Stereoselective C–O Silylation and Stannylation

Ying Hu,[1] Jiali Peng,[2],[4] Binjing Hu,[1] Jixin Wang,[1] Jing Jing,[1] Jie Lin,[1] Xingchen Liu,[1] Xiaotian Qi[2] and Jie Li[1,3]**

[1] Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Ren-Ai Road 199, 215123 Suzhou, P. R. China
[2] Engineering Research Center of Organosilicon Compounds & Materials, Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei 430072, P. R. China.
[3] Suzhou Key Laboratory of Pathogen Bioscience and Anti-infective Medicine, Soochow University, Ren-Ai Road 199, Suzhou 215123, P. R. China
[4] School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang Henan, 453003, P. R. China

* E-mail: jjackli@suda.edu.cn
qi7xiaotian@whu.edu.cn

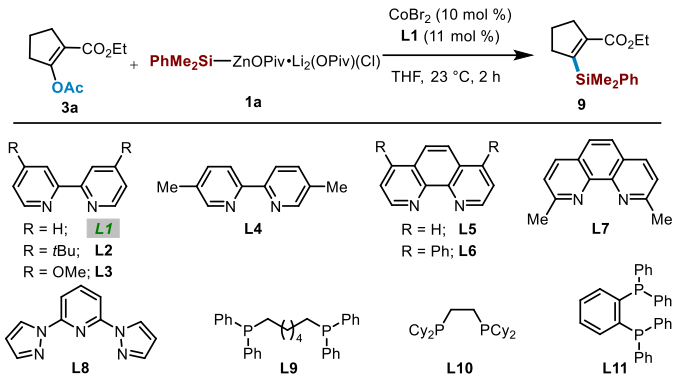
Contents

General Remarks

Unless otherwise indicated, all reactions were carried out with magnetic stirring and in flame-dried glassware under nitrogen. Syringes used to transfer reagents and solvents were purged with N_2 prior to use. The following starting materials were synthesized according to previously described methods: ketoesters,[1-8] esters S3as-S3av,[9] alkenyl acetates.[10-13] Other chemicals were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR and GC-analysis. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). TLC were performed using aluminum plates covered with SiO_2 (Merck 60, F-254) and visualized by UV detection. Purification *via* column chromatography was performed using Merck silica gel 60 (40–63 mm 230–400 mesh ASTM from Merck). THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. NMR spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in parts per million (ppm). Mass spectra and high resolution mass spectra (HR-MS) were recorded using electro ionization (EI) except where otherwise noted. GCs were recorded on machines of the type Hewlett-Packard 6890 (Hewlett Packard, 5% phenylmethylpolysiloxane; length: 15 m, diameter: 0.25 mm; film thickness: 0.25 μm).

Optimization Studies

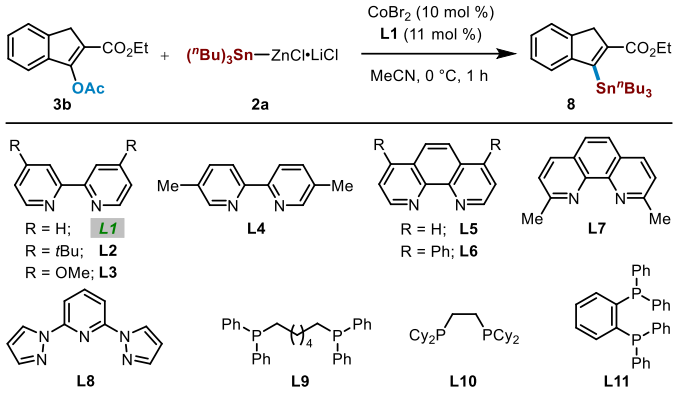
Table 1. Optimization for Cobalt-Catalyzed Silylation of Alkenyl Acetate 3a.[a]



entry	modified conditions	yield (%)[b]
1	none	81
2	**L2** instead of **L1**	40
3	**L3** instead of **L1**	Trace
4	**L4** instead of **L1**	80
5	**L5** instead of **L1**	Trace
6	**L7** instead of **L1**	Trace
7	**L11** instead of **L1**	Trace
8	PhMe or NMP or MeCN	0-20
9	Under 0 °C	57
10	CoI2 instead of $CoBr_2$ Under 0 °C	55
11	CoCl2 instead of $CoBr_2$	62
12	Co(acac)2 instead of $CoBr_2$	33
13	NiCl2 or FeCl2 or CrCl2	0-8
14	w/o [Co]	0

[a] Reaction conditions: **3a** (0.25 mmol, 1.0 equiv), **1a** (0.5 mmol, 2 equiv), $CoBr_2$ (10 mol %), **L1** (11 mol %), THF (1.5 mL), @ 23°C, 2 h. [b] Isolated yields.

Table 2. Optimization for Cobalt-Catalyzed Stannylation of Alkenyl Acetate 5a.[a]

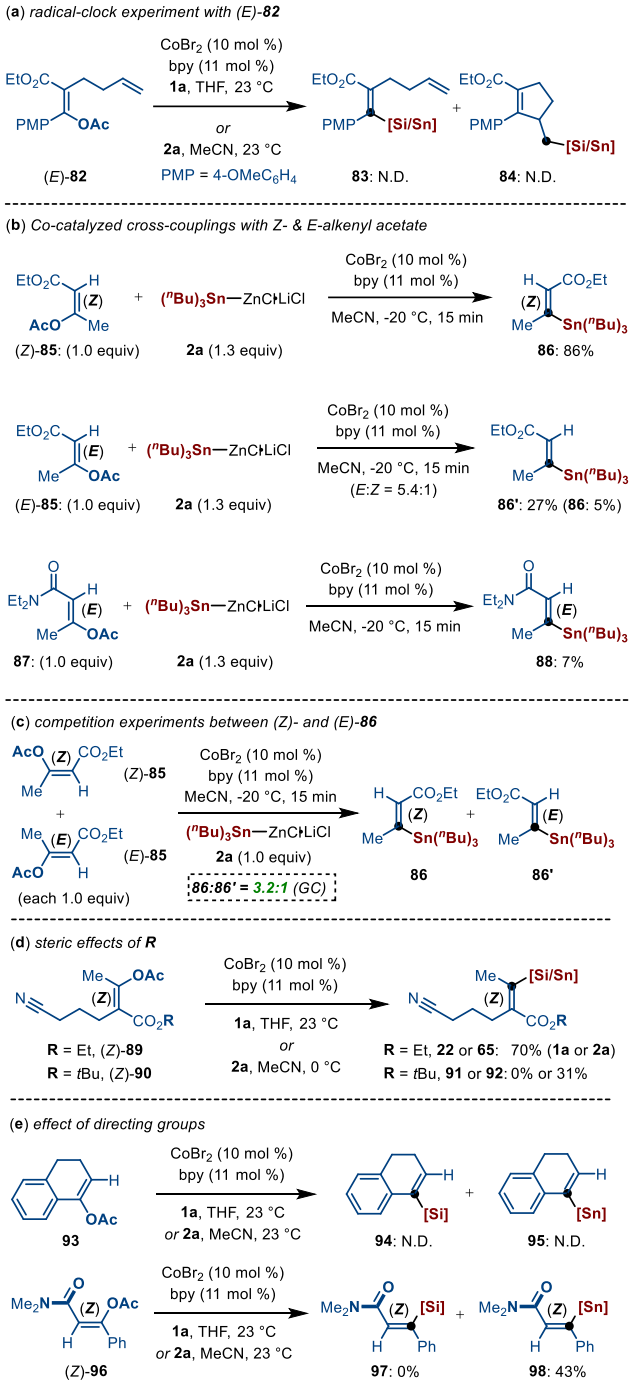


entry	modified conditions	yield (%)[b]
1	none	20
2	**L2** instead of **L1**	12
3	**L3** instead of **L1**	Trace
4	**L4** instead of **L1**	18
5	**L5** instead of **L1**	18
6	**L6** instead of **L1**	15
7	**L7** instead of **L1**	0
8	**L8** instead of **L1**	trace
9	**L9** instead of **L1**	14
10	**L10** instead of **L1**	18
11	**L11** instead of **L1**	20
12	THF, DMF, dioxane instead of MeCN	0
13	$NiCl_2$, $FeCl_2$, or $CrCl_2$ instead of $CoBr_2$	0–8
14	under -20 °C (or -30 °C)	53 (0r 0)
15	25 min**;** under -20 °C	54
16	**15 min; under -20 °C**	**66** (21)[c]

[a] Reaction conditions: **3b** (0.25 mmol, 1.0 equiv), **2a** (0.325 mmol, 1.3 equiv), $CoBr_2$ (10 mol %), **L1** (11 mol %), MeCN (1.5 mL), @ 0 °C, 1 h. [b] Isolated yields. [c] The number given in parentheses is the isolated yield of **6**.

Additional Experiments

Figure 5. Mechanistic Studies for Cobalt-Catalyzed Stereoselective C–O Bond Silylation and Stannylation.



Procedure for Figure 5a:

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous THF (0.5 mL) was added (*E*)-**82** (0.25 mmol, 1.0 equiv). Then the $PhMe_2Si$-ZnOPiv (0.9 mL, 0.5 mmol, 2 equiv) in THF (1 mL) was added and the reaction was stirred at 23 °C for 2 h under an atmosphere of N_2.

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous MeCN (0.5 mL) was added (*E*)-**82** (0.25 mmol, 1.0 equiv). Then the $(^nBu)_3Sn$–ZnCl•LiCl (1.3 mL, 0.325 mmol, 1.3 equiv) in MeCN (1 mL) was added and the reaction was stirred at 23 °C for 2 h under an atmosphere of N_2.

Procedure for Figure 5b:

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous MeCN (0.5 mL) was added corresponding alkenyl acetates (0.25 mmol, 1.0 equiv). Then the $(^nBu)_3Sn$–ZnCl•LiCl (1.3 mL, 0.325 mmol, 1.3 equiv) in MeCN (1 mL) was added and the reaction was stirred at -20 °C for 15 minutes under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **86**, **86'**, **88**.

Procedure for Figure 5c:

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous MeCN (0.5 mL) was added (*Z*)-**85** (0.25 mmol, 1.0 equiv) and (*E*)-**85** (0.25 mmol, 1.0 equiv). Then the $(^nBu)_3Sn$–ZnCl•LiCl (1.0 mL, 0.25 mmol, 1.0 equiv) in MeCN (1 mL) was added and the reaction was stirred at -20 °C for 15 minutes under an atmosphere of N_2. The reaction mixture was analyzed by GC.

Procedure for Figure 5d:

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous THF (0.5 mL) was added corresponding alkenyl acetates (0.25 mmol, 1.0 equiv). Then the $PhMe_2Si$-ZnOPiv (0.5 mmol, 2 equiv) in THF (1 mL) was added and the reaction was stirred at 23 °C under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield product **22**.

To a solution of $CoBr_2$ (8.2 mg, 15 mol %), 2,2'-bipyridyl (5.9 mg, 15 mol %) in anhydrous MeCN (0.5 mL) was added corresponding alkenyl acetates (0.25 mmol, 1.0 equiv). Then the $(^nBu)_3Sn–ZnCl•LiCl$ (0.325 mmol, 1.3 equiv) in MeCN (1 mL) was added and the reaction was stirred at 0 °C under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **65**, **92**.

Procedure for Figure 5e:

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous THF (0.5 mL) was added **93** (0.25 mmol, 1.0 equiv). Then the $PhMe_2Si$-ZnOPiv (0.9 mL, 0.5 mmol, 2 equiv) in THF (1 mL) was added and the reaction was stirred at 23 °C for 3 h under an atmosphere of N_2.

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous MeCN (0.5 mL) was added **93** (0.25 mmol, 1.0 equiv). Then the $(^nBu)_3Sn–ZnCl•LiCl$ (1.3 mL, 0.325 mmol, 1.3 equiv) in MeCN (1 mL) was added and the reaction was stirred at 23 °C for 3 h under an atmosphere of N_2.

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous THF (0.5 mL) was added (*Z*)-**96** (0.25 mmol, 1.0 equiv). Then the $PhMe_2Si$-ZnOPiv (0.9 mL, 0.5 mmol, 2 equiv) in THF (1 mL) was added and the reaction was stirred at 23 °C for 1 h under an atmosphere of N_2.

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous MeCN (0.5 mL) was added (*Z*)-**96** (0.25 mmol, 1.0 equiv). Then the $(^nBu)_3Sn–ZnCl•LiCl$ (1.3 mL, 0.325 mmol, 1.3 equiv) in MeCN (1 mL) was added and the reaction was stirred at 23 °C for 1 h under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield product **98**.

Representative Procedures

Typical procedure 1 (TP1) for the preparation of ketoesters:

1. Synthesis of substituted benzoylacetates from aryl ketones:[1]

S**3ac**-S**3af,** S**3ah**-S**3al** were prepared in the following manner: NaH (40 mmol, 2.0 eq, 60% in mineral oil) was added in 50 mL THF to form a suspension. And then commercial available ketone (20 mmol, 1.0 eq) was added to the mixture and stirred at rt for 10 min. Then diethyl carbonate (40 mmol, 2.0 eq) was added to the solution at rt and kept stirring at reflux conditions for 2-3 h. Upon completion as indicated by TLC, the reaction was quenched with saturated aqueous NH_4HCO_3 and followed by the addition of acetic acid (1 M) at rt. The reaction mixture was then extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give S**3ac**-S**3af,** S**3ah**-S**3al**.

Another syhthesis method:[2]

S**3ag** was prepared in the following manner: NaH (20 mmol, 2.0 eq, 60% in mineral oil) was added in 30 mL THF to form a suspension. And diethyl carbonate (20 mmol, 2 eq) was then added to the suspension at rt and subsequently the ketone (10 mmol, 1.0 eq) was added dropwise. The reaction mixture was allowed to stir at rt until hydrogen gas evolution ceased and then heated to reflux. Upon completion as indicated by TLC, the reaction mixture was cooled to 0 °C and quenched with aqueous NH_4Cl. The reaction mixture was then extracted with ethyl acetate, washed with brine, dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give S**3ag**.

According to Stubbing et al,[3] ethyl 3-(4-hydroxyphenyl)-3-oxopropanoate was prepared in the following manner: A solution of 4'-hydroxyacetophenone (10 mmol, 1.0 eq) in THF (26 mL) was added dropwise to a solution of LiHMDS (1 M in THF, 30 mmol, 3.0 eq) at -78 °C. The mixture was allowed to stir at this temperature for 2 h, then a solution of diethyl carbonate (11 mmol, 1.1 eq) in THF (10 mL) was added quickly. The mixture was allowed to slowly warm to rt and stirred overnight. The mixture was then poured onto a mixture of ice and concd HCl. The resulting solution was extracted with DCM and the combined organic extracts was washed with

water, dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified *via* flash column chromatography on silica gel (petroleum ether/EtOAc) to give ethyl 3-(4-hydroxyphenyl)-3-oxopropanoate.

2. Synthesis of cyclic ketoesters:[4]

S**3x**, S**3y** were prepared in the following manner: NaH (20 mmol, 2.0 eq, 60% in mineral oil) was added to THF (6 mL) followed by the addition of diethyl carbonate (20 mmol, 2.0 eq) to form a suspension. Then a solution of the starting material (10 mmol, 1.0 eq) in THF (20 mL) was added to the reaction mixture dropwise. The mixture was stirred at 75 ºC for 16 h, then extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give the cyclic ketoesters S**3x**, S**3y**.

3. Synthesis of α-alkyl substituted ketoesters from ethyl acetoacetate:[5]

S**3c-S3u,** S**3an** and S**3ap-S3ar** were prepared in the following manner: To a suspension of *t*-BuOK (22 mmol, 1.1 eq) in THF (40 mL) was added ethyl acetoacetate or tert-butyl acetoacetate (in case of S**5ay**) (20 mmol, 1.0 eq) at 0 °C. The resulting clear solution was stirred at 0 °C for 30 min, and then alkyl bromide or alkyl iodide (24 mmol, 1.2 eq) in THF (10 mL) was added to the solution. After heating under reflux conditions for 12 h, the reaction was quenched with saturated aqueous NH_4Cl. Then the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, then dried over Na_2SO_4, filtered and concentrated to give crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give α- alkyl substituted ketoesters S**3c-S3u,** S**3an** and S**3ap-S3ar**.

4. Synthesis of α-alkyl substituted benzoylacetates:[6]

S(*E*)**-82** was prepared in the following manner: A solution of ethyl 3-(4-methoxyphenyl)-3-oxopropanoate (15 mmol, 1.0 eq) in dry DMF (10 mL) was added dropwise to a suspension of NaH (18 mmol, 1.2 eq, 60% in mineral oil) in dry DMF (10 mL). The mixture was stirred for 1 h at rt. Then 4-bromobut-1-ene (16.5 mmol, 1.1 eq) in dry DMF (4 mL) was added dropwise, and the mixture was stirred for 20 h at rt. The reaction was quenched with water and neutralized with 10% aqueous HCl, extracted with ethyl actetate, dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give S(*E*)**-82**.

5. Synthesis of α-aryl substituted ethyl 3-oxooctanoate:[7]

S**3v** was slightly modified by Chegaev et al. To the solution of ethyl phenylacetate (10 mmol, 1.0 eq) in THF (20 mL), 16 mL of 1.3 M LiHMDS solution in THF was added dropwise at -70 °C. Then the solution was stirred at -70 °C for 15 min. The solution of hexanoyl chloride (10 mmol, 1.0 eq) in THF (20 mL) was added dropwise and the reaction was stirred at -70 °C for 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl and then extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered and concentrated to give the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give S**3v**.

6. Synthesis of ethyl 4-oxochromane-3-carboxylate S3z:[8]

S**3z** was slightly modified by Kenny et al. To a solution of 4-chromanone (10 mmol, 1.0 eq) in THF (20 mL) was added a solution of LiHMDS (15 mmol, 1.5 eq, 1.3 M in THF) dropwise at -78 °C and the mixture was stirred for 30 min. Ethyl cyanoformate (20 mmol, 2.0 eq) in THF (20 mL) was added dropwise and the reaction was stirred at -78 °C for 1 h. The mixture was allowed to warm to rt and quenched by the addition of aqueous NH_4Cl and water. The combined organic phases were washed with brine, dried over Na_2SO_4 and concentrated. Flash column chromatography on silica gel (petroleum ether/EtOAc) afforded S**3z**.

Typical procedure 2 (TP2) for the synthesis of esters S**3as-**S**3av:**[9]

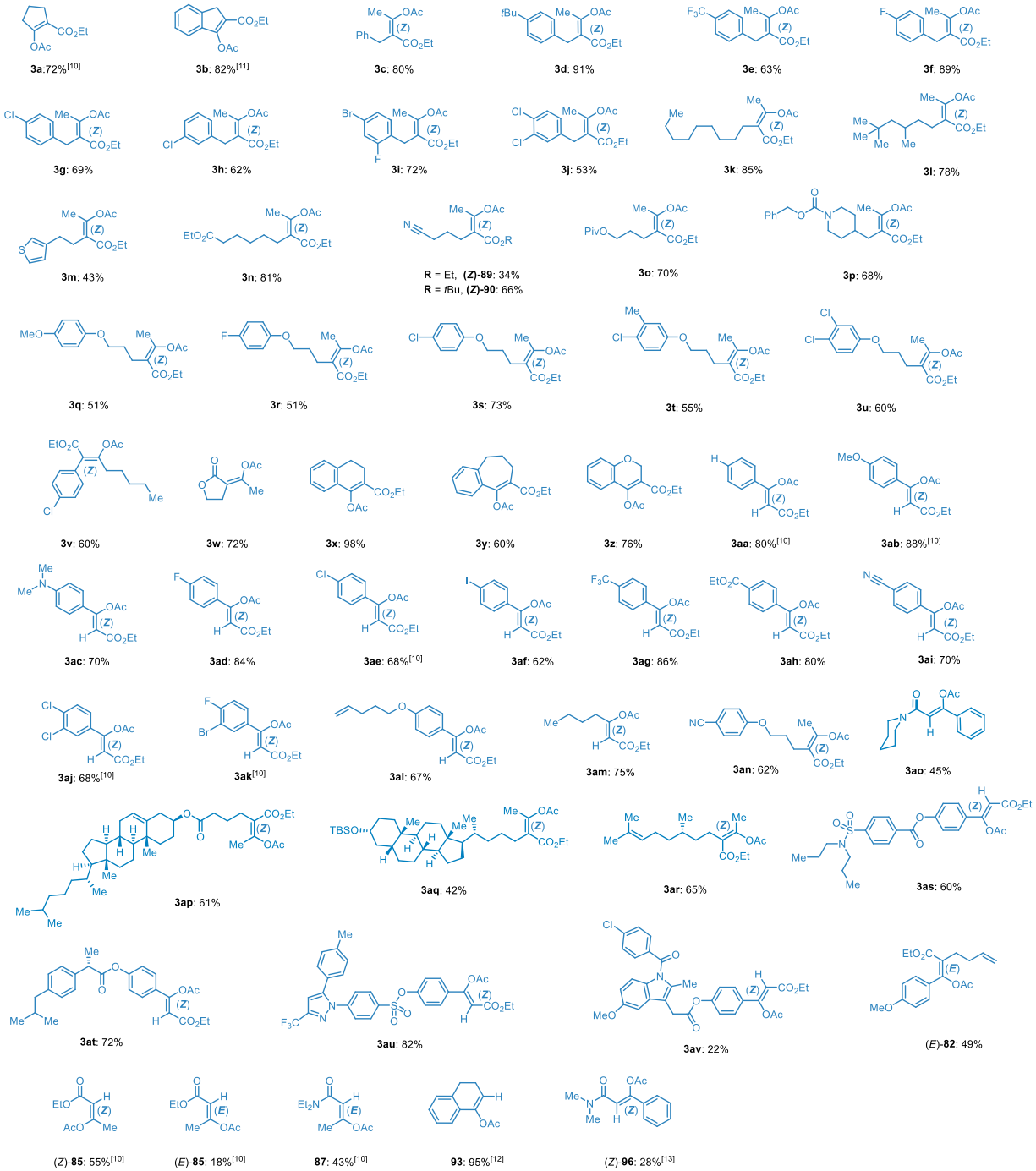
Take S**3at** for example: To a round-bottom flask were added (S)-(+)-ibuprofen (4 mmol, 1.0 eq), dicyclohexylcarbodiimide (6 mmol, 1.5 eq), and DCM (30 mL). Then ethyl 3-(4-hydroxyphenyl)-3-oxopropanoate (4 mmol, 1.0 eq) and 4-dimethylaminopyridine (0.4 mmol, 0.1 eq) were added to the mixture. The reaction mixture was stirred at rt for 24 h and then filtered. The filtrate was concentrated and purified by flash column chromatography on silica gel (petroleum ether/EtOAc) to give S**3at**.

Typical procedure 3 (**TP3) for the synthesis of alkenyl acetates 3a, 3b-3av:** [10]

To a solution of ketoester (10 mmol, 1.0 eq) in *iso*-propenyl acetate (10 mL) was added *p*-TSA·H_2O (1 mmol, 0.1 eq). The resulting mixture was heated under reflux conditions (130 ℃) for 18 hours (As for **3as-3av**, the resulting mixture were refluxing at 110 ℃). The mixture was allowed to cool to rt and the remaining *iso*-propenyl acetate was removed under reduced

pressure. The brown oily residue was extracted with ethyl acetate and washed with water. Afterwards the organic phase was dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The remaining residue was purified by column chromatography on silica gel (petroleum ether /EtOAc) to yield alkenyl acetates **3a, 3b-3av**.

***Starting materials synthesis of* TP3**:

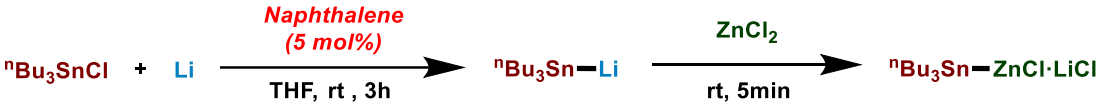


Preparation of $Zn(OPiv)_2$:

Pivalic acid (20.4 g, 22.6 mL, 200 mmol) was placed in a dry and argon-flushed 500 mL three-necked roundbottom flask, equipped with a magnetic stirring bar, a septum and a pressure equalizer, and was dissolved in dry THF (120 mL). The mixture was cooled to 0 °C, and a solution of Et_2Zn (13.0 g, 10.8 mL, 105 mmol) in dry THF (120 mL) was added over a period of 30 min under vigorous stirring. Then, the ice-bath was removed and stirring was continued at 25 °C for one additional hour at which point bubbling has ceased (a thick slurry was formed). The solvent was removed in vacuo and the solid residue was dried for at least 4 h longer. $Zn(OPiv)_2$ was obtained in quantitative yield, as a puffy amorphous white solid.

Preparation of $PhMe_2Si$-ZnOPiv and $(^nBu)_3Sn$–ZnCl•LiCl:

A 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar and was charged with lithium clippings (174 mg, 25 mmol) and dry THF (10.0 mL). Then Chlorodimethylphenylsilane (10 mmol, 1.0 equiv) was added dropwise at 0 °C and the mixture was stirred at same temperature for 12 h. The silyllithium was titrated against iodine according to Kofron's method. Next, this solution was added via syringe into a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring and $Zn(OPiv)_2$ (1.5 equiv with respect to titrated silyllithium) at rt, and the reaction mixture was stirred at rt for 10 min. The **$PhMe_2Si$-ZnOPiv** (**1a**) (routinely formed as an ~0.55 M solution) was titrated using Knochel's method.



To a solution of naphthalene (26 mg, 0.2 mmol) in THF (8 mL) were added lithium clippings (84 mg, 12 mmol). The resulting mixture was stirred at rt for 10 minutes under an nitrogen atmosphere. Then tributyltin chloride (1.1 mL, 4 mmol) was added and the mixture was stirred at rt for 3 h. The stannyllithium was titrated against iodine according to Kofron's method. A portion of 1.3 mL of the above solution (0.325 mmol) was added to a stirred solution of $ZnCl_2$ (0.5 mL, 1M solution in THF). The reaction was stirred at rt for 5 minutes. The **$(^nBu)_3Sn$–ZnCl•LiCl** (**2a**) (routinely formed as an ~0.25 M solution) was titrated using Knochel's method. Then the solvent was removed in vacuo and the liquid residue (**2a**) was obtained.

Typical procedure 4 (TP4) for the cobalt-catalyzed silylation of alkenyl acetates:

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous THF (0.5 mL) was added **alkenyl acetates 3** (0.25 mmol, 1.0 equiv). Then the **$PhMe_2Si$-ZnOPiv** (0.9 mL, 0.5 mmol, 2 equiv) in THF (1 mL) was added and the reaction was stirred at rt for 2 h under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **4, 21-22, 24, 26-31**.

Typical procedure 5 (TP5) for the cobalt-catalyzed silylation of alkenyl acetates:

To a solution of $CoBr_2$·5,5'-dimethyl-2,2'-bipyridine (10 mg, 10 mol %) in anhydrous THF (0.5 mL) was added **alkenyl acetates 3** (0.25 mmol, 1.0 equiv). Then the **$PhMe_2Si$-ZnOPiv** (0.9 mL, 0.5 mmol, 2 equiv) in THF (1 mL) was added and the reaction was stirred at rt for 2 h under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **9-20, 23, 25, 32, 73-76.**

Typical procedure 6 (TP6) for the cobalt-catalyzed stannylation of alkenyl acetates:

To a solution of $CoBr_2$ (5.5 mg, 10 mol %), 2,2'-bipyridyl (4.0 mg, 10 mol %) in anhydrous MeCN (0.5 mL) was added **alkenyl acetates 3** (0.25 mmol, 1.0 equiv). Then the **$(^nBu)_3Sn$–ZnCl•LiCl** (1.3 mL, 0.325 mmol, 1.3 equiv) in MeCN (1 mL) was added and the reaction was stirred at -20 °C for 15 minutes under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **7**, **40-45, 47, 49-52, 78-81.**

Typical procedure 7 (TP7) for the cobalt-catalyzed stannylation of alkenyl acetates:

To a solution of $CoBr_2$ (8.2 mg, 15 mol %), 2,2'-bipyridyl (5.9 mg, 15 mol %) in anhydrous MeCN (0.5 mL) was added **alkenyl acetates 3** (0.25 mmol, 1.0 equiv). Then the **$(^nBu)_3Sn$–ZnCl•LiCl** (1.3 ml, 0.325 mmol, 1.3 equiv) in MeCN (1 mL) was added and the reaction was stirred at 0 °C for 1h under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **35-39, 46, 48, 53-71, 77.**

Typical procedure 8 (TP8) for the MKS Reaction:

To a solution of $Pd(PPh_3)_4$ (6 mg, 5 mol %), CuI (9.5 mg, 50 mol %) in anhydrous DMF (0.5 mL) were added alkenyl stannanes (0.1 mmol, 1.0 equiv) and aryl or heteroaryl halides (0.12 mmol, 1.2 equiv). The reaction was stirred at 23 °C for 10 h under an atmosphere of N_2. The solvent was evaporated in vacuo and the remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **108-117**.

Typical procedure 9 (TP9) for the reduction of the ester:

To a solution of **ester** (1.0 equiv) in THF (1.5 mL), was added dropwise a solution of diisobutylaluminium hydride (3.0 equiv, 1.5 M in toluene) at –78 °C under nitrogen. After stirring for 20 min at 0 °C, diethyl ether and water were successively added at 0 °C. After stirring for 2 h, the reaction mixture was extracted with ethyl acetate, washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield product **8**.

Typical procedure 10 (TP10) for the reduction of the lactones:

To a suspended solution of **$LiAlH_4$** (1.5 equiv) in anhydrous Et_2O (1 mL) was added **lactones** (1 equiv) in Et_2O (1 mL) at 0 °C under N_2 atmosphere. After stirring for 1 h, the reaction was quenched with water at 0 °C.Then the reaction was extracted with CH_2Cl_2, washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield product **33, 72**.

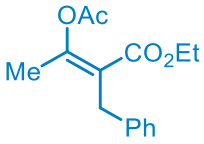
Typical procedure 11 (TP11) for the C—Si bond cleavage:

To a solution of tetrasubstituted alkenyl silanes (1.0 equiv) in CCl_4 (1.5 mL) was added iodine (1.5 equiv). The reaction mixture was stirred at 70 °C for 16 h. After cooling to room temperature, saturated $Na_2S_2O_3$ solution (4 mL) was added and the resulting mixture was extracted with CH_2Cl_2 (15 ml x 3). The organic phase was washed with brine (30 mL), dried over Na_2SO_4, filtered and concentrated. The remaining residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **118-119**.

Typical procedure 12 (TP12) for the Hiyama Cross-Coupling:

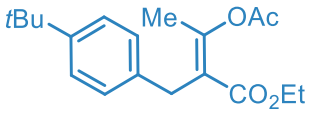
To a solution of alkenyl silane (1.0 equiv) in THF (1.5 mL) was added NaOH (2 equiv) at rt and the solution stirred for 5 min. **Ar-I** (1.5 equiv) was added and after 5min Pd_2dba_3 (2.5 mol%)

was added, then the mixture was stirred at 60 °C for 16 h. After cooling to room temperature, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc) to yield products **106-107**.



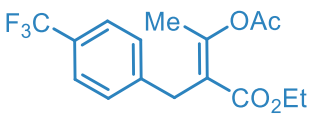
Ethyl (*Z*)-3-acetoxy-2-benzylbut-2-enoate (3c)

The general procedure **TP3** was followed using **ketoester** (3.7 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3c** (80%, 775 mg) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30 – 7.16 (m, 5H), 4.08 (q, J = 7.1 Hz, 2H), 3.71 (s, 2H), 2.20 (s, 3H), 2.06 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.9, 165.8, 154.4, 138.7, 128.6, 128.2, 126.4, 119.7, 60.7, 34.4, 21.1, 19.0, 14.2. HR-MS (EI) m/z calcd for $C_{15}H_{18}O_4$ [M+H$^+$] 263.1278, found 263.1280.



Ethyl (*Z*)-3-acetoxy-2-(4-(tert-butyl)benzyl)but-2-enoate (3d)

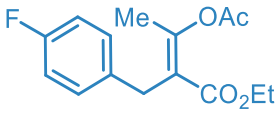
The general procedure **TP3** was followed using **ketoester** (3.6 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3d** (1.04 g, 91% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 4.09 (q, J = 7.1 Hz, 2H), 3.68 (s, 2H), 2.19 (s, 3H), 2.06 (s, 3H), 1.29 (s, 9H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 165.8, 154.1, 149.1, 135.5, 127.7, 125.4, 119.8, 60.6, 34.4, 33.8, 31.4, 21.0, 18.9, 14.1. HR-MS (EI) m/z calcd for $C_{19}H_{26}O_4$ [M+H$^+$] 319.1904, found 319.1908.



Ethyl (*Z*)-3-acetoxy-2-(4-(trifluoromethyl)benzyl)but-2-enoate (3e)

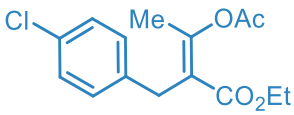
The general procedure **TP3** was followed using **ketoester** (2.2 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3e** (63%, 457 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 4.09

(q, J = 7.1 Hz, 2H), 3.76 (s, 2H), 2.21 (s, 3H), 2.06 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 165.5, 155.3, 143.0, 128.8 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 128.4, 125.6 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.4 (q, $^1J_{C\text{-}F}$ = 271.7 Hz), 118.9, 60.9, 34.3, 21.1, 19.1, 14.2. HR-MS (EI) m/z calcd for $C_{16}H_{17}F_3O_4$ [M+H$^+$] 331.1152, found 331.1157.



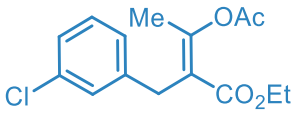
Ethyl (*Z*)-3-acetoxy-2-(4-fluorobenzyl)but-2-enoate (3f)

The general procedure **TP3** was followed using **ketoester** (4.8 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3f** (1.2 g, 89% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.19 (dd, J = 8.7, 5.4 Hz, 2H), 6.99 – 6.93 (m, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.67 (s, 2H), 2.20 (s, 3H), 2.06 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.9, 165.7, 161.6 (d, $^1J_{C\text{-}F}$ = 244.0 Hz), 154.5, 134.3 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 129.6 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 119.7, 115.3 (d, $^2J_{C\text{-}F}$ = 21.2 Hz), 60.7, 33.6, 21.0, 18.9, 14.2. HR-MS (EI) m/z calcd for $C_{15}H_{17}FO_4$ [M+H$^+$] 281.1184, found 281.1186.



Ethyl (*Z*)-3-acetoxy-2-(4-chlorobenzyl)but-2-enoate (3g)

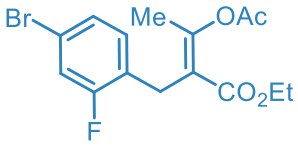
The general procedure **TP3** was followed using **ketoester** (4 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3g** (825 mg, 69% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.24 (dd, J = 8.6, 2.3 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 4.09 (q, J = 7.1 Hz, 2H), 3.67 (s, 2H), 2.20 (s, 3H), 2.05 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H). HR-MS (EI) m/z calcd for $C_{15}H_{17}ClO_4$ [M+H$^+$] 297.0888, found 297.0892.



Ethyl (*Z*)-3-acetoxy-2-(3-chlorobenzyl)but-2-enoate (3h)

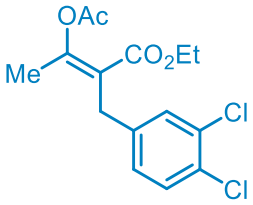
The general procedure **TP3** was followed using **ketoester** (3.2 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3h** (568 mg, 60% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.24 – 7.09 (m, 4H), 4.10 (q, J = 7.1 Hz, 2H),

3.68 (s, 2H), 2.21 (s, 3H), 2.06 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H). HR-MS (EI) m/z calcd for $C_{15}H_{17}ClO_4$ [M+H$^+$] 297.0888, found 297.0891.



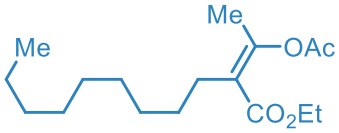
Ethyl (*Z*)-3-acetoxy-2-(4-bromo-2-fluorobenzyl)but-2-enoate (3i)

The general procedure **TP3** was followed using **ketoester** (5 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3i** (1.28 g, 72% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23 – 7.12 (m, 3H), 4.10 (q, J = 7.1 Hz, 2H), 3.66 (s, 2H), 2.21 (s, 3H), 2.05 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). HR-MS (EI) m/z calcd for $C_{15}H_{16}BrClFO_4$ [M+H$^+$] 359.0289, found 359.0292.



Ethyl (*Z*)-3-acetoxy-2-(3,4-dichlorobenzyl)but-2-enoate (3j)

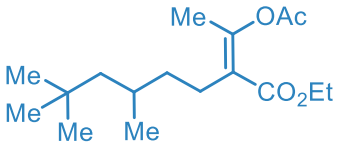
The general procedure **TP3** was followed using **ketoester** (2 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3j** (53%, 351 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.34 (t, J = 5.1 Hz, 2H), 7.08 (dd, J = 8.2, 2.0 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.65 (s, 2H), 2.21 (s, 3H), 2.05 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 165.4, 155.4, 139.1, 132.5, 130.5, 130.4, 130.2, 127.6, 118.8, 60.9, 33.6, 21.1, 19.2, 14.2. HR-MS (EI) m/z calcd for $C_{15}H_{16}Cl_2O_4$ [M+H$^+$] 331.0498, found 331.0501.



Ethyl (*Z*)-2-(1-acetoxyethylidene)undecanoate (3k)

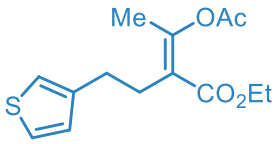
The general procedure **TP3** was followed using **ketoester** (7.3 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3k** (1.85 g, 85% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.18 (q, J = 7.1 Hz, 2H), 2.35 – 2.27 (m, 2H),

2.17 (s, 3H), 2.01 (s, 3H), 1.28 (dd, J = 9.3, 4.9 Hz, 17H), 0.89 (t, J = 6.8 Hz, 3H). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23 – 7.12 (m, 3H), 4.10 (q, J = 7.1 Hz, 2H), 3.66 (s, 2H), 2.21 (s, 3H), 2.05 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). HR-MS (EI) m/z calcd for $C_{17}H_{30}O_4$ [M+H$^+$] 299.2217, found 299.2220.



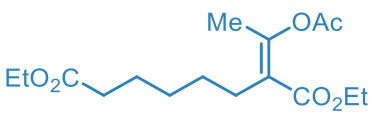
Ethyl (*Z*)-2-(1-acetoxyethylidene)-5,7,7-trimethyloctanoate (3l)

The general procedure **TP3** was followed using **ketoester** (7 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3l** (1.62 g, 78% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.16 (q, J = 7.1 Hz, 2H), 2.35 – 2.23 (m, 2H), 2.15 (s, 3H), 2.00 (s, 3H), 1.56 – 1.39 (m, 2H), 1.34 – 1.21 (m, 6H), 0.95 (d, J = 6.6 Hz, 3H), 0.89 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.7, 166.2, 151.9, 121.3, 60.4, 51.0, 38.4, 31.1, 30.0, 29.3, 26.8, 22.4, 20.9, 18.2, 14.2. HR-MS (EI) m/z calcd for $C_{17}H_{30}O_4$ [M+H$^+$] 299.2217, found 299.2219.



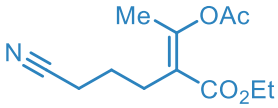
Ethyl (*Z*)-3-acetoxy-2-[2-(thiophen-3-yl)ethyl]but-2-enoate (3m)

The general procedure **TP3** was followed using **ketoester** (10.3 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3m** (43%, 1.25 g) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, J = 4.8, 3.0 Hz, 1H), 6.97 (dd, J = 8.7, 3.6 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 2.80 (t, J = 7.5 Hz, 2H), 2.59 (t, J = 7.6 Hz, 2H), 2.16 (s, 3H), 1.85 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.7, 166.1, 153.4, 141.4, 128.5, 125.4, 121.0, 120.0, 60.6, 30.3, 29.4, 21.0, 18.2, 14.3. HR-MS (EI) m/z calcd for $C_{14}H_{18}O_4S$ [M+H$^+$] 283.0999, found 283.1003.



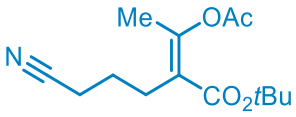
Diethyl (*Z*)-2-(1-acetoxyethylidene)octanedioate (3n)

The general procedure **TP3** was followed using **ketoester** (6.37 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3n** (81%, 1.61 g) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.17 – 4.08 (m, 4H), 2.30 – 2.24 (m, 4H), 2.13 (s, 3H), 1.97 (s, 3H), 1.65 – 1.58 (m, 2H), 1.43 (dd, *J* = 15.3, 7.7 Hz, 2H), 1.37 – 1.31 (m, 2H), 1.24 (m, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.8, 168.8, 166.3, 152.1, 121.0, 60.5, 60.3, 34.3, 28.8, 28.7, 28.6, 24.8, 21.0, 18.3, 14.3. HR-MS (EI) m/z calcd for $C_{16}H_{26}O_6$ [M+H$^+$] 315.1802, found 315.1808.



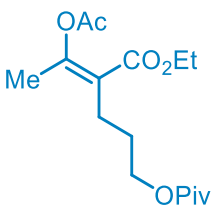
Ethyl (*Z*)-2-(1-acetoxyethylidene)-5-cyanopentanoate [(*Z*)-89]

The general procedure **TP3** was followed using **ketoester** (10.7 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 5:1) yielded (*Z*)-**89** (34%, 871 mg) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.18 (q, *J* = 7.1 Hz, 2H), 2.49 (t, *J* = 7.4 Hz, 2H), 2.40 (t, *J* = 7.0 Hz, 2H), 2.17 (s, 3H), 2.05 (s, 3H), 1.88 – 1.80 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.7, 165.7, 154.2, 119.6, 119.1, 60.9, 27.7, 24.8, 21.0, 18.8, 16.6, 14.4. HR-MS (EI) m/z calcd for $C_{12}H_{17}NO_4$ [M+H$^+$] 240.1230, found 240.1237.



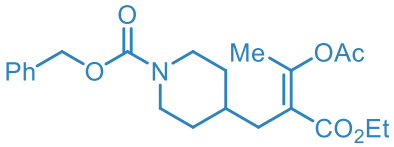
***tert*-Butyl (*Z*)-2-(1-acetoxyethylidene)-5-cyanopentanoate [(*Z*)-90]**

The general procedure **TP3** was followed using **ketoester** (5 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 50:1) yielded (*Z*)-**90** (66%, 887 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.43 – 2.39 (m, 2H), 2.38 (t, *J* = 5.9 Hz, 2H), 2.14 (s, 3H), 1.98 (s, 3H), 1.85 – 1.76 (m, 2H), 1.44 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.6, 165.3, 151.6, 120.6, 119.6, 81.4, 28.2, 27.8, 24.6, 21.0, 18.1, 16.4. HR-MS (EI) m/z calcd for $C_{14}H_{21}NO_4$ [M+H$^+$] 268.1543, found 268.1551.



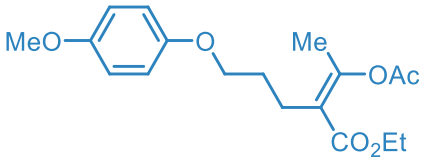
Ethyl (*Z*)-2-(1-acetoxyethylidene)-5-(pivaloyloxy)pentanoate (3o)

The general procedure **TP3** was followed using **ketoester** (5 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3o** (70%, 1.1 g) as a pale yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.15 (q, J = 7.1 Hz, 2H), 4.06 (t, J = 6.2 Hz, 2H), 2.40 – 2.33 (m, 2H), 2.14 (s, 3H), 1.99 (s, 3H), 1.77 (ddt, J = 12.4, 9.8, 6.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.18 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 178.5, 168.7, 165.9, 153.2, 120.1, 63.6, 60.6, 38.8, 28.1, 27.3, 25.5, 21.0, 18.4, 14.3. HR-MS (EI) m/z calcd for $C_{16}H_{26}O_6$ [M+H$^+$] 315.1806, found 315.1811.



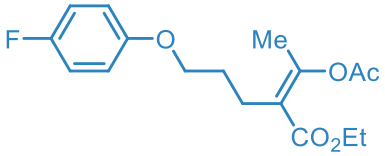
Benzyl (*Z*)-4-[3-acetoxy-2-(ethoxycarbonyl)but-2-en-1-yl]piperidine-1-carboxylate (3p)

The general procedure **TP3** was followed using **ketoester** (6.9 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 5:1) yielded **3p** (68%, 1.88 g) as an orange oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.34 (t, J = 7.3 Hz, 5H), 5.12 (s, 2H), 4.17 (dd, J = 14.2, 7.1 Hz, 4H), 2.72 (s, 2H), 2.27 (d, J = 7.1 Hz, 2H), 2.16 (s, 3H), 1.98 (s, 3H), 1.73 (d, J = 12.8 Hz, 2H), 1.60 (ddd, J = 11.3, 9.4, 5.5 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.13 (d, J = 10.5 Hz, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.7, 166.2, 155.2, 152.8, 136.9, 128.4, 127.9, 127.8, 119.2, 66.9, 60.6, 44.2, 36.1, 35.4, 31.8, 20.9, 18.7, 14.2. HR-MS (EI) m/z calcd for $C_{22}H_{29}NO_6$ [M+H$^+$] 404.2068, found 404.2075.



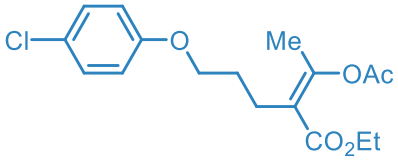
Ethyl (*Z*)-2-(1-acetoxyethylidene)-5-(4-methoxyphenoxy)pentanoate (3q)

The general procedure **TP3** was followed using **ketoester** (5.4 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3q** (51%, 922 mg) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.82 (s, 4H), 4.15 (q, J = 7.1 Hz, 2H), 3.92 (t, J = 5.9 Hz, 2H), 3.75 (s, 3H), 2.52 (t, J = 7.3 Hz, 2H), 2.15 (s, 3H), 1.98 (s, 3H), 1.92 (dt, J = 13.0, 6.5 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 166.2, 153.8, 153.3, 153.1, 120.0, 115.5, 114.7, 66.9, 60.6, 55.8, 28.4, 25.3, 21.0, 18.4, 14.3. HR-MS (EI) m/z calcd for $C_{18}H_{24}O_6$ [M+H$^+$] 337.1646, found 337.1651.



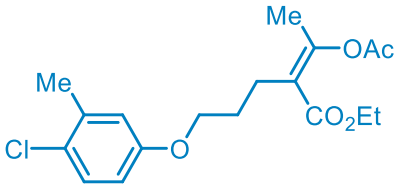
Ethyl (*Z*)-2-(1-acetoxyethylidene)-5-(4-fluorophenoxy)pentanoate (3r)

The general procedure **TP3** was followed using **ketoester** (3 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3r** (51%, 496 mg) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.97 – 6.90 (m, 2H), 6.84 – 6.78 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.92 (t, *J* = 6.0 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.14 (s, 3H), 1.96 (s, 3H), 1.91 (dd, *J* = 13.4, 6.9 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 166.1, 157.3 (d, $^{1}J_{C\text{-}F}$ = 237.8 Hz), 155.1 (d, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 153.2, 120.0, 115.8 (d, $^{2}J_{C\text{-}F}$ = 22.9 Hz), 115.5 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 66.9, 60.6, 28.3, 25.2, 21.0, 18.3, 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -124.30 (s). HR-MS (EI) m/z calcd for $C_{17}H_{21}FO_5$ [M+H$^+$] 325.1446, found 325.1448.



Ethyl (*Z*)-2-(1-acetoxyethylidene)-5-(4-chlorophenoxy)pentanoate (3s)

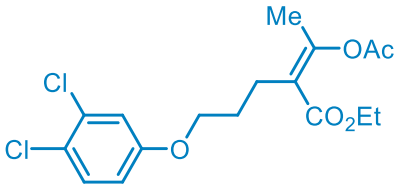
The general procedure **TP3** was followed using **ketoester** (2.9 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3s** (73%, 720 mg) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23 – 7.19 (m, 2H), 6.84 – 6.79 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.94 (t, *J* = 5.9 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.15 (s, 3H), 1.96 (s, 3H), 1.92 (dd, *J* = 13.3, 7.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 166.1, 157.6, 153.3, 129.4, 125.5, 119.9, 115.8, 66.6, 60.7, 28.2, 25.2, 21.0, 18.4, 14.3. HR-MS (EI) m/z calcd for $C_{17}H_{21}ClO_5$ [M+H$^+$] 341.1150, found 341.1156.



Ethyl (*Z*)-2-(1-acetoxyethylidene)-5-(4-chloro-3-methylphenoxy)pentanoate (3t)

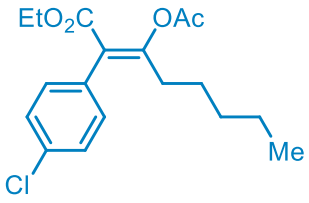
The general procedure **TP3** was followed using **ketoester** (1.2 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3t** (55%, 234 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 2.9 Hz, 1H), 6.66

(dd, *J* = 8.7, 3.0 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.93 (t, *J* = 5.9 Hz, 2H), 2.52 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.16 (s, 3H), 1.97 (s, 3H), 1.92 (dd, *J* = 13.3, 6.9 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 166.1, 157.5, 153.4, 137.1, 129.7, 125.8, 120.0, 117.1, 113.2, 66.6, 60.7, 28.3, 25.3, 21.1, 20.4, 18.4, 14.4. HR-MS (EI) m/z calcd for $C_{18}H_{23}ClO_5$ [M+H$^+$] 355.1307, found 355.1311.



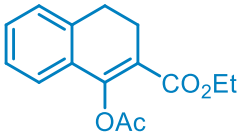
Ethyl (*Z*)-2-(1-acetoxyethylidene)-5-(3,4-dichlorophenoxy)pentanoate (3u)

The general procedure **TP3** was followed using **ketoester** (4 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3u** (60%, 900 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 8.9 Hz, 1H), 6.98 (d, *J* = 2.9 Hz, 1H), 6.74 (dd, *J* = 8.9, 2.9 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.94 (t, *J* = 5.9 Hz, 2H), 2.51 (t, *J* = 7.2 Hz, 2H), 2.16 (s, 3H), 1.97 (s, 3H), 1.93 (dd, *J* = 13.3, 6.9 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 166.1, 158.1, 153.4, 132.9, 130.8, 123.9, 119.8, 116.5, 114.5, 67.0, 60.7, 28.1, 25.2, 21.0, 18.5, 14.3. HR-MS (EI) m/z calcd for $C_{17}H_{20}Cl_2O_5$ [M+H$^+$] 375.0761, found 375.0764.



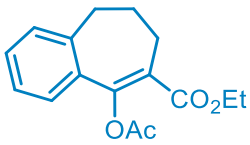
Ethyl (*Z*)-3-acetoxy-2-(4-chlorophenyl)oct-2-enoate (3v)

The general procedure **TP3** was followed using **ketoester** (8.6 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 80:1) yielded **3v** (60%, 1.76 g) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.29 (m, 2H), 7.23 – 7.16 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.24 (s, 3H), 2.17 – 2.10 (m, 2H), 1.45 – 1.39 (m, 2H), 1.22 – 1.12 (m, 7H), 0.82 (t, *J* = 6.9 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.6, 165.1, 158.8, 133.9, 133.6, 131.4, 128.6, 122.1, 61.0, 32.6, 31.4, 26.1, 22.4, 21.2, 14.2, 13.9. HR-MS (EI) m/z calcd for $C_{18}H_{23}ClO_4$ [M+H$^+$] 339.1358, found 339.1364.



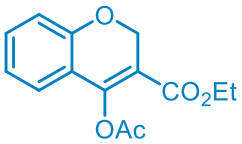
Ethyl 1-acetoxy-3,4-dihydronaphthalene-2-carboxylate (3x)

The general procedure **TP3** was followed using **ketoester** (6.8 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 30:1) yielded **3x** (1.729 g, 98% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.30 (m, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.17 (m, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.92 – 2.86 (m, 2H), 2.79 – 2.73 (m, 2H), 2.37 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.6, 165.8, 151.1, 138.3, 130.4, 130.2, 127.7, 126.8, 123.5, 116.7, 60.8, 27.4, 23.8, 21.0, 14.4. HR-MS (EI) m/z calcd for $C_{15}H_{16}O_4$ [M+H$^+$] 261.1121, found 261.1126.



Ethyl 9-acetoxy-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (3y)

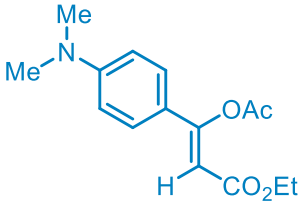
The general procedure **TP3** was followed using **ketoester** (4 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 70:1) yielded **3y** (657 mg, 60% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.36 (dt, *J* = 10.5, 5.1 Hz, 1H), 7.30 (ddd, *J* = 9.9, 7.3, 1.7 Hz, 2H), 7.23 (dd, *J* = 7.1, 1.6 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.77 (t, *J* = 6.7 Hz, 2H), 2.27 – 2.19 (m, 7H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.9, 166.1, 152.9, 142.1, 135.8, 129.9, 129.2, 126.7, 126.4, 120.8, 60.9, 34.7, 31.7, 25.1, 21.0, 14.4. HR-MS (EI) m/z calcd for $C_{16}H_{18}O_4$ [M+H$^+$] 275.1278, found 275.1280.



Ethyl 4-acetoxy-2*H*-chromene-3-carboxylate (3z)

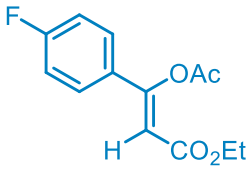
The general procedure **TP3** was followed using **ketoester** (3 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3z** (596 mg, 76% yield) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.26 (m, 1H), 7.24 (d, *J* = 1.5 Hz, 1H), 6.96 (td, *J* = 7.6, 1.1 Hz, 1H), 6.90 – 6.84 (m, 1H), 5.10 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.8, 162.8, 156.9, 149.8,

132.8, 124.0, 121.8, 119.1, 116.5, 109.7, 65.4, 60.9, 20.9, 14.3. HR-MS (EI) m/z calcd for $C_{14}H_{14}O_5$ [M+H$^+$] 263.0914, found 263.0918.



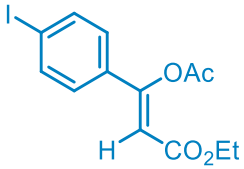
Ethyl (*Z*)-3-acetoxy-3-[4-(dimethylamino)phenyl]acrylate (3ac)

The general procedure **TP3** was followed using **ketoester** (4.5 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3ac** (873 mg, 70% yield) as a yellow solid. ^{1}H-MR (400 MHz, $CDCl_3$): δ = 7.49 – 7.44 (m, 2H), 6.68 – 6.62 (m, 2H), 6.09 (s, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.02 (s, 6H), 2.39 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.4, 165.1, 159.1, 152.3, 127.5, 119.8, 111.8, 101.1, 60.0, 40.2, 21.2, 14.5. HR-MS (EI) m/z calcd for $C_{15}H_{19}NO_4$ [M+H$^+$] 278.1387, found 278.1391.



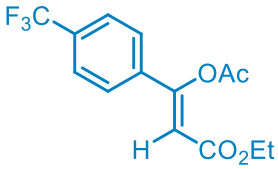
Ethyl (*Z*)-3-acetoxy-3-(4-fluorophenyl)acrylate (3ad)

The general procedure **TP3** was followed using **ketoester** (4.26 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 50:1) yielded **3ad** (84%, 898 mg) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.60 – 7.54 (m, 2H), 7.12 – 7.05 (m, 2H), 6.20 (s, 1H), 4.19 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.9 (d, $^1J_{C\text{-}F}$ = 243.6 Hz), 164.2, 163.2, 157.2, 129.8 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 128.2 (d, $^3J_{C\text{-}F}$ = 8.7 Hz), 116.1 (d, $^2J_{C\text{-}F}$ = 22.2 Hz), 106.1, 60.5, 21.1, 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -108.62 (s). HR-MS (EI) m/z calcd for $C_{13}H_{13}FO_3$ [M+H$^+$] 253.0871, found 253.0878.



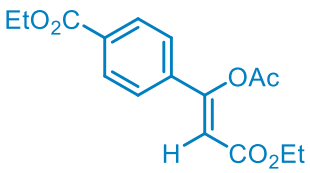
Ethyl (*Z*)-3-acetoxy-3-(4-iodophenyl)acrylate (3af)

The general procedure **TP3** was followed using **ketoester** (12 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3af** (62%, 2.67 g) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.77 – 7.73 (m, 2H), 7.32 – 7.28 (m, 2H), 6.25 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.0, 164.0, 157.2, 138.1, 133.0, 127.5, 106.7, 97.7, 60.5, 21.0, 14.3. HR-MS (EI) m/z calcd for $C_{13}H_{13}IO_4$ [M+H$^+$] 360.9931, found 360.9937.



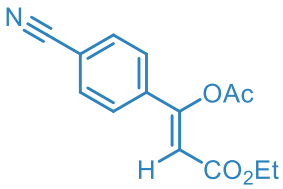
Ethyl (*Z*)-3-acetoxy-3-[4-(trifluoromethyl)phenyl]acrylate (3ag)

The general procedure TP3 was followed using ketoester (7.2 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 30:1) yielded **3ag** (86%, 1.87 g) as an orange oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.68 (q, J = 8.7 Hz, 4H), 6.32 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.1, 163.9, 156.5, 137.1, 132.7 (q, $^{2}J_{C\text{-}F}$ = 32.8 Hz), 126.4, 126.0 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz), 108.4, 60.8, 21.0, 14.4. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -63.01 (s). HR-MS (EI) m/z calcd for $C_{14}H_{13}F_3O_4$ [M+H$^+$] 303.0839, found 303.0841.



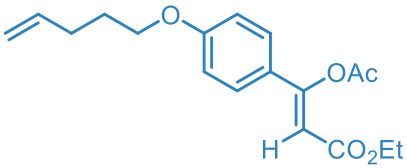
Ethyl (*Z*)-4-(1-acetoxy-3-ethoxy-3-oxoprop-1-en-1-yl)benzoate (3ah)

The general procedure **TP3** was followed using **ketoester** (3 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 15:1) yielded **3ah** (80%, 733 mg) as an white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.07 – 8.02 (m, 2H), 7.65 – 7.60 (m, 2H), 6.32 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 4.19 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.0, 165.7, 163.9, 156.8, 137.5, 132.5, 130.0, 125.9, 108.0, 61.3, 60.6, 20.9, 14.3, 14.3. HR-MS (EI) m/z calcd for $C_{16}H_{18}O_6$ [M+H$^+$] 307.1176, found 307.1179.



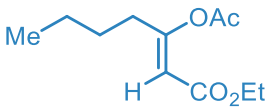
Ethyl (*Z*)-3-acetoxy-3-(4-cyanophenyl)acrylate (3ai)

The general procedure **TP3** was followed using **ketoester** (7 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 15:1) yielded **3ai** (70%, 1.27 g) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.72 – 7.66 (m, 4H), 6.32 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.9, 163.6, 155.7, 137.8, 132.6, 126.5, 118.1, 114.3, 109.1, 60.8, 20.9, 14.2. HR-MS (EI) m/z calcd for $C_{14}H_{13}NO_4$ [M+H$^+$] 260.0917, found 260.0922.



Ethyl (*Z*)-3-acetoxy-3-[4-(pent-4-en-1-yloxy)phenyl]acrylate (3al)

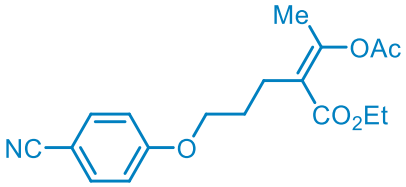
The general procedure **TP3** was followed using **ketoester** (2.87 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3al** (67%, 611 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.49 (m, 2H), 6.91 – 6.86 (m, 2H), 6.16 (s, 1H), 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.06 (ddd, *J* = 17.2, 3.2, 1.6 Hz, 1H), 5.01 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.99 (t, *J* = 6.4 Hz, 2H), 2.39 (s, 3H), 2.23 (dd, *J* = 14.6, 6.8 Hz, 2H), 1.93 – 1.85 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.2, 164.6, 161.5, 158.2, 137.6, 127.7, 125.6, 115.5, 114.8, 103.9, 67.4, 60.2, 30.1, 28.3, 21.1, 14.4. HR-MS (EI) m/z calcd for $C_{18}H_{22}O_5$ [M+H$^+$] 319.1540, found 319.1547.



Ethyl (*Z*)-3-acetoxyhept-2-enoate (3am)

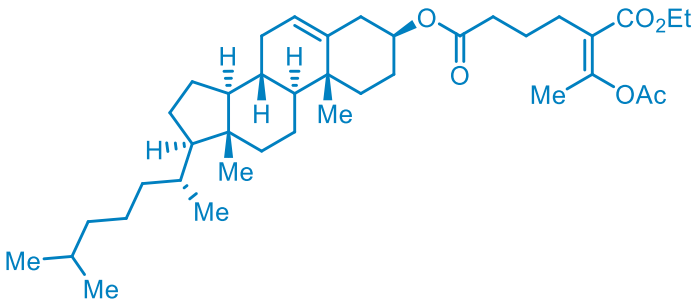
The general procedure **TP3** was followed using **ketoester** (6.7 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3am** (75%, 1.08g) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.58 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.26 (t, *J* = 7.4 Hz, 2H), 2.23 (s, 3H), 1.50 (dt, *J* = 15.2, 7.3 Hz, 2H), 1.36 (dd, *J* = 15.0, 7.4 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.1, 164.1,

163.6, 107.3, 60.1, 35.2, 28.0, 22.2, 21.1, 14.3, 13.8. HR-MS (EI) m/z calcd for $C_{11}H_{18}O_4$ [M+H$^+$] 215.1278, found 215.1281.



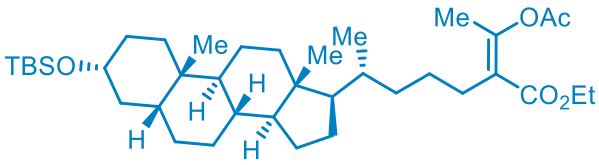
Ethyl (*Z*)-2-(1-acetoxyethylidene)-5-(4-cyanophenoxy)pentanoate (3an)

The general procedure **TP3** was followed using **ketoester** (3.3 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3an** (62%, 677 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.60 – 7.51 (m, 2H), 6.97 – 6.90 (m, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.03 (t, *J* = 6.0 Hz, 2H), 2.53 (t, *J* = 7.1 Hz, 2H), 2.15 (s, 3H), 2.01 – 1.95 (m, 2H), 1.95 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 166.0, 162.3, 153.4, 134.1, 119.8, 119.4, 115.3, 104.0, 66.8, 60.7, 28.0, 25.2, 21.0, 18.4, 14.3. HR-MS (EI) m/z calcd for $C_{18}H_{21}NO_5$ [M+H$^+$] 332.1492, found 332.1495.



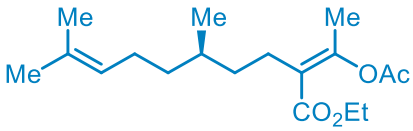
6-{(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-[(*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl} 1-ethyl (*Z*)-2-(1-acetoxyethylidene)hexanedioate (3ap)

The general procedure **TP3** was followed using **ketoester** (3.5 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3ap** (61%, 1.34 g) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 5.35 (d, *J* = 4.1 Hz, 1H), 4.65 – 4.54 (m, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.32 (ddd, *J* = 11.2, 10.4, 5.8 Hz, 6H), 2.14 (s, 3H), 2.04 – 1.91 (m, 5H), 1.87 – 1.71 (m, 5H), 1.58 – 0.90 (m, 30H), 0.84 (dd, *J* = 6.6, 1.6 Hz, 6H), 0.66 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.8, 168.7, 166.0, 153.2, 139.7, 122.7, 120.3, 74.0, 60.6, 56.8, 56.2, 50.1, 42.4, 39.8, 39.6, 38.2, 37.1, 36.7, 36.3, 35.9, 33.8, 32.0, 31.9, 28.3, 28.2, 28.1, 27.9, 24.4, 24.2, 23.9, 22.9, 22.7, 21.1, 21.0, 19.4, 18.8, 18.5, 14.3, 12.0. HR-MS (EI) m/z calcd for $C_{39}H_{62}O_6$ [M+H$^+$] 627.4619, found 627.4623.



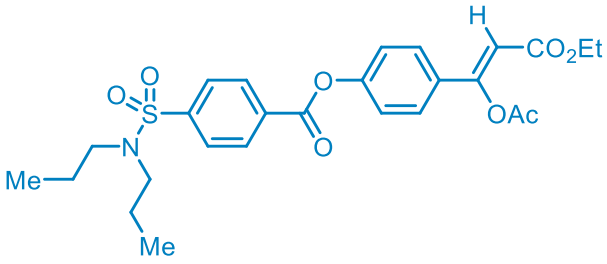
Ethyl (*R*,*Z*)-2-(1-acetoxyethylidene)-6-{(3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-[(tert-butyldimethylsilyl)oxy]-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl}heptanoate (3aq)

The general procedure **TP3** was followed using **ketoester** (2 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3aq** (42%, 529 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.17 (q, J = 7.1 Hz, 2H), 3.63 – 3.52 (m, 1H), 2.15 (s, 3H), 1.99 (s, 3H), 1.86 – 1.74 (m, 4H), 1.50 – 0.98 (m, 30H), 0.92 – 0.84 (m, 17H), 0.06 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.9, 166.5, 151.9, 121.5, 73.0, 60.5, 56.6, 56.3, 42.8, 42.5, 40.4, 40.3, 37.1, 36.0, 35.7, 35.7, 34.7, 31.2, 29.9, 29.4, 28.4, 27.5, 26.6, 26.1, 25.5, 24.4, 23.5, 21.1, 21.0, 18.7, 18.5, 18.4, 14.4, 12.2, -4.5. HR-MS (EI) m/z calcd for $C_{38}H_{66}O_5Si$ [M+H$^+$] 631.4752, found 631.4754.



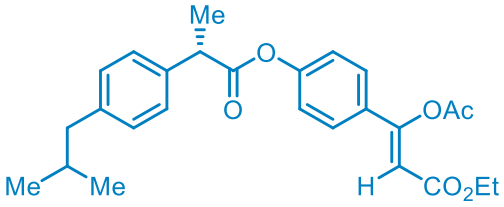
Ethyl (*R*,*Z*)-2-(1-acetoxyethylidene)-5,9-dimethyldec-8-enoate (3ar)

The general procedure **TP3** was followed using **ketoester** (4 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 20:1) yielded **3ar** (65%, 806 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.11 – 5.03 (m, 1H), 4.15 (q, J = 7.1 Hz, 2H), 2.36 – 2.19 (m, 2H), 2.14 (s, 3H), 2.02 – 1.89 (m, 5H), 1.67 (s, 3H), 1.59 (s, 3H), 1.44 (ddd, J = 12.7, 10.6, 5.3 Hz, 2H), 1.37 – 1.24 (m, 5H), 1.20 – 1.09 (m, 1H), 0.90 (d, J = 6.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.9, 166.4, 151.9, 131.3, 124.9, 121.5, 60.5, 36.9, 36.0, 32.5, 26.6, 25.8, 25.6, 21.0, 19.5, 18.2, 17.7, 14.3. HR-MS (EI) m/z calcd for $C_{18}H_{30}O_4$ [M+H$^+$] 311.2217, found 311.2218.



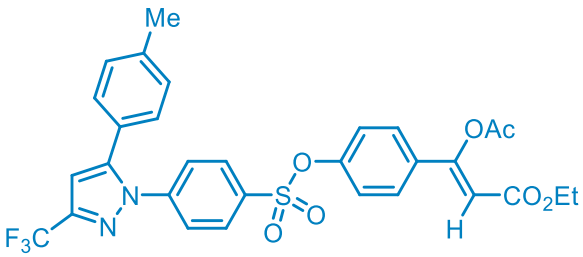
(*Z*)-4-(1-Acetoxy-3-ethoxy-3-oxoprop-1-en-1-yl)phenyl 4-(N,N dipropylsulfamoyl) benzoate (3as)

The general procedure **TP3** was followed using **ketoester** (2.44 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 5:1) yielded **3as** (60%, 757 mg) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.33 – 8.30 (m, 2H), 7.97 – 7.93 (m, 2H), 7.70 – 7.65 (m, 2H), 7.31 – 7.27 (m, 2H), 6.27 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.16 – 3.11 (m, 4H), 2.41 (s, 3H), 1.62 – 1.56 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.1, 164.1, 163.5, 157.1, 152.7, 145.3, 132.5, 131.6, 131.0, 127.5, 127.3, 122.1, 106.6, 60.5, 50.0, 22.0, 21.1, 14.3, 11.3. HR-MS (EI) m/z calcd for $C_{26}H_{31}NO_8S$ [M+H$^+$] 518.1843, found 518.1849.



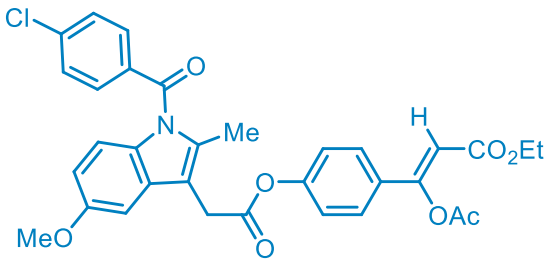
Ethyl (*S,Z*)-3-acetoxy-3-{4-{[2-(4-isobutylphenyl)propanoyl]oxy}phenyl}acrylate (3at)

The general procedure **TP3** was followed using **ketoester** (3.3 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 15:1) yielded **3at** (72%, 1.04 g) as an orange oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.57 – 7.53 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.07 – 7.03 (m, 2H), 6.20 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.94 (q, *J* = 7.1 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.37 (s, 3H), 1.87 (m, 1H), 1.60 (d, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.9, 168.1, 164.2, 157.4, 153.1, 141.1, 137.1, 131.1, 129.7, 127.3, 127.3, 122.0, 106.3, 60.5, 45.4, 45.2, 30.3, 22.5, 21.1, 18.6, 14.4. HR-MS (EI) m/z calcd for $C_{26}H_{30}O_6$ [M+H$^+$] 439.2115, found 439.2121.



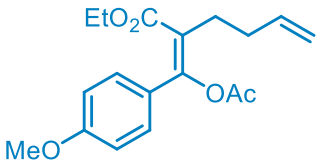
Ethyl (*Z*)-3-acetoxy-3-{4-{{{4-[5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]phenyl}sulfonyl}oxy}phenyl}acrylate (3au)

The general procedure **TP3** was followed using **ketoester** (1.4 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3au** (82%, 708 mg) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.82 – 7.78 (m, 2H), 7.54 – 7.48 (m, 4H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.06 – 7.00 (m, 2H), 6.75 (s, 1H), 6.20 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 2.37 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.1, 164.0, 156.5, 151.1, 145.6, 144.6 (q, $^{2}J_{C\text{-}F}$ = 38.5 Hz), 144.0, 140.2, 134.3, 132.9, 131.0, 129.6, 128.9, 127.7, 125.7, 125.5, 122.9, 121.1 (q, $^{1}J_{C\text{-}F}$ = 269.3 Hz), 107.3, 106.8, 60.6, 21.5, 21.0, 14.3. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.52 (s). HR-MS (EI) m/z calcd for $C_{30}H_{25}F_3N_2O_7S$ [M+H$^+$] 615.1407, found 615.1423.



Ethyl (*Z*)-3-acetoxy-3-{4-{2-[1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl]acetoxy}phenyl}acrylate (3av)

The general procedure **TP3** was followed using **ketoester** (2.5 mmol) for 18 h. Purification by column chromatography (petroleum ether/ EtOAc 10:1) yielded **3av** (22%, 320 mg) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.69 – 7.66 (m, 2H), 7.60 – 7.56 (m, 2H), 7.50 – 7.46 (m, 2H), 7.14 – 7.10 (m, 2H), 7.04 (d, *J* = 2.5 Hz, 1H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.70 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.21 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 2H), 3.83 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.0, 168.4, 168.1, 164.2, 157.2, 156.3, 152.8, 139.6, 136.5, 133.9, 131.3, 131.0, 130.5, 129.3, 127.4, 122.0, 115.2, 111.9, 111.8, 106.5, 101.3, 60.5, 55.9, 30.7, 21.1, 14.4, 13.6. HR-MS (EI) m/z calcd for $C_{32}H_{28}ClNO_8$ [M+H$^+$] 590.1576, found 590.1584.

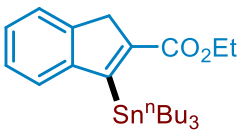


Ethyl (*E*)-2-[acetoxy(4-methoxyphenyl)methylene]hex-5-enoate [(*E*)-82]

The corresponding **ketoester** (3.2 mmol, 1.0 eq) was dissolved in acetic anhydride (6.4 mL), and 4-dimethylaminopyridine (1.6 mmol, 0.5 eq) and Et_3N (24.3 mmol, 7.6 eq) were added. The reaction mixture was stirred for 3 h at 23 °C. The solvent was evaporated and the residue was taken up in toluene and washed with a saturated solution of $NaHCO_3$, water and brine. The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ EtOAc 15:1) yielded (*E*)-**82** (49%, 499 mg) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.26 (m, 2H), 6.86 – 6.80 (m, 2H), 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.05 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.01 – 4.96 (m, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.45 (dd, *J* = 8.9, 6.6 Hz, 2H), 2.27 – 2.19 (m, 2H), 2.16 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.4, 168.3, 160.3, 152.4, 137.7, 129.7, 128.1, 123.4, 115.3, 113.5, 60.8, 55.3, 32.4, 28.4, 21.0, 13.9. HR-MS (EI) m/z calcd for $C_{18}H_{22}O_5$ [M+H$^+$] 319.1540, found 319.1544.

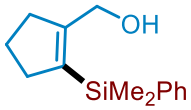
Ethyl 2-[dimethyl(phenyl)silyl]cyclopent-1-ene-1-carboxylate (4)

The general procedure **TP4** was followed using **3a** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 2 h. Purification by column chromatography (PE) yielded **4** (55 mg, 81%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 – 7.48 (m, 2H), 7.32 (dd, *J* = 4.2, 2.3 Hz, 3H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.71 (tt, *J* = 8.0, 2.5 Hz, 2H), 2.55 (tt, *J* = 7.6, 2.5 Hz, 2H), 1.89 – 1.81 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.44 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.1, 156.0, 145.5, 138.9, 133.7, 128.7, 127.6, 60.0, 41.0, 35.8, 23.5, 14.1, -2.0. HR-MS (EI) m/z calcd for $C_{16}H_{22}O_2Si$ [M+H$^+$] 275.1462, found 275.1466.



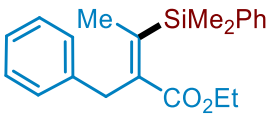
Ethyl 3-(tributylstannyl)-1*H*-indene-2-carboxylate (7)

The general procedure **TP6** was followed using **3b** (0.25 mmol) and **2a** (0.325 mmol) at -20 ℃ for 15 min. Purification by column chromatography (PE) yielded **7** (79 mg, 66%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.64 (dd, J = 5.8, 2.7 Hz, 1H), 7.51 (dd, J = 5.3, 2.7 Hz, 1H), 7.36 – 7.27 (m, 2H), 4.30 (q, J = 7.1 Hz, 2H), 3.81 – 3.65 (m, 2H), 1.52 (ddd, J = 11.0, 8.1, 3.7 Hz, 6H), 1.39 – 1.29 (m, 9H), 1.24 – 1.10 (m, 6H), 0.87 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.6, 161.8, 149.9, 145.8, 144.9, 127.0, 126.7, 125.2, 124.0, 60.6, 40.9, 29.3, 27.6, 14.6, 13.8, 11.5. HR-MS (EI) m/z calcd for $C_{24}H_{38}O_2Sn$ [M+H$^+$] 479.1967, found 479.1970.



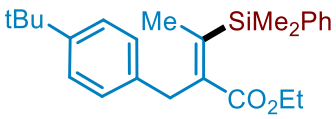
{2-[Dimethyl(phenyl)silyl]cyclopent-1-en-1-yl}methanol (8)

The general procedure **TP9** was followed using **4** (0.219 mmol) and **DIBAH** (0.66 mmol) at 0 °C for 2 h. Purification by column chromatography (petroleum ether/EtOAc 5:1) yielded **8** (38 mg, 74%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.47 (m, 2H), 7.39 – 7.32 (m, 3H), 4.09 (s, 2H), 2.56 – 2.47 (m, 4H), 1.88 – 1.78 (m, 2H), 1.18 (s, 1H), 0.39 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 154.6, 139.5, 136.9, 133.7, 129.2, 128.1, 61.8, 39.0, 36.7, 23.8, -1.4. HR-MS (EI) m/z calcd for $C_{14}H_{20}OSi$ [M+H$^+$] 233.1356, found 233.1358.



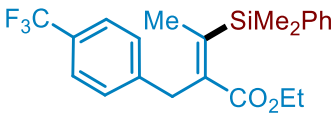
Ethyl (*Z*)-2-benzyl-3-[dimethyl(phenyl)silyl]but-2-enoate (9)

The general procedure **TP5** was followed using **3c** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1.5 h. Purification by column chromatography (PE) yielded **9** (48 mg, 57%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.47 (m, 2H), 7.31 (dd, J = 6.1, 2.6 Hz, 3H), 7.28 – 7.23 (m, 2H), 7.17 (t, J = 6.5 Hz, 3H), 3.82 (s, 2H), 3.77 (q, J = 7.1 Hz, 2H), 1.90 (s, 3H), 0.98 (t, J = 7.1 Hz, 3H), 0.43 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.2, 147.5, 142.3, 139.7, 139.4, 133.7, 128.6, 128.5, 128.4, 127.7, 126.1, 60.5, 35.9, 20.4, 14.0, -1.0. HR-MS (EI) m/z calcd for $C_{21}H_{26}O_2Si$ [M+H$^+$] 339.1775, found 339.1778.



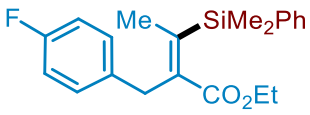
Ethyl (*Z*)-2-[4-(tert-butyl)benzyl]-3-[dimethyl(phenyl)silyl]but-2-enoate (10)

The general procedure **TP5** was followed using **3d** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (PE) yielded **10** (54 mg, 55%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.49 (m, 2H), 7.34 – 7.30 (m, 3H), 7.28 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 3.82 – 3.72 (m, 4H), 1.89 (s, 3H), 1.30 (s, 9H), 0.98 (t, J = 7.1 Hz, 3H), 0.43 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.3, 148.8, 147.1, 142.5, 139.7, 136.1, 133.7, 128.6, 128.0, 127.7, 125.4, 60.5, 35.4, 34.5, 31.5, 20.3, 14.0, -1.0. HR-MS (EI) m/z calcd for $C_{25}H_{34}O_2Si$ [M+H$^+$] 395.2401, found 395.2403.



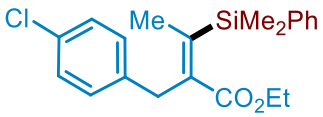
Ethyl (*Z*)-3-[dimethyl(phenyl)silyl]-2-[4-(trifluoromethyl)benzyl]but-2-enoate (11)

The general procedure **TP5** was followed using **3e** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (PE) yielded **11** (68 mg, 67%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.54 – 7.47 (m, 4H), 7.35 – 7.30 (m, 3H), 7.27 (d, J = 8.0 Hz, 2H), 3.86 (s, 2H), 3.77 (q, J = 7.1 Hz, 2H), 1.89 (s, 3H), 0.98 (t, J = 7.1 Hz, 3H), 0.44 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.9, 149.0 143.6 (d, $^{4}J_{C\text{-}F}$ = 1.0 Hz), 141.2, 139.4, 133.7, 128.8, 128.6, 128.2 (q, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 127.7, 125.5 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 124.5 (q, $^{1}J_{C\text{-}F}$ = 270.0 Hz), 60.7, 35.7, 20.6, 13.9, -1.0. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.33 (s). HR-MS (EI) m/z calcd for $C_{22}H_{25}F_3O_2Si$ [M+H$^+$] 407.1649, found 407.1652.



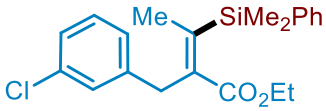
Ethyl (*Z*)-3-[dimethyl(phenyl)silyl]-2-(4-fluorobenzyl)but-2-enoate (12)

The general procedure **TP5** was followed using **3f** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 2 h. Purification by column chromatography (PE) yielded **12** (48 mg, 54%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.47 (m, 2H), 7.33 – 7.30 (m, 3H), 7.11 (dd, J = 8.6, 5.5 Hz, 2H), 6.98 – 6.92 (m, 2H), 3.76 (q, J = 7.1 Hz, 4H), 1.89 (s, 3H), 0.98 (t, J = 7.1 Hz, 3H), 0.42 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.1, 161.5 (d, $^{1}J_{C\text{-}F}$ = 243.6 Hz), 147.5, 142.2, 139.5, 134.9 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 133.7, 129.8 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 128.7, 127.7, 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 60.6, 35.1, 20.3, 14.0, -1.0. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -117.49 (s). HR-MS (EI) m/z calcd for $C_{21}H_{25}FO_2Si$ [M+H$^+$] 357.1681, found 357.1684.



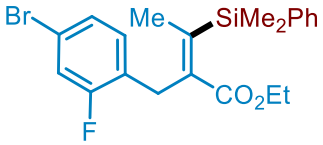
Ethyl (*Z*)-2-(4-chlorobenzyl)-3-[dimethyl(phenyl)silyl]but-2-enoate (13)

The general procedure **TP5** was followed using **3g** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (PE) yielded **13** (57 mg, 61%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.48 (dt, J = 7.9, 3.2 Hz, 2H), 7.34 – 7.30 (m, 3H), 7.23 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 3.77 (q, J = 7.3 Hz, 4H), 1.88 (s, 3H), 0.99 (t, J = 7.1 Hz, 3H), 0.42 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.0, 148.1, 141.8, 139.5, 137.9, 133.7, 131.8, 129.7, 128.7, 128.6, 127.7, 60.6, 35.3, 20.4, 14.0, -1.0. HR-MS (EI) m/z calcd for $C_{21}H_{25}ClO_2Si$ [M+H$^+$] 373.1385, found 373.1388.



Ethyl (*Z*)-2-(3-chlorobenzyl)-3-[dimethyl(phenyl)silyl]but-2-enoate (14)

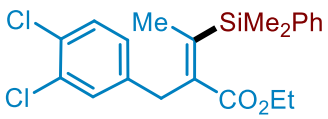
The general procedure **TP5** was followed using **3h** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (PE) yielded **14** (51 mg, 55%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (dd, J = 6.4, 3.0 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.21 – 7.13 (m, 3H), 7.04 (d, J = 7.1 Hz, 1H), 3.78 (q, J = 7.4 Hz, 4H), 1.89 (s, 3H), 0.99 (t, J = 7.1 Hz, 3H), 0.43 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.9, 148.7, 141.5, 141.4, 139.5, 134.3, 133.6, 129.7, 128.7, 128.6, 127.7, 126.5, 126.3, 60.6, 35.5, 20.5, 14.0, -1.0. HR-MS (EI) m/z calcd for $C_{21}H_{25}ClO_2Si$ [M+H$^+$] 373.1385, found 373.1388.



Ethyl (*Z*)-2-(4-bromo-2-fluorobenzyl)-3-[dimethyl(phenyl)silyl]but-2-enoate (15)

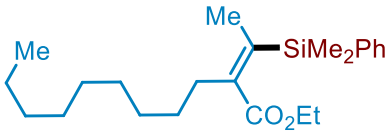
The general procedure **TP5** was followed using **3i** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 2 h. Purification by column chromatography (PE) yielded **15** (55 mg, 51%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 (dd, J = 6.5, 3.0 Hz, 2H), 7.32 (dd, J = 6.1, 2.6 Hz, 3H), 7.11 (t, J = 7.6 Hz, 1H), 7.02 (ddd, J = 15.8, 11.5, 4.7 Hz, 2H), 3.82 (s, 2H), 3.77 (q, J = 7.1 Hz, 2H), 1.88 (s, 3H), 0.98 (t, J = 7.1 Hz, 3H), 0.43 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.0, 161.1 (d, $^{1}J_{C\text{-}F}$ = 245.2 Hz), 148.3, 140.8, 139.6, 133.7, 129.8 (d, $^{4}J_{C\text{-}F}$ = 4.5 Hz), 128.7, 127.8 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 127.7, 126.2 (d, $^{2}J_{C\text{-}F}$ = 15.8 Hz), 124.1 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 115.2 (d, $^{2}J_{C\text{-}F}$ =

22.2 Hz), 60.6, 28.8 (d, $^{3}J_{C\text{-}F}$ = 3.5 Hz), 20.2, 13.9, -1.0. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -117.33 (s). HR-MS (EI) m/z calcd for $C_{21}H_{24}BrFO_2Si$ [M+H$^+$] 435.0786, found 435.0789.



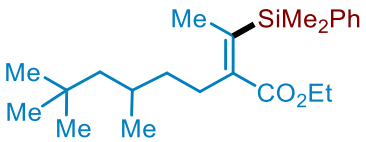
Ethyl (*Z*)-2-(3,4-dichlorobenzyl)-3-[dimethyl(phenyl)silyl]but-2-enoate (16)

The general procedure **TP5** was followed using **3j** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (PE) yielded **16** (60 mg, 60%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.46 (m, 2H), 7.35 – 7.31 (m, 4H), 7.26 (d, J = 2.0 Hz, 1H), 7.00 (dd, J = 8.2, 2.1 Hz, 1H), 3.78 (dd, J = 14.7, 7.5 Hz, 4H), 1.89 (s, 3H), 1.00 (t, J = 7.1 Hz, 3H), 0.43 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 149.3, 141.0, 139.8, 139.4, 133.6, 132.4, 130.4, 130.1, 129.7, 128.8, 127.8, 127.8, 60.7, 35.0, 20.6, 14.0, -1.0. HR-MS (EI) m/z calcd for $C_{21}H_{24}Cl_2O_2Si$ [M+H$^+$] 407.0995, found 407.0998.



Ethyl (*Z*)-2-{1-[dimethyl(phenyl)silyl]ethylidene}undecanoate (17)

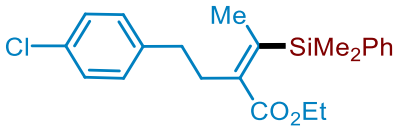
The general procedure **TP5** was followed using **3k** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (PE) yielded **17** (60 mg, 64%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.45 (m, 2H), 7.32 – 7.28 (m, 3H), 3.82 (q, J = 7.1 Hz, 2H), 2.46 – 2.34 (m, 2H), 1.83 (s, 3H), 1.43 – 1.36 (m, 2H), 1.31 – 1.24 (m, 12H), 1.09 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.0, 144.8, 143.4, 139.7, 133.7, 128.6, 127.6, 60.4, 32.1, 30.5, 29.7, 29.7, 29.6, 29.5, 28.7, 22.8, 19.3, 14.3, 14.1, -1.1. HR-MS (EI) m/z calcd for $C_{23}H_{38}O_2Si$ [M+H$^+$] 375.2714, found 375.2716.



Ethyl (*Z*)-2-{1-[dimethyl(phenyl)silyl]ethylidene}-5,7,7-trimethyloctanoate (18)

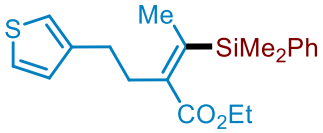
The general procedure **TP5** was followed using **3l** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (PE) yielded **18** (61 mg, 65%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.45 (m, 2H), 7.30 (dd, J = 3.7, 2.6 Hz, 3H), 3.82 (q,

J = 7.1 Hz, 2H), 2.46 – 2.31 (m, 2H), 1.84 (s, 3H), 1.48 (td, J = 11.7, 6.1 Hz, 1H), 1.43 – 1.33 (m, 1H), 1.27 – 1.21 (m, 2H), 1.09 (t, J = 7.1 Hz, 3H), 1.07 – 1.01 (m, 1H), 0.94 (d, J = 6.6 Hz, 3H), 0.89 (s, 9H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.0, 144.8, 143.7, 139.8, 133.7, 128.6, 127.6, 60.4, 51.2, 38.2, 31.2, 30.1, 29.6, 28.4, 22.7, 19.3, 14.1, -1.0. HR-MS (EI) m/z calcd for $C_{23}H_{38}O_2Si$ [M+H$^+$] 375.2714, found 375.2717.



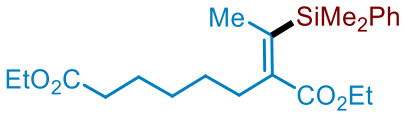
Ethyl (*Z*)-2-(4-chlorophenethyl)-3-[dimethyl(phenyl)silyl]but-2-enoate (19)

The general procedure **TP5** was followed using **corresponding alkenyl acetate** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 2 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **19** (51 mg, 52%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.52 – 7.48 (m, 2H), 7.38 – 7.34 (m, 3H), 7.13 (d, J = 8.4 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 2.51 – 2.44 (m, 2H), 2.41 – 2.35 (m, 2H), 1.92 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H), 0.39 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.8, 143.7, 139.8, 138.8, 138.5, 133.9, 131.7, 129.8, 129.4, 128.4, 128.2, 60.5, 36.3, 34.1, 20.9, 14.6, -1.1. HR-MS (EI) m/z calcd for $C_{22}H_{27}ClO_2Si$ [M+H$^+$] 387.1542, found 387.1544.



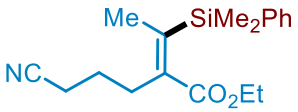
Ethyl (*Z*)-3-[dimethyl(phenyl)silyl]-2-[2-(thiophen-3-yl)ethyl]but-2-enoate (20)

The general procedure **TP5** was followed using **3m** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **20** (45 mg, 50%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (dt, J = 5.0, 2.7 Hz, 2H), 7.33 – 7.29 (m, 3H), 7.22 (dd, J = 4.9, 3.0 Hz, 1H), 6.94 (t, J = 3.5 Hz, 2H), 3.82 (q, J = 7.1 Hz, 2H), 2.79 – 2.69 (m, 4H), 1.71 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.6, 145.7, 143.0, 141.9, 139.6, 133.7, 128.6, 128.6, 127.6, 125.3, 120.7, 60.5, 31.4, 29.2, 19.4, 14.1, -1.1. HR-MS (EI) m/z calcd for $C_{20}H_{26}SO_2Si$ [M+H$^+$] 359.1496, found 359.1499.



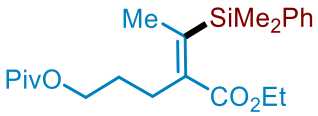
Diethyl (*Z*)-2-{1-[dimethyl(phenyl)silyl]ethylidene}octanedioate (21)

The general procedure **TP4** was followed using **3n** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **21** (53 mg, 54%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.47 (dd, J = 6.6, 2.9 Hz, 2H), 7.33 – 7.28 (m, 3H), 4.12 (q, J = 7.1 Hz, 2H), 3.82 (q, J = 7.1 Hz, 2H), 2.45 – 2.36 (m, 2H), 2.29 (t, J = 7.5 Hz, 2H), 1.83 (s, 3H), 1.69 – 1.62 (m, 2H), 1.47 – 1.33 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.9, 169.9, 144.3, 144.0, 139.6, 133.7, 128.6, 127.6, 60.4, 60.3, 34.4, 30.2, 29.2, 28.4, 24.9, 19.4, 14.4, 14.1, -1.1. HR-MS (EI) m/z calcd for $C_{22}H_{34}O_4Si$ [M+H$^+$] 391.2299, found 391.2302.



Ethyl (*Z*)-5-cyano-2-{1-[dimethyl(phenyl)silyl]ethylidene}pentanoate (22)

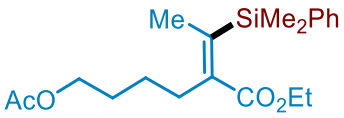
The general procedure **TP4** was followed using (*Z*)-**89** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **22** (55 mg, 70%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J = 6.4, 3.0 Hz, 2H), 7.31 (dd, J = 6.3, 2.7 Hz, 3H), 3.84 (q, J = 7.1 Hz, 2H), 2.62 – 2.52 (m, 2H), 2.36 (t, J = 7.1 Hz, 2H), 1.89 (s, 3H), 1.80 (m, 2H), 1.10 (t, J = 7.1 Hz, 3H), 0.40 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.2, 147.5, 141.6, 139.3, 133.6, 128.8, 127.7, 119.7, 60.7, 29.0, 24.6, 19.8, 17.0, 14.1, -1.1. HR-MS (EI) m/z calcd for $C_{18}H_{25}NO_2Si$ [M+H$^+$] 316.1727, found 316.1730.



Ethyl (*Z*)-2-{1-[dimethyl(phenyl)silyl]ethylidene}-5-(pivaloyloxy)pentanoate (23)

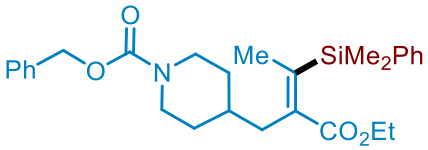
The general procedure **TP5** was followed using **3o** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 2 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **23** (55 mg, 56%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.44 (m, 2H), 7.33 – 7.29 (m, 3H), 4.07 (t, J = 6.3 Hz, 2H), 3.84 (q, J = 7.1 Hz, 2H), 2.53 – 2.44 (m, 2H), 1.85 (s, 3H), 1.75 (dq, J = 12.9, 6.3 Hz, 2H), 1.20 (s, 9H), 1.09 (t, J = 7.1 Hz, 3H), 0.39 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 178.7, 169.5, 145.8, 143.1, 139.6, 133.7, 128.6, 127.7, 64.0, 60.5, 38.9, 28.0,

27.4, 26.8, 19.5, 14.1, -1.1. HR-MS (EI) m/z calcd for $C_{22}H_{34}O_4Si$ [M+H$^+$] 391.2299, found 391.2301.



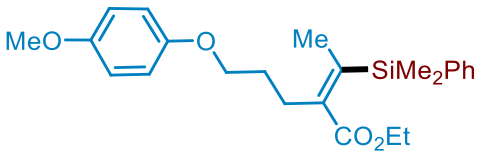
Ethyl (*Z*)-6-acetoxy-2-{1-[dimethyl(phenyl)silyl]ethylidene}hexanoate (24)

The general procedure **TP4** was followed using **corresponding alkenyl acetate** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **24** (52 mg, 58%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.44 (m, 2H), 7.33 – 7.28 (m, 3H), 4.07 (t, J = 6.6 Hz, 2H), 3.82 (q, J = 7.1 Hz, 2H), 2.49 – 2.39 (m, 2H), 2.04 (s, 3H), 1.84 (s, 3H), 1.71 – 1.62 (m, 2H), 1.48 (tt, J = 10.1, 6.4 Hz, 2H), 1.09 (t, J = 7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.3, 169.8, 144.6, 143.9, 139.6, 133.7, 128.6, 127.7, 64.4, 60.5, 29.9, 28.6, 25.1, 21.1, 19.5, 14.1, -1.1. HR-MS (EI) m/z calcd for $C_{20}H_{30}O_4Si$ [M+H$^+$] 363.1986, found 363.1989.



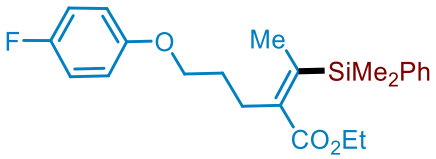
Benzyl (*Z*)-4-{3-[dimethyl(phenyl)silyl]-2-(ethoxycarbonyl)but-2-en-1-yl}piperidine-1-carboxylate (25)

The general procedure **TP5** was followed using **3p** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 5 h. Purification by column chromatography (petroleum ether/EtOAc 15:1) yielded **25** (60 mg, 50%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J = 6.4, 3.0 Hz, 2H), 7.35 (d, J = 4.2 Hz, 4H), 7.34 – 7.27 (m, 4H), 5.12 (s, 2H), 4.16 (s, 2H), 3.80 (q, J = 7.1 Hz, 2H), 2.72 (s, 2H), 2.39 (d, J = 7.1 Hz, 2H), 1.82 (s, 3H), 1.72 – 1.53 (m, 4H), 1.15 (d, J = 9.5 Hz, 1H), 1.08 (t, J = 7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.9, 155.4, 145.6, 142.3, 139.5, 137.1, 133.7, 128.7, 128.6, 128.1, 128.0, 127.7, 67.1, 60.5, 44.4, 36.8, 36.1, 32.1, 20.0, 14.1, -1.0. HR-MS (EI) m/z calcd for $C_{28}H_{37}NO_4Si$ [M+H$^+$] 480.2565, found 480.2567.



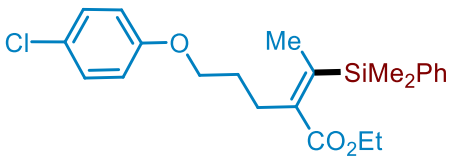
Ethyl (*Z*)-2-{1-[dimethyl(phenyl)silyl]ethylidene}-5-(4-methoxyphenoxy)pentanoate (26)

The general procedure **TP4** was followed using **3q** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 0.5 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **26** (59 mg, 57%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.42 (m, 2H), 7.35 – 7.27 (m, 3H), 6.81 (s, 4H), 3.91 (t, J = 6.3 Hz, 2H), 3.81 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 2.67 – 2.53 (m, 2H), 1.89 (dd, J = 8.6, 6.4 Hz, 2H), 1.85 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.7, 153.8, 153.2, 145.5, 143.3, 139.6, 133.7, 128.6, 127.7, 115.5, 114.8, 67.8, 60.5, 55.9, 28.4, 26.8, 19.5, 14.1, -1.0. HR-MS (EI) m/z calcd for $C_{24}H_{32}O_4Si$ [M+H$^+$] 413.2143, found 413.2145.



Ethyl (*Z*)-2-{1-[dimethyl(phenyl)silyl]ethylidene}-5-(4-fluorophenoxy)pentanoate (27)

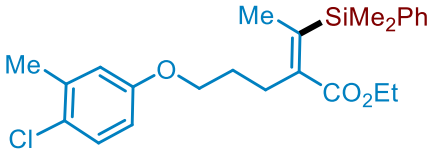
The general procedure **TP4** was followed using **3r** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **27** (55 mg, 55%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.48 – 7.43 (m, 2H), 7.32 – 7.27 (m, 3H), 6.98 – 6.91 (m, 2H), 6.84 – 6.77 (m, 2H), 3.91 (t, J = 6.2 Hz, 2H), 3.81 (q, J = 7.1 Hz, 2H), 2.67 – 2.56 (m, 2H), 1.91 (dt, J = 7.3, 6.4 Hz, 2H), 1.85 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.7, 157.3 (d, $^{1}J_{C\text{-}F}$ = 237.8 Hz), 155.2 (d, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 145.6, 143.2, 139.6, 133.7, 128.6, 127.7, 115.9 (d, $^{2}J_{C\text{-}F}$ = 23.2 Hz), 115.5 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 67.8, 60.5, 28.3, 26.7, 19.5, 14.1, -1.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -124.32 (s).. HR-MS (EI) m/z calcd for $C_{23}H_{29}FO_3Si$ [M+H$^+$] 401.1943 found 401.1945.



Ethyl (*Z*)-5-(4-chlorophenoxy)-2-{1-[dimethyl(phenyl)silyl]ethylidene}pentanoate (28)

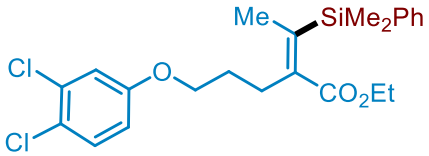
The general procedure **TP4** was followed using **3s** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **28** (90 mg, 86%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J = 6.5, 3.0 Hz, 2H), 7.30 (dd, J = 4.8, 1.8 Hz, 3H), 7.23 – 7.18 (m, 2H), 6.83 – 6.74 (m, 2H), 3.92 (t, J = 6.2 Hz, 2H), 3.80 (q, J = 7.1 Hz, 2H), 2.61 (t, J = 7.5 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.85 (s, 3H), 1.07 (t, J =

7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.6, 157.7, 145.7, 143.1, 139.5, 133.7, 129.4, 128.6, 127.7, 125.6, 115.9, 67.5, 60.5, 28.2, 26.7, 19.5, 14.1, -1.1. HR-MS (EI) m/z calcd for $C_{23}H_{29}ClO_3Si$ [M+H$^+$] 417.1647, found 417.1649.



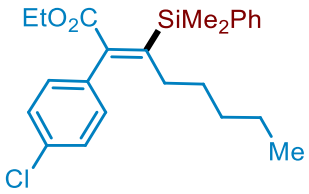
Ethyl (*Z*)-5-(4-chloro-3-methylphenoxy)-2-{1-[dimethyl(phenyl)silyl]ethylidene}pentanoate (29)

The general procedure **TP4** was followed using **3t** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **29** (77 mg, 71%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J = 6.4, 3.0 Hz, 2H), 7.31 – 7.29 (m, 3H), 7.19 (d, J = 8.7 Hz, 1H), 6.74 (d, J = 2.8 Hz, 1H), 6.64 (dd, J = 8.7, 2.9 Hz, 1H), 3.91 (t, J = 6.2 Hz, 2H), 3.81 (q, J = 7.1 Hz, 2H), 2.60 (t, J = 7.5 Hz, 2H), 2.32 (s, 3H), 1.93 – 1.86 (m, 2H), 1.85 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.7, 157.6, 145.7, 143.1, 139.6, 137.1, 133.7, 129.7, 128.6, 127.7, 125.8, 117.2, 113.1, 67.4, 60.5, 28.2, 26.7, 20.5, 19.6, 14.1, -1.0. HR-MS (EI) m/z calcd for $C_{24}H_{31}ClO_3Si$ [M+H$^+$] 431.1804, found 431.1808.



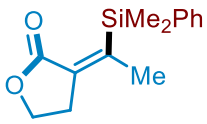
Ethyl (*Z*)-5-(3,4-dichlorophenoxy)-2-{1-[dimethyl(phenyl)silyl]ethylidene}pentanoate (30)

The general procedure **TP4** was followed using **3u** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **30** (59 mg, 52%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J = 6.4, 3.0 Hz, 2H), 7.30 (dd, J = 7.3, 3.7 Hz, 4H), 6.96 (d, J = 2.8 Hz, 1H), 6.72 (dd, J = 8.9, 2.8 Hz, 1H), 3.92 (t, J = 6.2 Hz, 2H), 3.81 (q, J = 7.1 Hz, 2H), 2.60 (t, J = 7.5 Hz, 2H), 1.95 – 1.86 (m, 2H), 1.85 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H), 0.39 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.6, 158.1, 145.9, 142.9, 139.5, 133.6, 132.9, 130.8, 128.7, 127.7, 123.9, 116.4, 114.7, 67.8, 60.6, 28.1, 26.6, 19.6, 14.1, -1.1. HR-MS (EI) m/z calcd for $C_{23}H_{28}Cl_2O_3Si$ [M+H$^+$] 451.1258, found 451.1260.



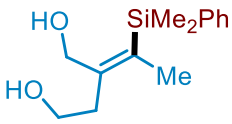
Ethyl (*Z*)-2-(4-chlorophenyl)-3-[dimethyl(phenyl)silyl]oct-2-enoate (31)

The general procedure **TP4** was followed using **3v** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **31** (64 mg, 62%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.59 – 7.52 (m, 2H), 7.36 – 7.29 (m, 5H), 7.15 – 7.08 (m, 2H), 3.75 (q, J = 7.1 Hz, 2H), 2.05 (dd, J = 9.4, 6.8 Hz, 2H), 1.22 – 1.15 (m, 2H), 1.08 – 1.01 (m, 2H), 1.01 – 0.92 (m, 5H), 0.73 (t, J = 7.2 Hz, 3H), 0.50 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.3, 153.9, 143.7, 139.5, 137.0, 133.9, 133.1, 130.6, 128.7, 128.4, 127.6, 60.9, 34.2, 31.9, 29.4, 22.2, 14.0, 13.9, -0.5. HR-MS (EI) m/z calcd for $C_{24}H_{31}ClO_2Si$ [M+H$^+$] 415.1855 found 415.1858.



(*Z*)-3-{1-[Dimethyl(phenyl)silyl]ethylidene}dihydrofuran-2(3*H*)-one (32)

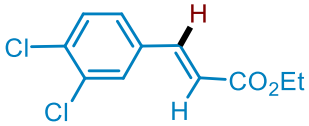
The general procedure **TP5** was followed using **3w** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **32** (50 mg, 81%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.58 – 7.51 (m, 2H), 7.36 – 7.30 (m, 3H), 4.37 (t, J = 7.5 Hz, 2H), 2.98 – 2.81 (m, 2H), 1.86 (t, J = 1.9 Hz, 3H), 0.52 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.2, 153.7, 139.0, 134.6, 134.1, 128.9, 127.7, 65.4, 28.4, 23.5, -2.0. HR-MS (EI) m/z calcd for $C_{14}H_{18}O_2Si$ [M+H$^+$] 247.1149 found 247.1151.



(*Z*)-2-[1-[dimethyl(phenyl)silyl]ethylidene]butane-1,4-diol (33)

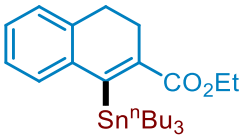
The general procedure **TP10** was followed using **32** (0.56 g, 2.2 mmol) and **LiAlH$_4$** (0.125 g, 3.3 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 2:1) yielded **33** (0.23 g, 41%) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.53 – 7.48 (m, 2H), 7.35 (dt, J = 4.1, 1.7 Hz, 3H), 4.01 – 3.93 (m, 2H), 3.71 (t, J = 5.9 Hz, 2H), 2.56 (t, J = 5.9 Hz, 4H), 1.82 (s, 3H), 0.42 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 147.9, 140.2, 135.1,

133.6, 129.2, 128.2, 66.4, 61.6, 35.5, 18.7, -0.4. HR-MS (EI) m/z calcd for $C_{14}H_{22}O_2Si$ [M+H$^+$] 251.1462 found 251.1464.



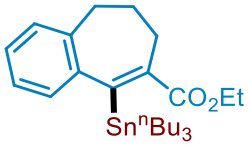
Ethyl (*E*)-3-(3,4-dichlorophenyl)acrylate (34)

The general procedure **TP4** was followed using **3aj** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 30 min. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **34** (47 mg, 77%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 2.0 Hz, 1H), 7.57 (d, J = 16.1 Hz, 1H), 7.46 (d, J = 8.3 Hz, 1H), 7.34 (dd, J = 8.4, 2.0 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H). HR-MS (EI) m/z calcd for $C_{11}H_{10}Cl_2O_2$ [M+H$^+$] 245.0131 found 245.0133.



Ethyl 1-(tributylstannyl)-3,4-dihydronaphthalene-2-carboxylate (35)

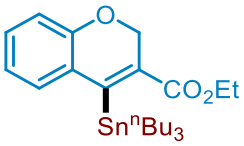
The general procedure **TP7** was followed using **3x** (0.25 mmol) and **2a** (0.325 mmol) at 0 ℃ for 15 min. Purification by column chromatography (PE) yielded **35** (86 mg, 70%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.20 (dt, J = 3.8, 2.2 Hz, 2H), 7.19 – 7.12 (m, 2H), 4.25 (q, J = 7.1 Hz, 2H), 2.78 – 2.62 (m, 2H), 2.59 – 2.41 (m, 2H), 1.51 – 1.41 (m, 6H), 1.34 – 1.24 (m, 9H), 1.06 – 0.93 (m, 6H), 0.85 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 159.2, 139.9, 139.2, 137.2, 130.4, 128.0, 127.2, 126.2, 61.1, 29.4, 29.0, 27.6, 24.1, 14.5, 13.9, 13.4. HR-MS (EI) m/z calcd for $C_{25}H_{40}O_2Sn$ [M+H$^+$] 493.2123, found 493.2125.



Ethyl 9-(tributylstannyl)-6,7-dihydro-5*H*-benzo[7]annulene-8-carboxylate (36)

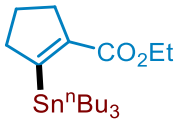
The general procedure **TP7** was followed using **3y** (0.25 mmol) and **2a** (0.325 mmol) at 0 ℃ for 50 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **36** (60 mg, 47%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.22 (td, J = 7.3, 1.9 Hz, 1H), 7.17 – 7.09 (m, 2H), 6.92 (d, J = 7.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.45 (t, J = 6.6 Hz, 2H), 2.13 – 2.05 (m, 2H), 1.34 (m, 10H), 1.22 (dq, J = 14.5, 7.1 Hz, 7H), 0.97 – 0.84 (m, 6H), 0.82

(t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.3, 164.8, 143.8, 140.6, 138.4, 128.8, 128.4, 126.6, 125.6, 61.0, 34.3, 31.5, 29.3, 27.6, 26.5, 14.5, 13.8, 12.5. HR-MS (EI) m/z calcd for $C_{26}H_{42}O_2Sn$ [M+H$^+$] 507.2280, found 507.2283.



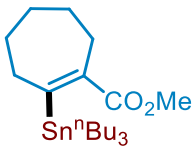
Ethyl 4-(tributylstannyl)-2*H*-chromene-3-carboxylate (37)

The general procedure **TP7** was followed using **3z** (0.25 mmol) and **2a** (0.325 mmol) at 0 ℃ for 1 h. Purification by column chromatography (PE) yielded **37** (71 mg, 58%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.28 – 7.24 (m, 1H), 7.19 (td, J = 7.8, 1.5 Hz, 1H), 7.04 – 6.88 (m, 2H), 4.81 – 4.72 (m, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.54 – 1.39 (m, 6H), 1.32 (ddd, J = 19.1, 7.1, 5.6 Hz, 9H), 1.13 – 0.97 (m, 6H), 0.86 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.4, 156.2, 154.4, 133.9, 131.1, 130.5, 128.7, 121.6, 116.4, 64.6, 61.2, 29.3, 27.5, 14.5, 13.8, 13.4. HR-MS (EI) m/z calcd for $C_{24}H_{38}O_3Sn$ [M+H$^+$] 495.1916, found 495.1918.



Ethyl 2-(tributylstannyl)cyclopent-1-ene-1-carboxylate (38)

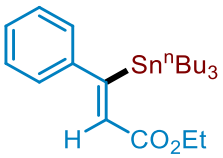
The general procedure **TP7** was followed using **3a** (0.25 mmol) and **2a** (0.325 mmol) at 0 ℃ for 20 min. Purification by column chromatography (PE) yielded **38** (92 mg, 85%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.19 (q, J = 7.1 Hz, 2H), 2.61 (t, J = 7.5 Hz, 4H), 1.98 – 1.82 (m, 2H), 1.60 – 1.42 (m, 6H), 1.42 – 1.18 (m, 9H), 1.00 – 0.93 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.7, 166.1, 143.9, 60.2, 41.8, 33.6, 29.4, 27.5, 24.6, 14.8, 13.8, 10.6. HR-MS (EI) m/z calcd for $C_{20}H_{38}O_2Sn$ [M+H$^+$] 431.1967, found 431.1969.



Methyl 2-(tributylstannyl)cyclohept-1-ene-1-carboxylate (39)

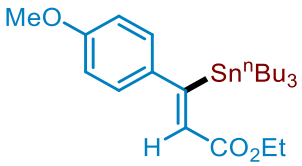
The general procedure **TP7** was followed using **corresponding alkenyl acetate** (0.25 mmol) and **2a** (0.325 mmol) at 0 ℃ for 30 min. Purification by column chromatography (PE) yielded

39 (67 mg, 60%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.71 (s, 3H), 2.70 – 2.60 (m, 2H), 2.60 – 2.40 (m, 2H), 1.80 (dt, *J* = 11.9, 6.0 Hz, 2H), 1.53 – 1.37 (m, 10H), 1.29 (dd, *J* = 14.7, 7.3 Hz, 6H), 0.98 – 0.81 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.1, 169.9, 144.3, 52.0, 35.3, 32.8, 29.4, 28.8, 27.6, 26.4, 25.0, 13.9, 11.7. HR-MS (EI) m/z calcd for $C_{21}H_{40}O_2Sn$ [M+H$^+$] 445.2123, found 445.2125.



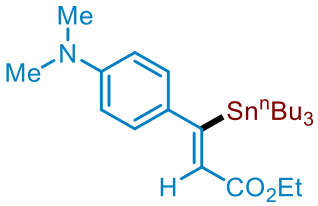
Ethyl (*Z*)-3-phenyl-3-(tributylstannyl)acrylate (40)

The general procedure **TP6** was followed using **3aa** (0.25 mmol) and **2a** (0.325 mmol) at -20 ℃ for 15 min. Purification by column chromatography (PE) yielded **40** (73 mg, 63%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38 – 7.25 (m, 2H), 7.26 – 7.18 (m, 1H), 7.09 – 7.00 (m, 2H), 6.67 – 6.30 (m, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.48 – 1.35 (m, 6H), 1.33 – 1.21 (m, 9H), 0.97 – 0.92 (m, 6H), 0.83 (t, *J* = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.8, 167.9, 145.9, 130.8, 128.2, 126.8, 126.3, 60.6, 29.2, 27.5, 14.5, 13.8, 12.1. HR-MS (EI) m/z calcd for $C_{23}H_{38}O_2Sn$ [M+H$^+$] 467.1967, found 467.1970.



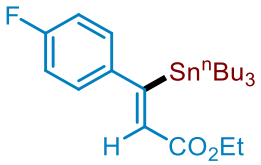
Ethyl (*Z*)-3-(4-methoxyphenyl)-3-(tributylstannyl)acrylate (41)

The general procedure **TP6** was followed using **3ab** (0.25 mmol) and **2a** (0.325 mmol) at -20 ℃ for 15 min. Purification by column chromatography (PE) yielded **41** (73 mg, 59%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.06 – 6.98 (m, 2H), 6.89 – 6.82 (m, 2H), 6.46 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.51 – 1.34 (m, 6H), 1.33 – 1.20 (m, 9H), 1.04 – 0.88 (m, 6H), 0.84 (t, *J* = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.1, 168.1, 159.1, 138.3, 129.9, 127.9, 113.7, 60.5, 55.5, 29.2, 27.5, 14.5, 13.8, 12.2. HR-MS (EI) m/z calcd for $C_{24}H_{40}O_3Sn$ [M+H$^+$] 497.2072, found 497.2075.



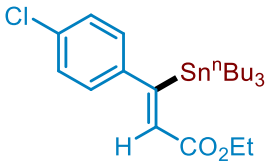
Ethyl (*Z*)-3-[4-(dimethylamino)phenyl]-3-(tributylstannyl)acrylate (42)

The general procedure **TP6** was followed using **3ac** (0.25 mmol) and **2a** (0.325 mmol) at 23 ℃ for 4.5 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **42** (89 mg, 70%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.10 – 7.00 (m, 2H), 6.68 (d, J = 8.9 Hz, 2H), 6.47 (s, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.96 (s, 6H), 1.52 – 1.38 (m, 6H), 1.36 – 1.20 (m, 9H), 1.00 – 0.94 (m, 6H), 0.84 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.3, 168.3, 150.1, 133.5, 128.2, 128.0, 112.1, 60.3, 40.6, 29.3, 27.5, 14.5, 13.9, 12.4. HR-MS (EI) m/z calcd for $C_{25}H_{43}NO_2Sn$ [M+H$^+$] 510.2389, found 510.2392.



Ethyl (*Z*)-3-(4-fluorophenyl)-3-(tributylstannyl)acrylate (43)

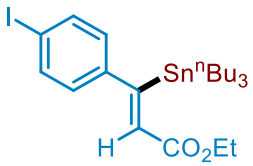
The general procedure **TP6** was followed using **3ad** (0.25 mmol) and **2a** (0.325 mmol) at -20 ℃ for 15 min. Purification by column chromatography (PE) yielded **43** (94 mg, 78%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.05 – 6.97 (m, 4H), 6.45 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.51 – 1.35 (m, 6H), 1.35 – 1.16 (m, 9H), 0.98 – 0.92 (m, 6H), 0.84 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.7, 167.8, 162.1 (d, $^1J_{C\text{-}F}$ = 245.8 Hz), 141.9 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 131.0, 128.0 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 60.7, 29.2, 27.5, 14.5, 13.8, 12.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -115.94 (d, J = 6.0 Hz). HR-MS (EI) m/z calcd for $C_{23}H_{37}FO_2Sn$ [M+H$^+$] 485.1872, found 485.1875.



Ethyl (*Z*)-3-(4-chlorophenyl)-3-(tributylstannyl)acrylate (44)

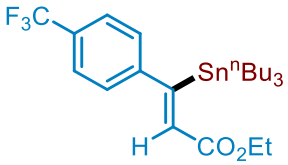
The general procedure **TP6** was followed using **3ae** (0.25 mmol) and **2a** (0.325 mmol) at -20 ℃ for 15 min. Purification by column chromatography (PE) yielded **44** (85 mg, 68%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.31 – 7.26 (m, 2H), 6.99 – 6.94 (m, 2H), 6.45 (s, 1H),

4.24 (q, J = 7.1 Hz, 2H), 1.45 – 1.34 (m, 6H), 1.33 – 1.19 (m, 9H), 0.97 – 0.92 (m, 6H), 0.84 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.5, 167.7, 144.4, 132.8, 131.2, 128.4, 127.6, 60.8, 29.2, 27.5, 14.5, 13.8, 12.1. HR-MS (EI) m/z calcd for $C_{23}H_{37}ClO_2Sn$ [M+H$^+$] 501.1577, found 501.1581.



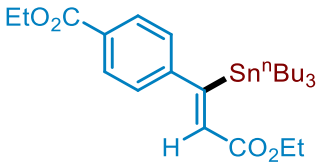
Ethyl (*Z*)-3-(4-iodophenyl)-3-(tributylstannyl)acrylate (45)

The general procedure **TP6** was followed using **3af** (0.25 mmol) and **2a** (0.275 mmol) at -20 °C for 10 min. Purification by column chromatography (PE) yielded **45** (71 mg, 49%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.76 – 7.50 (m, 2H), 6.90 – 6.67 (m, 2H), 6.56 – 6.29 (m, 1H), 4.23 (q, J = 7.1 Hz, 2H), 1.44 – 1.33 (m, 6H), 1.33 – 1.18 (m, 9H), 0.96 – 0.91 (m, 6H), 0.84 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.5, 167.7, 145.6, 137.3, 131.1, 128.2, 92.2, 60.8, 29.2, 27.5, 14.5, 13.8, 12.1. HR-MS (EI) m/z calcd for $C_{23}H_{37}IO_2Sn$ [M+H$^+$] 593.0933, found 593.0938.



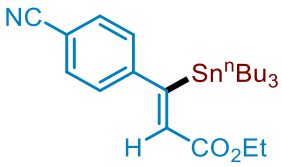
Ethyl (*Z*)-3-(tributylstannyl)-3-[4-(trifluoromethyl)phenyl]acrylate (46)

The general procedure **TP7** was followed using **3ag** (0.25 mmol) and **2a** (0.325 mmol) at -20 ℃ for 2.5 h. Purification by column chromatography (PE) yielded **46** (71 mg, 53%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 6.46 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 1.45 – 1.34 (m, 6H), 1.25 (m, 9H), 0.97 – 0.91 (m, 6H), 0.83 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.4, 167.6, 149.9, 131.7, 128.8 (q, $^2J_{C\text{-}F}$ = 32.4 Hz), 126.4, 125.2 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 124.4 (q, $^1J_{C\text{-}F}$ = 271.8 Hz), 60.9, 29.2, 27.5, 14.5, 13.8, 12.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.39 (s). HR-MS (EI) m/z calcd for $C_{24}H_{37}F_3O_2Sn$ [M+H$^+$] 535.1840, found 535.1844.



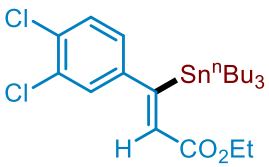
Ethyl (*Z*)-4-[3-ethoxy-3-oxo-1-(tributylstannyl)prop-1-en-1-yl]benzoate (47)

The general procedure **TP6** was followed using **3ah** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **47** (88 mg, 66%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.07 – 7.96 (m, 2H), 7.10 – 7.03 (m, 2H), 6.46 (s, 1H), 4.38 (q, J = 7.1 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 1.43 – 1.36 (m, 6H), 1.36 – 1.16 (m, 12H), 0.97 – 0.92 (m, 6H), 0.83 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.9, 167.6, 166.6, 151.0, 131.3, 129.6, 128.7, 126.1, 61.1, 60.8, 29.2, 27.4, 14.5, 14.5, 13.8, 12.1. HR-MS (EI) m/z calcd for $C_{26}H_{42}O_4Sn$ [M+H$^+$] 539.2178, found 539.2181.



Ethyl (*Z*)-3-(4-cyanophenyl)-3-(tributylstannyl)acrylate (48)

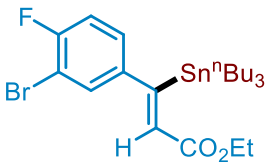
The general procedure **TP7** was followed using **3ai** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **48** (66 mg, 54%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.4 Hz, 2H), 7.15 – 7.06 (m, 2H), 6.44 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 1.40 – 1.33 (m, 6H), 1.33 – 1.18 (m, 10H), 0.95 – 0.91 (m, 5H), 0.84 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.0, 167.4, 151.2, 132.1, 131.9, 126.8, 119.1, 110.2, 61.0, 29.1, 27.4, 14.4, 13.8, 12.1. HR-MS (EI) m/z calcd for $C_{24}H_{37}NO_2Sn$ [M+H$^+$] 492.1919, found 492.1921.



Ethyl (*Z*)-3-(3,4-dichlorophenyl)-3-(tributylstannyl)acrylate (49)

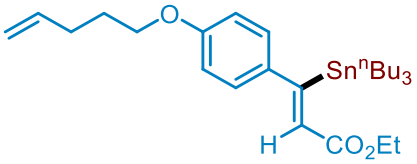
The general procedure **TP6** was followed using **3aj** (0.25 mmol) and **2a** (0.325 mmol) at -20 ℃ for 15 min. Purification by column chromatography (PE) yielded **49** (104 mg, 78%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.2 Hz, 1H), 7.13 (d, J = 2.1 Hz,

1H), 6.91 – 6.83 (m, 1H), 6.45 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.46 – 1.34 (m, 6H), 1.34 – 1.20 (m, 9H), 0.97 – 0.92 (m, 6H), 0.85 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.1, 167.5, 146.1, 132.3, 131.8, 130.7, 130.1, 128.0, 125.8, 60.9, 29.2, 27.5, 14.4, 13.8, 12.2. HR-MS (EI) m/z calcd for $C_{23}H_{36}Cl_2O_2Sn$ [M+H$^+$] 535.1187, found 535.1191.



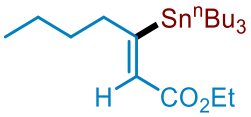
Ethyl (*Z*)-3-(3-bromo-4-fluorophenyl)-3-(tributylstannyl)acrylate (50)

The general procedure **TP6** was followed using **3ak** (0.25 mmol) and **2a** (0.325 mmol) at -20 ℃ for 15 min. Purification by column chromatography (PE) yielded **50** (93 mg, 66%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.10 – 6.98 (m, 3H), 6.45 (s, 1H), 4.24 (q, J = 7.1 Hz, 2H), 1.51 – 1.35 (m, 6H), 1.35 – 1.18 (m, 9H), 0.94 (m, 6H), 0.84 (td, J = 7.3, 4.1 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.6, 167.8, 162.1 (d, $^1J_{C\text{-}F}$ = 245.8 Hz), 141.9 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 131.8, 131.1 (d, $^3J_{C\text{-}F}$ = 6.2 Hz), 128.0 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 116.2 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 60.7, 29.2, 27.5, 14.5, 13.8, 12.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -116.04 (s). HR-MS (EI) m/z calcd for $C_{23}H_{36}BrFO_2Sn$ [M+H$^+$] 563.0977, found 563.0979.



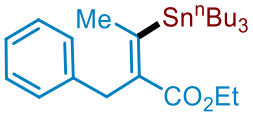
Ethyl (*Z*)-3-[4-(pent-4-en-1-yloxy)phenyl]-3-(tributylstannyl)acrylate (51)

The general procedure **TP6** was followed using **3al** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (PE) yielded **51** (98 mg, 71%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.05 – 6.98 (m, 2H), 6.88 – 6.82 (m, 2H), 6.46 (s, 1H), 5.85 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.11 – 4.95 (m, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.97 (t, J = 6.5 Hz, 2H), 2.30 – 2.19 (m, 2H), 1.97 – 1.82 (m, 2H), 1.51 – 1.36 (m, 6H), 1.26 (m, 9H), 0.98 – 0.92 (m, 6H), 0.84 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.2, 168.1, 158.6, 138.1, 137.9, 129.8, 127.9, 115.3, 114.3, 67.4, 60.5, 30.3, 29.2, 28.6, 27.5, 14.5, 13.8, 12.2. HR-MS (EI) m/z calcd for $C_{28}H_{46}O_3Sn$ [M+H$^+$] 551.2542, found 551.2547.



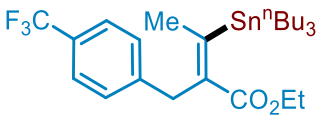
Ethyl (*Z*)-3-(tributylstannyl)hept-2-enoate (52)

The general procedure **TP6** was followed using **3am** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (PE) yielded **52** (85 mg, 76%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.36 (t, J = 1.2 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.39 (t, J = 6.7 Hz, 2H), 1.51 – 1.40 (m, 6H), 1.38 – 1.24 (m, 13H), 0.97 – 0.93 (m, 6H), 0.89 (dd, J = 13.6, 6.4 Hz, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 176.1, 168.1, 128.4, 60.3, 40.2, 31.5, 29.4, 27.6, 22.5, 14.5, 14.1, 13.9, 11.2. HR-MS (EI) m/z calcd for $C_{21}H_{42}O_2Sn$ [M+H$^+$] 447.2280, found 447.2284.



Ethyl (*Z*)-2-benzyl-3-(tributylstannyl)but-2-enoate (53)

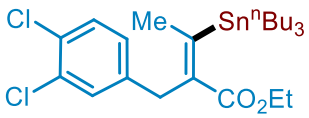
The general procedure **TP7** was followed using **3c** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **53** (85 mg, 69%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.24 (dd, J = 8.9, 5.8 Hz, 2H), 7.14 (dd, J = 13.6, 7.1 Hz, 3H), 4.11 (q, J = 7.1 Hz, 2H), 3.84 (s, 2H), 2.19 – 2.03 (m, 3H), 1.55 – 1.41 (m, 6H), 1.30 (dt, J = 14.7, 7.3 Hz, 6H), 1.16 (t, J = 7.1 Hz, 3H), 1.02 – 0.90 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.1, 165.1, 140.5, 137.9, 128.3, 128.2, 125.8, 60.9, 33.6, 29.5, 27.7, 22.9, 14.3, 14.0, 12.0. HR-MS (EI) m/z calcd for $C_{25}H_{42}O_2Sn$ [M+H$^+$] 495.2280, found 495.2283.



Ethyl (*Z*)-3-(tributylstannyl)-2-[4-(trifluoromethyl)benzyl]but-2-enoate (54)

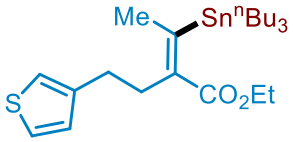
The general procedure **TP7** was followed using **3e** (0.15 mmol) and **2a** (0.195 mmol) at 0 ℃ for 1 h. Purification by column chromatography (PE) yielded **54** (62 mg, 73%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 3.88 (s, 2H), 2.17 – 2.06 (m, 3H), 1.52 – 1.42 (m, 6H), 1.33 – 1.27 (m, 6H), 1.16 (t, J = 7.1 Hz, 3H), 0.99 – 0.90 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.7, 166.4, 144.8, 137.0 128.5, 128.2 (q, $^{2}J_{C\text{-}F}$ = 32.4 Hz), 125.3 (q, $^{3}J_{C\text{-}F}$ = 3.8

Hz), 124.5 (q, $^{1}J_{C\text{-}F}$ = 272.0 Hz), 61.0, 33.6, 29.5, 27.7, 23.0, 14.3, 13.9, 12.0. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.30 (s). HR-MS (EI) m/z calcd for $C_{26}H_{41}F_3O_2Sn$ [M+H$^+$] 563.2153, found 563.2155.



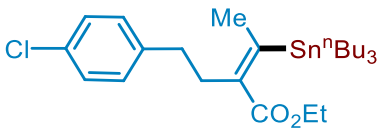
Ethyl (*Z*)-2-(3,4-dichlorobenzyl)-3-(tributylstannyl)but-2-enoate (55)

The general procedure **TP7** was followed using **3j** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (PE) yielded **55** (118 mg, 84%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.29 (d, J = 8.2 Hz, 1H), 7.21 (d, J = 1.8 Hz, 1H), 6.95 (dd, J = 8.3, 1.9 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.77 (s, 2H), 2.16 – 2.05 (m, 3H), 1.53 – 1.40 (m, 6H), 1.34 – 1.26 (m, 6H), 1.18 (t, J = 7.1 Hz, 3H), 1.01 – 0.91 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.6, 166.6, 140.9, 136.8, 132.3, 130.2, 130.2, 129.7, 127.6, 61.0, 32.8, 29.4, 27.6, 23.0, 14.3, 13.9, 12.0. HR-MS (EI) m/z calcd for $C_{25}H_{40}Cl_2O_2Sn$ [M+H$^+$] 563.1500, found 563.1503.



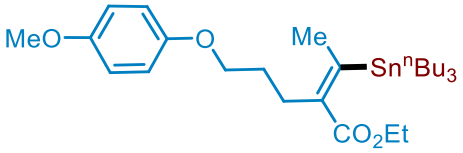
Ethyl (*Z*)-2-[2-(thiophen-3-yl)ethyl]-3-(tributylstannyl)but-2-enoate (56)

The general procedure **TP7** was followed using **3m** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (PE) yielded **56** (67 mg, 52%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.22 (dd, J = 4.9, 2.9 Hz, 1H), 6.94 (dd, J = 4.9, 1.2 Hz, 1H), 6.92 – 6.88 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.76 – 2.66 (m, 4H), 1.91 (d, J = 22.5 Hz, 3H), 1.49 – 1.40 (m, 6H), 1.28 (td, J = 7.1, 3.4 Hz, 9H), 0.92 – 0.86 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.2, 164.1, 142.5, 138.8, 128.6, 125.2, 120.4, 60.8, 30.0, 29.4, 29.3, 27.7, 22.1, 14.5, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{24}H_{42}O_2SSn$ [M+H$^+$] 515.2000, found 515.2005.



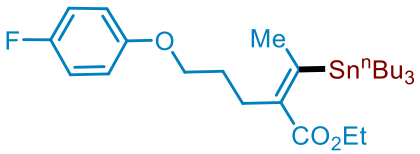
Ethyl (*Z*)-2-(4-chlorophenethyl)-3-(tributylstannyl)but-2-enoate (57)

The general procedure **TP7** was followed using corresponding alkenyl acetate (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **57** (77 mg, 57%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.22 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 2.67 (m, 4H), 2.04 – 1.81 (m, 3H), 1.50 – 1.39 (m, 6H), 1.32 – 1.25 (m, 9H), 0.95 – 0.84 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.1, 164.4, 140.6, 138.3, 131.7, 130.1, 128.4, 60.8, 35.1, 30.1, 29.4, 27.7, 22.2, 14.5, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{26}H_{43}ClO_2Sn$ [M+H$^+$] 543.2046, found 543.2049.



Ethyl (*Z*)-5-(4-methoxyphenoxy)-2-[1-(tributylstannyl)ethylidene]pentanoate(58)

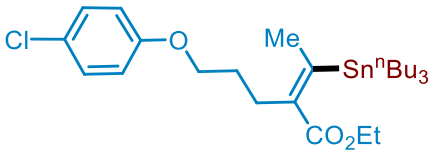
The general procedure **TP7** was followed using **3q** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 50 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **58** (74 mg, 52%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.81 (s, 4H), 4.17 (q, J = 7.1 Hz, 2H), 3.88 (t, J = 6.3 Hz, 2H), 3.76 (s, 3H), 2.62 (t, J = 7.4 Hz, 2H), 2.11 – 1.99 (m, 3H), 1.90 – 1.82 (m, 2H), 1.49 – 1.40 (m, 6H), 1.28 (m, 9H), 0.88 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.3, 163.9, 153.8, 153.3, 138.8, 115.5, 114.8, 67.9, 60.8, 55.9, 29.4, 29.1, 27.6, 24.4, 22.3, 14.5, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{28}H_{48}O_4Sn$ [M+H$^+$] 569.2647, found 569.2650.



Ethyl (*Z*)-5-(4-fluorophenoxy)-2-[1-(tributylstannyl)ethylidene]pentanoate (59)

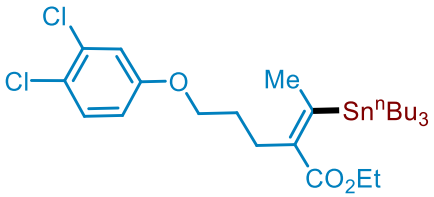
The general procedure **TP7** was followed using **3r** (0.25 mmol) and **2a** (0.325 mmol) at 0 ℃ for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **59** (112 mg, 81%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.98 – 6.91 (m, 2H), 6.87 – 6.75 (m, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.88 (t, J = 6.3 Hz, 2H), 2.63 (t, J = 7.4 Hz, 2H), 2.11 – 1.98 (m, 3H), 1.91 – 1.82 (m, 2H), 1.50 – 1.38 (m, 6H), 1.27 (dd, J = 15.0, 7.7 Hz, 9H), 0.93 – 0.84 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.2, 164.1, 157.3 (d, $^{1}J_{C\text{-}F}$ = 237.7 Hz), 155.3 (d, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 138.7, 115.9 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 115.4 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 67.9, 60.8, 29.4,

29.0, 27.6, 24.3, 22.3, 14.5, 13.9, 11.8. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -124.43 (s). HR-MS (EI) m/z calcd for $C_{27}H_{45}FO_3Sn$ [M+H$^+$] 557.2447, found 557.2450.



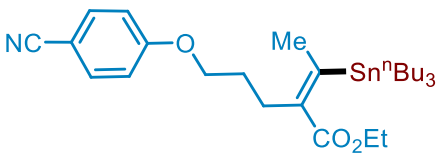
Ethyl (*Z*)-5-(4-chlorophenoxy)-2-[1-(tributylstannyl)ethylidene]pentanoate (60)

The general procedure **TP7** was followed using **3s** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **60** (89 mg, 62%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.24 – 7.15 (m, 2H), 6.87 – 6.74 (m, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.89 (t, J = 6.3 Hz, 2H), 2.62 (t, J = 7.4 Hz, 2H), 2.13 – 1.97 (m, 3H), 1.94 – 1.81 (m, 2H), 1.49 – 1.39 (m, 6H), 1.32 – 1.21 (m, 9H), 0.88 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.2, 164.2, 157.7, 138.6, 129.4, 125.5, 115.8, 67.6, 60.8, 29.4, 28.9, 27.6, 24.3, 22.4, 14.5, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{27}H_{45}ClO_3Sn$ [M+H$^+$] 573.2152, found 573.2155.



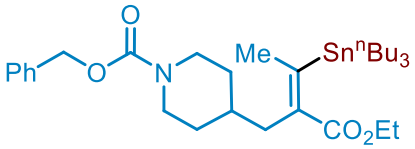
Ethyl (*Z*)-5-(3,4-dichlorophenoxy)-2-[1-(tributylstannyl)ethylidene]pentanoate (61)

The general procedure **TP7** was followed using **3u** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **61** (87 mg, 58%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.9 Hz, 1H), 6.96 (d, J = 2.8 Hz, 1H), 6.73 (dd, J = 8.9, 2.8 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.89 (t, J = 6.2 Hz, 2H), 2.61 (t, J = 7.4 Hz, 2H), 2.10 – 1.98 (m, 3H), 1.92 – 1.83 (m, 2H), 1.49 – 1.37 (m, 6H), 1.28 (dd, J = 13.6, 6.7 Hz, 9H), 0.88 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.1, 164.3, 158.2, 138.4, 133.9, 130.8, 123.9, 116.4, 114.6, 67.9, 60.9, 29.4, 28.8, 27.6, 24.3, 22.4, 14.5, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{27}H_{44}Cl_2O_3Sn$ [M+H$^+$] 607.1762, found 607.1764.



Ethyl (*Z*)-5-(4-cyanophenoxy)-2-[1-(tributylstannyl)ethylidene]pentanoate (62)

The general procedure **TP7** was followed using **3an** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **62** (66 mg, 47%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.9 Hz, 2H), 6.92 (d, J = 8.9 Hz, 2H), 4.17 (q, J = 7.1 Hz, 2H), 3.98 (t, J = 6.2 Hz, 2H), 2.64 (t, J = 7.4 Hz, 2H), 2.11 – 1.98 (m, 3H), 1.96 – 1.87 (m, 2H), 1.53 – 1.37 (m, 6H), 1.27 (dd, J = 14.8, 7.6 Hz, 9H), 0.95 – 0.82 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.1, 164.4, 162.4, 138.3, 134.1, 119.4, 115.2, 103.9, 67.7, 60.8, 29.4, 28.6, 27.6, 24.2, 22.3, 14.4, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{28}H_{45}NO_3Sn$ [M+H$^+$] 564.2494, found 564.2496.



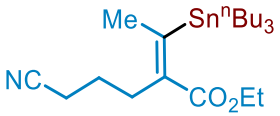
Benzyl (*Z*)-4-[2-(ethoxycarbonyl)-3-(tributylstannyl)but-2-en-1-yl]piperidine-1-carboxylate (63)

The general procedure **TP7** was followed using **3p** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 10:1) yielded **63** (89 mg, 56%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.40 – 7.26 (m, 5H), 5.12 (s, 2H), 4.18 (q, J = 7.1 Hz, 4H), 2.70 (s, 2H), 2.42 (d, J = 6.8 Hz, 2H), 2.11 – 1.94 (m, 3H), 1.59 – 1.34 (m, 11H), 1.34 – 1.09 (m, 9H), 0.92 – 0.84 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.4, 164.5, 155.4, 137.6, 137.1, 128.6, 128.0, 128.0, 67.1, 60.8, 44.5, 36.8, 34.2, 32.1, 29.4, 27.6, 23.0, 14.5, 13.9, 11.9. HR-MS (EI) m/z calcd for $C_{32}H_{53}NO_4Sn$ [M+H$^+$] 636.3069, found 636.3073.

Diethyl (*Z*)-2-[1-(tributylstannyl)ethylidene]octanedioate (64)

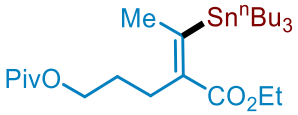
The general procedure **TP7** was followed using **corresponding alkenyl acetate** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **64** (74 mg, 54%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.18 (dd, J = 14.4, 7.3 Hz, 2H), 4.12 (dd, J = 14.4, 7.2 Hz, 2H), 2.53 – 2.34 (m, 2H), 2.29 (t, J = 7.6 Hz, 2H), 2.11 – 1.91 (m, 3H), 1.52 – 1.36 (m, 10H), 1.36 – 1.21 (m, 14H), 0.91 – 0.84 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 174.0, 169.4, 162.6, 139.9, 60.7, 60.3, 34.5, 29.4,

29.2, 29.1, 27.8, 27.6, 25.0, 22.3, 14.5, 14.4, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{26}H_{50}O_4Sn$ [M+H$^+$] 547.2804, found 547.2810.



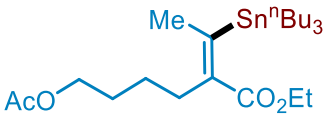
Ethyl (*Z*)-5-cyano-2-[1-(tributylstannyl)ethylidene]pentanoate (65)

The general procedure **TP7** was followed using (*Z*)**-89** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **65** (82 mg, 70%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.21 (q, J = 7.1 Hz, 2H), 2.62 – 2.57 (m, 2H), 2.32 (t, J = 7.1 Hz, 2H), 2.14 – 2.03 (m, 3H), 1.80 – 1.73 (m, 2H), 1.53 – 1.36 (m, 6H), 1.33 – 1.21 (m, 9H), 0.99 – 0.81 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.7, 165.8, 137.3, 119.8, 61.0, 29.3, 27.6, 26.8, 25.3, 22.5, 17.0, 14.4, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{22}H_{41}NO_2Sn$ [M+H$^+$] 472.2232, found 472.2236.



Ethyl (*Z*)-5-(pivaloyloxy)-2-[1-(tributylstannyl)ethylidene]pentanoate (66)

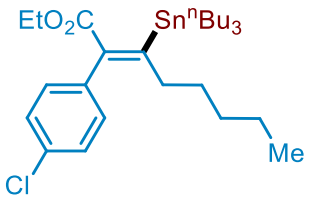
The general procedure **TP7** was followed using **3o** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **66** (84 mg, 62%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.19 (q, J = 7.1 Hz, 2H), 4.06 (t, J = 6.3 Hz, 2H), 2.58 – 2.45 (m, 2H), 2.12 – 1.99 (m, 3H), 1.78 – 1.66 (m, 2H), 1.51 – 1.39 (m, 6H), 1.32 – 1.25 (m, 9H), 1.24 – 1.19 (m, 9H), 0.93 – 0.83 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 178.7, 169.1, 164.1, 138.7, 64.2, 60.8, 38.9, 29.4, 28.7, 27.6, 27.4, 24.5, 22.2, 14.5, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{26}H_{50}O_4Sn$ [M+H$^+$] 547.2804, found 547.2808.



Ethyl (*Z*)-6-acetoxy-2-(1-(tributylstannyl)ethylidene)hexanoate (67)

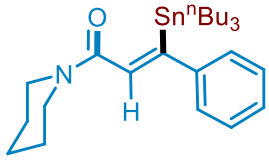
The general procedure **TP7** was followed using corresponding alkenyl acetate (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **67** (82 mg, 63%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.19 (q, J = 7.1 Hz, 2H), 4.07 (t, J = 6.7 Hz, 2H), 2.51 – 2.41 (m, 2H), 2.11 – 1.99 (m, 6H),

1.68 – 1.60 (m, 2H), 1.50 – 1.39 (m, 8H), 1.28 (dd, J = 14.3, 7.1 Hz, 9H), 0.88 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.3, 169.3, 163.2, 139.4, 64.6, 60.8, 29.4, 28.6, 27.6, 27.4, 25.8, 22.3, 21.1, 14.5, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{24}H_{46}O_4Sn$ [M+H$^+$] 519.2491, found 519.2493.



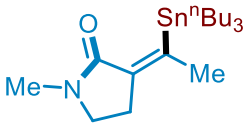
Ethyl (*Z*)-2-(4-chlorophenyl)-3-(tributylstannyl)oct-2-enoate (68)

The general procedure **TP7** was followed using **3v** (0.25 mmol) and **2a** (0.325 mmol) at 23 °C for 6 h. Purification by column chromatography (PE) yielded **68** (77 mg, 54%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.36 – 7.26 (m, 2H), 7.05 – 6.92 (m, 2H), 4.11 (q, J = 7.1 Hz, 2H), 2.26 – 2.05 (m, 2H), 1.55 – 1.43 (m, 6H), 1.32 (dd, J = 14.7, 7.3 Hz, 6H), 1.21 – 1.07 (m, 9H), 0.99 (m, 6H), 0.90 (t, J = 7.3 Hz, 9H), 0.79 (t, J = 7.0 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.6, 168.4, 139.6, 137.1, 132.6, 131.1, 128.1, 61.1, 36.3, 31.9, 29.5, 29.3, 27.7, 22.5, 14.4, 14.0, 13.9, 12.1. HR-MS (EI) m/z calcd for $C_{28}H_{47}ClO_2Sn$ [M+H$^+$] 571.2359, found 571.2363.



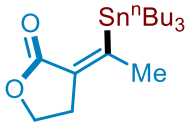
(*Z*)-3-Phenyl-1-(piperidin-1-yl)-3-(tributylstannyl)prop-2-en-1-one (69)

The general procedure **TP7** was followed using **3ao** (0.25 mmol) and **2a** (0.325 mmol) at 23 °C for 40 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **69** (70 mg, 56%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30 (t, J = 7.4 Hz, 2H), 7.25 – 7.16 (m, 1H), 7.11 – 7.03 (m, 2H), 7.03 – 6.77 (m, 1H), 3.71 – 3.46 (m, 4H), 1.65 (dd, J = 7.0, 3.5 Hz, 2H), 1.60 – 1.55 (m, 4H), 1.45 – 1.32 (m, 6H), 1.22 (dt, J = 14.3, 7.2 Hz, 6H), 1.00 – 0.86 (m, 6H), 0.82 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 168.8, 166.3, 147.0, 130.4, 128.1, 126.5, 126.4, 46.8, 43.6, 29.4, 27.6, 26.9, 25.8, 24.8, 13.9, 12.6. HR-MS (EI) m/z calcd for $C_{26}H_{43}NOSn$ [M+H$^+$] 506.2439, found 506.2444.



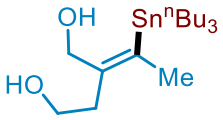
(*Z*)-1-Methyl-3-(1-(tributylstannyl)ethylidene)pyrrolidin-2-one (70)

The general procedure **TP7** was followed using corresponding alkenyl acetate (0.25 mmol) and **2a** (0.325 mmol) at 23 °C for 40 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **70** (45 mg, 43%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.45 – 3.34 (m, 2H), 2.92 (s, 3H), 2.76 – 2.66 (m, 2H), 2.06 – 1.92 (m, 3H), 1.52 – 1.37 (m, 6H), 1.29 (dd, J = 14.7, 7.3 Hz, 6H), 1.03 – 0.90 (m, 6H), 0.87 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.2, 149.6, 137.6, 46.5, 30.4, 29.5, 27.6, 23.7, 22.1, 13.9, 11.5. HR-MS (EI) m/z calcd for $C_{19}H_{37}NOSn$ [M+H$^+$] 416.1970, found 416.1974.



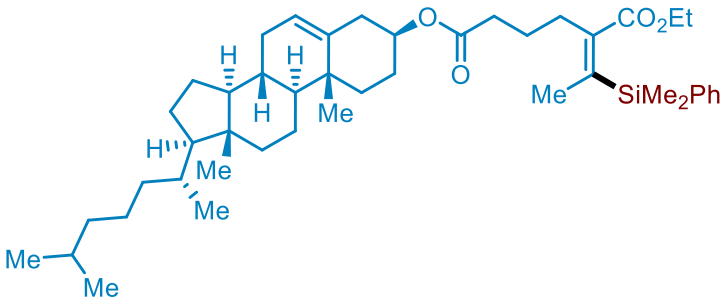
(*Z*)-3-[1-(tributylstannyl)ethylidene]dihydrofuran-2(3*H*)-one (71)

The general procedure **TP7** was followed using **3w** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 40 min. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **71** (68 mg, 68%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.32 (t, J = 7.6 Hz, 2H), 2.85 (td, J = 7.6, 1.8 Hz, 2H), 2.07 – 1.96 (m, 3H), 1.44 – 1.30 (m, 6H), 1.22 (dd, J = 14.7, 7.3 Hz, 6H), 0.95 – 0.84 (m, 6H), 0.84 – 0.77 (m, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.2, 163.0, 131.7, 65.5, 29.3, 27.5, 26.8, 24.0, 13.8, 11.0. HR-MS (EI) m/z calcd for $C_{18}H_{34}O_2Sn$ [M+H$^+$] 403.1654, found 403.1656.



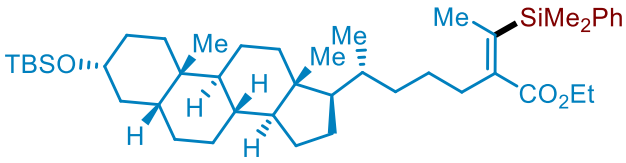
(*Z*)-2-[1-(Tributylstannyl)ethylidene]butane-1,4-diol (72)

The general procedure **TP10** was followed using **71** (0.5 mmol) and **LiAlH$_4$** (0.75 mmol) at 0 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 3:1) yielded **72** (120 mg, 59%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.99 (d, J = 4.6 Hz, 2H), 3.71 (q, J = 5.6 Hz, 2H), 2.77 (t, J = 5.0 Hz, 1H), 2.58 (t, J = 5.9 Hz, 2H), 2.53 (t, J = 4.8 Hz, 1H), 1.95 – 1.83 (m, 3H), 1.54 – 1.40 (m, 6H), 1.31 (dd, J = 14.6, 7.3 Hz, 6H), 0.91 (dt, J = 14.6, 7.8 Hz, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 144.9, 141.3, 70.4, 61.9, 33.9, 29.3, 27.5, 21.1, 13.8, 10.9. HR-MS (EI) m/z calcd for $C_{18}H_{38}O_2Sn$ [M+H$^+$] 407.1967, found 407.1969.



6-{(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-[(*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl} 1-ethyl (*Z*)-2-{1-[dimethyl(phenyl)silyl]ethylidene}hexanedioate (73)

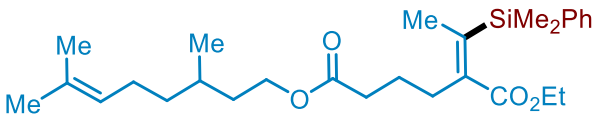
The general procedure **TP5** was followed using **3ap** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 2.5 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **73** (98 mg, 55%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.50 – 7.44 (m, 2H), 7.33 – 7.27 (m, 3H), 5.37 (d, J = 4.0 Hz, 1H), 4.69 – 4.57 (m, 1H), 3.83 (q, J = 7.1 Hz, 2H), 2.51 – 2.41 (m, 2H), 2.31 (t, J = 7.2 Hz, 4H), 2.05 – 1.93 (m, 2H), 1.90 – 1.81 (m, 6H), 1.75 (dd, J = 15.4, 7.6 Hz, 2H), 1.59 – 1.44 (m, 6H), 1.42 – 1.18 (m, 6H), 1.17 – 1.11 (m, 4H), 1.09 (t, J = 7.1 Hz, 5H), 1.02 (s, 4H), 0.96 (dd, J = 12.3, 4.7 Hz, 2H), 0.92 (d, J = 6.5 Hz, 3H), 0.86 (dd, J = 6.6, 1.7 Hz, 6H), 0.68 (s, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.9, 169.6, 145.6, 143.3, 139.8, 139.6, 133.6, 128.6, 127.6, 122.8, 74.0, 60.5, 56.8, 56.3, 50.2, 42.4, 39.9, 39.7, 38.3, 37.1, 36.7, 36.3, 35.9, 34.4, 32.0, 32.0, 29.6, 28.4, 28.1, 27.9, 24.4, 24.1, 24.0, 23.0, 22.7, 21.2, 19.6, 19.5, 18.9, 14.1, 12.0, -1.0. HR-MS (EI) m/z calcd for $C_{45}H_{70}O_4Si$ [M+H$^+$] 703.5116, found 703.5119.



Ethyl (*R*,*Z*)-6-{(3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-[(tert-butyldimethylsilyl)oxy]-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl}-2-{1-[dimethyl(phenyl)silyl]ethylidene}heptanoate (74)

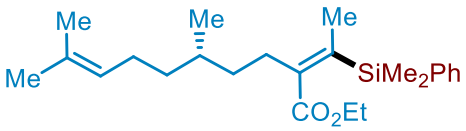
The general procedure **TP5** was followed using **3aq** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 100:1) yielded **74** (80 mg, 45%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51 – 7.46 (m, 2H), 7.33 – 7.28 (m, 3H), 3.83 (q, J = 7.1 Hz, 2H), 3.63 – 3.52 (m, 1H), 2.45 – 2.29 (m, 2H), 1.94 (d, J = 11.8

Hz, 1H), 1.85 – 1.72 (m, 7H), 1.53 (s, 2H), 1.38 (dt, J = 23.6, 15.1 Hz, 10H), 1.27 – 1.14 (m, 5H), 1.09 (t, J = 7.1 Hz, 5H), 1.04 (d, J = 8.7 Hz, 3H), 0.89 (s, 16H), 0.63 (s, 3H), 0.38 (s, 6H), 0.06 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.1, 144.8, 143.4, 139.7, 133.7, 128.6, 127.6, 73.0, 60.4, 56.6, 56.4, 42.8, 42.5, 40.4, 40.3, 37.1, 36.0, 35.8, 35.8, 34.8, 31.2, 30.8, 28.4, 27.5, 26.6, 26.1, 25.2, 24.4, 23.6, 21.0, 19.4, 18.8, 18.5, 14.1, 12.2, -1.0, -4.4. HR-MS (EI) m/z calcd for $C_{44}H_{74}O_3Si_2$ [M+H$^+$] 707.5249, found 707.5253.



6-(3,7-Dimethyloct-6-en-1-yl) 1-ethyl (*Z*)-2-{1-[dimethyl(phenyl)silyl]ethylidene}hexanedioate (75)

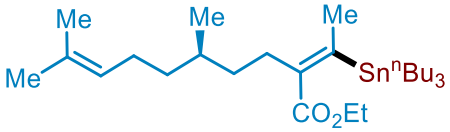
The general procedure **TP5** was followed using corresponding alkenyl acetate (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1.5 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **75** (48 mg, 41%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 – 7.45 (m, 2H), 7.32 – 7.29 (m, 3H), 5.08 (ddd, J = 7.1, 5.8, 1.3 Hz, 1H), 4.14 – 4.07 (m, 2H), 3.82 (q, J = 7.1 Hz, 2H), 2.48 – 2.43 (m, 2H), 2.33 (t, J = 7.4 Hz, 2H), 1.98 (dt, J = 17.1, 7.3 Hz, 2H), 1.85 (s, 3H), 1.76 (dd, J = 15.4, 7.7 Hz, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.49 (ddd, J = 20.8, 13.3, 7.0 Hz, 2H), 1.40 – 1.22 (m, 2H), 1.22 – 1.14 (m, 1H), 1.08 (t, J = 7.1 Hz, 3H), 0.91 (d, J = 6.6 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.7, 169.6, 145.7, 143.3, 139.6, 133.6, 131.5, 128.6, 127.6, 124.7, 63.1, 60.5, 37.1, 35.6, 34.0, 29.6, 25.8, 25.5, 24.0, 19.6, 19.5, 17.8, 14.1, -1.0. HR-MS (EI) m/z calcd for $C_{28}H_{44}O_4Si$ [M+H$^+$] 473.3082, found 473.3085.



Ethyl (*S*,*Z*)-2-{1-[dimethyl(phenyl)silyl]ethylidene}-5,9-dimethyldec-8-enoate (76)

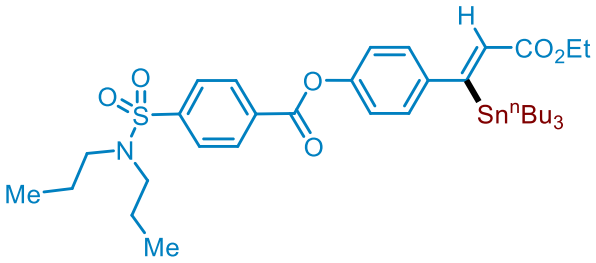
The general procedure **TP5** was followed using **3ar** (0.25 mmol) and **1a** (0.5 mmol) at 23 °C for 1 h. Purification by column chromatography (PE) yielded **76** (49 mg, 50%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.47 (dd, J = 6.1, 3.0 Hz, 2H), 7.35 – 7.27 (m, 3H), 5.10 (t, J = 7.0 Hz, 1H), 3.83 (q, J = 7.1 Hz, 2H), 2.49 – 2.32 (m, 2H), 1.98 (dd, J = 16.4, 10.2 Hz, 2H), 1.83 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H), 1.41 (m, 3H), 1.26 – 1.13 (m, 2H), 1.09 (t, J = 7.1 Hz, 3H), 0.91 (d, J = 6.4 Hz, 3H), 0.38 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.9, 144.9,

143.6, 139.8, 133.7, 131.2, 128.6, 127.6, 125.0, 60.4, 37.0, 35.7, 32.8, 28.1, 25.9, 25.7, 19.6, 19.3, 17.8, 14.1, -1.0. HR-MS (EI) m/z calcd for $C_{24}H_{38}O_2Si$ [M+H$^+$] 387.2714, found 387.2716.



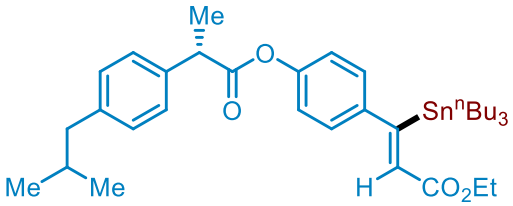
Ethyl (*R*,*Z*)-5,9-dimethyl-2-[1-(tributylstannyl)ethylidene]dec-8-enoate (77)

The general procedure **TP7** was followed using **3ar** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 1 h. Purification by column chromatography (PE) yielded **77** (80 mg, 59%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.22 – 5.04 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.48 – 2.34 (m, 2H), 2.11 – 1.95 (m, 5H), 1.69 (s, 3H), 1.61 (s, 3H), 1.42 (dddd, J = 17.3, 13.2, 7.7, 5.4 Hz, 9H), 1.31 – 1.25 (m, 9H), 1.21 – 1.12 (m, 2H), 0.89 (dt, J = 14.6, 6.9 Hz, 18H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.5, 162.0, 140.4, 131.2, 125.1, 60.7, 37.0, 36.5, 32.9, 29.4, 27.6, 25.9, 25.7, 25.6, 22.1, 19.7, 17.8, 14.5, 13.9, 11.8. HR-MS (EI) m/z calcd for $C_{28}H_{54}O_2Sn$ [M+H$^+$] 543.3219, found 543.3222.



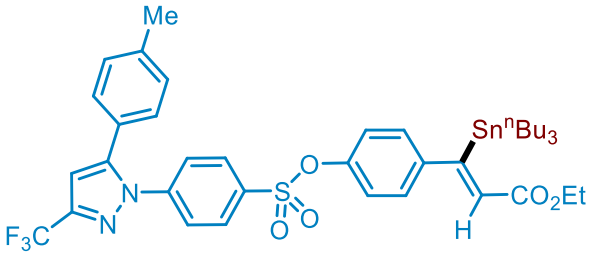
(*Z*)-4-[3-Ethoxy-3-oxo-1-(tributylstannyl)prop-1-en-1-yl]phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (78)

The general procedure **TP6** was followed using **3as** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **78** (133 mg, 71%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.4 Hz, 2H), 7.95 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 7.15 – 7.09 (m, 2H), 6.76 – 6.25 (m, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.17 – 3.11 (m, 4H), 1.57 (dd, J = 15.1, 7.5 Hz, 4H), 1.43 (ddd, J = 12.5, 8.5, 6.1 Hz, 6H), 1.34 – 1.22 (m, 9H), 1.04 – 0.94 (m, 6H), 0.87 (dt, J = 14.5, 7.3 Hz, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.5, 167.8, 163.9, 149.7, 145.0, 144.0, 133.0, 131.3, 130.9, 127.5, 127.3, 121.2, 60.7, 50.0, 29.2, 27.4, 22.1, 14.4, 13.8, 12.1, 11.3. HR-MS (EI) m/z calcd for $C_{36}H_{55}NO_6SSn$ [M+H$^+$] 750.2845, found 750.2851.



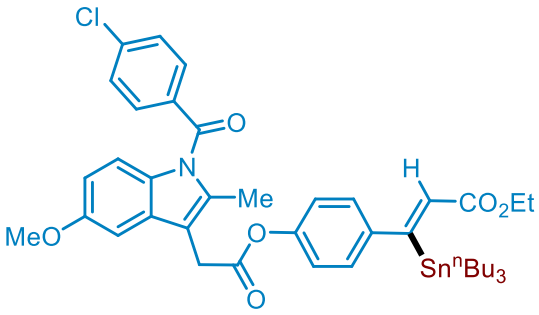
Ethyl (*S*,*Z*)-3-{4-{[2-(4-isobutylphenyl)propanoyl]oxy}phenyl}-3-(tributylstannyl)acrylate (79)

The general procedure **TP6** was followed using **3at** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **79** (91 mg, 54%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.07 – 6.98 (m, 2H), 6.98 – 6.91 (m, 2H), 6.60 – 6.27 (m, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.93 (q, J = 7.2 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 1.87 (dt, J = 13.5, 6.8 Hz, 1H), 1.60 (d, J = 7.2 Hz, 3H), 1.43 – 1.33 (m, 6H), 1.31 – 1.20 (m, 9H), 0.96 – 0.87 (m, 12H), 0.83 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 173.3, 172.7, 167.8, 150.0, 143.4, 141.0, 137.4, 131.1, 129.7, 127.4, 127.3, 121.2, 60.7, 45.4, 45.2, 30.3, 29.2, 27.5, 22.5, 18.7, 14.5, 13.8, 12.1. HR-MS (EI) m/z calcd for $C_{36}H_{54}O_4Sn$ [M+H$^+$] 671.3117, found 671.3121.



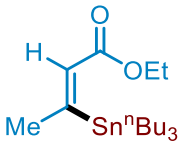
Ethyl (*Z*)-3-{4-{{{4-[5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl]phenyl}sulfonyl}oxy}phenyl}-3-(tributylstannyl)acrylate (80)

The general procedure **TP6** was followed using **3au** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **80** (100 mg, 47%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85 – 7.72 (m, 2H), 7.52 – 7.44 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 6.94 (ddd, J = 14.0, 7.8, 2.3 Hz, 4H), 6.75 (s, 1H), 6.57 – 6.30 (m, 1H), 4.23 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.38 – 1.31 (m, 6H), 1.31 – 1.17 (m, 9H), 0.91 (dd, J = 9.5, 6.6 Hz, 6H), 0.82 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.1, 167.6, 148.2, 145.5, 145.4, 144.5 (q, $^2J_{C\text{-}F}$ = 39.0 Hz), 143.8, 140.1, 134.6, 131.6, 129.9, 129.7, 128.9, 127.5, 125.7, 125.5, 122.1, 118.4 (dd, $^1J_{C\text{-}F}$ = 269.4 Hz), 106.8, 60.8, 29.1, 27.4, 21.5, 14.4, 13.8, 12.1. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -62.52 (s). HR-MS (EI) m/z calcd for $C_{40}H_{49}F_3N_2O_5SSn$ [M+H$^+$] 847.2409, found 847.2415.



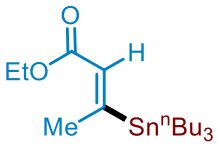
Ethyl (*Z*)-3-{4-{2-[1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl]acetoxy}phenyl}-3-(tributylstannyl)acrylate (81)

The general procedure **TP6** was followed using **3av** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (petroleum ether/EtOAc 10:1) yielded **49** (115 mg, 56%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 7.9 Hz, 2H), 7.09 – 7.00 (m, 5H), 6.90 (d, J = 9.0 Hz, 1H), 6.70 (dd, J = 9.0, 2.0 Hz, 1H), 6.59 – 6.29 (m, 1H), 4.23 (q, J = 7.0 Hz, 2H), 3.90 (s, 2H), 3.84 (d, J = 0.6 Hz, 3H), 2.46 (s, 3H), 1.39 (dt, J = 8.0, 6.3 Hz, 6H), 1.33 – 1.18 (m, 9H), 0.96 – 0.91 (m, 6H), 0.83 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 172.6, 169.4, 168.4, 167.8, 156.3, 149.8, 143.7, 139.5, 136.3, 134.0, 131.3, 131.2, 131.0, 130.6, 129.3, 127.4, 121.1, 115.2, 112.1, 112.0, 101.3, 60.7, 55.8, 30.7, 29.2, 27.4, 14.5, 13.8, 13.6, 12.1. HR-MS (EI) m/z calcd for $C_{42}H_{52}ClNO_6Sn$ [M+H$^+$] 822.2578, found 822.2582.



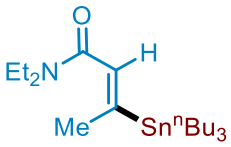
Ethyl (*Z*)-3-(tributylstannyl)but-2-enoate (86)

The general procedure **TP6** was followed using (*Z*)-**85** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (PE) yielded **86** (87 mg, 86%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.58 – 6.24 (m, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.18 – 2.08 (m, 3H), 1.53 – 1.41 (m, 6H), 1.39 – 1.23 (m, 9H), 0.99 – 0.94 (m, 6H), 0.88 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.7, 167.9, 129.4, 60.2, 29.4, 27.6, 27.5, 14.5, 13.9, 11.0. HR-MS (EI) m/z calcd for $C_{18}H_{36}O_2Sn$ [M+H$^+$] 405.1810, found 405.1815.



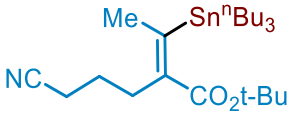
Ethyl (*E*)-3-(tributylstannyl)but-2-enoate (86')

The general procedure **TP6** was followed using (*E*)-**85** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (PE) yielded **86'** (27 mg, 27%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.10 – 5.83 (m, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.48 – 2.31 (m, 3H), 1.54 – 1.45 (m, 6H), 1.35 – 1.26 (m, 9H), 0.96 (dd, J = 9.5, 6.7 Hz, 6H), 0.89 (dd, J = 7.3, 5.1 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.3, 164.6, 128.3, 59.7, 29.1, 27.5, 22.5, 14.5, 13.8, 9.6. HR-MS (EI) m/z calcd for $C_{18}H_{36}O_2Sn$ [M+H$^+$] 405.1810, found 405.1815.



(*E*)-*N*,*N*-Diethyl-3-(tributylstannyl)but-2-enamide (88)

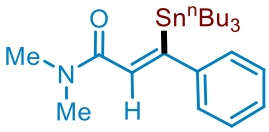
The general procedure **TP6** was followed using **87** (0.25 mmol) and **2a** (0.325 mmol) at -20 °C for 15 min. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **88** (8 mg, 7%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.77 (d, J = 1.6 Hz, 1H), 3.39 (m, 4H), 2.26 – 2.06 (m, 3H), 1.49 – 1.42 (m, 6H), 1.28 (m, 6H), 1.20 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H), 0.89 (dd, J = 7.0, 4.9 Hz, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.8, 166.5, 128.7, 42.0, 41.0, 29.5, 27.7, 27.3, 15.0, 14.0, 13.4, 11.7. HR-MS (EI) m/z calcd for $C_{20}H_{41}NOSn$ [M+H$^+$] 432.2283, found 432.2285.



***tert*-Butyl (*Z*)-5-cyano-2-[1-(tributylstannyl)ethylidene]pentanoate (92)**

The general procedure **TP7** was followed using (*Z*)-**90** (0.25 mmol) and **2a** (0.325 mmol) at 0 °C for 2 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **92** (39 mg, 31%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.62 – 2.48 (m, 2H), 2.31 (t, J = 7.1 Hz, 2H), 2.13 – 1.97 (m, 3H), 1.81 – 1.68 (m, 2H), 1.48 (s, 9H), 1.48 – 1.36 (m, 6H), 1.27 (dd, J = 14.6, 7.3 Hz, 6H), 0.93 – 0.83 (m, 15H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 167.8, 164.7, 138.1, 119.9, 80.7, 29.4, 28.2, 27.6, 26.9, 25.4, 22.3, 17.0, 13.9, 12.1. HR-MS (EI) m/z

calcd for $C_{24}H_{45}NO_2Sn$ [M+H$^+$] 500.2545, found 500.2549.

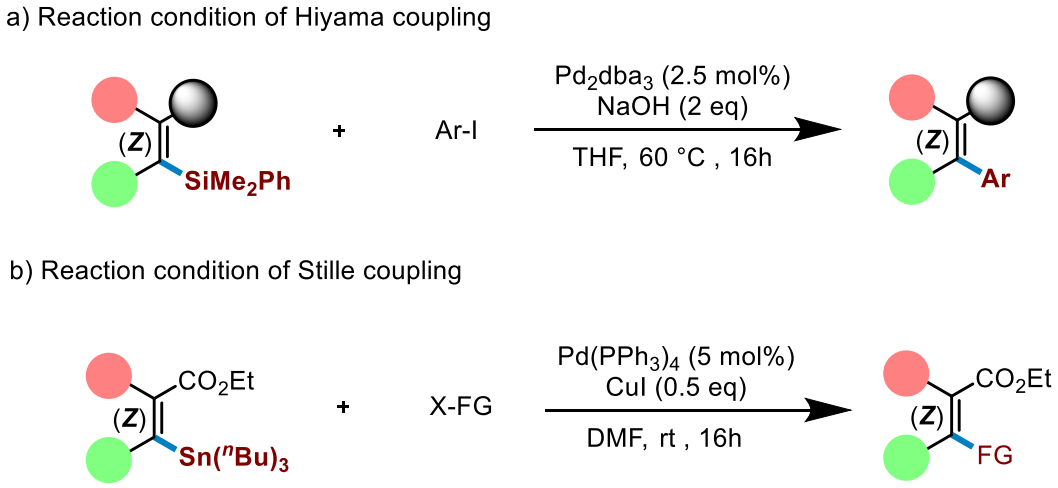


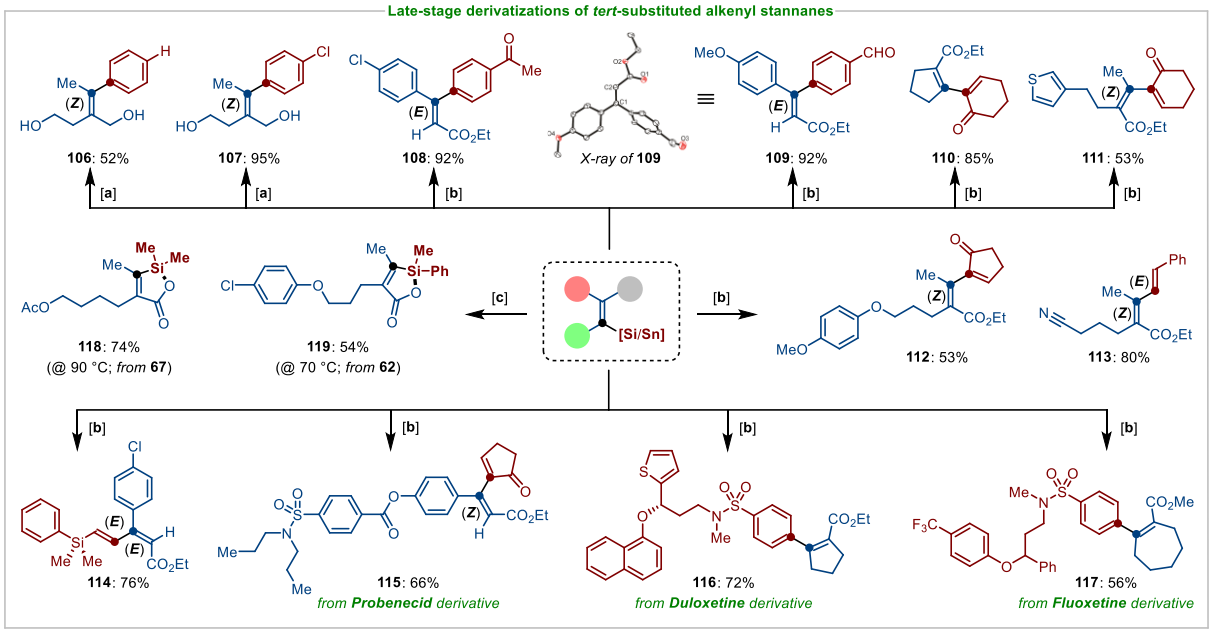
(*Z*)-*N*,*N*-Dimethyl-3-phenyl-3-(tributylstannyl)acrylamide (98)

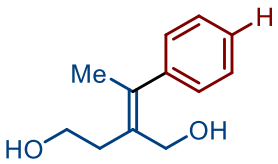
The general procedure **TP7** was followed using (*Z*)-**96** (0.25 mmol) and **2a** (0.325 mmol) at 23 °C for 1 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **98** (50 mg, 43%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.35 – 7.26 (m, 2H), 7.24 – 7.18 (m, 1H), 7.05 (dt, J = 8.0, 1.7 Hz, 2H), 7.02 – 6.74 (m, 1H), 3.13 (s, 3H), 3.03 (s, 3H), 1.45 – 1.34 (m, 6H), 1.23 (m, 6H), 0.90 (m, 6H), 0.82 (t, J = 7.3 Hz, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.6, 167.5, 147.0, 129.9, 128.1, 126.4, 126.4, 37.4, 36.2, 29.3, 27.6, 13.9, 12.6. HR-MS (EI) m/z calcd for $C_{23}H_{39}NOSn$ [M+H$^+$] 466.2126, found 466.2130.

Late-Stage Modifications of Alkenyl Silanes and Alkenyl Stannanes:

Figure S8: Synthetic Applicability of Alkenyl Silanes by Hiyama coupling and Alkenyl Stannanes by MKS Reaction.[14]

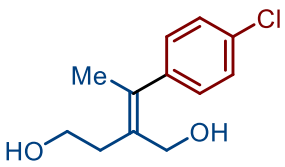






(*Z*)-2-(1-phenylethylidene)butane-1,4-diol (106)

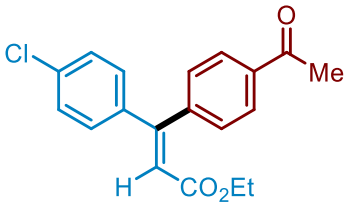
The general procedure **TP12** was followed using **33** (0.1 mmol) and **iodobenzene** (0.15 mmol) at 60 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 2:1) yielded **106** (10 mg, 52%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 (t, J = 7.3 Hz, 2H), 7.26 (s, 1H), 7.21 – 7.14 (m, 2H), 3.94 (s, 2H), 3.84 (t, J = 5.8 Hz, 2H), 2.61 (t, J = 5.7 Hz, 2H), 2.29 (s, 2H), 2.03 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 143.6, 138.4, 132.3, 128.3, 128.0, 126.8, 64.0, 62.0, 35.0, 21.2. HR-MS (EI) m/z calcd for $C_{12}H_{16}O_2$ [M+H$^+$] 193.1223, found 193.1225.



(*Z*)-2-[1-(4-chlorophenyl)ethylidene]butane-1,4-diol (107)

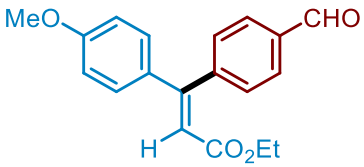
The general procedure **TP12** was followed using **33** (0.1 mmol) and **1-chloro-4-iodobenzene** (0.15 mmol) at 60 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 2:1) yielded **107** (19 mg, 56%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.33 – 7.26 (m, 2H), 7.16 – 7.09 (m, 2H), 3.91 (s, 2H), 3.82 (t, J = 5.7 Hz, 2H), 2.76 (s, 2H), 2.59 (t, J =

5.7 Hz, 2H), 2.00 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 142.0, 137.1, 133.0, 132.7, 129.5, 128.5, 63.9, 61.8, 35.0, 21.1. HR-MS (EI) m/z calcd for $C_{12}H_{15}ClO_2$ [M+H$^+$] 227.0833, found 227.0835.



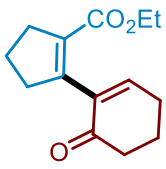
Ethyl (*E*)-3-(4-acetylphenyl)-3-(4-chlorophenyl)acrylate (108)

The general procedure **TP8** was followed using **44** (0.1 mmol) and **1-(4-iodophenyl)ethan-1-one** (0.12 mmol) at 23 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **108** (30 mg, 92%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.07 – 7.85 (m, 2H), 7.37 – 7.26 (m, 4H), 7.24 – 7.15 (m, 2H), 6.41 (s, 1H), 4.06 (q, J = 7.1 Hz, 2H), 2.64 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 197.7, 165.6, 154.3, 143.7, 138.5, 136.8, 136.1, 129.5, 129.4, 129.0, 128.2, 118.5, 60.5, 26.8, 14.1. HR-MS (EI) m/z calcd for $C_{19}H_{17}ClO_3$ [M+H$^+$] 329.0939, found 329.0943.



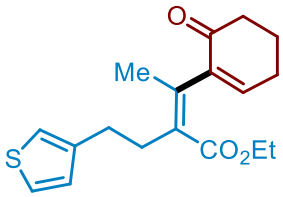
Ethyl (*E*)-3-(4-formylphenyl)-3-(4-methoxyphenyl)acrylate (109)

The general procedure **TP8** was followed using **41** (0.147 mmol) and **4-iodobenzaldehyde** (0.18 mmol) at 23 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **109** (43 mg, 95%) as a yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 10.06 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.25 – 7.16 (m, 2H), 6.93 – 6.77 (m, 2H), 6.39 (s, 1H), 4.04 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 192.0, 165.9, 161.2, 155.1, 146.1, 135.8, 132.0, 129.8, 129.7, 129.5, 116.0, 114.1, 60.2, 55.5, 14.1. HR-MS (EI) m/z calcd for $C_{19}H_{18}O_4$ [M+H$^+$] 311.1278, found 311.1282.



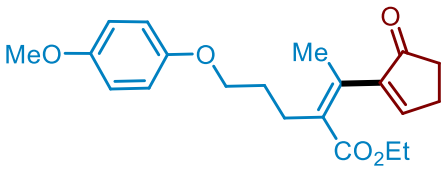
Ethyl 2-(6-oxocyclohex-1-en-1-yl)cyclopent-1-ene-1-carboxylate (110)

The general procedure **TP8** was followed using **38** (0.1 mmol) and **2-iodocyclohex-2-en-1-one** (0.12 mmol) at 23 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **110** (20 mg, 85%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.77 (t, J = 4.2 Hz, 1H), 4.09 (q, J = 7.1 Hz, 2H), 2.74 (ddd, J = 7.9, 4.9, 2.4 Hz, 2H), 2.62 (tt, J = 8.0, 2.4 Hz, 2H), 2.57 – 2.48 (m, 2H), 2.47 – 2.38 (m, 2H), 2.05 (dt, J = 12.4, 6.1 Hz, 2H), 1.99 – 1.84 (m, 2H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 197.0, 165.7, 149.6, 145.7, 138.1, 131.7, 60.0, 39.6, 38.8, 34.1, 26.1, 22.9, 21.9, 14.4. HR-MS (EI) m/z calcd for $C_{14}H_{18}O_3$ [M+H$^+$] 235.1329, found 235.1333.



Ethyl (*Z*)-3-(6-oxocyclohex-1-en-1-yl)-2-[2-(thiophen-3-yl)ethyl]but-2-enoate (111)

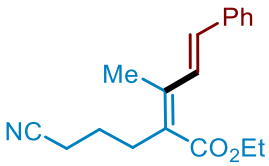
The general procedure **TP8** was followed using **56** (0.1 mmol) and **2-iodocyclohex-2-en-1-one** (0.12 mmol) at 23 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **111** (17 mg, 53%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.23 (dd, J = 4.7, 3.1 Hz, 1H), 6.98 (d, J = 4.9 Hz, 2H), 6.53 (t, J = 4.2 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 2.79 (t, J = 7.6 Hz, 2H), 2.67 (t, J = 7.6 Hz, 2H), 2.49 (dd, J = 8.6, 4.9 Hz, 2H), 2.37 (dd, J = 10.3, 6.0 Hz, 2H), 2.08 – 1.97 (m, 2H), 1.76 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 197.5, 168.7, 144.1, 143.1, 142.6, 141.9, 130.6, 128.7, 125.2, 120.8, 60.3, 38.8, 31.0, 29.4, 26.0, 22.9, 21.1, 14.4. HR-MS (EI) m/z calcd for $C_{18}H_{22}O_3S$ [M+H$^+$] 319.1362, found 319.1368.



Ethyl (*Z*)-5-(4-methoxyphenoxy)-2-[1-(5-oxocyclopent-1-en-1-yl)ethylidene]pentanoate (112)

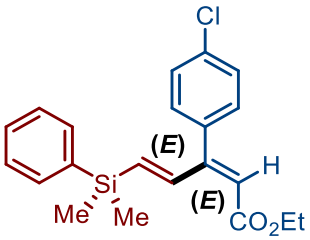
The general procedure **TP8** was followed using **58** (0.09 mmol) and **2-iodocyclopent-2-en-1-one** (0.108 mmol) at 23 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 5:1) yielded **112** (17 mg, 53%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.34 (t, J = 2.8 Hz, 1H), 6.83 (s, 4H), 4.06 (q, J = 7.1 Hz, 2H), 3.93 (t, J = 6.1 Hz, 2H), 3.76

(s, 3H), 2.71 – 2.59 (m, 4H), 2.53 – 2.37 (m, 2H), 1.99 – 1.83 (m, 5H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 206.5, 168.8, 156.9, 153.8, 153.2, 148.7, 135.5, 132.2, 115.5, 114.8, 67.5, 60.5, 55.9, 34.8, 28.5, 26.7, 26.5, 20.6, 14.3. HR-MS (EI) m/z calcd for $C_{21}H_{26}O_5$ [M+H$^+$] 359.1853, found 359.1857.



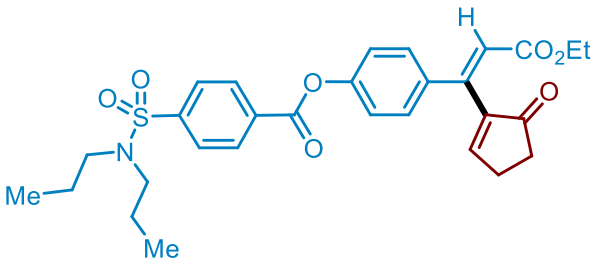
Ethyl (2*Z*,4*E*)-2-(3-cyanopropyl)-3-methyl-5-phenylpenta-2,4-dienoate (113)

The general procedure **TP8** was followed using **65** (0.127 mmol) and **(*E*)-(2-bromovinyl)benzene** (0.16 mmol) at 23 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 20:1) yielded **113** (29 mg, 80%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 16.1 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.27 – 7.24 (m, 1H), 6.79 (d, J = 16.1 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.73 – 2.56 (m, 2H), 2.40 (t, J = 7.0 Hz, 2H), 2.09 (s, 3H), 1.85 (t, J = 7.6 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.2, 141.1, 137.3, 132.3, 129.6, 128.8, 128.2, 128.2, 127.0, 119.6, 60.9, 29.7, 24.9, 16.9, 15.3, 14.5. HR-MS (EI) m/z calcd for $C_{18}H_{21}NO_2$ [M+H$^+$] 284.1645, found 284.1649.



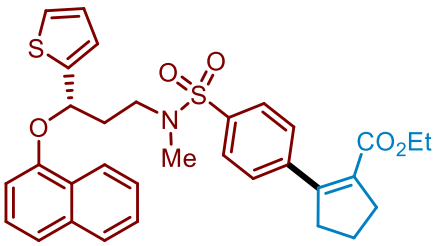
Ethyl (2*E*,4*E*)-3-(4-chlorophenyl)-5-[dimethyl(phenyl)silyl]penta-2,4-dienoate (114)

The general procedure **TP8** was followed using **44** (0.128 mmol) and **(*E*)-(2-iodovinyl)dimethyl(phenyl)silane** (0.15 mmol) at 23 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 50:1) yielded **114** (36 mg, 76%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 19.2 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.32 – 7.20 (m, 5H), 7.13 (d, J = 8.4 Hz, 2H), 6.07 (d, J = 19.2 Hz, 1H), 5.73 (s, 1H), 4.14 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H), 0.33 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 166.0, 154.8, 141.4, 141.1, 138.2, 138.0, 134.6, 133.9, 130.5, 129.3, 128.6, 128.0, 118.8, 60.4, 14.4, -2.7. HR-MS (EI) m/z calcd for $C_{21}H_{23}ClO_2Si$ [M+H$^+$] 371.1229, found 371.1231.



(*Z*)-4-[3-Ethoxy-3-oxo-1-(5-oxocyclopent-1-en-1-yl)prop-1-en-1-yl]phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (115)

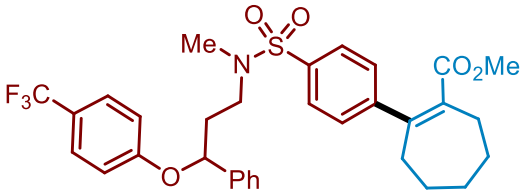
The general procedure **TP8** was followed using **78** (0.185 mmol) and **2-iodocyclopent-2-en-1-one** (0.23 mmol) at 23 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 5:1) yielded **115** (66 mg, 66%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, J = 8.6 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H), 7.52 – 7.41 (m, 3H), 7.25 – 7.18 (m, 2H), 6.39 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.18 – 3.09 (m, 4H), 2.81 (td, J = 4.7, 2.6 Hz, 2H), 2.67 – 2.57 (m, 2H), 1.58 (dt, J = 15.1, 7.5 Hz, 4H), 1.28 (t, J = 7.1 Hz, 3H), 0.89 (t, J = 7.4 Hz, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 205.8, 165.7, 163.7, 160.8, 151.7, 145.9, 145.3, 145.2, 137.3, 132.6, 131.0, 128.9, 127.3, 121.9, 120.2, 60.5, 50.1, 34.7, 27.4, 22.1, 14.3, 11.3. HR-MS (EI) m/z calcd for $C_{29}H_{33}NO_7S$ [M+H$^+$] 540.2050, found 540.2054.



Ethyl (*S*)-2-{4-{N-methyl-N-[3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl]sulfamoyl}phenyl}cyclopent-1-ene-1-carboxylate (116)

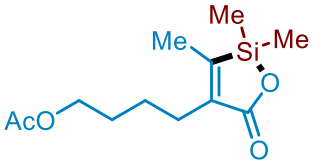
The general procedure **TP8** was followed using **38** (0.1 mmol) and **(*S*)-4-iodo-N-methyl-N-[3-(naphthalen-1-yloxy)-3-(thiophen-2-yl)propyl]benzenesulfonamide** (0.12 mmol) at 23 °C for 16 h. Purification by column chromatography (petroleum ether/EtOAc 10:1) yielded **116** (42 mg, 72%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 8.30 (dd, J = 6.2, 3.5 Hz, 1H), 7.77 (dd, J = 6.0, 3.4 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.38 (m, 3H), 7.30 – 7.25 (m, 1H), 7.20 (dd, J = 5.0, 1.1 Hz, 1H), 7.13 – 7.10 (m, 1H), 6.93 (dd, J = 5.0, 3.5 Hz, 1H), 6.88 (d, J = 7.6 Hz, 1H), 5.79 (dd, J = 7.8, 5.0 Hz, 1H), 4.04 (q, J = 7.1 Hz, 2H), 3.38 – 3.19 (m, 2H), 2.87 – 2.80 (m, 4H), 2.77 (s, 3H), 2.51 (dq, J = 7.6, 5.9 Hz, 1H), 2.41 – 2.26 (m, 1H), 2.00 (dt, J = 15.2, 7.7 Hz, 2H), 1.06 (t, J = 7.1 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 165.7, 153.1, 151.2, 144.5, 142.0, 136.3, 134.7, 131.7, 128.6, 127.7, 127.0, 126.8, 126.4,

126.2, 125.9, 125.4, 125.3, 125.1, 122.1, 121.0, 107.3, 73.8, 60.3, 47.3, 40.3, 37.8, 35.9, 35.3, 22.1, 14.1. HR-MS (EI) m/z calcd for $C_{32}H_{33}NO_5S_2$ [M+H$^+$] 576.1873, found 576.1875.



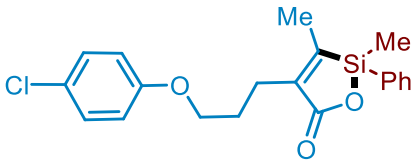
Methyl 2-{4-{N-methyl-N-{3-phenyl-3-[4-(trifluoromethyl)phenoxy]propyl}sulfamoyl}phenyl}cyclohept-1-ene-1-carboxylate (117)

The general procedure **TP8** was followed using **39** (0.149 mmol) and **4-iodo-N-methyl-N-{3-phenyl-3-[4-(trifluoromethyl)phenoxy]propyl}benzenesulfonamide** (0.179 mmol) at 23 ℃ for 16 h. Purification by column chromatography (petroleum ether/EtOAc 10:1) yielded **117** (50 mg, 56%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 4.4 Hz, 4H), 7.29 (dd, J = 8.3, 4.2 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 5.31 (dd, J = 8.6, 4.1 Hz, 1H), 3.34 (s, 3H), 3.29 (dd, J = 14.0, 7.0 Hz, 1H), 3.18 – 3.09 (m, 1H), 2.75 (s, 3H), 2.59 (dd, J = 10.5, 4.6 Hz, 4H), 2.22 (qd, J = 7.3, 5.3 Hz, 1H), 2.10 (dtd, J = 11.6, 7.4, 4.2 Hz, 1H), 1.87 (dt, J = 11.7, 5.9 Hz, 2H), 1.70 – 1.63 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 170.7, 160.4, 149.5, 149.5, 140.5, 135.5, 135.3, 129.0, 128.2, 127.4, 127.4, 126.9 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 126.0, 124.5 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 123.2 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 116.0, 51.5, 47.3, 37.4, 37.0, 35.7, 32.4, 31.0, 26.3, 25.8. ^{19}F-NMR (376 MHz, $CDCl_3$): δ = -61.58 (s). HR-MS (EI) m/z calcd for $C_{32}H_{34}F_3NO_5S$ [M+H$^+$] 602.2183, found 602.2185.



4-(2,2,3-Trimethyl-5-oxo-2,5-dihydro-1,2-oxasilol-4-yl)butyl acetate (118)

The general procedure **TP11** was followed using **24** (0.16 mmol) and **I$_2$** (0.24 mmol) at 90 °C overnight. Purification by column chromatography (petroleum ether/EtOAc 10:1) yielded **118** (30 mg, 74%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.07 (t, J = 6.5 Hz, 2H), 2.45 – 2.36 (m, 2H), 2.04 (s, 3H), 1.99 (s, 3H), 1.70 – 1.62 (m, 2H), 1.52 (m, 2H), 0.40 (s, 6H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 171.3, 169.7, 155.2, 145.8, 64.3, 28.6, 25.7, 25.0, 21.1, 13.9, -2.7. HR-MS (EI) m/z calcd for $C_{12}H_{20}O_4Si$ [M+H$^+$] 257.1204, found 257.1207.



4-[3-(4-Chlorophenoxy)propyl]-2,3-dimethyl-2-phenyl-1,2-oxasilol-5(2*H*)-one (119)

The general procedure **TP11** was followed using **28** (0.2 mmol) and **I_2** (0.3 mmol) at 70 °C overnight. Purification by column chromatography (petroleum ether/EtOAc 10:1) yielded **119** (40 mg, 54%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.58 – 7.46 (m, 3H), 7.45 – 7.36 (m, 2H), 7.21 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.5 Hz, 2H), 3.92 (t, J = 6.0 Hz, 2H), 2.65 (t, J = 7.3 Hz, 2H), 2.10 – 2.00 (m, 2H), 1.98 (s, 3H), 0.70 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 169.8, 157.6, 154.5, 145.9, 134.1, 131.7, 130.4, 129.5, 128.6, 125.7, 115.8, 67.4, 27.8, 22.8, 14.1, -5.1. HR-MS (EI) m/z calcd for $C_{20}H_{21}ClO_3Si$ [M+H$^+$] 373.1021, found 373.1023.

DFT Mechanistic Studies:

Density Functional Theory (DFT) Studies

1. Computational methods

All density functional theory (DFT) calculations were performed using the Gaussian 16 software package.[15] Geometries were optimized using the (U)B3LYP[16] functional and Grimme's D3(BJ) dispersion correction[17] with a mixed basis set of LANL2DZ for Zn, Sn, Co and 6-31G(d) for other atoms. Vibrational frequencies were calculated for all the stationary points to confirm if each optimized structure is a local minimum on the respective potential energy surface or a transition state structure with only one imaginary frequency. Solvation energy corrections were calculated in acetonitrile solvent with the SMD continuum solvation model[18] based on the gas phase optimized geometries. (U)B3LYP functional with a mixed basis set of SDD for Zn, Sn, Co and 6-311+G(d, p) for other atoms were used for single-point energy calculations. Moreover, M06[19] functional was also used for solvation single-point energy calculation. The corresponding results are summarized in Figure S2. Comparison between the computational results suggest that these two functionals afford similar computational data. The optimized transition state structures were plotted using CYLview.[20]

2. (U)B3LYP-calculated singlet free energy profile of cobalt(I)-catalyzed C–O oxidative addition

In our DFT studies, both singlet and triplet spin states have been considered for the Co(I) bromide complex. As shown in Figure S1, the relative free energy of the singlet structure is 29.7 kcal/mol higher than that of the triplet structure. Moreover, the activation free energy of singlet C–O oxidative addition transition state **^{1}TS-1** is determined to be 42.5 kcal/mol with respect to **^{3}99**. This energy barrier is 28.8 kcal/mol higher than the corresponding triplet transition state **^{3}TS-1**. Therefore, the C–O oxidative addition prefers to occur through the triplet free energy profile.

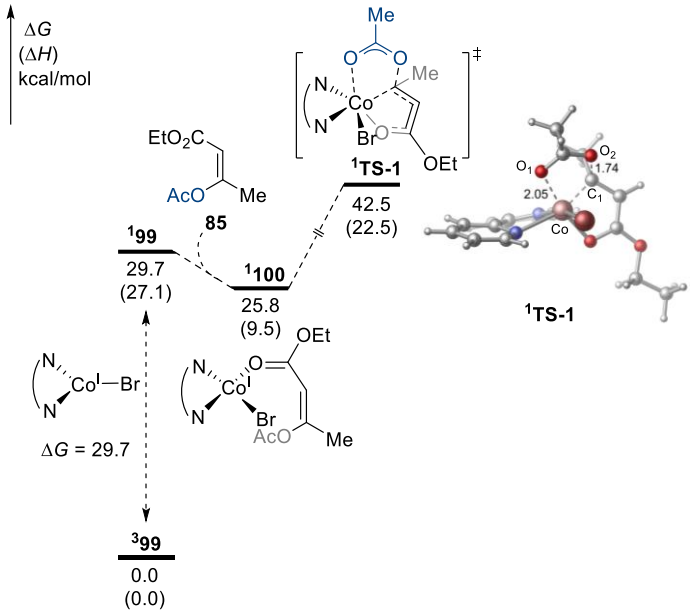
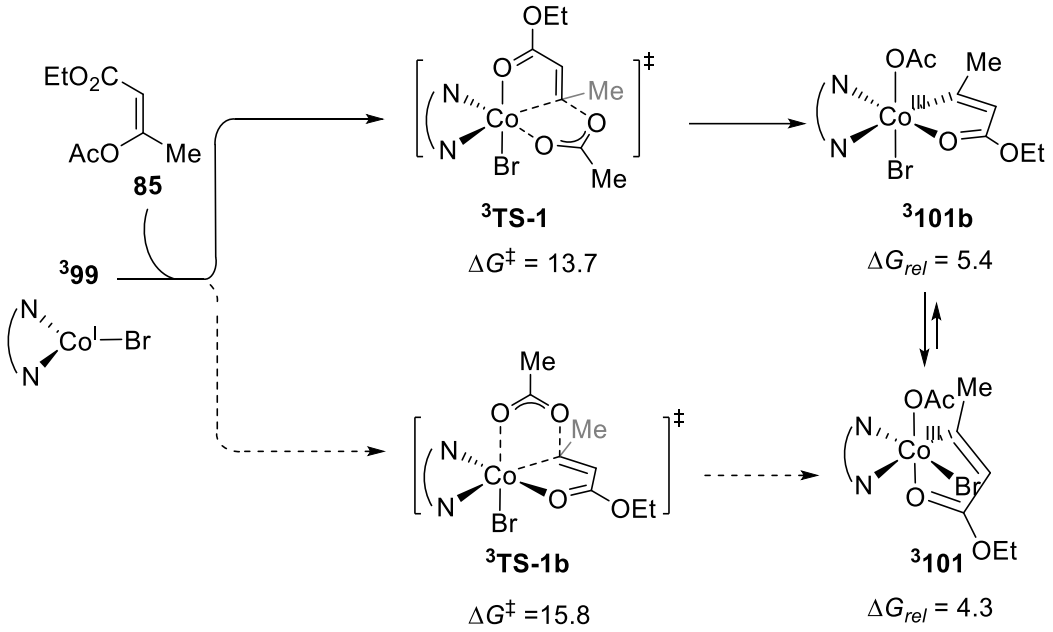


Figure S1. Singlet free energy profile of cobalt(I)-catalyzed C–O oxidative addition. Bipyridine ligand is used in DFT calculation. The energies were calculated at (U)B3LYP-D3/6-311+G(d,p)–SDD/SMD(acetonitrile)//(U)B3LYP-D3/6-31G(d)–LANL2DZ level of theory. All energies are with respect to triplet Co(I) complex **^{3}99**.

3. Conformations for the C–O oxidative addition transition state

As shown below, different conformations have been considered for the C–O oxidative addition transition state and the corresponding Co(III) intermediate. The most stable conformation was used for energy discussion in the main text.



4. M06-calculated free energy profile of cobalt-catalyzed cross-coupling reaction

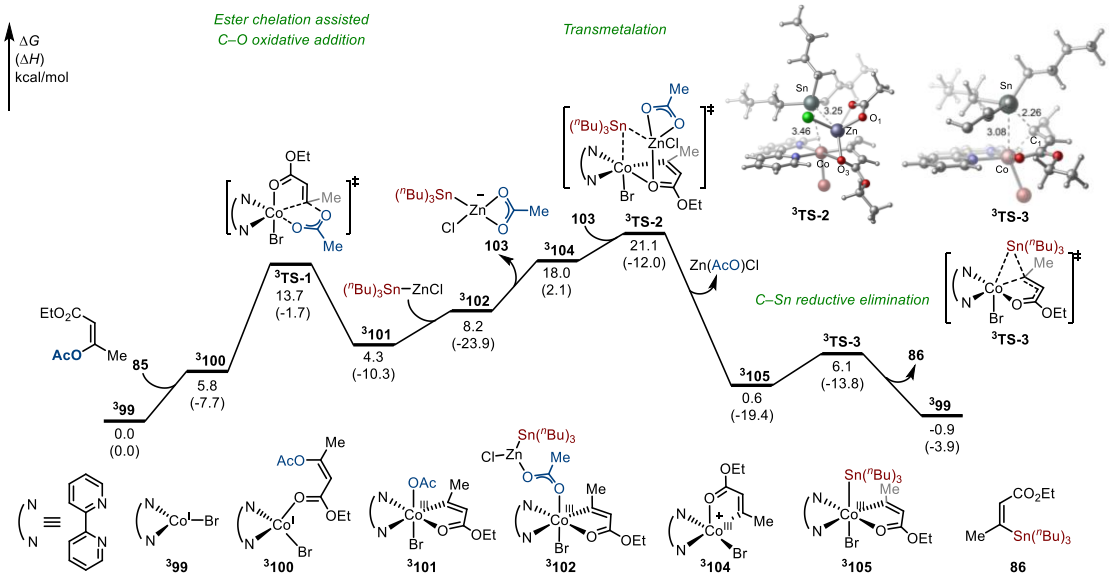


Figure S2. Free energy profile of cobalt(I)-catalyzed cross-coupling reaction of alkenyl acetate **85** with (^{n}Bu)$_3$Sn–ZnCl. Bipyridine ligand is used in DFT calculation. The energies were calculated at (U)M06/6-311+G(d,p)–SDD/SMD(acetonitrile)//(U)B3LYP-D3/6-31G(d)–LANL2DZ level of theory. All energies are with respect to triplet Co(I) complex ^{3}**99**.

5. M06-calculated singlet free energy profile of cobalt(I)-catalyzed C–O oxidative addition

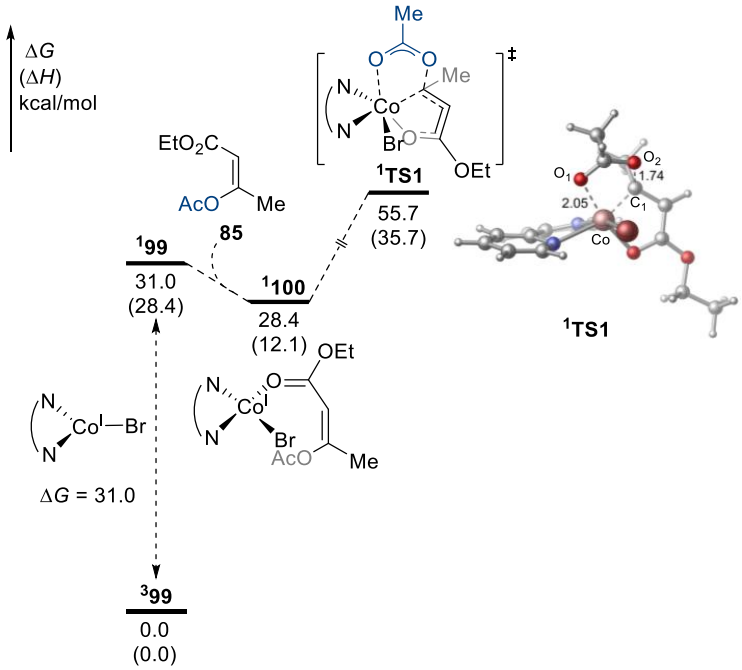


Figure S3. Free energy profile of cobalt(I)-catalyzed cross-coupling reaction of alkenyl acetate **85** with (^{n}Bu)$_3$Sn–ZnCl. Bipyridine ligand is used in DFT calculation. The energies were calculated at (U)M06/6-311+G(d,p)–SDD/SMD(acetonitrile)//(U)B3LYP-D3/6-31G(d)–LANL2DZ level of theory. All energies are with respect to triplet Co(I) complex ^{3}**99**.

6. Cartesian coordinates (Å) and energies of optimized structures

^{3}99

B3LYP SCF energy: -3212.01457958 a.u.

B3LYP enthalpy: -3211.840419 a.u.

B3LYP free energy: -3211.897773 a.u.

B3LYP SCF energy in solution: -3215.69263911 a.u.

B3LYP enthalpy in solution: -3215.518479 a.u.

B3LYP free energy in solution: -3215.575833 a.u.

M06 SCF energy in solution: -3215.12035339 a.u.

M06 enthalpy in solution: -3214.946193 a.u.

M06 free energy in solution: -3215.003547 a.u.

Cartesian coordinates

ATOM X Y Z

C -1.817609 -0.734449 0.000059

C	-0.478946	-2.642737	0.000773
C	-1.585093	-3.481177	0.000354
C	-2.860674	-2.906489	-0.000317
C	-2.975056	-1.521457	-0.000447
C	-1.816756	0.735781	0.000126
C	-0.475795	2.642506	0.000689
C	-1.580931	3.482213	0.000256
C	-2.857235	2.909050	-0.000237
C	-2.973275	1.524177	-0.000261
H	0.533284	-3.034339	0.001264
H	-1.449983	-4.557302	0.000518
H	-3.749761	-3.529086	-0.000742
H	-3.954278	-1.056845	-0.000965
H	0.536921	3.032831	0.001217
H	-1.444586	4.558184	0.000282
H	-3.745552	3.532744	-0.000578
H	-3.953042	1.060716	-0.000567
N	-0.579130	1.300083	0.000611
N	-0.580651	-1.300269	0.000585
Co	0.989012	-0.000464	-0.000516
Br	3.290581	-0.001074	-0.000023

85

B3LYP SCF energy: -613.00866752 a.u.

B3LYP enthalpy: -612.798793 a.u.

B3LYP free energy: -612.856045 a.u.

B3LYP SCF energy in solution: -613.22032621 a.u.

B3LYP enthalpy in solution: -613.010452 a.u.

B3LYP free energy in solution: -613.067704 a.u.

M06 SCF energy in solution: -612.79744408 a.u.

M06 enthalpy in solution: -612.587570 a.u.

M06 free energy in solution: -612.644822 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.611123	-0.813319	-0.288255
C	-0.662837	-1.717152	-0.006644
H	-0.978577	-2.727605	0.226029
C	0.801332	-1.548779	0.050752
O	1.554151	-2.481457	0.262357
O	1.233950	-0.279876	-0.133700
C	2.661981	-0.100404	-0.027140
C	2.946856	1.379417	-0.192859
H	3.153196	-0.703618	-0.797113
H	2.992613	-0.475050	0.946228
H	4.022931	1.563846	-0.105894
H	2.617794	1.733858	-1.175520
H	2.434023	1.962241	0.579041
C	-3.080854	-1.081344	-0.268183
H	-3.294553	-2.131405	-0.056113
H	-3.550759	-0.461196	0.505512
H	-3.532189	-0.808290	-1.229241
C	-1.086357	1.421905	0.292480
O	-1.233342	1.201311	1.467211
O	-1.302639	0.481242	-0.685362
C	-0.668206	2.722256	-0.338599
H	0.280547	2.577908	-0.863520
H	-1.410385	3.041079	-1.077135

H -0.556352 3.482985 0.434365

^{3}100

B3LYP SCF energy: -3825.05822185 a.u.

B3LYP enthalpy: -3824.672649 a.u.

B3LYP free energy: -3824.765791 a.u.

B3LYP SCF energy in solution: -3828.92669728 a.u.

B3LYP enthalpy in solution: -3828.541124 a.u.

B3LYP free energy in solution: -3828.634266 a.u.

M06 SCF energy in solution: -3827.93029983 a.u.

M06 enthalpy in solution: -3827.544727 a.u.

M06 free energy in solution: -3827.637869 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.583921	0.977605	0.670090
C	-3.327832	-0.091655	1.443712
H	-4.143231	-0.517095	2.017265
C	-2.043708	-0.792936	1.515108
O	-0.940639	-0.261258	1.372425
O	-2.200003	-2.085294	1.800051
C	-0.999677	-2.902357	1.807495
C	-1.420166	-4.307987	2.184411
H	-0.290659	-2.472604	2.521915
H	-0.563408	-2.856630	0.805588
H	-0.541865	-4.962262	2.196794
H	-1.881788	-4.329552	3.176866
H	-2.135267	-4.704693	1.457483
C	-4.910007	1.672561	0.631864

H	-5.562685	1.295467	1.422684
H	-4.766621	2.750583	0.773378
H	-5.389549	1.526858	-0.338972
C	-2.758503	1.647478	-1.471509
O	-3.769178	1.307337	-2.027897
O	-2.571819	1.525141	-0.098933
C	-1.526609	2.207664	-2.119109
H	-1.014226	2.923661	-1.473556
H	-0.850153	1.365694	-2.311726
H	-1.801217	2.664980	-3.070951
C	3.307900	0.287262	0.101153
C	2.962097	-1.948939	-0.489775
C	4.320178	-2.175381	-0.637906
C	5.205709	-1.108263	-0.417023
C	4.694133	0.128110	-0.054296
C	2.657893	1.537019	0.490403
C	0.605936	2.595810	0.871497
C	1.226455	3.754090	1.303517
C	2.631032	3.806167	1.312294
C	3.343626	2.686287	0.911665
H	2.225632	-2.721311	-0.688521
H	4.679696	-3.155430	-0.932546
H	6.275901	-1.243086	-0.539924
H	5.360229	0.969826	0.098388
H	-0.473837	2.495044	0.851878
H	0.629847	4.600104	1.628346
H	3.151547	4.699993	1.641287
H	4.427516	2.692013	0.940008
N	1.290981	1.510109	0.447914

N	2.456225	-0.756159	-0.119705
Br	-0.662044	-1.485462	-1.846108
Co	0.487079	-0.223358	-0.168373

^{3}TS-1

B3LYP SCF energy: -3825.03616094 a.u.

B3LYP enthalpy: -3824.652866 a.u.

B3LYP free energy: -3824.742978 a.u.

B3LYP SCF energy in solution: -3828.91496379 a.u.

B3LYP enthalpy in solution: -3828.531669 a.u.

B3LYP free energy in solution: -3828.621781 a.u.

Imaginary frequency: -138.7608 cm-1

M06 SCF energy in solution: -3827.91127605 a.u.

M06 enthalpy in solution: -3827.527981 a.u.

M06 free energy in solution: -3827.618093 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.787506	-0.878144	-1.281245
C	-2.522119	0.272476	-1.123036
H	-3.253347	0.601737	-1.859001
C	-2.373998	0.982760	0.108098
O	-1.453145	0.747098	0.920887
O	-3.277049	1.949821	0.342474
C	-3.109798	2.699119	1.562832
C	-4.195394	3.757692	1.591768
H	-2.106457	3.137549	1.576804
H	-3.182986	2.013906	2.413228
H	-4.111146	4.353800	2.506864

H	-4.107684	4.429009	0.731464
H	-5.187861	3.296789	1.568680
C	-1.800453	-1.712563	-2.515730
H	-1.254813	-1.188340	-3.308494
H	-1.299148	-2.666800	-2.359849
H	-2.832763	-1.890719	-2.845165
C	-1.787049	-2.612729	0.878447
O	-0.652568	-2.110142	1.133232
O	-2.536229	-2.258852	-0.072193
C	-2.266377	-3.739599	1.774252
H	-2.135799	-3.455500	2.822524
H	-3.310413	-3.984801	1.575076
H	-1.643809	-4.621895	1.588945
C	2.287168	0.886519	0.982541
C	1.831422	-0.982702	2.288124
C	2.924543	-0.733855	3.115433
C	3.718197	0.379748	2.848933
C	3.397688	1.201572	1.771615
C	1.868460	1.678591	-0.197451
C	0.314967	1.894315	-1.907456
C	0.963420	3.009841	-2.431484
C	2.116561	3.463175	-1.794613
C	2.575189	2.791339	-0.665289
H	1.168159	-1.828735	2.428467
H	3.143424	-1.400029	3.942845
H	4.579189	0.608362	3.469762
H	4.006352	2.070643	1.553155
H	-0.588921	1.492896	-2.352661
H	0.573780	3.500264	-3.316894

H	2.657240	4.325506	-2.172657
H	3.475011	3.126379	-0.163844
N	0.752902	1.251953	-0.822292
N	1.527589	-0.191305	1.255587
Br	1.468844	-1.808436	-1.637869
Co	-0.056985	-0.622890	-0.079131

^{3}TS-1b

B3LYP SCF energy: -3825.03194339 a.u.

B3LYP enthalpy: -3824.648897 a.u.

B3LYP free energy: -3824.739715 a.u.

B3LYP SCF energy in solution: -3828.91061102 a.u.

B3LYP enthalpy in solution: -3828.527565 a.u.

B3LYP free energy in solution: -3828.618383 a.u.

M06 SCF energy in solution: -3827.90603785 a.u.

M06 enthalpy in solution: -3827.522991 a.u.

M06 free energy in solution: -3827.613809 a.u.

Imaginary frequency: -213.4343 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-1.303344	-2.016639	-0.359223
C	-2.559484	-1.505595	-0.612024
H	-3.255052	-1.996523	-1.287844
C	-2.869872	-0.225996	-0.085391
O	-2.011034	0.517237	0.459565
O	-4.140203	0.187195	-0.226704
C	-4.429719	1.536344	0.181707
C	-5.889278	1.798116	-0.137953

H	-3.765201	2.220941	-0.356092
H	-4.222568	1.639622	1.252242
H	-6.160145	2.817560	0.157825
H	-6.076410	1.686406	-1.210479
H	-6.536043	1.097488	0.399677
C	-0.746348	-3.205875	-1.067635
H	-1.511391	-3.981094	-1.212195
H	-0.383044	-2.877525	-2.047744
H	0.081716	-3.656859	-0.514479
C	-0.533949	-1.960833	2.226035
O	0.142105	-0.941559	1.932896
O	-1.234360	-2.632809	1.404533
C	-0.546133	-2.427820	3.668443
H	-1.217045	-1.774056	4.237381
H	-0.903140	-3.455721	3.748279
H	0.455137	-2.332756	4.096067
C	2.901108	0.415460	0.164187
C	2.676191	-1.825271	-0.378572
C	4.053763	-1.996892	-0.492996
C	4.875189	-0.894980	-0.263946
C	4.294358	0.325522	0.067376
C	2.189492	1.674408	0.492999
C	0.112626	2.676493	0.793268
C	0.690163	3.916833	1.055569
C	2.079636	4.017822	1.030364
C	2.839875	2.886557	0.746015
H	1.988580	-2.643516	-0.560461
H	4.463696	-2.965238	-0.758799
H	5.954432	-0.980759	-0.345626

H	4.919959	1.192490	0.242107
H	-0.960432	2.518641	0.787588
H	0.063761	4.775925	1.269923
H	2.569890	4.966523	1.226979
H	3.920701	2.953732	0.719773
N	0.846110	1.593205	0.523455
N	2.118484	-0.657552	-0.057570
Br	0.066370	0.149111	-2.412964
Co	-0.057786	-0.264451	0.022842

^{3}101

B3LYP SCF energy: -3825.05094459 a.u.

B3LYP enthalpy: -3824.665862 a.u.

B3LYP free energy: -3824.757340 a.u.

B3LYP SCF energy in solution: -3828.93035445 a.u.

B3LYP enthalpy in solution: -3828.545272 a.u.

B3LYP free energy in solution: -3828.636750 a.u.

M06 SCF energy in solution: -3827.92730618 a.u.

M06 enthalpy in solution: -3827.542224 a.u.

M06 free energy in solution: -3827.633702 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.159104	-1.837201	-0.694173
C	-2.488043	-1.663722	-0.576110
H	-3.211902	-2.434935	-0.832173
C	-2.959353	-0.372144	-0.126538
O	-2.189356	0.564544	0.140173
O	-4.286168	-0.248227	-0.030077

C	-4.783416	1.037912	0.400727
C	-6.296391	0.947989	0.430323
H	-4.429364	1.802096	-0.298405
H	-4.364141	1.262947	1.386618
H	-6.719093	1.905380	0.753327
H	-6.691012	0.712517	-0.562927
H	-6.626224	0.170924	1.126897
C	-0.487830	-3.072996	-1.170760
H	-1.222268	-3.793338	-1.556295
H	0.221408	-2.834830	-1.970511
H	0.058513	-3.521800	-0.335176
C	0.205867	-1.941684	2.266936
O	-0.284900	-0.865827	1.723611
O	0.810236	-2.844029	1.684849
C	-0.043076	-2.002457	3.771551
H	-1.120781	-1.999517	3.967591
H	0.406035	-2.904235	4.191950
H	0.377220	-1.115185	4.257078
C	2.787823	0.545655	0.139013
C	2.697775	-1.728724	-0.292317
C	4.085585	-1.818211	-0.386178
C	4.839209	-0.661311	-0.208225
C	4.184495	0.536765	0.063185
C	2.002233	1.765598	0.435394
C	-0.129630	2.657048	0.702155
C	0.377635	3.922955	0.983177
C	1.759715	4.097817	0.983280
C	2.581656	3.009272	0.707669
H	2.065420	-2.598637	-0.390360

H	4.554249	-2.774875	-0.589347
H	5.922669	-0.687535	-0.274689
H	4.755536	1.445692	0.208659
H	-1.192565	2.450430	0.675278
H	-0.298092	4.744996	1.192470
H	2.196185	5.069143	1.195407
H	3.657912	3.129779	0.707851
N	0.663629	1.613287	0.437298
N	2.068766	-0.577498	-0.047406
Br	0.020336	0.236335	-2.454220
Co	-0.134356	-0.256974	-0.089181

^{3}101b

B3LYP SCF energy: -3825.04774376 a.u.

B3LYP enthalpy: -3824.662842 a.u.

B3LYP free energy: -3824.753441 a.u.

B3LYP SCF energy in solution: -3828.92924038 a.u.

B3LYP enthalpy in solution: -3828.544339 a.u.

B3LYP free energy in solution: -3828.634938 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.277152	-1.115468	1.621674
C	2.472247	-0.509794	1.465626
H	3.300887	-0.635931	2.160300
C	2.669424	0.262808	0.253989
O	1.758860	0.459894	-0.565006
O	3.904661	0.740806	0.075005
C	4.138065	1.468922	-1.152693

C	5.599520	1.870856	-1.165432
H	3.470539	2.336340	-1.178070
H	3.878389	0.822278	-1.995926
H	5.822837	2.427841	-2.081626
H	5.837351	2.506886	-0.306842
H	6.245168	0.987913	-1.131135
C	0.900189	-2.028894	2.727815
H	1.715989	-2.127442	3.456650
H	-0.011035	-1.680962	3.222242
H	0.664829	-3.013956	2.311264
C	-2.723989	-0.881924	1.381171
O	-1.489930	-1.307421	1.361527
O	-3.150087	0.161047	0.882062
C	-3.659144	-1.835422	2.120640
H	-3.661724	-2.808554	1.617285
H	-3.294830	-2.002585	3.140113
H	-4.673068	-1.430970	2.149818
C	-1.653205	1.302994	-1.223759
C	-1.542218	-0.712995	-2.376798
C	-2.361984	-0.231454	-3.395793
C	-2.824133	1.078478	-3.312537
C	-2.461589	1.857555	-2.216605
C	-1.241999	2.035299	-0.007163
C	-0.028397	1.928505	1.971080
C	-0.405932	3.217646	2.337482
C	-1.230842	3.932937	1.472179
C	-1.650031	3.338908	0.285674
H	-1.130405	-1.716977	-2.383034
H	-2.622237	-0.874167	-4.229569

H	-3.460979	1.493365	-4.087990
H	-2.817077	2.877160	-2.134939
H	0.622230	1.324678	2.593727
H	-0.061335	3.641002	3.274557
H	-1.550117	4.941105	1.718119
H	-2.301443	3.878715	-0.390161
N	-0.431388	1.362588	0.832309
N	-1.199145	0.036150	-1.326065
Br	0.756916	-2.691448	-0.788480
Co	-0.032560	-0.623874	0.243715

^{n}Bu3Sn-ZnCl

B3LYP SCF energy: -1002.84354332 a.u.

B3LYP enthalpy: -1002.448588 a.u.

B3LYP free energy: -1002.537159 a.u.

B3LYP SCF energy in solution: -1164.64253756 a.u.

B3LYP enthalpy in solution: -1164.247582 a.u.

B3LYP free energy in solution: -1164.336153 a.u.

M06 SCF energy in solution: -1164.13908601 a.u.

M06 enthalpy in solution: -1163.744131 a.u.

M06 free energy in solution: -1163.832702 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Zn	0.011577	0.007294	1.971103
Cl	0.027231	0.016525	4.194256
Sn	-0.006565	-0.002465	-0.699326
C	-1.912503	0.751549	-1.383573
C	-3.114867	0.088746	-0.699674

H	-1.961245	0.595905	-2.469954
H	-1.932787	1.836941	-1.223644
C	-4.467146	0.602044	-1.210499
H	-3.072779	-1.001629	-0.839288
H	-3.060821	0.253417	0.387309
C	-5.658756	-0.058998	-0.512736
H	-4.511230	1.690965	-1.070091
H	-4.528797	0.430434	-2.294143
H	-6.611075	0.324619	-0.895274
H	-5.651272	-1.145465	-0.663589
H	-5.634449	0.124851	0.568290
C	0.286094	-2.032172	-1.381913
C	1.471505	-2.738107	-0.711218
H	0.431265	-2.000781	-2.470303
H	-0.640918	-2.593034	-1.208029
C	1.699756	-4.166495	-1.221484
H	2.391753	-2.154658	-0.863264
H	1.315786	-2.771885	0.377980
C	2.878342	-4.863771	-0.536856
H	0.781842	-4.750782	-1.068286
H	1.865514	-4.135992	-2.307329
H	3.019864	-5.880841	-0.918907
H	3.812255	-4.312250	-0.700679
H	2.720757	-4.932611	0.546406
C	1.596040	1.264843	-1.404383
C	1.632387	2.639646	-0.724724
H	1.474875	1.382175	-2.489854
H	2.546731	0.738353	-1.252701
C	2.749126	3.551224	-1.248962

H	0.666410	3.149432	-0.856225
H	1.758619	2.513793	0.361540
C	2.780539	4.915743	-0.555466
H	3.714954	3.044262	-1.116345
H	2.621021	3.687326	-2.331815
H	3.585889	5.546716	-0.947499
H	1.835030	5.452998	-0.698928
H	2.937722	4.805719	0.524442

^{3}102

B3LYP SCF energy: -4827.96054531 a.u.

B3LYP enthalpy: -4827.178050 a.u.

B3LYP free energy: -4827.330042 a.u.

B3LYP SCF energy in solution: -4993.59706267 a.u.

B3LYP enthalpy in solution: -4992.814567 a.u.

B3LYP free energy in solution: -4992.966559 a.u.

M06 SCF energy in solution: -4992.08945976 a.u.

M06 enthalpy in solution: -4991.306964 a.u.

M06 free energy in solution: -4991.458956 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-3.324540	2.025487	0.754983
C	-4.344960	2.432913	-0.018727
H	-4.700685	3.460985	-0.043113
C	-5.010720	1.427857	-0.822018
O	-4.644365	0.240196	-0.827827
O	-6.044014	1.856678	-1.541981
C	-6.737318	0.865723	-2.339114

C	-7.864471	1.577478	-3.059498
H	-7.103344	0.079438	-1.671950
H	-6.020655	0.415646	-3.033029
H	-8.418023	0.862054	-3.676697
H	-8.559484	2.028347	-2.344577
H	-7.474419	2.366630	-3.709662
C	-2.541214	2.893019	1.670235
H	-2.964038	3.905635	1.708376
C	-0.931511	0.165113	-1.776315
O	-1.892800	0.741974	-1.175200
O	-0.363716	-0.889242	-1.380078
C	-0.471666	0.792811	-3.077237
H	0.619310	0.882041	-3.075949
H	-0.744591	0.127713	-3.904383
H	-0.926612	1.772145	-3.229142
C	-0.735761	-1.738693	1.442924
C	-0.209237	0.390614	2.192966
C	0.935271	-0.058796	2.847157
C	1.246952	-1.413085	2.774043
C	0.402600	-2.264325	2.064718
C	-1.674034	-2.566098	0.657086
C	-3.610302	-2.568883	-0.632916
C	-3.503537	-3.935629	-0.876051
C	-2.428308	-4.626291	-0.323693
C	-1.503598	-3.936552	0.455022
H	-0.481345	1.436760	2.210768
H	1.569273	0.643078	3.376378
H	2.143152	-1.804071	3.244033
H	0.645960	-3.313552	1.972188

H	-4.419607	-1.970812	-1.032953
H	-4.244852	-4.436107	-1.489334
H	-2.298870	-5.688901	-0.501884
H	-0.645627	-4.453848	0.859671
N	-2.716321	-1.908853	0.110520
N	-1.020467	-0.419199	1.508590
Br	-4.130927	-0.163693	2.500017
Co	-2.868897	0.112839	0.451793
Zn	1.534711	-1.410762	-0.850273
Cl	1.630167	-3.700540	-0.900982
Sn	3.221123	0.523962	-0.141632
C	4.510100	0.001494	1.530195
C	5.654012	1.002316	1.737165
H	4.914901	-1.004698	1.360285
H	3.902210	-0.063758	2.442289
C	6.571884	0.651778	2.916150
H	6.262147	1.065602	0.823458
H	5.245346	2.011915	1.894299
C	7.713605	1.654097	3.106738
H	5.970445	0.595728	3.834798
H	6.984082	-0.354919	2.760072
H	8.354067	1.381552	3.953398
H	8.346009	1.704237	2.211804
H	7.325248	2.663262	3.292379
C	2.288719	2.421110	0.392930
C	1.092528	2.772573	-0.496542
C	0.493424	4.163398	-0.254939
H	1.383747	2.704630	-1.555209
H	0.300052	2.025369	-0.358969

C	-0.710503	4.447151	-1.159781
H	0.199465	4.252145	0.801277
H	1.268778	4.925460	-0.412784
H	-1.160419	5.423092	-0.943700
H	-0.409777	4.446599	-2.214962
H	-1.485160	3.680277	-1.042409
C	4.607259	1.026825	-1.736790
C	5.518538	-0.142653	-2.129025
H	5.212712	1.881367	-1.404352
H	4.040638	1.373593	-2.611505
C	6.519946	0.199603	-3.239894
H	6.075827	-0.492690	-1.247267
H	4.908686	-0.999827	-2.452650
C	7.423277	-0.977811	-3.616810
H	5.967422	0.542148	-4.126278
H	7.135402	1.051084	-2.916581
H	8.128151	-0.708534	-4.411901
H	8.007674	-1.317551	-2.752754
H	6.830939	-1.831217	-3.969018
H	-2.536775	2.473886	2.681473
H	-1.505520	2.980145	1.325307
H	3.062244	3.196645	0.309141
H	1.986295	2.402090	1.448244

103

B3LYP SCF energy: -1231.46469061 a.u.

B3LYP enthalpy: -1231.014102 a.u.

B3LYP free energy: -1231.114210 a.u.

B3LYP SCF energy in solution: -1393.36224688 a.u.

B3LYP enthalpy in solution: -1392.911658 a.u.

B3LYP free energy in solution: -1393.011766 a.u.

M06 SCF energy in solution: -1392.72501534 a.u.

M06 enthalpy in solution: -1392.274427 a.u.

M06 free energy in solution: -1392.374535 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	3.676888	-0.407874	0.355360
O	3.397072	-0.062986	-0.835270
O	2.987244	-1.265697	0.986560
C	4.830704	0.280100	1.063943
H	4.454466	1.200872	1.526588
H	5.239070	-0.358934	1.850752
H	5.610248	0.555460	0.348821
Zn	1.626662	-1.334562	-0.710575
Cl	1.767957	-3.281715	-1.943718
Sn	-0.532772	0.204138	-0.202338
C	-2.249713	0.283936	-1.561526
C	-3.383893	1.186974	-1.064865
H	-2.624503	-0.737169	-1.717026
H	-1.898188	0.629340	-2.543904
C	-4.593380	1.251693	-2.009170
H	-3.729579	0.843312	-0.078477
H	-3.005819	2.208305	-0.906608
C	-5.718033	2.154007	-1.491457
H	-4.260189	1.605189	-2.995525
H	-4.978965	0.234100	-2.166221
H	-6.571054	2.184128	-2.181226

H	-6.086500	1.802513	-0.519168
H	-5.363148	3.183423	-1.353381
C	0.025924	2.319926	-0.028645
C	1.418363	2.522152	0.581517
C	1.837846	3.991701	0.722939
H	1.461959	2.049218	1.575423
H	2.163765	1.996195	-0.029073
C	3.240671	4.158270	1.316014
H	1.797692	4.471444	-0.265890
H	1.104998	4.522608	1.348720
H	3.527807	5.213804	1.407512
H	3.298859	3.708869	2.315991
H	3.989645	3.658843	0.689222
C	-1.543674	-0.169143	1.707839
C	-2.347977	-1.473020	1.721789
H	-2.206649	0.681889	1.922522
H	-0.791323	-0.186329	2.508047
C	-3.075907	-1.747052	3.045548
H	-3.091676	-1.461667	0.910195
H	-1.683018	-2.321572	1.501706
C	-3.879166	-3.051427	3.035882
H	-2.338240	-1.773191	3.860318
H	-3.744915	-0.902654	3.267854
H	-4.390160	-3.225852	3.991374
H	-4.641610	-3.036620	2.246481
H	-3.226259	-3.911780	2.843037
H	-0.732896	2.844913	0.570282
H	-0.006816	2.768485	-1.032323

^{3}104

B3LYP SCF energy: -3596.34305955 a.u.

B3LYP enthalpy: -3596.014358 a.u.

B3LYP free energy: -3596.092114 a.u.

B3LYP SCF energy in solution: -3600.19017808 a.u.

B3LYP enthalpy in solution: -3599.861477 a.u.

B3LYP free energy in solution: -3599.939233 a.u.

M06 SCF energy in solution: -3599.32657114 a.u.

M06 enthalpy in solution: -3598.997870 a.u.

M06 free energy in solution: -3599.075626 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.460303	0.186520	-1.718420
C	2.523466	0.674501	-1.055944
H	3.408755	1.078606	-1.542189
C	2.453534	0.602679	0.394088
O	1.402892	0.199772	0.955384
O	3.514442	0.977721	1.062871
C	3.471229	0.890249	2.524933
C	4.817824	1.349733	3.038729
H	3.249642	-0.146958	2.788407
H	2.648206	1.520980	2.871606
H	4.823654	1.296932	4.132058
H	5.620389	0.711143	2.658829
H	5.020162	2.383076	2.742353
C	1.246712	0.118558	-3.186844
H	2.004786	0.705468	-3.720956
C	-2.180958	1.366195	0.051475

C	-0.639989	2.463169	-1.320071
C	-1.415281	3.616442	-1.356435
C	-2.621271	3.626945	-0.658873
C	-3.003699	2.493516	0.054831
C	-2.494569	0.127616	0.799113
C	-1.734816	-2.005638	1.364915
C	-2.870594	-2.256113	2.131396
C	-3.847975	-1.267463	2.214956
C	-3.661734	-0.061539	1.539206
H	0.311833	2.408014	-1.832663
H	-1.075139	4.479364	-1.917310
H	-3.256254	4.506878	-0.662846
H	-3.931822	2.493556	0.612138
H	-0.949856	-2.742057	1.234078
H	-2.981102	-3.206855	2.640162
H	-4.750098	-1.429326	2.795898
H	-4.419865	0.709777	1.591761
N	-1.555549	-0.843817	0.724504
N	-1.013057	1.364091	-0.645250
Br	0.602299	-2.532597	-1.163556
Co	0.047006	-0.381709	-0.454846
H	1.302397	-0.923208	-3.519447
H	0.253136	0.487590	-3.469722

^{3}TS-2

B3LYP SCF energy: -4827.96513402 a.u.

B3LYP enthalpy: -4827.183488 a.u.

B3LYP free energy: -4827.334046 a.u.

B3LYP SCF energy in solution: -4993.57721640 a.u.

B3LYP enthalpy in solution: -4992.795570 a.u.

B3LYP free energy in solution: -4992.946128 a.u.

M06 SCF energy in solution: -4992.07602854 a.u.

M06 enthalpy in solution: -4991.294383 a.u.

M06 free energy in solution: -4991.444941 a.u.

Imaginary frequency: -47.5114 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-1.885595	1.043435	1.459072
C	-3.096849	1.632140	1.280830
H	-3.605273	2.177276	2.075382
C	-3.829440	1.494734	0.030605
O	-3.285365	1.227908	-1.065631
O	-5.132882	1.702226	0.122147
C	-5.908899	1.602589	-1.100383
C	-7.344423	1.929178	-0.743402
H	-5.801271	0.587035	-1.491972
H	-5.489623	2.298607	-1.832489
H	-7.970429	1.862299	-1.639456
H	-7.728754	1.226490	0.002085
H	-7.424318	2.943349	-0.340146
C	-1.170402	1.285708	2.763055
H	-1.792318	1.835604	3.481873
C	-0.310017	3.901129	-0.098493
O	-1.334620	3.751404	-0.838771
O	0.311638	2.893808	0.364089
C	0.193491	5.289017	0.221290
H	0.467701	5.352388	1.278003

H	1.099706	5.475141	-0.366760
H	-0.552908	6.045356	-0.026124
C	0.093968	-3.225076	0.129830
C	0.687033	-2.461009	2.242208
C	1.333289	-3.650224	2.553837
C	1.352102	-4.664779	1.596671
C	0.720572	-4.450943	0.376844
C	-0.654685	-2.940338	-1.112696
C	-2.165800	-1.525436	-2.167557
C	-2.201464	-2.329489	-3.302030
C	-1.401766	-3.468944	-3.338625
C	-0.621882	-3.780611	-2.229569
H	0.625731	-1.653916	2.960819
H	1.796353	-3.776694	3.526003
H	1.837061	-5.613804	1.801419
H	0.693875	-5.239305	-0.364577
H	-2.759755	-0.623732	-2.094260
H	-2.830208	-2.049942	-4.139780
H	-1.384146	-4.108895	-4.215236
H	0.010998	-4.659490	-2.239466
N	-1.401460	-1.813673	-1.105532
N	0.100432	-2.239727	1.056391
Br	-3.065752	-2.060829	1.885504
Co	-1.356115	-0.767023	0.700028
Zn	-1.220228	1.673402	-0.810236
Cl	-0.077208	0.898241	-2.702316
Sn	1.735205	0.416372	-0.318536
C	2.425681	-1.359481	-1.336668
C	3.385806	-2.210666	-0.500758

H	2.917860	-0.990144	-2.244691
H	1.571811	-1.948044	-1.676385
C	3.825712	-3.497485	-1.211331
H	4.279502	-1.624868	-0.240059
H	2.919808	-2.482557	0.454217
C	4.733646	-4.373841	-0.345521
H	2.928847	-4.064304	-1.498620
H	4.335577	-3.238482	-2.148973
H	5.033177	-5.289185	-0.868549
H	5.646931	-3.836615	-0.062643
H	4.224274	-4.666505	0.581203
C	2.227838	0.435752	1.801493
C	2.866682	1.756069	2.241760
C	3.135089	1.809934	3.751922
H	3.812368	1.918049	1.705933
H	2.210053	2.587633	1.960059
C	3.765394	3.133397	4.193784
H	2.187606	1.654794	4.287556
H	3.788612	0.973157	4.037011
H	3.941664	3.156280	5.275217
H	4.728033	3.297041	3.693907
H	3.114999	3.979838	3.941713
C	2.834917	2.059387	-1.175032
C	4.317109	1.699169	-1.341443
H	2.711008	2.916987	-0.508732
H	2.383846	2.318098	-2.136709
C	5.161832	2.872791	-1.858356
H	4.743877	1.360828	-0.384037
H	4.426928	0.853444	-2.035153

C	6.640014	2.514604	-2.032478
H	4.745121	3.215239	-2.815143
H	5.062549	3.716041	-1.161120
H	7.220566	3.368190	-2.400556
H	7.083030	2.194648	-1.081048
H	6.764636	1.692351	-2.747898
H	-0.870598	0.343950	3.239207
H	-0.262839	1.865375	2.566528
H	2.898073	-0.413647	1.990027
H	1.319140	0.259282	2.378424

ZnAcOCl

B3LYP SCF energy: -754.37135711 a.u.

B3LYP enthalpy: -754.310063 a.u.

B3LYP free energy: -754.353719 a.u.

B3LYP SCF energy in solution: -916.06375979 a.u.

B3LYP enthalpy in solution: -916.002466 a.u.

B3LYP free energy in solution: -916.046122 a.u.

M06 SCF energy in solution: -915.91431052 a.u.

M06 enthalpy in solution: -915.853016 a.u.

M06 free energy in solution: -915.896672 a.u.

Cartesian coordinates

ATOM	X	Y	Z
Zn	-0.520782	-0.000064	-0.001233
Cl	-2.695538	-0.001956	0.004647
O	1.196619	1.106623	-0.007441
C	1.845002	0.005806	-0.009110
O	1.196894	-1.097163	-0.007803

C	3.347120	-0.002645	0.008330
H	3.741814	0.984304	-0.234920
H	3.684320	-0.289292	1.011001
H	3.720632	-0.754487	-0.691449

^{3}105

B3LYP SCF energy: -4073.57313245 a.u.

B3LYP enthalpy: -4072.854222 a.u.

B3LYP free energy: -4072.981806 a.u.

B3LYP SCF energy in solution: -4077.52389992 a.u.

B3LYP enthalpy in solution: -4076.804989 a.u.

B3LYP free energy in solution: -4076.932573 a.u.

M06 SCF energy in solution: -4076.16795274 a.u.

M06 enthalpy in solution: -4075.449042 a.u.

M06 free energy in solution: -4075.576626 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	1.008763	0.698319	-1.905657
C	2.342062	0.438442	-1.866640
H	3.084392	0.988833	-2.442467
C	2.781579	-0.685636	-1.068988
O	1.993320	-1.485980	-0.542163
O	4.112936	-0.804981	-0.932704
C	4.583347	-1.957497	-0.203954
C	6.090417	-1.836040	-0.094527
H	4.278825	-2.861090	-0.742897
H	4.107578	-1.976544	0.780124
H	6.495158	-2.697593	0.447318

H	6.552527	-1.800672	-1.085936
H	6.365787	-0.925687	0.447835
C	0.464314	1.717209	-2.865366
H	1.256812	2.304530	-3.348666
H	-0.087004	1.182120	-3.649370
H	-0.233399	2.412330	-2.387946
C	-2.973627	-1.034704	-0.191511
C	-2.870450	0.693119	-1.737125
C	-4.245698	0.895367	-1.686524
C	-5.003291	0.085737	-0.839374
C	-4.362280	-0.891552	-0.085906
C	-2.197218	-2.045134	0.557774
C	-0.087904	-2.942888	0.957146
C	-0.599649	-3.875262	1.853556
C	-1.971371	-3.877198	2.103888
C	-2.779463	-2.957269	1.444690
H	-2.232253	1.284354	-2.383557
H	-4.706446	1.664137	-2.297119
H	-6.079220	0.210369	-0.768424
H	-4.937519	-1.529897	0.573212
H	0.964108	-2.890868	0.708400
H	0.065756	-4.580813	2.338868
H	-2.408712	-4.588193	2.798005
H	-3.848324	-2.951687	1.619033
N	-0.863967	-2.041714	0.337905
N	-2.250700	-0.237400	-1.002816
Br	-0.456883	-1.986542	-3.174835
Co	-0.149503	-0.716412	-1.122716
Sn	0.215905	1.155778	0.725463

C	-0.016877	3.250903	0.222075
C	1.280217	3.930419	-0.233699
H	-0.398793	3.744486	1.126808
H	-0.801507	3.373049	-0.535490
C	1.090417	5.395082	-0.647789
H	2.023446	3.880473	0.574973
H	1.723338	3.381063	-1.074084
C	2.393620	6.062204	-1.095694
H	0.352563	5.441821	-1.461497
H	0.654489	5.955161	0.191519
H	2.233347	7.104958	-1.392725
H	3.137327	6.054393	-0.289334
H	2.830941	5.533736	-1.951803
C	-1.300013	0.810592	2.254482
C	-2.613004	1.569601	2.022907
H	-0.855333	1.114592	3.212643
H	-1.490700	-0.264026	2.339534
C	-3.749104	1.119292	2.949990
H	-2.445089	2.647334	2.156197
H	-2.952157	1.453231	0.986257
C	-5.060723	1.865479	2.693984
H	-3.905713	0.039308	2.813042
H	-3.440398	1.251056	3.996183
H	-5.861690	1.520327	3.358014
H	-4.937725	2.943870	2.851546
H	-5.394798	1.720661	1.659095
C	2.121911	0.977207	1.732761
C	2.280058	-0.296385	2.570207
H	2.222617	1.865728	2.372970

H	2.924345	1.044391	0.989517
C	3.646450	-0.405684	3.259280
H	1.489970	-0.348854	3.333875
H	2.139805	-1.171901	1.925680
C	3.827046	-1.721211	4.021342
H	4.435762	-0.306998	2.500370
H	3.778307	0.443458	3.944069
H	4.807538	-1.778578	4.507612
H	3.060884	-1.835201	4.798262
H	3.738850	-2.581556	3.345114

^{3}TS-3

B3LYP SCF energy: -4073.56581319 a.u.

B3LYP enthalpy: -4072.848351 a.u.

B3LYP free energy: -4072.976137 a.u.

B3LYP SCF energy in solution: -4077.51353147 a.u.

B3LYP enthalpy in solution: -4076.796069 a.u.

B3LYP free energy in solution: -4076.923855 a.u.

M06 SCF energy in solution: -4076.16162815 a.u.

M06 enthalpy in solution: -4075.444166 a.u.

M06 free energy in solution: -4075.571952 a.u.

Imaginary frequency: -69.2747 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	0.703860	0.494536	-1.528208
C	1.799209	-0.283114	-1.885184
H	2.328308	-0.152416	-2.827233
C	2.186461	-1.391998	-1.044864

O	1.435529	-1.863136	-0.166659
O	3.411455	-1.889405	-1.272841
C	3.775656	-3.055560	-0.503699
C	5.116436	-3.536140	-1.022664
H	2.991276	-3.809863	-0.617649
H	3.823500	-2.777137	0.554956
H	5.437735	-4.419676	-0.460630
H	5.047438	-3.804903	-2.081237
H	5.879114	-2.758674	-0.911758
C	0.250380	1.543158	-2.527690
H	1.044776	2.267304	-2.749280
H	-0.020696	1.054276	-3.471532
H	-0.618569	2.106285	-2.176164
C	-3.327001	-0.320911	-0.006521
C	-2.983252	0.528694	-2.134802
C	-4.291977	0.995855	-2.220357
C	-5.140816	0.791233	-1.132768
C	-4.657851	0.112969	-0.018299
C	-2.741275	-1.107788	1.100625
C	-0.900911	-2.347232	1.801059
C	-1.529067	-2.709356	2.987115
C	-2.814144	-2.223623	3.234179
C	-3.430745	-1.424816	2.276375
H	-2.289918	0.631857	-2.960326
H	-4.633847	1.496685	-3.119638
H	-6.169250	1.137994	-1.157146
H	-5.312968	-0.084090	0.821564
H	0.092671	-2.691038	1.542210
H	-1.018568	-3.350732	3.697225

H	-3.334130	-2.471634	4.154304
H	-4.434459	-1.053616	2.444645
N	-1.477911	-1.544055	0.895483
N	-2.502444	-0.083538	-1.047937
Br	-1.069736	-2.618683	-2.647064
Co	-0.544209	-1.005981	-0.877040
Sn	0.834144	1.346901	0.558495
C	1.548712	3.297897	-0.046512
C	2.949956	3.258628	-0.668229
H	1.553391	3.931590	0.851706
H	0.834762	3.756940	-0.740823
C	3.446000	4.627565	-1.151556
H	3.667495	2.857141	0.062005
H	2.969131	2.557014	-1.514817
C	4.847969	4.572904	-1.764259
H	2.734073	5.024443	-1.889122
H	3.435727	5.332393	-0.308374
H	5.178244	5.560510	-2.105752
H	5.582221	4.208070	-1.035485
H	4.874568	3.894642	-2.626007
C	-0.894136	1.751150	1.786039
C	-1.935914	2.650844	1.106891
H	-0.508722	2.244872	2.689576
H	-1.350438	0.816536	2.121620
C	-3.196828	2.861258	1.954270
H	-1.489019	3.629064	0.879471
H	-2.233039	2.224860	0.140957
C	-4.244377	3.732528	1.257413
H	-3.630384	1.879303	2.190184

H	-2.915966	3.310158	2.917076
H	-5.138963	3.863850	1.877102
H	-3.843342	4.728862	1.035060
H	-4.555536	3.281207	0.307764
C	2.444278	0.520879	1.730074
C	2.059640	-0.560669	2.742840
H	2.897358	1.380557	2.245028
H	3.210030	0.140799	1.043176
C	3.234208	-1.042128	3.602490
H	1.257955	-0.198435	3.403601
H	1.652620	-1.417465	2.199942
C	2.834179	-2.155961	4.574108
H	4.036250	-1.399715	2.940675
H	3.654815	-0.193682	4.160243
H	3.683681	-2.493951	5.178255
H	2.049777	-1.815121	5.261517
H	2.442862	-3.026084	4.031631

86

B3LYP SCF energy: -861.52588857 a.u.

B3LYP enthalpy: -860.983670 a.u.

B3LYP free energy: -861.081121 a.u.

B3LYP SCF energy in solution: -861.80390863 a.u.

B3LYP enthalpy in solution: -861.261690 a.u.

B3LYP free energy in solution: -861.359141 a.u.

M06 SCF energy in solution: -861.02465455 a.u.

M06 enthalpy in solution: -860.482436 a.u.

M06 free energy in solution: -860.579887 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.176375	-0.128903	1.605075
C	-1.293624	0.592660	1.809728
H	-1.652790	0.858206	2.803731
C	-2.103453	1.062779	0.677491
O	-1.857982	0.831096	-0.502955
O	-3.167225	1.785626	1.068076
C	-4.016466	2.281779	0.009992
C	-5.142711	3.059397	0.661903
H	-4.383579	1.431301	-0.573154
H	-3.415309	2.905741	-0.658885
H	-5.814518	3.455675	-0.106956
H	-5.723518	2.416676	1.330979
H	-4.750240	3.898834	1.244474
C	0.631648	-0.617608	2.774660
H	0.201496	-0.320115	3.739080
H	0.714516	-1.712287	2.757558
H	1.660333	-0.238900	2.723503
Sn	0.488574	-0.620244	-0.414769
C	1.026675	1.145710	-1.521849
C	1.320022	2.352466	-0.619891
H	0.203896	1.380029	-2.205287
H	1.905944	0.912492	-2.136685
C	1.683425	3.620765	-1.401816
H	0.445976	2.561567	0.011297
H	2.141280	2.115451	0.072441
C	1.966191	4.821322	-0.494591
H	2.561062	3.416686	-2.031163

H	0.862418	3.861509	-2.091584
H	2.220734	5.715769	-1.074662
H	1.092532	5.061180	0.124184
H	2.802942	4.613744	0.183919
C	2.352037	-1.668648	-0.036896
C	3.531865	-0.738878	0.281727
H	2.590151	-2.270515	-0.925225
H	2.210313	-2.388173	0.781244
C	4.848942	-1.477718	0.551331
H	3.684644	-0.035089	-0.549254
H	3.297705	-0.112479	1.155921
C	6.014269	-0.533882	0.860499
H	4.703173	-2.174605	1.388701
H	5.094966	-2.098242	-0.321721
H	6.942525	-1.085200	1.049161
H	6.197216	0.152709	0.024631
H	5.802341	0.076576	1.747224
C	-0.871610	-1.997675	-1.355334
C	-1.852872	-2.648807	-0.371164
H	-0.282193	-2.768762	-1.868340
H	-1.425321	-1.447319	-2.124019
C	-2.841647	-3.608209	-1.045162
H	-1.301202	-3.197700	0.407004
H	-2.417589	-1.868110	0.154745
C	-3.824216	-4.243800	-0.057685
H	-3.396396	-3.060516	-1.819805
H	-2.281314	-4.395008	-1.569421
H	-4.523016	-4.921165	-0.561798
H	-3.293806	-4.821474	0.709528

H -4.415023 -3.476546 0.458002

^{1}99

B3LYP SCF energy: -3211.97432011 a.u.

B3LYP enthalpy: -3211.799646 a.u.

B3LYP free energy: -3211.852886 a.u.

B3LYP SCF energy in solution: -3215.64992773 a.u.

B3LYP enthalpy in solution: -3215.475254 a.u.

B3LYP free energy in solution: -3215.528494 a.u.

M06 SCF energy in solution: -3215.07553228 a.u.

M06 enthalpy in solution: -3214.900858 a.u.

M06 free energy in solution: -3214.954098 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.982511	-0.082243	-0.000137
C	-1.549359	-2.379142	0.000102
C	-2.903999	-2.673465	0.000030
C	-3.830476	-1.623526	-0.000278
C	-3.357894	-0.315471	-0.000401
C	-1.327776	1.219535	-0.000034
C	0.784295	2.235333	-0.000136
C	0.212315	3.499826	-0.000069
C	-1.181584	3.619783	0.000126
C	-1.956914	2.465334	0.000099
H	-0.795455	-3.160118	0.000072
H	-3.227129	-3.708805	0.000280
H	-4.896727	-1.823918	-0.000561
H	-4.048337	0.520959	-0.000724

H	1.855038	2.072749	-0.000068
H	0.852553	4.375101	-0.000189
H	-1.653542	4.596980	0.000305
H	-3.039652	2.525720	0.000294
N	0.033922	1.113766	-0.000073
N	-1.080204	-1.111933	-0.000038
Br	3.003280	-0.706114	-0.000245
Co	0.730586	-0.610863	0.000523

^{1}100

B3LYP SCF energy: -3825.03495033 a.u.

B3LYP enthalpy: -3824.648258 a.u.

B3LYP free energy: -3824.736871 a.u.

B3LYP SCF energy in solution: -3828.90045617 a.u.

B3LYP enthalpy in solution: -3828.513764 a.u.

B3LYP free energy in solution: -3828.602377 a.u.

M06 SCF energy in solution: -3827.90117348 a.u.

M06 enthalpy in solution: -3827.514481 a.u.

M06 free energy in solution: -3827.603094 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	3.907713	0.479496	-0.918183
C	3.675122	-0.116652	0.266079
H	4.514404	-0.535072	0.807461
C	2.358751	-0.327658	0.855998
O	1.317991	0.190049	0.428193
O	2.419444	-1.102501	1.931198
C	1.188979	-1.395874	2.645701

C	1.568791	-2.228057	3.852811
H	0.524620	-1.929169	1.961902
H	0.719466	-0.446837	2.923521
H	0.666765	-2.473235	4.423546
H	2.043449	-3.163355	3.540988
H	2.258260	-1.686988	4.509084
C	5.258494	0.620085	-1.538349
H	6.030498	0.133627	-0.938222
H	5.254352	0.182934	-2.543571
H	5.503757	1.684203	-1.646160
C	2.149822	2.048260	-1.327399
O	2.483736	2.779263	-0.430010
O	2.905086	0.960319	-1.725527
C	0.924046	2.150560	-2.183797
H	1.176483	2.023055	-3.239997
H	0.245859	1.334517	-1.898062
H	0.436166	3.110773	-2.013181
C	-2.564196	1.461653	0.414328
C	-0.500019	2.344339	1.053580
C	-1.084324	3.547039	1.417154
C	-2.467565	3.708753	1.278328
C	-3.208435	2.649563	0.768524
C	-3.214581	0.285482	-0.148224
C	-2.841052	-1.864255	-0.970372
C	-4.193298	-2.038893	-1.229598
C	-5.088127	-1.007060	-0.933257
C	-4.586476	0.167106	-0.386454
H	0.567037	2.189758	1.124656
H	-0.457482	4.346259	1.798046

H	-2.952624	4.639161	1.555316
H	-4.280979	2.741756	0.639047
H	-2.103978	-2.629062	-1.180224
H	-4.534094	-2.974851	-1.659340
H	-6.151125	-1.115976	-1.124371
H	-5.250513	0.988908	-0.143472
N	-2.342380	-0.727355	-0.436642
N	-1.213288	1.303612	0.560243
Br	0.399166	-2.459000	-0.762096
Co	-0.518644	-0.367020	-0.008181

^{1}TS-1

B3LYP SCF energy: -3825.00337960 a.u.

B3LYP enthalpy: -3824.618277 a.u.

B3LYP free energy: -3824.701029 a.u.

B3LYP SCF energy in solution: -3828.87821730 a.u.

B3LYP enthalpy in solution: -3828.493115 a.u.

B3LYP free energy in solution: -3828.575867 a.u.

M06 SCF energy in solution: -3827.86202289 a.u.

M06 enthalpy in solution: -3827.476920 a.u.

M06 free energy in solution: -3827.559672 a.u.

Imaginary frequency: -229.3499 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	1.160976	-0.194904	1.752796
C	2.504442	0.062138	1.330717
H	3.359594	0.057557	1.999871
C	2.601928	0.517107	0.025950

O	1.554074	0.696513	-0.726184
O	3.798790	0.867929	-0.476988
C	3.827242	1.303740	-1.848180
C	5.283526	1.526205	-2.211374
H	3.240379	2.223861	-1.950939
H	3.361333	0.539654	-2.477015
H	5.362936	1.863223	-3.250850
H	5.735576	2.285495	-1.564622
H	5.853803	0.598358	-2.102464
C	0.690991	0.407575	3.066584
H	0.862906	1.486132	3.088049
H	-0.369389	0.222322	3.260870
H	1.275454	-0.030309	3.885917
C	-0.431223	-2.091154	1.958864
O	-1.184623	-1.330131	1.282536
O	0.799305	-1.832729	2.201539
C	-0.970533	-3.398498	2.469338
H	-0.454697	-3.708400	3.380095
H	-2.047930	-3.328388	2.633166
H	-0.783965	-4.145781	1.689046
C	-2.666440	0.766269	-0.742653
C	-2.259392	-1.160827	-1.965046
C	-3.614016	-1.303919	-2.272047
C	-4.515820	-0.372066	-1.762403
C	-4.040663	0.680070	-0.980742
C	-2.031044	1.866059	0.017288
C	-0.053739	2.660011	0.956170
C	-0.591649	3.929023	1.142911
C	-1.916922	4.151316	0.774705

C	-2.636691	3.114305	0.189211
H	-1.501735	-1.872885	-2.279077
H	-3.948266	-2.136891	-2.881309
H	-5.579384	-0.465037	-1.960881
H	-4.726896	1.401069	-0.550667
H	0.974561	2.429994	1.204529
H	0.022664	4.718403	1.561469
H	-2.374472	5.126672	0.908719
H	-3.644429	3.279922	-0.172842
N	-0.767933	1.644479	0.452606
N	-1.806033	-0.144999	-1.231707
Br	0.849425	-2.237935	-0.925410
Co	0.069765	-0.174110	0.139342

***References*:**

[1] M. Dong, J. Wang, S. Wu, Y. Zhao, Y. Ma, Y. Xing, F. Cao, L. Li, Z. Li, H. Zhu, *Adv. Synth. Catal.* **2019**, *361*, 4602-4610.

[2] N. S. Y. Loy, S. Choi, S. Kim, C.-M. Park, *Chem. Commun.* **2016**, *52*, 7336-7339.

[3] L. A. Stubbing, F. F. Li, D. P. Furkert, V. E. Caprio, M. A. Brimble, *Tetrahedron.* **2012**, *68*, 6948-6956.

[4] G. Gu, J. Lu, O. Yu, J. Wen, Q. Yin, X. Zhang, *Org. Lett.* **2018**, *20*, 1888-1892.

[5] M. Hu, C. Ni, L. Li, Y. Han, J. Hu, *J. Am. Chem. Soc.* **2015**, *137*, 14496-14501.

[6] A. Bongers, C. Clavette, W. Gan, S. I. Gorelsky, L. Betit, K. Lavergne, T. Markiewicz, P. J. Moon, N. Das Neves, N. K. Obhi, A. B. Toderian, A. M. Beauchemin, *J. Org. Chem.* **2017**, *82*, 1175-1194.

[7] K. Chegaev, B. Rolando, D. Cortese, E. Gazzano, I. Buondonno, L. Lazzarato, M. Fanelli, C. M. Hattinger, M. Serra, C. Riganti, R. Fruttero, D. Ghigo, A. Gasco, *J. Med. Chem.* **2016**, *59*, 4881-4889.

[8] M. Kenny, J. Christensen, S. J. Coles, V. Franckevičius, *Org. Lett.* **2015**, *17*, 3926-3929.

[9] H. Zhang, X. Wu, Y. Wei, C. Zhu, *Org. Lett.* **2019**, *21*, 7568-7572.

[10] J. Li, Q. Ren, X. Cheng, K. Karaghiosoff, P. Knochel, *J. Am. Chem. Soc.* **2019**, *141*, 18127-18135.

[11] K. Gorlitzer, *Arch. Pharm. (Weinheim)* **1975**, *308*, 272-286.

[12] R.-D. He, C.-L. Li, Q.-Q. Pan, P. Guo, X.-Y. Liu, X.-Z. Shu, *J. Am. Chem. Soc.* **2019**, *141*, 12481-12486.

[13] F. Wang, W. Sun, Y. Wang, Y. Jiang, T.-P. Loh, *Org. Lett.* **2018**, *20*, 1256-1260.

[14] Y. Wang, L. Lu, D. J. Burton, *J. Org. Chem.* **2005**, *70*, 10743-10746.

[15] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; ; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., *Gaussian 16*, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2016.

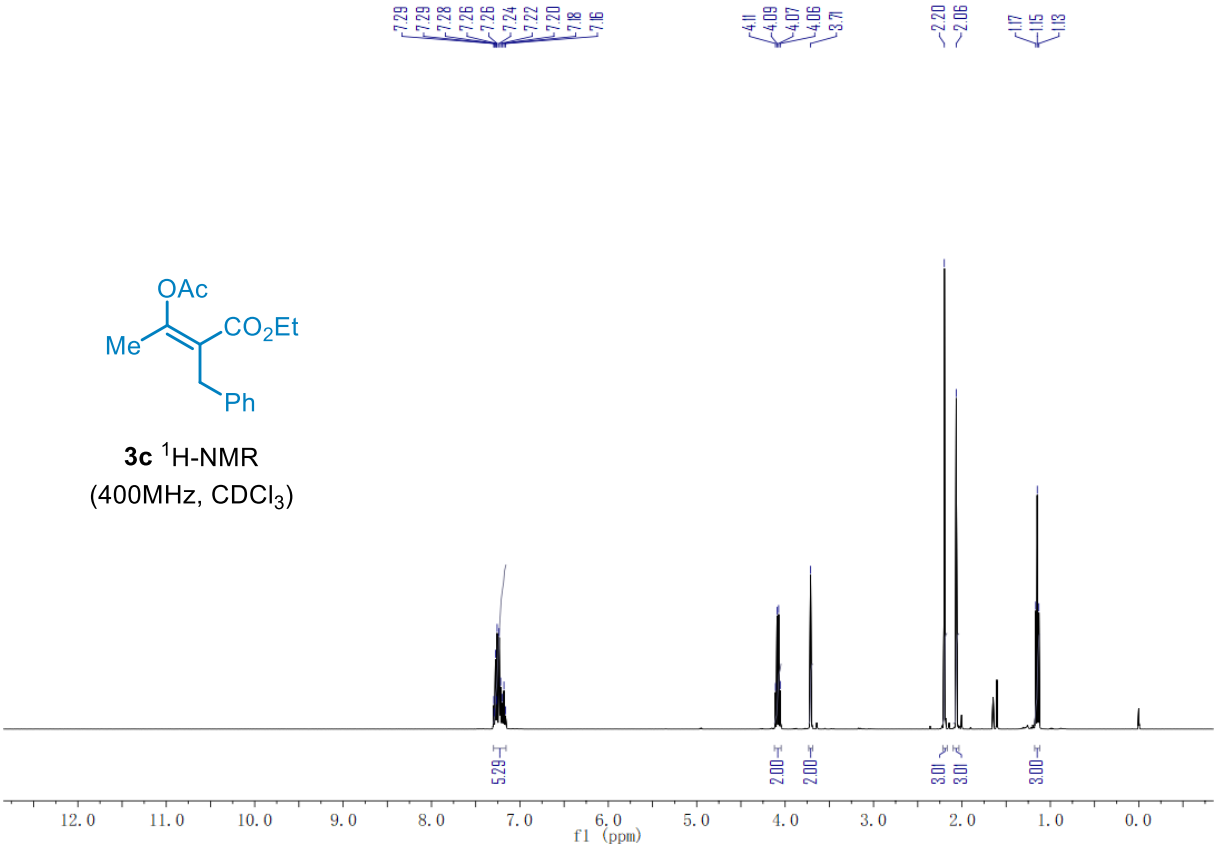
[16] a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

[17] a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.; b) Grimme, S.; Ehrlich, S.; Goerigk, L. *J. Comput. Chem.* **2011**, *32*, 1456-1465.

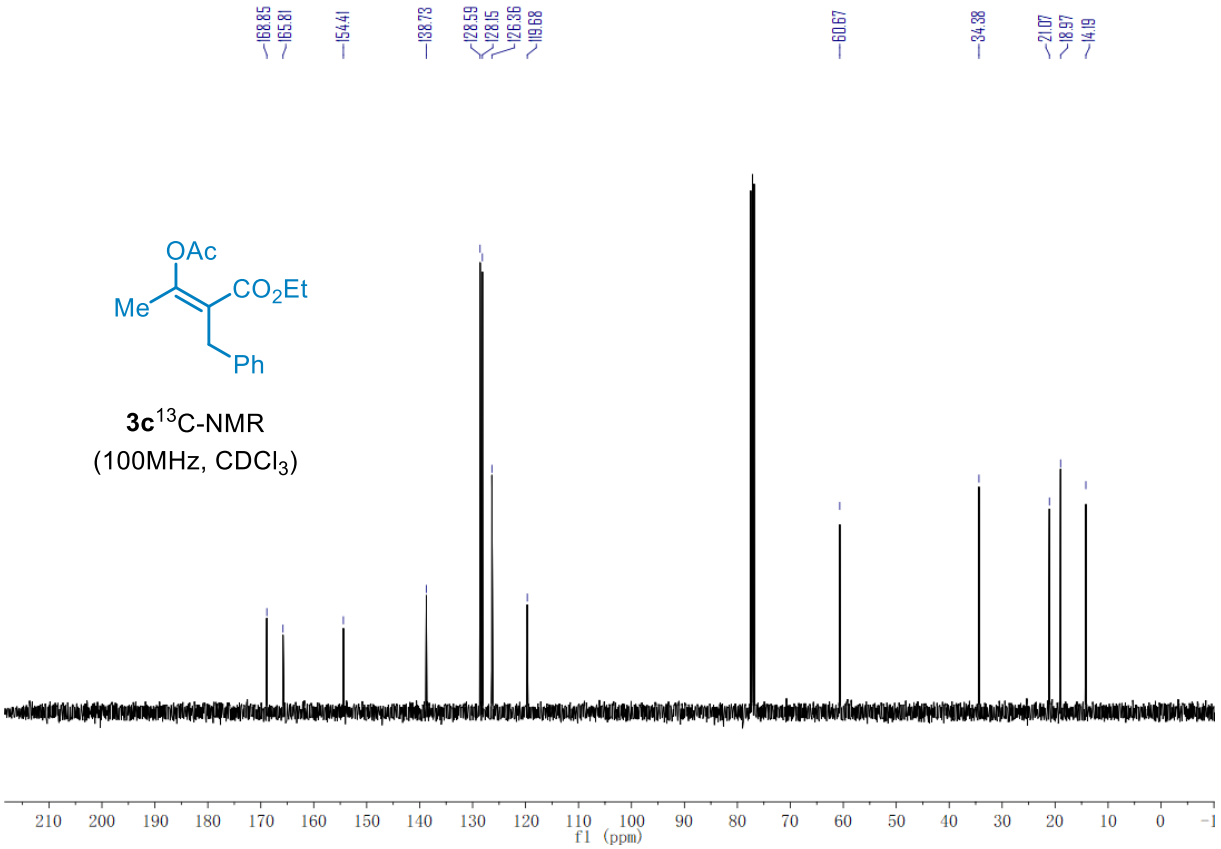
[18] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

[19] Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215-241.

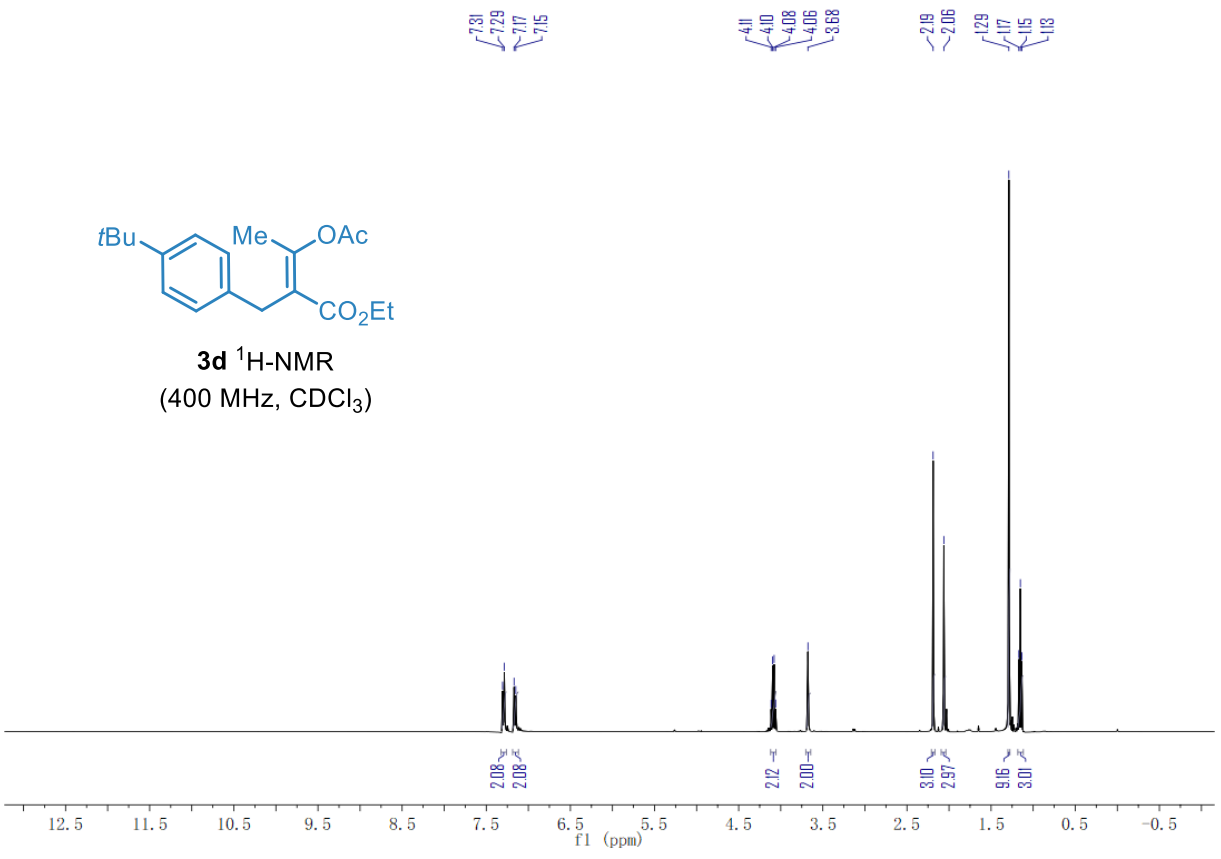
[20] Legault, C. Y. CYLView, 1.0b; Université de Sherbrooke: Canada, 2009, *http://www.cylview.org*.



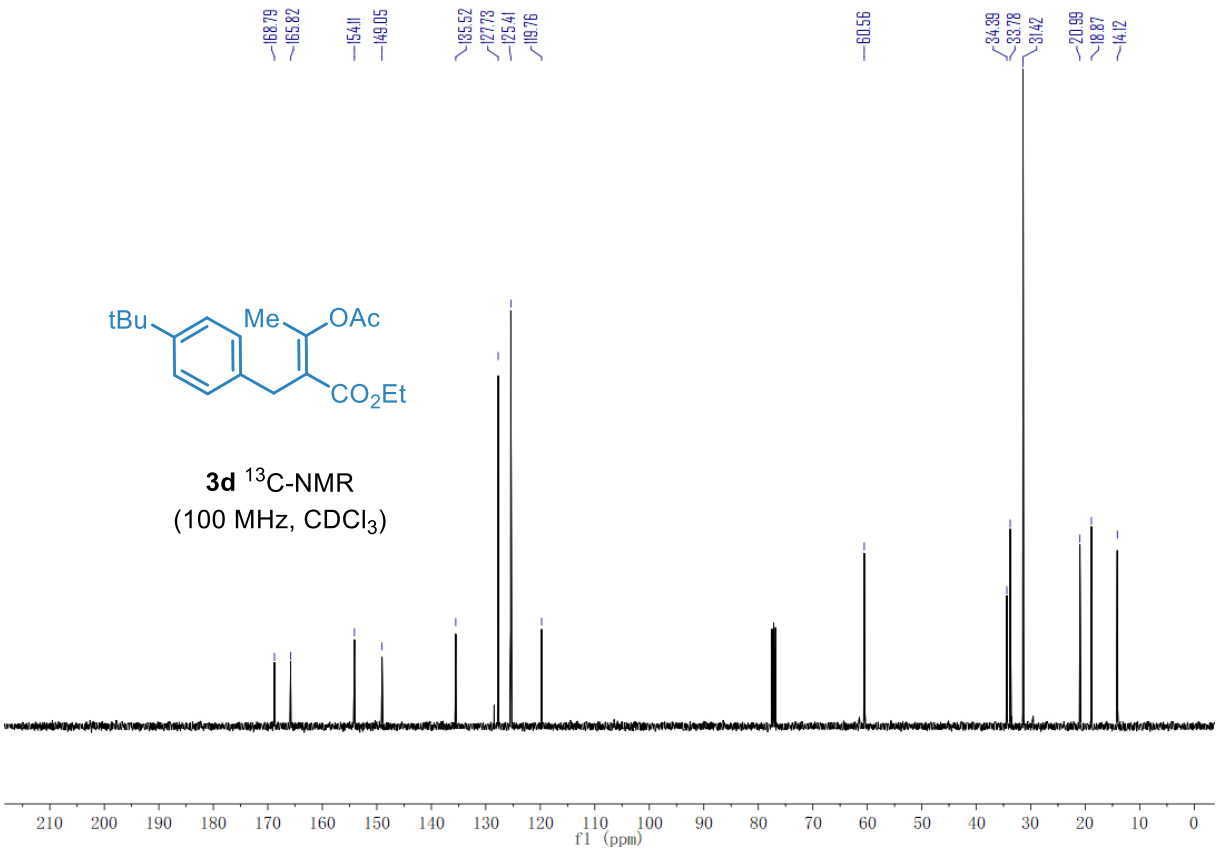
3c ^{1}H-NMR
(400MHz, $CDCl_3$)



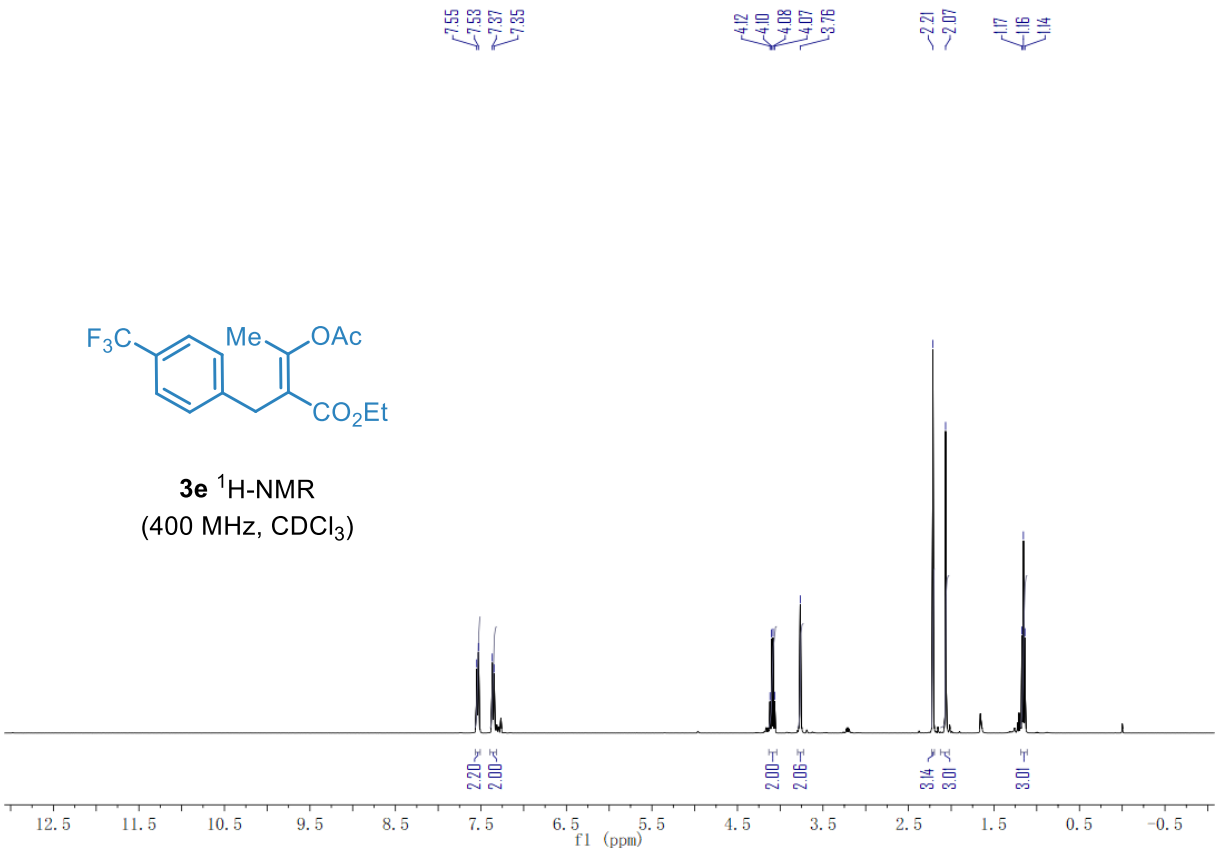
3c ^{13}C-NMR
(100MHz, $CDCl_3$)



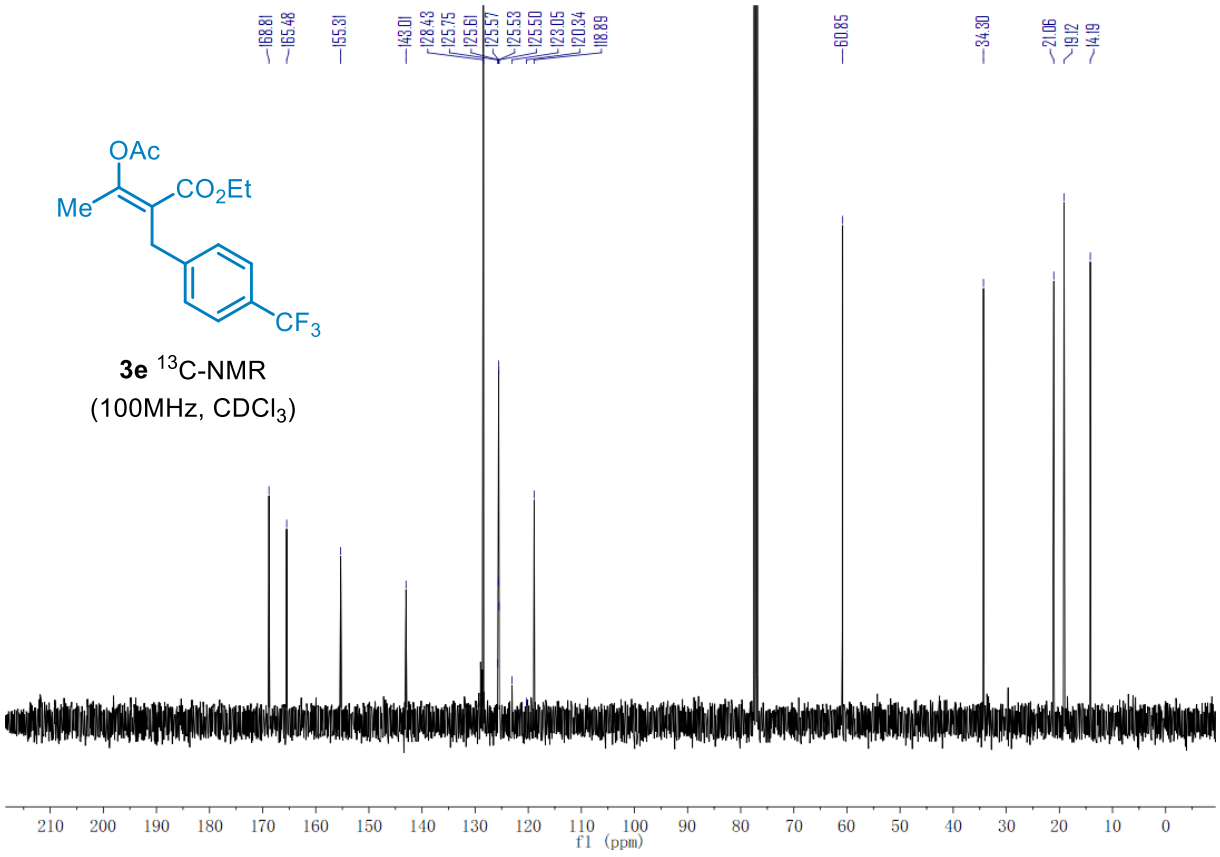
3d ^{1}H-NMR
(400 MHz, $CDCl_3$)



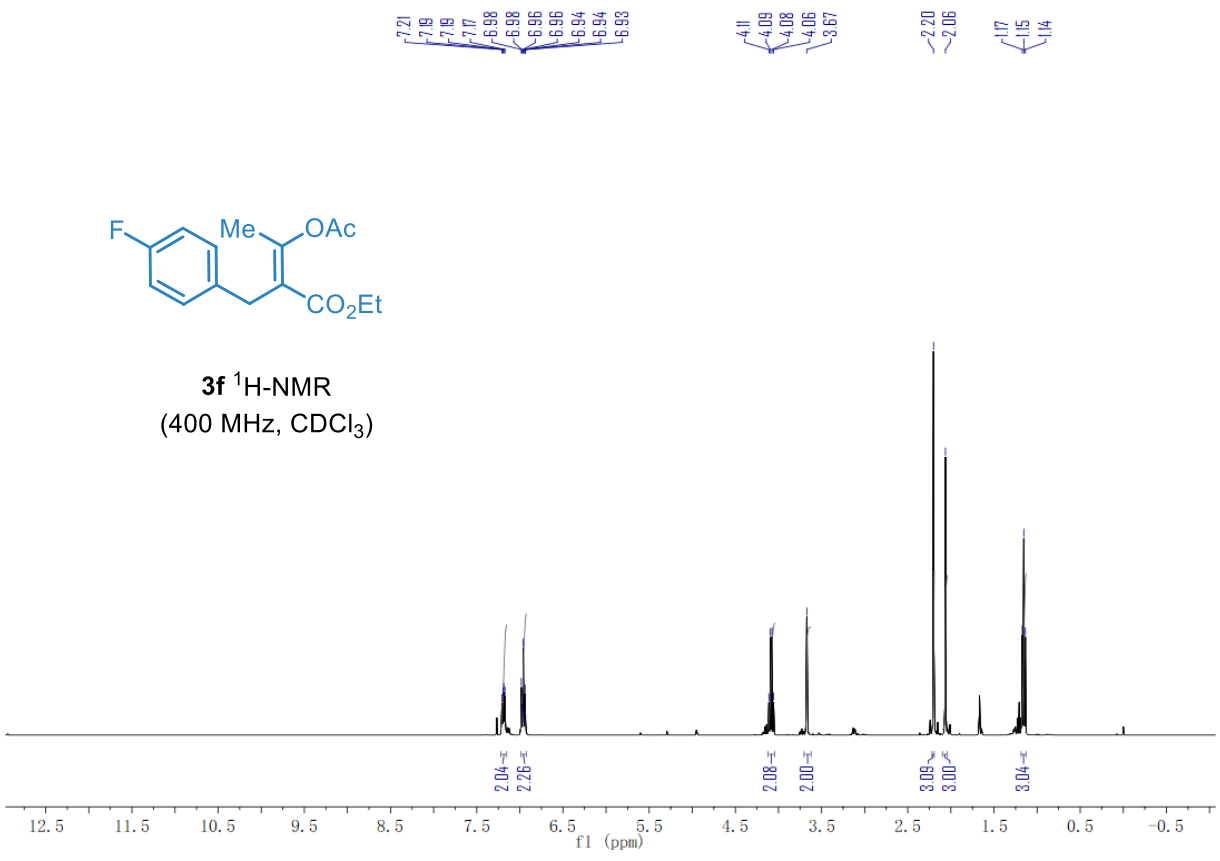
3d ^{13}C-NMR
(100 MHz, $CDCl_3$)



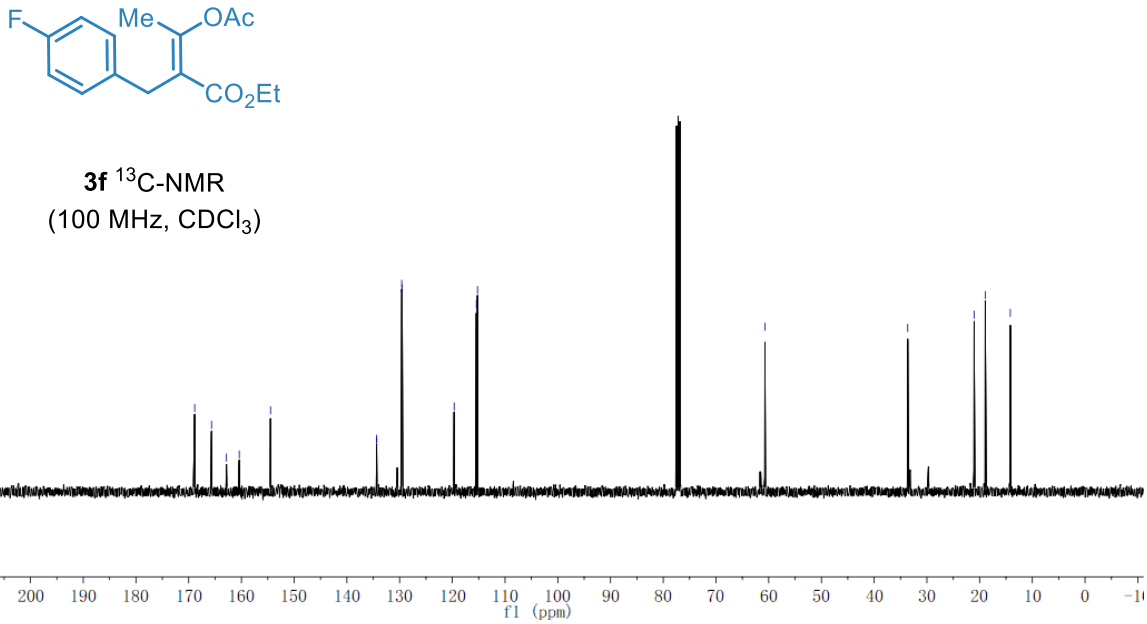
3e ^{1}H-NMR
(400 MHz, $CDCl_3$)



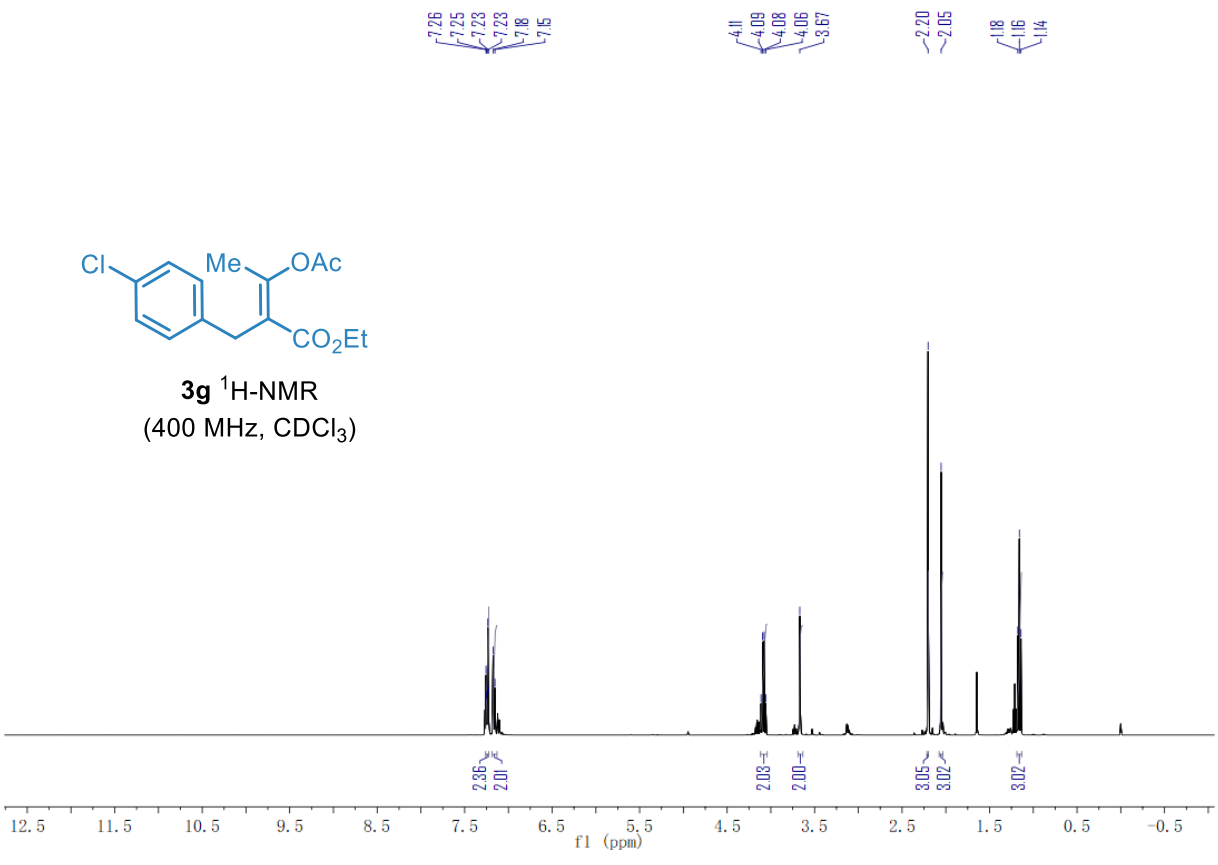
3e ^{13}C-NMR
(100MHz, $CDCl_3$)



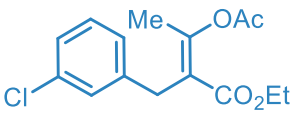
3f ^{1}H-NMR
(400 MHz, $CDCl_3$)



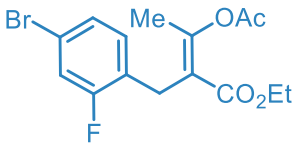
3f ^{13}C-NMR
(100 MHz, $CDCl_3$)



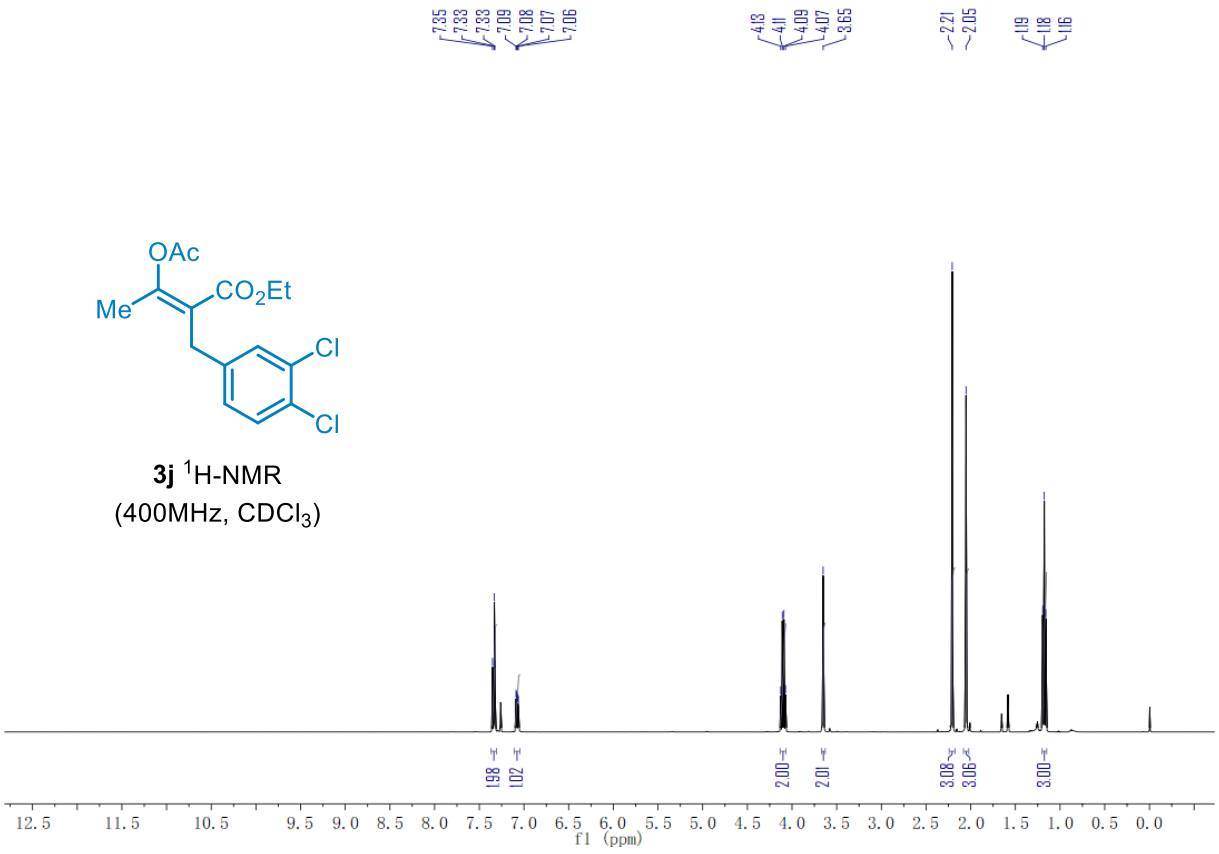
3g ^{1}H-NMR
(400 MHz, $CDCl_3$)



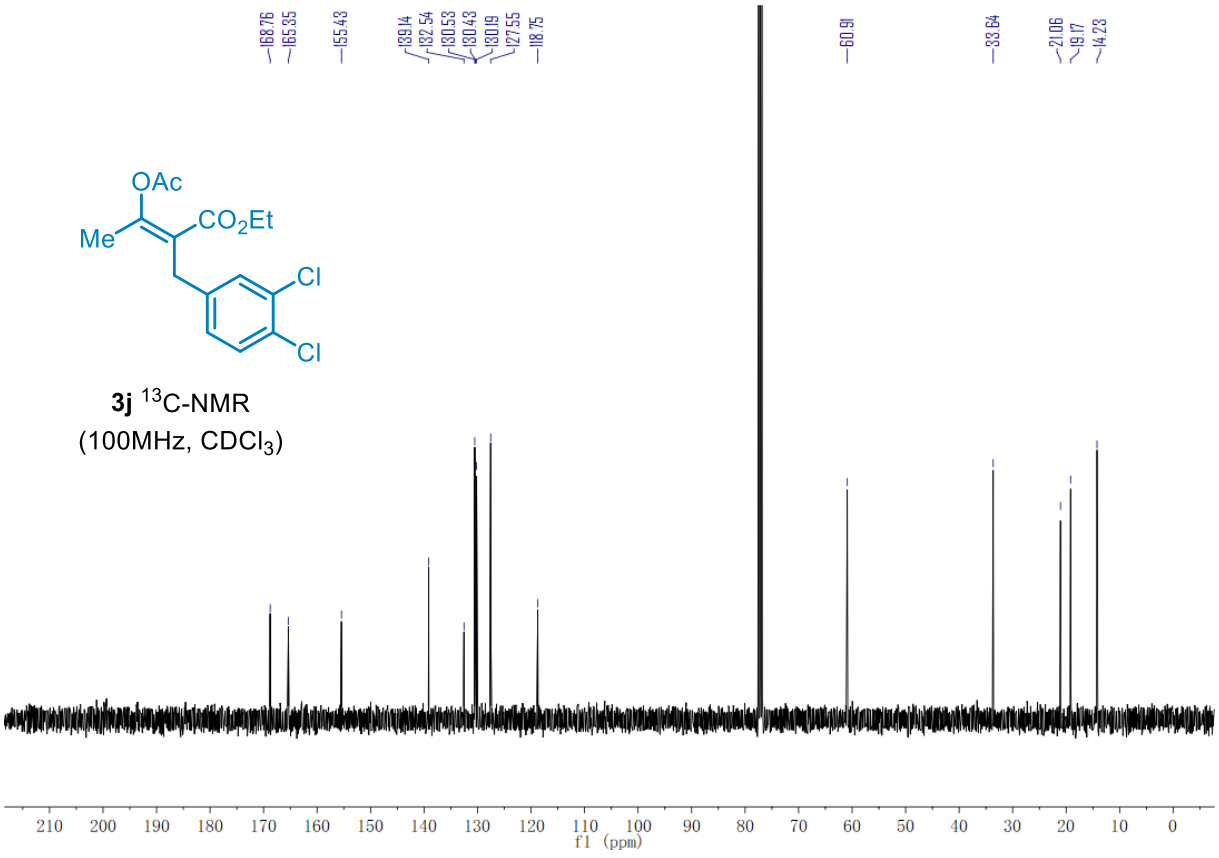
3h ^{1}H-NMR
(400 MHz, $CDCl_3$)



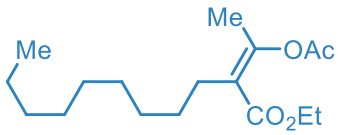
3i ^{1}H-NMR
(400 MHz, $CDCl_3$)



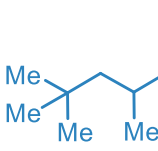
3j ^{1}H-NMR
(400MHz, $CDCl_3$)



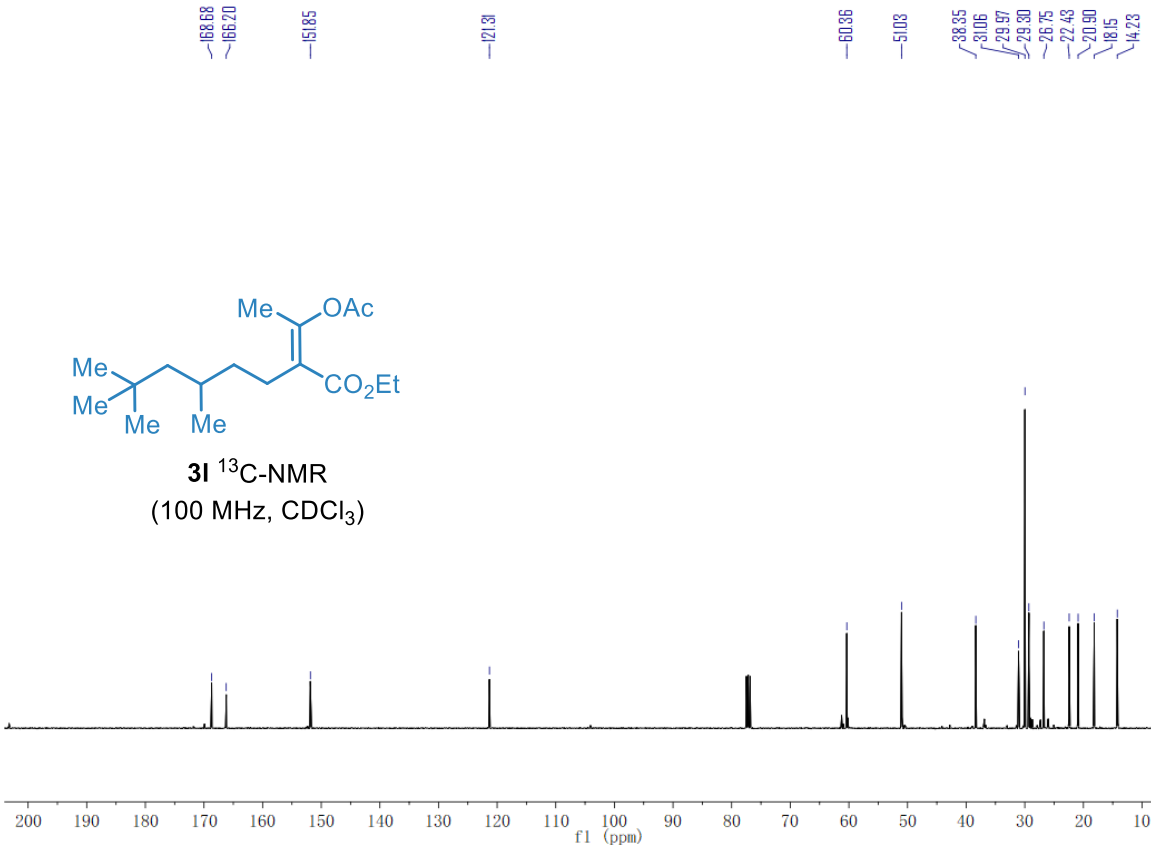
3j ^{13}C-NMR
(100MHz, $CDCl_3$)



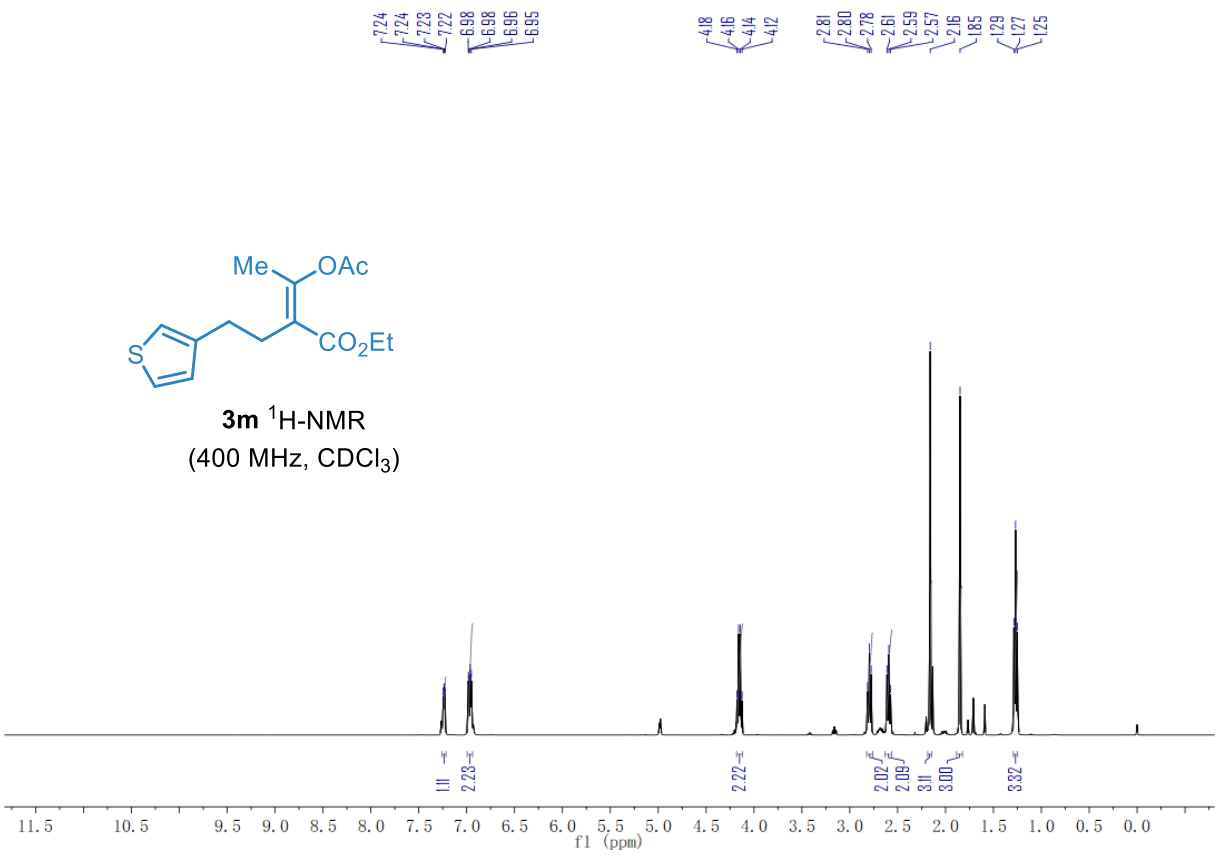
3k ^{1}H-NMR
(400 MHz, $CDCl_3$)



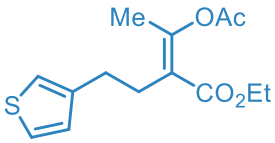
3l ^{1}H-NMR
(400 MHz, $CDCl_3$)



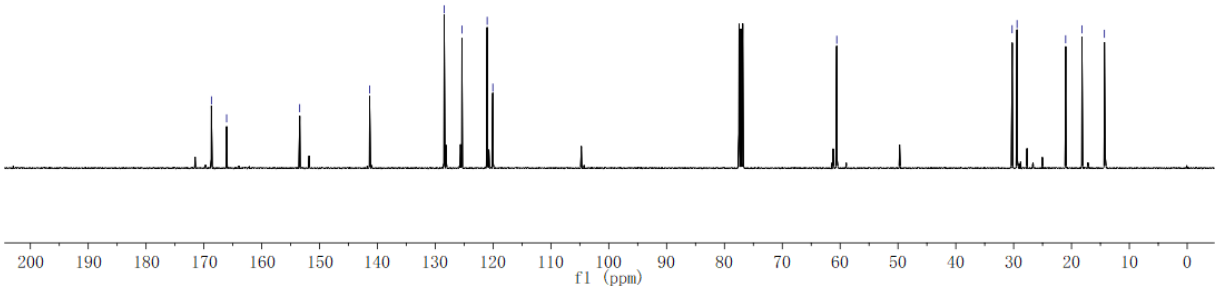
3l ^{13}C-NMR
(100 MHz, $CDCl_3$)

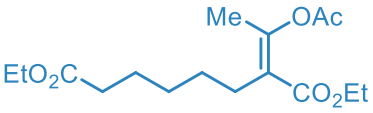


3m ^{1}H-NMR
(400 MHz, $CDCl_3$)

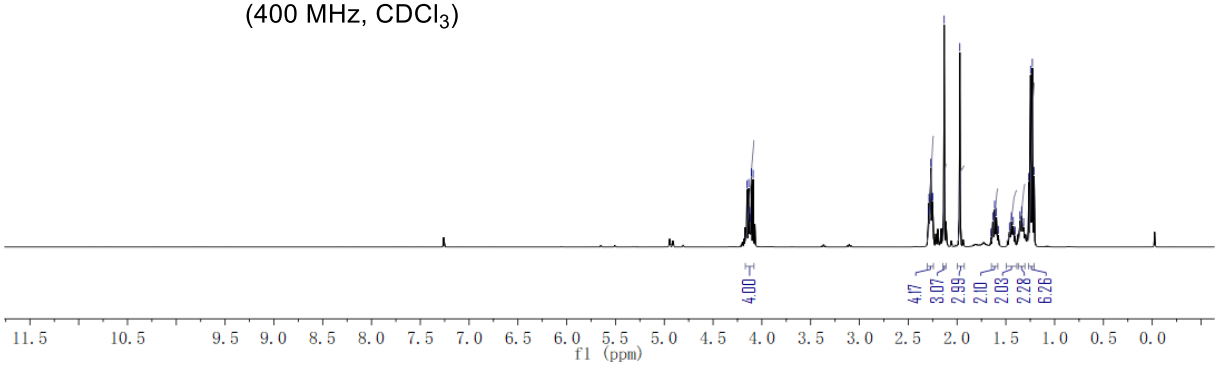


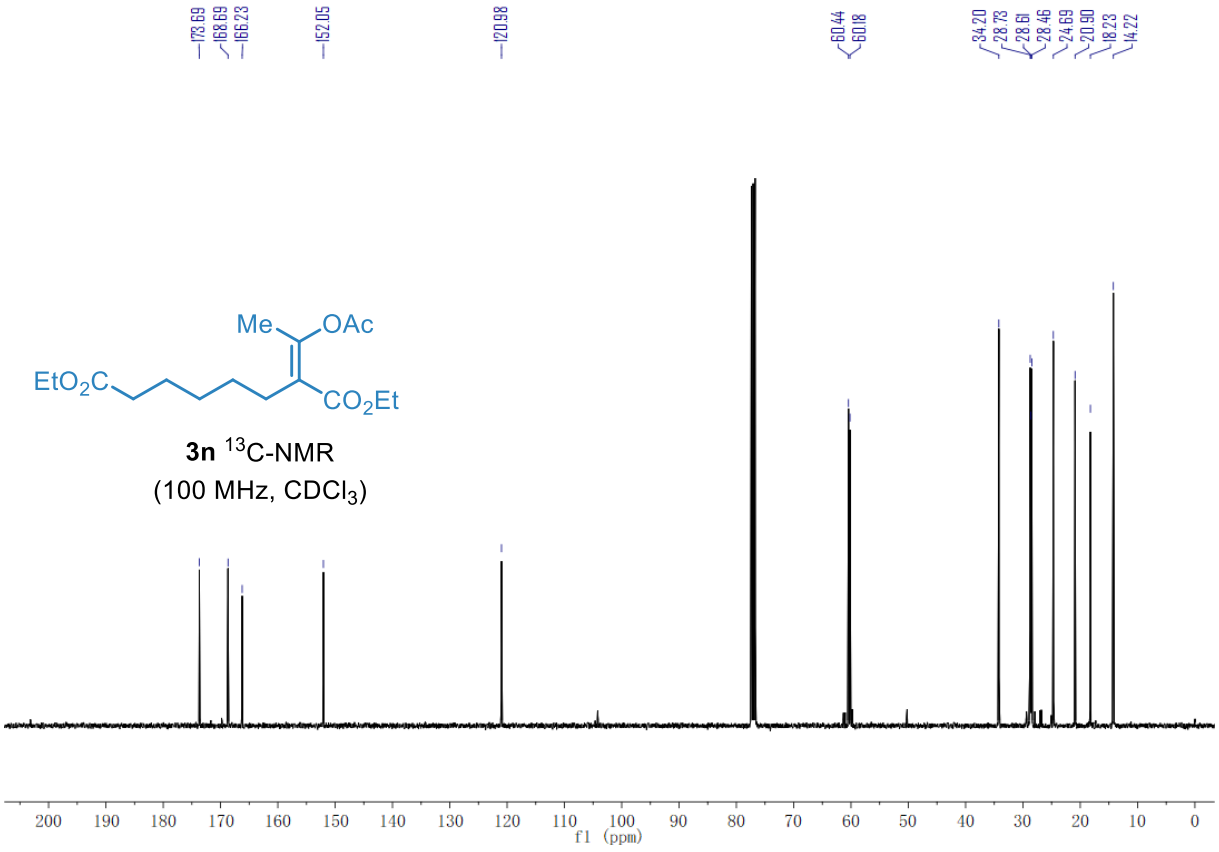
3m ^{13}C-NMR
(100 MHz, $CDCl_3$)



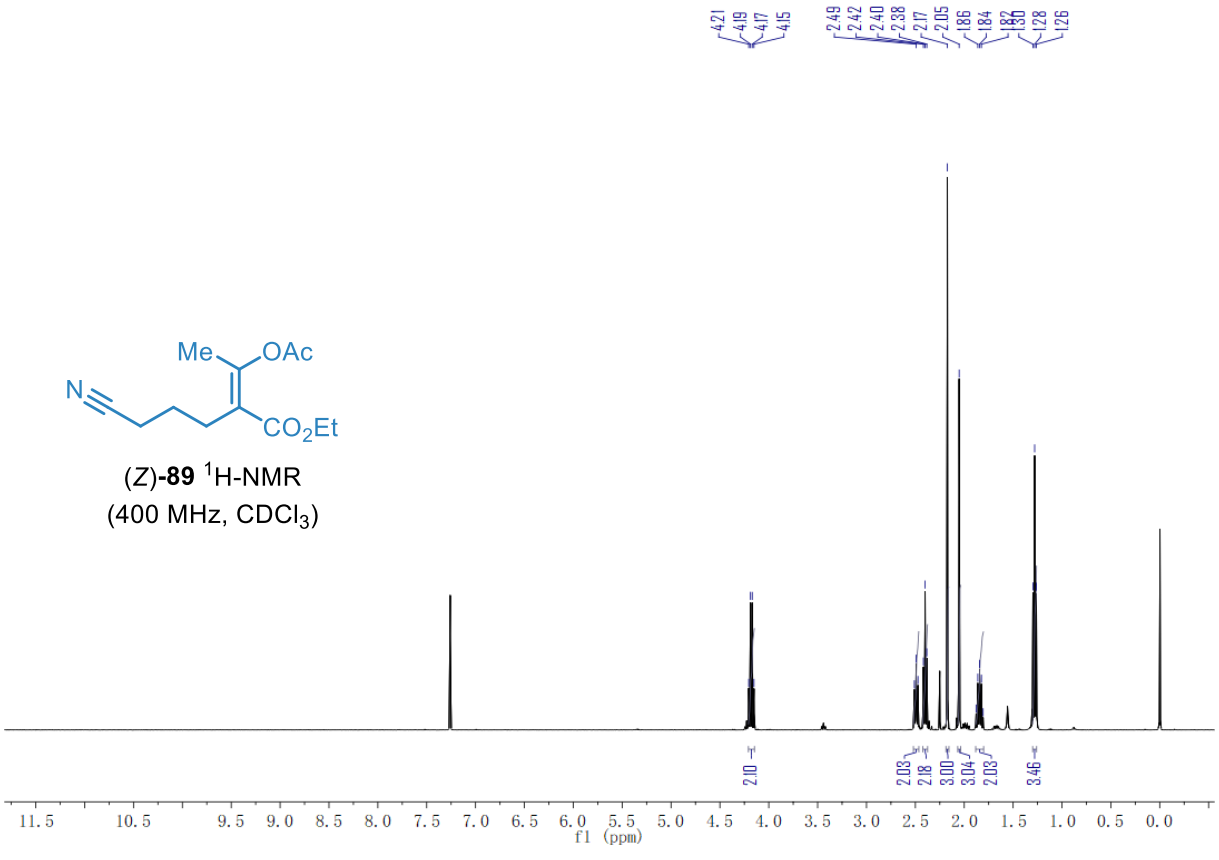


3n ^{1}H-NMR
(400 MHz, $CDCl_3$)

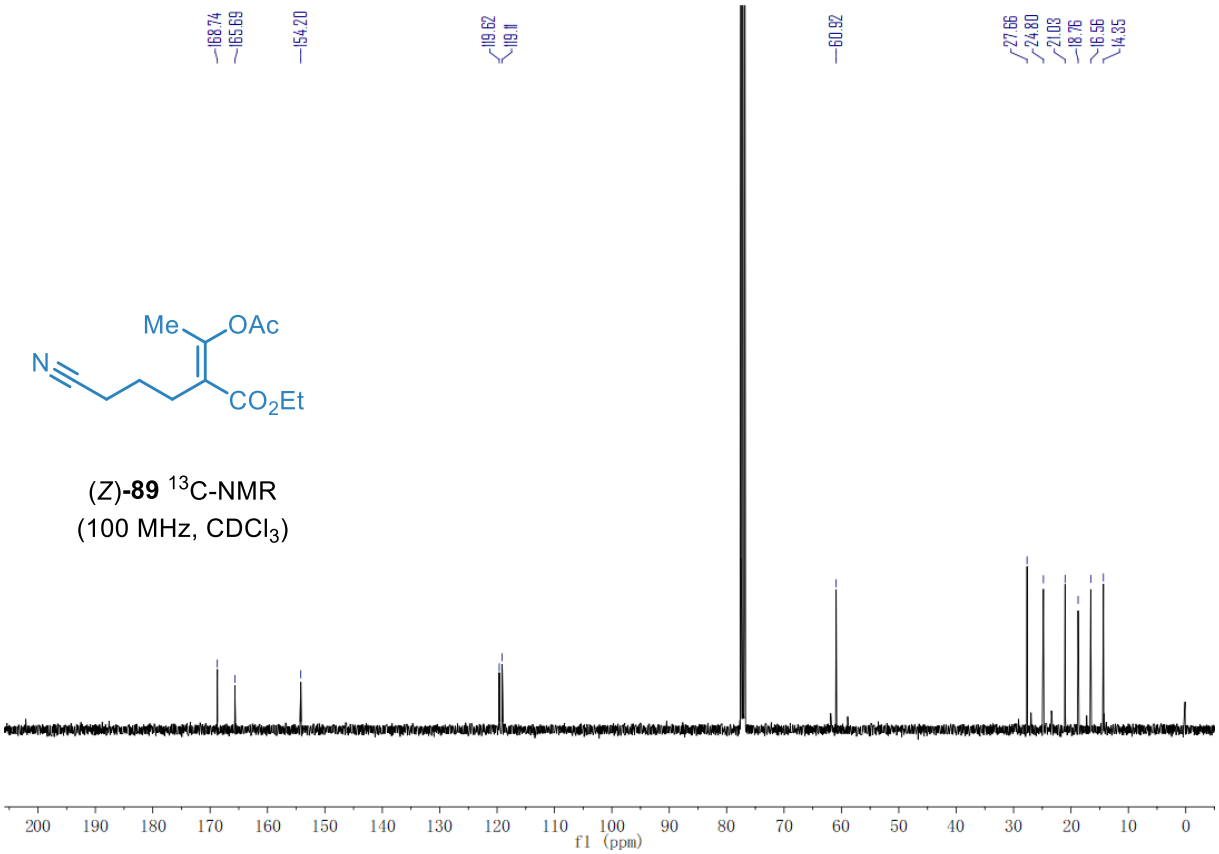




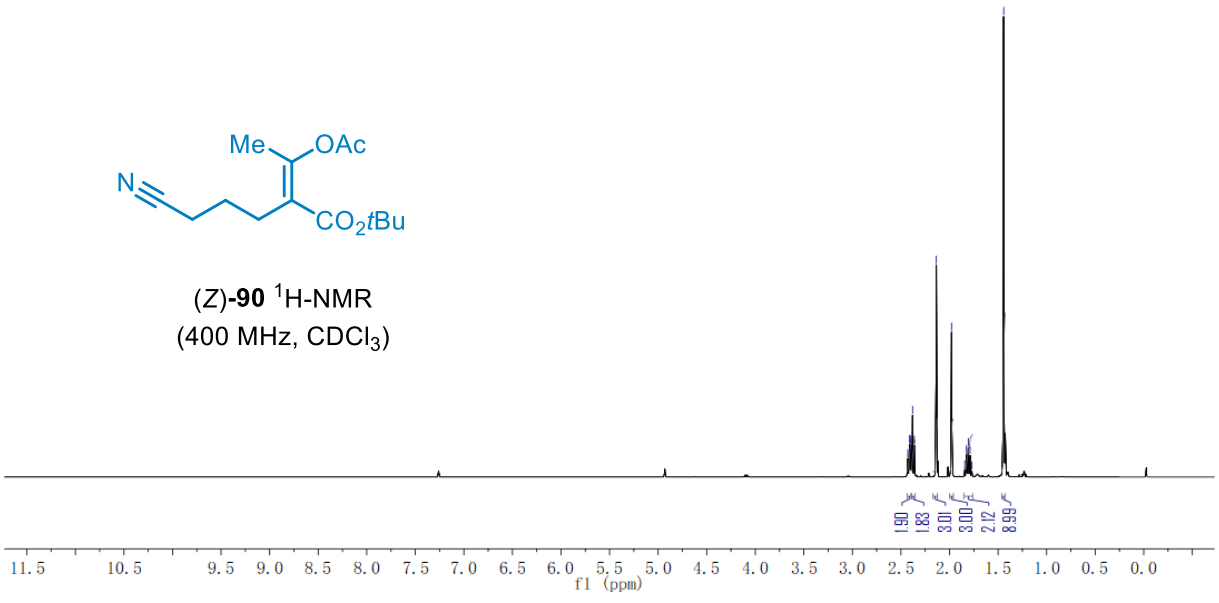
3n ^{13}C-NMR
(100 MHz, $CDCl_3$)



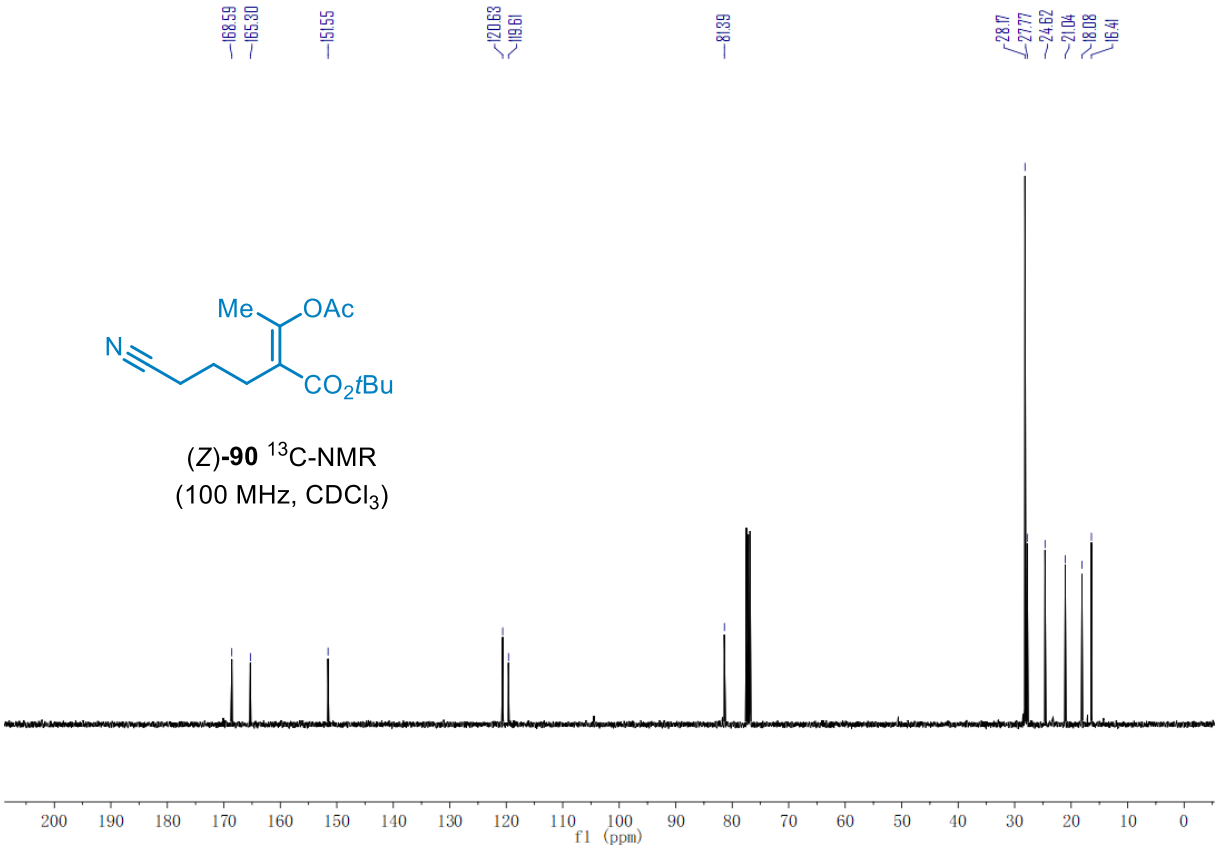
(*Z*)-**89** ^{1}H-NMR
(400 MHz, $CDCl_3$)



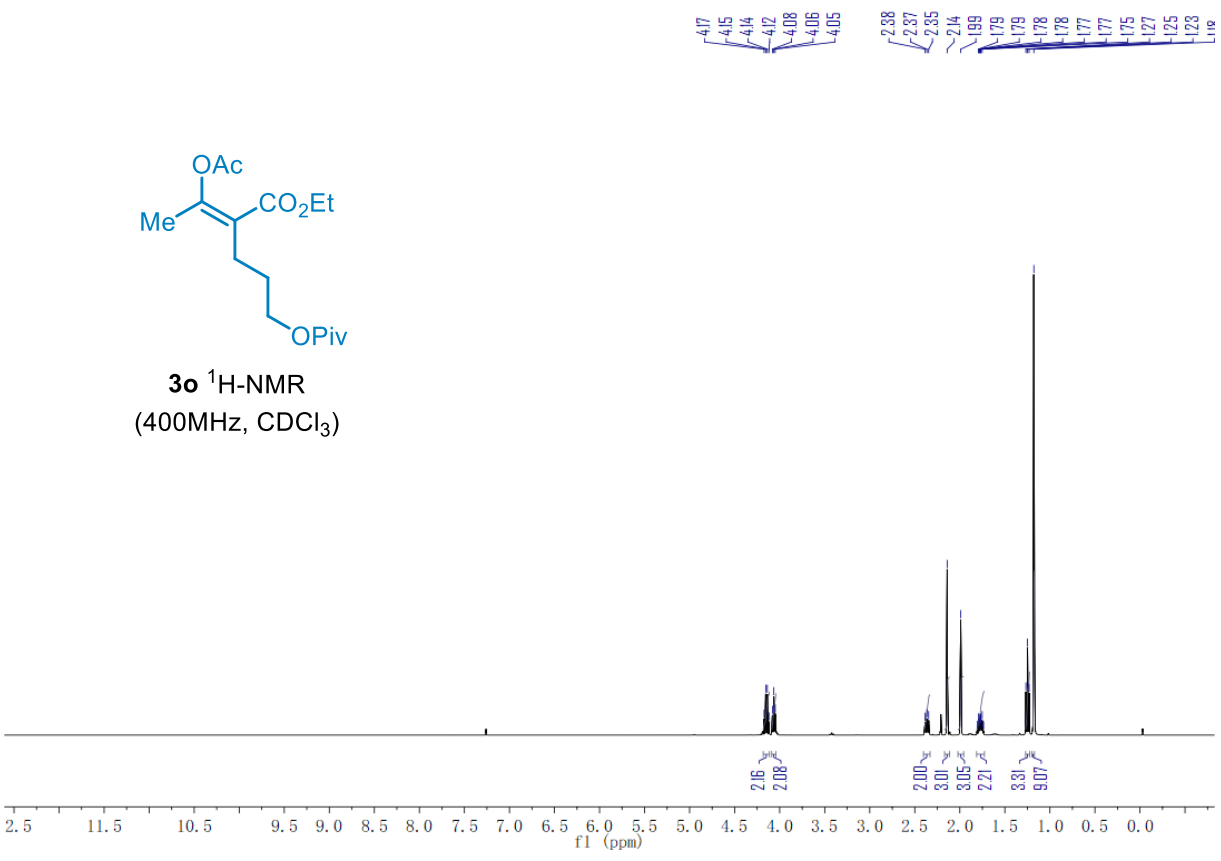
(*Z*)-**89** ^{13}C-NMR
(100 MHz, $CDCl_3$)



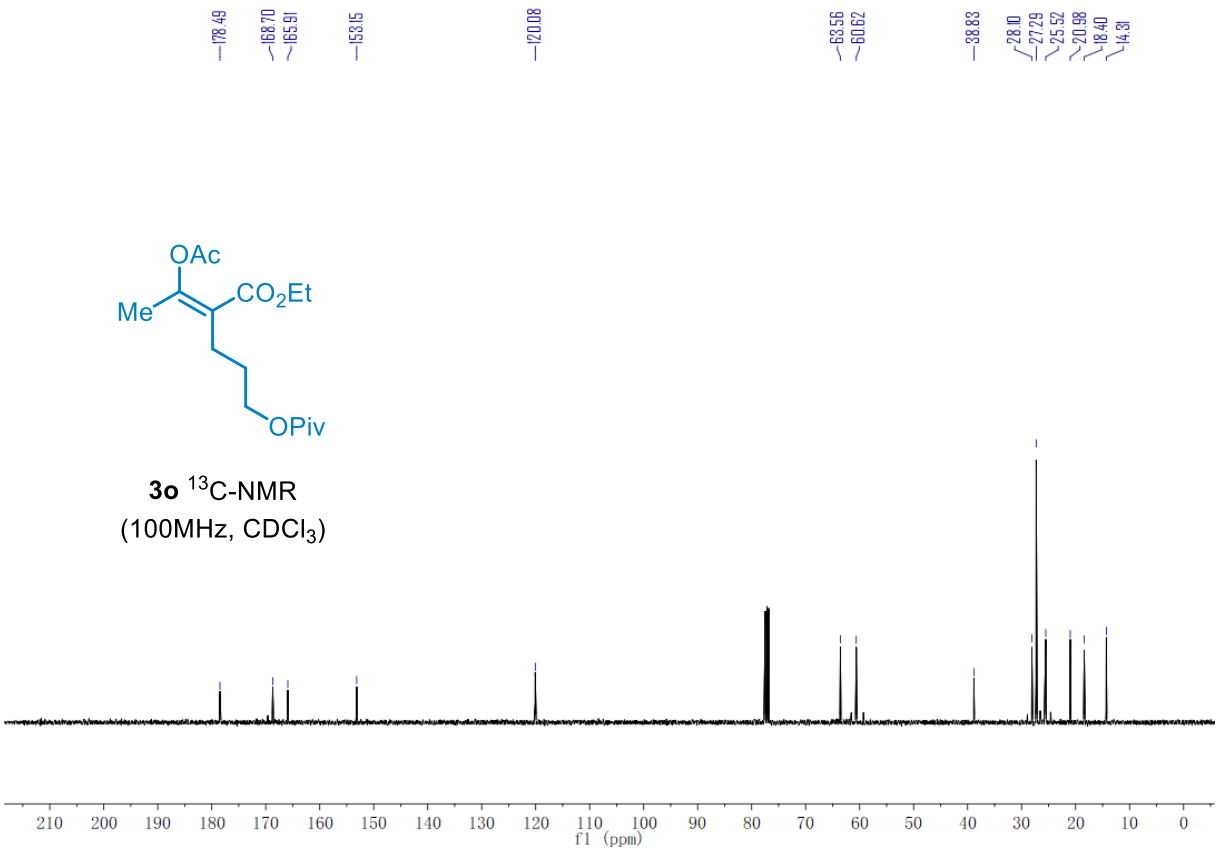
(*Z*)-**90** ^{1}H-NMR
(400 MHz, $CDCl_3$)



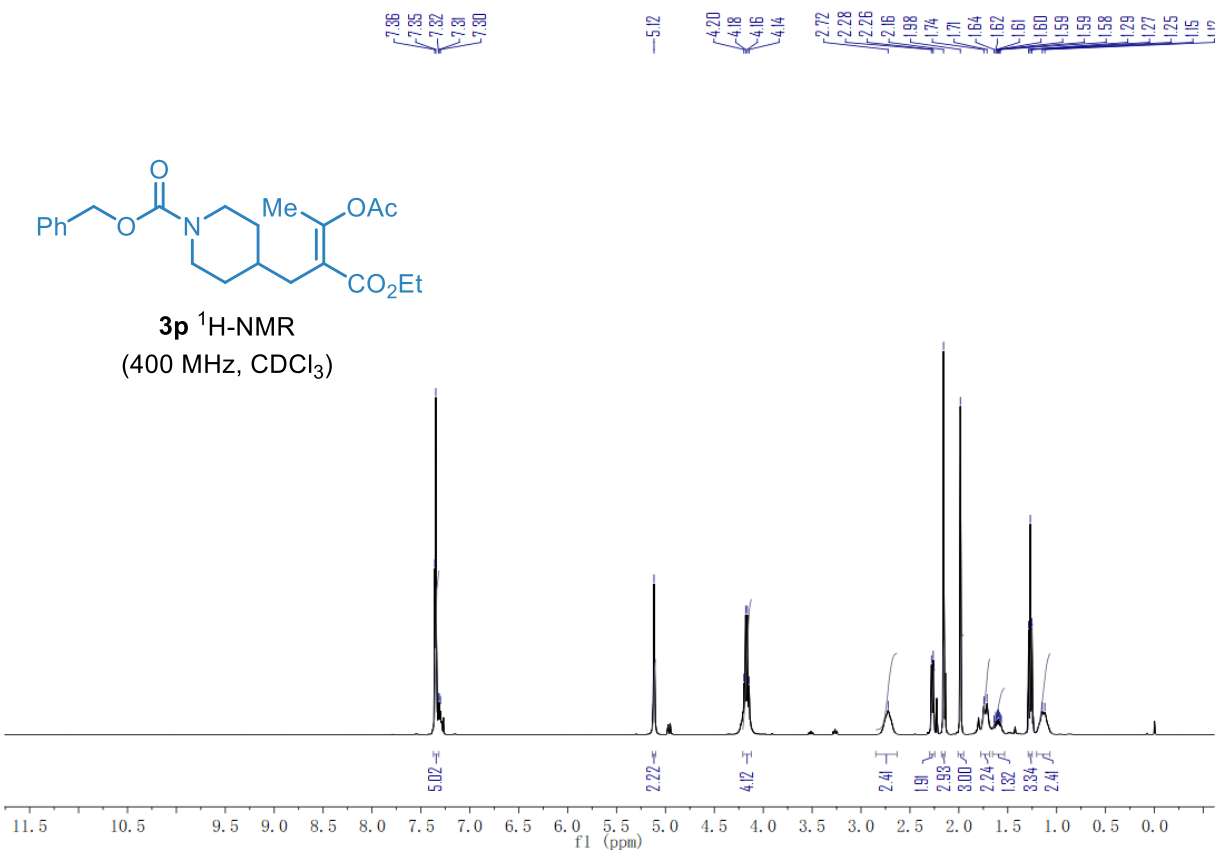
(*Z*)-**90** ^{13}C-NMR
(100 MHz, $CDCl_3$)



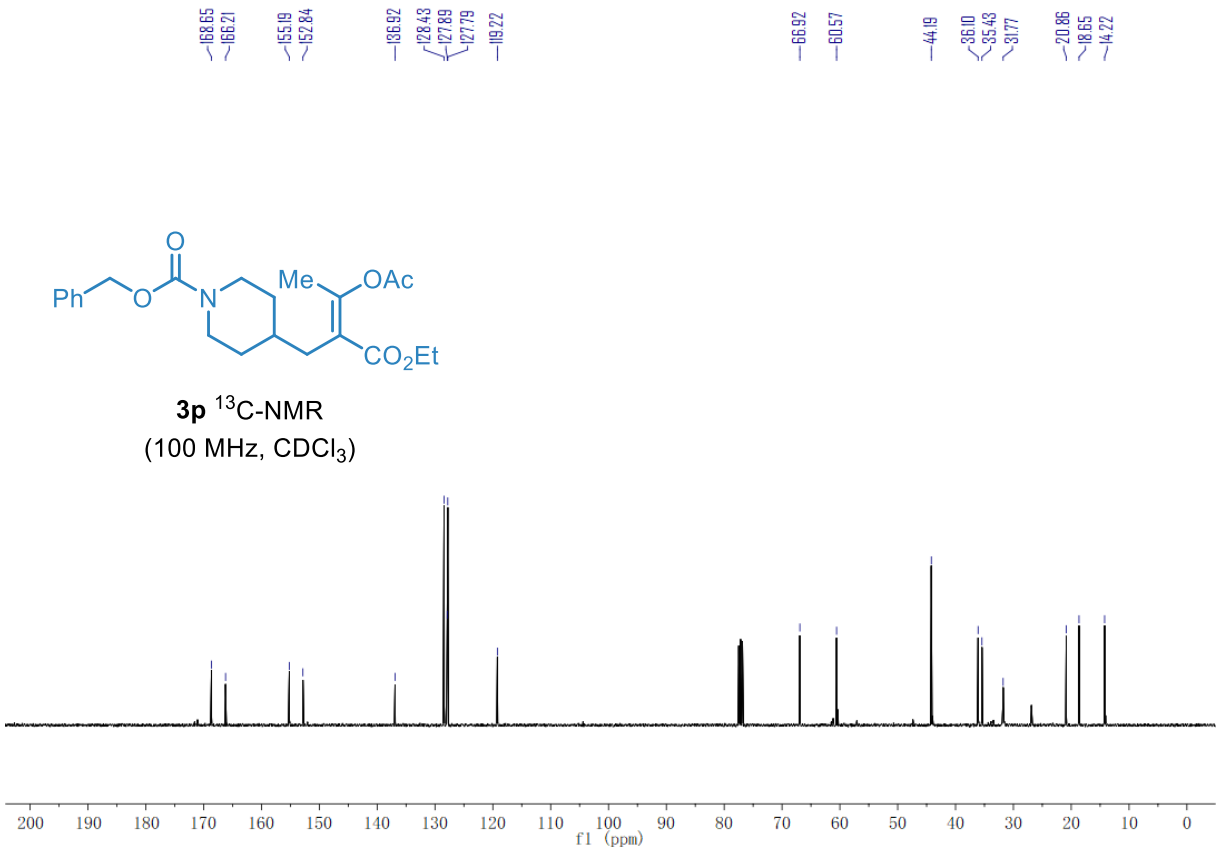
3o ^{1}H-NMR
(400MHz, $CDCl_3$)



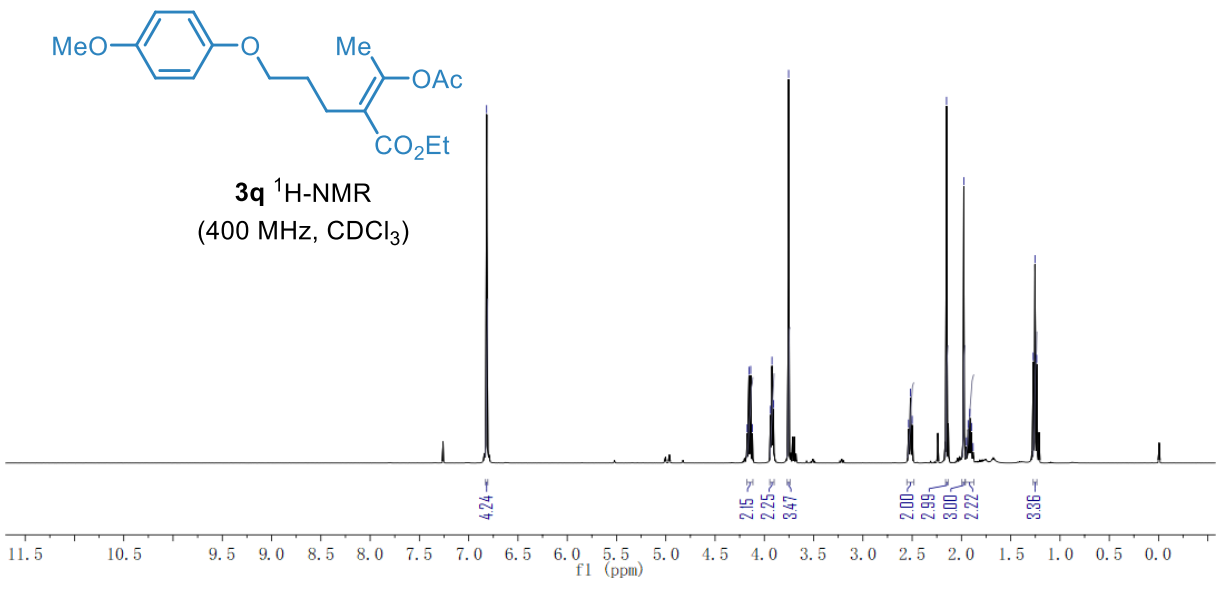
3o ^{13}C-NMR
(100MHz, $CDCl_3$)



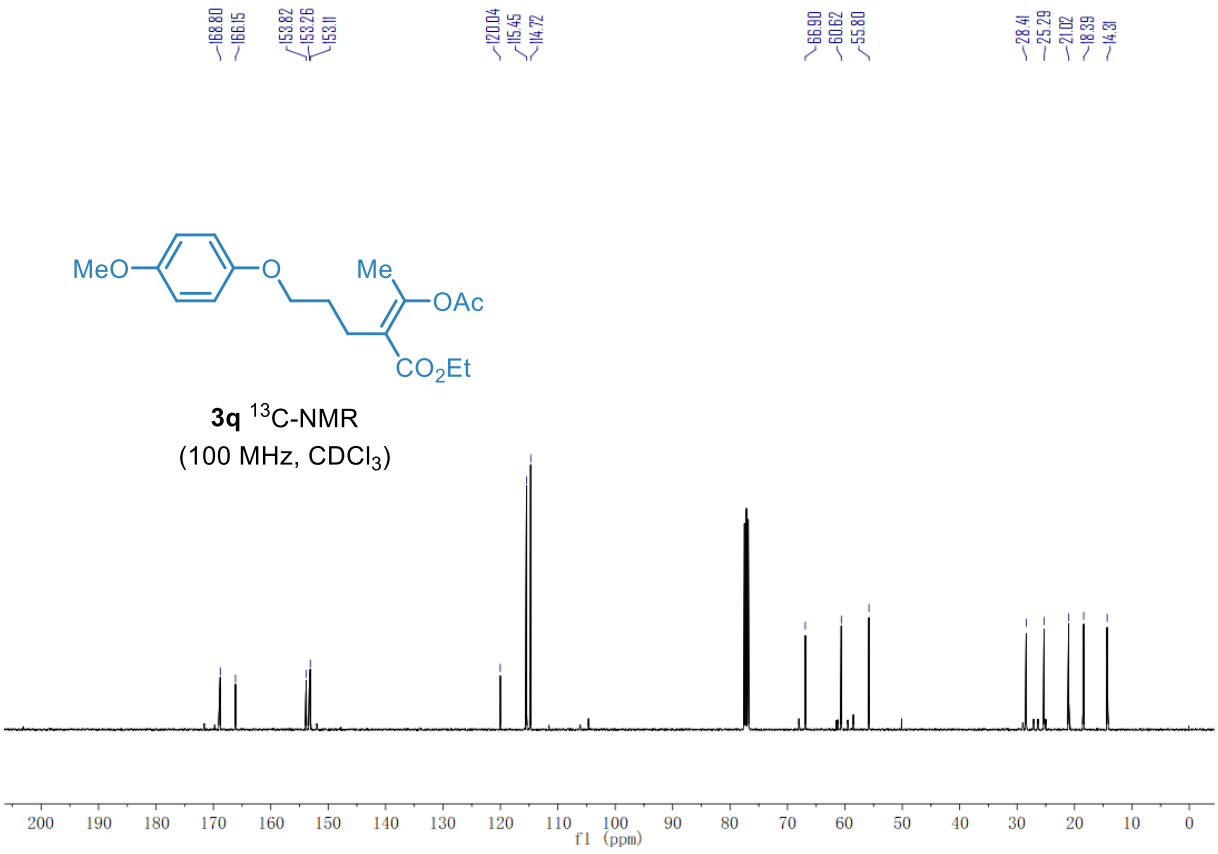
3p ^{1}H-NMR
(400 MHz, $CDCl_3$)



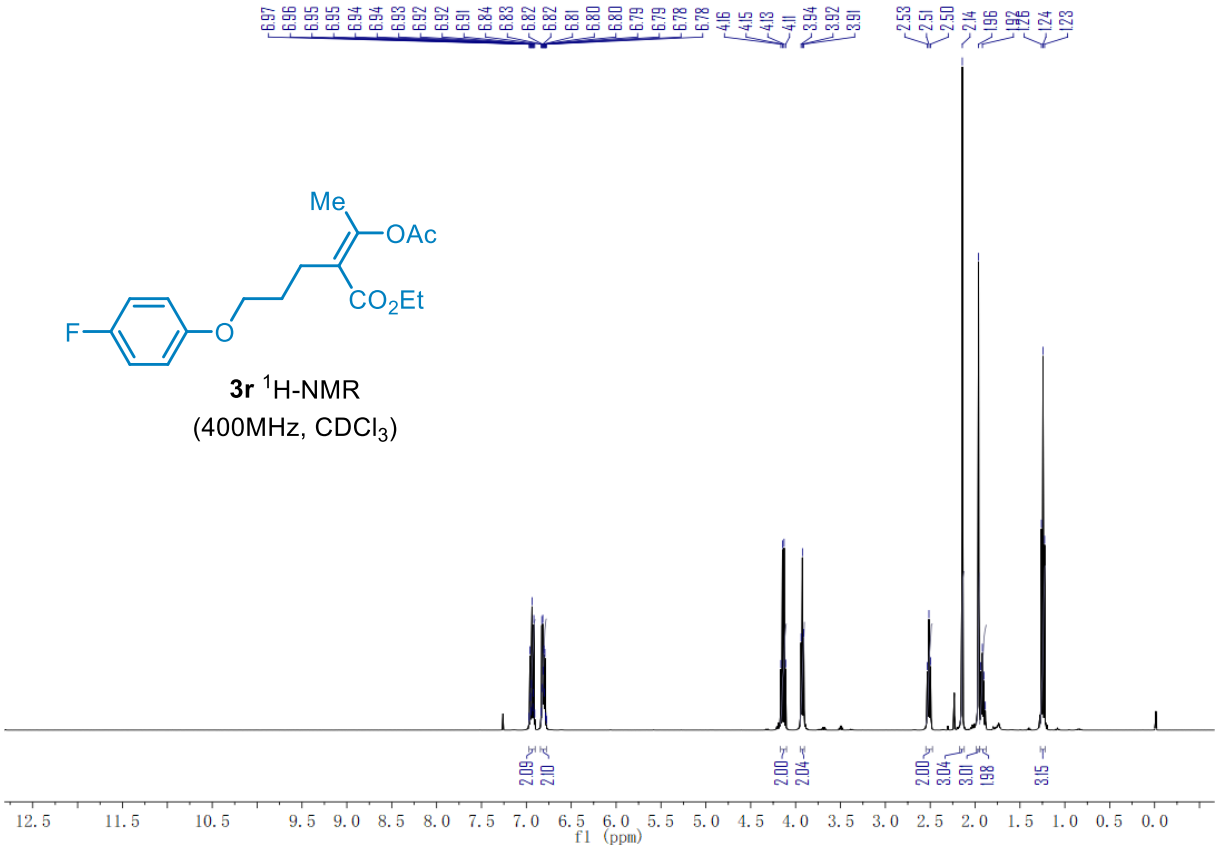
3p ^{13}C-NMR
(100 MHz, $CDCl_3$)



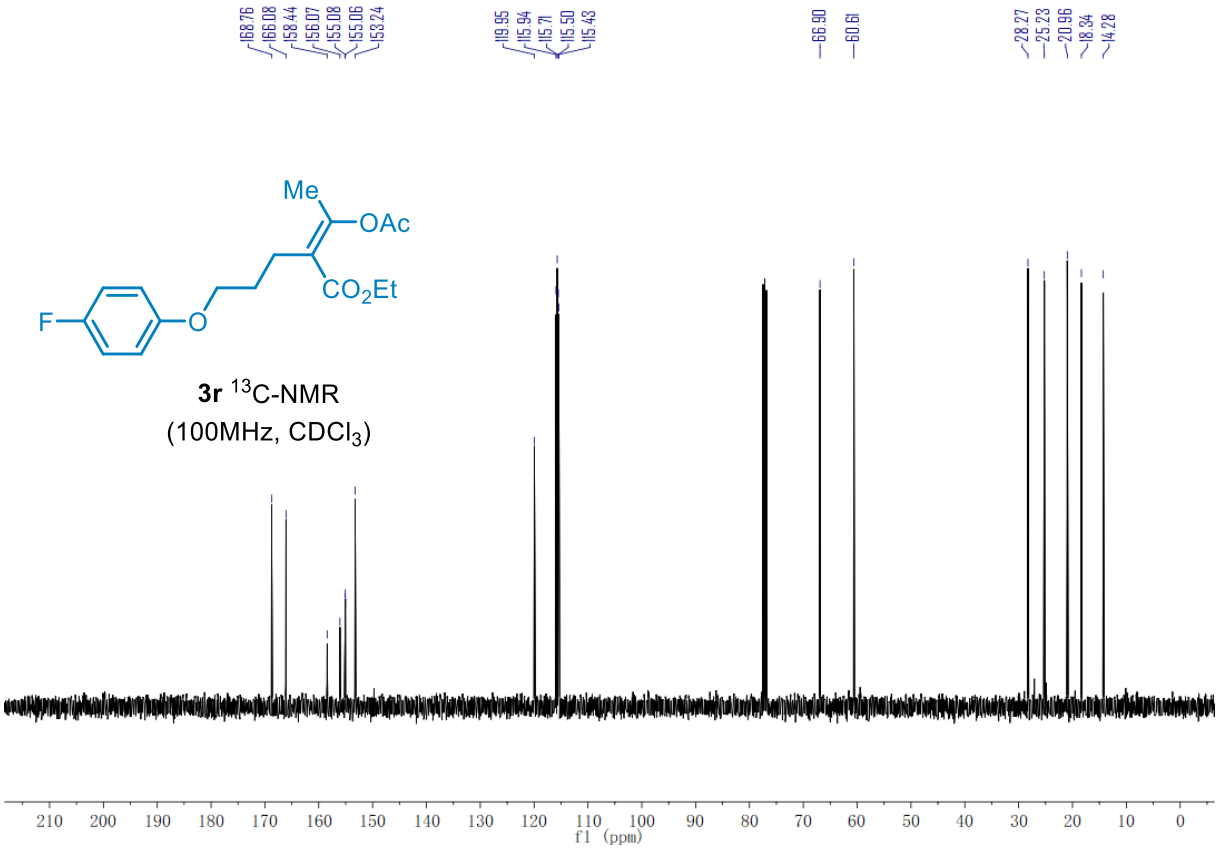
3q ^{1}H-NMR
(400 MHz, $CDCl_3$)



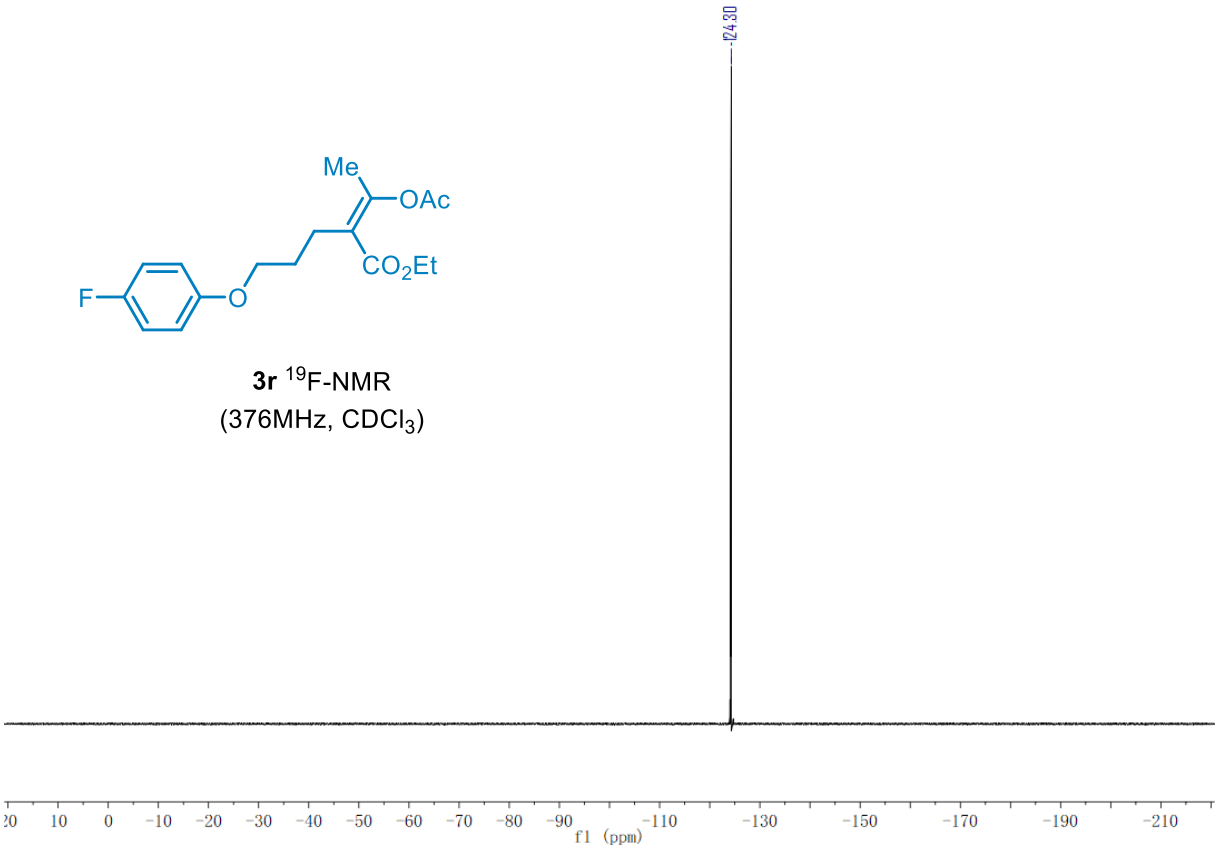
3q ^{13}C-NMR
(100 MHz, $CDCl_3$)



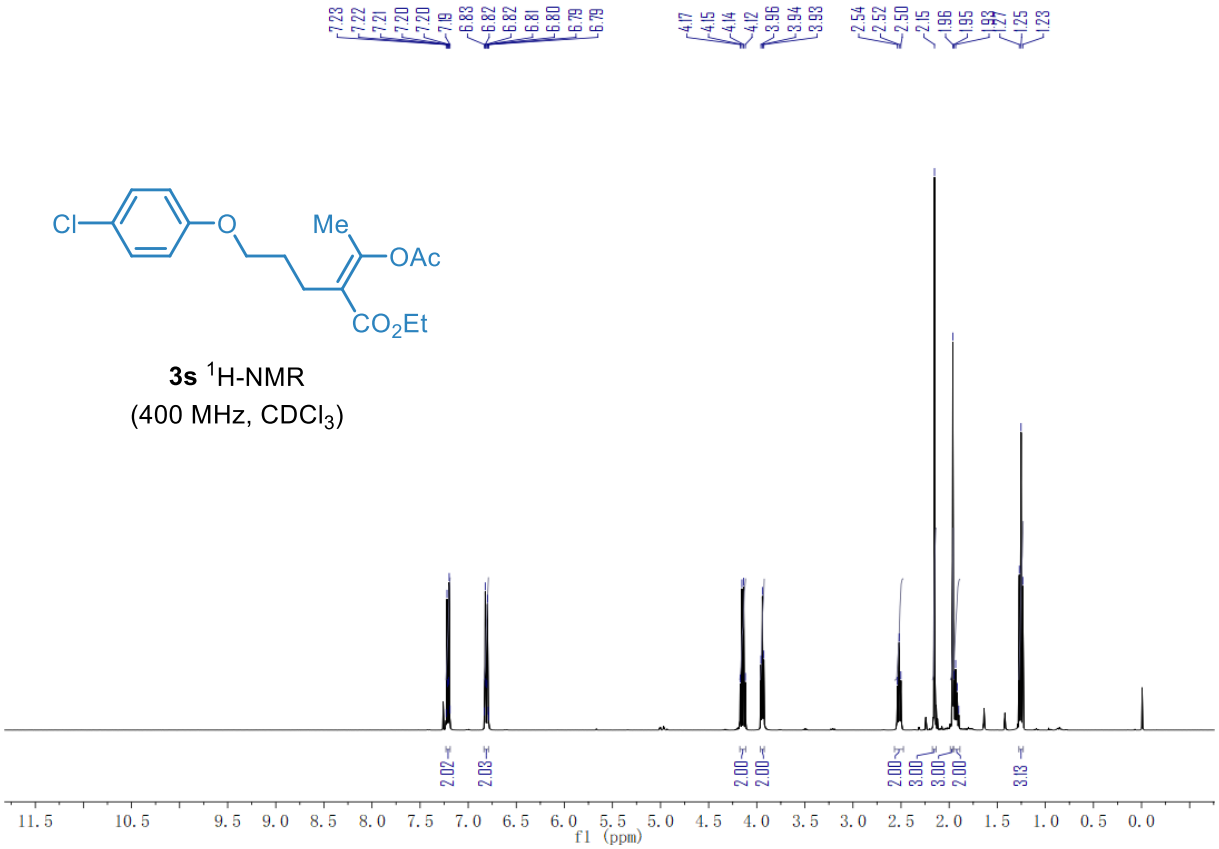
3r ^{1}H-NMR
(400MHz, $CDCl_3$)



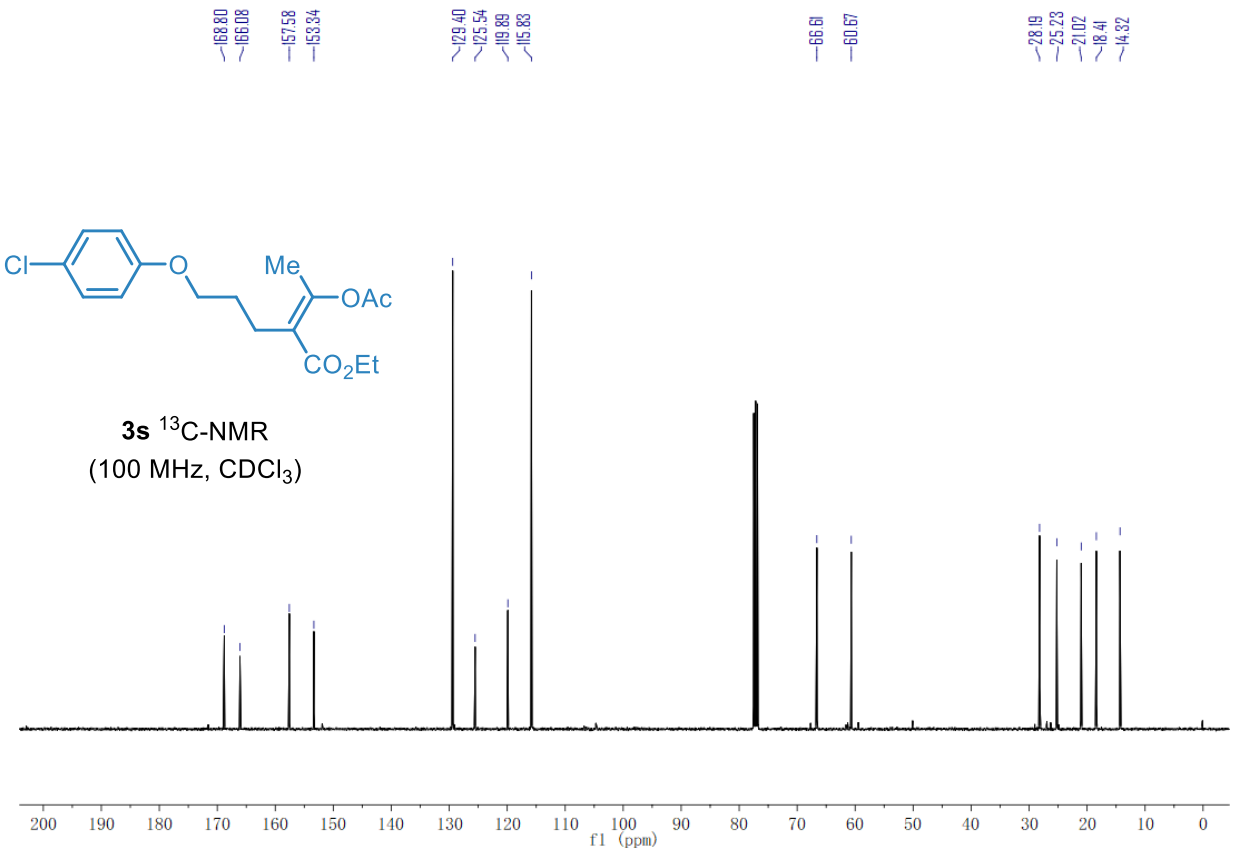
3r ^{13}C-NMR
(100MHz, $CDCl_3$)



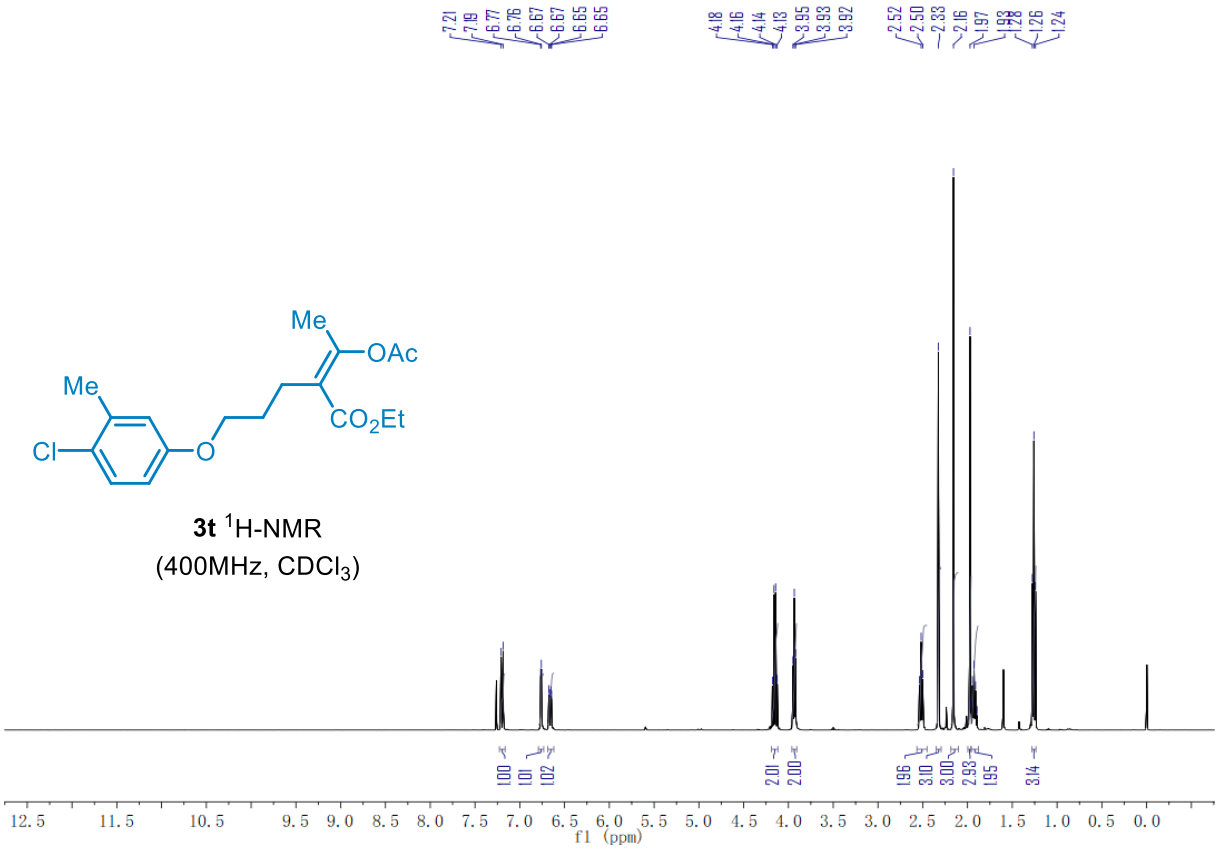
3r ^{19}F-NMR
(376MHz, $CDCl_3$)



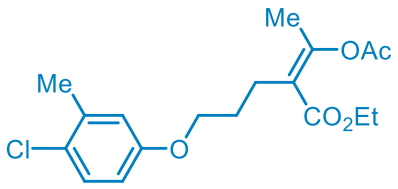
3s ^{1}H-NMR
(400 MHz, $CDCl_3$)



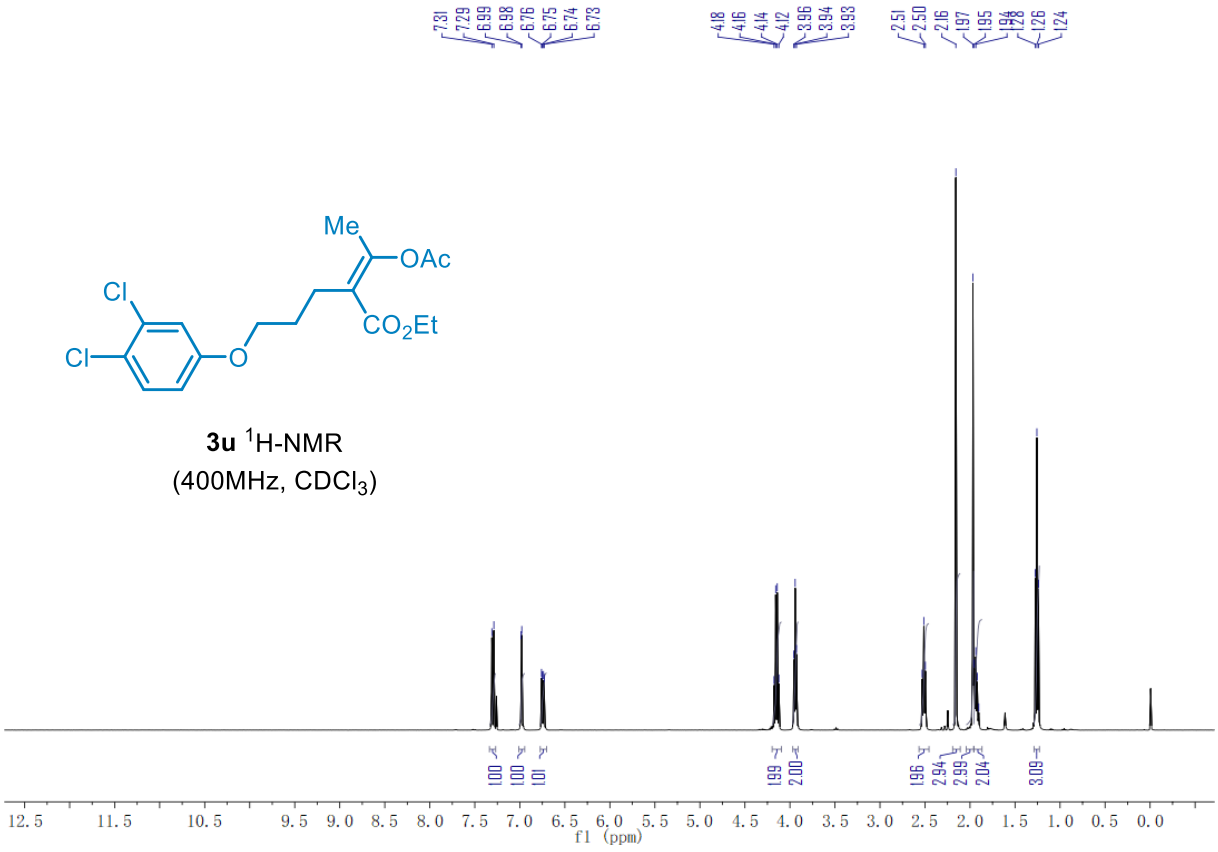
3s ^{13}C-NMR
(100 MHz, $CDCl_3$)



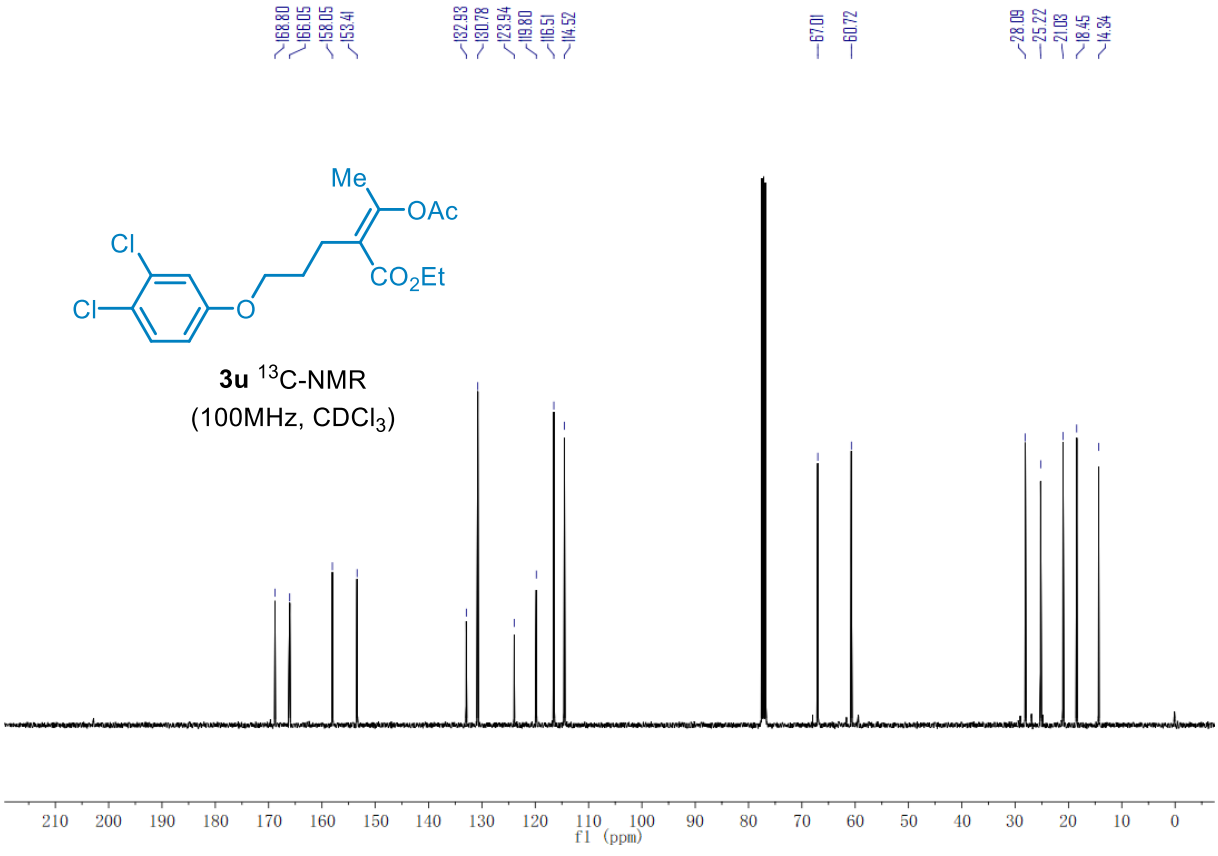
3t ^{1}H-NMR
(400MHz, $CDCl_3$)



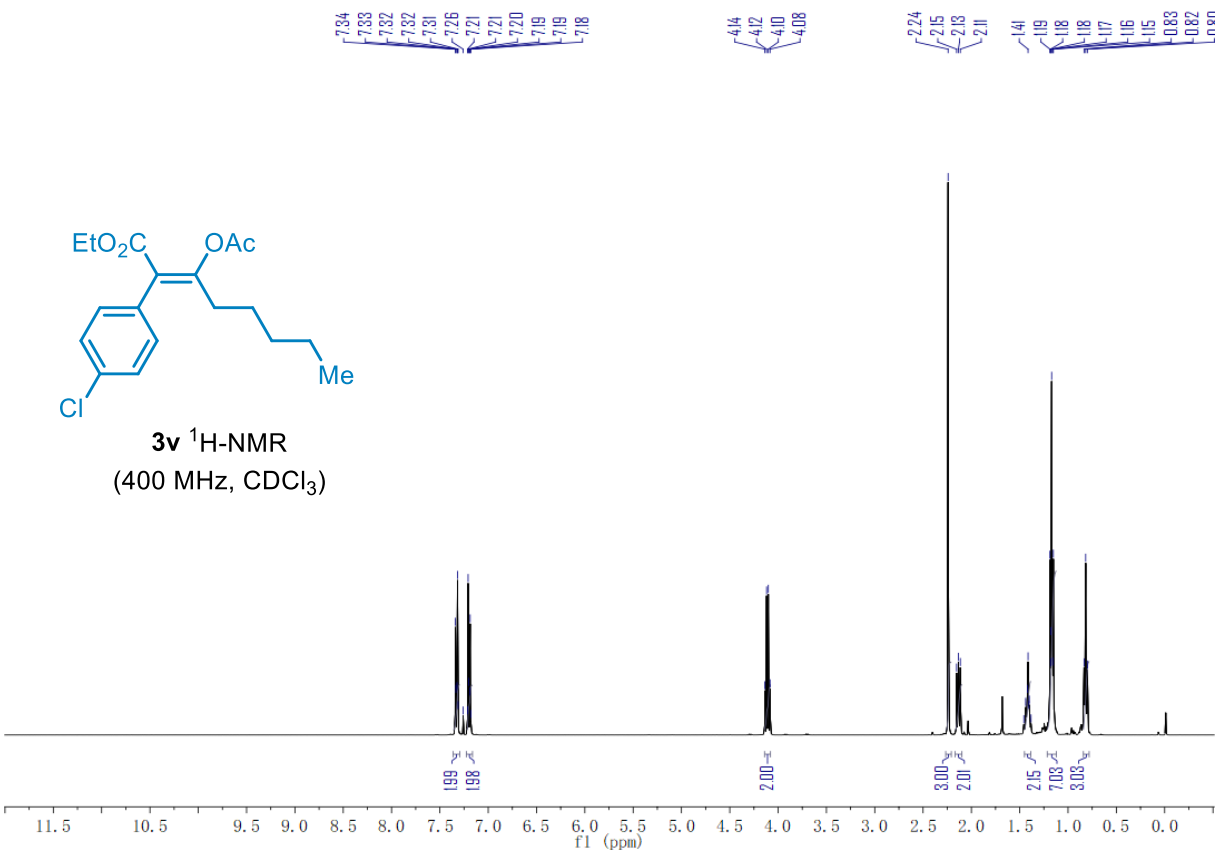
3t ^{13}C-NMR
(100MHz, $CDCl_3$)

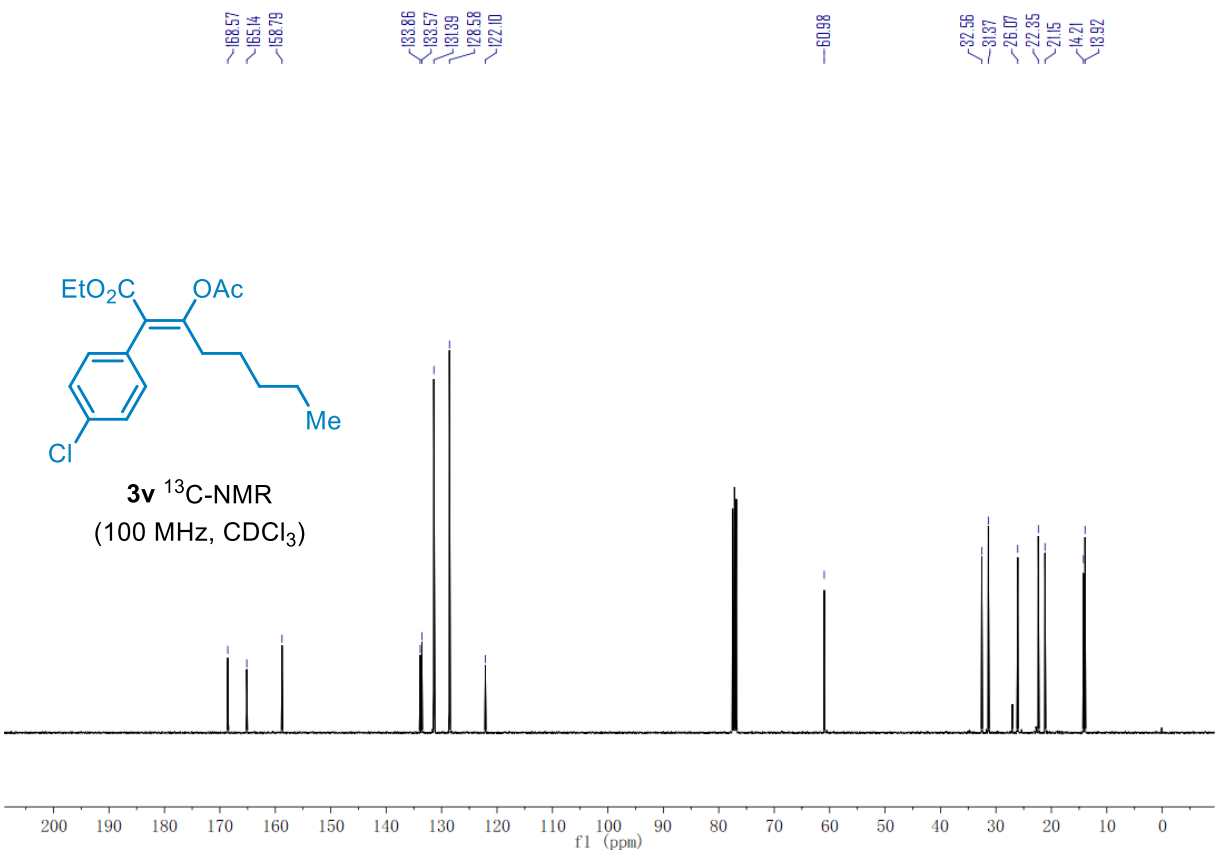


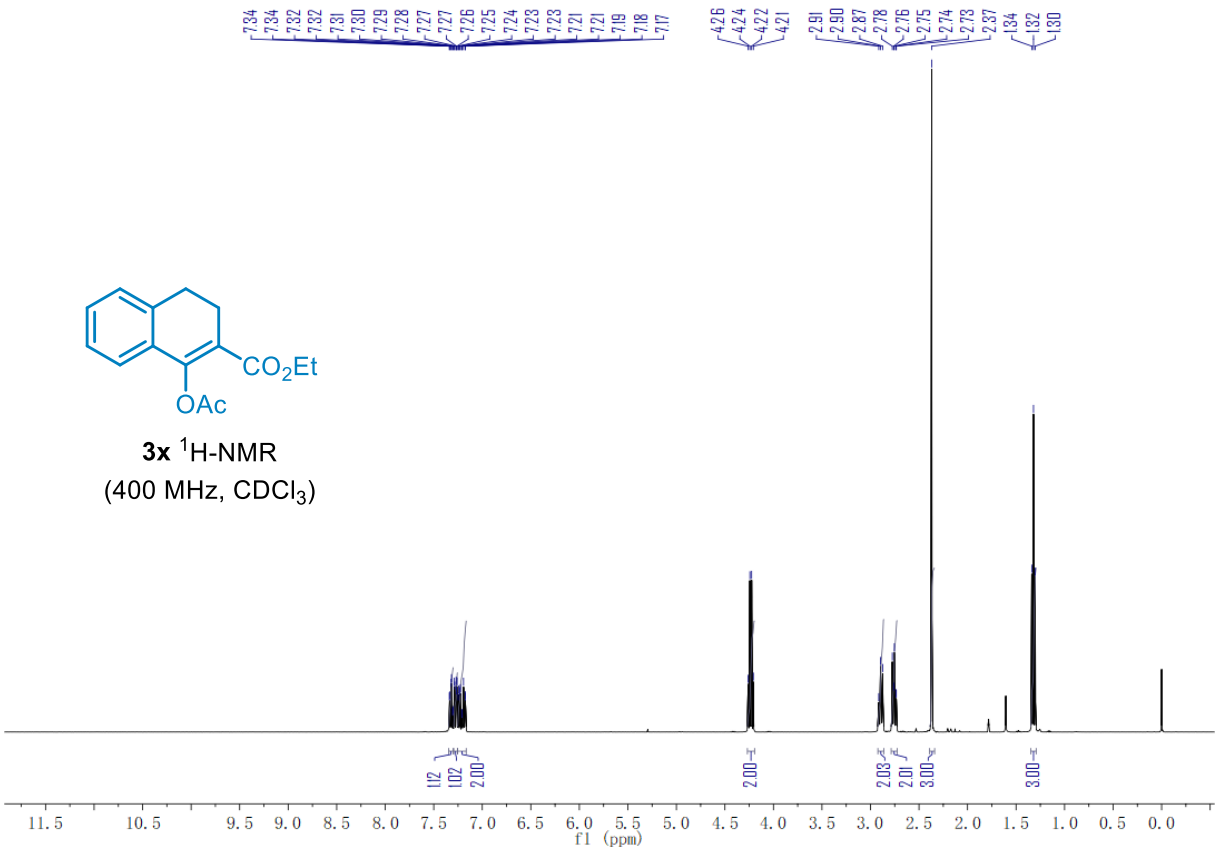
3u ^{1}H-NMR
(400MHz, $CDCl_3$)



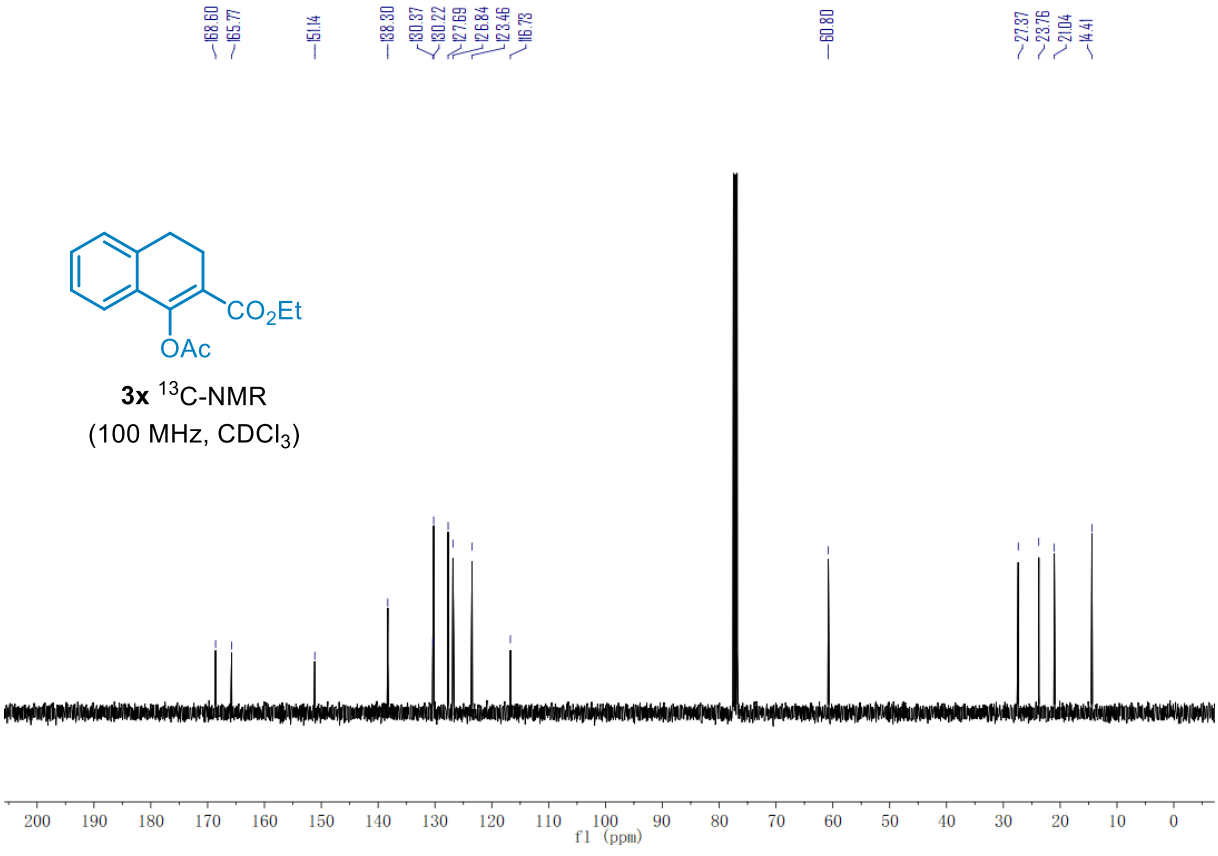
3u ^{13}C-NMR
(100MHz, $CDCl_3$)


EtO2C
OAc
Me
Cl
3v 1H-NMR
(400 MHz, CDCl3)
f1 (ppm)

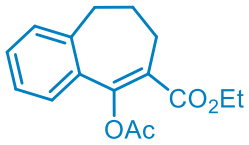

EtO2C
OAc
Me
Cl
3v 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)



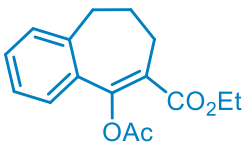
3x ^{1}H-NMR
(400 MHz, $CDCl_3$)



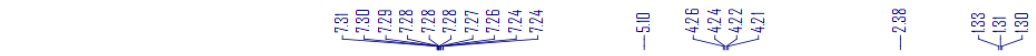
3x ^{13}C-NMR
(100 MHz, $CDCl_3$)

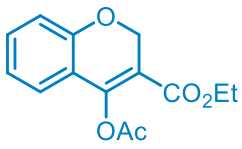


3y ^{1}H-NMR
(400 MHz, $CDCl_3$)

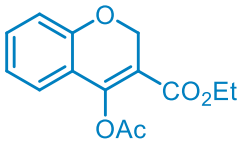


3y ^{13}C-NMR
(100 MHz, $CDCl_3$)

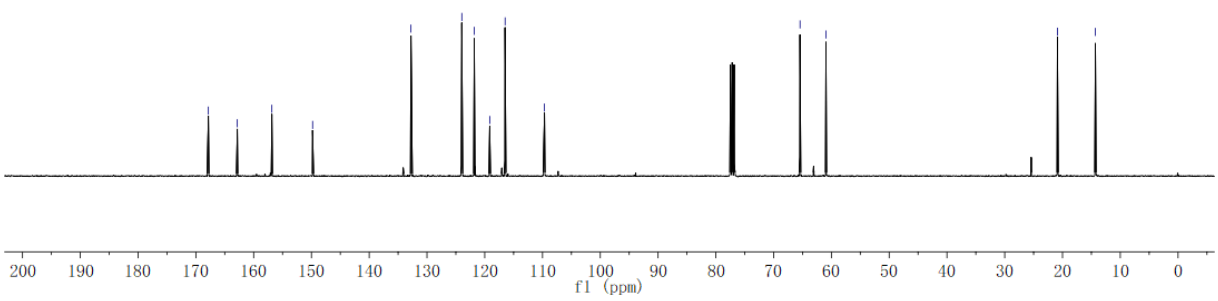


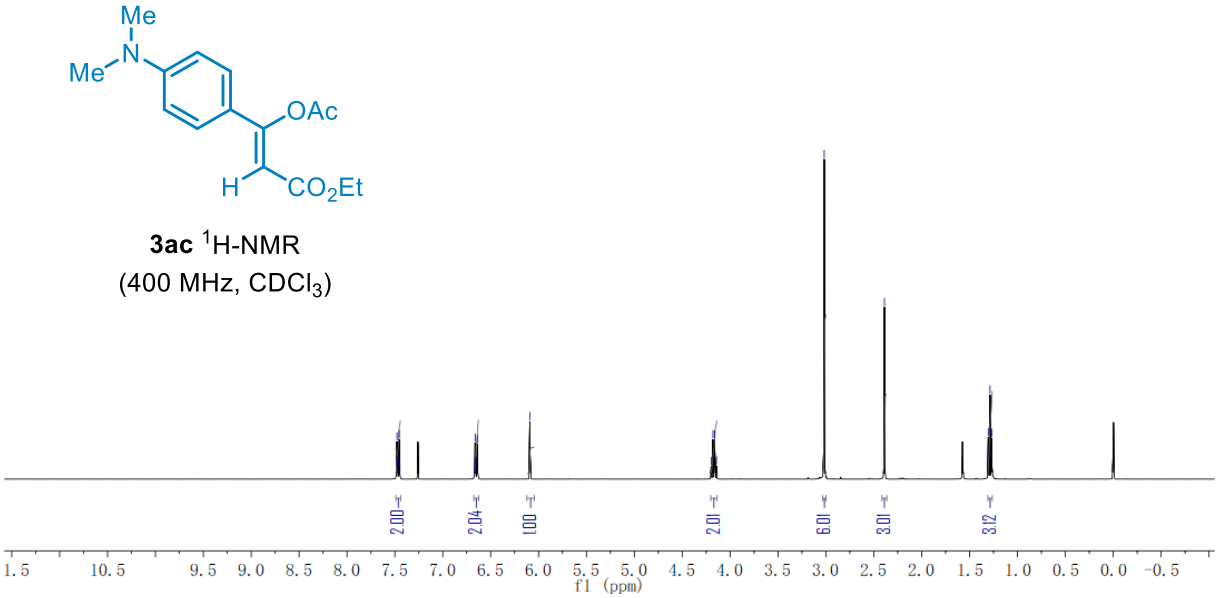


3z ^{1}H-NMR
(400 MHz, $CDCl_3$)

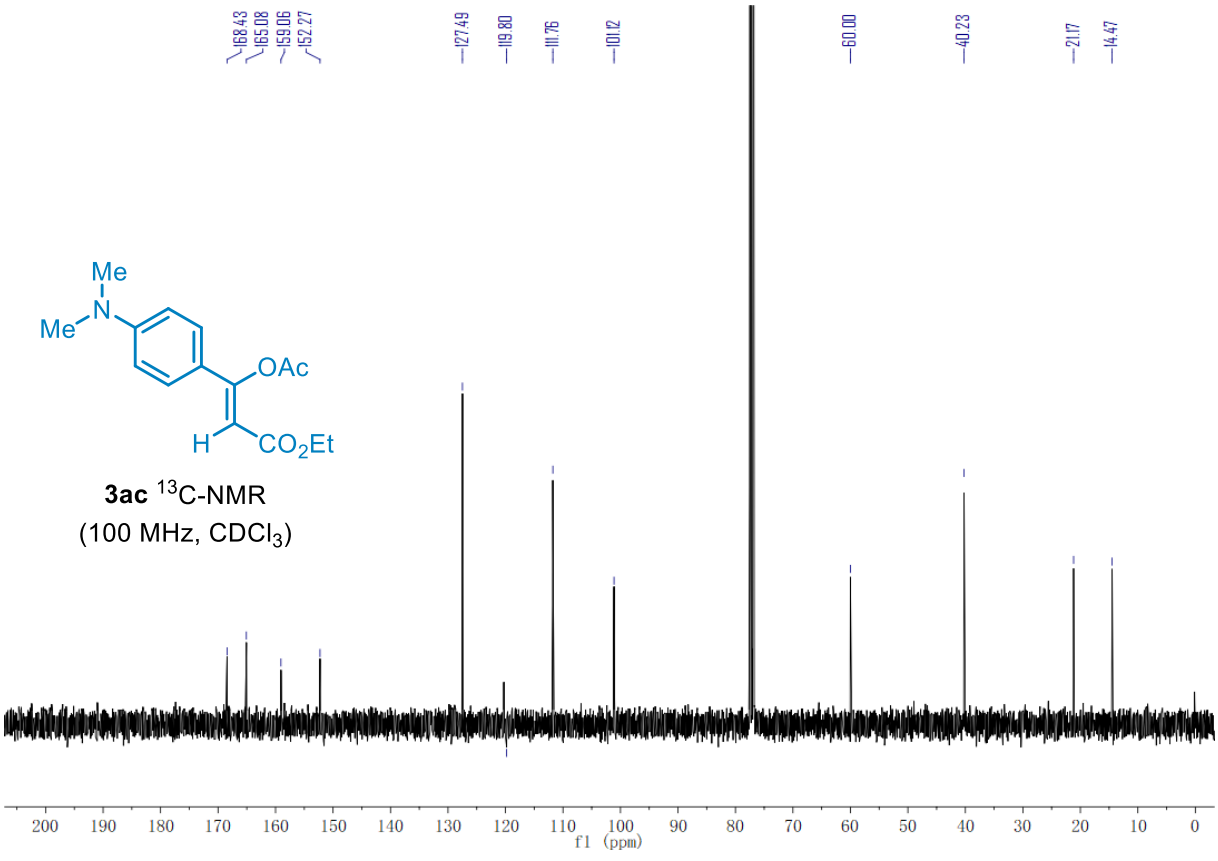


3z ^{13}C-NMR
(100 MHz, $CDCl_3$)

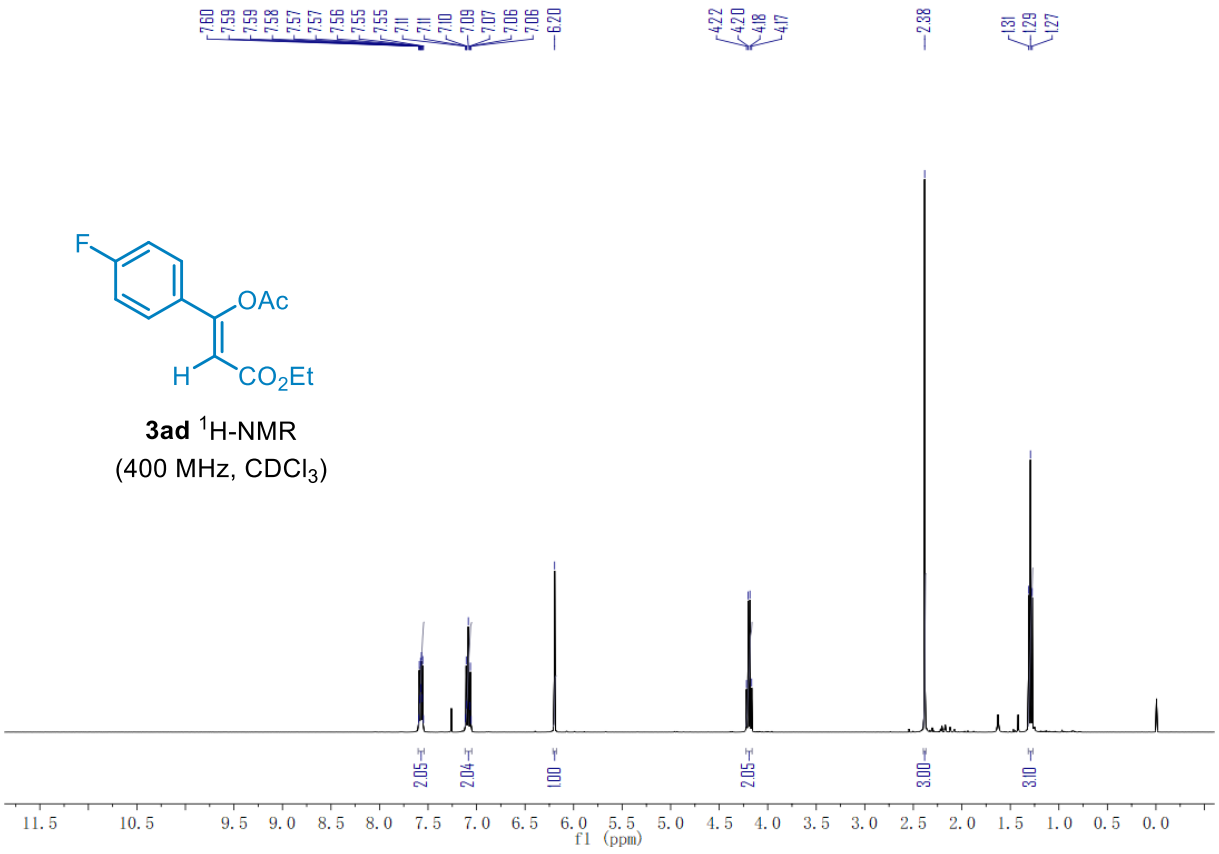




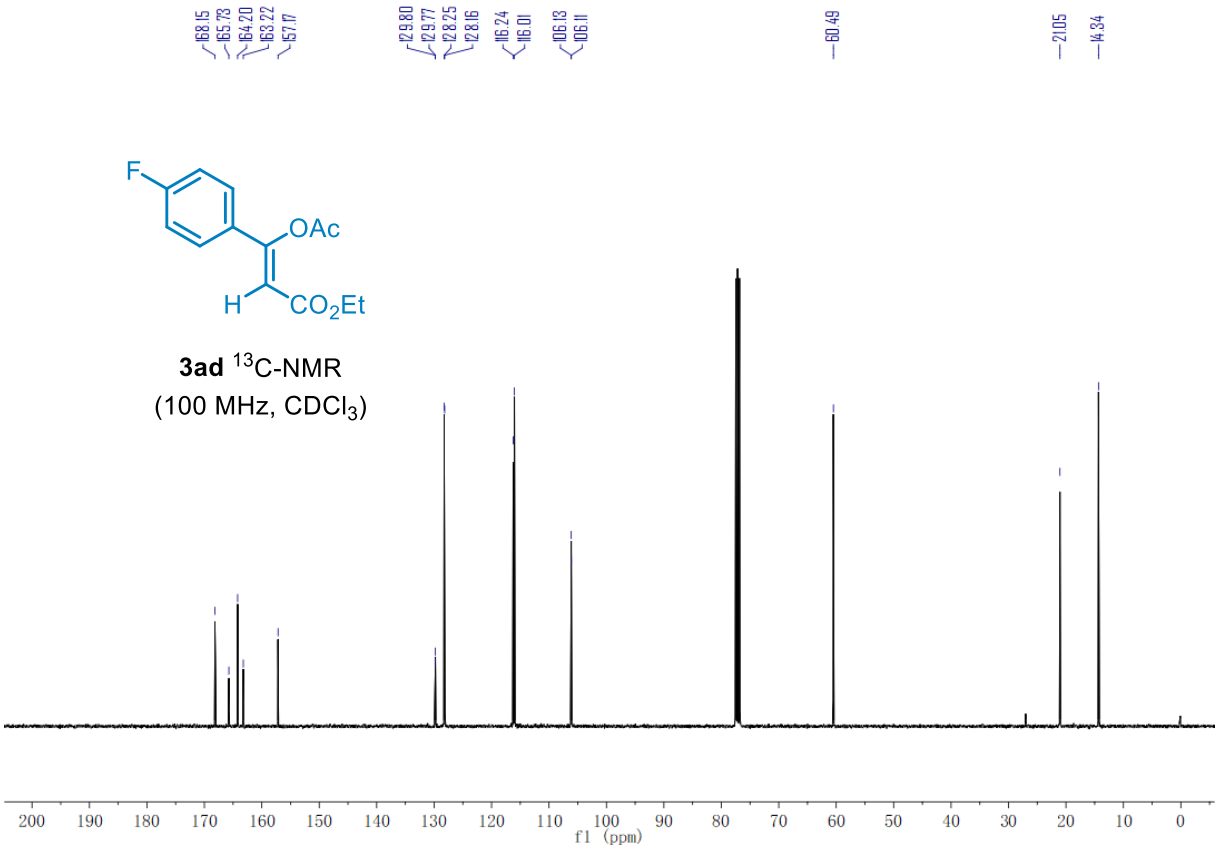
3ac ^{1}H-NMR
(400 MHz, $CDCl_3$)



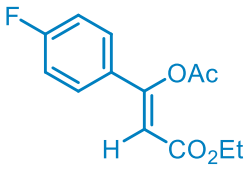
3ac ^{13}C-NMR
(100 MHz, $CDCl_3$)



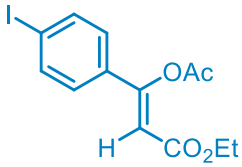
3ad ^{1}H-NMR
(400 MHz, $CDCl_3$)



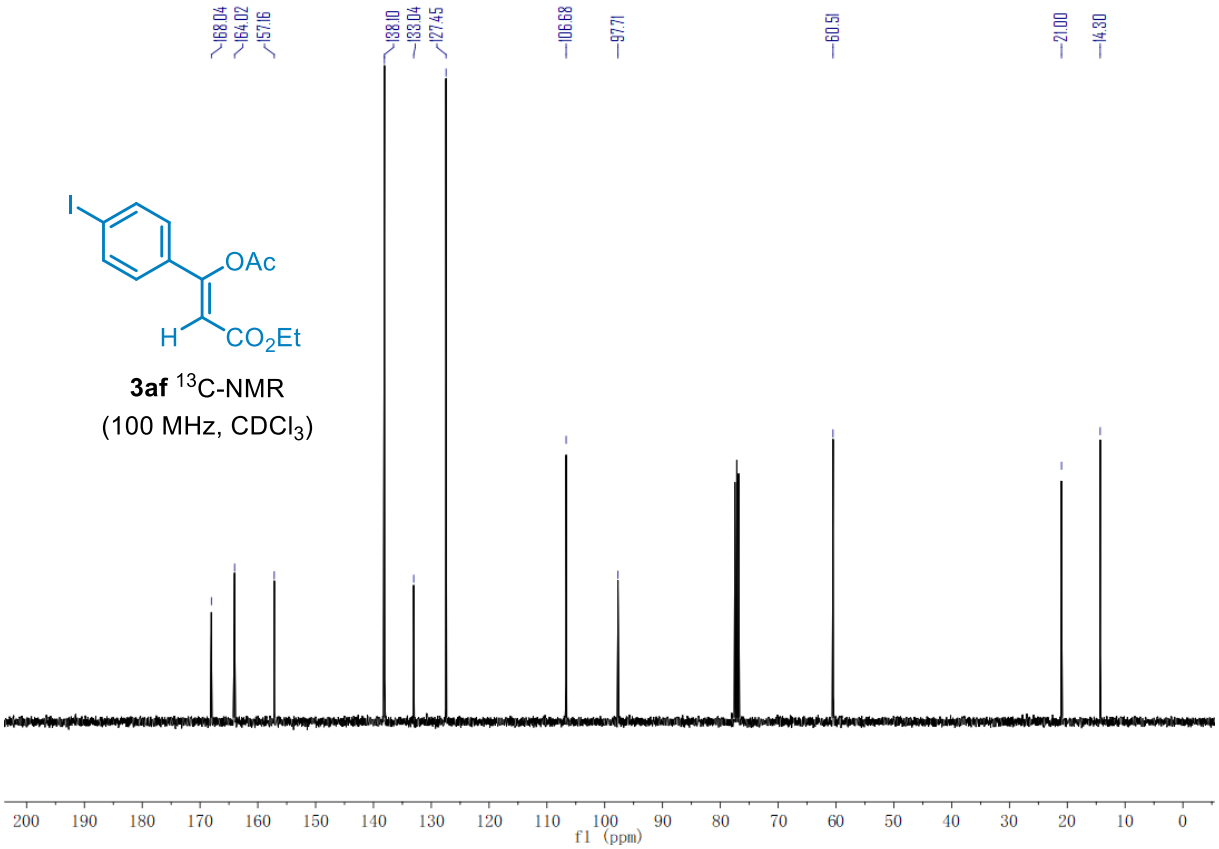
3ad ^{13}C-NMR
(100 MHz, $CDCl_3$)



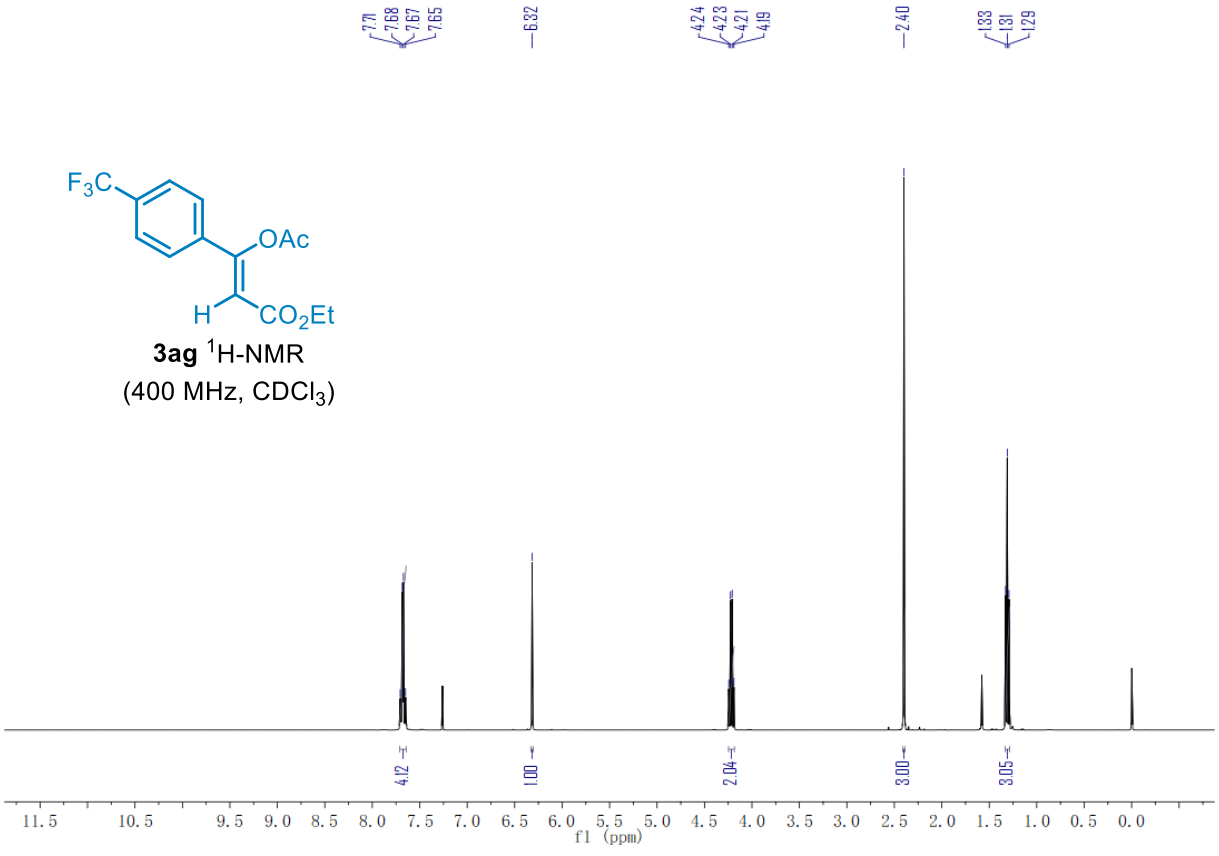
3ad ^{19}F-NMR
376 MHz, $CDCl_3$)



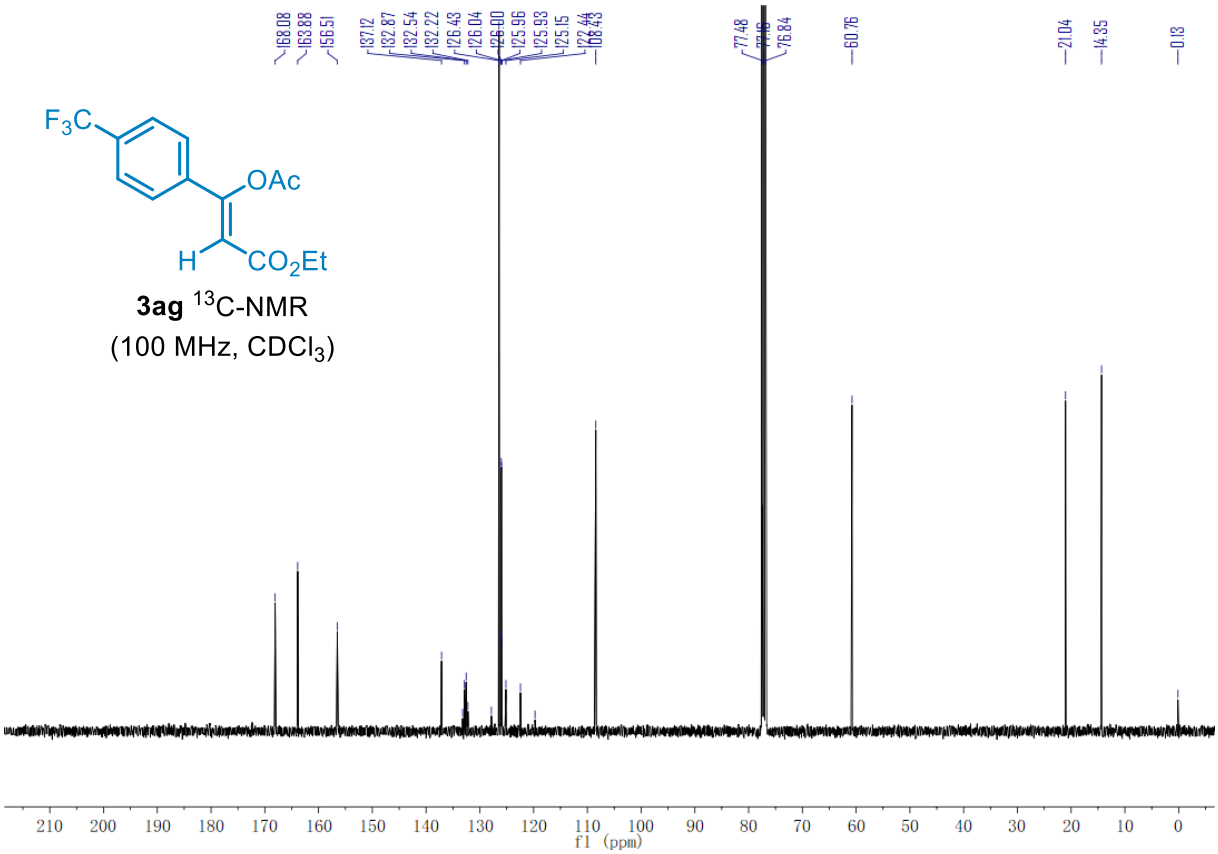
3af ^{1}H-NMR
(400 MHz, $CDCl_3$)



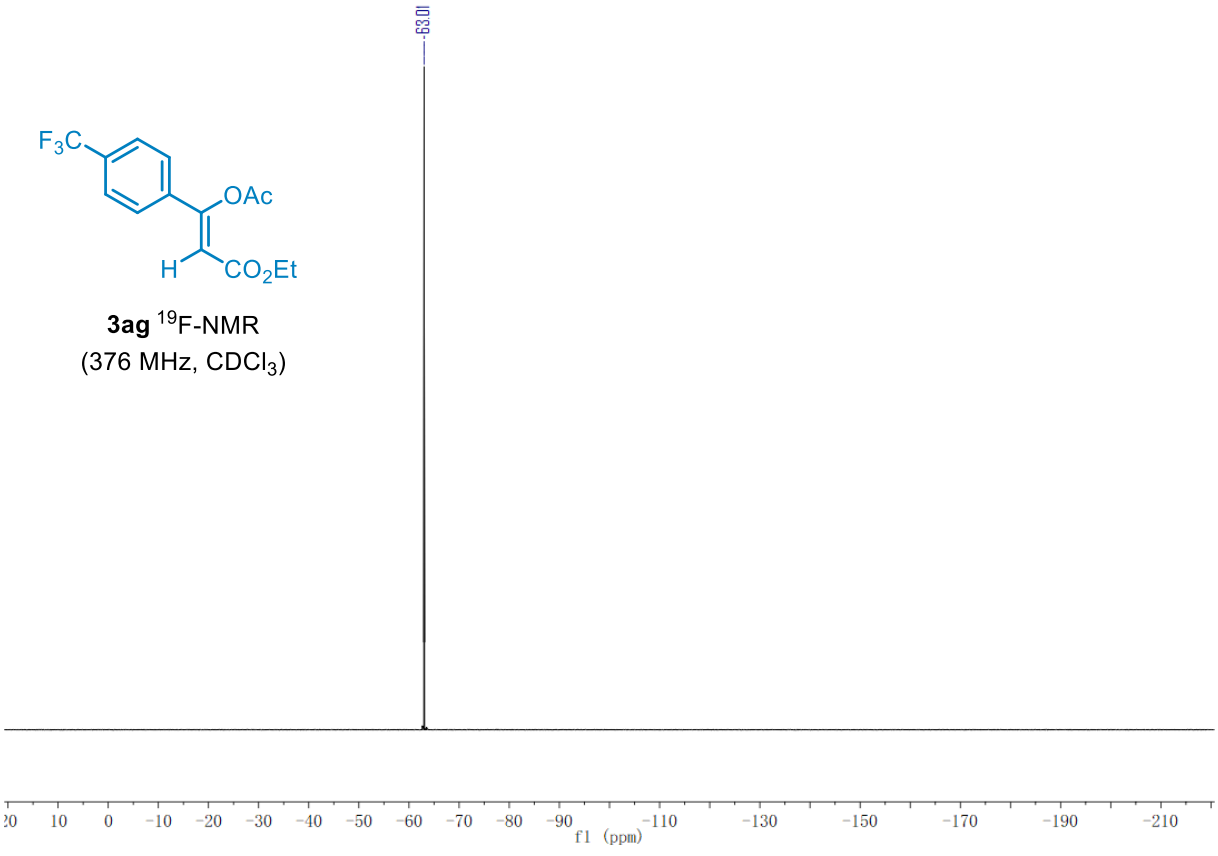
3af ^{13}C-NMR
(100 MHz, $CDCl_3$)



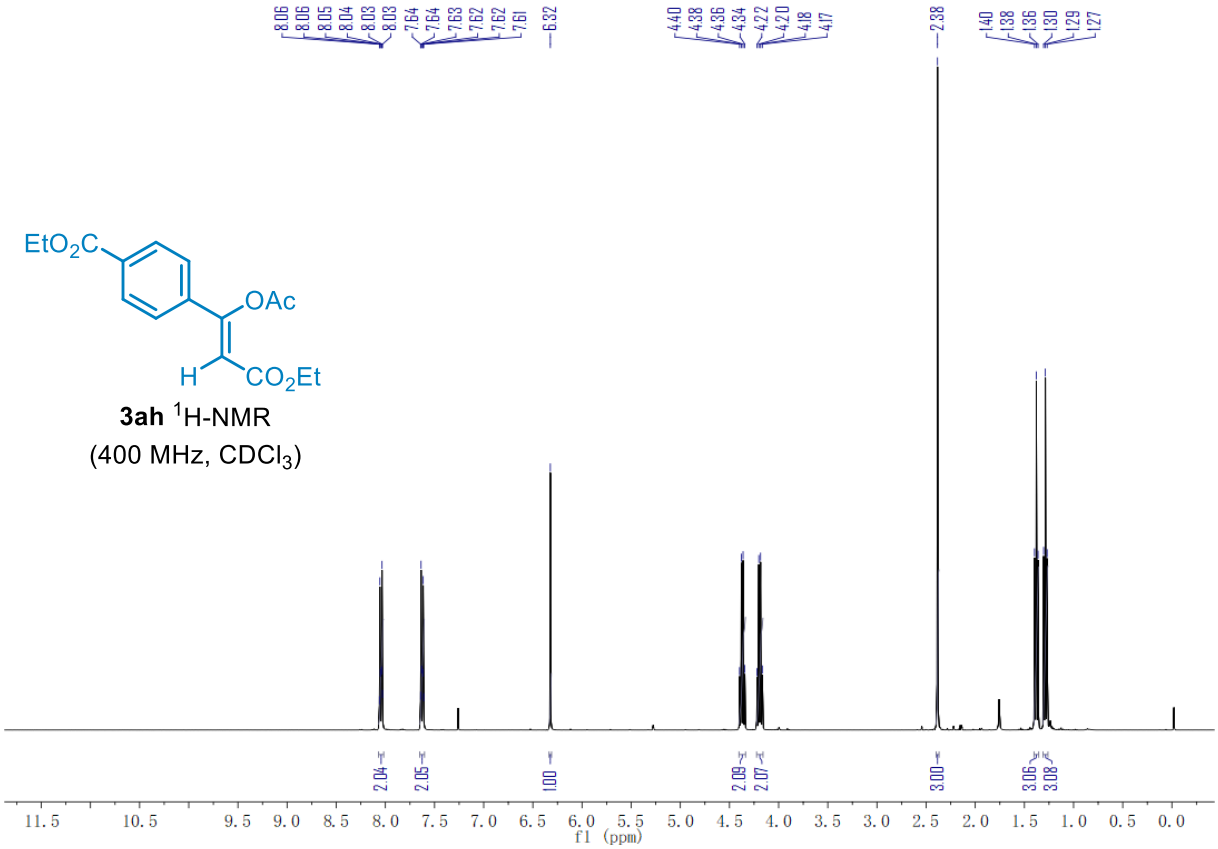
3ag ^{1}H-NMR
(400 MHz, $CDCl_3$)

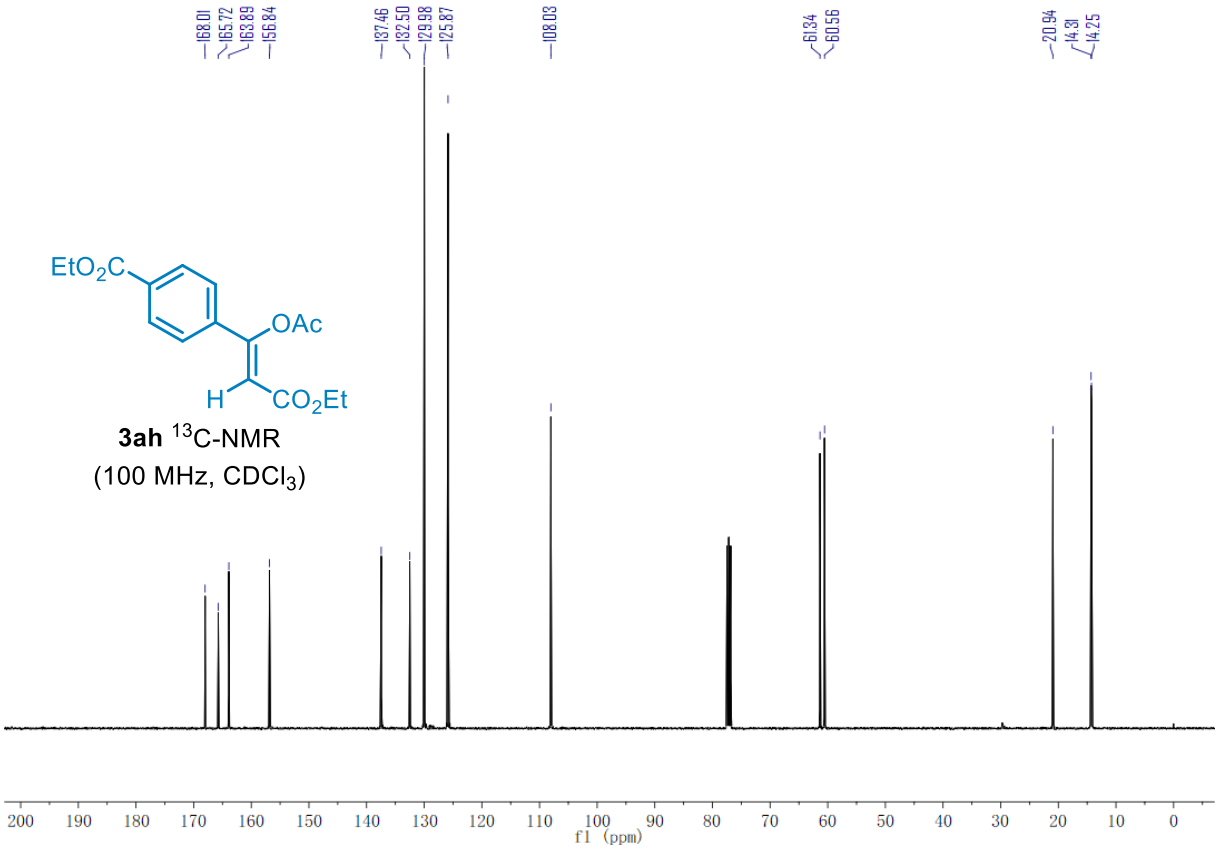


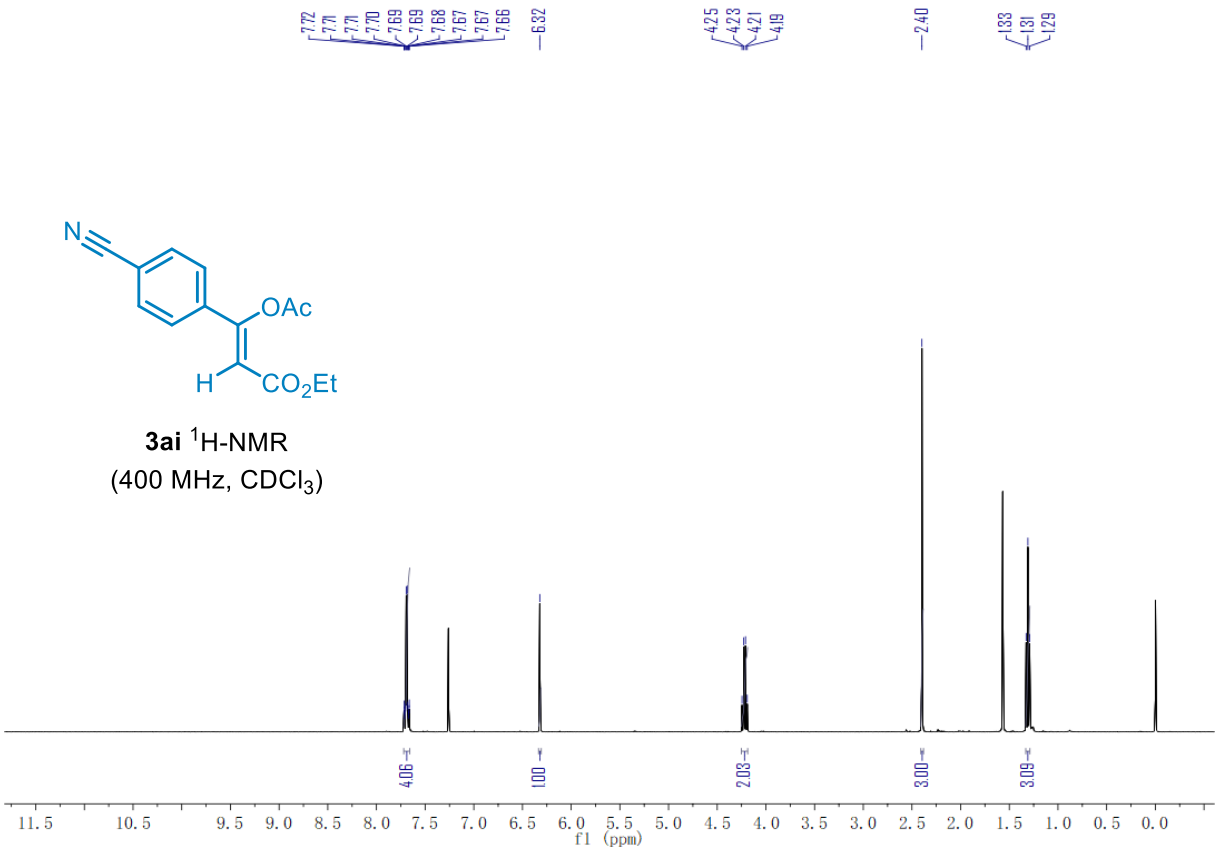
3ag ^{13}C-NMR
(100 MHz, $CDCl_3$)



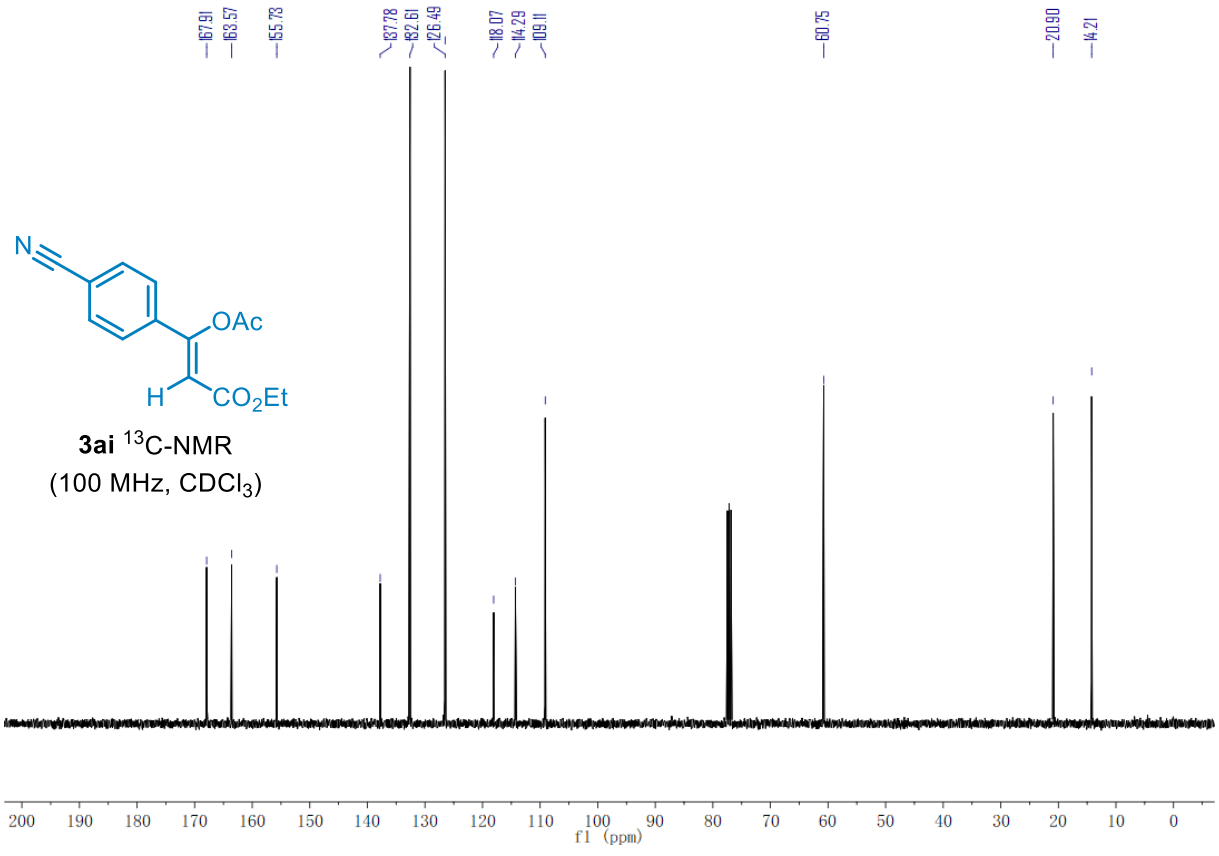
3ag ^{19}F-NMR
(376 MHz, $CDCl_3$)


8.06
8.06
8.05
8.04
8.03
8.03
7.64
7.64
7.63
7.62
7.62
7.61
6.32
4.40
4.38
4.36
4.34
4.22
4.20
4.18
4.17
2.38
1.40
1.38
1.36
1.30
1.29
1.27
EtO2C
OAc
H
CO2Et
3ah 1H-NMR
(400 MHz, CDCl3)
2.04
2.05
1.00
2.09
2.07
3.00
3.06
3.08
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

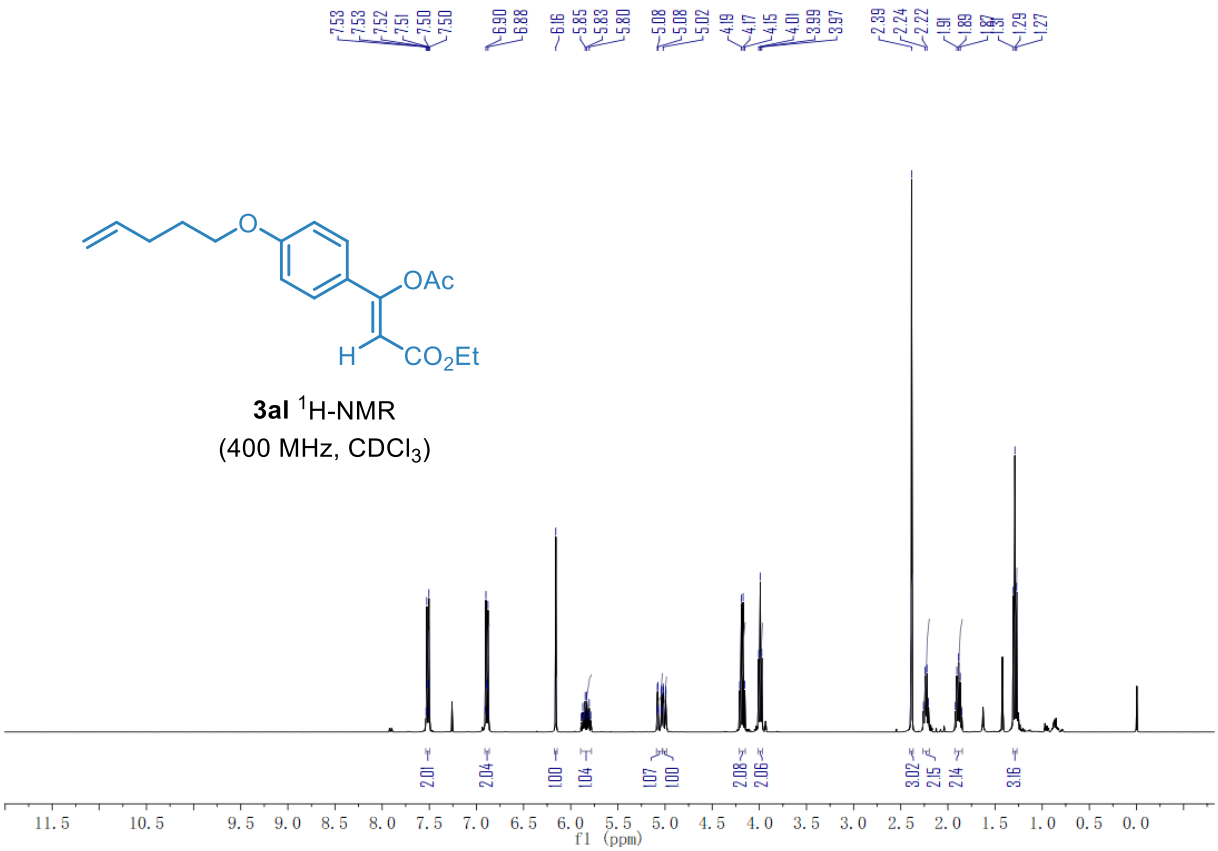

168.01
165.72
163.89
156.84
137.46
132.50
129.98
125.87
108.03
61.34
60.56
20.94
14.31
14.25
EtO2C
OAc
H
CO2Et
3ah 13C-NMR
(100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



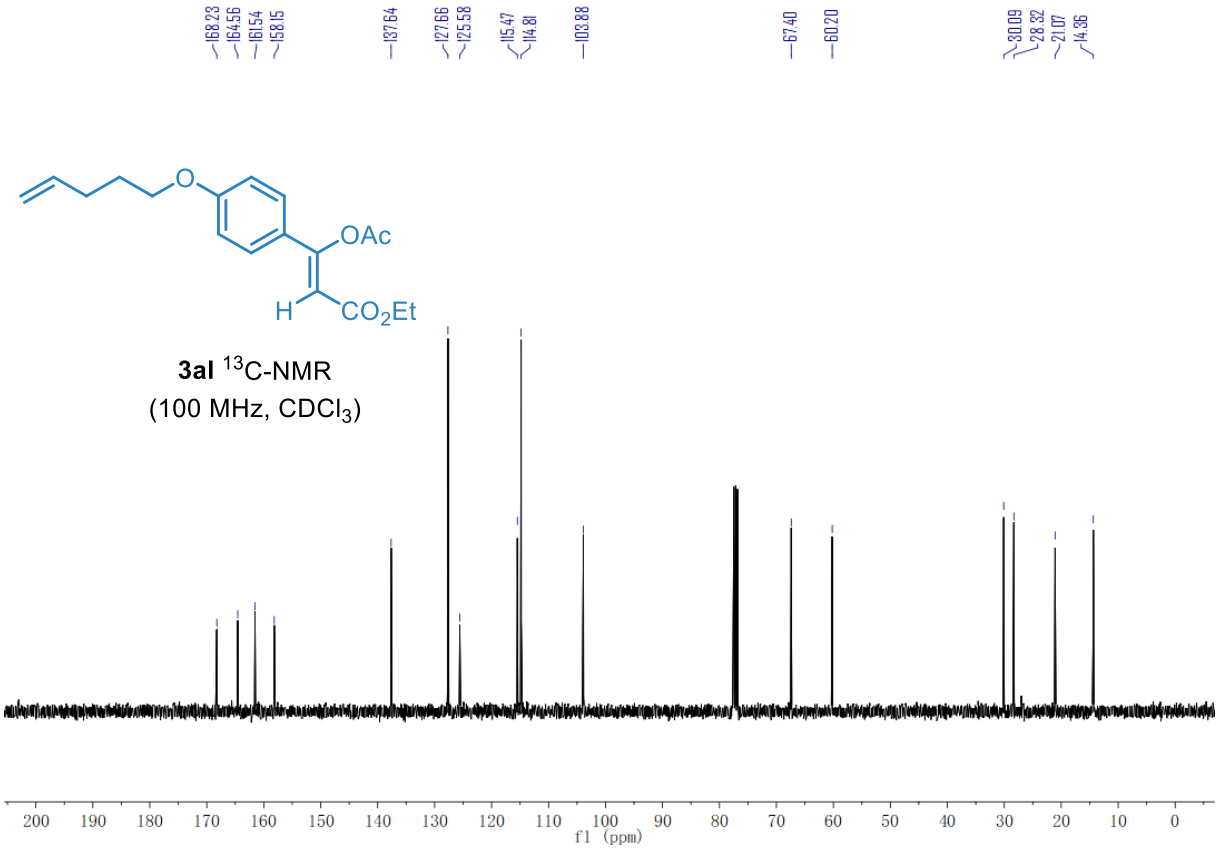
3ai ^{1}H-NMR
(400 MHz, $CDCl_3$)



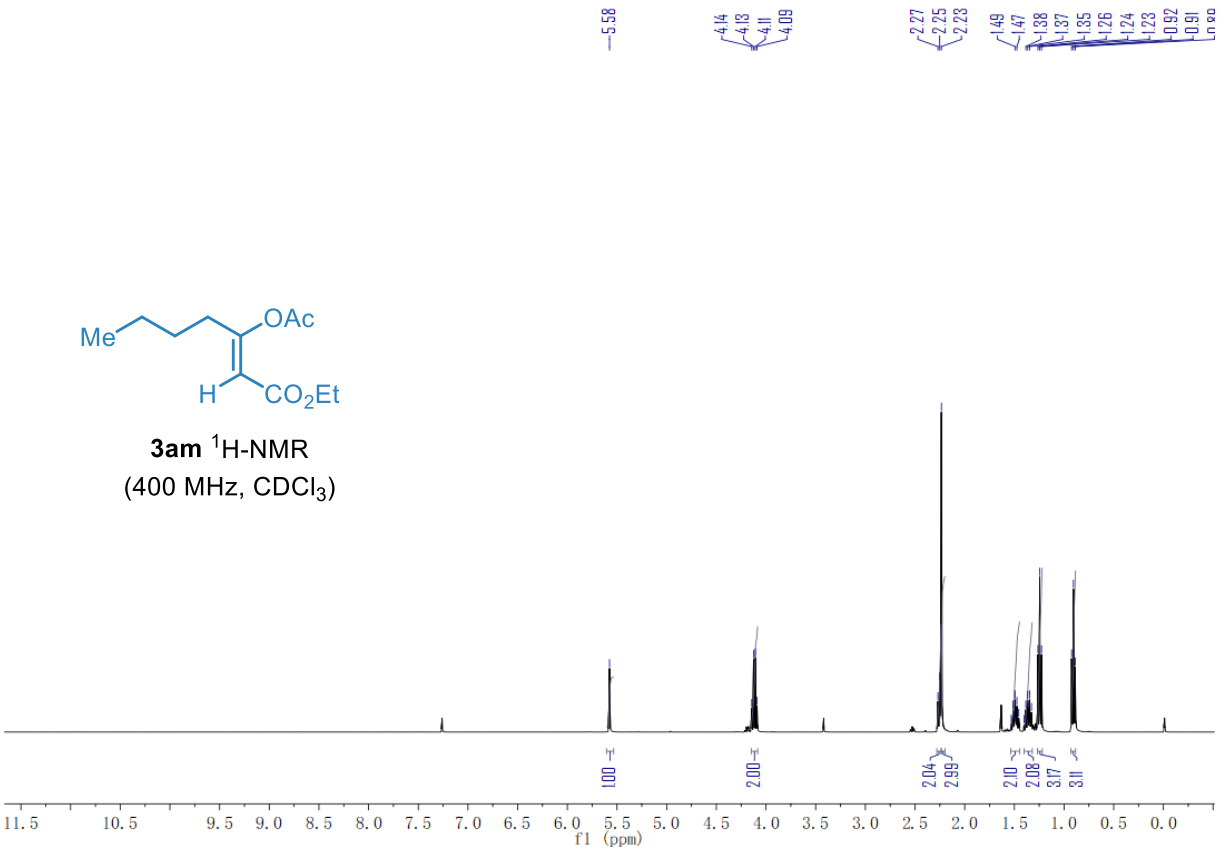
3ai ^{13}C-NMR
(100 MHz, $CDCl_3$)



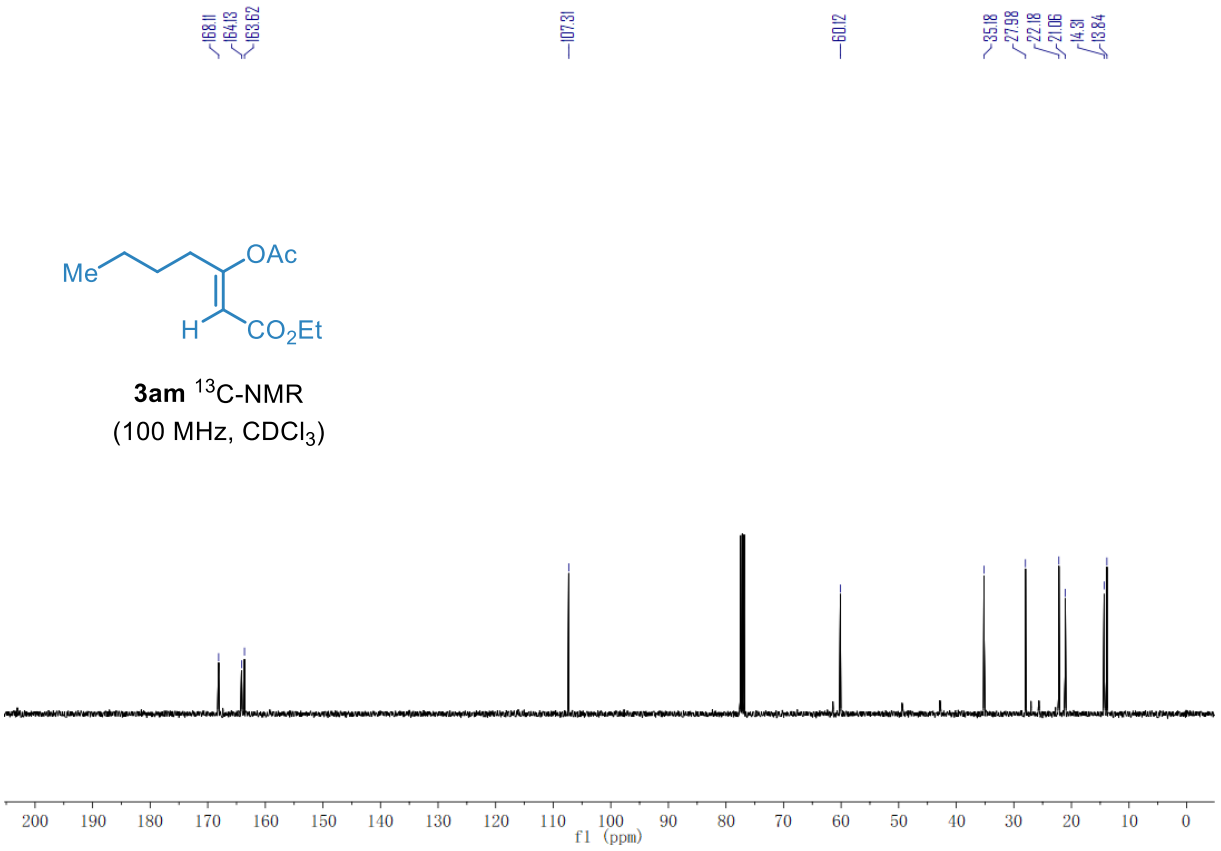
3al ^{1}H-NMR
(400 MHz, $CDCl_3$)



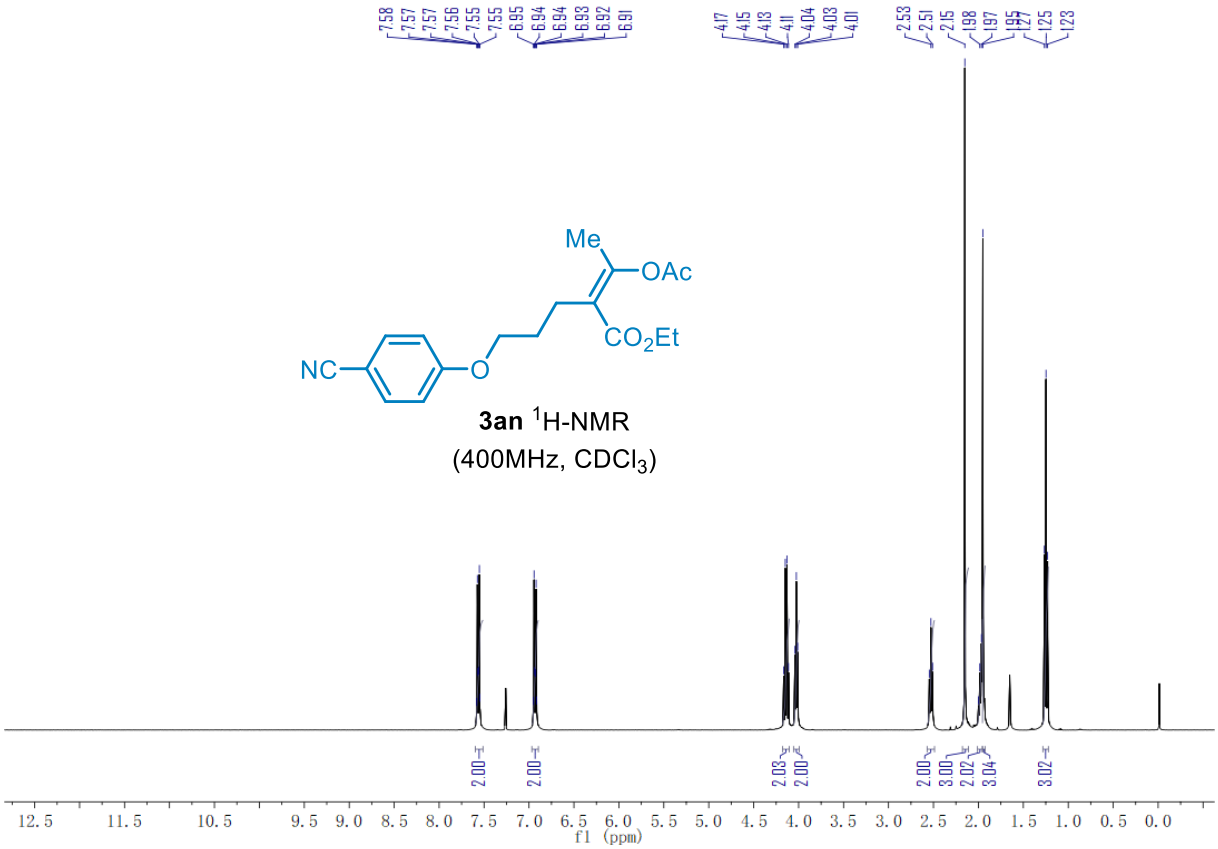
3al ^{13}C-NMR
(100 MHz, $CDCl_3$)



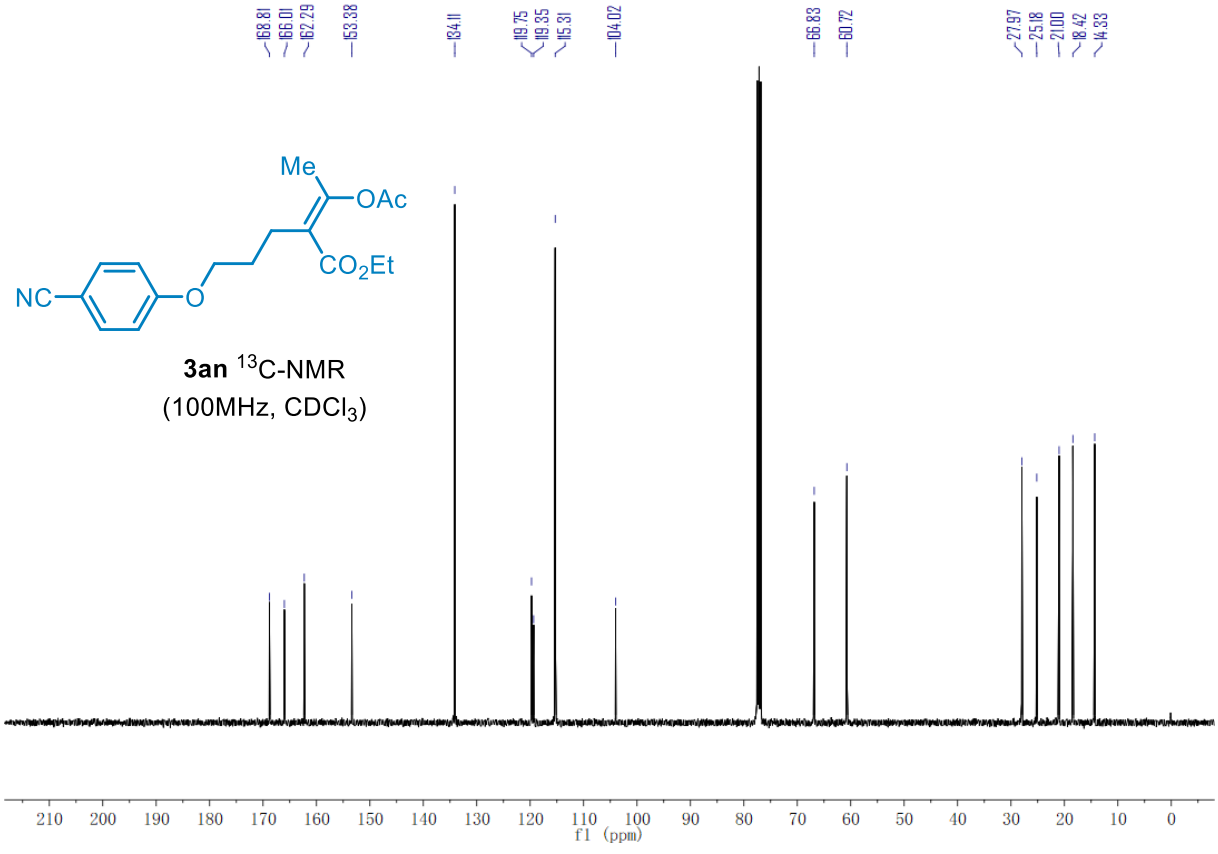
3am ^{1}H-NMR
(400 MHz, $CDCl_3$)



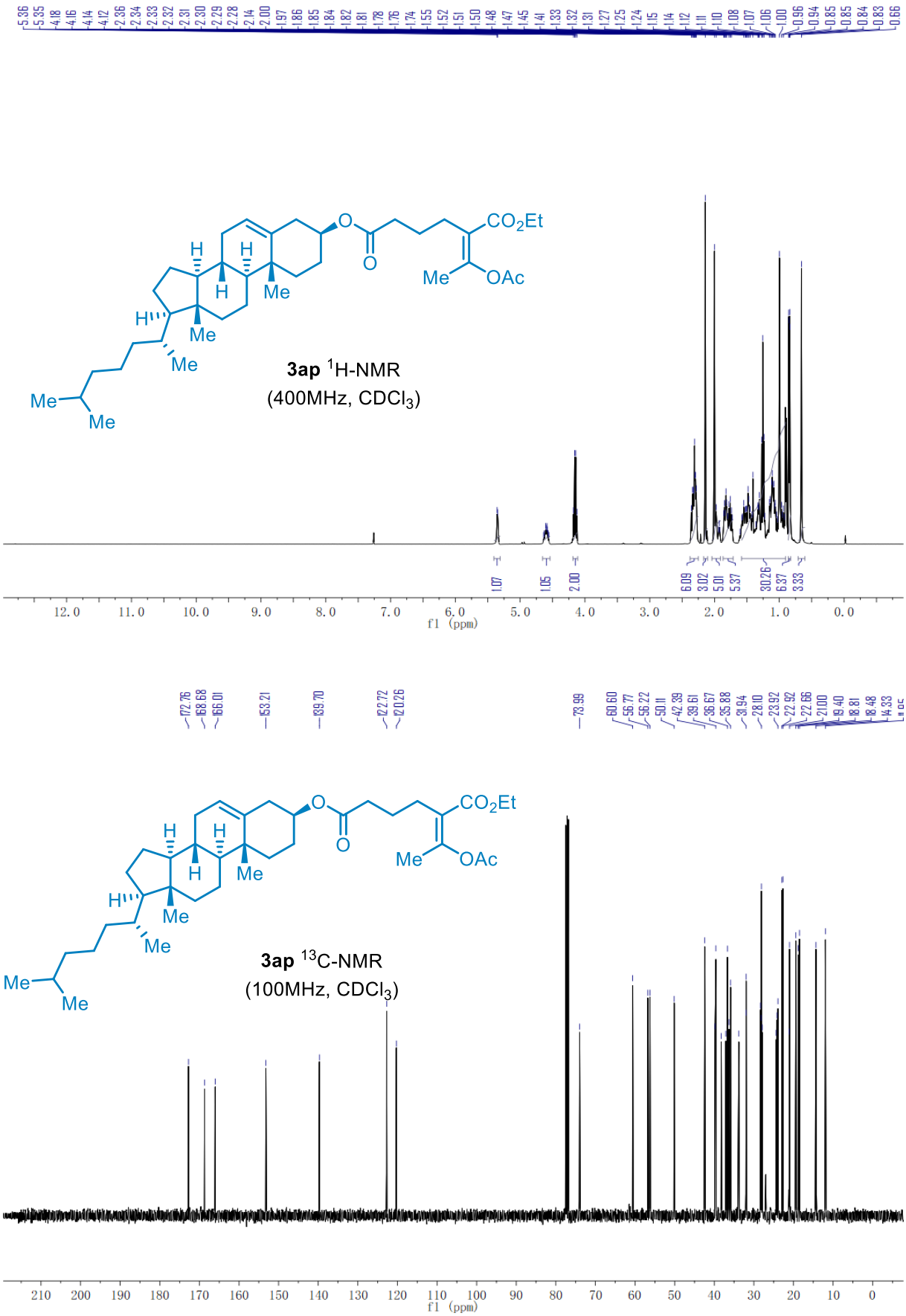
3am ^{13}C-NMR
(100 MHz, $CDCl_3$)

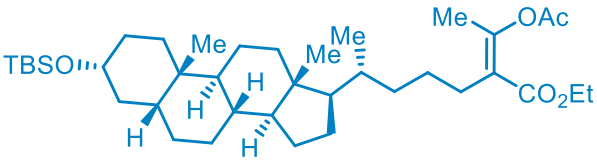


3an ^{1}H-NMR
(400MHz, $CDCl_3$)

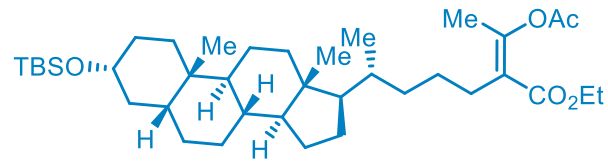


3an ^{13}C-NMR
(100MHz, $CDCl_3$)

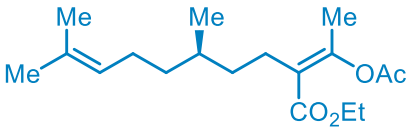

3ap 1H-NMR
(400MHz, CDCl3)
3ap 13C-NMR
(100MHz, CDCl3)
f1 (ppm)



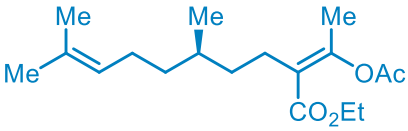
3aq ^{1}H-NMR
(400MHz, $CDCl_3$)



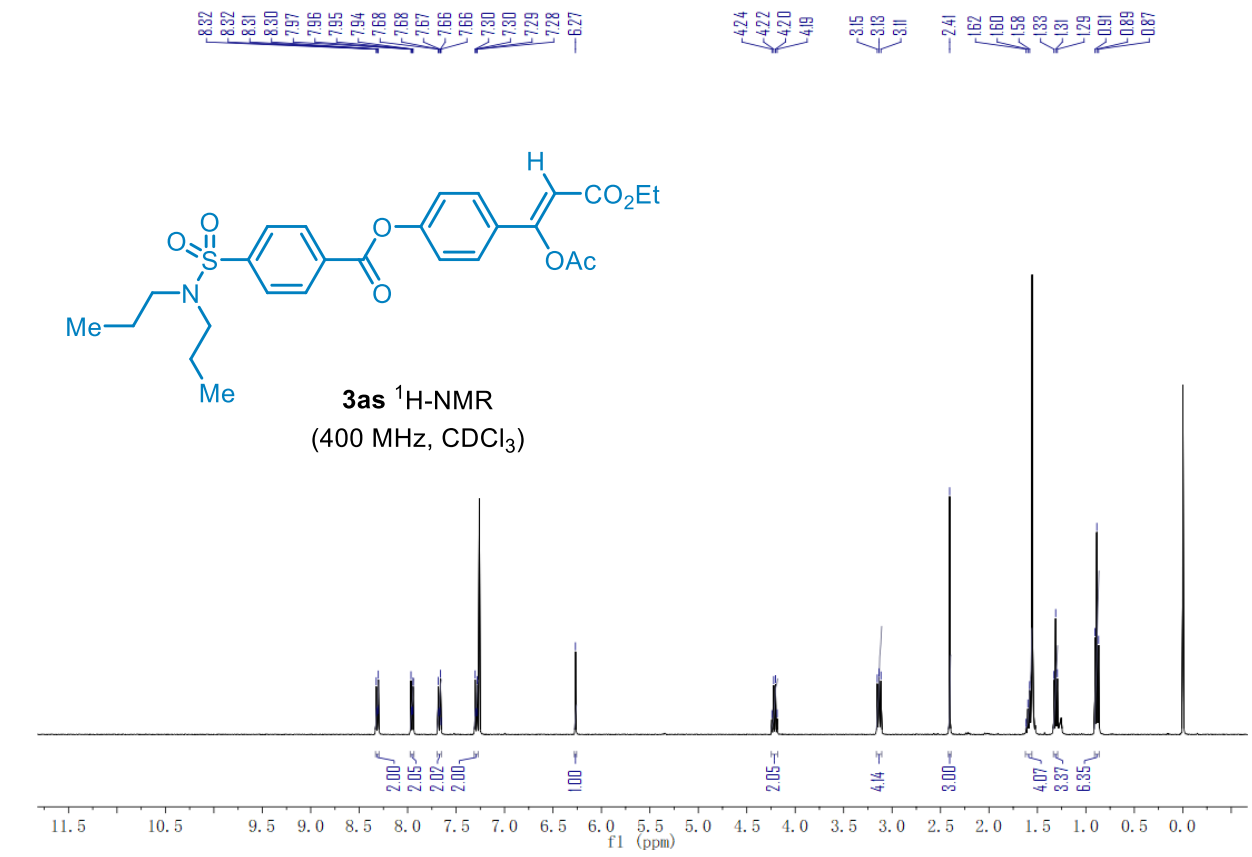
3aq ^{13}C-NMR
(100MHz, $CDCl_3$)

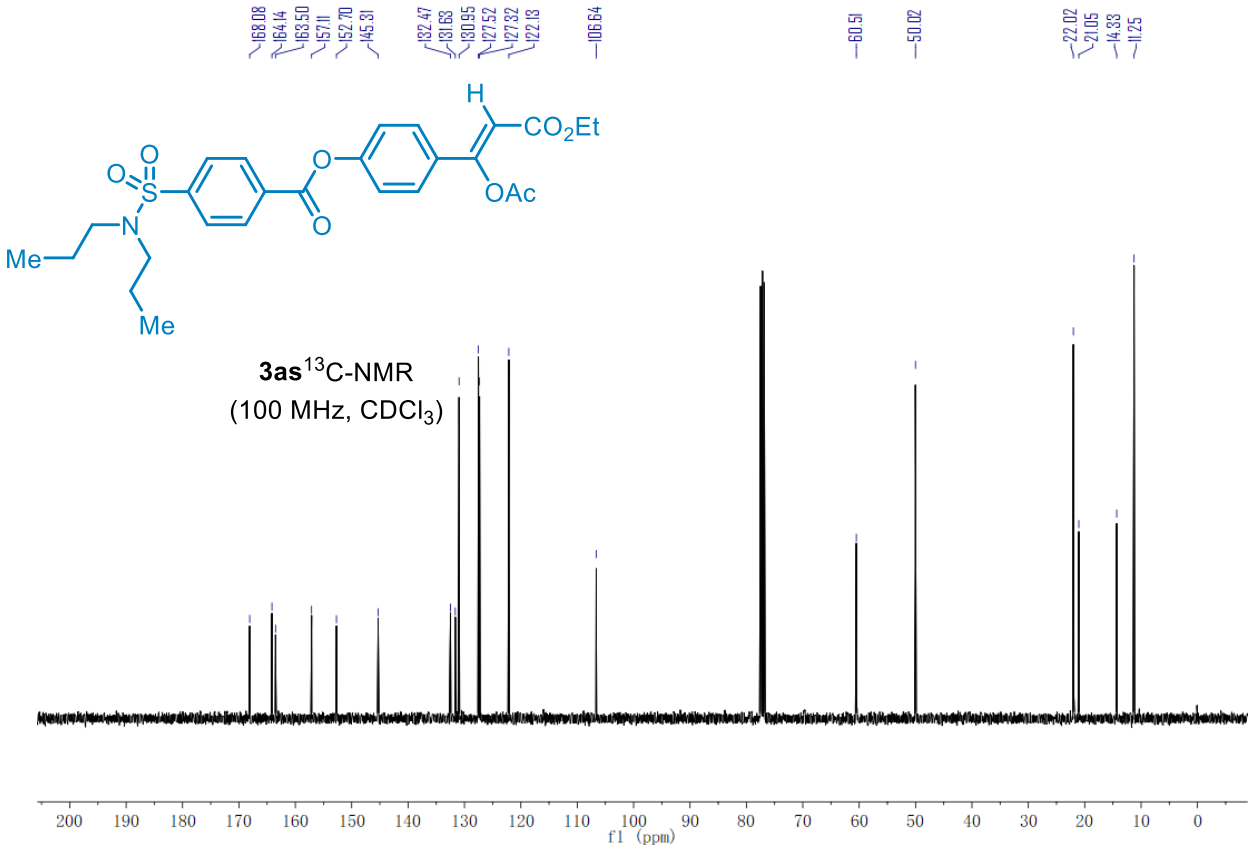


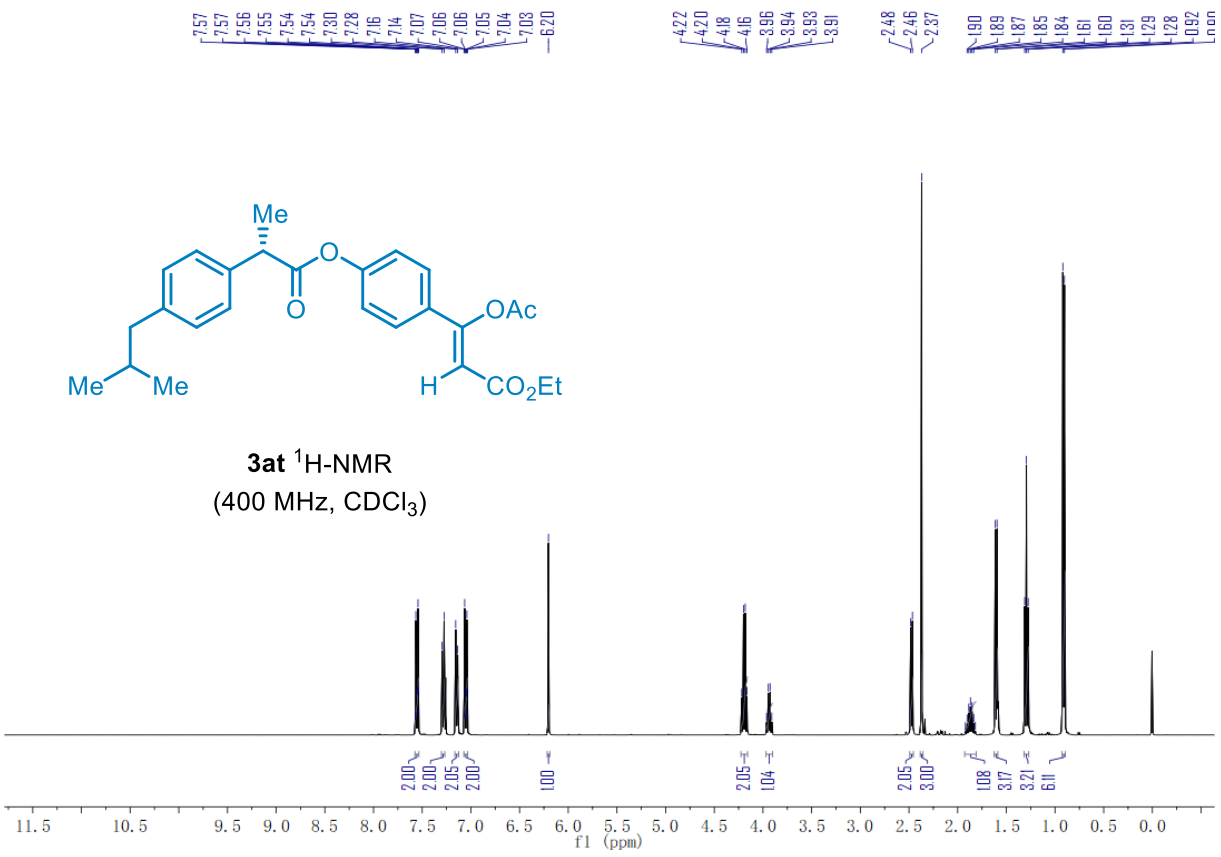
3ar ^{1}H-NMR
(400MHz, $CDCl_3$)

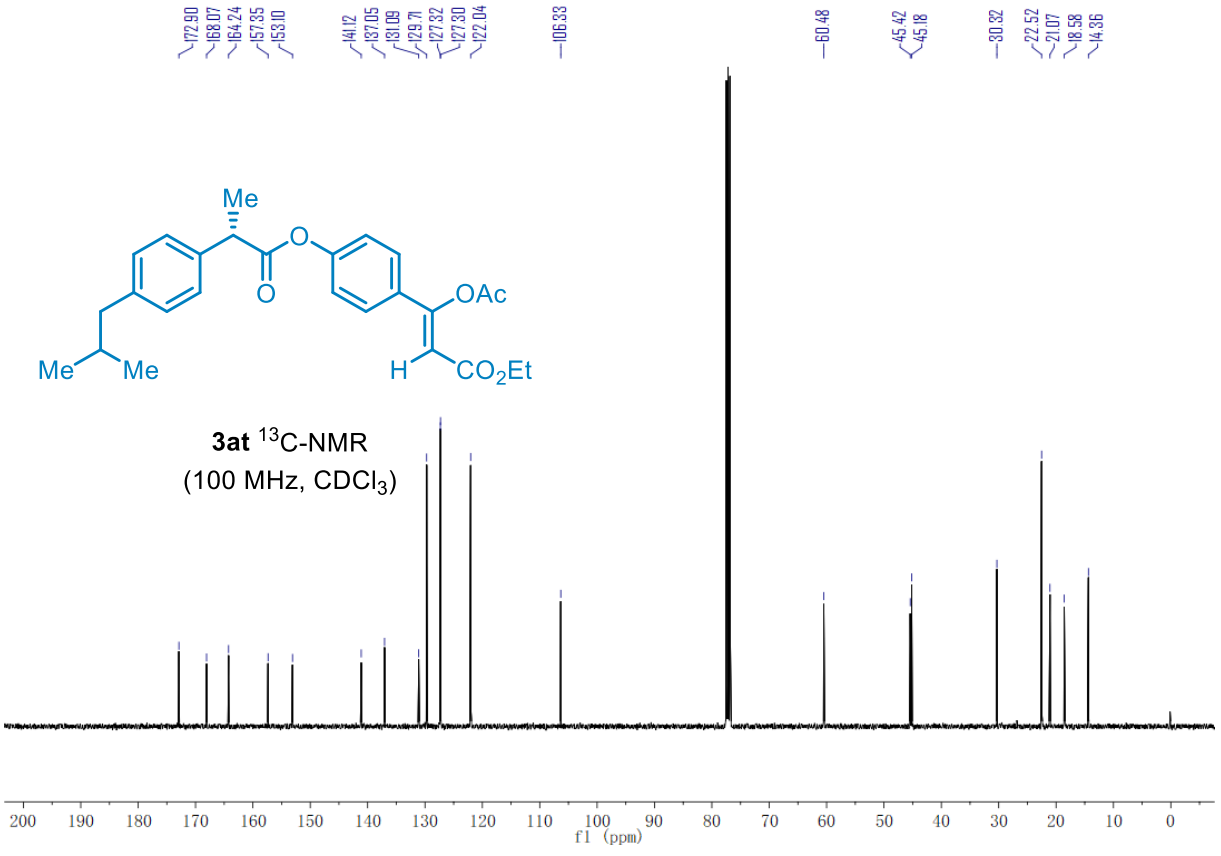


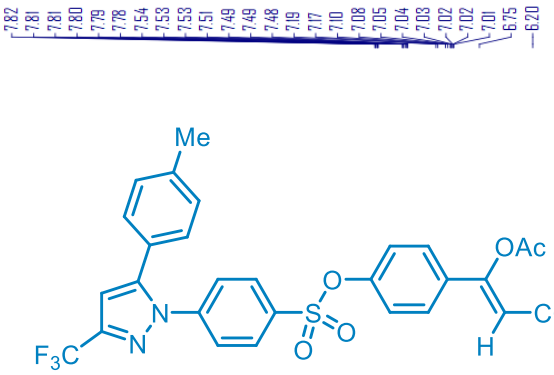
3ar ^{13}C-NMR
(100MHz, $CDCl_3$)


8.32
8.32
8.31
8.30
7.97
7.96
7.95
7.94
7.68
7.68
7.67
7.66
7.66
7.30
7.30
7.29
7.28
6.27
4.24
4.22
4.20
4.19
3.15
3.13
3.11
2.41
1.62
1.60
1.58
1.33
1.31
1.29
0.91
0.89
0.87
H
CO2Et
OAc
O
O
S
N
Me
Me
3as 1H-NMR
(400 MHz, CDCl3)
2.00
2.05
2.02
2.00
1.00
2.05
4.14
3.00
4.07
3.37
6.35
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

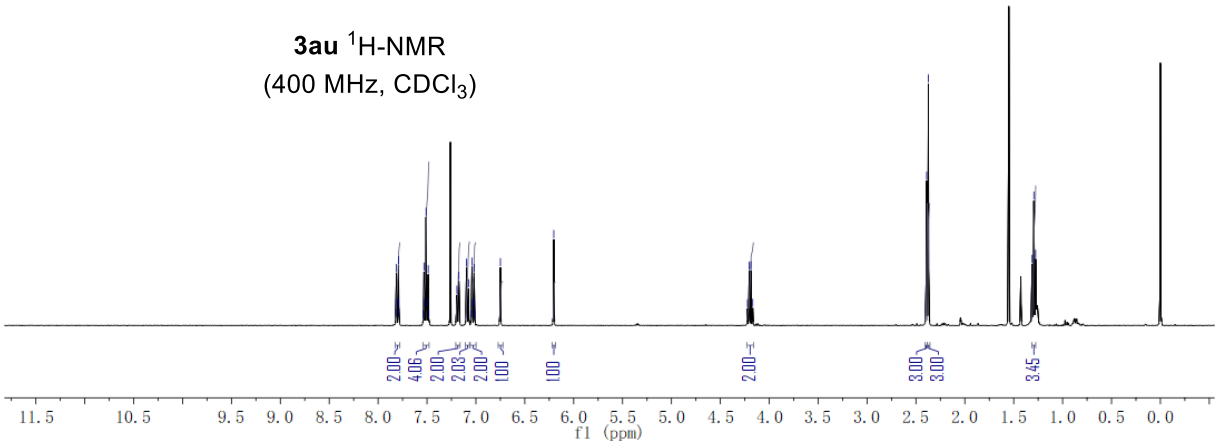

168.08
164.14
163.50
157.11
152.70
145.31
132.47
131.63
130.95
127.52
127.32
122.13
106.64
60.51
50.02
22.02
21.05
14.33
11.25
H
CO2Et
OAc
O
O
S
N
Me
Me
3as13C-NMR
(100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

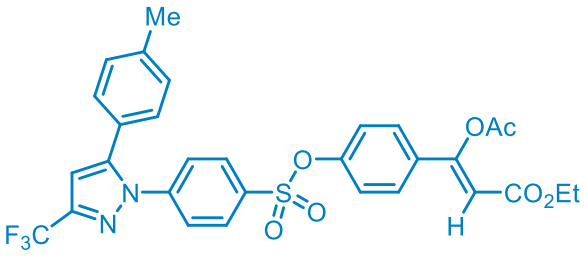

Me
O
O
OAc
Me
Me
H
CO2Et
3at 1H-NMR
(400 MHz, CDCl3)
f1 (ppm)


Me
O
O
OAc
Me
Me
H
CO2Et
3at 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)

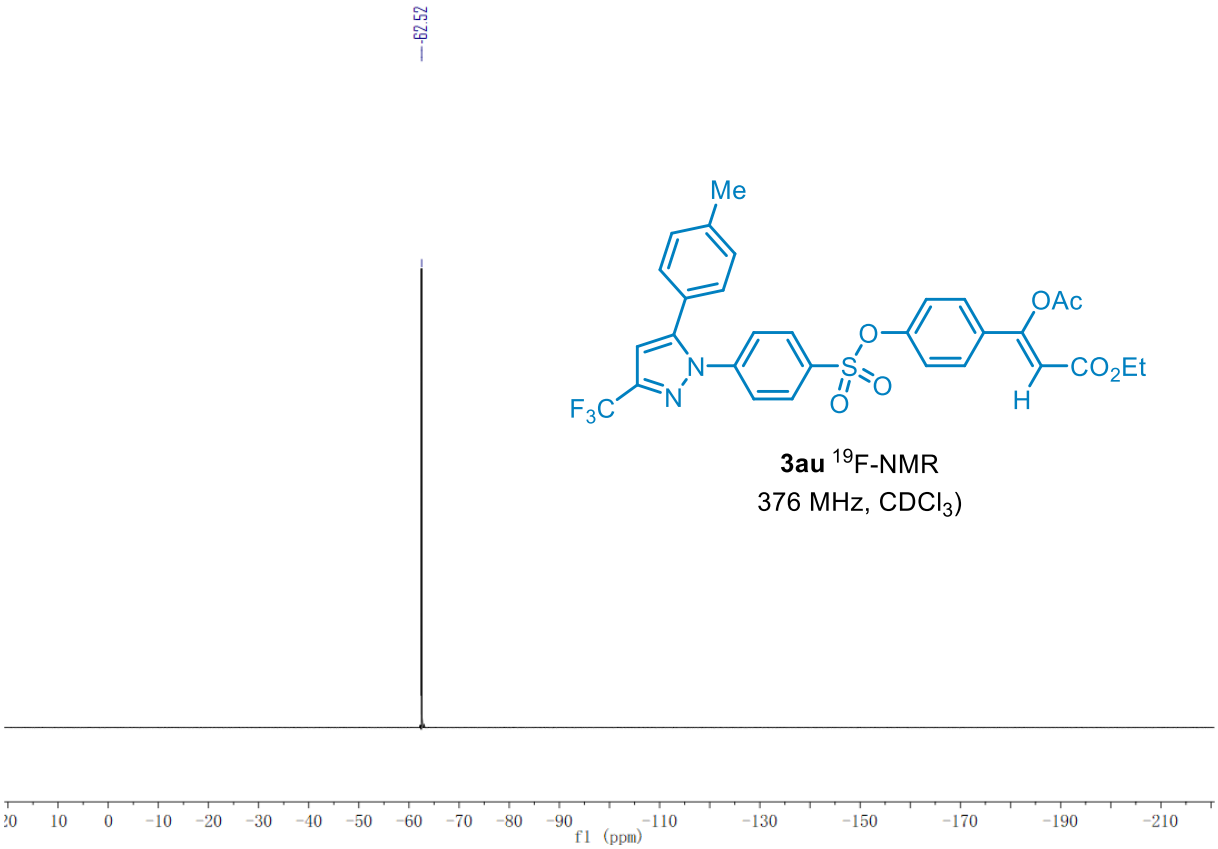


3au ^{1}H-NMR
(400 MHz, $CDCl_3$)

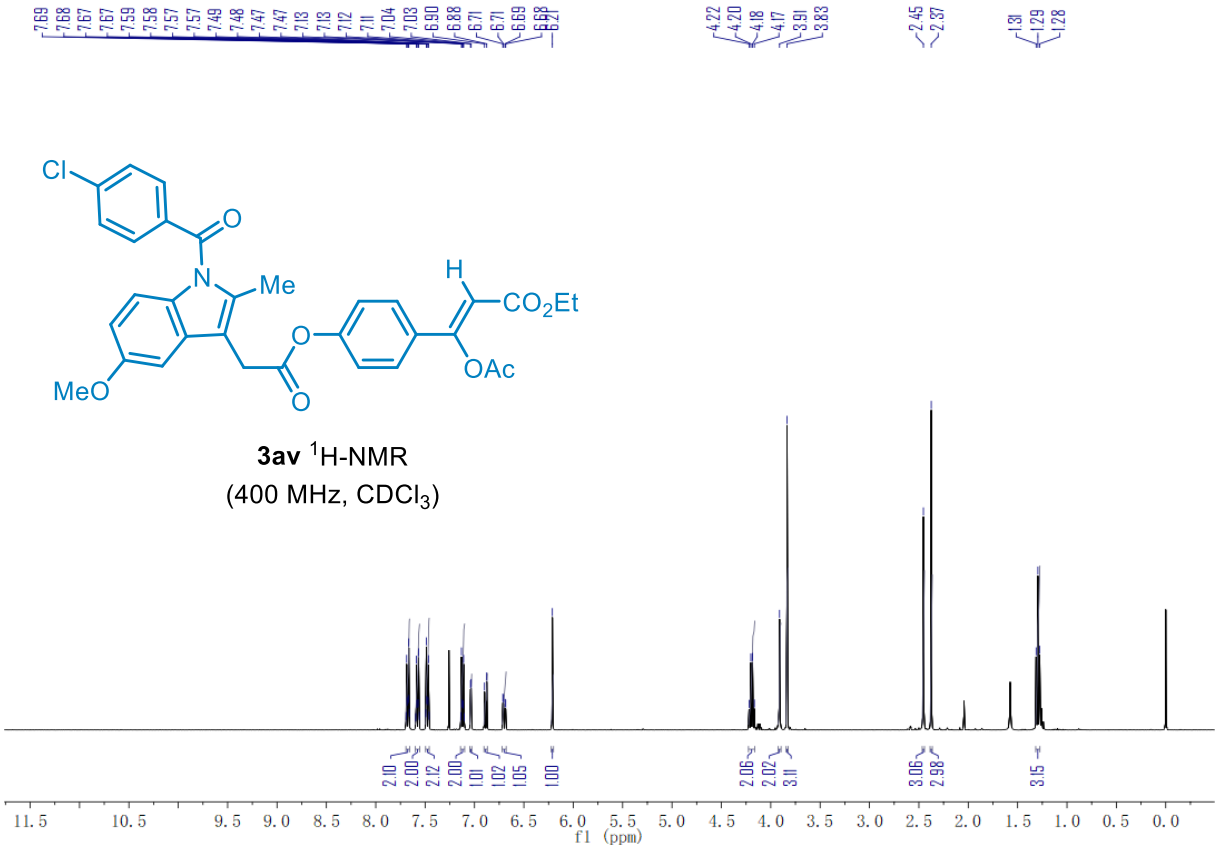




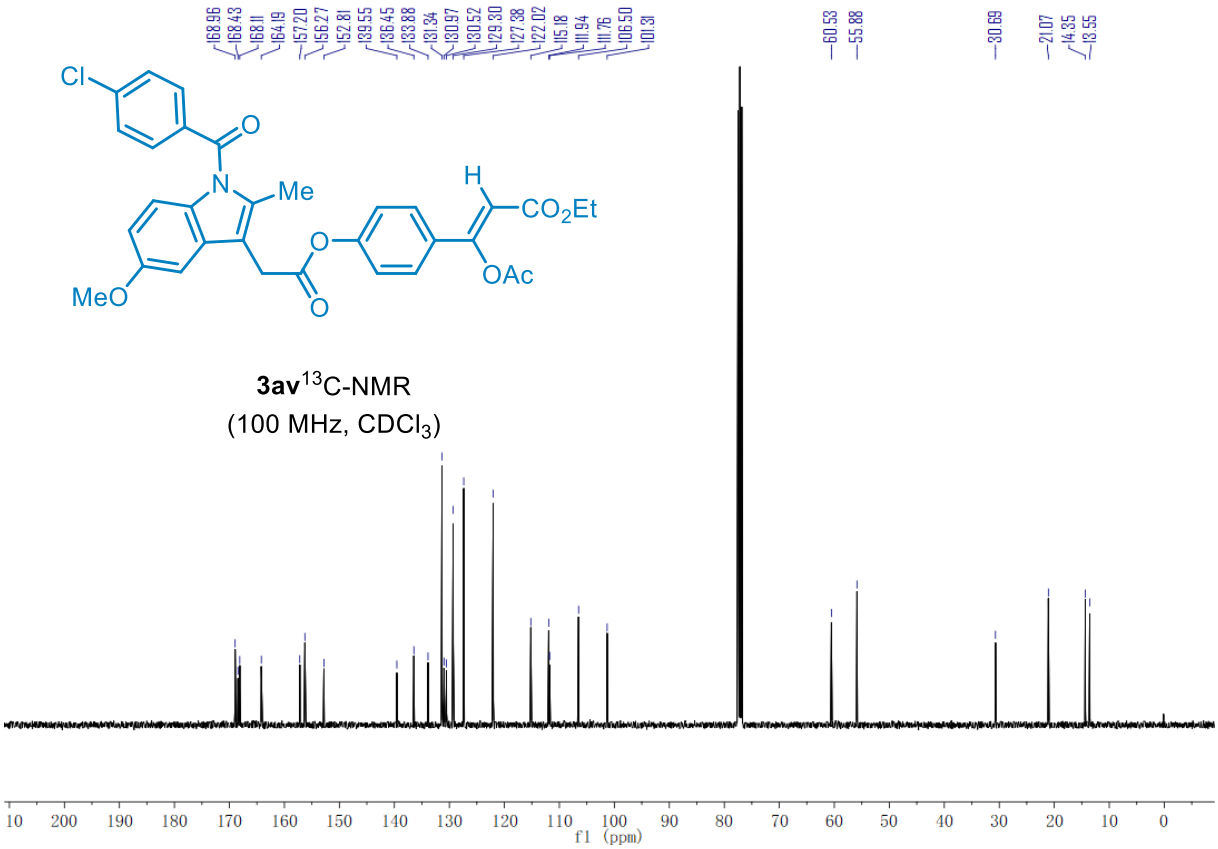
3au^{13}C-NMR
(100 MHz, $CDCl_3$)



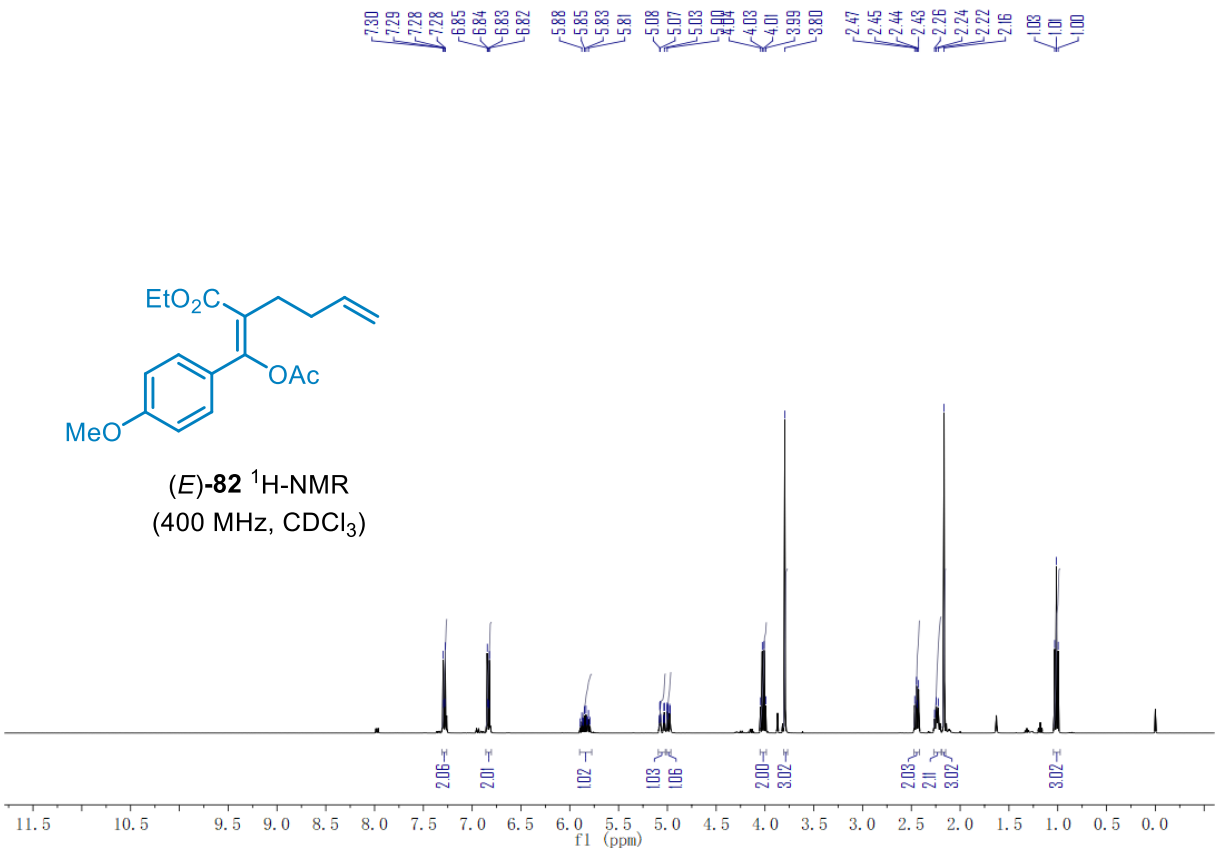
3au ^{19}F-NMR
376 MHz, $CDCl_3$)



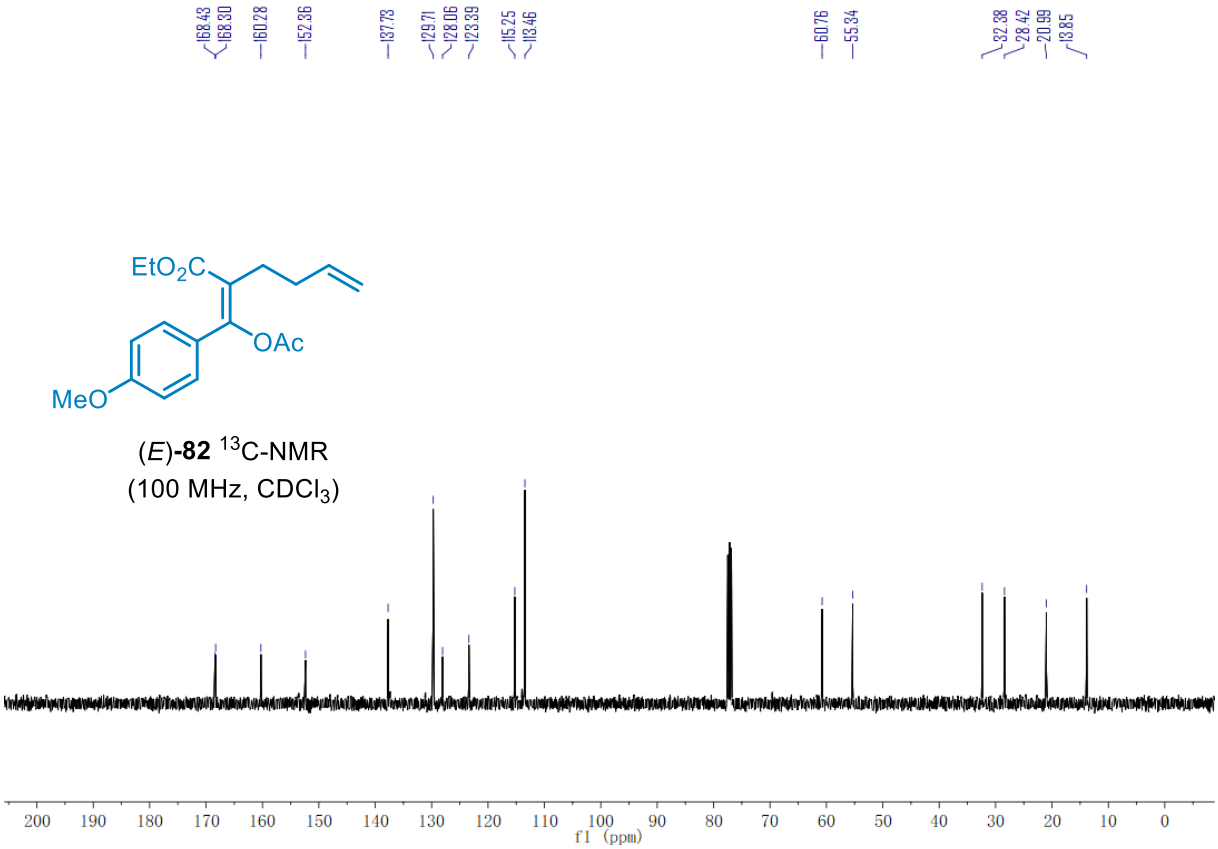
3av ^{1}H-NMR
(400 MHz, $CDCl_3$)



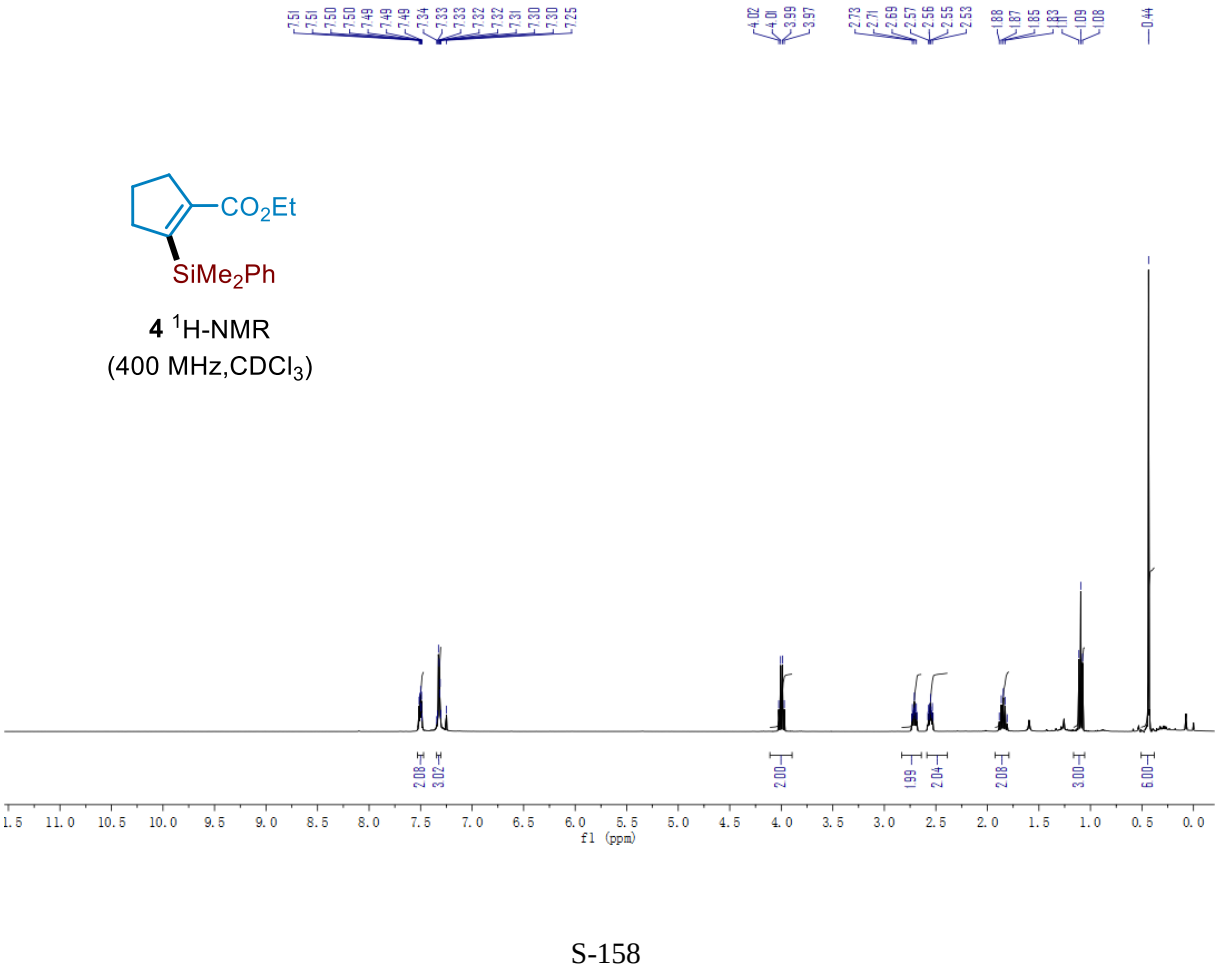
3av ^{13}C-NMR
(100 MHz, $CDCl_3$)



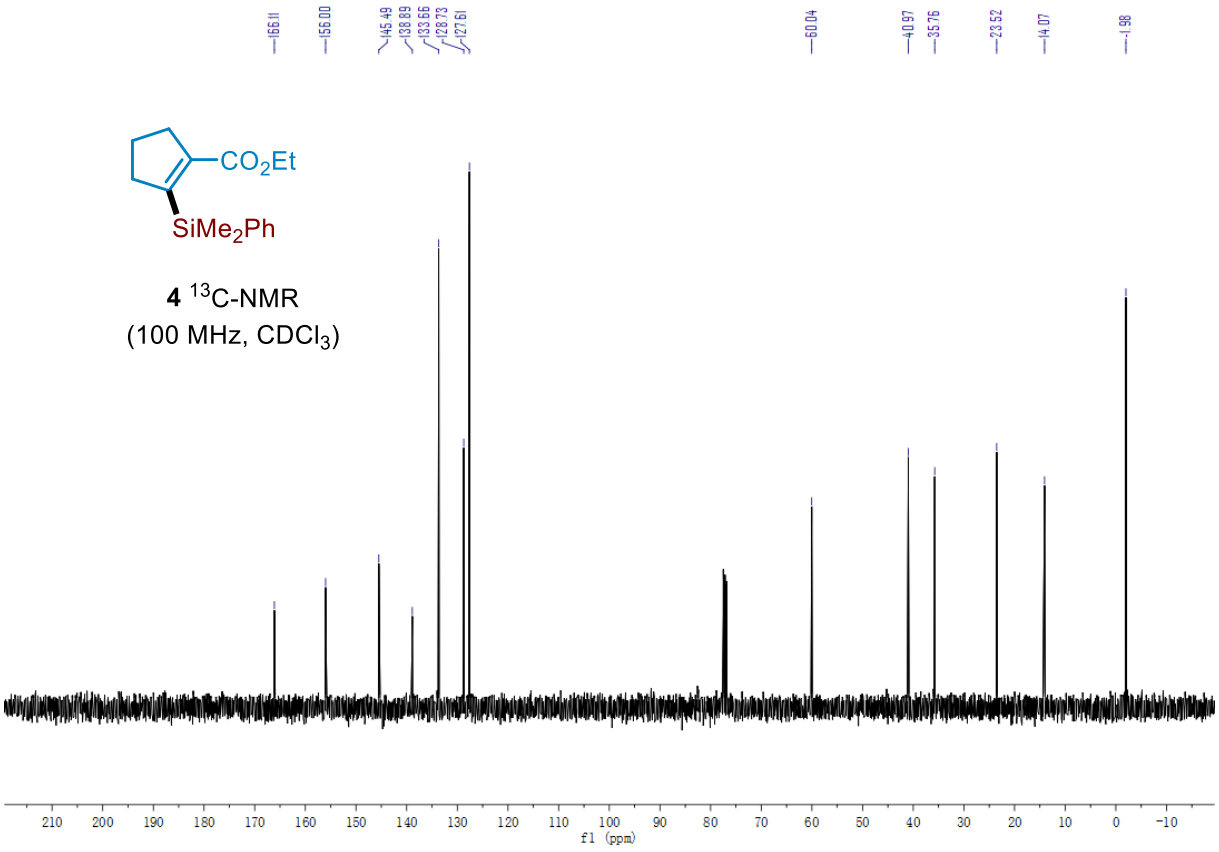
(*E*)-**82** ^{1}H-NMR
(400 MHz, $CDCl_3$)

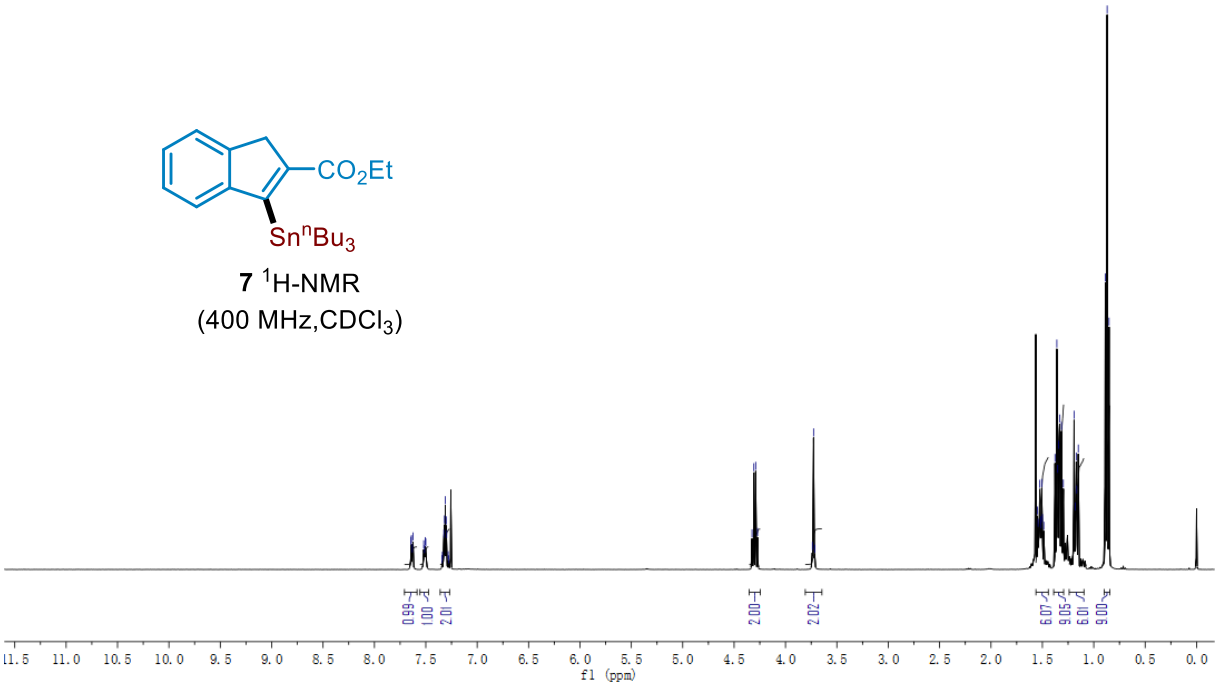


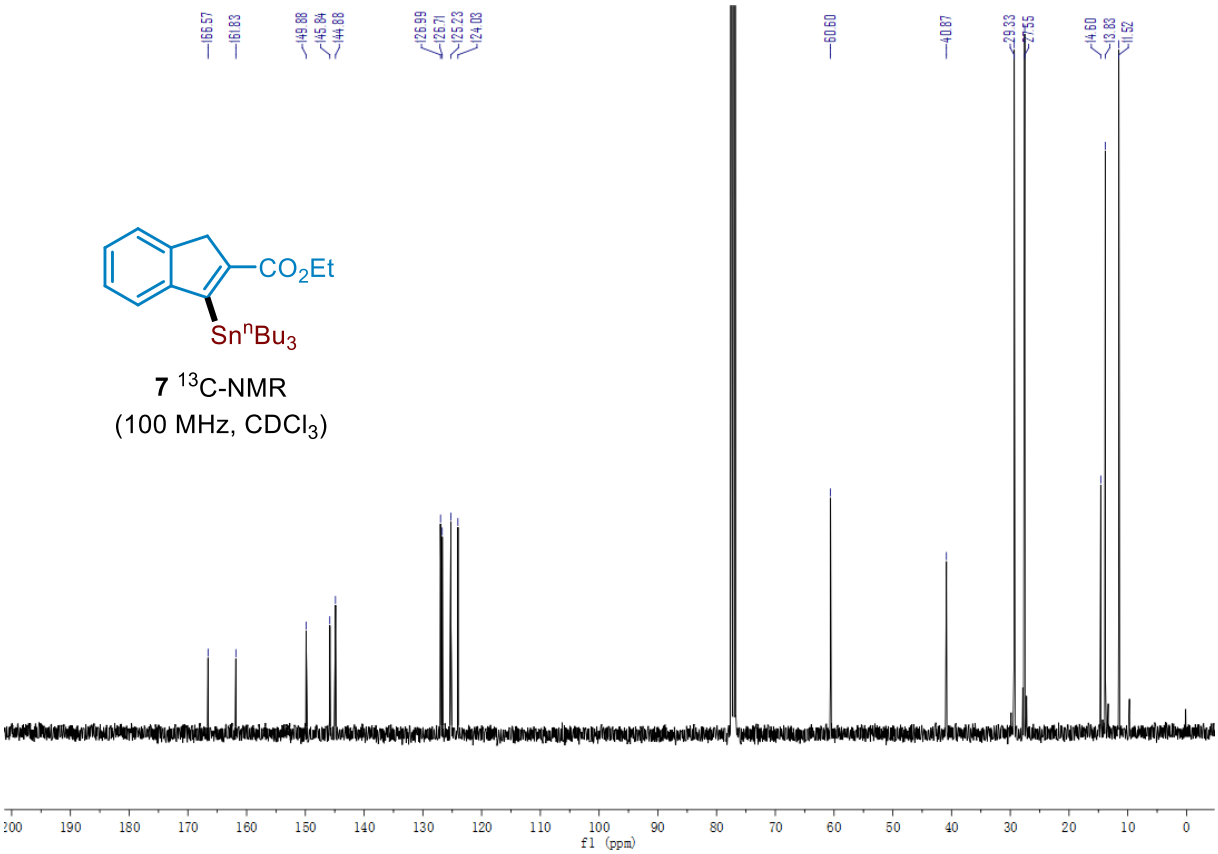
(*E*)-**82** ^{13}C-NMR
(100 MHz, $CDCl_3$)



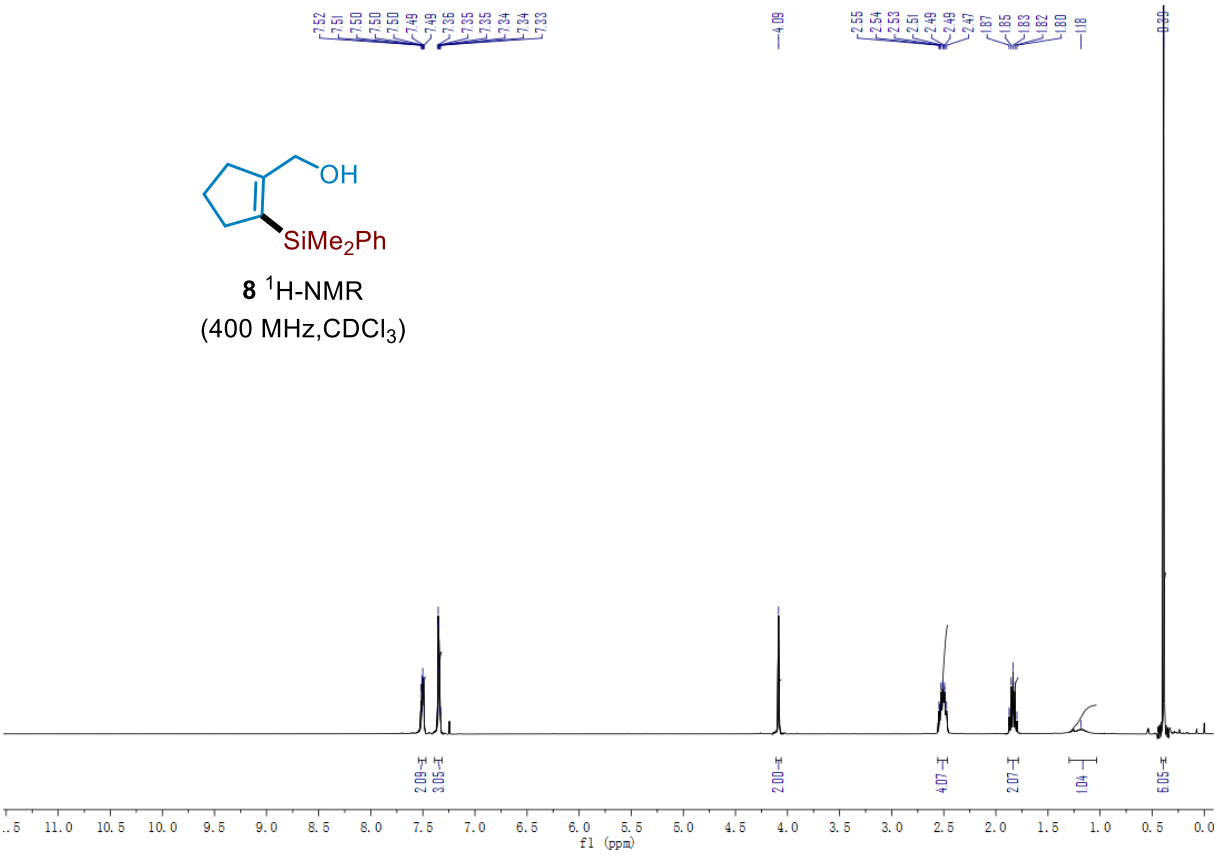
4 ^{1}H-NMR
(400 MHz,$CDCl_3$)


CO2Et
SiMe2Ph
4 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)

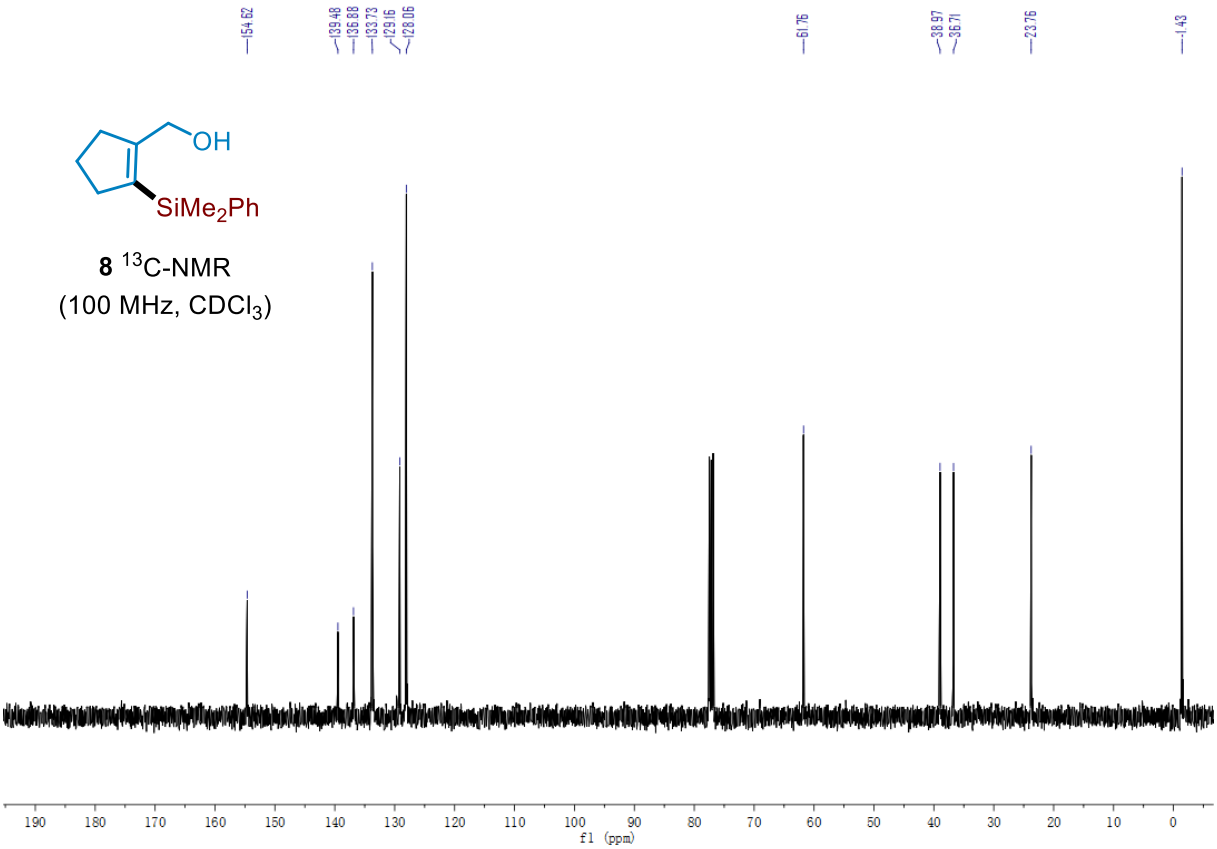

CO2Et
SnnBu3
7 1H-NMR
(400 MHz,CDCl3)
f1 (ppm)



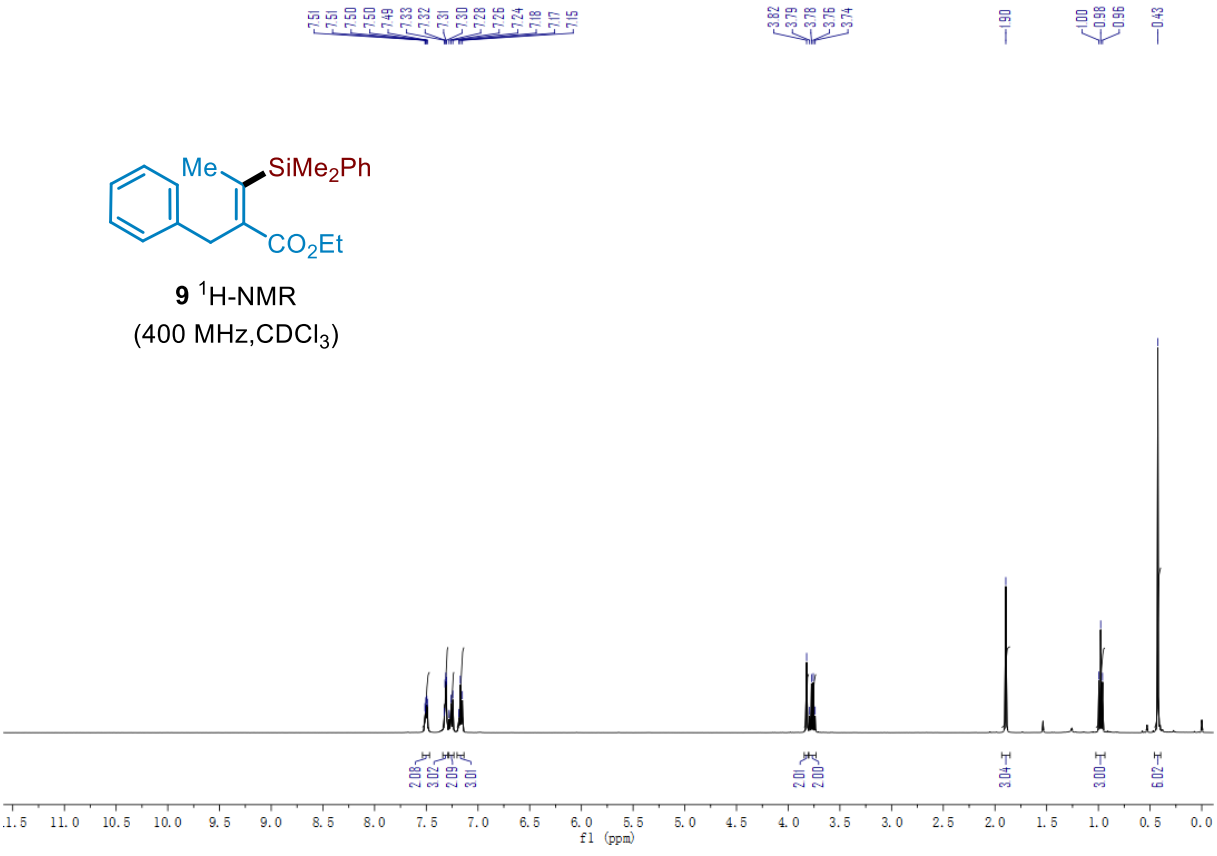
7 ^{13}C-NMR
(100 MHz, $CDCl_3$)



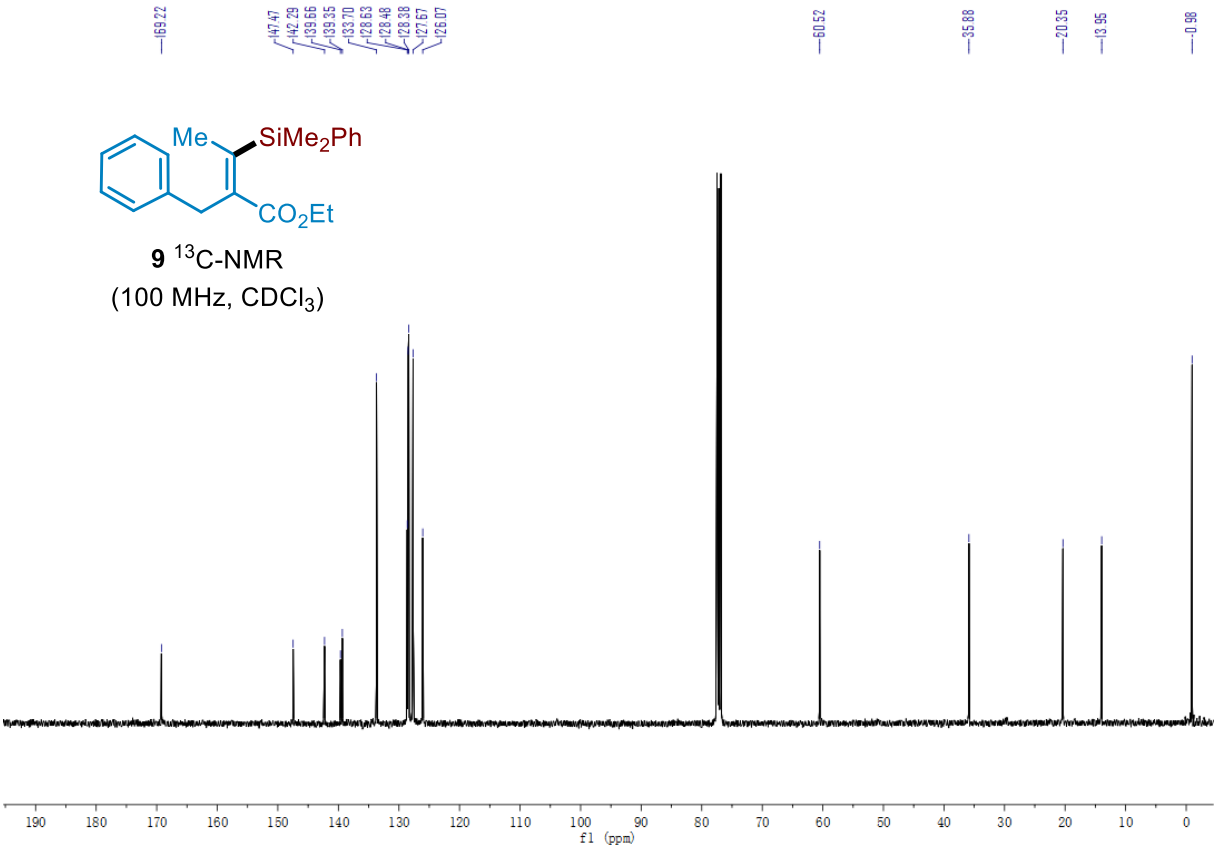
8 ^{1}H-NMR
(400 MHz,$CDCl_3$)



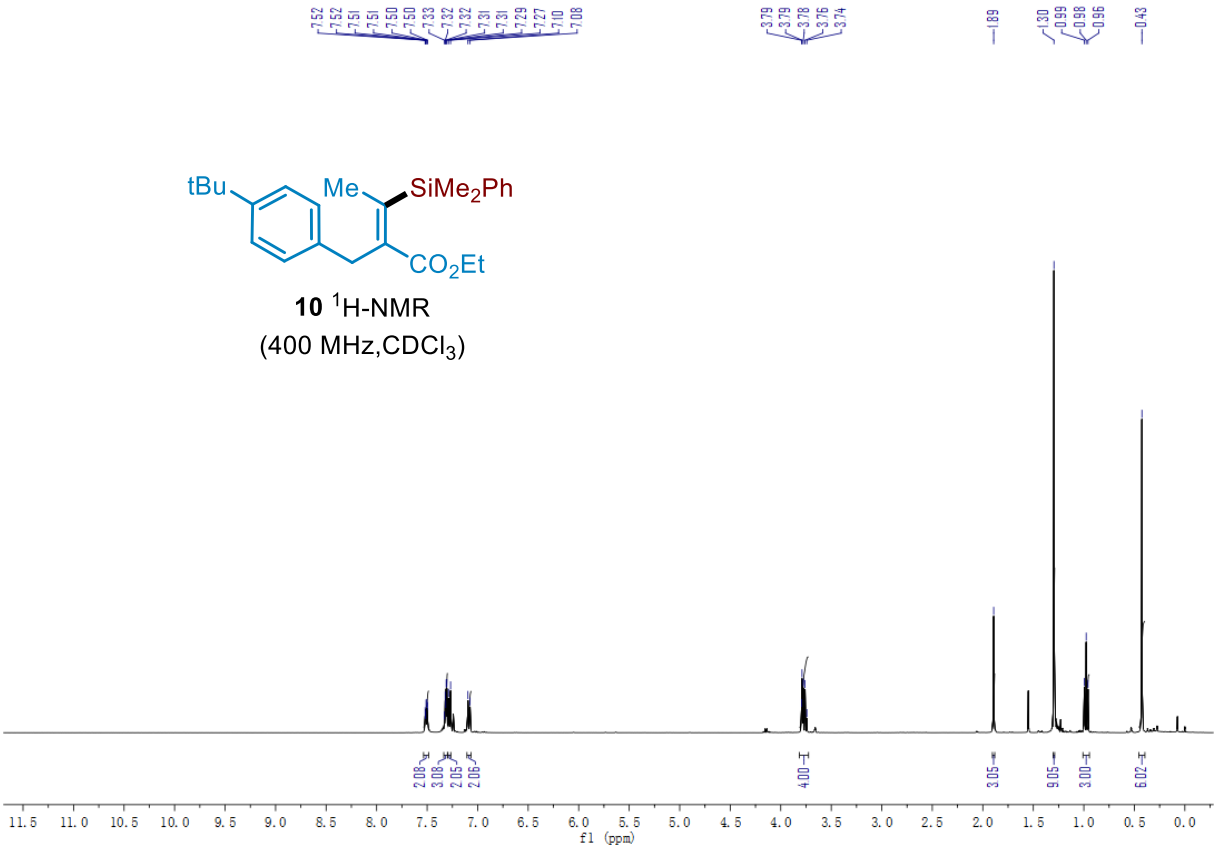
8 ^{13}C-NMR
(100 MHz, $CDCl_3$)



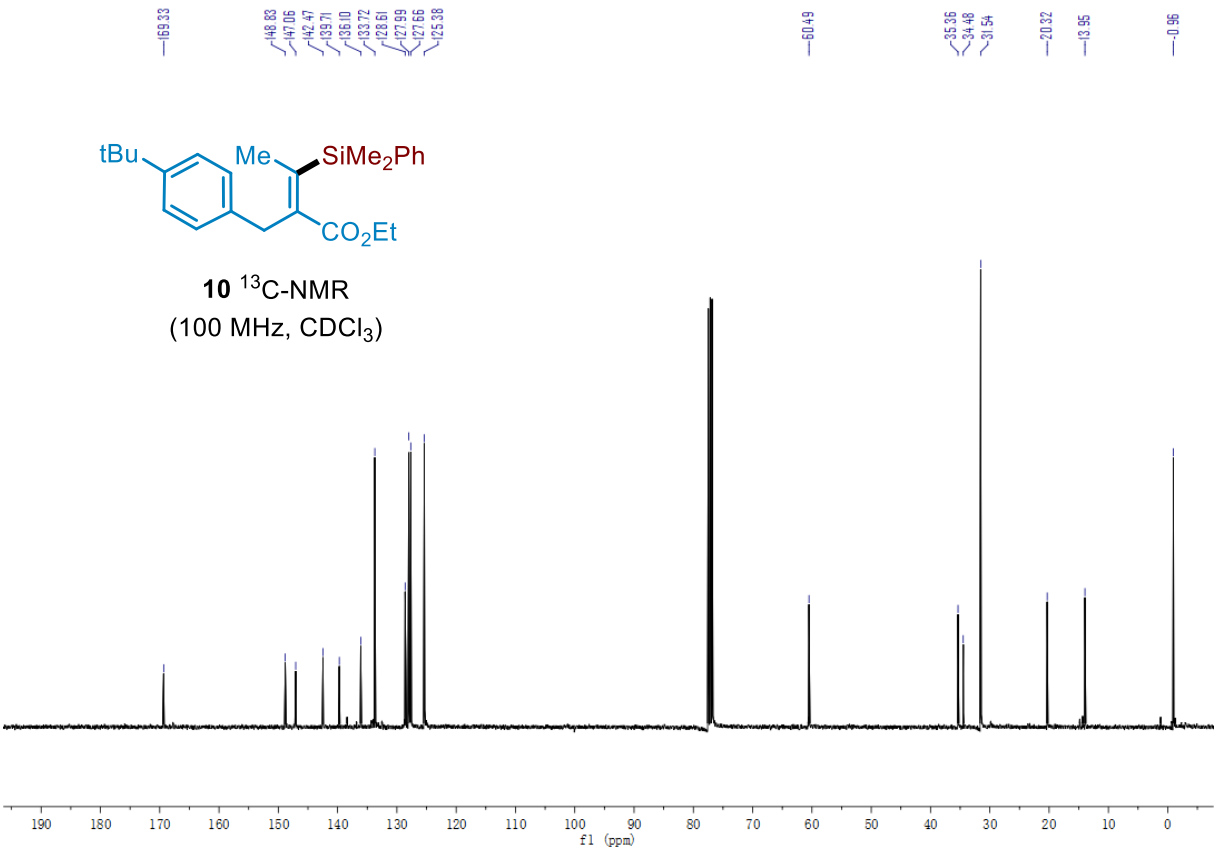
9 ^{1}H-NMR
(400 MHz,$CDCl_3$)



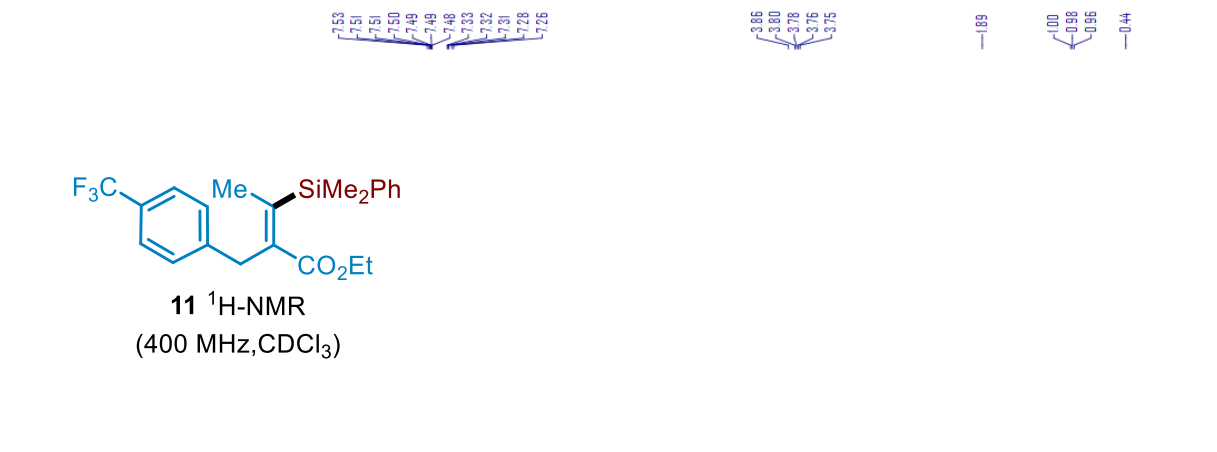
9 ^{13}C-NMR
(100 MHz, $CDCl_3$)

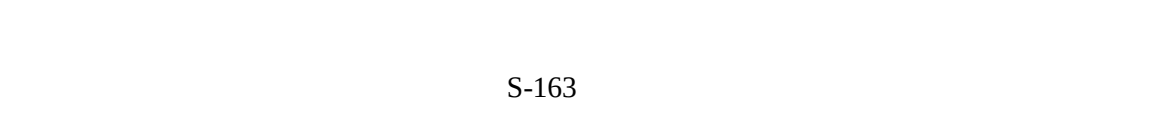


10 ^{1}H-NMR
(400 MHz,$CDCl_3$)

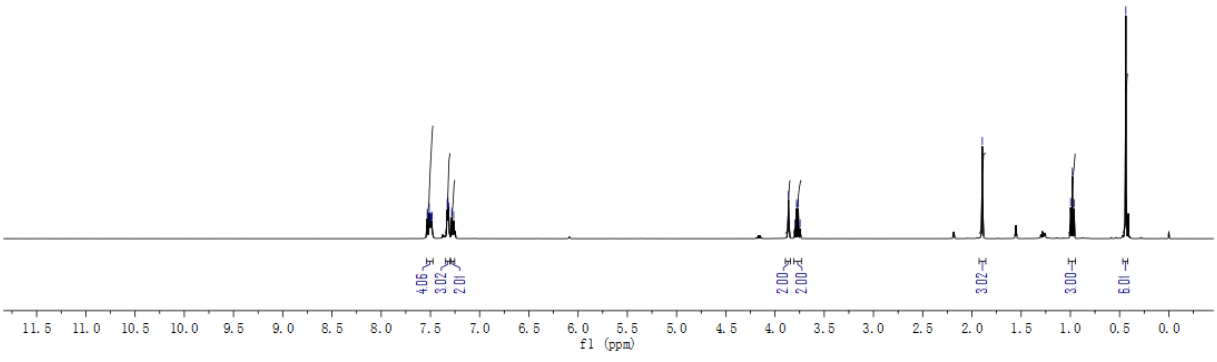


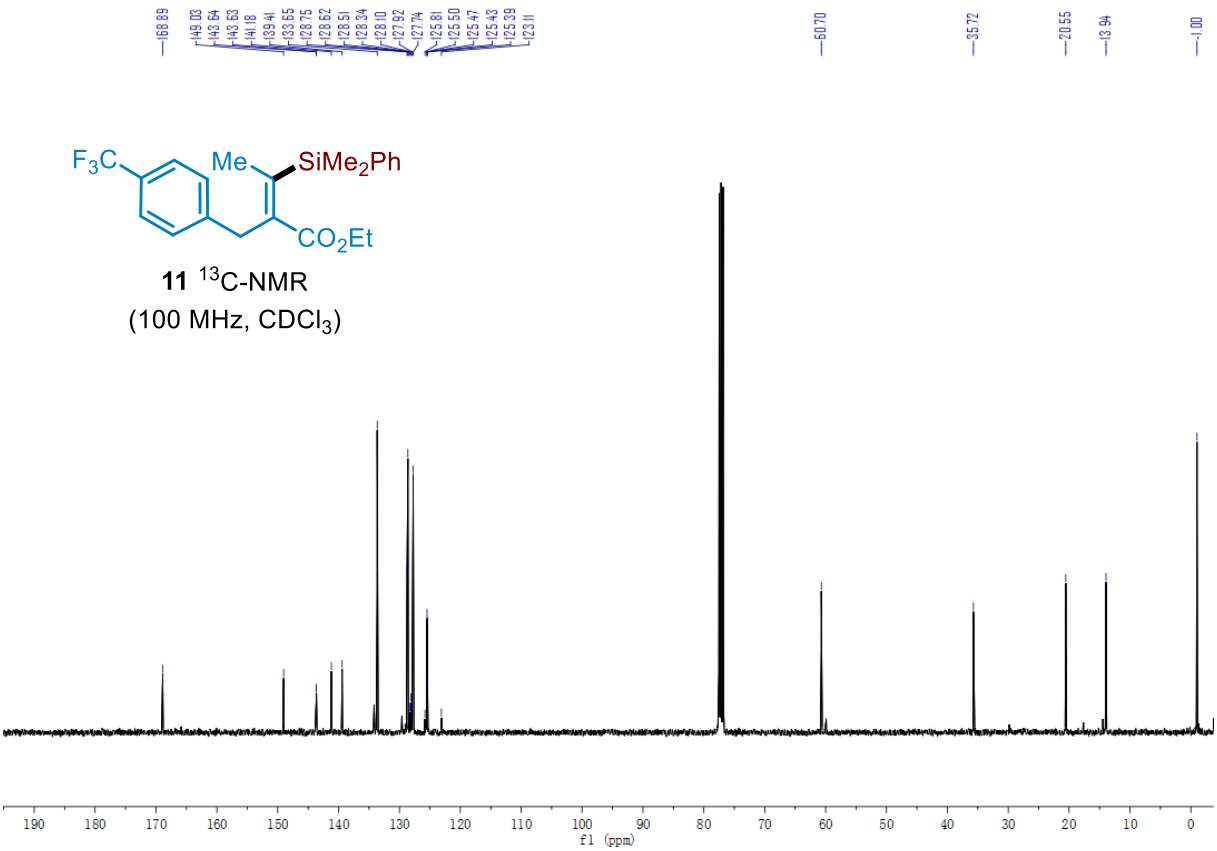
10 ^{13}C-NMR
(100 MHz, $CDCl_3$)



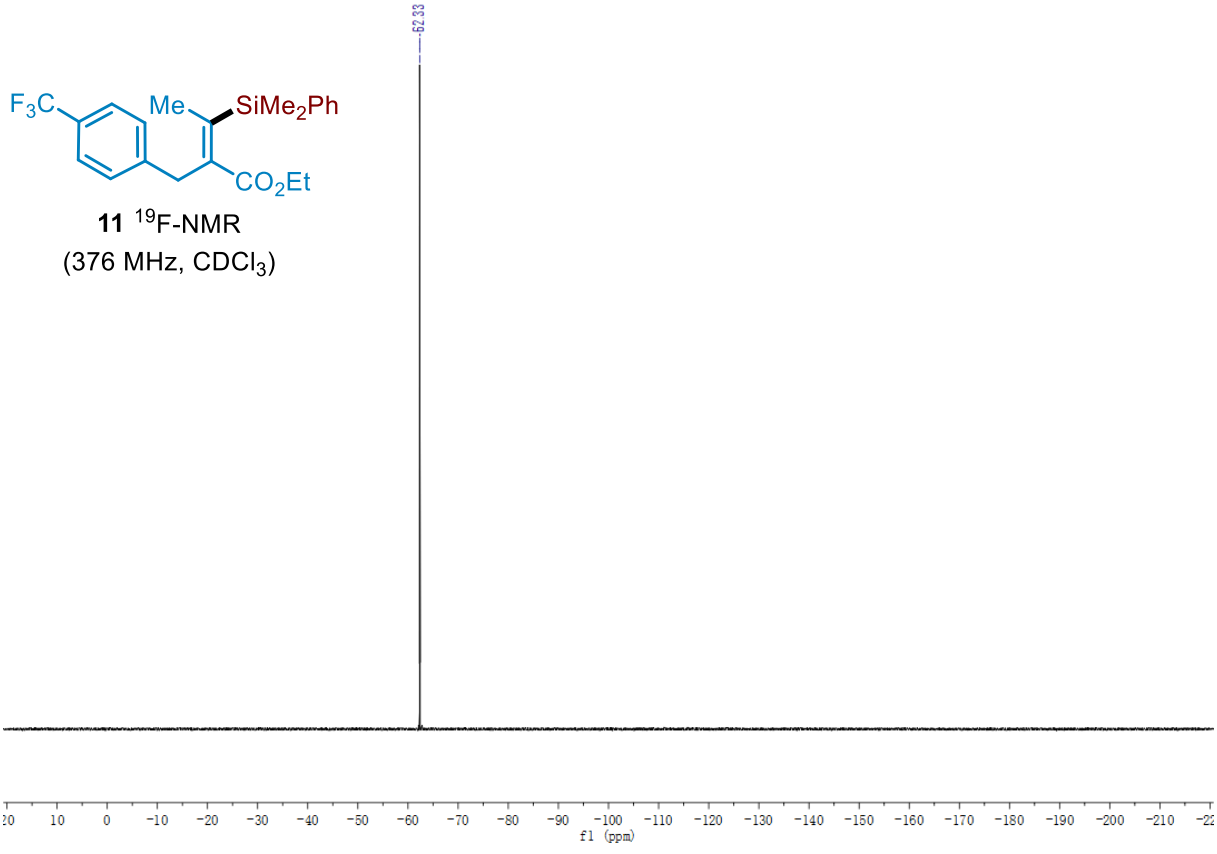


11 ^{1}H-NMR
(400 MHz,$CDCl_3$)

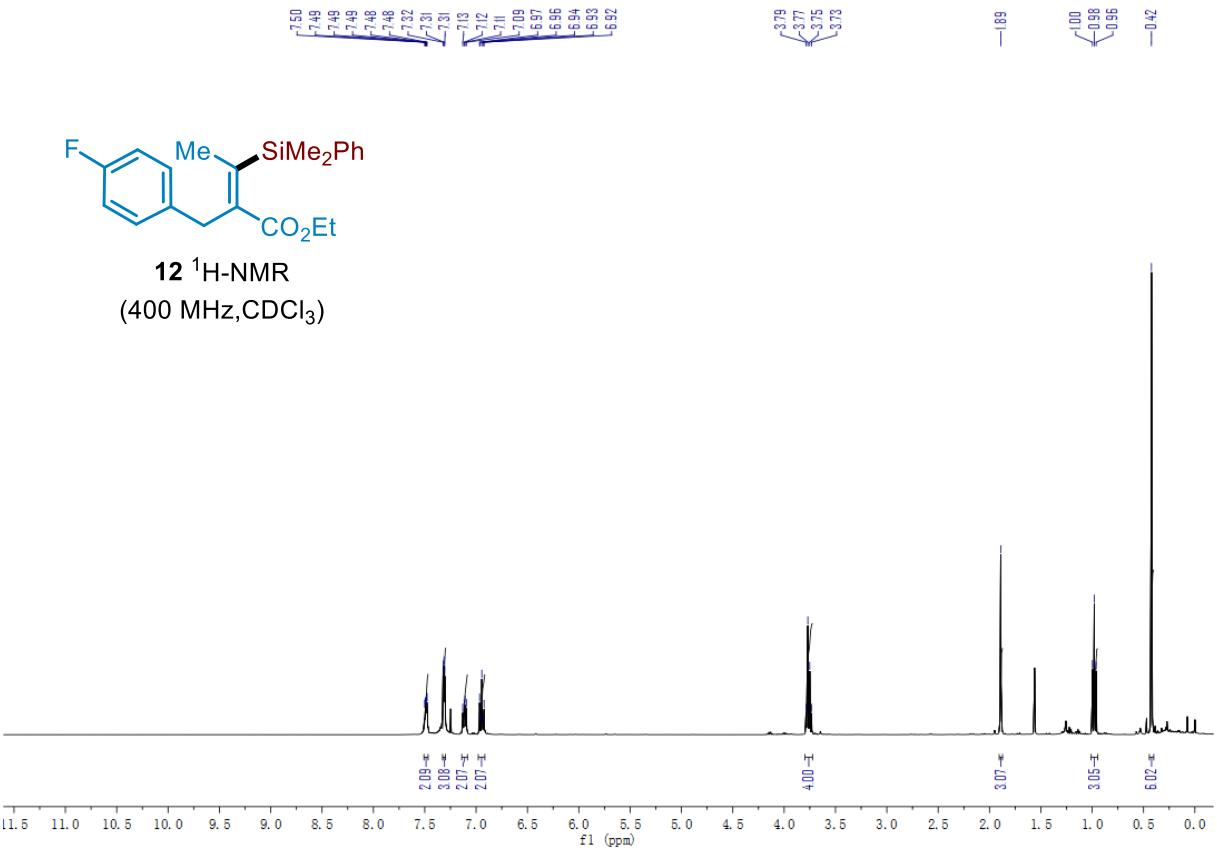


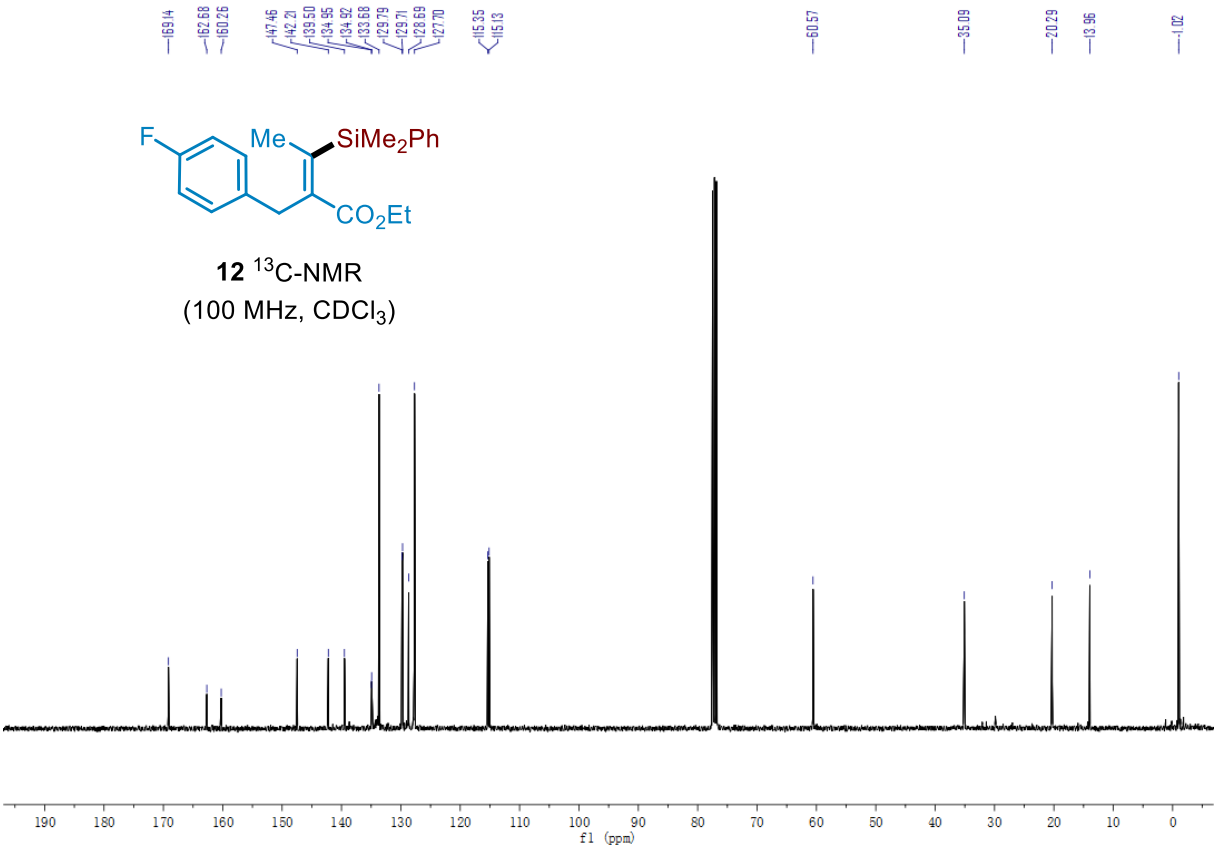


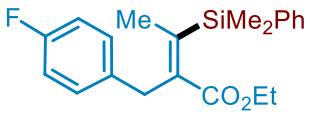
11 ^{13}C-NMR
(100 MHz, $CDCl_3$)



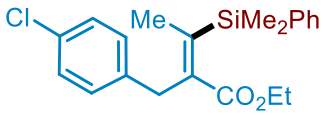
11 ^{19}F-NMR
(376 MHz, $CDCl_3$)


F
Me
SiMe2Ph
CO2Et
12 1H-NMR
(400 MHz,CDCl3)
f1 (ppm)

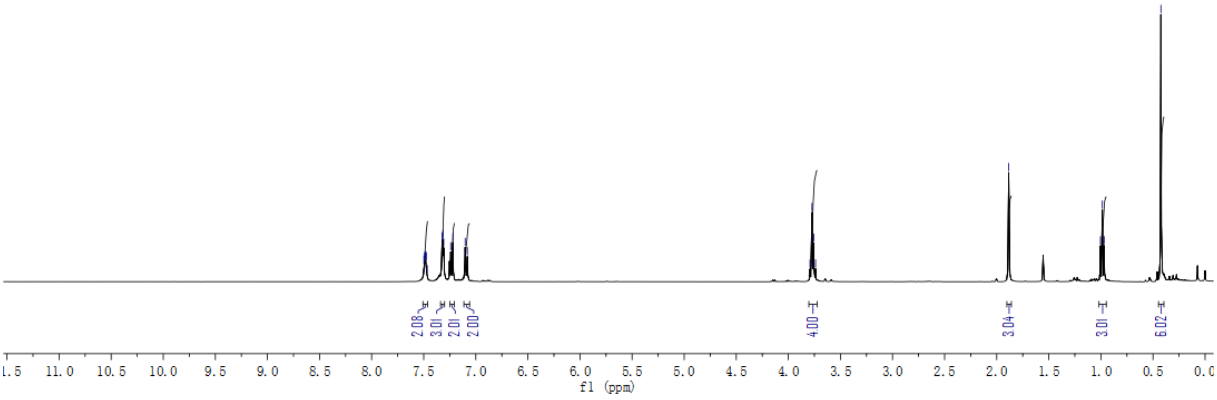

F
Me
SiMe2Ph
CO2Et
12 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)

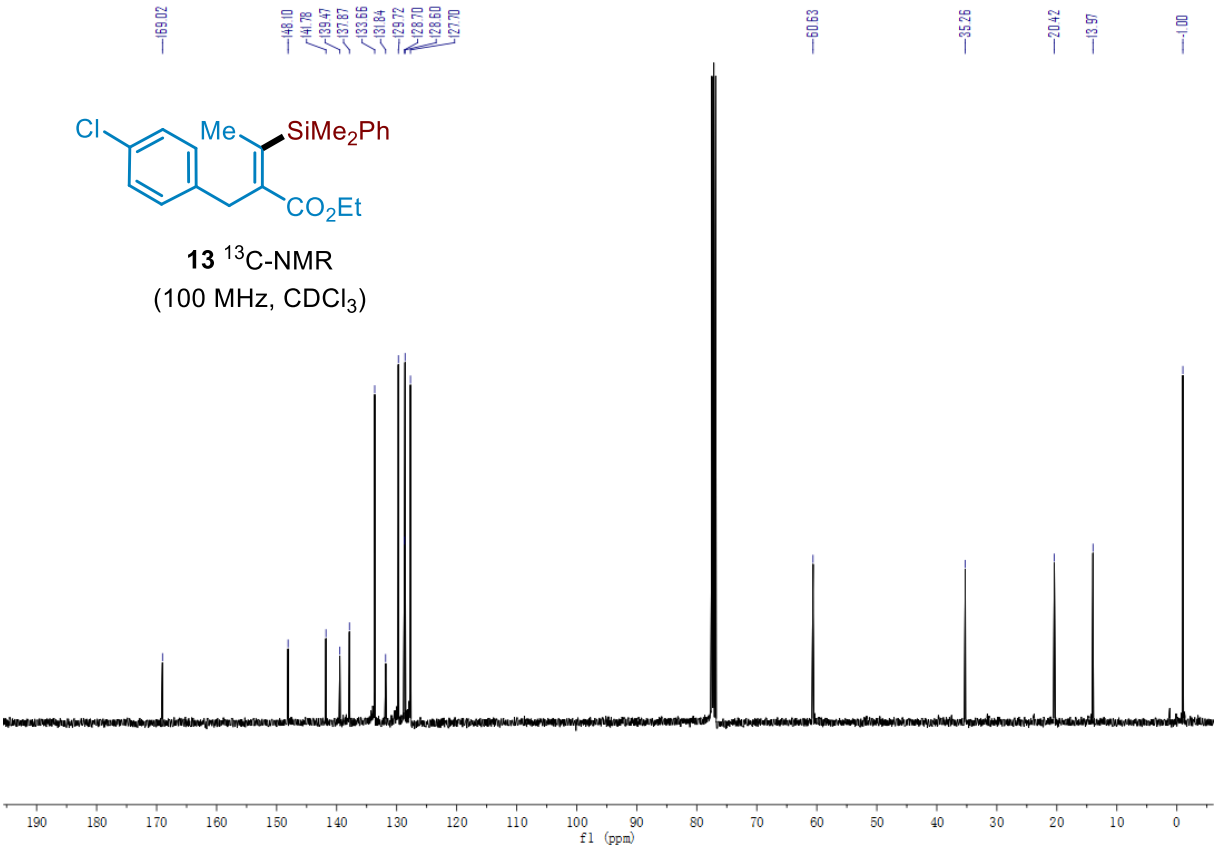


12 ^{19}F-NMR
(376 MHz, $CDCl_3$)

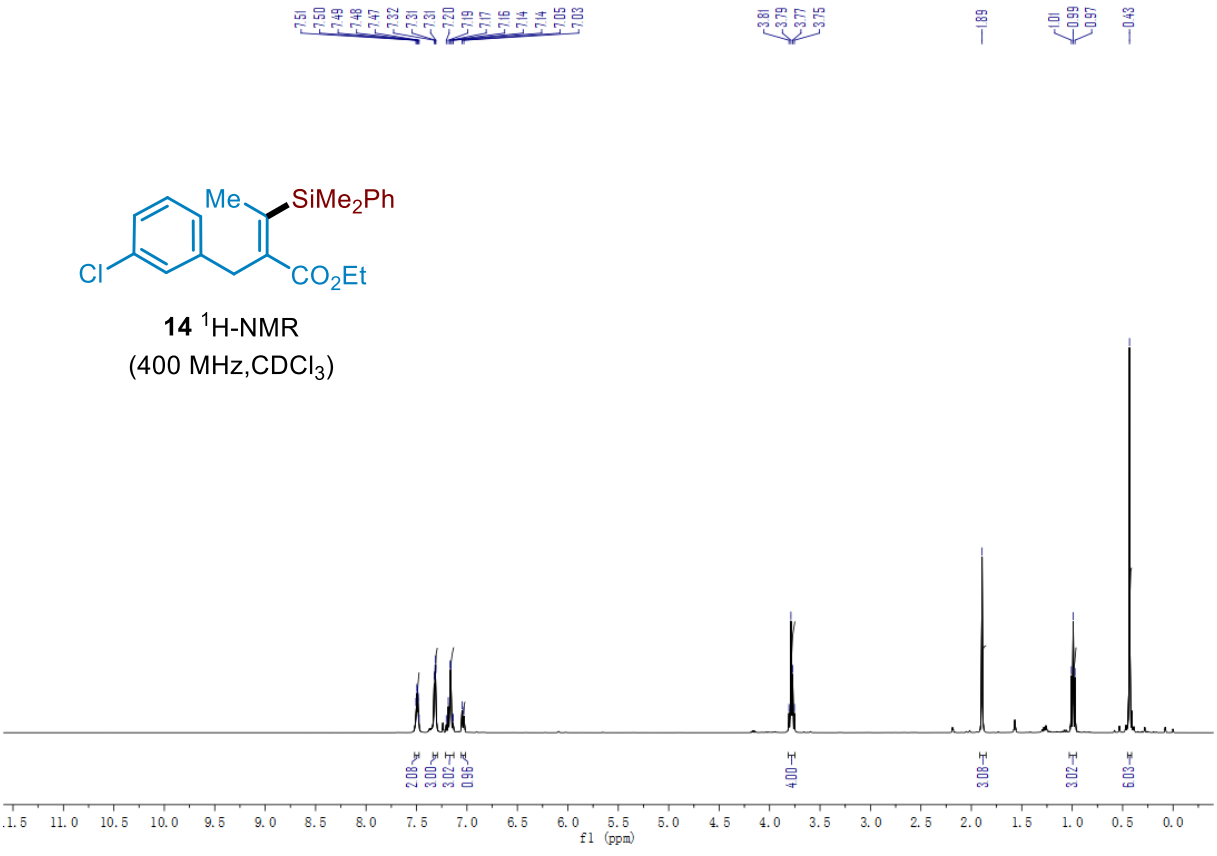


13 ^{1}H-NMR
(400 MHz,$CDCl_3$)

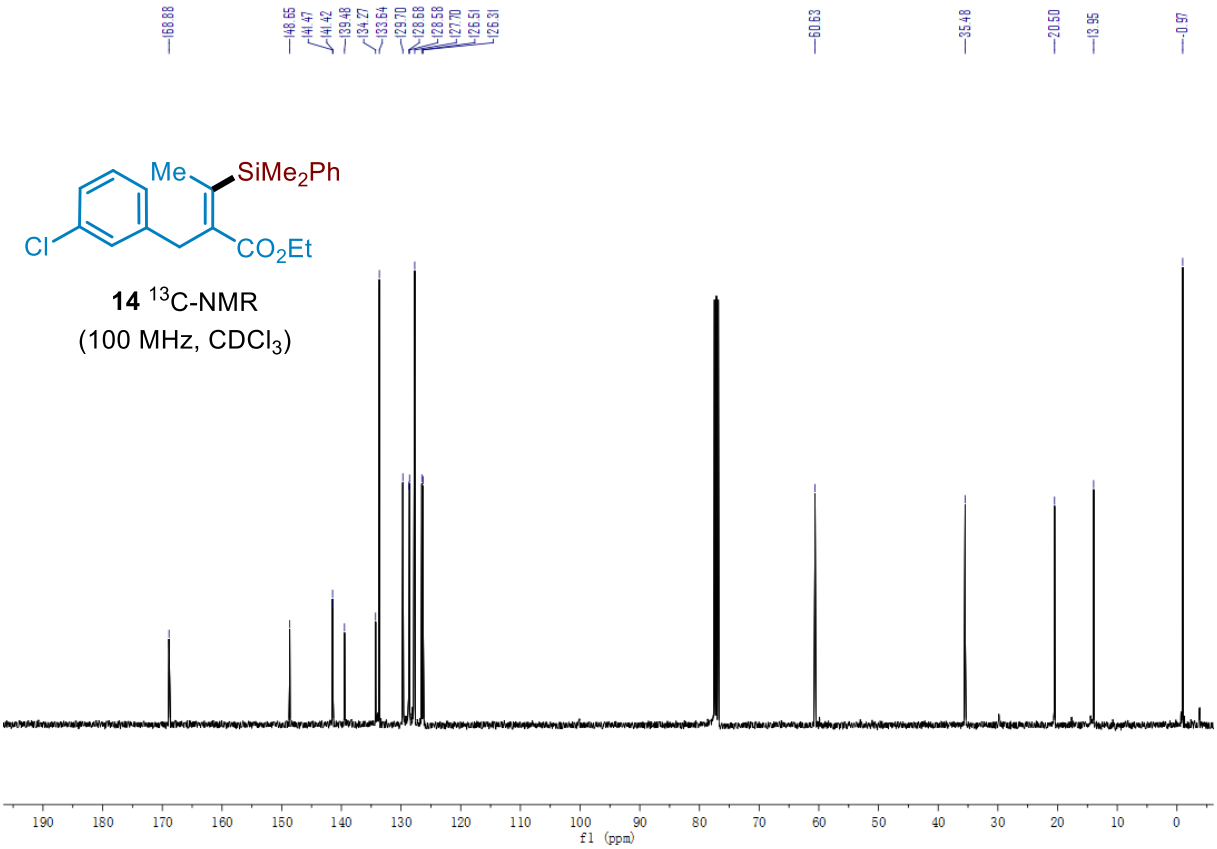




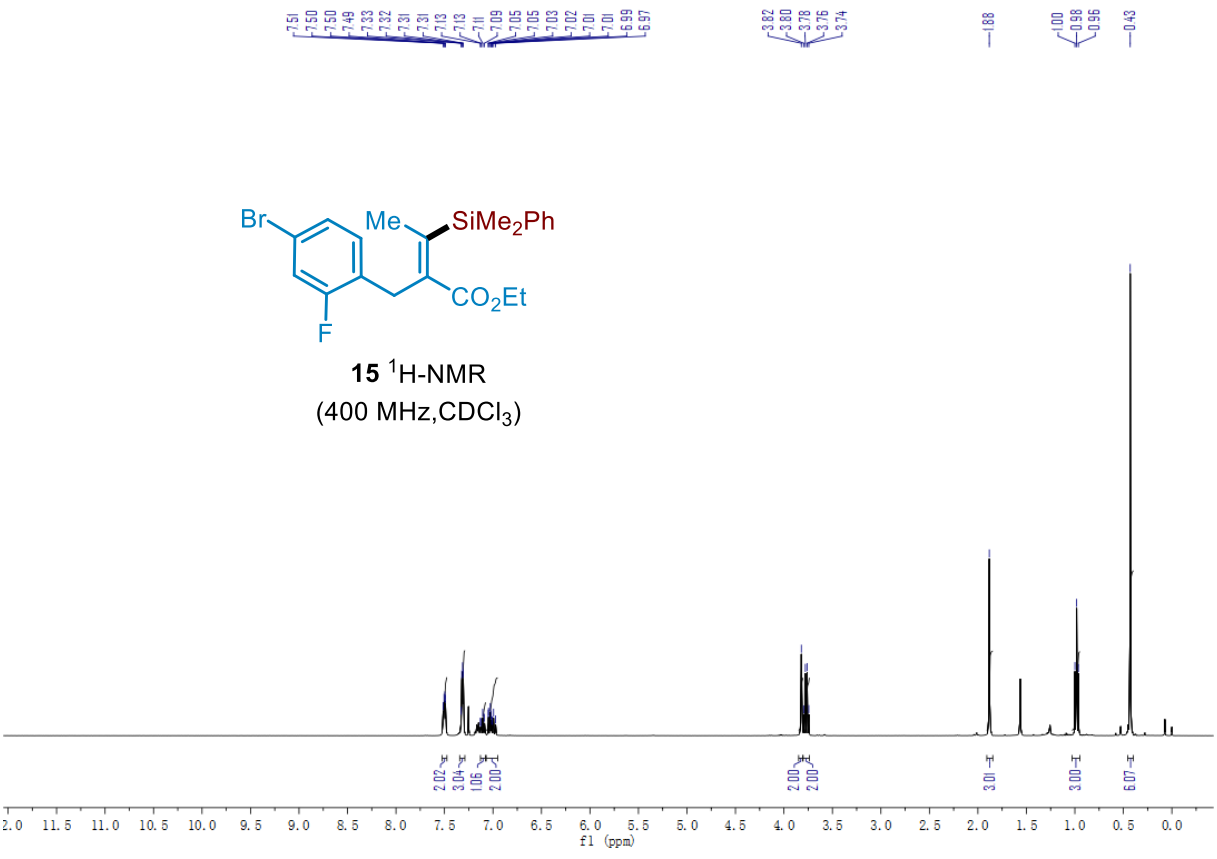
13 ^{13}C-NMR
(100 MHz, $CDCl_3$)



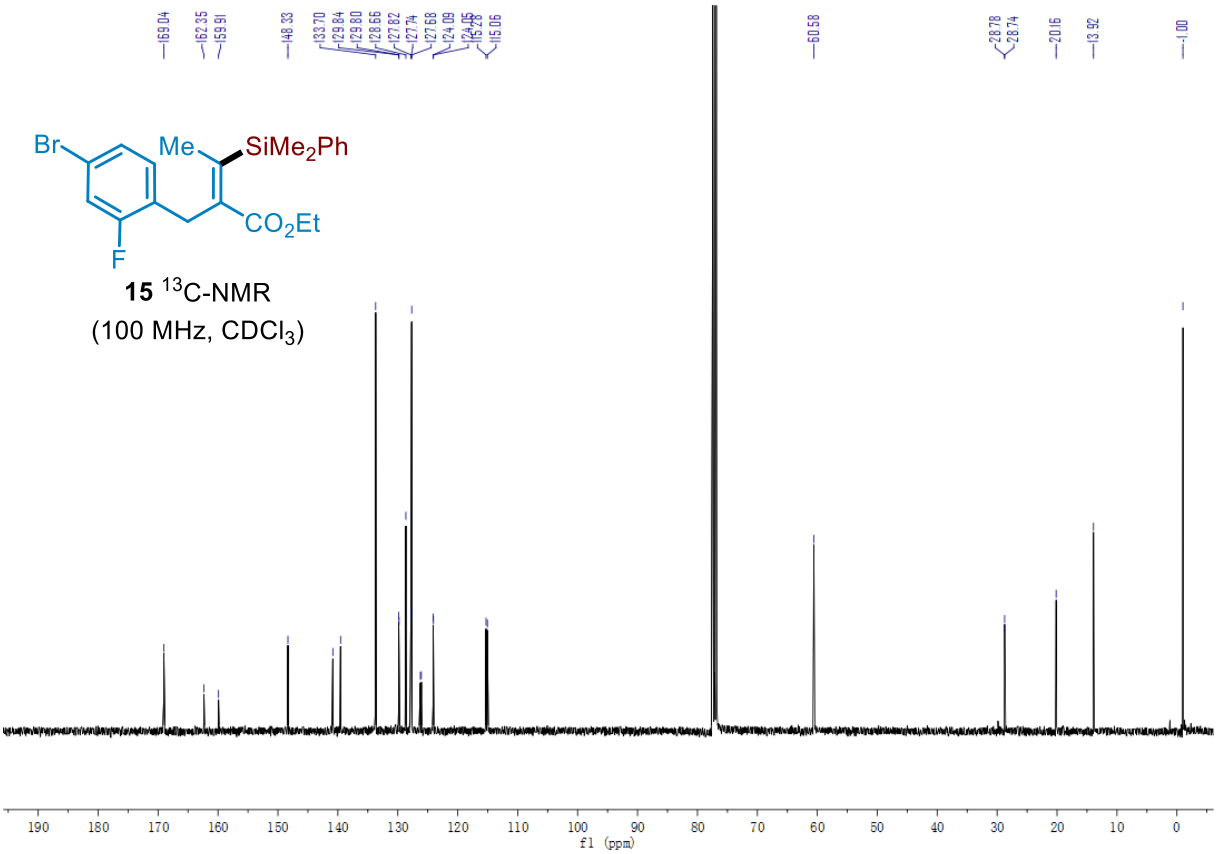
14 ^{1}H-NMR
(400 MHz,$CDCl_3$)



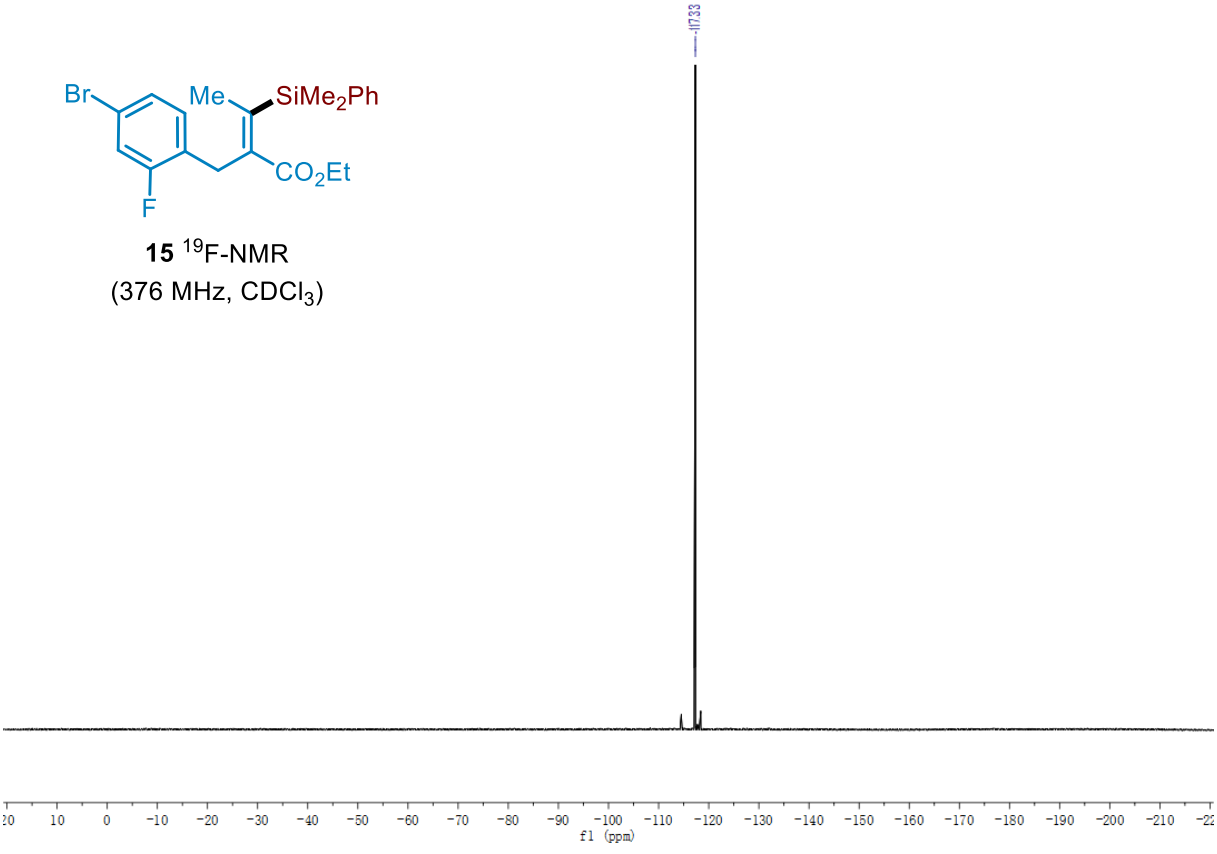
14 ^{13}C-NMR
(100 MHz, $CDCl_3$)



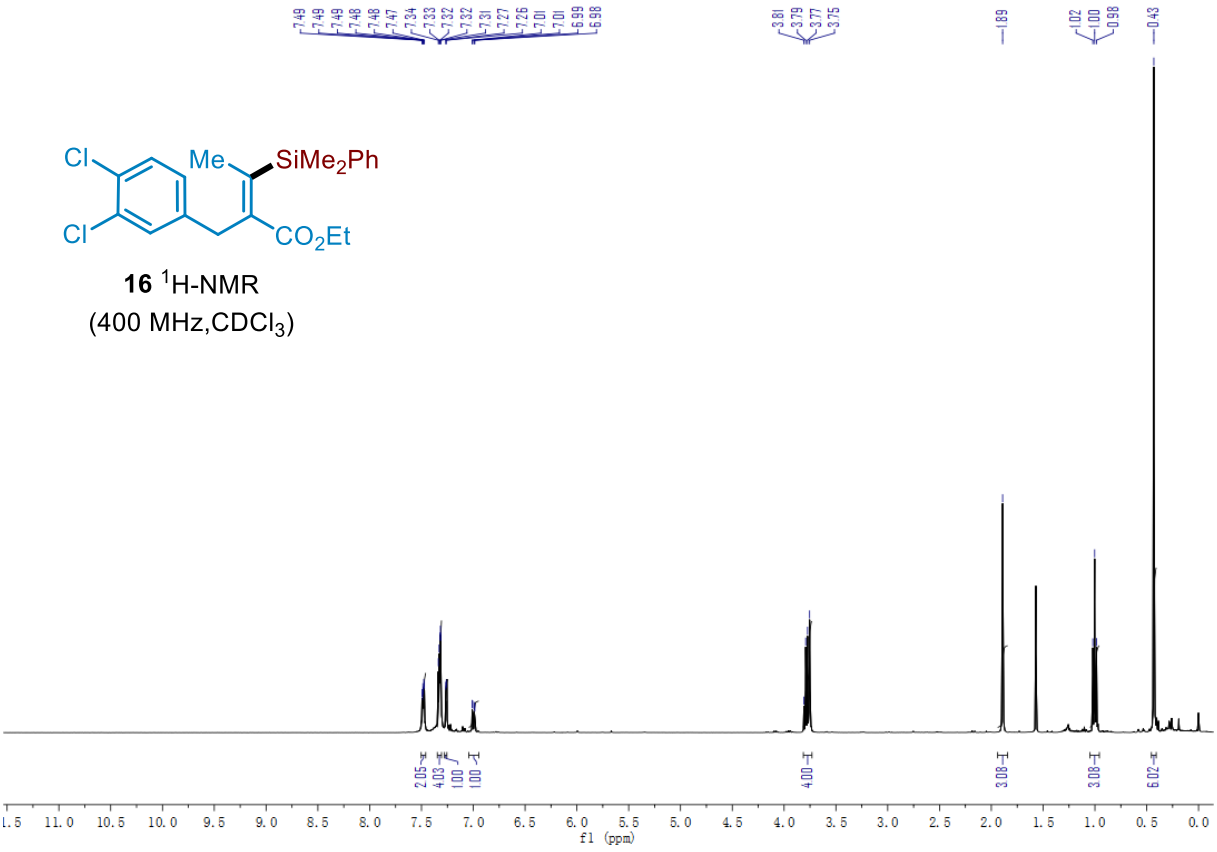
15 ^{1}H-NMR
(400 MHz,$CDCl_3$)



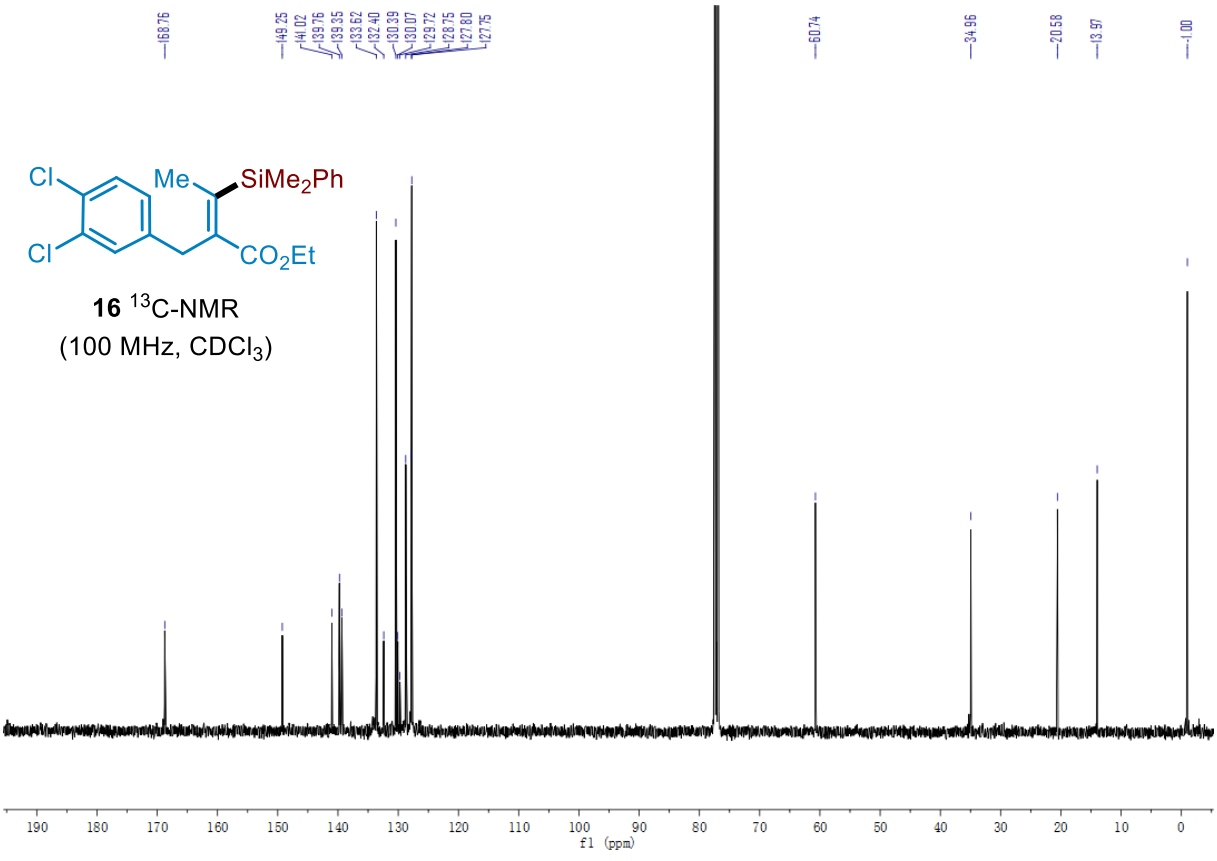
15 ^{13}C-NMR
(100 MHz, $CDCl_3$)



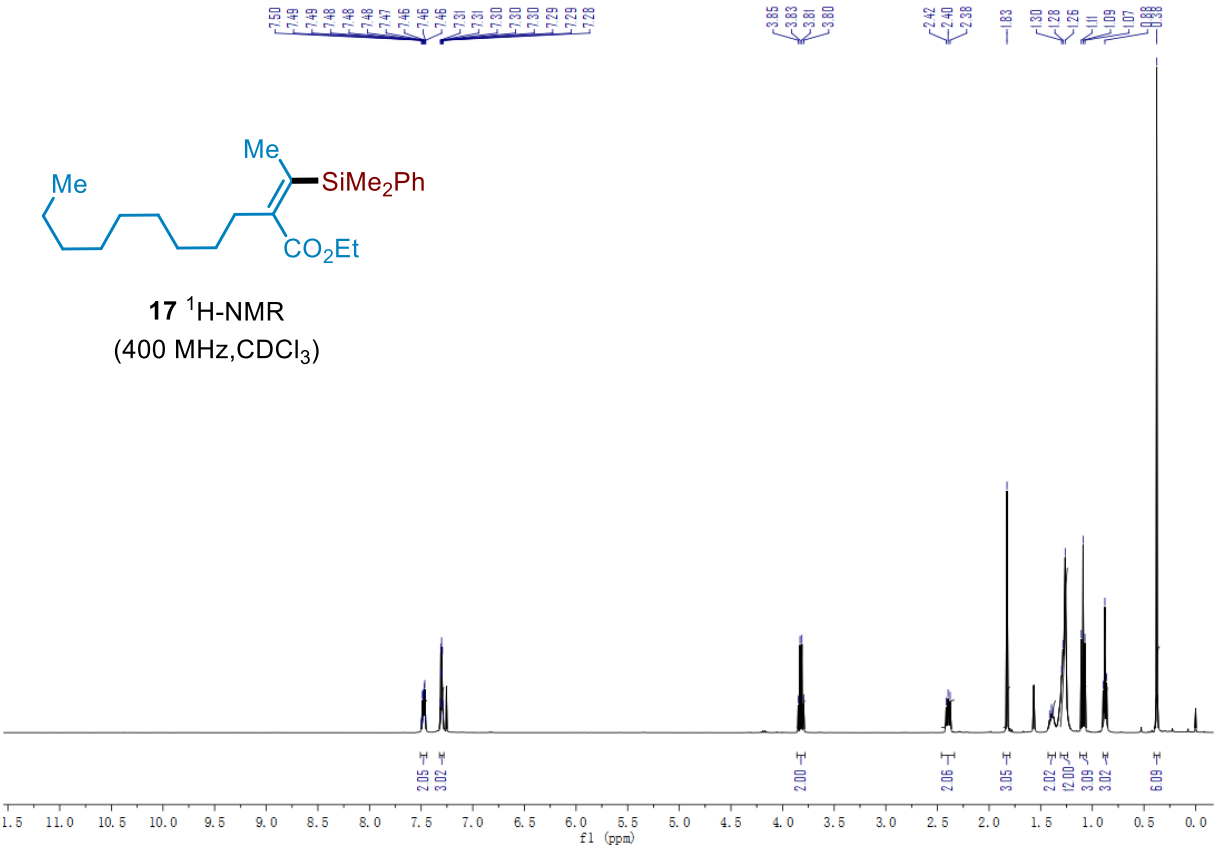
15 ^{19}F-NMR
(376 MHz, $CDCl_3$)



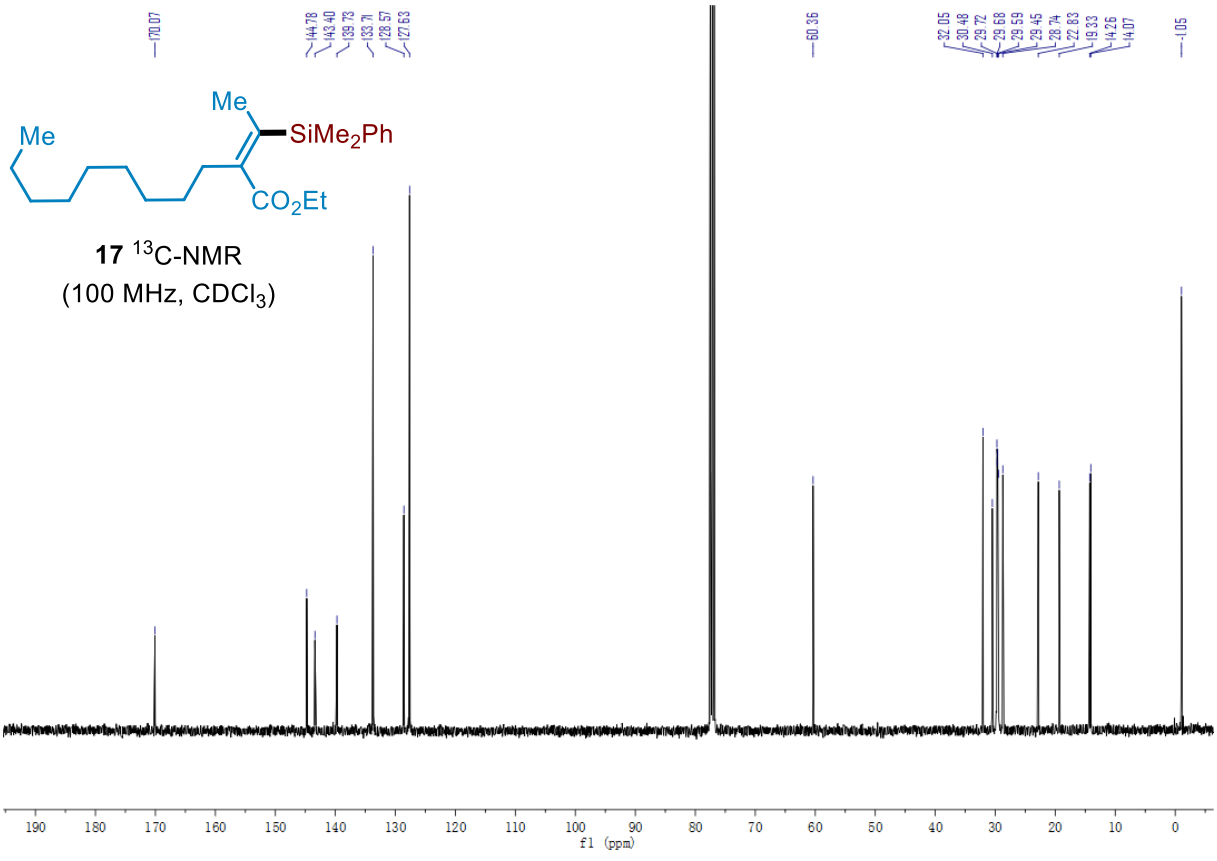
16 ^{1}H-NMR
(400 MHz,$CDCl_3$)



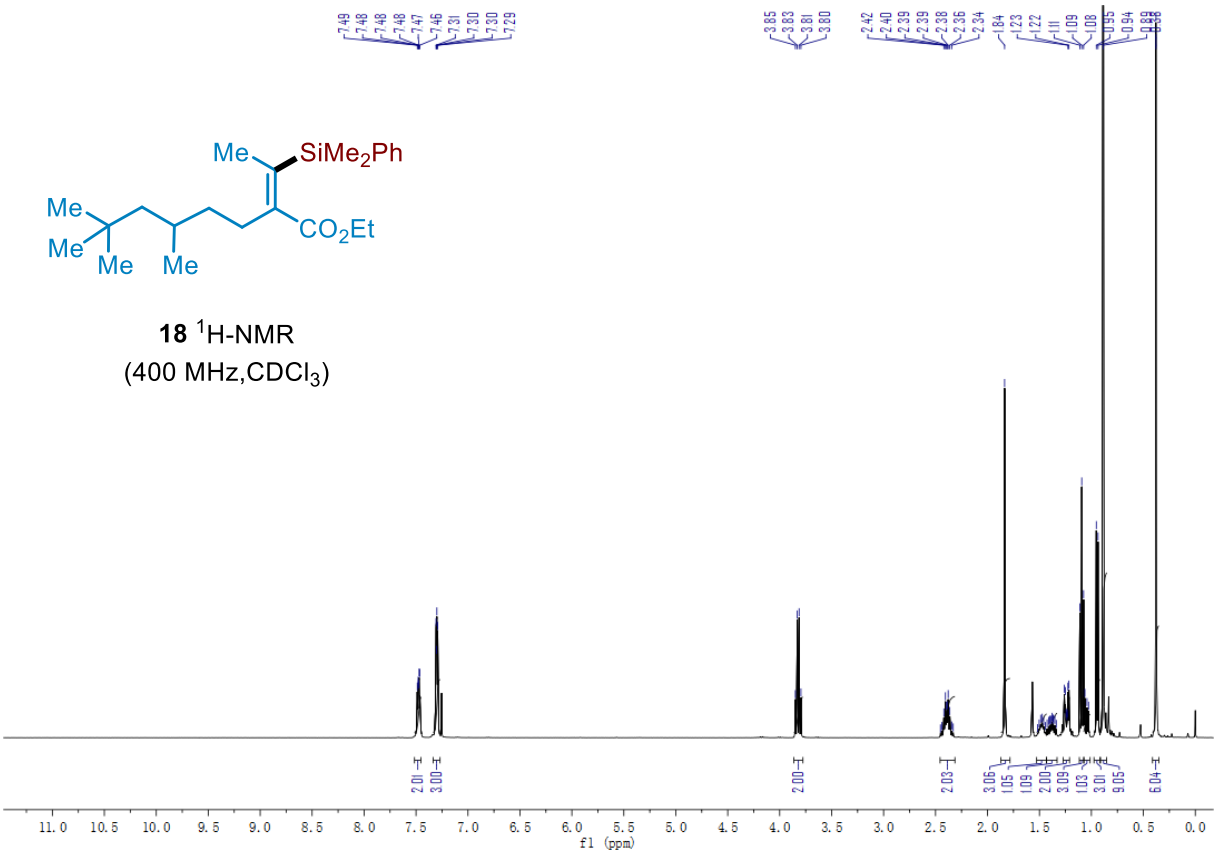
16 ^{13}C-NMR
(100 MHz, $CDCl_3$)



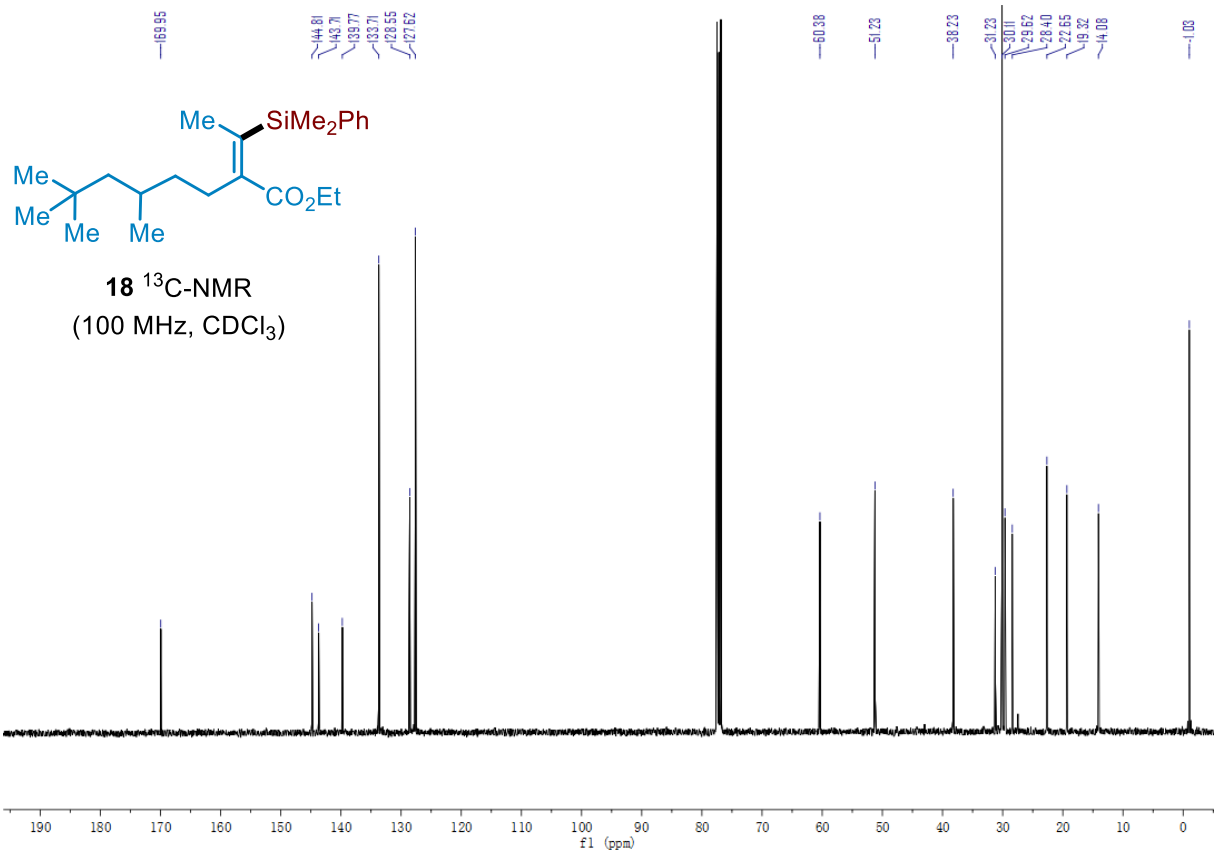
17 ^{1}H-NMR
(400 MHz,$CDCl_3$)



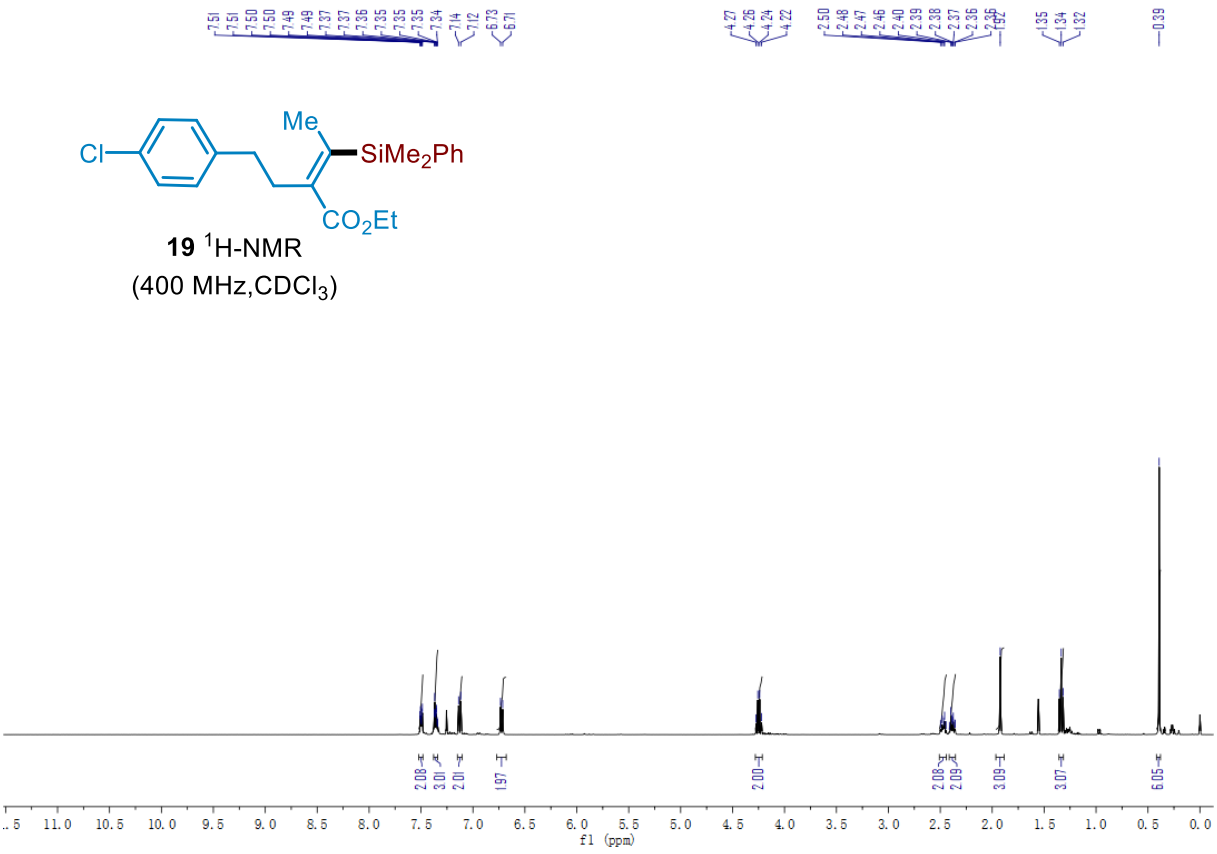
17 ^{13}C-NMR
(100 MHz, $CDCl_3$)



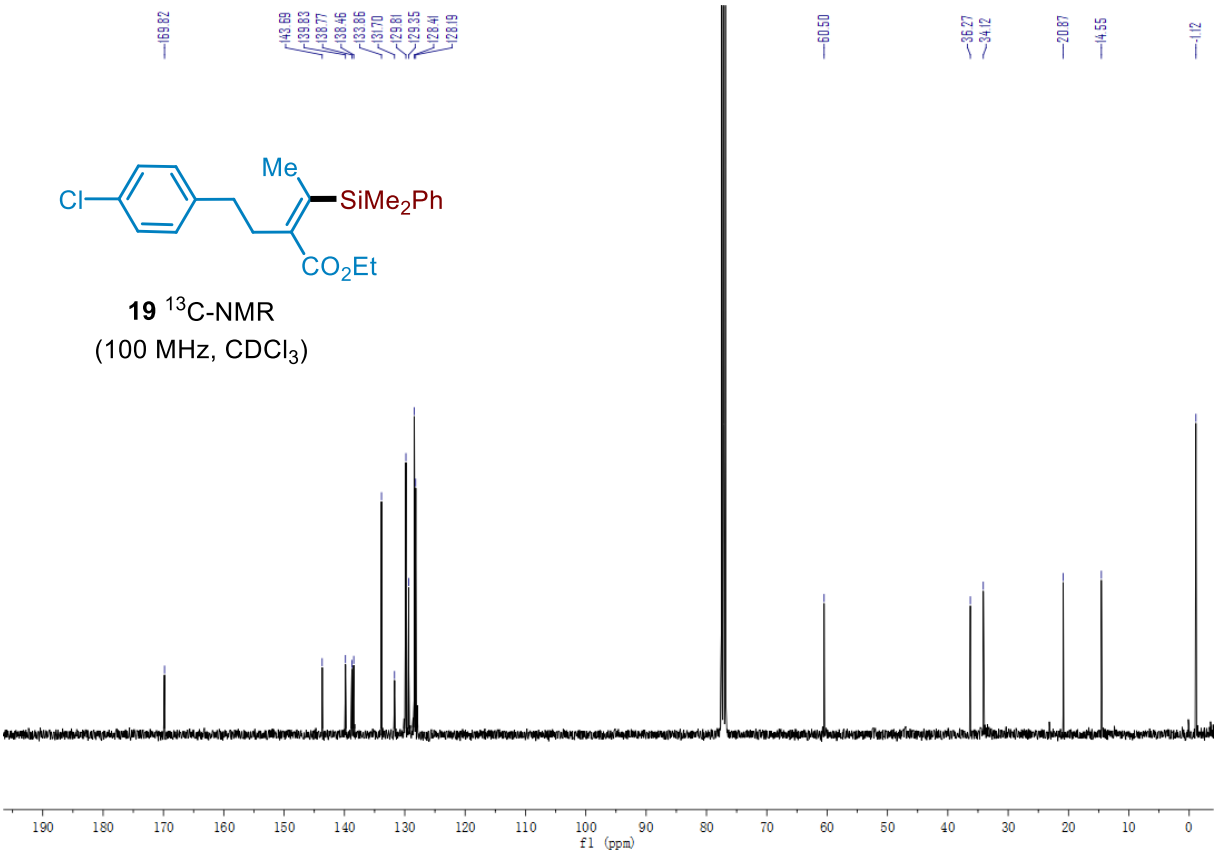
18 ^{1}H-NMR
(400 MHz,$CDCl_3$)



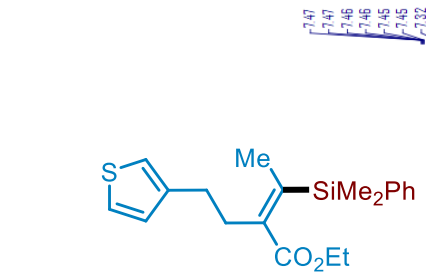
18 ^{13}C-NMR
(100 MHz, $CDCl_3$)



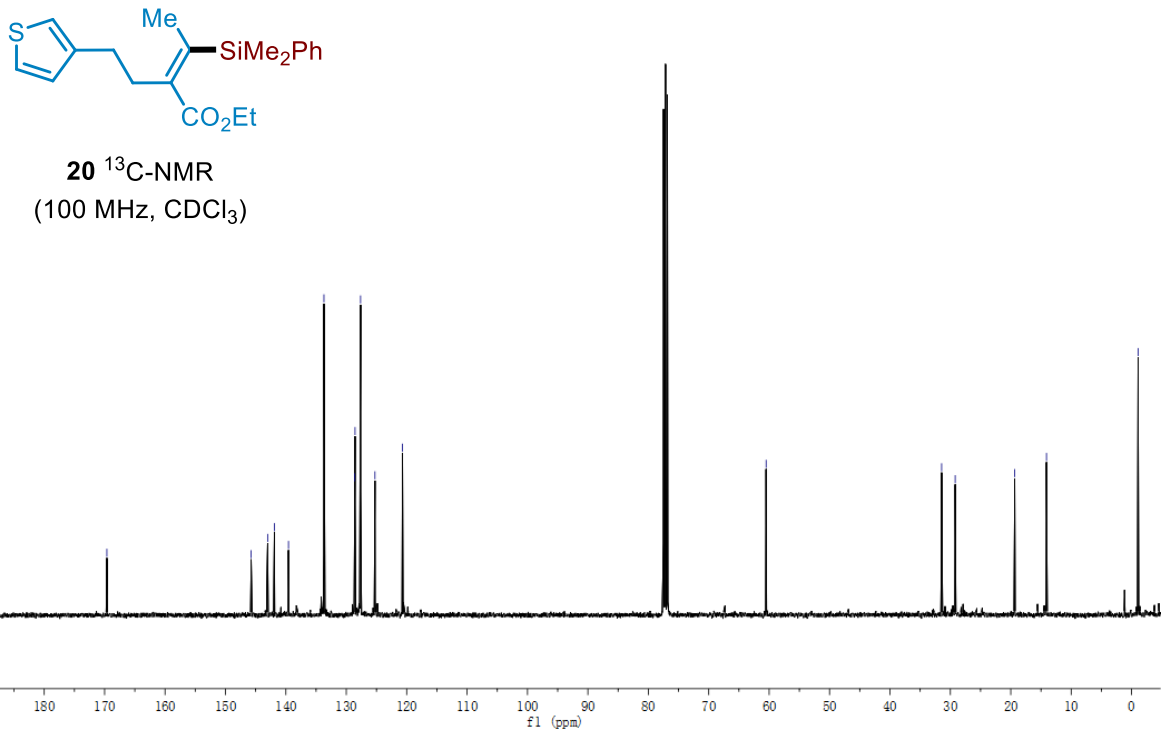
19 ^{1}H-NMR
(400 MHz,$CDCl_3$)



19 ^{13}C-NMR
(100 MHz, $CDCl_3$)

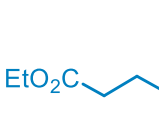


20 ^{1}H-NMR
(400 MHz,$CDCl_3$)

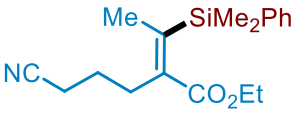


20 ^{13}C-NMR
(100 MHz, $CDCl_3$)

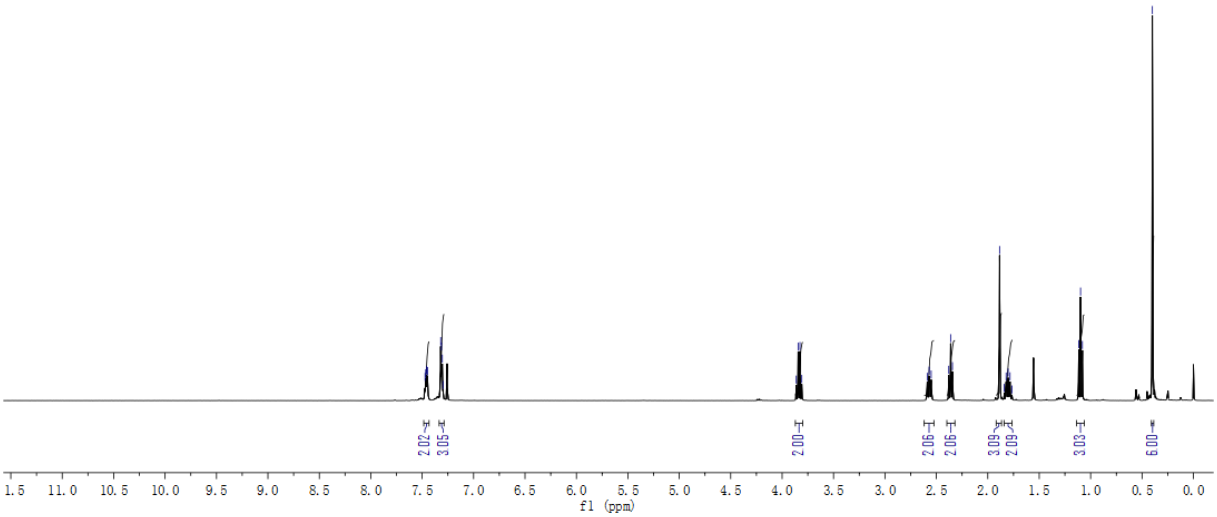
21 ^{1}H-NMR
(400 MHz,$CDCl_3$)

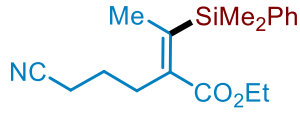


21 ^{13}C-NMR
(100 MHz, $CDCl_3$)

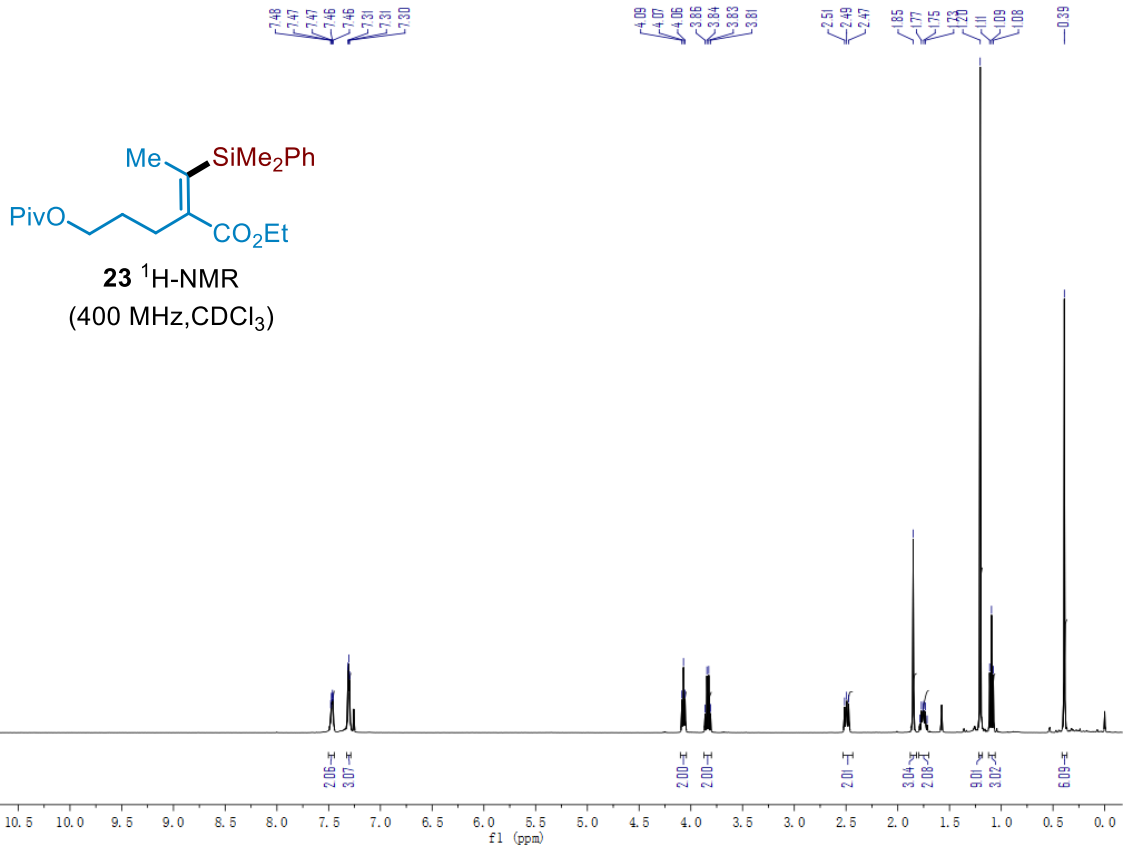


22 ^{1}H-NMR
(400 MHz,$CDCl_3$)

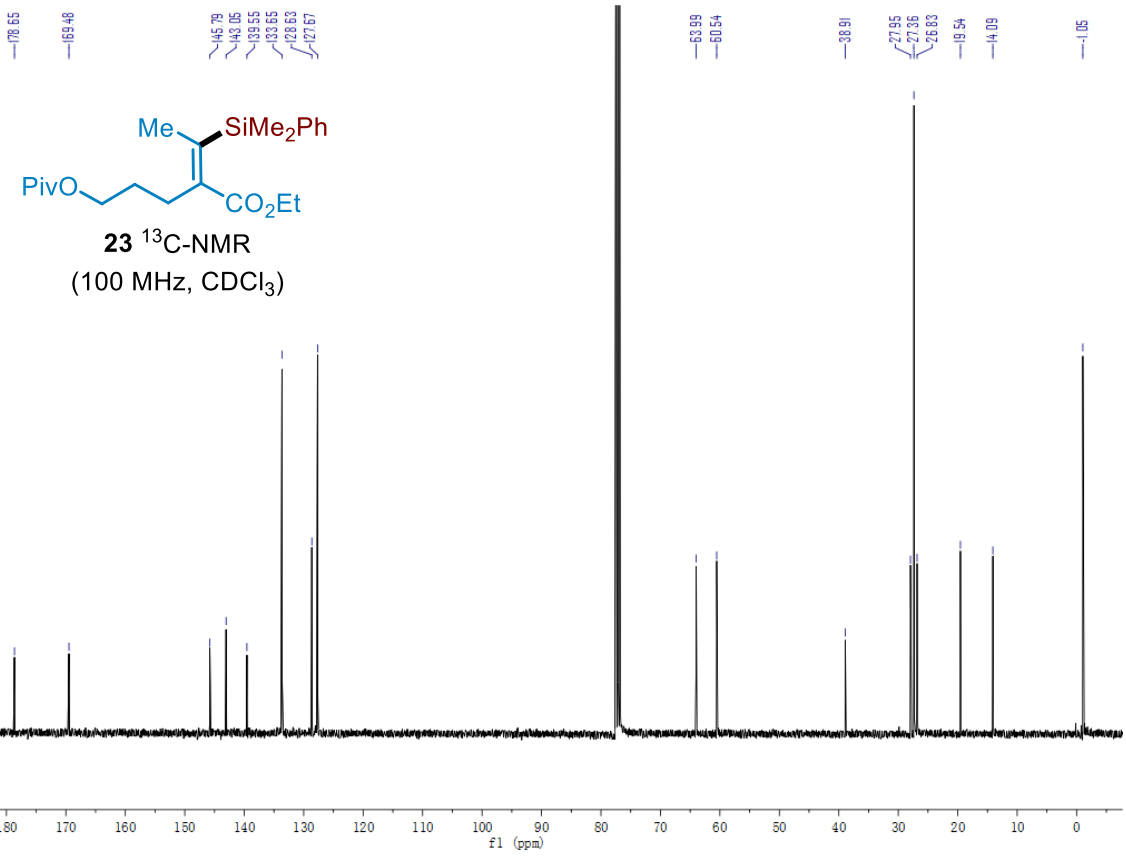




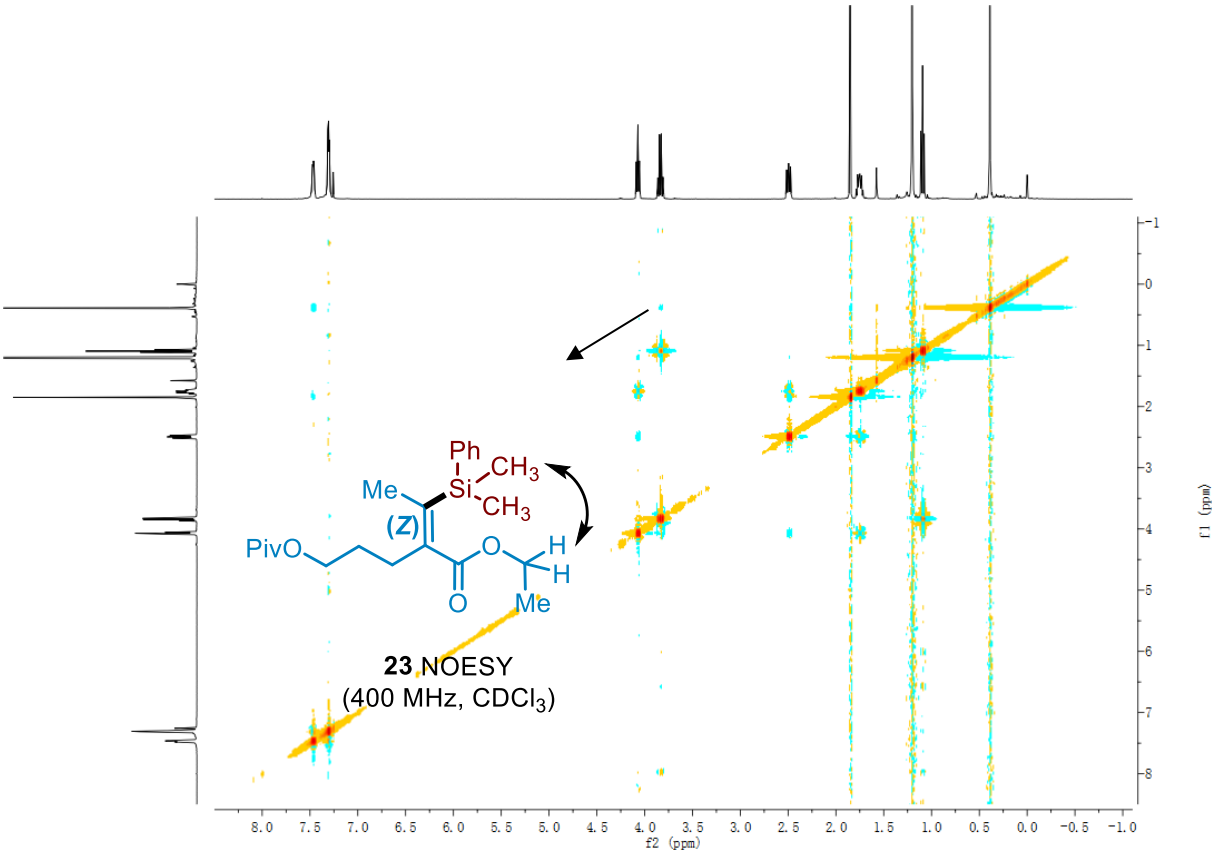
22 ^{13}C-NMR
(100 MHz, $CDCl_3$)



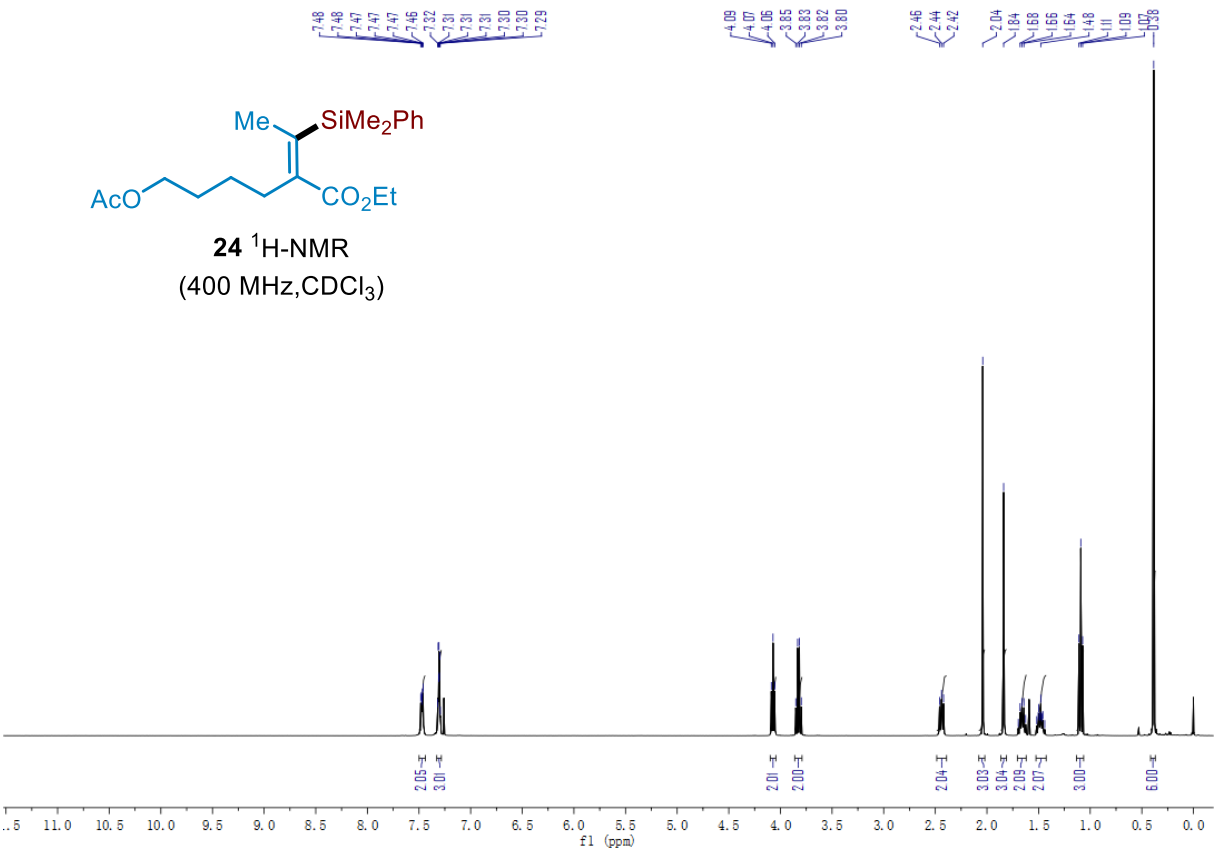
23 ^{1}H-NMR
(400 MHz,$CDCl_3$)



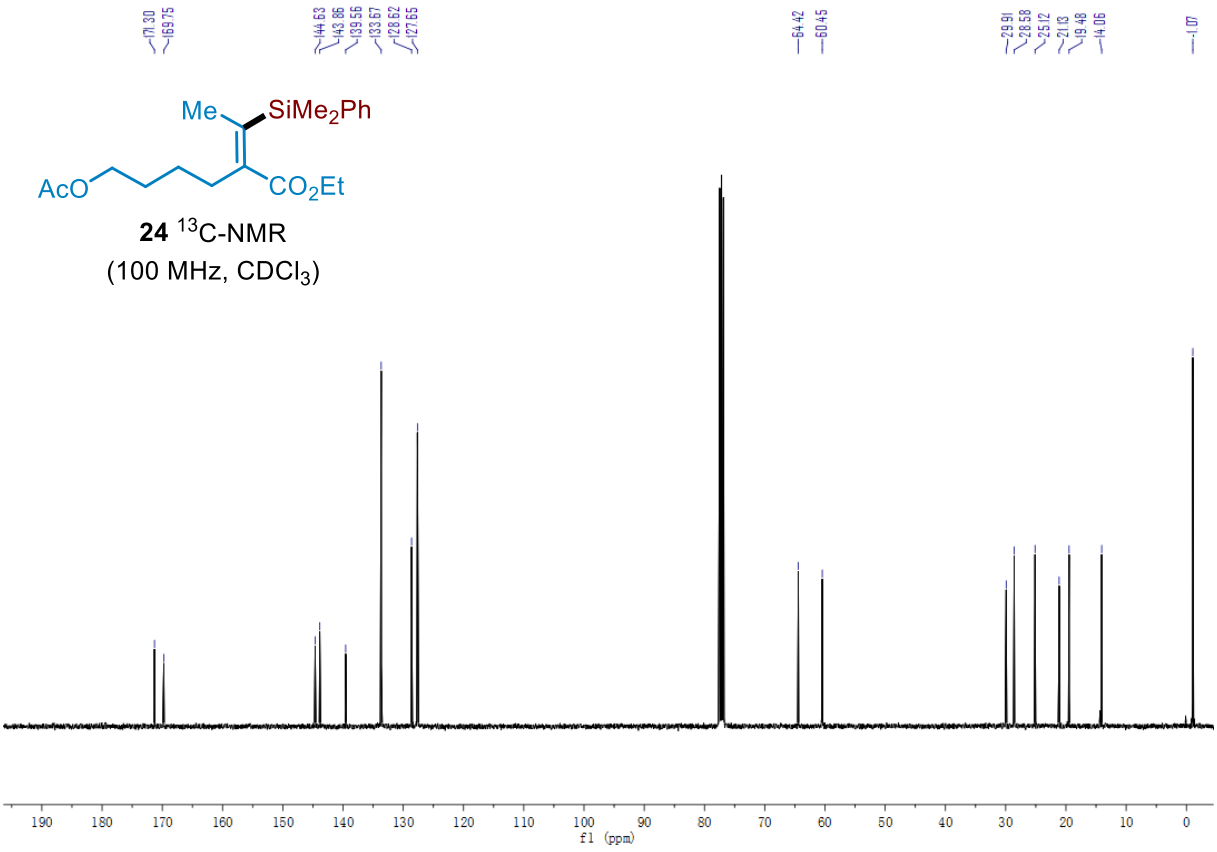
23 ^{13}C-NMR
(100 MHz, $CDCl_3$)



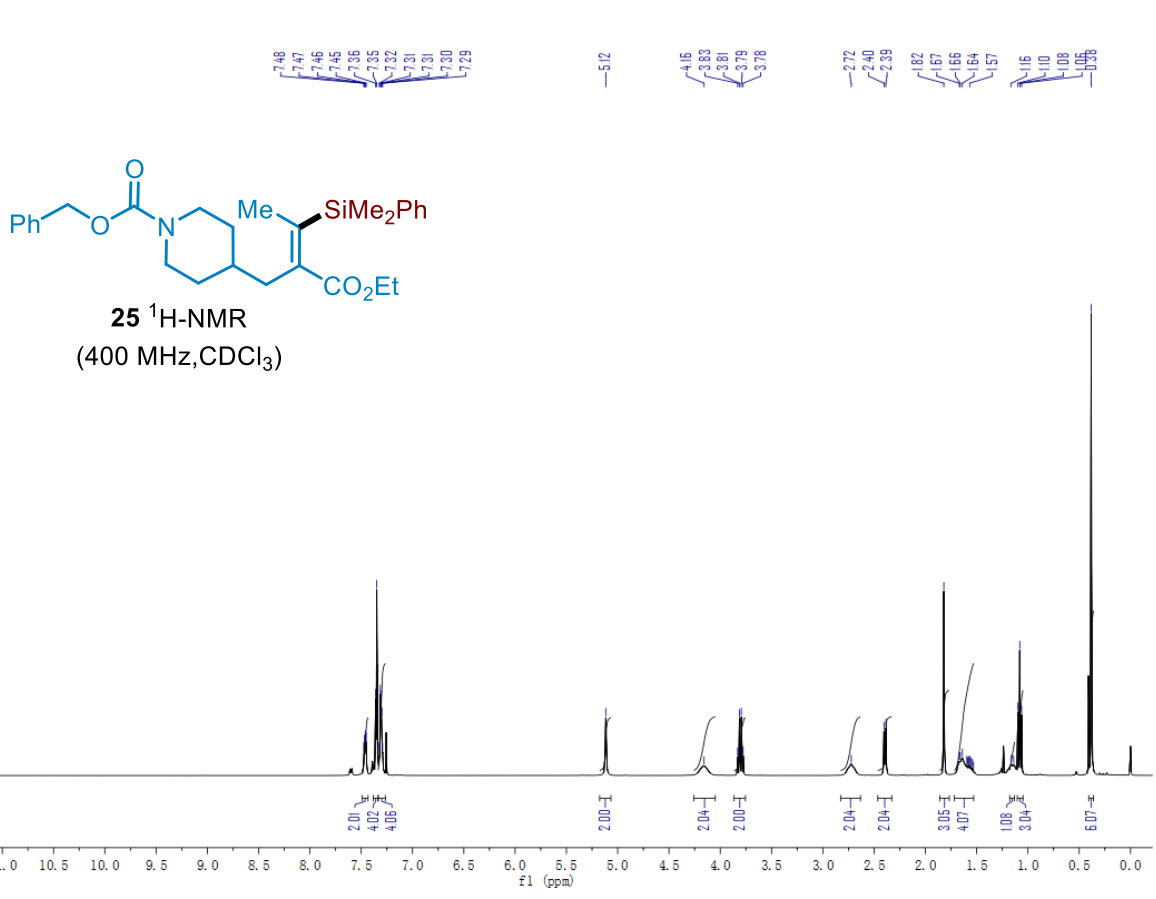
23 NOESY
(400 MHz, $CDCl_3$)



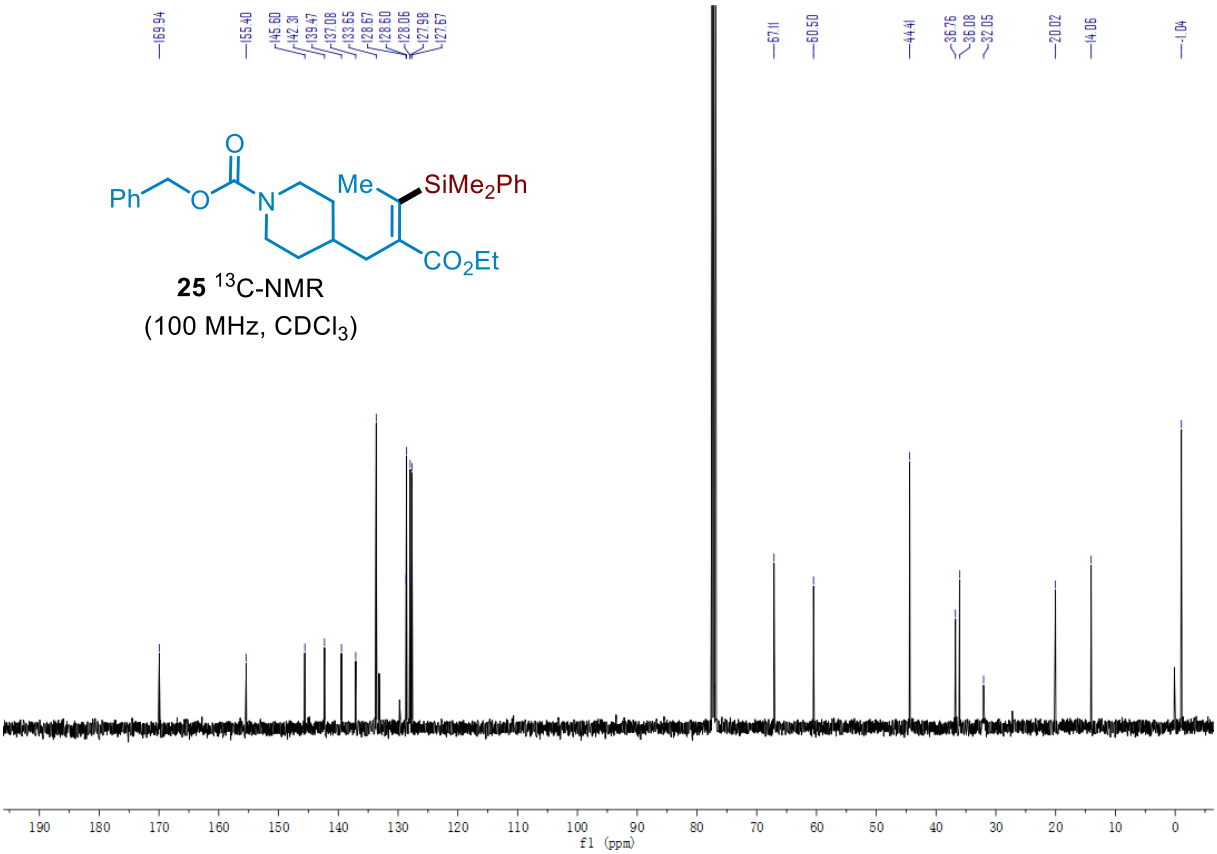
24 ^{1}H-NMR
(400 MHz,$CDCl_3$)



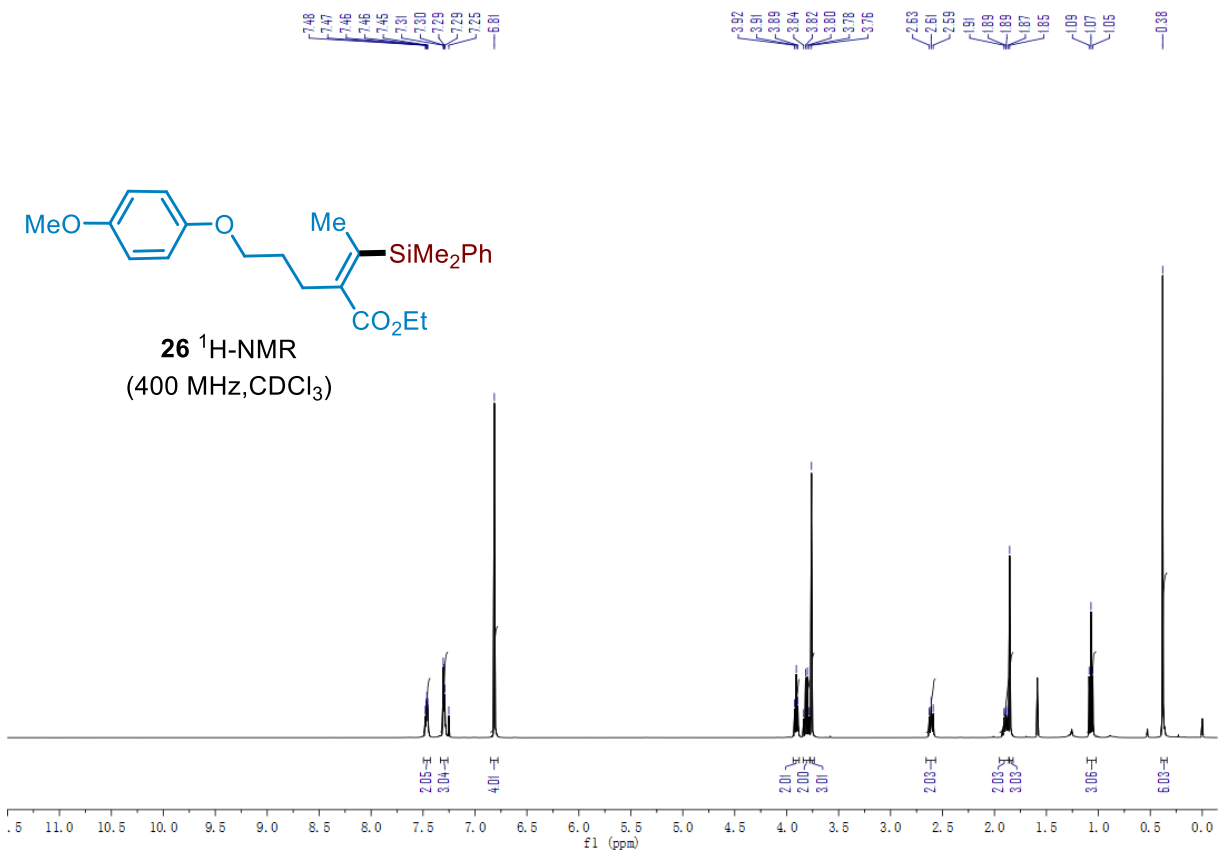
24 ^{13}C-NMR
(100 MHz, $CDCl_3$)



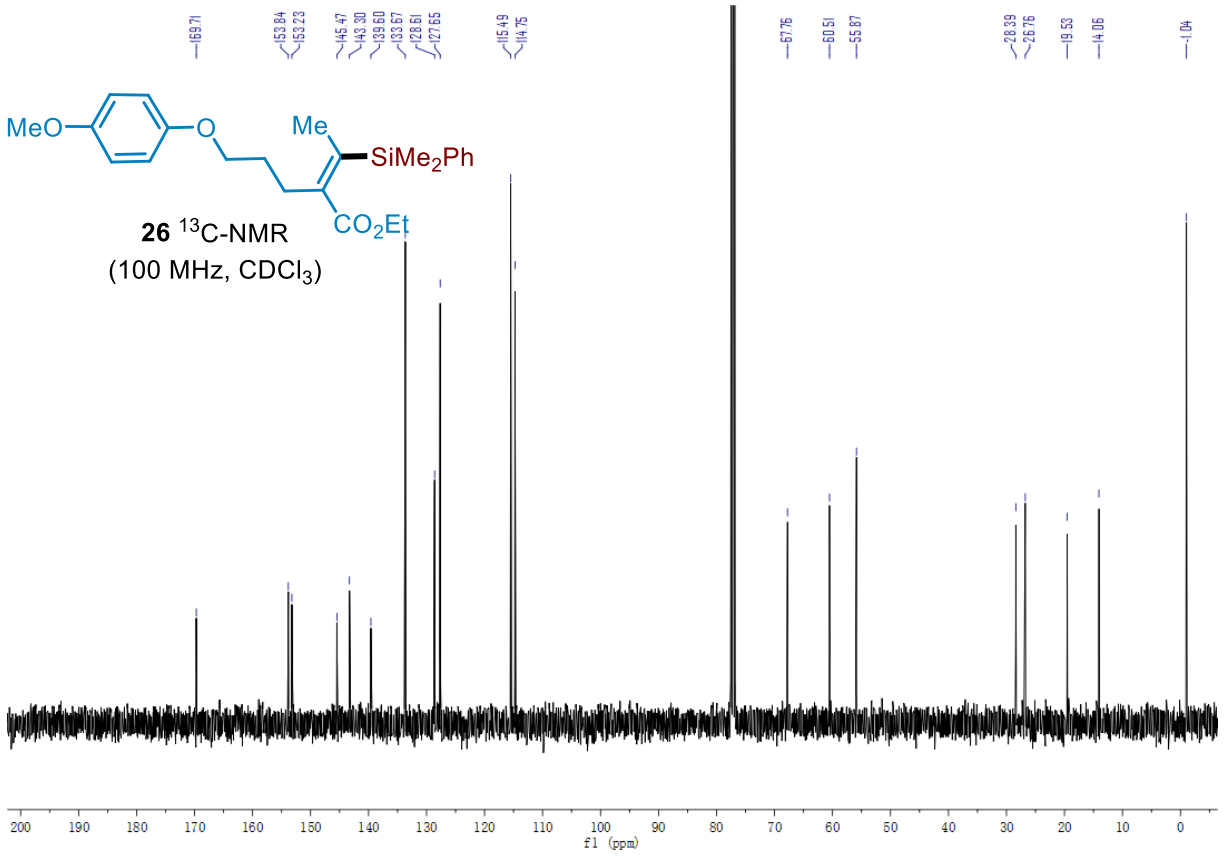
25 ^{1}H-NMR
(400 MHz,$CDCl_3$)



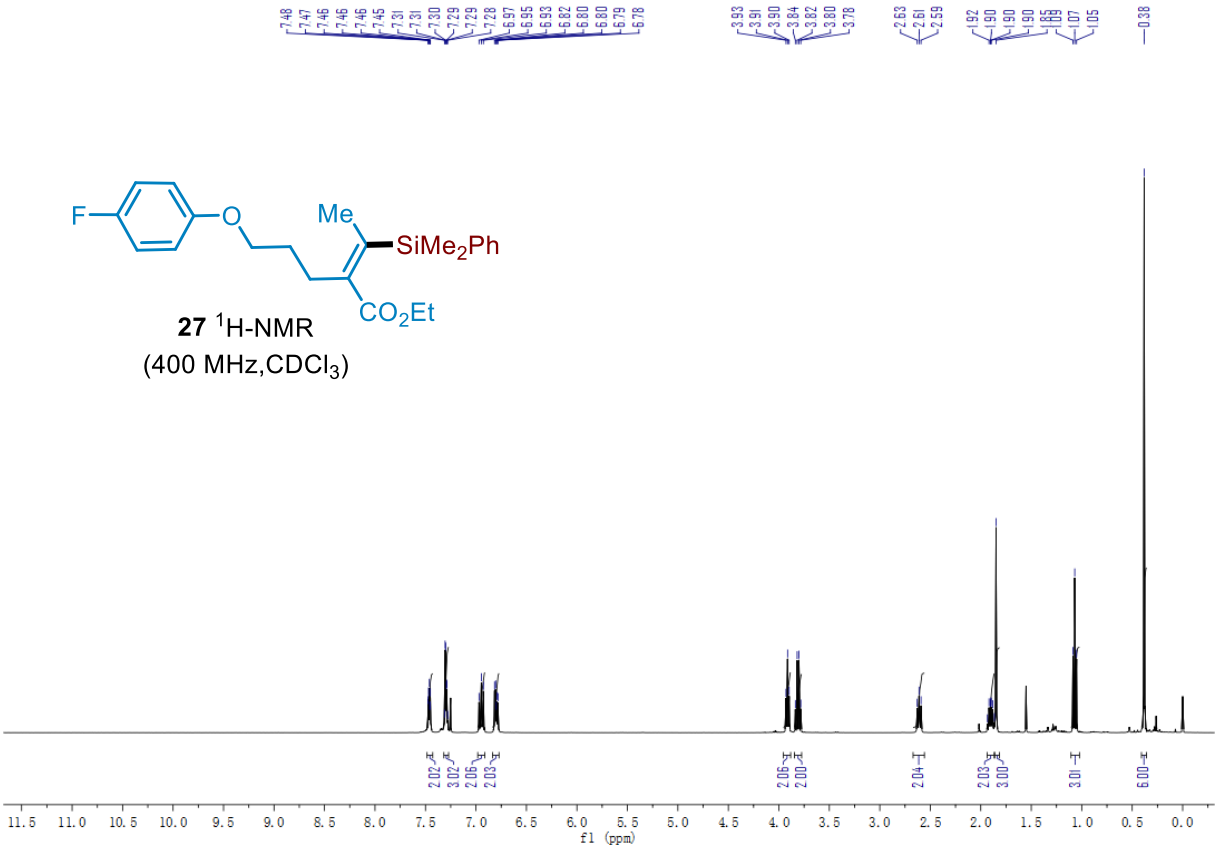
25 ^{13}C-NMR
(100 MHz, $CDCl_3$)



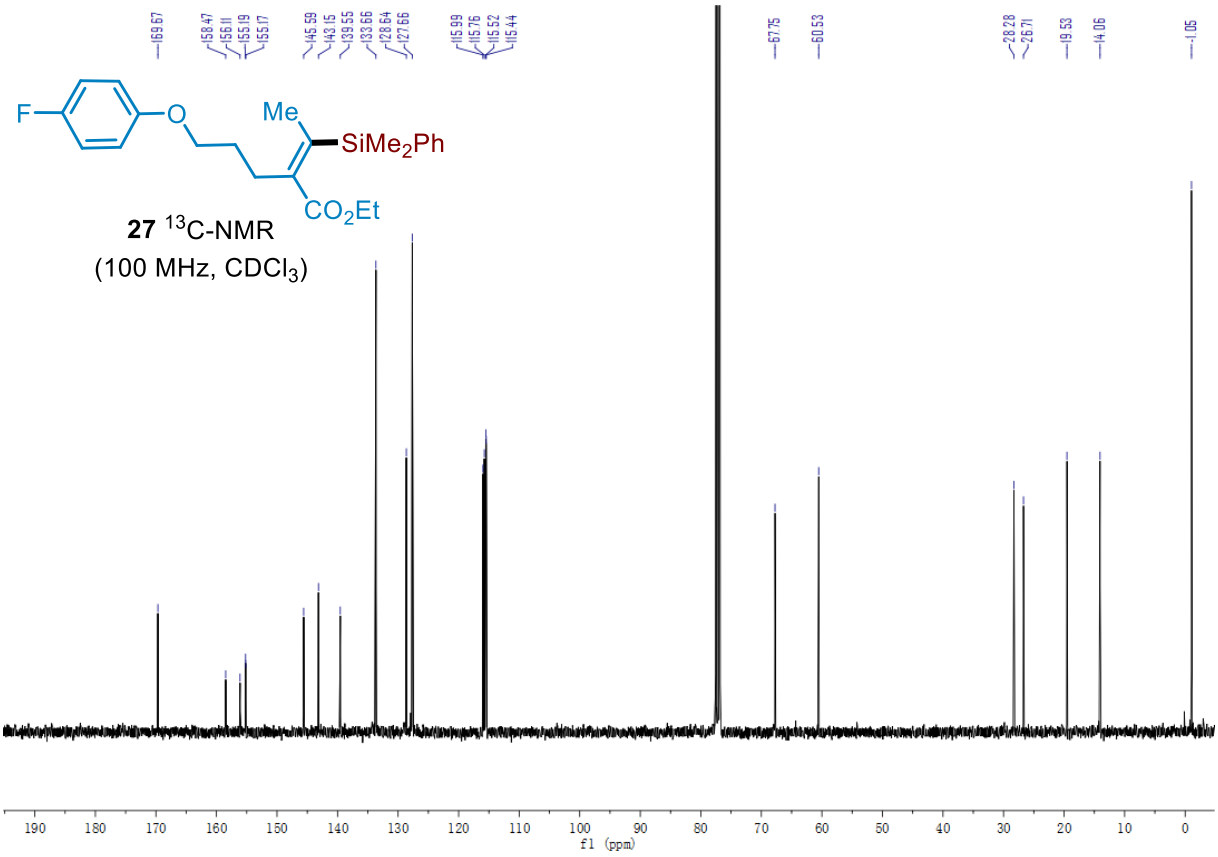
26 ^{1}H-NMR
(400 MHz,$CDCl_3$)



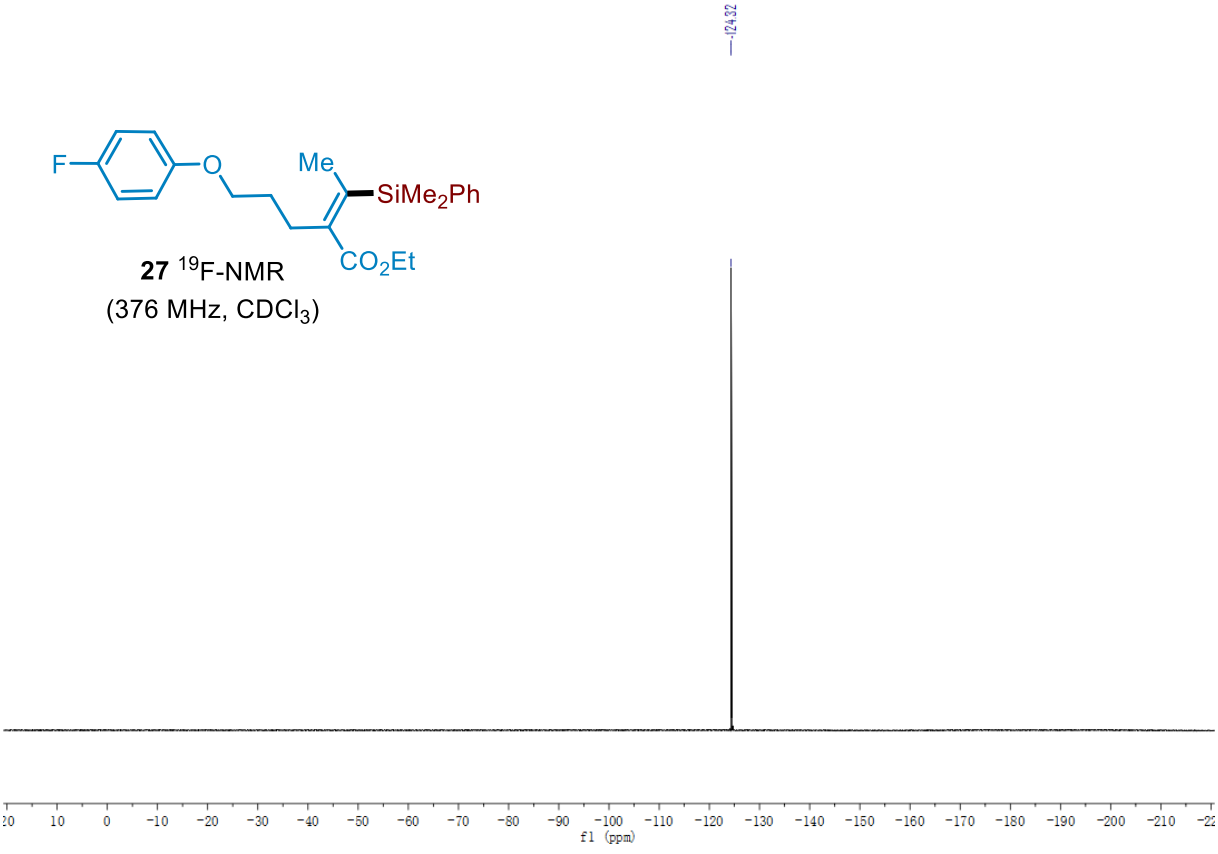
26 ^{13}C-NMR
(100 MHz, $CDCl_3$)



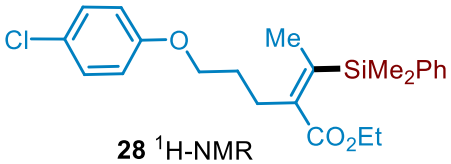
27 ^{1}H-NMR
(400 MHz,$CDCl_3$)



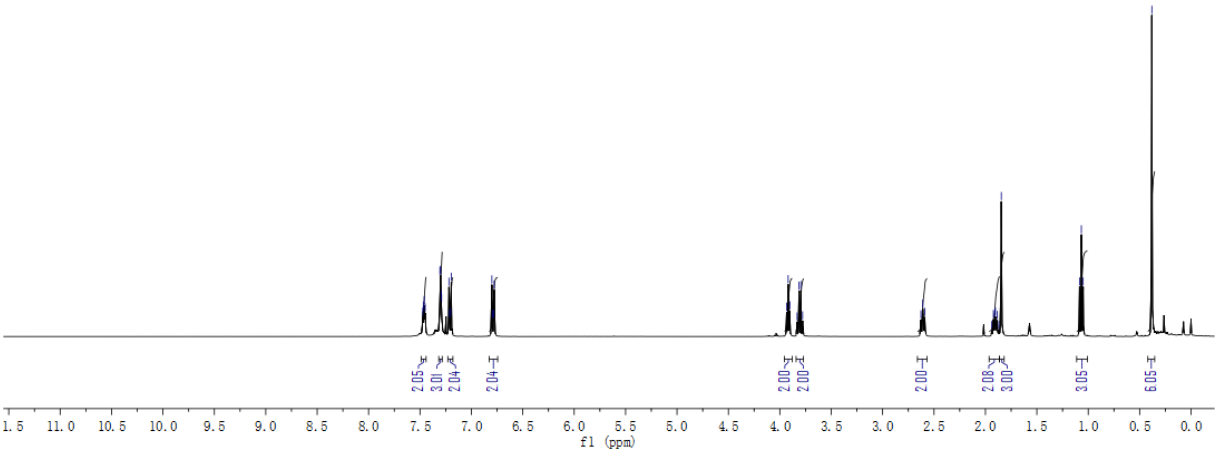
27 ^{13}C-NMR
(100 MHz, $CDCl_3$)

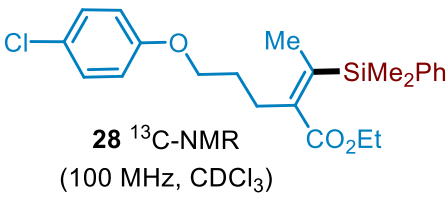


27 ^{19}F-NMR
(376 MHz, $CDCl_3$)

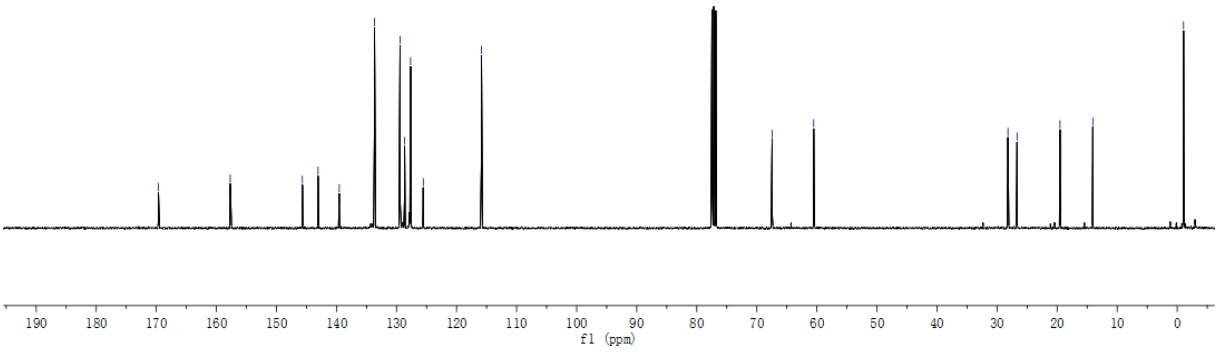


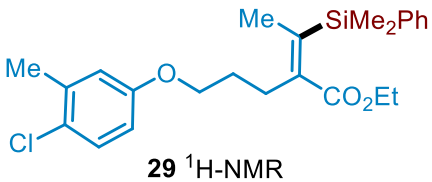
28 ^{1}H-NMR
(400 MHz,$CDCl_3$)



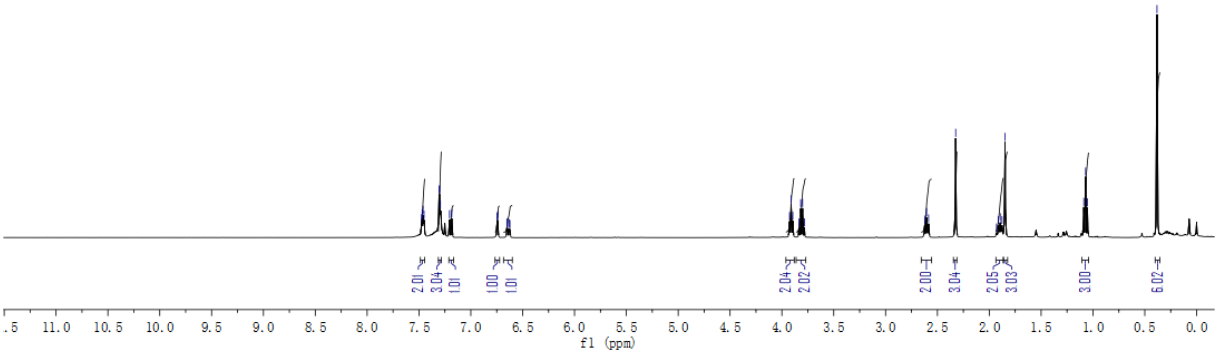


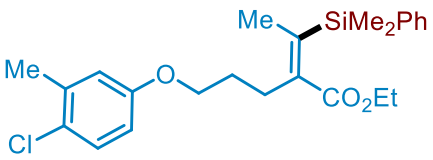
28 ^{13}C-NMR
(100 MHz, $CDCl_3$)



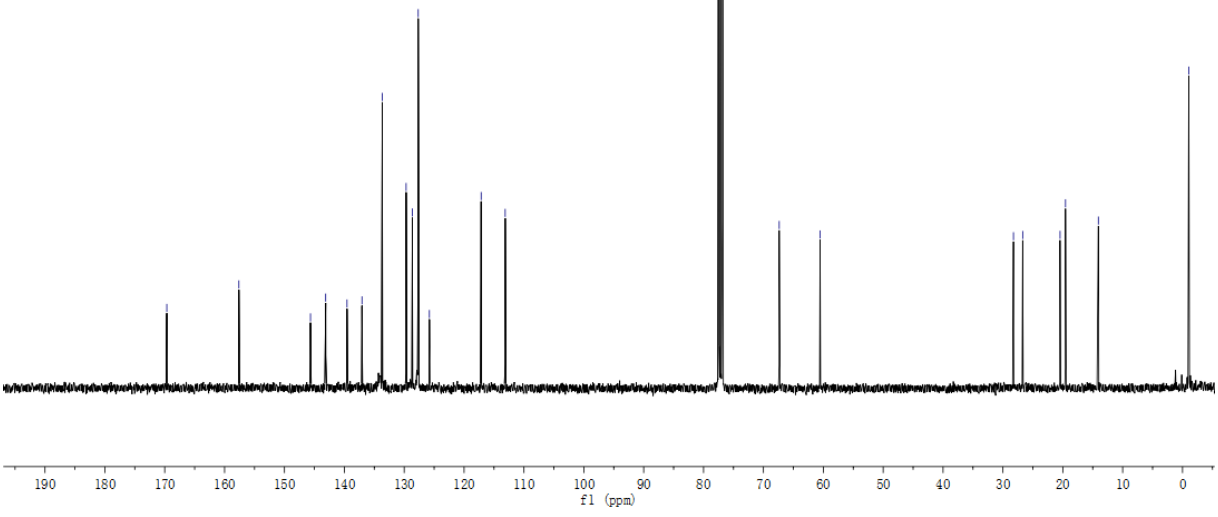


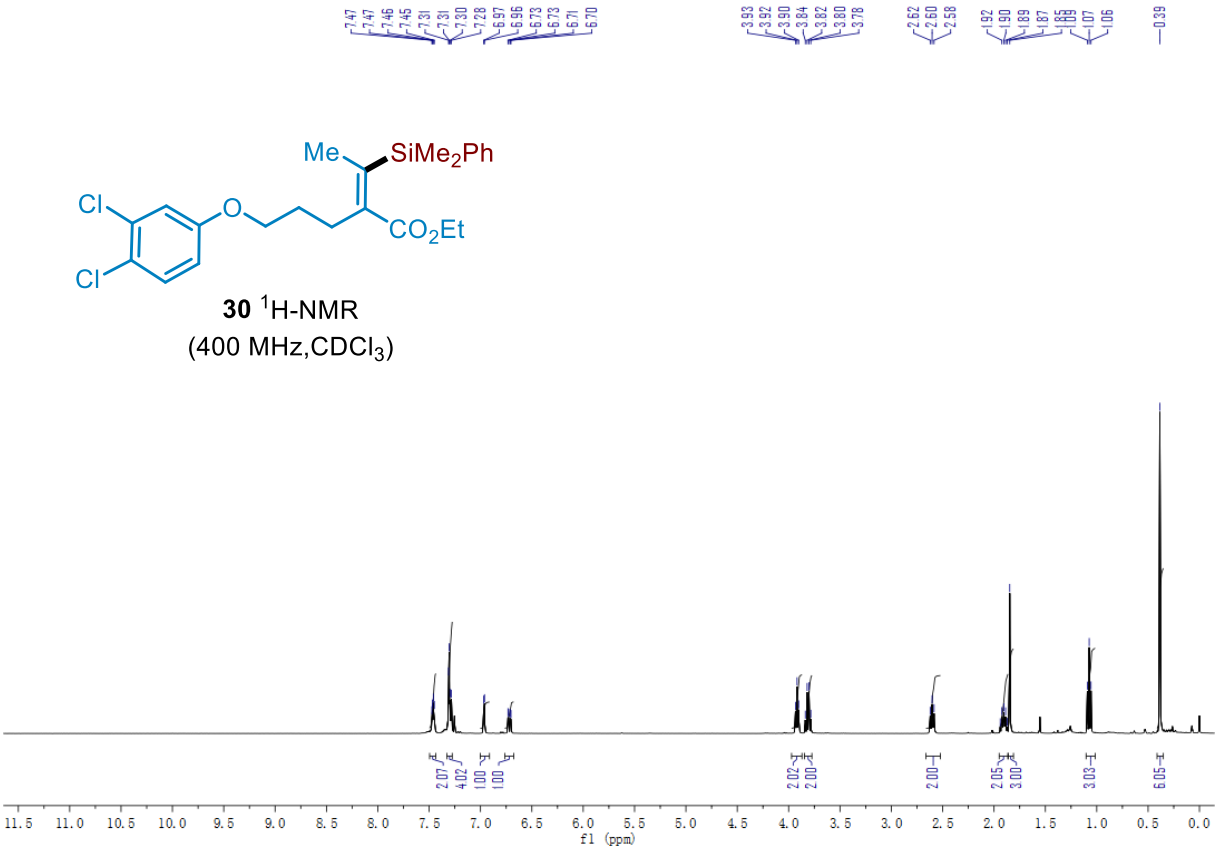
29 ^{1}H-NMR
(400 MHz,$CDCl_3$)



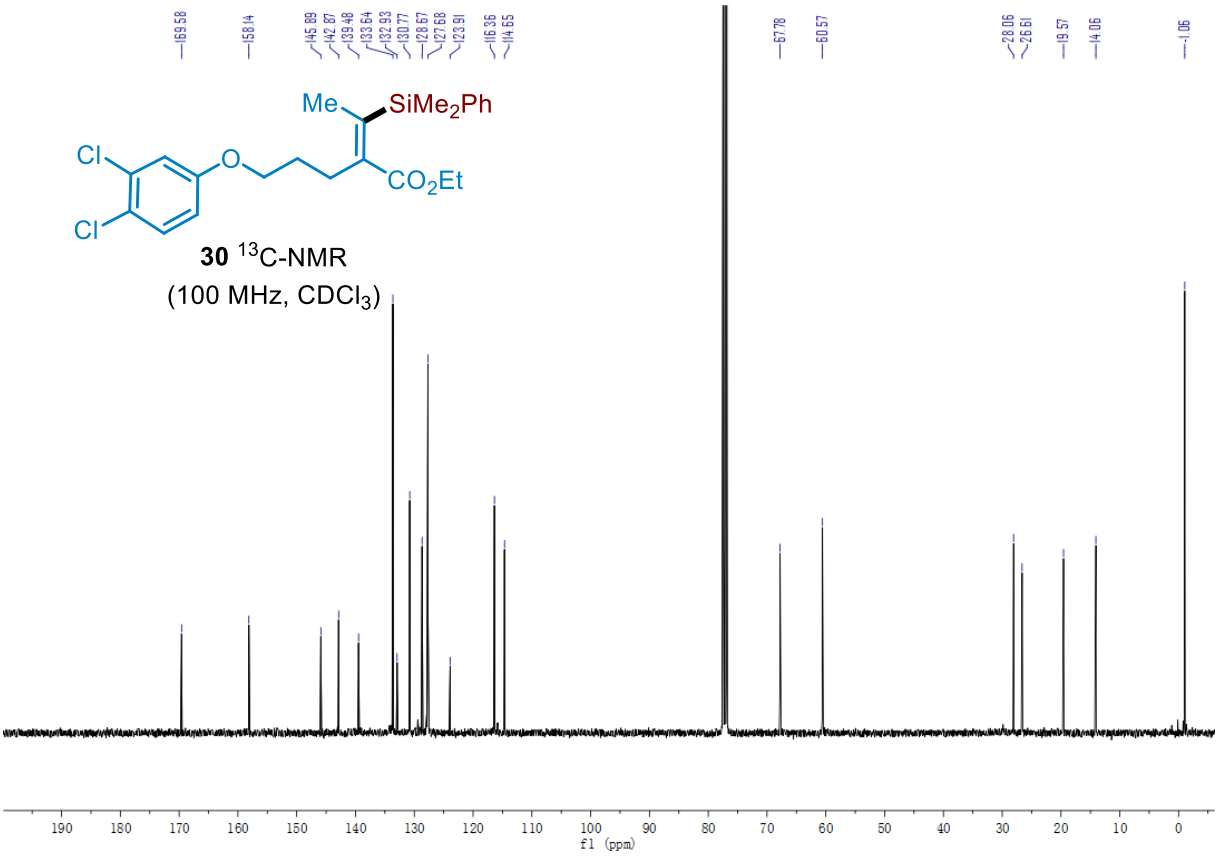


29 ^{13}C-NMR
(100 MHz, $CDCl_3$)

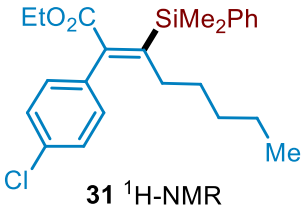




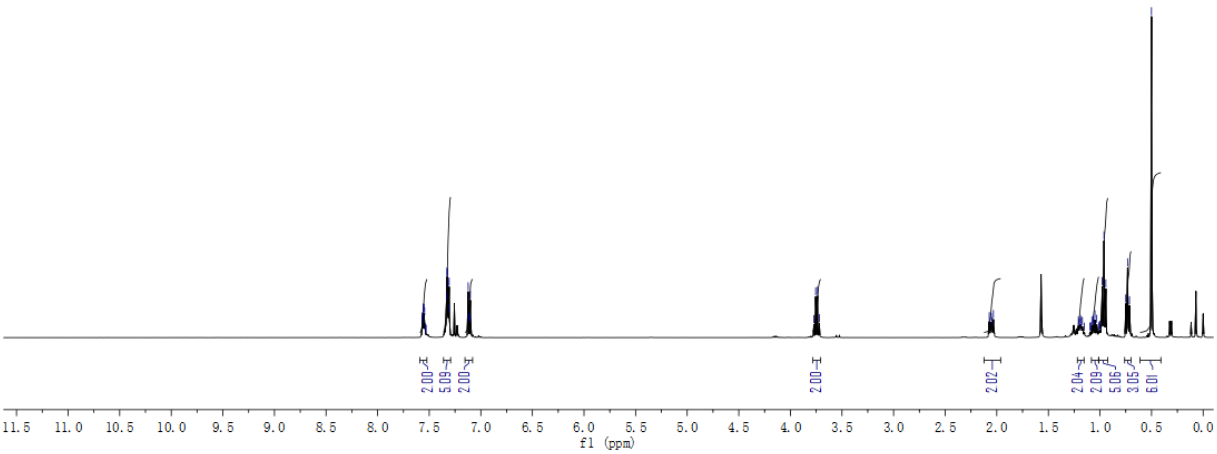
30 ^{1}H-NMR
(400 MHz,$CDCl_3$)

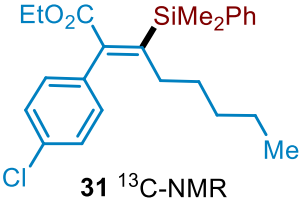


30 ^{13}C-NMR
(100 MHz, $CDCl_3$)

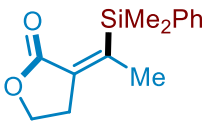


31 ^{1}H-NMR
(400 MHz,$CDCl_3$)

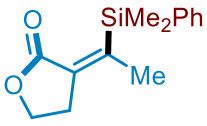




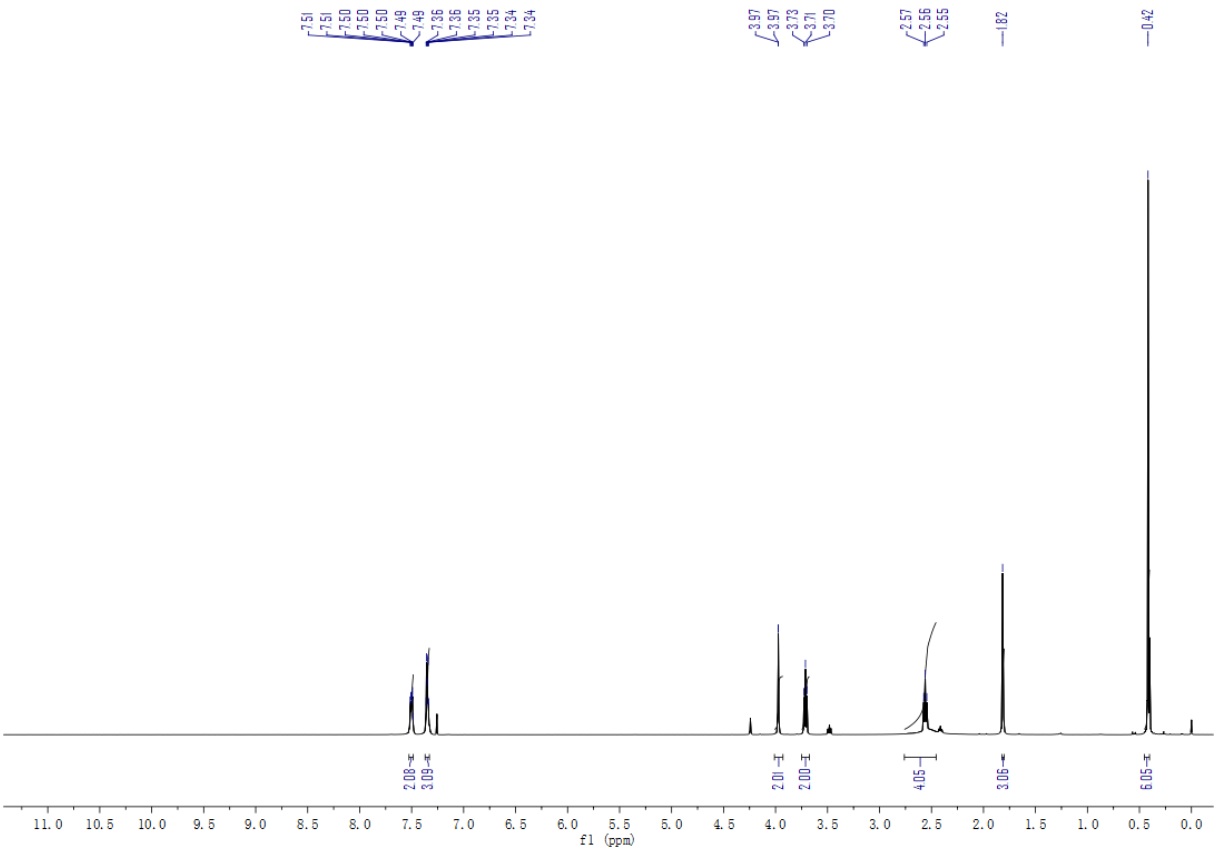
31 ^{13}C-NMR
(100 MHz, $CDCl_3$)

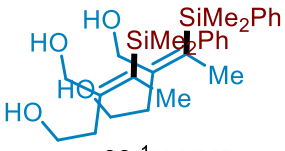


32 ^{1}H-NMR
(400 MHz,$CDCl_3$)

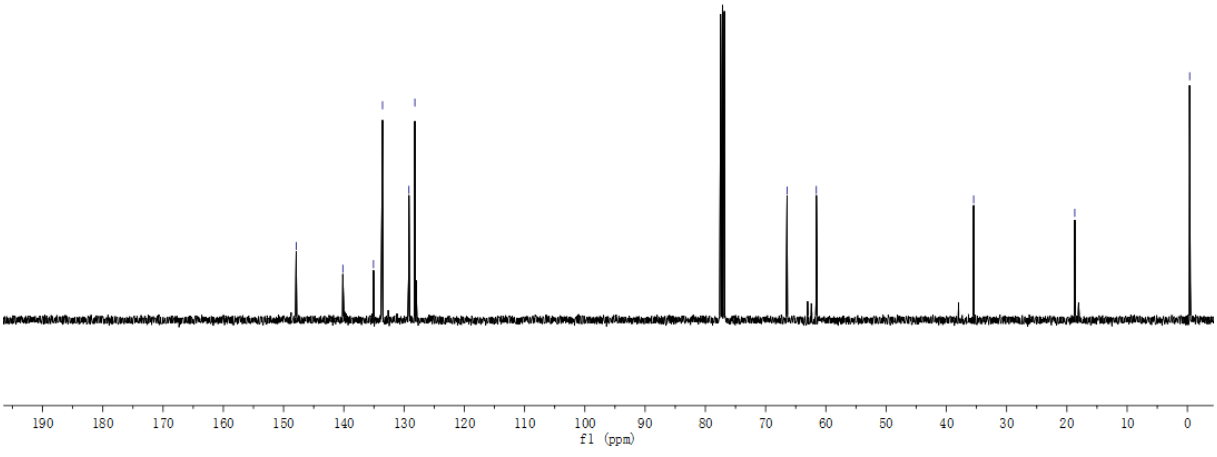


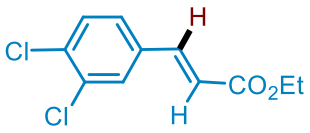
32 ^{13}C-NMR
(100 MHz, $CDCl_3$)



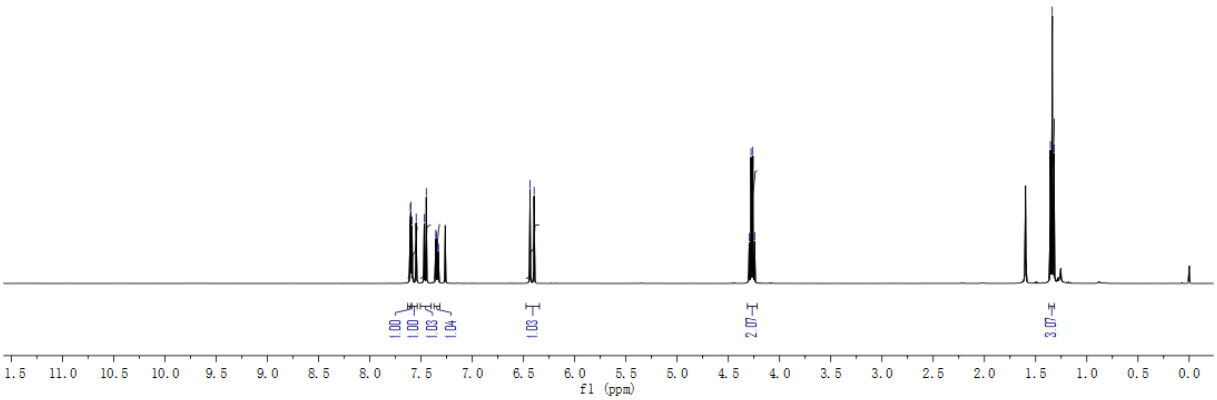


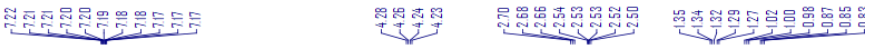
33 ^{1}H-NMR
33 ^{13}C-NMR
(400 MHz, $CDCl_3$)
(100 MHz, $CDCl_3$)

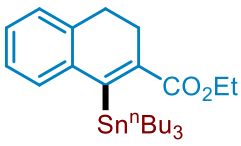




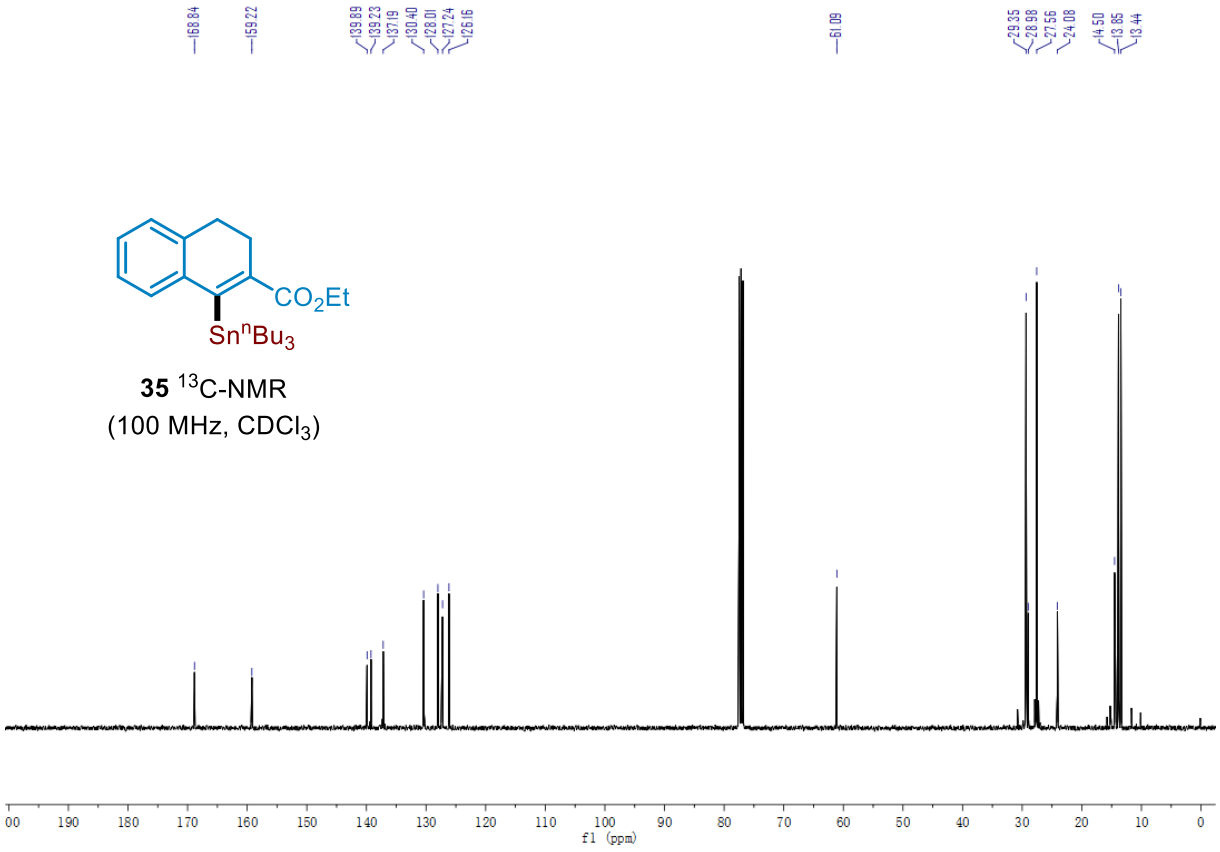
34 ^{1}H-NMR
(400 MHz,$CDCl_3$)



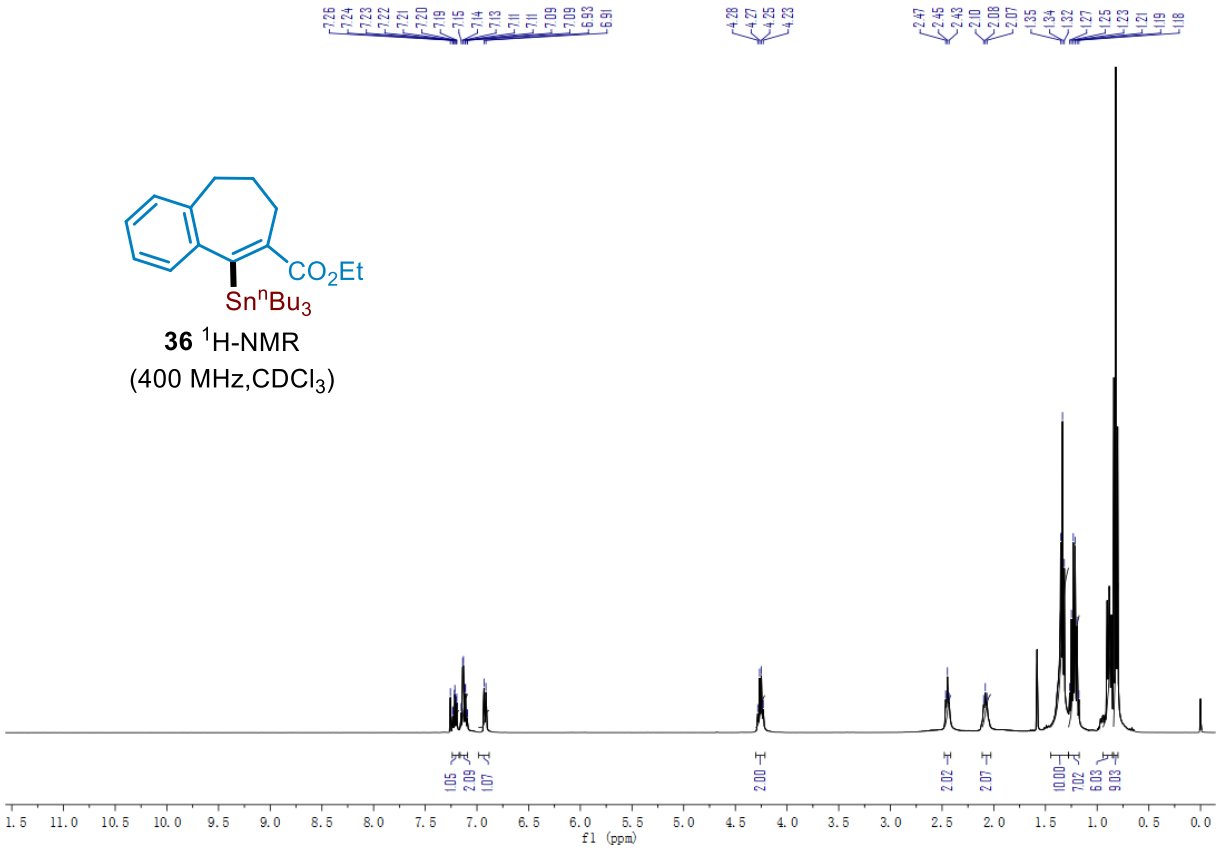




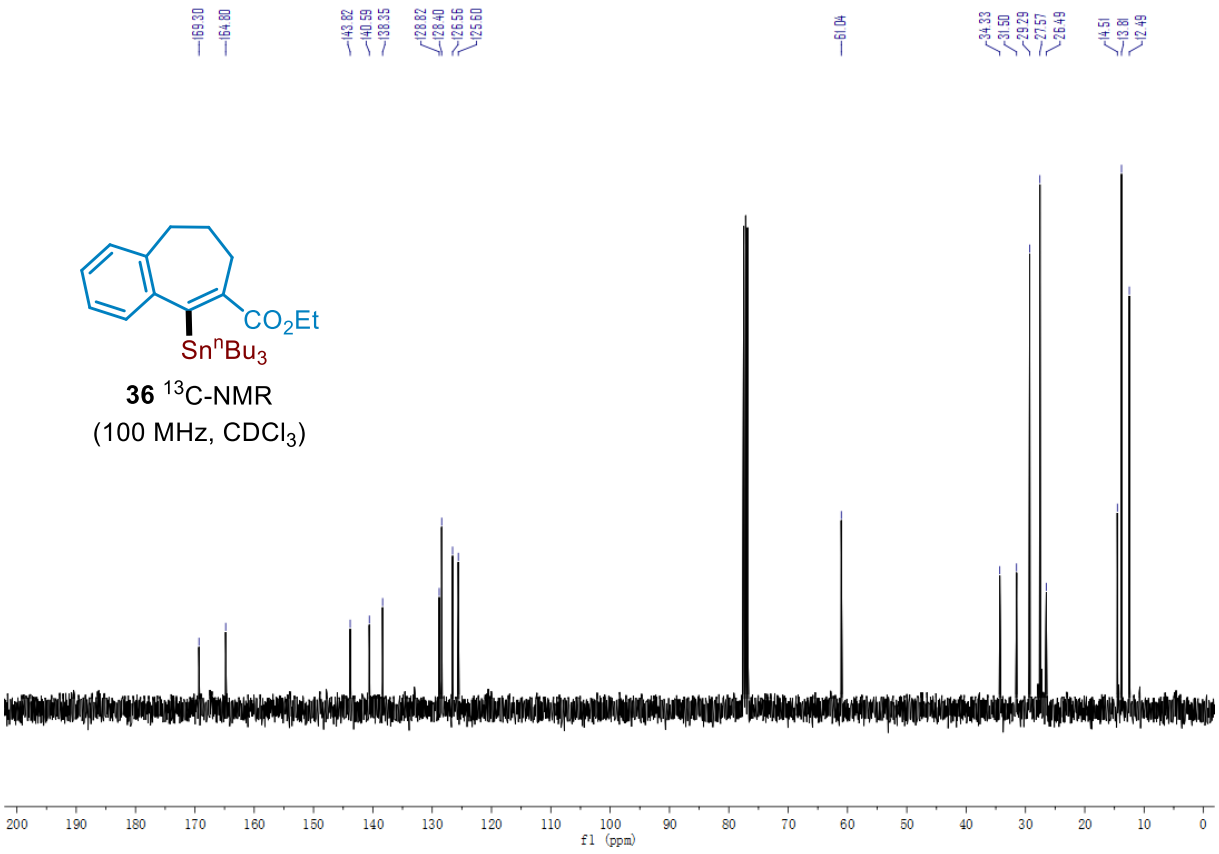
35 ^{1}H-NMR
(400 MHz,$CDCl_3$)



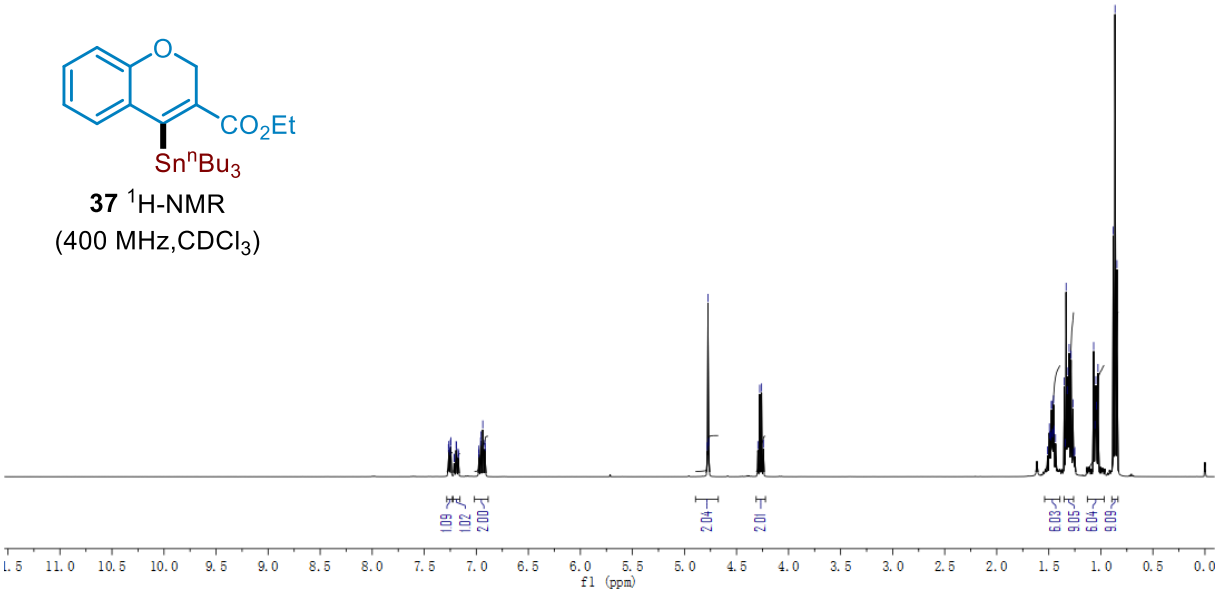
35 ^{13}C-NMR
(100 MHz, $CDCl_3$)



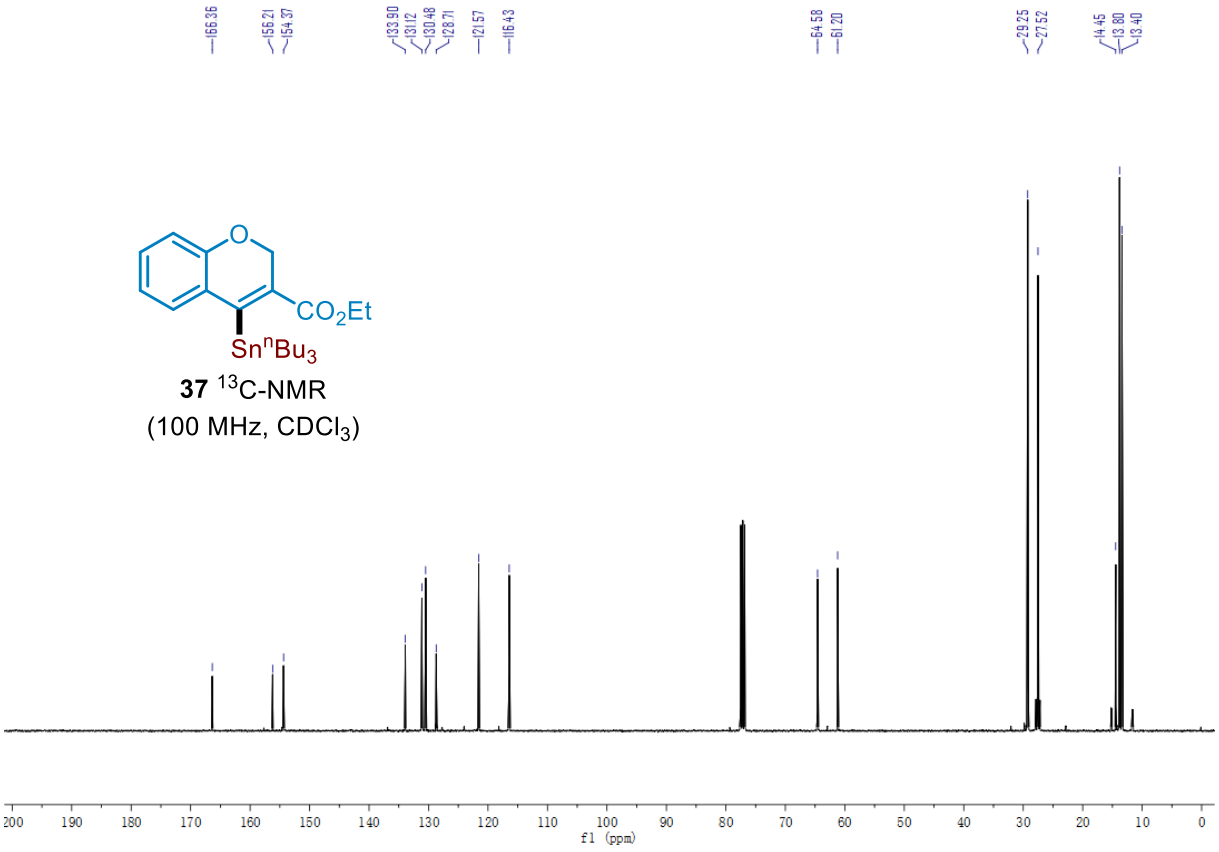
36 ^{1}H-NMR
(400 MHz,$CDCl_3$)



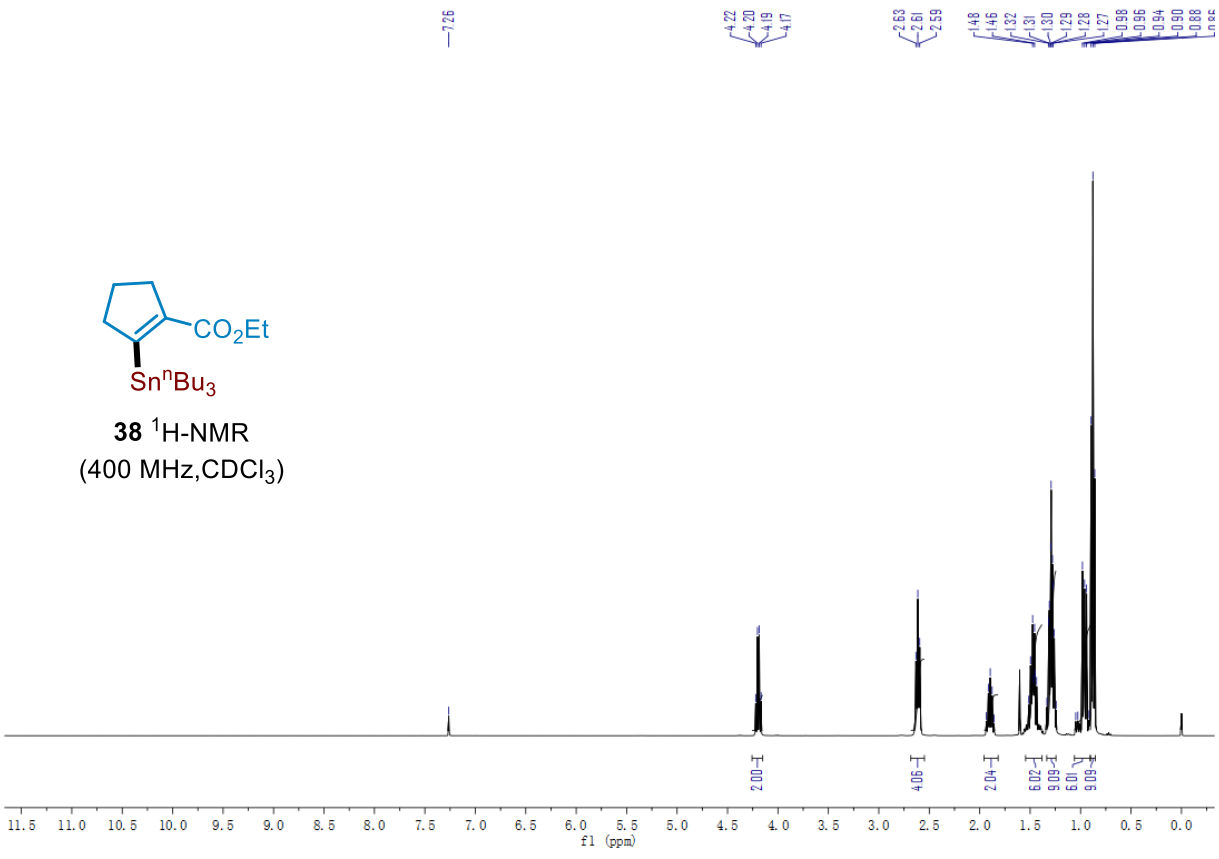
36 ^{13}C-NMR
(100 MHz, $CDCl_3$)



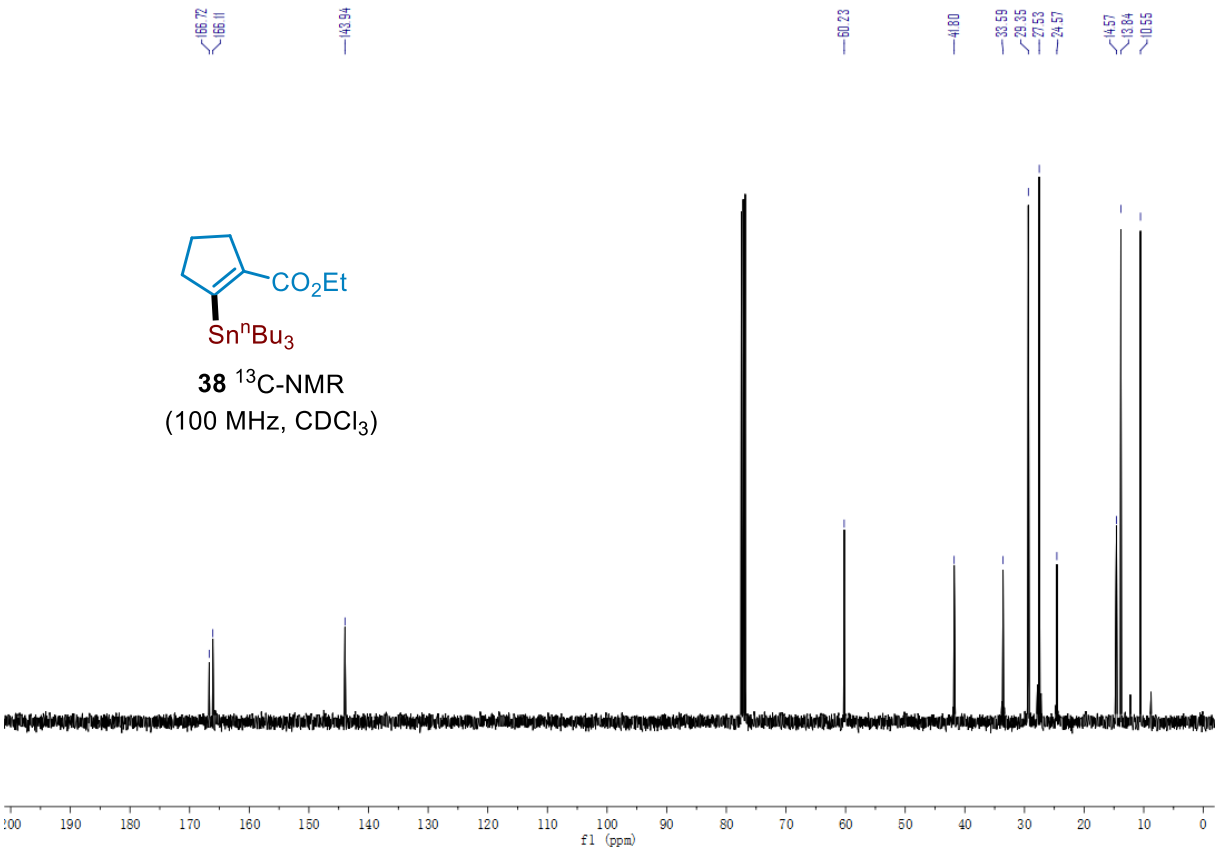
37 ^{1}H-NMR
(400 MHz,$CDCl_3$)



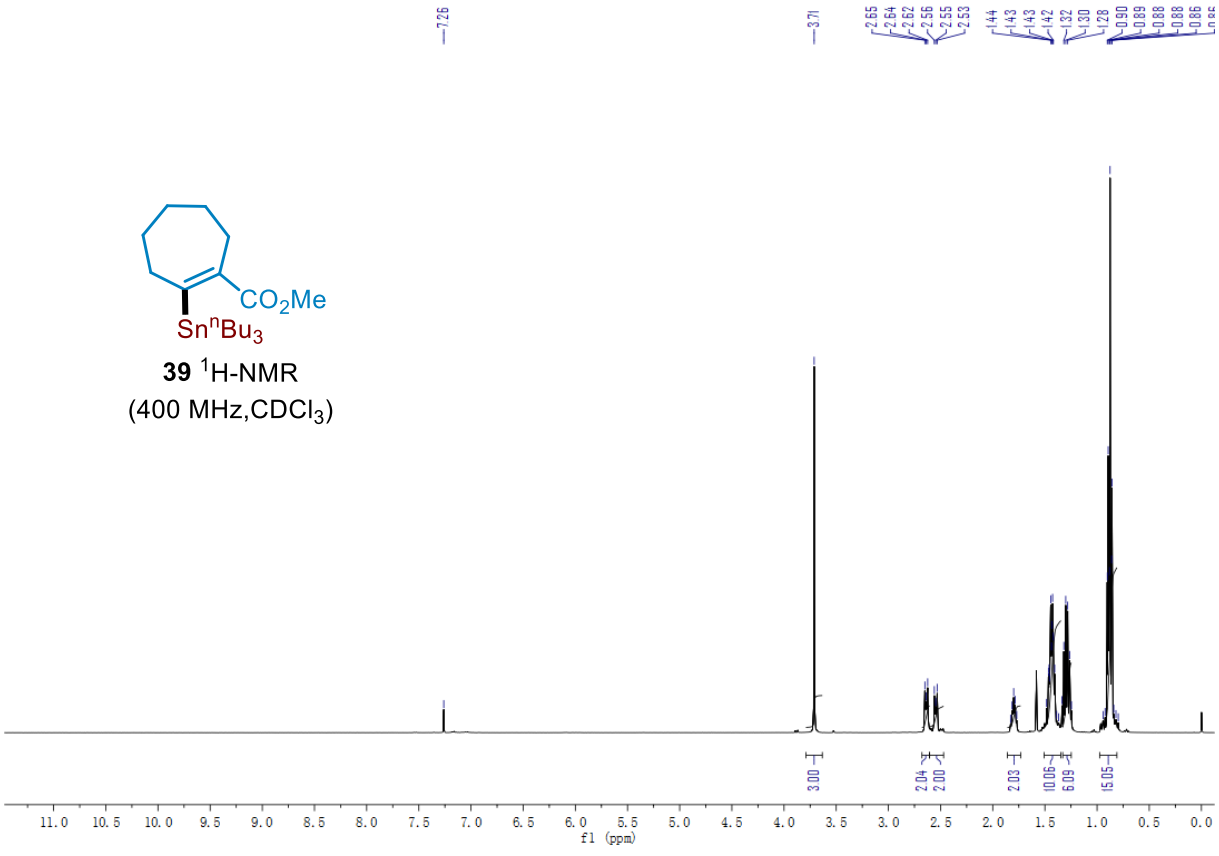
37 ^{13}C-NMR
(100 MHz, $CDCl_3$)



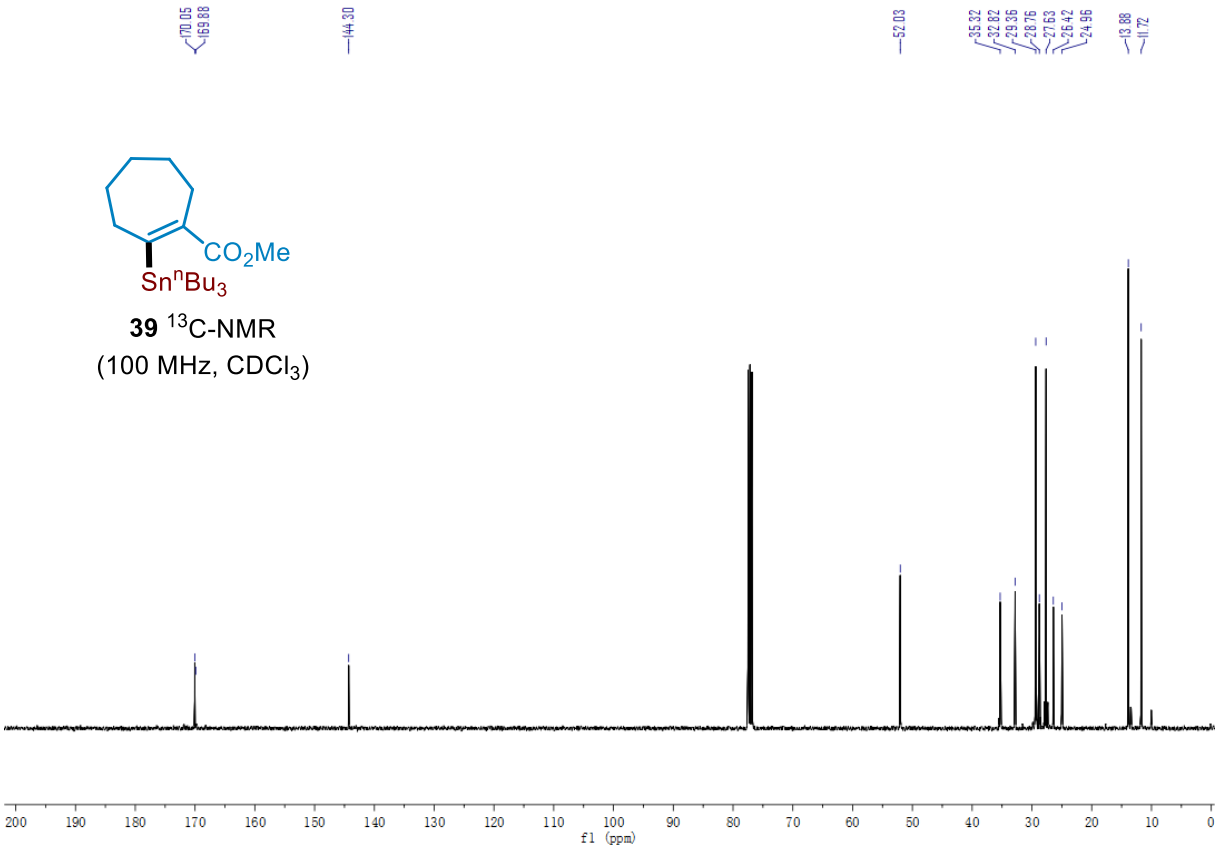
38 ^{1}H-NMR
(400 MHz,$CDCl_3$)



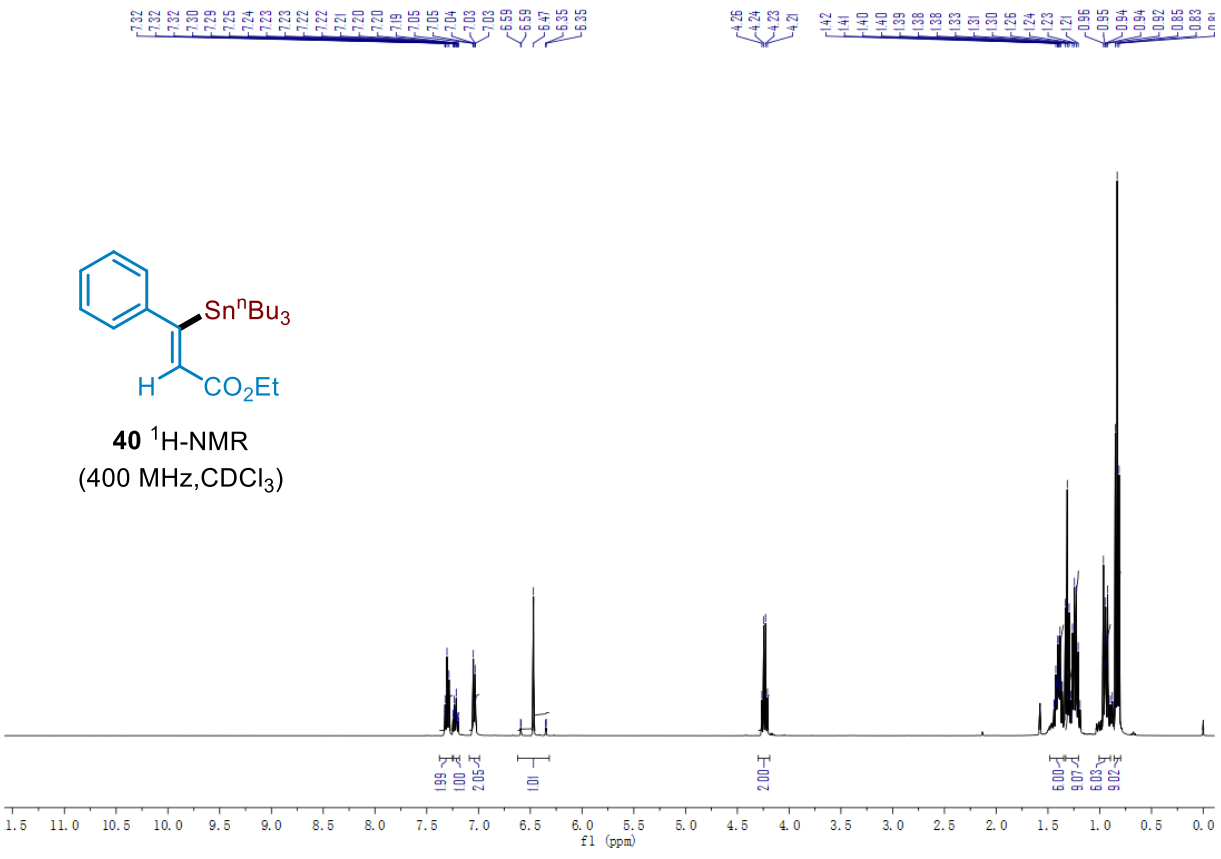
38 ^{13}C-NMR
(100 MHz, $CDCl_3$)



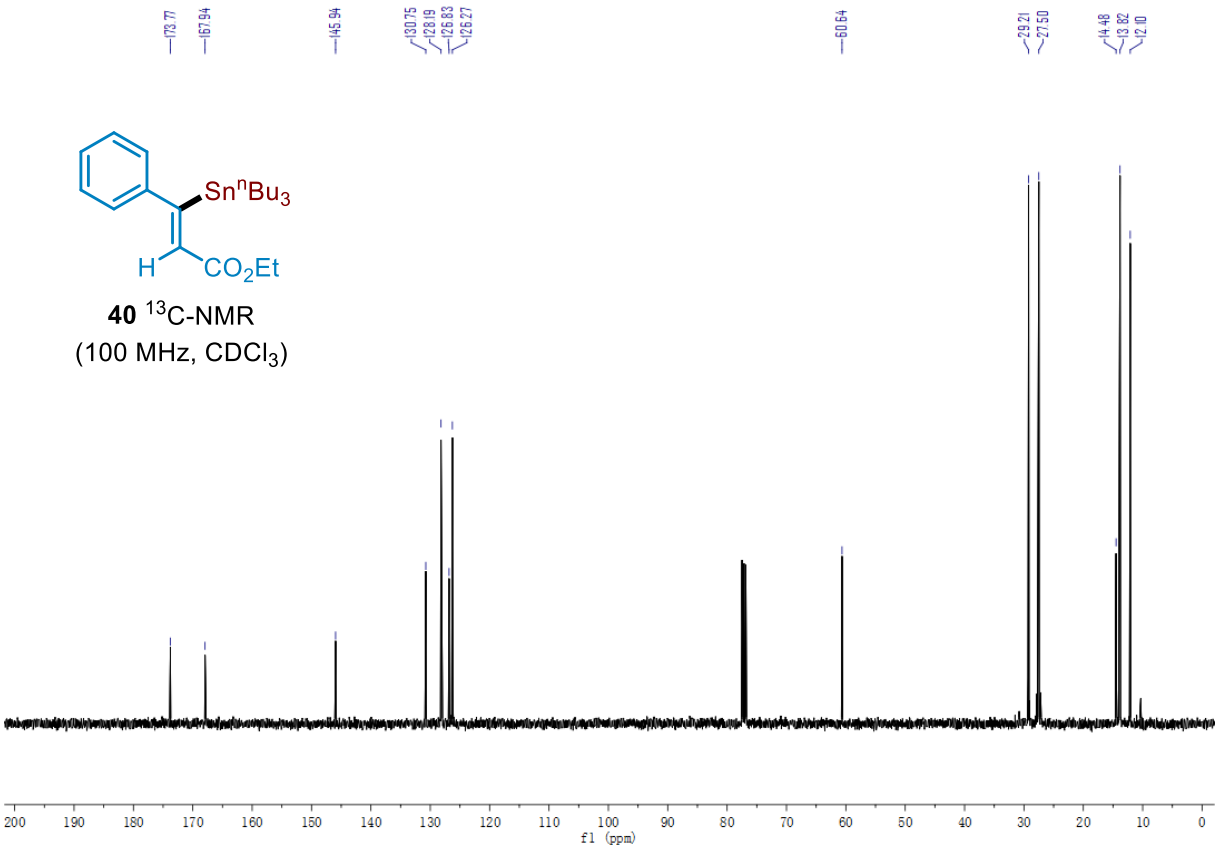
39 ^{1}H-NMR
(400 MHz,$CDCl_3$)



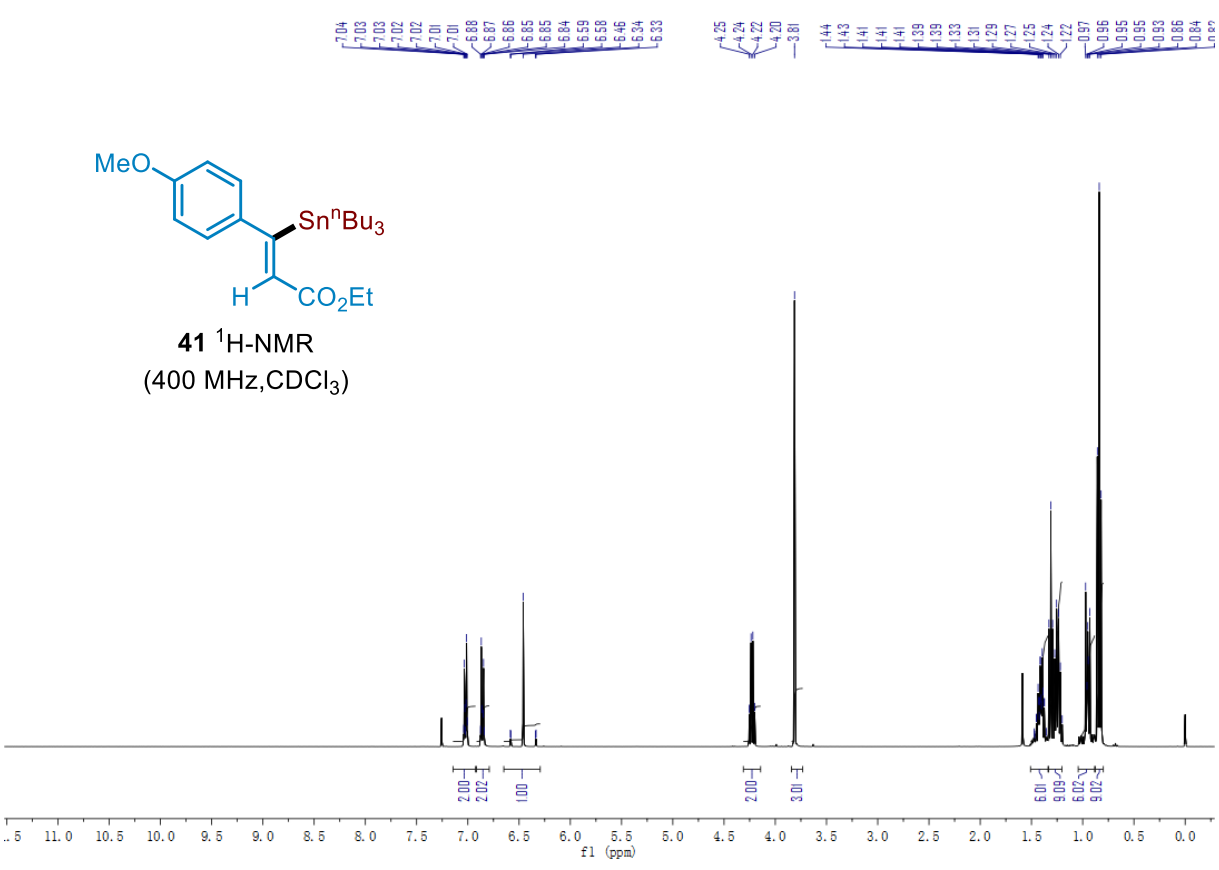
39 ^{13}C-NMR
(100 MHz, $CDCl_3$)



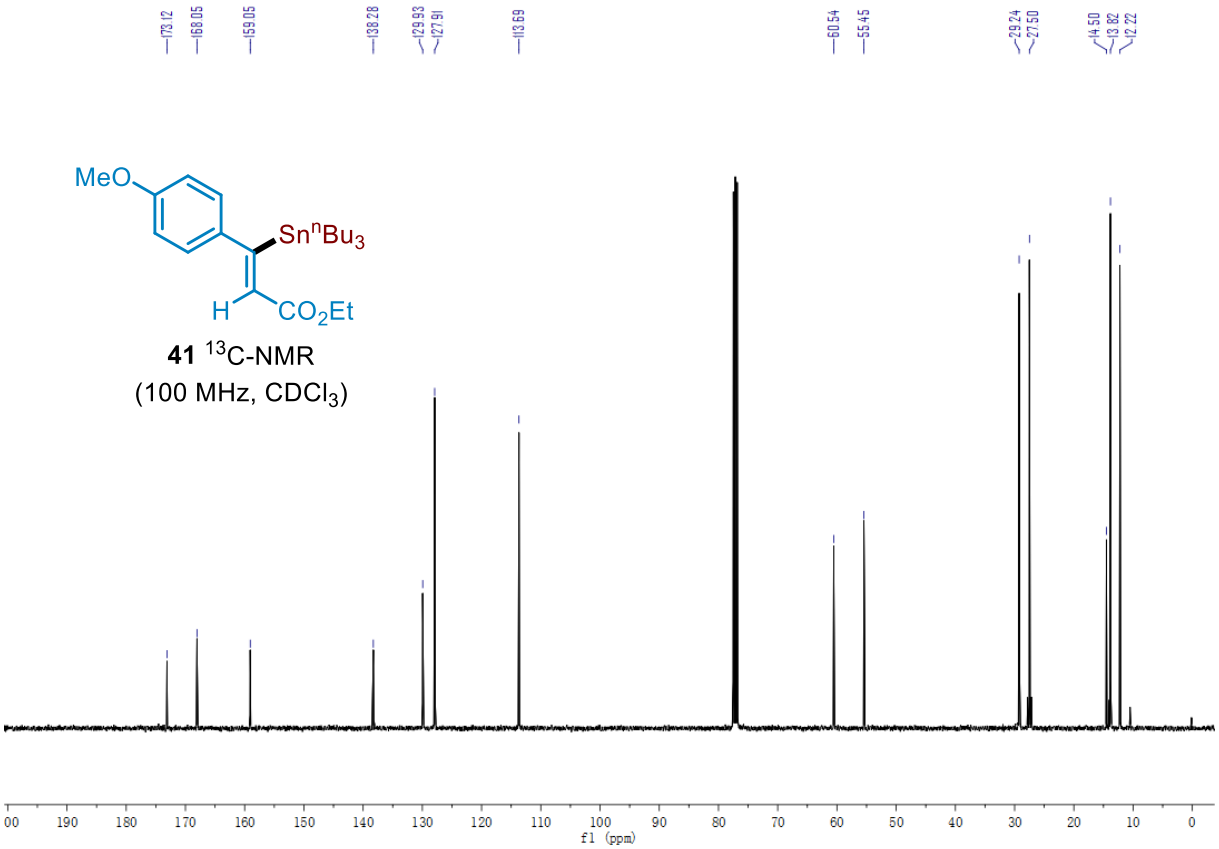
40 ^{1}H-NMR
(400 MHz,$CDCl_3$)



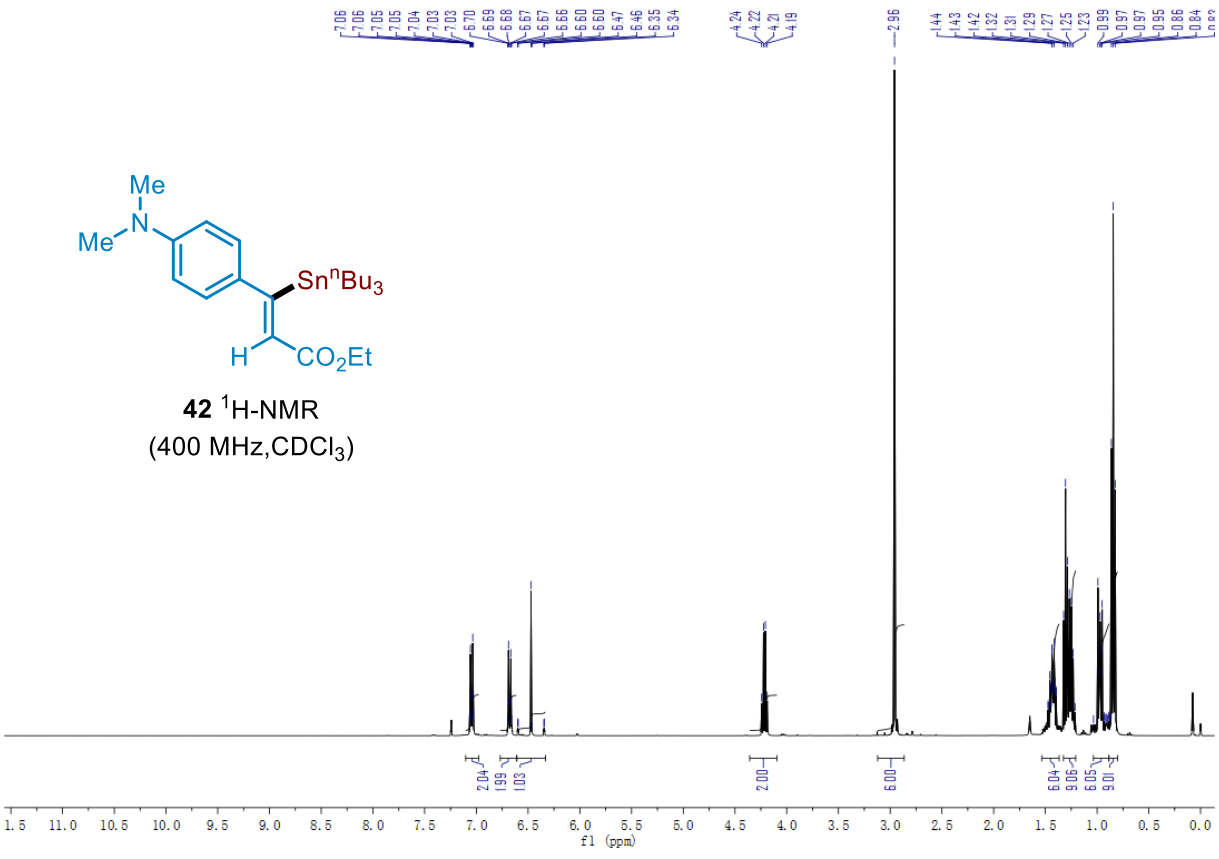
40 ^{13}C-NMR
(100 MHz, $CDCl_3$)



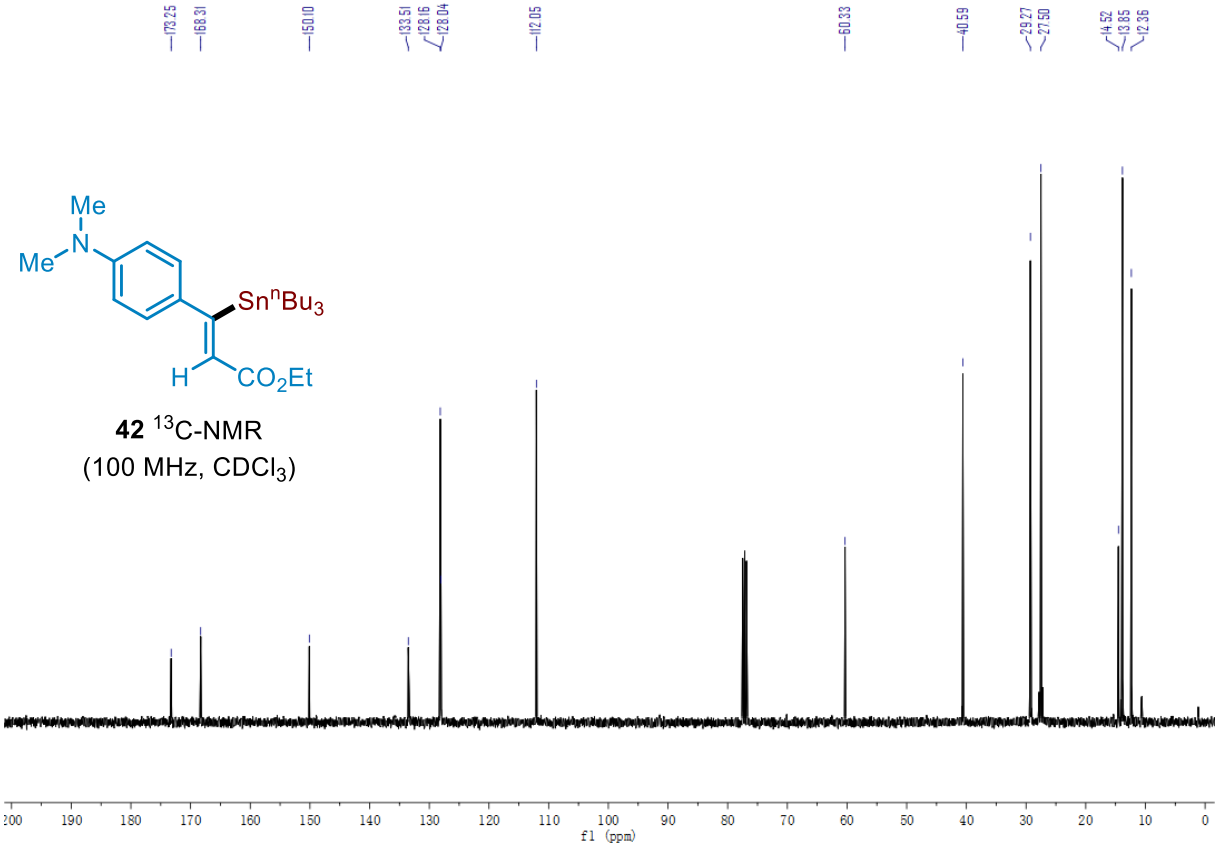
41 ^{1}H-NMR
(400 MHz,$CDCl_3$)



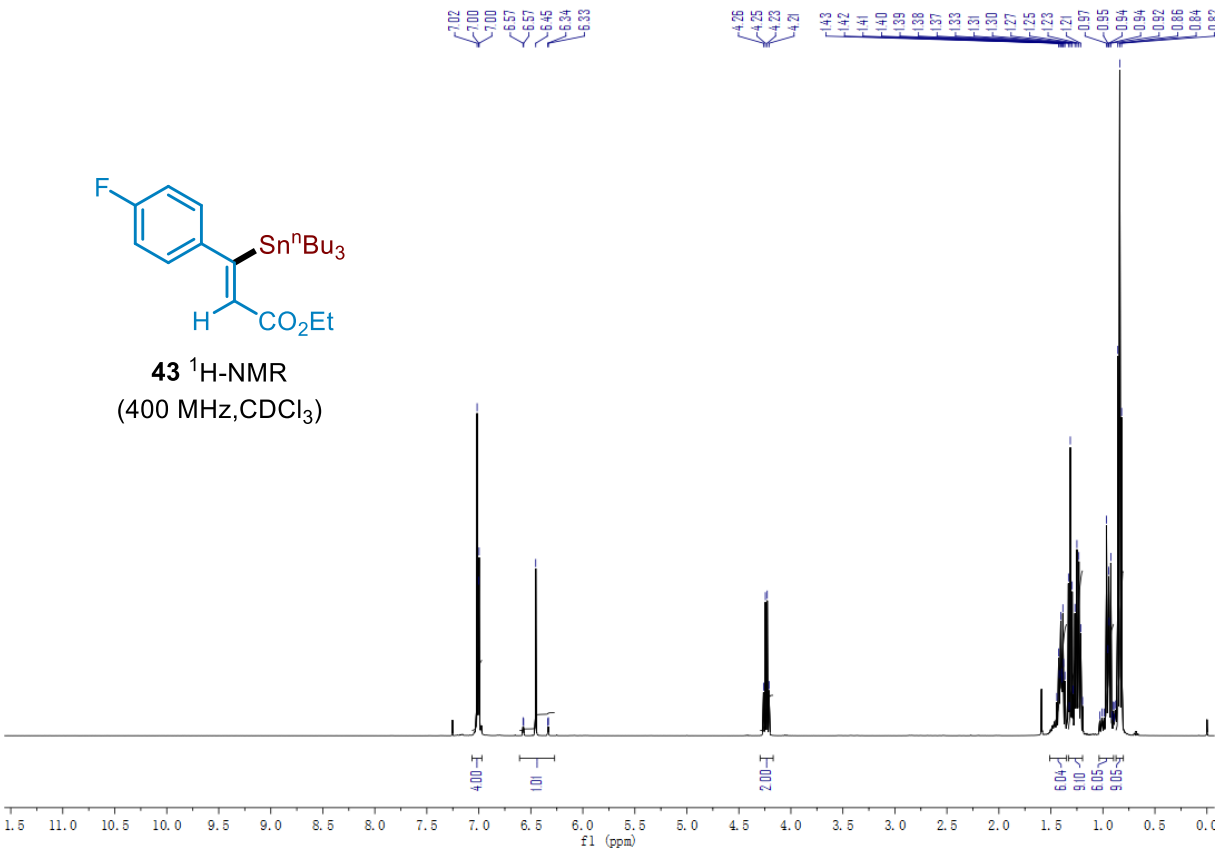
41 ^{13}C-NMR
(100 MHz, $CDCl_3$)



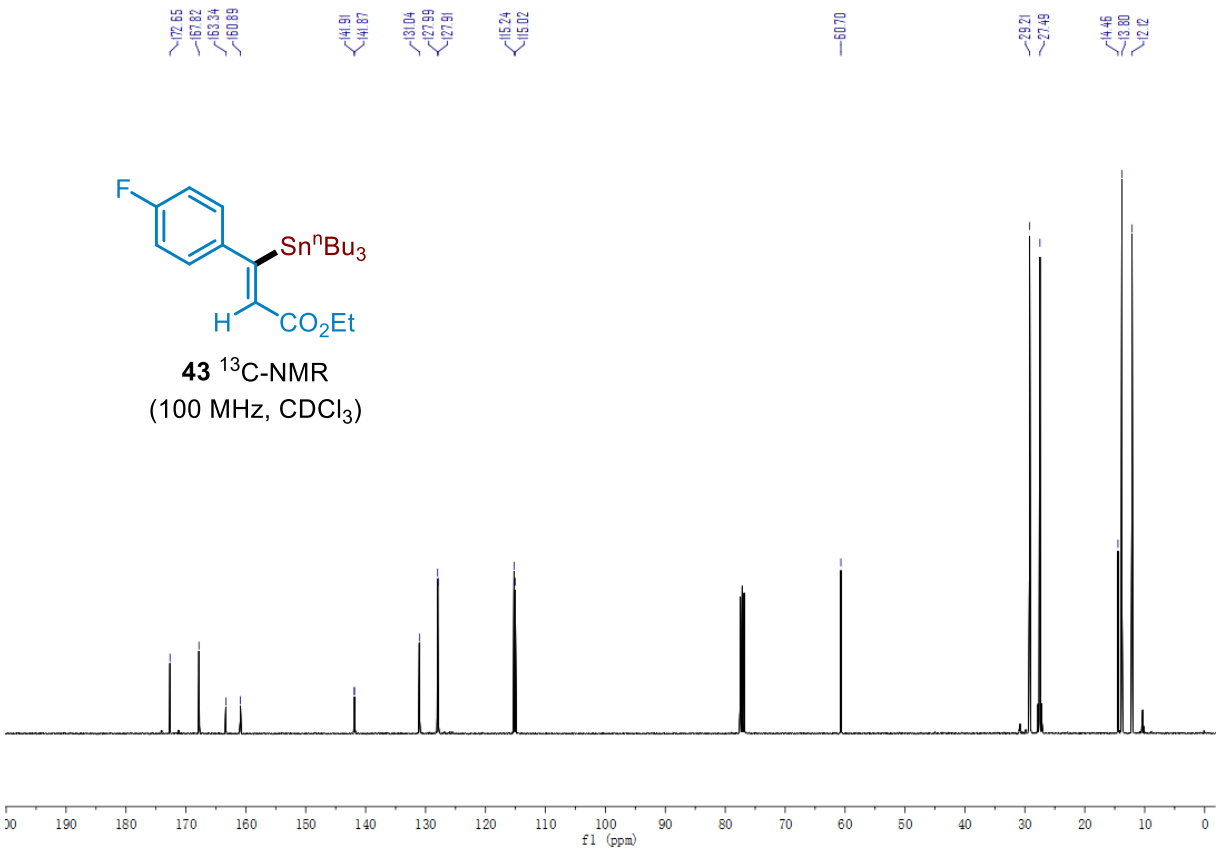
42 ^{1}H-NMR
(400 MHz,$CDCl_3$)



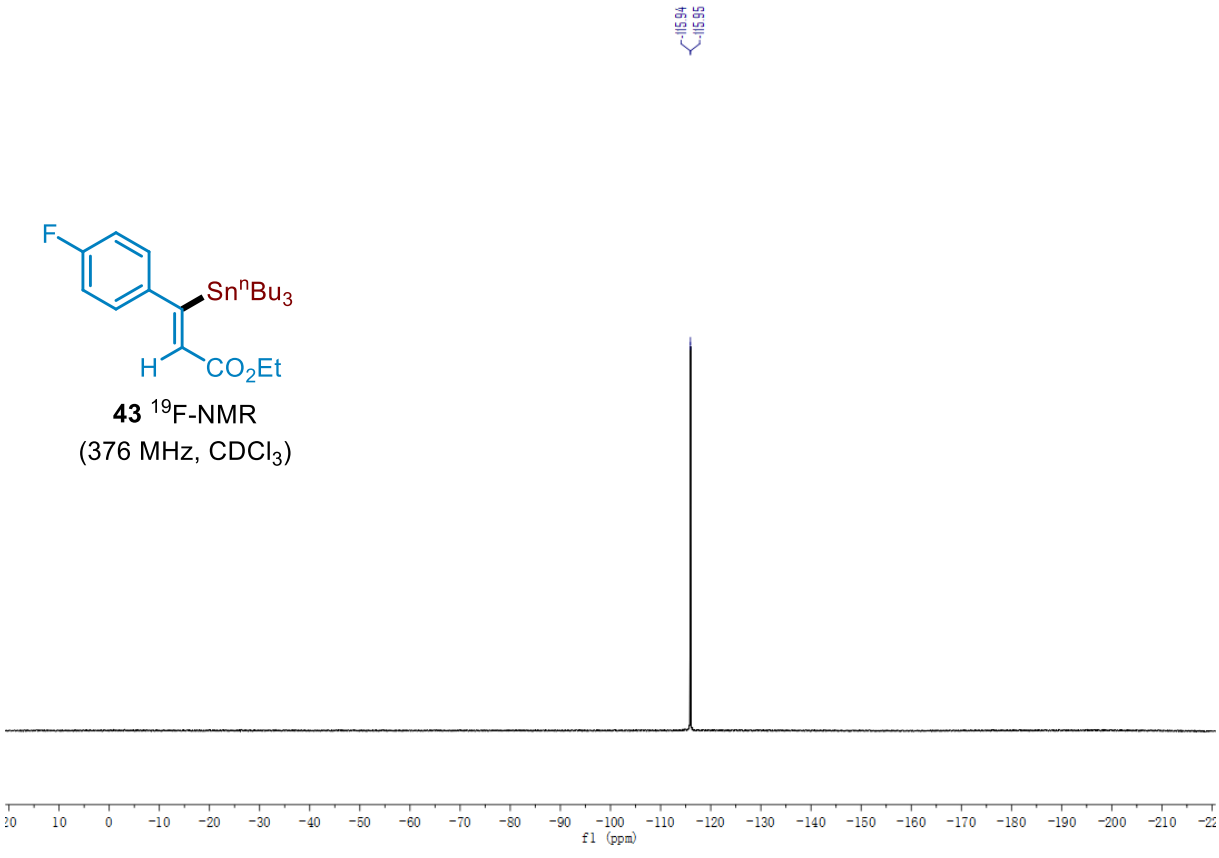
42 ^{13}C-NMR
(100 MHz, $CDCl_3$)



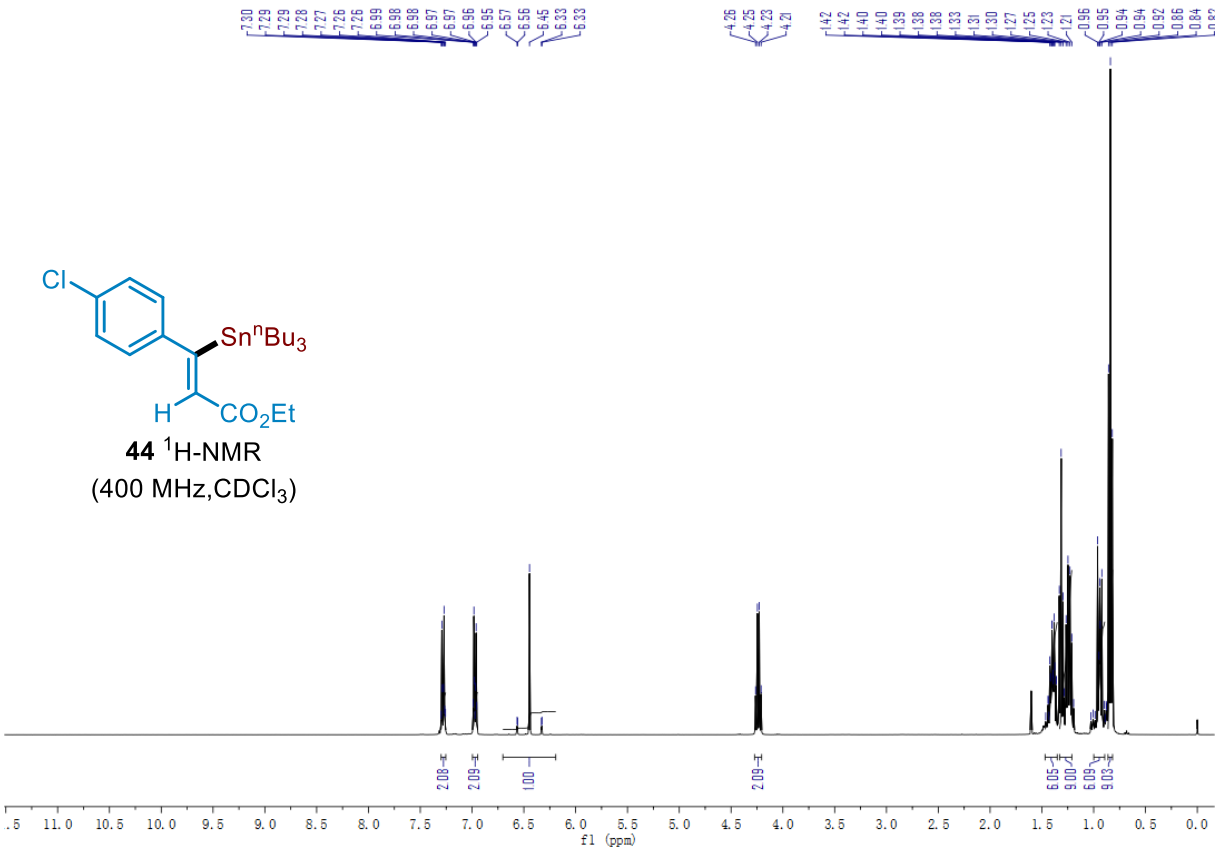
43 ^{1}H-NMR
(400 MHz,$CDCl_3$)



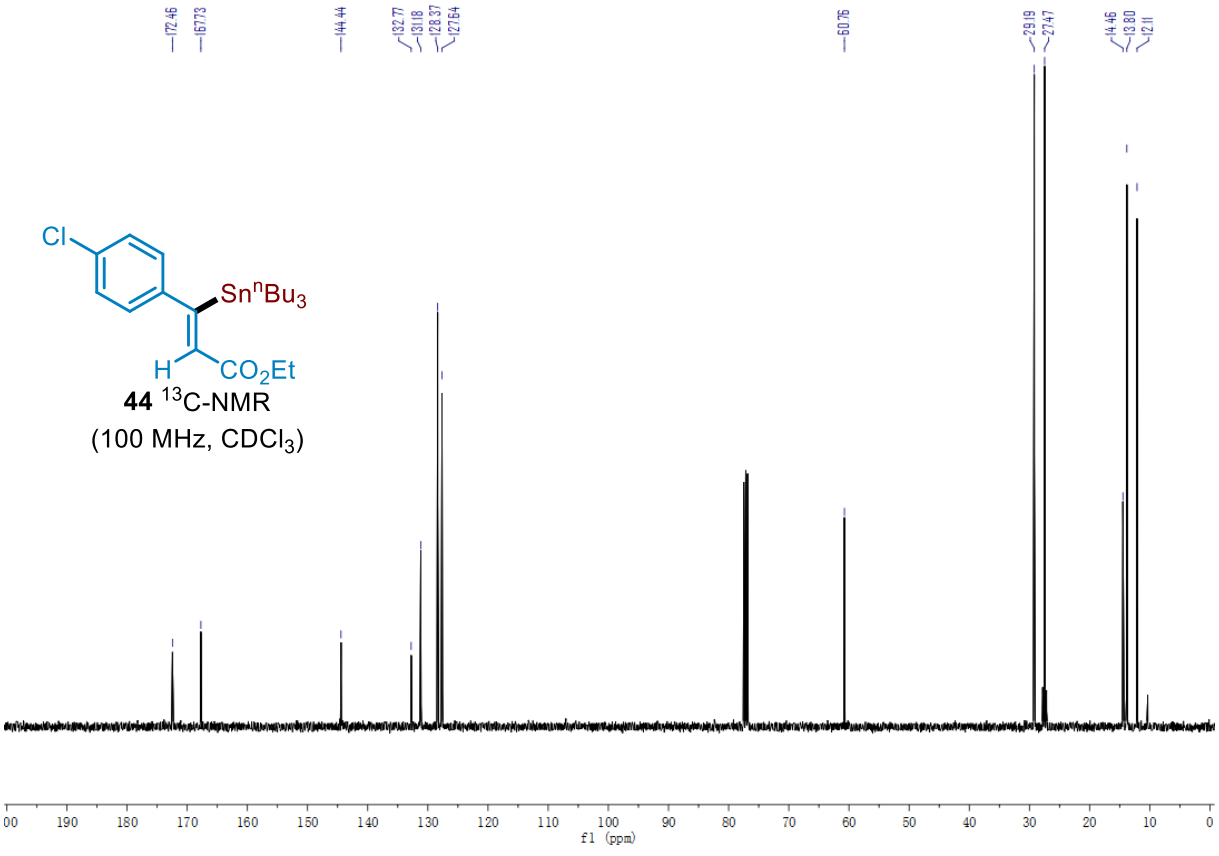
43 ^{13}C-NMR
(100 MHz, $CDCl_3$)



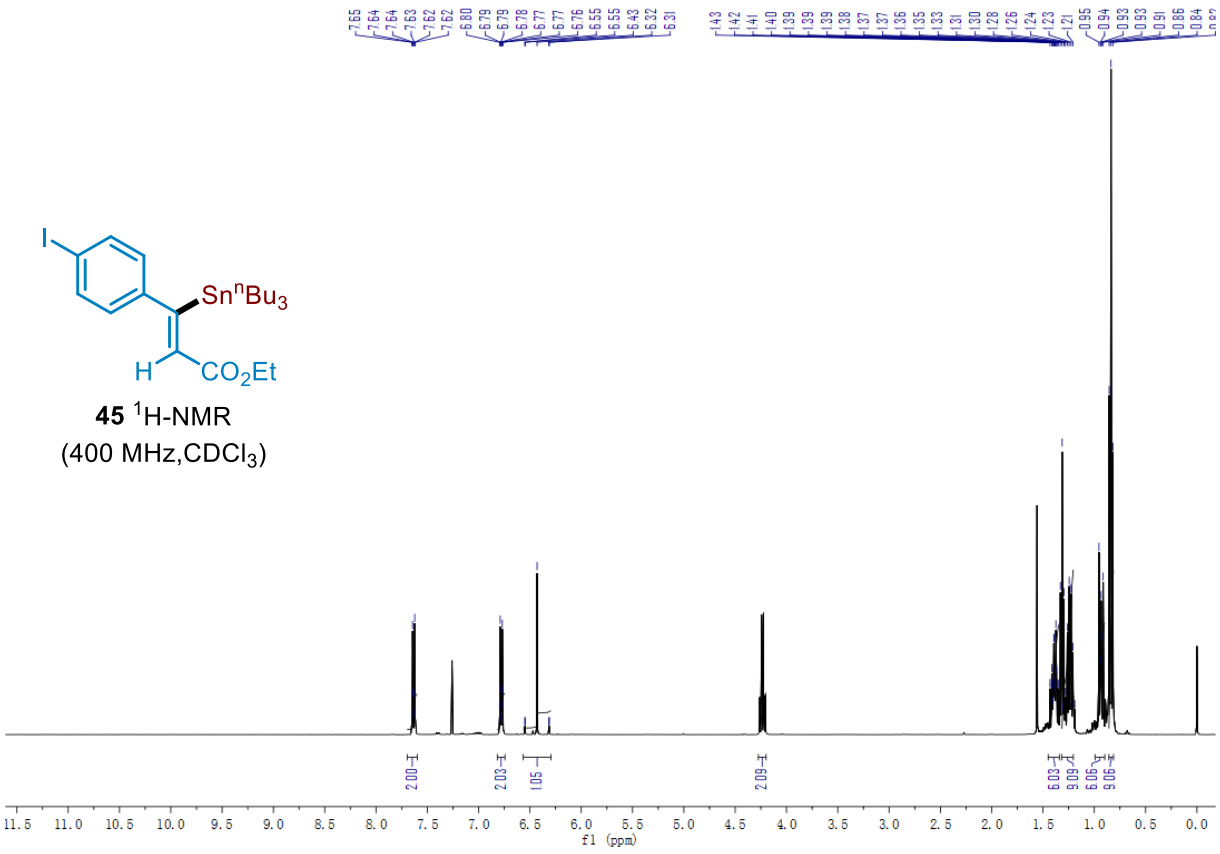
43 ^{19}F-NMR
(376 MHz, $CDCl_3$)



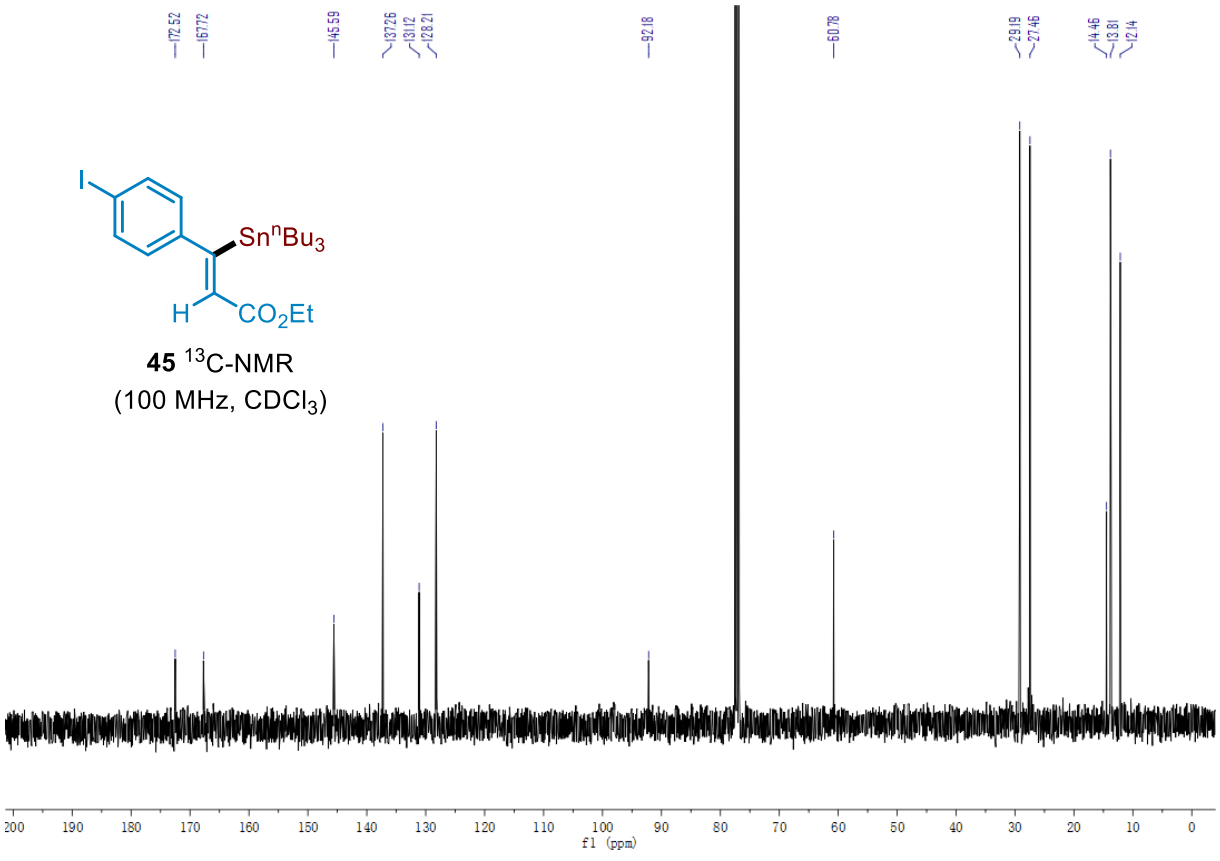
44 ^{1}H-NMR
(400 MHz,$CDCl_3$)



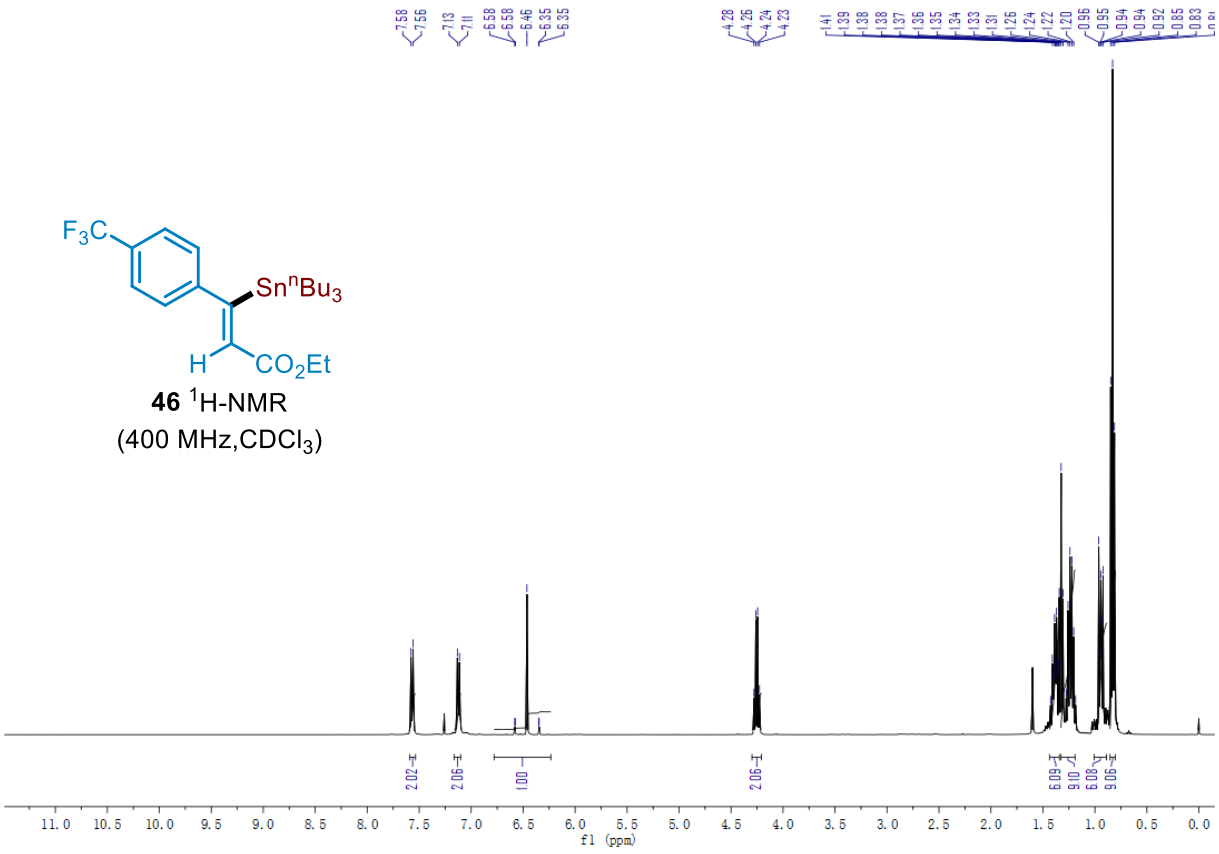
44 ^{13}C-NMR
(100 MHz, $CDCl_3$)



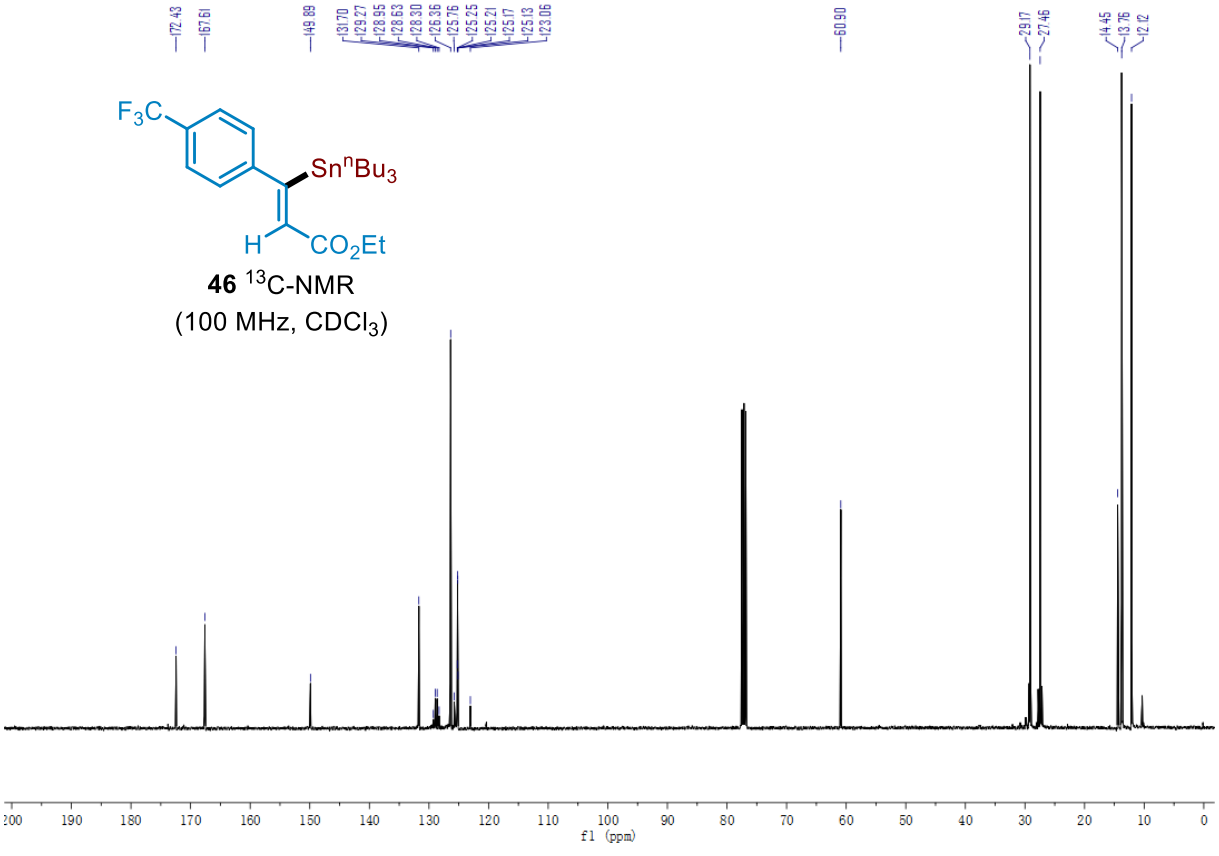
45 ^{1}H-NMR
(400 MHz,$CDCl_3$)



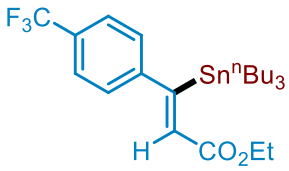
45 ^{13}C-NMR
(100 MHz, $CDCl_3$)



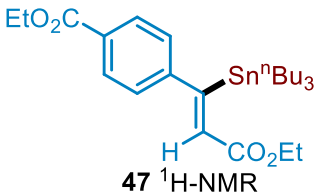
46 ^{1}H-NMR
(400 MHz,$CDCl_3$)



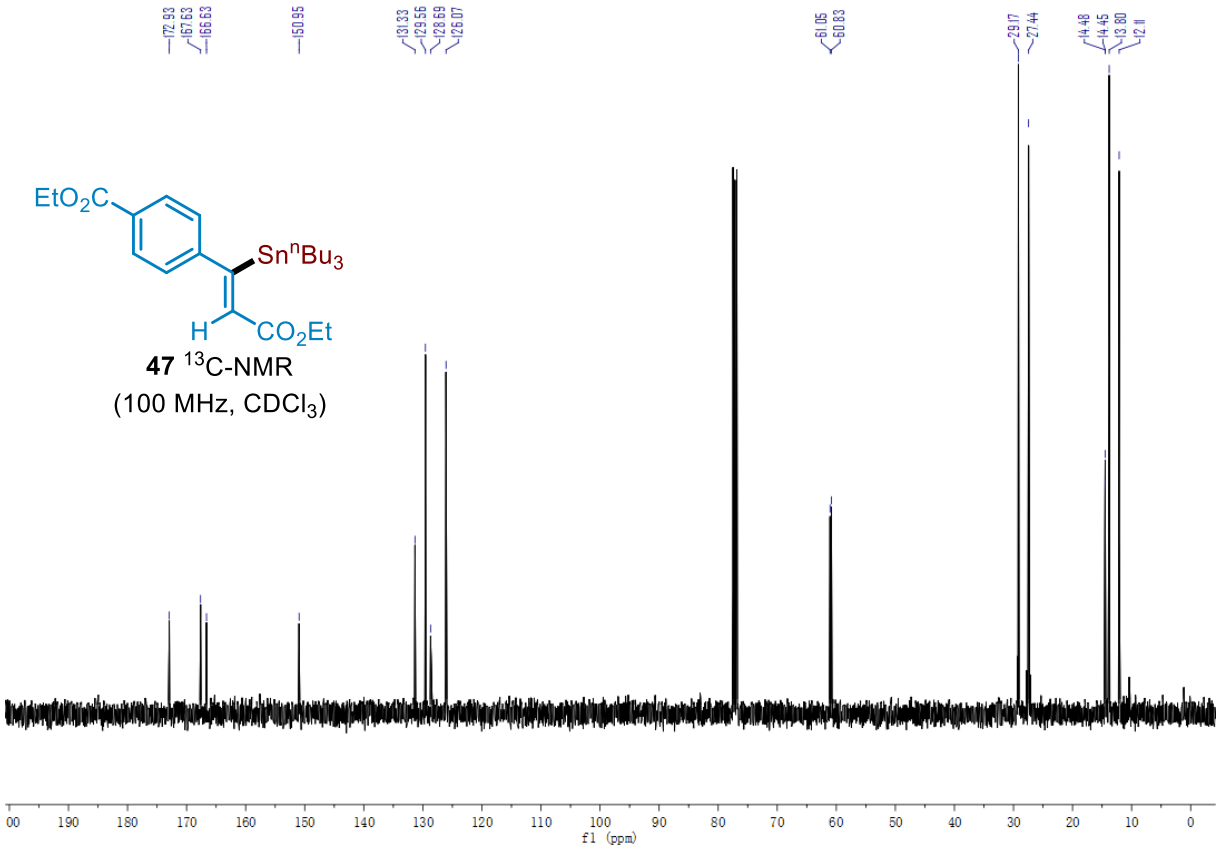
46 ^{13}C-NMR
(100 MHz, $CDCl_3$)



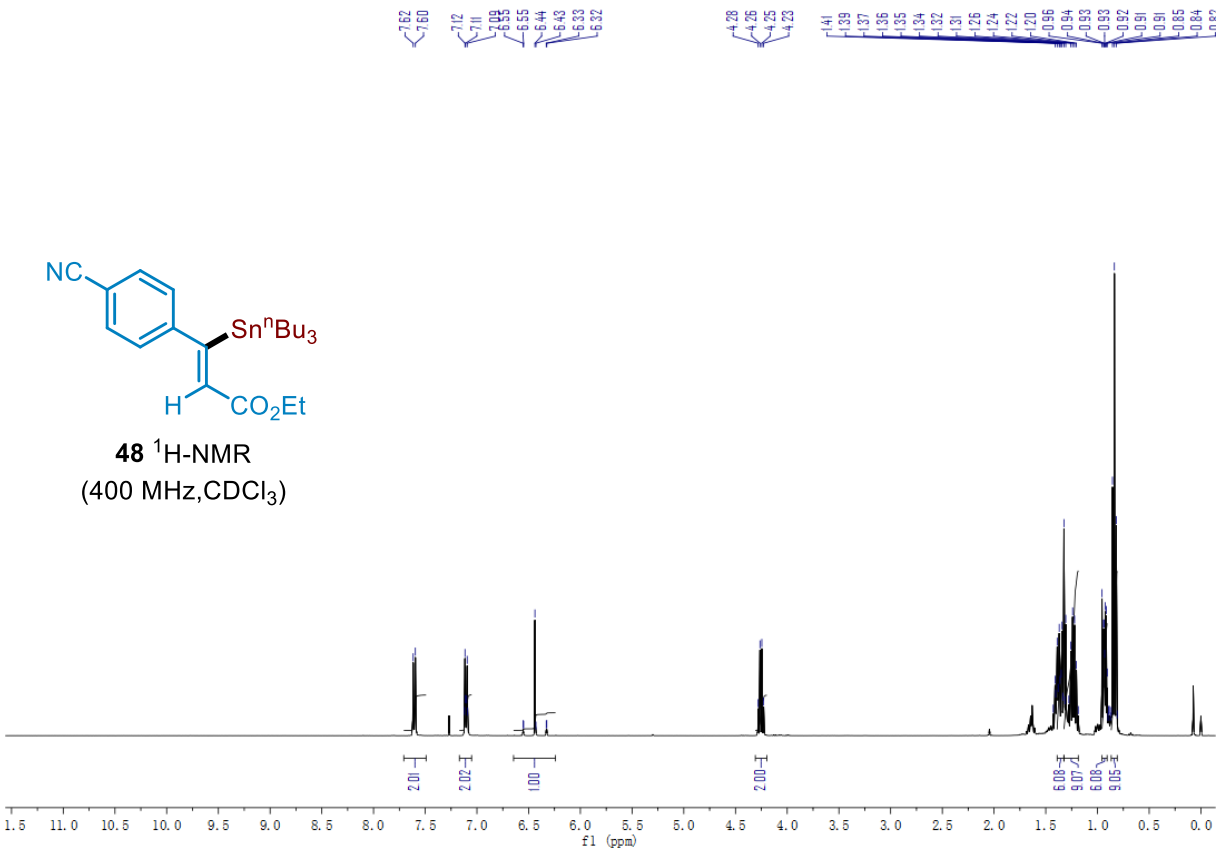
46 ^{19}F-NMR
(376 MHz, $CDCl_3$)



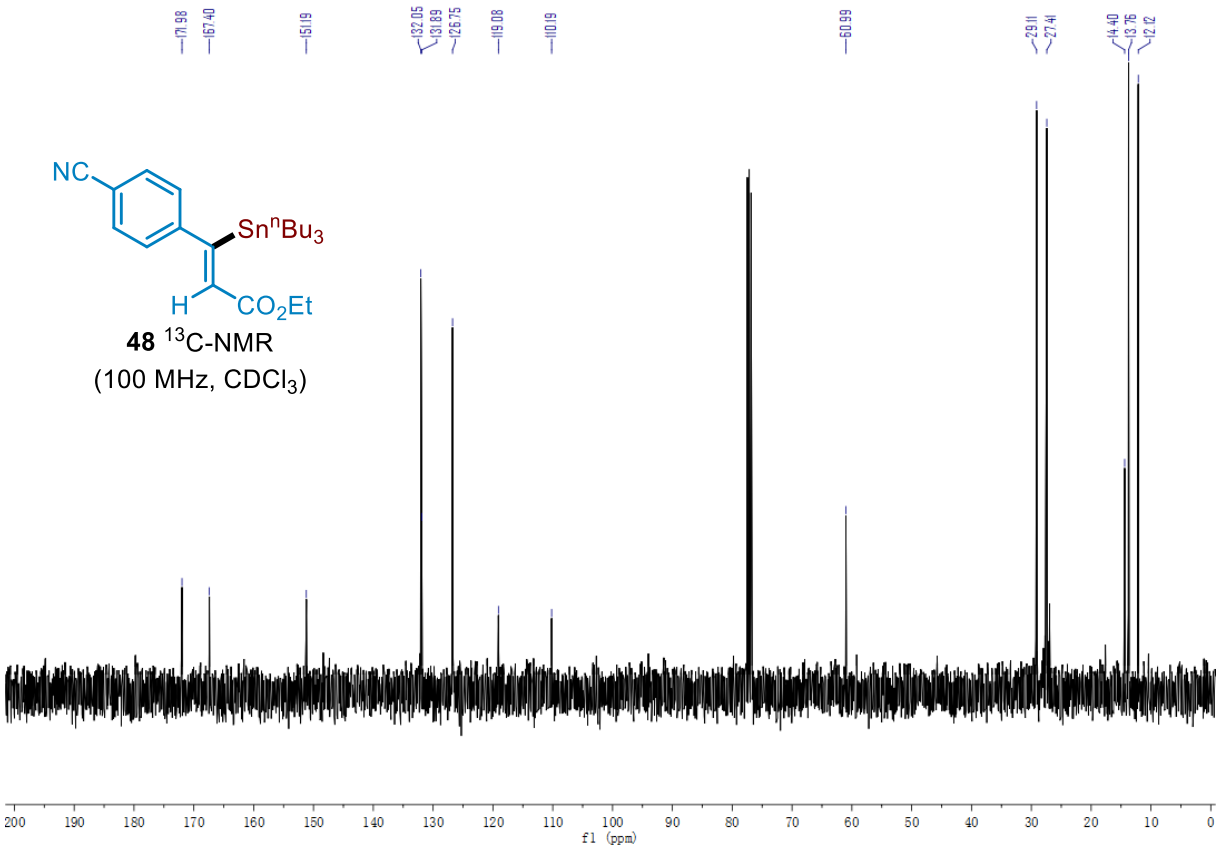
47 ^{1}H-NMR
(400 MHz,$CDCl_3$)



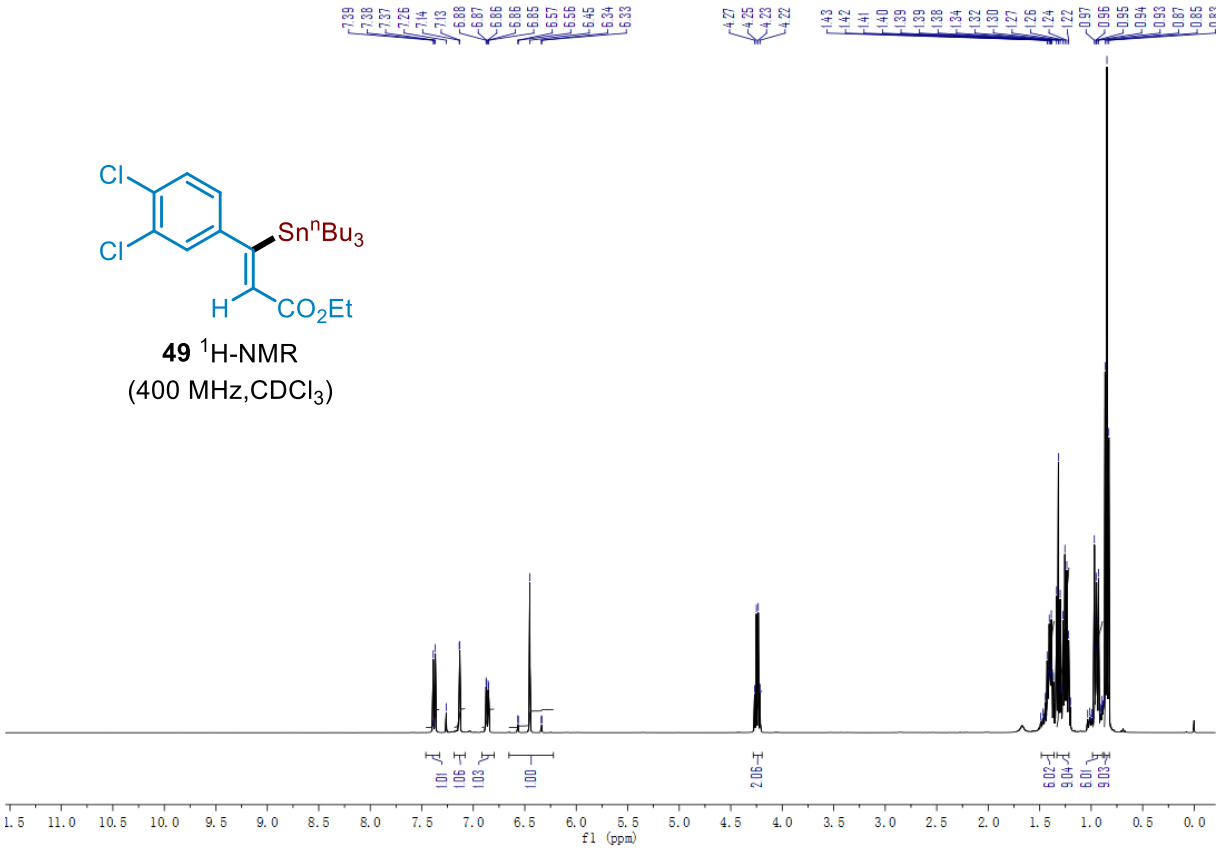
47 ^{13}C-NMR
(100 MHz, $CDCl_3$)



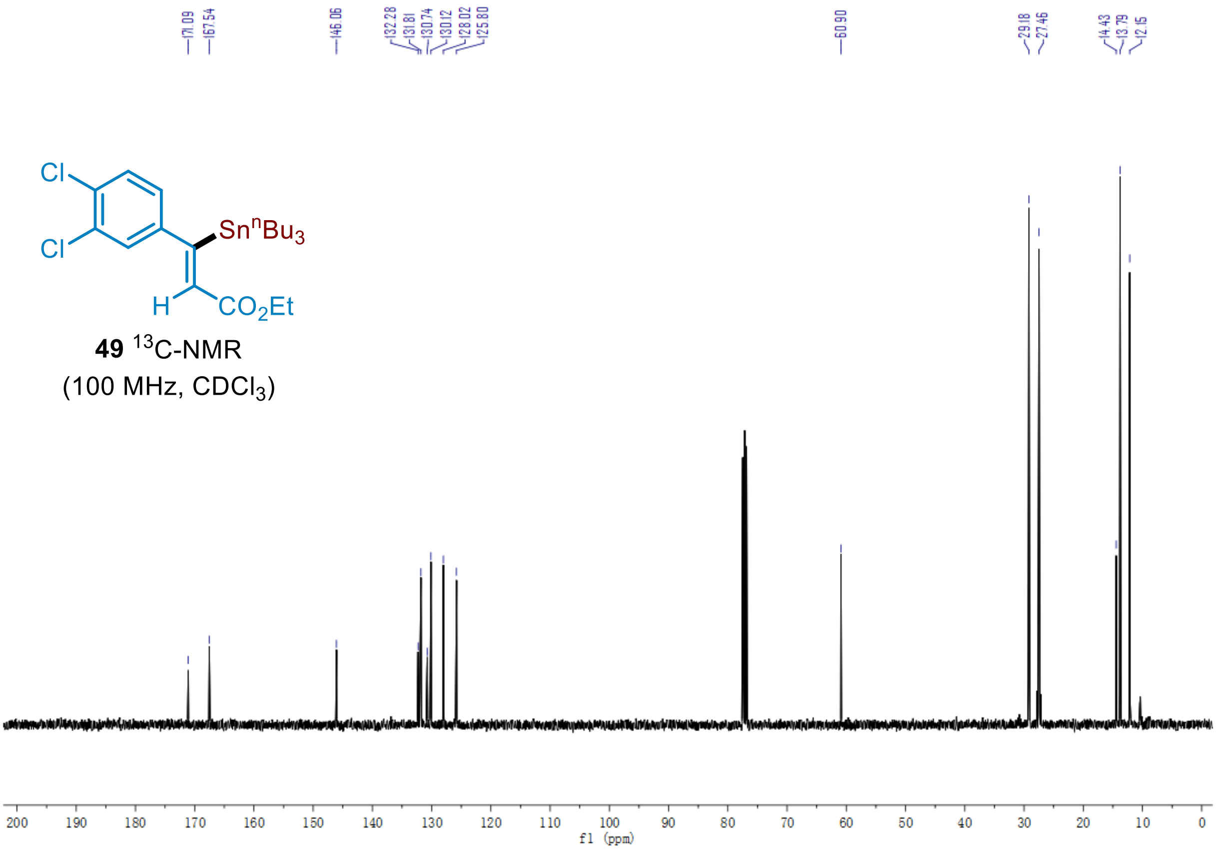
48 ^{1}H-NMR
(400 MHz,$CDCl_3$)



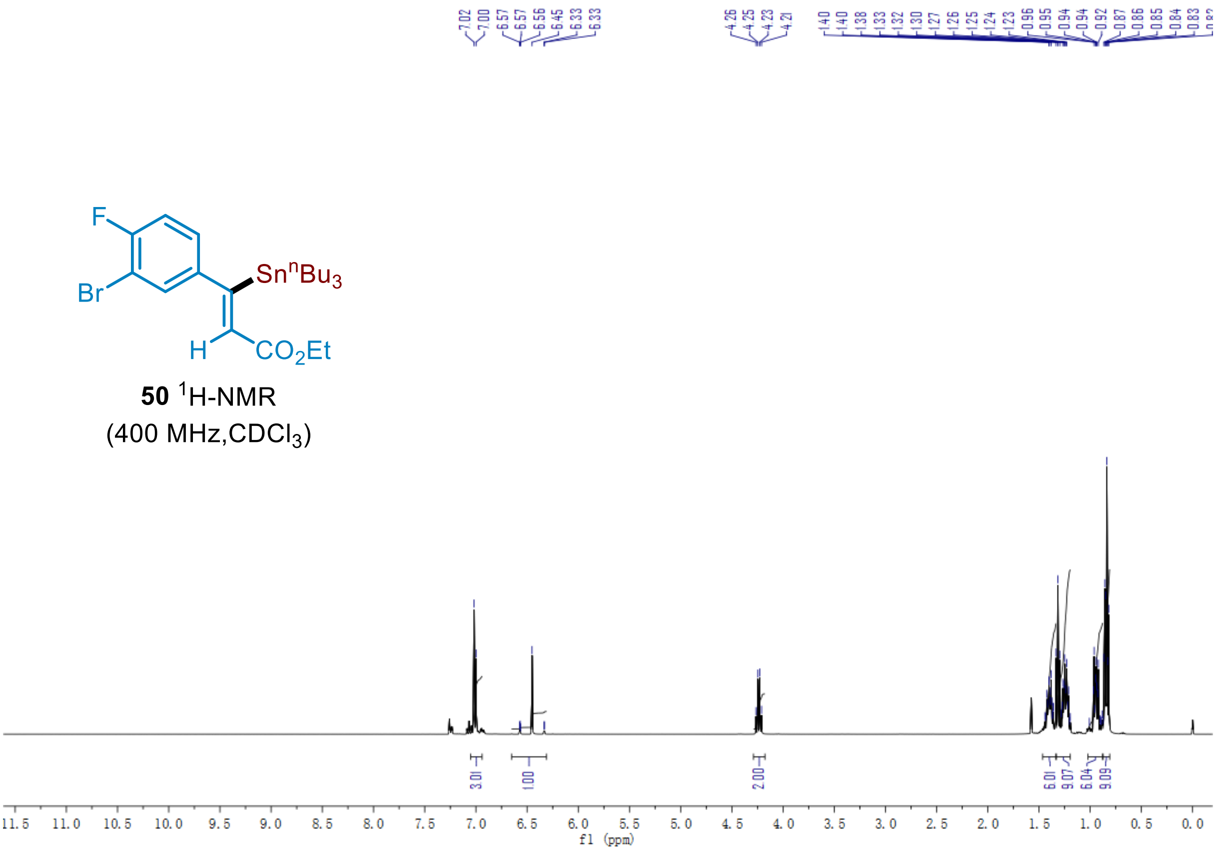
48 ^{13}C-NMR
(100 MHz, $CDCl_3$)



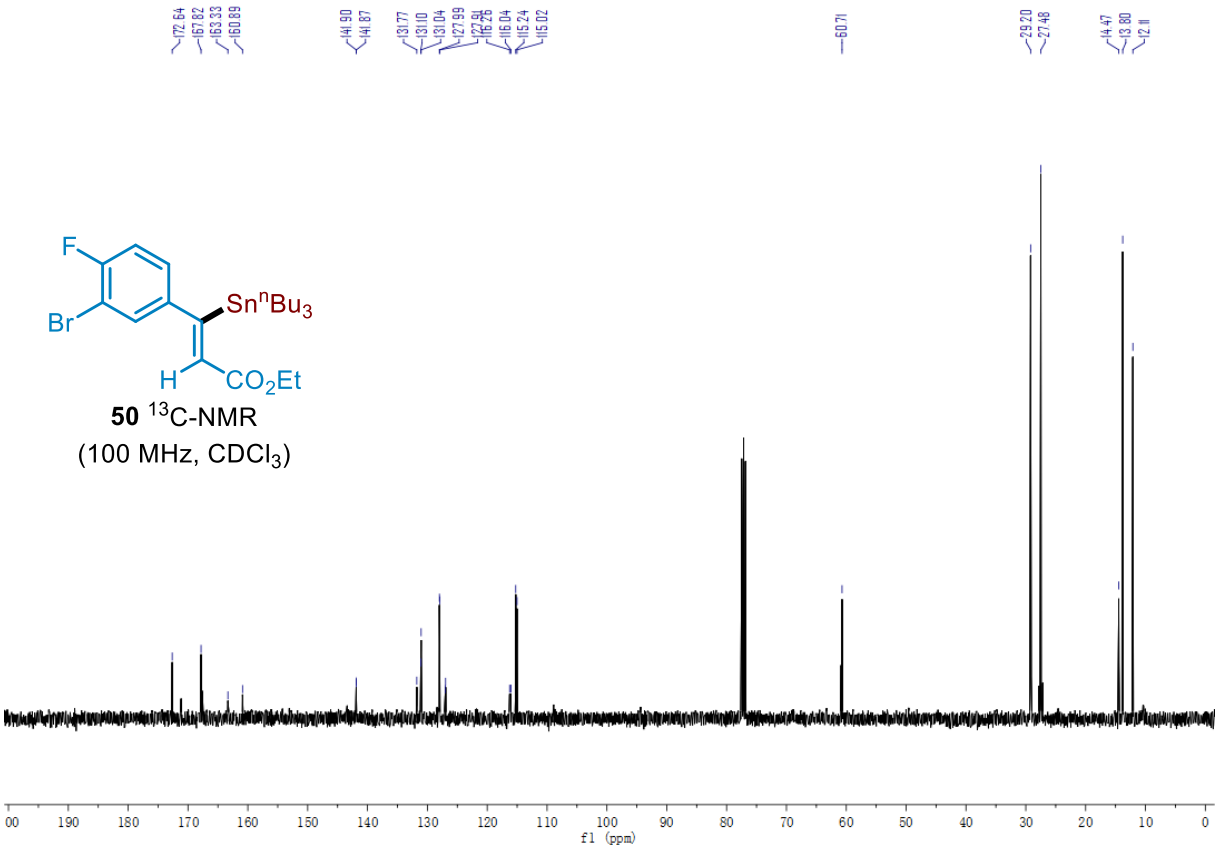
49 ^{1}H-NMR
(400 MHz,$CDCl_3$)



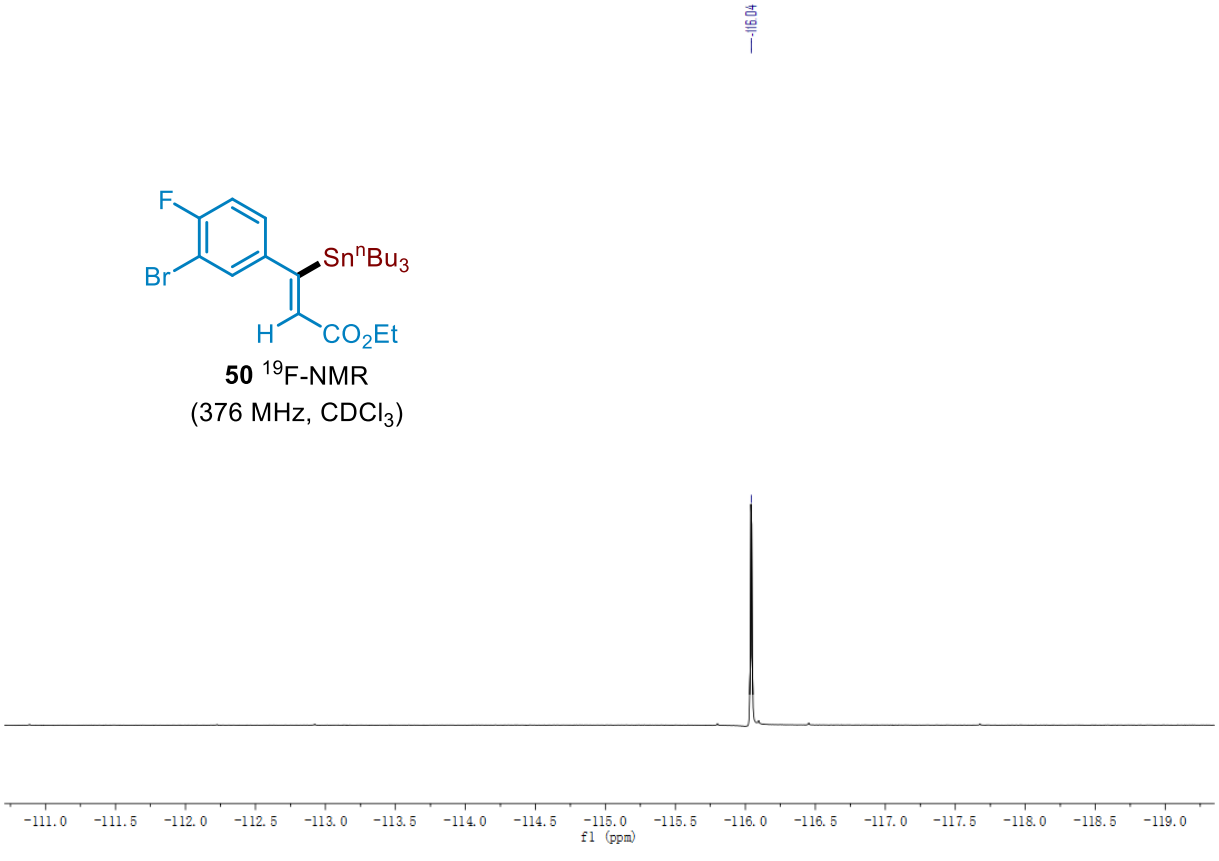
49 ^{13}C-NMR
(100 MHz, CDCl$_3$)



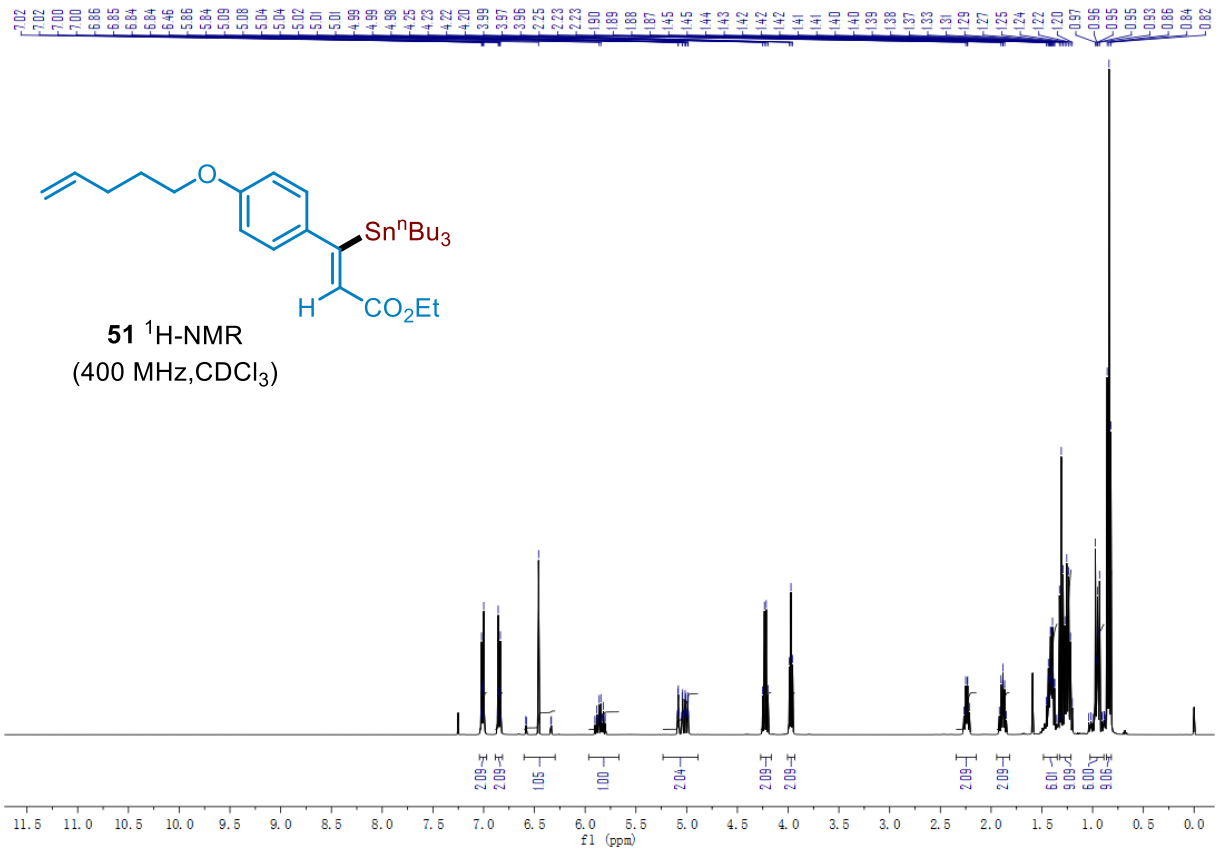
50 ^{1}H-NMR
(400 MHz,CDCl$_3$)



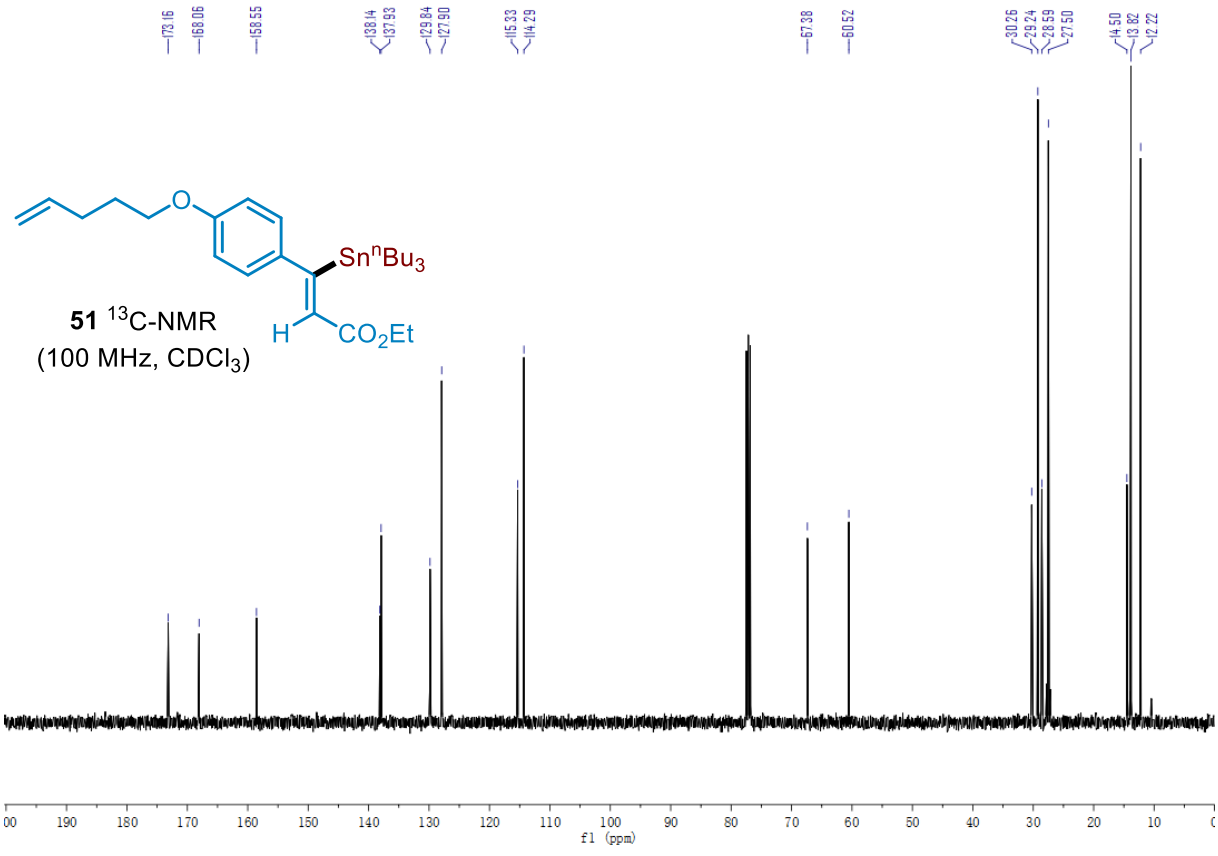
50 ^{13}C-NMR
(100 MHz, $CDCl_3$)



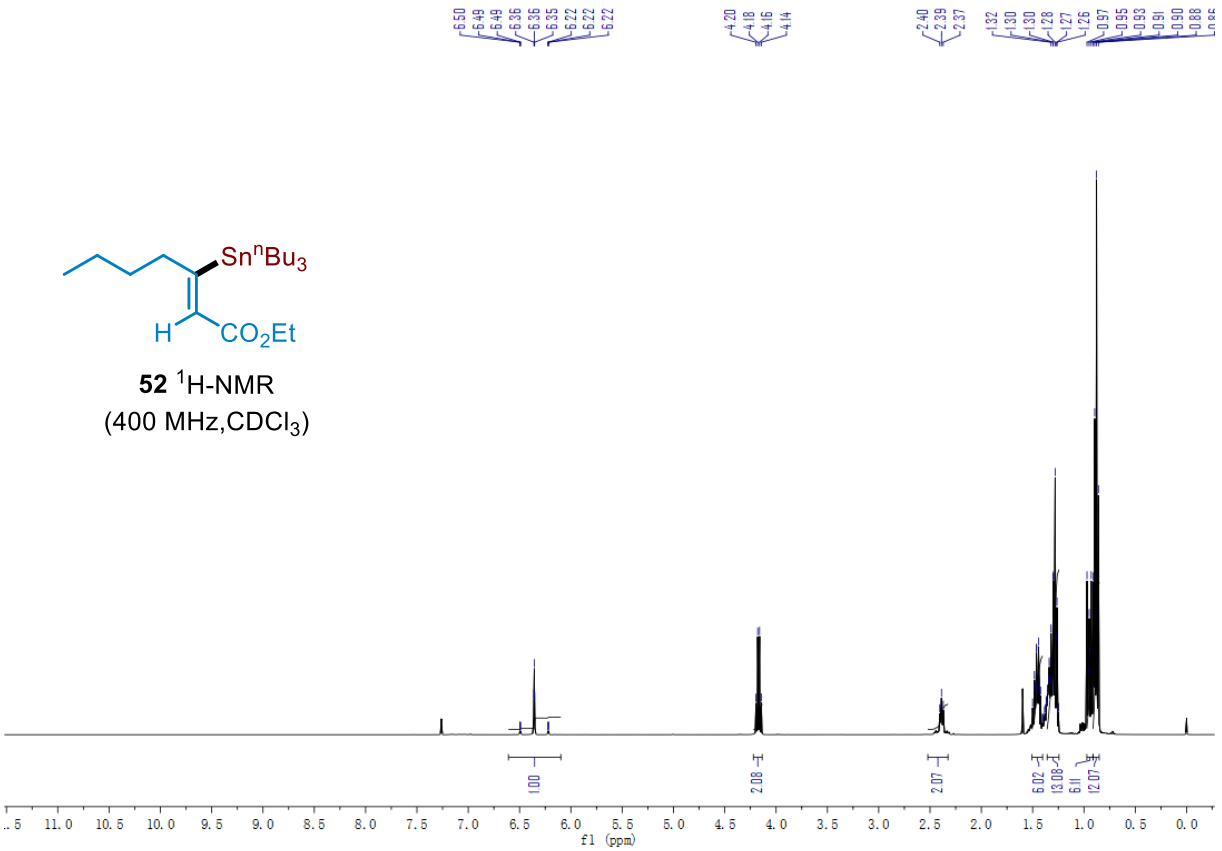
50 ^{19}F-NMR
(376 MHz, $CDCl_3$)



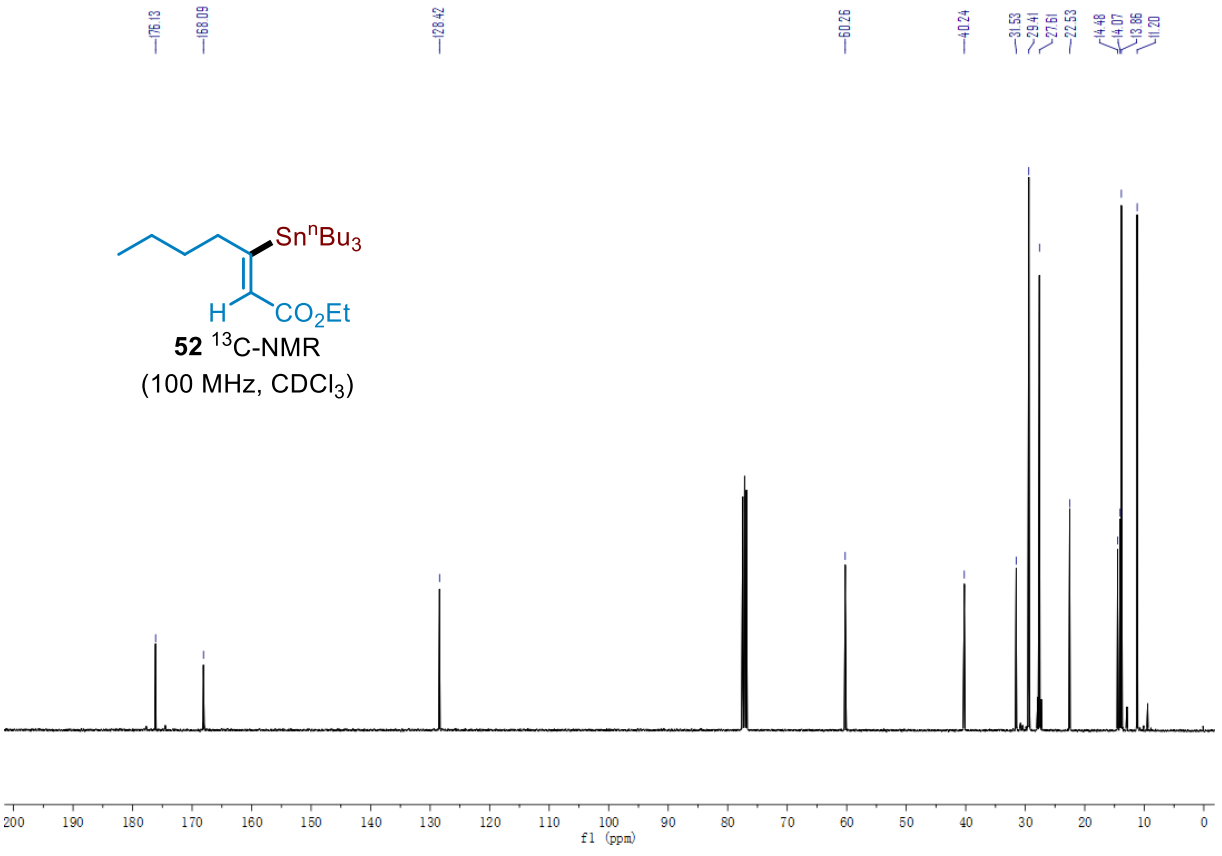
51 ^{1}H-NMR
(400 MHz,$CDCl_3$)



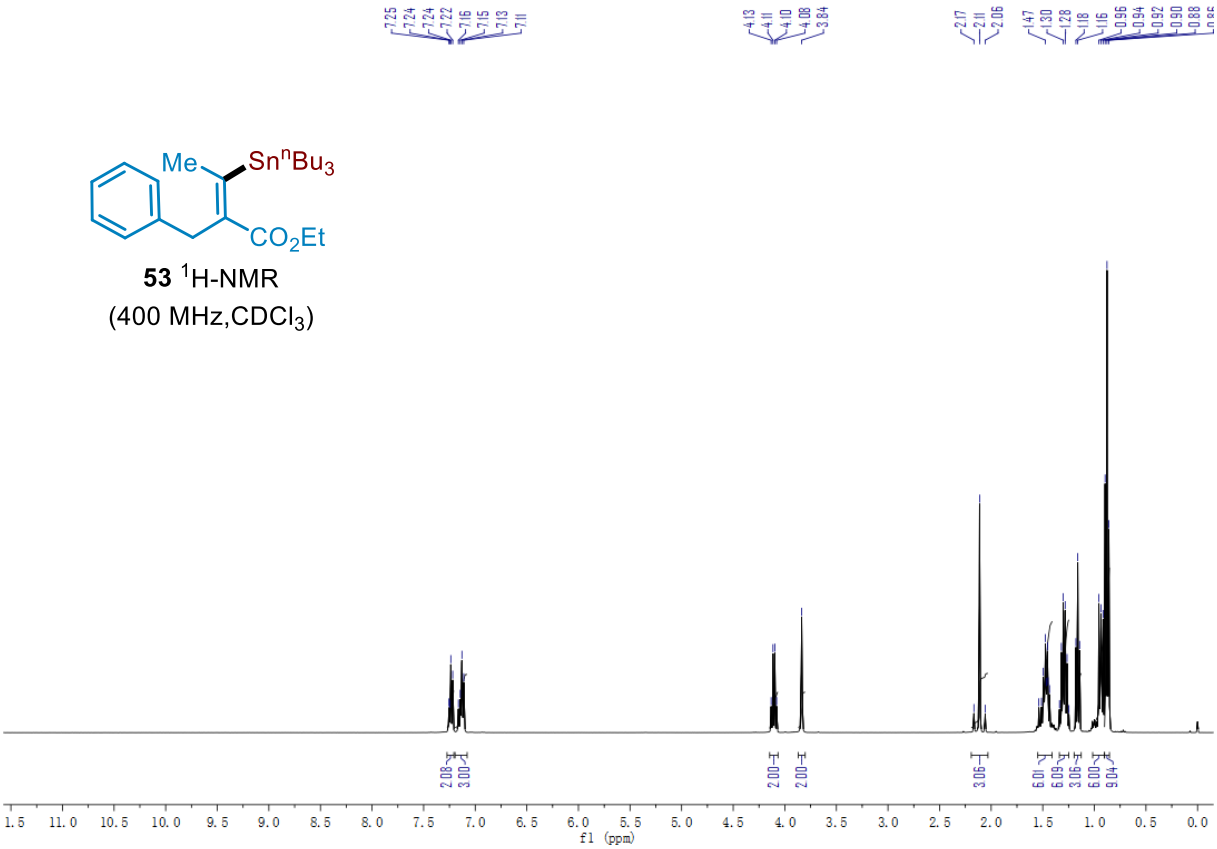
51 ^{13}C-NMR
(100 MHz, $CDCl_3$)



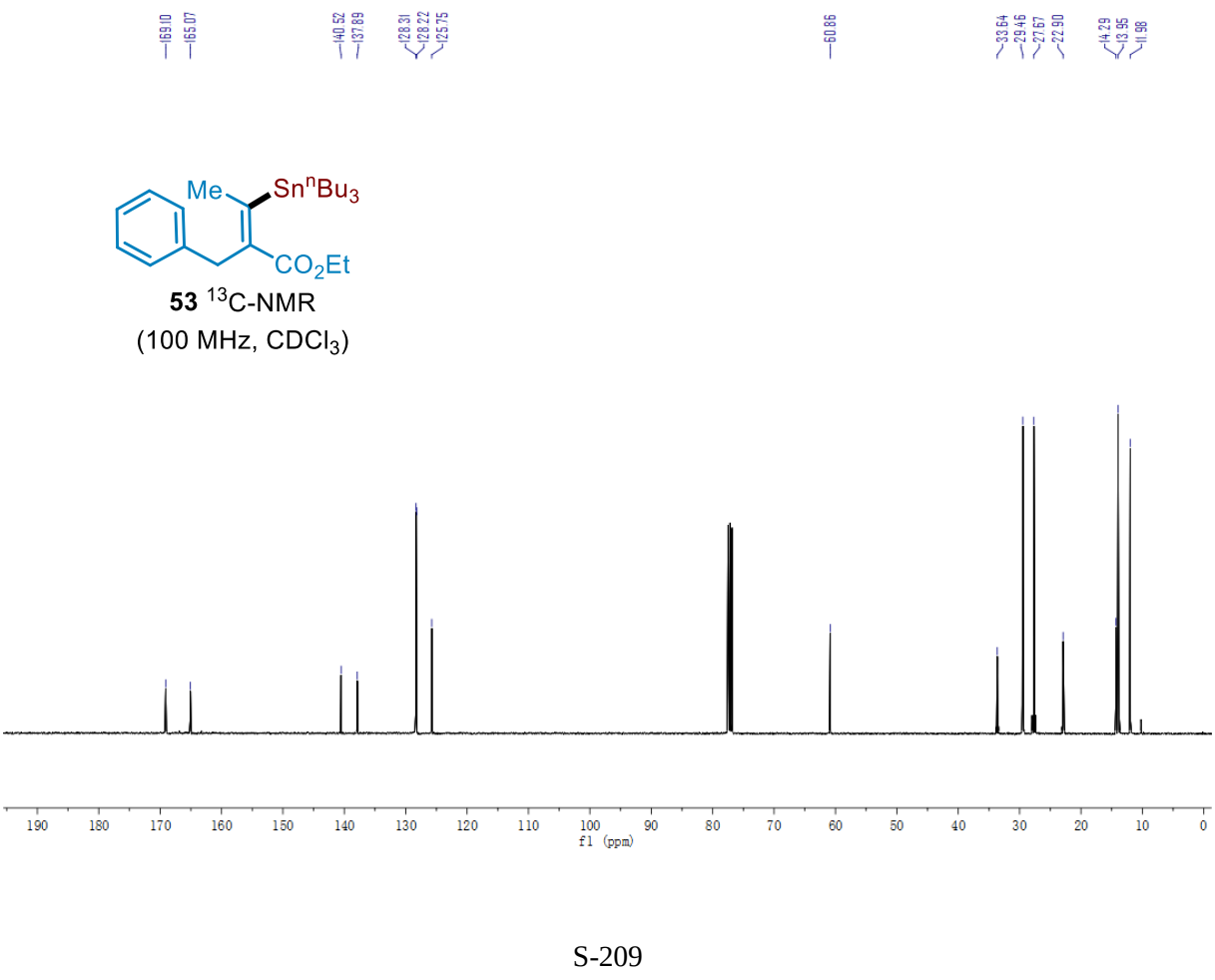
52 ^{1}H-NMR
(400 MHz,$CDCl_3$)



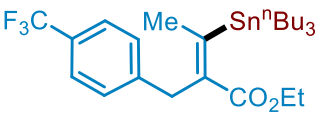
52 ^{13}C-NMR
(100 MHz, $CDCl_3$)



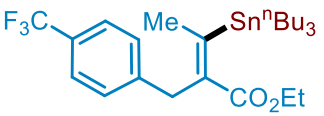
53 ^{1}H-NMR
(400 MHz,$CDCl_3$)



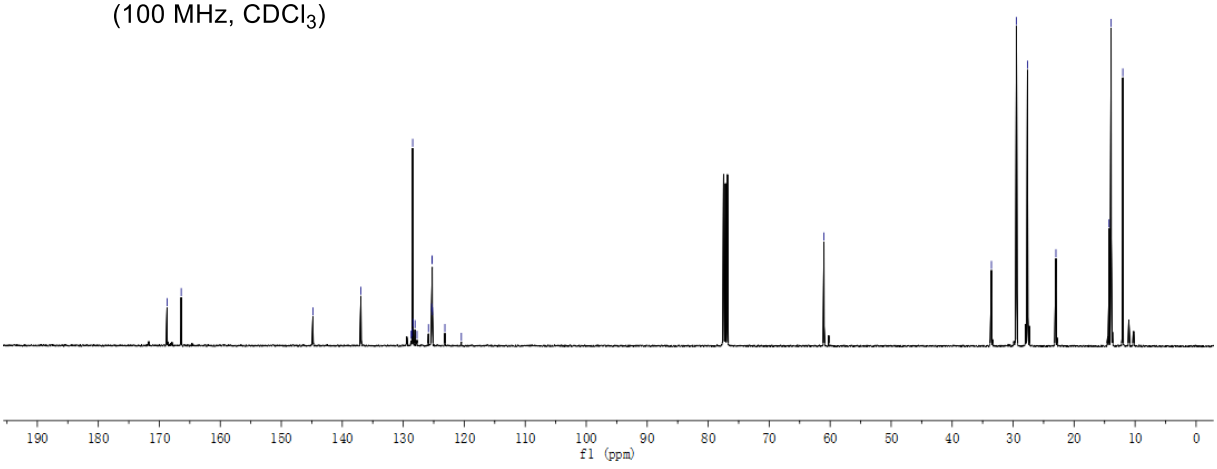
53 ^{13}C-NMR
(100 MHz, $CDCl_3$)

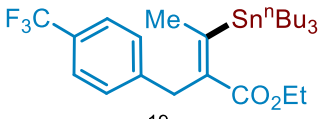


54 ^{1}H-NMR
(400 MHz,$CDCl_3$)



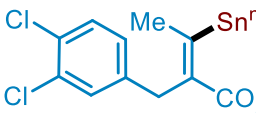
54 ^{13}C-NMR
(100 MHz, $CDCl_3$)





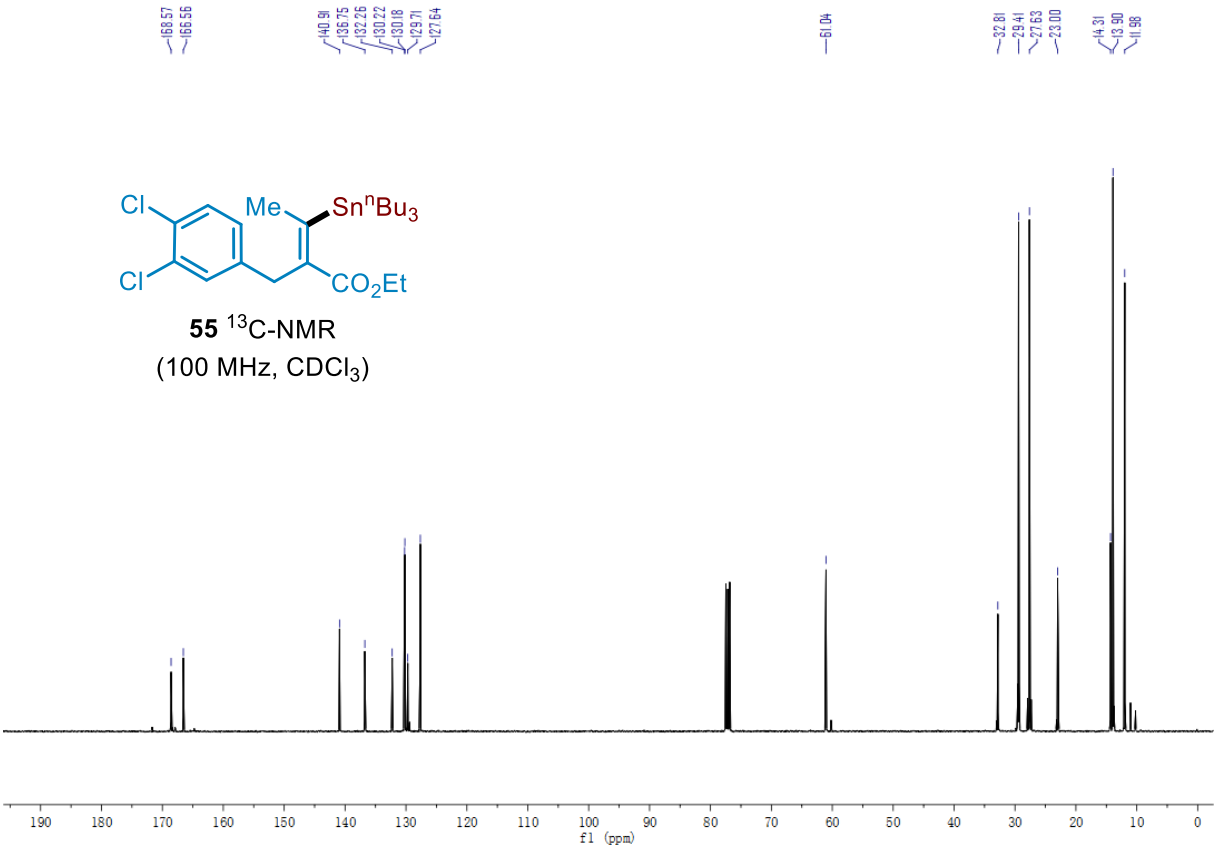
54 ^{19}F-NMR

(376 MHz, $CDCl_3$)

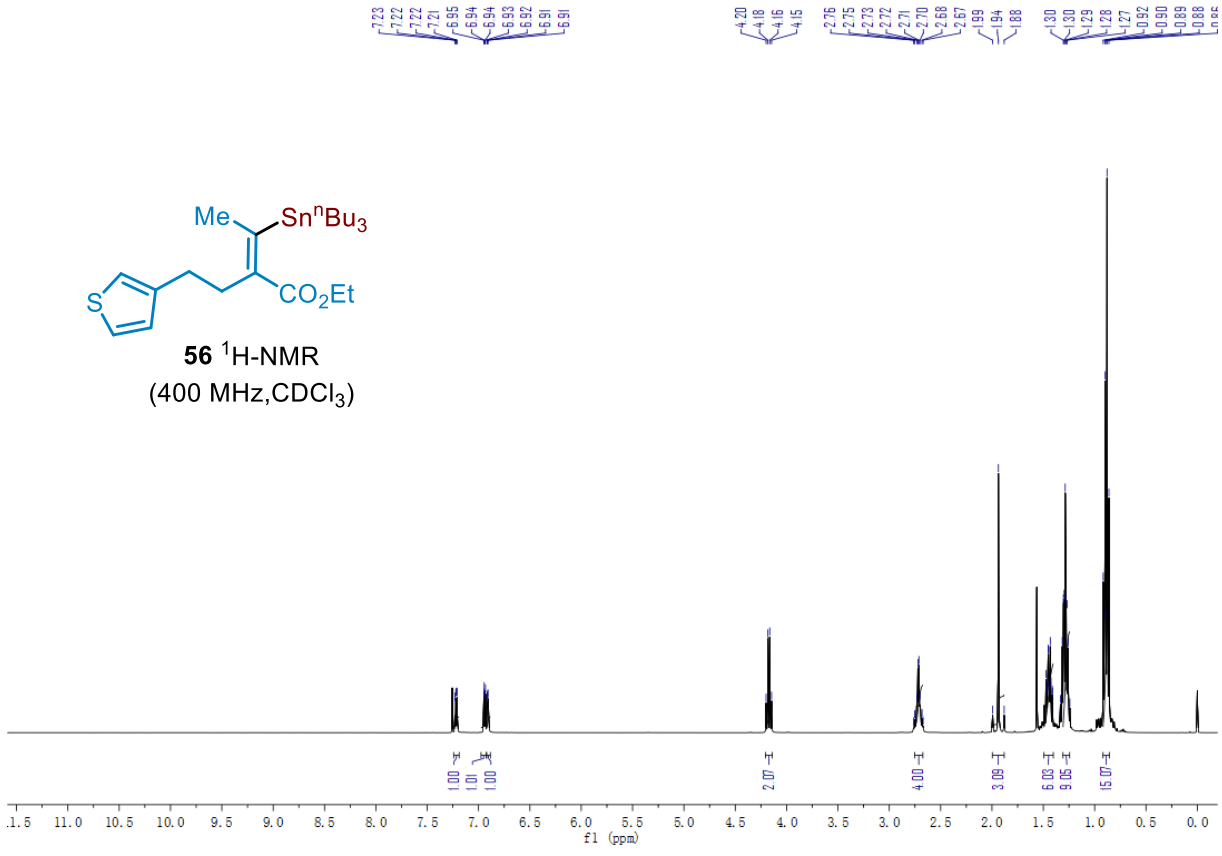


55 ^{1}H-NMR

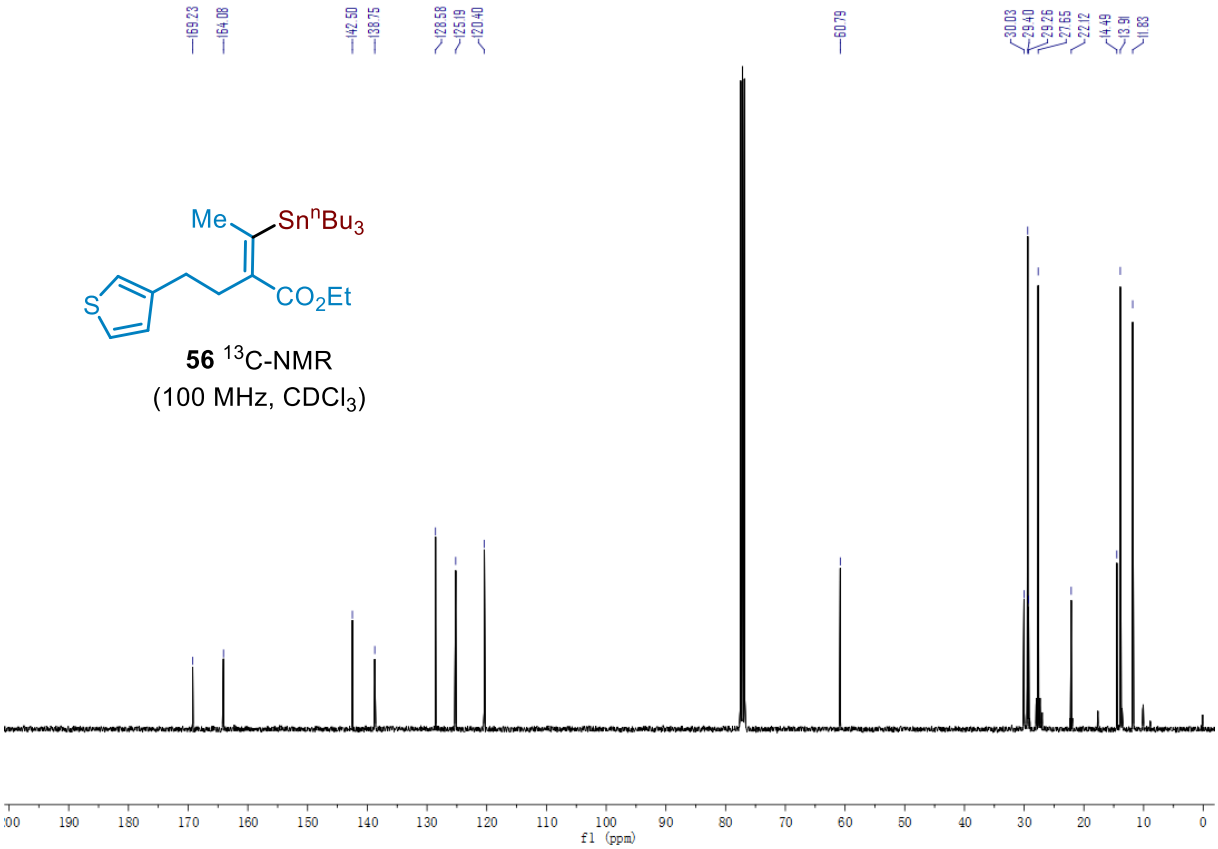
(400 MHz,$CDCl_3$)



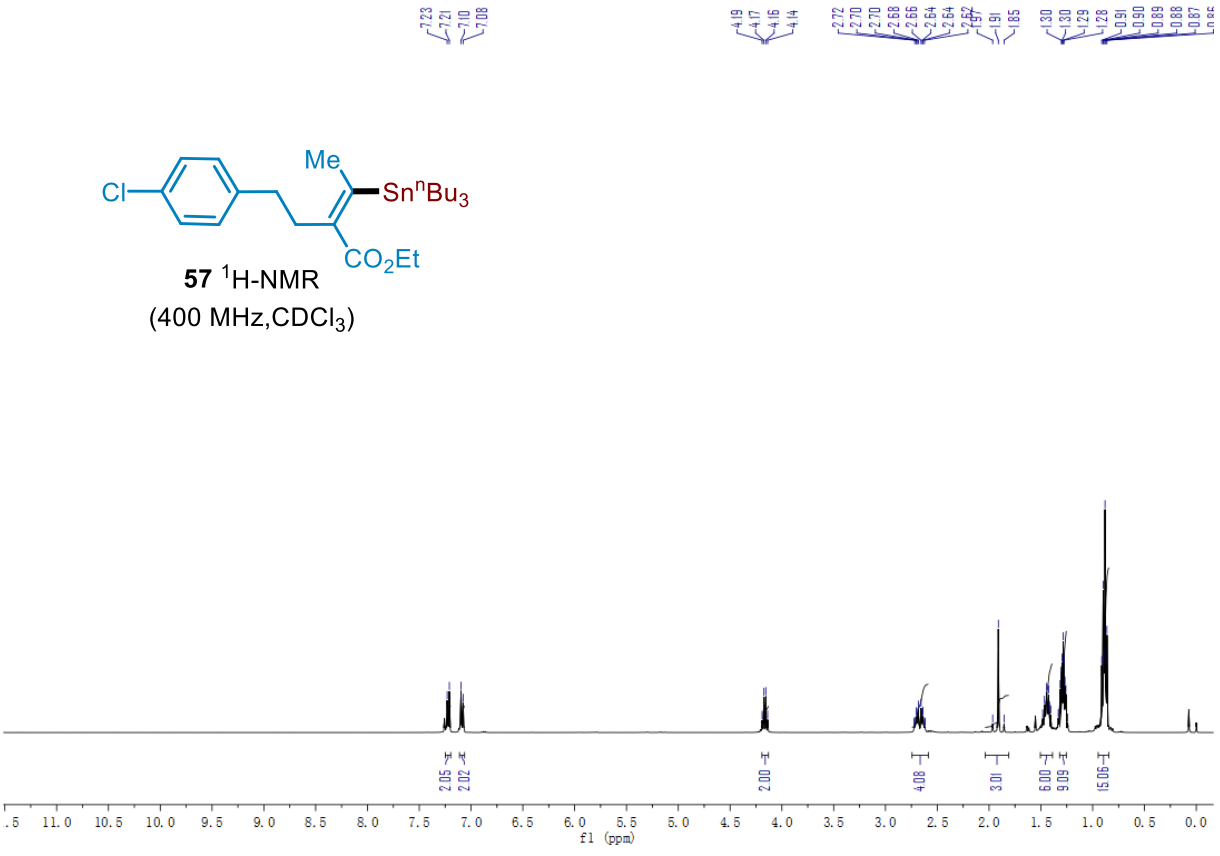
55 ^{13}C-NMR
(100 MHz, $CDCl_3$)



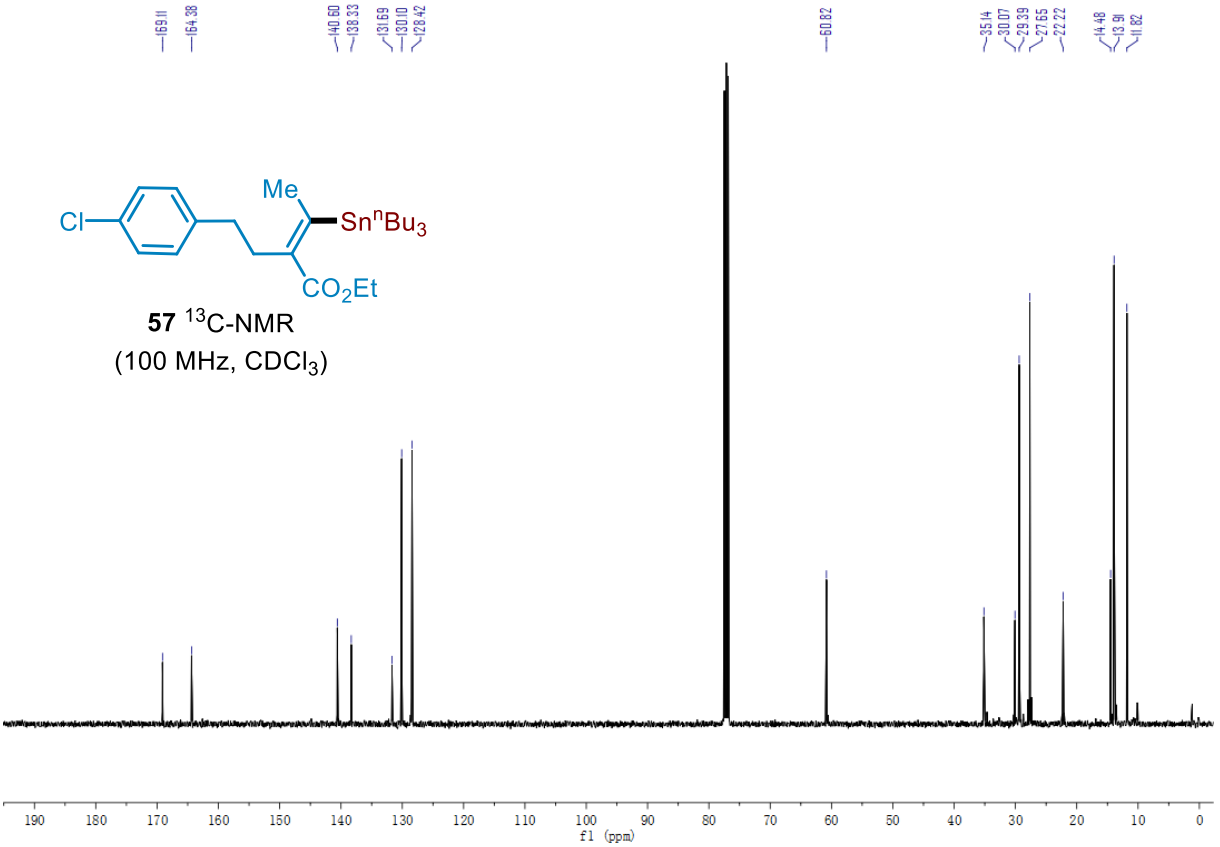
56 ^{1}H-NMR
(400 MHz,$CDCl_3$)



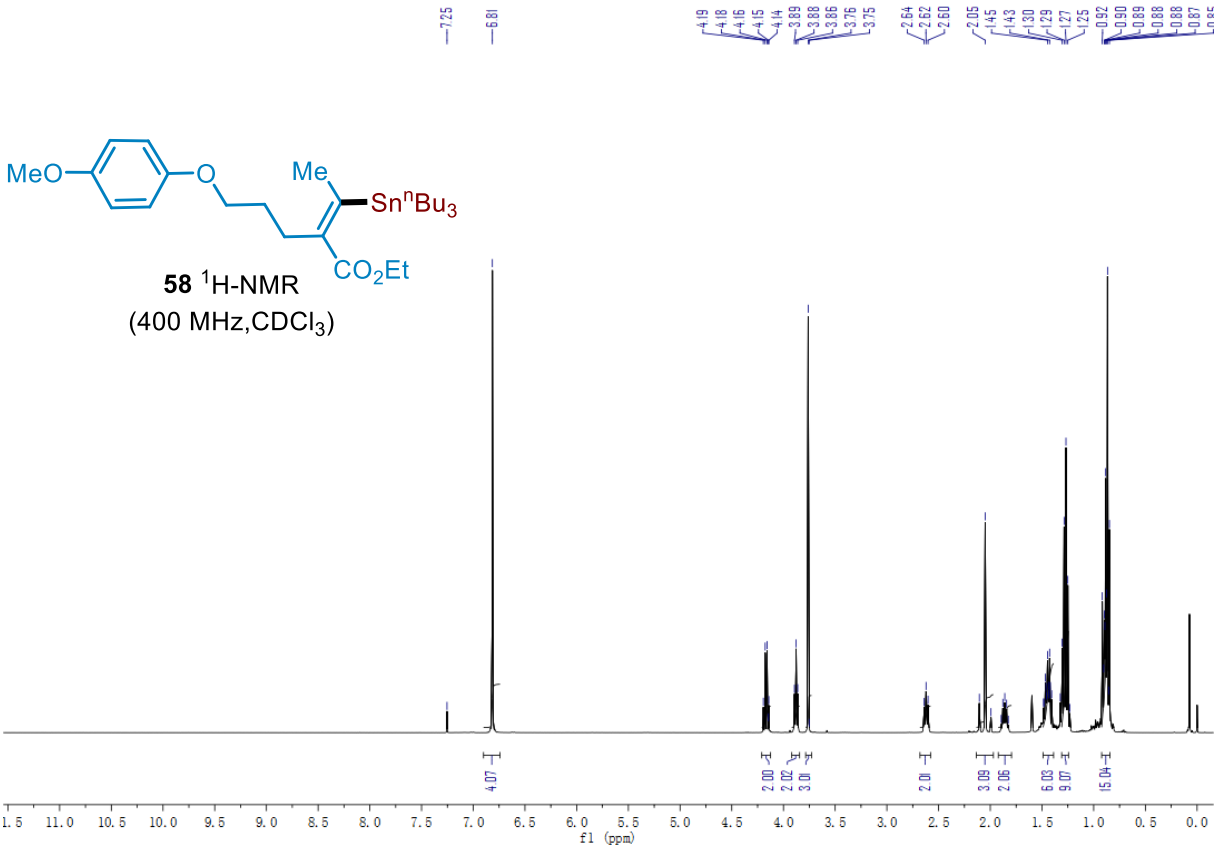
56 ^{13}C-NMR
(100 MHz, $CDCl_3$)



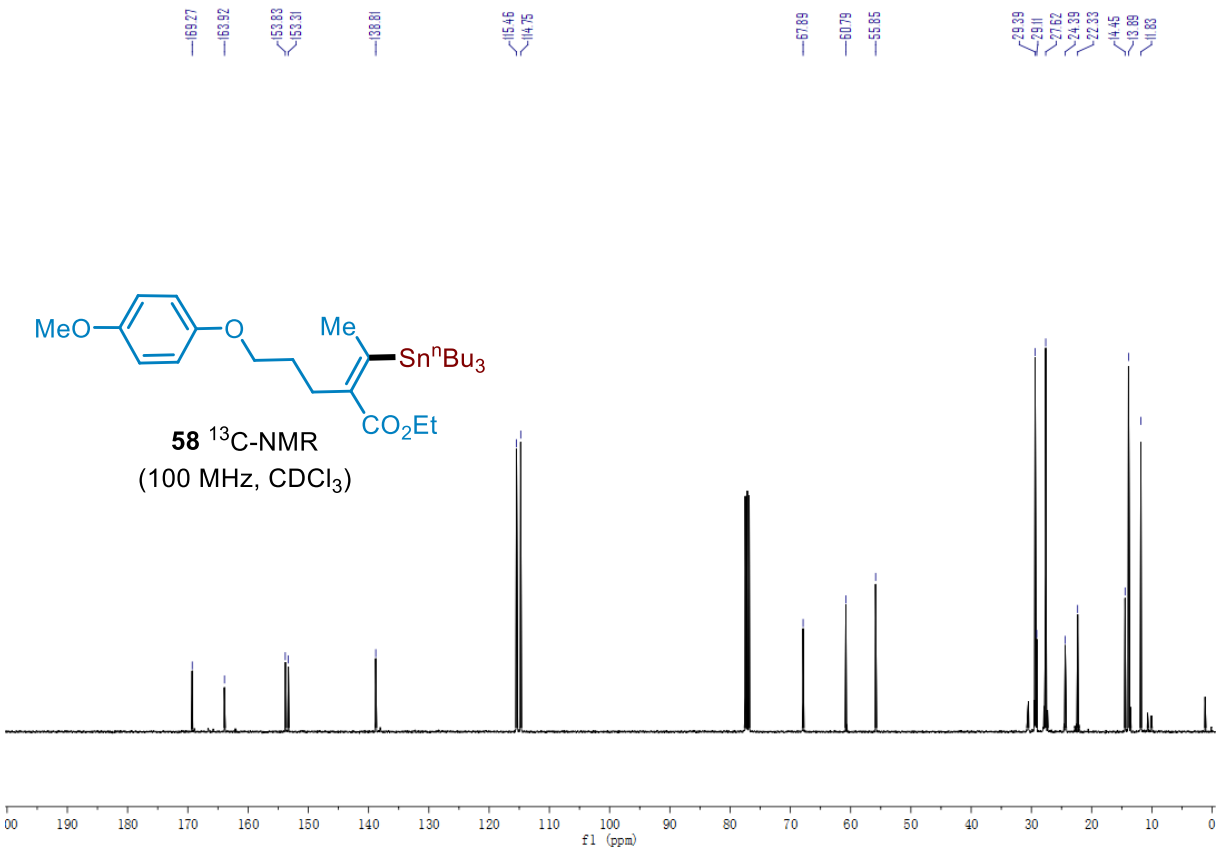
57 ^{1}H-NMR
(400 MHz,$CDCl_3$)



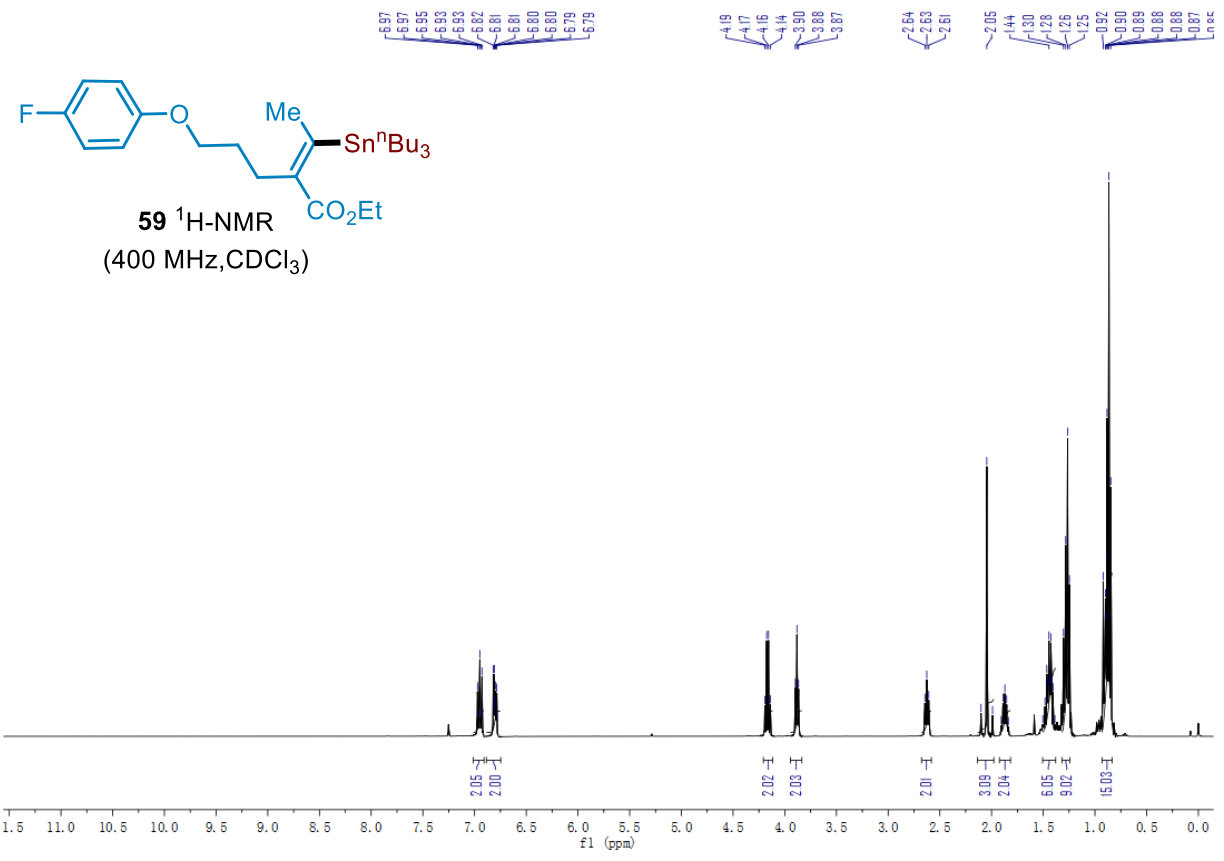
57 ^{13}C-NMR
(100 MHz, $CDCl_3$)



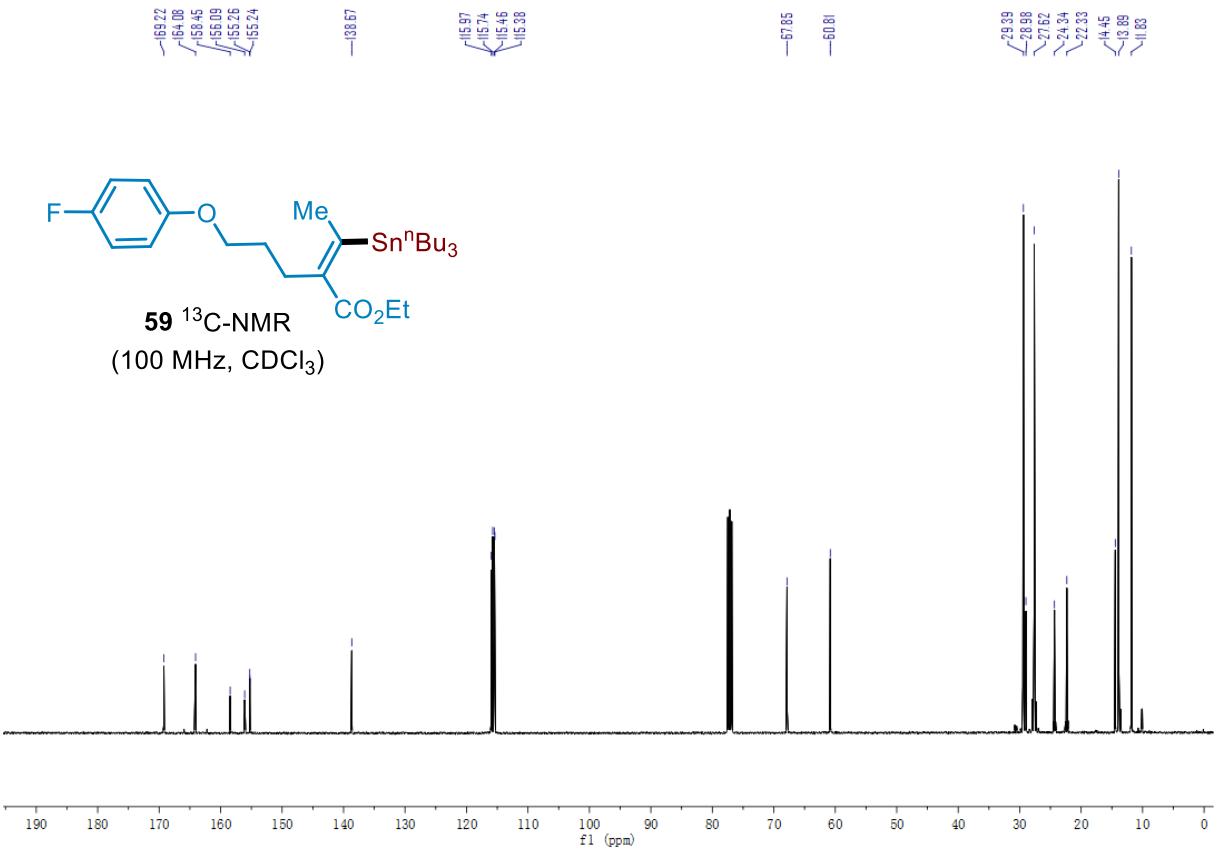
58 ^{1}H-NMR
(400 MHz,$CDCl_3$)



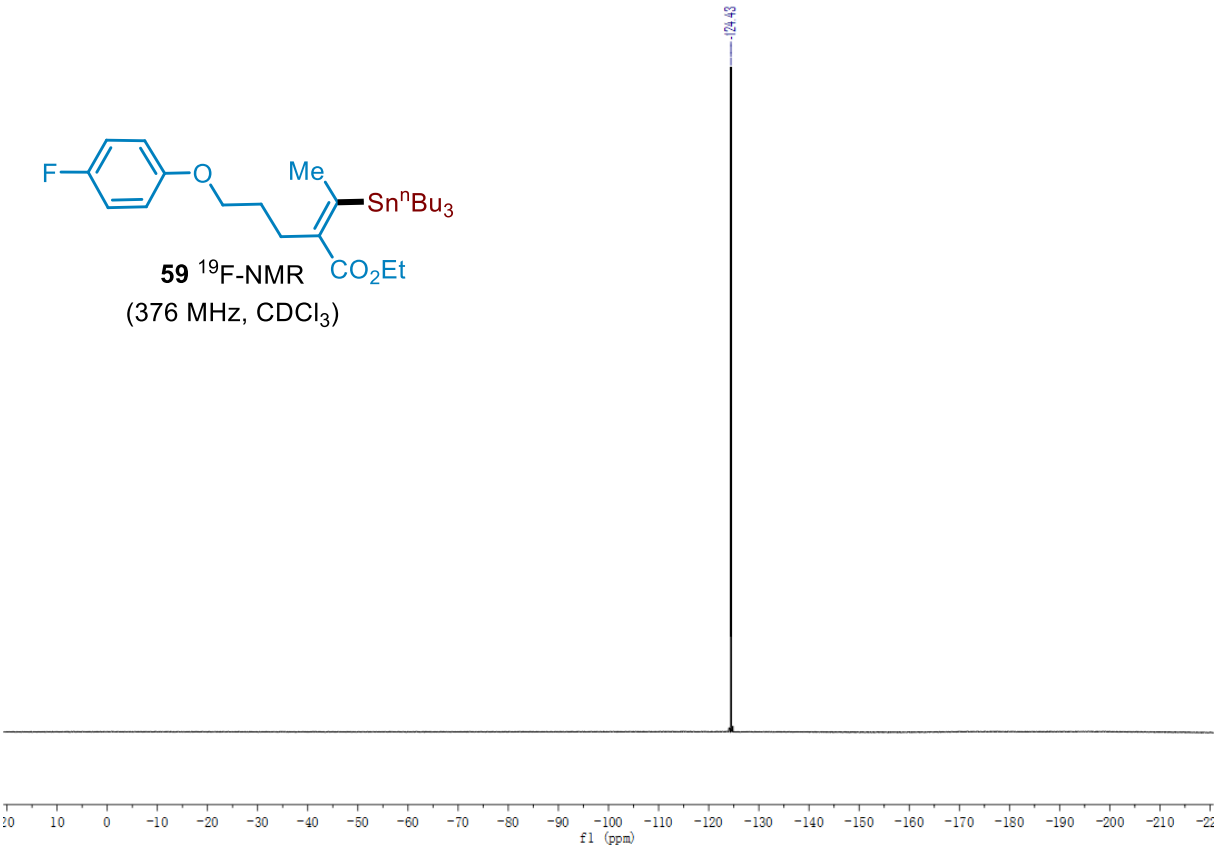
58 ^{13}C-NMR
(100 MHz, $CDCl_3$)



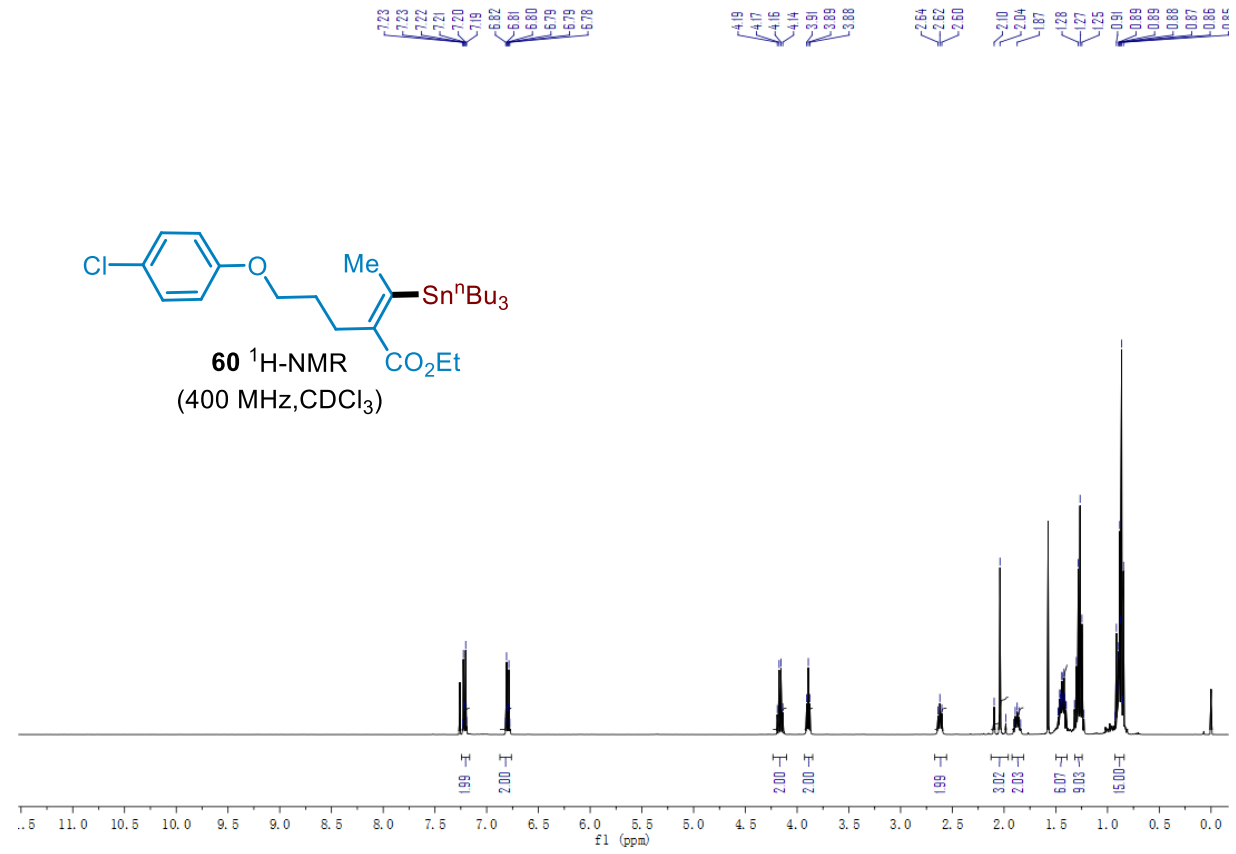
59 ^{1}H-NMR
(400 MHz,$CDCl_3$)

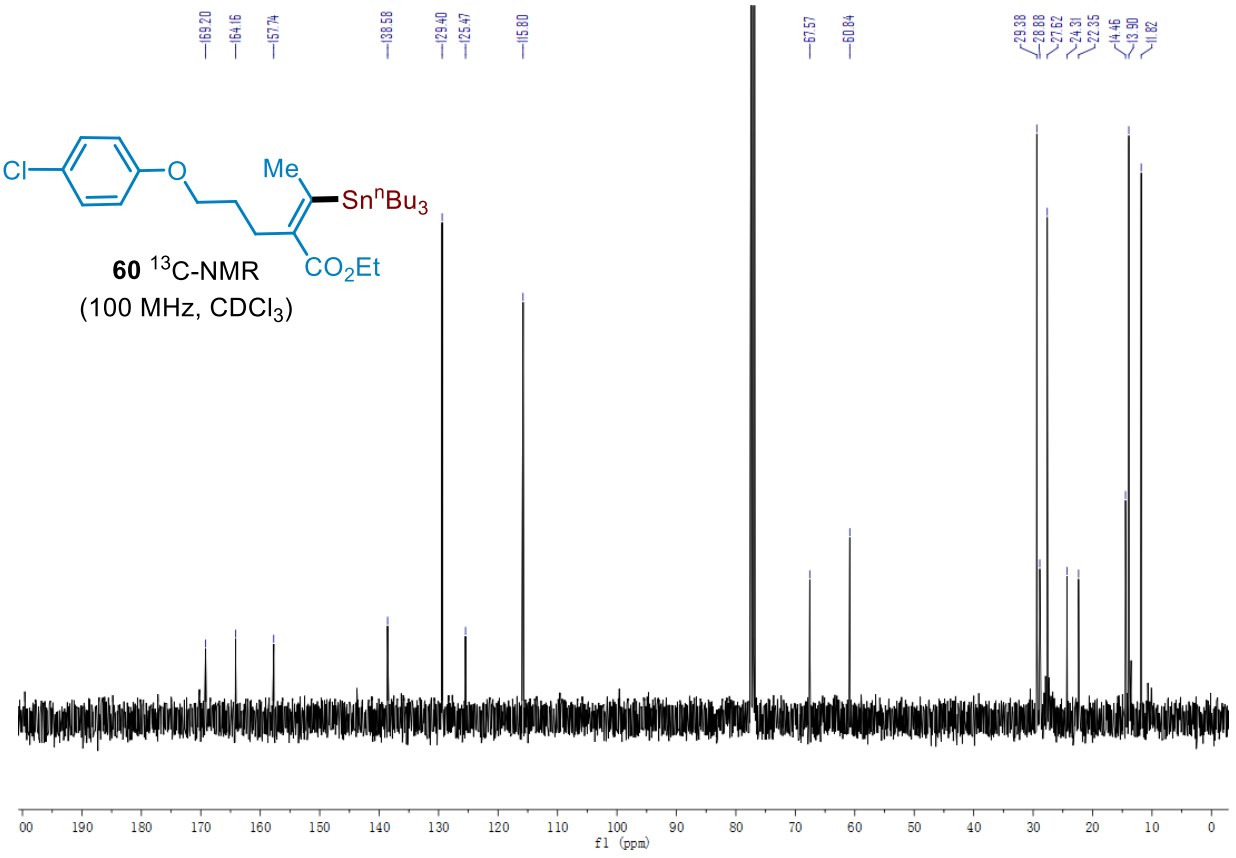


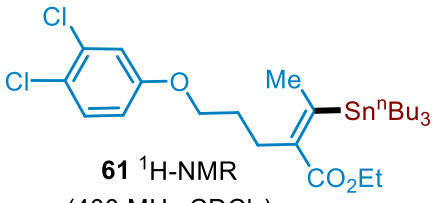
59 ^{13}C-NMR
(100 MHz, $CDCl_3$)



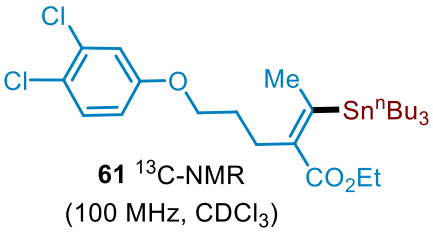
59 ^{19}F-NMR
(376 MHz, $CDCl_3$)


Cl
O
Me
Sn^{n}Bu$_3$
CO$_2$Et
60 ^{1}H-NMR
(400 MHz,CDCl$_3$)
f1 (ppm)

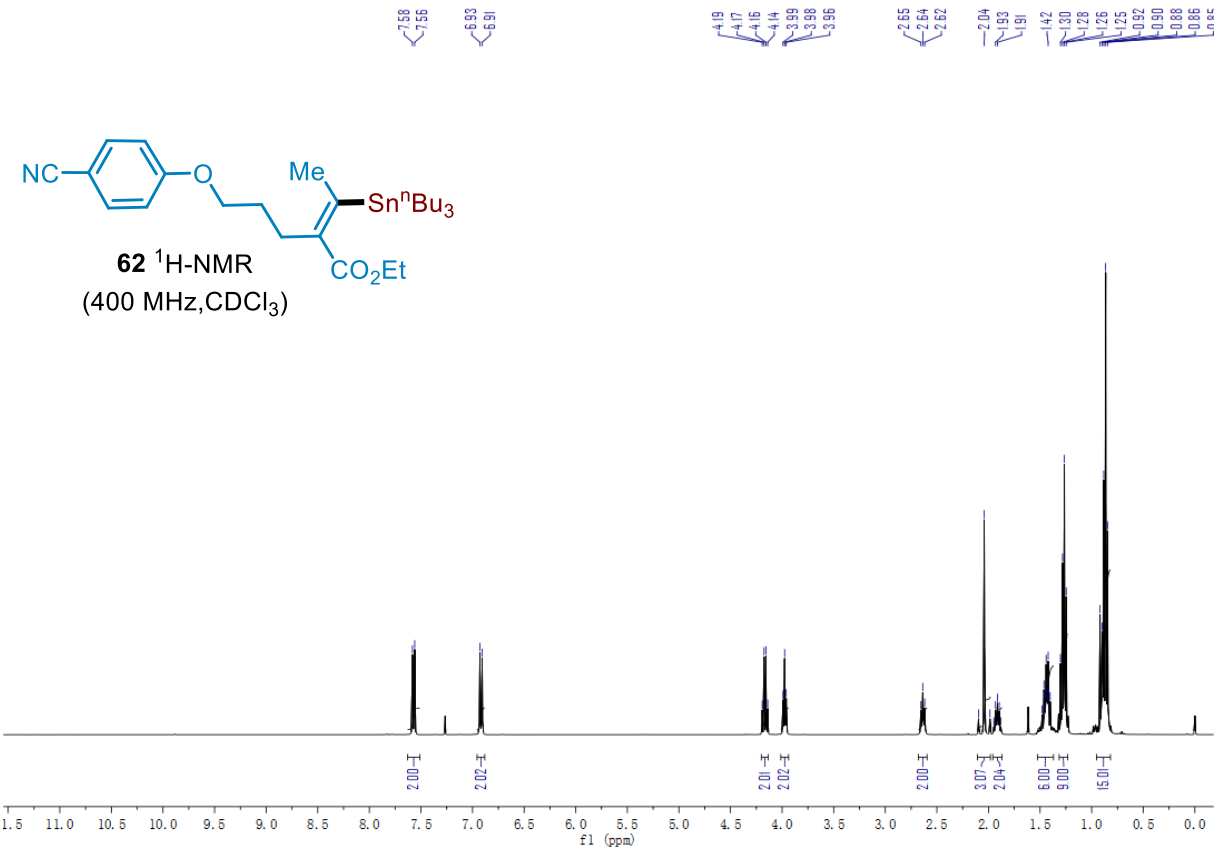

Cl
O
Me
Sn^{n}Bu$_3$
CO$_2$Et
60 ^{13}C-NMR
(100 MHz, CDCl$_3$)
f1 (ppm)

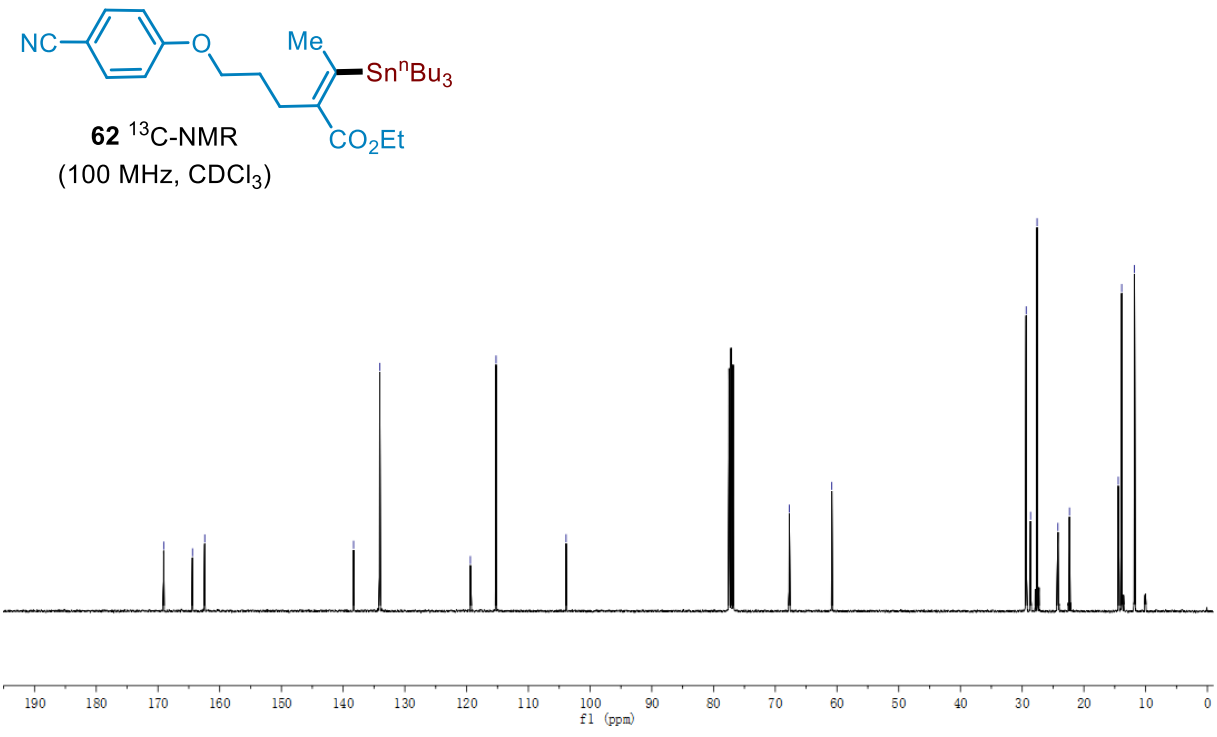


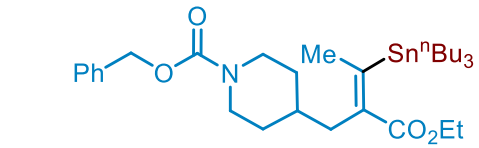
61 ^{1}H-NMR
(400 MHz,$CDCl_3$)



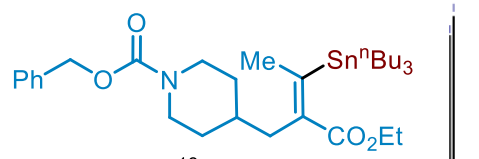
61 ^{13}C-NMR
(100 MHz, $CDCl_3$)


NC
O
Me
Sn^{n}Bu$_3$
CO$_2$Et
62 ^{1}H-NMR
(400 MHz,CDCl$_3$)
f1 (ppm)


NC
O
Me
Sn^{n}Bu$_3$
CO$_2$Et
62 ^{13}C-NMR
(100 MHz, CDCl$_3$)
f1 (ppm)



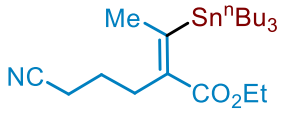
63 ^{1}H-NMR
(400 MHz,$CDCl_3$)



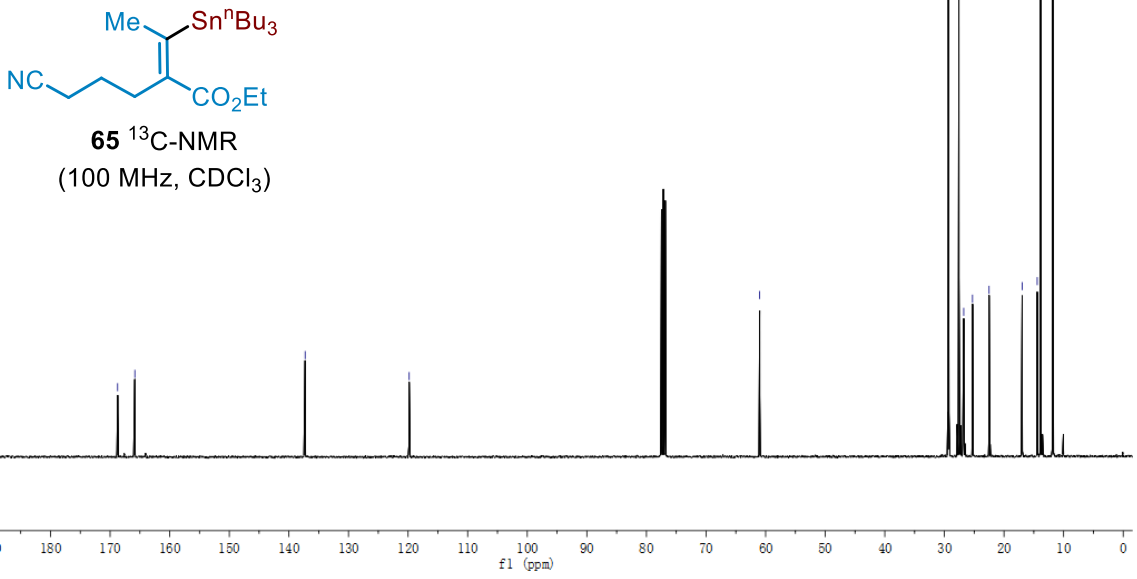
63 ^{13}C-NMR
(100 MHz, $CDCl_3$)

64 ^{1}H-NMR
(400 MHz,$CDCl_3$)

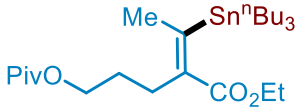
64 ^{13}C-NMR
(100 MHz, $CDCl_3$)



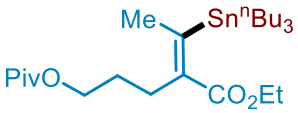
65 ^{1}H-NMR
(400 MHz,$CDCl_3$)



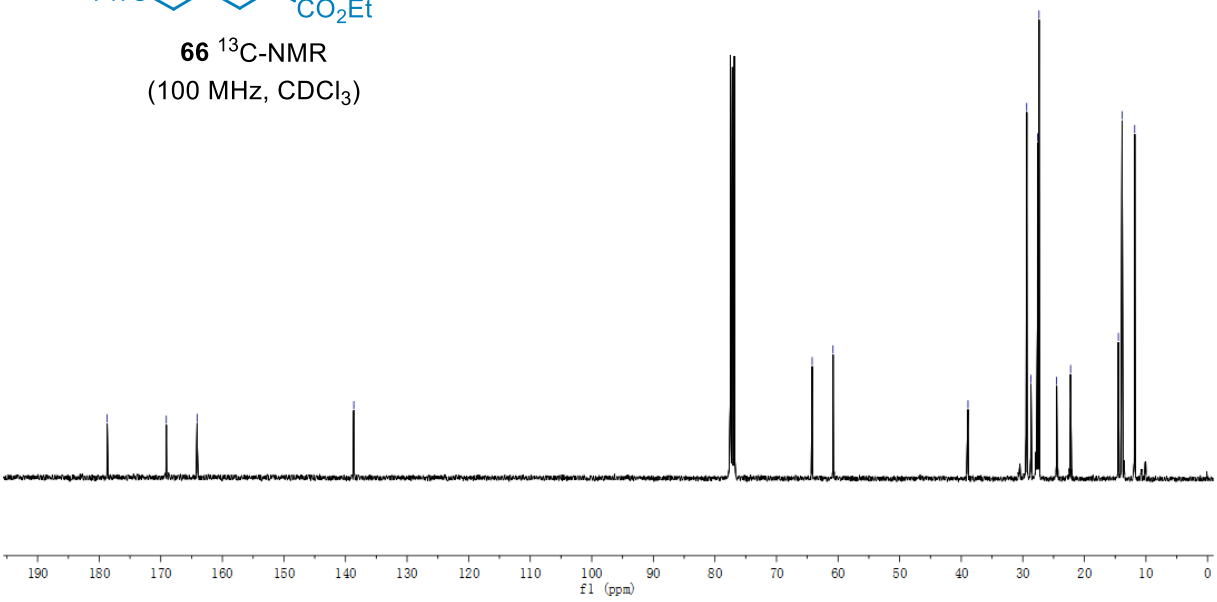
65 ^{13}C-NMR
(100 MHz, $CDCl_3$)

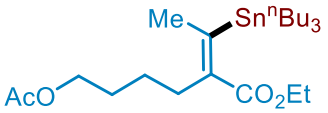


66 ^{1}H-NMR
(400 MHz,$CDCl_3$)

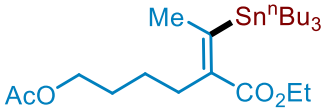


66 ^{13}C-NMR
(100 MHz, $CDCl_3$)

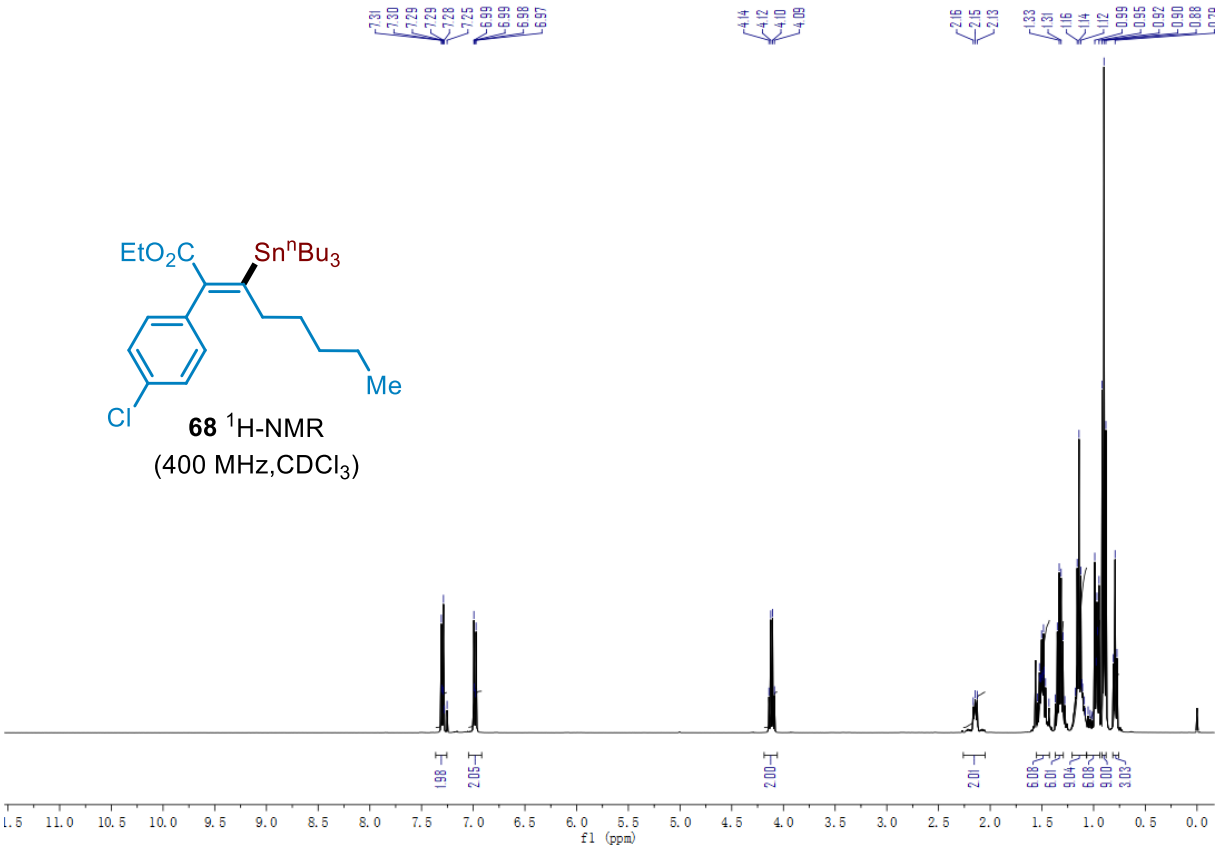


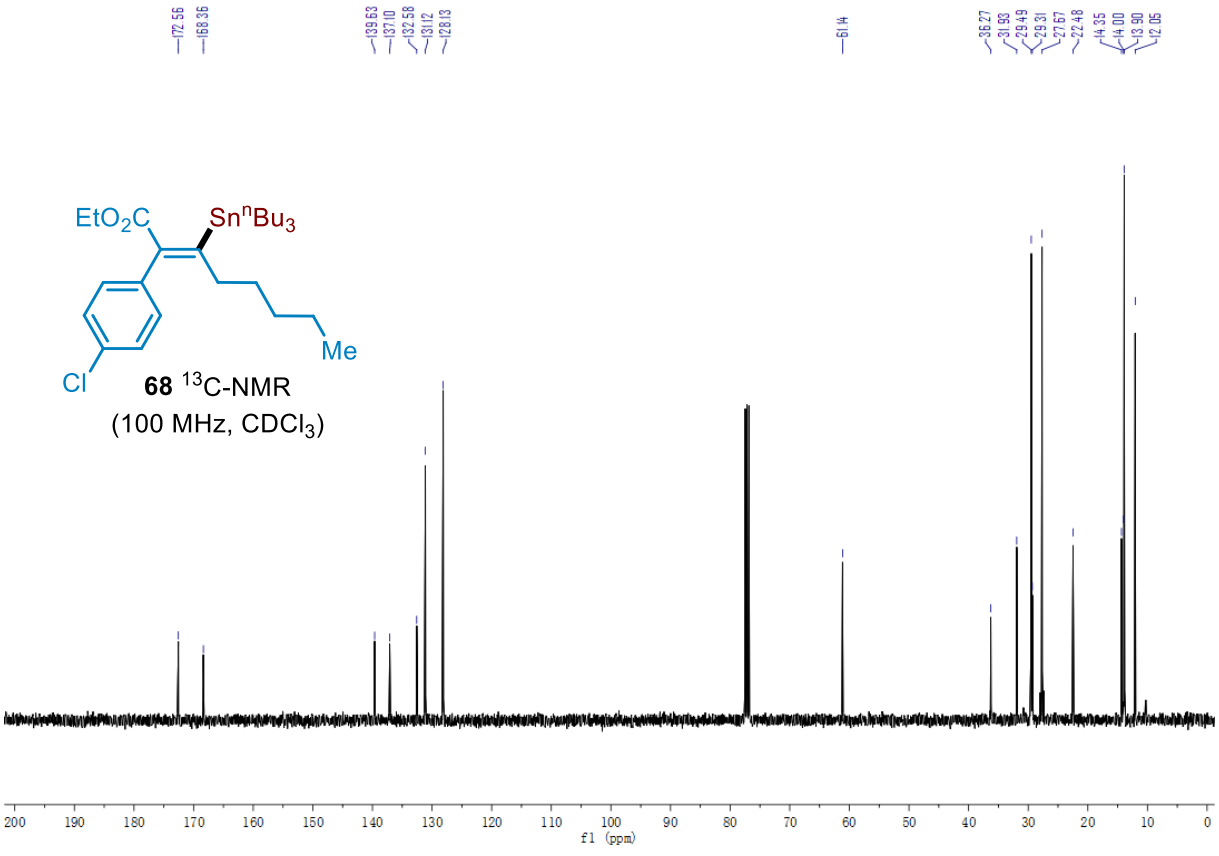


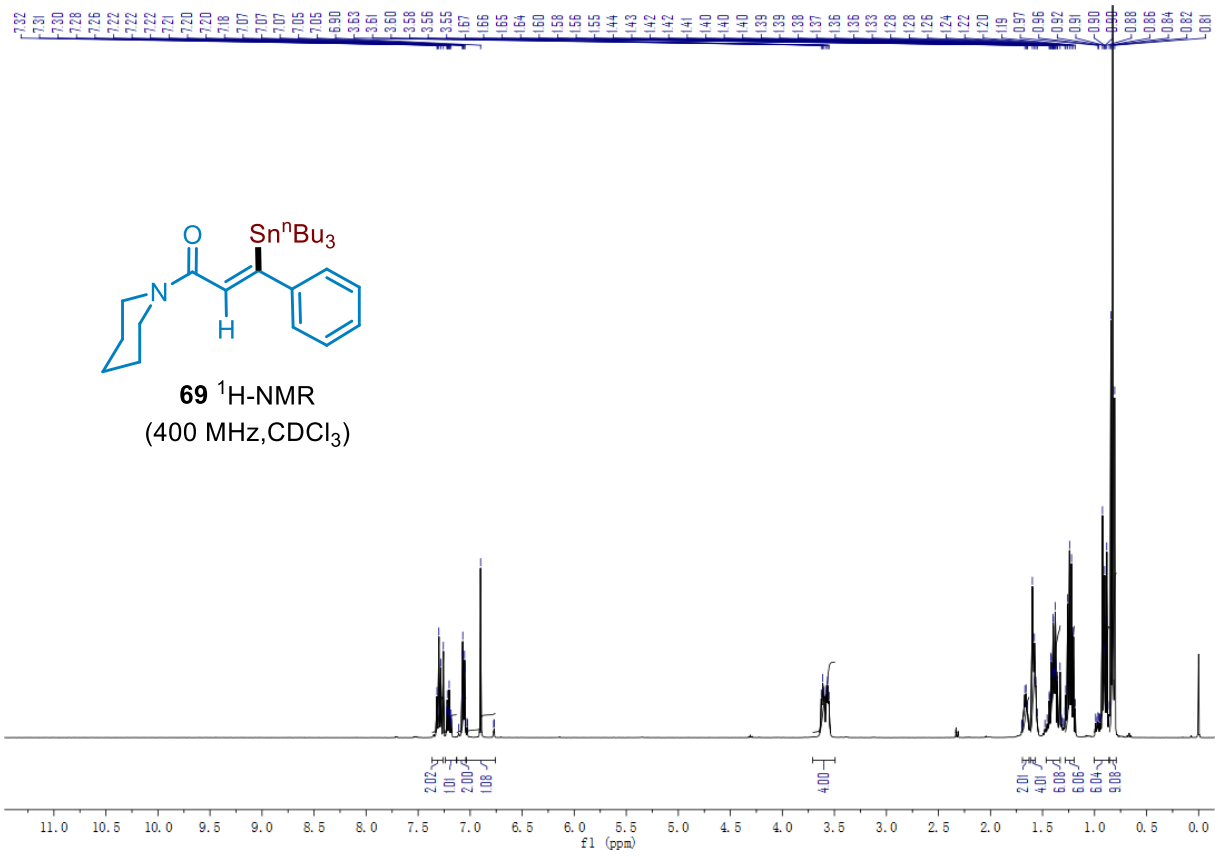
67 ^{1}H-NMR
(400 MHz,$CDCl_3$)



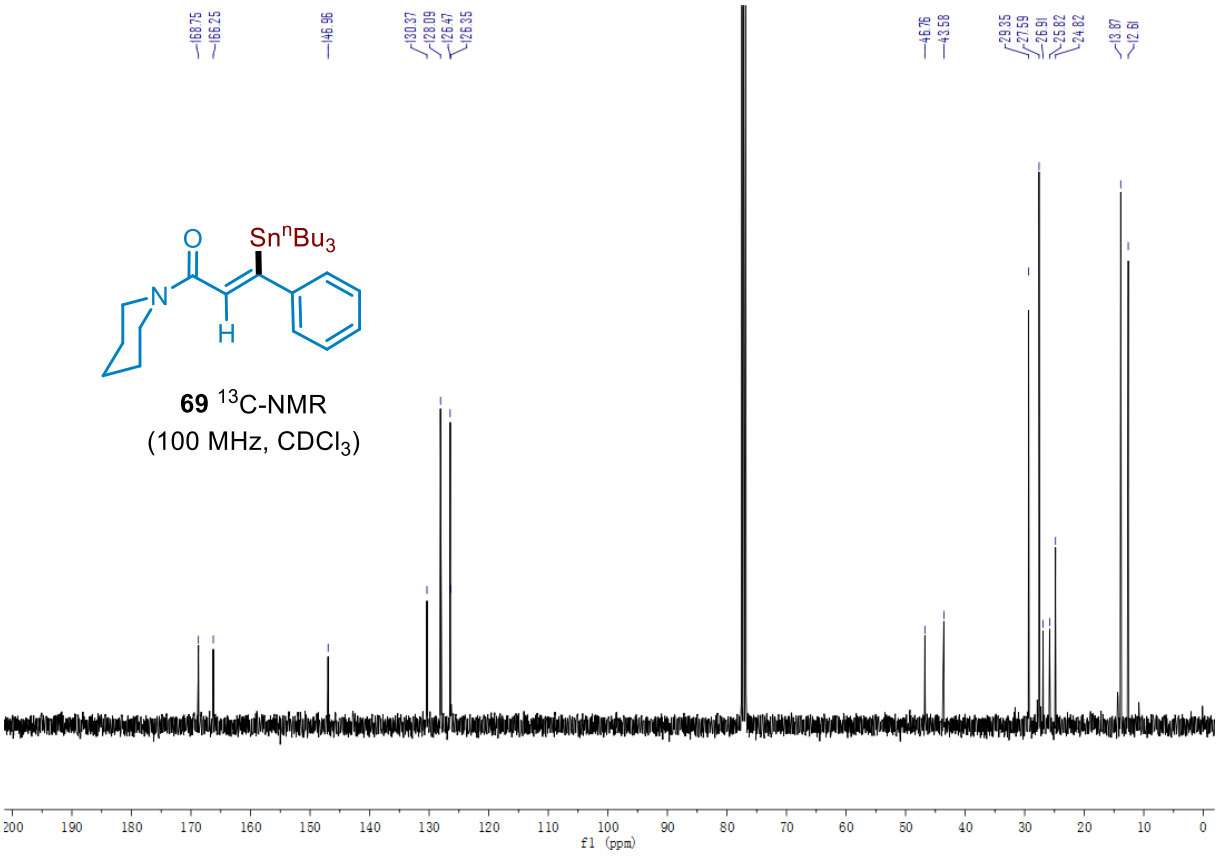
67 ^{13}C-NMR
(100 MHz, $CDCl_3$)


EtO2C
SnnBu3
Me
Cl
68 1H-NMR
(400 MHz,CDCl3)
f1 (ppm)


EtO2C
SnnBu3
Me
Cl
68 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)

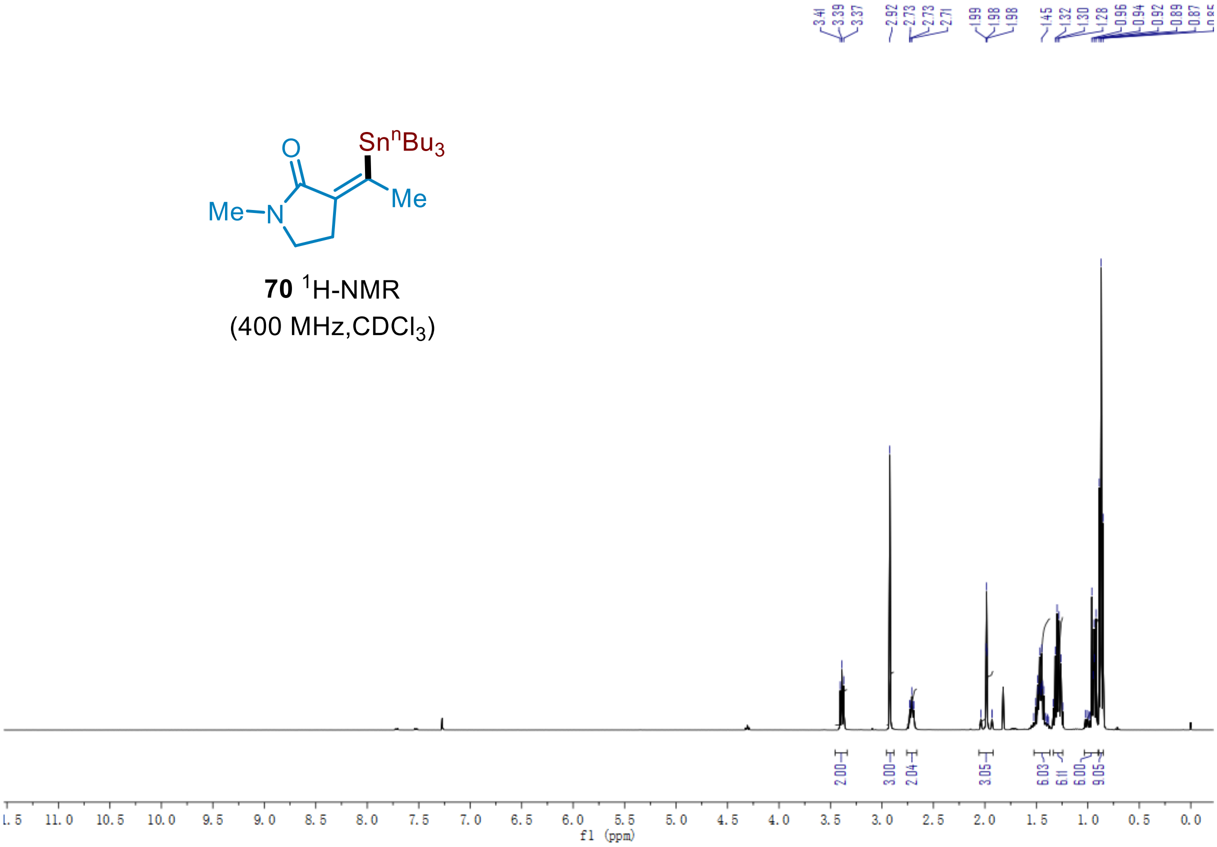


69 ^{1}H-NMR
(400 MHz,$CDCl_3$)

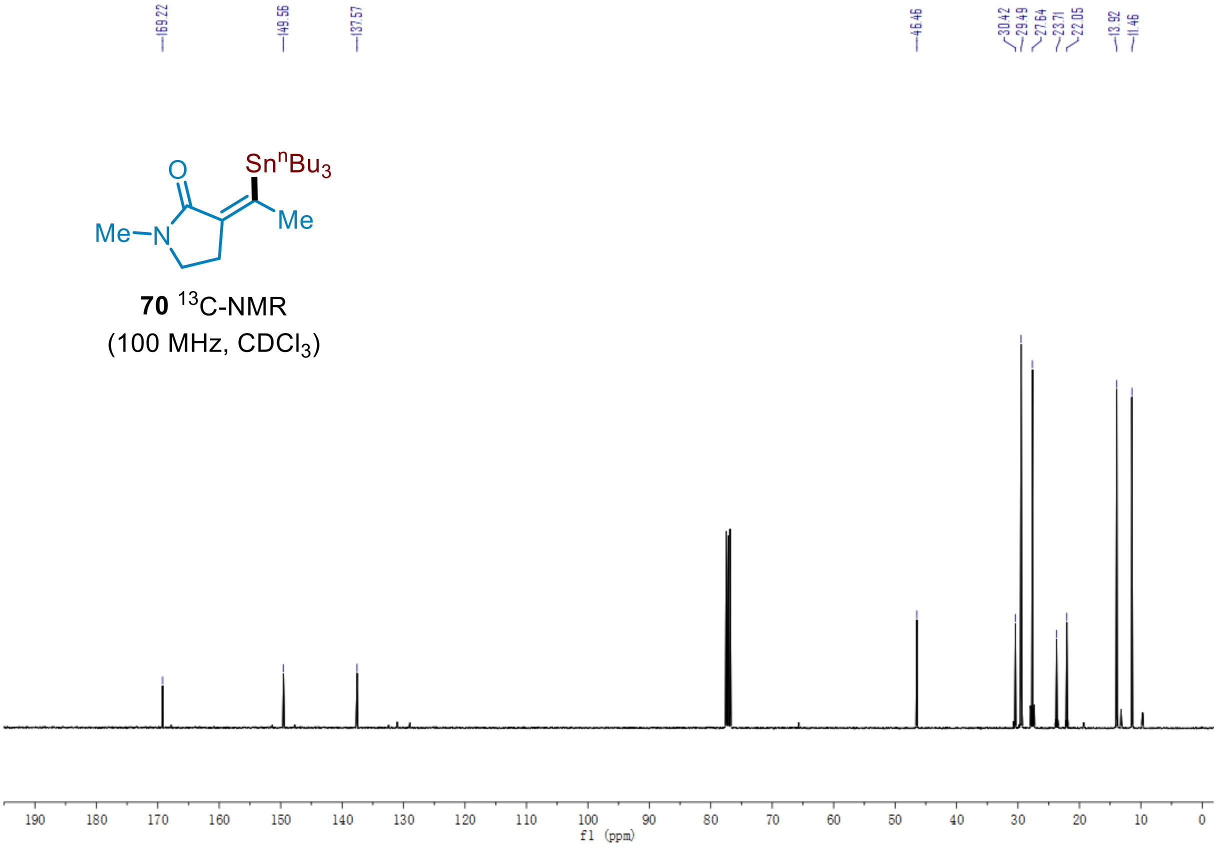


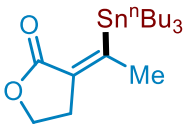
69 ^{13}C-NMR
(100 MHz, $CDCl_3$)

70 ^{1}H-NMR
(400 MHz,$CDCl_3$)

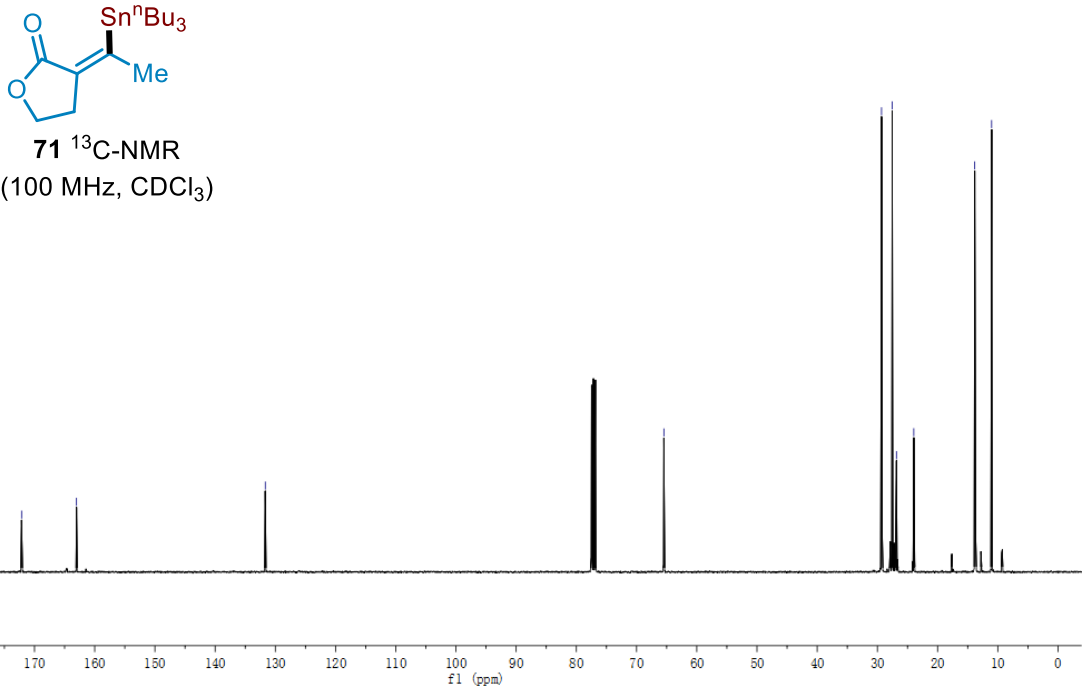


70 ^{13}C-NMR
(100 MHz, $CDCl_3$)

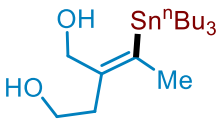




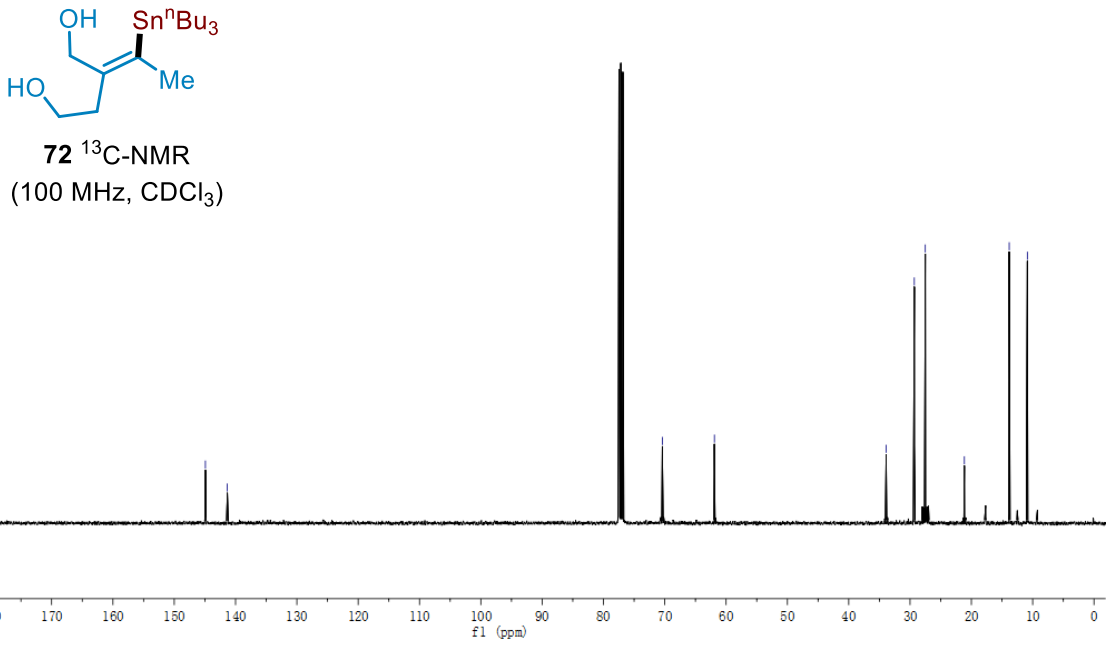
71 ^{1}H-NMR
(400 MHz,$CDCl_3$)



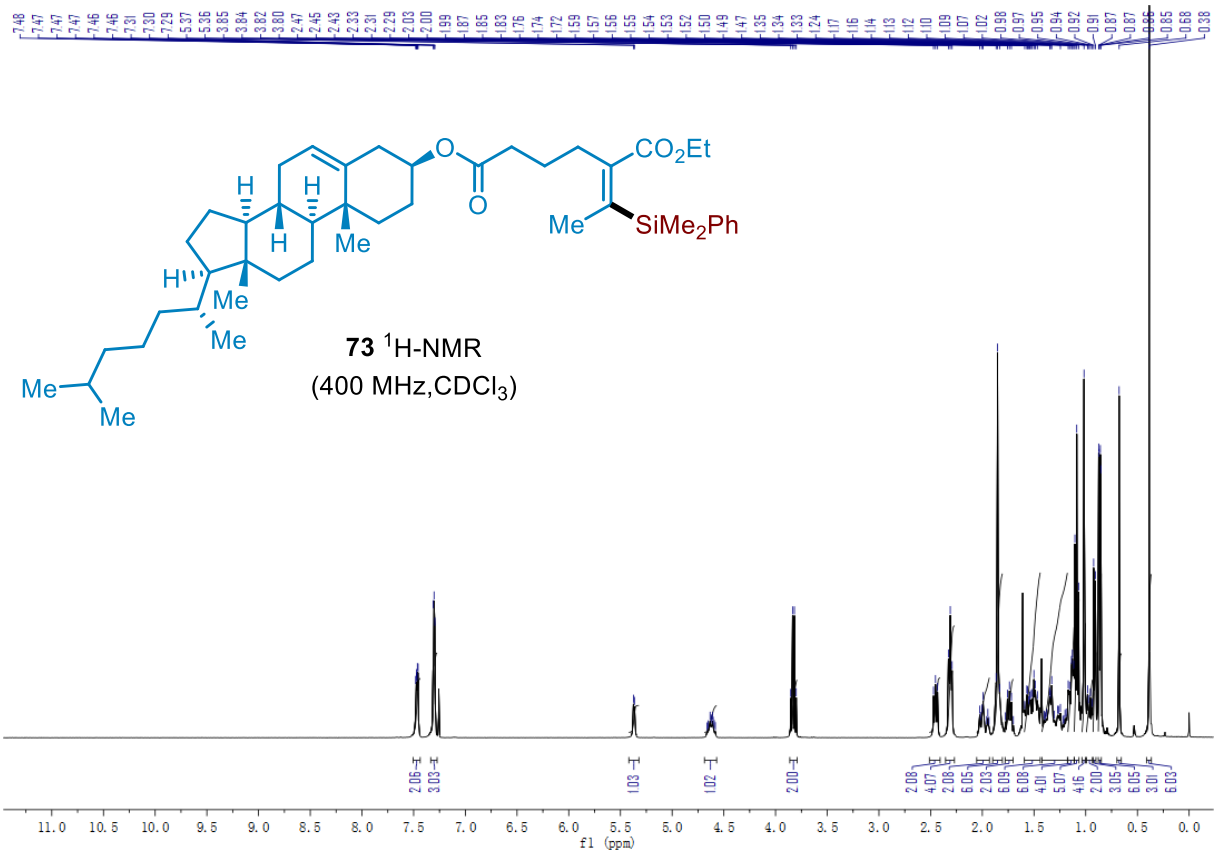
71 ^{13}C-NMR
(100 MHz, $CDCl_3$)

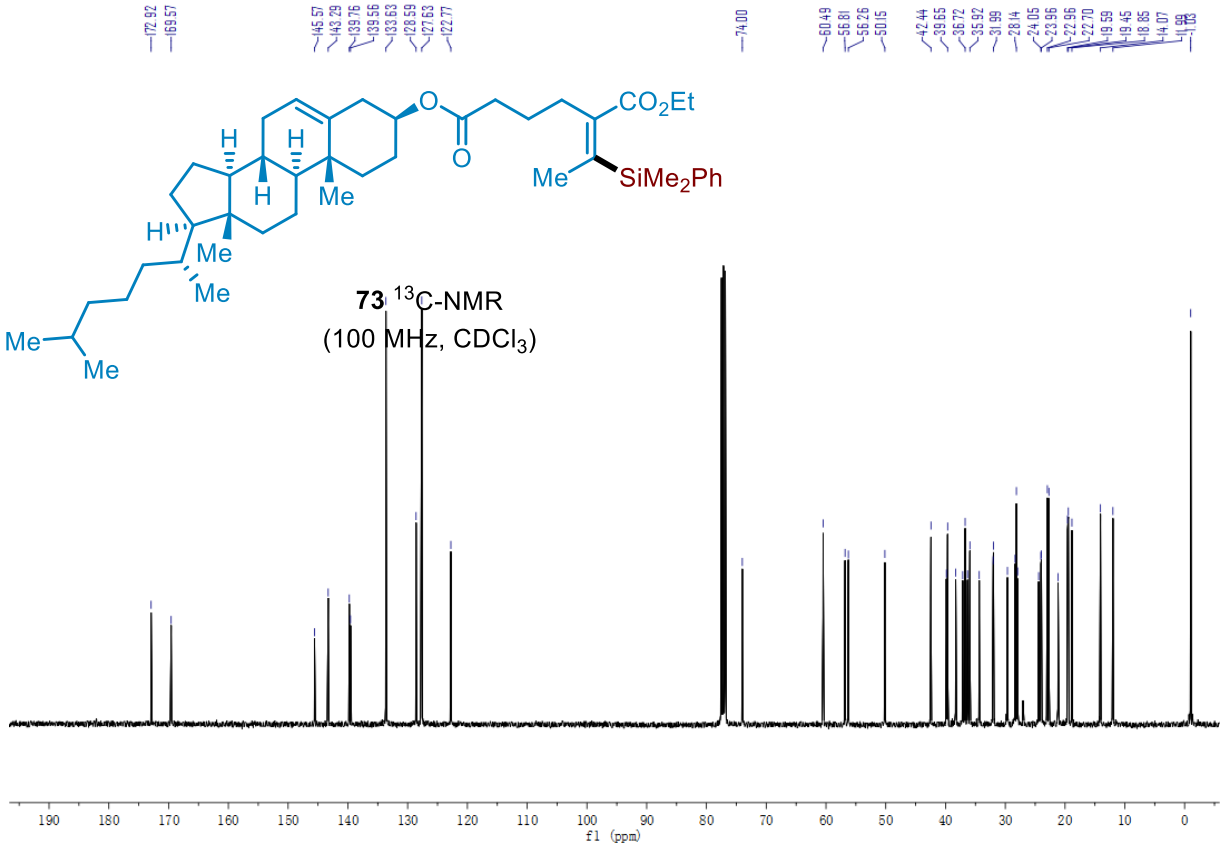


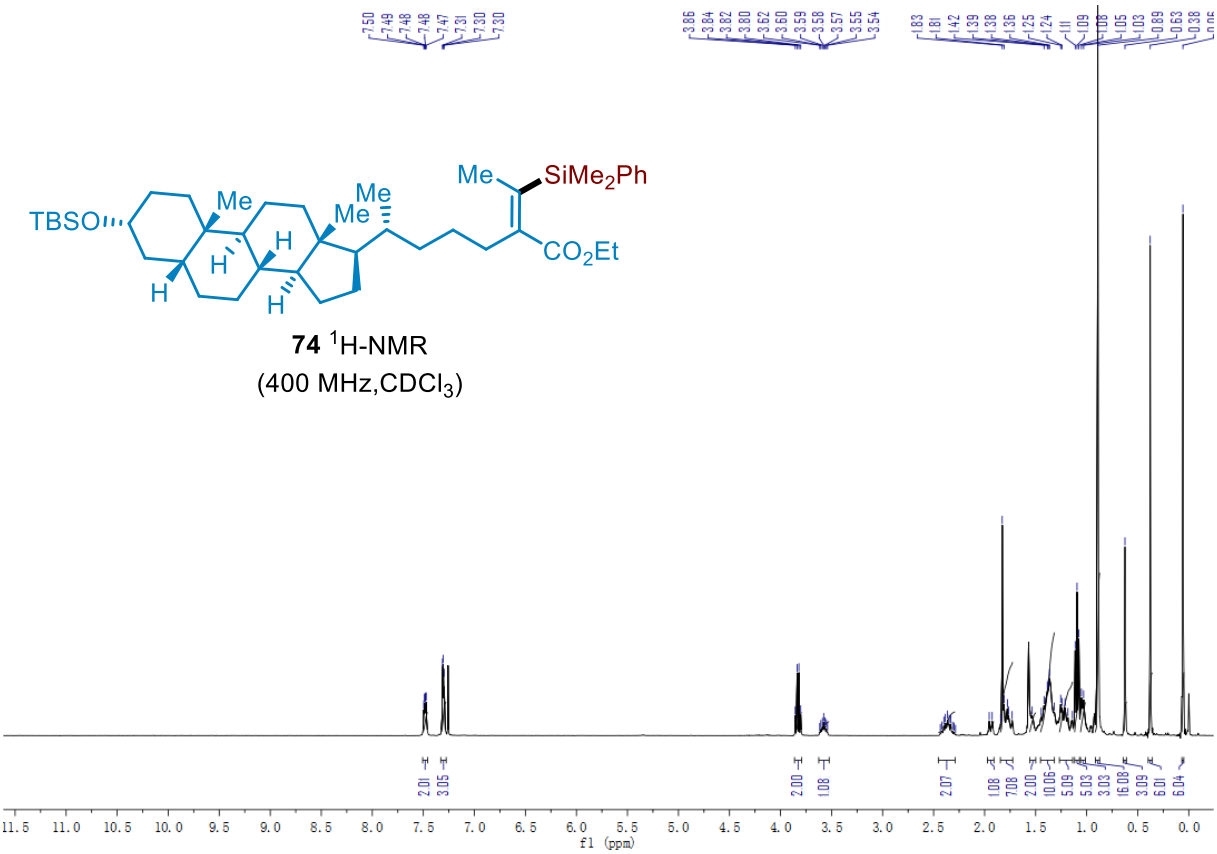
72 ^{1}H-NMR
(400 MHz,$CDCl_3$)



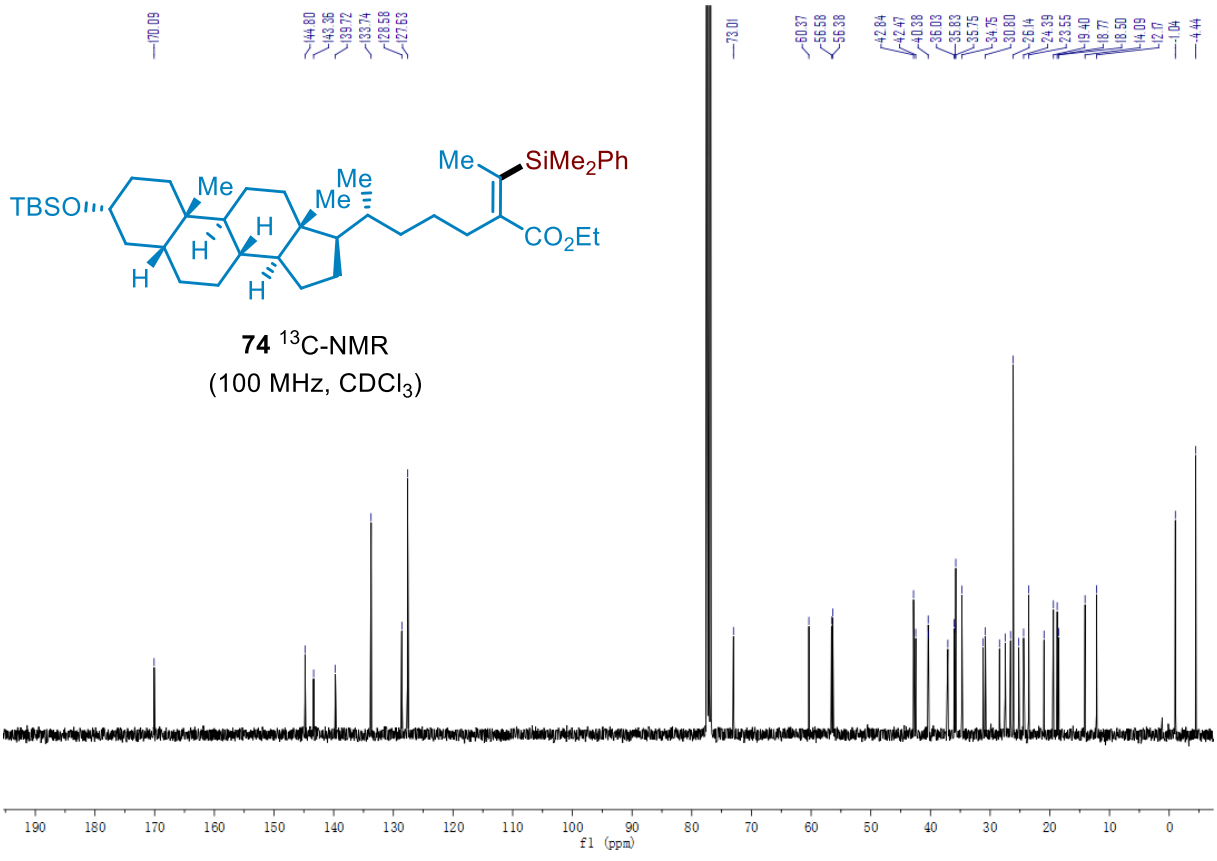
72 ^{13}C-NMR
(100 MHz, $CDCl_3$)


CO2Et
SiMe2Ph
Me
O
H
Me
73 1H-NMR
(400 MHz,CDCl3)
f1 (ppm)

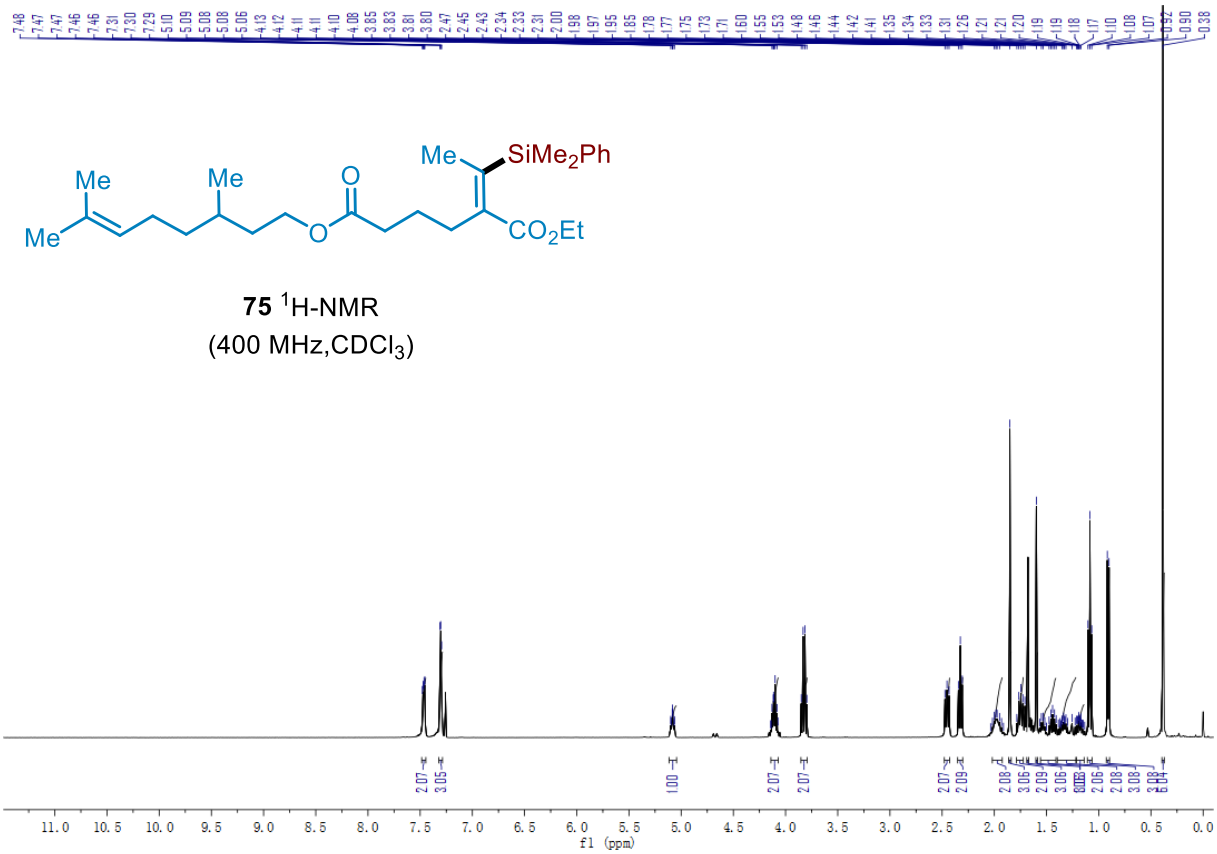

CO2Et
SiMe2Ph
Me
O
H
Me
73 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)



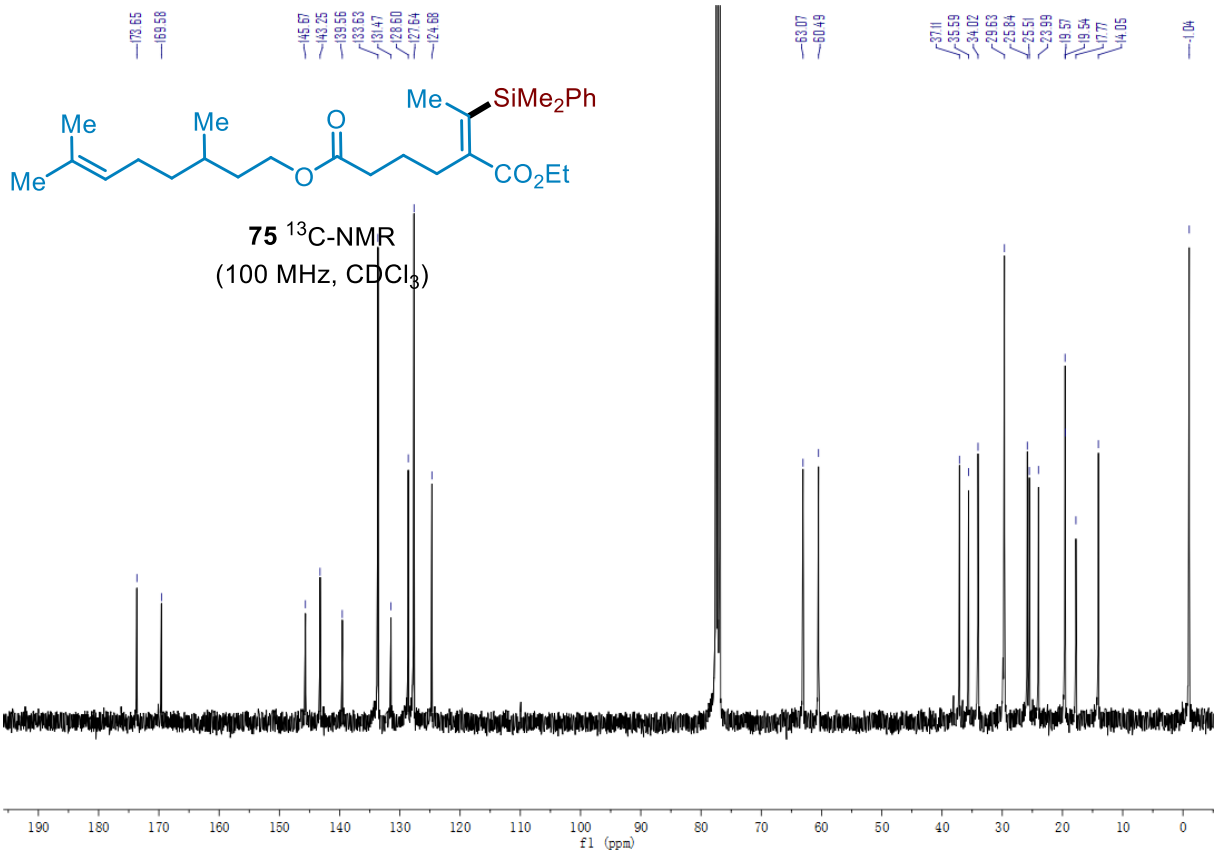
74 ^{1}H-NMR
(400 MHz,$CDCl_3$)



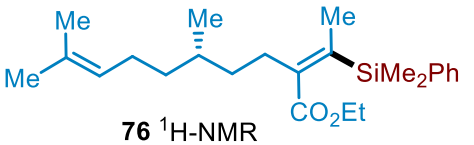
74 ^{13}C-NMR
(100 MHz, $CDCl_3$)



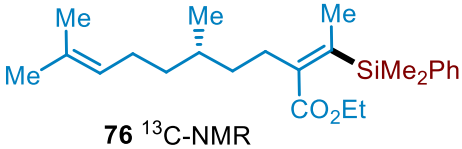
75 ^{1}H-NMR
(400 MHz,$CDCl_3$)



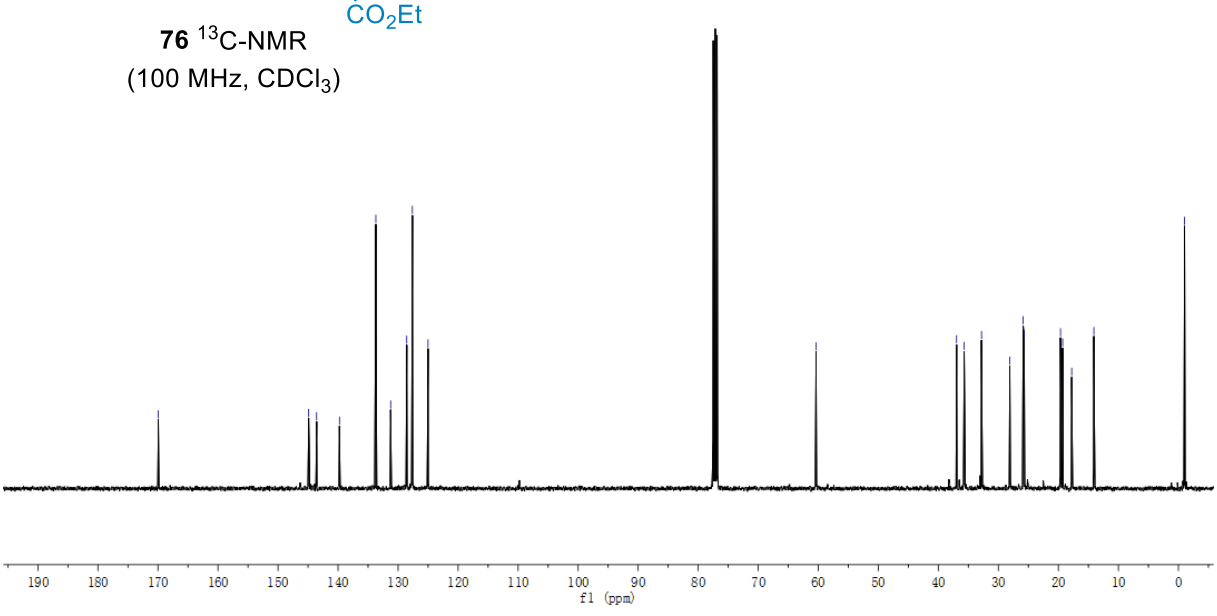
75 ^{13}C-NMR
(100 MHz, $CDCl_3$)

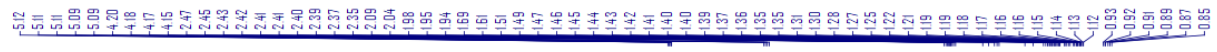


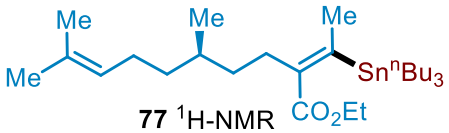
76 ^{1}H-NMR
(400 MHz,$CDCl_3$)



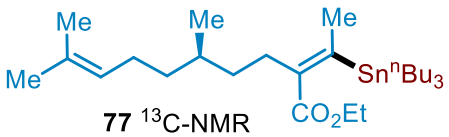
76 ^{13}C-NMR
(100 MHz, $CDCl_3$)



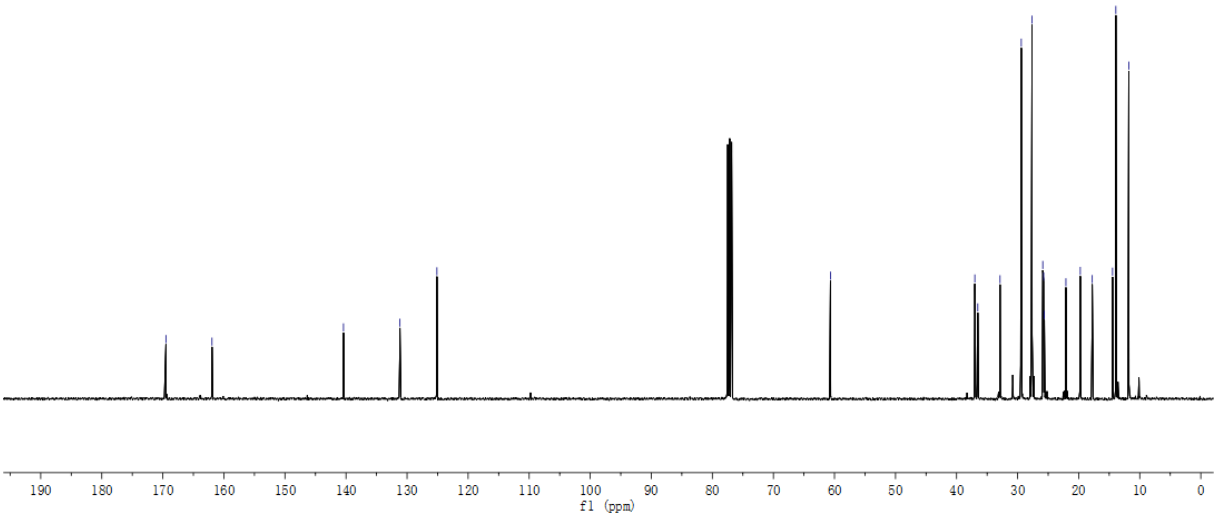


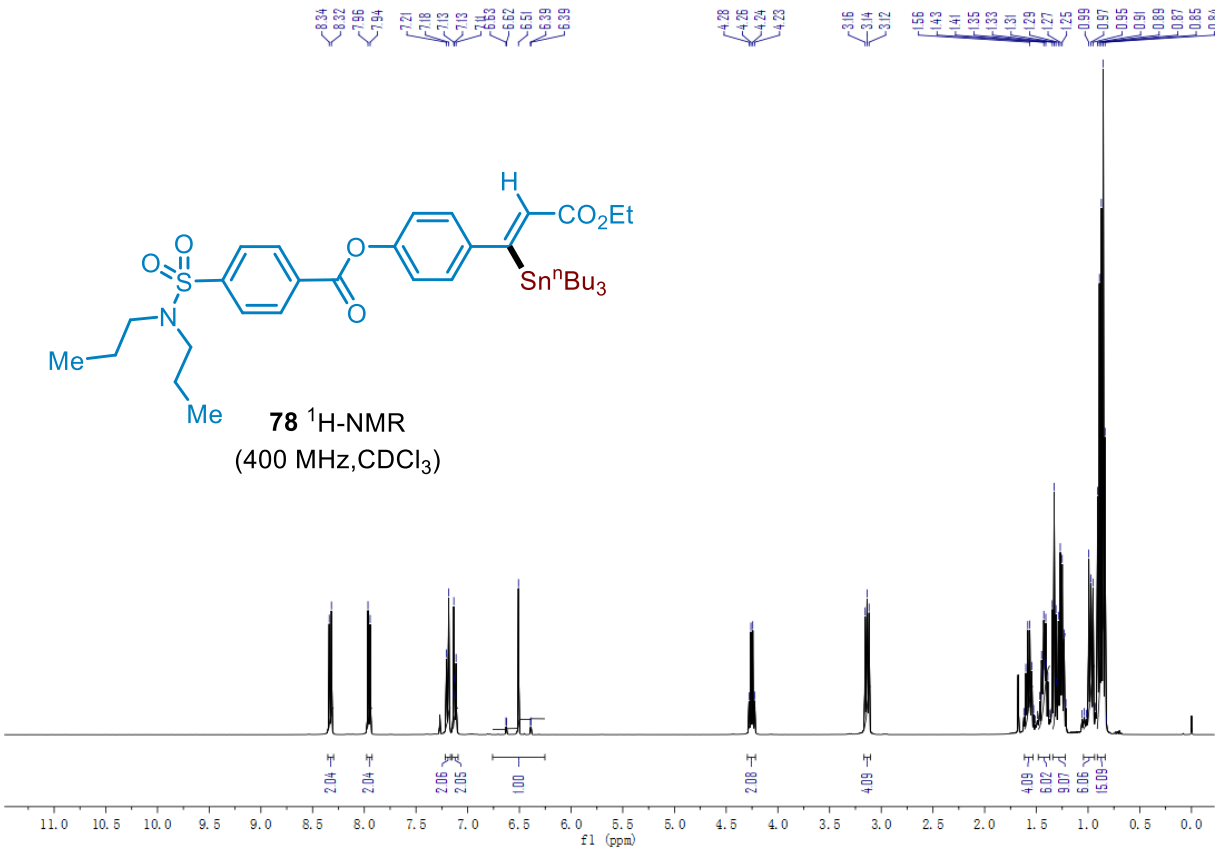


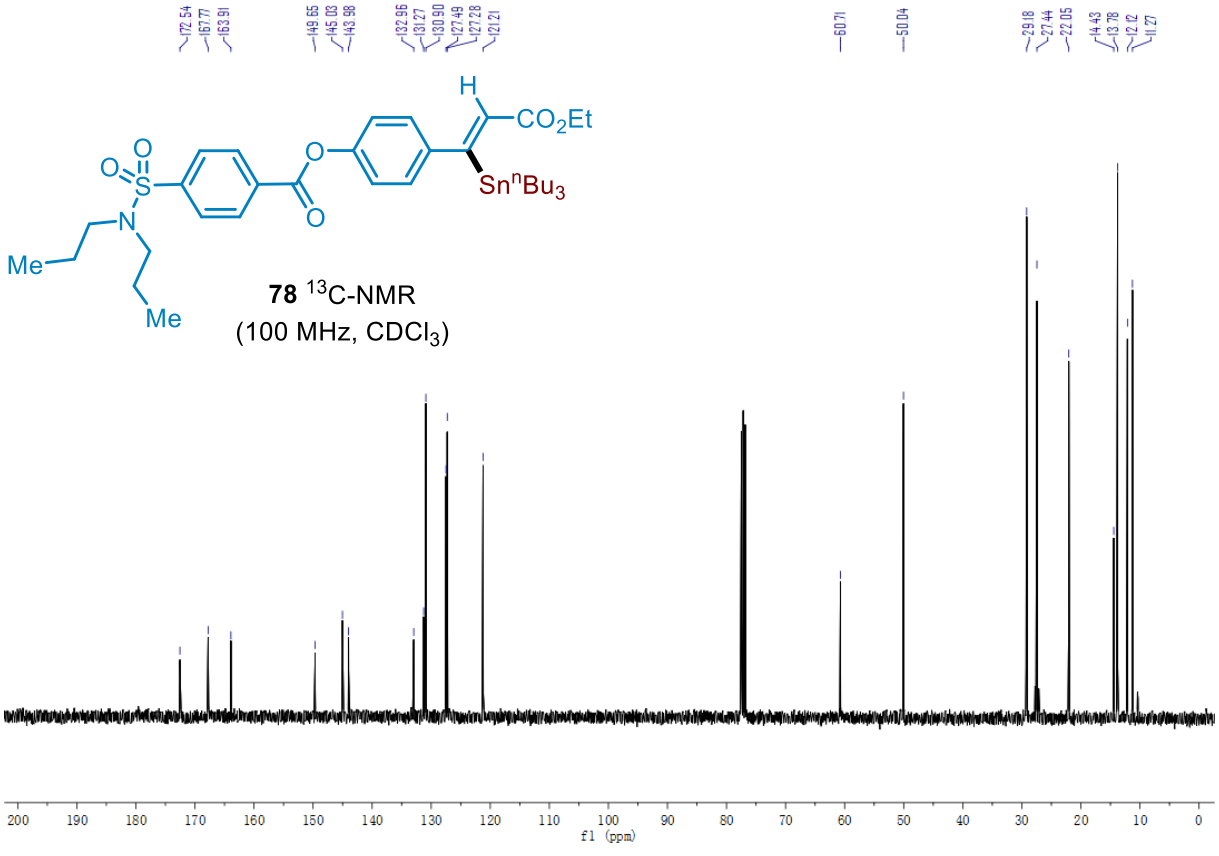
77 ^{1}H-NMR
(400 MHz,$CDCl_3$)

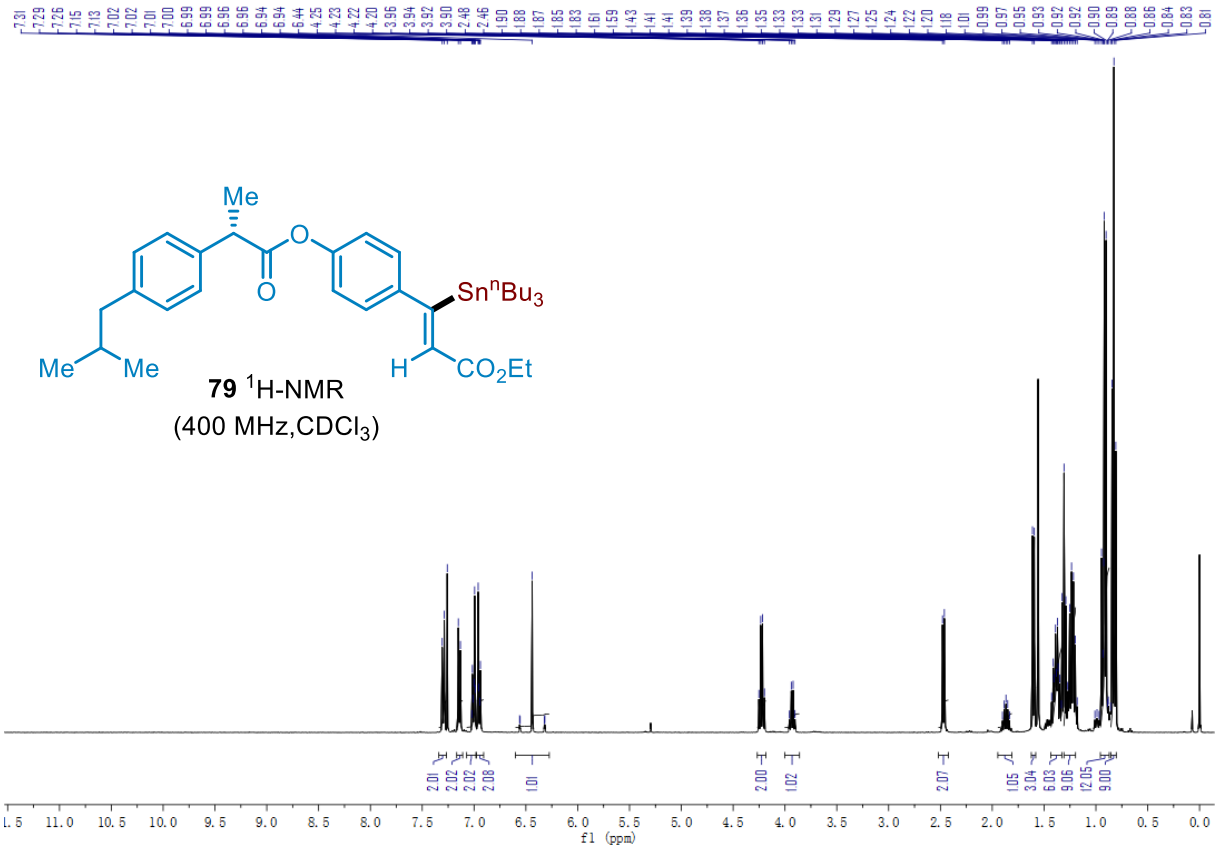


77 ^{13}C-NMR
(100 MHz, $CDCl_3$)

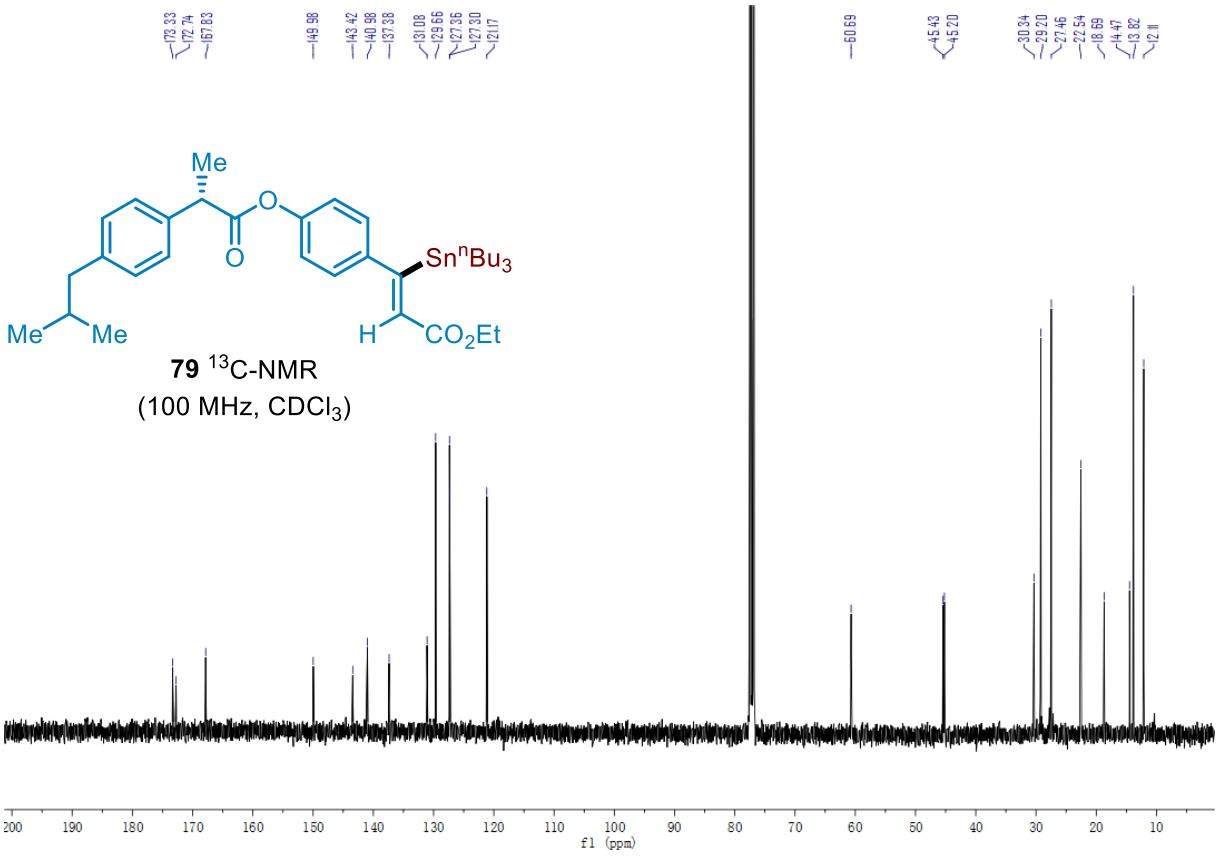



H
CO2Et
Sn^nBu3
O
S
N
Me
Me
78 1H-NMR
(400 MHz,CDCl3)
f1 (ppm)

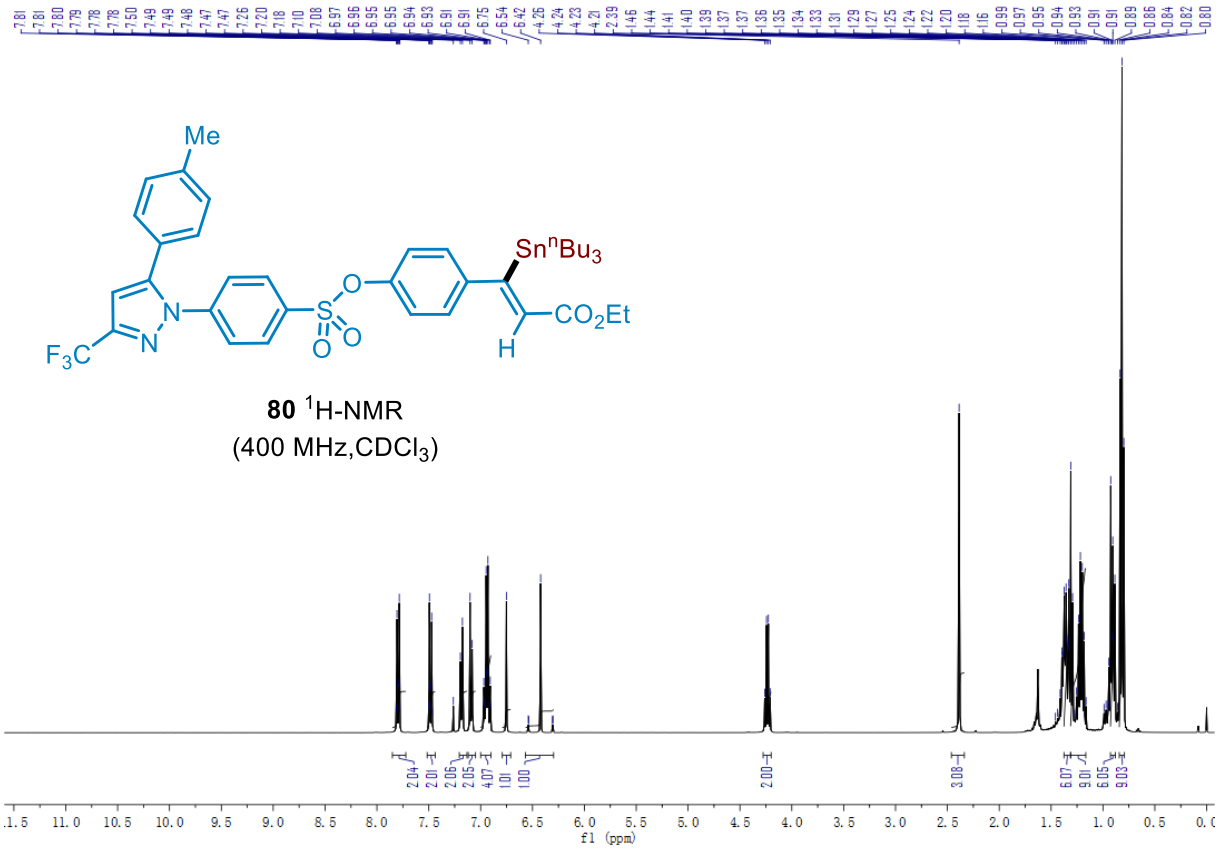

H
CO2Et
Sn^nBu3
O
S
N
Me
Me
78 13C-NMR
(100 MHz, CDCl3)
f1 (ppm)



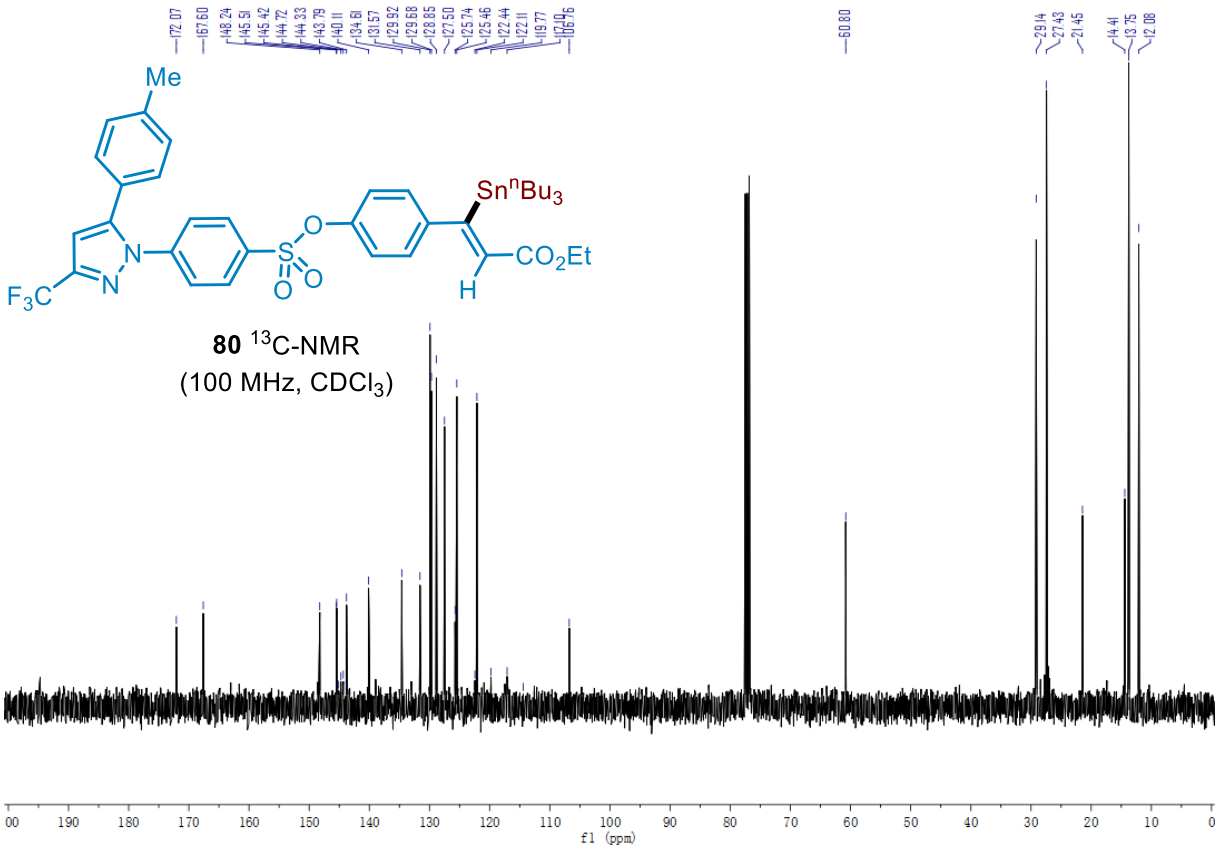
79 ^{1}H-NMR
(400 MHz,$CDCl_3$)



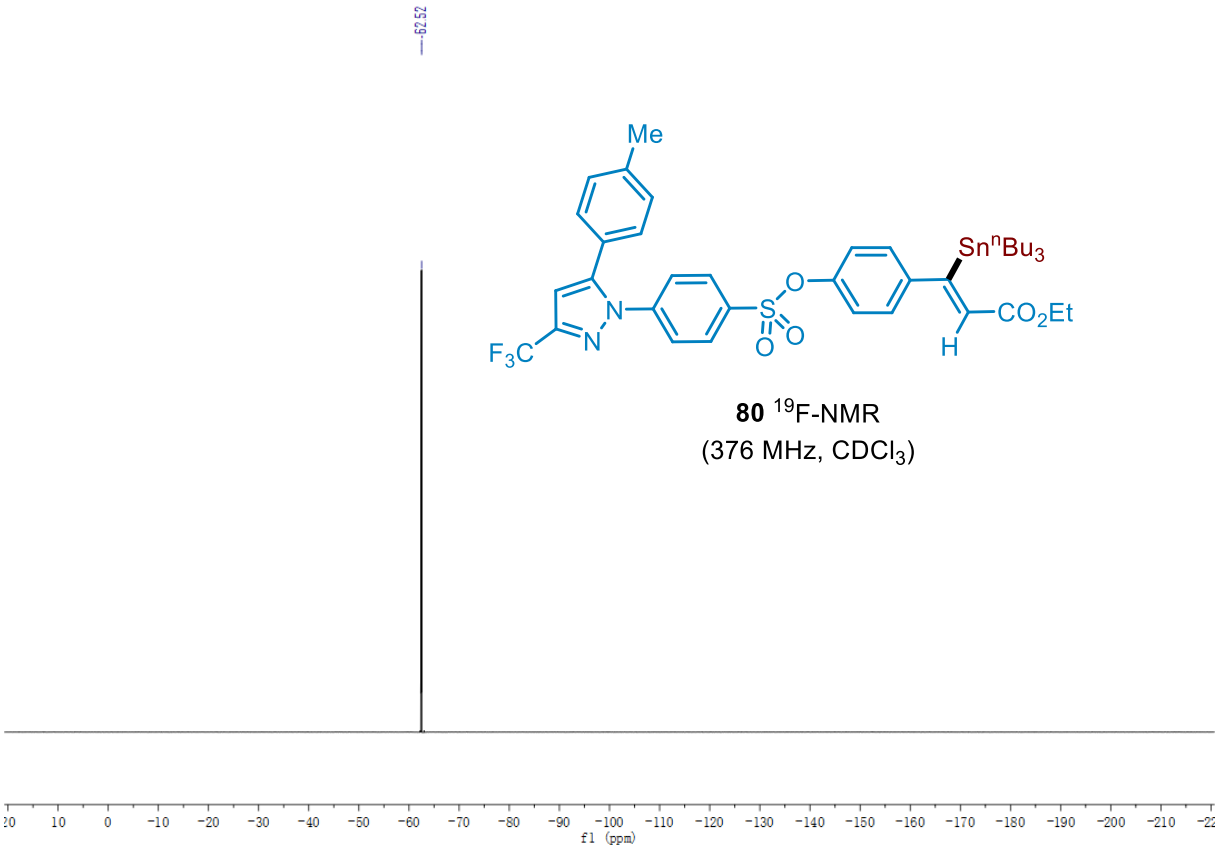
79 ^{13}C-NMR
(100 MHz, $CDCl_3$)



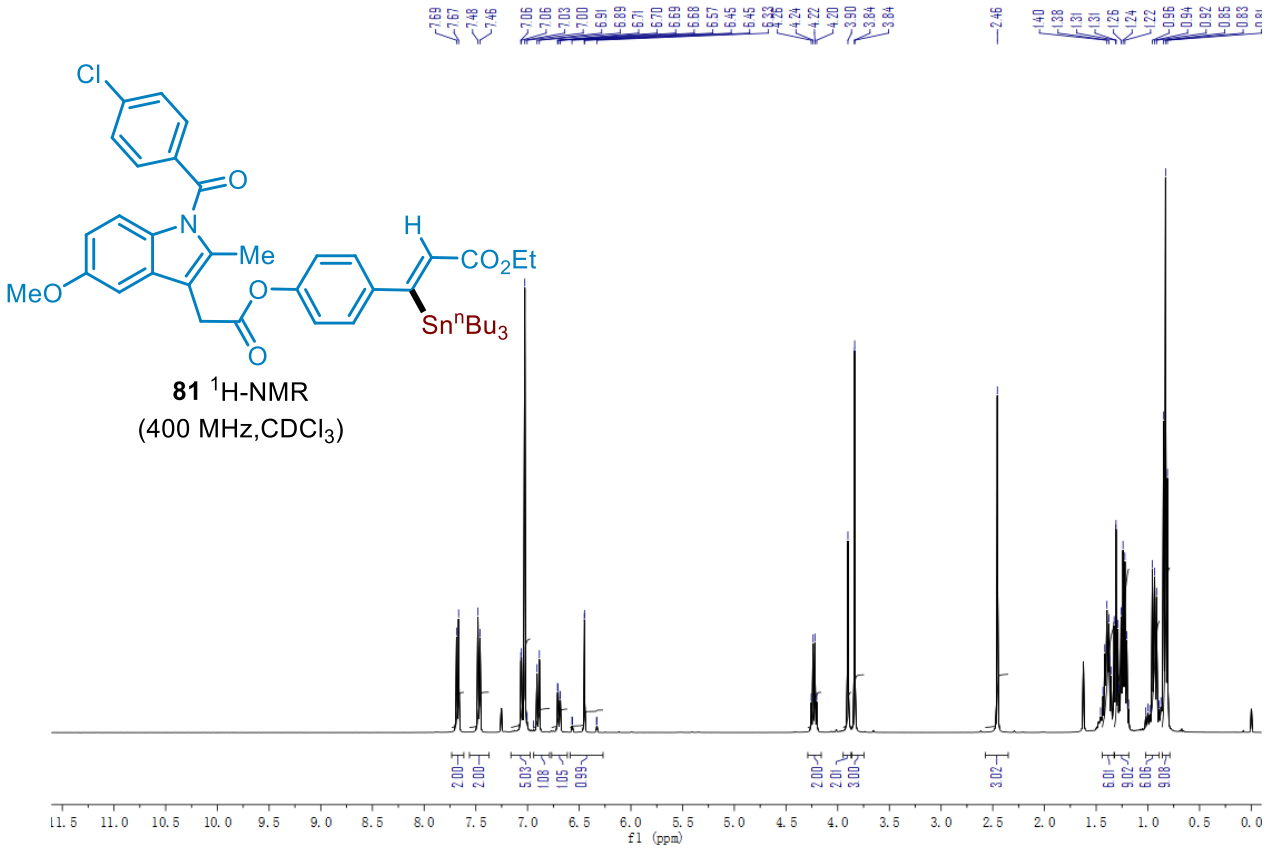
80 ^{1}H-NMR
(400 MHz,$CDCl_3$)



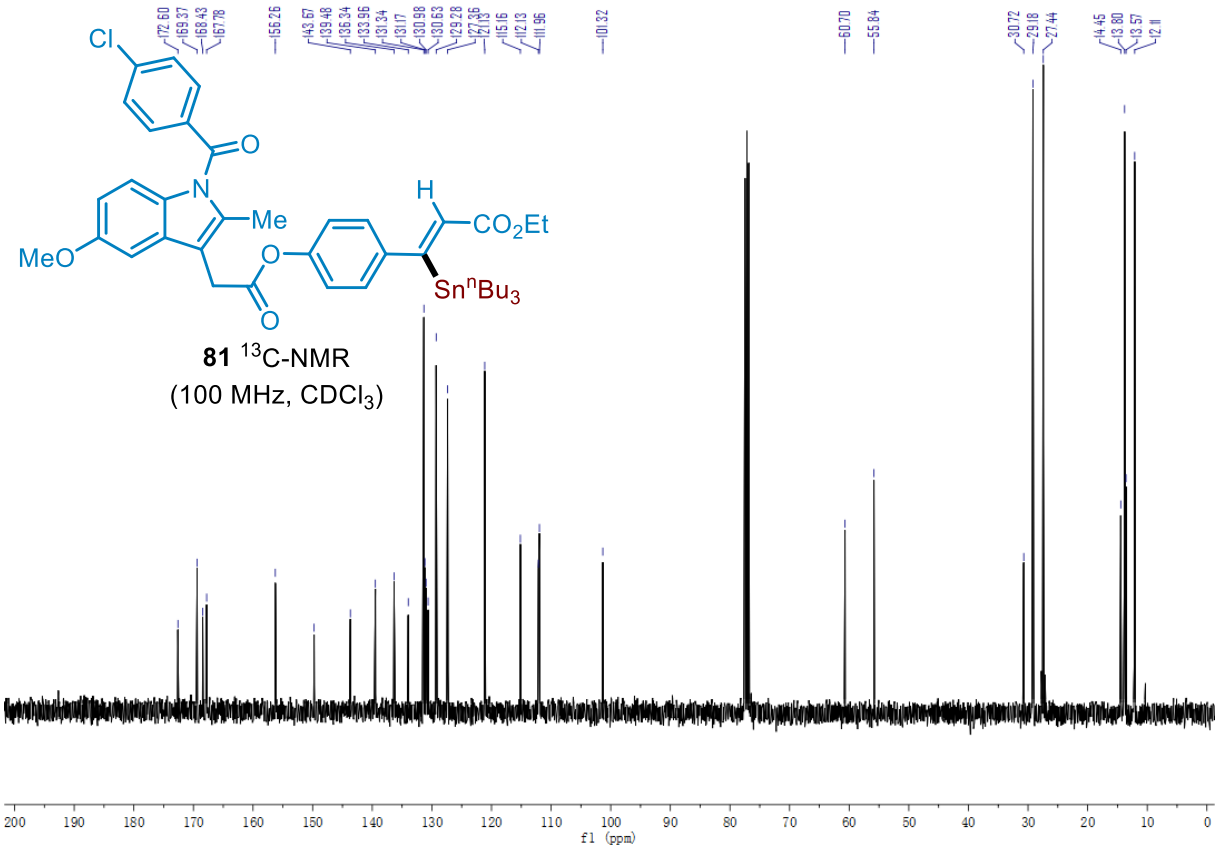
80 ^{13}C-NMR
(100 MHz, $CDCl_3$)



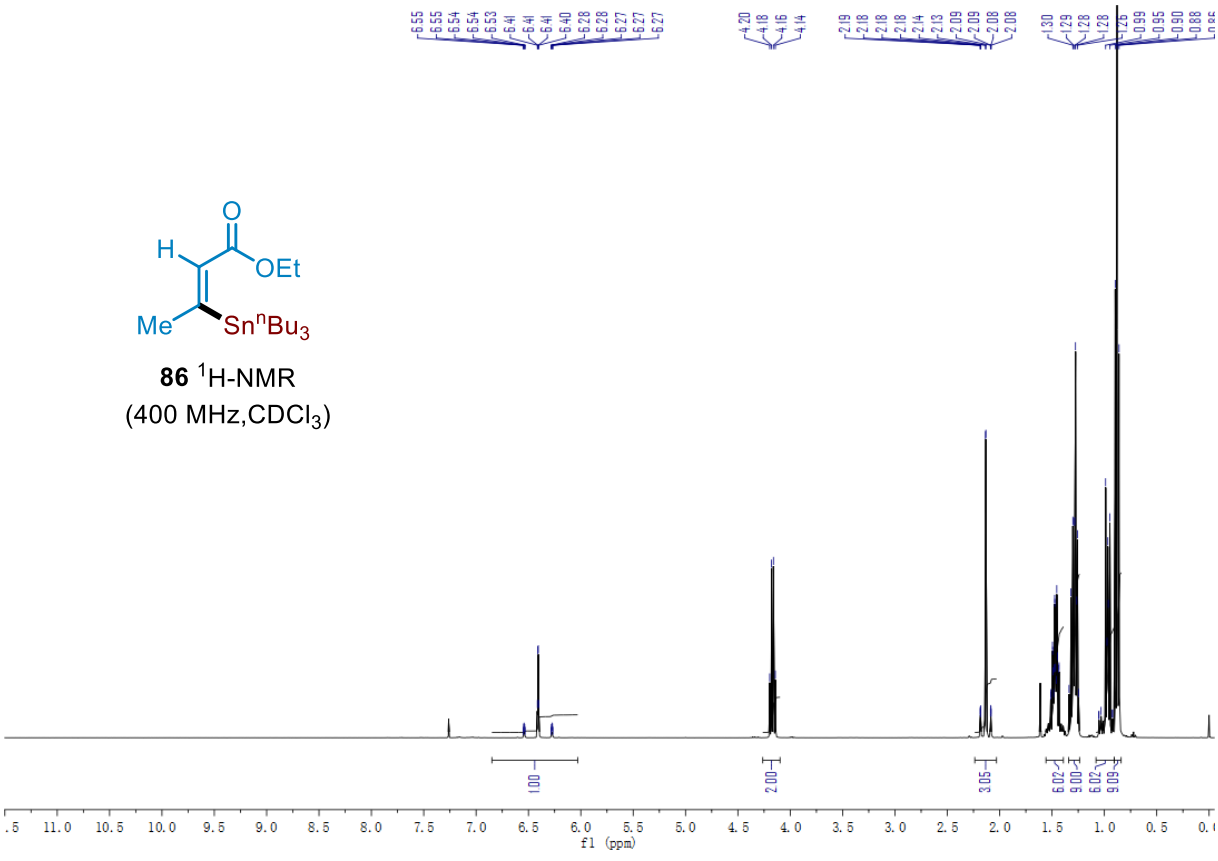
80 ^{19}F-NMR
(376 MHz, $CDCl_3$)



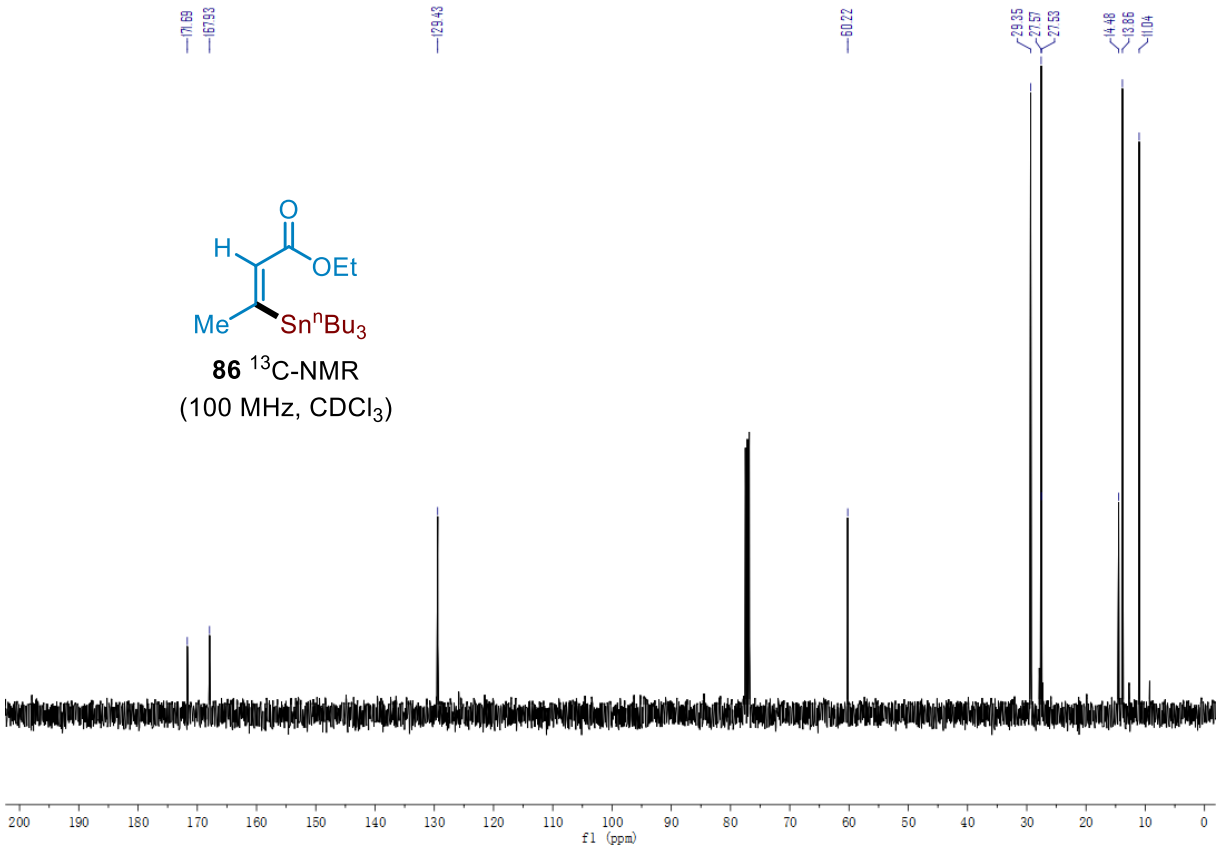
81 ^{1}H-NMR
(400 MHz,$CDCl_3$)



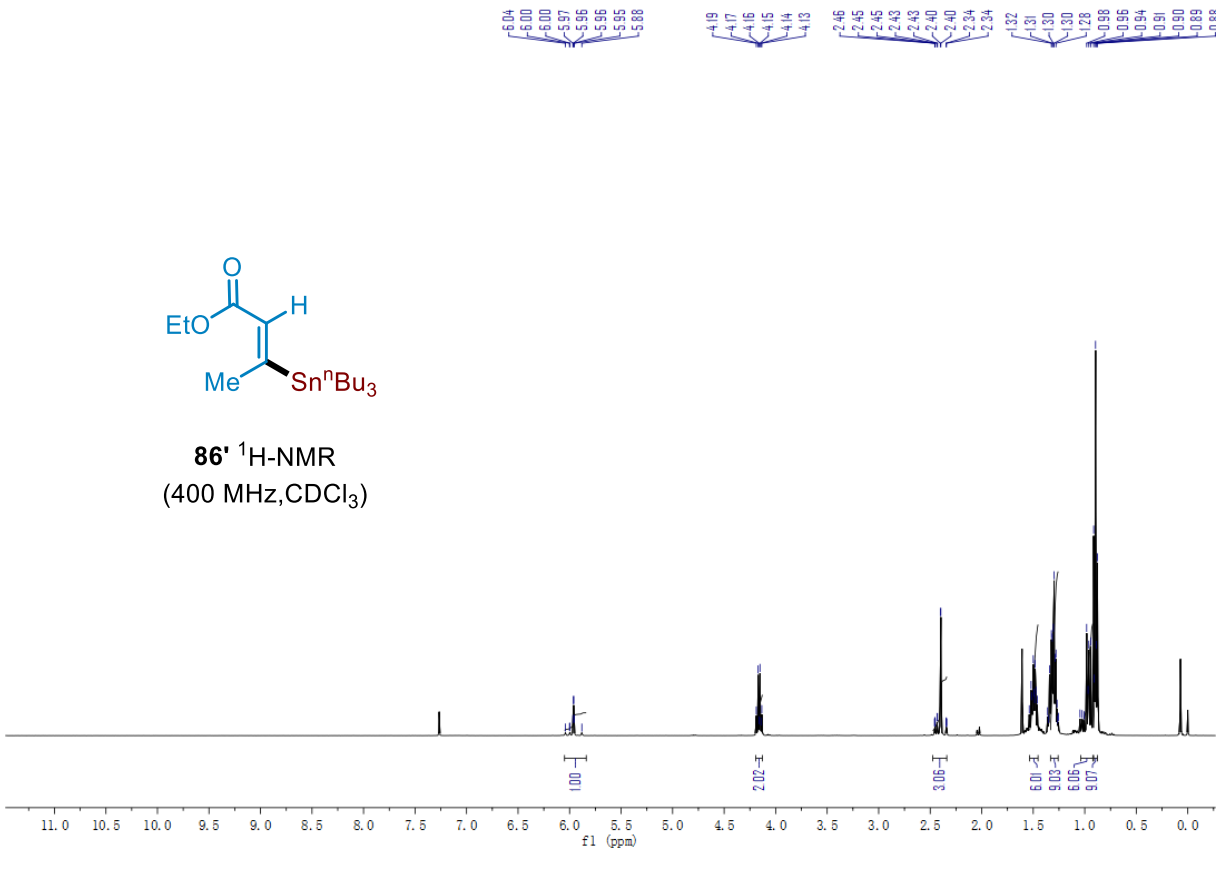
81 ^{13}C-NMR
(100 MHz, $CDCl_3$)



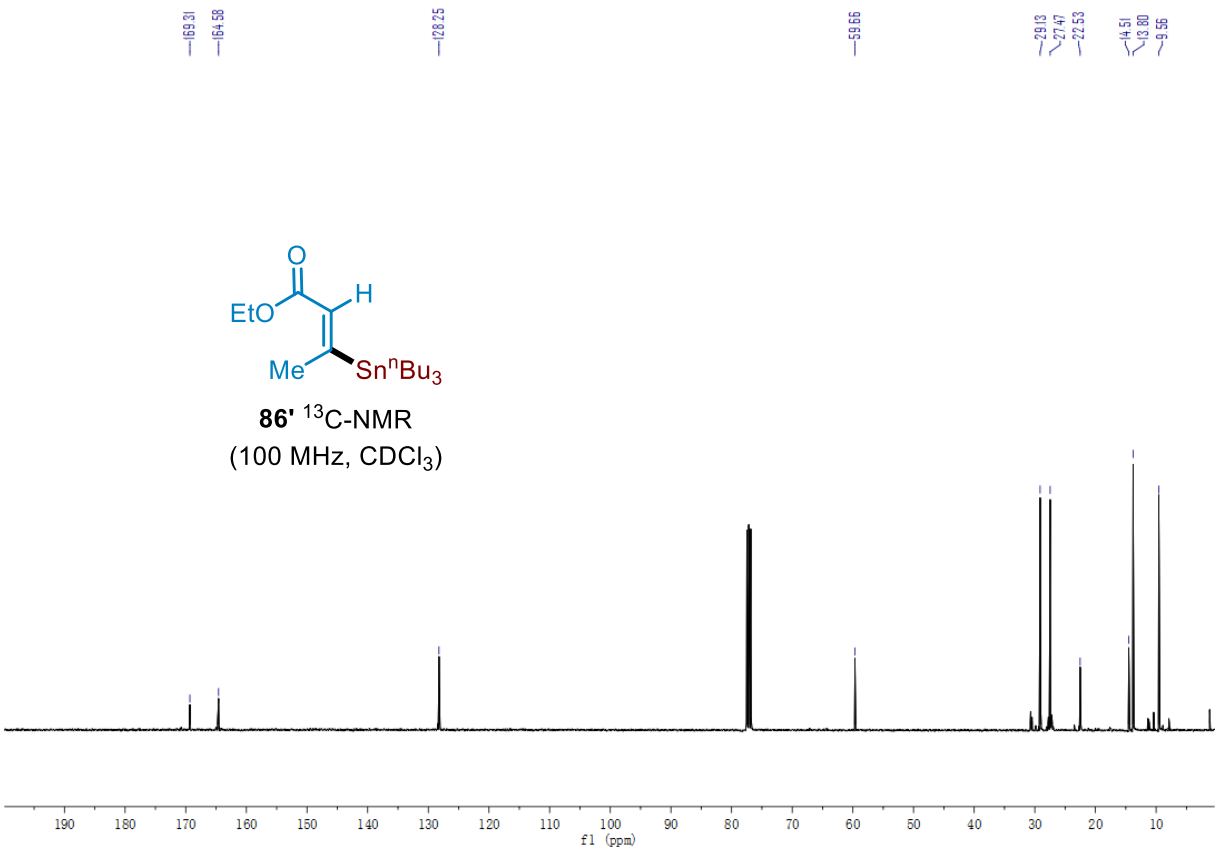
86 ^{1}H-NMR
(400 MHz,$CDCl_3$)



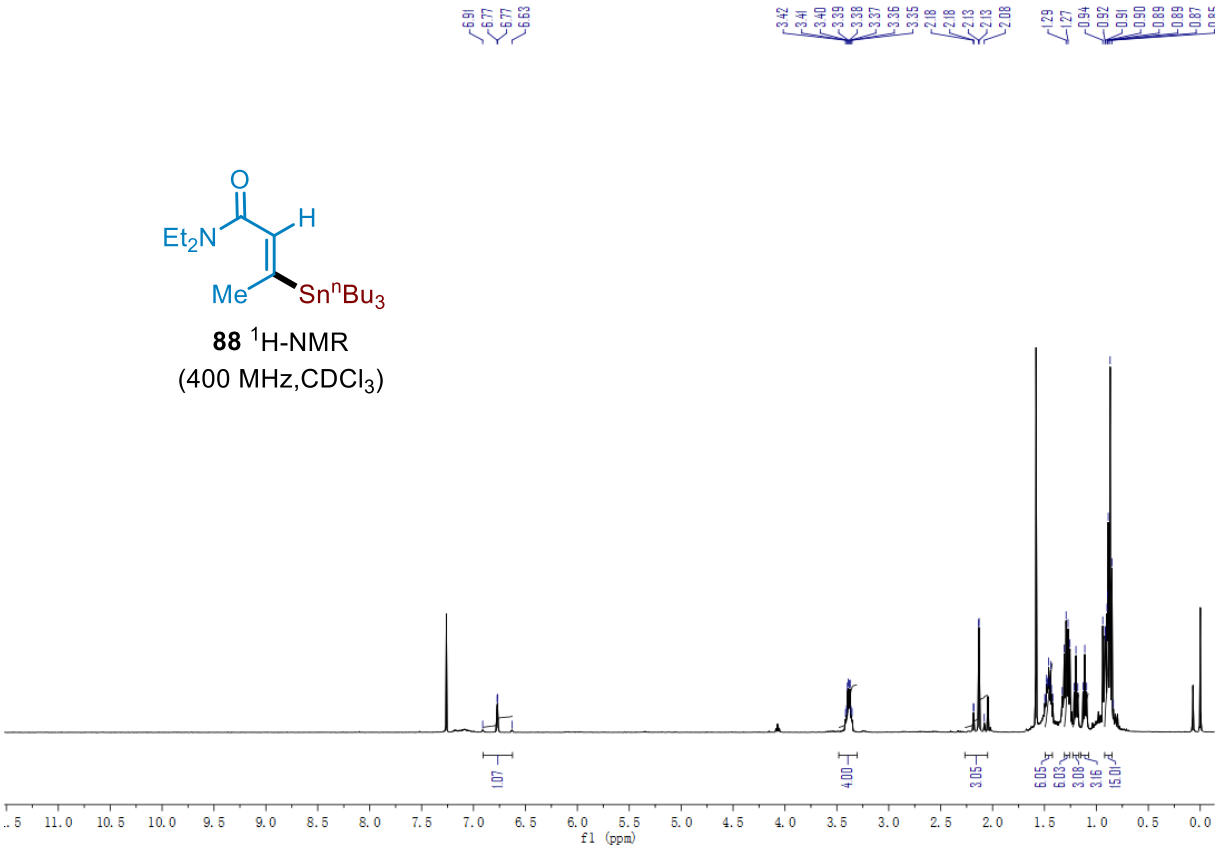
86 ^{13}C-NMR
(100 MHz, $CDCl_3$)



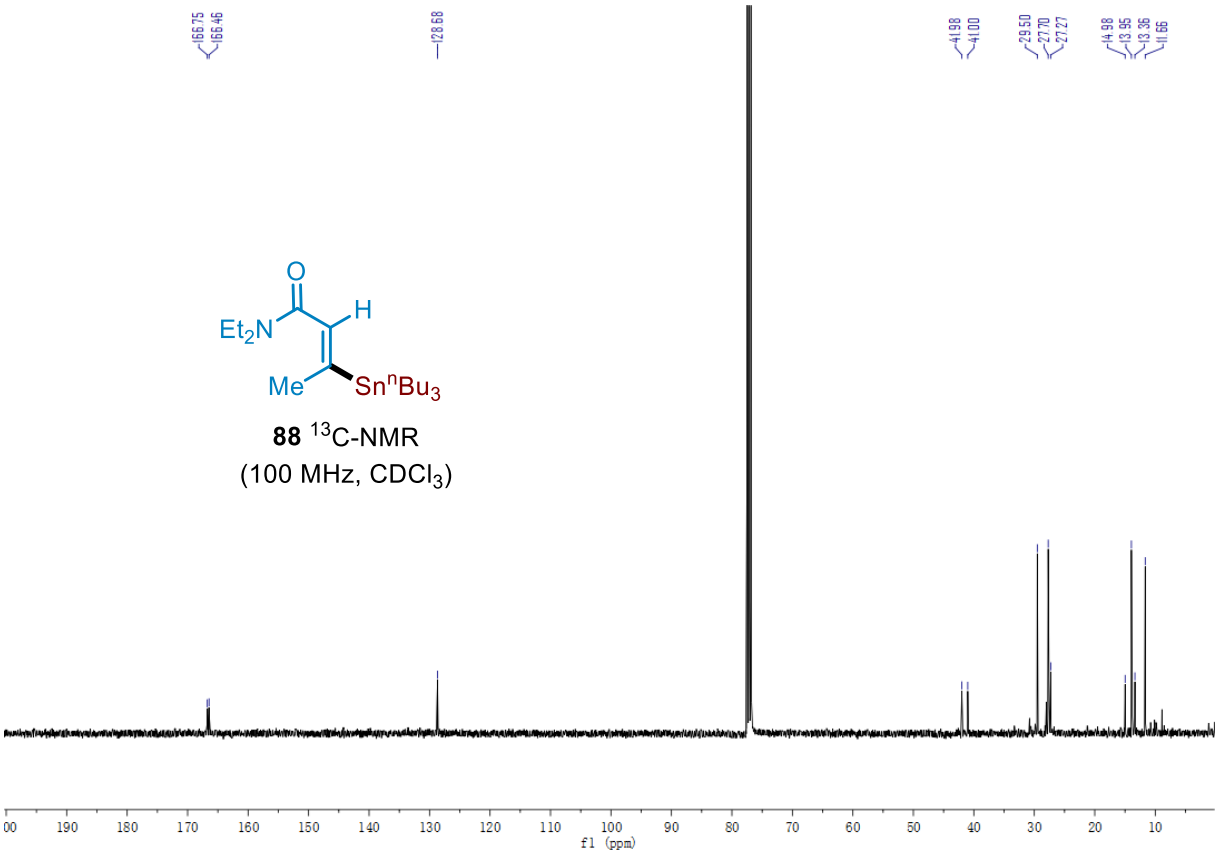
86' ^{1}H-NMR
(400 MHz,$CDCl_3$)



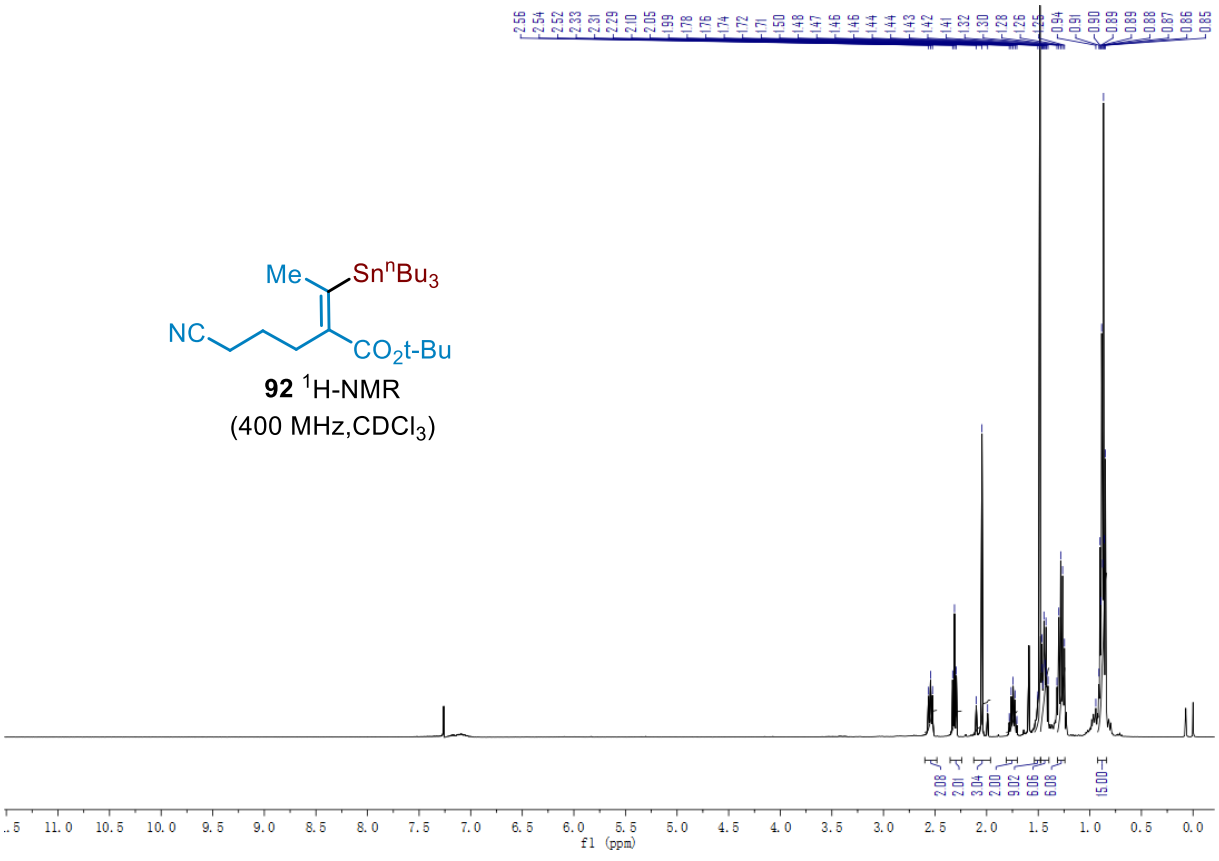
86' ^{13}C-NMR
(100 MHz, $CDCl_3$)



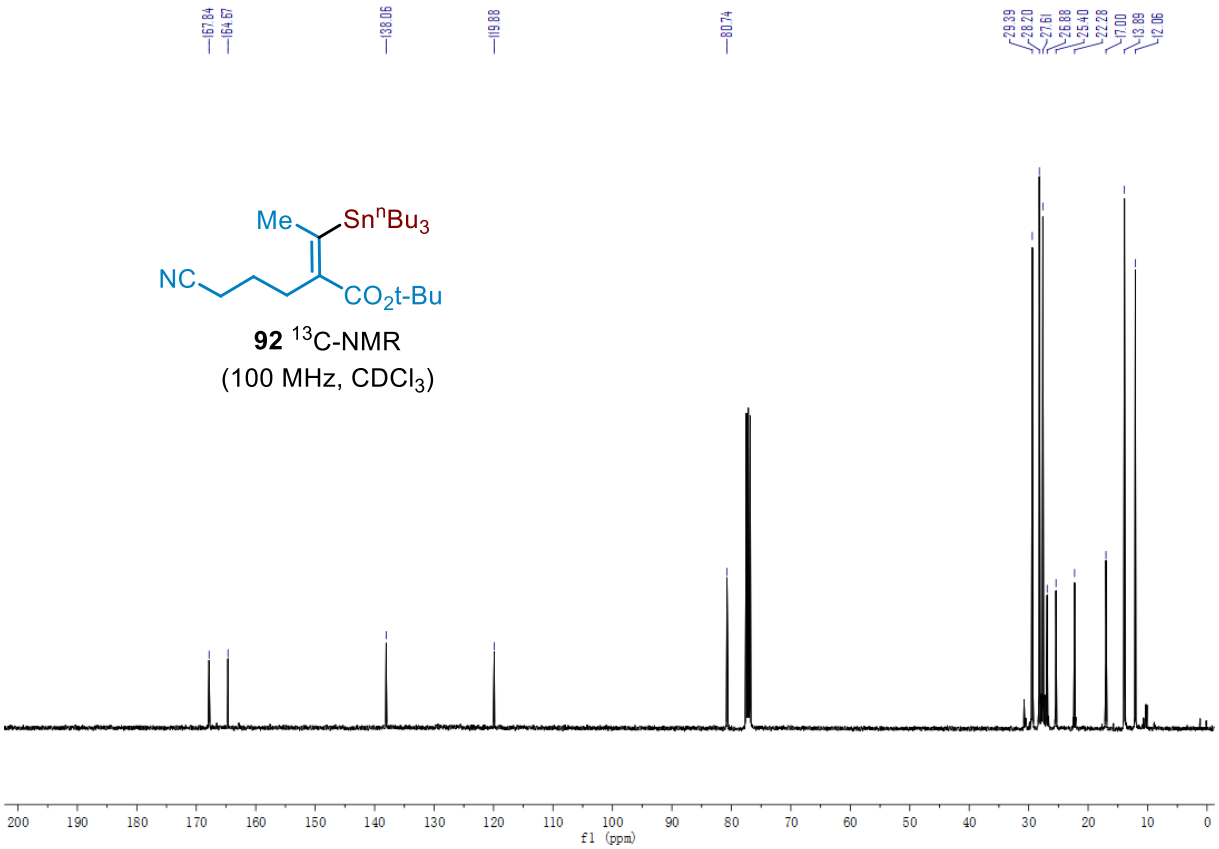
88 ^{1}H-NMR
(400 MHz,$CDCl_3$)



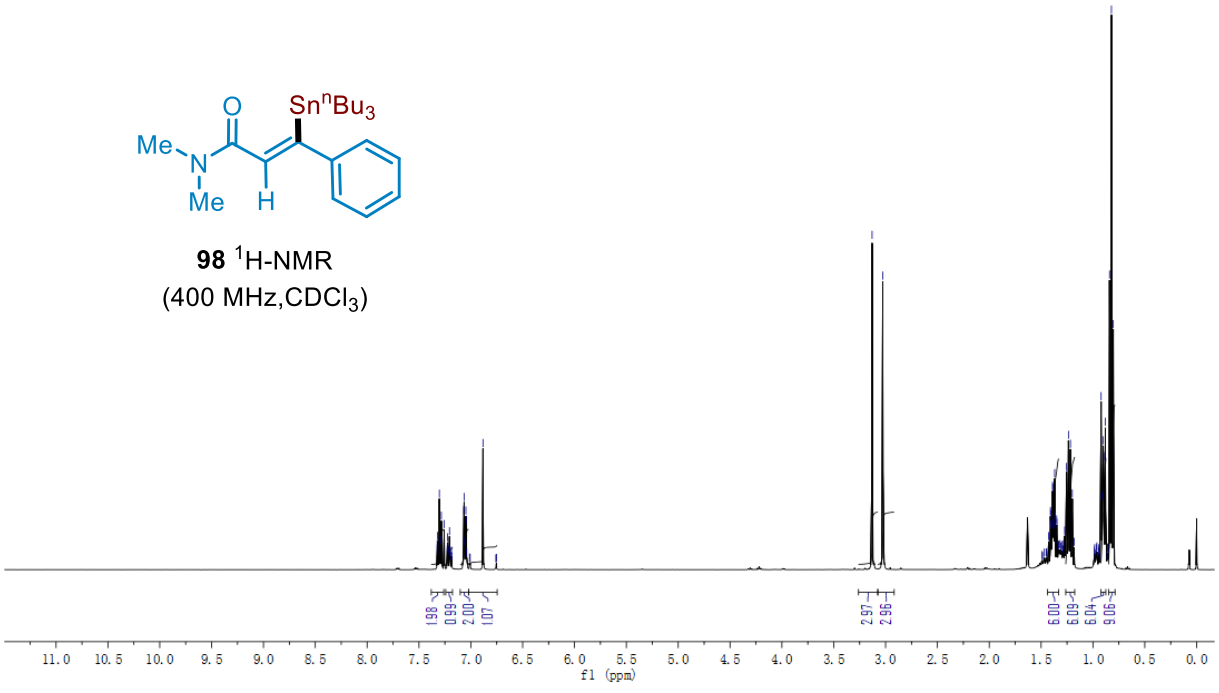
88 ^{13}C-NMR
(100 MHz, $CDCl_3$)



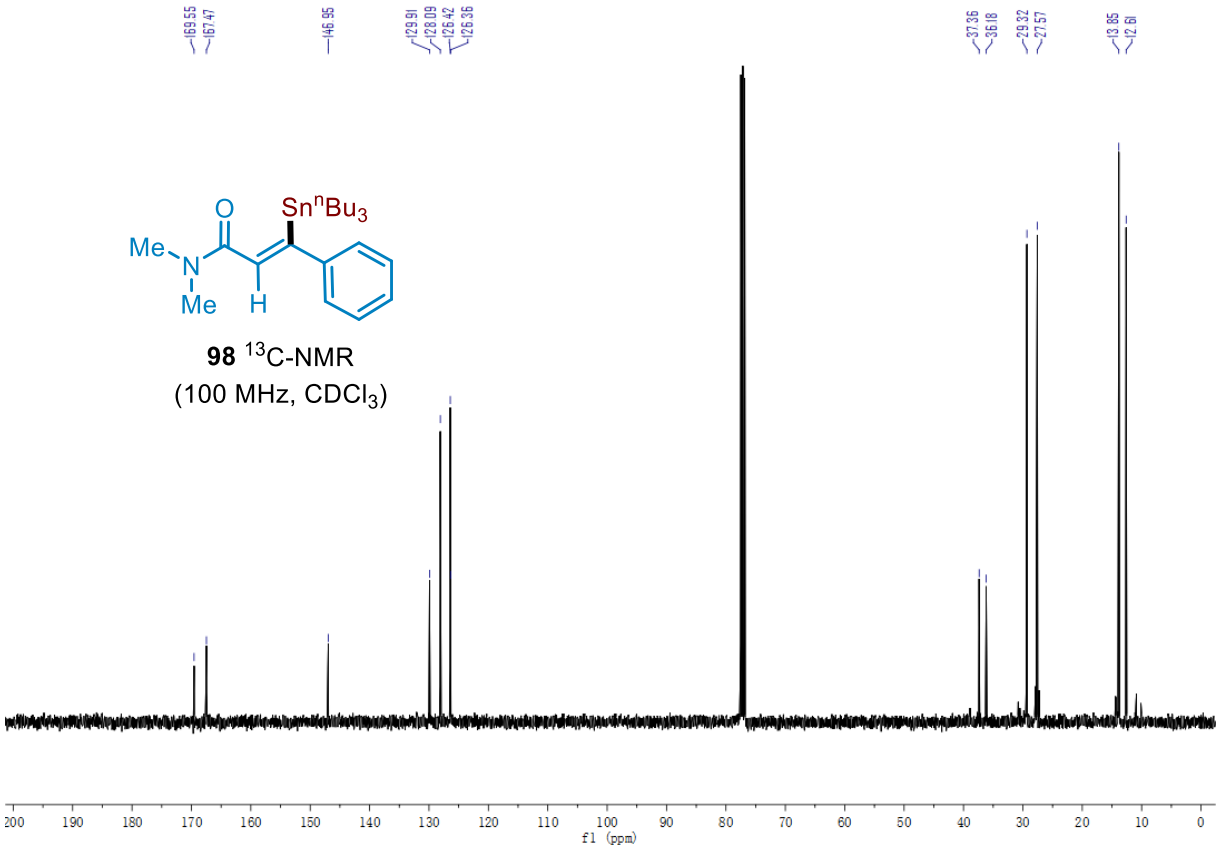
92 ^{1}H-NMR
(400 MHz,$CDCl_3$)



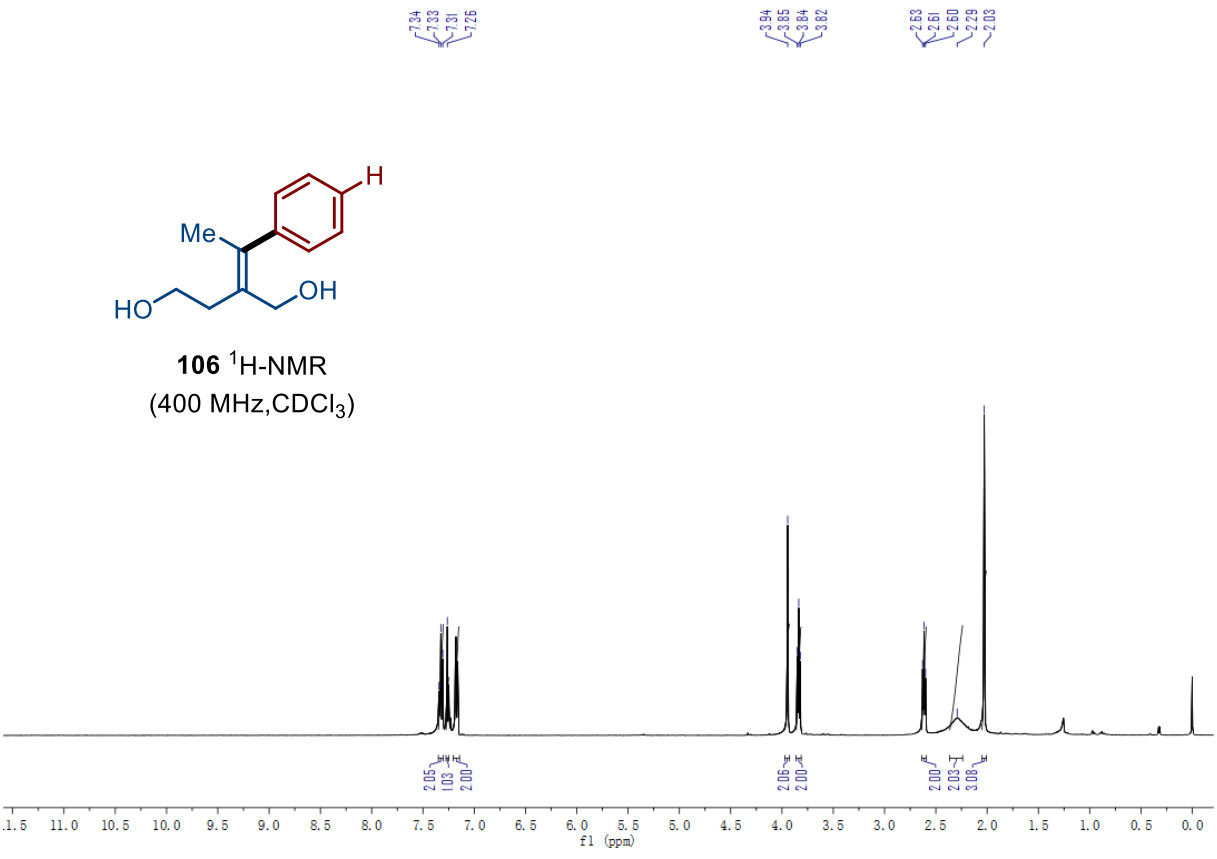
92 ^{13}C-NMR
(100 MHz, $CDCl_3$)



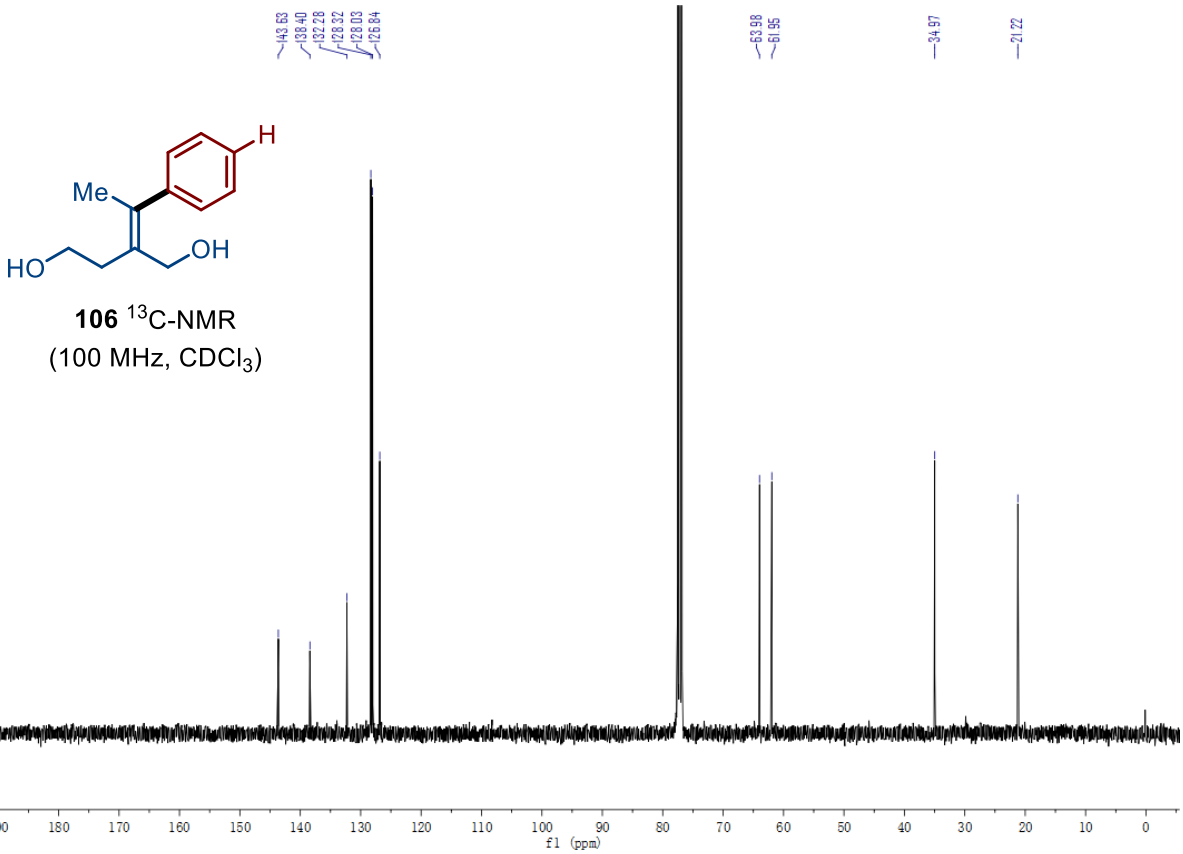
98 ^{1}H-NMR
(400 MHz,$CDCl_3$)



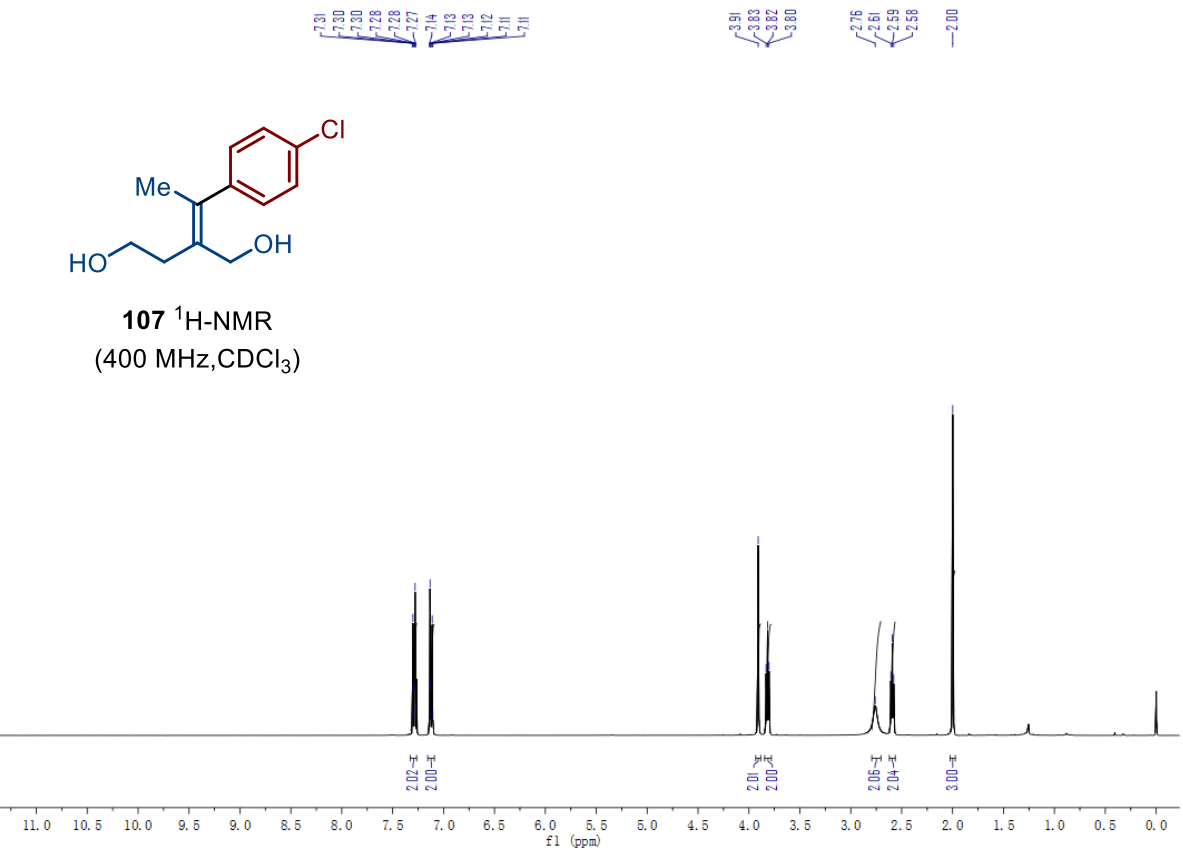
98 ^{13}C-NMR
(100 MHz, $CDCl_3$)



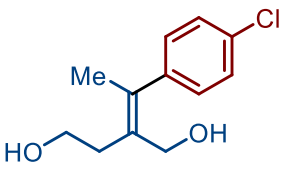
106 ^{1}H-NMR
(400 MHz,$CDCl_3$)



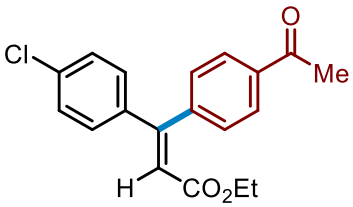
106 ^{13}C-NMR
(100 MHz, $CDCl_3$)



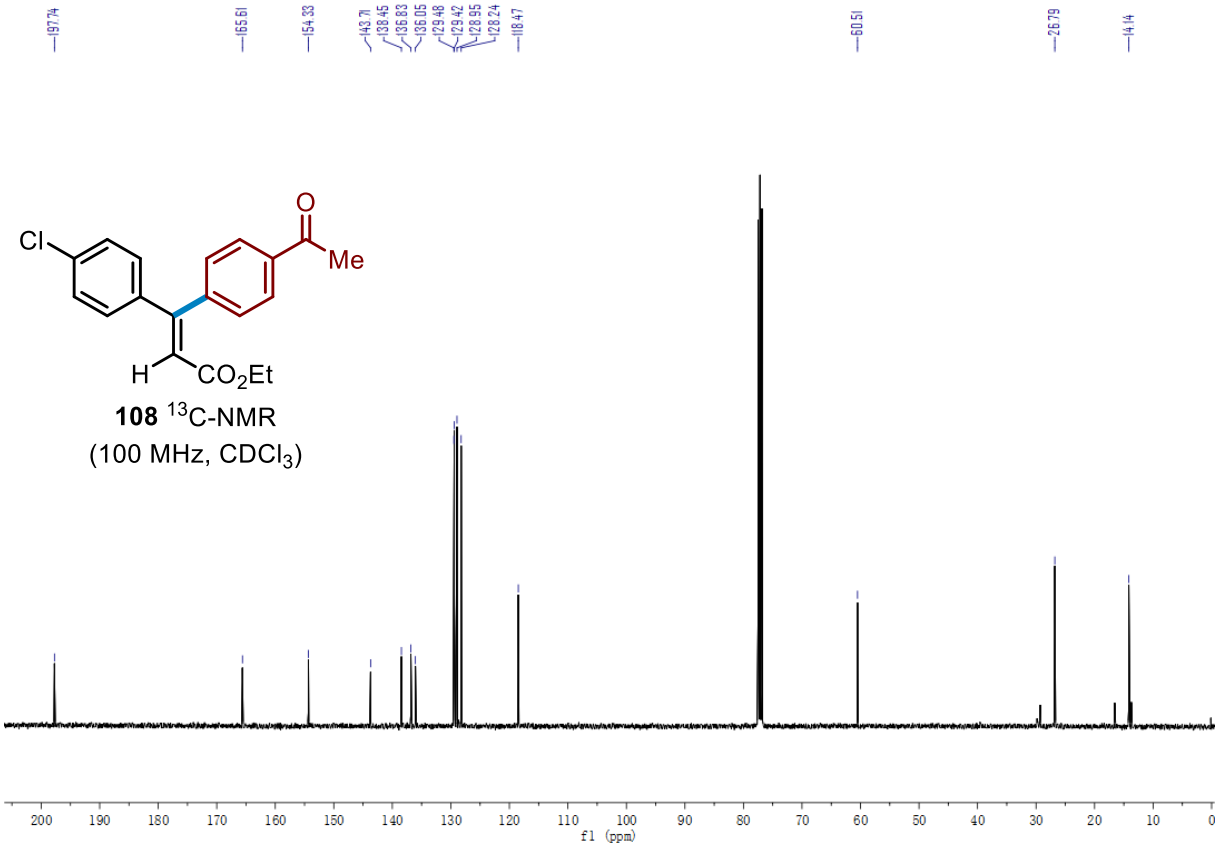
107 ^{1}H-NMR
(400 MHz,$CDCl_3$)



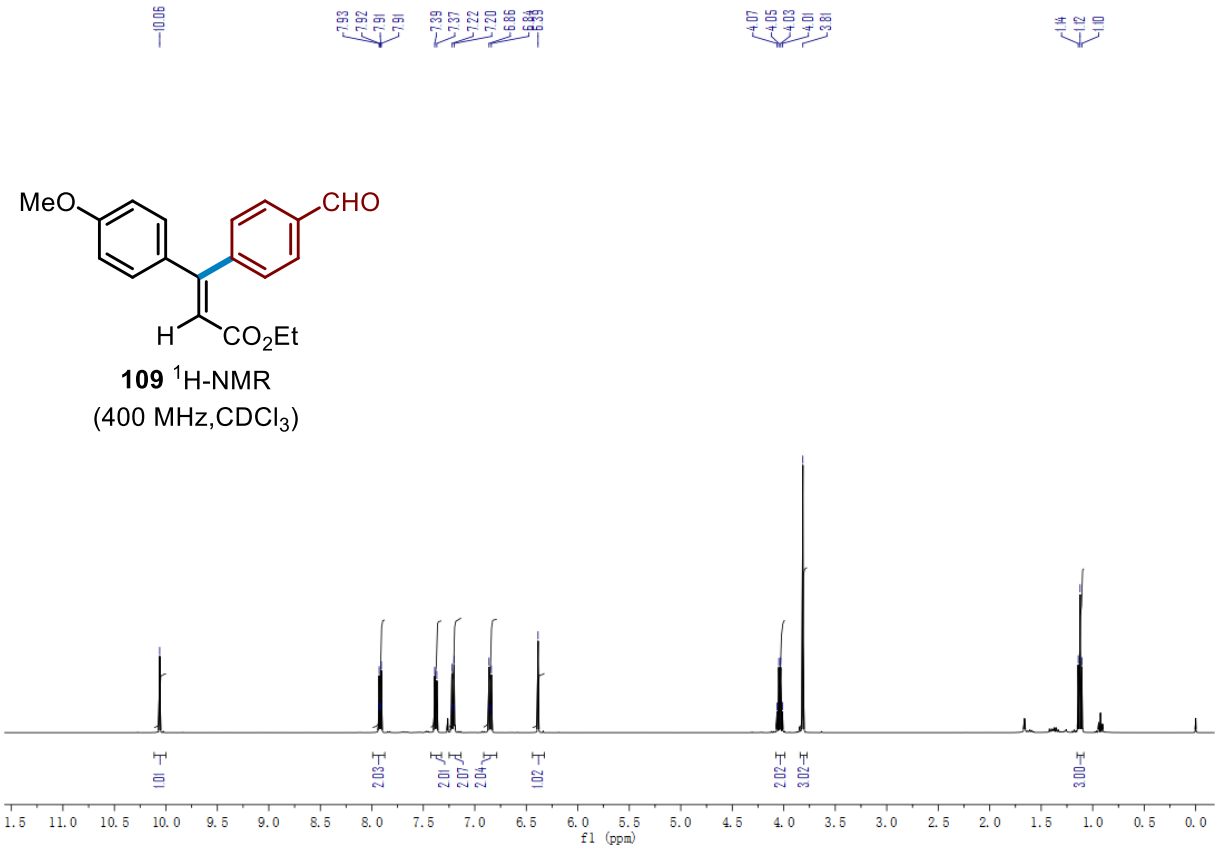
107 ^{13}C-NMR
(100 MHz, $CDCl_3$)



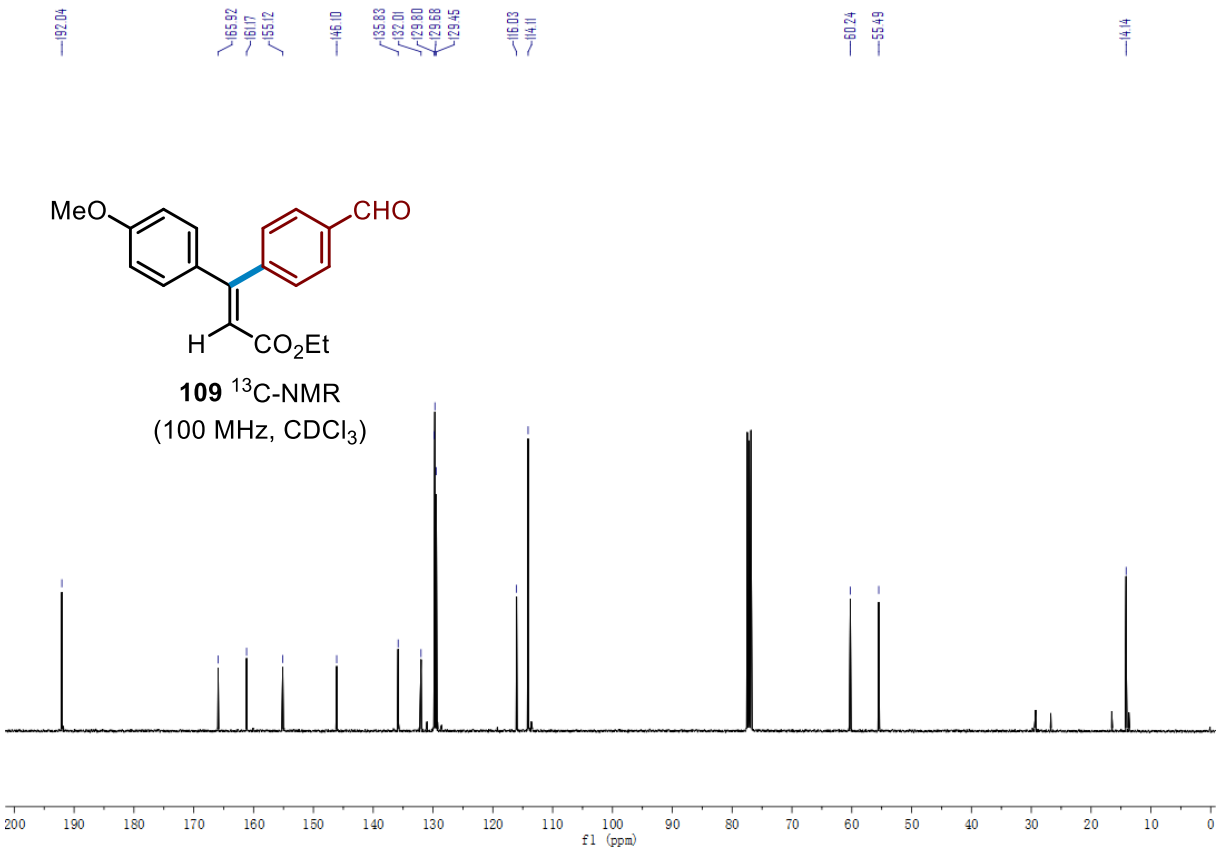
108 ^{1}H-NMR
(400 MHz,$CDCl_3$)



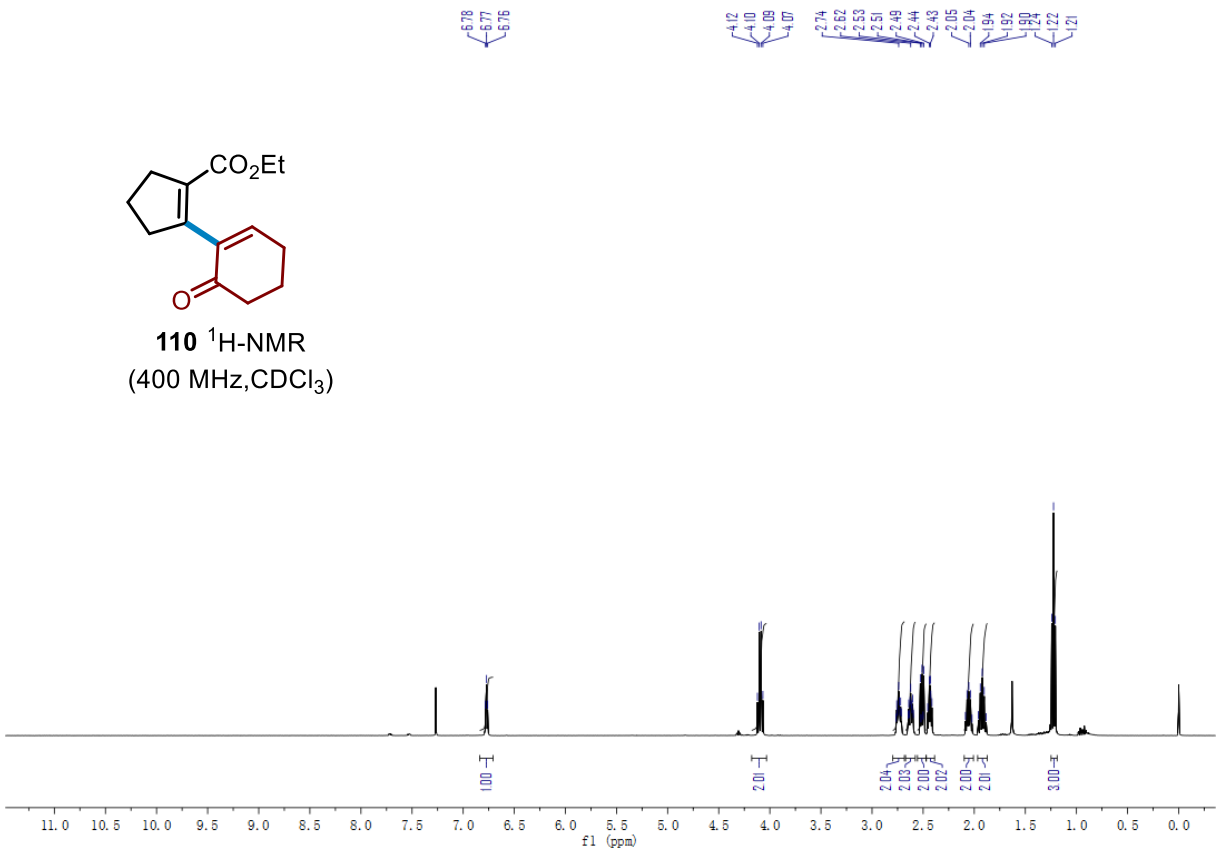
108 ^{13}C-NMR
(100 MHz, $CDCl_3$)



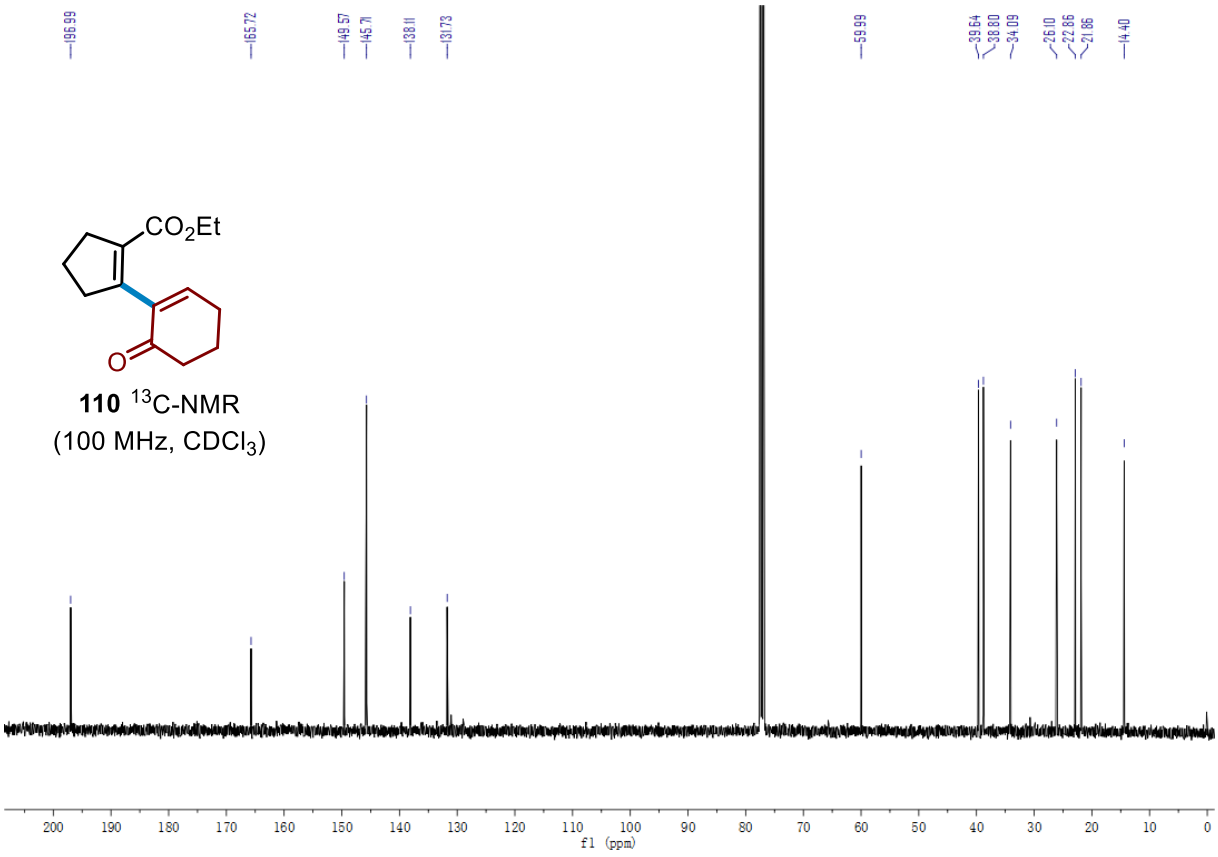
109 ^{1}H-NMR
(400 MHz,$CDCl_3$)



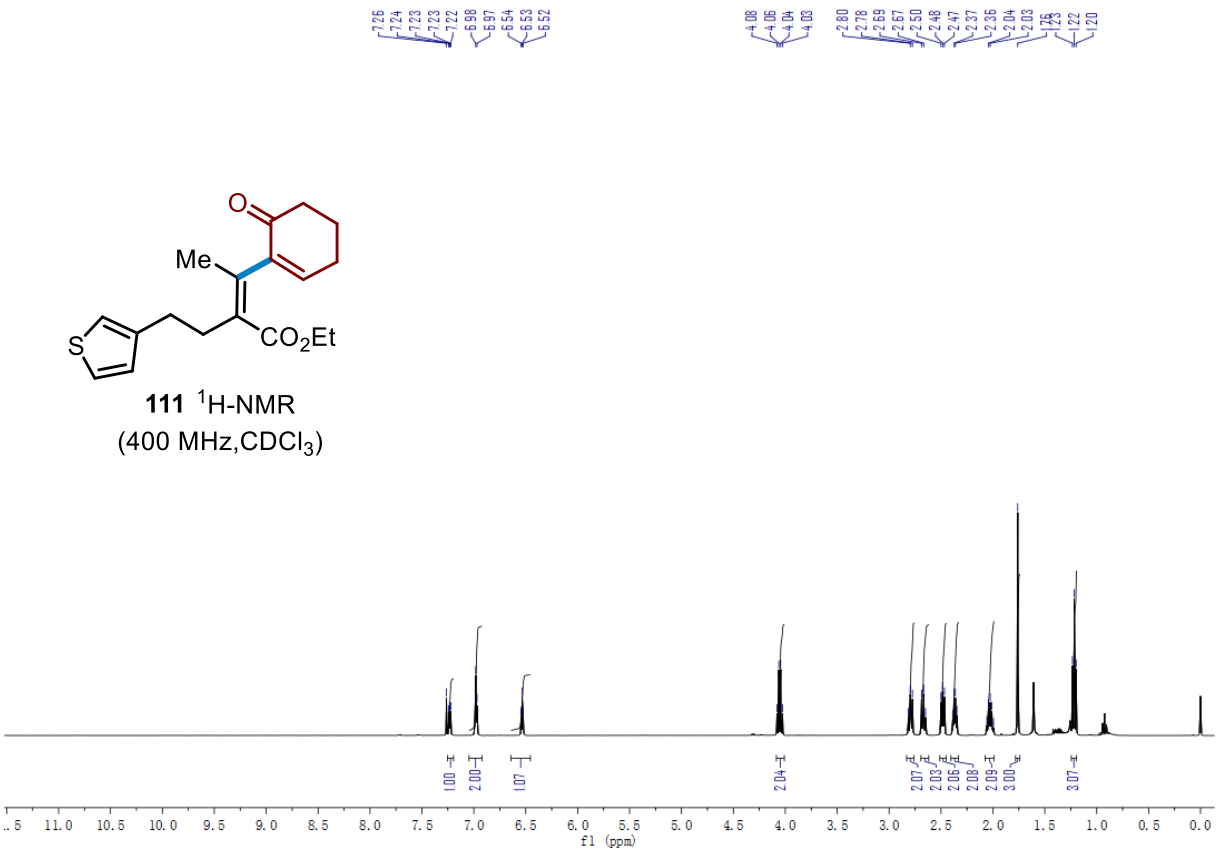
109 ^{13}C-NMR
(100 MHz, $CDCl_3$)



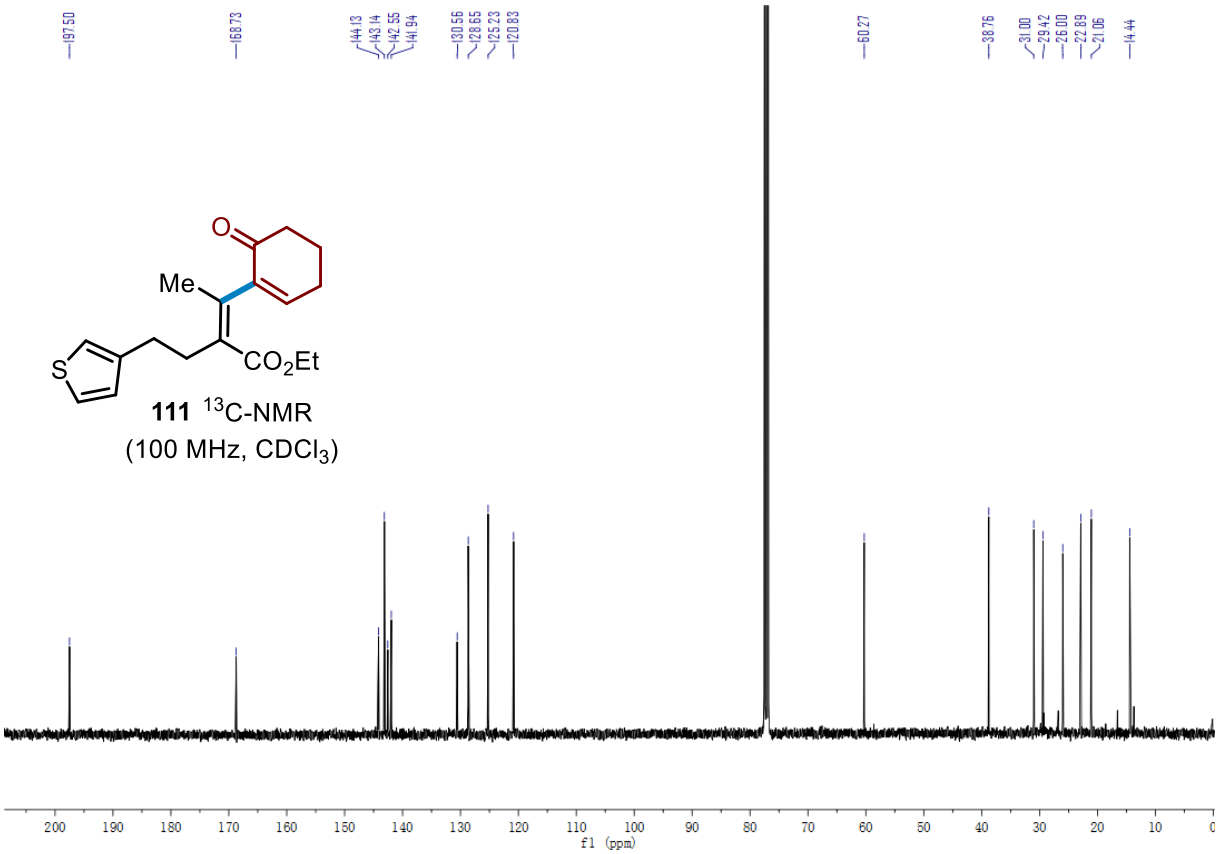
110 ^{1}H-NMR
(400 MHz,$CDCl_3$)



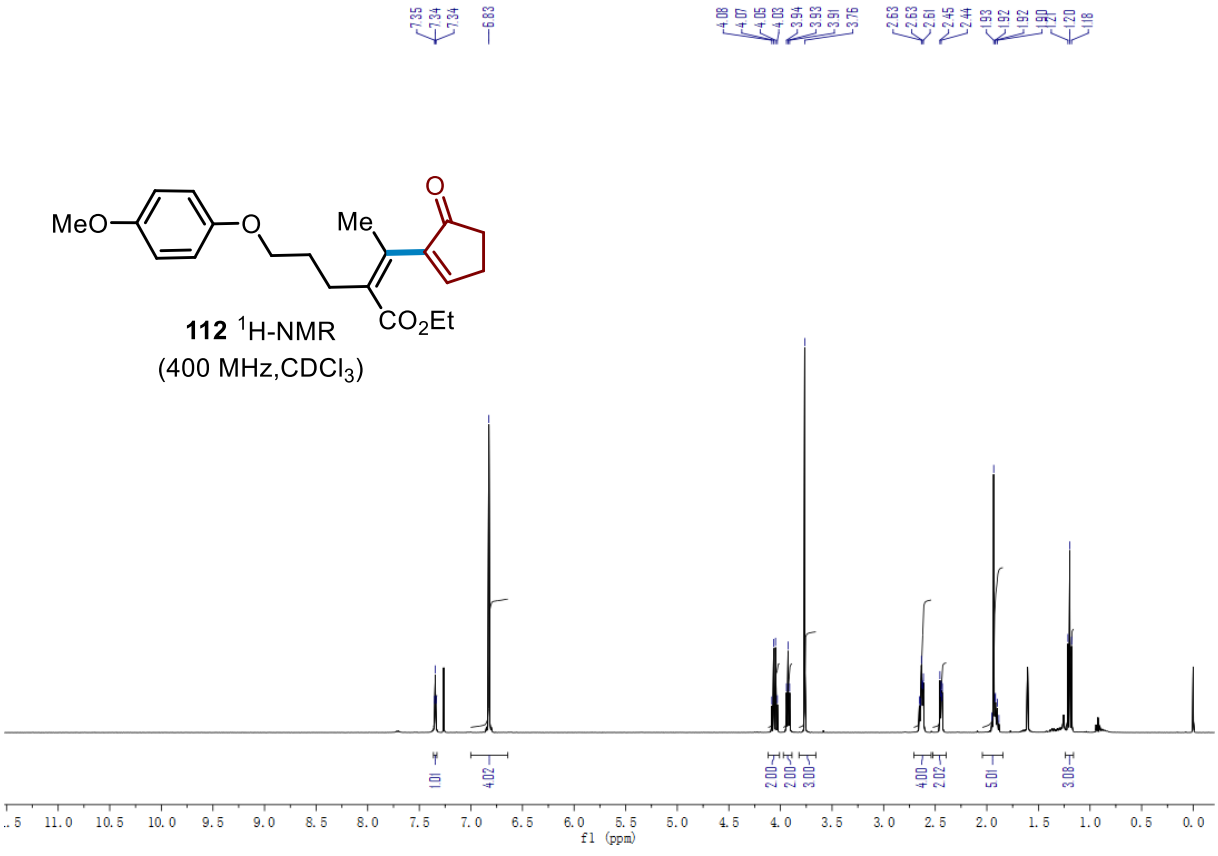
110 ^{13}C-NMR
(100 MHz, $CDCl_3$)



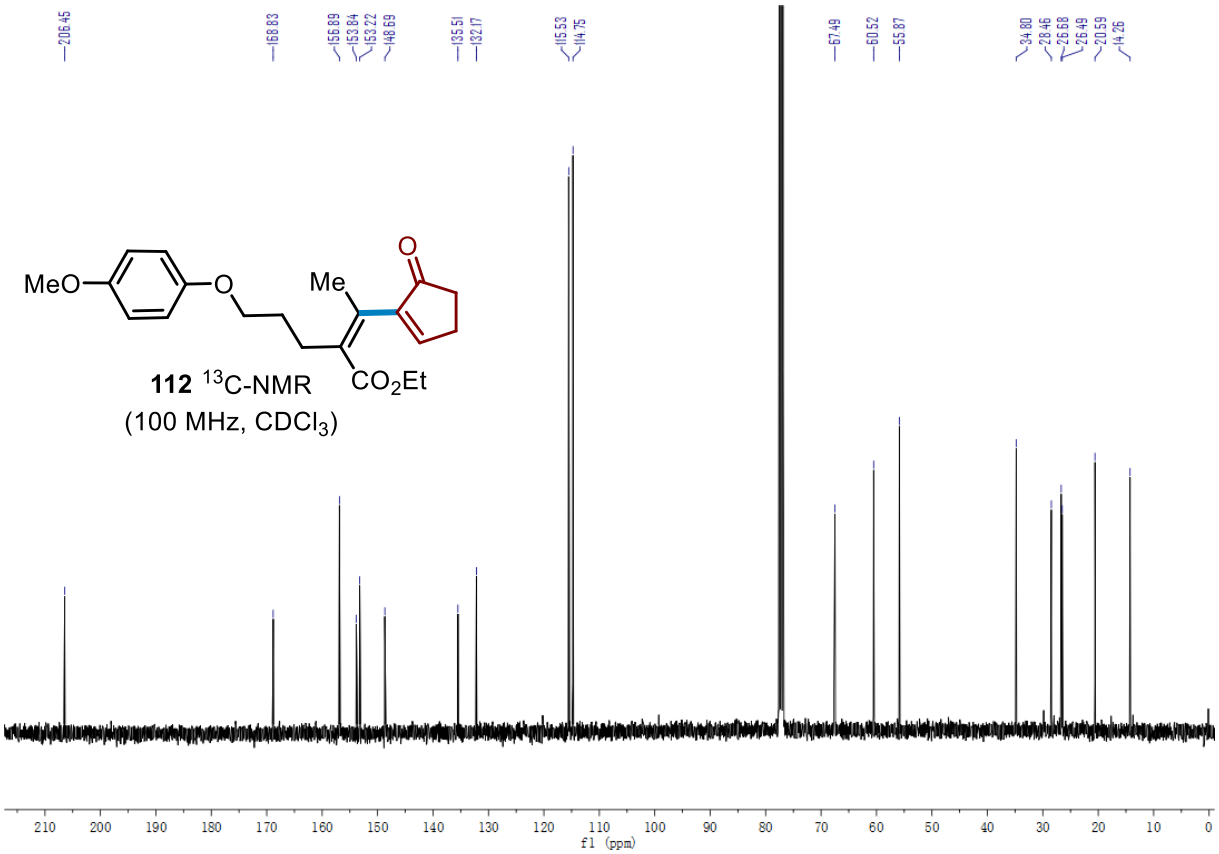
111 ^{1}H-NMR
(400 MHz,$CDCl_3$)



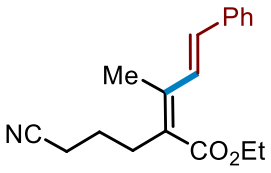
111 ^{13}C-NMR
(100 MHz, $CDCl_3$)



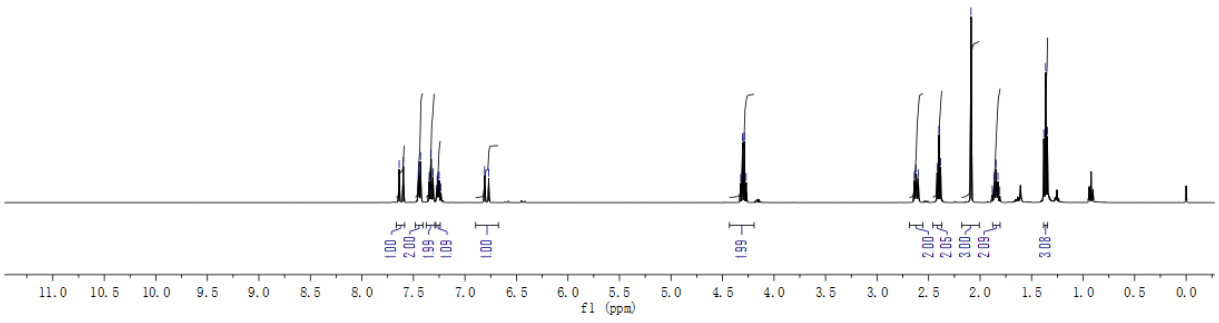
112 ^{1}H-NMR
(400 MHz,$CDCl_3$)

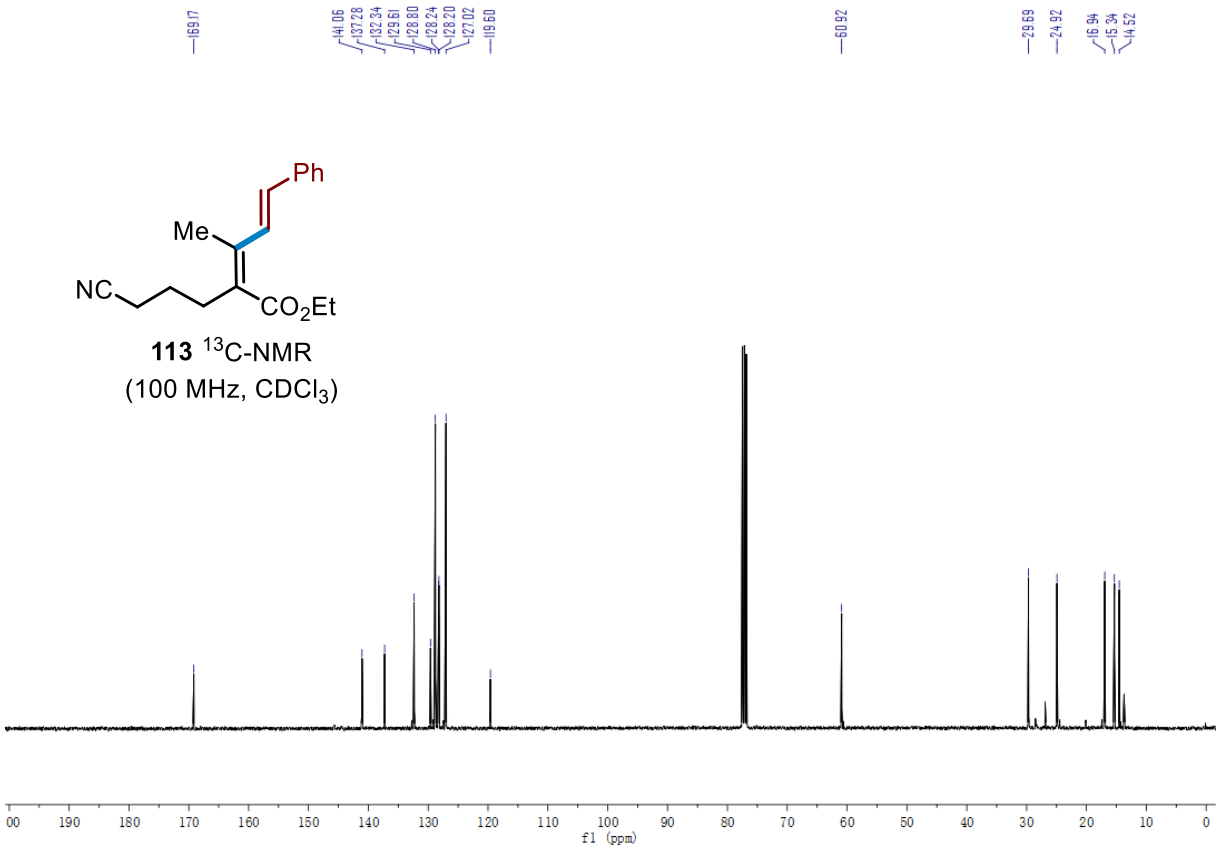


112 ^{13}C-NMR
(100 MHz, $CDCl_3$)

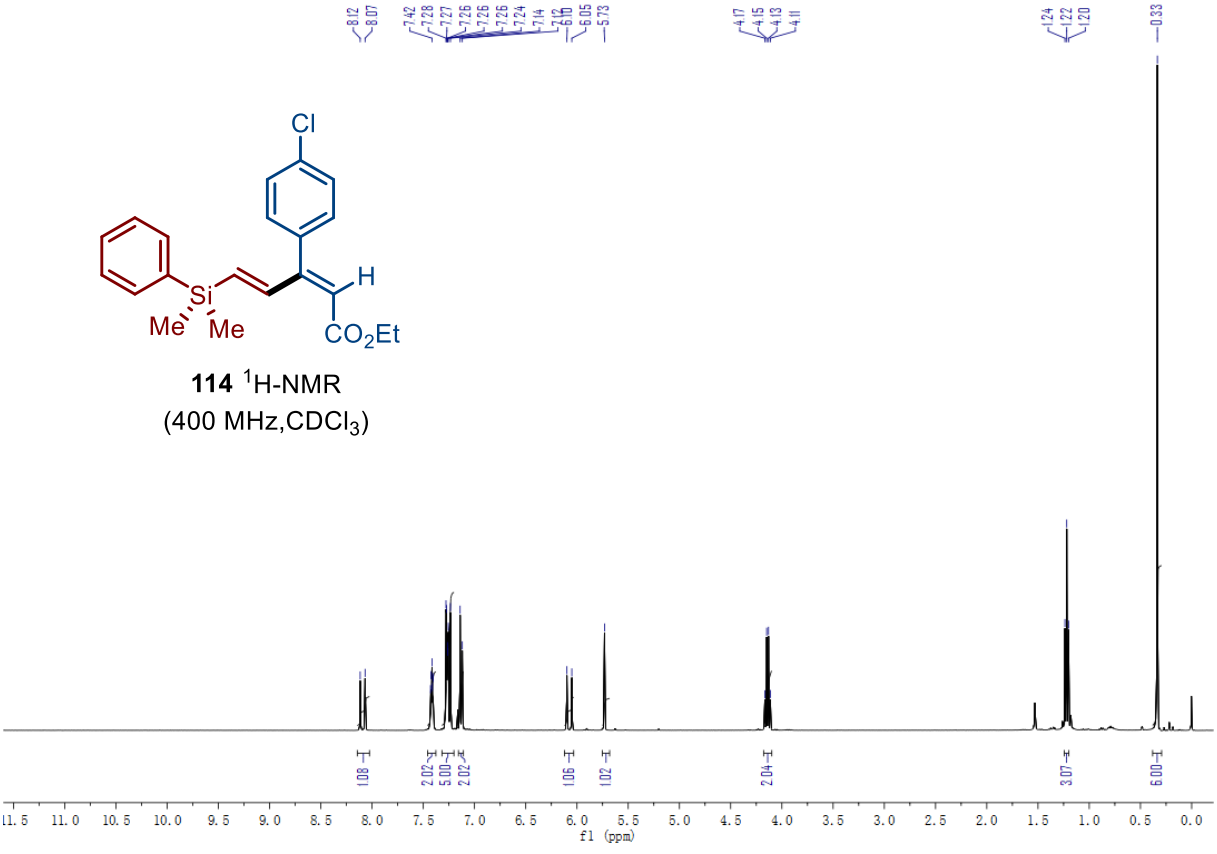


113 ^{1}H-NMR
(400 MHz,$CDCl_3$)

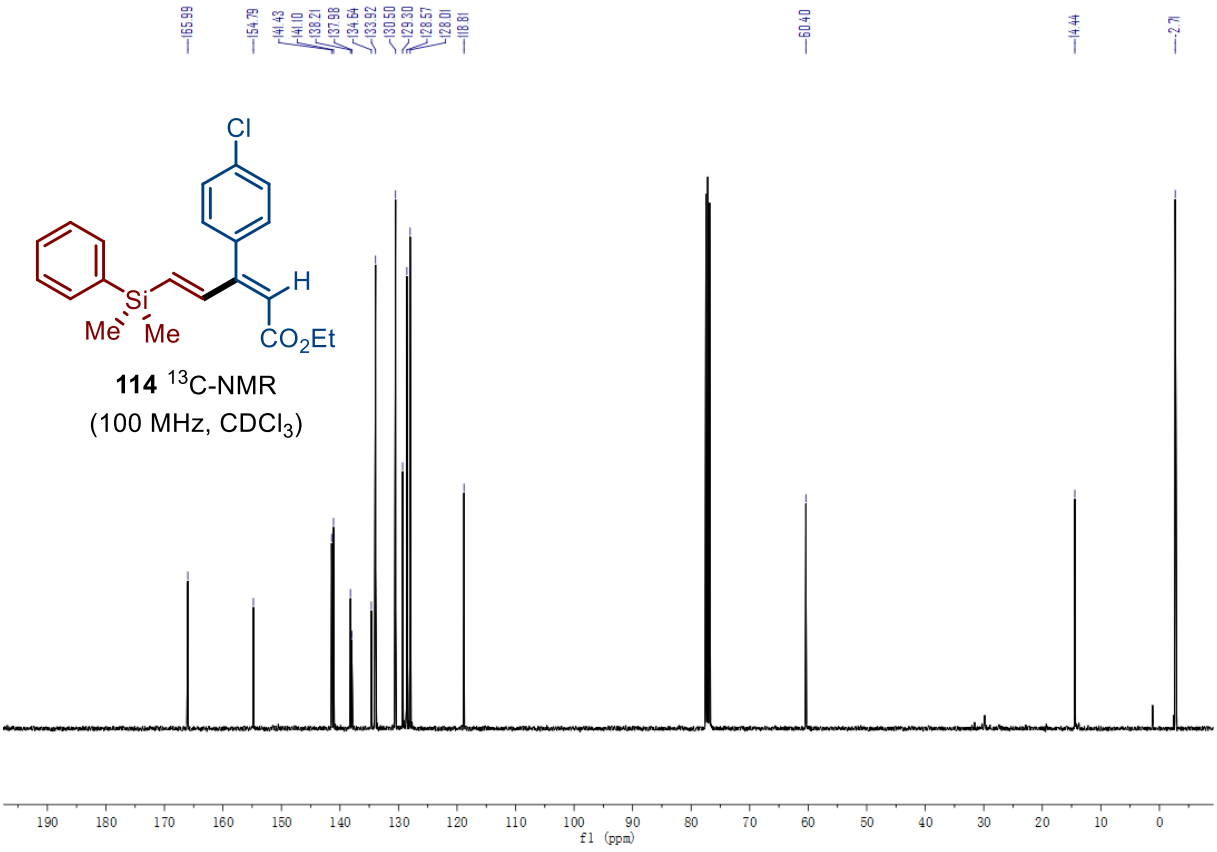




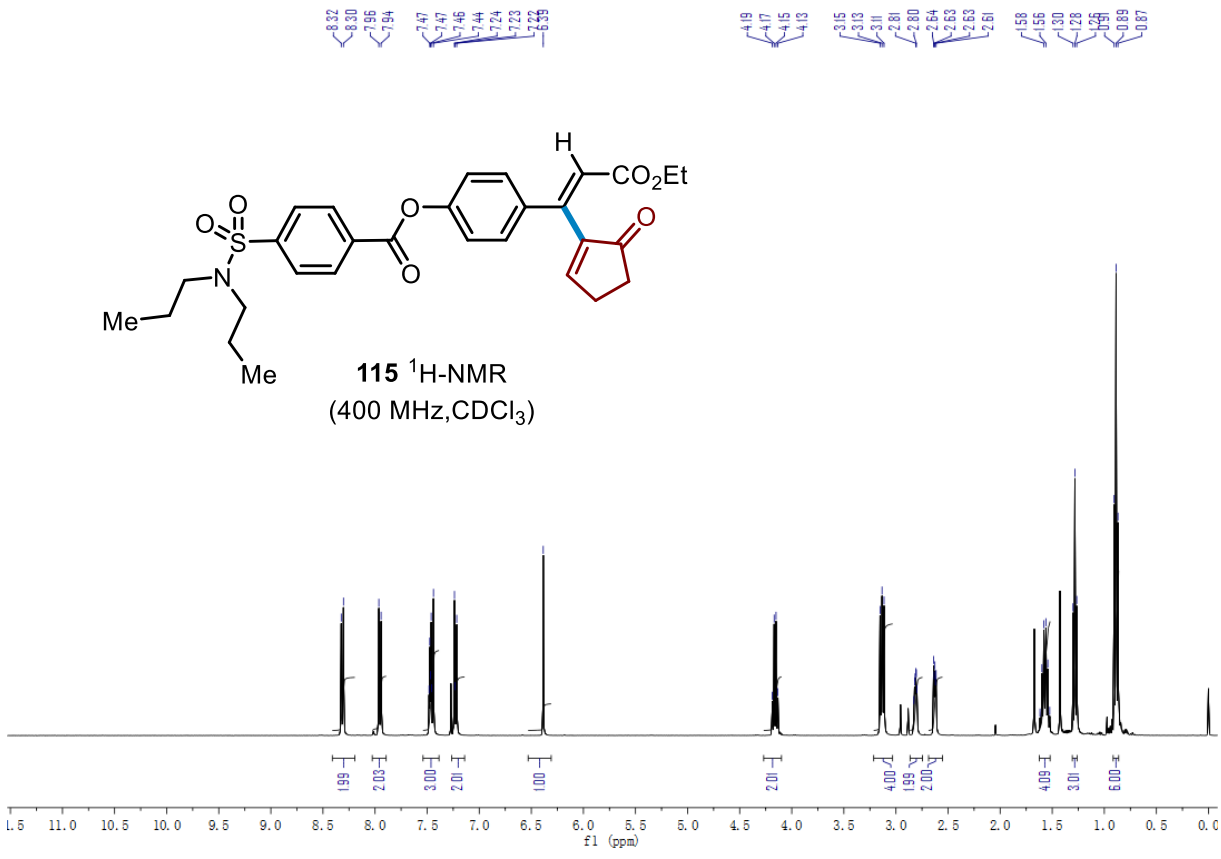
113 ^{13}C-NMR
(100 MHz, $CDCl_3$)



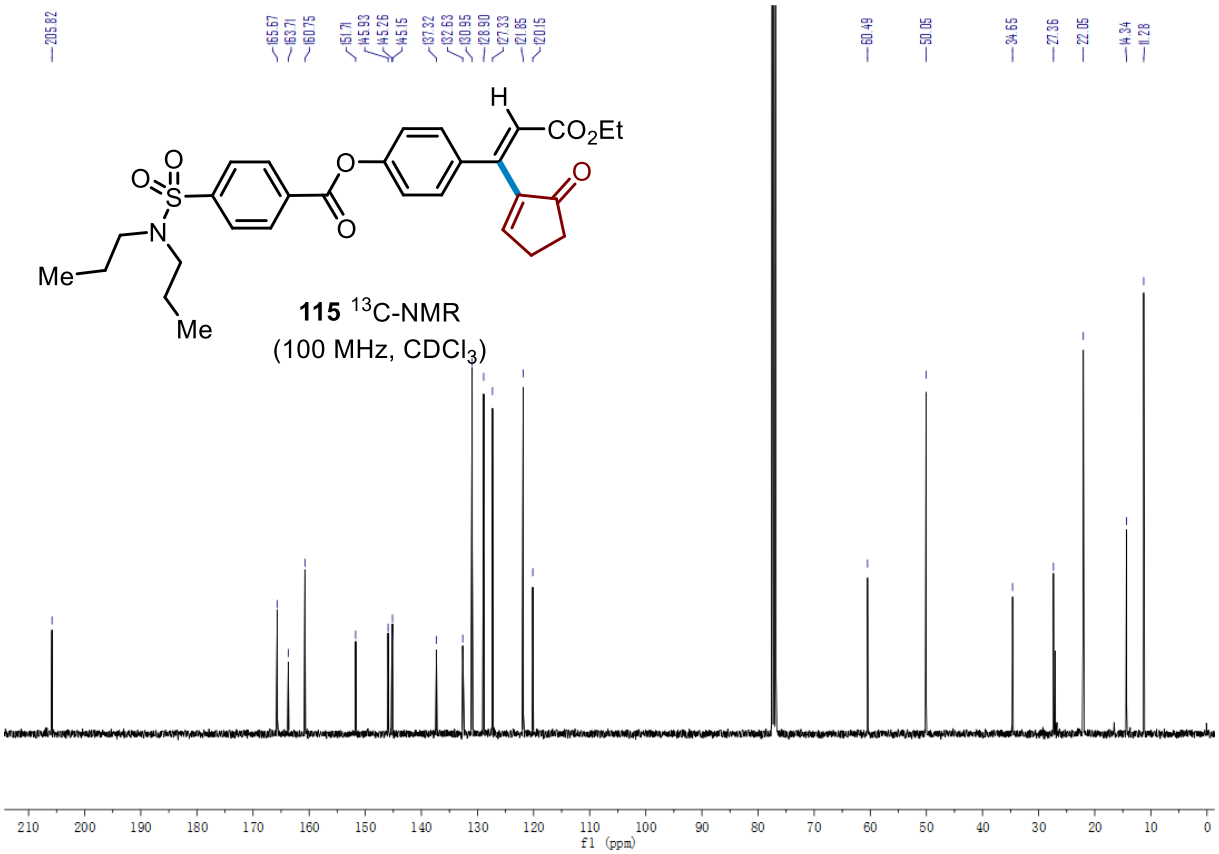
114 ^{1}H-NMR
(400 MHz,$CDCl_3$)



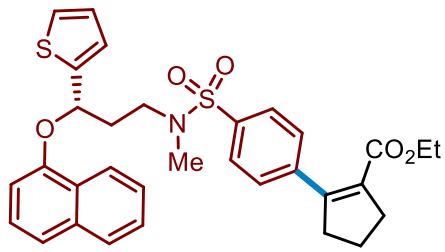
114 ^{13}C-NMR
(100 MHz, $CDCl_3$)



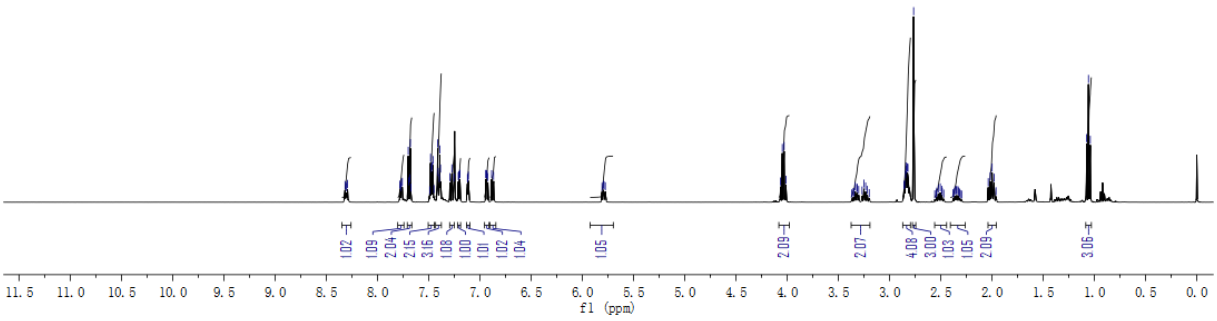
115 ^{1}H-NMR
(400 MHz,$CDCl_3$)

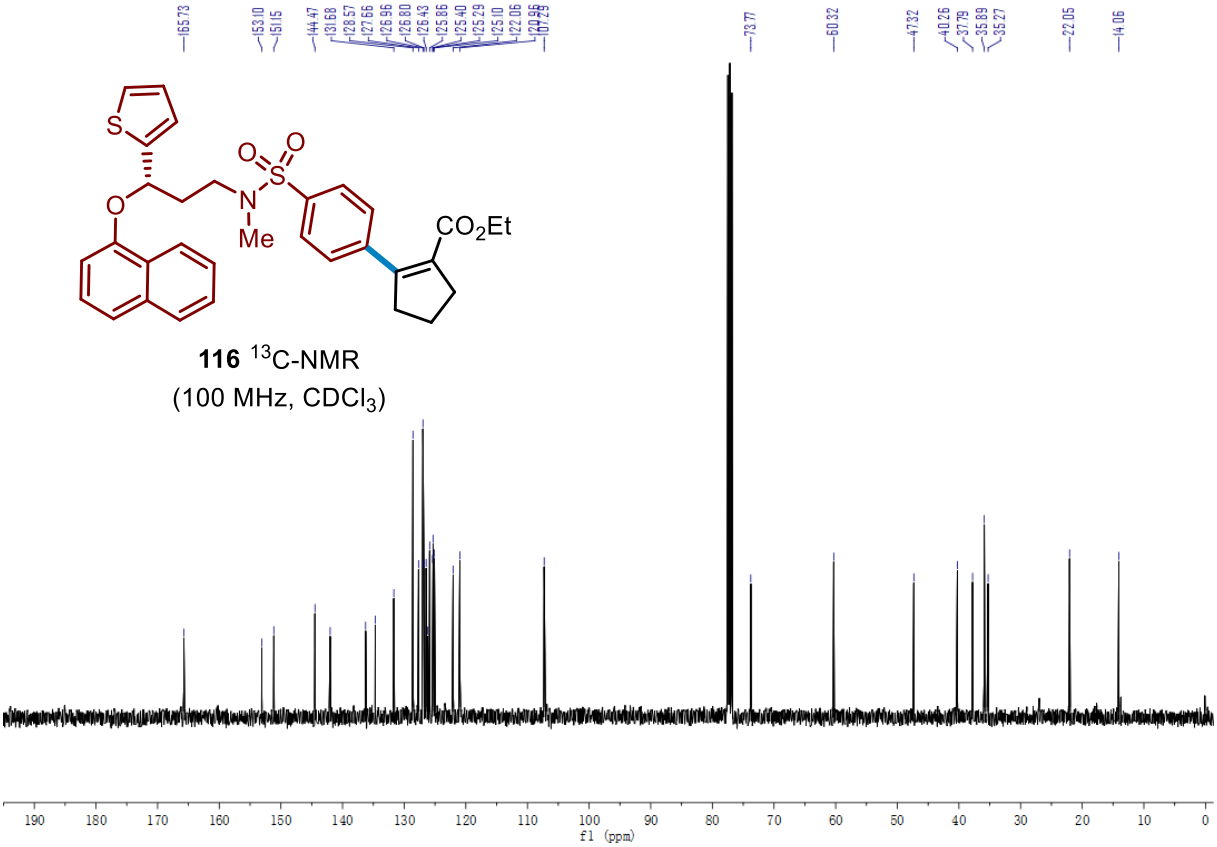


115 ^{13}C-NMR
(100 MHz, $CDCl_3$)

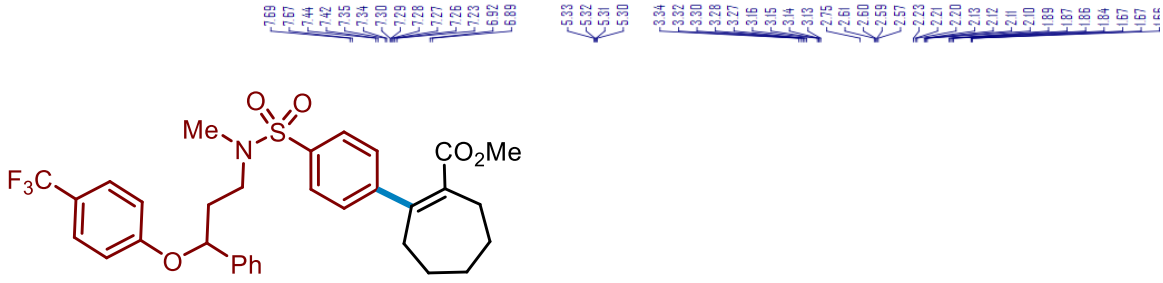


116 ^{1}H-NMR
(400 MHz,$CDCl_3$)

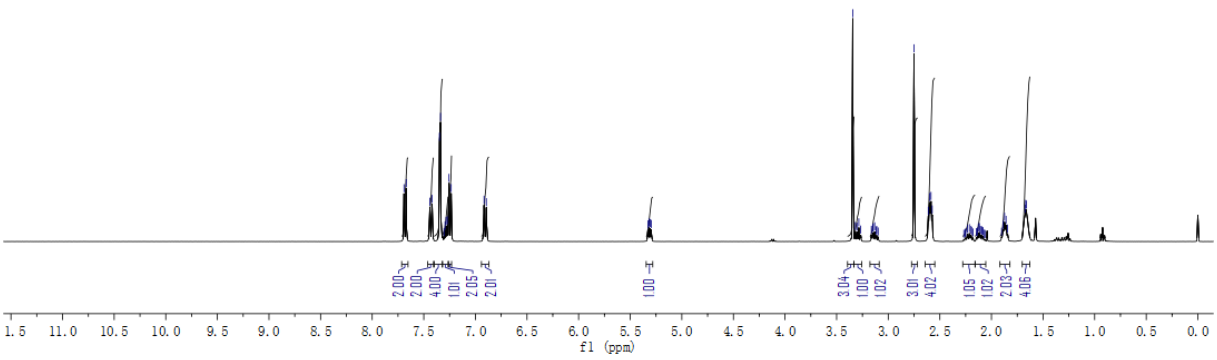


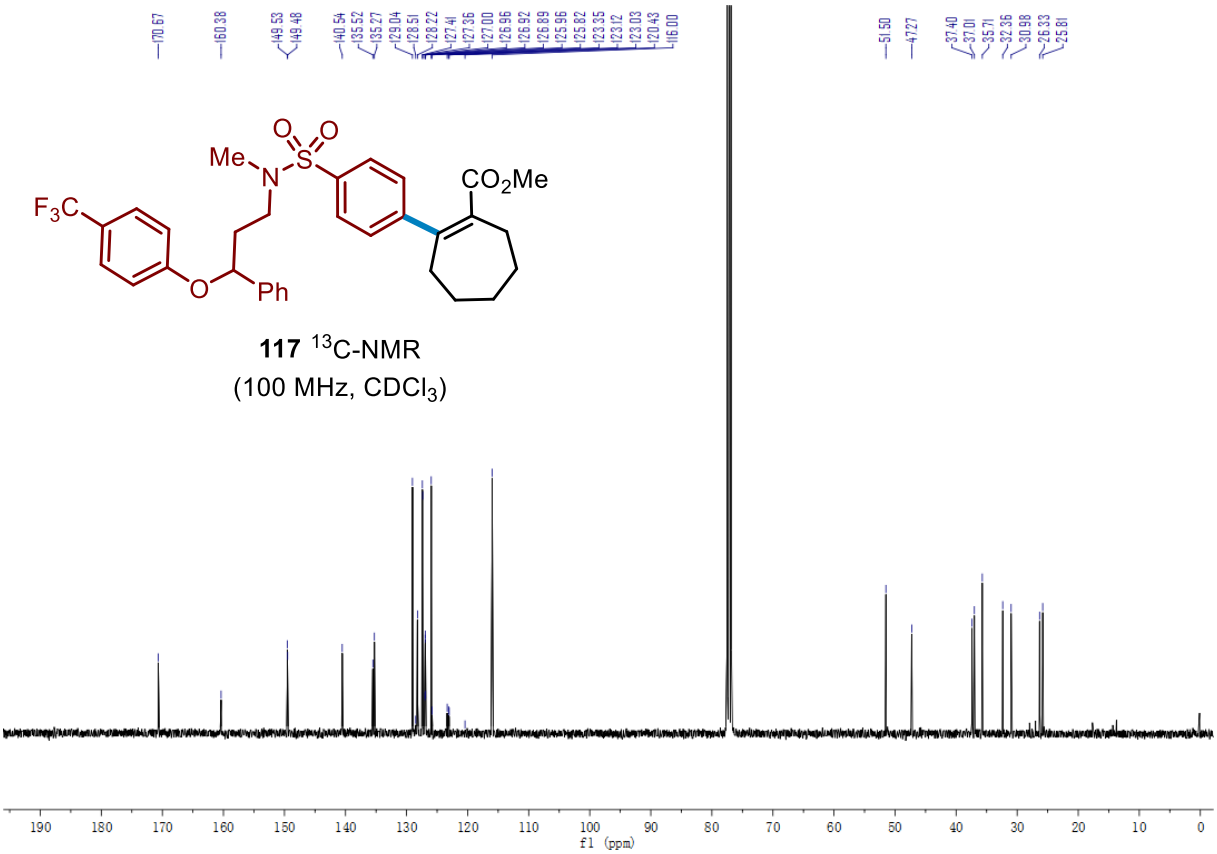


116 ^{13}C-NMR
(100 MHz, $CDCl_3$)

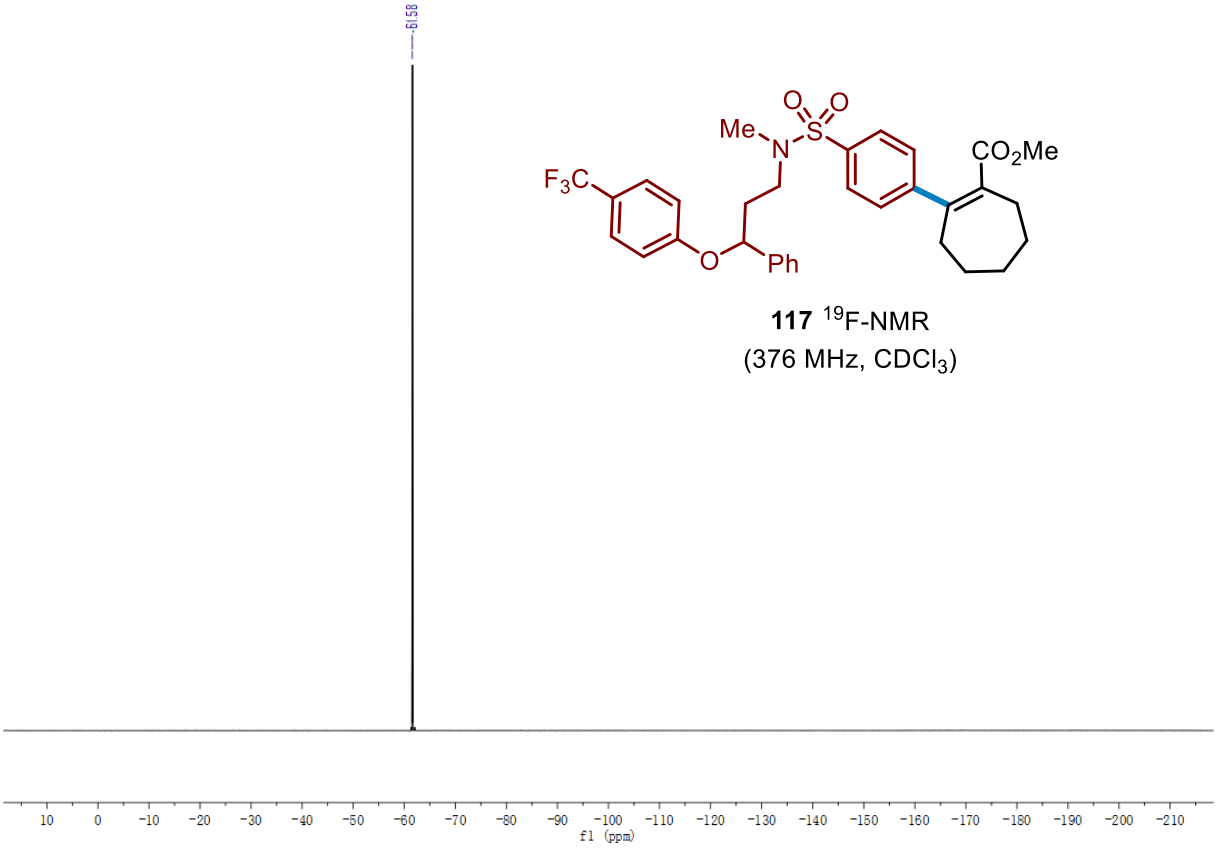


117 ^{1}H-NMR
(400 MHz,$CDCl_3$)

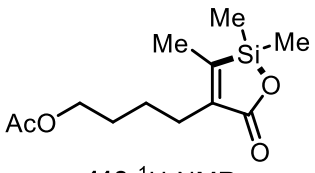




117 ^{13}C-NMR
(100 MHz, $CDCl_3$)

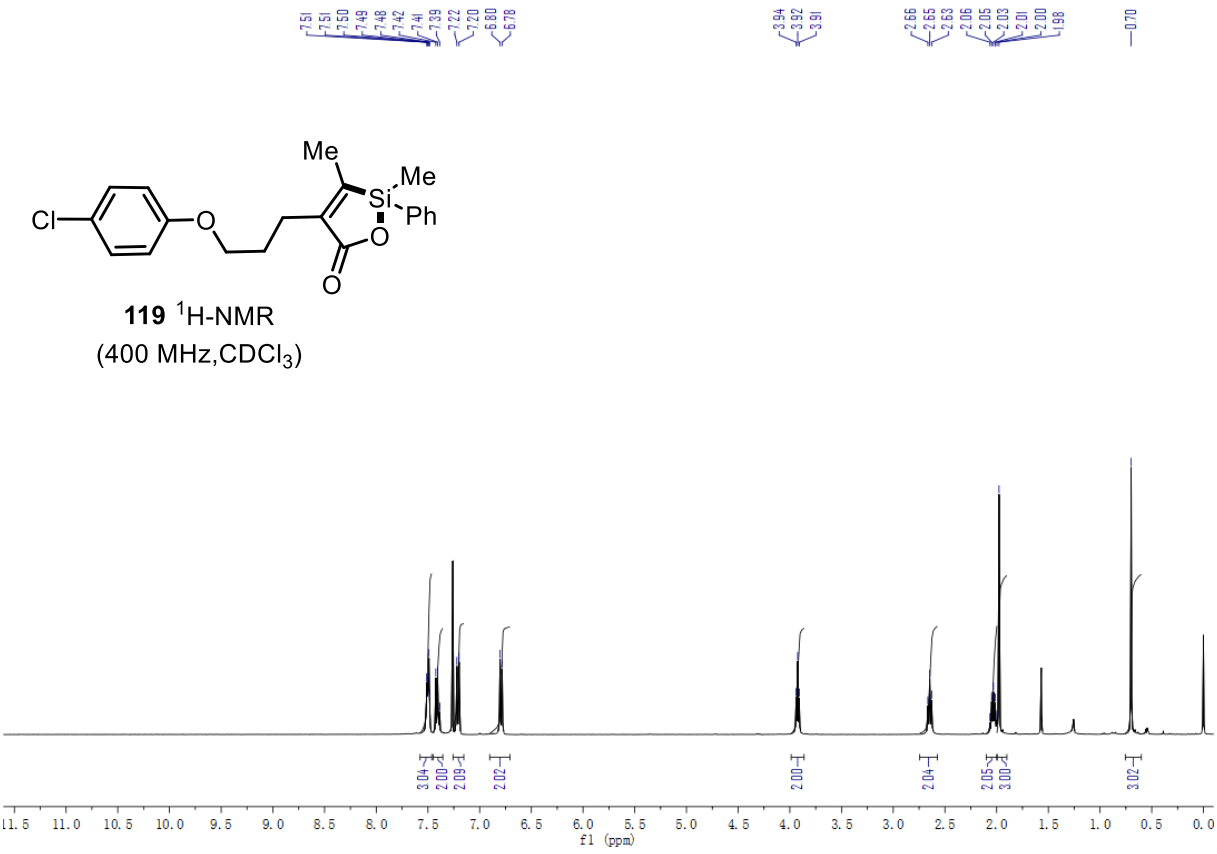


117 ^{19}F-NMR
(376 MHz, $CDCl_3$)

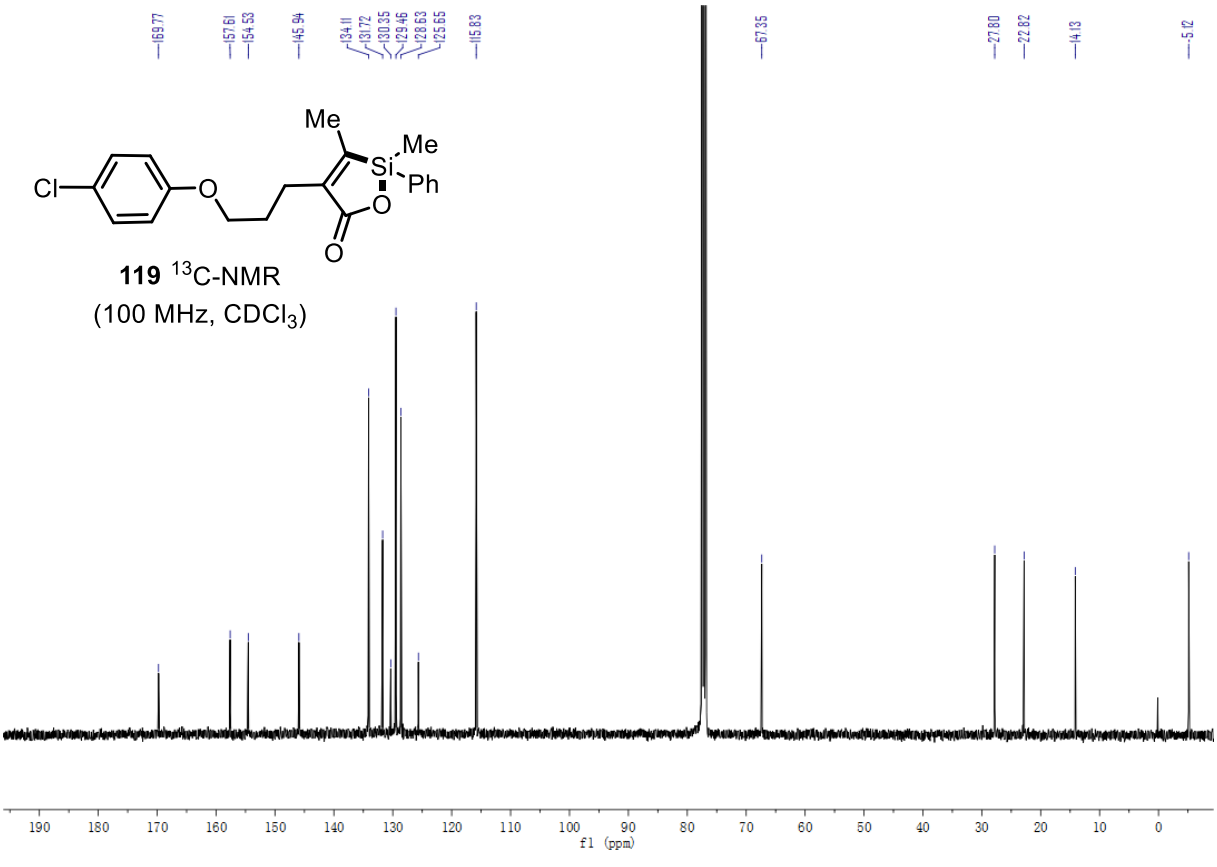


118 ^{1}H-NMR
(400 MHz,$CDCl_3$)

118 ^{13}C-NMR
(100 MHz, $CDCl_3$)



119 ^{1}H-NMR
(400 MHz,$CDCl_3$)



119 ^{13}C-NMR
(100 MHz, $CDCl_3$)