Electronic Supplementary Material (ESI) for Chemical Science.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Ni-Catalyzed Cross-Electrophile Coupling between Vinyl/Aryl and Alkl Sulfonates: Synthesis of Cycloalkenes and Modification of Peptides

Jicheng Duan, Yun-Fei Du, Xiaobo Pang, 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.

Table of Contents

1. General Information

Reagents and solvents:

Unless otherwise noted, all chemicals used in the preparation of starting materials were commercially available and were used as received without further purifications. All nickel catalysts, reductants, ligands 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.

Anhydrous *N*,*N*-dimethylacetamide (DMA), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile (CH_3CN), Tetrahydrofuran (THF), diethyl ether (Et_2O), dichloromethane (DCM), and toluene 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].

Analytical methods:

^1H and ^{13}C NMR spectra were collected on a Bruker AVANCE III 400MHz and Agilent-NMR-inova 600 MHz spectrometer at room temperature. All ^1H NMR spectra are reported in parts per million (ppm) downfield of tetramethylsilane (TMS) and were referenced to the signal of TMS (0 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.16 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 with Bruker-TENSOR27 spectrometer and only major peaks were reported in cm^{-1}. HRMS was performed on Bruker Apex II FT-ICR mass instrument (ESI) and waters GCT Premier TOFMS (EI). GC analysis was performed on Thermo Scientific TRACE 1300. GC-MS data was collected on Thermo Scientific TRACE DSQ GC-MS. HPLC analysis was recorded on Thermo Scientific UltiMate 3000 and SHIMADZU LC-20AD. Thin layer chromatography were carried out using XINNUO SGF254 TLC plates. Flash chromatography was performed with XINNUO silica gel (200-300 mesh). The yields reported in the manuscript refer to isolated yields.

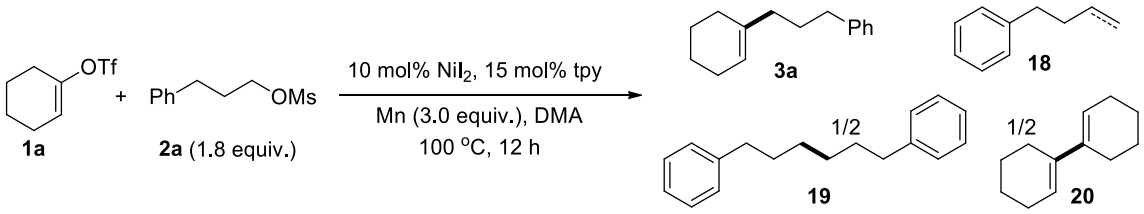
2. Optimization of Reaction Conditions

2.1 The reaction of vinyl triflate with alkyl mesylate

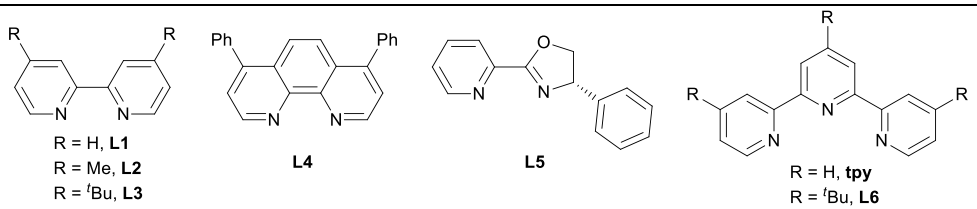
General procedure:

The procedure was conducted in the argon-filled glove box. To a reaction tube containing catalyst (0.02 mmol, 10 mol %), ligand (0.03 mmol, 15 mol %) and reductant (0.6 mmol, 3.0 equiv.) was added a solution of vinyl triflate **1a** (46.0 mg, 0.2 mmol) and alkyl mesylate **2a** (77.0 mg, 0.36 mmol) in DMA (2 mL). It was sealed and removed from the glove box, and the reaction mixture was stirred at 100 ^{o}C for 12 h. The reaction mixture was diluted with ethyl acetate (15 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).

Table S1 Optimization of reaction conditions[a]

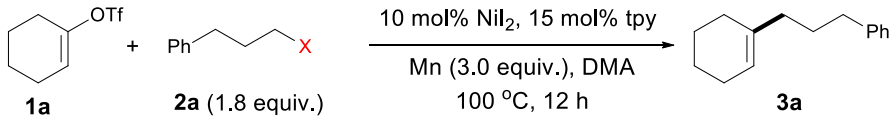


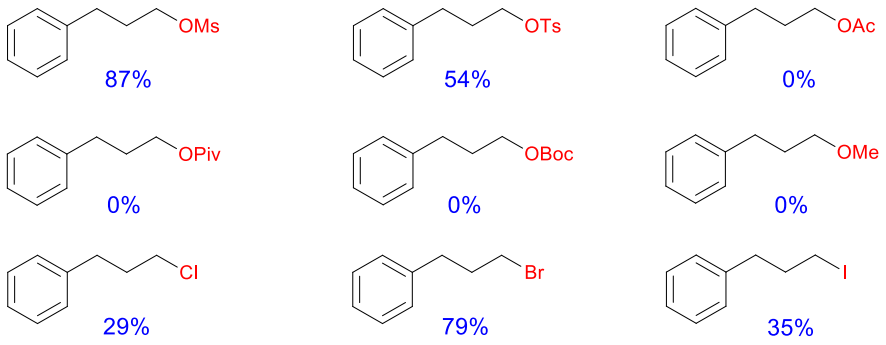
entry	change of conditions	**3a** (%)	**18** (%)	**19** (%)	**20** (%)
1	none	87 (81)[b]	20	16	5
2	$NiCl_2$ instead of NiI_2	trace	4	0	23
3	$NiBr_2$ instead of NiI_2	15	7	3	20
4	$NiBr_2$ with NaI (0.5 equiv.)	63	13	49	9
5	NiI_2 with NaI (0.5 equiv.)	38	17	63	13
6	**L1** instead of tpy	26	27	18	11
7	**L2** instead of tpy	34	55	10	38
8	**L3** instead of tpy	28	49	9	31
9	**L4** instead of tpy	37	75	3	30
10	**L5** instead of tpy	21	31	18	21
11	**L6** instead of tpy	77	10	41	8
12	Zn instead of Mn	4	6	0	6
13	TDAE[c] instead of Mn	8	82	trace	0
14	no Ni or Mn	0	0	0	0



[a]**1a** (0.2 mmol) was used and reacted for 12 h; the yields were determined by GC analysis with dodecane as internal standard. [b]Isolated yield. [c]TDAE: tetrakis(dimethylamino)ethylene.

Table S2 Reaction of vinyl triflate **1a** with various alkyl electrophiles[a]

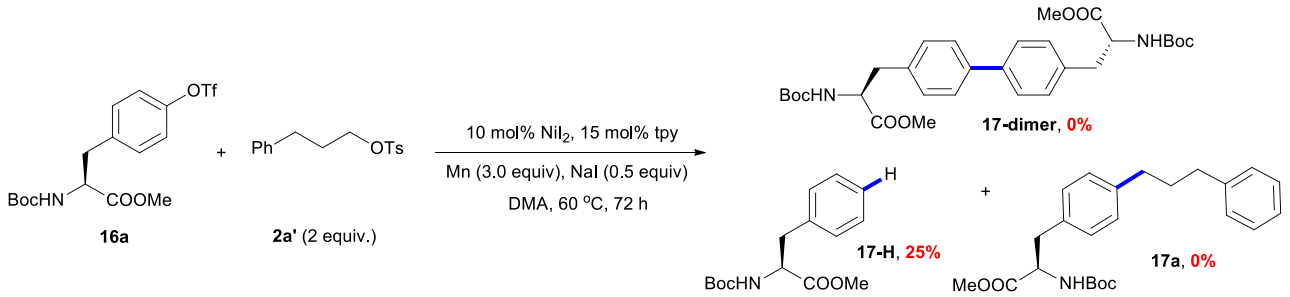




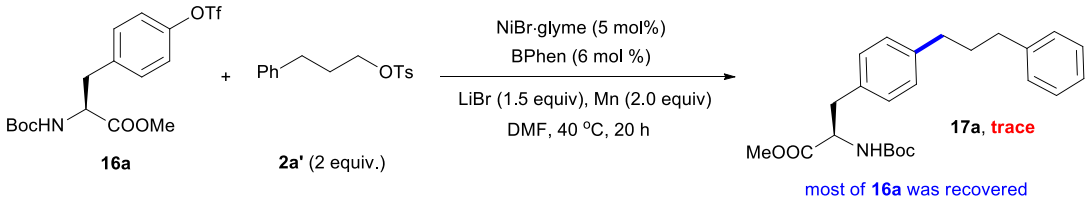
[a]**1a** (0.2 mmol) was used and reacted for 12 h; the yields were determined by GC analysis with dodecane as internal standard.

2.2 Modification of tyrosine in peptide with alkyl tosylate

(a) The reaction under the standard conditions for synthesis of cycloalkene



(b) The reaction under the Hosoya's conditions

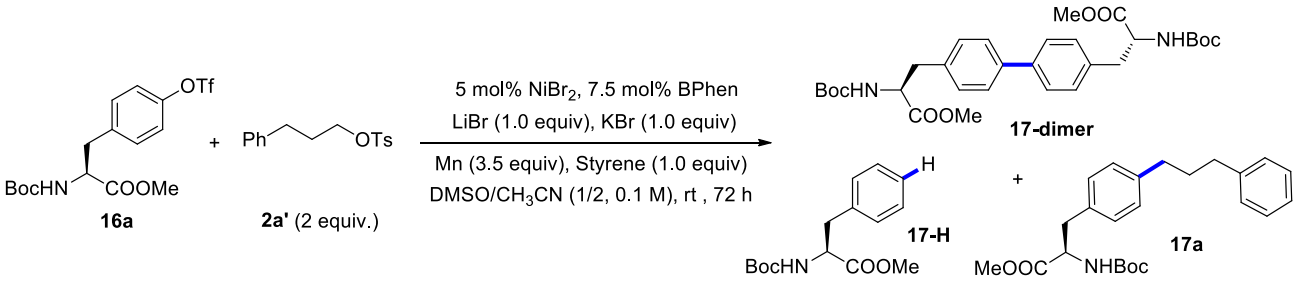


Scheme S1 Initial study of the reaction of **16a** and **2a′** under the established conditions

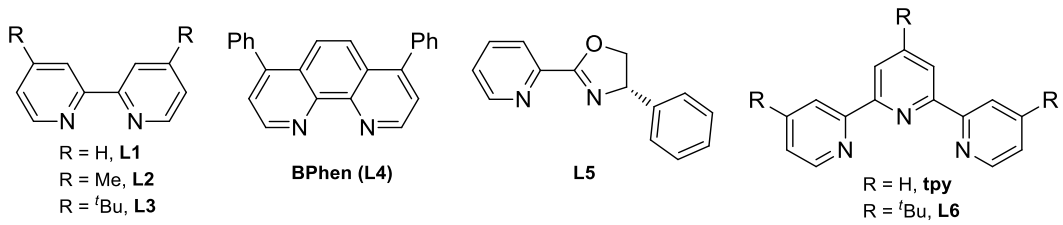
General procedure for reactions in Table S3-S4:

The procedure was conducted in an argon-filled glove box. To a reaction tube containing catalyst (0.005 mmol, 5 mol %), ligand (0.0075 mmol, 7.5 mol %), LiBr (9.0 mg, 0.1 mmol), KBr (12 mg, 0.1 mmol), and reductant (0.35 mmol) was added a solution of alkene additive (0.1 mmol), alkyl tosylate **2a′** (58 mg, 0.2 mmol) and tyrosine **16a** (42.7 mg, 0.1mmol) in DMSO/CH_3CN (1/2, 1 mL). It was sealed and moved from the glove box. The reaction mixture was stirred at room temperature for 72 h. The reaction mixture was diluted with ethyl acetate (15 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. A 0.2 mL of solution was collected, diluted with methanol (2 mL), and analyzed by HPLC. The yield was determined versus the internal standard (methyl benzoate).

Table S3 Optimization of reaction conditions[a]

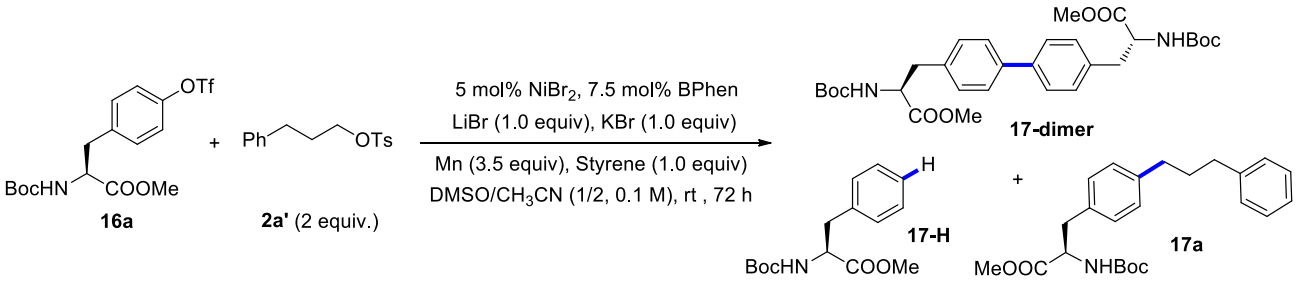


entry	change of conditions	**17a** (%)	**17-H** (%)	**17-dimer** (%)
1	none	84	0	6
2	NiI_2 instead of $NiBr_2$	28	0	8
3	$NiCl_2$ instead of $NiBr_2$	29	0	9
4	**L1** instead of BPhen	71	0	10
5	**L2** instead of BPhen	0	0	8
6	**L3** instead of BPhen	81	0	4
7	**L5** instead of BPhen	0	0	0
8	**tpy** instead of BPhen	0	0	0
9	**L6** instead of BPhen	0	0	0
10	no LiBr/KBr	38	0	11
11	LiBr (2 equiv) instead of LiBr/KBr	63	0	12
12	KBr (2 equiv) instead of LiBr/KBr	69	0	11
13	Zn instead of Mn	24	46	15
14	no styrene	78	18	2
15	no Ni or Mn	0	0	0

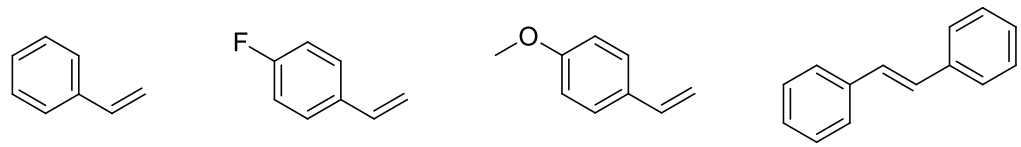


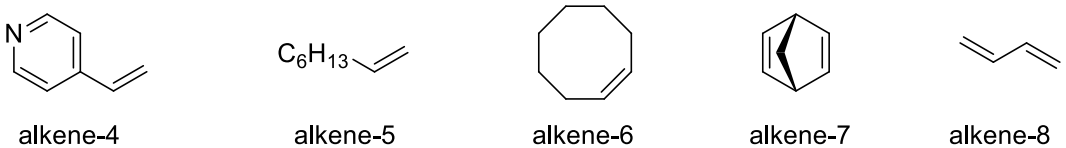
[a]**16a** (0.1 mmol) was used; the yields were determined by HPLC analysis with methyl benzoate as internal standard.

Table S4 Effect of alkene additives [a]



entry	additive	**17a**	**17-H**	**17-dimer**
1	styrene	84	0	6
2	Styrene (50 mol %)	66	0	14
3	alkene-1	46	0	8
4	alkene-2	79	9	5
5	alkene-3	78	13	4
6	alkene-4	12	18	9
7	alkene-5	76	20	2
8	alkene-6	80	16	2
9	alkene-7	7	0	0
10	alkene-8	41	0	7



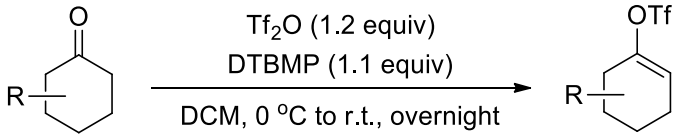


[a] **16a** (0.1 mmol) was used; the yields were determined by HPLC analysis with methyl benzoate as internal standard.

3. Preparation of Starting Materials

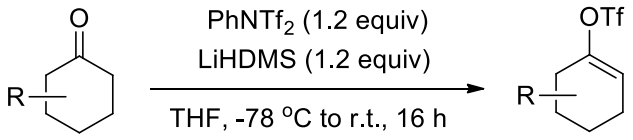
3.1 Preparation of vinyl triflates

General Procedure A[2]:



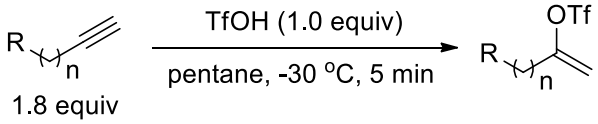
To a solution of ketone (10.0 mmol) in DCM (30 mL) was added 2,6-di-tert-butyl-4-methylpyridine (DTBMP, 11.0 mmol, 1.1 equiv) at 0 ℃. Tf_2O (12.0 mmol, 1.2 equiv) was added dropwise. The reaction mixture was then allowed to warm to room temperature, stirred overnight and evaporated to dryness. Petroleum ether was added and the mixture was filtered to remove pyridinium triflate. The petroleum ether solution was washed with cool HCl (1 M), brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to give the resulting vinyl triflate.

General Procedure B[2]:



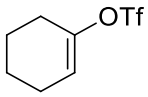
To a solution of ketone (10.0 mmol) in THF (45 mL) was dropwise added lithium hexamethyldisilazide (LiHMDS, 12.0 mmol, 1.2 equiv) at -78 ℃. After stirring for 1 h, a solution of $PhNTf_2$ (12.0 mmol, 1.2 equiv) in THF (10 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 16 h. The mixture was quenched with H_2O and extracted with ethyl acetate. The organic layer was washed with saturated NH_4Cl and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to give the resulting vinyl triflate.

General Procedure C[2]:



To a solution of alkyne (18.0 mmol, 1.8 equiv) in pentane (20 mL) was dropwise added Trifluoromethanesulfonic acid (10.0 mmol, 1.0 equiv) for 5 min at -30 ℃. The reaction mixture was

warmed to 0 ℃ and saturated aqueous $NaHCO_3$ was added to the reaction mixture. After stirring for another 5 min, the organic layer was separated and washed twice with saturated $NaHCO_3$. The combined solution was dried over anhydrous Na_2CO_3, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the resulting vinyl triflate.



Cyclohex-1-en-1-yl trifluoromethanesulfonate (**1a,** known compound)

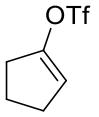
This compound was synthesized from cyclohexanone (0.98 g, 10.0 mmol) according to the General Procedure A, and was purified by distillation. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

1.24 g (54% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77-5.75 (m, 1 H), 2.33-2.30 (m, 2 H), 2.20-2.16 (m, 2 H), 1.80-1.76 (m, 2 H), 1.62-1.58 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 149.3, 118.6 (q, J_{C-F} = 318.0 Hz), 118.4, 27.6, 23.9, 22.6, 21.0.

^{19}F NMR (564 MHz, $CDCl_3$) δ -74.32.



Cyclopent-1-en-1-yl trifluoromethanesulfonate (**1b,** known compound)

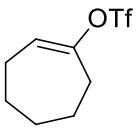
This compound was synthesized from cyclopentanone (0.84 g, 10.0 mmol) according to the General Procedure A, and was purified by distillation. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

0.86 g (40% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.64-5.62 (m, 1 H), 2.59-2.55 (m, 2 H), 2.43-2.40 (m, 2 H), 2.06-2.01 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 149.6, 118.6 (q, J_{C-F} = 319.0 Hz), 117.7, 30.8, 27.9, 20.8.

^{19}F NMR (564 MHz, $CDCl_3$) δ -73.86.



Cyclohept-1-en-1-yl trifluoromethanesulfonate (**1c,** known compound)

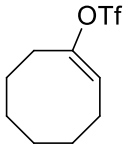
This compound was synthesized according to the General Procedure A, but cycloheptanone (1.12 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

1.12 g (46% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.88 (t, *J* = 6.6 Hz, 1 H), 2.53-2.50 (m, 2 H), 2.17-2.14 (m, 2 H), 1.70-1.66 (m, 4 H), 1.65-1.62 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.1, 123.0, 118.6 (q, J_{C-F} = 318.0 Hz), 33.2, 29.8, 26.3, 24.8, 24.7.

^{19}F NMR (564 MHz, $CDCl_3$) δ -74.00.



(*E*)-cyclooct-1-en-1-yl trifluoromethanesulfonate (**1d,** known compound)

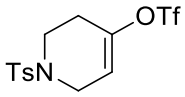
This compound was synthesized according to the General Procedure A, but cyclooctanone (1.26 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

1.81 g (70% yield), colourless oil.

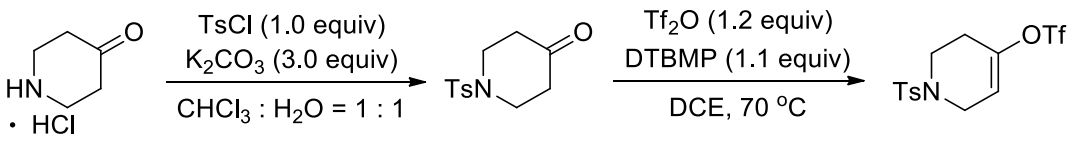
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.69 (t, *J* = 8.4 Hz, 1 H), 2.47 (t, *J* = 6.0 Hz, 2 H), 2.19-2.15 (m, 2 H), 1.74-1.70 (m, 2 H), 1.64-1.54 (m, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.0, 120.5, 118.6 (q, J_{C-F} = 318.0 Hz), 29.5, 29.1, 27.1, 25.8, 25.5, 24.9.

^{19}F NMR (564 MHz, $CDCl_3$) δ -74.42.



1-Tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate (**1e,** known compound)



Step 1[3]: To a solution of 4-oxopiperidinium chloride (3.84 g, 25.0 mmol) in $CHCl_3/H_2O$ (1:1) was added K_2CO_3 (10.40 g, 75.0 mmol) and tosyl chloride (4.80 g, 25.0 mmol). After stirring at room temperature for 4 h, the reaction mixture was extracted twice with CH_2Cl_2. The combined

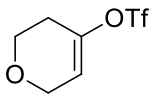
organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give 1-tosylpiperidin-4-one as a white solid (5.82 g, 92% yield).

Step 2: To a solution of 1-tosylpiperidin-4-one (2.90 g, 10.0 mmol) in DCE (30 mL) was added 2,6-di-tert-butyl-4-methylpyridine (2.46 g, 12.0 mmol) and trifluoromethanesulfonic anhydride (3.10 g, 11.0 mmol). After stirring at 70 ℃ for 6 h, the reaction was cooled to room temperature. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted twice with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the title product as a white solid (2.96 g, 77% yield). mp.: 71-73 ℃. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 4.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.8 Hz, 2 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 5.73 (m, 1 H), 3.80-3.78 (m, 2 H), 3.36 (t, *J* = 5.4 Hz, 2 H), 2.47 (m, 2H), 2.43 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 144.2, 133.5, 129.9, 127.4, 118.4 (q, J_{C-F} = 318.0 Hz), 114.4, 43.4, 42.6, 27.9, 21.4.

^{19}F NMR (564 MHz, $CDCl_3$) δ -73.80.



3,6-Dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate (**1f,** known compound)

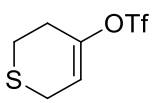
This compound was synthesized according to the General Procedure A, but tetrahydro-4*H*-pyran-4-one (1.00 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

0.93 g (40% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.82 (m, 1 H), 4.26-4.25 (m, 2 H), 3.89 (t, *J* = 5.4 Hz, 2 H), 2.46 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 145.8, 118.6 (q, J_{C-F} = 318.0 Hz), 116.9, 64.2, 64.0, 28.4.

^{19}F NMR (564 MHz, $CDCl_3$) δ -73.92.



3,6-Dihydro-2*H*-thiopyran-4-yl trifluoromethanesulfonate (**1g,** known compound)

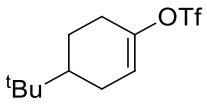
This compound was synthesized according to the General Procedure B, but tetrahydro-4*H*-thiopyran-4-one (1.16 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 5.

1.84 g (74% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.00-5.99 (m, 1 H), 3.30-3.28 (m, 2 H), 2.85 (t, *J* = 6.0 Hz, 2 H), 2.62-2.60 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 150.0, 118.4 (q, J_{C-F} = 318.0 Hz), 117.0, 29.2, 25.1, 24.8.

^{19}F NMR (564 MHz, $CDCl_3$) δ -71.71.



4-(*Tert*-butyl)cyclohex-1-en-1-yl trifluoromethanesulfonate (**1h,** known compound)

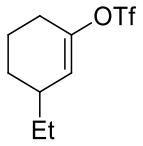
This compound was synthesized according to the General Procedure A, but 4-(*tert*-butyl)cyclohexan-1-one (1.54 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

2.20 g (77% yield), colourless oil.

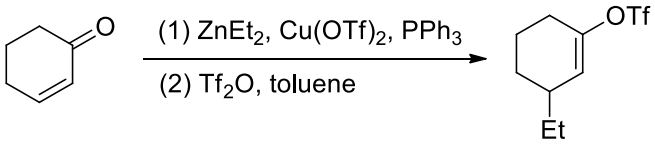
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.75-5.73 (m, 1 H), 2.42-2.30 (m, 2 H), 2.23-2.18 (m, 1 H), 1.98-1.92 (m, 2 H), 1.40-1.29 (m, 2 H), 0.89 (s, 9 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 149.2, 118.6 (q, J_{C-F} = 318.0 Hz), 118.4, 43.0, 32.06, 28.6, 27.2, 25.4, 24.1.

^{19}F NMR (564 MHz, $CDCl_3$) δ -74.15.



3-Ethylcyclohex-1-en-1-yl trifluoromethanesulfonate (**1i,** known compound)



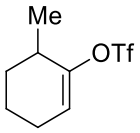
The mixture solution of $Cu(OTf)_2$ (72.3 mg, 0.2 mmol) and PPh_3 (105.0 mg, 0.4 mmol) in anhydrous toluene (50 mL) was stirred at room temperature for 0.5 h under argon. After addition of 2-cyclohexen-1-one (1.0 mL, 10.0 mmol), diethlyzinc (13.0 mL, 1M solution in toluene, 13.0 mmol)

was then dropwise added at -30 ^{o}C. The reaction mixture was stirred at the same temperature for 2 h. It was then warmed to 0 ^{o}C and was added trifluoromethanesulfonic anhydride (5.60g, 20.0 mmol). After stirring at room temperature for 12 h, the mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the title product as a colourless oil (1.68 g, 65% yield). ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 6.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.68 (s, 1 H), 2.34-2.21 (m, 3 H), 1.90-1.88 (m, 1 H), 1.78-1.76 (m, 1 H), 1.70-1.64 (m, 1 H), 1.45-1.35 (m, 2 H), 1.25-1.20 (m, 1 H), 0.93 (t, J = 7.2 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 149.4, 122.6, 118.6 (q, J_{C-F} = 318.0 Hz), 36.6, 28.3, 27.8, 27.2, 21.5, 11.2.

^{19}F NMR (564 MHz, $CDCl_3$) δ -74.02.



6-Methylcyclohex-1-en-1-yl trifluoromethanesulfonate (**1j,** known compound)

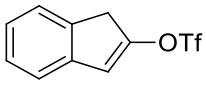
This compound was synthesized according to the General Procedure B, but 2-methylcyclohexan-1-one (1.12 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 6.

1.98 g (81% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.73 (td, J = 4.2 Hz, 1.2 Hz, 1 H), 2.56-2.52 (m, 1 H), 2.18-2.15 (m, 2 H), 1.96-1.91 (m, 1 H), 1.70-1.64 (m, 1 H), 1.60-1.53 (m, 1 H), 1.49-1.44 (m, 1 H), 1.14 (d, J = 6.6 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.4, 118.6 (q, J_{C-F} = 318.0 Hz), 118.1, 32.4, 31.5, 24.5, 19.2, 17.8.

^{19}F NMR (564 MHz, $CDCl_3$) δ -72.14.



1*H*-inden-2-yl trifluoromethanesulfonate (**1k,** known compound)

This compound was synthesized according to the General Procedure B, but 1,3-dihydro-2*H*-inden-2-one (1.32 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are

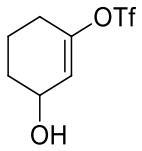
consistent with those reported in ref. 7.

2.14 g (81% yield), colourless oil.

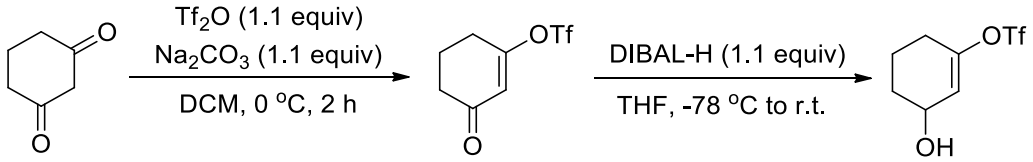
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2 H), 7.32-7.29 (m, 1 H), 7.27-7.25 (m, 1 H), 6.68 (m, 1 H), 3.66 (s, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.2, 140.2, 137.4, 127.3, 126.2, 123.8, 122.2, 119.5, 118.6 (q, J_{C-F} = 320.0 Hz), 37.7.

^{19}F NMR (564 MHz, $CDCl_3$) δ -72.89.



3-Hydroxycyclohex-1-en-1-yl trifluoromethanesulfonate (**1l,** known compound)



Step 1[8]**:** To a solution of cyclohexane-1,3-dione (2.30 g, 20.0 mmol) in DCM (50 mL) was added Na_2CO_3 (2.40 g, 22.0 mmol). The mixture was cooled to 0 °C and trifluoromethanesulfonic anhydride (6.20g, 22.0 mmol) was added dropwise. After stirring at 0 °C for 2 h, the reaction mixture was filtered. The filtrate was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 twice. The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give 5-oxocyclohex-1-en-1-yl trifluoromethanesulfonate as a colourless oil (2.60 g, 53% yield).

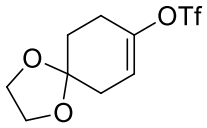
Step 2: To a solution of 5-oxocyclohex-1-en-1-yl trifluoromethanesulfonate (2.44 g, 10.0 mmol) in THF (30 mL) was slowly added diisobutylaluminum hydride (DIBAL-H, 7.4 mL, 1.5 M solution in toluene, 11.0 mmol) at -78 °C under argon. The reaction mixture was stirred at -78 °C for 10 min, at 0 °C for 10 min and then at room temperature for 30 min. The reaction mixture was quenched with saturated aqueous NH_4Cl, and was added a solution of potassium sodium tartrate in water (50 mL). After stirring overnight, the reaction mixture was extracted with EtOAc twice. The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the title product as a colourless oil (2.19 g, 89% yield). ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 9.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.84-5.83 (m, 1 H), 4.43-4.41 (m, 1 H), 2.42 (s, 1 H), 2.39-2.27

(m, 2 H), 1.97-1.90 (m, 1 H), 1.88-1.83 (m, 1 H), 1.77-1.71 (m, 1 H), 1.65-1.60 (m, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 120.6, 118.5 (q, J_{C-F} = 318.0 Hz), 65.1, 30.5, 27.6, 18.7.

^{19}F NMR (564 MHz, $CDCl_3$) δ -74.14.



1,4-Dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate (**1m,** known compound)

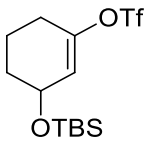
This compound was synthesized according to the General Procedure A, but 1,4-dioxaspiro[4.5]decan-8-one (1.56 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 2.

1.30 g (45% yield), colourless oil.

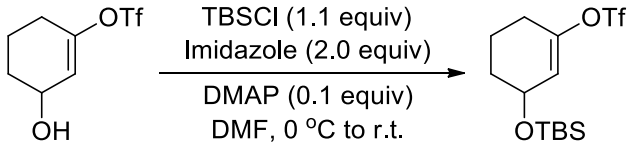
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.67-5.66 (m, 1 H), 4.01-3.96 (m, 4 H), 2.55-2.53 (m, 2 H), 2.40 (m, 2 H), 1.90 (t, *J* = 6.6 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 148.2, 118.5 (q, J_{C-F} = 318.0 Hz), 115.8, 106.1, 64.6, 34.1, 31.0, 26.3.

^{19}F NMR (564 MHz, $CDCl_3$) δ -71.72.



3-((*Tert*-butyldimethylsilyl)oxy)cyclohex-1-en-1-yl trifluoromethanesulfonate (**1n**)



To a solution of **1l** (1.23 g, 5.0 mmol), imidazole (0.68 g, 10.0 mmol) and DMAP (0.06 g, 0.5 mmol) in DMF (30 mL) was added TBSCl (0.83g, 5.5 mmol) at 0 °C. The reaction mixture was stirred at room temperature overnight and was then quenched with water, extracted twice with EtOAc. The combine 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 the title product as a colorless oil (1.30 g, 72% yield).

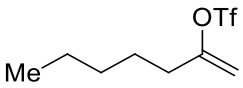
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.71-5.70 (m, 1 H), 4.43-4.40 (m, 1 H), 2.37-2.24 (m, 2 H), 1.98-1.92 (m, 1 H), 1.77-1.66 (m, 2 H), 1.62-1.57 (m, 1 H), 0.89 (s, 9 H), 0.08 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.1, 121.4, 118.6 (q, J_{C-F} = 318.0 Hz), 65.7, 31.1, 27.6, 25.7, 18.8, 18.1, -4.7.

^{19}F NMR (564 MHz, $CDCl_3$) δ -74.10.

IR (neat, cm^{-1}): 2956, 2889, 2860, 1685, 1642, 1465, 1421, 1366, 1334, 1247, 1212, 1144, 1122, 1098, 1072, 1056, 1022, 981, 895, 839, 777, 667, 611.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{13}H_{24}F_3O_4SSi$ 361.1111, found 361.1115.



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

This compound was synthesized according to the General Procedure C, but hept-1-yne (0.96 g, 10.0 mmol) was used.

1.28 g (52% yield), colourless oil.

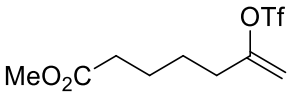
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.08 (d, *J* = 3.6 Hz, 1 H), 4.92 (d, *J* = 3.6 Hz, 1 H), 2.33 (t, *J* = 7.8 Hz, 2 H), 1.58-1.53 (m, 2 H), 1.36-1.32 (m, 4 H), 0.92-0.90 (m, 3 H).

^{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.

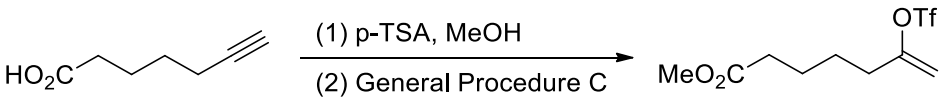
^{19}F NMR (564 MHz, $CDCl_3$) δ -74.32.

IR (neat, cm^{-1}): 2962, 2937, 2875, 1671, 1419, 1251, 1213, 1142, 1094, 947, 907, 793, 705, 613.

HRMS (ESI): $[M+H]^+$ calcd. for $C_8H_{14}F_3O_3S$ 247.0610, found 247.0604.



Methyl 6-(((trifluoromethyl)sulfonyl)oxy)hept-6-enoate (**1p**)



Step 1: To a solution of hept-6-ynoic acid (2.52 g, 20.0 mmol) and MeOH (4 mL) in CH_2Cl_2 (15 mL) was added *p*-TSA (20 mg, 0.1 mmol). The reaction mixture was refluxed for 24 h, quenched with saturated aqueous $NaHCO_3$, and extracted twice with CH_2Cl_2. The combine organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give methyl hept-6-ynoate as a colorless oil (2.55 g, 91% yield).

Step 2: The title product compound was synthesized from methyl hept-6-ynoate (1.40 g, 10.0 mmol) according to the General Procedure C.

1.10 g (38% yield), colourless oil.

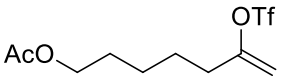
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.11 (d, *J* = 3.6 Hz, 1 H), 4.97 (d, *J* = 3.6 Hz, 1 H), 3.68 (s, 3 H), 2.38-2.34 (m, 4 H), 1.72-1.70 (m, 2 H), 1.62-1.57 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.5, 156.3, 118.5 (q, J_{C-F} = 318.0 Hz), 104.3, 51.4, 33.5, 33.4, 25.4, 23.8.

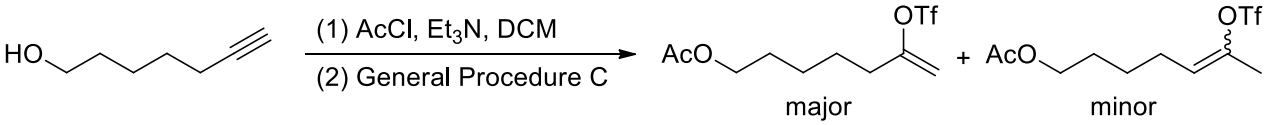
^{19}F NMR (564 MHz, $CDCl_3$) δ -71.92.

IR (neat, cm^{-1}): 2956, 2874, 1740, 1671, 1417, 1211, 1144, 1073, 943, 893, 830, 791, 708, 638, 613.

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 (**1q**)



Step 1: To a solution of hept-6-yn-1-ol (2.24 g, 20.0 mmol) and Et_3N (4.05 g, 40.0 mmol) in CH_2Cl_2 (40 mL) was added acetyl chloride (2.40 g, 30.0 mmol) at 0 ^{o}C. The reaction mixture was stirred at room temperature overnight and then quenched with water, extracted twice with CH_2Cl_2. The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give hept-6-yn-1-yl acetate as a colorless oil (2.77 g, 90% yield).

Step 2: The title product was produced from hept-6-yn-1-yl acetate (1.54 g, 10.0 mmol) according to the General Procedure C.

1.28 g (42% yield), colourless oil, triflate **1q** mixed with 20% of unisolable isomers.

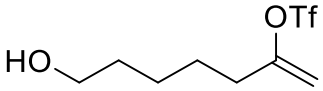
^{1}H NMR (400 MHz, $CDCl_3$, 1q) δ 5.10 (d, *J* = 3.6 Hz, 1 H), 4.94 (d, *J* = 3.6 Hz, 1 H), 4.06 (t, *J* = 6.4 Hz, 2 H), 2.36 (t, *J* = 7.6 Hz, 2 H), 2.04 (s, 3 H), 1.69-1.55 (m, 4 H), 1.50-1.38 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$, 1q) δ 171.1, 156.6, 118.5 (q, J_{C-F} = 318.0 Hz), 104.2, 64.0, 33.7, 28.2, 25.6, 25.0, 20.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -74.23.

IR (neat, cm^{-1}): 2954, 2870, 1739, 1643, 1417, 1210, 1141, 1046, 900, 706, 637.

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



7-Hydroxyhept-1-en-2-yl trifluoromethanesulfonate (**1r**)

This compound was synthesized according to the General Procedure C, but hept-6-yn-1-ol (1.12 g, 10.0 mmol) was used.

0.79 g (30% yield), colourless oil.

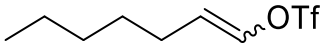
^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.07 (d, *J* = 4.0 Hz, 1H), 4.92 (d, *J* = 4.0 Hz, 1H), 3.60 (t, *J* = 8.0 Hz, 2H), 2.33 (t, *J* = 8.0 Hz, 2H), 2.05 (s, 1H), 1.59–1.52 (m, 4H), 1.44–1.37 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.9, 118.6 (q, J_{C-F} = 320.0 Hz), 104.3, 62.5, 33.9, 32.2, 25.8, 24.9.

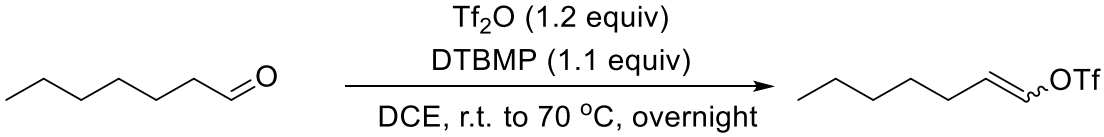
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = −74.29.

IR (cm^{-1}): 2940, 2868, 1671, 1417, 1249, 1210, 1145, 1073, 945, 902, 705, 613.

HRMS (EI): [M] calcd for $C_8H_{13}F_3O_4S$ 262.0487, found 262.0484.



Hept-1-en-1-yl trifluoromethanesulfonate (**1s**)



To a solution of heptanal (1.14g, 10.0 mmol) in DCE (30 mL) was added 2,6-di-tert-butyl-4-methylpyridine (DTBMP, 2.26 g, 11.0 mmol). Tf_2O (3.40 g, 12.0 mmol) was added dropwise. The reaction mixture was allowed to warm to 70 ℃, stirred overnight, and evaporated to dryness. Petroleum ether was added, and the mixture was filtered to remove pyridinium triflate. The petroleum ether solution was washed with cool HCl (1 M), brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by distillation.

1.1 g (45% yield, *E*:*Z* = 1:9), colourless oil. The E/Z isomers were determined by comparison with the related compounds reported in reference 10.

^{1}H NMR (600 MHz, $CDCl_3$, the *Z* isomer) δ: 6.53 (d, *J* = 5.4 Hz, 1H), 5.28-5.24 (m, 1H),

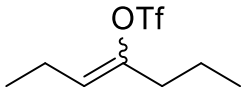
2.21-2.17 (m, 2H), 1.44-1.39 (m, 2H), 1.34-1.27 (m, 4H), 0.90 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$, the *Z* isomer) δ: 135.3, 121.1, 118.8 (q, $J_{C\text{-}F}$ = 330.0 Hz), 31.3, 28.5, 24.2, 22.5, 14.0.

^{19}F NMR (564 MHz, $CDCl_3$, the *Z* isomer) δ (ppm): −74.0.

IR (cm^{-1}): 1668, 1425, 1246, 1215, 1146, 1019, 971, 854, 742, 642.

HRMS (EI): [M] calcd. for $C_8H_{13}F_3O_3S$ 246.0537, found 246.0539.



Hept-3-en-4-yl trifluoromethanesulfonate (**1t**)

This compound was synthesized from heptan-4-one (1.14 g, 10.0 mmol) according to the General Procedure A, and was purified by distillation.

1.13 g (46% yield, *E*:*Z* = 3:1), colourless oil. The E/Z isomers were determined by comparison with the related compounds reported in reference 2.

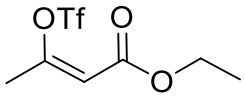
^{1}H NMR (400 MHz, $CDCl_3$, the E isomer) δ: 5.23 (t, *J* = 8.0 Hz, 1H), 2.29 (t, *J* = 8.0 Hz, 2H), 2.23-2.15 (m, 2H), 1.59-1.50 (m, 2H), 1.02 (t, *J* = 8.0 Hz, 3H), 0.94 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, the E isomer) δ: 148.5, 122.9, 118.7 (q, $J_{C\text{-}F}$ = 320.0 Hz), 118.6 (q, $J_{C\text{-}F}$ = 320.0 Hz), 35.5, 19.7, 19.4, 13.5, 13.2.

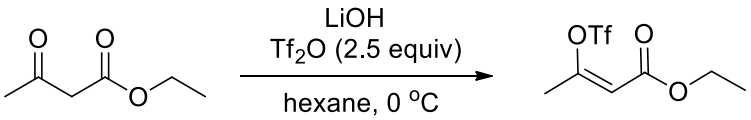
^{19}F NMR (376 MHz, $CDCl_3$, the E isomer) δ (ppm): −75.2.

IR (cm^{-1}): 2971, 2940, 2881, 1697, 1462, 1414, 1243, 1212, 1140, 999, 925, 905, 789, 725, 653.

HRMS (EI): [M] calcd. for $C_8H_{13}F_3O_3S$ 246.0537, found 246.0535.



Ethyl (Z)-2-methyl-3-(((trifluoromethyl)sulfonyl)oxy)acrylate (**Z-1u**)



To a solution of ethyl 3-oxobutanoate (0.65 g, 5.0 mmol) in hexane (30 mL) was added saturated aqueous solution of LiOH (6 mL) in one portion at 0 °C. The mixture was vigorously stirred at the same temperature for 5 minutes, and Tf_2O (3.53 g, 12.5 mmol) was added dropwise. After the reaction was completed as monitored by TLC, it was quenched with water (30 mL) and extracted twice with EtOAc (30 mL). The combined organic layers were washed with brine, dried over

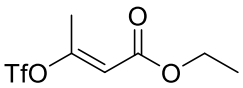
anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by flash chromatography on silica gel to afford **1u**. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 11.

1.05 g (80% yield), colourless oil.

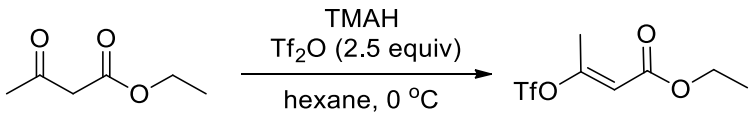
^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.76 (m, 1H), 4.27-4.22 (m, 2H), 2.15 (s, 3H), 1.30 (t, J = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.4, 155.2, 118.5 (q, J_{C-F} = 310.0 Hz), 113.0, 61.4, 21.0, 14.1.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): −74.15.



Ethyl (E)-3-(((trifluoromethyl)sulfonyl)oxy)but-2-enoate (E-1u)



To a solution of ethyl 3-oxobutanoate (0.65 g, 5.0 mmol) in hexane (30 mL) was added water (5 mL). The mixture was cooled with an ice bath, and an aqueous solution of tetramethylammonium hydroxide (10 mL of a 25 wt% solution in water, 25 mmol) was added in one portion. The mixture was vigorously stirred at the same temperature for 5 minutes, and Tf_2O (3.53 g, 12.5 mmol) was added dropwise. After the reaction was completed as monitored by TLC, it was diluted with water (30 mL) and extracted twice with EtOAc (30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by flash chromatography on silica gel to afford title compound. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 11.

0.84 g (64% yield), colourless oil.

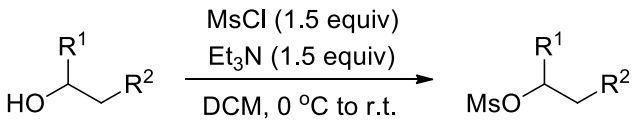
^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.95 (s, 1H), 4.25-4.20 (m, 2H), 2.51 (s, 3H), 1.31 (t, J = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3, 162.1, 118.5 (q, J_{C-F} = 318.4 Hz), 113.5, 61.3, 18.5, 14.2.

^{19}F NMR (564 MHz, $CDCl_3$) δ (ppm): −73.90.

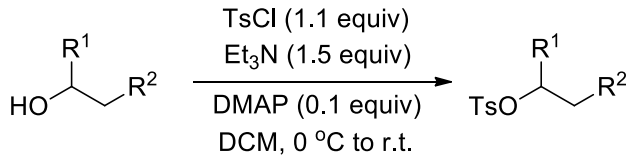
3.2 Preparation of alkyl sulfonates

General Procedure D[12]:

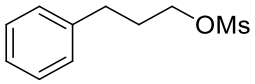


To a solution of alcohol (10.0 mmol, 1.0 equiv) and Et_3N (15.0 mmol, 1.5 equiv) in CH_2Cl_2 (30 mL) was added MsCl (15.0 mmol, 1.5 equiv) at 0 °C. The reaction mixture was stirred at room temperature overnight and then quenched with water, extracted twice with CH_2Cl_2. The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by flash chromatography on silica gel to give the alkyl mesylate.

General Procedure E[13]:



To a solution of alcohol (10.0 mmol, 1.0 equiv), Et_3N (15.0 mmol, 1.5 equiv) and DMAP (1.0 mmol, 0.1 equiv) in CH_2Cl_2 (30 mL) was added TsCl (11.0 mmol, 1.1 equiv). The reaction mixture was stirred at room temperature overnight and then quenched with water, extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give the alkyl tosylate.



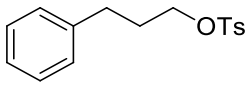
3-Phenylpropyl methanesulfonate (**2a,** known compound)

This compound was synthesized according to the General Procedure D, but 3-phenylpropan-1-ol (1.36 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 12.

2.03 g (95% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2 H), 7.24-7.18 (m, 3 H), 4.21 (t, *J* = 6.0 Hz, 2 H), 2.97 (s, 3 H), 2.74 (t, *J* = 7.2 Hz, 2 H), 2.10-2.03 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 128.6, 128.5, 126.3, 69.3, 37.3, 31.5, 30.6.



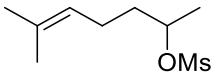
3-Phenylpropyl 4-methylbenzenesulfonate (**2a',** known compound)

This compound was synthesized according to the General Procedure E, but 3-phenylpropan-1-ol (1.36 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 13.

2.64 g (91% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.23-7.20 (m, 2 H), 7.17-7.13 (m, 1 H), 7.05 (d, *J* = 7.2 Hz, 2 H), 4.01 (t, *J* = 6.0 Hz, 2 H), 2.62 (t, *J* = 7.6 Hz, 2 H), 2.43 (s, 3 H), 1.97-1.90 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 140.5, 133.3, 130.0, 128.6, 128.5, 128.0, 126.2, 69.8, 31.6, 30.6, 21.7.



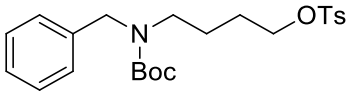
6-Methylhept-5-en-2-yl methanesulfonate (**2b,** known compound)

This compound was synthesized according to the General Procedure D, but 6-methylhept-5-en-2-ol (1.28 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 14.

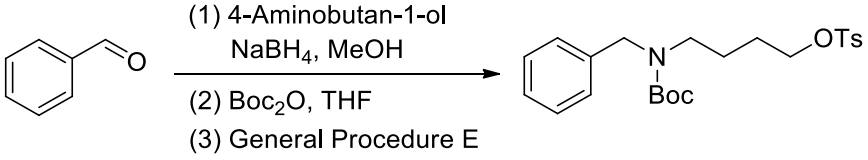
1.77 g (86% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.10-5.07 (m, 1 H), 4.83-4.77 (m, 1 H), 2.99 (s, 3 H), 2.14-2.03 (m, 2 H), 1.80-1.74 (m, 1 H), 1.69 (s, 3 H), 1.65-1.60 (m, 4 H), 1.43 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 132.8, 122.7, 80.0, 38.6, 36.7, 25.6, 23.7, 21.1, 17.7.



4-(Benzyl(tert-butoxycarbonyl)amino)butyl 4-methylbenzenesulfonate (**2c**)



Step 1: To a solution of 4-aminobutan-1-ol (0.89 g, 10.0 mmol) in MeOH (20 mL) was added benzaldehyde (1.38 g, 13.0 mmol). After stirring for 12 h, the mixture was cooled to 0 ^{o}C and $NaBH_4$ (0.50 g, 13.0 mmol) was slowly added. The reaction mixture was stirred at 0 ^{o}C for 1 h and at room temperature for 5 h. The mixture was quenched with H_2O at 0 ^{o}C and extracted twice with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The crude product was used for the next step without further purification.

Step 2: To a solution of the above crude product in THF was added Boc_2O (2.40 g, 11.0 mmol). The reaction mixture was stirred at room temperature overnight, and then quenched with water and extracted twice with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give *tert*-butyl benzyl(4-hydroxybutyl)carbamate as a colourless oil (1.81 g, 65% yield).

Step 3: The title product was synthesized according to the General Procedure E, but tert-butyl benzyl(4-hydroxybutyl)carbamate (1.81 g, 6.5 mmol) was used.

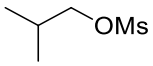
2.11 g (75% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$, mixture of amide rotamers): δ 7.76 (d, *J* = 8.4 Hz, 2 H), 7.33-7.28 (m, 4 H), 7.25-7.20 (m, 3 H), 4.39-4.37 (m, br, 2 H), 3.99 (t, *J* = 5.6 Hz, 2 H), 3.17-3.10 (m, br, 2 H), 2.43 (s, 3 H), 1.59-1.42 (m, 13 H).

^{13}C NMR (100 MHz, $CDCl_3$, major isomer): δ 155.7, 144.8, 138.4, 133.1, 129.9, 128.5, 127.9, 127.6, 127.2, 79.8, 70.2, 50.4, 45.7, 28.4, 26.2, 23.9, 21.6.

IR (neat, cm^{-1}): 2975, 2930, 2873, 1691, 1459, 1416, 1363, 1244, 1176, 1135, 1098, 1019, 937, 875, 816, 774, 733, 701, 664.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{32}NO_5S$ 434.1996, found 434.1994.



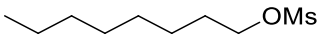
Isobutyl methanesulfonate (**2d,** known compound)

This compound was synthesized according to the General Procedure D, but 2-methylpropan-1-ol (0.74 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 15.

1.25 g (92% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (d, *J* = 6.4 Hz, 2 H), 3.01 (s, 3 H), 2.11-1.98 (m, 1 H), 1.00 (d, *J* = 6.4 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 75.7, 37.2, 28.2, 18.6.



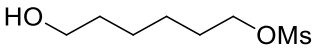
Octyl methanesulfonate (**2e,** known compound)

This compound was synthesized according to the General Procedure D, but octan-1-ol (1.30 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 16.

1.98 g (95% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (t, *J* = 6.8 Hz, 2 H), 3.00 (s, 3 H), 1.78-1.71 (m, 2 H), 1.42-1.28 (m, 10 H), 0.89 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 70.3, 37.5, 31.8, 29.3, 29.2, 29.1, 25.5, 22.7, 14.2.



6-Hydroxyhexyl methanesulfonate (**2f**)

This compound was synthesized according to the General Procedure D, but hexane-1,6-diol (5.90 g, 50.0 mmol, 5.0 equiv) and MsCl (1.14 g, 10.0 mmol) was used.

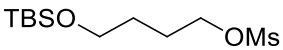
0.74 g (38% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (t, *J* = 6.4 Hz, 2 H), 3.59 (m, 2 H), 3.02 (s, 3 H), 2.94 (brs, 1 H), 1.80-1.73 (m, 2 H), 1.59-1.53 (m, 2 H), 1.48-1.38 (m, 4 H).

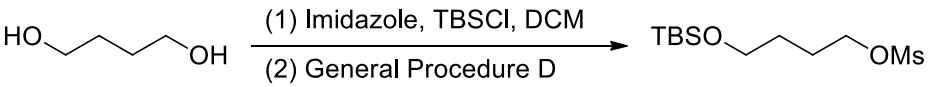
^{13}C NMR (100 MHz, $CDCl_3$) δ 70.0, 61.8, 36.8, 31.9, 28.6, 24.8, 24.8.

IR (neat, cm^{-1}): 2939, 2863, 1644, 1463, 1342, 1172, 1055, 928, 820.

HRMS (ESI): $[M+H]^+$ calcd. For $C_7H_{17}O_4S$ 197.0842, found 197.0842.



4-((*Tert*-butyldimethylsilyl)oxy)butyl methanesulfonate (**2g**)



Step 1: To a solution of butane-1,4-diol (1.35 g, 15.0 mmol) and imidazole (1.36 g, 20.0 mmol) in CH_2Cl_2 (40 mL) was added TBSCl (1.50 g, 10.0 mmol). The reaction mixture was stirred at room temperature overnight and then quenched with water, extracted twice with CH_2Cl_2. The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude residue was purified by flash chromatography on silica gel to give

4-((*tert*-butyldimethylsilyl)oxy)butan-1-ol as a colorless oil (1.02 g, 50% yield).

Step 2: The title product was synthesized according to the General Procedure D, but 4-((tert-butyldimethylsilyl)oxy)butan-1-ol (1.02 g, 5.0 mmol) was used.

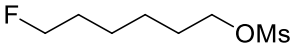
1.34 g (95% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (t, *J* = 6.8 Hz, 2 H), 3.65 (t, *J* = 6.0 Hz, 2 H), 3.01 (s, 3 H), 1.88-1.80 (m, 2 H), 1.66-1.59 (m, 2 H), 0.89 (s, 9 H), 0.05 (s, 6 H).

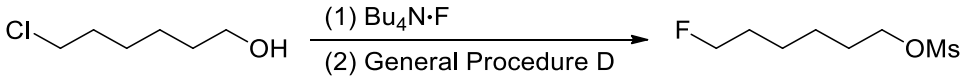
^{13}C NMR (100 MHz, $CDCl_3$) δ 70.1, 62.2, 37.3, 28.5, 25.89, 25.85, 18.3, -5.4.

IR (neat, cm^{-1}): 2955, 2930, 2857, 1644, 1341, 1173, 1093, 980, 840, 836, 776.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{11}H_{27}O_4SSi$ 283.1394, found 283.1395.



6-Fluorohexyl methanesulfonate (**2h**)



Step 1: The mixture of 1-chloro-6-fluorohexane (2.73 g, 20.0 mmol) and tetrabutylammonium fluoride (10.5 g, 40.0 mmol) was stirred at 80 °C for 7 h. The reaction was quenched with water, extracted twice with EtOAc. The combine organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by silica gel column to give a colorless oil. The crude product was further purified by distillation to give 6-fluorohexan-1-ol as a colorless oil (0.79 g, 33% yield).

Step 2: The title product was synthesized according to the General Procedure D, but 6-fluorohexan-1-ol (0.79 g, 6.6 mmol) was used.

1.23 g (94% yield), colourless oil.

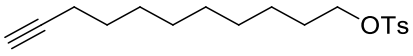
^{11}H NMR (400 MHz, $CDCl_3$) δ 4.51 (dt, *J* = 47.6, 6.0 Hz, 2 H), 4.24 (t, *J* = 6.4 Hz, 2 H), 3.01 (s, 3 H), 1.81-1.67 (m, 4 H), 1.48-1.45 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 83.9 (d, J_{C-F} = 163.3 Hz), 69.9, 37.3, 30.2 (d, J_{C-F} = 19.5 Hz), 29.0, 25.1, 24.7 (d, J_{C-F} = 5.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -218.53.

IR (neat, cm^{-1}): 3030, 2943, 2866, 1703, 1648, 1466, 1355, 1174, 976, 928, 817, 742.

HRMS (ESI): $[M+H]^+$ calcd. for $C_7H_{16}FO_3S$ 199.0799, found 199.0799.



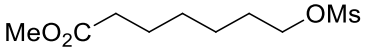
Undec-10-yn-1-yl tosylate (**2i,** known compound)

This compound was synthesized according to the General Procedure E, but undec-10-yn-1-ol (1.68 g, 10.0 mmol) was used directly. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 17.

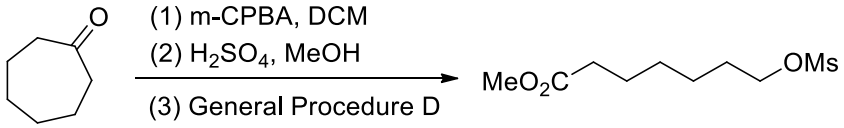
2.93 g (91% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.02 (t, *J* = 6.4 Hz, 2 H), 2.45 (s, 3 H), 2.17 (td, *J* = 6.8 Hz, 2.4 Hz, 2 H), 1.93 (t, *J* = 2.8 Hz, 1 H), 1.67-1.60 (m, 2 H), 1.54-1.47 (m, 2 H), 1.40-1.24 (m, 10 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 133.3, 129.8, 127.8, 84.6, 70.6, 68.1, 29.2, 28.9, 28.79, 28.76, 28.6, 28.4, 25.3, 21.6, 18.3.



Methyl 7-((methylsulfonyl)oxy)heptanoate (**2j,** known compound)



Step 1: To a solution of *m*-CPBA (9.20 g, 53.5 mmol) in CH_2Cl_2 (100 mL) was added cycloheptanone (9.20 g, 107.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 5 days and filtered. The filtrate was washed with saturated aqueous $NaHCO_3$, water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The oxocan-2-one was obtained as a colourless oil quantitatively and used without further purification.

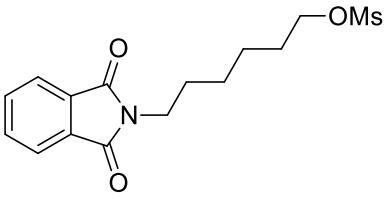
Step 2: A mixture of oxocan-2-one (about 107.0 mmol) and H_2SO_4 (1 mL) in MeOH (150 mL) was stirred at room temperature for 8 h. The solvent was removed under reduced pressure. The residue was dissolved in EtOAc, washed with water twice, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by silica gel column to give methyl 7-hydroxyheptanoate as a colorless oil (12.00 g, 70% yield).

Step 3: The title product was synthesized according to the General Procedure D, but methyl 7-hydroxyheptanoate (1.60 g, 10 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 18.

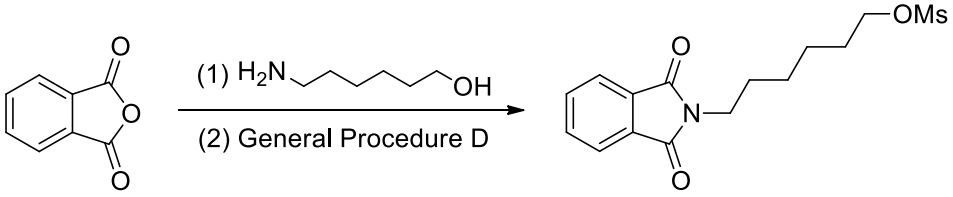
2.02 g (85% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.22 (t, *J* = 6.6 Hz, 2 H), 3.67 (s, 3 H), 3.01 (s, 3 H), 2.32 (t, *J* = 7.2 Hz, 2 H), 1.78-1.74 (m, 2 H), 1.67-1.62 (m, 2 H), 1.46-1.41 (m, 2 H), 1.40-1.34 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.9, 69.8, 51.4, 37.3, 33.8, 28.9, 28.4, 25.1, 24.6.



6-(1,3-Dioxoisoindolin-2-yl)hexyl methanesulfonate (**2k**)



Step 1: The mixture of 6-aminohexan-1-ol (2.34 g, 20.0 mmol) and isobenzofuran-1,3-dione (3.26 g, 22.0 mmol) was stirred at 160 °C for 2 h. The reaction mixture was cooled to room temperature and dissolved in EtOAc. The mixture was purified by silica gel column to give 2-(6-hydroxyhexyl)isoindoline-1,3-dione (3.95 g, 80% yield).

Step 2: The title product was synthesized according to the General Procedure D, but 2-(6-hydroxyhexyl)isoindoline-1,3-dione (2.47 g, 10 mmol) was used.

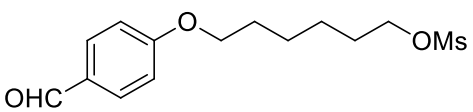
2.93 g (90% yield), white solid, mp.: 44-45 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.82 (m, 2 H), 7.75-7.71 (m, 2 H), 4.23 (t, *J* = 6.4 Hz, 2 H), 3.69 (t, *J* = 7.2 Hz, 2 H), 3.03 (s, 3 H), 1.80-1.67 (m, 4 H), 1.51-1.36 (m, 4 H).

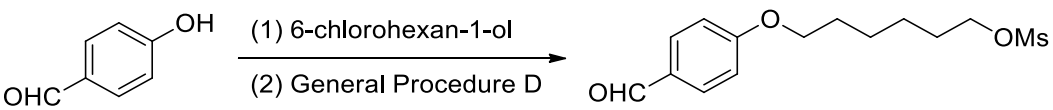
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 133.8, 131.8, 123.0, 69.8, 37.5, 37.1, 28.7, 28.1, 26.0, 24.8.

IR (neat, cm^{-1}): 2933, 2862, 1769, 1699, 1645, 1462, 1394, 1169, 1048, 914, 792, 712.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{15}H_{20}NO_5S$ 326.1057, found 326.1055.



6-(4-Formylphenoxy)hexyl methanesulfonate (**2l**)



Step 1: To a solution of 4-hydroxybenzaldehyde (1.22 g, 10.0 mmol) and K_2CO_3 (4.15 g, 30.0 mmol) in DMF (30mL) was added 6-chlorohexan-1-ol (1.78 g, 13.0 mmol). The reaction mixture was stirred at 160 ^oC for 12 h, and then cooled to room temperature and filtered. The filtrate was diluted with EtOAc, washed with water twice, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give 4-((6-hydroxyhexyl)oxy)benzaldehyde as a colorless oil (1.55 g, 70% yield).

Step 2: The title product was synthesized according to the General Procedure D, but 4-((6-hydroxyhexyl)oxy)benzaldehyde (1.55 g, 7.0 mmol) was used.

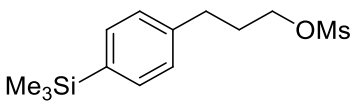
1.72 g (82% yield), white solid, mp.: 42-44 ^oC.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.88 (s, 1 H), 7.83 (d, *J* = 9.0 Hz, 2 H), 6.99 (d, *J* = 8.4 Hz, 2 H), 4.25 (t, *J* = 6.6 Hz, 2 H), 4.05 (t, J = 6.0 Hz, 2 H), 3.01 (s, 3 H), 1.86-1.78 (m, 4 H), 1.57-1.49 (m, 4 H).

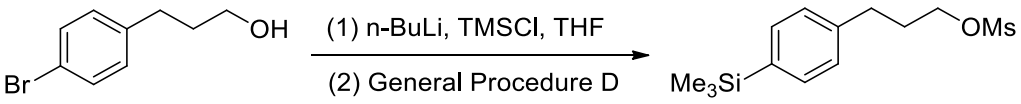
^{13}C NMR (150 MHz, $CDCl_3$) δ 190.7, 164.0, 131.9, 129.8, 114.7, 69.8, 68.0, 37.3, 29.0, 28.8, 25.4, 25.2.

IR (neat, cm^{-1}): 2924, 2853, 1689, 1599, 1511, 1463, 1424, 1394, 1344, 1258, 1215, 1159, 973, 831, 649, 616.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{14}H_{21}O_5S$ 301.1104, found 301.1105.



3-(4-(Trimethylsilyl)phenyl)propyl methanesulfonate (**2m**)



Step 1: To a solution of 3-(4-bromophenyl)propan-1-ol (2.15 g, 10.0 mmol) in THF (40 mL) was dropwise added *n*-BuLi (10 mL, 25.0 mmol, 2.5 M hexane solution) at -78 ^oC. After stirring at -78 ℃ for 60 min, TMSCl (3.26 g, 30.0 mmol) was then dropwise added. The reaction mixture was stirred at room temperature overnight and then quenched with water, extracted twice with EtOAc. The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by silica gel column to give 3-(4-(trimethylsilyl)phenyl)propan-1-ol as a colorless oil (1.28 g, 60% yield).

Step 2: The title product was synthesized according to the General Procedure D, but

3-(4-(trimethylsilyl)phenyl)propan-1-ol (1.28 g, 6.0 mmol) was used.

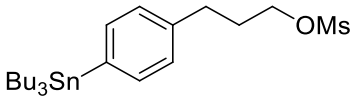
1.55 g (90% yield), white solid, mp.: 39-41 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 4.23 (t, *J* = 6.4 Hz, 2 H), 2.99 (s, 3 H), 2.74 (t, *J* = 7.2 Hz, 2 H), 2.11-2.04 (m, 2 H), 0.26 (s, 9 H).

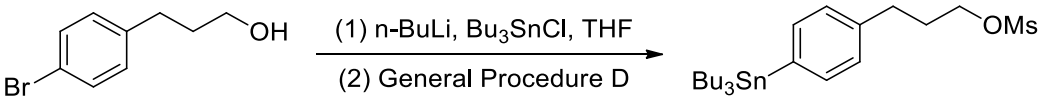
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.0, 133.6, 127.9, 69.1, 37.3, 31.4, 30.5, -1.1.

IR (neat, cm^{-1}): 2955, 2857, 1643, 1459, 1355, 1248, 1174, 1109, 1005, 973, 928, 837, 756, 723, 660.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{13}H_{23}O_3SSi$ 287.1132, found 287.1133.



3-(4-(Tributylstannyl)phenyl)propyl methanesulfonate (**2n**)



Step 1: To a solution of 3-(4-bromophenyl)propan-1-ol (2.15 g, 10.0 mmol) in THF (40 mL) was dropwise added *n*-BuLi (10 mL, 25.0 mmol, 2.5 M hexane solution) at -78 ^{o}C. After stirring at -78 ℃ for 60 min, chlorotributyltin (3.90 g, 12.0 mmol) was then dropwise added. The reaction mixture was stirred at room temperature overnight and then quenched with water, extracted twice with EtOAc. The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by silica gel column to give 3-(4-(tributylstannyl)phenyl)propan-1-ol as a colorless oil (1.98 g, 46% yield).

Step 2: The title product was synthesized according to the General Procedure D, but 3-(4-(tributylstannyl)phenyl)propan-1-ol (1.98 g, 4.6 mmol) was used.

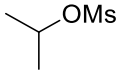
1.97 g (85% yield), colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.28 (m, 2 H), 7.20-7.14 (m, 2 H), 4.23 (d, *J* = 6.0 Hz, 2 H), 2.98 (s, 3 H), 2.72 (t, *J* = 7.6 Hz, 2 H), 2.11-2.04 (m, 2 H), 1.67-1.44 (m, 6 H), 1.37-1.26 (m, 6 H), 1.12-0.96 (m, 6 H), 0.88 (t, *J* = 7.2 Hz, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 139.3, 136.7, 128.1, 69.2, 37.3, 31.4, 30.5, 29.0, 27.3, 13.6, 9.5.

IR (neat, cm^{-1}): 2956, 2925, 2852, 1702, 1650, 1545, 1460, 1420, 1360, 1175, 1072, 928, 690.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{41}O_3SSn$ 505.1793, found 505.1796.



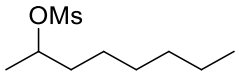
Isopropyl methanesulfonate (**2o,** known compound)

This compound was synthesized according to the General Procedure D, but propan-2-ol (0.60 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 19.

1.30 g (94% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.97-4.92 (m, 1 H), 2.99 (s, 3 H), 1.42 (d, *J* = 6.0 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 76.7, 38.6, 23.0.



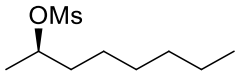
Octan-2-yl methanesulfonate (**2p,** known compound)

This compound was synthesized according to the General Procedure D, but octan-2-ol (1.30 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 14.

1.81 g (87% yield), colourless oil.

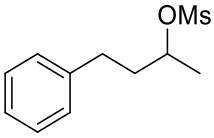
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.81-4.77z (m, 1 H), 2.99 (s, 3 H), 1.75-1.69 (m, 1 H), 1.62-1.58 (m, 1 H), 1.42 (d, *J* = 6.0 Hz, 3 H), 1.36-1.27 (m, 8 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 80.4, 38.6, 36.7, 31.6, 28.9, 25.1, 22.5, 21.1, 14.0.



(R)-octan-2-yl methanesulfonate (**chiral-2p**)

This compound was synthesized according to the General Procedure D, but (R)-octan-2-ol (99% ee., 1.30 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are the same with 2p.



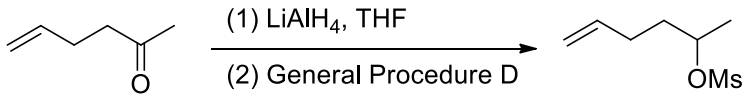
4-Phenylbutan-2-yl methanesulfonate (**2q,** known compound)

This compound was synthesized according to the General Procedure D, but 4-phenylbutan-2-ol (1.50 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 20.

2.05 g (90% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.28 (m, 2 H), 7.22-7.19 (m, 3 H), 4.88-4.80 (m, 1 H), 2.99 (s, 3 H), 2.81-2.66 (m, 2 H), 2.11-2.01 (m, 1 H), 1.97-1.88 (m, 1 H), 1.46 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 128.5, 128.3, 126.2, 79.5, 38.7, 38.2, 31.4, 21.2.



Hex-5-en-2-yl methanesulfonate (**2r,** known compound)

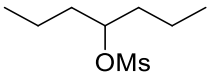
Step 1: To a slurry of $LiAlH_4$ (0.76 g, 20.0 mmol) in THF (10 ml) was dropwise added a solution of hex-5-en-2-one (1.96 g, 20.0 mmol) in THF (10 ml) at 0 ^oC. The reaction mixture was stirred at room temperature for 3 h, and then quenched with 5% HCl aqueous solution (50 ml) and extracted with ethyl acetate (3 × 50 ml). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by flash chromatography on silica gel to give pentane-1,4-diol (1.80 g, 90% yield).

Step 2: The title product was synthesized according to the General Procedure D, but hex-5-en-2-ol (1.80 g, 18.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 14.

2.63 g (82% yield), colourless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.83-5.77 (m, 1 H), 5.09-5.00 (m, 2 H), 4.84-4.79 (m, 1 H), 3.00 (s, 3 H), 2.22-2.12 (m, 2 H), 1.87-1.81 (m, 1 H), 1.73-1.67 (m, 1 H), 1.44 (d, *J* = 6.0 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 136.9, 115.6, 79.5, 38.7, 35.7, 29.2, 21.1.



Heptan-4-yl methanesulfonate (**2s**)

This compound was synthesized according to the General Procedure D, but heptan-4-ol (1.16 g, 10.0 mmol) was used.

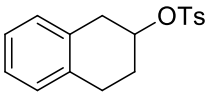
1.55 g (80% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76-4.70 (m, 1 H), 2.30 (s, 3 H), 1.75-1.60 (m, 4 H), 1.52-1.33 (m, 4 H), 0.95 (t, *J* = 7.6 Hz, 6 H).

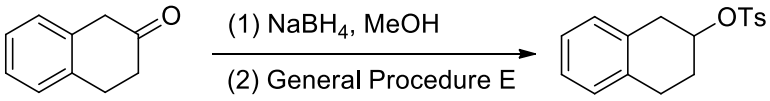
^{13}C NMR (100 MHz, $CDCl_3$) δ 83.9, 38.7, 36.6, 18.3, 13.8.

IR (neat, cm^{-1}): 2965, 2876, 1639, 1461, 1340, 1174, 968.

HRMS (ESI): $[M+Na]^+$ calcd. For $C_8H_{18}NaO_3S$ 217.0869, found 217.0866.



1,2,3,4-Tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate (**2t,** known compound)



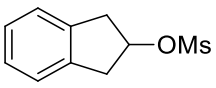
Step 1: To a stirred solution of 3,4-dihydronaphthalen-2(1*H*)-one (1.46 g, 10.0 mmol) in MeOH (10 mL) was slowly added sodium borohydride (0.57 g, 15.0 mmol) at 0 ^{o}C. After stirring at 0 ℃ for 60 min, the reaction mixture was warmed to room temperature and stirred until it was completed as monitored by TLC. The reaction mixture was then quenched with water and extracted twice with EtOAc. The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was directly used for the next step without further purification.

Step 2: The title product was synthesized from the above compound according to the General Procedure E. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 21.

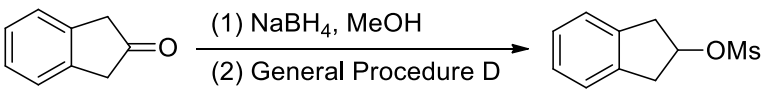
2.72 g (90% yield for 2 steps), white solid, mp.: 78-80 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.12-7.07 (m, 2 H), 7.05-7.03 (m, 1 H), 6.97-6.94 (m, 1 H), 4.94-4.89 (m, 1 H), 3.04-2.89 (m, 3 H), 2.79-2.72 (m, 1 H), 2.43 (s, 3 H), 2.03-1.98 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 134.8, 134.2, 132.3, 129.7, 129.1, 128.5, 127.6, 126.2, 126.0, 78.2, 35.0, 28.5, 26.0, 21.5.



2,3-Dihydro-1H-inden-2-yl methanesulfonate (**2u,** known compound)



Step 1: To a stirred solution of 1,3-dihydro-2*H*-inden-2-one (1.32 g, 10.0 mmol) in MeOH (10 mL) was slowly added sodium borohydride (0.57 g, 15.0 mmol) at 0 ^{o}C. After stirring at 0 ℃ for 60 min, the reaction mixture was warmed to room temperature and stirred until it was completed as

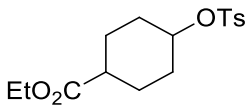
monitored by TLC. The reaction mixture was then quenched with water and extracted twice with EtOAc. The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was directly used for the next step without further purification.

Step 2: The title product was synthesized from the above compound according to the General Procedure D. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 22.

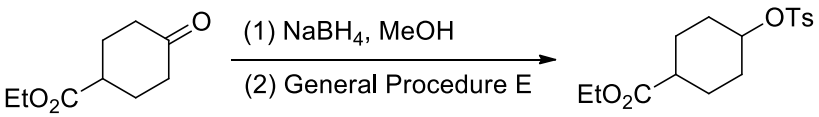
1.89 g (89% yield for 2 steps), brown solid, mp.: 78-80 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.20 (m, 4 H), 5.55-5.50 (m, 1 H), 3.39-3.23 (m, 4 H), 3.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 127.1, 124.6, 81.8, 40.1, 38.5.



Ethyl 4-(tosyloxy)cyclohexane-1-carboxylate (**2v**)



Step 1: To a stirred solution of ethyl 4-oxocyclohexane-1-carboxylate (1.70 g, 10.0 mmol) in MeOH (10 mL) was slowly added sodium borohydride (0.57 g, 15.0 mmol) at 0 ^{o}C. After stirring at 0 ℃ for 60 min, the reaction mixture was warmed to room temperature and stirred until it was completed as monitored by TLC. The reaction mixture was then quenched with water and extracted twice with EtOAc. The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was directly used for the next step without further purification.

Step 2: The title product was synthesized from the above compound according to the General Procedure E.

3.03 g (93% yield for 2 steps), colourless oil.

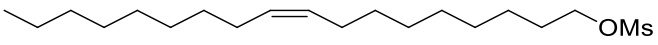
^{1}H NMR (400 MHz, $CDCl_3$, diastereomers) δ 7.79 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), [4.72-4.68 (m), 4.45-4.39 (m), 1 H], 4.15-4.07 (m, 2 H), 2.45 (s, 3 H), 2.35-2.22 (m, 1 H), 1.99-1.43 (m, 8 H), 1.26-1.20 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, diastereomers) δ 174.6, (144.5, 144.4), (134.5, 134.3), 129.7, (127.52, 127.49), (80.4, 78.4), (60.34, 60.29), (41.1, 41.0), (31.0, 29.7), (26.3, 23.2), 21.5, (14.12,

14.08).

IR (neat, cm^{-1}): 2954, 2929, 2869, 1717, 1646, 1457, 1365, 1173, 1096, 1042, 928, 844, 813, 666.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{16}H_{23}O_5S$ 327.1261, found 327.1261.



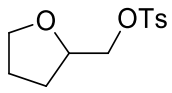
(*Z*)-octadec-9-en-1-yl methanesulfonate (**2x,** known compound)

This compound was synthesized according to the General Procedure D, but Oleyl alcohol (2.68 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 23.

3.11 g (90% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39-5.30 (m, 2 H), 4.22 (t, *J* = 6.4 Hz, 2 H), 3.00 (s, 3 H), 2.10-1.99 (m, 3 H), 1.78-1.71 (m, 2 H), 1.40-1.26 (m, 23 H), 0.88 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 130.0, 129.7, 70.1, 37.3, 31.9, 29.7, 29.6, 29.5, 29.3, 29.1, 29.0, 27.2, 27.1, 25.4, 22.6, 14.1.



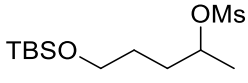
(Tetrahydrofuran-2-yl)methyl 4-methylbenzenesulfonate (**2y,** known compound)

This compound was synthesized according to the General Procedure E, but (tetrahydrofuran-2-yl)methanol (1.02 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 24.

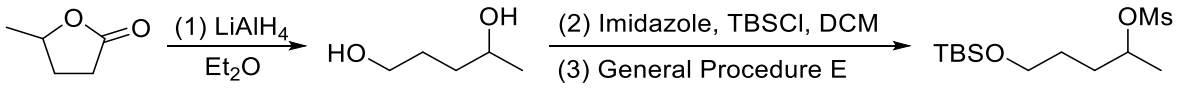
2.12 g (83% yield), white solid. Mp.: 33-35 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.12-4.07 (m, 1 H), 4.03-3.96 (m, 2 H), 3.81-3.70 (m, 2 H), 2.45 (s, 3 H), 2.07-1.94 (m, 1 H), 1.92-1.80 (m, 2 H), 1.70-1.62 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 133.0, 129.8, 127.9, 75.9, 71.4, 68.6, 27.8, 25.5, 21.6.



5-((Tert-butyldimethylsilyl)oxy)pentan-2-yl methanesulfonate (**2z**)



Step 1: To a slurry of $LiAlH_4$ (1.52 g, 40.0 mmol) in dry diethyl ether (100 ml) was dropwise

added a solution of 5-methyldihydrofuran-2(3*H*)-one (1.00 g, 10.0 mmol) in dry diethyl ether (10 ml) at 0 ^{o}C under argon. The reaction mixture was stirred at room temperature for 3 h, and then quenched with water (2.0 ml), 15% NaOH aqueous solution (2.0 ml) and water (5 ml). The mixture was filtered through a pad of silica gel and the filter bed was washed with ethyl acetate (3 × 50 ml). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by flash chromatography on silica gel to give pentane-1,4-diol (0.83 g, 80% yield).

Step 2: To a solution of pentane-1,4-diol (0.83 g, 8.0 mmol) and imidazole (0.68 g, 10 mmol) in CH_2Cl_2 (30 mL) was added TBSCl (1.21 g, 8.0 mmol). The reaction mixture was stirred at room temperature overnight and then quenched with water, extracted twice with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by silica gel column to give 5-((tert-butyldimethylsilyl)oxy)pentan-2-ol (1.05 g, 60% yield).

Step 3: The title compound was synthesized according to the General Procedure D, but 5-((tert-butyldimethylsilyl)oxy)pentan-2-ol (1.05 g, 4.8 mmol) was used.

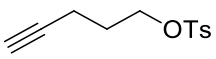
1.30 g (91% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87-4.80 (m, 1 H), 3.67-3.58 (m, 2 H), 2.98 (s, 3 H), 1.80-1.68 (m, 2 H), 1.66-1.52 (m, 2 H), 1.42 (d, *J* = 6.4 Hz, 3 H), 0.88 (s, 9 H), 0.04 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 80.2, 62.4, 38.6, 33.2, 28.3, 25.9, 21.2, 18.3, -5.4.

IR (neat, cm^{-1}): 2955, 2932, 2858, 1642, 1466, 1355, 1255, 1176, 1099, 1047, 1005, 973, 905, 837, 777.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{12}H_{29}O_4SSi$ 297.1550, found 297.1551.



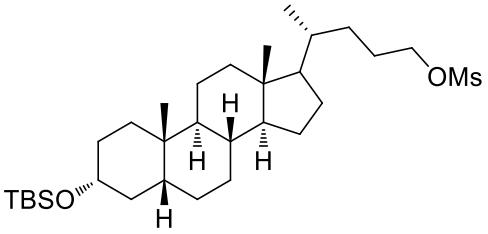
Pent-4-yn-1-yl 4-methylbenzenesulfonate (**2aa,** known compound)

This compound was synthesized according to the General Procedure E, but pent-4-yn-1-ol (0.84 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 25.

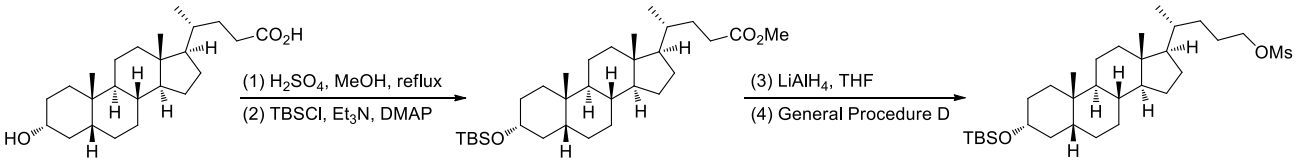
2.14 g (90% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 4.15 (t, *J* = 6.4 Hz, 2 H), 2.46 (s, 3 H), 2.26 (td, J_1= 6.8 Hz, 2.4 Hz, 2 H), 1.90-1.83 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 132.8, 129.8, 127.9, 82.1, 69.4, 68.7, 27.6, 21.6, 14.6.



(4*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*)-3-((*tert*-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentyl methanesulfonate (**7**)



Step 1: To a solution of Lithocholic acid (3.76 g, 10.0 mmol) in MeOH (30 mL) was added H_2SO_4 (1.8 mL). The reaction mixture was refluxed for 2 h. After removing the solvent, the crude mixture was diluted with EtOAc (50 ml), washed with H_2O (40 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in DCM (40 ml) and triethylamine (2.2 ml, 15.0 mmol), DMAP (241 mg, 2.0 mmol) and TBSCl (1.52 g, 11.9 mmol) were added. The reaction mixture was stirred at room temperature for 12 h, and then quenched with a saturated aqueous NH_4Cl (50 ml), extracted twice with CH_2Cl_2 (50 ml). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by silica gel column to give the corresponding protected alcohol (3.53 g).

Step 2: To a solution of the above compound in THF (20 ml) was added $LiAlH_4$ (0.68 g, 18.0 mmol) slowly. The reaction mixture was stirred for 2 h, quenched by addition of water (20 mL), and extracted with EtOAc (2 ×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was purified by silica gel column to give alcohol as a white solid (3.33 g, 70% yield).

The title compound was synthesized from the above alcohol (3.33 g, 7.0 mmol) according to the General Procedure D.

2.18 g (80% yield), white solid, mp.: 128-130 ^{o}C.

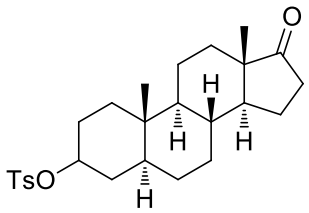
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.23-4.17 (m, 2 H), 3.60-3.55 (m, 1 H), 3.00 (s, 3 H), 1.95-1.93 (m, 1 H), 1.84-1.74 (m, 5 H), 1.66-1.54 (m, 3 H), 1.49-1.33 (m, 9 H), 1.26-1.17 (m, 3 H), 1.15-0.99 (m, 6 H), 0.96-0.89 (m, 16 H), 0.64 (s, 3 H), 0.06 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 72.8, 70.6, 56.4, 56.1, 42.7, 42.3, 40.2, 40.2, 37.4, 36.9, 35.9,

35.6, 35.3, 34.6, 31.5, 31.0, 28.3, 27.3, 26.4, 26.0, 25.9, 24.2, 23.4, 20.8, 18.5, 18.3, 12.0, -4.6.

IR (neat, cm^{-1}): 2927, 2859, 1648, 1544, 1462, 1347, 1250, 1176, 1099, 985, 959, 918, 872, 836, 772, 669.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{31}H_{59}O_4SSi$ 555.3898, found 555.3891.



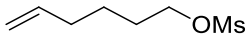
(4*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*)-3-((*tert*-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentyl methanesulfonate (**9,** known compound)

This compound was synthesized according to the general Procedure E, but epiandrosterone (2.90 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 26.

3.11 g (90% yield), white solid, mp.: 140-142 ^{o}C

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 2 H), 7.33 (d, *J* = 7.8 Hz, 2 H), 4.43-4.39 (m, 1 H), 2.44-2.40 (m, 4 H), 2.08-2.02 (m, 1 H), 1.93-1.90 (m, 1 H), 1.78-1.69 (m, 4 H), 1.64-1.42 (m, 6 H), 1.29-1.19 (m, 5 H), 1.12-1.08 (m, 1 H), 0.96-0.91 (m, 2 H), 0.82 (d, *J* = 19.2 Hz, 6 H), 0.67-0.63 (m, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 220.8, 144.3, 134.9, 129.7, 127.5, 110.0, 82.1, 54.17, 51.3, 47.6, 44.8, 36.7, 35.7, 35.3, 34.9, 34.8, 31.5, 30.7, 28.3, 28.1, 21.7, 21.5, 20.4, 13.7, 12.1.



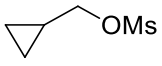
Hex-5-en-1-yl methanesulfonate (**13,** known compound)

This compound was synthesized according to the General Procedure D, but hex-5-en-1-ol (1.00 g, 10.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 14.

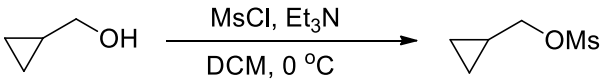
1.64 g (92% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84-5.74 (m, 1 H), 5.05-4.97 (m, 2 H), 4.23 (t, *J* = 6.8 Hz, 2 H), 3.00 (s, 3 H), 2.13-2.08 (m, 2 H), 1.80-1.73 (m, 2 H), 1.56-1.48 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 155.1, 69.9, 37.3, 32.9, 28.4, 24.5.



Cyclopropylmethyl methanesulfonate (**2ab,** known compound)

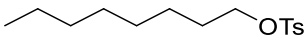


To a solution of cyclopropylmethanol (0.36g, 5.0 mmol) in DCM (10 mL) at -30 ℃ was added MsCl (0.86g, 7.5 mmol) in one portion. Et_3N (0.81 g, 8.0 mmol) was added dropwise. The reaction mixture was warmed to 0 ℃. When the reaction was completed as monitored by TLC, it was quenched with a cold aqueous solution of HCl (5 mL, 3 M) and cold brine (5 mL), extracted twice with CH_2Cl_2 (20 mL). The combined organic layers were washed with cold brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting yellow liquid was used without further purification. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 27.

0.68 g (90% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (d, *J* = 4.0 Hz, 2H), 3.03 (s, 3H), 1.29-1.21 (m, 1H), 0.72-0.67 (m, 2H), 0.42-0.38 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 75.5, 38.0, 10.3, 4.0.



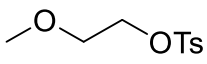
Octyl 4-methylbenzenesulfonate (2ad, known compound**)**

This compound was synthesized according to the General Procedure E, but octan-1-ol (650 mg, 5.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 28.

1.3 g (93% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 4.02 (t, *J* = 4.0 Hz, 2H), 2.44 (s, 3H), 1.66-1.59 (m, 2H), 1.29-1.22 (m, 10H), 0.86 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 133.3, 129.9, 127.9, 70.8, 31.7, 29.1, 28.93, 28.87, 25.4, 22.7, 21.7, 14.1.



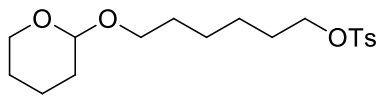
2-Methoxyethyl 4-methylbenzenesulfonate (2ae, known compound**)**

This compound was synthesized according to the General Procedure E, but 2-methoxyethan-1-ol (380 mg, 5.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 29.

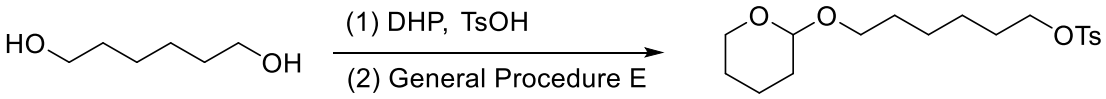
1.05 g (91% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.16 (t, *J* = 4.0 Hz, 2H), 3.58 (t, *J* = 4.0 Hz, 2H), 3.30 (s, 3H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 133.1, 129.9, 128.1, 70.0, 69.2, 59.1, 21.7.



6-((Tetrahydro-2*H*-pyran-2-yl)oxy)hexyl 4-methylbenzenesulfonate (2af, known compound**)**



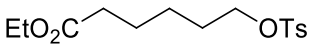
Step 1: To a stirred solution of hexane-1,6-diol (1.18 g, 10.0 mmol) and *p*-toluenesulfonic acid monohydrate (7.5 g, 40 mmol) in THF (10 mL) was slowly added dihydropyran (0.42 g, 5.0 mmol) at 0 ^{o}C. After stirring at room temperature for 24 h, the reaction mixture was warmed to room temperature. The reaction mixture was then quenched with water and extracted twice with EtOAc (30 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was directly used for the next step without further purification.

Step 2: The title product was synthesized from the above compound according to the General Procedure E. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 30.

1.3 g (72% yield for 2 steps), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.55 (t, *J* = 4.0 Hz, 1H), 4.02 (t, *J* = 8.0 Hz, 2H), 3.88-3.82 (m, 1H), 3.73-3.67 (m, 1H), 3.52-3.47 (m, 1H), 3.37-3.32 (m, 1H), 2.45 (s, 3H), 1.84-1.52 (m, 10H), 1.34 -1.32 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 132.9, 129.7, 127.6, 98.7, 70.4, 67.1, 62.2, 30.6, 29.3, 28.5, 25.4, 25.3, 25.0, 21.4, 19.5.



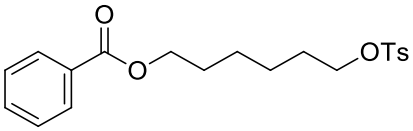
Ethyl 6-(tosyloxy)hexanoate (2ag, known compound**)**

This compound was synthesized according to the General Procedure E, but 2-methoxyethan-1-ol (870 mg, 5.0 mmol) was used. ^{1}H NMR data are consistent with those reported in ref. 31.

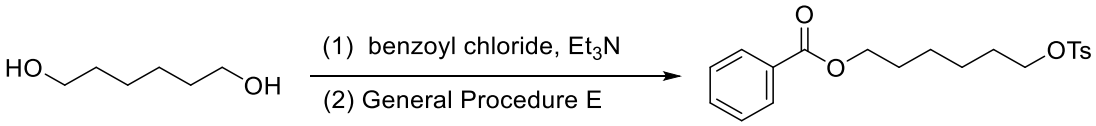
1.40 g (85% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.14-4.09 (m, 2H), 4.02 (t, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.25 (t, *J* = 8.0 Hz, 2H), 1.70-1.54 (m, 4H), 1.39-1.31 (m, 2H), 1.25 (t, *J* = 4.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 144.8, 133.3, 130.0, 128.0, 70.4, 60.4, 34.1, 28.7, 25.1, 24.4, 21.8, 14.4.



6-(Tosyloxy)hexyl benzoate (2ah)



Step 1: To a stirred solution of hexane-1,6-diol (1.18 g, 10.0 mmol), Et_3N (1.52 g, 15.0 mmol), and DMAP (122.2 mg, 1.0 mmol) in CH_2Cl_2 (30 mL) was added benzoyl chloride (1.55 g, 11.0 mmol). The reaction mixture was stirred at room temperature overnight, and then quenched with water (20 mL), extracted twice with CH_2Cl_2 (20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel.

Step 2: The title product was synthesized from the above compound according to the General Procedure E.

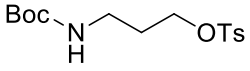
2.44 g (65% yield for two steps), white solid, mp.: 29-30 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.26 (t, *J* = 8.0 Hz, 2H), 4.03 (t, *J* = 4.0 Hz, 2H), 2.41 (s, 3H), 1.70-1.66 (m, 4H), 1.37 (s, 4H).

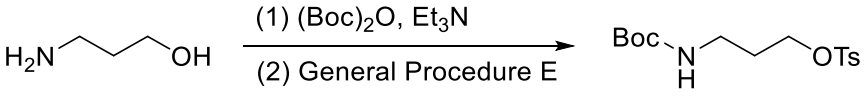
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 144.6, 132.9, 132.8, 130.2, 129.7, 129.3, 128.2, 127.7, 70.3, 64.6, 28.5, 23.3, 25.3, 24.9, 21.4.

IR (neat, cm^{-1}): 2952, 2927, 2863, 1716, 1599, 1453, 1359, 1275, 1176, 1099, 963, 926, 815, 713, 663.

HRMS (ESI): $[M+H]^+$ calcd for $C_{20}H_{25}O_5S$ 377.1417, found 377.1416.



3-((Tert-butoxycarbonyl)amino)propyl 4-methylbenzenesulfonate (2ai, known compound**)**



Step 1: To a solution of 3-aminopropan-1-ol (0.75 g, 10.0 mmol) and Et_3N (2.00 g, 20.0 mmol)

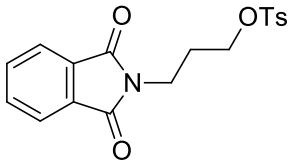
in CH_2Cl_2 (30 mL) was added $(Boc)_2O$ (2.40 g, 11.0 mmol) at 0 ^oC. The reaction mixture was stirred at room temperature overnight, and then quenched with water, extracted twice with CH_2Cl_2. The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The residue was directly used for the next step without further purification.

Step 2: The title product was synthesized from the above compound according to the General Procedure E. ^1H NMR and ^{13}C NMR data are consistent with those reported in ref. 32.

2.7 g (84% yield, yield for two steps), colourless oil.

^1H NMR (600 MHz, $CDCl_3$) δ 7.79-7.78 (d, *J* = 6.0 Hz, 2H), 7.36-7.35 (d, *J* = 6.0 Hz, 2H), 4.83 (bs, 1H), 4.08 (t, *J* = 6.0 Hz, 2H), 3.15 (s, 2H), 2.45 (s, 3H), 1.87-1.81 (m, 2H), 1.41 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 155.9, 144.9, 132.8, 129.9, 127.8, 79.2, 68.1, 36.7, 29.2, 28.3, 21.5



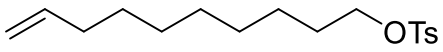
3-(1,3-Dioxoisoindolin-2-yl)propyl 4-methylbenzenesulfonate (2aj, known compound**)**

The title product was synthesized according to the General Procedure E. ^1H NMR and ^{13}C NMR data are consistent with those reported in ref. 33.

1.60 g (91% yield), colourless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.71 (m, 6H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.11 (t, *J* = 4.0 Hz, 2H), 3.74 (t, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.09-2.03 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 145.0, 134.2, 132.9, 132.0, 130.0, 128.1, 123.4, 67.9, 34.7, 28.1, 21.8.



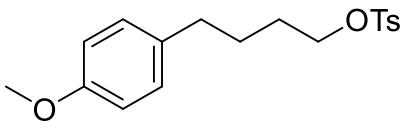
Dec-9-en-1-yl 4-methylbenzenesulfonate (2ak, known compound**)**

This compound was synthesized according to the General Procedure E, but dec-9-en-1-ol (780 mg, 5.0 mmol) was used. ^1H NMR and ^{13}C NMR data are consistent with those reported in ref. 34.

1.38 g (89% yield), colourless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.84-5.74 (m, 1H), 5.01-4.91 (m, 2H), 4.01 (t, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.05-1.99 (m, 2H), 1.66-1.59 (m, 2H), 1.36-1.23 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.7, 139.1, 133.2, 129.9, 127.9, 114.2, 70.7, 33.8, 29.2, 29.0, 28.88, 28.86, 28.81, 25.3, 21.7.



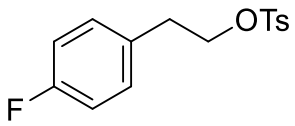
4-(4-Methoxyphenyl)butyl 4-methylbenzenesulfonate (2al, known compound**)**

This compound was synthesized according to the General Procedure E, but 4-(4-methoxyphenyl)butan-1-ol (900 mg, 5.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 35.

1.50 g (90% yield), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 4.01 (t, *J* = 8.0 Hz, 2H), 3.76 (s, 3H), 2.49 (t, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 1.66-1.56 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 144.8, 133.6, 133.0, 129.9, 129.2, 127.9, 113.7, 70.5, 55.2, 34.1, 28.3, 27.3, 21.6.



4-Fluorophenethyl 4-methylbenzenesulfonate (2am)

This compound was synthesized according to the General Procedure E, but 2-(4-fluorophenyl)ethan-1-ol (700 mg, 5.0 mmol) was used.

1.40 g (92% yield), colourless oil.

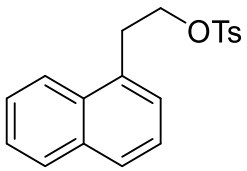
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.08 – 7.03 (m, 2H), 6.94 – 6.88 (m, 2H), 4.18 (t, *J* = 8.0 Hz, 2H), 2.91 (t, *J* = 4.0 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, $J_{C\text{-}F}$ = 244.0 Hz), 144.9, 132.8, 132.1 (d, $J_{C\text{-}F}$ = 2.9 Hz), 130.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.8, 127.8, 115.4 (d, $J_{C\text{-}F}$ = 21.1 Hz), 70.6, 34.5, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ –116.02.

IR (neat, cm^{-1}): 3046, 2959, 2926, 1922, 1892, 1601, 1511, 1360, 1224, 1176, 1099, 1056, 967, 903, 866, 829, 750, 705, 663.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{16}FO_3S$ 295.0799, found 295.0796.



2-(Naphthalen-1-yl)ethyl 4-methylbenzenesulfonate (2an)

This compound was synthesized according to the General Procedure E, but 2-(naphthalen-1-yl)ethan-1-ol (860 mg, 5.0 mmol) was used. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 36.

1.40 g (85% yield), colourless oil.

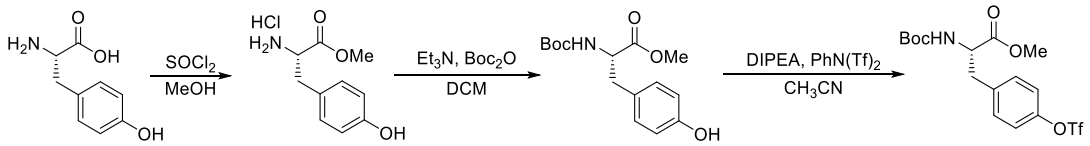
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.45-7.40 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.30 (t, *J* = 8.0 Hz, 2H), 3.38 (t, *J* = 8.0 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 133.8, 132.6, 131.9, 131.6, 129.7, 128.9, 127.8, 127.7, 127.5, 126.3, 125.7, 125.5, 123.0, 69.9, 32.5, 21.6.

3.3 Preparation of peptide substrates

3.3.1 Synthesis of tyrosine 16a

General Procedure F

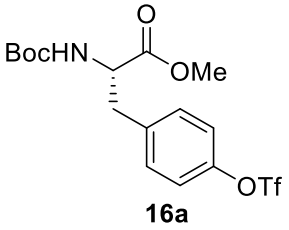


Step 1: To a stirred solution of tyrosine (1.8 g, 10 mmol) in MeOH (15 mL) at 0 ℃ was added thionyl chloride (2.4 g, 20 mmol) dropwise. The reaction mixture was refluxed. When the reaction was completed as monitored by TLC, the reaction mixture was concentrate under the reduced pressure to give a crude ester product, which was used for the next step without purification.

Step 2: To a solution of the above product and Et_3N (2.5 g, 25 mmol) in DCM (15 mL) was added a solution of Boc_2O (2.2 g, 10 mmol) in DCM (5 mL) at 0 ^{o}C. The reaction mixture was stirred at room temperature overnight. The reaction was quenched with water and extracted twice with DCM. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The crude product was used for the next step without further purification.

Step 3: To a solution of the above crude product in CH_3CN (30 mL) was added DIPEA (1.9 g, 15 mmol), N-Phenyl-bis(trifluoromethanesulfonimide) [$PhN(Tf)_2$, 4.3 g, 12 mmol] at 0 ℃. The reaction was stirred at 0 ^{o}C for 10 min, and at room temperature overnight. The solvent was removed under the reduced pressure. The residue was diluted with CH_2Cl_2, washed with water twice, dried over anhydrous Mg_2SO_4, concentrated under reduced pressure. The residue was purified by flash

chromatography on silica gel to give the title product.



16a

Methyl(*S*)-2-((tert-butoxycarbonyl)amino)-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoate (16a)

This compound was synthesized according to the General Procedure F. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 37.

3.5 g (82% yield), colourless oil.

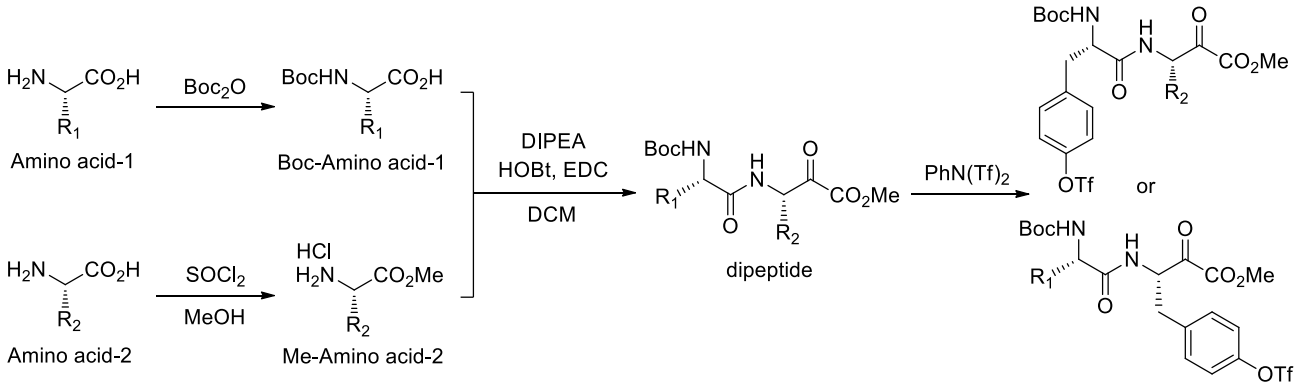
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.19 (m, 4H), 5.04 (m, 1H), 4.60 (m, 1H), 3.71 (s, 3H), 3.20-3.01 (m, 2H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 155.1, 148.8, 137.1, 131.3, 121.5, 118.9 (q, $J_{C\text{-}F}$ = 319.0Hz), 80.4, 54.4, 52.5, 38.1, 28.4.

^{19}F NMR (564 MHz, $CDCl_3$) δ –72.73.

3.3.2 Synthesis of tyrosine containing dipeptides, tripeptides, and tetrapeptides

General Procedure G



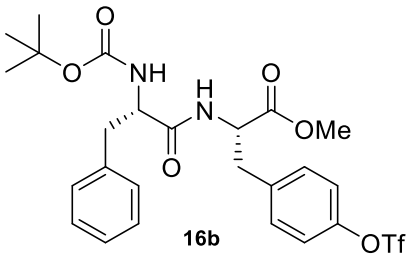
Step 1: To a stirred solution of amino acid-1 (10 mmol, 1.0 equiv) in H_2O/dioxane (1:1, 10 mL) was added aqueous solution of NaOH (2.0 M) until a pH ~ 11-12 was achieved. Di-tert-butyl dicarbonate (Boc_2O, 11 mmol, 1.1 equiv) was then added over 30 min. Additional aqueous solution of NaOH (2.0 M) was added at 0 ℃ to keep the pH alkaline. After stirring at the same temperature for 60 min, the reaction mixture was warmed to room temperature and stirred until it was completed

as monitored by TLC. The solvent was removed under the reduced pressure. The crude mixture was acidified to pH 2.5-3 with saturated citric acid, extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were washed with H_2O, brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product (Boc-Amino acid-1) was used for the next step without further purification.

To another round bottom flask charged with amino acid-2 (10 mmol, 1.0 equiv) and MeOH (15 mL), thionyl chloride ($SOCl_2$, 20 mmol, 1.0 equiv) was added dropwise at 0 ℃. The reaction was refluxed. When the reaction was completed as monitored by TLC, the solvent was removed under the reduced pressure. The crude product (Me-Amino acid-2) was used for the next step without purification.

Step 2: To a solution of crude product Boc-Amino acid-1 in CH_2Cl_2 (100 mL) was added DIPEA (1.7 mL, 10 mmol), crude product Me-Amino acid-2, 1-hydroxybenzotriazole (HOBt, 2.0 g), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC, 1.9 g, 10 mmol) at 0 ℃. The reaction was warmed to room temperature and stirred for 24 h. The reaction mixture was washed with sat. aq. $NaHCO_3$ (2 × 100 mL), 10 wt% aq. citric acid (2 × 50 mL), brine, and dried over anhydrous Mg_2SO_4. The solvent was removed under the reduced pressure. The residue was purified by flash chromatography on silica gel to give dipeptide.

Step 3: The desired triflate substrates were prepared according to the procedure described in General Procedure G, step 3.



16b

Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoate (16b)

This compound was synthesized according to the General Procedure G.

4.5 g (78% yield yield for 3 steps), white solid, mp.: 130-132 ^{o}C

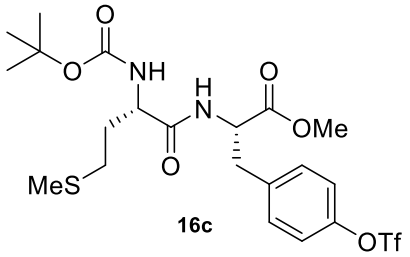
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.10 (m, 9H), 6.41 (d, *J* = 12 Hz, 1H), 4.94 (s, 1H), 4.77 (m, 1H), 4.32 (m, 1H), 3.65 (s, 3H), 3.13-3.03 (m, 4H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 171.0, 155.5, 148.7, 136.6, 136.5, 131.2, 129.4, 128.9, 127.2, 121.5, 118.8 (q, J_{C-F} = 318.9Hz), 80.6, 55.9, 53.2, 52.6, 38.1, 37.5, 28.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ −72.92.

IR (cm^{-1}): 3332, 3298, 2981, 2932, 1740, 1661, 1519, 1421, 1250, 1213, 1167, 1142, 1018, 891, 749, 699, 610.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{25}H_{30}F_3N_2O_8S$ 575.1669, found 575.1666.



methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-4-(methylthio)butanamido)-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoate (16c)

This compound was synthesized according to the General Procedure G.

4.3 g (76% yield for 3 steps), white solid, mp.: 72-74 ^oC

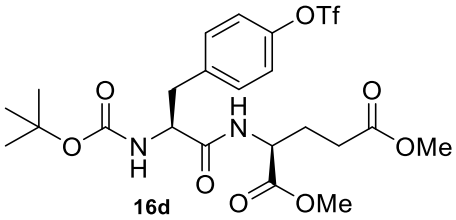
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.99-6.97 (m, 1H), 5.39-5.37 (m, 1H), 4.89-4.84 (m, 1H), 4.31-4.29 (m, 1H), 3.70 (s, 3H), 3.22-3.06 (m, 2H), 2.54 (t, *J* = 8.0 Hz, 2H), 2.17-1.83 (m, 5H), 1.44 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 171.3, 155.6, 148.6, 136.7, 131.2, 121.4, 118.7 (q, J_{C-F} = 320 Hz), 80.2, 53.4, 53.1, 52.5, 37.3, 31.4, 30.1, 28.3, 15.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.75.

IR (cm^{-1}): 3322, 2980, 2922, 2252, 1745, 1661, 1503, 1424, 1368, 1215, 1142, 1049, 1020, 891, 735.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{30}F_3N_2O_8S_2$ 559.1390, found 559.1384.



Dimethyl((S)-2-((tert-butoxycarbonyl)amino)-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoyl)-L-glutamate (16d)

This compound was synthesized according to the General Procedure G.

4.1 g (72% yield for 3 steps), white solid, mp.: 134-136 ^oC

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.67 (m, 1H), 5.01 (m, 1H), 4.59-4.52 (m, 1H), 4.41-4.31 (m, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 3.17-3.02 (m, 2H),

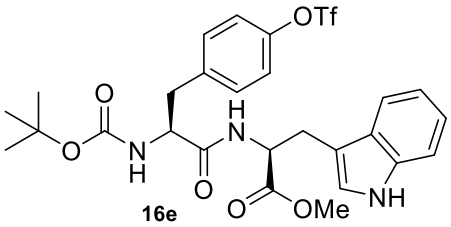
2.15-2.41 (m, 3H), 1.91-2.00 (m, 1H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 171.8, 170.8, 155.4, 148.7, 137.4, 131.4, 121.5, 118.8 (q, J_{C-F} = 322.2 Hz), 80.6, 55.5, 52.7, 52.0, 51.9, 37.6, 29.9, 28.3, 27.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ -73.54.

IR (cm^{-1}): 3311, 2980, 2956, 1742, 1659, 1529, 1504, 1424, 1369, 1213, 1142, 1019, 891, 750, 639, 611.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{30}F_3N_2O_{10}S$ 571.1568, found 571.1566.



16e

methyl((S)-2-((tert-butoxycarbonyl)amino)-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoyl)-L-tryptophanate (16e)

This compound was synthesized according to the General Procedure G.

4.6 g (73% yield for 3 steps), white solid, mp.: 144-146 ^oC

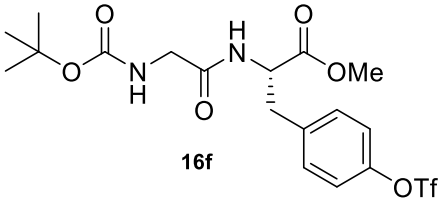
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.15-7.19 (m, 3H), 7.06-7.10 (m, 3H), 6.87 (m, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.06 (d, *J* = 8.0 Hz, 1H), 4.85 (m, 1H), 4.36 (m, 1H), 3.65 (s, 3H), 3.25 (d, *J* = 4.0 Hz, 2H), 3.07-3.02 (m, 1H), 2.81-2.91 (m, 1H), 1.36 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 170.6, 155.4, 148.5, 137.5, 136.2, 131.3, 127.6, 123.1, *122*.4, 121.4, 119.8, 118.8 (q, J_{C-F} = 322.2 Hz), 118.4, 111.6, 109.5, 80.4, 55.4, 53.1, 52.5, 37.9, 28.3, 27.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ –73.36.

IR (cm^{-1}): 3322, 2980, 2955, 2933, 1741, 1658, 1503, 1424, 1368, 1250, 1215, 1168, 1142, 1019, 891, 741, 639, 610.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{27}H_{31}F_3N_3O_8S$ 614.1778, found 614.1777.



16f

Methyl (S)-2-(2-((tert-butoxycarbonyl)amino) acetamido)-3-(4-(((trifluoromethyl) sulfonyl)oxy) phenyl)propanoate (16f)

This compound was synthesized according to the General Procedure G.

3.4 g (70% yield for 3 steps), white solid, mp.: 64-65 °C.

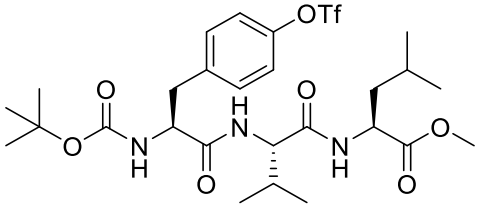
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 4H), 6.65 (m, 1 H), 5.06 (s, 1 H), 4.91-4.86 (m, 1 H), 3.86-3.80 (m, 1H), 3.75 (d, *J* = 8.0 Hz, 1 H), 3.71 (s, 3H), 3.22-3.09 (m, 2H), 1.45 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 171.5, 169.5, 156.2, 148.8, 136.8, 131.2, 121.5, 118.9 (q, J_{C-F} = 318 Hz), 80.5, 53.1, 52.5, 44.4, 37.4, 28.3.

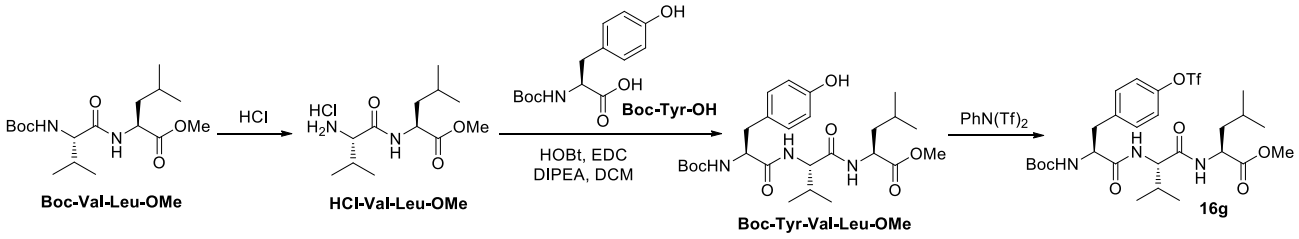
^{19}F NMR (376 MHz, $CDCl_3$) δ −72.92.

IR (cm^{-1}): 3328, 3071, 2981, 2936, 1672, 1503, 1424, 1369, 1214, 1052, 1019, 942, 891, 783, 738, 639, 611.

HRMS (ESI): $[M+H]^+$ calcd for $C_{18}H_{24}F_3N_2O_8S$ 485.1200, found 485.1194.



Methyl((S)-2-((tert-butoxycarbonyl)amino)-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propanoyl)-L-valyl-L-leucinate (16g)



Boc-Val-Leu-OMe was synthesized according the General Procedure G.

Boc-Val-Leu-OMe (3.5g, 10 mmol) was dissolved in a solution of HCl in dioxane (4.0 M, 50 mL), and stirred for 2 h at room temperature. The reaction mixture was concentrated under the reduced pressure to afford HCl-Val-Leu-OMe as a white solid. The crude product was pure enough for the next step.

Tripeptide **16g** was prepared according the General Procedure G.

4.2 g (66% yield for 3 steps), white solid, mp.: 108-110 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (bs, 1H), 7.35 (bs, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.82-5.72 (m, 1H), 4.69 (bs, 1H), 4.63-4.57 (m, 1H), 4.47(t, *J* = 8.0 Hz, 1H), 3.73 (s, 3H), 3.11-2.94(m, 2H), 2.13-2.02 (m, 1H), 1.72-1.59 (m, 3H), 1.35 (s, 9H), 0.98-0.90 (m, 12H).

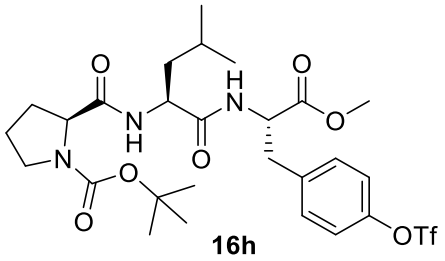
^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 171.9, 171.4, 155.7, 148.5, 137.9, 131.4, 121.1, 118.8 (q,

$J_{C\text{-}F}$ = 315 Hz), 80.0, 58.7, 55.3, 52.2, 51.0, 41.0, 37.8, 31.4, 28.3, 25.0, 22.7, 22.0, 19.0, 18.5.

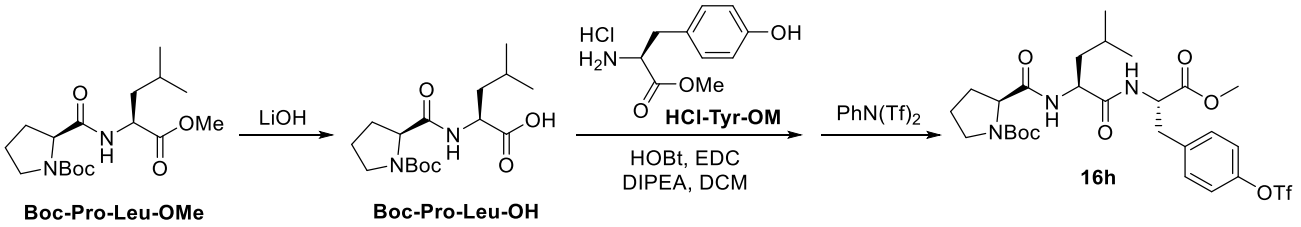
^{19}F NMR (564 MHz, $CDCl_3$) δ −73.11.

IR (cm^{-1}): 3291, 3076, 2962, 1875, 1750, 1688, 1643, 1526, 1426, 1393, 1369, 1214, 1143, 1021, 891, 829, 740, 639, 610.

HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{41}F_3N_3O_9S$ 640.2510, found 640.2509.



Tert-butyl(S)-2-(((S)-1-(((S)-1-methoxy-1-oxo-3-(4-(((trifluoromethyl) sulfonyl)oxy) phenyl)propan-2-yl)amino)-4-methyl-1-oxopentan-2-yl) carbamoyl) pyrrolidine-1- carboxylate (16h)



Boc-Pro-Leu-OMe was synthesized according to the General Procedure G.

To a stirred solution of Boc-Pro-Leu-OMe (3.4g, 10 mmol) in THF/H_2O (3/1, 30 mL) was added LiOH (10 mL, 2.0 M in H_2O, 2.0 equiv) at 0 ℃. The reaction mixture was stirred at the same temperature for 30 min. It was then stirred at room temperature until complete conversion of the methyl ester was determined by TLC. $KHSO_4$ was slowly added until a pH ~ 2-3 was achieved. The reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give crude Boc-Pro-Leu-OH (assumed quantitative yield) which was directly used for the next step.

Tripeptide **16h** was prepared according the General Procedure G.

3.9 g (61% yield for 3 steps), white solid, mp.: 61-63 ^oC.

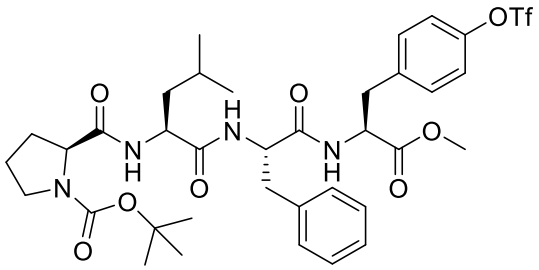
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 6.0 Hz, 2H), 7.20 (d, *J* = 6.0 Hz, 2H), 7.01 (s, 1H), 6.56 (s, 1H), 4.73-7.69 m, 1H), 4.31 (s, 1H), 4.17 (s, 1H), 3.61 (s, 3H), 3.32-3.28 (m, 2H), 3.10-2.98 (m, 2H), 2.19-1.99 (m, 2H), 1.81 (m, 2H), 1.56-1.49 (m, 2H), 1.38 (s, 10H), 0.83-0.79 (m, 6H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 172.4, 171.8, 156.0, 148.5, 137.0, 131.2, 121.2, 118.7 (q, $J_{C\text{-}F}$ = 315 Hz), 80.6, 59.9, 53.1, 52.3, 51.9, 47.1, 40.2, 37.1, 28.2, 27.9, 24.7, 22.9, 21.6.

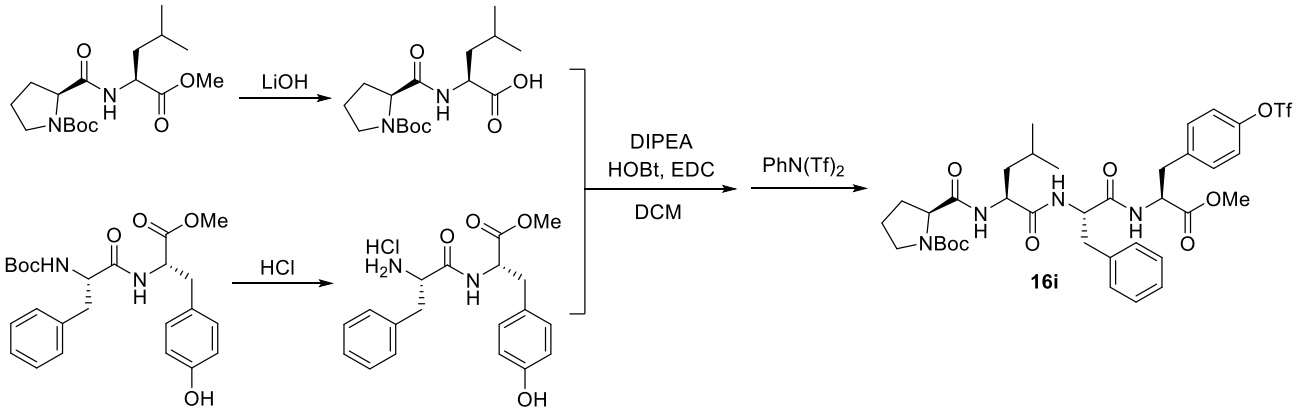
^{19}F NMR (376 MHz, $CDCl_3$) δ −73.11.

IR (cm^{-1}): 3297, 3066, 2961, 2875, 1745, 1661, 1545, 1503, 1422, 1367, 1214, 1142, 1020, 995, 890, 775, 735, 701, 610.

HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{39}F_3N_3O_9S$ 638.2354, found 638.2349.



Tert-butyl(S)-2-(((S)-1-(((S)-1-(((S)-1-methoxy-1-oxo-3-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)propan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-methyl-1-oxopentan-2-yl) carbamoyl) pyrrolidine-1-carboxylate (16i)



Tetrapeptide 16i was prepared according to the General Procedure G.

5.2 g (66% yield for 3 steps), white solid, mp.: 64-66 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.10 (m, 12H), 4.83-4.74 (m, 2 H), 4.32-4.07 (m, 2 H), 3.67-3.60 (m, 3H), 3.44-3.40 (m, 2H), 3.24-2.91 (m, 4 H), 2.09-1.86 (m, 4H), 1.57-1.43 (m, 12H), 0.89-0.83 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 171.9, 171.1, 170.9, 156.3, 148.5, 137.5, 137.0, 131.2, 129.0, 128.5, 126.7, 121.3, 118.8 (q, J_{C-F} = 310 Hz), 81.2, 60.5, 53.7, 53.3, 52.9, 47.4, 39.9, 37.0, 28.6, 28.3, 24.9, 24.7, 23.0, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ −73.17.

IR (cm^{-1}): 3293, 3068, 3033, 2957, 2931, 2873, 2250, 1746, 1646, 1545, 1503, 1422, 1214, 1175, 1142, 1019, 890, 738, 700, 641, 610.

HRMS (ESI): $[M+H]^+$ calcd for $C_{36}H_{48}F_3N_4O_{10}S$ 785.3038, found 785.3033.

4. Cross-Coupling of Alkyl Sulfonates with Vinyl Triflates

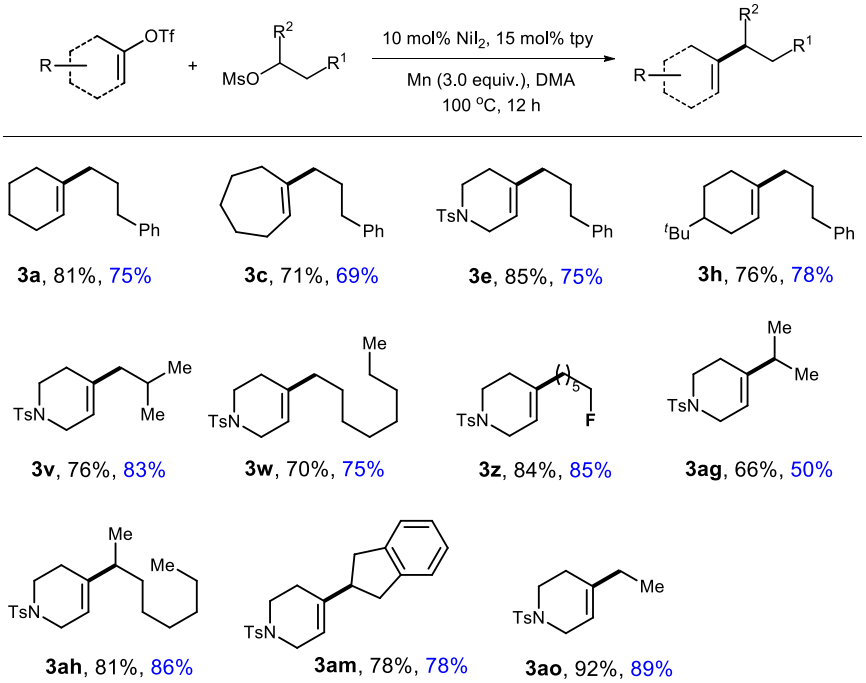
4.1 General Procedure H (glove box technique)

The procedure was conducted in the argon-filled glove box. To a reaction tube containing NiI_2 (6.3 mg, 10 mol %), tpy (7.0 mg, 15 mol %) and Mn (33 mg, 3.0 equiv.) was added a solution of alkyl sulfonate (1.8 equiv.) and vinyl triflate (1.0 equiv.) in DMA (2mL). It was then removed from the glove box, and the reaction mixture was stirred at 100 ^{o}C for 12 h. The reaction was quenched with water (20 mL), extracted twice with ethyl acetate (2 × 15 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 to give the desired product.

4.2 General Procedure I (bench air-free technique)

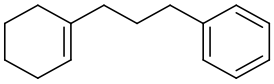
To a Schlenk tube containing NiI_2 (6.3 mg, 10 mol %), tpy (7.0 mg, 15 mol %) and Mn (33 mg, 3.0 equiv.) was added a solution of alkyl sulfonate (1.8 equiv.) and vinyl triflate (1.0 equiv.) in DMA (2 mL). The reaction tube was cooled with liquid N_2, vacuumed and refilled with argon for three times. The reaction mixture was stirred at 100 ^{o}C for 12 h. The reaction was quenched with water (20 mL), extracted twice with ethyl acetate (2 × 15 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 to give the desired product.

Table S5 Comparison of the two procedures[a]



[a]Isolated yields from procedure H (black) and procedure I (blue)

4.3 Characterization Data



(3-(Cyclohex-1-en-1-yl)propyl)benzene (**3a**)

The title compound was prepared according to the General Procedure from the reaction of cyclohex-1-en-1-yl trifluoromethanesulfonate **1a** (46 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

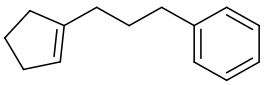
33.6 mg, 81% yield from Procedure H; 30 mg, 75% yield from Procedure I; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 2 H), 7.18-7.14 (m, 3 H), 5.41 (m, 1 H), 2.58 (t, *J* = 7.6 Hz, 2 H), 1.99-1.95 (m, 4 H), 1.90 (m, 2 H), 1.75-1.68 (m, 2 H), 1.64-1.51 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.6, 128.6, 128.4, 125.7, 121.2, 37.8, 35.8, 29.6, 28.5, 25.4, 23.2, 22.8.

IR (neat, cm^{-1}): 3027, 2930, 2857, 2835, 1496, 1454, 918, 746, 698.

HRMS (EI): [M^+] calcd. for $C_{15}H_{20}$ 200.1565, found 200.1567.



(3-(Cyclopent-1-en-1-yl)propyl)benzene (**3b**)

The title compound was prepared according to the General Procedure H from the reaction of cyclopent-1-en-1-yl trifluoromethanesulfonate **1b** (43 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

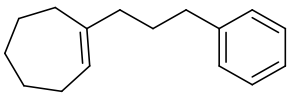
23.4 mg, 63% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2 H), 7.19-7.15 (m, 3 H), 5.36-5.33 (m, 1 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.32-2.27 (m, 2 H), 2.24-2.21 (m, 2 H), 2.10 (t, *J* = 7.6 Hz, 2 H), 1.88-1.73 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 142.8, 128.6, 128.4, 125.8, 123.6, 35.9, 35.2, 32.6, 30.9, 29.7, 23.6.

IR (neat, cm^{-1}): 3028, 2933, 2846, 1455, 746, 698.

HRMS (EI): [M^+] calcd. for $C_{14}H_{18}$ 186.1409, found 186.1405.



1-(3-Phenylpropyl)cyclohept-1-ene (**3c**)

The title compound was prepared according to the General Procedure from the reaction of cyclohept-1-en-1-yl trifluoromethanesulfonate **1c** (49 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

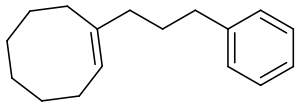
30.4 mg, 71% yield from Procedure H; 30.3 mg, 69% yield from Procedure I; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 2 H), 7.18-7.14 (m, 3 H), 5.55 (t, *J* = 6.4 Hz, 1 H), 2.58 (t, *J* = 7.6 Hz, 2 H), 2.10-2.04 (m, 4 H), 2.01 (t, *J* = 7.6 Hz, 2 H), 1.75-1.66 (m, 4H), 1.49-1.43 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 143.0, 128.6, 128.4, 126.4, 125.7, 40.0, 35.8, 32.9, 32.9, 30.0, 28.5, 27.6, 27.1.

IR (neat, cm^{-1}): 3027, 2924, 2852, 1497, 1454, 747, 699.

HRMS (EI): [M^+] calcd. for $C_{16}H_{22}$ 214.1722, found 214.1719.



(E)-1-(3-phenylpropyl)cyclooct-1-ene (**3d**)

The title compound was prepared according to the General Procedure H from the reaction of (*E*)-cyclooct-1-en-1-yl trifluoromethanesulfonate **1d** (52 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

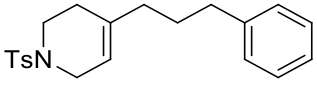
24.2 mg, 52% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2 H), 7.19-7.15 (m, 3 H), 5.35 (t, *J* = 8.0 Hz, 1 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.15-2.12 (m, 2 H), 2.08 (m, 2 H), 2.03 (t, *J* = 7.6 Hz, 2 H), 1.77-1.70 (m, 2H), 1.46 (s, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 140.6, 128.6, 128.4, 125.7, 124.1, 37.4, 36.0, 30.12, 30.07, 29.7, 29.05, 26.7, 26.5, 26.4.

IR (neat, cm^{-1}): 2932, 2858, 2835, 1639, 1454, 746, 698.

HRMS (EI): [M^+] calcd. for $C_{17}H_{24}$ 228.1878, found 228.1878.



4-(3-Phenylpropyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3e**)

The title compound was prepared according to the General Procedure from the reaction of

1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

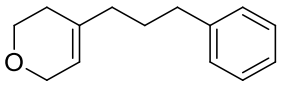
60.4 mg, 85% yield from Procedure H; 54.0 mg, 75% yield from Procedure I; colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31-7.24 (m, 4 H), 7.18-7.12 (m, 3 H), 5.31 (m, 1 H), 3.55 (m, 2 H), 3.16 (t, *J* = 5.4 Hz, 2 H), 2.53 (t, *J* = 7.2 Hz, 2 H), 2.40 (s, 3 H), 2.10 (m, 2H), 1.97 (t, *J* = 7.2 Hz, 2 H), 1.70-1.62 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 143.6, 142.2, 136.4, 133.6, 129.7, 128.5, 128.4, 127.8, 125.9, 116.6, 44.9, 43.0, 36.5, 35.4, 29.0, 28.4, 21.6.

IR (neat, cm^{-1}): 3027, 2927, 2855, 1648, 1600, 1495, 1456, 1343, 1244, 1211, 1165, 1096, 1031, 942, 816, 732, 701, 681, 640.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{26}NO_2S$ 356.1679, found 356.1681.



4-(3-Phenylpropyl)-3,6-dihydro-2*H*-pyran (**3f**)

The title compound was prepared according to the General Procedure H from the reaction of 3,6-dihydro-2*H*-pyran-4-yl trifluoromethanesulfonate **1f** (46 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

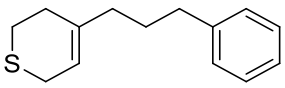
33.1 mg, 82% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2 H), 7.18-7.16 (m, 3 H), 5.40 (m, 1 H), 4.11 (m, 2 H), 3.77 (t, *J* = 5.6 Hz, 2 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.03 (m, 4 H), 1.79-1.71 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 135.4, 128.5, 128.4, 125.8, 119.9, 65.6, 64.5, 36.7, 35.5, 28.9, 28.5.

IR (neat, cm^{-1}): 2933, 1457, 1283, 1125, 747, 699.

HRMS (ESI): $[M+Na]^+$ calcd. for $C_{14}H_{18}NaO$ 225.1250, found 225.1250.



4-(3-Phenylpropyl)-3,6-dihydro-2*H*-thiopyran (**3g**)

The title compound was prepared according to the General Procedure H from the reaction of 3,6-dihydro-2*H*-thiopyran-4-yl trifluoromethanesulfonate **1g** (50 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

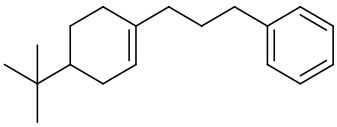
33.1 mg, 76% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2 H), 7.19-7.16 (m, 3 H), 5.60 (s, 1 H), 3.14-3.12 (m, 2 H), 2.71 (t, *J* = 6.0 Hz, 2 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.21 (m, 2 H), 2.01 (t, *J* = 7.6 Hz, 2 H), 1.78-1.70 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 138.5, 128.5, 128.4, 125.8, 118.1, 38.6, 35.6, 29.4, 29.1, 25.8, 25.4.

IR (neat, cm^{-1}): 2931, 1455, 1422, 1286, 1030, 747, 699.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{14}H_{19}S$ 219.1202, found 219.1202.



(3-(4-(*Tert*-butyl)cyclohex-1-en-1-yl)propyl)benzene (**3h**)

The title compound was prepared according to the General Procedure from the reaction of 4-(*tert*-butyl)cyclohex-1-en-1-yl trifluoromethanesulfonate **1h** (57 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

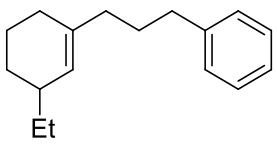
38.9 mg, 76% yield from Procedure H; 40.6 mg, 78% yield from Procedure I; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2 H), 7.19-7.15 (m, 3 H), 5.41-5.40 (m, 1 H), 2.58 (t, *J* = 7.6 Hz, 2 H), 2.04-1.97 (m, 5 H), 1.82-1.68 (m, 4 H), 1.25-1.08 (m, 2H), 0.86 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.4, 128.6, 128.4, 125.7, 121.4, 44.4, 37.3, 35.8, 32.4, 29.9, 29.6, 27.4, 27.0, 24.5.

IR (neat, cm^{-1}): 3027, 2937, 1457, 1364, 745, 698.

HRMS (EI): $[M^+]$ calcd. for $C_{19}H_{28}$ 256.2191, found 256.2194.



(3-(3-Ethylcyclohex-1-en-1-yl)propyl)benzene (**3i**)

The title compound was prepared according to the General Procedure H from the reaction of 3-ethylcyclohex-1-en-1-yl trifluoromethanesulfonate **1i** (52 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

34.7 mg, 76% yield, colorless oil.

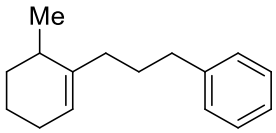
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2 H), 7.19-7.15 (m, 3 H), 5.31 (s, 1 H), 2.58 (t, *J* =

7.6 Hz, 2 H), 1.98 (t, *J* = 7.6 Hz, 2 H), 1.94-1.88 (m, 3 H), 1.76-1.68 (m, 4 H), 1.51-1.44 (m, 1 H), 1.39-1.19 (m, 2 H), 1.14-1.06 (m, 1 H), 0.90 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 137.3, 128.6, 128.4, 126.4, 125.7, 37.7, 37.2, 35.7, 29.7, 29.5, 28.9, 28.7, 22.2, 11.7.

IR (neat, cm^{-1}): 3027, 2930, 2856, 1455, 1079, 887, 746, 698.

HRMS (EI): [M^+] calcd. for $C_{17}H_{24}$ 228.1878, found 228.1878.



(3-(6-Methylcyclohex-1-en-1-yl)propyl)benzene (**3j**)

The title compound was prepared according to the General Procedure H from the reaction of 6-methylcyclohex-1-en-1-yl trifluoromethanesulfonate **1j** (49 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

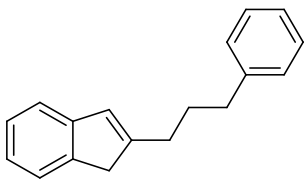
21.4 mg, 50% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2 H), 7.18-7.14 (m, 3 H), 5.38 (s, 1 H), 2.66-2.51 (m, 2 H), 2.15-2.05 (m, 2 H), 1.99-1.92 (m, 3 H), 1.81-1.58 (m, 4 H), 1.52-1.43 (m, 1 H), 1.39-1.32 (m, 1 H), 0.98 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 141.8, 128.6, 128.4, 125.7, 121.4, 35.9, 35.0, 31.8, 31.5, 29.9, 25.8, 20.0, 19.8.

IR (neat, cm^{-1}): 3027, 2930, 2856, 1455, 1031, 745, 698.

HRMS (EI): [M^+] calcd. for $C_{16}H_{22}$ 214.1722, found 214.1718.



2-(3-Phenylpropyl)-1*H*-indene (**3k**)

The title compound was prepared according to the General Procedure H from the reaction of 1*H*-inden-2-yl trifluoromethanesulfonate **1k** (53 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

30.0 mg, 61% yield, colorless oil.

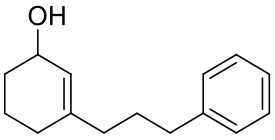
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 1 H), 7.31-7.26 (m, 3 H), 7.21-7.17 (m, 4 H),

7.10 (td, *J* = 7.6 Hz, 1.2 Hz, 1 H), 6.53 (s, 1 H), 3.31 (s, 2 H), 2.68 (t, *J* = 7.6 Hz, 2 H), 2.52 (t, *J* = 7.6 Hz, 2 H), 1.99-1.91 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 145.8, 143.2, 142.4, 128.6, 128.5, 126.6, 126.4, 125.9, 123.7, 123.5, 120.0, 41.2, 35.7, 30.9, 30.8.

IR (neat, cm^{-1}): 3025, 2932, 1609, 1458, 1392, 1077, 910, 750, 717, 699.

HRMS (EI): [M^+] calcd. for $C_{18}H_{18}$ 234.1409, found 234.1403.



2-(3-Phenylpropyl)cyclohex-2-en-1-ol (**3l**)

The title compound was prepared according to the General Procedure H from the reaction of 3-hydroxycyclohex-1-en-1-yl trifluoromethanesulfonate **1l** (49 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

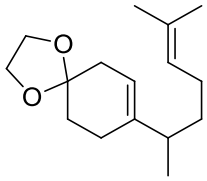
28.9 mg, 67% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2 H), 7.20-7.16 (m, 3 H), 5.51 (m, 1 H), 4.19 (s, 1 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.02 (t, *J* = 7.6 Hz, 2 H), 1.98-1.83 (m, 2 H), 1.81-1.67 (m, 4 H), 1.61-1.53 (m, 2 H), 1.41 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 142.2, 128.5, 128.4, 125.8, 124.1, 66.0, 37.3, 35.7, 32.1, 29.3, 28.6, 19.2.

IR (neat, cm^{-1}): 3027, 2933, 1651, 1455, 1031, 909, 747, 699.

HRMS (ESI): [M+H]$^+$ calcd. for $C_{15}H_{21}O$ 217.1587, found 217.1585.



8-(6-Methylhept-5-en-2-yl)-1,4-dioxaspiro[4.5]decane (**3m**)

The title compound was prepared according to the General Procedure H from 1,4-dioxaspiro[4.5]dec-7-en-8-yl trifluoromethanesulfonate **1m** (58 mg, 0.2 mmol) and 6-Methylhept-5-en-2-yl mesylate **2b** (74 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol). The reaction was conducted at 80 ℃ for 12 h.

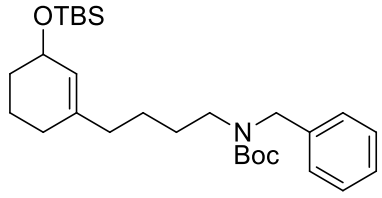
35.5 mg, 71% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.31-5.29 (m, 1 H), 5.11-5.07 (m, 1 H), 3.99-3.95 (m, 4 H), 2.28-2.26 (m, 2 H), 2.19-2.06 (m, 3 H), 1.92-1.87 (m, 2 H), 1.74 (t, *J* = 6.4 Hz, 2 H), 1.68 (s, 3 H), 1.58 (s, 3 H), 1.45-1.36 (m, 1 H), 1.32-1.23 (m, 1 H), 0.99 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 131.3, 124.9, 117.5, 108.5, 64.5, 64.4, 40.3, 35.9, 35.4, 31.4, 26.2, 25.9, 24.2, 19.6, 17.8.

IR (neat, cm^{-1}): 2958, 2924, 2876, 1649, 1455, 1377, 1258, 1211, 1118, 1041, 947, 863.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{16}H_{27}O_2$ 251.2006, found 251.2003.



***Tert*-butyl benzyl(4-(3-((*tert*-butyldimethylsilyl)oxy)cyclohex-1-en-1-yl)butyl)carbamate** (**3n**)

The title compound was prepared according to the General Procedure H from 3-((*tert*-butyldimethylsilyl)oxy)cyclohex-1-en-1-yl trifluoromethanesulfonate **1n** (72 mg, 0.2 mmol) and 4-(benzyl(*tert*-butoxycarbonyl)amino)butyl 4-methylbenzenesulfonate **2c** (156 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol). The reaction was conducted at 100 ℃ for 12 h.

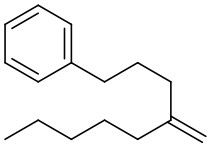
57.7 mg, 61% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, mixture of amide rotamers): δ 7.32-7.29 (m, 2 H), 7.26-7.23 (m, 3 H), 5.33 (s, 1 H), 4.43-4.40 (m, br, 2 H), 4.21 (s, 1 H), 3.21-3.12 (m, br, 2 H), 1.92-1.88 (m, 3 H), 1.82-1.75 (m, 3 H), 1.49-1.35 (m, 16 H), 0.90 (s, 9 H), 0.07 (d, *J* = 3.6 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$, major isomer):δ 156.0, 140.1, 138.7, 128.4, 127.6, 127.0, 125.3, 79.5, 67.3, 49.8, 46.4, 37.2, 32.6, 28.5, 28.3, 27.8, 26.0, 24.7, 19.9, 18.3, -4.5.

IR (neat, cm^{-1}): 2932, 2858, 1696, 1460, 1415, 1365, 1252, 1170, 1076, 1020, 879, 836, 774, 732, 699.

HRMS (ESI): $[M+Na]^+$ calcd. for $C_{28}H_{47}NNaO_3Si$ 496.3217, found 496.3217.



(4-Methylenenonyl)benzene (**3o**)

The title compound was prepared according to the General Procedure H from the reaction of hept-1-en-2-yl trifluoromethanesulfonate **1o** (49 mg, 0.2 mmol) with 3-phenylpropyl

4-methylbenzenesulfonate **2a'** (105 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol). The reaction was conducted at 60 ℃ for 12 h.

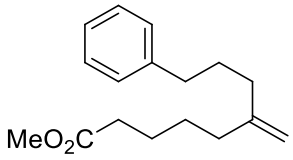
27.2 mg, 63% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2 H), 7.21-7.15 (m, 3 H), 4.72 (s, 2 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.05 (t, *J* = 7.6 Hz, 2 H), 2.00 (t, *J* = 7.6 Hz, 2 H), 1.79-1.72 (m, 2 H), 1.45-1.37 (m, 2 H), 1.34-1.23 (m, 4 H), 0.89 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 142.7, 128.6, 128.4, 125.8, 108.9, 36.2, 35.8, 35.8, 31.8, 29.7, 27.6, 22.7, 14.2.

IR (neat, cm^{-1}): 3083, 3028, 2030, 2858, 1644, 1497, 1456, 1031, 888, 747, 698.

HRMS (EI): [M^+] calcd. for $C_{16}H_{24}$ 216.1878, found 216.1882.



Methyl 6-methylene-9-phenylnonanoate (**3p**)

The title compound was prepared according to the General Procedure H from the reaction of methyl 6-(((trifluoromethyl)sulfonyl)oxy)hept-6-enoate **1p** (58 mg, 0.2 mmol) with 3-phenylpropyl 4-methylbenzenesulfonate **2a'** (105 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol). The reaction was conducted at 60 ℃ for 12 h.

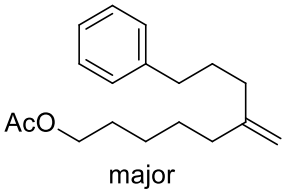
26.5 mg, 51% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2 H), 7.19-7.15 (m, 3 H), 4.73 (s, 2 H), 3.65 (s, 3 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 2.31 (t, *J* = 7.2 Hz, 2 H), 2.06-2.00 (m, 4 H), 1.79-1.71 (m, 2 H), 1.66-1.58 (m, 2 H), 1.48-1.40 (m, 2 H).

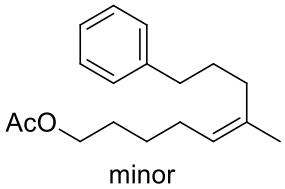
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 149.0, 142.6, 128.5, 128.4, 125.8, 109.4, 51.6, 35.71, 35.66, 35.6, 34.0, 29.6, 27.2, 24.7.

IR (neat, cm^{-1}): 2937, 2861, 1740, 1644, 1454, 1173, 889, 748, 699.

HRMS (ESI): [M+H]$^+$ calcd. for $C_{17}H_{25}O_2$ 261.1849, found 261.1848.



major



minor

6-Methylene-9-phenylnonyl acetate (**3q**)

The title compound was prepared according to the General Procedure H from the reaction of triflate **1q** (61 mg, 0.16 mmol of **1q** mixed with 0.04 mmol of unisolable isomers) with $Ph(CH_2)_3$-OTs **2a'** (104 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol). The reaction was conducted at 60 ℃ for 12 h.

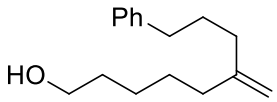
31 mg (**3q**/unisolable isomers is 9:1). The NMR yield of **3q** is 63%.

^{1}H NMR (400 MHz, $CDCl_3$, 3q) δ 7.29-7.25 (m, 2 H), 7.19-7.15 (m, 3 H), 4.73 (s, 2 H), 4.07-4.03 (m, 2 H), 2.63-2.55 (m, 2 H), 2.07-2.00 (m, 7 H), 1.79-1.68 (m, 2 H), 1.66-1.59 (m, 2 H), 1.48-1.30 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$, 3q) δ 171.3, 149.4, 142.6, 128.5, 128.39, 125.8, 109.2, 64.7, 36.0, 35.70, 35.68, 29.6, 28.6, 27.5, 25.8, 21.1.

IR (neat, cm^{-1}): 3065, 3027, 2935, 2859, 1740, 1646, 1497, 1455, 1366, 1239, 1045, 890, 749, 700.

HRMS (ESI): $[M+Na]^+$ calcd. for $C_{18}H_{26}NaO_2$ 297.1825, found 297.1825.



6-Methylene-9-phenylnonan-1-ol (**3r**)

The title compound was prepared according to the General Procedure H from the reaction of triflate **1r** (52.4 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

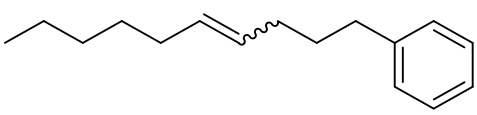
24 mg, 52% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2H), 7.19-7.16 (m, 3H), 4.73 (s, 2H), 3.63 (t, *J* = 8.0 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.07-2.00 (m, 4H), 1.79-1.72 (m, 2H), 1.61-1.54 (m, 2H), 1.48-1.41 (m, 2H), 1.39-1.33 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 142.7, 128.6, 128.4, 125.8, 109.2, 63.1, 36.1, 35.72, 35.70, 32.8, 29.6, 27.7, 25.6.

IR (cm^{-1}): 3359, 2931, 2857, 1600, 1495, 1454, 1428, 1074, 888, 748, 698.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{16}H_{25}O$ 233.1900, found 233.1902.



Dec-4-en-1-ylbenzene (**3s**)

The title compound was prepared according to the General Procedure H from the reaction of

triflate **1s** (147.6 mg, 0.6 mmol) with mesylate **2a'** (58 mg, 0.2 mmol).

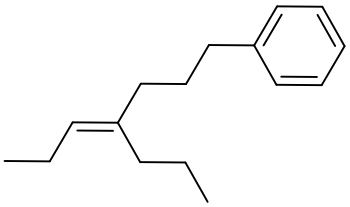
27 mg, 62% yield, E:Z = 2:1, colorless oil. The E/Z isomers were determined by comparison with related compounds reported in ref. 38.

^{1}H NMR (400 MHz, $CDCl_3$, the E isomer) δ 7.28-7.24 (m, 2H), 7.18-7.15 (m, 3H), 5.45-5.38 (m, 2H), 2.60 (t, *J* = 4.0 Hz, 2H),2.04-1.96 (m, 4H), 1.70-1.65 (m, 2H), 1.37-1.32 (m, 2H), 1.31-1.24 (m, 4H), 0.88 (t, *J* = 4.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, the E isomer) δ 142.8, 131.2, 129.9, 128.6, 128.4, 125.7, 35.5, 32.7, 32.3, 31.6, 31.5, 29.5, 22.7, 14.2.

IR (cm^{-1}): 2956, 2926, 2855, 1603, 1496, 1455, 1030, 968, 745, 697.

HRMS (EI): [M] calcd for $C_{16}H_{24}$ 216.1878, found 216.1883.



(E)-(4-propylhept-4-en-1-yl)benzene (**3t**)

The title compound was prepared according to the General Procedure H from the reaction of triflate **1t** (147.6 mg, 0.6 mmol) with mesylate **2a'** (58 mg, 0.2 mmol).

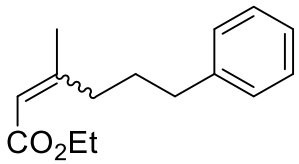
22 mg, 50% yield, colorless oil. The E/Z isomers were determined by NOE.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 7.18-7.15 (m, 3H), 3.14 (t, *J* = 4.0 Hz, 1H), 2.58 (t, *J* = 8.0 Hz, 2H), 2.03-1.97 (m, 6H), 1.74-1.68 (m, 2H), 1.40-1.34 (m, 2H), 0.94 (t, *J* = 4.0 Hz, 3H), 0.88 (t, *J* = 4.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 143.0, 138.4, 128.6, 128.4, 127.3, 125.7, 36.7, 35.9, 32.2, 30.2, 21.8, 21.2, 14.9, 14.3.

IR (cm^{-1}): 2959, 2931, 2870, 1602, 1496, 1455, 1377, 1030, 747, 698.

HRMS (EI): [M] calcd. for $C_{16}H_{24}$ 216.1878, found 216.1870.



Ethyl -2-methyl-6-phenylhex-2-enoate (**3u**)

The title compound was prepared according to the General Procedure H from the reaction of triflate **1u** (52.4 mg, 0.2 mmol) with mesylate **2a** (77 mg, 0.36 mmol).

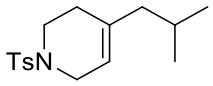
28 mg, 60% yield, E:Z = 1:4, colorless oil. The E/Z isomers were determined by comparison with related componds reported in ref. 39.

^{1}H NMR (400 MHz, $CDCl_3$, the Z isomer) δ = 7.29-7.25 (m, 2H), 7.20-7.16 (m, 3H), 5.67 (s, 1H), 4.16-4.11 (m, 2H), 2.71-2.64 (m, 4H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.83-1.75 (m, 2H), 1.26 (t, *J* = 4.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, the Z isomer) δ = 166.5, 160.0, 142.5, 128.5, 128.4, 125.9, 116.6, 59.6, 36.2, 33.4, 30.1, 25.2, 14.5.

IR (cm^{-1}): 2978, 2935, 2859, 1714, 1648, 1452, 1376, 1222, 1153, 1084, 1032, 857, 749, 699.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{15}H_{21}O_2$ 233.1536, found 233.1537.



4-Isobutyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3v**)

The title compound was prepared according to the General Procedure from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with isobutyl methanesulfonate **2d** (55 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

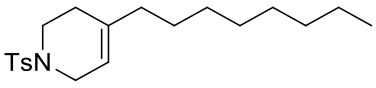
44.5 mg, 76% yield from Procedure H; 48.1mg, 83% yield from Procedure I; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.28 (m, 1 H), 3.56 (m, 2 H), 3.16 (t, *J* = 6.0 Hz, 2 H), 2.42 (s, 3 H), 2.09 (m, 2 H), 1.81 (d, *J* = 7.2 Hz, 2 H), 1.71-1.61 (m, 1 H), 0.80 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 135.9, 133.5, 129.7, 127.8, 117.5, 46.8, 44.9, 43.1, 28.4, 25.9, 22.4, 21.6.

IR (neat, cm^{-1}): 2955, 2924, 2868, 1598, 1461, 1346, 1246, 1208, 1164, 1093, 1047, 946, 815, 754, 738, 710, 684, 643.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{16}H_{24}NO_2S$ 294.1522, found 294.1521.



4-Octyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3w**)

The title compound was prepared according to the General Procedure from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with octyl methanesulfonate **2e** (75 mg, 0.36 mmol).

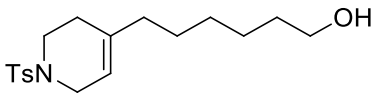
48.9 mg, 70% yield from Procedure H; 52.5mg, 75% yield from Procedure I; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.30-5.28 (m, 1 H), 3.54 (m, 2 H), 3.16 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.12-2.09 (m, 2 H), 1.92 (t, *J* = 6.8 Hz, 2 H), 1.35-1.24 (m, 12 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.8, 133.3, 129.5, 127.7, 115.9, 44.8, 42.9, 36.9, 31.8, 29.4, 29.20, 29.16, 28.3, 27.2, 22.6, 21.5, 14.1.

IR (neat, cm^{-1}): 2955, 2926, 2855, 1460, 1345, 1166, 1094, 949, 815, 711, 682, 642.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{32}NO_2S$ 350.2148, found 350.2144.



6-(1-Tosyl-1,2,3,6-tetrahydropyridin-4-yl)hexan-1-ol (**3x**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 6-hydroxyhexyl methanesulfonate **2f** (71 mg, 0.36 mmol).

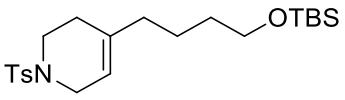
51.2 mg, 76% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.30-5.28 (m, 1 H), 3.62 (t, *J* = 6.4 Hz, 2 H), 3.55-3.52 (m, 2 H), 3.16 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.10 (m, 2 H), 1.93 (t, *J* = 6.8 Hz, 2 H), 1.57-1.50 (m, 3 H), 1.38-1.20 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.7, 133.4, 129.7, 127.8, 116.1, 63.0, 44.9, 43.0, 36.9, 32.7, 29.0, 28.4, 27.3, 25.7, 21.6.

IR (neat, cm^{-1}): 2929, 2856, 1598, 1460, 1341, 1244, 1210, 1164, 1094, 1053, 943, 816, 727, 682, 641.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{28}NO_3S$ 338.1784, found 338.1786.



4-(4-((*Tert*-butyldimethylsilyl)oxy)butyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3y**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 4-((*tert*-butyldimethylsilyl)oxy)butyl methanesulfonate **2g** (102 mg, 0.36 mmol).

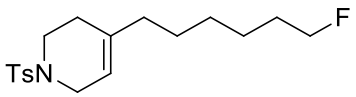
72.8 mg, 86% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.30 (m, 1 H), 3.57 (t, *J* = 6.4 Hz, 2 H), 3.54 (m, 2 H), 3.16 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.11 (m, 2 H), 1.95 (t, *J* = 7.2 Hz, 2 H), 1.48-1.34 (m, 4 H), 0.88 (s, 9 H), 0.03 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.7, 133.4, 129.7, 127.9, 116.3, 63.0, 44.9, 43.1, 36.7, 32.4, 28.4, 26.1, 23.6, 21.6, 18.5, -5.2.

IR (neat, cm^{-1}): 2930, 2857, 1599, 1464, 1387, 1352, 1253, 1168, 1099, 1007, 944, 836, 815, 776, 732, 681, 665, 641.

HRMS (ESI): $[M+Na]^+$ calcd. for $C_{22}H_{37}NNaO_3SSi$ 446.2156, found 446.2166.



4-(6-Fluorohexyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3z**)

The title compound was prepared according to the General Procedure from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 6-fluorohexyl methanesulfonate **2h** (71 mg, 0.36 mmol).

57.0 mg, 84% yield from Procedure H; 57.8 mg, 85% yield from Procedure I; colorless oil.

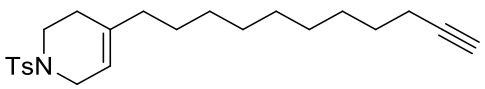
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.30-5.28 (m, 1 H), 4.42 (dt, *J* = 47.6, 6.0 Hz, 2 H), 3.54 (m, 2 H), 3.16 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.11 (m, 2 H), 1.94 (t, *J* = 6.8 Hz, 2 H), 1.73-1.60 (m, 2 H), 1.41-1.24 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.6, 133.3, 129.5, 127.7, 116.1, 84.1 (d, J_{C-F} = 164.1 Hz), 44.8, 42.9, 36.7, 30.3 (d, J_{C-F} = 19.3 Hz), 28.7, 28.3, 27.1, 25.0 (d, J_{C-F} = 5.2 Hz), 21.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -218.21.

IR (neat, cm^{-1}): 2935, 2857, 1460, 1342, 1163, 1093.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{27}FNO_2S$ 340.1741, found 340.1741.



1-Tosyl-4-(undec-10-yn-1-yl)-1,2,3,6-tetrahydropyridine (**3aa**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with undec-10-yn-1-yl 4-methylbenzenesulfonate **2i** (116 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol). The reaction was conducted at 40 ℃ for 24 h.

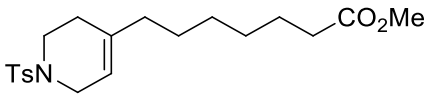
48.0 mg, 61% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.29 (m, 1 H), 3.54 (m, 2 H), 3.16 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.17 (td, *J* = 6.8 Hz, 2.8 Hz, 2 H), 2.10 (m, 2 H), 1.94-1.90 (m, 3 H), 1.55-1.48 (m, 2 H), 1.39-1.25 (m, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.9, 133.6, 129.7, 127.9, 116.1, 84.9, 68.2, 45.0, 43.1, 37.0, 29.5, 29.5, 29.3, 29.2, 28.8, 28.6, 28.4, 27.4, 21.6, 18.5.

IR (neat, cm^{-1}): 2927, 2854, 1650, 1460, 1344, 1165, 1093, 952, 816, 730, 682, 637.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{34}NO_2S$ 388.2305, found 388.2302.



Methyl 7-(1-tosyl-1,2,3,6-tetrahydropyridin-4-yl)heptanoate (**3ab**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with methyl 7-((methylsulfonyl)oxy)heptanoate **2j** (86 mg, 0.36 mmol).

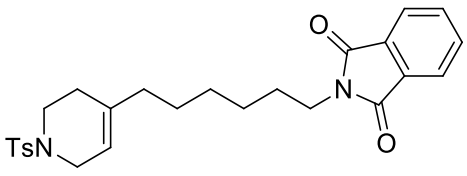
44.0 mg, 58% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.29 (m, 1 H), 3.66 (s, 3 H), 2.54 (m, 2 H), 3.16 (t, *J* = 6.0 Hz, 2 H), 2.42 (s, 3 H), 2.29 (t, *J* = 7.6 Hz, 2 H), 2.10 (m, 2 H), 1.92 (t, *J* = 7.2 Hz, 2 H), 1.63-1.56 (m, 2 H), 1.37-1.19 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 143.5, 136.7, 133.4, 129.7, 127.8, 116.2, 51.6, 44.9, 43.1, 36.9, 34.1, 29.0, 28.9, 28.4, 27.1, 24.9, 21.6.

IR (neat, cm^{-1}): 2928, 2855, 1735, 1650, 1459, 1342, 1164, 1096, 953, 816, 728, 681, 639.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{30}NO_4S$ 380.1890, found 380.1885.



2-(6-(1-Tosyl-1,2,3,6-tetrahydropyridin-4-yl)hexyl)isoindoline-1,3-dione (**3ac**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 6-(1,3-dioxoisoindolin-2-yl)hexyl methanesulfonate **2k** (117 mg, 0.36 mmol).

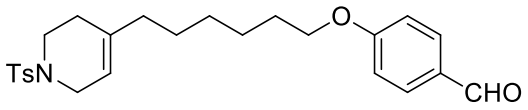
75.5 mg, 81% yield, white solid, mp.: 194-196 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2 H), 7.72-7.70 (m, 2 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.28 (s, 1 H), 3.66 (t, *J* = 7.2 Hz, 2 H), 3.53 (s, 2 H), 3.15 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.09 (m, 2 H), 1.91 (m, 2 H), 1.68-1.61 (m, 2 H), 1.34-1.26 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 143.5, 136.6, 134.0, 133.4, 132.2, 129.6, 127.8, 123.2, 116.2, 44.9, 43.0, 38.0, 36.8, 28.7, 28.5, 28.3, 27.1, 26.7, 21.6.

IR (neat, cm^{-1}): 2929, 2855, 1709, 1642, 1461, 1397, 1342, 1164, 1094, 1050, 942, 815, 722, 682.

HRMS (ESI): $[M+Na]^+$ calcd. for $C_{26}H_{30}N_2NaO_4S$ 489.1818, found 489.1809.



4-((6-(1-Tosyl-1,2,3,6-tetrahydropyridin-4-yl)hexyl)oxy)benzaldehyde (**3ad**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 6-(4-formylphenoxy)hexyl methanesulfonate **2l** (108 mg, 0.36 mmol).

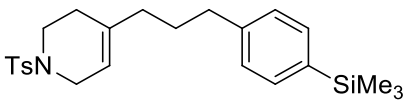
52.9 mg, 60% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1 H), 7.82 (d, *J* = 8.8 Hz, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 6.98 (d, *J* = 8.4 Hz, 2 H), 5.30 (m, 1 H), 4.02 (t, *J* = 6.4 Hz, 2 H), 3.53 (m, 2 H), 3.16 (t, *J* = 6.0 Hz, 2 H), 2.42 (s, 3 H), 2.12 (m, 2 H), 1.95 (t, *J* = 6.8 Hz, 2 H), 1.82-1.75 (m, 2 H), 1.52-1.28 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 164.3, 143.5, 136.6, 133.4, 132.1, 129.9, 129.7, 127.8, 116.3, 114.8, 68.4, 44.9, 43.0, 36.9, 29.1, 28.9, 28.4, 27.2, 25.9, 21.6.

IR (neat, cm^{-1}): 2927, 2855, 2738, 1690, 1600, 1510, 1462, 1429, 1396, 1343, 1312, 1258, 1216, 1160, 1094, 1018, 945, 833, 816, 734, 681, 642, 618.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{25}H_{32}NO_4S$ 442.2047, found 442.2043.



1-Tosyl-4-(3-(4-(trimethylsilyl)phenyl)propyl)-1,2,3,6-tetrahydropyridine (**3ae**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 3-(4-(trimethylsilyl)phenyl)propyl methanesulfonate **2m** (103 mg, 0.36 mmol).

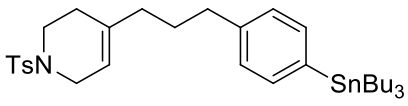
59.8 mg, 70% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 7.6 Hz, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 5.32 (m, 1 H), 3.56 (m, 2 H), 3.16 (t, *J* = 5.6 Hz, 2 H), 2.52 (t, *J* = 7.6 Hz, 2 H), 2.39 (s, 3 H), 2.11 (m, 2 H), 1.98 (t, *J* = 7.6 Hz, 2 H), 1.70-1.62 (m, 2 H), 0.25 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.9, 137.5, 136.4, 133.5, 133.5, 129.7, 128.0, 127.8, 116.6, 44.9, 43.0, 36.6, 35.4, 28.9, 28.4, 21.6, -0.9.

IR (neat, cm^{-1}): 2929, 2857, 1599, 1462, 1348, 1252, 1167, 1098, 944, 836, 815, 776, 732, 681, 640.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{24}H_{34}NO_2SSi$ 428.2074, found 428.2073.



1-Tosyl-4-(3-(4-(tributylstannyl)phenyl)propyl)-1,2,3,6-tetrahydropyridine (**3af**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 3-(4-(tributylstannyl)phenyl)propyl methanesulfonate **2n** (181 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

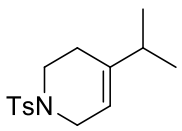
94.0 mg, 73% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.41-7.29 (m, 4 H), 7.12-7.08 (m, 2 H), 5.32 (m, 1 H), 3.56 (m, 2 H), 3.16 (t, *J* = 6.0 Hz, 2 H), 2.50 (t, *J* = 7.6 Hz, 2 H), 2.39 (s, 3 H), 2.11 (m, 2 H), 1.98 (t, *J* = 7.2 Hz, 2 H), 1.69-1.62 (m, 2 H), 1.59-1.43 (m, 6 H), 1.37-1.28 (m, 6 H), 1.11-0.94 (m, 6 H), 0.88 (t, *J* = 7.2 Hz, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 141.8, 138.6, 136.5, 136.4, 129.6, 128.3, 128.1, 127.7, 116.4, 44.8, 42.9, 36.5, 35.3, 29.1, 28.8, 28.3, 27.4, 21.5, 13.7, 9.5.

IR (neat, cm^{-1}): 2928, 2856, 1598, 1459, 1348, 1166, 1096, 953, 815, 731, 713, 679, 641.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{33}H_{52}NO_2SSn$ 646.2735, found 646.2734.



4-Isopropyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ag**)

The title compound was prepared according to the General Procedure from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with isopropyl methanesulfonate **2o** (50 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

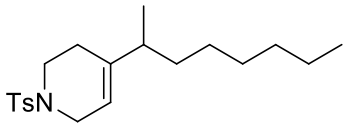
36.8 mg, 66% yield from Procedure H; 28.0 mg, 50% yield from Procedure I; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.29 (m, 1 H), 3.56 (m, 2 H), 3.17 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.18-2.12 (m, 3 H), 0.94 (d, *J* = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 142.3, 133.6, 129.7, 127.8, 114.2, 45.0, 43.2, 34.6, 26.2, 21.6, 21.0.

IR (neat, cm^{-1}): 2961, 2927, 2872, 1598, 1461, 1347, 1247, 1213, 1165, 1096, 945, 816, 731, 662, 627.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{15}H_{22}NO_2S$ 280.1366, found 280.1365.



4-(Octan-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ah**)

The title compound was prepared according to the General Procedure from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with octan-2-yl methanesulfonate **2p** (75 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

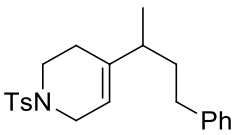
56.5 mg, 81% yield from Procedure H; 60.2 mg, 86% yield from Procedure I; colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.29 (m, 1 H), 3.56 (m, 2 H), 3.21-3.10 (m, 2 H), 2.42 (s, 3 H), 2.15-1.98 (m, 3 H), 1.32-1.05 (m, 10 H), 0.91 (d, *J* = 6.8 Hz, 3 H), 0.86 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 141.1, 133.5, 129.7, 127.8, 115.6, 45.0, 43.2, 40.5, 34.8, 31.9, 29.5, 27.5, 25.2, 22.8, 21.6, 19.4, 14.2.

IR (neat, cm^{-1}): 2926, 2855, 1650, 1459, 1164, 1097.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{20}H_{32}NO_2S$ 350.2148, found 350.2146.



4-(4-Phenylbutan-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ai**)

The title compound was prepared according to the General Procedure H from the reaction of

1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 4-phenylbutan-2-yl methanesulfonate **2q** (82 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

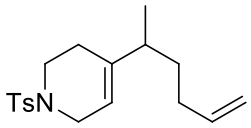
59.0 mg, 80% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.23 (d, *J* = 7.6 Hz, 2 H), 7.16-7.09 (m, 3 H), 5.33 (m, 1 H), 3.58 (m, 2 H), 3.22-3.10 (m, 2 H), 2.44 (t, *J* = 7.6 Hz, 2 H), 2.40 (s, 3 H), 2.16-2.04 (m, 3 H), 1.67-1.49 (m, 2 H), 0.96 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.5, 140.5, 133.5, 129.7, 128.44, 128.41, 127.8, 125.8, 116.4, 45.0, 43.2, 40.2, 36.4, 33.8, 25.1, 21.6, 19.4.

IR (neat, cm^{-1}): 2925, 2855, 1600, 1457, 1343, 1165, 1097, 946, 816, 729, 700, 661, 626.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{28}NO_2S$ 370.1835, found 370.1832.



4-(Hex-5-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3aj**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with hex-5-en-2-yl methanesulfonate **2r** (64 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

53 mg, 83% yield, colorless oil.

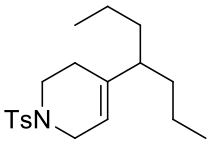
The gram-scale reaction was conducted with the same procedure and gave **3af** with 72% yield (1.15 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.79-5.69 (m, 1 H), 5.31 (m, 1 H), 4.97-4.90 (m, 2 H), 3.57 (m, 2 H), 3.22-3.11 (m, 2 H), 2.42 (s, 3 H), 2.15-2.03 (m, 3 H), 1.92-1.86 (m, 2 H), 1.43-1.25 (m, 2 H), 0.93 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 140.6, 138.7, 133.5, 129.7, 127.8, 116.1, 114.5, 44.9, 43.2, 39.9, 33.8, 31.6, 25.1, 21.6, 19.3.

IR (neat, cm^{-1}): 2960, 2925, 1641, 1598, 1459, 1346, 1246, 1211, 1164, 1098, 946, 816, 730, 662.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{26}NO_2S$ 320.1679, found 320.1673.



4-(Heptan-4-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ak**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with heptan-4-yl methanesulfonate **2s** (70 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

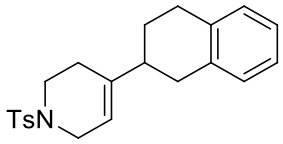
34.2 g, 51% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.28 (m, 1 H), 3.59-3.57 (m, 2 H), 3.16 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.02-2.00 (m, 2 H), 1.97-1.90 (m, 1 H), 1.24-1.17 (m, 4 H), 1.16-1.04 (m, 4 H), 0.82 (t, *J* = 7.6 Hz, 6 H) .

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 139.0, 133.7, 129.7, 127.8, 117.4, 46.2, 44.9, 43.2, 35.6, 24.3, 21.6, 20.7, 14.2.

IR (neat, cm^{-1}): 2956, 2926, 2870, 1560, 1460, 1347, 1164, 943, 816, 727, 661, 625.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{19}H_{30}NO_2S$ 336.1992, found 336.1990.



4-(1,2,3,4-Tetrahydronaphthalen-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3al**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 1,2,3,4-tetrahydronaphthalen-2-yl 4-methylbenzenesulfonate **2t** (109 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

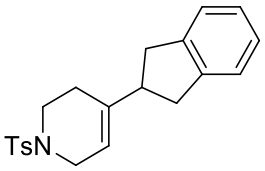
41.1 mg, 56% yield, a white solid, mp.: 136-138 ^{o}C.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.08-7.01 (m, 4 H), 5.38 (m, 1 H), 3.63-3.57 (m, 2 H), 3.25-3.18 (m, 2 H), 2.82-2.73 (m, 3 H), 2.63-2.58 (m, 1H), 2.43 (s, 3 H), 2.28-2.22 (m, 3 H), 1.89-1.86 (m, 1 H), 1.59-1.53 (m, 1 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 140.3, 136.3, 136.2, 133.75, 129.7, 129.1, 128.9, 127.9, 125.8, 125.7, 115.8, 45.1, 43.2, 41.1, 34.6, 29.3, 27.8, 26.9, 21.6.

IR (neat, cm^{-1}): 2923, 1597, 1494, 1456, 1343, 1211, 1164, 1094, 916, 816, 744, 713, 693, 648.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{22}H_{26}NO_2S$ 368.1679, found 368.1674.



4-(2,3-Dihydro-1*H*-inden-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3am**)

The title compound was prepared according to the General Procedure from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 2,3-dihydro-1*H*-inden-2-yl methanesulfonate **2u** (76 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

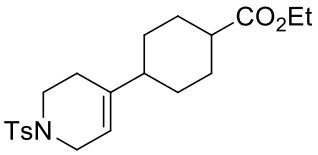
55.1 mg, 78% yield from Procedure H; 55.0 mg, 78% yield from Procedure I; white solid, mp.: 122-124 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.18-7.11 (m, 4 H), 5.42(m, 1 H), 3.58 (m, 2 H), 3.19 (t, *J* = 5.6 Hz, 2 H), 3.00-2.94 (m, 3 H), 2.78-2.71 (m, 2 H), 2.42 (s, 3 H), 2.18 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 142.8, 138.8, 133.4, 129.7, 127.9, 126.4, 124.4, 115.8, 46.3, 45.0, 43.1, 37.3, 37.3, 26.9, 21.6.

IR (neat, cm^{-1}): 2927, 2851, 1343, 1164, 1094, 943, 746, 695.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{24}NO_2S$ 354.1522, found 354.1520.



Ethyl 4-(1-tosyl-1,2,3,6-tetrahydropyridin-4-yl)cyclohexane-1-carboxylate (**3an**)

The title compound was prepared according to the General Procedure H from the reaction of triflate **1e** (77 mg, 0.2 mmol) with ethyl 4-(tosyloxy)cyclohexanecarboxylate **2v** (117 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

31.3 mg, 40% yield, colorless oil.

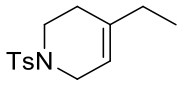
^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers) δ 7.67 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.30 (m, 1 H), 4.16-4.08 (m, 2 H), 3.56 (m, 2 H), 3.17-3.13 (m, 2 H), 2.42 (s, 3 H), 2.17-1.99 (m, 4 H), 1.85-1.69 (m, 3 H), 1.53-1.08 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$, mixture of diastereomers) δ 175.9, 175.1, 143.6, 140.8, 140.7, 133.5, 129.7, 127.9, 115.2, 115.1, 60.3, 45.0, 43.9, 43.6, 43.22, 43.15, 39.3, 30.5, 29.0, 27.6, 27.1,

26.9, 21.6, 14.4, 14.3.

IR (neat, cm^{-1}): 2932, 2858, 1728, 1455, 1344, 1248, 1165, 1095, 1041, 944, 817, 746, 713, 693, 647.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{21}H_{30}NO_4S$ 392.1890, found 392.1894.



4-Ethyl-1-tosyl-1,2,3,6-tetrahydropyridine (**3ao**)

The title compound was prepared according to the General Procedure from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with ethyl methanesulfonate **2w** (45 mg, 0.36 mmol).

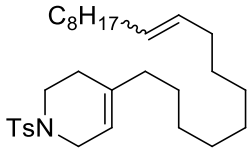
48.8 mg, 92% yield from Procedure H; 48.1 mg, 89% yield from Procedure I; white solid, mp.: 172-174 ^oC.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.30-5.28 (m, 1 H), 3.56-3.54 (m, 2 H), 3.17 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.12 (m, 2 H), 1.97-1.92 (m, 2 H), 0.94 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 138.3, 133.5, 129.7, 127.8, 115.0, 44.9, 43.1, 29.7, 28.4, 21.6, 11.9.

IR (neat, cm^{-1}): 2852, 1340, 1162, 1097, 940, 820, 737, 668, 635.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{14}H_{20}NO_2S$ 266.1209, found 266.1208.



(E)-4-(octadec-9-en-1-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ap**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with (Z)-octadec-9-en-1-yl methanesulfonate **2x** (125 mg, 0.36 mmol).

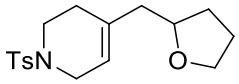
87.7 mg, 90% yield, colorless oil, a mixture of E/Z isomers with a ratio of about 4:1.

^{1}H NMR (400 MHz, $CDCl_3$, the E isomer) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.42-5.33 (m, 2 H), 5.28 (m, 1 H), 3.54 (m, 2 H), 3.16 (t, *J* = 5.6 Hz, 2 H), 2.42 (s, 3 H), 2.11 (m, 2 H), 1.96-1.90 (m, 6 H), 1.31-1.24 (m, 24 H), 0.88 (t, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$, the E isomer) δ 143.5, 136.9, 133.5, 130.5, 130.4, 129.7, 127.9, 116.1, 44.9, 43.1, 37.0, 32.74, 32.72, 32.0, 29.79, 29.75, 29.62, 29.56, 29.4, 29.33, 29.31, 29.27, 28.4, 27.4, 22.8, 21.6, 14.2.

IR (neat, cm^{-1}): 2925, 2854, 1460, 1344, 1165, 1094.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{30}H_{50}NO_2S$ 488.3557, found 488.3553.



4-((Tetrahydrofuran-2-yl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3aq**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with (tetrahydrofuran-2-yl)methyl 4-methylbenzenesulfonate **2y** (92 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

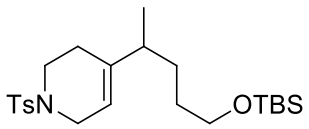
45.6 mg, 71% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.40 (m, 1 H), 3.91-3.81 (m, 2 H), 3.71-3.65 (m, 1 H), 3.56 (s, 2 H), 2.22-3.11 (m, 2 H), 3.42 (s, 3 H), 2.23-2.09 (m, 4 H), 1.96-1.79 (m, 3 H), 1.47-1.38 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 134.3, 133.2, 129.7, 127.8, 118.2, 77.4, 67.9, 44.9, 43.01, 42.98, 31.4, 28.9, 25.6, 21.6.

IR (neat, cm^{-1}): 2293, 1597, 1459, 1344, 1165, 1095, 1063, 952, 816, 742, 711, 681, 642.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{17}H_{24}NO_3S$ 322.1471, found 322.1470.



4-(5-((*Tert*-butyldimethylsilyl)oxy)pentan-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**3ar**)

The title compound was prepared according to the General Procedure H from the reaction of 1-tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate **1e** (77 mg, 0.2 mmol) with 5-((*tert*-butyldimethylsilyl)oxy)pentan-2-yl methanesulfonate **2z** (107 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol).

41.1 mg, 47% yield, colorless oil.

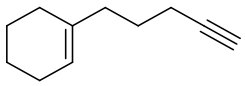
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.29 (m, 1 H),

3.60-3.49 (m, 4 H), 3.22-3.16 (m, 1 H), 3.13-3.07 (m, 1 H), 2.42 (s, 3 H), 2.16-2.02 (m, 3 H), 1.43-1.20 (m, 4 H), 0.92 (d, *J* = 6.8 Hz, 3 H), 0.87 (s, 9 H), 0.02 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 140.8, 133.5, 129.7, 127.9, 115.9, 63.3, 45.0, 43.2, 40.3, 30.83, 30.76, 26.1, 25.2, 21.6, 19.4, 18.5, -5.2.

IR (neat, cm^{-1}): 2955, 2930, 2857, 1462, 1351, 1252, 1212, 1165, 1098, 945, 836, 815, 776, 729, 661.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{23}H_{40}NO_3SSi$ 438.2493, found 438.2493.



1-(Pent-4-yn-1-yl)cyclohex-1-ene (**5**)

The title compound was prepared according to the General Procedure H from the reaction of cyclohex-1-en-1-yl trifluoromethanesulfonate **1a** (86 mg, 0.2 mmol) with pent-4-yn-1-yl 4-methylbenzenesulfonate **2aa** (116 mg, 0.36 mmol) in the presence of NaI (15 mg, 0.1 mmol). The reaction was conducted at 40 ℃ for 24 h.

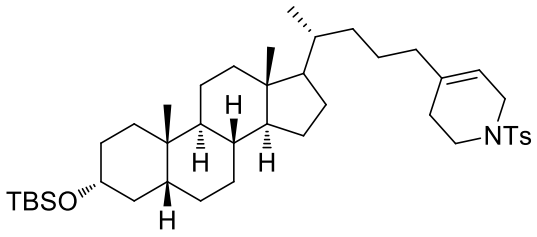
23.1 mg, 78% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 (m, 1 H), 2.16 (td, *J* = 7.2 Hz, 2.8 Hz, 2 H), 2.04-1.91 (m, 7 H), 1.67-1.59 (m, 4 H), 1.57-1.52 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 121.8, 84.9, 68.3, 37.1, 28.3, 26.7, 25.4, 23.1, 22.7, 18.1.

IR (neat, cm^{-1}): 3312, 2937, 2858, 1455, 1261, 1085, 1022, 799, 628.

HRMS (EI): $[M^+]$ calcd. for $C_{11}H_{16}$ 148.1252, found 148.1258.



4-((4*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*)-3-((*Tert*-butyldimethylsilyl)oxy)-10,13-dimethylhexade-cahydro-1H-cyclopenta[a]phenanthren-17-yl)pentyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**8**)

The title compound was prepared according to the General Procedure H from the reaction of mesylate **7** (200 mg, 0.36 mmol) with triflate **1e** (77 mg, 0.2 mmol).

125.3 mg, 90% yield, colorless oil.

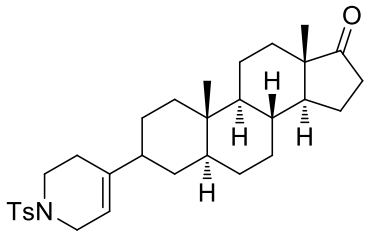
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 5.27 (m, 1 H),

3.60-3.53 (m, 3 H), 3.15 (t, *J* = 6.0 Hz, 2 H), 2.40 (s, 3 H), 2.09 (m, 2 H), 1.93-1.71 (m, 7 H), 1.54-1.52 (m, 2 H), 1.42-1.28 (m, 10 H), 1.24-1.13 (m, 5 H), 1.10-0.94 (m, 6 H), 0.88-0.85 (m, 15 H), 0.60 (s, 3 H), 0.04 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.9, 133.6, 129.6, 127.8, 116.0, 72.9, 56.5, 56.3, 44.9, 43.0, 42.8, 42.4, 40.34, 40.26, 37.4, 37.0, 35.9, 35.69, 35.67, 35.6, 34.7, 31.1, 28.4, 27.4, 26.5, 26.1, 24.3, 23.9, 23.5, 21.6, 20.9, 18.7, 18.4, 12.1, -4.5.

IR (neat, cm^{-1}): 2929, 2859, 1649, 1461, 1351, 1251, 1167, 1094, 952, 911, 870, 836, 815, 775, 734, 681, 642.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{42}H_{70}NO_3SSi$ 696.4840, found 696.4847.



(5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-3-(1-tosyl-1,2,3,6-tetrahydropyridin-4yl)hexadecahy-dro-17*H*-cyclopenta[a]phenanthren-17-one (**10**)

The title compound was prepared according to the General Procedure H from the reaction of tosylate **9** (160 mg, 0.36 mmol) with triflate **1e** (77 mg, 0.2 mmol) in the presence of NaI (15 mg, 0.1 mmol).

95.7 mg, 94% yield, white solid, mp.: 224-226 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 5.29 (m, 1 H), 3.56 (m, 2 H), 3.16 (t, *J* = 6.0 Hz, 2 H), 2.46-2.39 (m, 4 H), 2.13 (m, 2 H), 2.09-2.00 (m, 1 H), 1.95-1.88 (m, 1 H), 1.85-1.63 (m, 5 H), 1.55-1.46 (m, 3 H), 1.32-1.17 (m, 7 H), 1.15-1.10 (m, 2 H), 1.10-0.91 (m, 2 H), 0.85 (s, 3 H), 0.76 (s, 3 H), 0.73-0.67 (m, 1 H).

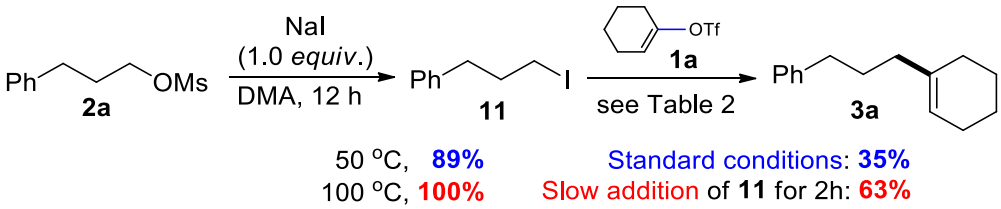
^{13}C NMR (100 MHz, $CDCl_3$) δ 221.2, 143.4, 141.1, 133.4, 129.6, 127.7, 114.5, 54.6, 51.5, 47.8, 46.6, 44.94, 44.88, 43.1, 38.4, 36.0, 35.8, 35.1, 33.4, 31.6, 30.9, 28.6, 26.8, 26.6, 21.8, 21.5, 20.3, 13.8, 12.3.

IR (neat, cm^{-1}): 2922, 2854, 1736, 1597, 1455, 1341, 1247, 1211, 1164, 1095, 1057, 1012, 943, 916, 815, 732, 712, 696, 648.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{31}H_{44}NO_3S$ 510.3036, found 510.3032.

5. Mechanistic Investigation

5.1 Experiments to investigate the effect of NaI



5.1.1 The possibility of mesylate/iodide exchange.

To a solution of mesylate 2a (43 mg, 0.2 mmol) in DMA (2 mL) was added NaI (30 mg, 0.2 mmol). The reaction mixture was stirred at listed temperature for 12 h. The GC analysis revealed that 89% and 100% of alkyl iodide **11** were formed at 50 and 100 °C, respectively. The isolated yield of **11** from the reaction at 100 °C was 91%, 45 mg. ^{1}H NMR and ^{13}C NMR data are consistent with those reported in ref. 40.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2 H), 7.21-7.18 (m, 3 H), 3.16 (t, *J* = 6.8 Hz, 2 H), 2.72 (t, *J* = 7.3 Hz, 2 H), 2.15- 2.10 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 140.4, 128.51, 128.47, 126.2, 36.2, 34.9, 6.2.

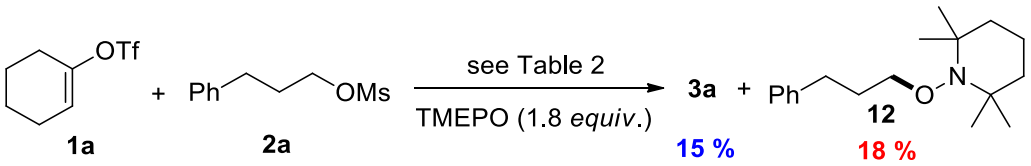
5.1.2 The reaction of triflate 1a with alkyl iodide 11.

Procedure 1 (Standard conditions): The procedure was conducted in the argon-filled glove box. To a reaction tube containing NiI_2 (6.3 mg, 10 mol %), tpy (7.0 mg, 15 mol %) and Mn (33 mg, 3.0 equiv.) was added a solution of vinyl triflate **1a** (46 mg, 0.2 mmol) and alkyl iodide **11** (89 mg, 0.36 mmol) in DMA (2 mL). It was then removed from the glove box, and the reaction mixture was stirred at 100 °C for 12 h. The reaction was quenched with water (20 mL), extracted twice with ethyl acetate (2 × 15 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 to give the desired product **3a** with 35% yield (14 mg).

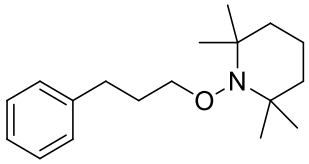
Procedure 2 (Slow addition of iodide 11): To a solution of NiI_2 (6.3 mg, 10 mol %), tpy (7.0 mg, 15 mol %), Mn (33 mg, 3.0 equiv.) and vinyl triflate **1a** (46 mg, 0.2 mmol) in DMA (1 mL) was slowly added a solution of alkyl iodide **11** (89 mg, 0.36 mmol) in DMA (1 mL) by syringe pump under argon at 100 °C for 2h. The reaction was stirred at the same temperature for 10 h. The reaction was quenched with water (20 mL), extracted twice with ethyl acetate (2 × 15 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 to give the desired product **3a** with 63% yield (25 mg).

5.2 Radical inhibition experiments



The procedure was conducted in the argon-filled glove box. To a reaction tube containing NiI_2 (6.3 mg, 10 mol %), tpy (7.0 mg, 15 mol %), TEMPO (57 mg, 0.36 mmol) and Mn (33 mg, 3.0 equiv.) was added a solution of vinyl triflate **1a** (46 mg, 0.2 mmol) and mesylate **2a** (77 mg, 0.36 mmol) in DMA (2 mL). It was then removed from the glove box, and the reaction mixture was stirred at 100 ^oC for 12 h. The reaction was quenched with water (20 mL), extracted twice with ethyl acetate (2 × 15 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 to give **3a** with 15% yield (6 mg) and radical trapping product **12** with 18% yield (10 mg).



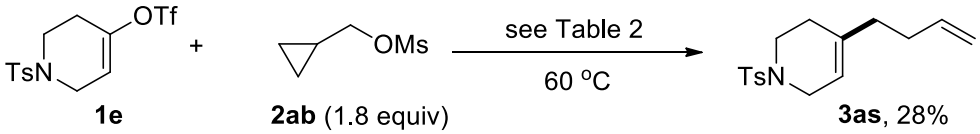
2,2,6,6-Tetramethyl-1-(3-phenylpropoxy)piperidine (12)

Colorless oil, the ^1H NMR data of **12** is consistent with those reported in ref. 41.

^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.25 (m, 2 H), 7.22-7.15 (m, 3 H), 3.77 (t, *J* = 6.5 Hz, 2 H), 2.73-2.69 (m, 32 H), 1.89-1.82 (m, 2 H), 1.62-1.43 (m, 6 H), 1.12 (d, *J* = 12.6 Hz, 12 H).

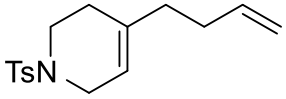
GC-MS (EI) m/z (rel intensity, ion): 275.26 (2.62, M+).

5.3 Radical clock experiments



The procedure was conducted in an argon-filled glove box. To a reaction tube containing NiI_2 (6.3 mg, 10 mol %), tpy (7.0 mg, 15 mol %), NaI (15 mg, 0.1 mmol) and Mn (33 mg, 0.6 mmol) was added a solution of vinyl triflate **1e** (77 mg, 0.2 mmol) and mesylate **2ab** (54 mg, 0.36 mmol) in

DMA (2 mL). It was sealed and removed from the glove box. The reaction mixture was stirred at 60 ^{o}C for 12 h. The reaction was quenched with water (20 mL), extracted twice with ethyl acetate (2 × 15 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 **3as** with 28% yield (16 mg).



4-(But-3-en-1-yl)-1-tosyl-1,2,3,6-tetrahzydropyridine (**3as**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.78-5.69 (m, 1H), 5.32 (m, 1H), 5.01-4.92 (m, 2H), 3.55 (s, 2H), 3.17 (t, *J* = 4.0 Hz, 2H), 2.43 (s, 3H), 2.12-2.01 (m, 6H).

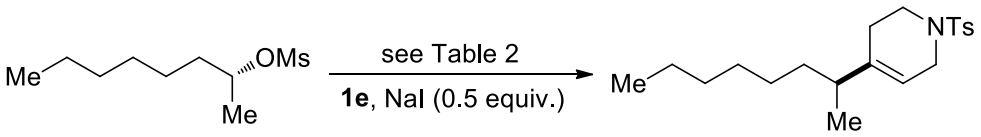
^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.1, 136.1, 133.6, 129.7, 127.9, 116.7, 115.0, 44.9, 43.0, 36.3, 31.6, 28.5, 21.7.

IR (neat, cm^{-1}): 3421, 2922, 2851, 1595, 1459, 1423, 1343, 1163, 1121, 1093, 1019, 951, 815, 685, 668.

HRMS (ESI): $[M+H]^+$ calcd for $C_{16}H_{22}NO_2S$ 292.1366, found 292.1370.

5.4 Chirality transfer and asymmetric catalysis

5.4.1 Chirality transfer reaction



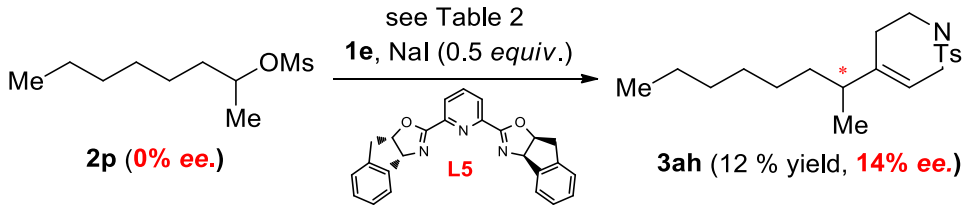
Chiral-2p (99% *ee.*) **3ah** (72 % yield, 0% *ee.*)

Chiral-2p was synthesized from chiral alcohol (99% ee., commercial available) according to the General Procedure D.

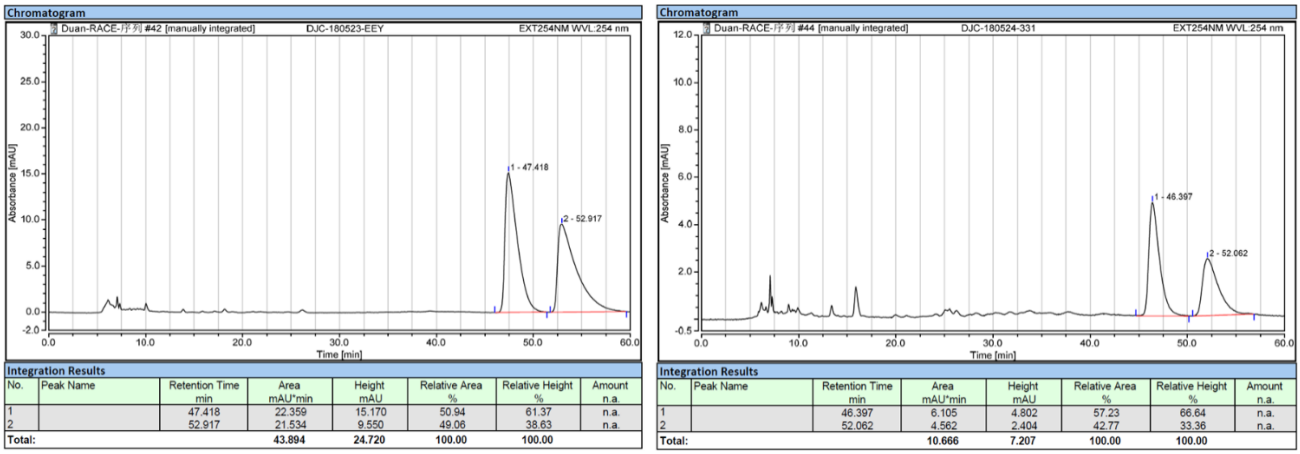
The procedure was conducted in the argon-filled glove box. To a reaction tube containing NiI_2 (6.3 mg, 10 mol %), tpy (7.0 mg, 15 mol %), NaI (15 mg, 0.1 mmol) and Mn (33 mg, 0.6 mmol) was added a solution of vinyl triflate **1e** (77 mg, 0.2 mmol) with mesylate **chiral-2p** (75 mg, 0.36 mmol) in DMA (2 mL). It was then removed from the glove box, and the reaction mixture was stirred at 100 ^{o}C for 12 h. The reaction was quenched with water (20 mL), extracted twice with ethyl acetate (2 × 15 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 to give **3ah** with 72% yield (50 mg) and 0% ee. The enantiomeric excess was determined by

chiral HPLC analysis (Chiralpak IA column, Hexane/*i*-PrOH = 98:2, flow rate = 0.5 mL/min, wave length = 254 nm).

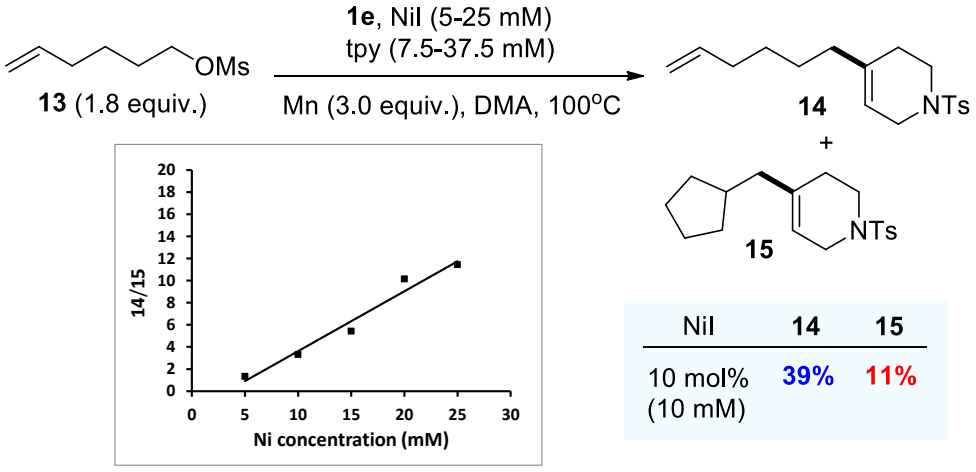
5.4.2 Enantioselective catalysis



This reaction was conducted according to the above procedure, but racemic mesylate **2p** (75 mg, 0.36 mmol) and chiral ligand **L5** (12 mg, 15 mol %) were used instead of **chiral-2p** and tpy respectively. The desired product **3ah** was obtained with 12% yield (8.2 mg) and 14% ee. The enantiomeric excess was determined by chiral HPLC analysis [Chiralpak IA column, Hexane/*i*-PrOH = 98:2, flow rate = 0.5 mL/min, wave length = 254 nm, t_R = 46.397 min (major), t_R = 52.062min (minor)].



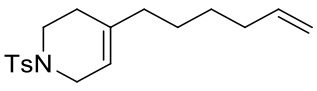
5.5 Effect of catalyst concerntration on 14/15



The procedure was conducted in the argon-filled glove box. To a reaction tube containing NiI_2 (5-25 mol %, 5-25 mM), tpy (7.5-37.5 mol %, 7.5-37.5 mM), and Mn (33 mg, 0.6 mmol) was added a solution of vinyl triflate **1e** (77 mg, 0.2 mmol) and alkyl mesylate **13** (64 mg, 0.36 mmol) in DMA (2 mL). It was then removed from the glove box, and the reaction mixture was stirred at 100 ^{o}C for 12 h. The reaction was quenched with water (20 mL), extracted twice with ethyl acetate (2 × 15 mL). The yields of **14** and **15** were determined by GC Analysis using n-dodecane as internal standard. The results were listed in Table S6.

Table S6. the effect of catalyst concentration on the formation of **14** and **15**.

entry	NiI_2	tpy	14	15
1	5% 5mM	7.5% 7.5mM	16%	12%
2	10% 10mM	15% 15mM	39%	11%
3	15% 15mM	22.5% 22.5mM	55%	9%
4	20% 20mM	30% 30mM	71%	6%
5	25% 25mM	37.5% 37.5mM	75%	6%



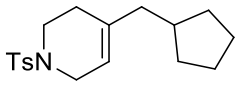
4-(Hex-5-en-1-yl)-1-tosyl-1,2,3,6-tetrahydropyridine (**14**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.82-5.72 (m, 1 H), 5.29 (m, 1 H), 5.00-4.92 (m, 2 H), 3.54 (m, 2 H), 3.16 (t, *J* = 5.7 Hz, 2 H), 2.43 (s, 3 H), 2.11 (m, 2 H), 2.05-2.00 (m, 2 H), 1.95-1.92 (m, 2 H), 1.34-1.32 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 138.9, 136.7, 133.3, 129.7, 127.8, 116.2, 114.6, 44.9, 43.1, 36.8, 33.7, 28.5, 28.4, 26.8, 21.6.

IR (neat, cm^{-1}): 2928, 2855, 1641, 1598, 1460, 1346, 1245, 1211, 1166, 1095, 946, 911, 816, 730, 682, 639.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{26}NO_2S$ 320.1679, found 320.1679.



4-(Cyclopentylmethyl)-1-tosyl-1,2,3,6-tetrahydropyridine (**15**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 5.28 (m, 1 H), 3.55 (m, 2 H), 3.17 (t, *J* = 5.7 Hz, 2 H), 2.42 (s, 3 H), 2.11 (m, 2 H), 1.93-1.85 (m, 3 H), 1.67-1.45 (m, 6 H), 1.07-0.99 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.6, 133.7, 129.7, 127.9, 116.8, 44.9, 43.7, 43.1, 37.8, 32.6, 28.6, 25.2, 21.6.

IR (neat, cm^{-1}): 2948, 2865, 1650, 1458, 1344, 1164, 1095, 952, 815, 741, 710, 682, 642.

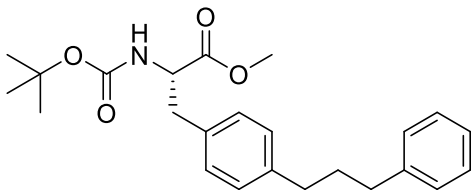
HRMS (ESI): $[M+H]^+$ calcd. for $C_{18}H_{26}NO_2S$ 320.1679, found 320.1675.

6. Catalytic Modification of Tyrosine in Peptides

6.1 General Procedure

The procedure was conducted in an argon-filled glove box. To a reaction tube containing $NiBr_2$ (1.1 mg, 5 mol %), 4,7-diphenyl-1,10-phenanthroline (Bphen, 2.5 mg, 7.5 mol %), LiBr (9.0 mg, 0.1 mmol), KBr (12 mg, 0.1 mmol) and Mn (19.3 mg, 0.35 mmol) was added a solution of styrene (10.4 mg, 0.1 mmol), alkyl tosylate (0.2 mmol) and peptide substrate (0.1 mmol) in DMSO/CH_3CN (1/2, 1 mL). It was sealed and moved from the glove box. The reaction mixture was stirred at room temperature for 72 h. The reaction was quenched with water (20 mL), extracted twice with ethyl acetate (2 × 15 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 the desired product.

6.2 Characterization Data



Methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-(3-phenylpropyl)phenyl)propanoate (17a)

The title compound was prepared according to the General Procedure from triflate **16a** (42.7 mg, 0.1 mmol) and tosylate **2a′** (58 mg, 0.2 mmol).

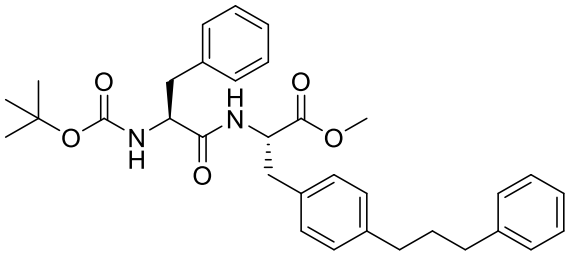
33.0 mg, 83% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 2H), 7.18-7.16 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.96 (s, 1H), 4.57 (m, 1H), 3.70 (s, 3H), 3.10-3.02(m, 2H), 2.66-2.59 (m, 4H), 1.98-1.90 (m, 2H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 155.2, 142.3, 141.1, 133.4, 129.3, 128.7, 128.5, 128.4, 125.9, 80.0, 54.6, 52.2, 38.1, 35.6, 35.1, 33.0, 28.4.

IR (cm^{-1}): 3440, 3362, 3025, 3006, 2977, 2933, 2857, 1746, 1716, 1497, 1452, 1391, 1365, 1251, 1214, 1167, 1058, 1022, 700.

HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{31}NO_4$ 420.2145, found 420.2139.



Methyl (S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(3-phenylpropyl) phenyl) propanoate (17b)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2a′** (58 mg, 0.2 mmol).

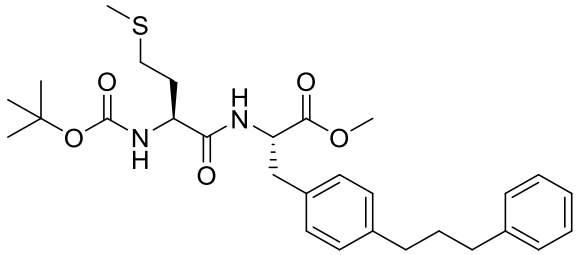
40.3 mg, 74% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.16 (m, 10H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.25 (d, *J* = 8.0 Hz, 1H), 4.94 (m, 1H), 4.75 (m, 1H), 4.32 (m, 1H), 3.66 (s, 3H), 3.06-2.96 (m, 4H), 2.65-2.58 (m, 4H), 1.96-1.88 (m, 2H), 1.39 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.8, 155.4, 142.3, 141.2, 136.6, 133.0, 129.5, 129.3, 128.8, 128.7, 128.5, 128.4, 127.1, 125.9, 80.3, 55.8, 53.4, 52.4, 38.4, 37.7, 35.6, 35.1, 33.0, 28.4.

IR (cm^{-1}): 3299, 2931, 2856, 1744, 1658, 1515, 1366, 1249, 1169, 1117, 1021, 747, 699.

HRMS (ESI): $[M+H]^+$ calcd for $C_{33}H_{41}N_2O_5$ 545.3010, found 545.3007.



Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-4-(methylthio)butanamido)-3-(4-(3-phenylpropyl)phenyl)propanoate (17c)

The title compound was prepared according to the General Procedure from triflate **16c** (55.9 mg, 0.1 mmol) and tosylate **2a′** (58 mg, 0.2 mmol).

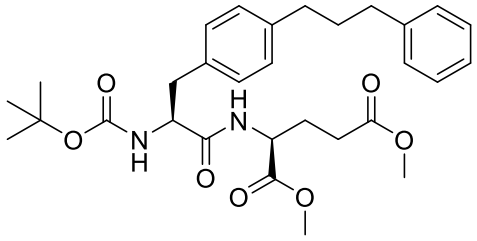
24.3 mg, 46% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (d, *J* = 7.6 Hz, 2H), 7.18-7.16(m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.04-7.00 (m, 2H), 6.57 (d, *J* = 8 Hz, 1H), 5.15 (m, 1H), 4.84-4.79 (m, 1H), 4.25 (m, 1H), 3.70 (s, 3H), 3.12-3.02 (m, 2H), 2.65-2.59 (m, 4H), 2.52 (t, *J* = 8.0 Hz, 2H), 2.04-1.89 (m, 7H), 1.43 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 171.2, 155.5, 142.3, 141.4, 133.0, 129.3, 128.9, 128.6, 128.4, 125.9, 80.2, 53.3, 53.3, 52.5, 37.6, 35.6, 35.2, 33.0, 31.7, 30.2, 28.4, 15.2.

IR (cm^{-1}): 3423, 2977, 2929, 2856, 1744, 1658, 1515, 1451, 1367, 1251, 1169, 1026, 748, 700.

HRMS (ESI): $[M+H]^+$ calcd for $C_{29}H_{41}N_2O_5S$ 529.2731, found 529.2731.



dimethyl((S)-2-((tert-butoxycarbonyl)amino)-3-(4-(3-phenylpropyl)phenyl)propanoyl)-L-glutamate (17d)

The title compound was prepared according to the General Procedure from triflate **16d** (57.1 mg, 0.1 mmol) and tosylate **2a′** (58 mg, 0.2 mmol).

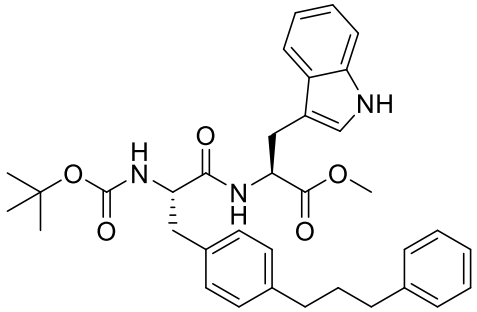
27.1 mg, 50% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.19-7.16 (m, 3H), 7.11 (s, 4H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.94 (bs, 1H), 4.59-4.54 (m, 1H), 4.33-4.32 (m, 1H), 3.69 (s, 3H), 3.64 (s, 3H), 3.09-2.98 (m, 2H), 2.66-2.59 (m, 4H), 2.38-2.15 (m, 3H), 1.97-1.89 (m, 3H), 1.41 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 171.8, 171.4, 155.5, 142.3, 141.2, 133.8, 129.4, 128.9, 128.6, 128.4, 125.9, 81.2, 55.9, 52.6, 51.9, 51.7, 37.8, 35.6, 35.2, 33.0, 29.9, 28.4, 27.5.

IR (cm^{-1}): 3318, 3027, 2929, 2855, 2251, 1741, 1661, 1516, 1440, 1368, 1259, 1209, 1170, 1120, 1047, 1022, 911, 800, 737, 700.

HRMS (ESI): $[M+H]^+$ calcd for $C_{30}H_{41}N_2O_7$ 541.2908, found 541.2909.



Methyl((S)-2-((tert-butoxycarbonyl)amino)-3-(4-(3-phenylpropyl)phenyl)propanoyl)-L-tryptophanate (17e)

The title compound was prepared according to the General Procedure from triflate **16e** (61.4 mg, 0.1 mmol) and tosylate **2a′** (58 mg, 0.2 mmol).

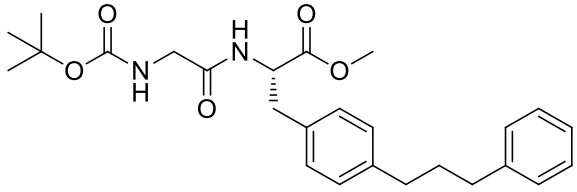
45 mg, 77% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.24-7.35 (m, 4H), 7.21-7.13 (m, 4H), 7.06-7.02 (m, 5H), 6.84 (s, 1H), 6.43 (m, 1H), 4.92-4.86 (m, 2H), 4.33 (s, 1H), 3.58 (s, 3H), 3.28-3.18 (m, 2H), 3.02-2.97 (m, 2H), 2.64-2.56 (m, 4H), 1.94-1.86 (m, 2H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 171.0, 155.4, 142.3, 141.1, 136.2, 133.9, 129.5, 128.8, 128.5, 128.4, 127.6, 125.9, 123.1, 122.3, 119.7, 118.6, 111.4, 109.8, 80.2, 55.8, 53.1, 52.4, 38.0, 35.5, 35.1, 33.1, 28.3, 27.8.

IR (cm^{-1}): 3334, 3059, 3026, 2978, 2931, 2857, 2248, 1740, 1659, 1515, 1440, 1367, 1252, 1213, 1169, 1105, 1050, 1023, 910, 741, 700.

HRMS (ESI): $[M+H]^+$ calcd for $C_{35}H_{42}N_3O_5$ 584.3119, found 584.3116.



Methyl (S)-2-(2-((tert-butoxycarbonyl) amino) acetamido)-3-(4-(3-phenylpropyl) phenyl) propanoate (17f)

The title compound was prepared according to the General Procedure from triflate **16f** (48.4 mg, 0.1 mmol) and tosylate **2a′** (58 mg, 0.2 mmol).

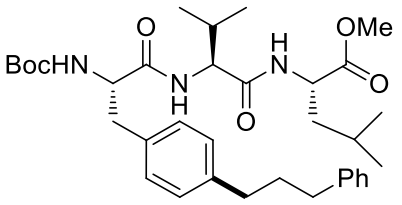
35.5 mg, 78% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.2 Hz, 2H), 7.19-7.16 (m, 3H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 7.6, 2H), 6.51 (d, *J* = 8.0 Hz, 1H), 5.10 (s, 1H), 4.88-4.83 (m, 1H), 3.89-3.75 (m, 2H), 3.70 (s, 3H), 3.15-3.04 (m, 2H), 2.66-2.59 (m, 4H), 1.97-1.89 (m, 2H), 1.43 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.2, 156.0, 142.3, 141.3, 133.0, 129.3, 128.8, 128.5, 128.4, 125.9, 80.3, 53.2, 52.4, 44.3, 37.6, 35.6, 35.1, 33.0, 28.4.

IR (cm^{-1}): 3313, 3026, 2978, 2933, 2858, 1744, 1678, 1514, 1452, 1367, 1277, 1249, 1213, 1170, 1120, 1050, 1029, 864, 748, 700.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{26}H_{35}N_2O_5$ 455.2540, found 455.2539.



Methyl ((S)-2-((tert-butoxycarbonyl) amino)-3-(4-(3-phenylpropyl) phenyl) propanoyl)-L-valyl-L-leucinate (17g)

The title compound was prepared according to the General Procedure from triflate **16g** (64 mg, 0.1 mmol) and tosylate **2a′** (58 mg, 0.2 mmol).

34.8 mg, 57% yield, colorless oil.

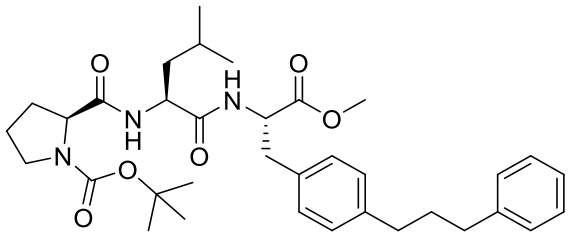
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.19-7.16 (m, 3H),7.10 (s, 4H), 6.63(d, *J* = 12

Hz, 1H), 6.53 (m, 1H), 5.02 (m, 1H), 4.60-4.55 (m, 1H), 4.37 (m, 1H), 4.29-4.25 (m, 1H), 3.72 (s, 3H), 3.10-3.00 (m, 2H), 2.66-2.59 (m, 4H), 2.15-2.13 (m, 1H), 1.97-1.89 (m, 2H), 1.81 (s, 1H), 1.67-1.53 (m, 2H), 1.39(s, 9H), 0.93-0.90 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 171.6, 170.7, 155.7, 142.3, 141.1, 133.9, 129.4, 128.9, 128.5, 128.4, 125.9, 80.5, 58.6, 56.0, 52.4, 50.9, 41.3, 37.5, 35.6, 35.1, 33.0, 30.8, 28.4, 24.9, 22.9, 22.0, 19.2, 18.0.

IR (cm^{-1}): 3279, 2959, 2934, 2872, 1751, 1689, 1643, 1523, 1452, 1391, 1367, 1250, 1210, 1172, 1048, 1023, 892, 748, 699.

HRMS (ESI): $[M+H]^+$ calcd. for $C_{35}H_{52}N_3O_6$ 610.3851, found 610.3854.



Tert-butyl (S)-2-(((S)-1-(((S)-1-methoxy-1-oxo-3-(4-(3-phenylpropyl) phenyl) propan-2-yl)amino)-4-methyl-1-oxopentan-2-yl) carbamoyl) pyrrolidine-1-carboxylate (17h)

The title compound was prepared according to the General Procedure from triflate **16h** (63.9 mg, 0.1 mmol) and tosylate **2a′** (58 mg, 0.2 mmol).

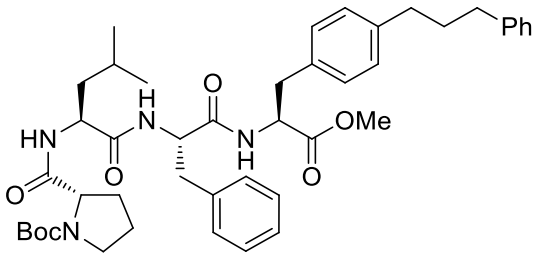
39.5 mg, 65% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 2H), 7.19-7.16 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 6.46 (m, 1H),4.81-4.76 (m, 1H), 4,35 (m, 1H), 4.22 (m, 1H), 3.69 (s, 3H), 3.38 (m, 2H), 3.06 (m, 2H), 2.66-2.59 (m, 4H), 2.30 (s, 1H), 1.97-1.86 (m, 5H), 1.72 (m, 1H), 1.61-1.51 (m, 2H), 1.46 (s, 9H), 0.89-0.86 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.9, 171.6, 156.2, 142.4, 141.1, 133.3, 129.3, 128.7, 128.6, 128.4, 125.9, 80.8, 59.8, 53.4, 52.4, 51.9, 47.2, 40.3, 37.6, 35.6, 35.2, 33.0, 28.5, 27.8, 24.8, 23.2, 21.8.

IR (cm^{-1}): 3293, 2956, 2929, 2870, 1744, 1702, 1660, 1548, 1453, 1400, 1366, 1275, 1251, 1211, 1172, 1122, 1028, 749, 699.

HRMS (ESI): $[M+H]^+$ calcd for $C_{35}H_{50}N_3O_6$ 608.3694, found 608.3697.



Tert-butyl (S)-2-(((S)-1-(((S)-1-(((S)-1-methoxy-1-oxo-3-(4-(3-phenylpropyl) phenyl)propan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-methyl-1-oxopentan-2-yl)carbamoyl) pyrrolidine-1-carboxylate (17i)

The title compound was prepared according to the General Procedure from triflate **16i** (78.5 mg, 0.1 mmol) and tosylate **2a′** (58 mg, 0.2 mmol).

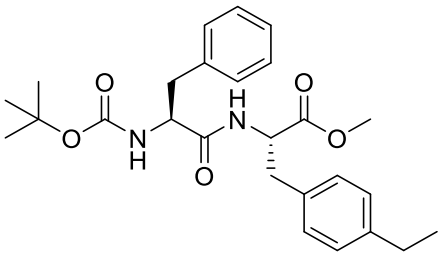
55.1 mg, 73% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.13 (m, 11H), 7.10-7.01 (m, 3H), 7.00 (m, 1H), 6.84 (m, 1H), 6.64 (m, 1H), 4.74-4.69 (m, 2H), 4.24 (m, 1H), 4.10 (m, 1H), 3.65 (s, 3H), 3.37 (m, 2H), 3.14-2.99 (m, 4H), 2.65-2.58 (m, 4H), 2.18-1.88 (m, 7H), 1.59-1.51 (m, 2H), 1.46 (s, 9H), 0.87-0.83 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.8, 171.6, 170.6, 156.2, 142.3, 140.9, 137.0, 133.6, 129.2, 129.2, 128.6, 128.5, 128.5, 128.4, 126.8, 125.8, 80.9, 60.1, 53.9, 53.7, 53.6, 52.6, 52.3, 52.2, 47.4, 40.0, 37.5, 35.6, 35.1, 33.0, 28.4, 24.8, 23.1, 21.6.

IR (cm^{-1}): 3296, 3062, 3028, 2955, 2869, 1747, 1642, 1546, 1453, 1396, 1247, 1210, 1166, 1124, 989, 920, 735, 699.

HRMS (ESI): $[M+H]^+$ calcd for $C_{44}H_{59}N_4O_7$ 755.4378, found 755.4373.



Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-ethylphenyl)propanoate (17j)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2ac** (40 mg, 0.2 mmol).

38.7 mg, 85% yield, colorless oil.

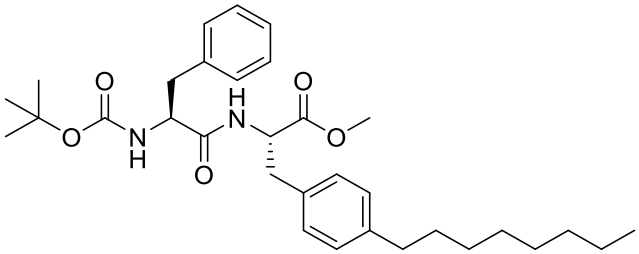
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 6.27 (m, 1 H), 4.97 (m, 1H), 4.77-4.75 (m, 1H), 4.35-4.33 (m, 1H), 3.67 (s, 3H), 3.06-2.96 (m,

4H), 2.63-2.57 (m, 2H), 1.39 (s, 9H), 1.21 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.8, 155.3, 143.1, 136.6, 132.8, 129.5, 129.2, 128.7, 128.2, 127.0, 80.3, 55.7, 53.4, 52.4, 38.4, 37.6, 28.5, 28.3, 15.6.

IR (cm^{-1}): 3331, 3306, 3028, 2965, 2930, 2872, 1743, 1659, 1520, 1442, 1367, 1249, 1170, 1120, 10461022, 912, 825, 736, 699.

HRMS (ESI): $[M+H]^+$ calcd for $C_{26}H_{35}N_2O_5$ 455.2540, found 455.2538.



Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-octylphenyl) propanoate（17k）

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2ad** (56.8 mg, 0.2 mmol).

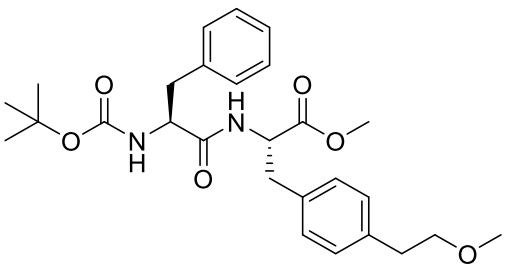
42.0 mg, 78% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 6.28 (m, 1 H), 4.97 (m, 1H), 4.76 (m, 1H), 4.33 (m, 1H), 3.66 (s, 3H), 3.05-2.95 (m, 4H), 2.54 (t, *J* = 8.0 Hz, 2 H), 1.59-1.53 (m, 2H), 1.40 (s, 9H), 1.29-1.26 (m, 10H), 0.88 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 170.8, 155.4, 141.9, 136.6, 132.8, 129.5, 129.2, 128.7, 128.6, 127.0, 80.2, 55.8, 53.4, 52.3, 38.4, 37.7, 35.7, 32.0, 31.5, 29.6, 29.5, 29.4, 28.3, 22.8, 14.2.

IR (cm^{-1}): 3332, 2954, 2925, 2853, 1741, 1665, 1522, 1446, 1368, 1296, 1248, 1169, 1022, 751, 689.

HRMS (ESI): $[M+H]^+$ calcd for $C_{32}H_{47}N_2O_5$ 539.3479, found 539.3478.



Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(2-methoxyethyl)phenyl)propanoate (17l)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2ae** (46 mg, 0.2 mmol).

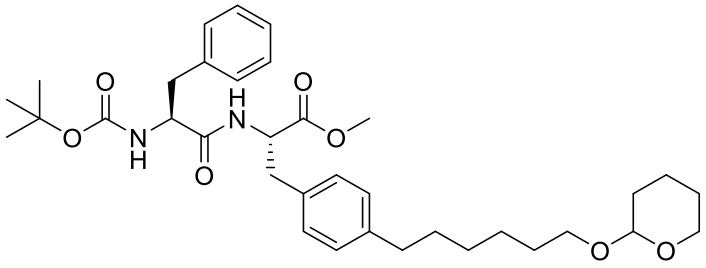
36.4 mg, 75% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.29 (m, 1H), 4.99 (m, 1H), 4.77-4.75 (m, 1H), 4.33 (m, 1H), 3.67 (s, 3H), 3.57 (t, *J* = 8.0 Hz, 2H), 3.40 (s, 3H), 3.07-2.96 (m, 4H), 2.83 (t, *J* = 8.0 Hz, 2H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.8, 155.4, 137.8, 136.6, 133.5, 129.5, 129.3, 129.1, 128.7, 127.1, 80.3, 73.6, 58.7, 55.8, 53.4, 52.4, 38.4, 37.6, 35.9, 28.3.

IR (cm^{-1}): 3427, 2978, 2929, 2869, 1744, 1660, 1519, 1367, 1251, 1171, 1116, 1048, 1022, 735, 700.

HRMS (ESI): $[M+H]^+$ calcd for $C_{27}H_{37}N_2O_6$ 485.2646, found 485.2646.



Methyl(2S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(6-((tetrahydro-2H-pyran-2-yl)oxy)hexyl)phenyl)propanoate (17m)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2af** (71.2mg, 0.2 mmol).

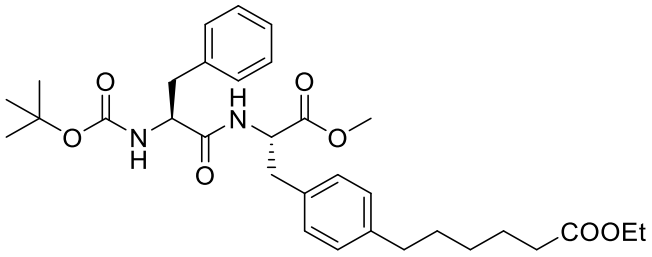
47.0 mg, 77% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.27 (m, 1H), 4.98 (m, 1H), 4.76-4.74 (m, 1H), 4.58-4.56 (m, 1H), 4.33 (m, 1 H), 3.89-3.83 (m, 1H), 3.75-3,69 (m, 1H), 3.67(s, 3H), 3.52-3.47 (m, 1H), 3.40-3.34 (m, 1H), 3.04-2.95 (m, 4H), 2.55 (t, *J* = 8.0 Hz, 2H), 1.85-1.79 (m, 1H), 1.74-1.68 (m, 1H), 1.63-1.50 (m, 8H), 1.40-1.36 (m, 13H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.8, 155.3, 141.7, 136.6, 132.8, 129.5, 129.2, 128.8, 128.7, 127.1, 98.9, 80.3, 67.7, 62.5, 55.7, 53.4, 52.4, 38.4, 37.6, 35.6, 31.5, 30.9, 29.8, 29.3, 28.3, 26.2, 25.6, 19.8.

IR (cm^{-1}): 3421, 2934, 2857, 1745, 1660, 1517, 1441, 1367, 1251, 1203, 1171, 1120, 1024, 908, 885, 867, 813, 734, 700.

HRMS (ESI): $[M+H]^+$ calcd for $C_{35}H_{51}N_2O_7$ 611.3691, found 611.3693.



ethyl6-(4-((S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-methoxy-3-oxopropyl)phenyl)hexanoate（17n）

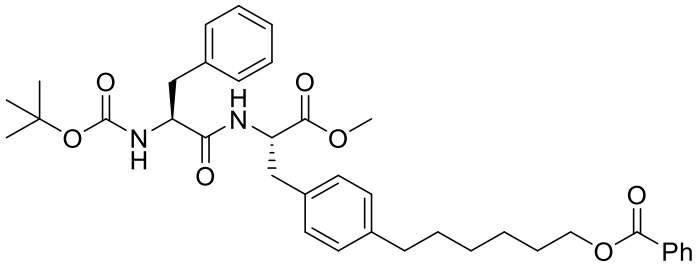
The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2ag** (62.8 mg, 0.2 mmol).

38.7 mg, 68% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H）, 7.24-7.18 (m, 3H), 7.03 (d, *J* = 8.0 Hz, 2 H), 6.88 (d, *J* = 8.0 Hz, 2 H), 6.29 (s, 1 H), 4.99 (s, 1H), 4.75 (m, 1H), 4.33 (s, 1H), 4.14-4.09 (m, 2H), 3.66 (s, 3H), 3.05-2.95 (m, 4H), 2.55 (t, *J* = 8.0 Hz, 2 H), 2.28 (t, *J* = 8.0 Hz, 2H), 1.68-1.57 (m, 4H), 1.40 (s, 9H), 1.26-1.22 (m, 5H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 173.8, 171.5, 170.8, 155.4, 141.4, 136.7, 133.0, 129.5, 129.2, 128.7, 128.6, 127.0, 80.3, 60.3, 55.8, 53.4, 52.3, 38.4, 37.7, 35.4, 34.4, 31.1, 29.8, 28.4, 24.9, 14.4.

HRMS (ESI): $[M+H]^+$ calcd for $C_{32}H_{45}N_2O_7$ 569.3221, found 569.3220.



6-(4-((S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-methoxy-3-oxopropyl)phenyl)hexyl benzoate (17o)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2ah** (75.2 mg, 0.2 mmol).

42.9 mg, 68% yield, colorless oil.

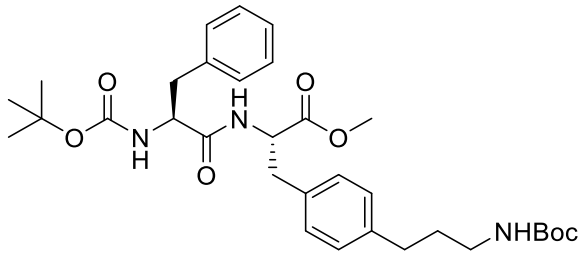
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 7.44 (t, *J* = 4.0 Hz, 2 H), 7.29-7.27 (m, 2H), 7.24-7.18 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 6.28 (m, 1 H), 4.99 (m, 1H), 4.76 (m, 1H), 4.34-4.29 (m, 3H), 3.67 (s, 3H), 3.04-2.96 (m, 4H), 2.56 (t, *J* = 8.0 Hz, 2 H), 1.78-1.74 (m, 2H), 1.64-1.59 (m, 2H), 1.49-1.44 (m, 2H), 1.39 (m, 11H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.8, 166.8, 155.4, 141.5, 136.6, 132.95, 132.88, 130.6,

129.6, 129.5, 129.2, 128.8, 128.7, 128.4, 127.1, 80.2, 65.1, 55.7, 53.4, 52.4, 38.4, 37.6, 35.6, 31.4, 29.0, 28.7, 28.3, 26.0.

IR (cm^{-1}): 3322, 2932, 2857, 1719, 1660, 1516, 1452, 1390, 1367, 1275, 1172, 1117, 1026, 746, 714.

HRMS (ESI): $[M+H]^+$ calcd for $C_{37}H_{47}N_2O_7$ 631.3378, found 631.3378.



Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(3-((tert-butoxycarbonyl)amino)propyl)phenyl)propanoate (17p)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2ai** (65.8 mg, 0.2 mmol).

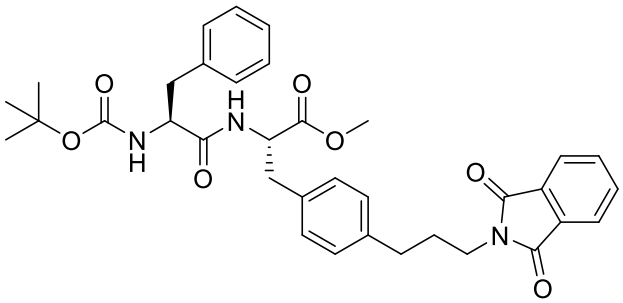
35.0 mg, 60% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 6.29 (m, 1H), 5.04 (m, 1H), 4.75 (m, 1H), 4.56 (m, 1H), 4.32 (m, 1H), 3.67 (s, 3H), 3.15-3.10 (m, 2H), 3.06-2.95 (m, 4H), 2.59 (t, *J* = 8.0 Hz, 2H), 1.81-1.74 (m, 2H), 1.44 (s, 9H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.9, 156.5, 156.1, 140.5, 136.7, 133.3, 129.5, 129.4, 128.75, 128.67, 127.0, 80.2, 79.3, 55.8, 53.4, 52.4, 40.3, 38.4, 37.7, 32.8, 31.8, 28.5, 28.4.

IR (cm^{-1}): 3340, 2978, 2931, 2865, 2249, 1744, 1693, 1515, 1453, 1392, 1367, 1251, 1170, 1047, 1022, 912, 733, 700.

HRMS (ESI): $[M+H]^+$ calcd for $C_{32}H_{46}N_3O_7$ 584.3330, found 584.3328.



Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(3-(1,3-dioxoisoindolin-2-yl)propyl)phenyl)propanoate (17q)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2aj** (71.8 mg, 0.2 mmol).

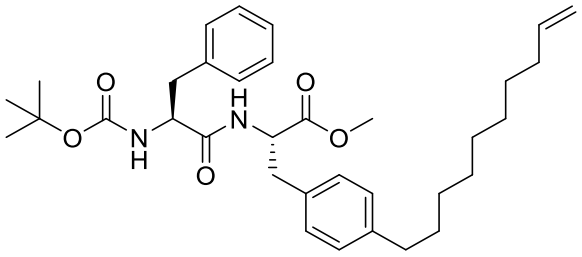
49.7 mg, 81% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 7.72-7.69 (m, 2H), 7.29-7.18 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 6.32 (m, 1 H), 5.07 (m, 1H), 4.75-4.74 (m, 1H), 4.35-4.33 (m, 1H), 3.72-3.67 (m, 5H), 3.08-2.93 (m, 4H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.04-1.96 (m, 2H), 1.38 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.9, 168.5, 155.4, 139.9, 136.7, 134.0, 133.3, 132.2, 129.4, 129.3, 128.7, 128.6, 127.0, 123.3, 80.2, 55.7, 53.3, 52.4, 38.3, 37.7, 37.6, 32.8, 29.9, 28.3.

IR (cm^{-1}): 3343, 2977, 2932, 2860, 1712, 1516, 1440, 1397, 1368, 1251, 1170, 1089, 1022, 913, 858, 794, 725.

HRMS (ESI): $[M+H]^+$ calcd for $C_{35}H_{40}N_3O_7$ 614.2861, found 614.2858.



Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(dec-9-en-1-yl) phenyl) propanoate (17r)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2ak** (62 mg, 0.2 mmol).

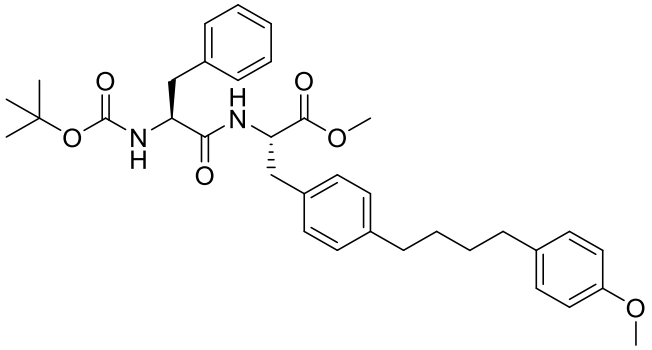
22.6 mg, 40% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.18 (m, 5H), 7.04 (d, *J* = 8.0 Hz, 2 H), 6.87 (d, *J* = 8.0 Hz, 2 H), 6.24 (m, 1 H), 5.86-5.76 (m, 1H), 5.02-4.91 (m, 3H), 4.76-4.74 (m, 1H), 4.32 (m, 1H), 3.67 (s, 3H), 3.05-2.95 (m, 4H), 2.54 (t, *J* = 8.0 Hz, 2 H), 2.06-2.01 (m, 2 H), 1.58-1.55 (m, 2H), 1.40 (s, 9H), 1.37-1.25 (m, 11 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.8, 155.3, 141.8, 139.3, 136.6, 132.7, 129.5, 129.2, 128.8, 128.7, 127.1, 114.2, 80.3, 55.7, 53.4, 52.4, 38.4, 37.7, 35.7, 33.9, 31.5, 29.8, 29.54, 29.46, 29.2, 29.0, 28.3.

IR (cm^{-1}): 3337, 2978, 2927, 2855, 1745, 1659, 1518, 1440, 1367, 1250, 1213, 1171, 1048, 1021, 910, 749, 699.

HRMS (ESI): $[M+H]^+$ calcd for $C_{34}H_{49}N_2O_5$ 565.3636, found 565.3636.



Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(4-(4-methoxyphenyl)butyl)phenyl)propanoate (17s)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2al** (66.8 mg, 0.2 mmol).

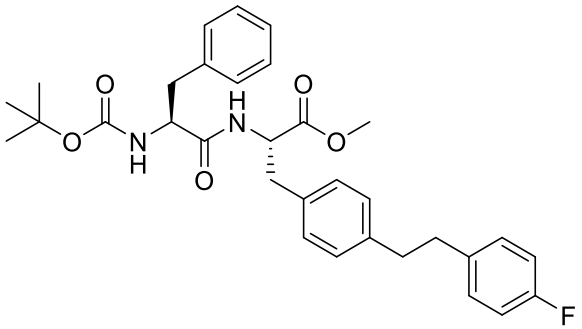
48.9 mg, 83% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.27 (m, 1H), 4.97 (m, 1H), 4.75 (m, 1H), 4.33 (m, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 3.05-2.98 (m, 4H), 2.57-2.56 (m, 4H), 1.63-1.60 (m, 4H), 1.39 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.8, 157.7, 155.4, 141.5, 136.6, 134.7, 132.9, 129.5, 129.3, 129.2, 128.8, 128.7, 127.1, 113.8, 80.2, 55.8, 55.3, 53.4, 52.4, 38.4, 37.6, 35.5, 34.9, 31.5, 31.0, 28.3.

IR (cm^{-1}): 3343, 2978, 2932, 2856, 1744, 1659, 1613, 1513, 1442, 1367, 1247, 1214, 1174, 1034, 912, 820, 734, 700.

HRMS (ESI): $[M+H]^+$ calcd for $C_{35}H_{45}N_2O_6$ 589.3272, found 589.3271.



Methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(4-fluorophenethyl)phenyl)propanoate (17t)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2am** (78.8 mg, 0.2 mmol).

69.0 mg, 84% yield, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.18 (m, 5H), 7.09-7.05 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H),

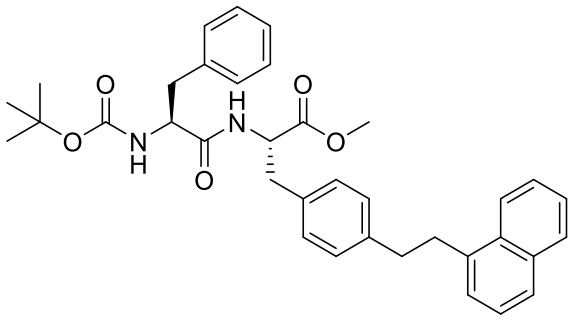
6.97-6.92 (m, 2H), 6.88 (d, J = 8.0 Hz, 2H), 6.28 (m, 1H), 4.98 (m, 1H), 4.76-4.75 (m, 1H), 4.35-4.33 (m, 1H), 3.66 (s, 3H), 3.06-2.96 (m, 4H), 2.84 (s, 4H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.8, 161.4 (q, J_{C-F} = 242.0 Hz), 155.4, 140.3, 137.3 (q, J_{C-F} = 2.9 Hz), 136.6, 133.3, 129.9 (q, J_{C-F} = 7.7 Hz), 129.87, 129.5, 129.3, 128.8, 127.1, 115.1 (q, J_{C-F} = 20.9 Hz), 80.3, 55.8, 53.4, 52.4, 38.4, 37.7, 37.7, 37.0, 28.3.

^{19}F NMR (376 MHz, $CDCl_3$) δ −116.02.

IR (cm^{-1}): 3331, 3027, 2981, 2926, 2859, 1739, 1664, 1511, 1451, 1368, 1295, 1248, 1219, 1168, 1021, 913, 826, 749, 698.

HRMS (ESI): $[M+H]^+$ calcd for $C_{32}H_{38}FN_2O_5$ 549.2759, found 549.2755.



methyl(S)-2-((S)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-3-(4-(2-(naphthalen-1-yl)ethyl)phenyl)propanoate (17u)

The title compound was prepared according to the General Procedure from triflate **16b** (57.5 mg, 0.1 mmol) and tosylate **2an** (65.2 mg, 0.2 mmol).

27.3 mg, 47% yield, colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J = 6.0 Hz, 1H), 7.87 (d, J = 6.0 Hz, 1H), 7.73 (d, J = 6.0 Hz, 1H), 7.54-7.48 (m, 2H), 7.38 (t, J = 6.0 Hz, 1H), 7.30-7.20 (m, 6H), 7.11 (d, J = 6.0 Hz, 2H), 6.92 (d, J = 6.0 Hz, 2H), 6.27 (m, 1H), 4.97 (m, 1H), 4.78 (m, 1H), 4.35 (m, 1H), 3.68 (s, 3H), 3.35-3.33 (m, 2H), 3.08-3.00 (m, 6H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 170.8, 155.4, 140.9, 137.8, 136.6, 134.0, 133.3, 131.9, 129.5, 129.4, 129.0, 128.8, 128.7, 127.1, 126.9, 126.1, 126.0, 125.7, 125.6, 123.7, 80.3, 55.8, 53.5, 52.4, 38.5, 37.7, 36.8, 35.1, 28.4.

IR (cm^{-1}): 3429, 2978, 2930, 2868, 1743, 1658, 1515, 1440, 1392, 1367, 1251, 1215, 1169, 1048, 1021, 911, 797, 778, 734, 700.

HRMS (ESI): $[M+H]^+$ calcd for $C_{36}H_{41}N_2O_5$ 581.3010, found 581.3008.

7. References

1. Armarego, W. L. F.; Chai, C. L. L. *Purification of laboratory chemicals*, 5th ed., Butterworth-Heinemann, **2003**.

2. Su, X.; Huang, H.; Yuan, Y.; Li, Y. *Angew. Chem. Int. Ed.* **2017**, *56*, 1338.

3. Thakur, A.; Manohar, S.; Gerena, C. E.; Zayas, B.; Kumar, V.; Malhotra S. V.; Rawat, D. S. *Med. Chem. Commun.* **2014**, *5*, 576.

4. Jana, N.; Nguyen, Q.; Driver, T. G. *J. Org. Chem.* **2014**, *79*, 2781.

5. Lippincott, D. J.; Linstadt, R. T. H.; Maser, M. R.; Lipshutz, B. H. *Angew. Chem. Int. Ed.* **2017**, *56*, 847.

6. Lim, B.-Y.; Jung, B.-E.; Cho, C.-G. *Org. Lett.* **2014**, *16*, 4492

7. Ueda, T.; Konishi, H.; Manabe, K. *Org. Lett.* **2012**, *14*, 5370.

8. Burger, M. T. *J. Med. Chem.* **2015**, *58*, 8373.

9. Kamijo, S.; Dudley, G. B. *Tetrahedron Letters* **2006**, *47*, 5629.

10. McCammant, M; Liao, L; Sigman, M. *J. Am. Chem. Soc.* **2013**, *135*, 4167.

11. Babinski, D.; Soltani, O.; Frantz D. E. *Org. Lett.* **2008**, *10*, 2901.

12. Said, M. S.; Khandare, L.; Shinde, S. S. *Tetrahedron Letters* **2017**, *58*, 59.

13. Peng, L.; Li, Y.; Li, Y.; Wang, W.; Pang, H.; Yin, G. *ACS Catal.* **2018**, *8*, 310.

14. Marcotullio, M. C.; Campagna, V.; Sternativo, S.; Costantino, F.; Curini, M. *Synthesis* **2006**, *16*, 2760.

15. Hansen, D. J.; Manuguerra, I.; Kjelstrup, M. B.; Gothelf, K. V. *Angew. Chem. Int. Ed.* **2014**, *53*, 14415.

16. Hong, Y.-R.; Gorman, C. B. *J. Org. Chem.* **2003**, *68*, 9019.

17. Bélard, A.-C.; Collins, S. K. *Org. Lett.* **2014**, *16*, 5286.

18. Solladié, G.; Rubio, A.; Carreño, M. C.; Ruano, J. G. *Tetrahedron: Asymmetry* **1990**, *1*, 187.

19. Willemsen, J. S.; Hest, J. C. M.; Rutjes, F. P. J. T. *Beilstein J. Org. Chem.* **2013**, *9*, 960.

20. Liu, Y.; Xu, Y.; Jung, S. H.; Chae, J. *Synlett* **2012**, *23*, 2692.

21. Orsini, F.; Sello, G.; Travaini, E.; Gennaro, P. D. *Tetrahedron: Asymmetry* **2002**, *13*, 253.

22. Pujala, B.; Pham, S. M. *ACS Med. Chem. Lett.* **2016**, *7*, 1161.

23. Pan, D.; Sun, J.; Jin, H.; Li, Y.; Li, L.; Wu, Y.; Zhang, L.; Yang, Z. *Chem. Commun.* **2015**, *51*, 469.

24. Gichinga, M. G.; Striegler, S. *Tetrahedron* **2009**, *65*, 4917.

25. Lewis, J. E. M.; Modicom, F.; Goldup, S. M. *J. Am. Chem. Soc.* **2018**, *140*, 4787.

26. Bume, D. D.; Pitts, C. R. S.; Ghorbani, F.; Harry, S. A.; Capilato, J. N.; Siegler, M. A.; Lectka, T. *Chem. Sci.* **2017**, *8*, 6918.

27. Blasco, I; Péreza, H; Guijarroa, A. *J. Phys. Org. Chem.* **2015**, *28*, 388.

28. Sergeev, M. E.; Morgia, F.; Lazari, M.; Wang, C.; Dam, R. M. *J. Am. Chem. Soc.* **2015**, *137*, 5686.

29. Wang, Y.; Deng, L.; Deng, Y.; Han, J. *J. Org. Chem.* **2018**, *83*, 4674.

30. Zhang, Q.; Ren, H.; Baker, G. L. *Tetrahedron Letters*, **2014**, *55*, 3384.

31. Yoshida, Y. *Synthesis*, **1999**, *9*, 1633.

32. Guo, Z.; Zhang, R.; Liang, F. *RSC Advances*, **2014**, *4*, 11400.

33. Hisashi, U.; Mitsuhiko, I.; Hatsuho, U. *Bulletin of the Chemical Society of Japan*, **1989**, *62*, 198.

34. Matos, J. L. M.; Vásquez-Céspedes, S.; Gu, J.; Oguma, T.; Shenvi, R. A. *J. Am. Chem. Soc.* **2018**, *140*, 16976.

35. Liu, Y.; Cornella, J.; Martin, R. *J. Am. Chem. Soc.* **2014**, *136*, 11212.

36. Gardner, R. A. *J. Med. Chem.* **2004**, *47*, 6055.

37. Horatscheck, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 9441.

38. Belhomme, M. C.; Wang, D.; Szabó, K. J. *Organic Letters*, **2016**, *18*, 2503.

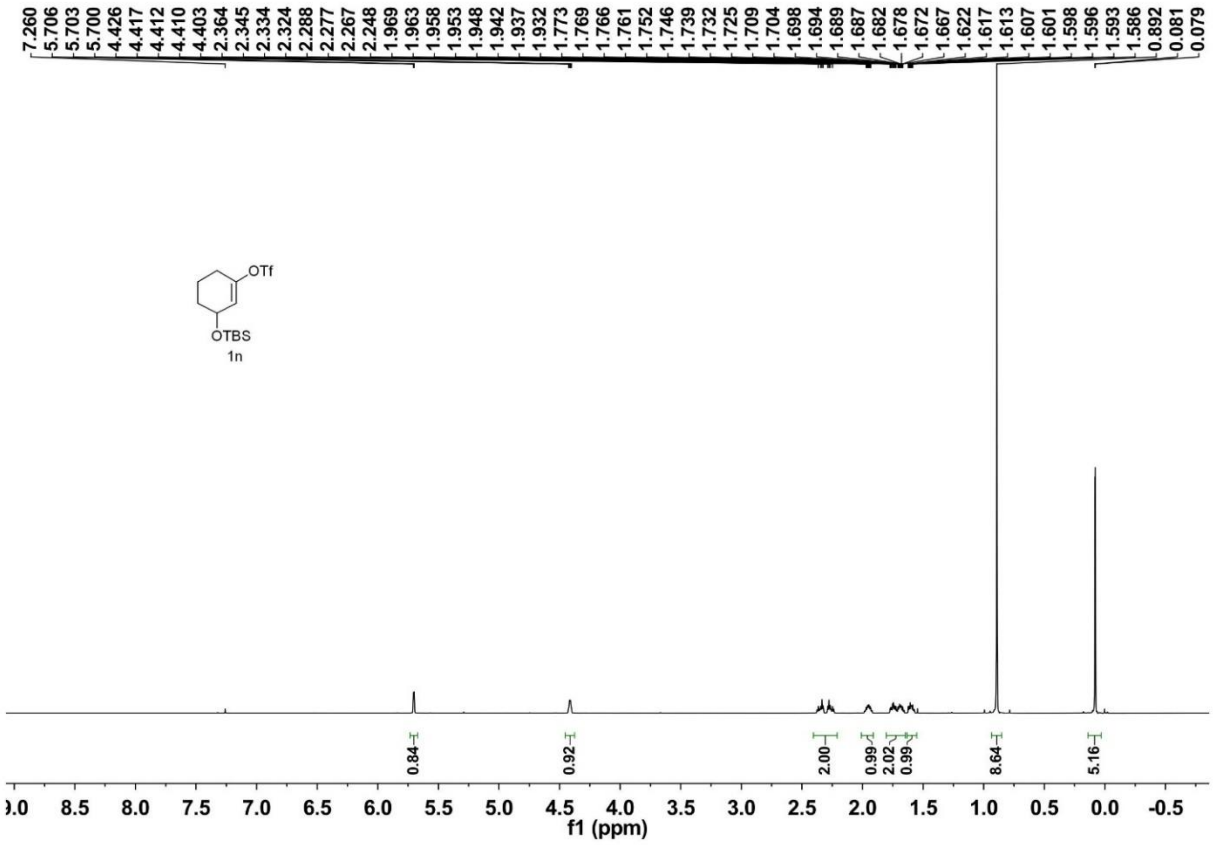
39. Hennum, M.; Odden, H. H.; Gundersen, L. L. *Eur. J. Org. Chem.* **2017**, *2017*, 846.

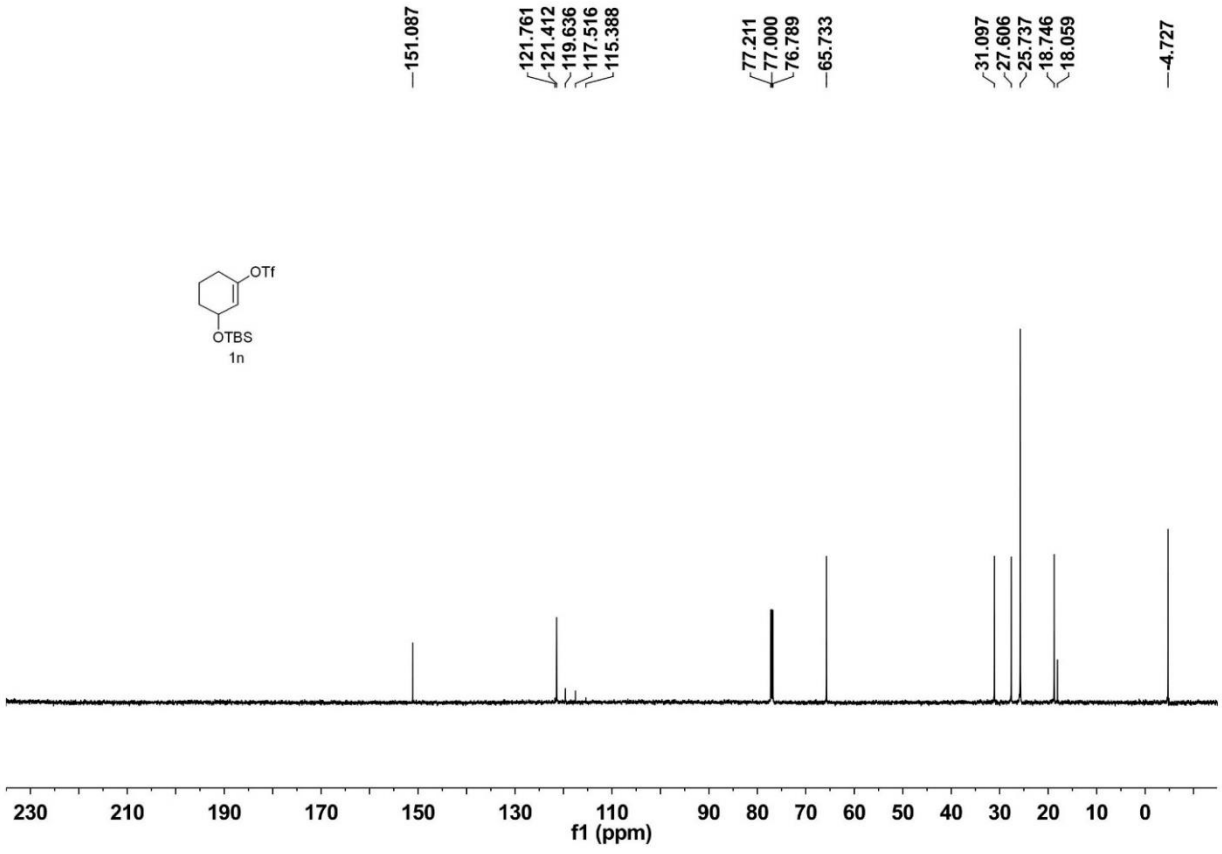
40. Wang, X.; Ji, X.; Shao, C.; Zhang, Y.; Zhang, Y. *Org. Biomol. Chem.* **2017**, *15*, 5616.

41. Bose, S. K.; Brand, S.; Omoregie, H. O.; Haehnel, M.; Maier, J.; Bringmann, G.; Marder, T. B. *ACS Catal.* **2016**, *6*, 8332.

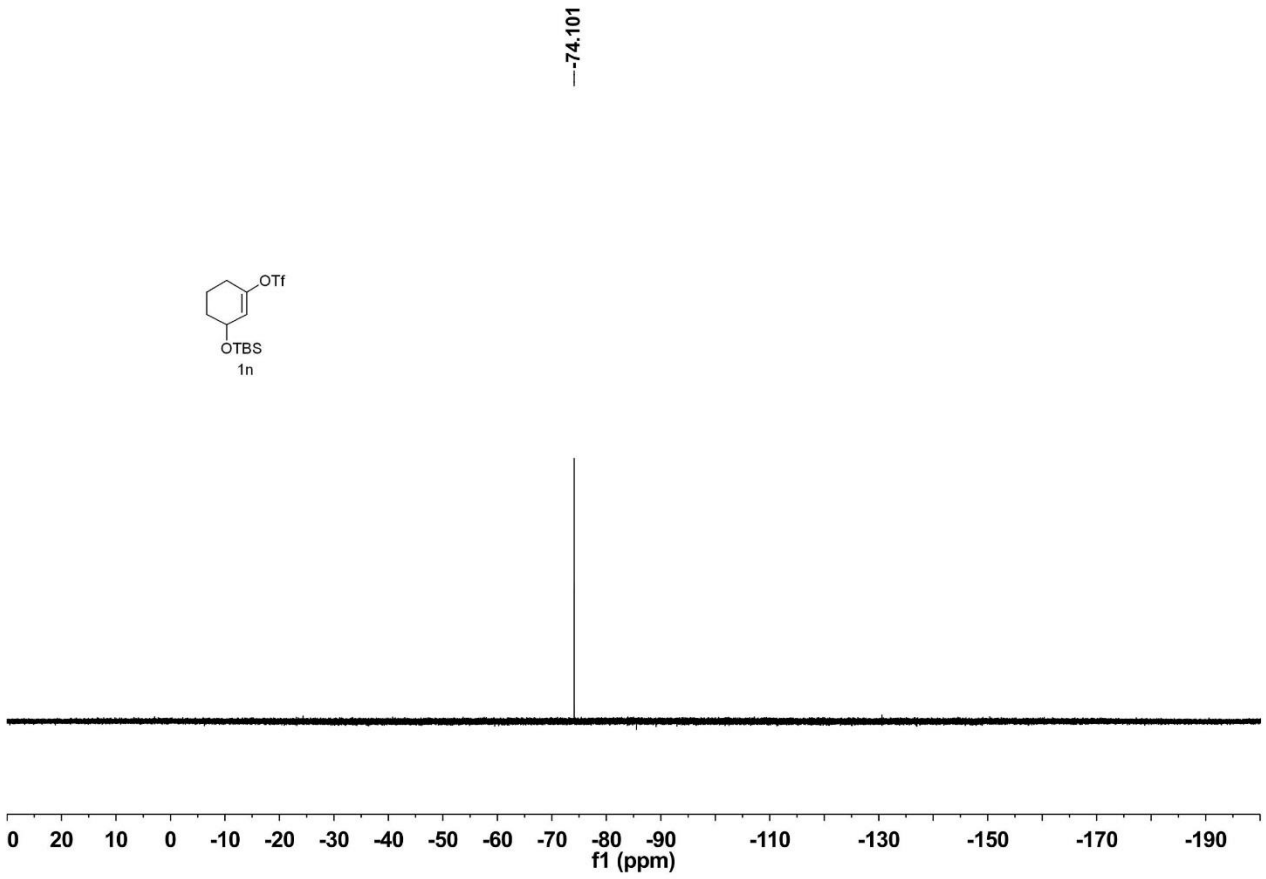
8. Copies of NMR Spectra for Compounds

1n; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

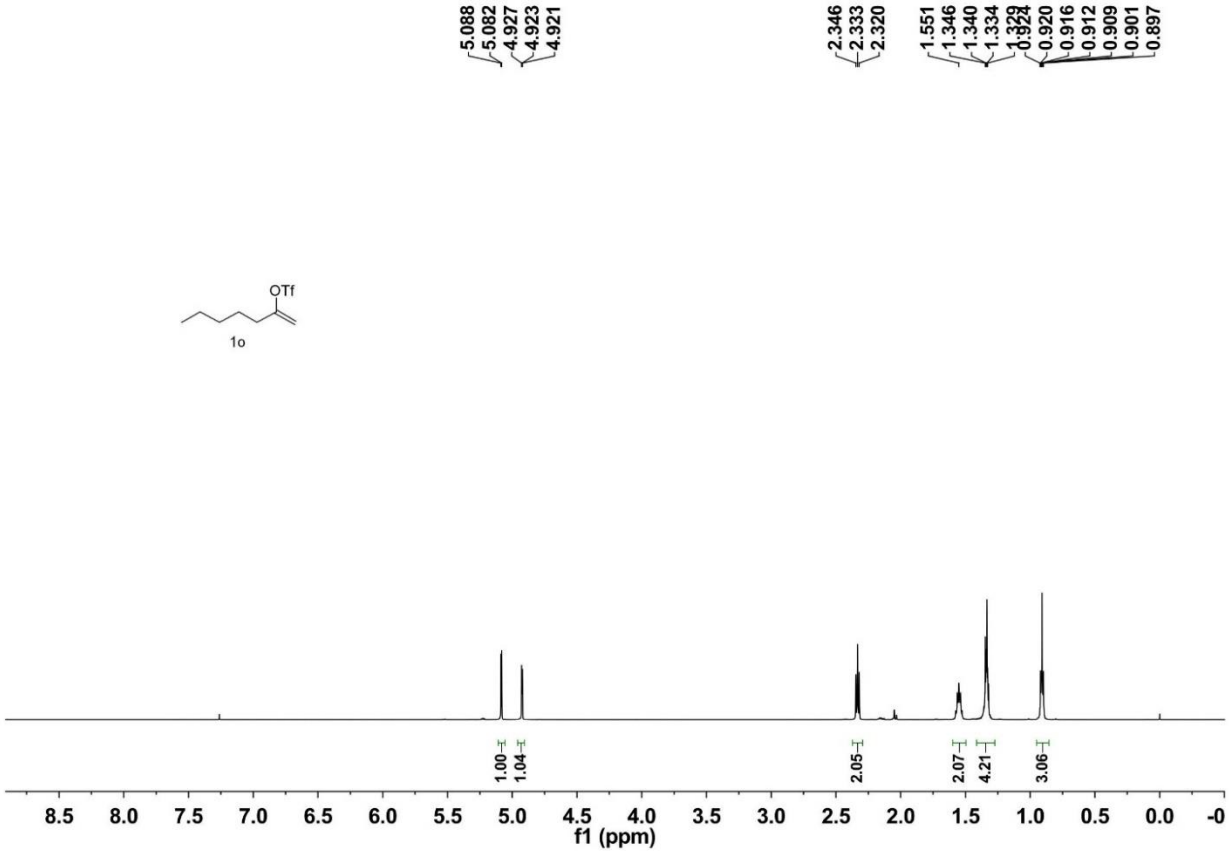


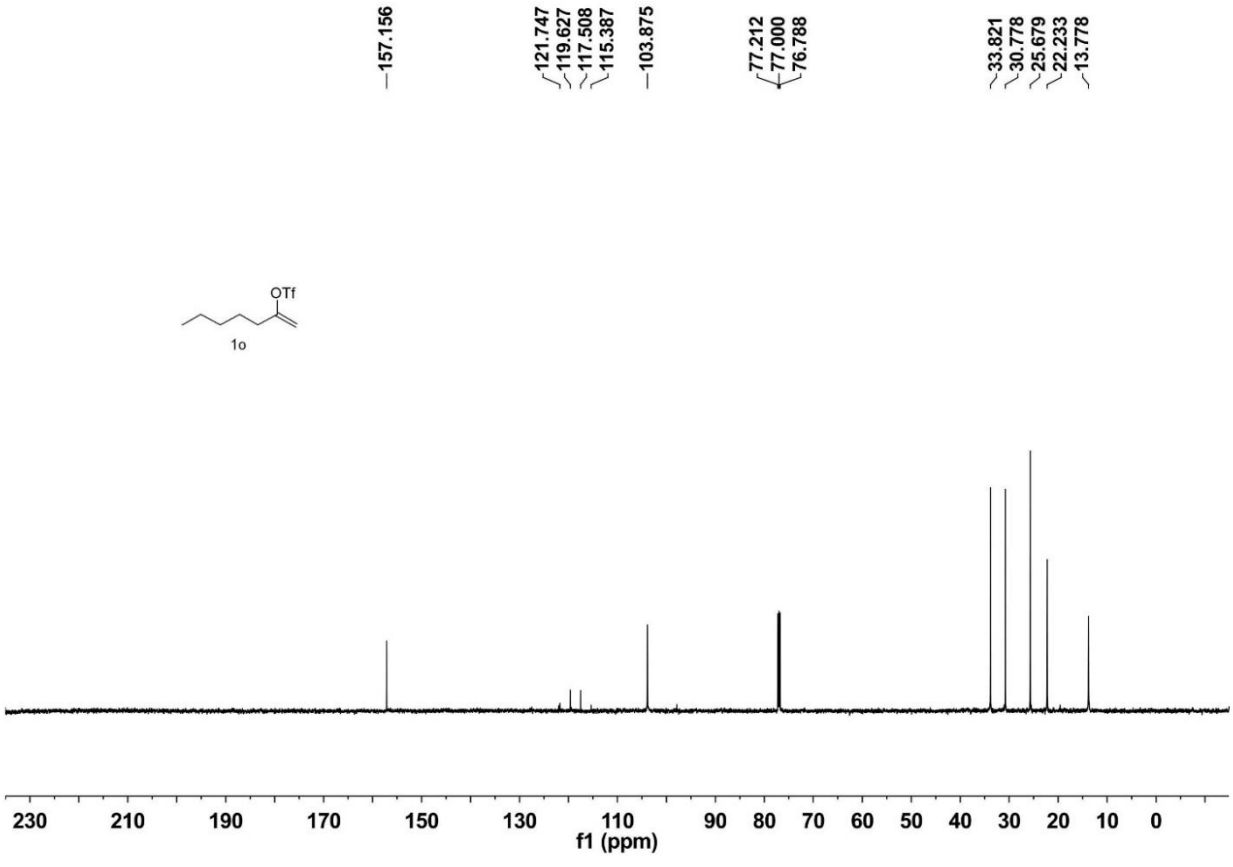


1n; ^{19}F NMR (564MHz, $CDCl_3$)

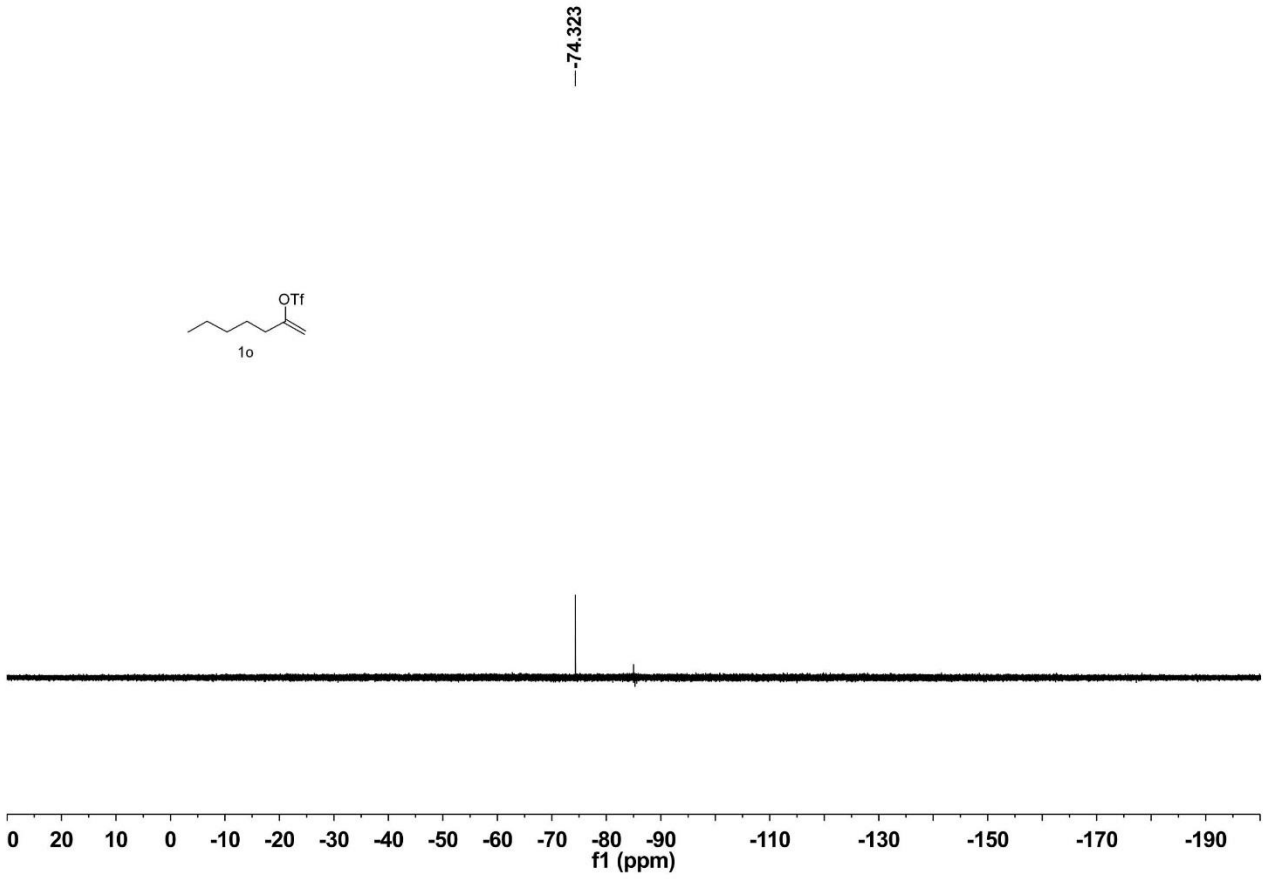


1o; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

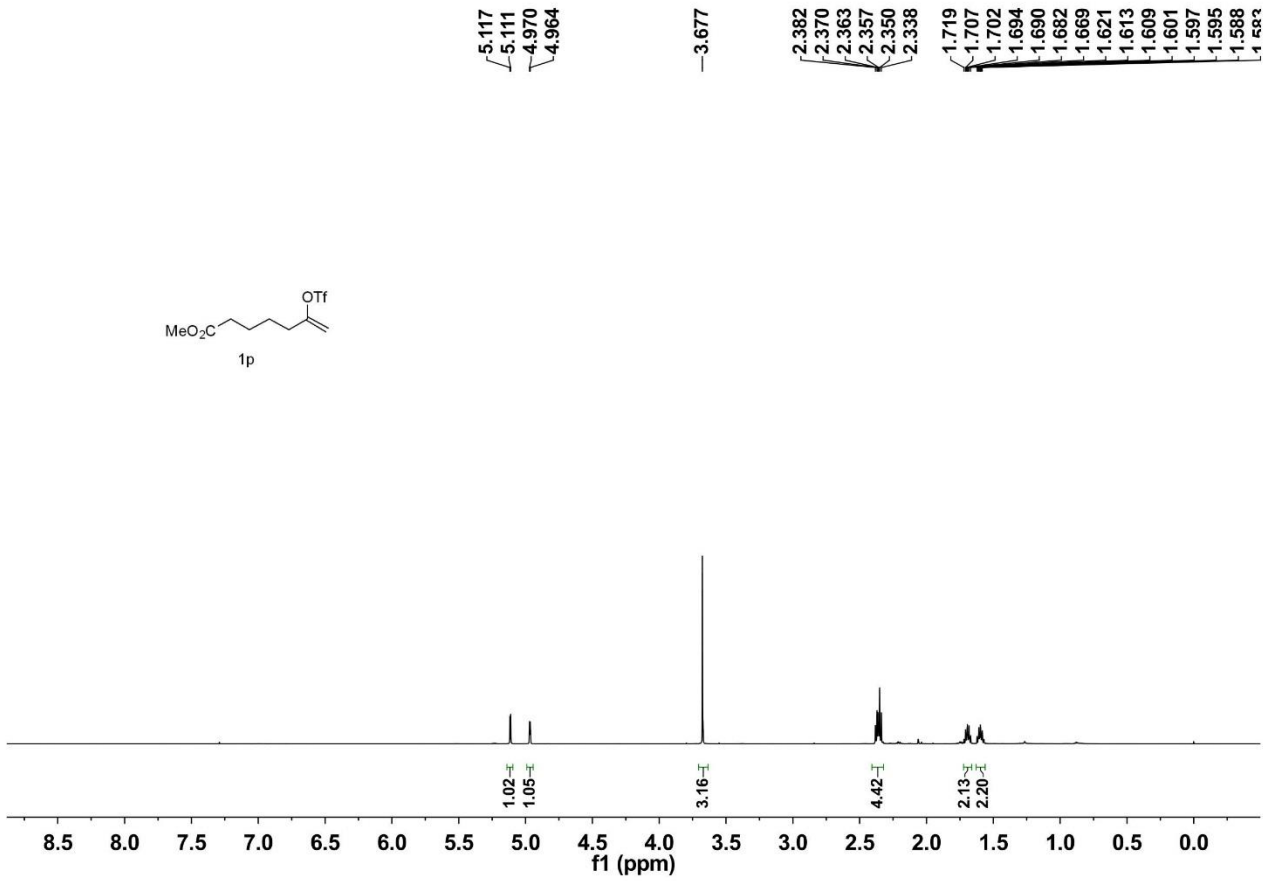


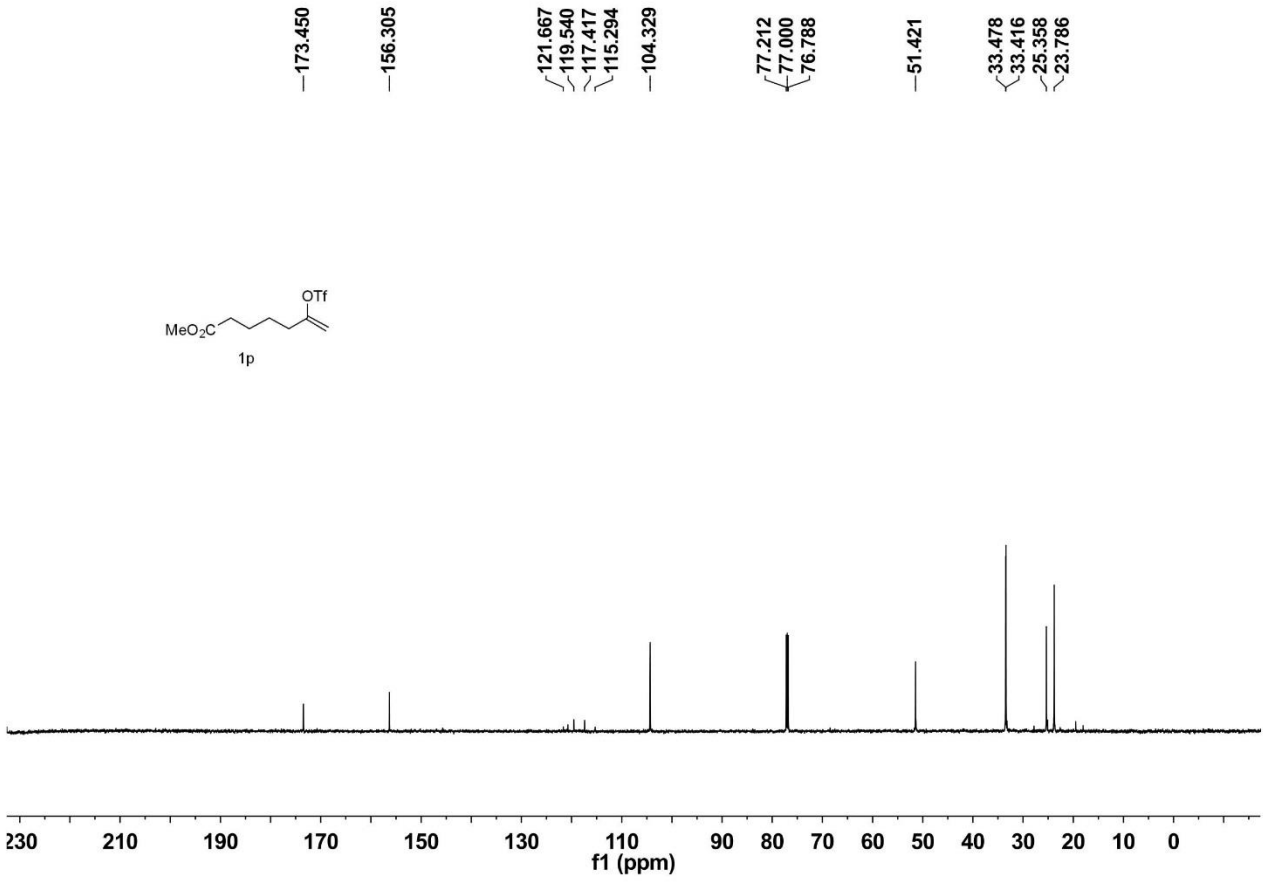


1o; ^{13}F NMR (564MHz, $CDCl_3$)

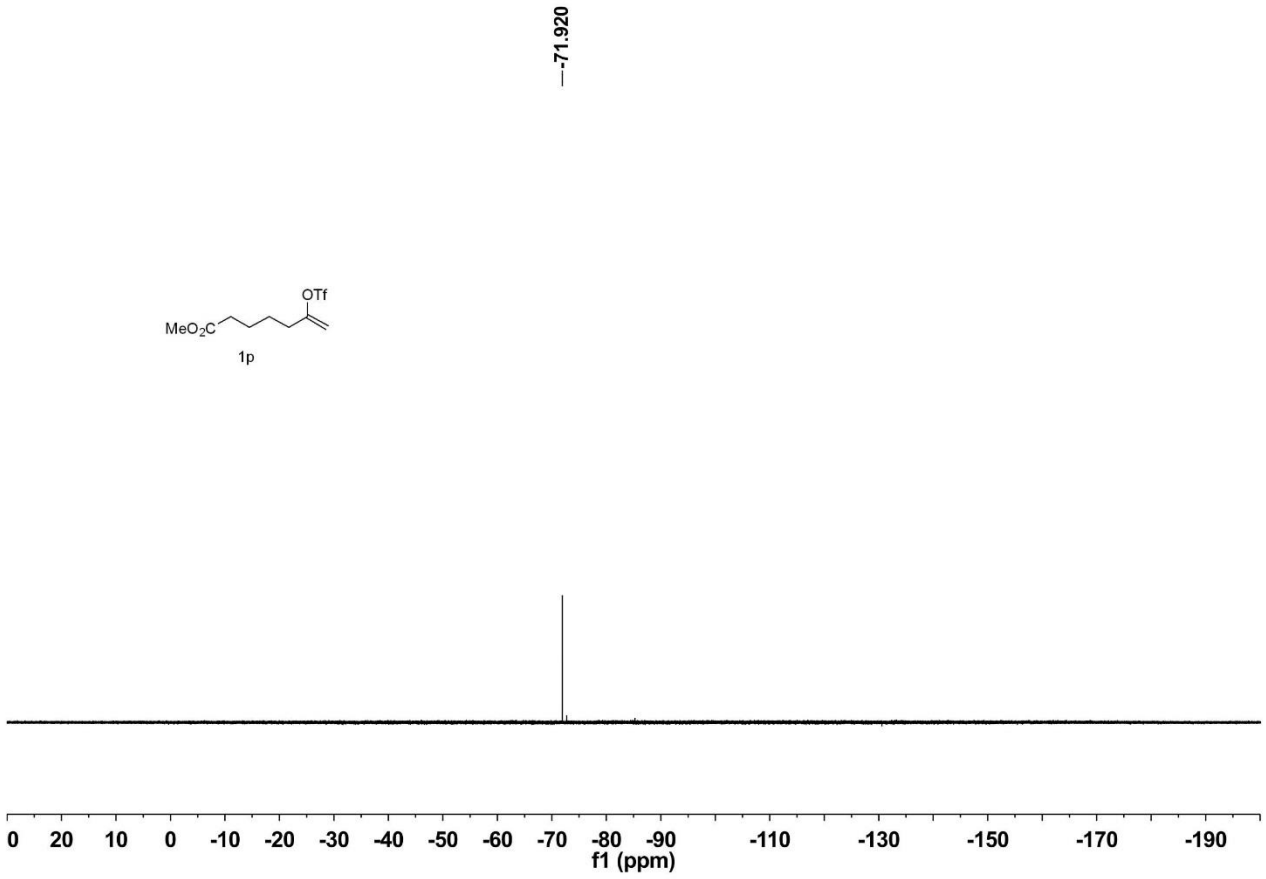


1p; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

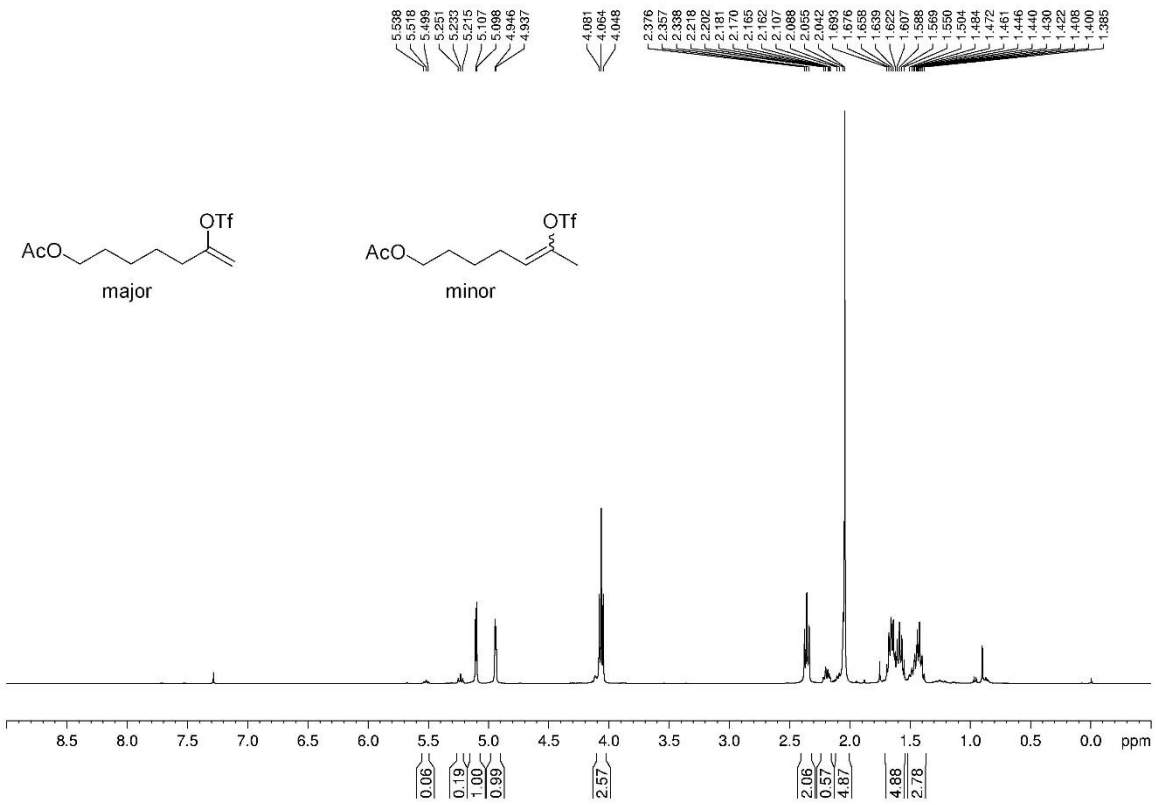


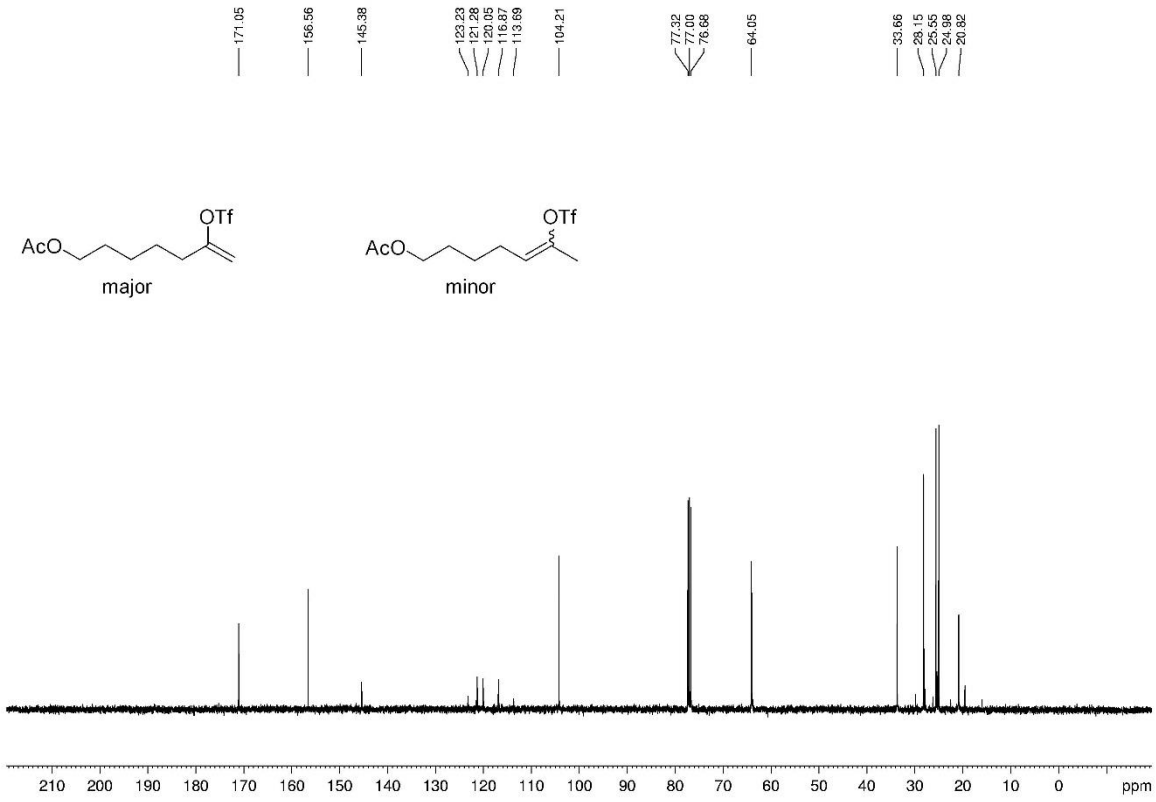


1p; ^{19}F NMR (564MHz, $CDCl_3$)

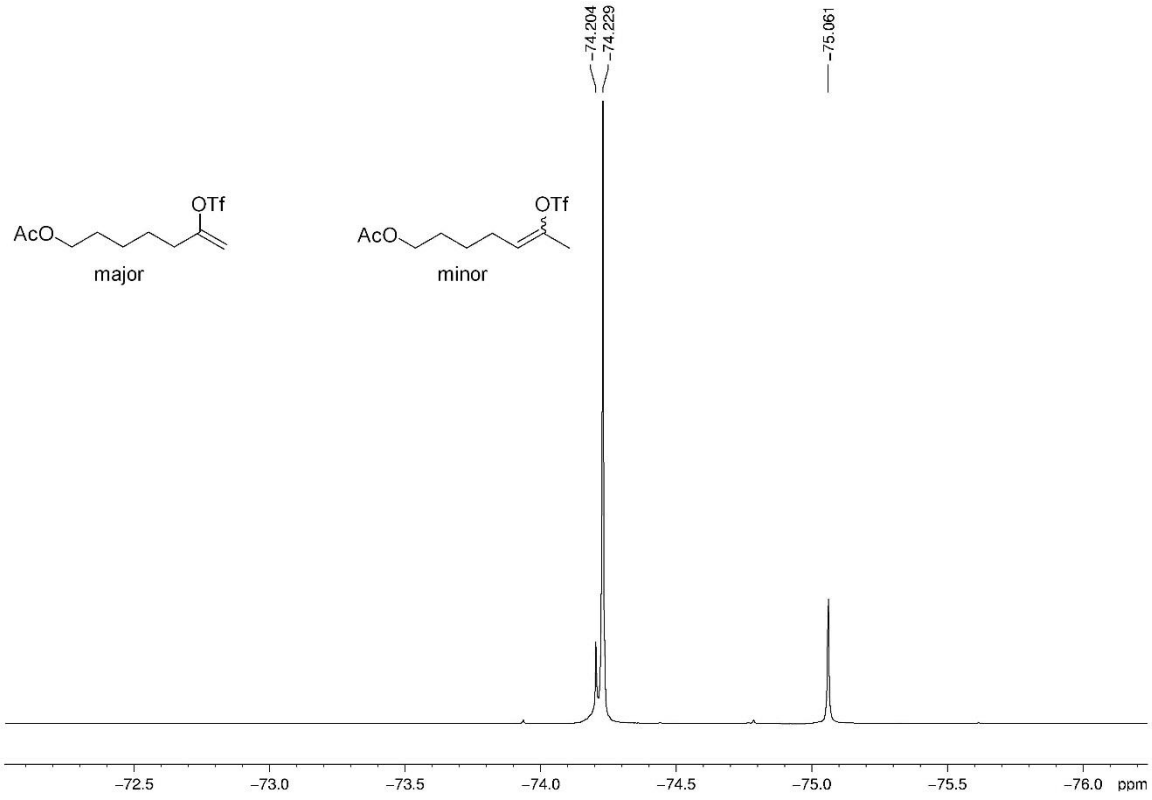


1q; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

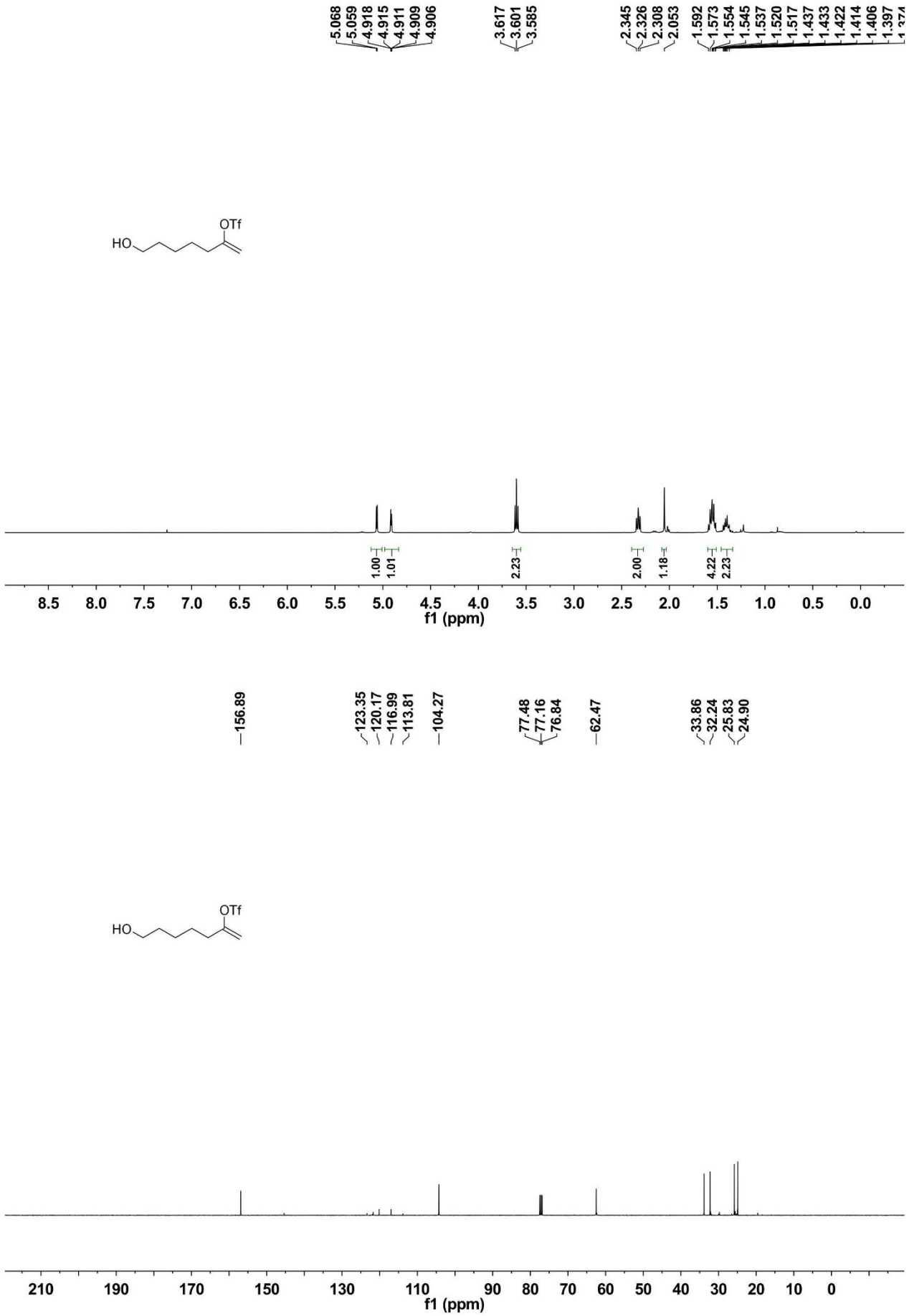




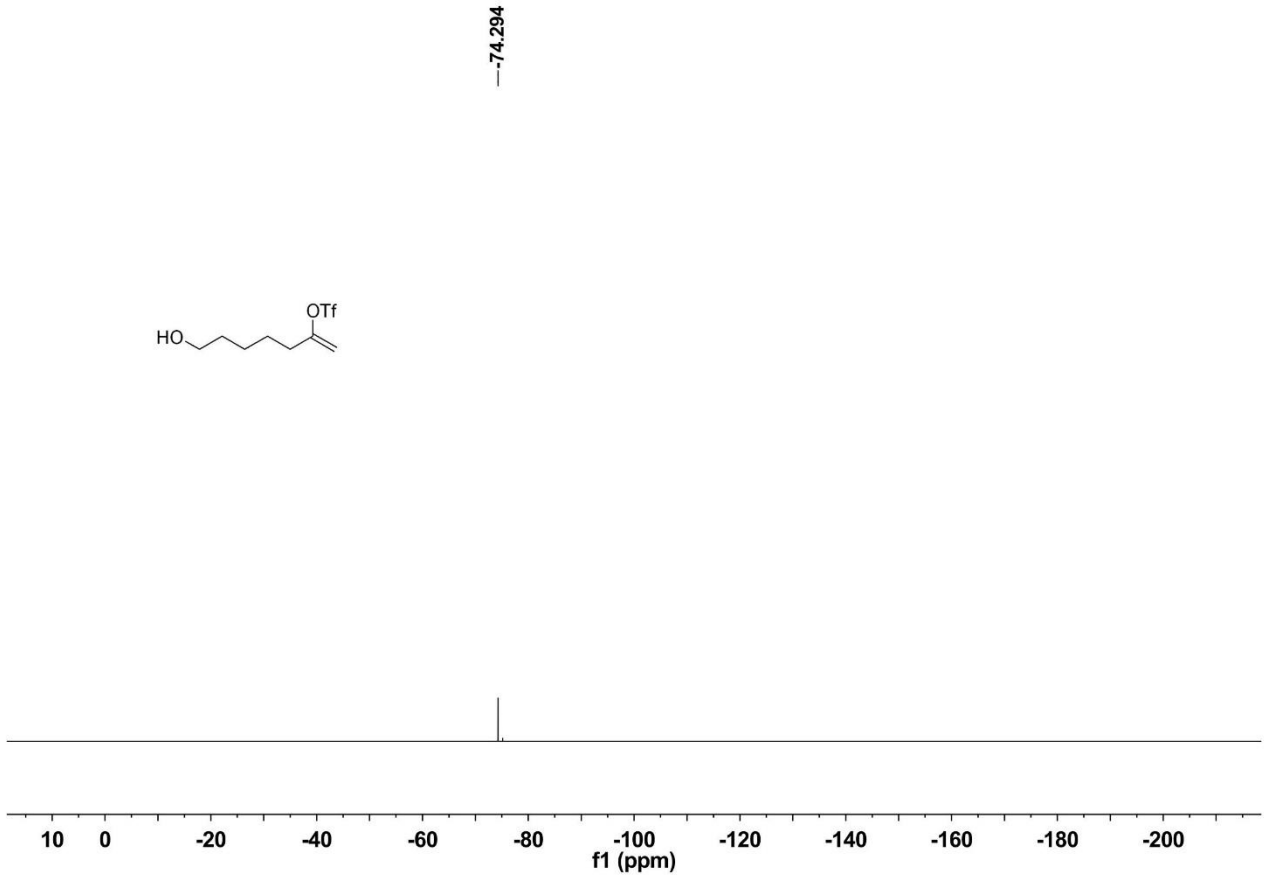
1q; ^{18}F NMR (376MHz, $CDCl_3$)



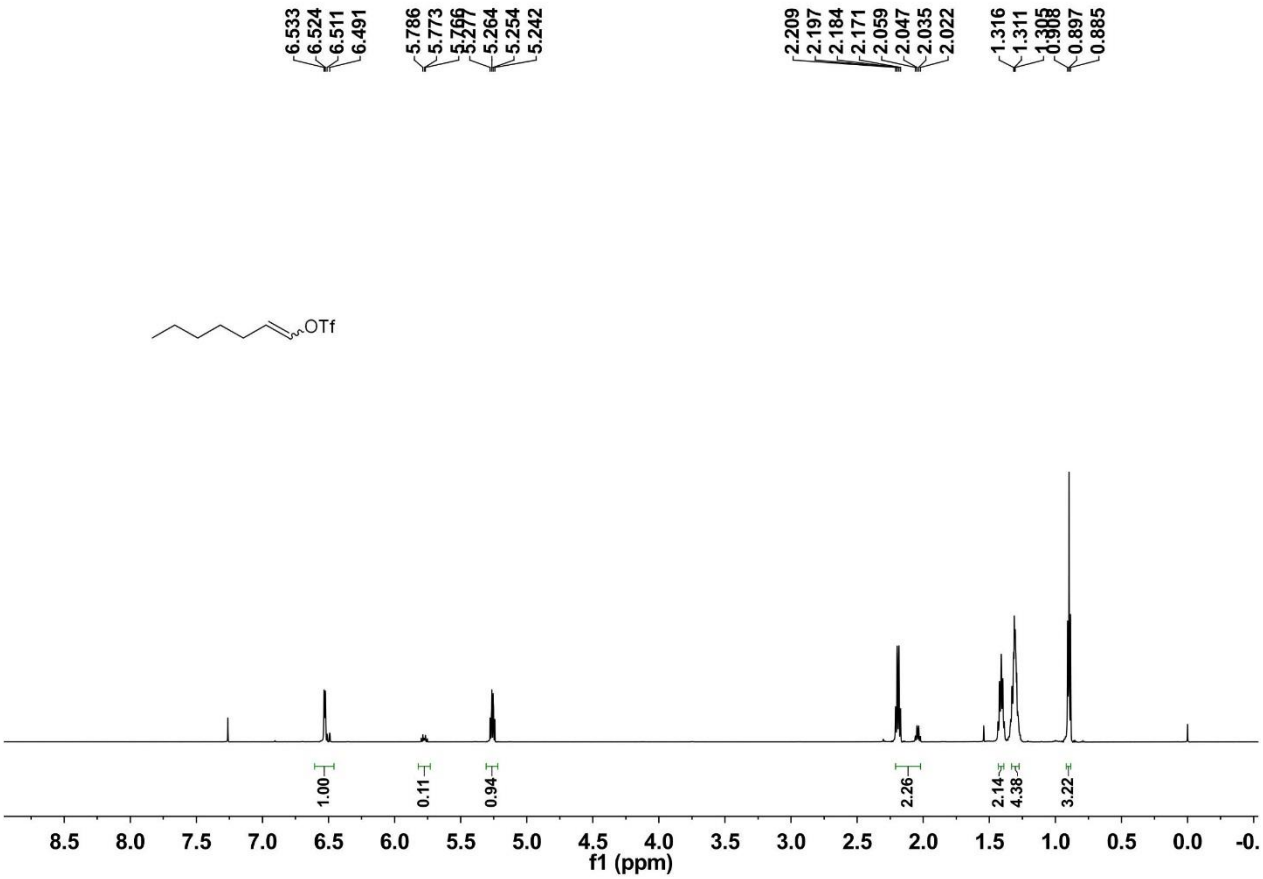
1r; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

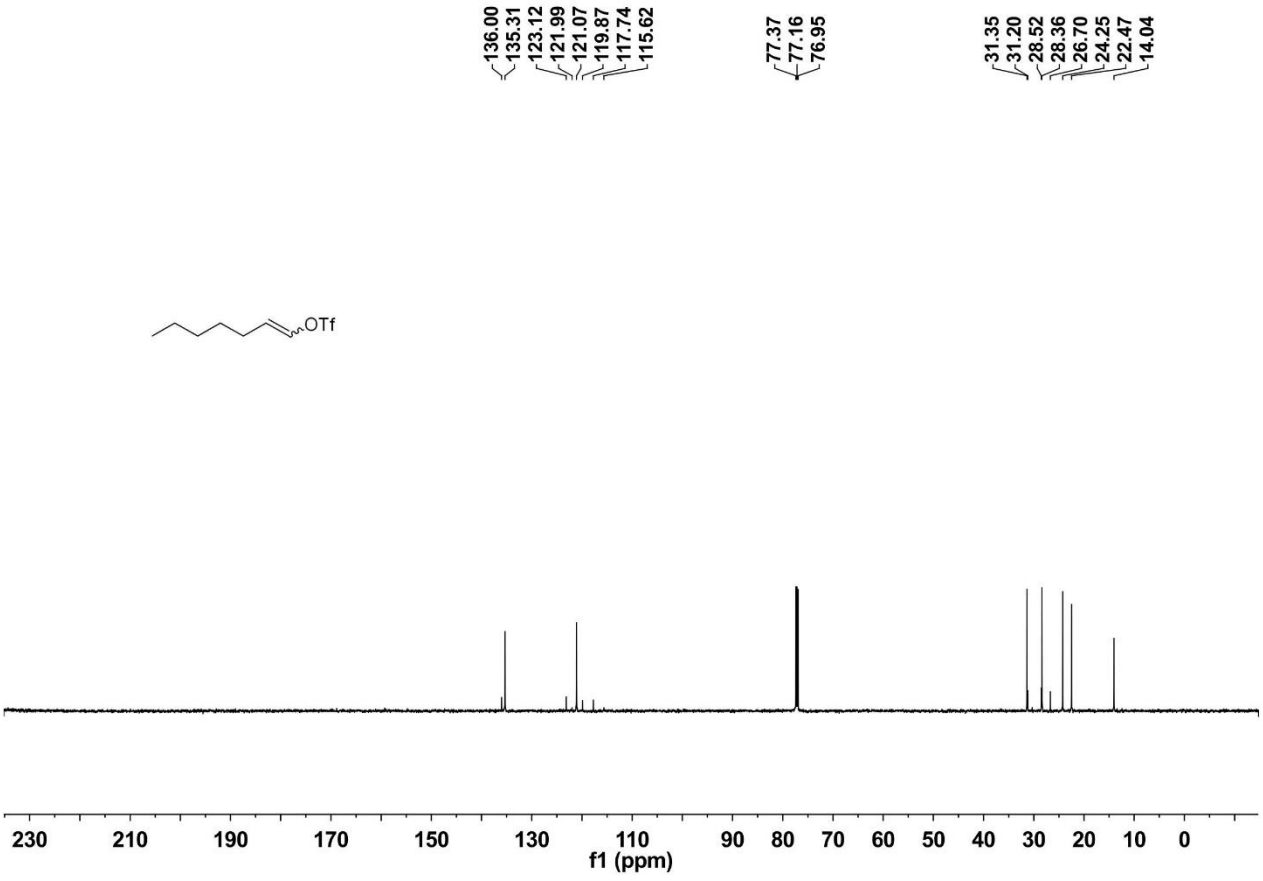


1r; ^{13}F NMR (376MHz, $CDCl_3$)

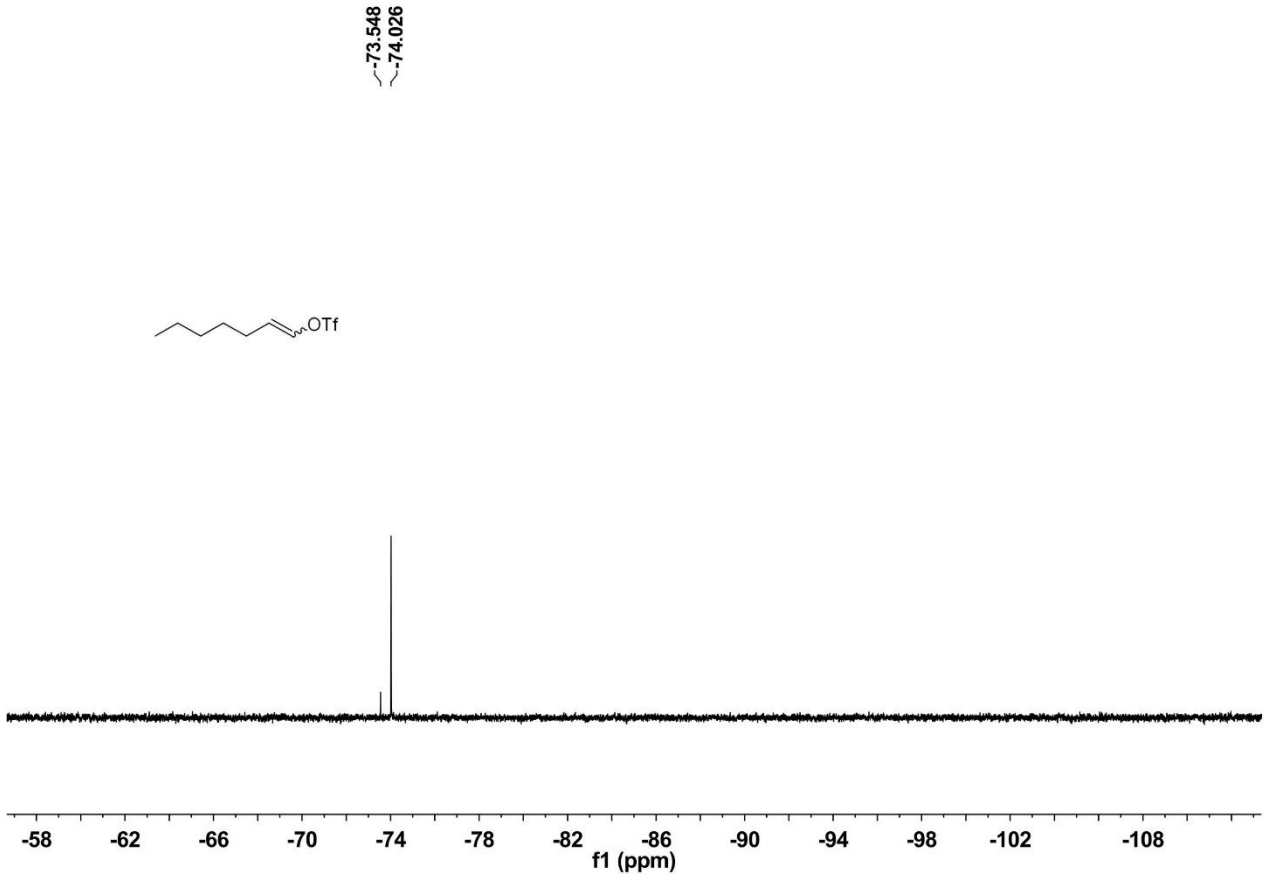


1s; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

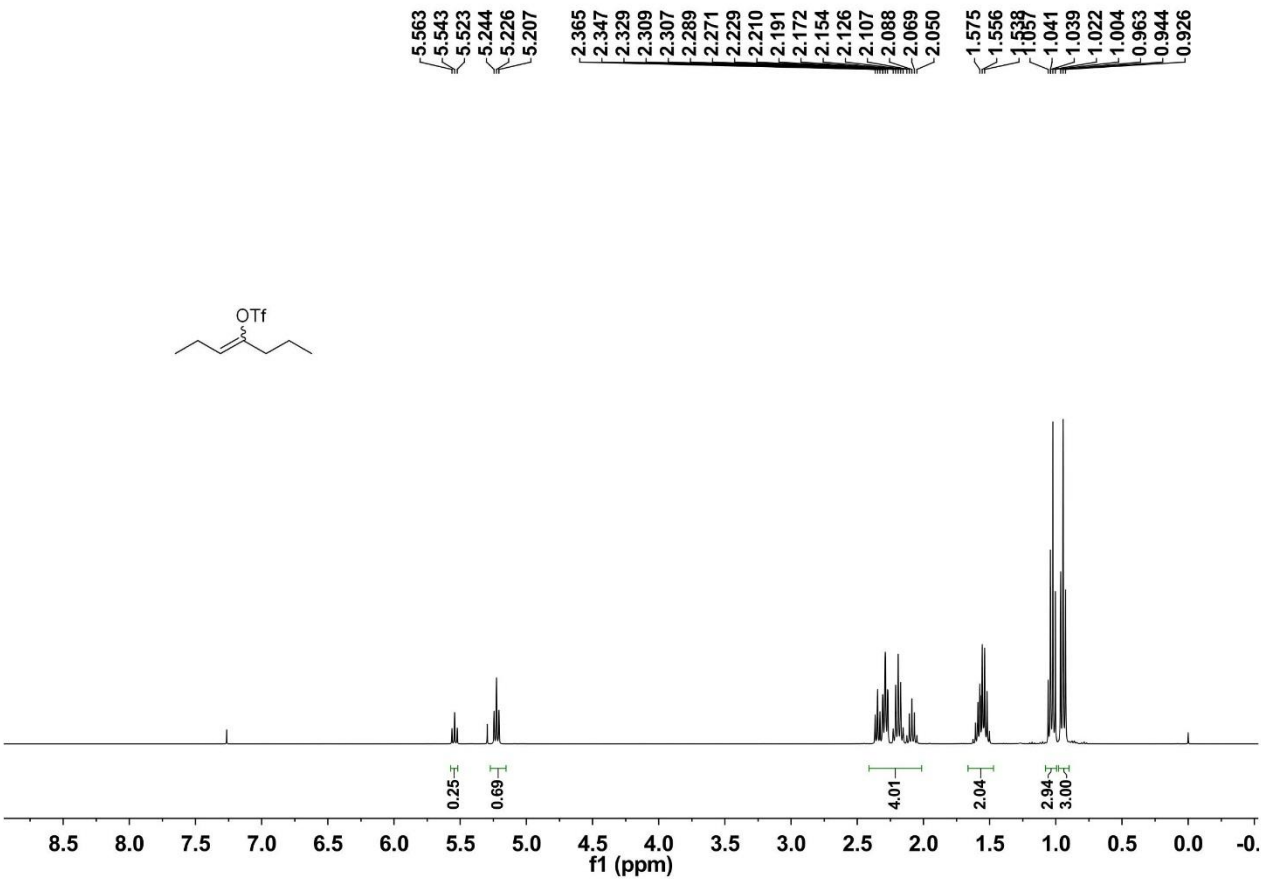


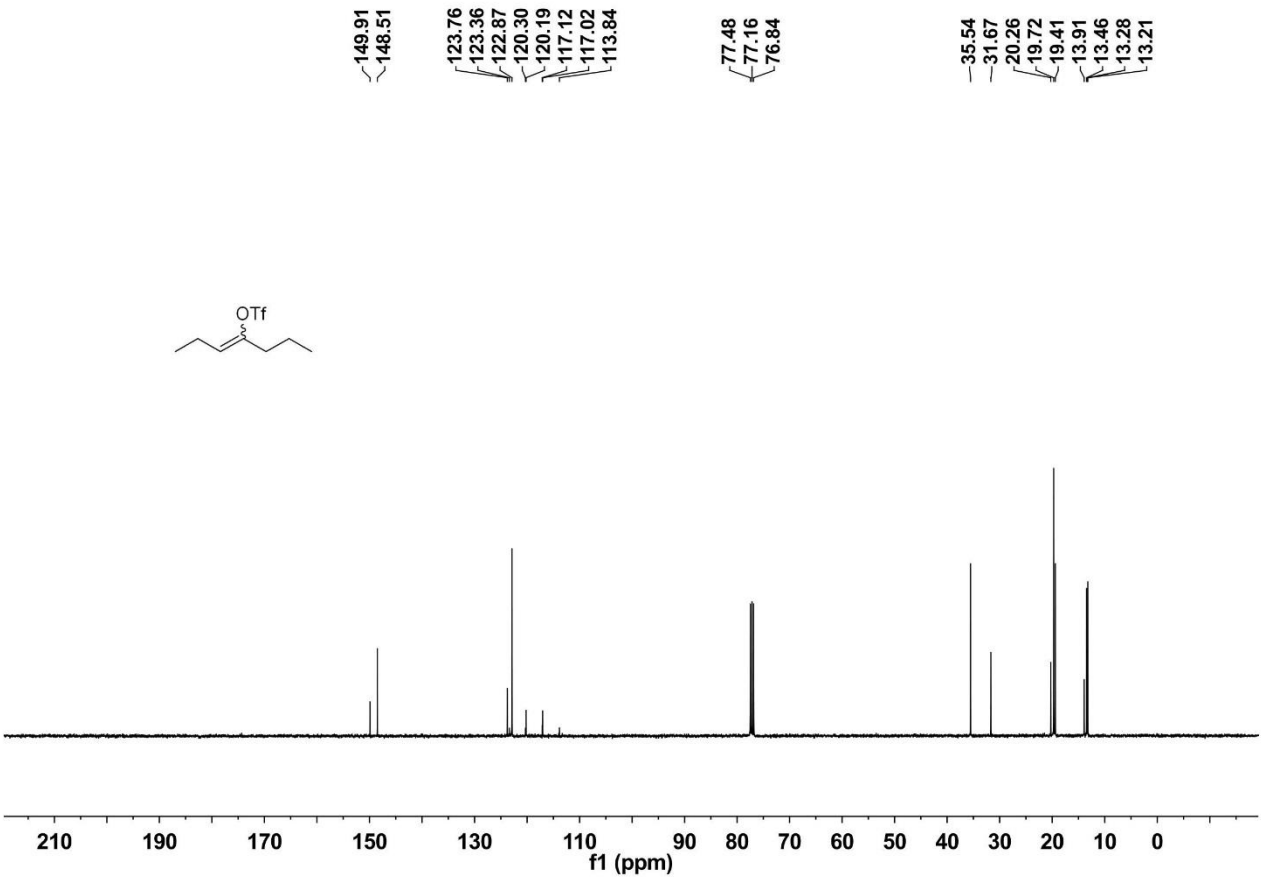


1s; ^{13}F NMR (564MHz, $CDCl_3$)

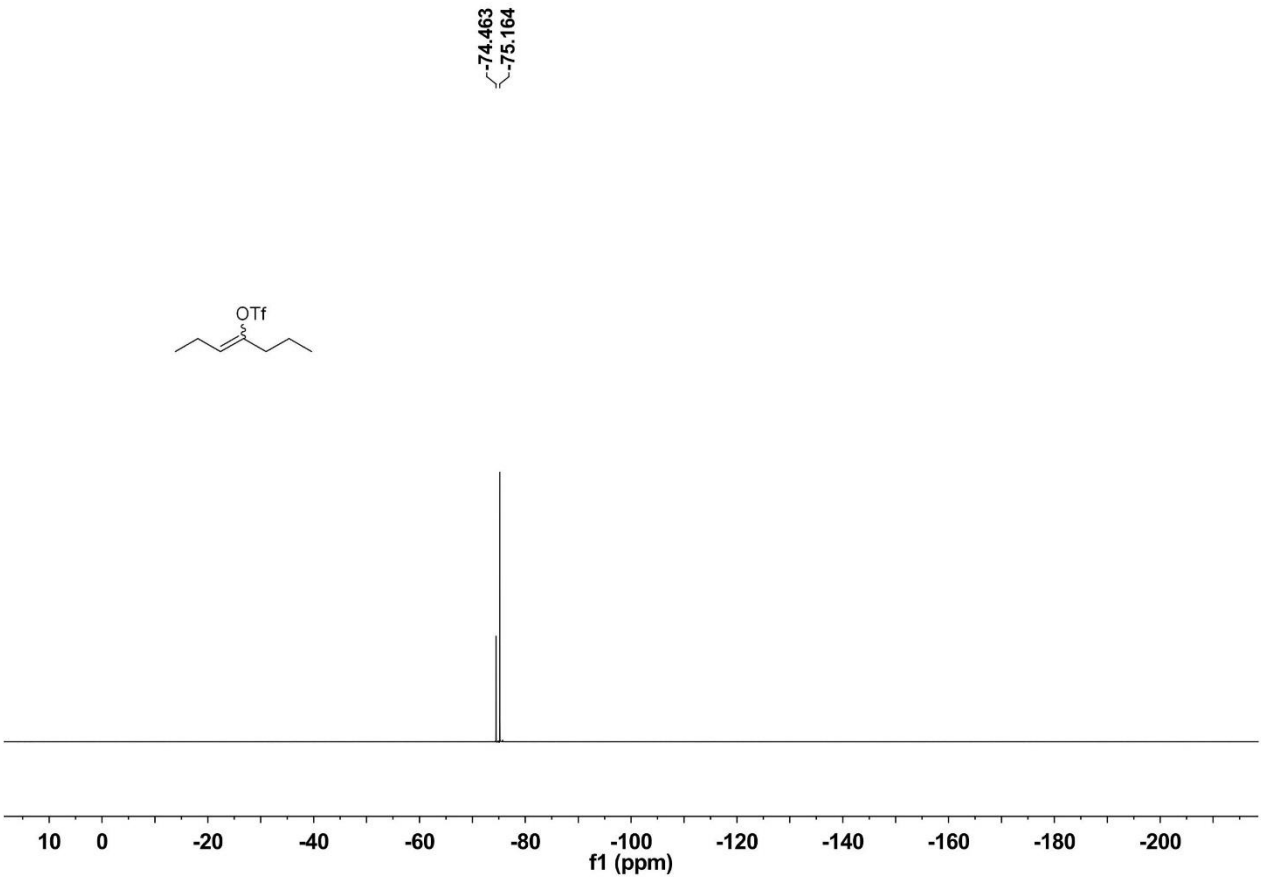


1t; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

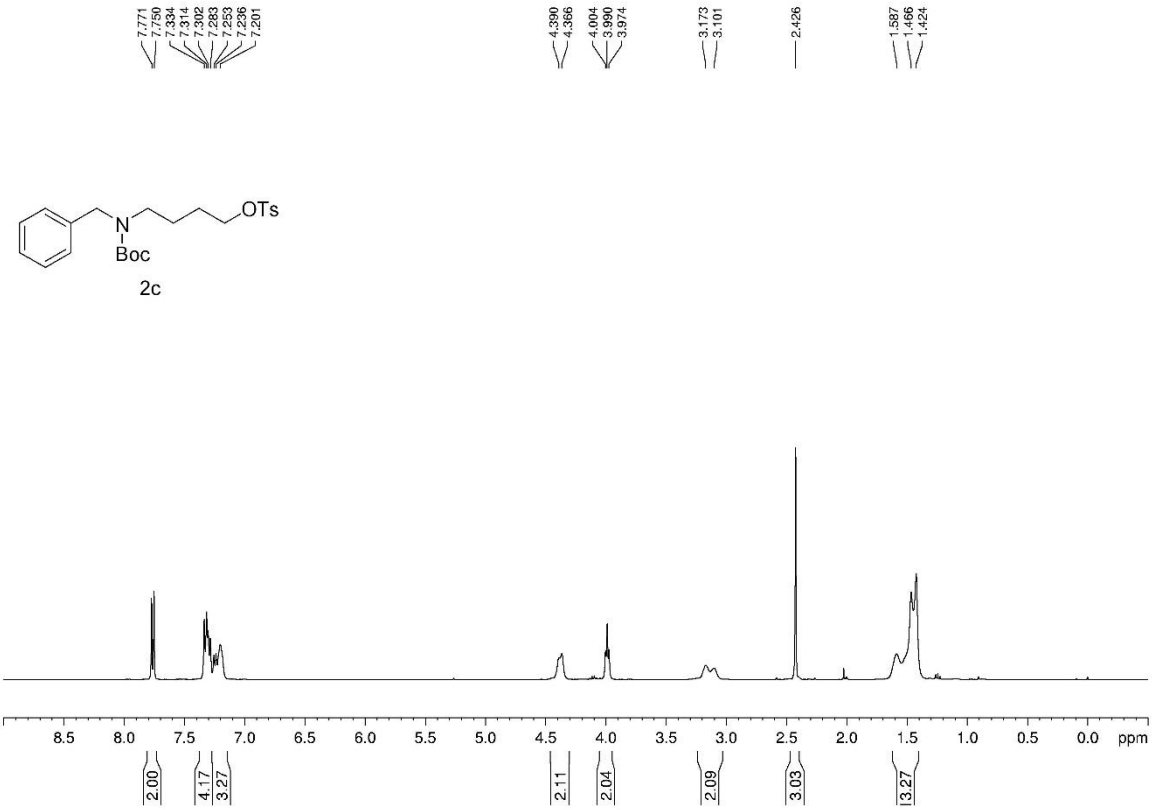


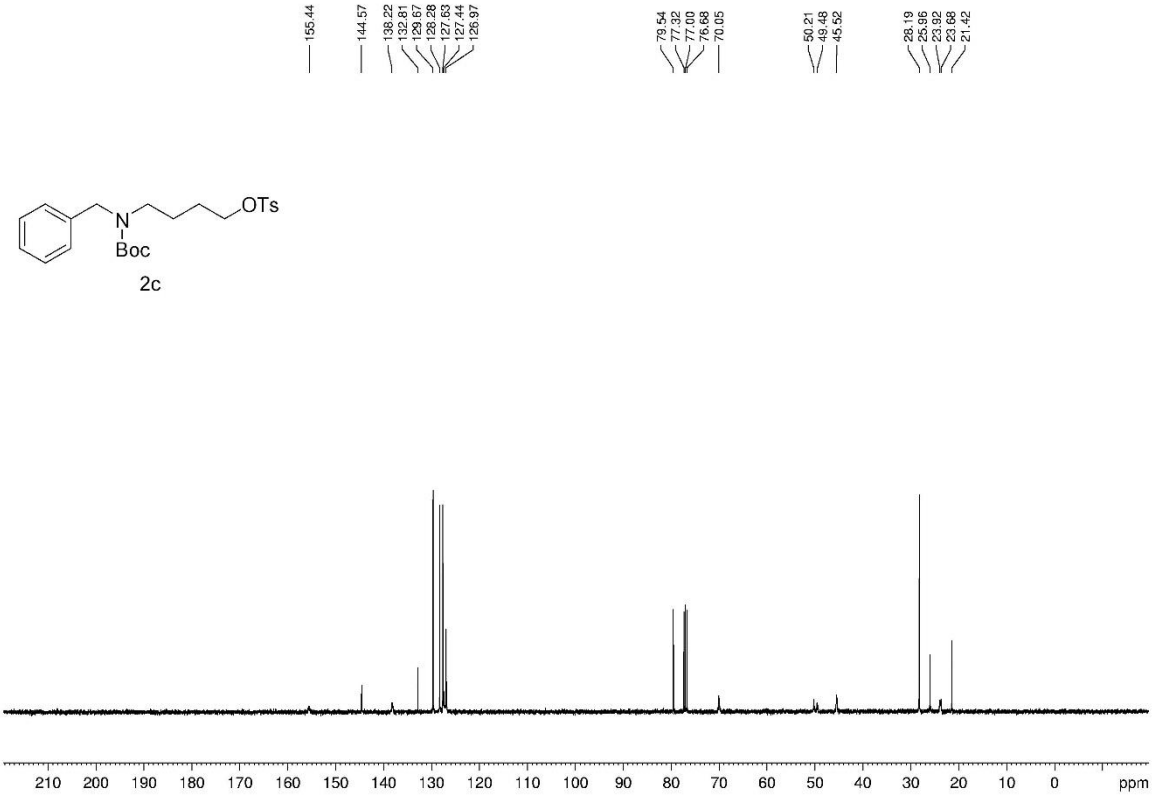


1t; ^{13}F NMR (376MHz, $CDCl_3$)

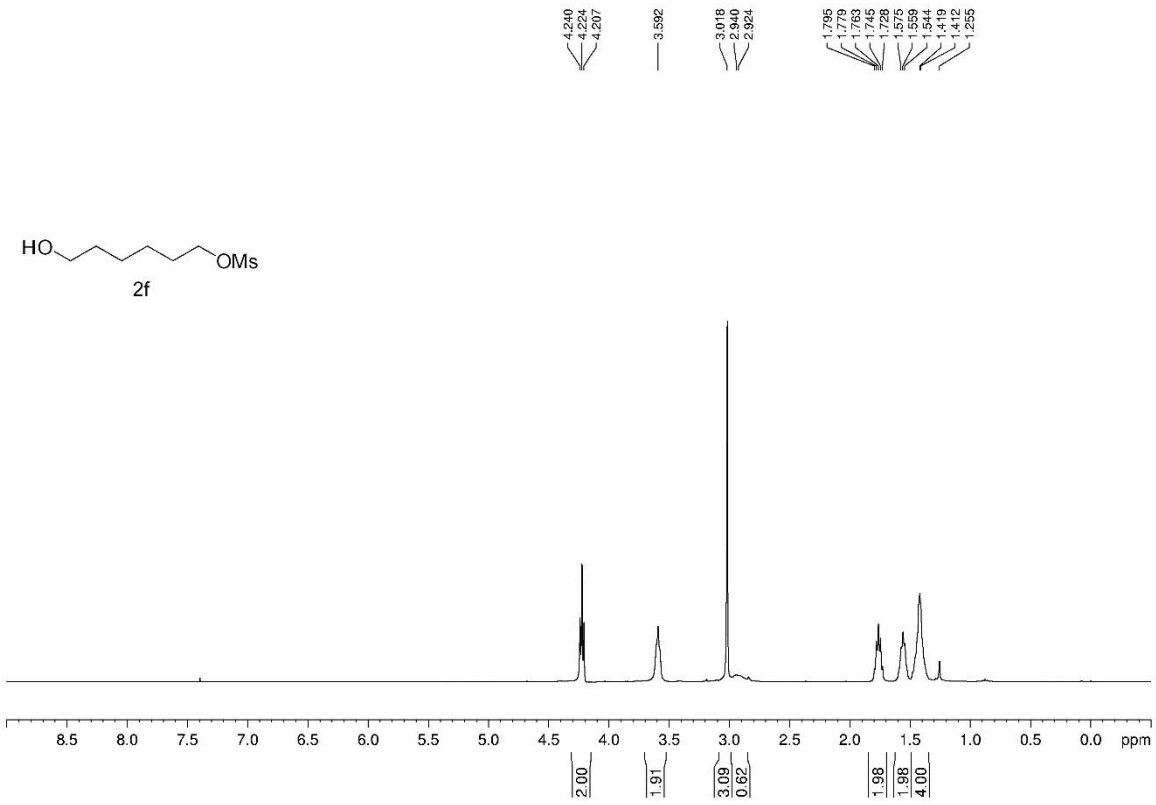


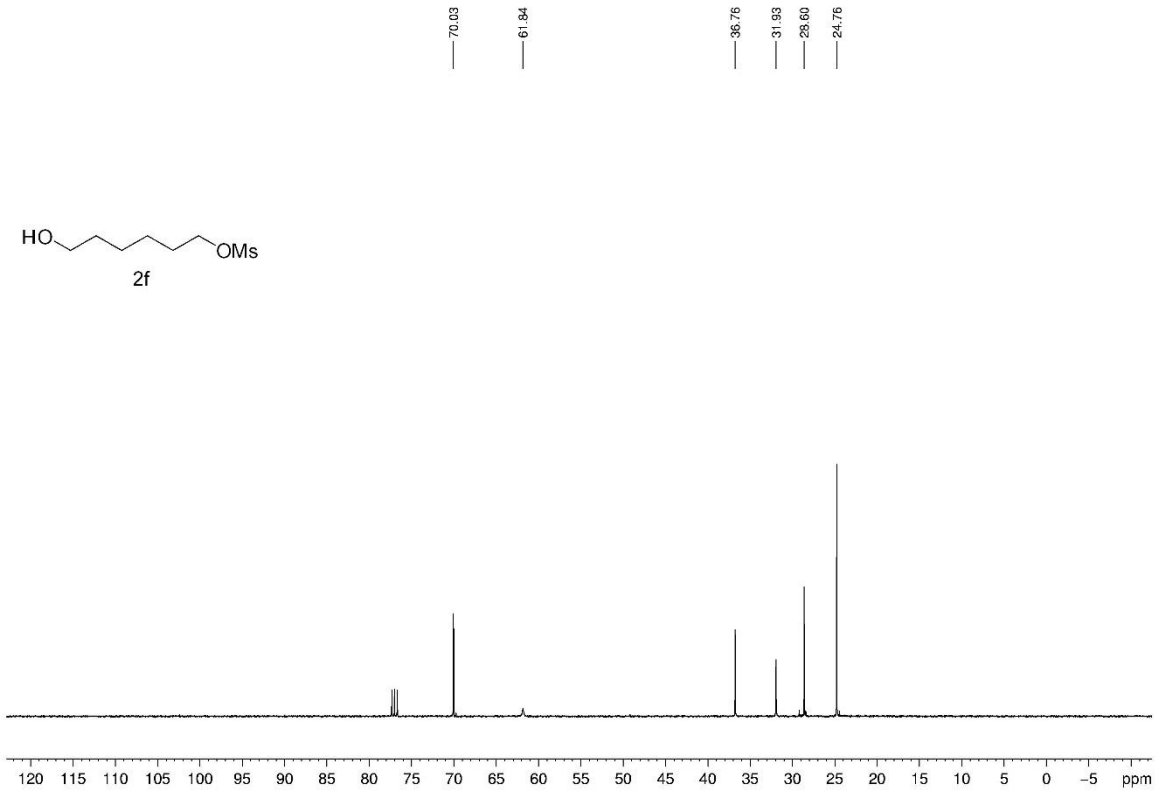
2c; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



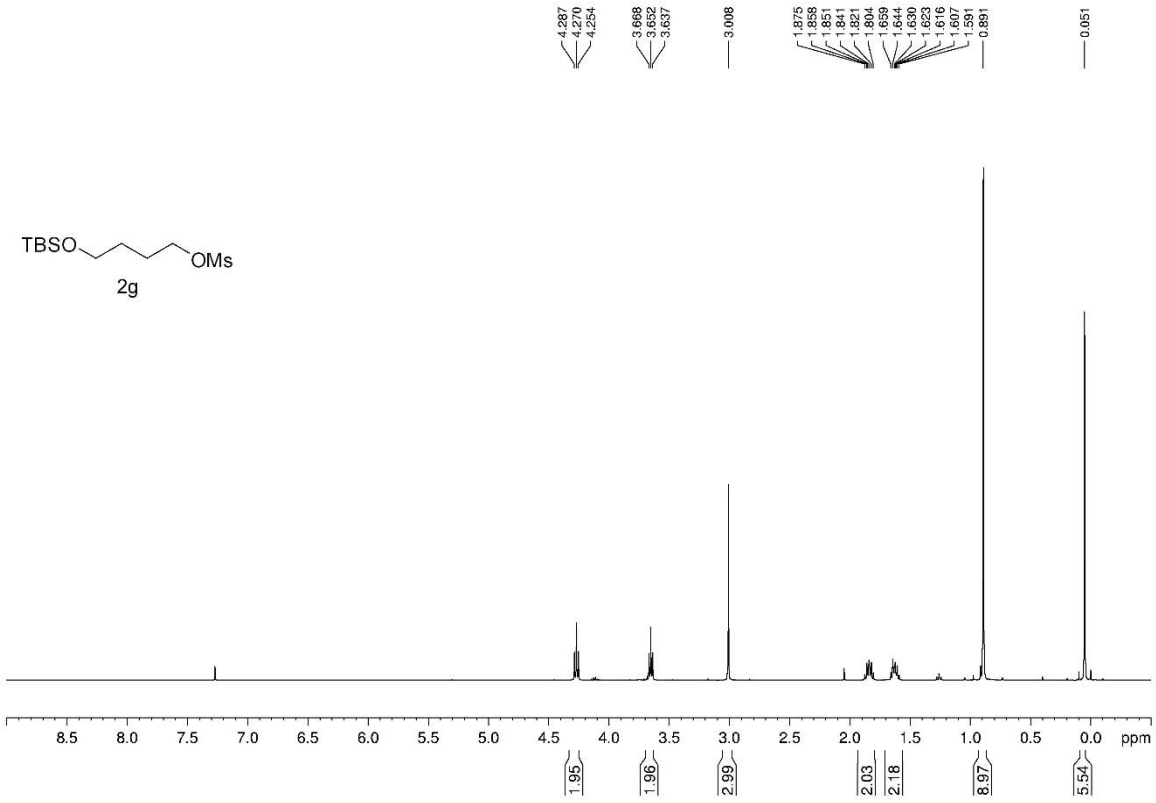


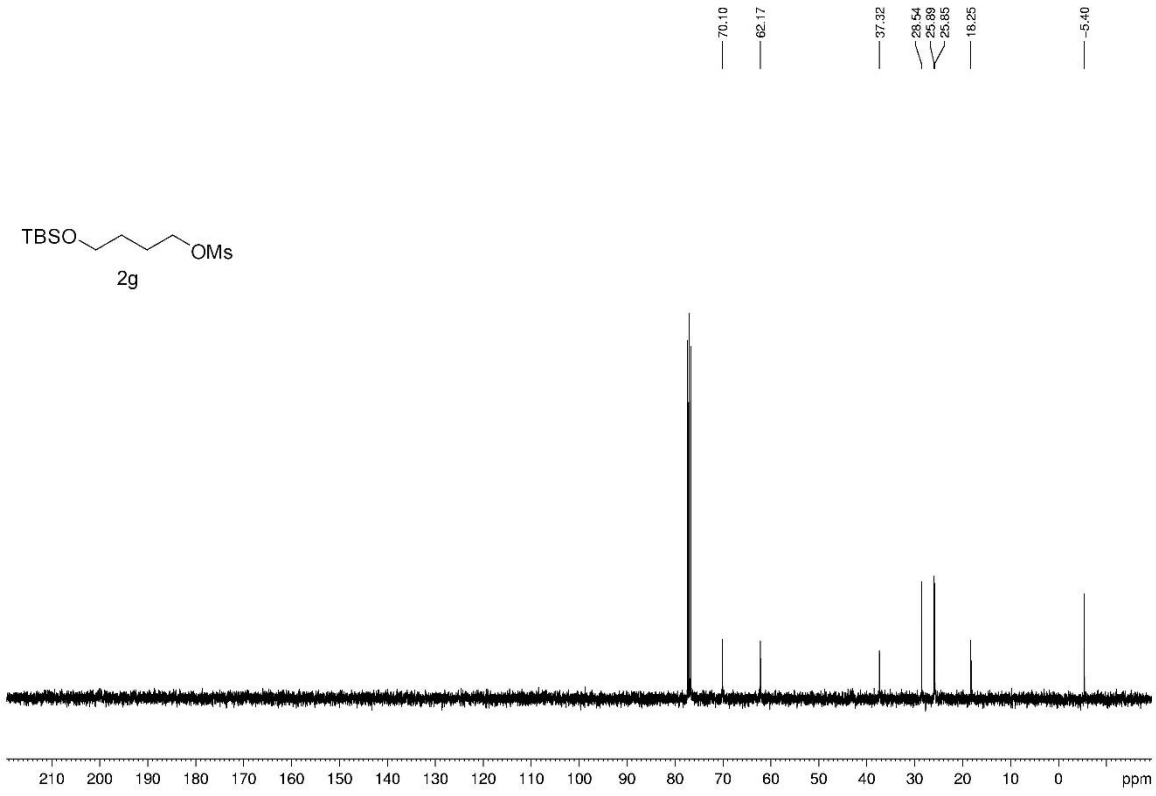
2f; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



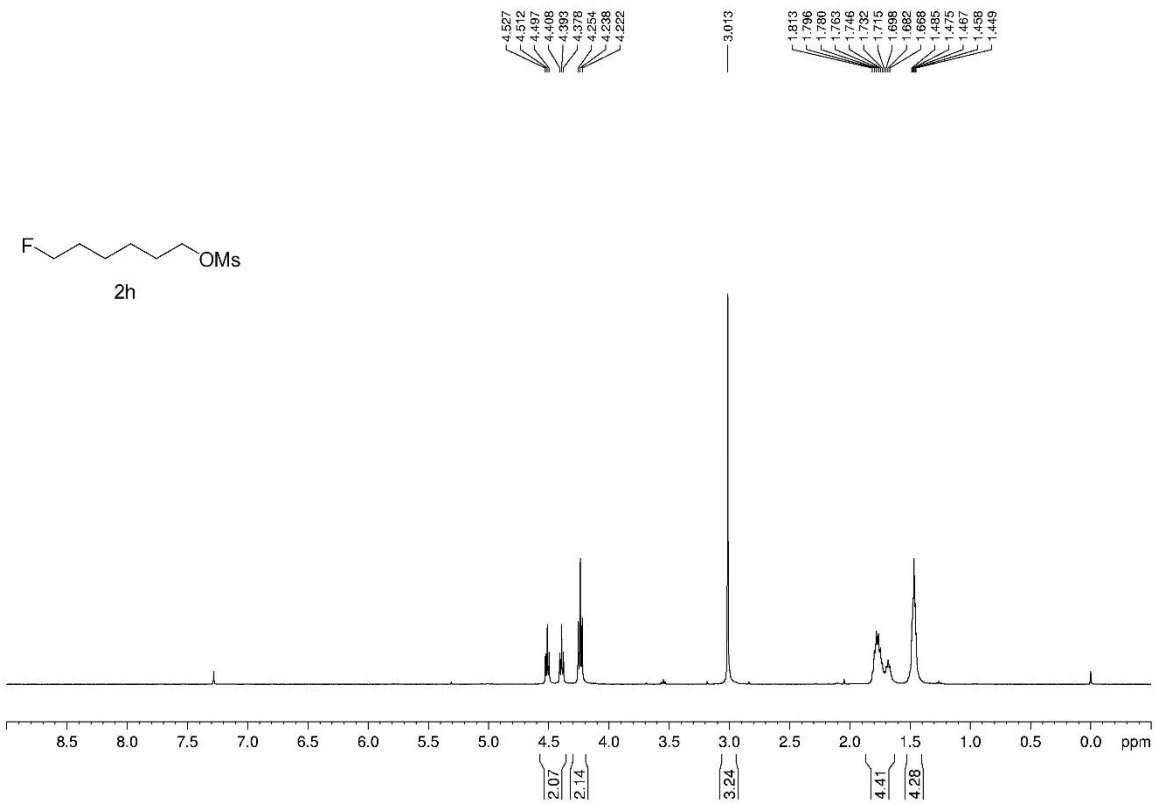


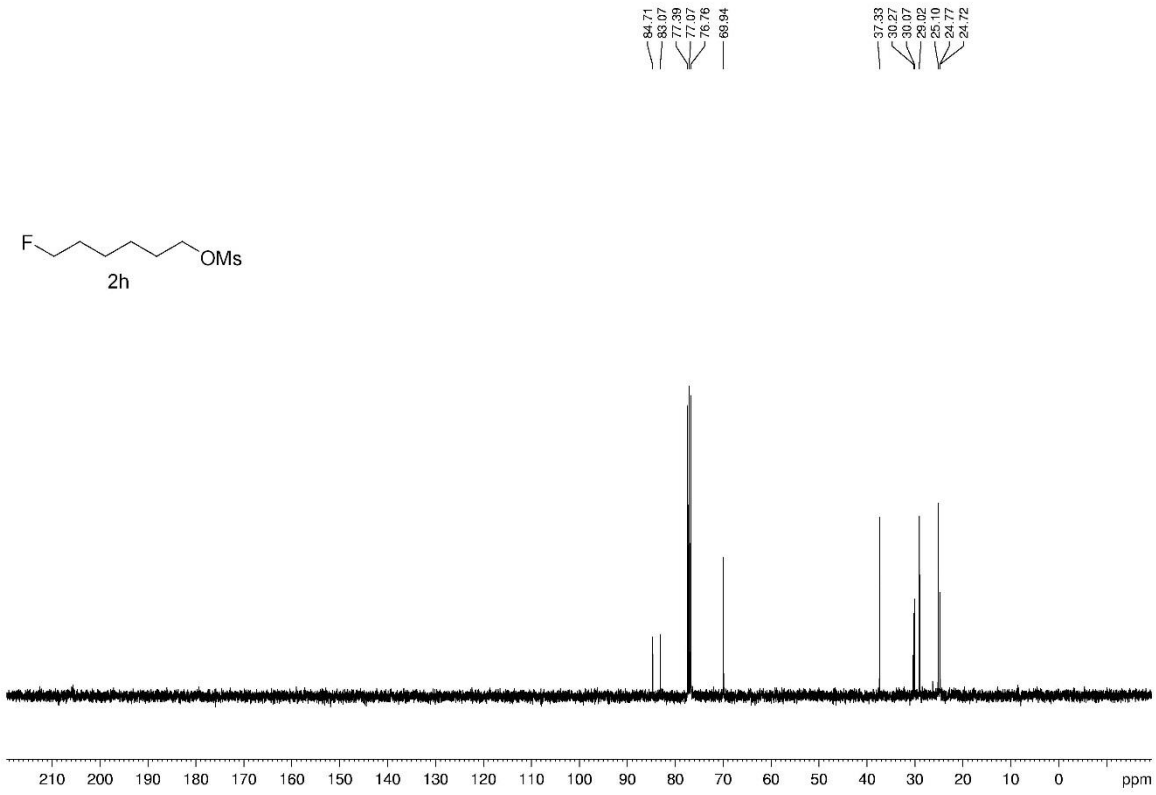
2g; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



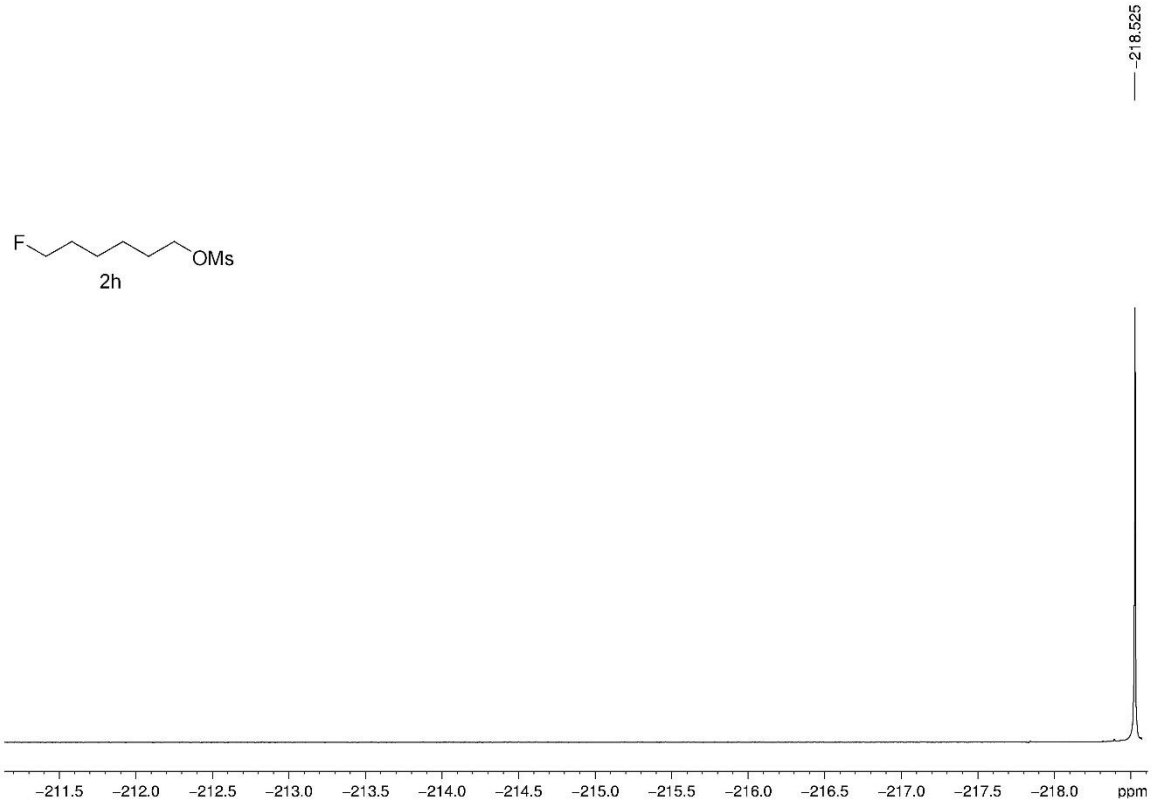


2h; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

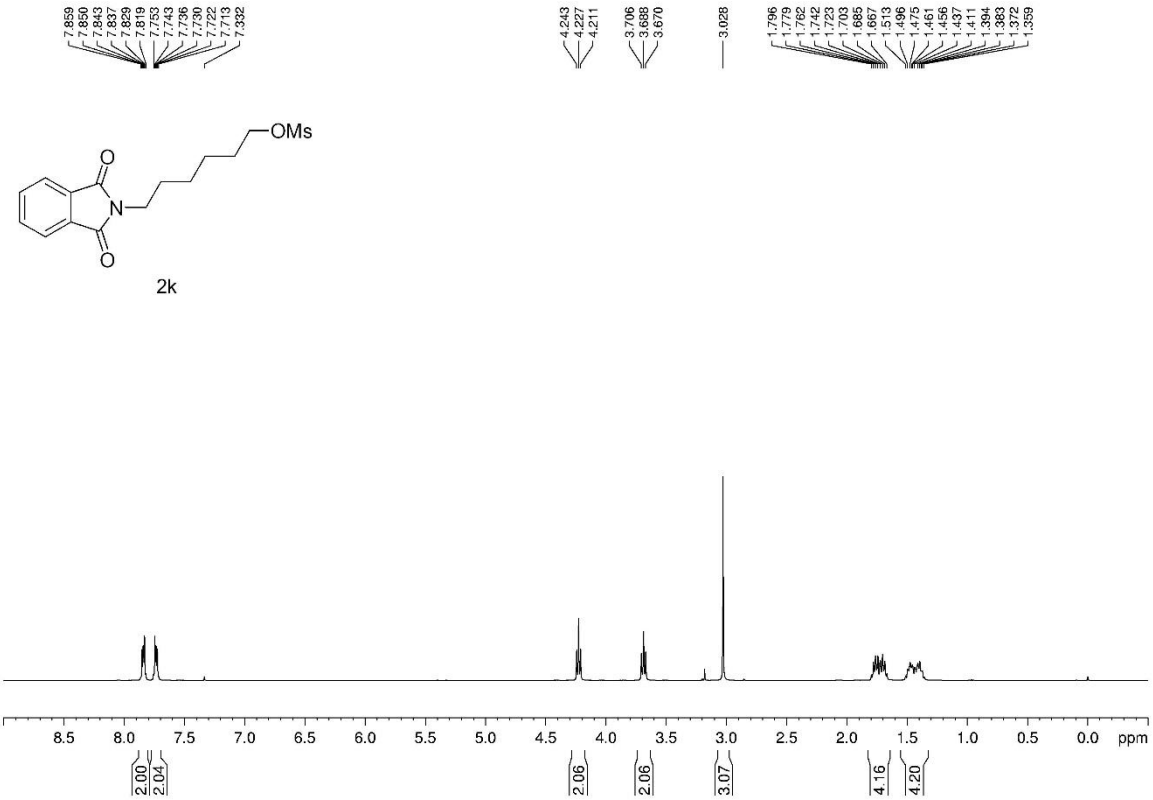


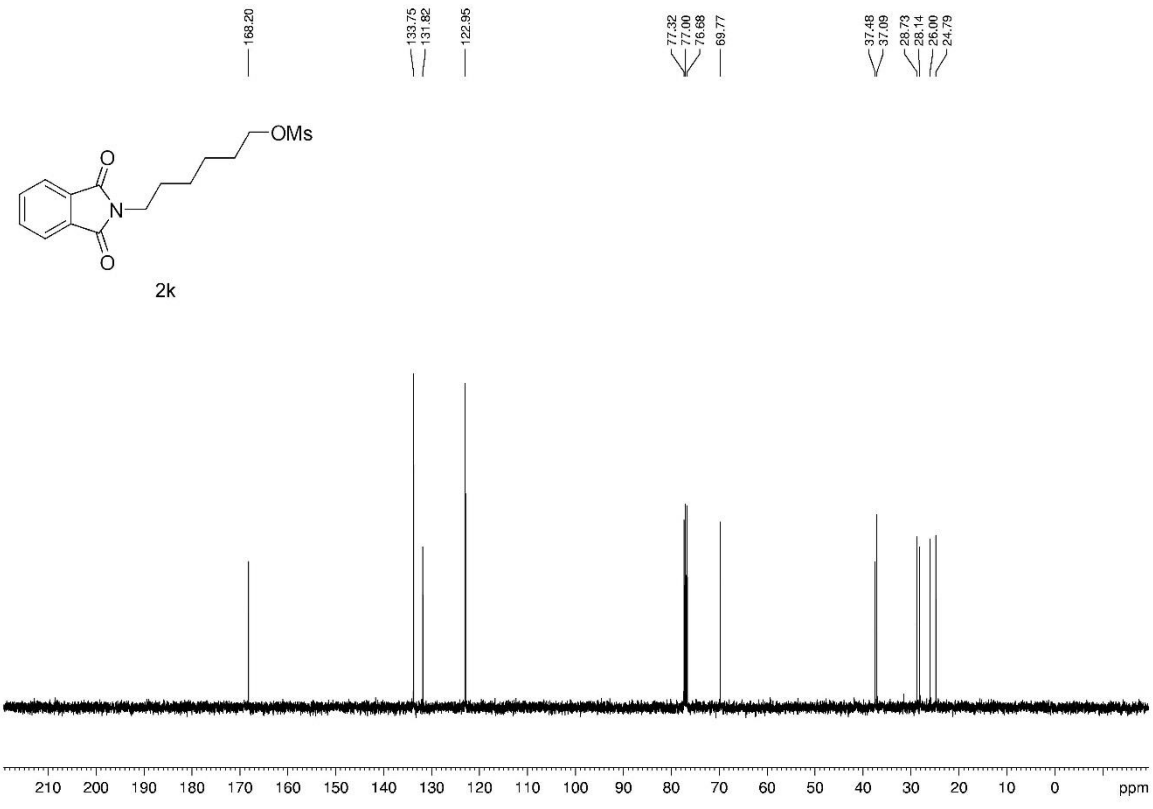


2h; ^{13}F NMR (376MHz, $CDCl_3$)

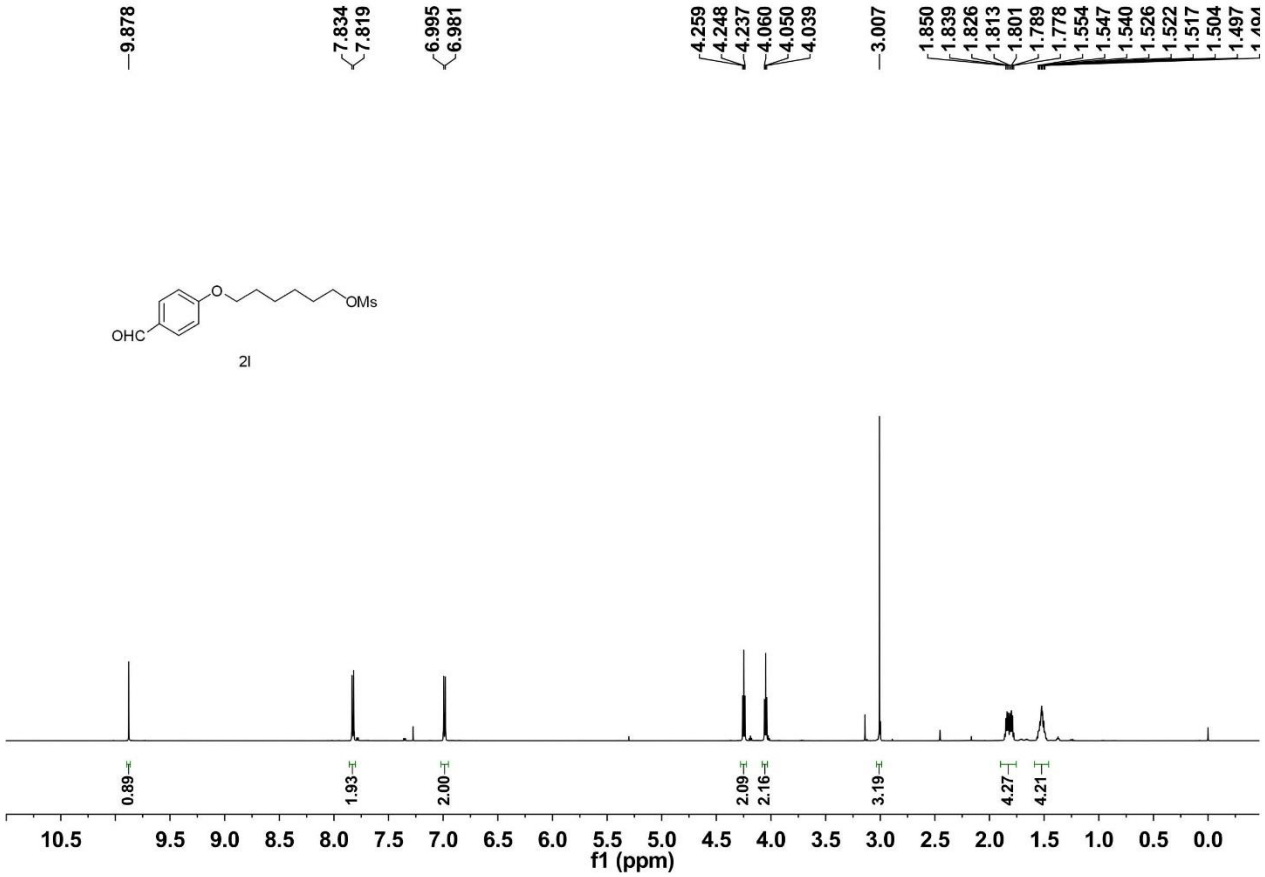


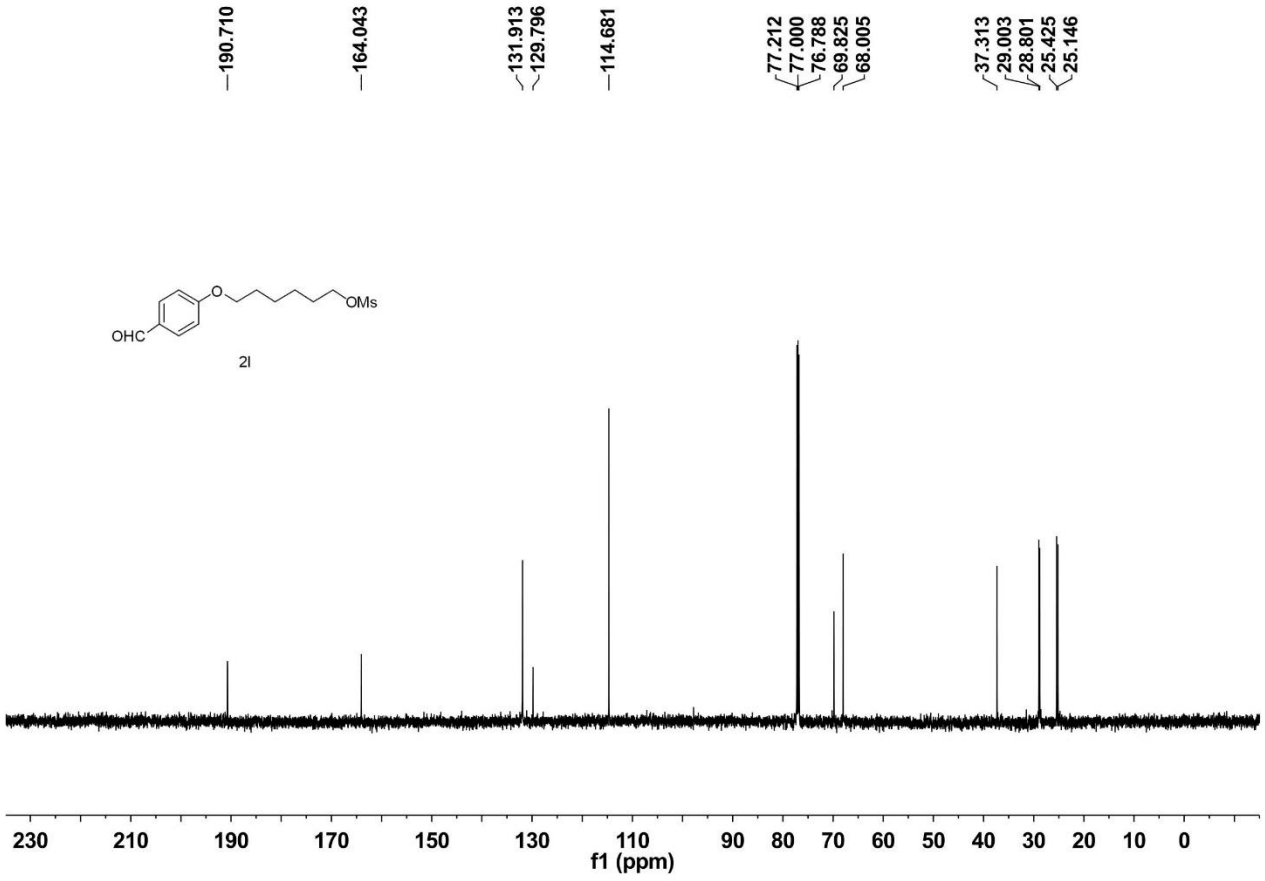
2k; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



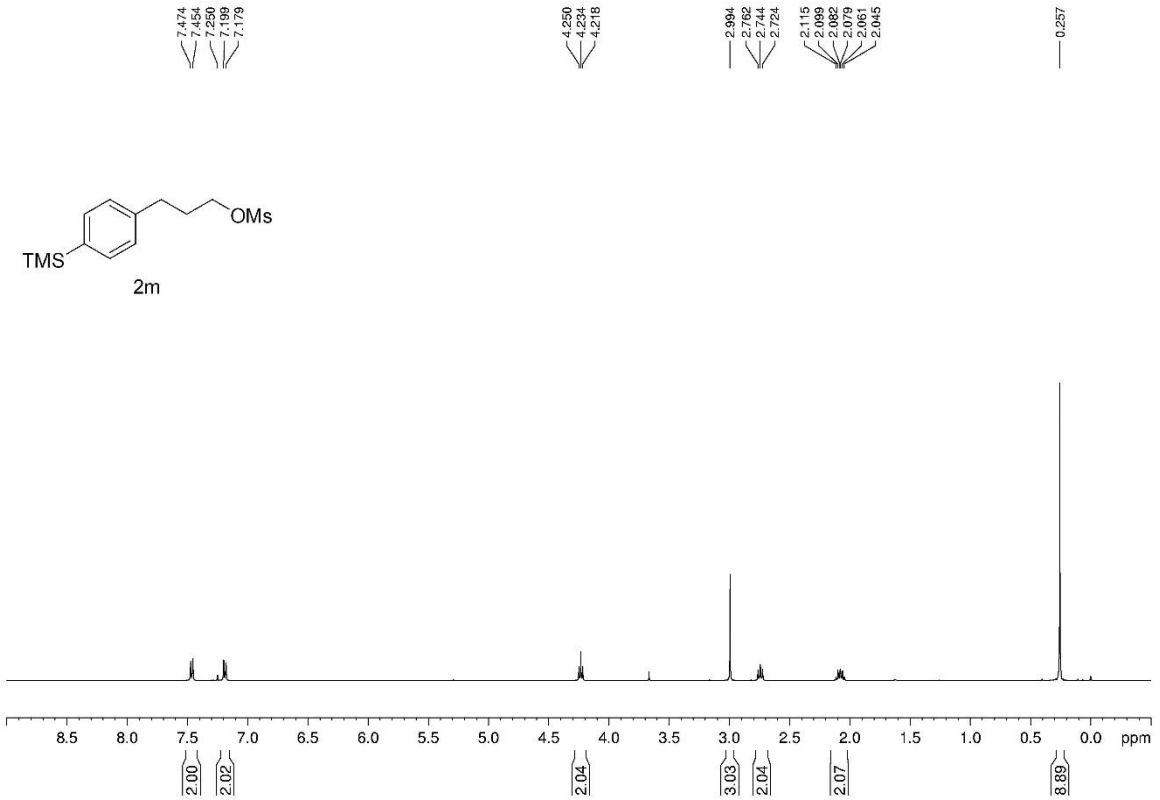


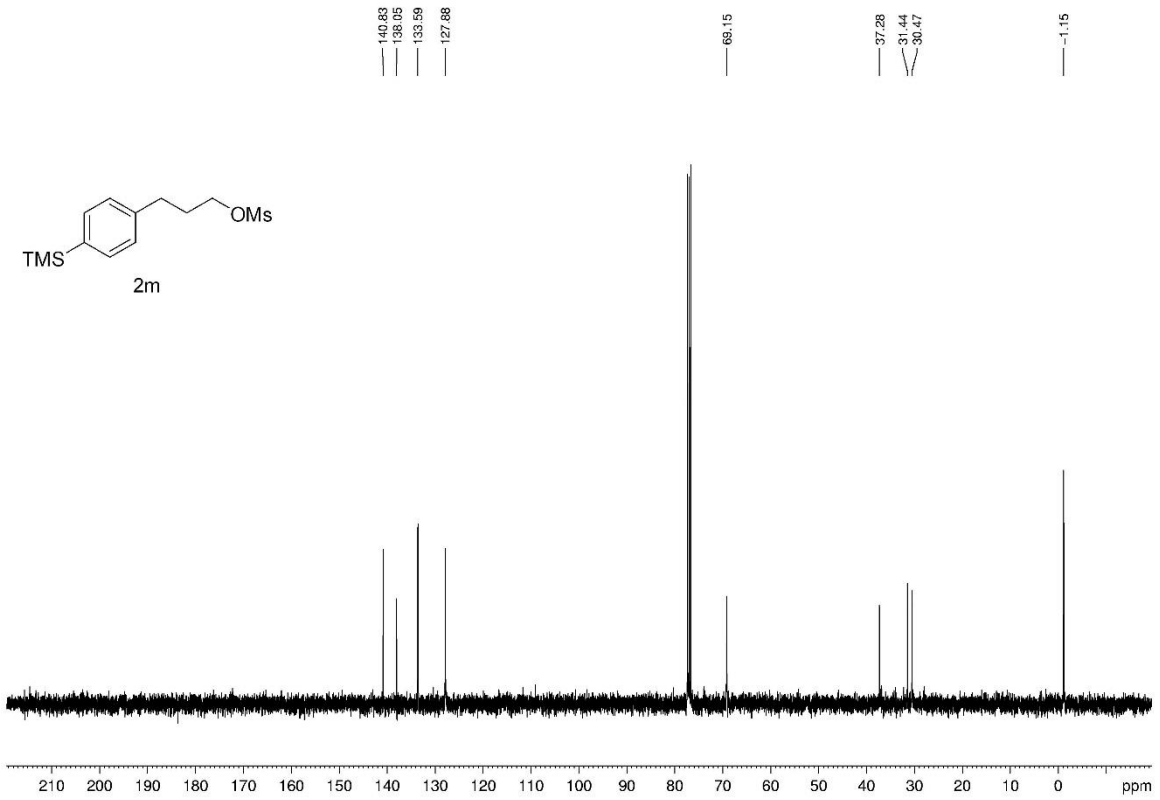
2l; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)



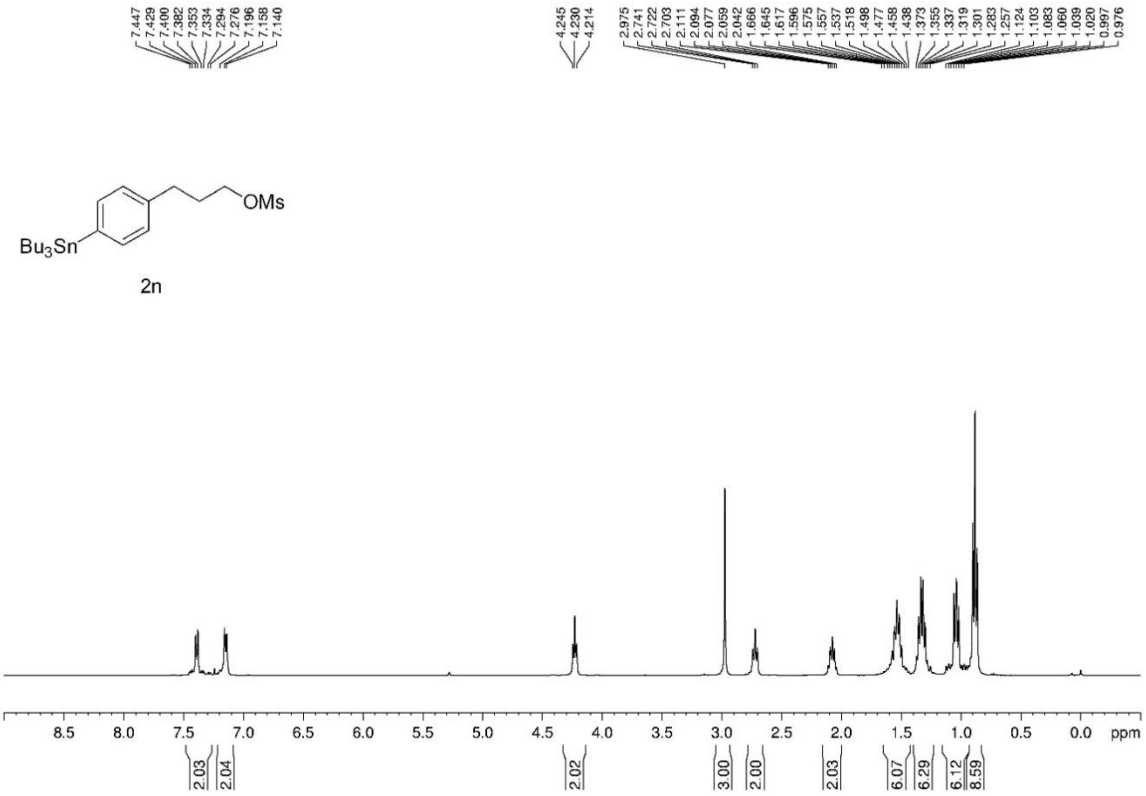


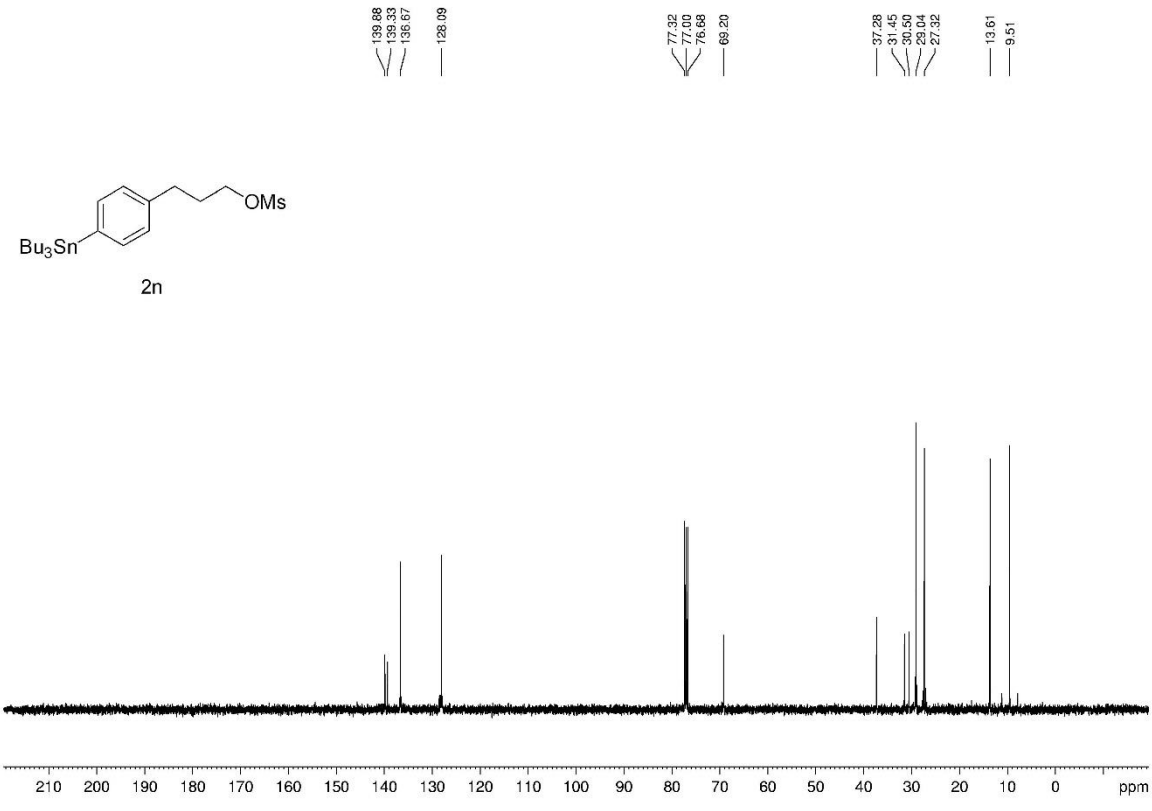
2m; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



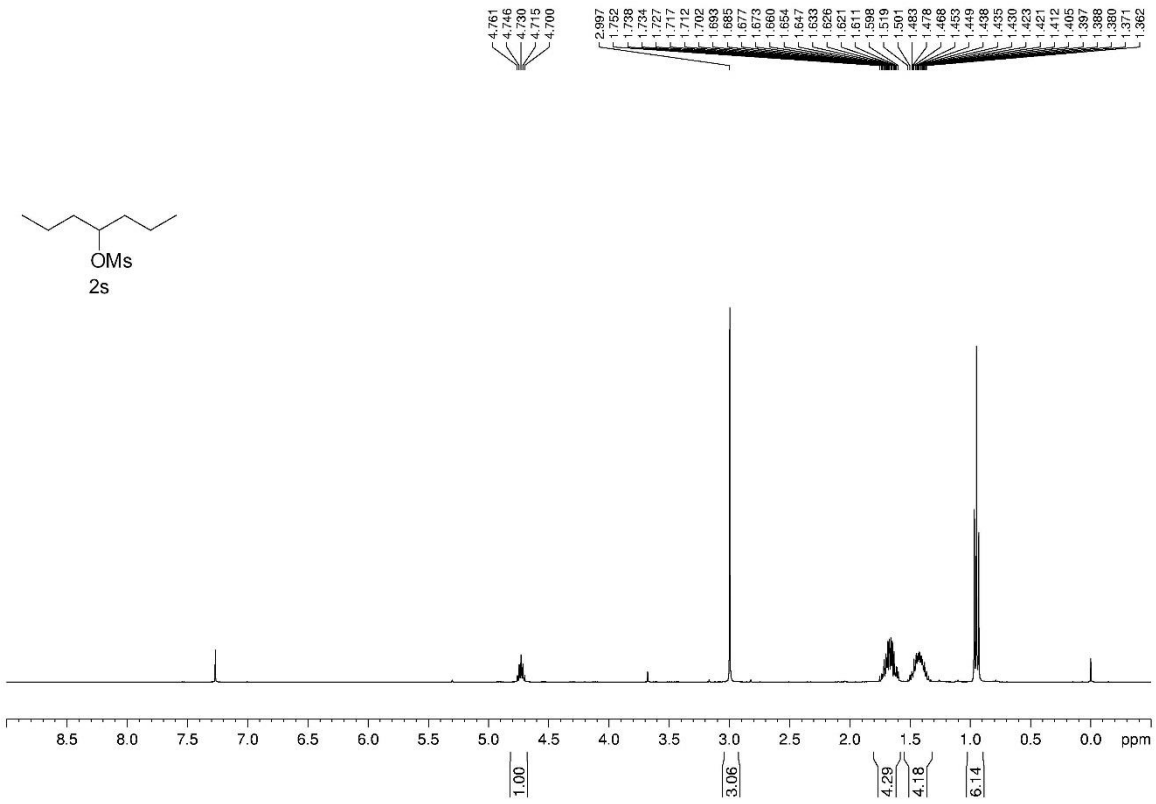


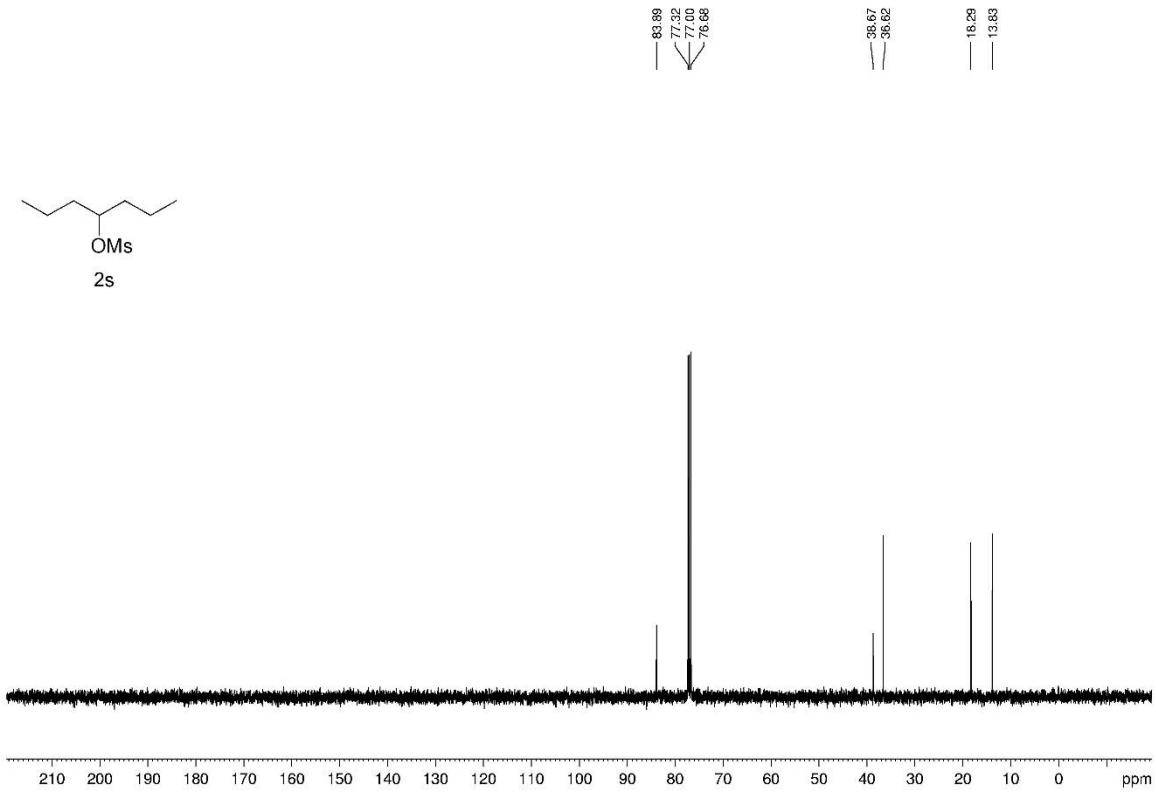
2n; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



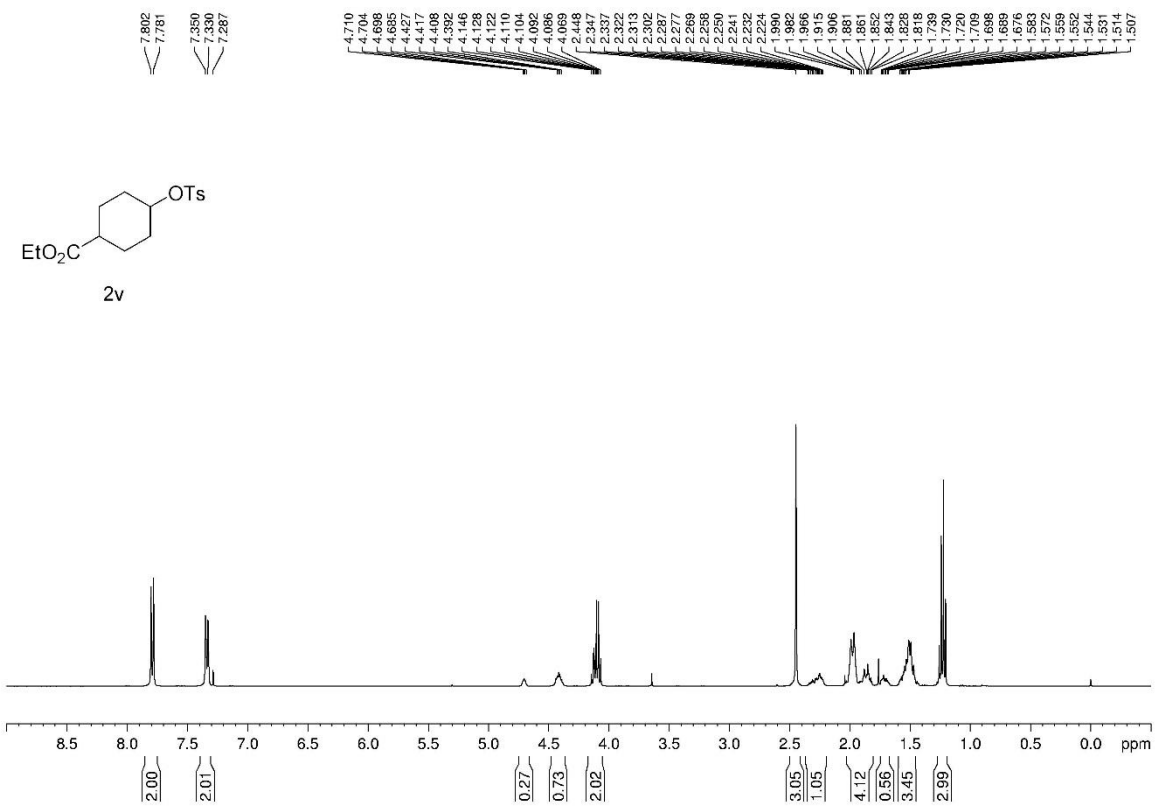


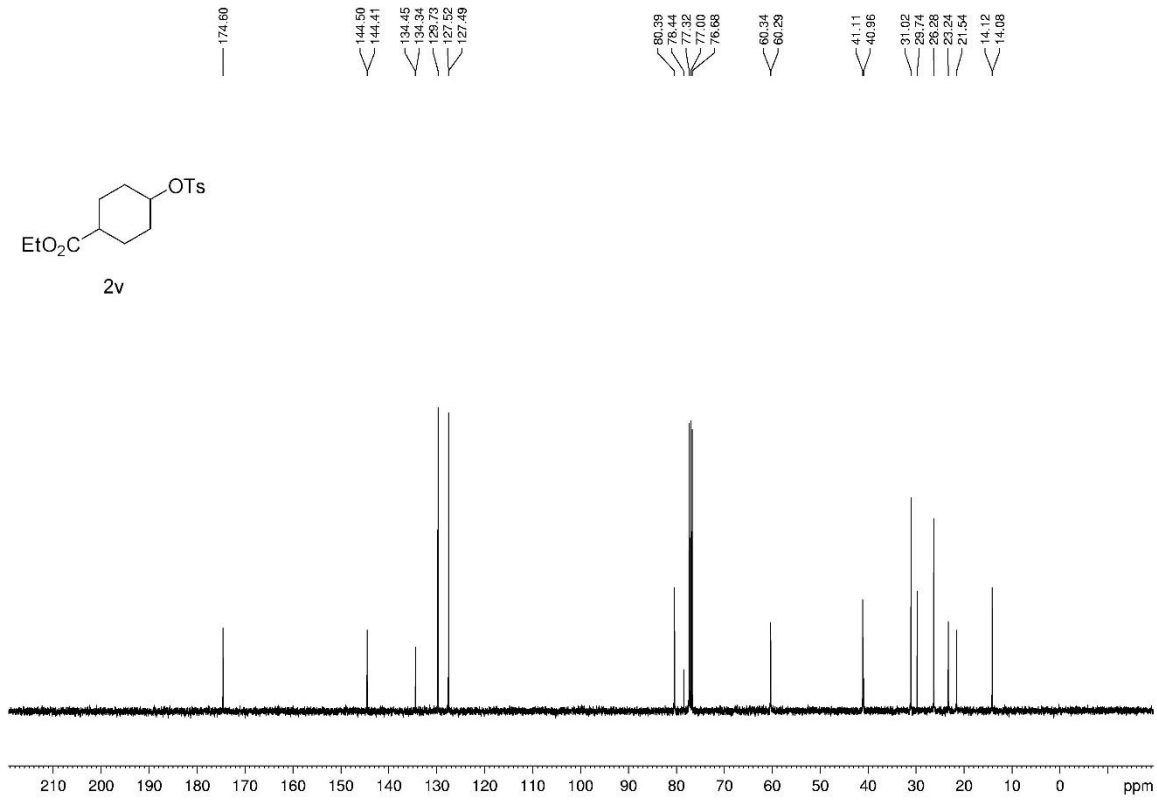
2s; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



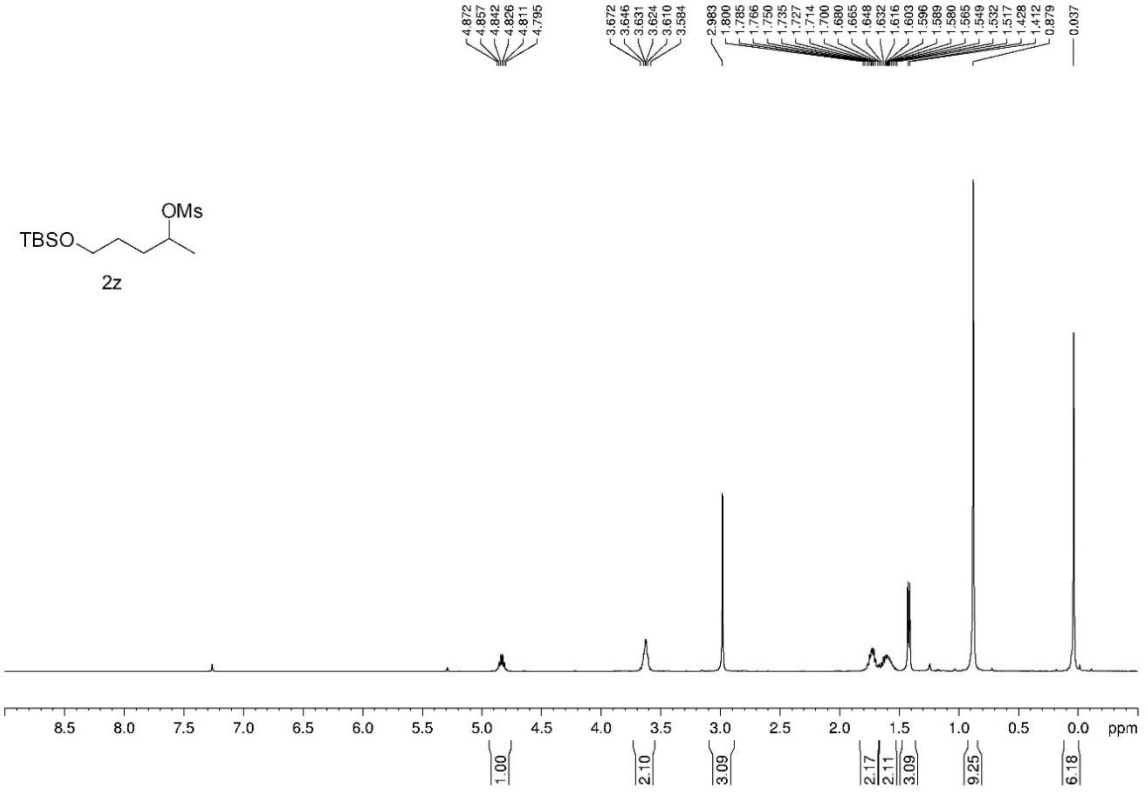


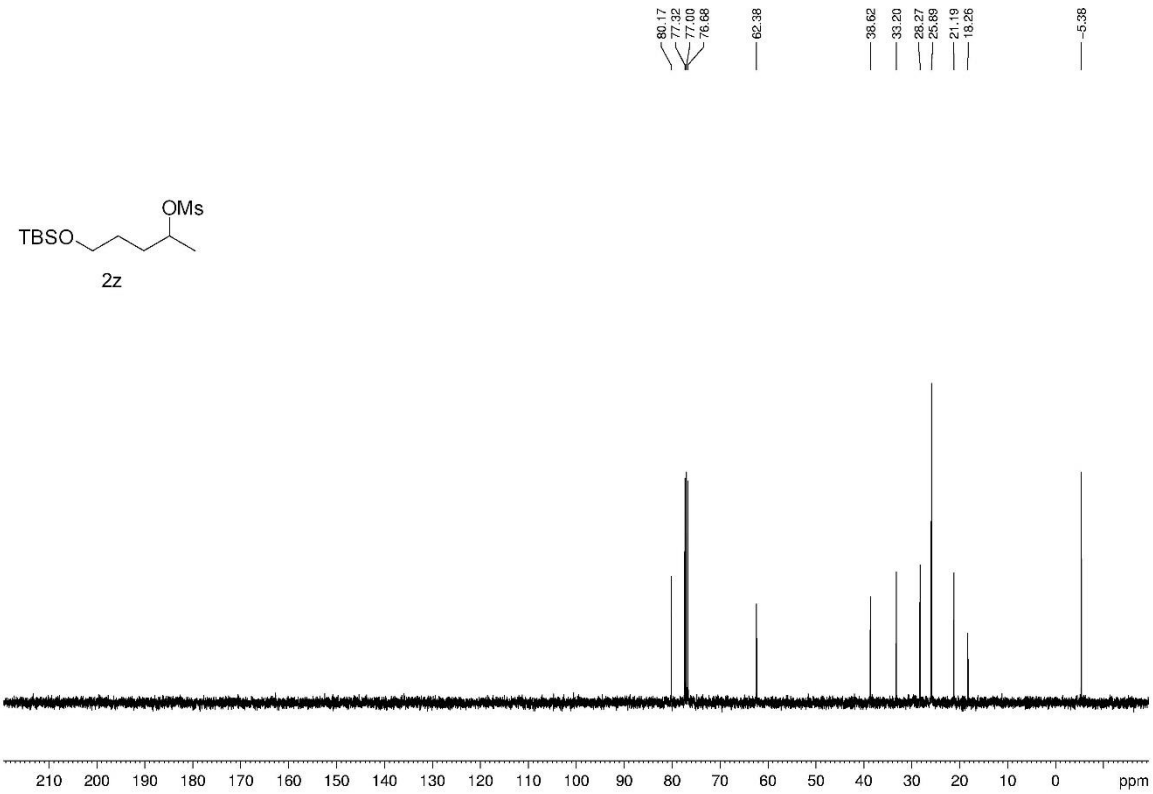
2v; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



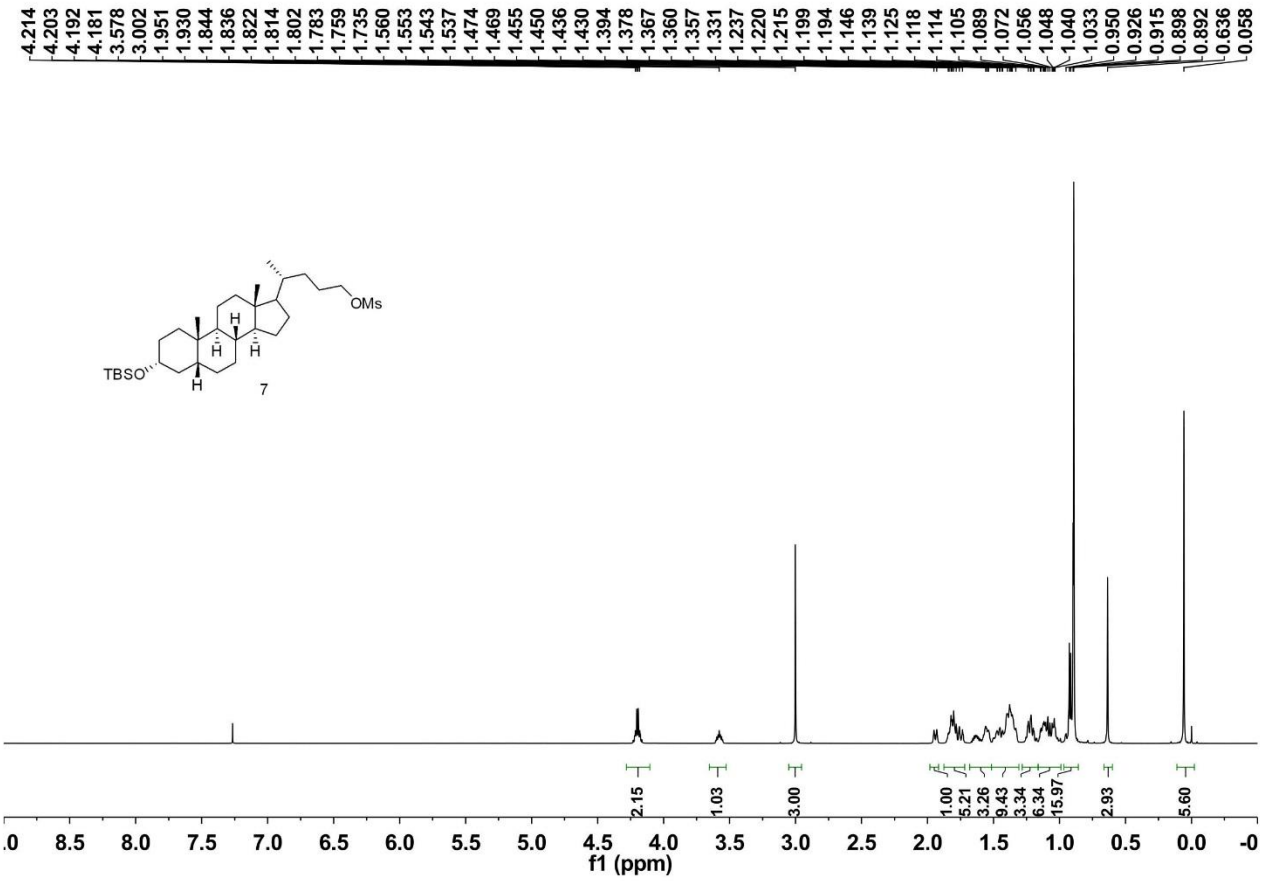


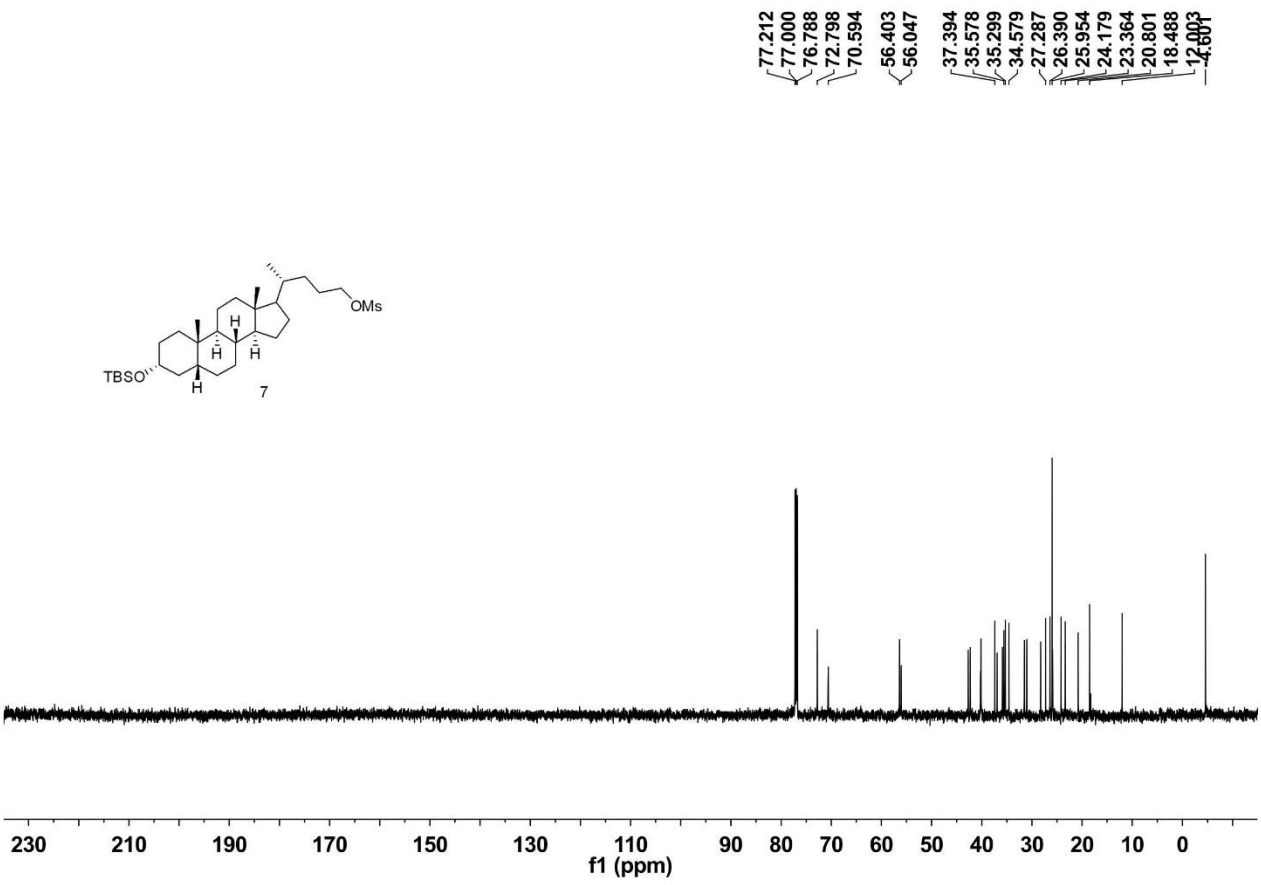
2z; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



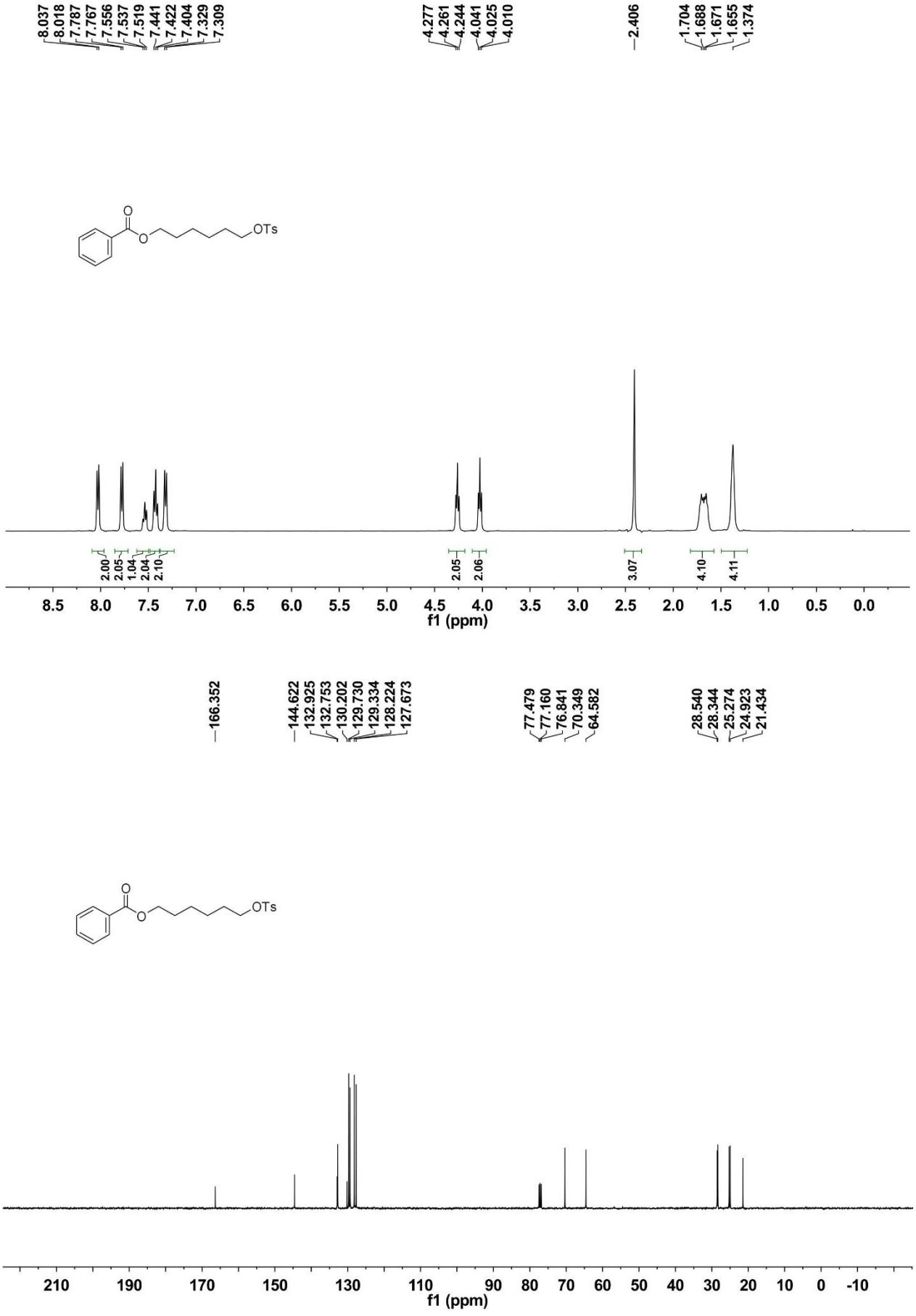


7; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

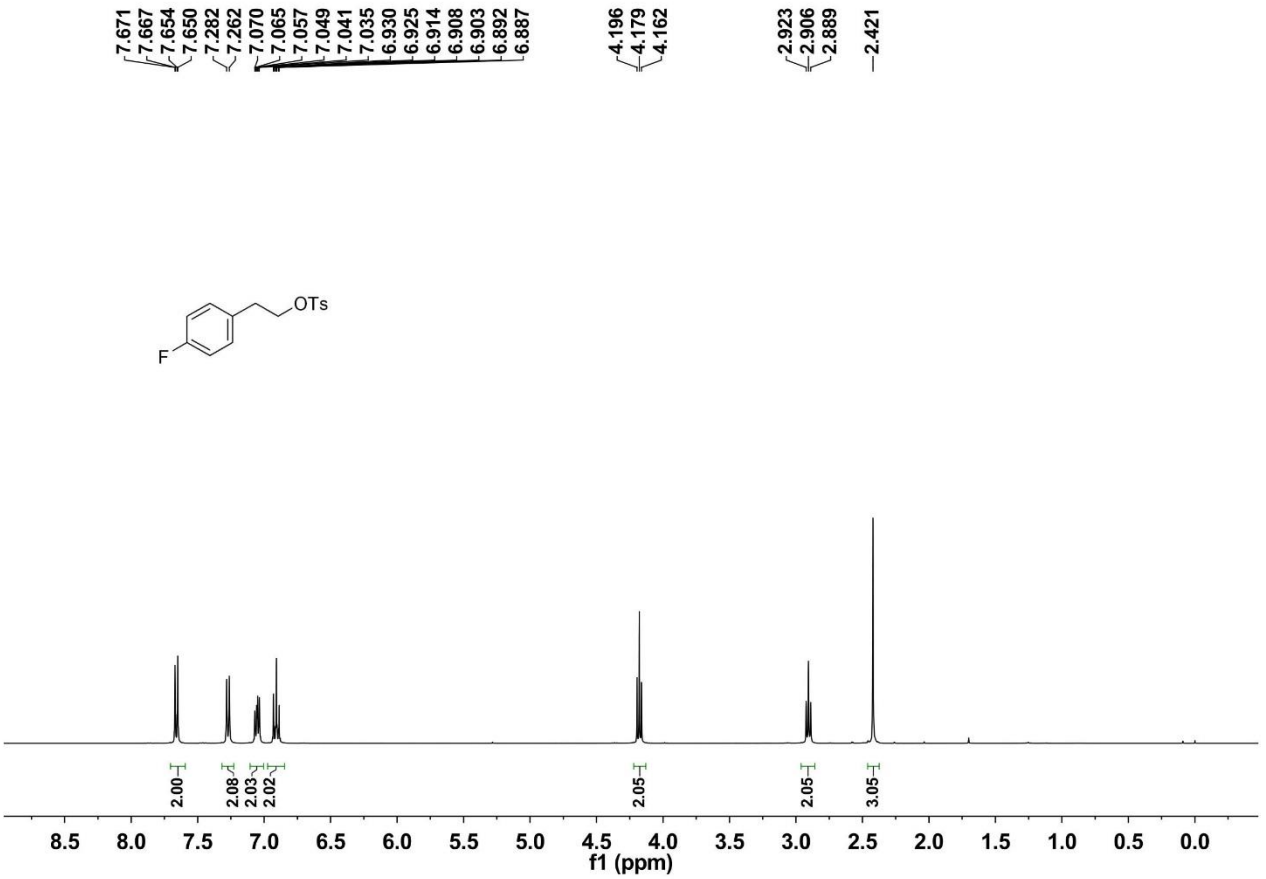


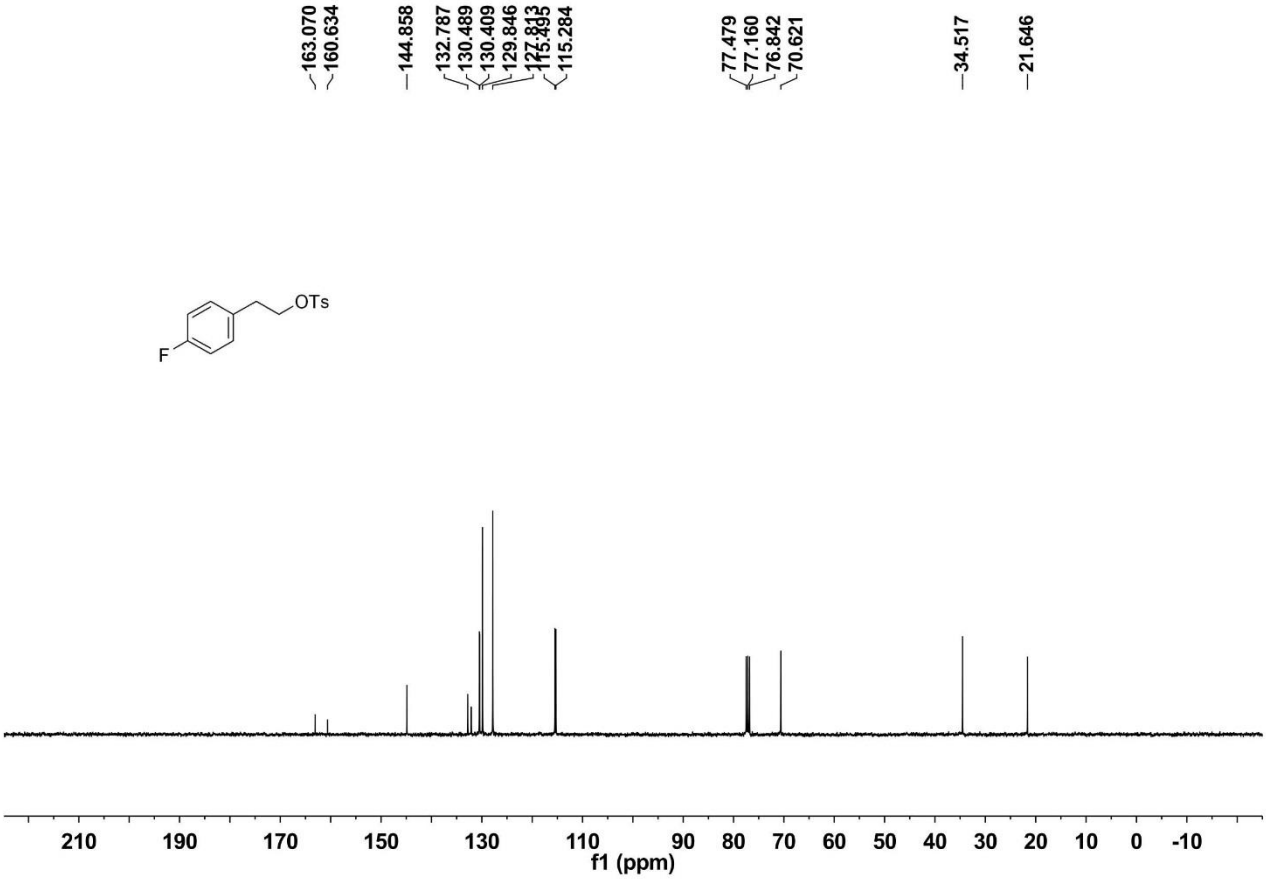


2ah; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

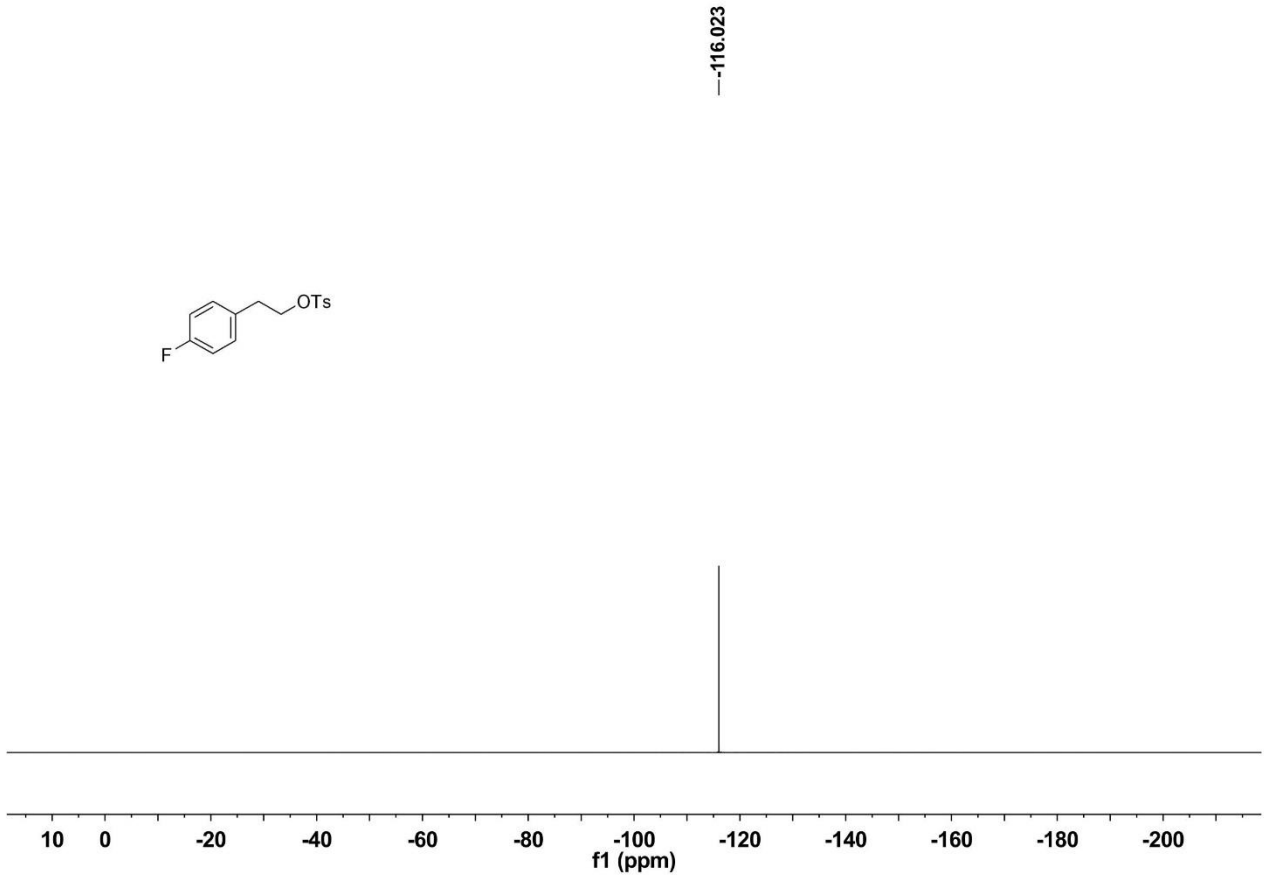


2am; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

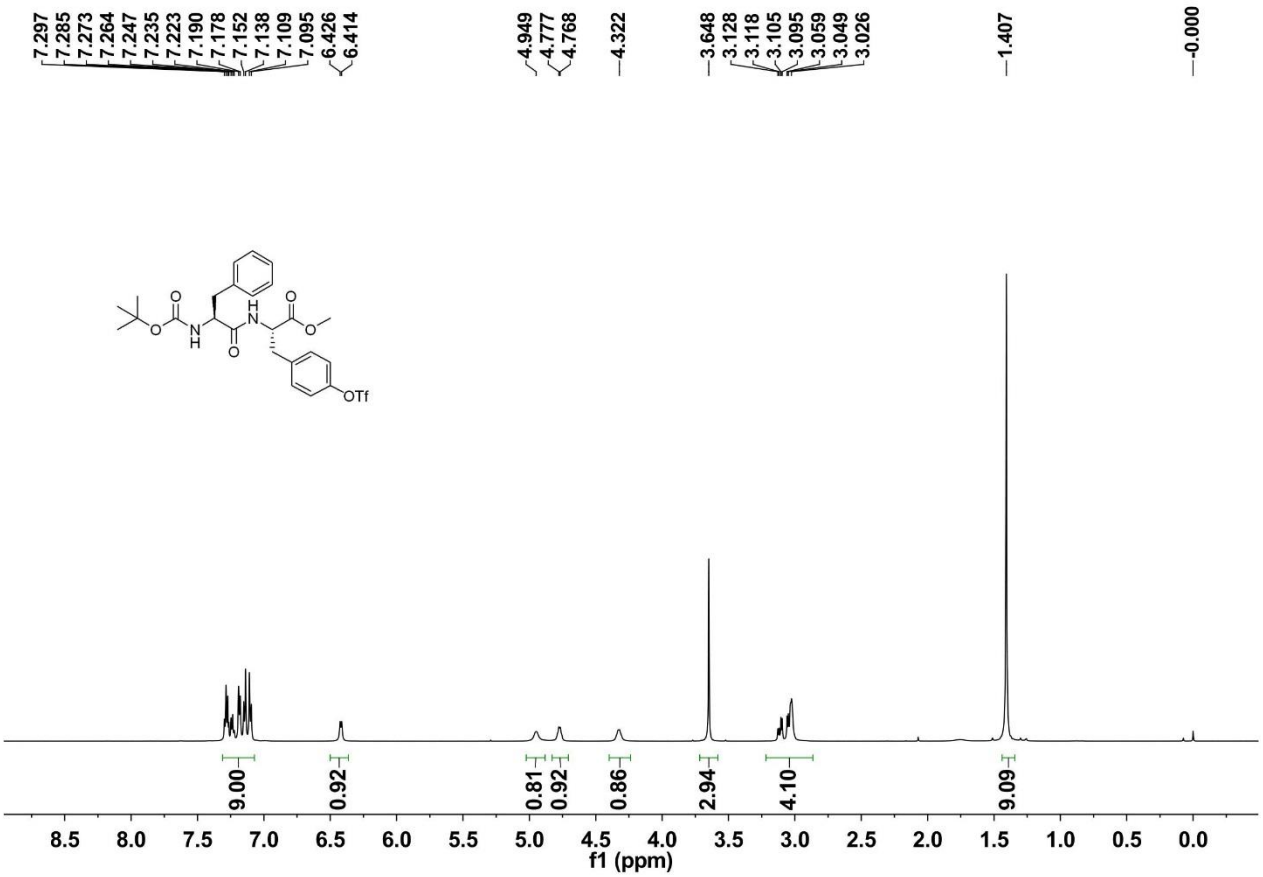


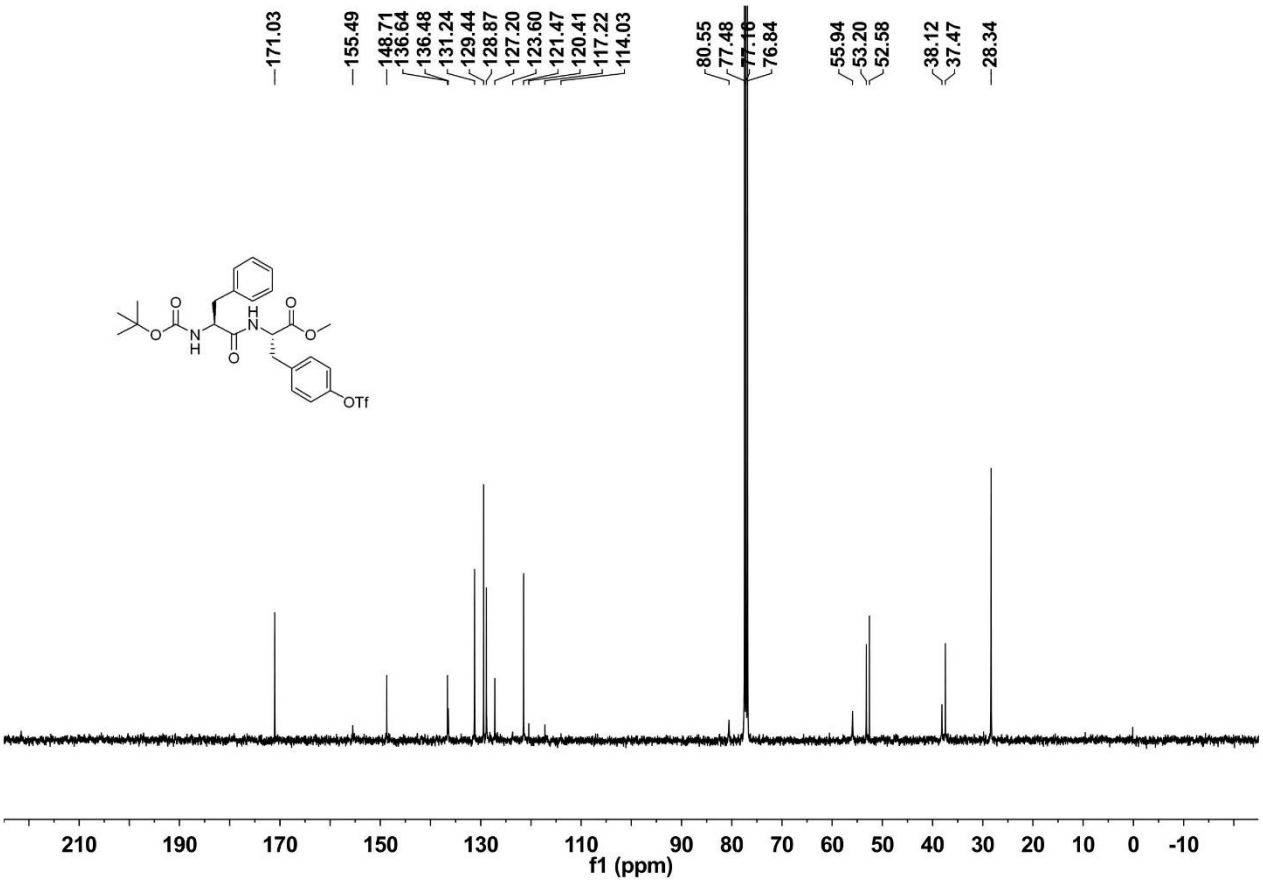


2am; ^{13}F NMR (376MHz, $CDCl_3$)

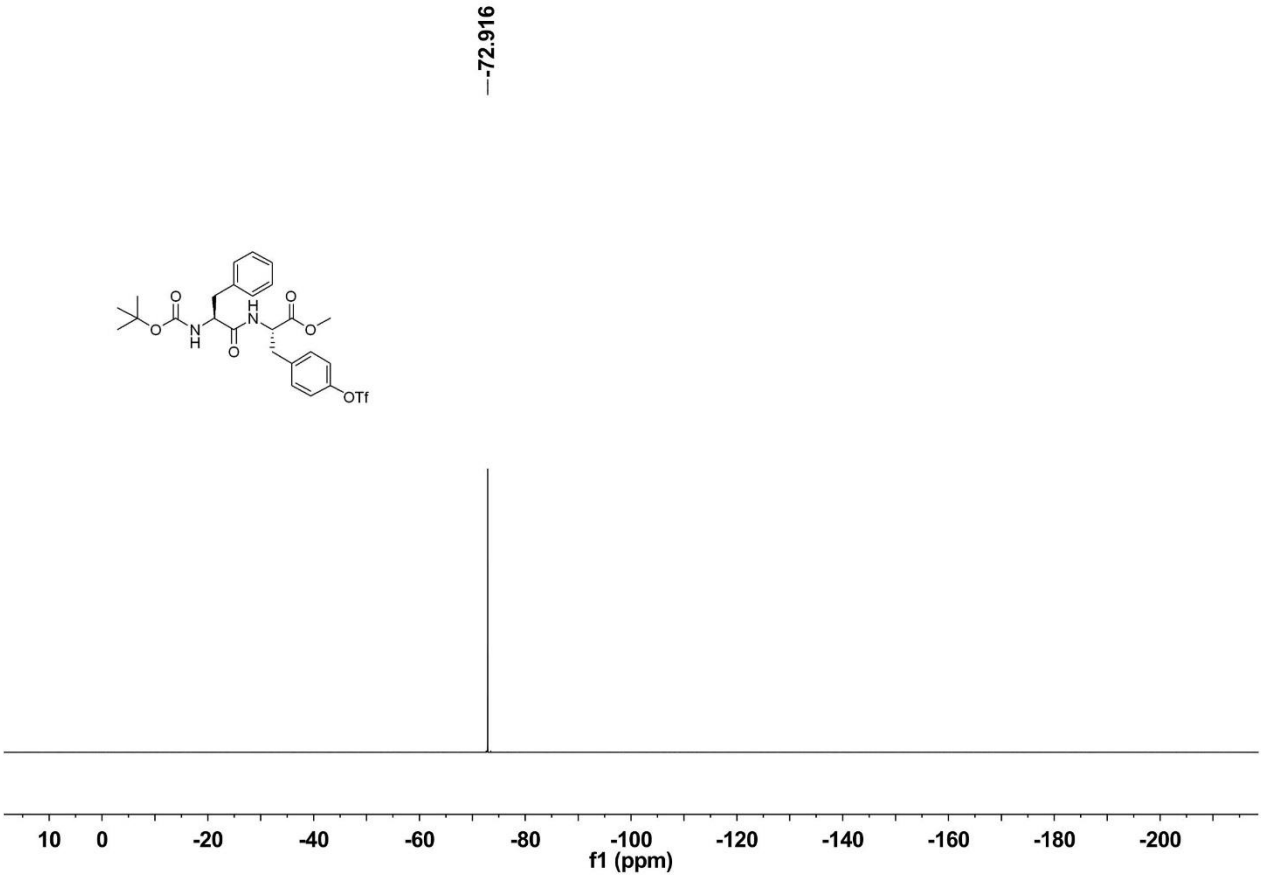


16b; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

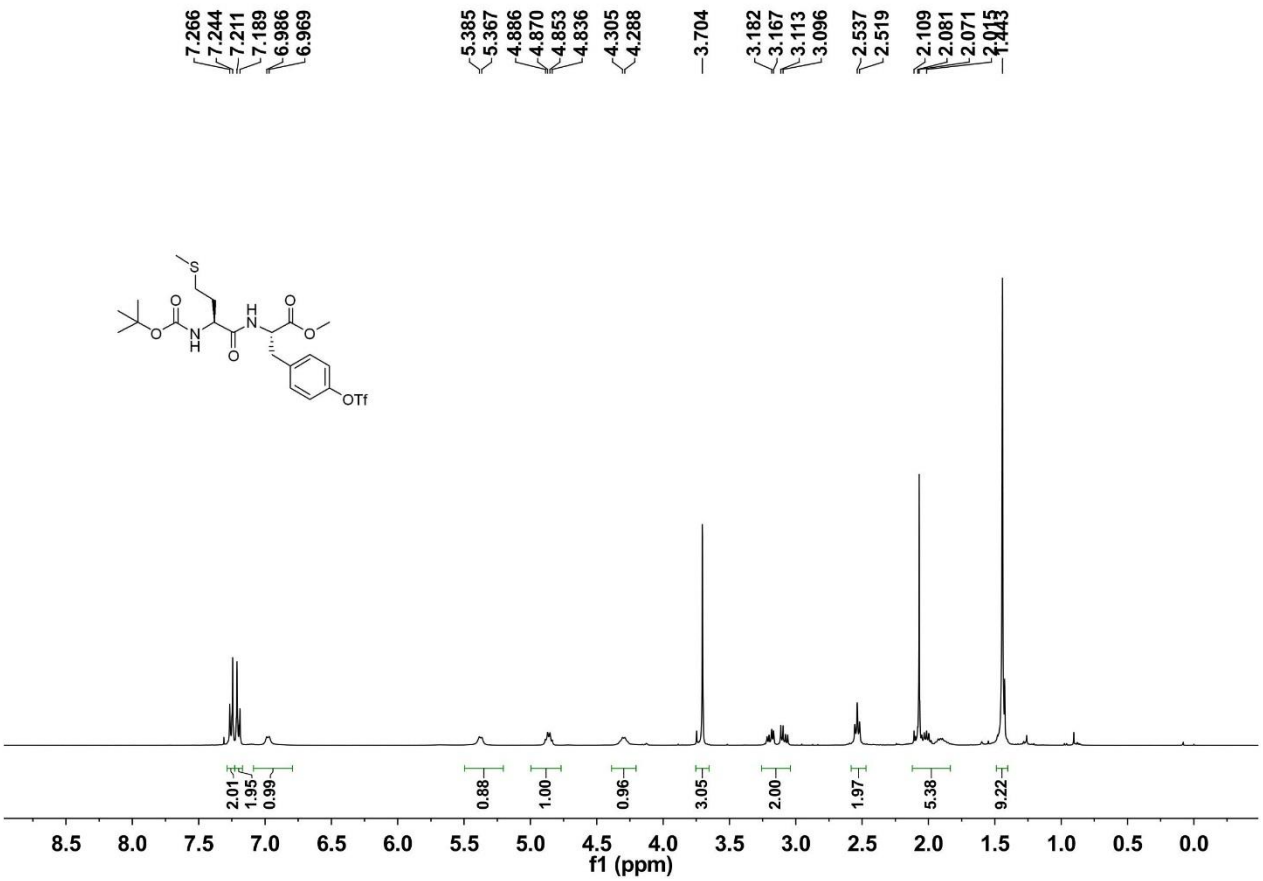


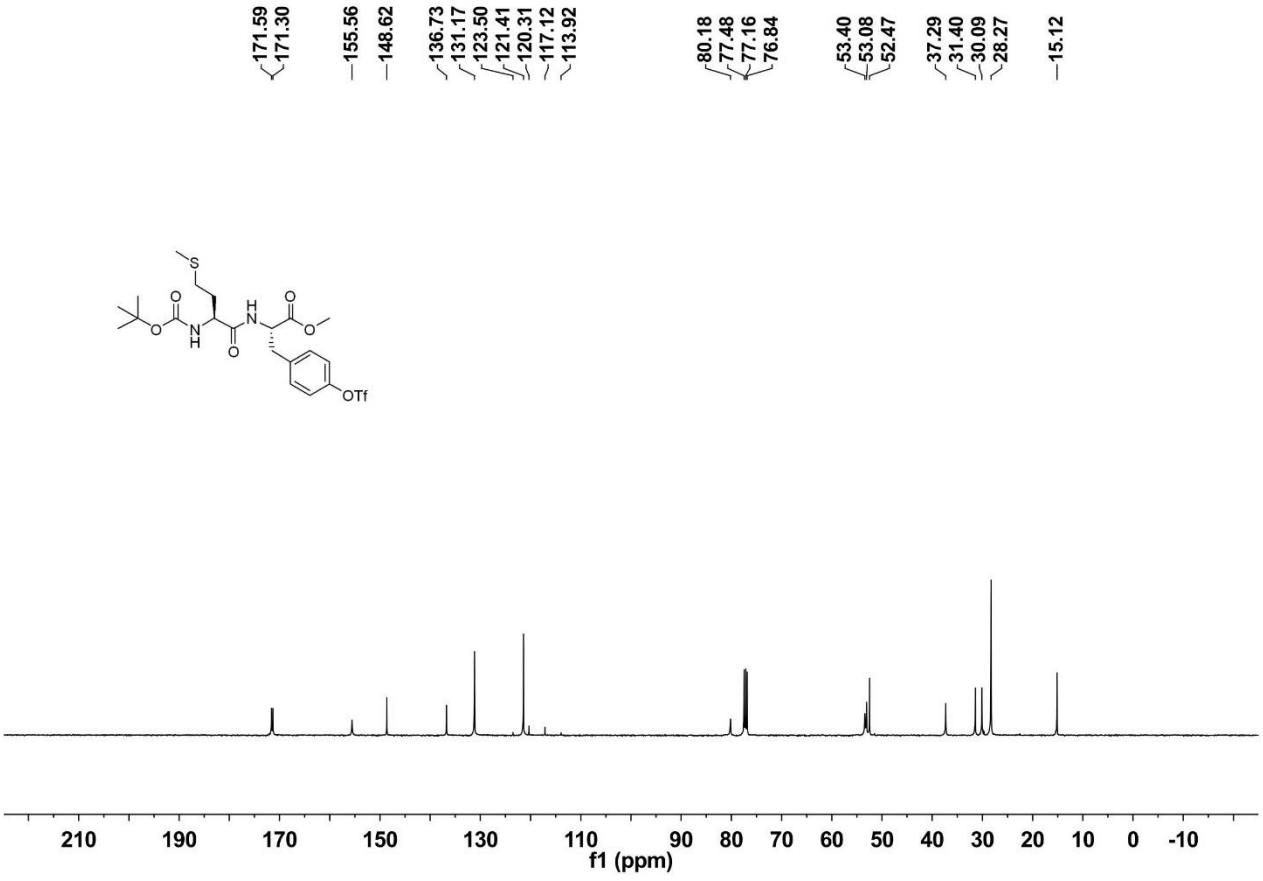


16b; ^{13}F NMR (376MHz, $CDCl_3$)

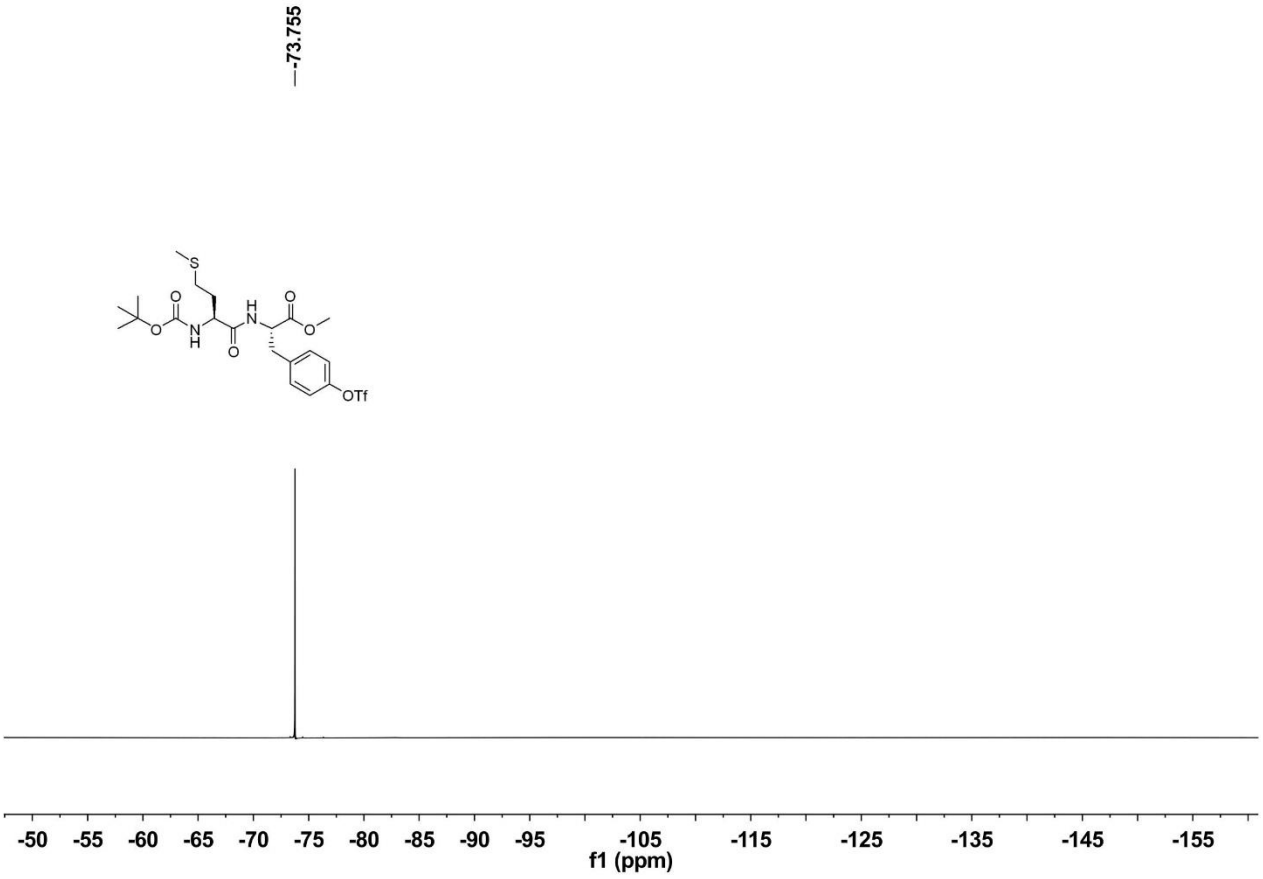


16c; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

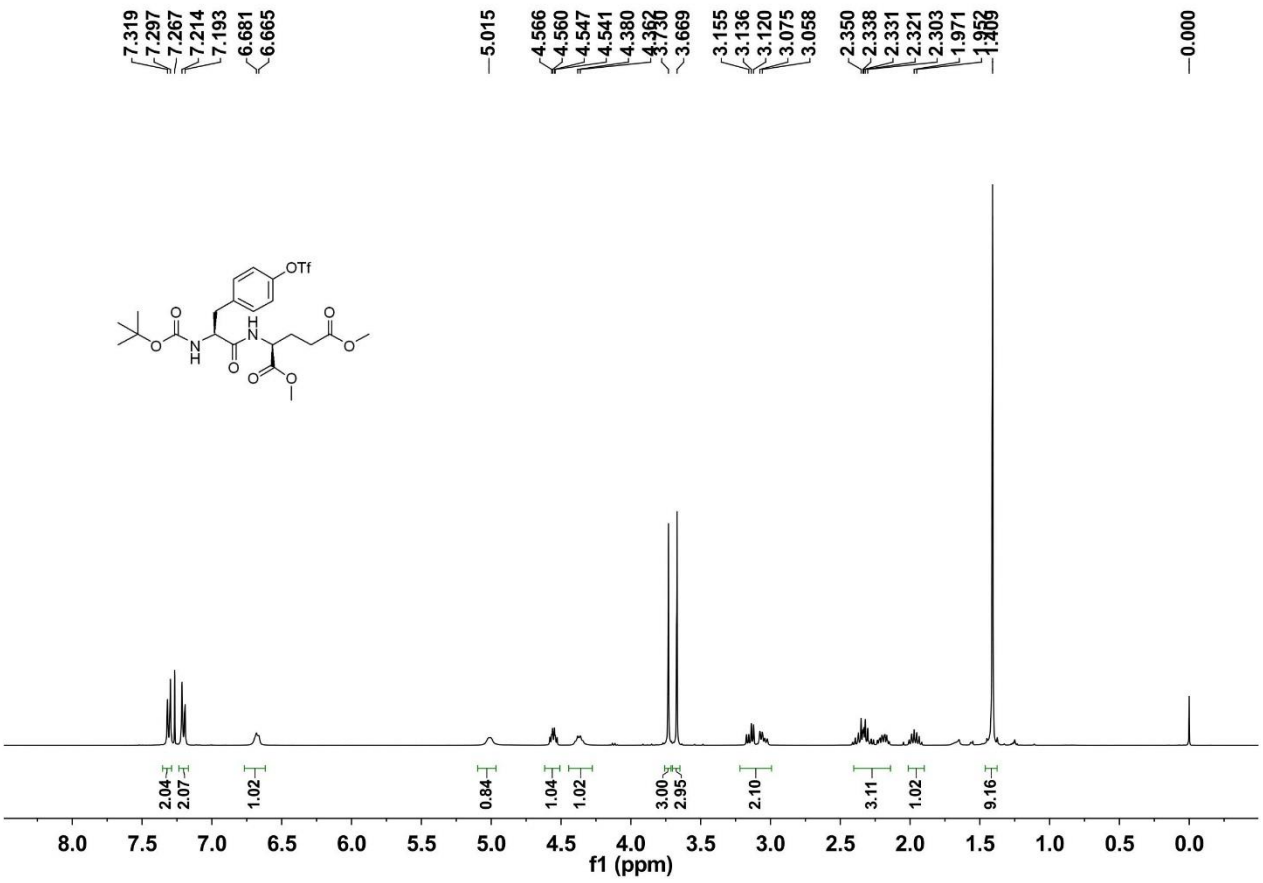


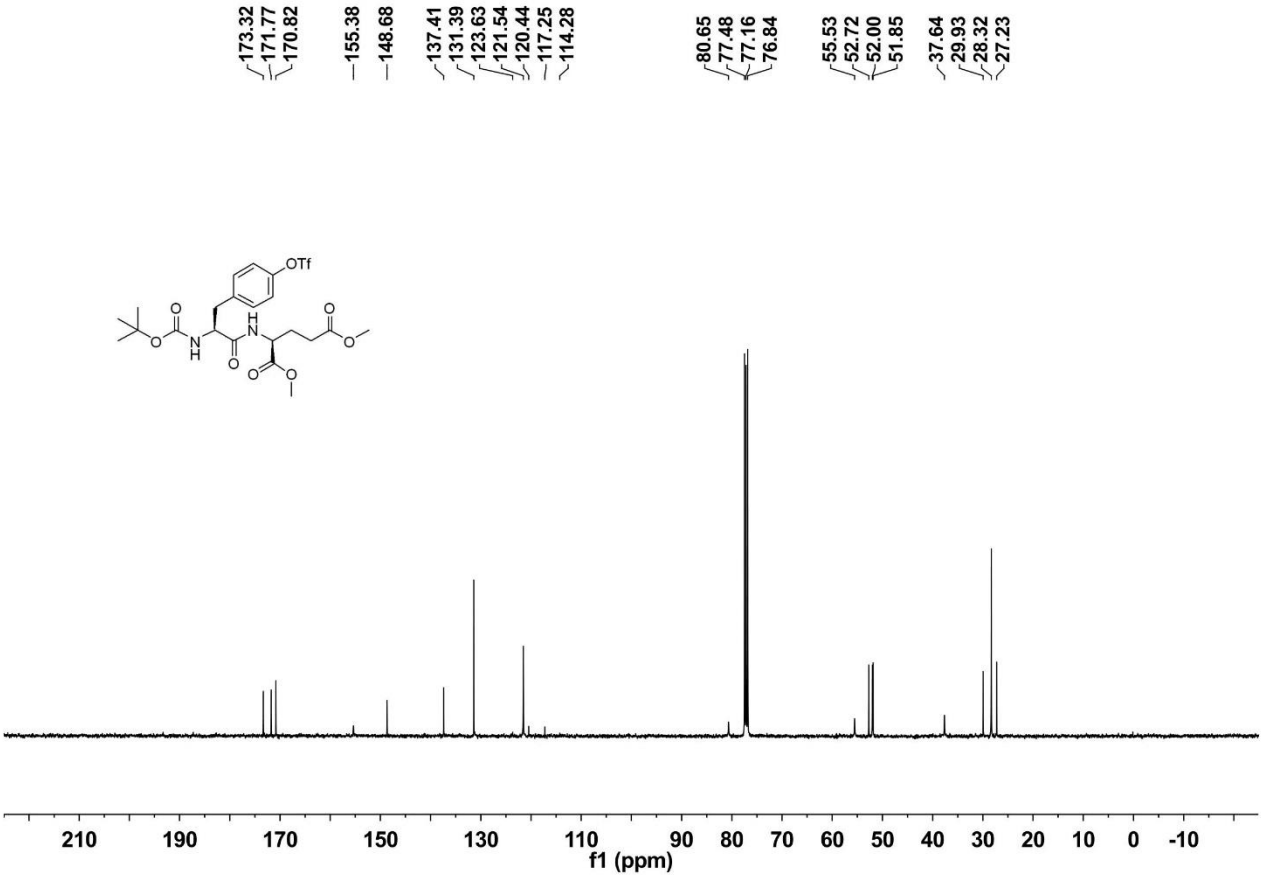


16c; ^{13}F NMR (282MHz, $CDCl_3$)

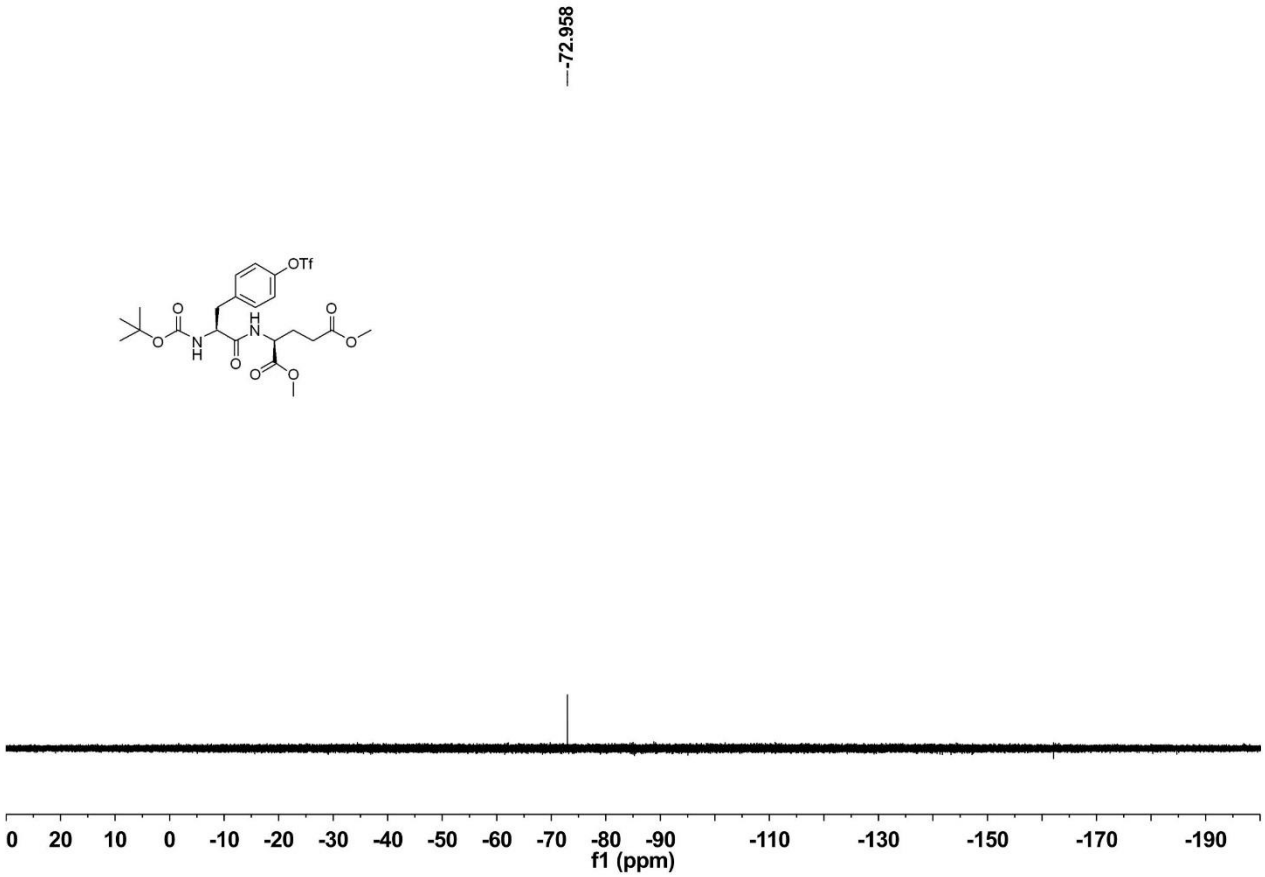


16d; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

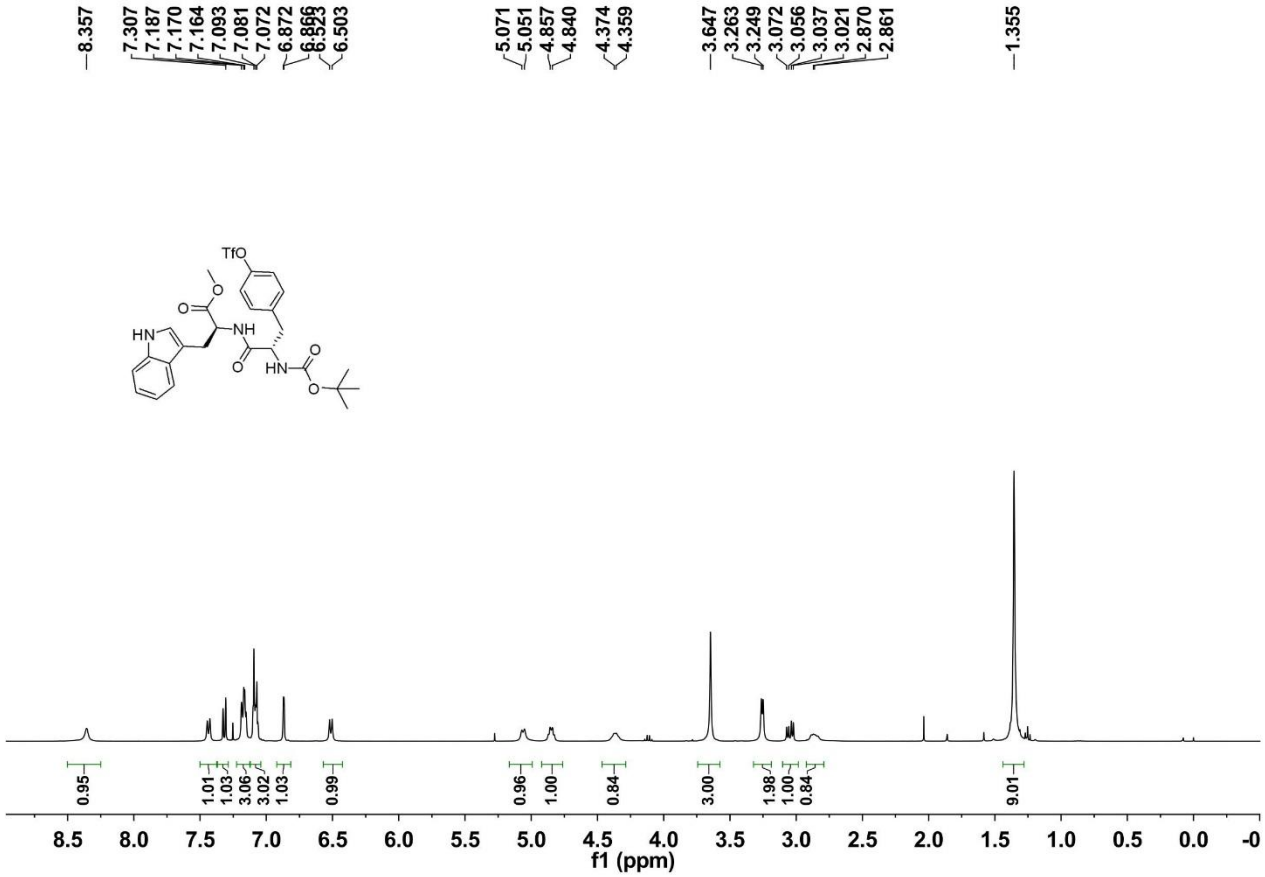


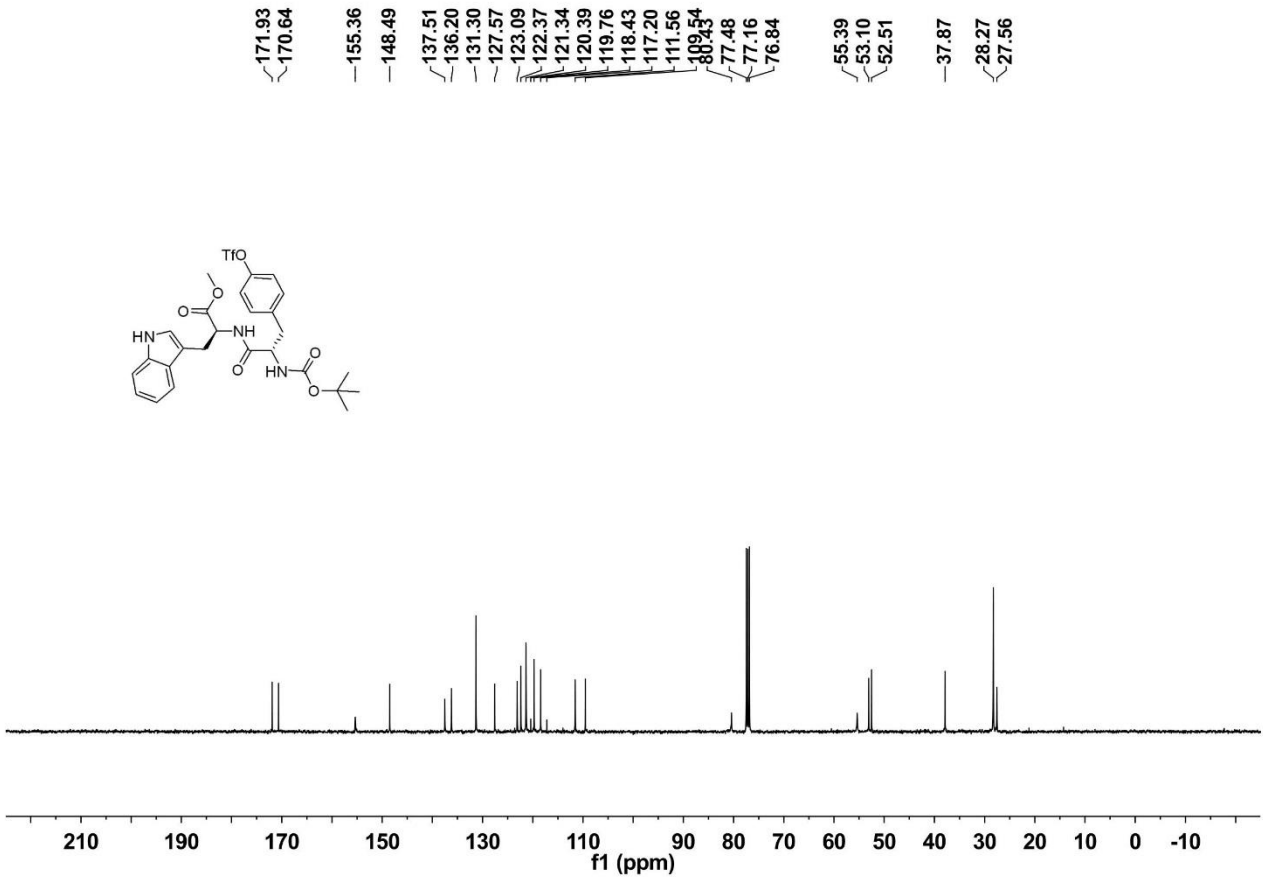


16d; ^{13}F NMR (282MHz, $CDCl_3$)

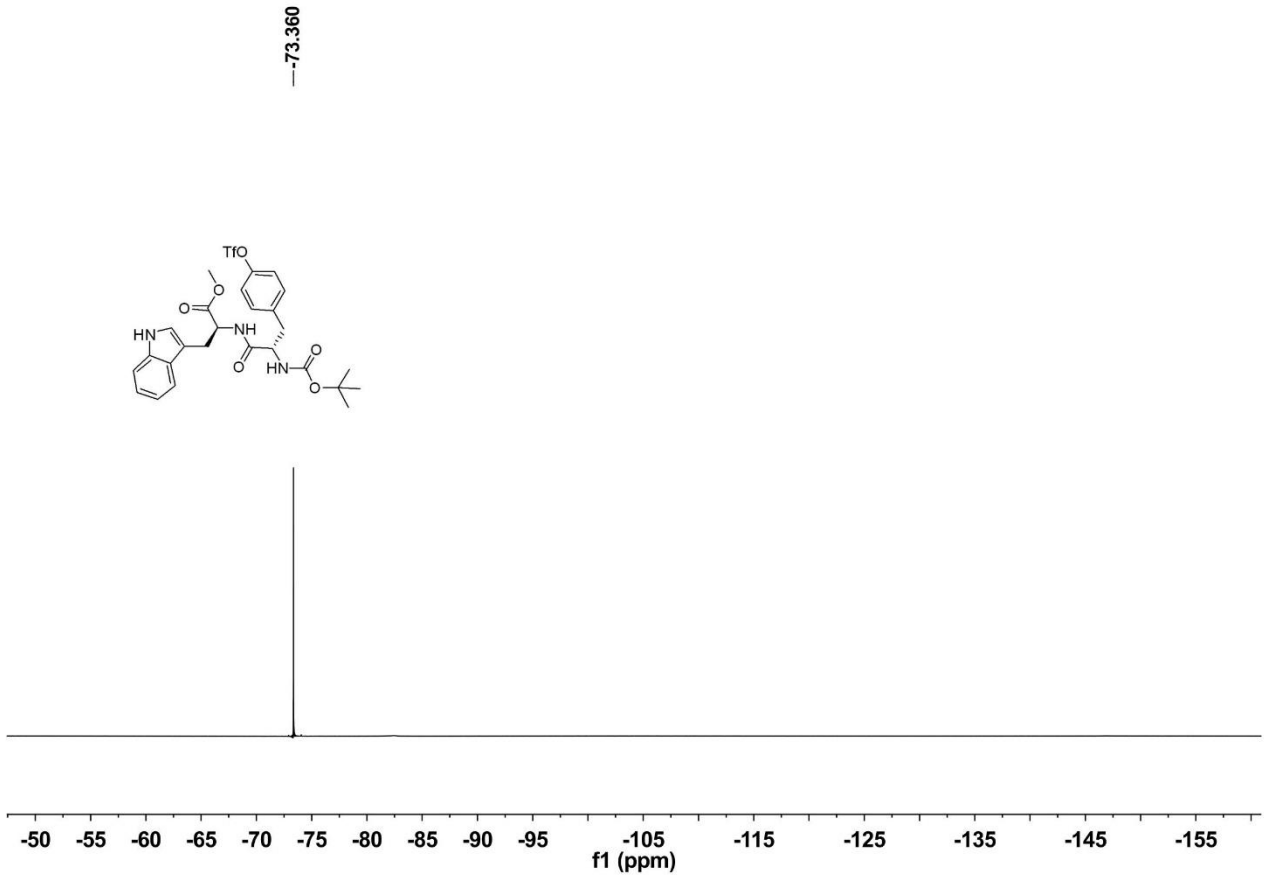


16e; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

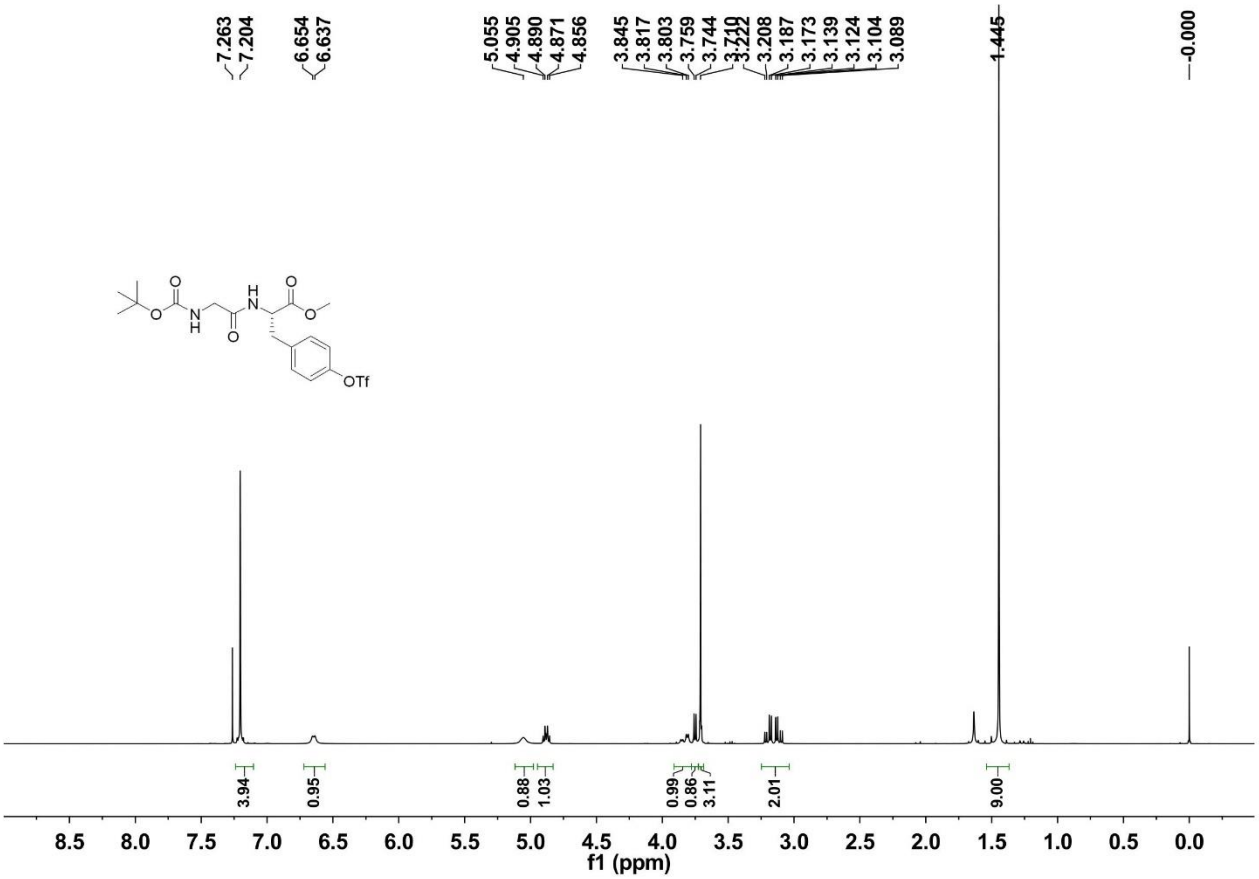


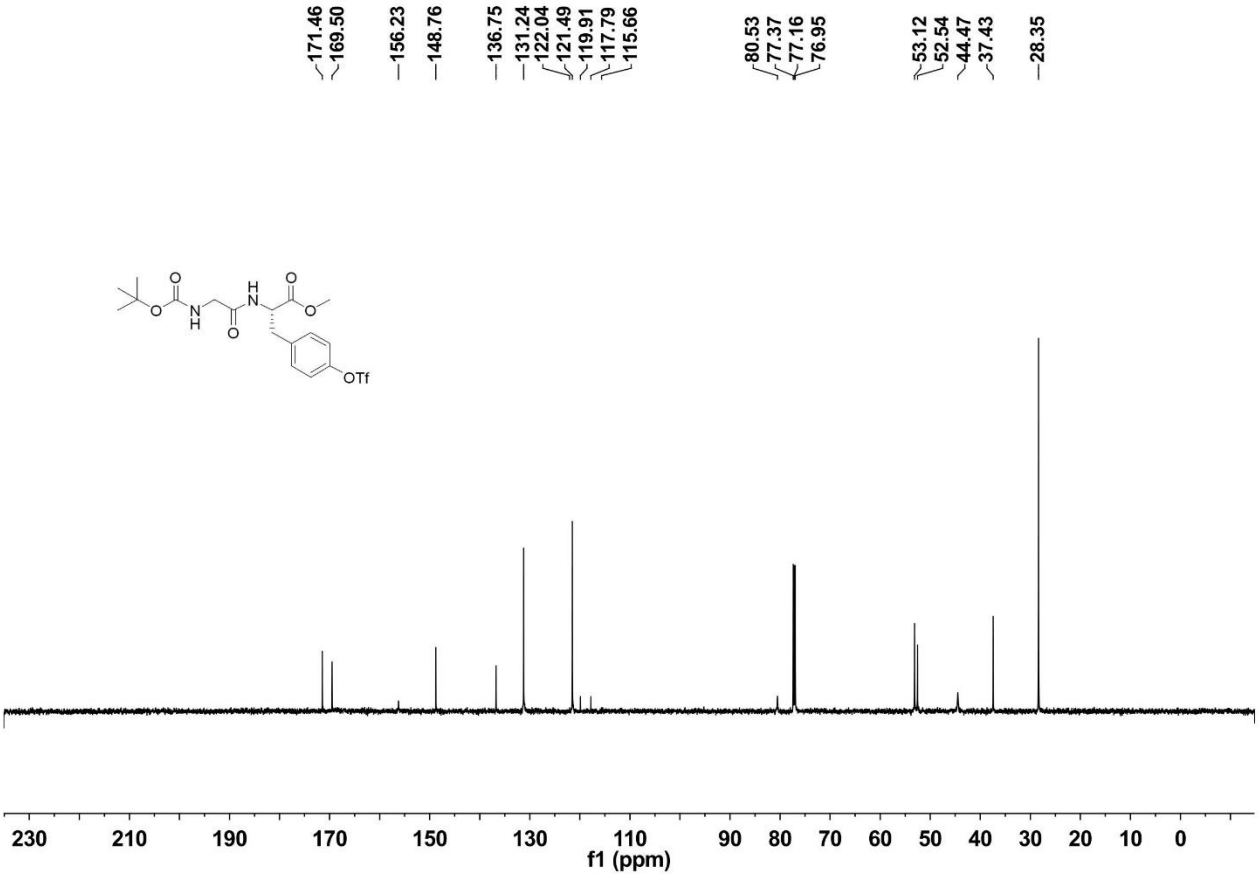


16e; ^{13}F NMR (282MHz, $CDCl_3$)

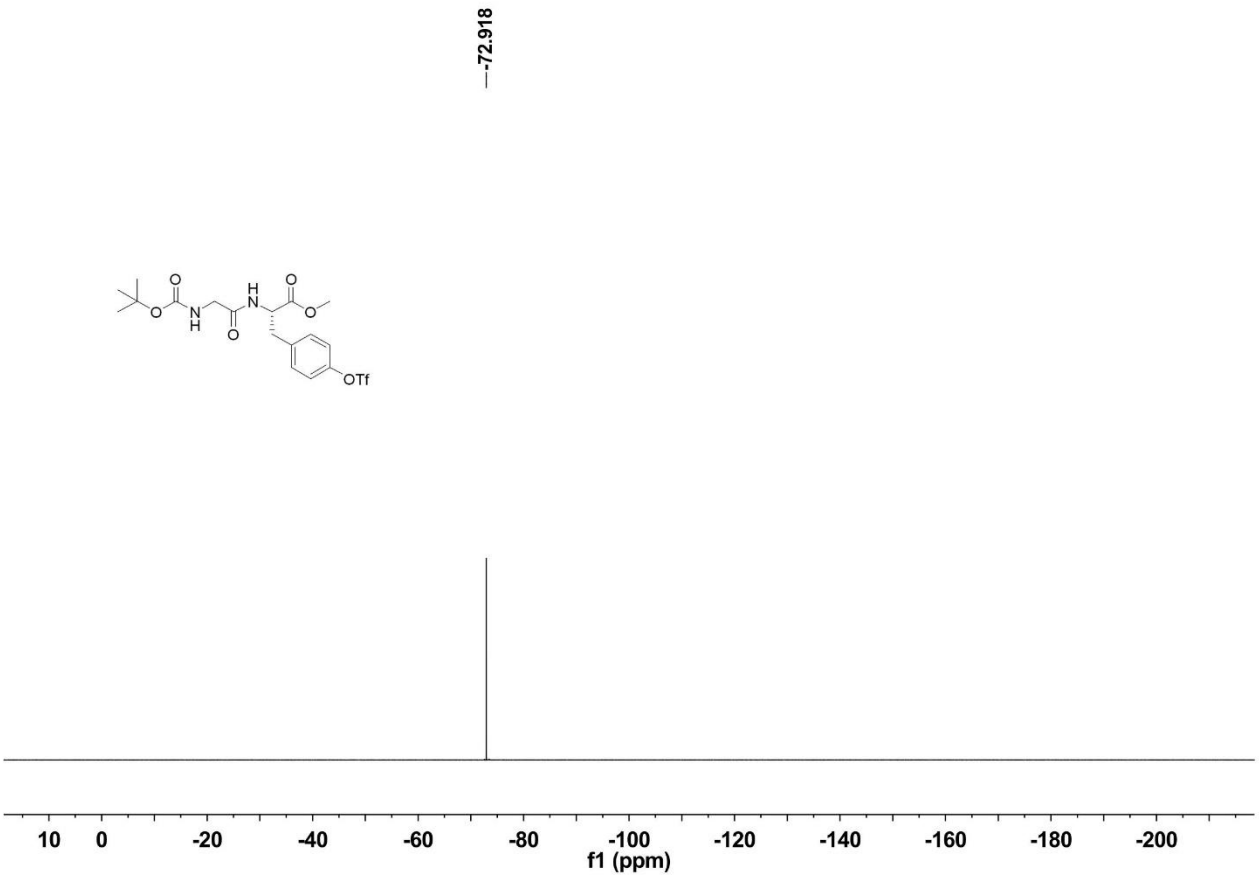


16f; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

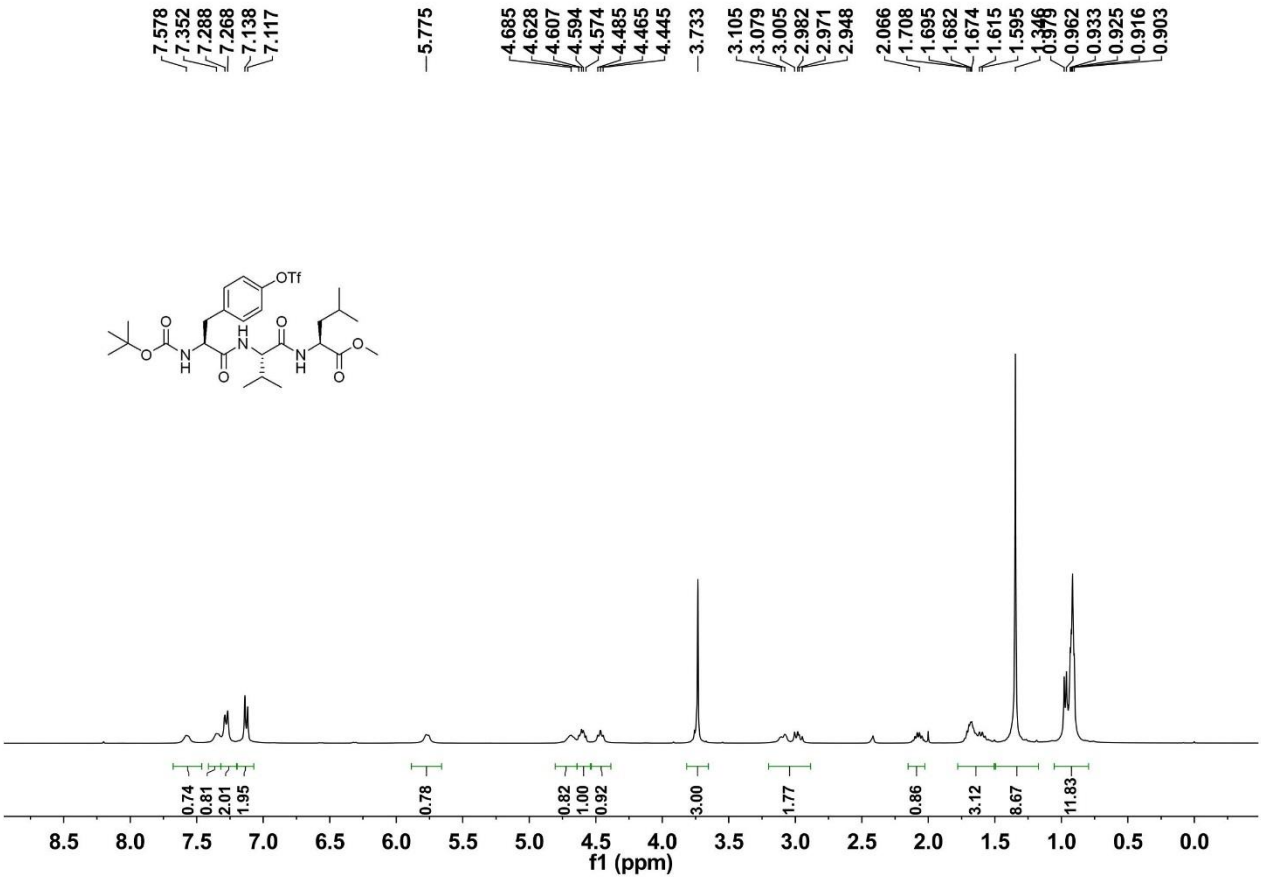


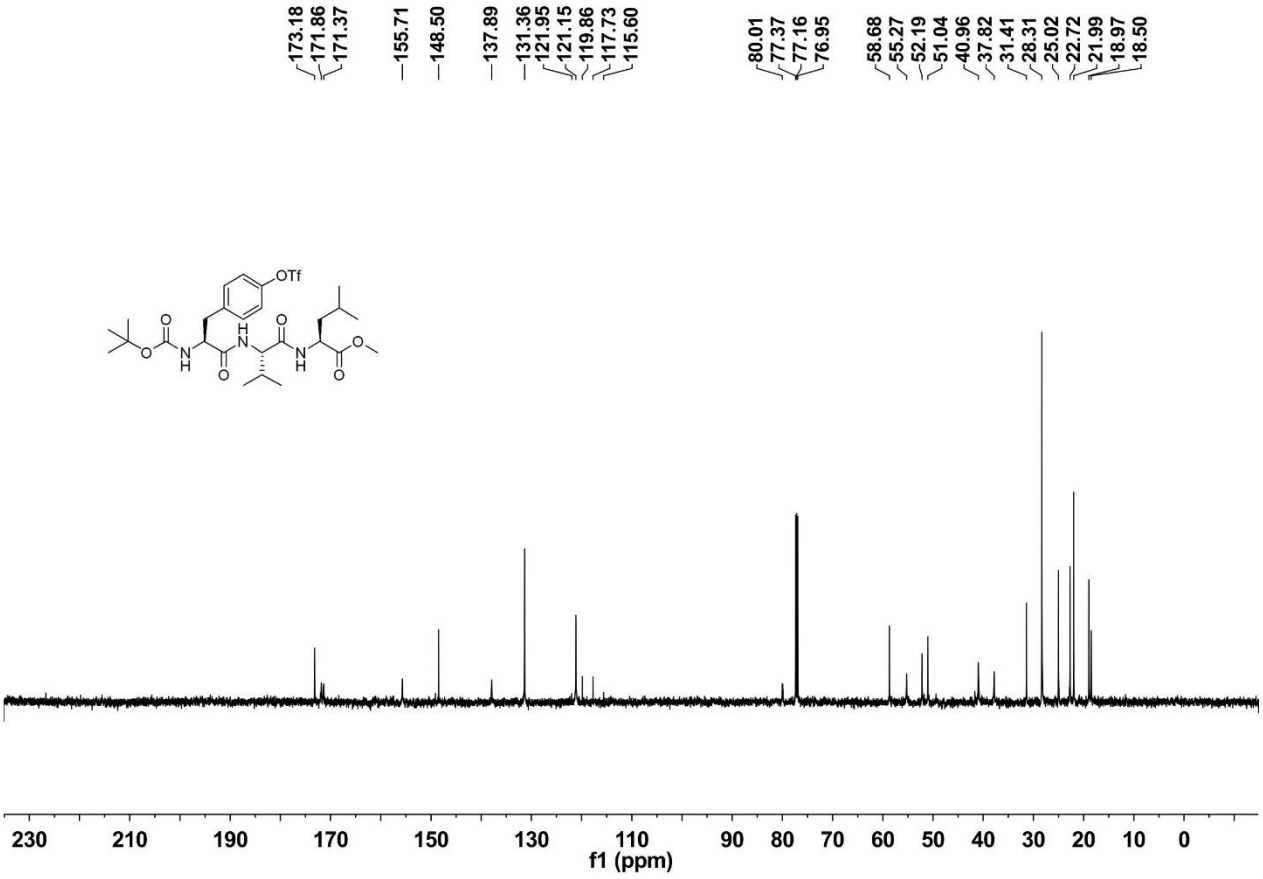


16f; ^{13}F NMR (376MHz, $CDCl_3$)

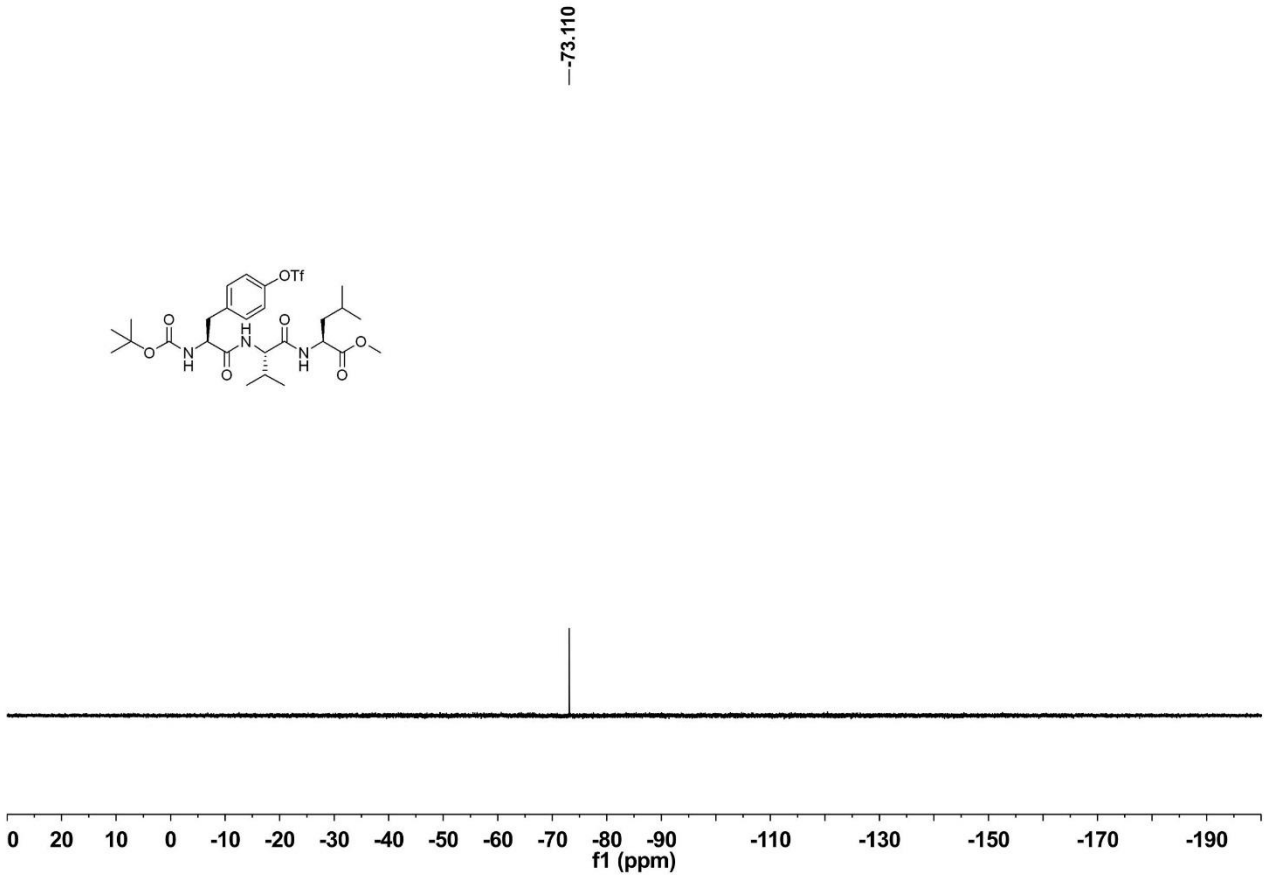


16g; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

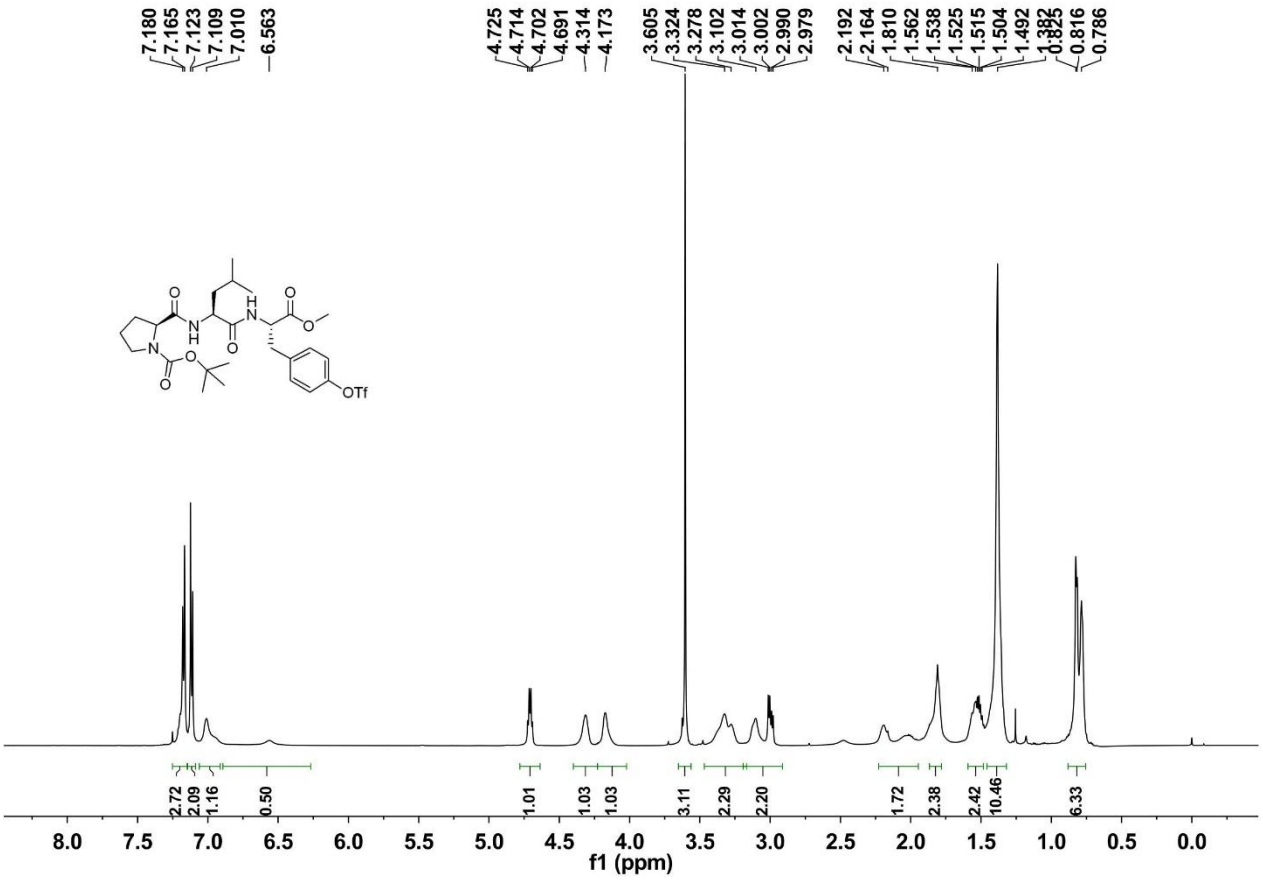


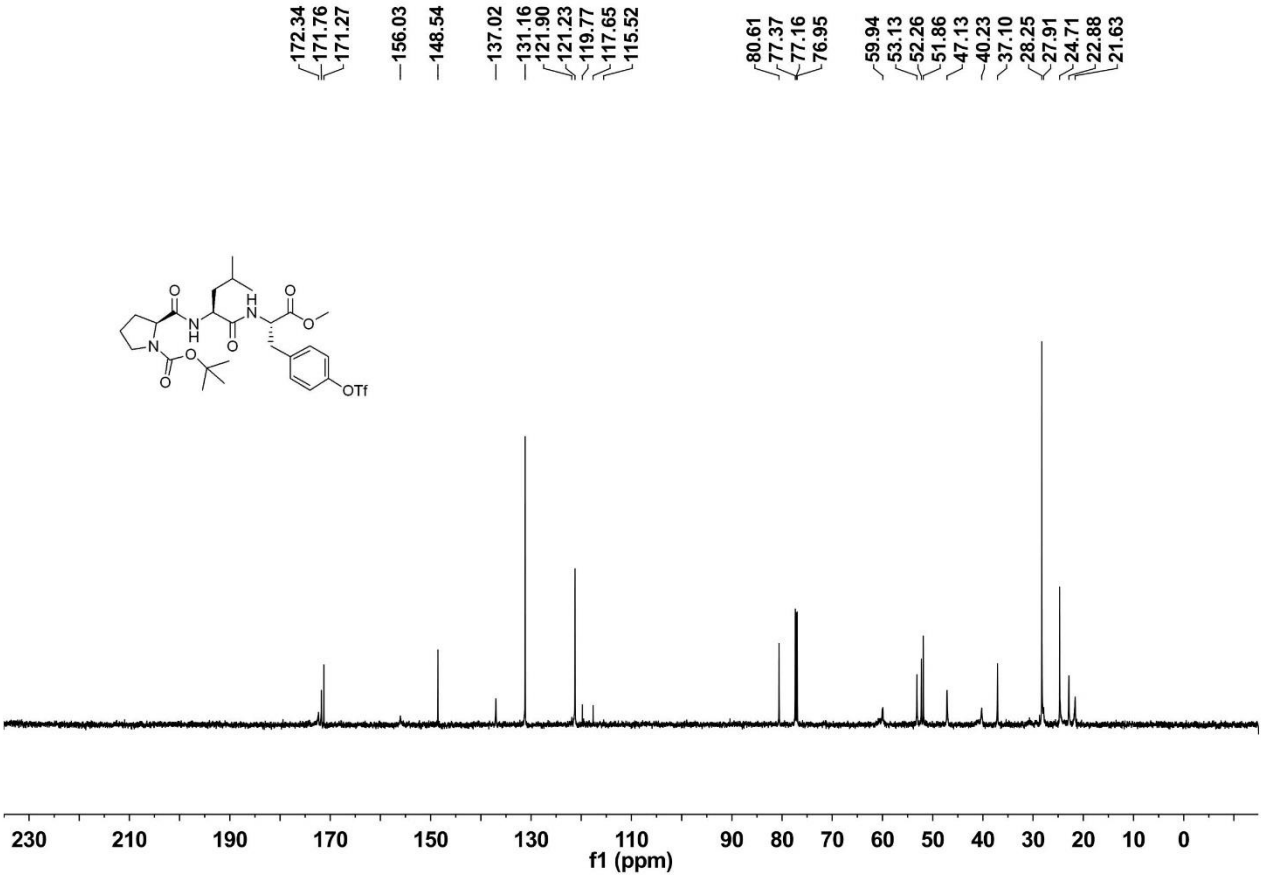


16g; ^{13}F NMR (564MHz, $CDCl_3$)

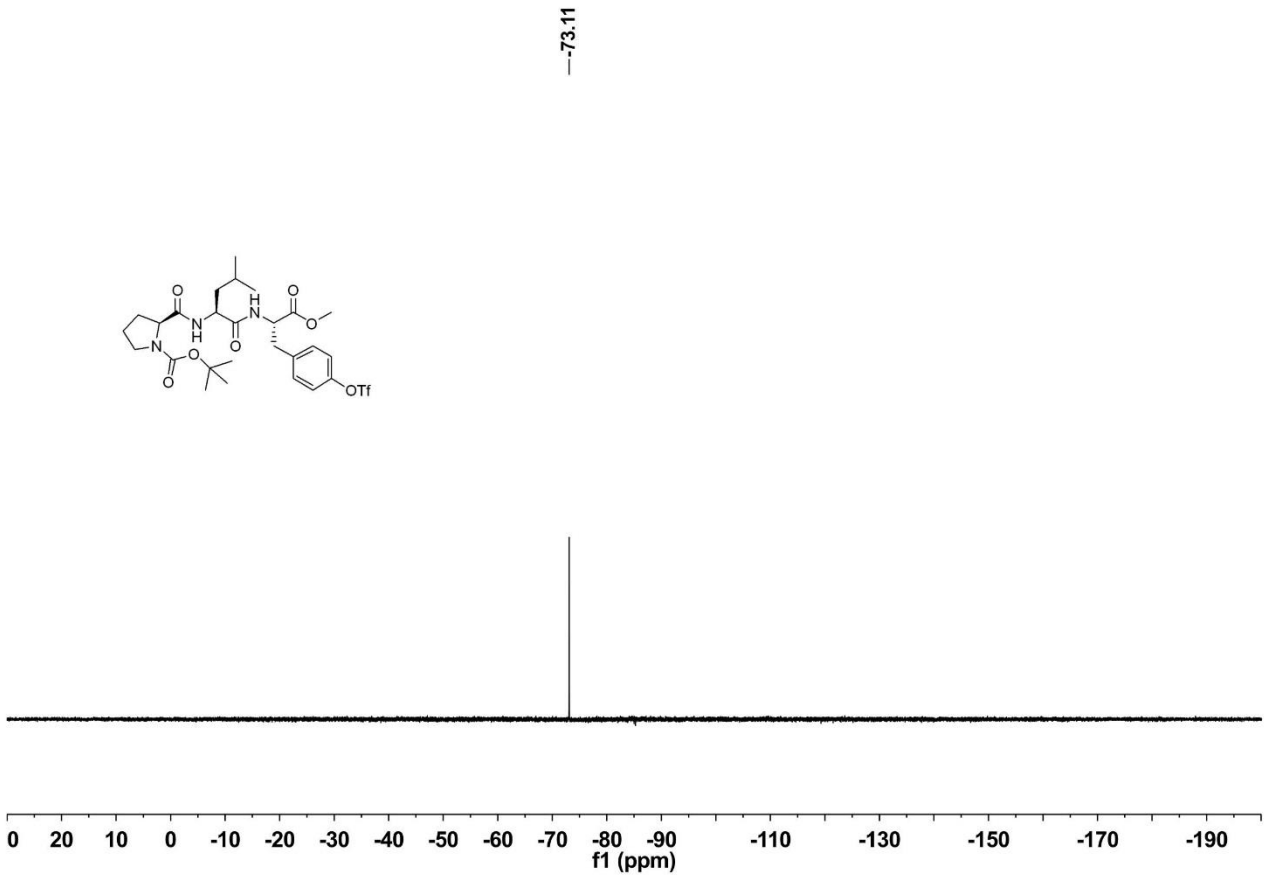


16h; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

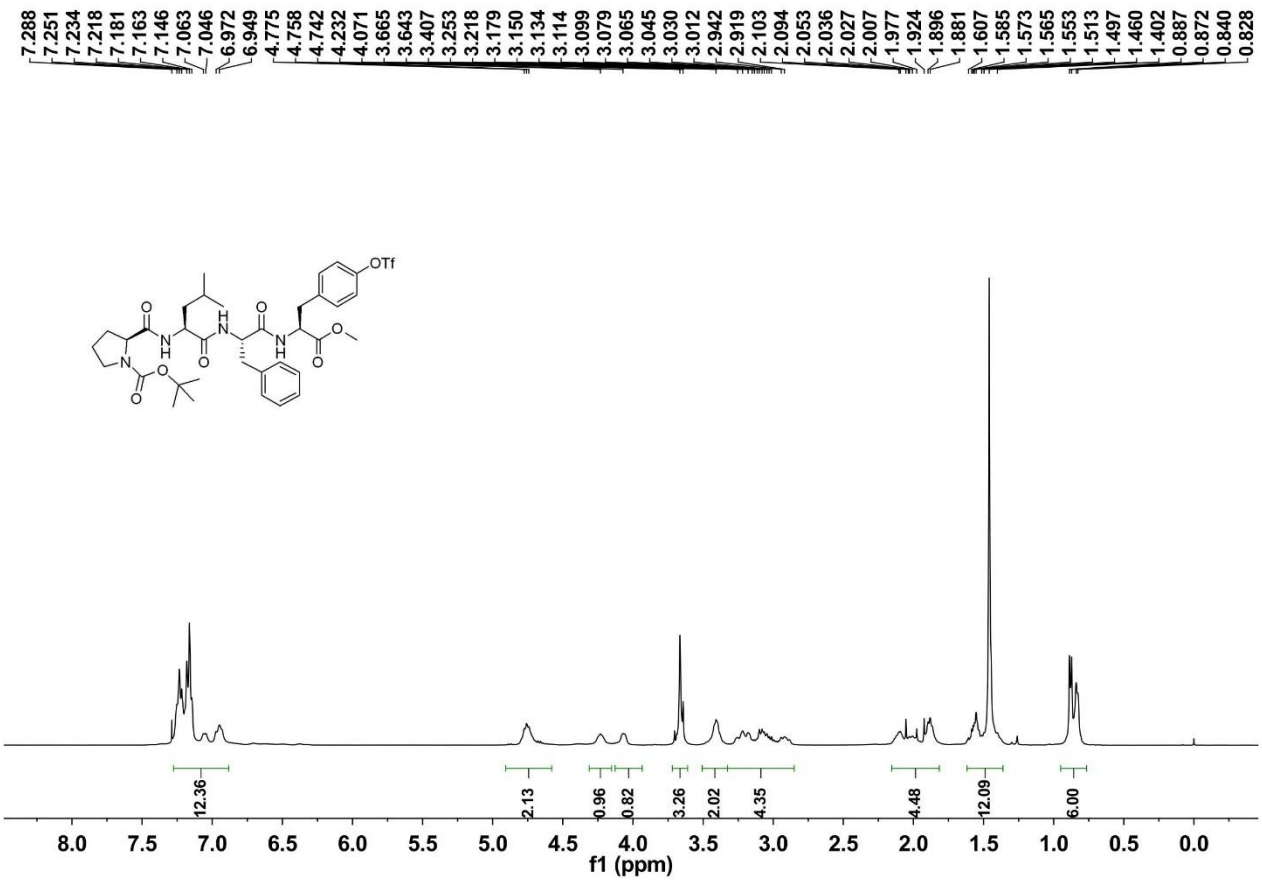


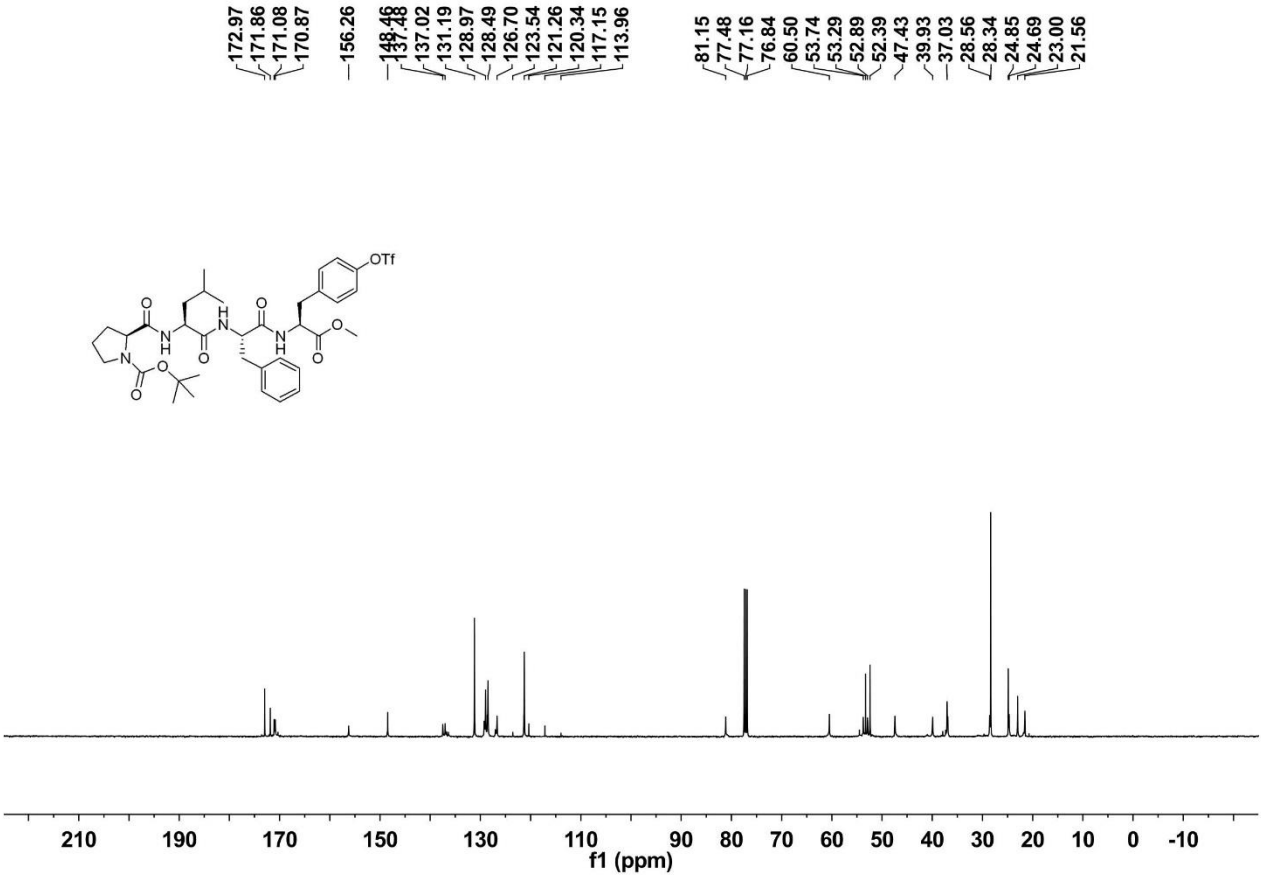


16h; ^{13}F NMR (376MHz, $CDCl_3$)

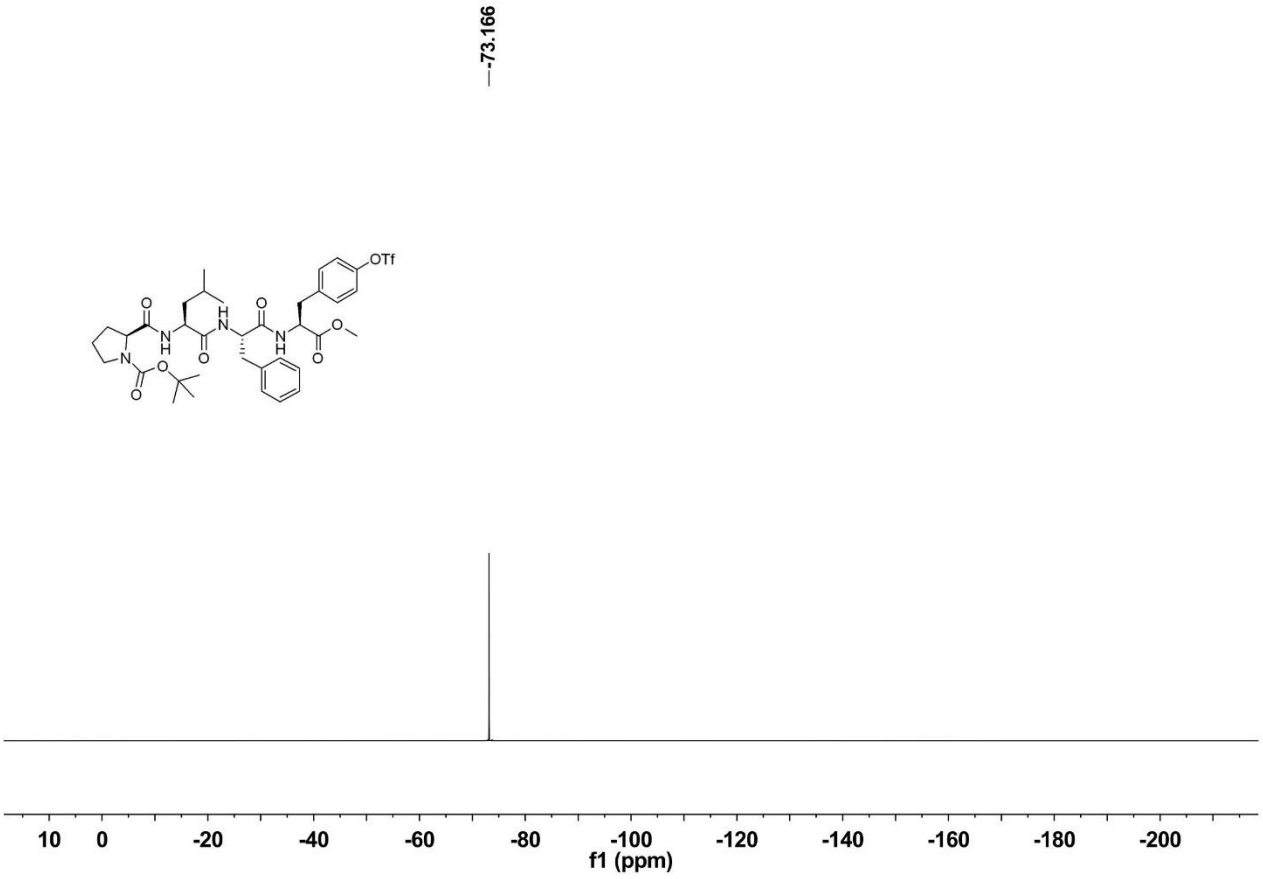


16i; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

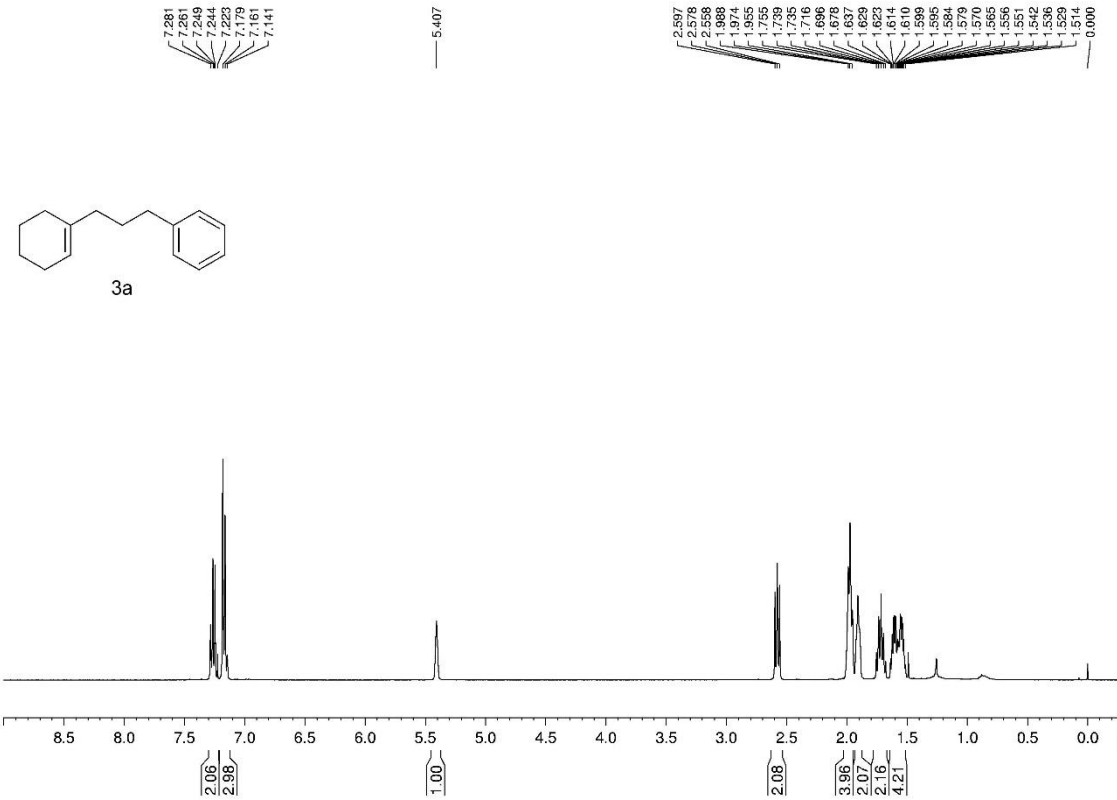


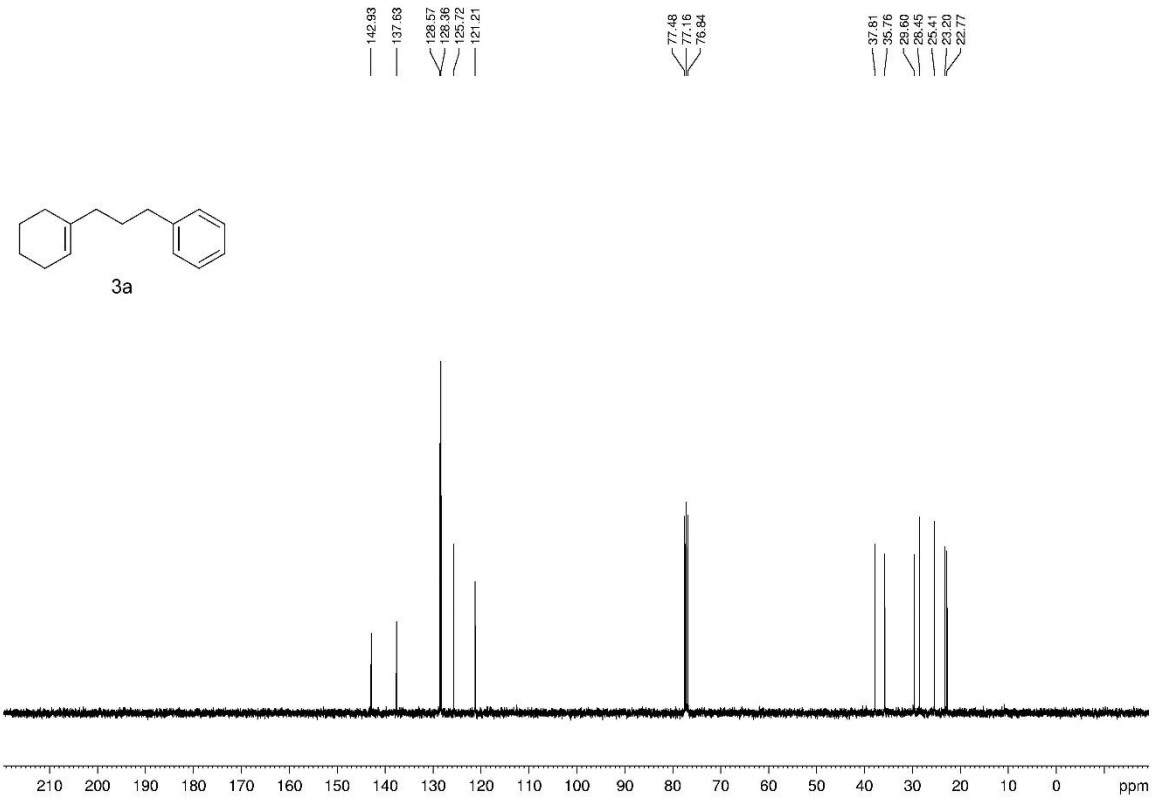


16i; ^{13}F NMR (376MHz, $CDCl_3$)

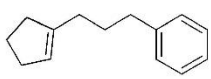


3a; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

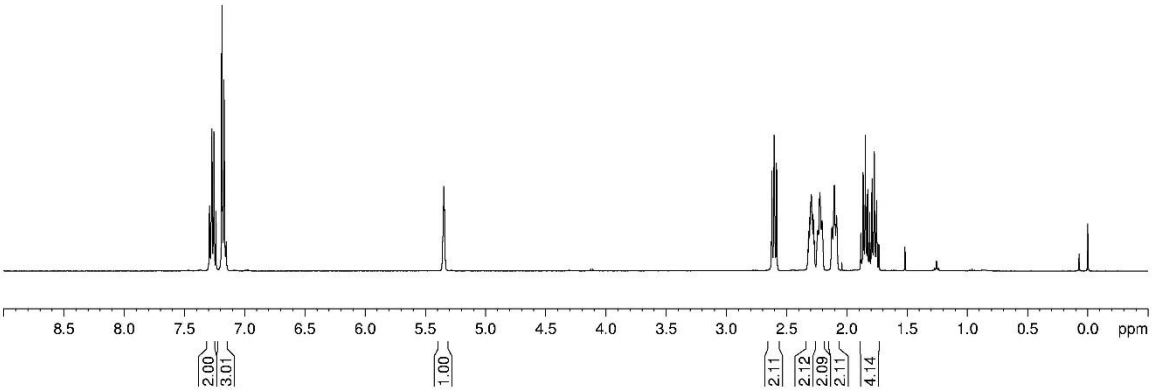


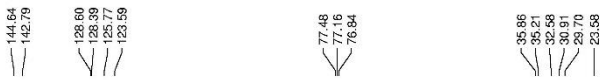


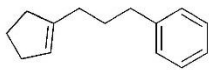
3b; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



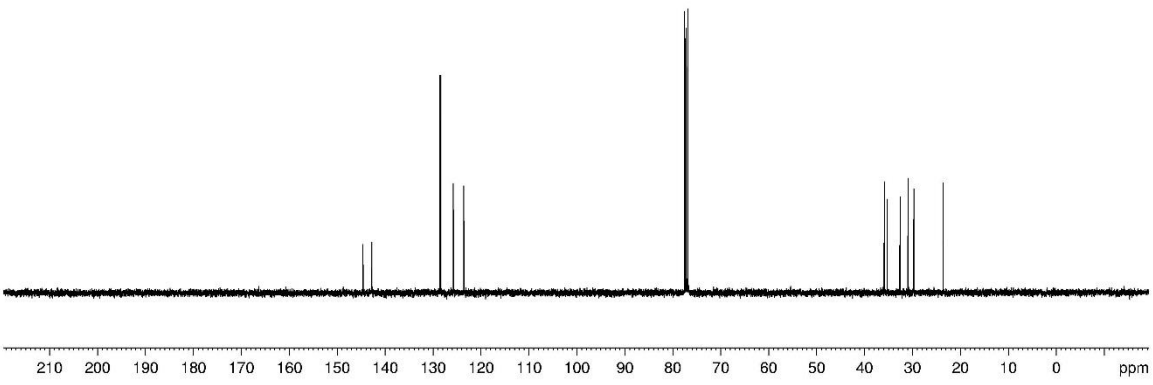
3b



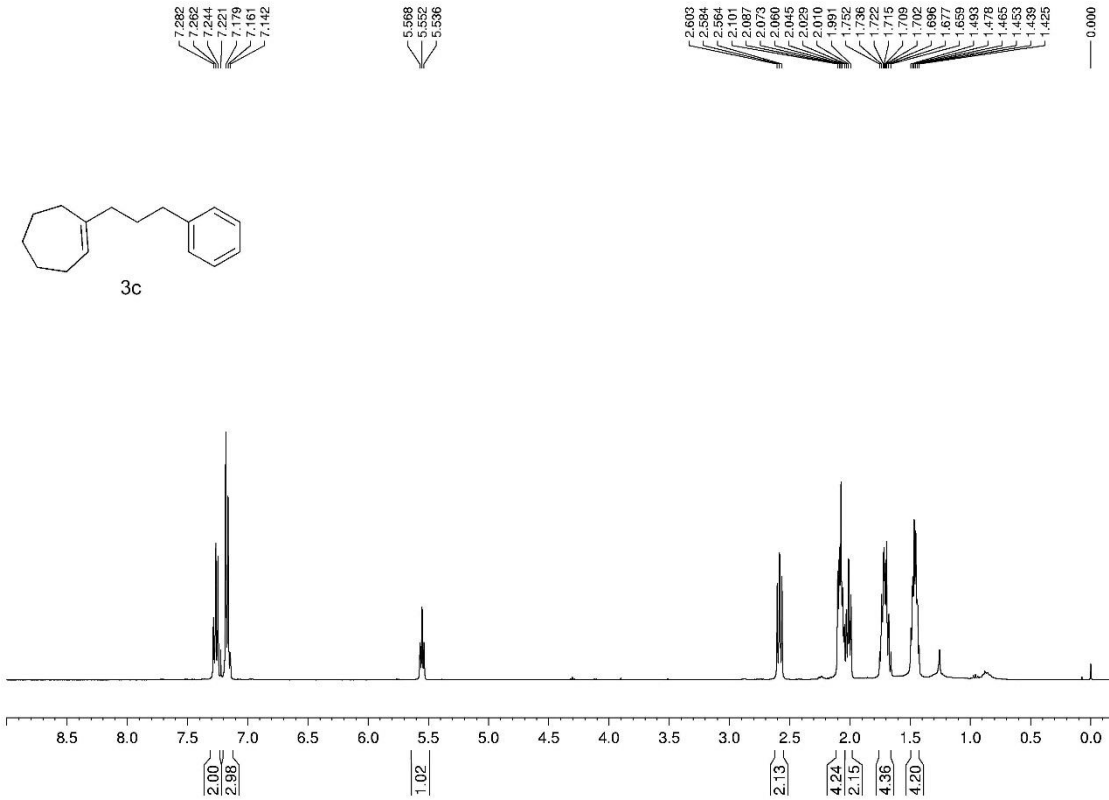


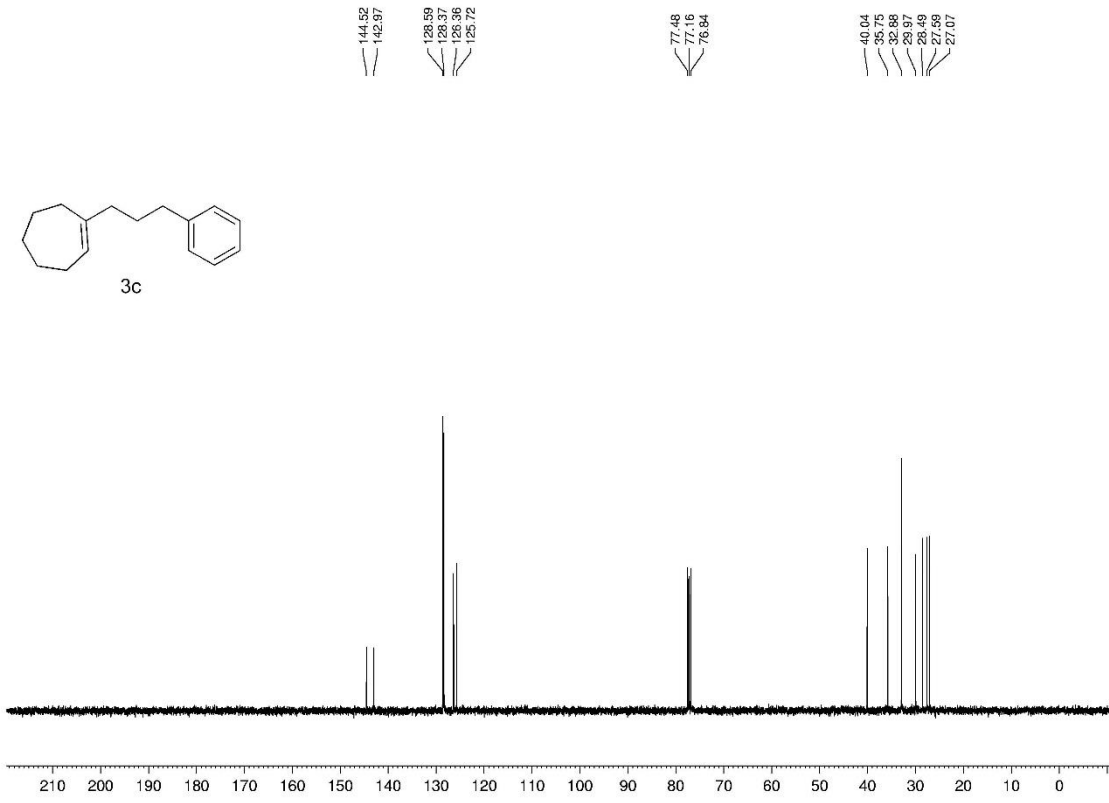


3b

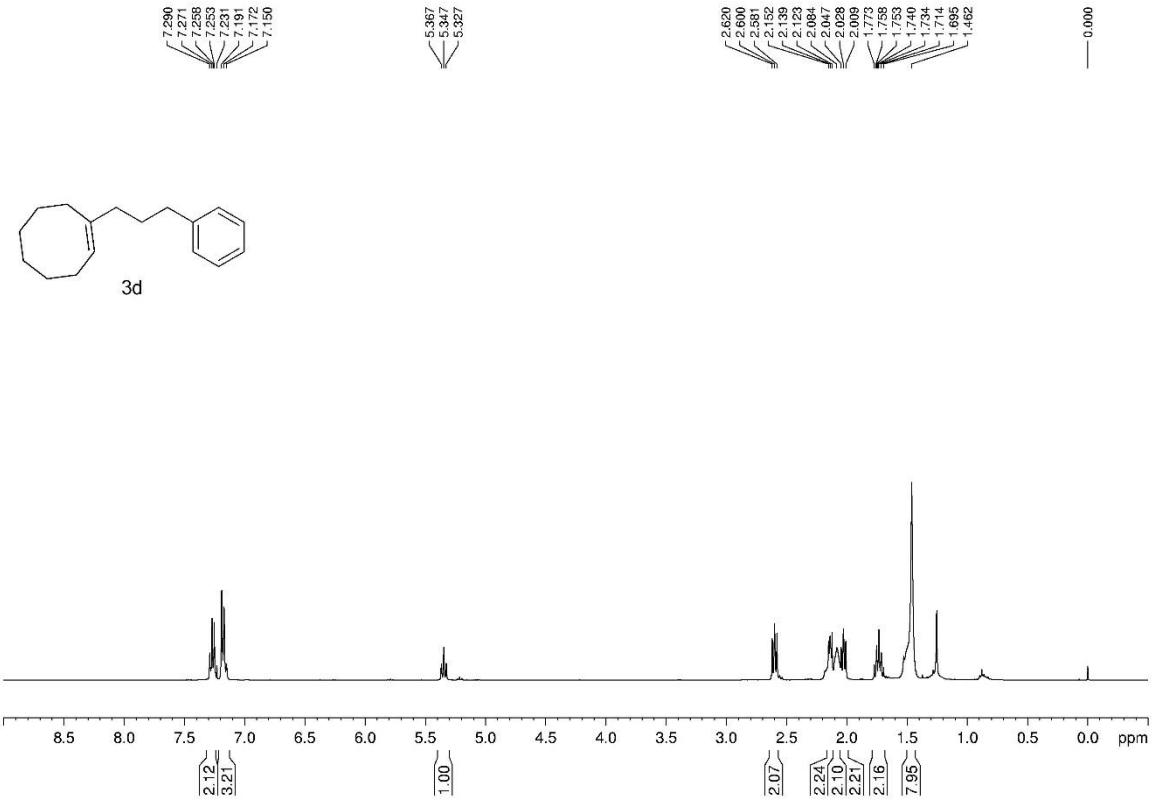


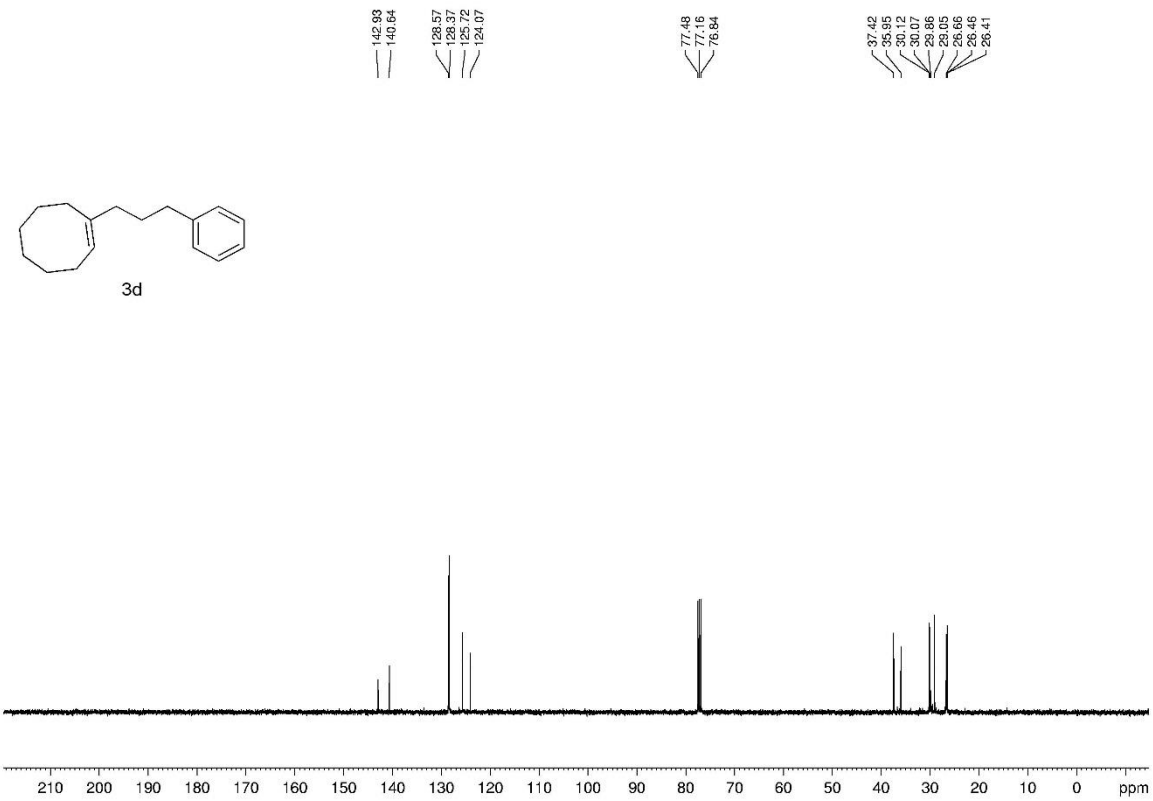
3c; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



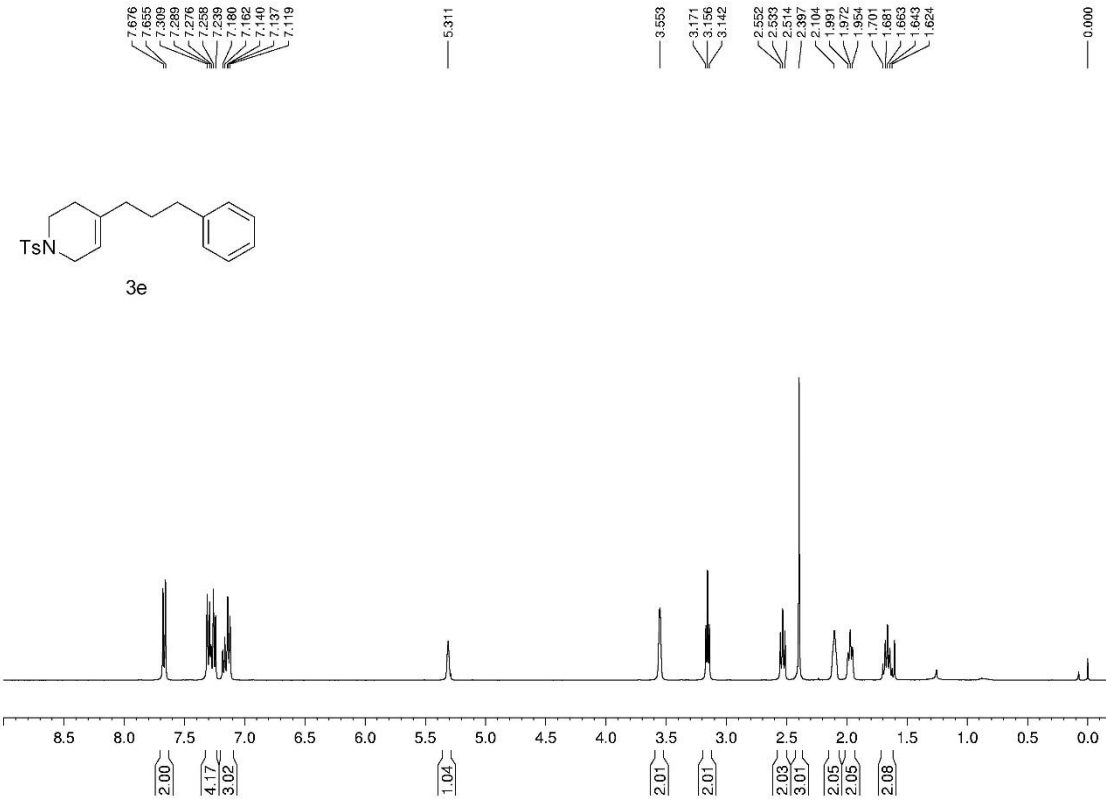


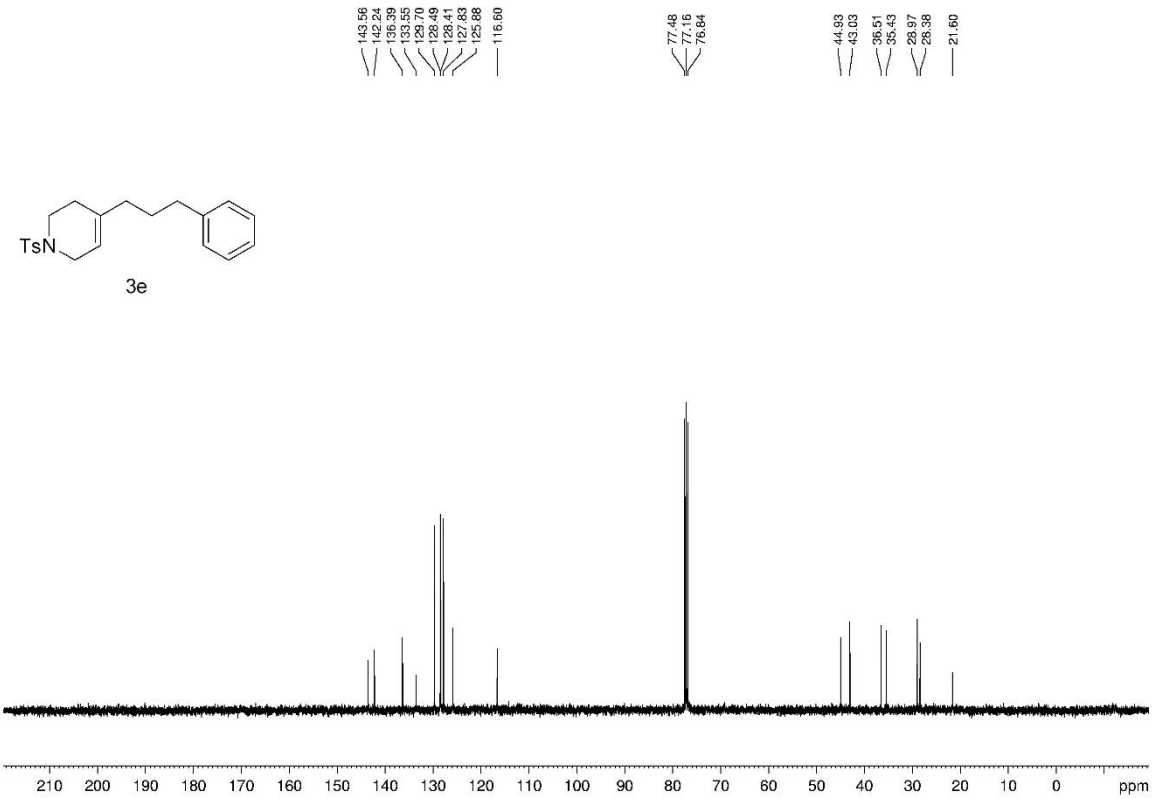
3d; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



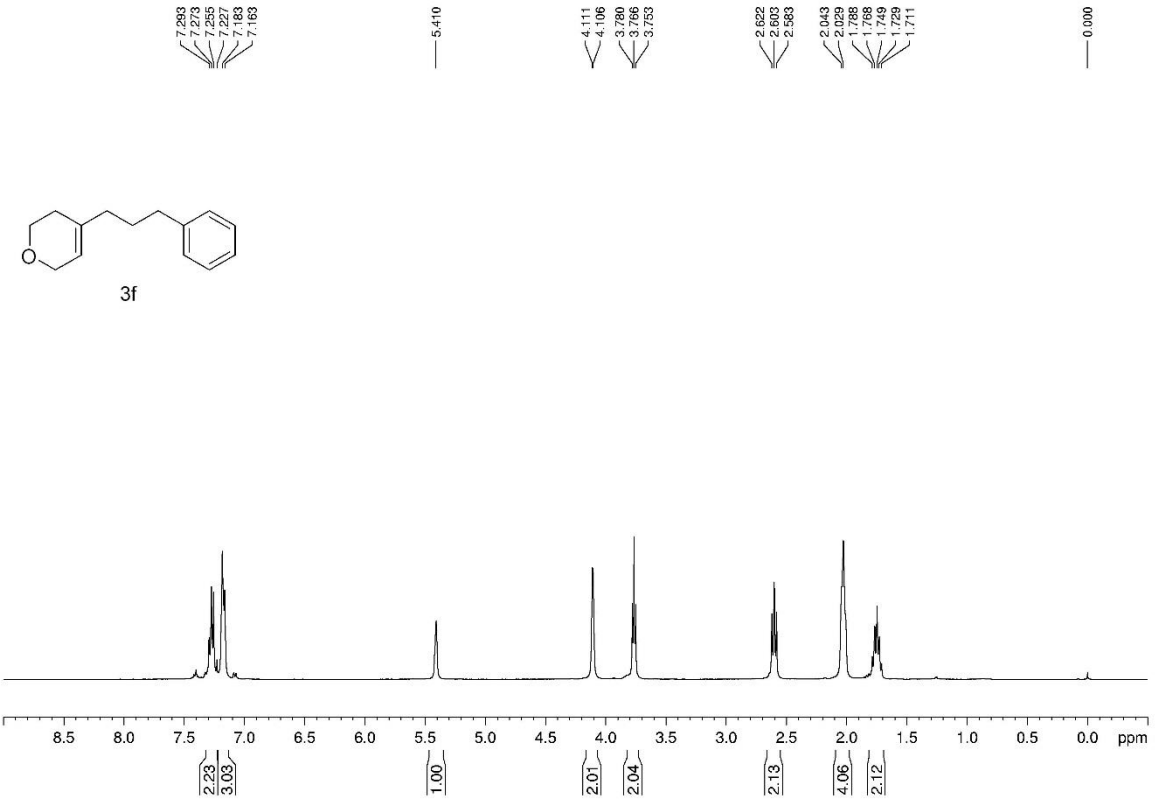


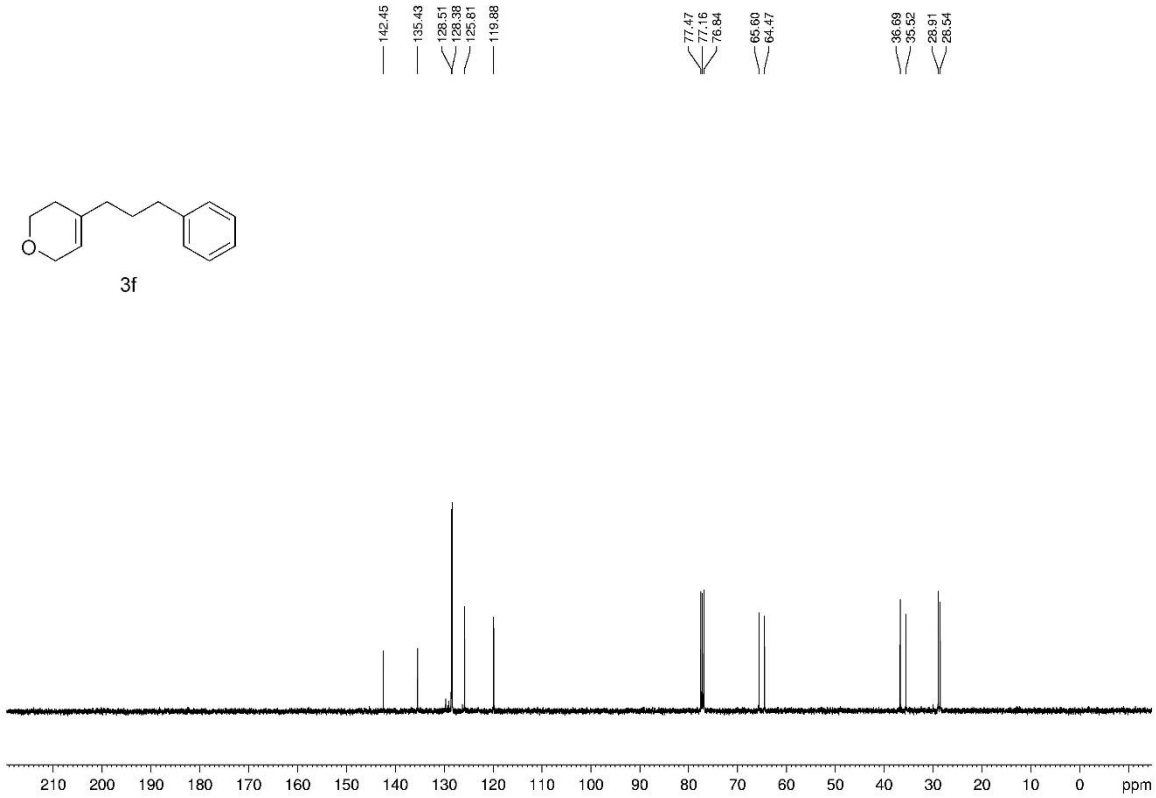
3e; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)



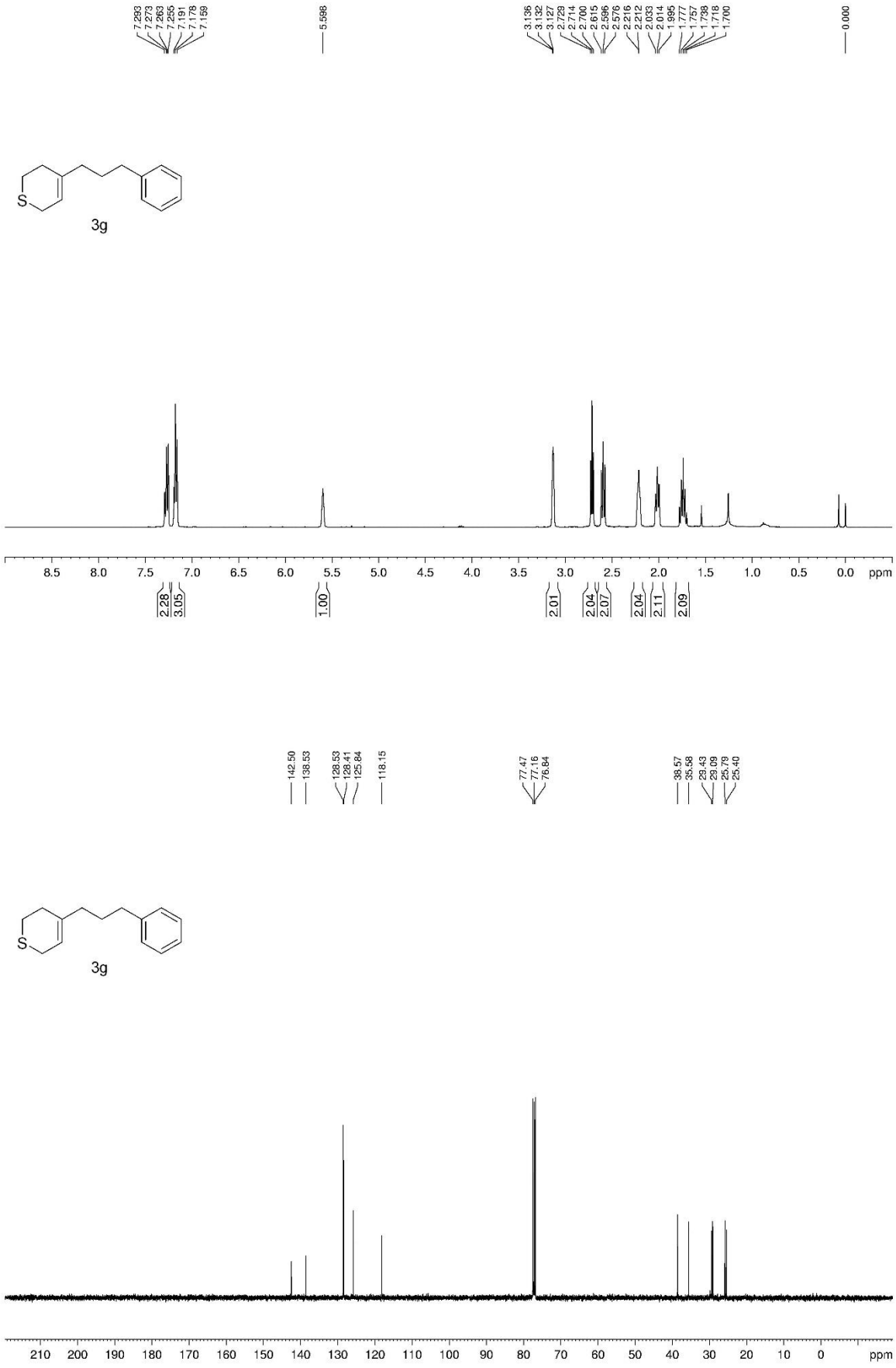


3f; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

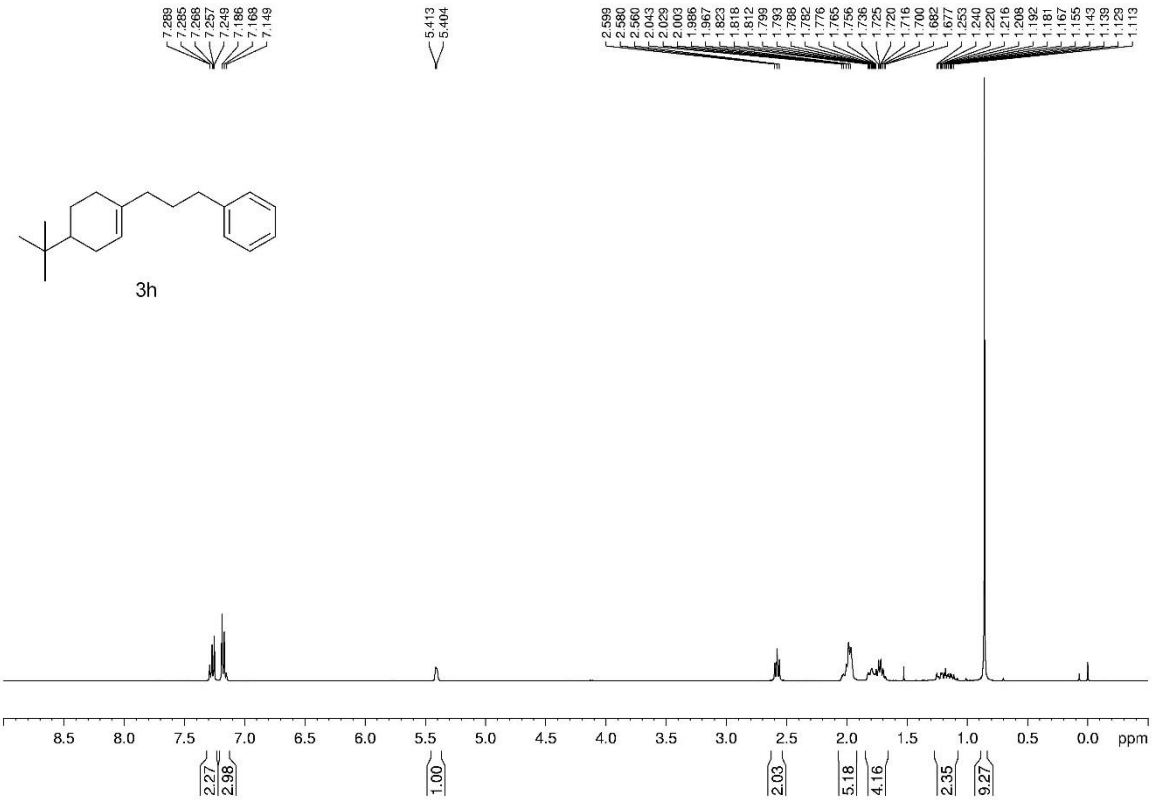


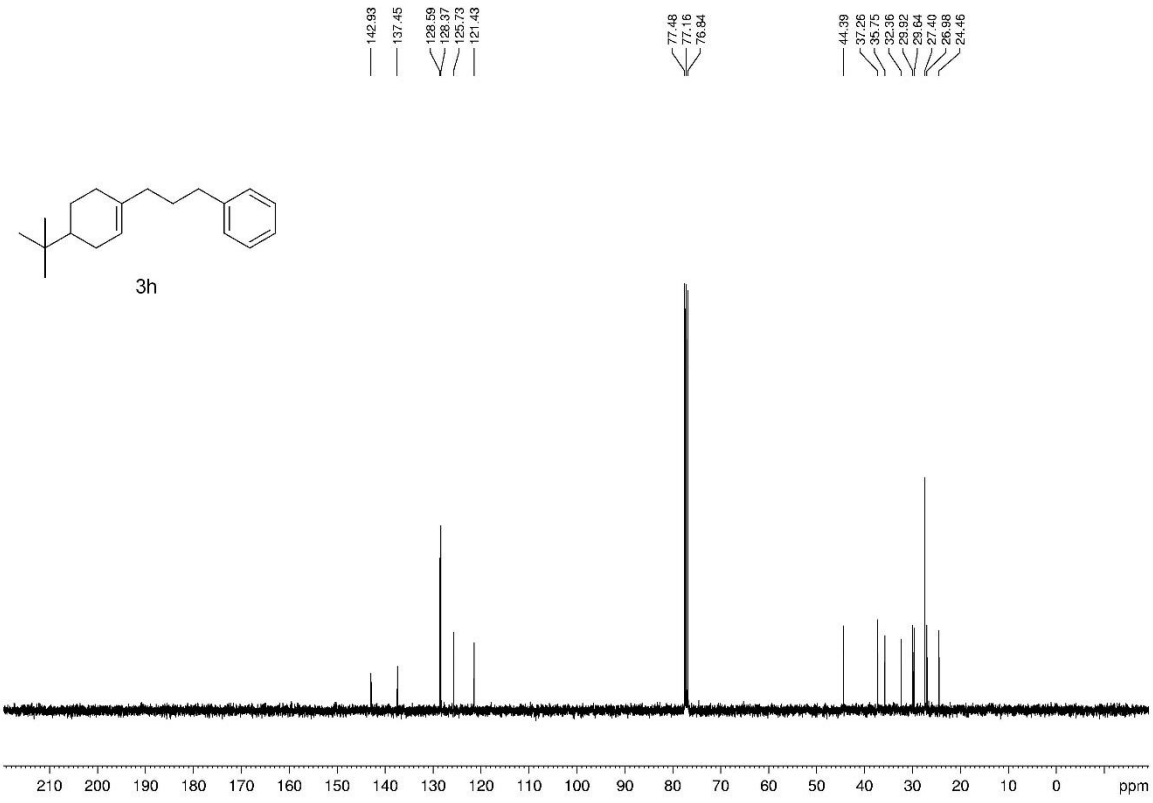


3g; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

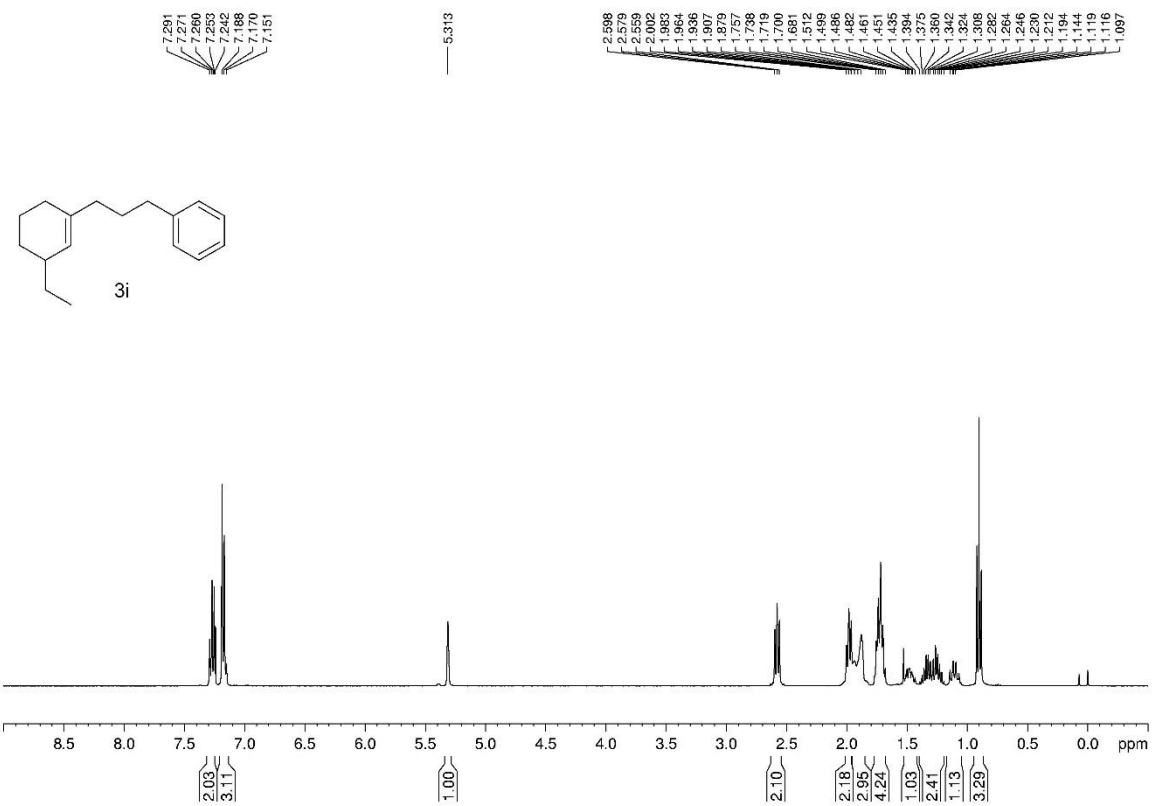


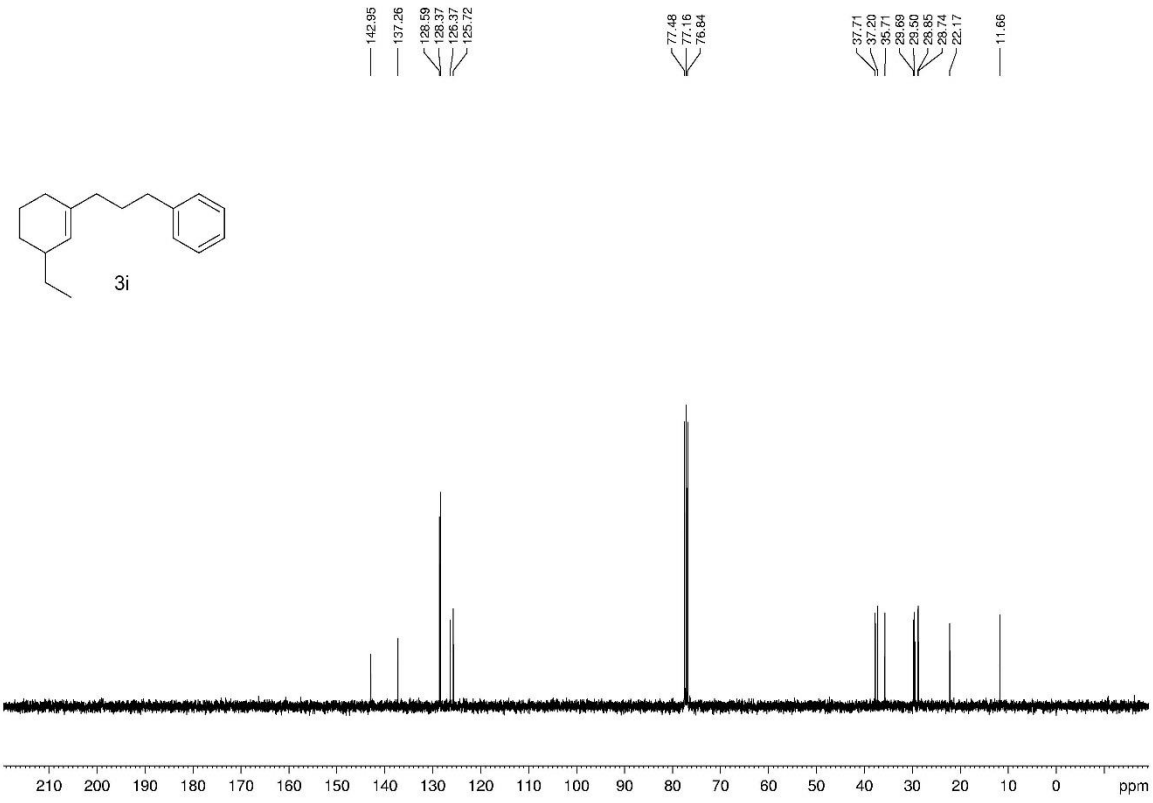
3h; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



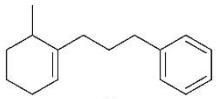


3i; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

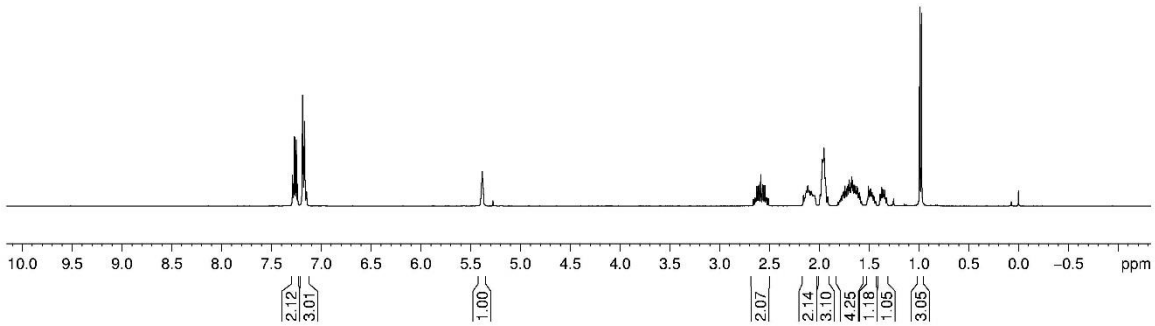


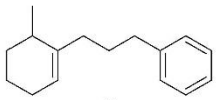


3j; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

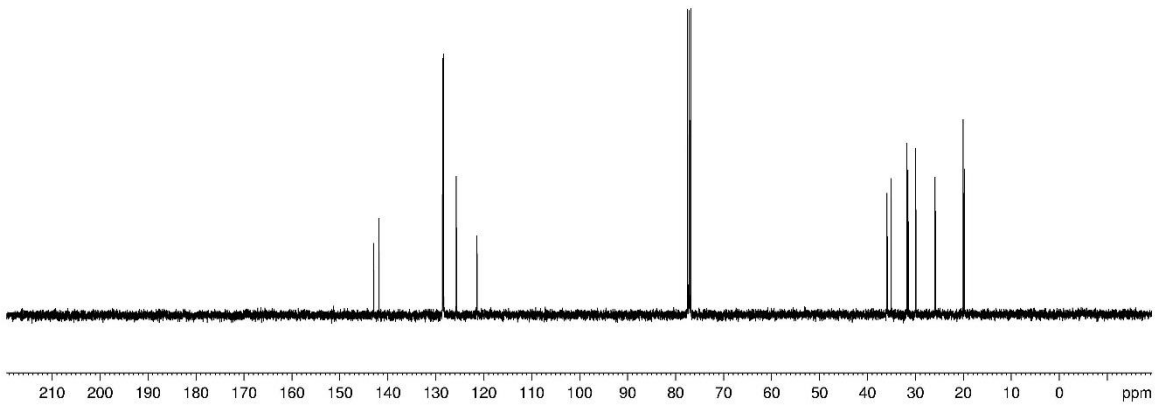


3j

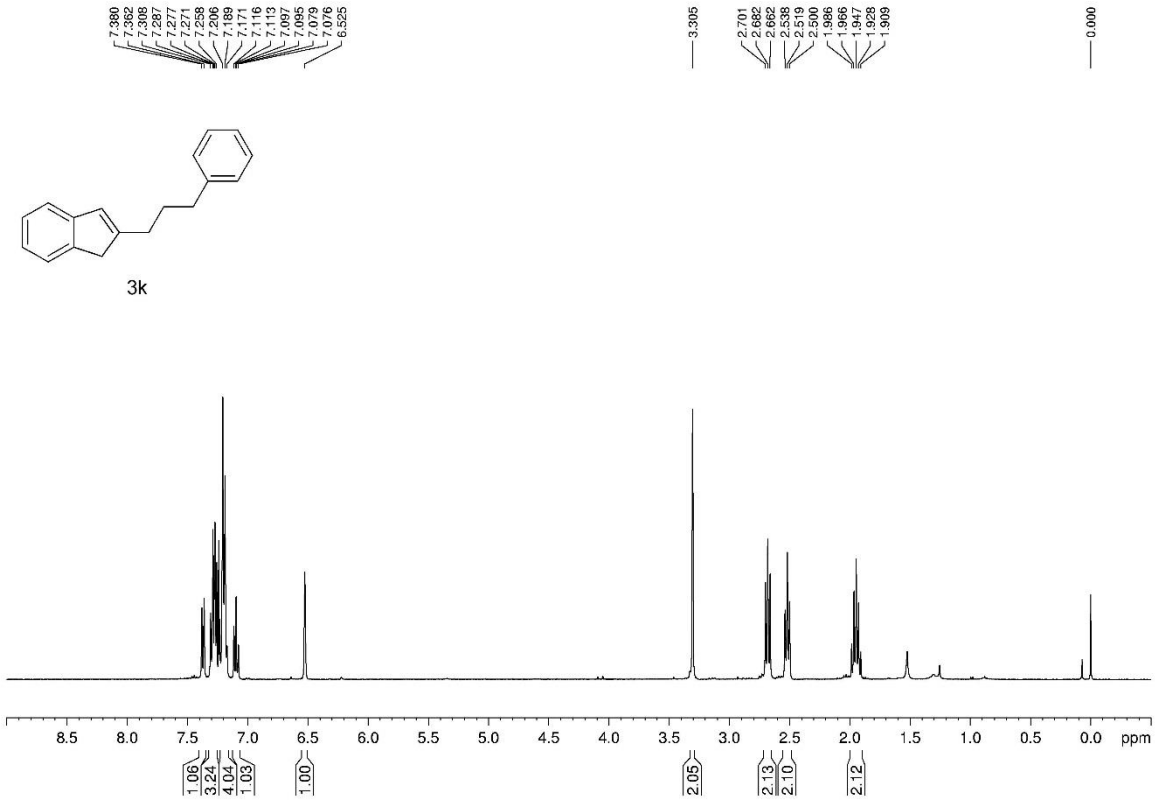


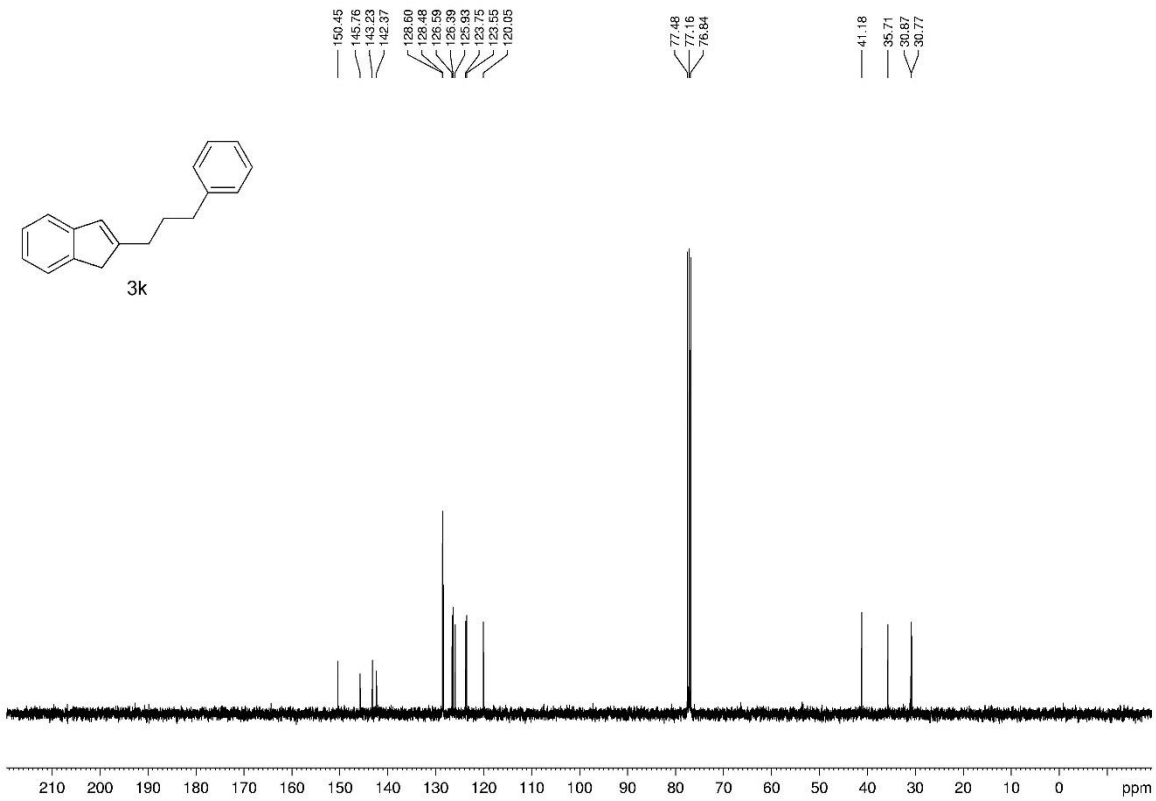


3j

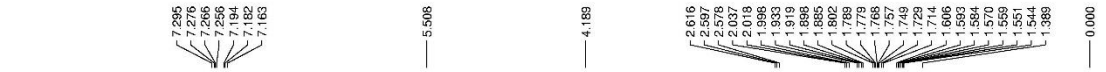


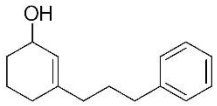
3k; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

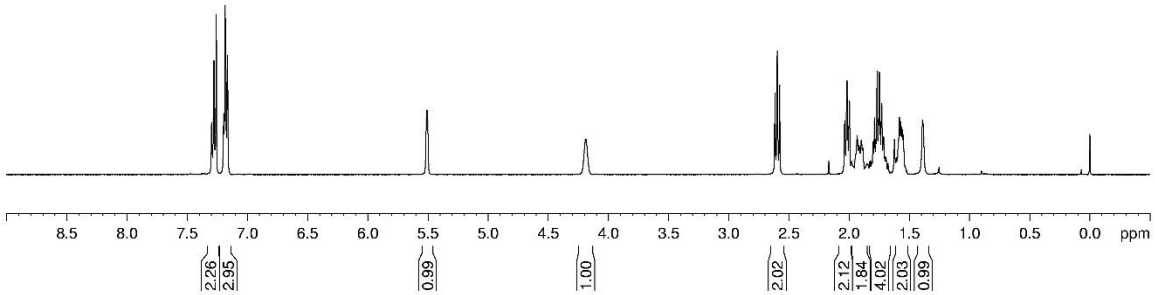


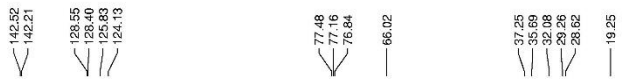


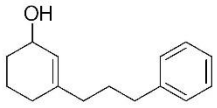
3l; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

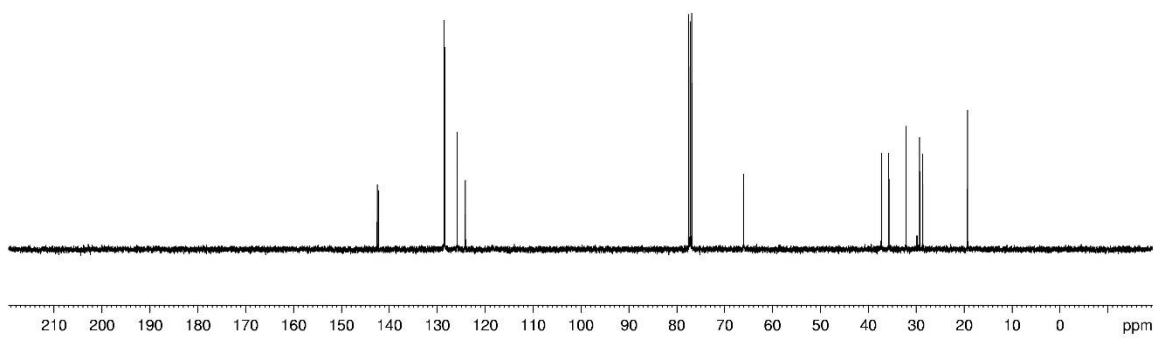




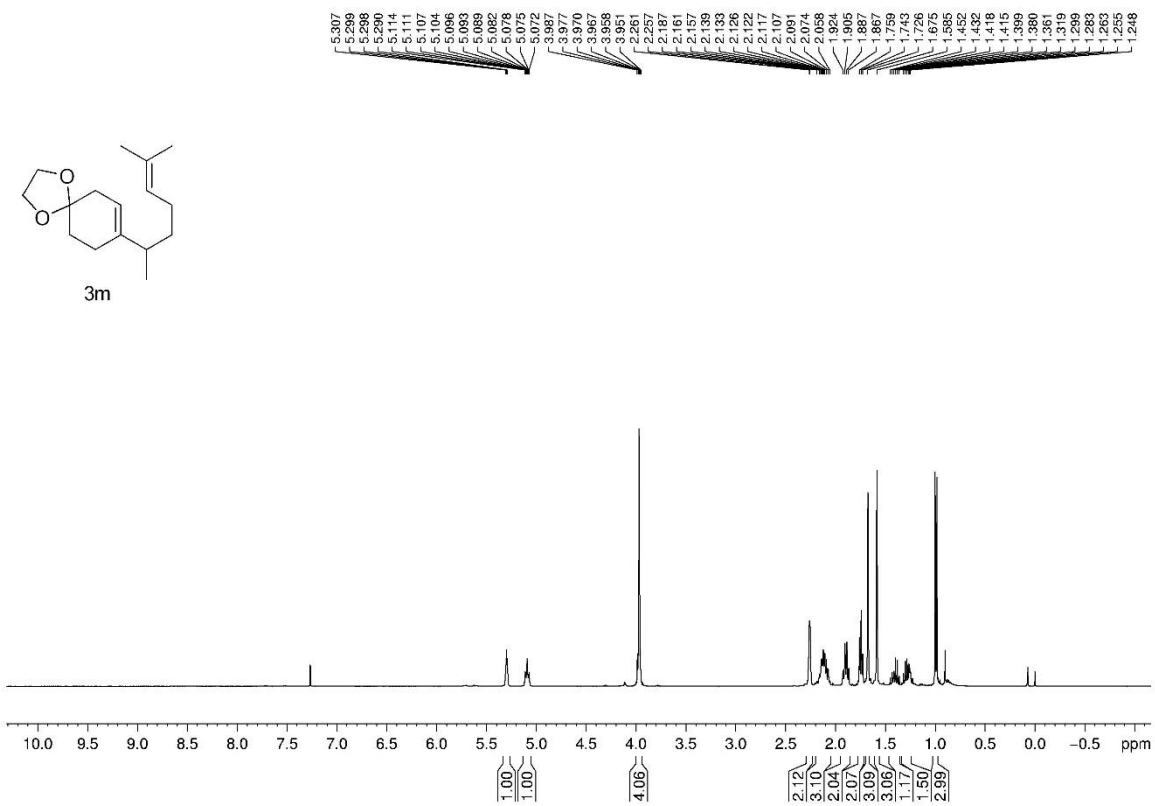


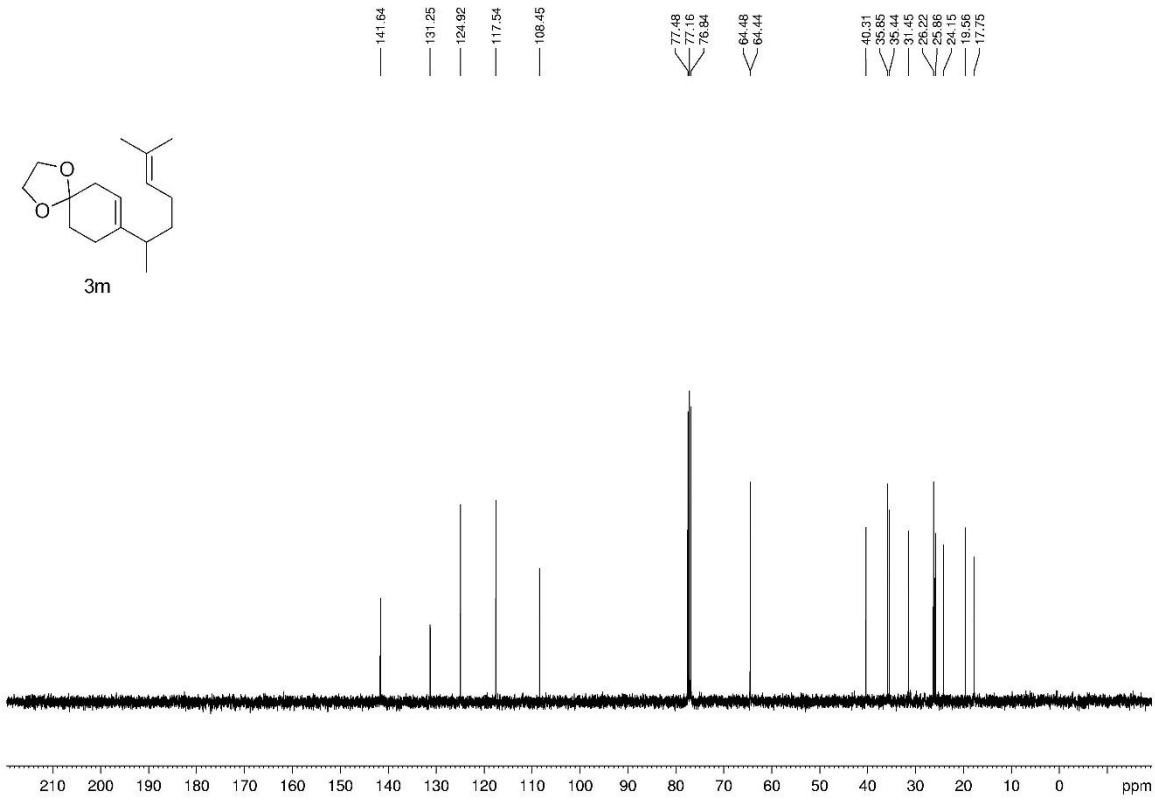




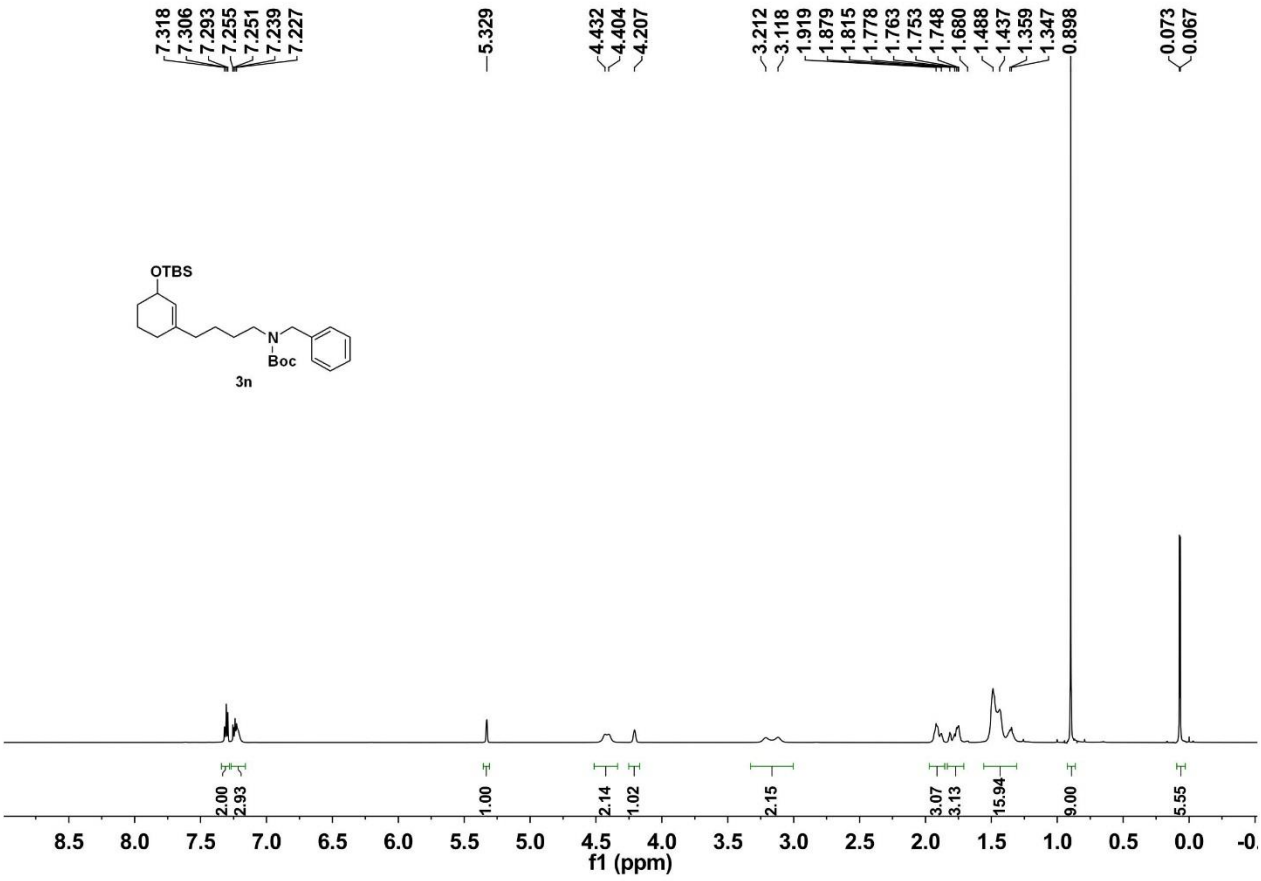


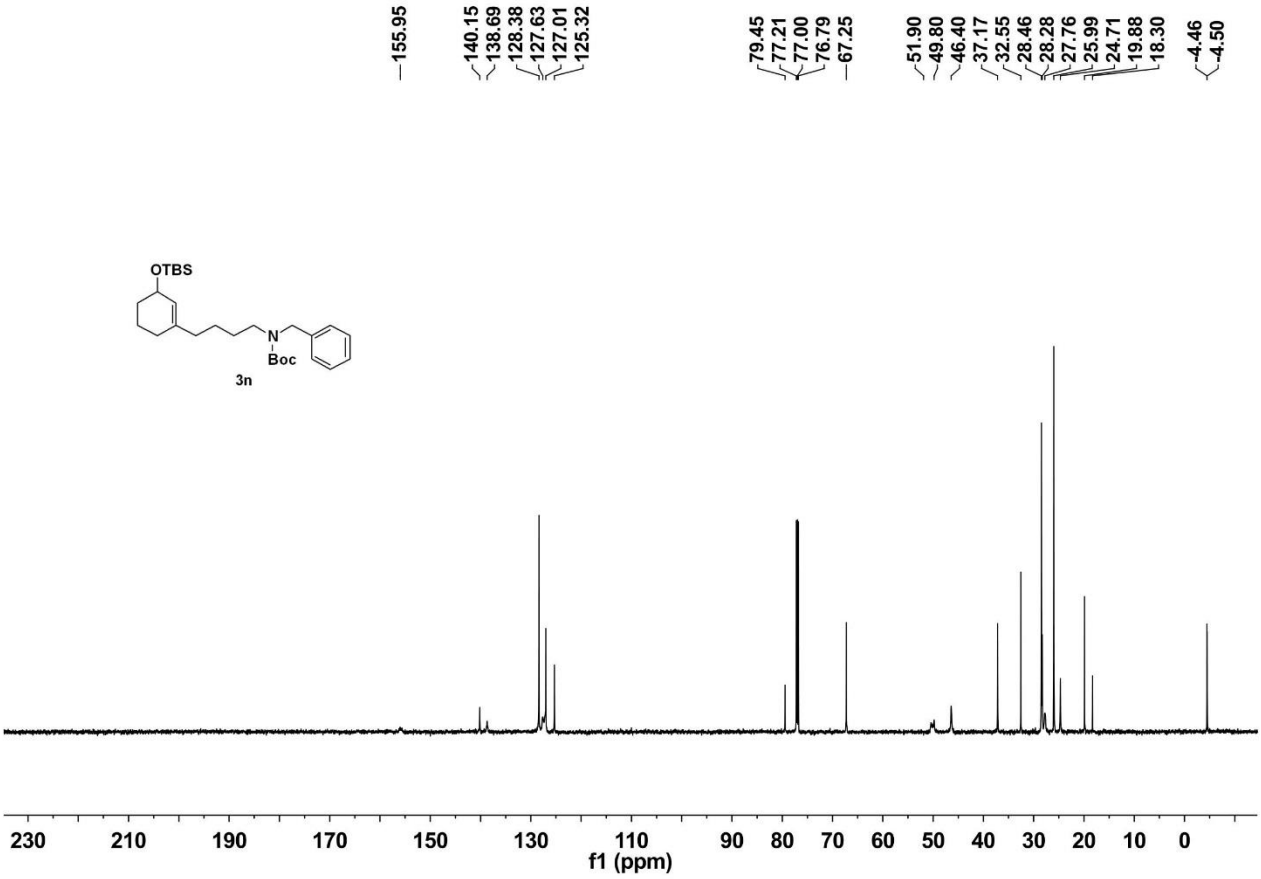
3m; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



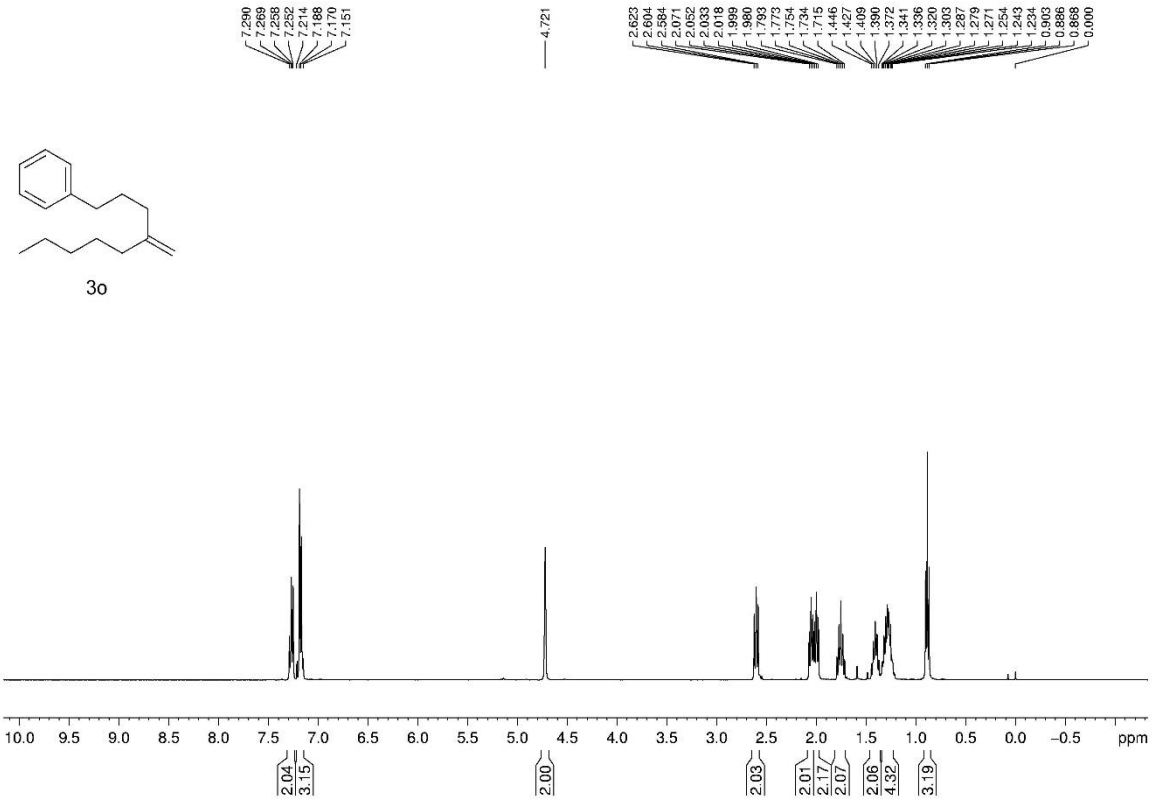


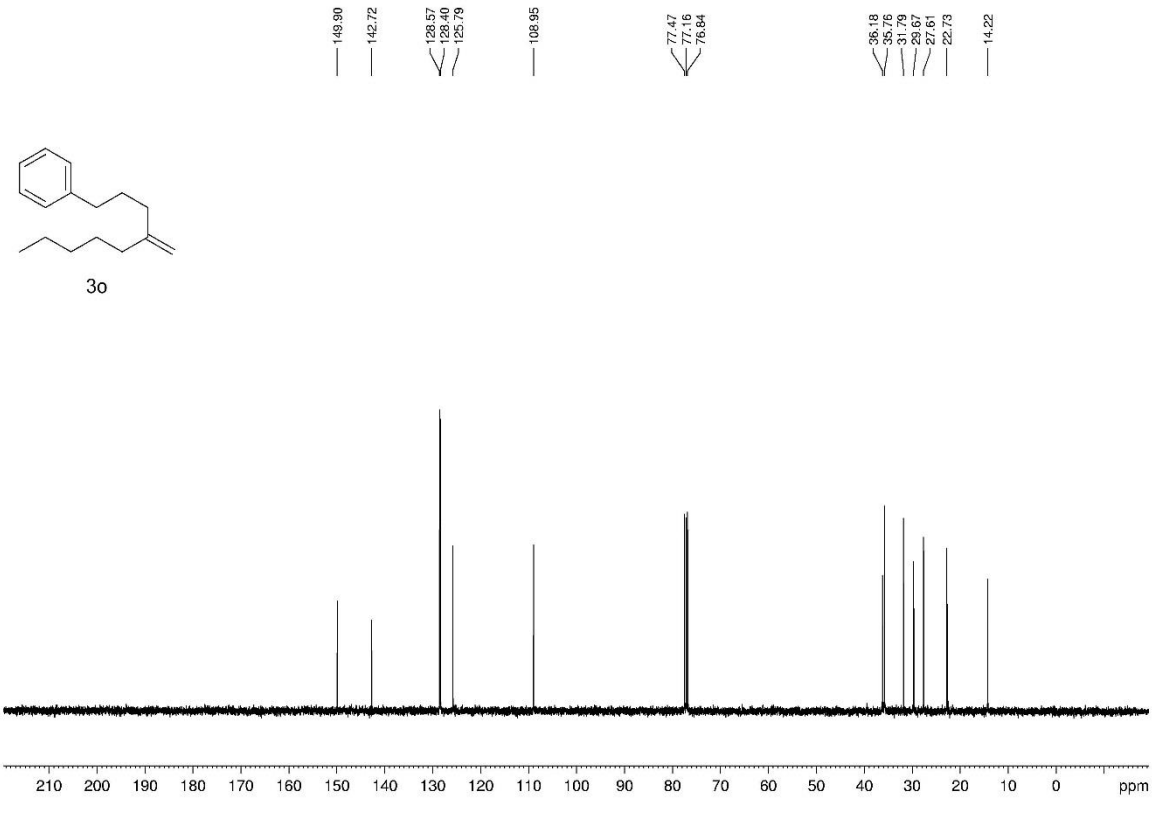
3n; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)



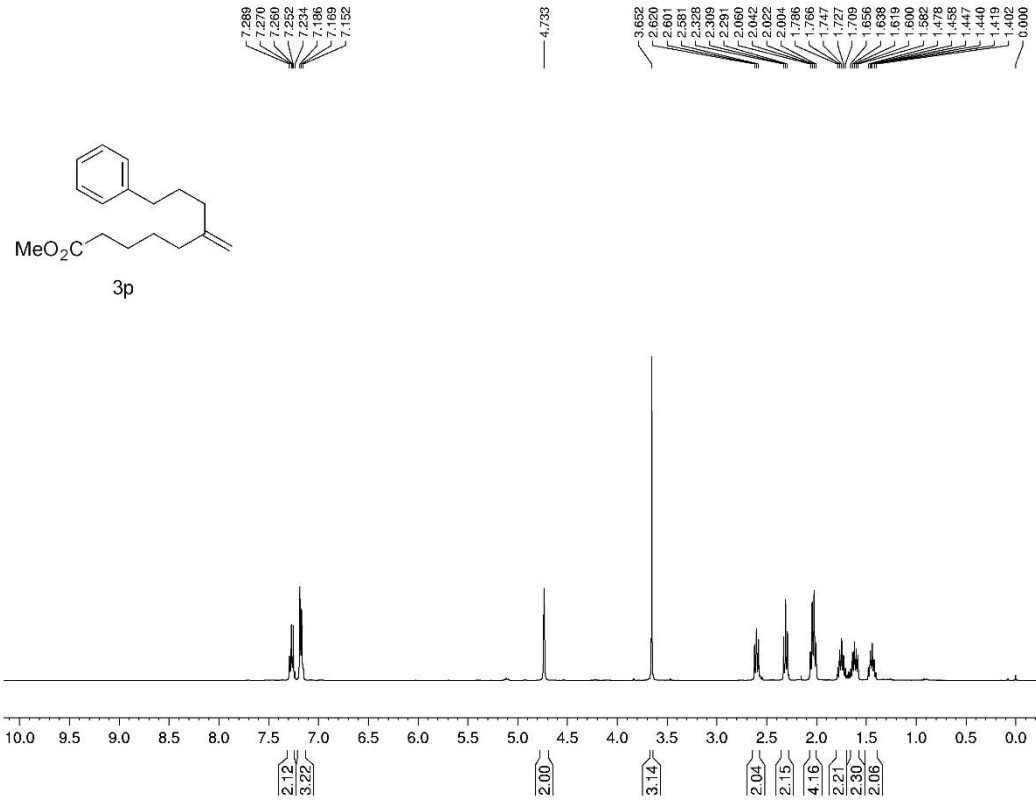


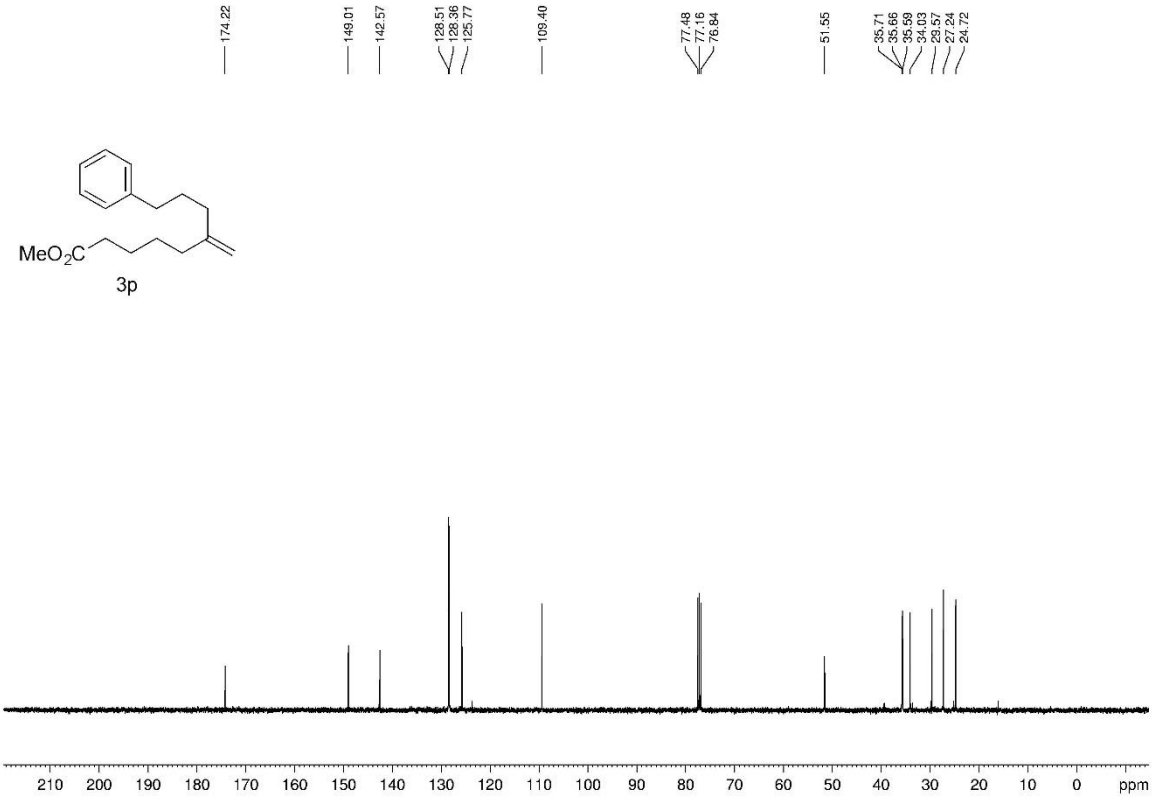
3o; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



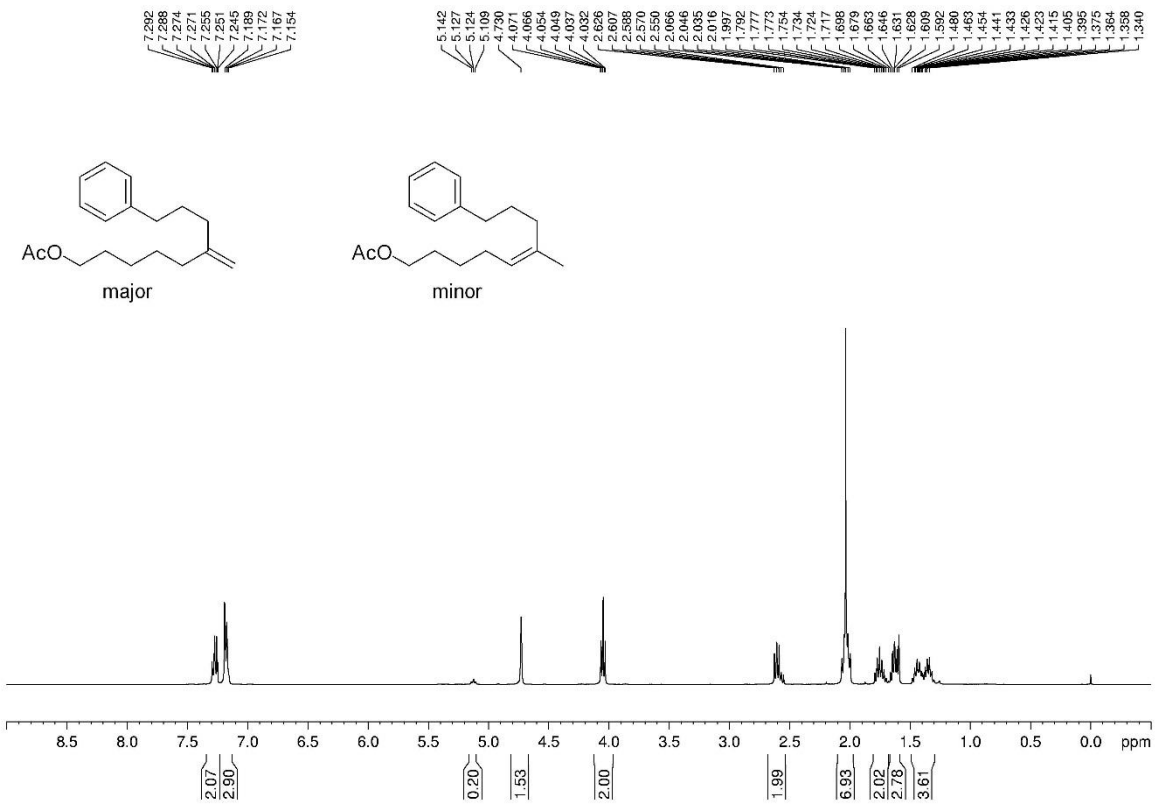


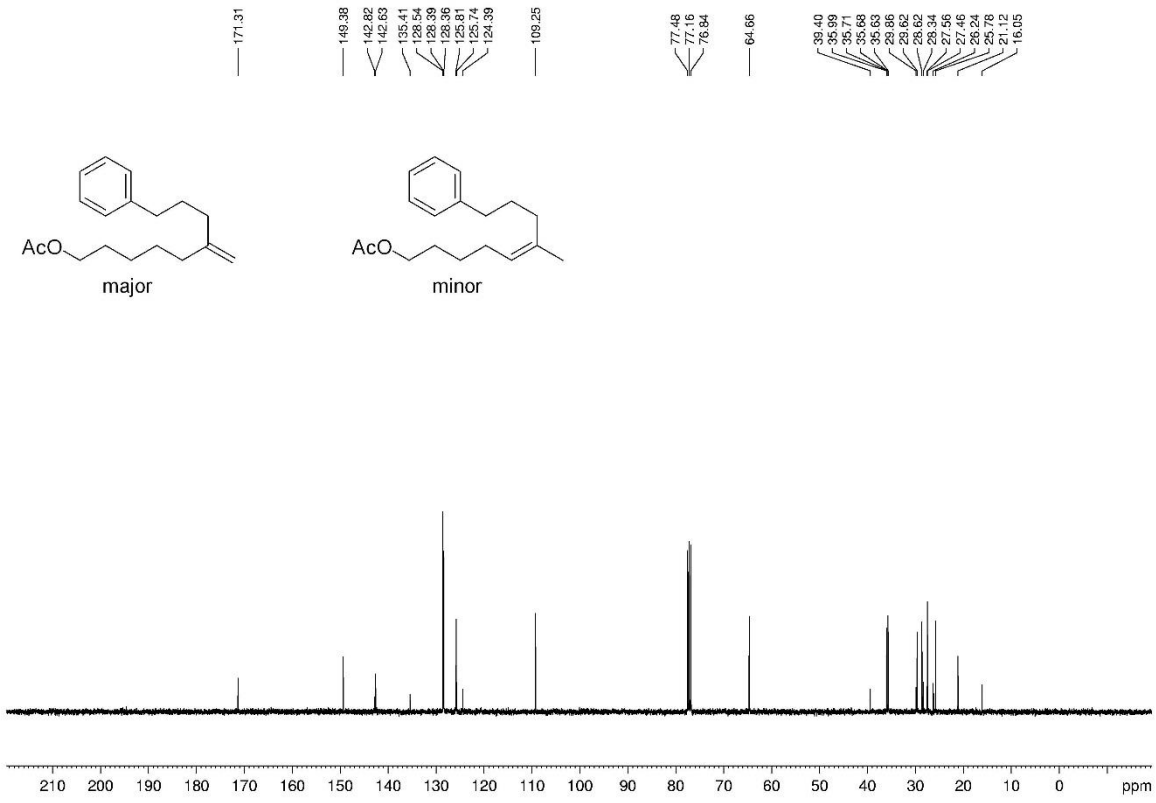
3p; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



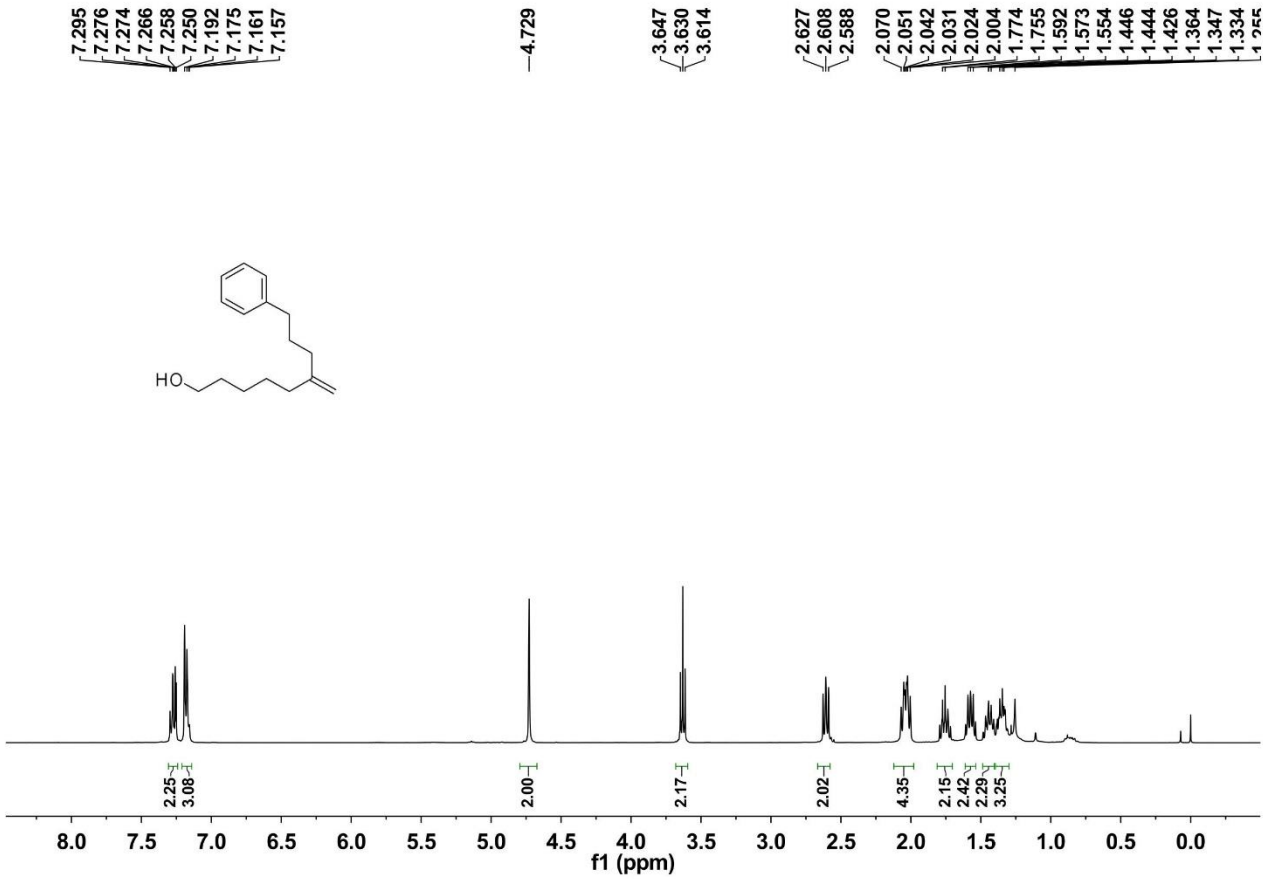


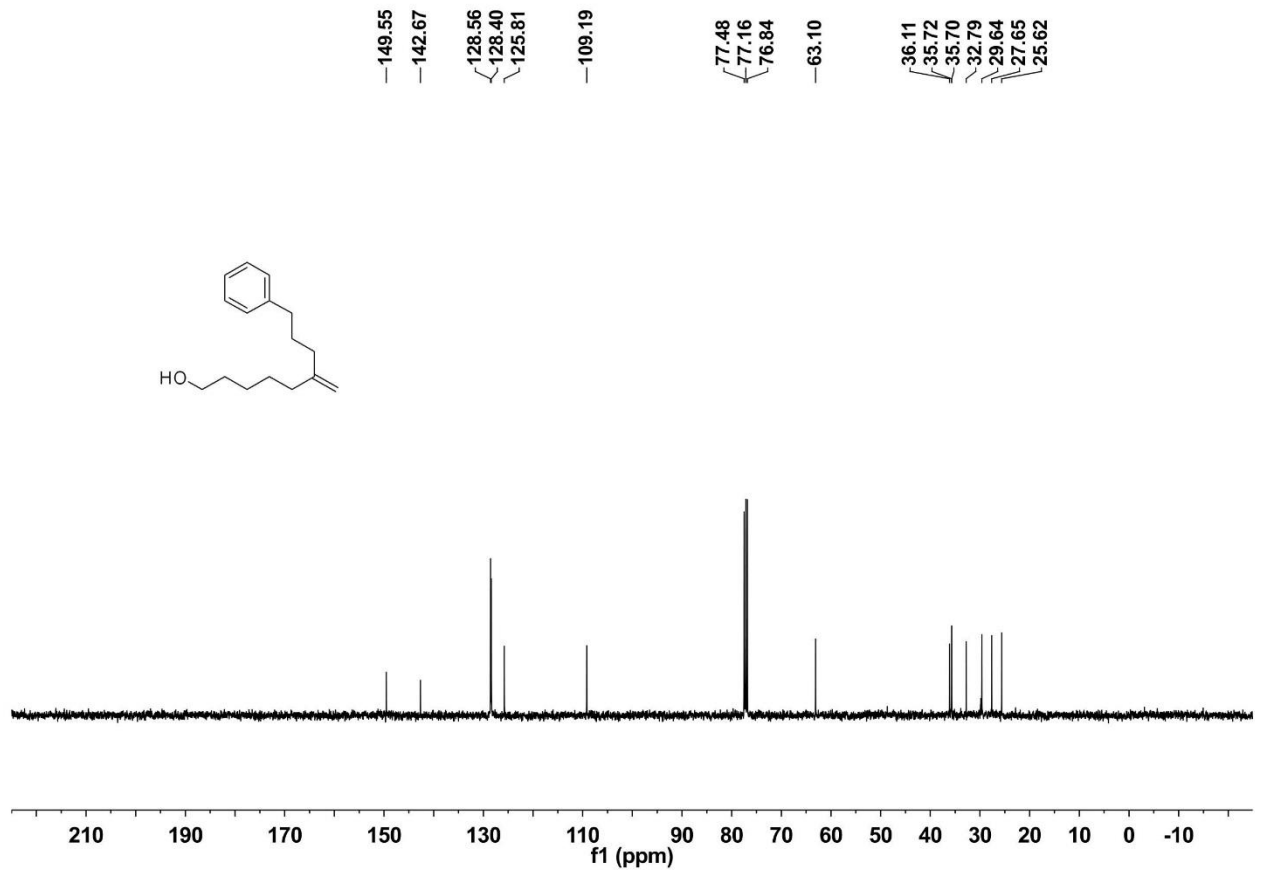
3q; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



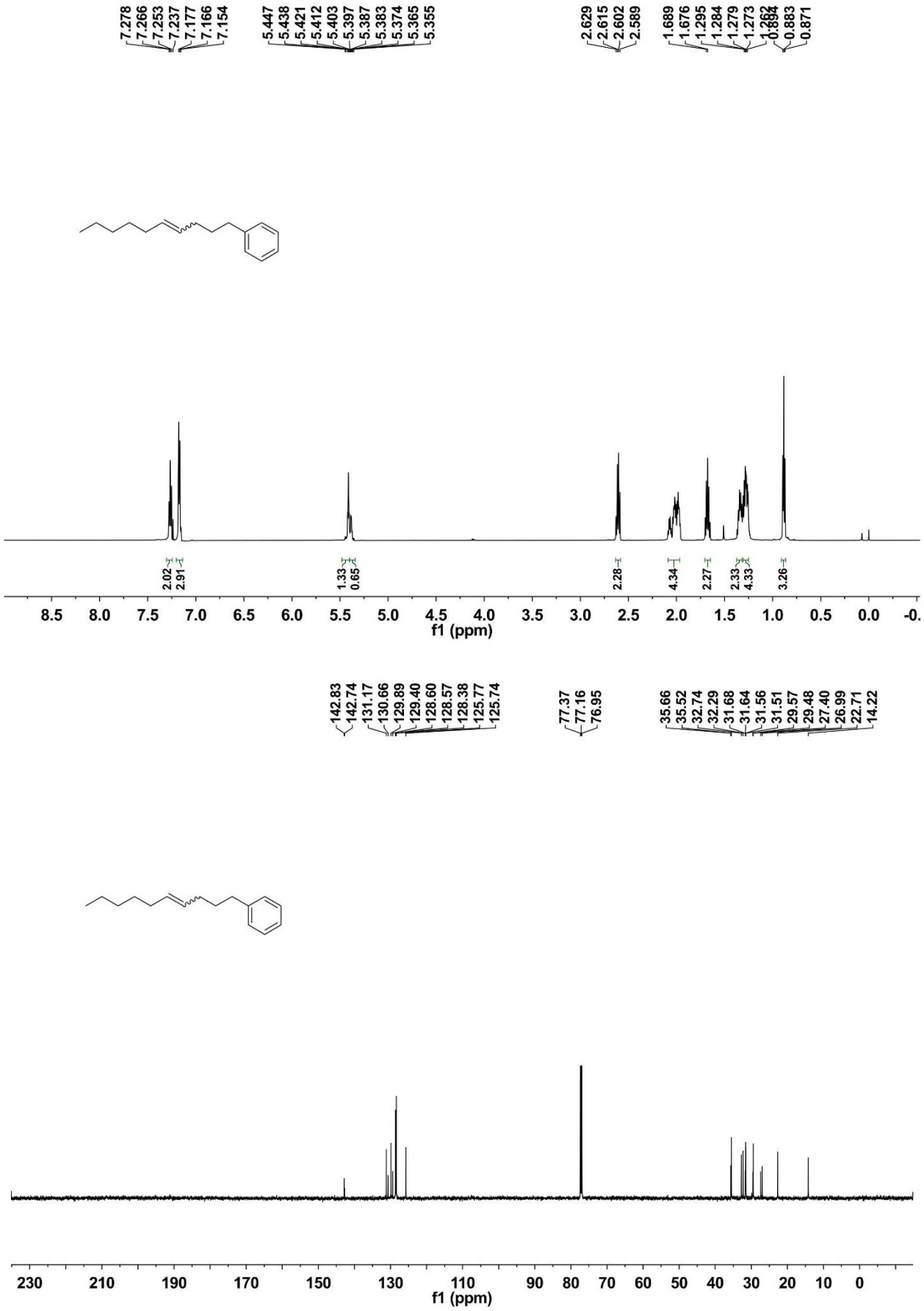


3r; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

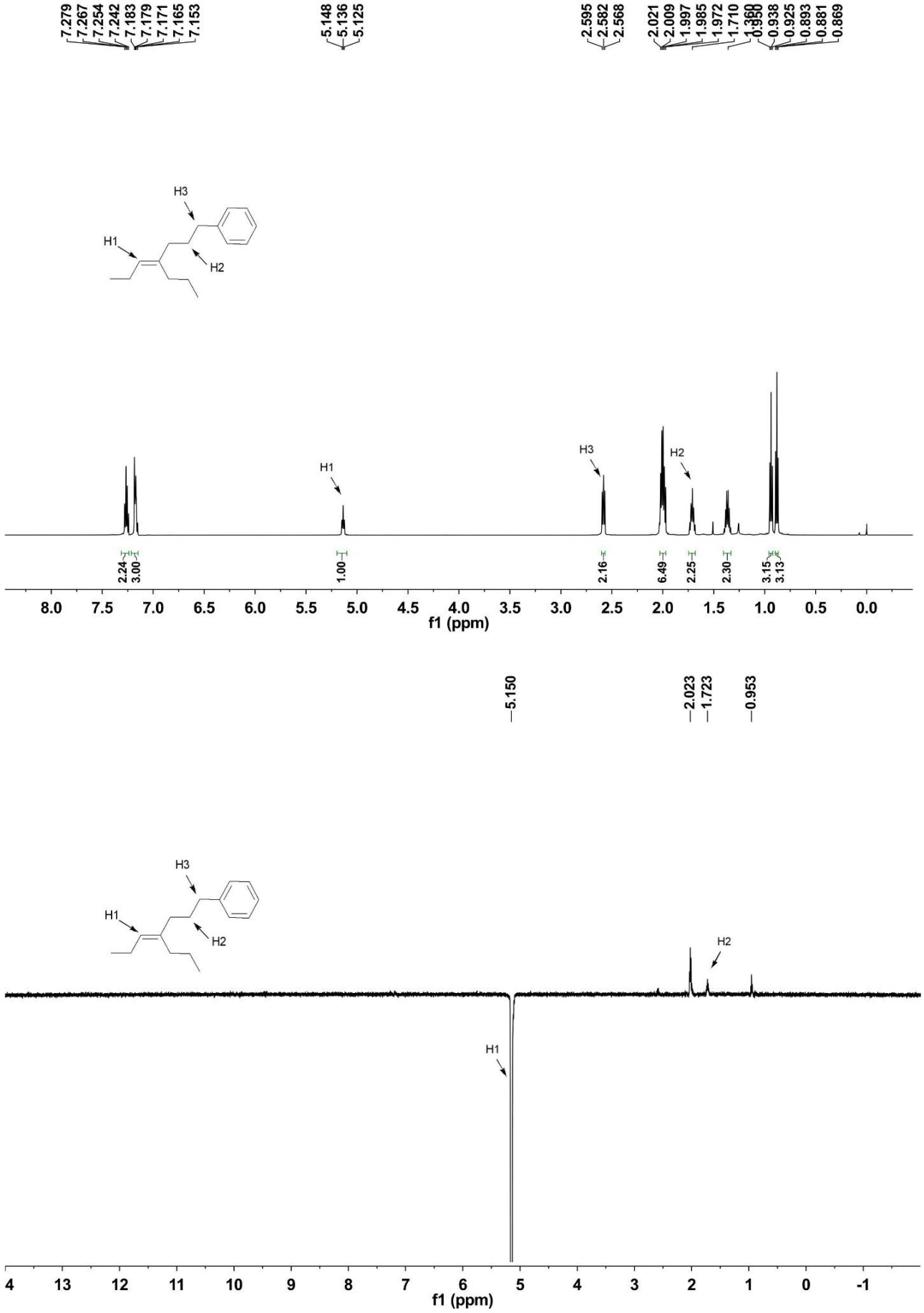




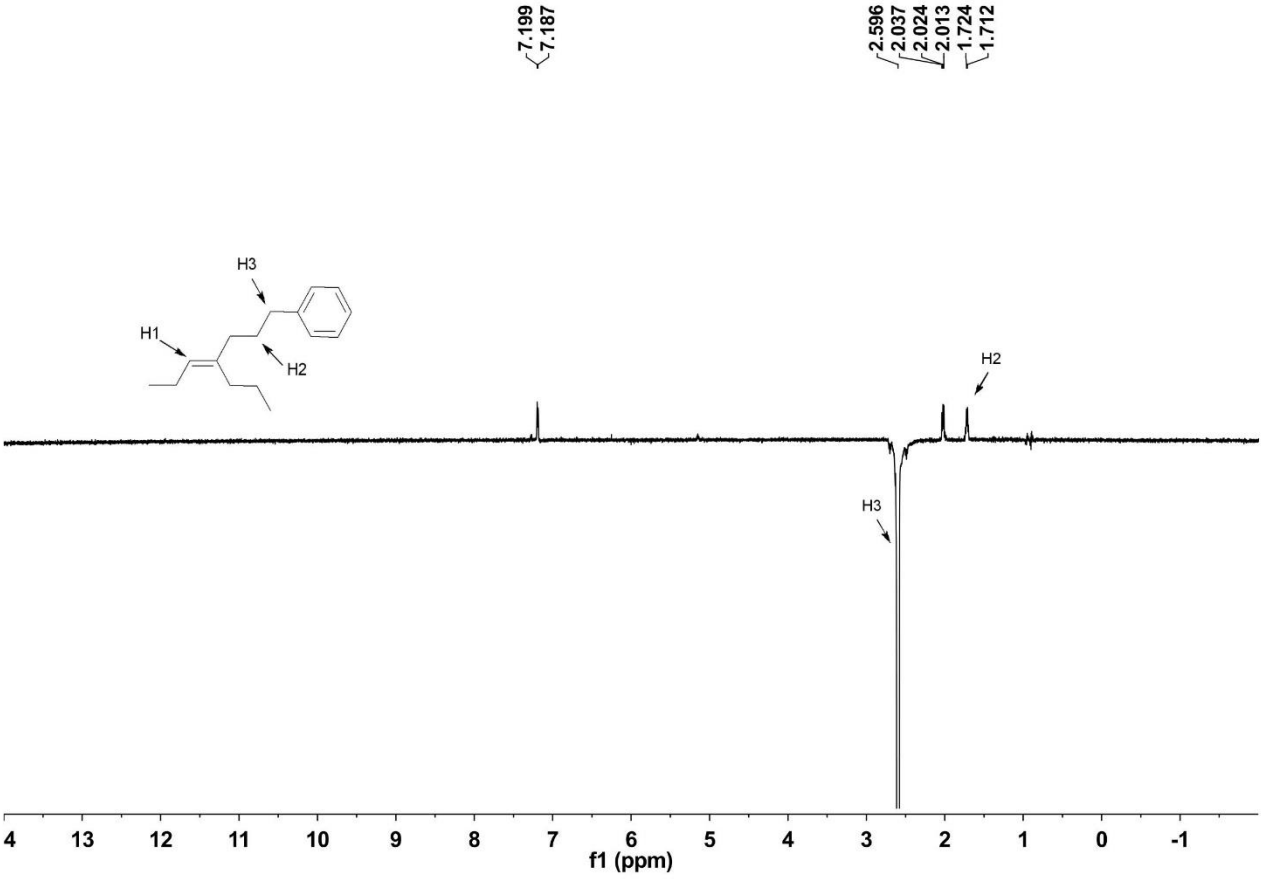
3s; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

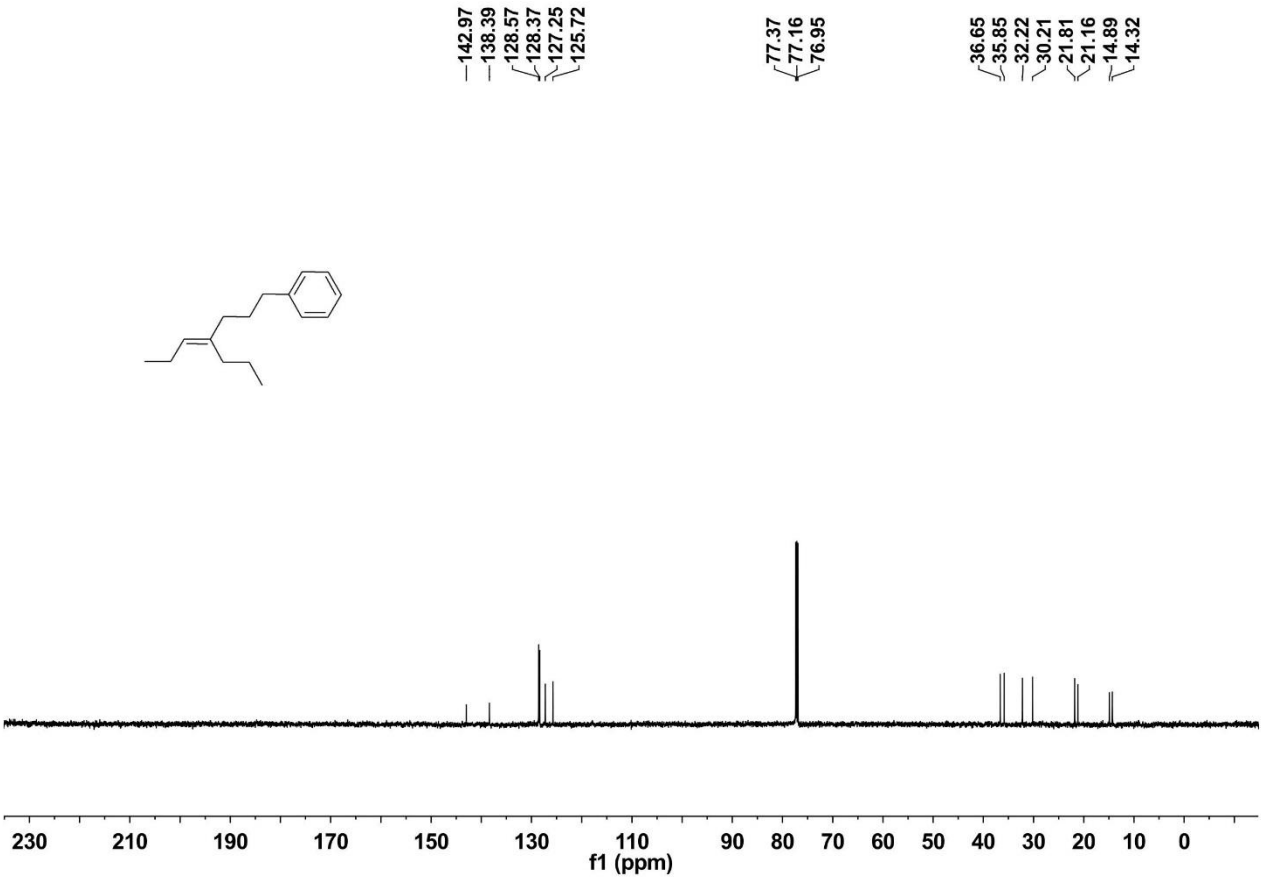


3t; ^{1}H NMR (600MHz, $CDCl_3$); NOE (600MHz, $CDCl_3$)

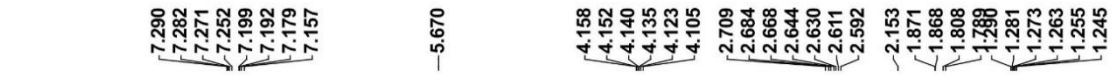


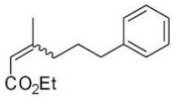
3t; NOE (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

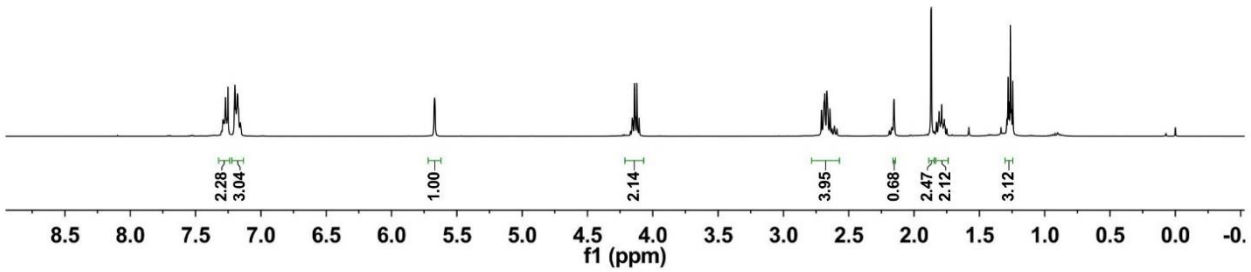


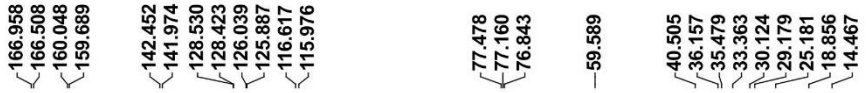


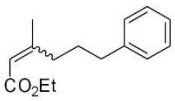
3u; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

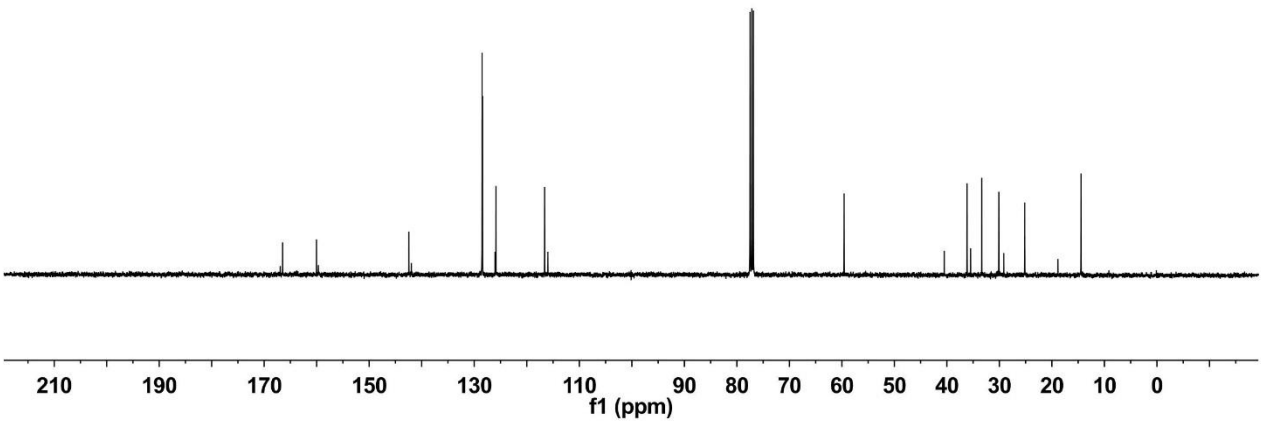




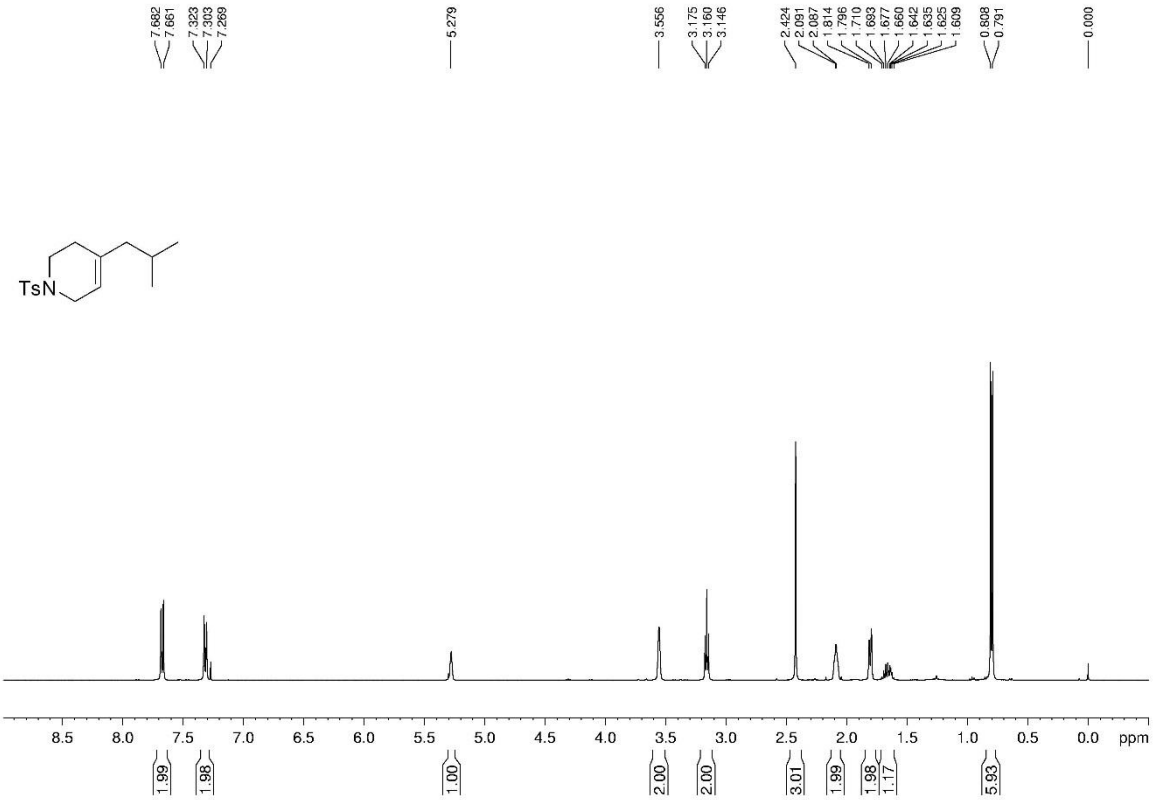


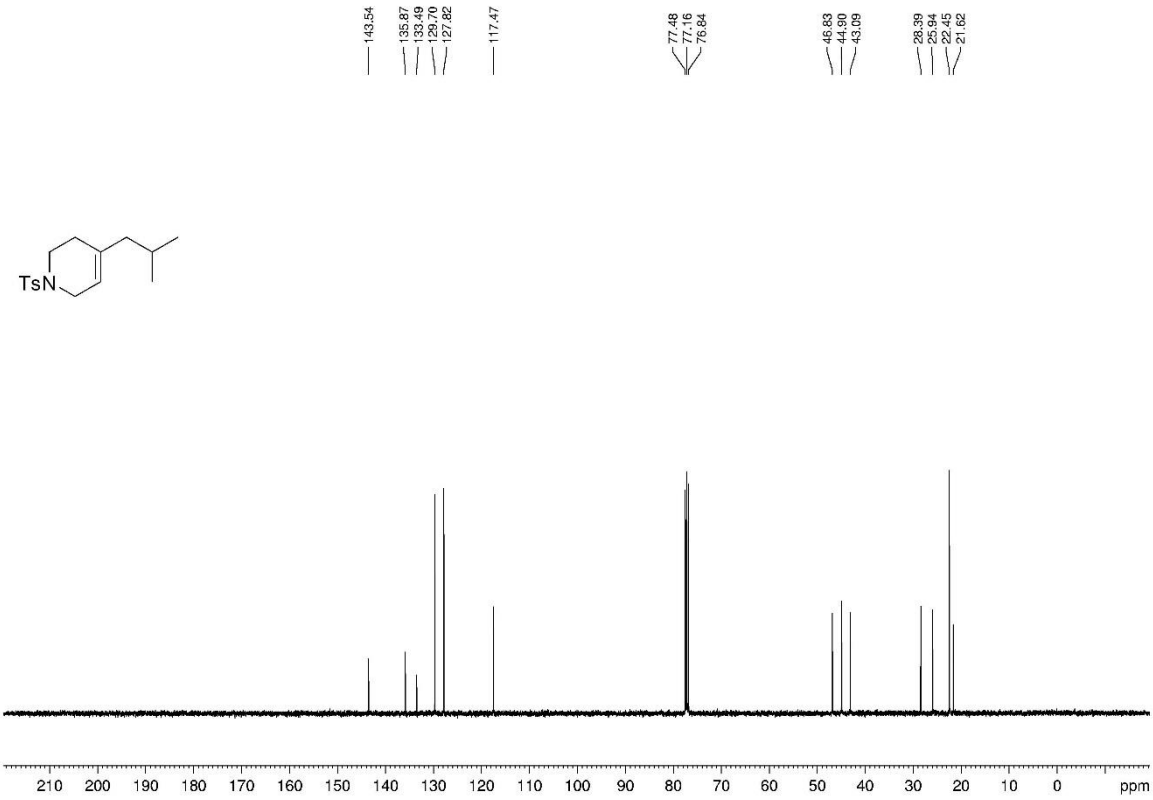




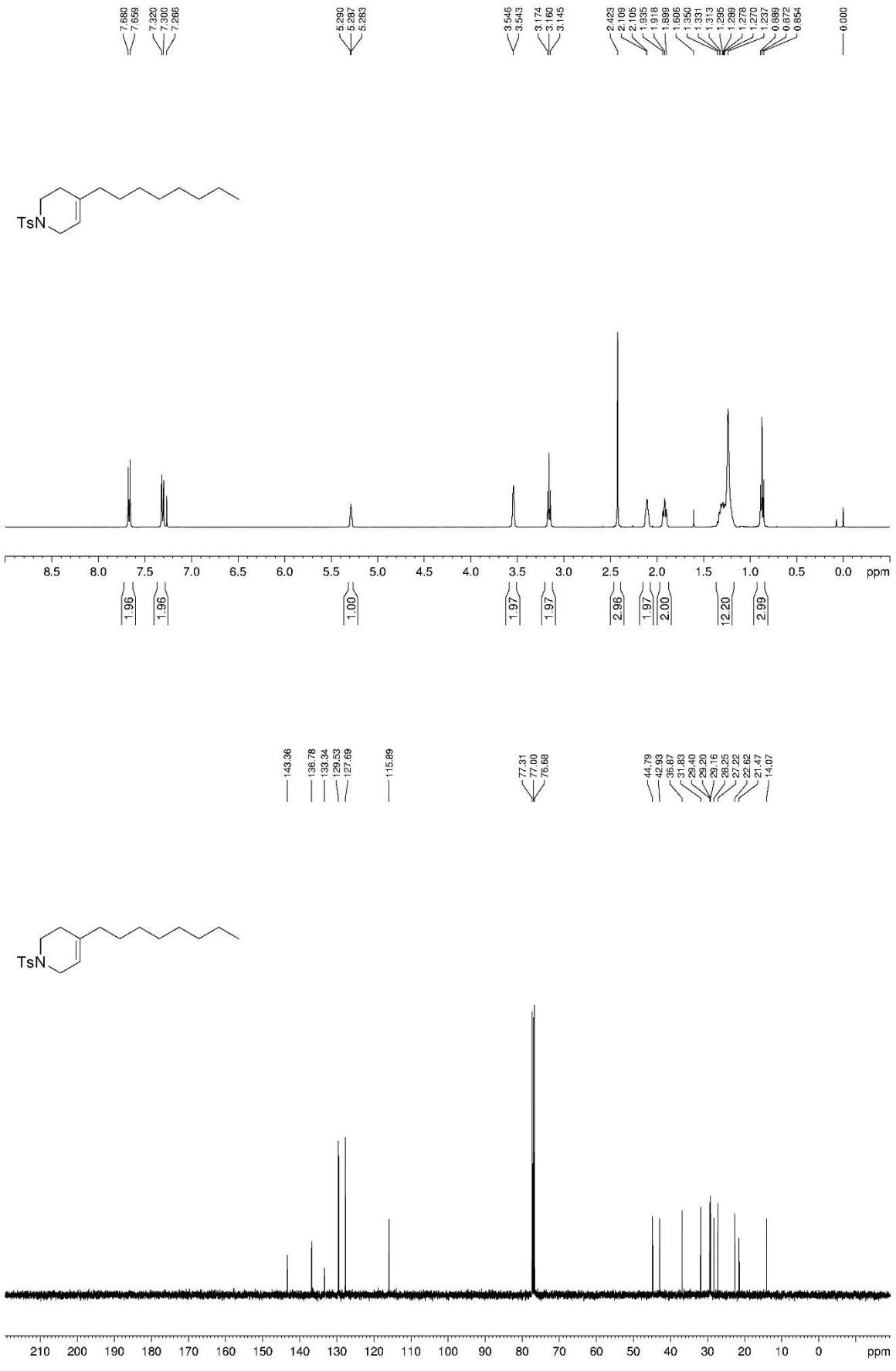


3v; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

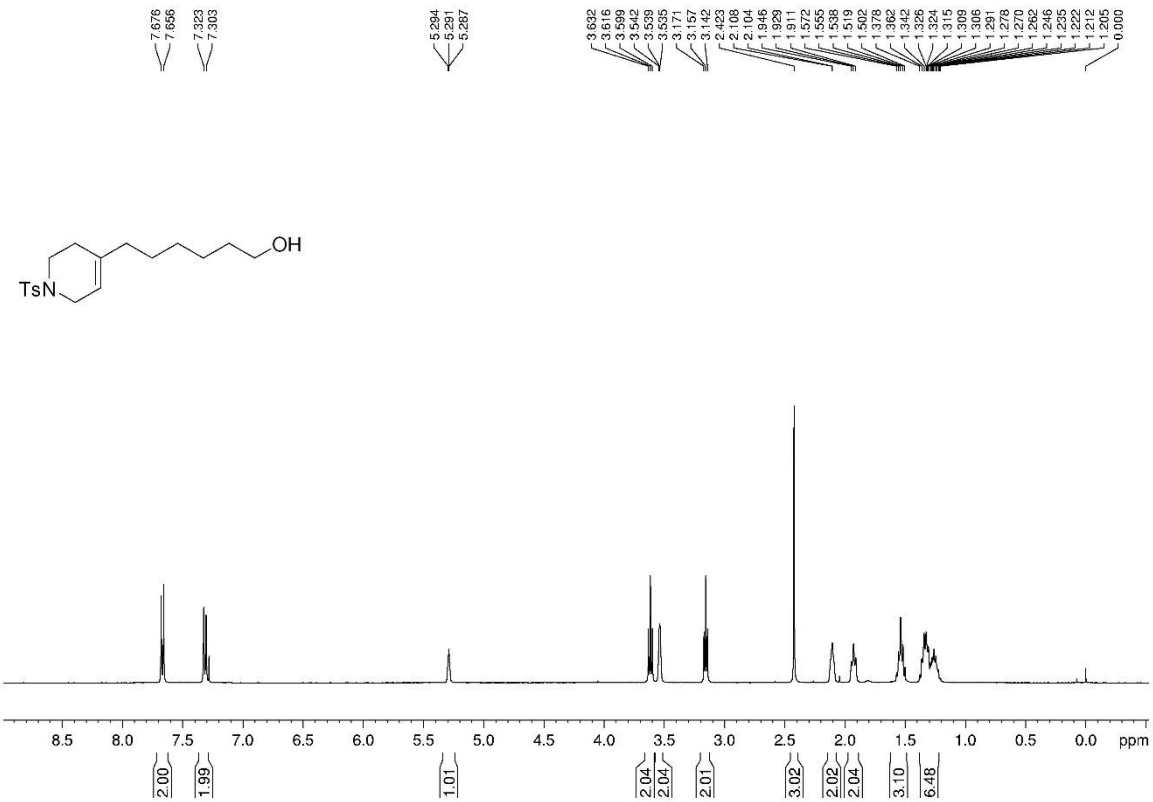


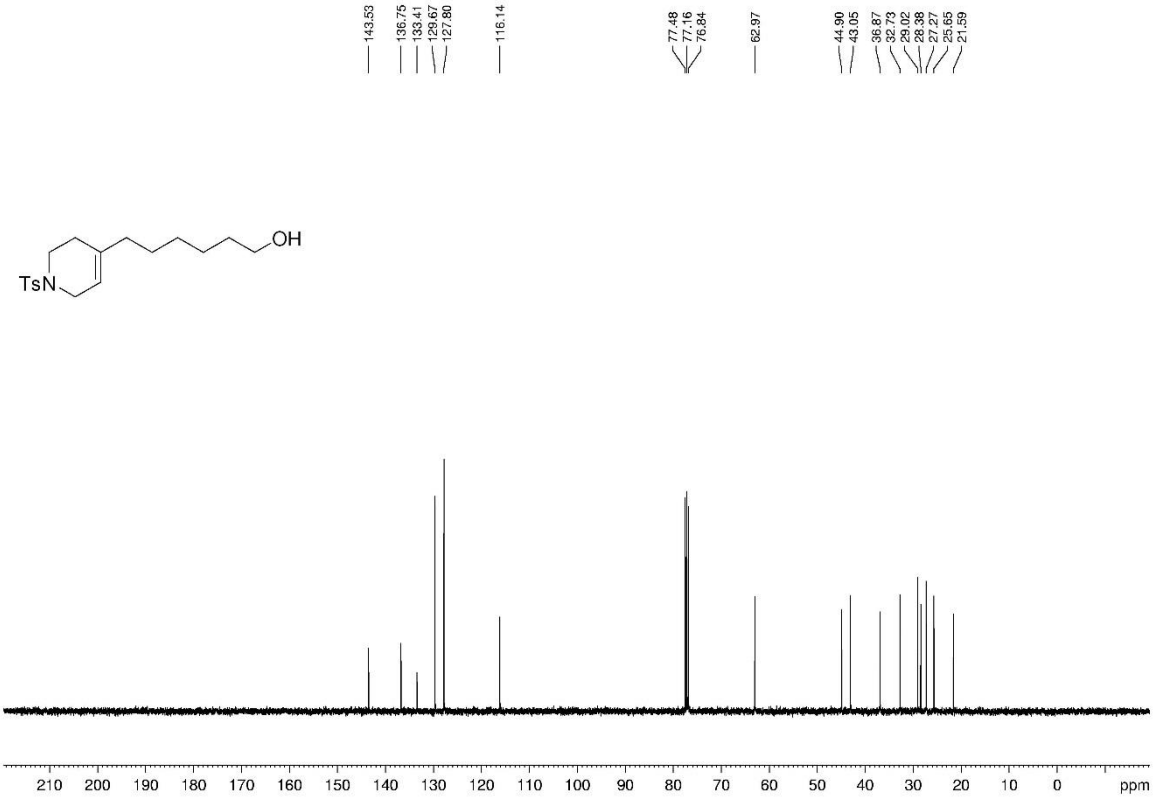


3w; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

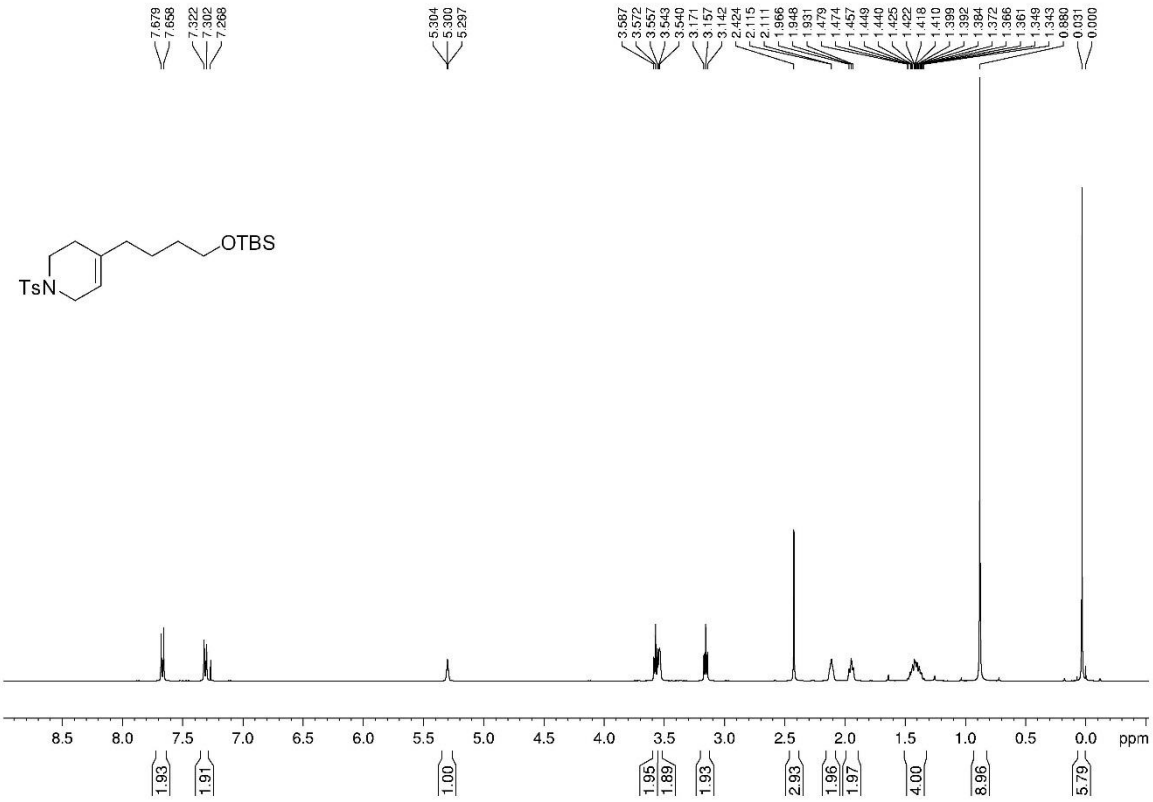


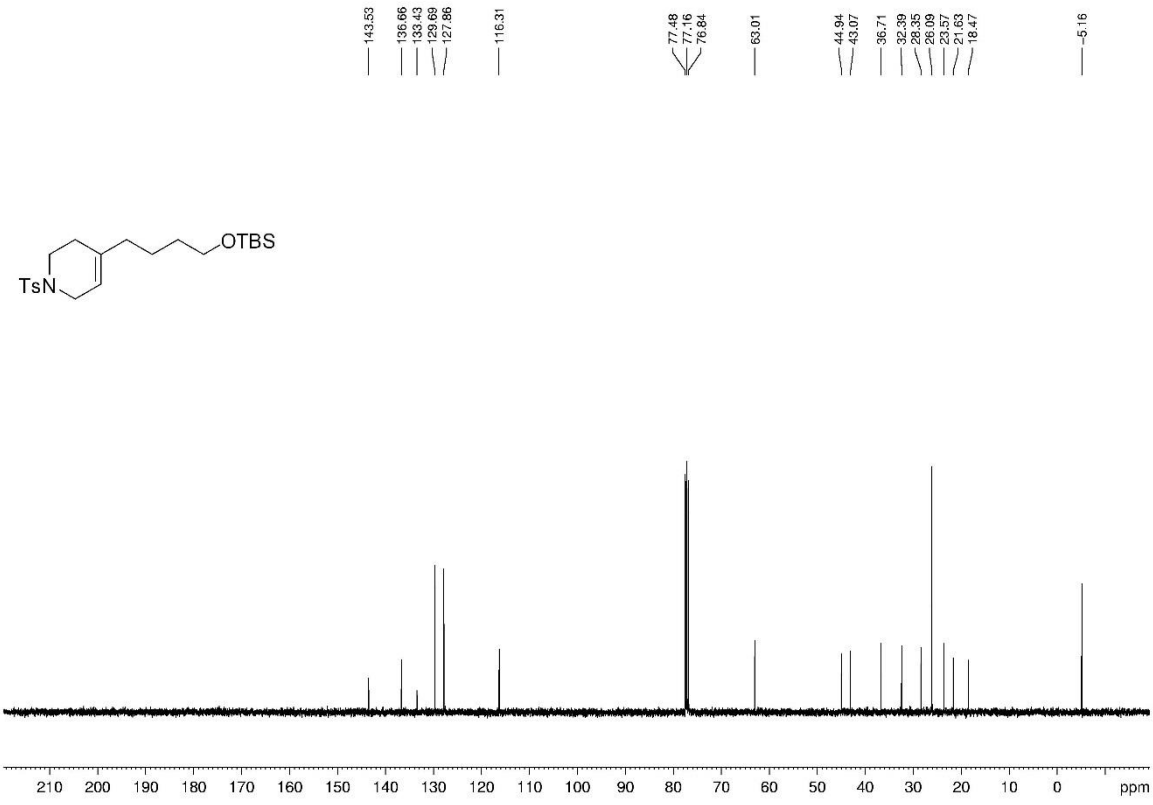
3x; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



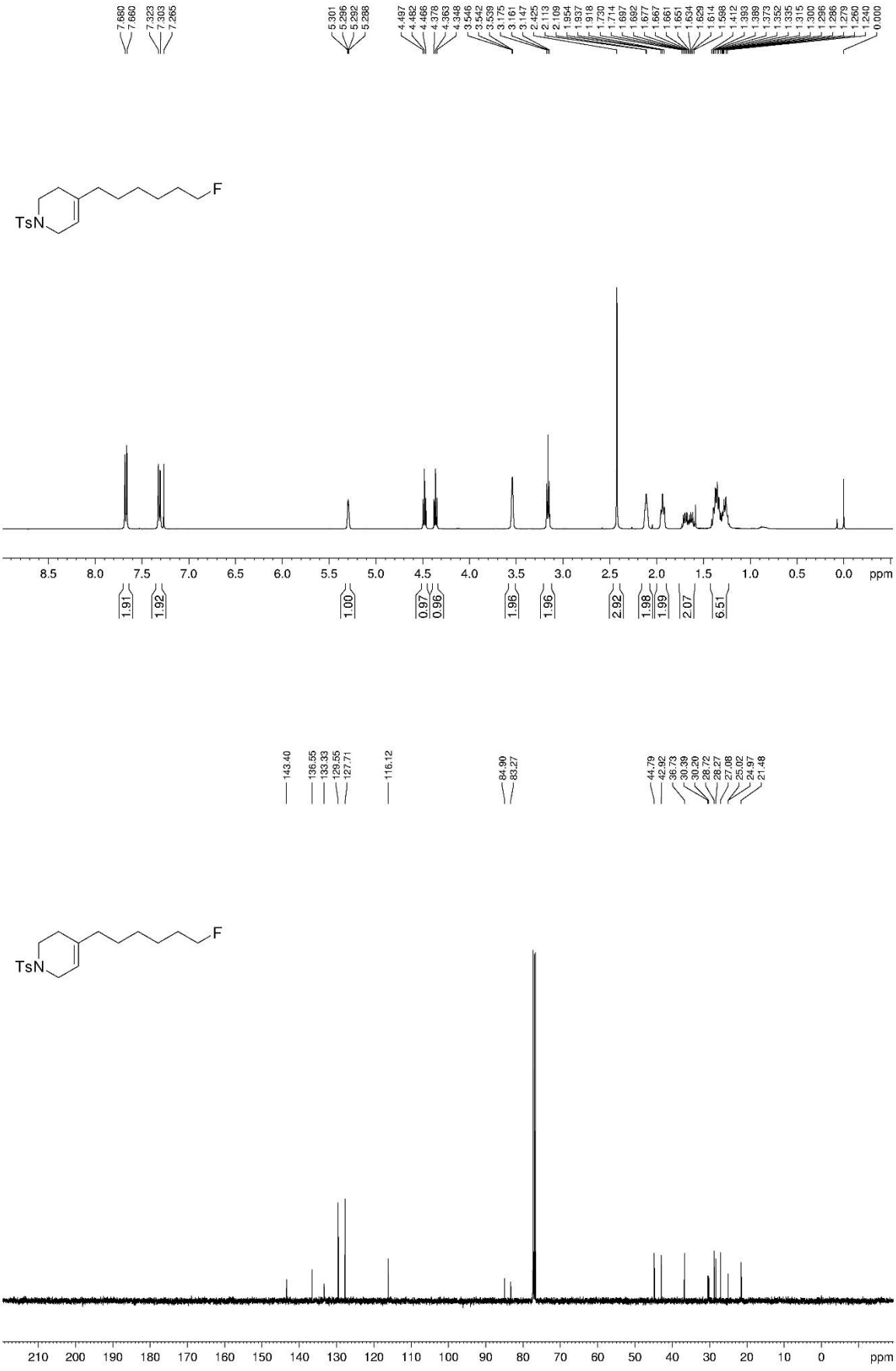


3y; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

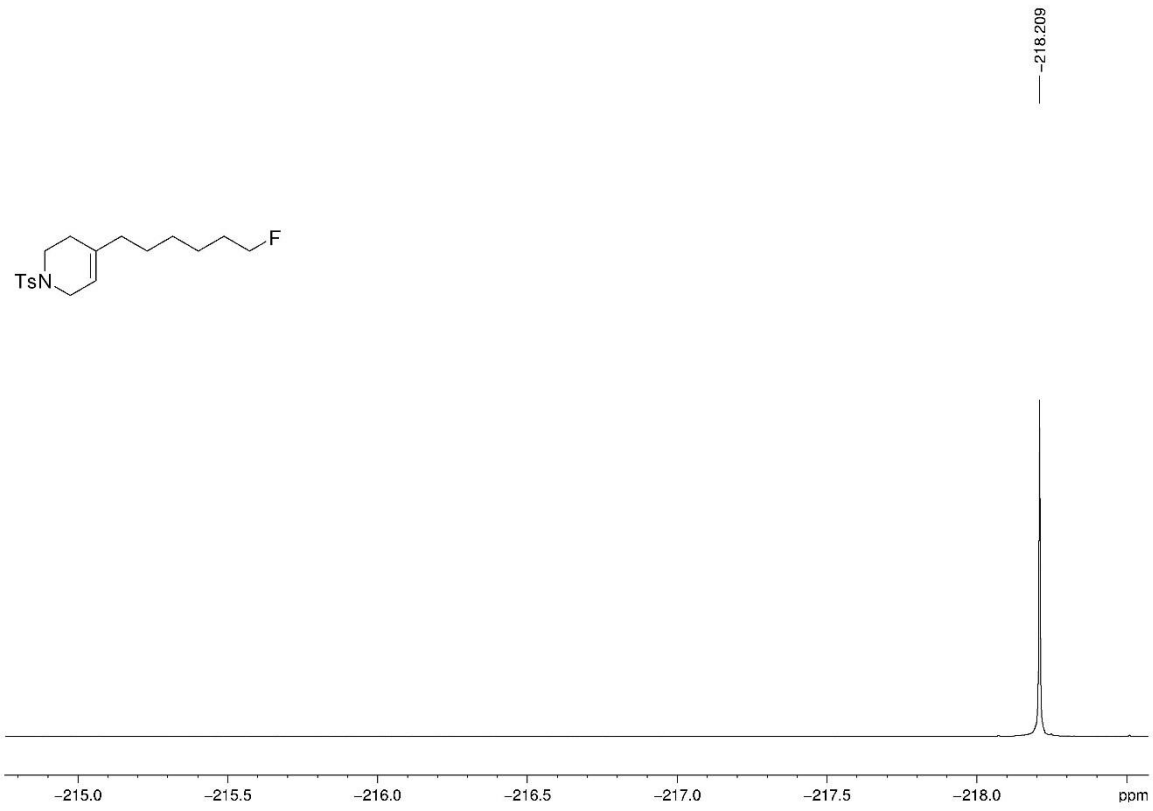




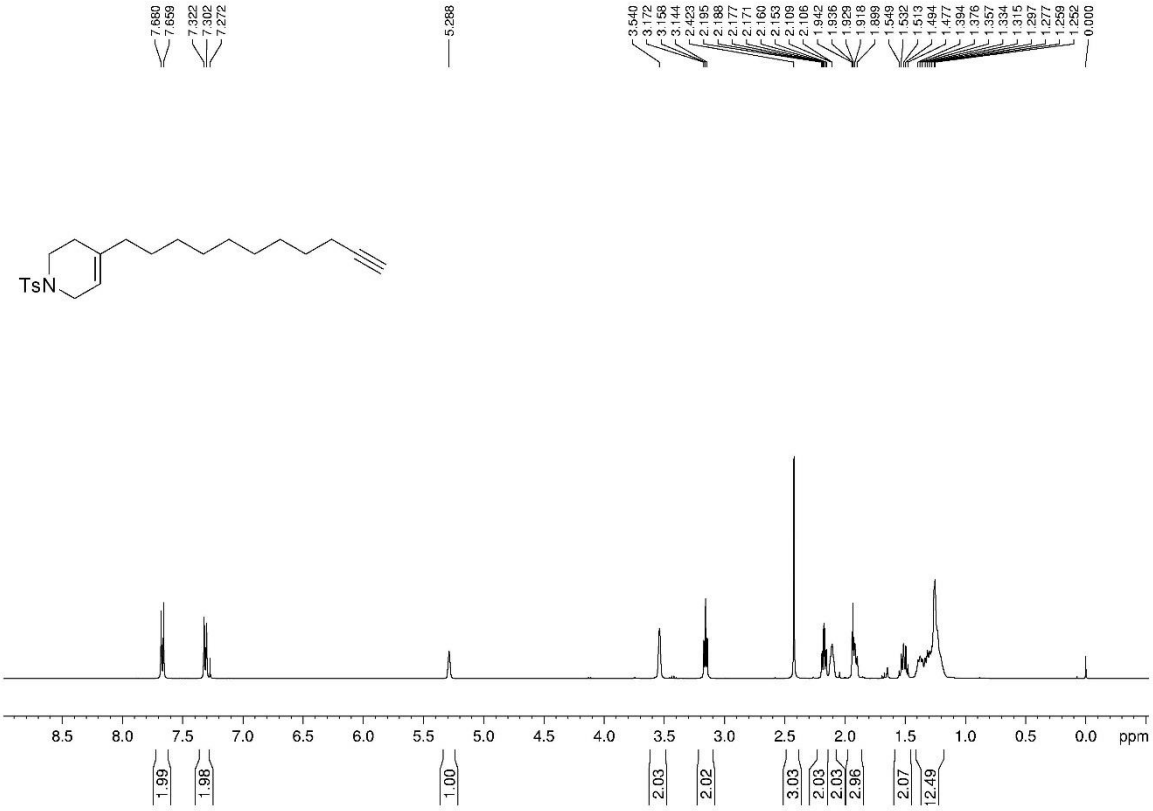
3z; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

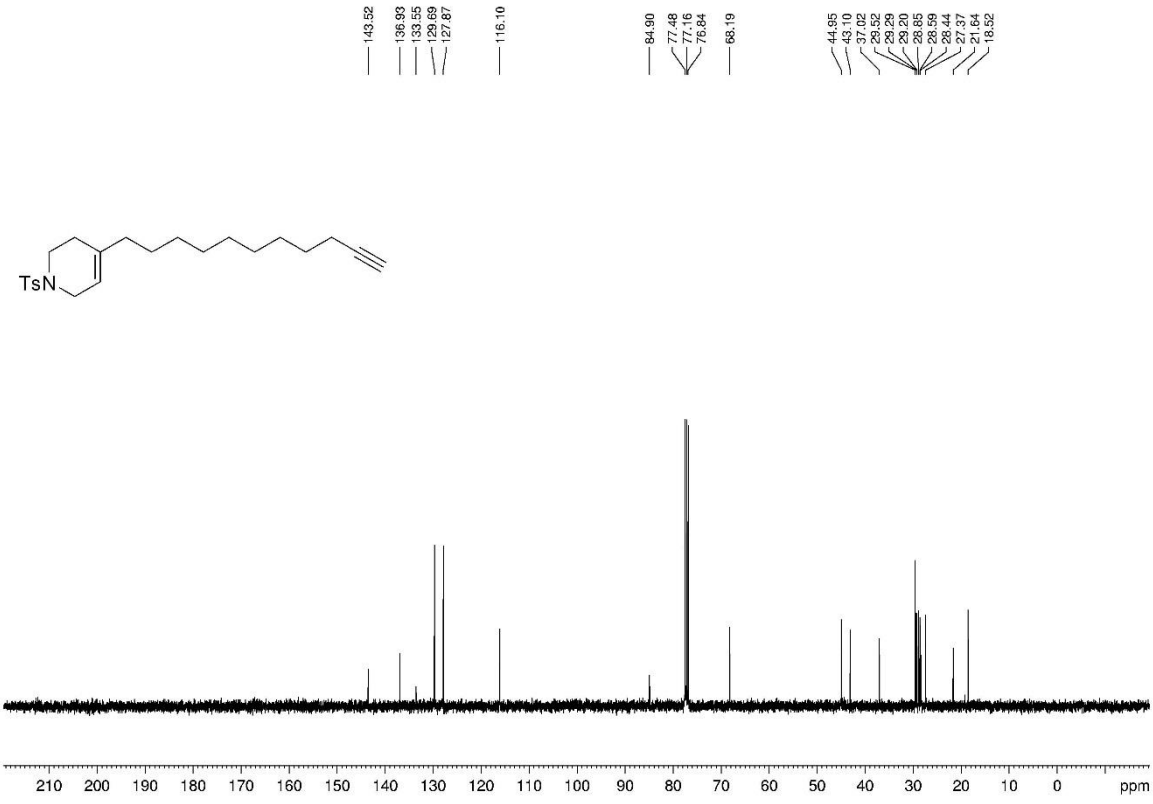


3z; ^{13}F NMR (376MHz, $CDCl_3$)

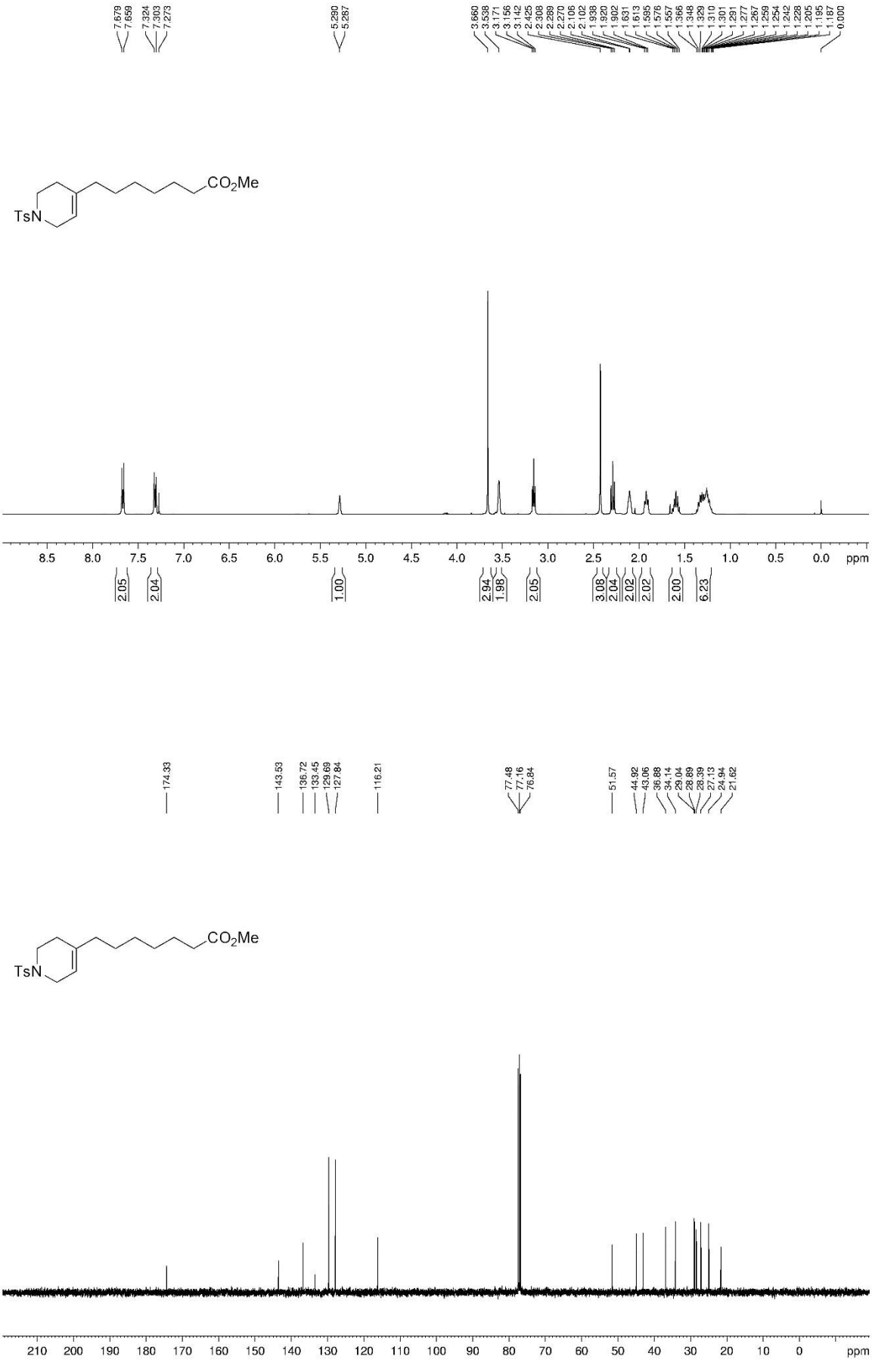


3aa; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

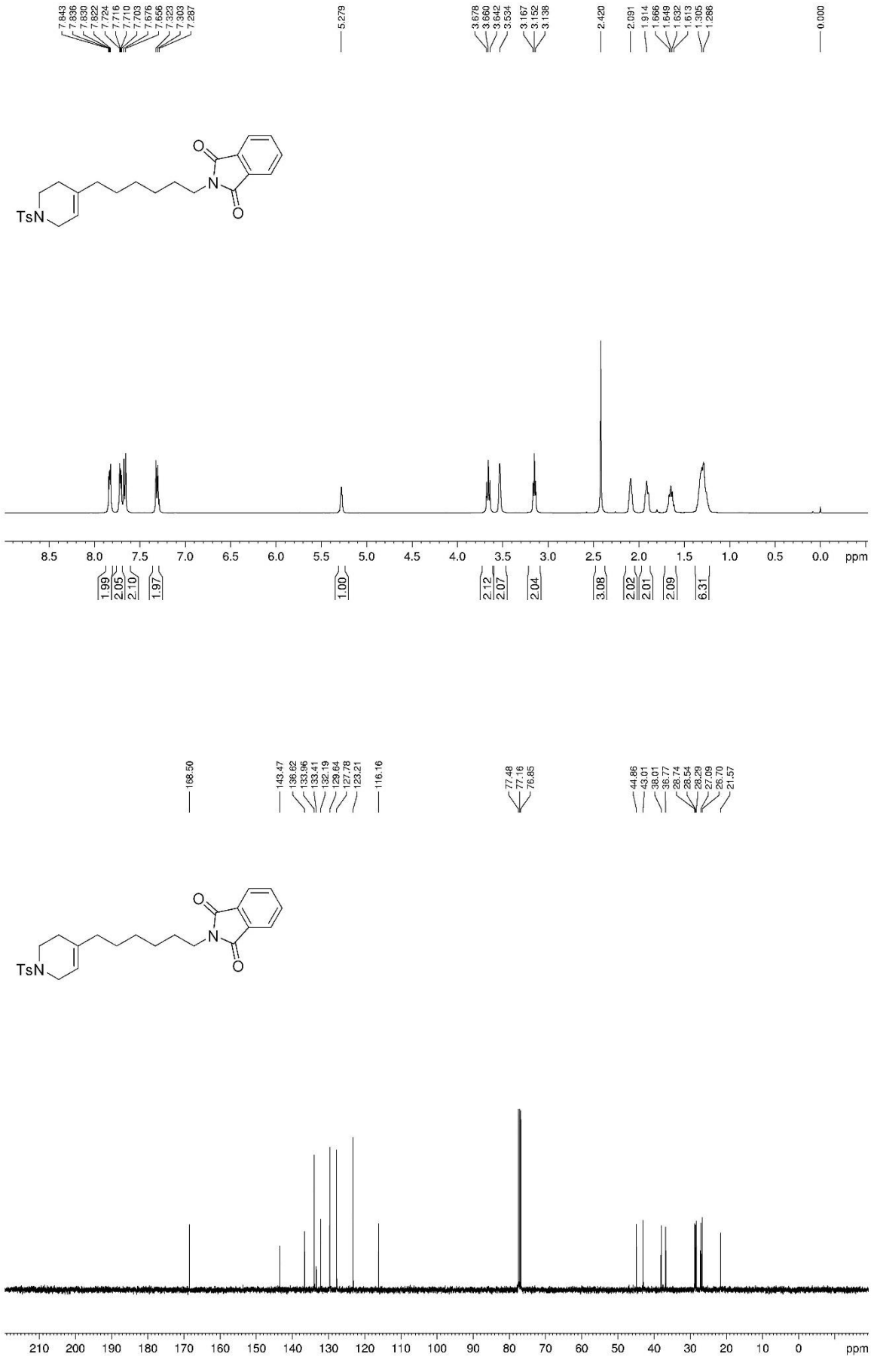




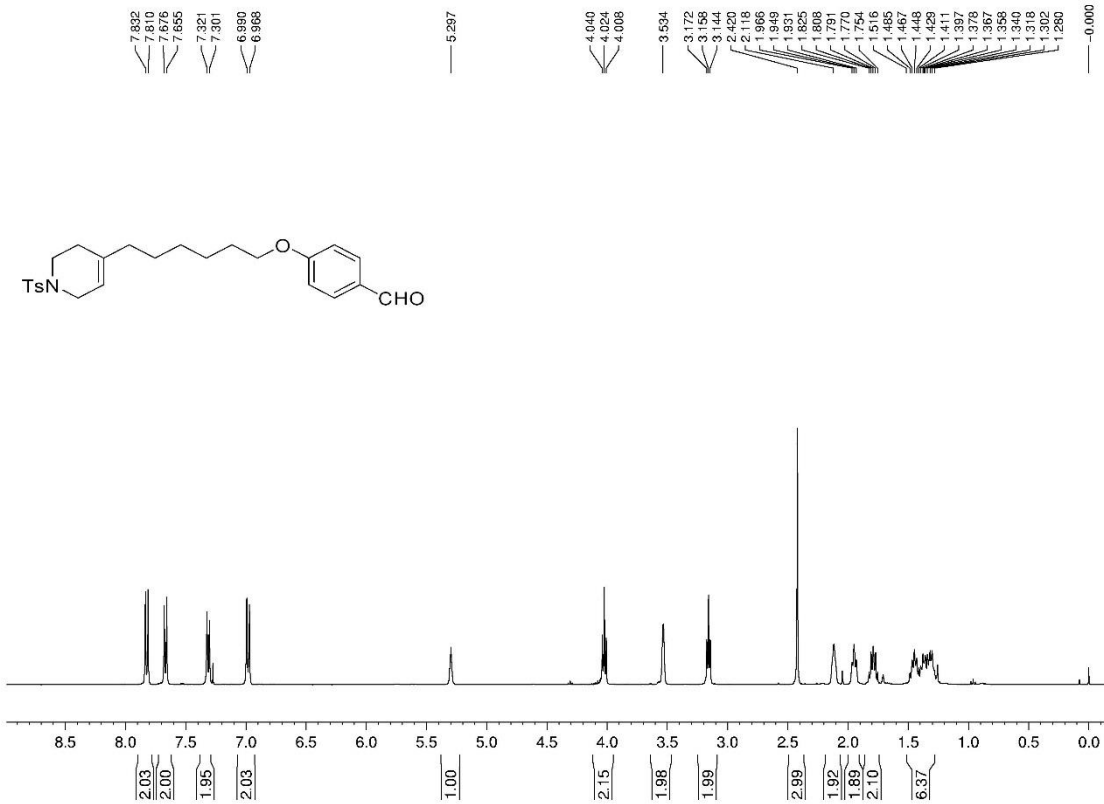
3ab; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

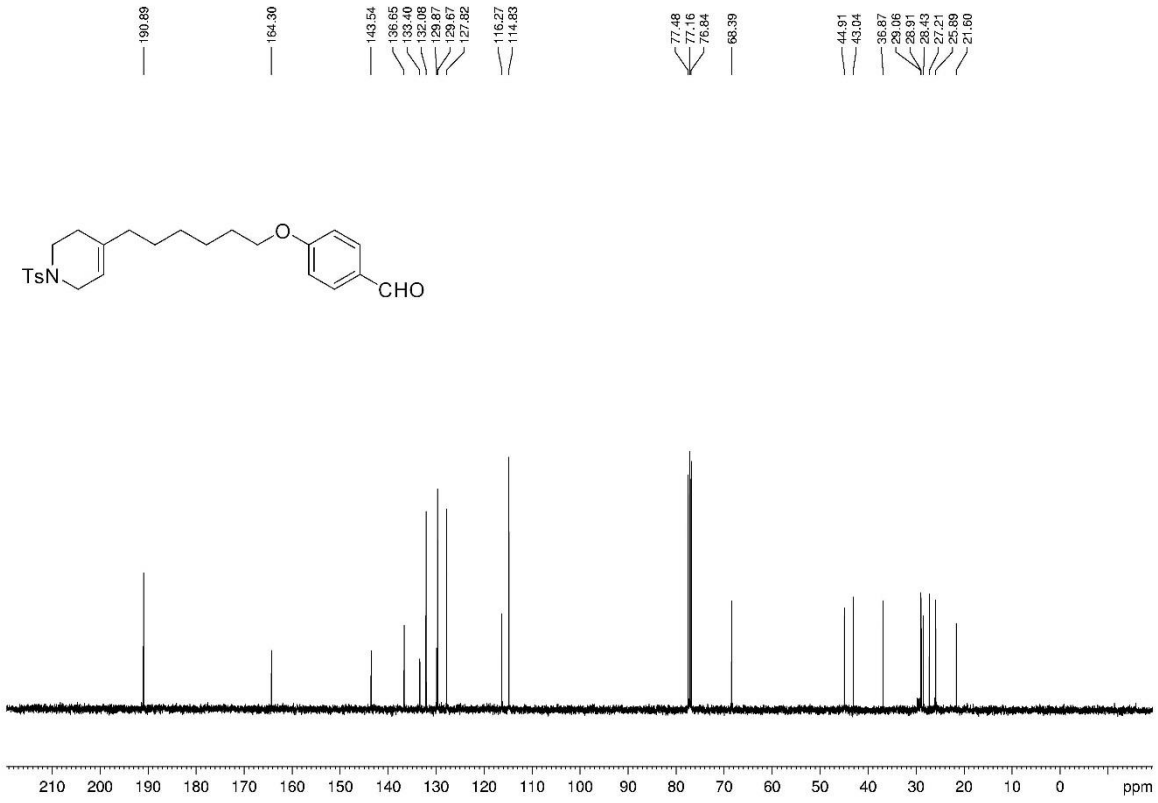


3ac; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

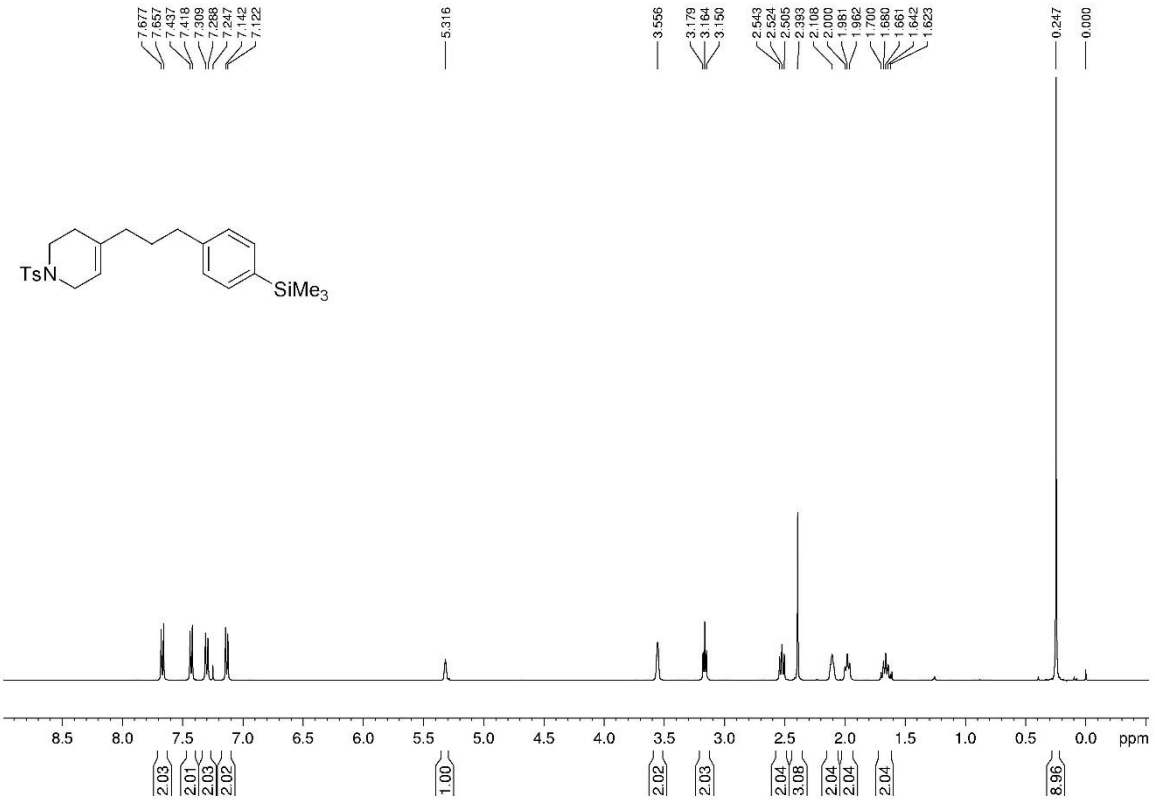


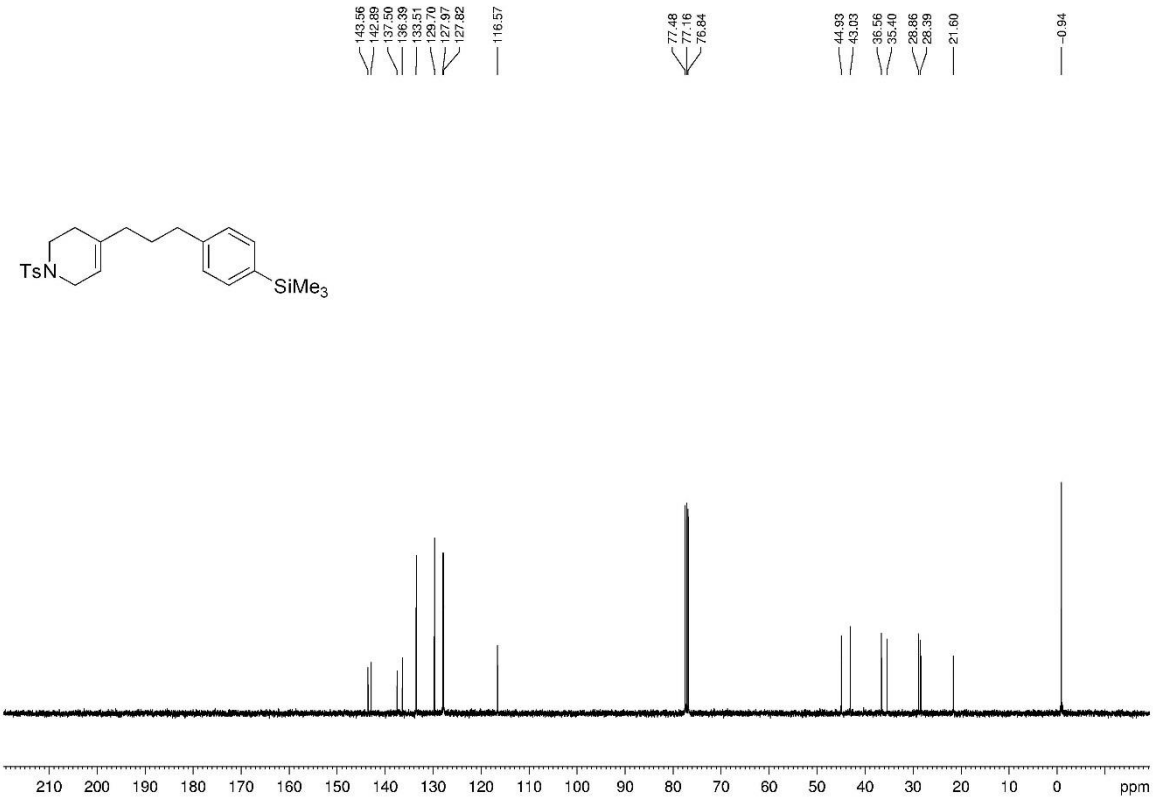
3ad; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



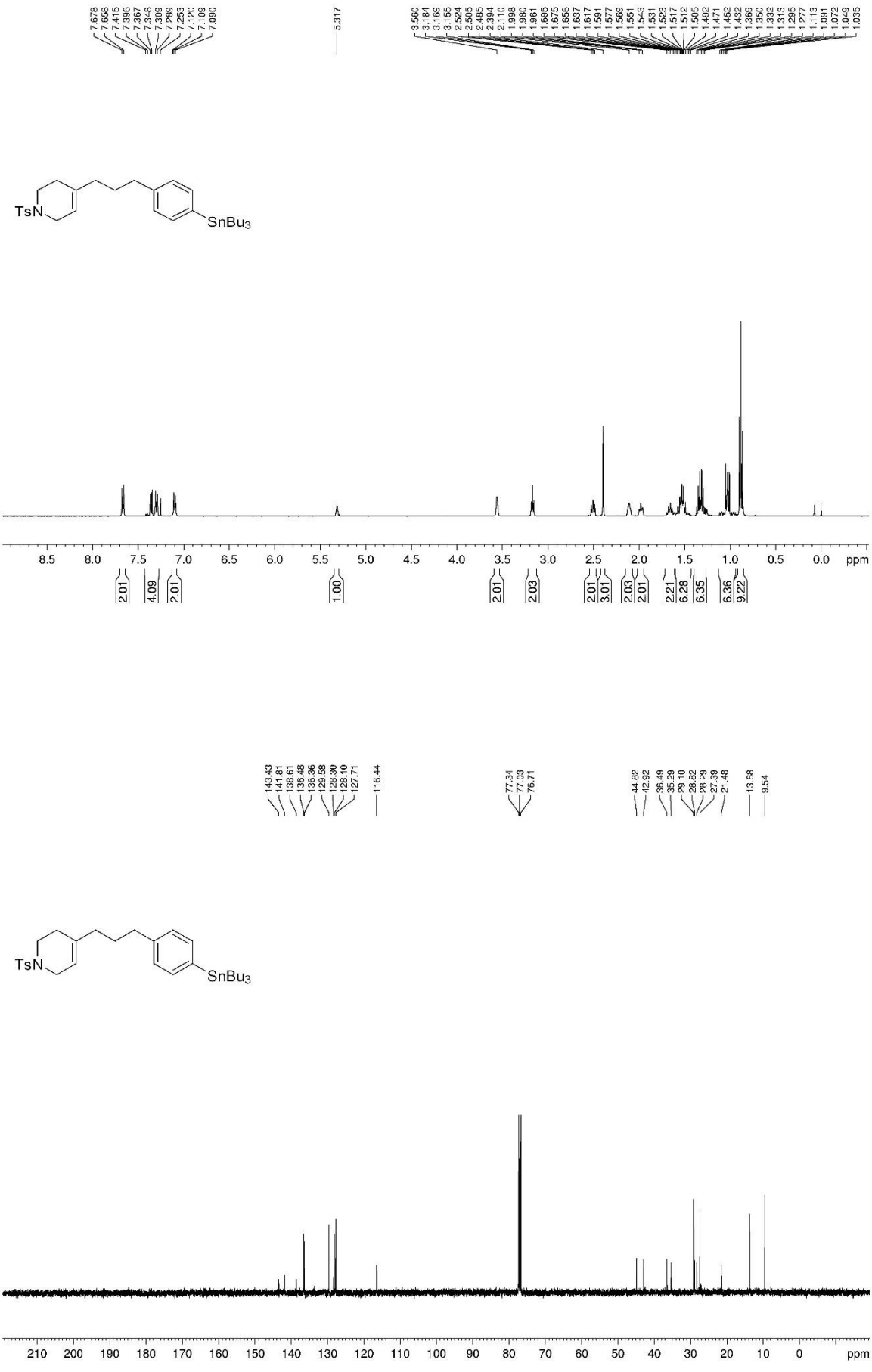


3ae; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

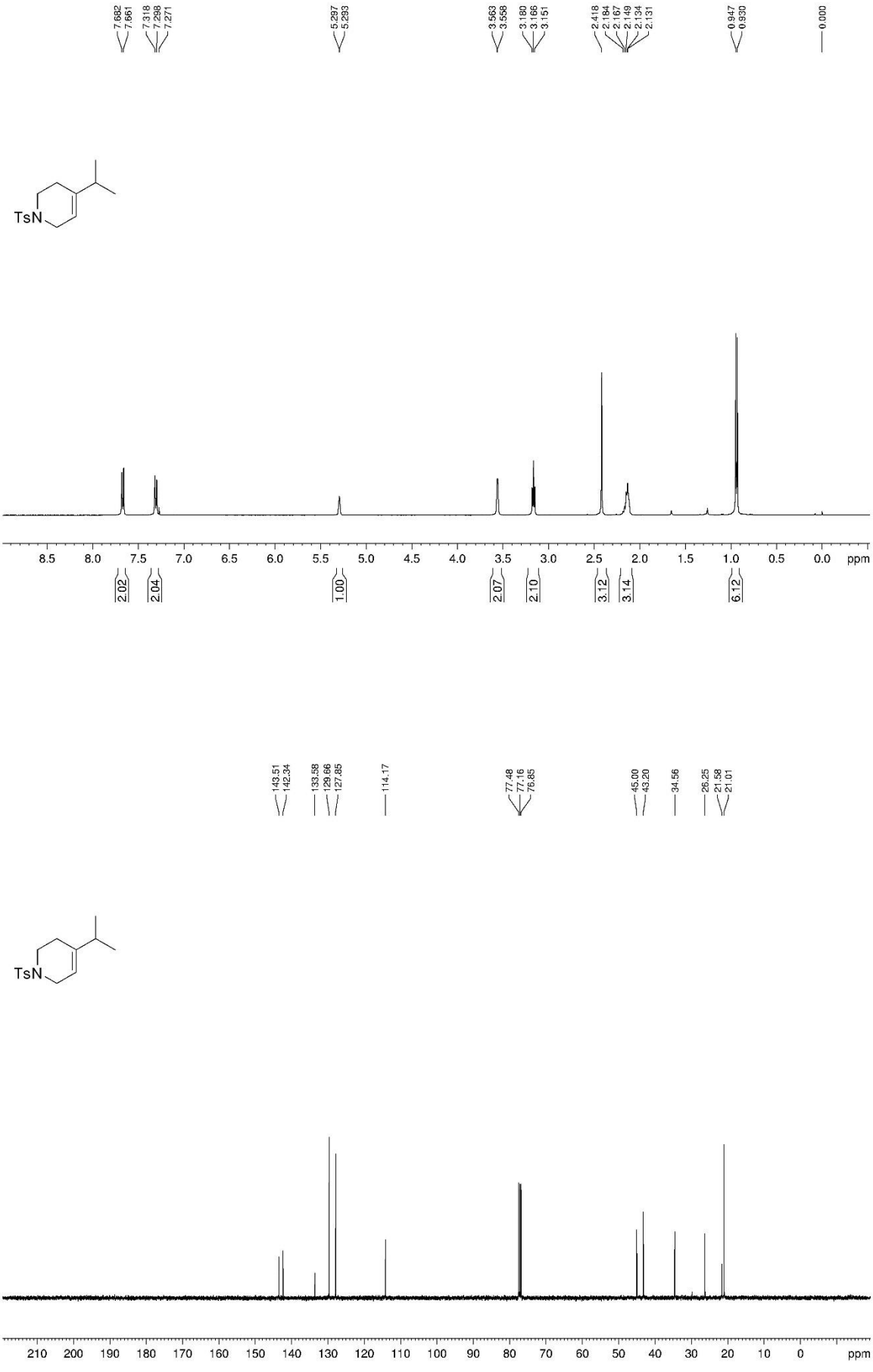




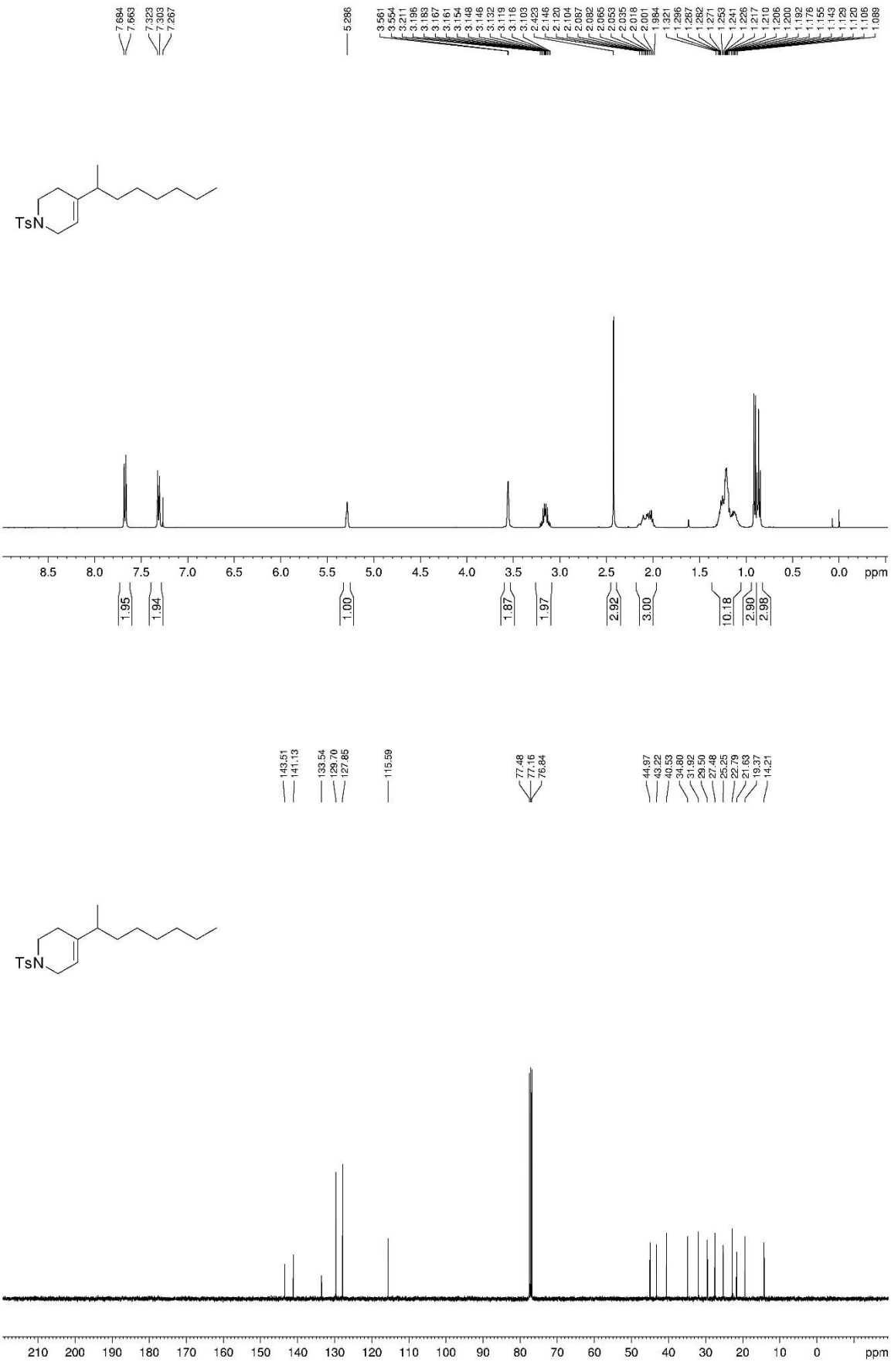
3af; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



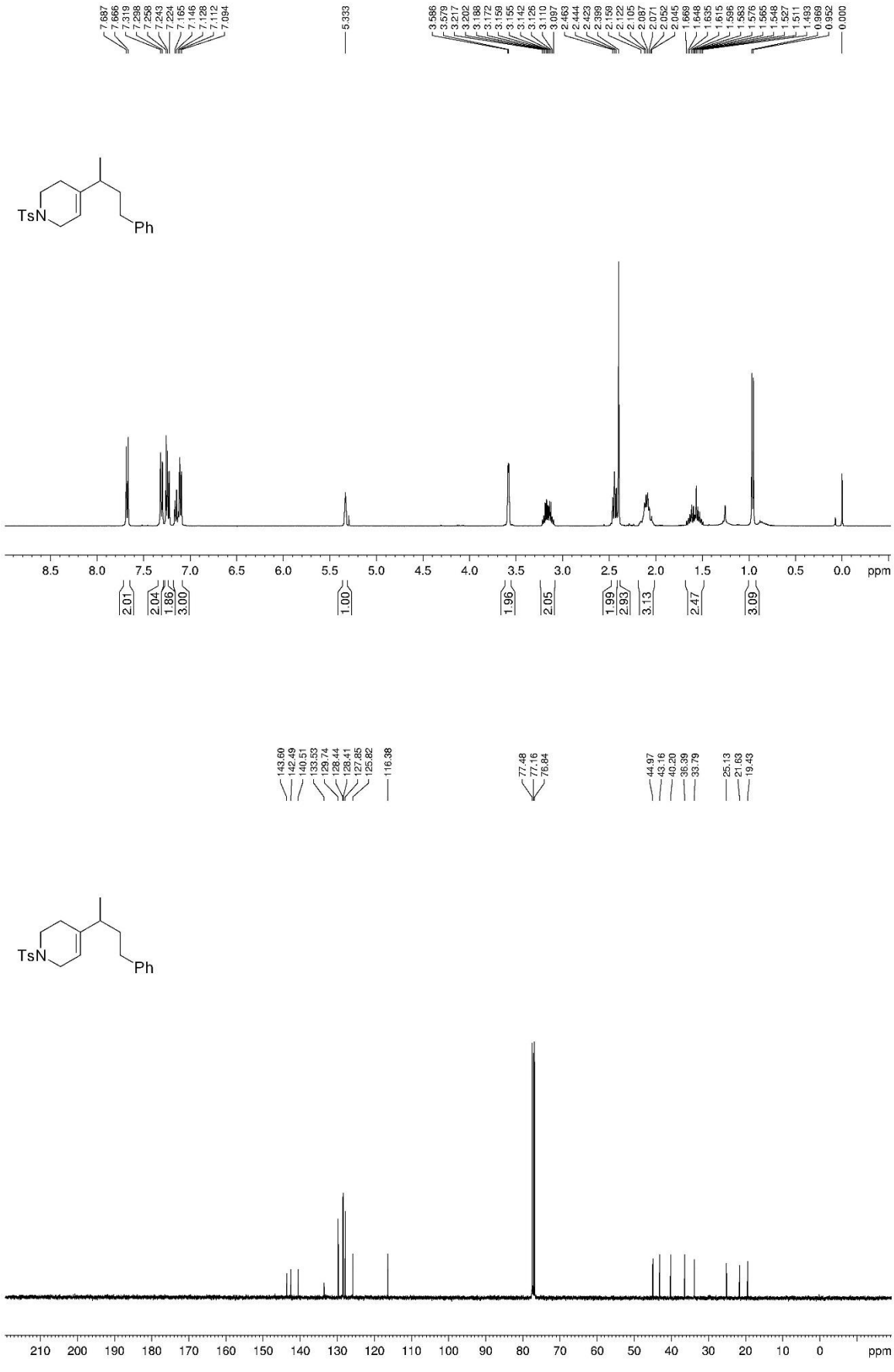
3ag; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



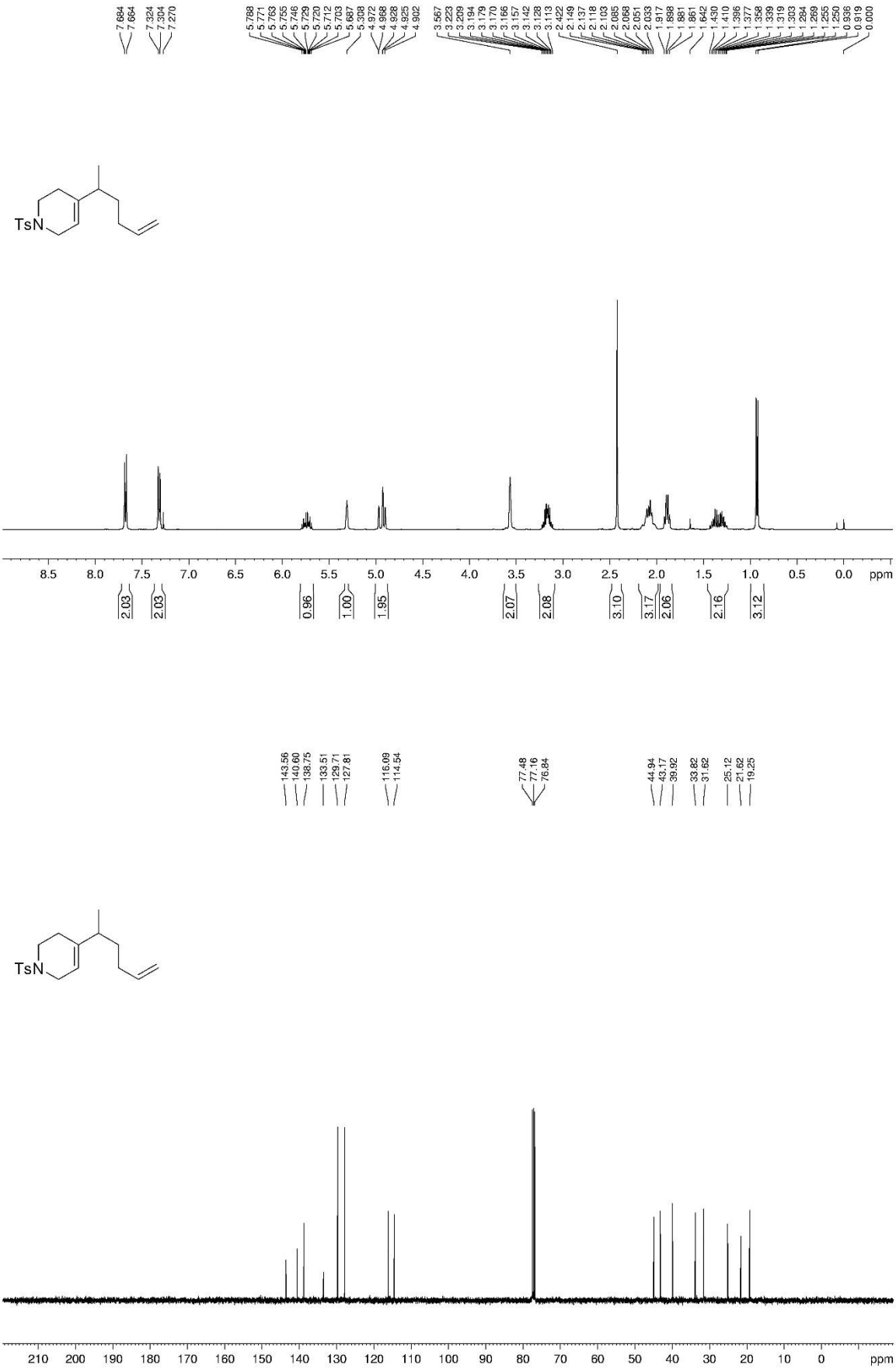
3ah; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



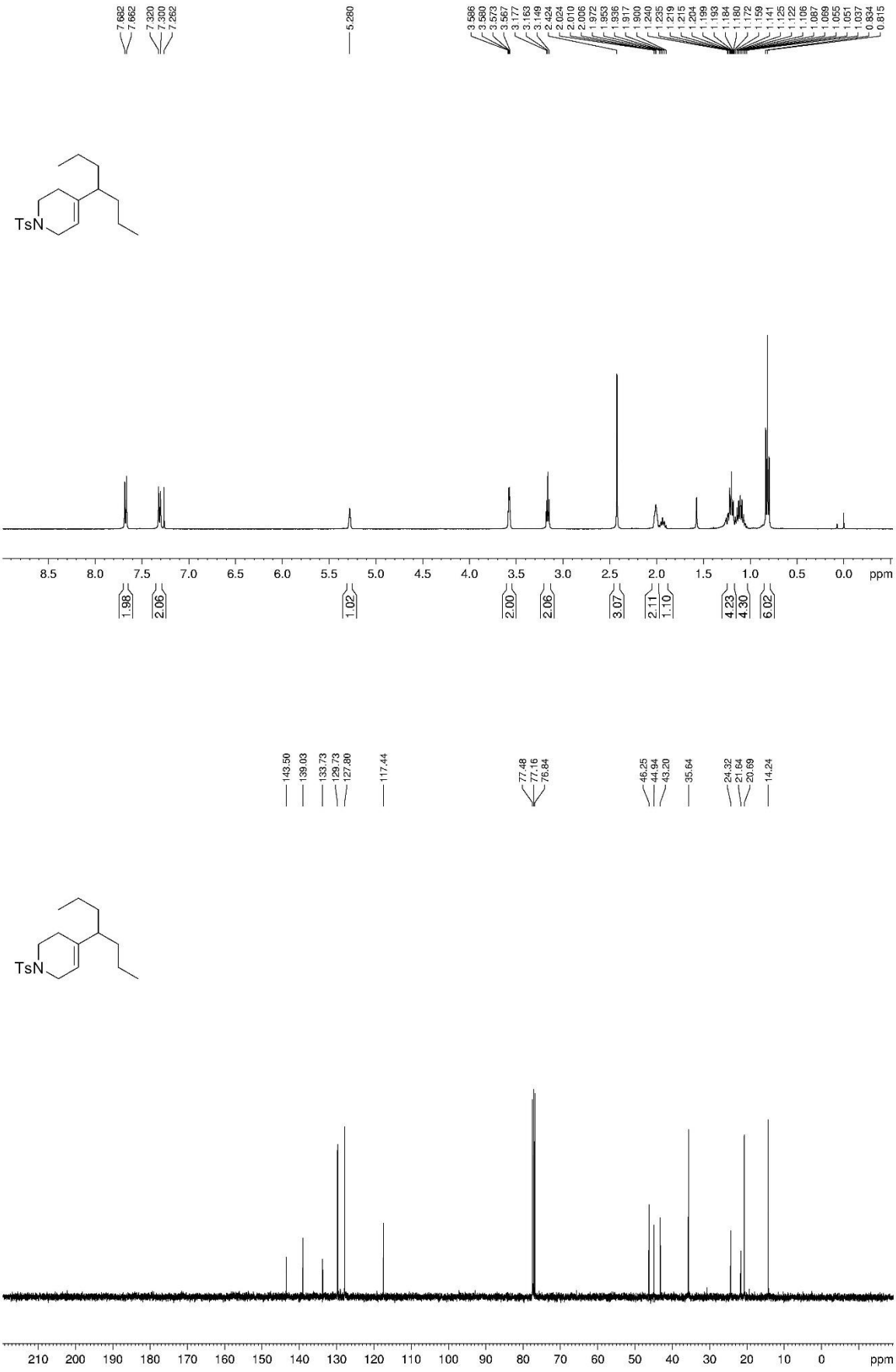
3ai; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



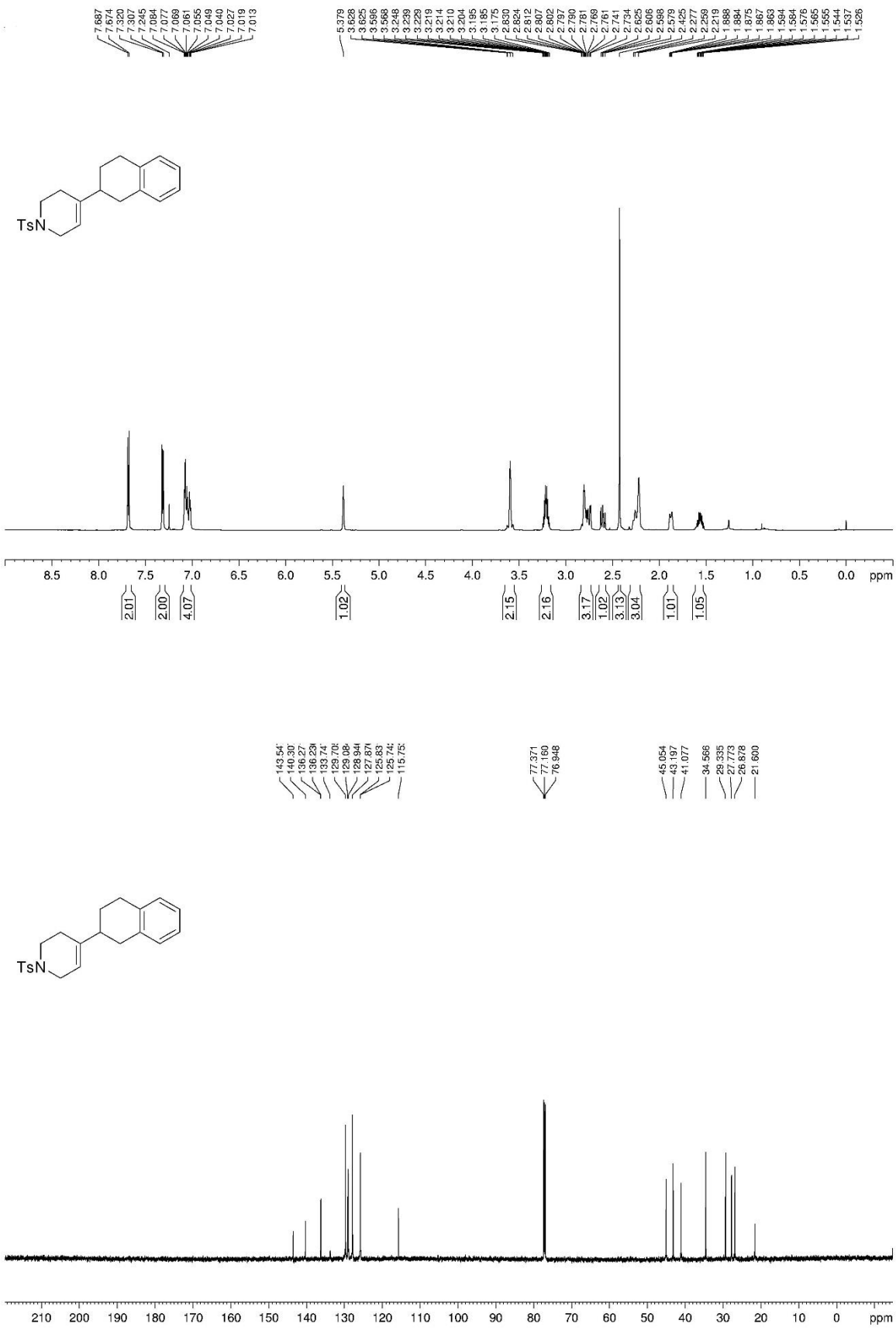
3aj; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



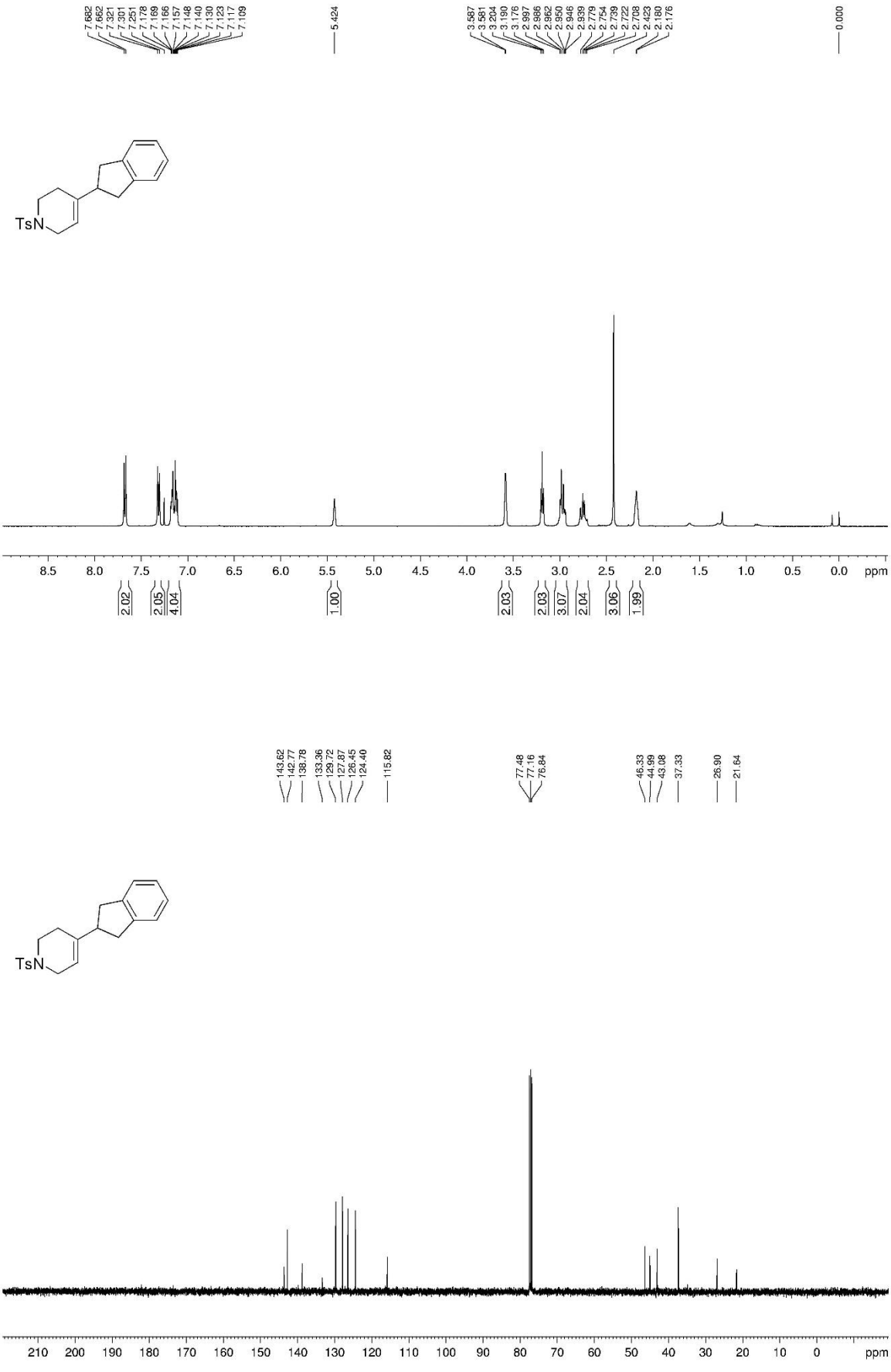
3ak; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



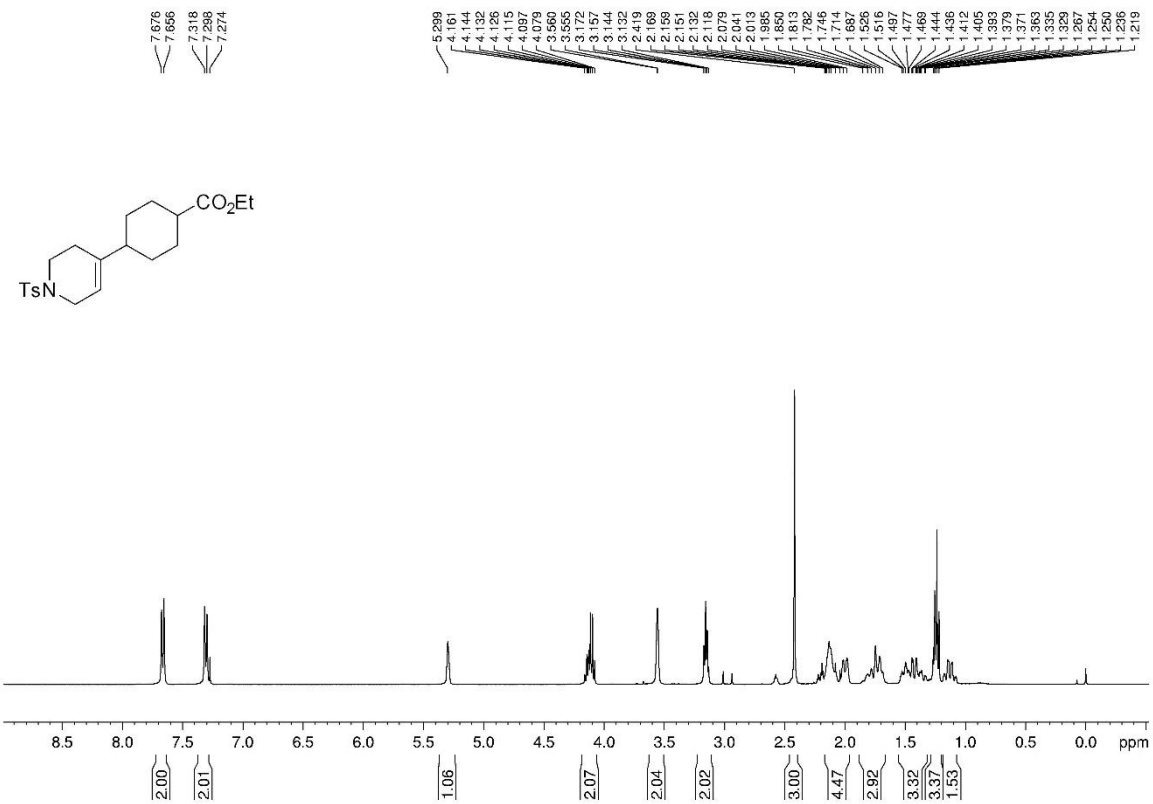
3al; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

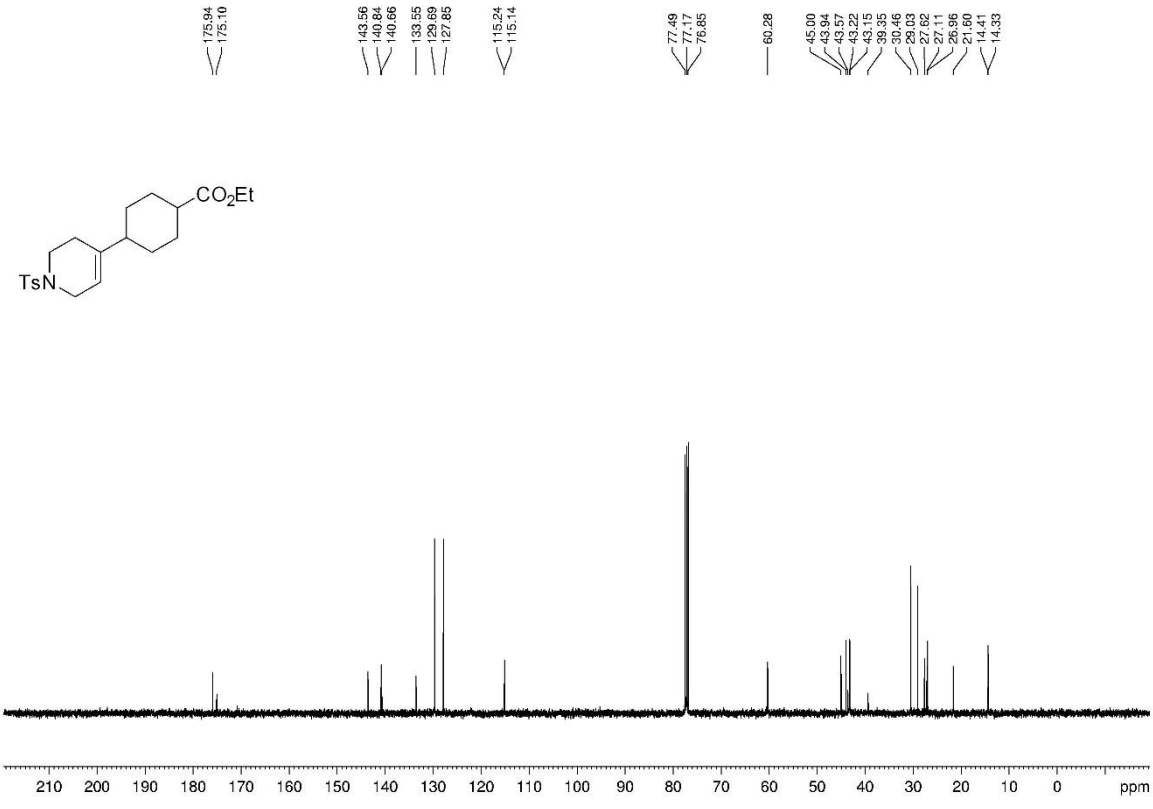


3am; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

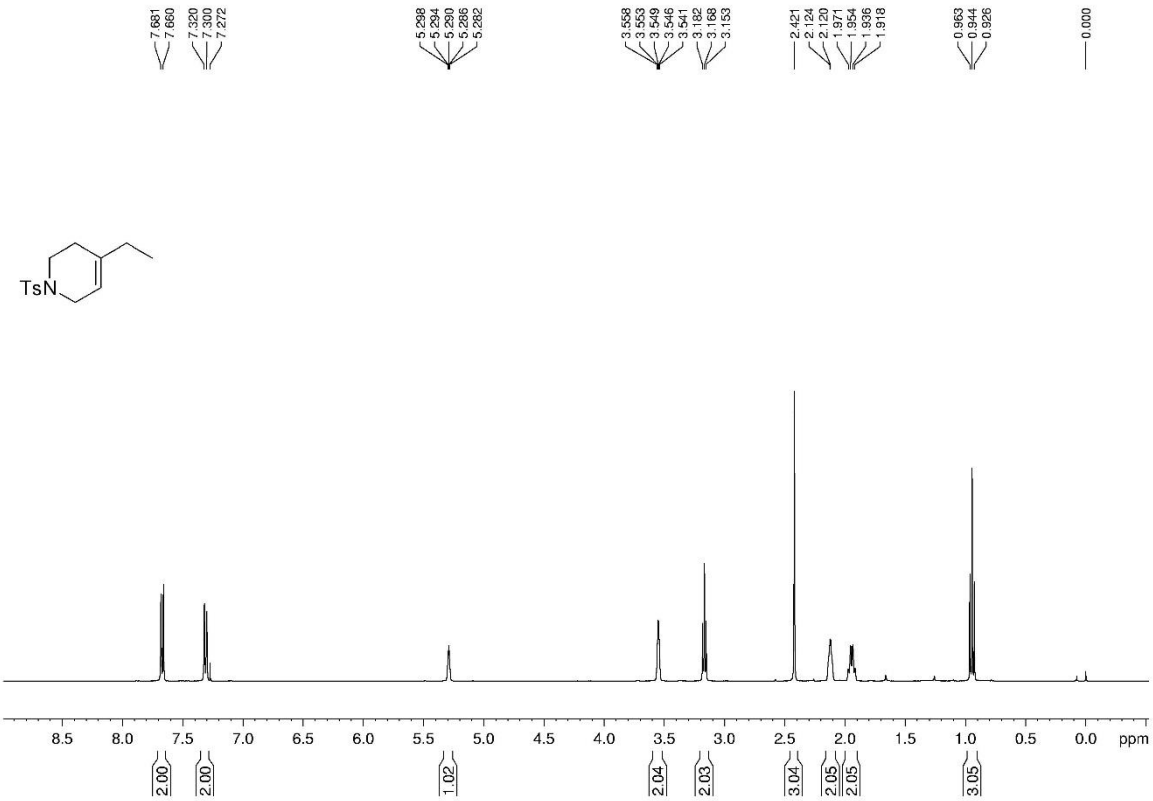


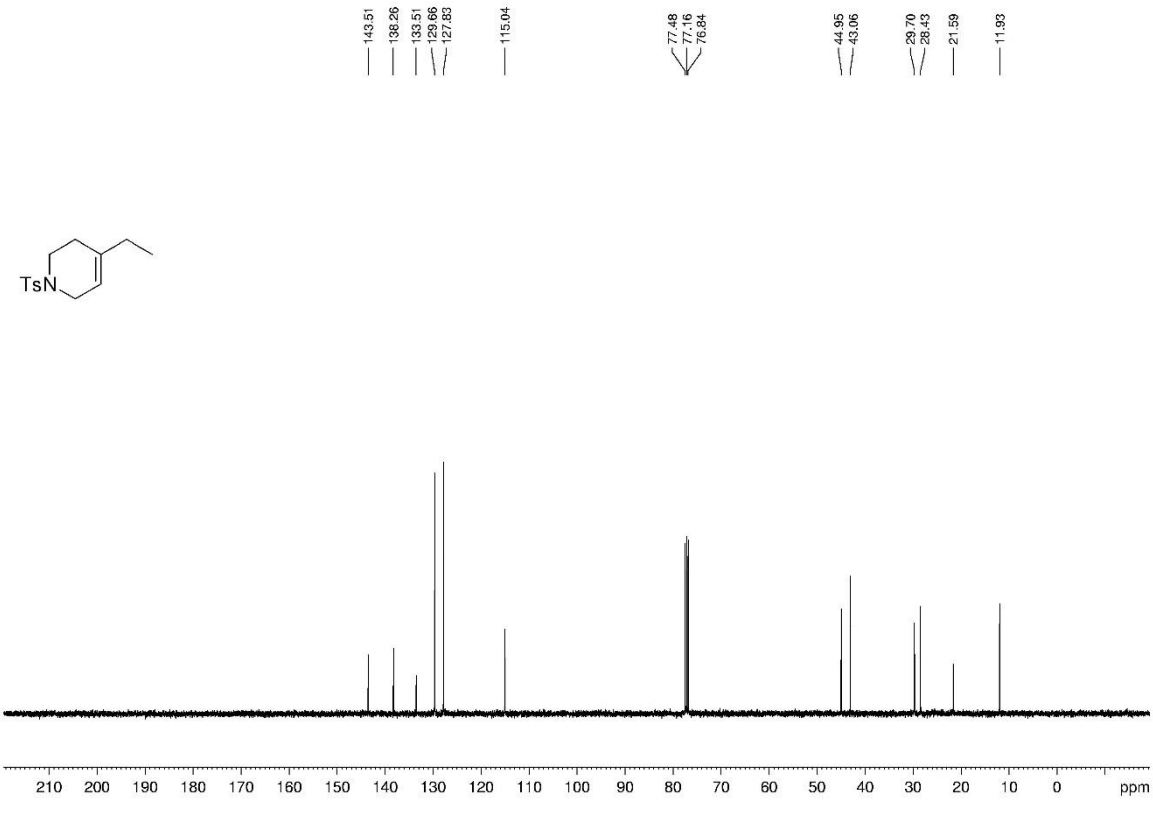
3an; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



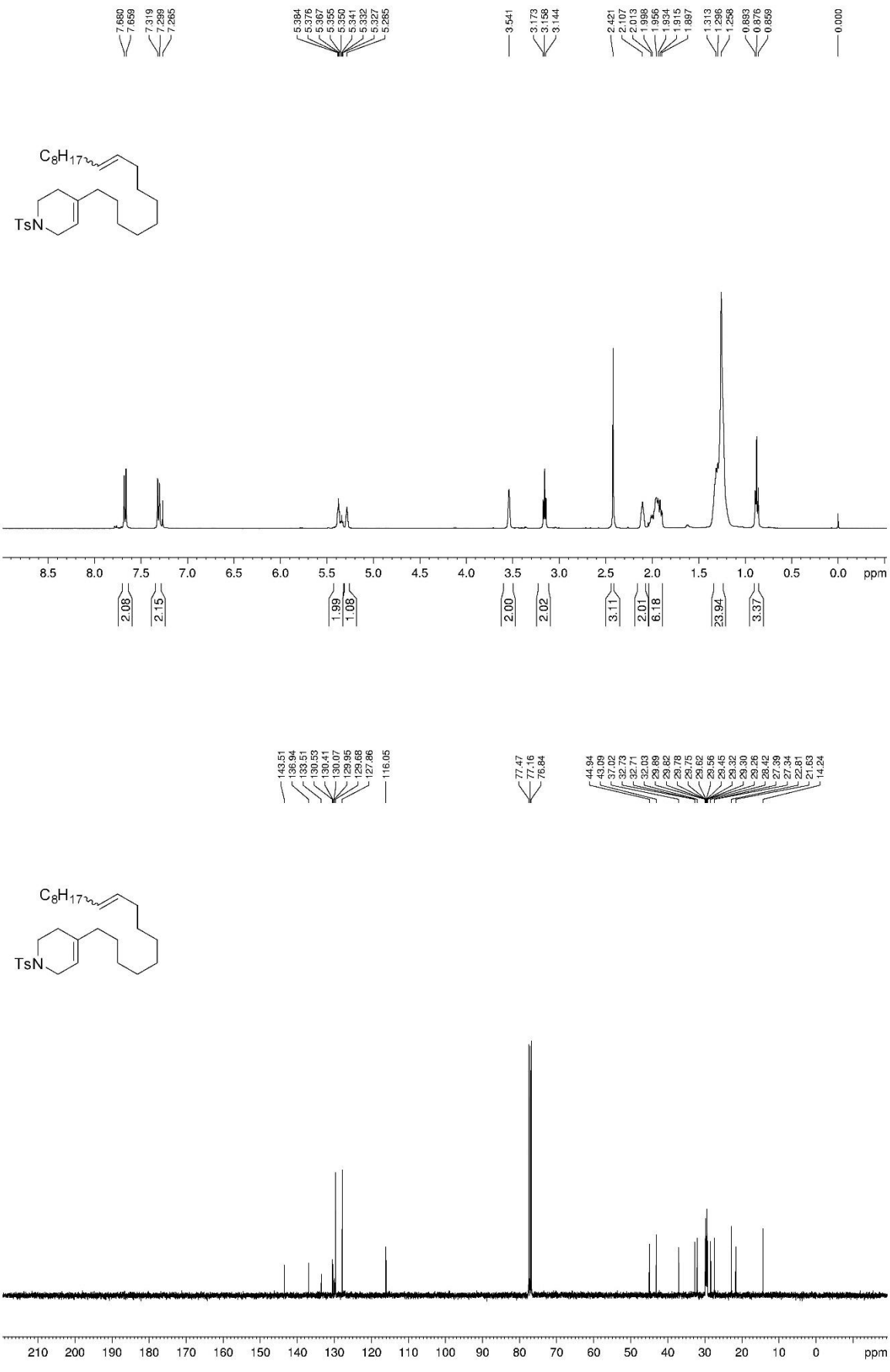


3ao; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

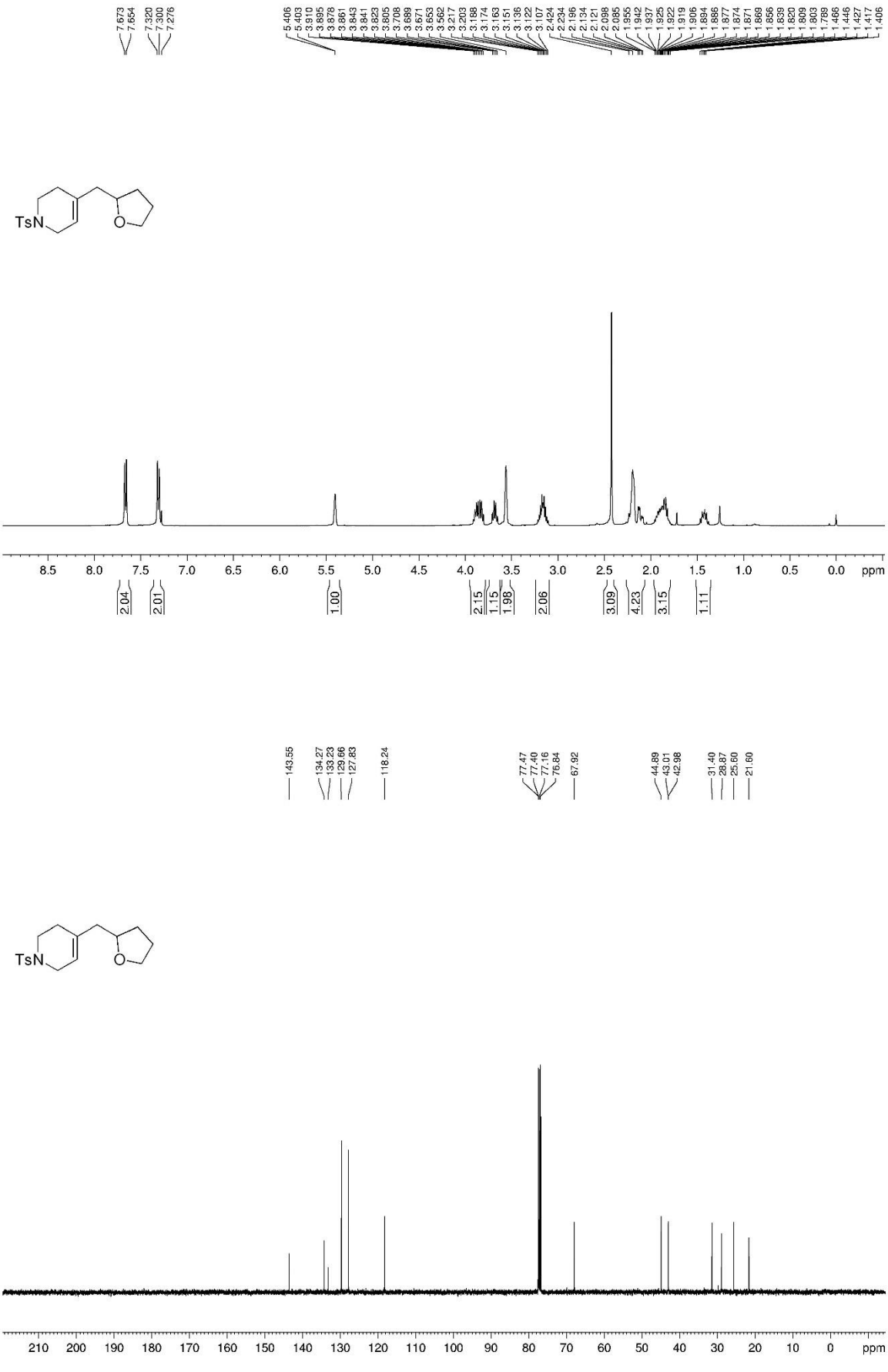




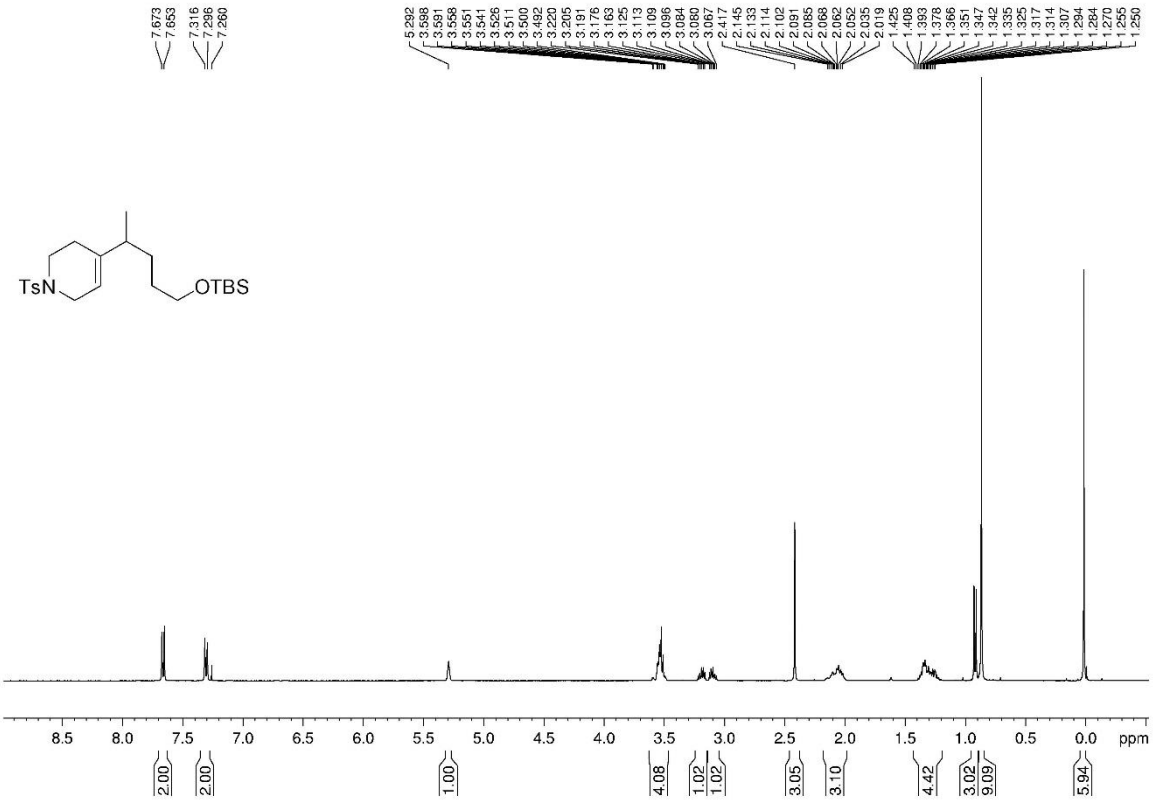
3ap; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

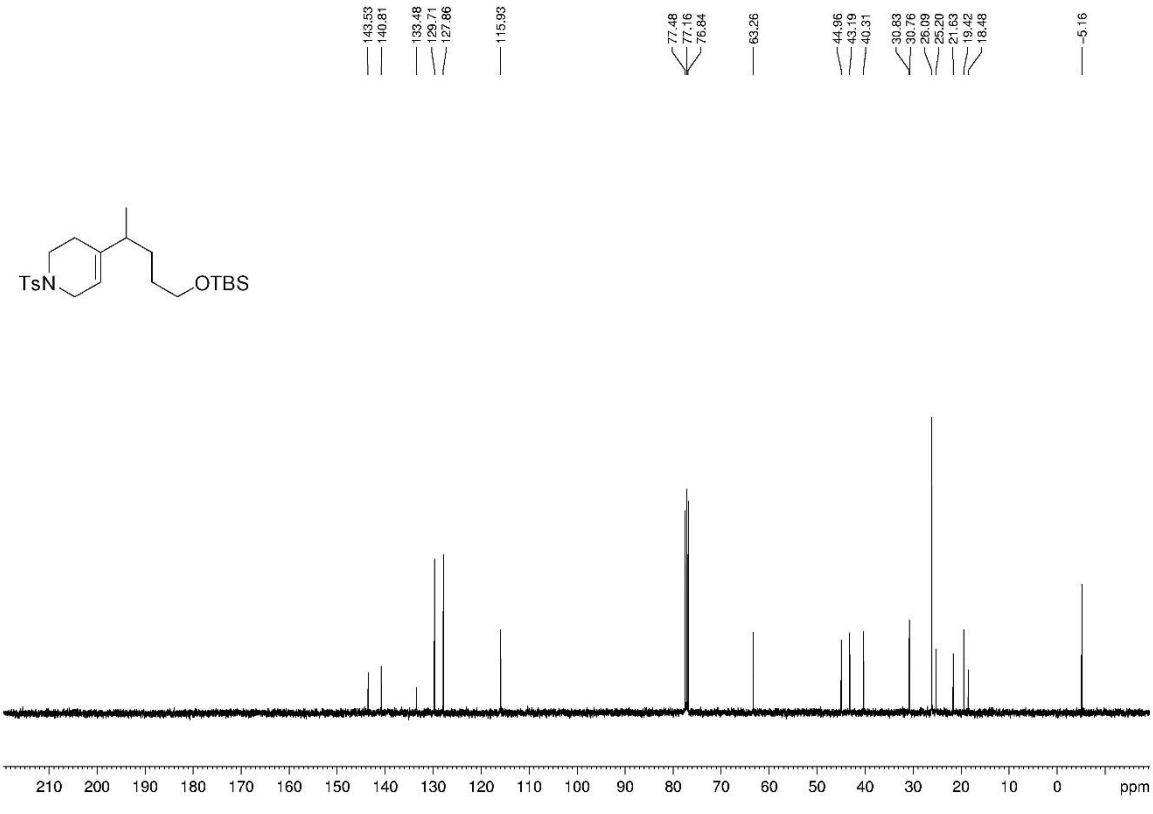


3aq; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

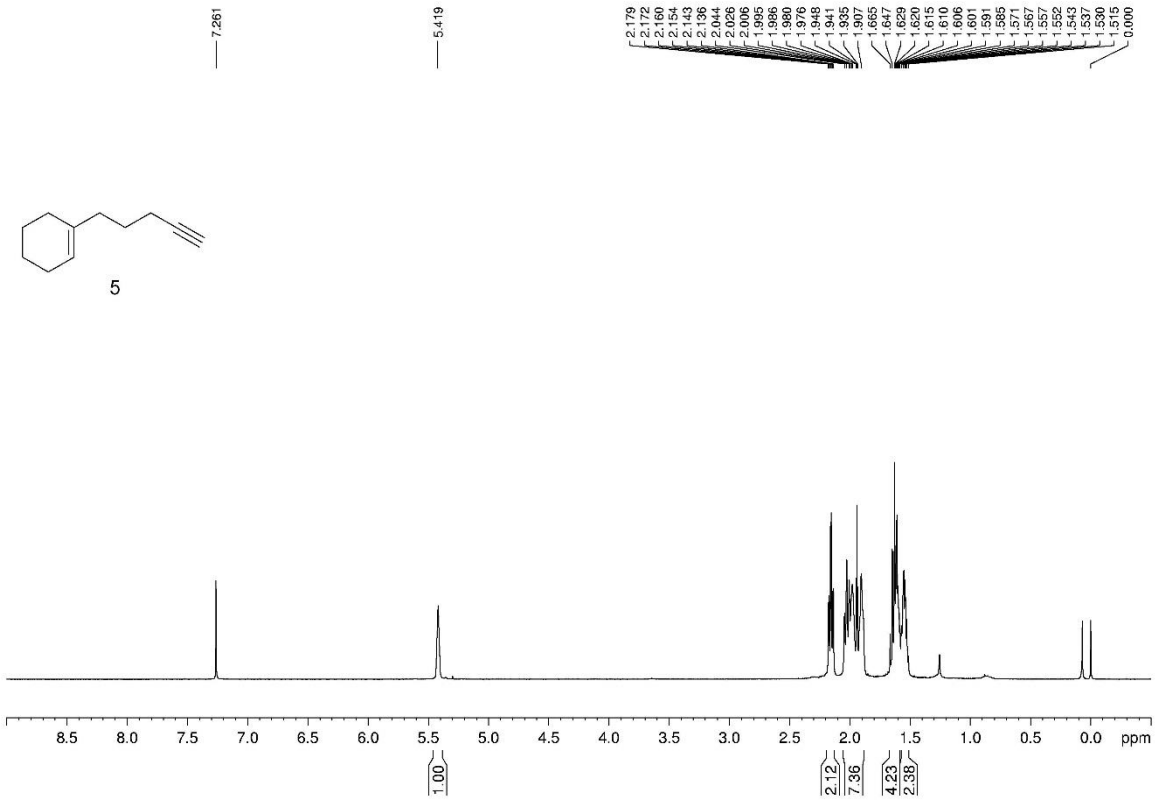


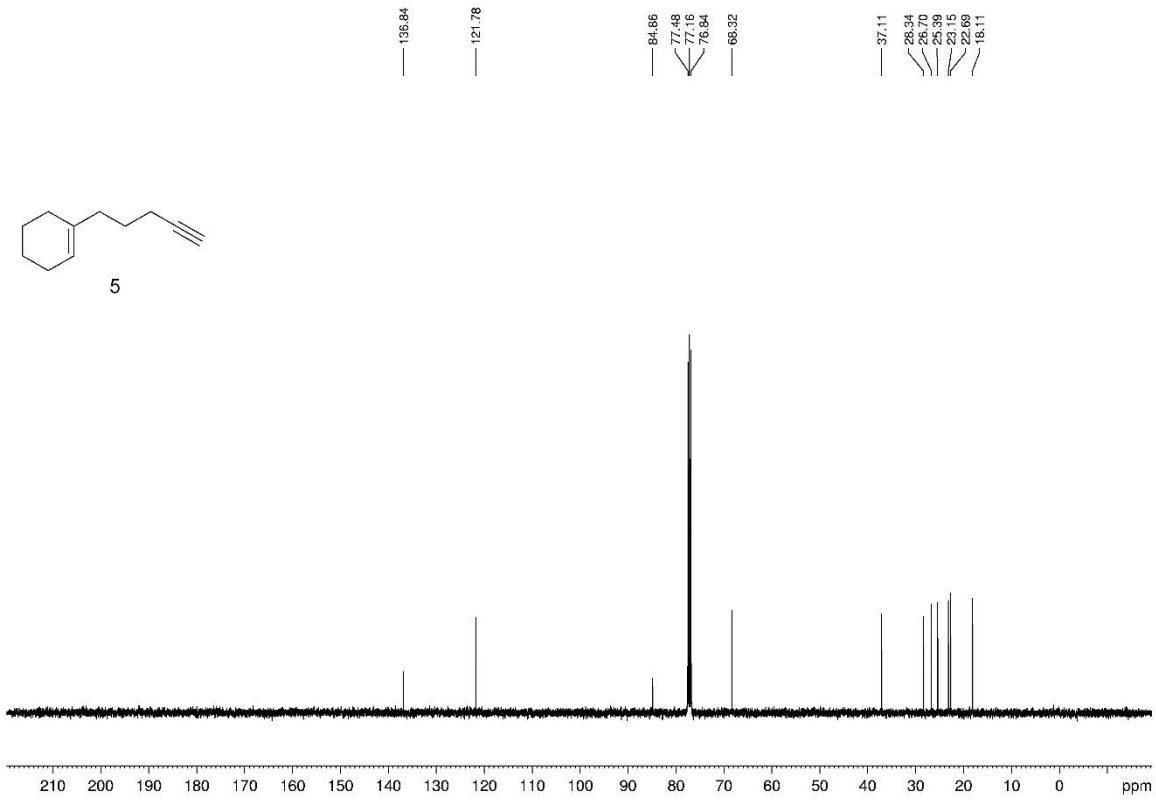
3ar; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



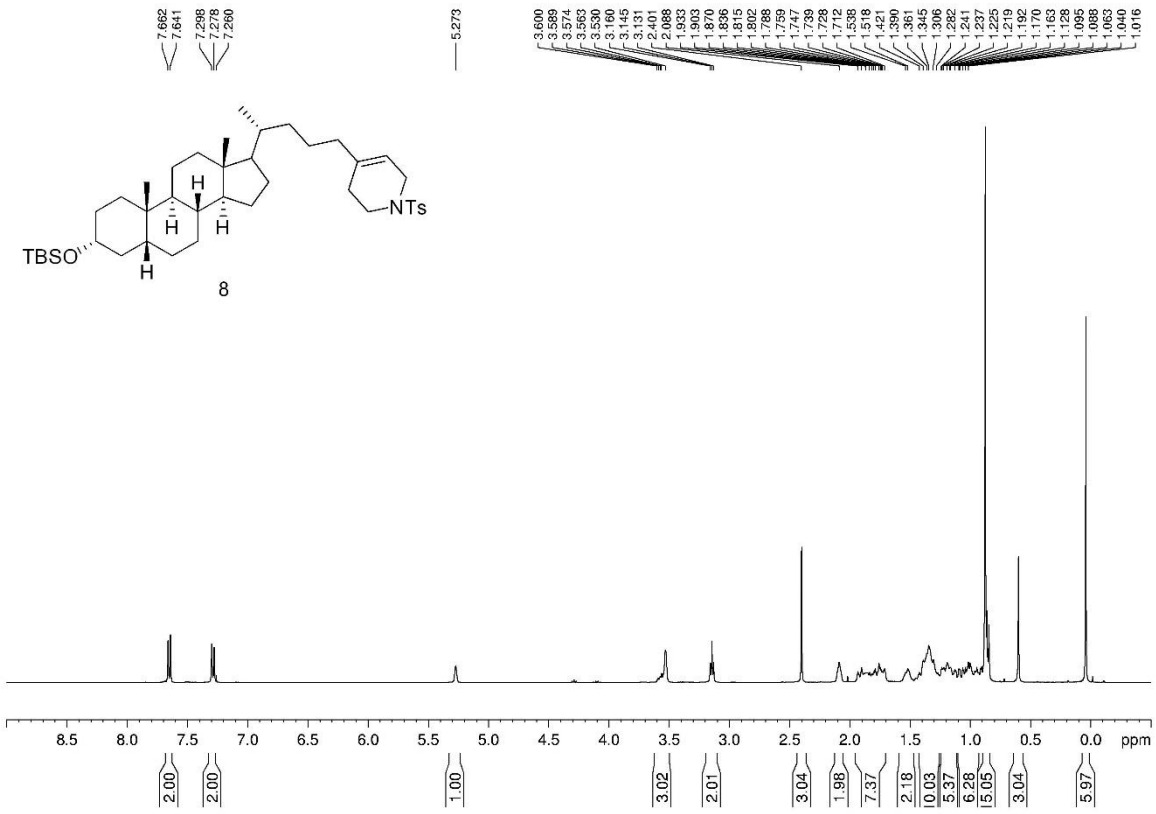


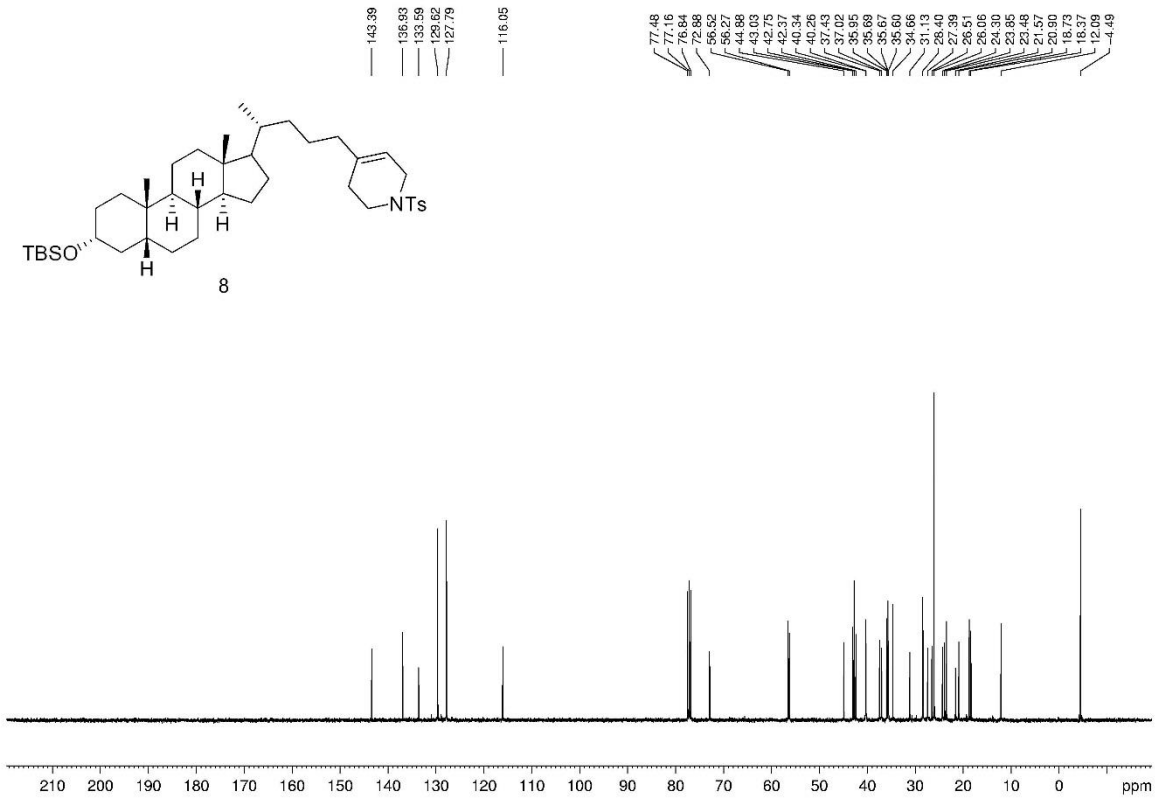
5; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



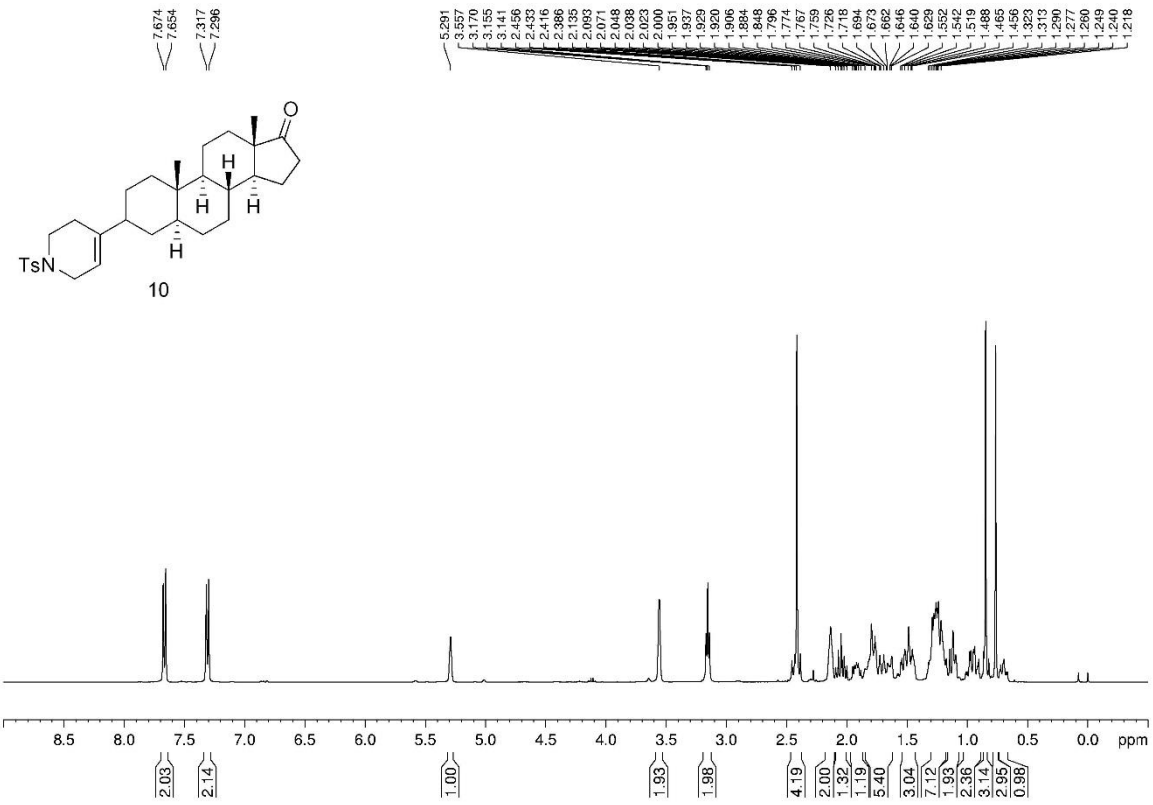


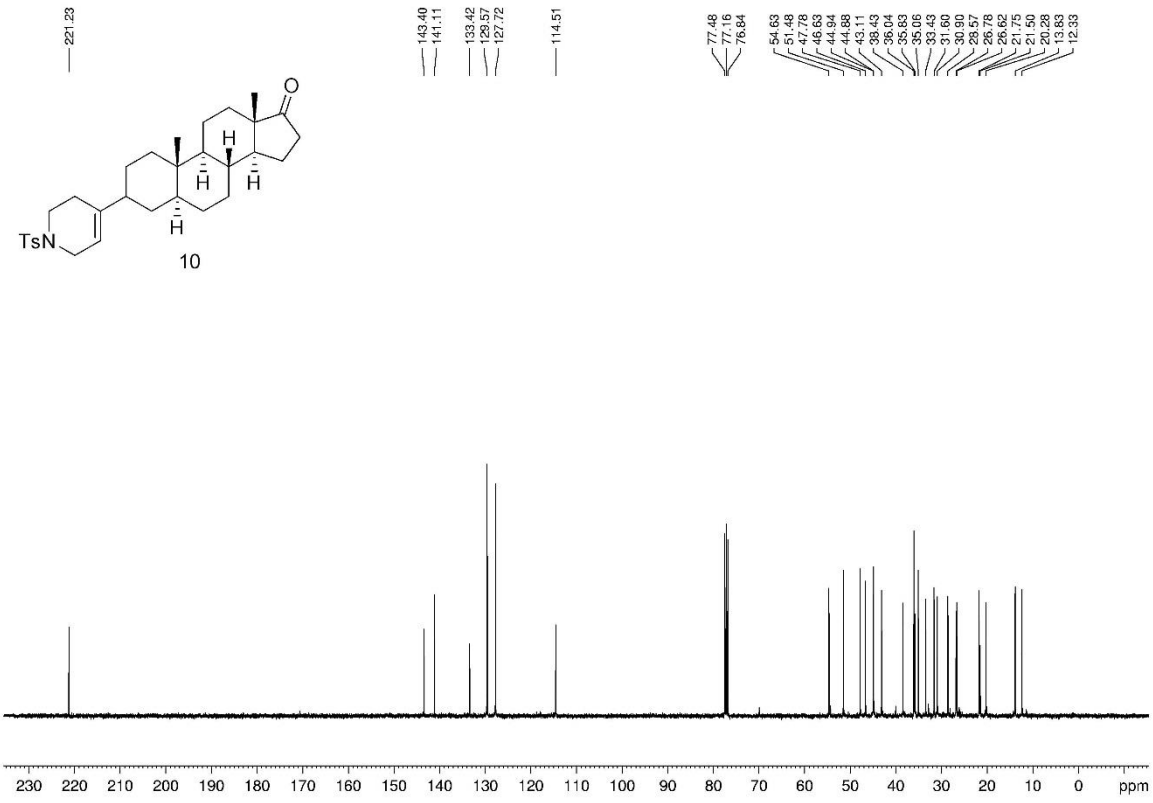
8; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



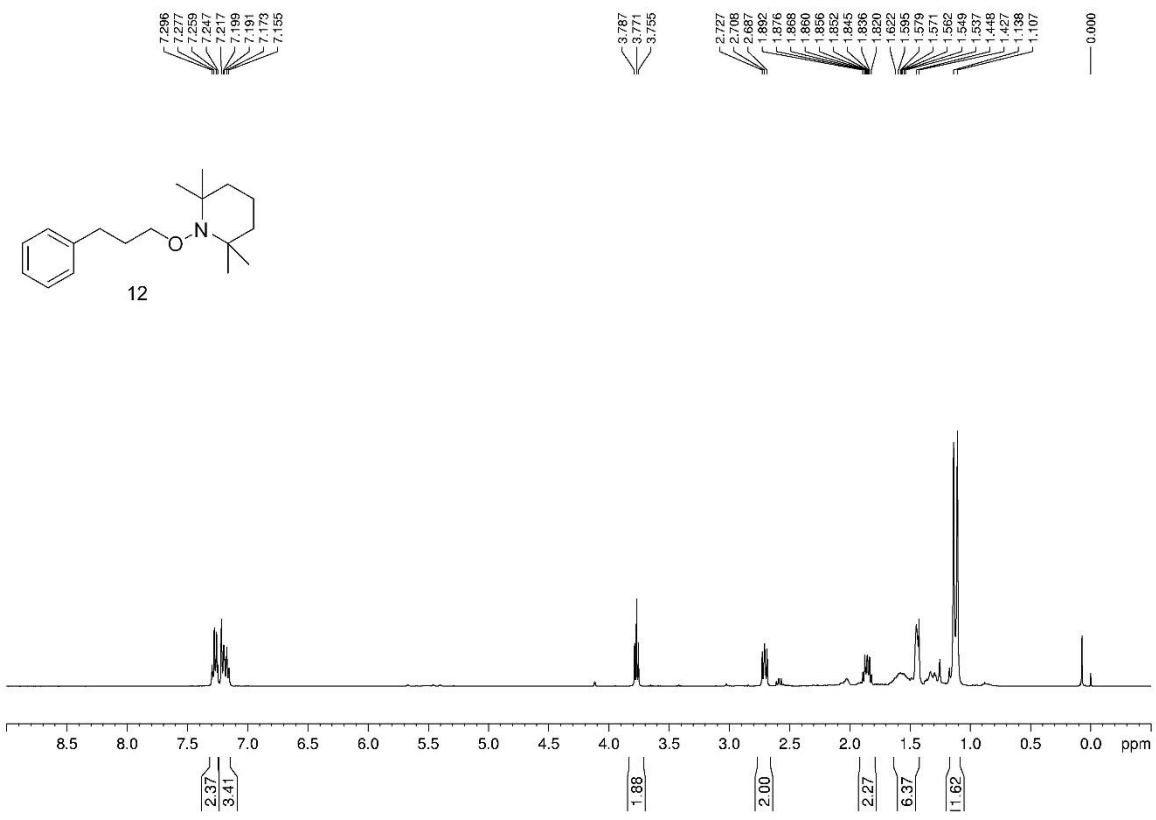


10; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

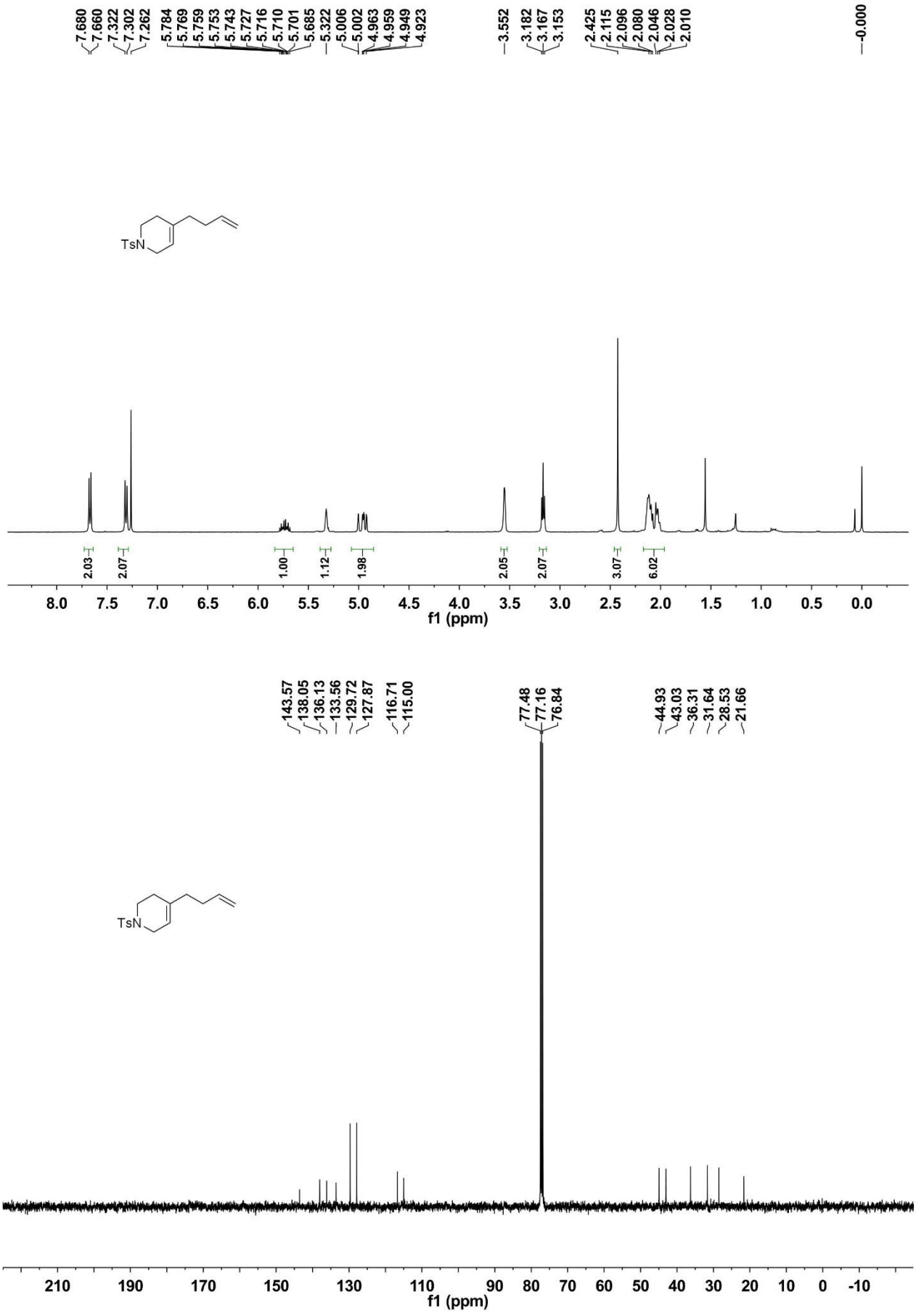




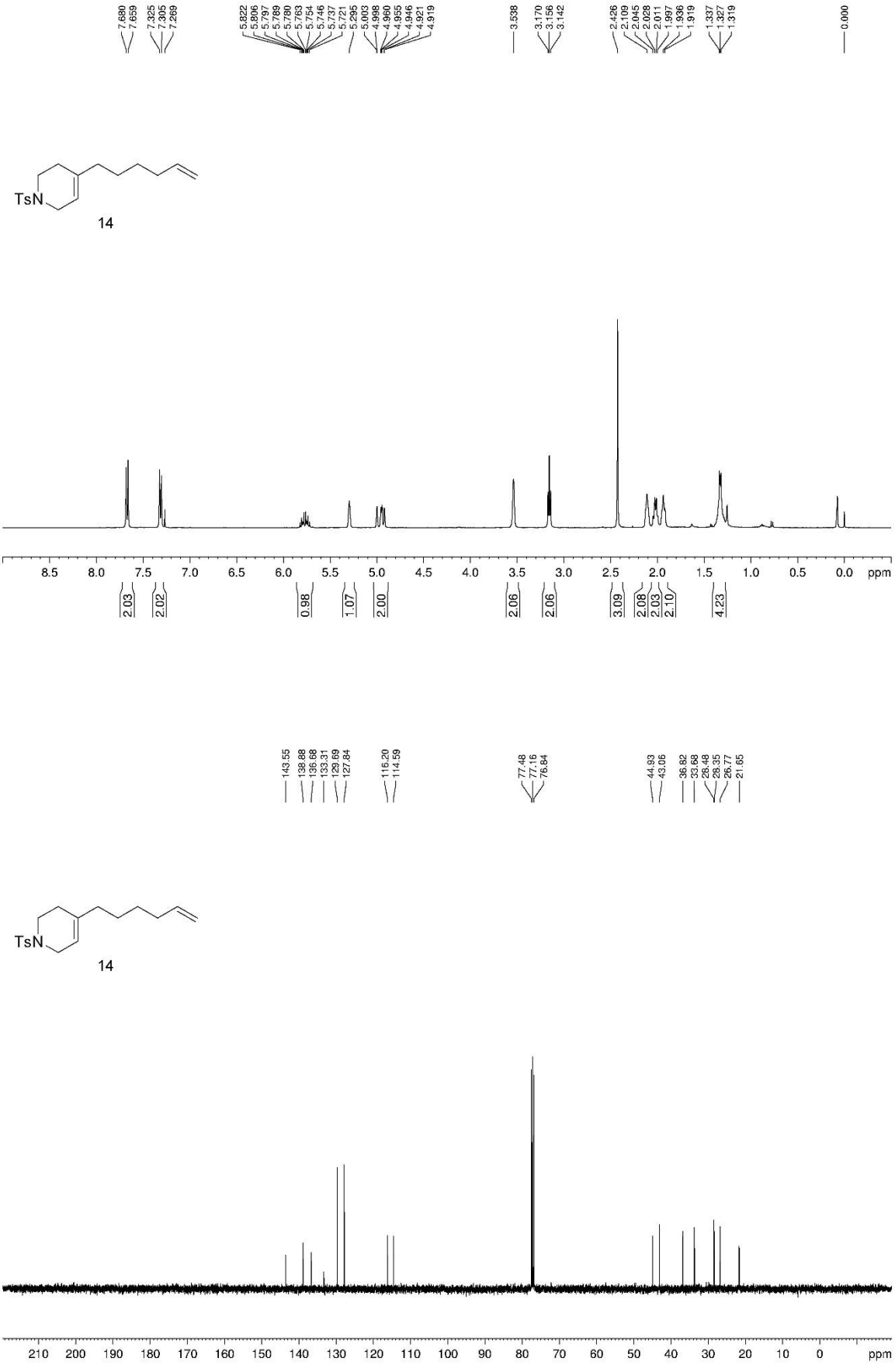
12; ^{1}H NMR (400MHz, $CDCl_3$)



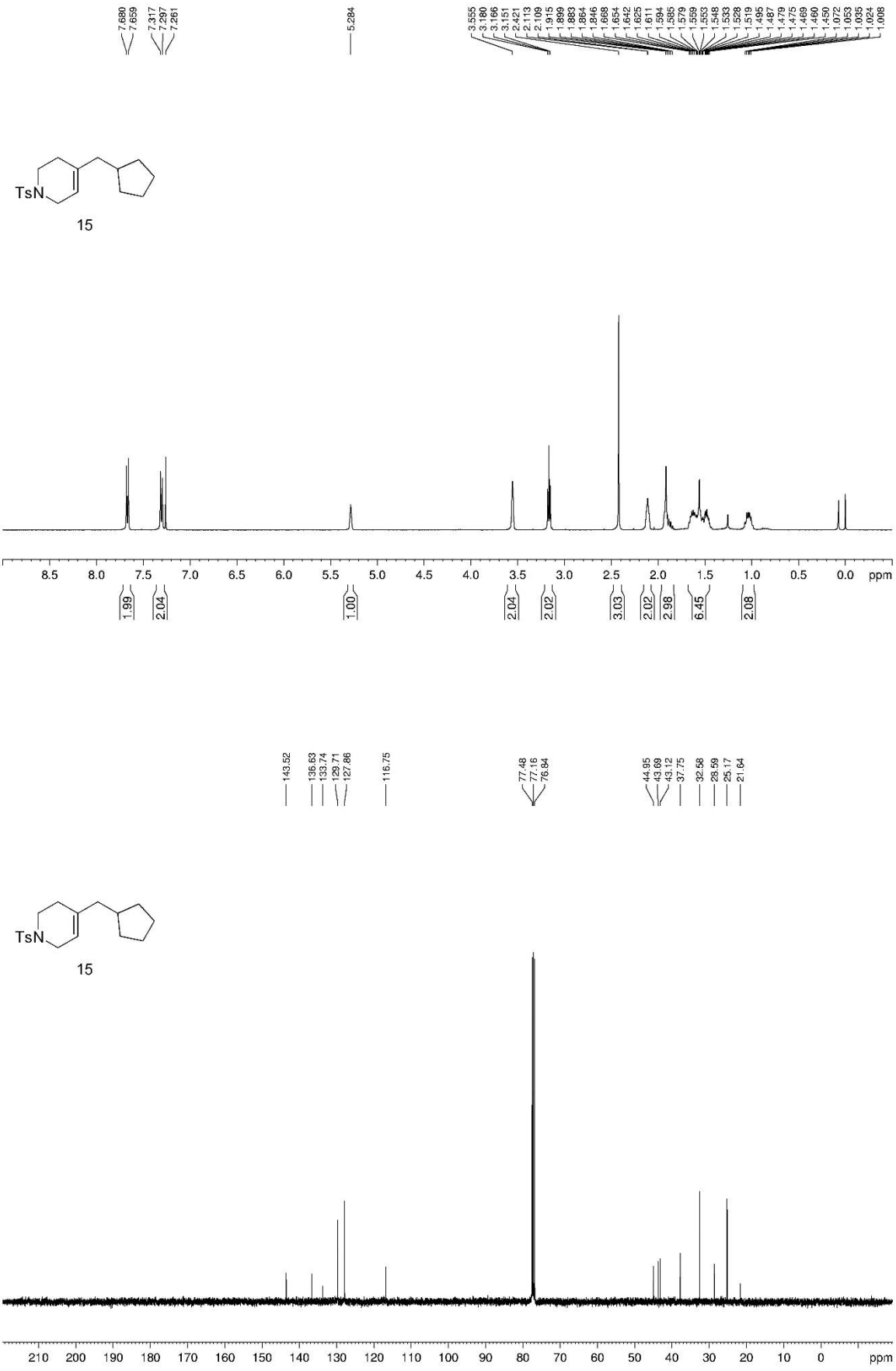
3as; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



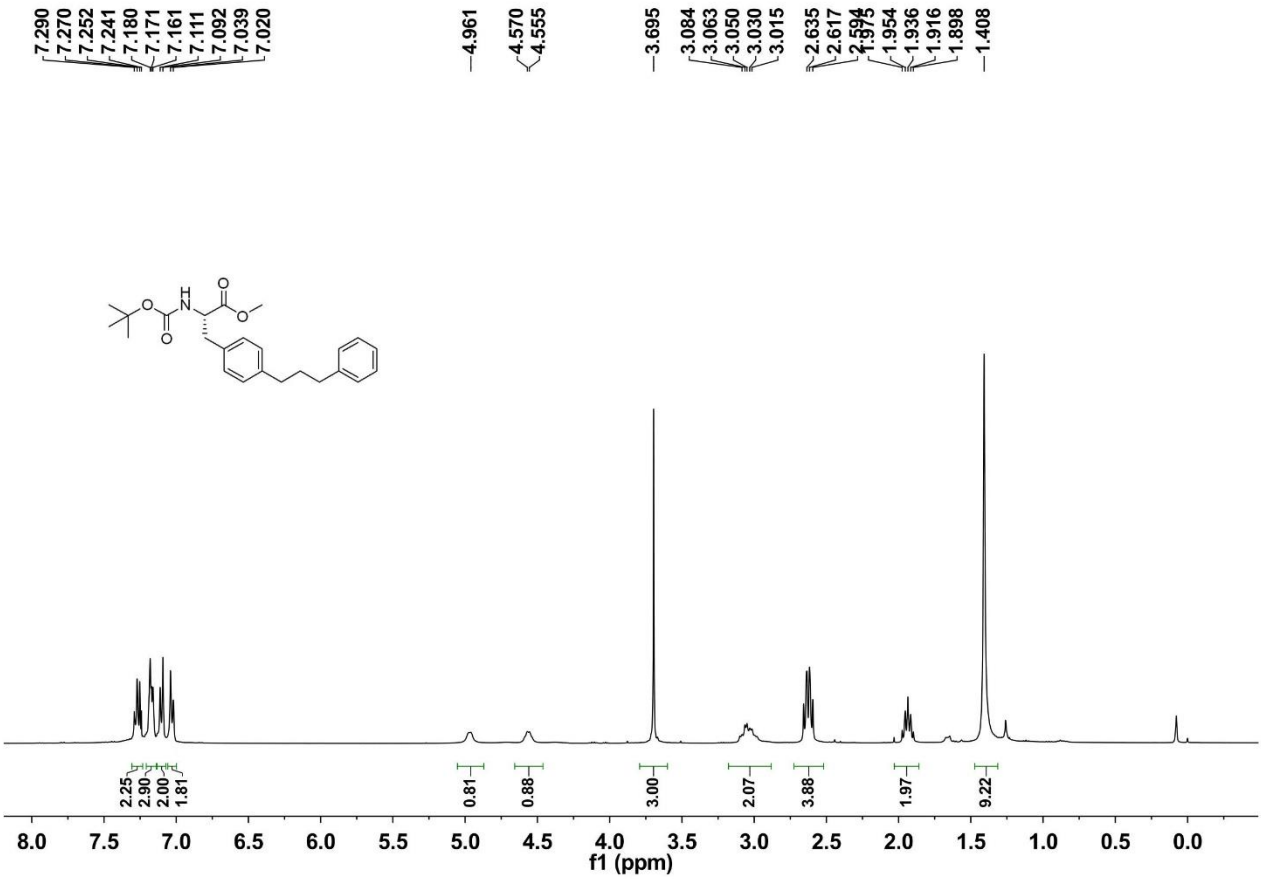
14; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

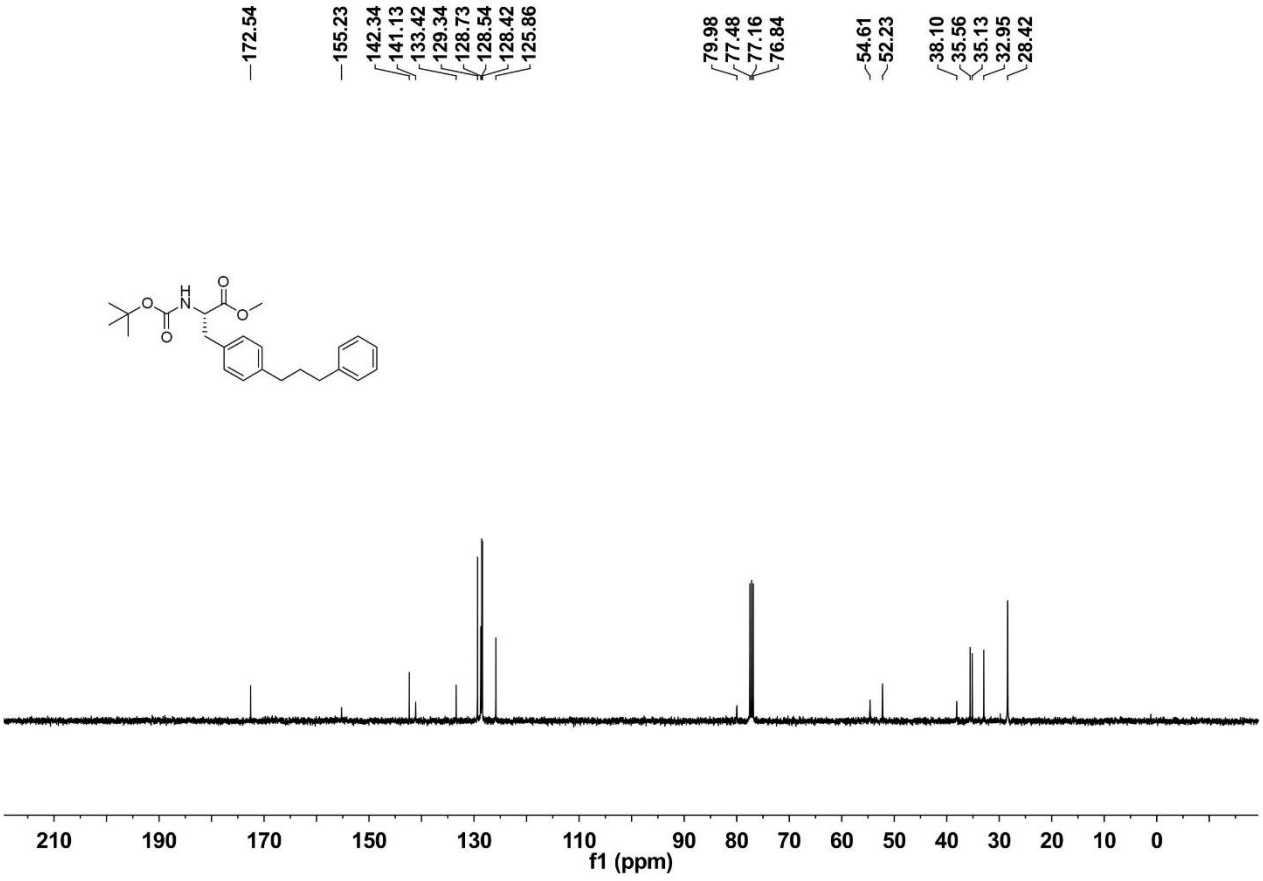


15; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

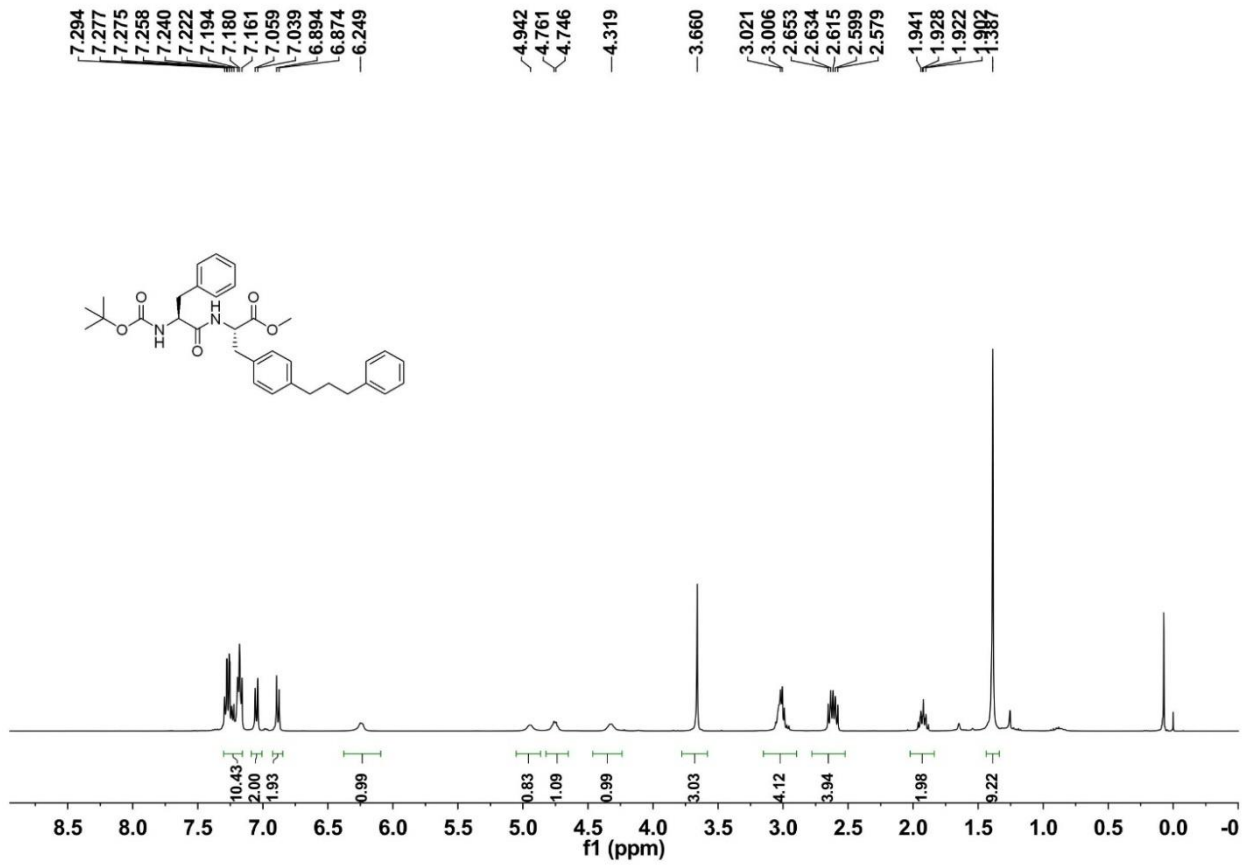


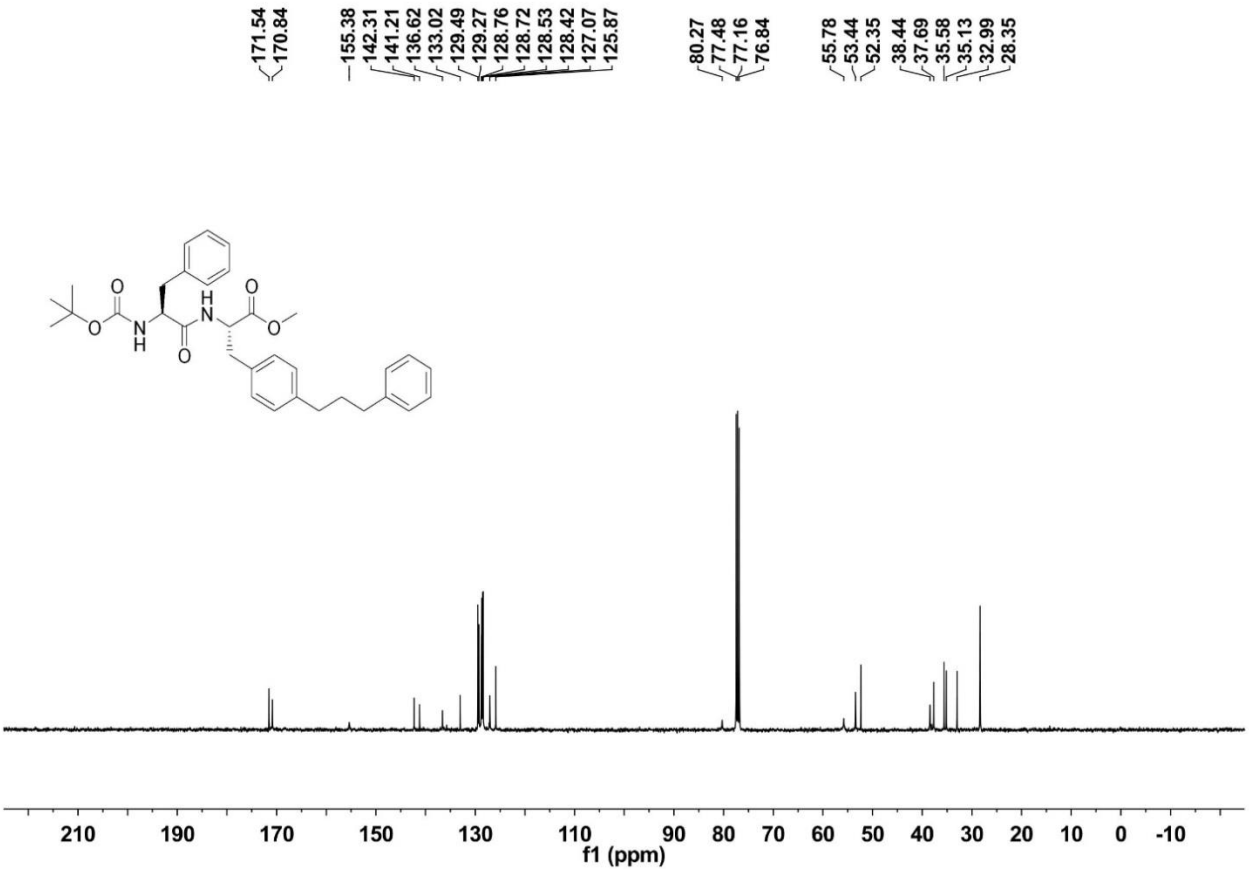
17a; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



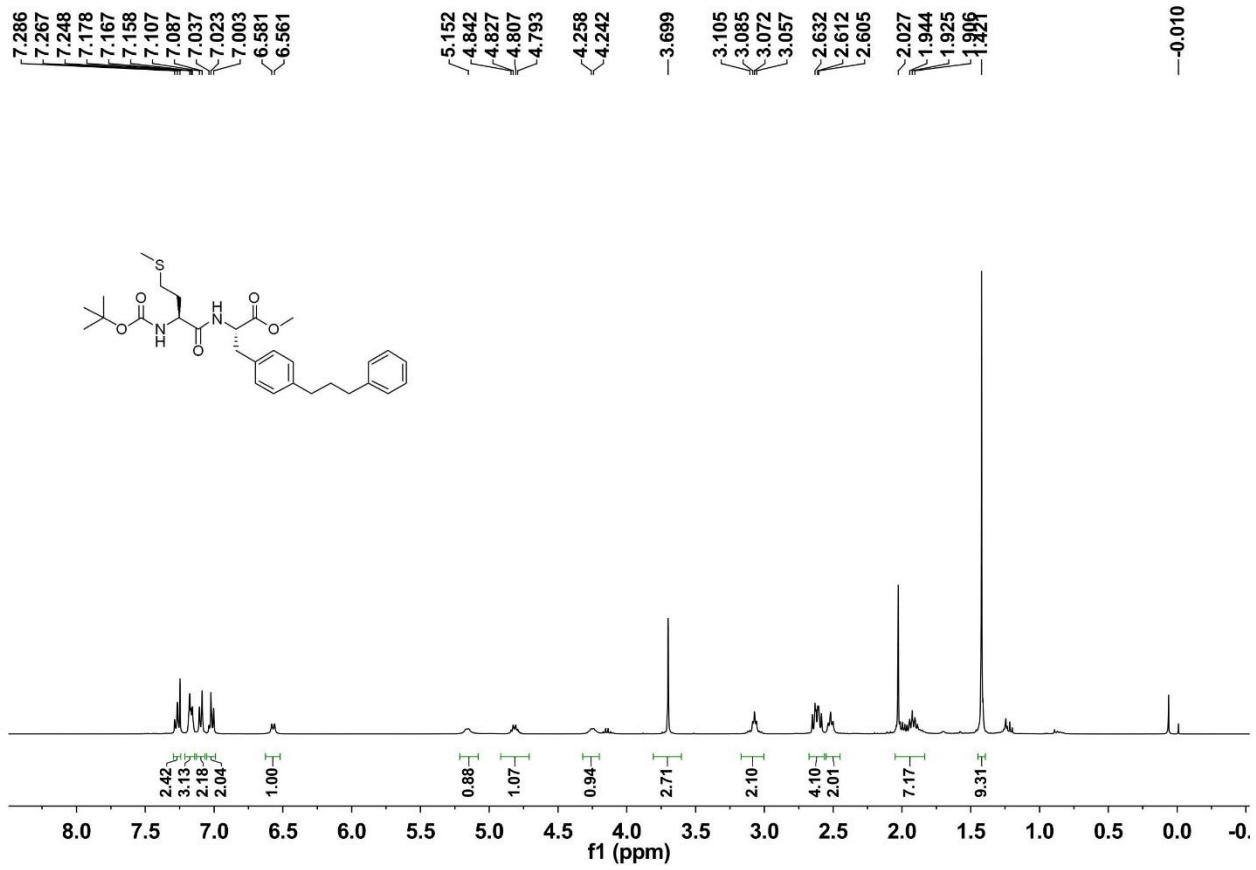


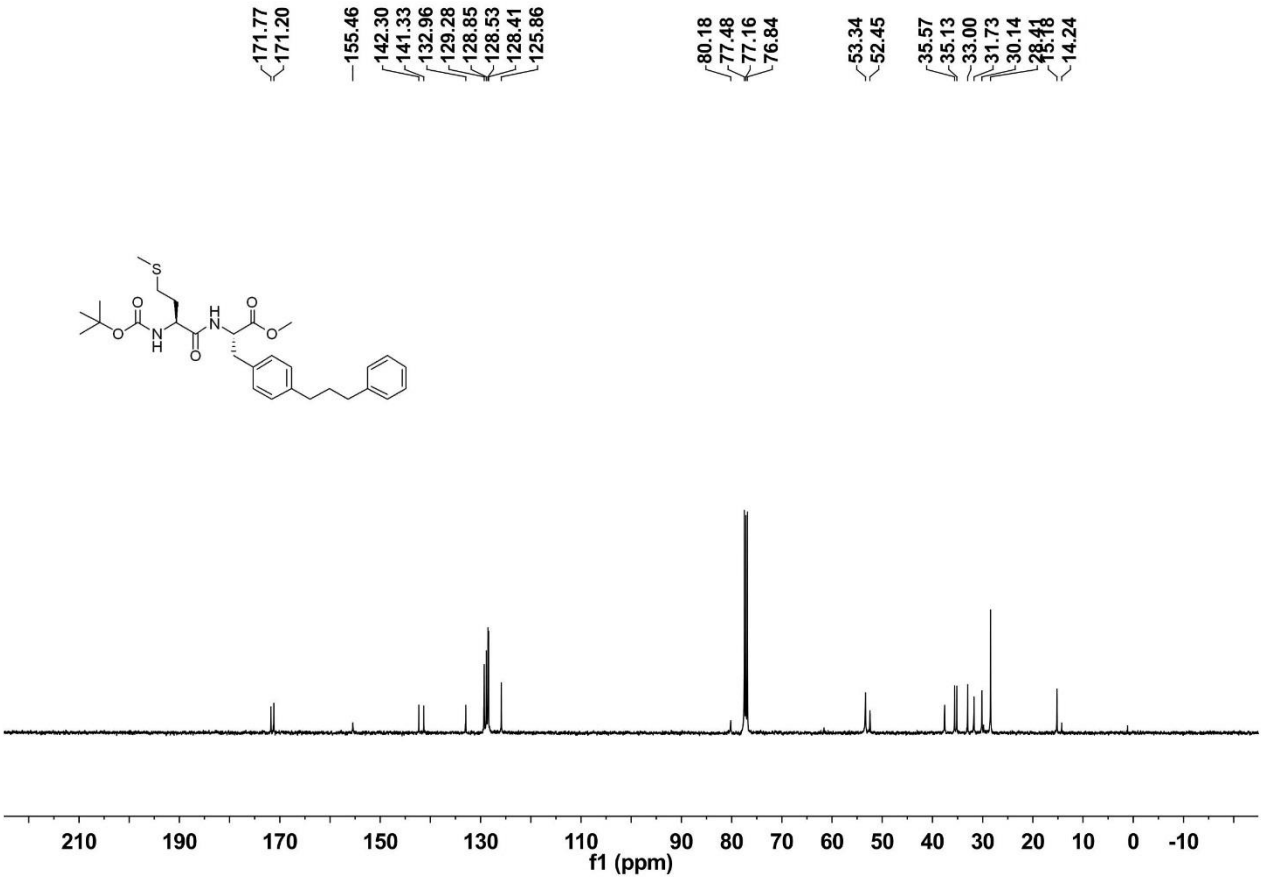
17b; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



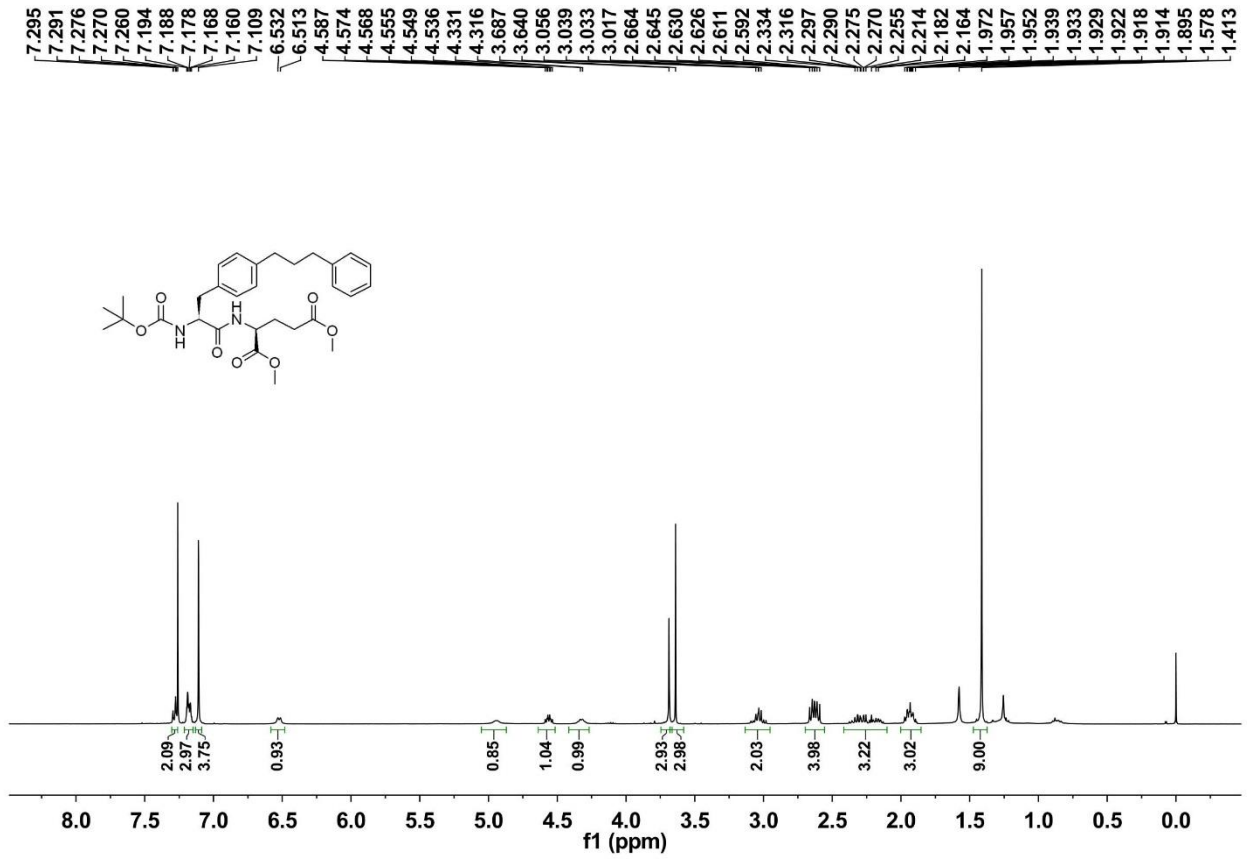


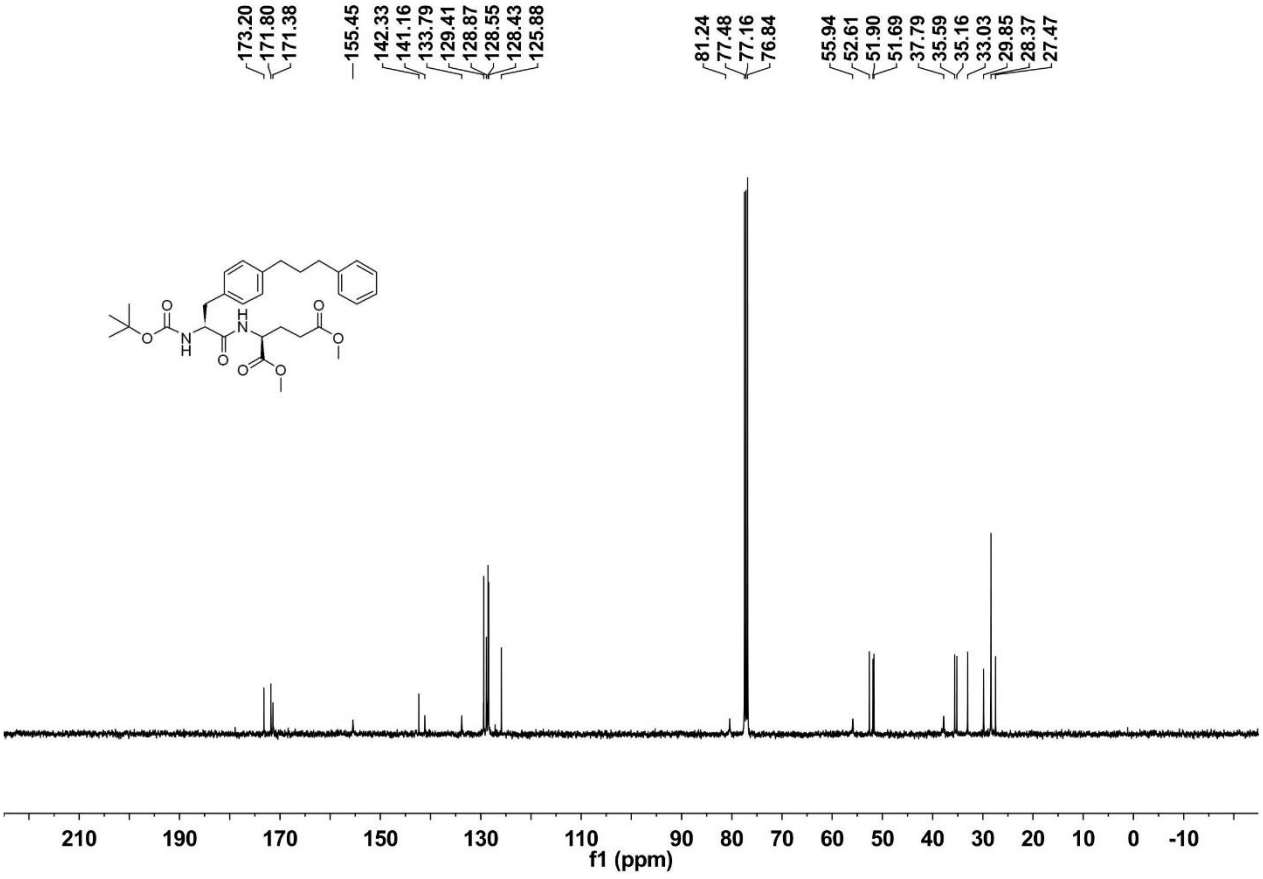
17c; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



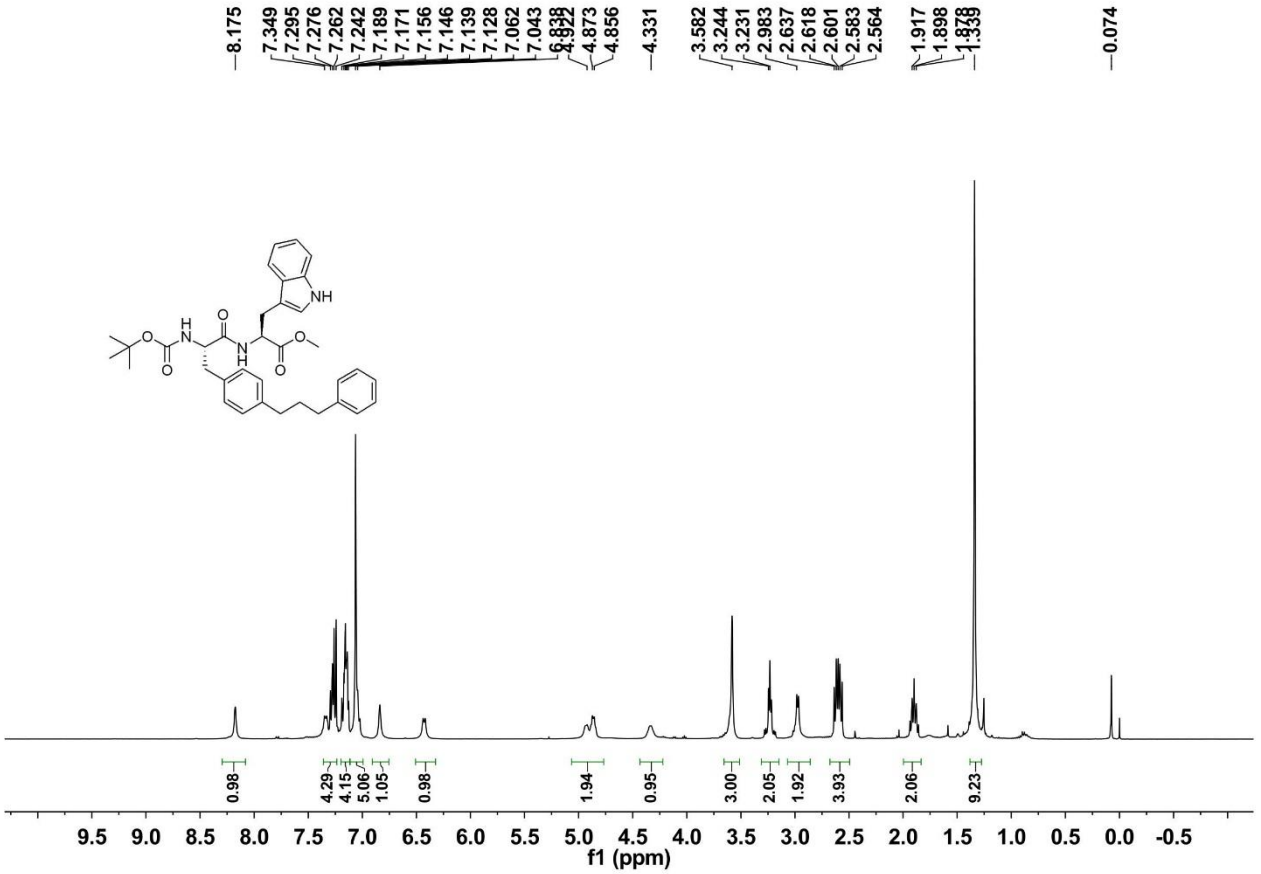


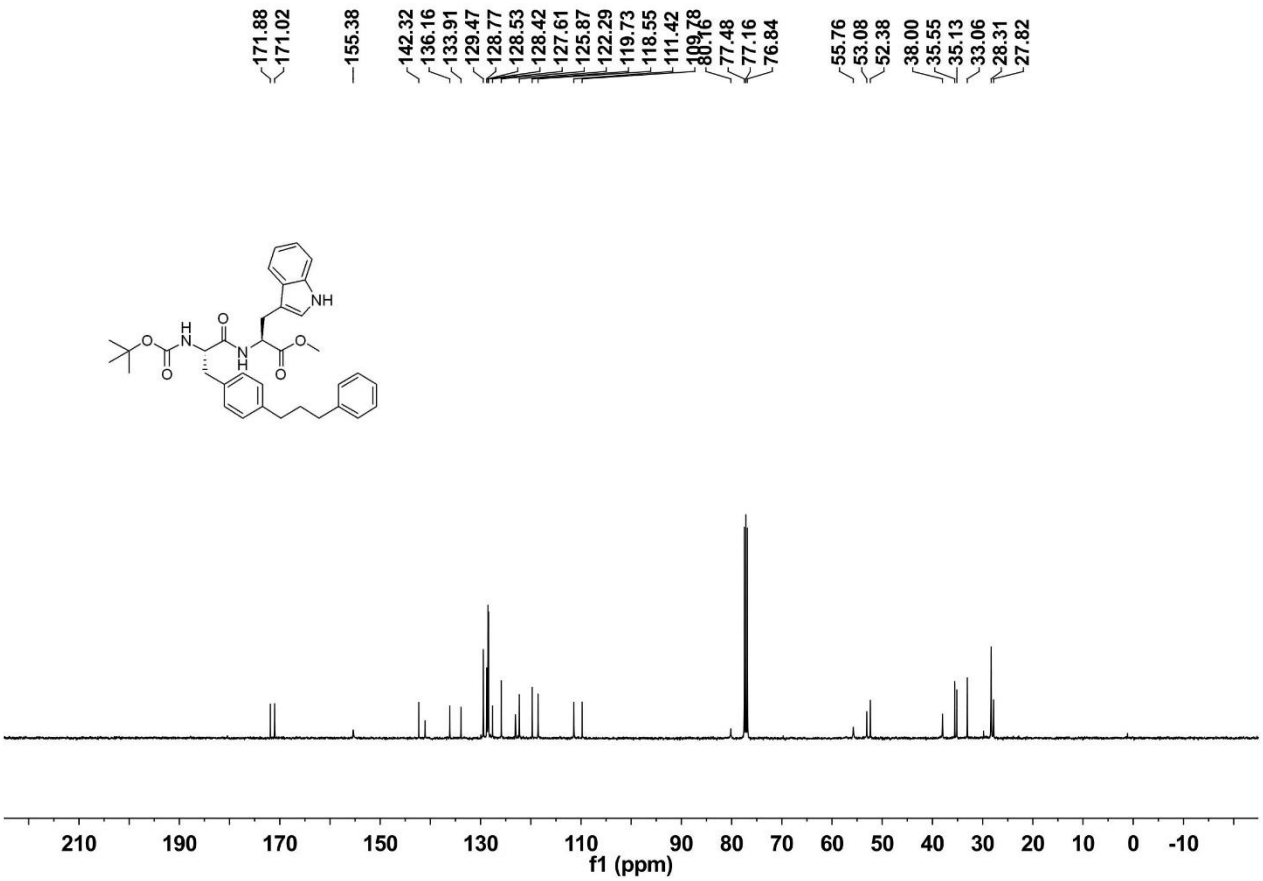
17d; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



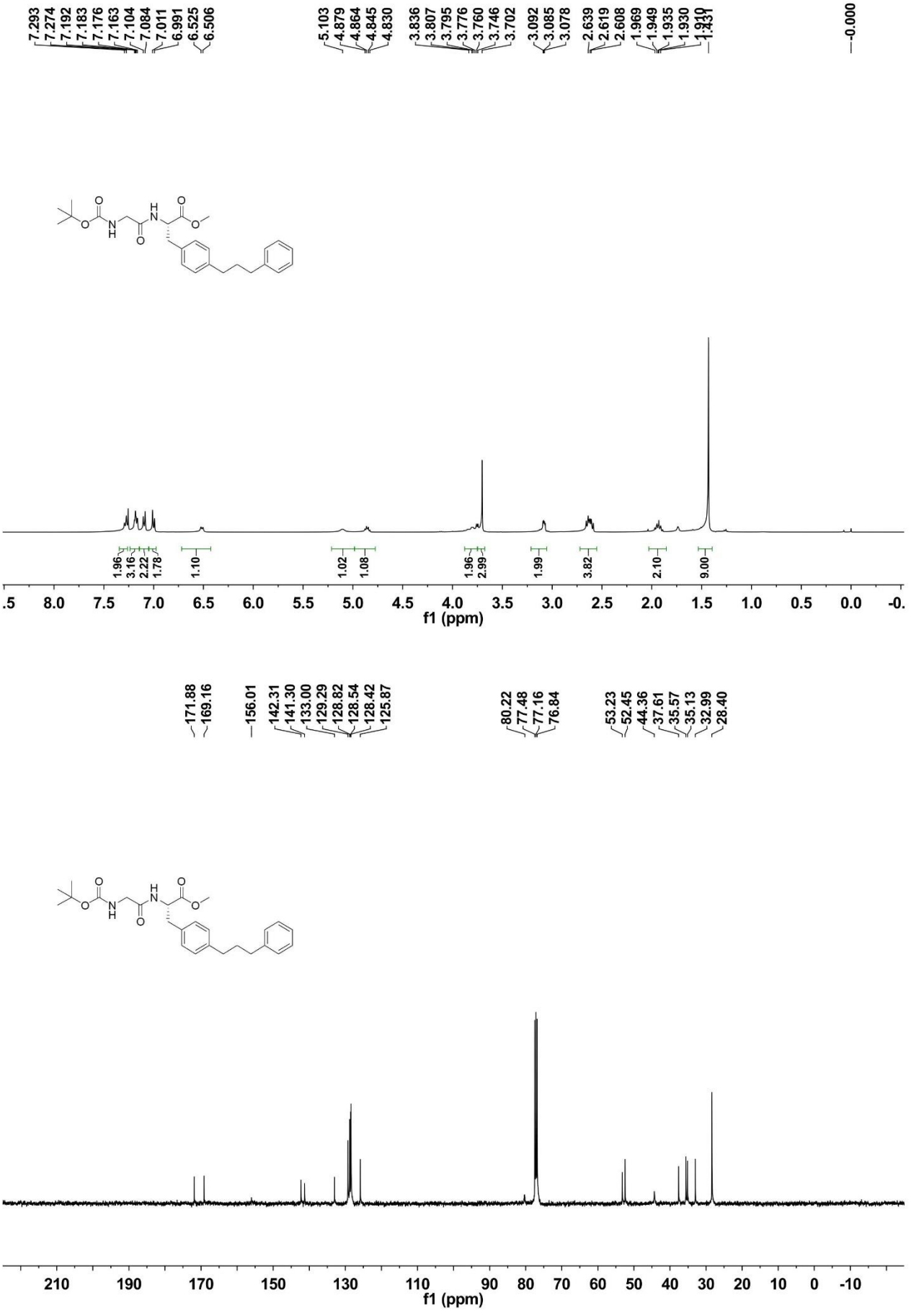


17e; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

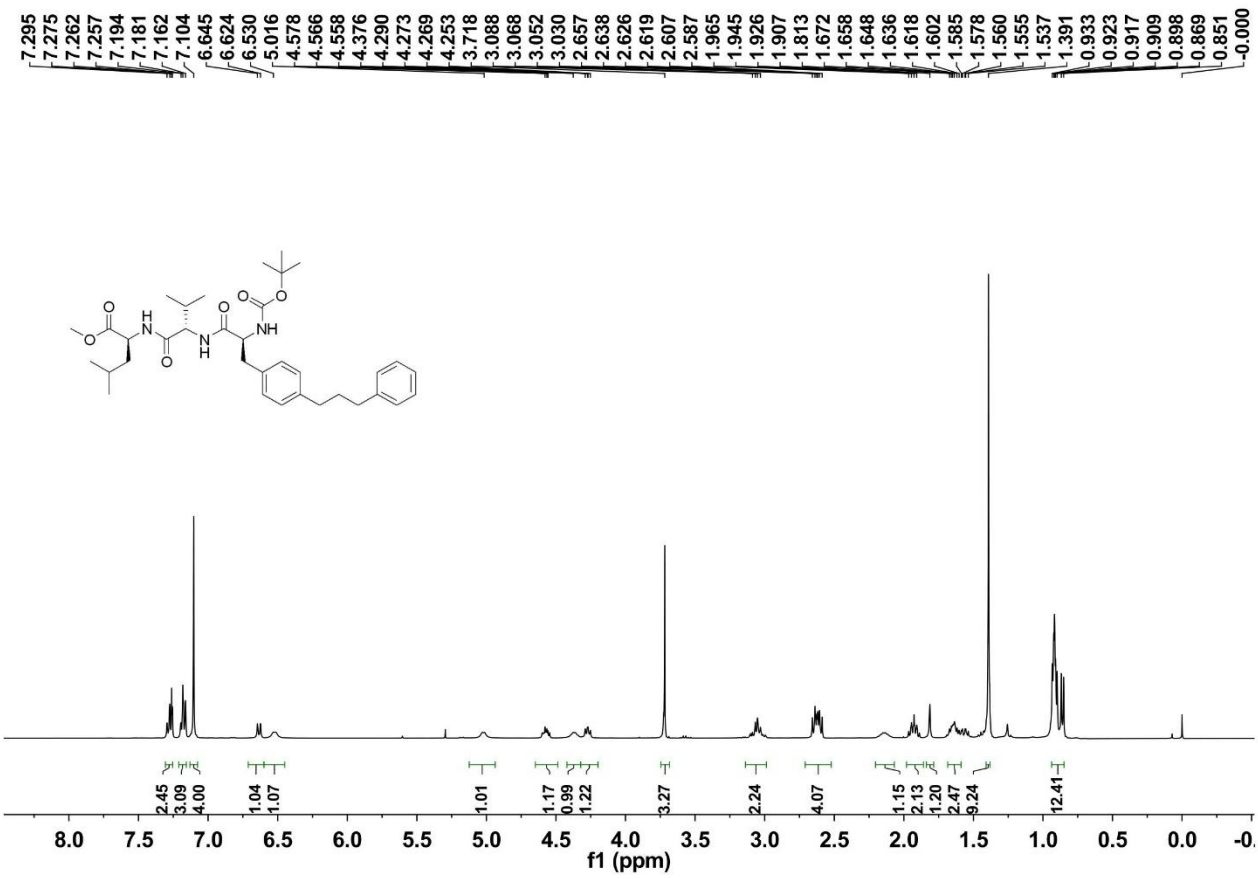


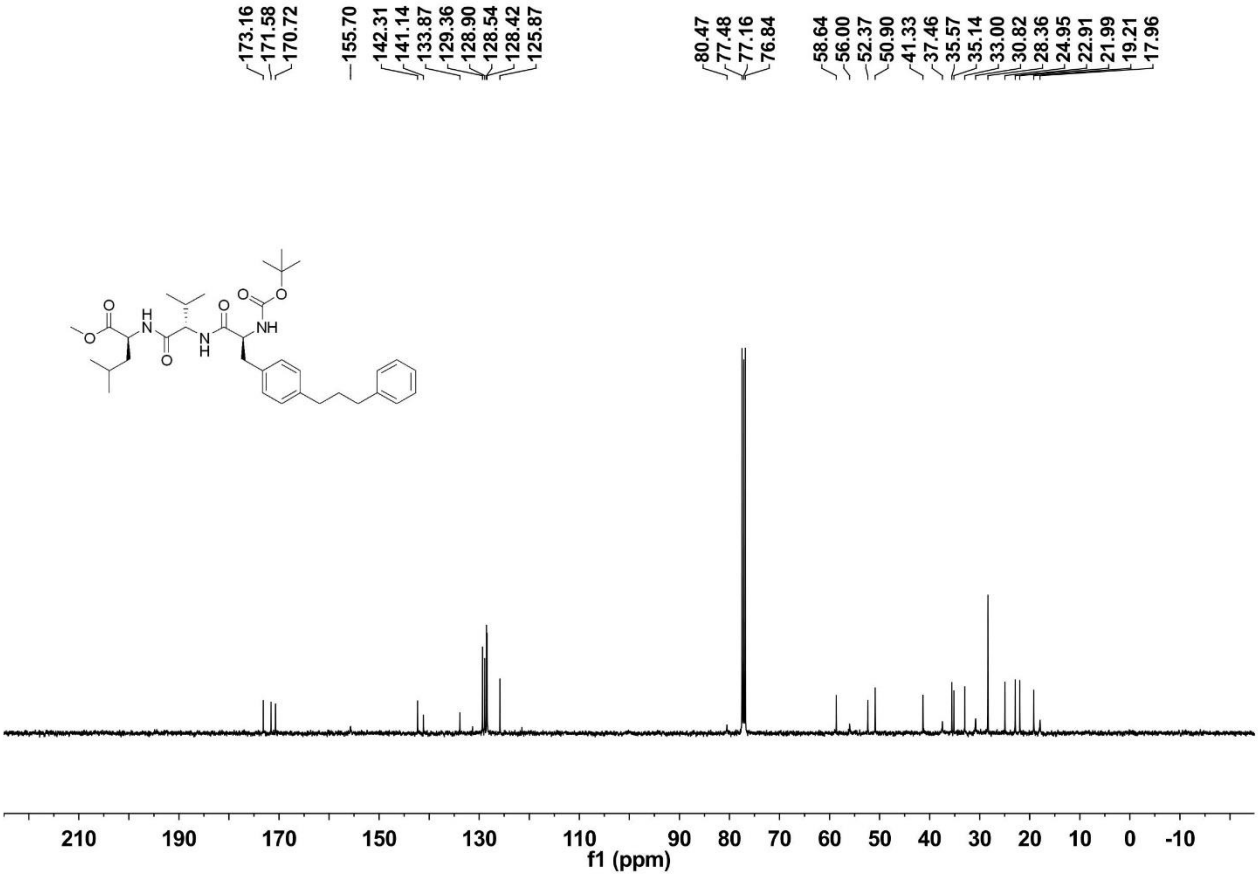


17f; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

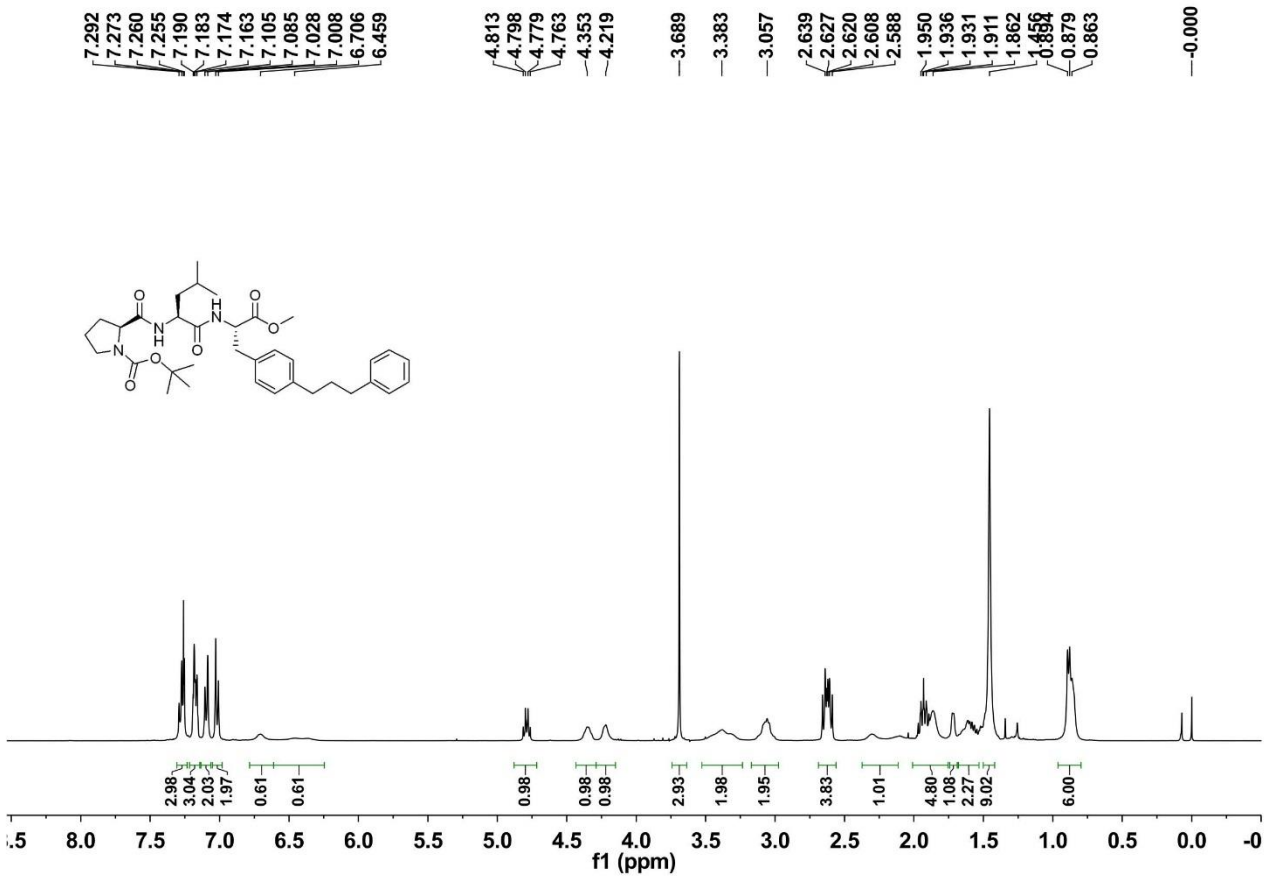


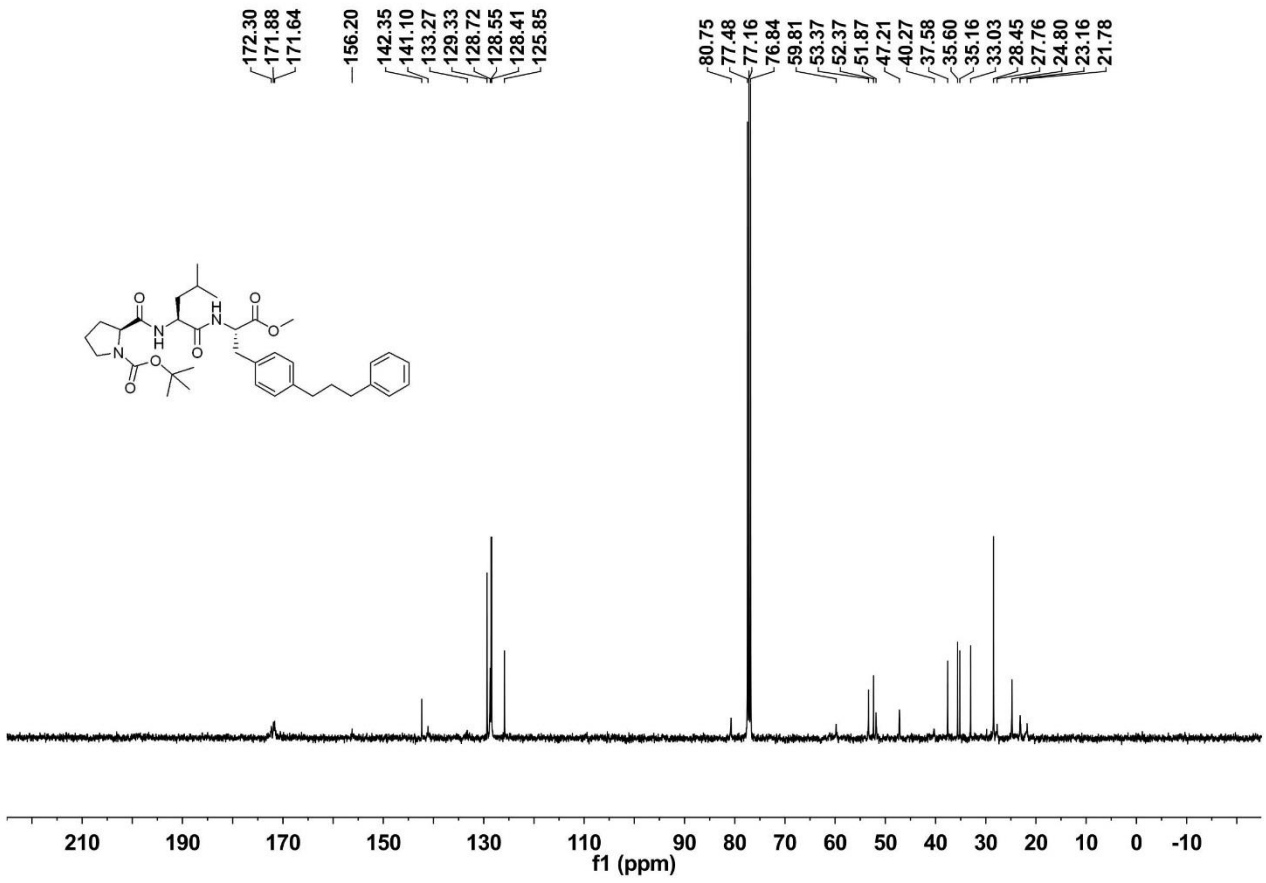
17g; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



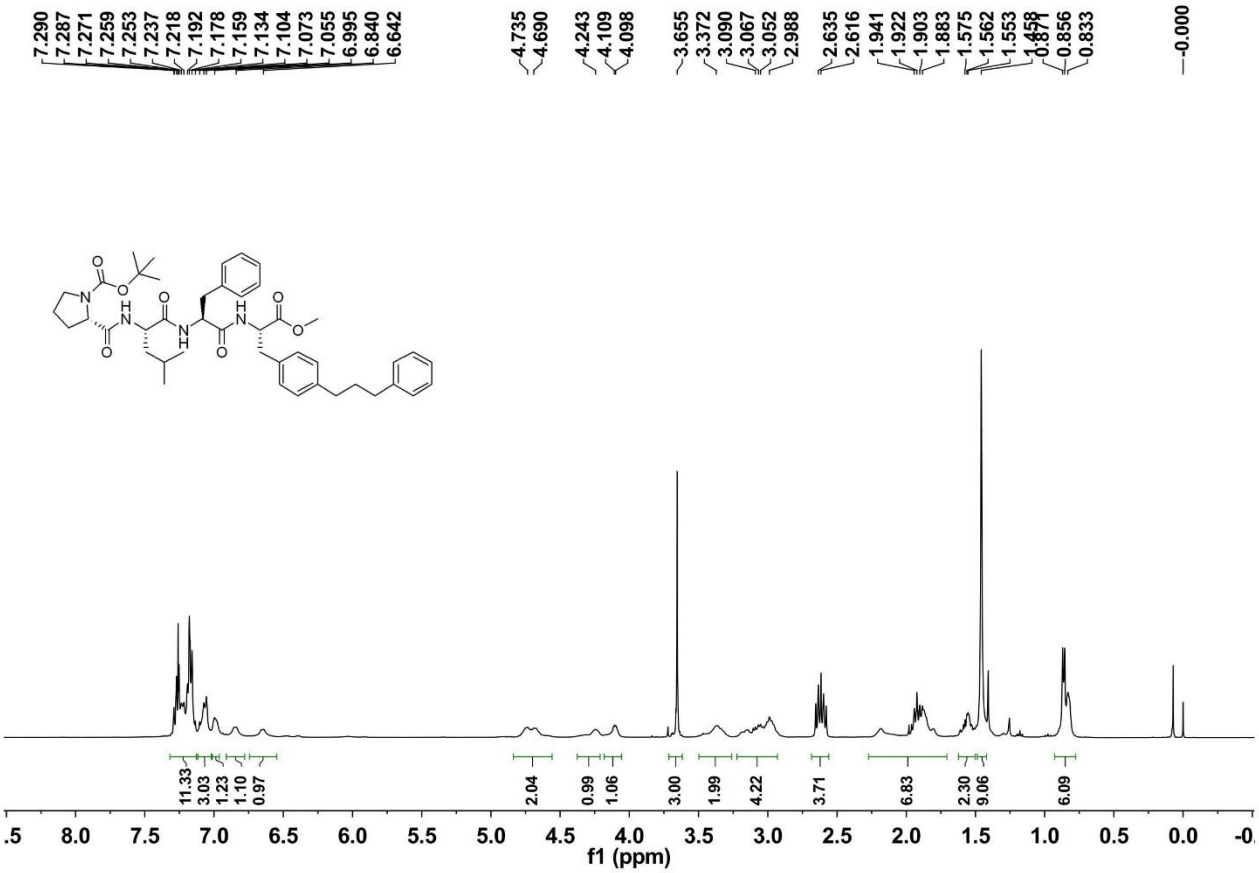


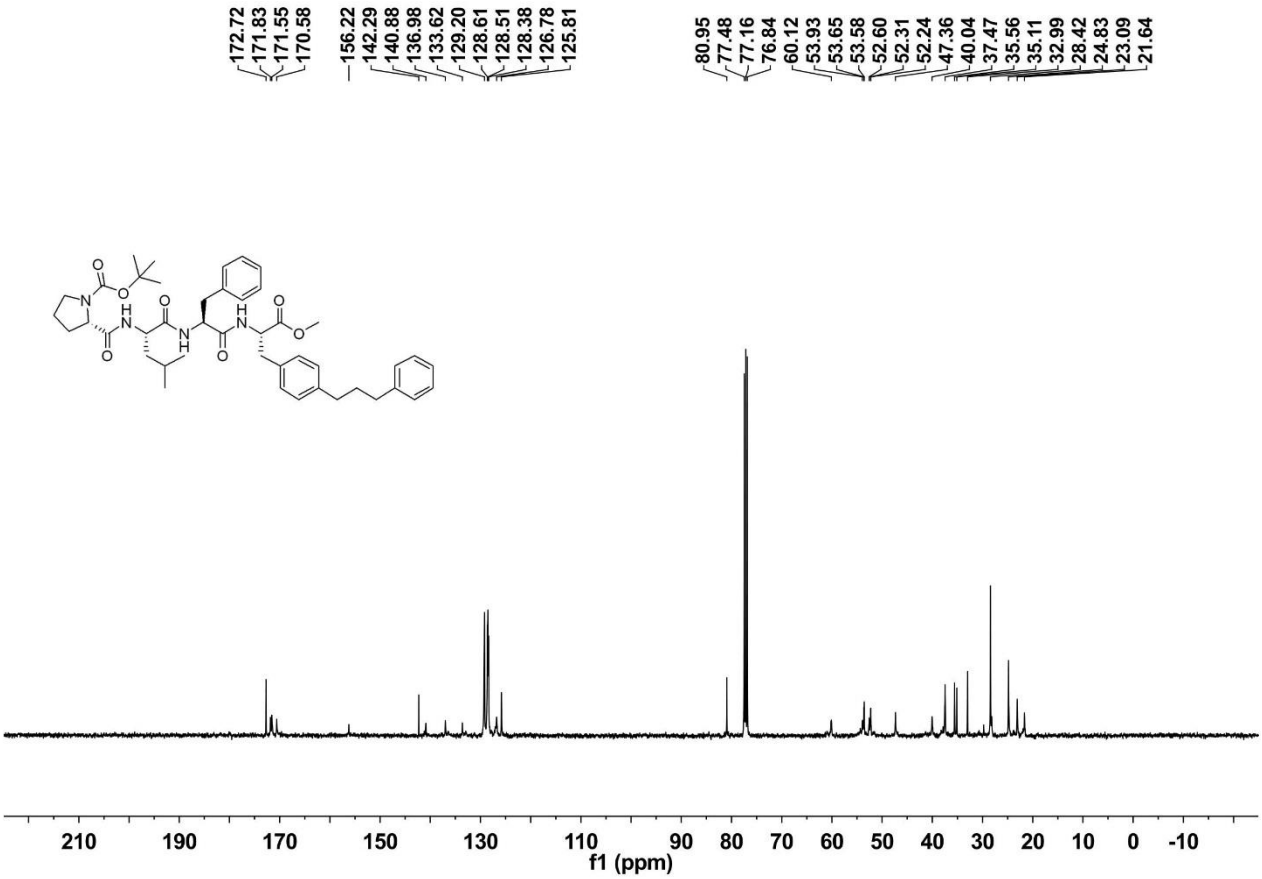
17h; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



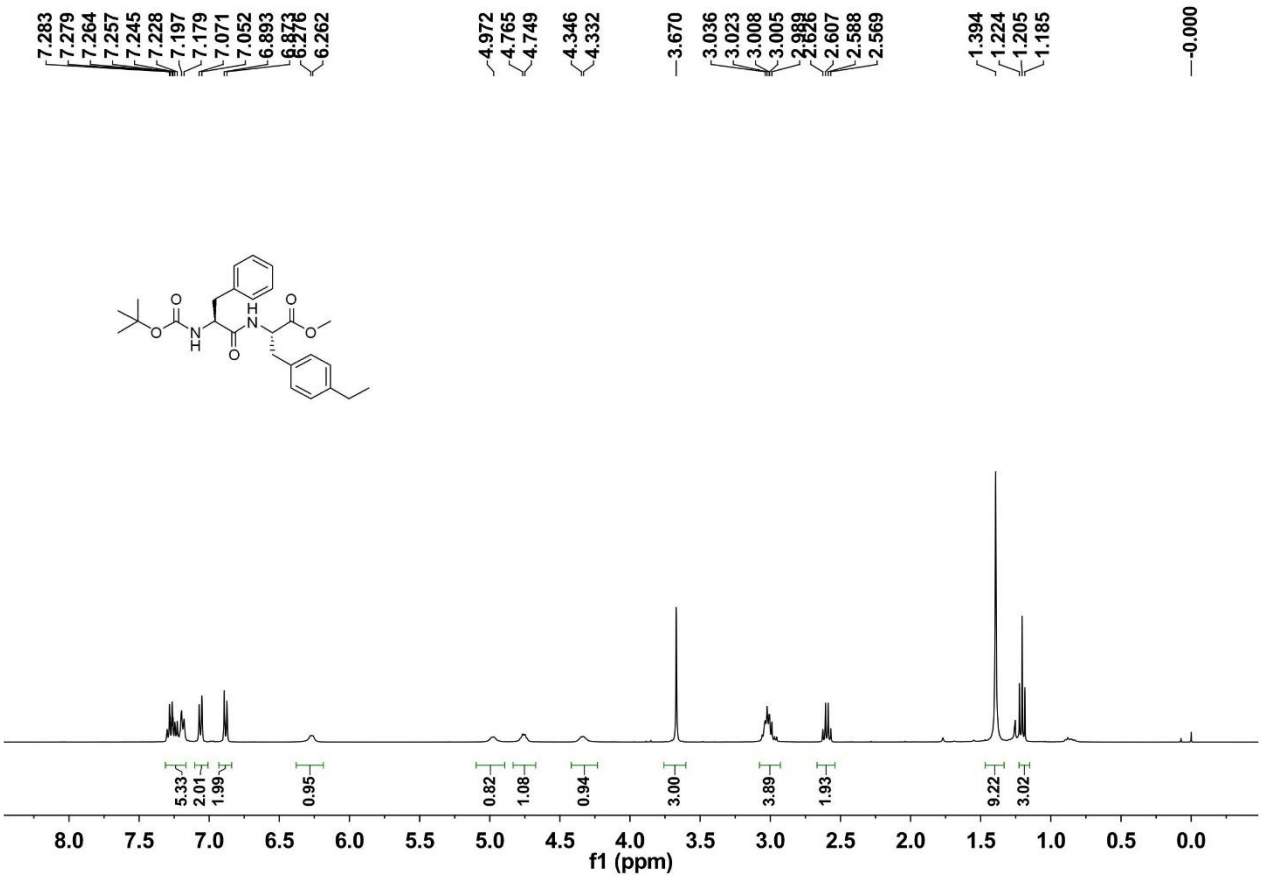


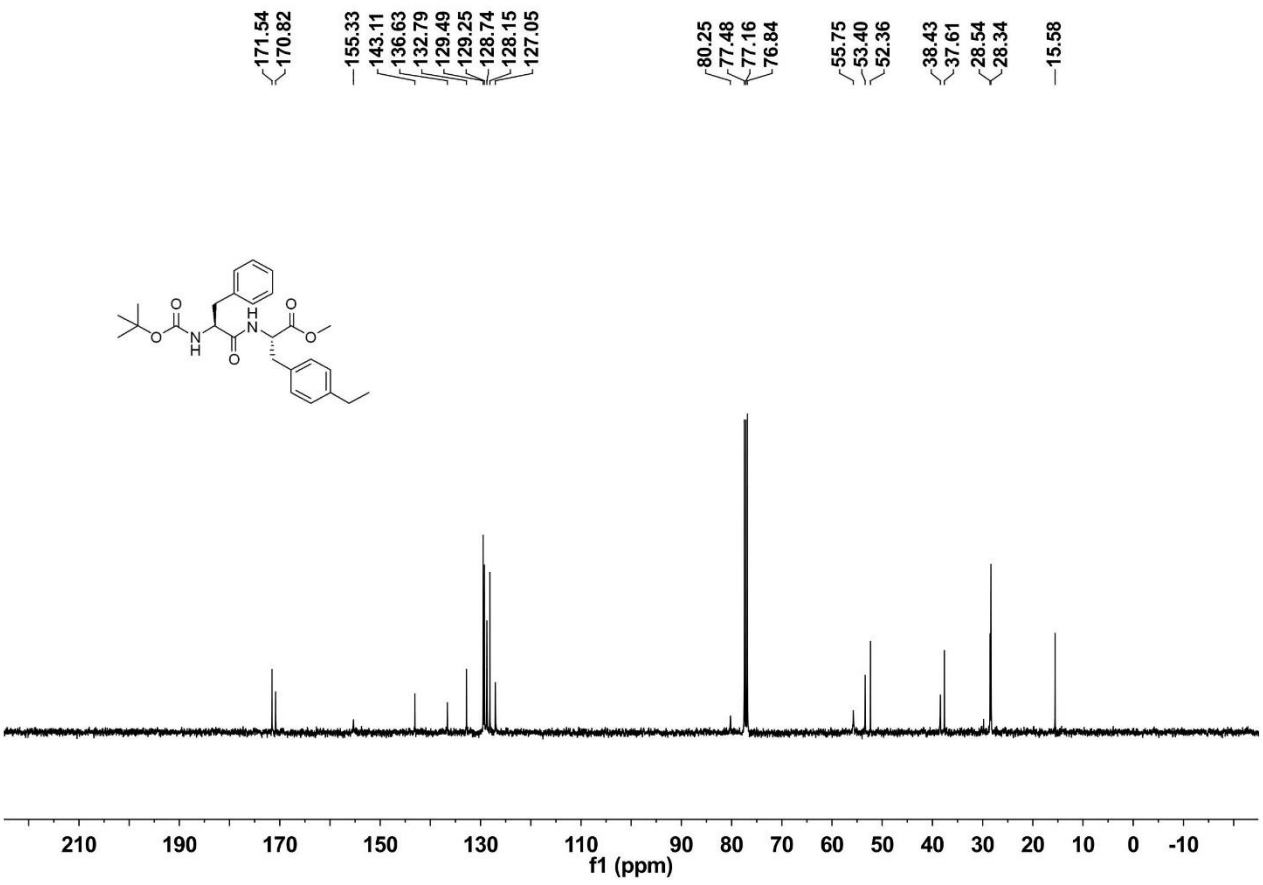
17i; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



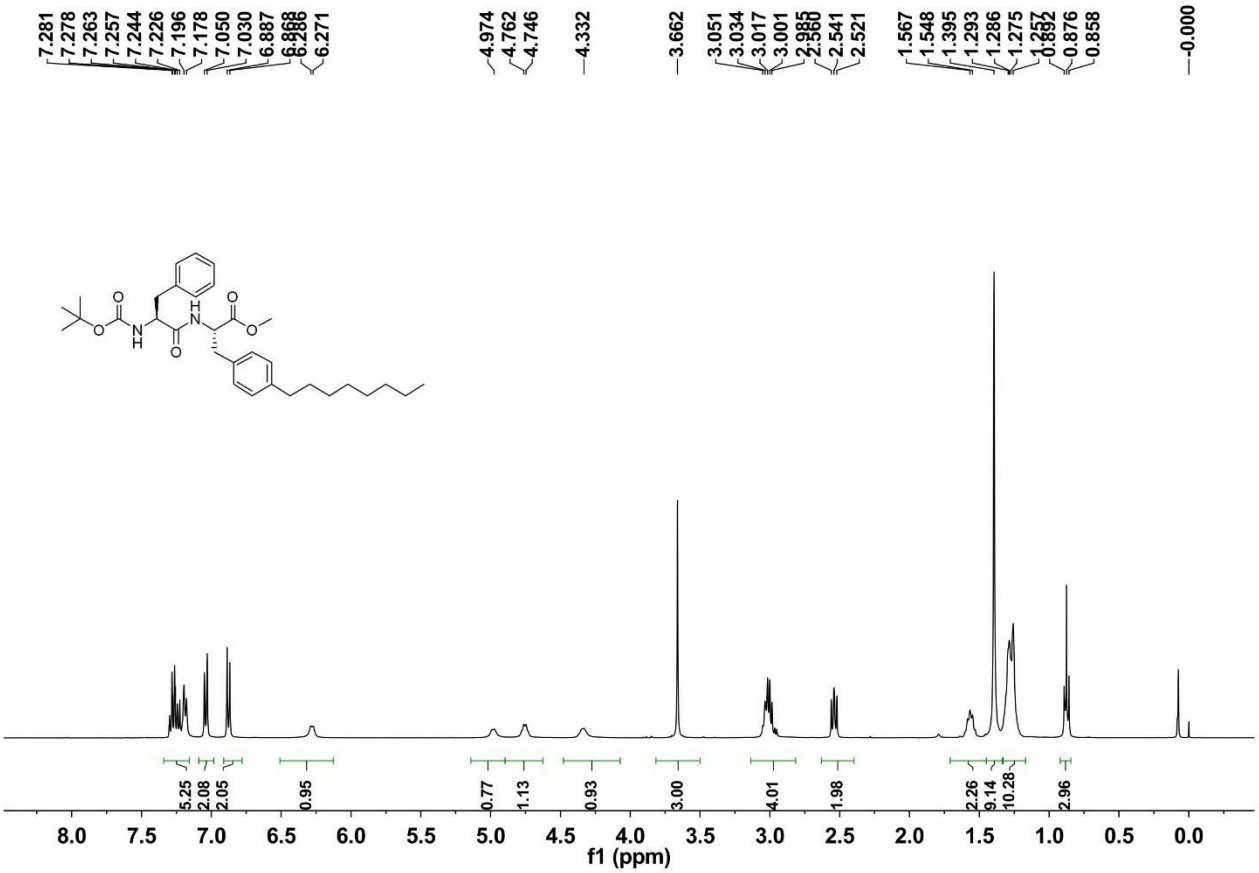


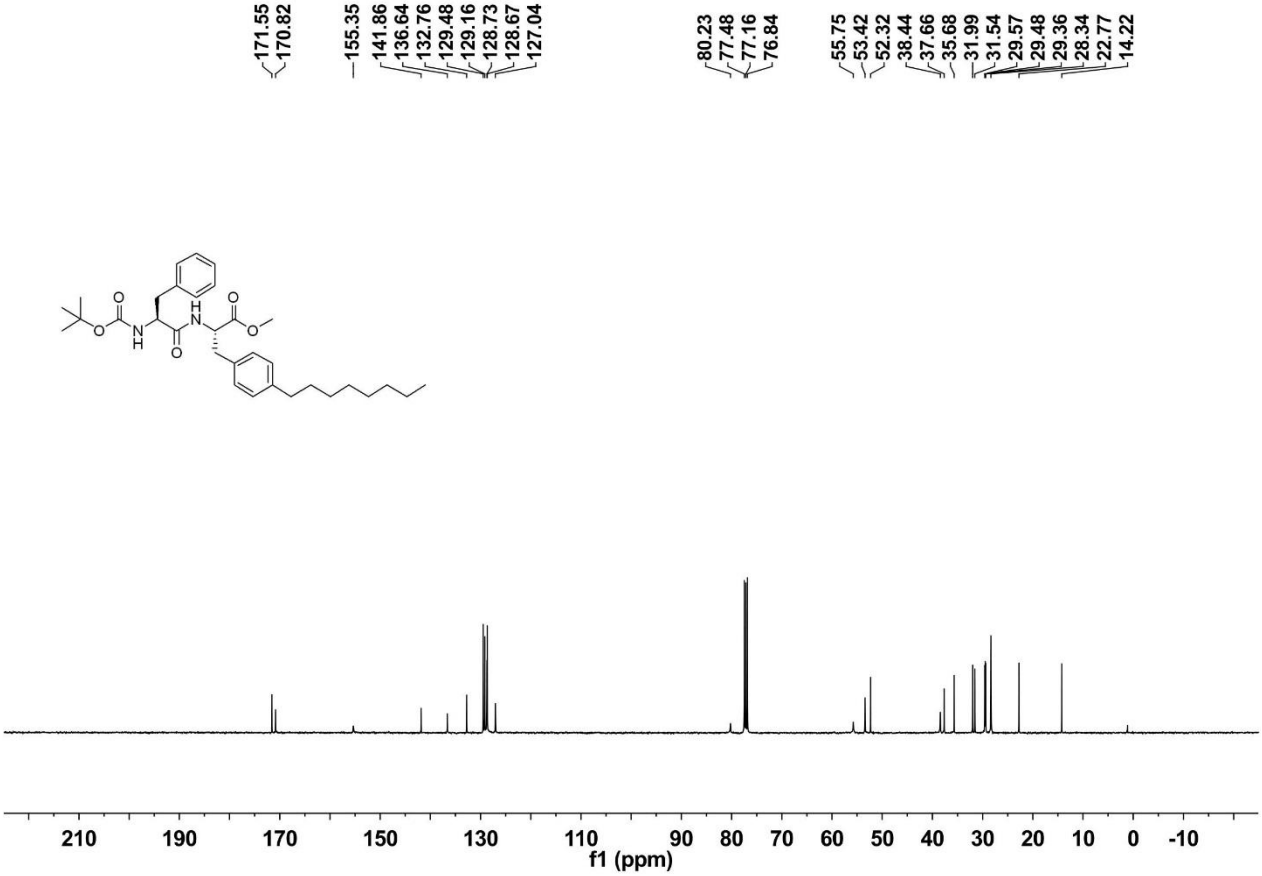
17j; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



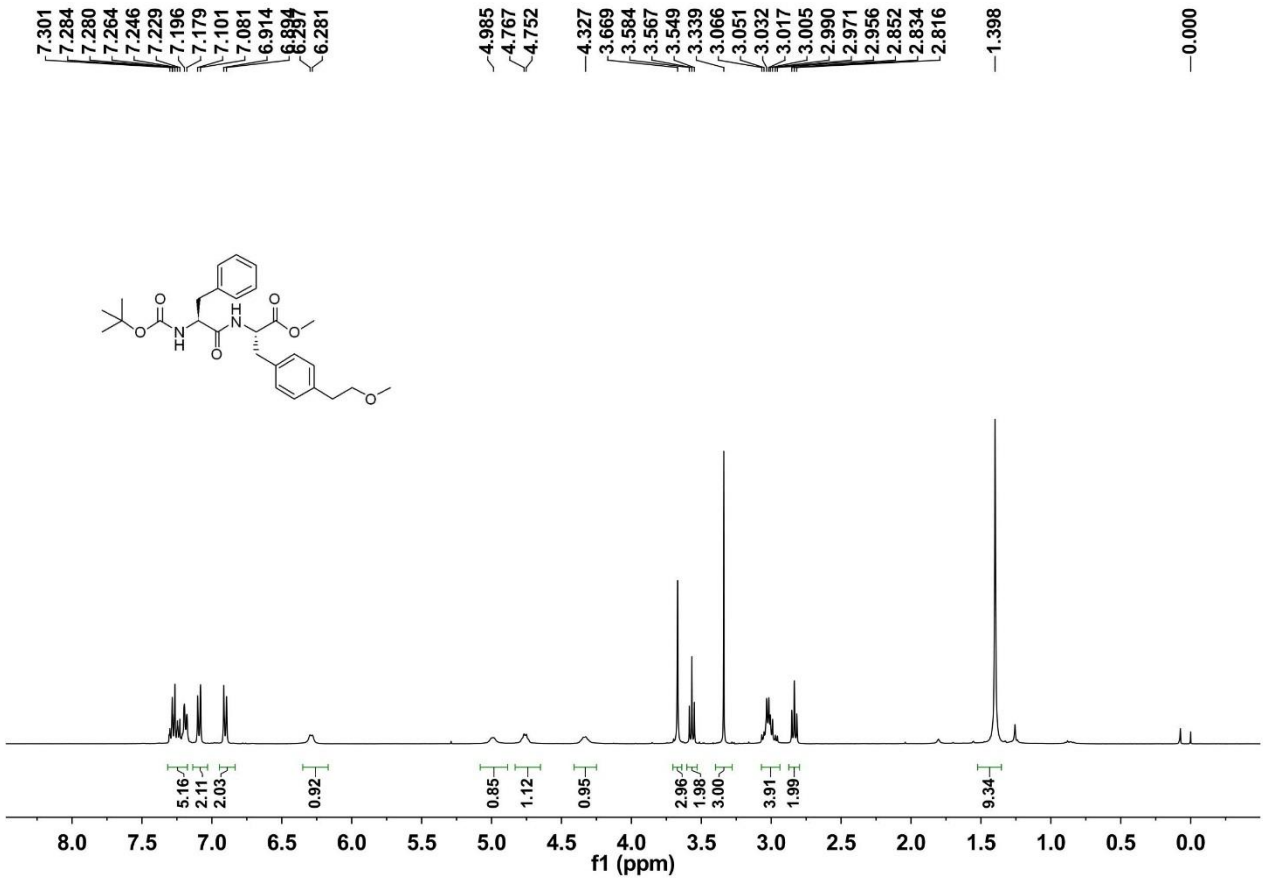


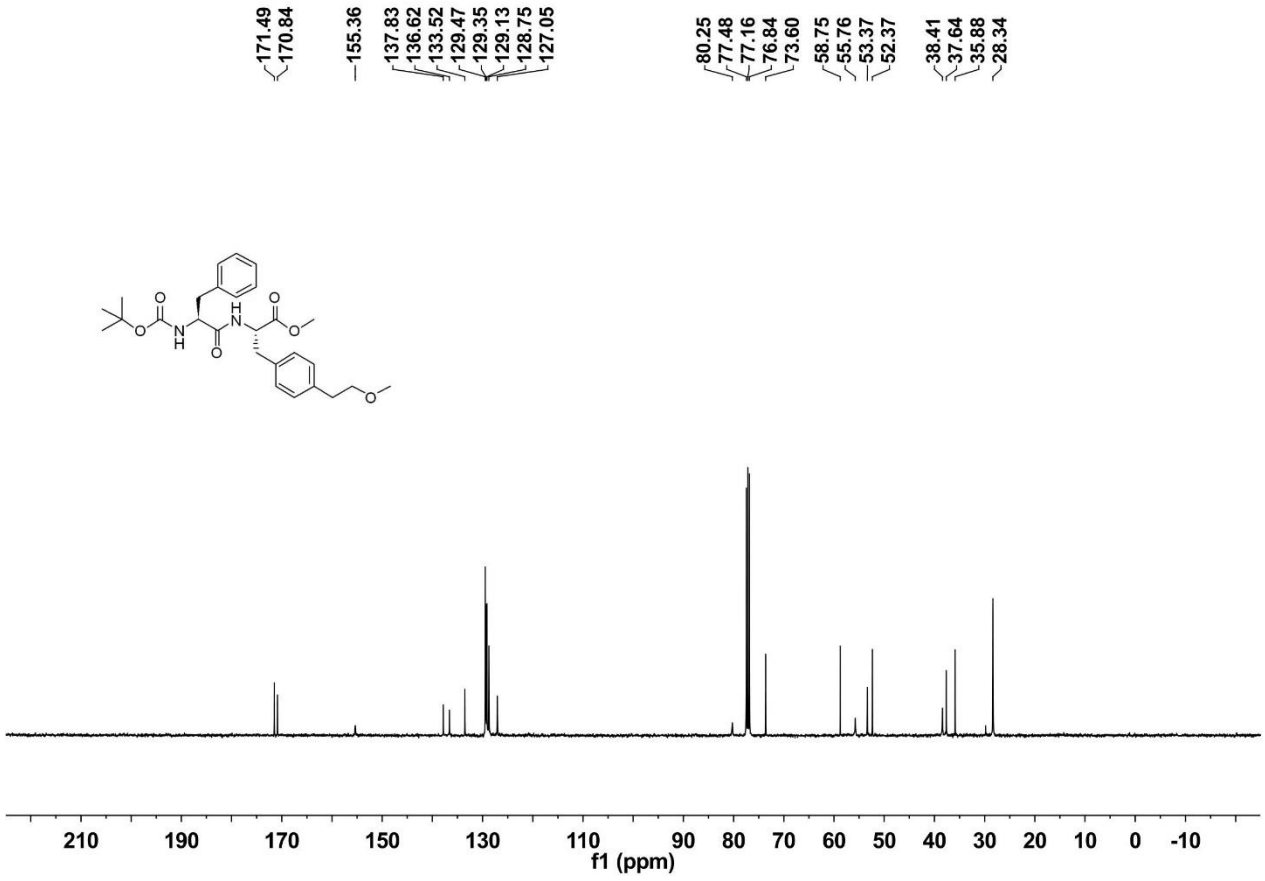
17k; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



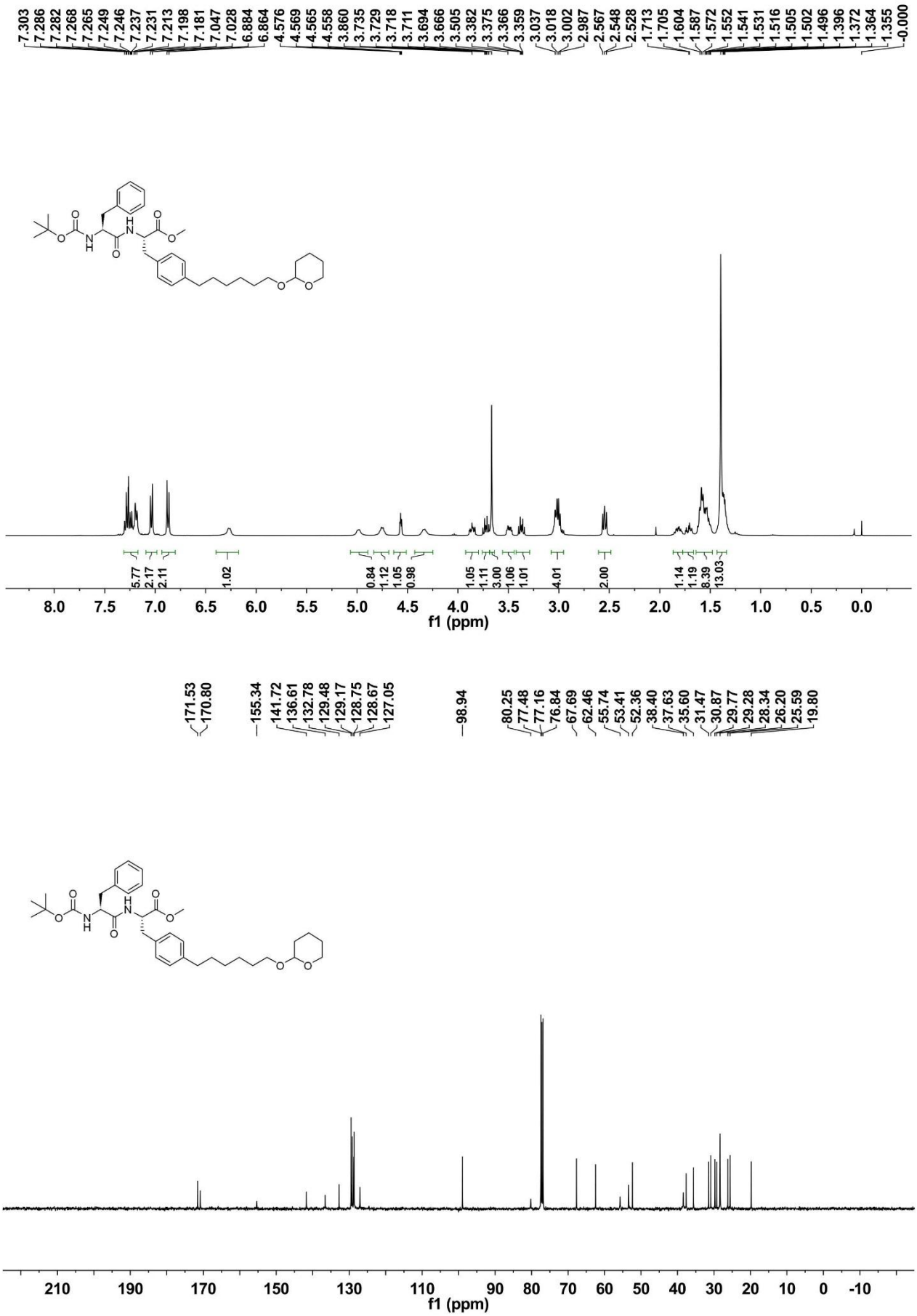


17l; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

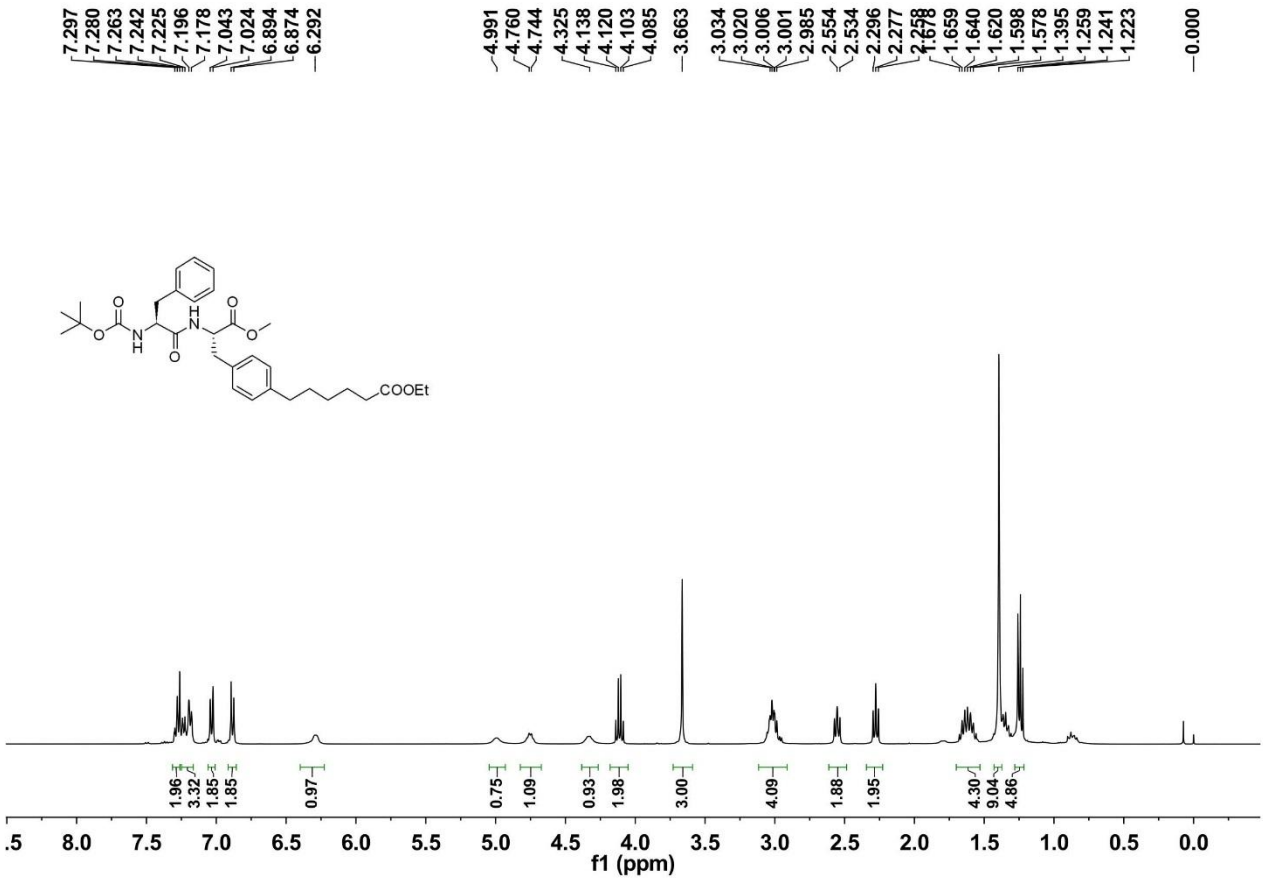


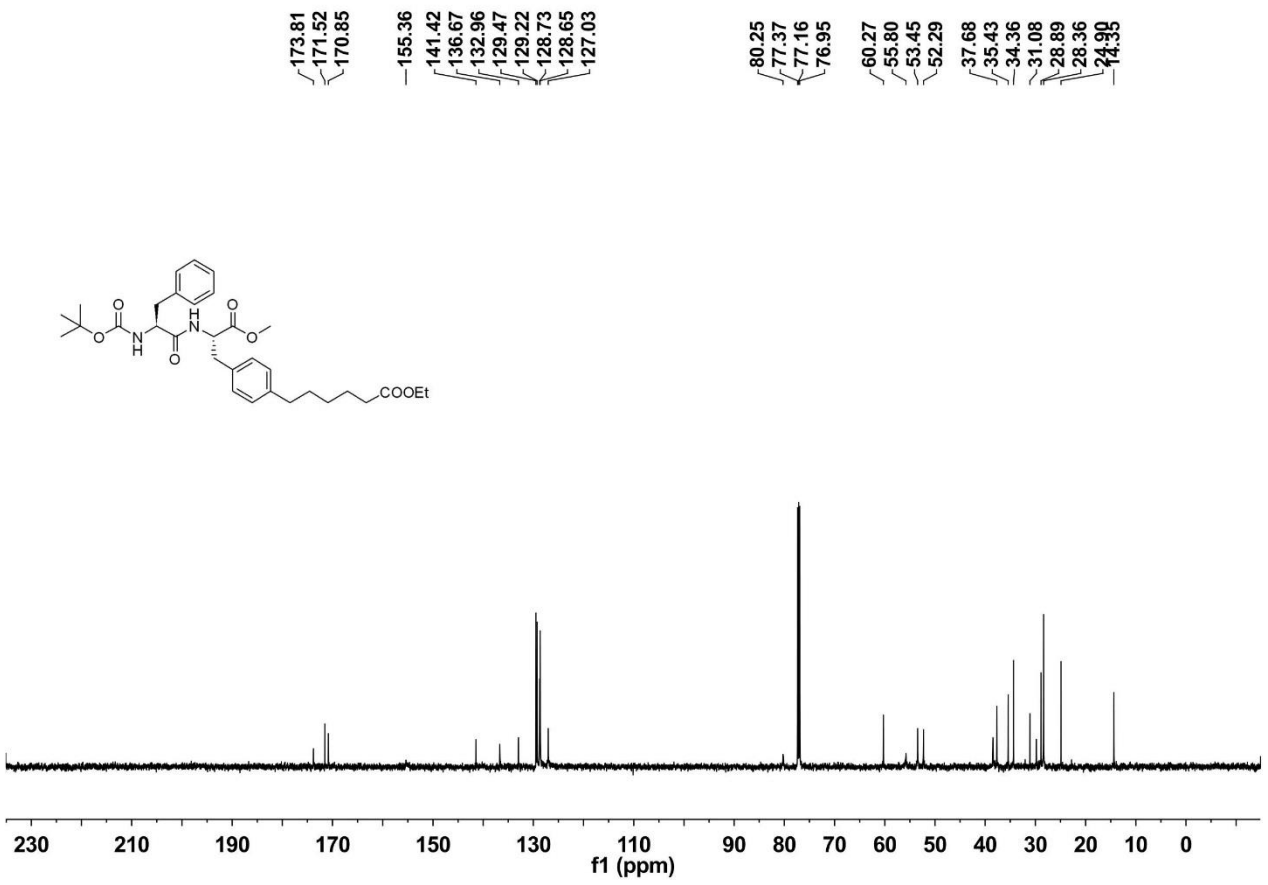


17m; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

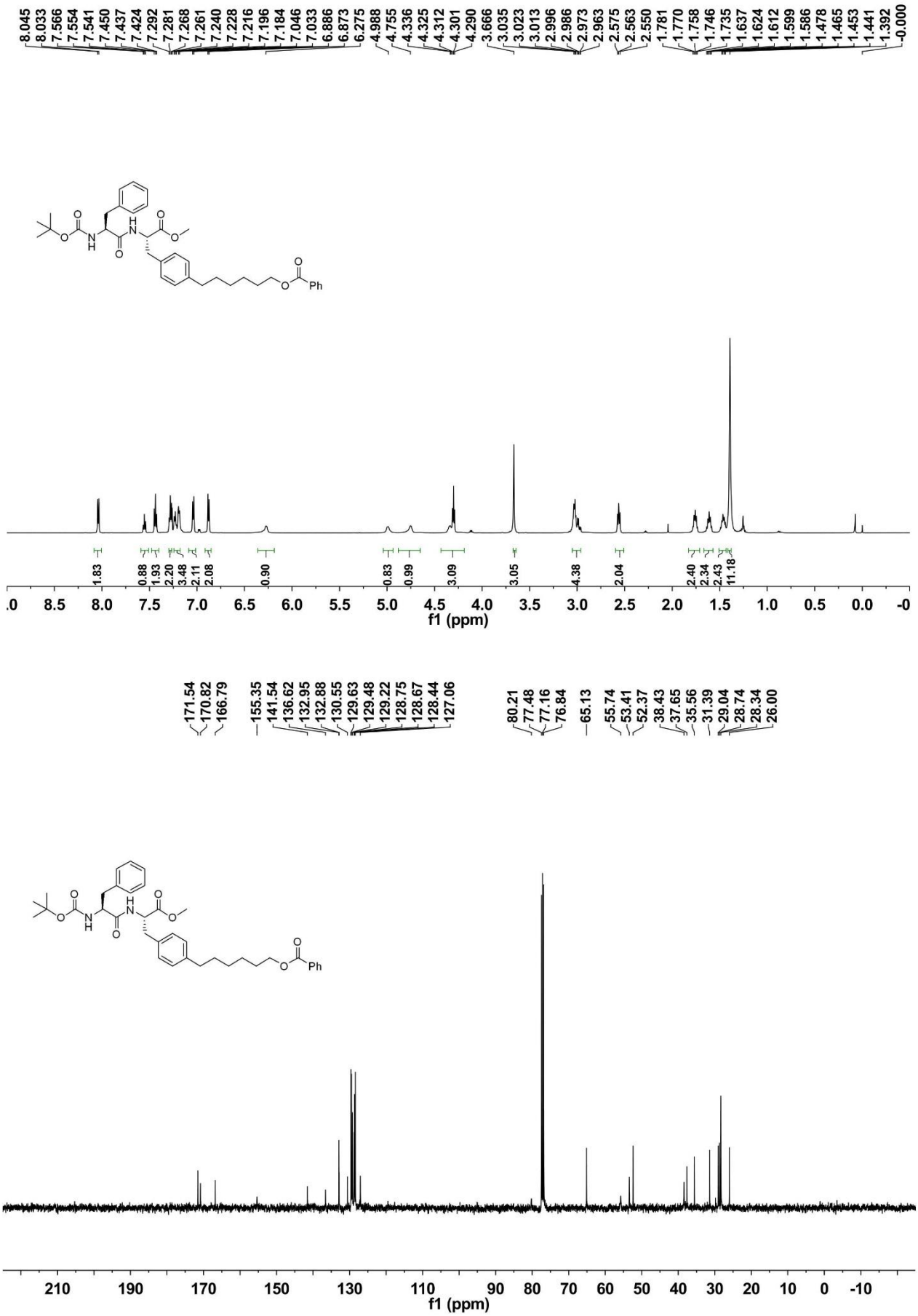


17n; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (150MHz, $CDCl_3$)

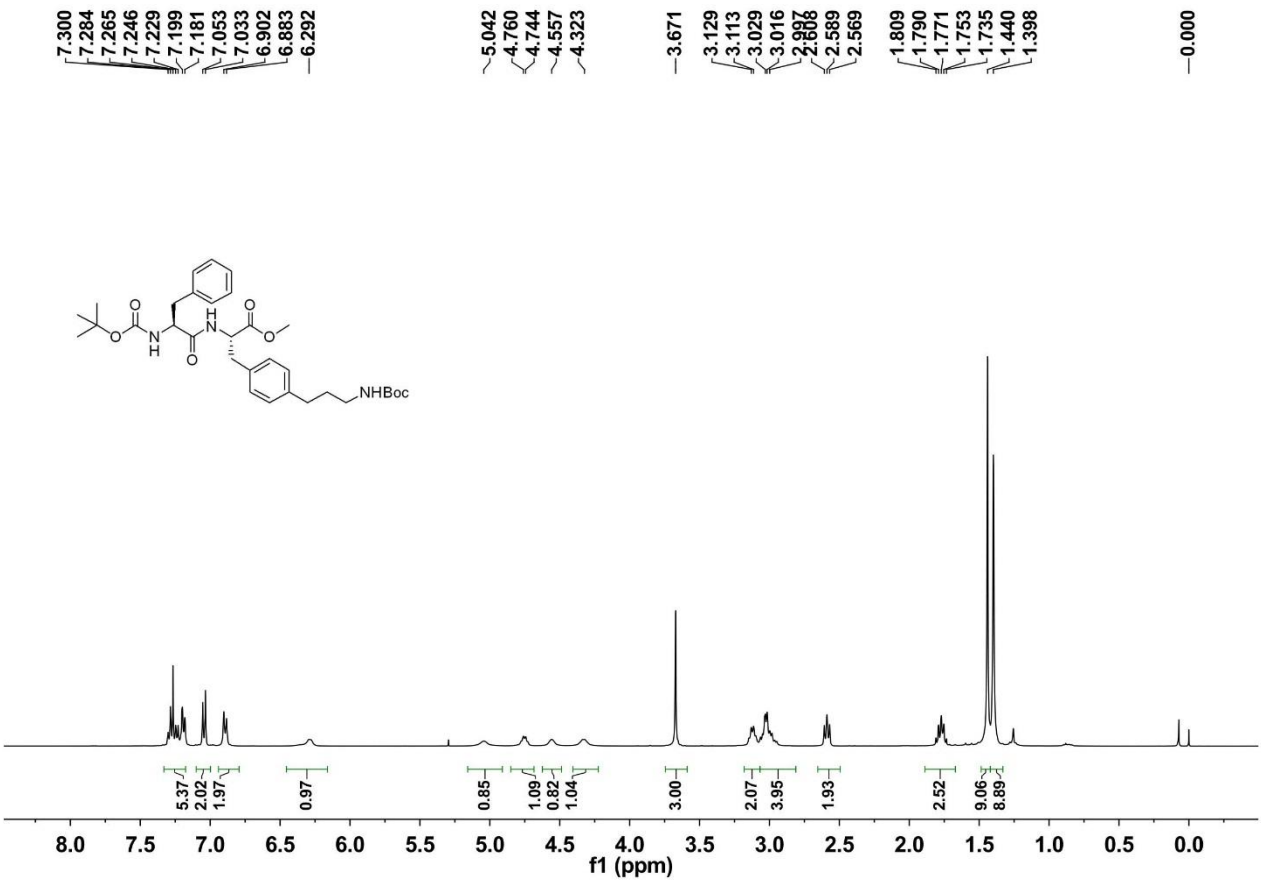


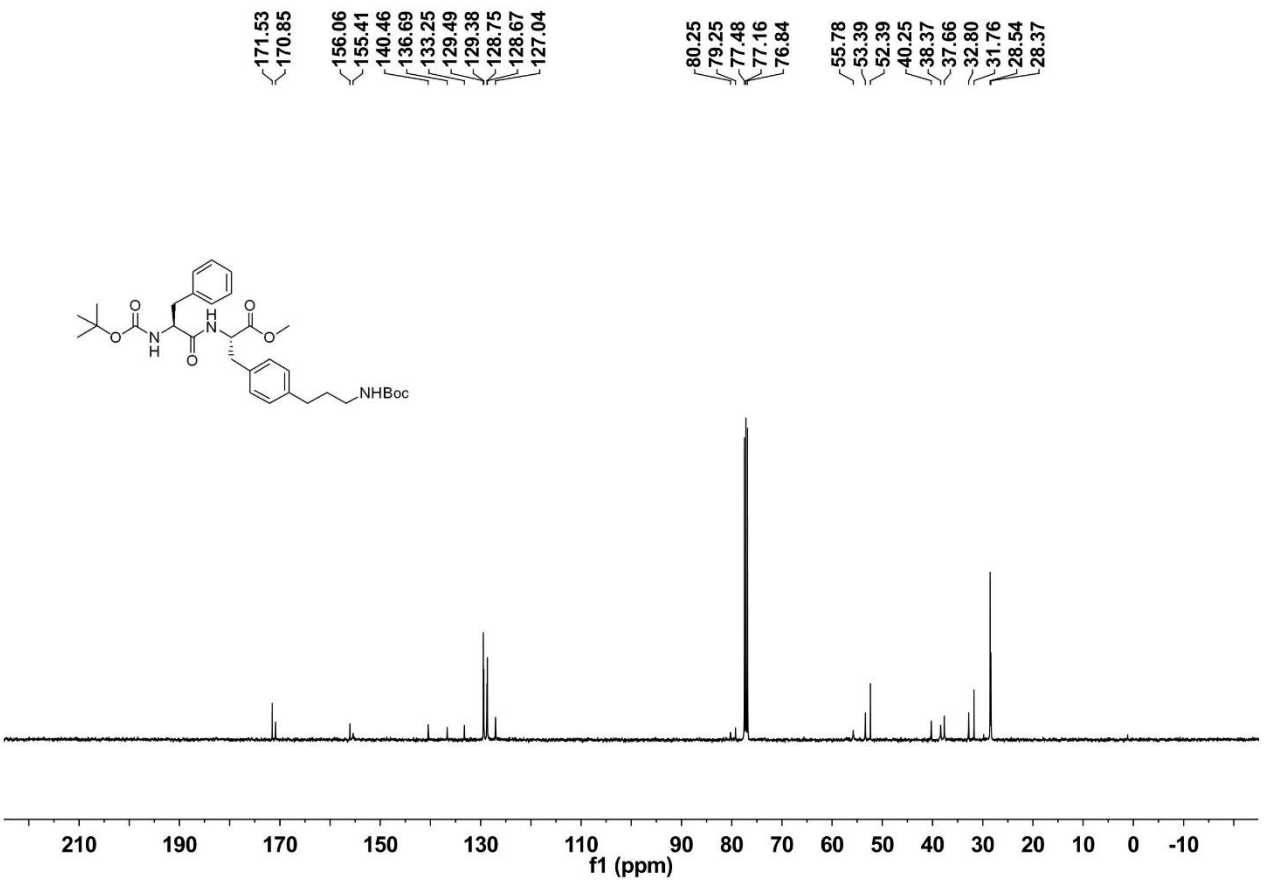


17o; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)

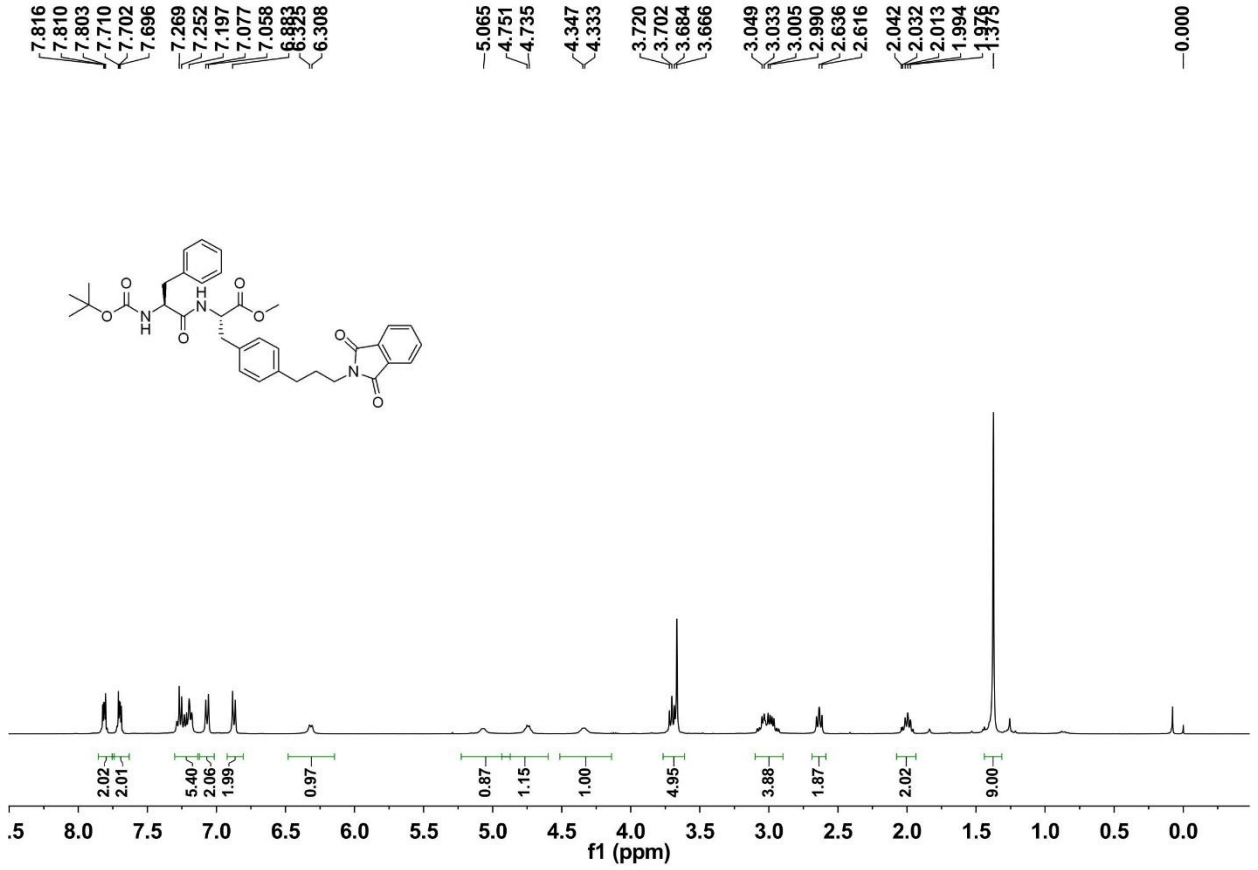


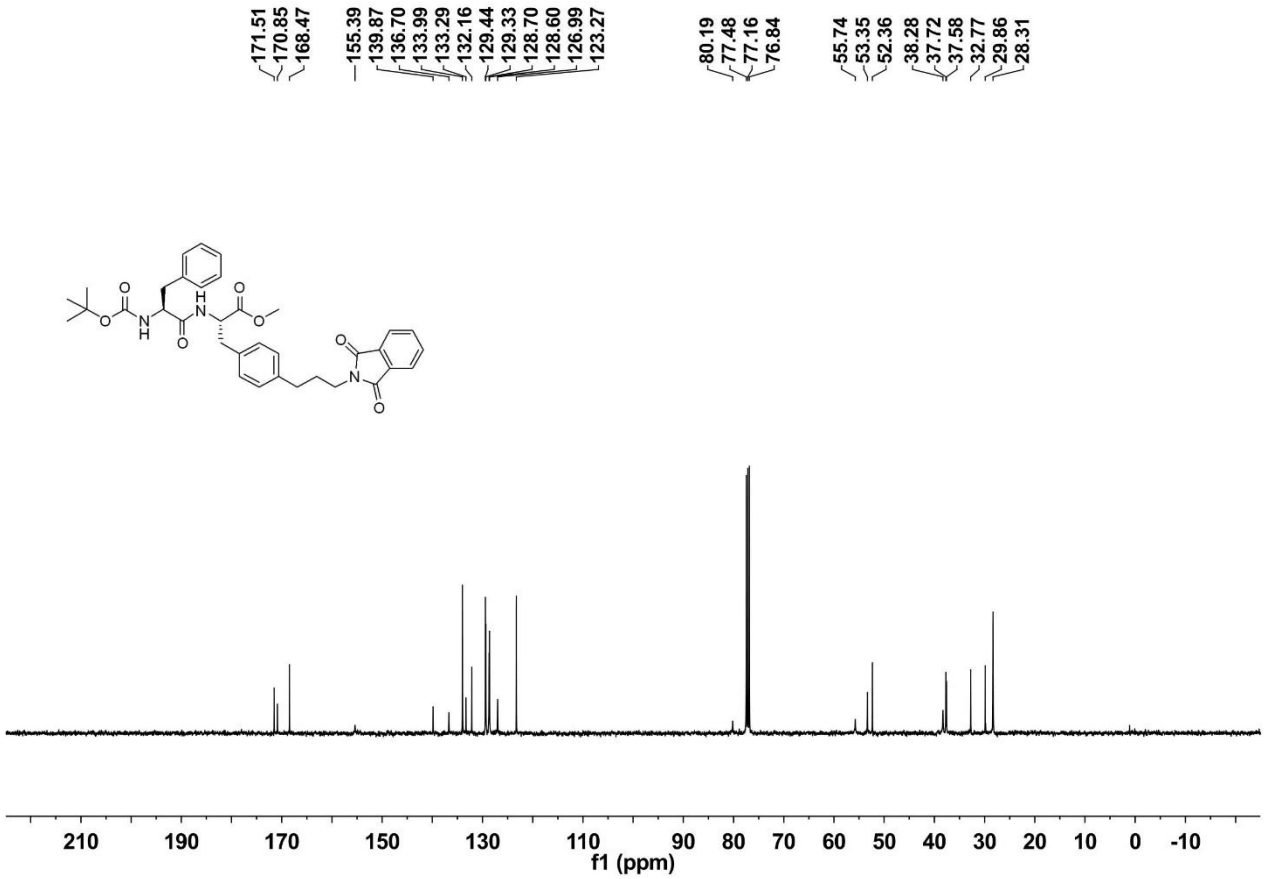
17p; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



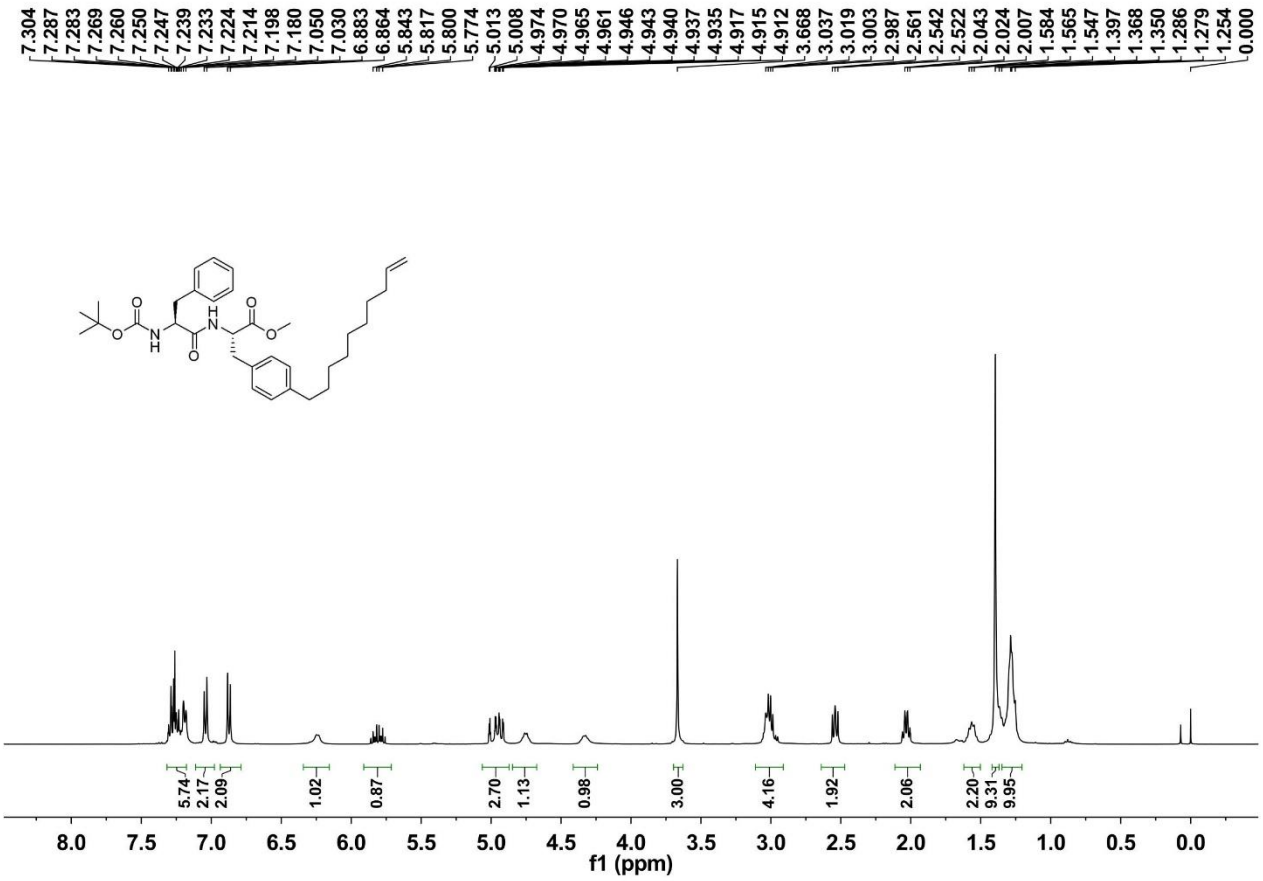


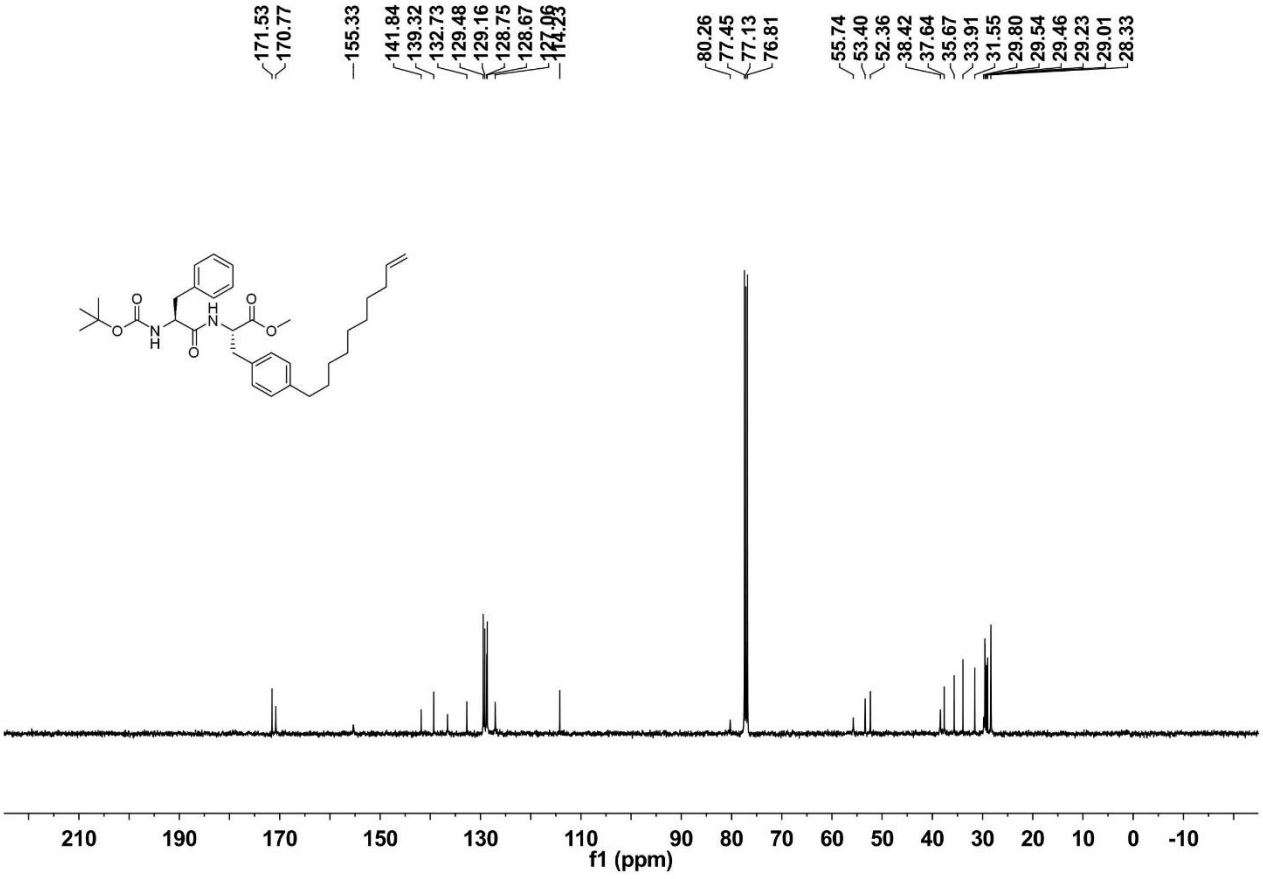
17q; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



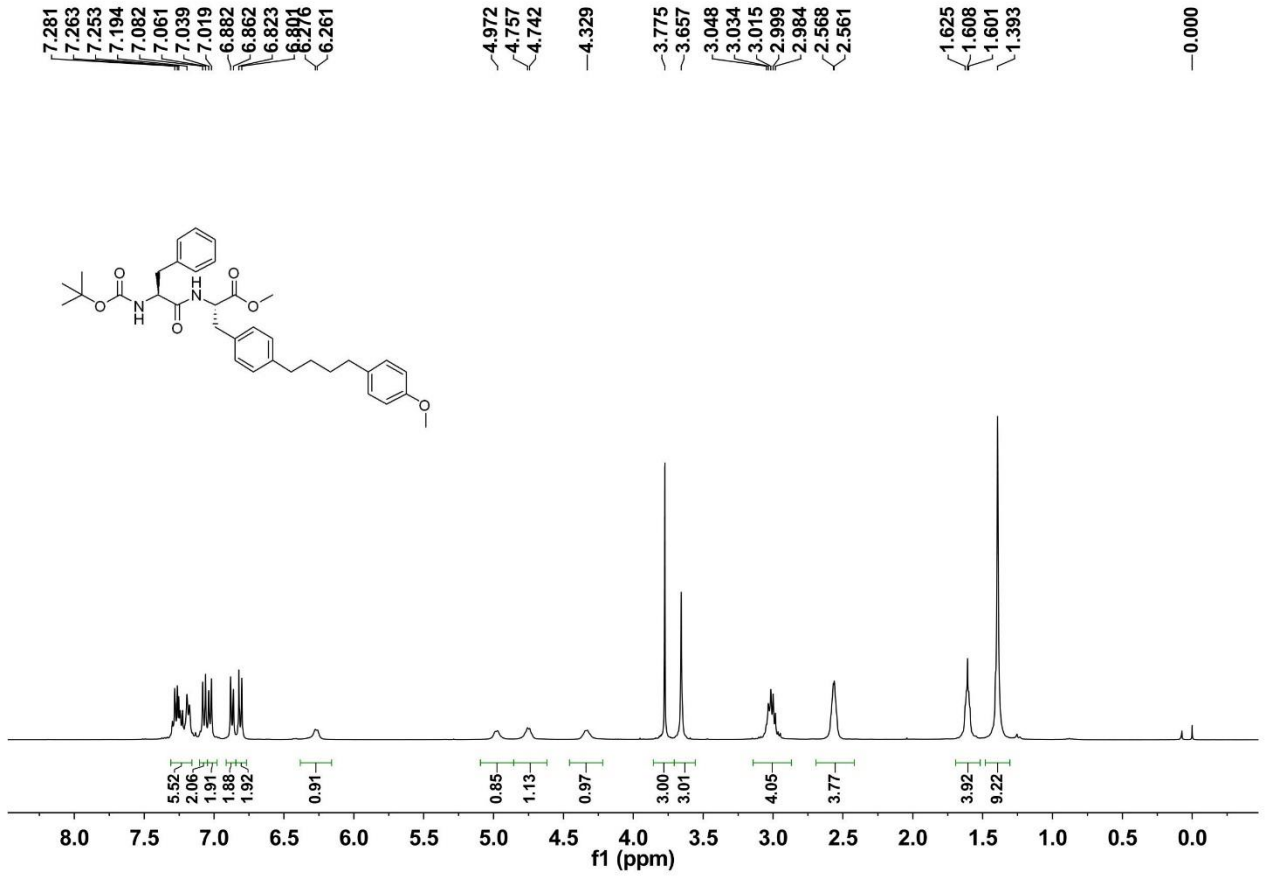


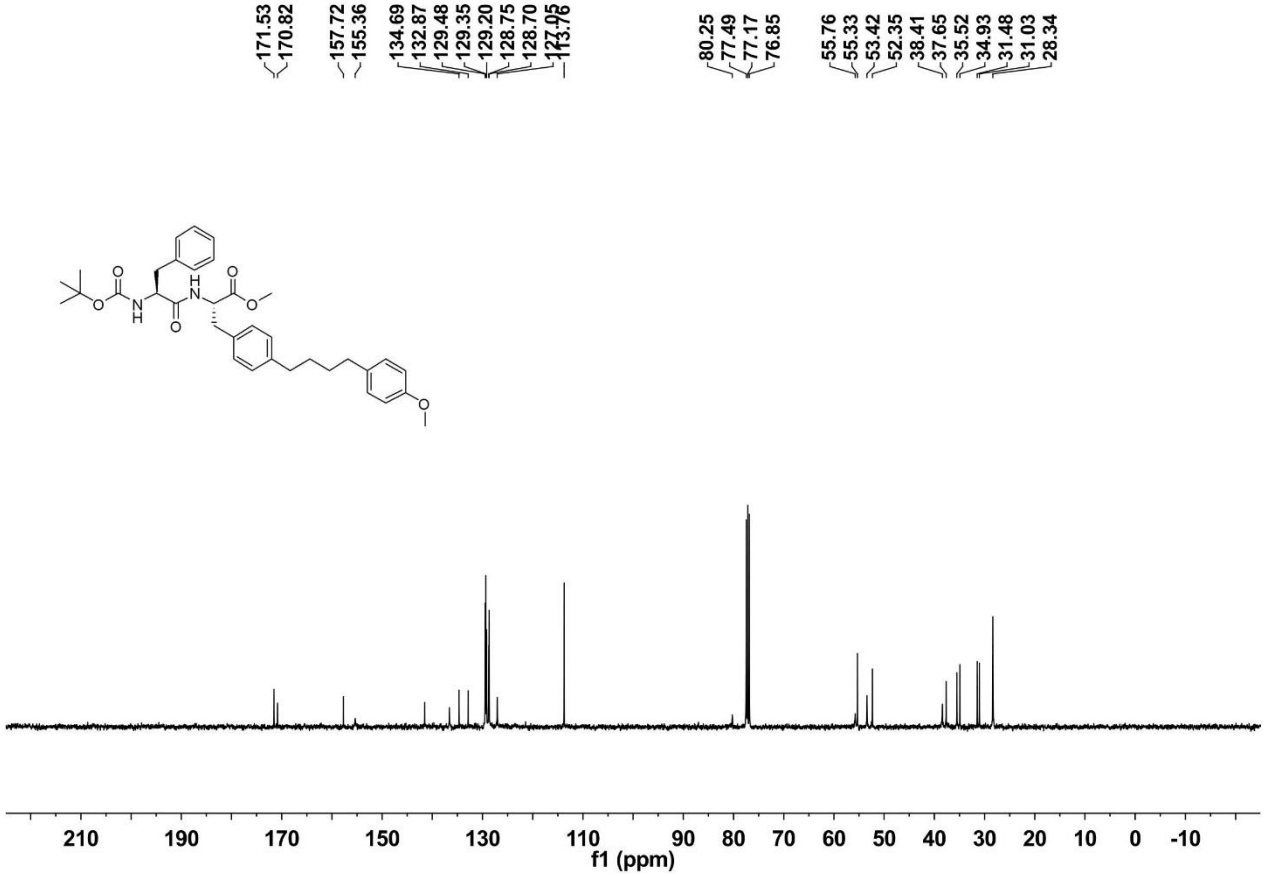
17r; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



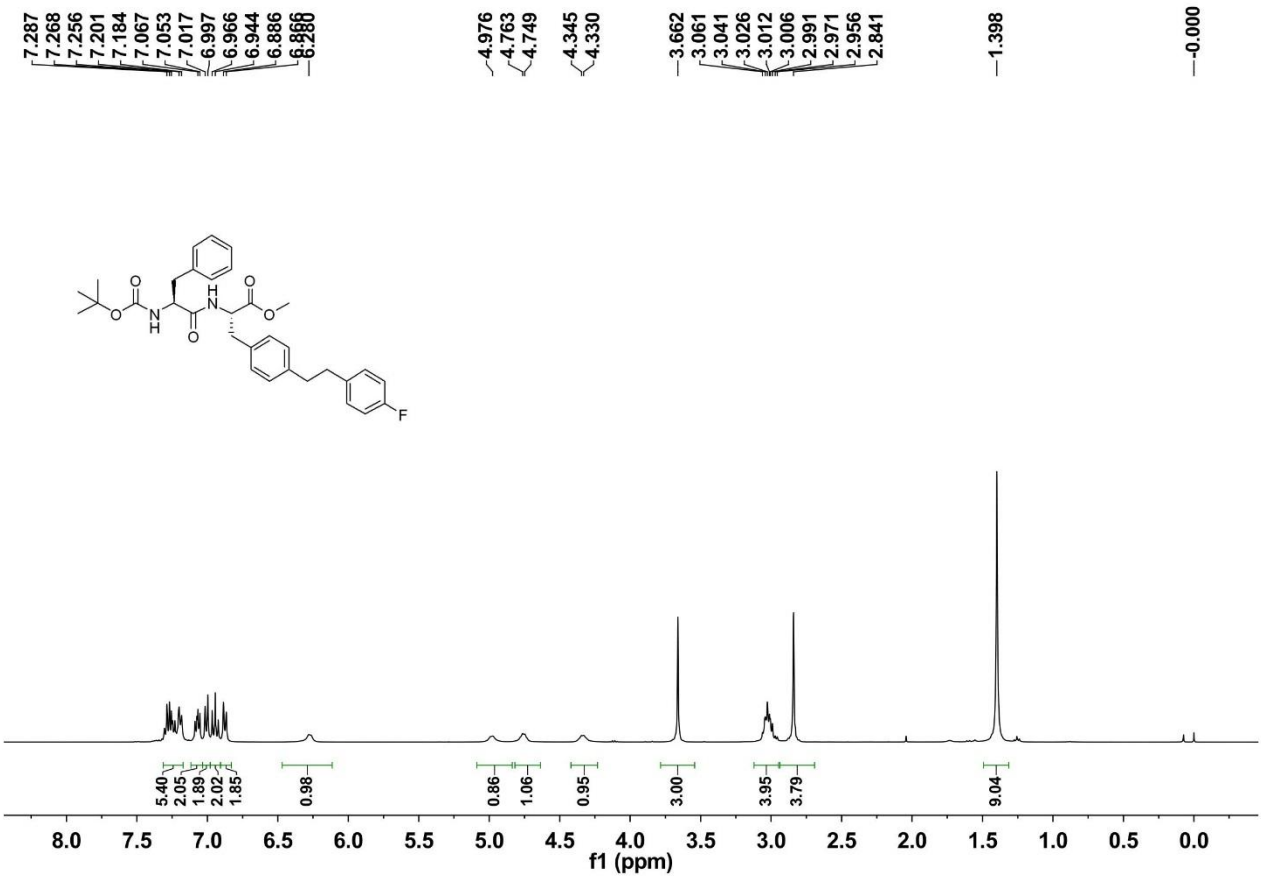


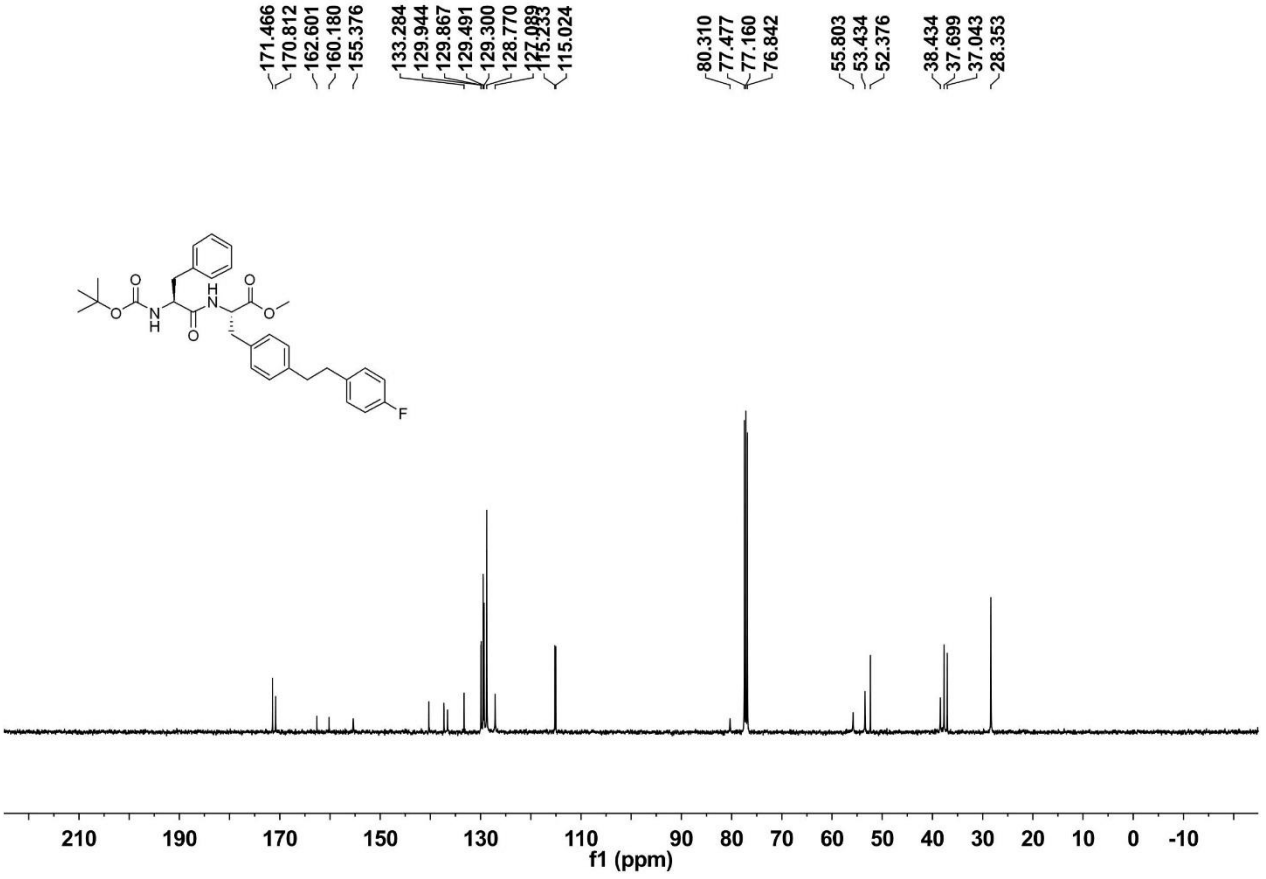
17s; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)



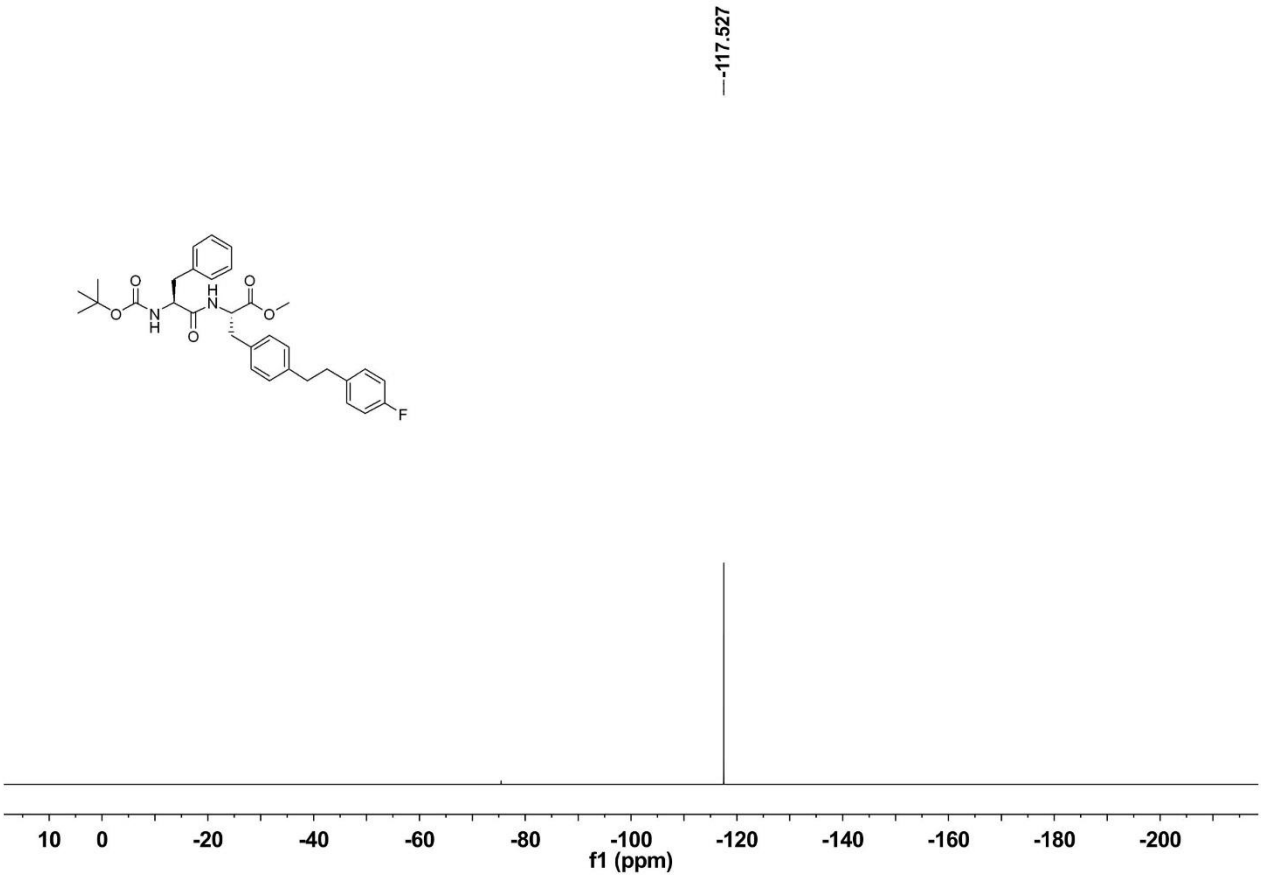


17t; ^{1}H NMR (400MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)





17t; ^{13}F NMR (376MHz, $CDCl_3$)



17u; ^{1}H NMR (600MHz, $CDCl_3$); ^{13}C NMR (100MHz, $CDCl_3$)