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Supporting Information for

Highly enantioselective Pd-catalyzed indole allylic alkylation using binaphthyl-based phosphoramidite-thioether ligands

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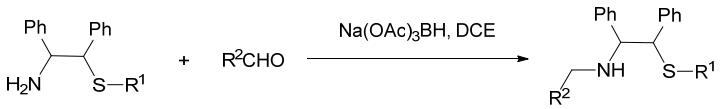
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 or 600 MHz spectrophotometers. Chemical shifts were reported on the delta (δ) scale in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass spectra were measured on a MS spectrometer (EI). The high resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer by ESI. Enantiomeric ratios were determined by chiral HPLC with chiral columns (chiralpak AS-H column, chiralpak AD-H column, chiralcel OJ-H column, chiralpak IC-H column or chiralcel OD-H column) with hexane and *i*-PrOH as solvents. Optical rotations were measured with a polarimeter.

2. Preparation and Spectral Data of Ligands

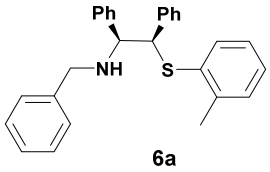
2.1 General procedure for the preparation secondary amine



Aminosulfide (2.0 mmol) and aldyhyde (2.0 mmol) were dissolved in DCE (10 mL) in a flask. Then, $NaB(OAc)_3H$ (1.4 eq, 2.8 mmol) was added and stired at room temperature until the aminosulfide was totally consumed. Then was purified by flash column chromatrography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding products.

2.2 Characterization data of secondary amine

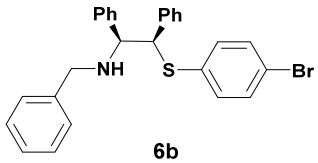
(1S,2R)-N-benzyl-1,2-diphenyl-2-(o-tolylthio)ethan-1-amine (6a)



6a

87% yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 6.74 (m, 19H), 4.25 (d, J = 7.7 Hz, 1H), 4.03 (d, J = 7.7 Hz, 1H), 3.59 (d, J = 13.5 Hz, 1H), 3.34 (d, J = 13.6 Hz, 1H), 2.16 (s, 3H), 1.95 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.5, 139.9, 139.8, 139.1, 132.9, 129.8, 128.6, 128.2, 128.0, 127.9, 127.8, 127.4, 127.2, 126.9, 126.6, 125.8, 65.4, 60.2, 51.2, 20.6.

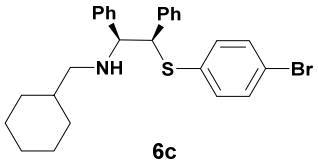
(1S,2R)-N-benzyl-2-((4-bromophenyl)thio)-1,2-diphenylethan-1-amine (6b)



6b

67% yield; white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.08 (m, 15H), 7.08 – 7.01 (m, 2H), 6.91 – 6.83 (m, 2H), 4.31 (d, *J* = 7.7 Hz, 1H), 4.01 (d, *J* = 7.7 Hz, 1H), 3.61 (d, *J* = 13.6 Hz, 1H), 3.34 (d, *J* = 13.6 Hz, 1H), 1.92 (s, 1H). 13C NMR (100 MHz, cdcl3) δ 140.0, 139.6, 138.5, 133.9, 133.5, 131.3, 128.6, 128.2, 128.1, 128.0, 128.0, 127.8, 127.6, 127.4, 126.7, 120.9, 77.3, 77.0, 76.6, 65.5, 60.9, 51.0.

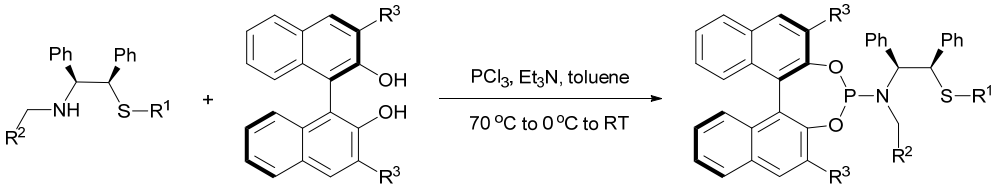
(1S,2R)-2-((4-bromophenyl)thio)-N-(cyclohexylmethyl)-1,2-diphenylethan-1-amine (6c)



6c

90% yield; white solid **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.14 (m, 12H), 6.95 – 6.89 (m, 2H), 4.31 (d, *J* = 7.5 Hz, 1H), 3.97 (d, *J* = 7.5 Hz, 1H), 2.12 (d, *J* = 6.7 Hz, 2H), 1.69 – 1.52 (m, 5H), 1.45 (d, *J* = 12.9 Hz, 1H), 1.36-1.25 (m, 1H), 1.20-0.95 (m, 3H), 0.85 – 0.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.9, 134.3, 133.4, 132.6, 131.5, 128.7, 128.2, 128.2, 127.9, 127.5, 120.8, 67.1, 60.8, 54.2, 37.6, 31.2, 31.1, 26.6, 25.9, 25.9.

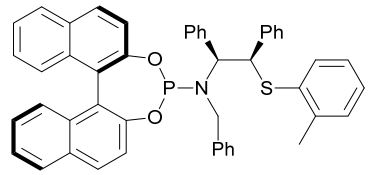
2.3 General procedure for the preparation of ligands



PCl_3 (1.0 eq, 1.0 mmol) and Et_3N (1.1 eq, 1.1 mmol) were mixed in toluene (5 mL). Then, aminosulfide (1.0 mmol) was added in toluene (1 mL) and stirred for 7 h at 70 °C. Then, the mixture was cooled to 0 °C, Et_3N (3.3 eq, 3.3 mmol)and *R*-BINOL (1.0 mmol) in toluene (1 mL) were added and stired at room temperature until the aminosulfide was totally consumed. Then, the mixture was purified by flash column chromatrography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding ligand.

2.4 Characterization data of ligands

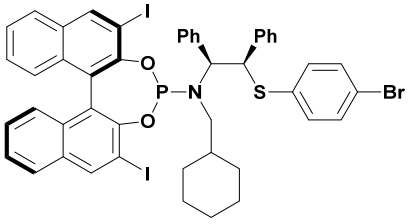
N-benzyl-N-((1S,2R)-2-(naphthalen-2-ylthio)-1,2-diphenylethyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine(L4)



L4

75% yield; white solid; melting point 142 °C **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (t, *J* = 9.2 Hz, 2H), 7.71 (d, *J* = 6.7 Hz, 3H), 7.64 (d, *J* = 8.9 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.48 (d, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.35-7.09 (m, 13H), 7.05-6.90 (m, 2H), 6.90-6.75(m, 6H), 6.68 (d, *J* = 8.8 Hz, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 4.29 (dd, *J* = 17.7, 12.2 Hz, 1H), 3.81 (d, *J* = 14.4 Hz, 1H), 2.88 (d, *J* = 14.4 Hz, 1H), 1.98 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.3, 149.2, 141.3, 140.1, 139.5, 136.8, 135.1, 133.3, 132.7, 132.4, 131.4, 130.5, 130.1, 129.9, 129.8, 129.3, 129.3, 128.9, 128.3, 128.0, 127.8, 127.6, 127.2, 127.0, 126.8, 126.0, 125.8, 124.8, 124.4, 124.1, 122.1, 121.6, 65.4(d, *J* = 65.5 Hz), 57.2(d, *J* = 57.2 Hz), 48.6, 20.5(d, *J* = 20.5Hz). **^{31}P NMR** (160 MHz $CDCl_3$) δ 137.9. HRMS m/z: anal. calcd for C48H37NO2PS $[M-H]^+$: 722.2277, found: 722.2269.

N-((1S,2R)-2-((4-bromophenyl)thio)-1,2-diphenylethyl)-N-(cyclohexylmethyl)-2,6-diiododinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L5)

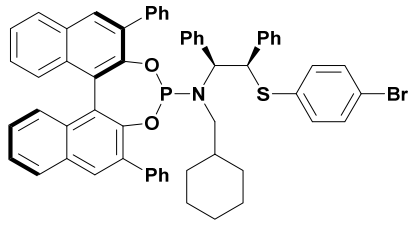


L5

60% yield; whitle solid; melting point 136 °C **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.28 (s, 1H), 7.76 (d, J = 8.3 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.50 – 7.29 (m, 6H), 7.26 (s, 1H), 7.21 (t, J = 7.6 Hz, 2H), 7.18 – 7.11 (m, 4H), 7.02 (dd, J = 14.8, 8.7 Hz, 2H), 6.88 – 6.76 (m, 2H), 5.29 (d , J = 6 Hz 1H), 4.61 (dd, J = 20.0, 11.0 Hz, 1H), 2.55 (s, 1H), 2.30 (s, 1H), 1.24 (dd, J = 75.8, 31.9 Hz, 6H), 1.02 (d, J = 11.2 Hz, 1H), 0.70 (d, J = 10.2 Hz, 2H), 0.24 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7, 147.8, 140.0, 139.6, 139.4, 139.2, 135.5, 134.9, 133.1, 132.4, 132.4, 132.3, 132.2, 131.4, 131.3, 131.1, 130.0, 130.0, 129.6, 128.9, 128.3, 128.3, 127.3, 127.0, 126.9, 126.8, 126.7, 126.5, 126.3, 125.6, 125.1, 124.4, 121.8, 121.1, 91.5, 91.5, 90.0, δ 58.50 (d, *J* = 22.6 Hz), 51.9, 34.2, 30.9,

30.3, 26.0, 25.8, 25.3. **^{31}P NMR** (160 MHz $CDCl_3$) δ 143.56. HRMS m/z: anal. calcd for $C_{48}H_{37}NO_2PS$ $[M+K]^+$: 1083.9343, found:1083.9342.

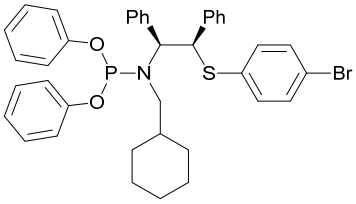
N-((1S,2R)-2-((4-bromophenyl)thio)-1,2-diphenylethyl)-N-(cyclohexylmethyl)-2,6-diphenyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L6)



L6

63% yield; whitle solid; melting point 151 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.81-7.65 (m, 4H), 7.56-7.35 (m, 10H), 7.32-7.25 (m, 2H), 7.19-7.01 (m, 6H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.78-6.59 (m, 4H), 6.25-6.13 (m, 2H), 4.40 (dd, *J* = 9.1, 3.4 Hz, 1H), 4.16 (dd, *J* = 7.1, 3.4 Hz, 1H), 2.55-2.41 (m, 1H), 1.84 (dt, *J* = 13.7, 3.9 Hz, 1H), 1.54 (d, *J* = 4.0 Hz, 1H), 1.46 (s, 1H), 1.43 – 1.36 (m, 2H), 1.28 (d, *J* = 14.8 Hz, 1H), 0.97 – 0.79 (m, 6H), 0.67 (t, *J* = 11.4 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 148.0, 146.9, 139.8, 138.2, 138.1, 135.1, 134.8, 134.4, 133.9, 132.5, 132.2, 131.4, 131.4, 131.1, 131.0, 130.5, 130.1, 130.0, 129.9, 129.1, 128.6, 128.3, 128.1, 128.0, 127.7, 127.6, 127.3, 127.2, 127.1, 126.9, 126.9, 126.8, 125.9, 125.6, 125.5, 124.9, 124.5, 122.7, 119.8, δ 67.59 (d, *J* = 18.8 Hz), 57.40 (d, *J* = 41.4 Hz), 49.2, 34.0, 31.0, 30.2, 26.3, 25.7, 25.6. **^{31}P NMR** (160 MHz $CDCl_3$) δ 136.90. HRMS m/z: anal. calcd for $C_{59}H_{49}BrNO_2PS$ $[M]^+$: 945.2399, found: 945.2327.

Diphenyl ((1S,2R)-2-((4-bromophenyl)thio)-1,2-diphenylethyl)(cyclohexylmethyl)phosphoramidite (L8)

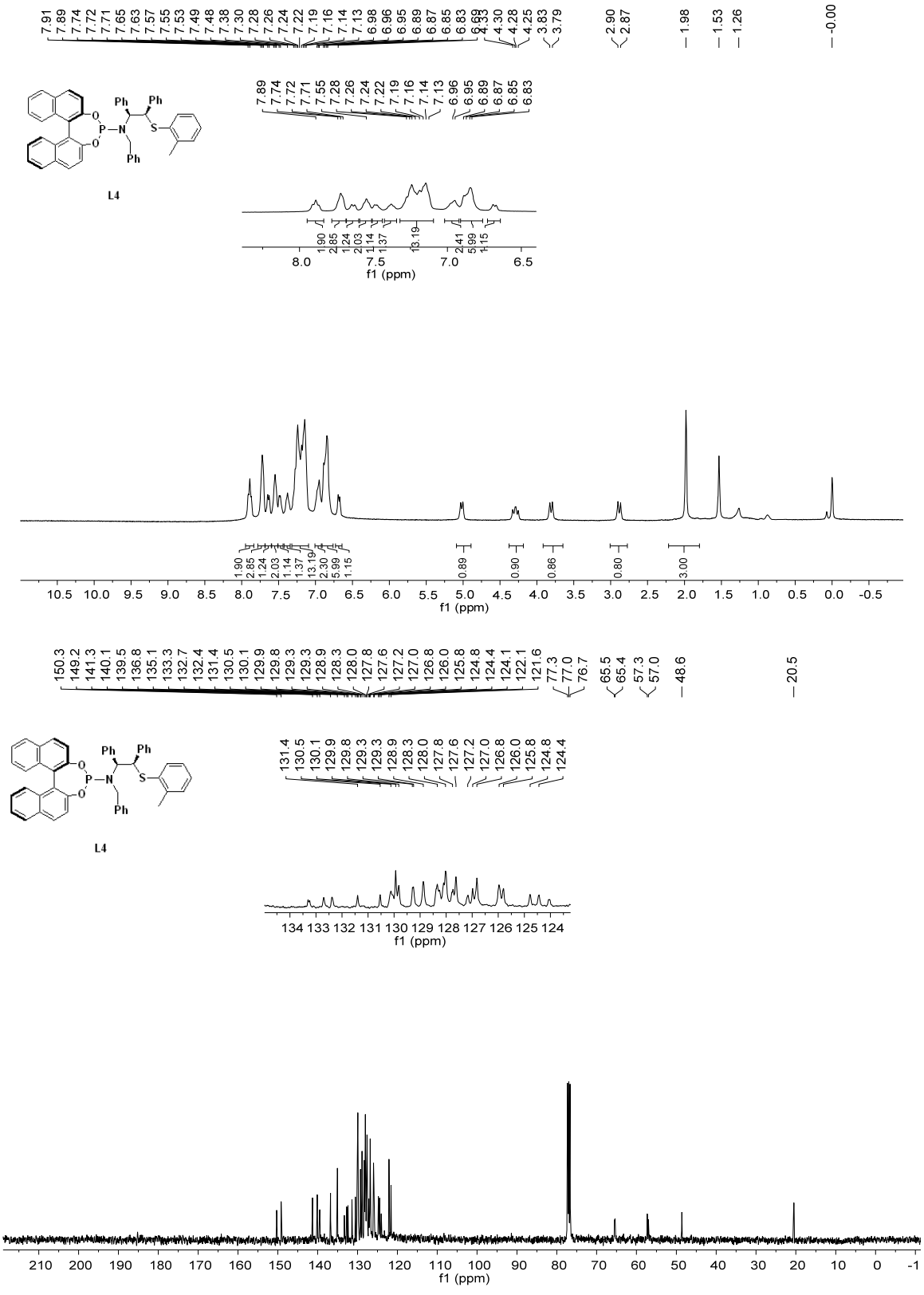


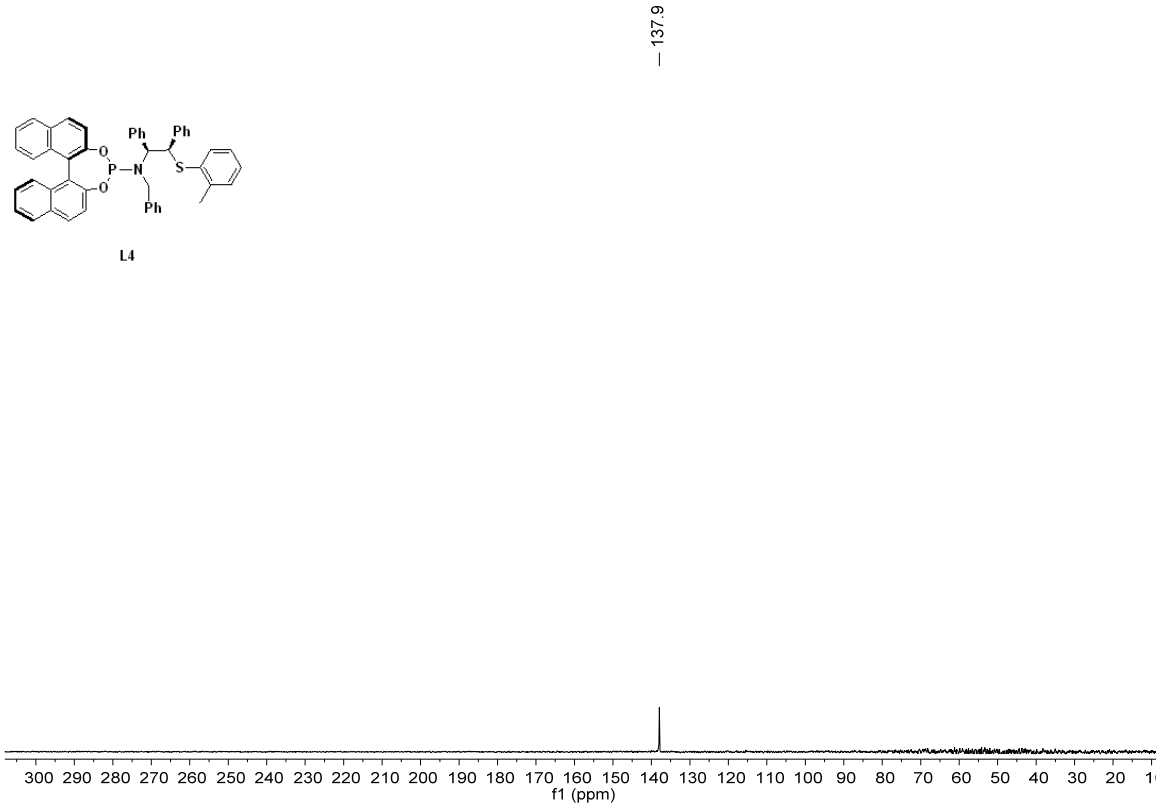
L8

68% yield; whitle solid; melting point 101 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.4 Hz, 2H), 7.34 – 7.20 (m, 5H), 7.20 – 7.06 (m, 8H), 7.00 (d, *J* = 7.4 Hz, 2H), 6.78 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 7.9 Hz, 2H), 6.62 (d, *J* = 7.9 Hz, 2H), 5.03 (d, *J* = 11.7 Hz, 1H), 4.68 (dd, *J* = 19.7, 11.7 Hz, 1H), 3.08 – 2.97 (m, 1H), 2.54 (d, *J* = 14.3 Hz, 1H), 1.72-1.60 (m, 1H), 1.52-1.42 (m, 1H), 1.25-1.21 (m, 4H), 1.09-1.01 (m, 2H), 0.95 – 0.71 (m, 2H), 0.69-0.52 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.5, 139.1, 135.0, 131.2, 129.1, 129.1, 128.8, 128.8, 128.6, 128.6, 128.0, 127.9, 127.7, 127.1, 122.7, 122.5, 120.2, 120.1, 119.8, 119.7, 66.5 (d, *J* = 23.4 Hz), 57.9 (d, *J* = 21.3 Hz), 49.9, 35.2, 31.5, 29.8, 26.7, 26.5, 26.2. **^{31}P NMR** (160 MHz $CDCl_3$) δ 137.25. HRMS m/z: anal. calcd for $C_{39}H_{39}BrNO_2PS$ $[M+H]^+$: 696.1701, found: 696.1683.

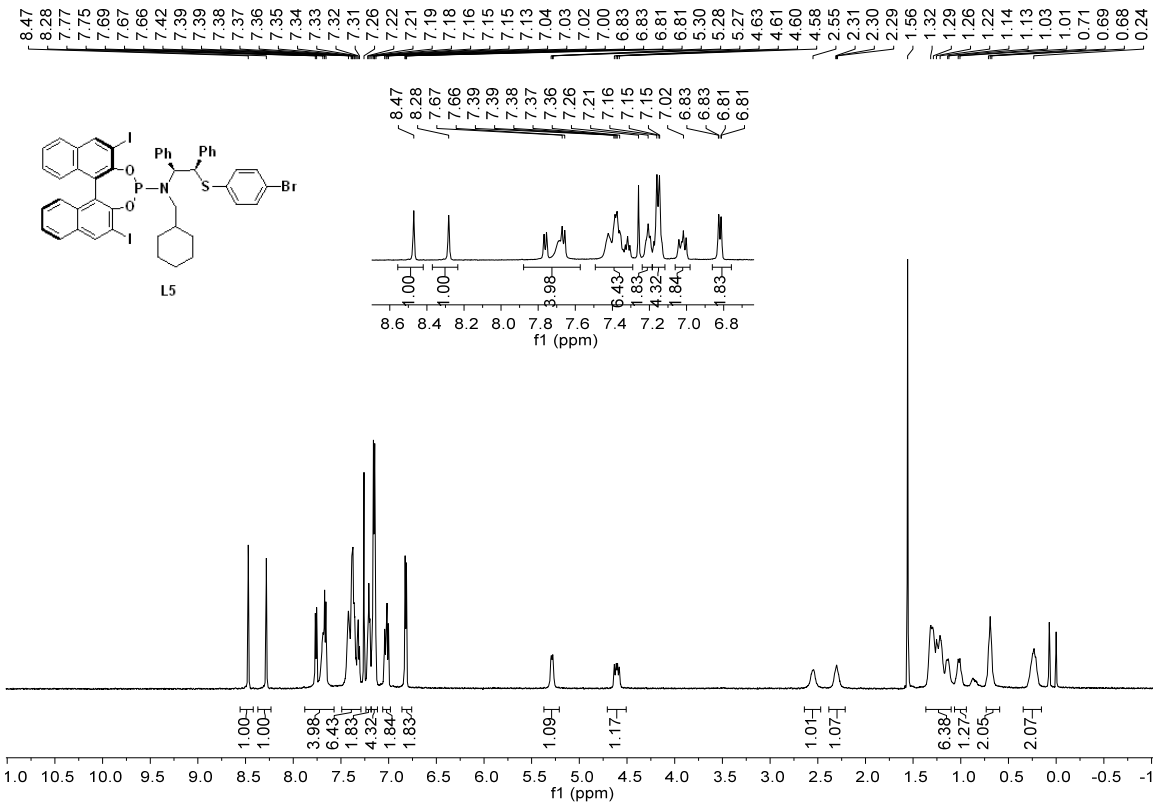
2.5 Copies of ^{1}H NMR, ^{13}C NMR and ^{31}P NMR Spectra of ligands

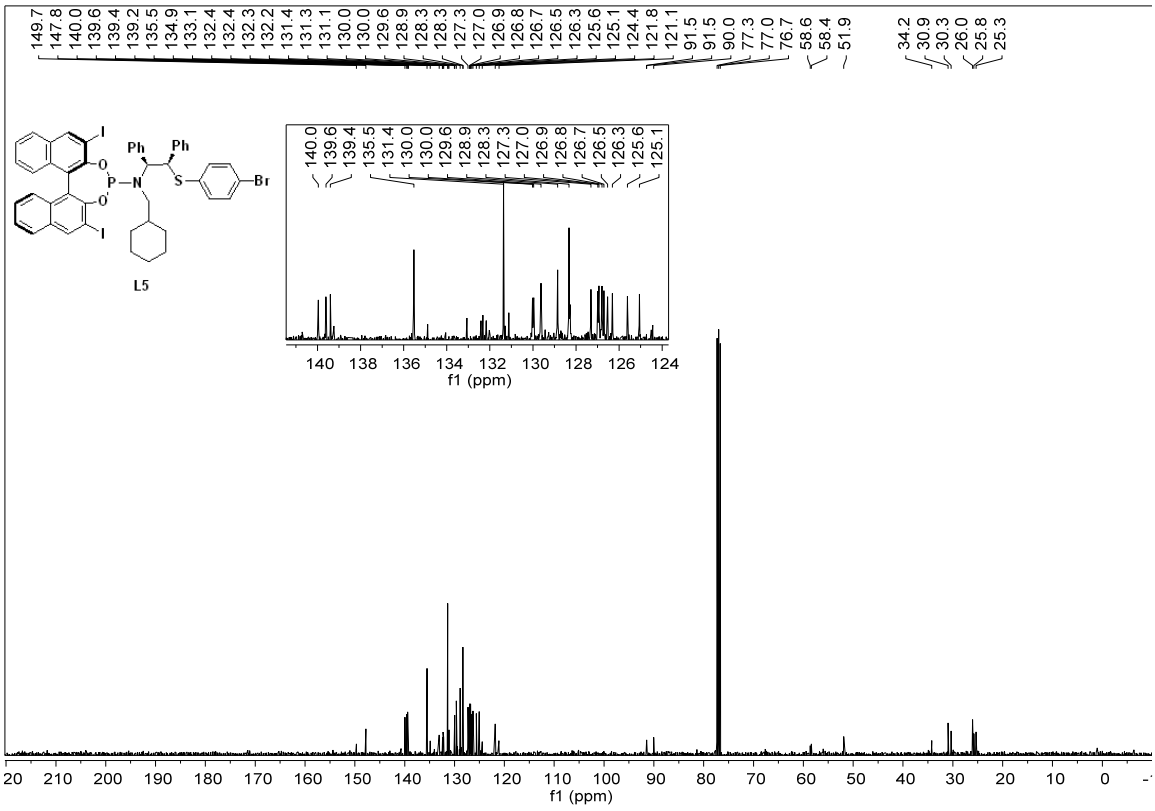
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (160 MHz, $CDCl_3$) spectra of product L4





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (160 MHz, $CDCl_3$) spectra of product L5

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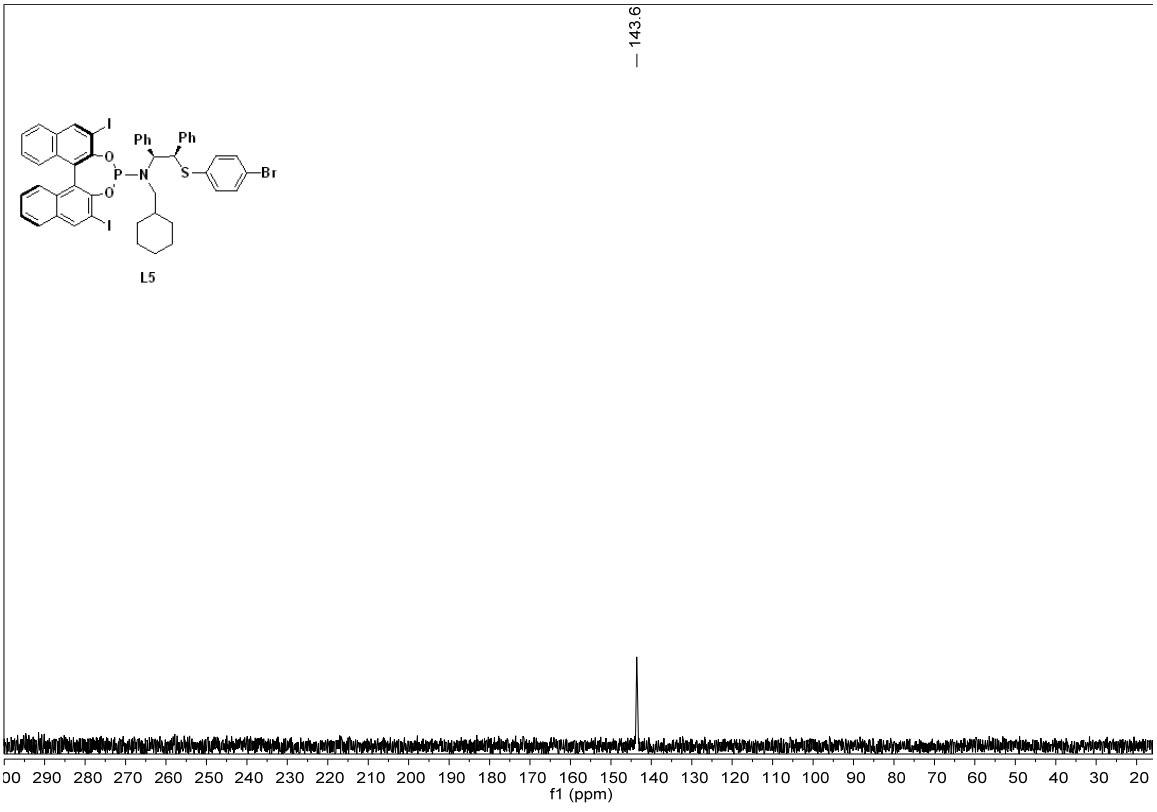
f1 (ppm)


143.6
L5
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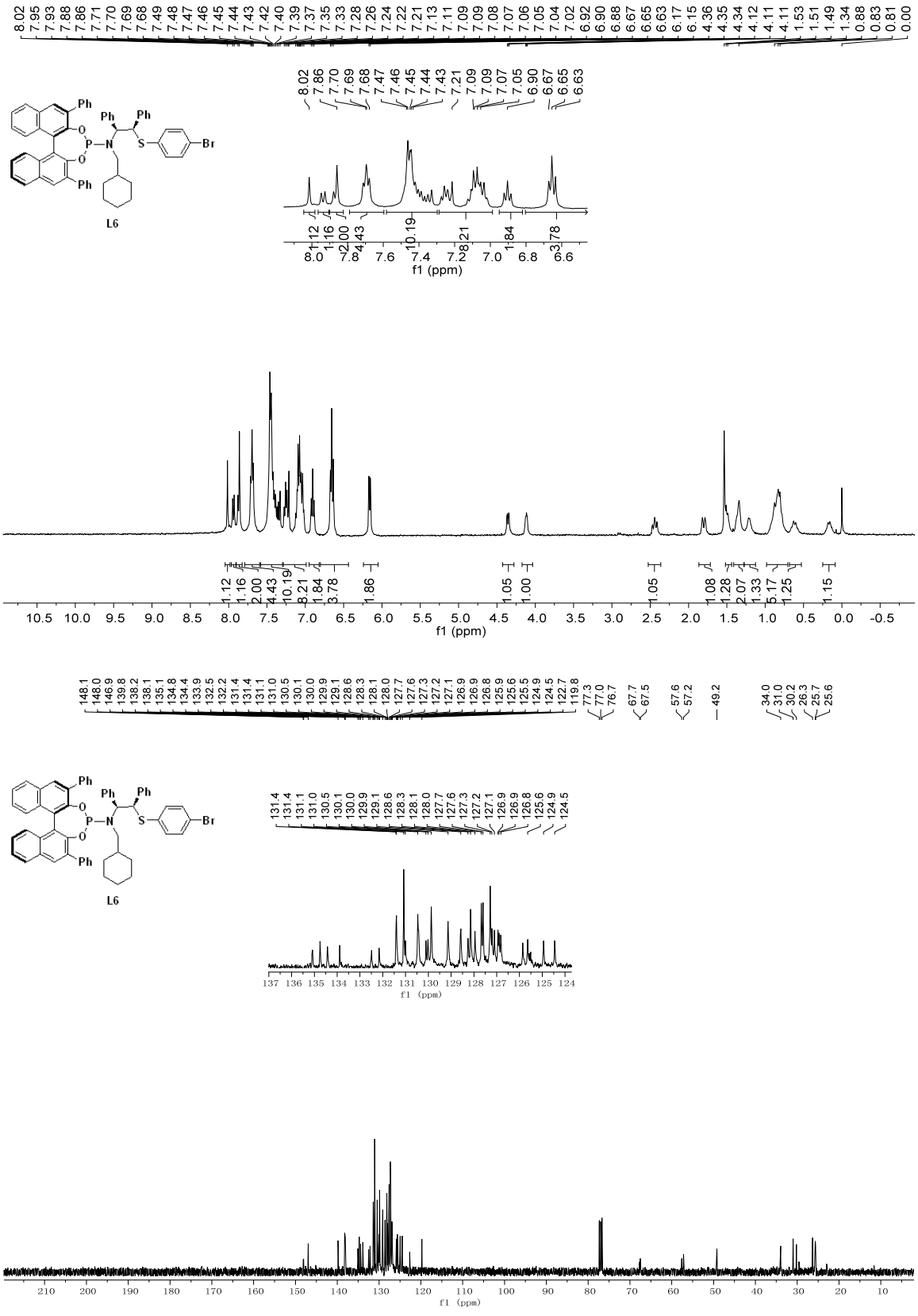
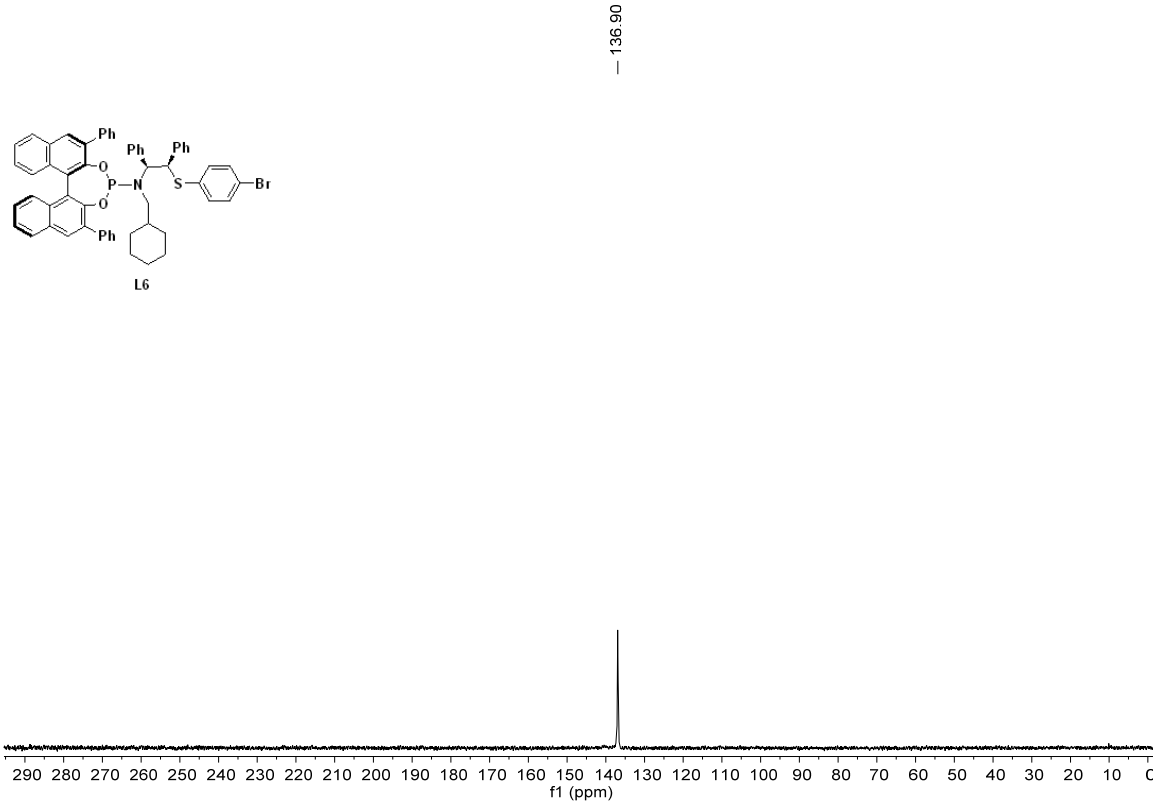
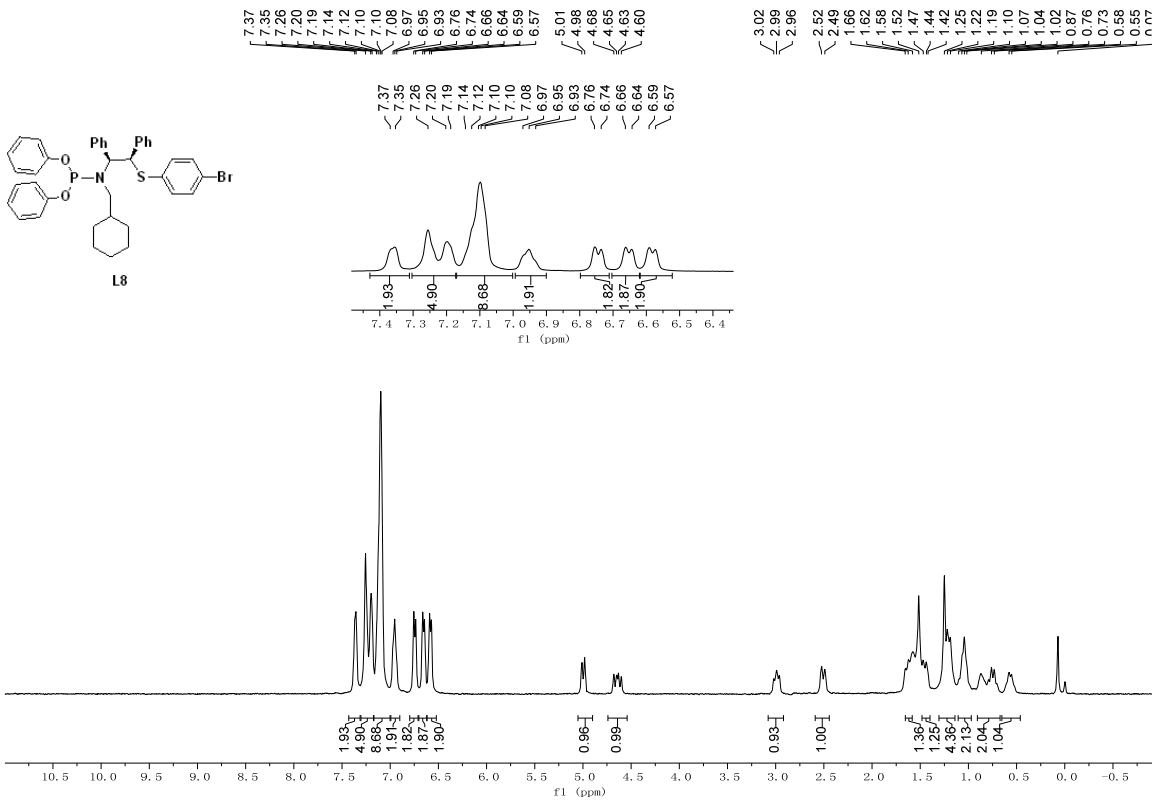
f1 (ppm)

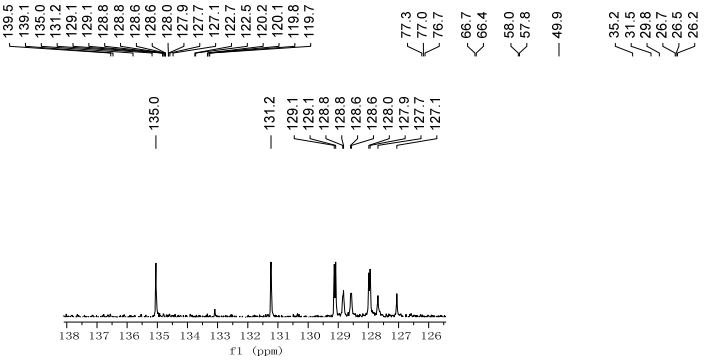
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (160 MHz, $CDCl_3$) spectra of product L6





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{31}P NMR (160 MHz, $CDCl_3$) spectra of product L8

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35.2
31.5
29.8
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26.2
135.0
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129.1
128.8
128.8
128.6
128.6
128.0
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Ph
Ph
O
P
N
S
Br
O
L8
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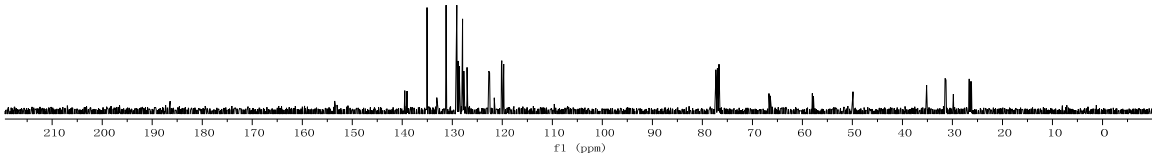
f1 (ppm)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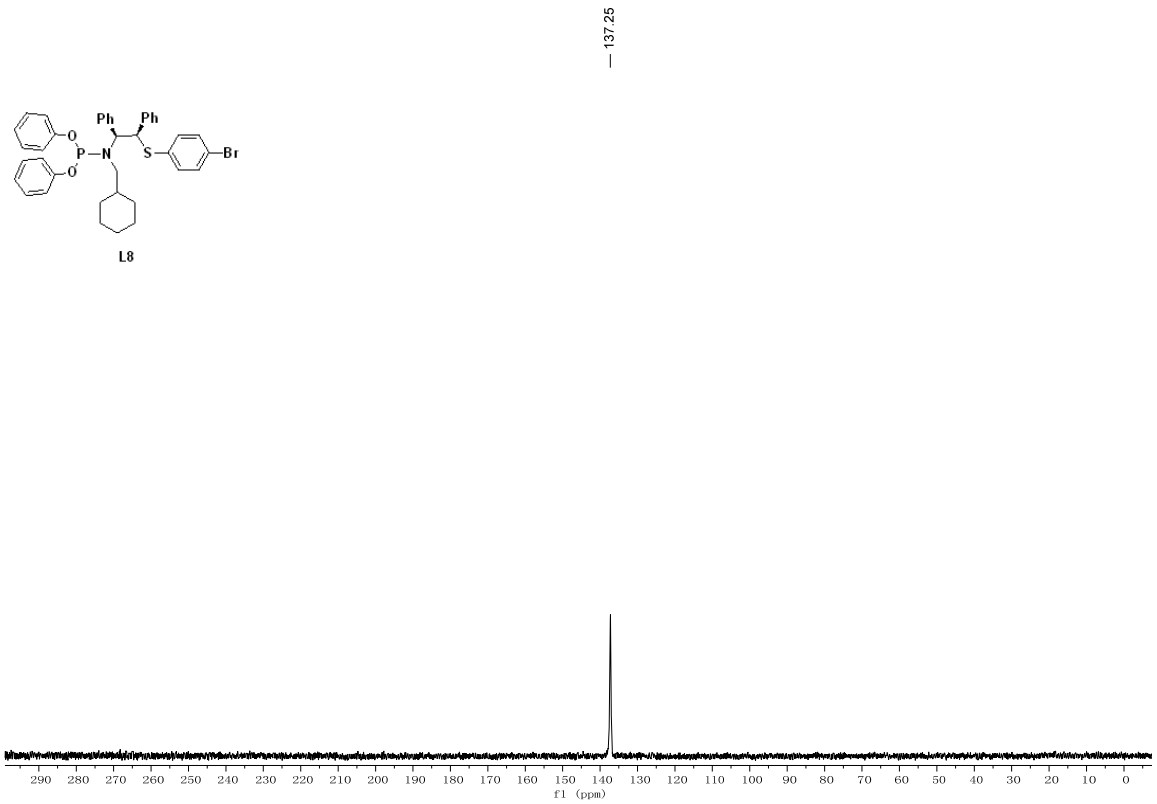
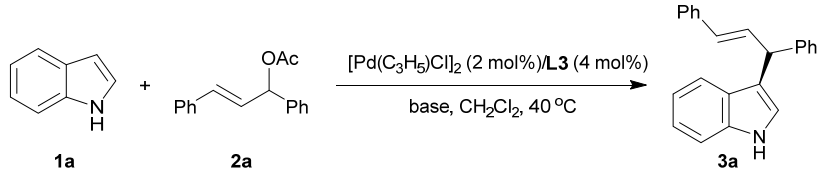
f1 (ppm)


137.25
Ph
Ph
O
P
N
S
Br
O
L8
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3. Detailed Optimization of Reaction Conditions

Table S1. Screen of the bases for the enantioselective allylic reaction[a]



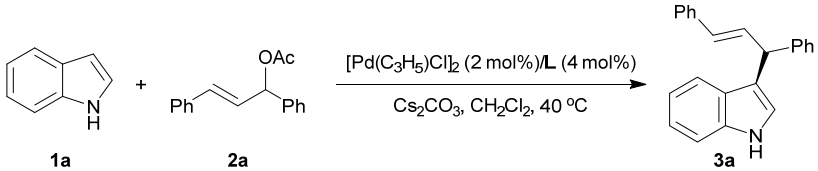
1a 2a 3a

Entry	Base	t (h)	Yield [b] (%)	ee [c] (%)
1	K_2CO_3 (2.0 eq.)	18	82	71
2	*Cs_2CO_3 (2.0 eq.)*	*10*	*87*	*71*
3[d]	Cs_2CO_3 (2.0 eq.)	48	85	50
4	BSA (2.0 eq.)+LiOAc (0.1 eq.)	24	85	71
5	BSA (2.0 eq.)+KOAc (0.1 eq.)	24	88	71

[a] Unless otherwise noted, reactions were carried out with **1a** (0.90 mmol), **2a** (0.30 mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **L3** (0.012 mmol) in CH_2Cl_2 (2.0 mL). [b] Isolated yield. [c] Determined by chiral HPLC. [d] React at room temperature.

As shown in Table S1, among all the bases, the Cs_2CO_3 (2 eq.) in CH_2Cl_2 at 40 °C gave the best result in terms of reaction efficiency, and was thus selected for further optimization studies.

Table S2. Screen of ligands for the the enantioselective allylic reaction[a]



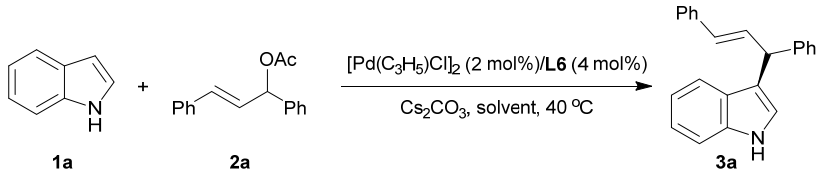
1a 2a 3a

Entry	Ligand	Time (h)	Yield[b] (%)	ee[c] (%)
1	**L3**	24	87	71
2	**L4**	24	97	89
4	**L5**	24	84	83
5	***L6***	***24***	***90***	***94***
6	**L7**	24	60	30
7	**L8**	10	85	35

[a] Unless otherwise noted, reactions were carried out with **1a** (0.90 mmol), **2a** (0.30 mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **ligand** (0.012 mmol), Cs_2CO_3 (0.60 mmol) in CH_2Cl_2 (2.0 mL) at 40 °C. [b] Isolated yield. [c] Determined by chiral HPLC.

As shown in Table S2, among the ligands tested, ligand **L6** gave the best results (entry 5), and was thus selected for further studies.

Table S3. Screen the solvents for the enantioselective allylic reaction[a]



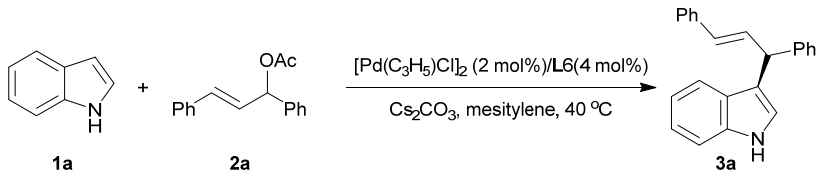
1a 2a 3a

Entry	Solvent	t (h)	Yield[b] (%)	ee[c] (%)
1	CH_2Cl_2	10	90	94
2	$CHCl_3$	10	80	94
3	Toluene	5	88	96
4	xylenes	5	89	97
5	*mesitylene*	*5*	*90*	*97*

[a] Unless otherwise noted, reactions were carried out with 1**a** (0.90 mmol), **2a** (0.30 mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **L6** (0.012 mmol), Cs_2CO_3 (0.60 mmol) in solvent (2.0 mL) at 40 °C. [b] Isolated yield. [c] Determined by chiral HPLC.

As shown in Table S3, among the solvents tested, mesitylene gave the best result in terms of yield and enantioselectivity (entry 5), and was thus selected for further studies.

Table S4. Screen the ratio of indole to allylic acetate [a]



1a 2a 3a

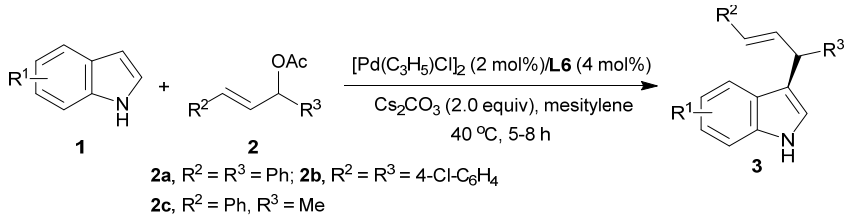
Entry	Ratio (x:y)	t (h)	Yield[b] (%)	ee[c] (%)
1	3:1	5	90	97
2	1.5:1	5	89	96
3	*1:1.5*	*5*	*92*	*97*
4	1:2	5	90	86

[a] Unless otherwise noted, reactions were carried out with **1a** (0.3x mmol), **2a** (0.3y mmol), $[Pd(C_3H_5)Cl]_2$ (0.006 mmol), **L6** (0.012 mmol), Cs_2CO_3 (0.60 mmol) in mesitylene (2.0 mL) at 40 °C. [b] Isolated yield. [c] Determined by chiral HPLC.

As shown in Table S4, among the ratio tested, the ratio of 1:1.5 of **1a** to **2a** gave the best result in terms of yield and enantioselectivity (entry 3), and thus the optimized reaction condition was confirmed: **1** (0.3 mmol), **2** (0.45 mmol), 2 mol% of $[Pd(C_3H_5Cl)]_2$, 4 mol% of ligand **L6**, and 2.0 equivalents of Cs_2CO_3 in mesitylene at 40 °C.

4. General Procedure for Pd-Catalyzed Enantioselective Allylic Substitution Reactions and Spectral Data

4.1 General procedure for Pd-catalyzed enantioselective allylic substitution reactions



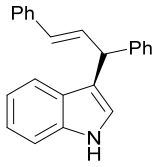
2a, $R^2 = R^3$ = Ph; **2b**, $R^2 = R^3$ = 4-Cl-C_6H_4

2c, R^2 = Ph, R^3 = Me

Ligand **L6** (11.3 mg, 0.012 mmol, 4 mol%) and $[Pd(C_3H_5)Cl]_2$ (2.2 mg, 0.006 mmol, 2 mol%) were dissolved in mesitylene (1.0 mL) in a Schlenk tube under Ar. After stirring at room temperature for 1 h, allylic acetate **2** (0.45 mmol) in mesitylene (1.0 mL) was added, followed by indoles **1** (0.3 mmol), Cs_2CO_3 (197 mg, 0.6 mmol). The mixture was stirred at 40 °C until indoles was totally consumed, and then was purified by flash column chromatrography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding product **3**.

4.2 Spectral data of allylic reaction products

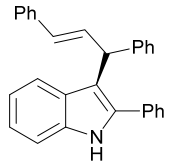
(*S*, E)-3-(1,3-diphenylallyl)-1H-indole (3a) [1]



3a

Yield: 90%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90：10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 20.995 min (minor) for (*R*)-isomer, t_R = 23.581 min (major) for (*S*)-isomer. ee = 97%. $[\alpha]_D^{21}$ 255.6 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.15 (m, 12 H), 7.03-6.95 (m, 1H), 6.89 (dd, *J* = 2.4, 1.0 Hz, 1H), 6.76 (dd, *J* = 15.7, 7.3 Hz, 1H), 6.47 (d, *J* = 16, 1H), 5.16 (d, *J* = 7.4 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.1, 137.2, 136.4, 132.3, 130.3, 128.3, 128.2, 127.0, 126.6, 126.2, 126.1, 122.4, 121.9, 119.7, 119.2, 118.5, 111.0, 46.2. MS m/z: anal. calcd for $C_{23}H_{19}N$ $[M]^+$: 309.15, found: 309.14.

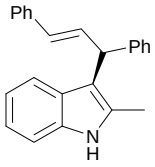
(*S*, E)-3-(1,3-diphenylallyl)-2-phenyl-1H-indole (3b) [1]



3b

Yield: 70%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 85：15 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 6.860 min (major) for (*S*)-isomer, t_R = 7.438 min (minor) for (*R*)-isomer. ee = 82%. $[\alpha]_D^{21}$ 312 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.56 – 7.46 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.29 (m, 5H), 7.26 – 7.20 (m, 4H), 7.19 – 7.03 (m, 4H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.86 (dd, *J* = 15.7, 7.3 Hz, 1H), 6.46 – 6.28 (m, 1H), 5.26 (d, *J* = 7.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 137.3, 136.0, 135.4, 132.8, 132.1, 130.9, 128.6, 128.5, 128.4, 128.3, 128.1, 128.1, 128.0, 127.8, 127.7, 126.9, 126.1, 125.9, 121.9, 121.0, 119.5, 113.7, 110.8, 45.2.MS m/z: anal. calcd for $C_{29}H_{23}N$ $[M]^+$: 385.18, found: 385.51.

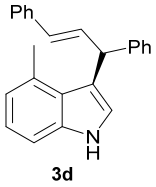
(*S*, E)-3-(1,3-diphenylallyl)-2-methyl-1H-indole (3c) [1]



3c

Yield: 82%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 95:5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 33.353 min (major) for (*S*)-isomer, t_R = 35.932 min (major) for (*R*)-isomer. ee = 95%. $[\alpha]_D^{21}$ 163.9 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.21 – 7.03 (m, 10 H), 6.97 (d, J = 8.3 Hz, 1H), 6.91 (t, J = 7.6 Hz, 1H), 6.73 – 6.52 (m, 3H), 6.09 (d, J = 15.8 Hz, 1H), 5.31 (d, J = 6.5 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2, 137.3, 135.1, 132.0, 131.5, 130.4, 128.3, 128.1, 128.1, 127.8, 126.9, 126.1, 125.9, 120.8, 119.3, 119.1, 112.7, 110.1, 45.1, 12.6. MS m/z: anal. calcd for $C_{24}H_{21}N$ $[M]^+$: 323.17, found: 323.44.

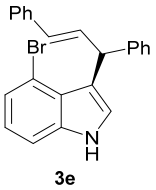
(*S*, E)-(3-((4-methoxybenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (3d) [1]



3d

Yield: 99%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 91:10 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 14.322 min (major) for (*S*)-isomer, t_R = 16.066 min (minor) for (*R*)-isomer. ee = 86%. $[\alpha]_D^{23}$ 185 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl^3$) δ 7.62 (s, 1H), 7.28 – 7.00 (m, 11H), 7.00 – 6.87 (m, 2H), 6.73 – 6.52 (m, 3H), 6.09 (d, J = 15.8 Hz, 1H), 5.31 (d, J = 6.5 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.0, 143.8, 137.2, 136.6, 133.7, 130.8, 130.4, 128.6, 128.3, 128.2, 128.1, 126.9, 126.1, 126.1, 125.3, 123.3, 122.0, 121.0, 118.6, 108.9, 46.5, 20.5. MS m/z: anal. calcd for $C_{24}H_{21}N$ [M]+: 323.17, found: 323.21.

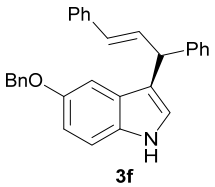
(*S*, E)-4-bromo-3-(1,3-diphenylallyl)-1H-indole (3e) [1]



3e

Yield: 82%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 16.107 min (major) for (*S*)-isomer, t_R = 18.383 min (minor) for (*R*)-isomer. ee = 93%. $[\alpha]_D^{23}$ 220 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.41 – 6.98 (m, 12H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.63 (dd, *J* = 15.7, 7.3 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.01 (d, *J* = 7.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 137.2, 135.2, 132.0, 130.7, 128.5, 128.3, 127.2, 126.5, 126.3, 124.9, 123.8, 122.2, 118.3, 112.7, 112.6, 45.8. MS m/z: anal. calcd for $C_{23}H_{18}BrN$ $[M]^+$: 387.06, found: 387.15.

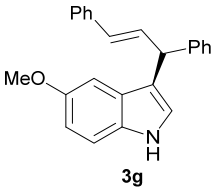
(*S*, E)-(3-((4-chlorobenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (3f) [1]



3f

Yield: 80%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 34.259 min (minor) for (*R*)-isomer, t_R = 39.353 min (major) for (*S*)-isomer. ee = 97%. $[\alpha]_D^{23}$ 203.7 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.38 – 7.10 (m, 16H), 6.94 – 6.82 (m, 2H), 6.78 (d, *J* = 2.4 Hz, 1H), 6.65 (dd, *J* = 15.7, 7.3 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.01 (d, *J* = 7.3 Hz, 1H), 4.91 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 143.0, 137.3, 137.2, 132.2, 131.7, 130.3, 128.3, 128.3, 128.2, 128.2, 127.5, 127.4, 127.0, 126.9, 126.2, 126.1, 123.3, 118.1, 112.7, 111.7, 103.1, 70.7, 46.2. MS m/z: anal. calcd for $C_{30}H_{25}NO$ $[M]^+$: 415.19, found: 415.27.

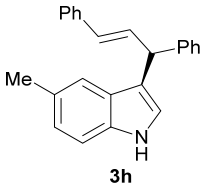
(S, E)-3-(1,3-diphenylallyl)-5-methoxy-1H-indole (3g) [1]



3g

Yield: 82%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 23.104 min (minor) for (*R*)-isomer, t_R = 28.418 min (major) for (*S*)-isomer. ee = 98%. $[\alpha]_D^{23}$ 387.6 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.18 (d, *J* = 7.1 Hz, 4H), 7.14 – 7.08 (m, 3H), 7.08 – 6.98 (m, 3H), 6.97 – 6.93 (m, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 6.66 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.59 (dd, *J* = 2.6, 1.1 Hz, 1H), 6.54 (dd, *J* = 15.7, 7.3 Hz, 1H), 6.28 (d, *J* = 15.8 Hz, 1H), 4.90 (d, *J* = 7.3 Hz, 1H), 3.54 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 143.2, 137.4, 132.4, 131.7, 130.4, 128.4, 128.3, 127.1, 126.3, 126.2, 123.4, 118.0, 111.9, 111.8, 101.7, 55.7, 46.1. MS m/z: anal. calcd for $C_{24}H_{21}NO$ $[M]^+$: 339.16, found: 339.21.

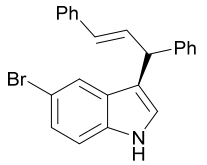
(*S*, E)-3-(1,3-diphenylallyl)-5-methyl-1H-indole (3h) [1]



3h

Yield: 83%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 97:3 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 16.069 min (minor) for (*R*)-isomer, t_R = 17.578 min (major) for (*S*)-isomer. ee = 97%. $[\alpha]_D^{21}$ 278.8 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, CDCl3) δ 7.56 (s, 1H), 7.38 – 7.03 (m, 12H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.76 – 6.59 (m, 2H), 6.35 (d, *J* = 15.7 Hz, 1H), 5.03 (d, *J* = 7.3 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.6, 143.0, 137.3, 137.2, 132.2, 131.7, 130.3, 128.3, 128.3, 128.2, 128.2, 127.5, 127.4, 127.0, 126.9, 126.2, 126.1, 123.3, 118.1, 112.7, 111.7, 103.1, 70.7, 46.2. MS m/z: anal. calcd for $C_{24}H_{21}N$ $[M]^+$: 323.17, found: 323.20.

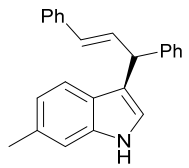
(*S*, E)-5-bromo-3-(1,3-diphenylallyl)-1H-indole (3i) [1]



3i

Yield: 88%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 16.862 min (minor) for (*R*)-isomer, t_R = 19.425 min (major) for (*S*)-isomer. ee = 95%. $[\alpha]_D^{21}$ 278.8 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.34 – 7.08 (m, 12H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.63 (dd, *J* = 15.7, 7.3 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.01 (d, *J* = 7.3 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.6, 137.0, 134.9, 131.8, 130.5, 128.3, 128.3, 128.2, 127.1, 126.4, 126.1, 124.8, 123.7, 122.0, 118.1, 112.5, 45.9. MS m/z: anal. calcd for $C_{23}H_{18}BrN$ $[M]^+$: 387.06, found: 387.17

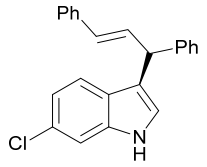
(*S*, E)-3-(1,3-diphenylallyl)-6-methyl-1H-indole (3j) [1]



3j

Yield: 72%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 22.039 min (minor) for (*R*)-isomer, t_R = 26.249 min (major) for (*S*)-isomer. ee = 96%. $[\alpha]_D^{23}$ 429.9 (c = 1.0, $CHCl_3$)**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.35 – 7.10 (m, 11H), 7.03 (s, 1H), 6.83 (d, *J* = 8.1 Hz, 1H), 6.74 – 6.60 (m, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 5.05 (d, *J* = 7.4 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.2, 137.3, 136.9, 132.4, 131.7, 130.2, 128.3, 128.2, 127.0, 126.2, 126.1, 124.5, 121.8, 121.0, 119.4, 118.2, 111.0, 46.3, 21.8. MS m/z: anal. calcd for $C_{24}H_{21}N$ $[M]^+$: 323.17, found: 323.22.

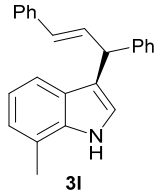
(*S*, E)-6-chloro-3-(1,3-diphenylallyl)-1H-indole (3k) [1]



3k

Yield: 73%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 95:5 v/v, flow rate 1 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 41.833 min (minor) for (*R*)-isomer, t_R = 43.818 min (major) for (*S*)-isomer. ee = 97%. $[\alpha]_D^{23}$ 213.7 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, CDCl3) δ 7.92 (s, 1H), 7.49 (d, J = 1.8 Hz, 1H), 7.41 – 6.98 (m, 12H), 6.81 (d, *J* = 2.5 Hz, 1H), 6.63 (dd, *J* = 15.7, 7.3 Hz, 1H), 6.36 (d, *J* = 15.7 Hz, 1H), 5.01 (d, *J* = 7.3 Hz, 1H). **^{13}C NMR** (100 MHz, CDCl3) ^{13}C NMR (101 MHz, cdcl$_3$) δ 143.0, 137.2, 136.9, 132.1, 130.7, 128.5, 128.5, 128.4, 127.9, 127.2, 126.5, 126.3, 125.3, 123.2, 120.7, 120.1, 118.7, 111.0, 77.3, 77.0, 76.7, 46.0.MS m/z: anal. calcd for $C_{23}H_{18}ClN$ $[M]^+$: 343.11, found: 343.15.

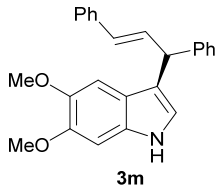
(*S*, E)-3-(1,3-diphenylallyl)-7-methyl-1H-indole (3l) [1]



3l

Yield: 88%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 95:5 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 19.152 min (minor) for (*R*)-isomer, t_R = 21.002 min (major) for (*S*)-isomer. ee = 96%. $[\alpha]_D^{23}$ -202.3 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.39 – 7.07 (m, 16H), 6.92 – 6.82 (m, 2H), 6.78 (d, *J* = 2.4 Hz, 1H), 6.65 (dd, *J* = 15.7, 7.3 Hz, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.01 (d, *J* = 7.3 Hz, 1H), 4.91 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 137.4, 136.1, 132.5, 130.4, 128.4, 128.4, 128.3, 127.1, 126.3, 126.2, 122.5, 122.3, 120.2, 119.5, 118.9, 117.5, 46.2, 16.5. MS m/z: anal. calcd for $C_{24}H_{21}N$ $[M]^+$: 323.17, found: 323.17.

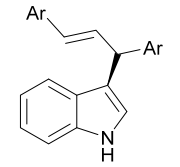
(*S*, E)-3-(1,3-diphenylallyl)-5,6-dimethoxy-1H-indole (3m)[1]



3m

Yield: 99%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 34.794 min (minor) for (*R*)-isomer, t_R = 45.927 min (major) for (*S*)-isomer. ee = 98%. $[\alpha]_D^{23}$ 71.8 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.38 – 7.02 (m, 10H), 6.75 (s, 1H), 6.69 (s, 1H), 6.67 – 6.56 (m, 2H), 6.40 (d, *J* = 15.7 Hz, 1H), 5.00 (d, *J* = 7.3 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 144.4, 143.3, 137.4, 132.5, 130.8, 130.3, 128.4, 128.3, 127.1, 126.3, 126.2, 121.2, 119.5, 118.1, 101.5, 94.4, 56.1, 56.0, 46.3. MS m/z: anal. calcd for $C_{25}H_{23}NO_2$ $[M]^+$: 369.17, found: 369.20.

(*S*,E)-3-(1,3-bis(4-chlorophenyl)allyl)-1H-indole (3n) [1]

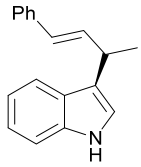


$R^2 = R^3 = 4\text{-Cl-}C_6H_4$

3m

Yield: 82%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 16.589 min (major) for (*S*)-isomer, t_R = 23.700 min (minor) for (*R*)-isomer. ee = 98%. $[\alpha]_D^{23}$ 155.5 (c = 1.0, $CHCl_3$). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.26 (q, *J* = 8.1 Hz, 8H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.65 (dd, *J* = 15.8, 7.2 Hz, 1H), 6.35 (d, *J* = 15.8 Hz, 1H), 5.08 (d, *J* = 7.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 136.4, 135.5, 132.6, 132.4, 131.9, 129.6, 129.5, 128.4, 128.4, 127.3, 126.3, 122.4, 122.1, 119.5, 119.4, 117.7, 111.1, 45.5. MS m/z: anal. calcd for $C_{23}H_{17}Cl_2N$ $[M]^+$: 377.07, found: 377.15.

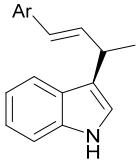
(*R*, E)-3-(4-phenylbut-3-en-2-yl)-1H-indole (3o) [1]



3o

Yield: 89%. The ee was determined by chiral HPLC (Chiralcel OJ-H, hexane/isopropanol 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 32.053 min (minor) for (*R*)-isomer, t_R = 34.850 min (major) for (*S*)-isomer. ee = 53%. $[\alpha]_D^{23}$ 151.6 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.29 (m, 3H), 7.28 – 7.20 (m, 3H), 7.18 – 7.12 (m, 2H), 7.09 – 7.03 (m, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.56 – 6.37 (m, 2H), 3.91 (q, *J* = 6.6 Hz, 1H), 1.57 (d, *J* = 6.9 Hz 5H including H_2O). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.7, 136.5, 135.4, 128.4, 128.1, 126.8, 126.7, 126.1, 121.9, 120.4, 120.3, 119.6, 119.2, 111.1, 34.2, 20.7. MS m/z: anal. calcd for $C_{18}H_{17}N$ $[M]^+$: 247.14, found: 247.14.

(*R*, E)-3-(4-(pyridin-4-yl)but-3-en-2-yl)-1H-indole

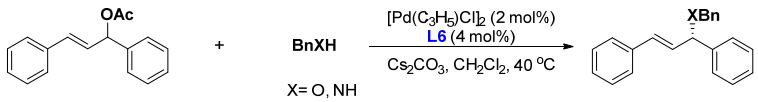


Ar = Pyridinyl

3p

Yield: 89%. The ee was determined by chiral HPLC (Chiralcel AD-H, hexane/isopropanol 80:20 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 18.511 min (minor) for (*R*)-isomer, t_R = 23.694 min (major) for (*S*)-isomer. ee = 41%. $[\alpha]_D^{23}$ -551.5 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.3 Hz, 2H), 8.34 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.13 (m, 3H), 7.07 (p, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.67 (dd, *J* = 15.8, 6.9 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 3.95 (t, *J* = 7.0 Hz, 1H), 1.57 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.5, 145.1, 140.4, 136.4, 126.4, 125.8, 121.9, 120.7, 120.5, 119.2, 111.2, 34.4, 20.4. HRMS m/z: anal. calcd for $C_{13}H_{13}NO_2$[M+Na]$^+$: 271.1211, found: 271.1238.

4.3 General procedure for Pd-catalyzed enantioselective allylic etherification and amination reactions

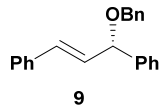


2a

Ligand **L6** (11.3 mg, 0.012 mmol, 4 mol%) and $[Pd(C_3H_5)Cl]_2$ (2.2 mg, 0.006 mmol, 2 mol%) were dissolved in CH_2Cl_2 (1.0 mL) in a Schlenk tube under Ar. After stirring at room temperature for 1 h, allylic acetate **2a** (0.45 mmol) in CH_2Cl_2 (1.0 mL) was added, followed by benzylamine or benzylalcohol (0.3 mmol), Cs_2CO_3 (197 mg, 0.6 mmol). The mixture was stirred at 40 °C until indoles was totally consumed, and then was purified by flash column chromatrography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding product **9** and **11**.

4.4 Spectral Data of Allylic Reaction Products

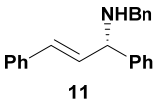
(*S*,E)-(3-(benzyloxy)prop-1-ene-1,3-diyl)dibenzene (9) [2]



9

Yield: 95%. The ee was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol 97:3 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 6.028 min (major) for (*S*)-isomer, t_R = 6.525 min (minor) for (*R*)-isomer. ee = 98%. $[\alpha]_D^{23}$ -15.9 (c = 1.0, toluene). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.3 Hz, 2H), 7.41-7.33 (m, 8H), 7.21-7.28 (m, 4H), 7.24-7.20 (m, 1H), 6.63 (d, *J* = 16.2 Hz, 1H), 6.34 (dd, *J* = 16.7, 7.2 Hz, 1H), 5.01 (d, *J* = 7.2 Hz, 1H), 4.57 (dd, *J* = 15.6, 12.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.0, 138.3, 136.5, 131.5, 130.2, 128.5, 128.5, 128.3, 127.7, 127.7, 127.7, 127.5, 126.9, 126.5, 81.5, 70.0.HRMS (EI) m/z: calcd for $C_{22}H_{20}O$ $[M]^+$: 300.1514, found: 300.1520.

(*S*,*E*)-N-benzyl-1,3-diphenylprop-2-en-1-amine (11) [2]



11

Yield: 90%. The ee was determined by chiral HPLC (Chiralpak AD-H, hexane/isopropanol 90:10 v/v, flow rate 1.0 mL/min, λ = 254 nm, 25 °C). Retension times: t_R = 8.627 min (minor) for (*R*)-isomer, t_R = 9.228 min (major) for (*S*)-isomer. ee = 97%. $[\alpha]_D^{23}$ -19.66 (c = 1.0, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.39 (m, 2H), 7.36-7.32 (m, 7H), 7.30 (s, 1H), 7.29 – 7.12 (m, 5H). 6.58 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.9, 7.5 Hz, 1H), 4.40 (d, *J* = 7.5 Hz, 1H), 3.79 (dd, *J* = 17.6 Hz, *J* = 9.2 Hz, 2H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 140.3, 136.8, 132.5, 130.3, 128.6, 128.5, 128.4, 128.2, 127.4, 127.3, 127.3, 126.9, 126.4, 64.5, 51.3. MS m/z: anal. calcd for $C_{22}H_{21}N$ $[M]^+$: 299.17, found: 299.22

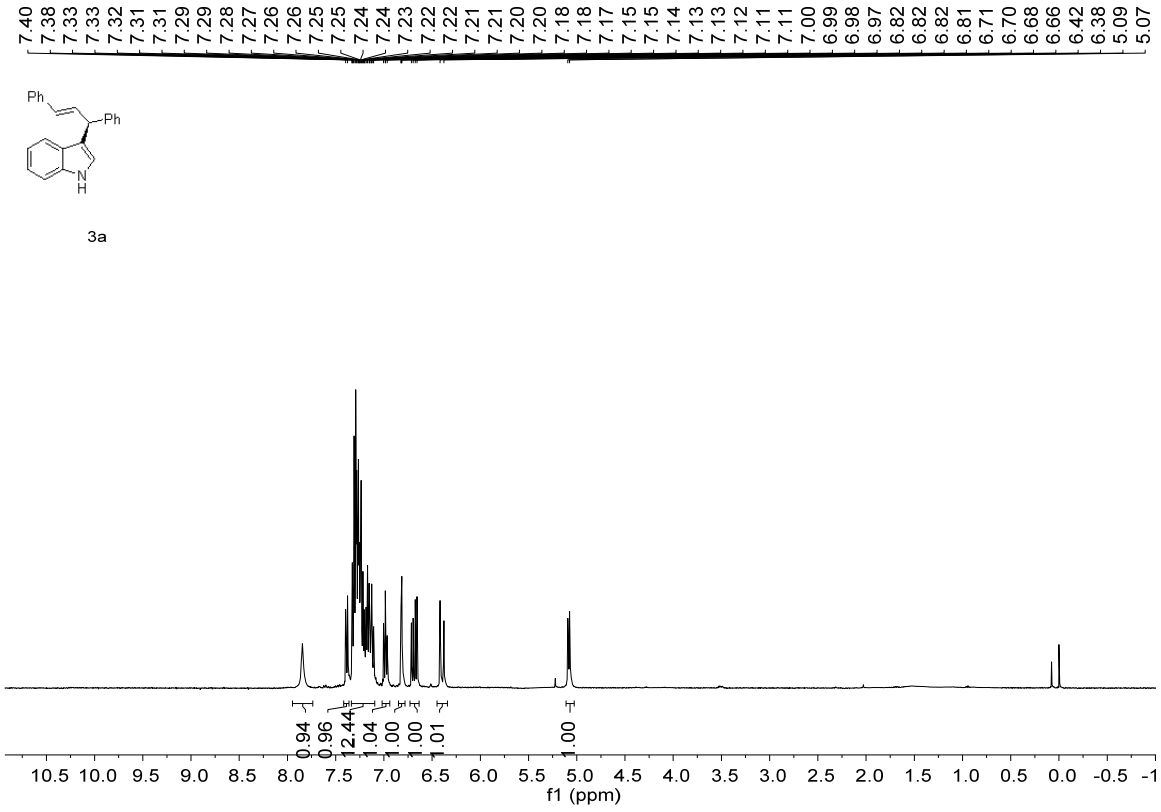
5. References

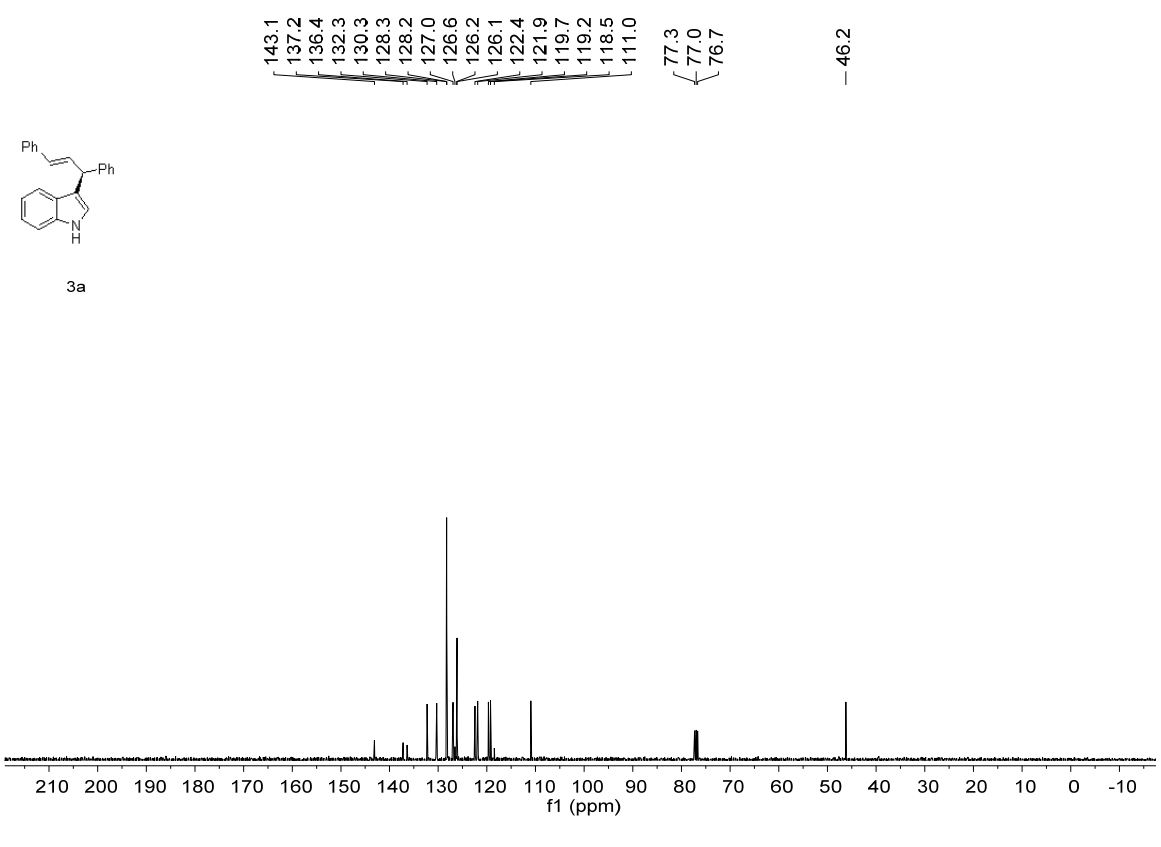
[1] (a) Z. Liu, Z. Cao and H.-F. Du, *Org. Biomol. Chem.*, 2011, **9**, 5369; (b) H. Y. Cheung, W.-Y. Yu, F. L. Lam, T.-T. Au-Yeung, Z.-Y. Zhou, T. H. Chan and A. S. Chan, *Org. Lett.*, 2007, **9**, 4295; (c) Y. Liu and H.-F. Du, *Org. Lett.*, 2013, **15**, 740; (*c*) Z. Cao, Y. Liu, Z. Liu, X. Feng, M. Zhuang and H.-F. Du, *Org. Lett.*, 2011, **13**, 2164; (d) T. Hoshi, K. Sasaki, S. Sato, Y. Ishii, T. Suzuki and H. Hagiwara, *Org. Lett.*, 2011, **13**, 932.

[2] (a) M. Coll, O. Pàmies and M. Diéguez, *Org. Lett.,* 2014, **16**, 1892; (b) M. Brichacek, M. N. Villalobos, A. Plichta and J. Njardarson, *Org. Lett.,* 2011, **13**, 1110; (c) Z. Cao, Y. Liu and H.-F. Du, *J. Org. Chem.,* 2011, **76**, 6401; (d) L. Du, P. Cao and J. Liao, *Acta Chim. Sinica.*, 2013, **71**, 1239.

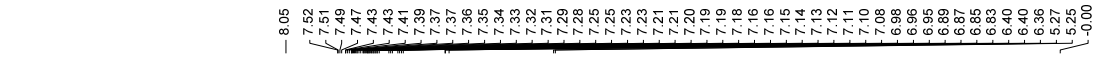
6. Copies of ^{1}H NMR and ^{13}C NMR Spectra

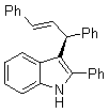
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3a



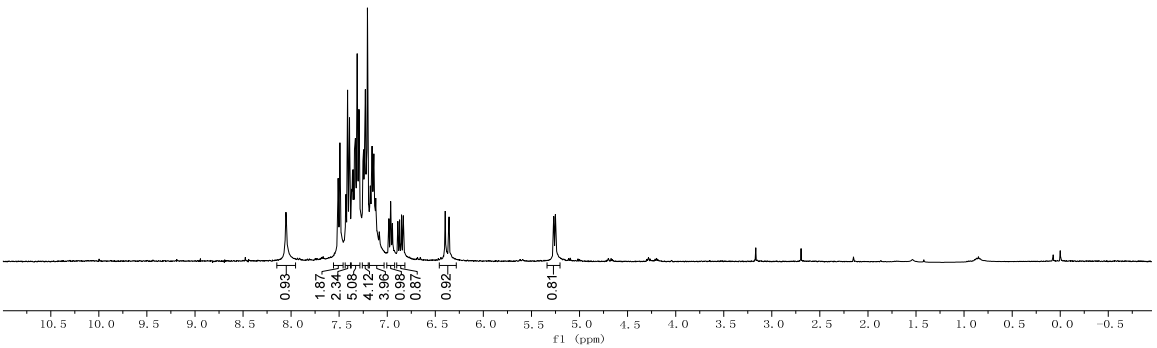


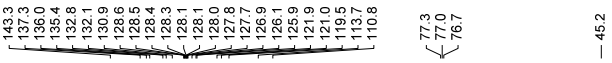
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3b

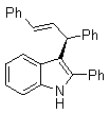




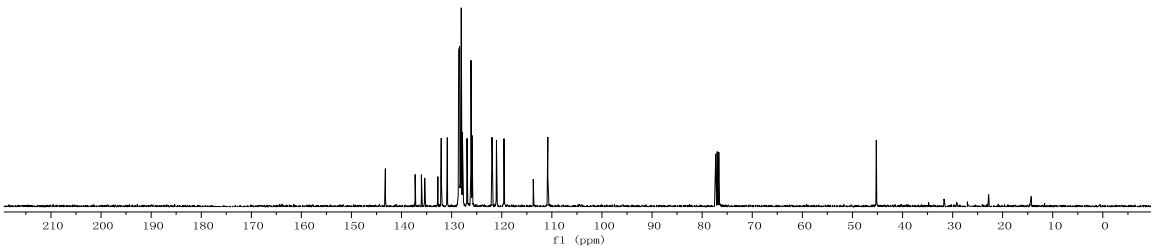
3b



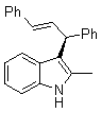




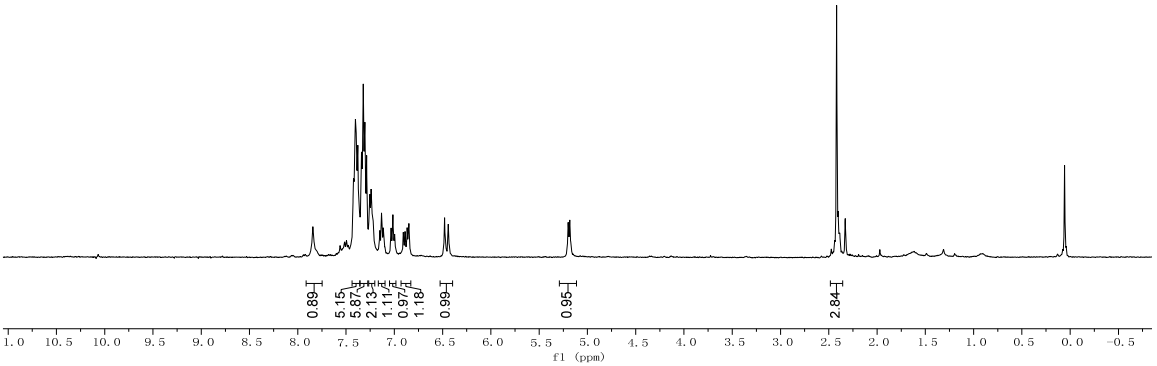
3b

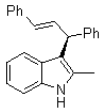


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3c

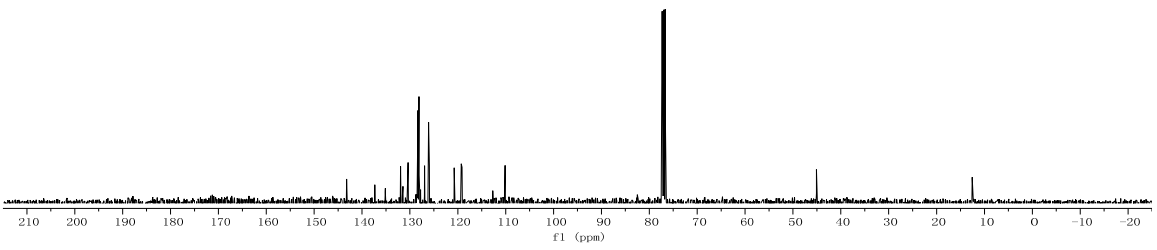


3c

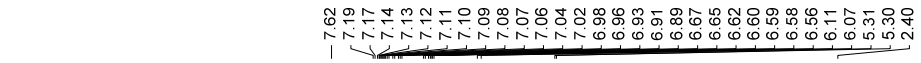


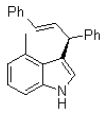


3c

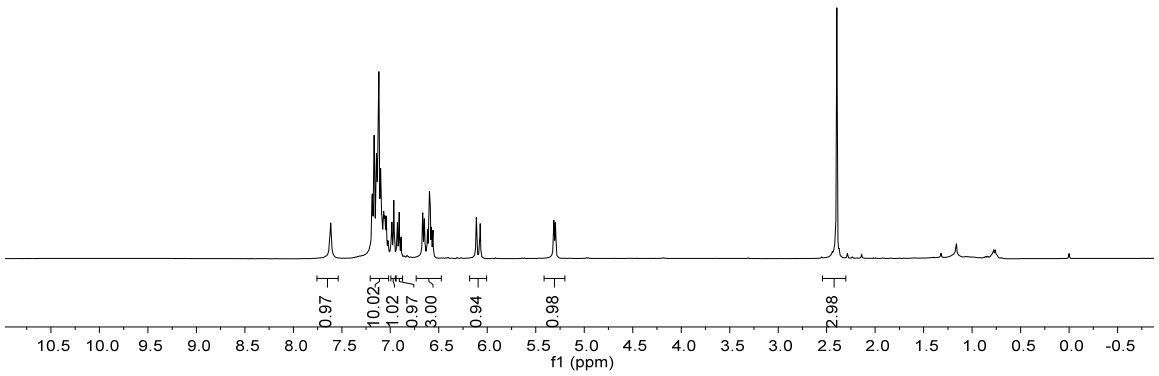


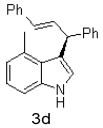
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3d



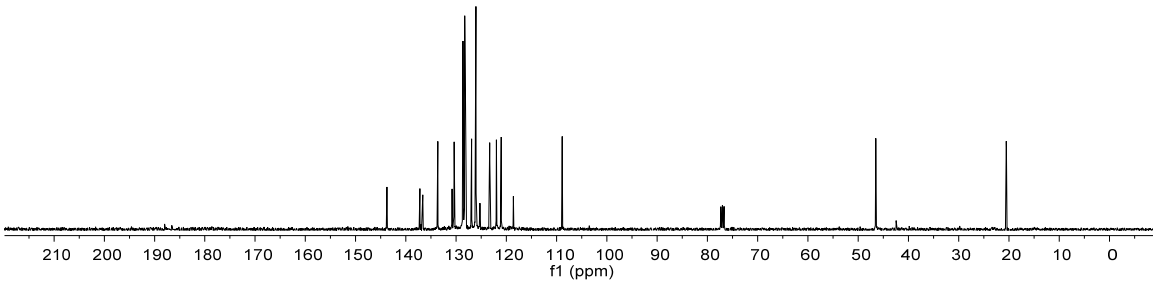


3d

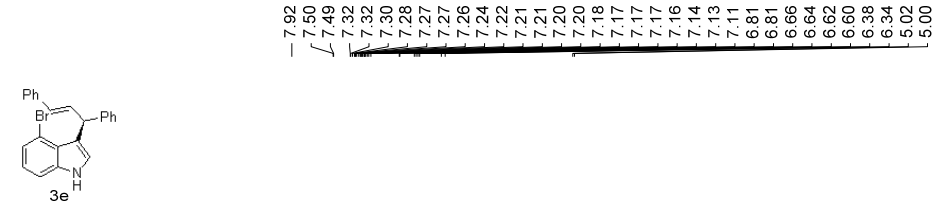




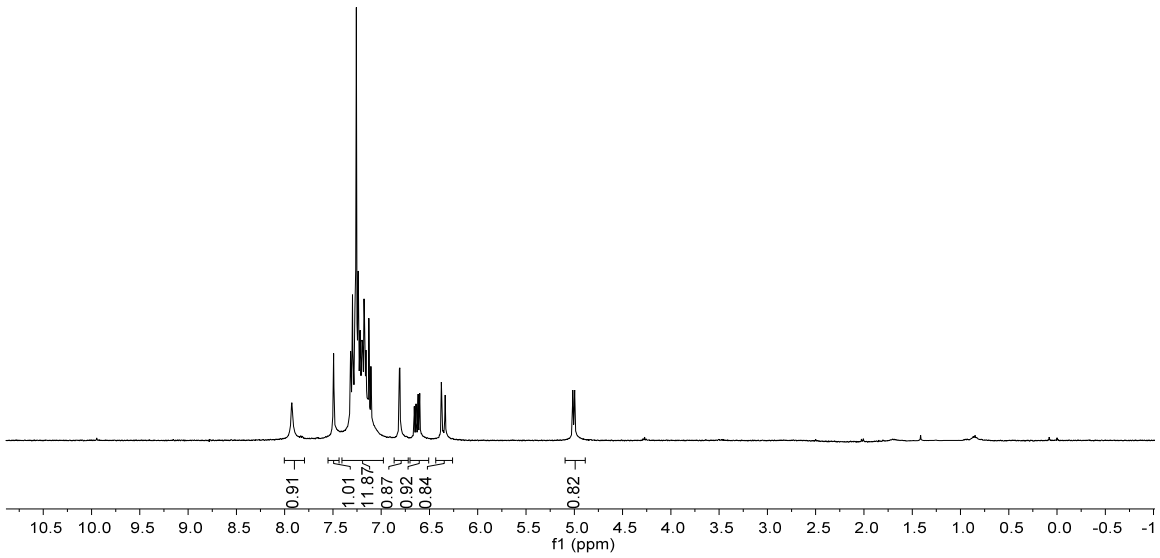
3d

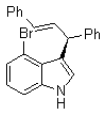


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3e

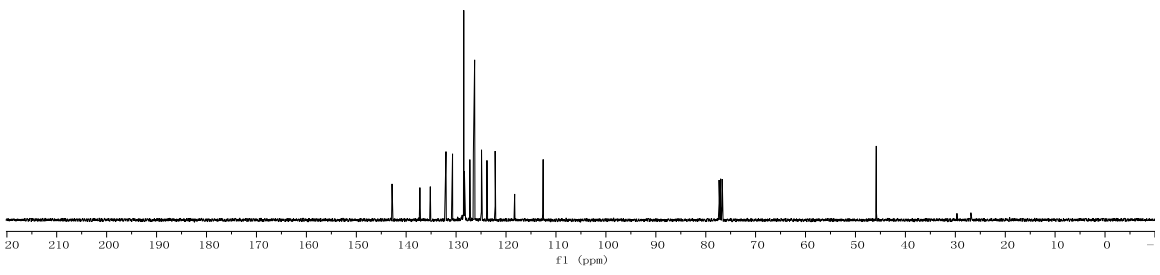


3e

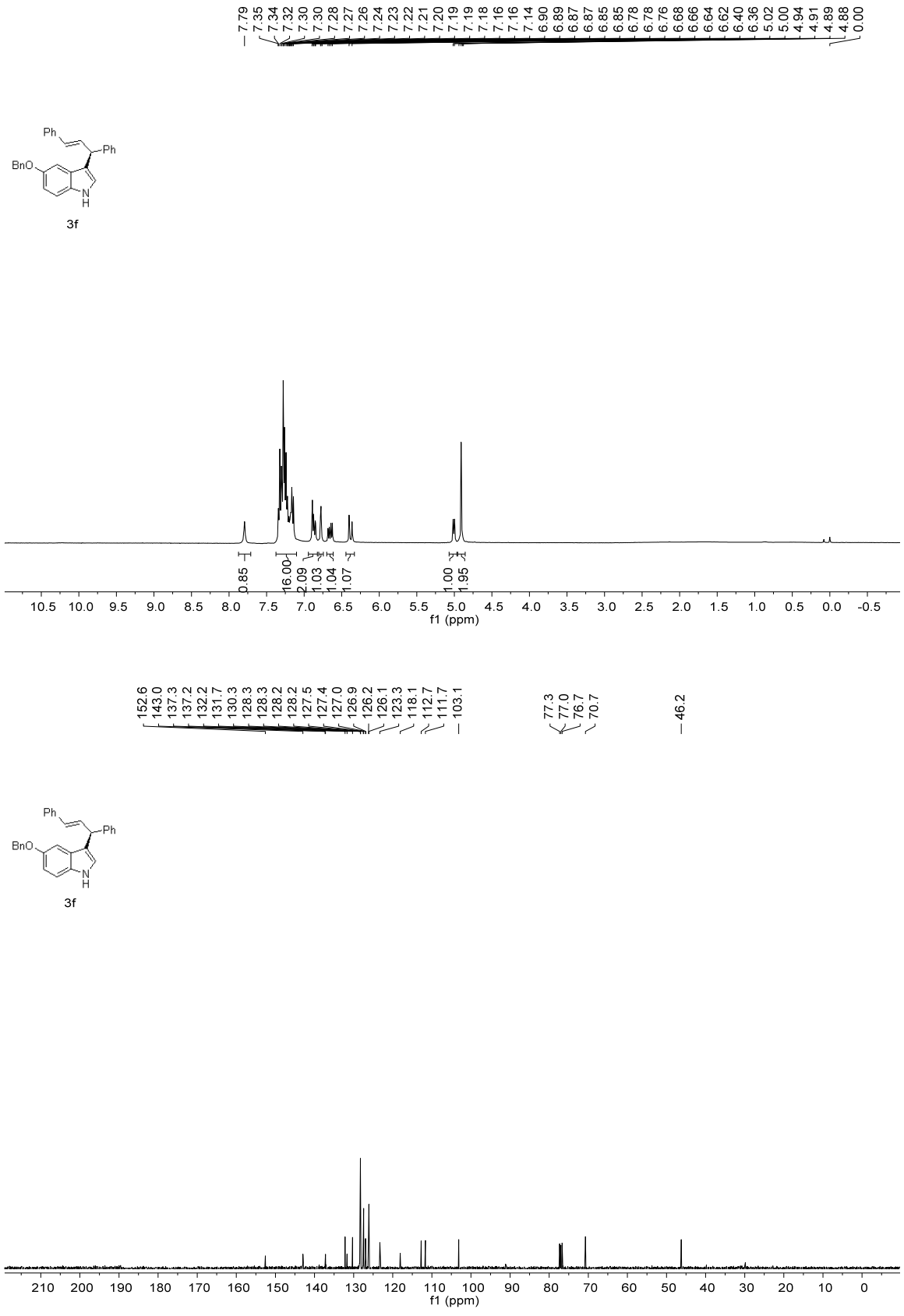




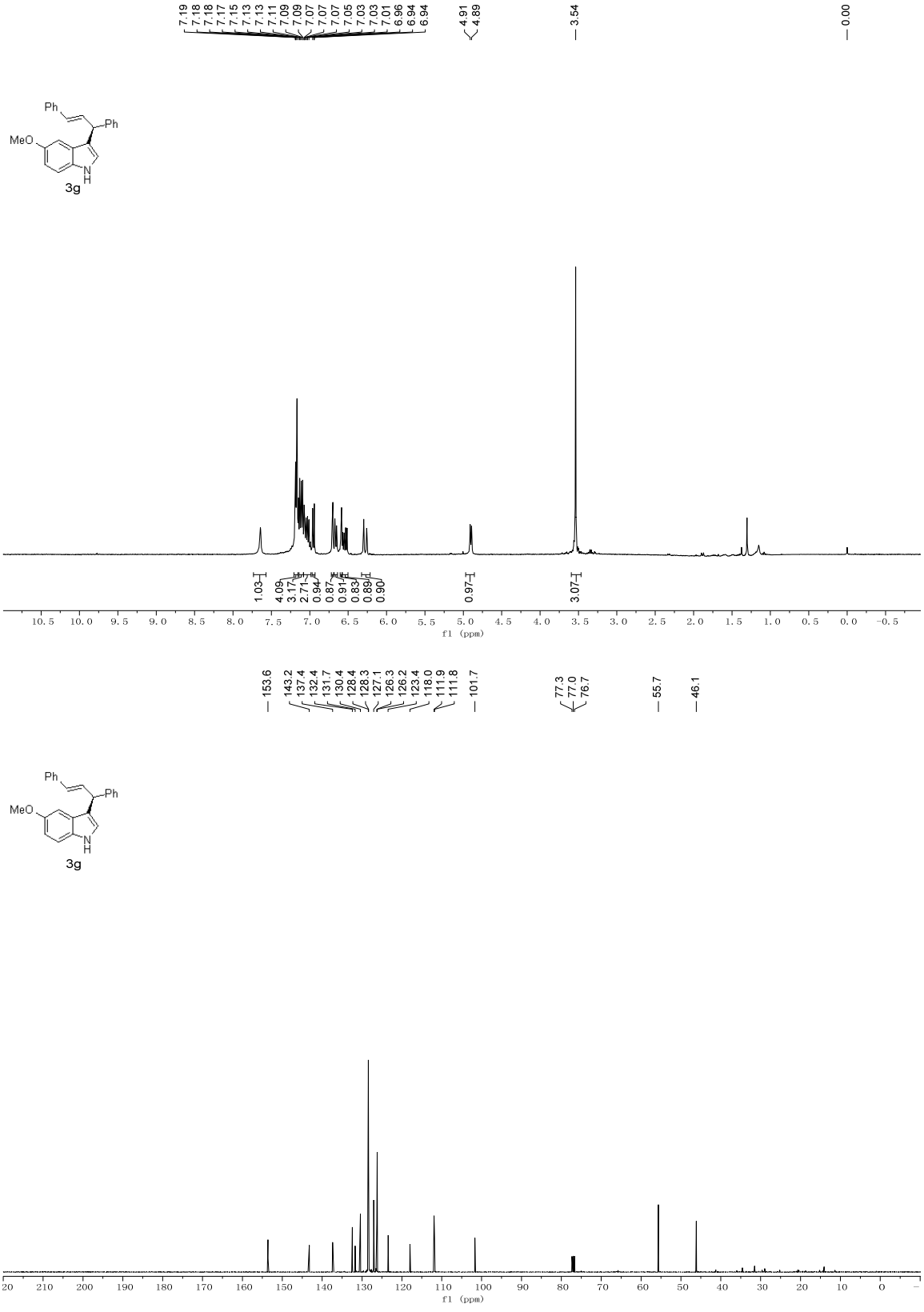
3e



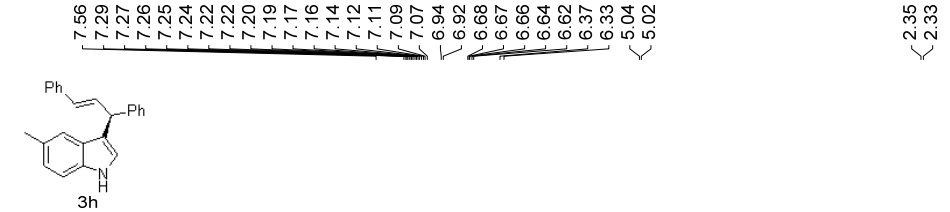
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3f



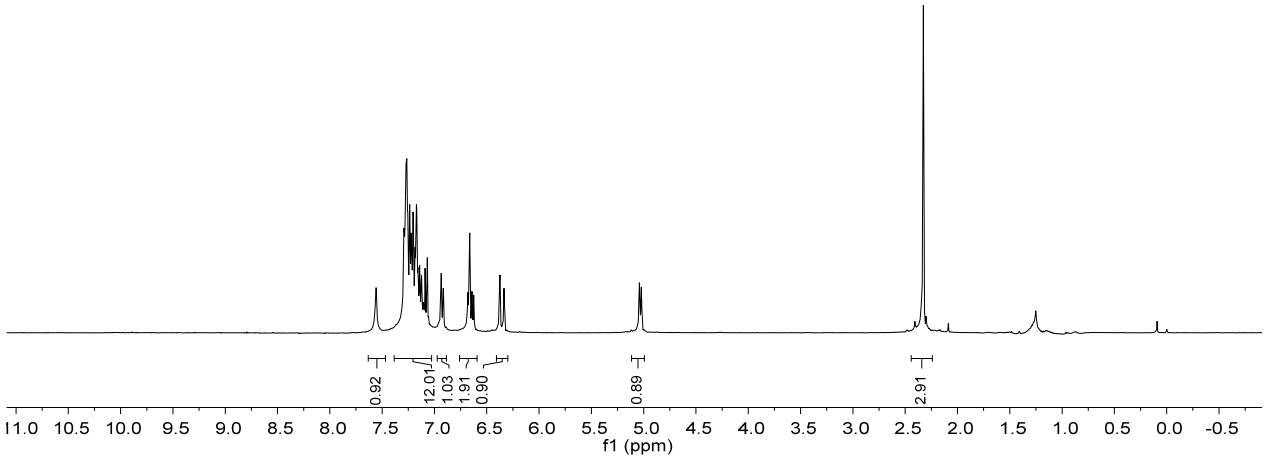
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3g

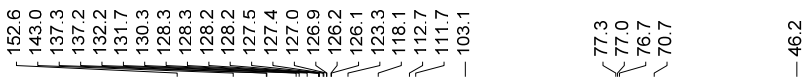


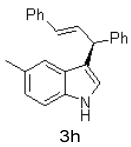
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3h



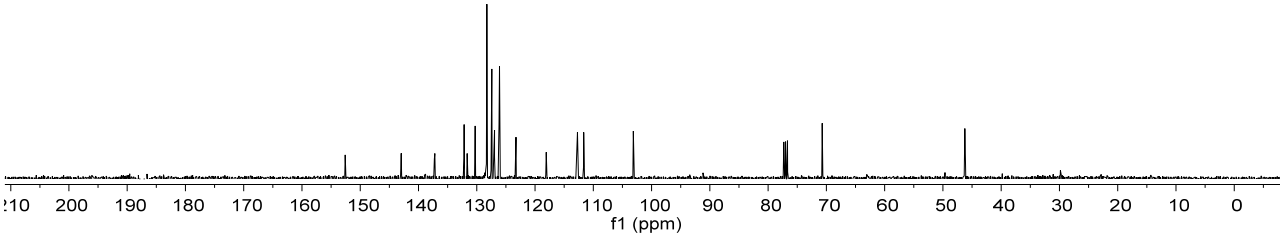
3h



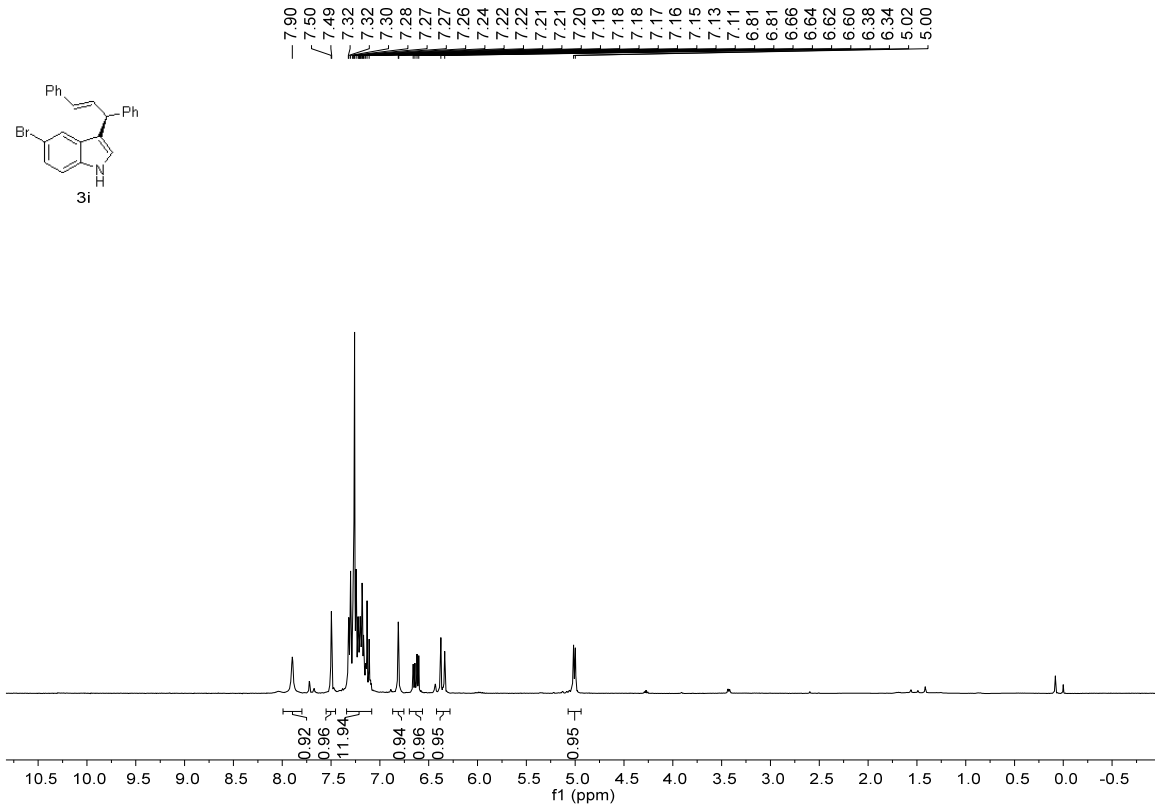


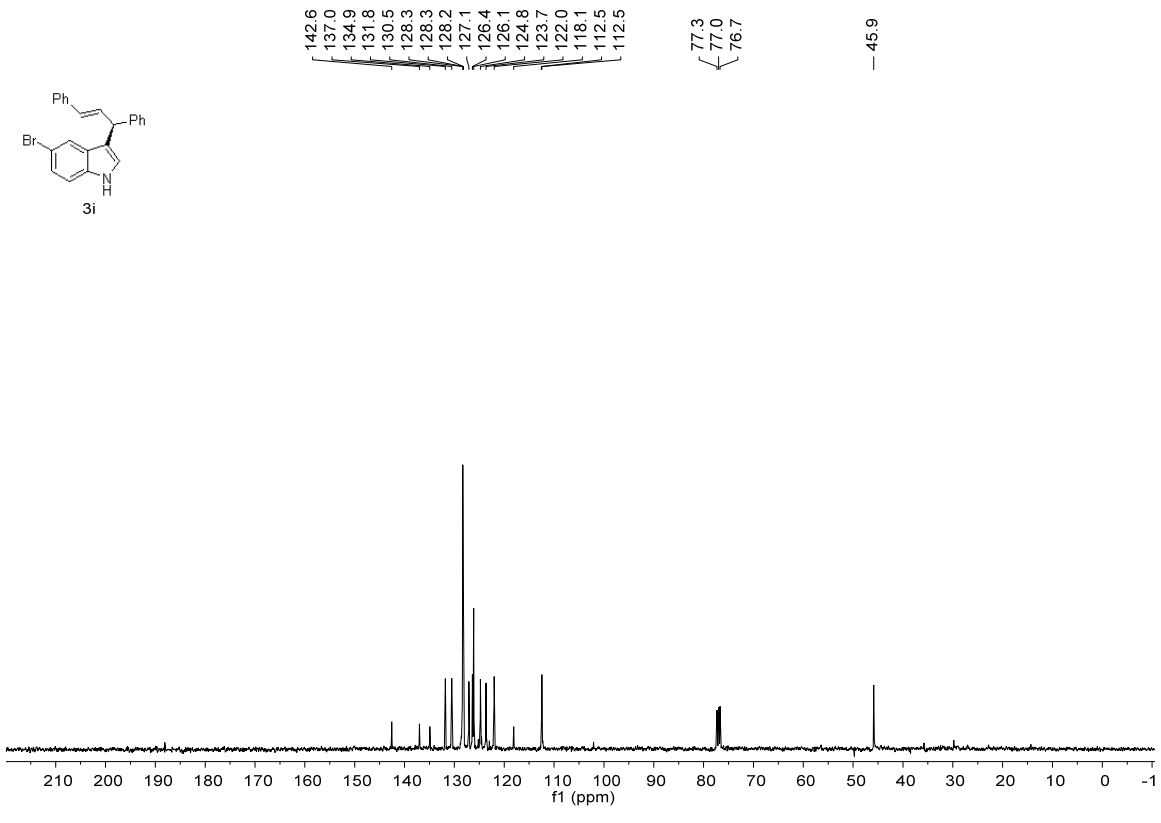


3h

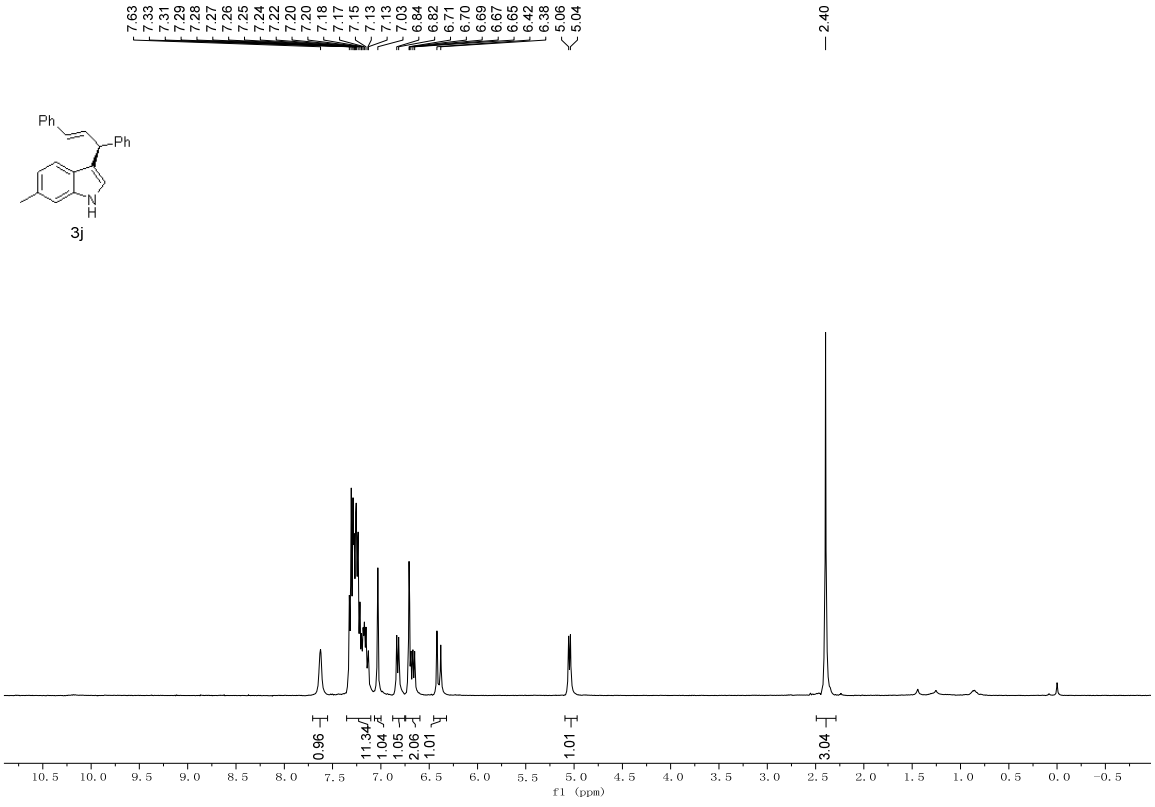


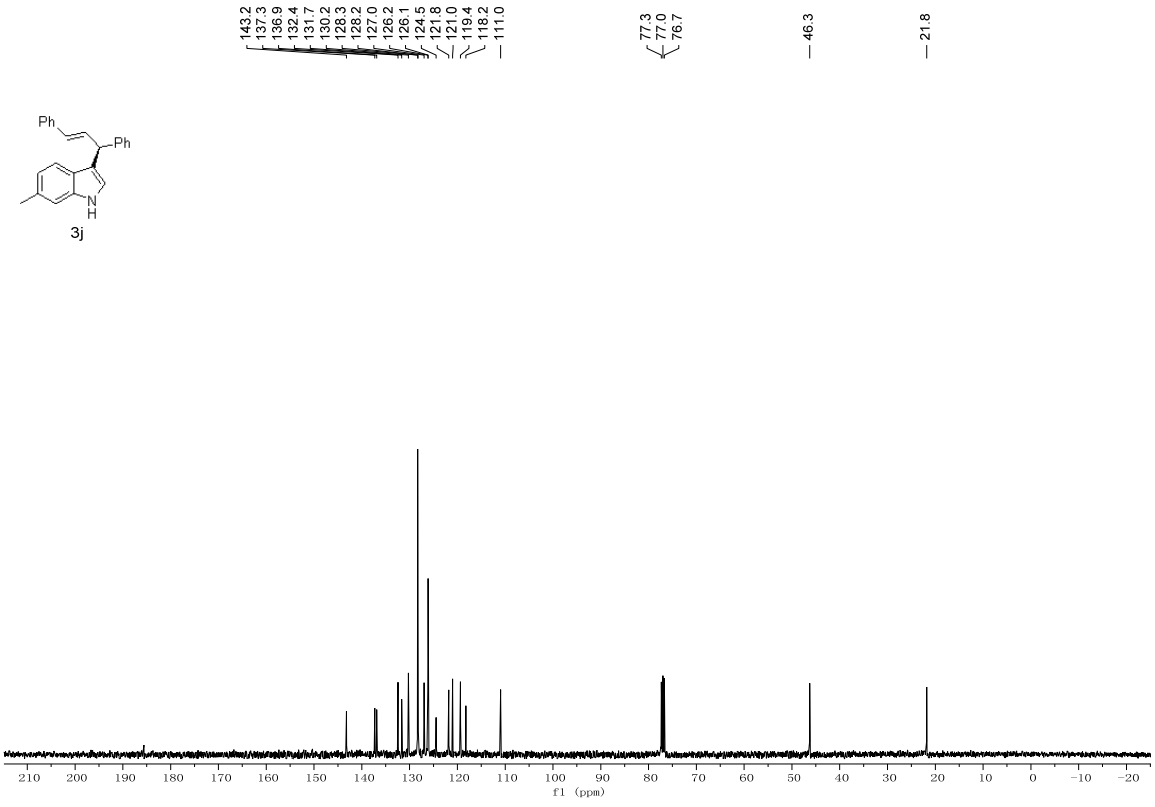
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3i



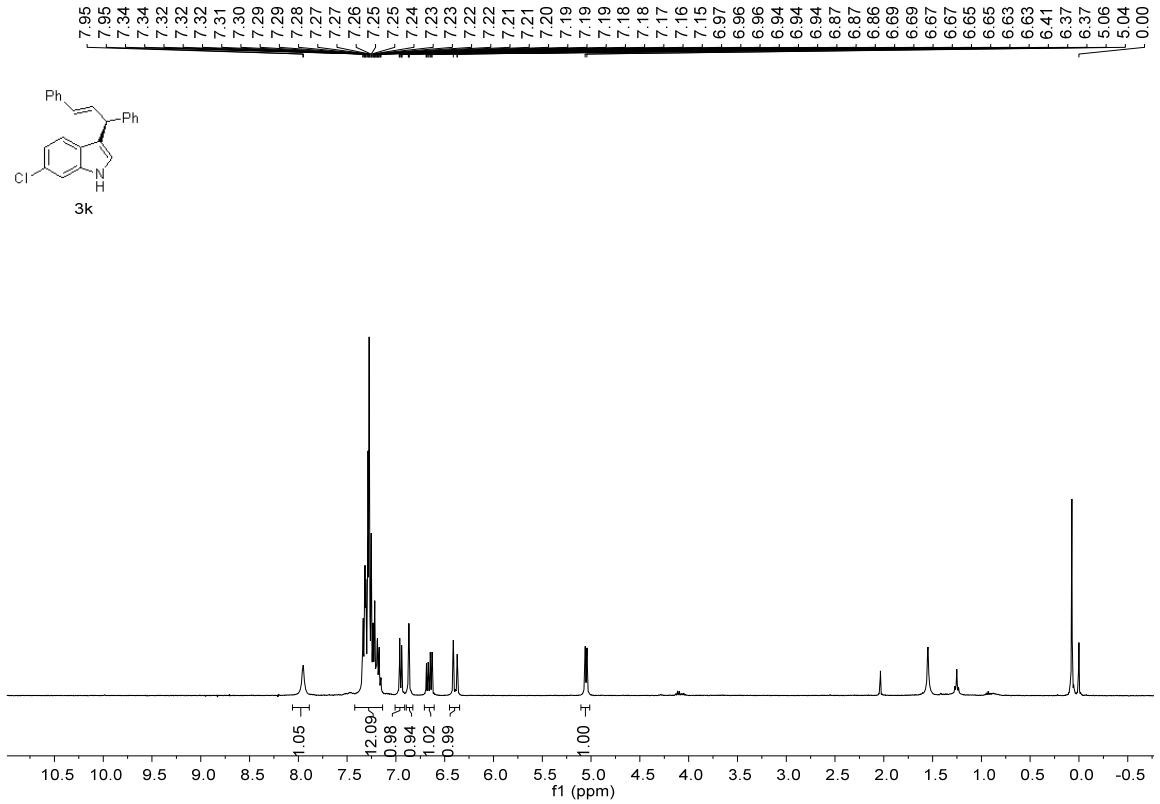


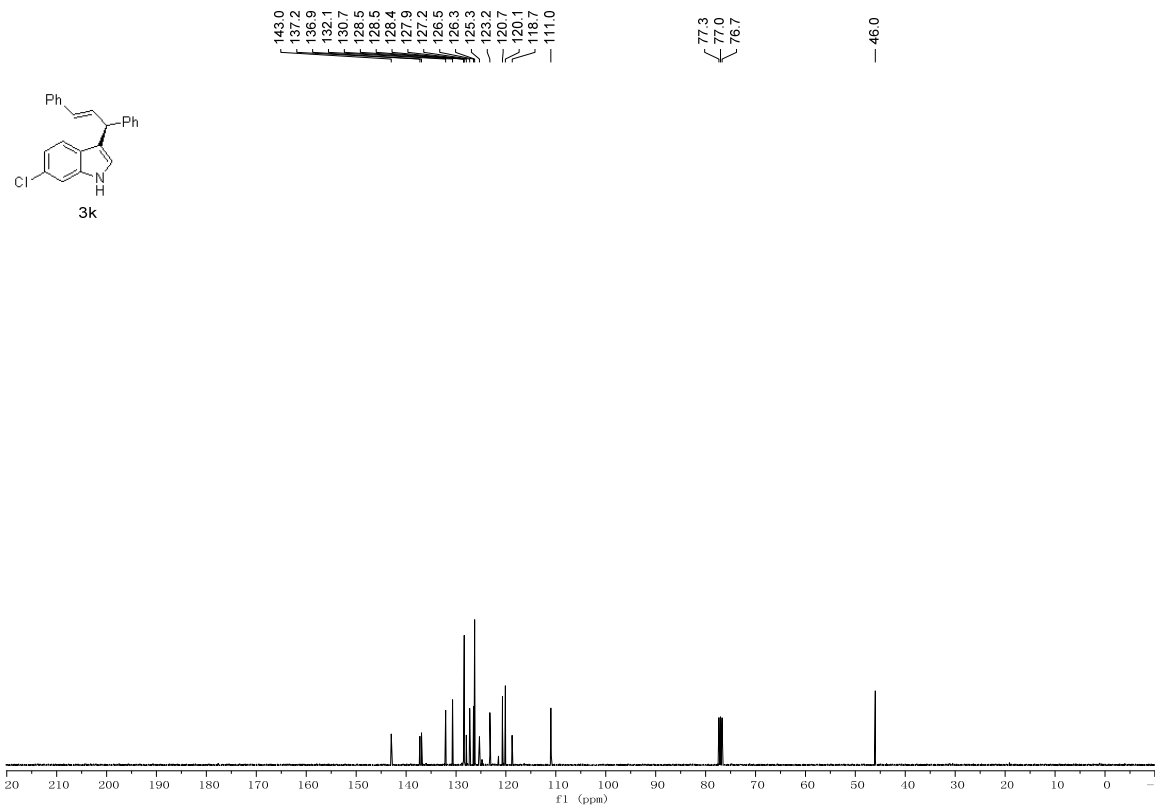
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3j



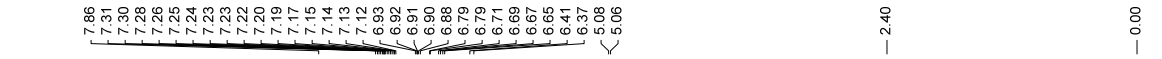


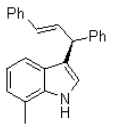
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3k



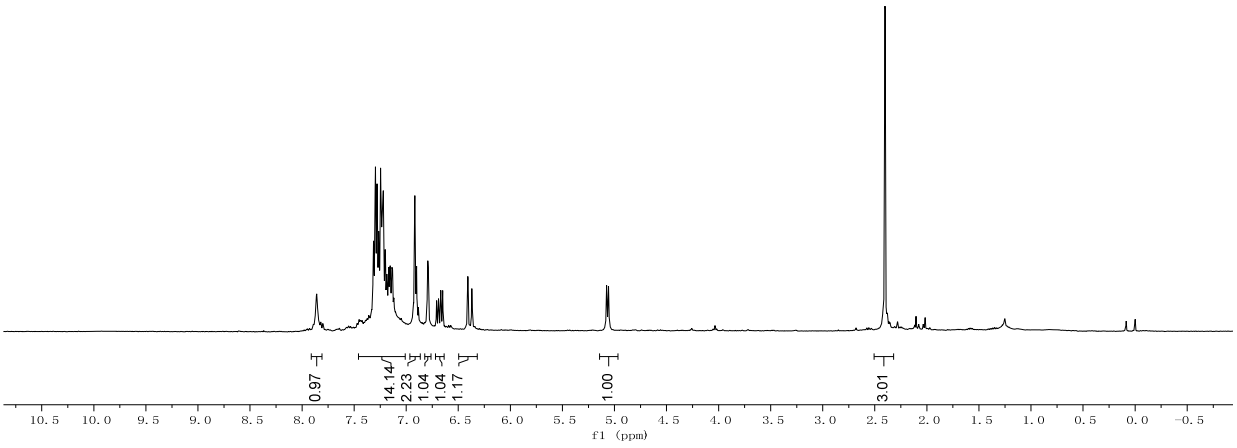


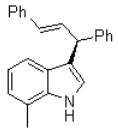
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3l



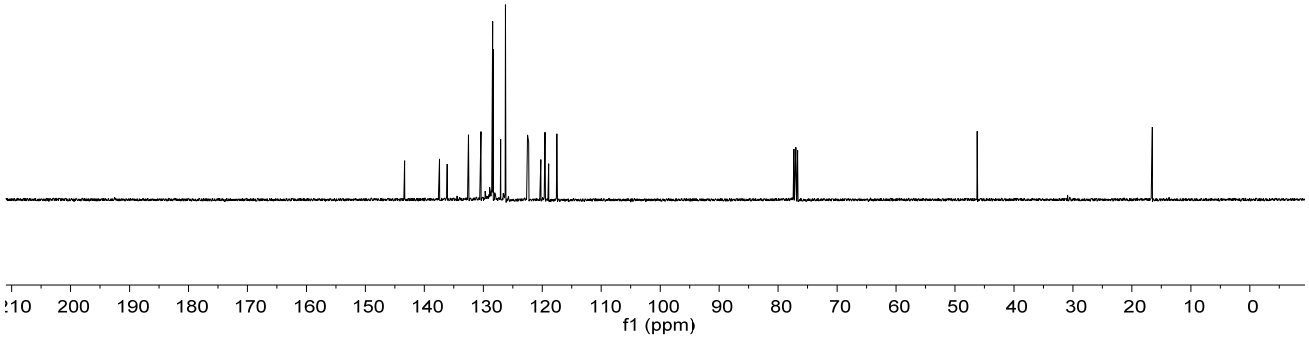


3l

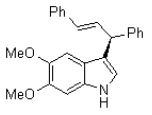




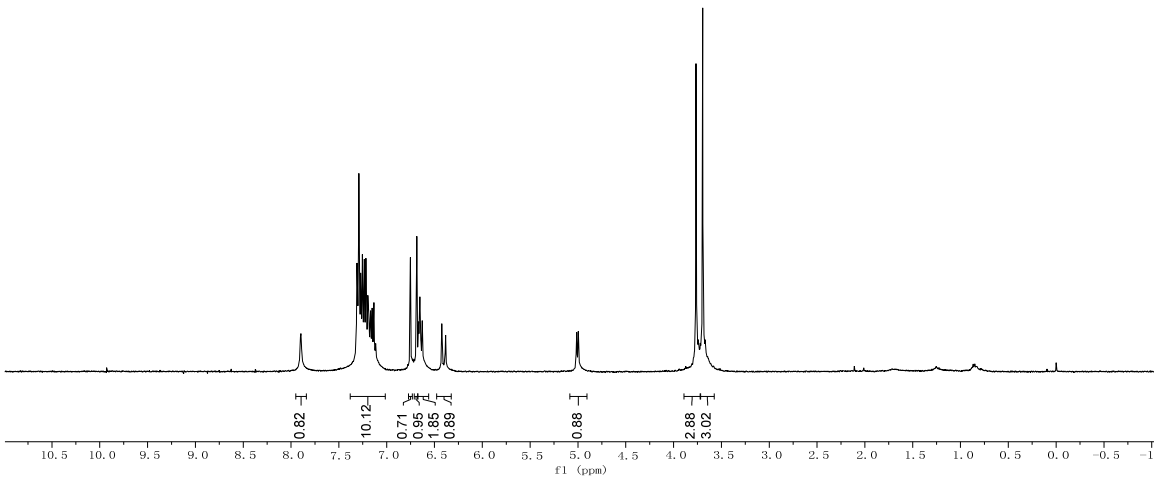
3l

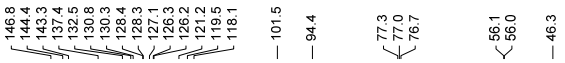


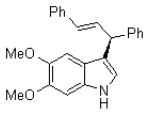
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3m



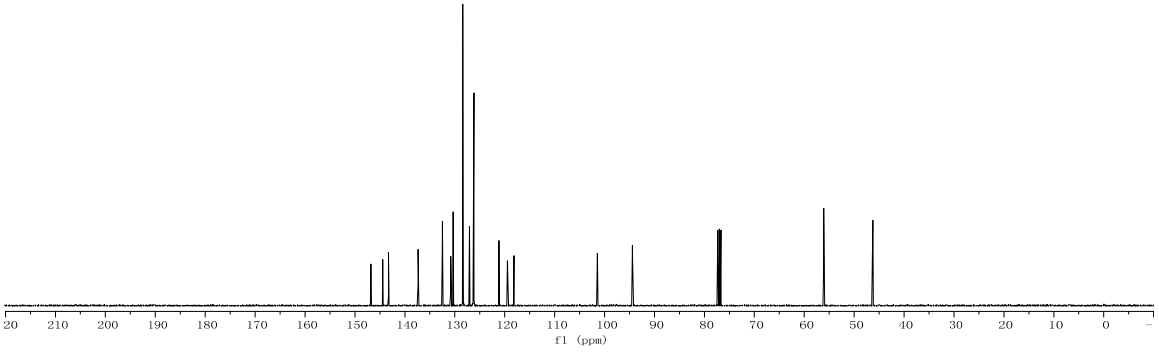
3m



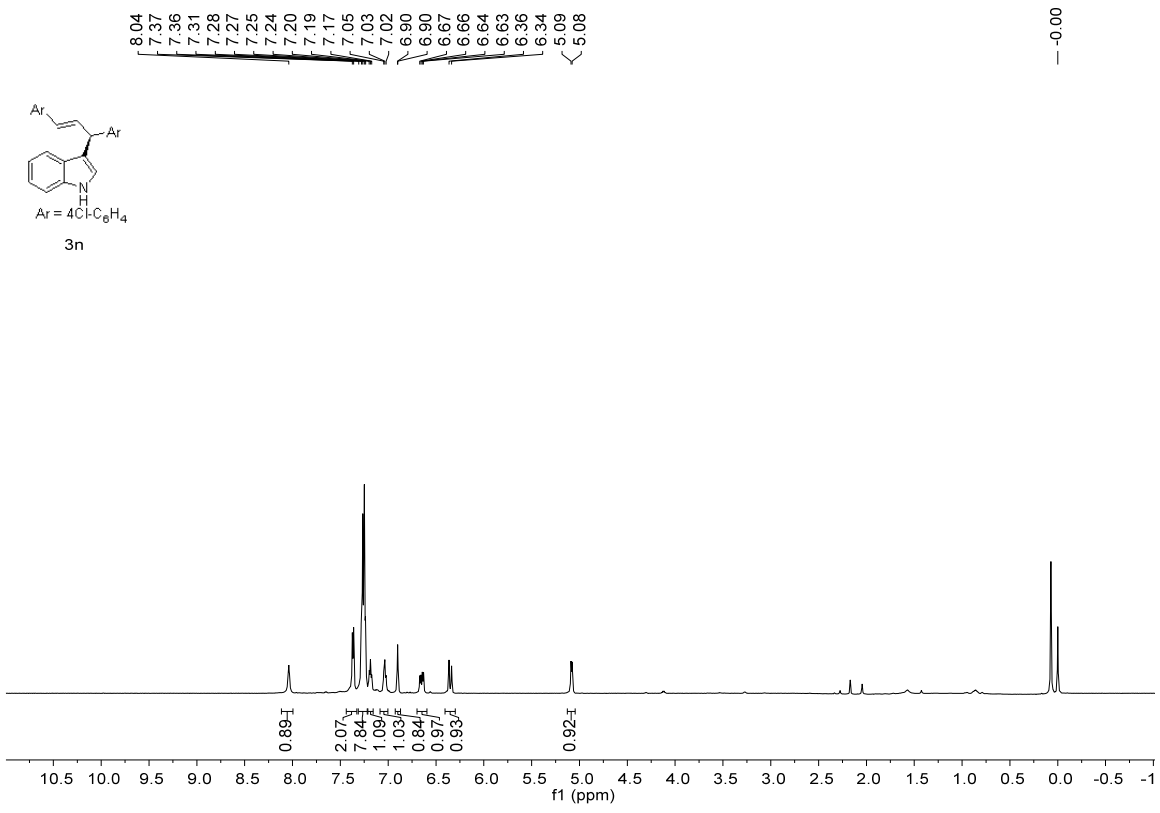


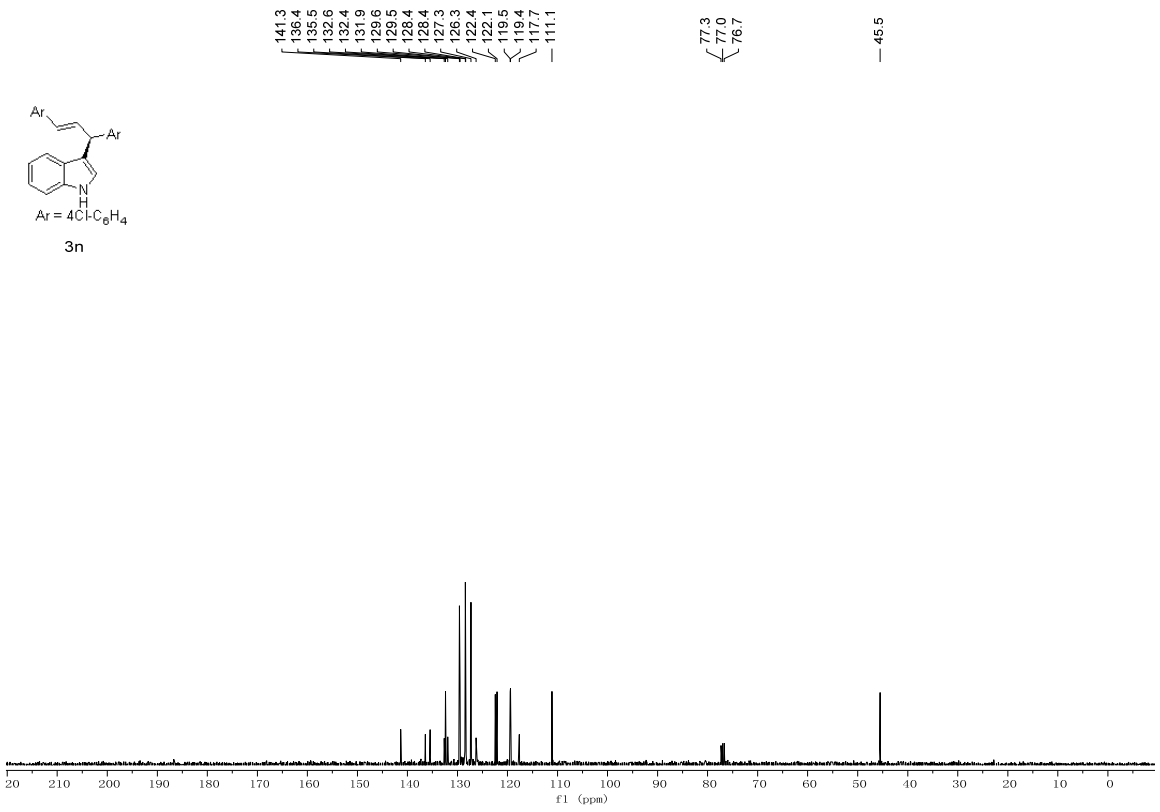


3m

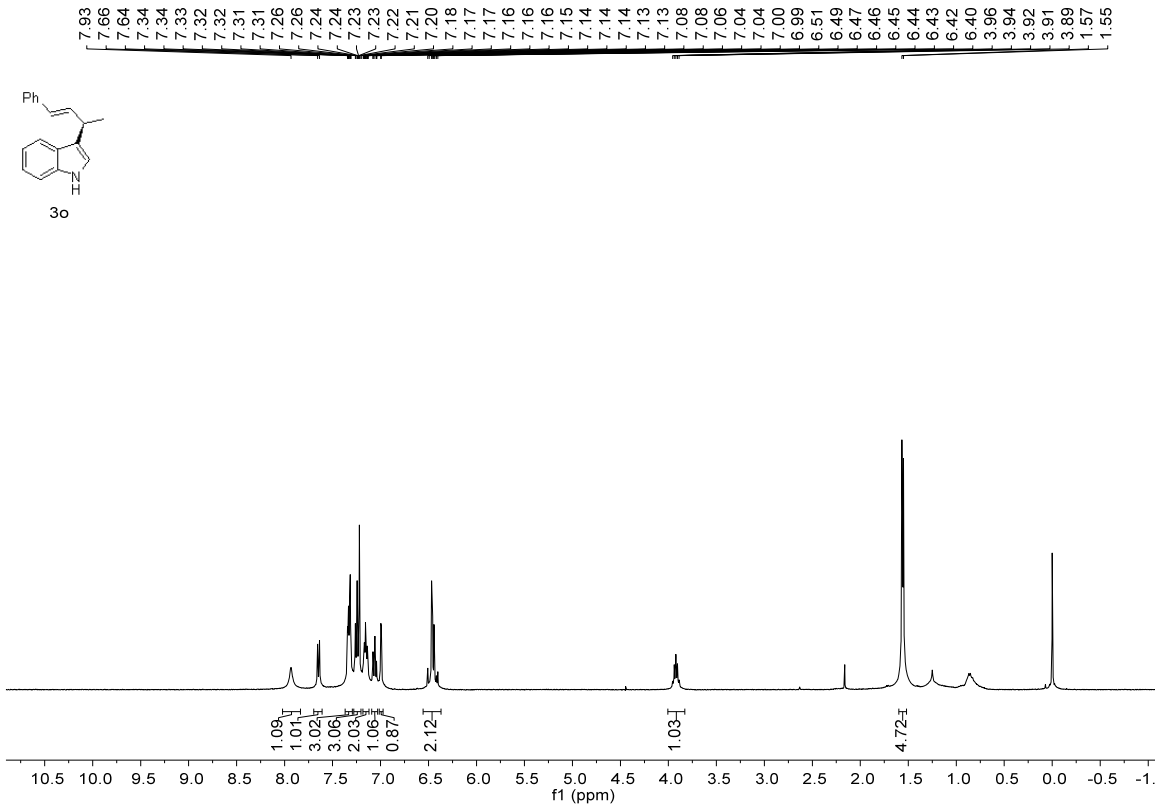


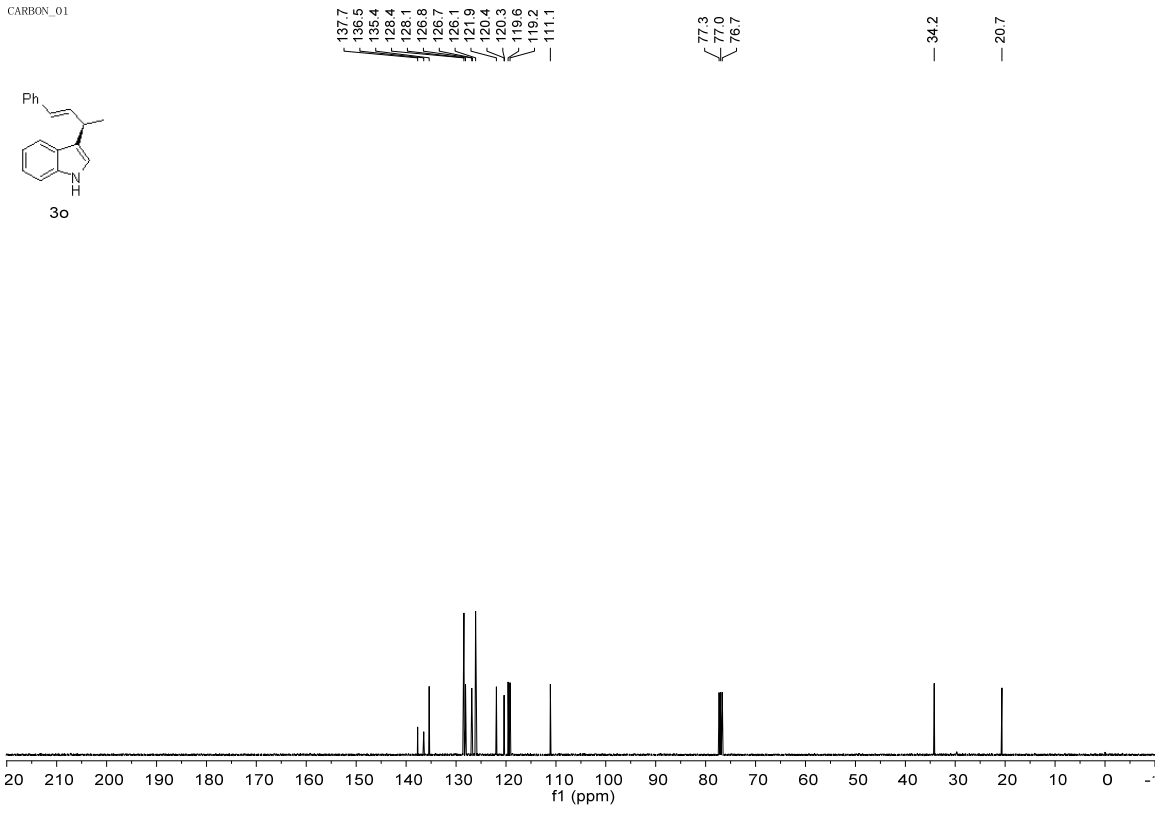
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3n



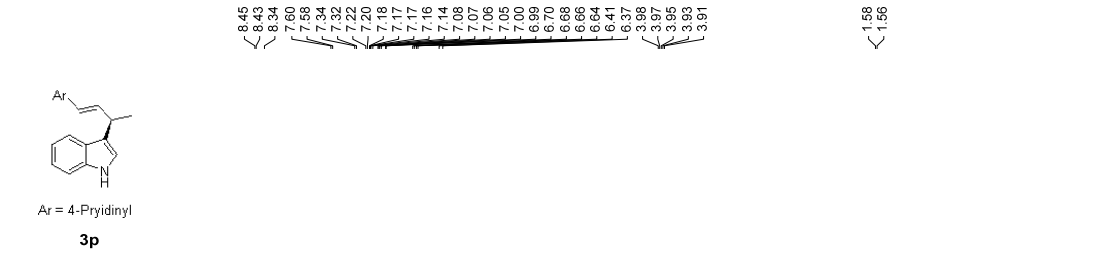


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3o



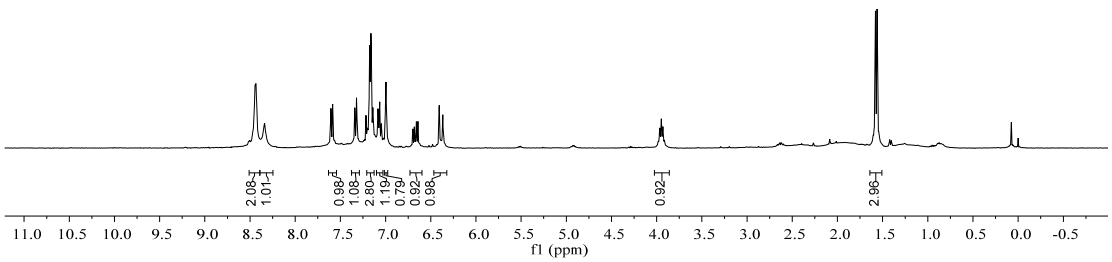


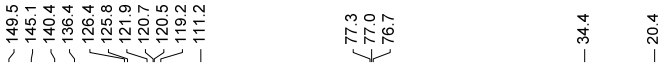
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3p

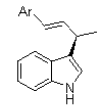


Ar = 4-Pryidinyl

3p

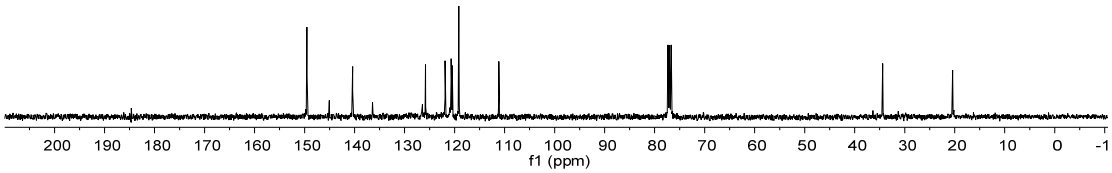




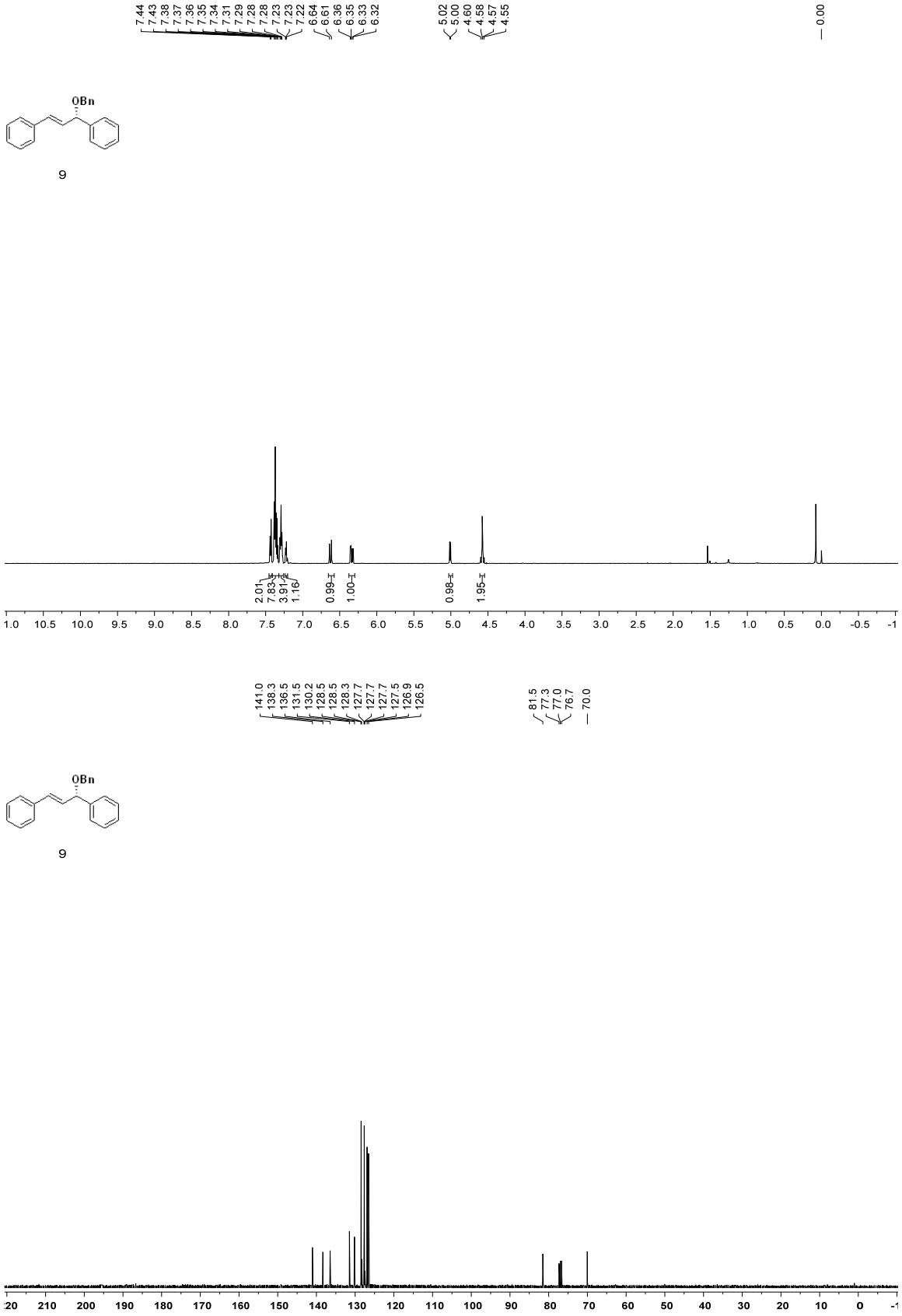


Ar = 4-Pryidinyl

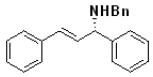
3p



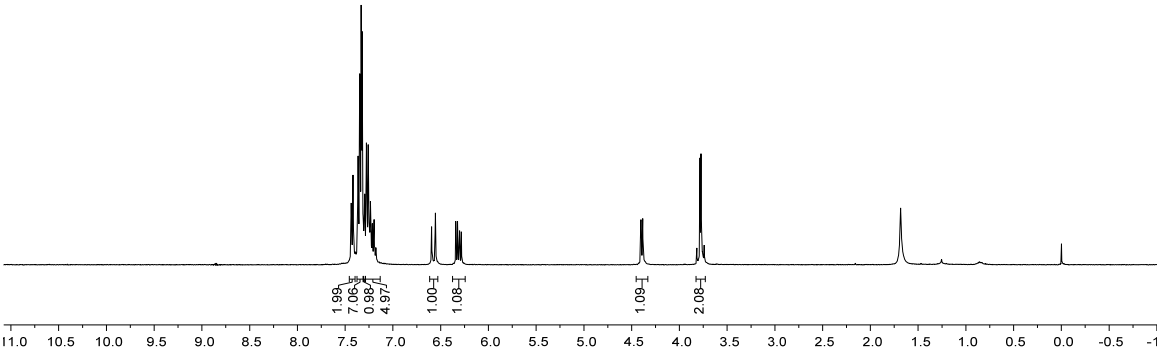
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 9

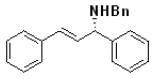


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 11

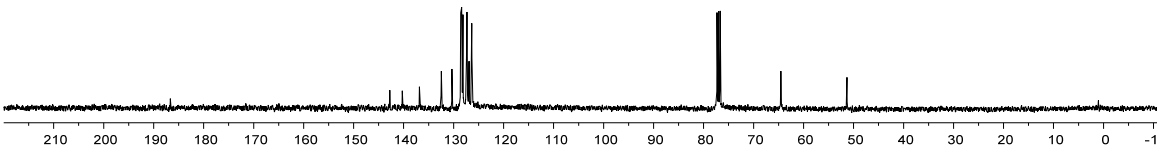


11

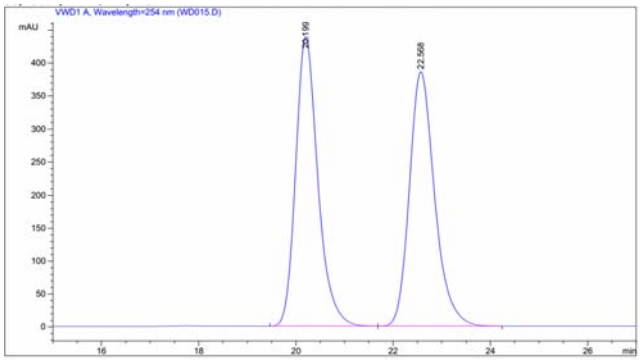


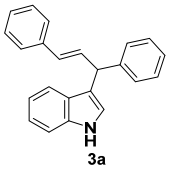


11



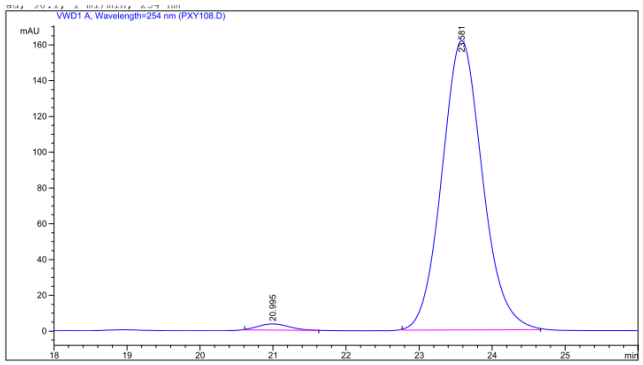
7. Copies of HPLC Chromatograms

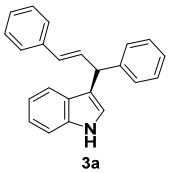




3a

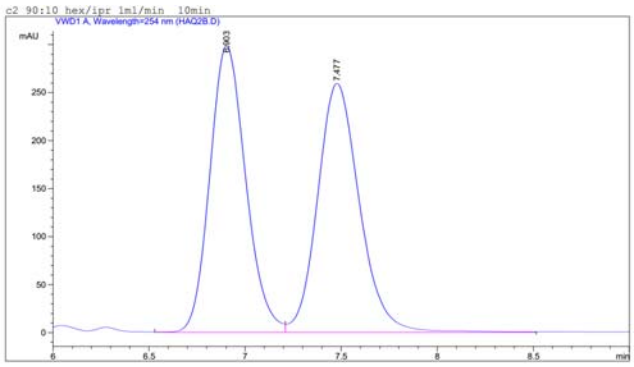
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.199	PV	0.4840	1.39360e4	438.95880	49.9929
2	22.568	VB	0.5491	1.39201e4	385.80133	49.9359

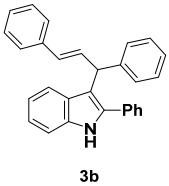




3a

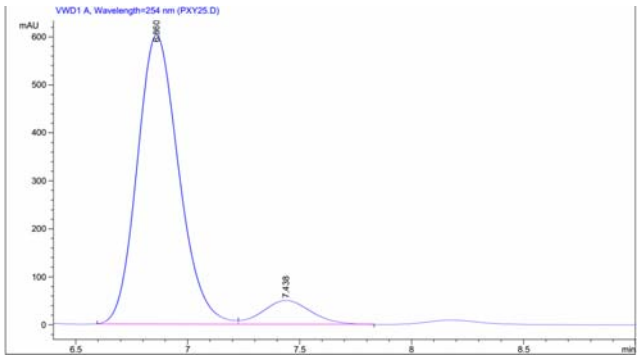
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.995	BB	0.4295	105.61577	3.54086	1.6634
2	23.581	BB	0.5943	6243.64893	161.82333	98.3366

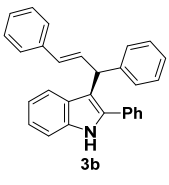




3b

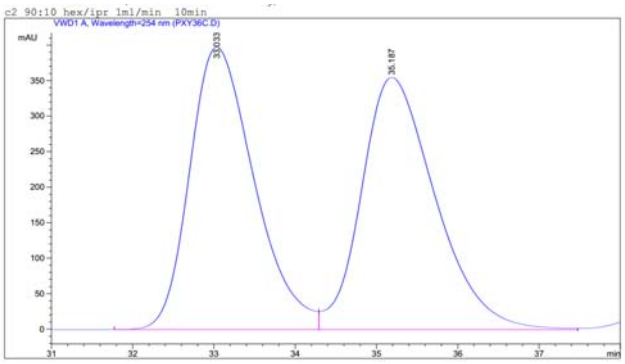
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.903	VV	0.2014	3890.48950	298.78192	49.5586
2	7.477	VB	0.2333	3959.79639	259.52771	50.4414

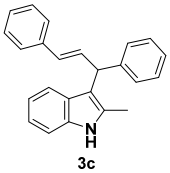




3b

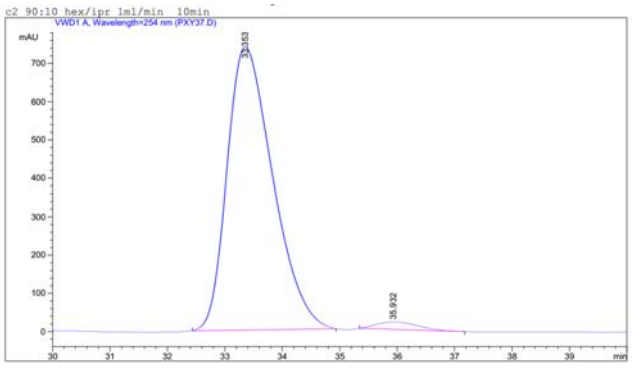
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.860	BB	0.2001	7774.27100	602.31647	91.2898
2	7.438	BB	0.2296	741.76172	49.66985	8.7102

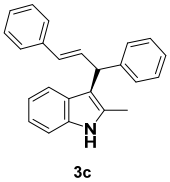




3c

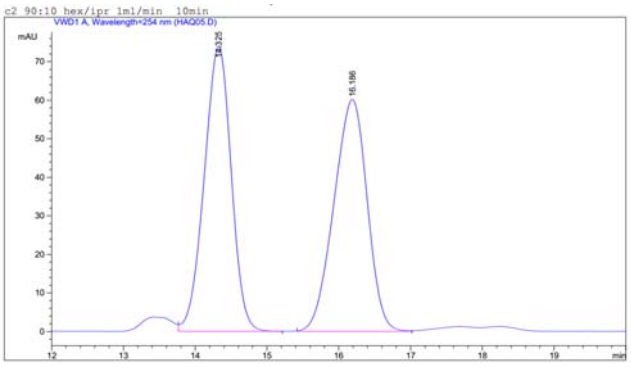
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.033	BV	0.8531	2.19511e4	397.98581	49.4644
2	35.187	VV	0.9665	2.24265e4	355.25589	50.5356

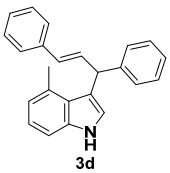




3c

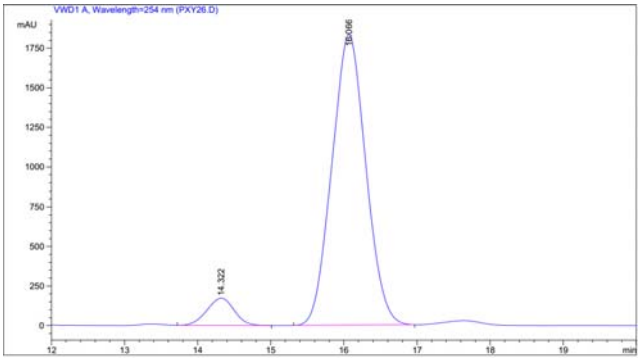
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.353	BB	0.8097	4.09202e4	739.90649	97.6095
2	35.932	BP	0.7775	1002.14142	19.77868	2.3905

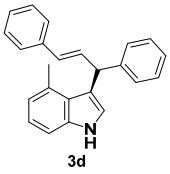




3d

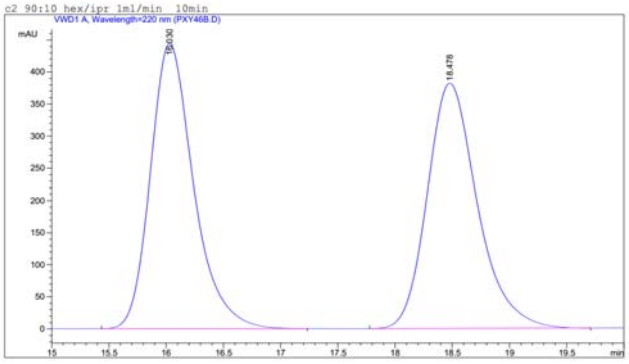
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.325	VB	0.4069	1932.80505	73.93610	49.9042
2	16.186	BV	0.5102	1940.22205	60.15617	50.0958

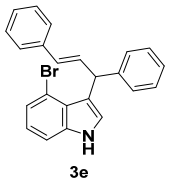




3d

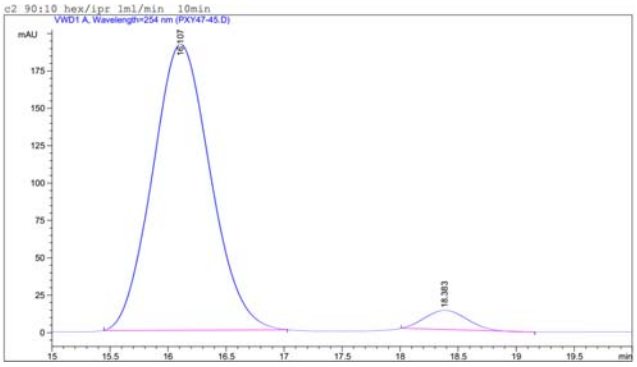
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.322	VB	0.4039	4509.14697	173.35382	7.0750
2	16.066	BB	0.4872	5.92240e4	1834.93286	92.9250

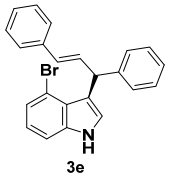




3e

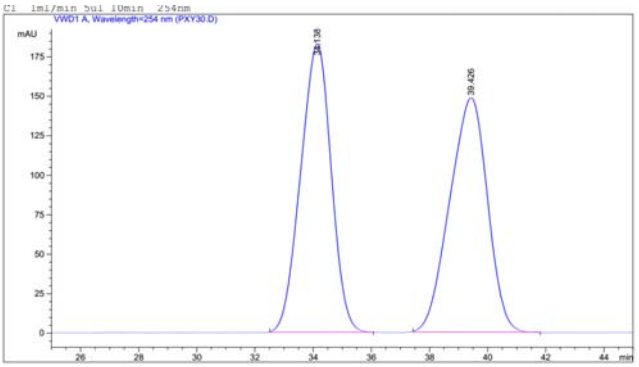
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.030	BB	0.3992	1.16447e4	444.01630	50.0622
2	18.478	BP	0.4642	1.16158e4	381.76508	49.9378

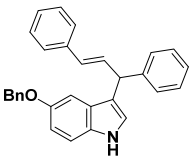




3e

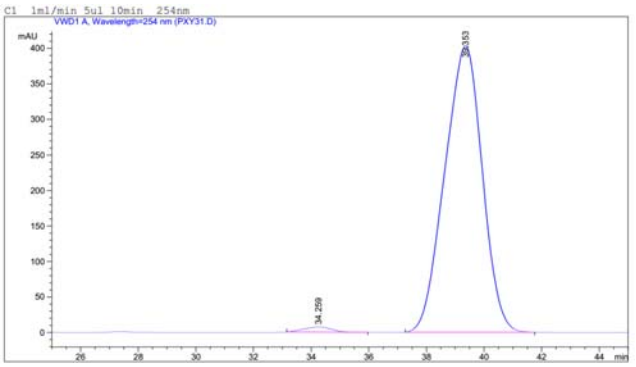
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.107	BB	0.5337	6628.55127	191.34755	95.3852
2	18.383	BP	0.4086	320.69064	12.80602	4.6148

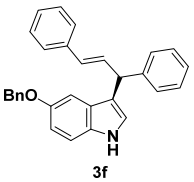




3f

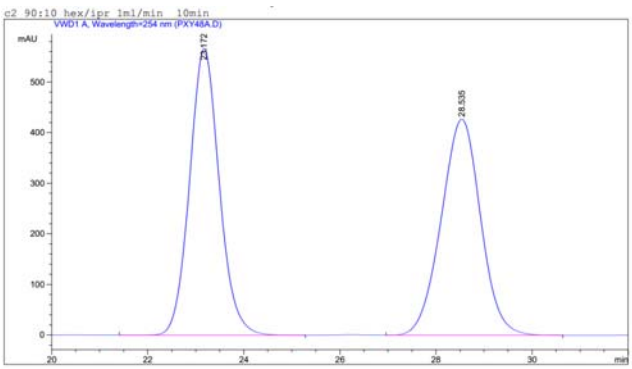
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.138	BB	1.1183	1.33661e4	182.73970	49.9327
2	39.426	BB	1.3299	1.34022e4	148.44897	50.0673

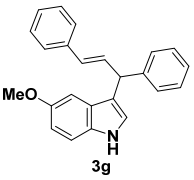




3f

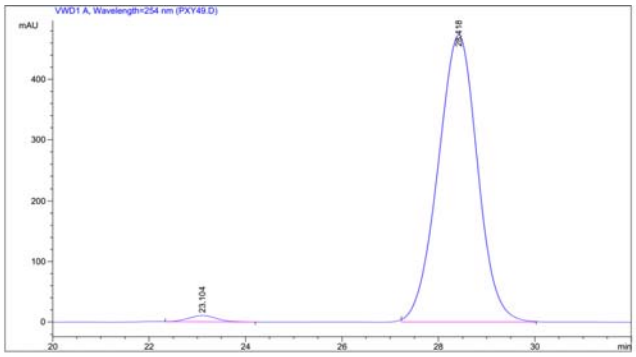
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.259	BP	0.8412	494.83313	7.40051	1.3358
2	39.353	BB	1.3351	3.65486e4	403.41574	98.6642

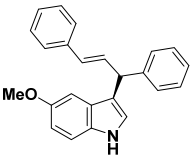




3g

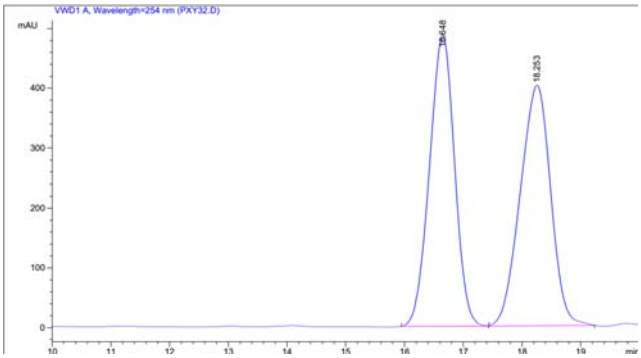
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.172	VB	0.6595	2.43914e4	566.58282	50.0250
2	28.535	VB	0.8810	2.43670e4	427.16690	49.9750

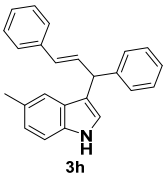




3g

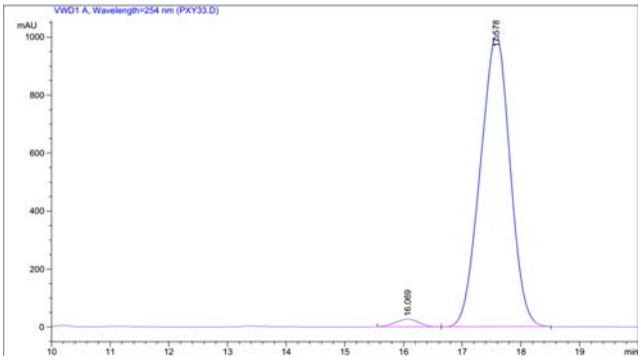
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.104	BP	0.6585	446.38608	10.51260	1.6307
2	28.418	BB	0.8855	2.69272e4	472.98013	98.3693

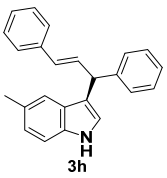




3h

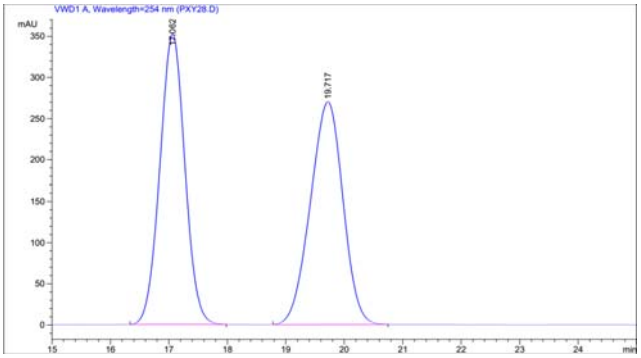
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.648	BB	0.4643	1.44585e4	486.94351	49.9045
2	18.253	BB	0.5680	1.45138e4	402.25812	50.0955

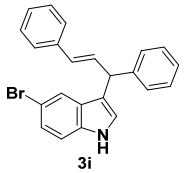




3h

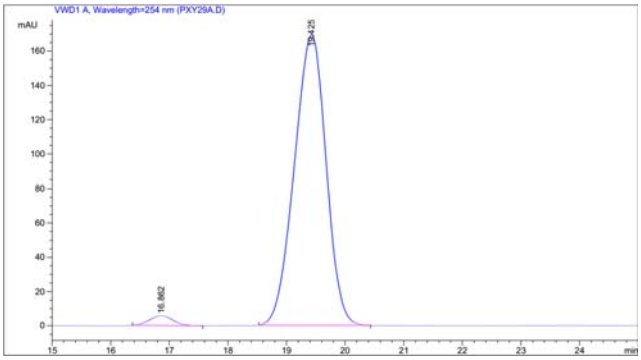
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.069	BP	0.4368	735.32397	26.42523	2.0401
2	17.578	VB	0.5420	3.53086e4	1005.89111	97.9599

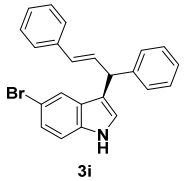




3i

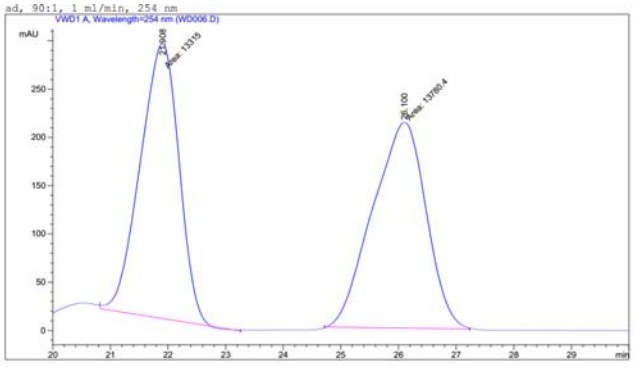
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.062	BB	0.4589	1.04805e4	352.62350	49.9730
2	19.717	BB	0.6059	1.04918e4	270.18921	50.0270

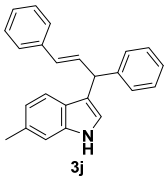




3i

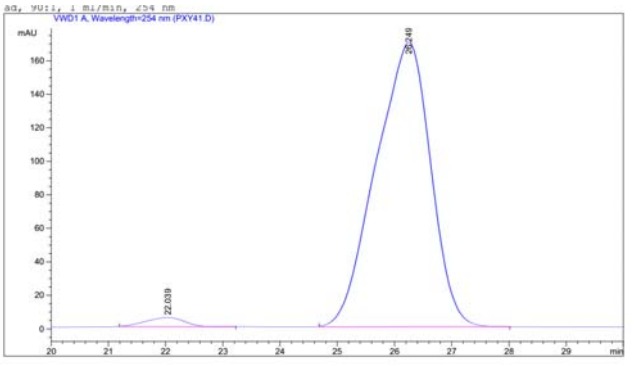
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.862	BB	0.4074	158.44281	5.69770	2.4298
2	19.425	BB	0.5899	6362.32959	169.27892	97.5702

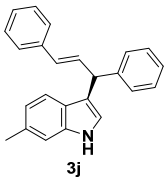




3j

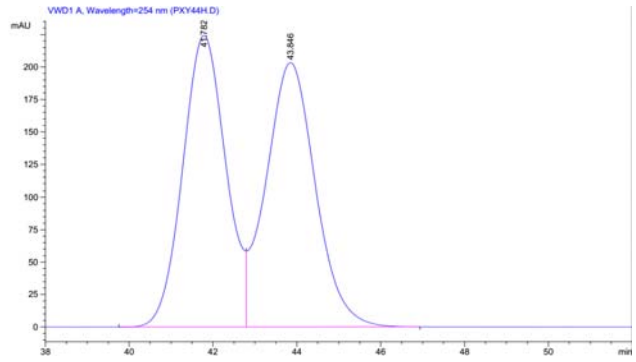
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.908	MM	0.7795	1.33150e4	284.69598	49.1411
2	26.100	MM	1.0764	1.37804e4	213.37245	50.8589

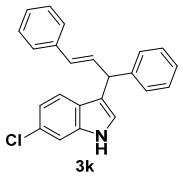




3j

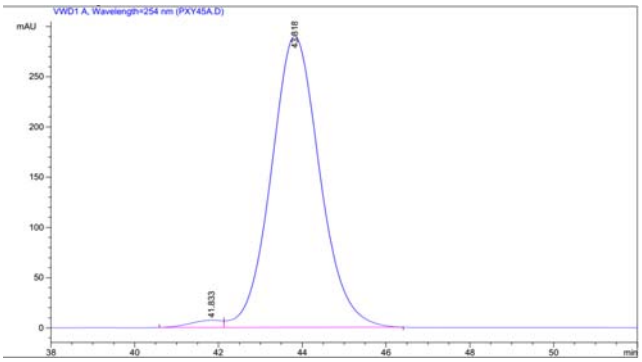
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.039	BB	0.6698	256.30084	5.49107	2.2159
2	26.249	BB	0.9638	1.13101e4	169.73598	97.7841

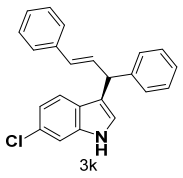




3k

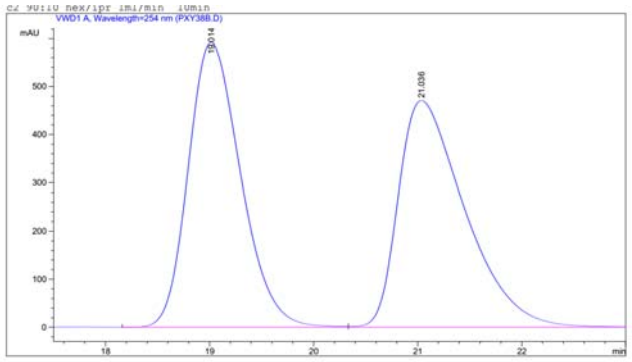
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.782	BV	1.0982	1.60314e4	224.47896	49.0461
2	43.846	VB	1.2315	1.66551e4	203.48674	50.9539

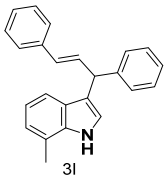




3k

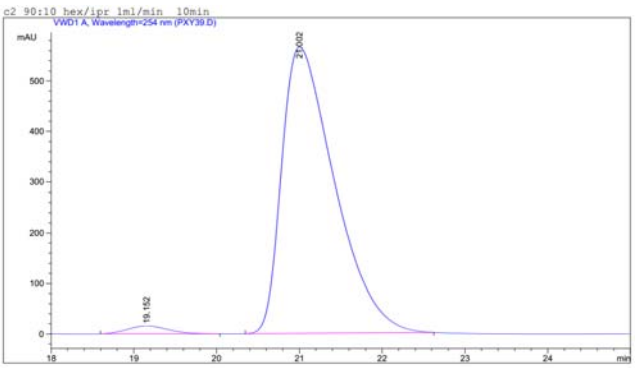
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.833	BV	0.6514	381.94278	7.22801	1.6053
2	43.818	VB	1.2185	2.34109e4	289.98016	98.3947

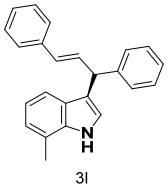




3l

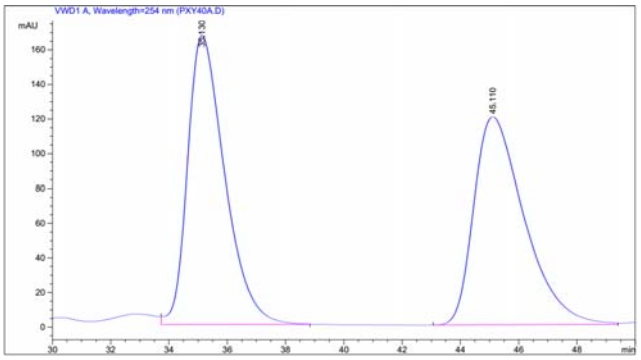
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.014	VV	0.5423	2.07160e4	591.86401	49.7549
2	21.036	VB	0.6726	2.09201e4	470.92886	50.2451

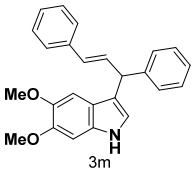




3l

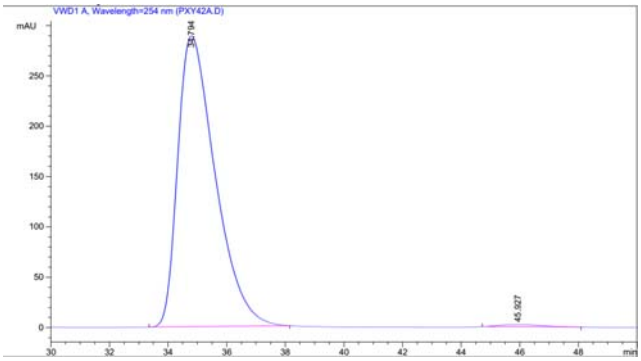
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.152	BB	0.5252	527.02032	15.65555	2.0533
2	21.002	BB	0.6707	2.51399e4	566.43872	97.9467

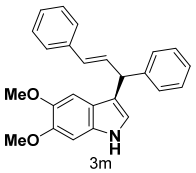




3m

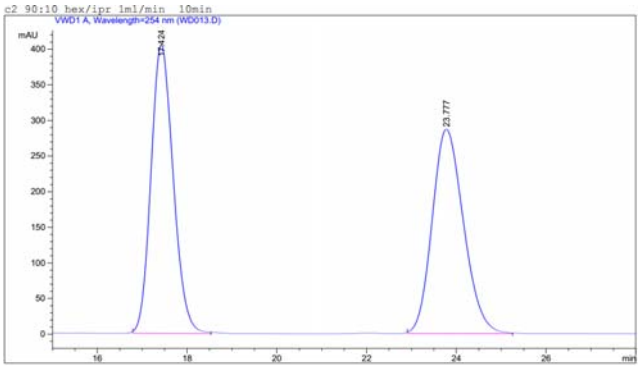
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.130	VB	1.3484	1.47938e4	166.93011	50.5887
2	45.110	BB	1.8299	1.44495e4	120.00943	49.4113

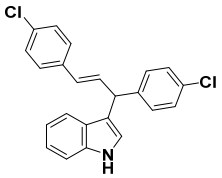




3m

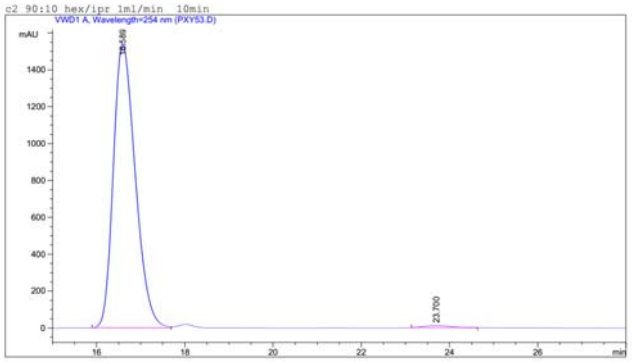
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.794	BB	1.3428	2.56608e4	289.08572	99.0717
2	45.927	BB	1.1992	240.43529	2.35633	0.9283

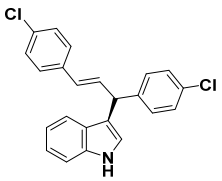




3n

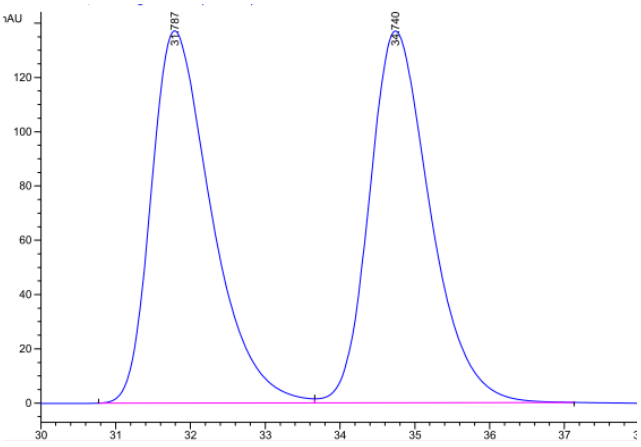
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.424	BB	0.5422	1.39571e4	404.60382	50.0522
2	23.777	BB	0.7527	1.39280e4	286.90149	49.9478

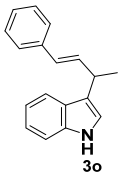




3n

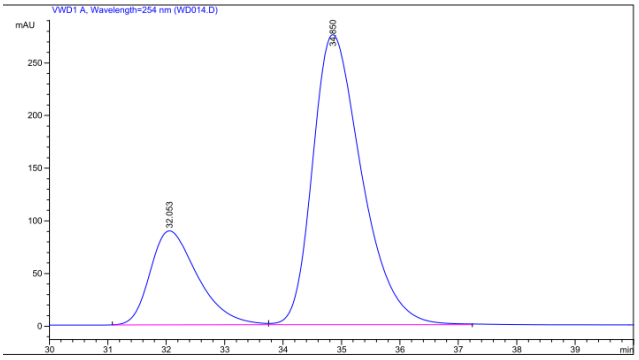
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.589	BB	0.5357	5.31962e4	1539.27161	99.1077
2	23.700	BB	0.6124	478.94327	11.40214	0.8923

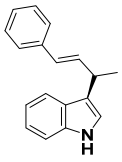




3o

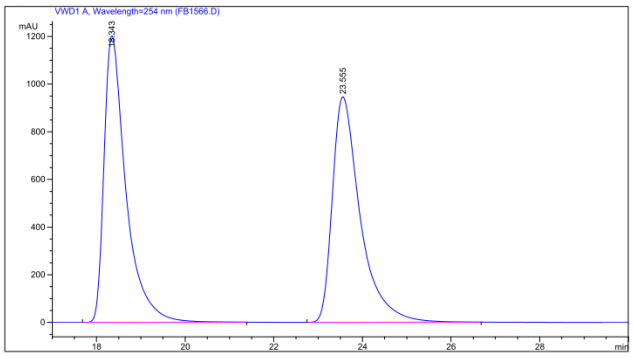
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	31.787	BV	0.8490	7691.15186	137.22783	49.7441
2	34.740	VB	0.8681	7770.28955	137.07729	50.2559

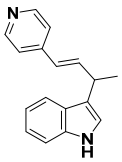




3o

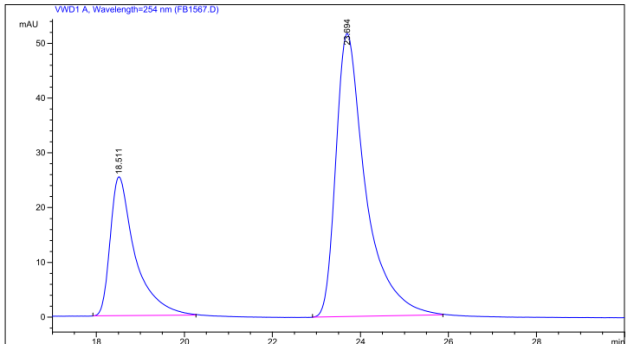
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.053	BV	0.8651	5064.81592	89.35329	23.9255
2	34.850	VB	0.8917	1.61043e4	275.48511	76.0745

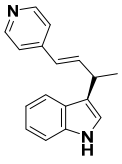




3p

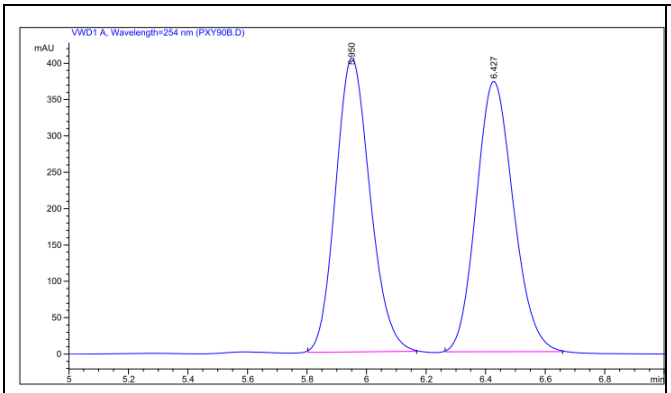
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.343	BB	0.5104	4.12040e4	1202.63586	49.9461
2	23.555	BB	0.6534	4.12930e4	945.90649	50.0539

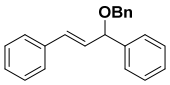




3p

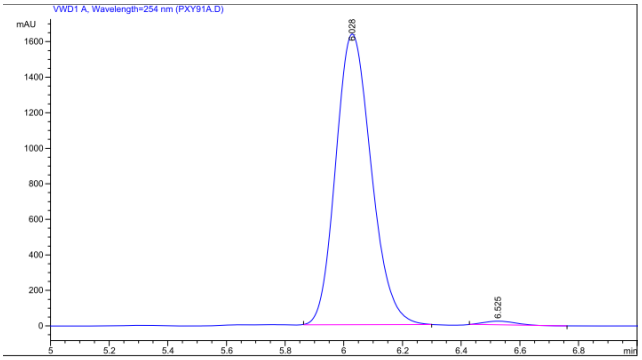
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.511	BB	0.5710	992.00275	25.37877	29.0197
2	23.694	BB	0.6890	2426.37769	51.68048	70.9803

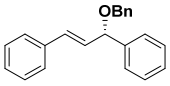




9

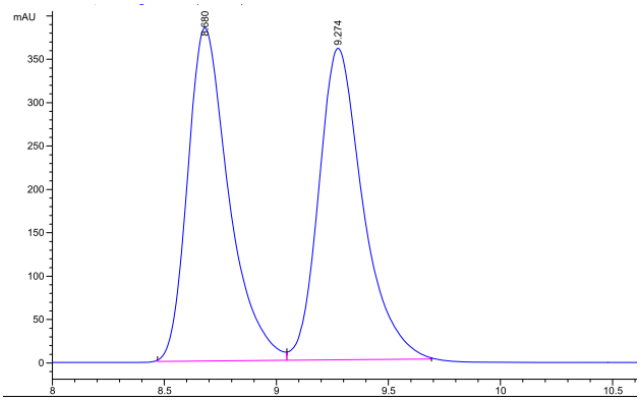
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.950	BB	0.1241	3247.01050	404.89063	50.1361
2	6.427	BB	0.1347	3229.38403	372.14075	49.8639

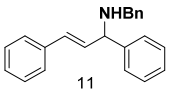




9

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.028	BB	0.1316	1.37731e4	1637.34143	98.8783
2	6.525	BP	0.1211	156.24391	21.14914	1.1217





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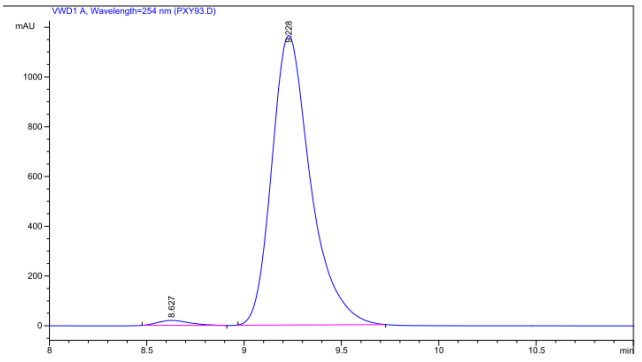
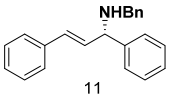
#	[min]		[min]	mAU *s	[mAU]	%
1	8.680	BB	0.1915	4913.24902	384.08768	49.9578
2	9.274	BB	0.2064	4921.54883	359.21280	50.0422





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Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.627	BB	0.1741	226.86583	20.07676	1.3869
2	9.228	BB	0.2098	1.61303e4	1163.66492	98.6131