Supporting information

Highly Enantioselective Cross-Electrophile Aryl-Alkenylation of Unactivated Alkenes

Zhi-Xiong Tian, Jin-Bao Qiao, Guang-Li Xu, Xiaobo Pang, Liangliang Qi, Wei-Yuan Ma, Zhen-Zhen Zhao, Jicheng Duan, Yun-Fei Du, Peifeng Su, Xue-Yuan Liu, Xing-Zhong Shu*

State Key Laboratory of Applied Organic Chemistry (SKLAOC), College of Chemistry and Chemical Engineering, Lanzhou University, 222 South Tianshui Road, Lanzhou, 730000, China.

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1. General Information

All reactions were carried out under an atmosphere of argon in sealed tube with magnetic stirring. Dry DMF, THF, CH_2Cl_2 were purified using a solvent-purification system that contained activated alumina and molecular sieves. Other solvents were dried and purified according to the procedure from ‘‘Purification of Laboratory Chemicals’’.[1]

Nickel catalysts, reductants were purchased from Acros, Alfa Aesar, Aldrich, Ark Pharm, and Strem. Other chemicals were purchased from TCI, Adamas, and Energy chemicals, and were directly used without further purifications.

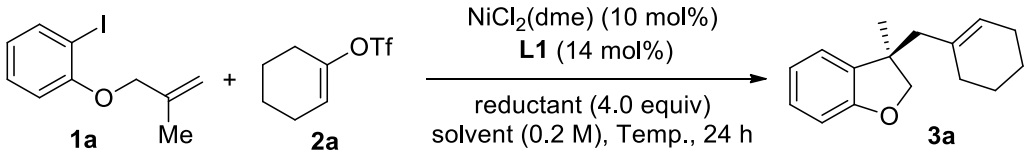
^1H and ^{13}C NMR spectra were collected on a Bruker AVANCE III 400MHz, JEOL JNM-ECS 400M and Agilent-NMR-inova 600 MHz spectrometer at room temperature. ^1H NMR spectra were reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were referenced to the signal of TMS (0 ppm). ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.00 ppm). Coupling constants, *J*, are reported in hertz (Hz). ^{19}F NMR spectra were also collected on Bruker AVANCE III 400 MHz spectrometers and Agilent-NMR-inova 600 MHz spectrometer at room temperature. Melting points were determined on a microscopic apparatus. IR spectra were collected using Bruker-TENSOR 27 spectrometer and Agilent Technologies Cary 630 FTIR, and only major peaks were reported in cm^{-1}. HRMS was performed on Bruker Apex II FT-ICR mass instrument (ESI). GC analysis was performed on Thermo Scientific TRACE 1300. GC-MS data was collected on Thermo Scientific TRACE DSQ GC-MS. The enantiomeric excess (ee) of the products was determined by chiral HPLC (Thermo Scientific UltiMate 3000) using Daicel CHIRALCEL® columns and Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 μm). Optical rotations were measured on an AUTOPOL IV Automatic polarimeter (Rudolph Research Analytical). The X-RAY was measured on Agilent SUPERNOVA. Thin layer chromatography was carried out using XINNUO SGF254 TLC plates. Flash chromatography was performed using XINNUO silica gel (200-300 mesh).

2. Optimization of Reaction Parameters

General Procedure

The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with catalyst (10 mol %, 0.010 mmol), **L1** (14 mol %, 3.8 mg, 0.014 mmol), reductant (4 equiv, 0.4 mmol), and solvent (0.5 mL). The reaction mixture was stirred for 5 min. Substrates **1a** (27.4 mg, 0.1 mmol) and **2a** (23.0 mg, 0.1 mmol) were then added. The reaction tube was sealed with a rubber septum, and removed from the glove box. The reaction mixture was stirred at appreciate temperature for 24 h. The reaction mixture was diluted with ethyl acetate (10 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected, diluted with ethyl acetate (2 mL), and analyzed by GC. The yield was determined versus the internal standard (dodecane). The rest solution was concentrated under the reduced pressure, and part of the residue was purified by thin layer chromatography on silica gel. The enantiomeric excess (ee) of the products was determined by chiral HPLC.

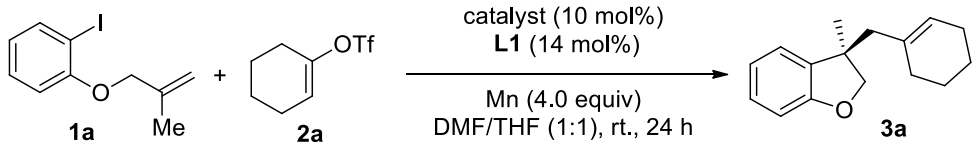
Table S1. Effect of reductant, solvent and temperature[a]



entry	reductant	solvent	temperature	yield (%)	ee (%)
1	Mn	DMF	rt.	59	93
2	Zn	DMF	rt.	trace	-
3	Mg	DMF	rt.	0	-
4	Mn	CH_3CN	rt.	0	-
5	Mn	DMSO	rt.	48	90
6	Mn	DMA	rt.	52	91
7	Mn	Toluene	rt.	0	-
8	Mn	THF	rt.	trace	-
9	Mn	Dioxane	rt.	0	-
10	Mn	DMF/THF(4/1)	rt.	60	94
11	Mn	DMF/THF(3/2)	rt.	63	94
12	Mn	DMF/THF(1/1)	rt.	67	95
13	Mn	DMF/THF(2/3)	rt.	55	95
14	Mn	DMF/THF(1/4)	rt.	31	94
15	Mn	DMF/THF(1/1)	0 ^{o}C	trace	-
16	Mn	DMF/THF(1/1)	10 ^{o}C	34	95
17	Mn	DMF/THF(1/1)	40 ^{o}C	60	95
18	Mn	DMF/THF(1/1)	60 ^{o}C	54	93

[a]**1a** (0.1 mmol) and **2a** (0.1 mmol) was used. The yields were determined by GC analysis with doecane as an internal standard. The ees were determined by chiral HPLC.

Table S2. Effect of catalyst[a]

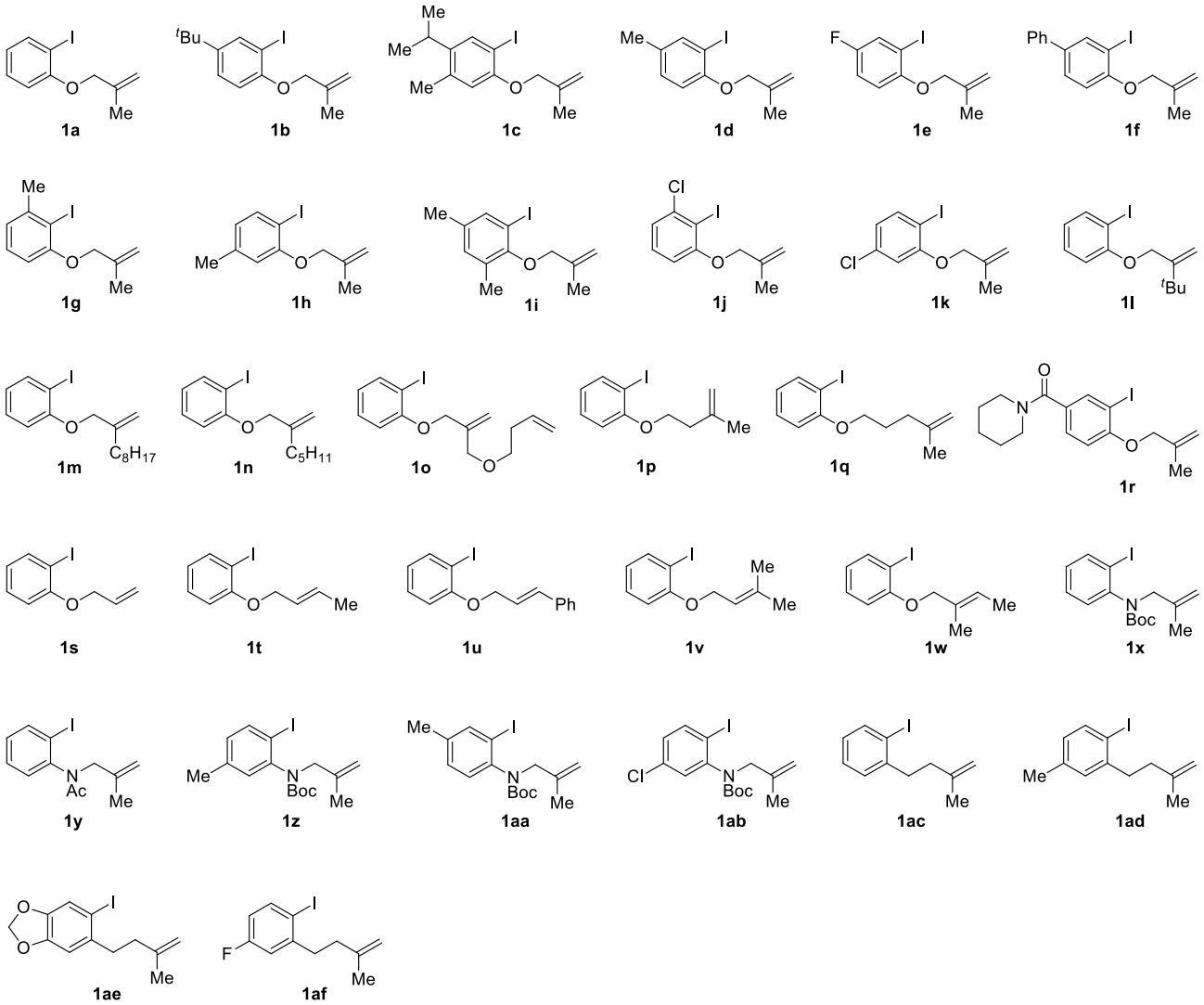


entry	catalyst	yield (%)	ee (%)
1	NiF_2	0	-
2	$NiCl_2$	30	91
3	$NiBr_2$	69	97
4	NiI_2	79 (77)[b]	98
5	$NiCl_2$(dme)	67	95
6	$Ni(cod)_2$	68	95
7	$NiCl_2$(dppp)	45	94
8	$NiCl_2$(dppf)	0	-
9	$CoCl_2$	0	-
10	$CoBr_2$	0	-
11	$PdCl_2$	0	-
12	$CuCl_2$	0	-

[a]**1a** (0.1 mmol) and **2a** (0.1 mmol) was used. The yields were determined by GC analysis with doecane as an internal standard. The ees were determined by chiral HPLC. [b]Isolated yield.

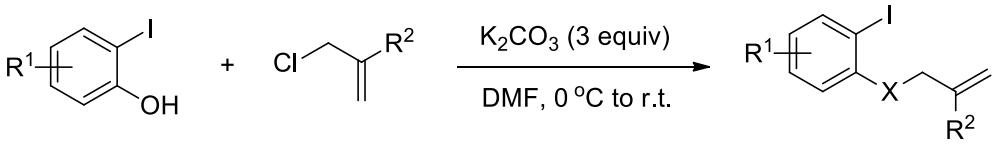
3. Synthesis of Substrates

3.1 Synthesis of Aryl Iodide tethered Alkenes



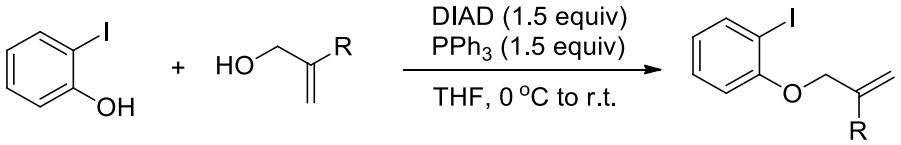
Known compounds **1a**,[2] **1b**,[2] **1d**,[3] **1e**,[4] **1f**,[5] **1h**[5], **1k**[6], **1y**[2], were prepared according to the literature procedure in ref.2. Known compound **1n**[7], **1p**[2], **1s**[8], **1t**[9], **1u**[10], **1v**[11], **1w**[12], was prepared according to the literature procedure in ref.13. Known compound **1x**[14] was prepared according to the literature procedure in ref.14, Known compound **1ac**[15] was prepared according to the literature procedure in ref.15. The preparation of new compounds, and their characterization data are provided as follows.

General procedure A:



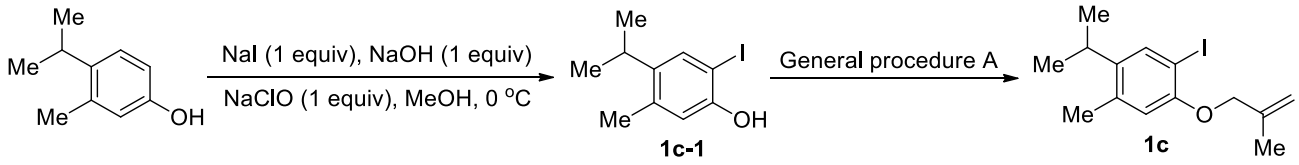
These compounds were synthesized according to the literature procedure.[2] To a solution of phenol (10.0 mmol) in DMF (30.0 mL) was added K_2CO_3 (4.15 g, 30.0 mmol) at 0 °C, followed by slowly addition of allyl halide (10.0 mmol) after 20 min. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water (40.0 mL), and extracted with ethyl acetate (3 × 30.0 mL). The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$, brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the product.

General procedure B:



These compounds were synthesized according to the literature procedure.[13] To a solution of alcohol (10.0 mmol) and phenol (10.0 mmol) in THF (30.0 mL) was added PPh_3 (2.62 g, 10.0 mmol) at 0 °C, followed by slowly addition of diisopropyl azodicarboxylate (DIAD, 2.02 g, 10.0 mmol) after 20 min under argon. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water (40.0 mL), and extracted with ethyl acetate (3 × 30.0 mL). The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$, brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the product.

1-Iodo-5-isopropyl-4-methyl-2-((2-methylallyl)oxy)benzene (1c)



Step 1: Compound **1c-1** was synthesized according to the literature procedure.[16] To a solution of phenol (10.0 mmol) in MeOH (30.0 mL) at 0 °C was added NaI·$2H_2O$ (1.86 g, 10.0 mmol) and

NaOH (0.40 g, 10.0 mmol), followed by slowly addition of NaClO (15.0 ml, 10.0 mmol, 5% aqueous solution,) after 20 min. The reaction mixture was stirred overnight at the same temperature. The MeOH was removed under reduced pressure, and water (30.0 mL) was added. The reaction mixture was neutralized with aqueous HCl (2.0 M) to pH < 7, and extracted with ethyl acetate (3 × 20.0 mL). The combined organic layers were washed with water, saturated aqueous $Na_2S_2O_3$, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give 2-iodo-4-isopropyl-5-methylphenol **(1c-1)**.

1.55 g, 56% yield, white solid, mp: 40-42 ^oC, R_f = 0.3 (silica gel, petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1 H), 6.78 (s, 1 H), 5.05 (s, 1 H), 3.03-2.97 (m, 1 H), 2.25 (s, 3 H), 1.18 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 141.6, 137.7, 134.3, 116.6, 82.4, 28.6, 23.3, 19.0.

IR (neat, cm^{-1}): 2963, 1481, 1459, 1398, 1299, 1269, 1200, 880, 762, 725.

HRMS (ESI): $[M+H]^+$ calcd for $C_{10}H_{14}IO$ 277.0084, found 277.0093.

Step 2: Compound **1c** was prepared from 2-iodo-4-isopropyl-5-methylphenol (**1c-1**, 1.38 g, 5.0 mmol) and 3-chloro-2-methylprop-1-ene (0.45 g, 5.0 mmol) according to the General procedure A.

1.39 g, 84% yield, colorless oil, R_f = 0.7 (silica gel, petroleum ether).

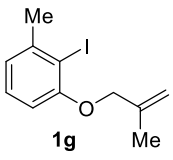
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1 H), 6.57 (s, 1 H), 5.19 (s, 1 H), 5.00 (s, 1 H), 4.43 (s, 2 H), 3.03-2.96 (m, 1 H), 2.27 (s, 3 H), 1.86 (s, 3 H), 1.18 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 141.4, 140.5, 136.4, 135.7, 114.4, 112.6, 83.3, 72.6, 28.6, 23.3, 19.5, 19.4.

IR (neat, cm^{-1}): 2963, 2872, 1654, 1591, 1490, 1252, 1053, 1030, 902, 716.

HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{20}IO$ 331.0553, found 331.0562.

2-Iodo-1-methyl-3-((2-methylallyl)oxy)benzene (1g)



1g

This compound was prepared from 2-iodo-3-methylphenol (2.34 g, 10.0 mmol) and 3-chloro-2-methylprop-1-ene (0.91 g, 10.0 mmol) according to General procedure A.

22.5g, 78% yield, colorless oil, R_f = 0.7 (silica gel, petroleum ether).

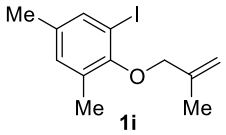
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (t, *J* = 8.0 Hz, 1 H), 6.87 (d, *J* = 8.0 Hz, 1 H), 6.60 (d, *J* = 8.0 Hz, 1 H), 5.22 (s, 1 H), 5.01 (s, 1 H), 4.47 (s, 2 H), 2.47 (s, 3 H), 1.88 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 143.5, 140.4, 128.5, 122.4, 112.8, 109.2, 93.6, 72.7, 28.8, 19.5.

IR (neat, cm^{-1}): 3290, 2918, 1959, 1650, 1565, 1450, 1260, 1057, 902, 764.3

HRMS (ESI): [M+H] $^{+}$ calcd for $C_{11}H_{14}IO$ 289.0084, found 289.0091.

1-Iodo-3,5-dimethyl-2-((2-methylallyl)oxy)benzene (1i)



1i

This compound was prepared from 2-iodo-4,6-dimethylphenol (2.48 g, 10.0 mmol) and 3-chloro-2-methylprop-1-ene (0.91 g, 10.0 mmol) according to General procedure A.

2.48 g, 82% yield, colorless oil, R_f = 0.7 (silica gel, petroleum ether).

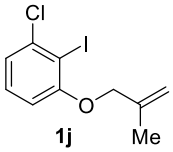
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1 H), 6.94 (s, 1 H), 5.19 (s, 1 H), 5.01 (s, 1 H), 4.23 (s, 2 H), 2.29 (s, 3 H), 2.23(s, 3 H), 1.93 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 141.2, 137.3, 135.6, 132.2, 131.8, 113.0, 91.8, 76.04, 20.2, 19.9, 17.0.

IR (neat, cm^{-1}): 3077, 2973, 2858, 1653, 1469, 1272, 1123, 1041, 995, 853.

HRMS (ESI): [M+H] $^{+}$ calcd for $C_{12}H_{16}IO$ 303.0240, found 303.0247.

1-Chloro-2-iodo-3-((2-methylallyl)oxy)benzene (1j)



1j

This compound was prepared from 3-chloro-2-iodophenol (2.54 g, 10.0 mmol) and 3-chloro-2-methylprop-1-ene (0.91 g, 10.0 mmol) according to General procedure A.

22.5g, 78% yield, colorless oil, R_f = 0.7 (silica gel, petroleum ether).

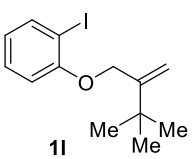
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 8.0 Hz, 1 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 6.65 (d, *J* = 8.0 Hz, 1 H), 5.20 (s, 1 H), 5.03 (s, 1 H), 4.48 (s, 2 H), 1.87 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 139.8, 139.8, 129.6, 121.9, 113.2, 109.7, 91.7, 73.0, 19.5.

IR (neat, cm^{-1}): 2975, 2920, 1572, 1440, 1259, 1060, 1014, 904, 766, 697

HRMS (ESI): [M+H] $^{+}$ calcd for $C_{10}H_{11}ClIO$ 308.9538, found 308.9542.

1-(3, 3-Dimethyl-2-methylenebutoxy)-2-iodobenzene (1l)



1l

This compound was prepared from 2-iodophenol (2.20 g, 10.0 mmol) and 3,3-dimethyl-2-methylenebutan-1-ol (1.14 g, 10.0 mmol) according to General procedure B.

1.96 g, 62% yield, colorless oil, R_f = 0.8 (silica gel, petroleum ether).

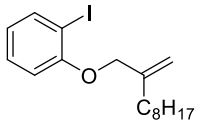
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.29-7.24 (m, 1 H), 6.79 (dd, *J* = 1.2, 8.4 Hz, 1 H), 6.69 (m, 1 H), 5.33 (d, *J* =1.2 Hz, 1 H), 5.13 (d, *J* =0.8 Hz, 1 H), 4.61 (s, 2 H), 1.18 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 151.2, 139.5, 129.3, 122.4, 112.1, 110.0, 86.4, 69.1, 34.8, 29.5.

IR (neat, cm^{-1}): 2961, 2868, 1638, 1582, 1472, 1438, 1274, 1019, 909, 747 cm^{-1}.

HRMS (ESI): $[M+H]^+$ calcd for $C_{13}H_{18}IO$ 317.0397, found 317.0400.

1-Iodo-2-((2-methylenedecyl)oxy)benzene (1m)



1m

This compound was prepared from 2-iodophenol (2.20 g, 10.0 mmol) and 2-methylenedecan-1-ol (1.70 g, 10.0 mmol) according to the General procedure B.

2.42 g, 65% yield, colorless oil, R_f = 0.8 (silica gel, petroleum ether).

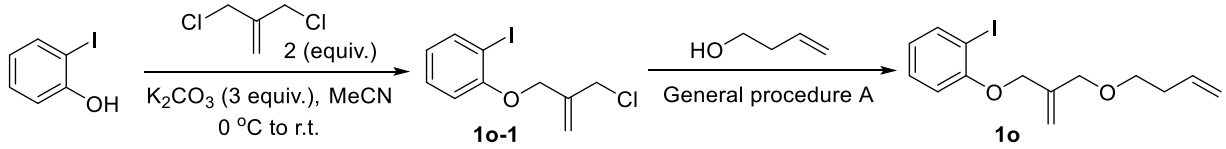
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 1.6, 7.6 Hz, 1 H), 7.29-7.25 (m, 1 H), 6.79 (dd, *J* = 0.8, 8.4 Hz, 1 H), 6.70 (m, 1 H), 5.22 (s, 1 H), 5.01 (d, *J* =0.8 Hz, 1 H), 4.50 (s, 2 H), 2.18 (t, *J* = 8.0 Hz, 2 H), 1.54-1.47 (m, 2 H), 1.31-1.27 (m, 10 H), 0.88 (t, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 144.3, 139.5, 129.3, 122.5, 112.3, 111.9, 86.6, 71.6, 33.2, 31.9, 29.44, 29.41, 29.3, 27.6, 22.7, 14.1.

IR (neat, cm^{-1}): 2926, 2857, 1582, 1472, 1439, 1291, 1244, 1019, 746, 727.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{26}IO$ 373.1023, found 373.1024.

1-((2-((But-3-en-1-yloxy)methyl)allyl)oxy)-2-iodobenzene (1o)



Compound **1o-1** was synthesized according to the literature procedure.[17] To a solution of K_2CO_3 (4.15 g, 30.0 mmol), 3-chloro-2-(chloromethyl)prop-1-ene (2.32 mL, 20.0 mmol) in acetonitrile (25.0 mL) was added 2-iodophenol (2.20 g, 10.0 mmol) at 0 ℃. The reaction mixture was stirred at room temperature overnight, and filtered through a pad of celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford 2.16 g of **1o-1** (93% purity, mixed with dichloromethyl ethylene).

Compound **1o** was prepared from the above crude **1o-1** and but-3-en-1-ol (0.50 g, 7.0 mmol) according to the General procedure A.

1.69 g, 49% yield for two steps, colorless oil, R_f = 0.3 (silica gel, petroleum ether/ethyl acetate = 50:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.30-7.25 (m, 1 H), 6.82 (dd, *J* = 8.4, 1.2 Hz, 1 H), 6.71 (m, 1 H), 5.87-5.77 (m, 1 H), 5.43 (d, *J* = 0.4 Hz, 1 H), 5.29 (d, *J* = 0.8 Hz, 1 H),

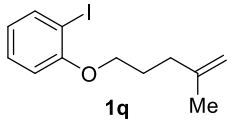
5.12-5.01 (m, 2 H), 4.59 (s, 2 H), 4.13 (s, 2 H), 3.52 (t, *J* = 6.8 Hz, 2 H), 2.38-2.33 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 140.9, 139.4, 135.2, 129.3, 122.6, 116.4, 114.8, 112.2, 86.5, 71.6, 69.7, 69.4, 34.2.

IR (neat, cm^{-1}): 3071, 2857, 1582, 1474, 1440, 1247, 1098, 1018, 917, 747.

HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{18}IO_2$ 345.0346, found 345.0352.

1-Iodo-2-((4-methylpent-4-en-1-yl)oxy)benzene (1q)



1q

This compound was prepared from 2-iodophenol (2.20 g, 10.0 mmol) and 4-methylpent-4-en-1-ol (1.00 g, 10.0 mmol) according to General procedure B. 2.05g, 68% yield, colorless oil, R_f = 0.7 (silica gel, petroleum ether).

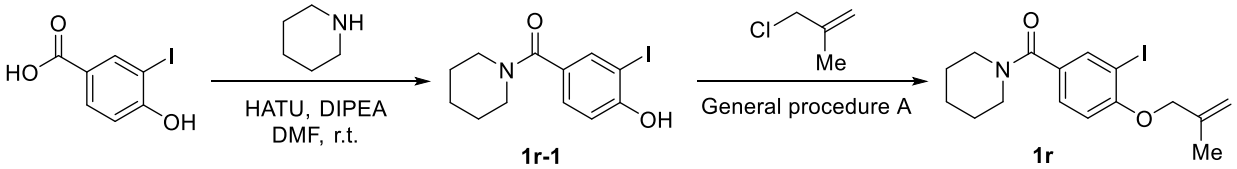
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 1.6 Hz, *J* = 7.6 Hz, 1 H), 7.29-7.24 (m, 1 H), 6.78 (dd, *J* = 0.8 Hz, *J* = 8.4 Hz, 1 H), 6.68 (dt, *J* = 1.2 Hz, *J* = 7.6 Hz, 1 H), 4.75 (s, 2 H), 4.00 (t, *J* = 6.0 Hz, 2 H), 2.27 (t, *J* = 7.2 Hz, 2 H), 2.01-1.94 (m, 2 H),1.77 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 144.8, 139.3, 129.3, 122.3, 112.0, 110.5, 86.7, 68.4, 34.0, 27.0, 22.4.

IR (neat, cm^{-1}): 3072, 2918, 2874, 1694, 1464, 1275, 1052, 1018, 889, 746

HRMS (ESI): $[M+H]^+$ calcd for $C_{12}H_{16}IO$ 303.0240, found 303.0248

(3-Iodo-4-((2-methylallyl)oxy)phenyl)(piperidin-1-yl)methanone (1r)



1r-1 **1r**

Step 1: Compound **1r-1** was synthesized according to the literature procedure.[18] To a solution of 4-hydroxy-3-iodobenzoic acid (2.64 g, 10.0 mmol) in DMF (25.0 mL) at 0 ℃ was added 1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate (HATU, 5.70 g, 15.0 mmol) and *N*, *N*-Diisopropylethylamine (DIPEA, 2.50 mL, 15.0 mmol). The reaction mixture was stirred at room temperature for 1 h, and piperidine (1.0 mL, 12.0 mmol) was dropwise added. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with H_2O, and extracted with ethyl acetate (3 × 20.0 mL). The combined organic layers were washed with saturated aqueous NH_4Cl, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give **1r-1** as a white solid (2.71 g, 82% yield, mp: 181-183 ^oC).

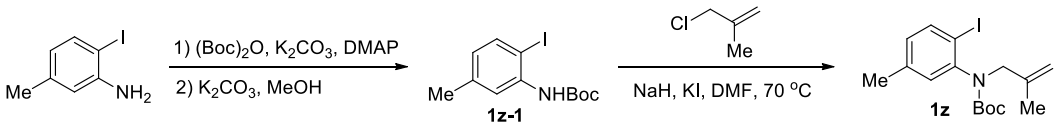
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1 H), 7.44 (s, 1 H), 7.20 (d, *J* = 6.8 Hz, 1 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 3.67 (brs, 2 H), 3.41 (brs, 2 H), 1.68-1.60 (m, 6 H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 157.3, 137.5, 128.8, 128.7, 115.0, 84.8, 49.1, 43.6, 26.3, 25.6, 24.4.
IR (neat, cm^{-1}): 3728, 2937, 2621, 1699, 1507, 1277, 1114, 1025, 832, 761.
HRMS (ESI): $[M+H]^+$ calcd for $C_{12}H_{15}INO_2$ 332.0142, found 332.0150.

Step 2: Compound **1r** was prepared from **1r-1** (1.66 g, 5.0 mmol) and 3-chloro-2-methylprop-1-ene (0.5 mL, 5.0 mmol) according to the General procedure A.

1.48 g, 77% yield, white solid, mp: 62-64 ^oC, R_f = 0.3 (silica gel, petroleum ether/ethyl acetate = 4:1).

^{1}H NMR (400 MHz , $CDCl_3$): δ 7.84 (d, *J* = 2.0 Hz, 1 H), 7.35 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.78 (d, *J* = 8.4 Hz, 1 H), 5.19 (s, 1 H), 5.03 (s, 1 H), 4.51 (s, 2 H), 3.60 (brs, 2 H), 3.45 (brs, 2 H), 1.87 (s, 3 H), 1.68-1.59 (m, 6 H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 157.7, 139.5, 138.1, 130.3, 128.4, 113.0, 111.3, 86.0, 72.4, 48.8, 43.2, 26.2, 25.4, 24.4, 19.3.
IR (neat, cm^{-1}): 3474, 3459, 2910, 2823 1634, 1437, 1277, 1262, 776, 751.
HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{21}INO_2$ 386.0611, found 386.0616.

***Tert*-butyl (2-iodo-4-methylphenyl)(2-methylallyl)carbamate (1z)**



General Procedure:

Compound **1z-1** was synthesized according to the literature procedure.[14] To a solution of 2-iodo-5-methylaniline (2.33 g, 10.0 mmol) in THF (30.0 mL) was added K_2CO_3 (2.77 g, 20.0 mmol) and DMAP (0.12 g, 1.0 mmol) at 0 ^oC, followed by slowly addition of $(Boc)_2O$ (2.29 g, 10.5 mmol) after 10 min. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was quenched with saturated aqueous solution of $NaHCO_3$ (30.0 mL), and extracted with ethyl acetate (3 × 30.0 mL). The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$, brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude product. The residue was then engaged in the known procedure (K_2CO_3 (4.15 g, 30.0 mmol), MeOH (30.0 mL), 3 h, 70 ℃) to obtain the crude product **1z-1**.

To a solution of the above crude compound **1z-1** in DMF (20.0 mL) was added KI (1.99 g, 12.0 mmol) and NaH (0.36 g, 15.0 mmol) at 0 ^oC, followed by slowly addition of 3-chloro-2-methylprop-1-ene (0.91 g, 10.0 mmol) after 20 min. The reaction mixture was allowed to

warm to room temperature and stirred at 70 ^{o}C for 3 h. The reaction was quenched with water (40.0 mL), and extracted with ethyl acetate (3 × 30.0 mL). The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the product **1z**.

2.79 g, 72% yield, colorless oil, R_f = 0.7 (silica gel, petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ 7.70 (d, *J* = 8.0 Hz, 1 H), [7.04 (s), 6.95 (s), 1 H], 6.79 (d, *J* = 7.2 Hz, 1 H), 4.85 (s, 1 H), 4.77 (s, 1 H), [4.56 (d, *J* = 15.6 Hz), 4.48 (d, *J* = 16.0 Hz), 1 H], 3.48 (d, *J* = 15.6 Hz, 1 H), 2.29 (s, 3 H), 1.82 (s, 3 H), [1.52 (s), 1.37 (s), 9 H].

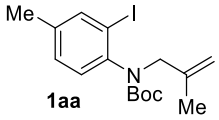
^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ154.2, 144.4, 141.2, 139.2, 138.9, 138.7, 130.9, 130.3, 129.9, 129.6, 112.8, 112.6, 95.8, 80.6, 80.2, 56.3, 55.2, 28.2, 20.9, 20.6.

IR (neat, cm^{-1}): 2974, 2925, 1706, 1593, 1367, 1299, 1170, 937, 861, 759.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{23}INO_2$ 388.0768, found 388.0774.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **1z** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.

***Tert*-butyl (2-iodo-5-methylphenyl)(2-methylallyl)carbamate (1aa)**



1aa

This compound was prepared from 2-iodo-4-methylaniline (2.33 g, 10.0 mmol) according to the General Procedure for the synthesis of **1z**.

2.94 g, 76% yield, colorless oil, R_f = 0.7 (silica gel, petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ 7.68 (s, 1 H), 7.26-6.99 (m, 2 H), 4.83 (s, 1 H), 4.74 (s, 1 H), [4.58 (d, *J* = 15.2 Hz), 4.49 (d, *J* = 15.2 Hz), 1 H], 3.47 (d, *J* = 16.0 Hz, 1 H), 2.29 (s, 3 H), 1.81 (s, 3 H), [1.52 (s), 1.36 (s), 9 H].

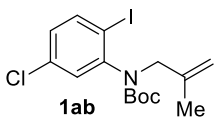
^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ154.3, 142.0, 141.8, 141.4, 141.2, 140.0, 139.7, 139.0, 138.6, 129.6, 129.3, 129.1, 113.0, 112.8, 99.7, 80.5, 80.0, 56.2, 55.1, 28.2, 20.5, 20.4.

IR (neat, cm^{-1}): 3077, 2976, 2925, 1706, 1487, 1368, 1297, 1171, 866, 763.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{23}INO_2$ 388.0768, found 388.0774.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **1aa** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.

***Tert*-butyl (5-chloro-2-iodophenyl)(2-methylallyl)carbamate (1ab)**



1ab

This compound was prepared from 5-chloro-2-iodoaniline (2.53 g, 10.0 mmol)

according to the General Procedure for the synthesis of **1z**.

3.30 g, 81% yield, white solid, mp: 184-186 ^{o}C, R_f = 0.6 (silica gel, petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ 7.77 (d, *J* = 8.4 Hz, 1 H), [7.26 (s), 7.20 (s), 1 H], 6.70 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 1 H), 4.88 (s, 1 H), 4.75 (s, 1 H), 4.58-4.54 (m, 1 H), 3.50-3.46 (m, 1 H), 1.82 (s, 3 H), [1.52 (s), 1.37 (s), 9 H].

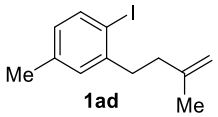
^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ 153.7, 145.7, 140.8, 140.0, 134.2, 129.8, 128.8, 113.5, 97.6, 80.7, 56.1, 55.0, 28.2, 20.48.

IR (neat, cm^{-1}): 2976, 1708, 1572, 1463, 1366, 1289, 1165, 863, 729.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{20}ClINO_2$ 408.0222, found 408.0219.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **1ab** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.

1-Iodo-4-methyl-2-(3-methylbut-3-en-1-yl)benzene (1ad)



1ad

This compound was prepared from (2-iodo-5-methylphenyl)methanol (2.48 g, 10.0 mmol) according to the literature reference 15.

1.86 g, 65% yield, colorless oil, R_f = 0.8 (silica gel, petroleum ether).

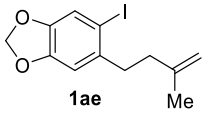
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 2.0 Hz, 1 H), 6.70 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1 H), 4.76 (s, 2 H), 2.81-2.77 (m, 2 H), 2.31-2.23 (m, 5 H), 1.81 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 144.4, 139.1, 138.2, 130.2, 128.7, 110.3, 96.3, 39.3, 38.4, 22.6, 20.9.

IR (neat, cm^{-1}): 3075, 2951, 2924, 2854, 1648, 1592, 1467, 1122, 1011, 886.

HRMS (APCI): $[M+H]^+$ calcd for $C_{12}H_{15}I$ 287.0291, found 287.0300.

5-Iodo-6-(3-methylbut-3-en-1-yl)benzo[d][1,3]dioxole (1ae)



1ae

This compound was prepared from 5-(bromomethyl)-6-iodobenzo[d][1,3]dioxole[21] (1.52 g, 10.0 mmol) according to the literature reference 15.

2.40 g, 76% yield, colorless oil, R_f = 0.4 (silica gel, petroleum ether).

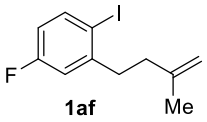
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (s, 1 H), 6.73 (s, 1 H), 5.93 (s, 2 H), 4.75 (d, *J* = 9.6 Hz, 2 H), 2.78-2.74 (m, 2 H), 2.24-2.20 (m, 2 H), 1.80 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 146.6, 144.9, 137.9, 118.5, 110.5, 109.1, 101.4, 87.6, 39.3, 38.4, 22.6.

IR (neat, cm^{-1}): 3074, 2925, 1648, 1596, 1226, 1107, 1041, 935, 889, 826.

HRMS (ESI): [M+H]$^+$ calcd for $C_{12}H_{14}IO_2$ 317.0041, found 317.0033.

4-Fluoro-1-iodo-2-(3-methylbut-3-en-1-yl)benzene (1af)



1af

This compound was prepared from (5-fluoro-2-iodophenyl)methanol (2.52 g, 10.0 mmol) according to the literature reference 15.

1.62 g, 56% yield, colorless oil, R_f = 0.4 (silica gel, petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.19 (m, 1 H), 6.96 (d, *J* = 8.0 Hz, 1 H), 6.91-6.85 (m, 1 H), 4.72-4.70 (m, 2 H), 2.77-2.73 (m, 2 H), 2.33-2.29 (m, 2 H), 1.76 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (d, J_{C-F} = 325 Hz), 144.8 (d, J_{C-F} = 8.0 Hz), 144.7, 129.6 (d, J_{C-F} = 9.0 Hz), 124.0, 115.1 (d, J_{C-F} = 21.0 Hz), 112.6 (d, J_{C-F} = 21.0 Hz), 110.5, 39.2, 33.9, 22.5.

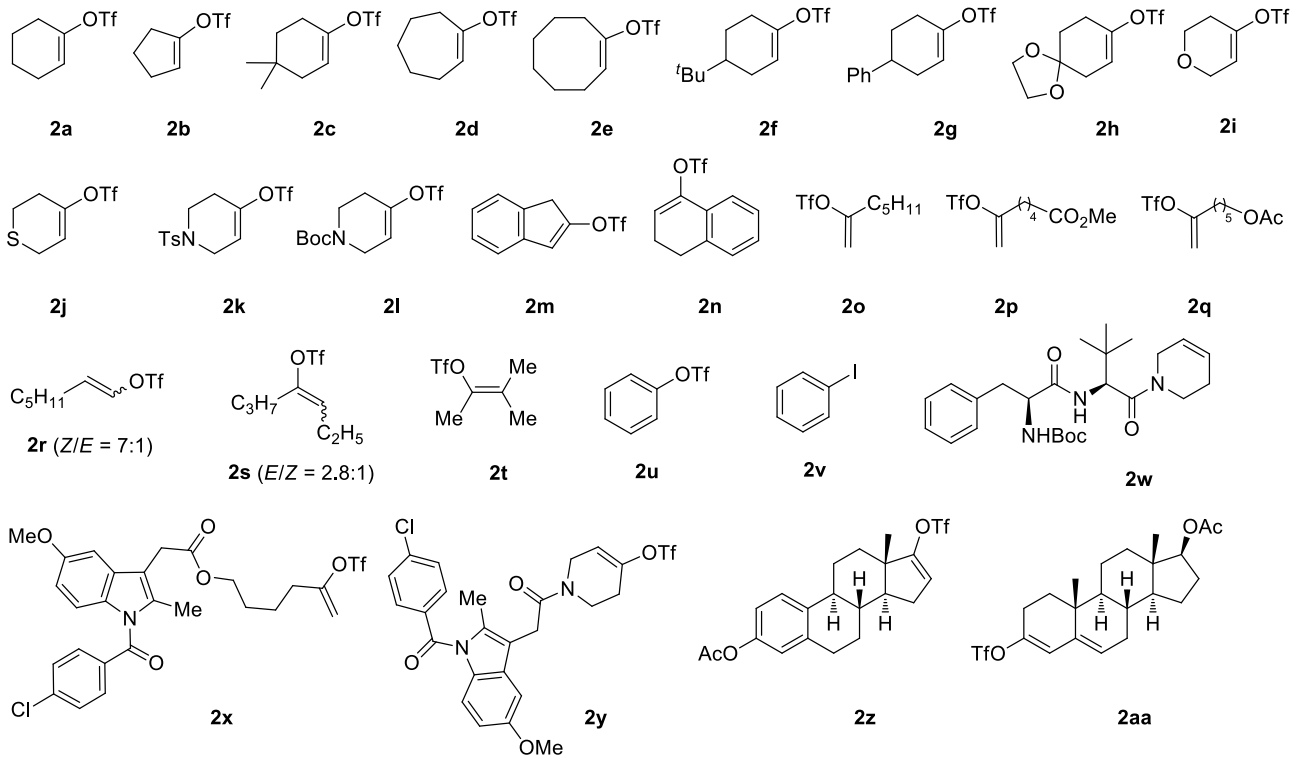
148.4, 146.6, 144.9, 137.9, 118.5, 110.5, 109.1, 101.4, 87.6, 39.3, 38.4, 22.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -114.0

IR (neat, cm^{-1}): 2917, 2849, 1590, 1453, 1417, 1270, 1112, 887, 781, 688.

HRMS (ESI): [M+H]$^+$ calcd for $C_{11}H_{13}FI$ 291.0040, found 291.0049.

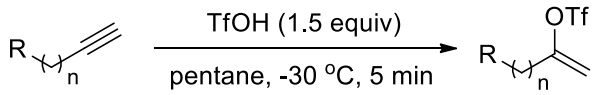
3.2 Synthesis of Alkenyl Triflate Reagents 2a-2v



Alkenyl triflates **2a,**[22] **2b,**[22] **2c**[23,] **2d**,[22] **2e**,[22] **2f**,[22] **2g**,[24] **2h**,[22] **2i,**[22] **2j**,[25] **2k**,[26] **2l**,[27] **2m**,[28] **2n**,[22] **2z**,[29] **2aa**,[30] are known compounds, and were synthesized according the literature procedure.[22] Known

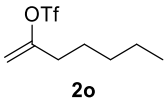
compound **2r** was prepared according to the literature procedure.[31] Known compound **2s** was prepared according to the literature procedure.[32] Known compound **2t** was prepared according to the literature procedure.[33] Known compound **2u** was prepared according to the literature procedure.[34] The preparation of new compounds, and their characterization data are provided as follows.

General procedure C:



These compounds were synthesized according the literature procedure.[22] To a solution of alkyne (10.0 mmol) in pentane (20.0 mL) was dropwise added trifluoromethanesulfonic acid (1.33 mL, 15.0 mmol) at -30 °C. The reaction mixture was warmed to 0 °C after 1 h, and quenched with saturated aqueous $NaHCO_3$. The organic layer was separated after 5 min, washed twice with saturated aqueous $NaHCO_3$, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give alkenyl triflates.

Hept-1-en-2-yl trifluoromethanesulfonate (2o)



2o

This compound was prepared from hept-1-yne (0.96 g, 10.0 mmol) according to the General procedure C.

1.79 g, 73% yield, colorless oil, R_f = 0.8 (silica gel, petroleum ether).

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.08 (d, *J* = 3.6 Hz, 1 H), 4.92 (d, *J* = 3.6 Hz, 1 H), 2.33 (t, *J* = 7.8 Hz, 2 H), 1.56-1.54 (m, 2 H), 1.36-1.32 (m, 4 H), 0.92-0.90 (m, 3 H).

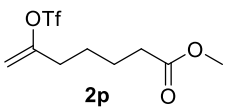
^{13}C NMR (150 MHz, $CDCl_3$): δ 157.2, 118.6 (q, J_{C-F} = 318.0 Hz), 103.9, 33.8, 30.8, 25.7, 22.2, 13.8.

^{19}F NMR (564 MHz, $CDCl_3$): δ -74.3.

IR (neat, cm^{-1}): 2962, 2875, 1671, 1419, 1251, 1142, 1094, 947, 705, 613.

HRMS (ESI): $[M+H]^+$ calcd for $C_8H_{14}F_3O_3S$ 247.0610, found 247.0610.

Methyl 6-(((trifluoromethyl)sulfonyl)oxy)hept-6-enoate (2p)



2p

This compound was prepared from methyl hept-6-ynoate[35] (1.40 g, 10.0 mmol) according to the General procedure C.

2.37 g, 82% yield, colorless oil, R_f = 0.4 (silica gel, petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12 (d, *J* = 3.6 Hz, 1 H), 4.97 (d, *J* = 3.6 Hz, 1 H), 3.68 (s, 3 H),

2.39-2.34 (m, 4 H), 1.72-1.66 (m, 2 H), 1.63-1.57 (m, 2 H).

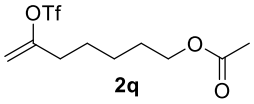
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 156.2, 118.4 (q, J_{C-F} = 318.0 Hz), 104.5, 51.5, 33.5, 33.4, 25.3, 23.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.2.

IR (neat, cm^{-1}): 2956, 2874, 1740, 1417, 1211, 1073, 943, 830, 791, 638.

HRMS (ESI): $[M+H]^+$ calcd for $C_9H_{14}F_3O_5S$ 291.0509, found 291.0510.

6-(((Trifluoromethyl)sulfonyl)oxy)hept-6-en-1-yl acetate (2q)



This compound was prepared from hept-6-yn-1-yl acetate[36] (1.54 g, 10.0 mmol) according to the General procedure C.

2.37 g, 78% yield, colorless oil, R_f = 0.4 (silica gel, petroleum ether/ethyl acetate = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.11 (d, *J* = 3.6 Hz, 1 H), 4.95 (d, *J* = 3.6 Hz, 1 H), 4.07 (t, *J* = 6.4 Hz, 2 H), 2.36 (t, *J* = 7.2 Hz, 2 H), 2.06 (s, 3 H), 1.70-1.55 (m, 4 H), 1.46-1.39 (m, 2 H).

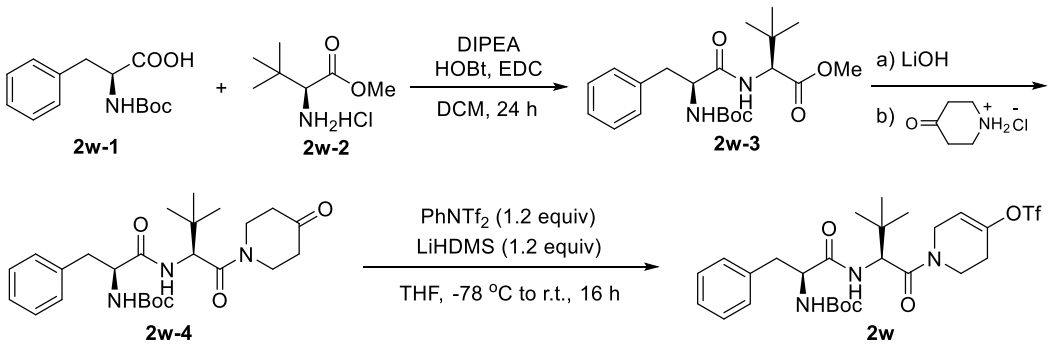
^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 156.5, 118.4 (q, J_{C-F} = 318.0 Hz), 104.3, 64.1, 33.7, 28.1, 25.5, 25.0, 20.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.2.

IR (neat, cm^{-1}): 2954, 2870, 1739, 1643, 1417, 1210, 1141, 900, 706, 637.

HRMS (ESI): $[M+H]^+$ calcd for $C_{10}H_{16}F_3O_5S$ 305.0665, found 305.0665.

1-((*S*)-2-((S)-2-((Tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3,3-dimethylbutanoyl)-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate (2w)



To a stirred solution of acid **2w-1**[37] (2.65 g, 10.0 mmol) and ester **2w-2**[38] (1.81 g, 10.0 mmol) in CH_2Cl_2 (20.0 mL) at 0 °C was added DIPEA (1.65 mL, 10.0 mmol), hydroxybenzotriazole (HOBt, 1.49 g, 11.0 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, 1.92 g, 10.0 mmol). The reaction mixture was stirred at the same temperature for 10 min, and then room temperature for 24 h. The reaction was quenched with saturated aqueous $NaHCO_3$, extracted with ethyl acetate (3 ×

30.0 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give peptide **2w-3** as a white solid (2.74 g, 70% yield, mp: 114-116 ^oC).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.20 (m, 5 H), 6.46 (d, *J* = 9.2 Hz, 1 H), 5.09 (d, *J* = 7.2 Hz, 1 H), 4.39-4.33 (m, 2 H), 3.67 (s, 3 H), 3.06 (d, *J* = 6.8 Hz, 2 H), 1.42 (s, 9 H), 0.91 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 170.9, 155.4, 136.6, 129.2, 128.6, 126.8, 80.1, 60.0, 56.0, 51.7, 37.8, 34.7, 28.2, 26.4.

IR (neat, cm^{-1}): 3317, 2973, 1743, 1655, 1537, 1368, 1168, 1023, 881, 700.

HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{33}N_2O_5$ 393.2384, found 393.2388.

To a solution of peptide **2w-3** (5.0 mmol, 1.96 g) in THF/H_2O (10.0 mL/10.0 mL) was added LiOH·H_2O (1.05 g, 25.0 mmol) at 0 ^oC. The reaction mixture was stirred at the same temperature for 20 min, then room temperature for 24 h. The reaction was quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate (3 × 30.0 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was used for the next step without purification.

To a stirred solution of the above residue in THF/CH_2Cl_2 (10.0 mL/10.0 mL) at room temperature was added 1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate (HATU, 3.81 g, 10.0 mmol) and N,N-diisopropylethylamine (DIPEA, 2.06 mL, 12.5 mmol), followed by 4-oxopiperidinium chloride (0.68 g, 5.0 mmol) after 10 min. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate (3 × 20.0 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was used for the next step without purification.

To a stirred solution of above crude ketone in THF (20.0 mL) was dropwise added Lithium bis(trimethylsilyl)amide (LiHMDS, 0.80 g, 4.8 mmol) at -78 ^oC. A solution of $PhNTf_2$ (1.72 g, 4.8 mmol) in THF (10.0 mL) was dropwise added after 1h. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The reaction was quenched with H_2O and extracted with ethyl acetate (3 × 20.0 mL). The organic layers were washed with saturated aqueous NH_4Cl, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give alkenyl triflate **2w**.

1.89 g, 64% yield for 3 steps, white solid, mp: 70-72 ^oC, R_f = 0.4 (silica gel, petroleum ether/ethyl

acetate = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamors): δ 7.30-7.13 (m, 5 H), 7.03-7.01 (m, 1 H), 5.81-5.79 (m, 1 H), 5.29-5.24 (m, 1 H), 4.91-4.80 (m, 1 H), 4.51-3.54 (m, 5 H), 3.14-3.03 (m, 2 H), 2.57-2.44 (m, 2 H), 1.40-1.37 (m, 9 H), 0.96-0.87 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamors): δ 171.3, 171.0, 170.1, 169.8, 169.7, 169.5, 155.2, 155.1, 147.5, 145.9, 136.6, 136.53, 136.47, 129.1, 129.0, 128.5, 128.3, 126.8, 126.6, 118.3(q, $J_{C\text{-}F}$ = 319.0 Hz), 115.5, 115.4, 114.7, 79.8, 55.6, 54.7, 54.11, 54.05, 43.7, 43.0, 42.8, 40.2, 40.1, 38.6, 38.5, 38.4, 37.9, 35.7, 35.6, 35.5, 35.3, 28.5, 28.10, 28.05, 27.7, 26.3, 26.23, 26.19, 26.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.76, -73.80.

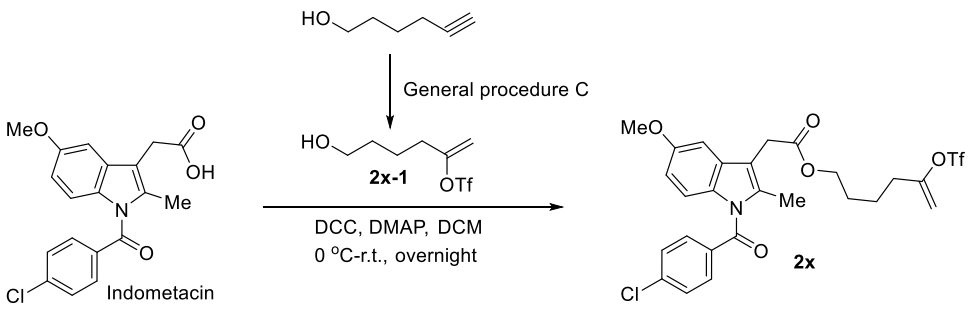
IR (neat, cm^{-1}): 3423, 2976, 1701, 1638, 1422, 1368, 1215, 1142, 870, 747.

HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{37}F_3N_3O_7S$ 592.2299, found 592.2309.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **2w** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20

5-(((trifluoromethyl)sulfonyl)oxy)hex-5-en-1-yl

2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (2x)



Step 1: Triflate **2x-1** (4.22 g, 85% yield) was prepared as a colorless oil from hex-5-yn-1-ol (2.21 mL, 20.0 mmol) according to the General procedure C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.11 (d, J = 3.6 Hz, 1 H), 4.97 (d, J = 3.6 Hz, 1 H), 3.66 (q, J = 6.0 Hz, 2 H), 2.39 (t, J = 6.8 Hz, 2 H), 1.99 (s, 1 H), 1.69-1.58 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 118.4 (q, $J_{C\text{–}F}$ = 318.0 Hz), 104.3, 62.1, 33.5, 31.4, 22.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.2.

IR (neat, cm^{-1}): 3347, 2947, 2878, 1672, 1418, 1213, 1148, 1066, 948, 706.

HRMS (ESI): $[M+K]^+$ calcd for $C_7H_{11}F_3O_4SK$ 286.9962, found 286.9967.

Step2: To a solution of Indomethacin (5.37 g, 15.0 mmol) in DCM (30.0 mL) was added dicyclohexylcarbodiimide (DCC, 3.09 g, 15.0 mmol) and 4-dimethylaminopyridine (DMAP, 0.12 g,

1.0 mmol) at 0 ^{o}C. The reaction mixture was stirred for 30 min, and a solution of triflate **2x-1** (2.48 g, 10.0 mmol) in DCM (10.0 mL) was added. The reaction mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure, and the residue was treated with water, extracted with ethyl acetate (3 × 30.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the product **2x**.

4.23 g, 72% yield, colorless oil, R_f = 0.4 (silica gel, petroleum ether/ethyl acetate = 4:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 6.96 (d, *J* = 2.4 Hz, 1 H), 6.86 (d, *J* = 8.8 Hz, 1 H), 6.67 (dd, *J* = 2.4, 9.2 Hz, 1 H), 5.08 (d, *J* = 3.2 Hz, 1 H), 4.86 (d, *J* = 3.6 Hz, 1 H), 4.13 (t, *J* = 6.4 Hz, 2 H), 3.83 (s, 3 H), 3.67 (s, 2 H), 2.39 (s, 3 H), 2.33 (t, *J* = 7.6 Hz, 2 H), 1.72-1.52 (m, 4 H).

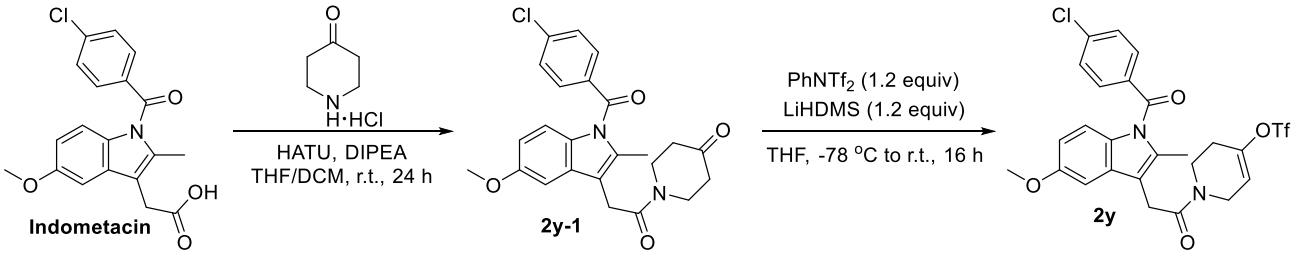
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 168.2, 156.0, 155.9, 139.2, 135.9, 133.7, 131.1, 130.7, 130.5, 129.0, 118.4 (q, J_{C-F} = 318 Hz), 114.9, 112.4, 111.4, 104.6, 101.2, 64.2, 55.6, 33.3, 30.2, 27.5, 22.4, 13.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.0.

IR (neat, cm^{-1}): 3470, 2959, 1735, 1683, 1480, 1418, 1215, 1069, 926, 755.

HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{26}ClF_3NO_7S$ 588.1065, found 588.1076.

1-(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetyl)-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate (2y)



Step 1: To a solution of Indomethacin (1.97 g, 5.5 mmol) in THF/CH_2Cl_2 (10.0 mL/10.0 mL) was added 1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate (HATU, 4.18 g, 11.0 mmol) and N,N-diisopropylethylamine (DIPEA, 2.06 mL, 12.0 mmol) at room temperature. 4-Oxopiperidinium chloride (0.68 g, 5.0 mmol) was added after 10 min. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated aqueous $NaHCO_3$, and extracted with ethyl acetate (3 × 20.0 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced

pressure. The residue was used for the next step without purification.

Step 2: To a solution of the above residue in THF (30.0 mL) was dropwise added Lithium bis(trimethylsilyl)amide (LiHMDS, 1.00 g, 6.0 mmol) at -78 ^{o}C. A solution of $PhNTf_2$ (2.15 g, 6.0 mmol) in THF (10.0 mL) was dropwise added after 1 h. The reaction mixture was allowed to warm to room temperature, and stirred for 16 h. The reaction was quenched with H_2O, and extracted with ethyl acetate (3 × 20.0 mL). The organic layers were washed with saturated aqueous NH_4Cl, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give alkenyl triflate **2y**.

2.05 g, 72% yield for two steps, white solid, mp: 184-186 ^{o}C, R_f = 0.4 (silica gel, petroleum ether/ethyl acetate = 2:1), approximate 1.4:1 ratio of rotamers.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 6.94 (m, 1 H), 6.82-6.80 (m, 1 H), 6.66-6.65 (m, 1 H), [5.81 (s), 5.75 (s), 1 H), [4.25 (d, *J* = 3.0 Hz), 4.14 (d, *J* = 1.8 Hz), 2 H), 3.86-3.67 (m, 7 H), 2.47 (s, 1 H), 2.38 (d, *J* = 6.0 Hz, 3 H), 2.32 (s, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 168.9, 168.2, 156.0, 147.7, 145.7, 139.3, 135.3, 131.1, 130.7, 130.3, 129.1, 118.3 (q, J_{C-F} = 319.5 Hz), 116.0, 114.9, 114.4, 112.4, 111.6, 111.4, 101.2, 55.6, 43.2, 42.3, 40.4, 38.6, 30.6, 30.5, 28.4, 27.7, 13.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.6, -73.8.

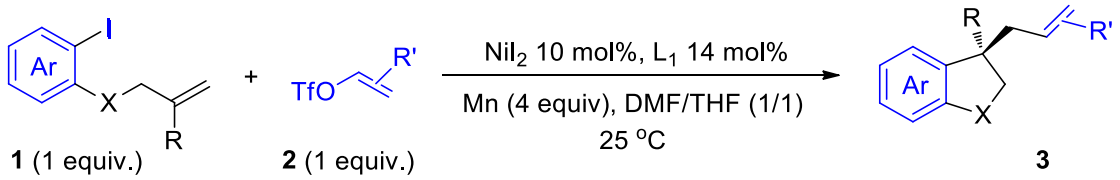
IR (neat, cm^{-1}): 2928, 2842, 1679, 1418, 1316, 1213, 1142, 1053, 868, 776.

HRMS (ESI): $[M+H]^+$ calcd for $C_{25}H_{23}ClF_3N_2O_6S$ 571.0912, found 571.0922.

NOTE: Because of the amide bond rotation equilibrium, two rotamers of **2y** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 37-38

4. Ni-catalyzed Enantioselective Cross-electrophile Aryl-alkenylation of Alkene

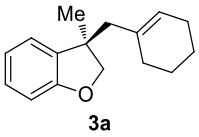
4.1. General Procedure



The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with NiI_2 (6.3 mg, 0.020 mmol), **L1** (7.6 mg, 0.028 mmol), Mn (44.0 mg, 0.8 mmol), and DMF/THF (0.5 mL/0.5 mL). The reaction mixture was stirred for 5 min. Substrates **1** (0.2 mmol) and **2** (0.2 mmol) were then added. The reaction tube was sealed with a rubber septum, and removed from the glove box. The reaction mixture was stirred at 25 ^{o}C for 24 h. The reaction was quenched with water (20.0 mL), and extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **3**.

4.2. Characterization Data of Products

(*R*)-3-(cyclohex-1-en-1-ylmethyl)-3-methyl-2,3-dihydrobenzofuran (3a)



3a

This compound was prepared according to the General procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol).

35.1 mg, 77% yield, 98% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm. t_R(major) = 9.1 min, t_R(minor) = 11.1 min.

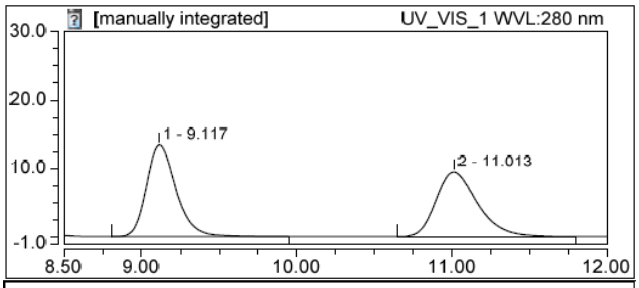
$[\alpha]_D^{25}$ = -12 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.07 (m, 2 H), 6.86 (dt, *J* = 0.8, 7.6 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 5.41 (s, 1 H), 4.47 (d, *J* = 8.4 Hz, 1 H), 4.14 (d, *J* = 8.4 Hz, 1 H), 2.33-2.25 (m, 2 H), 1.99 (s, 2 H), 1.78-1.61 (m, 2 H), 1.54-1.44 (m, 4 H), 1.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 135.8, 134.6, 127.9, 125.9, 122.9, 120.2, 109.5, 82.3, 49.0, 45.5, 30.1, 26.3, 25.4, 23.0, 22.1.

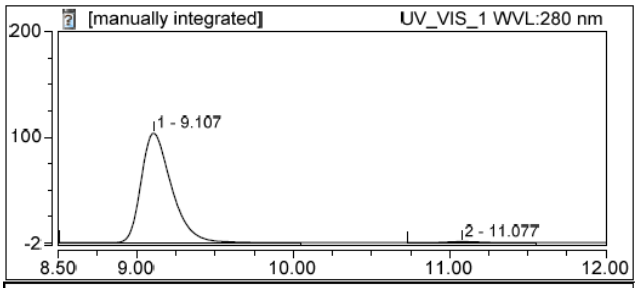
IR (neat, cm^{-1}): 2926, 2838, 1597, 1482, 1459, 1230, 1016, 980, 831, 747.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{21}O$ 229.1587, found 229.1597.



Integration Results

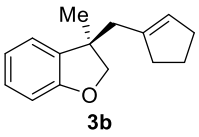
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.117	2.961	50.28
2	11.013	2.928	49.72
Total:		5.889	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	9.107	23.346	98.82
2	11.077	0.278	1.18
Total:		23.624	100.00

(*R*)-3-(cyclopent-1-en-1-ylmethyl)-3-methyl-2,3-dihydrobenzofuran (3b)



3b

The compound was prepared according to the General procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2b** (43.2 mg, 0.2 mmol).

33.8 mg, 79% yield, 98% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm, t_R(major) = 10.5 min, t_R(minor) =12.8 min.

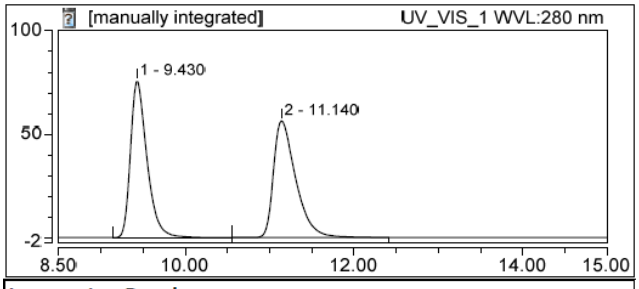
$[\alpha]_D^{20}$= +20 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.07 (m, 2 H), 6.86 (d, *J* = 7.2 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 5.37 (t, *J* = 0.8 Hz, 1 H), 4.45 (d, *J* = 8.4 Hz, 1 H), 4.16 (d, *J* = 8.8 Hz, 1 H), 2.51-2.40 (m, 2 H), 2.28-2.24 (m, 2 H), 2.11-1.93 (m, 2 H), 1.82-1.74 (m, 2 H), 1.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 140.8, 135.7, 128.5, 128.0, 122.8, 120.3, 109.5, 82.2, 45.3, 42.1, 36.4, 32.3, 26.5, 24.0.

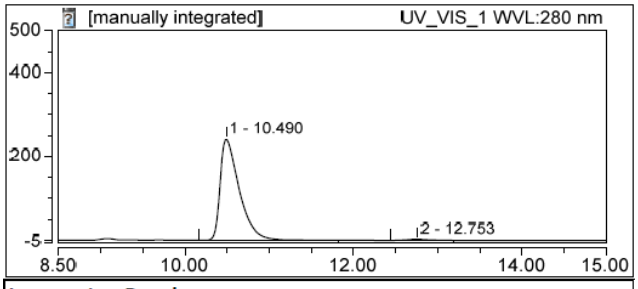
IR (neat, cm^{-1}): 3051, 2957, 2849, 1599, 1482, 1232, 1018, 980, 833, 747.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{19}O$ 215.1430, found 215.1438.



Integration Results

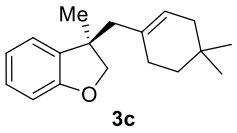
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.430	17.117	49.99
2	11.140	17.124	50.01
Total:		34.240	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	10.490	63.790	98.75
2	12.753	0.806	1.25
Total:		64.595	100.00

(*R*)-3-((4,4-dimethylcyclohex-1-en-1-yl)methyl)-3-methyl-2,3-dihydrobenzofuran (3c)



3c

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) with **2c** (51.6 mg, 0.2 mmol).

36.9 mg, 72% yield, 99% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm, t_R(minor) = 8.1 min, t_R(major) = 8.6 min.

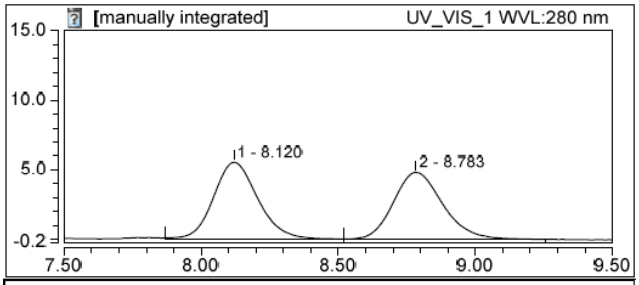
$[\alpha]_D^{20}$ = -5 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.07 (m, 2 H), 6.86 (dt, *J* = 0.8, 7.2 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.33 (s, 1 H), 4.48 (d, *J* = 8.8 Hz, 1 H), 4.15 (d, *J* = 8.4 Hz, 1 H), 2.34-2.27 (m, 2 H), 1.77-1.59 (m, 4 H), 1.32 (s, 3 H). 1.26-1.23 (m, 2 H), 0.85 (s, 3 H), 0.83 (s, 3 H).

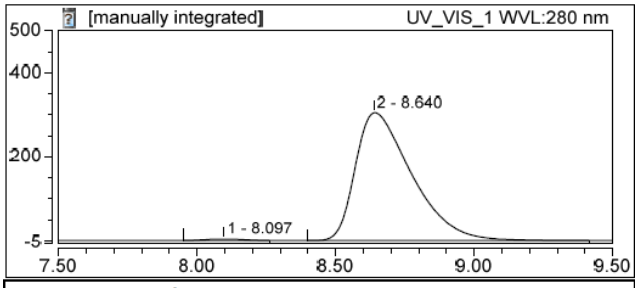
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 135.8, 133.2, 127.9, 125.1, 122.9, 120.3, 109.5, 82.3, 48.9, 45.6, 39.6, 35.8, 28.9, 28.2, 27.8, 27.4, 26.4.

IR (neat, cm^{-1}): 2956, 2920, 1613, 1482, 1459, 1232, 1018, 982, 833, 747.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{25}O$ 257.1900, found 257.1896.

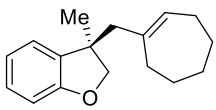


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	8.120	1.048	51.08
2	8.783	1.004	48.92
Total:		2.052	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	8.097	0.525	0.73
2	8.640	71.825	99.27
Total:		72.350	100.00

(*R*)-3-(cyclohept-1-en-1-ylmethyl)-3-methyl-2,3-dihydrobenzofuran (3d)



3d

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2d** (48.8 mg, 0.2 mmol).

31.5 mg, 65% yield, 97% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 279 nm, t_R(major) = 8.1 min, t_R(minor) = 9.9 min.

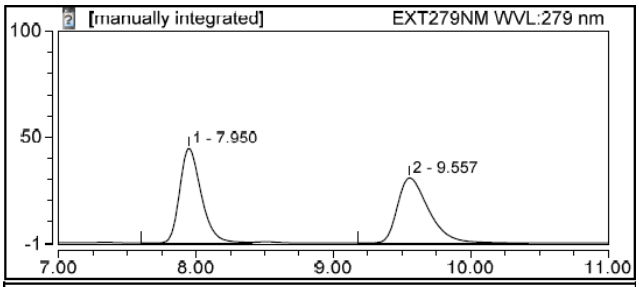
$[\alpha]_D^{19}$ = +2 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12-7.07 (m, 2 H), 6.85 (dt, *J* = 0.8, 7.6 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 5.53 (t, *J* = 6.4 Hz, 1 H), 4.51 (d, *J* = 8.4 Hz, 1 H), 4.09 (d, *J* = 8.8 Hz, 1 H), 2.35-2.27 (m, 2 H), 2.08-1.87 (m, 4 H), 1.69-1.65 (m, 2 H), 1.45-1.31 (m, 4 H), 1.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 141.3, 135.6, 131.4, 127.9, 123.1, 120.2, 109.5, 81.8, 50.7, 45.9, 34.4, 32.5, 28.6, 27.0, 26.5, 26.1.

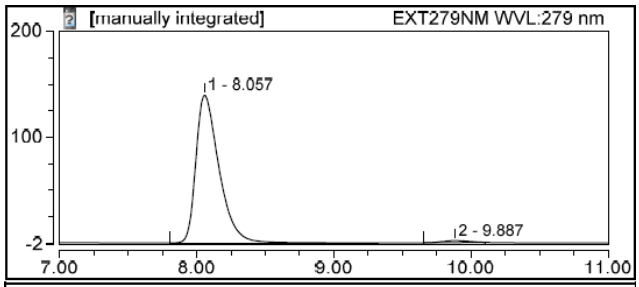
IR (neat, cm^{-1}): 2922, 2846, 1597, 1482, 1450, 1230, 1016, 978, 831, 747.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{23}O$ 243.1743, found 243.1746.



Integration Results

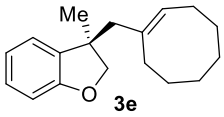
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.950	8.142	50.24
2	9.557	8.064	49.76
Total:		16.206	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	8.057	27.290	98.63
2	9.887	0.380	1.37
Total:		27.670	100.00

(R,E)-3-(cyclooct-1-en-1-ylmethyl)-3-methyl-2,3-dihydrobenzofuran (3e)



3e

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2e** (51.6 mg, 0.2 mmol).

21.5 mg, 42% yield, 97% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm, t_R(major) = 10.1 min, t_R(minor) = 15.5 min.

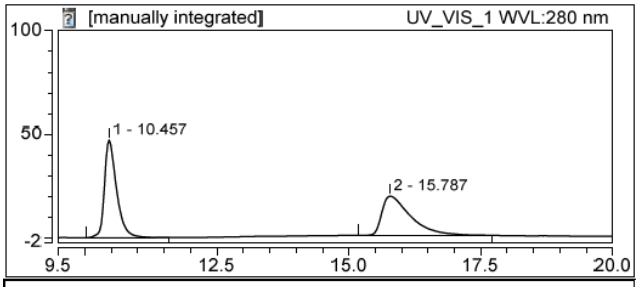
$[\alpha]_D^{19}$ = +2 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12-7.07 (m, 2 H), 6.87-6.83 (t, *J* = 7.2 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 5.35 (t, *J* = 8.0 Hz, 1 H), 4.50 (d, *J* = 8.4 Hz, 1 H), 4.14 (d, *J* = 8.4 Hz, 1 H), 2.36-2.25 (m, 2 H), 2.10-1.90 (m, 4 H), 1.45-1.41 (m, 8 H), 1.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 137.1, 135.8, 129.0, 127.9, 123.0, 120.2, 109.5, 82.1, 46.8, 45.7, 29.9, 29.6, 28.3, 26.7, 26.6, 26.0, 26.0.

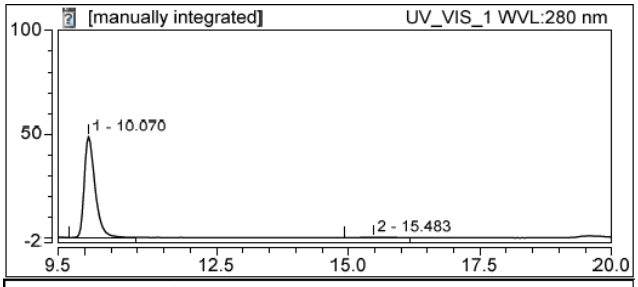
IR (neat, cm^{-1}): 2924, 2853, 1482, 1459, 1277, 1262, 1018, 980, 713, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{25}O$ 257.1900, found 257.1902.



Integration Results

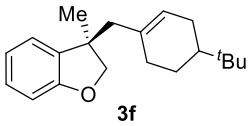
No.	Retention Time min	Area mAU*min	Relative Area %
1	10.457	12.553	51.09
2	15.787	12.018	48.91
Total:		24.571	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	10.070	11.539	98.68
2	15.483	0.154	1.32
Total:		11.694	100.00

(3*R*)-3-((4-(*tert*-butyl)cyclohex-1-en-1-yl)methyl)-3-methyl-2,3-dihydrobenzofuran (3f)



3f

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2f** (57.2 mg, 0.2 mmol).

31.8 mg, 56% yield, 98% ee, dr = 1.2/1, white solid, mp 34-36 ^{o}C.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 0.1/99.9, 0.4 mL/min, 280 nm. t_{R1}(major) = 24.2 min, t_{R1}(minor) = 30.3 min; t_{R2}(major) = 25.0 min, t_{R2}(minor) = 26.0 min.

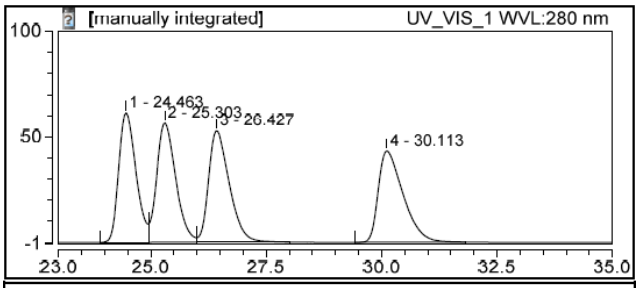
$[\alpha]_D^{23}$= +11 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.07 (m, 2 H), 6.88-6.84 (m, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), [5.43 (t, *J* = 2.4 Hz), 5.39 (d, *J* = 3.2 Hz), 1 H], 4.48-4.45 (m, 1 H), 4.16-4.12 (m, 1 H), 2.32-2.25 (m, 2 H), 2.04-1.68 (m, 5 H), 1.33-1.30 (m, 3 H). 1.20-1.07 (m, 2 H), 0.84 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 136.0, 135.8, 134.5, 134.4, 127.93, 127.90, 126.3, 126.2, 122.9, 120.3, 120.2, 109.5, 82.3, 82.2, 48.6, 48.3, 45.6, 45.5, 43.83, 43.76, 32.1, 31.7, 31.6, 27.18, 27.15, 27.1, 26.4, 26.2, 24.5, 24.3.

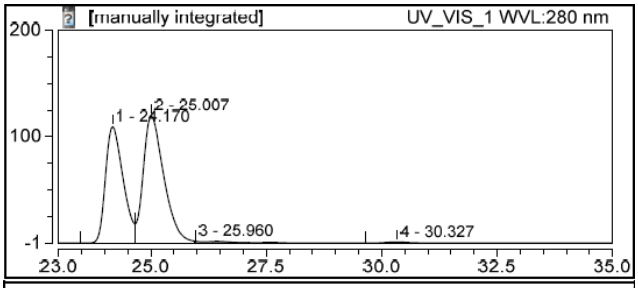
IR (neat, cm^{-1}): 3008, 2965, 1654, 1547, 1480, 1460, 1277, 1262, 767, 751.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{20}H_{28}ONa$ 302.2032, found 302.2034.



Integration Results

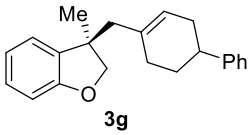
No.	Retention Time min	Area mAU*min	Relative Area %
1	24.463	26.570	24.59
2	25.303	27.070	25.06
3	26.427	27.504	25.46
4	30.113	26.898	24.90
Total:		108.043	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	24.170	48.208	43.22
2	25.007	61.938	55.53
3	25.960	0.933	0.84
4	30.327	0.464	0.42
Total:		111.544	100.00

(3*R*)-3-methyl-3-((1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)methyl)-2,3-dihydrobenzofuran (3g)



3g

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2g** (61.2 mg, 0.2 mmol).

34.7 mg, 57% yield, 98% ee, dr = 1.1:1, white solid, mp: 69-71^{o}C.

Chiral HPLC: CHIRALPAK IB, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 1 mL/min, 203 nm. t_{R1}(minor) = 17.0 min, t_{R1}(major) = 21.5 min; t_{R2}(minor) = 18.0 min, t_{R2}(major) = 18.8 min.

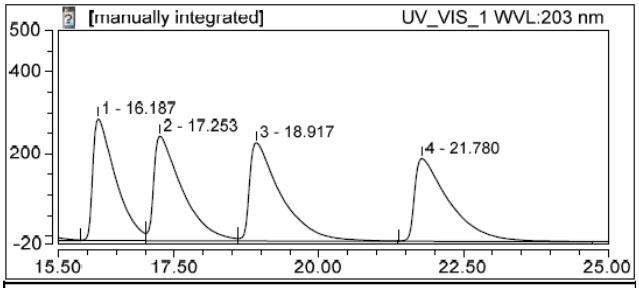
$[\alpha]_D^{23}$ = +12 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.09 (m, 7 H), 6.89-6.85 (t, *J* = 7.2 Hz, 1 H), 6.80-6.76 (m, 1 H), [5.52 (d, *J* = 2.4 Hz), 5.48 (d, *J* = 1.2 Hz), 1 H), 4.50 (d, *J* = 8.4 Hz, 1 H), 4.17 (t, *J* = 8.4 Hz, 1 H), 2.71-2.67 (m, 1 H), 2.37-1.63 (m, 8 H), 1.34 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 147.0, 146.9, 135.7, 135.6, 134.6, 134.5, 128.29, 128.26, 128.01, 127.96, 126.82, 126.78, 125.92, 125.90, 125.6, 125.5, 122.9, 120.3, 109.5, 82.2, 48.7, 48.5, 45.6, 45.4, 39.7, 39.5, 33.8, 33.4, 30.8, 30.3, 30.1, 30.0, 26.4, 26.2.

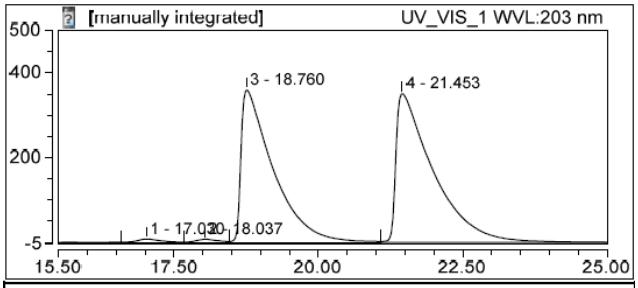
IR (neat, cm^{-1}): 3407, 2917, 1655, 1482, 1459, 1277, 1262, 1016, 751, 699.

HRMS (ESI): [M+Na]$^+$ calcd for $C_{22}H_{24}NaO$ 327.1719, found 327.1720.



Integration Results

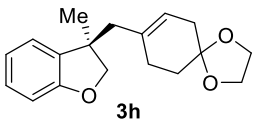
No.	Retention Time min	Area mAU*min	Relative Area %
1	16.187	135.708	23.69
2	17.253	145.632	25.43
3	18.917	151.248	26.41
4	21.780	140.146	24.47
Total:		**572.733**	**100.00**



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	17.030	3.704	0.74
2	18.037	3.169	0.63
3	18.760	232.358	46.25
4	21.453	263.191	52.38
Total:		**502.424**	**100.00**

(*R*)-8-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-1,4-dioxaspiro[4.5]dec-7-ene (3h)



3h

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2h** (57.6 mg, 0.2 mmol) in DMF.

46.9 mg, 82% yield, 98% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 4/96, 0.8 mL/min, 281 nm, t_R(major) = 16.7 min, t_R(minor) =18.7 min.

$[\alpha]_D^{22}$ = -7 (c = 1.0, CH_2Cl_2).

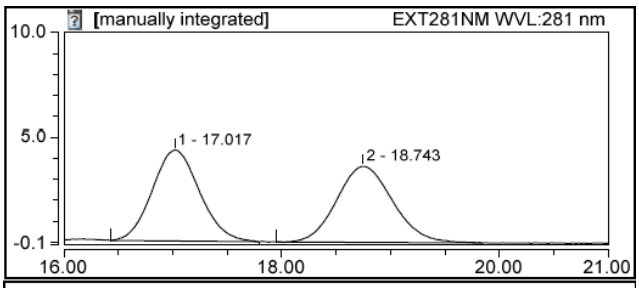
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.07 (m, 2 H), 6.86 (t, *J* = 7.2 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1

H), 5.31 (s, 1 H), 4.45 (d, *J* = 8.8 Hz, 1 H), 4.16 (d, *J* = 8.4 Hz, 1 H), 3.97-3.93 (m, 4 H), 2.37-2.29 (m, 2 H), 2.26 (s, 2 H), 2.01-1.89 (m, 2 H), 1.67-1.63 (m, 2 H), 1.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 135.5, 134.3, 128.0, 123.04, 122.95, 120.3, 109.6, 107.6, 82.4, 64.3, 47.7, 45.5, 35.8, 31.2, 29.1, 25.9.

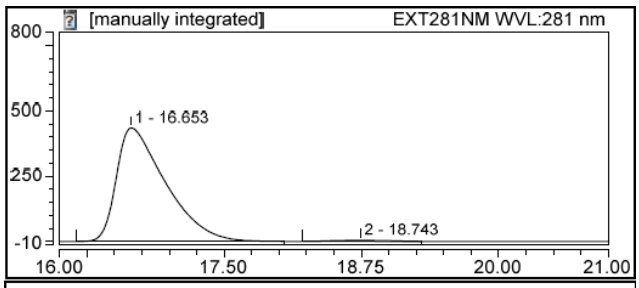
IR (neat, cm^{-1}): 2956, 2883, 1597, 1482, 1243, 1116, 1060, 1016, 833, 753.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{23}O_3$ 287.1642, found 287.1643.



Integration Results

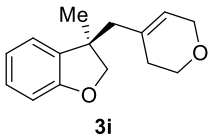
No.	Retention Time min	Area mAU*min	Relative Area %
1	17.017	2.190	50.32
2	18.743	2.162	49.68
Total:		4.352	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	16.653	225.342	98.97
2	18.743	2.340	1.03
Total:		227.682	100.00

(*R*)-3-((3,6-dihydro-2*H*-pyran-4-yl)methyl)-3-methyl-2,3-dihydrobenzofuran (3i)



3i

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2i** (46.4 mg, 0.2 mmol) in DMF. 30.8 mg, 67% yield, 98% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 280 nm, t_R(major) = 5.6 min, t_R(minor) = 6.2 min.

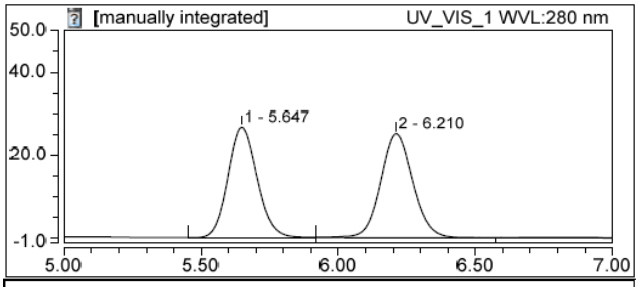
$[\alpha]_D^{21}$ = +1 (c = 1.0, CH_2Cl_2).

1H NMR (400 MHz, $CDCl_3$): δ 7.14-7.08 (m, 2 H), 6.88-6.84 (dt, *J* = 0.8, 7.2 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 5.40 (s, 1 H), 4.46 (d, *J* = 8.8 Hz, 1 H), 4.16 (d, *J* = 8.4 Hz, 1 H), 4.10-4.06 (m, 2 H), 3.69-3.59 (m, 2 H), 2.38-2.30 (m, 2 H), 1.86-1.74 (m, 2 H), 1.35 (s, 3 H).

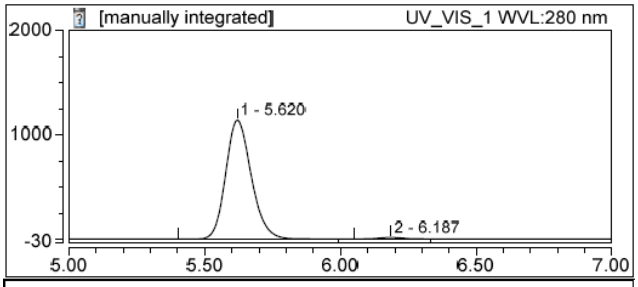
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 135.2, 132.6, 128.1, 124.4, 122.9, 120.3, 109.6, 82.0, 65.4, 64.2, 48.2, 45.4, 30.2, 26.2.

IR (neat, cm^{-1}): 2962, 2752, 1722, 1597, 1481, 1235, 1128, 978, 832, 752.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{19}O_2$ 231.1380, found 231.1381.

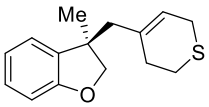


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	5.647	3.287	48.89
2	6.210	3.436	51.11
Total:		6.723	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	5.620	124.961	98.76
2	6.187	1.571	1.24
Total:		126.532	100.00

(*R*)-3-((3,6-dihydro-2*H*-thiopyran-4-yl)methyl)-3-methyl-2,3-dihydrobenzofuran (3j)



3j

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2j** (49.6 mg, 0.2 mmol) in DMF.

32.0 mg, 65% yield, 96% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 2/98, 1 mL/min, 260 nm, t_R(major) = 12.0 min, t_R(minor) =13.2 min.

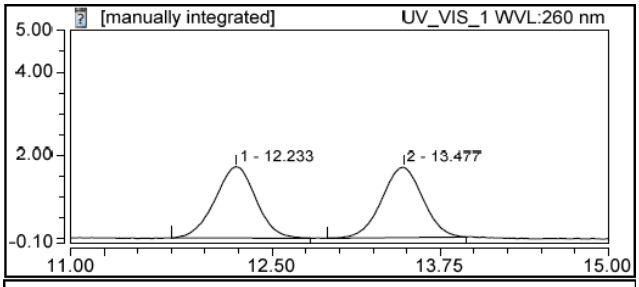
$[\alpha]_D^{21}$ = -17 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.07 (m, 2 H), 6.87 (dt, *J* = 0.8, 7.6 Hz, 1 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 5.57 (s, 1 H), 4.45 (d, *J* = 8.8 Hz, 1 H), 4.14 (d, *J* = 8.8 Hz, 1 H), 3.19-3.09 (m, 2 H), 2.64-2.53 (m, 2 H), 2.36-2.27 (m, 2 H), 2.04-1.88 (m, 2 H),, 1.34 (s, 3 H).

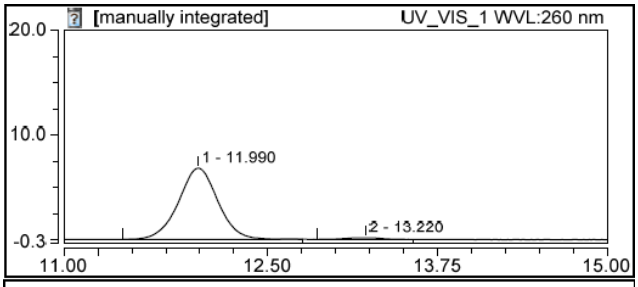
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 135.6, 135.1, 128.2, 123.0, 122.5, 120.3, 109.7, 82.1, 49.8, 45.6, 30.8, 26.0, 25.7, 25.1.

IR (neat, cm^{-1}): 2961, 2883, 1663, 1596, 1480, 1230, 1017, 975, 831, 753.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{19}OS$ 247.1151, found 247.1153.

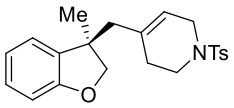


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	12.233	0.605	50.23
2	13.477	0.599	49.77
Total:		1.204	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	11.990	2.302	97.78
2	13.220	0.052	2.22
Total:		2.354	100.00

(*R*)-4-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (3k)



3k

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol).

59.7 mg, 78% yield, 98% ee, white solid, mp: 87-89 ^{o}C.

Chiral HPLC: CHIRALPAK ID, 25 ^{o}C, ^{i}PrOH-hexanes 8/92, 1 mL/min, 203 nm, t_R(minor) = 56.5 min, t_R(major) = 57.8 min.

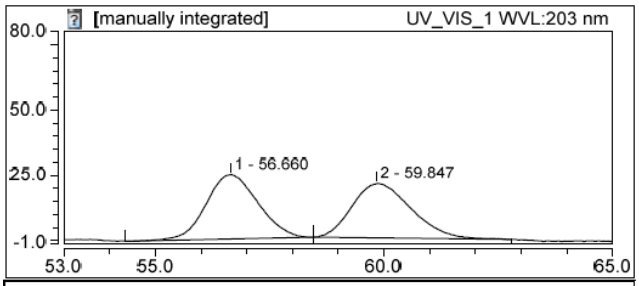
$[\alpha]_D^{23}$ = -8 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.12-7.08 (m, 1 H), 7.02 (dd, *J* = 0.8, 7.2 Hz, 1 H), 6.84 (dt, *J* =0.8, 7.6 Hz, 1 H), 6.73 (d, *J* = 8.0 Hz, 1 H), 5.29 (s, 1 H), 4.35 (d, *J* = 8.4 Hz, 1 H), 4.08 (d, *J* = 8.8 Hz, 1 H), 3.61-3.47 (m, 2 H), 3.12-2.94 (m, 2 H), 2.42 (s, 3 H), 2.32-2.24 (m, 2 H), 1.94-1.78 (m, 2 H), 1.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 143.5, 134.8, 133.5, 133.2, 129.6, 128.2, 127.6, 122.8, 121.0, 120.4, 109.6, 81.7, 47.9, 45.3, 44.7, 42.8, 29.9, 26.0, 21.4.

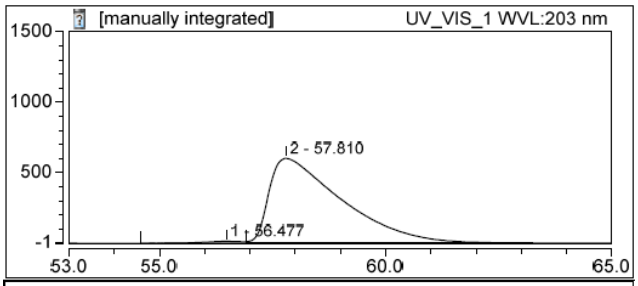
IR (neat, cm^{-1}): 2963, 2922, 1597, 1482, 1344, 1165, 1094, 952, 754, 688.

HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{26}NO_3S$ 384.1628, found 384.1627.



Integration Results

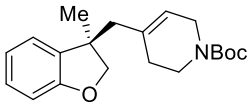
No.	Retention Time min	Area mAU*min	Relative Area %
1	56.660	32.330	50.86
2	59.847	31.232	49.14
Total:		63.563	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	56.477	11.633	1.03
2	57.810	1113.654	98.97
Total:		1125.286	100.00

***Tert*-butyl (*R*)-4-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-3,6-dihydropyridine-1(2*H*)-carboxylate (3l)**



3l

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2l** (66.2 mg, 0.2 mmol).

52.0 mg, 79% yield, 96% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 2/98, 1 mL/min, 260 nm, t_R(major) = 12.4 min, t_R(minor) =17.0 min.

$[\alpha]_D^{23}$ = -6 (c = 1.0, CH_2Cl_2).

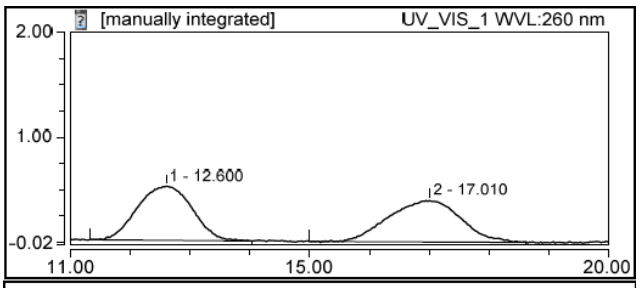
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.06 (m, 2 H), 6.86 (dt, *J* = 0.8, 7.6 Hz, 1 H), 6.77 (d, *J* = 8.0

Hz, 1 H), 5.34 (s, 1 H), 4.44 (d, *J* = 8.4 Hz, 1 H), 4.14 (d, *J* = 8.8 Hz, 1 H), 3.91-3.76 (m, 2 H), 3.41 (s, 1 H), 3.29-3.23 (m, 1 H), 2.38-2.31 (m, 2 H), 1.82-1.76 (m, 2 H), 1.45 (s, 9 H), 1.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 154.9, 135.0, 133.6, 128.2, 122.9, 122.3, 120.4, 109.6, 81.9, 79.4, 48.3, 45.5, 43.5, 40.9, 30.0, 28.4, 26.1.

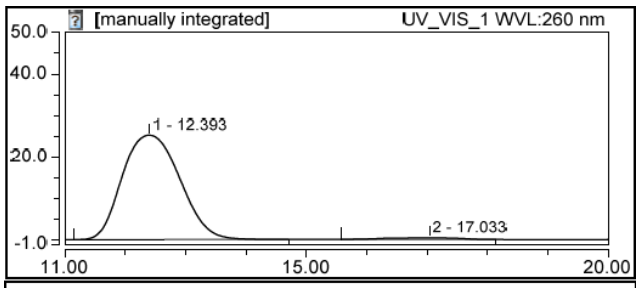
IR (neat, cm^{-1}): 2976, 2932, 1698, 1481, 1420, 1366, 1172, 980, 845, 753.

HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{28}NO_3$ 330.2064, found 330.2062.



Integration Results

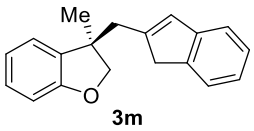
No.	Retention Time min	Area mAU*min	Relative Area %
1	12.600	0.551	50.05
2	17.010	0.550	49.95
Total:		1.100	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	12.393	27.826	98.06
2	17.033	0.551	1.94
Total:		28.377	100.00

(*R*)-3-((1*H*-inden-2-yl)methyl)-3-methyl-2,3-dihydrobenzofuran (3m)



3m

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2m** (52.8 mg, 0.2 mmol) in DMF. 37.2 mg, 71% yield, 96% ee, colorless oil.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 280 nm, t_R(major) = 6.2 min, t_R(minor) = 6.8 min.

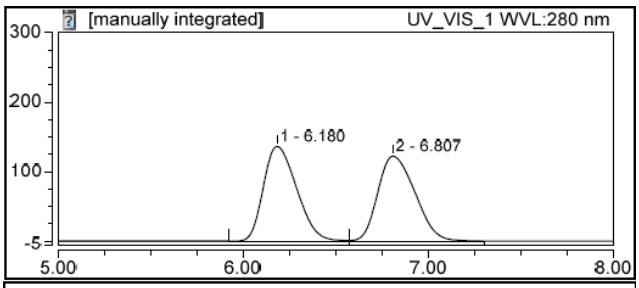
$[\alpha]_D^{22}$ = +66 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.07 (m, 6 H), 6.89 (dt, *J* = 1.2, 7.6 Hz, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.52 (m, 1 H), 4.52 (d, *J* = 8.8 Hz, 1 H), 4.19 (d, *J* = 8.4 Hz, 1 H), 3.15-2.95 (m, 2 H), 2.81 (s, 2 H), 1.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 145.8, 144.8, 143.4, 134.9, 130.4, 128.3, 126.2, 124.0, 123.3, 122.8, 120.5, 120.1, 109.7, 81.8, 45.8, 42.4, 42.1, 26.5.

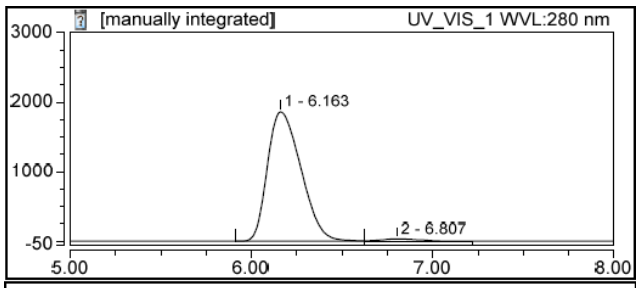
IR (neat, cm^{-1}): 2962, 2885, 1610, 1481, 1392, 1265, 1101, 978, 831, 752.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{19}O$ 263.1430, found 263.1431.



Integration Results

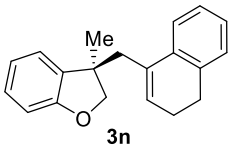
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.180	28.276	49.98
2	6.807	28.295	50.02
Total:		56.572	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	6.163	398.223	98.11
2	6.807	7.687	1.89
Total:		405.910	100.00

(*R*)-3-((3,4-dihydronaphthalen-1-yl)methyl)-3-methyl-2,3-dihydrobenzofuran (3n)



3n

The compound was prepared according to the General Procedure from the reaction of **1a** (49 mg, 0.2 mmol) and **2n** (55.6 mg, 0.2 mmol) in DMF. 39.7 mg, 72% yield, 97% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 260 nm, t_R(minor) = 11.5 min, t_R(major) = 15.3 min.

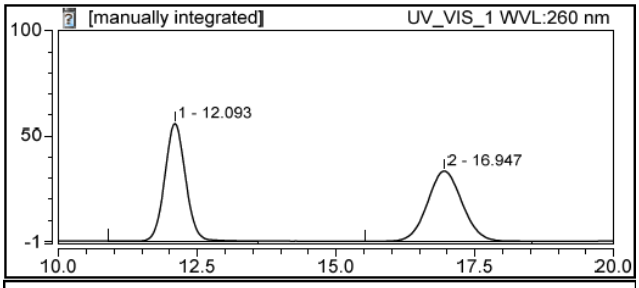
$[\alpha]_D^{22}$ = -25 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.19 (m, 1 H), 7.12-7.05 (m, 5 H), 6.82-6.75 (m, 2 H), 5.72 (t, *J* = 4.8 Hz, 1 H), 4.47 (d, *J* = 8.8 Hz, 1 H), 4.00 (d, *J* = 8.8 Hz, 1 H), 2.85-2.67 (m, 4 H), 2.20-2.15 (m, 2 H), 1.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 136.5, 135.5, 135.4, 133.1, 129.4, 128.0, 127.5, 126.5, 126.1, 123.1, 123.0, 120.2, 109.6, 82.1, 46.1, 41.7, 28.6, 25.0, 23.2.

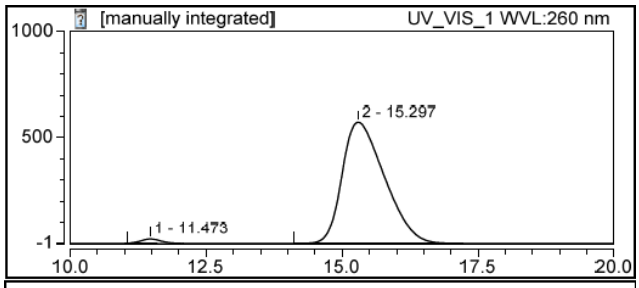
IR (neat, cm^{-1}): 2963, 2881, 1655, 1597, 1480, 1234, 1016, 975, 833, 744.

HRMS (ESI): $[M+K]^+$ calcd for $C_{20}H_{20}OK$ 315.1146, found 315.1145.



Integration Results

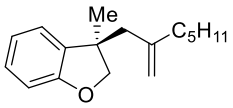
No.	Retention Time min	Area mAU*min	Relative Area %
1	12.093	24.237	49.91
2	16.947	24.321	50.09
Total:		48.558	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	11.473	8.712	1.66
2	15.297	516.295	98.34
Total:		525.007	100.00

(*R*)-3-methyl-3-(2-methyleneheptyl)-2,3-dihydrobenzofuran (3o)



3o

The compound was prepared according to the General Procedure from the reaction of **1a** (109.6 mg, 0.4 mmol) and **2o** (49.2 mg, 0.2 mmol) in THF. 34.6 mg, 71% yield, 90% ee, colorless oil.

Chiral HPLC: CHIRALPAK IB, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm, t_R(major) = 7.3 min, t_R(minor) = 11.6 min.

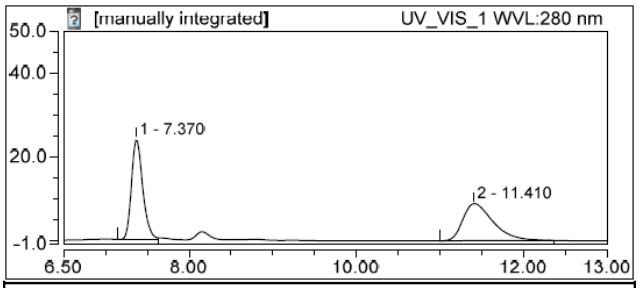
$[\alpha]_D^{20}$ = +8 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.09 (m, 2 H), 6.88-6.84 (m, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 4.85 (d, *J* = 1.6 Hz, 1 H), 4.70 (s, 1H), 4.50 (d, *J* = 8.4 Hz, 1 H), 4.16 (d, *J* = 8.8 Hz, 1 H), 2.44-2.32 (m, 2 H), 1.84-1.68 (m, 2 H), 1.38-1.14 (m, 9 H), 0.86 (t, *J* = 7.2 Hz, 3 H).

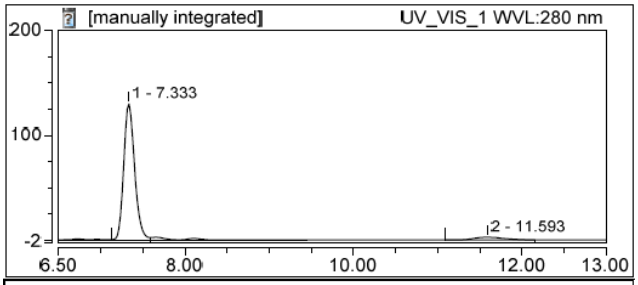
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 146.6, 135.5, 128.0, 122.9, 120.3, 113.4, 109.6, 82.0, 46.3, 45.3, 37.0, 31.5, 27.6, 26.3, 22.5, 14.0.

IR (neat, cm^{-1}): 2958, 2876, 1638, 1599, 1482, 1232, 1018, 982, 896, 747.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{25}O$ 245.1900, found 245.1902.

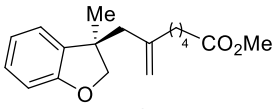


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.370	3.754	50.28
2	11.410	3.712	49.72
Total:		7.466	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.333	19.423	94.94
2	11.593	1.036	5.06
Total:		20.459	100.00

Methyl (*R*)-6-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)hept-6-enoate (3p)



3p

The compound was prepared according to the General Procedure from the reaction of **1a** (164.4 mg, 0.6 mmol) and **2p** (58.0 mg, 0.2 mmol). 32.8 mg, 57% yield, 92% ee, colorless oil.

Chiral HPLC: CHIRALPAK ID, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 203 nm, t_R(major) = 5.7 min, t_R(minor) = 6.4 min.

$[\alpha]_D^{20}$ = +4 (c = 1.0, CH_2Cl_2).

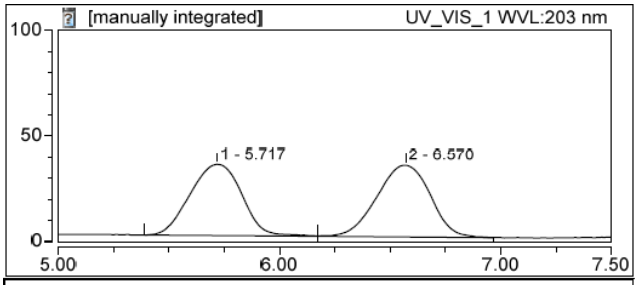
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.09 (m, 2 H), 6.87 (t, *J* = 7.2 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 4.86 (d, *J* = 0.8 Hz, 1 H), 4.72 (s, 1 H), 4.50 (d, *J* = 8.8 Hz, 1 H), 4.16 (d, *J* = 8.4 Hz, 1 H), 3.66 (s, 3 H), 2.43-2.31 (m, 2 H), 2.27-2.23 (m, 2 H), 1.81-1.64 (m, 2 H), 1.56-1.42 (m, 2 H), 1.40-1.25

(m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 159.3, 145.9, 135.3, 128.1, 122.8, 120.3, 113.9, 109.6, 81.9, 51.5, 46.3, 45.3, 36.5, 33.8, 27.3, 26.3, 24.4.

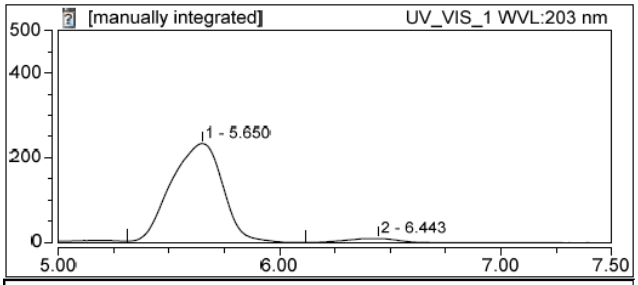
IR (neat, cm^{-1}): 3006, 2959, 1739, 1482, 1459, 1276, 1262, 976, 776, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{25}O_3$ 289.1798, found 289.1800.



Integration Results

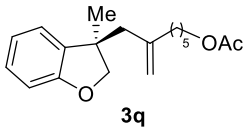
No.	Retention Time min	Area mAU*min	Relative Area %
1	5.717	9.172	49.02
2	6.570	9.538	50.98
Total:		18.710	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	5.650	64.017	95.96
2	6.443	2.696	4.04
Total:		66.714	100.00

(*R*)-6-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)hept-6-en-1-yl acetate (3q)



3q

The compound was prepared according to the General Procedure from the reaction of **1a** (164.4 mg, 0.6 mmol) and **2q** (60.8 mg, 0.2 mmol).

34.6 mg, 54% yield, 93% ee, colorless oil.

Chiral HPLC: CHIRALPAK ID, 25 ^{o}C, ^{i}PrOH-hexanes 4/96, 1 mL/min, 280 nm, t_R(major) = 6.0 min, t_R(minor) = 6.6 min.

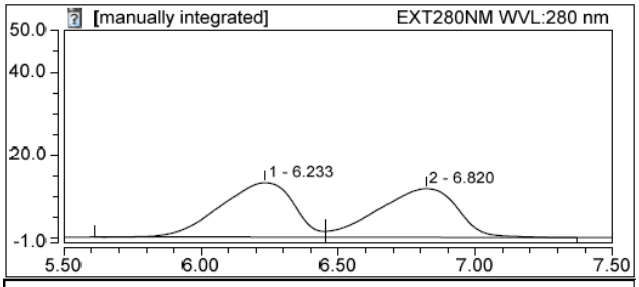
$[\alpha]_D^{20}$ = +5 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.09 (m, 2 H), 6.86 (dt, *J* = 0.8, 7.2 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 4.85 (d, *J* = 1.2 Hz, 1 H), 4.72 (s, 1 H), 4.50 (d, *J* = 8.4 Hz, 1 H), 4.16 (d, *J* = 8.8 Hz, 1 H), 4.02 (t, *J* = 6.8 Hz, 2H), 2.43-2.31 (m, 2 H), 2.04 (s, 3 H), 1.84-1.64 (m, 2 H), 1.60-1.53 (m, 2 H), 1.40-1.19 (m, 7 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 159.3, 146.1, 135.3, 128.1, 122.8, 120.3, 113.7, 109.6, 81.9, 64.5, 46.3, 45.3, 36.8, 28.4, 27.4, 26.3, 25.5, 21.0.

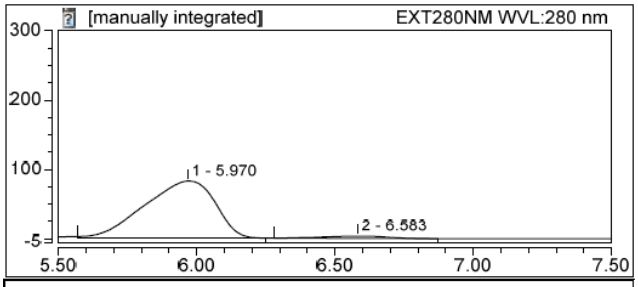
IR (neat, cm^{-1}): 2939, 2866, 1739, 1597, 1482, 1366, 1239, 1046, 978, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{27}O_3$ 303.1955, found 303.1953.



Integration Results

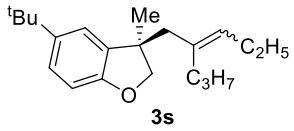
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.233	4.081	50.85
2	6.820	3.945	49.15
Total:		8.026	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	5.970	24.450	96.55
2	6.583	0.873	3.45
Total:		25.323	100.00

(R)-5-(tert-butyl)-3-methyl-3-(2-propylpent-2-en-1-yl)-2,3-dihydrobenzofuran (3s)



3s

This compound was prepared according to the General Procedure from the reaction of **1b** (66.0 mg, 0.2 mmol) and **2s** (49.2mg, 0.2 mmol) in DMF. 18.0 mg, 30% yield, *E*/*Z*= 2.5/1, 91% ee, colorless oil. The *E*- and *Z*-isomers were determined by 1-D NOE experiments.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 0.4/99.6, 0.3 mL/min, 280 nm, t_{R1}(major) = 18.6 min, t_{R1}(minor) = 21.9 min; t_{R2}(major) = 19.4 min, t_{R2}(minor) = 20.9 min.

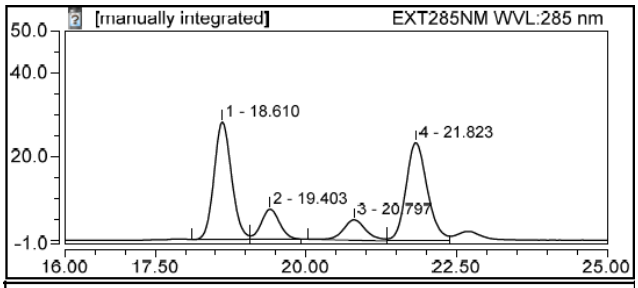
$[\alpha]_D^{23}$ = +33 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (td, *J* = 2.0 Hz, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 1 H), 5.123 (t, *J* = 6.8 Hz, 1 H), 4.47 (d, *J* = 8.4 Hz, 1 H), 4.12 (d, *J* = 8.4 Hz, 1 H), 2.40-2.21 (m, 2 H), 2.03-1.92 (m, 2 H), 1.87-1.58 (m, 2 H), 1.32-1.30 (m, 2 H), 1.32 (s, 3 H), 1.30 (s, 9 H), 0.92 (t, *J* = 7.6 Hz, 3 H), 0.78 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 143.2, 135.5, 135.1, 131.9, 124.6, 119.9, 108.6, 82.3, 46.7, 45.9, 40.0, 34.3, 31.8, 26.2, 21.7, 21.1, 14.6, 14.0.

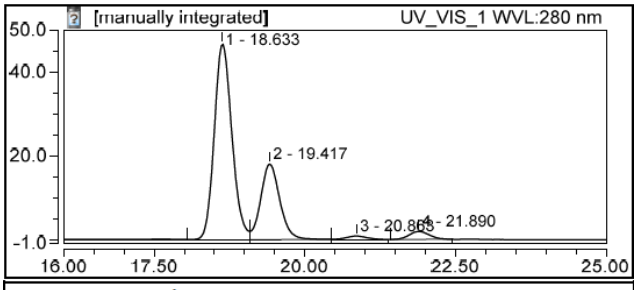
IR (neat, cm^{-1}): 2960, 2931, 1594, 1490, 1363, 1261, 1186, 1057, 989, 816.

HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{33}O$ 301.2526, found 301.2533.



Integration Results

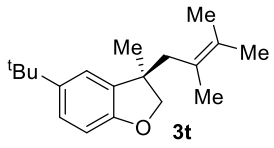
No.	Retention Time min	Area mAU*min	Relative Area %
1	18.610	9.506	39.79
2	19.403	2.530	10.59
3	20.797	2.145	8.98
4	21.823	9.708	40.64
Total:		**23.889**	**100.00**



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	18.633	15.919	67.28
2	19.417	6.668	28.18
3	20.863	0.328	1.39
4	21.890	0.745	3.15
Total:		**23.659**	**100.00**

(R)-5-(tert-butyl)-3-(2,3-dimethylbut-2-en-1-yl)-3-methyl-2,3-dihydrobenzofuran (3t)



3t

The compound was prepared according to the General Procedure from the reaction of **1b** (66.0 mg, 0.2 mmol) and **2t** (43.6 mg, 0.2 mmol) in DMF. 23.4 mg, 43% yield, 99.8% ee, colorless oil.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 0.4/99.6, 0.3 mL/min, 280 nm, t_R(minor) = 21.6 min, t_R(major) = 22.7 min.

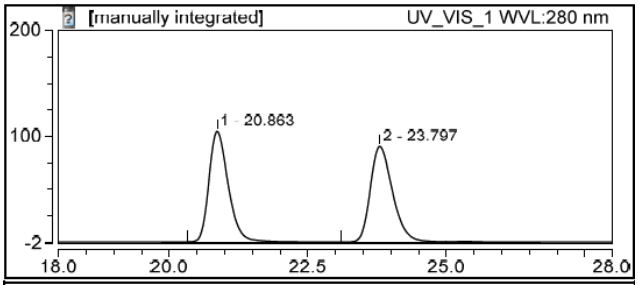
$[\alpha]_D^{22}$ = +38 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1 H), 7.20 (d, *J* = 2.0 Hz, 1 H), 7.08 (d, *J* = 8.4 Hz, 1 H), 4.37 (d, *J* = 8.4 Hz, 1 H), 4.09 (d, *J* = 8.4 Hz, 1 H), 2.61 (d, *J* = 13.6 Hz, 1 H), 2.23 (d, *J* = 13.6 Hz, 1 H), 1.63 (s, 3 H), 1.56 (s, 3 H), 1.41 (s, 3 H), 1.35 (s, 3 H), 1.28 (m, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 143.2, 135.0, 128.6, 124.6, 124.5, 120.2, 108.5, 83.4, 46.7, 44.5, 34.3, 31.8, 25.4, 20.9, 20.84, 20.82.

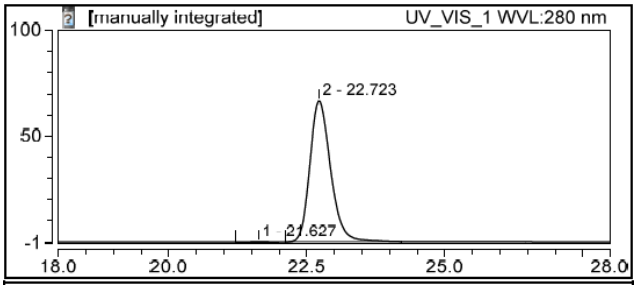
IR (neat, cm^{-1}): 2961, 2917, 1738, 1648, 1490, 1462, 1262, 1057, 993, 815.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{29}O$ 273.2213, found 273.2219.



Integration Results

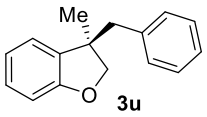
No.	Retention Time min	Area mAU*min	Relative Area %
1	20.863	42.465	50.20
2	23.797	42.119	49.80
Total:		**84.585**	**100.00**



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	21.627	0.028	0.10
2	22.723	28.950	99.90
Total:		**28.978**	**100.00**

(R)-3-benzyl-3-methyl-2,3-dihydrobenzofuran (3u)



3u

The compound was prepared according to the General Procedure from the reaction of **1a** (54.8 mg, 0.2 mmol) and **2v** (40.8 mg, 0.2 mmol).

31.4 mg, 70% yield, 98% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 220 nm, t_R(major) = 19.1 min, t_R(minor) = 22.7 min.

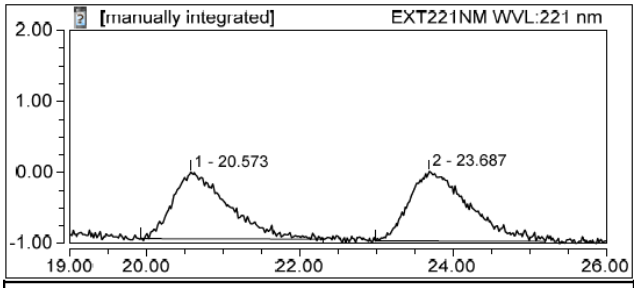
$[\alpha]_D^{21}$ = +1 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.20 (m, 3 H), 7.15-7.11 (m, 1 H), 7.00-6.98 (m, 2 H), 6.95-6.92 (m, 1 H), 6.88-6.84 (m, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 4.50 (d, *J* = 8.8 Hz, 1 H), 4.05 (d, *J* = 8.8 Hz, 1 H), 2.91-2.83 (m, 2 H), 1.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 137.5, 134.8, 130.3, 128.1, 127.9, 126.4, 123.3, 120.2, 109.7, 81.8, 46.6, 46.2, 24.5.

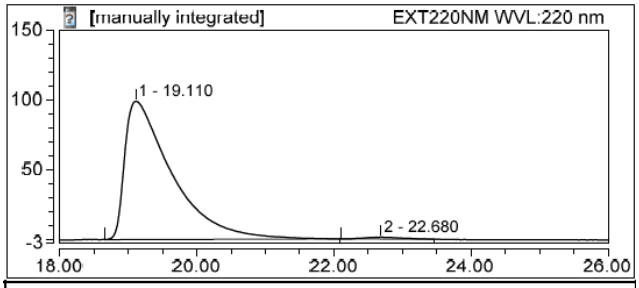
IR (neat, cm^{-1}): 3432, 2086, 1637, 1479, 1418, 1261, 1122, 1042, 750, 702.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{17}O$ 225.1274, found 225.1272.



Integration Results

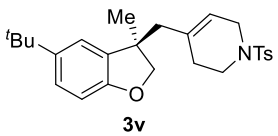
No.	Retention Time min	Area mAU*min	Relative Area %
1	20.573	0.791	47.03
2	23.687	0.891	52.97
Total:		1.682	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	19.110	79.310	98.91
2	22.680	0.870	1.09
Total:		80.180	100.00

(*R*)-4-((5-(*tert*-butyl)-3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (3v)



3v

The compound was prepared according to the General Procedure from the reaction of **1b** (66.0 mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol).

65.9 mg, 75% yield, 97% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 3/97, 1 mL/min, 279 nm, t_R(minor) = 32.7 min, t_R(major) = 37.8 min.

$[\alpha]_D^{24}$ = +14 (c = 1.0, CH_2Cl_2).

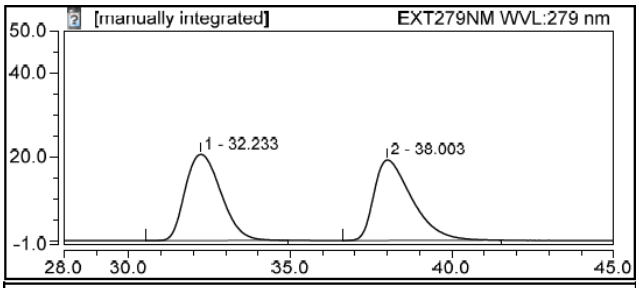
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.12 (dd, *J* = 2.0, 8.0 Hz, 1 H), 7.02 (d, *J* = 2.0 Hz, 1 H), 6.66 (d, *J* = 8.4 Hz, 1 H), 5.29 (s, 1 H), 4.33 (d, *J* = 8.4 Hz, 1

H), 4.07 (d, *J* = 8.8 Hz, 1 H), 3.60-3.46 (m, 2 H), 3.11-2.92 (m, 2 H), 2.42 (s, 3 H), 2.28 (s, 2 H), 1.91-1.79 (m, 2 H), 1.29 (s, 3 H), 1.27 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 143.5, 143.4, 134.1, 133.6, 133.2, 129.6, 127.6, 124.9, 120.9, 119.7, 108.7, 82.2, 47.9, 45.5, 44.8, 42.9, 34.3, 31.7, 29.9, 25.7, 21.5.

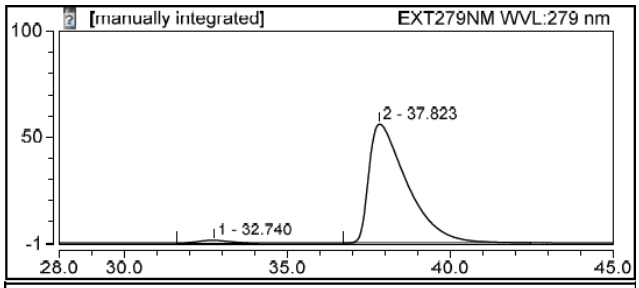
IR (neat, cm^{-1}): 2963, 2873, 1490, 1461, 1349, 1165, 1094, 950, 818, 736.

HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{34}NO_3S$ 440.2254, found 440.2253.



Integration Results

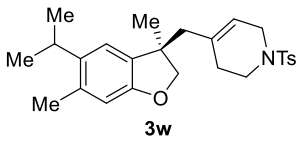
No.	Retention Time min	Area mAU*min	Relative Area %
1	32.233	26.305	50.04
2	38.003	26.261	49.96
Total:		**52.567**	**100.00**



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	32.740	1.229	1.59
2	37.823	76.299	98.41
Total:		**77.528**	**100.00**

(*R*)-4-((5-isopropyl-3,6-dimethyl-2,3-dihydrobenzofuran-3-yl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (3w)



3w

The compound (a colorless oil, 72.0 mg, 82% yield, 97% ee) was prepared according to the General Procedure from the reaction of **1c** (66.0 mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol). The gram scale reaction was conducted with **1c** (1.32 g, 4.0 mmol) and **2k** (1.54 g, 4.0 mmol) to afford **3w** with 72% yield (1.27 g) and 97% ee.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 3/97, 1 mL/min, 287 nm, t_R(minor) = 30.2 min, t_R(major) = 33.2 min.

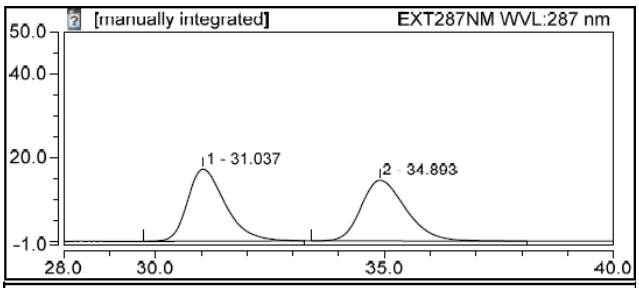
$[\alpha]_D^{24}$ = +9 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 6.87 (s, 1 H), 6.53 (s, 1 H), 5.29 (s, 1 H), 4.30 (d, *J* = 8.8 Hz, 1 H), 4.05 (d, *J* = 8.8 Hz, 1 H), 3.61-3.46 (m, 2 H), 3.13-3.03 (m, 3 H), 2.42 (s, 3 H), 2.27 (s, 5 H), 1.93-1.82 (m, 2 H), 1.27 (s, 3 H), 1.18-1.14 (m, 6 H).

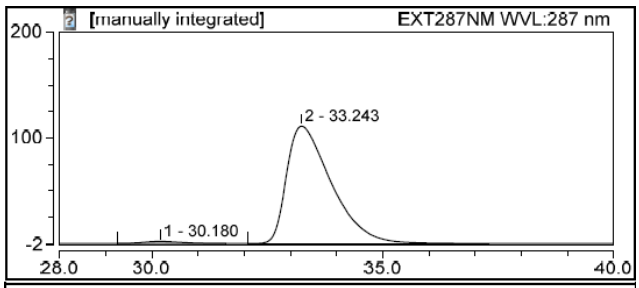
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 143.4, 138.9, 135.0, 133.7, 133.2, 132.2, 129.6, 127.6, 120.8, 118.9, 111.0, 82.1, 47.9, 45.4, 44.8, 42.9, 29.9, 28.8, 25.9, 23.7, 23.4, 21.4, 19.6.

IR (neat, cm^{-1}): 2960, 2926, 1489, 1459, 1349, 1165, 1094, 948, 818, 738.

HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{34}NO_3S$ 440.2254, found 440.2252.

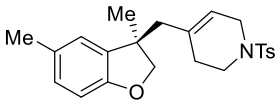


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	31.037	16.436	50.02
2	34.893	16.420	49.98
Total:		32.857	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	30.180	1.732	1.37
2	33.243	124.493	98.63
Total:		126.225	100.00

(*R*)-4-((3,5-dimethyl-2,3-dihydrobenzofuran-3-yl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (3x)



3x

The compound was prepared according to the General Procedure from the reaction of **1d** (57.6 mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol).

47.6 mg, 63% yield, 97% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 10/90, 1 mL/min, 281 nm, t_R(minor) = 17.3 min, t_R(major) = 27.3 min.

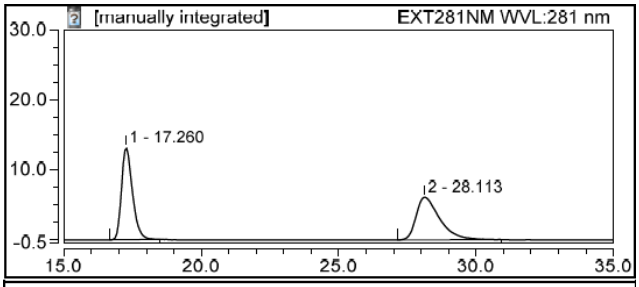
$[\alpha]_D^{24}$ = +12 (c = 0.68, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 6.89 (d, *J* = 8.0 Hz, 1 H), 6.83 (s, 1 H), 6.62 (d, *J* = 8.0 Hz, 1 H), 5.30 (s, 1 H), 4.32 (d, *J* = 8.4 Hz, 1 H), 4.05 (d, *J* = 8.8 Hz, 1 H), 3.61-3.49 (m, 2 H), 3.11-2.95 (m, 2 H), 2.42 (s, 3 H), 2.31-2.23 (m, 2 H), 2.26 (s, 3 H), 1.94-1.80 (m, 2 H), 1.26 (s, 3 H).

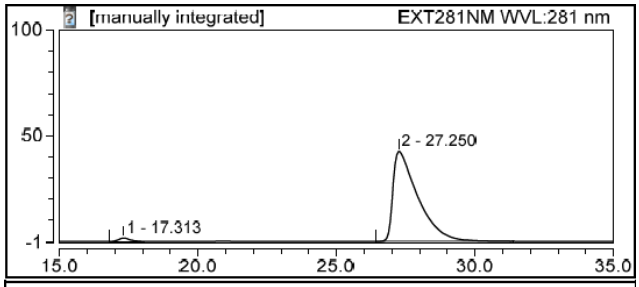
^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 143.5, 134.9, 133.6, 133.4, 129.7, 129.6, 128.6, 127.6, 123.3, 120.9, 109.2, 81.8, 47.8, 45.4, 44.8, 42.8, 30.0, 26.0, 21.5, 20.8.

IR (neat, cm^{-1}): 2967, 2924, 1490, 1459, 1344, 1165, 1094, 982, 814, 688.

HRMS (ESI): $[M+H]^+$ calcd for $C_{23}H_{28}NO_3S$ 398.1784, found 229.1785.

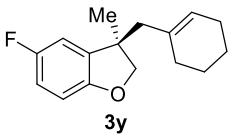


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	17.260	6.092	50.10
2	28.113	6.067	49.90
Total:		12.159	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	17.313	0.678	1.51
2	27.250	44.336	98.49
Total:		45.014	100.00

(*R*)-3-(cyclohex-1-en-1-ylmethyl)-5-fluoro-3-methyl-2,3-dihydrobenzofuran (3y)



3y

The compound was prepared according to the General Procedure from the reaction of **1e** (105.1 mg, 0.36 mmol) and **2a** (46.0 mg, 0.2 mmol). NiI_2 (9.5 mg, 0.030 mmol) and **L1** (11.4 mg, 0.042 mmol) were used.

16.7 mg, 38% yield, 99% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 289 nm, t_R(major) = 13.2 min, t_R(minor) = 21.6 min.

$[\alpha]_D^{21}$ = -5 (c = 1.0, CH_2Cl_2).

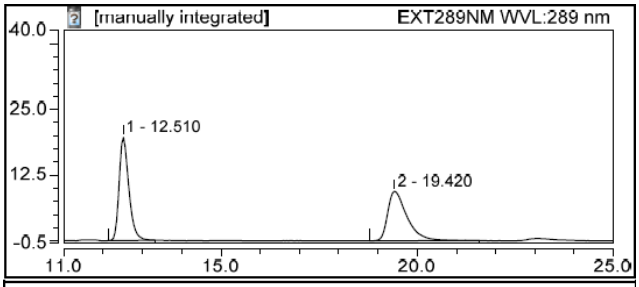
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81-6.76 (m, 2 H), 6.68-6.65 (m, 1 H), 5.40 (s, 1 H), 4.48 (d, *J* = 8.8 Hz, 1 H), 4.16 (d, *J* = 8.8 Hz, 1 H), 2.31-2.22 (m, 2 H), 1.99 (s, 2 H), 1.78-1.62 (m, 2 H), 1.56-1.45 (m, 4 H), 1.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 (d, J_{C-F} = 236.0 Hz), 155.1, 137.3 (d, J_{C-F} = 8.0 Hz), 134.2, 126.3, 114.0 (d, J_{C-F} = 24.0 Hz), 110.2 (d, J_{C-F} = 24.0 Hz), 109.6 (d, J_{C-F} = 8.0 Hz), 82.9, 48.8, 46.0, 30.2, 26.1, 25.4, 23.0, 22.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -124.40.

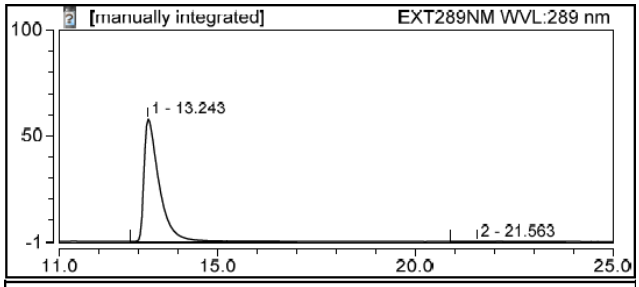
IR (neat, cm^{-1}): 2961, 2850, 1591, 1486, 1261, 1175, 1092, 1039, 807, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{20}FO$ 247.1493, found 247.1509.



Integration Results

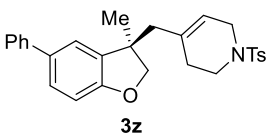
No.	Retention Time min	Area mAU*min	Relative Area %
1	12.510	5.589	51.06
2	19.420	5.358	48.94
Total:		10.947	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	13.243	25.627	99.56
2	21.563	0.113	0.44
Total:		25.740	100.00

(*R*)-4-((3-methyl-5-phenyl-2,3-dihydrobenzofuran-3-yl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (3z)



3z

The compound was prepared according to the General Procedure from the reaction of **1f** (70.0 mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol).

48.7 mg, 55% yield, 95% ee, white solid, mp: 60-62 ^{o}C.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 280 nm, t_R(major) =

45.9 min, t_R(minor) = 54.3 min.

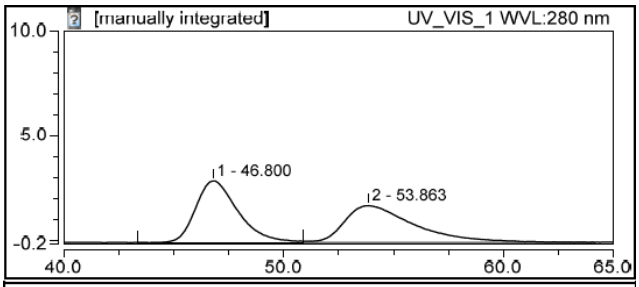
$[\alpha]_D^{24}$ = +75 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2 H), 7.52-7.50 (m, 2 H), 7.40 (t, *J* = 8.0 Hz, 2 H), 7.35 (dd, *J* = 2.0, 8.0 Hz, 1 H), 7.31-7.28 (m, 3 H), 7.25 (d, *J* = 2.0 Hz, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 5.33 (s, 1 H), 4.41 (d, *J* = 8.8 Hz, 1 H), 4.14 (d, *J* = 8.8 Hz, 1 H), 3.62-3.47 (m, 2 H), 3.14-2.93 (m, 2 H), 2.42 (s, 3 H), 2.37-2.29 (m, 2 H), 1.97-1.85 (m, 2 H), 1.33 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 143.5, 141.2, 135.5, 134.0, 133.5, 133.2, 129.6, 128.7, 127.6, 127.4, 126.7, 126.6, 121.6, 121.1, 109.8, 82.2, 47.9, 45.4, 44.8, 42.8, 30.0, 26.1, 21.5.

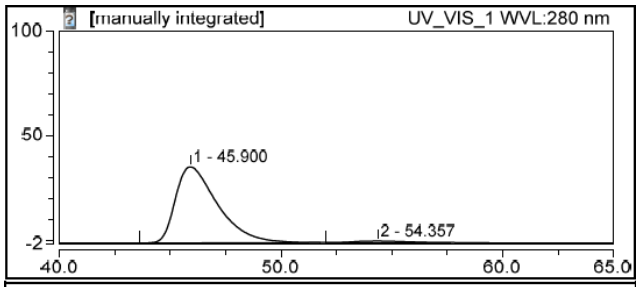
IR (neat, cm^{-1}): 2963, 2853, 1601, 1482, 1344, 1165, 1096, 958, 818, 738.

HRMS (ESI): $[M+H]^+$ calcd for $C_{28}H_{30}NO_3S$ 460.1941, found 460.1941.



Integration Results

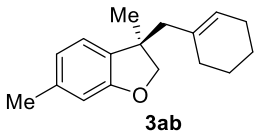
No.	Retention Time min	Area mAU*min	Relative Area %
1	46.800	6.595	50.32
2	53.863	6.512	49.68
Total:		**13.107**	**100.00**



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	45.900	80.080	97.64
2	54.357	1.936	2.36
Total:		**82.016**	**100.00**

(R)-3-(cyclohex-1-en-1-ylmethyl)-3,6-dimethyl-2,3-dihydrobenzofuran (3ab)



3ab

The compound was prepared according to the General Procedure from the reaction of **1h** (57.6 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol).

29.0 mg, 60% yield, 98% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 284 nm, t_R(major) = 11.4 min, t_R(minor) = 13.5 min.

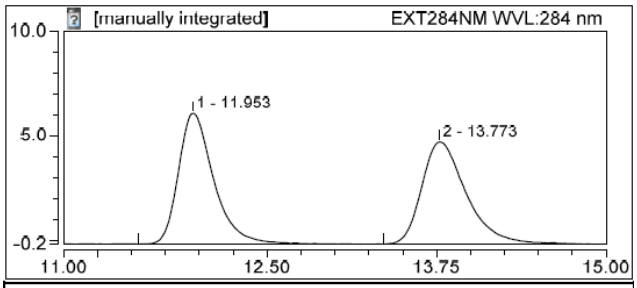
$[\alpha]_D^{21}$ = -8 (c = 1.0, CH_2Cl_2)

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95 (d, *J* = 7.6 Hz, 1 H), 6.83 (dd, *J* = 0.4 Hz, *J* = 7.2 Hz, 1 H), 6.59 (s, 1 H), 5.41 (s, 1 H), 4.45 (d, *J* = 8.4 Hz, 1 H), 4.13 (d, *J* = 8.4 Hz, 1 H), 2.30 (s, 3 H), 2.27 (d, *J* = 6.0 Hz, 2 H), 1.99 (s, 2 H), 1.77-1.64 (m, 2 H), 1.58-1.45 (m, 4 H), 1.28 (s, 3 H).

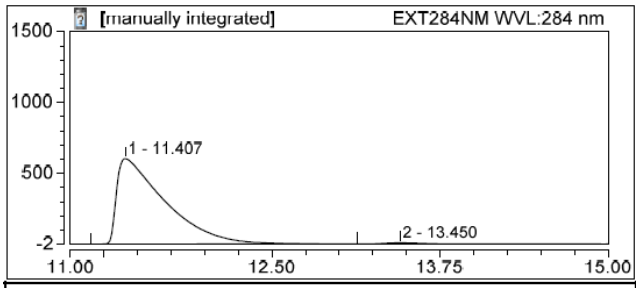
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 138.0, 134.7, 133.0, 125.8, 122.5, 121.0, 110.2, 82.6, 49.0, 45.2, 30.2, 26.3, 25.4, 23.0, 22.2, 21.5.

IR (neat, cm^{-1}): 2923, 2836, 1592, 1495, 1425, 1251, 1122, 1007, 980, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{23}O$ 243.1743, found 243.1749.

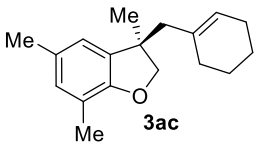


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	11.953	1.905	50.16
2	13.773	1.893	49.84
Total:		3.798	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	11.407	251.311	98.93
2	13.450	2.719	1.07
Total:		254.030	100.00

(R)-3-(cyclohex-1-en-1-ylmethyl)-3,5,7-trimethyl-2,3-dihydrobenzofuran (3ac)



3ac

The compound was prepared according to the General Procedure from the reaction of **1i** (60.4 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol).

33.3 mg, 65% yield, 90% ee, colorless oil.

Chiral HPLC: CHIRALCEL OD-H, 25 ^oC, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 290 nm, t_R(major) = 10.9 min, t_R(minor) = 12.6 min.

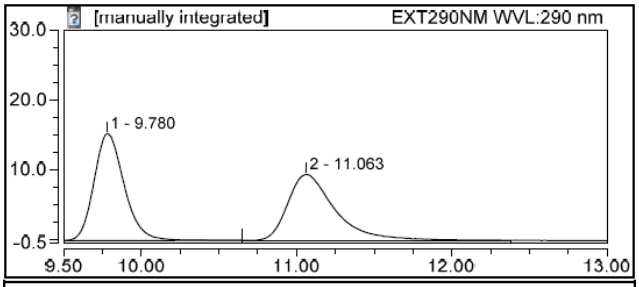
$[\alpha]_D^{21}$ = -2 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (d, *J* = 0.8 Hz, 1 H), 6.72 (d, *J* = 0.4 Hz, 1 H), 5.42 (s, 1 H), 4.44 (d, *J* = 8.4 Hz, 1 H), 4.12 (d, *J* = 8.4 Hz, 1 H), 2.30-2.22 (m, 5 H), 2.17(s, 3 H), 2.00 (s, 2 H), 1.78-1.65 (m, 2 H), 1.57-1.45 (m, 4 H), 1.27 (s, 3 H).

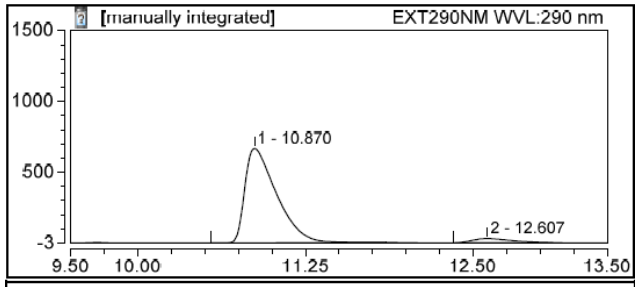
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 135.3, 134.8, 129.7, 129.4, 125.7, 120.8, 119.0, 82.3, 48.9, 45.8, 30.2, 25.9, 25.5, 23.1, 22.2, 20.8, 15.0.

IR (neat, cm^{-1}): 3429, 2923, 2836, 1638, 1482, 1200, 1123,1003, 854, 749.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{25}O$ 257.1900, found 257.1903.

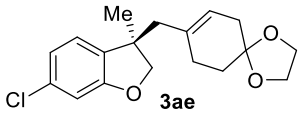


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.780	3.450	50.82
2	11.063	3.338	49.18
Total:		6.789	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	10.870	181.991	94.98
2	12.607	9.617	5.02
Total:		191.607	100.00

(R)-8-((6-chloro-3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-1,4-dioxaspiro[4.5]dec-7-ene (3ae)



The compound was prepared according to the General Procedure from the reaction of **1k** (61.6 mg, 0.2 mmol) and **2h** (57.6 mg, 0.2 mmol) in DMF. 41.0 mg, 64% yield, 98% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 260 nm, t_R(minor) = 10.4 min, t_R(major) = 12.5 min.

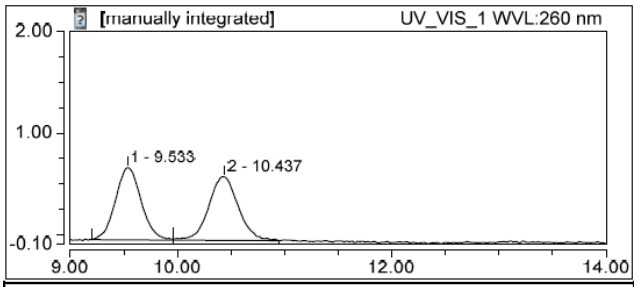
$[\alpha]_D^{21}$ = -8 (c = 0.5, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (d, *J* = 8.0 Hz, 1 H), 6.83 (dd, *J* = 1.6 Hz, *J* = 8.0 Hz, 1 H), 6.76 (d, *J* = 1.6 Hz, 1 H), 5.30 (s, 1 H), 4.47 (d, *J* = 8.4 Hz, 1 H), 4.18 (d, *J* = 8.4 Hz, 1 H), 3.96 (d, *J* = 2.4 Hz, 4 H), 2.31-2.26 (m, 4 H), 1.96 (d, *J* = 5.6 Hz, 2 H), 1.66 (t, *J* = 6.4 Hz, 2 H), 1.32 (s, 3 H).

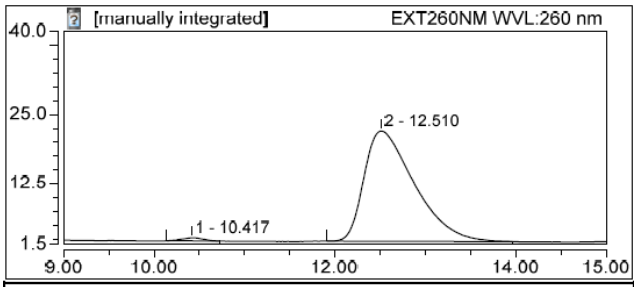
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 134.3, 134.0, 133.3, 123.6, 123.4, 120.4, 110.4, 107.6, 83.2, 64.4, 47.6, 45.3, 35.8, 31.2, 29.2, 26.0.

IR (neat, cm^{-1}): 2917, 1593, 1480, 1417, 1316, 1260, 1118, 1042, 875, 804.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{22}ClO_3$ 321.1252, found 321.1259.

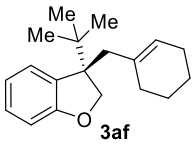


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.533	0.199	49.80
2	10.437	0.200	50.20
Total:		0.399	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	10.417	0.153	1.17
2	12.510	12.859	98.83
Total:		13.011	100.00

(*S*)-3-(*tert*-butyl)-3-(cyclohex-1-en-1-ylmethyl)-2,3-dihydrobenzofuran (3af)



The compound was prepared according to the General Procedure from the reaction of **1l** (63.2 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol).

33.0 mg, 65% yield, 98% ee, colorless oil.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 295 nm, t_R(major) = 7.7 min, t_R(minor) = 10.9 min.

$[\alpha]_D^{21}$ = +68 (c = 0.5, CH_2Cl_2).

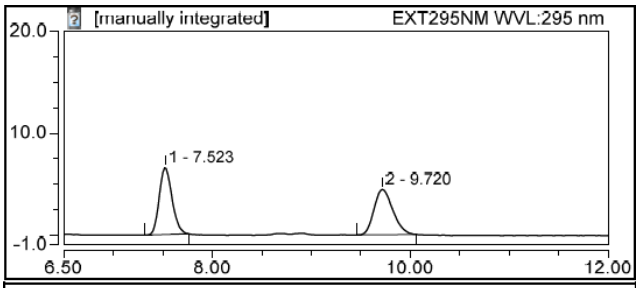
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.17 (m, 1 H), 7.10 (dt, *J* = 1.2, 7.6 Hz, 1 H), 6.80 (m, 1 H),

6.70 (d, *J* = 8.0 Hz, 1 H), 5.31 (s, 1 H), 4.49-4.41 (m, 2 H), 2.56-2.53 (m, 1 H), 2.36-2.33 (m, 1 H), 1.92 (s, 2 H), 1.44-1.34 (m, 6 H), 0.93 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 135.9, 131.9, 127.9, 126.4, 125.6, 119.2, 109.0, 76.1, 54.4, 42.3, 37.2, 30.0, 25.6, 25.5, 23.0, 22.1.

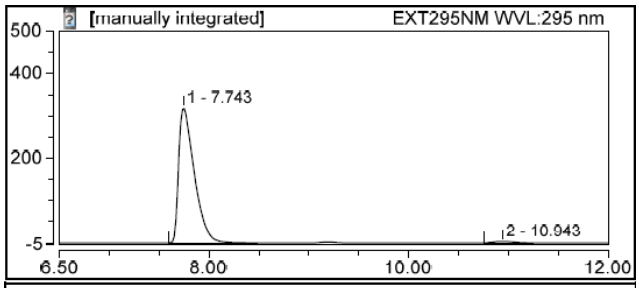
IR (neat, cm^{-1}): 2961, 2935, 1687, 1655, 1459, 1217, 1112, 1084, 835, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{27}O$ 271.2056, found 271.2058.



Integration Results

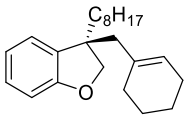
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.523	0.987	50.13
2	9.720	0.981	49.87
Total:		**1.968**	**100.00**



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	7.743	57.854	98.76
2	10.943	0.724	1.24
Total:		**58.578**	**100.00**

(*R*)-3-(cyclohex-1-en-1-ylmethyl)-3-octyl-2,3-dihydrobenzofuran (3ag)



3ag

The compound was prepared according to the General Procedure from the reaction of **1m** (74.4 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol).

42.4 mg, 68% yield, 95% ee, colorless.

Chiral HPLC: CHIRALPAK IB, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.5 mL/min, 280 nm, t_R(major) = 9.0 min, t_R(minor) = 10.1 min.

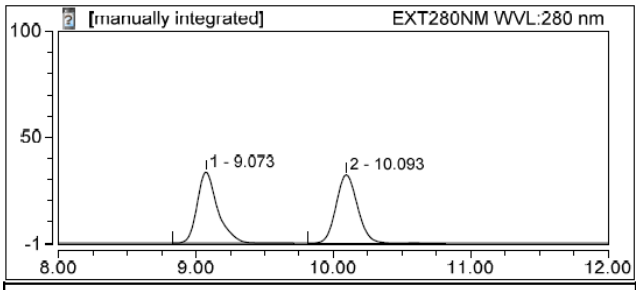
$[\alpha]_D^{22}$ = -2 (c = 0.5, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (dt, *J* = 1.2, 7.6 Hz, 1 H), 7.04 (dd, *J* = 1.2, 7.6 Hz, 1 H), 6.84 (dt, *J* = 0.8, 7.6 Hz, 1 H), 6.74 (d, *J* = 7.8 Hz, 1 H), 5.38 (s, 1 H), 4.41 (d, *J* = 8.8 Hz, 1 H), 4.26 (d, *J* = 8.4 Hz, 1 H), 2.33 (s, 2 H), 1.98 (s, 2 H), 1.70-1.42 (m, 8 H), 1.32-1.00 (m, 12 H), 0.86 (t, *J* = 6.8 Hz, 3 H).

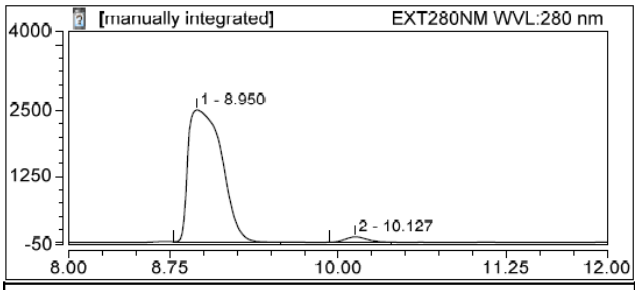
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 134.6, 134.0, 127.9, 125.9, 123.7, 120.0, 109.3, 80.5, 48.9, 47.6, 39.5, 31.8, 30.2, 30.1, 29.4, 29.3, 25.5, 24.2, 23.0, 22.6, 22.1, 14.1.

IR (neat, cm^{-1}): 2924, 2857, 1597, 1482, 1459, 1230, 1019, 975, 831, 745.

HRMS (ESI): $[M+H]^+$ calcd for $C_{23}H_{35}O$ 327.2682, found 327.2682.

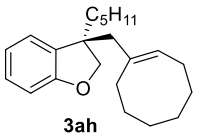


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.073	5.795	49.95
2	10.093	5.806	50.05
Total:		11.601	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	8.950	725.404	97.48
2	10.127	18.751	2.52
Total:		744.155	100.00

(*R*,*E*)-3-(cyclooct-1-en-1-ylmethyl)-3-pentyl-2,3-dihydrobenzofuran (3ah)



3ah

The compound was prepared according to the General Procedure from the reaction of **1n** (66.0 mg, 0.2 mmol) and **2e** (51.6 mg, 0.2 mmol).

26.8 mg, 46% yield, 93% ee, colorless oil.

Chiral HPLC: CHIRALPAK IB, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm, t_R(major) = 7.1 min, t_R(minor) = 7.5 min.

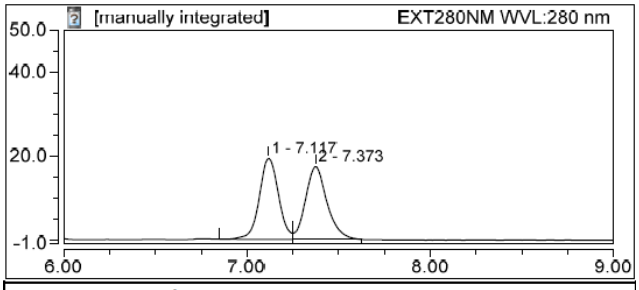
$[\alpha]_D^{22}$= +10 (c = 0.5, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12-7.08 (m, 1 H), 7.04 (d, *J* = 7.6 Hz, 1 H), 6.84 (t, *J* = 7.2 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.33 (t, *J* = 8.0 Hz, 1 H), 4.45 (d, *J* = 8.8 Hz, 1 H), 4.28 (d, *J* = 8.8 Hz, 1 H), 2.42-2.31 (m, 2 H), 2.07-1.81 (m, 4 H), 1.69-1.57 (m, 2 H), 1.45-0.88 (m, 14 H), 0.83 (t, *J* = 6.8 Hz, 3 H).

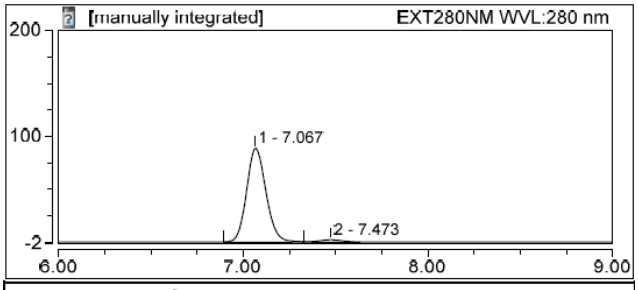
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 137.0, 134.0, 129.0, 127.8, 123.6, 120.0, 109.3, 80.3, 49.1, 45.4, 39.3, 32.4, 30.0, 29.4, 28.2, 26.70, 26.68, 26.0, 23.9, 22.5, 14.0.

IR (neat, cm^{-1}): 2963, 2851, 1595, 1459, 1260, 1122, 1093, 978, 803, 748.

HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{33}O$ 313.2526, found 313.2527..

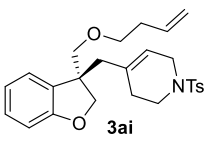


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.117	2.355	50.00
2	7.373	2.356	50.00
Total:		4.711	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.067	10.870	96.69
2	7.473	0.372	3.31
Total:		11.242	100.00

(*R*)-4-((3-((but-3-en-1-yloxy)methyl)-2,3-dihydrobenzofuran-3-yl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (3ai)



3ai

The compound was prepared according to the General Procedure from the reaction of **1o** (68.8 mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol) in DMF at 60 ^{o}C.

37.2 mg, 43% yield, 95% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 10/90, 1 mL/min, 285 nm, t_R(minor) = 20.7 min, t_R(major) = 24.2 min.

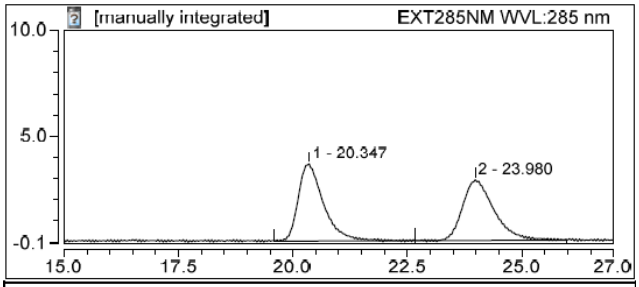
$[\alpha]_D^{22}$ = -1 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.15-7.07 (m, 2 H), 6.82 (dt, *J* = 1.2, 7.6 Hz, 1 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 5.82-5.75 (m, 1 H), 5.31 (s, 1 H), 5.09-5.01 (m, 2 H), 4.28 (s, 2 H), 3.60-3.36 (m, 6 H), 3.10-2.89 (m, 2 H), 2.52-2.27 (m, 4 H), 2.42, (s, 3 H), 1.87-1.81 (m, 2 H).

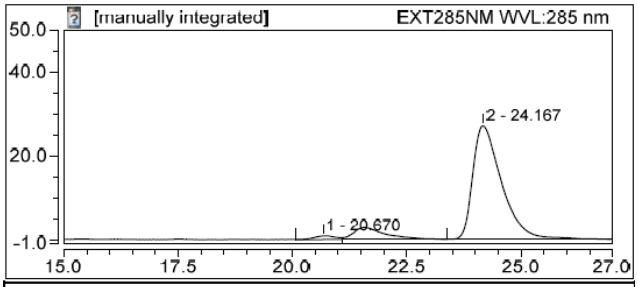
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 143.5, 135.1, 133.3, 132.9, 131.1, 129.6, 128.8, 127.6, 124.2, 121.1, 120.1, 116.4, 109.7, 78.3, 75.7, 70.6, 49.9, 44.8, 42.8, 42.6, 34.0, 30.0, 21.5.

IR (neat, cm^{-1}): 2924, 2857, 1597, 1482, 1347, 1165, 1098, 954, 755, 690.

HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{33}NO_4S$ 454.2047, found 454.2061.

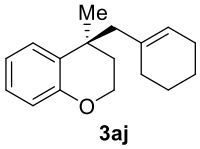


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	20.347	2.333	50.45
2	23.980	2.292	49.55
Total:		4.625	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	20.670	0.486	2.37
2	24.167	20.027	97.63
Total:		20.513	100.00

(S)-4-(cyclohex-1-en-1-ylmethyl)-4-methylchromane (3aj)



3aj

The compound was prepared according to the General Procedure from the reaction of **1p** (57.6 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol).

28.1 mg, 58% yield, 94% ee, colorless oil.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 0/100, 0.3 mL/min, 226 nm, t_R(major) = 18.5 min, t_R(minor) = 19.0 min.

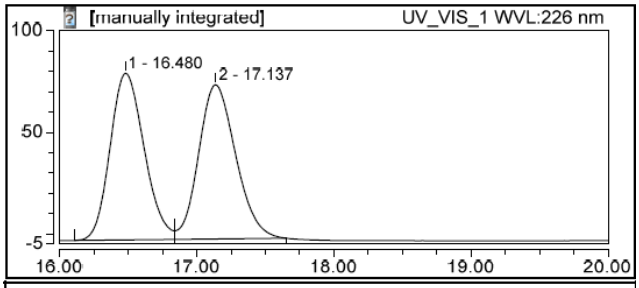
$[\alpha]_D^{21}$ = +1 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.24 (m, 1 H), 7.06 (t, *J* = 8.0 Hz, 1 H), 6.88-6.84 (m, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 5.39 (s, 1 H), 4.21-4.14 (m, 2 H), 2.44-2.22 (m, 2 H), 2.05-1.66 (m, 6 H), 1.55-1.46 (m, 4 H), 1.31 (s, 3 H).

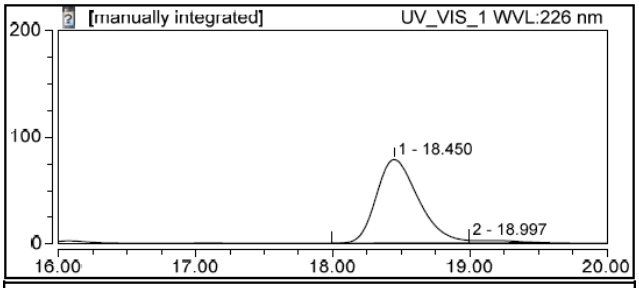
^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 135.0, 131.1, 127.5, 126.9, 126.2, 120.1, 116.9, 63.0, 51.2, 34.5, 33.8, 30.7, 30.4, 25.5, 23.1, 22.2.

IR (neat, cm^{-1}): 3410, 2918, 1594, 1447, 1420, 1261, 1117, 1042, 892, 750.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{23}O$ 243.1743, found 243.1748.

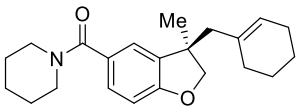


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	16.480	23.612	49.82
2	17.137	23.781	50.18
Total:		47.394	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	18.450	27.891	97.13
2	18.997	0.823	2.87
Total:		28.714	100.00

(*R*)-(3-(cyclohex-1-en-1-ylmethyl)-3-methyl-2,3-dihydrobenzofuran-5-yl)(piperidin-1-yl)methanone (3al)



3al

The compound was prepared according to the General Procedure from the reaction of **1r** (138.6 mg, 0.36 mmol) and **2a** (46.0 mg, 0.2 mmol).

30.6 mg, 45% yield, 92% ee, white solid, mp: 77-79 °C.

Chiral HPLC: CHIRALPAK IA, 25 °C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 280 nm, t_R(major) = 13.8 min, t_R(minor) = 15.6 min.

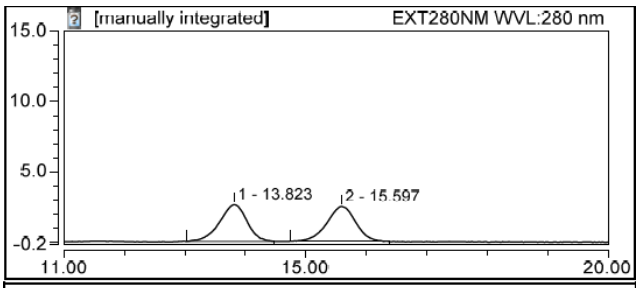
$[\alpha]_D^{22}$ = +22 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (dd, *J* = 2.0, 4.0 Hz, 2 H), 6.74 (d, *J* = 8.8 Hz, 1 H), 5.40 (s, 1 H), 4.51 (d, *J* = 8.4 Hz, 1 H), 4.19 (d, *J* = 8.4 Hz, 1 H), 3.53 (brs, 4 H), 2.33-2.25 (m, 2 H), 1.98 (s, 2 H), 1.77-1.43 (m, 12 H), 1.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 160.4, 136.0, 134.2, 128.4, 127.5, 126.2, 122.6, 108.9, 82.8, 49.0, 48.7, 45.4, 43.6, 30.1, 26.4, 26.2, 25.8, 25.3, 24.6, 22.9, 22.0.

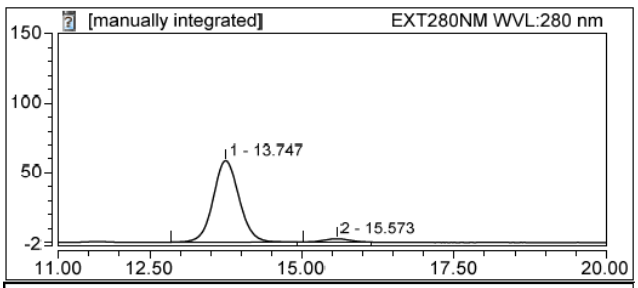
IR (neat, cm^{-1}): 3569, 3450, 1655, 1638, 1473, 1277, 1262, 1074, 766, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{30}NO_2$ 340.2271, found 340.2272.



Integration Results

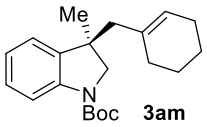
No.	Retention Time min	Area mAU*min	Relative Area %
1	13.823	1.373	49.97
2	15.597	1.375	50.03
Total:		2.748	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	13.747	28.995	96.12
2	15.573	1.169	3.88
Total:		30.164	100.00

***Tert*-butyl (R)-3-(cyclohex-1-en-1-ylmethyl)-3-methylindoline-1-carboxylate (3am)**



3am

The compound was prepared according to the General Procedure from the reaction of **1x** (74.6 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol) in DMF.

30.1 mg, 46% yield, 83% ee, colorless oil.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 284 nm, t_R(major) = 21.5 min, t_R(minor) = 24.2 min.

$[\alpha]_D^{22}$ = -25 (c = 2.0, CH_2Cl_2).

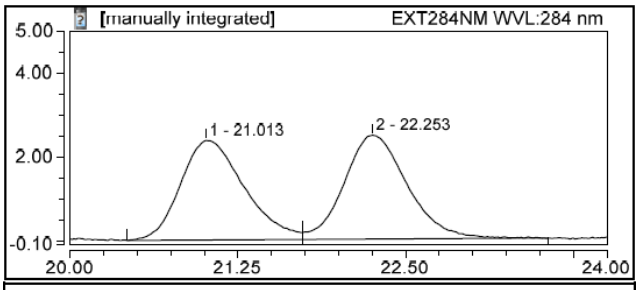
^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ [7.81 (s), 7.42 (s), 1 H], 7.15 (t, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 6.94 (t, *J* = 8.0 Hz, 1 H), 5.37 (s, 1 H), 3.97 (s, 1 H), 3.56 (s, 1 H), 2.22(s, 2 H), 1.96 (s, 2 H), 1.64-1.40 (m, 15 H), 1.30 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ 152.5, 142.1, 141.1, 140.2, 139.2, 134.6, 127.5, 125.8, 122.5, 122.1, 114.6, 81.3, 80.2, 59.7, 50.1, 43.1, 42.44, 30.1, 28.5, 27.3, 25.5, 23.0, 22.1.

IR (neat, cm^{-1}): 2927, 1704, 1600, 1485, 1393, 1291, 1147, 1017, 859, 750.

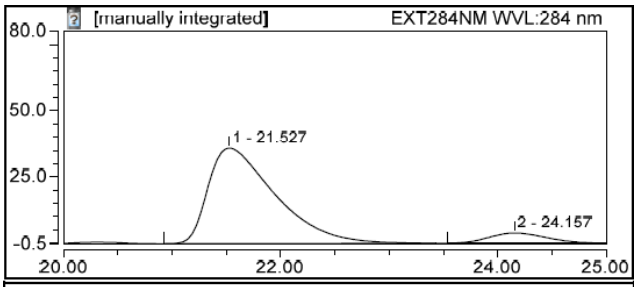
HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{30}NO_2$ 328.2271, found 328.2277.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **3am** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.



Integration Results

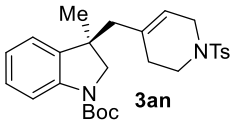
No.	Retention Time min	Area mAU*min	Relative Area %
1	21.013	1.310	49.24
2	22.253	1.351	50.76
Total:		2.661	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	21.527	25.807	91.65
2	24.157	2.352	8.35
Total:		28.159	100.00

Tert-butyl(R)-3-methyl-3-((1-tosyl-1,2,3,6-tetrahydropyridin-4-yl)methyl)indoline-1-carboxylate (3an)



The compound was prepared according to the General Procedure from the reaction of **1x** (74.6mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol) in DMF.

48.2 mg, 50% yield, 91% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 10/90, 1 mL/min, 280 nm, t_R(major) = 15.2 min, t_R(minor) = 16.7 min.

$[\alpha]_D^{22}$ = -13 (c = 2.0, CH_2Cl_2).

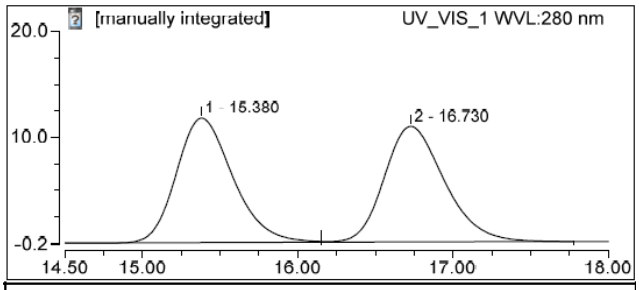
^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ [7.78 (s), 7.35 (s), 1 H], 7.62 (t, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.15 (t, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 4.0 Hz, 1 H), 6.94-6.91 (m, 1 H), 5.29 (d, *J* = 4.0 Hz, 1 H), 3.87 (s, 1 H), 3.50 (m, 3 H), 2.97 (d, *J* = 4.0 Hz, 2 H), 2.42 (s, 3 H), 2.23 (s, 2 H), 1.89-1.67 (m, 2 H), 1.51 (s, 9 H), 1.27 (d, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ 152.2, 143.4, 141.9, 138.9, 133.5, 133.1, 129.6, 127.9, 127.6, 122.5, 122.2, 120.1, 114.7, 81.4, 59.3, 48.6, 44.7, 42.8, 42.5, 29.9, 28.4, 27.1, 21.5.

IR (neat, cm^{-1}): 2975, 2925, 1698, 1598, 1484, 1393, 1164, 1018, 951, 712.

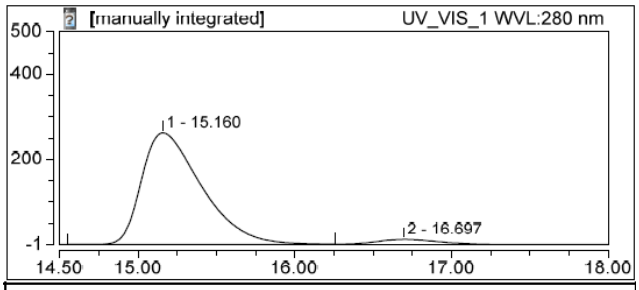
HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{35}N_2O_4S$ 483.2312, found 483.2321.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **3an** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.



Integration Results

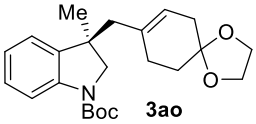
No.	Retention Time min	Area mAU*min	Relative Area %
1	15.380	4.970	50.25
2	16.730	4.920	49.75
Total:		**9.890**	**100.00**



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	15.160	116.761	95.63
2	16.697	5.338	4.37
Total:		**122.099**	**100.00**

Tert-butyl(R)-3-((1,4-dioxaspiro[4.5]dec-7-en-8-yl)methyl)-3-methylindoline-1-carboxylate (3ao)



3ao

The compound was prepared according to the General Procedure from the reaction of **1x** (74.6mg, 0.2 mmol) and **2h** (57.6 mg, 0.2 mmol) in DMF. 29.3 mg, 38% yield, 84% ee, colorless oil.

Chiral HPLC: CHIRALPAK ID, 25 ^{o}C, ^{i}PrOH-hexanes 2/98, 1 mL/min, 280 nm, t_R(major) = 9.7 min, t_R(minor) = 12.7 min.

$[\alpha]_D^{21}$ = -11 (c = 1.0, CH_2Cl_2).

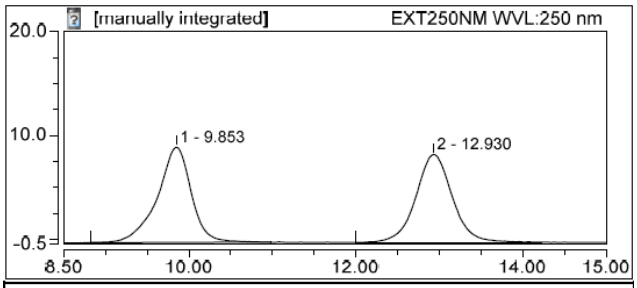
^{1}H NMR (400 MHz, $CDCl_3$): δ [7.81(s), 7.41 (s), 1 H], 7.16 (t, *J* = 8.0 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 6.95 (t, *J* = 4.0 Hz, 1 H), 5.30 (s, 1 H), 3.97-3.89 (m, 5 H), 3.59 (s, 1 H), 2.27-2.23 (d, *J* = 4.0 Hz), 1.89-176 (m, 2 H), 1.64-1.57 (m, 11 H), 1.32 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$, mixture of rotamers): δ 152.5, 142.1, 139.9, 134.3, 127.7, 122.7, 122.1, 114.7, 107.6, 81.4, 80.4, 64.3, 59.9, 48.7, 43.1, 35.9, 31.3, 29.1, 28.5, 27.0.

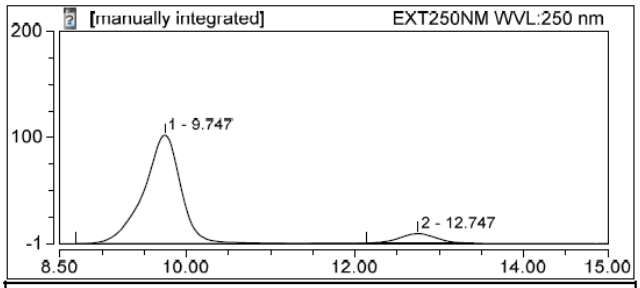
IR (neat, cm^{-1}): 2925, 1703, 1599, 1485, 1393, 1256, 1147, 1080, 857, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{23}H_{32}NO_4$ 386.2326, found 386.2337.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **3ao** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.

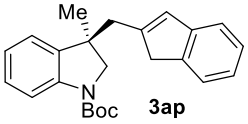


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.853	4.322	50.33
2	12.930	4.266	49.67
Total:		8.588	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	9.747	52.292	91.80
2	12.747	4.668	8.20
Total:		56.961	100.00

***Tert*-butyl (R)-3-((1H-inden-2-yl)methyl)-3-methylindoline-1-carboxylate (3ap)**



3ap

The compound was prepared according to the General Procedure from the reaction of **1x** (74.6 mg, 0.2 mmol) and **2m** (52.8 mg, 0.2 mmol) in DMF. 38.3 mg, 53% yield, 97% ee, colorless oil.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 4/96, 1 mL/min, 284 nm, t_R(major) = 5.4 min, t_R(minor) = 6.1 min.

$[\alpha]_D^{21}$ = -24 (c = 1.0, CH_2Cl_2).

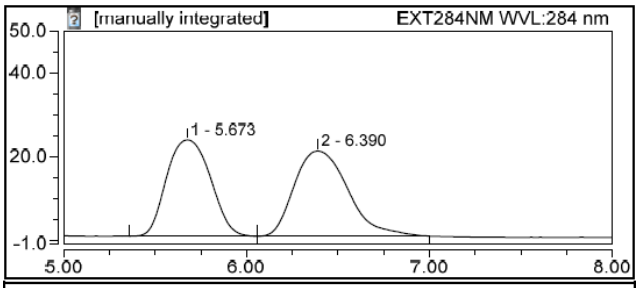
^{1}H NMR (400 MHz, $CDCl_3$, mixture of isomers): δ [7.82 (s), 7.39 (s), 1 H], 7.37-7.07 (m, 6 H), 7.01-6.97 (m, 1 H), 6.51 (d, *J* = 4.0 Hz, 1 H), 4.04-3.98 (m, 1 H), 3.65 (s, 1 H), 3.12-2.89 (m, 2 H), 2.81 (s, 2 H), 1.50 (s, 9 H), 1.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of isomers): δ 152.4, 145.8, 144.9, 143.4, 142.1, 139.1, 130.4, 127.9, 126.2, 123.9, 123.3, 122.7, 122.3, 120.2, 114.8, 81.8, 80.5, 59.4, 43.5, 42.8, 42.5, 28.4, 27.9.

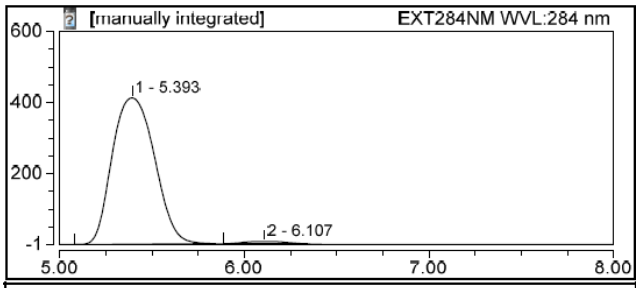
IR (neat, cm^{-1}): 3424, 2975, 2928, 1700, 1599, 1460, 1392, 1147, 857, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{24}H_{28}NO_2$ 362.2125, found 362.2123.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **3ap** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.

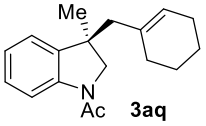


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	5.673	6.398	48.03
2	6.390	6.924	51.97
Total:		13.322	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	5.393	109.721	98.41
2	6.107	1.777	1.59
Total:		111.498	100.00

(R)-1-(3-(cyclohex-1-en-1-ylmethyl)-3-methylindolin-1-yl)ethan-1-one (3aq)



3aq

The compound was prepared according to the General Procedure from the reaction of **1y** (63.0 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol) in DMF.

24.7 mg, 46% yield, 92% ee, colorless oil.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 10/90, 1 mL/min, 280 nm, t_R(major) = 6.7 min, t_R(minor) = 8.3 min.

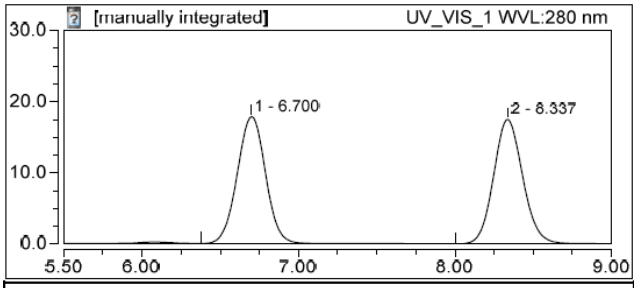
$[\alpha]_D^{21}$ = -13 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.0 Hz, 1 H), 7.15 (t, *J* = 8.0 Hz, 1 H), 7.12 (d, *J* = 8.0 Hz, 1 H), 7.04 (d, *J* = 8.0 Hz, 1 H), 5.42 (s, 1 H), 4.03 (d, *J* = 8.0 Hz, 1 H), 3.64 (d, *J* = 8.0 Hz, 1 H), 2.26-1.97 (m, 5 H), 1.65 (s, 2 H), 1.57-1.36 (m, 6 H), 1.31 (s, 3 H).

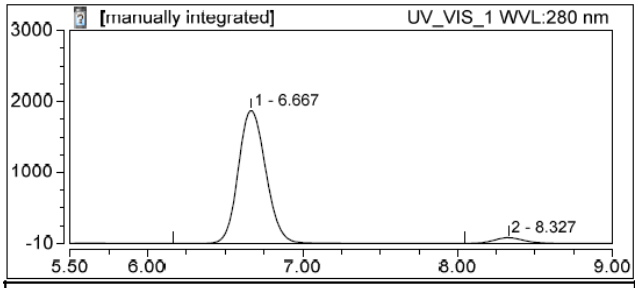
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4, 142.1, 139.6, 134.9, 127.8, 125.9, 123.6, 122.4, 116.9, 60.8, 50.3, 43.8, 30.0, 27.4, 25.5, 24.2, 22.9, 22.1.

IR (neat, cm^{-1}): 2923, 1663, 1597, 1481, 1460, 1402, 1120, 1043, 753, 618.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{23}NO$ 270.1852, found 270.1859.

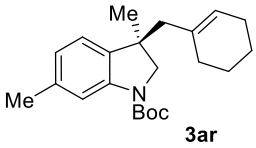


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.700	3.726	49.53
2	8.337	3.797	50.47
Total:		7.524	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.667	384.636	95.82
2	8.327	16.788	4.18
Total:		401.425	100.00

***Tert*-butyl (R)-3-(cyclohex-1-en-1-ylmethyl)-3,6-dimethylindoline-1-carboxylate (3ar)**



3ar

The compound was prepared according to the General Procedure from the reaction of **1z** (77.4 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol) in DMF. 51.2 mg, 75% yield, 83% ee, colorless oil.

$[\alpha]_D^{21}$ = -21 (c = 2.0, CH_2Cl_2).

Chiral HPLC: CHIRALCEL OD-H, 25 ^oC, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm, t_R(major) = 23.8 min, t_R(minor) = 25.4 min.

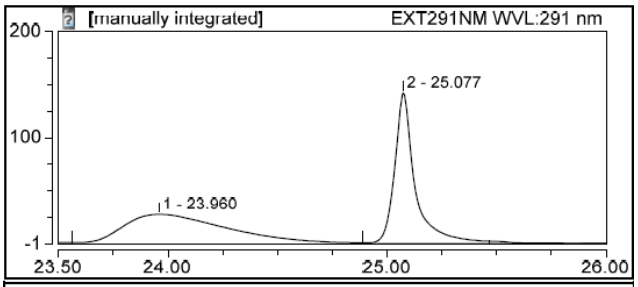
^{1}H NMR (600 MHz, $CDCl_3$, mixture of rotamers): δ [7.67 (s), 7.26 (s), 1 H], 6.97 (d, *J* = 6.0 Hz, 1 H), 6.77 (d, *J* = 6.0 Hz, 1 H), 5.37 (s, 1 H), 3.96 (s, 1 H), 3.59-3.53 (m, 1 H), 2.32 (s, 3 H), 2.21 (t, *J* = 12.0 Hz, 2 H), 1.97 (s, 2 H), 1.65-1.42 (m, 15 H), 1.28 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$, mixture of rotamers): δ 152.5, 142.3, 137.5, 136.7, 134.8, 125.7, 122.8, 122.3, 115.4, 80.2, 60.1, 50.1, 42.8, 30.2, 28.5, 27.4, 25.5, 23.1, 22.2, 21.7.

IR (neat, cm^{-1}): 2926, 2836, 1705, 1592, 1498, 1389, 1243, 1161, 1027, 764.

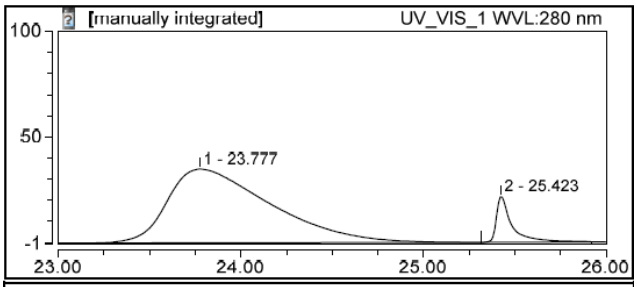
HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{32}NO_2$ 342.2428, found 342.2434.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **3ar** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.



Integration Results

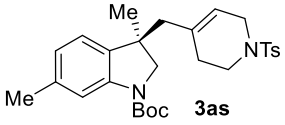
No.	Retention Time min	Area mAU*min	Relative Area %
1	23.960	15.431	49.72
2	25.077	15.604	50.28
Total:		31.034	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	23.777	22.871	91.44
2	25.423	2.140	8.56
Total:		25.011	100.00

***Tert*-butyl(R)-3,6-dimethyl-3-((1-tosyl-1,2,3,6-tetrahydropyridin-4-yl)methyl)indoline-1-carboxylate (3as)**



3as

The compound was prepared according to the General Procedure from the reaction of **1z** (77.4 mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol) in DMF. 91.3 mg, 92% yield, 96% ee, colorless oil.

Chiral HPLC: CHIRALPAK IB, 25 ^oC, ^{i}PrOH-hexanes 2/98, 1 mL/min, 290 nm, t_R(major) = 30.0 min, t_R(minor) = 33.7 min.

$[\alpha]_D^{21}$ = -25 (c = 2.0, CH_2Cl_2).

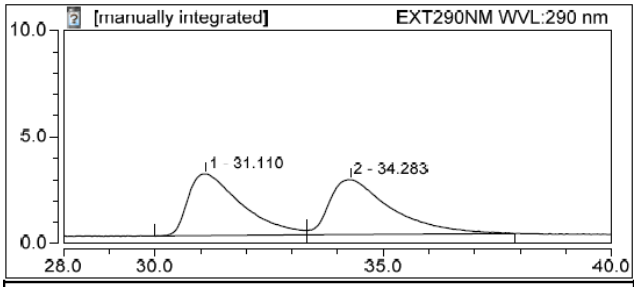
^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): [δ 7.64 (s), 7.27 (s), 1 H], 7.63 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 6.91 (d, *J* = 7.6 Hz, 1 H), 6.74 (d, *J* = 7.6 Hz, 1 H), 5.29 (s, 1 H), 3.85 (s, 1 H), 3.51 (s, 3 H), 2.98 (s, 2 H), 2.41 (s, 3 H), 2.31 (s, 3 H), 2.22 (s, 2 H), 1.89-1.72 (m, 2 H), 1.51 (s, 9 H), 1.25 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ 152.3, 143.4, 142.0, 137.7, 135.6, 133.6, 133.1, 129.5, 127.6, 122.8, 122.1, 120.7, 115.4, 81.4, 80.3, 59.5, 48.6, 44.7, 42.8, 42.5, 29.9, 28.3, 27.2, 21.6, 21.4.

IR (neat, cm^{-1}): 3428, 2974, 1699, 1595, 1497, 1347, 1163, 1028, 890, 737.

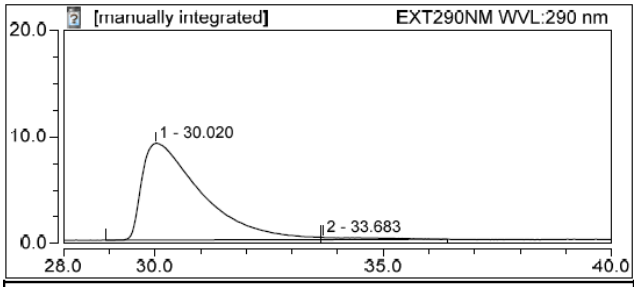
HRMS (ESI): $[M+H]^+$ calcd for $C_{28}H_{37}N_2O_4S$ 497.2477, found 497.2469.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **3as** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.



Integration Results

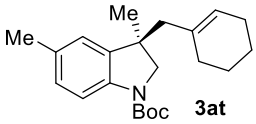
No.	Retention Time min	Area mAU*min	Relative Area %
1	31.110	3.938	49.26
2	34.283	4.057	50.74
Total:		7.995	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	30.020	13.751	97.94
2	33.683	0.289	2.06
Total:		14.040	100.00

***Tert*-butyl (R)-3-(cyclohex-1-en-1-ylmethyl)-3,5-dimethylindoline-1-carboxylate (3at)**



3at

The compound wasprepared according to the General Procedure from the reaction of **1aa** (77.4 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol) in DMF. 49.1 mg, 72% yield, 85% ee, colorless oil.

$[\alpha]_D^{21}$ = -7 (c = 1.5, CH_2Cl_2).

Chiral HPLC: CHIRALCEL OD-H, 25 ^oC, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm, t_R(minor) = 17.3 min, t_R(major) = 18.7 min.

^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ [7.67 (s), 7.28 (s), 1 H], 6.95 (d, *J* = 8.0 Hz, 1 H), 6.88 (s, 1 H), 5.38 (s, 1 H), 3.96 (s, 1 H), 3.53 (m, 1 H), 2.30 (s, 3 H), 2.21 (s, 2 H), 1.96 (s, 2 H), 1.55-1.44 (m, 15 H), 1.28 (s, 3 H).

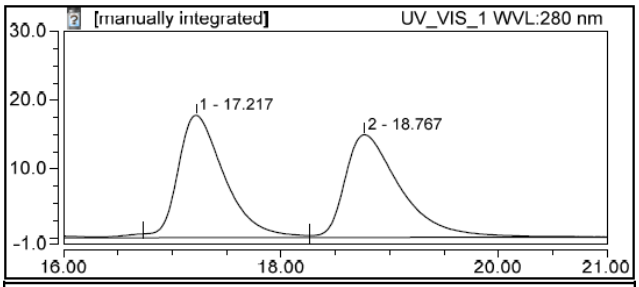
^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ 152.5, 139.8, 134.7, 131.5, 128.0, 125.7, 123.3, 114.3, 81.0, 80.1, 59.8, 50.0, 43.1, 42.5, 30.1, 28.5, 27.2, 25.5, 23.0, 22.2, 21.0.

HRMS (ESI): $[M+H]^+$ calcd for $C_{22}H_{32}NO_2$ 342.2428, found 342.2434.

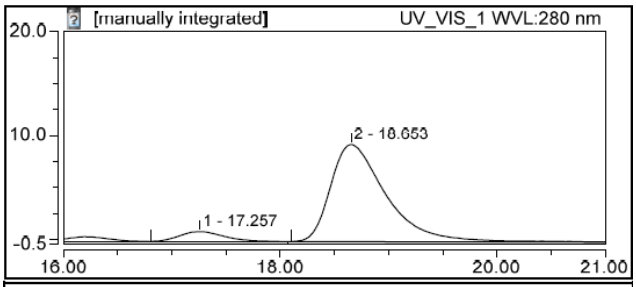
IR (neat, cm^{-1}): 3424, 2927, 1701, 1637, 1494, 1456, 1390, 1243, 1019, 858, 763.

HRMS (ESI): [M+H]$^+$ calcd for $C_{22}H_{32}NO_2$ 342.2428, found 342.2432.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **3at** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.

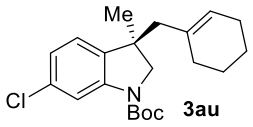


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	17.217	8.838	49.80
2	18.767	8.908	50.20
Total:		17.746	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	17.257	0.466	7.73
2	18.653	5.564	92.27
Total:		6.030	100.00

***Tert*-butyl(R)-6-chloro-3-(cyclohex-1-en-1-ylmethyl)-3-methylindoline-1-carboxylate (3au)**



3au

The compound was prepared according to the General Procedure from the reaction of **1ab** (81.4 mg, 0.2 mmol) and **2a** (46.0 mg, 0.2 mmol) in DMF. 41.9 mg, 58% yield, 96% ee, colorless oil.

[α]$_D^{21}$ = -49 (c = 1.0, CH_2Cl_2).

Chiral HPLC: CHIRALCEL OD-H, 25 ^oC, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm, t_R(minor) = 13.8 min, t_R(major) = 16.3 min.

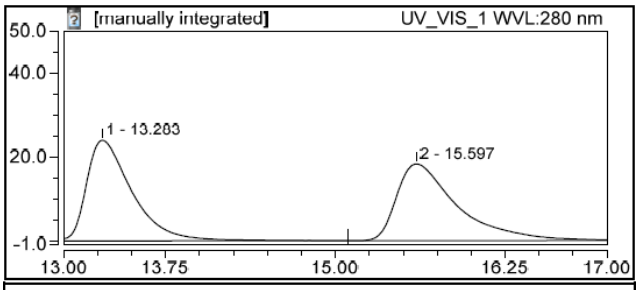
^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ [7.85 (s), 7.40 (s), 1 H], 6.97 (d, *J* = 8.0 Hz, 1 H), 6.91 (dd, *J* = 4.0 Hz, 1 H), 5.36 (s, 1 H), 3.98 (d, *J* = 8.0 Hz, 1 H), 3.57 (s, 1 H), 2.20-2.19 (m, 2 H), 1.96 (d, *J* = 8.0 Hz, 2 H), 1.60-1.44 (m, 15 H), 1.29 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ 152.2, 143.3, 137.8, 134.3, 133.1, 126.1, 123.3, 122.0, 115.0, 81.9, 80.7, 60.0, 50.0, 42.9, 42.2, 30.2, 28.4, 27.4, 25.5, 23.0, 22.1.

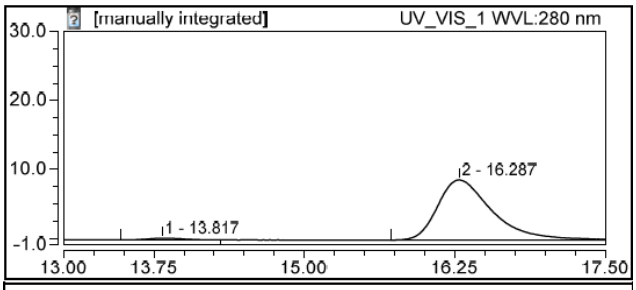
IR (neat, cm^{-1}): 2928, 2836, 1706, 1599, 1486, 1386, 1152, 1081, 921, 860.

HRMS (ESI): [M+H]$^+$ calcd for $C_{21}H_{29}ClNO_2$ 362.1881, found 362.1889.

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **3au** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.

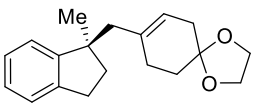


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	13.283	9.340	49.56
2	15.597	9.505	50.44
Total:		18.845	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	13.817	0.092	1.96
2	16.287	4.616	98.04
Total:		4.708	100.00

(*R*)-8-((1-methyl-2,3-dihydro-1*H*-inden-1-yl)methyl)-1,4-dioxaspiro[4.5]dec-7-ene (3av)



3av

The compound was prepared according to the General Procedure from the reaction of **1ac** (54.4 mg, 0.2 mmol) and **2h** (57.6 mg, 0.2 mmol). 43.2 mg, 76% yield, 90% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 273 nm, t_R(major) = 7.1 min, t_R(minor) = 8.1 min.

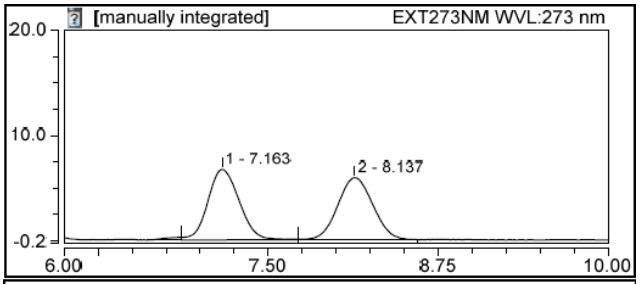
$[\alpha]_D^{25}$ = +18 (c = 0.78, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.10 (m, 4 H), 5.28 (d, *J* = 3.2 Hz, 1 H), 3.97-3.90 (m, 4 H), 2.93-2.78 (m, 2 H), 2.28-2.20 (m, 4 H), 2.14-2.08 (m, 1 H), 1.89-1.81 (m, 3 H), 1.66-1.59 (m, 2 H), 1.26 (s, 3 H).

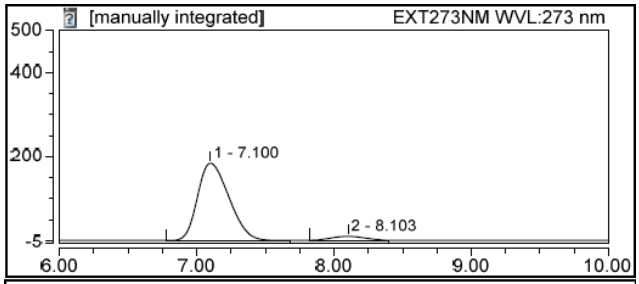
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 143.1, 135.5, 126.2, 126.0, 124.4, 122.7, 122.0, 107.8, 64.2, 48.5, 47.7, 38.9, 35.8, 31.3, 30.3, 29.3, 27.5.

IR (neat, cm^{-1}): 2956, 2928, 1479, 1450, 11377, 1256, 1112, 1060, 863, 759.

HRMS (ESI): $[M+H]^+$ calcd for $C_{19}H_{25}O_2$ 285.1849, found 285.1851.

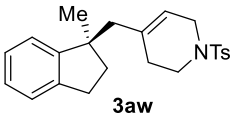


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.163	1.798	50.41
2	8.137	1.768	49.59
Total:		3.566	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.100	48.776	94.87
2	8.103	2.635	5.13
Total:		51.411	100.00

(R)-4-((1-methyl-2,3-dihydro-1H-inden-1-yl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (3aw)



3aw

The compound was prepared according to the General Procedure from the reaction of **1ac** (54.4 mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol) in DMF.

43.4 mg, 57% yield, 84% ee, colorless oil.

Chiral HPLC: CHIRALCEL AS-H, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 260 nm, t_R(minor) = 29.1 min, t_R(major) = 30.6 min.

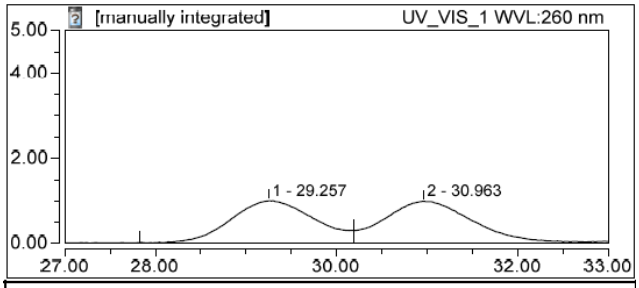
$[\alpha]_D^{22}$ = -4 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.26-7.04 (m, 4 H), 5.26 (s, 1 H), 3.63-3.45 (m, 2 H), 3.15-2.88 (m, 2 H), 2.83-2.80 (m, 2 H), 2.42 (s, 3 H), 2.26-2.18 (m, 2 H), 2.05-2.00 (m, 1 H), 1.98-1.74 (m, 3 H), 1.20 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 143.4, 142.9, 134.7, 133.3, 129.5, 127.6, 126.4, 126.1, 124.5, 122.5, 120.0, 48.8, 47.6, 44.8, 42.9, 38.4, 30.3, 30.2, 27.6, 21.4.

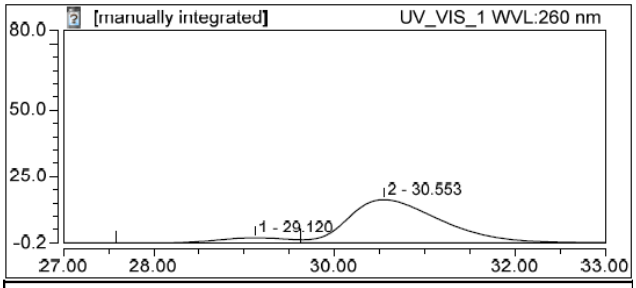
IR (neat, cm^{-1}): 3386, 2924, 1600, 1458, 1346, 1162, 1096, 1039, 816, 761.

HRMS (ESI): $[M+H]^+$ calcd for $C_{23}H_{28}NO_2S$ 382.1835, found 382.1842.



Integration Results

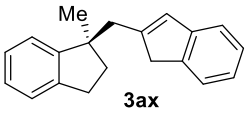
No.	Retention Time min	Area mAU*min	Relative Area %
1	29.257	1.041	49.01
2	30.963	1.084	50.99
Total:		2.125	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	29.120	1.717	8.10
2	30.553	19.473	91.90
Total:		21.190	100.00

(R)-2-((1-methyl-2,3-dihydro-1H-inden-1-yl)methyl)-1H-indene (3ax)



3ax

The compound was prepared according to the General Procedure from the reaction of **1ac** (54.4 mg, 0.2 mmol) and **2m** (52.8 mg, 0.2 mmol) in DMF.

23.4 mg, 45% yield, 92% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 260 nm, t_R(minor) = 8.0 min, t_R(major) = 10.6 min.

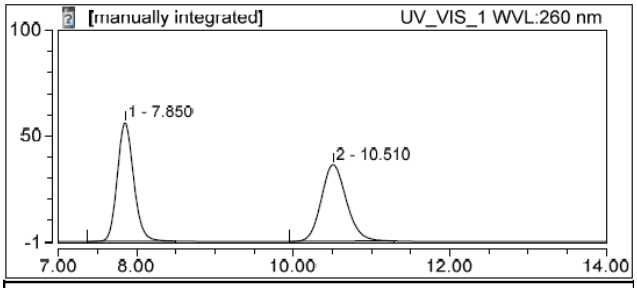
$[\alpha]_D^{21}$ = -1 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.18 (m, 2 H), 7.15-7.00 (m, 5 H), 6.99 (d, *J* = 1.2 Hz, 1 H), 6.43 (s, 1 H), 3.05-2.85 (m, 2 H), 2.79-2.65 (m, 4 H), 2.15-1.76 (m, 2 H), 1.26 (s, 3 H).

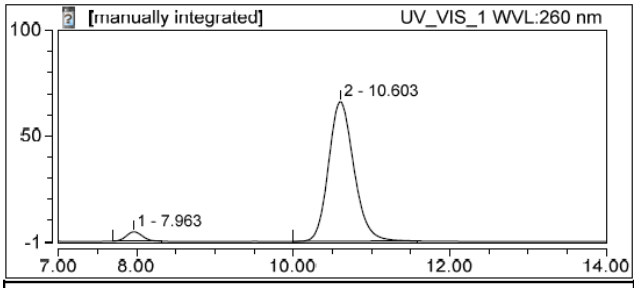
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 147.7, 145.3, 143.6, 143.2, 129.7, 126.5, 126.3, 126.1, 124.6, 123.6, 123.3, 122.6, 119.9, 48.1, 43.0, 42.8, 38.3, 30.2, 27.9.

IR (neat, cm^{-1}): 3440, 2962, 1636, 1459, 1416, 1316, 1260, 1094, 798, 755

HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{21}$ 261.1644, found 261.1638.

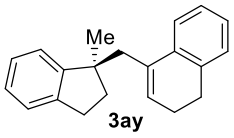


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.850	13.595	50.12
2	10.510	13.527	49.88
Total:		27.122	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	7.963	1.054	4.07
2	10.603	24.852	95.93
Total:		25.906	100.00

(R)-4-((1-methyl-2,3-dihydro-1H-inden-1-yl)methyl)-1,2-dihydronaphthalene (3ay)



The compound was prepared according to the General Procedure from the reaction of **1ac** (54.4 mg, 0.2 mmol) and **2n** (55.6 mg, 0.2 mmol) in DMF. 25.2mg, 46% yield, 89% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^oC, ^{i}PrOH-hexanes 4/96, 1 mL/min, 260 nm, t_R(minor) = 5.1 min, t_R(major) = 5.8 min.

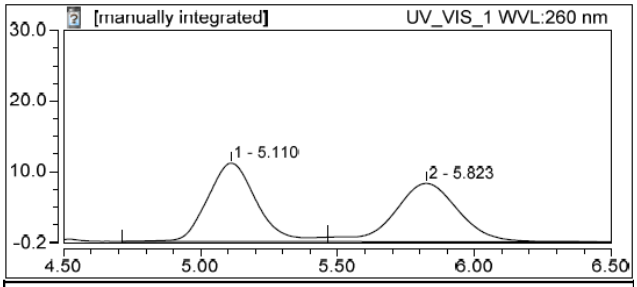
$[\alpha]_D^{23}$ = -1 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.06 (m, 8 H), 5.66 (t, *J* = 4.8 Hz, 1 H), 2.88-2.60 (m, 6 H), 2.18-2.08 (m, 3 H), 1.76-1.69 (m, 1 H), 1.25 (s, 3 H).

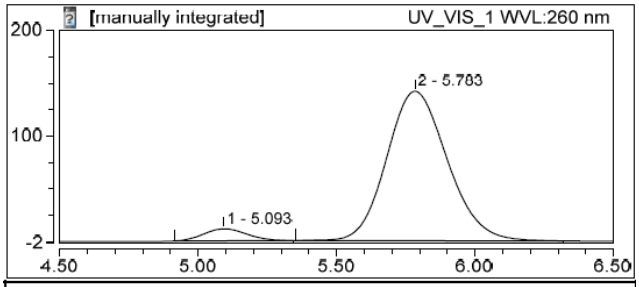
^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 143.2, 136.4, 136.1, 134.1, 128.8, 127.4, 126.3, 126.2, 125.9, 125.9, 124.4, 123.1, 123.0, 48.3, 42.3, 39.1, 30.2, 28.8, 27.1, 23.3.

IR (neat, cm^{-1}): 3023, 2930, 1945, 1600, 1478, 1311, 1109, 1023, 756, 670.

HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{23}$ 275.1797, found 275.1794.

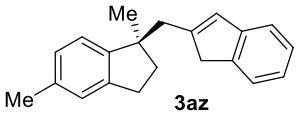


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	5.110	2.301	50.84
2	5.823	2.225	49.16
Total:		4.527	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	5.093	2.028	5.32
2	5.783	36.078	94.68
Total:		38.106	100.00

(R)-2-((1,5-dimethyl-2,3-dihydro-1H-inden-1-yl)methyl)-1H-indene (3az)



3az

The compound was prepared according to the General Procedure from the reaction of **1ad** (57.2 mg, 0.2 mmol) and **2m** (57.6 mg, 0.2 mmol) in DMF. 18.6 mg, 34% yield, 95% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 260 nm, t_R(minor) = 8.5 min, t_R(major) = 9.2 min.

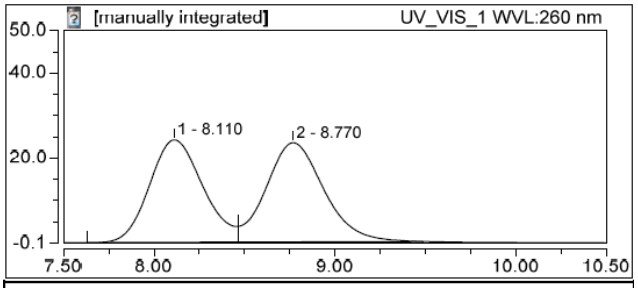
$[\alpha]_D^{21}$ = +12 (c = 0.5, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.20 (m, 3 H), 7.09-7.00 (m, 4 H), 6.50 (s, 1 H), 3.14-2.96 (m, 2 H), 2.82-2.70 (m, 4 H), 2.33 (s, 3 H), 2.18-1.87 (m, 2 H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 147.5, 145.3, 143.6, 143.4, 136.1, 129.6, 127.1, 126.1, 125.3, 123.6, 123.3, 122.4, 119.9, 47.7, 43.1, 42.8, 38.6, 30.1, 27.9, 21.3.

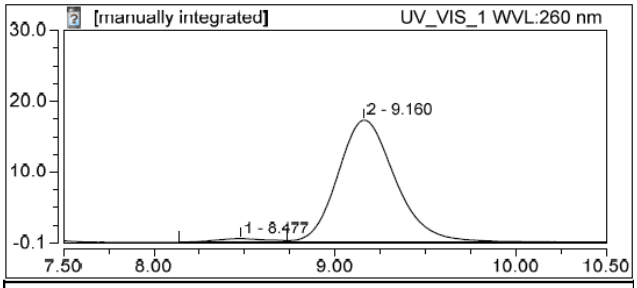
IR (neat, cm^{-1}): 2922, 1959, 1593, 1460, 1421, 1260, 1119, 1037, 831, 799.

HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{23}$ 275.1794, found 275.1783.



Integration Results

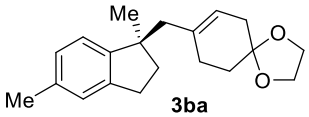
No.	Retention Time min	Area mAU*min	Relative Area %
1	8.110	8.265	48.87
2	8.770	8.647	51.13
Total:		16.911	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	8.477	0.170	2.60
2	9.160	6.378	97.40
Total:		6.547	100.00

(R)-8-((1,5-dimethyl-2,3-dihydro-1H-inden-1-yl)methyl)-1,4-dioxaspiro[4.5]dec-7-ene (3ba)



3ba

The compound was prepared according to the General Procedure from the reaction of **1ad** (57.2 mg, 0.2 mmol) and **2h** (57.6 mg, 0.2 mmol) in DMF. 22.1 mg, 37% yield, 90% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 271 nm, t_R(major) = 6.0 min, t_R(minor) = 7.5 min.

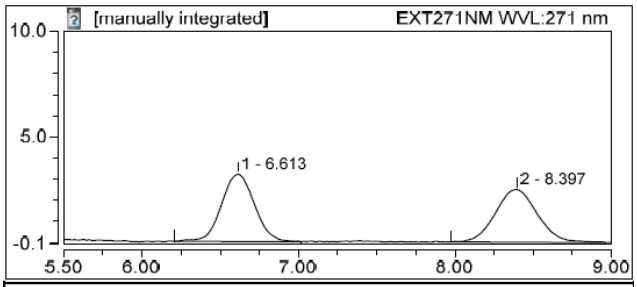
$[\alpha]_D^{21}$ = +7 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02-6.96 (m, 3 H), 5.28 (s, 1 H), 3.97-3.93 (m, 4 H), 2.87-2.79 (m, 2 H), 2.31 (s, 3 H), 2.25-2.18 (m, 4 H), 2.13-2.07 (m, 1 H), 1.92 (s, 2 H), 1.90-1.79 (m, 1 H), 1.65-1.56 (m, 2 H), 1.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 143.3, 135.9, 135.7, 126.8, 125.1, 122.5, 121.9, 107.9, 64.3, 48.5, 47.4, 39.2, 35.9, 31.4, 30.2, 29.4, 27.5, 21.2.

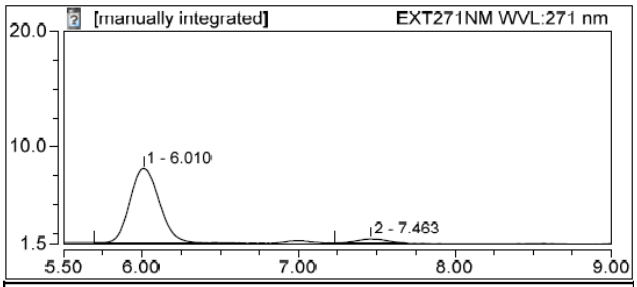
IR (neat, cm^{-1}): 3370, 2921, 1590, 1453, 1424, 1378, 1259, 1115, 862, 816.

HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{27}O$ 298.1933, found 298.1939.



Integration Results

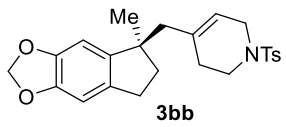
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.613	0.777	50.02
2	8.397	0.777	49.98
Total:		1.554	100.00



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	6.010	1.394	94.93
2	7.463	0.074	5.07
Total:		1.469	100.00

(R)-4-((5-methyl-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxol-5-yl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (3bb)



3bb

The compound was prepared according to the General Procedure from the reaction of **1ae** (63.2 mg, 0.2 mmol) and **2k** (77.0 mg, 0.2 mmol) in DMF. 42.5 mg, 50% yield, 94% ee, colorless oil.

Chiral HPLC: CHIRALCEL OD-H, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 293 nm, t_R(minor) = 29.0 min, t_R(major) = 31.0 min.

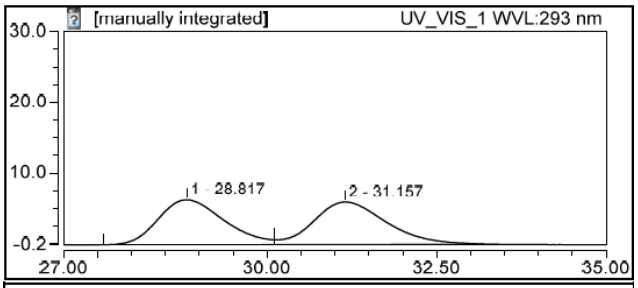
$[\alpha]_D^{21}$ = +14 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 6.61 (s, 1 H), 6.53 (s, 1 H), 5.90 (dd, *J* = 1.2 Hz, *J* = 7.2 Hz, 2 H), 5.27 (s, 1 H), 3.63-3.44 (m, 2 H), 3.17-2.88 (m, 2 H), 2.72-2.68 (m, 2 H), 2.42 (s, 3 H), 2.20-2.13 (m, 2 H), 2.06-1.99 (m, 1 H), 1.86-1.73 (m, 3 H), 1.15 (s, 3 H).

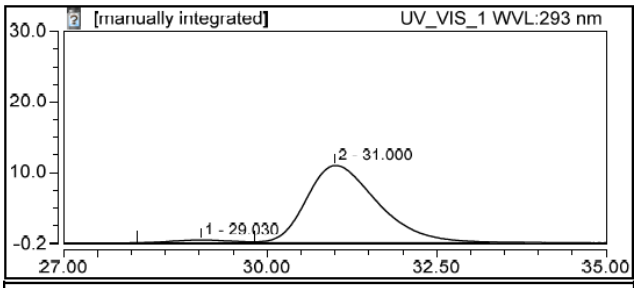
^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 146.4, 143.9, 143.4, 135.5, 134.7, 133.3, 129.6, 127.6, 120.0, 105.0, 103.2, 100.9, 49.0, 47.4, 44.8, 43.0, 38.7, 30.3, 30.2, 30.0, 21.5.

IR (neat, cm^{-1}): 3435, 2086, 1638, 1474, 1417, 1349, 1162, 1097, 943, 711.

HRMS (ESI): $[M+H]^+$ calcd for $C_{24}H_{28}NO_4S$ 426.1734, found 426.1743.

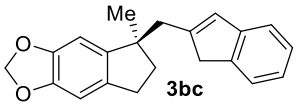


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	28.817	7.157	49.21
2	31.157	7.387	50.79
Total:		14.544	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	29.030	0.406	2.95
2	31.000	13.333	97.05
Total:		13.739	100.00

(R)-5-((1H-inden-2-yl)methyl)-5-methyl-6,7-dihydro-5H-indeno[5,6-d][1,3]dioxole (3bc)



3bc

The compound was prepared according to the General Procedure from the reaction of **1ae** (63.2 mg, 0.2 mmol) and **2m** (77.0 mg, 0.2 mmol) in DMF. 31.0 mg, 51% yield, 94% ee, colorless oil.

Chiral HPLC: CHIRALCEL OJ-H, 25 ^{o}C, ^{i}PrOH-hexanes 10/90, 1 mL/min, 260 nm, t_R(minor) = 13.0 min, t_R(major) = 24.9 min.

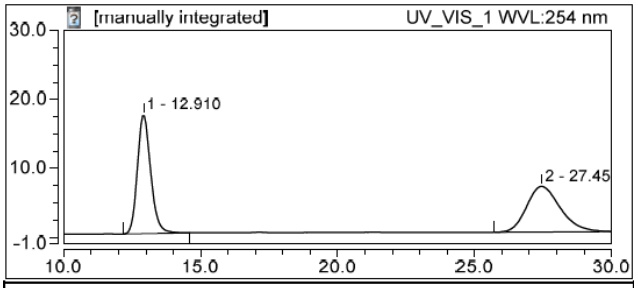
$[\alpha]_D^{21}$ = +55 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2 H), 7.20 (d, *J* = 8.0 Hz, 1 H), 7.08 (t, *J* = 8.0 Hz, 1 H), 6.65 (s, 1 H), 6.61 (s, 1 H), 6.49 (s, 1 H), 5.93 (d, *J* = 16.0 Hz, 2 H), 3.15-2.96 (m, 2 H), 2.77-2.65 (m, 4 H), 2.20-1.87 (m, 2 H), 1.28 (s, 3 H).

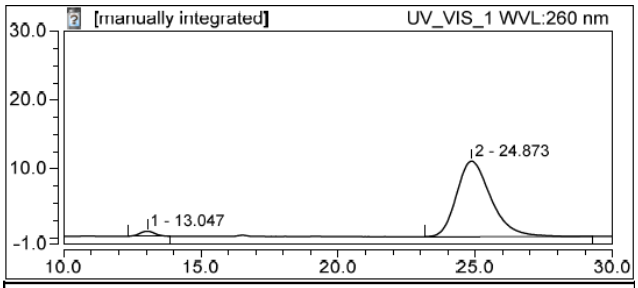
^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 146.6, 146.5, 145.3, 144.0, 143.6, 135.8, 129.7, 126.1, 123.7, 123.3, 120.0, 105.0, 103.3, 100.9, 47.9, 43.2, 42.7, 38.7, 30.2, 28.2.

IR (neat, cm^{-1}): 2922, 1594, 1474, 1422, 1304, 1248, 1121, 1039, 941, 857.

HRMS (ESI): $[M+H]^+$ calcd for $C_{21}H_{21}O_2$ 305.1536, found 305.1552.



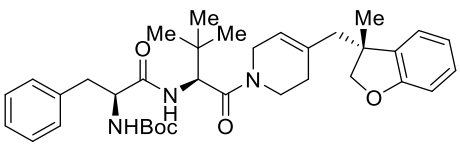
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	12.910	9.726	50.76
2	27.457	9.433	49.24
Total:		19.158	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	13.047	0.450	2.73
2	24.873	16.018	97.27
Total:		16.468	100.00

***Tert*-butyl ((*S*)-1-(((*S*)-3,3-dimethyl-1-(4-(((*R*)-3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-**

3,6-dihydropyridin-1(2*H*)-yl)-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate (4)



4

The compound was prepared according to the General Procedure from the reaction of **1a** (98.3 mg, 0.36 mmol) and **2w** (118.2 mg, 0.2 mmol).

91.9 mg, 78% yield, 97% de, white solid, mp: 66-68 ^{o}C.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 18/82, 0.2 mL/min, 280 nm, t_R(minor) = 131.5 min, t_R(major) = 138.2 min.

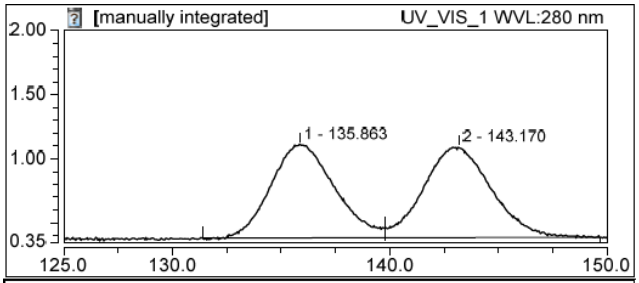
$[\alpha]_D^{23}$= -18 (c = 0.5, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, mixture of rotamers): δ 7.25-7.06 (m, 7 H), 6.89-6.71 (m, 3 H), 5.40-5.34 (m, 1 H), 5.15 (s, 1 H), 4.82-4.76 (m, 1 H), 4.46-4.33 (m, 2 H), 4.16-3.02 (m, 7 H), 2.39-2.31 (m, 2 H), 1.91-1.56 (m, 2 H), 1.40-1.33 (m, 12 H), 0.92-0.83 (m, 9 H).

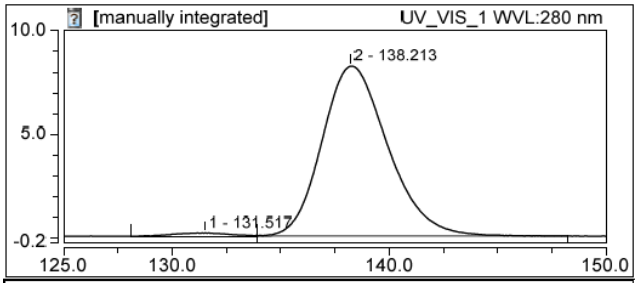
^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers): δ 170.8, 170.6, 169.5, 169.4, 169.0, 159.28, 159.25, 159.22, 159.15, 155.1, 155.0, 136.5, 135.1, 134.8, 134.5, 134.4, 133.4, 133.2, 129.14, 129.10, 129.0, 128.5, 128.34, 128.25, 128.20, 128.15, 126.8, 126.6, 122.8, 122.7, 122.1, 121.2, 121.1, 120.33, 120.29, 109.6, 109.5, 81.8, 81.7, 81.6, 81.4, 79.8, 55.7, 54.6, 54.2, 54.0, 48.4, 48.0, 45.6, 45.43, 45.41, 45.3, 43.4, 43.3, 42.04, 42.00, 38.8, 38.7, 38.3, 38.0, 37.9, 35.80, 35.75, 35.7, 35.5, 30.2, 30.1, 29.7, 29.6, 28.13, 28.08, 26.4, 26.3, 26.1, 26.0, 25.9.

IR (neat, cm^{-1}): 2993, 2963, 1675, 1477, 1362, 1321, 1226, 1182, 1088, 754, 688.

HRMS (ESI): $[M+H]^+$ calcd for $C_{35}H_{48}N_3O_5$ 590.3588, found 590.3602.



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	135.863	2.477	49.38
2	143.170	2.539	50.62
Total:		5.016	100.00

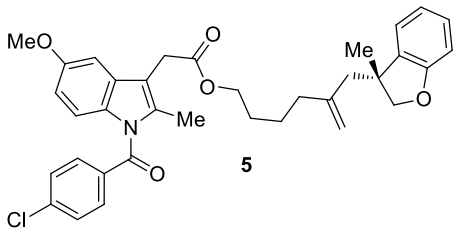


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	131.517	0.466	1.59
2	138.213	28.939	98.41
Total:		29.405	100.00

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **4** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.

(*R*)-5-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)hex-5-en-1-yl 2-(1-(4-chlorobenzoyl)-5-

methoxy-2-methyl-1H-indol-3-yl)acetate (5)



5

The compound was prepared according to the General Procedure from the reaction of **1a** (164.4 mg, 0.6 mmol) and **2x** (115.6 mg, 0.2 mmol).

49.1 mg, 42% yield, 94% ee, colorless oil.

Chiral HPLC: CHIRALPAK IB, 25 ^{o}C, ^{i}PrOH-hexanes 3/97, 1 mL/min, 203 nm, t_R(minor) = 31.8 min, t_R(major) = 33.8 min.

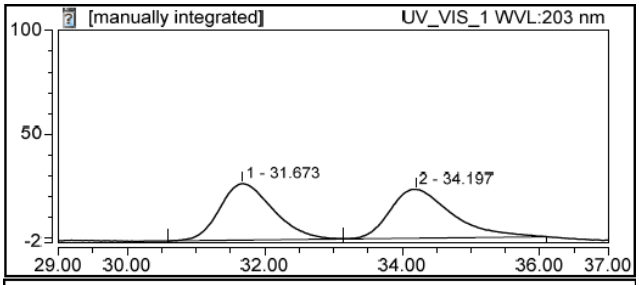
$[\alpha]_D^{21}$= +1 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.13-7.05 (m, 2 H), 6.96 (d, *J* = 2.4 Hz, 1 H), 6.87-6.82 (m, 2 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.67-6.65 (m, 1 H), 4.80 (s, 1 H), 4.71 (s, 1 H), 4.47 (d, *J* = 8.8 Hz, 1 H), 4.14 (d, *J* = 8.4 Hz, 1 H), 4.03 (m, 2 H), 3.82 (s, 3 H), 3.65 (s, 2 H), 2.38 (s, 3 H), 2.34-2.27 (m, 2 H), 1.79-1.65 (m, 2 H), 1.54-1.44 (m, 2 H), 1.37-1.30 (m, 2 H), 1.34 (s, 3 H).

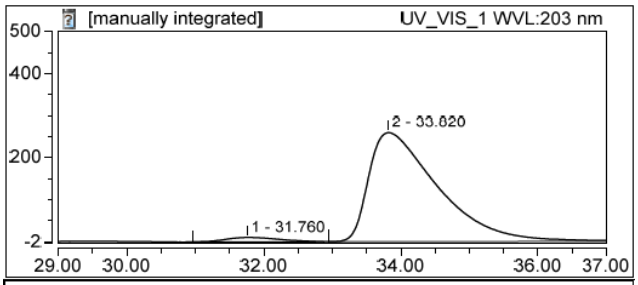
^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 168.2, 159.3, 156.0 145.7, 139.2, 135.8, 135.2, 133.9, 131.1, 130.8, 130.6, 129.1, 128.1, 122.8, 120.3, 114.9, 113.9, 112.7, 111.6, 109.6, 101.3, 81.8, 64.8, 55.6, 46.3, 45.3, 36.3, 30.4, 28.1, 26.3, 24.1, 13.3.

IR (neat, cm^{-1}): 2943, 1735, 1687, 1597, 1480, 1321, 1224, 1167, 833, 755.

HRMS (ESI): $[M+H]^+$ calcd for $C_{35}H_{37}ClNO_5$ 586.2355, found 586.2361.

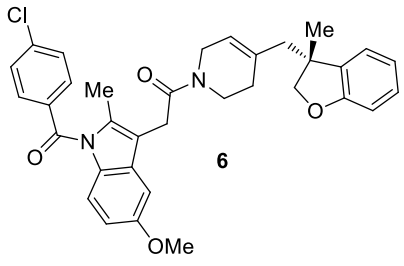


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	31.673	24.693	50.11
2	34.197	24.583	49.89
Total:		49.276	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	31.760	9.443	3.03
2	33.820	302.615	96.97
Total:		312.057	100.00

(*R*)-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)-1-(4-((3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-3,6-dihydropyridin-1(2*H*)-yl)ethan-1-one (6)



6

The compound was prepared according to the General Procedure from the reaction of **1a** (98.6 mg, 0.36 mmol) and **2y** (114.0 mg, 0.2 mmol).

73.8 mg, 65% yield, >99% ee, white solid, mp: 66-68 °C.

Chiral HPLC: CHIRALCEL OD-H, 25 °C, ^{i}PrOH-hexanes 30/70, 1 mL/min, 260 nm, t_R(minor) = 19.7 min, t_R(major) = 33.2 min. Approximate 1.25:1 ratio of rotamers.

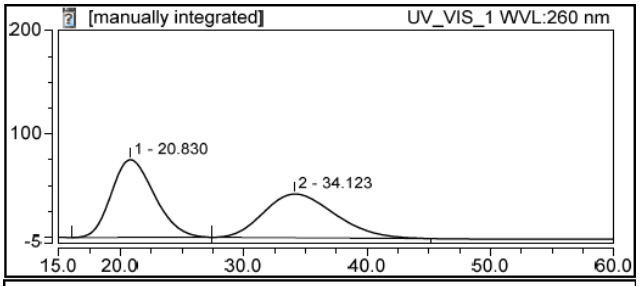
$[\alpha]_D^{23}$ = -6 (c = 0.5, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 7.6 Hz, 2 H), 7.12-7.08 (m, 1 H), 7.02 (t, *J* = 6.4 Hz, 1 H), 6.98 (d, *J* = 2.4 Hz, 1 H), 6.86-6.81 (m, 2 H), 6.73 (dd, *J* = 2.0, 8.0 Hz, 1 H), 6.64 (dd, *J* = 2.4, 9.2 Hz, 1 H), [5.38 (s), 5.27 (s), 1 H], 4.39-4.34 (m, 1 H), 4.16-3.90 (m, 3 H), 3.80 (d, *J* = 2.8 Hz, 3 H), 3.68-3.32 (m, 4 H), 2.36-2.29 (m, 5 H), 1.89-1.54 (m, 2 H), 1.30-1.25 (m, 3 H).

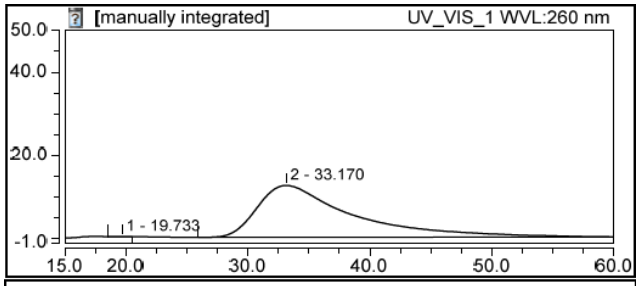
^{13}C NMR (100 MHz, $CDCl_3$): δ 168.71, 168.67, 168.1, 159.2, 155.8, 139.1, 139.0, 135.1, 135.0, 134.9, 134.7, 134.6, 133.81, 133.75, 132.9, 131.1, 130.70, 130.68, 130.62, 130.60, 128.98, 128.96, 128.20, 128.15, 122.7, 120.9, 120.31, 120.28, 114.7, 113.2, 111.4, 111.3, 109.6, 109.5, 101.4, 101.3, 81.70, 81.65, 55.54, 55.52, 48.2, 45.4, 45.3, 44.9, 42.8, 42.2, 38.7, 30.5, 30.4, 30.1, 29.6, 25.9, 25.8, 13.4, 13.3.

IR (neat, cm^{-1}): 3302, 2970, 1709, 1627, 1482, 1455, 1262, 1172, 1017, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{34}H_{34}ClN_2O_4$ 569.2202, found 569.2209.



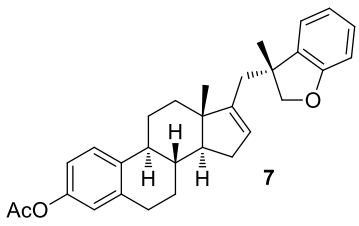
Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	20.830	303.509	51.83
2	34.123	282.110	48.17
Total:		585.619	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	19.733	0.037	0.03
2	33.170	112.038	99.97
Total:		112.075	100.00

NOTE: Because of the amide bond rotation equilibrium, the rotamers of **4** were observed on the NMR. This phenomenon is seen with many tertiary amides. For related references, see: ref. 19-20.

(8*S*,9*S*,13*S*,14*S*)-13-methyl-17-(((*R*)-3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-7,8,9,11,12,13,14,15-octahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl acetate (7)



7

The compound was prepared according to the General Procedure from the reaction of **1a** (98.6 mg, 0.36 mmol) and **2z** (88.8 mg, 0.2 mmol). 75.1 mg, 85% yield, 99% de, white solid, mp: 123-125 °C.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 288 nm, t_R(major) = 6.4 min, t_R(minor) = 7.8 min.

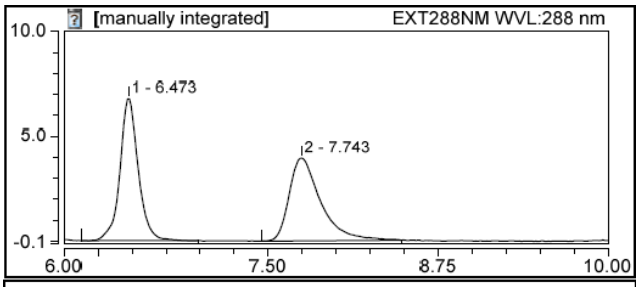
$[\alpha]_D^{20}$ = -61 (c = 1.36, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.23 (m, 1 H), 7.15-7.09 (m, 2 H), 6.90-6.78 (m, 4 H), 5.16 (d, *J* = 1.2 Hz, 1 H), 4.53 (d, *J* = 8.4 Hz, 1 H), 4.27 (d, *J* = 8.4 Hz, 1 H), 2.90-2.86 (m, 2 H), 2.46-2.11 (m, 8 H), 1.96-1.88 (m, 2 H), 1.76-11.73 (m, 1 H), 1.62-1.33 (m, 8 H), 1.33 (s, 3 H).

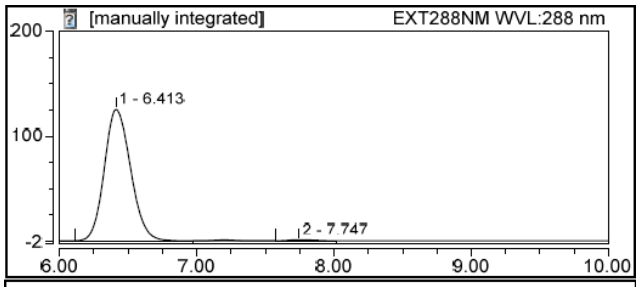
^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 159.0, 150.8, 148.3, 138.2, 138.2, 136.2, 128.0, 126.0, 123.4, 122.6, 121.4, 120.4, 118.4, 109.5, 81.9, 55.3, 47.5, 44.5, 44.4, 37.2, 37.0, 34.4, 31.3, 29.4, 27.5, 26.9, 26.2, 21.1, 15.4.

IR (neat, cm^{-1}): 2930, 2851, 1765, 1597, 1482, 1370, 1207, 1016, 974, 751.

HRMS (ESI): $[M+H]^+$ calcd for $C_{30}H_{35}O_3$ 443.2581, found 443.2587.

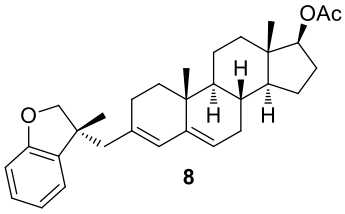


Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.473	1.051	49.78
2	7.743	1.061	50.22
Total:		2.112	100.00



Integration Results			
No.	Retention Time min	Area mAU*min	Relative Area %
1	6.413	27.970	99.30
2	7.747	0.198	0.70
Total:		28.168	100.00

(8*R*,9*S*,10*R*,13*S*,14*S*,17*S*)-10,13-dimethyl-3-(((*R*)-3-methyl-2,3-dihydrobenzofuran-3-yl)methyl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl acetate (8)



8

The compound was prepared according to the General Procedure from the reaction of **1a** (98.6 mg, 0.36 mmol) and **2aa** (92.4 mg, 0.2 mmol). 49.7 mg, 54% yield, 94% de, white solid, mp: 47-49 ^{o}C.

Chiral HPLC: CHIRALPAK IA, 25 ^{o}C, ^{i}PrOH-hexanes 5/95, 1 mL/min, 280 nm, t_R(major) = 4.8 min, t_R(minor) = 8.2 min.

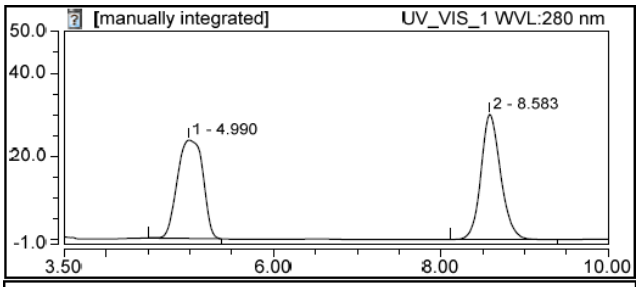
$[\alpha]_D^{21}$ = -73 (c = 1.0, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.09 (m, 2 H), 6.86 (t, *J* = 7.2 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 5.75 (s, 1 H), 5.34 (d, *J* = 2.8 Hz, 1 H), 4.62-4.58 (m, 1 H), 4.49 (d, *J* = 8.8 Hz, 1 H), 4.16 (d, *J* = 8.4 Hz, 1 H), 2.38-2.33 (m, 2 H), 2.20-2.14 (m, 2 H), 2.04 (s, 3 H), 1.77-0.94 (m, 18 H), 0.85 (s, 3 H), 0.82 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 159.4, 141.7, 135.4, 133.5, 128.5, 128.0, 123.0, 121.9, 120.3, 109.5, 82.7, 82.1, 51.2, 49.2, 48.2, 45.8, 42.5, 36.7, 34.7, 34.2, 31.6, 31.3, 27.9, 27.5, 26.4, 23.5, 21.2, 20.5, 18.7, 12.0.

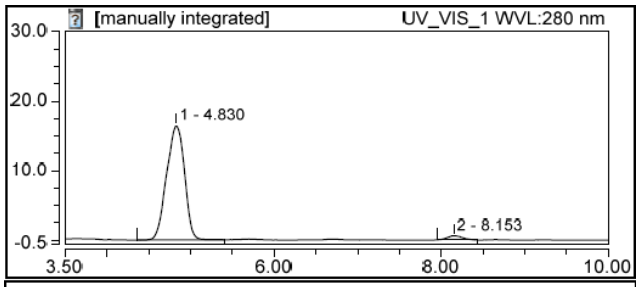
IR (neat, cm^{-1}): 2963, 1735, 1481, 1459, 1373, 1247, 1034, 978, 751, 689.

HRMS (ESI): $[M+H]^+$ calcd for $C_{31}H_{41}O_3$ 461.3050, found 461.3068.



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	4.990	8.353	50.48
2	8.583	8.195	49.52
Total:		**16.548**	**100.00**

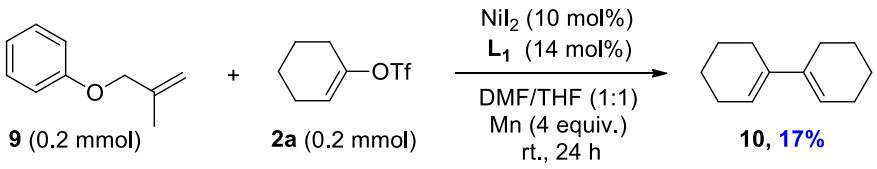


Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	4.830	4.074	97.15
2	8.153	0.120	2.85
Total:		**4.193**	**100.00**

5. Mechanistic Investigation

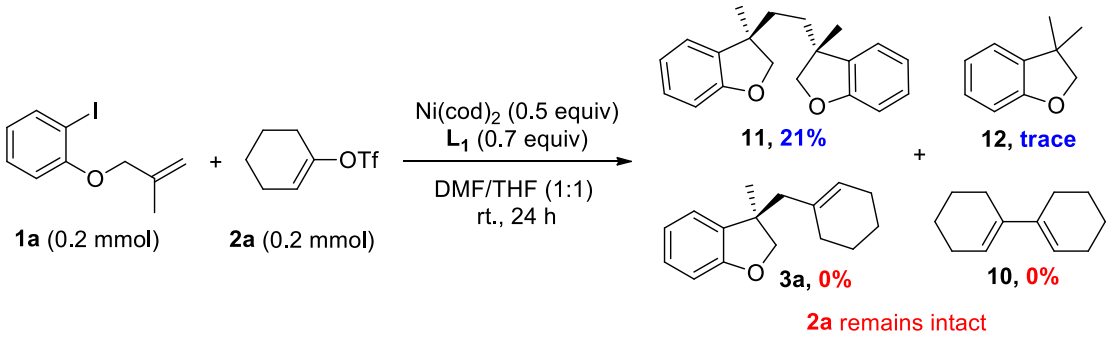
5.1 Study of the Reaction of Alkenyl Triflate with Alkene



The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with NiI_2 (6.3 mg, 0.020 mmol), **L1** (7.6 mg, 0.028 mmol), Mn (44.0 mg, 0.8 mmol), and DMF/THF (0.5 mL/0.5 mL). The reaction mixture was stirred for 5 min. Substrates **9** (29.6 mg, 0.2 mmol) and **2a** (46 mg, 0.2 mmol) were then added. The reaction tube was sealed with a rubber septum, and removed from the glove box. The reaction mixture was stirred at 25 ^{o}C for 24 h. The reaction mixture was diluted with ethyl acetate (10 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected, diluted with ethyl acetate (2 mL), and analyzed by GC.

The reaction afforded alkenyl dimer **10** with 17% yield and trace of protonated product alkenyl-H. No cross product was observed, and substrate **9** remained intact.

5.2 The reactivity of alkene tethered Ar-I and alkenyl-OTf towards Ni(0)

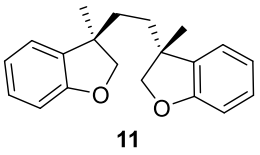


The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with $Ni(cod)_2$ (27.4 mg, 0.10 mmol), **L1** (38.2 mg, 0.14 mmol), and DMF/THF (0.5 mL/0.5 mL). The reaction mixture was stirred for 5 min. Substrates **1a** (54.8 mg, 0.2 mmol) and **2a** (46 mg, 0.2 mmol) were then added. The reaction tube was sealed with a rubber septum, and removed from the glove box. The reaction mixture was stirred at 25 ^{o}C for 24 h. The reaction mixture was diluted with ethyl acetate (10 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected, diluted with ethyl acetate (2 mL), and

analyzed by GC.

The reaction afforded dimer **11** with 21% yield, and trace of protonated product **12**. Alkenyl triflate **2a** remained intact.

1,2-Bis((R)-3-methyl-2,3-dihydrobenzofuran-3-yl)ethane (11, known[39])

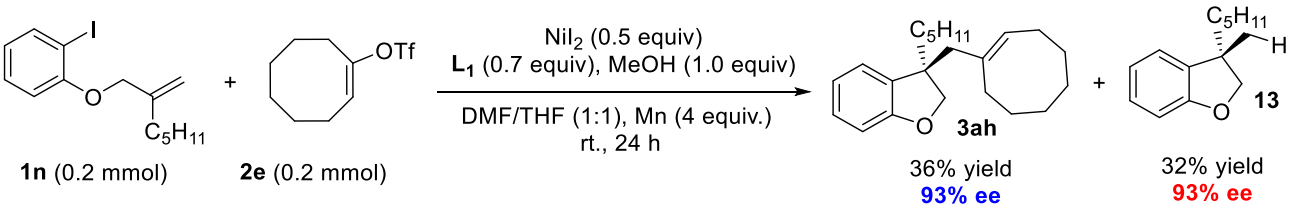


11

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15-7.09 (m, 4 H), 6.86 (t, *J* = 8.0 Hz, 2 H), 6.75 (d, *J* = 8.0 Hz, 2 H), 4.59 (d, *J* = 8.0 Hz, 2 H), 4.05 (d, *J* = 8.0 Hz, 2 H), 1.84 (s, 4 H), 1.35 (s, 6 H).

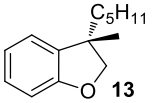
^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 135.4, 128.0, 126.5, 120.1, 109.6, 82.2, 46.8, 39.2, 25.0.

5.3 Enantioselectivity of the Formation of Cross-product 3x and Protonated Byproduct 13



The procedure was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was charged with NiI_2 (31.5 mg, 0.10 mmol), **L1** (38.2 mg, 0.14 mmol), Mn (44.0 mg, 4.0 equiv.), and DMF/THF (0.5 mL/0.5 mL). The reaction mixture was stirred for 5 min. Substrates **1n** (66.0 mg, 0.2 mmol), **2e** (51.6 mg, 0.2 mmol) and MeOH (6.4 mg, 0.2 mmol) were then added. The reaction tube was sealed with a rubber septum, and removed from the glove box. The reaction mixture was stirred at 25 ^{o}C for 24 h. The reaction mixture was diluted with ethyl acetate (10 mL), washed with water, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **3ah** (22.4 mg, 36% yield, 93% ee) and **13** (13.9 mg, 32% yield, 93% ee).

(*S*)-3-methyl-3-pentyl-2,3-dihydrobenzofuran (13, known)



13.9 mg, 32% yield, 93% ee, colorless oil. The ^{1}H NMR and ^{13}C NMR are consistent with that reported in ref.7.

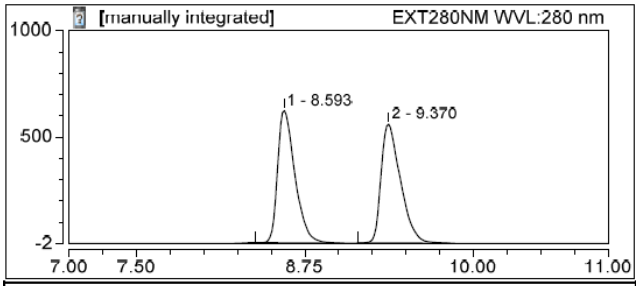
Chiral HPLC: CHIRALPAK IB, 25 ^{o}C, ^{i}PrOH-hexanes 0.2/99.8, 0.75 mL/min, 280 nm, t_R(major)= 7.6 min, t_R(minor)= 8.3 min.

$[\alpha]_D^{22}$= +2 (c = 0.5, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14-7.10 (m, 1 H), 7.08-7.06 (m, 1 H), 6.87 (dt, *J* = 0.8, 7.2 Hz, 1

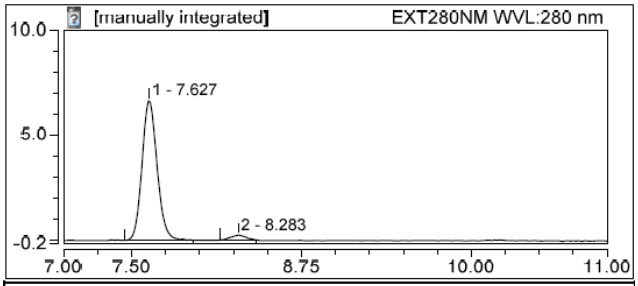
H), 6.78 (d, *J* = 8.0 Hz, 1 H), 4.35 (d, *J* = 8.4 Hz, 1 H), 4.15 (d, *J* = 8.4 Hz, 1 H), 1.62-1.20 (m, 8 H), 1.33 (s, 3 H), 0.85 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 135.5, 127.9, 122.8, 120.4, 109.5, 82.5, 45.2, 40.9, 32.3, 25.6, 24.3, 22.5, 14.0.



Integration Results

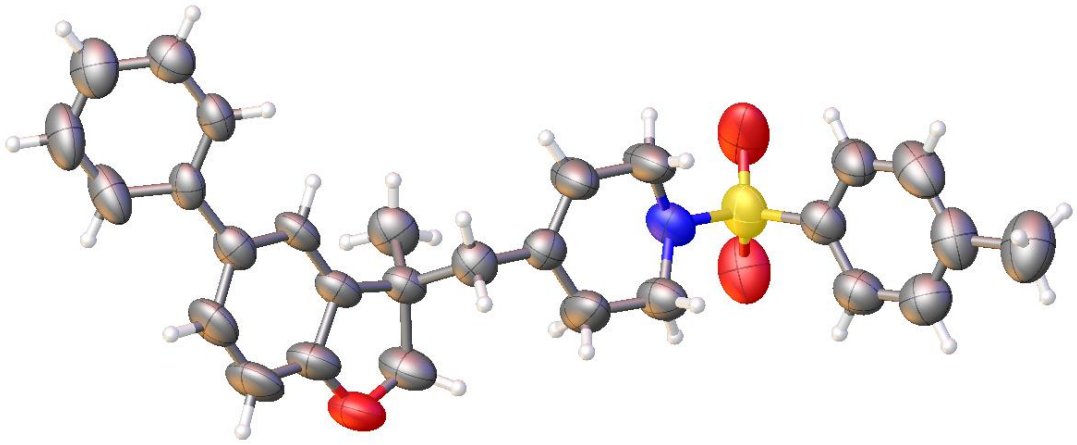
No.	Retention Time min	Area mAU*min	Relative Area %
1	8.593	92.645	49.82
2	9.370	93.310	50.18
Total:		**185.955**	**100.00**



Integration Results

No.	Retention Time min	Area mAU*min	Relative Area %
1	7.627	0.865	96.64
2	8.283	0.030	3.36
Total:		**0.895**	**100.00**

6. Crystallographic Data for Compound 3z (CCDC 1890459)



tianzhx_1015

Table 1 Crystal data and structure refinement for tianzhx_1015.

Identification code	tianzhx_1015
Empirical formula	$C_{28}H_{29}NO_3S$
Formula weight	460.59
Temperature/K	295.6(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.5255(6)
b/Å	10.9187(9)
c/Å	26.122(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2431.7(4)
Z	4
ρ_{calc}g/cm^3	1.258
μ/mm^{-1}	1.413
F(000)	980.0
Crystal size/mm^3	0.21 × 0.15 × 0.14
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	8.78 to 133.18
Index ranges	$-6 \leq h \leq 10$, $-12 \leq k \leq 12$, $-31 \leq l \leq 29$
Reflections collected	7508
Independent reflections	4101 [R_{int} = 0.0426, R_{sigma} = 0.0706]
Data/restraints/parameters	4101/0/300
Goodness-of-fit on F^2	1.121
Final R indexes [I>=2σ (I)]	R_1 = 0.0730, wR_2 = 0.1894
Final R indexes [all data]	R_1 = 0.1101, wR_2 = 0.2606
Largest diff. peak/hole / e $Å^{-3}$	0.22/-0.57
Flack parameter	-0.07(5)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for tianzhx_1015. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	-7953.1(18)	-5233.5(19)	-1431.7(7)	83.3(5)
O1	-16535(6)	-5867(5)	-2890(2)	93.8(16)
O2	-6624(5)	-4766(8)	-1707(2)	124(2)
O3	-8104(7)	-6521(5)	-1341(2)	104.8(18)
N1	-9511(5)	-4815(5)	-1751(2)	74.0(14)
C1	-15865(6)	-1118(5)	-4366(2)	64.1(14)
C2	-15793(7)	-320(6)	-4773(3)	76.9(17)
C3	-16732(9)	-510(7)	-5196(3)	92(2)
C4	-17749(10)	-1480(7)	-5193(3)	100(3)
C5	-17808(8)	-2271(6)	-4788(3)	90(2)
C6	-16866(6)	-2107(5)	-4358(2)	57.5(12)
C7	-16885(6)	-3006(5)	-3934(2)	61.7(13)
C8	-18210(6)	-3694(6)	-3825(3)	83(2)
C9	-18188(7)	-4643(7)	-3454(3)	96(2)
C10	-16782(7)	-4917(6)	-3234(3)	78.0(18)

C11	-15439(6)	-4256(5)	-3319(2)	60.5(14)
C12	-15497(5)	-3300(5)	-3677(2)	62.1(14)
C13	-14100(6)	-4756(5)	-3016(2)	60.2(13)
C14	-14910(8)	-5917(6)	-2782(3)	90(2)
C15	-12688(7)	-5088(6)	-3341(3)	80.5(18)
C16	-13666(7)	-3817(5)	-2590(2)	67.4(15)
C17	-12237(7)	-4108(5)	-2283(2)	60.4(13)
C18	-10875(8)	-3444(6)	-2329(3)	85(2)
C19	-9535(8)	-3563(7)	-1979(3)	97(3)
C20	-11012(7)	-5163(6)	-1526(3)	78.9(18)
C21	-12284(8)	-5084(9)	-1905(3)	100(3)
C22	-7990(7)	-4483(5)	-846(2)	67.2(15)
C23	-7293(8)	-3357(6)	-784(3)	83.2(19)
C24	-7248(10)	-2772(6)	-318(4)	99(3)
C25	-7870(10)	-3356(7)	108(3)	93(2)
C26	-8583(9)	-4458(7)	65(3)	90(2)
C27	-8636(7)	-5048(6)	-417(3)	79.9(18)
C28	-7765(14)	-2741(8)	635(4)	131(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for tianzhx_1015. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	51.2(7)	111.1(13)	87.7(11)	-5.9(10)	-7.5(7)	15.6(8)
O1	68(3)	88(3)	125(4)	18(3)	5(3)	-25(2)
O2	47(2)	229(7)	97(4)	-7(5)	6(2)	12(4)
O3	101(4)	91(3)	122(4)	-17(3)	-26(3)	40(3)
N1	45(2)	82(3)	95(4)	0(3)	2(2)	0(2)
C1	50(3)	74(3)	68(3)	-12(3)	-13(2)	4(2)

C2	63(3)	72(4)	96(5)	1(4)	-6(3)	6(3)
C3	89(5)	85(4)	103(5)	-2(4)	-23(4)	27(4)
C4	106(6)	95(5)	101(6)	-12(4)	-55(5)	19(4)
C5	78(4)	74(4)	118(6)	-16(4)	-45(4)	6(3)
C6	41(2)	71(3)	61(3)	-8(3)	-10(2)	13(2)
C7	41(2)	66(3)	79(4)	-9(3)	-3(2)	4(2)
C8	37(3)	94(4)	118(6)	-4(4)	-13(3)	-5(3)
C9	42(3)	105(5)	141(7)	18(5)	1(3)	-22(3)
C10	51(3)	72(4)	111(5)	7(4)	9(3)	-14(3)
C11	36(2)	62(3)	83(4)	-5(3)	6(2)	-7(2)
C12	32(2)	65(3)	89(4)	-7(3)	-2(2)	-8(2)
C13	47(2)	62(3)	72(3)	-1(3)	4(2)	-7(2)
C14	68(4)	66(4)	134(7)	13(4)	-2(4)	-11(3)
C15	58(3)	88(4)	95(5)	-10(4)	5(3)	12(3)
C16	58(3)	68(3)	77(4)	-5(3)	2(3)	8(2)
C17	58(3)	59(3)	64(3)	-3(3)	4(3)	1(2)
C18	72(4)	81(4)	102(5)	24(4)	-17(4)	-21(3)
C19	67(4)	105(5)	120(6)	42(5)	-20(4)	-30(4)
C20	53(3)	82(4)	102(5)	18(4)	-2(3)	-2(3)
C21	55(3)	148(7)	97(5)	38(5)	-5(3)	-20(4)
C22	50(3)	70(3)	81(4)	-1(3)	-1(3)	4(3)
C23	83(4)	79(4)	88(5)	12(4)	-21(4)	-10(3)
C24	97(5)	64(4)	138(7)	2(4)	-38(5)	2(4)
C25	95(5)	81(5)	101(5)	-21(4)	-23(5)	23(4)
C26	84(4)	87(5)	99(5)	10(4)	-1(4)	13(4)
C27	63(3)	75(4)	102(5)	3(4)	0(3)	-1(3)
C28	162(10)	113(7)	118(7)	4(6)	-35(7)	32(7)

Table 4 Bond Lengths for tianzhx_1015.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.436(6)	C10	C11	1.371(7)
S1	O3	1.431(6)	C11	C12	1.401(8)
S1	N1	1.633(5)	C11	C13	1.494(8)
S1	C22	1.735(6)	C13	C14	1.566(8)
O1	C10	1.390(8)	C13	C15	1.516(7)
O1	C14	1.415(8)	C13	C16	1.557(8)
N1	C19	1.492(8)	C16	C17	1.493(8)
N1	C20	1.458(7)	C17	C18	1.374(8)
C1	C2	1.376(9)	C17	C21	1.452(9)
C1	C6	1.377(8)	C18	C19	1.468(9)
C2	C3	1.381(10)	C20	C21	1.471(9)
C3	C4	1.369(11)	C22	C23	1.376(9)
C4	C5	1.367(11)	C22	C27	1.394(9)
C5	C6	1.392(8)	C23	C24	1.376(10)
C6	C7	1.480(8)	C24	C25	1.389(12)
C7	C8	1.386(8)	C25	C26	1.353(10)
C7	C12	1.398(7)	C25	C28	1.533(11)
C8	C9	1.421(10)	C26	C27	1.415(10)
C9	C10	1.362(9)			

Table 5 Bond Angles for tianzhx_1015.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	N1	106.7(3)	C12	C11	C13	130.8(4)
O2	S1	C22	106.7(4)	C7	C12	C11	121.4(5)
O3	S1	O2	120.2(4)	C11	C13	C14	99.5(5)
O3	S1	N1	106.6(3)	C11	C13	C15	113.4(5)

O3	S1	C22	108.5(3)	C11	C13	C16	108.7(5)
N1	S1	C22	107.6(3)	C15	C13	C14	112.0(5)
C10	O1	C14	107.8(5)	C15	C13	C16	111.7(5)
C19	N1	S1	118.2(4)	C16	C13	C14	111.0(5)
C20	N1	S1	115.8(5)	O1	C14	C13	108.9(6)
C20	N1	C19	112.8(5)	C17	C16	C13	115.9(5)
C2	C1	C6	122.5(5)	C18	C17	C16	122.0(6)
C1	C2	C3	119.8(7)	C18	C17	C21	118.1(6)
C4	C3	C2	118.6(8)	C21	C17	C16	119.9(5)
C5	C4	C3	121.1(7)	C17	C18	C19	123.8(6)
C4	C5	C6	121.4(6)	C18	C19	N1	109.9(5)
C1	C6	C5	116.5(6)	N1	C20	C21	111.2(6)
C1	C6	C7	122.6(5)	C17	C21	C20	118.6(6)
C5	C6	C7	120.8(6)	C23	C22	S1	121.2(5)
C8	C7	C6	121.4(5)	C23	C22	C27	118.2(6)
C8	C7	C12	117.8(6)	C27	C22	S1	120.5(5)
C12	C7	C6	120.2(5)	C24	C23	C22	122.1(7)
C7	C8	C9	121.7(6)	C23	C24	C25	119.1(7)
C10	C9	C8	117.3(5)	C24	C25	C28	119.7(8)
C9	C10	O1	124.7(5)	C26	C25	C24	120.9(8)
C9	C10	C11	123.5(7)	C26	C25	C28	119.4(9)
C11	C10	O1	111.8(6)	C25	C26	C27	119.6(8)
C10	C11	C12	118.1(5)	C22	C27	C26	120.1(6)
C10	C11	C13	111.1(5)				

Table 6 Torsion Angles for tianzhx_1015.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N1	C19	C18	169.1(6)	C10	O1	C14	C13	9.7(8)

S1	N1	C20	C21	-162.9(6)	C10	C11	C12	C7	1.2(9)
S1	C22	C23	C24	-177.1(6)	C10	C11	C13	C14	5.4(7)
S1	C22	C27	C26	176.5(5)	C10	C11	C13	C15	124.5(6)
O1	C10	C11	C12	177.2(5)	C10	C11	C13	C16	-110.8(6)
O1	C10	C11	C13	0.1(8)	C11	C13	C14	O1	-9.1(8)
O2	S1	N1	C19	-39.6(7)	C11	C13	C16	C17	-173.8(5)
O2	S1	N1	C20	-178.0(6)	C12	C7	C8	C9	2.0(10)
O2	S1	C22	C23	23.9(6)	C12	C11	C13	C14	-171.3(6)
O2	S1	C22	C27	-151.6(5)	C12	C11	C13	C15	-52.2(9)
O3	S1	N1	C19	-169.2(6)	C12	C11	C13	C16	72.6(8)
O3	S1	N1	C20	52.4(6)	C13	C11	C12	C7	177.7(6)
O3	S1	C22	C23	154.7(5)	C13	C16	C17	C18	109.4(7)
O3	S1	C22	C27	-20.9(6)	C13	C16	C17	C21	-73.5(8)
N1	S1	C22	C23	-90.3(6)	C14	O1	C10	C9	175.3(8)
N1	S1	C22	C27	94.2(5)	C14	O1	C10	C11	-6.3(9)
N1	C20	C21	C17	-36.0(10)	C14	C13	C16	C17	77.8(6)
C1	C2	C3	C4	1.7(11)	C15	C13	C14	O1	-129.2(6)
C1	C6	C7	C8	155.2(6)	C15	C13	C16	C17	-48.0(7)
C1	C6	C7	C12	-33.5(8)	C16	C13	C14	O1	105.3(7)
C2	C1	C6	C5	0.5(9)	C16	C17	C18	C19	169.6(7)
C2	C1	C6	C7	176.6(5)	C16	C17	C21	C20	-165.6(6)
C2	C3	C4	C5	-2.0(12)	C17	C18	C19	N1	27.0(11)
C3	C4	C5	C6	1.5(12)	C18	C17	C21	C20	11.7(11)
C4	C5	C6	C1	-0.7(10)	C19	N1	C20	C21	56.6(9)
C4	C5	C6	C7	-176.9(6)	C20	N1	C19	C18	-51.3(9)
C5	C6	C7	C8	-28.8(9)	C21	C17	C18	C19	-7.6(12)
C5	C6	C7	C12	142.5(6)	C22	S1	N1	C19	74.6(6)
C6	C1	C2	C3	-1.0(9)	C22	S1	N1	C20	-63.8(6)
C6	C7	C8	C9	173.5(6)	C22	C23	C24	C25	2.7(12)

C6	C7	C12	C11	-171.8(5)	C23	C22	C27	C26	0.8(10)
C7	C8	C9	C10	-4.9(12)	C23	C24	C25	C26	-3.3(12)
C8	C7	C12	C11	-0.2(9)	C23	C24	C25	C28	177.3(7)
C8	C9	C10	O1	-175.7(7)	C24	C25	C26	C27	2.7(11)
C8	C9	C10	C11	6.1(12)	C25	C26	C27	C22	-1.5(10)
C9	C10	C11	C12	-4.4(11)	C27	C22	C23	C24	-1.4(10)
C9	C10	C11	C13	178.5(7)	C28	C25	C26	C27	-177.9(7)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for tianzhx_1015.

Atom	*x*	*y*	*z*	U(eq)
H1	-15214	-985	-4086	77
H2	-15113	346	-4763	92
H3	-16676	11	-5477	111
H4	-18411	-1603	-5471	121
H5	-18493	-2934	-4800	108
H8	-19136	-3530	-4000	99
H9	-19098	-5061	-3364	115
H12	-14593	-2852	-3744	74
H14A	-14459	-6652	-2930	107
H14B	-14743	-5939	-2415	107
H15A	-13018	-5592	-3622	121
H15B	-11943	-5529	-3136	121
H15C	-12211	-4354	-3469	121
H16A	-13519	-3023	-2748	81
H16B	-14549	-3749	-2357	81
H18	-10797	-2887	-2597	102
H19A	-9615	-2956	-1709	117

H19B	-8567	-3418	-2165	117
H20A	-11245	-4627	-1240	95
H20B	-10945	-5994	-1397	95
H21A	-12318	-5856	-2089	120
H21B	-13265	-5010	-1719	120
H23	-6836	-2979	-1067	100
H24	-6808	-1996	-289	119
H26	-9035	-4825	351	108
H27	-9104	-5815	-447	96
H28A	-8182	-3282	891	197
H28B	-8359	-1994	632	197
H28C	-6689	-2562	712	197

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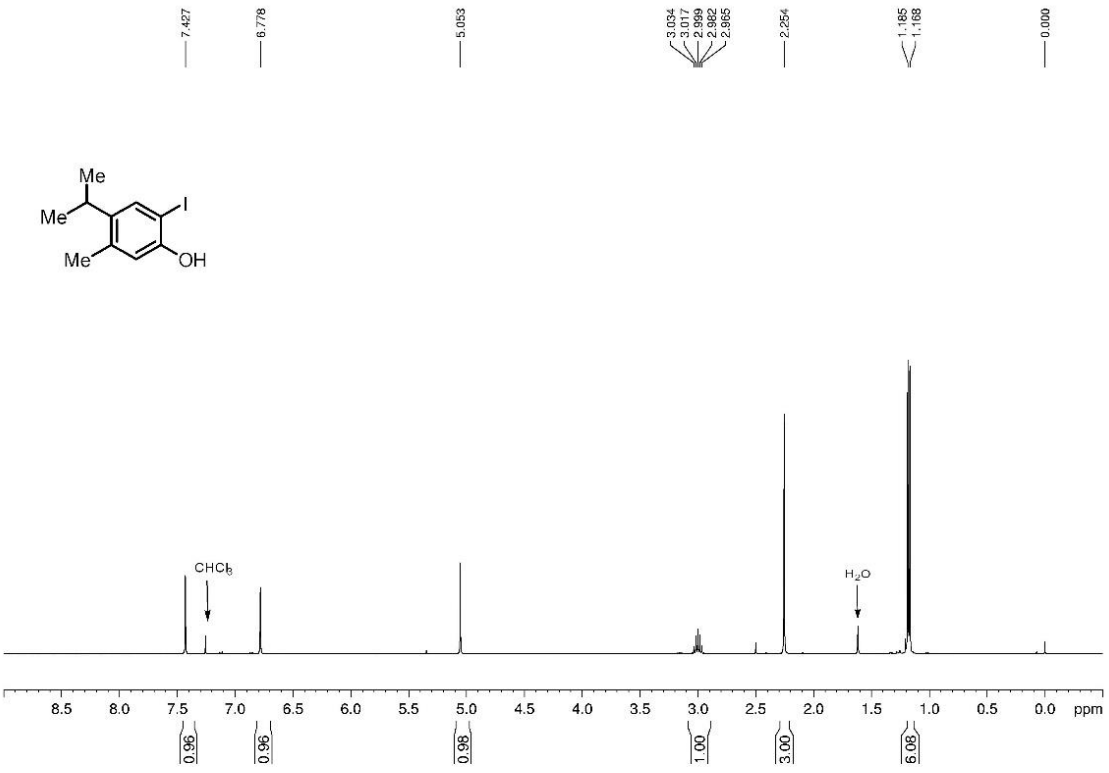
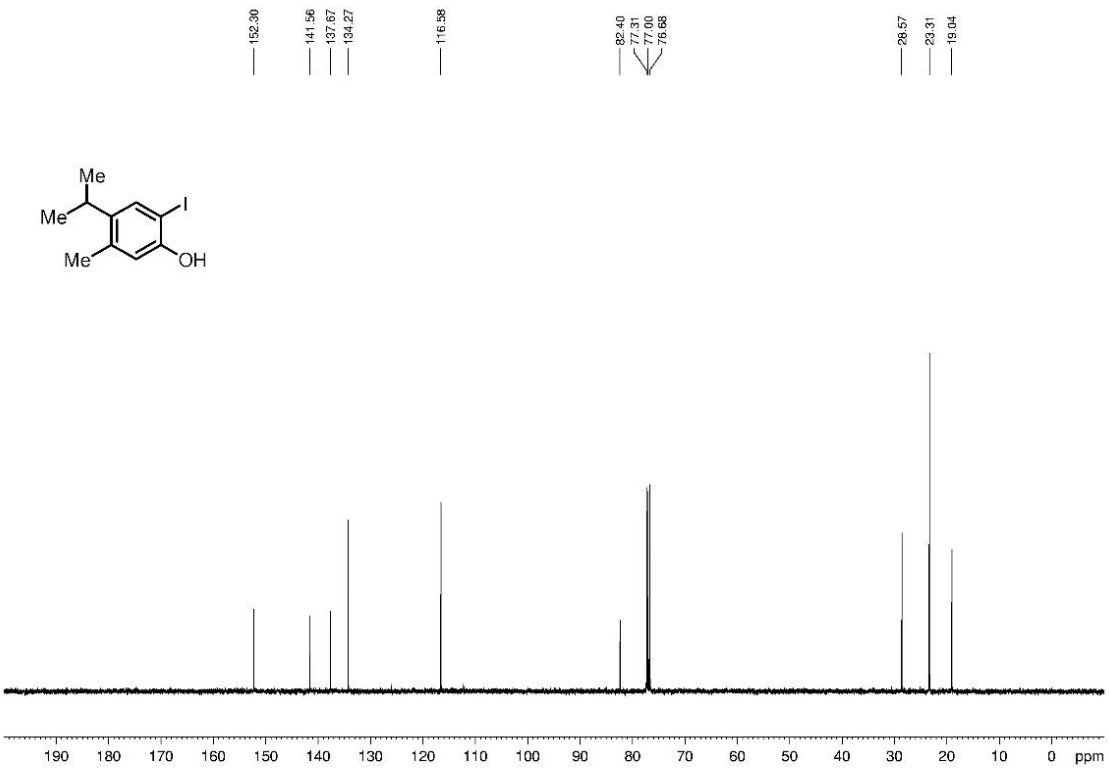
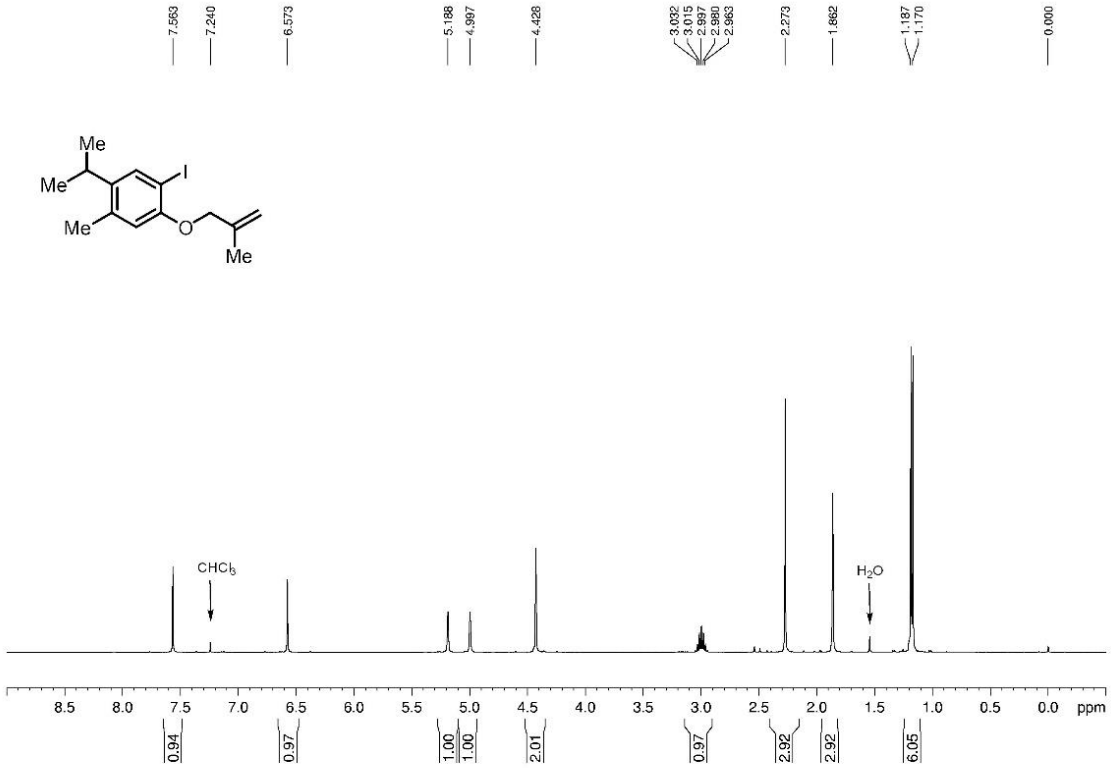
8. Copies of NMR Spectra

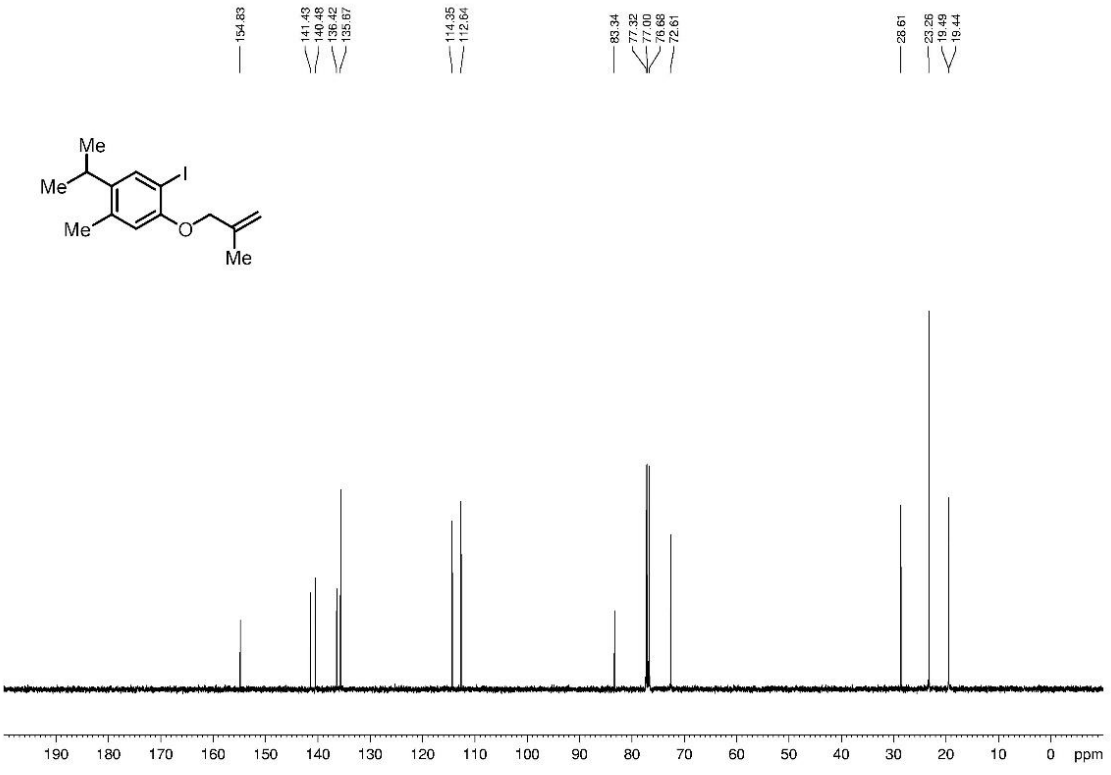
1c-1; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



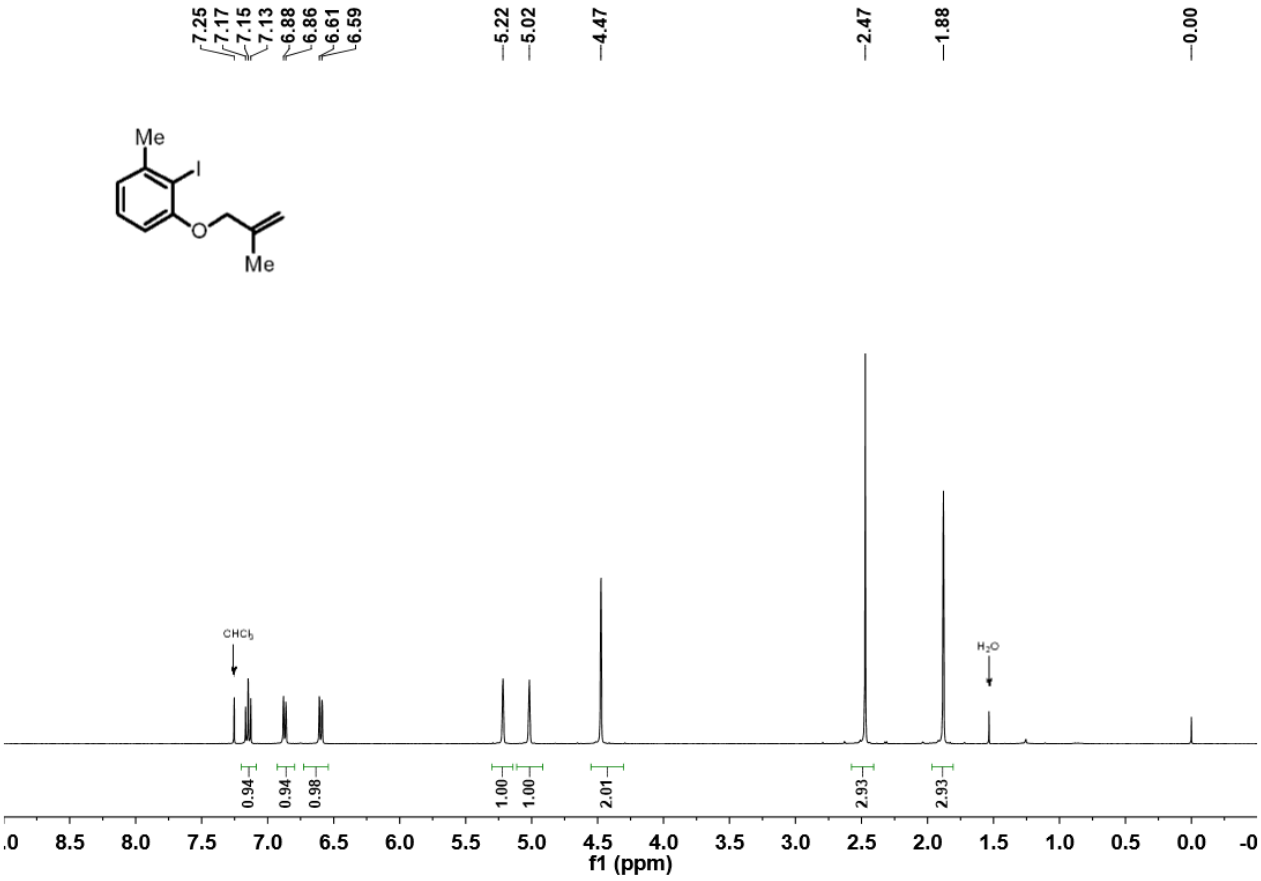


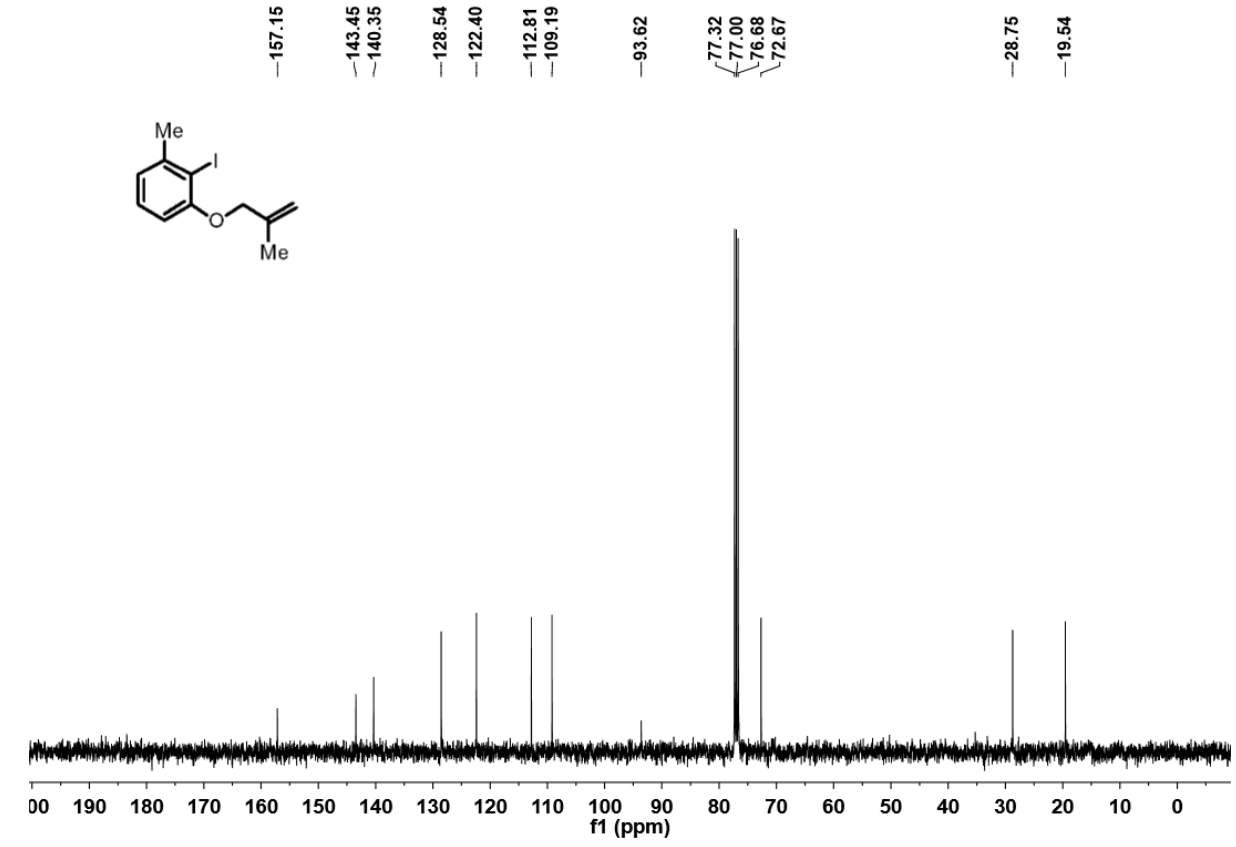
1c; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



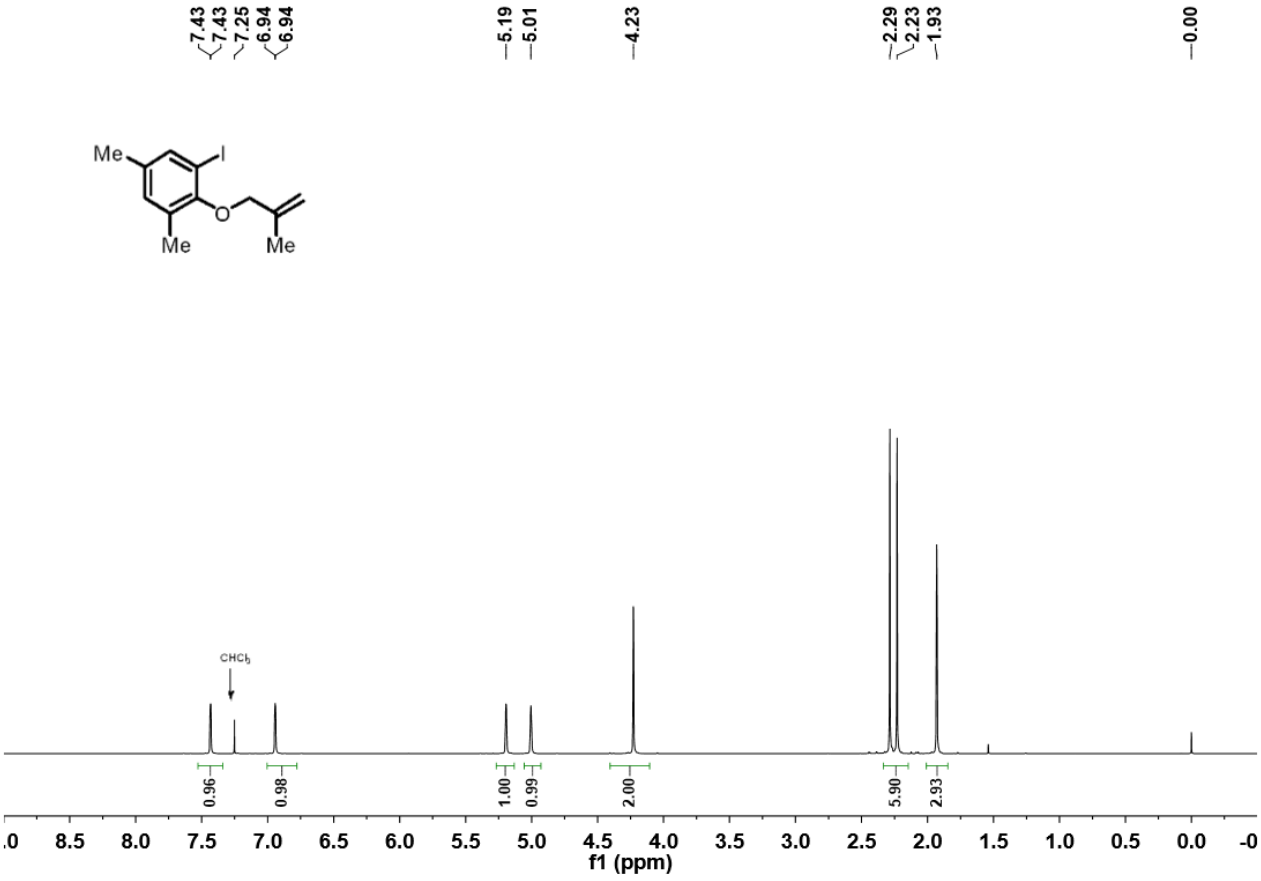


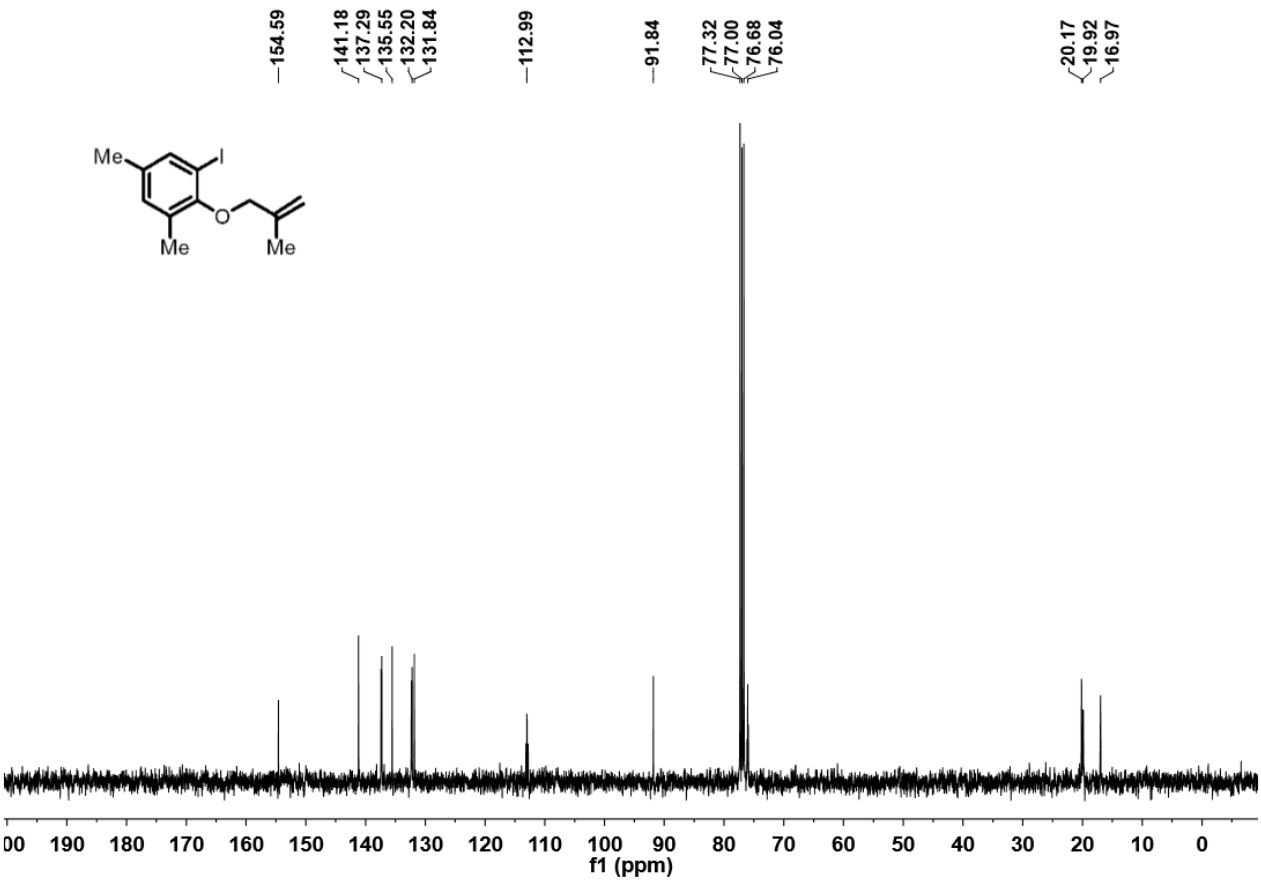
1g; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



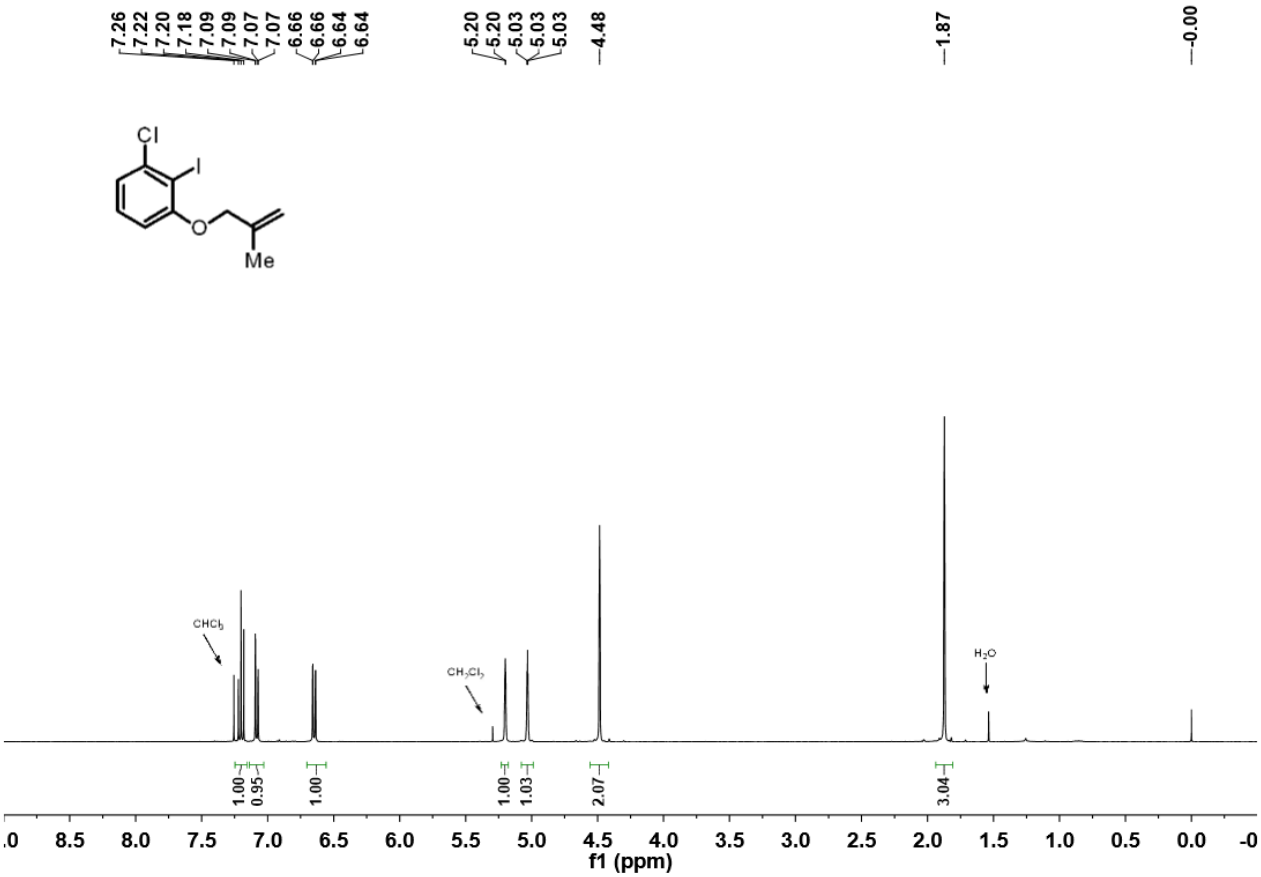


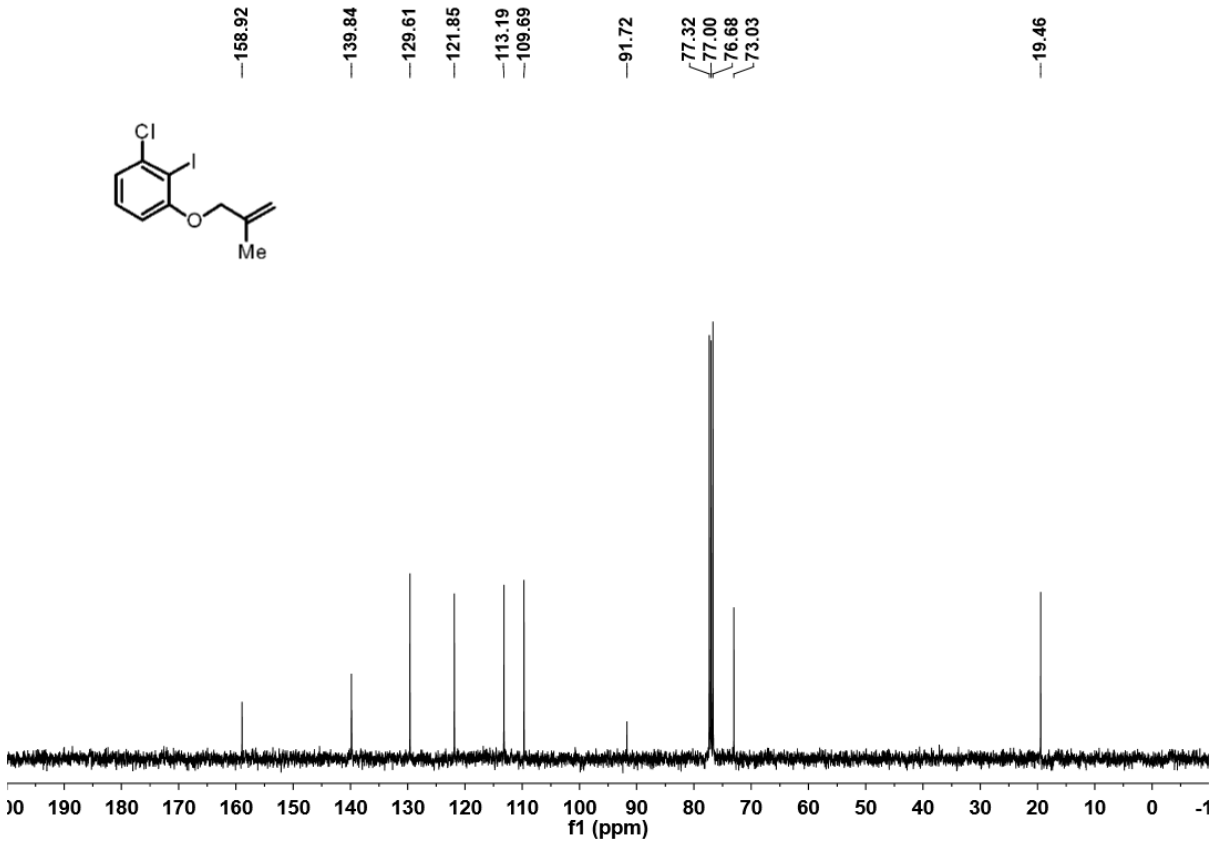
1i; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



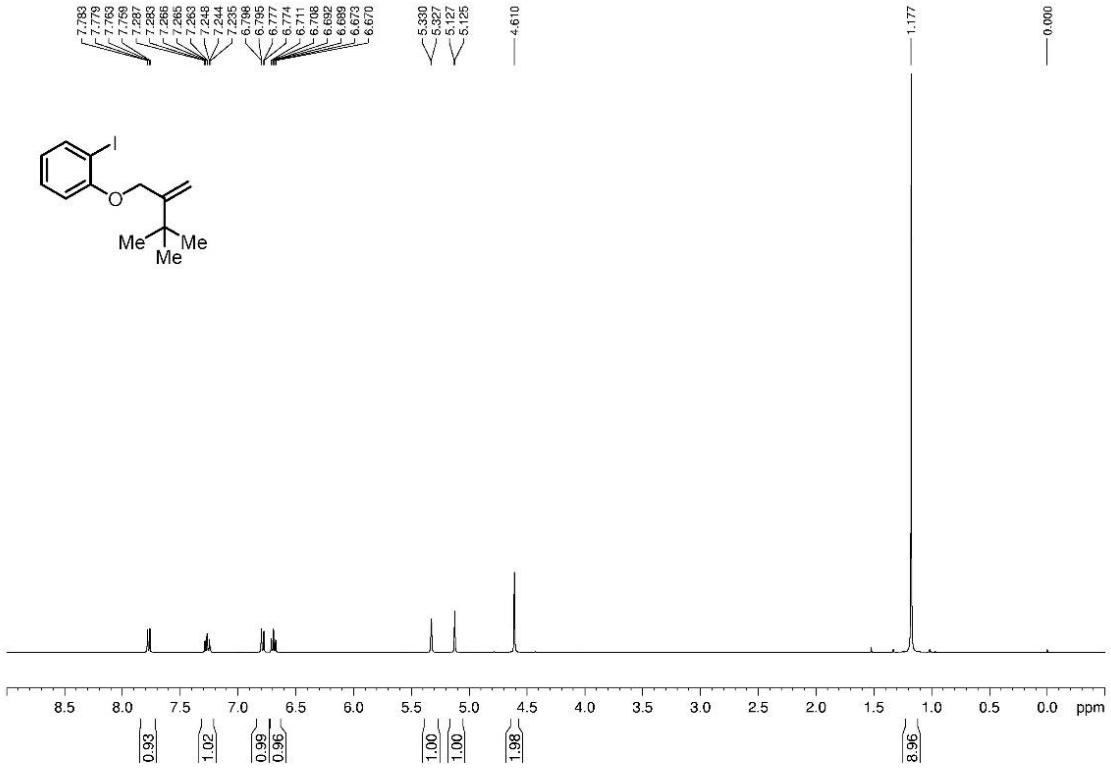


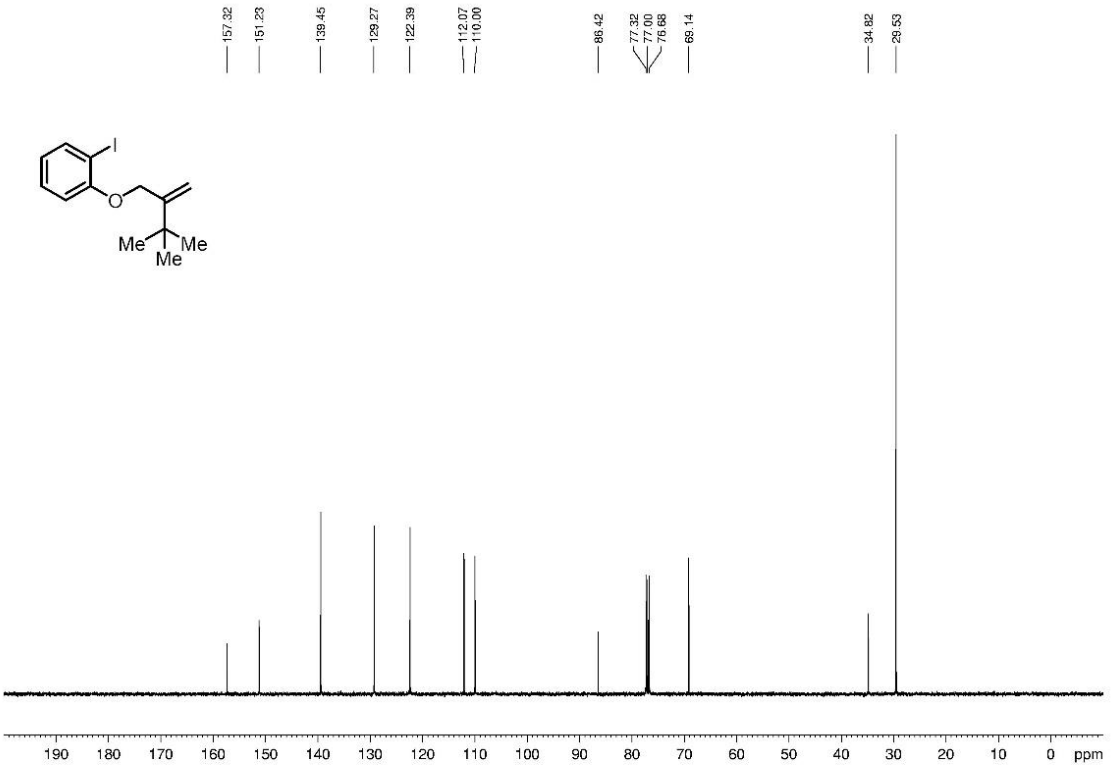
1j; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



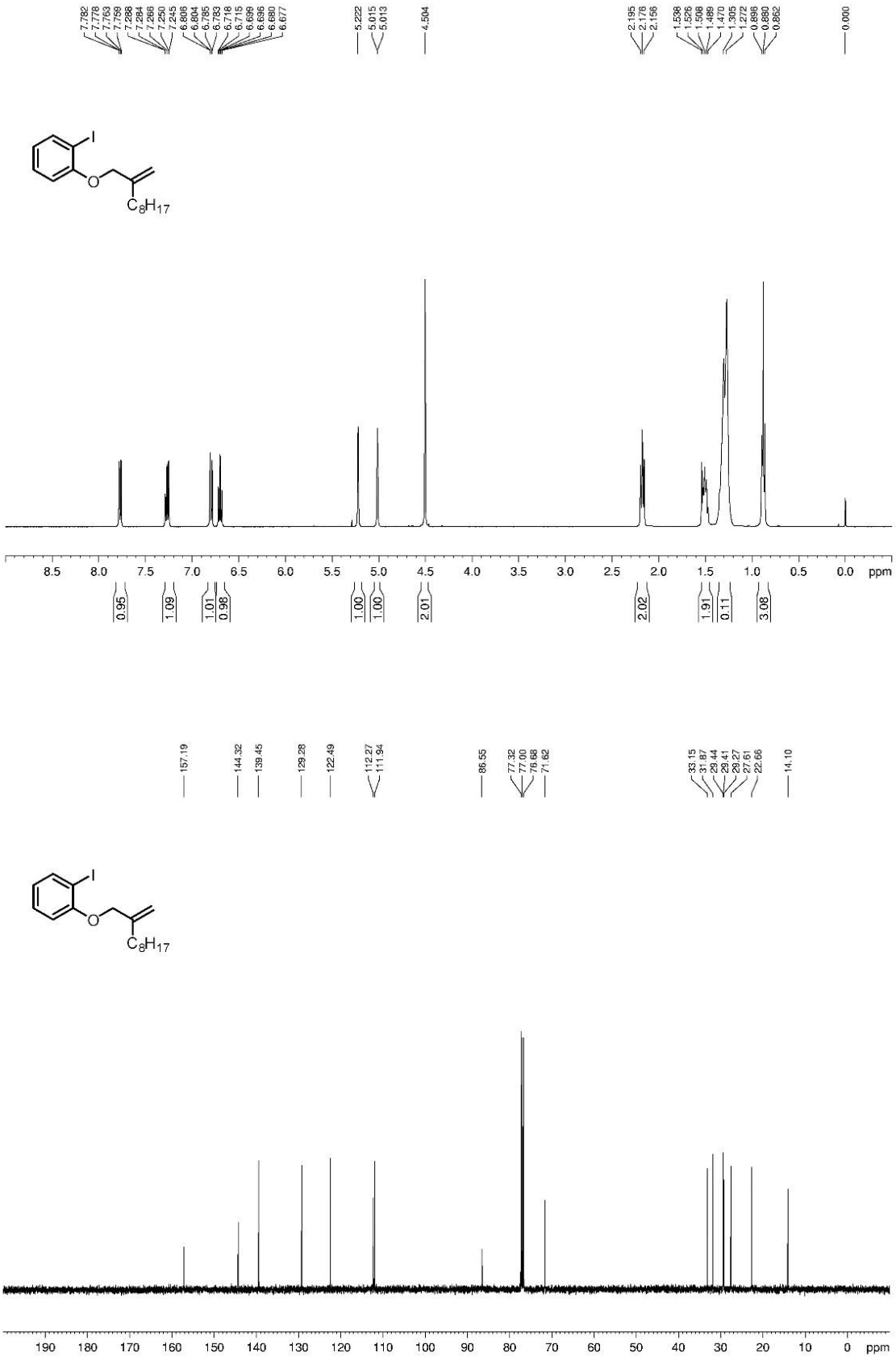


1l; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

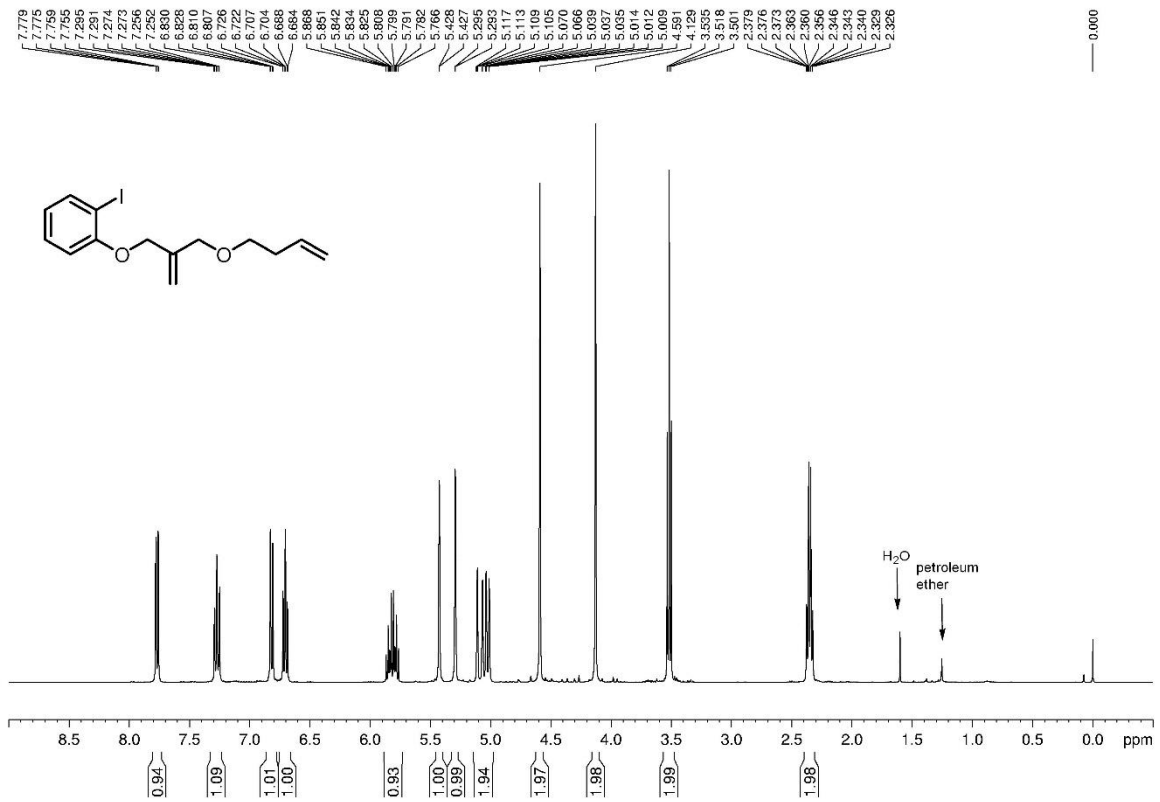


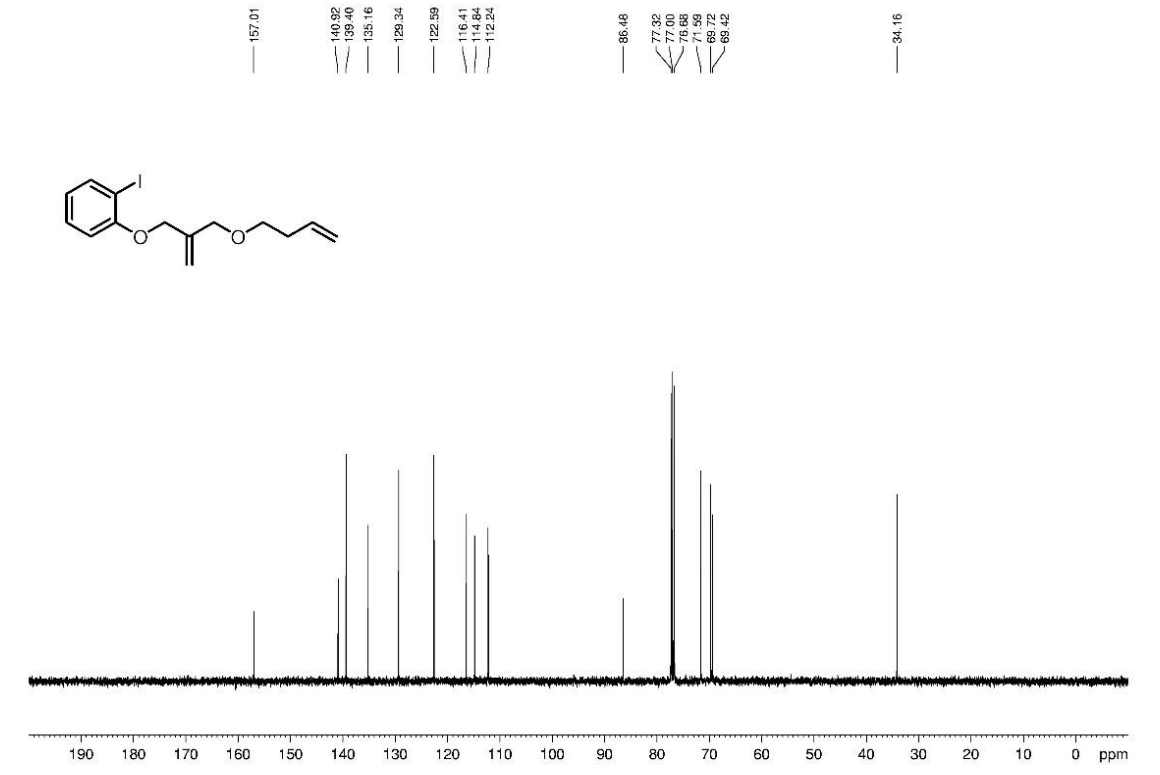


1m; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

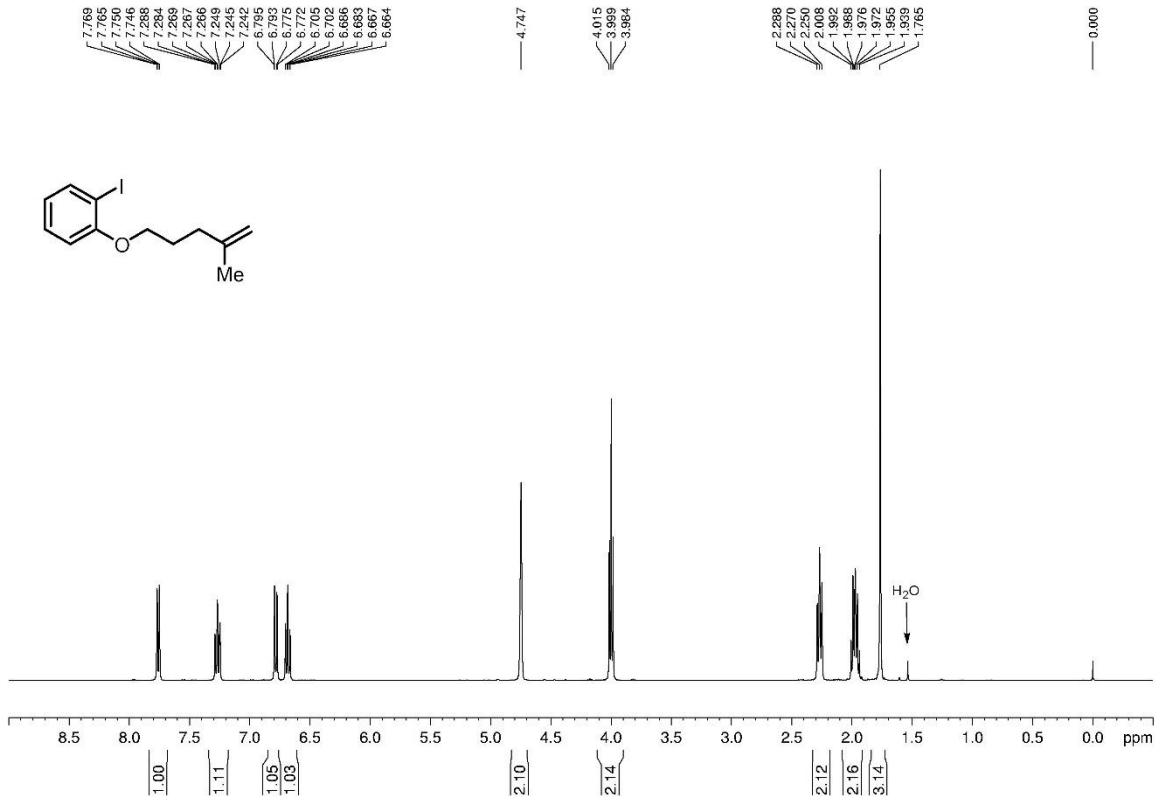


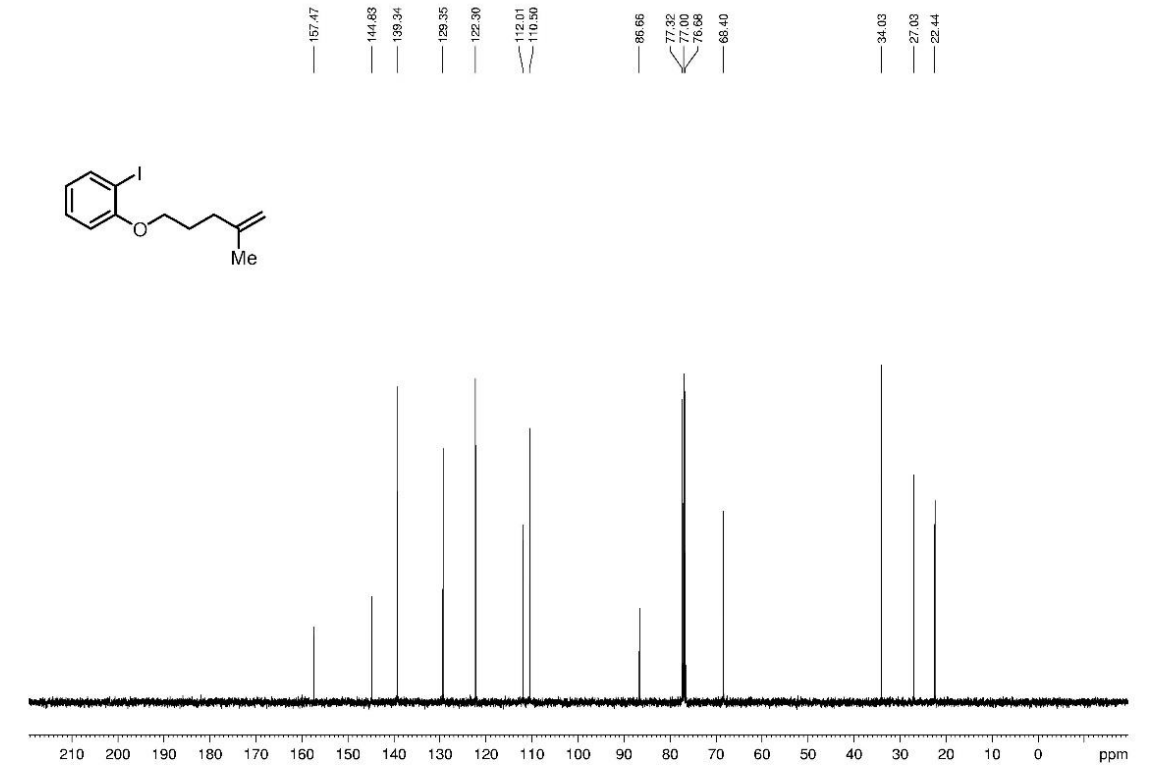
1o; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



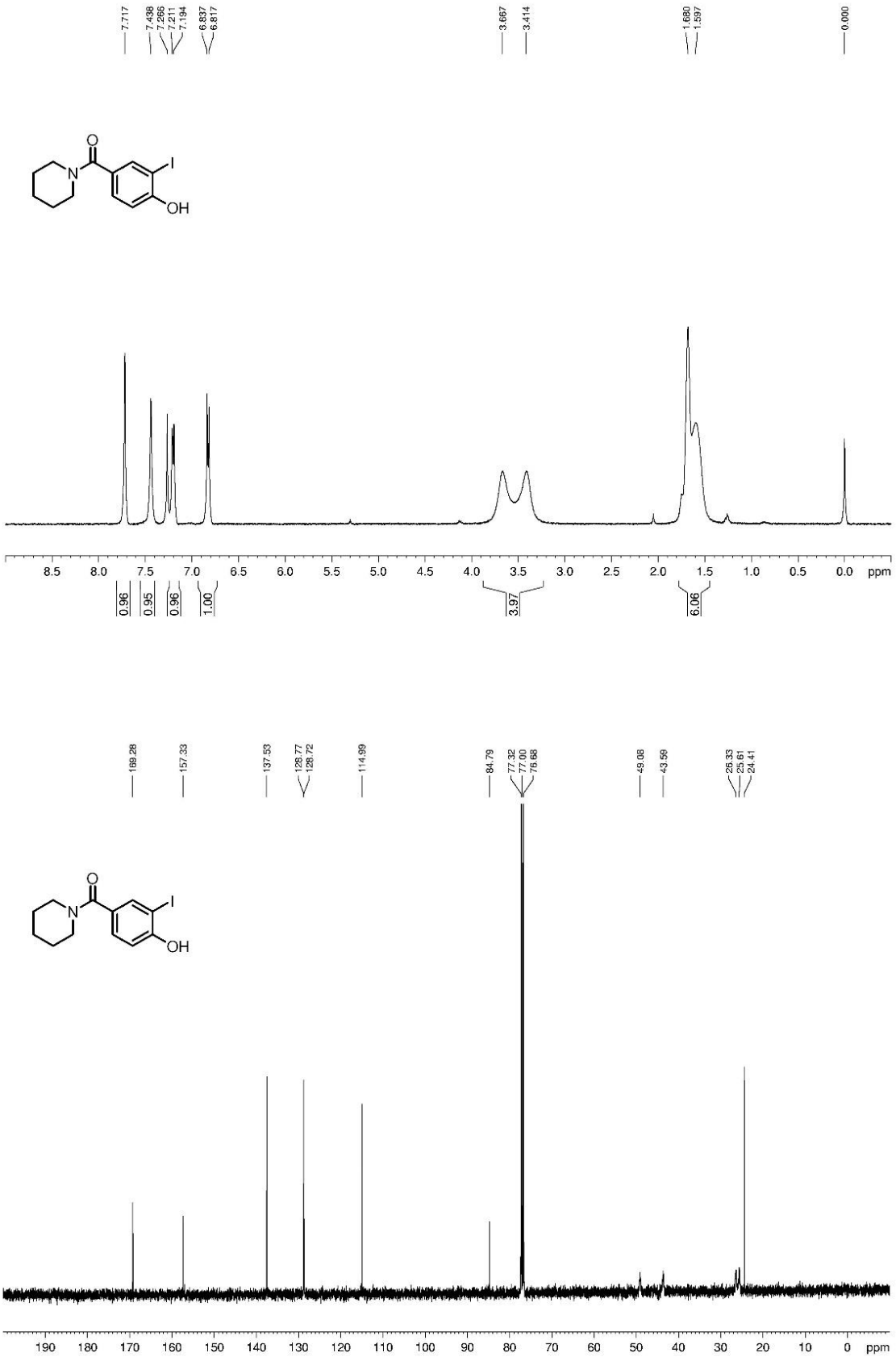


1q; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

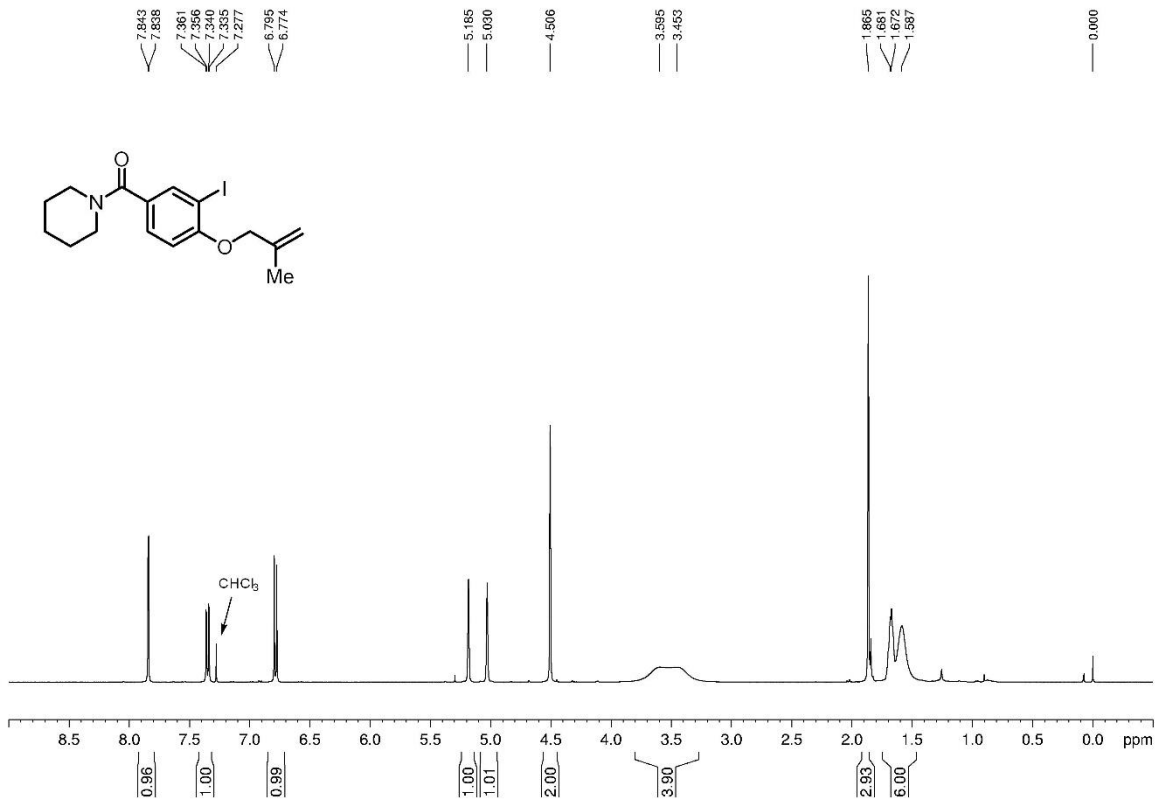


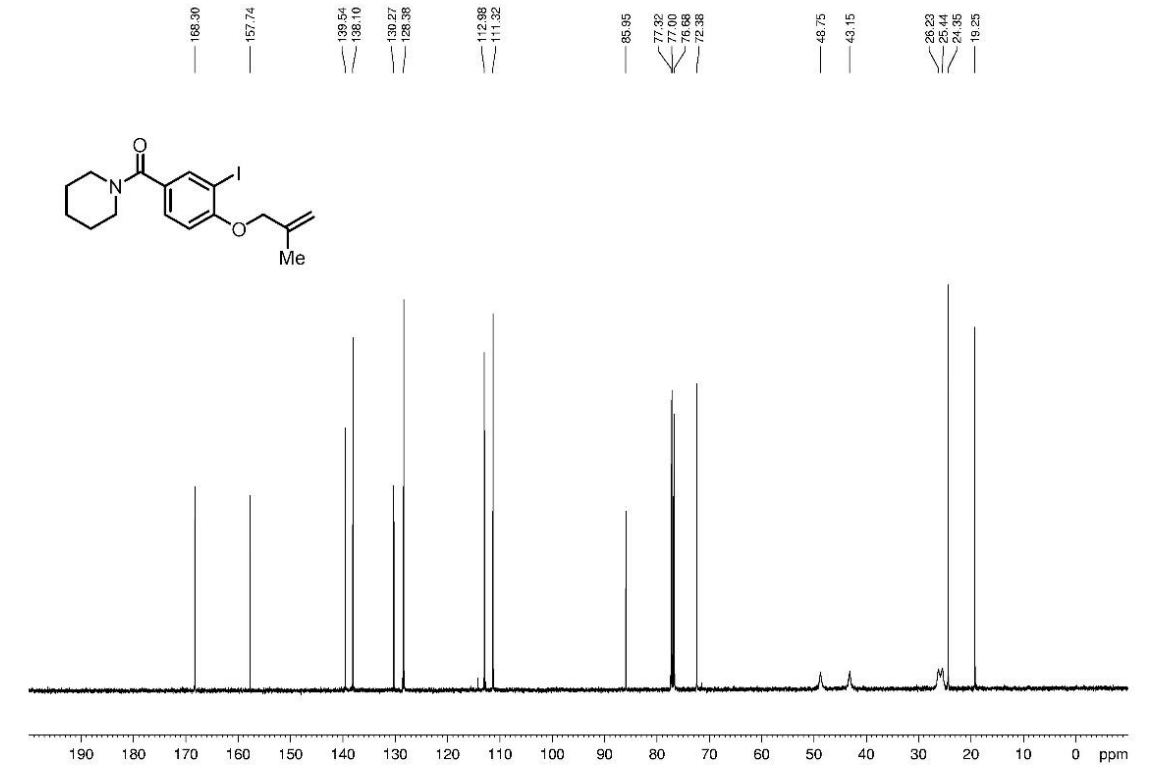


1r-1; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

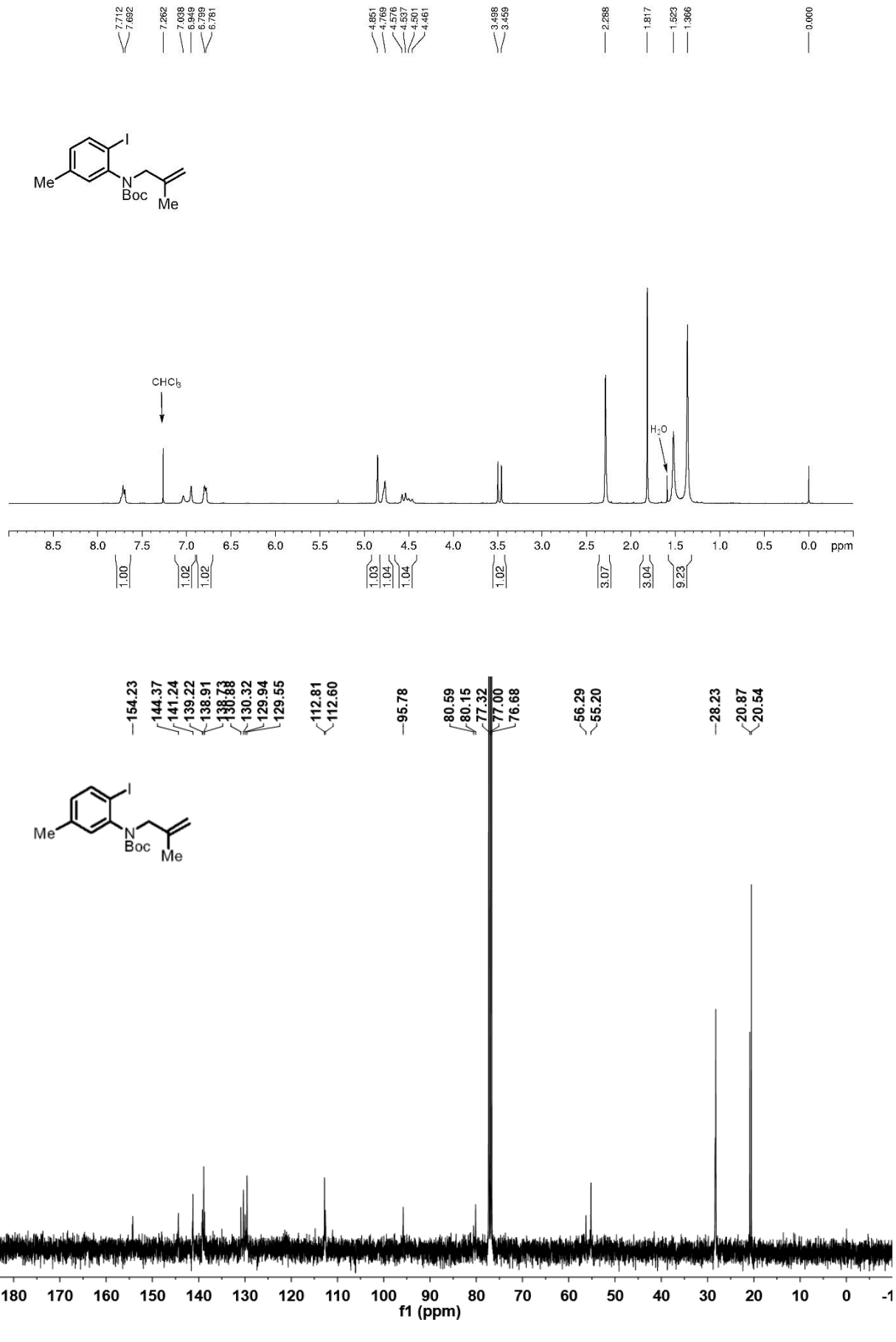


1r; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

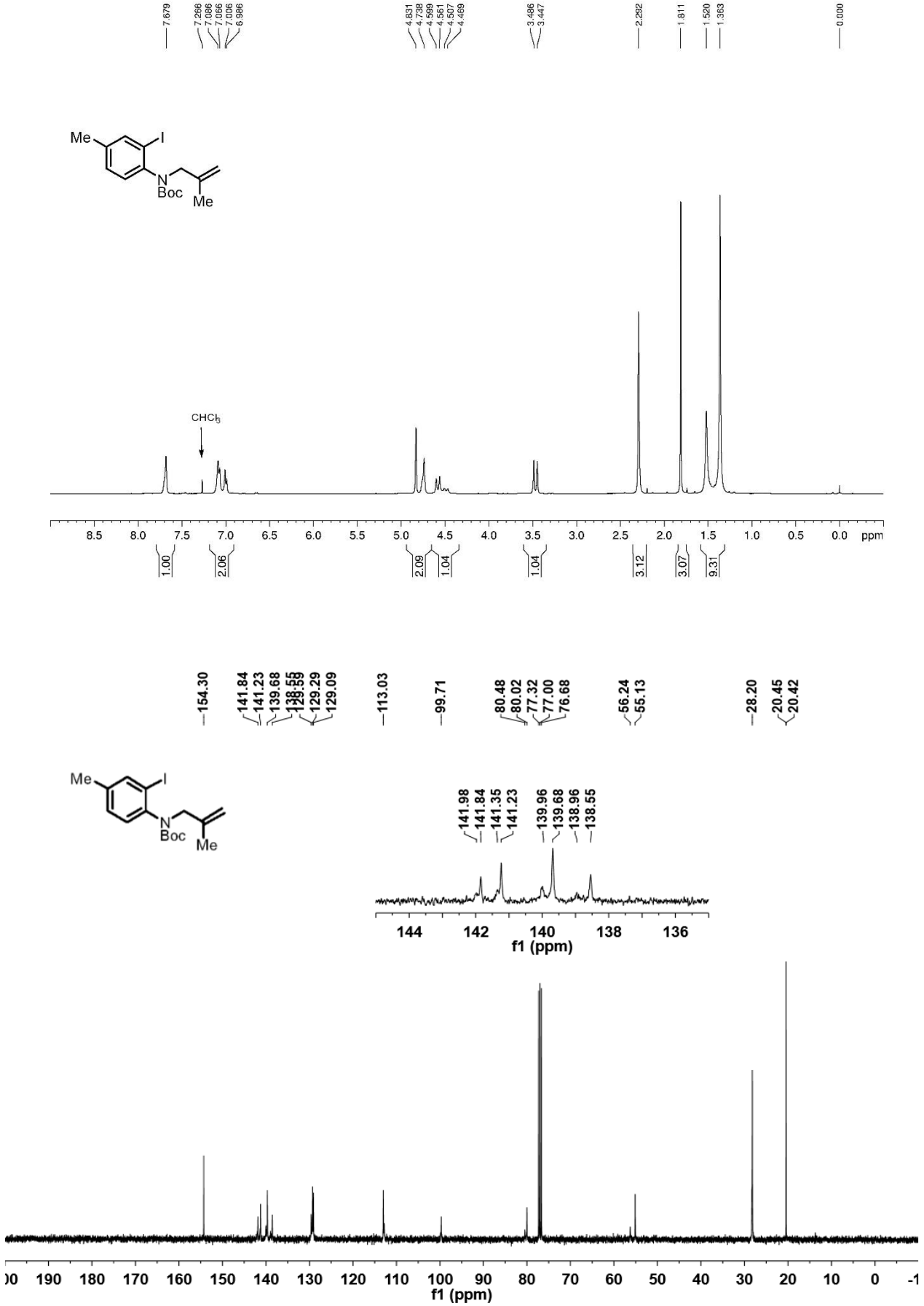




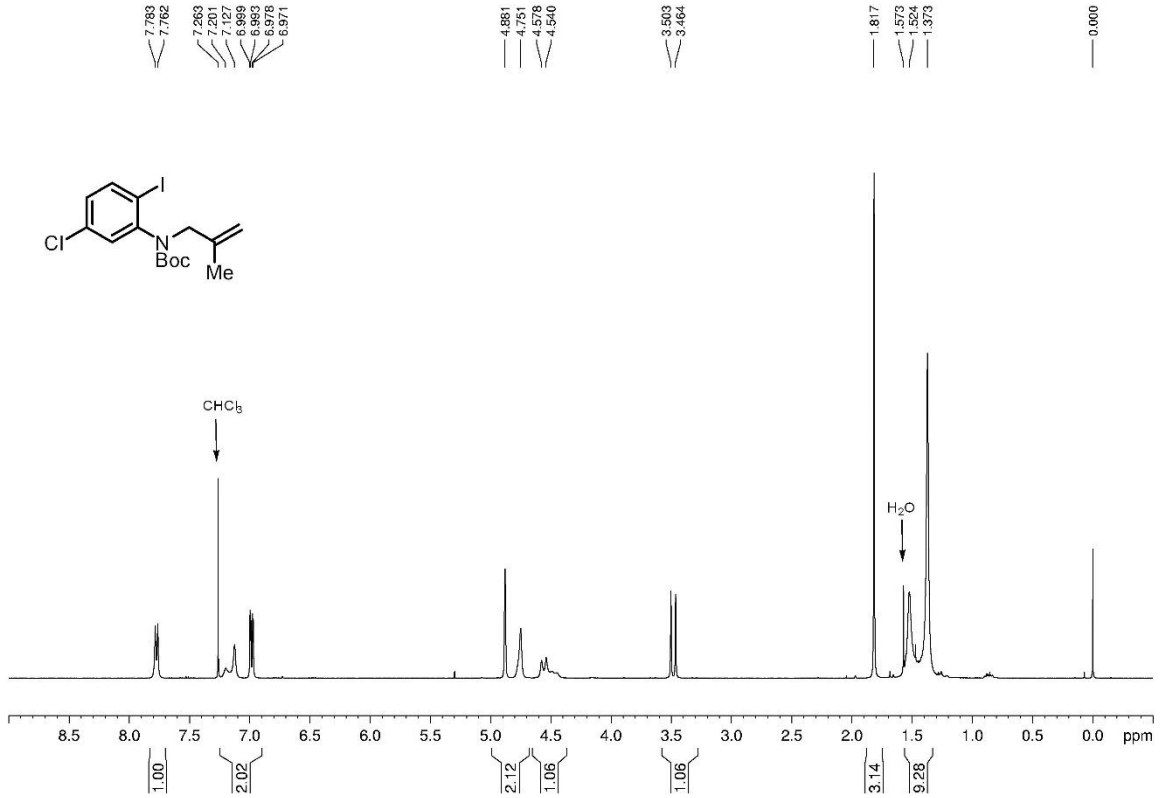
1z; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

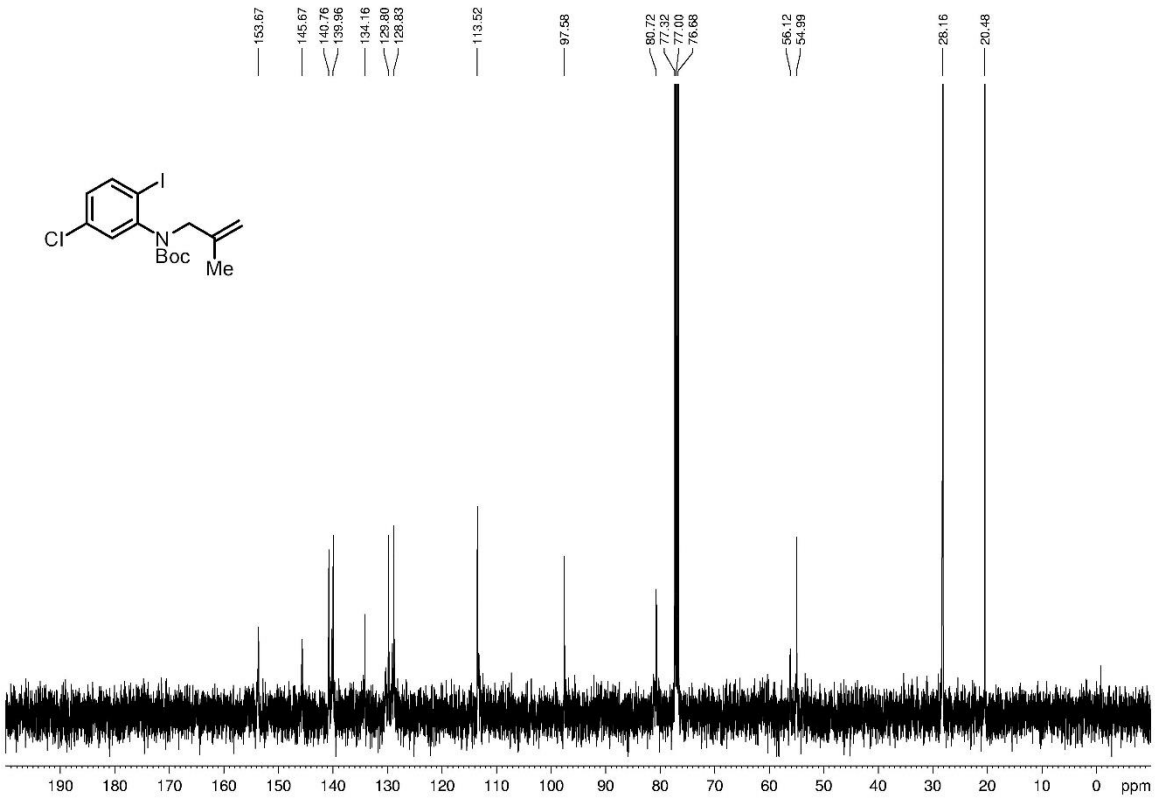


1aa; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

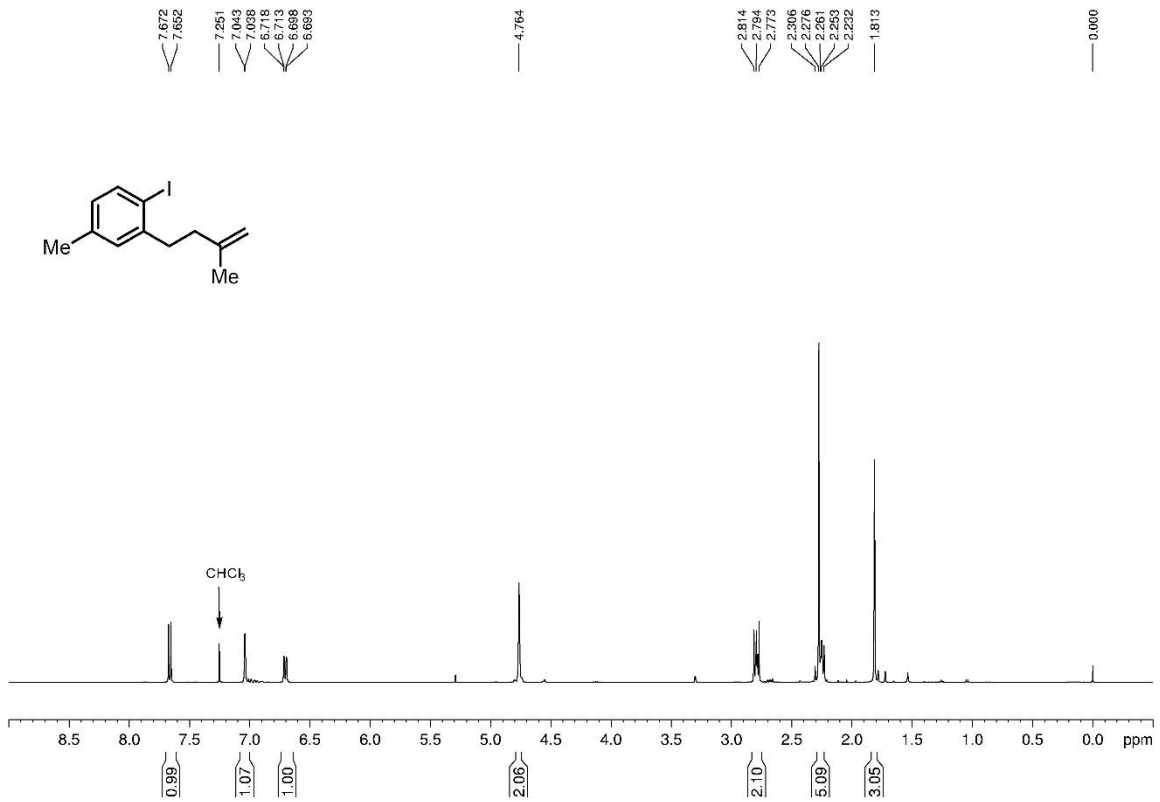


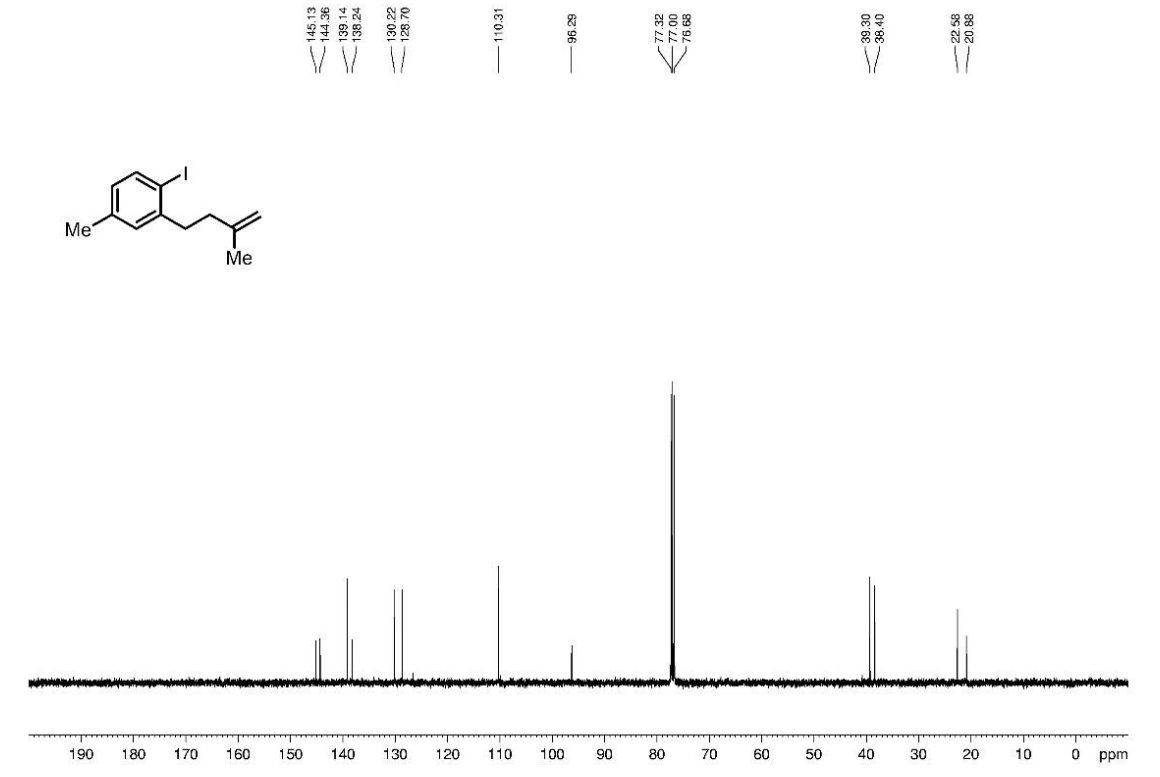
1ab; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



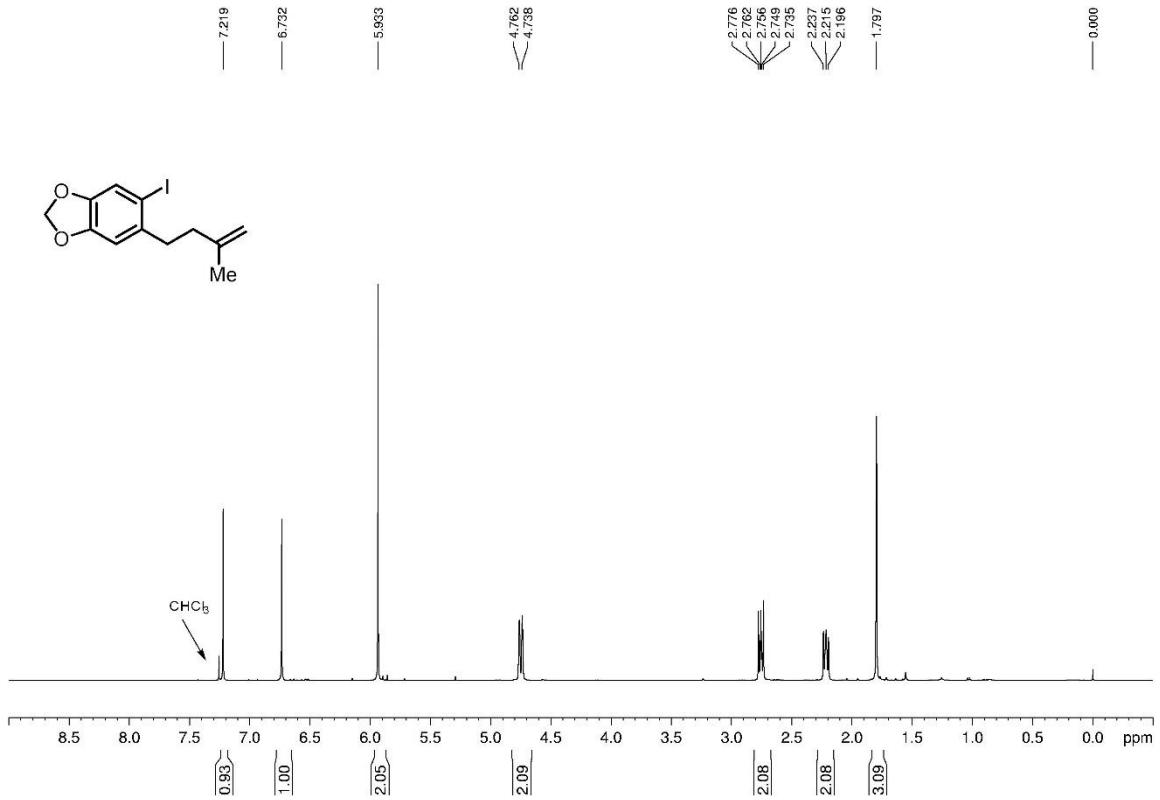


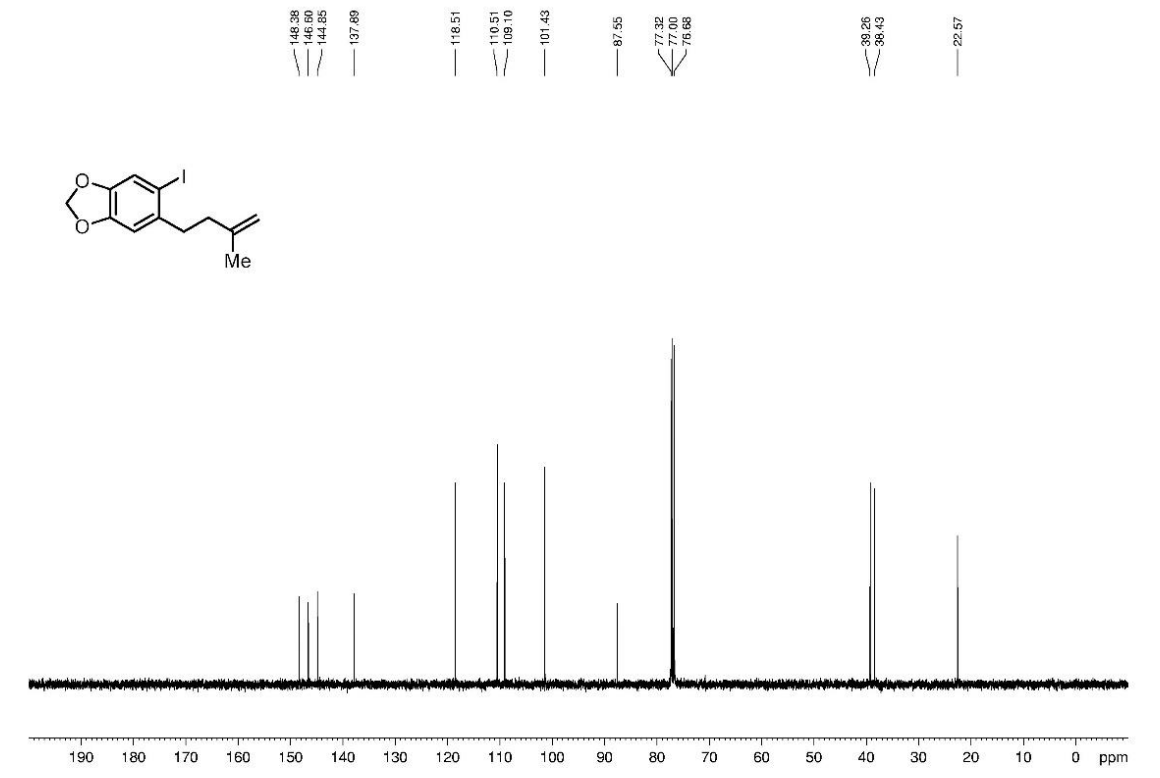
1ad; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



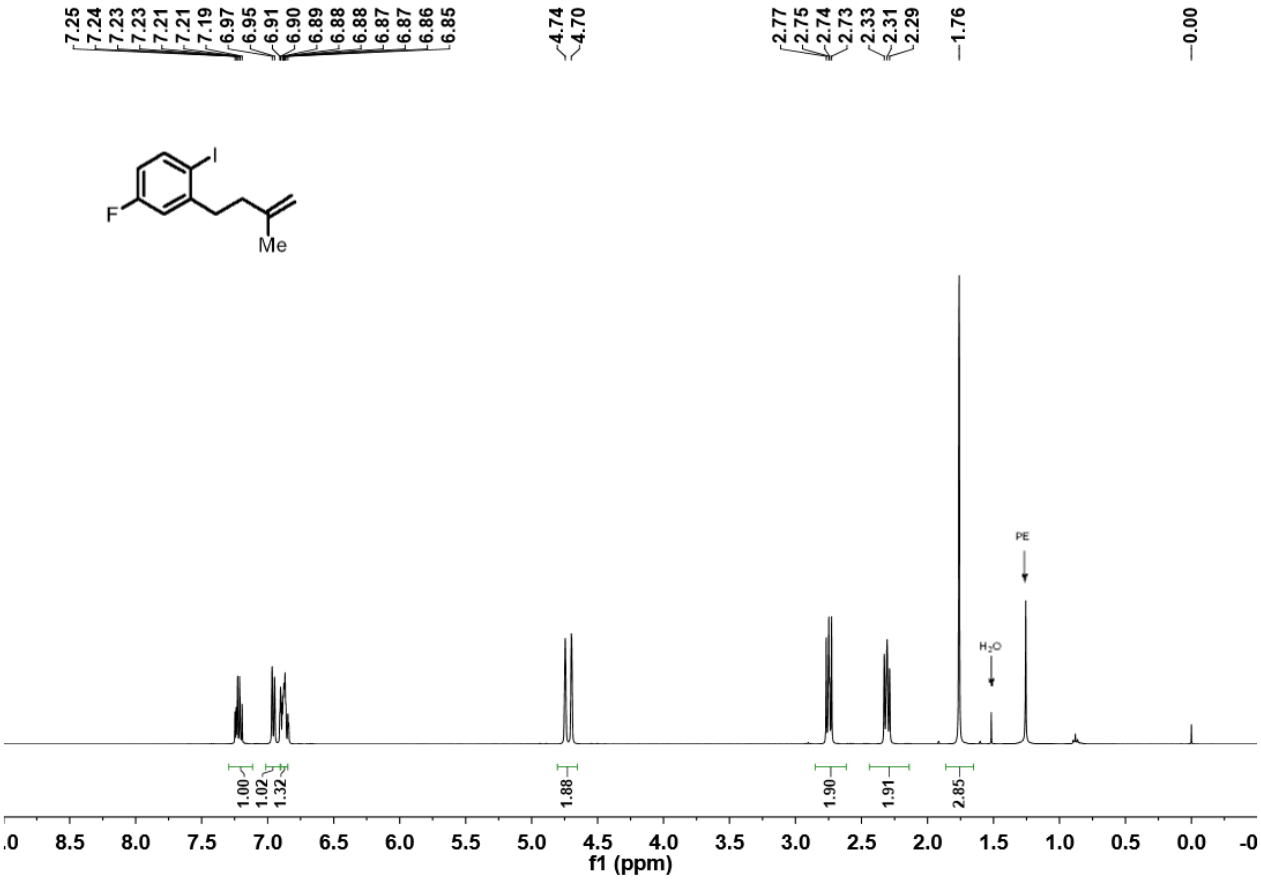


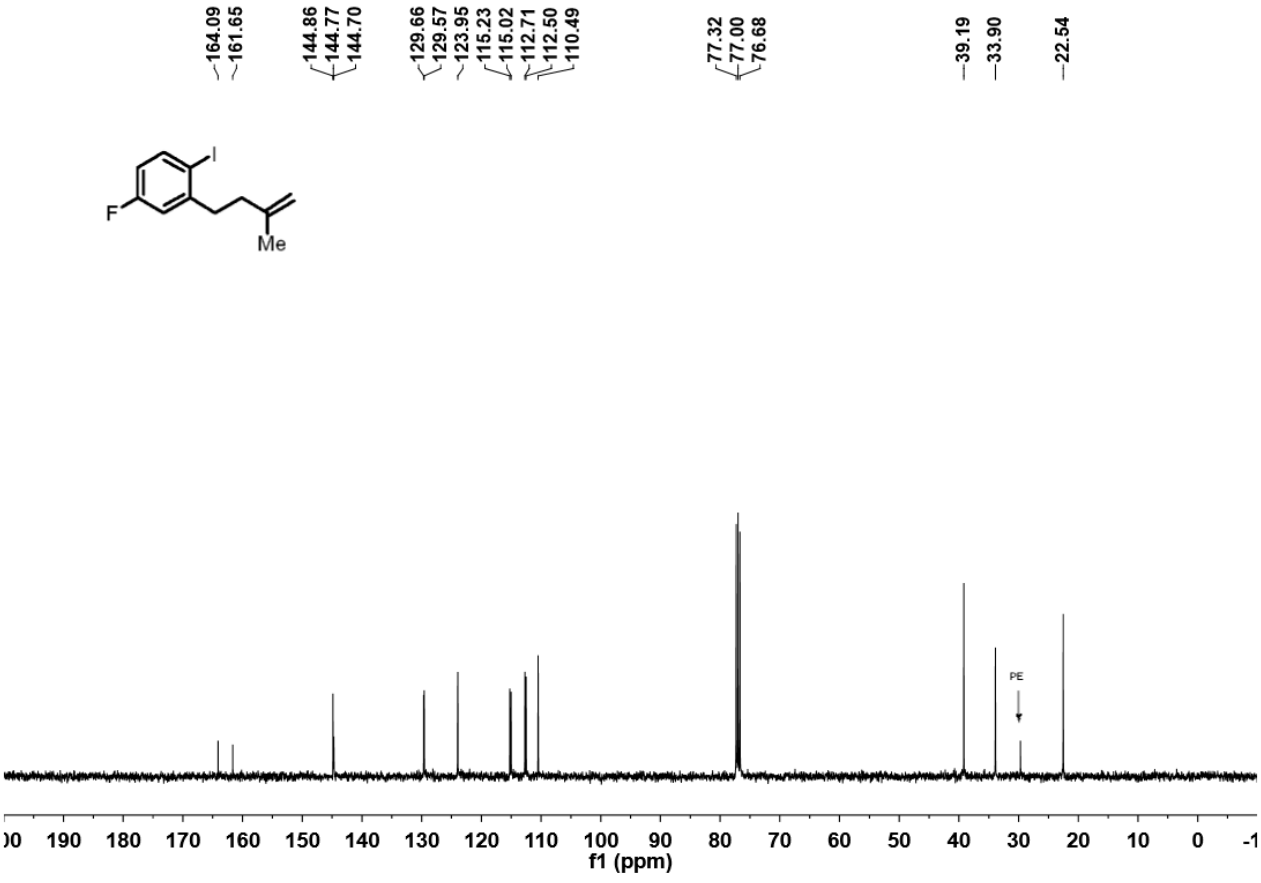
1ae; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



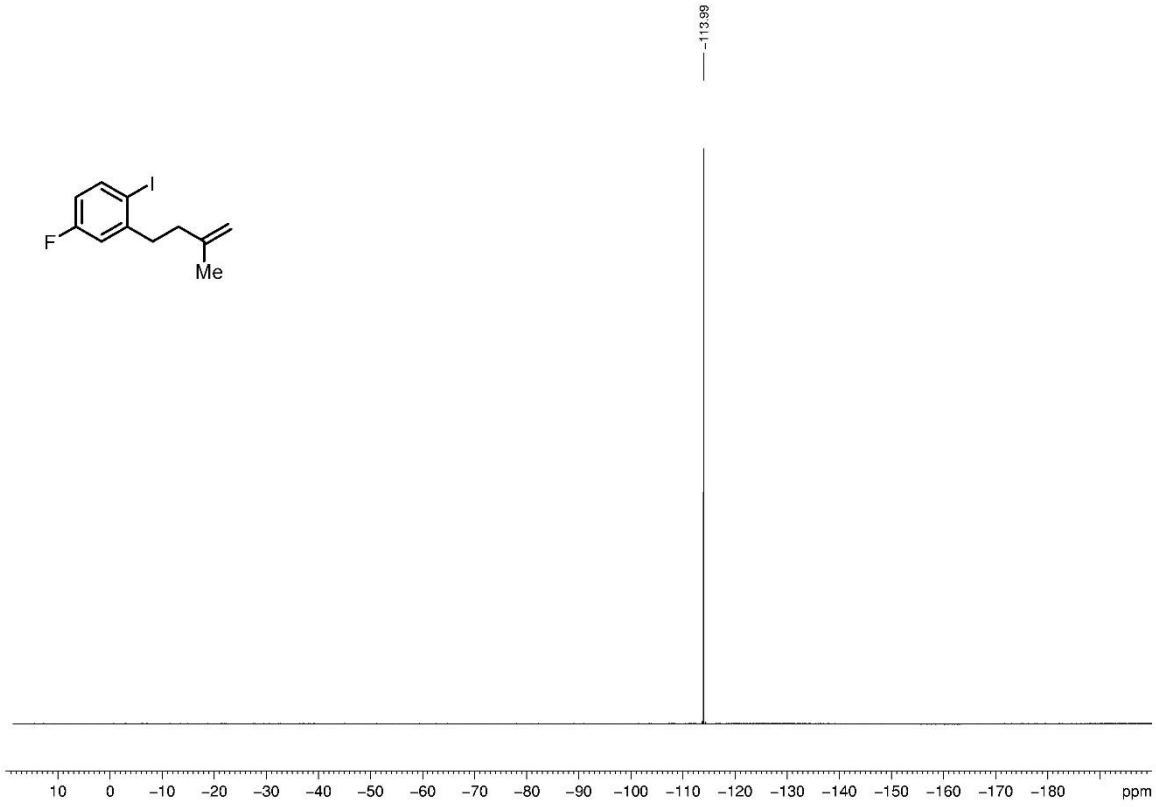


1af; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

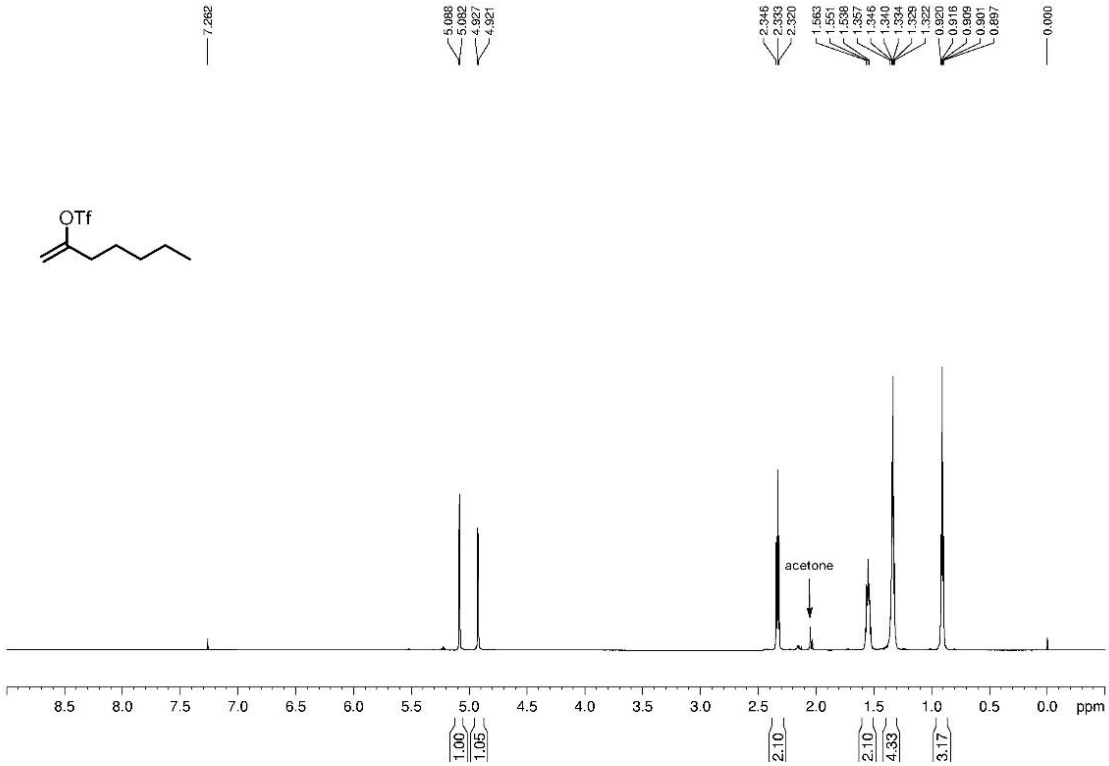


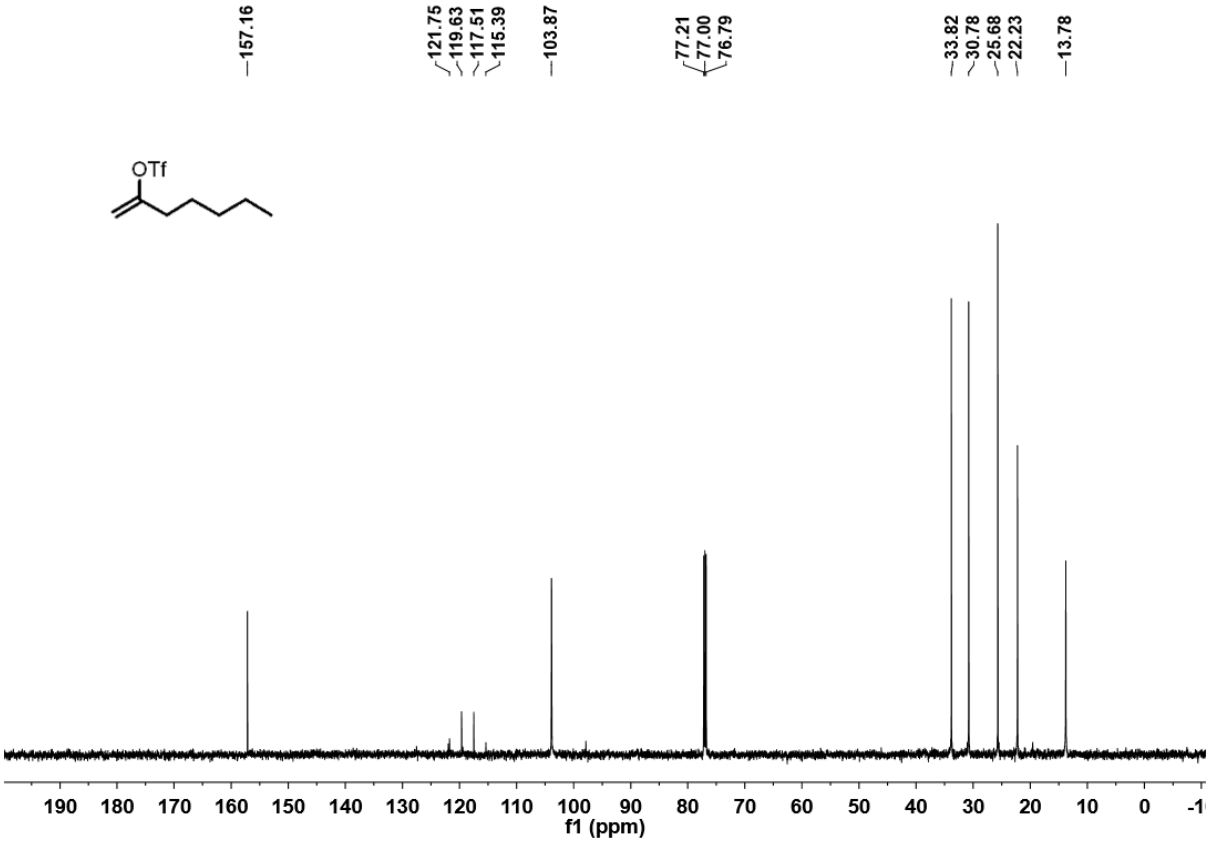


1af; ^{19}F NMR (376MHz, $CDCl_3$)

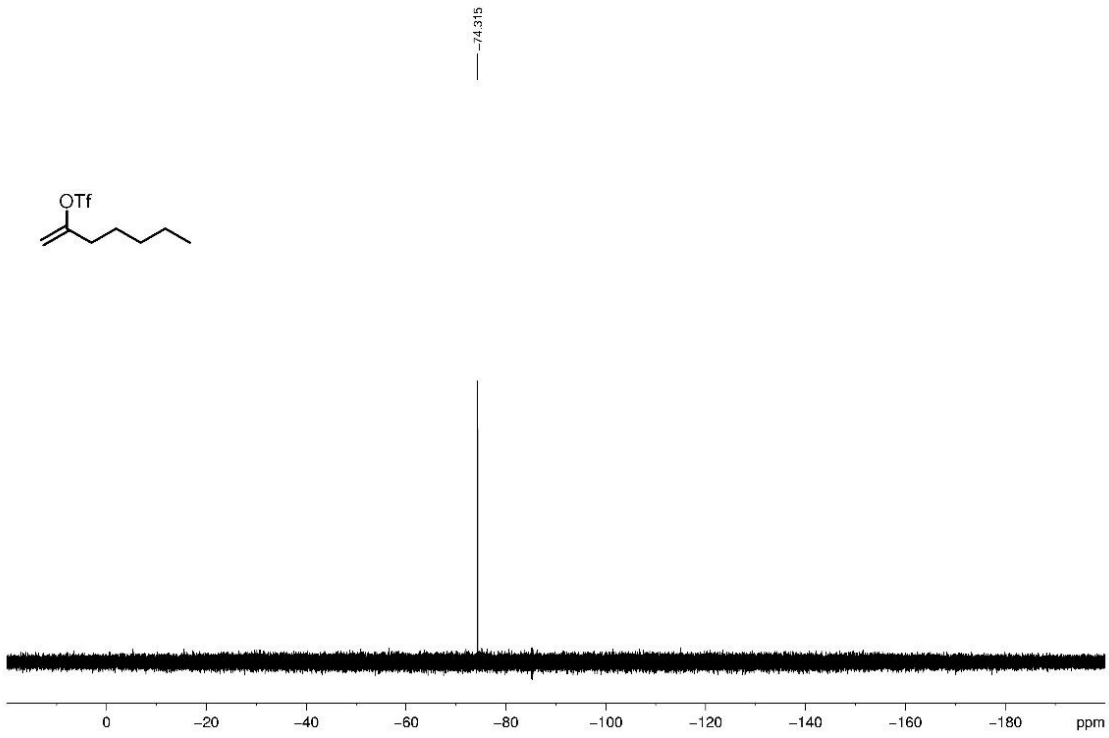


2o; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

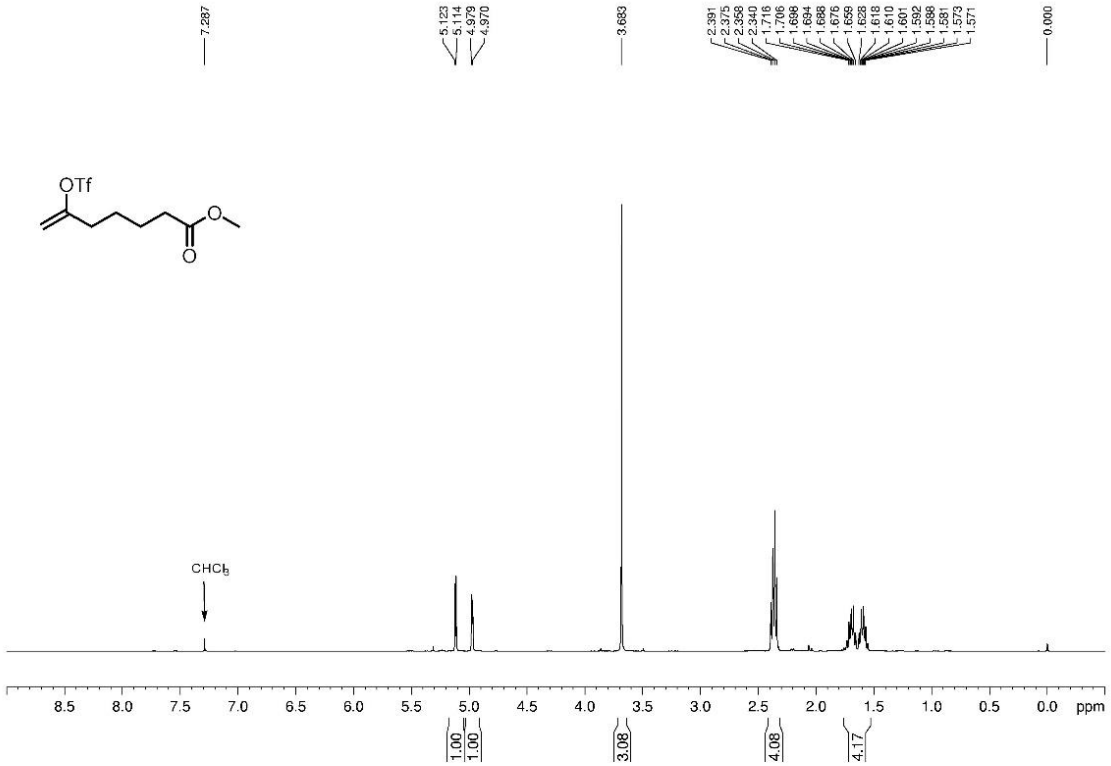


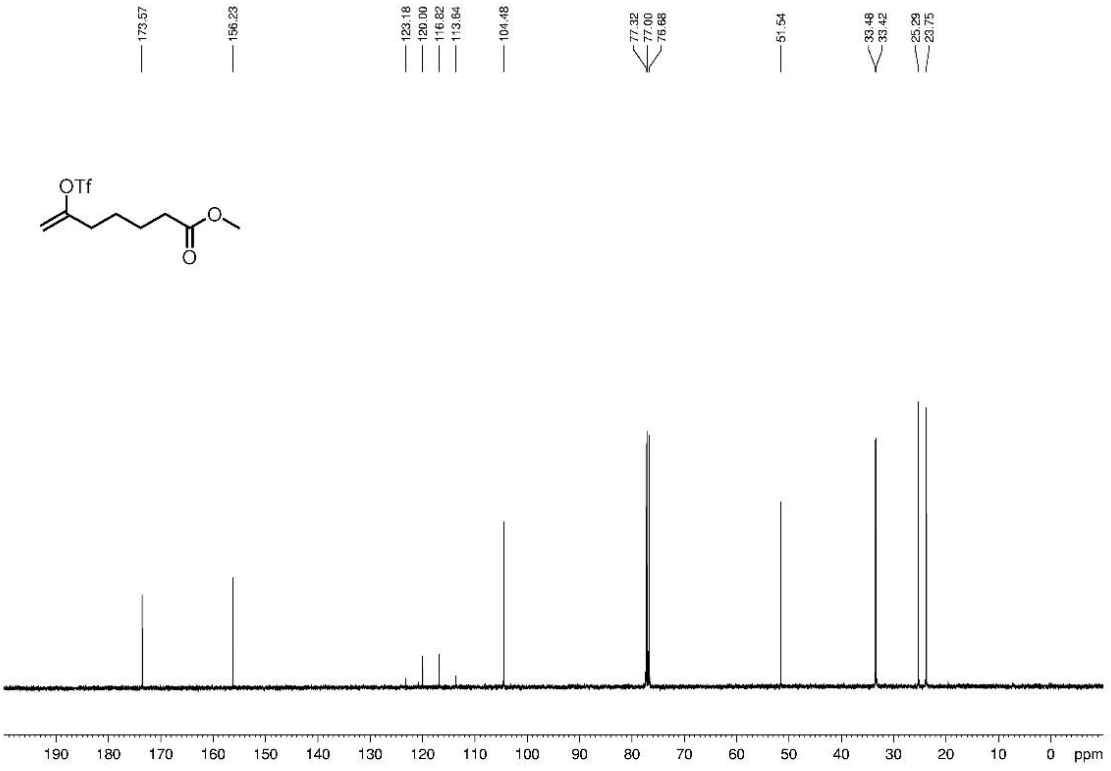


2o; ^{19}F NMR (564MHz, $CDCl_3$)

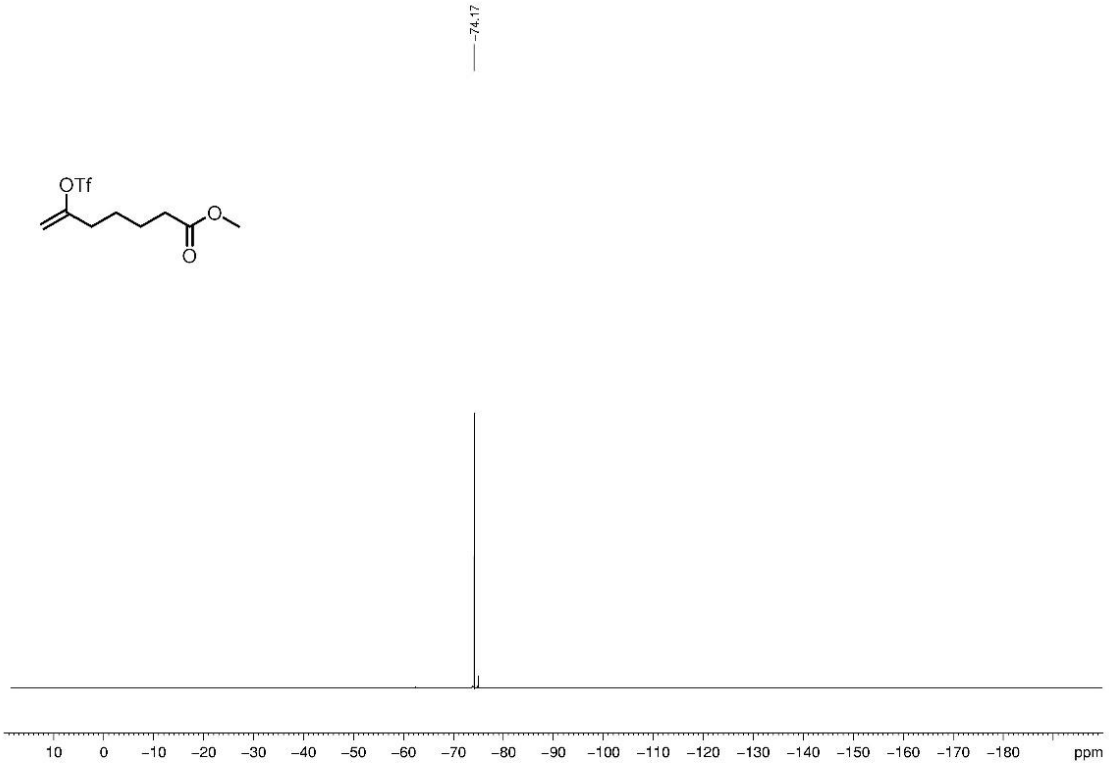


2p; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

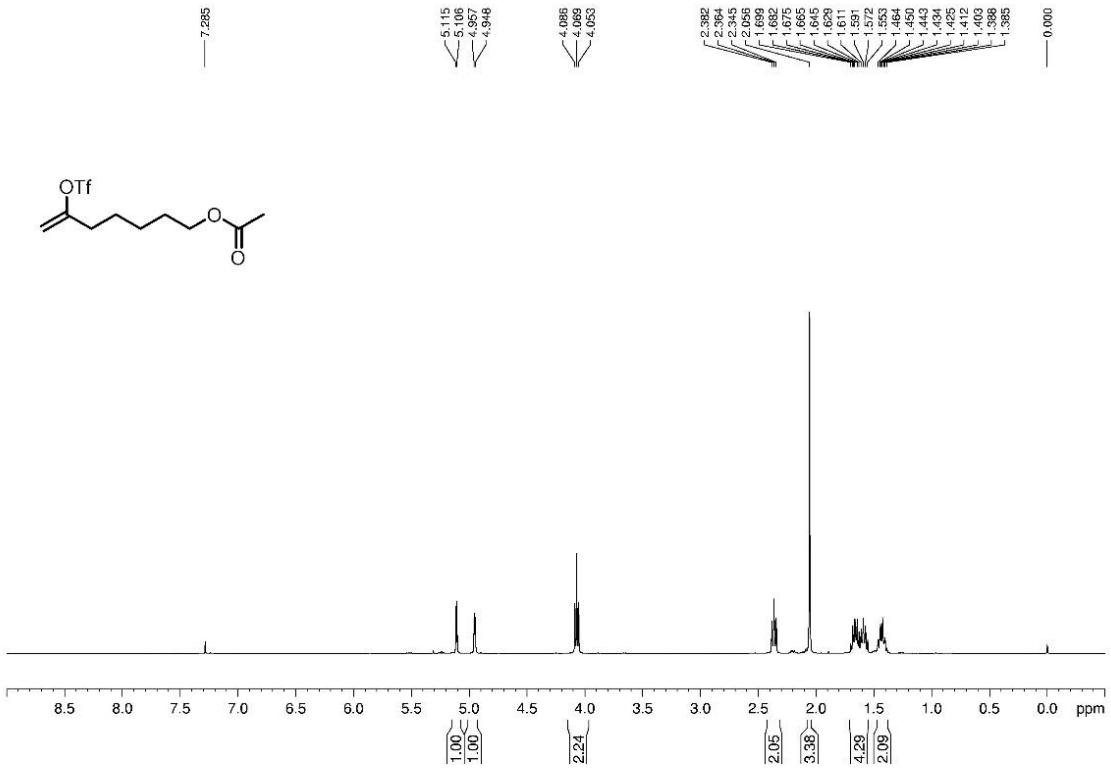


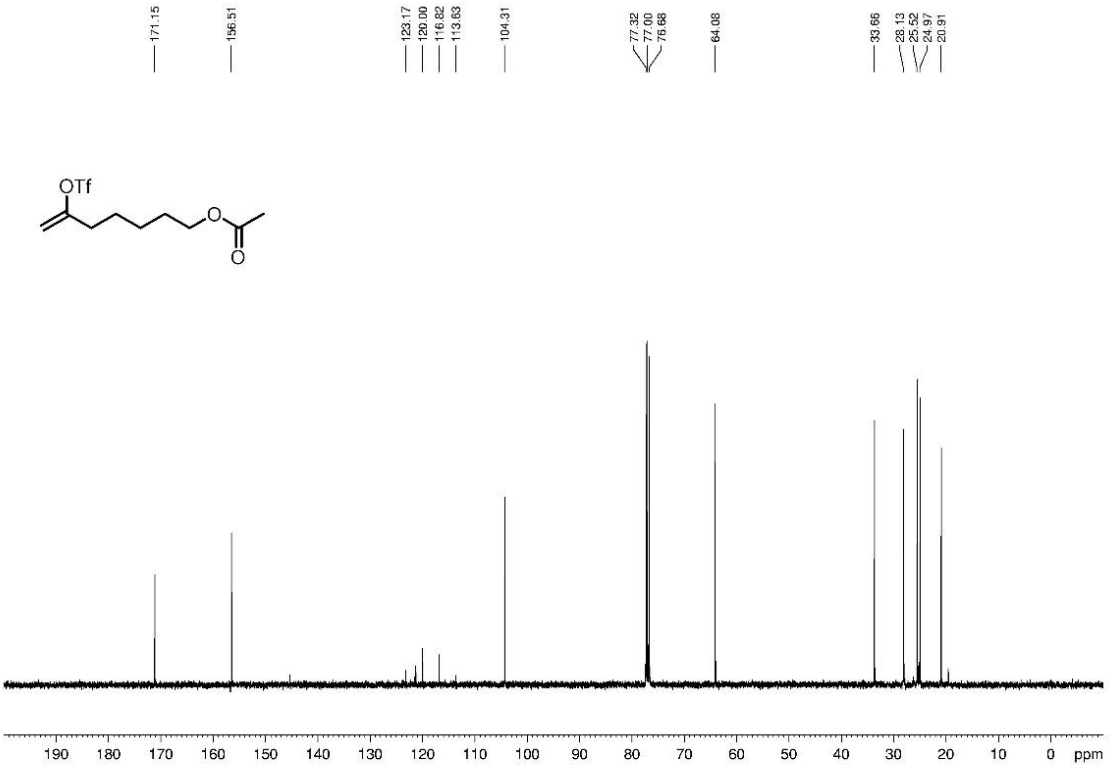


2p; ^{19}F NMR (376MHz, $CDCl_3$)



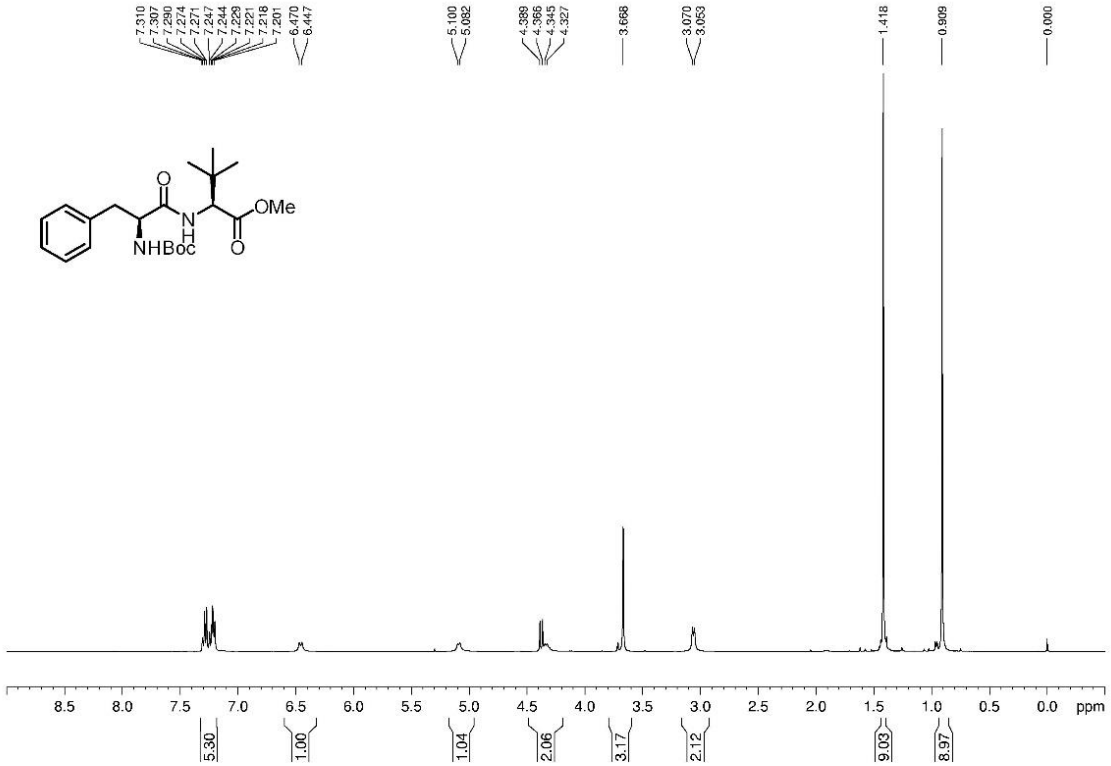
2q; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

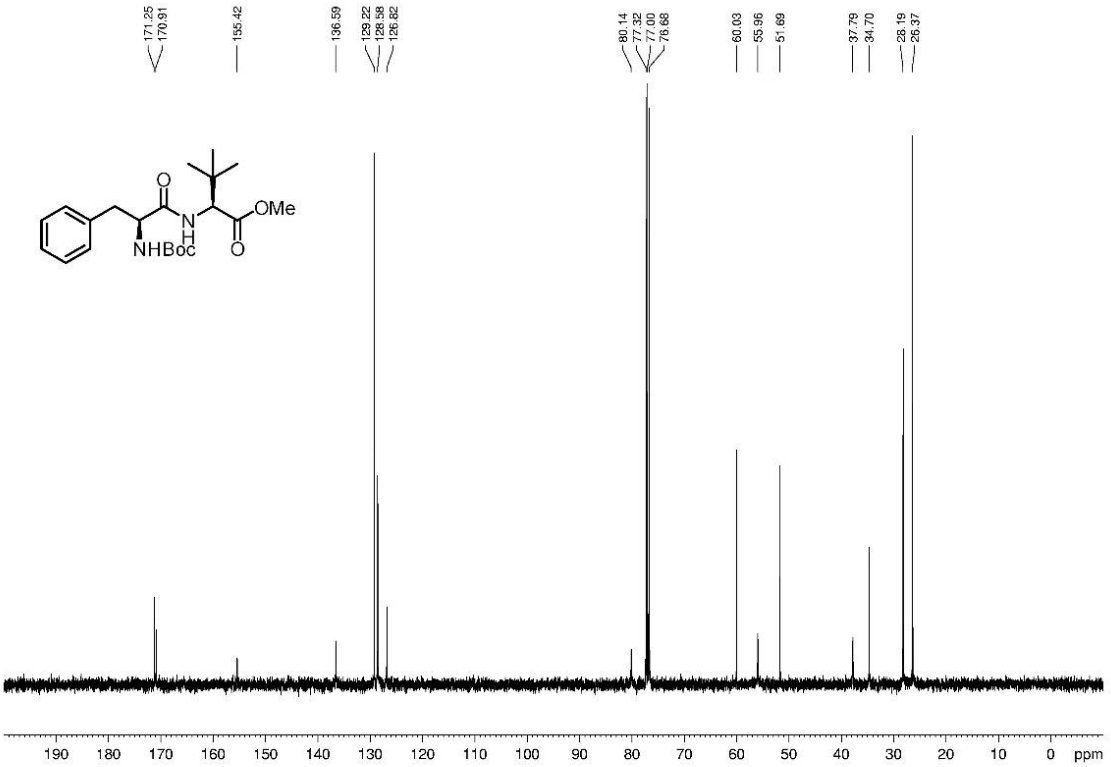




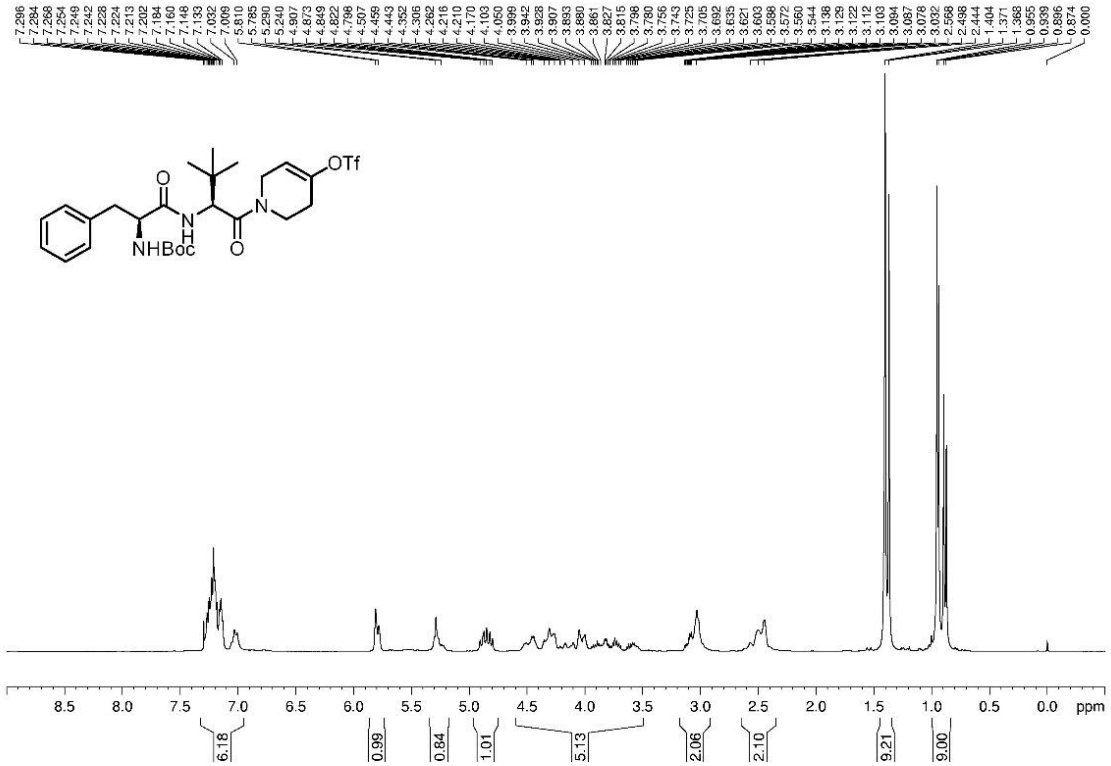
2q; ^{19}F NMR (376MHz, $CDCl_3$)

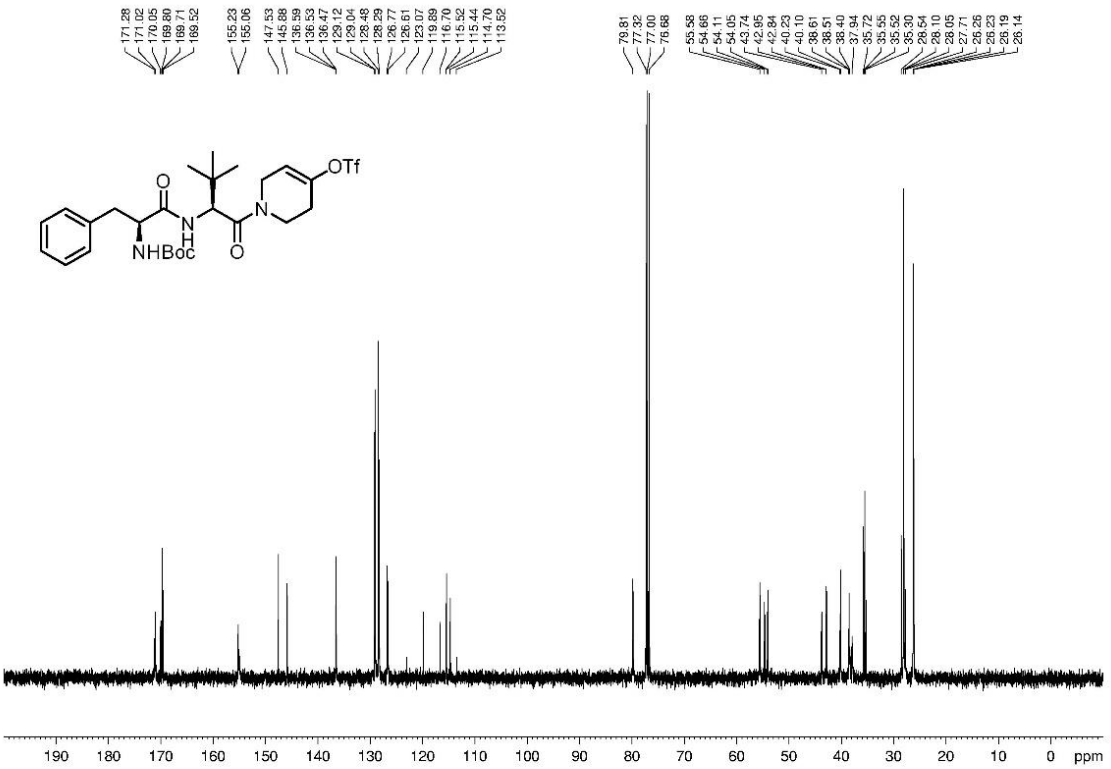
2w-1; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



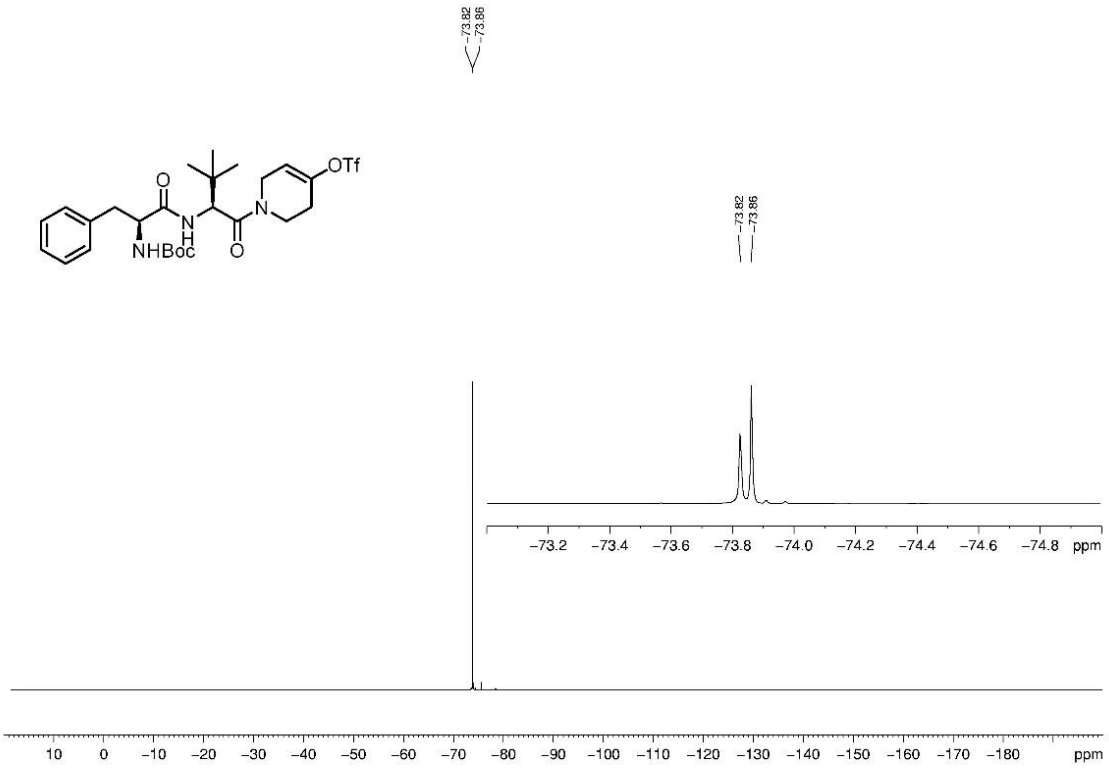


2w; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

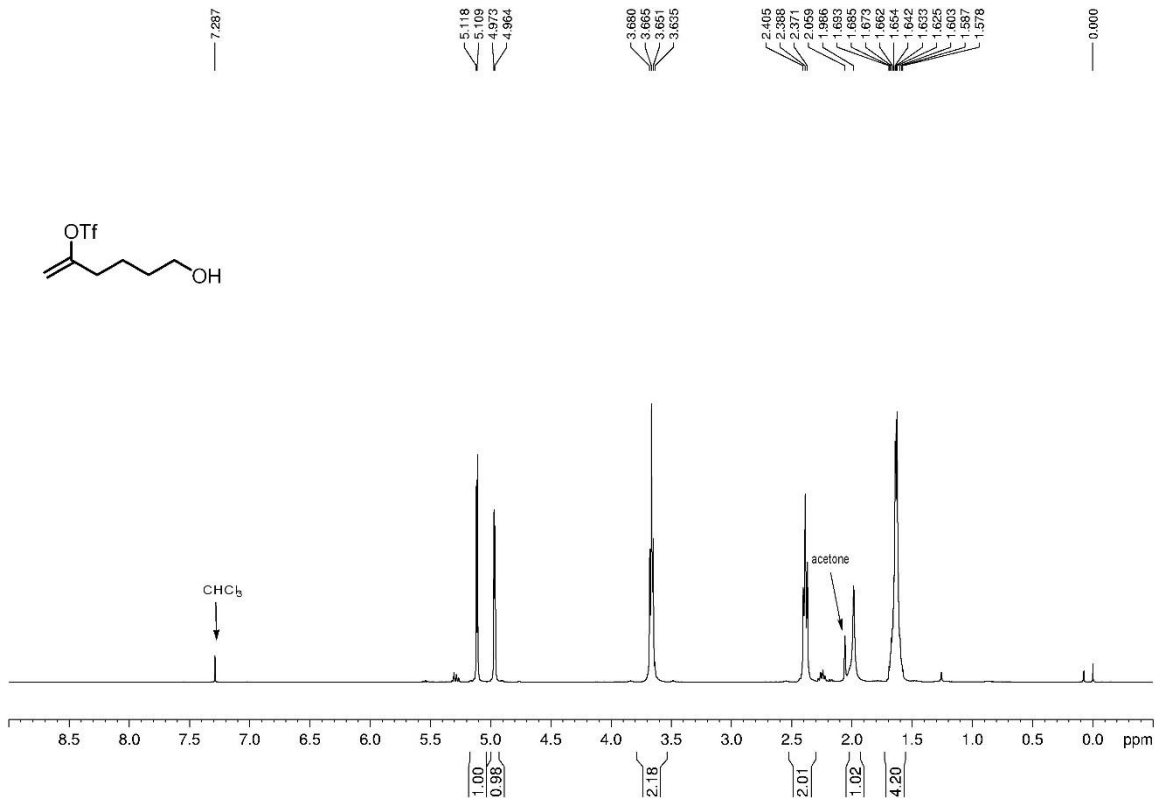


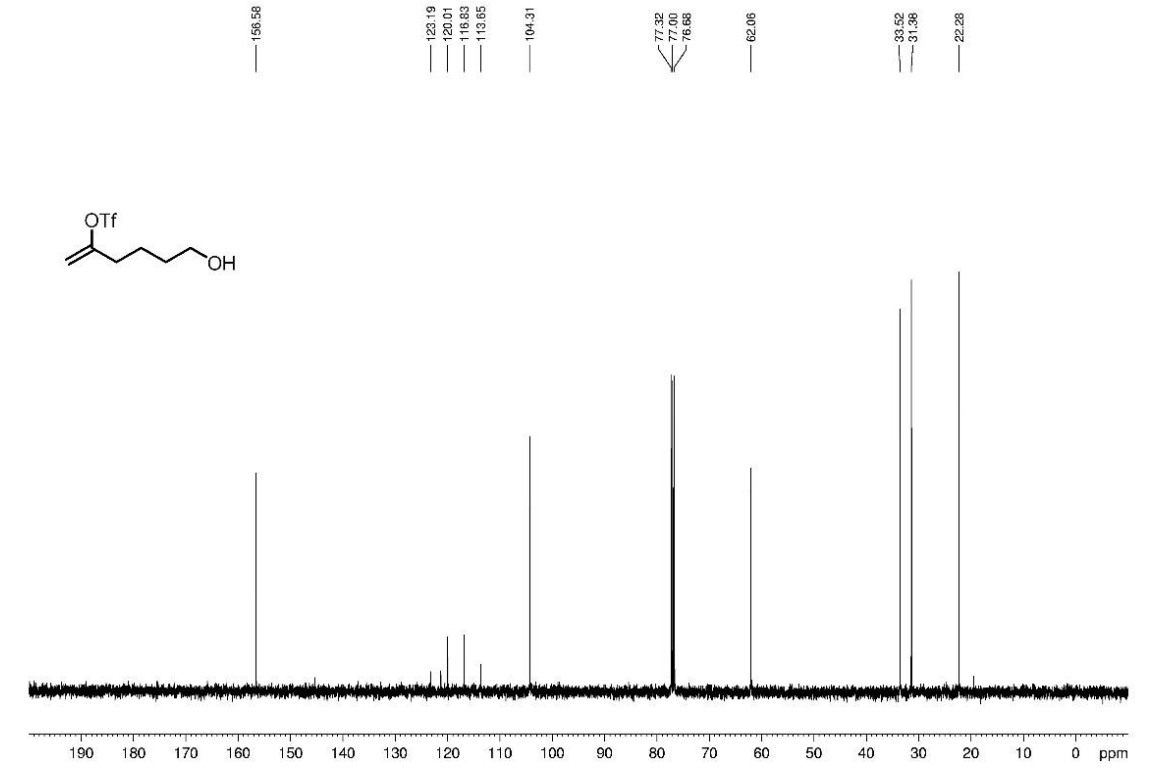


2w; ^{19}F NMR (376MHz, $CDCl_3$)

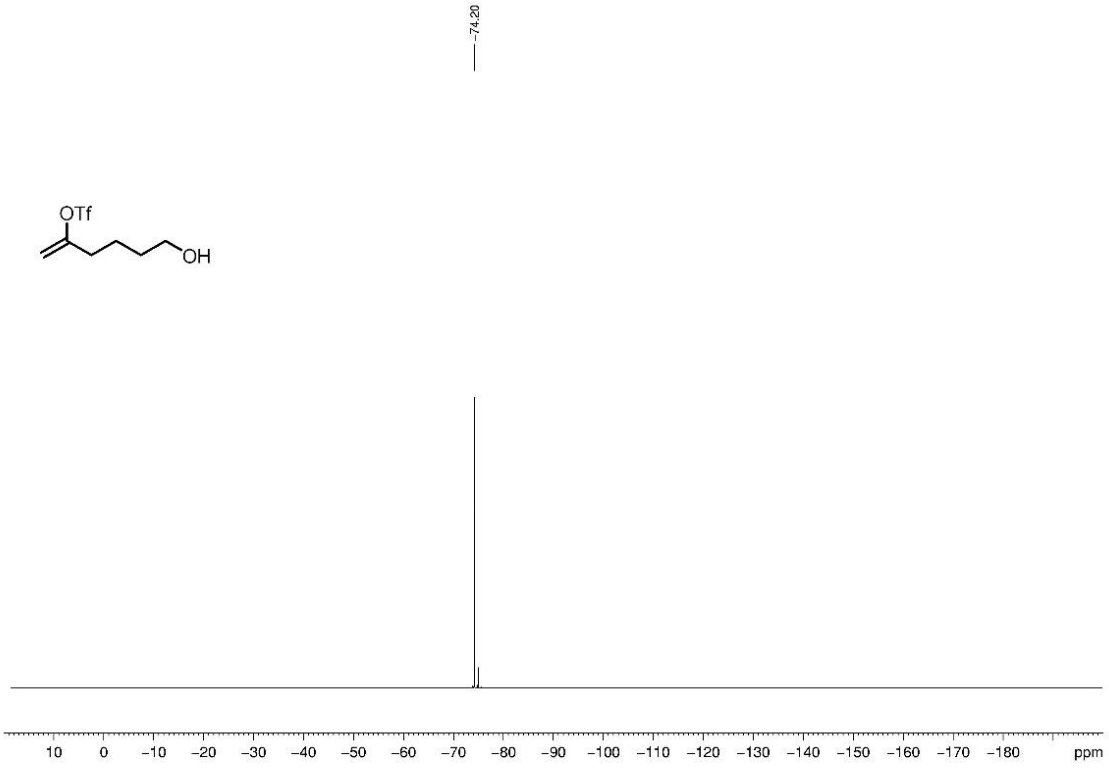


2x-1; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

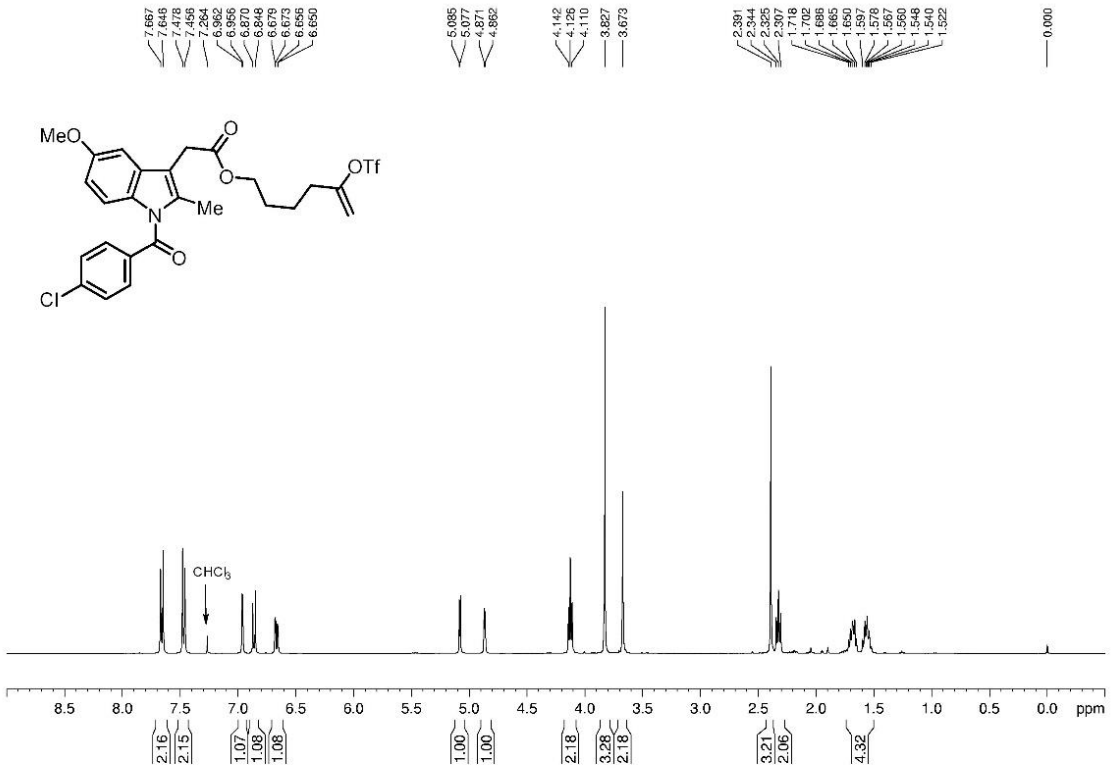


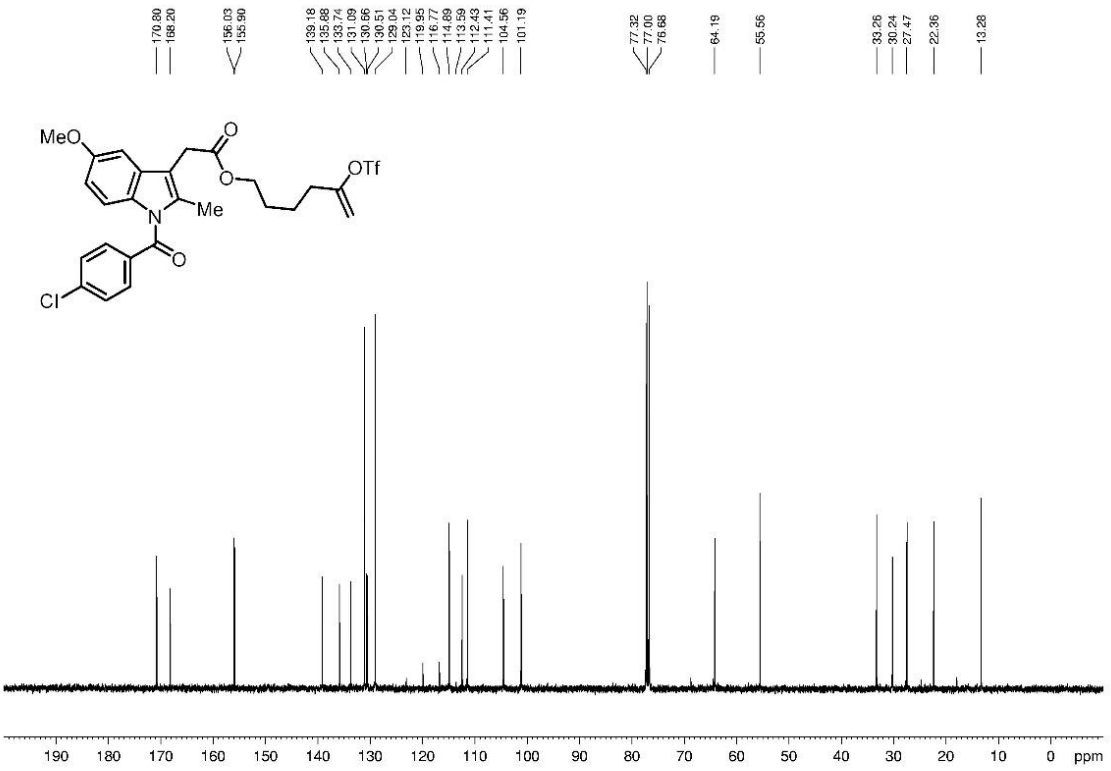


2x-1; ^{19}F NMR (376MHz, $CDCl_3$)

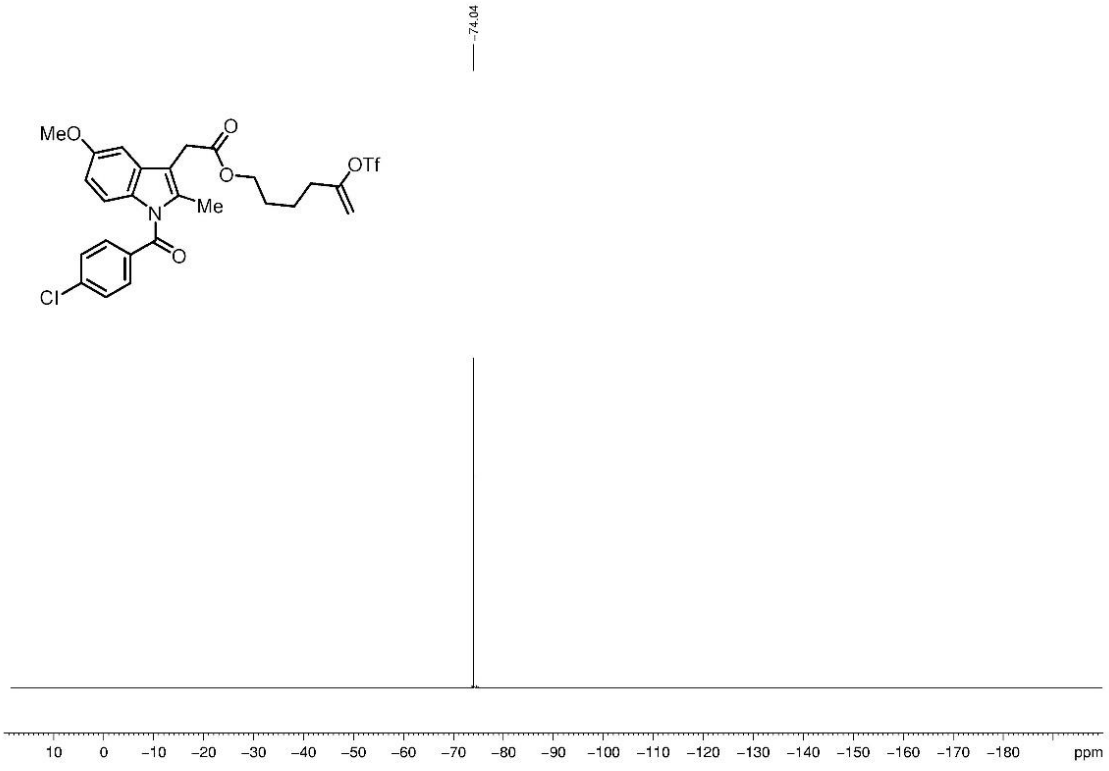


2x; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

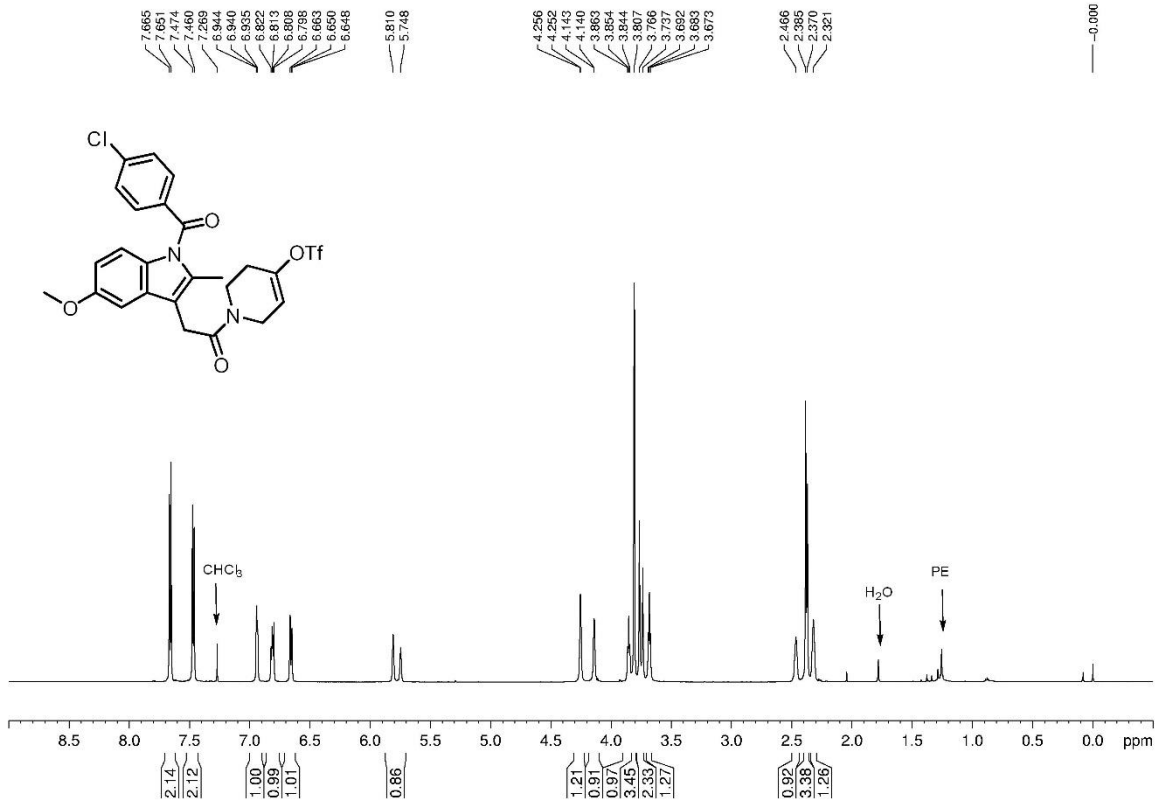


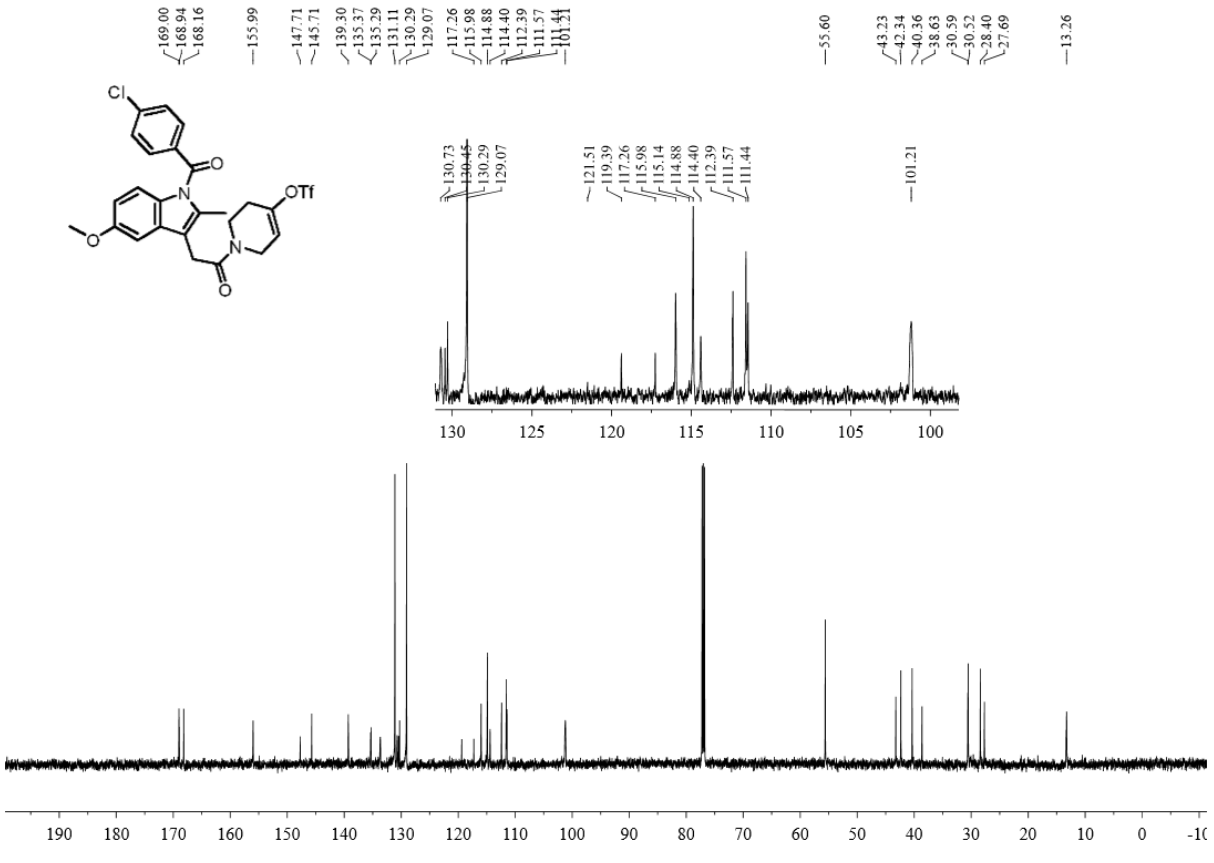


2x; ^{19}F NMR (376MHz, $CDCl_3$)

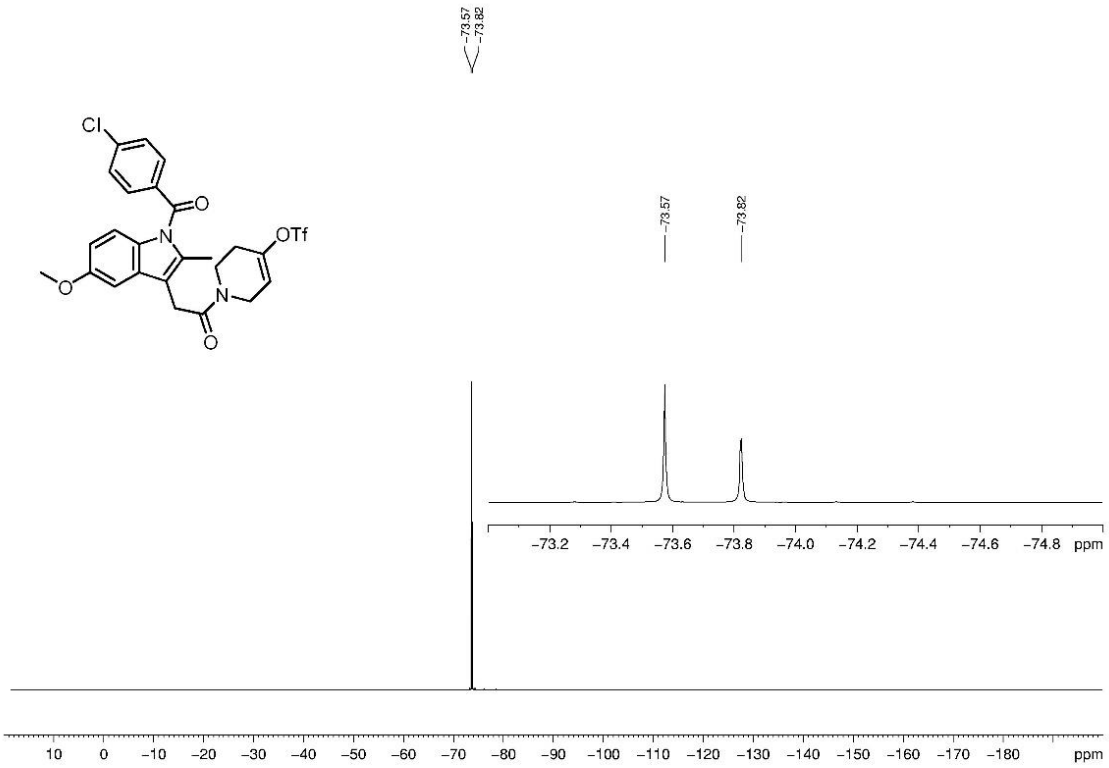


2y; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

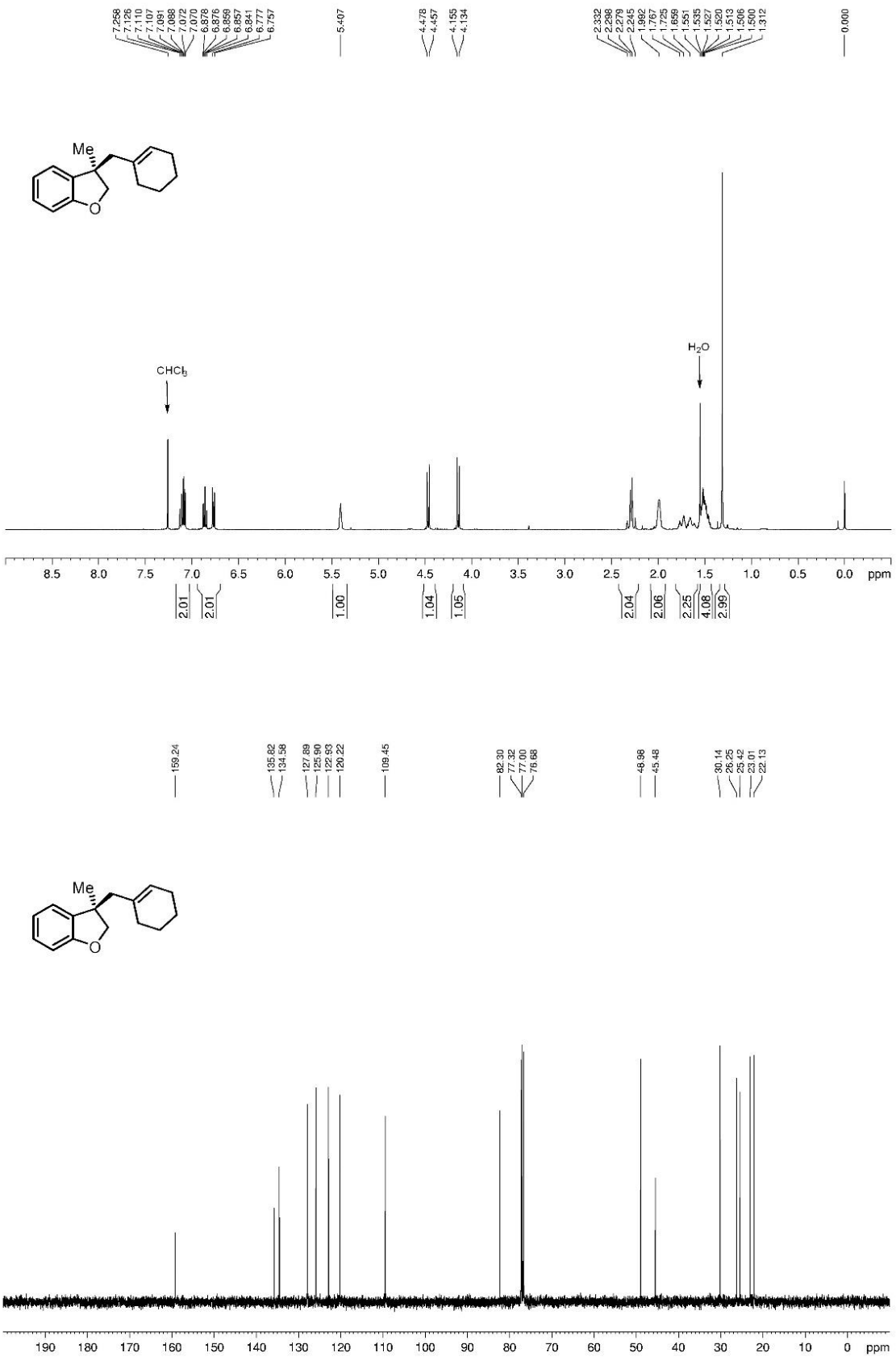




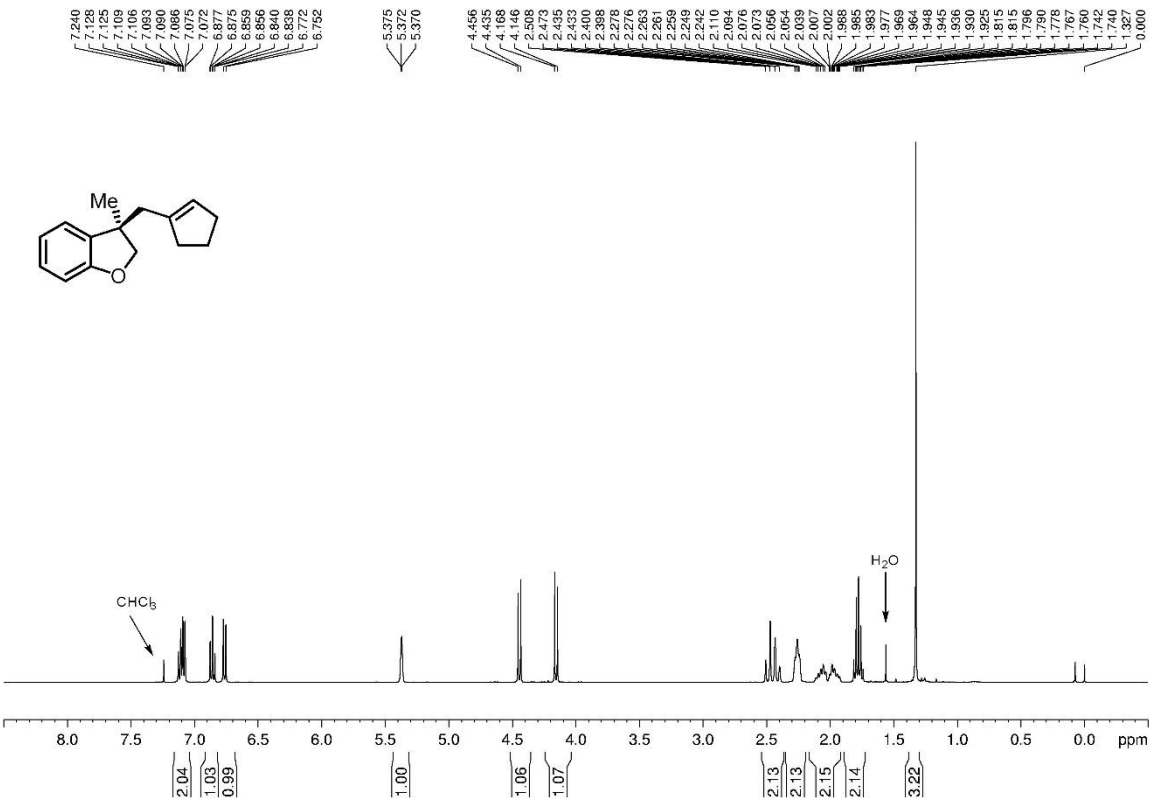
2y; ^{19}F NMR (376MHz, $CDCl_3$)

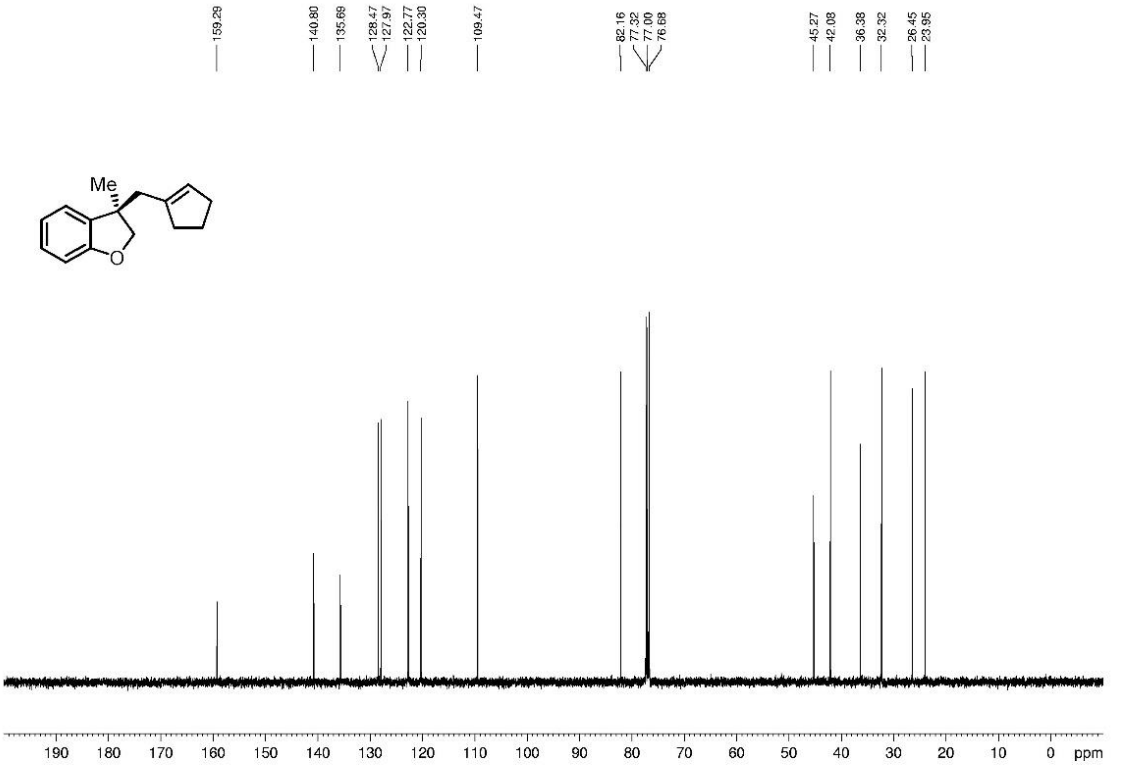


3a; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

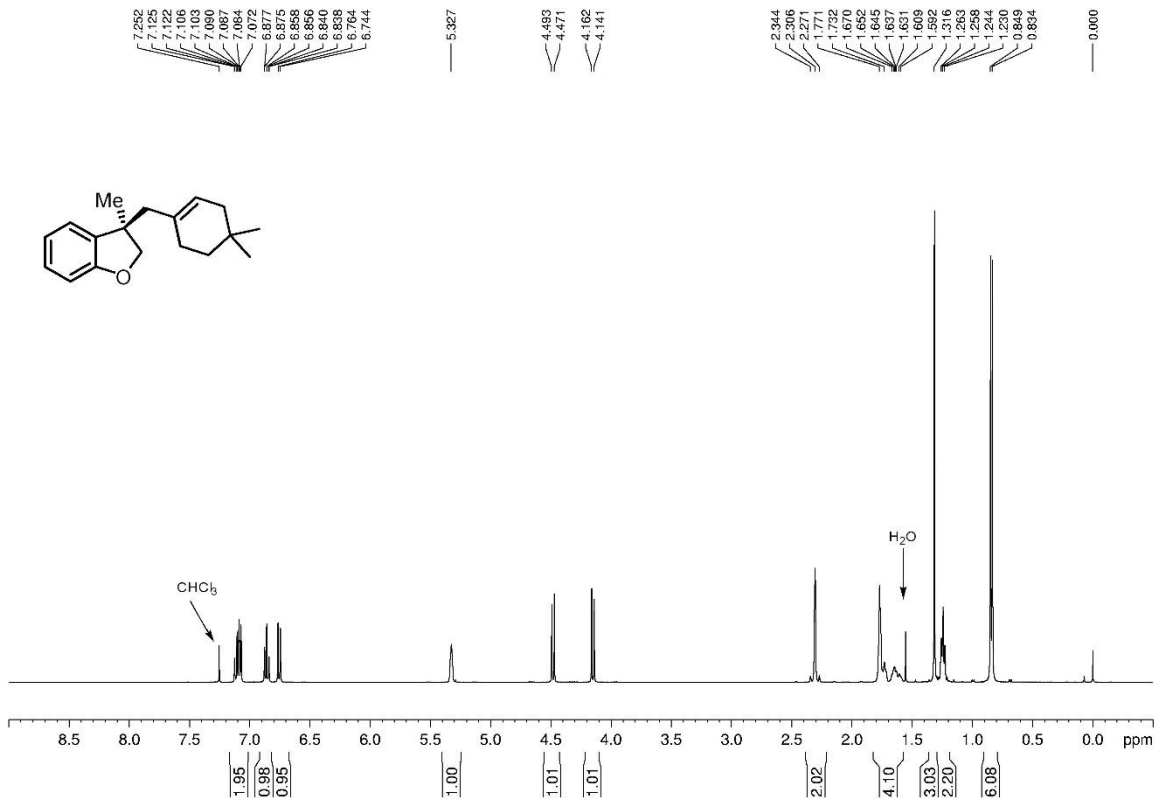


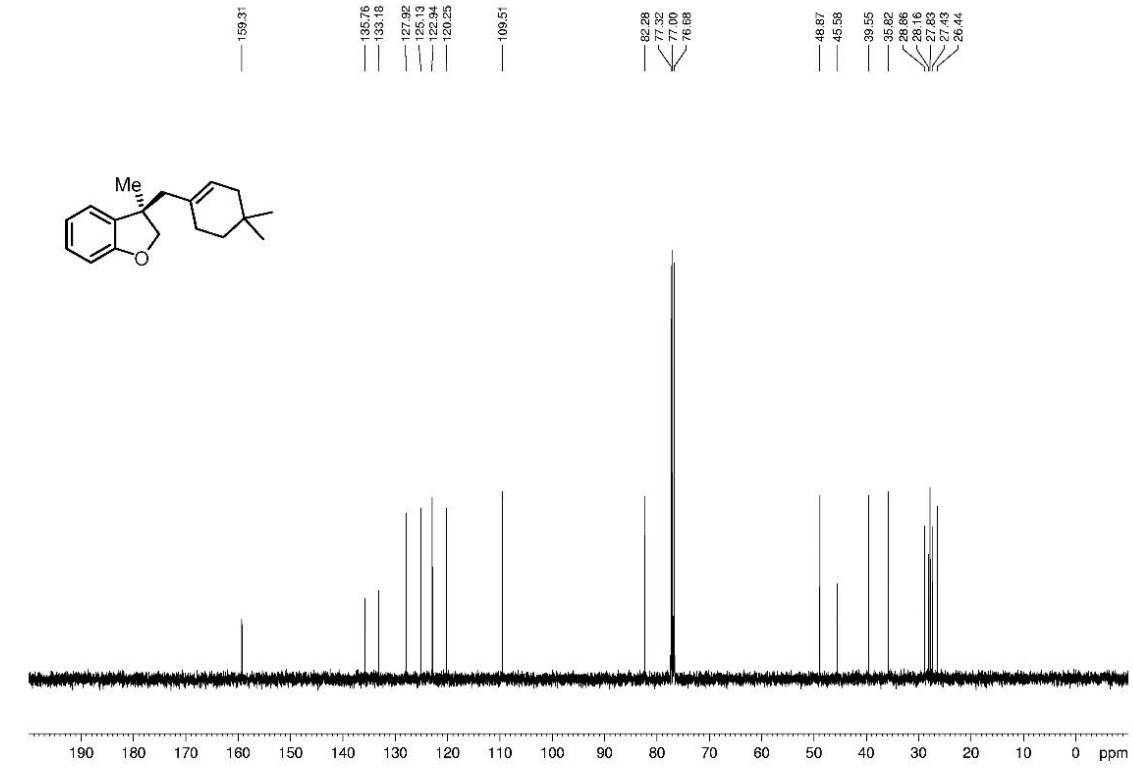
3b; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



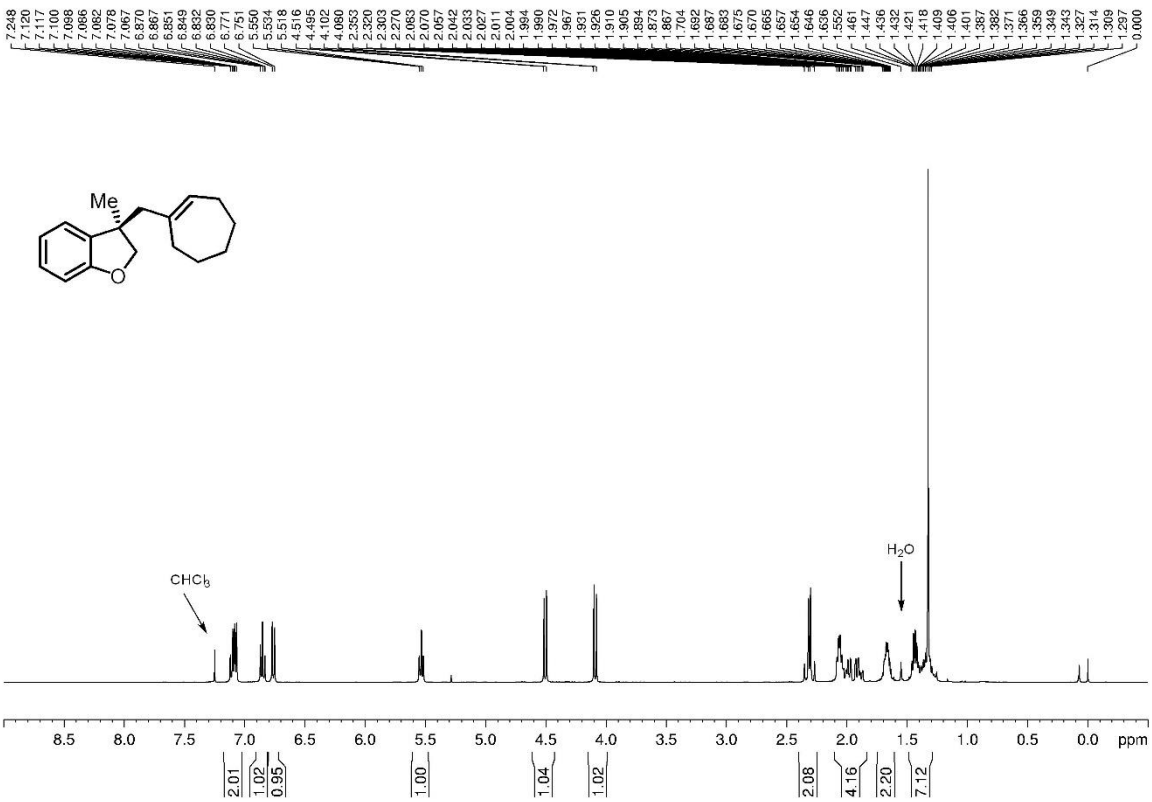


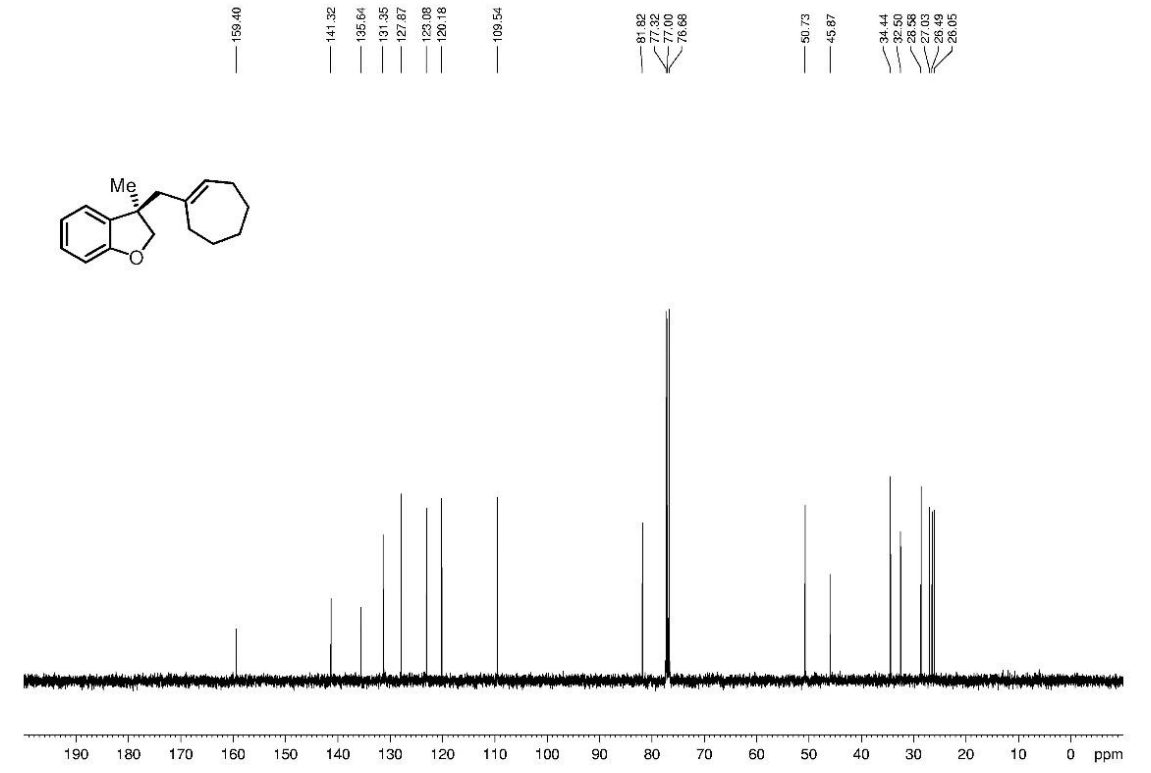
3c; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



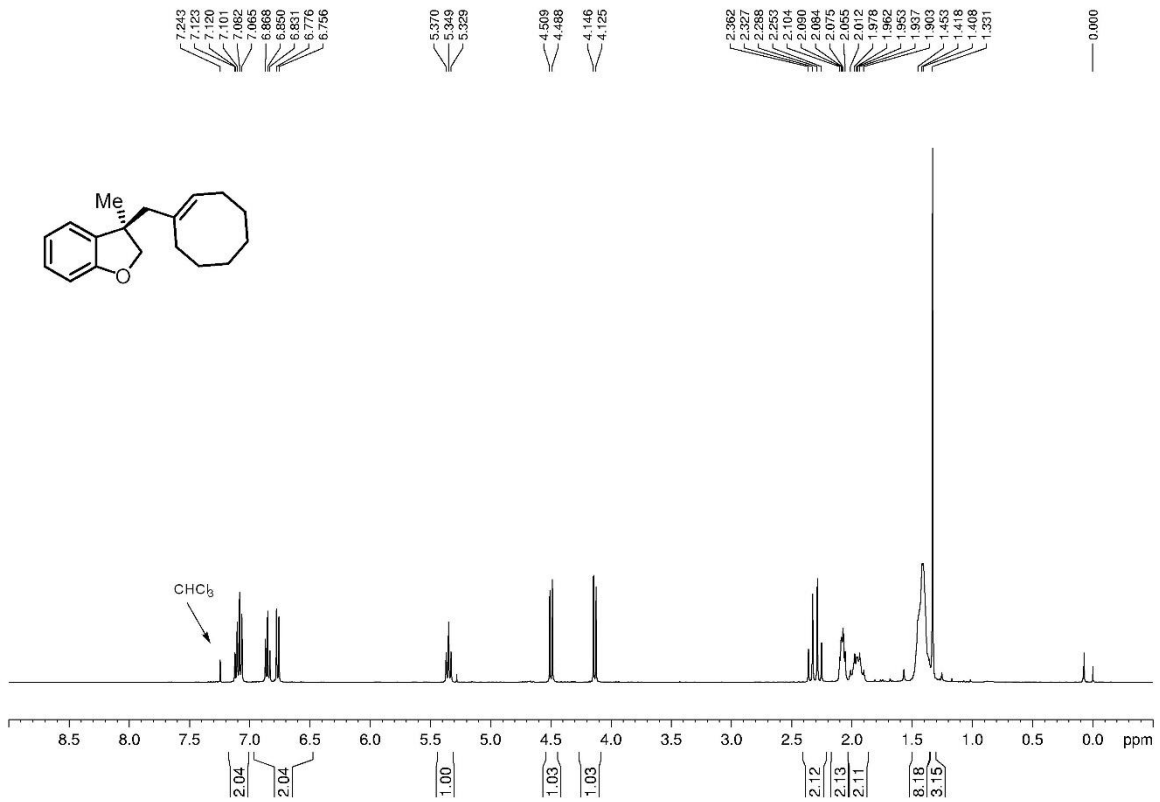


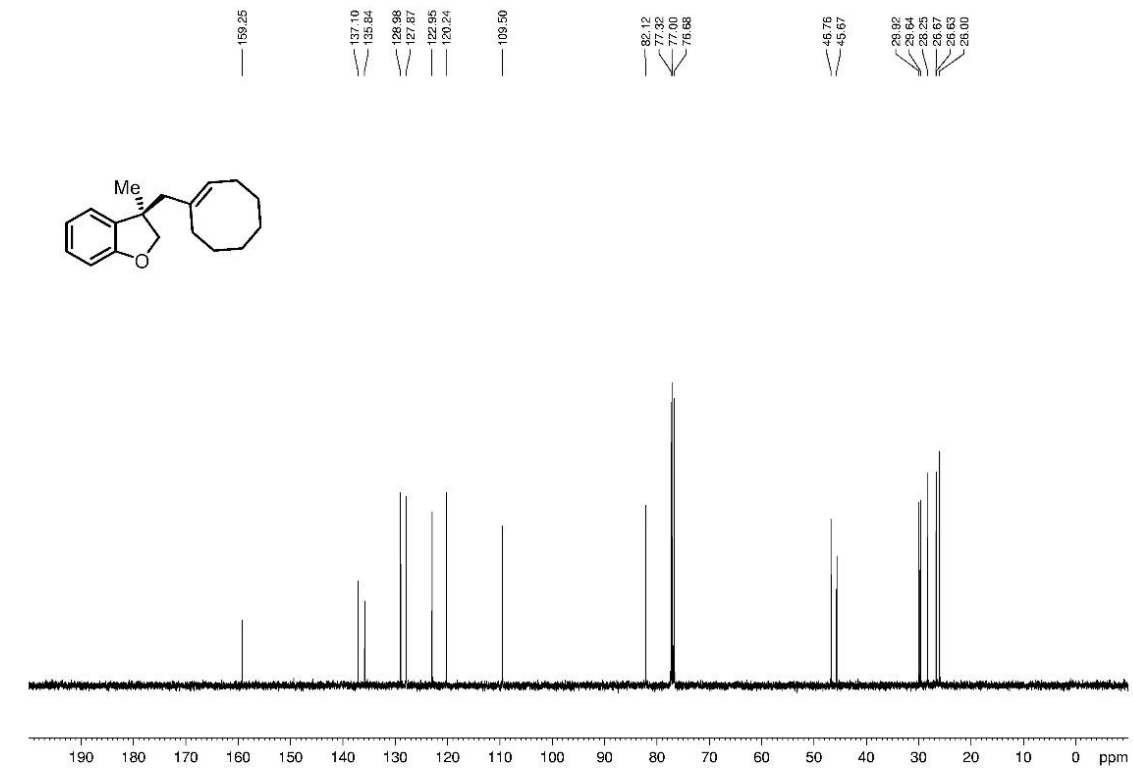
3d; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



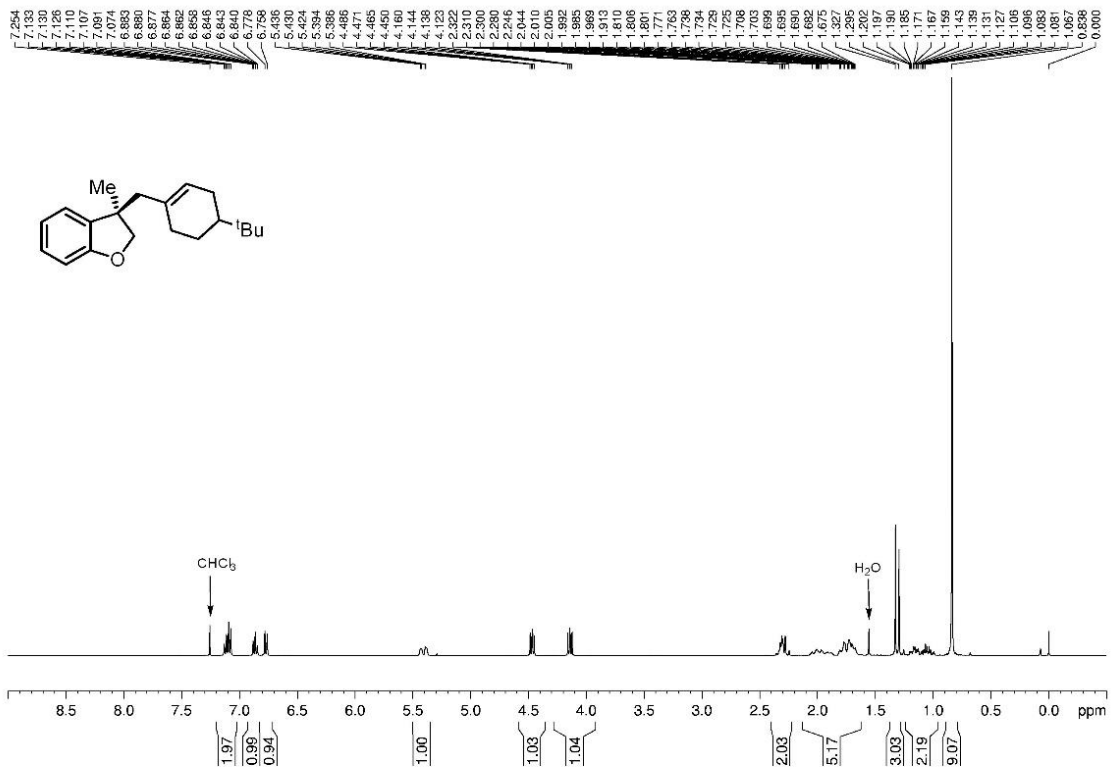


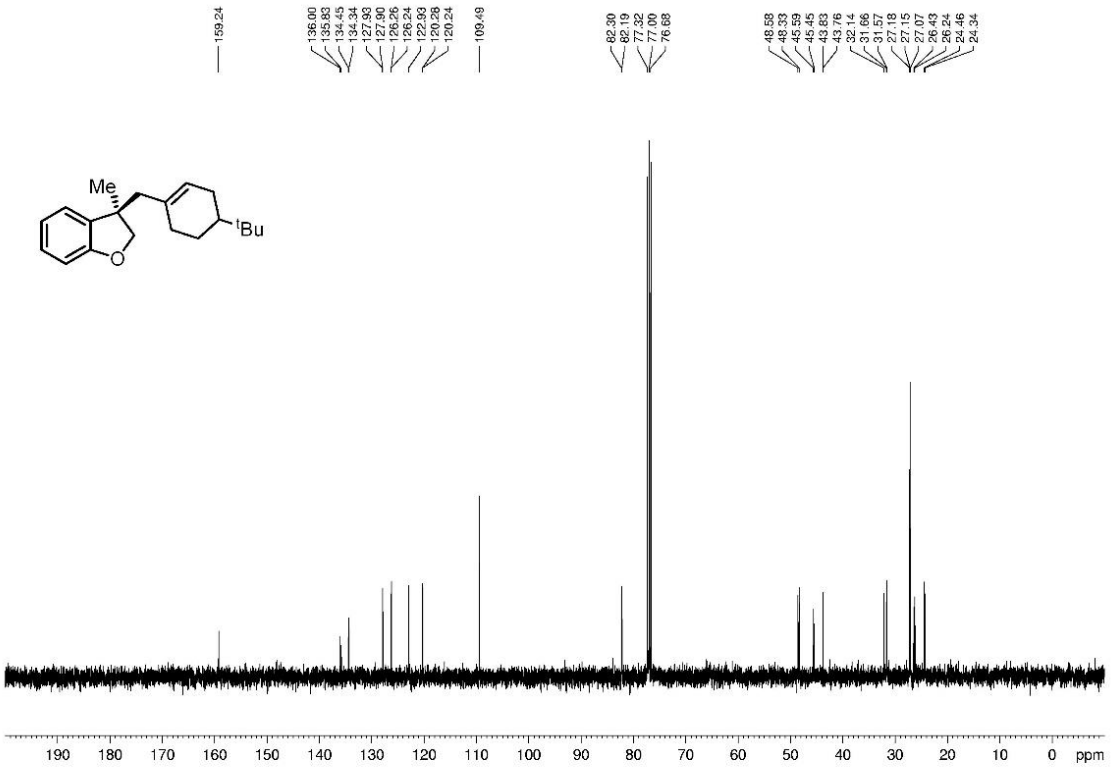
3e; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



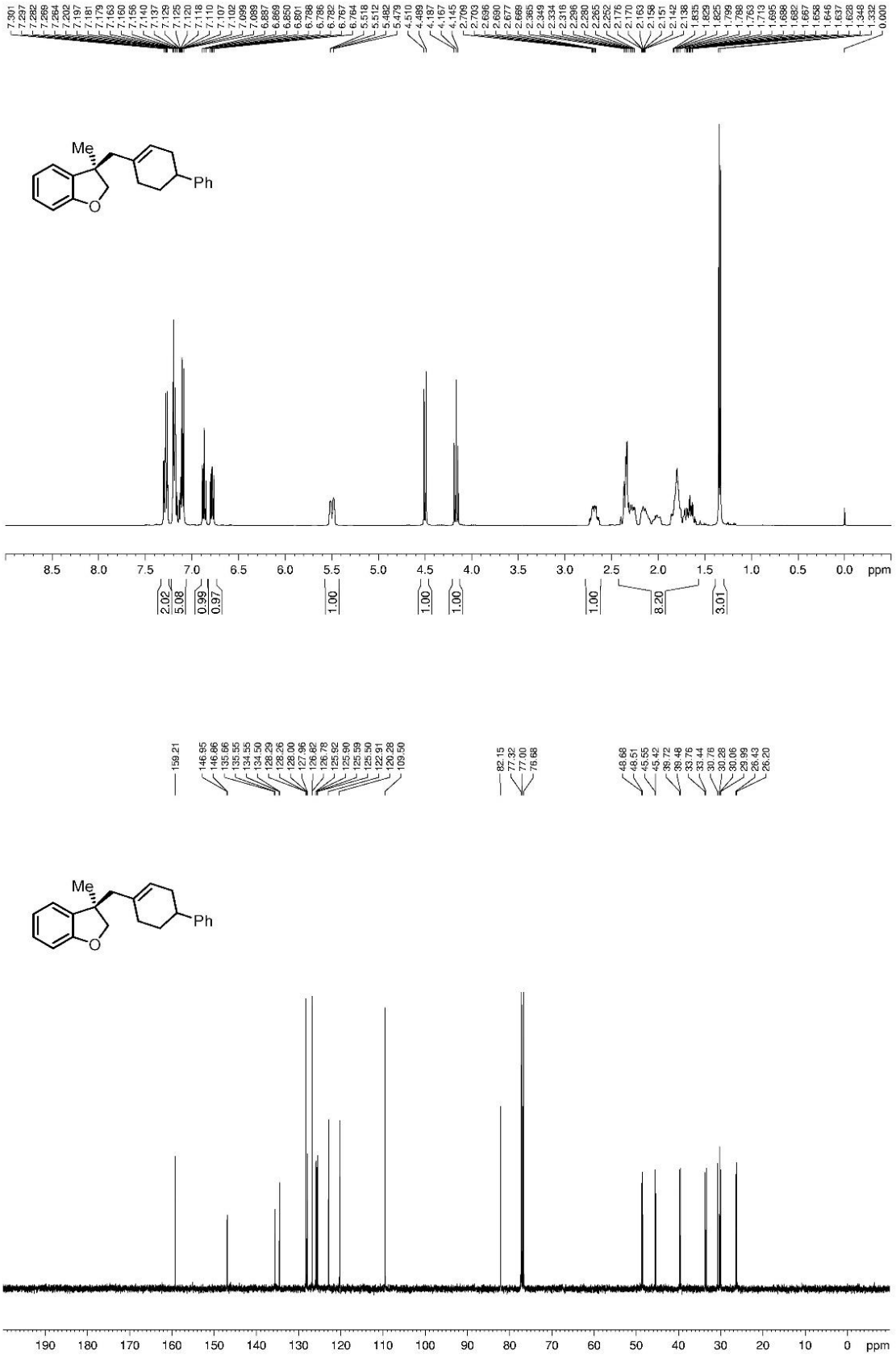


3f; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

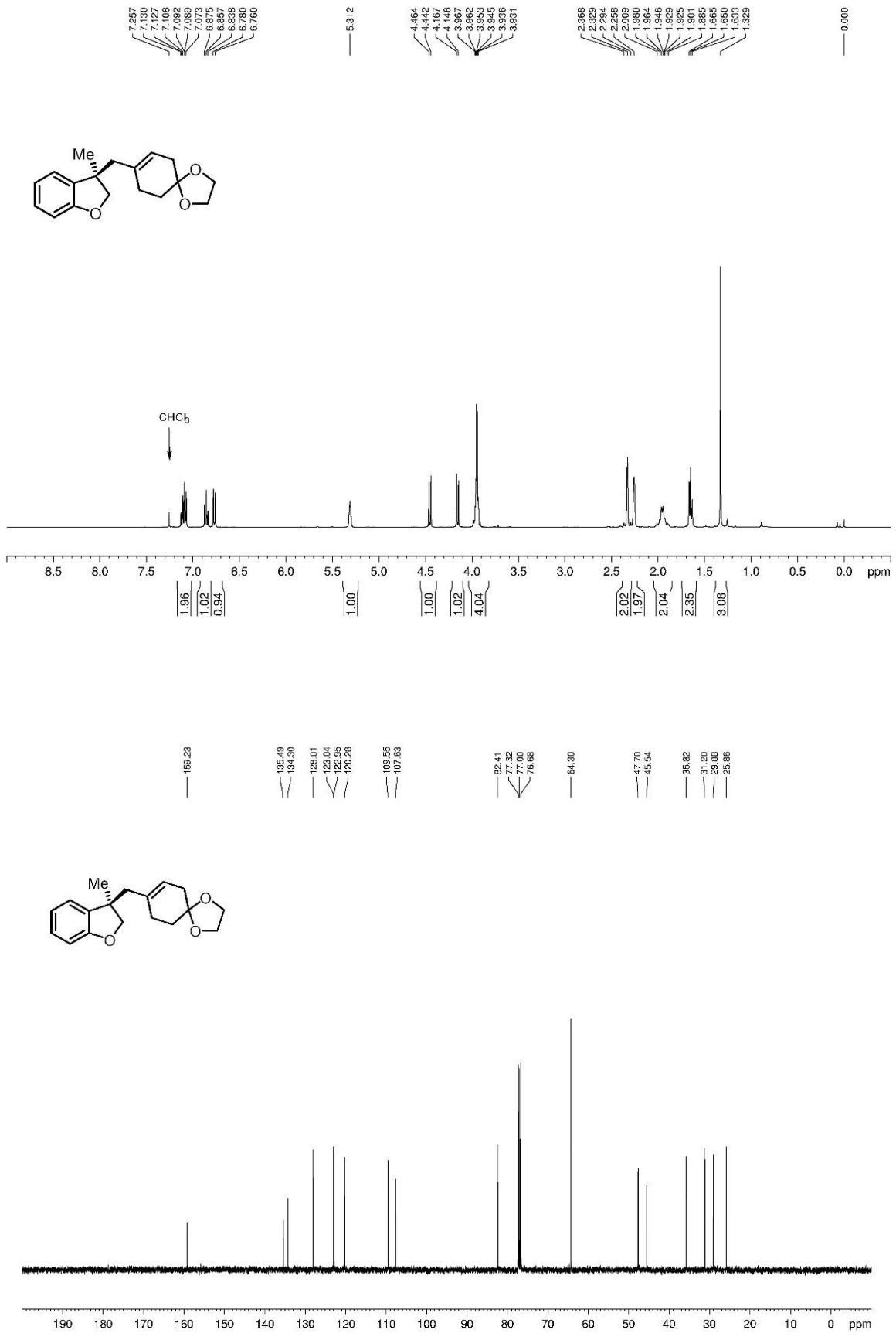




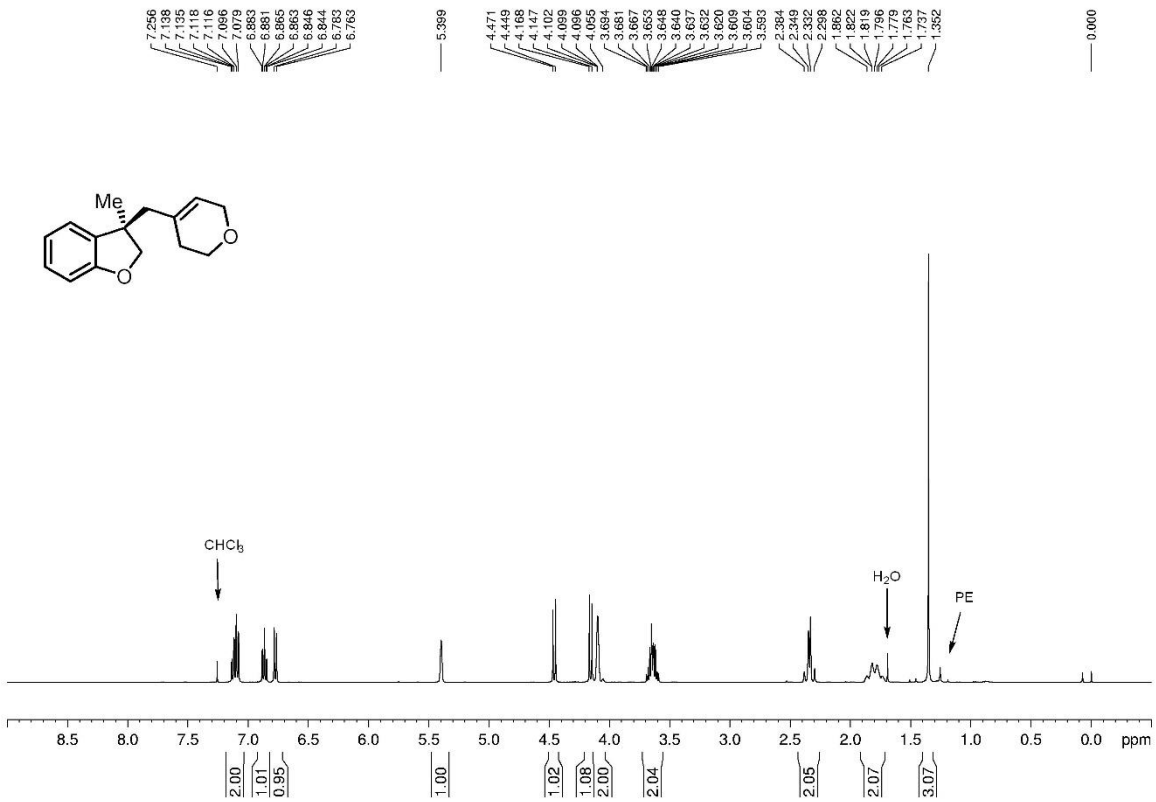
3g; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

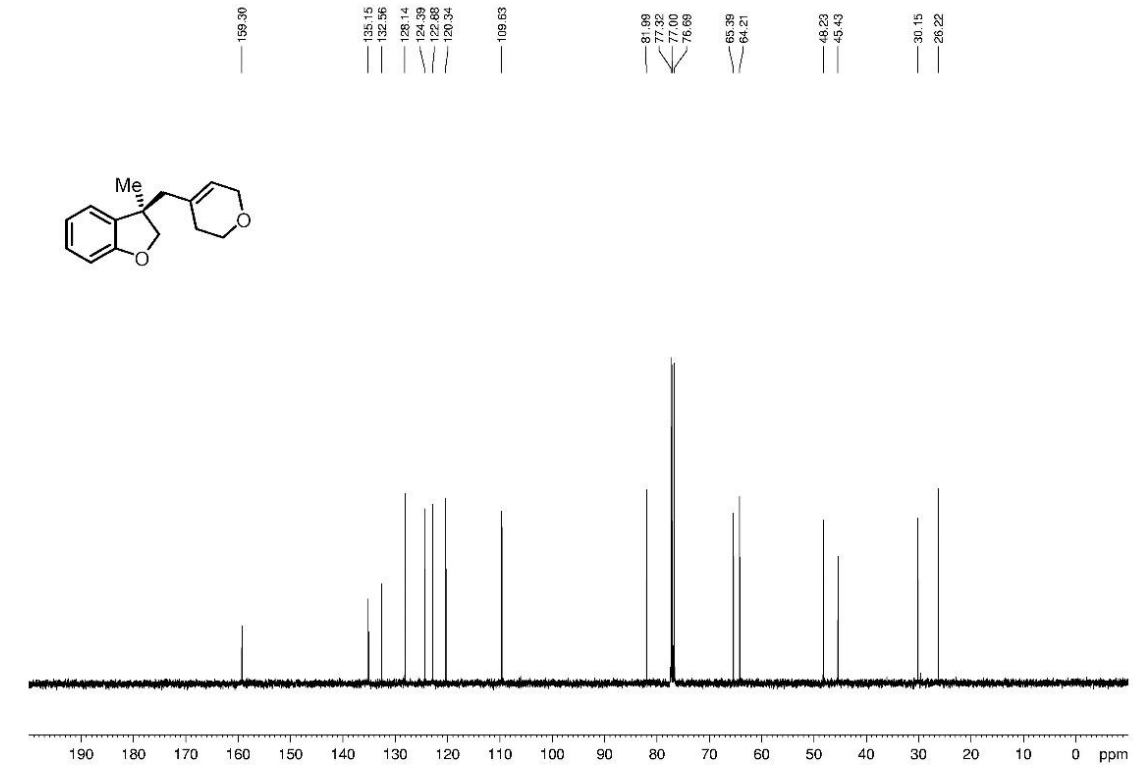


3h; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

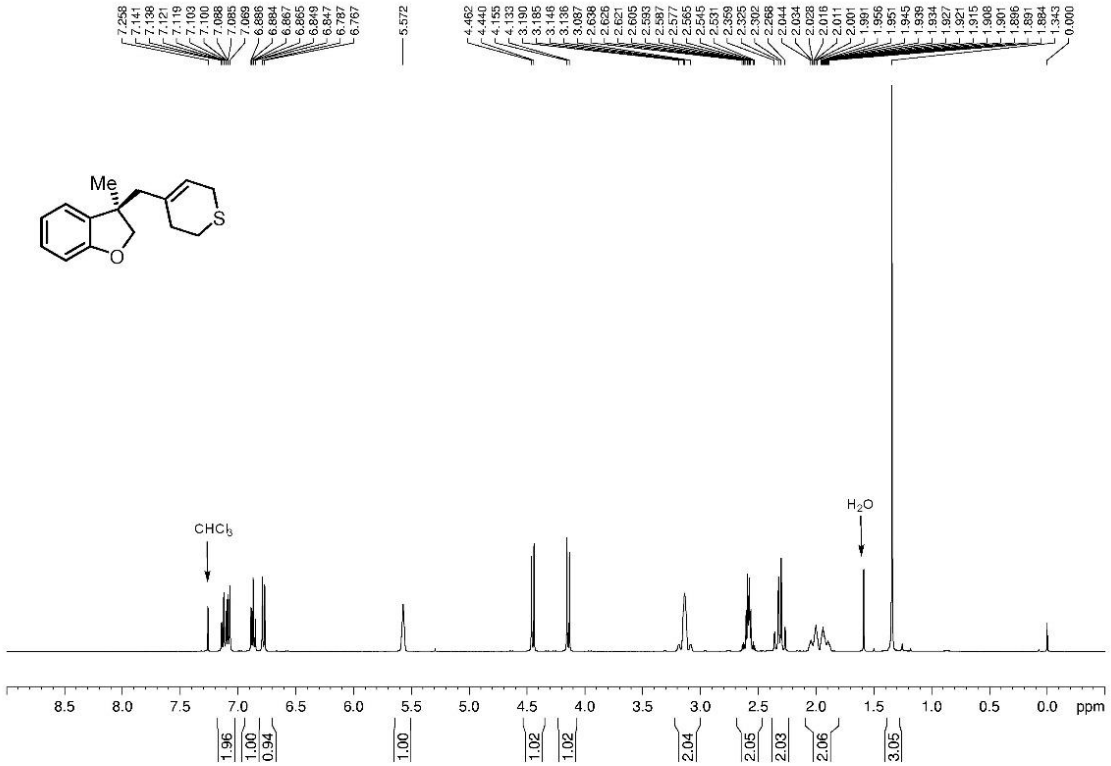


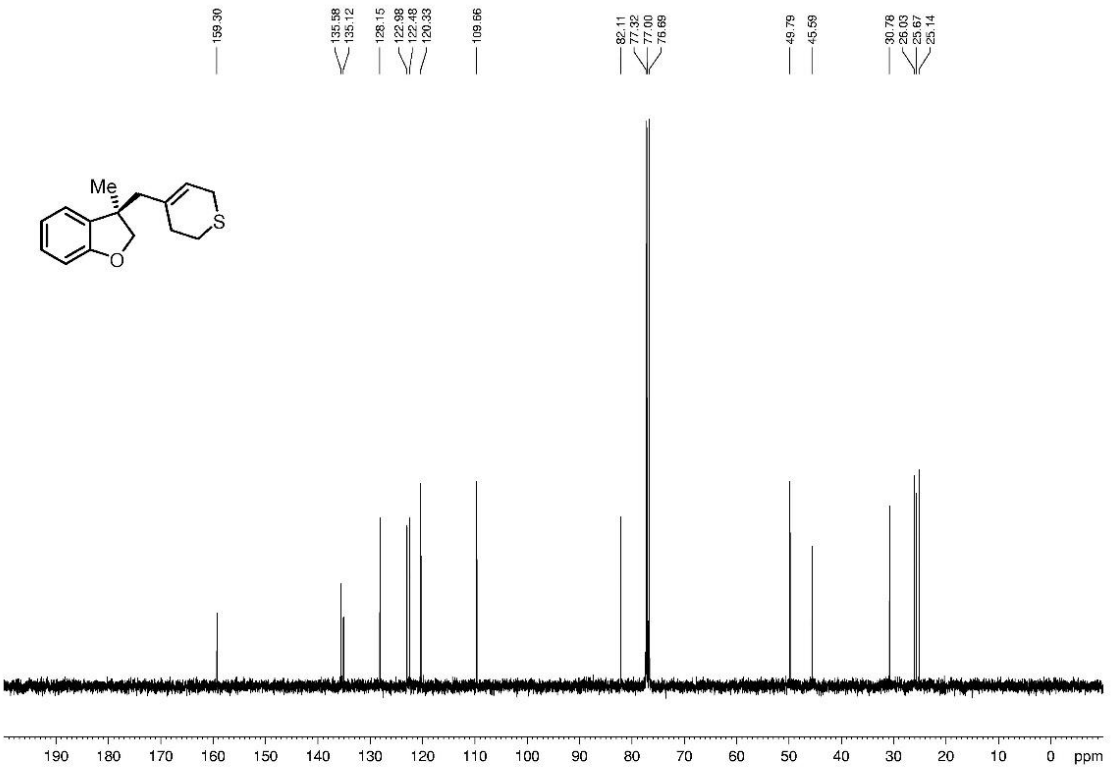
3i; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



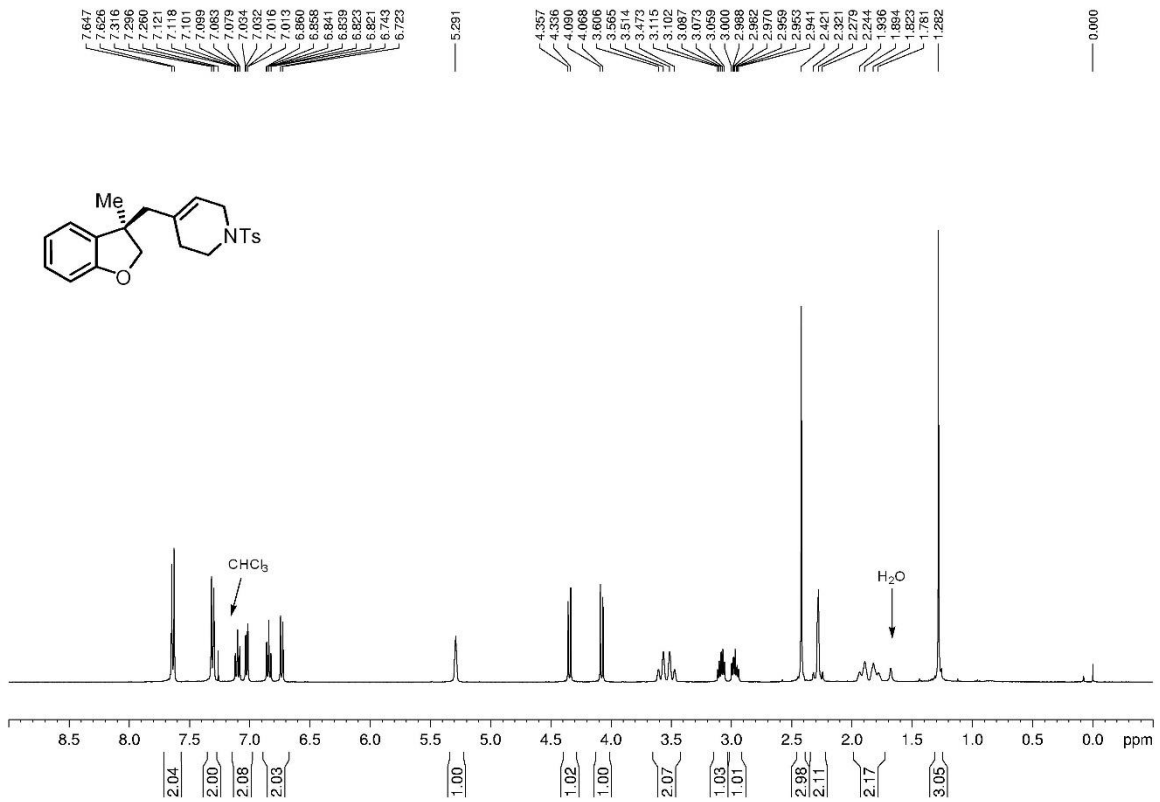


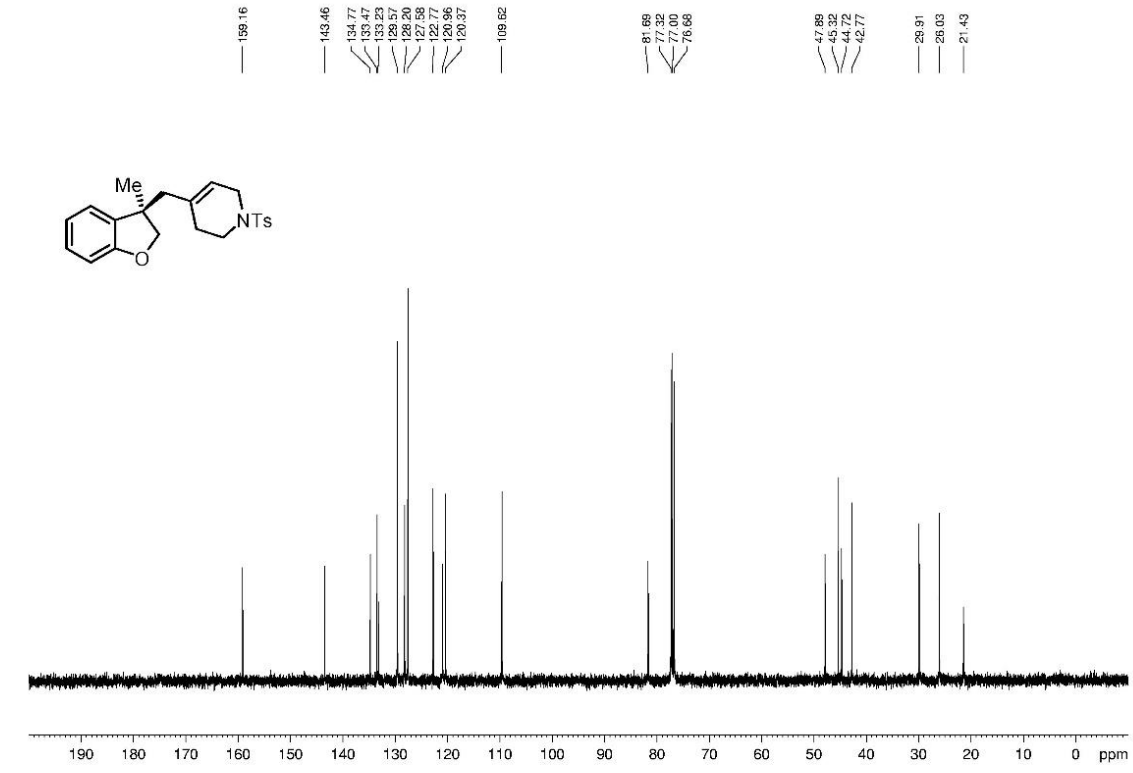
3j; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



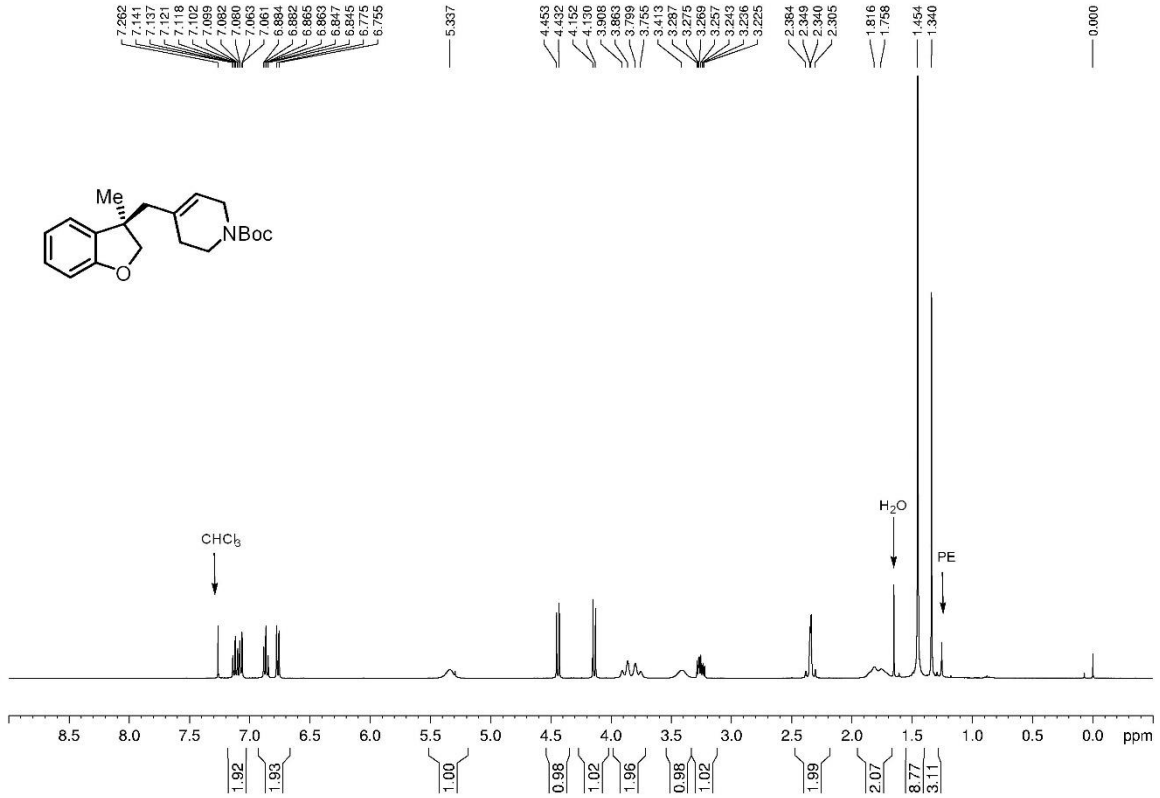


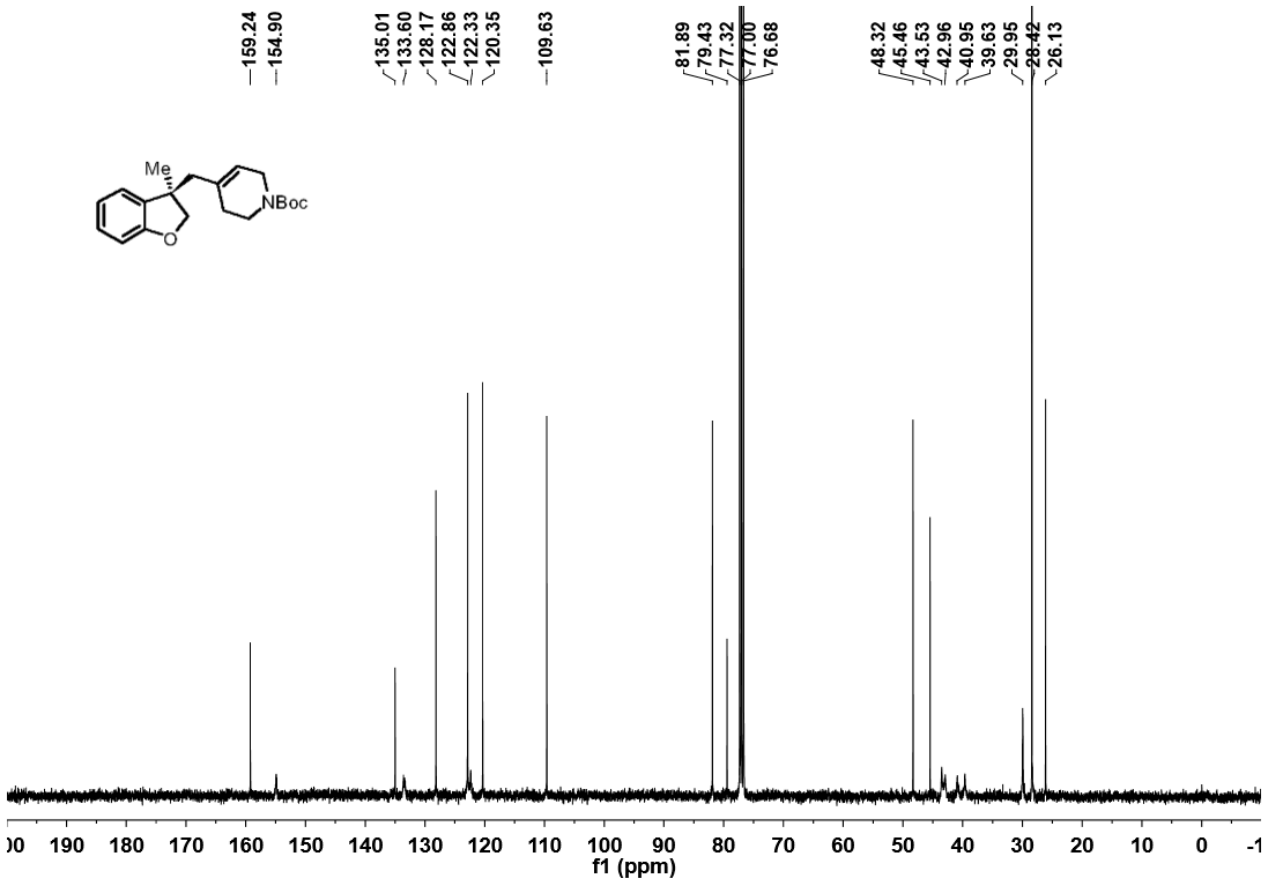
3k; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



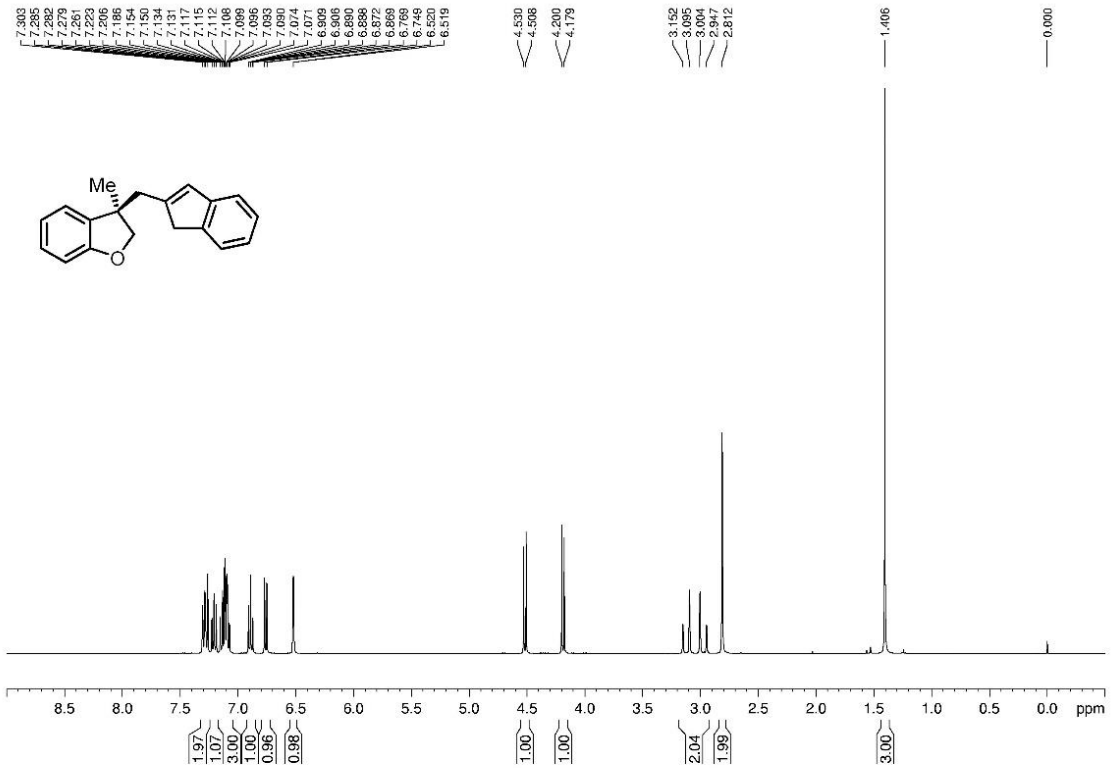


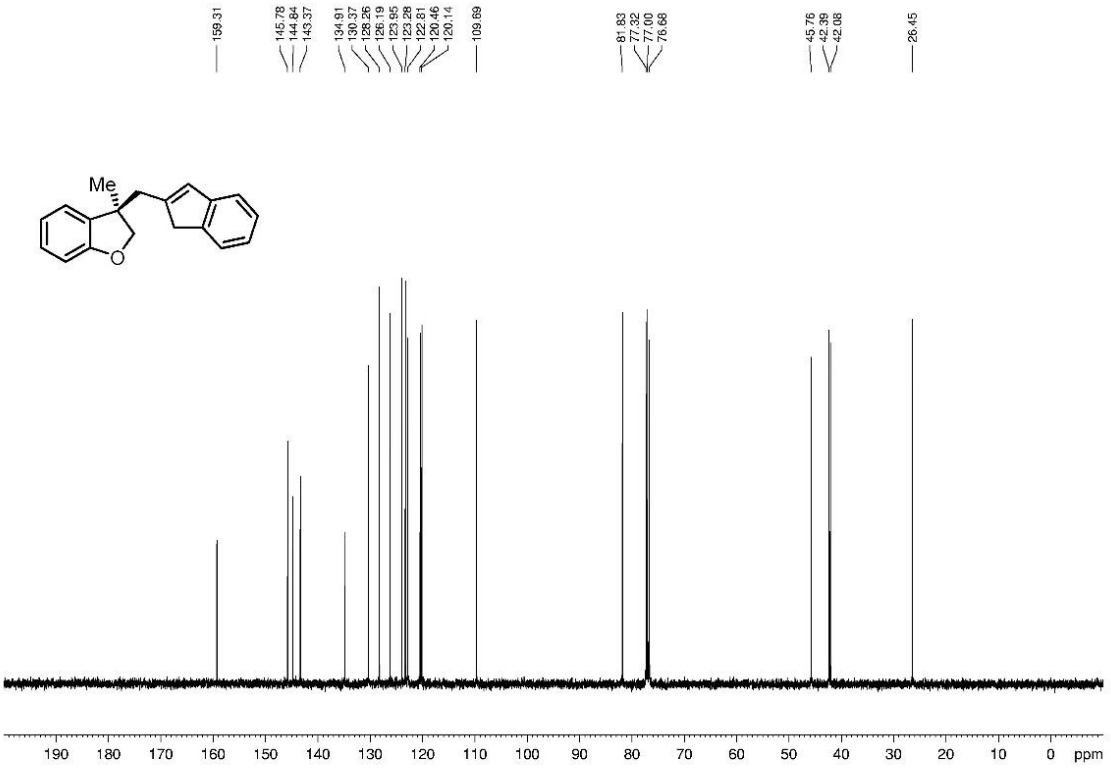
3l; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



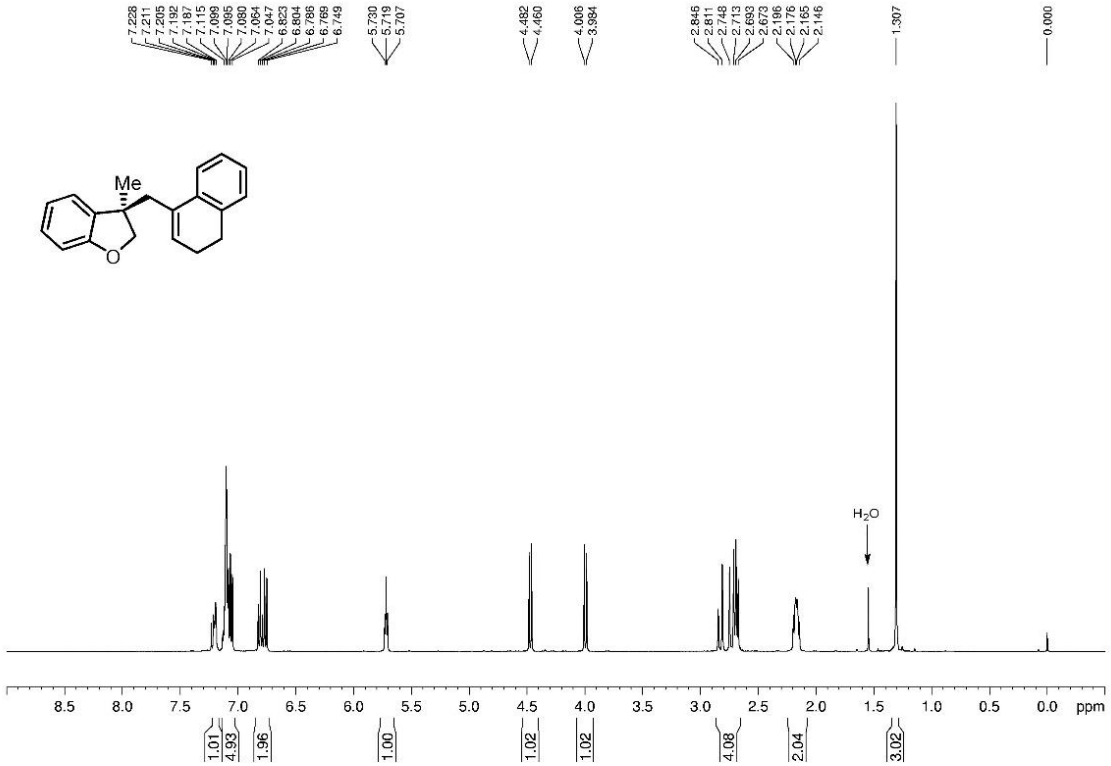


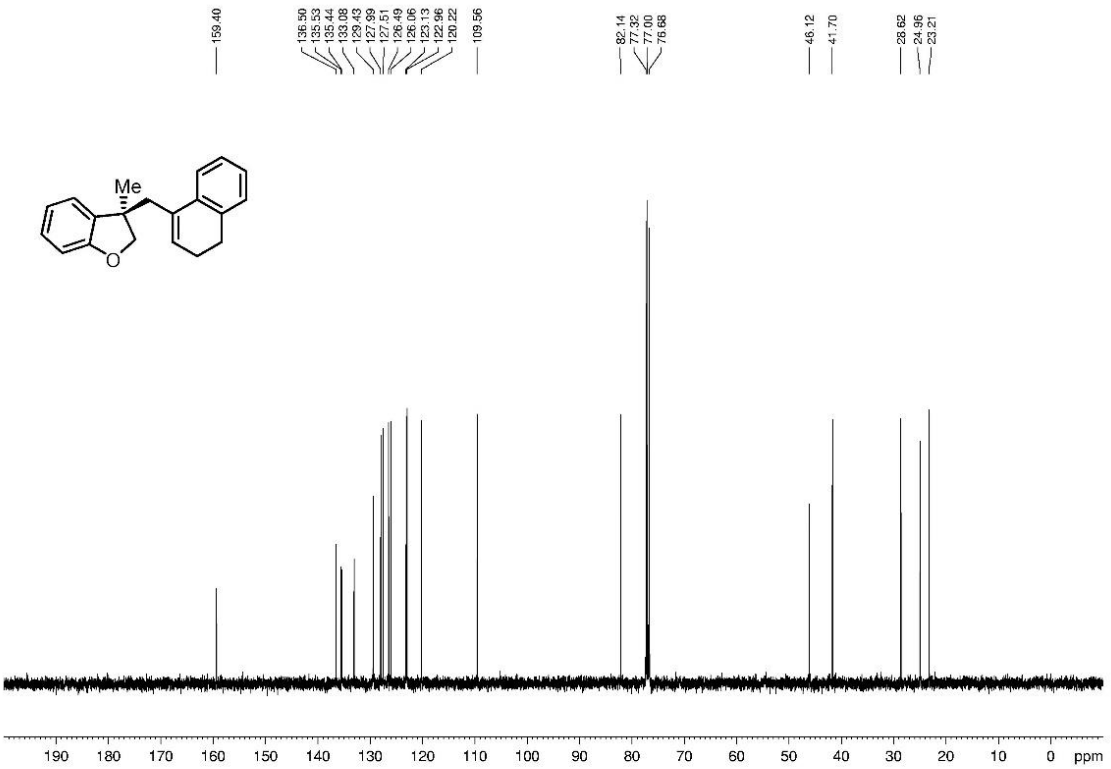
3m; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



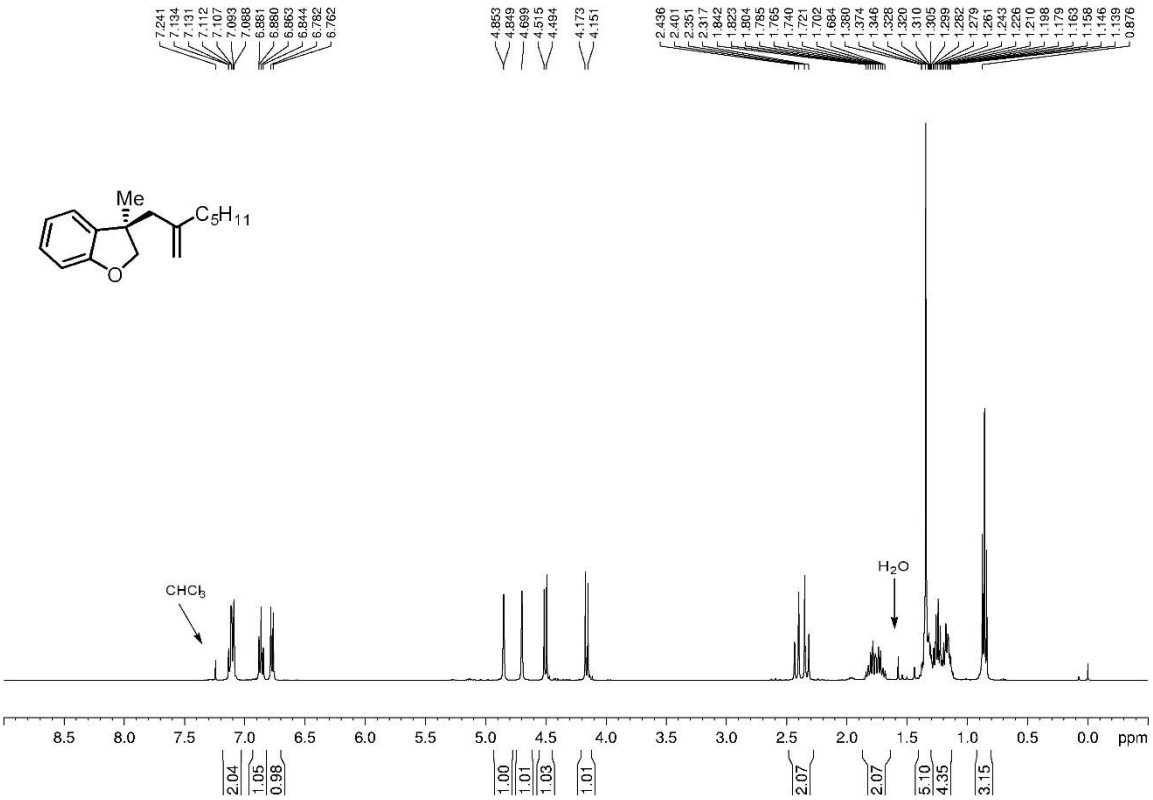


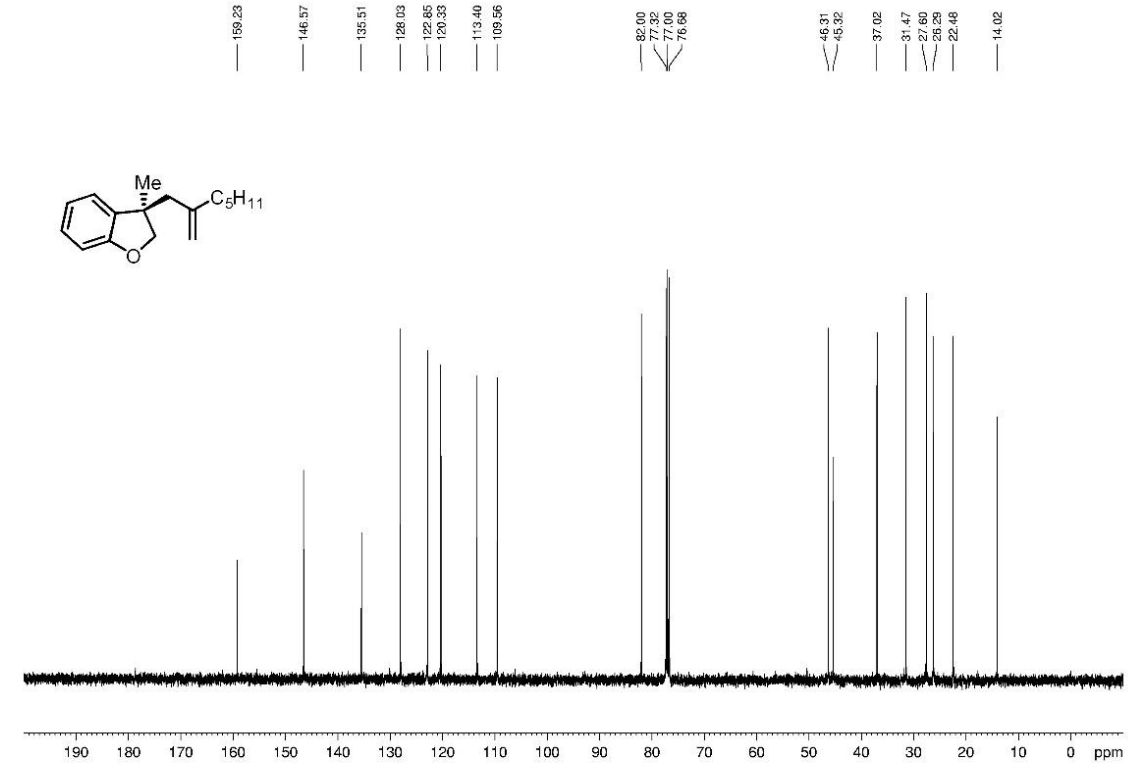
3n; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



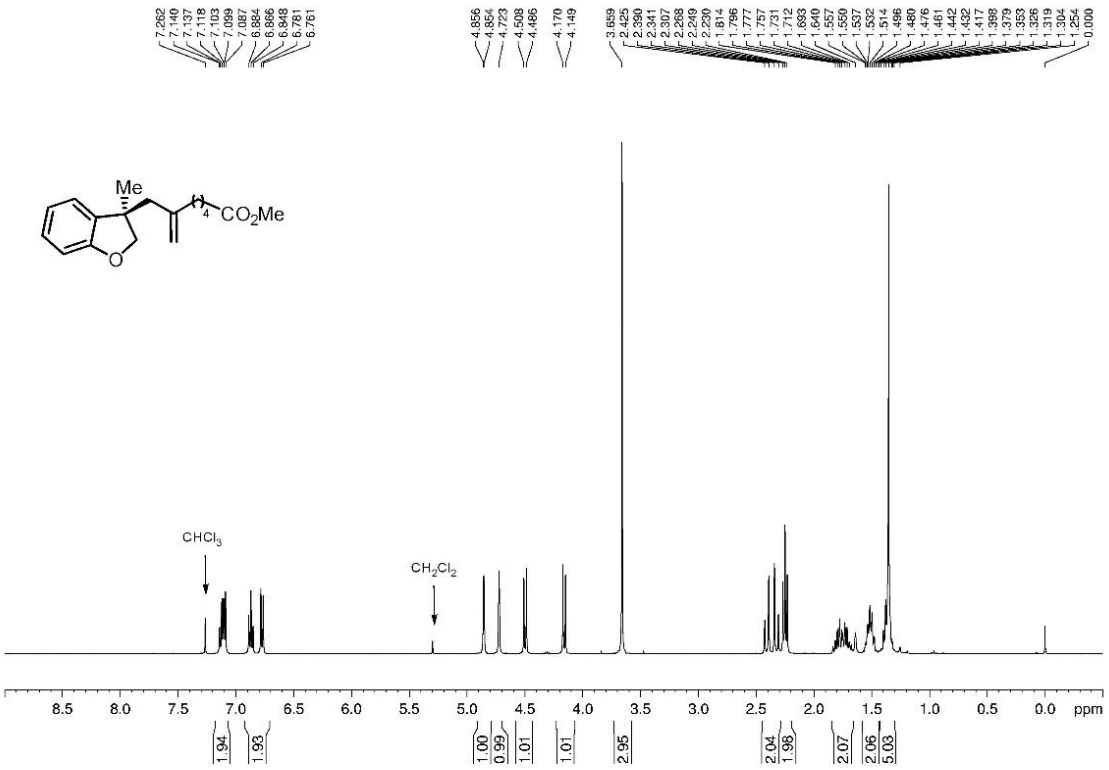


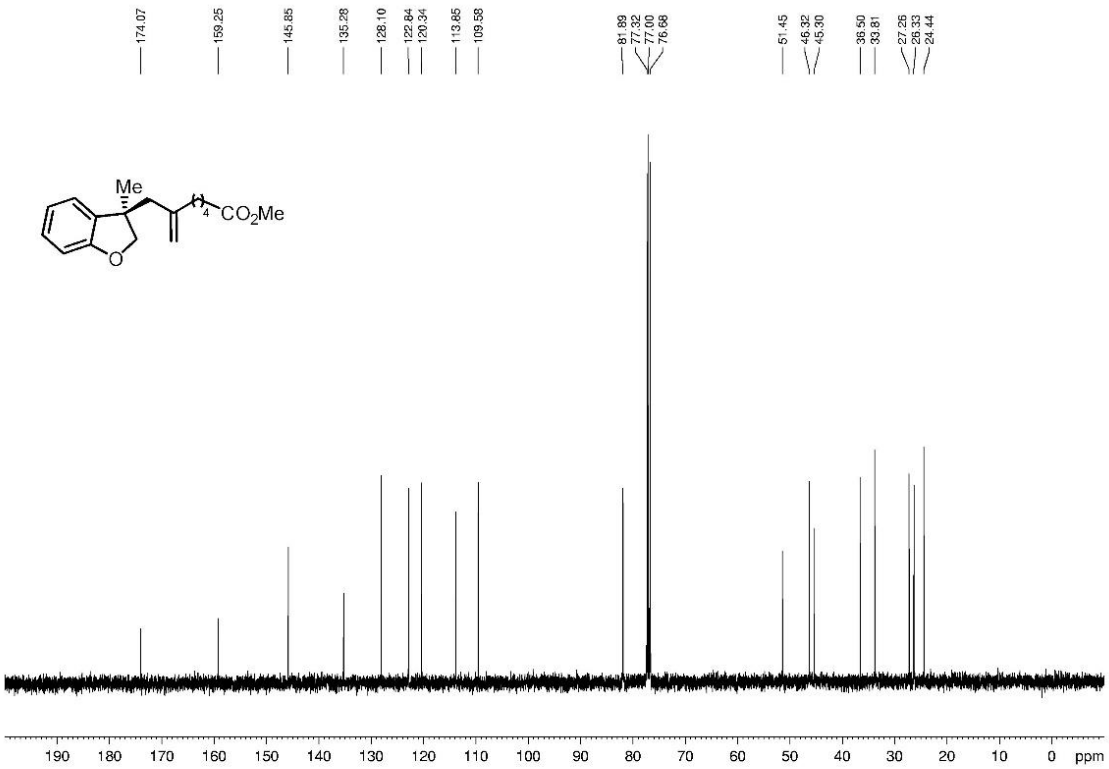
3o; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



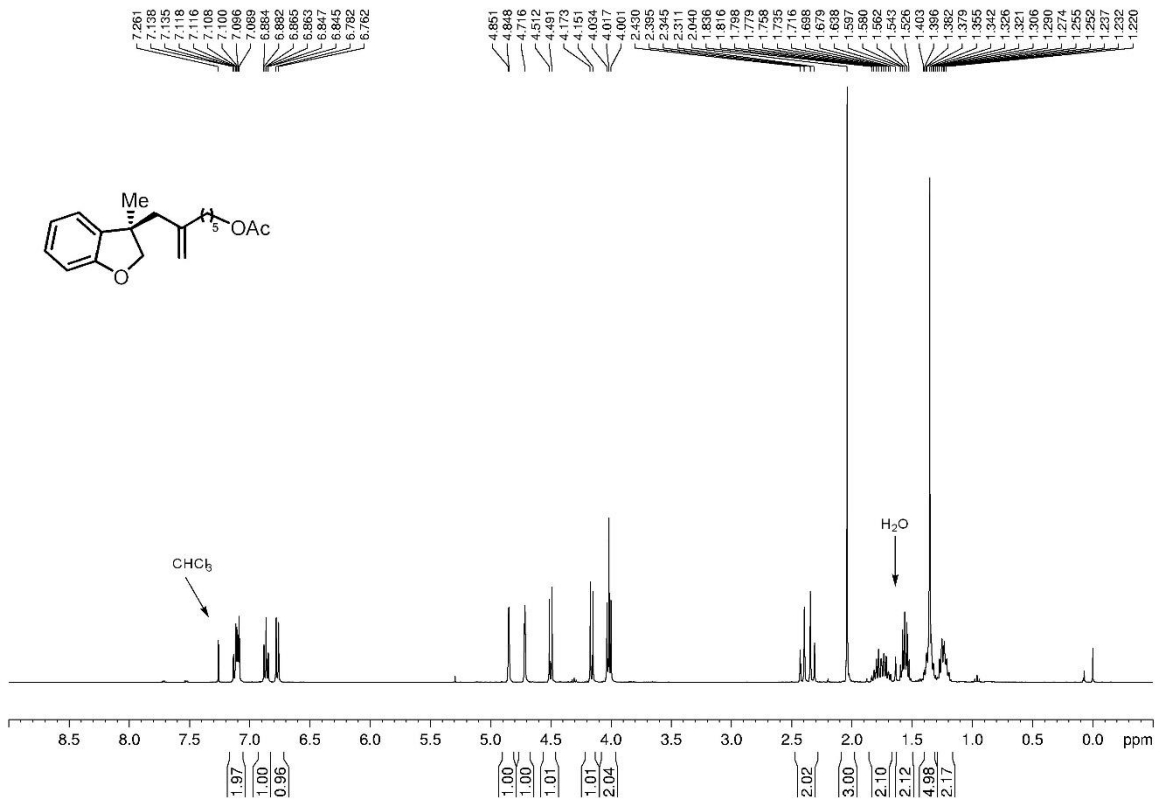


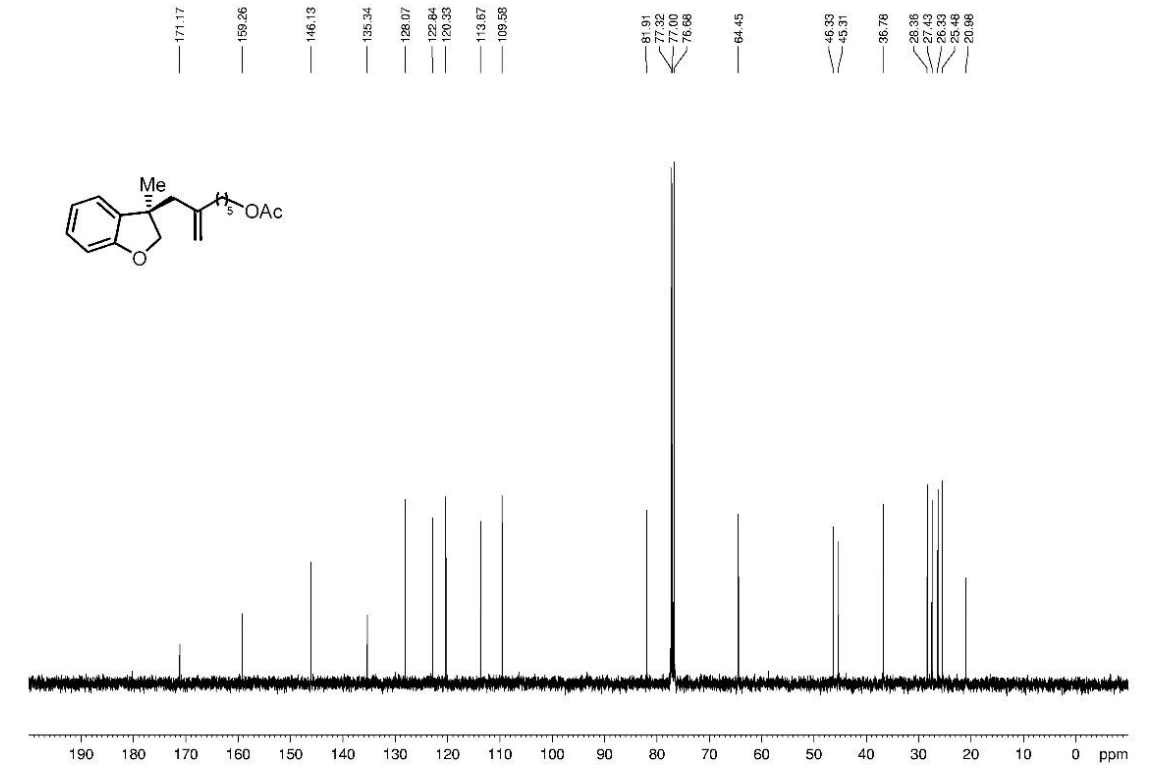
3p; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



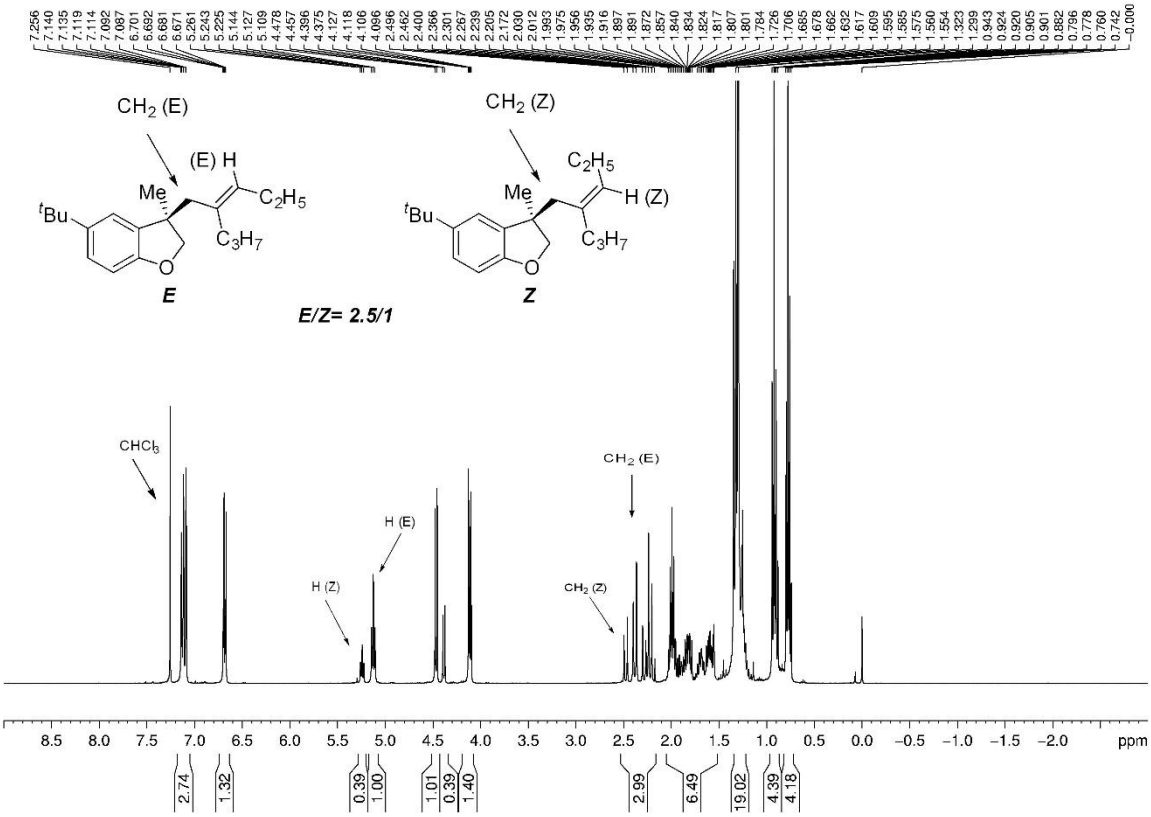


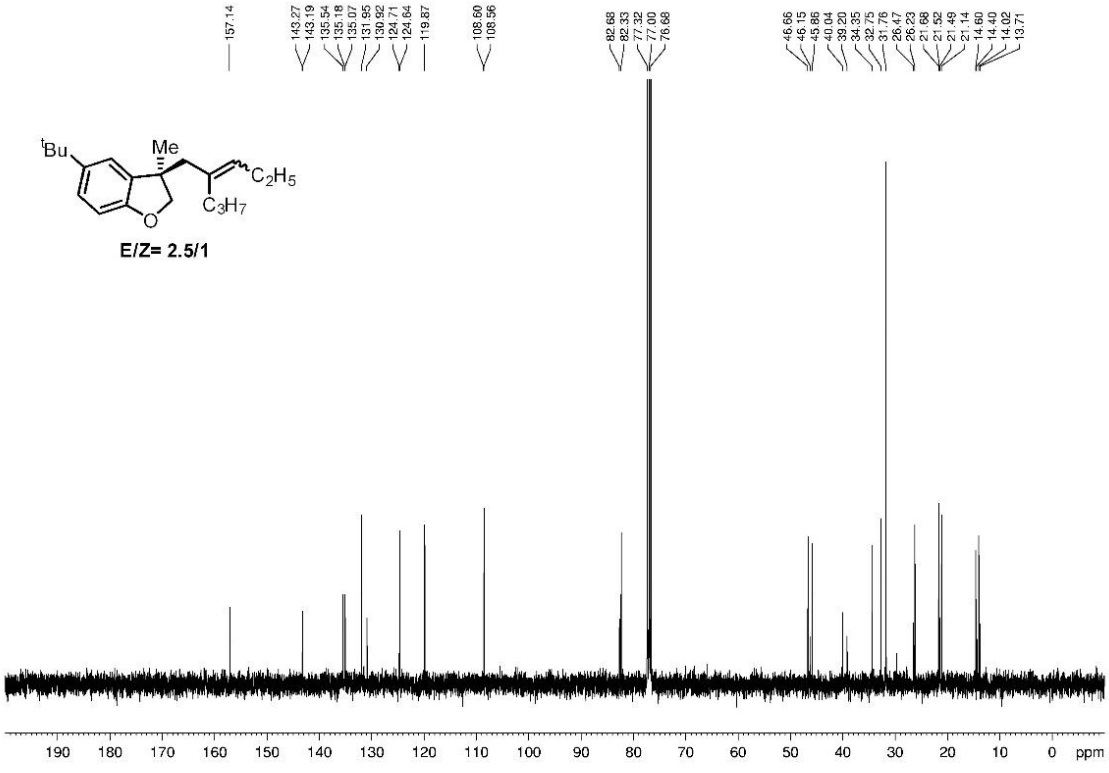
3q; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



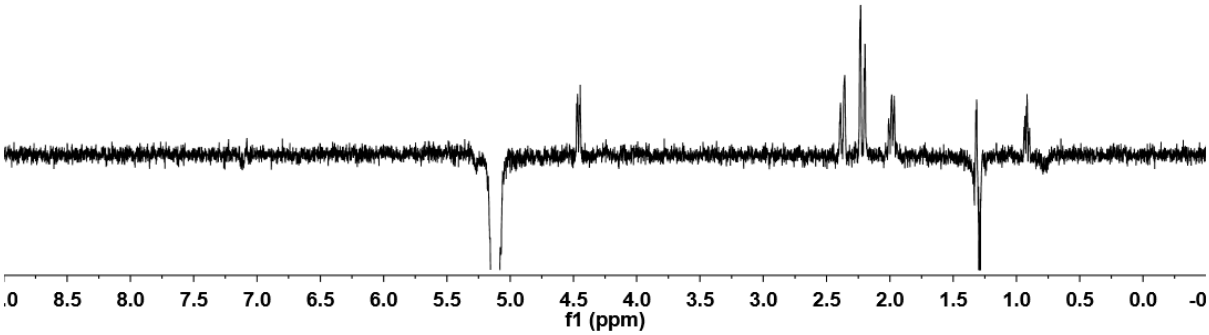


3s; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

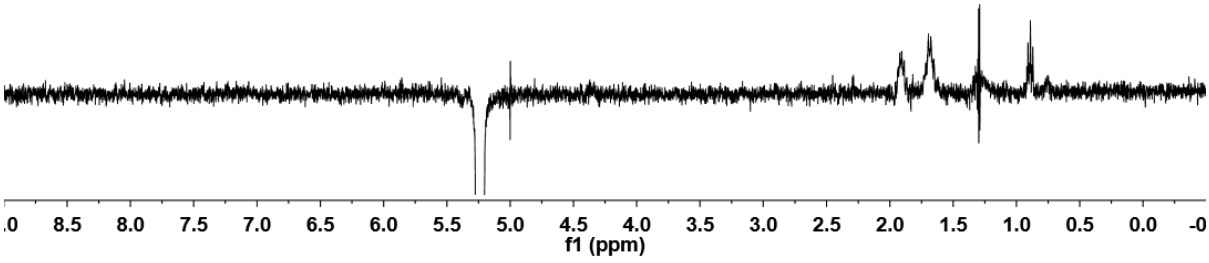




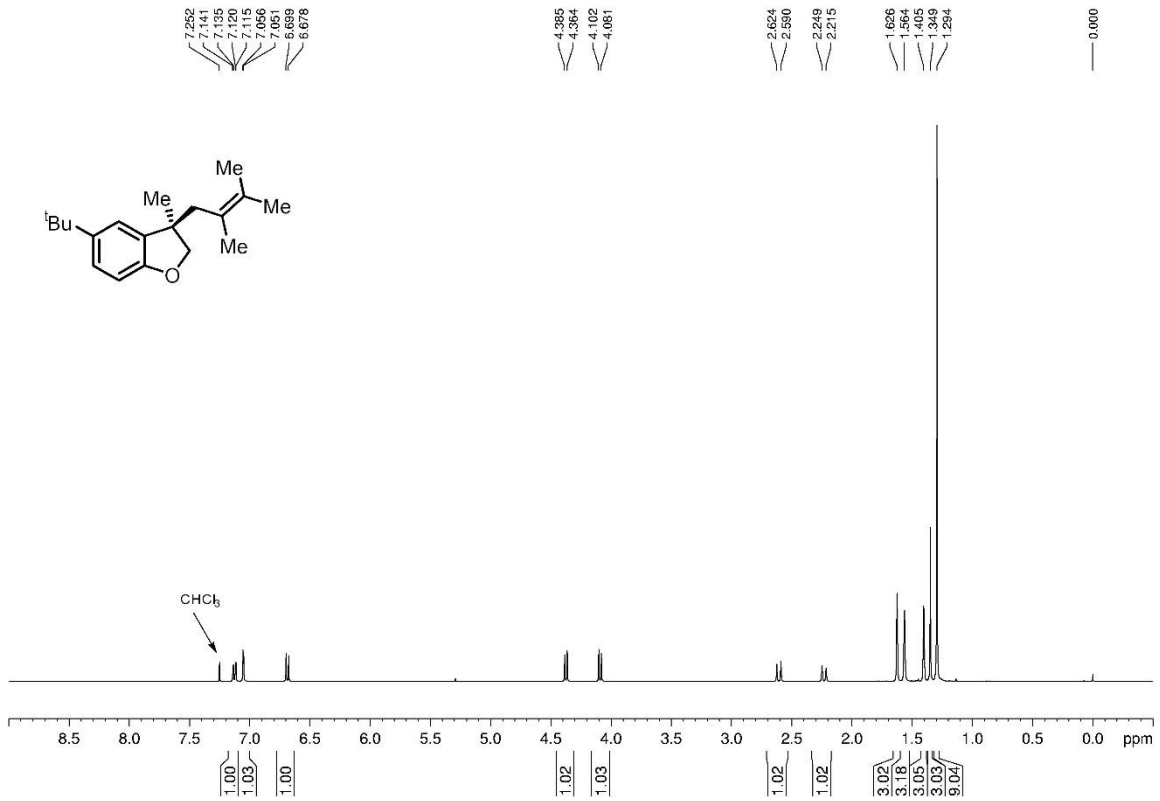
1D-NOE spectra of *E*-3s

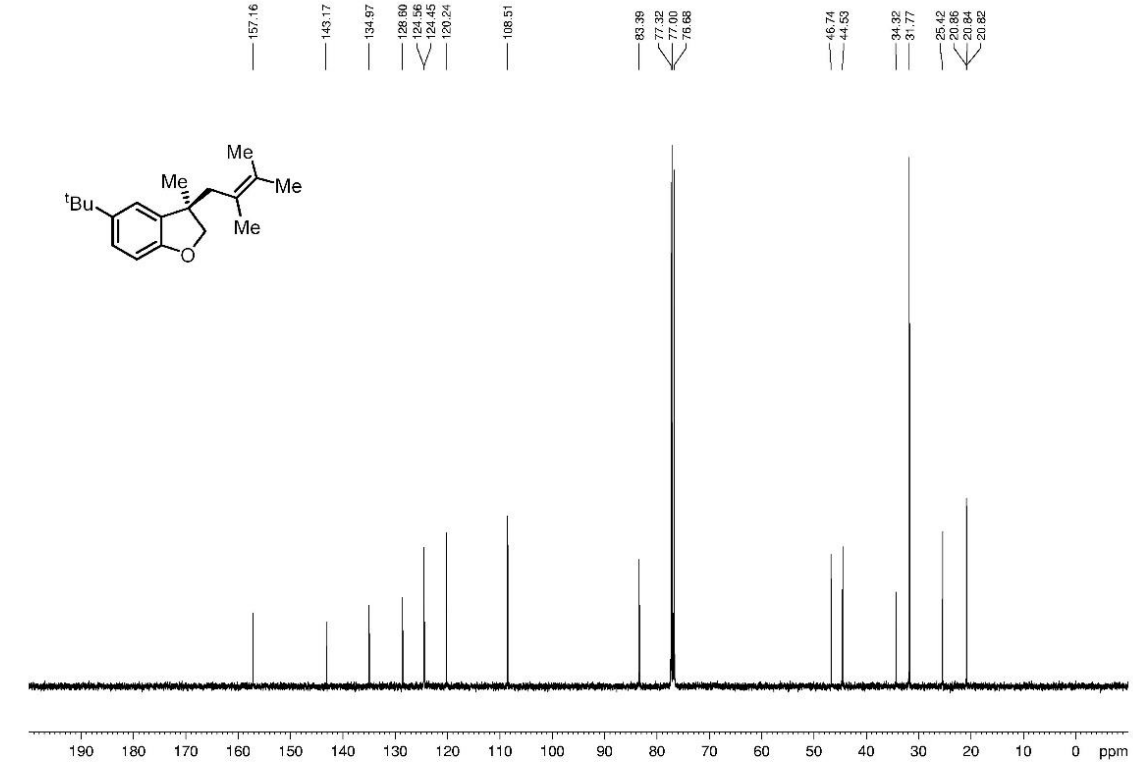


1D-NOE spectra of *Z*-3s

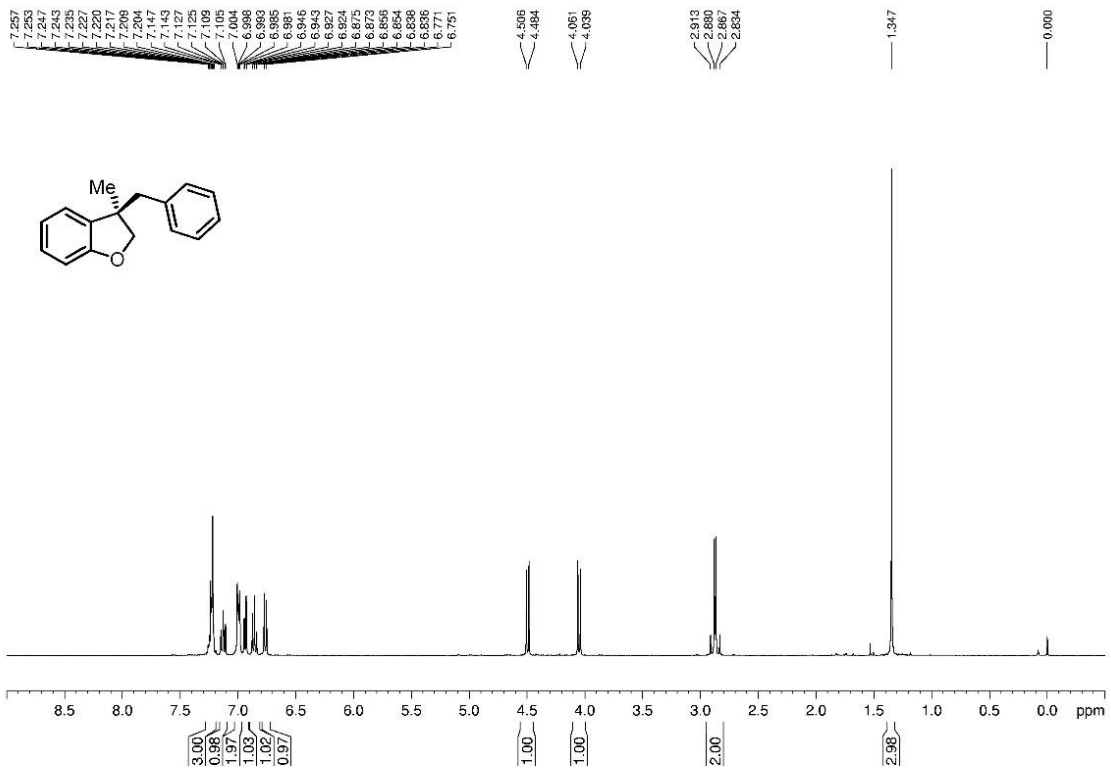


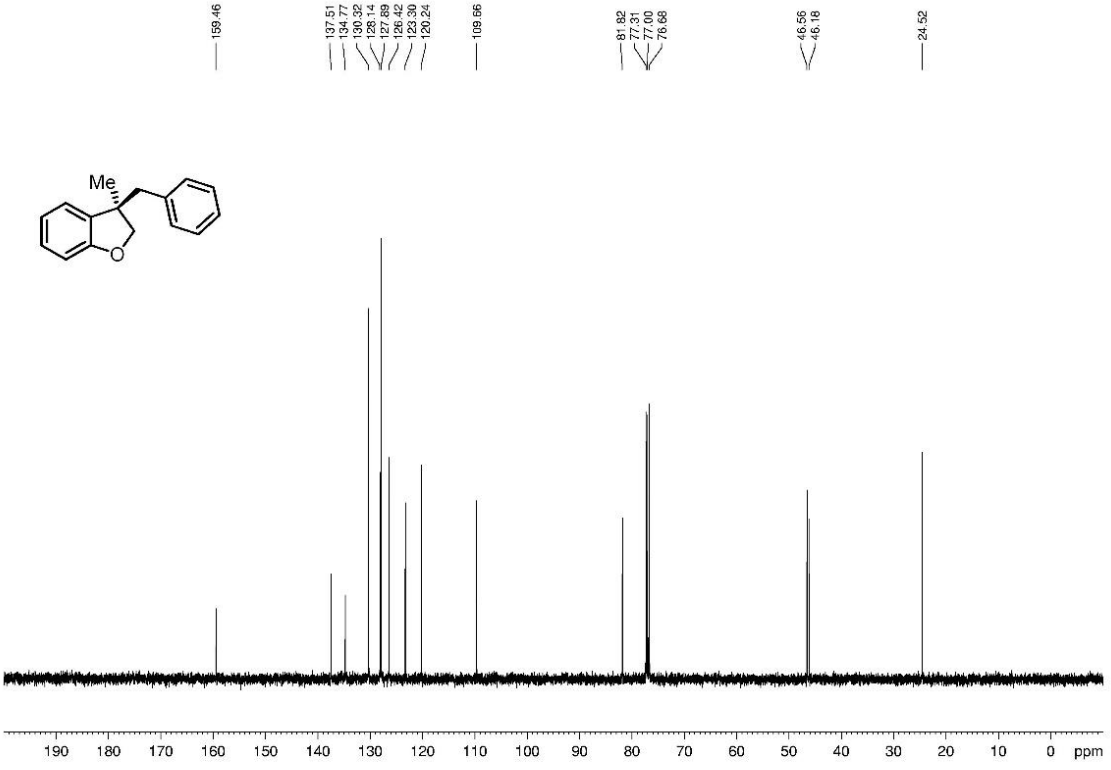
3t; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



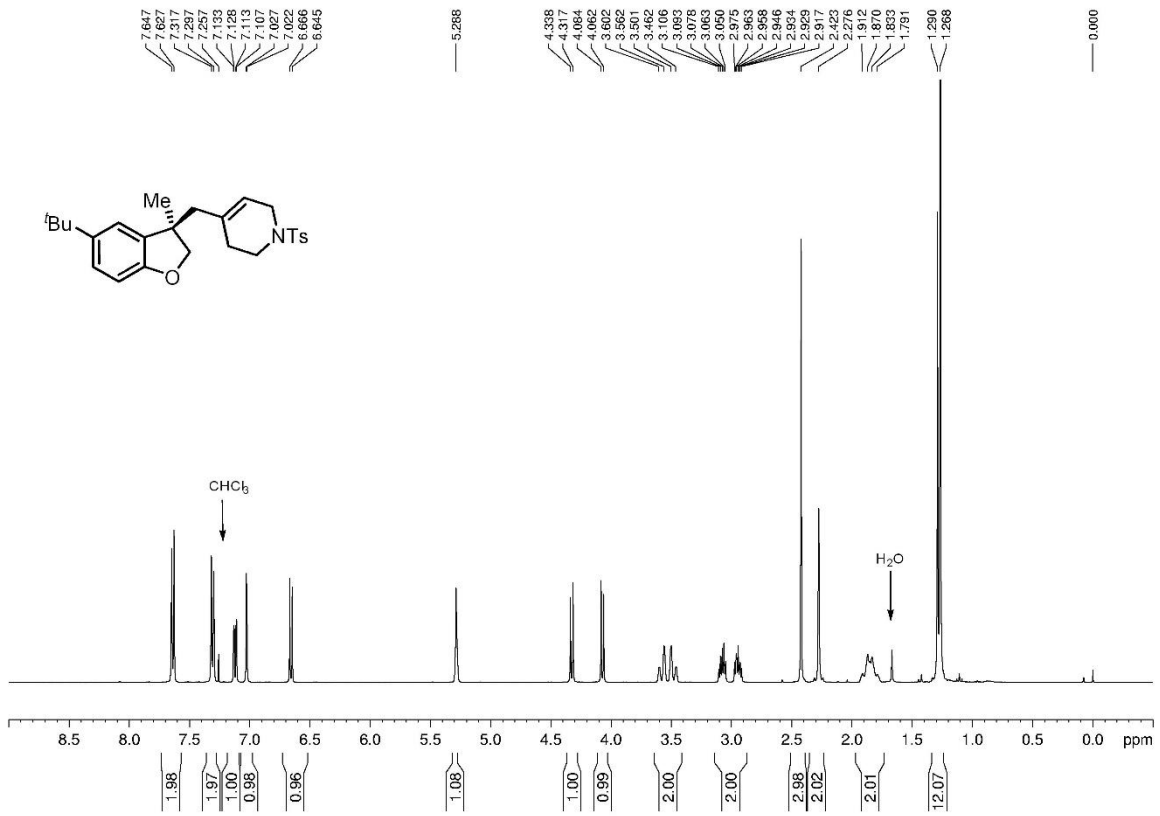


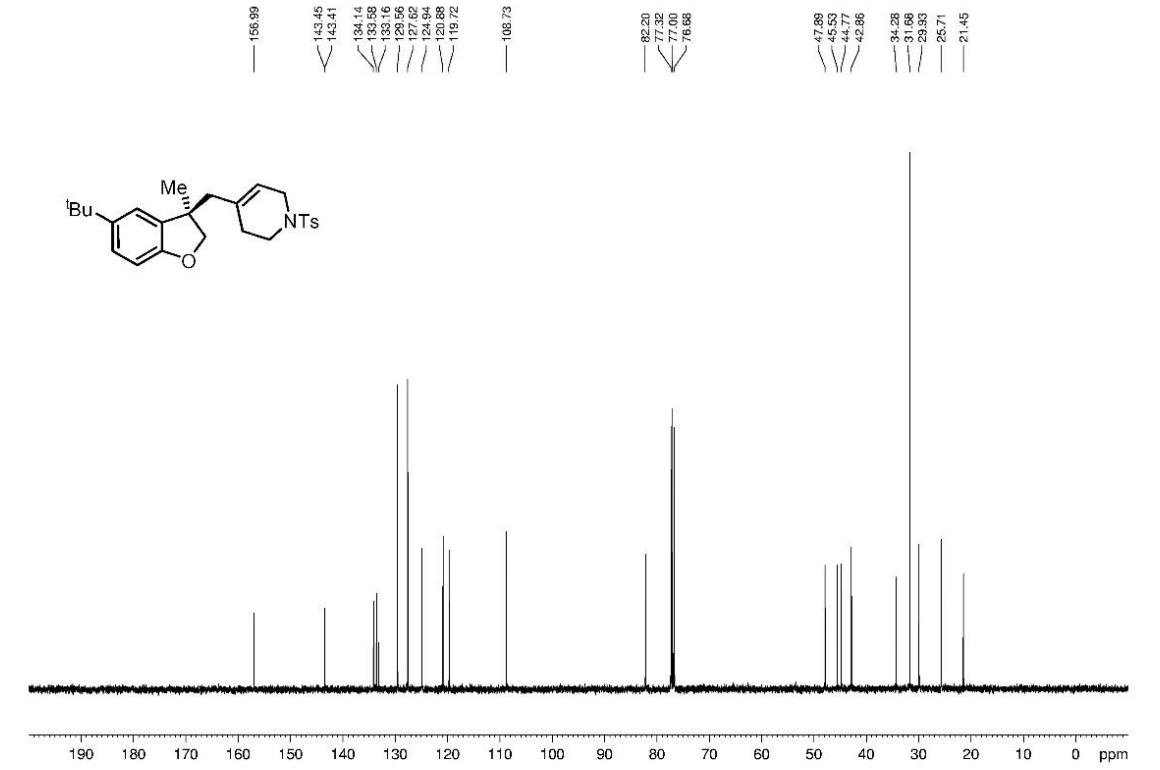
3u; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



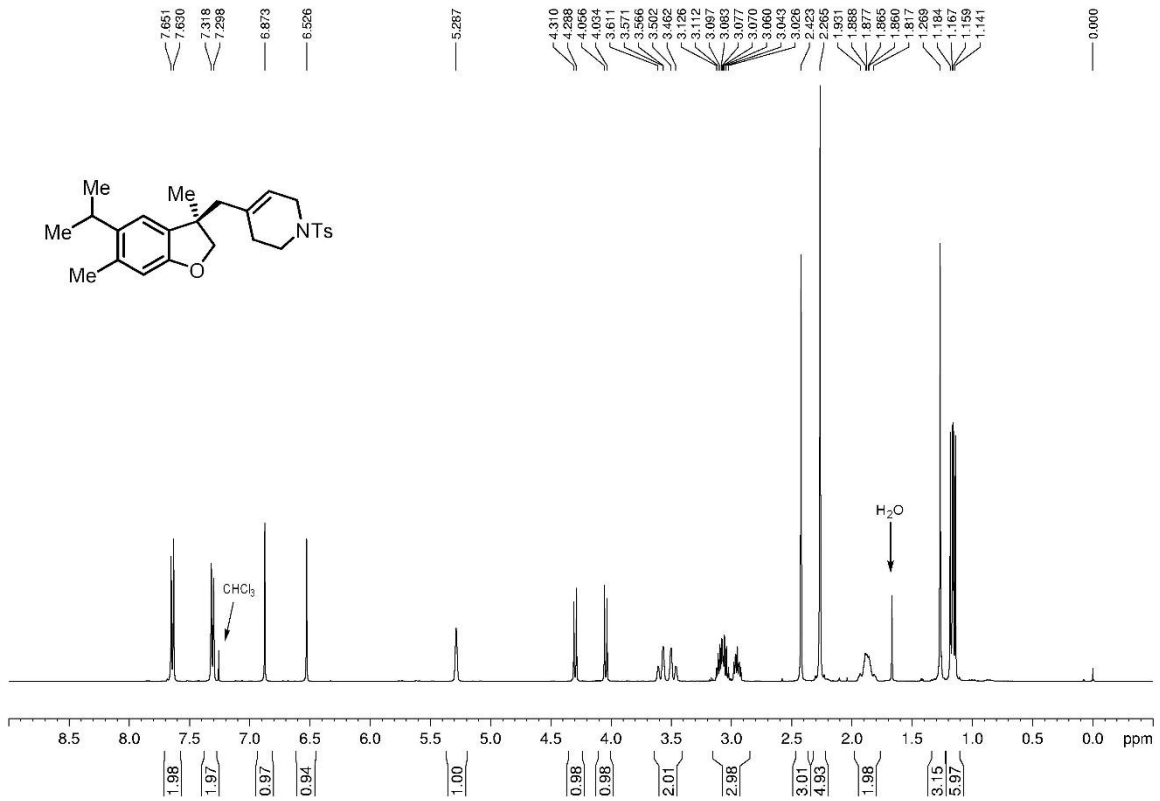


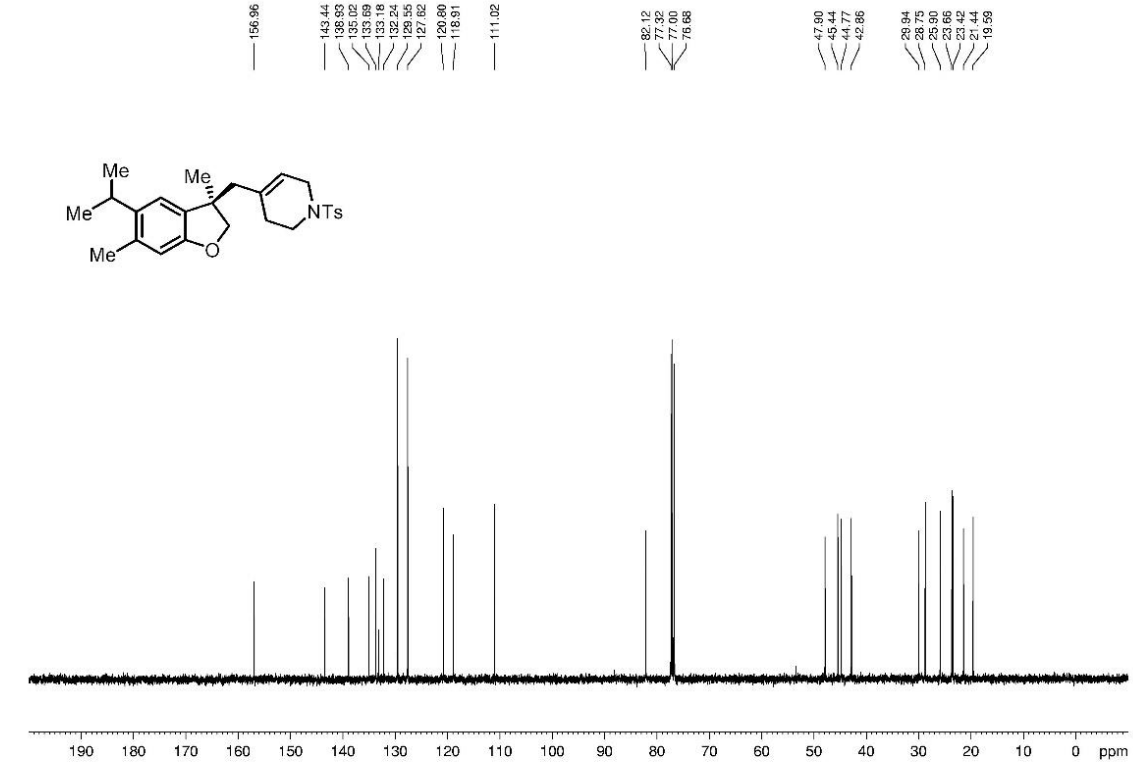
3v; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



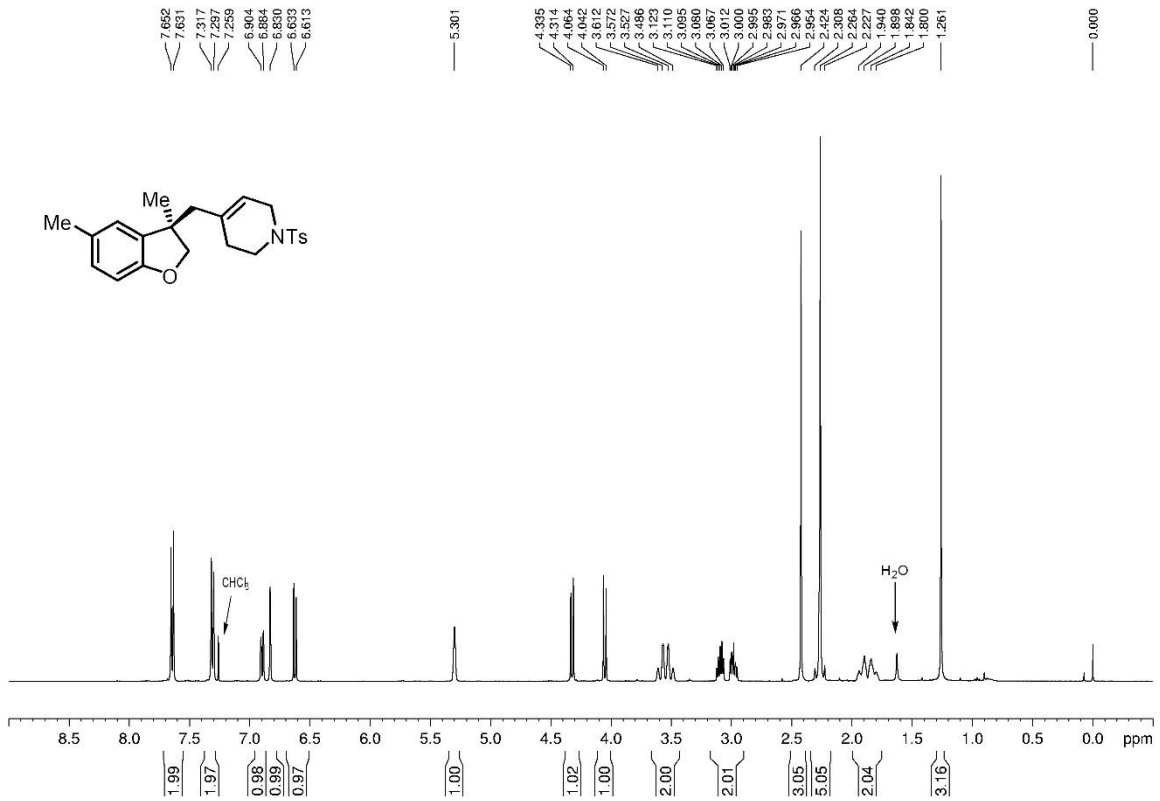


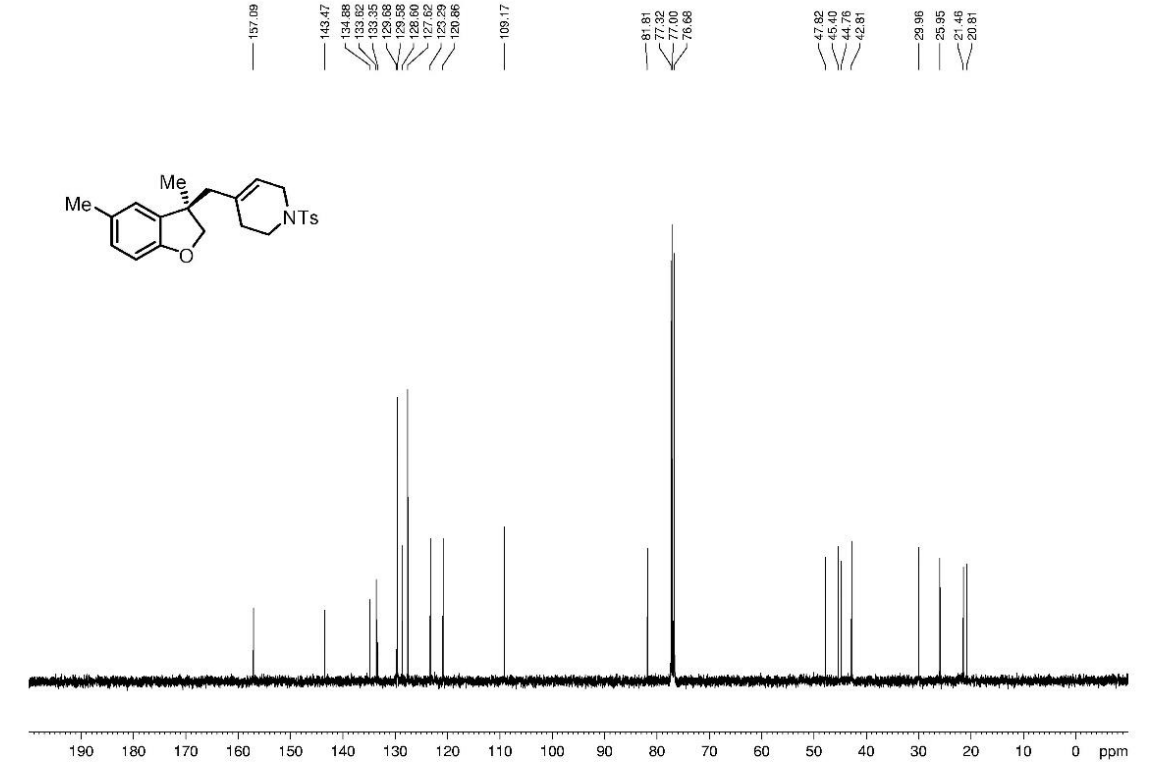
3w; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



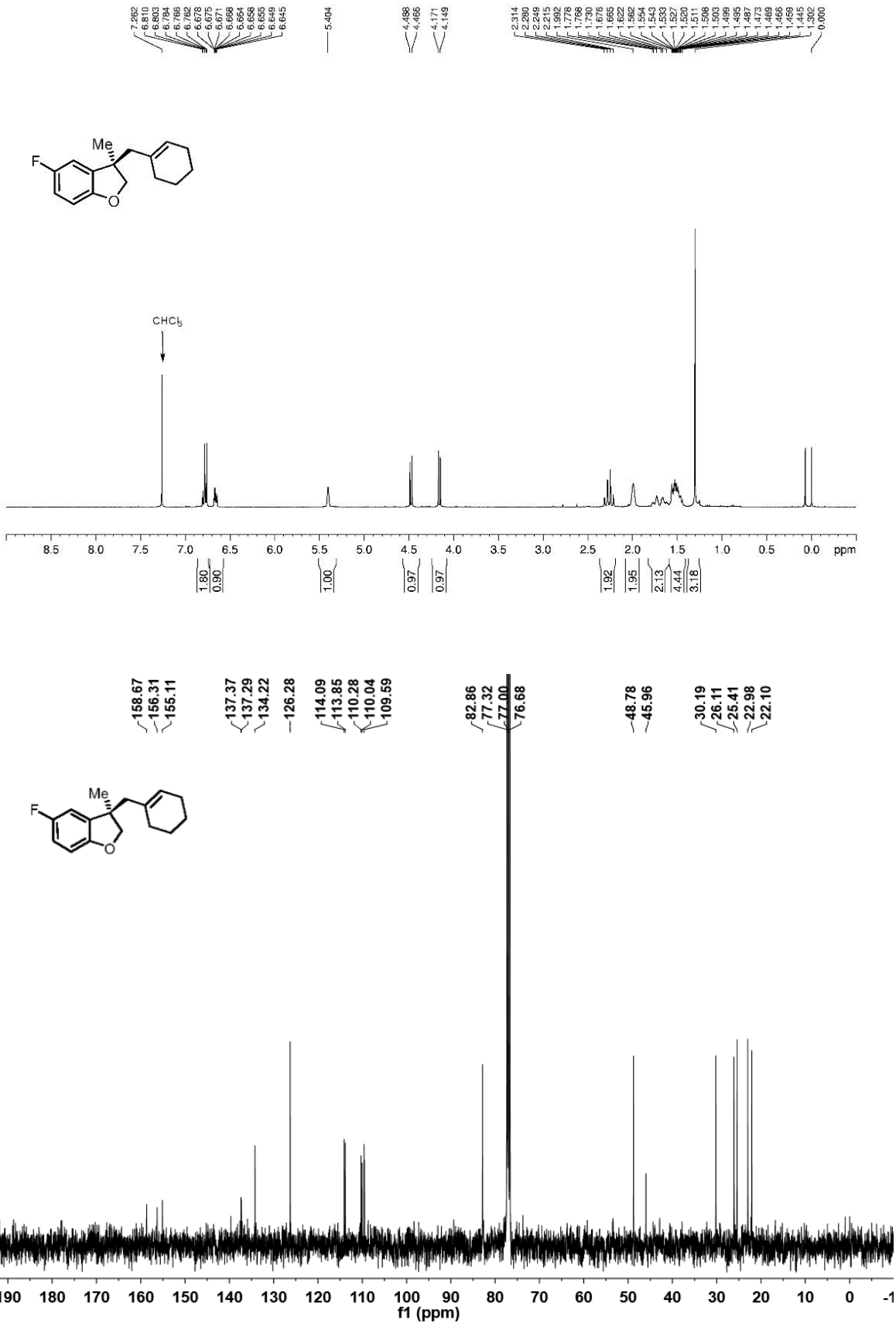


3x; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

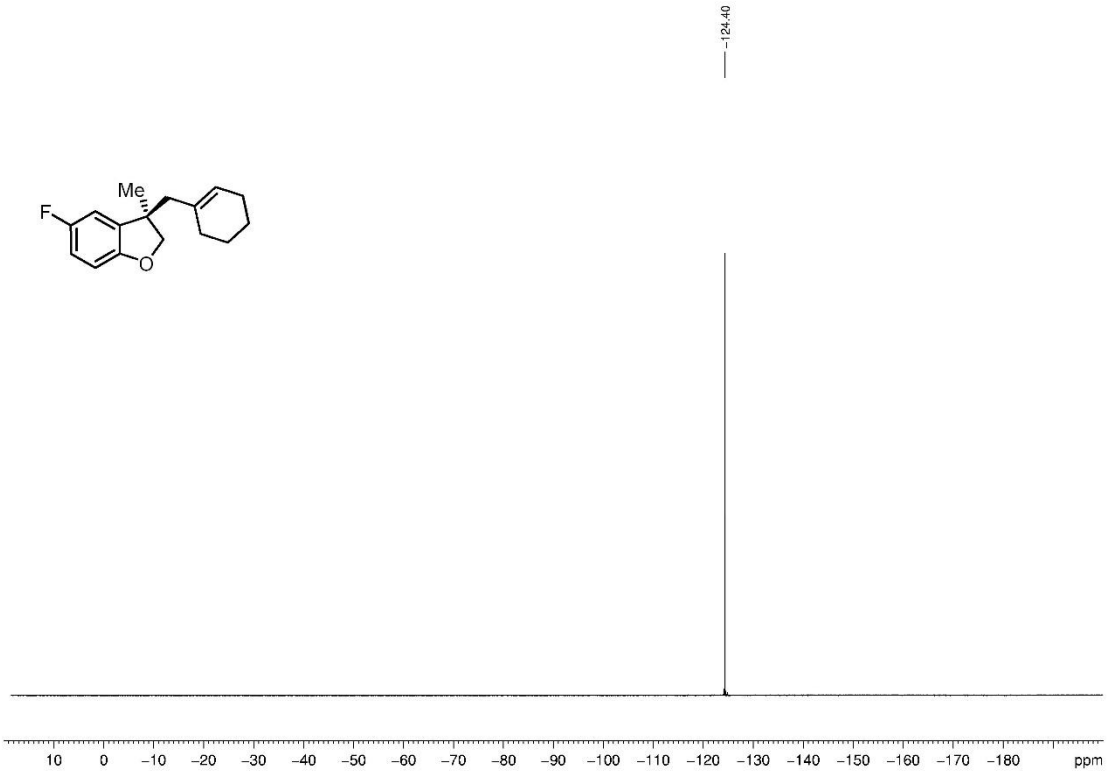




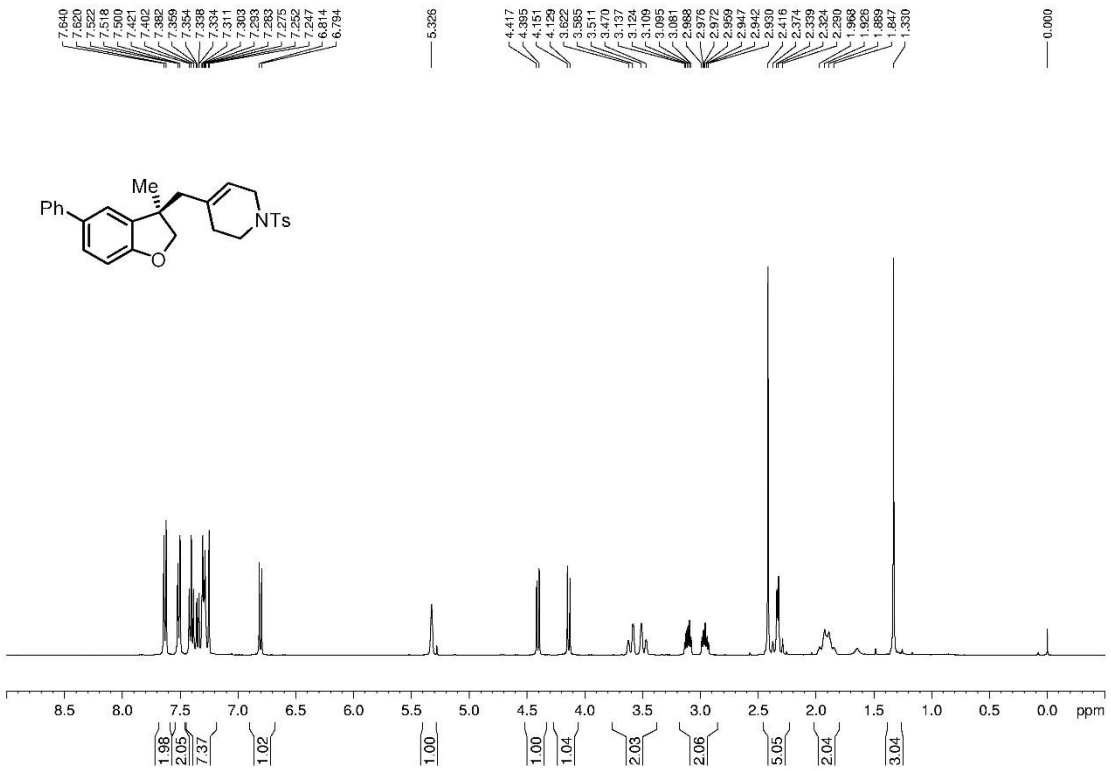
3y; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

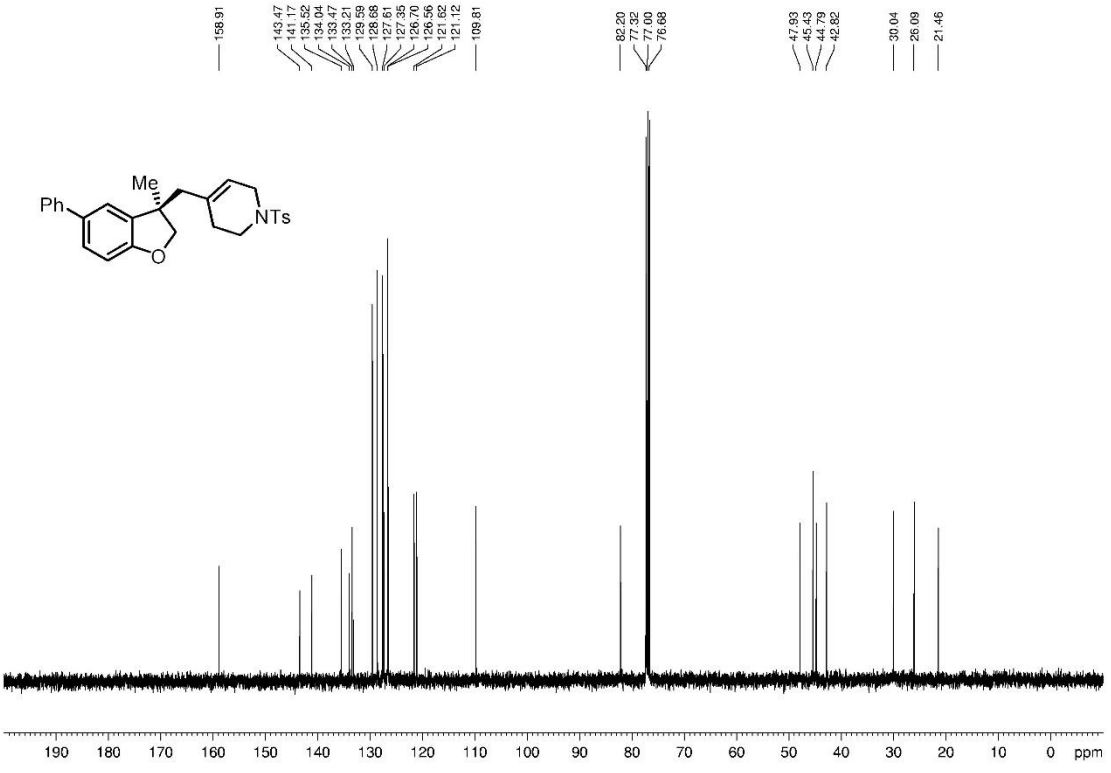


3y; ^{19}F NMR (376MHz, $CDCl_3$)

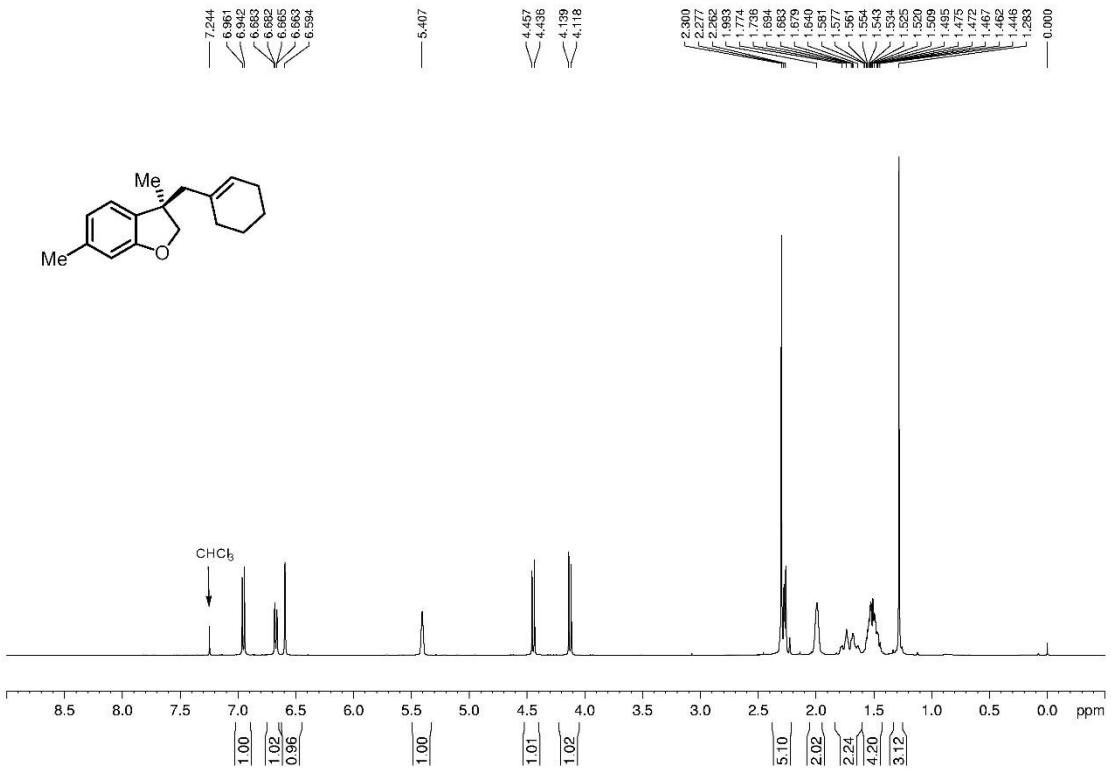


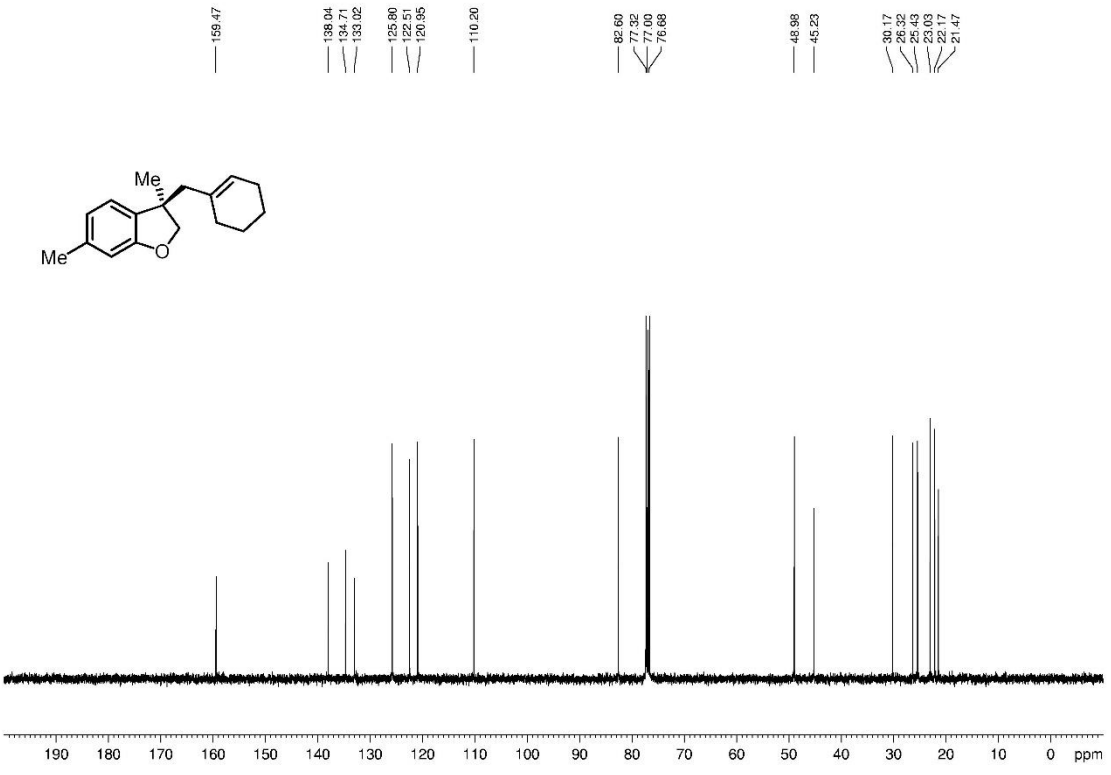
3z; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



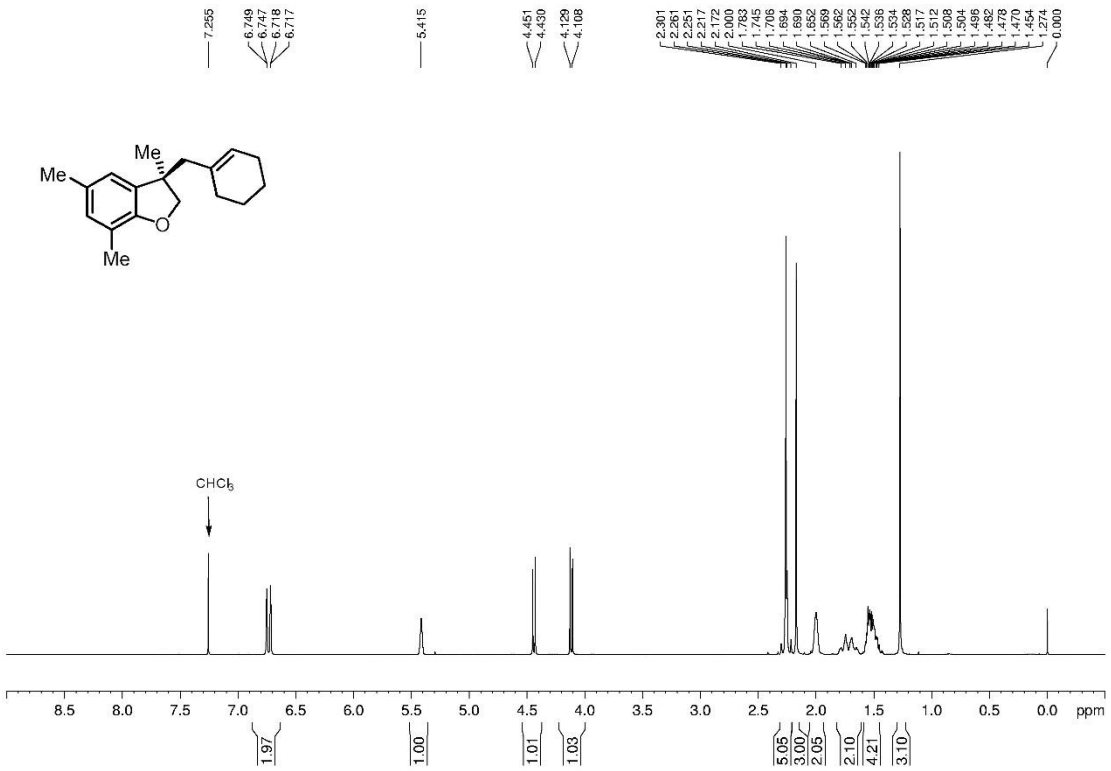


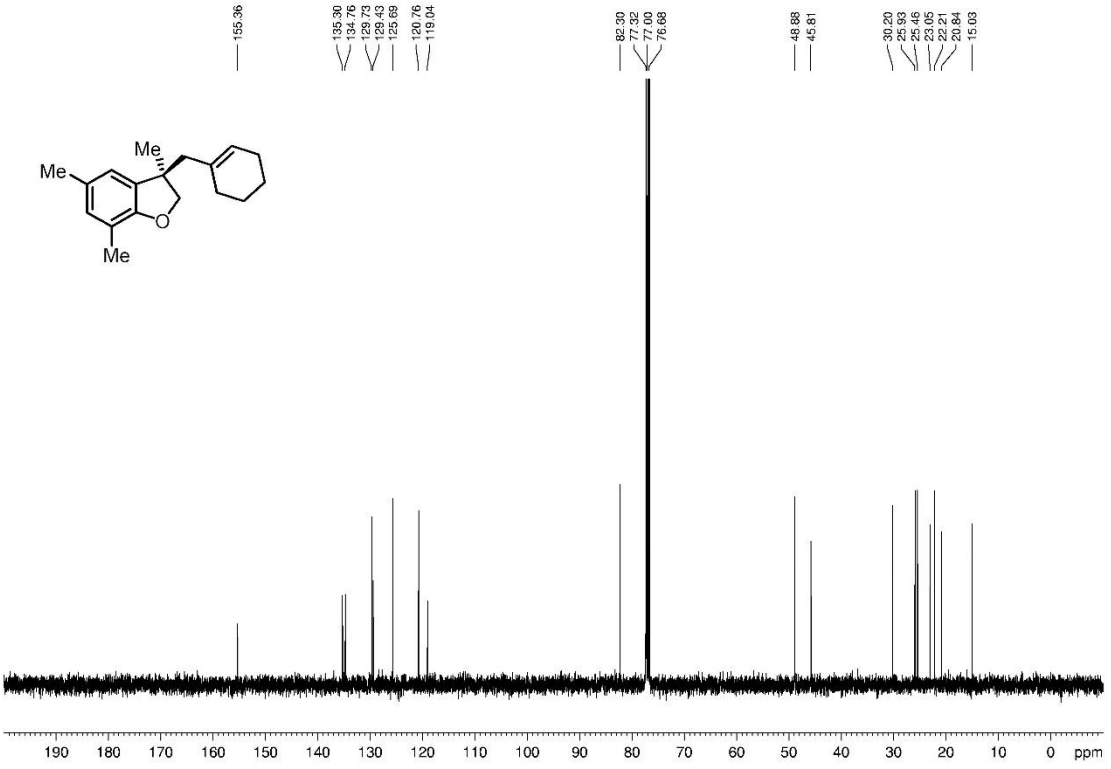
3ab; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



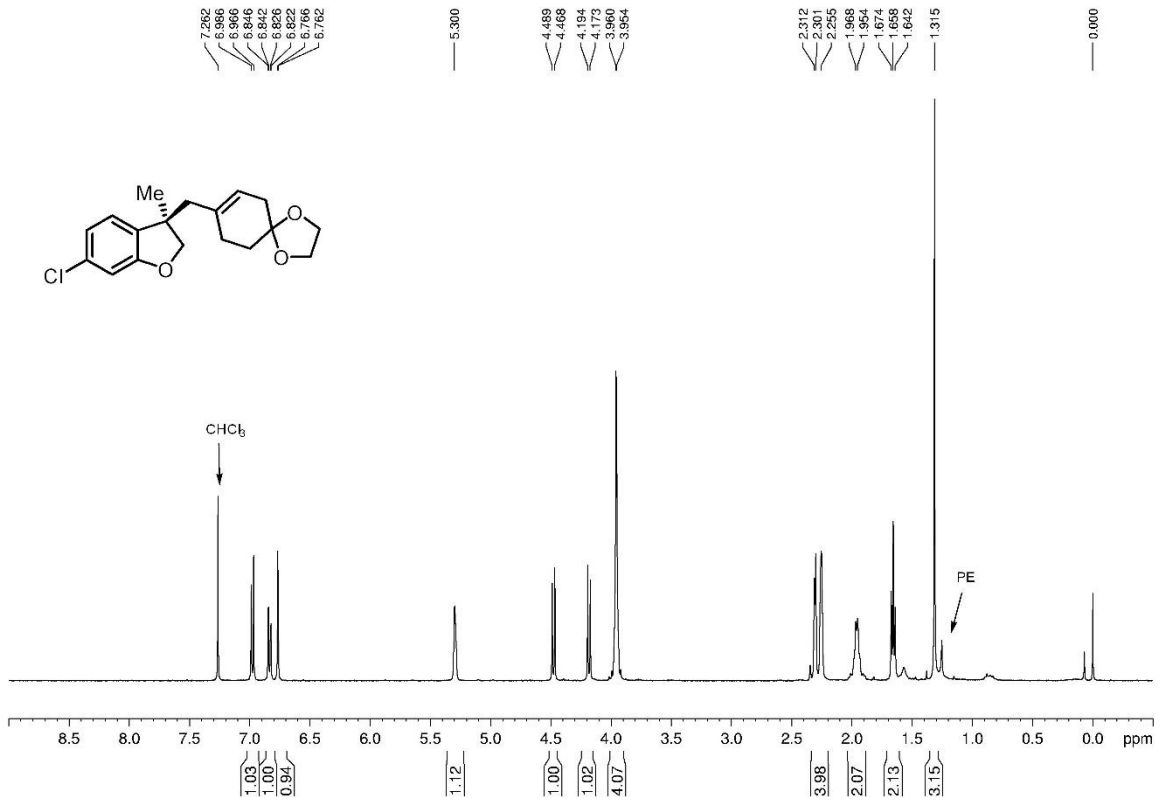


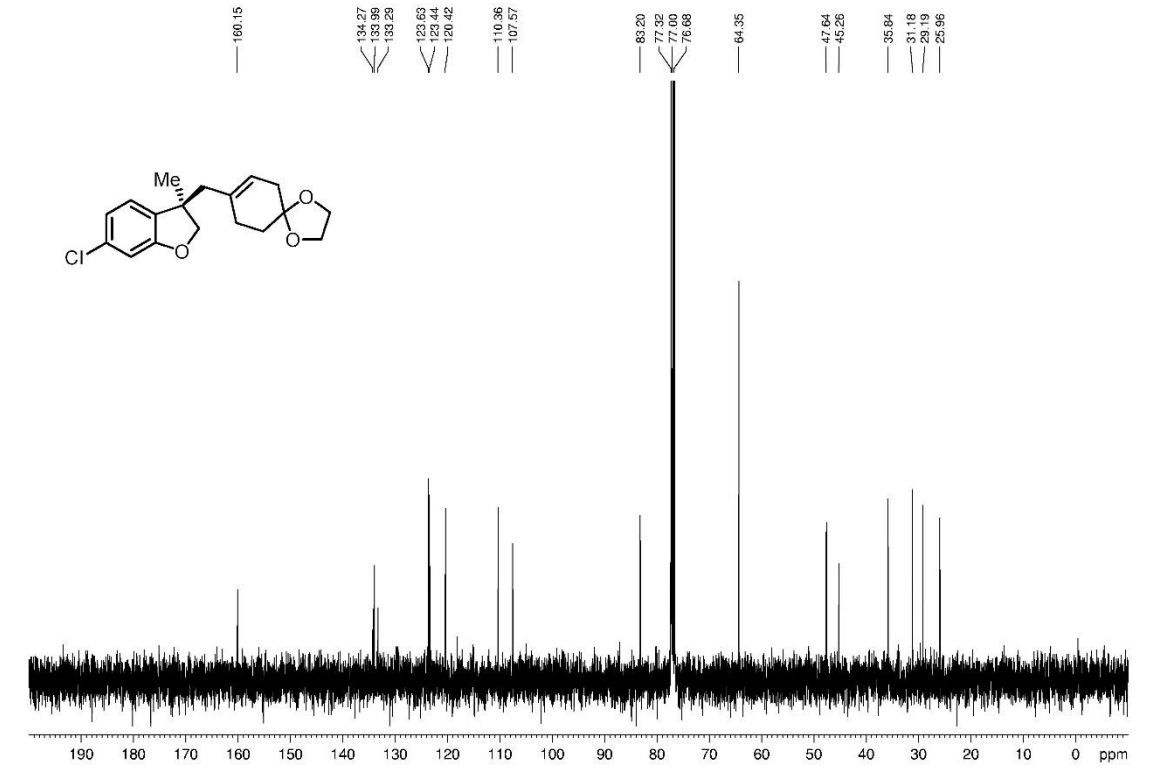
3ac; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



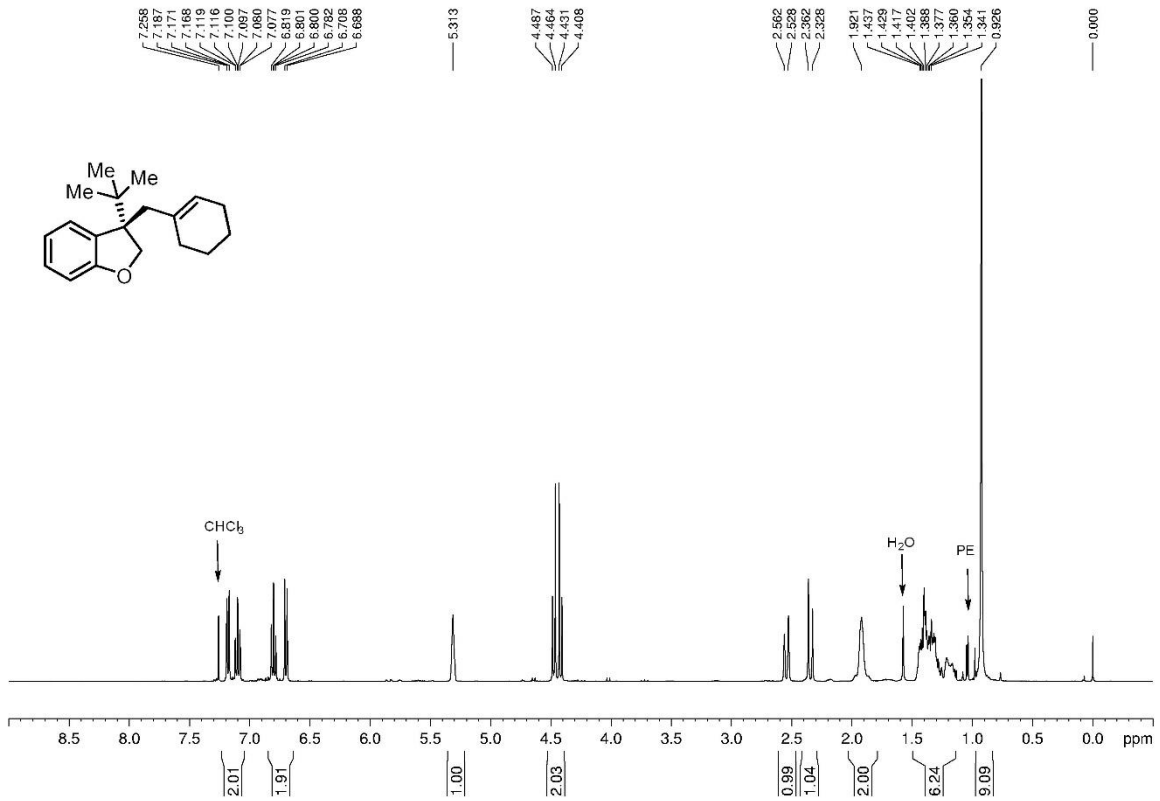


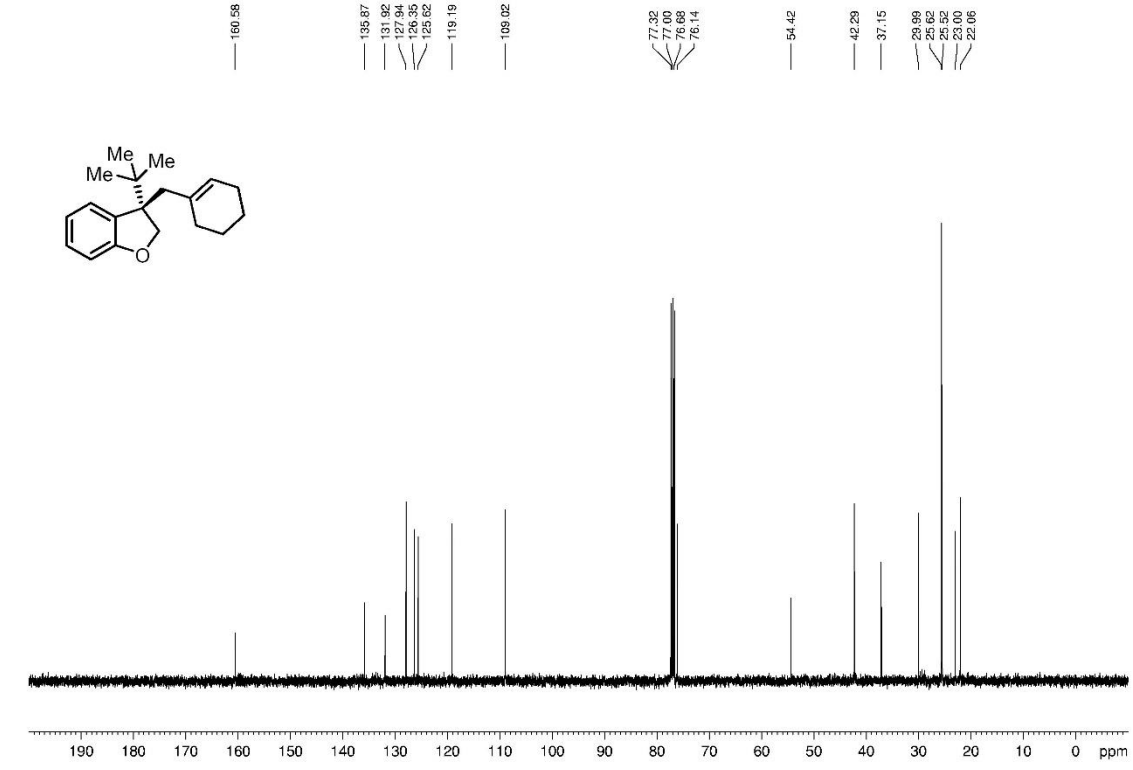
3ae; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



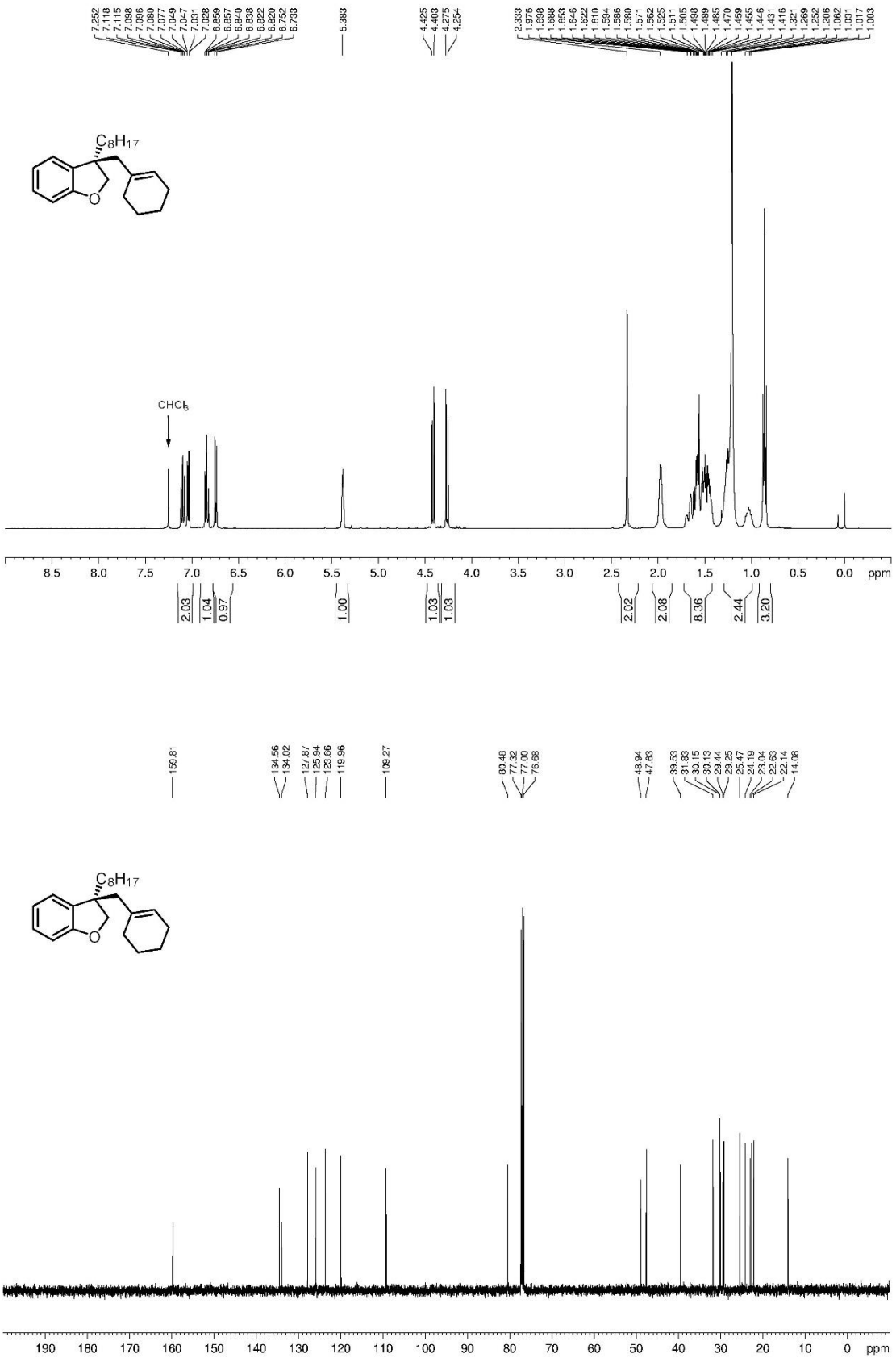


3af; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

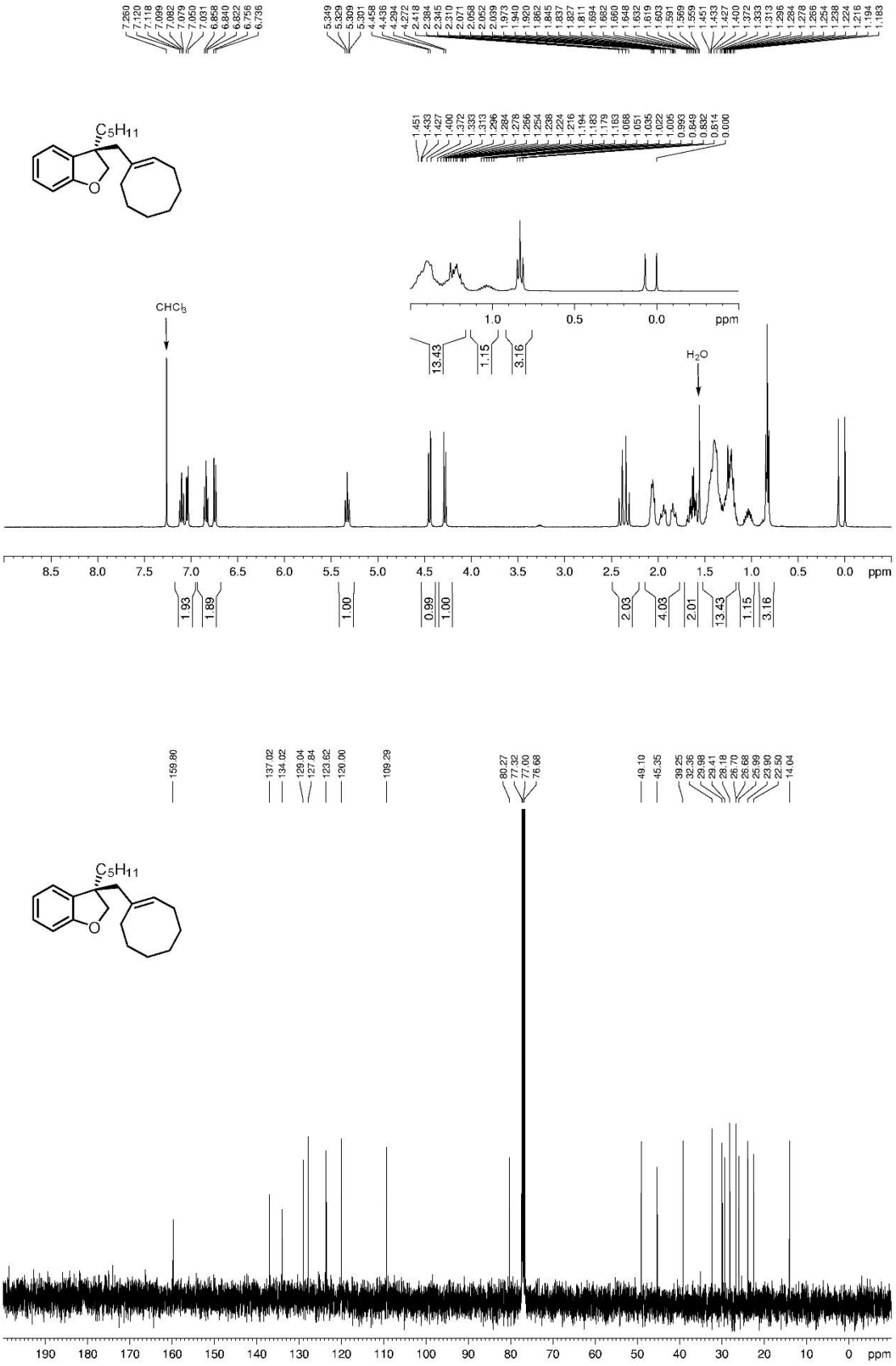




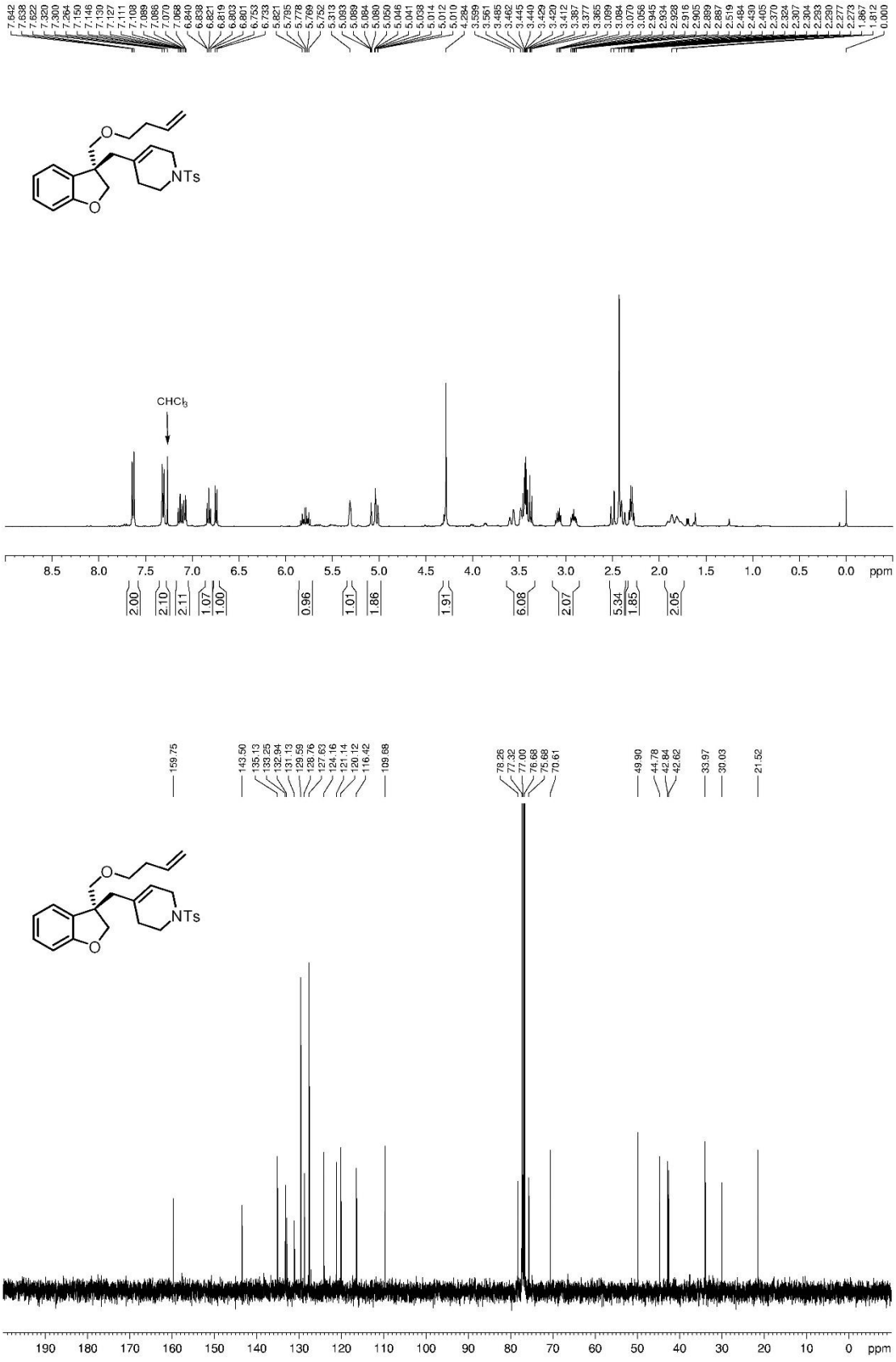
3ag; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



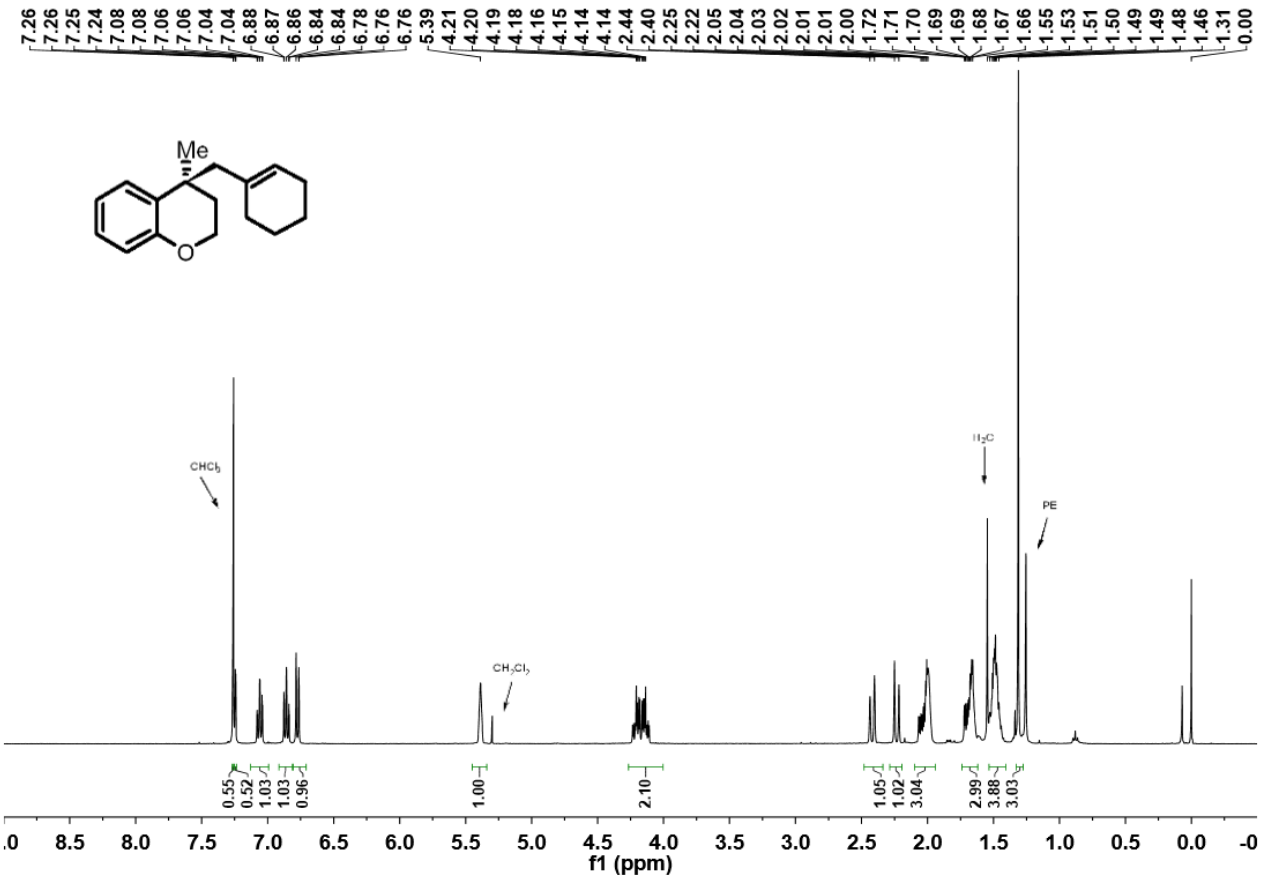
3ah; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

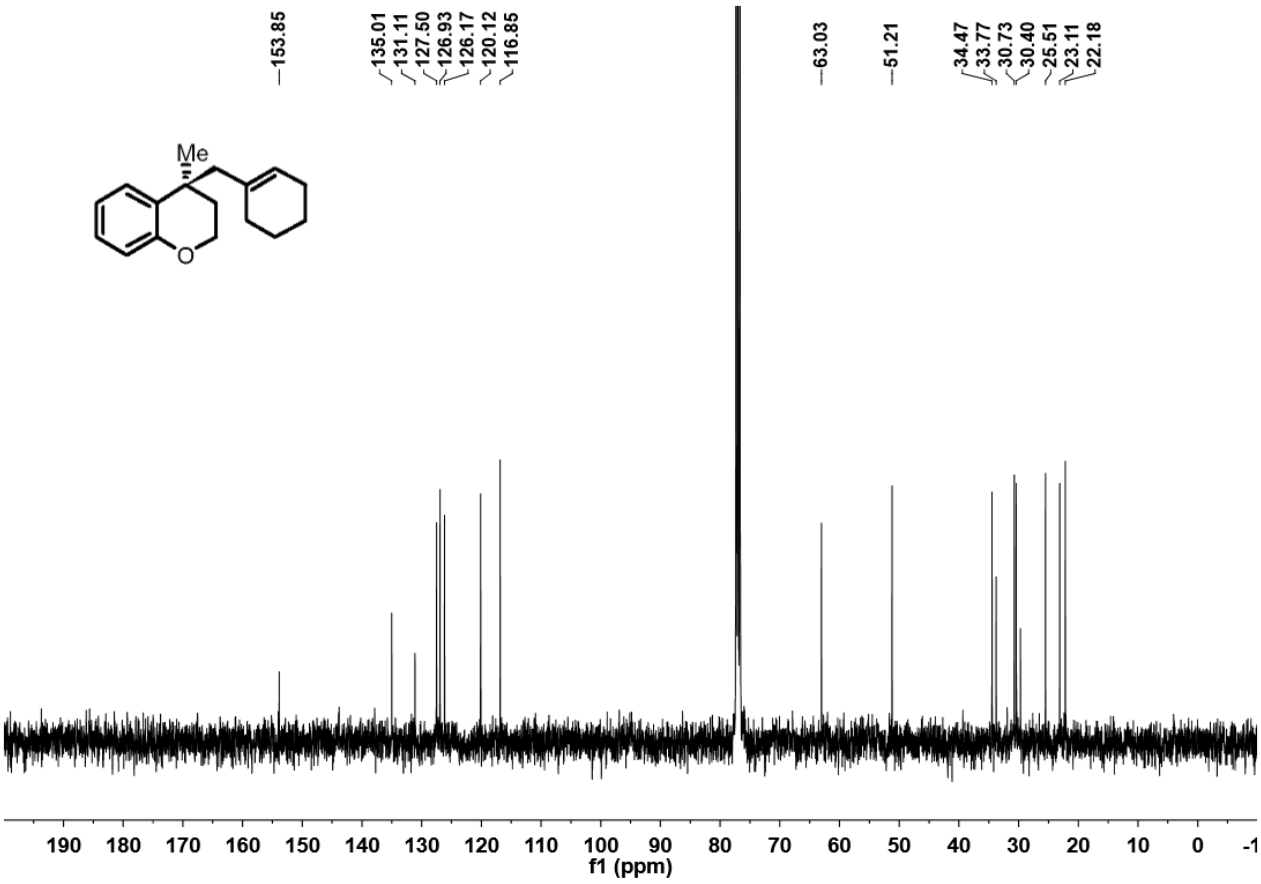


3ai; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

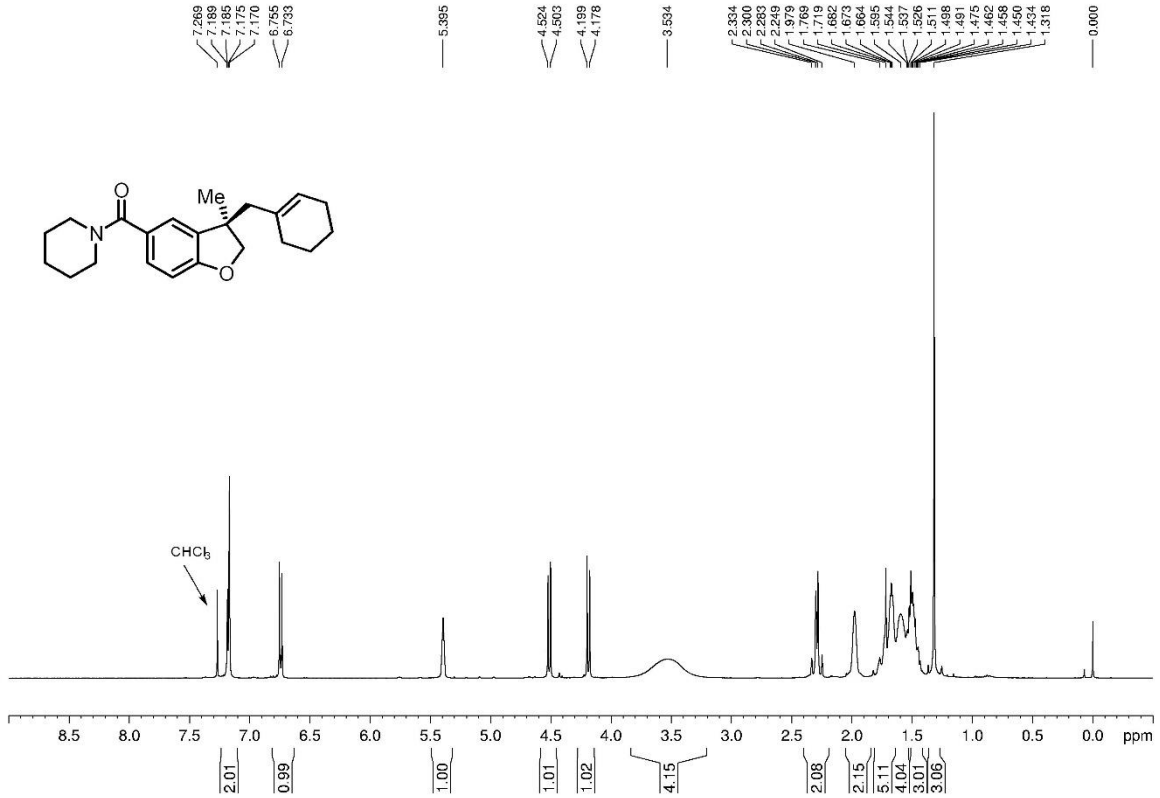


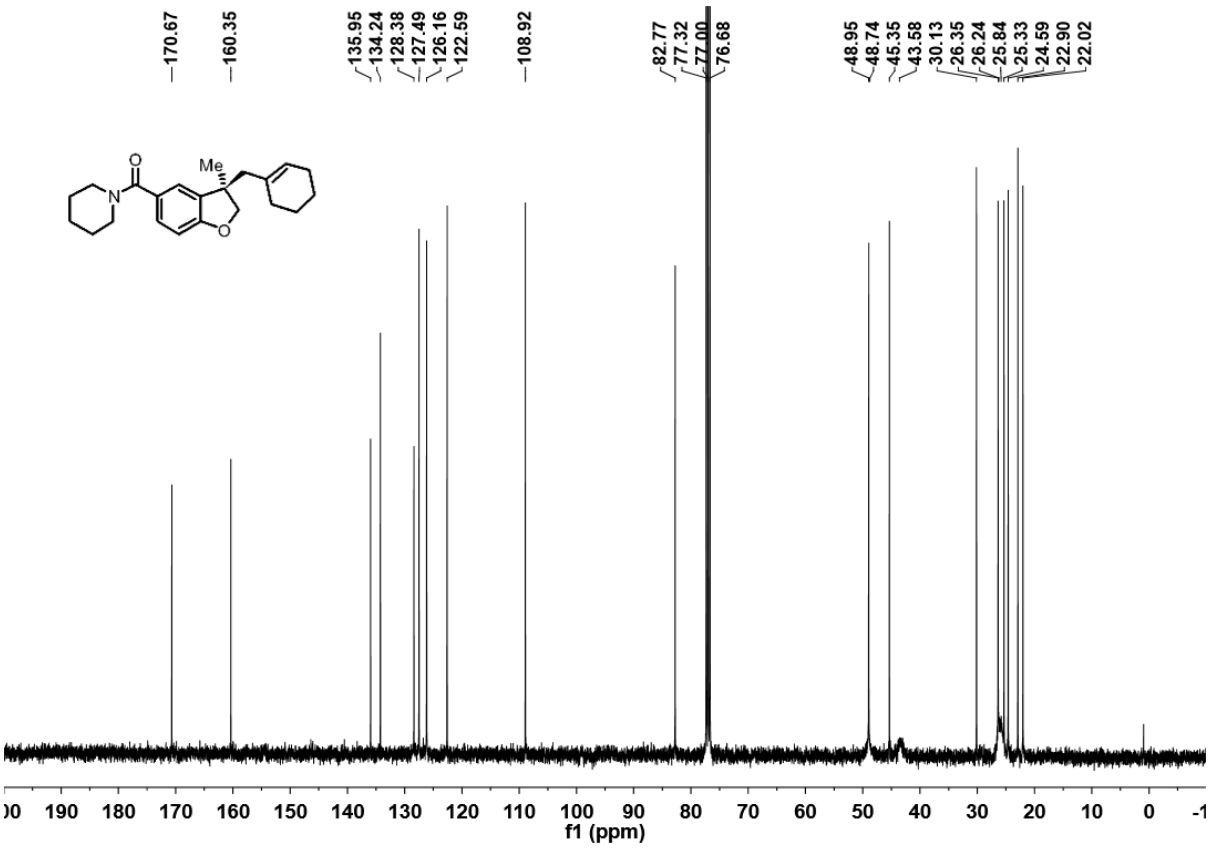
3aj; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



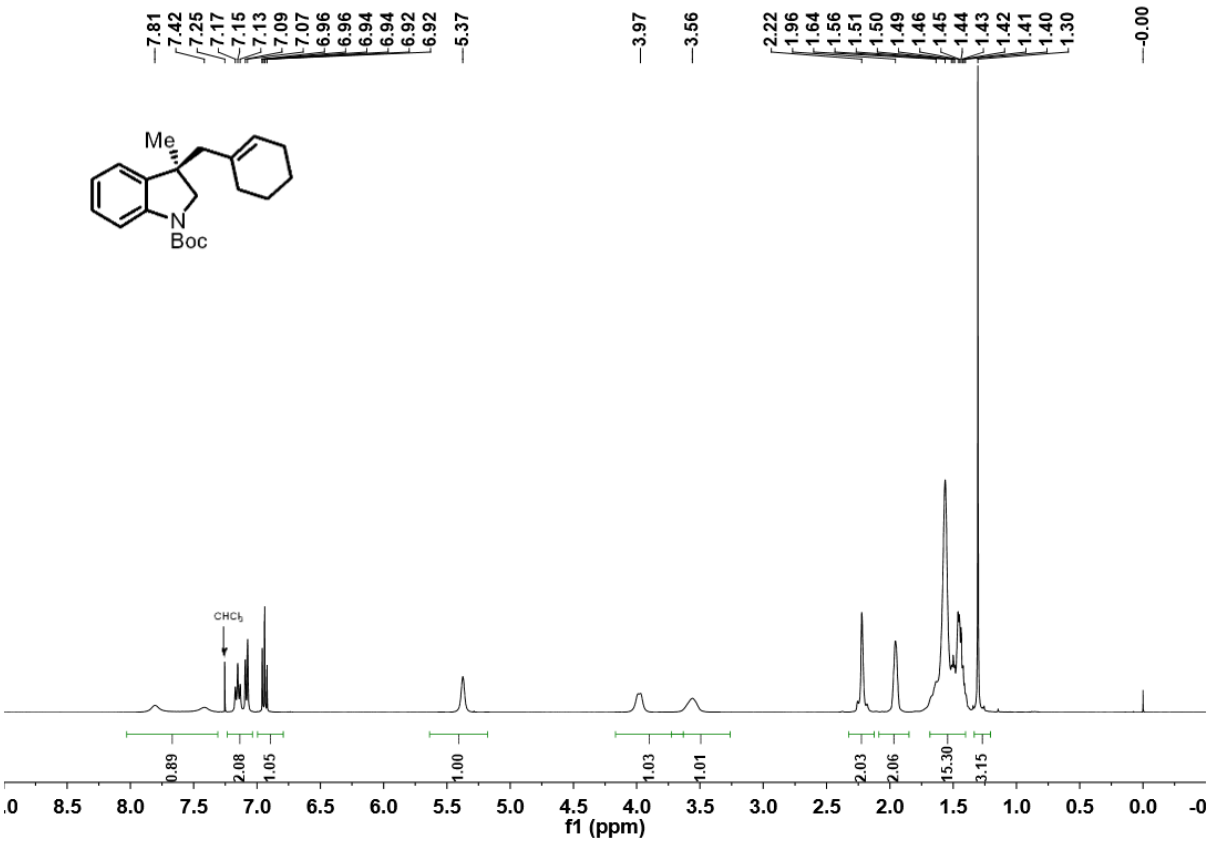


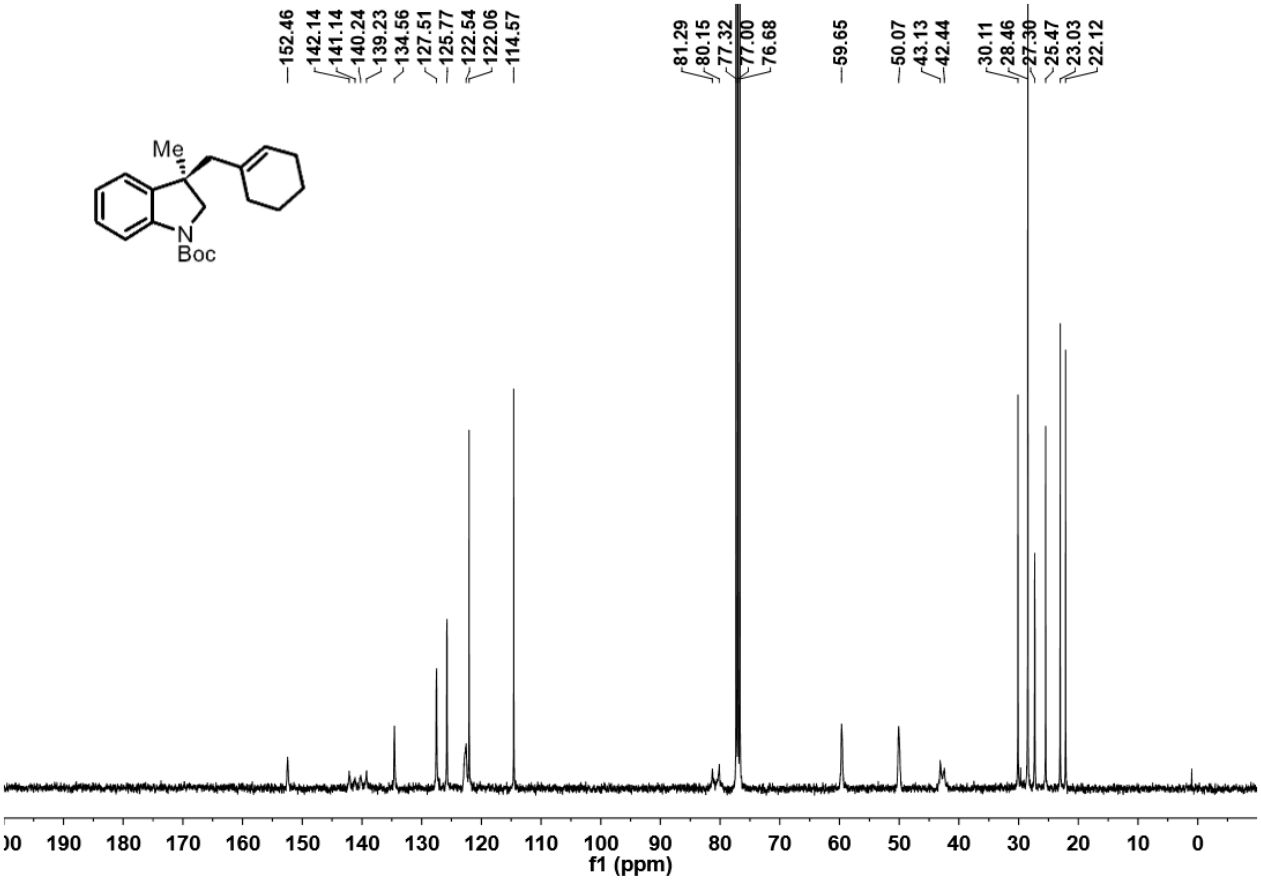
3al; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



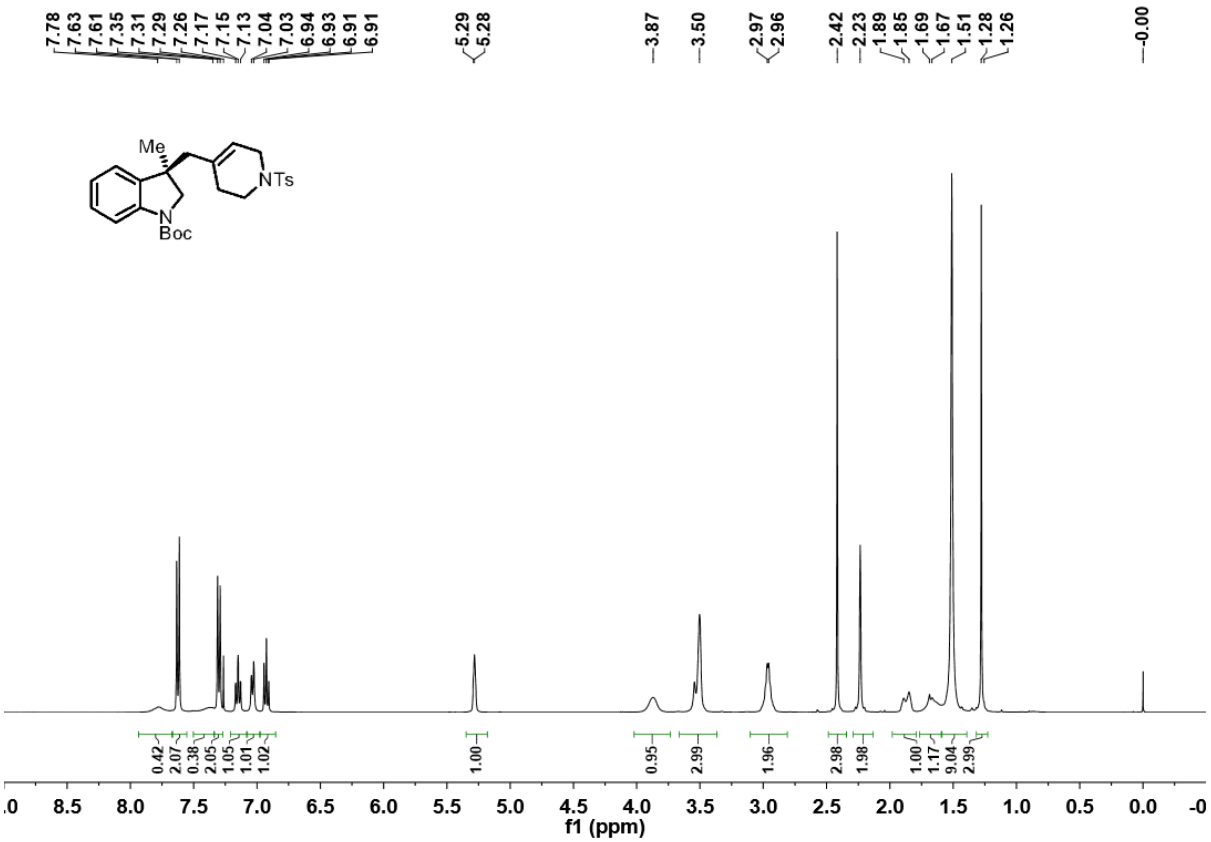


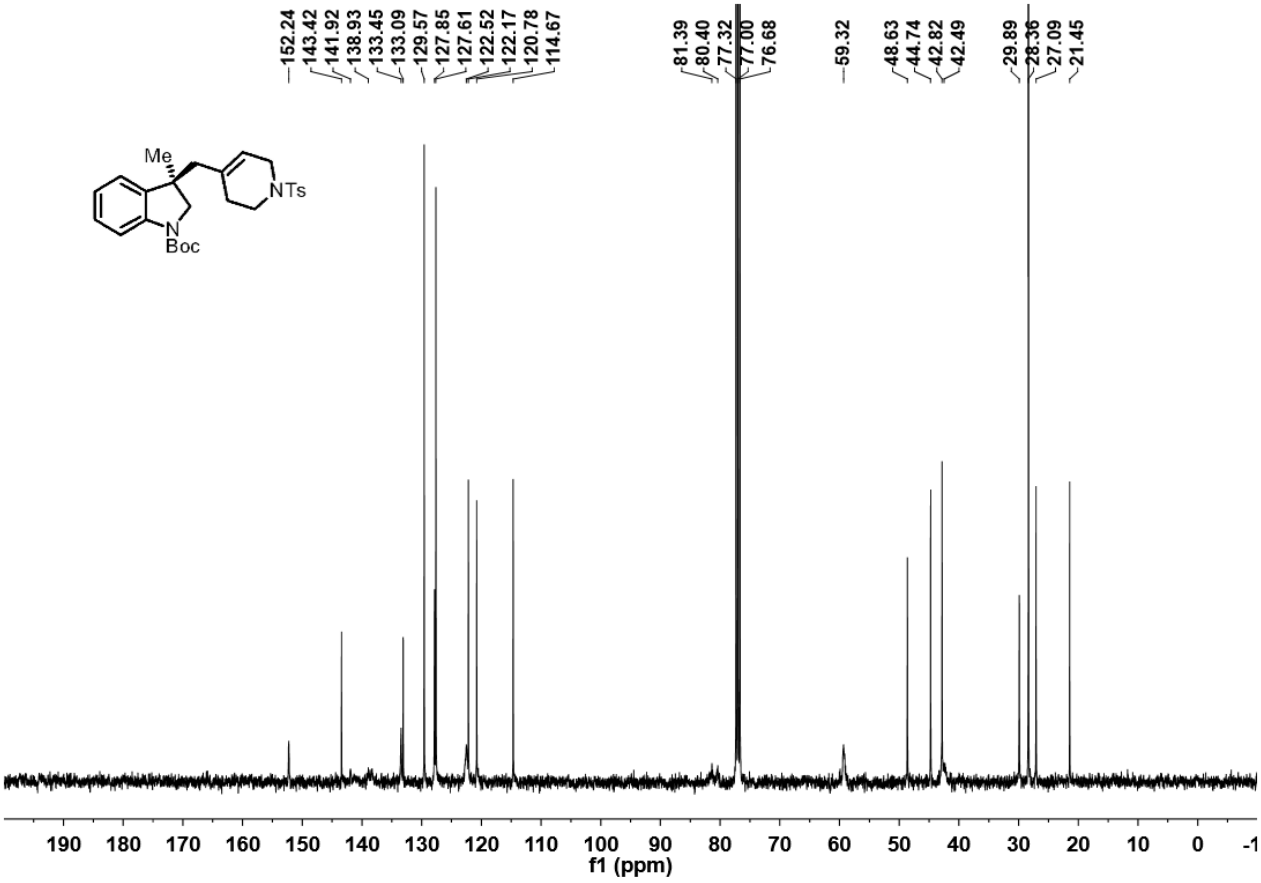
3am; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



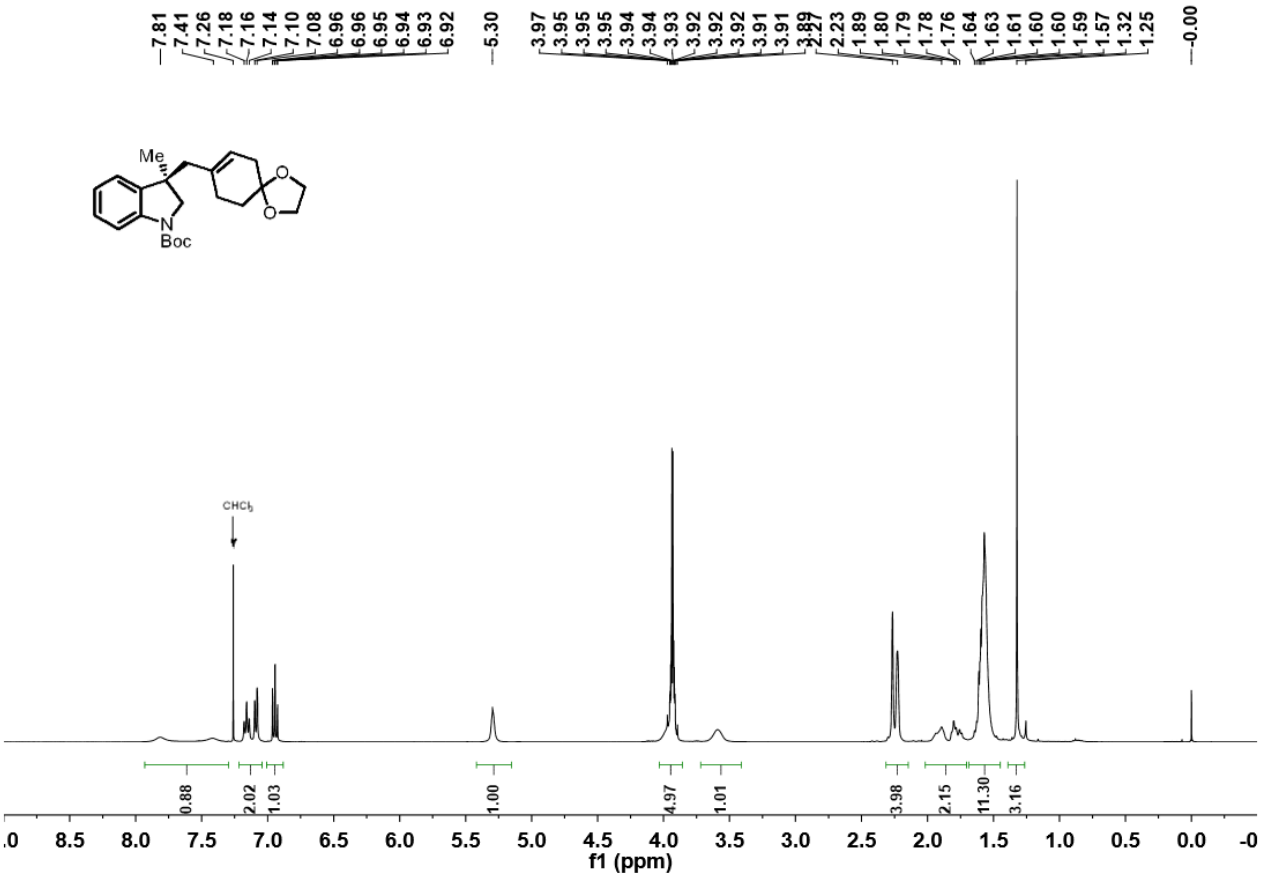


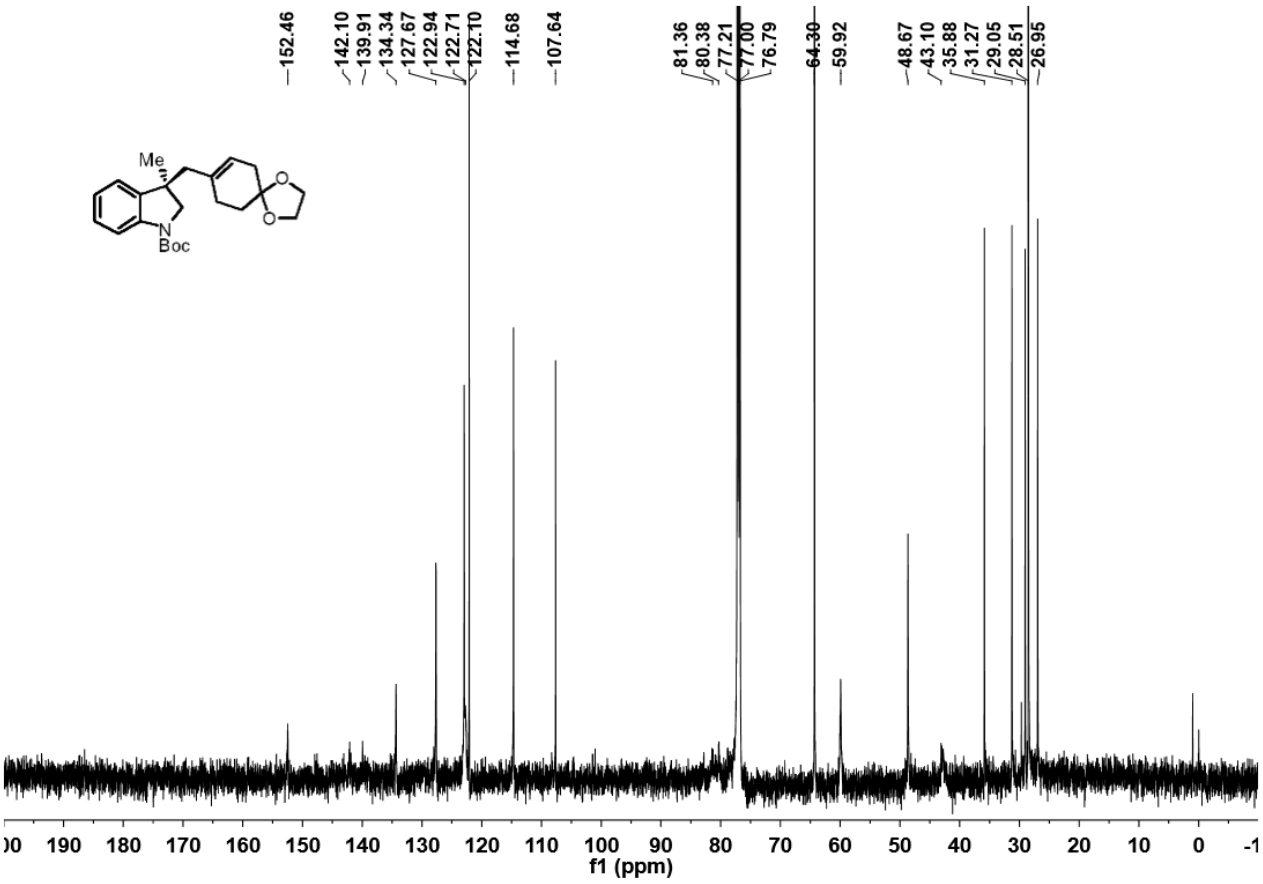
3an; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



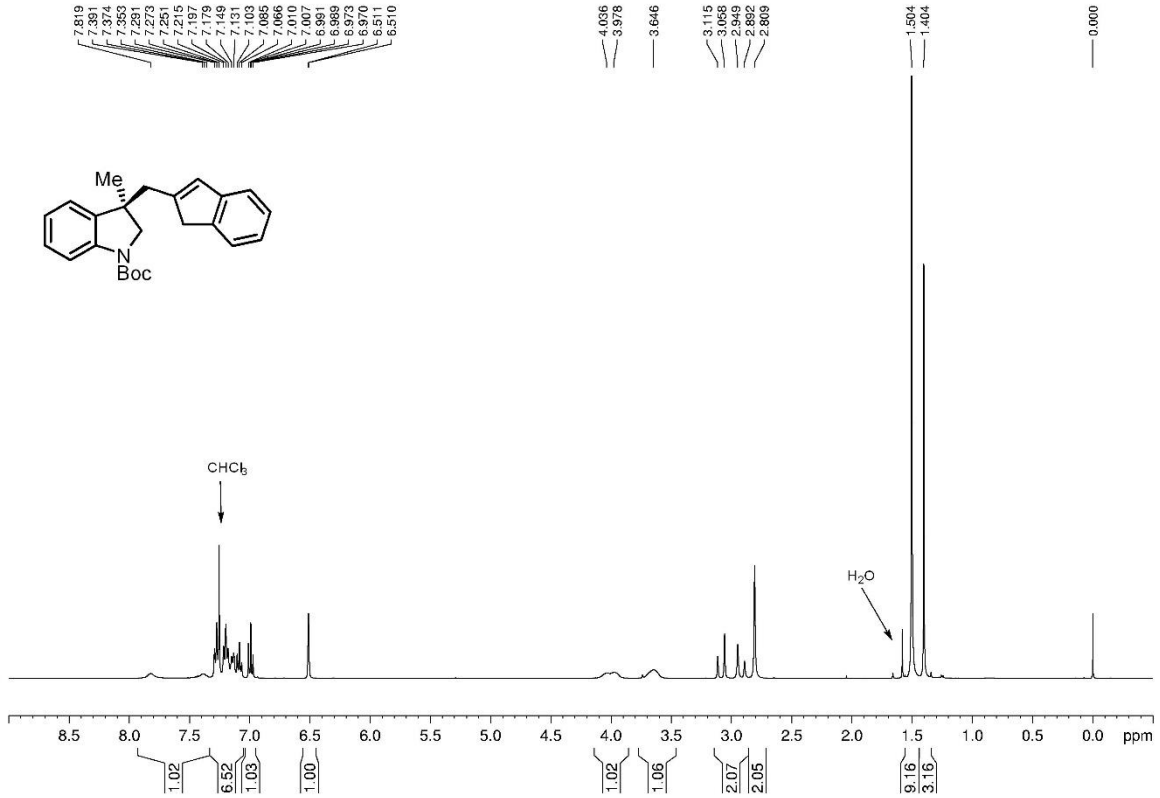


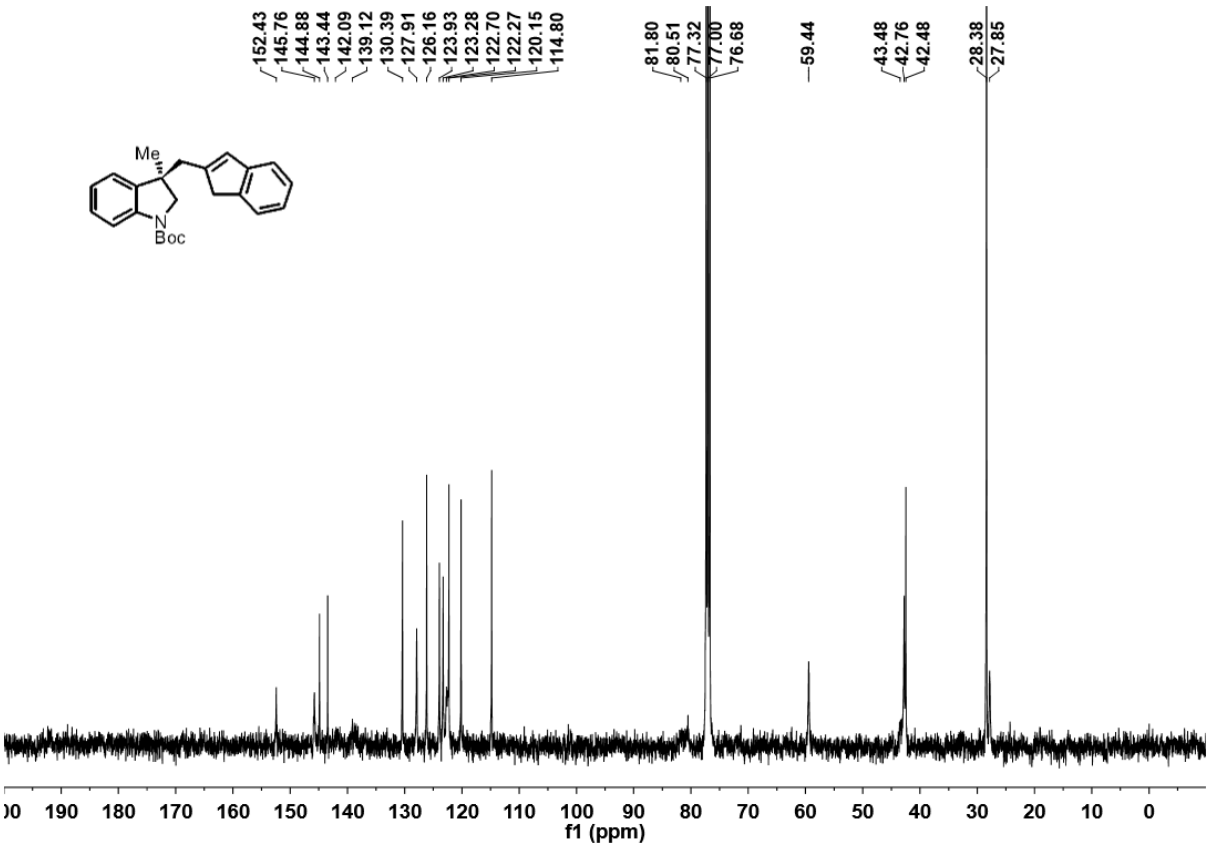
3ao; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)



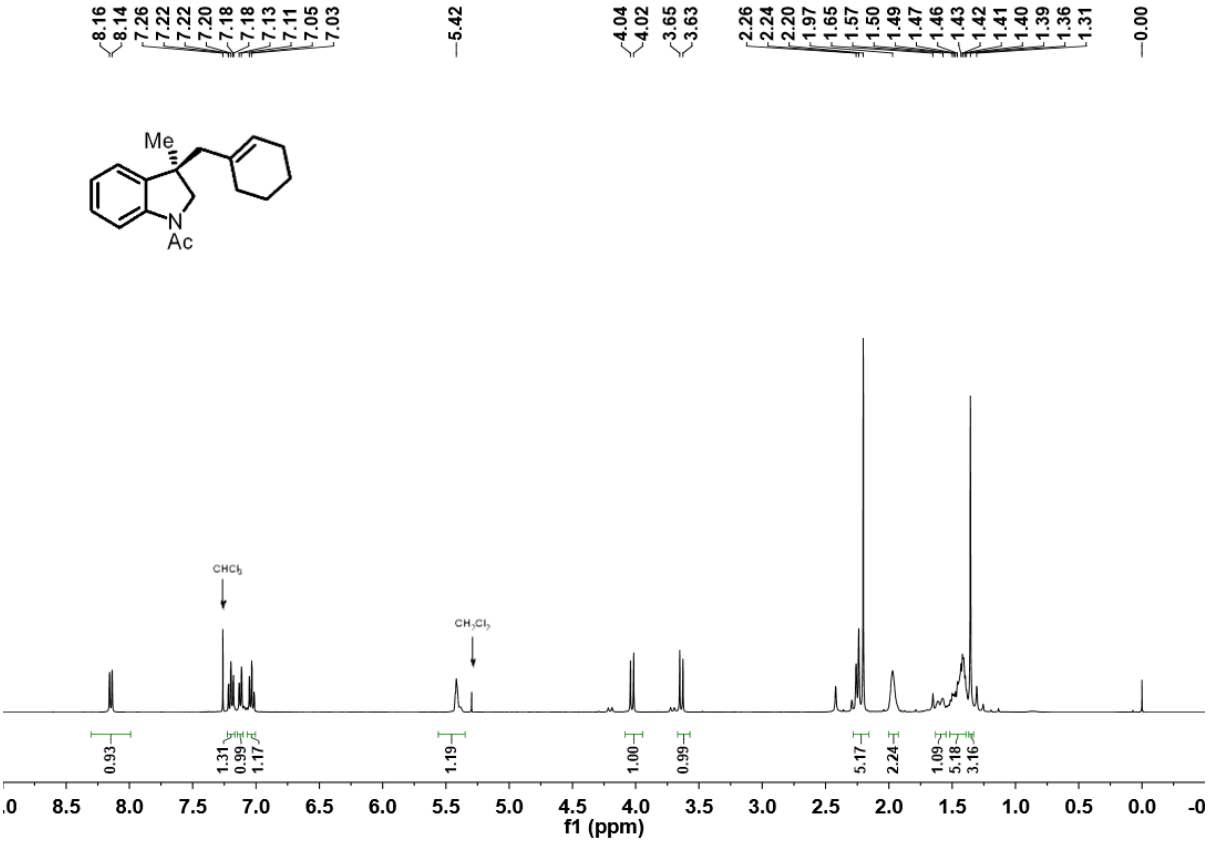


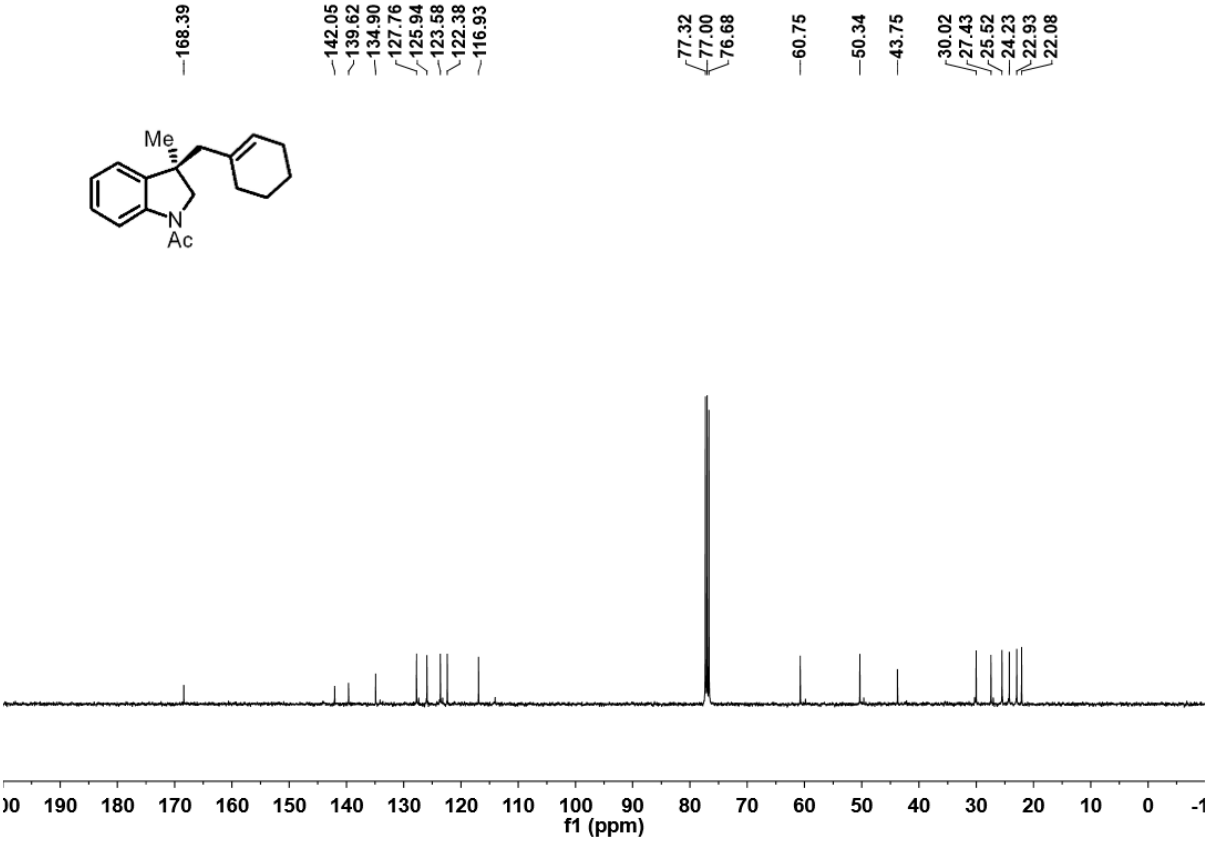
3ap; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



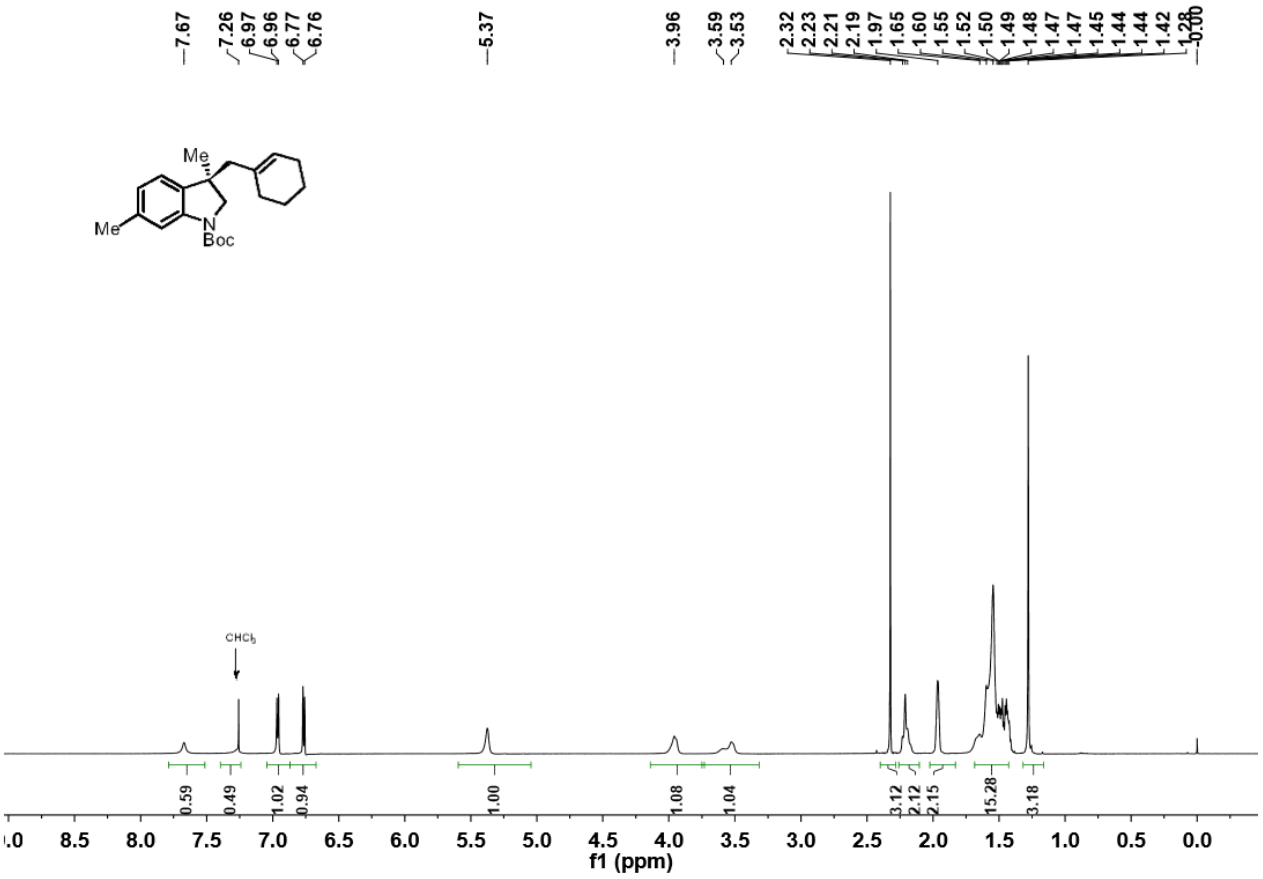


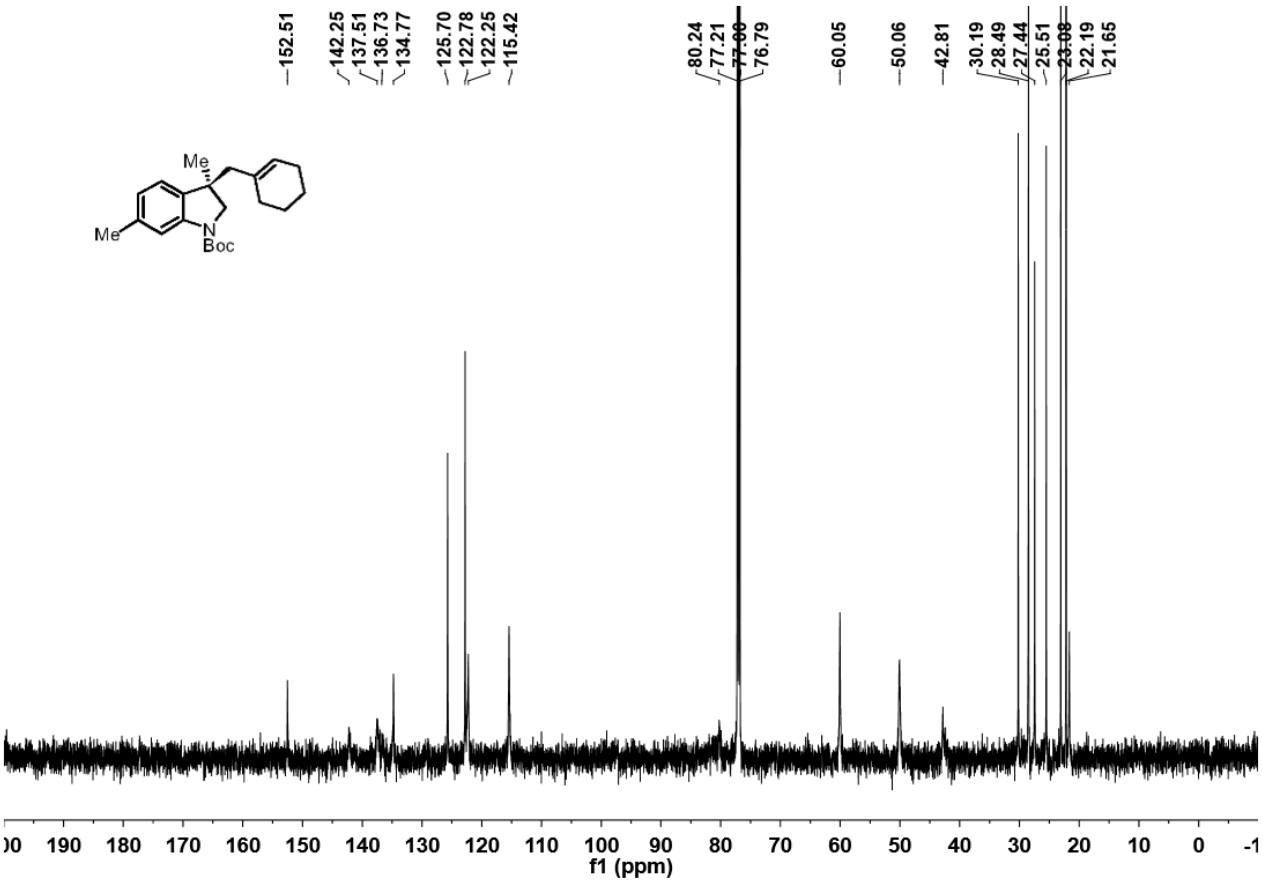
3aq; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



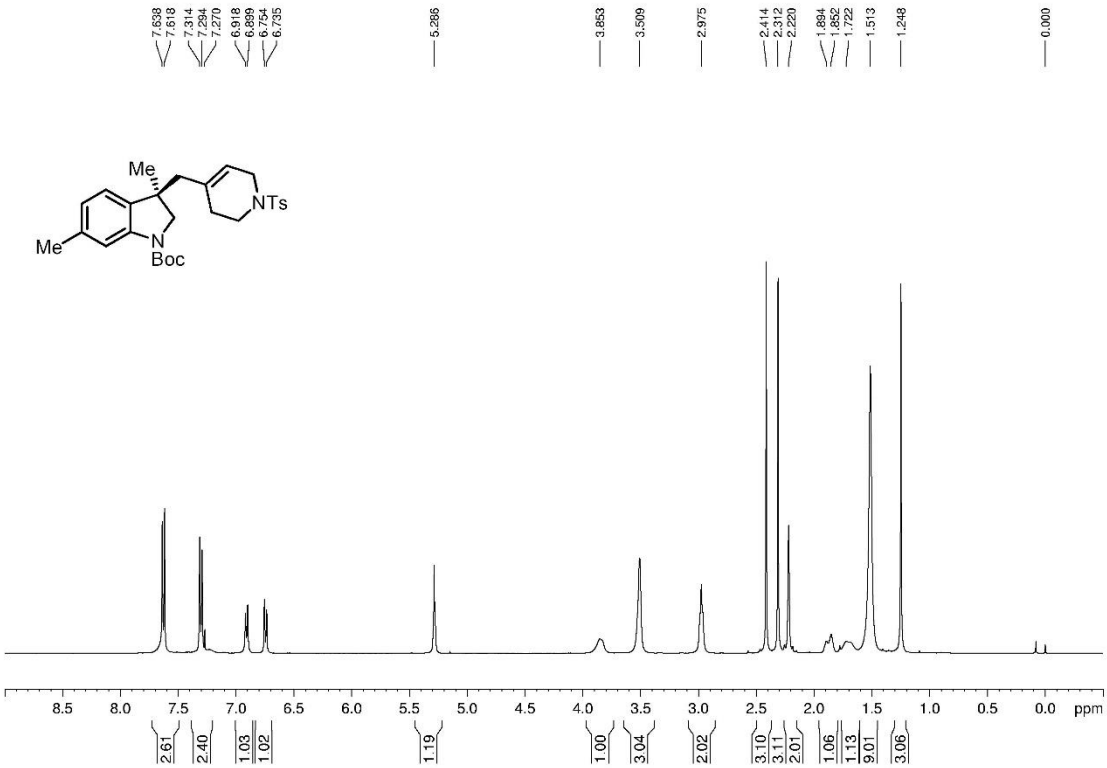


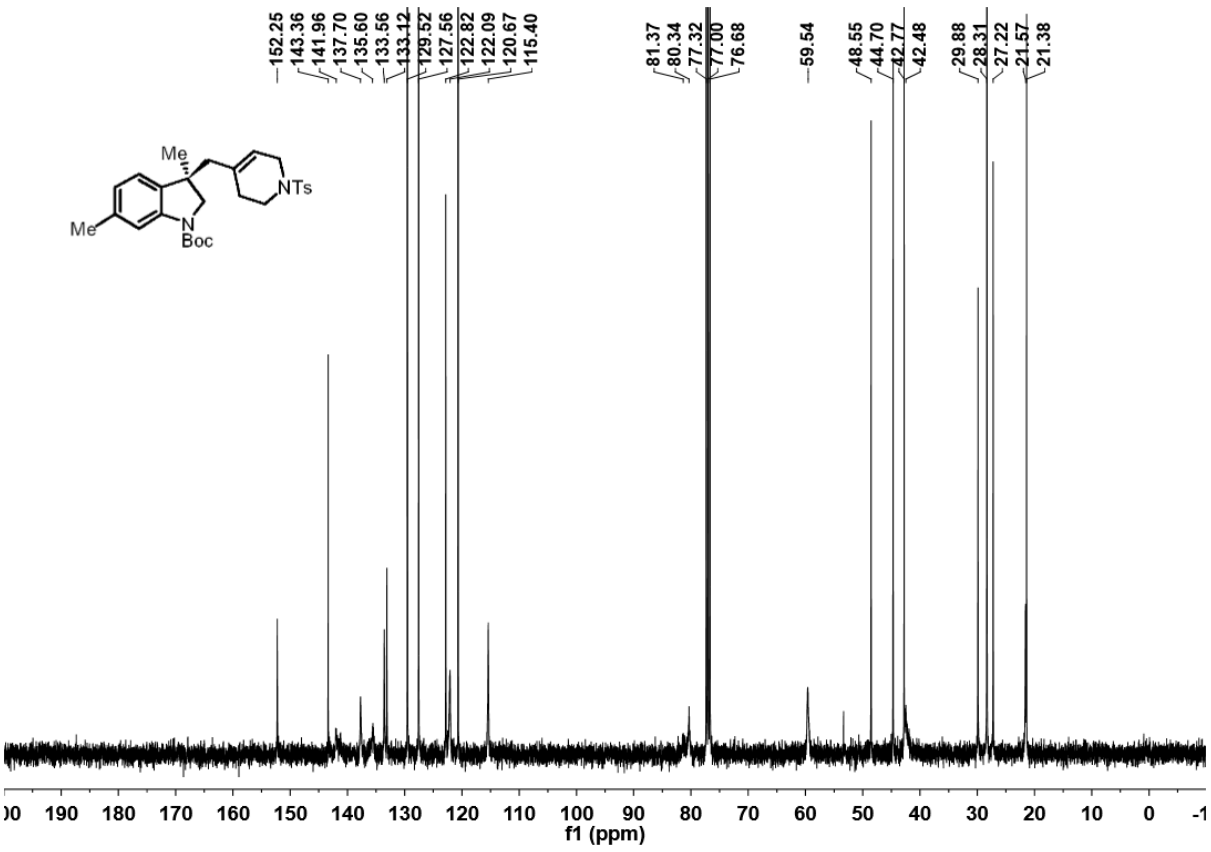
3ar; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)



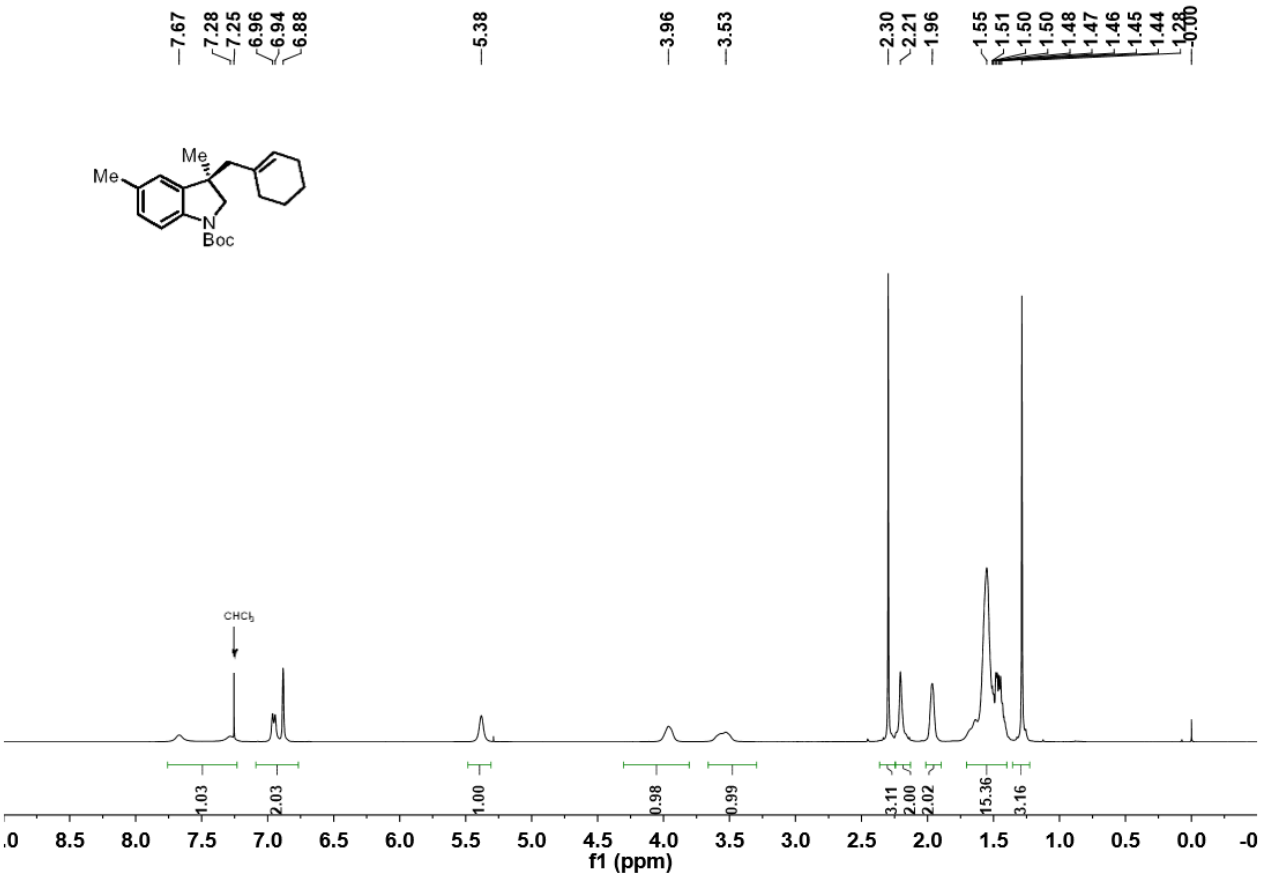


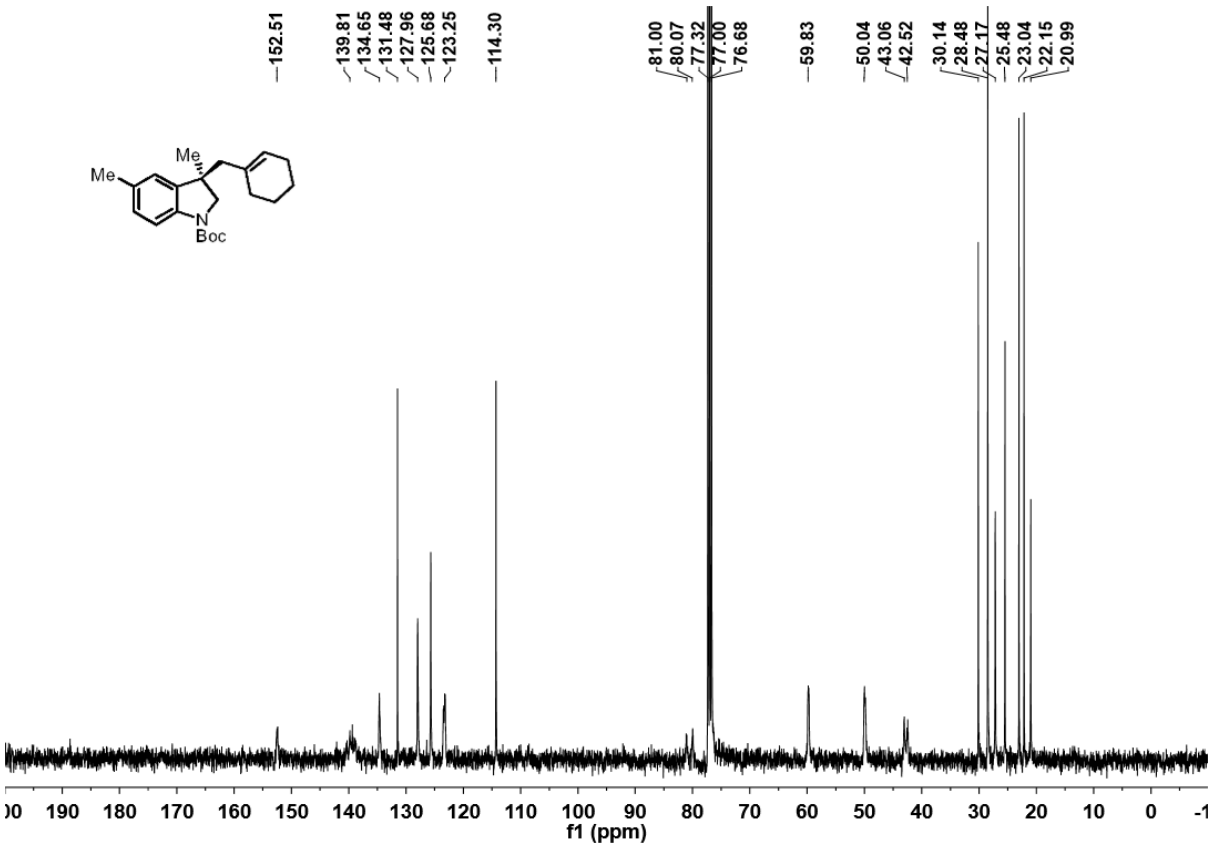
3as; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



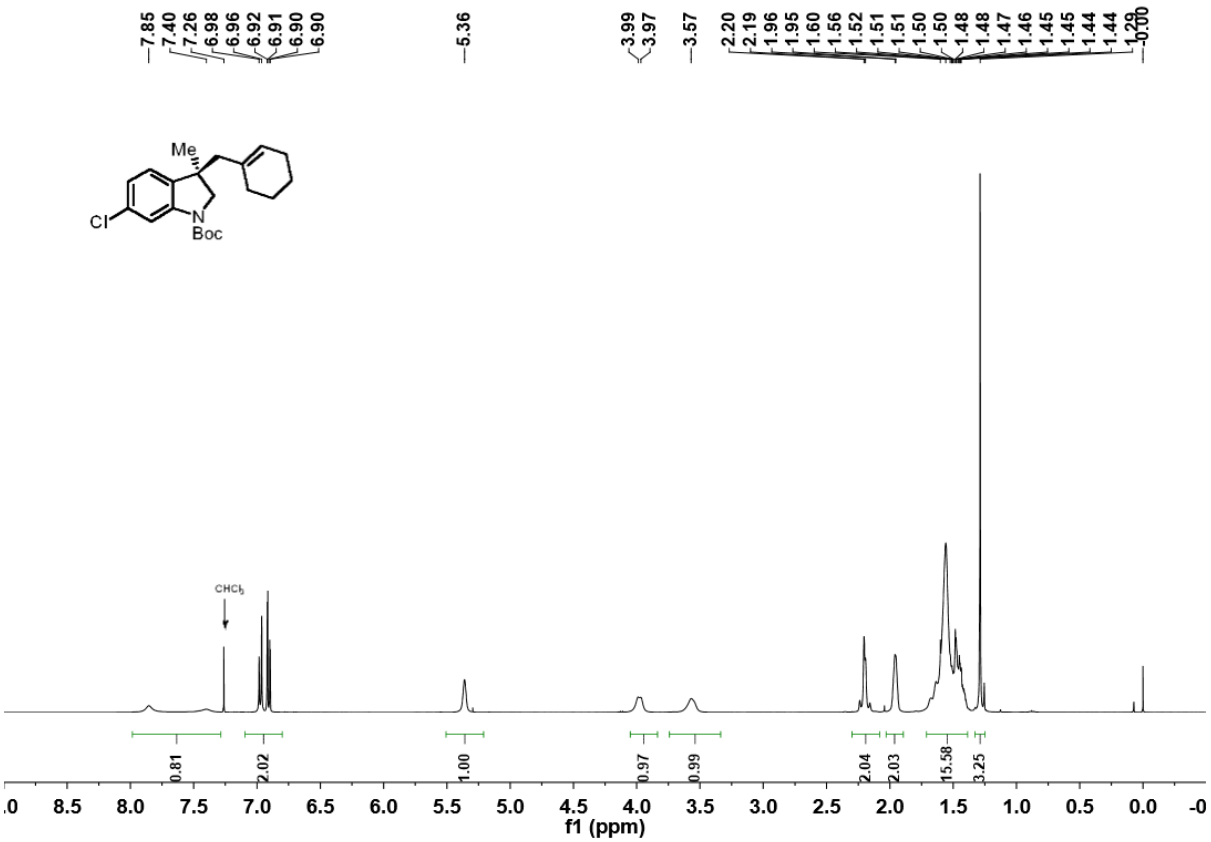


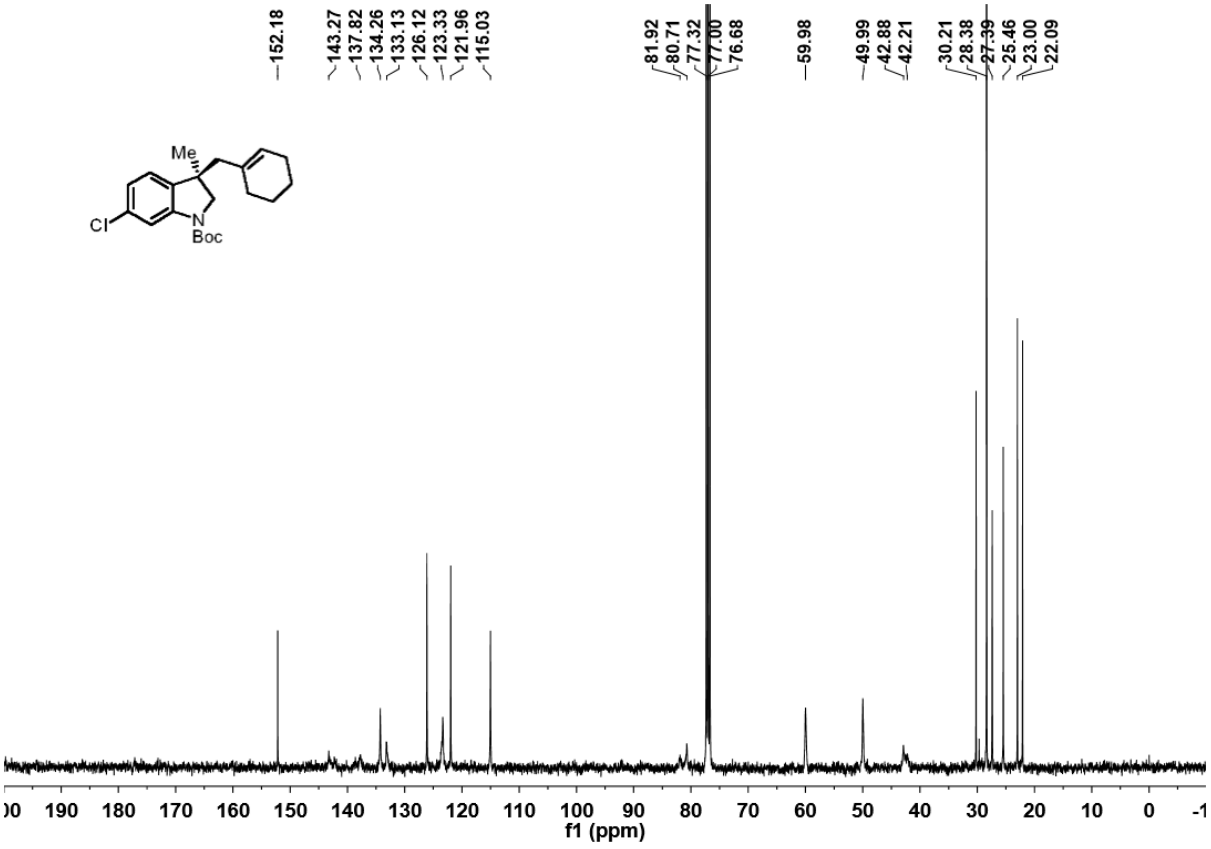
3at; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



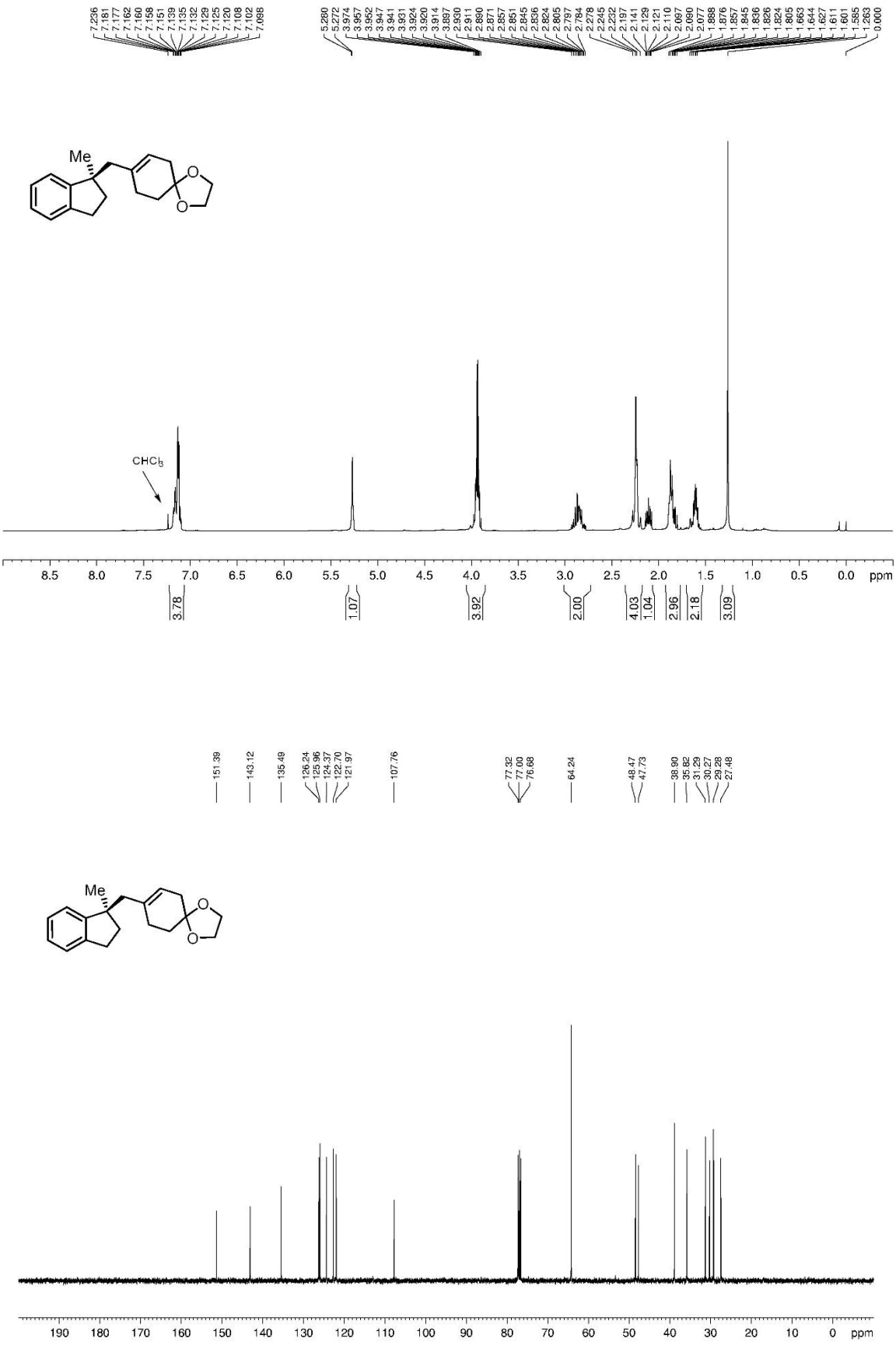


3au; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

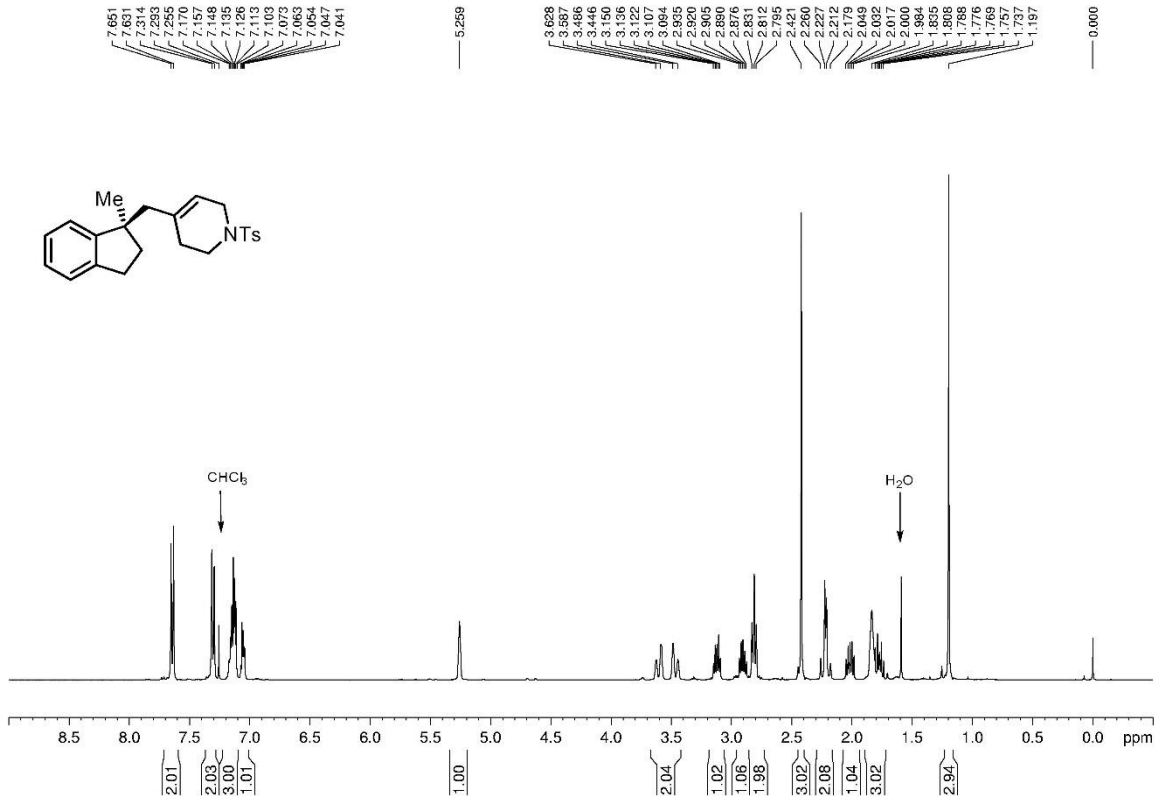


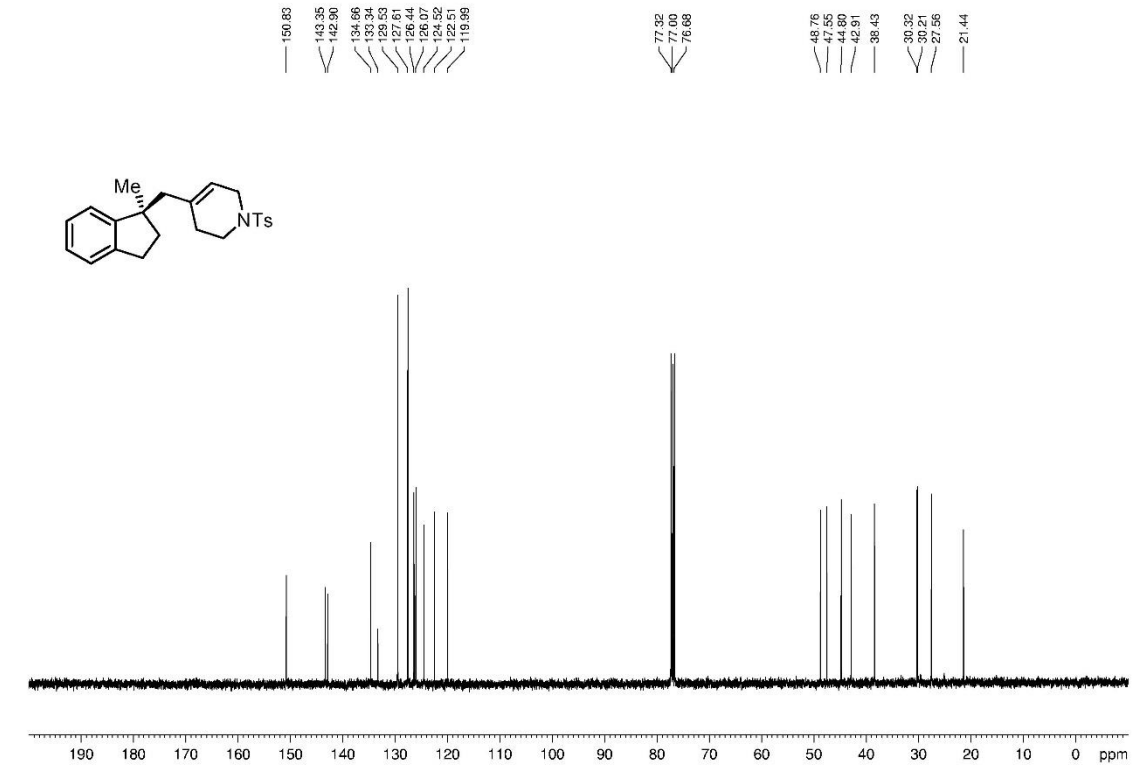


3av; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

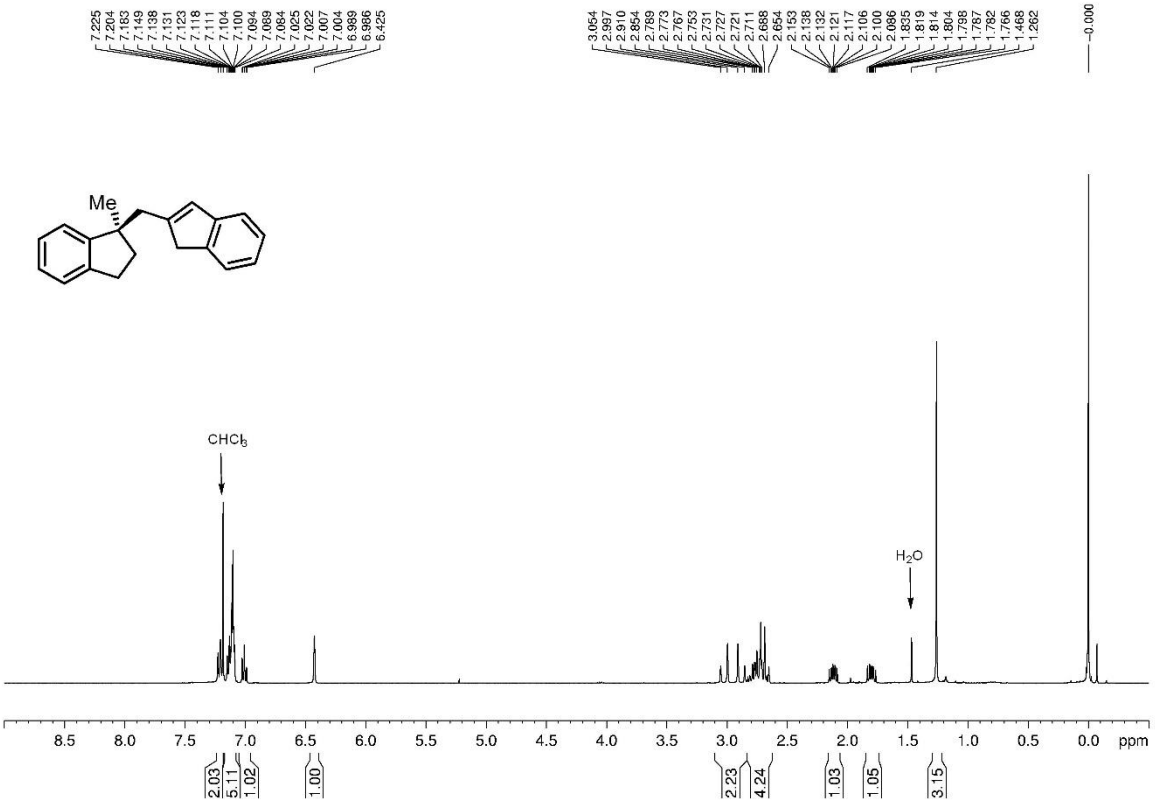


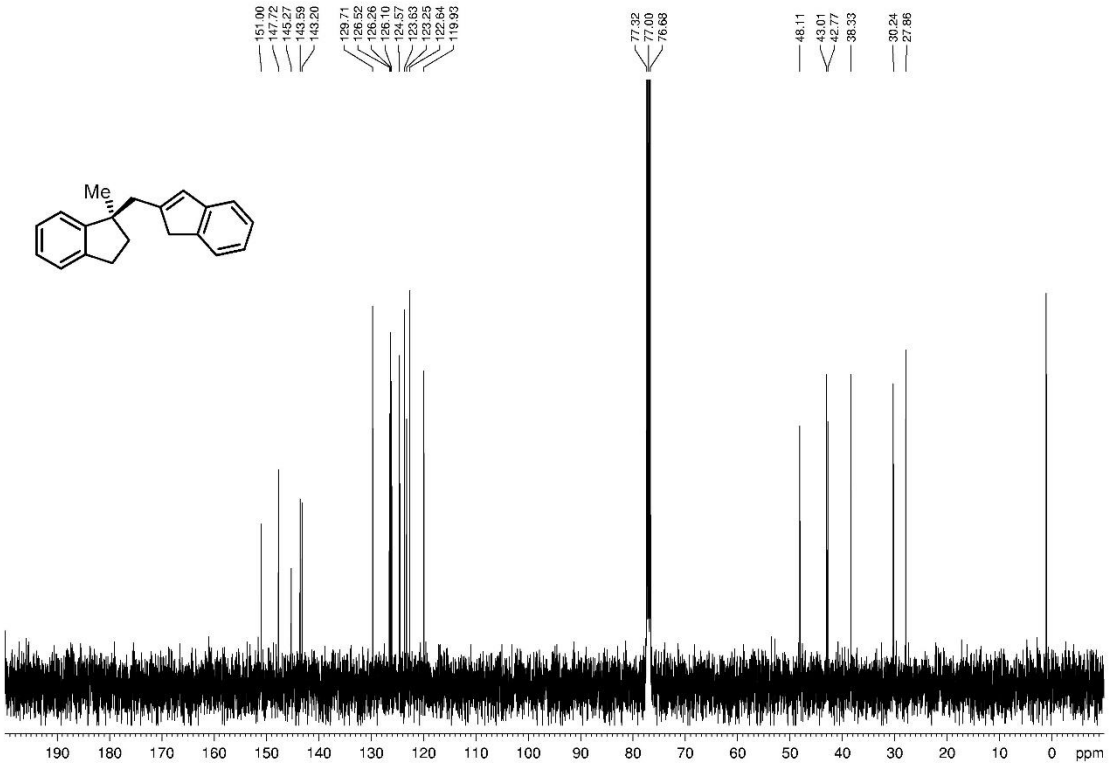
3aw; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



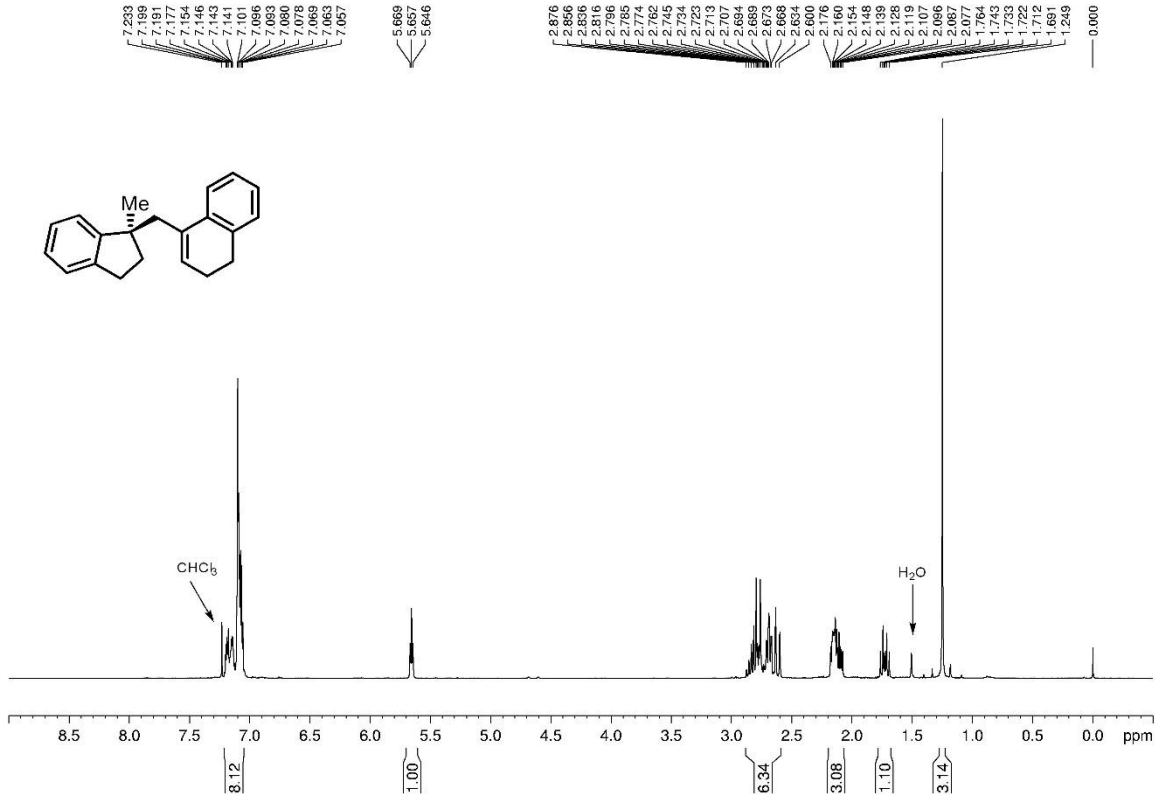


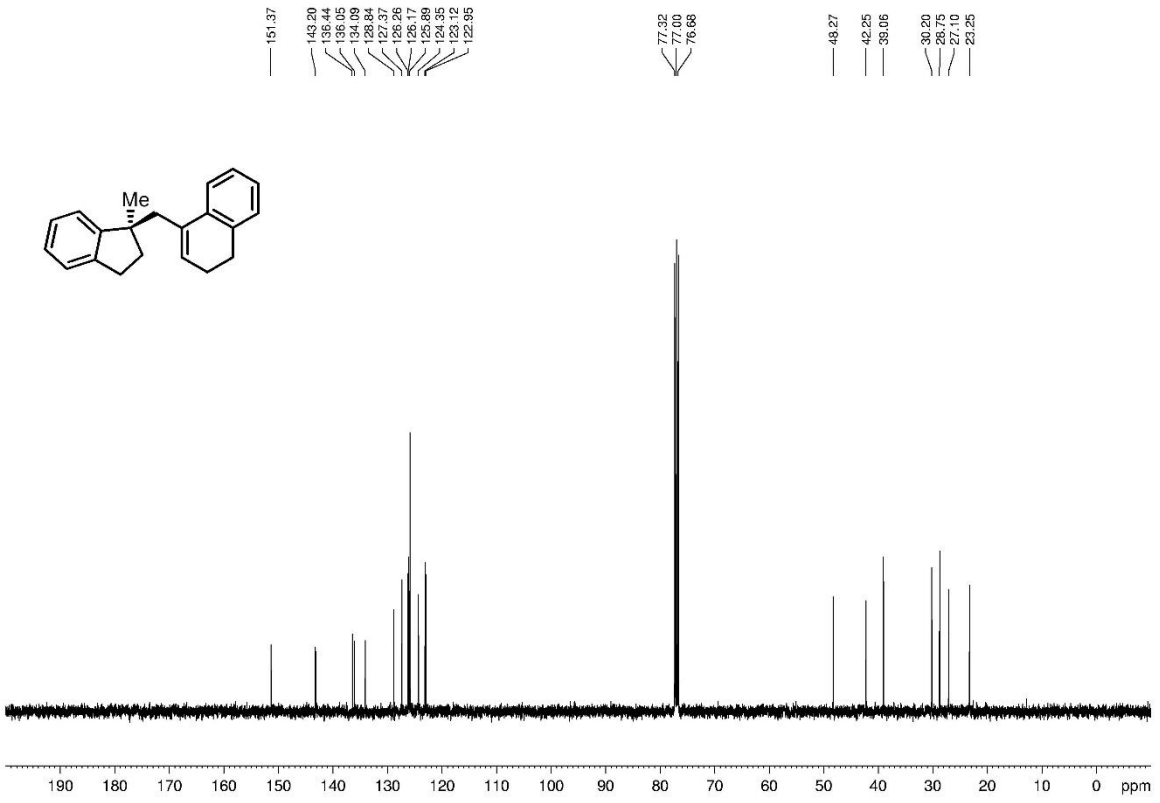
3ax; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



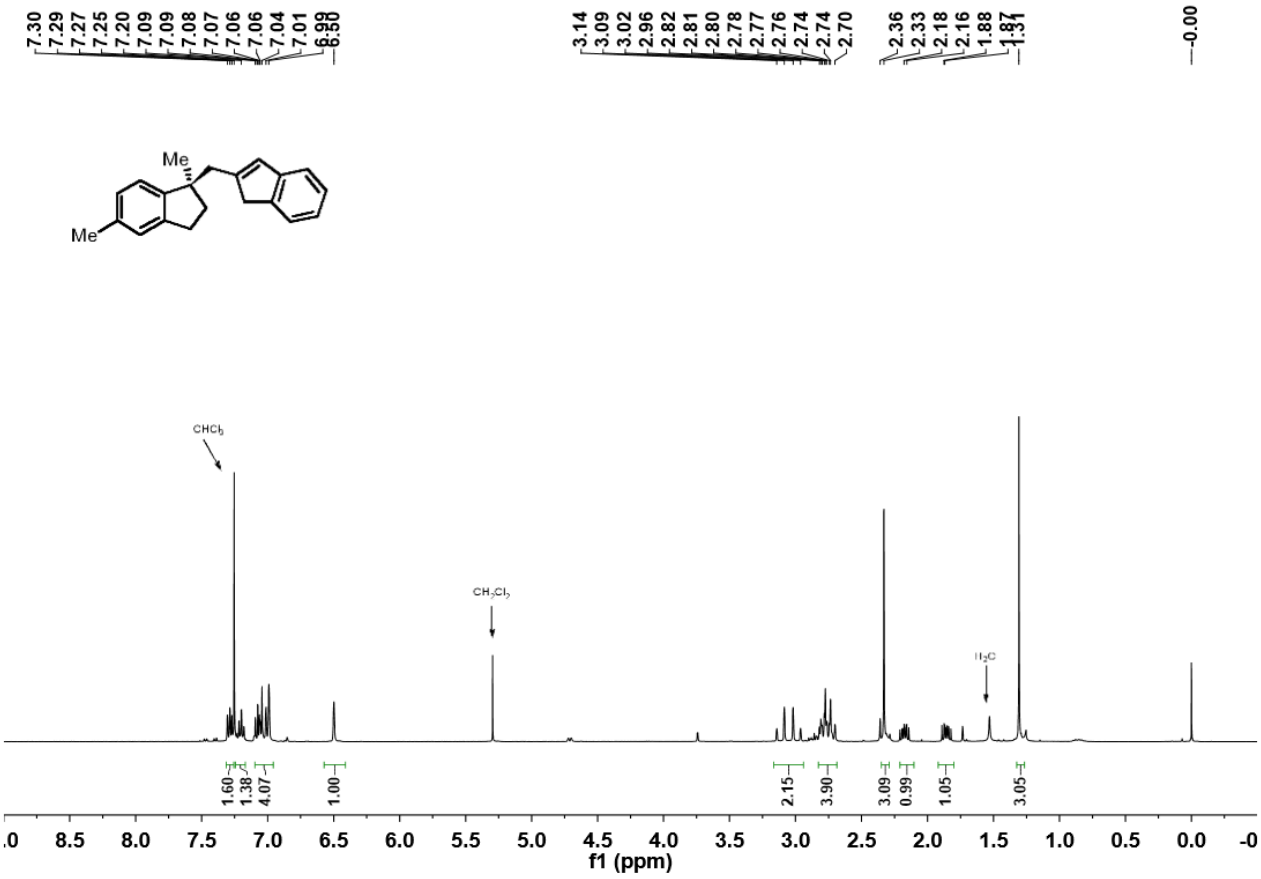


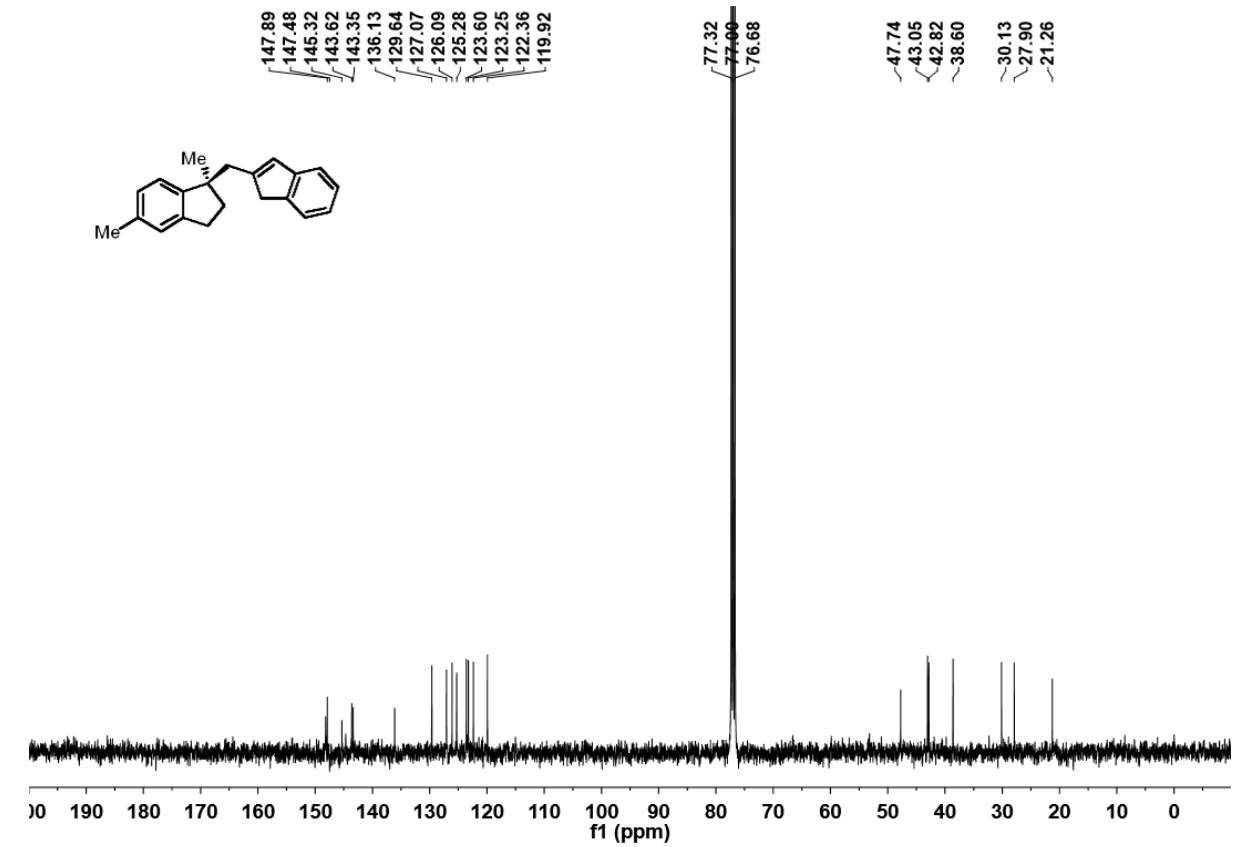
3ay; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



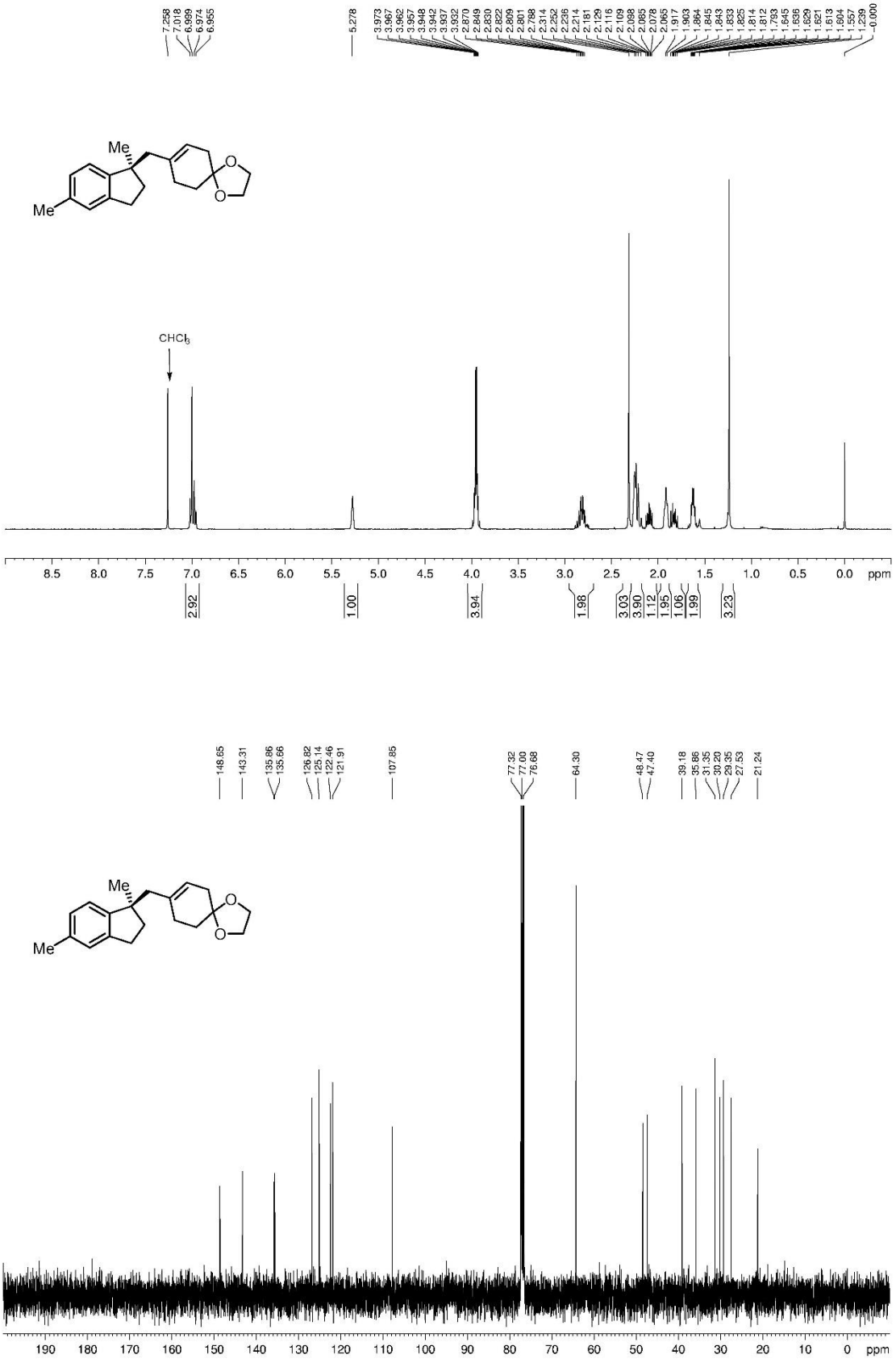


3az; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

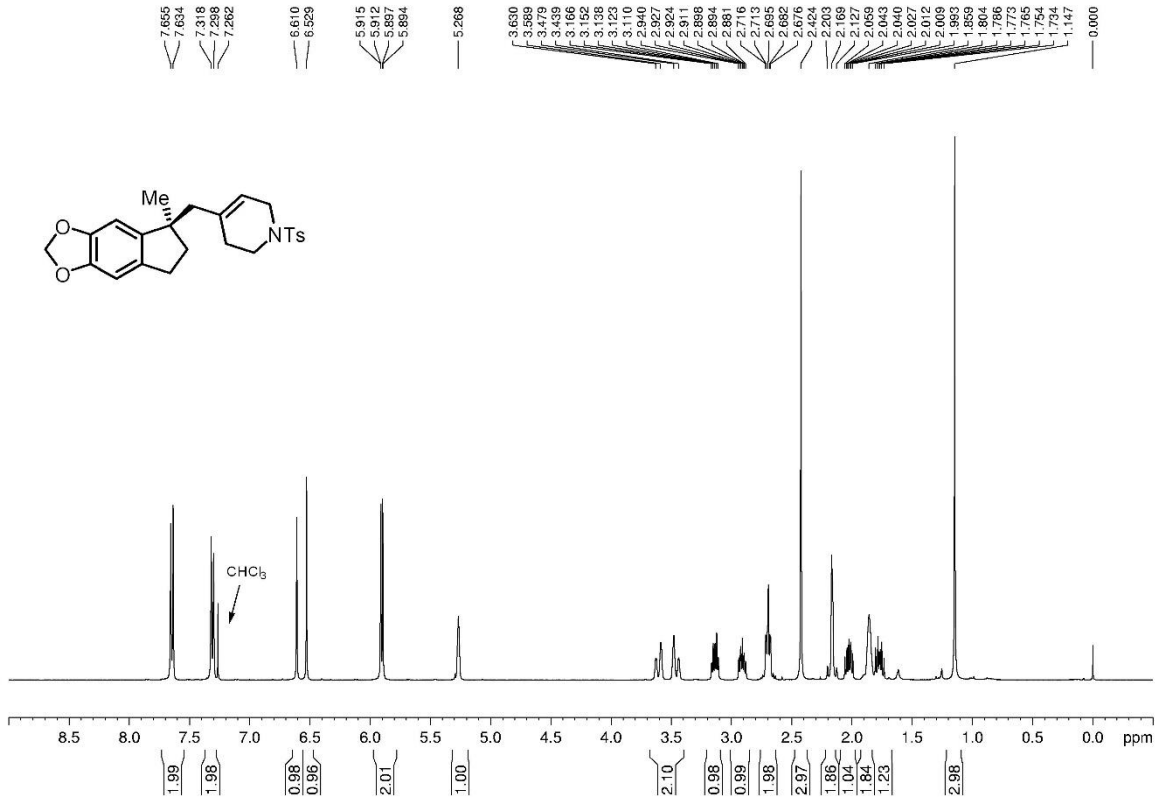


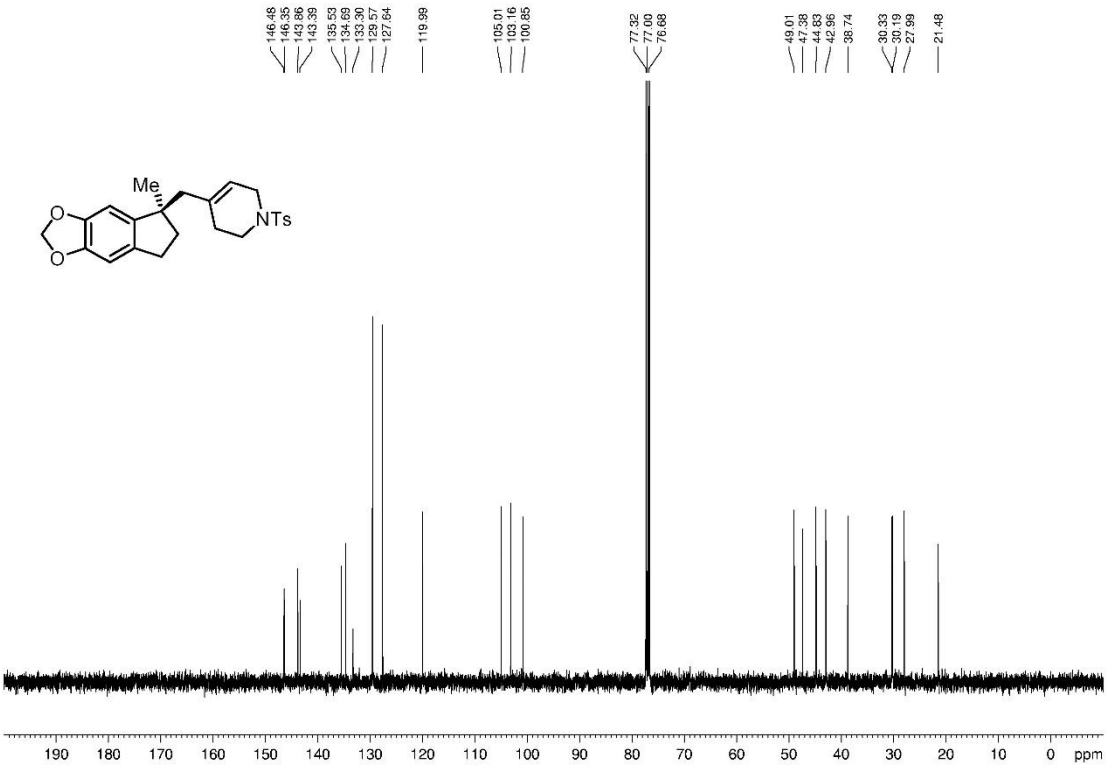


3ba; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

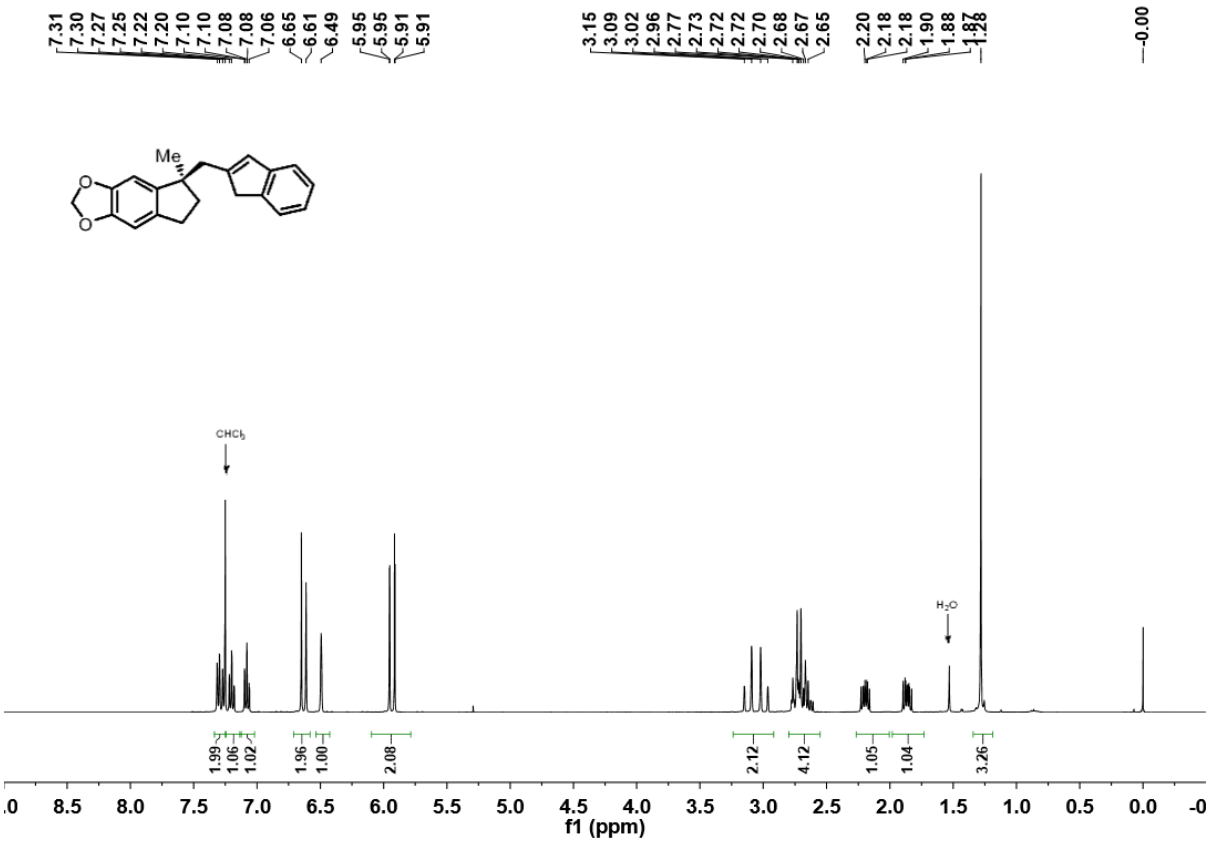


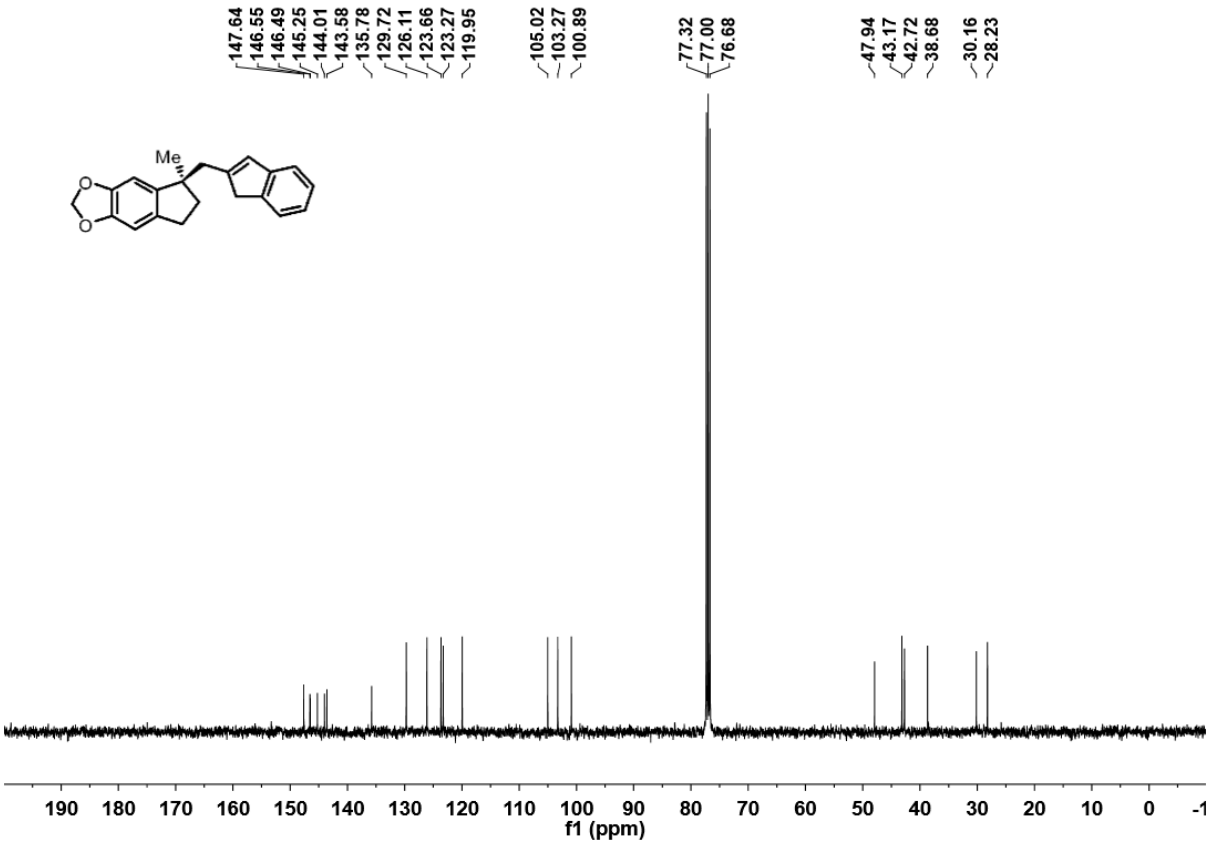
3bb; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



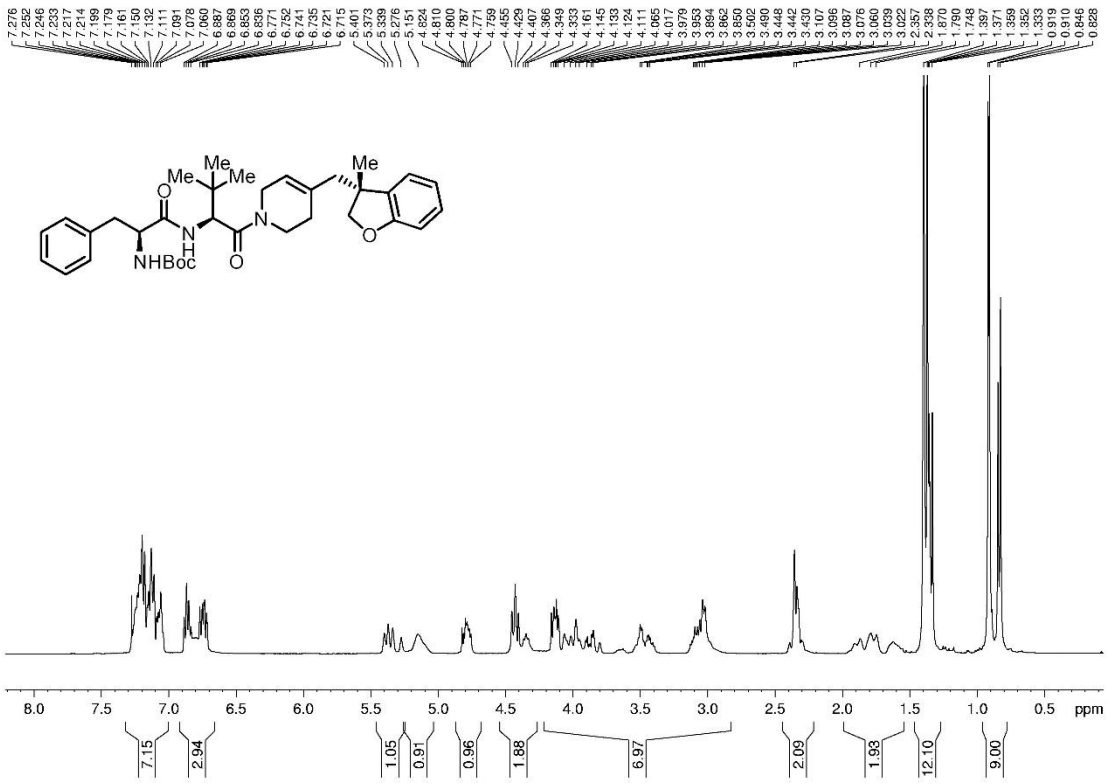


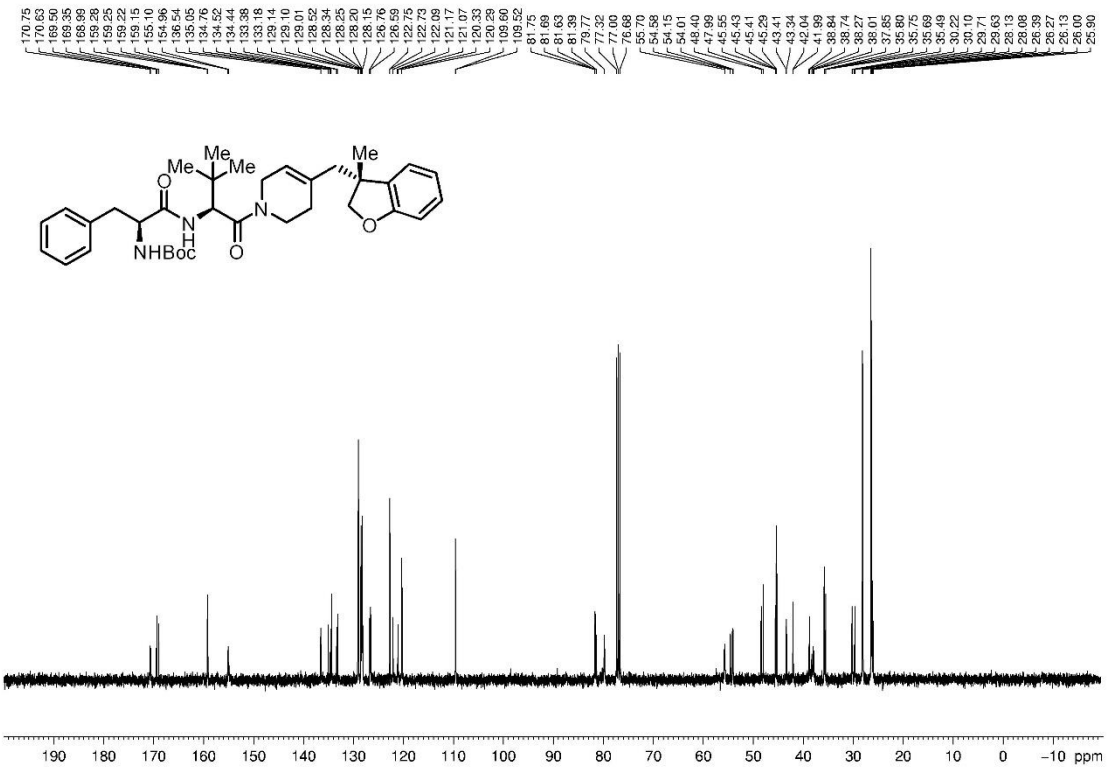
3bc; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



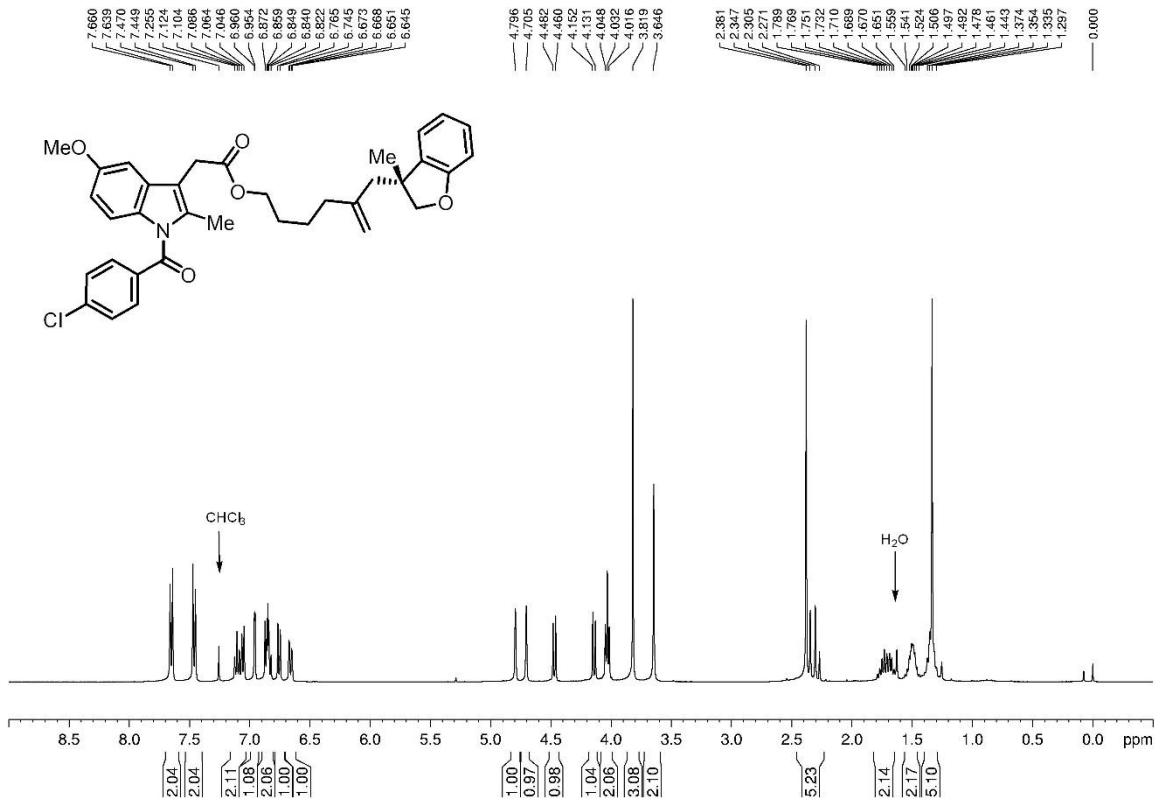


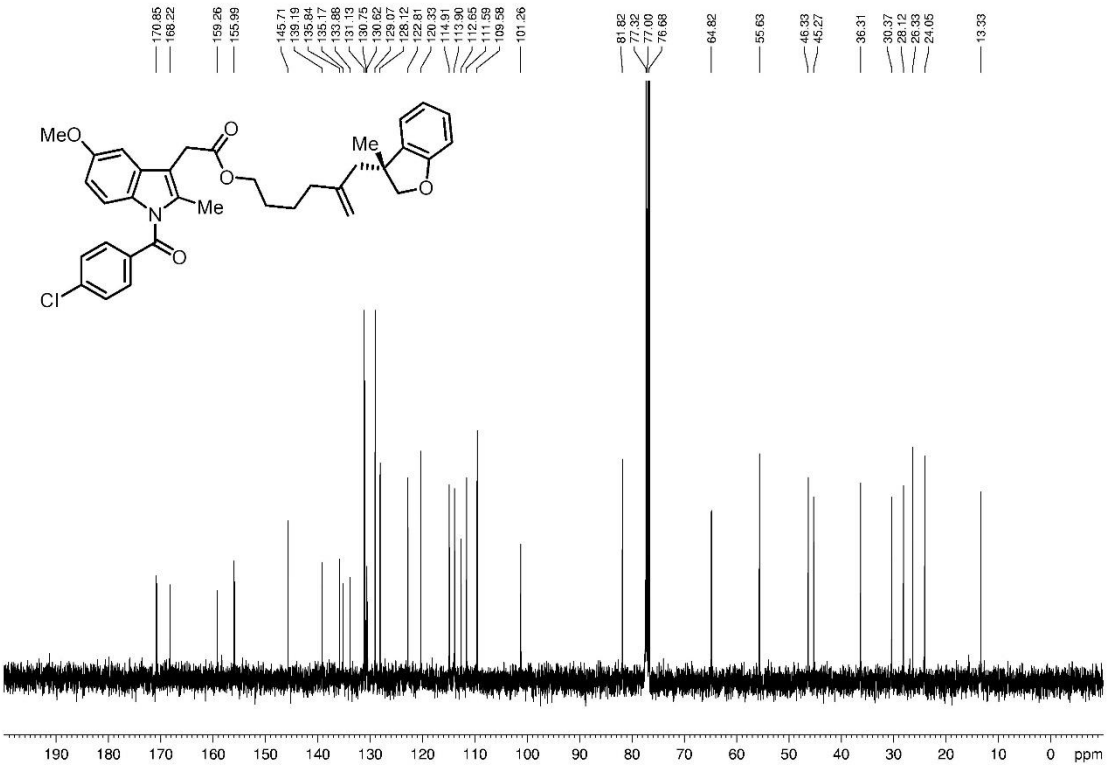
4; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



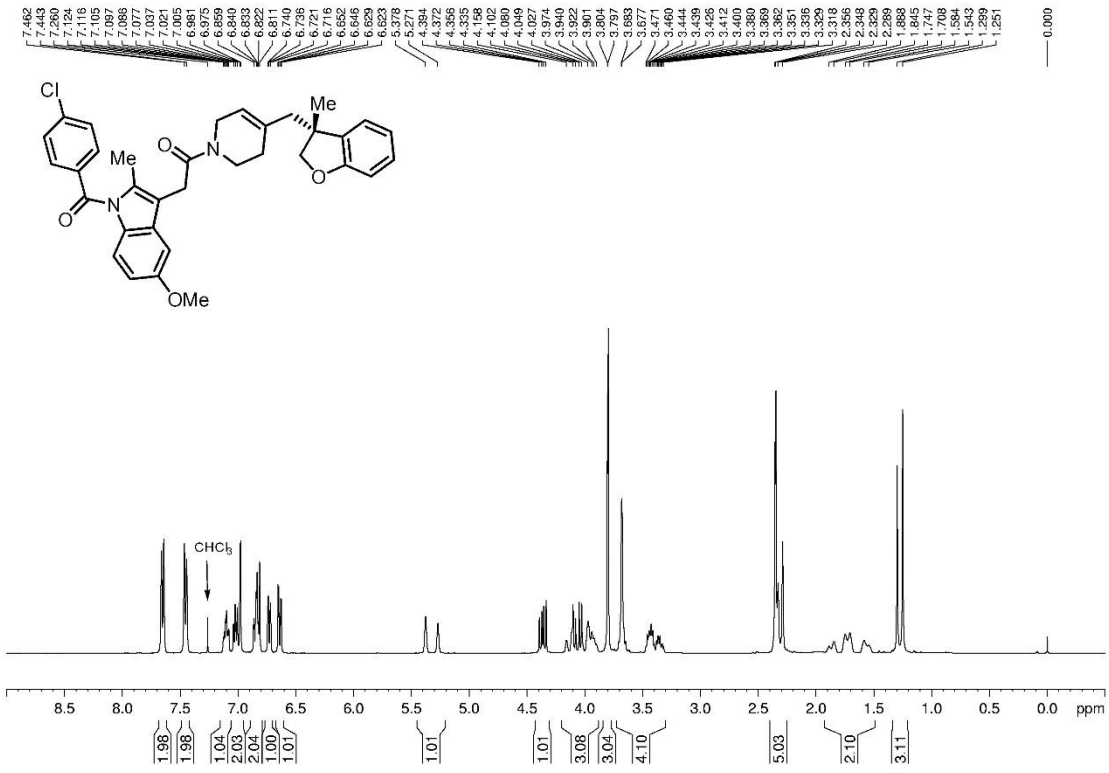


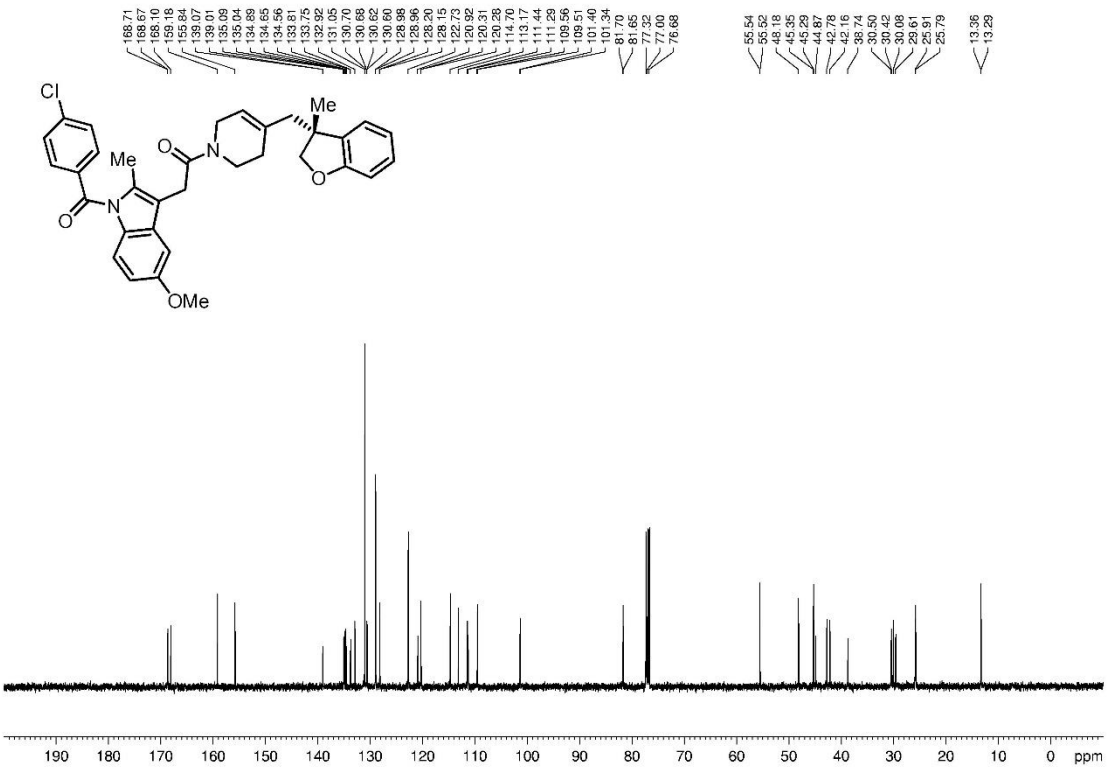
5; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



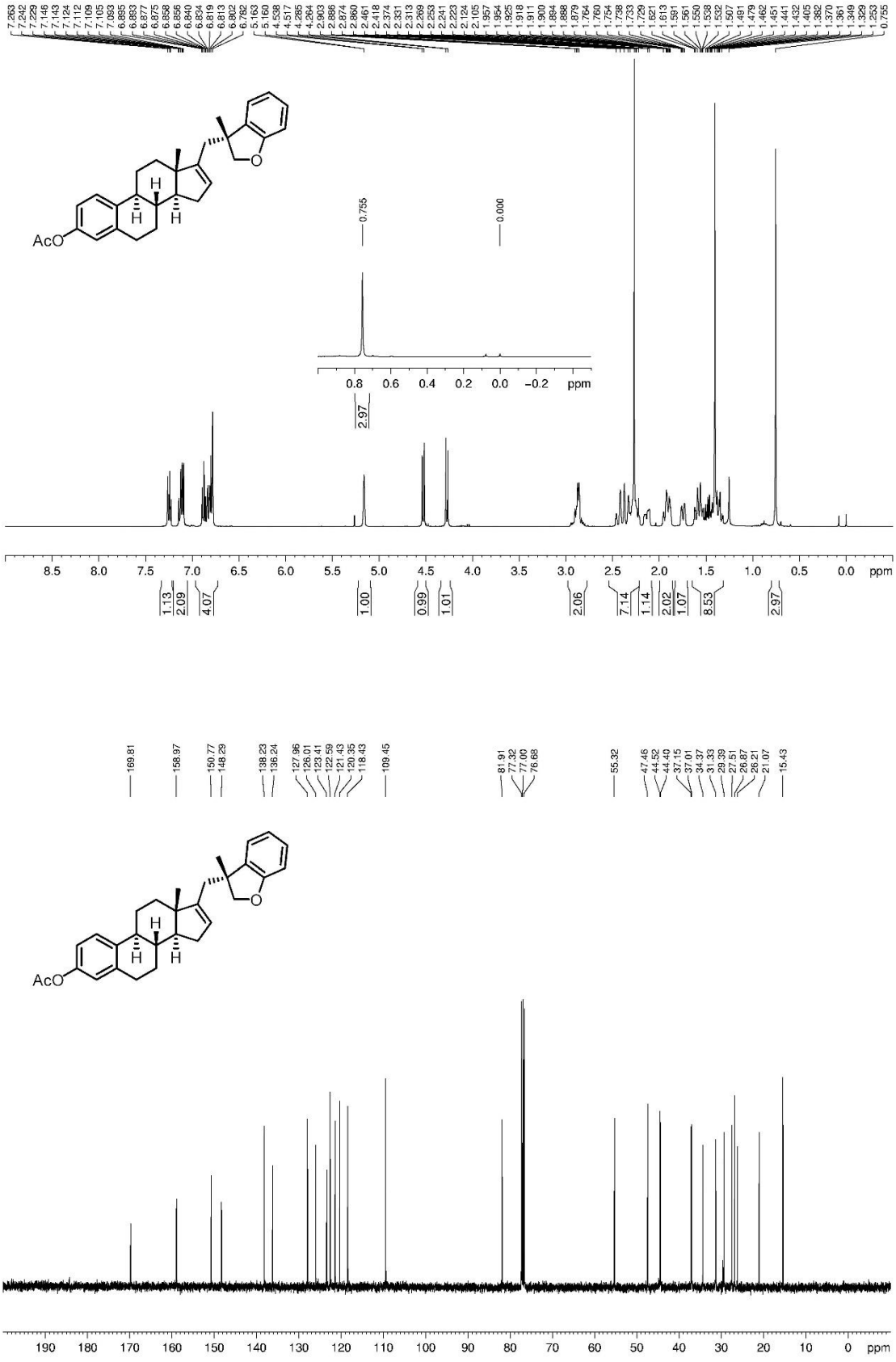


6; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)





7; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



8; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)