Synthesis of C5-Allylindoles through an Iridium-Catalyzed Asymmetric Allylic Substitution/Oxidation Reaction Sequence of *N*-alkyl Indolines

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I General information:

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate.

Flash column chromatography was performed using Merck aluminium oxide90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use.

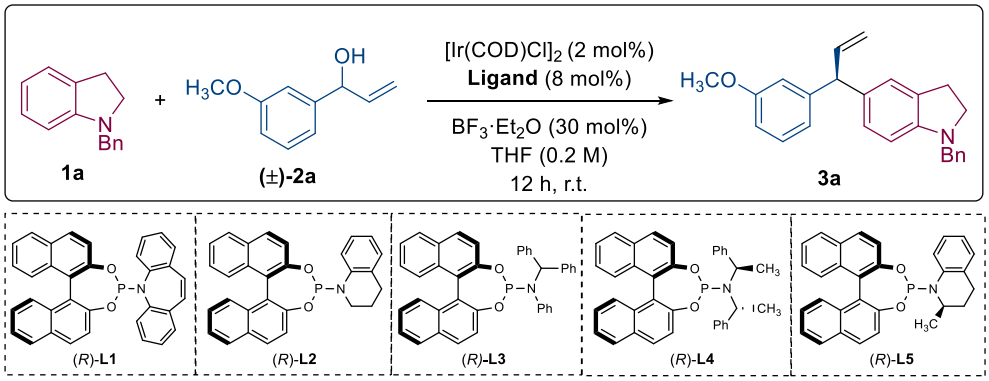
Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-d (7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (0.0) and relative to the signal of chloroform-d (77.0, triplet).

Enantiomeric excesses were determined by high performance liquid chromatography (HPLC) analysis on a chiral stationary phase, CHIRALCEL OD-H, CHIRALCEL IC or CHIRALCEL AD-H. Optical rotations were measured in $CHCl_3$ on a Schmidt + Haensdchpolarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL).

High resolution mass spectrometry (HRMS) was recorded on QTOF perimer for ESI^{+}.

II Optimization of reaction conditions:

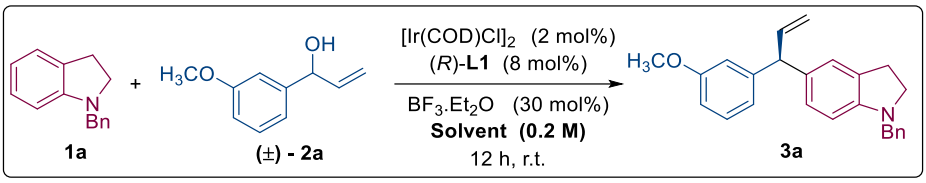
Table S1. Screening of various chiral phosphoramidite ligands[a]



entry	ligand	yield (%)[b]	*ee* (%)[c]
1	**(*R*)-L1**	**67**	**96**
2	(*R*)-**L2**	n.r.	-
3	(*R*)-**L3**	n.r.	-
4	(*R*)-**L4**	n.r.	-
5	(*R*)-**L5**	< 5	-

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 8 mol% of ligand, 30 mol% of $BF_3{\cdot}Et_2O$, 0.2 mmol of **1a**, 0.4 mmol of **2a** in THF (0.2 M) at room temperature, 12 h. [b]Isolated yields of **3a**. [c]Determined by HPLC analysis. n.r. = no reaction, n.d. = not determined.

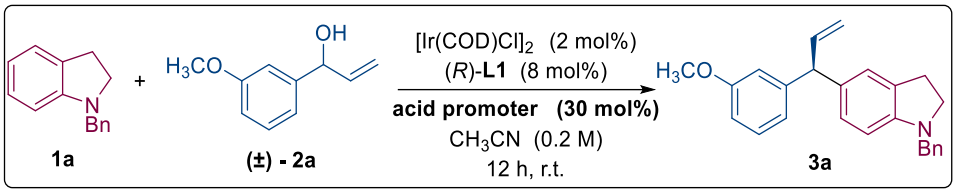
Table S2. Comparison of various solvents[a]



entry	solvent	yield (%)[b]	*ee* (%)[c]
1	THF	67	96
2	DCM	74	81
3	DCE	83	80
4	Dioxane	68	97
5	Et_2O	57	95
6	Toluene	60	96
7	**CH_3CN**	**62**	**98**
8	MTBE	56	97

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 8 mol% of (*R*)-**L1**, 30 mol% of $BF_3{\cdot}Et_2O$, 0.2 mmol of **1a**, 0.4 mmol of **2a** in solvents (0.2 M) at room temperature, 12 h. [b]Isolated yields of **3a**. [c]Determined by HPLC analysis.

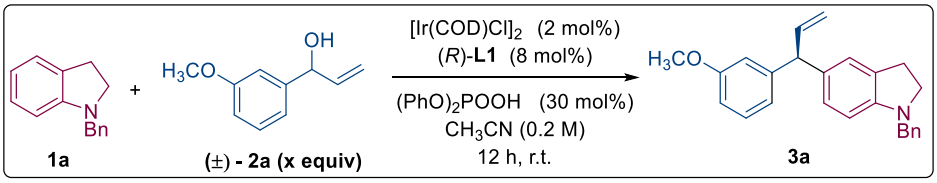
Table S3. Comparison of various acid promoters[a]



entry	acid	yield (%)[b]	*ee* (%)[c]
1	$BF_3{\cdot}Et_2O$	62	98
2	**$(PhO)_2POOH$**	**71**	**99**
3	$(CF_3SO_2)_2NH$	72	96
4	(±) - CSA	69	99
5	CF_3COOH	67	99
6	$La(OTf)_3$	42	> 99
7	$Fe(OTf)_2$	22	98
8	$Sc(OTf)_3$	48	84
9	$Zn(OTf)_2$	12	96

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 8 mol% of (*R*)-**L1**, 30 mol% of acid promoters, 0.2 mmol of **1a**, 0.4 mmol of **2a** in CH_3CN (0.2 M) at room temperature, 12 h. [b]Isolated yields of **3a**. [c]Determined by HPLC analysis. (±) - CSA = (±) - camphorsulfonic acid, n.r. = no reaction, n.d. = not determined.

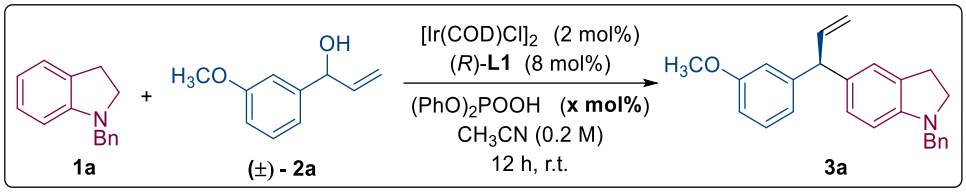
Table S4. Comparison of the equivalent of starting materials[a]



entry	x	yield (%)[b]	*ee* (%)[c]
1	2.0	71	99
2	1.0	31	95
3	1.2	53	> 99
4	1.5	56	> 99
5	**2.5**	**72**	**> 99**
6	0.5	57	98
7	0.67	35	96
8	0.83	37	> 99

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 8 mol% of (*R*)-**L1**, 30 mol% of $(PhO)_2POOH$, 0.2 mmol of **1a**, x equivalent of **2a** in CH_3CN (0.2 M) at room temperature, 12 h. [b]Isolated yields of **3a**. [c]Determined by HPLC analysis.

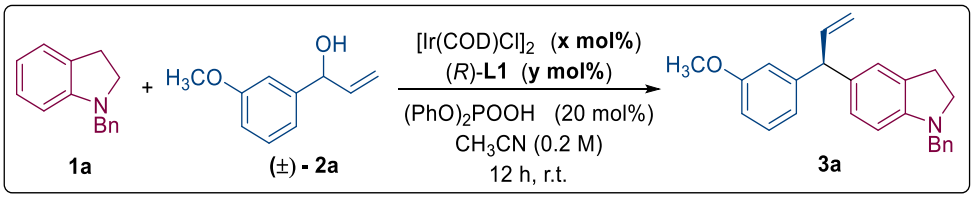
Table S5. Comparison of the equivalent of acid promoters[a]



entry	x	yield (%)[b]	*ee* (%)[c]
1	30	72	> 99
2	10	40	96
3	**20**	**83**	**> 99**
4	40	72	> 99

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 8 mol% of (*R*)-**L1**, x mol% of $(PhO)_2POOH$, 0.2 mmol of **1a**, 0.5 mmol of **2a** in CH_3CN (0.2 M) at room temperature, 12 h. [b]Isolated yields of **3a**. [c]Determined by HPLC analysis.

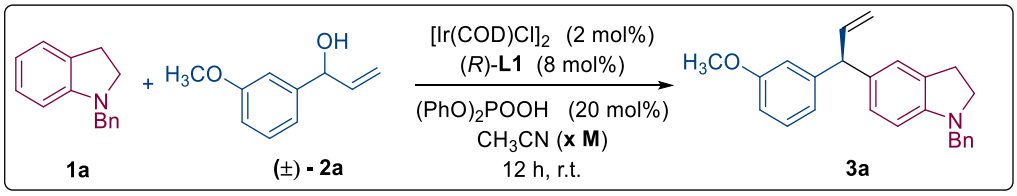
Table S6. Comparison of the equivalent of $[Ir(COD)Cl]_2$ and ligand[a]



entry	x	y	yield (%)[b]	*ee* (%)[c]
1	**2**	**8**	**83**	**> 99**
2	1	4	18	94
3	1.25	5	21	95
4	1.5	6	68	> 99

[a]Reaction conditions: x mol% of $[Ir(COD)Cl]_2$, y mol% of (*R*)-**L1**, 20 mol% of $(PhO)_2POOH$, 0.2 mmol of **1a**, 0.5 mmol of **2a** in CH_3CN (0.2 M) at room temperature, 12 h. [b]Isolated yields of **3a**. [c]Determined by HPLC analysis.

Table S7. Comparison of the solvent's concentration[a]



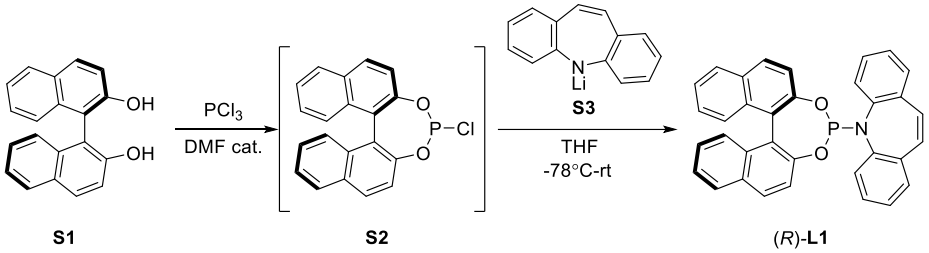
entry	x	yield (%)[b]	*ee* (%)[c]
1	0.20	83	> 99

2	0.10	82	> 99
3	0.15	87	> 99
4	**0.25**	**93**	**> 99**

[a]Reaction conditions: 2 mol% of $[Ir(COD)Cl]_2$, 8 mol% of (*R*)-**L1**, 20 mol% of $(PhO)_2POOH$, 0.2 mmol of **1a**, 0.5 mmol of **2a** in CH_3CN (0.25 M) at room temperature, 12 h. [b]Isolated yields of **3a**. [c]Determined by HPLC analysis.

III Experimental section

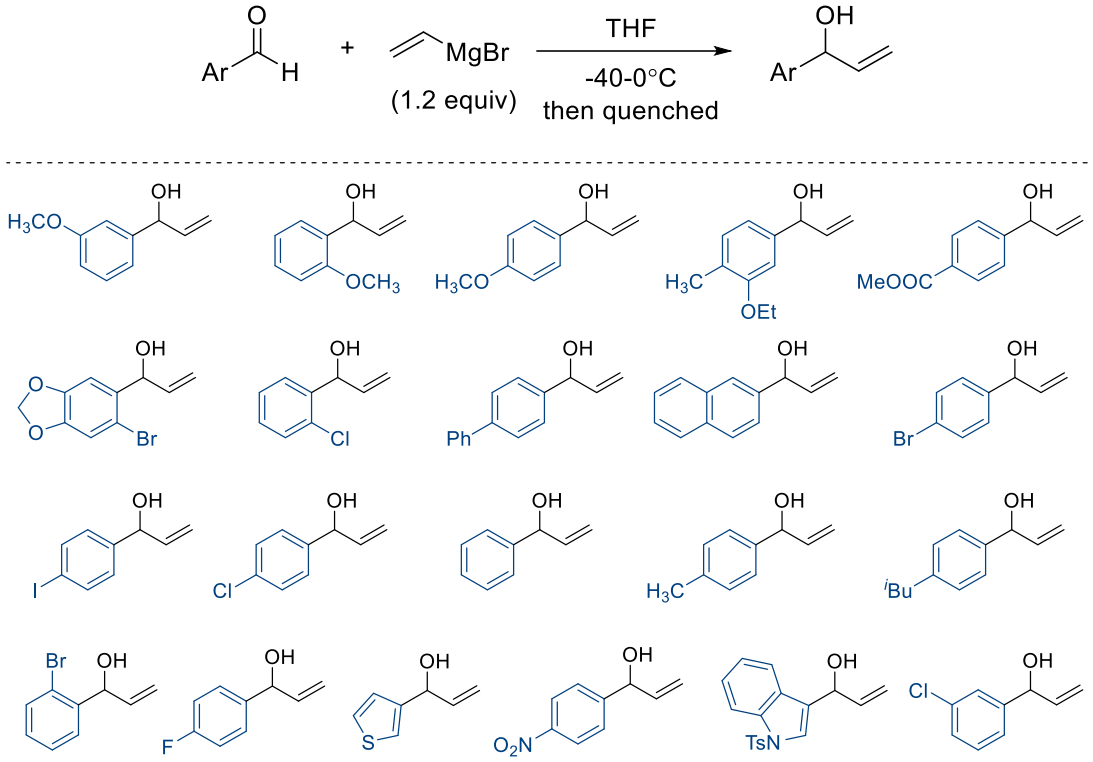
3.1. General synthesis for *Carreira* ligand (*R*)-L1:



Scheme S1. Synthesis of *Carreira* ligand (*R*)-**L1**

The synthetic protocol of *Carreira* ligand was accorded to the relevant literature[1]. To an oven-dried flask charged with stir bar and **S1** (1.574 g, 5.5 mmol), then refilled with argon 3 times. Redistilled PCl_3 (5.76 mL, 66.0 mmol, 12.0 equiv) and DMF (12.6 μL, 0.165 mmol, 0.03 equiv) were added sequentially. The system was oil bath heated to 55 °C smoothly and stirred for 1.5 hour to give colorless oil. After reaction completion, the excess PCl_3 was removed under the reduced pressure to afford product **S2** with white foam, then dissolved in 200 mL anhydrous THF. **S3** (prepared from iminostilbene and *n*-BuLi) in 50 mL THF was added dropwise to the above solution via syringe at -78 °C. The dark blue homogeneous solution was warmed to room temperature slowly and stirred for additional 6-8 h. Afterwards, the organics was quenched by water. The mixture was extracted with EtOAc 3 times, then separated. The organic mixture was washed with water and brine, then dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography with eluent (PE/EA/Et_3N = 20/1/0.1% to 8/1/0.1%) to give the final product, then recrystallized with DCM/pentane to afford the high ee value (>99%) compound (*R*)-**L1**. The characterization data of compound (*R*)-**L1** was reported as reference.

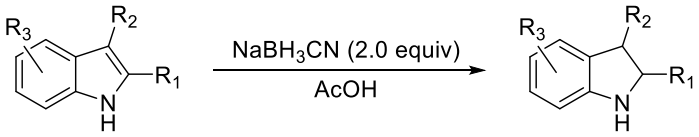
3.2. General synthesis for allylic alcohols:

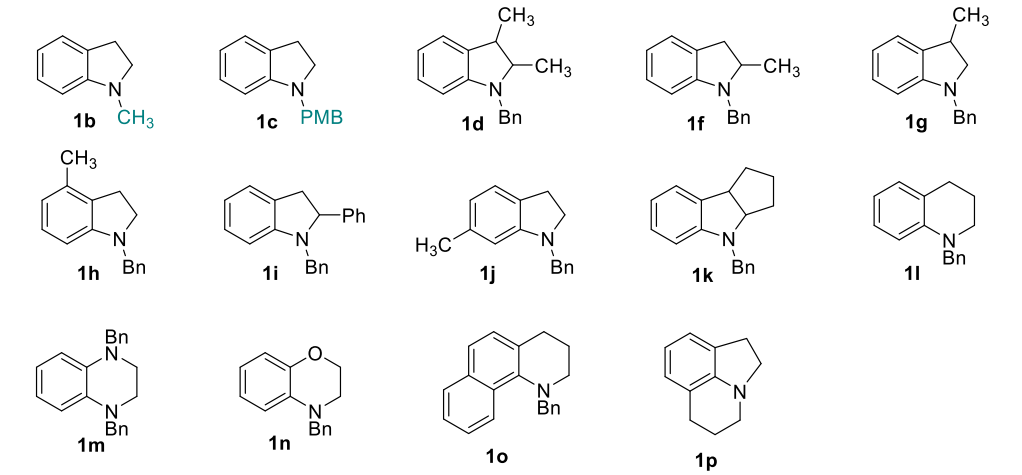


Scheme S2. Synthesis for allylic alcohols

The synthetic protocol of branched allylic alcohols was according to the relevant literature[2]. Aryl aldehyde was added to an oven-dried round bottom flask and refilled with argon twice times, followed by the addition of anhydrous THF solvent (0.1 M). After completely cooled to -40 °C, vinylmagnesium bromide (1.2 equiv, 1.0 M in THF) was then added slowly via syringe. The system was warmed to 0 °C and stirred for extra 4~8 h. The organic mixture was quenched by the saturated aqueous NH_4Cl and extracted with EtOAc twice times. The organic phase was separated and washed with water and brine, dried over anhydrous Na_2SO_4, filtrated, concentrated under then reduced pressure. The residue was purified by flash chromatography (PE:EA=10:1) to give the desired product. The characterization data of allylic alcohols were reported as reference.

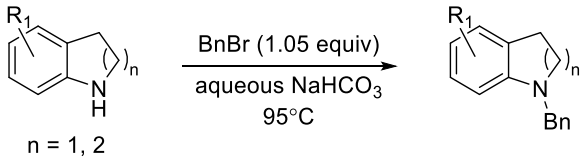
3.3. General procedure for the synthesis for *N*-protected hydro-heterocyclic compounds:





Scheme S3. Synthesis of allylic alcohols indolines

The synthetic protocol of substituted indolines **1b-1i**, **1k**, **1l**, **1n-1p** was according to the relevant literature[3]. Compounds **1j**, **1m** were synthesized according to the following method. At ambient temperature, to a 50 mL of oven-dried flask, commercially available substituted indole (8 mmol) was added glacial acetic acid (16 mL). After completely dissolved, $NaBH_3CN$ (2.0 equiv) was added portionwise. Afterwards, the organic mixture was stirred for 2~6 h. The solvent was removed under the reduced pressure, and the residue was treated by the 1.0 M aqueous NaOH. The mixture was extracted with DCM twice times before separated. The organic layer was washed with water and brine, dried over Na_2SO_4, filtrated, concentrated *in vacuo*. The crude product was purified by column chromatography (PE/EA) to afford the desired compound.

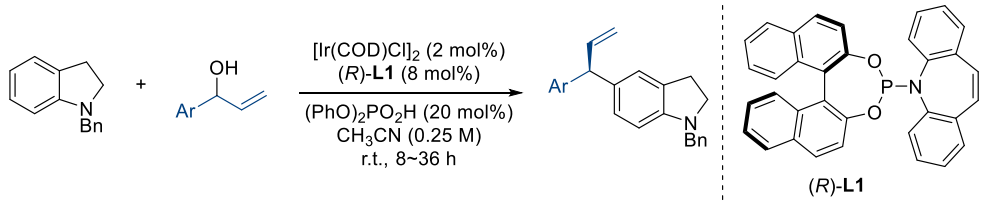


Scheme S4. Synthesis of *N*-protected indoles

The synthetic protocol of *N*-Bn indolines/*N*-Bn hydroheterocyclic compounds were accorded to the relevant literature[4]. To a two-necked flask charged with stir bar and indolines/hydroheterocyclic compounds (5 mmol) was added saturated aqueous $NaHCO_3$ (20 mL) and oil bath heated to 95°C slowly. BnBr (1.05 equiv) was added dropwise over 5 min to the above solution and stirred vigorously for additional 2 h. After completion, the reaction mixture was extracted with DCM twice times after cooled to the room temperature. The combined organic layer was then wash with brine, dried over Na_2SO_4, filtrated, concentrated *in vacuo*. The crude mixture was purified by the flash

chromatography (PE/EA) to yield the corresponding product. The characterization data of substituted indolines were listed as follows.

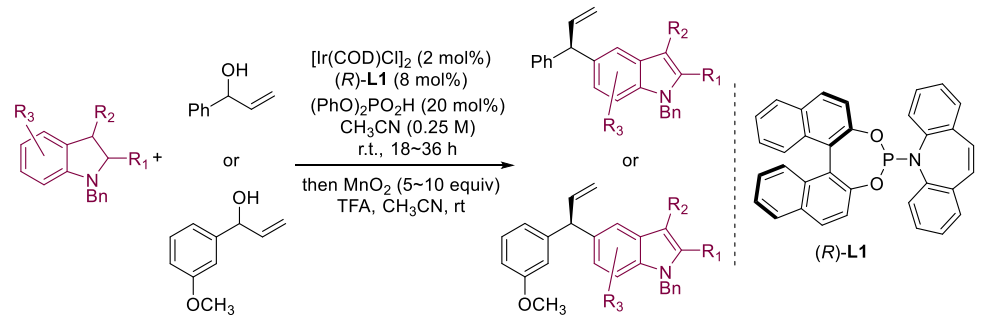
3.4. General procedure A: the synthesis of compound 3a-3y:



Scheme S5. General procedure for the AAS reaction

At room temperature, to an oven-dried Schlenk tube charged with stir bar, $[Ir(COD)Cl]_2$ (0.004 mmol, 2 mol%) and (*R*)-**L1** (0.016 mmol, 8 mol%) refilled with argon two times. Redistilled CH_3CN (0.8 mL, 0.25 M) was added via syringe and the combined mixture was stirred for 30 min. After complexation, the organic heterogeneous solution was followed by the addition of indoline (0.2 mmol, 1.0 equiv), allylic alcohol (0.5 mmol, 2.5 equiv) and diphenyl phosphate (0.04 mmol, 20 mol%) sequentially. The reaction was stirred for additional 8~36 h. After completion, the mixture was directly concentrated *in vacuo*, and the residue was purified by silica gel column chromatography (PE/EA) rapidly to afford the desired compounds. The characterization data of C5-substituted indolines were listed as follows.

3.5. General procedure B: the synthesis of compound 4a-4h:



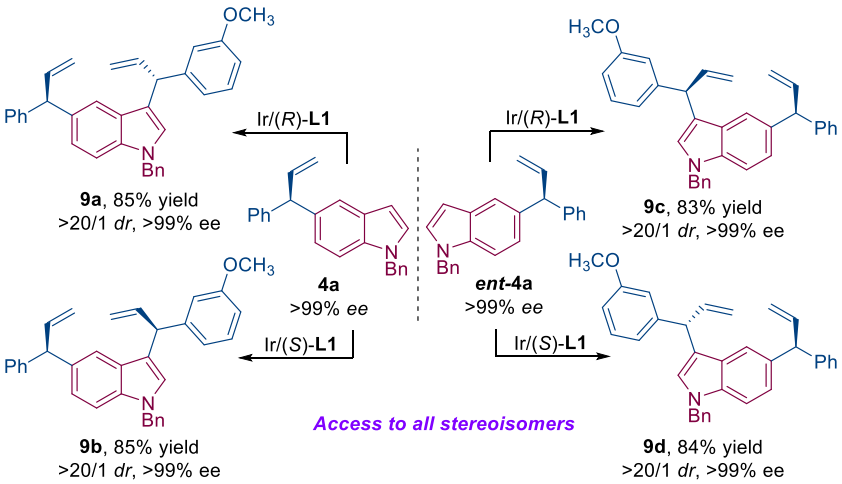
Scheme S6. General procedure for the AAS/oxidation reaction

At room temperature, to an oven-dried Schlenk tube charged with stir bar, $[Ir(COD)Cl]_2$ (0.004 mmol, 2 mol%) and (*R*)-**L1** (0.016 mmol, 8 mol%) refilled with argon two times. Redistilled CH_3CN (0.8 mL, 0.25 M) was added via syringe and the combined mixture was stirred for 30 min. After complexation, the organic heterogeneous solution was followed by the addition of indoline (0.2

mmol, 1.0 equiv), allylic alcohol (0.3 mmol, 1.5 equiv) and diphenyl phosphate (0.04 mmol, 20 mol%) sequentially. The reaction was stirred for additional 18~36 h. After completion, the mixture was added trimethylamine (30 mol%), CH_3CN (1 mL) and activated MnO_2 (5~10 equiv) and stirred for 6~12 h. The mixture was filtrated with celite and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EA) rapidly to afford the desired compounds. The characterization data of C5-substituted indoles were reported as follows.

3.6 Stereodivergent synthesis of diallylated indoles

Then, a second iridium catalyzed AAS reaction was carried out by using **4a** and **2a**, the desired diallylated product **9a** was obtained in 85% yield and >20:1 *dr* without any erosion of the enantioselectivity. Recently, the stereodivergent synthetic route to access all stereoisomers of chiral compounds has gained much attention, since it would significantly enhance the efficiency for the chiral compound library design and diversity-oriented synthesis of natural product analogues and drug discovery.[4] Thus, the enantiomeric isomers **4a** and ***ent*-4a** were applied to the second AAS reaction for the stereodivergent synthesis of diallylated products. It could be seen that all four stereoisomers **9a**-**9d** were afforded in 83-85% yields in >20:1 *dr*, and the *ee* values were all >99%. (Scheme 4)

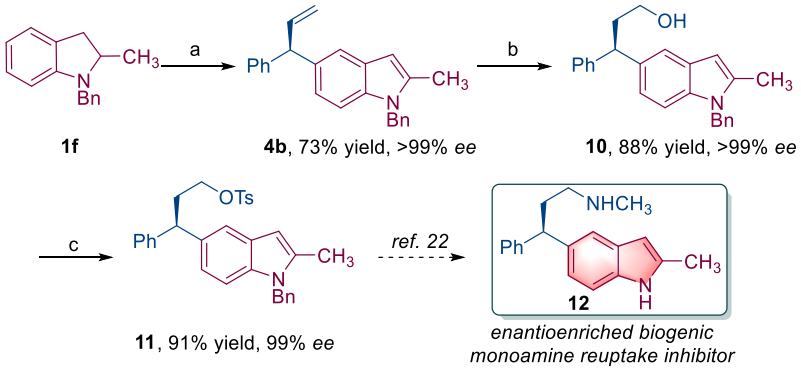


Scheme S5. Enantiodivergent synthesis of compound 9a-d

3.7 Deca-mmol scale preparation for a key chiral intermediate.

5-Indolyl aryl propylamines, which exhibited good activities for inhibition of Dopamine Transporter (DAT), were discovered and used as monoamine reuptake inhibitors and have attracted the attention of the scientific community.[5] To test the reliability of our method, we applied

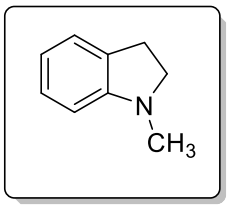
it in the rapid asymmetric construction of a key indole intermediate **10** for the synthesis of chiral 3-amino-1-arylpropyl indoles. Firstly, the allylation/oxidation reaction of *N*-benzyl-2-methylindoline (**1f**) with **2a** provided **4f** in 73% yield with >99% *ee*; secondly, **4f** was converted to **10** by a 9-BBN mediated hydroboration oxidation reaction, which could be further converted to **11** by a tosylation reaction in high yield and *ee*, which could be further converted to the chiral biogenic monoamine reuptake inhibitor **12** by following the literature. (Scheme 5)[6]



Scheme S6. Deca-mmol scale preparation for a key chiral intermediate. Conditions: a) standard condition; b) 9-BBN, then $NaBO_3 \cdot 4H_2O$, 0 °C to rt.; c) TsCl, DMAP, TEA, DCM. 9-BBN = 9-borabicyclo[3.3.1]nonane.

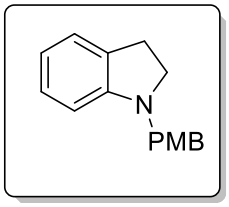
IV Characterization of products:

1-methylindoline (1b)[3a]



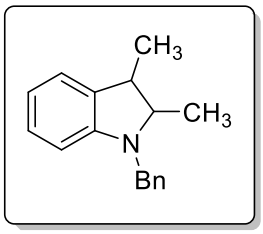
Brown oil, 59.2 mg, yield (89%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.03 (m, 2H), 6.70 – 6.63 (m, 1H), 6.50 – 6.46 (m, 1H), 3.28 (t, *J* = 8.1 Hz, 2H), 2.93 (t, *J* = 8.1 Hz, 2H), 2.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 130.3, 127.4, 124.3, 117.8, 107.3, 56.2, 36.3, 28.8.

1-(4-methoxybenzyl)indoline (1c)[3b]



White solid, 105.1 mg, yield (88%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 3H), 7.11 – 7.03 (m, 2H), 6.90 – 6.85 (m, 2H), 6.67 – 6.64 (m, 1H), 6.54 – 6.50 (m, 1H), 4.19 (s, 2H), 3.81 (s, 3H), 3.27 (t, *J* = 8.3 Hz, 2H), 2.95 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 152.6, 130.4, 130.1, 129.2, 127.3, 124.5, 117.6, 113.9, 107.1, 55.3, 53.4, 53.0, 28.5.

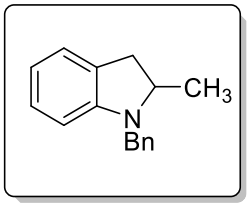
1-benzyl-2,3-dimethylindoline (1d) [3a]



Colorless oil, 80.6 mg, yield (68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.27 – 7.23 (m, 1H), 7.23 – 7.13 (m, 1H), 7.04 – 6.92 (m, 2H), 6.69 – 6.60 (m, 1H), 6.35 – 6.23 (m, 1H), 4.31 (dd, *J* = 29.2, 16.0 Hz, 1H), 4.09 (dd, *J* = 24.7, 16.0 Hz, 1H), 3.65 (dq, *J* = 13.3, 6.6 Hz, 1H, minor),

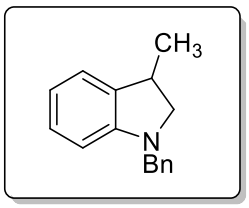
3.25 – 3.06 (m, 1H), 2.82 (dq, *J* = 13.7, 6.8 Hz, 1H, major), 1.26 (dd, *J* = 8.9, 6.5 Hz, 4H), 1.11 (dd, *J* = 18.3, 6.8 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6, 151.8, 139.6, 139.5, 135.1, 134.0, 128.8, 128.7, 127.8, 127.7, 127.7, 127.6, 127.2, 123.7, 123.0, 117.9, 117.9, 107.3, 107.2, 69.3, 63.1, 51.8, 50.4, 43.9, 39.4, 18.7, 17.5, 15.1, 13.2.

1-benzyl-2-methylindoline (1f) [3a]



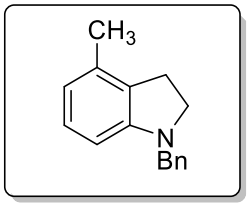
Yellowish oil, 91.4 mg, yield (82%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.32 – 7.25 (m, 2H), 7.25 – 7.20 (m, 1H), 7.06 – 7.02 (m, 1H), 6.99 – 6.94 (m, 1H), 6.64 – 6.58 (m, 1H), 6.33 – 6.28 (m, 1H), 4.34 (d, *J* = 16.1 Hz, 1H), 4.17 (d, *J* = 16.1 Hz, 1H), 3.71 (tq, *J* = 9.2, 6.1 Hz, 1H), 3.14 (dd, *J* = 15.5, 8.6 Hz, 1H), 2.66 (dd, *J* = 15.5, 9.5 Hz, 1H), 1.28 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 139.4, 128.9, 128.5, 127. 5, 127.4, 127.0, 124.2, 117.5, 106.9, 60.7, 51.2, 37.5, 19.8.

1-benzyl-3-methylindoline (1g) [3c]



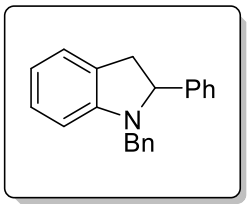
Reddish oil, 79.1 mg, yield (72%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.26 – 7.20 (m, 1H), 7.08 – 7.01 (m, 2H), 6.68 (m, 1H), 6.49 (m, 1H), 4.33 (d, *J* = 14.8 Hz, 1H), 4.08 (d, *J* = 14.8 Hz, 1H), 3.47 (t, *J* = 8.6 Hz, 1H), 3.31 – 3.22 (m, 1H), 2.80 (t, *J* = 8.5 Hz, 1H), 1.28 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 138.7, 135.2, 128.6, 128.0, 127.6, 127.2, 123.3, 117.9, 107.2, 61.8, 53.6, 35.3, 18.8.

1-benzyl-4-methylindoline (1h) [3c]



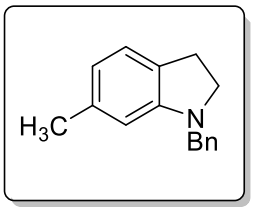
Reddish oil, 69.1 mg, yield (62%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.27 – 7.23 (m, 1H), 6.99 – 6.93 (m, 1H), 6.53 – 6.47 (m, 1H), 6.37 – 6.33 (m, 1H), 4.24 – 4.20 (s, 2H), 3.30 (t, *J* = 8.4 Hz, 2H), 2.87 (t, *J* = 8.3 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 138.7, 134.1, 128.6, 128.6, 128.0, 127.5, 127.2, 119.2, 104.7, 53.9, 53.4, 27.3, 18.7.

1-benzyl-2-phenylindoline (1i) [3c]



White solid, 92.6 mg, yield (65%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 2H), 7.36 – 7.26 (m, 2H), 7.26 – 7.15 (m, 6H), 7.10 – 6.97 (m, 2H), 6.73 – 6.68 (m, 1H), 6.43 – 6.25 (m, 1H), 4.62 (t, *J* = 9.5 Hz, 1H), 4.36 (d, *J* = 15.8 Hz, 1H), 3.94 (d, *J* = 15.8 Hz, 1H), 3.37 (dd, *J* = 15.4, 9.1 Hz, 1H), 3.01 (dd, *J* = 15.1, 10.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5, 142.6, 138.4, 128.7, 128.5, 127.8, 127.7, 127.6, 126.9, 124.2, 118.0, 107.5, 77.4, 77.1, 76.9, 69.4, 51.0, 39.6.

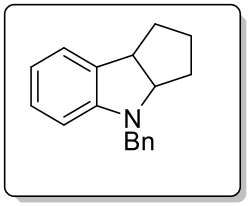
1-benzyl-6-methylindoline (1j)



Colorless oil, 73.6 mg, yield (66%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 7.00 – 6.95 (m, 1H), 6.51 – 6.47 (m, 1H), 6.36 – 6.33 (m, 1H), 4.23 (s, 2H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.92 (t, *J* = 8.2 Hz, 2H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 137.6, 136.1, 127.4, 126.9, 126.0, 126.0, 123.2, 117.3, 106.9, 52.8, 52.6, 27.2, 20.7.

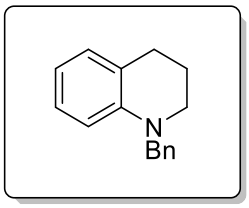
HRMS (ESI) m/z: [M + H]+ Calcd for $C_{16}H_{17}N$ 224.1434; Found 224.1441.

4-benzyl-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indole (1k) [3d]



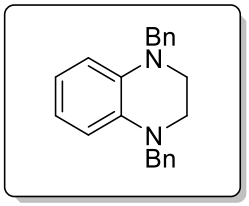
Colorless oil, 97.1 mg, yield (78%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 4H), 7.24 – 7.19 (m, 1H), 7.03 – 6.99 (m, 1H), 6.97 – 6.92 (m, 1H), 6.60 – 6.53 (m, 1H), 6.24 – 6.18 (m, 1H), 4.39 (d, *J* = 16.2 Hz, 1H), 4.27 (d, *J* = 16.2 Hz, 1H), 4.21 – 4.16 (m, 1H), 3.73 (td, *J* = 9.0, 2.7 Hz, 1H), 2.01 – 1.91 (m, 1H), 1.84 – 1.75 (m, 2H), 1.66 – 1.51 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 139.3, 133.6, 128.6, 127.6, 127.3, 126.9, 124.2, 116.7, 105.4, 69.9, 51.2, 45.9, 35.2, 33.3, 24.7.

1-benzyl-1,2,3,4-tetrahydroquinoline (1l) [3d]



Pink solid, 98.1 mg, yield (88%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 7.26 – 7.18 (m, 3H), 6.98 – 6,92 (m, 2H), 6.58 – 6.53 (m, 1H), 6.50 – 6.45 (m, 1H), 4.45 (s, 2H), 3.33 (m, 2H), 2.79 (t, *J* = 6.3 Hz, 2H), 2.03 – 1.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 139.1, 129.1, 128.7, 127.3, 126.9, 126.7, 122.3, 116.0, 111.1, 55.3, 50.0, 28.4, 22.5.

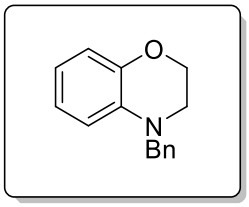
1,4-dibenzyl-1,2,3,4-tetrahydroquinoxaline (1m)



White solid, 124.0 mg, yield (79%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 7H), 7.21 – 7.15 (m, 3H), 6.55 – 6.47 (m, 4H), 4.38 (s, 4H), 3.33 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6, 135.8, 128.6, 127.2, 126.9, 118.1, 111.5, 55.6, 47.9.

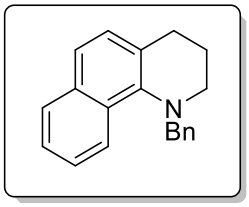
HRMS (ESI) m/z: [M + H]+ Calcd for $C_{22}H_{22}N_2$ 315.1856; Found 315.1857.

4-benzyl-3,4-dihydro-2H-benzo[b][1,4]oxazine (1n) [3d]



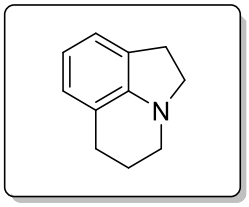
Brown solid, 75.4 mg, yield (67%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 5H), 6.85 – 6.73 (m, 2H), 6.70 – 6.56 (m, 2H), 4.43 (s, 2H), 4.28 – 4.23 (m, 2H), 3.39 – 3.29 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 138.2, 135.7, 128.7, 127.2, 127.2, 121.7, 117.9, 116.4, 112.6, 64.7, 55.0, 47.4.

1-benzyl-1,2,3,4-tetrahydrobenzo[h]quinoline (1o) [3d]



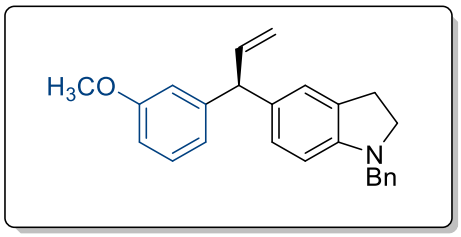
Ivory oil, 102.7 mg, yield (76%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.12 (m, 1H), 7.78 – 7.74 (m, 1H), 7.65 – 7.60 (m, 2H), 7.47 – 7.40 (m, 3H), 7.39 – 7.31 (m, 3H), 7.19 – 7.14 (m, 1H), 4.34 (s, 2H), 3.18 – 3.13 (m, 2H), 2.94 (t, J = 6.7 Hz, 2H), 1.92 – 1.85 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 139.8, 133.5, 128.9, 128.7, 128.4, 128.2, 127.4, 127.0, 125.3, 125.3, 125.0, 122.9, 122.1, 59.1, 46.9, 28.0, 16.5.

1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinoline (1p) [3d]



Yellowish oil, 49.3 mg, yield (62%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 – 6.91 (m, 1H), 6.84 – 6.78 (m, 1H), 6.64 – 6.58 (m, 1H), 3.24 (t, *J* = 7.8 Hz, 2H), 2.99 – 2.95 (m, 2H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 6.6 Hz, 2H), 2.12 – 2.06 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0, 128.8, 126.3, 121.9, 119.6, 118.6, 55.3, 47.5, 28.8, 24.0, 23.3.

(*S*)-1-benzyl-5-(1-(3-methoxyphenyl)allyl)indoline (3a)



Yellowish oil, 66.0 mg, yield (93%); $[\alpha]_D^{20}$ = -30.3 (c 1.25, $CHCl_3$);

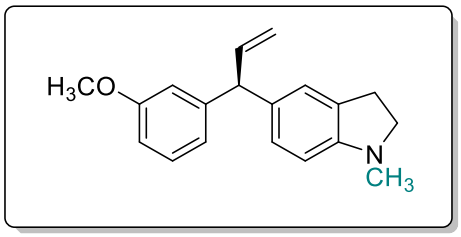
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.28 – 7.24 (m, 1H), 7.23 – 7.17 (m, 1H), 6.94 – 6.88 (m, 1H), 6.87 – 6.85 (m, 1H), 6.83 – 6.72 (m, 3H), 6.45 – 6.41 (m, 1H), 6.30 – 6.22 (m, 1H), 5.19 – 5.13 (m, 1H), 5.03 – 4.96 (m, 1H), 4.61 – 4.56 (m, 1H), 4.21 (s, 2H), 3.77 (s, 3H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.91 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 151.2, 145.8, 141.2, 138.6, 132.6, 130.4, 129.2, 128.5, 128.0, 127.3, 127.1, 124.8, 121.1, 115.7, 114.6, 111.2, 106.8, 55.2, 54.6, 54.0, 53.9, 28.6.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 0.5 mL/min, l = 254 nm) t_R = 19.1 min (major), 18.2 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{26}NO$ 356.2009; Found 356.2009.

(*S*)-5-(1-(3-methoxyphenyl)allyl)-1-methylindoline (3b)



Yellowish oil, 35.7 mg, yield (64%); $[\alpha]_D^{20}$ = +5.4 (c 1.25, $CHCl_3$);

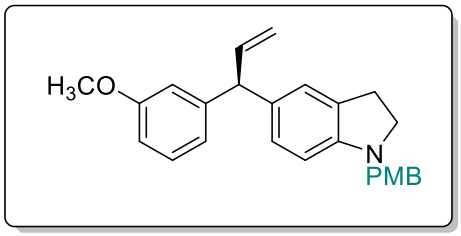
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.17 (m, 1H), 6.93 – 6.87 (m, 2H), 6.82 – 6.77 (m, 1H), 6.77 – 6.71 (m, 2H), 6.43 – 6.39 (m, 1H), 6.30 – 6.22 (m, 1H), 5.19 – 5.14 (m, 1H), 5.02 – 4.95 (m, 1H), 4.61 – 4.56 (m, 1H), 3.77 (s, 3H), 3.26 (t, *J* = 8.1 Hz, 2H), 2.88 (t, *J* = 8.1 Hz, 2H), 2.73 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 151.0, 144.8, 140.2, 131.6, 129.6, 128.2, 126.3, 123.5, 120.0, 114.6, 113.5, 110.2, 106.0, 55.3, 54.1, 53.5, 35.4, 27.7.

>99% *ee* as determined by HPLC (AD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 5.1 min (major), 4.6 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{19}H_{22}NO$ 280.1696; Found 280.1698.

(*S*)-1-(4-methoxybenzyl)-5-(1-(3-methoxyphenyl)allyl)indoline (3c)



Yellowish oil, 63.3 mg, yield (82%); $[\alpha]_D^{20}$ = +4.5 (c 1.25, $CHCl_3$);

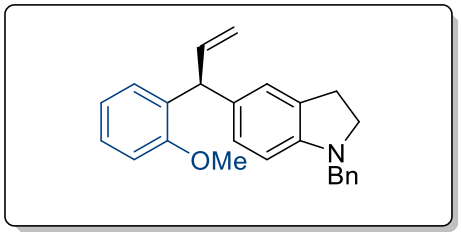
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.24 – 7.17 (m, 1H), 6.93 – 6.88 (m, 1H), 6.88 – 6.84 (m, 3H), 6.81 – 6.71 (m, 3H), 6.46 – 6.42 (m, 1H), 6.30 – 8.22 (m, 1H), 5.18 – 5.14 (m, 1H), 5.03 – 4,95 (m, 1H), 4.60 – 4.55 (m, 1H), 4.14 (s, 2H), 3.77 (d, *J* = 13.5 Hz, 6H), 3.23 (t, *J* = 8.2 Hz, 2H), 2.88 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 158.8, 151.3, 145.9, 141.3, 132.6, 130.6, 130.5, 129.2, 129.2, 127.3, 124.8, 121.1, 115.7, 114.6, 113.9, 111.2, 106.9, 55.3, 55.2, 54.6, 53.8, 53.4, 28.6.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 10.1 min (major), 8.9 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{26}H_{28}NO_2$ 386.2115; Found 386.2110.

(*S*)-1-benzyl-5-(1-(2-methoxyphenyl)allyl)indoline (3d)



Yellowish oil, 55.4 mg, yield (78%); $[\alpha]_D^{20}$ = +229.3 (c 1.25, $CHCl_3$);

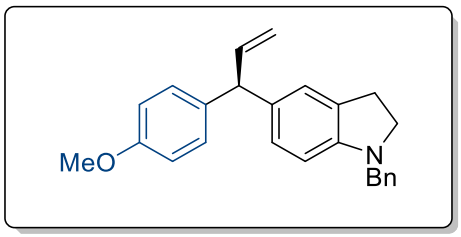
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.28 – 7.24 (m, 1H), 7.20 – 7.15 (m, 1H), 7.14 – 7.08 (m, 1H), 6.95 – 6.82 (m, 4H), 6.45 – 6.37 (m, 1H), 6.33 – 6.23 (m, 1H), 5.17 – 5.12 (m, 1H), 5.11 – 5.05 (m, 1H), 4.93 – 4.85 (m, 1H), 4.19 (s, 2H), 3.78 (s, 3H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.91 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 151.0, 141.3, 138.7, 132.6, 132.5, 130.1, 129.4, 128.5, 128.0, 127.4, 127.2, 127.1, 125.0, 120.5, 115.2, 110.8, 106.8, 55.7, 54.2, 54.0, 46.8, 28.6.

99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 0.5 mL/min, l = 254 nm) t_R = 22.5 min (major), 21.6 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{26}NO$ 356.2009; Found 356.2015.

(*R*)-1-benzyl-5-(1-(4-methoxyphenyl)allyl)indoline (3e)



Yellowish oil, 41.9 mg, yield (59%); $[\alpha]_D^{20}$ = +2.8 (c 1.25, $CHCl_3$);

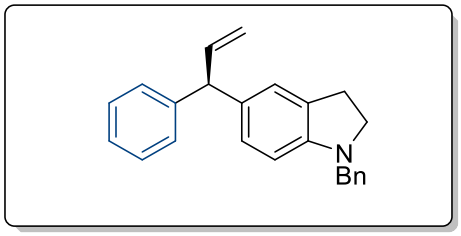
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 4H), 7.27 – 7.22 (m, 1H), 7.14 – 7.07 (m, 2H), 6.92 – 6.87 (m, 1H), 6.86 – 6.80 (m, 3H), 6.45 – 6.40 (m, 1H), 6.30 – 6.20 (m, 1H), 5.16 – 5.11 (m, 1H), 4.99 – 4.93 (m, 1H), 4.60 – 4.55 (m, 1H), 4.20 (s, 2H), 3.77 (s, 3H), 3.27 (t, *J* = 8.3 Hz, 2H), 2.90 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 151.3, 141.8, 138.7, 136.3, 133.2, 130.4, 129.50, 128.5, 128.0, 127.3, 127.1, 124.8, 115.4, 113.7, 106.8, 55.3, 54.1, 54.0, 53.7, 28.6.

91% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 0.5 mL/min, l = 254 nm) t_R = 32.3 min (major), 30.7 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{26}NO$ 356.2009; Found 356.2001.

(*R*)-1-benzyl-5-(1-phenylallyl)indoline (3f)



Yellowish oil, 50.0 mg, yield (77%); $[\alpha]_D^{20}$ = +7.6 (c 1.25, $CHCl_3$);

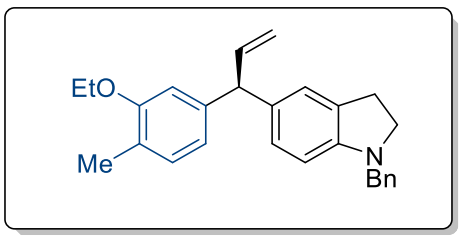
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 7H), 7.21 – 7.16 (m, 3H), 6.93 – 6.88 (m, 1H), 6.87 – 6.84 (m, 1H), 6.45 – 6.40 (m, 1H), 6.33 – 6.23 (m, 1H), 5.20 – 5.13 (m, 1H), 5.02 – 4.94 (m, 1H), 4.65 – 4,57 (m, 1H), 4.20 (s, 2H), 3.27 (t, *J* = 8.3 Hz, 2H), 2.90 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 144.3, 141.5, 138.7, 132.9, 130.4, 128.6, 128.5, 128.4, 128.0, 127.4, 127.1, 126.2, 124.9, 115.7, 106.9, 54.6, 54.1, 54.0, 28.6.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) t_R = 9.8 min (major), 10.5 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{24}N$ 326.1903; Found 326.1910.

(*S*)-1-benzyl-5-(1-(3-ethoxy-4-methylphenyl)allyl)indoline (3g)



Yellowish oil, 57.6 mg, yield (75%); $[\alpha]_D^{20}$ = +7.69 (c 1.25, $CHCl_3$);

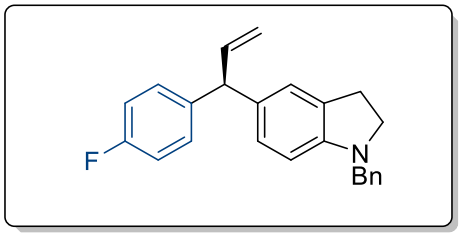
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 4H), 7.28 – 7.21 (m, 1H), 6.93 – 6.87 (m, 1H), 6.92 – 6.83 (m, 1H), 6.83 – 6.77 (m, 1H), 6.76 – 6.68 (m, 2H), 6.47 – 6.40 (m, 1H), 6.30 – 6.19 (m, 1H), 5.10 – 5.13 (m, 1H), 5.03 – 4.95 (m, 1H), 4.58 – 4.52 (m, 1H), 4.20 (s, 2H), 4.04 (q, *J* = 7.0 Hz, 2H), 3.83 (s, 3H), 3.27 (t, *J* = 8.3 Hz, 2H), 2.91 (t, *J* = 8.2 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 148.1, 147.7, 141.7, 138.6, 136.7, 133.0, 130.4, 128.5, 128.0, 127.3, 127.1, 124.8, 120.5, 115.4, 113.6, 111.4, 106.9, 64.3, 56.0, 54.1, 54.1, 53.9, 28.6, 14.9.

93% *ee* as determined by HPLC (AD-H, *i*-PrOH /*n*-hexane = 3/97, flow rate = 1.0 mL/min, l = 254 nm) t_R = 9.6 min (major), 10.3 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{27}H_{30}NO$ 384.2322; Found 384.2329.

(*R*)-1-benzyl-5-(1-(4-fluorophenyl)allyl)indoline (3h)



Yellowish oil, 59.0 mg, yield (86%); $[\alpha]_D^{20}$ = +233.8 (c 1.25, $CHCl_3$);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 1H), 7.37 – 7.30 (m, 4H), 7.28 – 7.22 (m, 2H), 7.20 – 7.16 (m, 1H), 7.08 – 7.02 (m, 1H), 6.93 – 6.89 (m, 1H), 6.89 – 6.84 (m, 1H), 6.46 – 6.41 (m, 1H), 6.26 – 6.18 (m, 1H), 5.24 – 5.17 (m, 1H), 5.15 – 5.10 (m, 1H), 4.93 – 4.86 (m, 1H), 4.21 (s, 2H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.92 (t, *J* = 8.2 Hz, 2H).

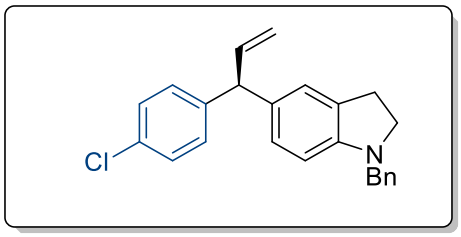
^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (C-F, $1J_{C\text{-}F}$ = 242. 7 Hz), 160.4 (C-F, $1J_{C\text{-}F}$ = 242. 7 Hz), 151.4, 141.3, 139.9, 139.8, 138.6, 132.6, 130.5, 130.0 (C-F, $3J_{C\text{-}F}$ = 7.7 Hz), 130.0 (C-F, $3J_{C\text{-}F}$ = 7.7 Hz), 128.5, 128.0, 127.4, 127.2, 124.8, 115.8, 115.1 (C-F, $2J_{C\text{-}F}$ = 21.0 Hz), 115.1 (C-F, $2J_{C\text{-}F}$ = 21.0 Hz), 106.9, 54.0, 53.9, 53.8, 28.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -117.3.

>99% *ee* as determined by HPLC (OJ, *i*-PrOH /*n*-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) t_R = 12.8 min (major), 16.2 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{23}NF$ 344.1809; Found 344.1804.

(*R*)-1-benzyl-5-(1-(4-chlorophenyl)allyl)indoline (3i)



Yellowish viscous oil, 62.6 mg, yield (87%); $[\alpha]_D^{20}$ = +2.5 (c 1.25, $CHCl_3$);

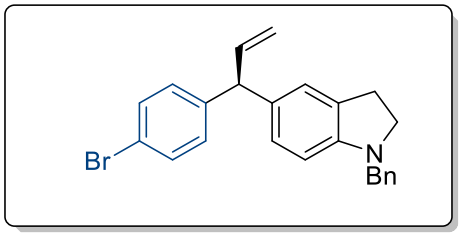
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.27 – 7.21 (m, 3H), 7.14 – 7.09 (m, 2H), 6.89 – 6.85 (m, 1H), 6.85 – 6.81 (m, 1H), 6.45 – 6.39 (m, 1H), 6.26 – 6.18 (m, 1H), 5.20 – 5.14 (m, 1H), 5.00 – 4.91 (m, 1H), 4.62 – 4.55 (m, 1H), 4.20 (s, 2H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.90 (t, *J* = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 142.7, 141.0, 138.6, 132.2, 131.9, 130.6, 130.0, 128.5, 128.4, 128.0, 127.4, 127.2, 124.8, 116.0, 106.9, 54.0, 53.9, 53.9, 28.6.

>99% *ee* as determined by HPLC (OJ, *i*-PrOH /*n*-hexane = 1/99, flow rate = 0.5 mL/min, l = 254 nm) t_R = 44.5 min (major), 26.2 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{23}ClN$ 360.1514; Found 360.1518.

(*R*)-1-benzyl-5-(1-(4-bromophenyl)allyl)indoline (3j)



Yellowish solid, 64.6 mg, yield (80%); mp. = 77.1-78.9 °C; $[\alpha]_D^{20}$ = -35.6 (c 1.25, $CHCl_3$);

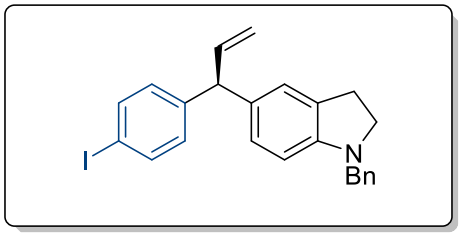
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.29 (m, 4H), 7.27 – 7.23 (m, 1H), 7.09 – 7.03 (m, 2H), 6.89 – 6.85 (m, 1H), 6.85 – 6.80 (m, 1H), 6.46 – 6.39 (m, 1H), 6.26 – 6.17 (m, 1H), 5.21 – 5.15 (m, 1H), 4.99 – 4.92 (m, 1H), 4.60 – 4.52 (m, 1H), 4.20 (s, 2H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.91 (t, *J* = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 143.2, 140.9, 138.5, 132.1, 131.4, 130.6, 130.4, 128.5, 128.0, 127.4, 127.2, 124.8, 120.0, 116.1, 106.9, 54.0, 53.9, 53.9, 28.6.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 2/98, flow rate = 1.0 mL/min, l = 254 nm) t_R = 10.1 min (major), 10.9 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{23}NBr$ 404.1008; Found 404.1000.

(*R*)-1-benzyl-5-(1-(4-iodophenyl)allyl)indoline (3k)



Yellowish solid, 74.0 mg, yield (82%); mp. = 78.0-79.1 °C; $[\alpha]_D^{20}$ = +0.4 (c 1.25, $CHCl_3$);

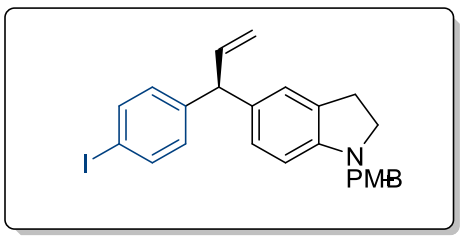
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.36 – 7.29 (m, 4H), 7.27 – 7.23 (m, 1H), 6.96 – 6.91 (m, 2H), 6.88 – 6.85 (m, 1H), 6.84 – 6.80 (m, 1H), 6.44 – 6.40 (m, 1H), 6.25 – 6.16 (m, 1H), 5.20 – 5.14 (m, 1H), 5.00 – 4.92 (m, 1H), 4.58 – 4.52 (m, 1H), 4.20 (s, 2H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.90 (t, *J* = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 143.9, 140.8, 138.5, 137.4, 132.1, 130.8, 130.6, 128.5, 128.0, 127.4, 127.2, 124.8, 116.1, 106.9, 91.5, 54.0, 54.0, 53.9, 28.6.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 0.5 mL/min, l = 254 nm) t_R = 17.7 min (major), 19.4 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{23}NI$ 452.0870; Found 452.0866.

(*R*)-5-(1-(4-iodophenyl)allyl)-1-(4-methoxybenzyl)indoline (3l)



Yellowish oil, 73.1 mg, yield (76%); $[\alpha]_D^{20}$ = -0.3 (c 1.25, $CHCl_3$);

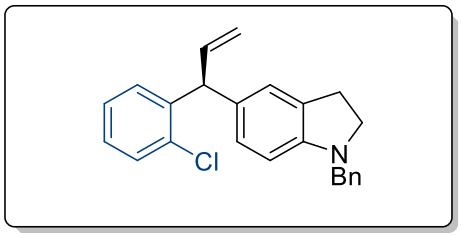
^1H NMR (500 MHz, CDCl3) δ 7.61 – 7.56 (m, 2H), 7.63 – 7.24 (m, 2H), 6.97 – 6.91 (m, 2H), 6.88 – 6.80 (m, 4H), 6.46 – 6.42 (m, 1H), 6.25 – 6.16 (m, 1H), 5.20 – 5.15 (m, 1H), 4.98 – 4.93 (m, 1H), 4.57 – 4.52 (m, 1H), 4.14 (s, 2H), 3.79 (s, 3H), 3.25 (t, J = 8.3 Hz, 2H), 2.89 (t, J = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, CDCl3) δ 158.8, 151.3, 143.9, 140.8, 137.3, 132.0, 130.7, 130.6, 130.4, 129.2, 127.3, 124.7, 116.1, 113.9, 106.9, 91.4, 55.3, 54.0, 53.7, 53.3, 28.5.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 1.0 mL/min, l = 254 nm) t_R = 22.1 min (major), 24.3 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{25}INO$ 482.0975; Found 482.0973.

(*S*)-1-benzyl-5-(1-(2-chlorophenyl)allyl)indoline (3m)



Yellowish oil, 36.0 mg, yield (50%); $[\alpha]_D^{20}$ = -5.4 (c 1.25, $CHCl_3$);

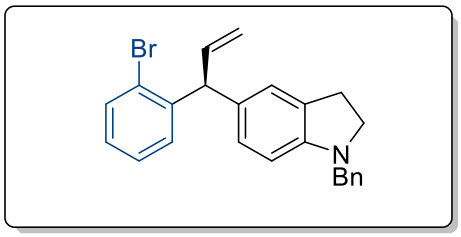
^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 5H), 7.26 – 7.22 (m, 1H), 7.21 – 7.15 (m, 2H), 7.13 – 7.08 (m, 1H), 6.93 – 6.87 (m, 1H), 6.87 – 6.83 (m, 1H), 6.46 – 6.38 (m, 1H), 6.27 – 6.17 (m, 1H), 5.23 – 5.16 (m, 1H), 5.15 – 5.10 (m, 1H), 4.93 – 4.85 (m, 1H), 4.20 (s, 2H), 3.27 (t, *J* = 8.1 Hz, 2H), 2.90 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 141.5, 140.2, 138.6, 134.2, 131.2, 130.4, 130.2, 129.7, 128.5, 128.0, 127.7, 127.5, 127.2, 126.7, 125.1, 116.4, 106.8, 54.0, 53.9, 50.4, 28.6.

97% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 0.5 mL/min, l = 254 nm) t_R = 19.7 min (major), 18.2 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{23}ClN$ 360.1514; Found 360.1522.

(*S*)-1-benzyl-5-(1-(2-bromophenyl)allyl)indoline (3n)



Yellowish solid, 54.1 mg, yield (67%); mp. = 52.8-58.4 °C; $[\alpha]_D^{20}$ = +5.6 (c 1.25, $CHCl_3$);

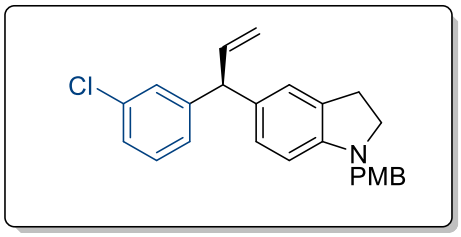
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.28 – 7.23 (m, 1H), 7.17 – 7.11 (m, 2H), 6.99 – 6.93 (m, 2H), 6.90 – 6.86 (m, 1H), 6.85 – 6.81 (m, 1H), 6.45 – 6.40 (m, 1H), 6.28 – 6.19 (m, 1H), 5.19 – 5.14 (m, 1H), 4.98 – 4.92 (m, 1H), 4.62 – 4.57 (m, 1H), 4.20 (s, 2H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.91 (t, *J* = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ151.3, 141.3, 139.8, 139.8, 138.6, 130.0, 129.9, 128.5, 128.0, 127.3, 127.2, 124.8, 115.8, 115.1, 115.0, 106.9, 54.0, 53.9, 53.8, 28.6.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) t_R = 8.4 min (major), 7.4 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{23}BrN$ 404.1008; Found 404.1000.

(*S*)-5-(1-(3-chlorophenyl)allyl)-1-(4-methoxybenzyl)indoline (3o)



Yellowish oil, 47.6 mg, yield (61%); $[\alpha]_D^{20}$ = -3.0 (c 1.25, $CHCl_3$);

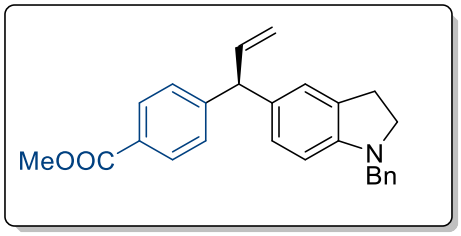
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 3H), 7.23 – 7.13 (m, 3H), 7.10 – 7.05 (m, 1H), 6.90 – 6.81 (m, 4H), 6.48 – 6.42 (m, 1H), 6.27 – 6.18 (m, 1H), 5.23 – 5.17 (m, 1H), 5.01 – 4.93 (m, 1H), 4.61 – 4.54 (m, 1H), 4.15 (s, 2H), 3.80 (d, *J* = 0.7 Hz, 3H), 3.26 (t, *J* = 8.1 Hz, 2H), 2.90 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 151.4, 146.3, 140.7, 134.1, 131.8, 130.6, 130.4, 129.5, 129.2, 128.6, 127.3, 126.8, 126.3, 124.7, 116.2, 113.9, 106.9, 55.3, 54.2, 53.7, 53.3, 28.5.

98% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 1.0 mL/min, l = 254 nm) t_R = 13.1 min (major), 12.3 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{25}ClNO$ 390.1619; Found 390.1613.

methyl (*R*)-4-(1-(1-benzylindolin-5-yl)allyl)benzoate (3p)



Yellowish oil, 54.5 mg, yield (75%); $[\alpha]_D^{20}$ = +0.3 (c 1.25, $CHCl_3$);

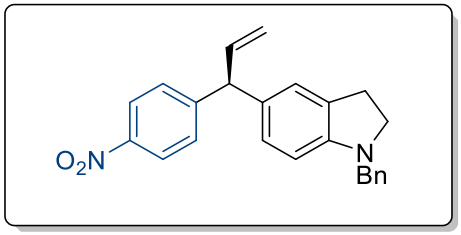
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.37 – 7.29 (m, 4H), 7.29 – 7.21 (m, 3H), 6.90 – 6.86 (m, 1H), 6.86 – 6.82 (m, 1H), 6.45 – 6.40 (m, 1H), 6.30 – 6.20 (m, 1H), 5.22 – 5.17 (m, 1H), 5.00 – 4.94 (m, 1H), 4.68 – 4.64 (m, 1H), 4.21 (s, 2H), 3.88 (s, 3H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.91 (t, *J* = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 151.4, 149.6, 140.6, 138.5, 131.9, 130.6, 129.7, 128.6, 128.5, 128.1, 128.0, 127.4, 127.2, 124.8, 116.3, 106.9, 54.5, 53.9, 53.9, 52.0, 28.6.

>99% *ee* as determined by HPLC (AD-H, *i*-PrOH /*n*-hexane = 3/97, flow rate = 1.0 mL/min, l = 254 nm) t_R = 10.2 min (major), 9.5 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{26}H_{26}NO_2$ 384.1958; Found 384.1968.

(*R*)-1-benzyl-5-(1-(4-nitrophenyl)allyl)indoline (3q)



Brown oil, 35.5 mg, yield (48%); $[\alpha]_D^{20}$ = -1.8 (c 1.25, $CHCl_3$);

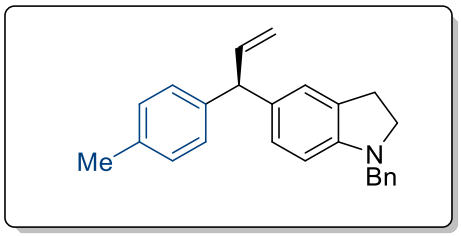
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 2H), 7.38 – 7.30 (m, 6H), 7.29 – 7.25 (m, 1H), 6.88 – 6.85 (m, 1H), 6.85 – 6.80 (m, 1H), 6.46 – 6.42 (m, 1H), 6.28 – 6.20 (m, 1H), 5.27 – 5.21 (m, 1H), 5.03 – 4.95 (m, 1H), 4.74 – 4.67 (m, 1H), 4.23 (s, 2H), 3.31 (t, *J* = 8.3 Hz, 2H), 2.93 (t, *J* = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 151.6, 146.4, 139.9, 138.4, 131.0, 130.8, 129.4, 128.5, 127.9, 127.4, 127.2, 124.7, 123.6, 116.9, 106.9, 54.3, 53.8, 29.7, 28.5.

97% *ee* as determined by HPLC (OJ, *i*-PrOH /*n*-hexane = 10/90, flow rate = 0.5 mL/min, l = 254 nm) t_R = 50.5 min (major), 46.6 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{23}N_2O_2$ 371.1754; Found 371.1761.

(*R*)-1-benzyl-5-(1-(p-tolyl)allyl)indoline (3r)



Yellowish oil, 54.6 mg, yield (79%); $[\alpha]_D^{20}$ = -102.8 (c 1.25, $CHCl_3$);

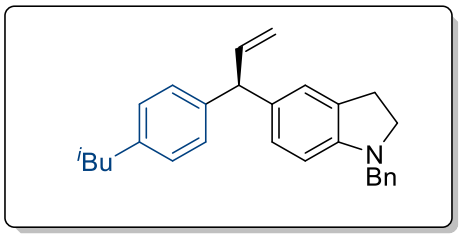
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 7.27 – 7.20 (m, 1H), 7.12 – 7.06 (m, 4H), 6.93 – 6.88 (m, 1H), 6.87 – 6.84 (m, 1H), 6.46 – 6.37 (m, 1H), 6.30 – 6.20 (m, 1H), 5.17 – 5.12 (m, 1H), 5.00 – 4.94 (m, 1H), 4.62 – 4.54 (m, 1H), 4.20 (s, 2H), 3.26 (t, *J* = 8.3 Hz, 2H), 2.90 (t, *J* = 8.2 Hz, 2H), 2.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 141.7, 141.2, 138.7, 135.6, 133.1, 130.4, 129.1, 128.5, 128.5, 128.0, 127.3, 127.1, 124.8, 115.4, 106.9, 54.2, 54.1, 54.0, 28.6, 21.1.

>99% *ee* as determined by HPLC (OJ, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 18.5 min (major), 16.2 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{26}N$ 340.2060; Found 340.2063.

(*R*)-1-benzyl-5-(1-(4-isobutylphenyl)allyl)indoline (3s)



Yellowish oil, 53.5 mg, yield (70%); $[\alpha]_D^{20}$ = -456.8 (c 1.25, $CHCl_3$);

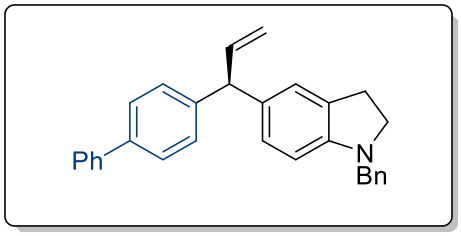
^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 7.27 – 7.21 (m, 1H), 7.11 – 7.08 (m, 2H), 7.07 – 7.03 (m, 2H), 6.94 – 6.90 (m, 1H), 6.88 – 6.84 (m, 1H), 6.45 – 6.40 (m, 1H), 6.32 – 6.23 (m, 1H), 5.17 – 5.13 (m, 1H), 5.00 – 4.93 (m, 1H), 4.63 – 4.55 (m, 1H), 4.20 (s, 2H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.90 (t, *J* = 8.3 Hz, 2H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.90 – 1.77 (m, 1H), 0.89 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 141.7, 141.4, 139.4, 138.7, 133.1, 130.4, 129.1, 128.5, 128.2, 128.0, 127.4, 127.1, 124.9, 115.4, 106.9, 54.3, 54.1, 54.0, 45.1, 30.3, 28.6, 22.5.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 0.5 mL/min, l = 254 nm) t_R = 13.6 min (major), 12.9 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{28}H_{32}N$ 382.2529; Found 382.2533.

(*R*)-5-(1-([1,1'-biphenyl]-4-yl)allyl)-1-benzylindoline (3t)



Yellowish viscous oil, 78.0 mg, yield (97%); mp. = 77.2-79.1 °C; $[\alpha]_D^{20}$ = +0.1 (c 1.25, $CHCl_3$);

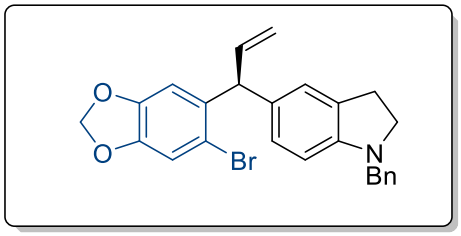
^1H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.54 – 7.49 (m, 2H), 7.44 – 7.39 (m, 2H), 7.38 – 7.29 (m, 5H), 7.29 – 7.23 (m, 3H), 6.98 – 6.93 (s, 1H), 6.92 – 6.88 (m, 1H), 6.47 – 6.42 (m, 1H), 6.35 – 6.26 (m, 1H), 5.23 – 5.17 (m, 1H), 5.06 – 4.98 (m, 1H), 4.69 – 4.61 (m, 1H), 4.22 (s, 2H), 3.29 (t, *J* = 8.3 Hz, 2H), 2.93 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 143.3, 141.3, 141.0, 139.0, 138.6, 132.7, 130.4, 128.9, 128.7, 128.5, 127.9, 127.3, 127.1, 127.0, 127.0, 124.8, 115.7, 106.8, 54.2, 54.0, 53.9, 28.6.

98% *ee* as determined by HPLC (AD-H, *i*-PrOH /*n*-hexane = 3/97, flow rate = 1.0 mL/min, l = 254 nm) t_R = 5.6 min (major), 5.2 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{30}H_{28}N$ 402.2216; Found 402.2210.

(*S*)-1-benzyl-5-(1-(6-bromobenzo[d][1,3]dioxol-5-yl)allyl)indoline (3u)



Green oil, 87.8 mg, yield (98%); $[\alpha]_D^{20}$ = -13.5 (c 1.25, $CHCl_3$);

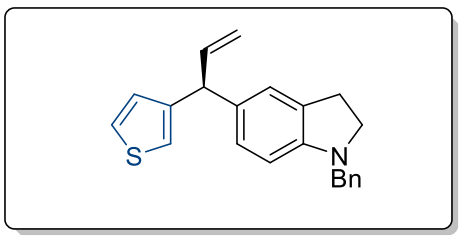
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 4H), 7.27 – 7.23 (m, 1H), 7.03 – 6.98 (m, 1H), 6.92 – 6.88 (m, 1H), 6.87 – 6.84 (m, 1H), 6.67 – 6.63 (m, 1H), 6.45 – 6.40 (m, 1H), 6.20 – 6.12 (m, 1H), 5.91 (dd, *J* = 7.3, 1.3 Hz, 2H), 5.22 – 5.17 (m, 1H), 5.18 – 5.03 (m, 1H), 4.93 – 4.86 (m, 1H), 4.21 (s, 2H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.92 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.4, 147.3, 146.6, 140.1, 138.6, 136.4, 131.3, 130.4, 128.5, 128.0, 127.5, 127.1, 125.0, 116.4, 115.0, 112.7, 110.0, 106.8, 101.6, 54.0, 53.9, 52.6, 28.6.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 9.4 min (major), 16.4 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{23}BrNO_2$ 448.0907; Found 448.0911.

(*S*)-1-benzyl-5-(1-(thiophen-3-yl)allyl)indoline (3v)



Yellowish oil, 56.9 mg, yield (86%); $[\alpha]_D^{20}$ = +264.8 (c 1.25, $CHCl_3$);

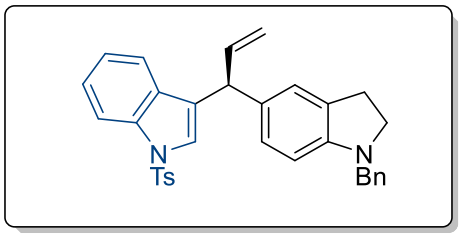
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.28 – 7.22 (m, 2H), 6.94 – 6.91 (m, 2H), 6.91 – 6.87 (m, 2H), 6.46 – 6.41 (m, 1H), 6.28 – 6.19 (m, 1H), 5.16 – 5.12 (m, 1H), 5.05 – 4.99 (m, 1H), 4.65 – 4.61 (m, 1H), 4.21 (s, 2H), 3.29 (t, *J* = 8.3 Hz, 2H), 2.92 (t, *J* = 8.3 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 145.0, 141.1, 138.6, 132.5, 130.4, 128.5, 128.3, 127.9, 127.1, 127.1, 125.2, 124.5, 121.1, 115.1, 106.9, 54.0, 53.9, 50.4, 28.6.

99% *ee* as determined by HPLC (OJ, *i*-PrOH /*n*-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) t_R = 39.5 min (major), 30.1 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{22}H_{22}NS$ 332.1467; Found 332.1457.

(*S*)-3-(1-(1-benzylindolin-5-yl)allyl)-1-tosyl-1H-indole (3w)



Green oil, 88.2 mg, yield (85%); $[\alpha]_D^{20}$ = +13.2 (c 1.25, $CHCl_3$);

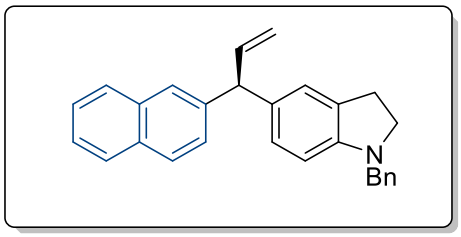
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 1H), 7.74 – 7.69 (m, 2H), 7.37 – 7.28 (m, 5H), 7.28 – 7.22 (m, 3H), 7.20 – 7.16 (m, 2H), 7.14 – 7.09 (m, 1H), 6.90 – 6.87 (m, 1H), 6.85 – 6.81 (m, 1H), 6.42 – 6.38 (m, 1H), 6.27 – 6.19 (m, 1H), 5.18 – 5.13 (m, 1H), 5.01 – 4.94 (m, 1H), 4.73 – 4.68 (m, 1H), 4.21 (s, 2H), 3.28 (t, *J* = 8.3 Hz, 2H), 2.89 (td, *J* = 8.0, 3.4 Hz, 2H), 2.31 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 144.7, 139.7, 138.6, 135.7, 135.3, 130.6, 130.5, 130.5, 129.8, 128.5, 128.0, 127.2, 126.8, 126.1, 124.6, 124.5, 124.1, 123.0, 120.7, 115.8, 113.8, 106.9, 54.0, 53.9, 46.1, 28.6, 21.6.

96% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 15.7 min (major), 18.2 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{33}H_{31}N_2O_2S$ 519.2101; Found 519.2101.

(*R*)-1-benzyl-5-(1-(naphthalen-2-yl)allyl)indoline (3x)



Yellowish viscous oil, 70.7 mg, yield (94%); $[\alpha]_D^{20}$ = +6.4 (c 1.25, $CHCl_3$);

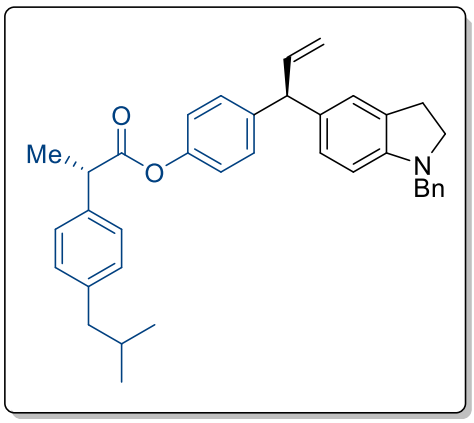
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.72 (m, 3H), 7.67 – 7.63 (m, 1H), 7.46 – 7.39 (m, 2H), 7.38 – 7.29 (m, 5H), 7.28 – 7.22 (m, 1H), 6.95 – 6.88 (m, 2H), 6.47 – 6.42 (m, 1H), 6.41 – 6.33 (m, 1H), 5.26 – 5.18 (m, 1H), 5.07 – 4.99 (m, 1H), 4.82 – 4.73 (m, 1H), 4.21 (s, 2H), 3.27 (t, *J* = 8.3 Hz, 2H), 2.90 (t, *J* = 8.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.2, 141.6, 141.2, 138.6, 133.5, 132.6, 132.1, 130.4, 128.5, 127.9, 127.8, 127.8, 127.6, 127.5, 127.5, 127.1, 126.6, 125.8, 125.4, 124.9, 115.9, 106.8, 54.6, 54.0, 53.9, 28.5.

98% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) t_R = 44.6 min (major), 53.7 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{28}H_{26}N$ 376.2060; Found 376.2065.

4-((*R*)-1-(1-benzylindolin-5-yl)allyl)phenyl (*S*)-2-(4-isobutylphenyl)propanoate (3y)



Yellowish oil, 94.3 mg, yield (89%); $[\alpha]_D^{20}$ = -120.7 (c 1.25, $CHCl_3$);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 7H), 7.16 – 7.10 (m, 4H), 6.93 – 6.88 (m, 2H), 6.87 – 6.84 (s, 1H), 6.84 – 6.80 (m, 1H), 6.45 – 6.40 (m, 1H), 6.26 – 6.17 (m, 1H), 5.17 – 5.13 (m, 1H),

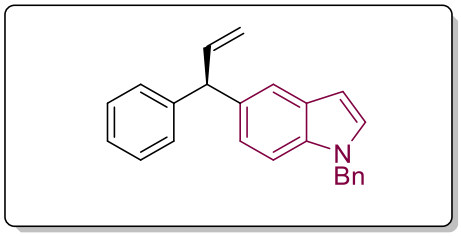
4.98 – 4.92 (m, 1H), 4.63 – 4.55 (m, 1H), 4.20 (s, 2H), 3.91 (q, *J* = 7.1 Hz, 1H), 3.26 (t, *J* = 8.3 Hz, 2H), 2.89 (t, *J* = 8.2 Hz, 2H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.90 – 1.81 (m, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 173.3, 151.3, 149.2, 141.5, 141.2, 140.8, 138.6, 137.3, 132.5, 130.4, 129.5, 129.4, 128.5, 128.0, 127.4, 127.3, 127.1, 124.8, 121.1, 115.8, 106.8, 54.0, 53.9, 53.9, 45.3, 45.1, 30.2, 28.6, 22.5, 18.6.

93% *ee*, >20/1 *dr* as determined by HPLC (AD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 1.0 mL/min, l = 254 nm) t_R = 31.1 min (major), 26.9 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{37}H_{40}NO$ 529.7240; Found 529.7244.

(*R*)-1-benzyl-5-(1-phenylallyl)-1H-indole (4a)



White solid, 53.0 mg, yield (82%); mp. = 51.7-53.0 °C; $[\alpha]_D^{20}$ = +2.2 (c 1.25, $CHCl_3$);

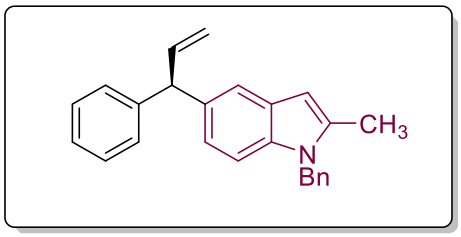
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 1H), 7.29 – 7.21 (m, 7H), 7.20 – 7.16 (m, 2H), 7.11 – 7.07 (m, 3H), 7.01 – 6.97 (m, 1H), 6.49 – 6.46 (m, 1H), 6.41 – 6.33 (m, 1H), 5.26 (s, 2H), 5.21 – 5.18 (m, 1H), 5.02 – 4.97 (m, 1H), 4.84 – 4.80 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 141.6, 137.6, 135.2, 134.6, 128.8, 128.8, 128.7, 128.5, 128.3, 127.6, 126.9, 126.1, 123.0, 120.5, 115.8, 109.6, 101.7, 55.1, 50.2.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 1.0 mL/min, l = 254 nm) t_R = 29.1 min (major), 21.7 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{22}N$ 324.1747; Found 324.1746.

(*R*)-1-benzyl-2-methyl-5-(1-phenylallyl)-1H-indole (4b)



Yellowish solid, 49.2 mg, yield (73%); mp. = 92.1-93.4 °C; $[\alpha]_D^{20}$ = 0.5 (c 1.25, $CHCl_3$);

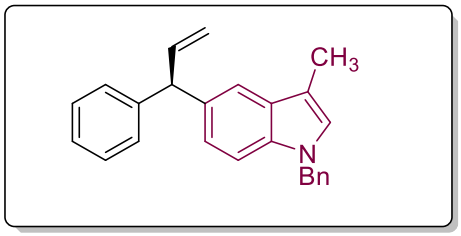
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 1H), 7.28 – 7.16 (m, 8H), 7.12 – 7.08 (m, 1H), 6.98 – 6.95 (m, 2H), 6.94 – 6.89 (m, 1H), 6.42 – 6.33 (m, 1H), 6.27 – 6.24 (m, 1H), 5.24 (s, 2H), 5.21 – 5.16 (m, 1H), 5.02 – 4.96 (m, 1H), 4.83 – 4.79 (m, 1H), 2.25 (d, *J* = 5.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 141.6, 137.9, 136.9, 136.0, 134.5, 128.7, 128.7, 128.2, 128.2, 127.2, 126.0, 126.0, 121.9, 119.3, 115.6, 109.1, 100.4, 55.1, 46.5, 12.8.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 1.0 mL/min, l = 254 nm) t_R = 16.0 min (major), 14.1 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{24}N$ 338.1903; Found 338.1897.

(*R*)-1-benzyl-3-methyl-5-(1-phenylallyl)-1H-indole (4c)



Yellowish oil, 49.9 mg, yield (74%); $[\alpha]_D^{20}$ = -0.9 (c 1.25, $CHCl_3$);

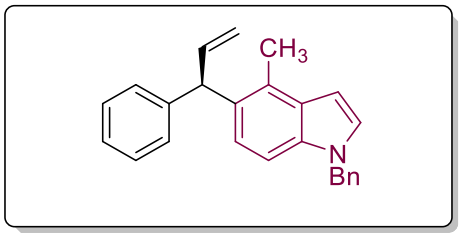
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 1H), 7.29 – 7.21 (m, 7H), 7.18 – 7.14 (m, 2H), 7.14 – 7.08 (m, 2H), 7.00 – 6.96 (m, 1H), 6.87 – 6.84 (m, 1H), 6.43 – 6.35 (m, 1H), 5.23 – 5.18 (m, 1H), 5.22 – 5.20 (s, 1H), 5.04 – 5.98 (m, 1H), 4.86 – 4.82 (m, 1H), 2.29 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 141.7, 137.9, 135.5, 133.9, 129.0, 128.7, 128.7, 128.3, 127.5, 126.9, 126.1, 126.1, 122.8, 118.6, 115.8, 110.8, 109.4, 55.2, 49.9, 9.7.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 1.0 mL/min, l = 254 nm) t_R = 19.6 min (major), 21.4 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{24}N$ 338.1903; Found 338.1899.

(*R*)-1-benzyl-4-methyl-5-(1-phenylallyl)-1H-indole (4d)



Yellowish oil, 43.1 mg, yield (64%); $[\alpha]_D^{20}$ = -13.3 (c 1.25, $CHCl_3$);

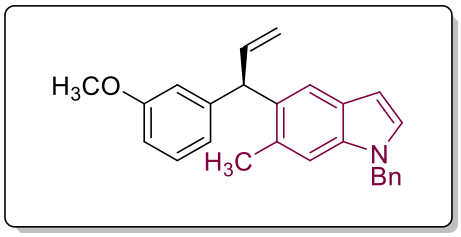
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 5H), 7.19 – 7.11 (m, 5H), 7.11 – 7.07 (m, 2H), 6.99 – 6.95 (m, 1H), 6.57 – 6.53 (m, 1H), 6.38 – 6.30 (m, 1H), 5.26 (s, 2H), 5.22 – 5.18 (m, 1H), 5.11 – 5.06 (m, 1H), 4.92 – 4.85 (d, *J* = 7.2 Hz, 1H), 2.48 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 141.3, 137.6, 134.9, 131.7, 129.4, 128.9, 128.8, 128.2, 128.1, 127.8, 127.6, 126.9, 125.9, 123.0, 115.8, 107.2, 100.5, 50.7, 50.2, 15.3.

>99% *ee* as determined by HPLC (AD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 6.8 min (major), 4.6 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{24}N$ 338.1903; Found 338. 1901.

(*R*)-1-benzyl-5-(1-(3-methoxyphenyl)allyl)-6-methyl-1H-indole (4e)



Orange oil, 63.1 mg, yield (86%); $[\alpha]_D^{20}$ = -13.3 (c 1.25, $CHCl_3$);

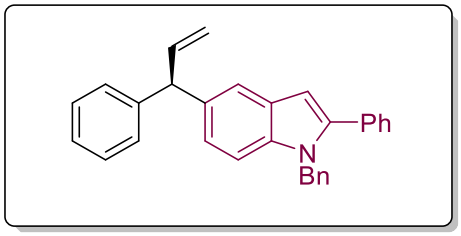
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 1H), 7.31 – 7.23 (m, 3H), 7.20 – 7.15 (m, 1H), 7.14 – 7.09 (m, 2H), 7.08 – 7.04 (m, 1H), 7.03 – 6.99 (m, 1H), 6.78 – 6.70 (m, 3H), 6.47 – 6.43 (m, 1H), 6.39 – 6.31 (m, 1H), 5.26 (s, 2H), 5.23 – 5.19 (m, 1H), 4.95 – 4.91 (m, 1H), 4.89 – 4.83 (m, 1H), 3.74 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 145.0, 141.4, 137.8, 135.5, 133.1, 130.6, 129.1, 128.8, 127.6, 127.5, 126.9, 126.8, 121.6, 120.7, 115.9, 115.1, 111.0, 110.8, 101.5, 55.1, 51.4, 50.0, 20.7.

99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 30.4 min (major), 37.8 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{26}H_{26}NO$ 368.2009; Found 368.2008.

(*R*)-1-benzyl-2-phenyl-5-(1-phenylallyl)-1H-indole (4f)



Yellowish oil, 55.2 mg, yield (69%); $[\alpha]_D^{20}$ = +0.3 (c 1.25, $CHCl_3$);

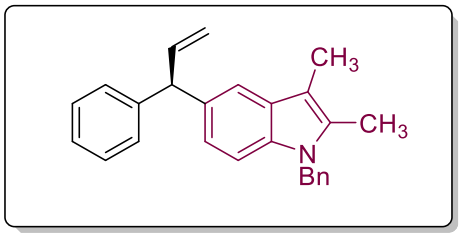
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 1H), 7.43 – 7.40 (m, 2H), 7.39 – 7.33 (m, 3H), 7.30 – 7.18 (m, 8H), 7.12 – 7.08 (m, 1H), 7.06 – 7.01 (m, 1H), 7.00 – 6.95 (m, 1H), 6.60 – 6.55 (m, 1H), 6.43 – 6.34 (m, 1H), 5.32 (s, 2H), 5.24 – 5.18 (m, 1H), 5.05 – 4.98 (m, 1H), 4.86 – 4.82 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 142.1, 141.5, 138.3, 136.9, 135.3, 132.7, 129.2, 128.7, 128.7, 128.6, 128.4, 128.3, 128.0, 127.2, 126.1, 126.1, 123.2, 120.1, 115.8, 110.5, 102.3, 55.1, 47.84.

86% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 0.5 mL/min, l = 254 nm) t_R = 18.0 min (major), 19.7 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{30}H_{26}N$ 400.2060; Found 400.2064.

(*R*)-1-benzyl-2,3-dimethyl-5-(1-phenylallyl)-1H-indole (4g)



Yellowish oil, 50.5 mg, yield (72%); $[\alpha]_D^{20}$ = +2.9 (c 1.25, $CHCl_3$);

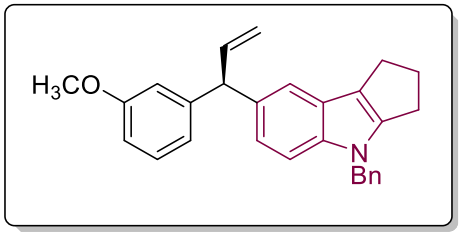
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 1H), 7.27 – 7.16 (m, 8H), 7.12 – 7.08 (m, 1H), 7.00 – 6.95 (m, 2H), 6.93 – 6.89 (m, 1H), 6.44 – 6.35 (m, 1H), 5.24 (s, 2H), 5.22 – 5.18 (m, 1H), 5.03 – 4.98 (m, 1H), 4.86 – 4.82 (m, 1H), 2.25 (d, *J* = 5.2 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 141.7, 138.3, 135.2, 133.8, 132.7, 128.7, 128.7, 128.6, 128.2, 127.1, 126.1, 126.00, 121.8, 117.6, 115.6, 108.7, 106.9, 55.2, 46.6, 10.2, 8.9.

99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 0.5 mL/min, l = 254 nm) t_R = 12.4 min (major), 13.1 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{26}H_{26}N$ 352.2060; Found 352.2066.

(*S*)-4-benzyl-7-(1-(3-methoxyphenyl)allyl)-1,2,3,4-tetrahydrocyclopenta[b]indole (4h)



Reddish oil, 56.7 mg, yield (72%); mp. = 79.5-80.0 °C; $[\alpha]_D^{20}$ = -1.2 (c 1.25, $CHCl_3$);

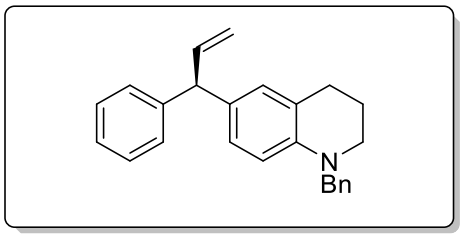
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 9H), 7.20 – 7.15 (m, 1H), 7.13 – 7.05 (m, 3H), 6.92 – 6.86 (m, 1H), 6.43 – 6.33 (m, 1H), 5.24 – 5.15 (m, 1H), 5.17 (s, 2H), 5.03 – 4.95 (m, 1H), 4.85 – 4.77 (m, 1H), 2.83 (d, *J* = 6.9 Hz, 1H), 2.73 (d, *J* = 6.7 Hz, 6H), 2.48 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 144.5, 141.7, 140.0, 138.1, 134.2, 128.7, 128.7, 128.3, 127.4, 126.7, 126.0, 124.6, 121.3, 118.3, 118.2, 115.7, 109.8, 55.2, 48.4, 28.5, 25.2, 24.8.

96% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 1.0 mL/min, l = 254 nm) t_R = 14.2 min (major), 16.0 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{28}H_{28}NO$ 394.2165; Found 394.2168.

(*R*)-1-benzyl-6-(1-phenylallyl)-1,2,3,4-tetrahydroquinoline (5a)



Light green solid, 38.6 mg, yield (57%); mp. = 61.7-62.9 °C; $[\alpha]_D^{20}$ = +3.8 (c 1.25, $CHCl_3$);

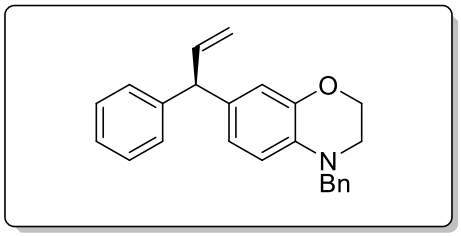
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.15 (m, 10H), 6.81 – 6.74 (m, 2H), 6.47 – 6.42 (m, 1H), 6.30 – 6.21 (m, 1H), 5.17 – 5.12 (m, 1H), 5.00 – 4.93 (m, 1H), 4.58 – 4.54 (m, 1H), 4.42 (s, 2H), 3.35 – 3.28 (m, 2H), 2.76 (t, *J* = 6.2 Hz, 2H), 2.02 – 1.94 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 144.2, 141.5, 139.2, 130.6, 129.1, 128.6, 128.3, 127.1, 126.80, 126.7, 126.1, 122.2, 115.5, 111.0, 55.5, 54.3, 49.9, 28.3, 22.5.

98% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 3/97, flow rate = 1.0 mL/min, l = 254 nm) t_R = 6.3 min (major), 5.9 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{26}N$ 340.2060; Found 340.2058.

(*R*)-4-benzyl-7-(1-phenylallyl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (5b)



Yellowish oil, 32.7 mg, yield (48%); $[\alpha]_D^{20}$ = +1.6 (c 1.25, $CHCl_3$);

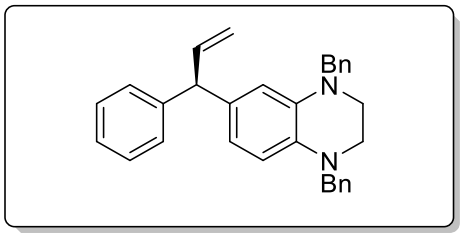
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 7H), 7.21 – 7.16 (m, 3H), 6.67 – 6.64 (m, 1H), 6.62 – 6.57 (m, 2H), 6.30 – 6.20 (m, 1H), 5.18 – 5.14 (m, 1H), 5.03 – 4.95 (m, 1H), 4.59 – 4.55 (m, 1H), 4.39 (s, 2H), 4.25 (dd, *J* = 5.6, 3.3 Hz, 2H), 3.33 – 3.29 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 143.8, 141.1, 138.3, 134.2, 133.2, 128.8, 128.6, 128.4, 127.3, 127.3, 126.3, 121.6, 116.6, 115.9, 112.6, 64.9, 55.3, 54.3, 47.4.

82% *ee* as determined by HPLC (AD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 5.5 min (major), 6.1 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{24}NO$ 342.1852; Found 342.1856.

(*R*)-1,4-dibenzyl-6-(1-phenylallyl)-1,2,3,4-tetrahydroquinoxaline (5c)



Brown oil, 43.1 mg, yield (50%); $[\alpha]_D^{20}$ = +1.8 (c 1.25, $CHCl_3$);

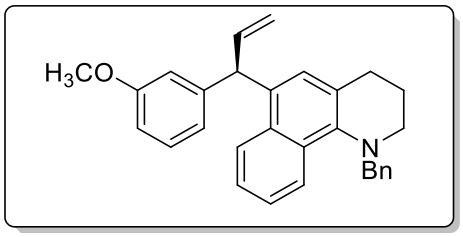
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 6H), 7.25 – 7.19 (m, 6H), 7.15 – 7.08 (m, 3H), 6.51 – 6.46 (m, 1H), 6.43 – 6.37 (m, 2H), 6.23 – 6.13 (m, 1H), 5.09 – 5.05 (m, 1H), 4.94 – 4.83 (m, 1H), 4.51 – 4.42 (m, 1H), 4.39 (s, 2H), 4.35 (d, *J* = 2.9 Hz, 2H), 3.39 – 3.32 (m, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 141.3, 138.8, 138.6, 135.6, 134.4, 132.9, 128.6, 128.6, 128.5, 128.2, 127.4, 127.3, 127.0, 126.9, 126.0, 118.0, 115.4, 112.2, 111.4, 55.8, 55.6, 54.7, 48.0, 47.9.

98% *ee* as determined by HPLC (AD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 5.5 min (major), 4.8 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{31}H_{31}N_2$ 431.2482; Found 431.2481.

(*R*)-1-benzyl-6-(1-(3-methoxyphenyl)allyl)-1,2,3,4-tetrahydrobenzo[h]quinoline (5d)



Yellowish oil, 61.3 mg, yield (73%); $[\alpha]_D^{20}$ = -11.8 (c 1.25, $CHCl_3$);

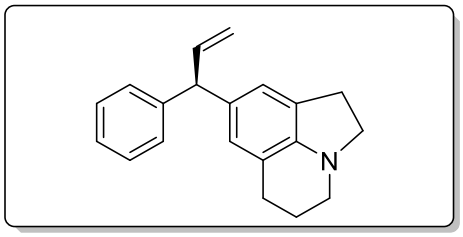
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 – 8.16 (m, 1H), 7.94 – 7.89 (m, 1H), 7.64 – 7.59 (m, 2H), 7.46 – 7.41 (m, 2H), 7.35 – 7.29 (m, 3H), 7.22 – 7.18 (m, 1H), 7.03 (s, 1H), 6.85 – 6.72 (m, 3H), 6.44 – 6.36 (m, 1H), 5.39 – 5.33 (m, 1H), 5.28 – 5.24 (m, 1H), 4.98 – 4.91 (m, 1H), 4.32 (s, 2H), 3.76 (s, 3H), 3.19 – 3.12 (m, 2H), 2.90 (td, *J* = 6.6, 1.2 Hz, 2H), 1.94 – 1.85 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 144.9, 143.4, 140.8, 139.8, 132.4, 131.6, 129.4, 129.3, 128.6, 128.5, 127.4, 127.0, 125.0, 24.9, 124.7, 124.6, 123.4, 121.4, 116.6, 115.1, 111.1, 59.2, 55.2, 50.6, 46.9, 28.0, 16.5.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 10.4 min (major), 5.3 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{30}H_{30}NO$ 420.2322; Found 420.2320.

(*R*)-8-(1-phenylallyl)-1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-ij]quinoline (5e)



Light green oil, 41.3 mg, yield (75%); $[\alpha]_D^{20}$ = +1.3 (c 1.25, $CHCl_3$);

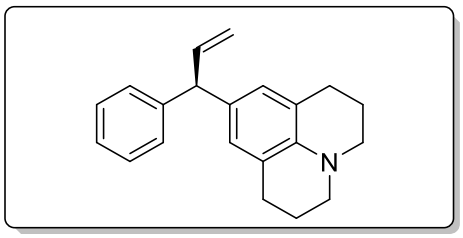
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.24 – 7.15 (m, 3H), 6.78 – 6.72 (m, 1H), 6.70 – 6.62 (m, 1H), 6.32 – 6.22 (m, 1H), 5.19 – 5.12 (m, 1H), 5.03 – 4.93 (m, 1H), 4.65 – 4.55 (m, 1H), 3.22 (t, *J* = 7.6 Hz, 2H), 2.99 – 2.92 (m, 2H), 2.85 (t, *J* = 7.7 Hz, 2H), 2.64 (t, *J* = 6.5 Hz, 2H), 2.07 (dt, *J* = 11.4, 5.9 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 144.3, 141.6, 133.8, 129.0, 128.6, 128.3, 126.3, 126.0, 122.2, 119.3, 115.5, 55.4, 54.9, 47.6, 28.8, 24.0, 23.3.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 1.0 mL/min, l = 254 nm) t_R = 4.7 min (major), 7.4 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{20}H_{22}N$ 276.1747; Found 276.1752.

(*R*)-9-(1-phenylallyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline (5f)



Reddish oil, 31.2 mg, yield (54%); $[\alpha]_D^{20}$ = -5.3 (c 1.25, $CHCl_3$);

^1H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.22 – 7.14 (m, 3H), 6.62 – 6.57 (m, 2H), 6.30 – 6.21 (m, 1H), 5.17 – 5.12 (m, 1H), 5.00 – 4.94 (m, 1H), 4.54 – 4.90 (m, 1H), 3.10 – 3.05 (m, 4H), 2.70 (t, *J* = 6.6 Hz, 4H), 1.98 – 1.90 (m, 4H).

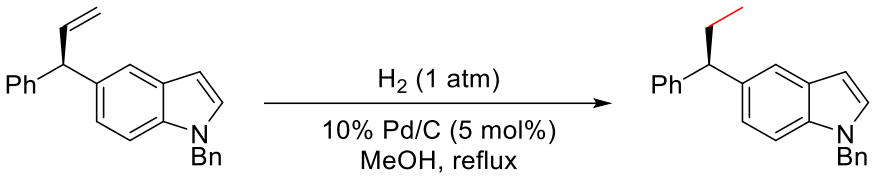
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 141.5, 141.5 130.5, 128.5, 128.2, 126.9, 126.0, 121.6, 115.3, 54.4, 50.1, 27.6, 22.2.

97% *ee* as determined by HPLC (OJ, *i*-PrOH /*n*-hexane = 5/95, flow rate = 1.0 mL/min, l = 254 nm) t_R = 7.5 min (major), 8.7 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{21}H_{24}N$ 290.1903; Found 290.1902.

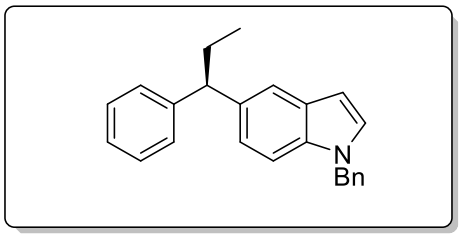
V. Transformations of Compound 4a

4.1. Pd/C-catalyzed Hydrogenation of Compound 4a:



The synthetic protocol of substituted indolines were accorded to the relevant literature. In a glove box, a 10 mL oven-dried flask charged with stir bar, allyl indole (0.1 mmol, 1.0 equiv), 10% Pd/C (0.005 mmol, 5 mol%) and MeOH (2 mL). The organic mixture was reacted under the H_2 (1 atm) and then oil bath heated to reflux to stir for 12 h until the starting material was consumed completely detected by TLC. The solution was filtrated with celite and the filtrate was concentrated under the reduced pressure. The residue was purified by column chromatography to afford the desired compound **6** as a yellowish oil, affording 20.5 mg of **6** in 63% yield and 93% ee.

(*R*)-1-benzyl-5-(1-phenylpropyl)-1H-indole (6)



Yellowish oil, 20.5 mg, yield (63%); $[\alpha]_D^{20}$ = -0.7 (c 1.25, $CHCl_3$);

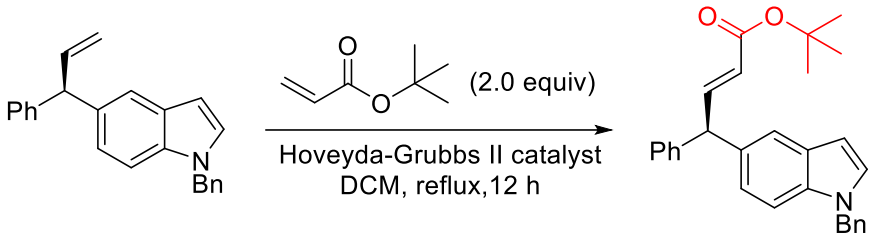
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.31 – 7.24 (m, 8H), 7.18 – 7.00 (m, 6H), 6.50 – 6.45 (m, 1H), 5.26 (s, 2H), 3.87 (t, *J* = 7.6 Hz, 1H), 2.15 – 2.09 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 137.6, 136.4, 135.0, 128.7, 128.7, 128.3, 128.2, 128.0, 127.6, 126.0, 125.7, 122.4, 119.6, 109.5, 101.5, 53.3, 50.1, 29.0, 13.0.

93% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 0.8/99.2, flow rate = 1.0 mL/min, l = 254 nm) t_R = 23.0 min (major), 28.3 min (minor).

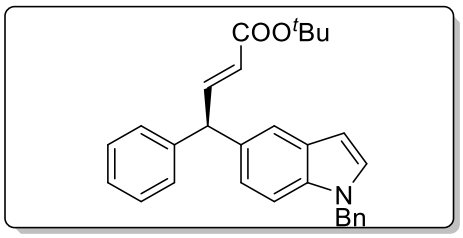
HRMS (ESI) m/z: [M + H]+ Calcd for $C_{24}H_{24}N$ 326.1903; Found 326.1897.

4.2. Ru-catalyzed Olefin Metathesis of Compound 4a:



To an oven-dried flask charged with stir bar and Hoveyda-Grubbs II catalyst (0.0045 mmol, 4.5 mol%) carefully refilled with argon 3 times, then followed by anhydrous DCM (0.2 M), allyl indole (0.1 mmol, 1.0 equiv) and tert-butyl acylate (0.2 mmol, 2.0 equiv). The homogeneous solution was oil bath heated to reflux and stirred for 12 h. After completion, the solvent was removed under the reduced pressure and the residue was purified by flash chromatography to give the product **7** as a yellowish solid, affording 23.7 mg of **7** in 56% yield.

tert-butyl (*R*,*E*)-4-(1-benzyl-1H-indol-5-yl)-4-phenylbut-2-enoate (7)



Yellowish solid, 23.7 mg, yield (56%); mp. = 116.7-118.0 °C; $[\alpha]_D^{20}$ = +1.6 (c 1.25, $CHCl_3$);

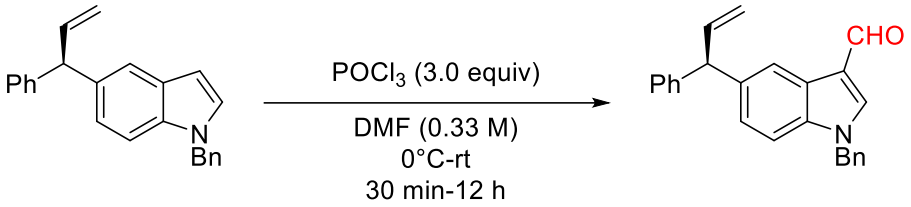
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.43 (m, 1H), 7.42 – 7.35 (m, 1H), 7.28 – 7.16 (m, 9H), 7.14 – 7.10 (m, 3H), 6.98 – 6.94 (m, 1H), 6.51 – 6.46 (m, 1H), 5.70 – 5.63 (m, 1H), 5.29 (s, 2H), 4.97 – 4.90 (m, 1H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 149.6, 142.7, 137.4, 135.3, 133.0, 128.9, 128.8, 128.7, 128.7, 128.5, 127.7, 126.9, 126.6, 124.2, 122.8, 120.7, 109.9, 101.7, 80.3, 53.4, 50.2, 28.2.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 4/96, flow rate = 0.5 mL/min, l = 254 nm) t_R = 46.3 min (major), 42.4 min (minor).

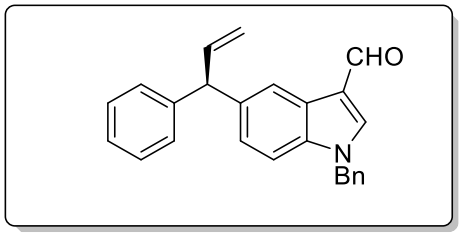
HRMS (ESI) m/z: [M + H]+ Calcd for $C_{29}H_{30}NO_2$ 424.2271; Found 424.2269.

.3. Vilsmeier-Haack Formylation of Compound 4a:



To an oven-dried flask charged with stir bar and allyl indole (0.1 mmol, 1.0 equiv) refilled with argon twice, followed by anhydrous DMF solvent (0.33mL). The system was cooled at 0°C atmosphere (ice-bath). 3.0 equivalent of $POCl_3$ was added to the reaction mixture dropwise over 5 min via syringe. Afterwards, the mixture was proceeded 30 min under the same condition, then removed from ice-bath and warmed to ambient temperature to stir for another 12 h. The mixture was quenched and washed with cool water (10 mL) and extracted with Et_2O (3×10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, concentrated *in vacuo* and purified by the flash chromatography to give the product **8** as a yellowish oil, affording 27.0 mg of **8** in 77% yield.

(*R*)-1-benzyl-5-(1-phenylallyl)-1H-indole-3-carbaldehyde (8)



Yellowish oil, 27.0 mg, yield (77%); $[\alpha]_D^{20}$ = +1.5 (c 1.25, $CHCl_3$);

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.25 – 8.20 (m, 1H), 7.70 – 7.64 (m, 1H), 7.36 – 7.31 (m, 3H), 7.29 – 7.15 (m, 8H), 7.13 – 7.08 (m, 1H), 6.42 – 6.34 (m, 1H), 5.30 (s, 2H), 5.25 – 5.20 (m, 1H), 5.04 – 4.98 (m, 1H), 4.89 – 4.85 (m, 1H).

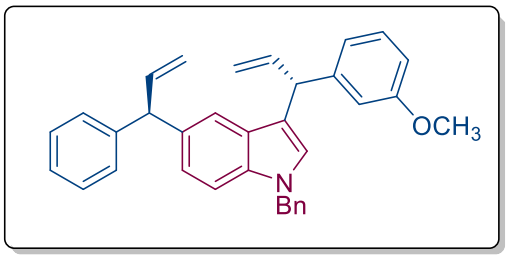
^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6, 143.8, 140.9, 138.7, 138.7, 136.3, 135.3, 129.1, 128.6, 128.4, 128.4, 127.3, 126.3, 125.7, 125.2, 121.8, 118.5, 116.4, 110.4, 55.1, 51.0.

>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 10/90, flow rate = 1.0 mL/min, l = 254 nm) t_R = 20.1 min (major), 24.3 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{22}NO$ 368.1645; Found 368.1645.

VI. Enantiodivergent Synthesis of Compound 9a-d

1-benzyl-3-((*R*)-1-(3-methoxyphenyl)allyl)-5-((*R*)-1-phenylallyl)-1H-indole (9a)



Yellowish oil, 79.9 mg, yield (85%); $[\alpha]_D^{20}$ = +3.7 (c 1.25, $CHCl_3$);

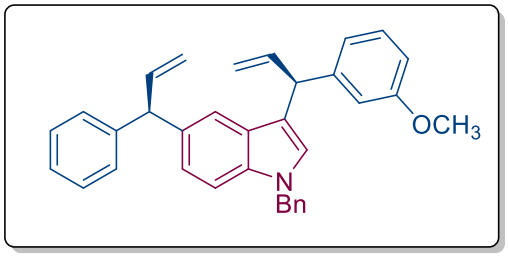
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 7H), 7.17 – 7.11 (m, 4H), 7.11 – 7.06 (m, 2H), 6.97 – 6.93 (m, 1H), 6.89 – 6.86 (m, 1H), 6.84 – 6.81 (m, 1H), 6.81 – 6.78 (m, 1H), 6.76 – 6.72 (m, 1H), 6.34 – 6.24 (m, 2H), 5.21 (s, 2H), 5.17 – 5.13 (m, 2H), 5.09 – 5.03 (m, 1H), 4.97 – 4.92 (m, 1H), 4.92 – 4.87 (m, 1H), 4.77 – 4.71 (m, 1H), 3.73 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 145.0, 144.2, 141.5, 140.4, 137.8, 135.8, 134.0, 129.2, 128.7, 128.6, 128.2, 127.6, 127.5, 126.9, 126.7, 126.0, 122.9, 120.9, 119.6, 117.5, 115.6, 115.4, 114.2, 111.6, 109.6, 55.1, 55.1, 50.1, 47.0.

>20/1 *dr* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) t_R = 25.1 min (major), 18.7 min (minor), 21.5 min (minor), 23.8 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{34}H_{32}NO$ 470.2478; Found 470.2479.

1-benzyl-3-((*S*)-1-(3-methoxyphenyl)allyl)-5-((*R*)-1-phenylallyl)-1H-indole (9b)



Yellowish oil, 79.9 mg, yield (85%); $[\alpha]_D^{20}$ = -18.1 (c 1.25, $CHCl_3$);

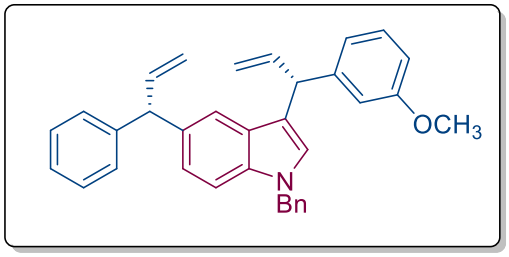
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 7H), 7.19 – 7.14 (m, 3H), 7.14 – 7.10 (m, 1H), 7.09 – 7.05 (m, 2H), 6.97 – 6.92 (m, 1H), 6.89 – 6.85 (m, 1H), 6.84 – 6.82 (m, 1H), 6.81 – 6.75 (m, 1H), 6.74 – 6.73 (m, 1H), 6.35 – 6.23 (m, 2H), 5.19 (s, 2H), 5.17 – 5.11 (m, 2H), 5.10 – 5.03 (m, 1H), 4.97 – 4.92 (m, 1H), 4.92 – 4.87 (m, 1H), 4.77 – 4.71 (m, 1H), 3.73 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 145.0, 144.2, 141.5, 140.4, 137.8, 135.8, 134.0, 129.2, 128.7, 128.6, 128.2, 127.6, 127.5, 126.9, 126.7, 126.0, 122.9, 120.9, 119.6, 117.5, 115.6, 115.4, 114.2, 111.6, 109.6, 55.1, 55.1, 50.1, 47.0.

>20/1 *dr* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) t_R = 22.0 min (major), 19.8 min (minor), 25.7 min (minor), 26.4 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{34}H_{32}NO$ 470.2478; Found 470.2476.

1-benzyl-3-((*R*)-1-(3-methoxyphenyl)allyl)-5-((*S*)-1-phenylallyl)-1H-indole (9c)



Yellowish oil, 78.0 mg, yield (83%); $[\alpha]_D^{20}$ = +16.8 (c 1.25, $CHCl_3$);

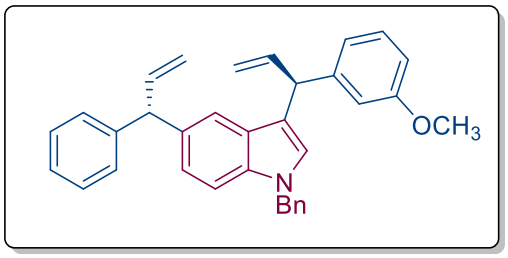
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 7H), 7.18 – 7.14 (m, 3H), 7.13 – 7.10 (m, 1H), 7.09 – 7.05 (m, 2H), 6.96 – 6.92 (m, 1H), 6.89 – 6.86 (m, 1H), 6.85 – 6.82 (m, 1H), 6.80 – 6.77 (m, 1H), 6.76 – 6.72 (m, 1H), 6.33 – 6.24 (m, 2H), 5.20 (s, 2H), 5.17 – 5.12 (m, 2H), 5.09 – 5.03 (m, 1H), 4.97 – 4.91 (m, 1H), 4.91 – 4.86 (m, 1H), 4.77 – 4.72 (m, 1H), 3.73 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 145.0, 144.2, 141.5, 140.4, 137.8, 135.9, 134.0, 129.3, 128.7, 128.6, 128.3, 127.6, 127.5, 126.9, 126.7, 126.1, 122.9, 120.9, 119.6, 117.5, 115.7, 115.4, 114.2, 111.7, 109.6, 55.2, 55.1, 50.1, 47.0.

>20/1 *dr* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) t_R = 18.4 min (major), 21.8 min (minor), 24.1 min (minor), 24.6 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{34}H_{32}NO$ 470.2478; Found 470.2475.

1-benzyl-3-((*S*)-1-(3-methoxyphenyl)allyl)-5-((*S*)-1-phenylallyl)-1H-indole (9d)



Yellowish oil, 79.0 mg, yield (84%); $[\alpha]_D^{20}$ = -5.86 (c 1.25, $CHCl_3$);

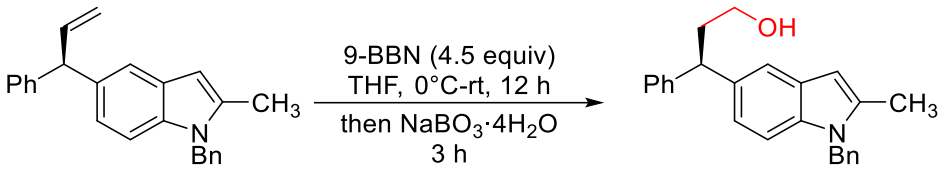
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 7H), 7.18 – 7.11 (m, 4H), 7.10 – 7.05 (m, 2H), 6.97 – 6.93 (m, 1H), 6.89 – 6.85 (m, 1H), 6.84 – 6.77 (m, 2H), 6.77 – 6.70 (m, 1H), 6.35 – 6.23 (m, 2H), 5.21 (s, 2H), 5.17 – 5.12 (m, 2H), 5.08 – 5.03 (m, 1H), 4.98 – 4.92 (m, 1H), 4.92 – 4.86 (m, 1H), 4.76 – 4.70 (m, 1H), 3.73 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6, 145.0, 144.2, 141.5, 140.4, 137.8, 135.9, 134.0, 129.3, 128.7, 128.6, 128.3, 127.6, 127.5, 126.9, 126.7, 126.1, 122.9, 120.9, 119.6, 117.5, 115.7, 115.4, 114.2, 111.7, 109.6, 55.2, 55.1, 50.1, 47.0.

>20/1 *dr* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 1/99, flow rate = 1.0 mL/min, l = 254 nm) t_R = 24.1 min (major), 18.0 min (minor), 20.3 min (minor), 22.5 min (minor).

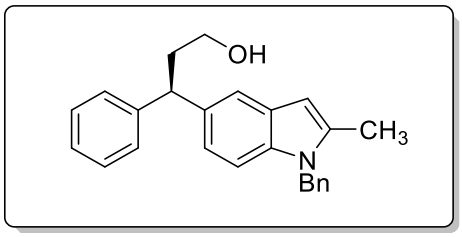
HRMS (ESI) m/z: [M + H]+ Calcd for $C_{34}H_{32}NO$ 470.2478; Found 470.2477.

VII. Synthesis of Chiral Analogue 11



The synthetic protocol of substituted indolines were accorded to the relevant literature. An oven-dried Schlenk flask was equipped with stir bar and allyl indole (0.2 mmol, 1.0 equiv), followed by anhydrous THF (1.0 mL). The organic mixture was cooled at 0°C and 9-BBN (0.9 mmol, 0.5 M in THF, 4.5 equiv) was added dropwise via syringe over 5 min. The mixture was warmed to room temperature and stirred for 12 h, followed by the addition of $NaBO_3·4H_2O$ (2 mmol, 10 equiv) and distilled water (1.0 mL). The mixture was reacted for another 3 h. After completion, the homogeneous solution was diluted in water and extracted with Et_2O 3 times. The combined organic phase was washed with water and brine, dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by flash chromatography (PE/EA = 8/1) to yield the terminal product **9** as a white solid.

(*R*)-3-(1-benzyl-2-methyl-1H-indol-5-yl)-3-phenylpropan-1-ol (10)



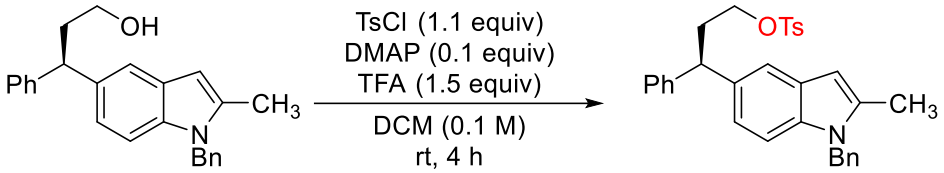
White solid, 62.5 mg, yield (88%); mp. = 116.7-118.0 °C; $[\alpha]_D^{20}$ = -2.4 (c 1.25, $CHCl_3$);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 1H), 7.31 – 7.19 (m, 7H), 7.16 – 7.06 (m, 2H), 6.98 – 6.94 (m, 3H), 6.27 – 6.23 (m, 1H), 5.23 (s, 2H), 4.18 (t, *J* = 7.9 Hz, 1H), 3.62 (t, *J* = 6.4 Hz, 2H), 2.39 – 2.31 (m, 2H), 2.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 137.9, 137.1, 136.0, 135.6, 128.8, 128.4, 128.3, 127.9, 127.3, 126.1, 126.0, 121.2, 118.5, 109.3, 100.3, 61.6, 47.6, 46.6, 38.8, 12.8.

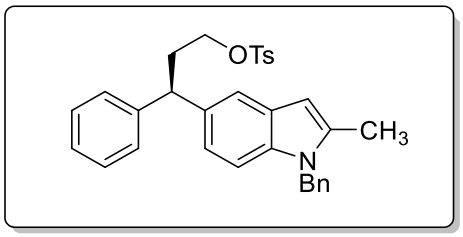
>99% *ee* as determined by HPLC (OD-H, *i*-PrOH /*n*-hexane = 10/90, flow rate = 1.0 mL/min, l = 254 nm) t_R = 44.7 min (major), 49.7 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{25}H_{26}NO$ 356.2009; Found 356.2011.



To a dry 25 mL round-bottom flask equipped with a stir bar under Ar atmosphere were added alcohol (0.1 mmol, 1.0 equiv), TsCl (0.11mmol, 1.1 equiv), DMAP (0.01 mmol, 0.1 equiv) and DCM (1 mL, 0.1 M), followed by the addition of trimethylamine (0.15 mmol, 1.5 equiv). The reaction was stirred for 4 h at room temperature. After completion, the solution was washed with saturated aqueous $NaHCO_3$ and water. The organic layer was reextracted with DCM twice and the combined organic phases were separated, dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The residue was purified by flash chromatography to give the desired product **10** as a reddish oil.

(*R*)-3-(1-benzyl-2-methyl-1H-indol-5-yl)-3-phenylpropyl 4-methylbenzenesulfonate (11)



Reddish oil, 46.4 mg, yield (91%); $[\alpha]_D^{20}$ = +2.2 (c 1.25, $CHCl_3$);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.30 – 7.09 (m, 12H), 7.05 – 7.02 (m, 1H), 6.97 – 6.93 (m, 2H), 6.85 – 6.80 (m, 1H), 6.25 – 6.20 (m, 1H), 5.23 (s, 2H), 4.08 (t, *J* = 7.9 Hz, 1H), 3.99 (td, *J* = 6.3, 1.1 Hz, 2H), 2.44 – 2.38 (m, 2H), 2.39 (s, 2H), 2.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 144.5, 137.8, 137.1, 136.1, 134.3, 133.1, 129.8, 128.8, 128.4, 128.2, 127.9, 127.8, 127.3, 126.1, 126.0, 121.0, 118.4, 109.3, 100.3, 69.2, 46.7, 46.5, 35.06, 21.63, 12.8.

99% *ee* as determined by HPLC (AD-H, *i*-PrOH /*n*-hexane = 10/90, flow rate = 1.0 mL/min, l = 254 nm) t_R = 20.4 min (major), 22.0 min (minor).

HRMS (ESI) m/z: [M + H]+ Calcd for $C_{32}H_{32}NO_3S$ 510.2097; Found 510.2099.

VIII. Absolute Configuration of 3a

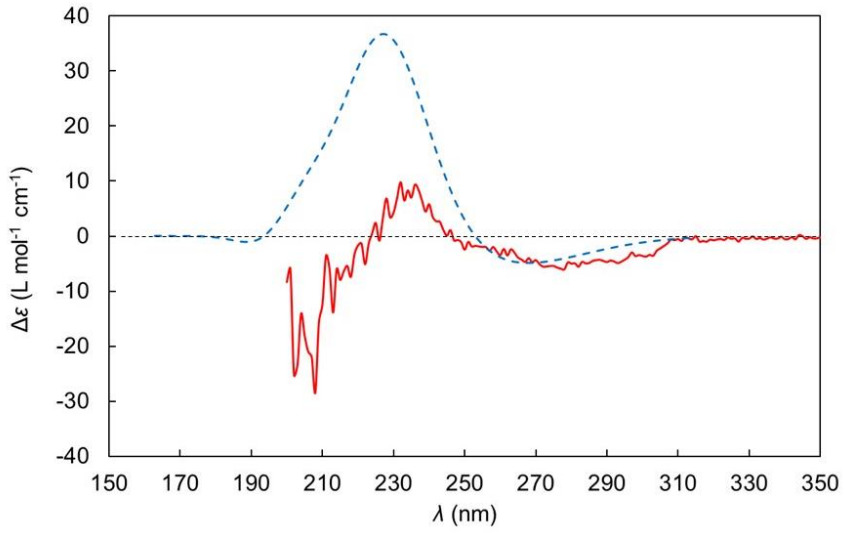


Figure S1. Experimental (solid red line, CH_3CN) and calculated (dashed blue line) ECD spectra of compound **3a**.

The absolute configuration is *R*.

Computational details

There are 16 conformations of compound **3a** as shown in Fig. S2. The structures were optimized with the PBE0 functional[7] at the 6-311G(d,p) basis set with the IEFPCM solvation model[8] in CH_3CN. Subsequent frequency calculations were performed to confirm the structures are local minima. The obtained Gibbs free energy corrections were approximately used as corrections in vacuum. More accurate gas phase single point energies were computed at the PBE0/def2-TZVPP level. The solvation free energies were calculated from the difference between M05-2X[9]/6-31G(d) and M05-2X/6-31G(d)/SMD[10]/CH_3CN single point energies. The relative Gibbs free energies and populations of the 16 conformations are listed in Table S1. Calculations of the ECD spectra were performed using the time-dependent density functional theory (TD-DFT) at the PBE0/def2-TZVP/IEFPCM/CH_3CN level (solving for 20 states). All calculations were performed using Gaussian 16 program.[11]

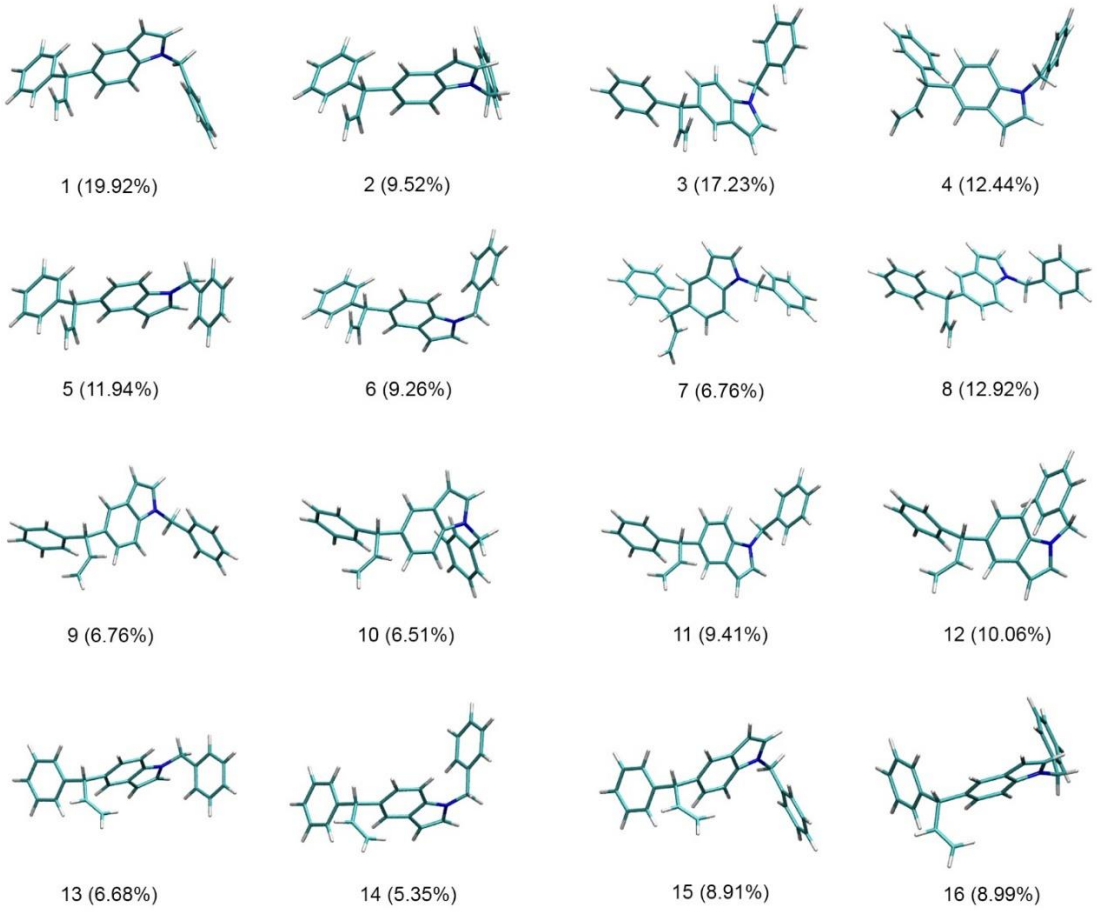


Figure S2. Optimized structures and relative populations of the 16 conformations.

Table S1. Relative Gibbs free energies and populations of the 16 conformations.

Conformation	ΔG (kcal/mol)	Population
1	0.00	19.92%
2	0.44	9.52%
3	0.09	17.23%
4	0.28	12.44%
5	0.30	11.94%
6	0.45	9.26%
7	0.64	6.76%
8	0.26	12.92%
9	0.64	6.76%
10	0.66	6.51%
11	0.44	9.41%
12	0.40	10.06%
13	0.65	6.68%
14	0.78	5.35%
15	0.48	8.91%
16	0.47	8.99%

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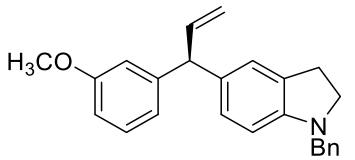
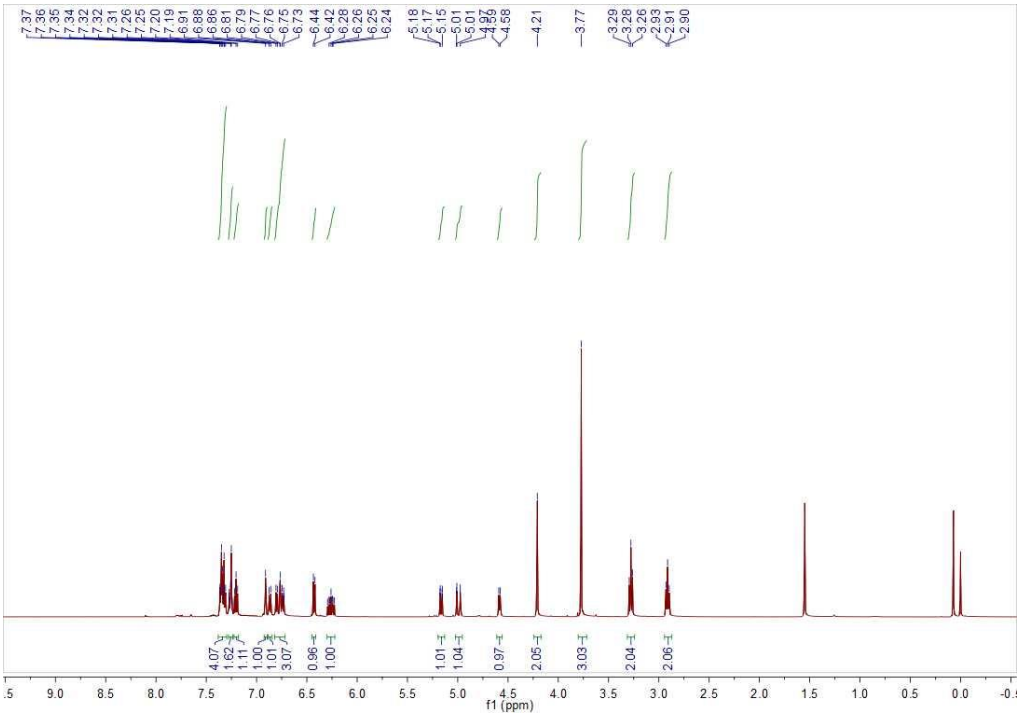
11. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16 Rev. A.03, Wallingford, CT, 2016.

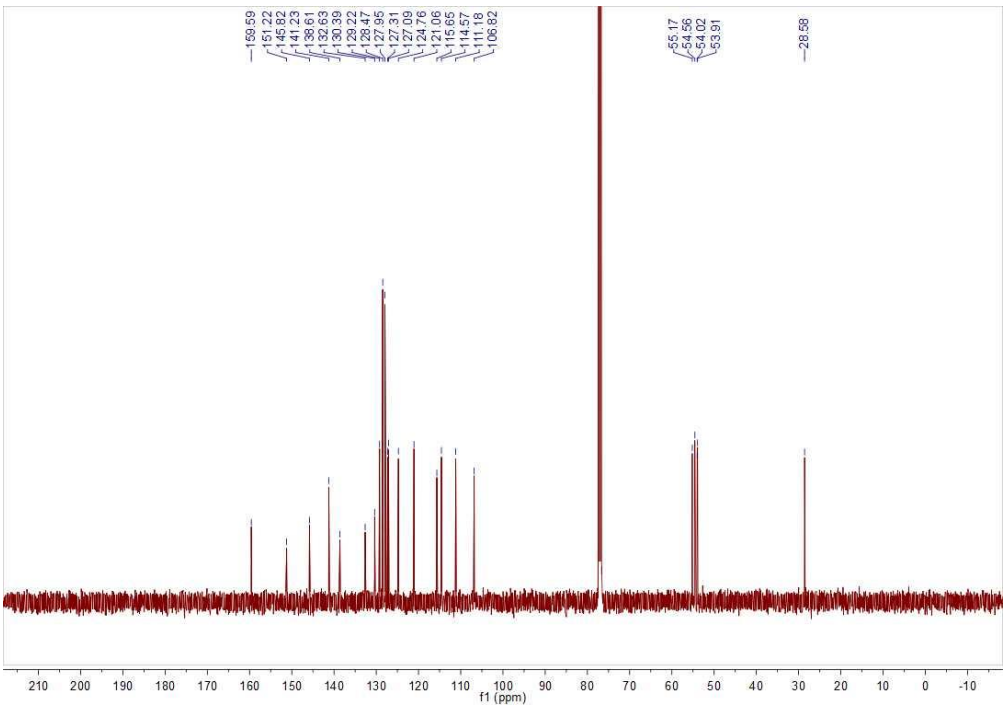
IX. Data of NMR Spectra:



3a



$CDCl_3$; 500Hz



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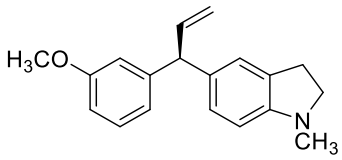

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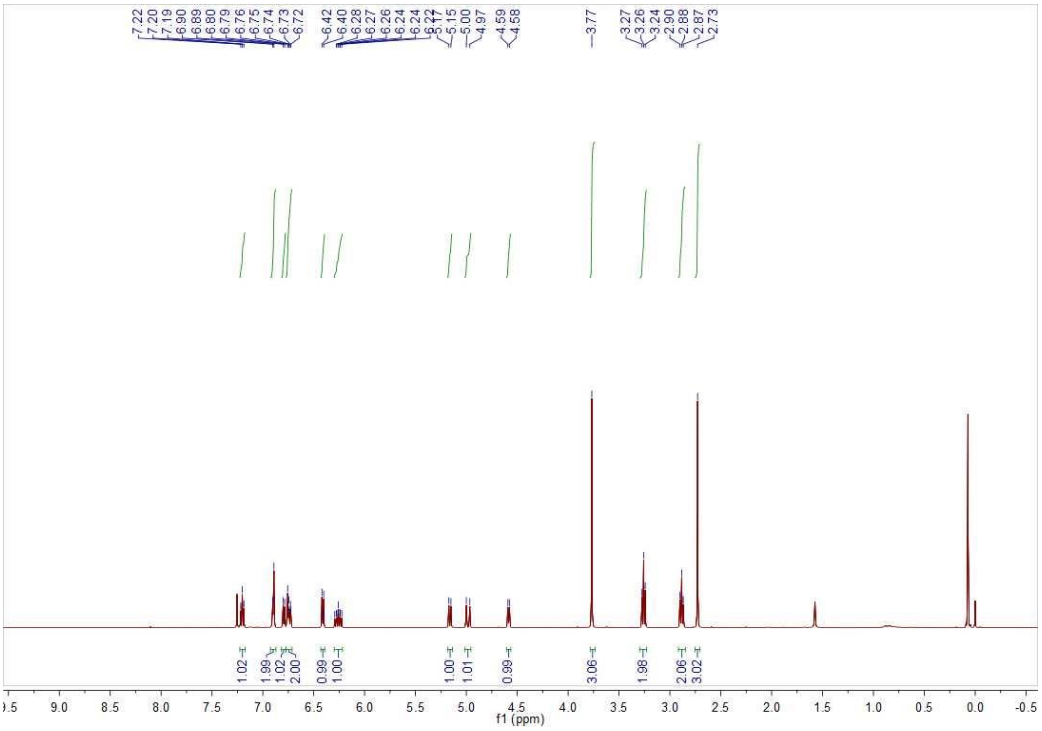

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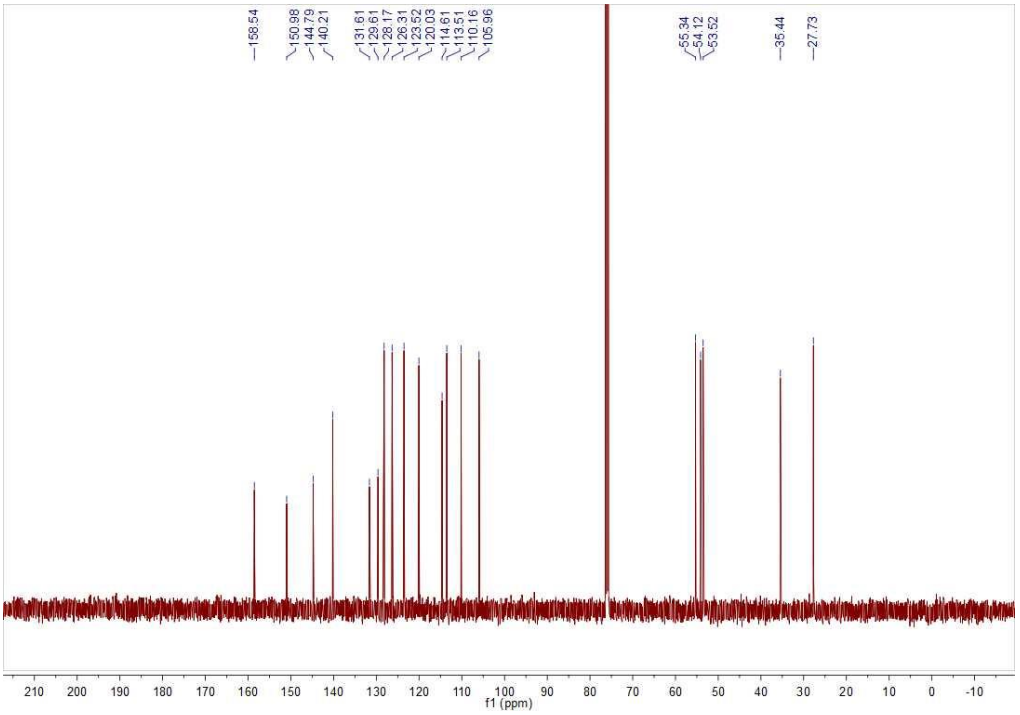

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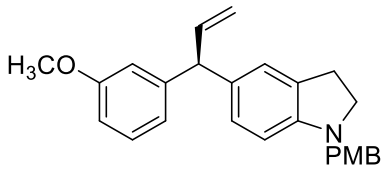

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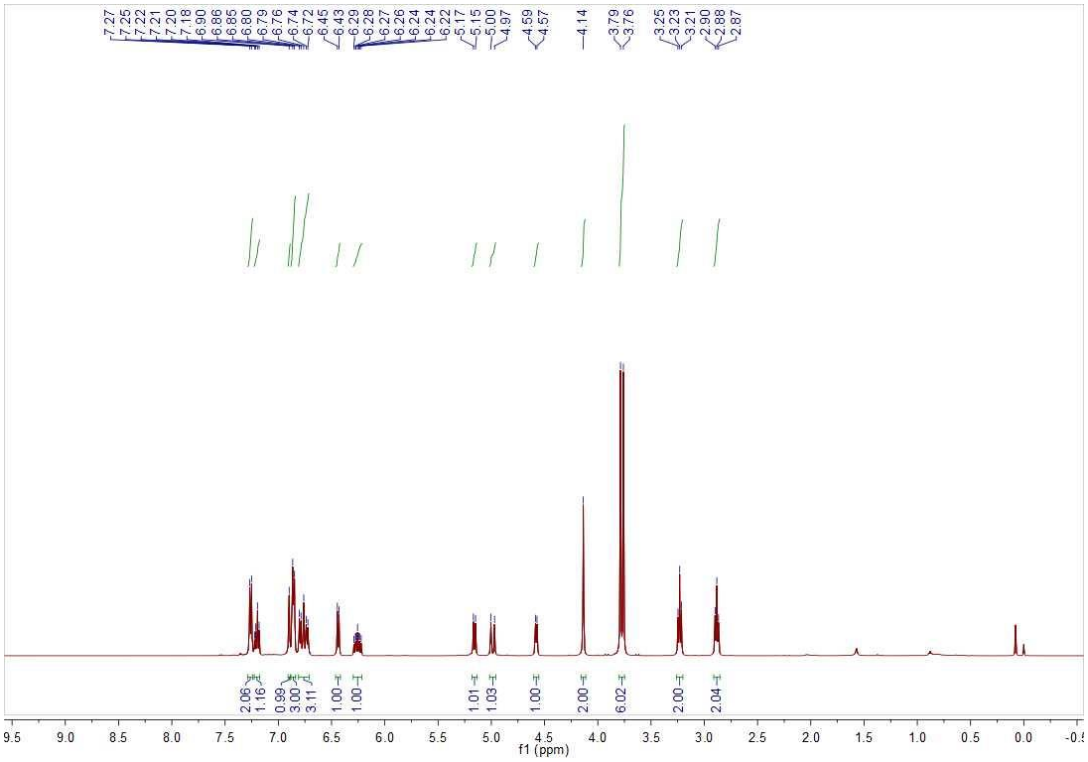

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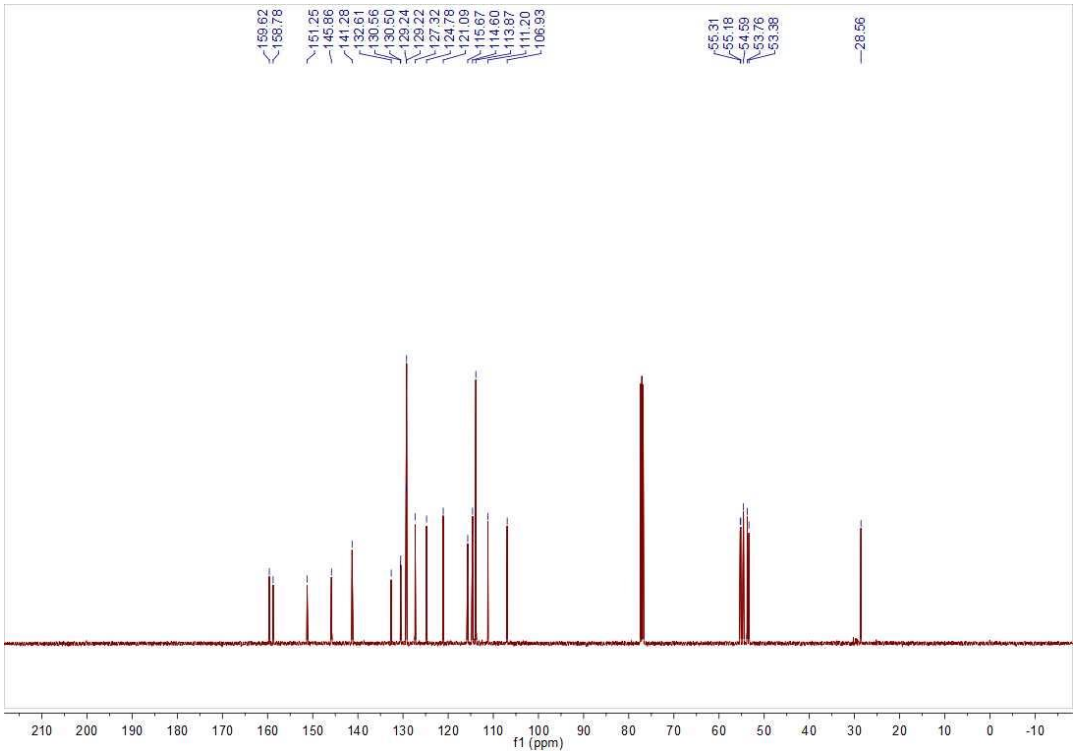

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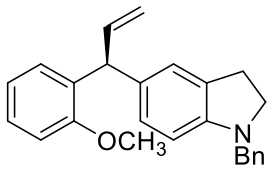

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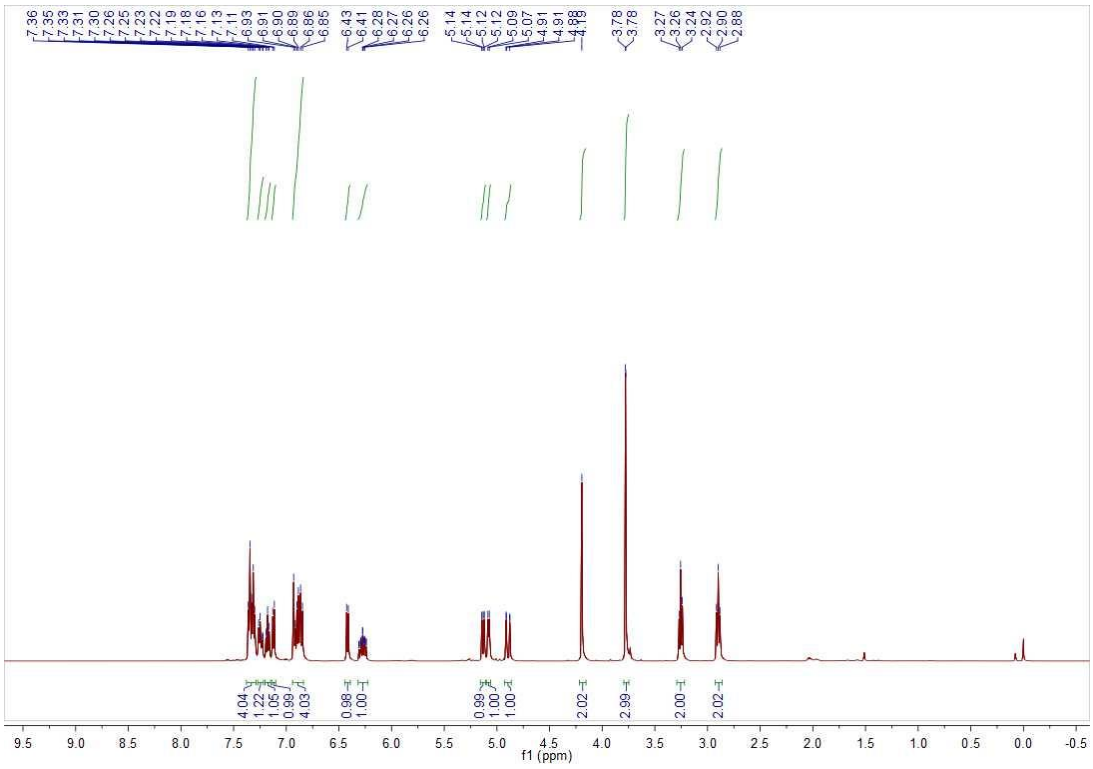

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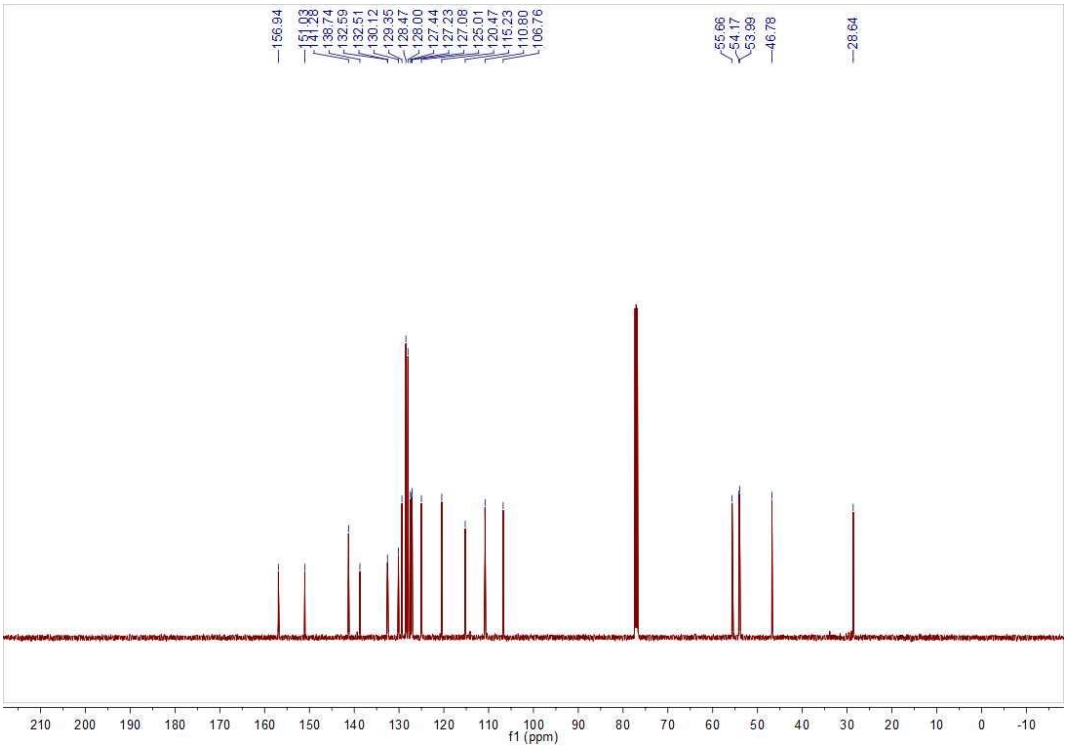

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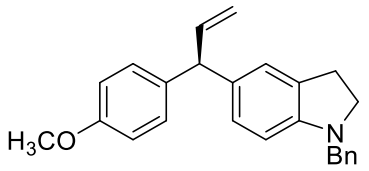

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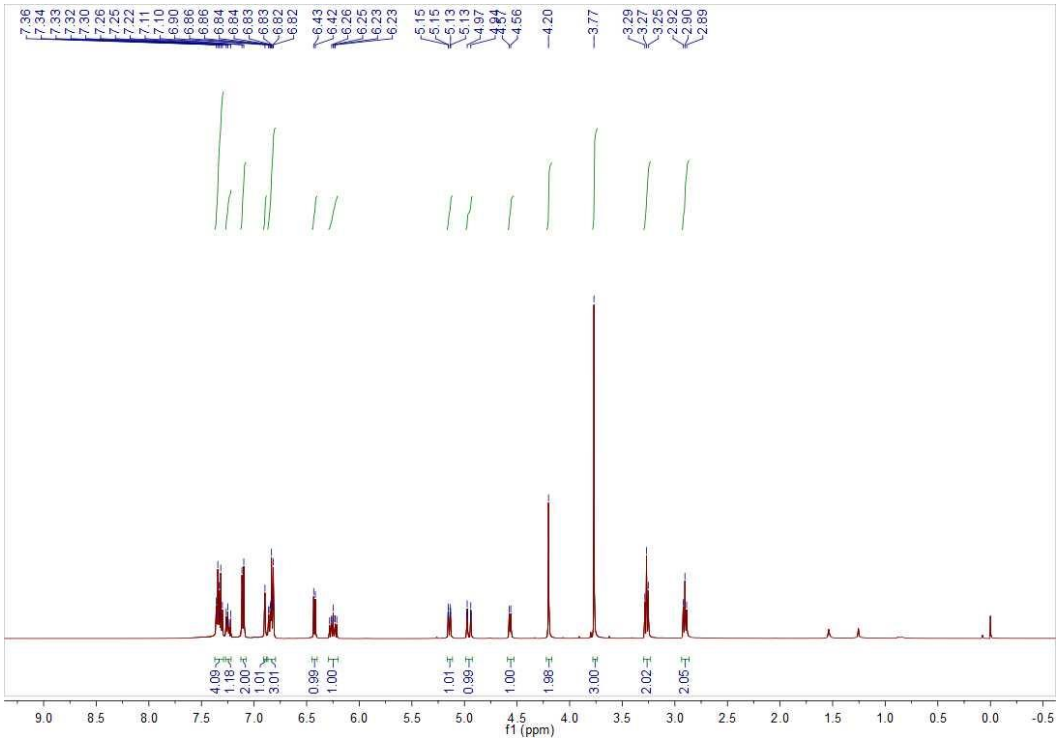

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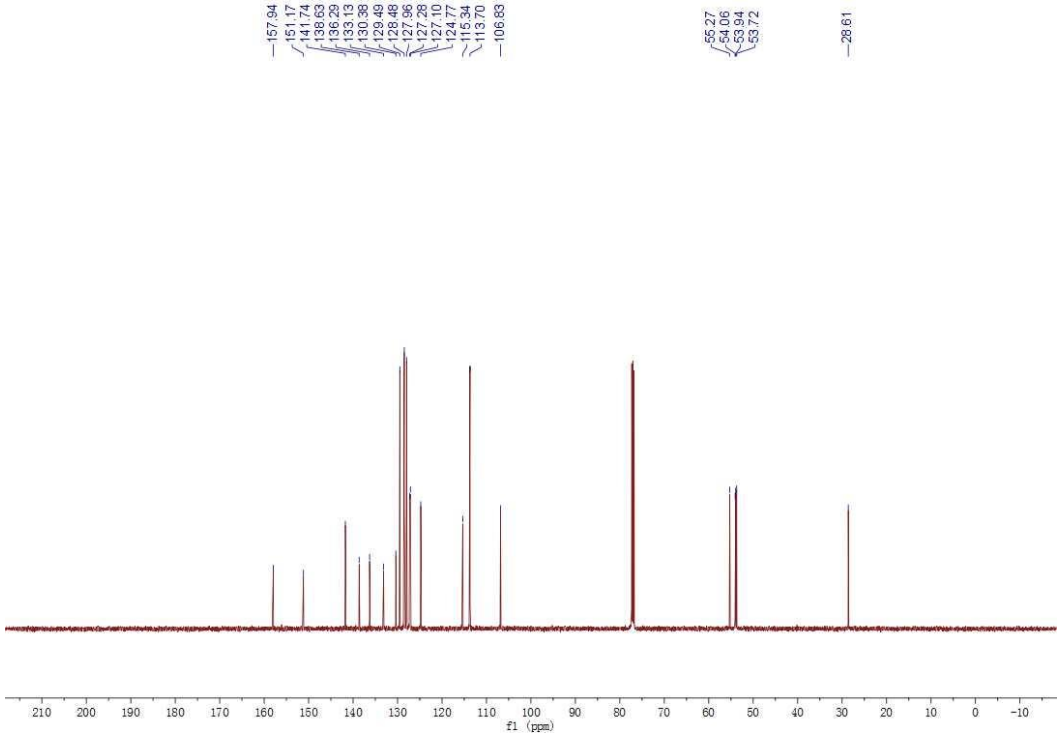

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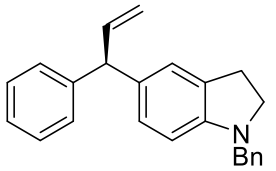

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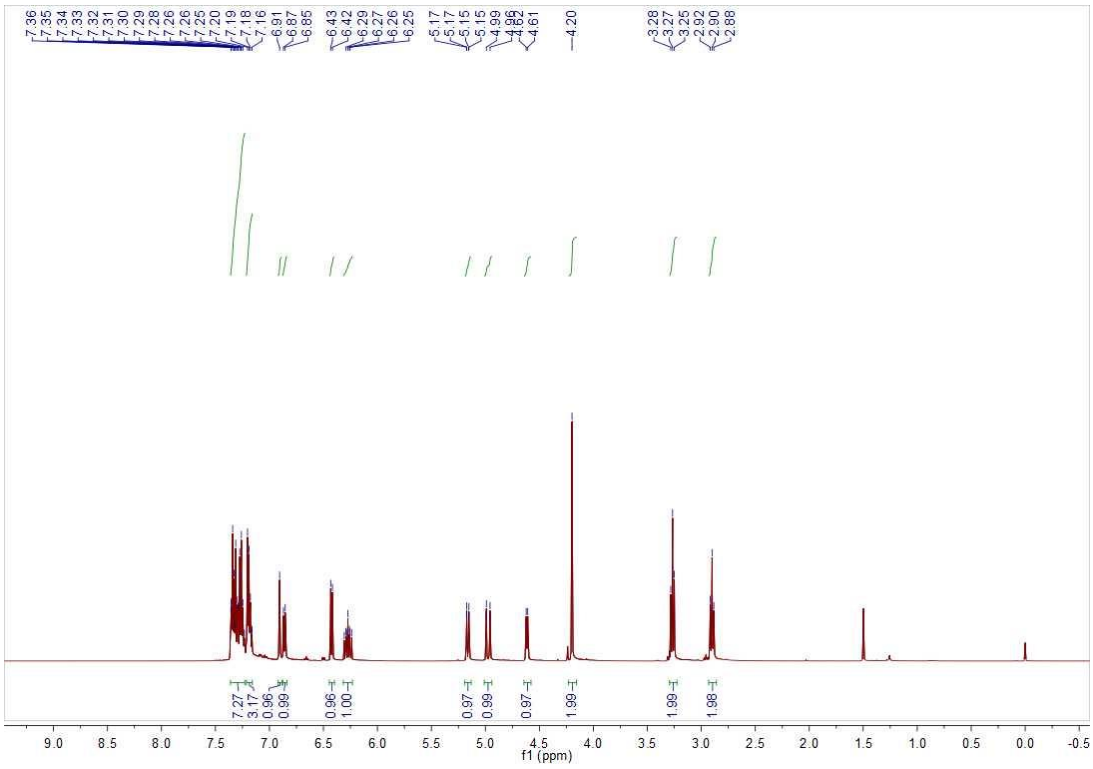

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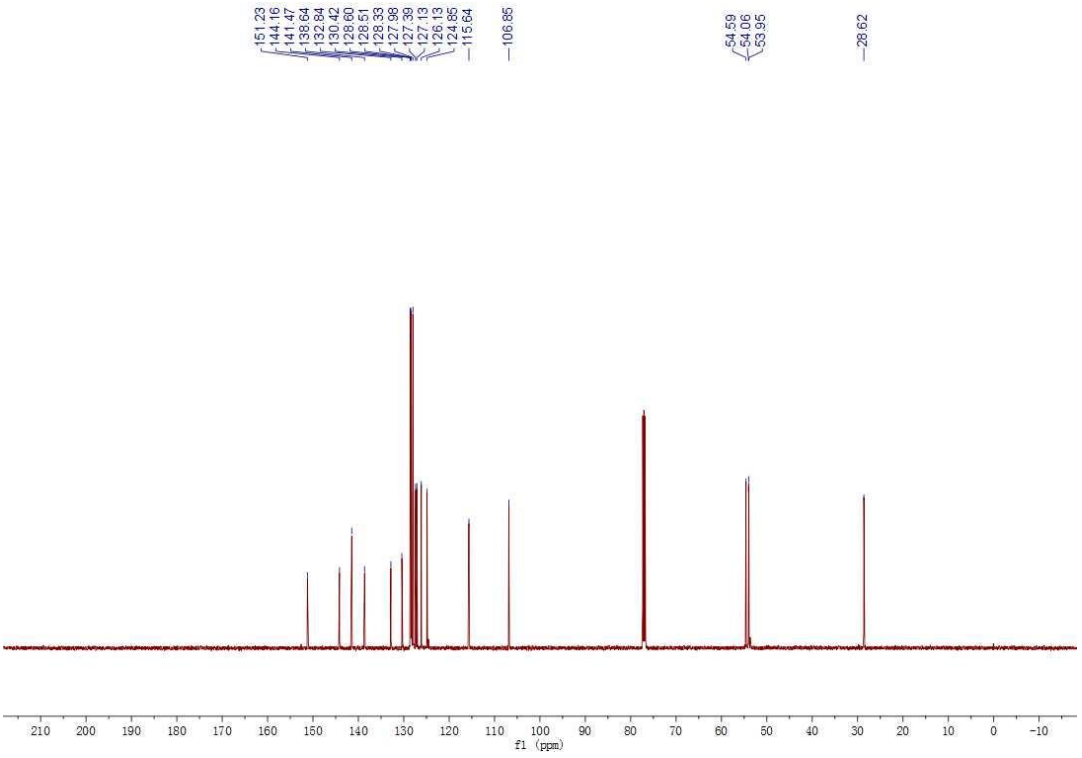

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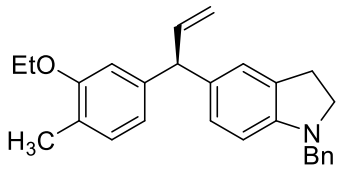

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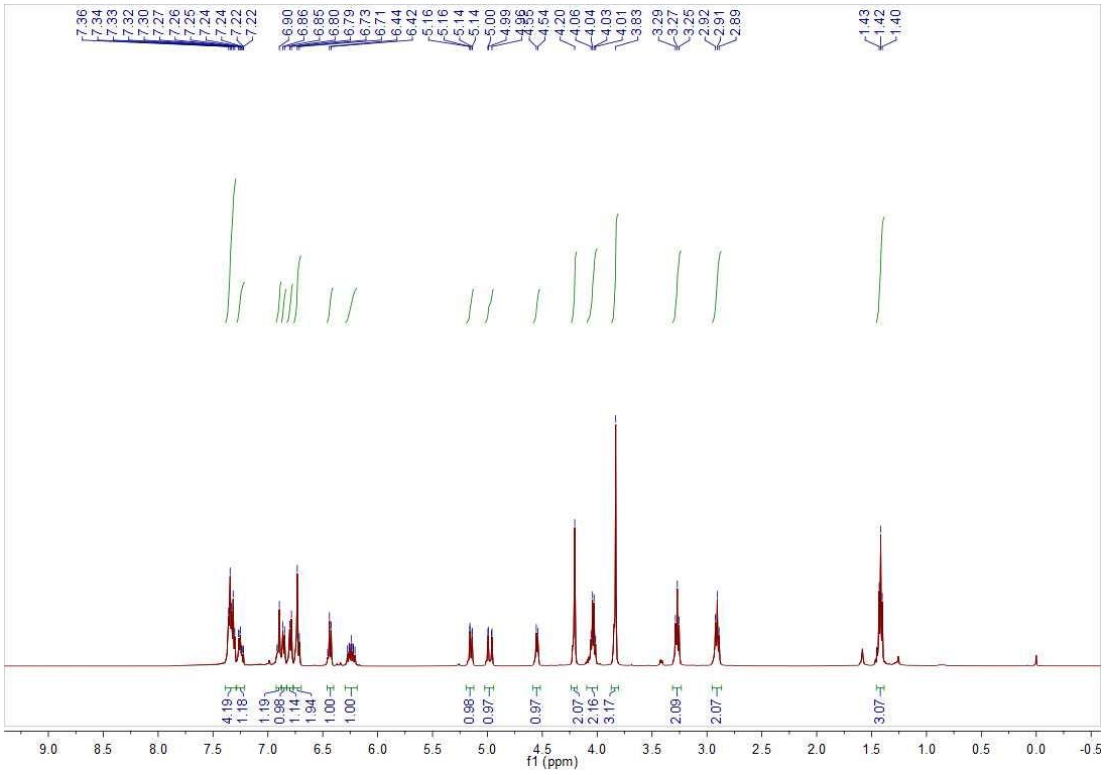

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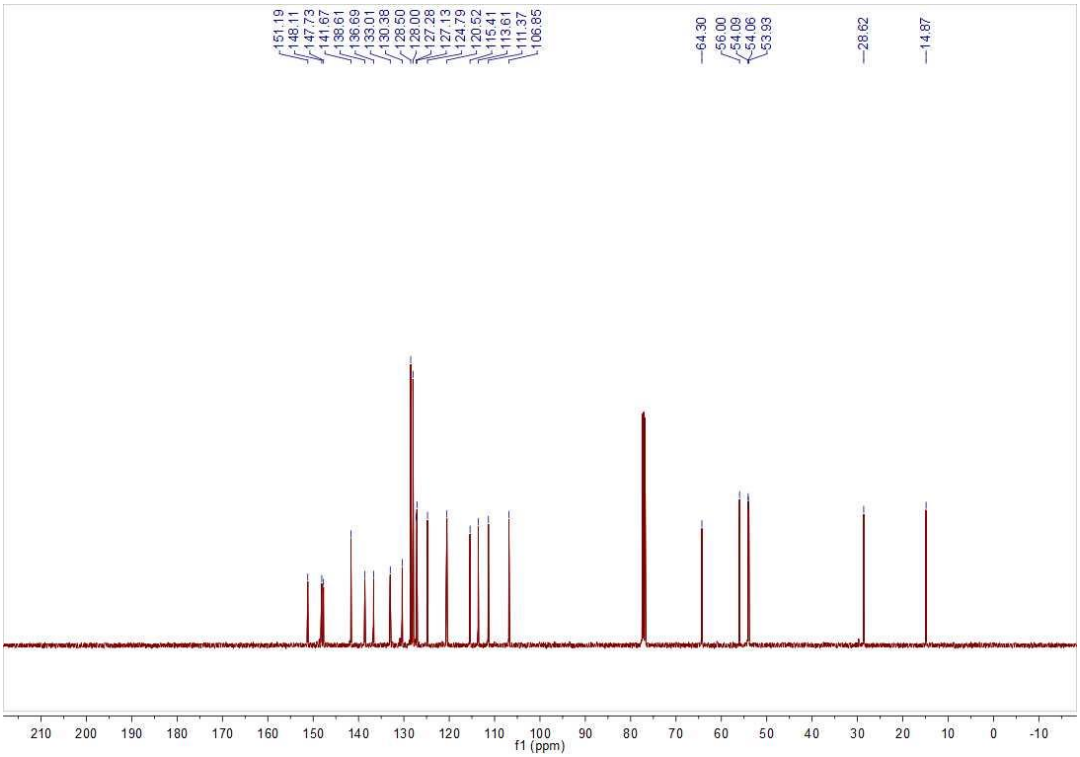

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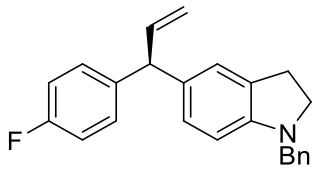

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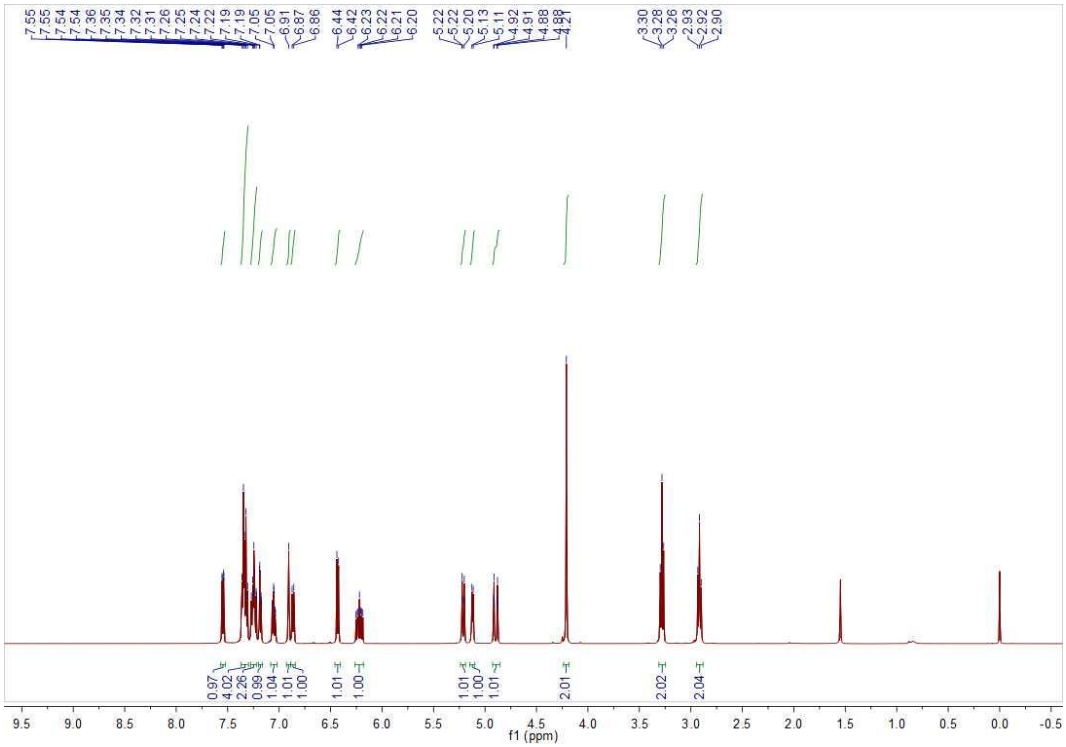

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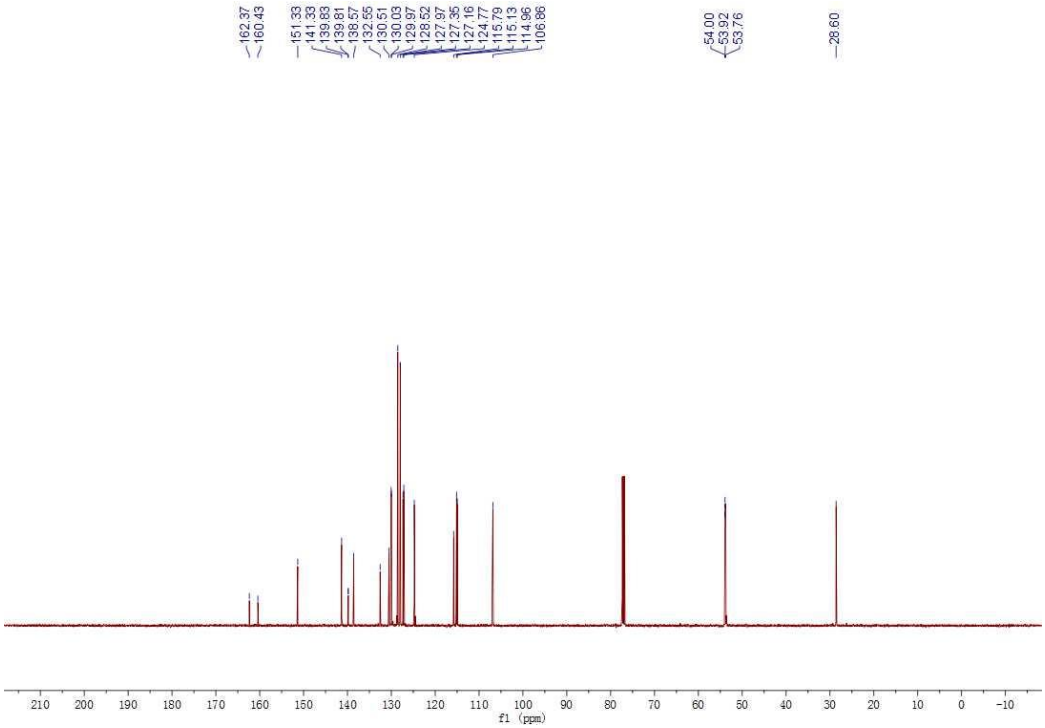

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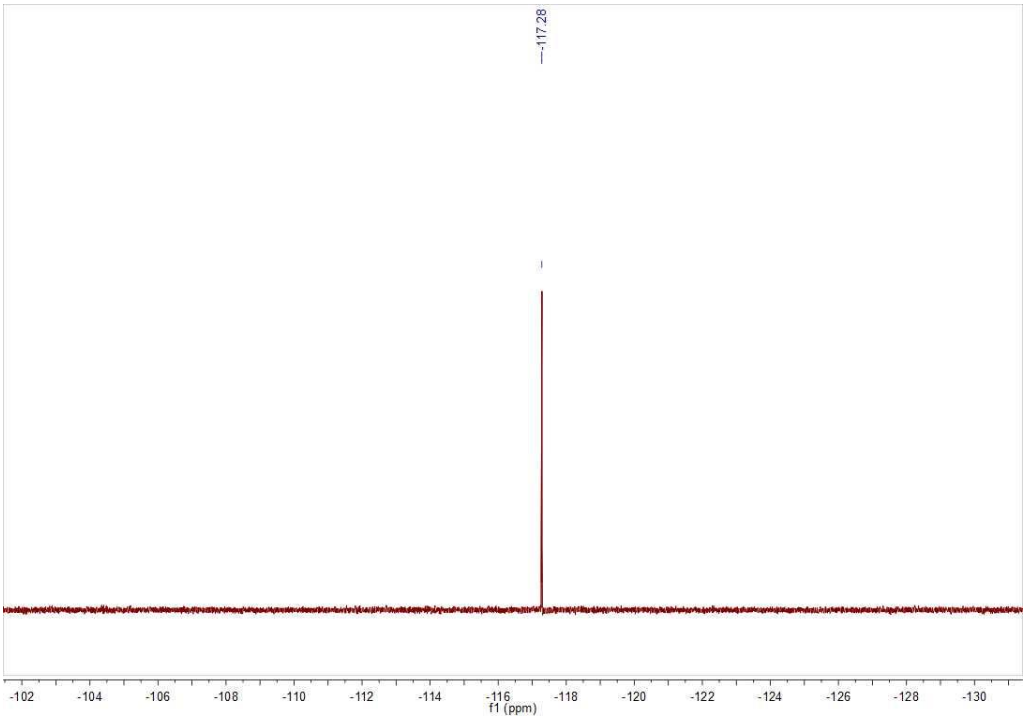

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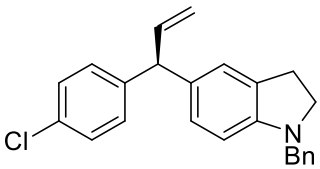

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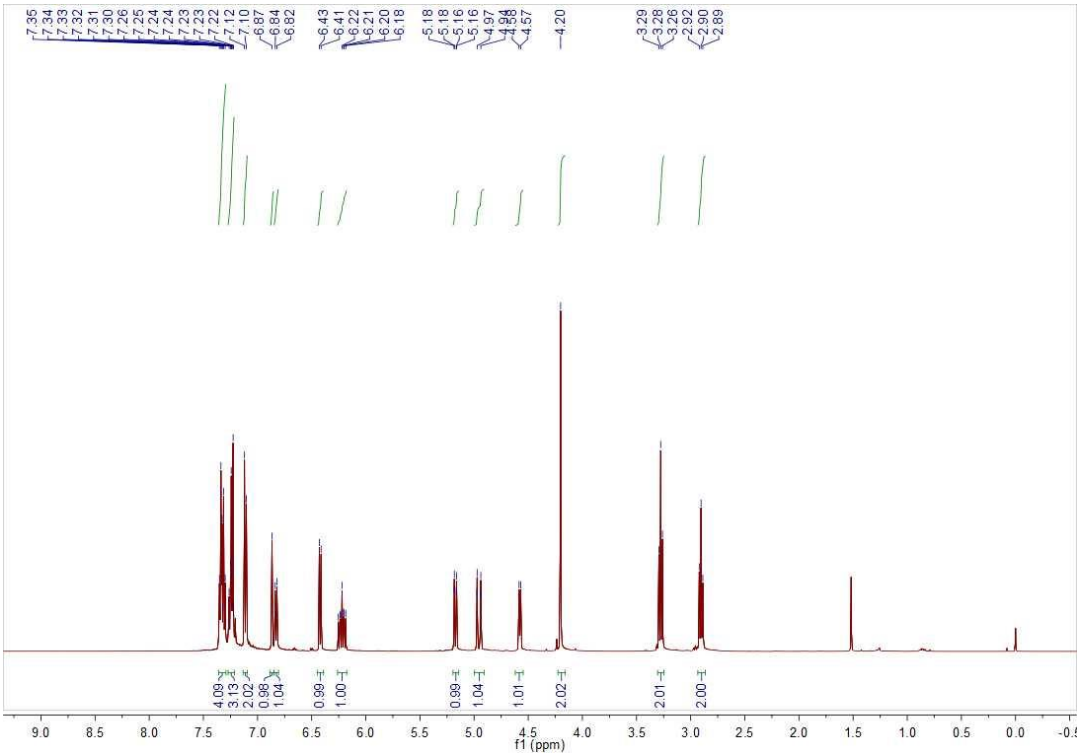

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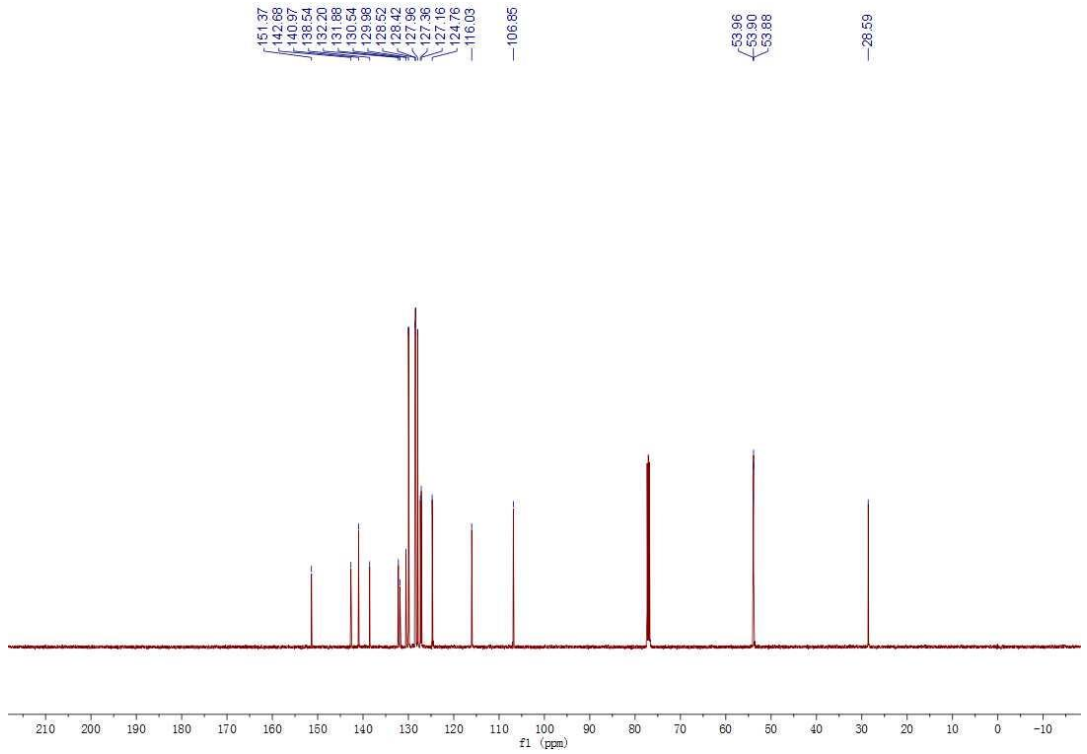

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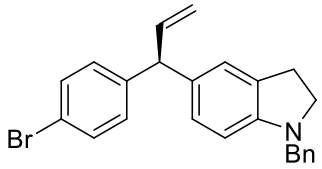

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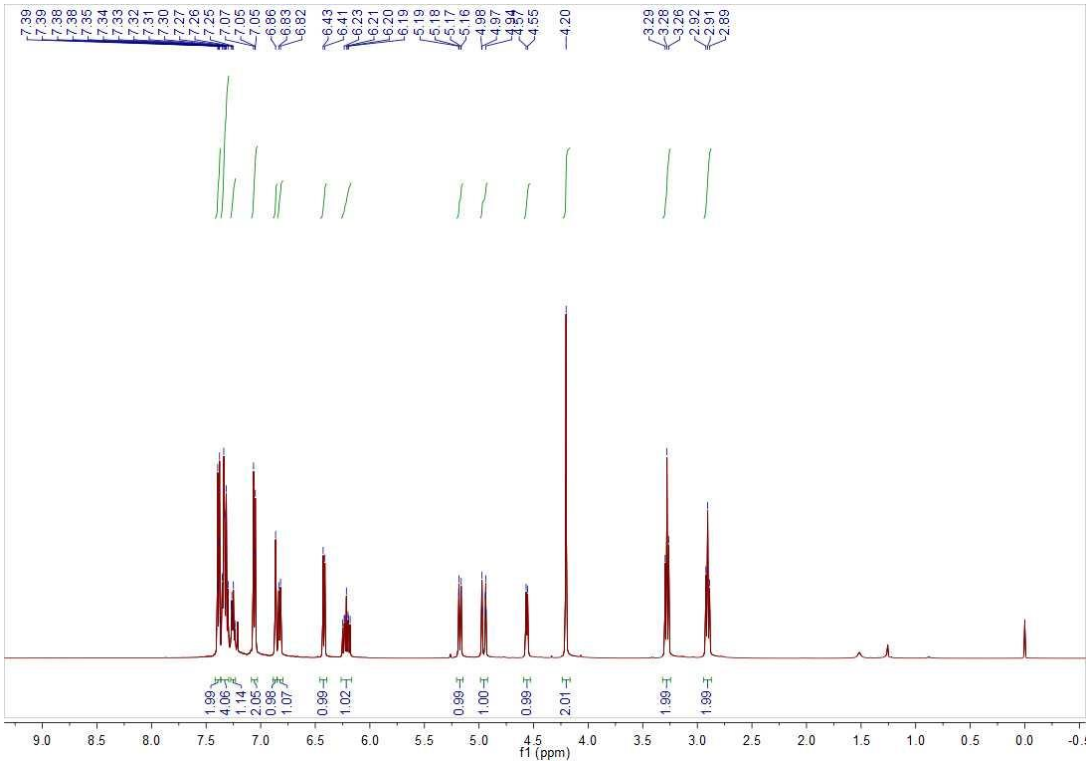

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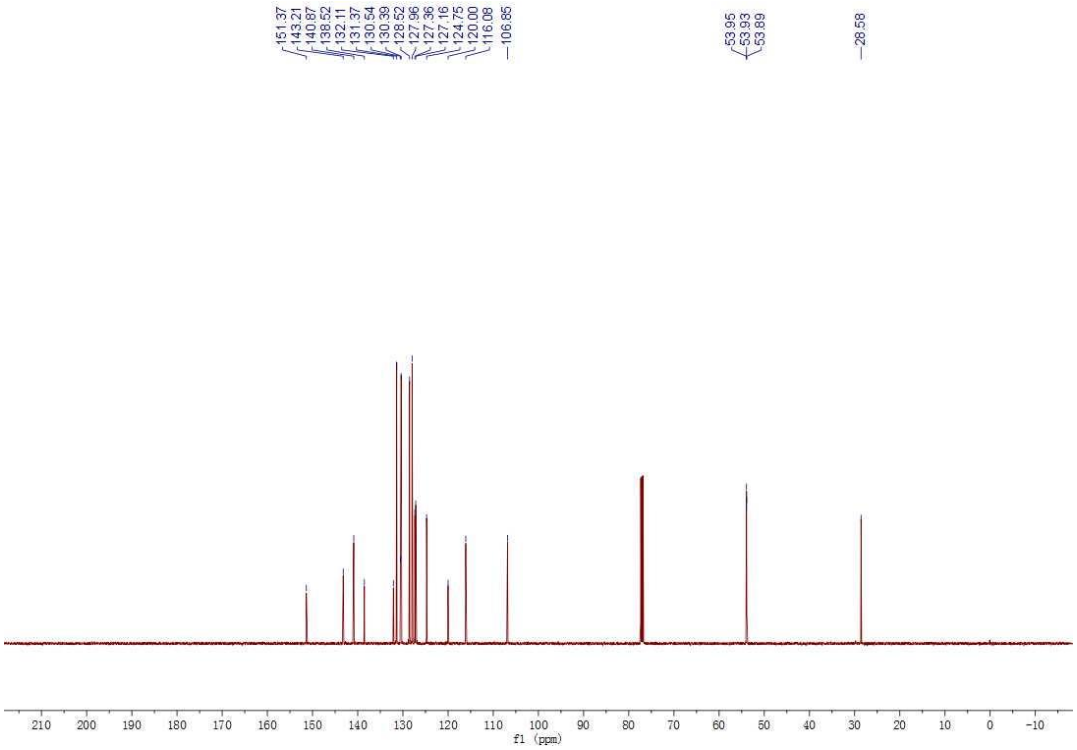

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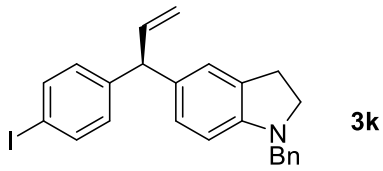

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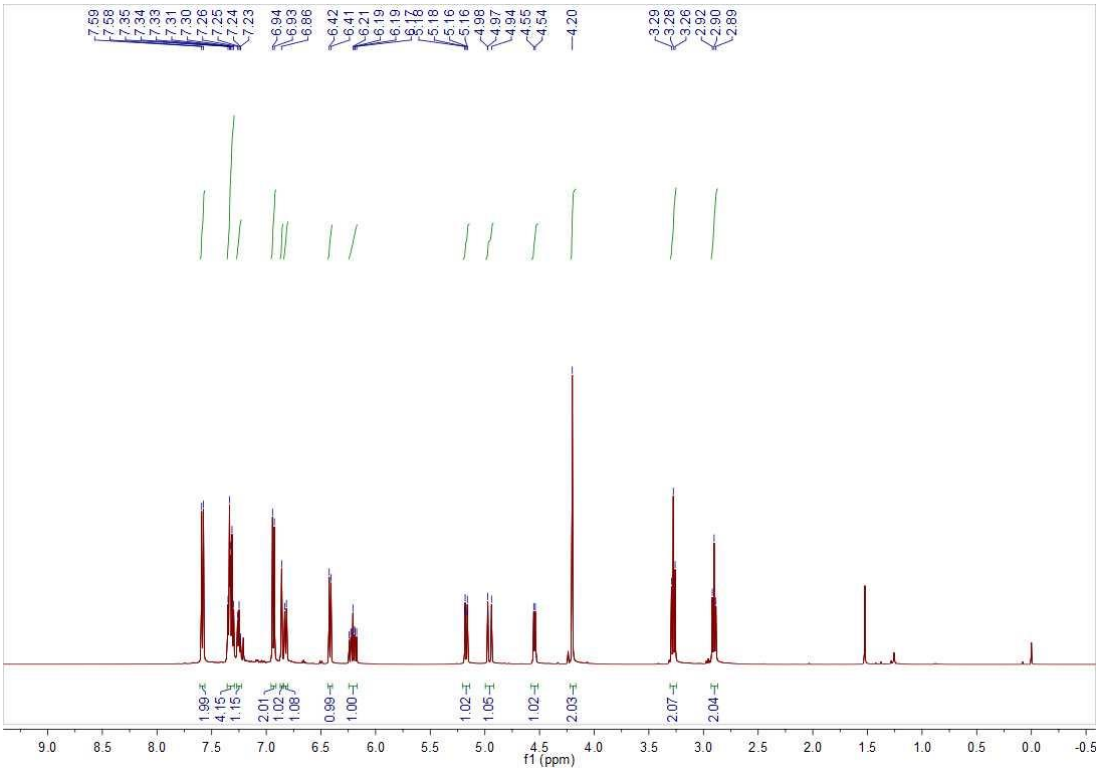

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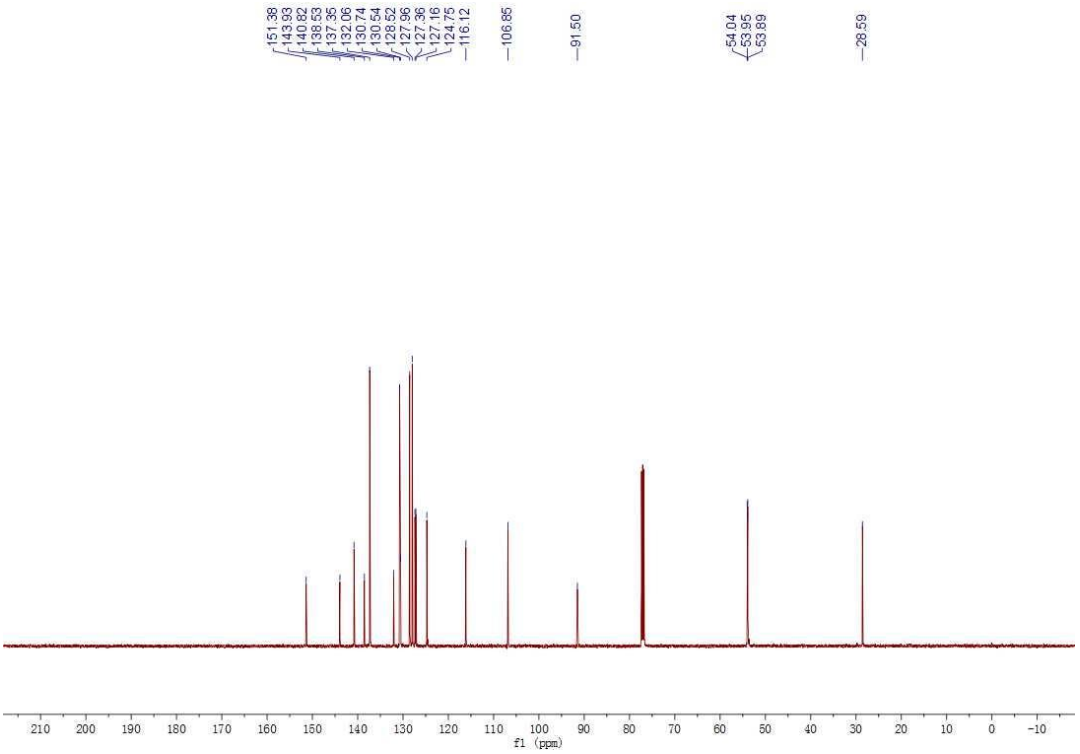

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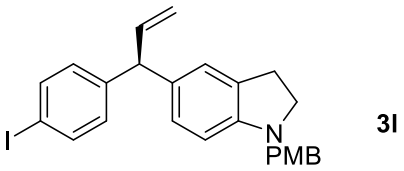

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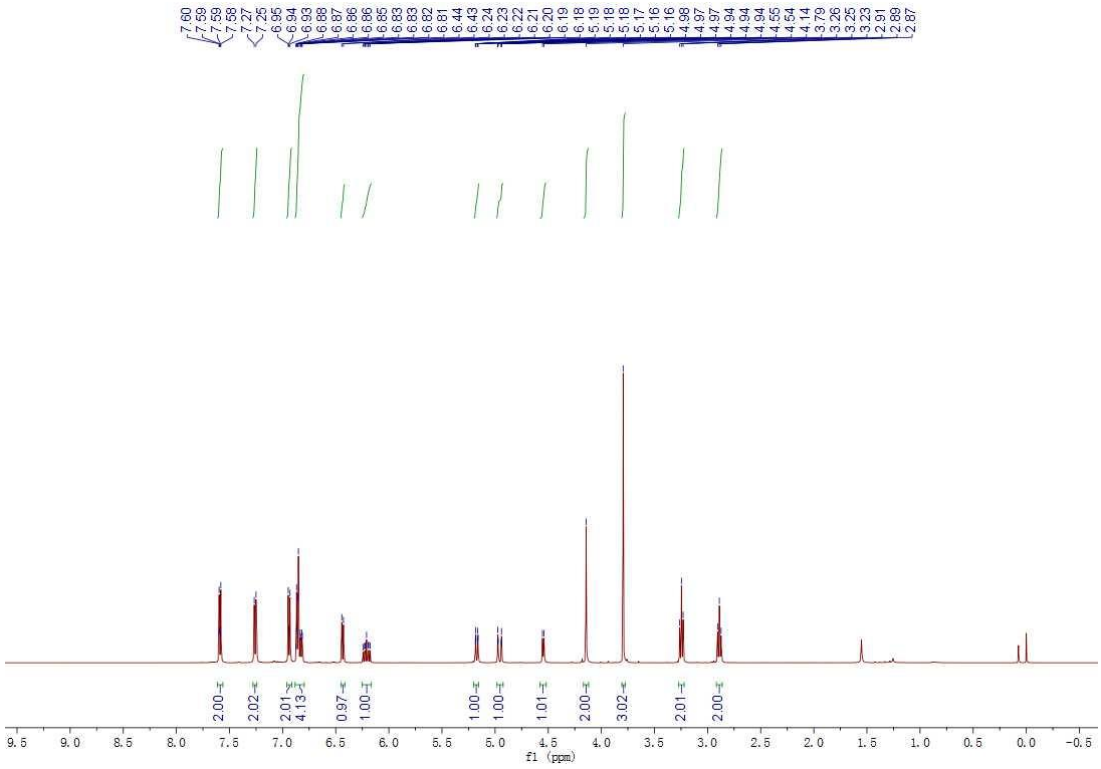

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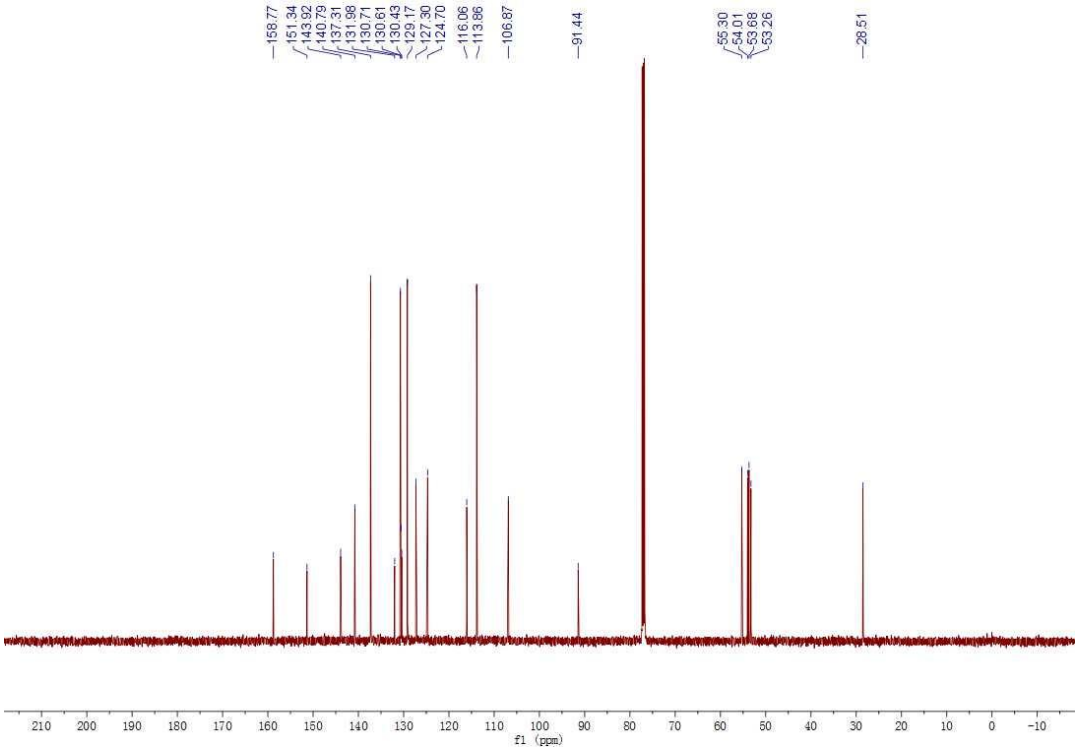

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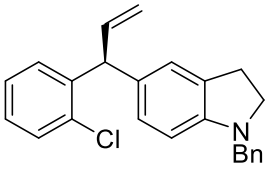

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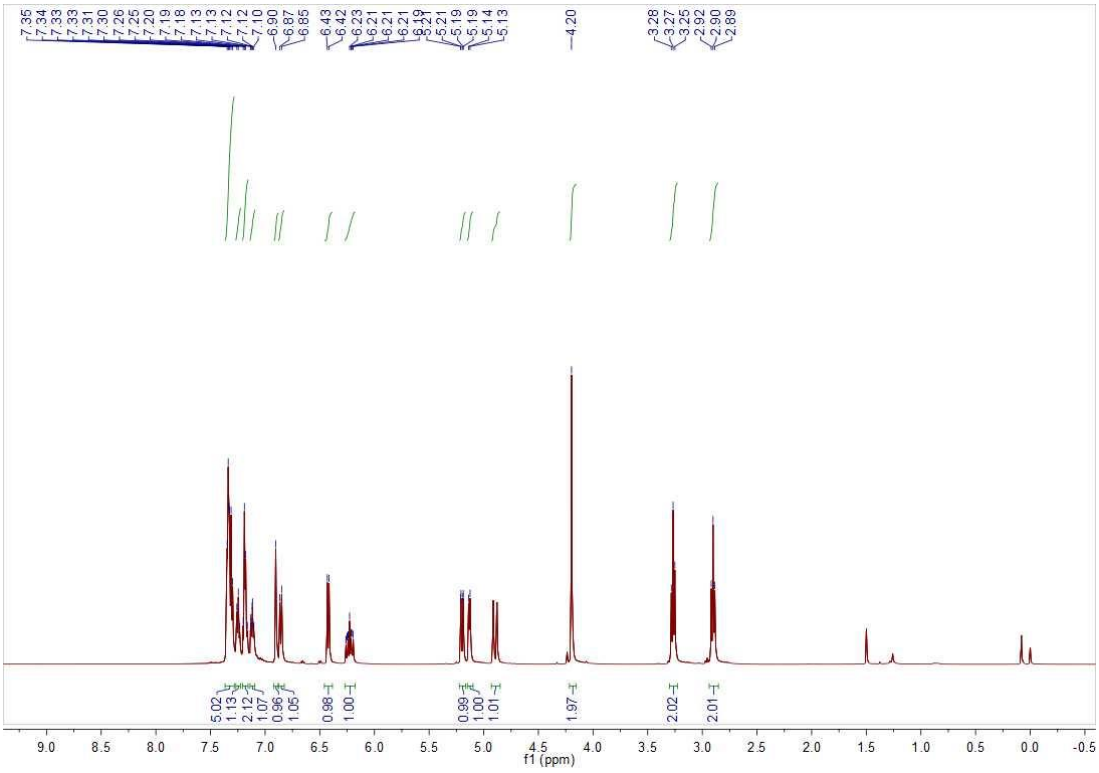

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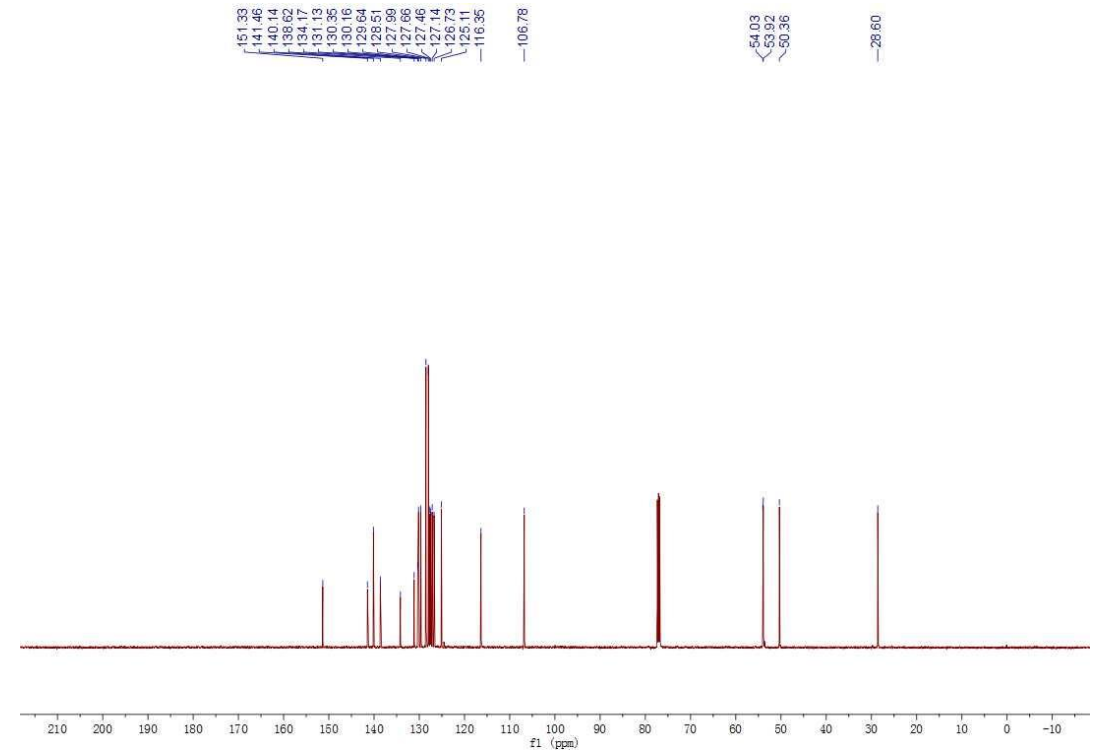

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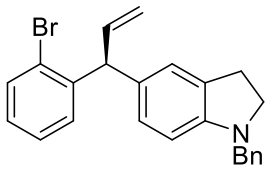

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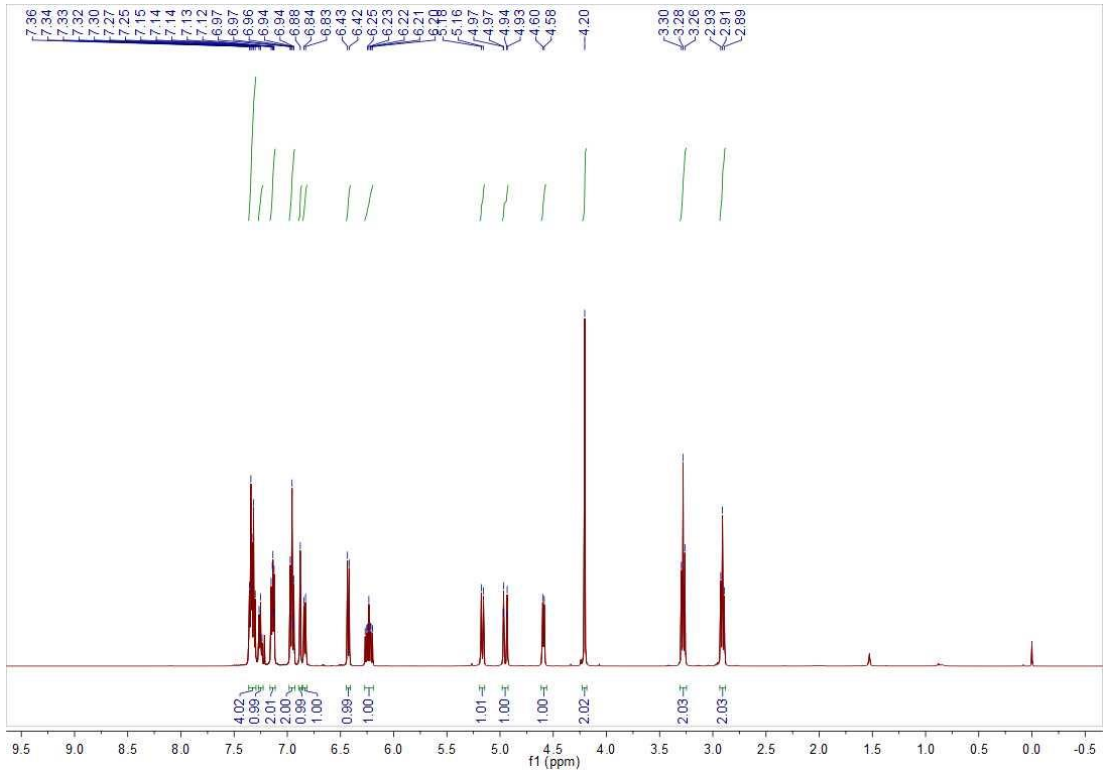

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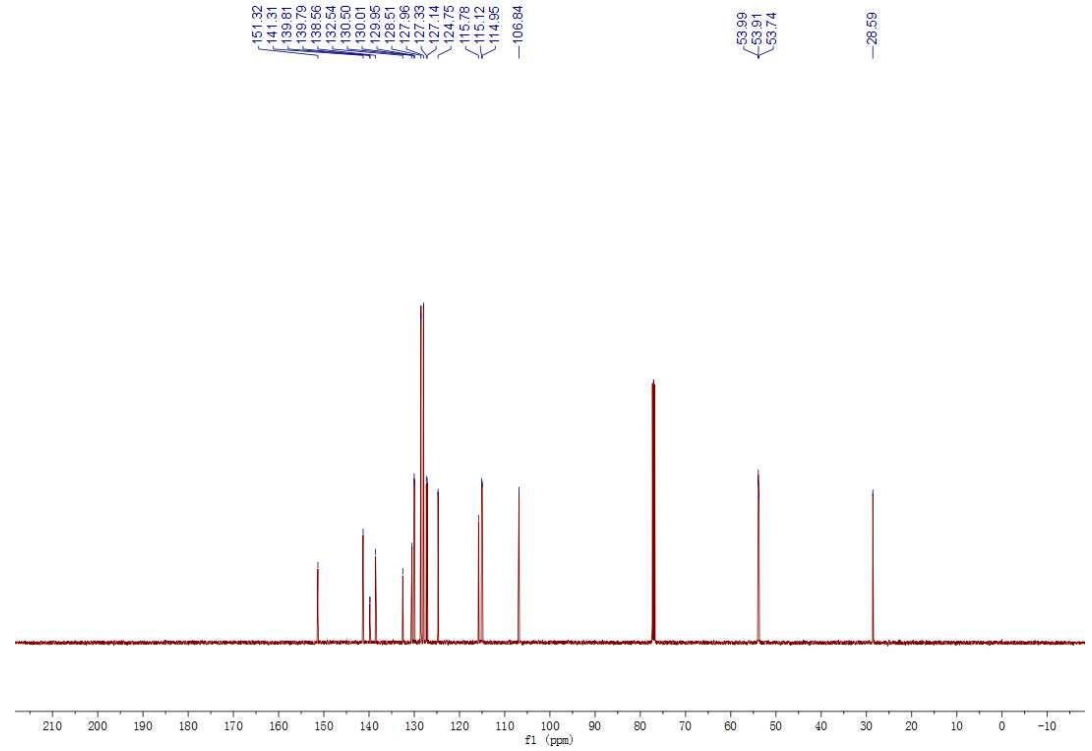

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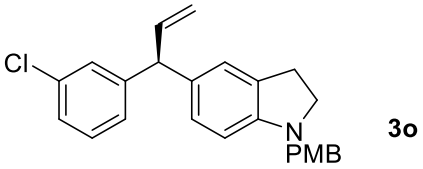

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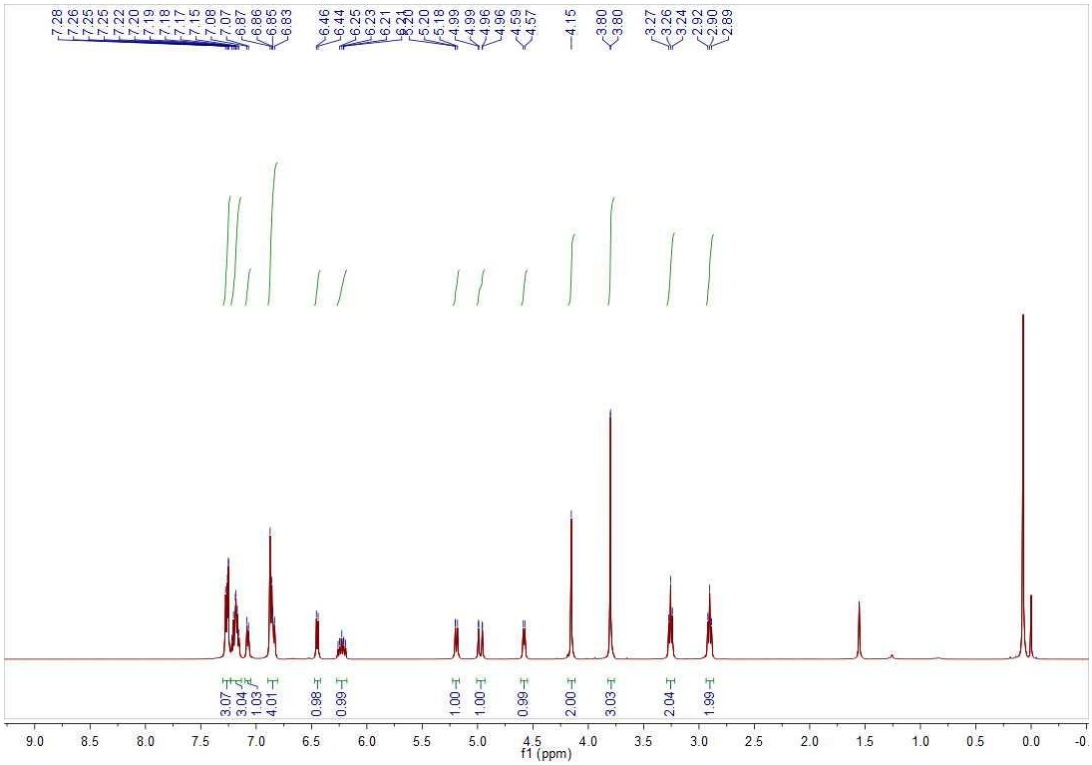

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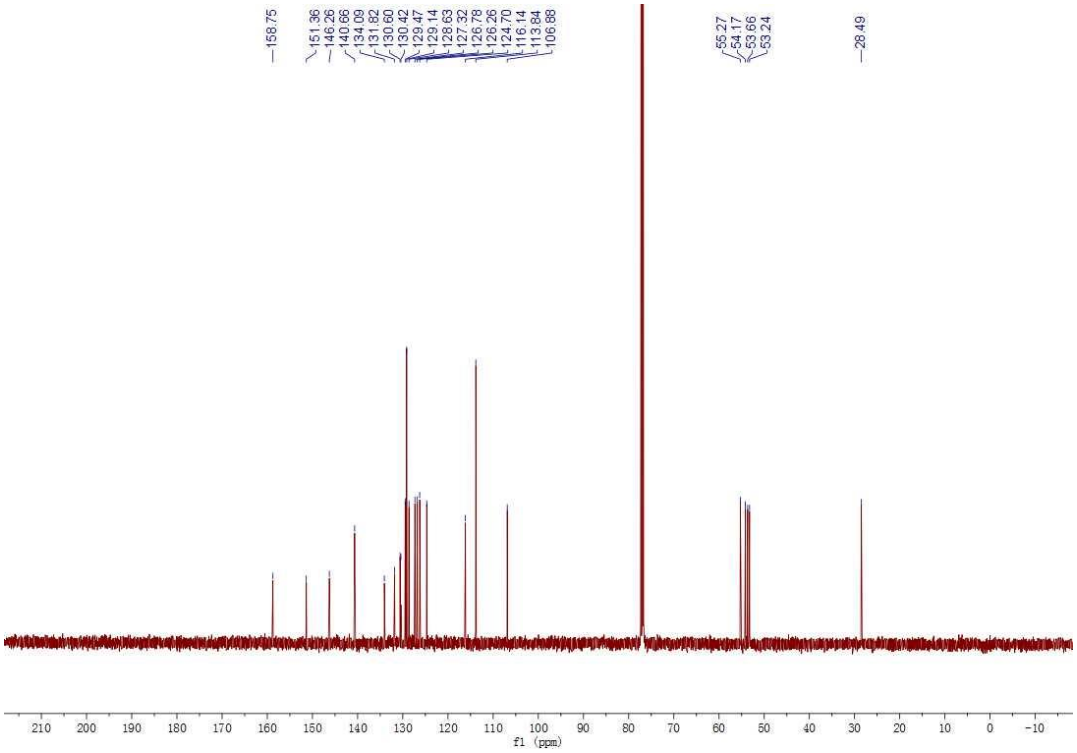

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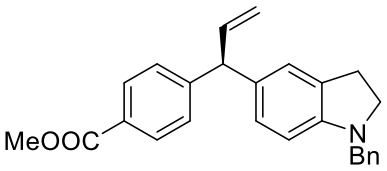

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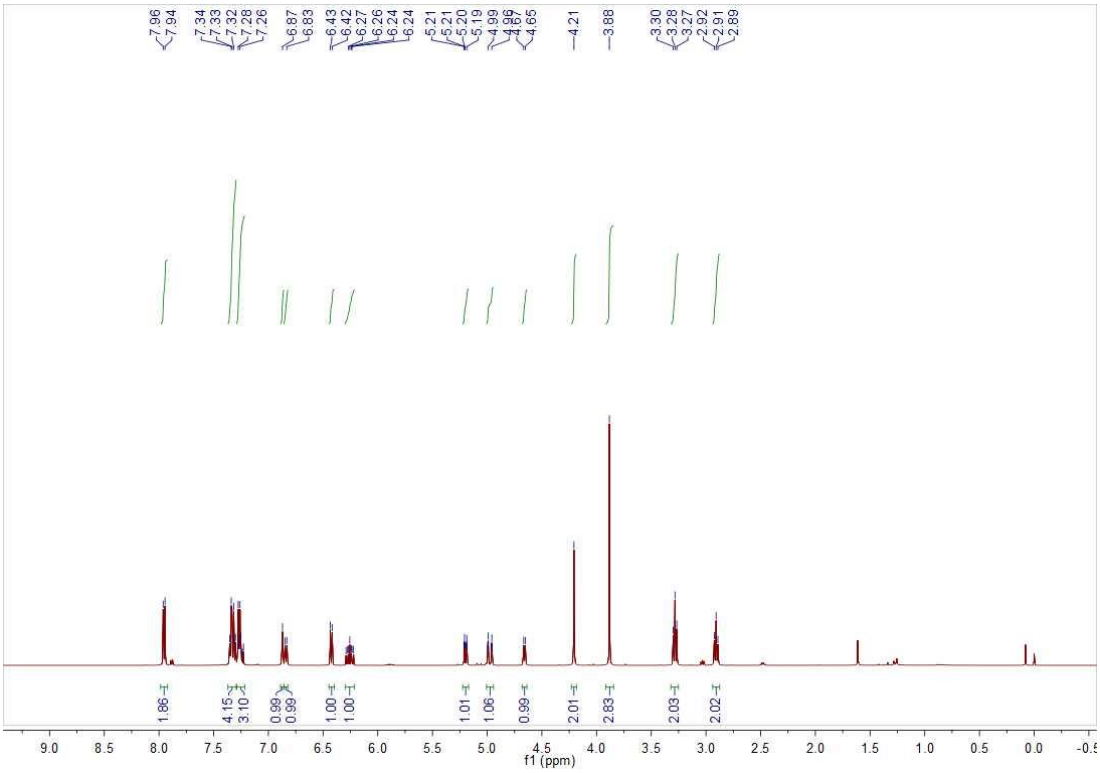

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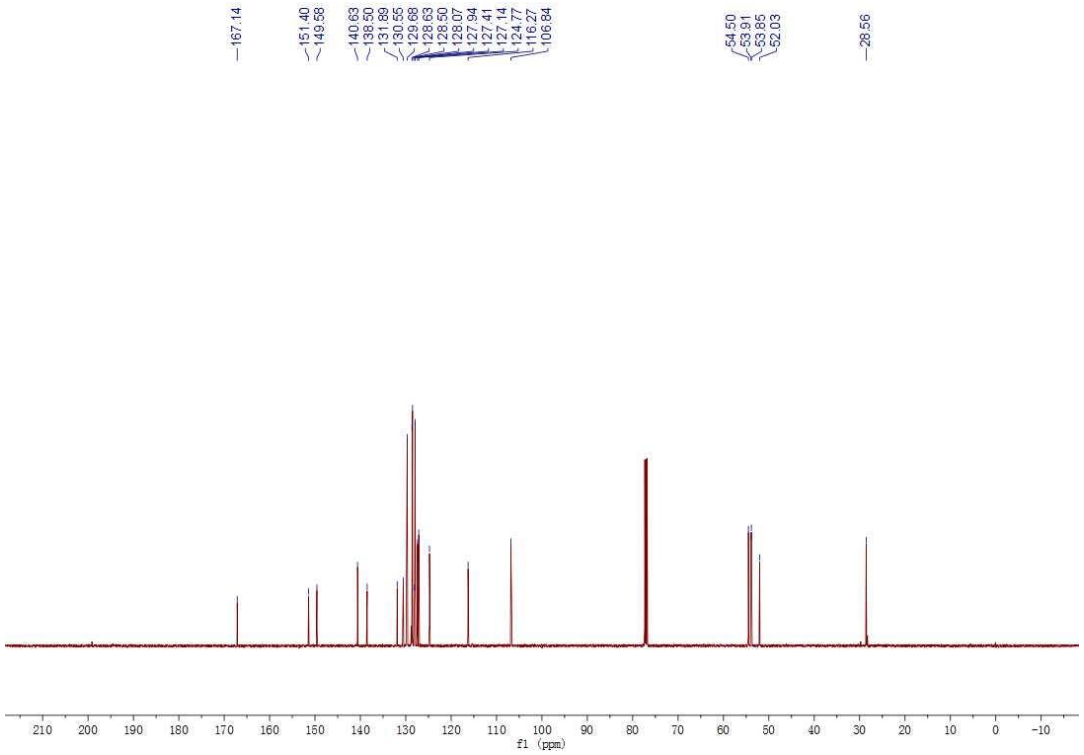

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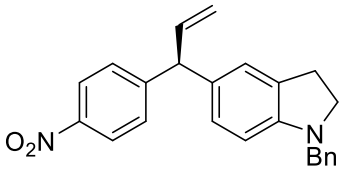

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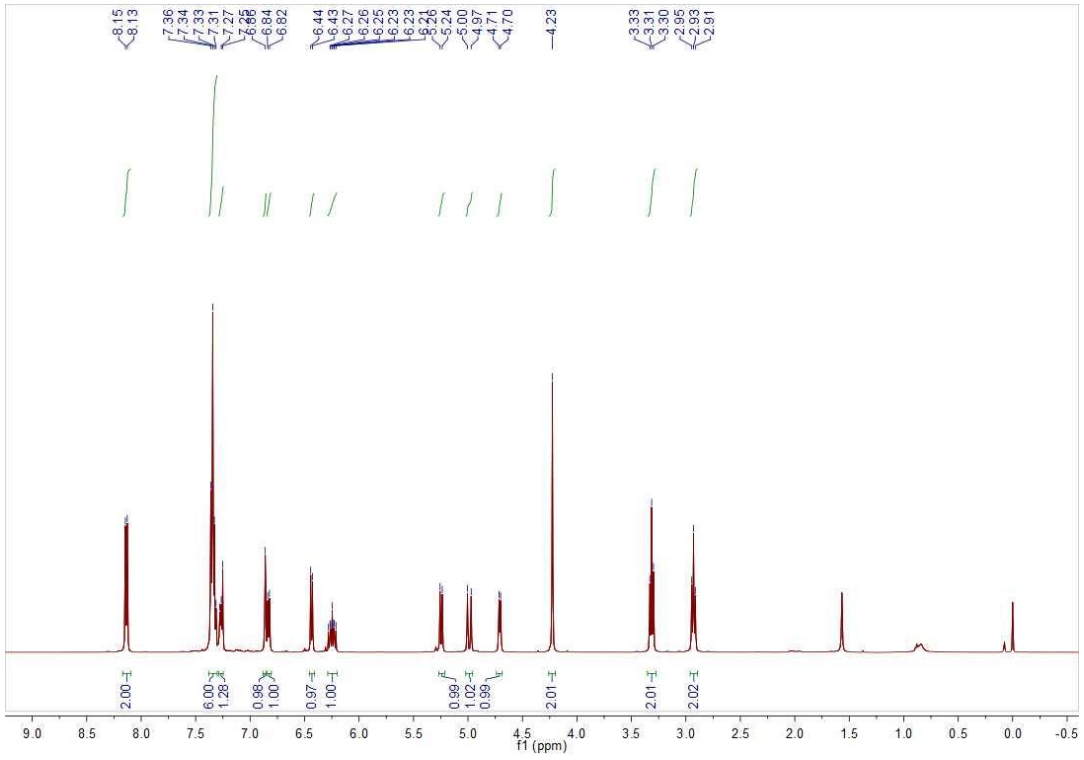

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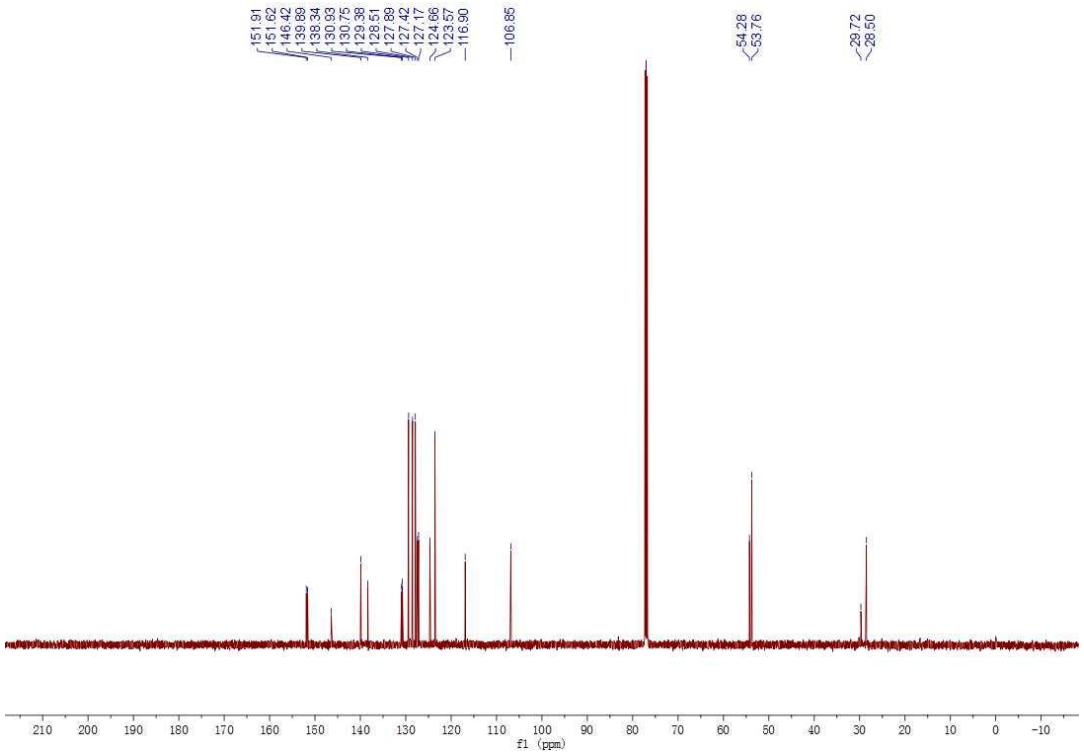

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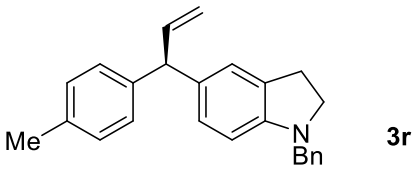

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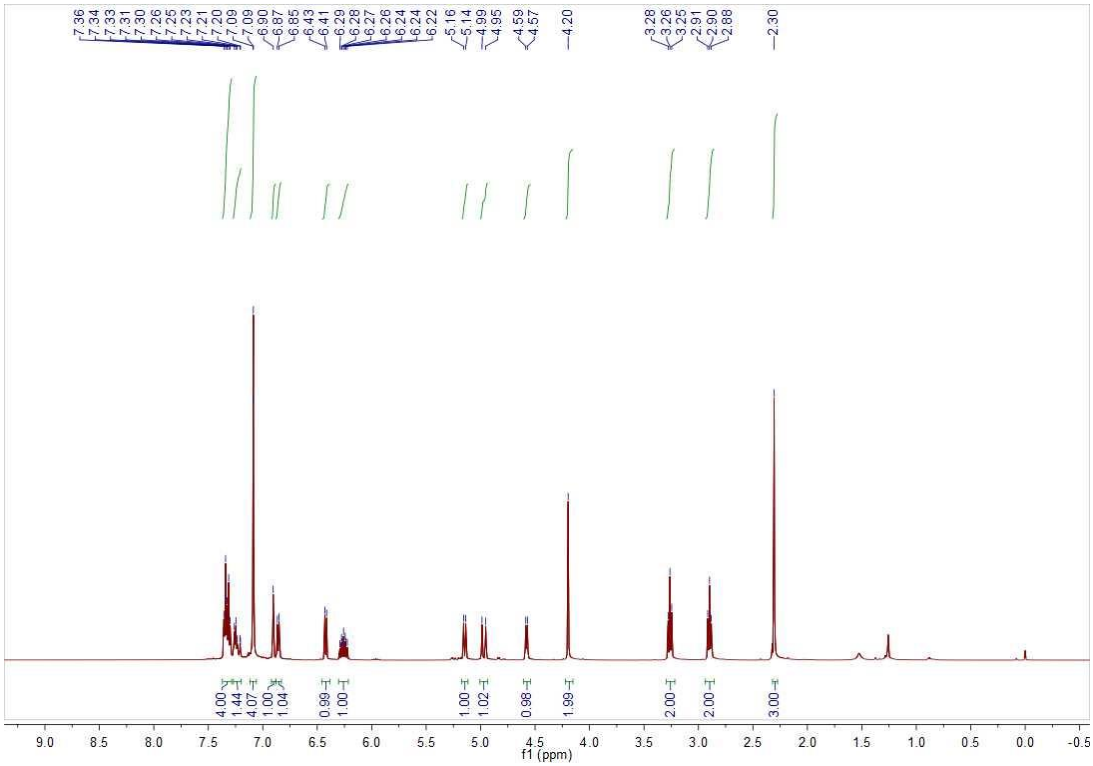

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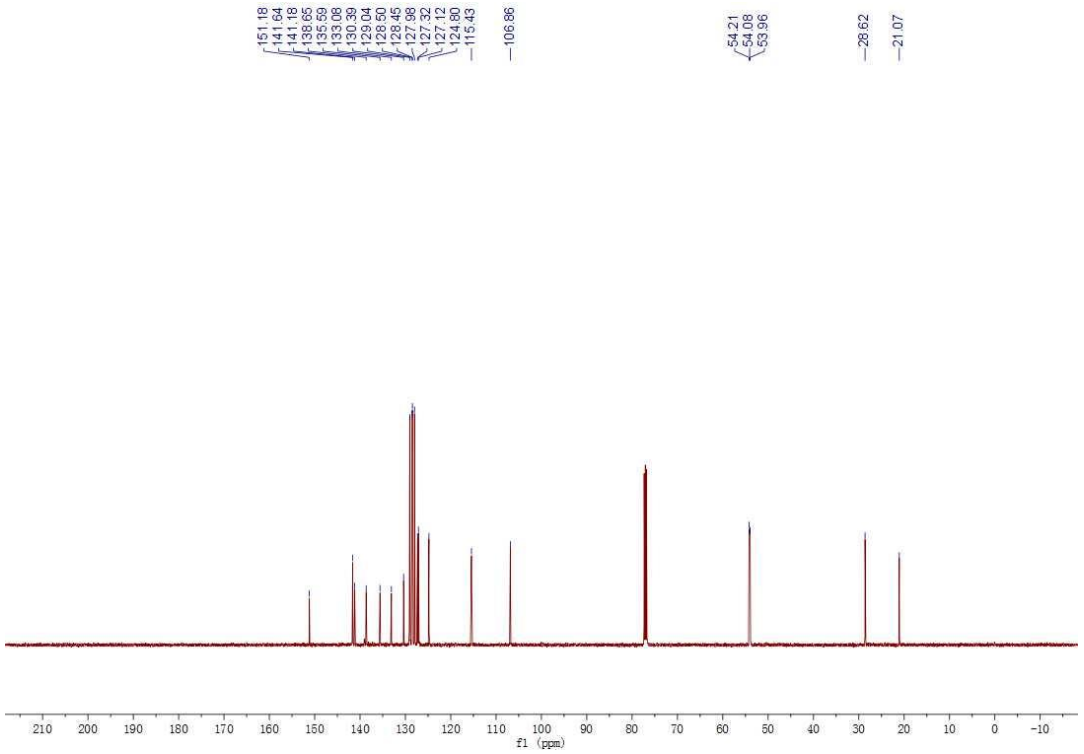

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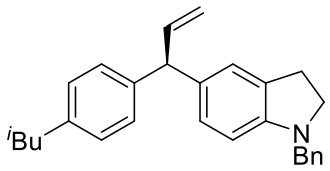
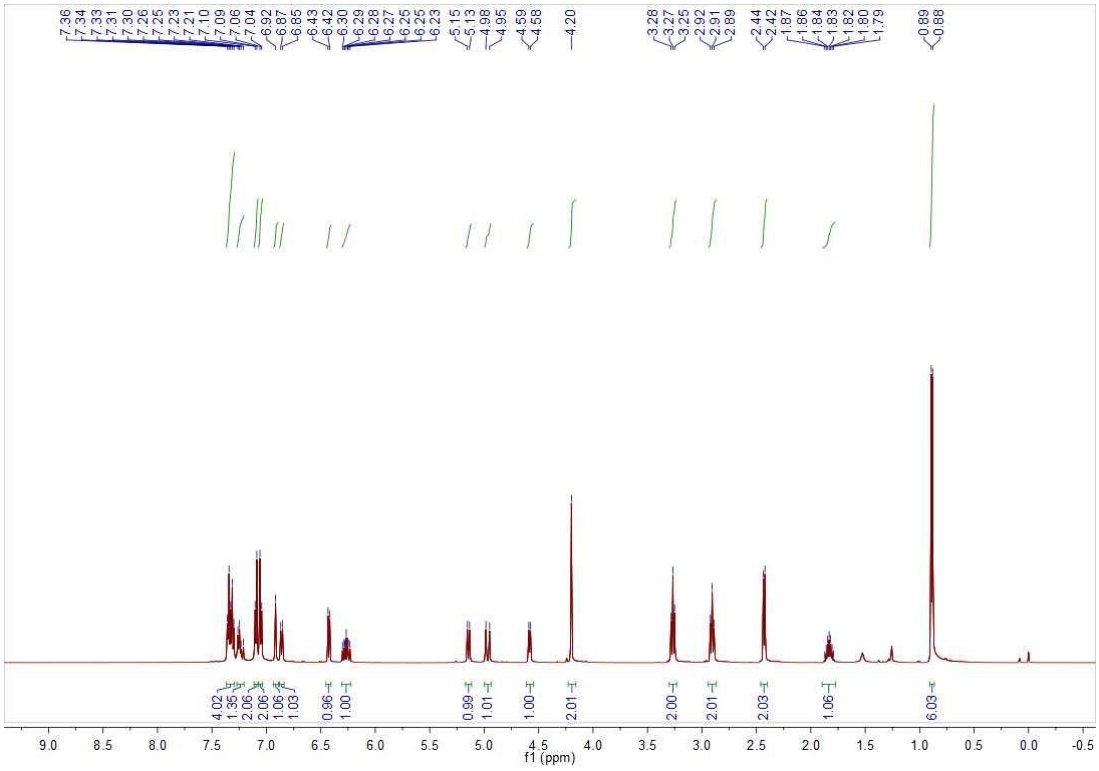
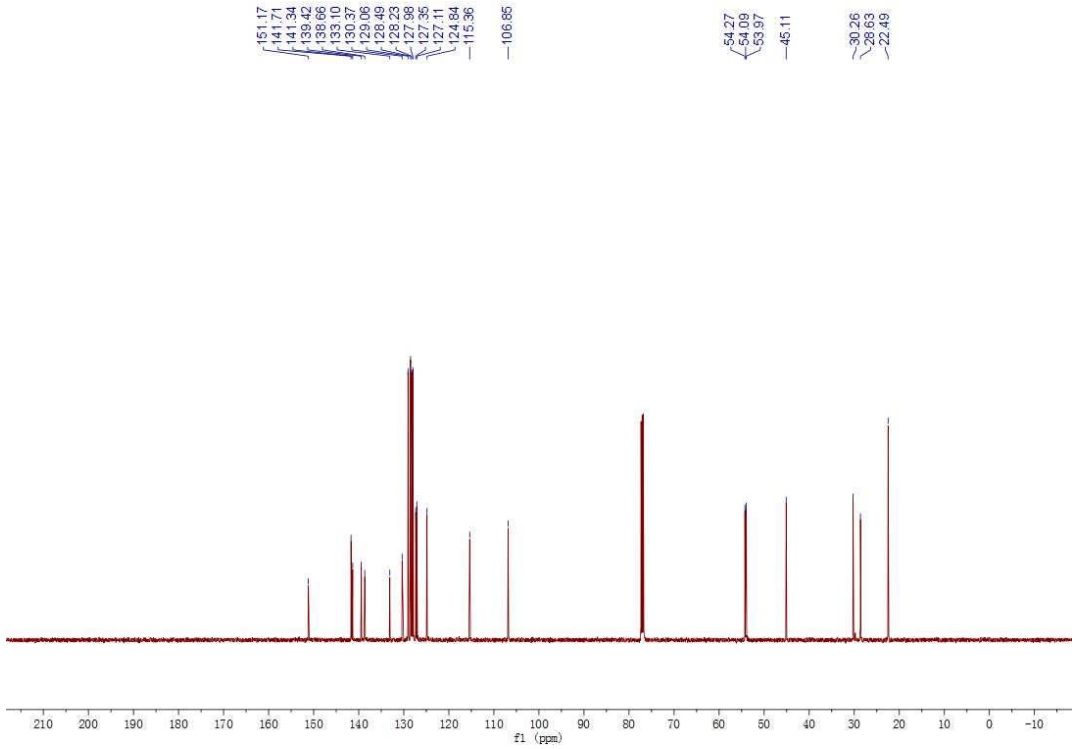


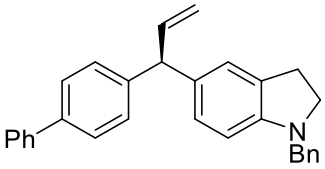
3r



$CDCl_3$; 500Hz



$CDCl_3$; 125Hz



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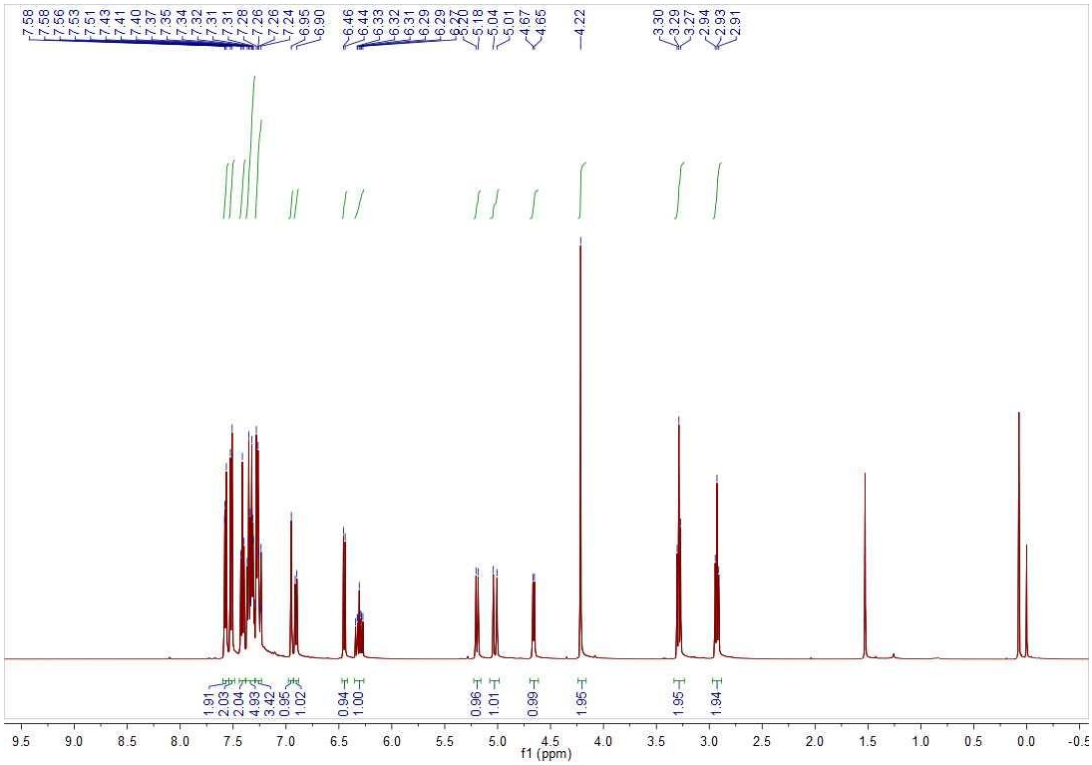

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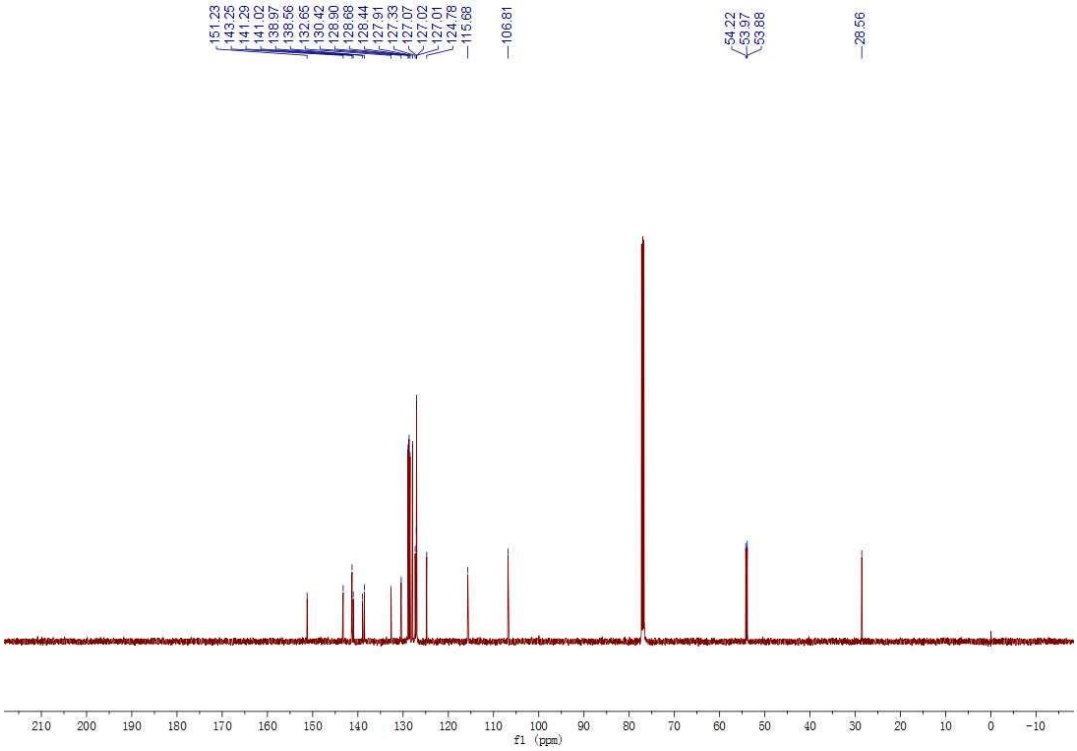

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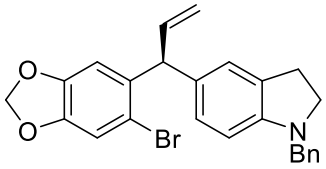

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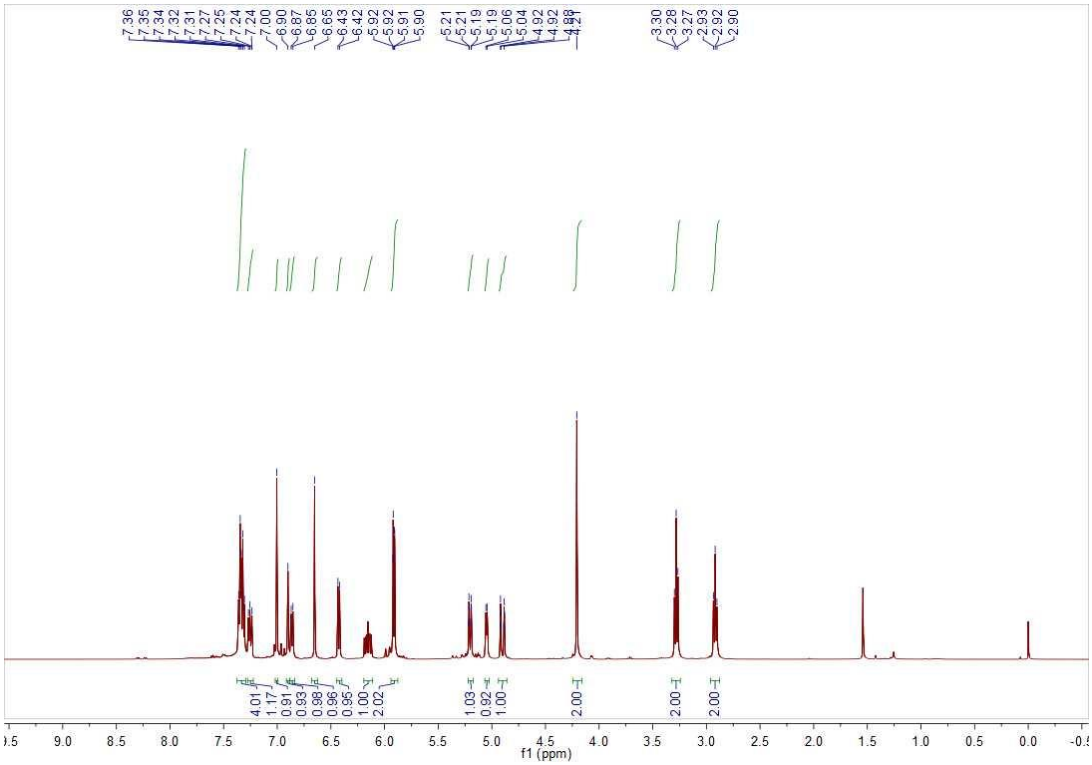
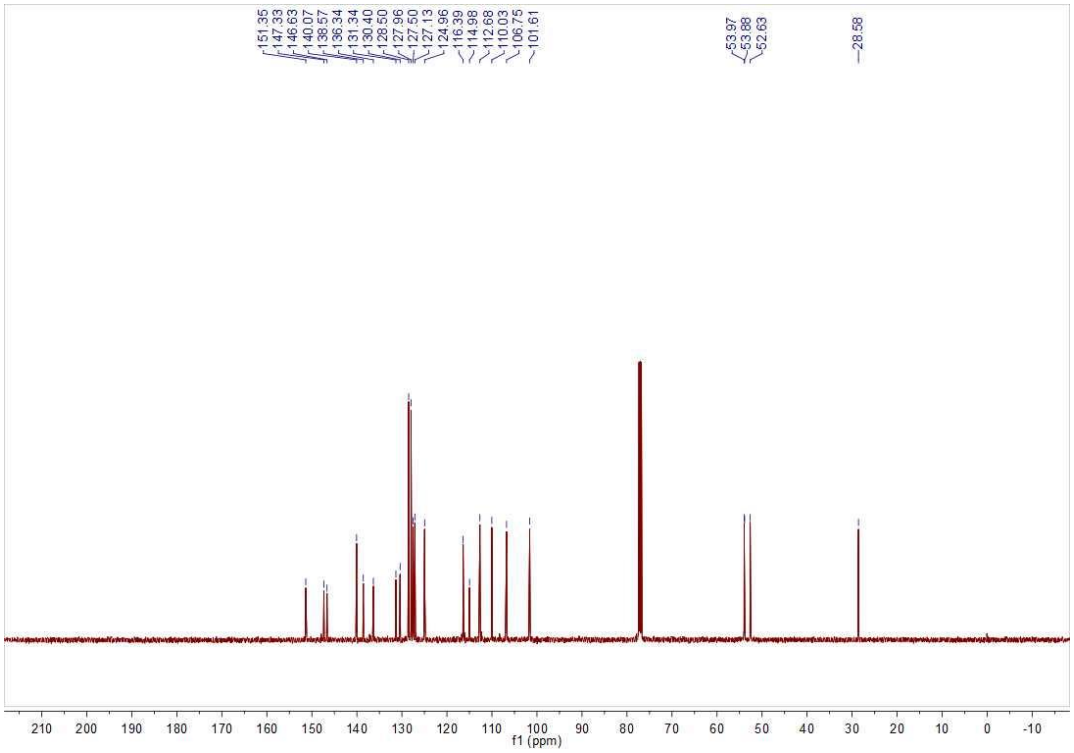
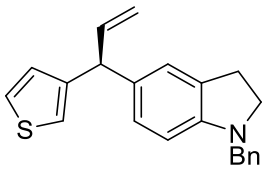


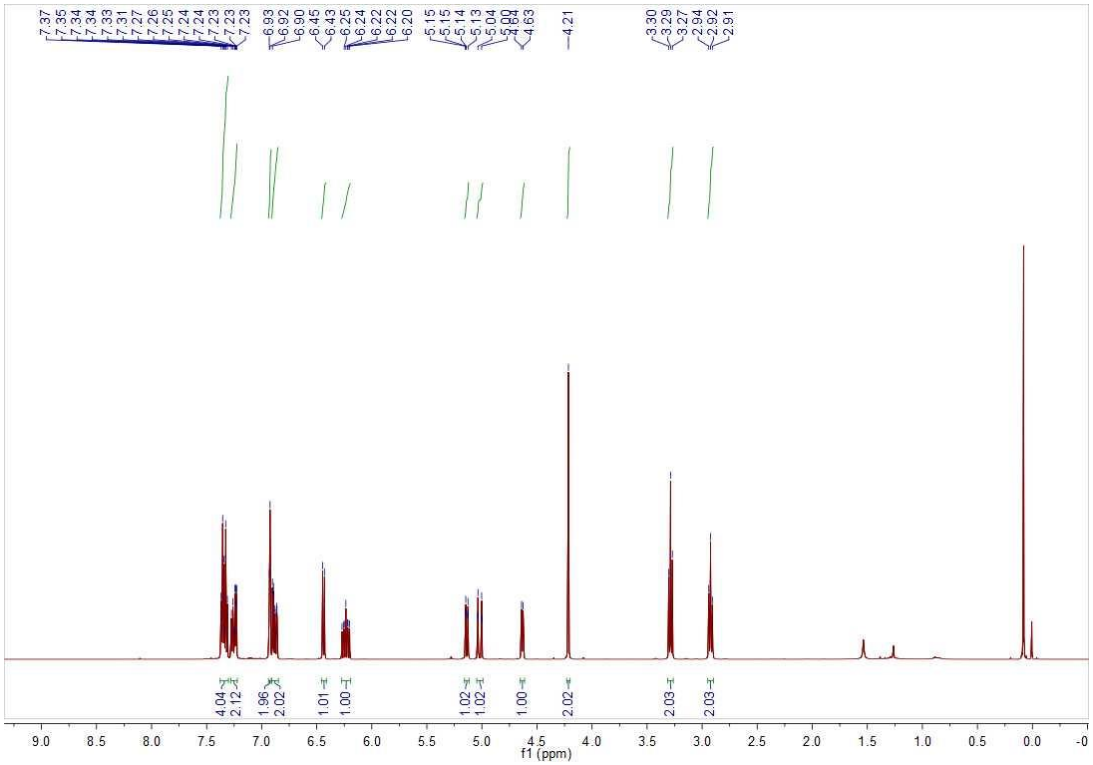
$CDCl_3$; 500Hz



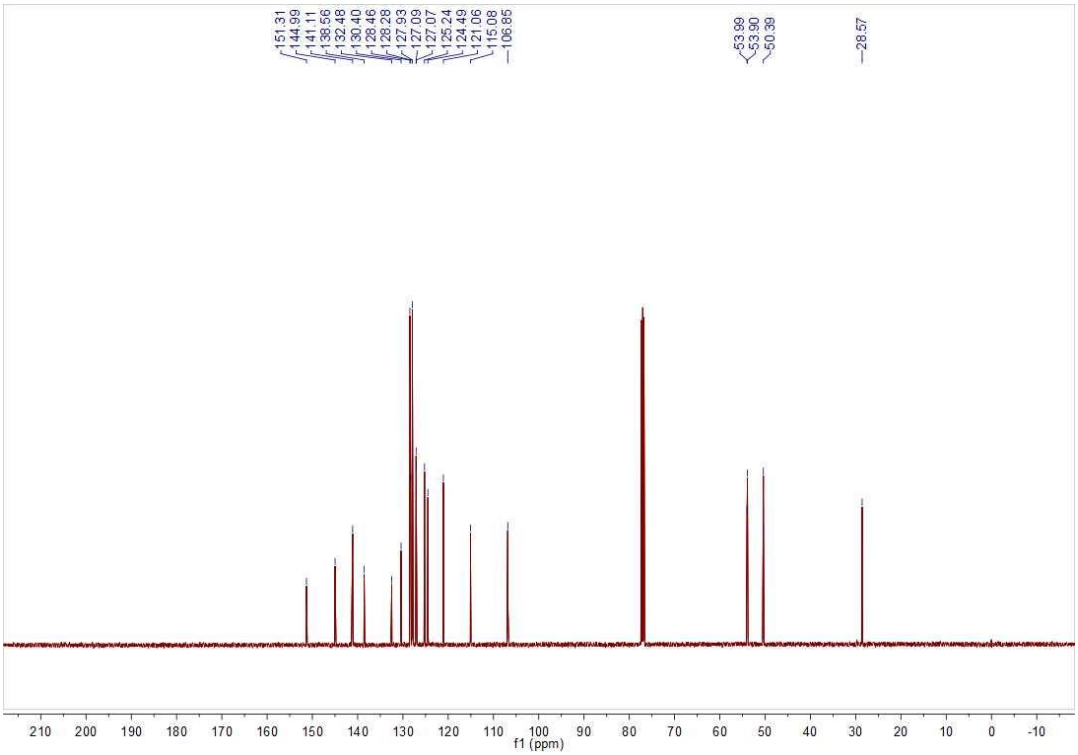
$CDCl_3$; 125Hz



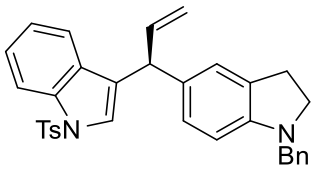
3v



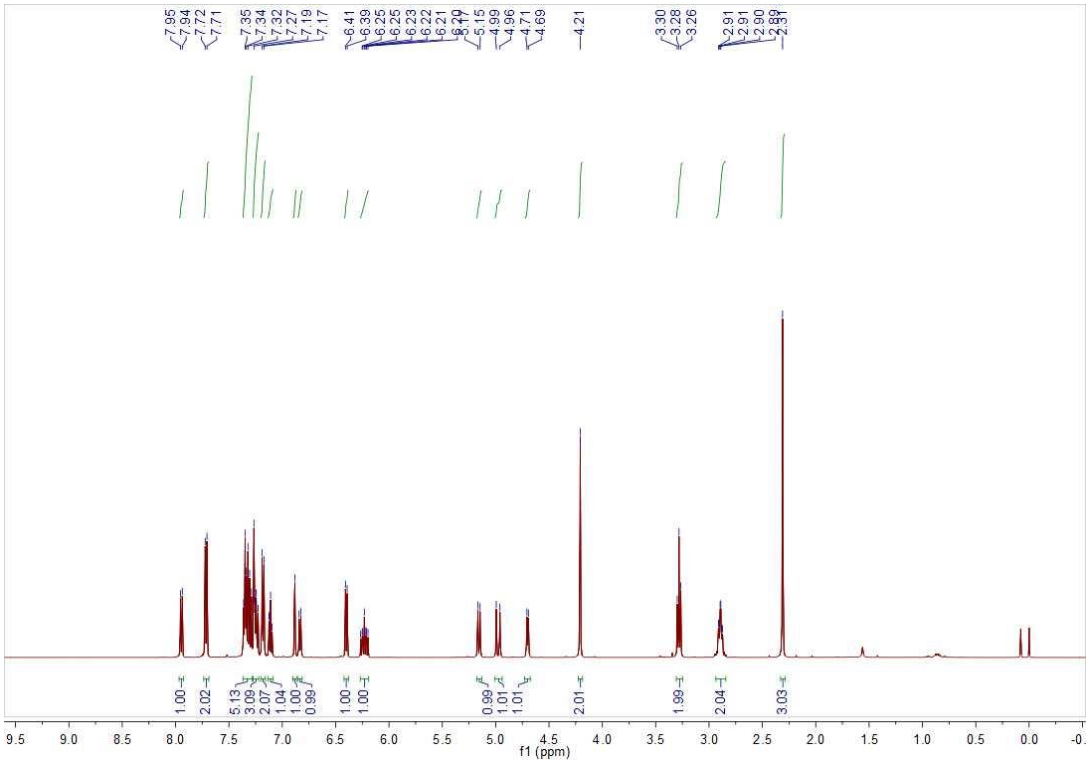
$CDCl_3$; 500Hz



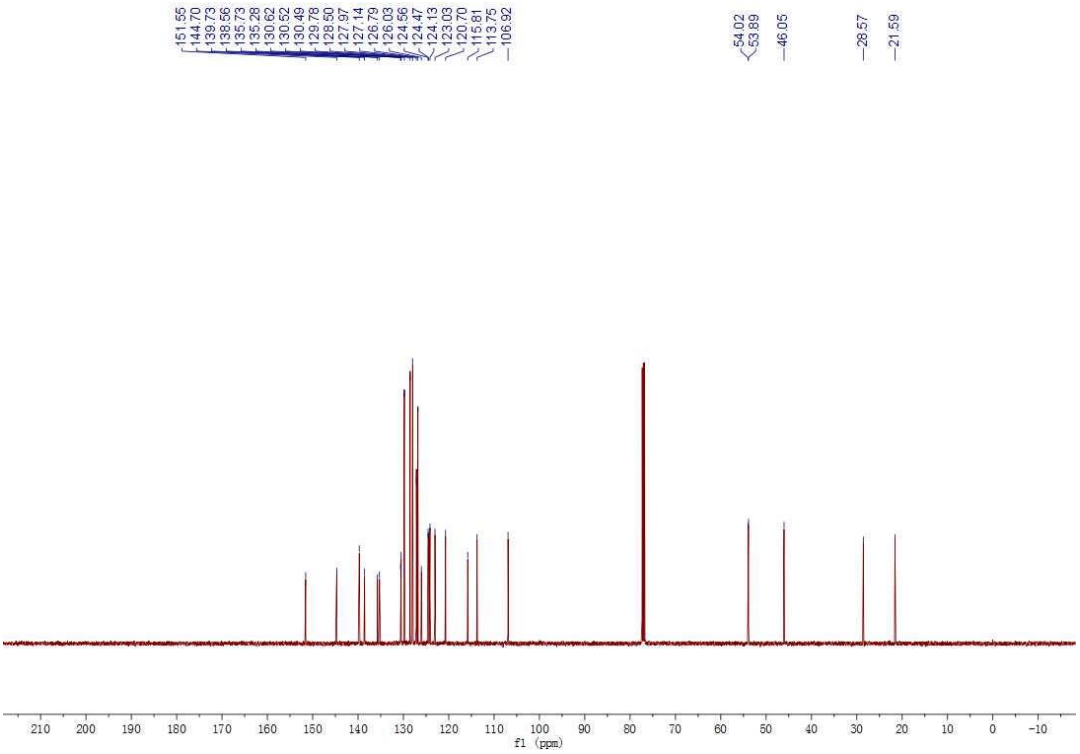
$CDCl_3$; 125Hz



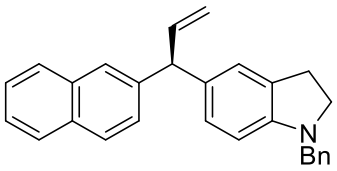
3w



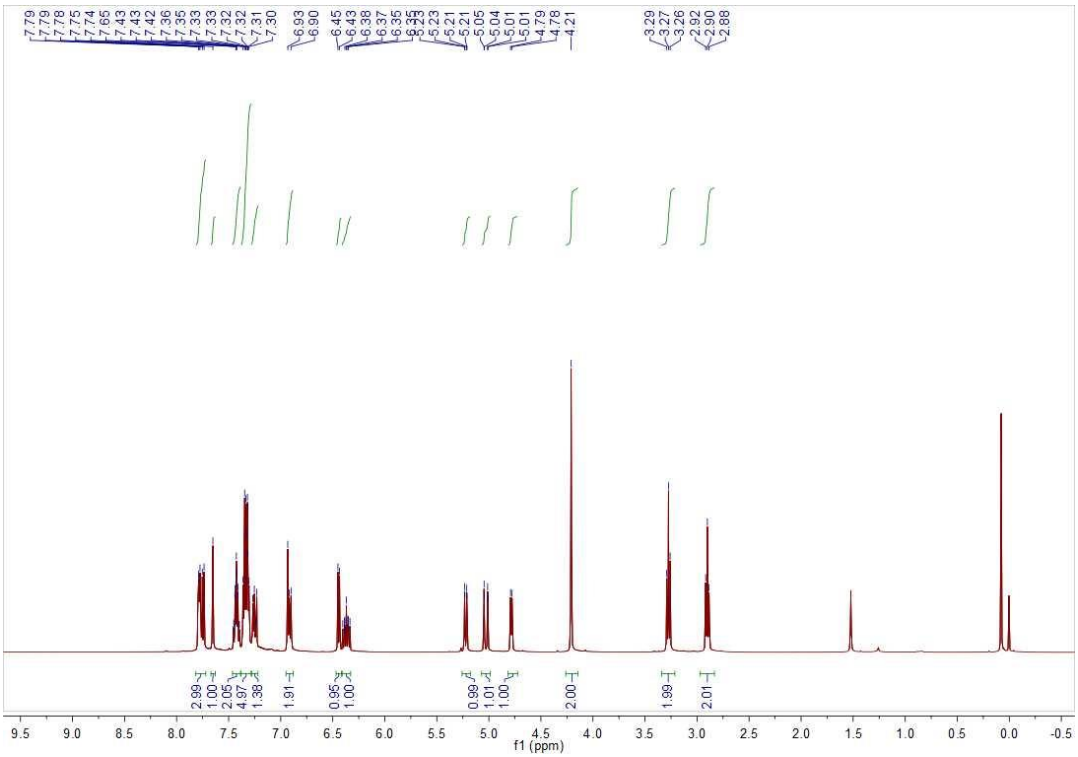
$CDCl_3$; 500Hz


151.55
144.70
139.73
138.66
135.73
135.28
130.62
130.52
130.49
129.78
128.50
127.97
127.14
126.79
126.03
124.56
124.47
124.13
123.03
120.70
115.81
113.75
106.92
54.02
53.89
46.05
28.57
21.59
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

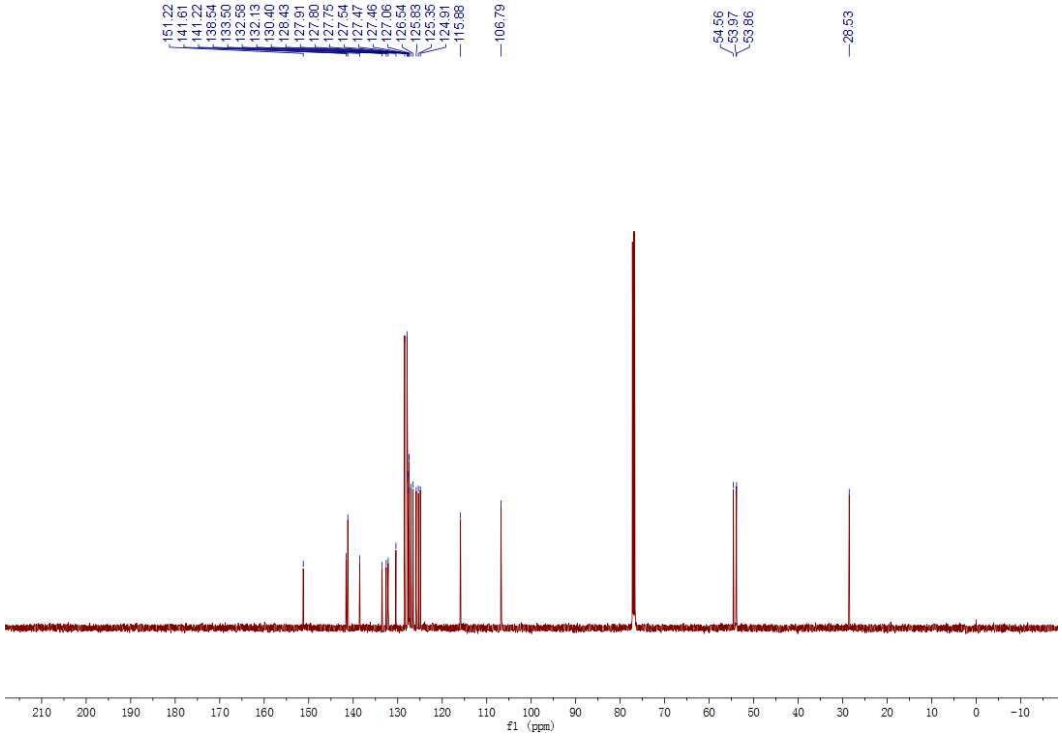
$CDCl_3$; 125Hz



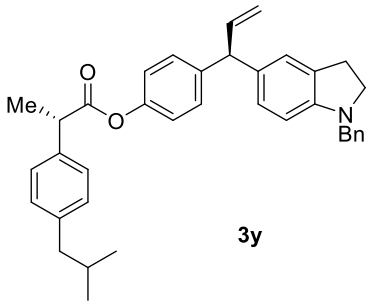
3x



$CDCl_3$; 500Hz



$CDCl_3$; 125Hz



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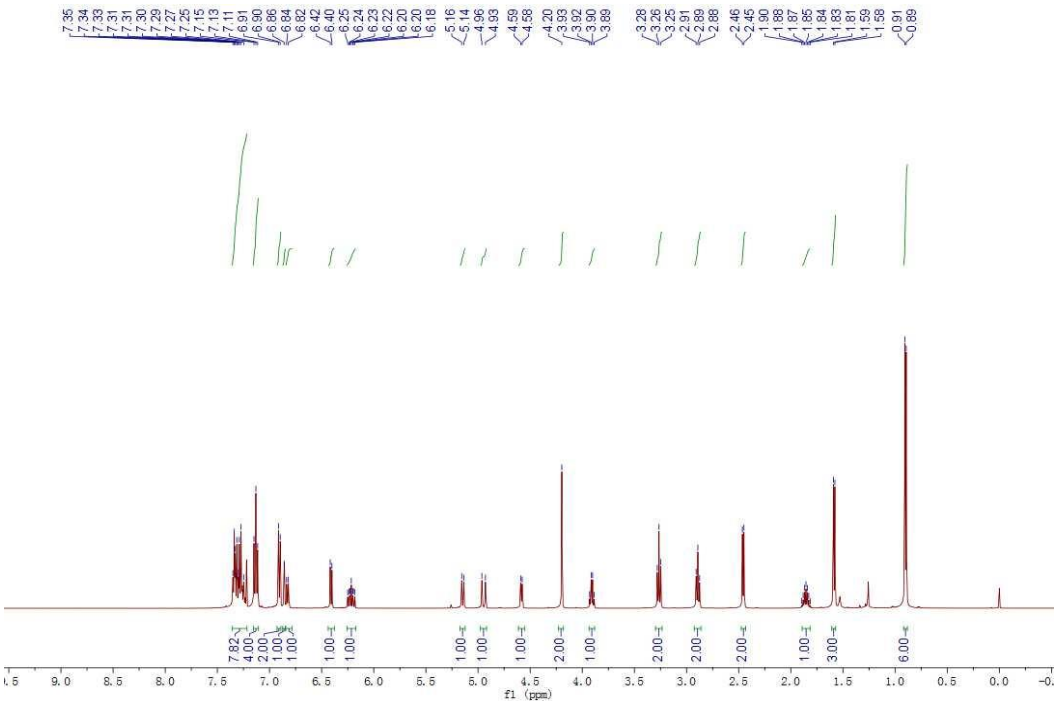
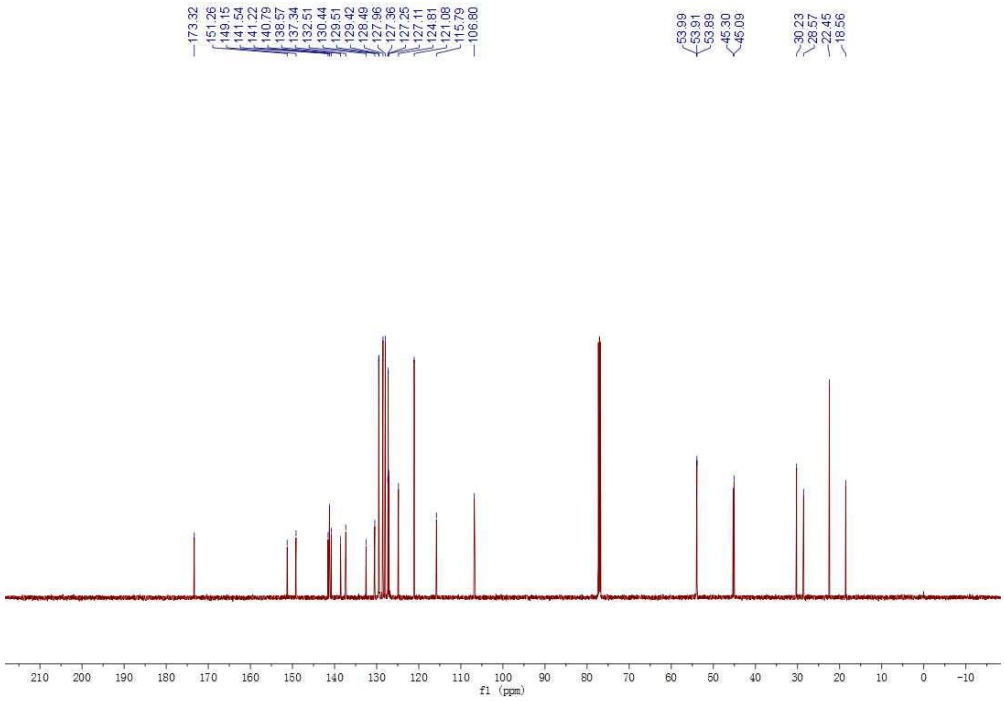
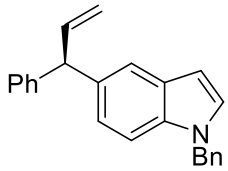


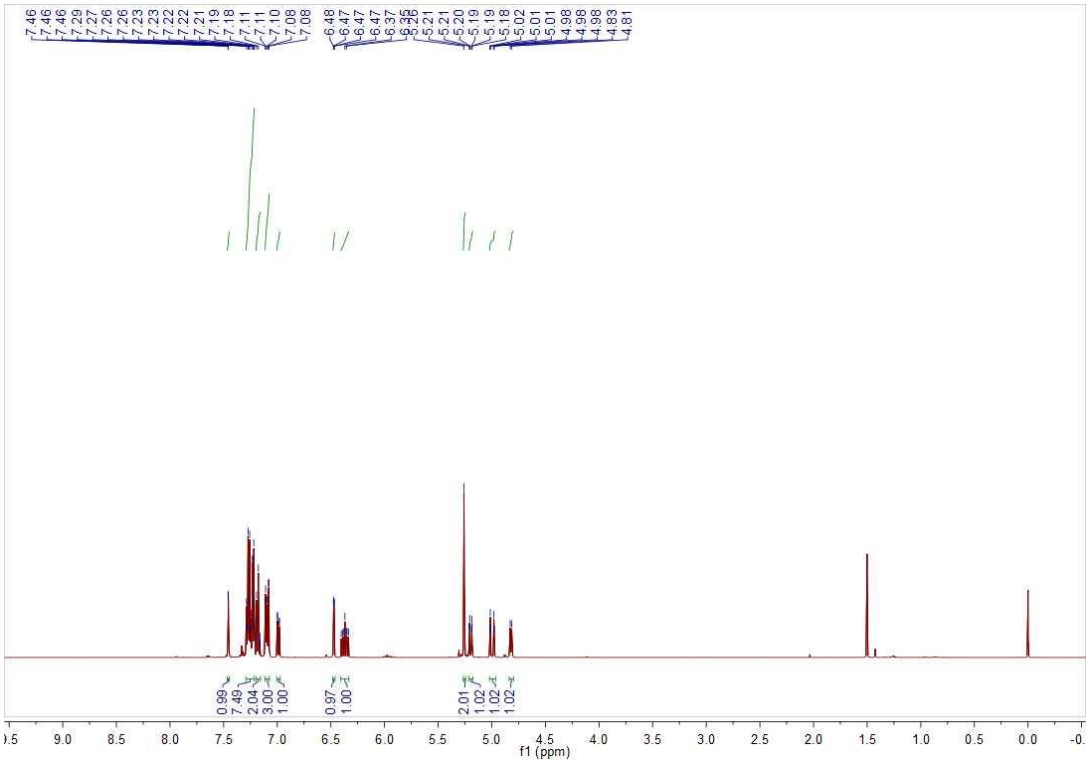
$CDCl_3$; 500Hz



$CDCl_3$; 125Hz



4a



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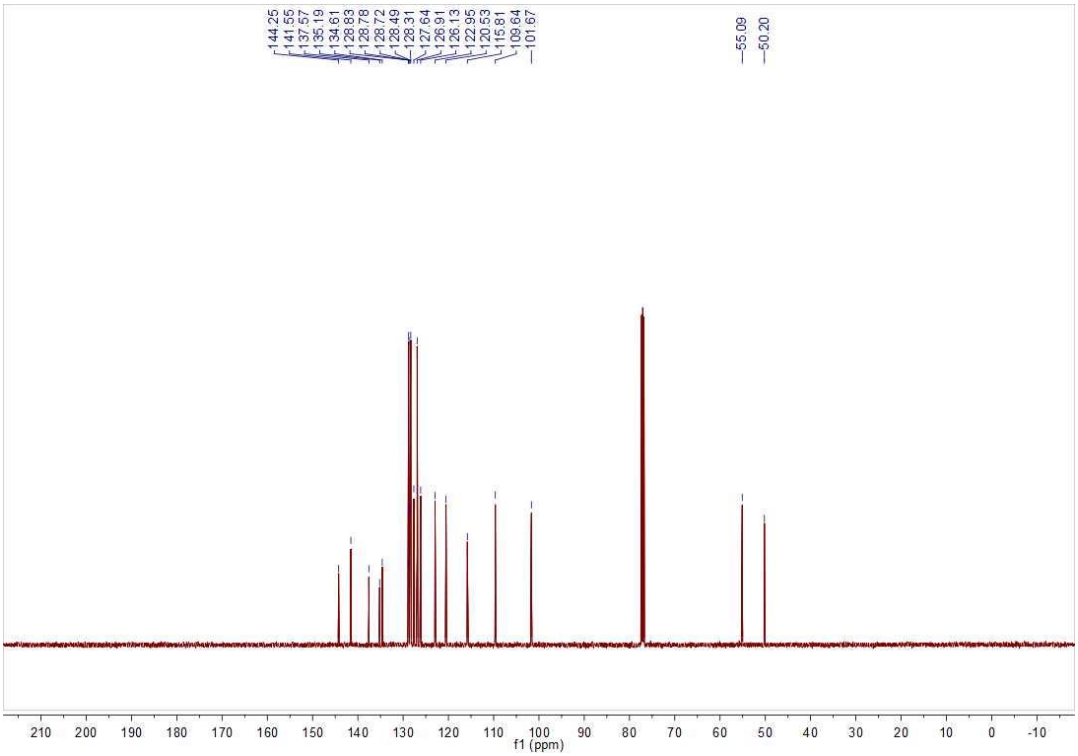

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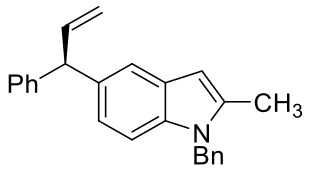
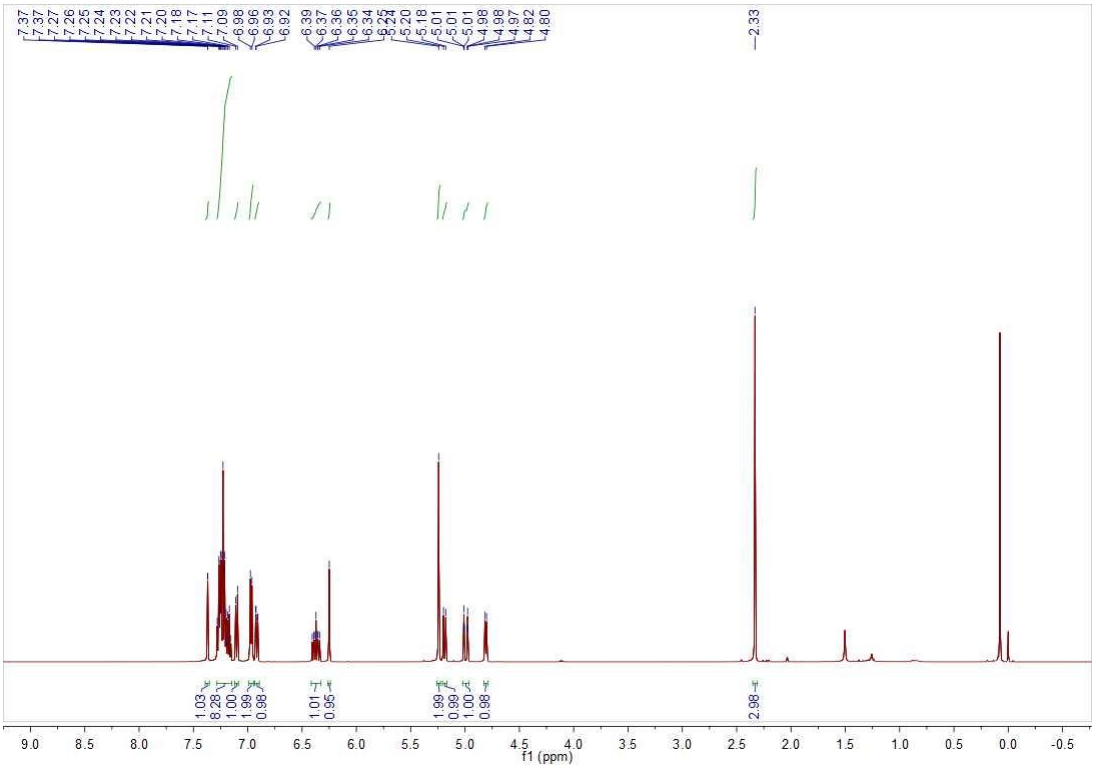


4b



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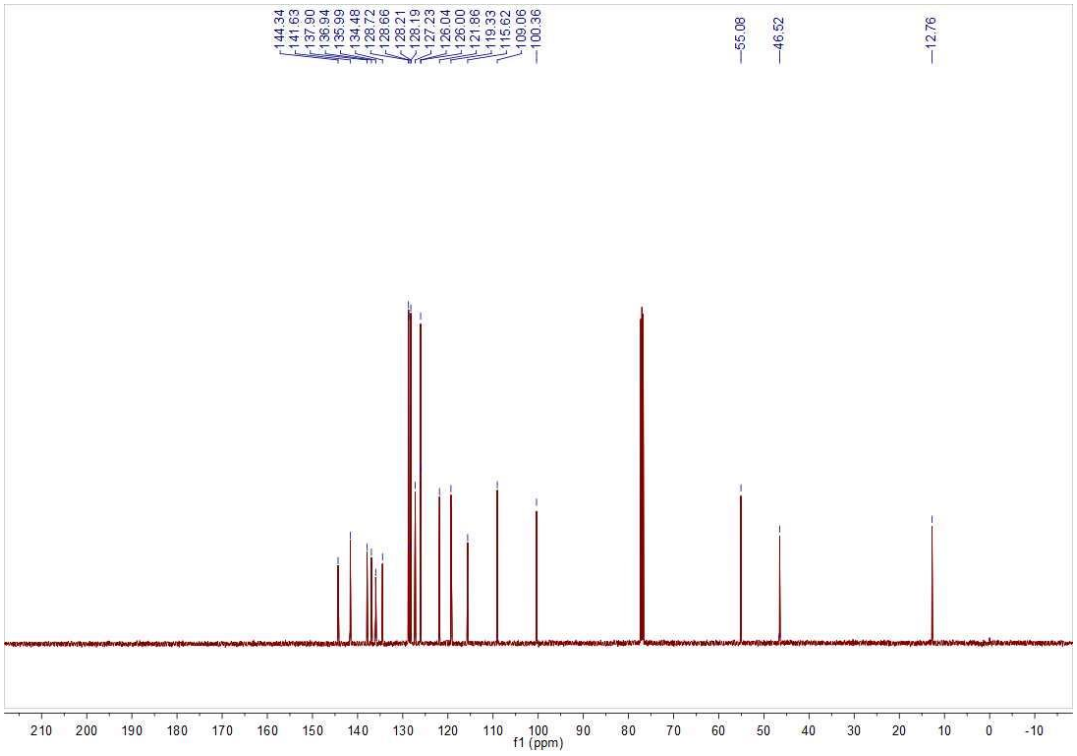

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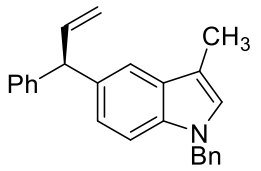
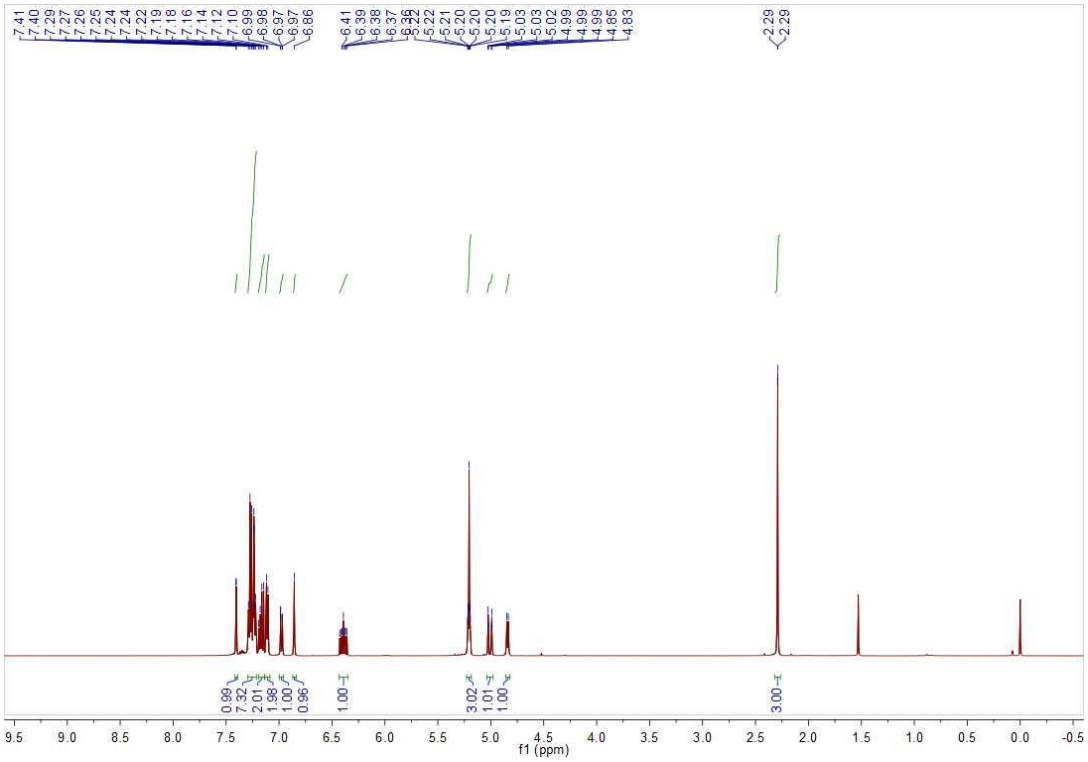


4c



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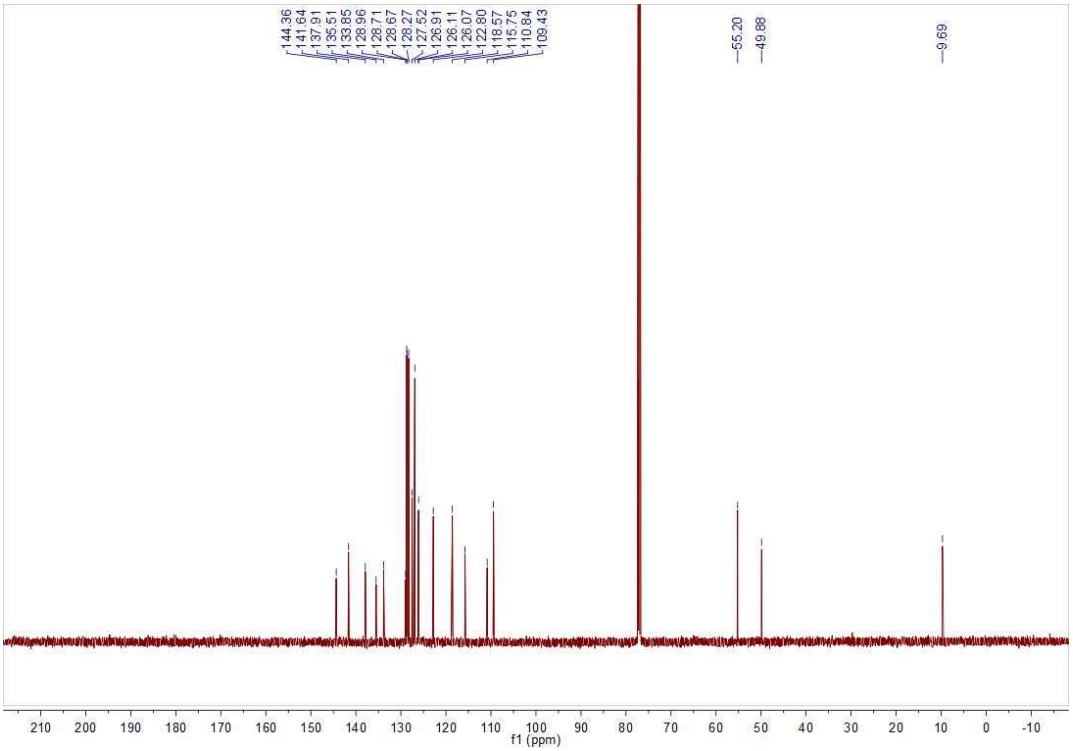

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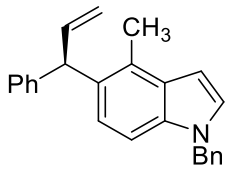

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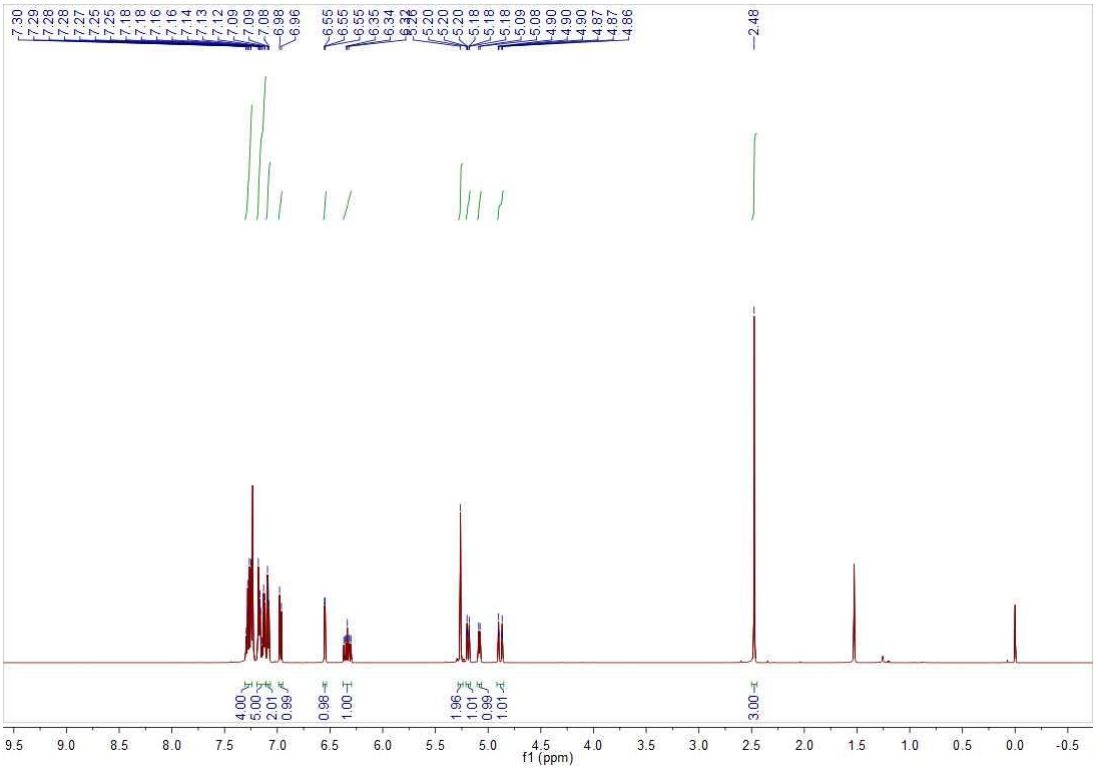

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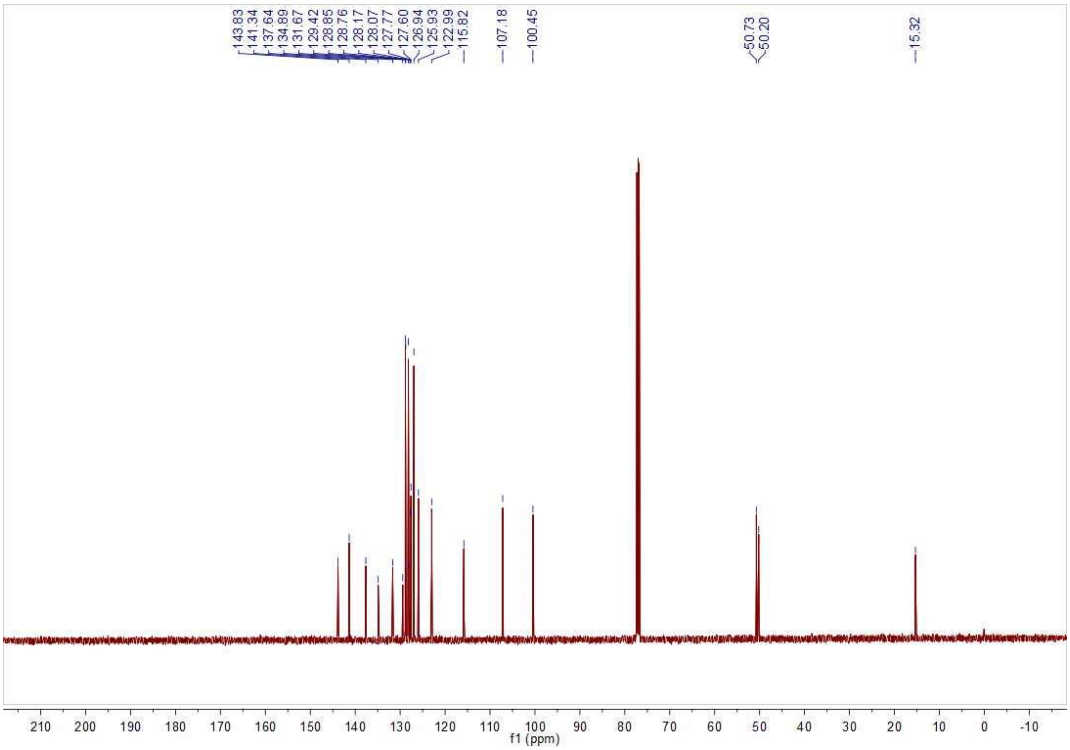

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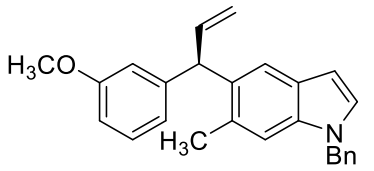
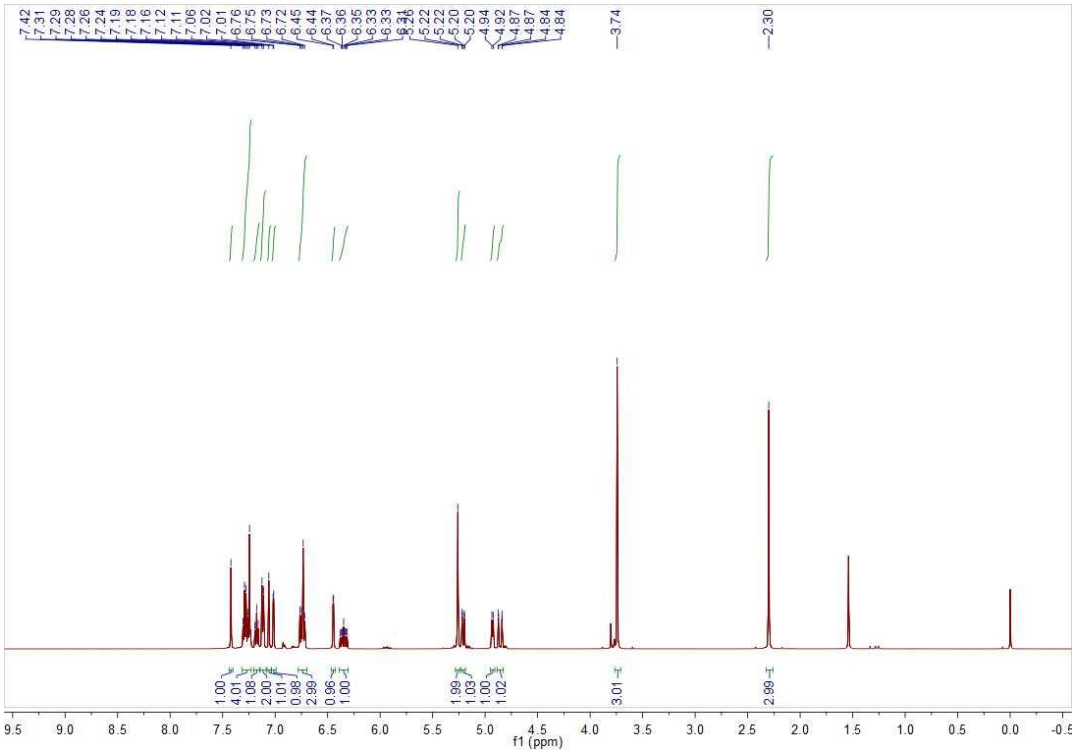


4e



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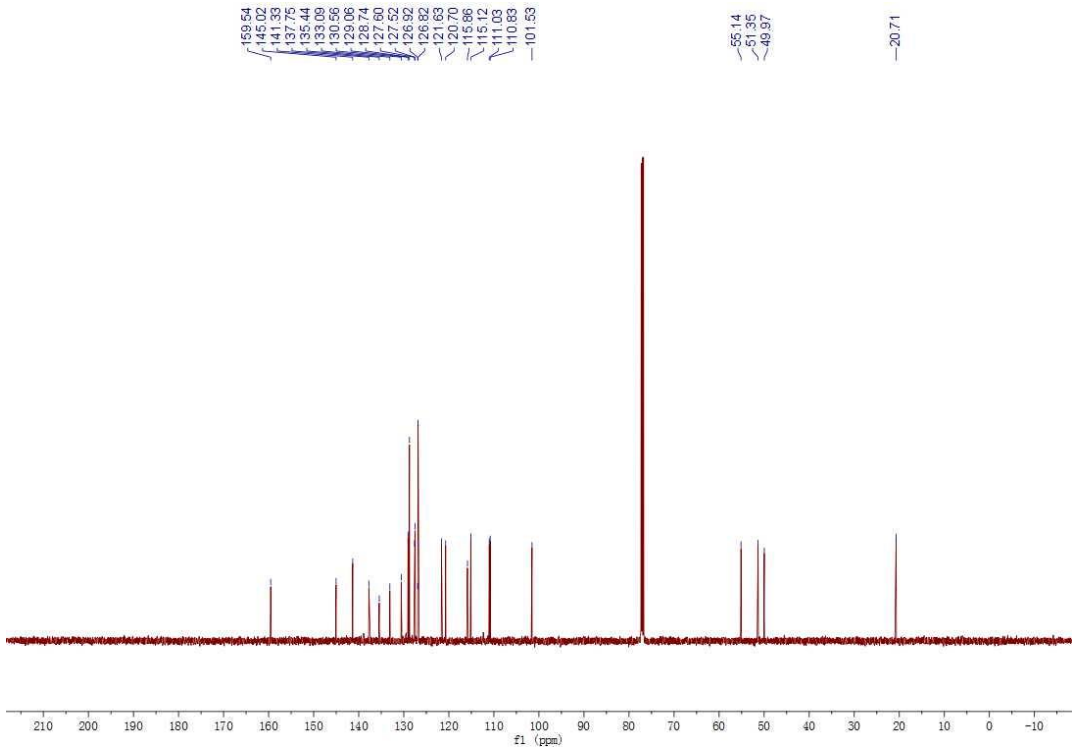

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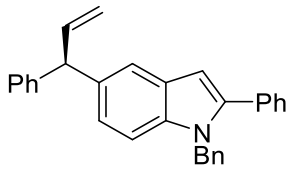

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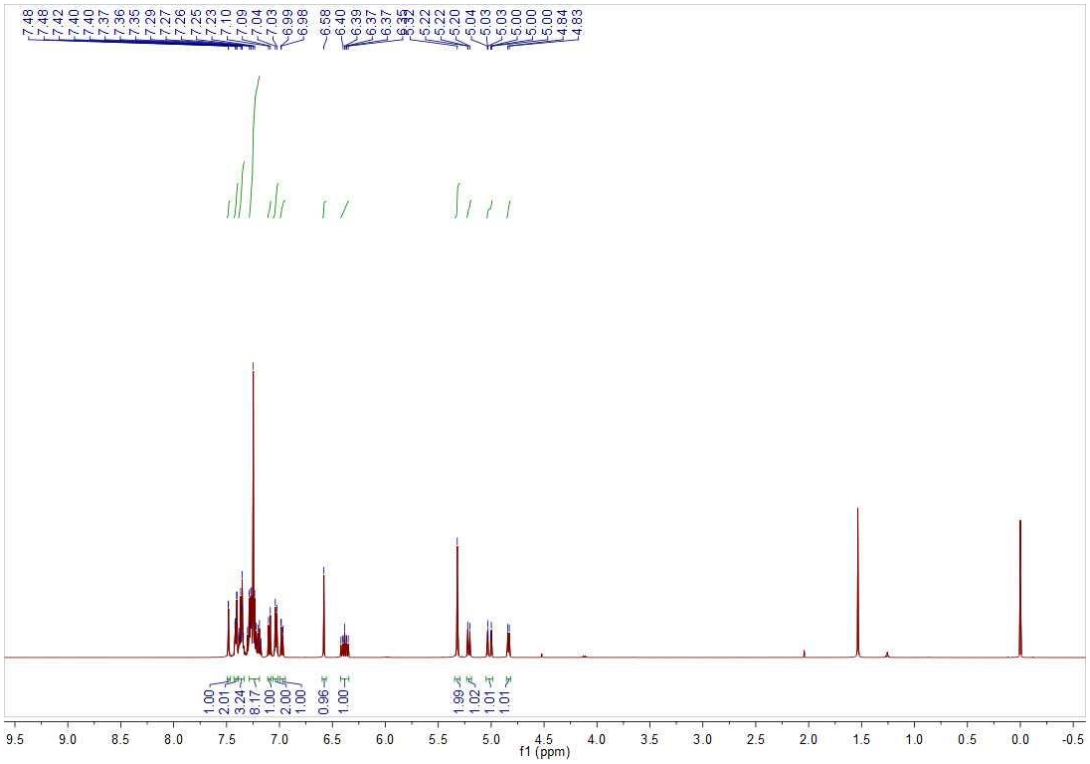

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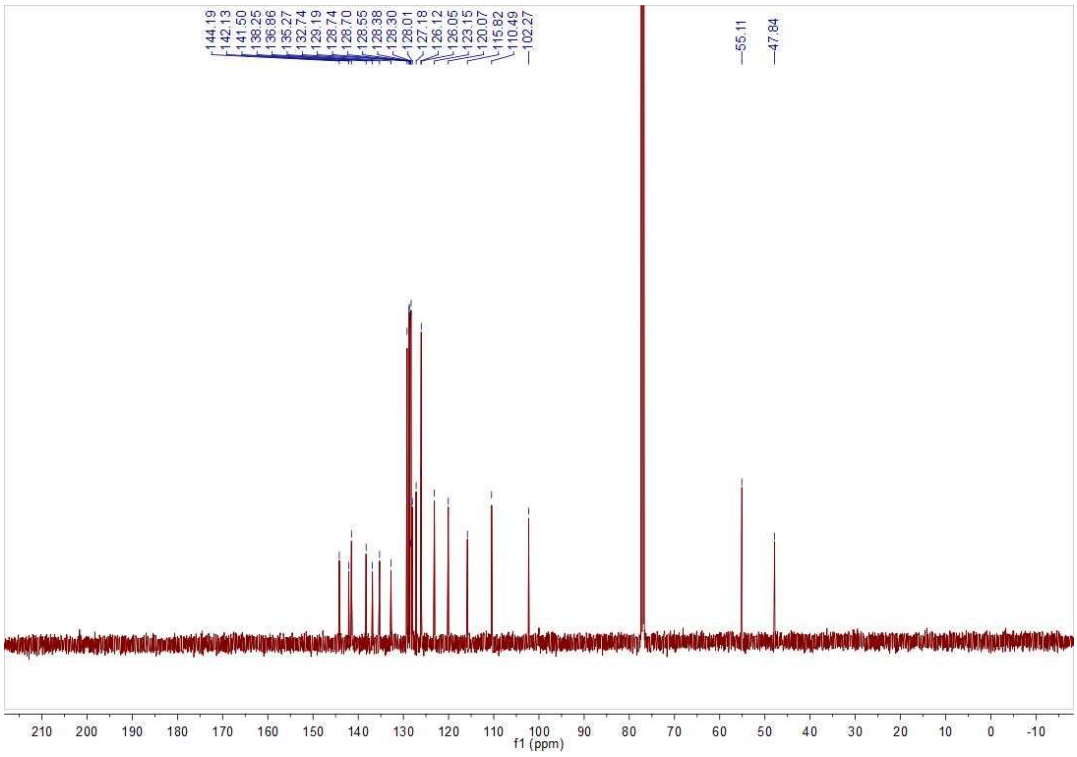

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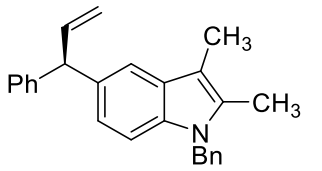
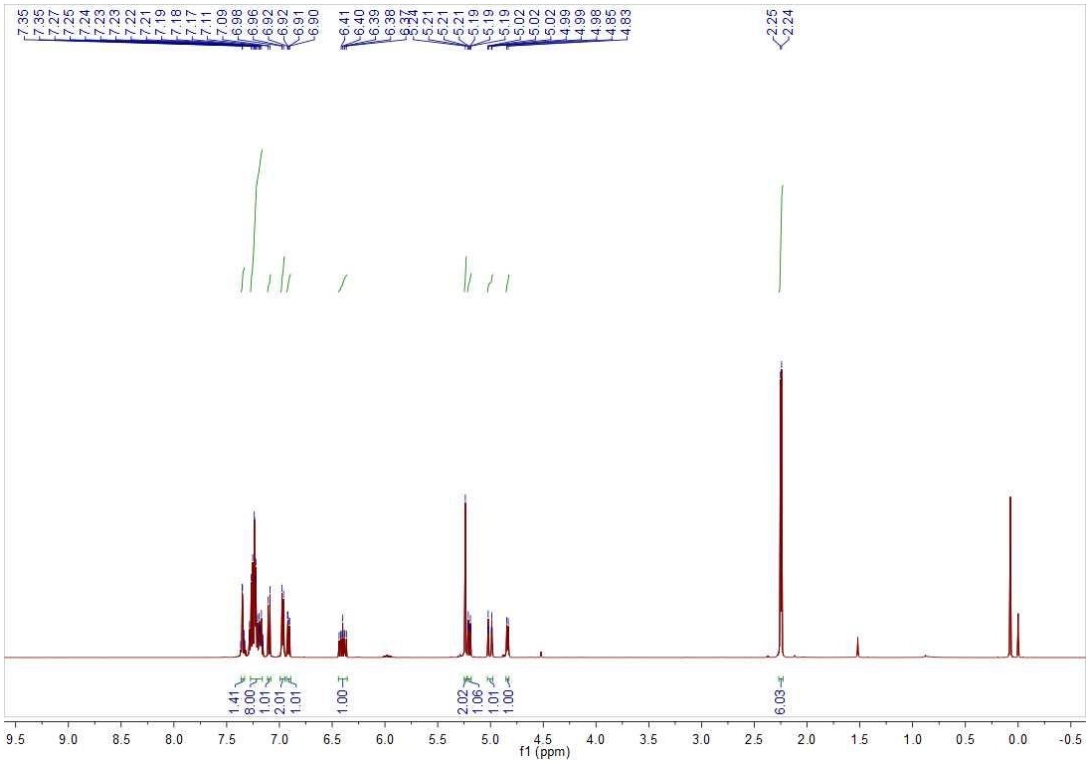
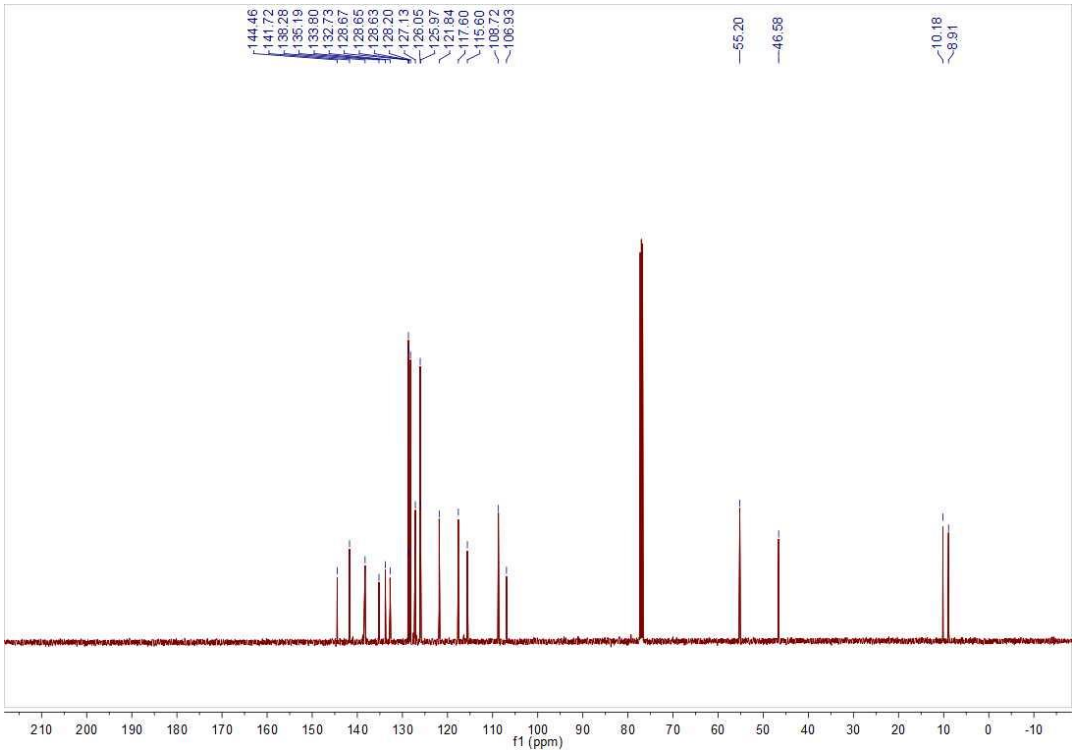


4g



$CDCl_3$; 500Hz



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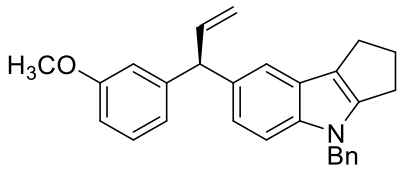
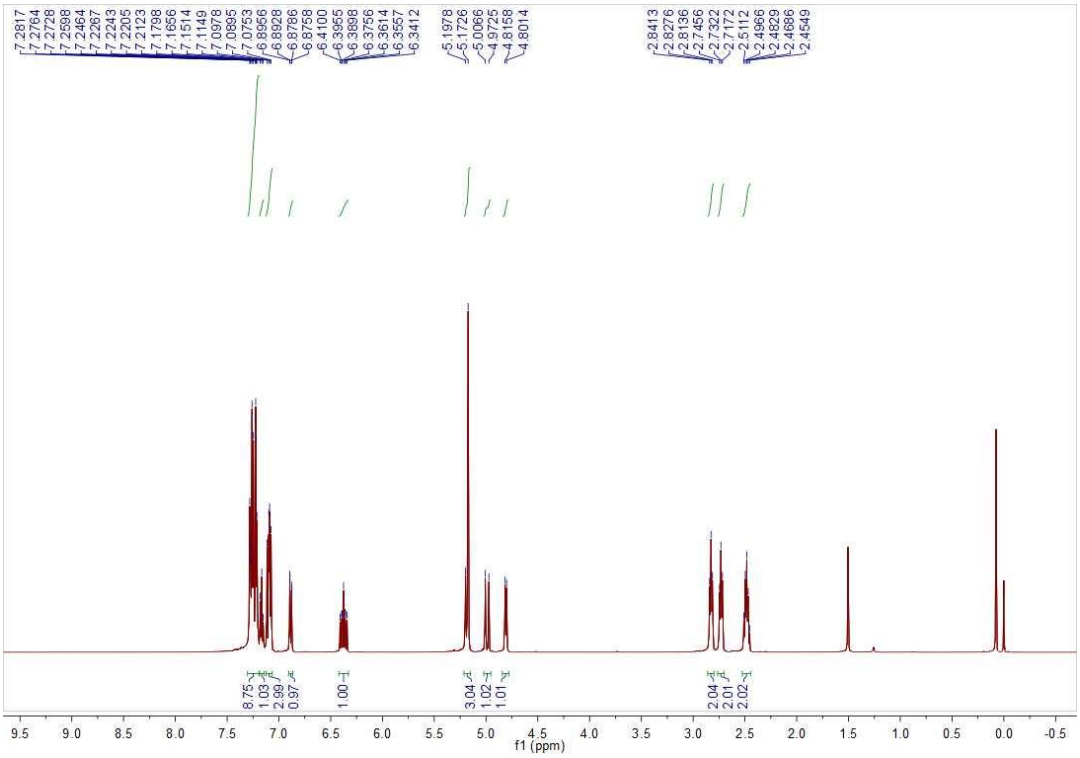


4h



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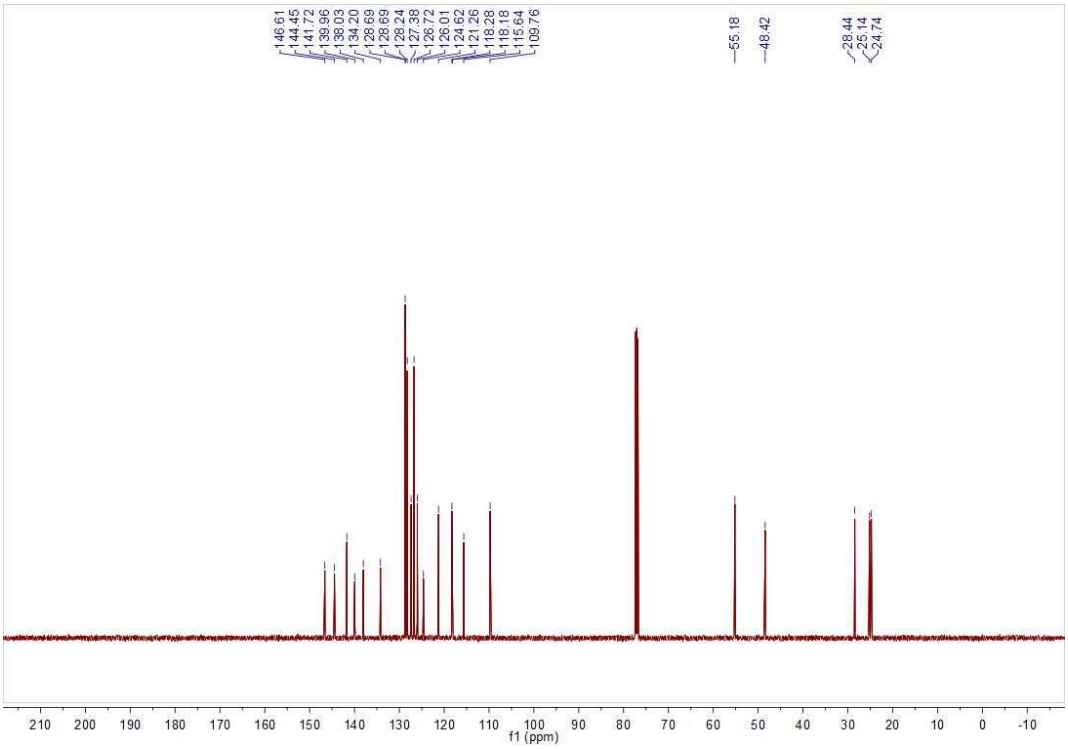
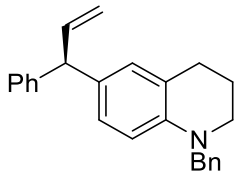
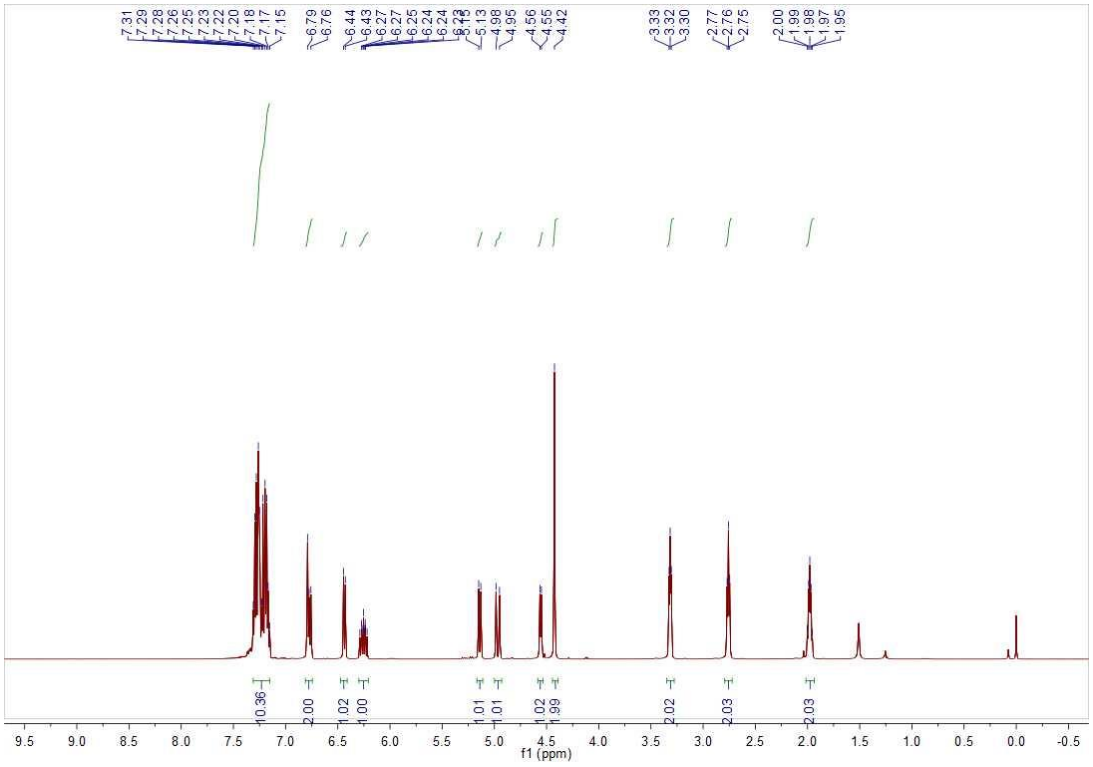


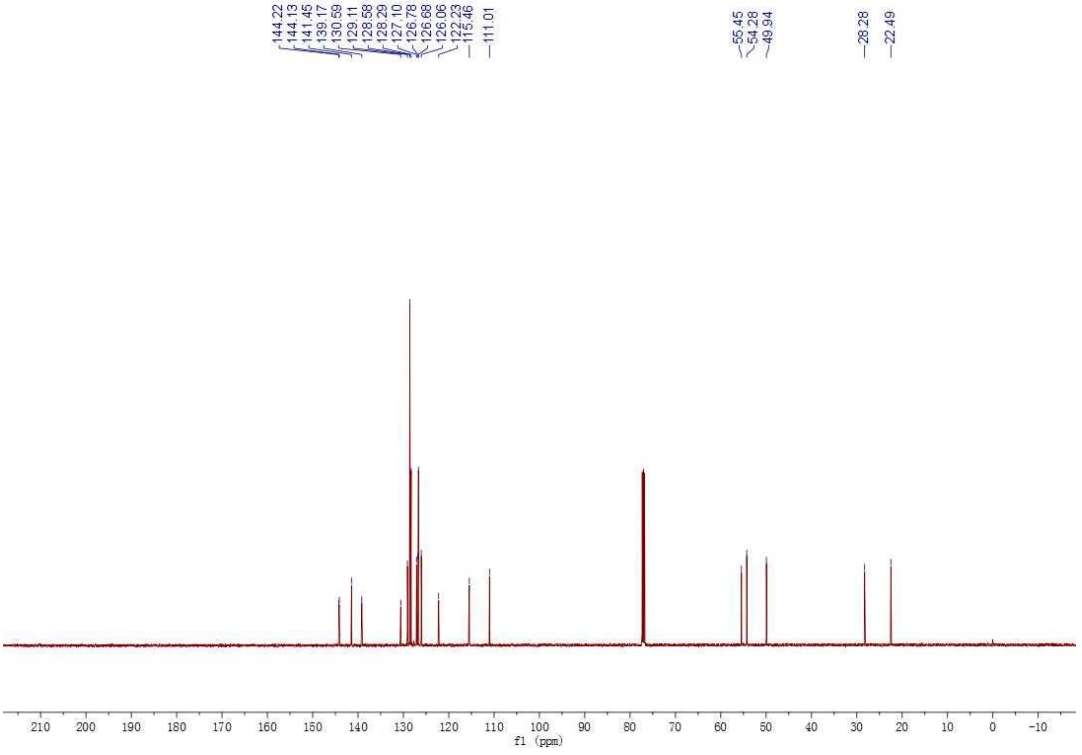
$CDCl_3$; 125Hz



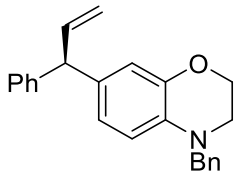
5a



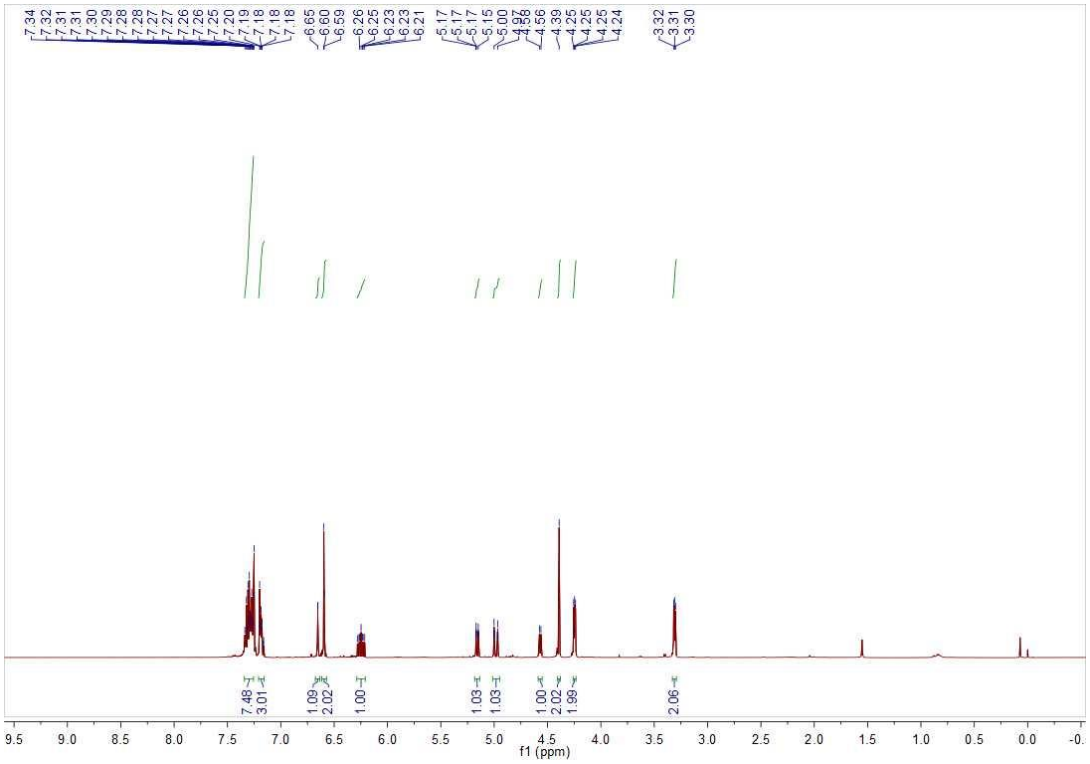
$CDCl_3$; 500Hz



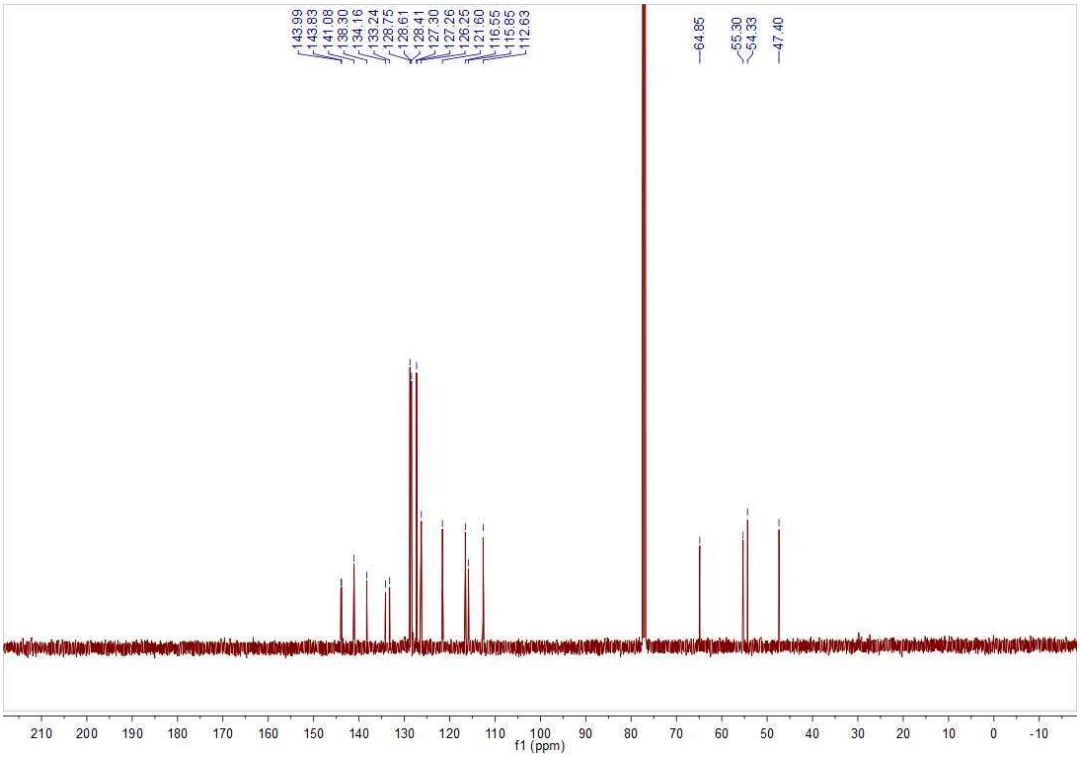
$CDCl_3$; 125Hz



5b



$CDCl_3$; 500Hz



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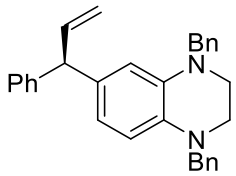
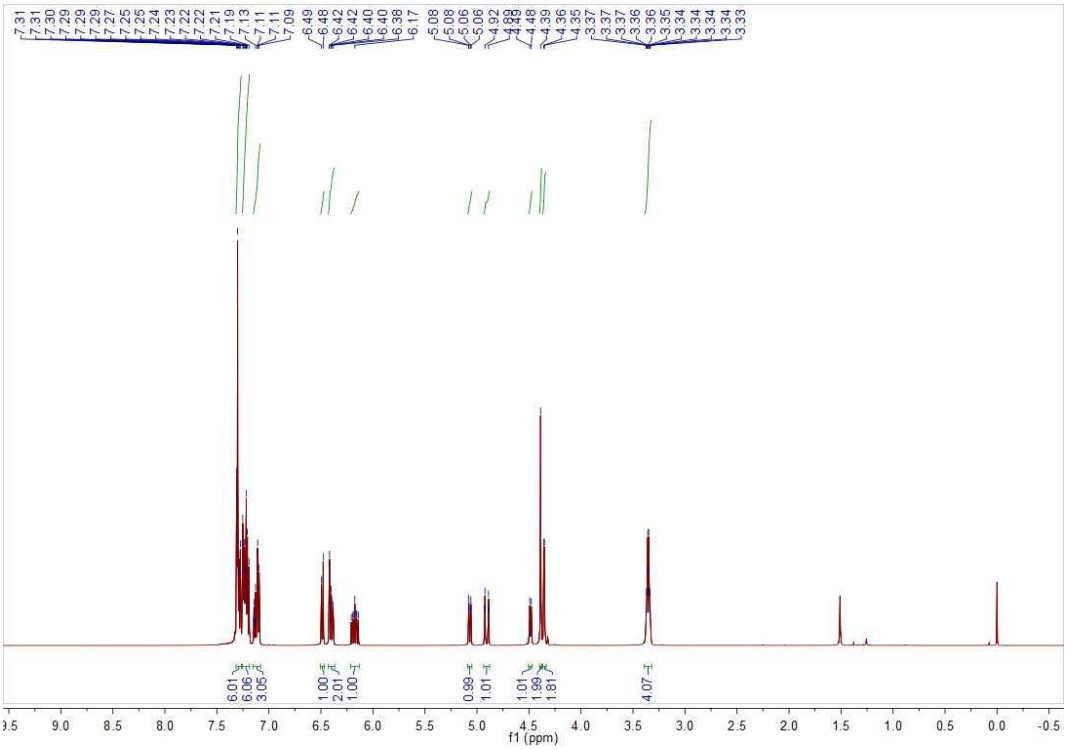
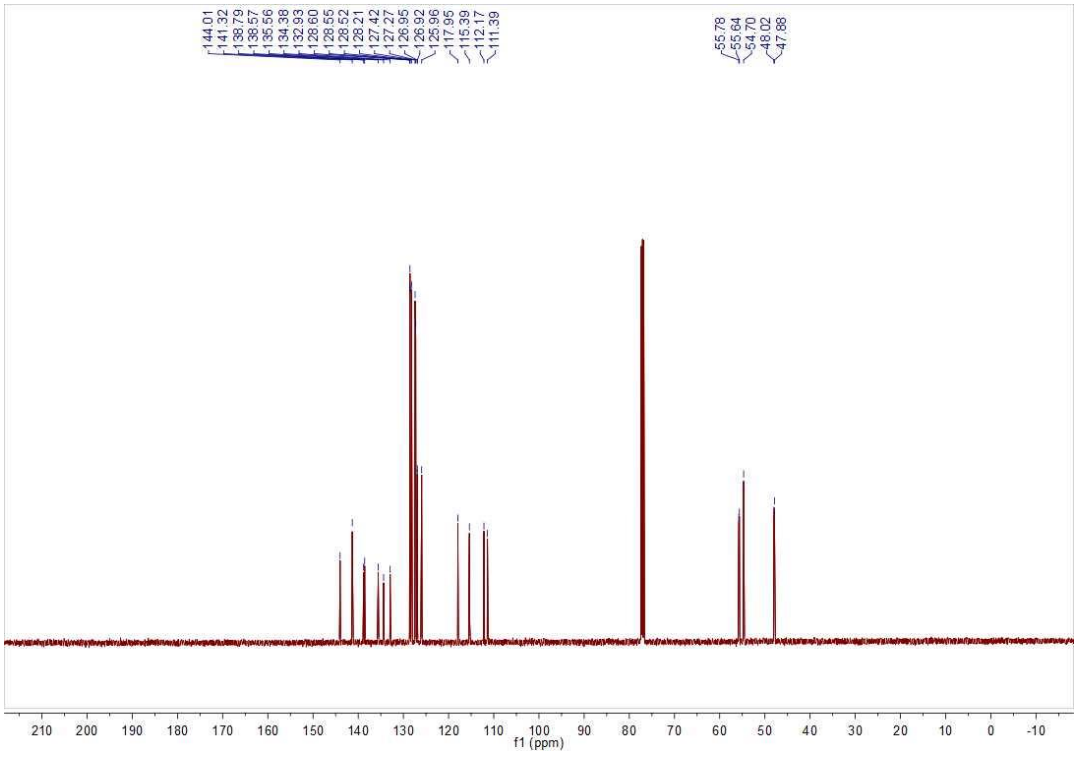


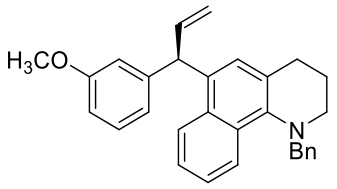
5c



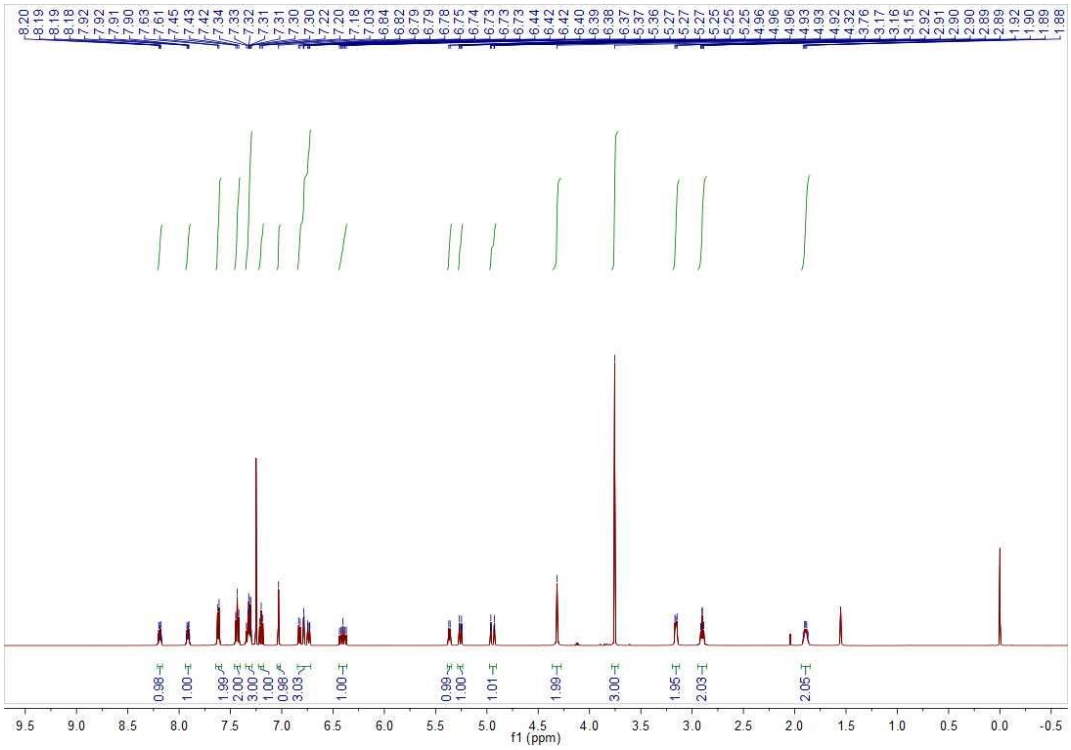
$CDCl_3$; 500Hz



$CDCl_3$; 125Hz



5d



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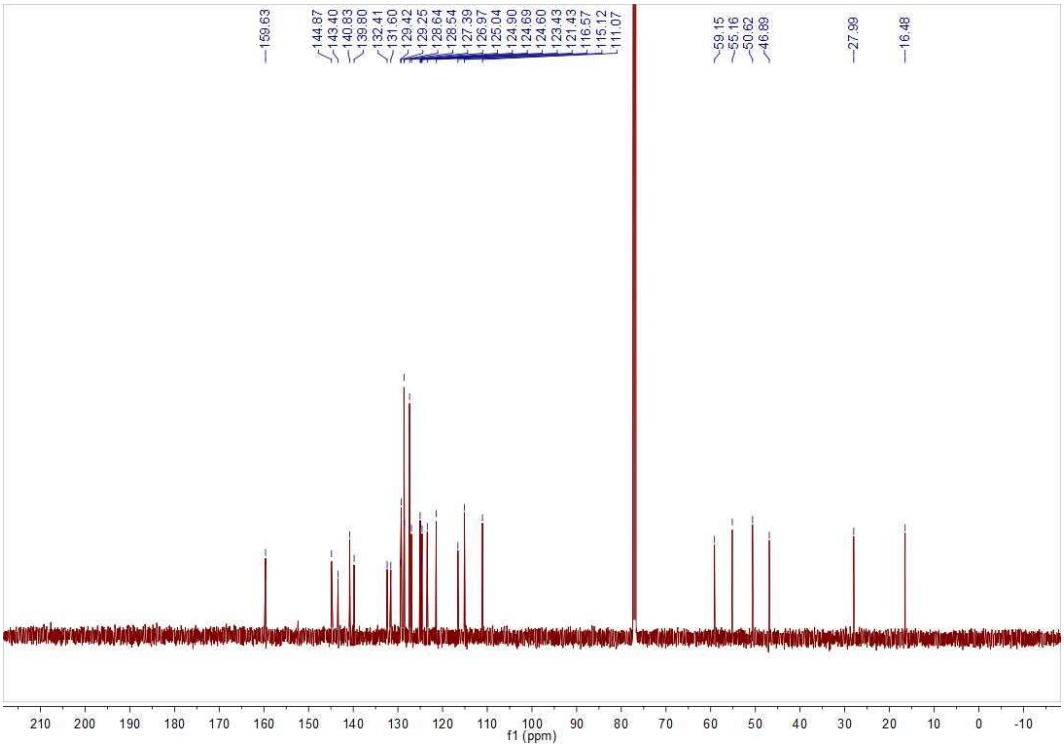

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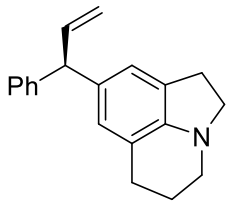
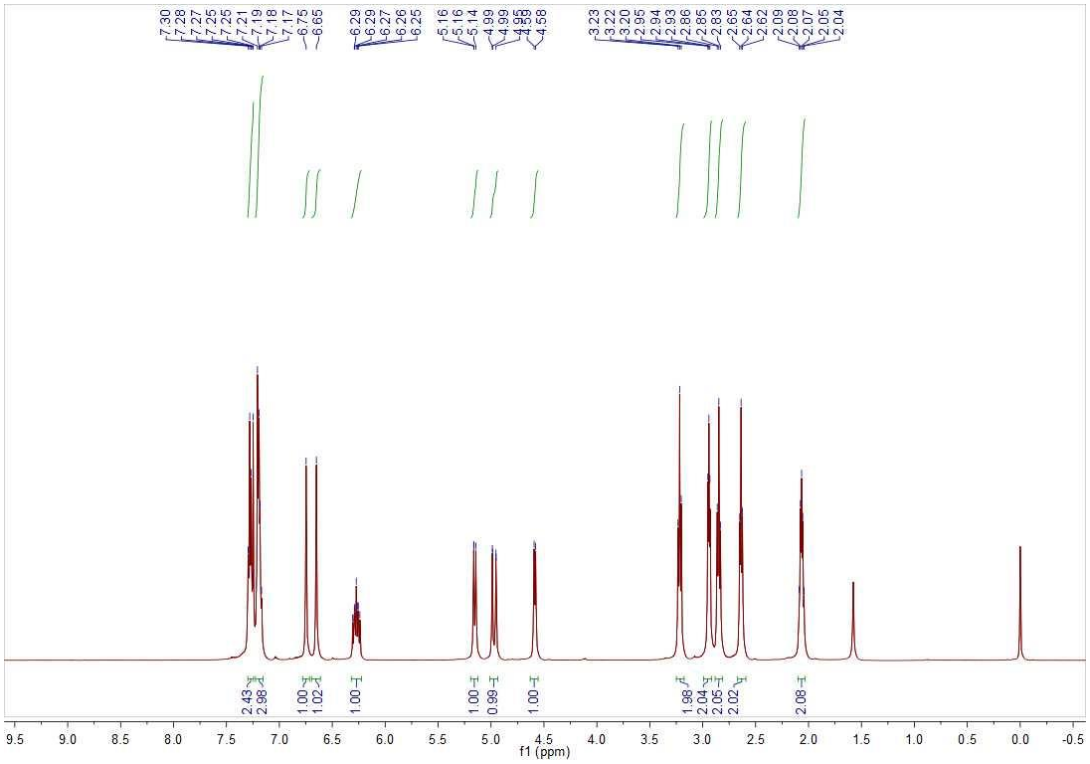
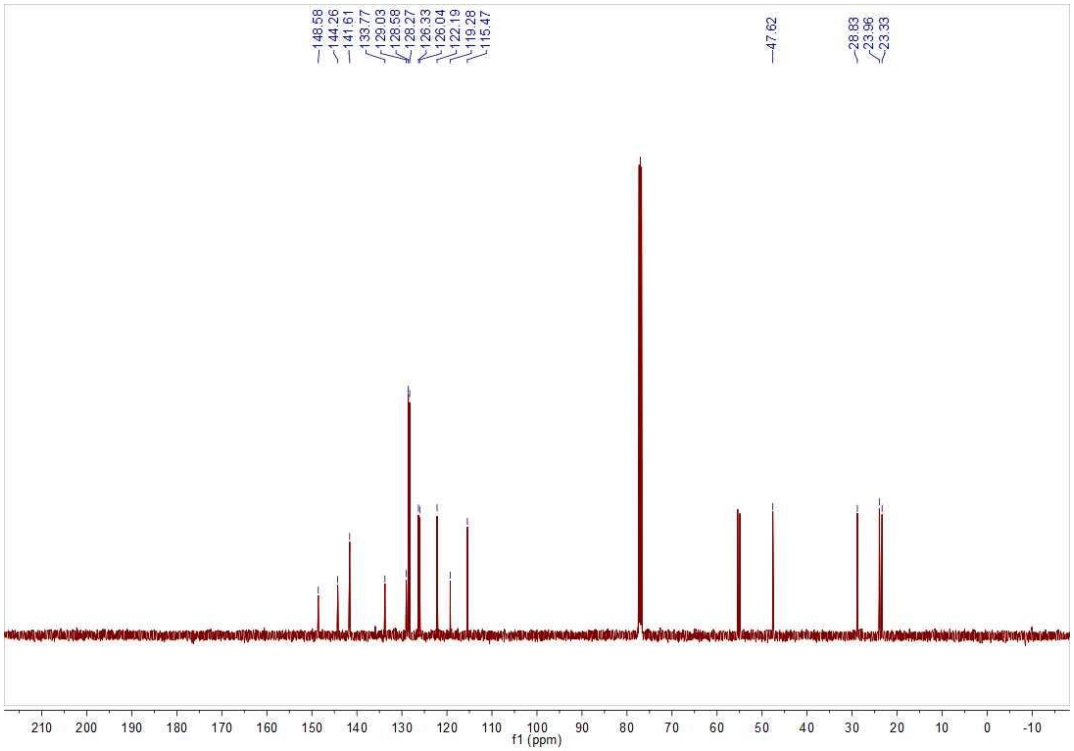


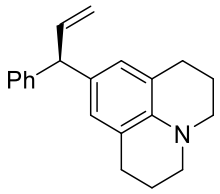
5e



$CDCl_3$; 500Hz



$CDCl_3$; 125Hz



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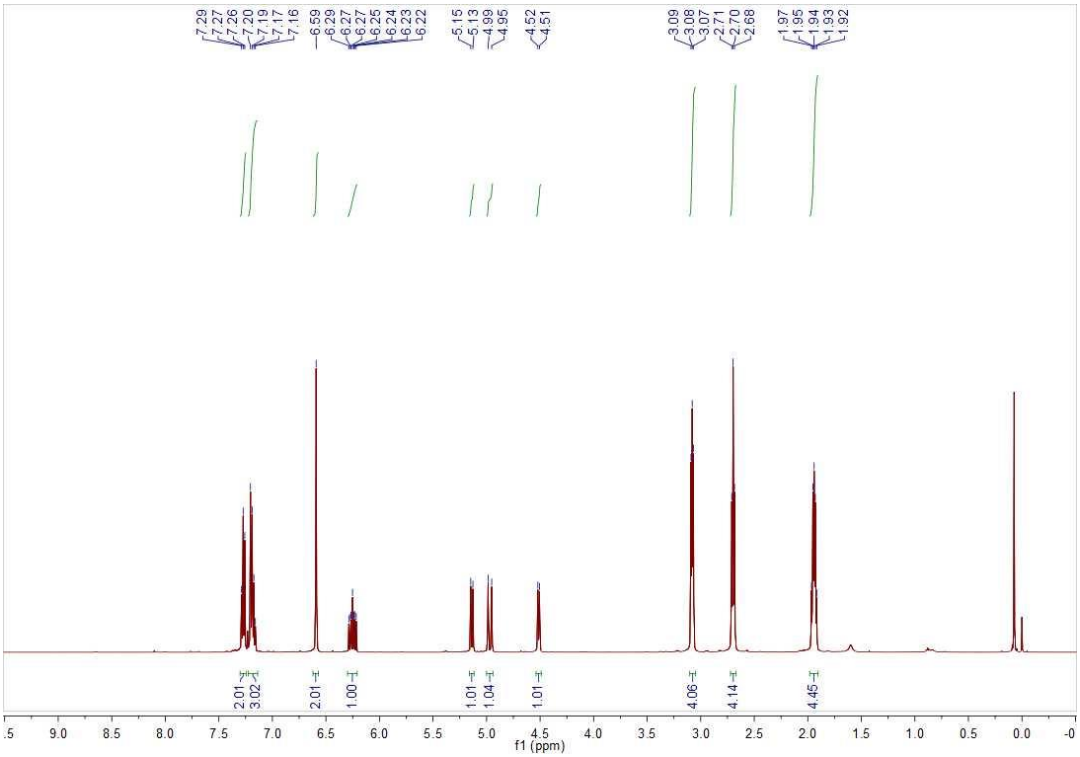

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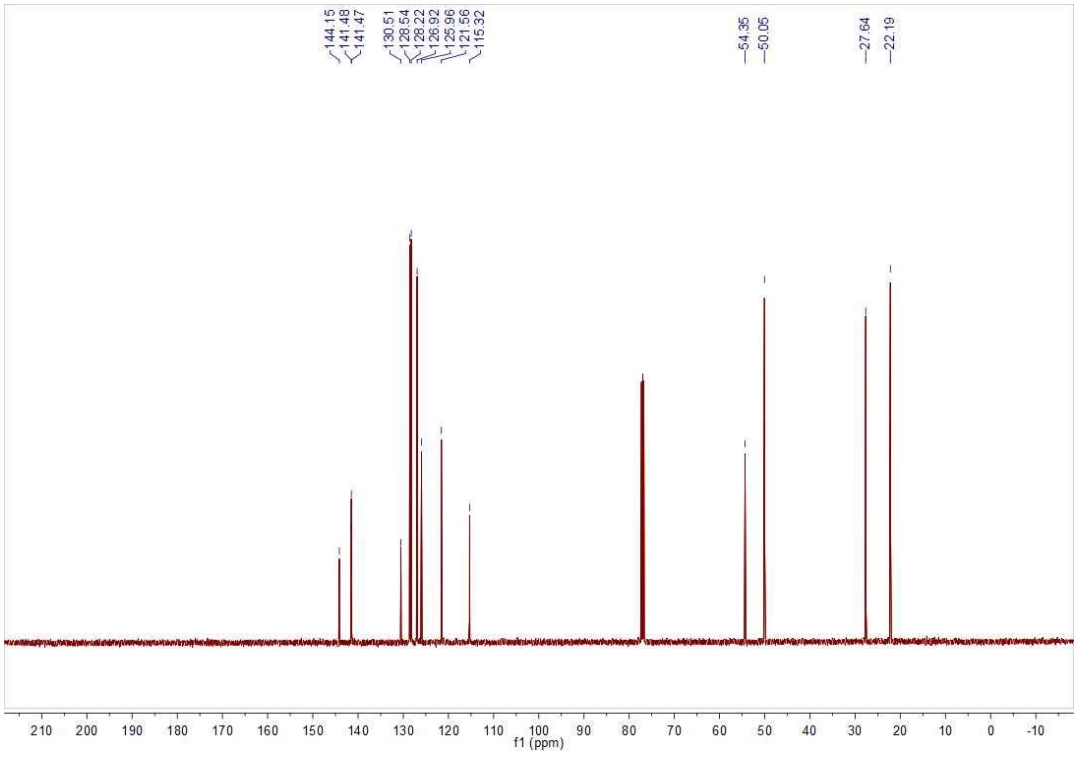

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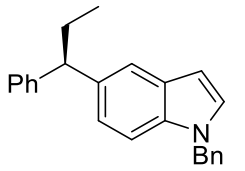

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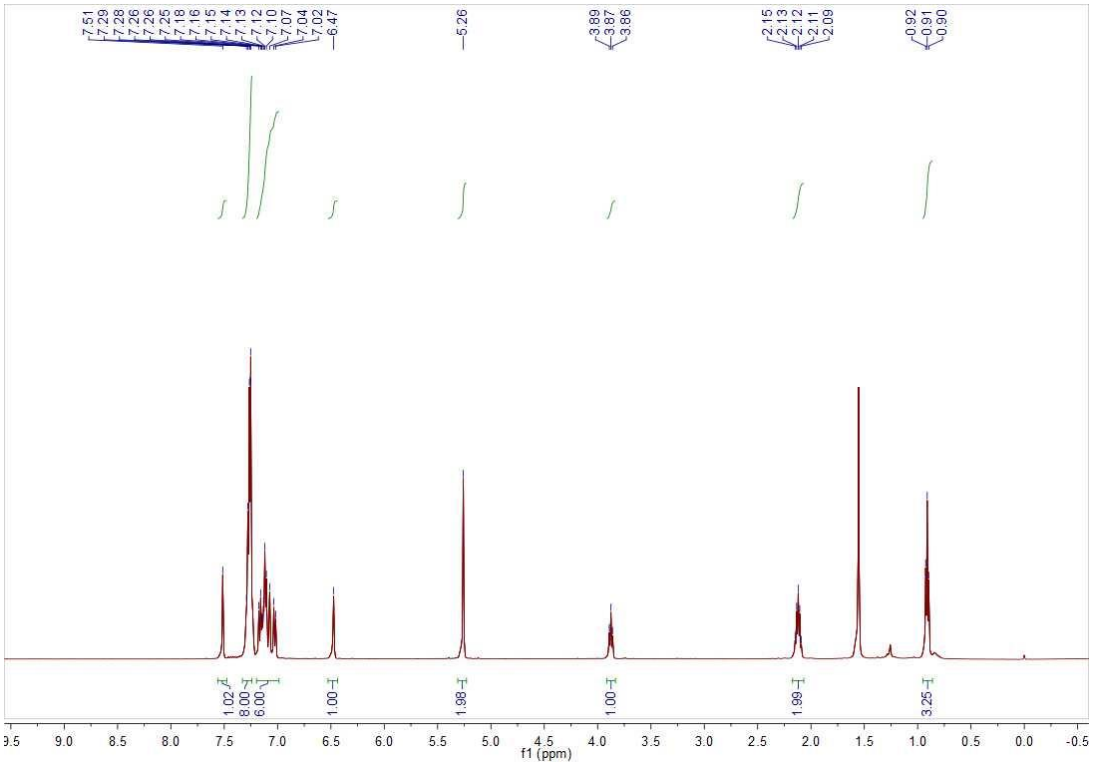

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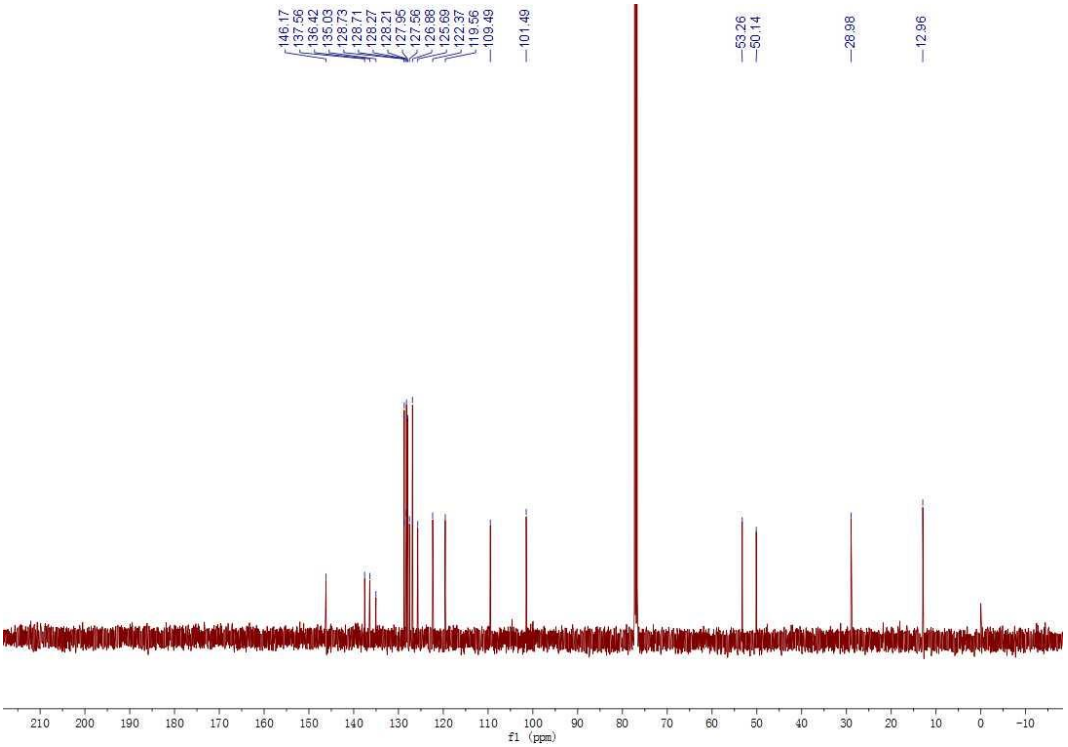

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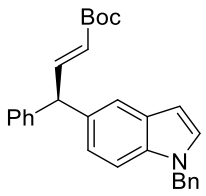

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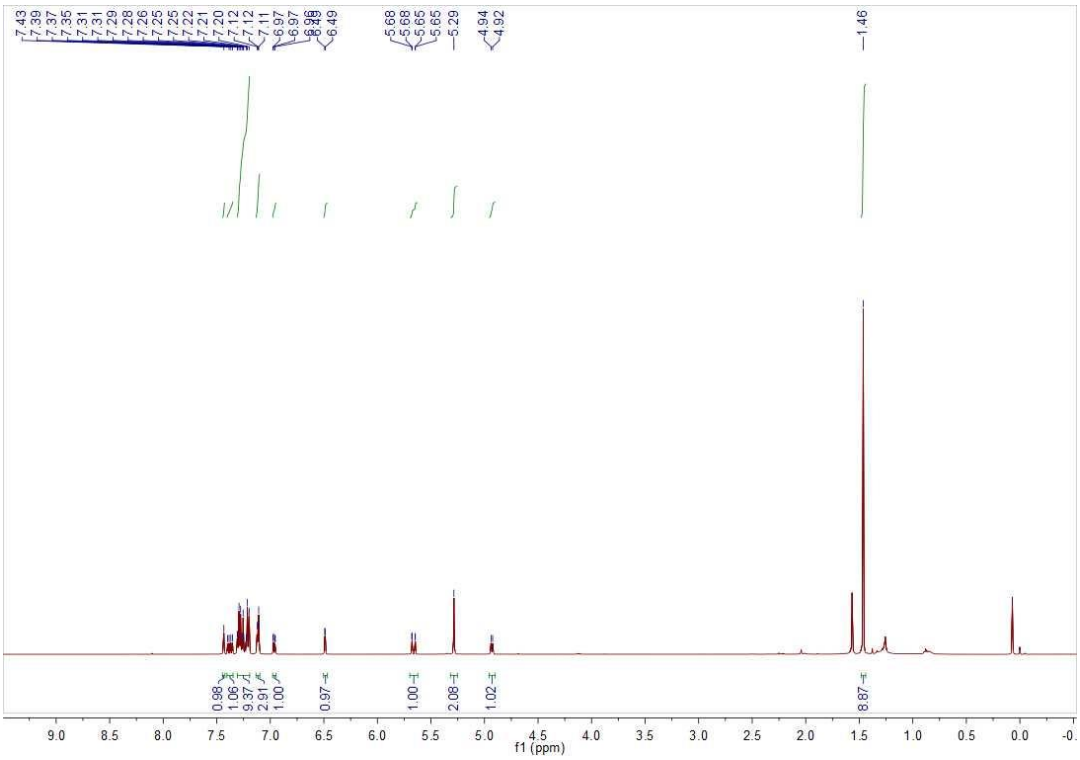
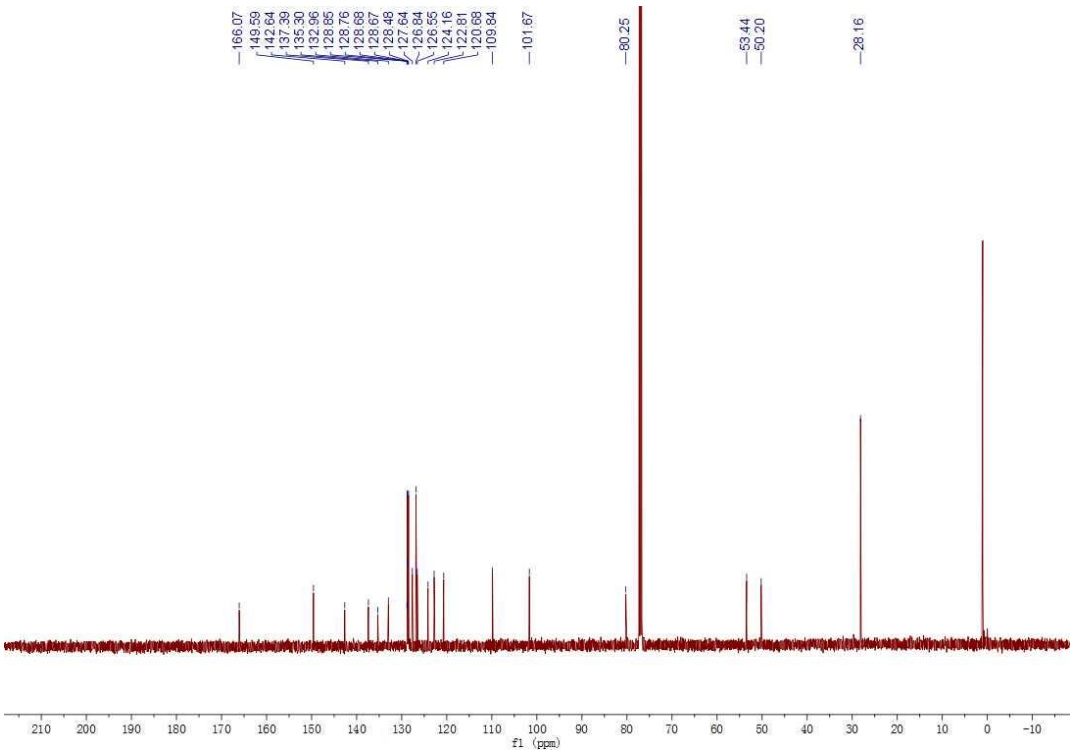


$CDCl_3$; 500Hz



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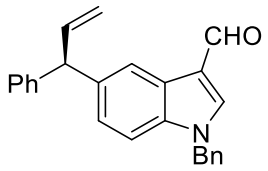

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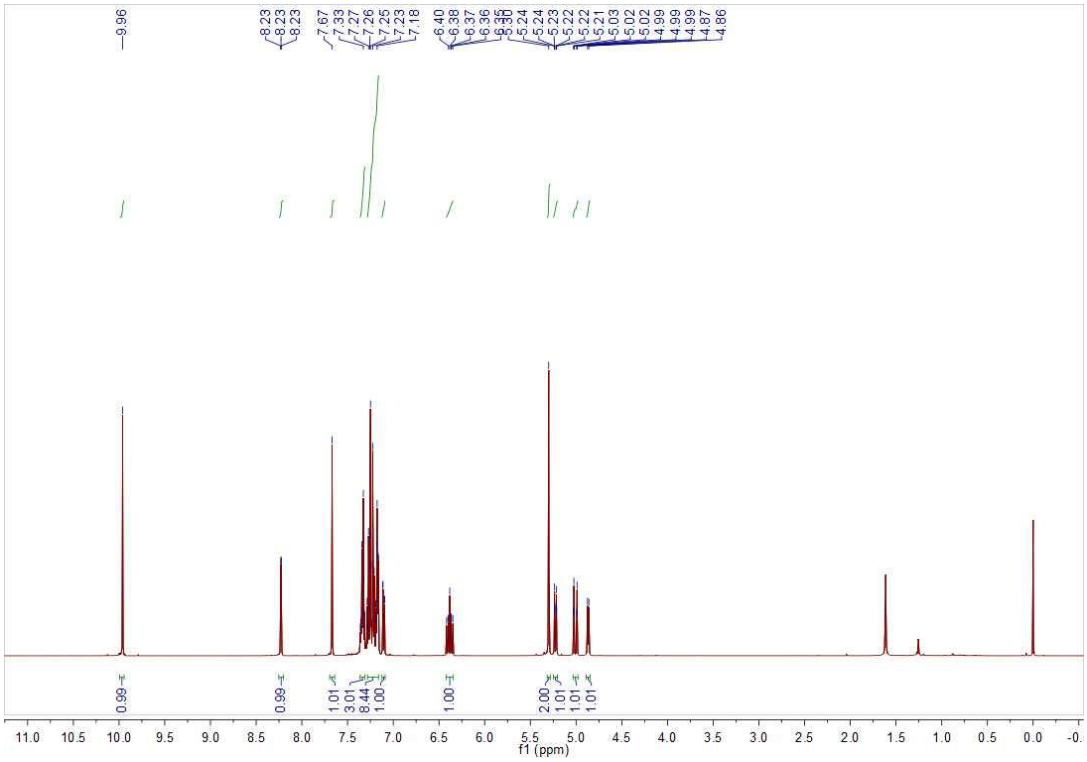

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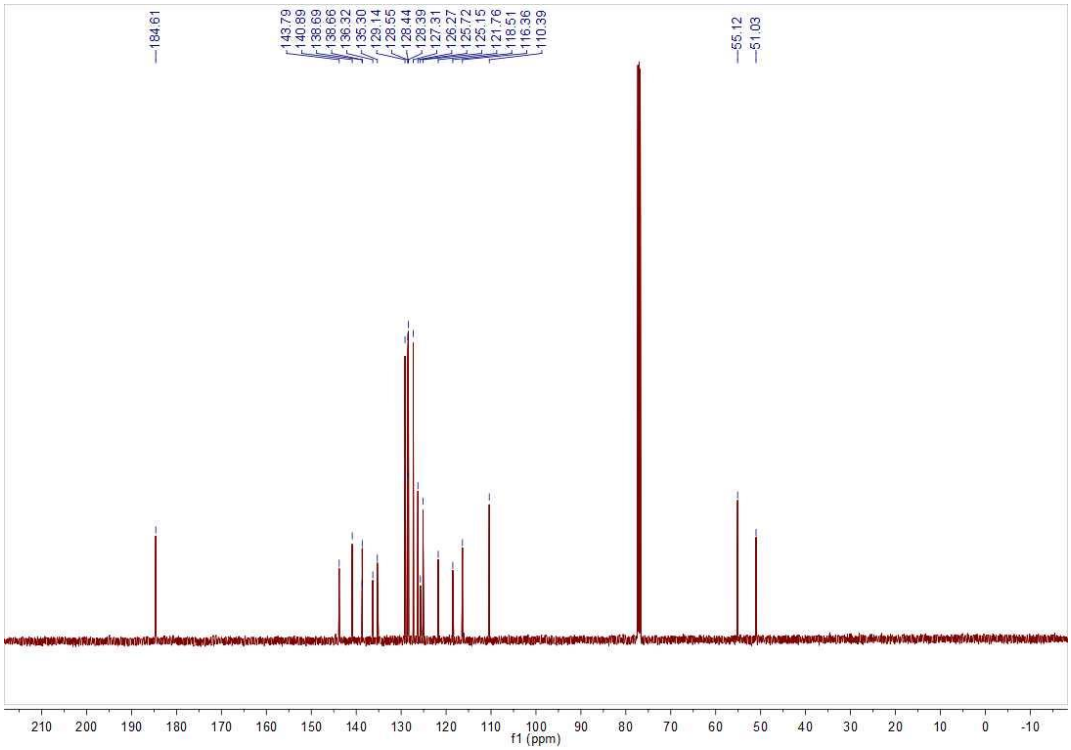
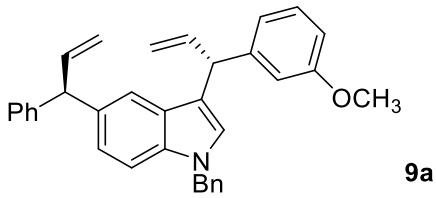


$CDCl_3$; 125Hz



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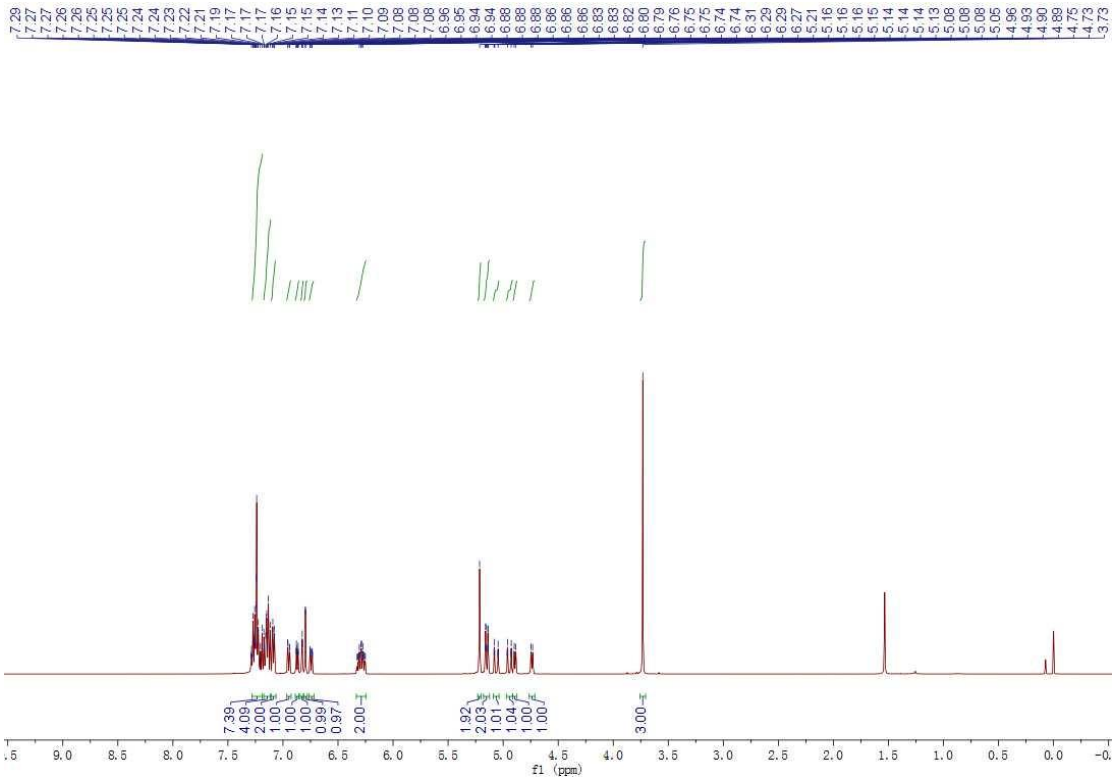
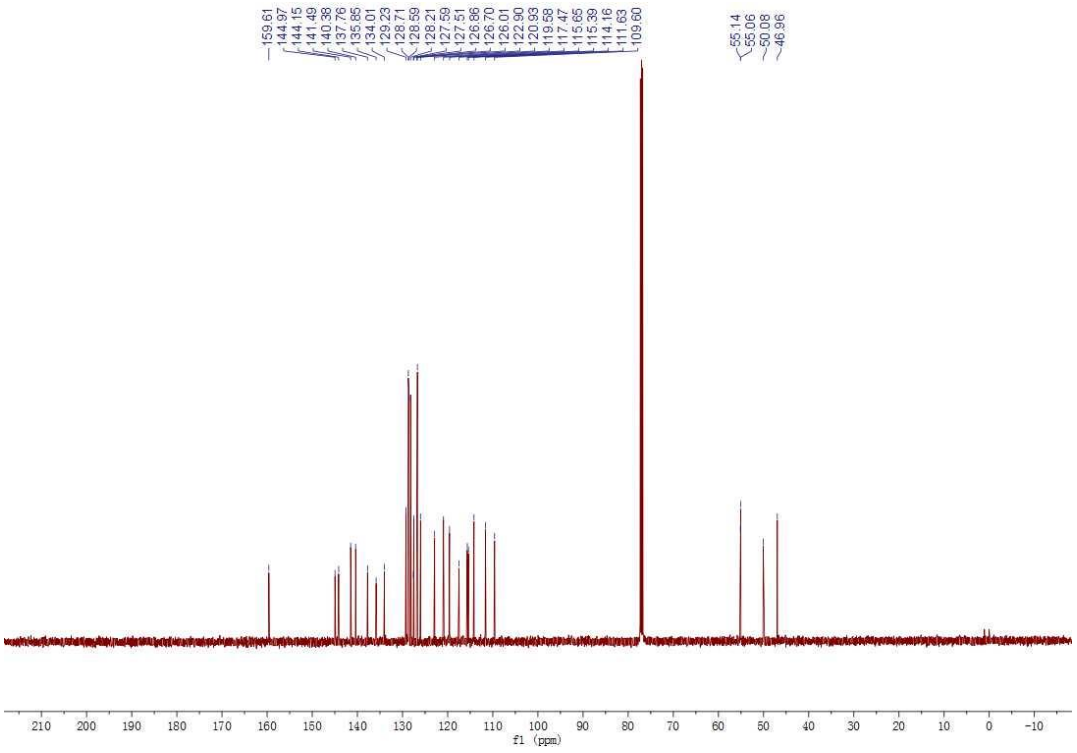


$CDCl_3$; 500Hz



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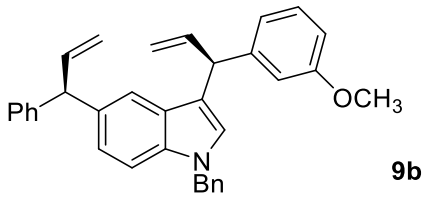

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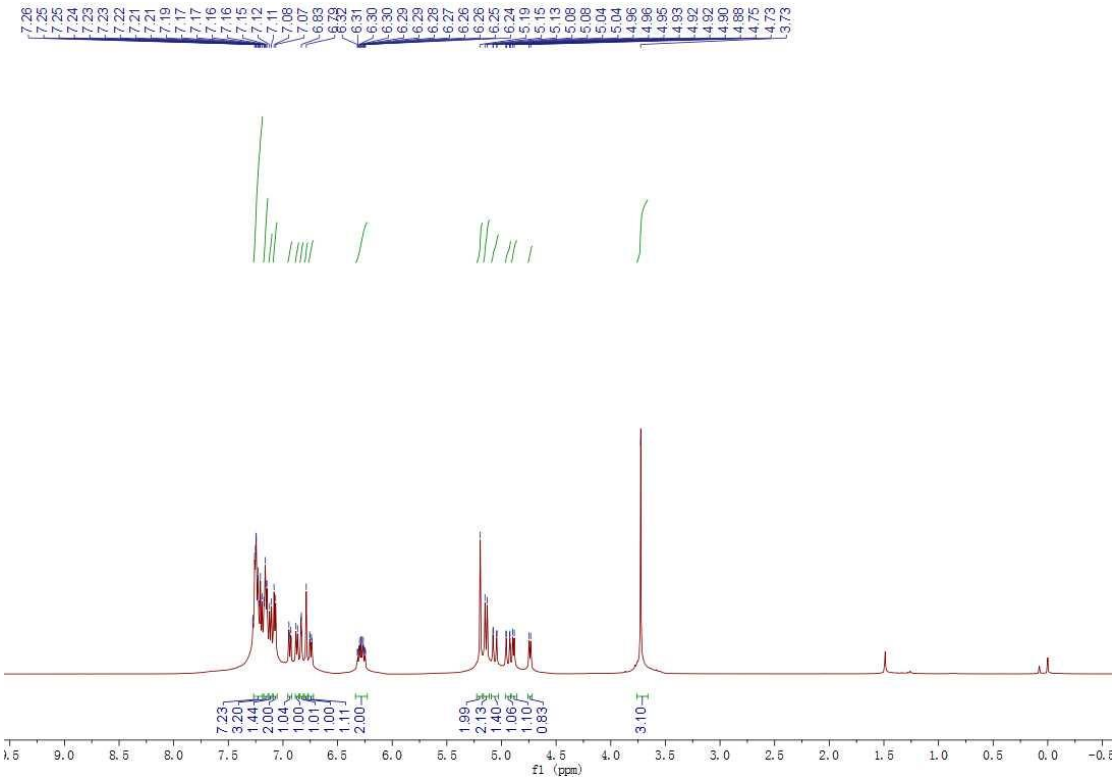

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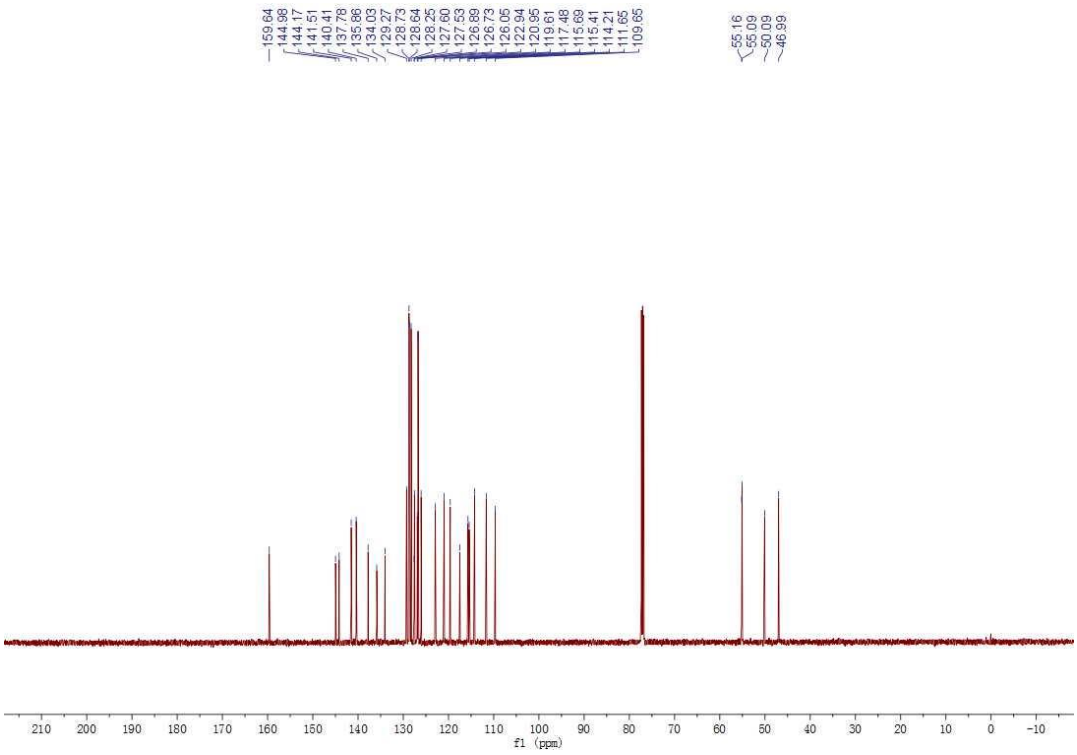

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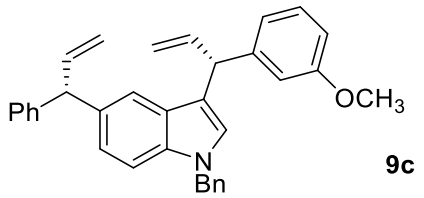

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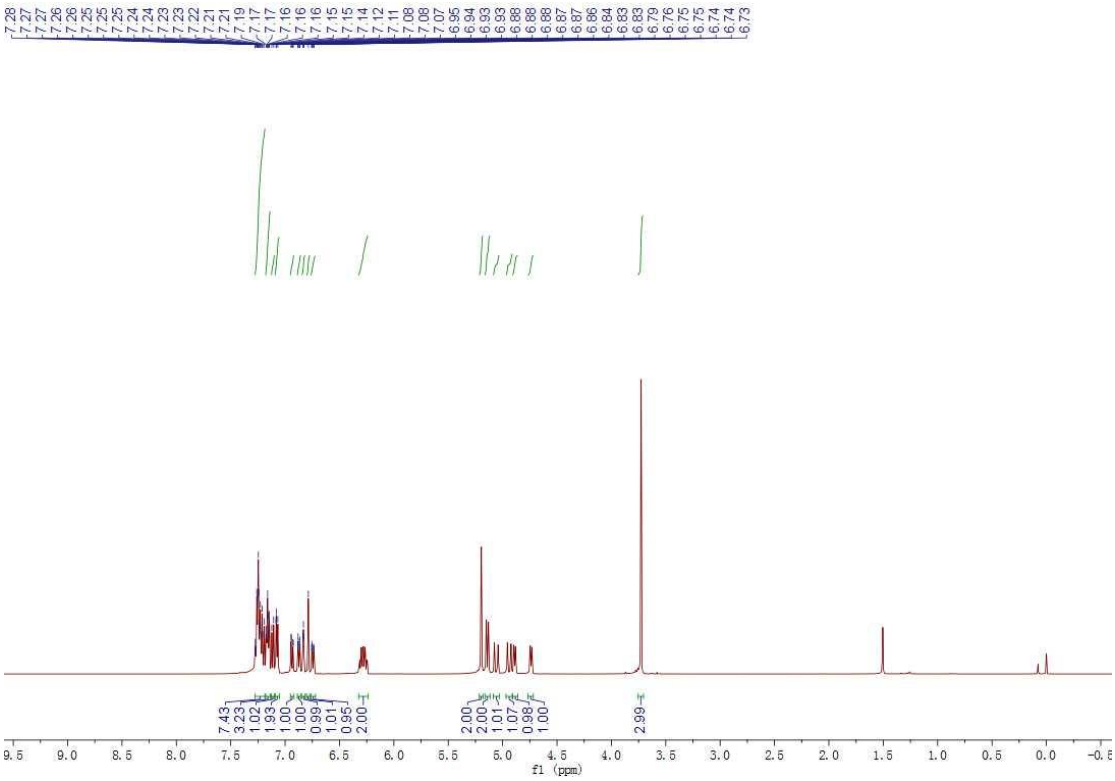

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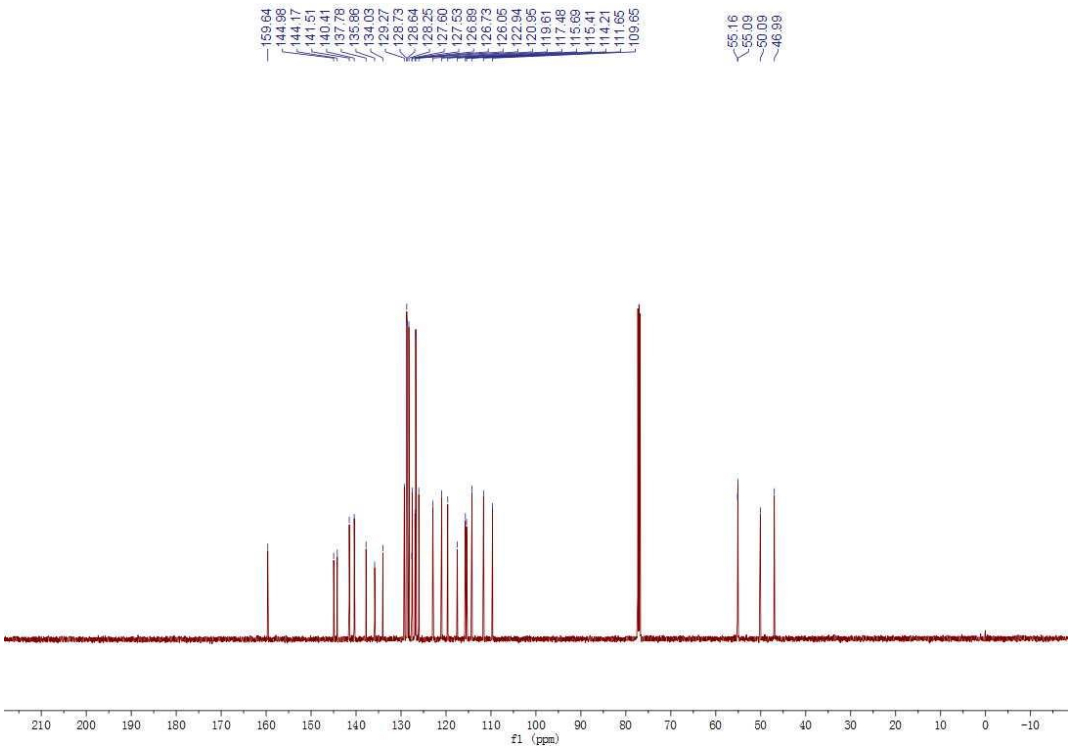

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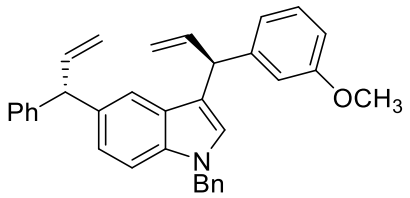

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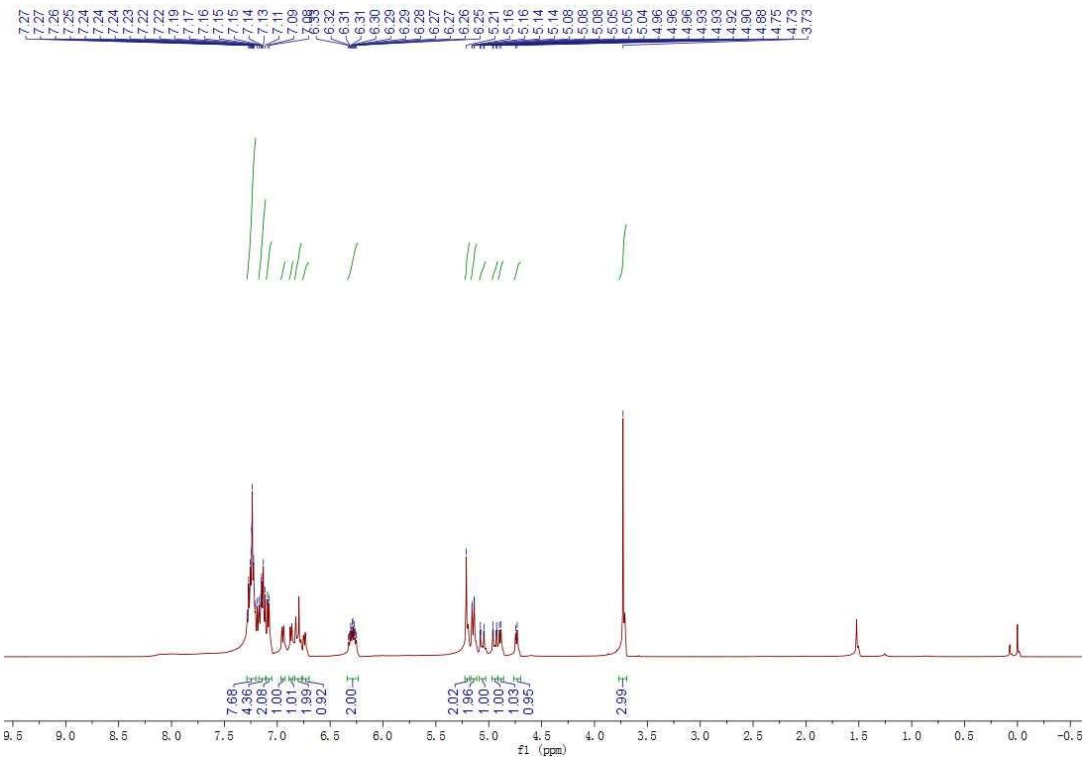

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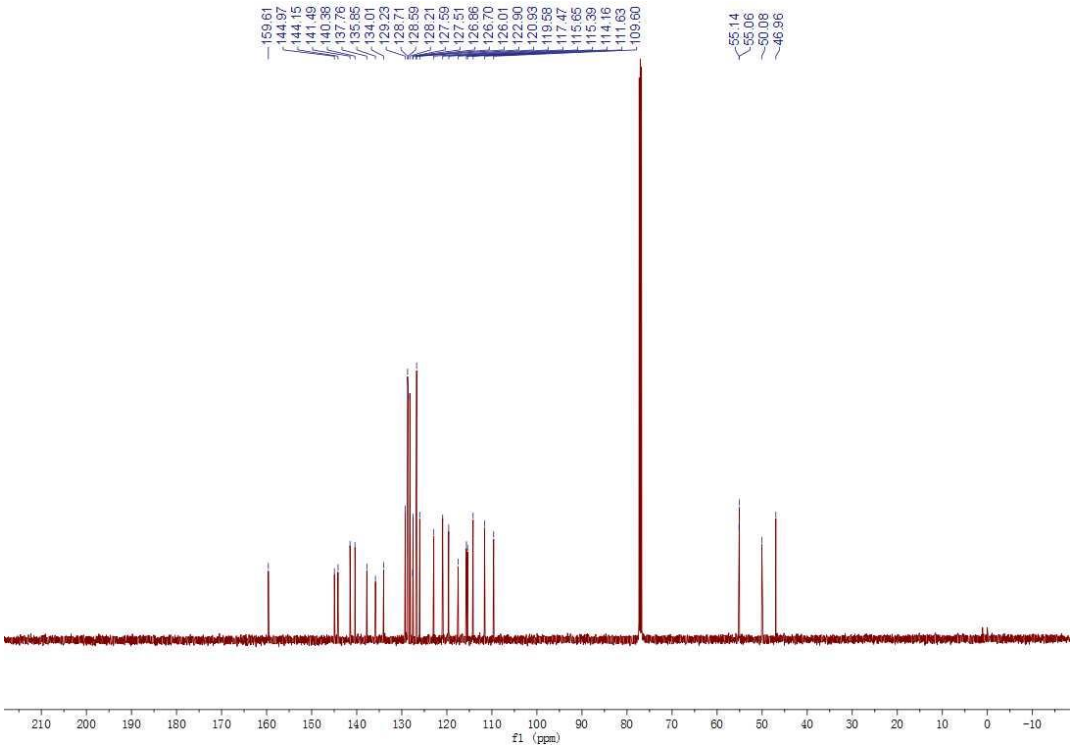

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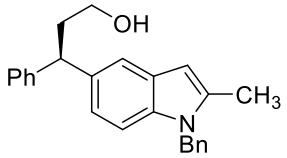

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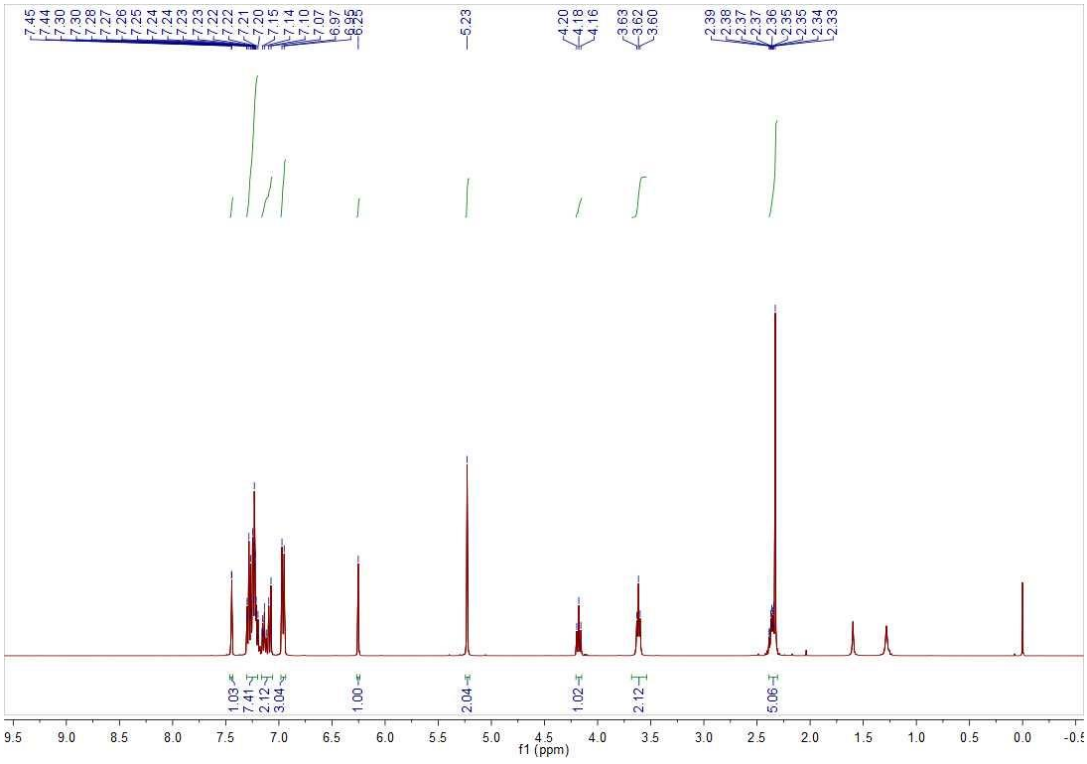

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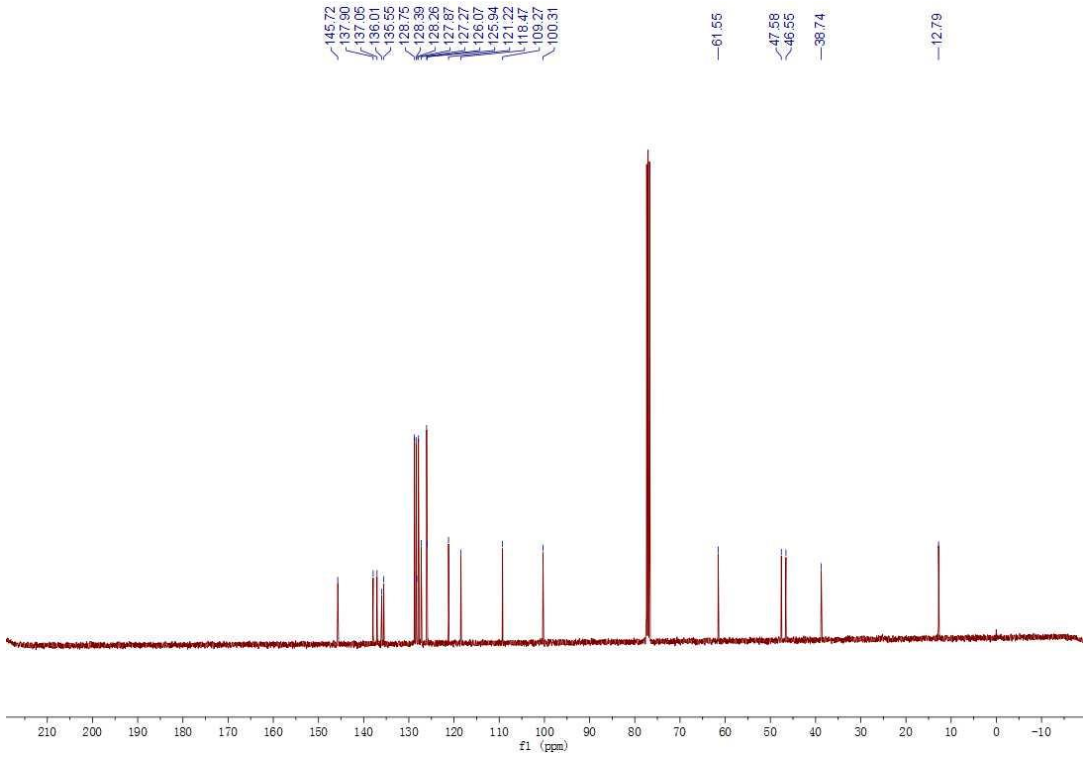

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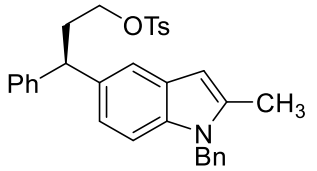

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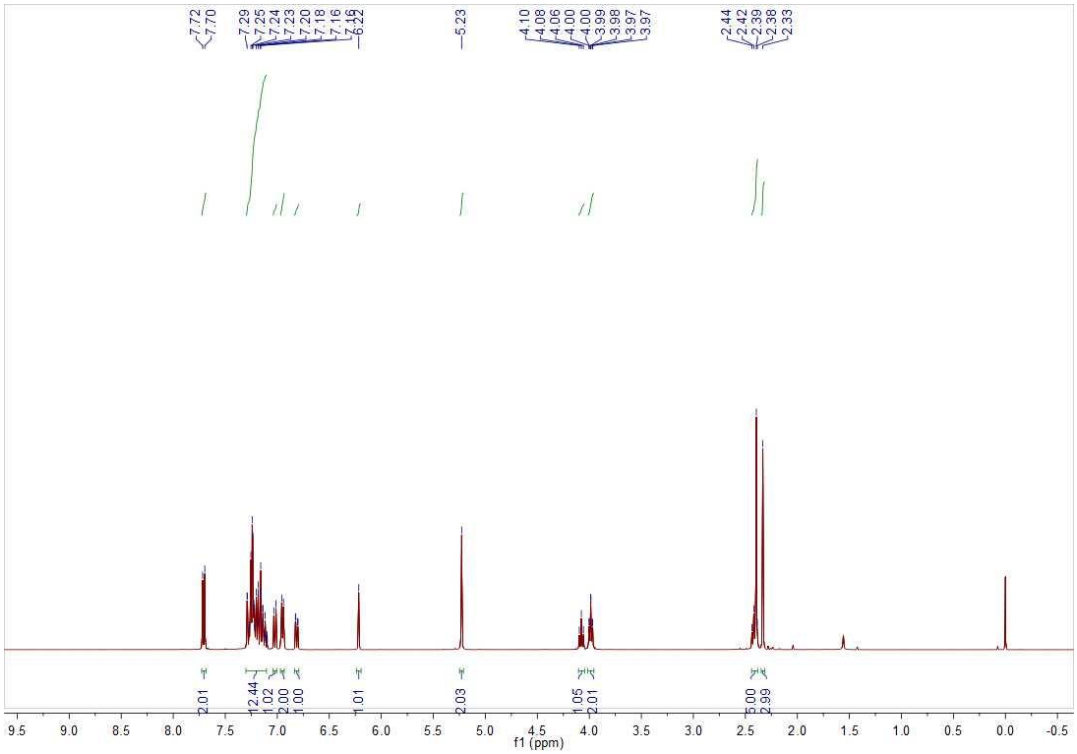

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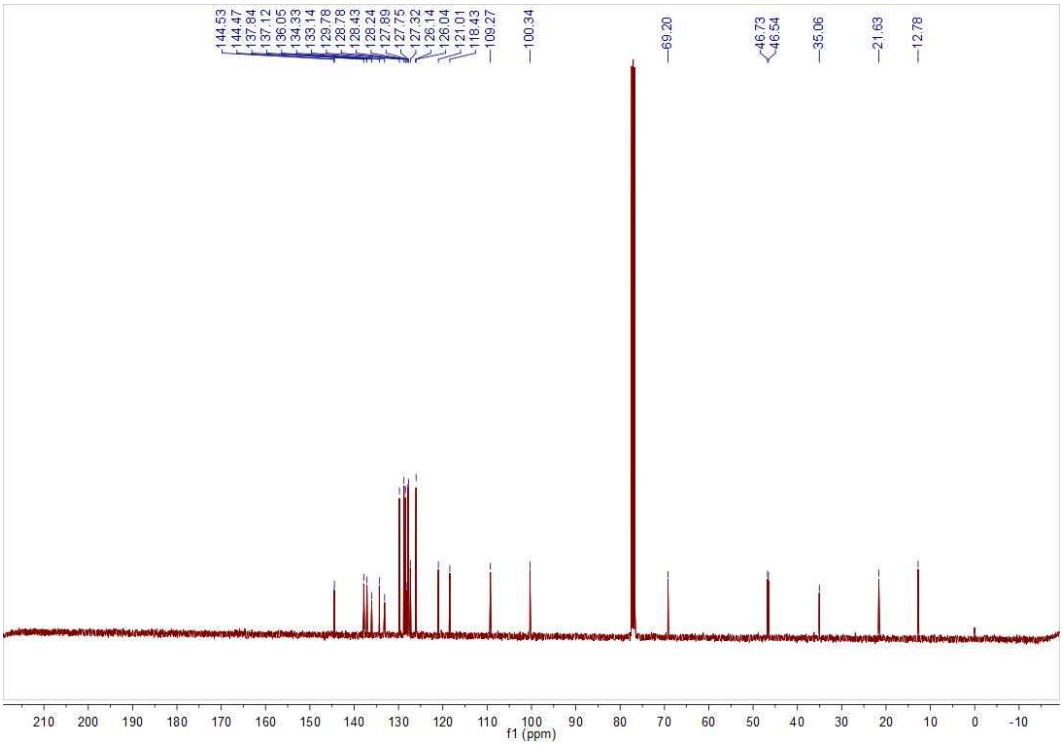
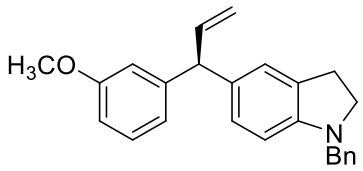


$CDCl_3$; 125Hz

X. Data of HPLC Chromatography:



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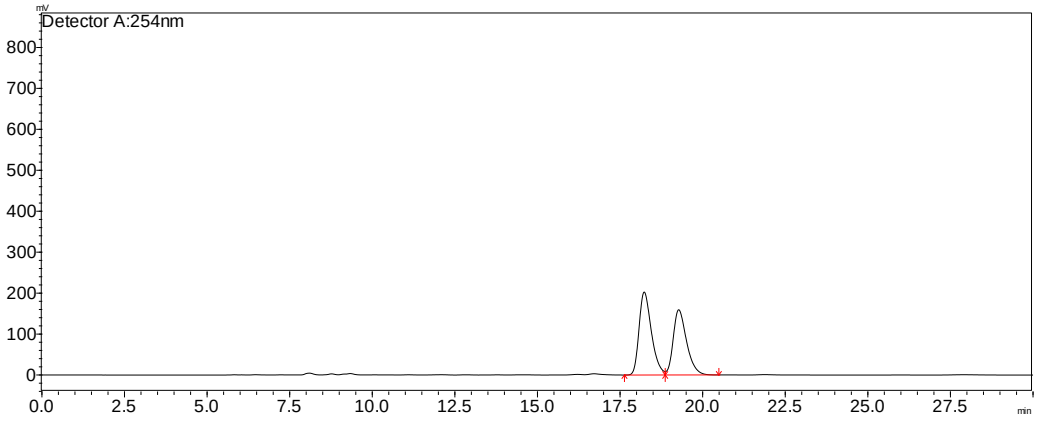
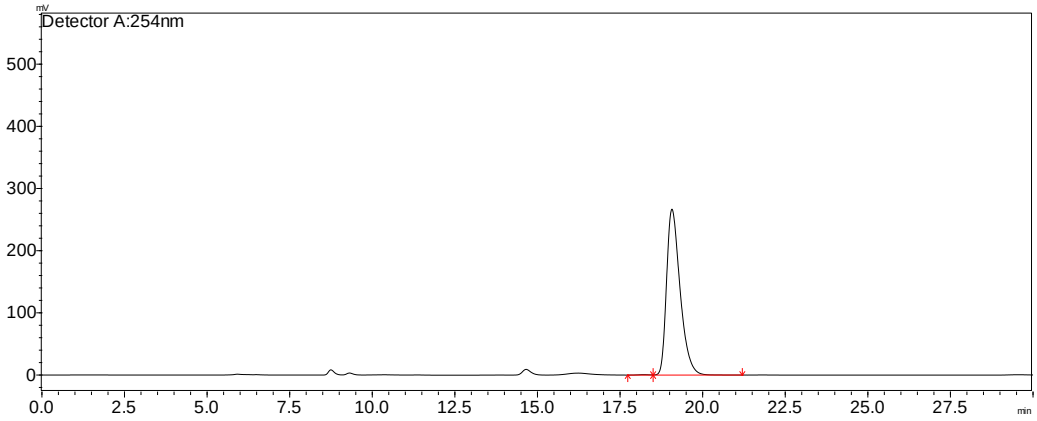
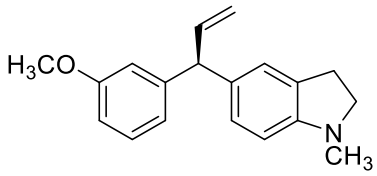


Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.227	5272029	202572	54.018	55.981
2	19.272	4487729	159290	45.982	44.019
Total		9759758	361862	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.209	14699	623	0.193	0.233
2	19.067	7597717	266818	99.807	99.767
Total		7612416	267441	100.000	100.000



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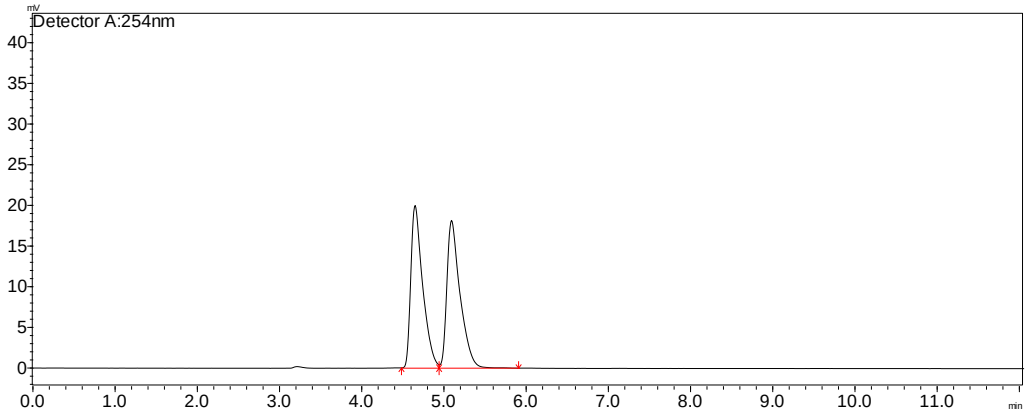
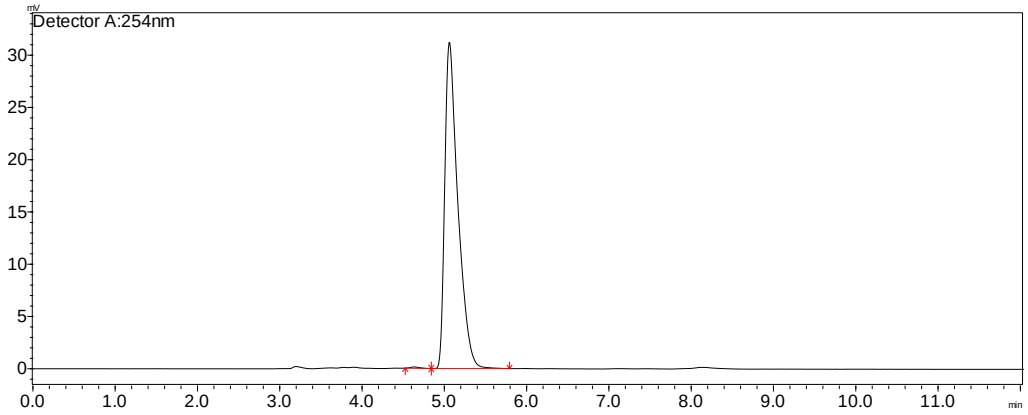
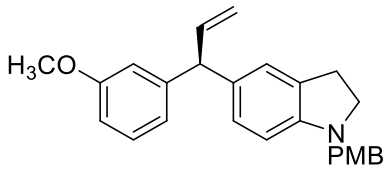


Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.645	200890	20000	49.745	52.405
2	5.088	202946	18165	50.255	47.595
Total		403836	38165	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.627	996	124	0.286	0.396
2	5.057	347323	31214	99.714	99.604
Total		348319	31338	100.000	100.000



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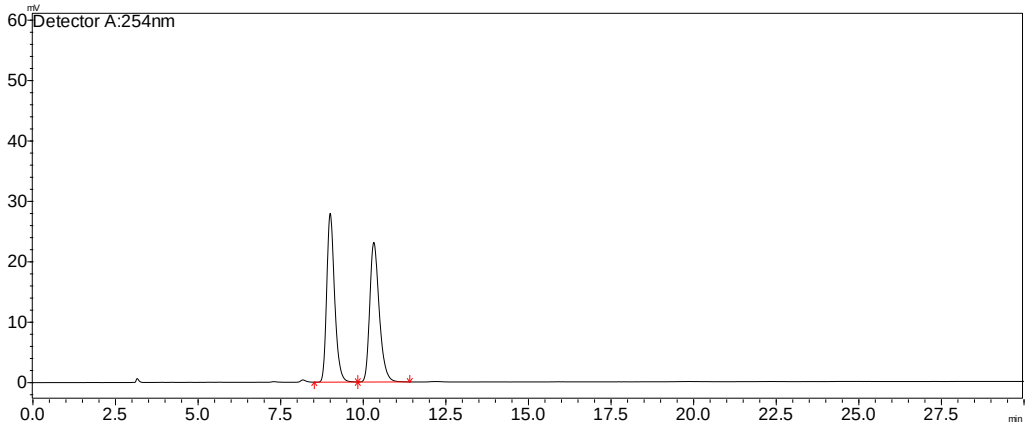
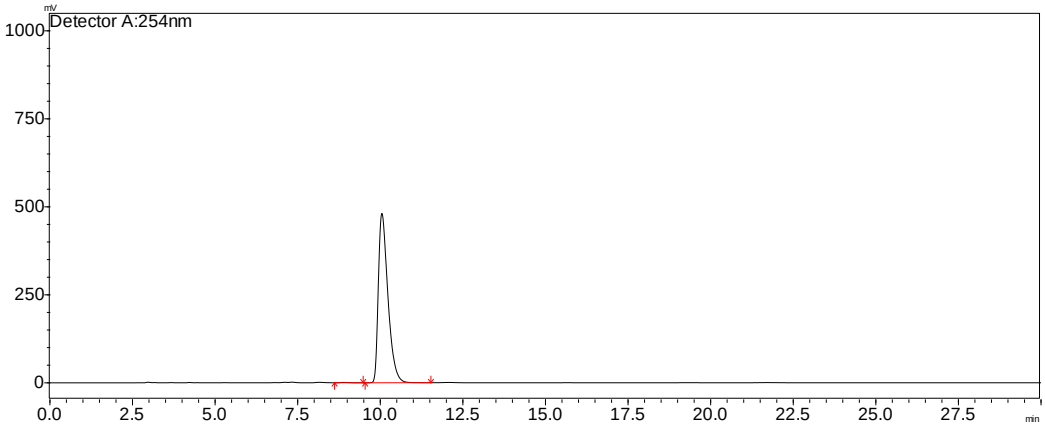
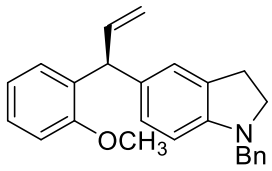


Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.995	464312	27952	49.993	54.726
2	10.315	464451	23124	50.007	45.274
Total		928763	51076	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.884	17019	1035	0.175	0.215
2	10.045	9690673	481162	99.825	99.785
Total		9707692	482197	100.000	100.000



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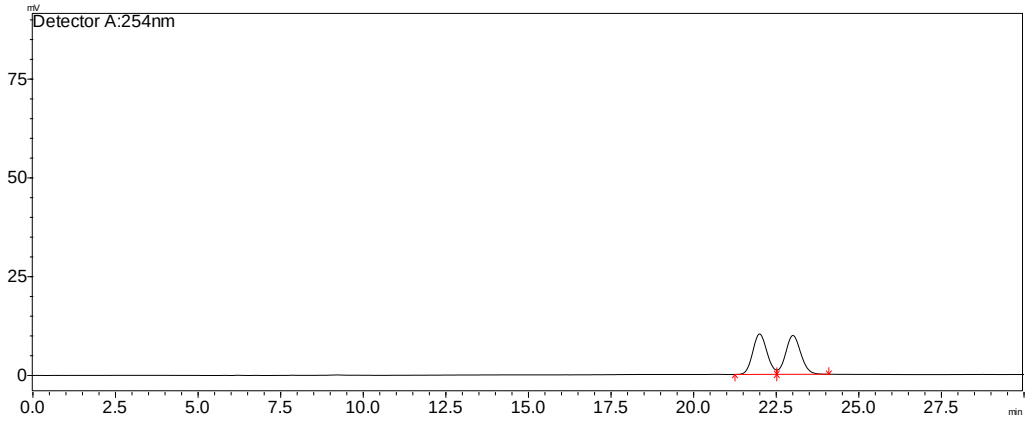
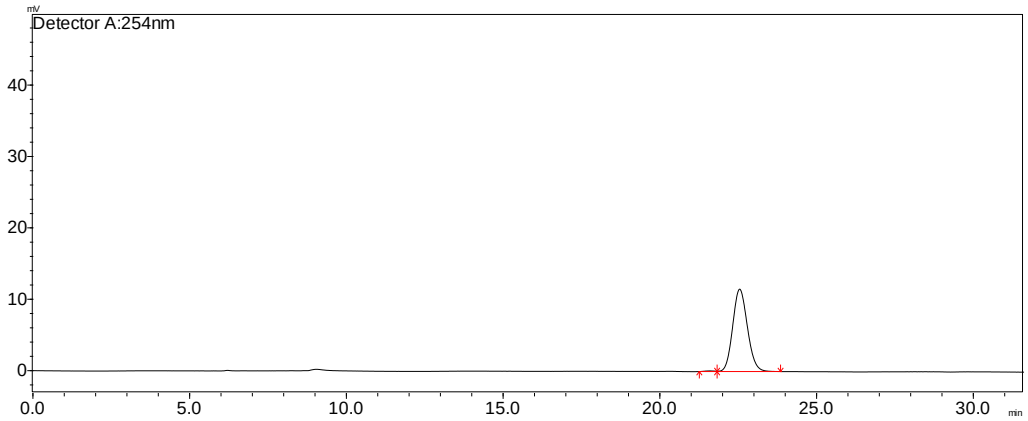
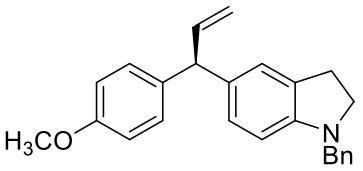


Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.991	307685	10230	49.529	50.999
2	23.000	313538	9829	50.471	49.001
Total		621223	20060	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.593	1990	92	0.526	0.791
2	22.541	376112	11540	99.474	99.209
Total		378102	11632	100.000	100.000



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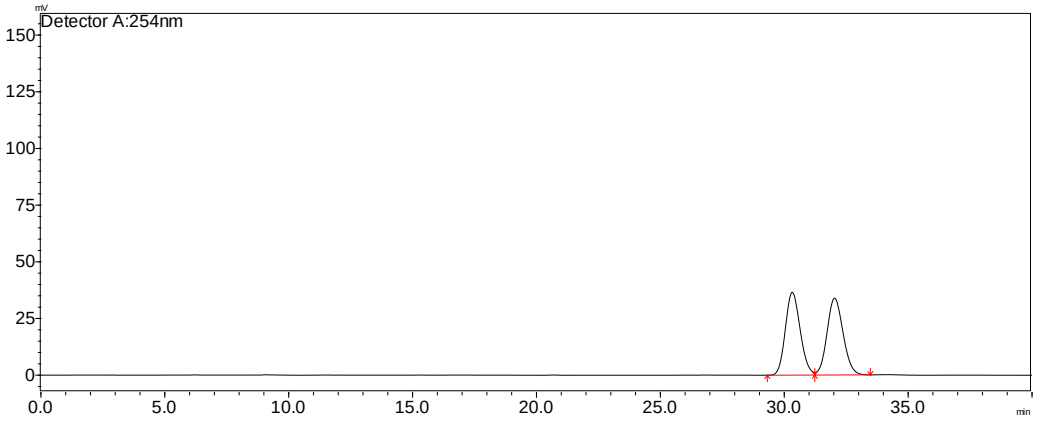
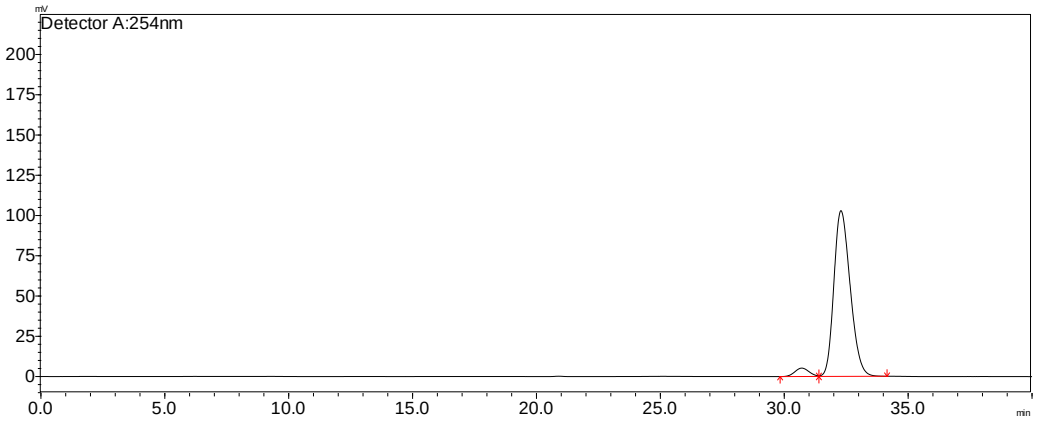
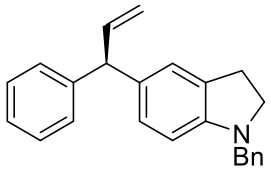


Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.320	1521251	36540	49.929	51.879
2	32.027	1525560	33893	50.071	48.121
Total		3046811	70433	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.701	211093	5235	4.285	4.839
2	32.285	4714700	102953	95.715	95.161
Total		4925793	108187	100.000	100.000



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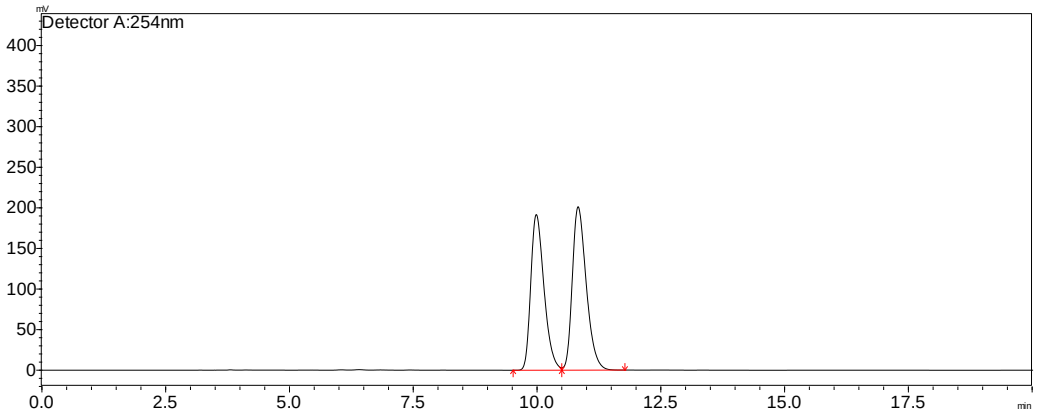
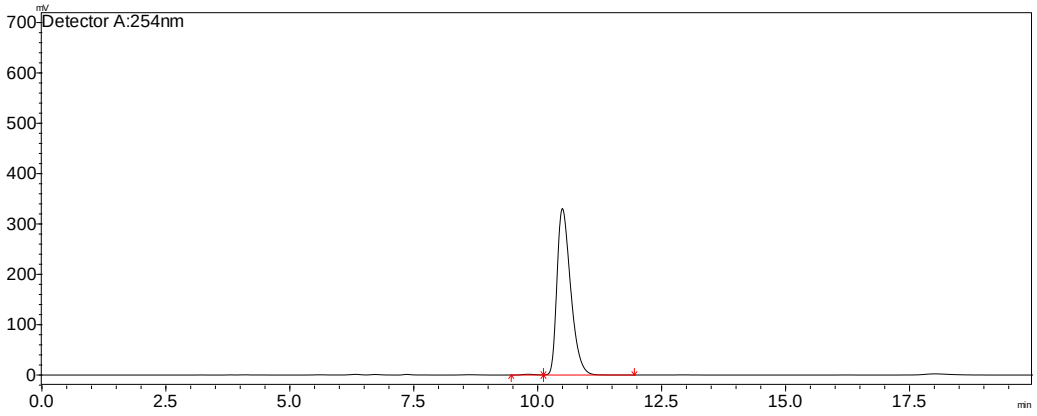
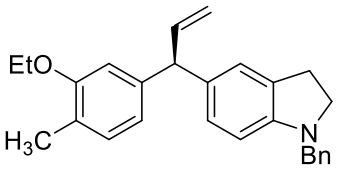


Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.981	3572133	191796	47.480	48.792
2	10.825	3951240	201289	52.520	51.208
Total		7523372	393085	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.802	26437	1526	0.415	0.459
2	10.494	6344132	330670	99.585	99.541
Total		6370569	332197	100.000	100.000



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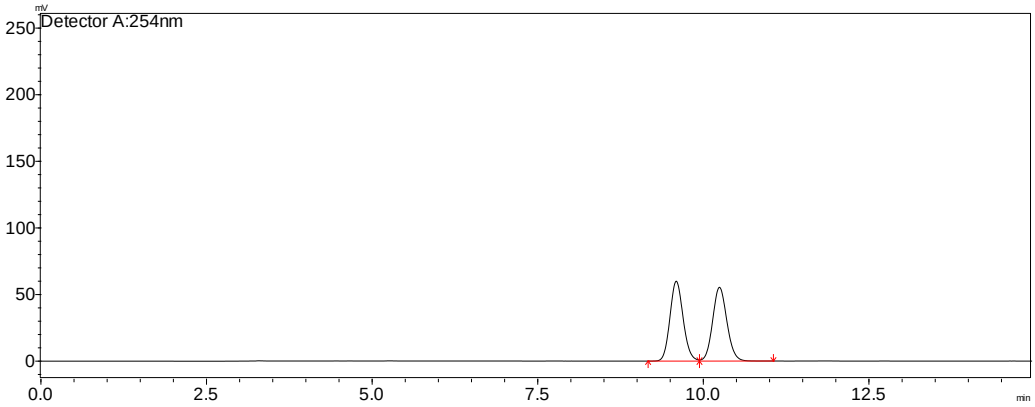
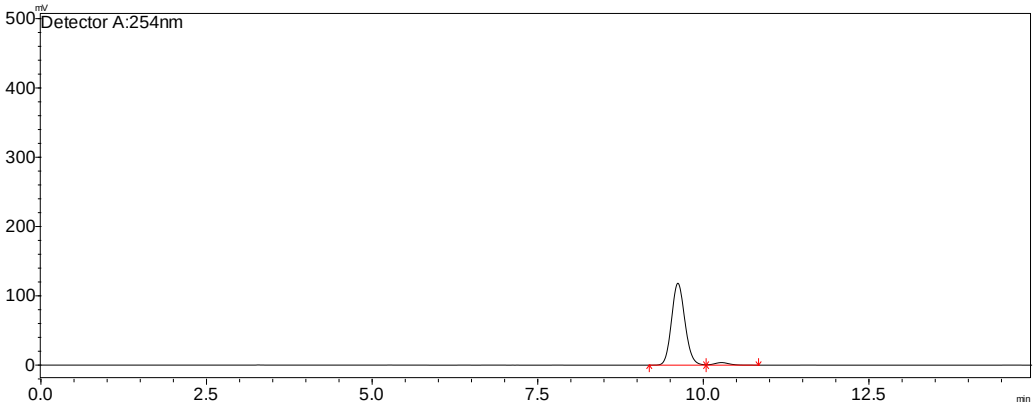
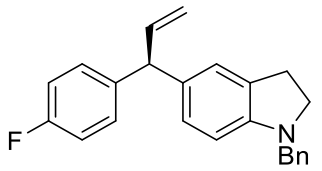


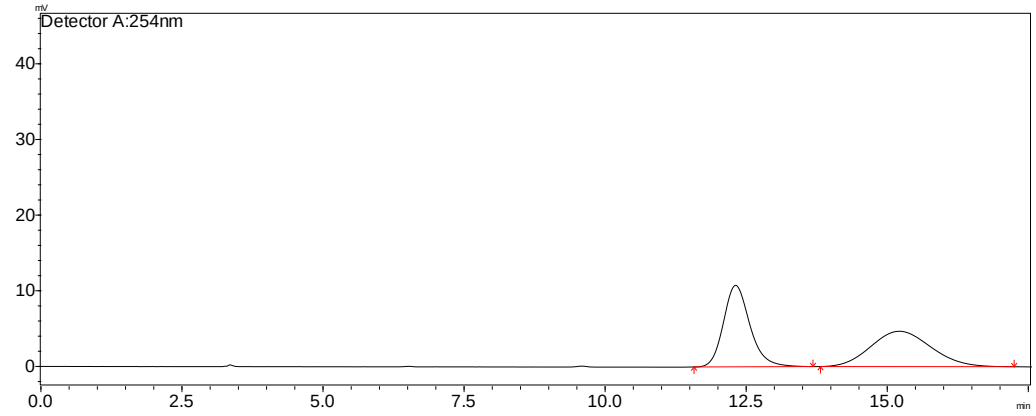
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.587	830254	59973	50.019	51.995
2	10.239	829611	55372	49.981	48.005
Total		1659865	115345	100.000	100.000



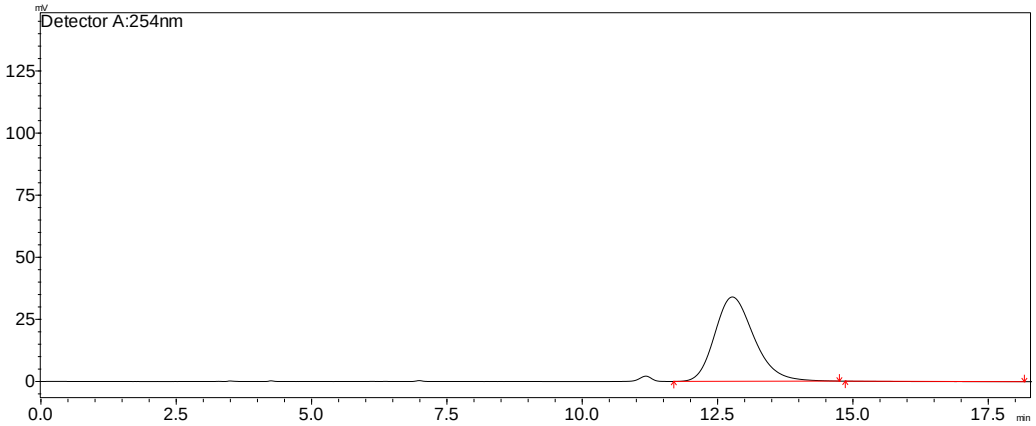
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.611	1663410	118233	96.732	96.975
2	10.270	56189	3688	3.268	3.025
Total		1719599	121921	100.000	100.000



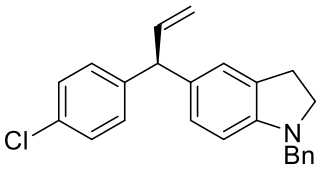
3h



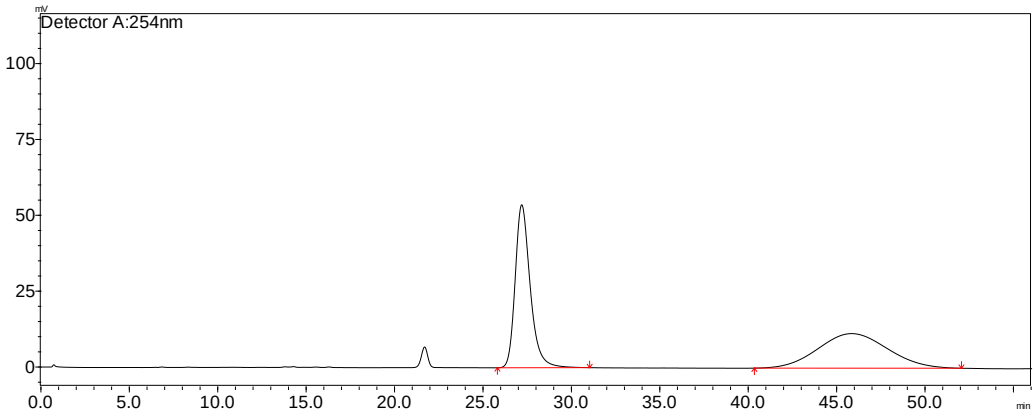
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.309	351565	10773	50.324	69.755
2	15.218	347035	4671	49.676	30.245
Total		698600	15444	100.000	100.000



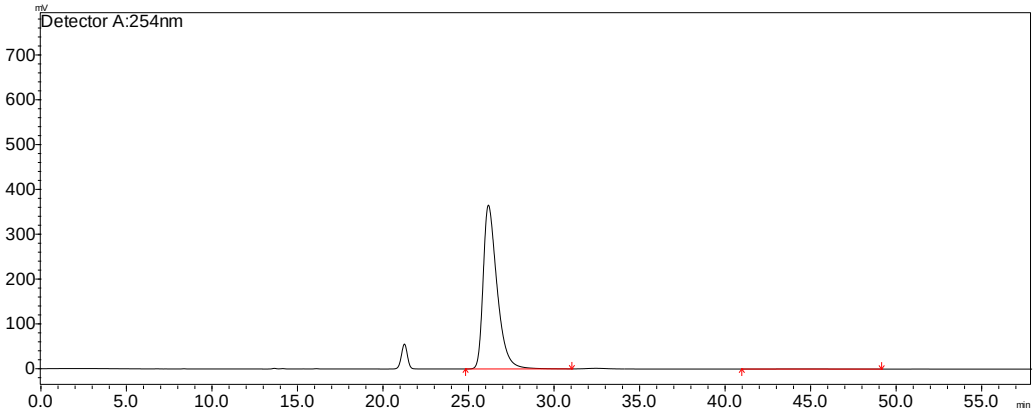
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.769	1734728	34020	99.927	99.962
2	16.183	1259	13	0.073	0.038
Total		1735987	34033	100.000	100.000



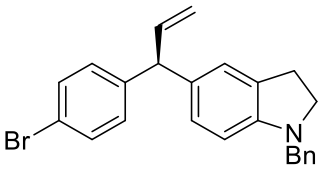
3i



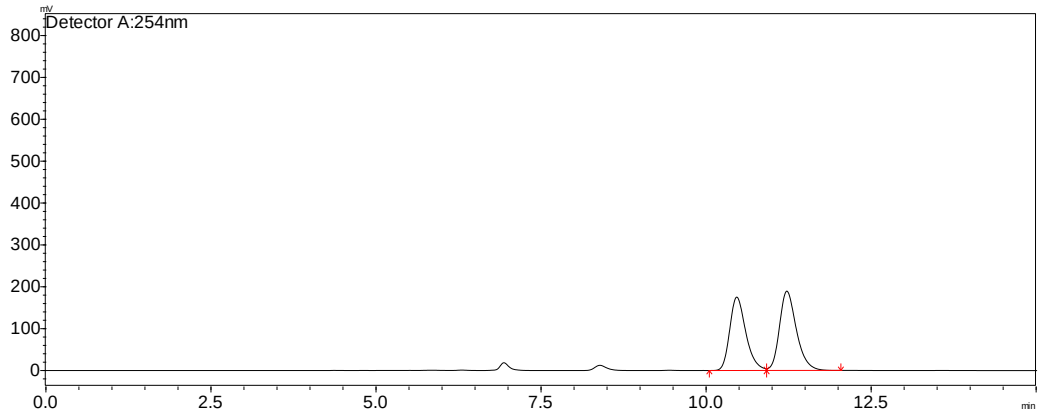
Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.188	3175907	53707	50.402	82.495
2	45.825	3125243	11396	49.598	17.505
Total		6301150	65103	100.000	100.000



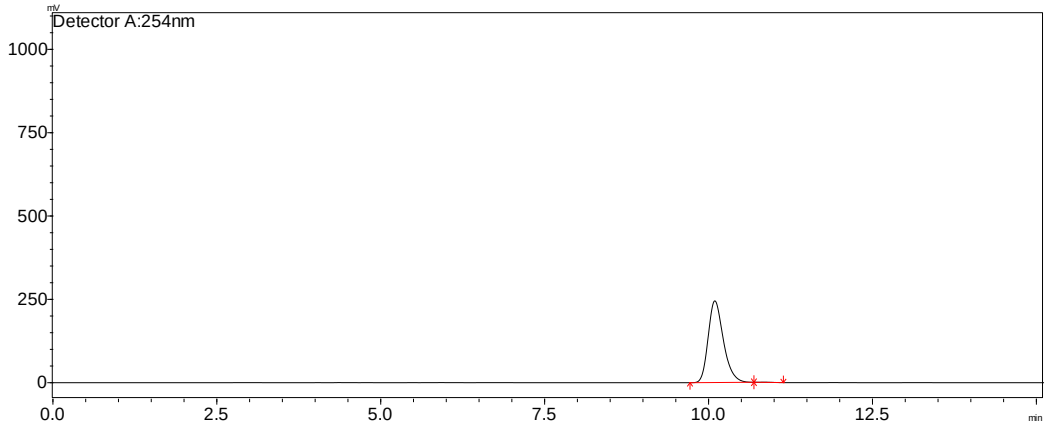
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.159	20634682	365476	99.761	99.942
2	44.522	49528	214	0.239	0.058
Total		20684210	365689	100.000	100.000



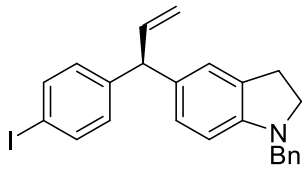
3j



Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.461	2983962	175338	46.844	48.056
2	11.219	3386099	189522	53.156	51.944
Total		6370062	364860	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.092	3961666	244872	99.802	99.761
2	10.849	7851	586	0.198	0.239
Total		3969517	245459	100.000	100.000



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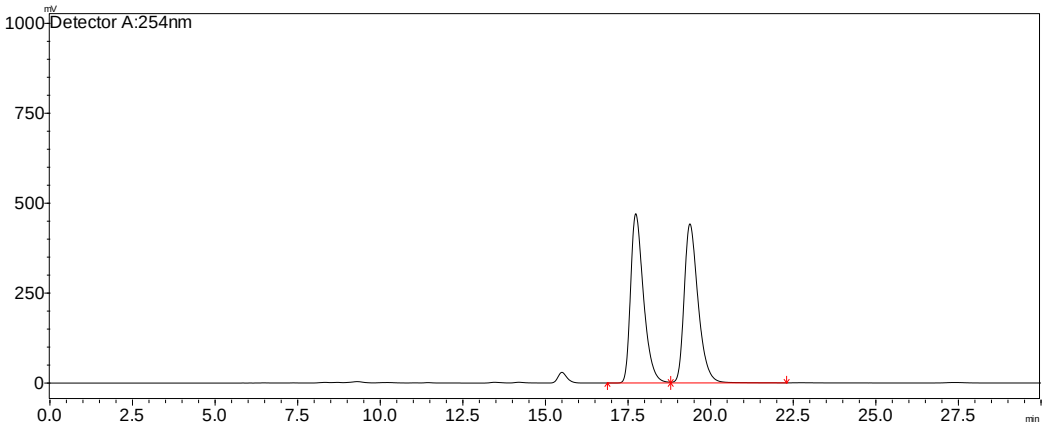
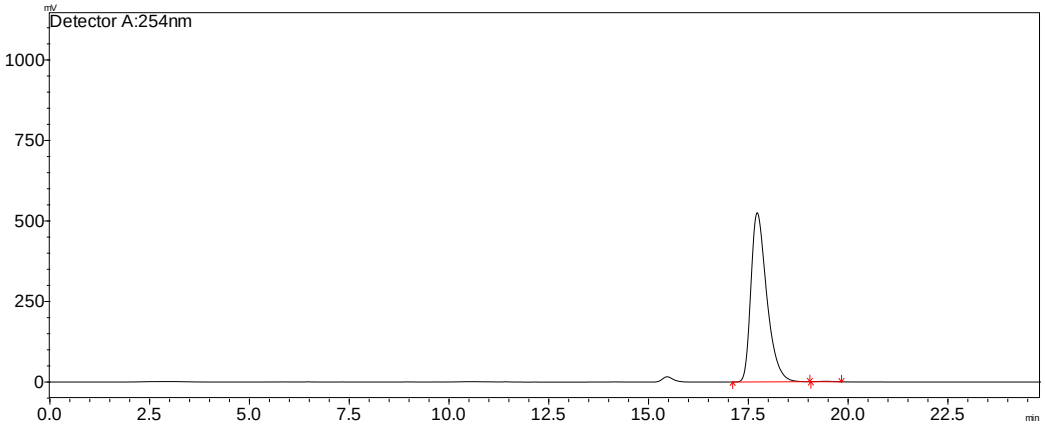
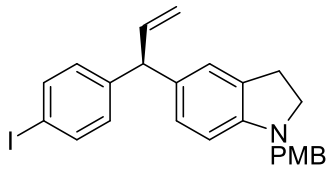


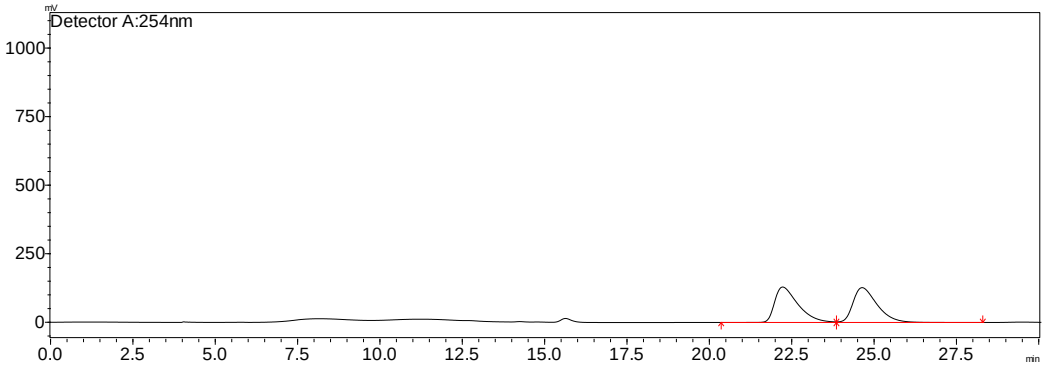
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.729	12817253	470736	49.611	51.566
2	19.368	13018414	442136	50.389	48.434
Total		25835667	912871	100.000	100.000



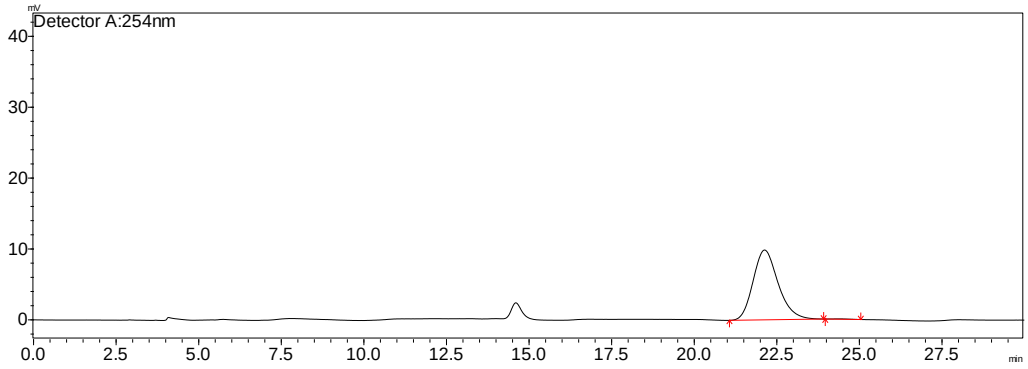
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.718	14540737	525471	99.757	99.719
2	19.441	35360	1483	0.243	0.281
Total		14576097	526954	100.000	100.000



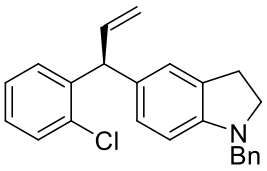
3l



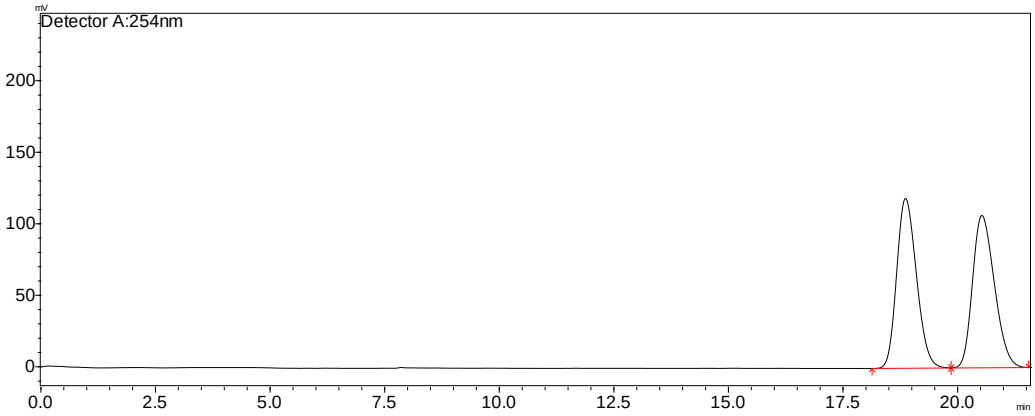
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.222	6416264	129400	49.703	50.445
2	24.633	6493067	127118	50.297	49.555
Total		12909331	256518	100.000	100.000



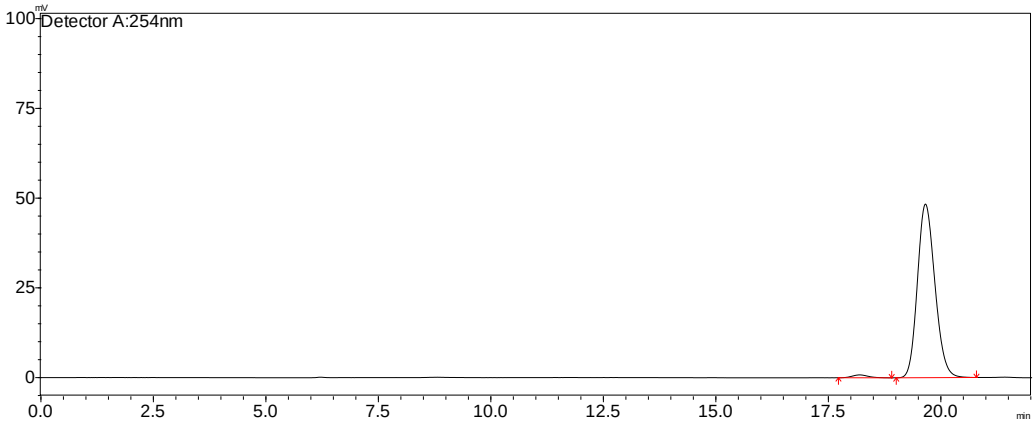
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.125	520539	9855	99.685	99.558
2	24.339	1644	44	0.315	0.442
Total		522183	9898	100.000	100.000



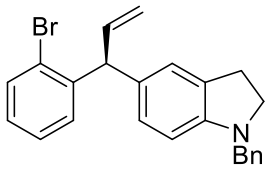
3m



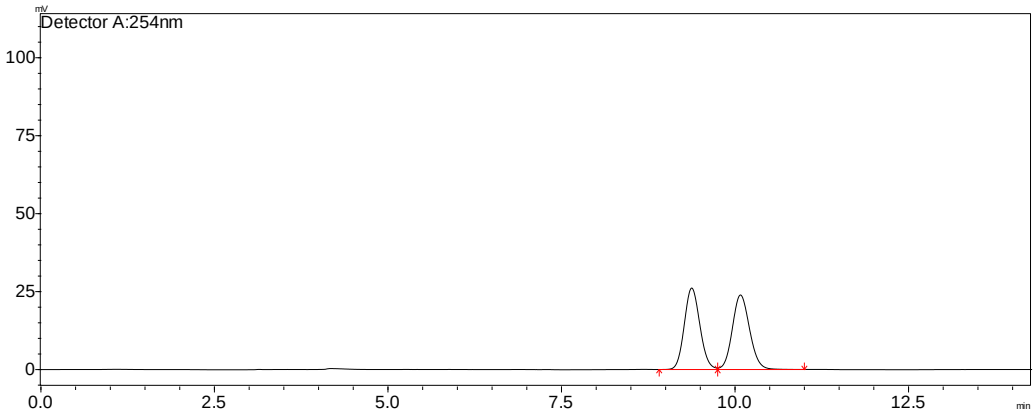
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.859	3565846	118748	50.169	52.709
2	20.526	3541790	106542	49.831	47.291
Total		7107636	225290	100.000	100.000



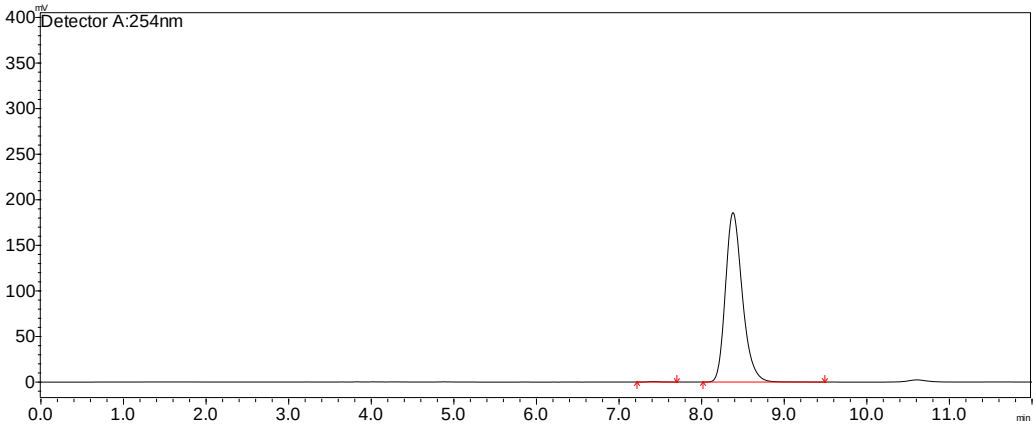
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.192	19789	797	1.488	1.622
2	19.654	1309735	48369	98.512	98.378
Total		1329524	49166	100.000	100.000



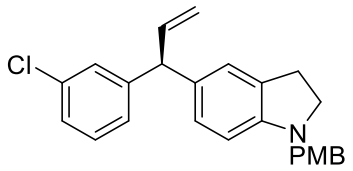
3n



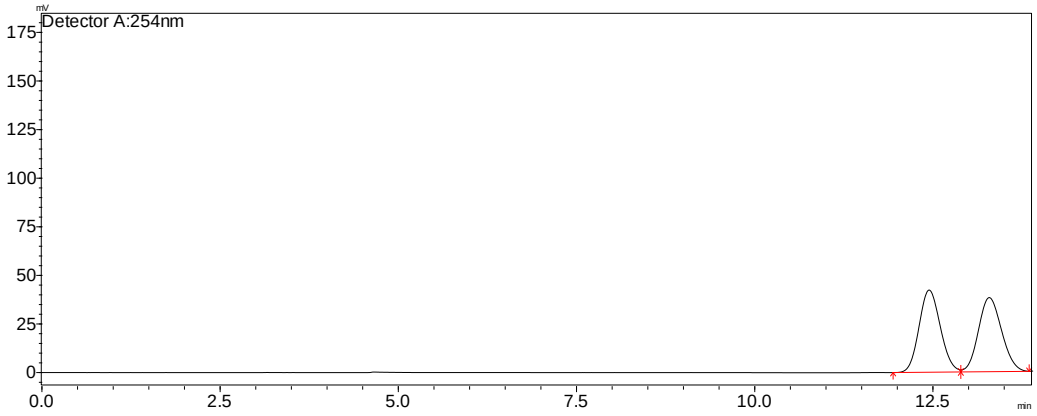
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.372	408595	26145	49.670	52.246
2	10.074	414020	23898	50.330	47.754
Total		822615	50043	100.000	100.000



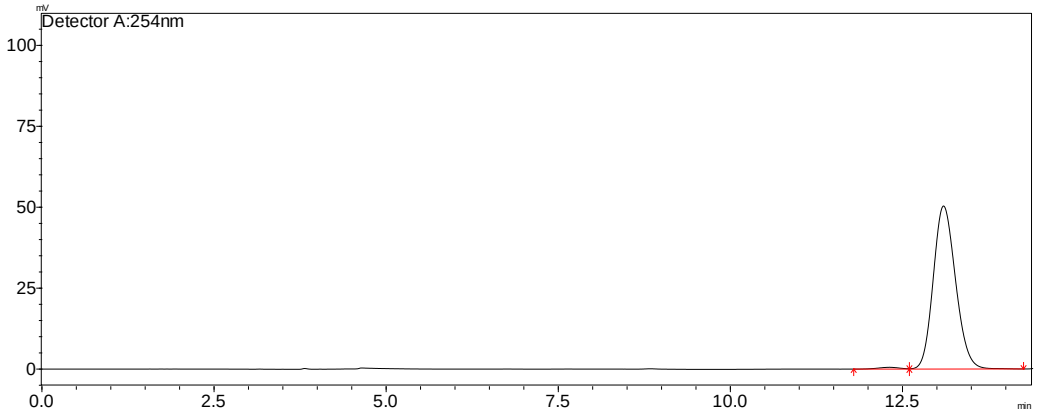
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.404	4763	487	0.180	0.261
2	8.375	2641507	185784	99.820	99.739
Total		2646270	186271	100.000	100.000



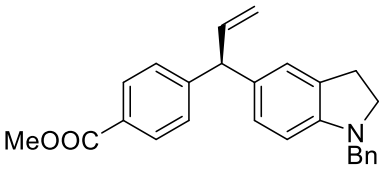
3o



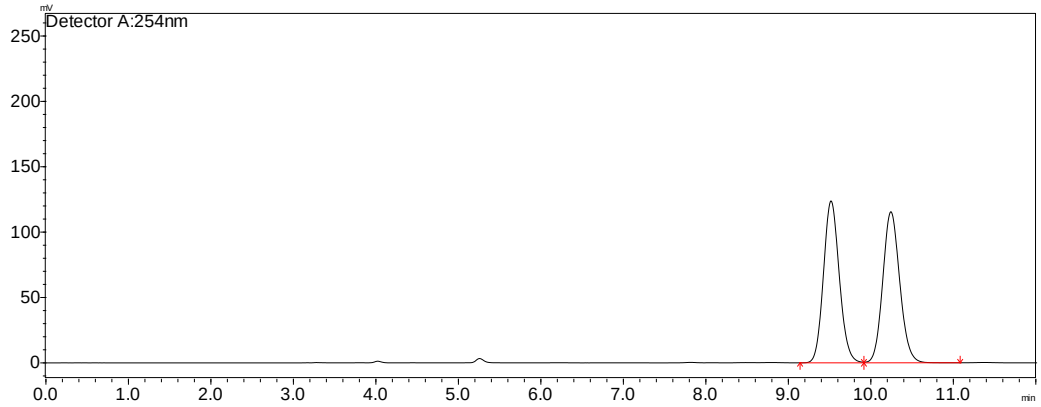
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.442	878208	42278	50.469	52.581
2	13.286	861871	38127	49.531	47.419
Total		1740079	80405	100.000	100.000



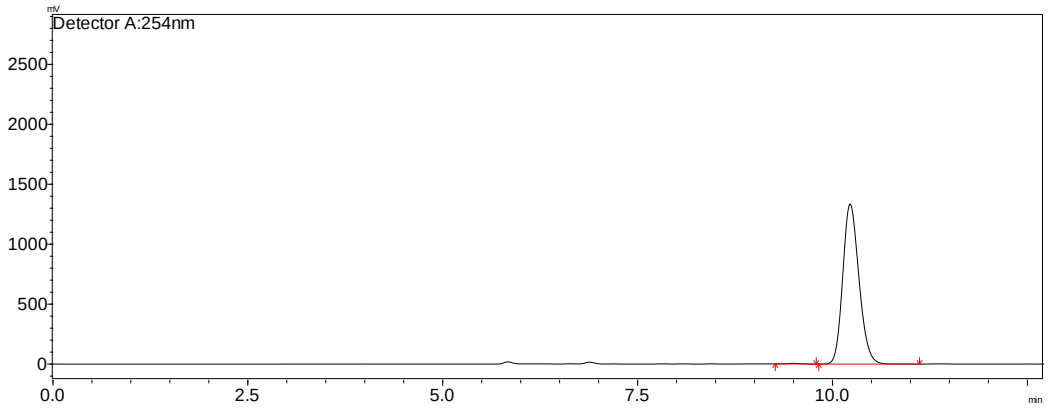
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.306	12110	552	1.053	1.083
2	13.092	1138048	50360	98.947	98.917
Total		1150158	50912	100.000	100.000



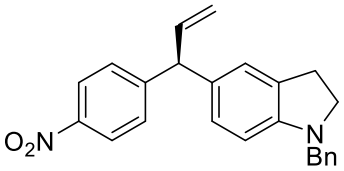
3p



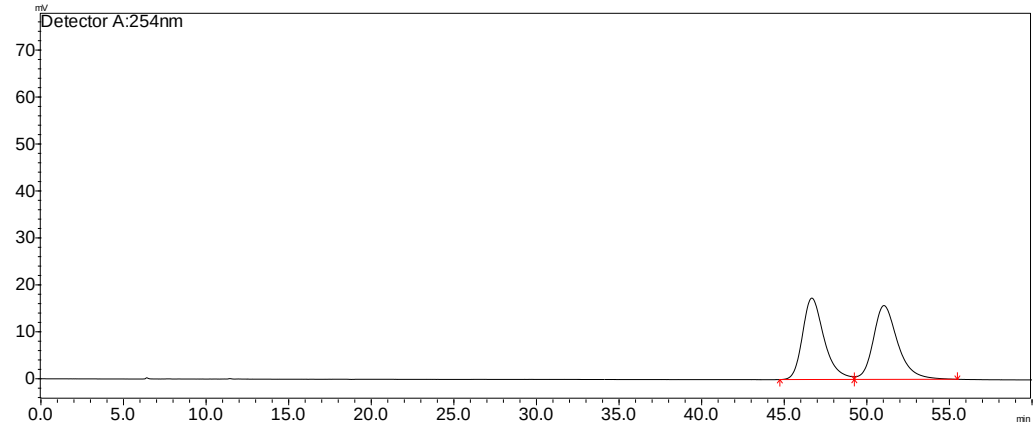
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.513	1655432	123878	50.025	51.728
2	10.239	1653758	115600	49.975	48.272
Total		3309190	239479	100.000	100.000



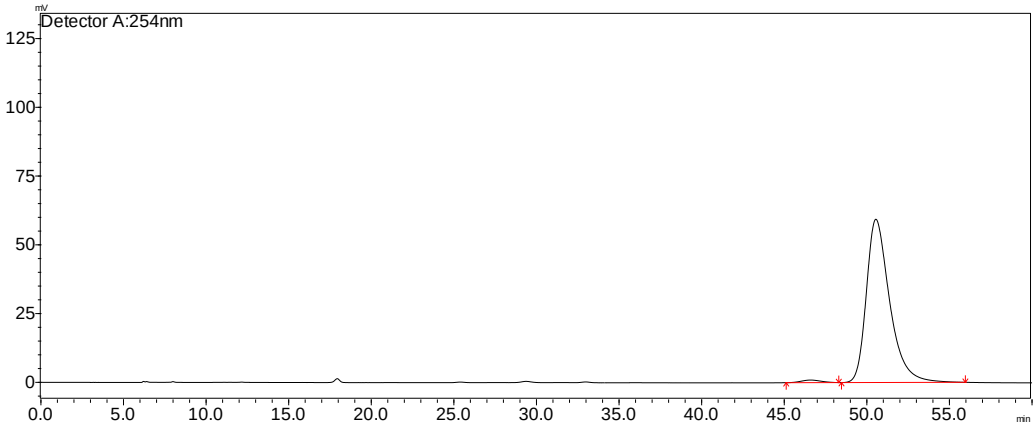
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.501	66933	5290	0.346	0.394
2	10.222	19268894	1335872	99.654	99.606
Total		19335827	1341162	100.000	100.000



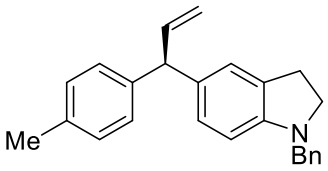
3q



Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.665	1581064	17341	49.379	52.436
2	51.031	1620834	15730	50.621	47.564
Total		3201899	33070	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.588	77494	935	1.310	1.551
2	50.543	5836123	59357	98.690	98.449
Total		5913617	60292	100.000	100.000



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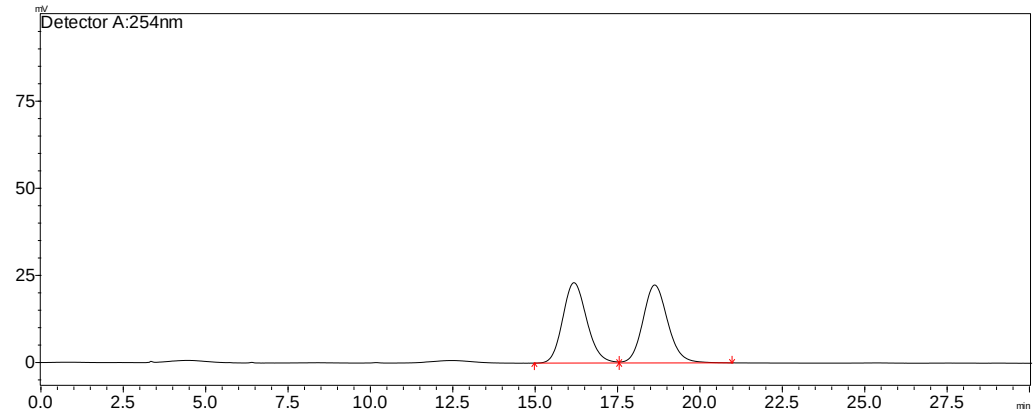
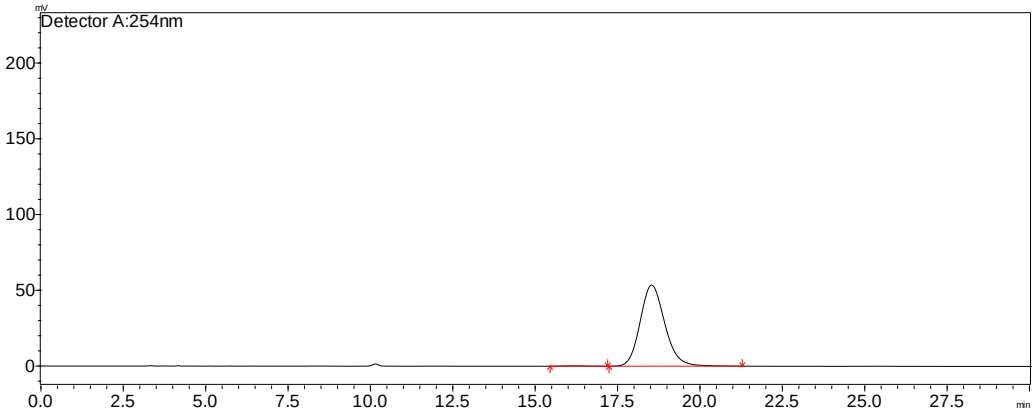
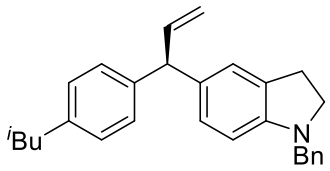


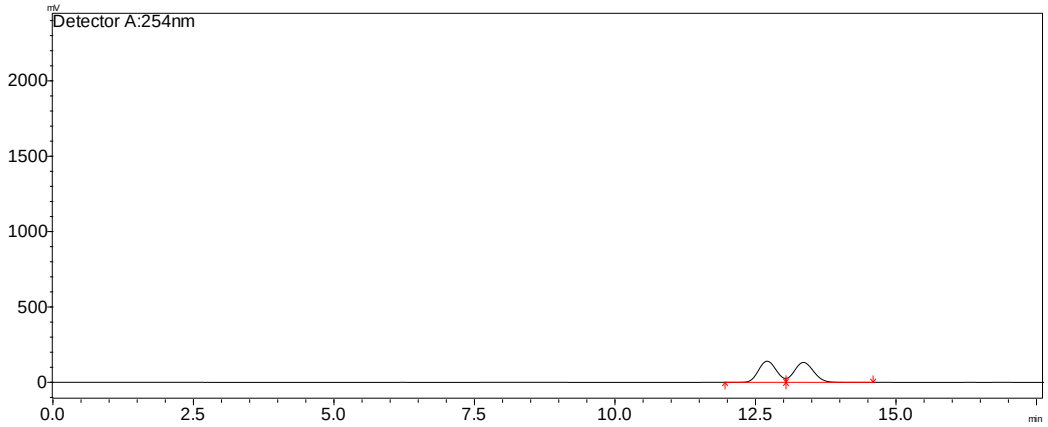
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.172	1173846	23068	49.968	50.761
2	18.622	1175348	22376	50.032	49.239
Total		2349194	45444	100.000	100.000



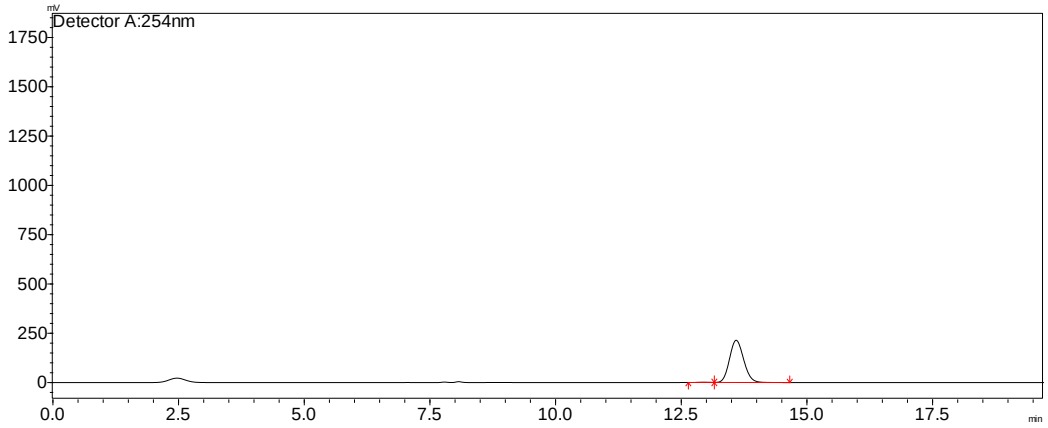
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.180	11627	251	0.416	0.466
2	18.529	2784293	53524	99.584	99.534
Total		2795920	53775	100.000	100.000



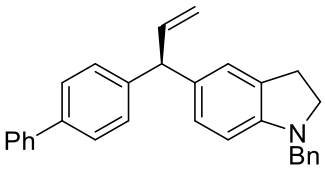
3s



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.702	3106343	140264	49.657	51.524
2	13.349	3149256	131964	50.343	48.476
Total		6255599	272228	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.941	19717	1311	0.469	0.609
2	13.588	4185946	214159	99.531	99.391
Total		4205662	215471	100.000	100.000



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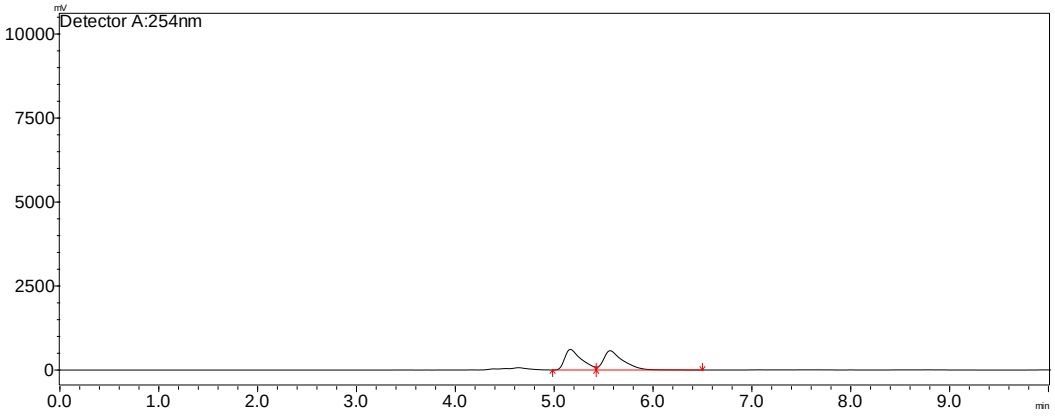
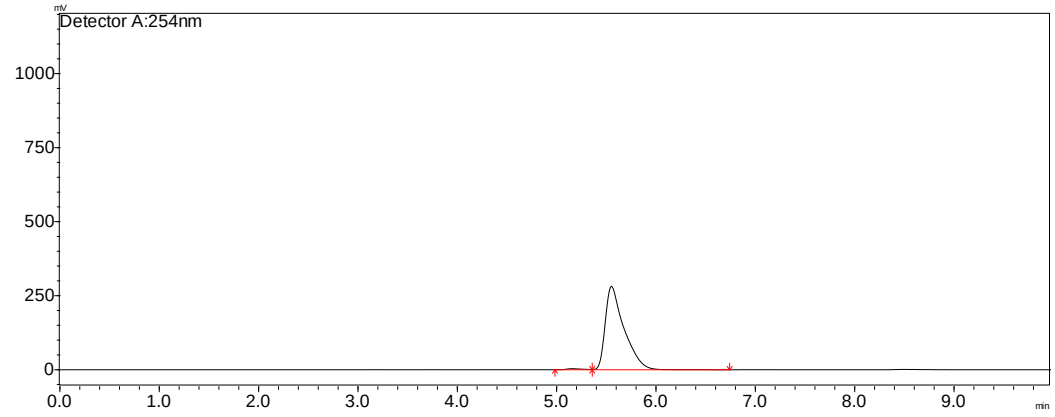
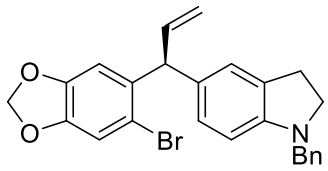


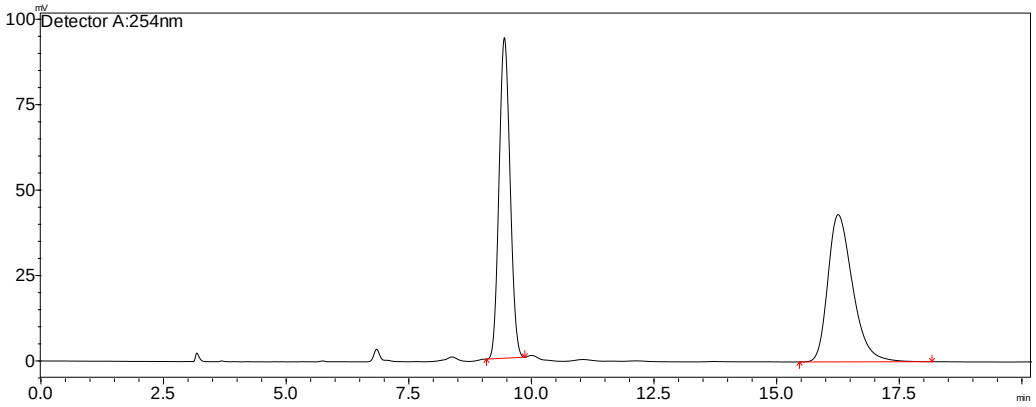
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.159	7229405	612320	47.993	51.568
2	5.561	7834065	575086	52.007	48.432
Total		15063470	1187406	100.000	100.000



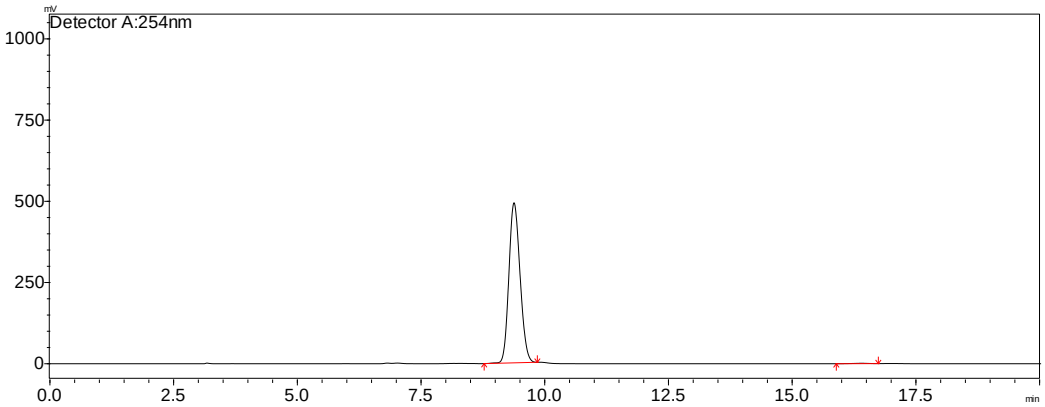
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.153	39171	3500	1.050	1.227
2	5.548	3690856	281729	98.950	98.773
Total		3730028	285229	100.000	100.000



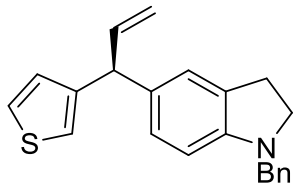
3u



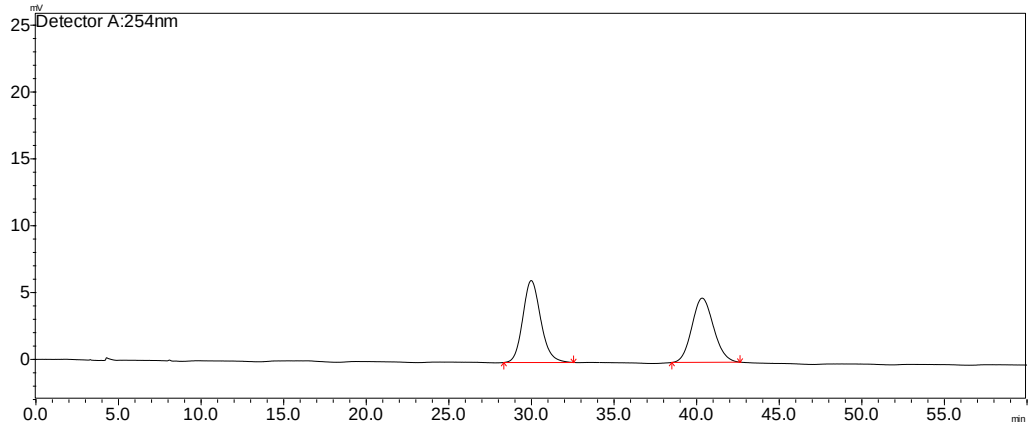
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.445	1468280	93799	49.220	68.516
2	16.251	1514806	43101	50.780	31.484
Total		2983086	136900	100.000	100.000



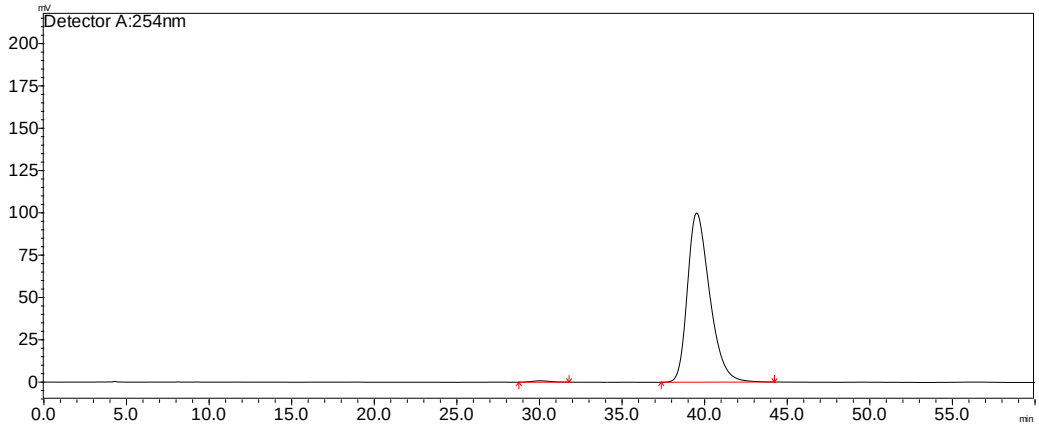
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.375	7726090	492792	99.648	99.758
2	16.399	27285	1195	0.352	0.242
Total		7753375	493986	100.000	100.000



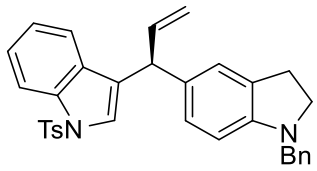
3v



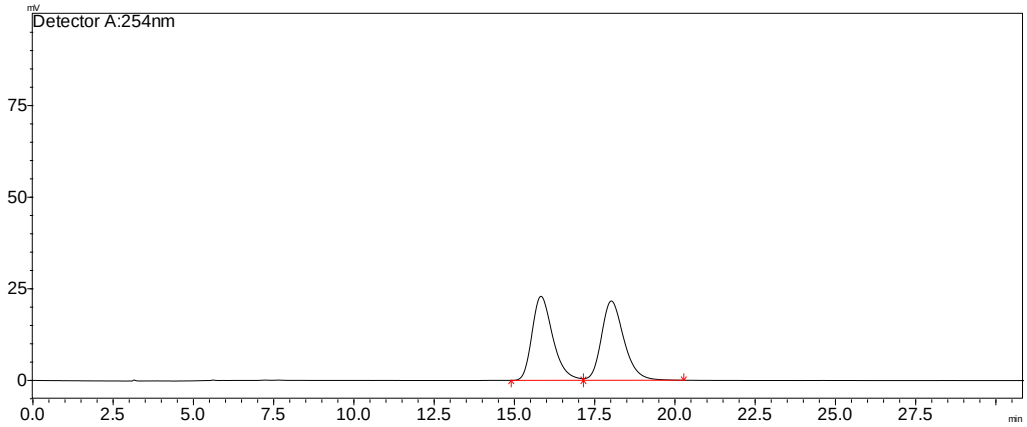
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.978	464249	6128	51.348	56.074
2	40.335	439871	4801	48.652	43.926
Total		904121	10929	100.000	100.000



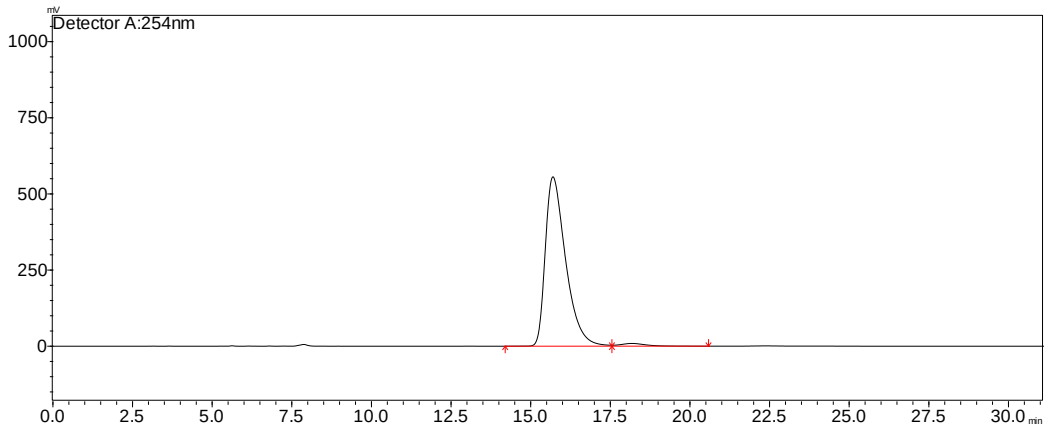
Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.068	62477	825	0.663	0.819
2	39.512	9366485	99953	99.337	99.181
Total		9428962	100779	100.000	100.000



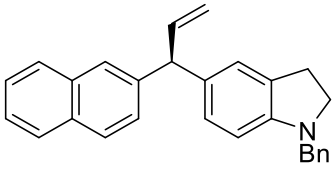
3w



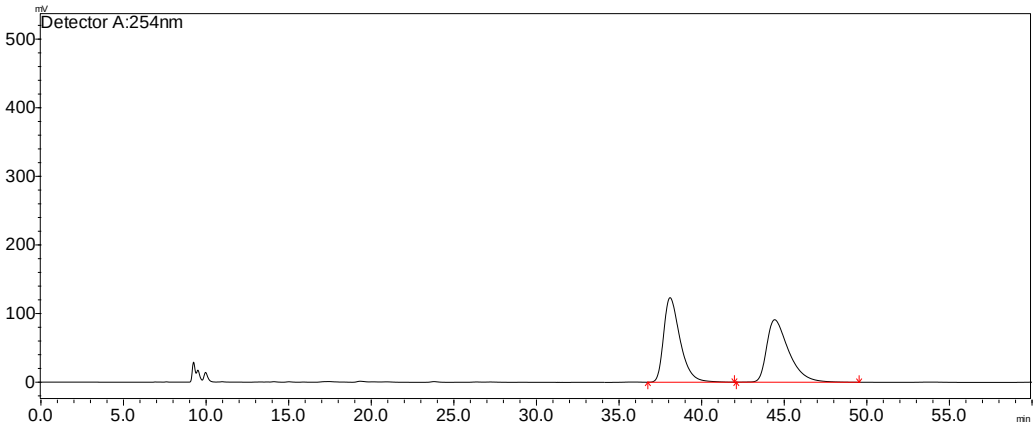
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.823	1035122	22929	49.505	51.443
2	18.015	1055826	21642	50.495	48.557
Total		2090948	44572	100.000	100.000



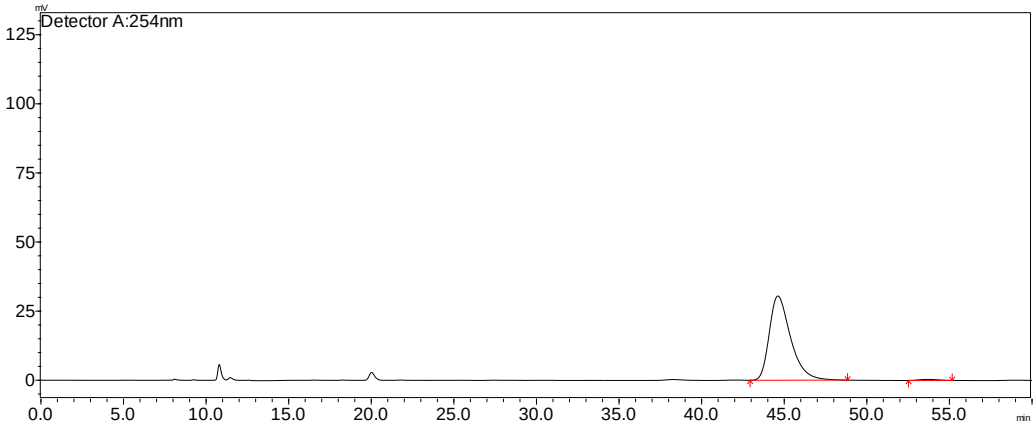
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.695	24720255	556088	98.016	98.412
2	18.173	500333	8973	1.984	1.588
Total		25220588	565061	100.000	100.000



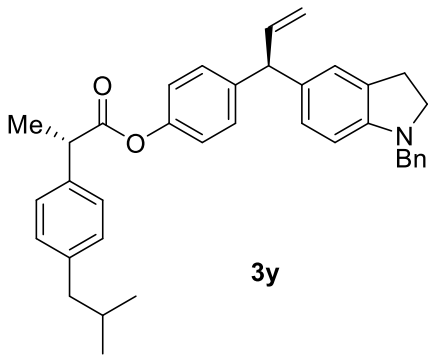
3x



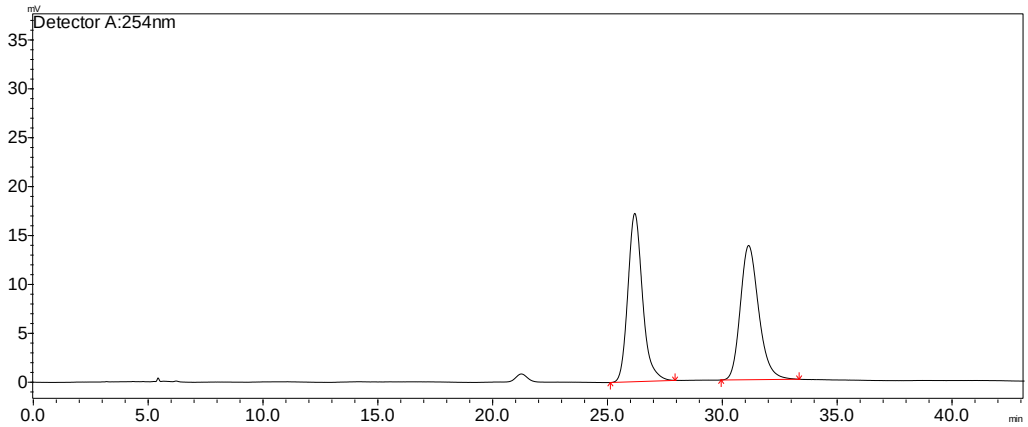
Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.084	8549588	123210	50.350	57.508
2	44.418	8430770	91038	49.650	42.492
Total		16980359	214248	100.000	100.000



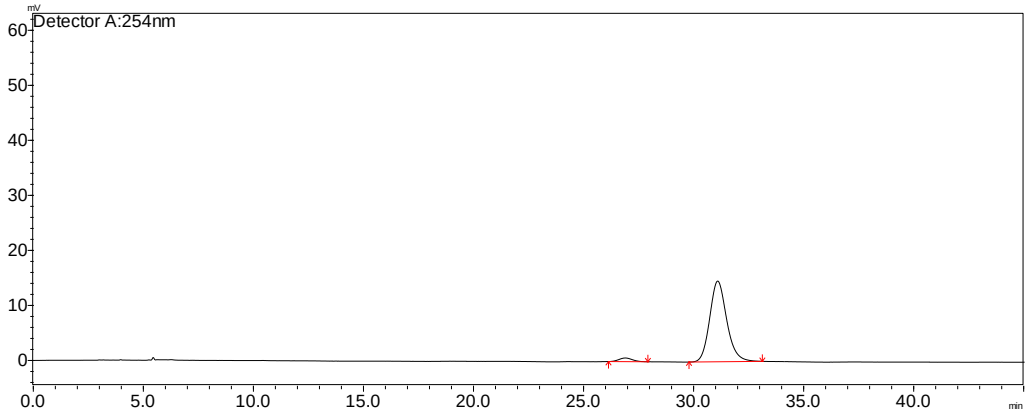
Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.611	2742099	30470	98.935	98.767
2	53.678	29516	380	1.065	1.233
Total		2771615	30850	100.000	100.000



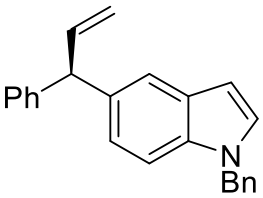
3y



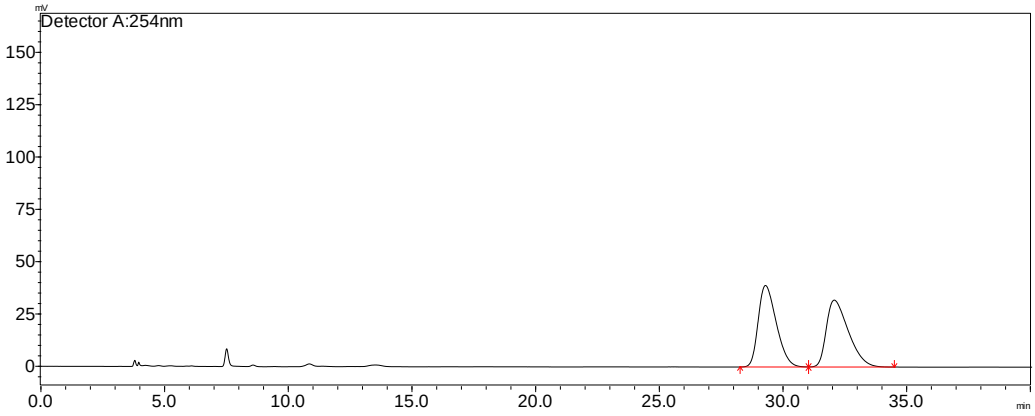
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.183	763868	17218	49.989	55.629
2	31.140	764194	13733	50.011	44.371
Total		1528061	30951	100.000	100.000



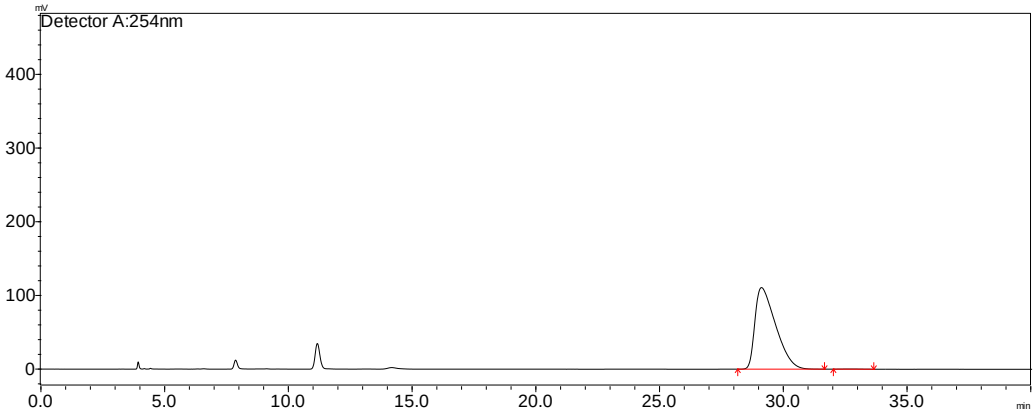
Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.895	28326	664	3.464	4.328
2	31.091	789416	14667	96.536	95.672
Total		817742	15330	100.000	100.000



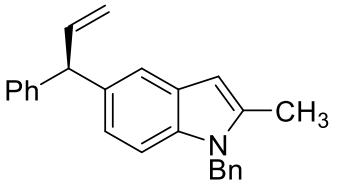
4a



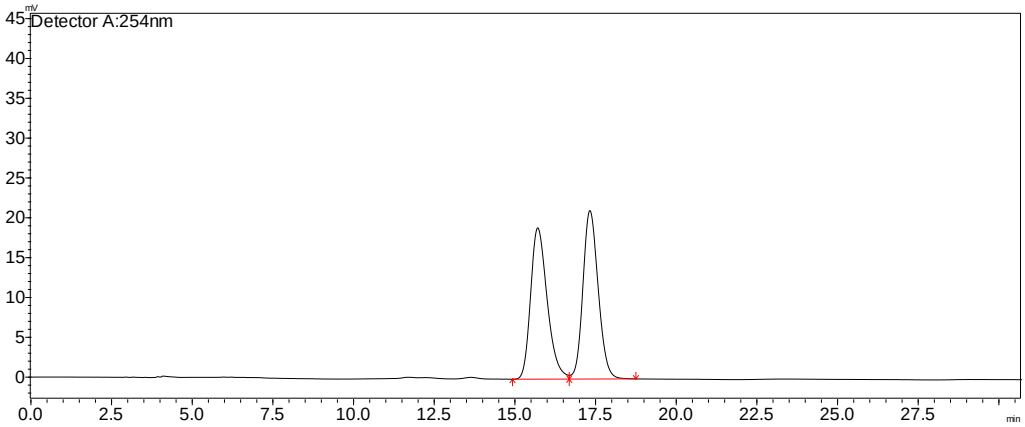
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.288	1984412	38950	50.044	54.923
2	32.068	1980947	31968	49.956	45.077
Total		3965359	70918	100.000	100.000



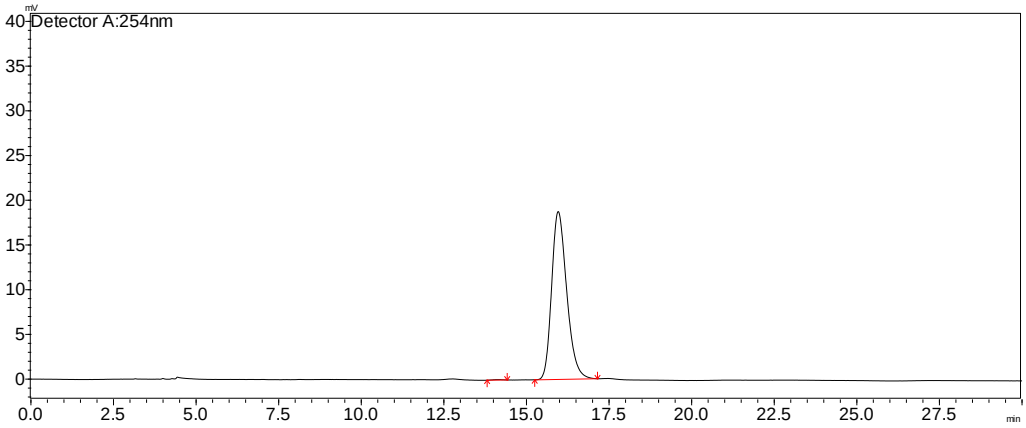
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.115	6438474	110724	99.829	99.799
2	32.715	11015	223	0.171	0.201
Total		6449489	110947	100.000	100.000



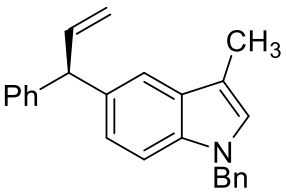
4b



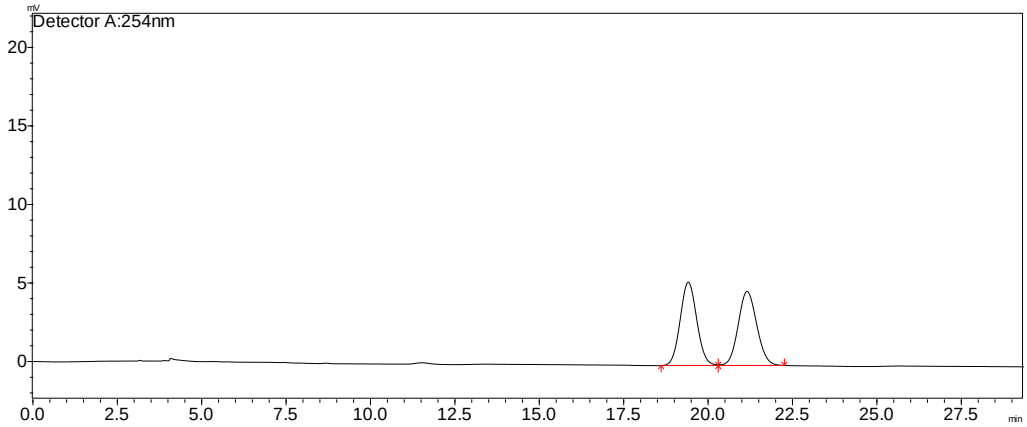
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.704	680556	18992	49.379	47.315
2	17.320	697681	21148	50.621	52.685
Total		1378237	40141	100.000	100.000



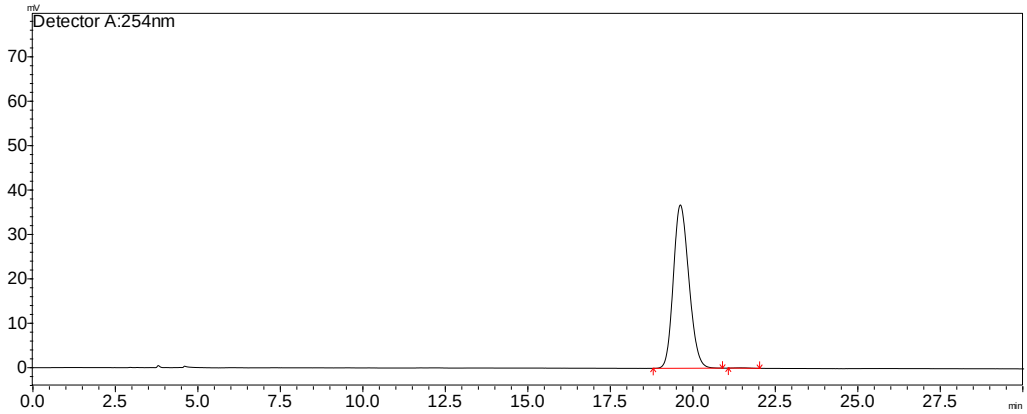
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.128	1013	49	0.170	0.259
2	15.957	595772	18769	99.830	99.741
Total		596784	18818	100.000	100.000



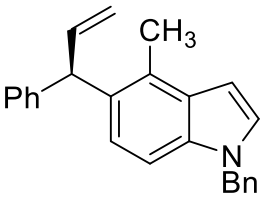
4c



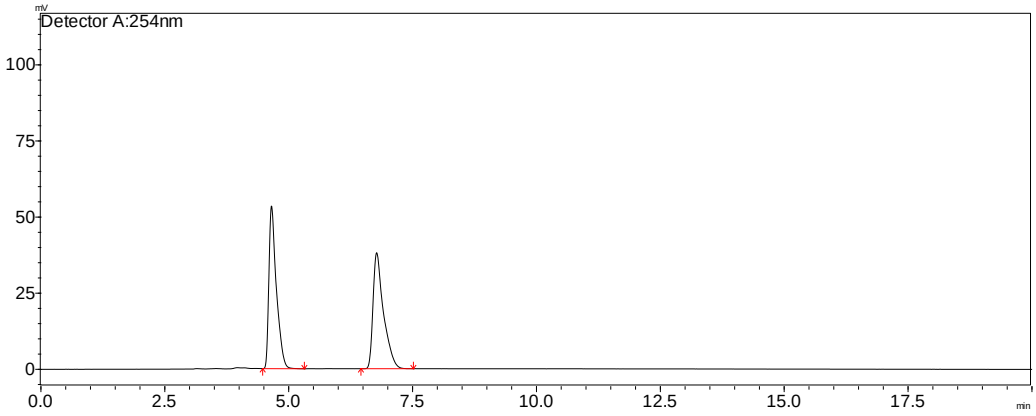
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.409	181714	5307	50.197	52.963
2	21.152	180288	4713	49.803	47.037
Total		362001	10021	100.000	100.000



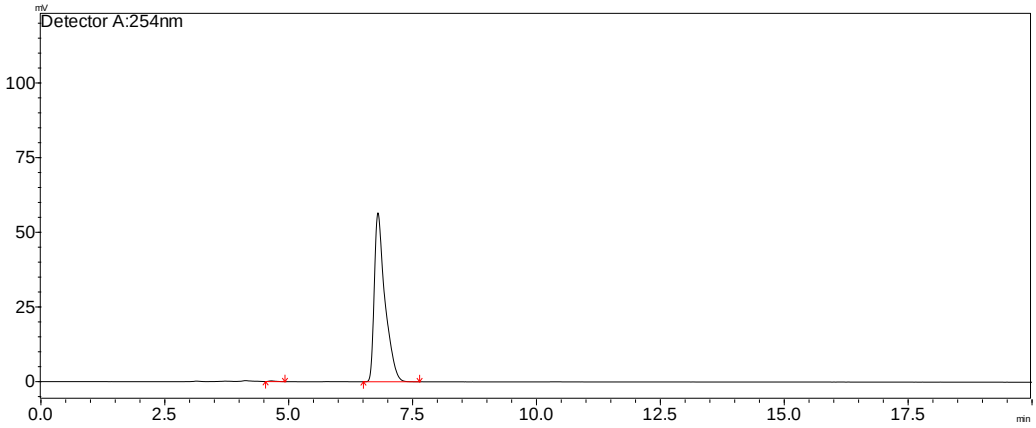
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.618	1203796	36771	99.799	99.781
2	21.427	2422	81	0.201	0.219
Total		1206218	36852	100.000	100.000



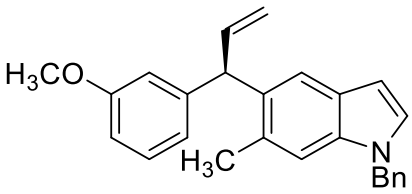
4d



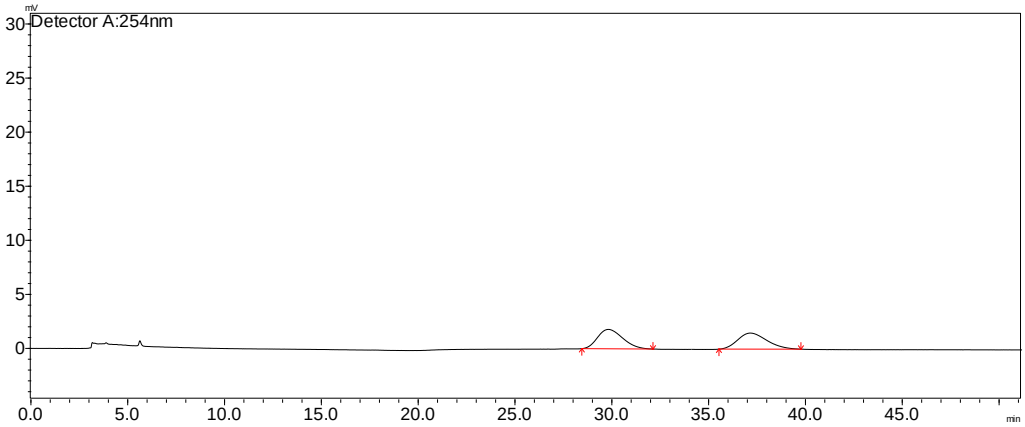
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.650	561189	53397	50.097	58.348
2	6.772	559019	38118	49.903	41.652
Total		1120209	91515	100.000	100.000



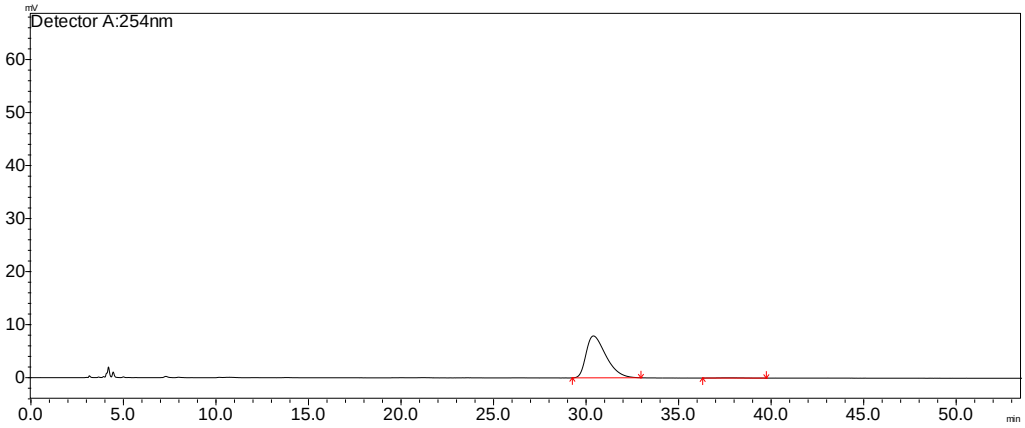
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.644	2234	234	0.264	0.412
2	6.798	844707	56564	99.736	99.588
Total		846941	56798	100.000	100.000



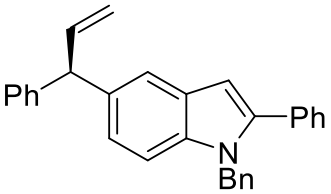
4e



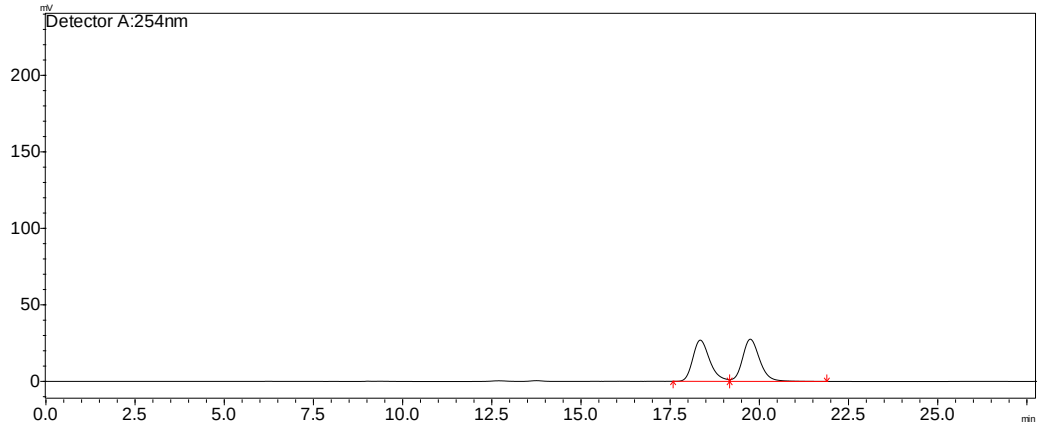
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.823	161896	1793	50.951	54.688
2	37.133	155853	1486	49.049	45.312
Total		317748	3279	100.000	100.000



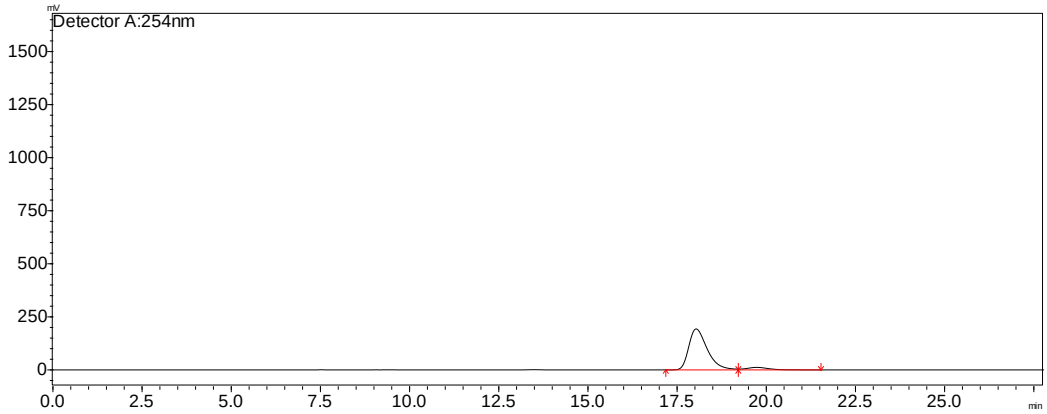
Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.394	591139	7908	99.292	99.473
2	37.753	4217	42	0.708	0.527
Total		595356	7949	100.000	100.000



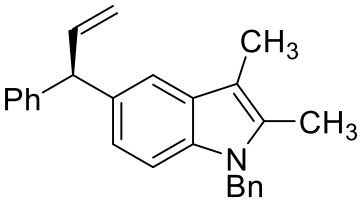
4f



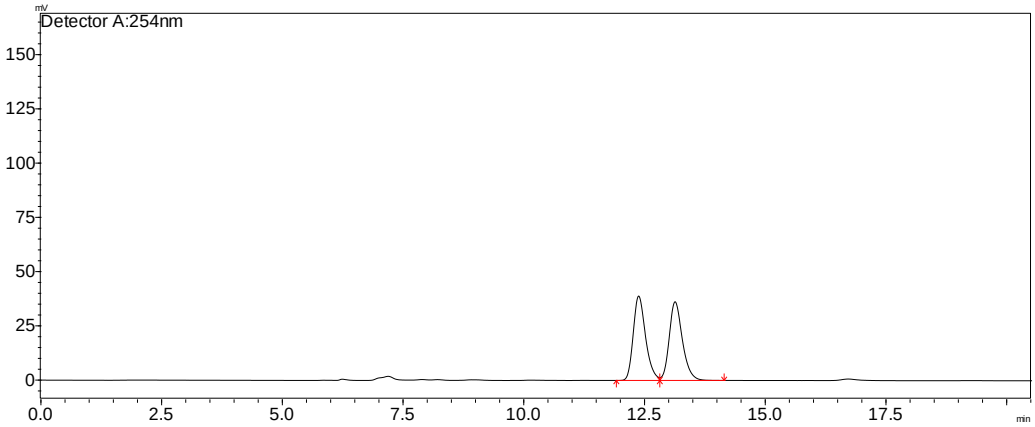
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.339	890775	26949	49.073	49.435
2	19.741	924420	27565	50.927	50.565
Total		1815195	54514	100.000	100.000



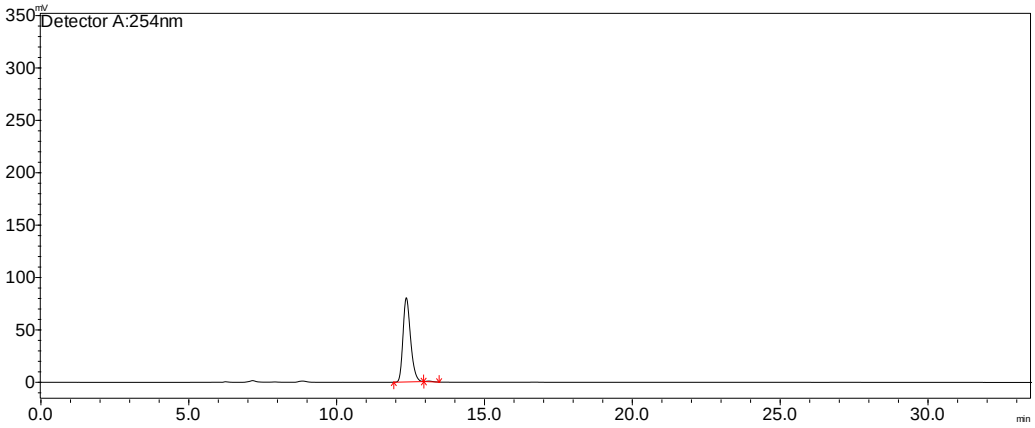
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.030	6963940	193042	93.160	94.212
2	19.729	511293	11860	6.840	5.788
Total		7475233	204902	100.000	100.000



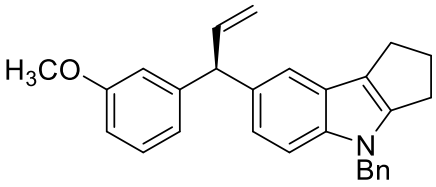
4g



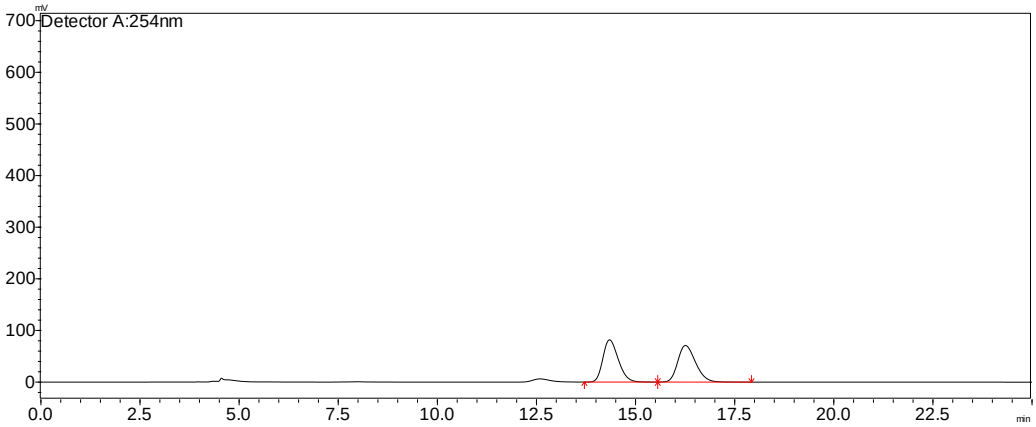
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.375	692001	38878	50.101	51.740
2	13.129	689214	36263	49.899	48.260
Total		1381214	75141	100.000	100.000



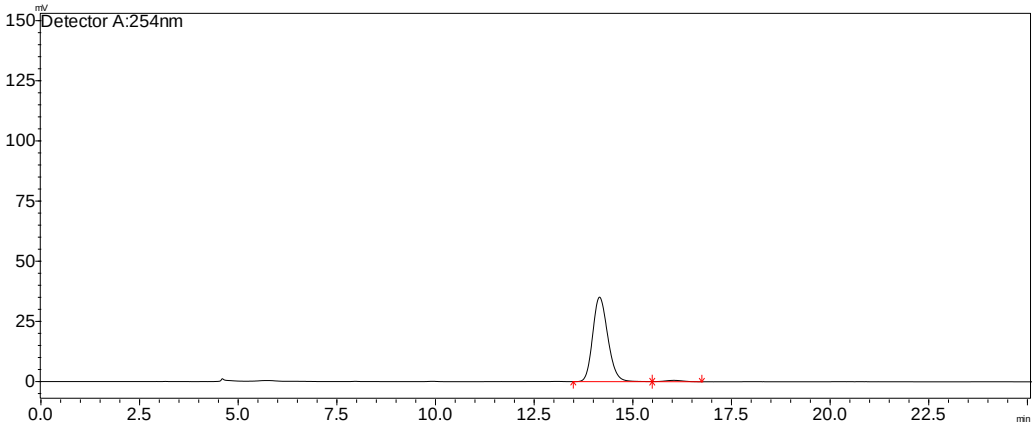
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.353	1425537	80376	99.419	99.270
2	13.111	8326	591	0.581	0.730
Total		1433863	80967	100.000	100.000



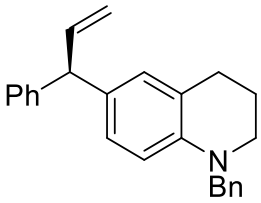
4h



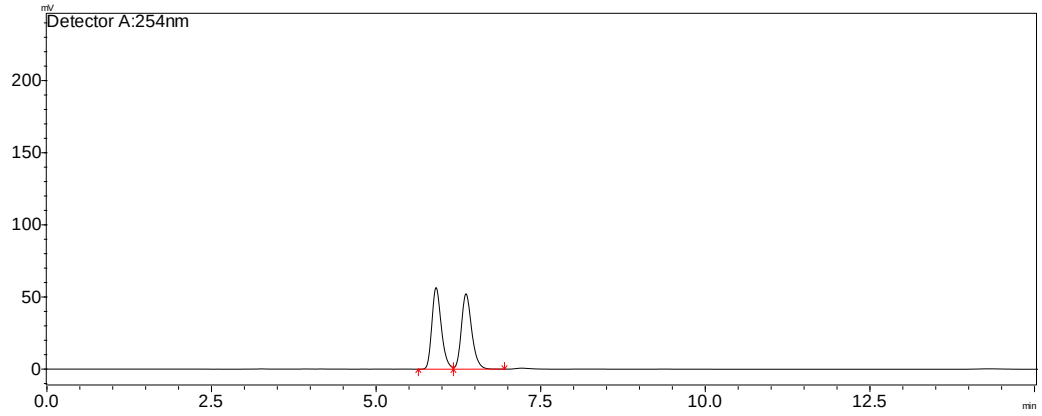
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.339	2216451	81836	49.936	53.558
2	16.254	2222126	70962	50.064	46.442
Total		4438577	152798	100.000	100.000



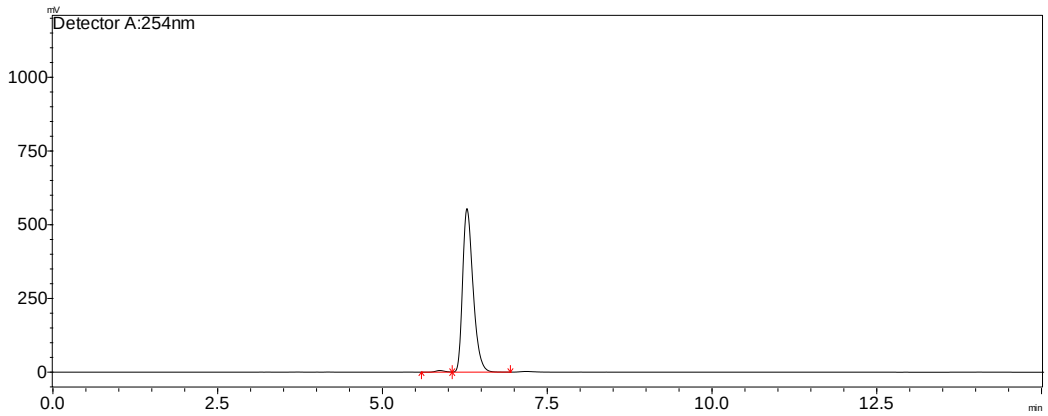
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.152	937593	35128	98.086	98.394
2	16.037	18296	573	1.914	1.606
Total		955889	35702	100.000	100.000



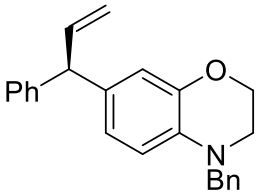
5a



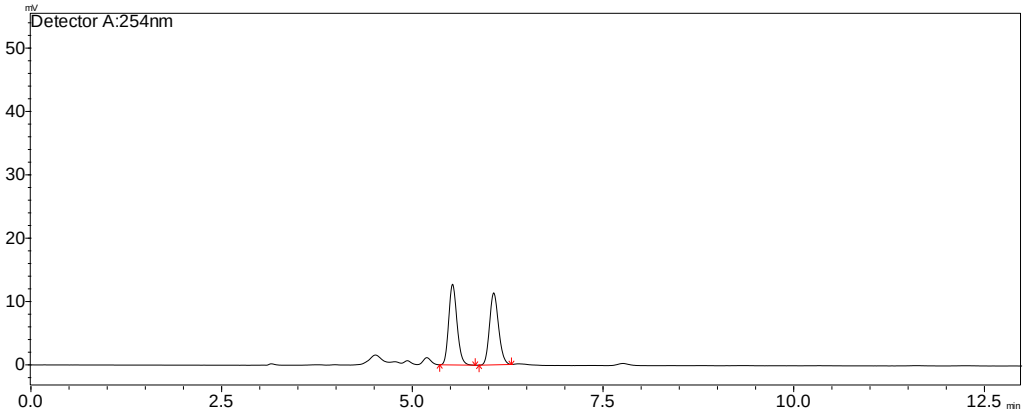
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.907	566651	56559	49.765	51.954
2	6.361	571995	52305	50.235	48.046
Total		1138645	108864	100.000	100.000



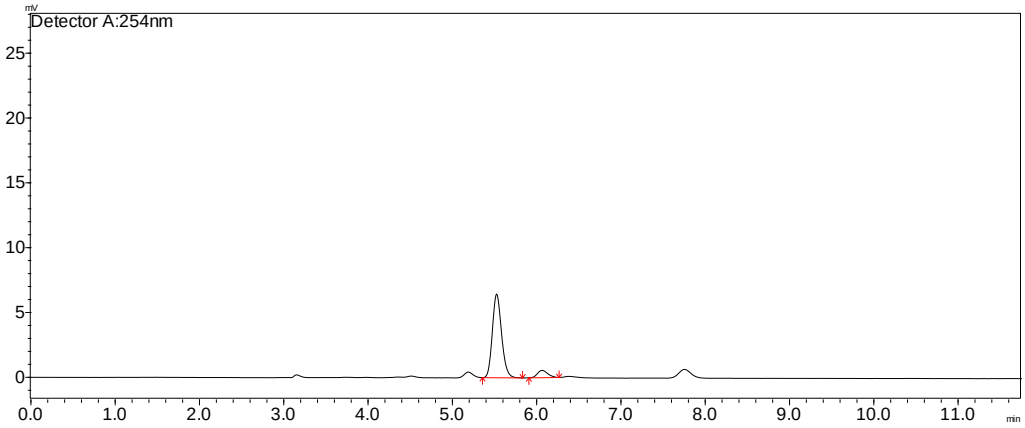
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.866	53583	5501	0.870	0.982
2	6.278	6103972	554581	99.130	99.018
Total		6157555	560082	100.000	100.000



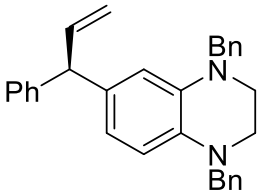
5b



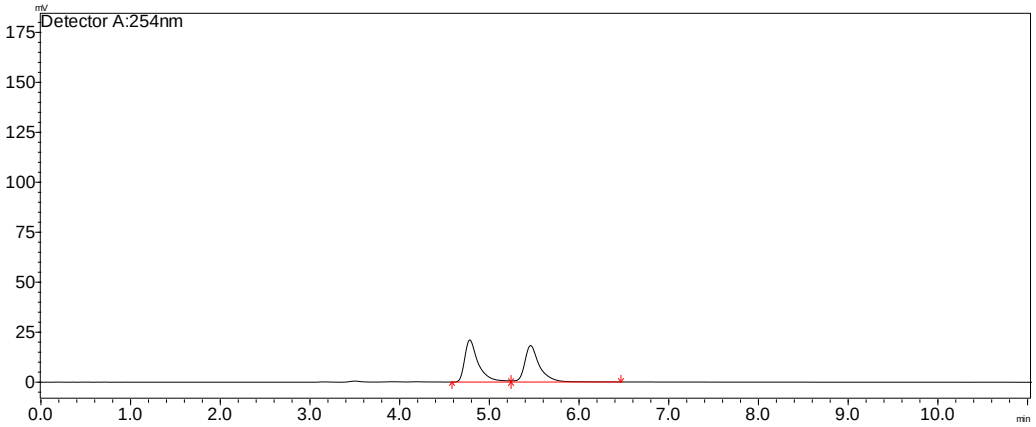
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.523	96663	12739	50.757	52.823
2	6.063	93779	11378	49.243	47.177
Total		190442	24117	100.000	100.000



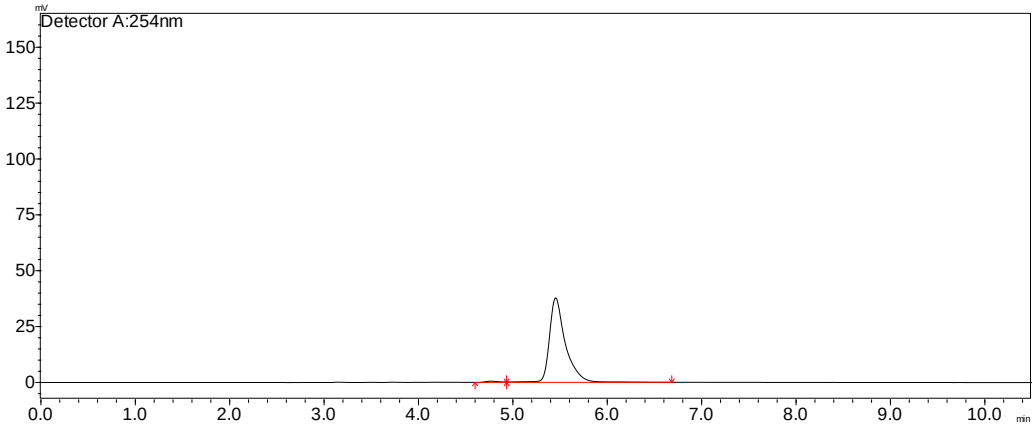
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.521	49139	6461	91.022	91.927
2	6.061	4847	567	8.978	8.073
Total		53985	7029	100.000	100.000



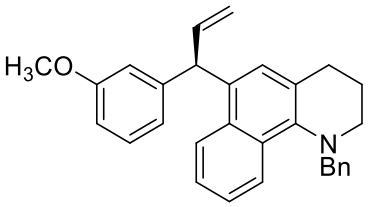
5c



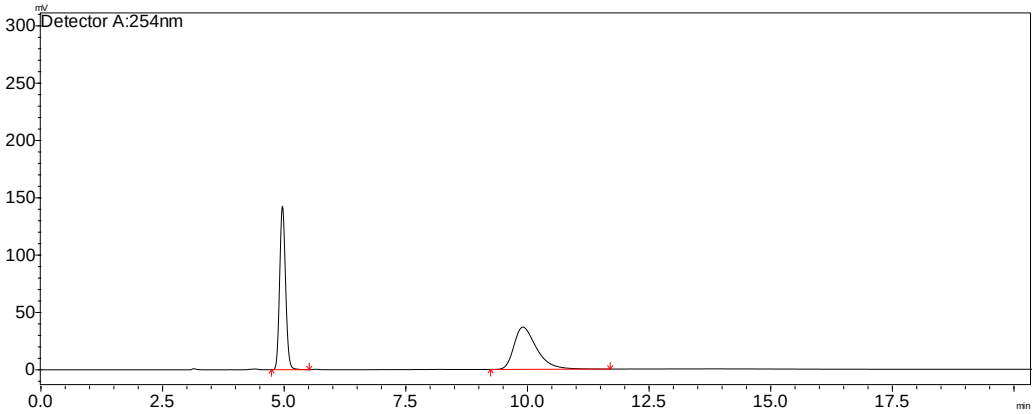
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.777	223810	21101	51.730	53.592
2	5.455	208842	18273	48.270	46.408
Total		432652	39373	100.000	100.000



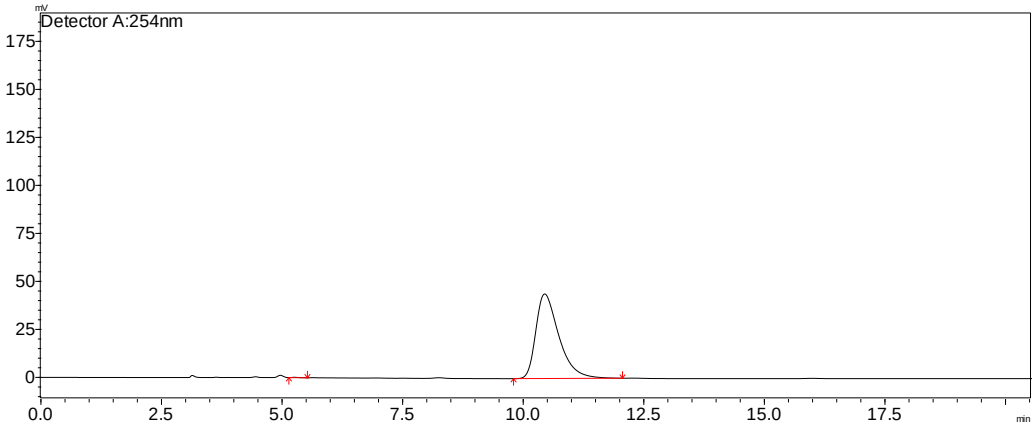
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.762	5389	545	1.194	1.422
2	5.449	445843	37808	98.806	98.578
Total		451233	38354	100.000	100.000



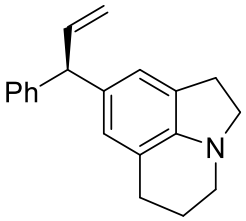
5d



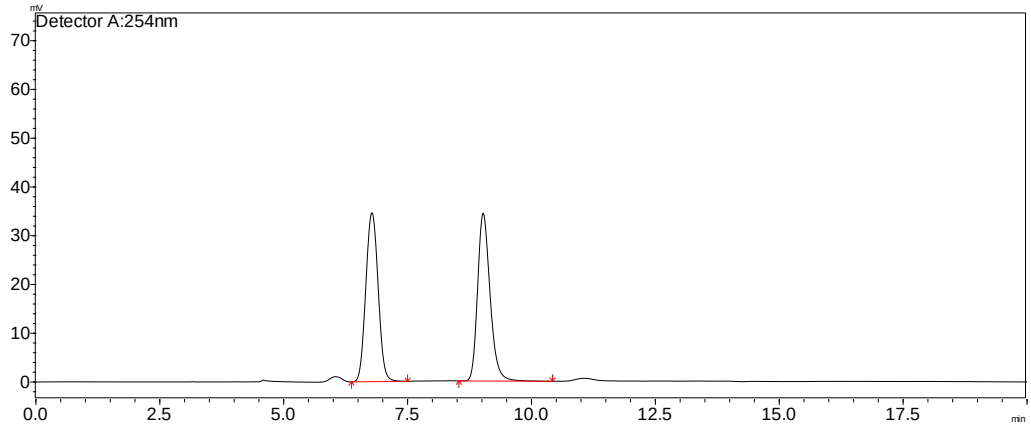
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.961	1208918	142636	50.382	79.471
2	9.902	1190569	36846	49.618	20.529
Total		2399487	179482	100.000	100.000



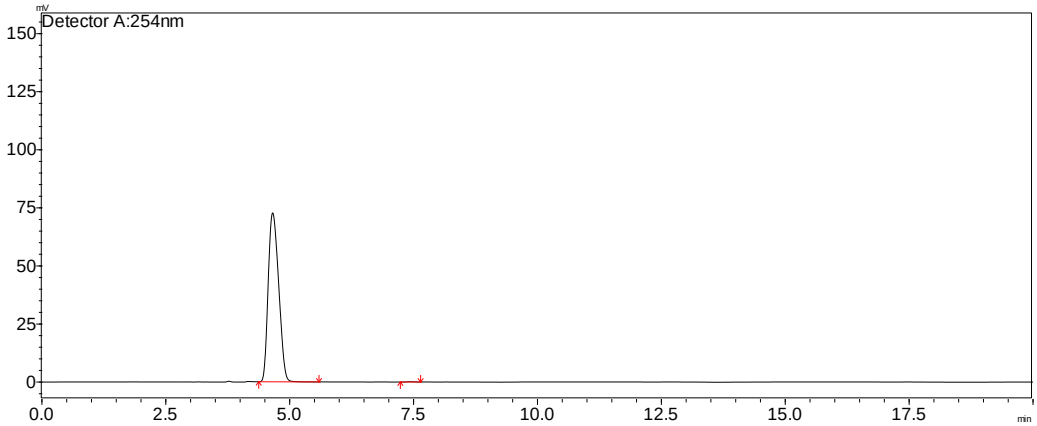
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.254	1806	203	0.123	0.458
2	10.441	1464299	44044	99.877	99.542
Total		1466106	44246	100.000	100.000



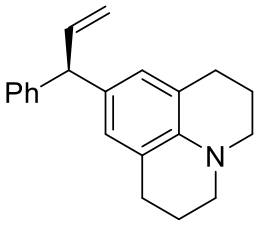
5e



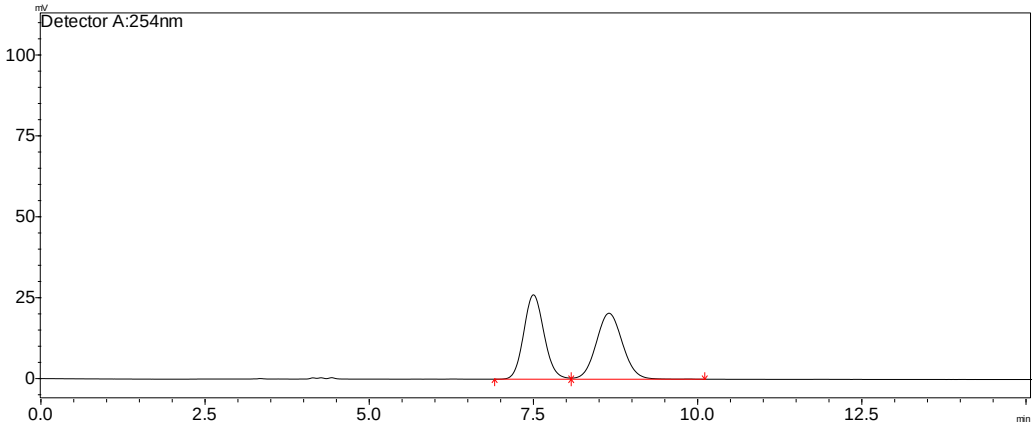
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.777	600274	34634	49.876	50.152
2	9.021	603249	34424	50.124	49.848
Total		1203522	69059	100.000	100.000



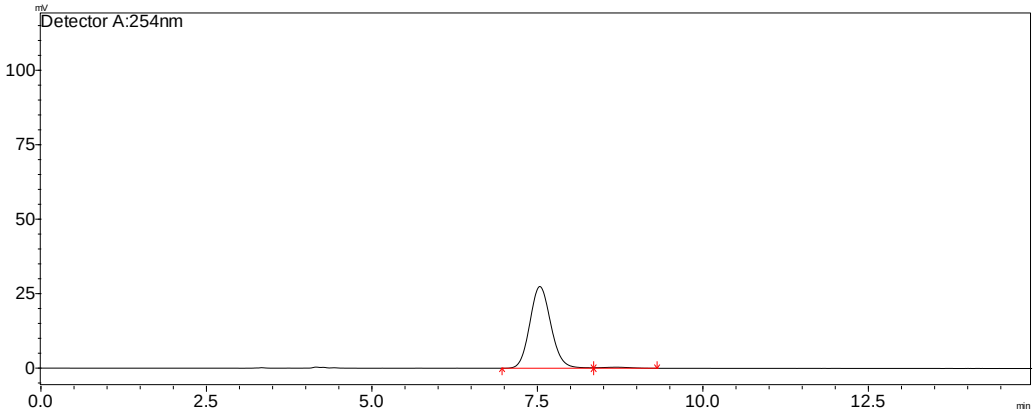
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.652	1069238	72752	99.868	99.818
2	7.431	1408	133	0.132	0.182
Total		1070646	72885	100.000	100.000



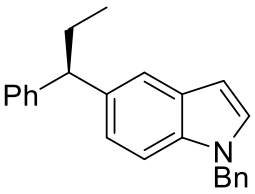
5f



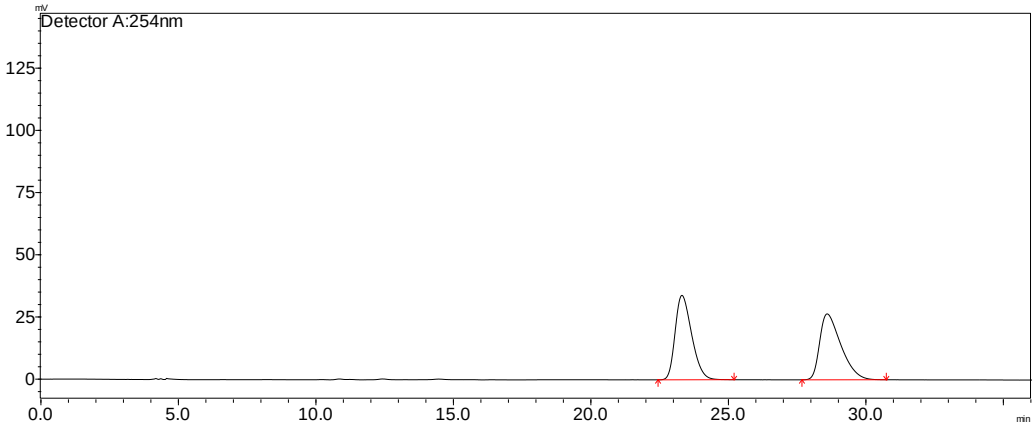
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.495	562650	26075	49.724	56.117
2	8.646	568896	20390	50.276	43.883
Total		1131545	46466	100.000	100.000



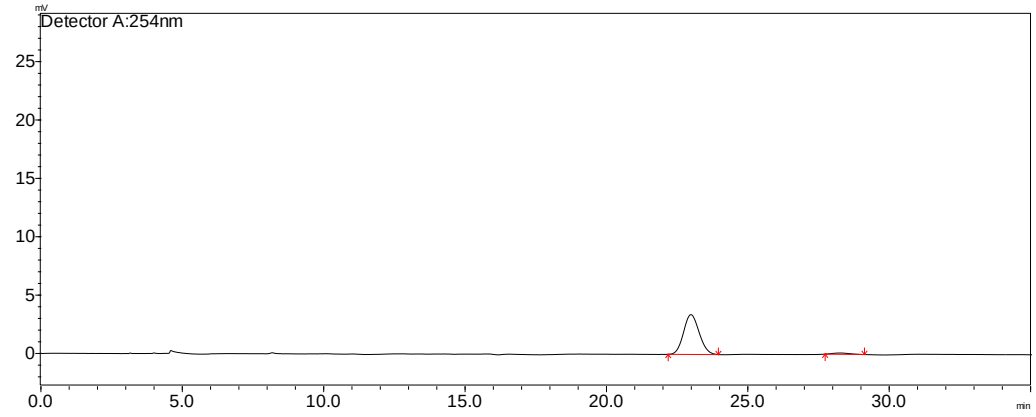
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.533	608336	27440	98.313	98.763
2	8.701	10436	344	1.687	1.237
Total		618772	27784	100.000	100.000



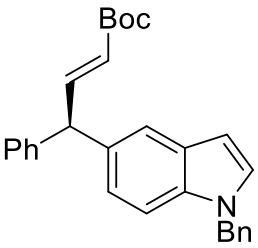
6



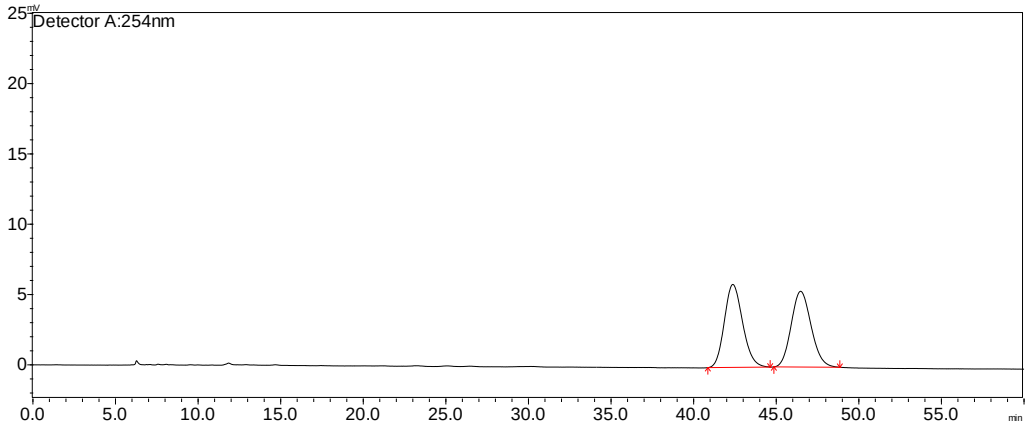
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.307	1421142	33940	50.011	56.171
2	28.589	1420522	26483	49.989	43.829
Total		2841664	60422	100.000	100.000



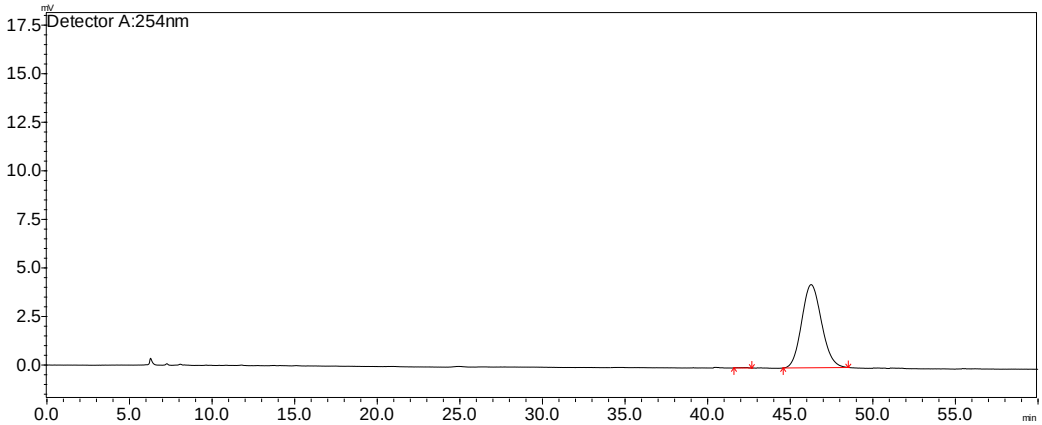
Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.984	131150	3408	96.548	96.882
2	28.258	4690	110	3.452	3.118
Total		135839	3518	100.000	100.000



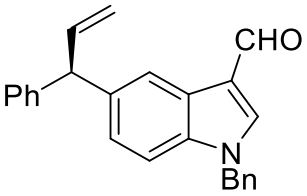
7



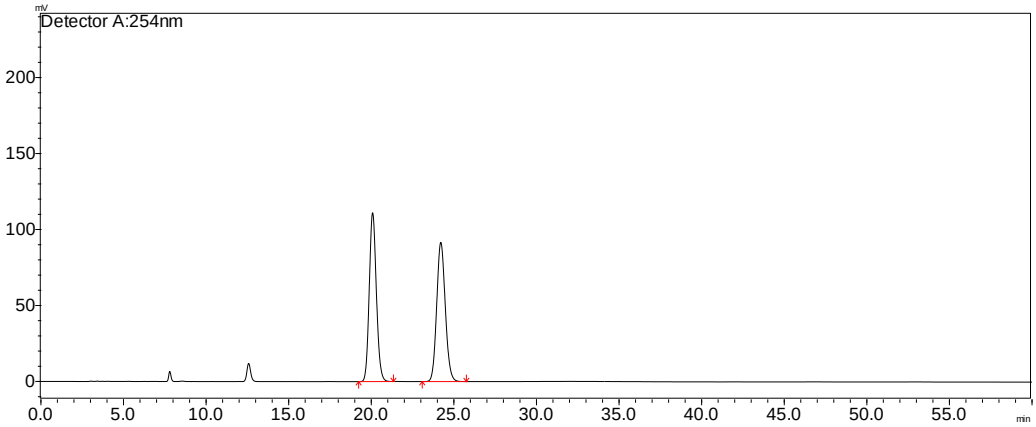
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.373	454283	5898	50.158	52.266
2	46.472	451420	5386	49.842	47.734
Total		905703	11284	100.000	100.000



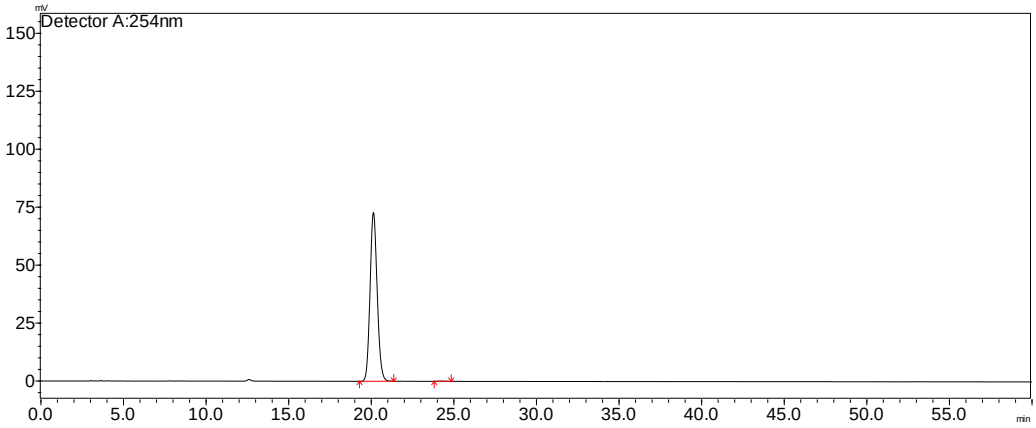
Peak#	Ret. Time	Area	Height	Area %	Height %
1	42.403	695	19	0.194	0.452
2	46.263	358445	4283	99.806	99.548
Total		359140	4303	100.000	100.000



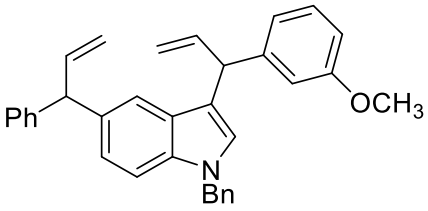
8



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.077	3319199	111144	50.003	54.815
2	24.204	3318863	91619	49.997	45.185
Total		6638063	202763	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.126	2180887	72798	99.834	99.844
2	24.288	3616	114	0.166	0.156
Total		2184504	72912	100.000	100.000



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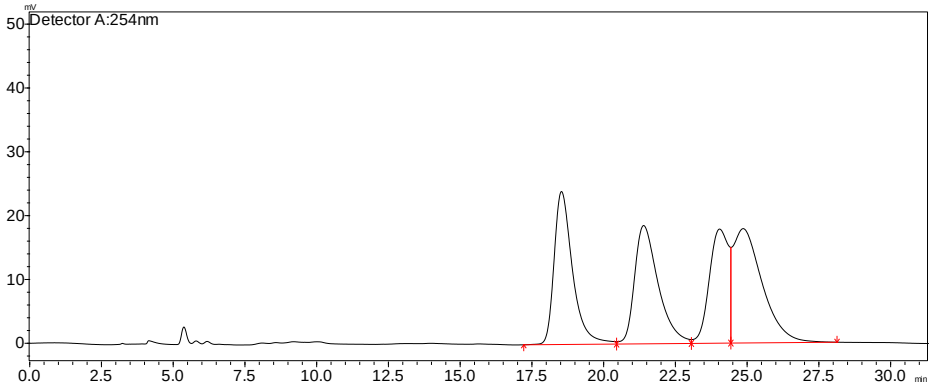
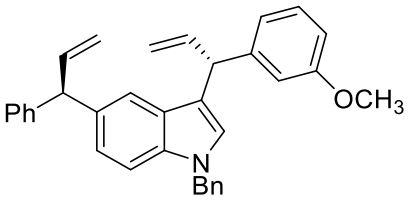
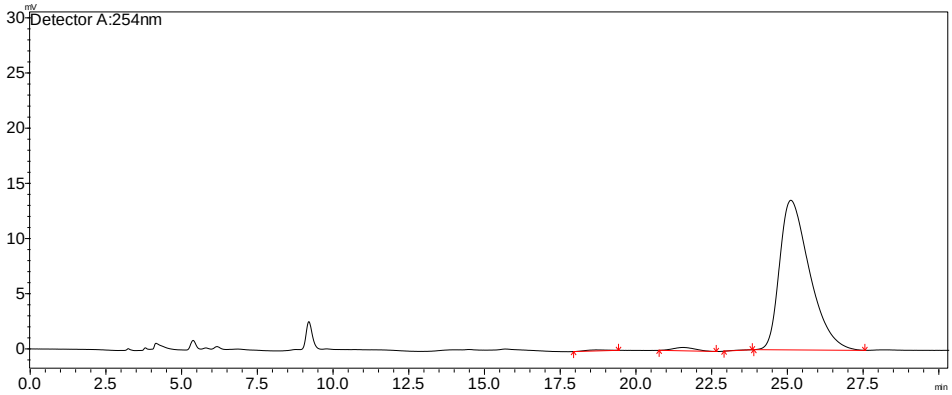


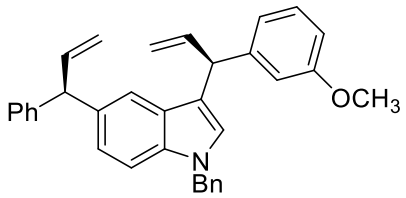
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.526	1076700	23974	25.365	30.611
2	21.388	1066243	18535	25.119	23.667
3	24.035	837772	17885	19.737	22.837
4	24.860	1264047	17923	29.779	22.885
Total		4244762	78317	100.000	100.000



9a



Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.678	4648	98	0.485	0.699
2	21.534	15550	304	1.621	2.181
3	23.827	817	3	0.085	0.019
4	25.108	938224	13556	97.809	97.101
Total		959238	13961	100.000	100.000



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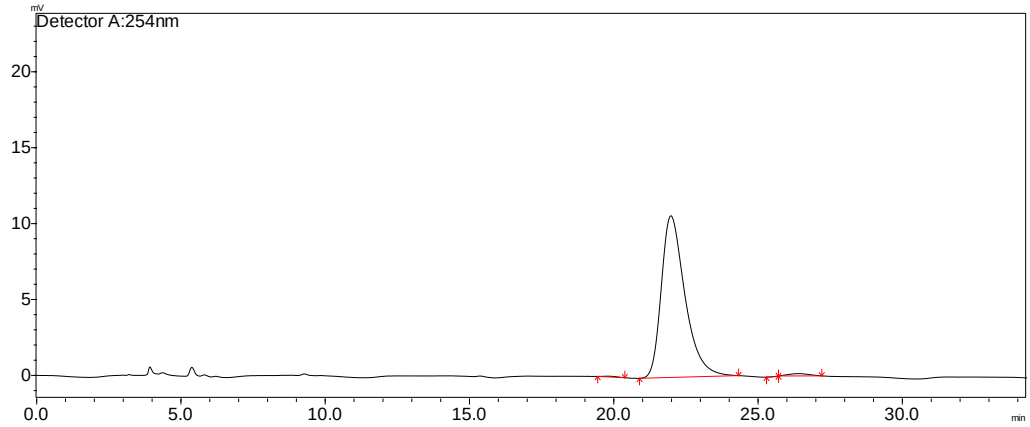
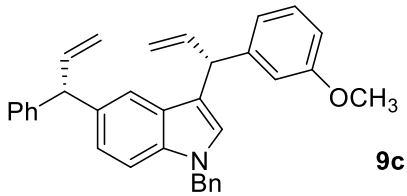


Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.797	1548	48	0.251	0.438
2	21.974	607917	10651	98.460	97.873
3	25.700	350	32	0.057	0.292
4	26.374	7613	152	1.233	1.397
Total		617427	10882	100.000	100.000



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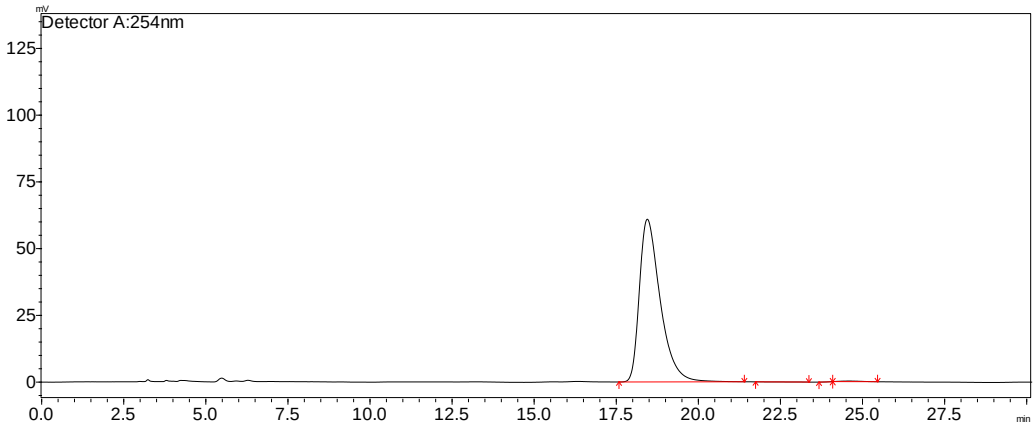
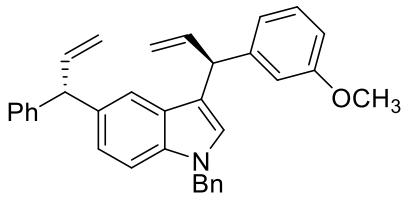


Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.442	2689985	60930	99.591	99.541
2	21.745	685	0	0.025	0.001
3	24.083	498	67	0.018	0.109
4	24.547	9874	214	0.366	0.349
Total		2701042	61210	100.000	100.000



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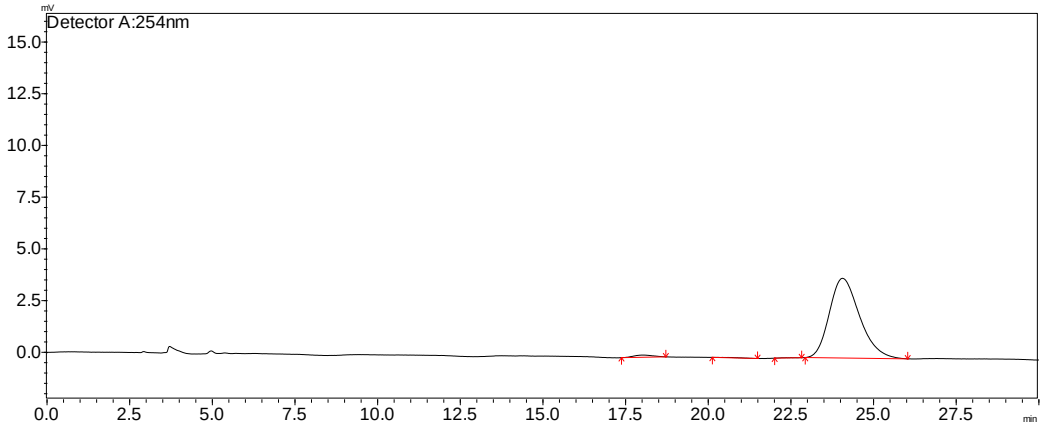
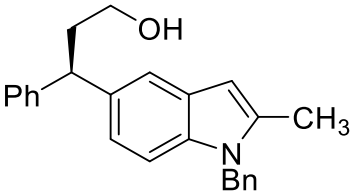
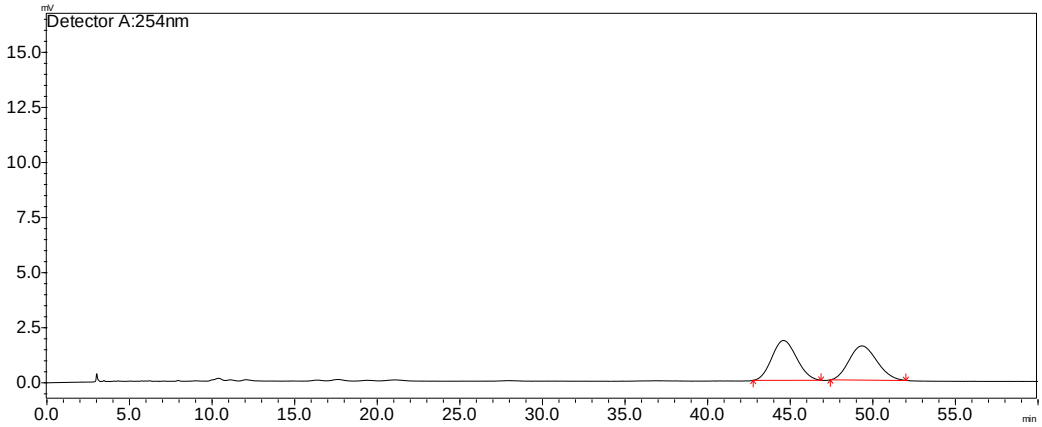


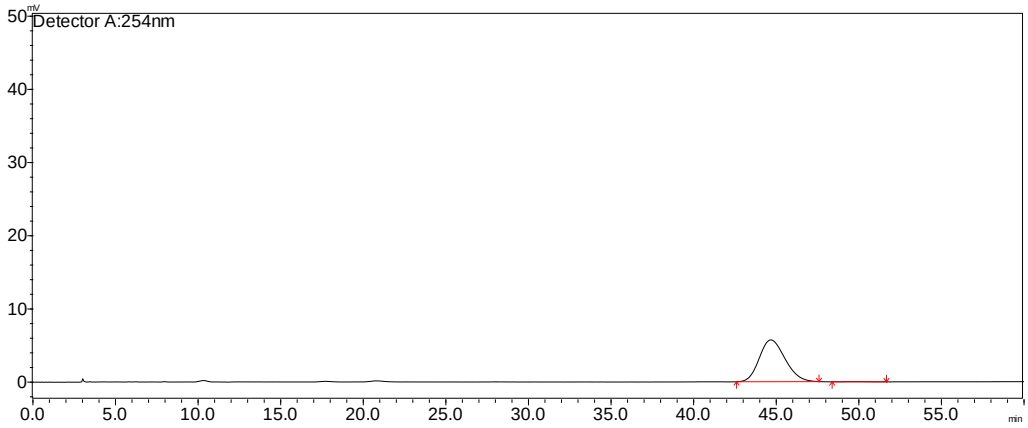
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.011	4335	108	1.728	2.711
2	20.269	610	8	0.243	0.211
3	22.497	197	9	0.079	0.228
4	24.052	245793	3852	97.951	96.849
Total		250936	3978	100.000	100.000



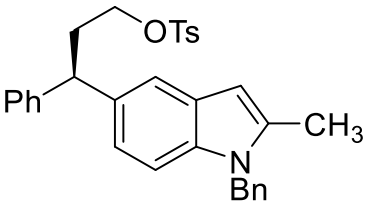
10



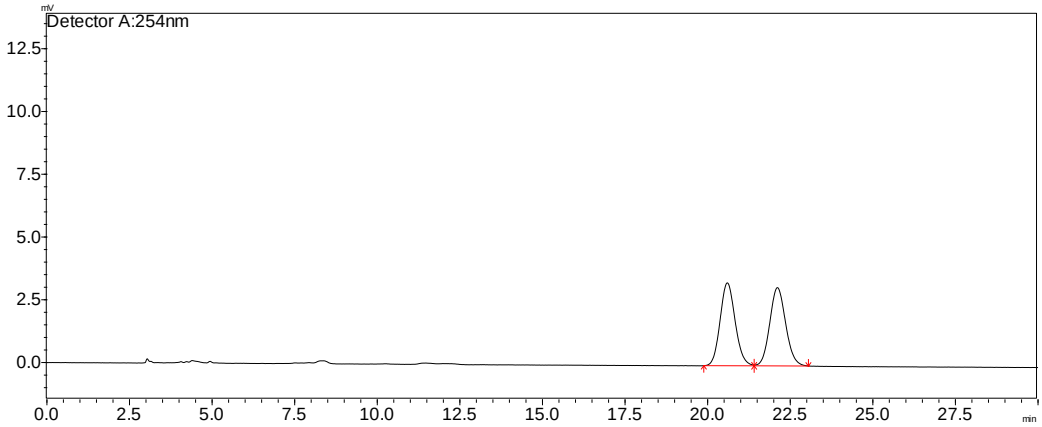
Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.598	189099	1808	50.852	53.829
2	49.321	182760	1551	49.148	46.171
Total		371858	3360	100.000	100.000



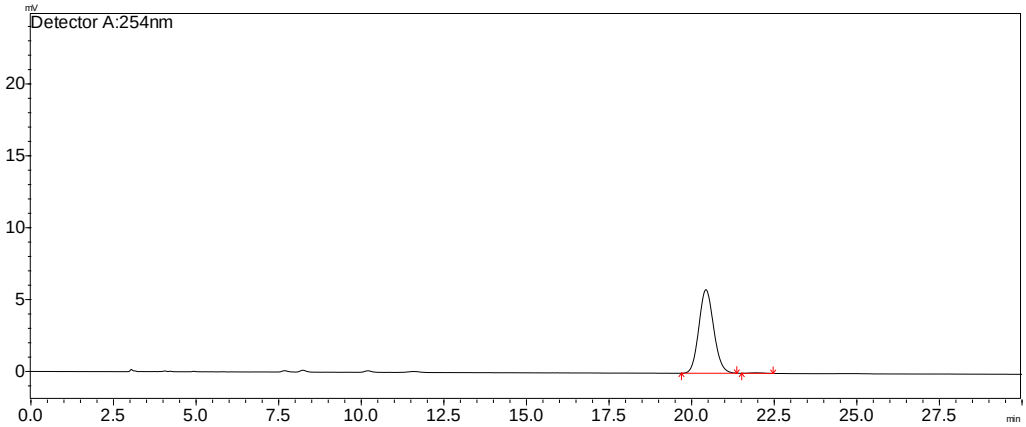
Peak#	Ret. Time	Area	Height	Area %	Height %
1	44.676	620290	5713	99.658	99.562
2	49.711	2127	25	0.342	0.438
Total		622417	5738	100.000	100.000



11



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.592	104672	3301	50.020	51.421
2	22.108	104589	3119	49.980	48.579
Total		209261	6420	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.428	182110	5813	99.434	99.371
2	21.972	1037	37	0.566	0.629
Total		183147	5850	100.000	100.000