Supporting Information

Cobalt-Catalyzed Chemoselective Dehydrogenation through Radical Translocation under Visible Light

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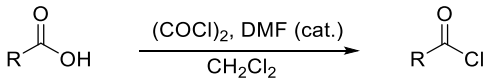
1. General Information

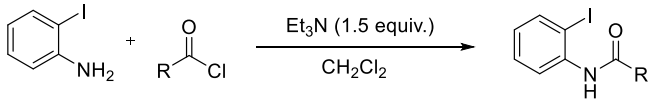
All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200−300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz and 600 MHz spectrometer. The spectra were recorded in deuterochloroform ($CDCl_3$) as solvent at room temperature, and ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet doublet, br = broad), integration, coupling constant (Hz), and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS analysis was performed on a Bruker Apex II mass instrument (ESI).

2. General Preparation of Substrates

a) General Procedure for Preparation of *N*-(2-iodophenyl)acylamides

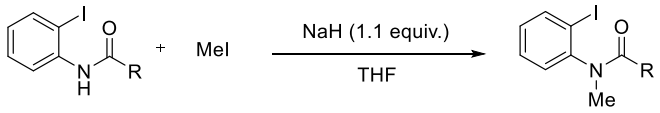


To a solution of the carboxylic acid (1.0 equiv.) in CH_2Cl_2 (0.2 M) at 0 °C was added oxalyl chloride (2.0 equiv.) dropwise followed by 1 to 2 drops of DMF. The resulting solution was stirred for 2-4 h and then concentrated to remove excess oxalyl chloride to give the acid chloride, which was used without further purification.

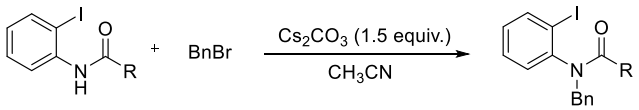


To a solution of 2-iodoaniline (2.0 mmol, 1.0 equiv.) in dicholoromethane (5.0 mL) was slowly added respective acid chlorides (2.4 mmol, 1.2 equiv.) followed by triethylamine (3.0 mmol, 1.5 equiv.) at 0 °C. After complete addition, the reaction was allowed to stir continuously until all the starting material was consumed completely (monitored by TLC, approx. 8-12 h). After completion, the reaction mixture was quenched with water and extracted with dichloromethane. The combined

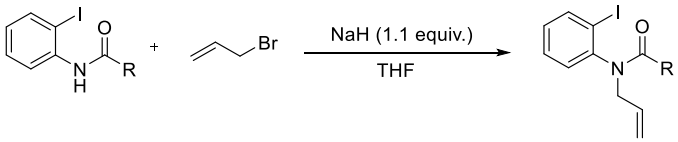
organic layer was washed with brine solution, dried over Na_2SO_4. The product was purified by column chromatography on silica gel to afford pure compounds.



To a stirred suspension of NaH (1.1 equiv.) in dry THF (0.2 M) at 0 °C, the respective amide (1.0 equiv.) dissolved in THF (0.4 M) was added dropwise within 10 min. The reaction mixture was stirred until the solution became clear (30 min, hydrogen gas evolved), and the solution of MeI (1.2 equiv.) in THF (0.4 M) was added dropwise within 10 min. The solution was warmed up to room temperature and stirred for 3 h. Then the reaction mixture was quenched with water. The resulting solution was extracted with ethyl acetate. Combined organic layers were washed with brine and dried over Na_2SO_4. Ethyl acetate was removed under reduced pressure to give crude products. The product was purified by column chromatography on silica gel to afford pure compounds.



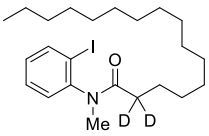
To a solution of the respective amide (1.0 equiv.), cesium carbonate (1.5 equiv.) in acetonitrile (0.1 M) at 0 °C was added benzyl bromide (1.5 equiv.). The resulting mixture was then stirred at room temperature for 12 h. After filtration through a short column of silica gel and washed with ethyl acetate for 3 times. The combined organic phases were concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to afford pure compounds.



To a stirred suspension of NaH (1.1 equiv.) in dry THF (0.2) at 0 °C, the respective amide (1.0 equiv.) dissolved in THF was added dropwise within 10 min. The reaction mixture was stirred until the solution became clear (30 min, with hydrogen gas evolved), and the solution of allyl bromide (1.3 equiv.) in THF (0.5 M) was added dropwise within 10 min. The solution was warmed up to room temperature. The reaction mixture was monitored by TLC and quenched with water. The resulting solution was extracted with ethyl acetate. Combined organic layers were washed with brine and dried over Na_2SO_4. Ethyl acetate was removed under reduced pressure to give the crude product,

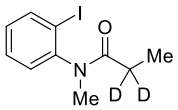
which was purified by column chromatography on silica gel to afford the pure compounds.

N-(2-iodophenyl)-N-methylhexadecanamide-2,2-d2 (D_2-28')



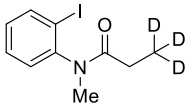
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.94 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.42 (td, *J* = 7.7, 1.4 Hz, 1H), 7.25 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.08 (td, *J* = 7.7, 1.6 Hz, 1H), 3.17 (s, 3H), 1.62-1.52 (m, 2H), 1.30-1.20 (m, 24H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 172.7, 146.3, 140.1, 129.8, 129.6, 129.0, 99.7, 35.8, 33.8-33.4 (m), 31.8, 29.60, 29.58, 29.57, 29.52, 29.4, 29.3, 29.23, 29.21, 25.0, 24.9, 22.6, 14.0; HRMS (ESI) for $C_{23}H_{37}D_2INO$ $[M+H]^+$ calcd 474.2196, found 474.2197.

N-(2-iodophenyl)-N-methylpropanamide-2,2-d2 (114a')



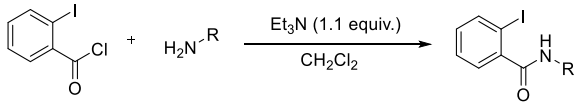
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.94 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.4 Hz, 1H), 7.27 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.08 (td, *J* = 7.7, 1.6 Hz, 1H), 3.18 (s, 3H), 1.06 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 173.4, 146.3, 140.1, 129.9, 129.7, 129.0, 99.7, 35.9, 27.3-26.8 (m), 9.2; HRMS (ESI) for $C_{10}H_{11}D_2INO$ $[M+H]^+$ calcd 292.0162, found 292.0166.

N-(2-iodophenyl)-N-methylpropanamide-3,3,3-d3 (114b')

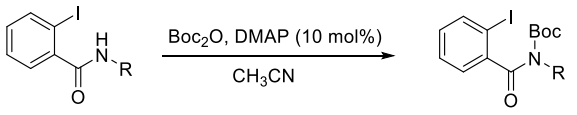


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.93 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.43 (td, *J* = 7.6, 1.4 Hz, 1H), 7.26 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.08 (td, *J* = 7.7, 1.6 Hz, 1H), 3.18 (s, 3H), 1.94 (s, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 173.5, 146.3, 140.2, 129.9, 129.7, 129.0, 99.8, 35.9, 27.5, 8.9-8.5 (m); HRMS (ESI) for $C_{10}H_{10}D_3INO$ $[M+H]^+$ calcd 293.0225, found 293.0219.

b) General Procedure for Preparation of N-2-iodobenzoylamides

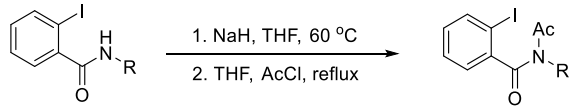


The 2-iodobenzoyl chloride (1.0 equiv.) was dissolved in dichloromethane (0.2 M). Amine or amine HCl salt (1.5 equiv.) and NEt_3 (3.0 equiv.) were added and the mixture was stirred at 0 °C until consumption of starting material for 2-12 h. The reaction was filtered through a pad of silica gel, which was purified by column chromatography on silica gel to afford pure compounds.

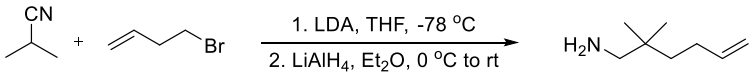


Prepared according to the procedure previously described.[1] To a solution of the amide (1.0 equiv.) prepared from above in acetonitrile was then added 4-(*N*,*N*-dimethylamino)pyridine (DMAP, 10 mol %), and di-*tert*-butyl dicarbonate (1.5 equiv.). The resulting mixture was stirred at 40 °C

overnight. After the reaction, the mixture was dried *in vacuo*, and the crude product was washed with ethyl acetate and dilute with 1M HCl solution. The organic fraction was further washed with saturated $NaHCO_3$ solution followed by saturated NaCl solution. The organic fraction was then concentrated *in vacuo*, and the residue was purified by column chromatography on silica gel to afford the Boc-activated amide.



Prepared according to the modified procedure previously described.[2] To a stirred suspension of NaH (60% in mineral oil, 1.1 equiv.) in dry THF (0.25 M) at room temperature was added a solution of amide (1.0 equiv.) in THF. The reaction mixture was kept at 60 °C for 3 h, and then a solution of acetylchloride in THF (0.5 M) was added dropwise. The reaction mixture was heated to reflux for 12 h, and then the mixture was cooled to room temperature, quenched with saturated NH_4Cl, extracted with ethyl acetate, and washed with brine. The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to give pure product.

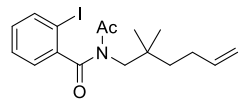


Prepared according to the procedure previously described.[3] To a solution of the isobutyronitrile (1.0 equiv.) in THF (0.2 M) was added LDA (1.1 equiv. 2.0 M in THF) at −78 °C and stirring was continued for 30 min. Then, 4-bromo-1-butene (1.2 equiv.) was also added. The reaction mixture was maintained at -78 °C for 30 min and then it was allowed to warm to room temperature. Saturated aqueous ammonium chloride solution was added and the mixture was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to yield crude 2,2-dimethyl-5-hexenenitrile that was employed without further purification.

This crude product was dissolved in diethyl ether (0.1 M) and it was added dropwise to a suspension of $LiAlH_4$ (2.0 equiv.) in diethyl ether (0.5 M) at 0 °C. The reaction mixture was allowed to reach room temperature until GC-MS revealed the disappearance of the nitrile. Then, it was quenched with ice with vigorous stirring until grey aluminum salts turned white. The suspension was then filtered through a short pad of Celite® washing with diethyl ether 3 times. The filtrate was dried

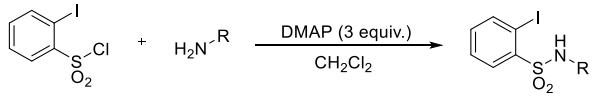
with Na_2SO_4, filtered and concentrated under vacuum, obtaining a yellow oil that was employed without further purification.

N-acetyl-N-(2,2-dimethylhex-5-en-1-yl)-2-iodobenzamide (80')



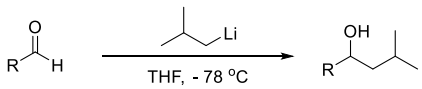
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 (d, *J* = 7.9 Hz, 1H), 7.43 (td, *J* = 7.6, 0.9 Hz, 1H), 7.37 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.16 (td, *J* = 7.9, 1.7 Hz, 1H), 5.83-5.72 (m, 1H), 5.04-4.87 (m, 2H), 3.69 (s, 2H), 2.21 (s, 3H), 2.04-1.96 (m, 2H), 1.31-1.27 (m, 2H), 0.88 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 173.6, 173.5, 141.3, 140.3, 139.1, 131.8, 130.0, 128.3, 114.1, 93.1, 54.0, 40.1, 36.7, 28.3, 26.6, 25.6; HRMS (ESI) for $C_{17}H_{23}INO_2$ $[M+H]^+$ calcd 400.0768, found 400.0767.

c) General Procedure for Preparation of Sulfamides.

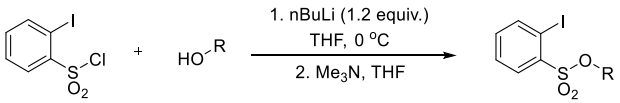


To a solution of 2-iodobenzene sulfonyl chloride (1.0 equiv.) in dry dichloromethane (0.2 M) was added amine or amine HCl salt (1.5 equiv.) followed by dropwise addition of DMAP (3 mmol) solution in dichloromethane (0.5 M). The reaction was stirred for 3-12 h (monitored by TLC), filtered through a pad of silica gel and rinsed with dichloromethane, which was purified by flash chromatography to afford pure compounds.

d) General Procedure for Preparation of Sulfonates.



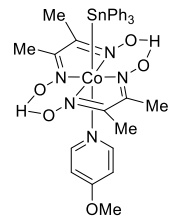
Prepared according to the procedure previously described.[4] To a solution of aldehyde (1.0 equiv) in anhydrous THF (0.75 M) under argon atmosphere was added *i*BuLi (1.1 equiv.) at -78 °C over a period of 1 h. The reaction mixture was allowed to warm to rt and stirring was continued for 2 h. After quenching by addition of saturated NH_4Cl solution, the aqueous layer was extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to obtain the desired alcohol which was used without further purification.



A Schlenk flask was charged with the alcohol (1.0 equiv.) in anhydrous THF (0.2 M) under argon.

*n*BuLi (1.2 equiv) was added slowly at 0 °C and stirring was continued for 30 min. At the same time, a second Schlenk flask was charged with the sulfonyl chloride (1.2 equiv.) in anhydrous THF and treated with Me_3N (1.5 equiv, 2.0 M in THF) at 0 °C and stirring was continued for 30 min. The alcoholate solution was then transferred via a cannula to the sulfonyl chloride solution. The reaction progress was monitored by TLC and after the alcohol was completely consumed, imidazole was added until no remaining sulfonyl chloride was observed by TLC. The reaction mixture was transferred onto a column and directly purified by flash chromatography.

3. Preparation of Cobaloxime



$Co(dmgH)_2(4\text{-OMe-Py})SnPh_3$ (III)

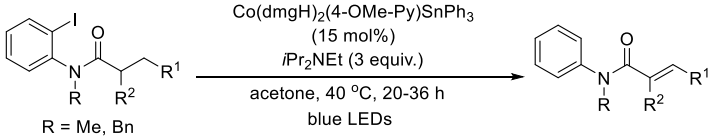
$[Co(dmgH)_2(4\text{-OMe-Py})SnPh_3]$ (**III**) Following the literature procedure,[5] reaction conducted in the dark. To a solution of $CoCl_2$ (1.11 g, 8.6 mmol) in degassed MeOH (40 ml) was added dimethylglyoxime (2.0 g, 17.2 mmol, 2.0 equiv.) and the resulting brown suspension was stirred for 10 min at rt. 4-Methoxypyridine (0.92 ml, 9.0 mmol, 1.05 equiv.) and NaOH (1.07 M in degassed H_2O, 16.2 ml, 17.3 mmol, 2.0 equiv.) was added and the dark solution was stirred for 10 min at rt before cooling to 0 °C. A suspension of Ph_3SnCl (3.34 g, 8.7 mmol, 1.0 equiv.) in degassed MeOH (10 ml) and NaOH (1.07 M in degassed H_2O, 8.1 ml, 8.7 mmol, 1.0 equiv.) was then added at 0°C. $NaBH_4$ (0.65 g, 17.1 mmol, 2 equiv.) was added portion wise at 0 °C, the cooling bath was removed and the resulting orange-red mixture was stirred for 90 min at rt. H_2O (80 ml) was added carefully and the mixture was stirred for another 60 min open to air. The orange precipitate was collected on a glass filter and rinsed with H_2O (15 ml), MeOH (10 ml), diethyl ether (10 ml) and hexanes (10 ml). The filter cake was dissolved in DCM (50 ml), dried over Na_2SO_4, filtrated and concentrated in vacuo in a conical flask until small red needles started to crystallize from the solution. The deep red solution was carefully over layered with hexanes (80 ml) and allowed mix by diffusion over 16 h at rt. The resulting crystals were collected on a glass filter, rinsed with hexanes (20 ml) and dried in high vacuum to afford $Co(dmgH)_2(4\text{-OMe-Py})SnPh_3$ (4.35 g, 5.8 mmol, 67%) as dark red crystals.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.35 (d, *J* = 6.8 Hz, 2H), 7.57-7.38 (m, 6H), 7.33-7.17 (m, 9H), 6.78 (d, *J* = 6.9 Hz, 2H), 3.77 (s, 3H), 1.71 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) =

166.4, 150.4, 150.1, 141.0, 137.0, 128.0, 127.5, 111.5, 55.4, 11.8; HRMS (ESI) for $C_{32}H_{36}CoN_5NaO_5Sn^+$ $[M+Na]^+$ calcd 772.0963, found 772.0959.

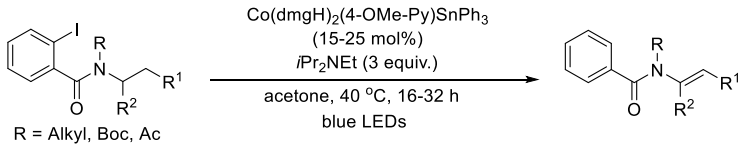
4. General Procedure for the Site-Selective Dehydrogenative Reaction

General procedure A for synthesis of α,β-unsaturated amides:



A Schlenk flask equipped with a magnetic stir bar was charged with substrate (0.1 mmol) and *i*Pr_2NEt (0.3 mmol), $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (15 mol%) in dry acetone 2 mL at room temperature. The heterogenous mixture was degassed carefully by three cycles of freeze-pump-thaw under argon and then placed in the irradiation apparatus equipped with 18 W blue light emitting diodes (LED, λ = 450-460 nm). The resulting mixture was stirred at 40 °C until the starting material was completely consumed after 20-36 h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:5-1:2), which furnished the title compounds as described.

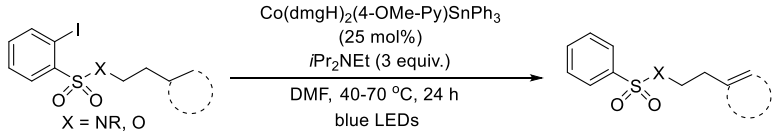
General procedure B for synthesis of enamides:



A Schlenk flask equipped with a magnetic stir bar was charged with substrate (0.1 mmol) and *i*Pr_2NEt (0.3 mmol), $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (15-25 mol%) in dry acetone 2 mL at room temperature. The heterogenous mixture was degassed carefully by three cycles of freeze-pump-thaw under argon and then placed in the irradiation apparatus equipped with 18 W blue light emitting diodes (LED, λ = 450-460 nm). The resulting mixture was stirred at 40 °C until the starting material was completely consumed after 16-32 h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by column

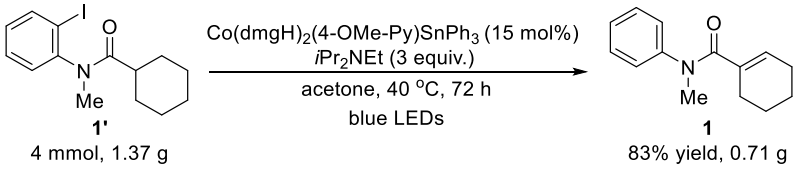
chromatography on silica gel (EtOAc/petroleum ether = 1:15-1:8), which furnished the title compounds as described.

General procedure C for synthesis of allylic and homoallylic sulfonamides and sulfonates:



A Schlenk flask equipped with a magnetic stir bar was charged with substrate (0.1 mmol) and *i*Pr$_2$NEt (0.3 mmol), Co(dmgH)$_2$(4-OMe-Py)SnPh$_3$ (25 mol%) in dry DMF 2 mL at room temperature. The heterogenous mixture was degassed carefully by three cycles of freeze-pump-thaw under argon and then placed in the irradiation apparatus equipped with 18 W blue light emitting diodes (LED, λ = 450-460 nm). The resulting mixture was stirred at 40-70 °C until the starting material was completely consumed after 24 h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:50-1:4), which furnished the title compounds as described.

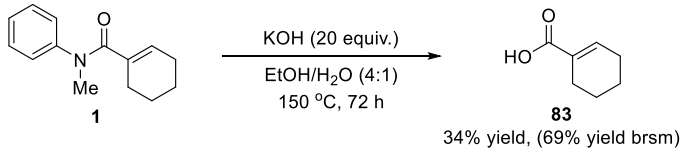
Gram-Scale Preparation of 1



To a 150 mL round-bottom flask equipped with a magnetic stir bar was added Co(dmgH)$_2$(4-OMe-Py)SnPh$_3$ (15 mol%, 0.6 mmol). Dry acetone (50 mL, 0.08 M) was added, after which the substrate **1'** (4 mmol) and *i*Pr$_2$NEt (12 mmol) were added respectively at room temperature. The heterogeneous mixture was degassed by three cycles of freeze−pump−thaw under argon and then placed in the irradiation apparatus equipped with 18 W blue light emitting diodes (LED, λ = 450-460 nm). The resulting mixture was stirred at 40 °C until the starting material was completely consumed as monitored by TLC after 72 h. Upon completion of the reaction, the reaction mixture

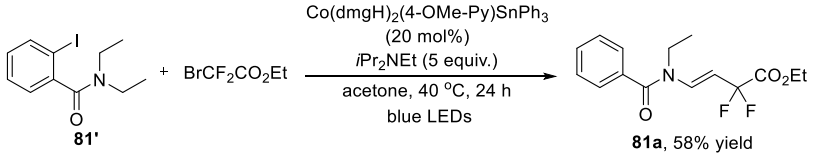
was concentrated under reduced pressure. Then mixture was quenched with water and extracted with EtOAc (20 ml × 3), and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5:1), which furnished the title compounds **1** as described (715 mg, 83% yield).

Hydrolysis of compound 1



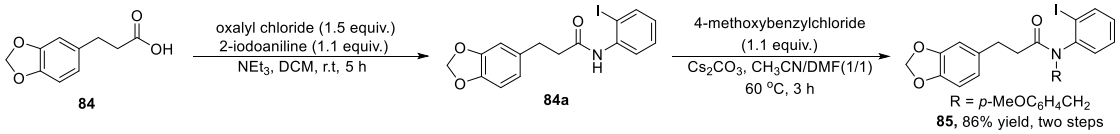
To a solution of **1** (0.1 mmol) in 4:1 mixture of EtOH/H_2O (1 mL) added KOH (2 mmol) and stirred in a Teflon lined sealed tube at 150 ºC after 72 h. The reaction mixture was cooled, acidified with 2 M HCl and extracted with EtOAc (10 mL). The combined organic phase was dried with anhydrous $NaSO_4$ and concentrated in reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:10) to afford pure compound **83** (4.3 mg, 34% yield; 69% yield based on recovered starting material).

Two-step cascade reaction

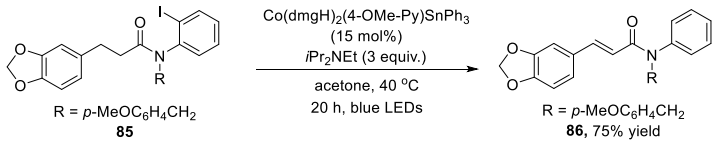


A Schlenk flask equipped with a magnetic stir bar was charged with **81'** (0.1 mmol) and *i*Pr_2NEt (5.0 equiv.), $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (20 mol%) in dry acetone 2 mL at room temperature. The heterogenous mixture was degassed carefully by three cycles of freeze-pump-thaw under argon and then placed in the irradiation apparatus equipped with 18 W blue light emitting diodes (LED, λ = 450-460 nm) at 40 °C for 10 h then ethyl bromodifluoroacetate (0.2 mmol) was added. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:3) to afford the pure compound **81a** (17.2 mg, 58% yield).

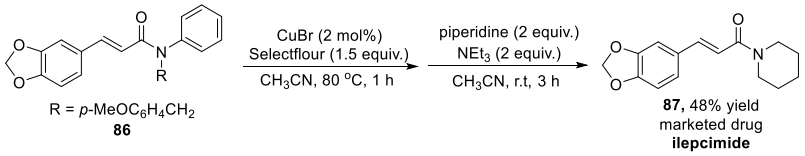
Synthesis of Ilepcimide



To a solution of the 3-(3,4-methylenedioxyphenyl)propionic acid **84** (1 mmol) in CH_2Cl_2 (5 ml) at 0 °C was added oxalyl chloride (1.5 mmol) slowly followed by 10 μl DMF. The resulting solution was stirred at r.t for 2 h and then concentrated to remove excess oxalyl chloride. The residue was dissolved in CH_2Cl_2 (10 ml) and 2-iodoaniline (1.1 mmol) and NEt_3 (1.2 mmol) were added at 0 °C. The mixture was stirred at r.t for 3 h. The solvent was evaporated under reduced pressure and the residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the amide **84a** (376 mg, 95% yield). Next, to a solution of the **84a** (1.0 equiv.), Cs_2CO_3 (1.2 equiv.) in CH_3CN/DMF (10 ml, 1:1 v/v) at 0 ℃ was added 4-methoxybenzylchloride (1.1 equiv.). The resulting mixture was then stirred at 60 ºC for 3 h. After filtration through a short column of silica gel and washed with ethyl acetate for 3 times. The combined organic phases were concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:5) to afford pure compound **85** (443 mg, 86% yield, two steps).



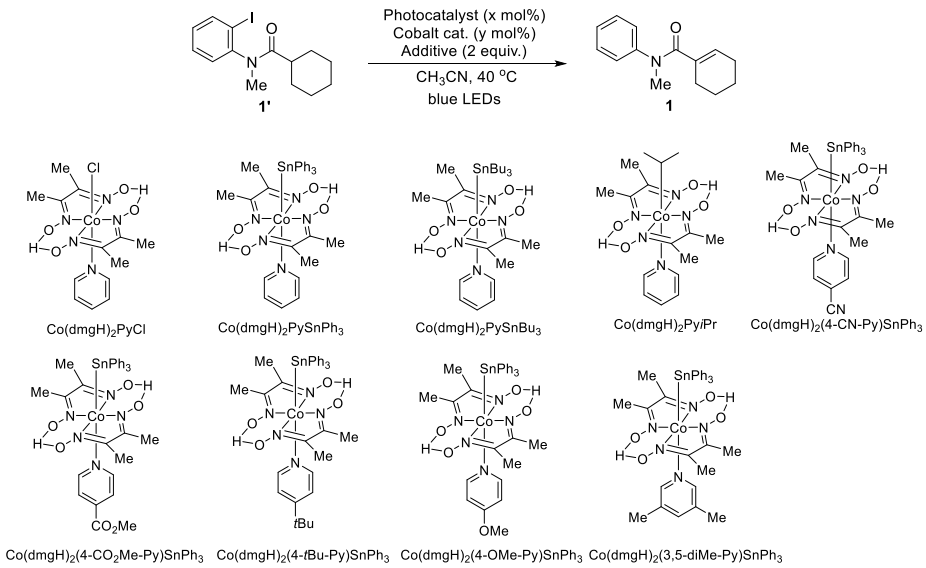
A Schlenk flask equipped with a magnetic stir bar was charged with **85** (0.1 mmol, 1.0 equiv.) and *i*Pr_2NEt (3.0 equiv.), $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (15 mol%) in dry acetone 2 mL at room temperature. The heterogenous mixture was degassed carefully by three cycles of freeze-pump-thaw under argon and then placed in the irradiation apparatus equipped with 18 W blue light emitting diodes (LED, λ = 450-460 nm). The resulting mixture was stirred at 40 °C after 20 h. Upon completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:3) to afford the pure compound **86** (29.2 mg, 75% yield).



$CuBr_2$ (2 mol% of Cu), Selectfluor (1.5 equiv.), and **86** (0.1 mmol, 1.0 equiv.), were placed in an oven dried 10 mL Schlenk tube. The tube was evacuated and then re-filled with argon gas for 3 cycles. CH_3CN (0.5 mL) were added successively. The tube was placed in a preheated oil bath at 80 °C and stirred for 1 h equipped with argon balloon. Subsequently, piperidine (2.0 equiv.) and Et_3N (2.0 equiv.) was added in sequence to the reaction mixture at 0 ˚C and the reaction was stirred at r.t for 3 h with argon balloon. The reaction mixture was concentrated under reduced pressure, and the resulting crude mixtures was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:3) to afford the pure compound **87** (12.5 mg, 48% yield).

5. Initial Studies and Reaction Optimization

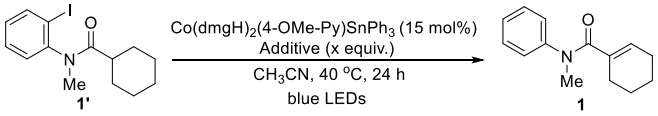
Table S1. Screen of the cobaloxime catalysts



Entry	Photocatalyst	Cobalt Cat.	Additive	Time (h)	Yield (%)[a,b]
1	4CzIPN (5 mol%)	$Co(dmgH)_2PyCl$ (10 mol%)	NEt_3	36	trace
2	$Ir(ppy)_3$ (5 mol%)	$Co(dmgH)_2PyCl$ (10 mol%)	NEt_3	36	0
3	-	$Co(dmgH)_2PySnPh_3$ (10 mol%)	NEt_3	24	68
4	-	Vitamin B_{12} (10 mol%)	NEt_3	36	0
5	-	$Co(dmgH)_2PySnBu_3$ (10 mol%)	NEt_3	36	22
6	-	$Co(dmgH)_2Py$*i*Pr (10 mol%)	NEt_3	36	trace
7	-	$Co(dmgH)_2$(4-CN-Py)$SnPh_3$ (10 mol%)	NEt_3	24	70
8	-	$Co(dmgH)_2$(4-CO_2Me-Py)$SnPh_3$ (10 mol%)	NEt_3	24	65
9	-	$Co(dmgH)_2$(4-*t*Bu-Py)$SnPh_3$ (10 mol%)	NEt_3	24	63
10	-	$Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (10 mol%)	NEt_3	24	72
11	-	$Co(dmgH)_2$(3,5-diMe-Py)$SnPh_3$ (10 mol%)	NEt_3	24	56
12	-	$Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (15 mol%)	NEt_3	24	79
13	-	$Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (5 mol%)	NEt_3	36	50

[a] Unless otherwise noted, reaction conditions are as follows: reactant (0.1 mmol), photocatalyst (0.005 mmol), cobalt catalyst (0.01-0.015 mmol), additive (0.2 mmol), solvent (2 mL), blue LEDs (λ = 450-460 nm), 40 ℃ and under Ar atmosphere. [b] Isolated yield.

Table S2. Screen of the additives

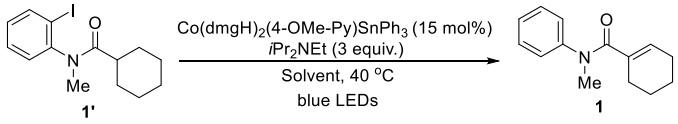


Entry	Additive	Yield (%)[a,b]
1	*i*Bu$_3$N (2 equiv.)	59
2	*n*Pr$_3$N (2 equiv.)	49
3	Cy$_2$NMe (2 equiv.)	57
4	N-Methylpyrrolidine (2 equiv.)	12
5	*i*Pr$_2$NEt (2 equiv.)	83
6	TMEDA (2 equiv.)	41
7	Na_2CO_3 (2 equiv.)	0
8[c]	Na_2CO_3 (2 equiv.)	19
9	Pyridine (2 equiv.)	0
10[c]	Pyridine (2 equiv.)	25
11	DMAP (2 equiv.)	17
12	Tetramethylpiperidine (2 equiv.)	36
13	DABCO (2 equiv.)	31
14	Na_2CO_3 (2 equiv.) + $NaBH_4$ (1.5 equiv.)	trace
15[c]	Na_2CO_3 (2 equiv.) + $NaBH_4$ (1.5 equiv.)	28
16	Pyridine (2 equiv.) + $NaBH_4$ (1.5 equiv.)	39
17	Na_2CO_3 (2 equiv.) + Zn (1.5 equiv.)	58
18	$NaBH_4$ (1.5 equiv.)	trace
19	Zn (1.5 equiv.)	trace
20	*i*Pr$_2$NEt (1 equiv.)	65
21	*i*Pr$_2$NEt (2.5 equiv.)	85

22	*i*Pr$_2$NEt (3 equiv.)	90
23	*i*Pr$_2$NEt (3.5 equiv.)	89

[a] Unless otherwise noted, reaction conditions are as follows: reactant (0.1 mmol), [Co] (0.015 mmol), additive (0.15-0.35 mmol), CH_3CN (2 mL), blue LEDs (λ = 450-460 nm), 40 ℃ and under Ar atmosphere. [b] Isolated yield. [c] reaction was carried out at 50 ℃ for 36 h.

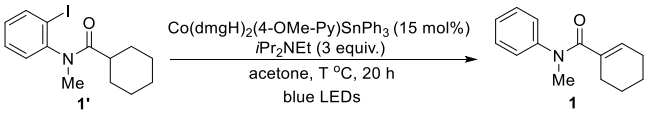
Table S3. Screen of the solvents



Entry	Solvent	Time (h)	Yield (%)[a,b]
1	DCM	36	44
2	DCE	36	60
3	toluene	36	62
4	DMF	20	94
5	DMSO	20	84
6	NMP	20	82
7	acetone	20	96
8	THF	48	90
9	MeOH	20	77

[a] Unless otherwise noted, reaction conditions are as follows: reactant (0.1 mmol), [Co] (0.015 mmol), *i*Pr$_2$NEt (0.3 mmol), solvent (2 mL), blue LEDs (λ = 450-460 nm), 40 ℃ and under Ar atmosphere. [b] Isolated yield.

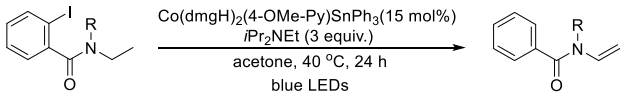
Table S4. Control experiments



Entry	Co cat.	Blue LEDs	*i*Pr$_2$NEt	Temperature (°C)	Yield (%)[a,b]
1	√	√	√	25	65
2	×	√	√	40	0
3	√	×	√	40	0
4	√	√	×	40	0

[a] Unless otherwise noted, reaction conditions are as follows: reactant (0.1 mmol), [Co] (0.015 mmol), *i*Pr$_2$NEt (0.3 mmol), acetone (2 mL), blue LEDs (λ = 450-460 nm), under Ar atmosphere. [b] Isolated yield.

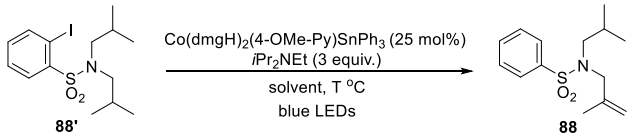
Table S5. Screen of N-protecting groups



Entry	R	Yield (%)[a,b]
1	Me	decomposition
2	H	0
3	Bn	0
4	Boc	76

[a] Unless otherwise noted, reaction conditions are as follows: reactant (0.1 mmol), [Co] (0.015 mmol), *i*Pr$_2$NEt (0.3 mmol), acetone (2 mL), blue LEDs (λ = 450-460 nm), 40 °C and under Ar atmosphere. [b] Isolated yield.

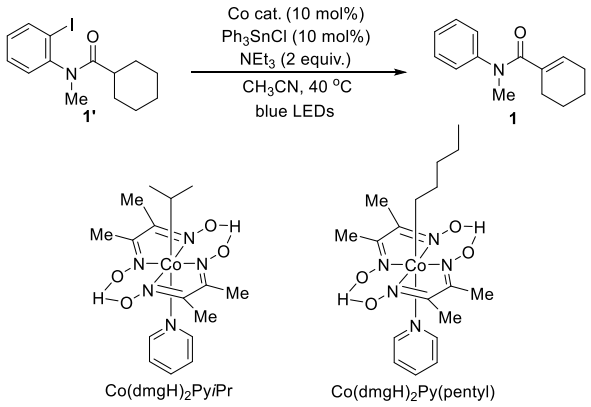
Table S6. Screen of reaction temperature of β,γ-desaturation



Entry	Solvent	Temperature (℃)	Time (h)	Yield (%)[a,b]
1	CH_3CN	40	24	trace
2	CH_3CN	50	24	11
3	CH_3CN	60	24	45
4	CH_3CN	70	24	66
5	DMF	70	24	71
6	DMSO	70	24	58
7	toluene	70	24	30
8	DCE	70	24	55
9	DMF	80	20	67

[a] Unless otherwise noted, reaction conditions are as follows: reactant (0.1 mmol), [Co] (0.025 mmol), *i*Pr$_2$NEt (0.3 mmol), solvent (2 mL), blue LEDs (λ = 450-460 nm), under Ar atmosphere. [b] Isolated yield.

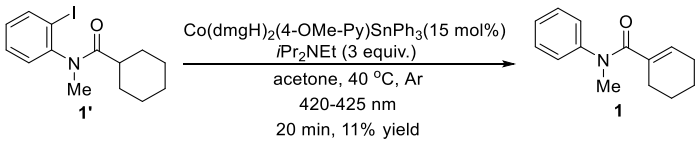
Table S7. Investigation of Ph_3SnCl



Entry	Cobaloxime (10 mol%)	Ph_3SnCl (10 mol%)	Time (h)	Yield (%)[a,b]
1	Co(dmgH)$_2$Py*i*Pr	-	36	trace
2	Co(dmgH)$_2$Py(pentyl)	-	36	trace
3	Co(dmgH)$_2$Py*i*Pr	√	24	55
4	Co(dmgH)$_2$Py(pentyl)	√	24	47

[a] Unless otherwise noted, reaction conditions are as follows: **1** (0.1 mmol), [Co] (0.01 mmol), Ph_3SnCl (0.01 mmol), NEt_3 (0.2 mmol), CH_3CN (2 mL), blue LEDs (λ = 450-460 nm), under Ar atmosphere. [b] Isolated yield.

6. Determination of the Quantum Yield



Following the literature procedure,[6] the reaction was conducted under standard conditions in a quartz tube: reactant (0.1 mmol) and *i*Pr_2NEt (0.3 mmol) were added to a solution of $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (0.015 mmol) in dry acetone 2 mL in an oven-dried 8 mL quartz vial with a magnetic stirring bar was degassed by three cycles of freeze-pump-thaw. The mixture was stirred under argon atmosphere at 40 ℃ while irradiated by blue light (420-425 nm) for 20 minutes (1200 s).

The reaction was irradiated in Parallel Light Reactor (WP-TEC-1020) (the diameter of hole was 16 mm with intensity of 191.24 $mW \cdot cm^{-2}$). After irradiation, the yield of the product **1** was determined by ^1H NMR based on a 1,3,5-trimethoxybenzene standard and the final yield was 11%.

Next, we determined the absorbance of the catalyst $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ in the reaction. The absorbance of $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ in acetone was measured at the reaction concentration of 7.5×10^{-3} M. The absorbance of $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ at 420 nm in a 7.5×10^{-3} M solution is 0.923 (A = 0. 923).

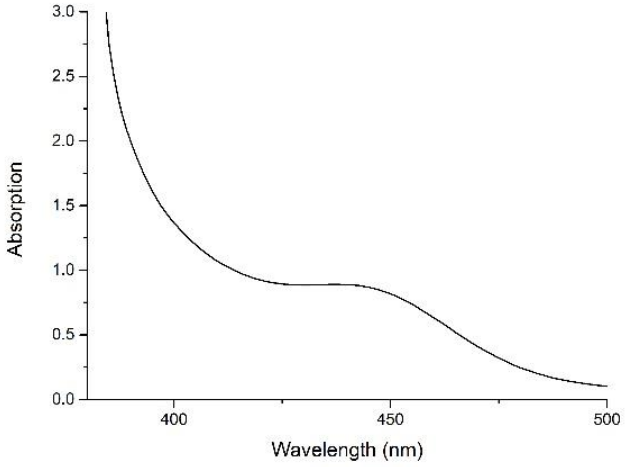


Figure S1. UV-Vis absorption spectra: $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (7.5×10^{-3} M) in acetone under argon atmosphere

The quantum yield was calculated by following equation:

Φ = Mole number for product /Mole number for absorption of photon = $\frac{N_A \times n_1 \times h \times c}{f \times P \times \lambda \times t}$ = 0.0078

n_1: the mole number of the product **1** (n_1 = 1.1 ×10^{-5} mol); t: the reaction time (t = 1200 s); N_A = 6.02×10^{23} mol^{-1}; f = 1-10^{-A} = 0.881 (420 nm, A = 0.923); P = E×S (E: illumination intensity, E = 0.19124 W/cm^2; S: the area irradiated S = 2.0 cm^2); λ: wavelength (λ = 4.20 ×10^{-7} m); h: planck constant (*h* = 6.626 ×10^{-34} J·s); c: velocity of light (c = 3 ×10^8 m/s). The result excluded the chain process.

7. Cyclic Voltammetry (CV) Experiments

Determination of the potential was performed by cyclic voltammetry using a CHI660D potentiostation. The electrochemical measurements were made using a polished glassy carbon electrode (Ø = 2 mm) as the working electrode, platinum mesh as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

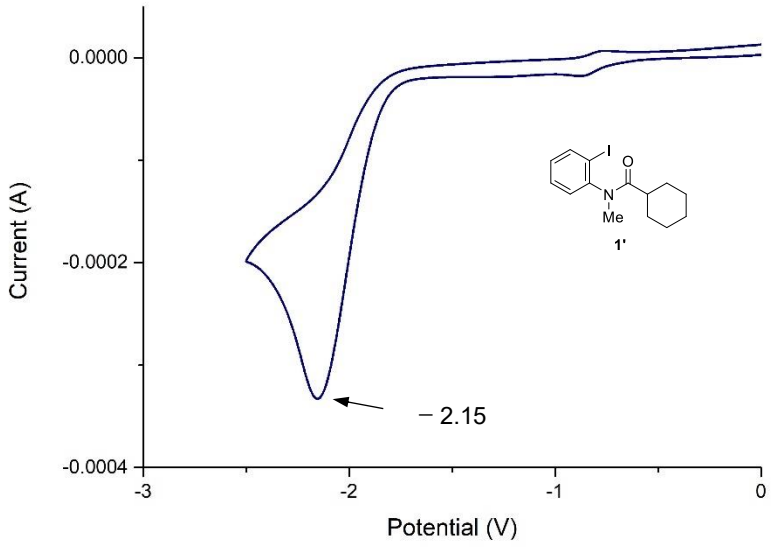


Figure S2. The cyclic voltammetry experiment of amide **1'** (0.01 M) and *n*Bu_4NPF_6 (0.1 M) in CH_3CN with a sweep rate of 100 mV/s under anhydrous and anaerobic conditions. The redox potentials of **1'** was E_p^{red} = − 2.15 V vs SCE.

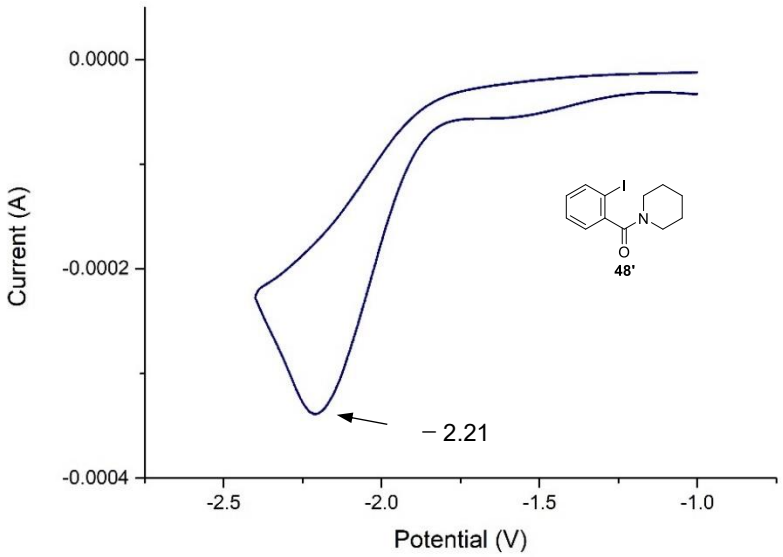


Figure S3. The cyclic voltammetry experiment of amide **48'** (0.01 M) and nBu$_4$NPF$_6$ (0.1 M) in CH$_3$CN with a sweep rate of 100 mV/s under anhydrous and anaerobic conditions. The redox potentials of **48'** was $E_{\mathrm{p}}^{\mathrm{red}} = -2.21$ V vs SCE.

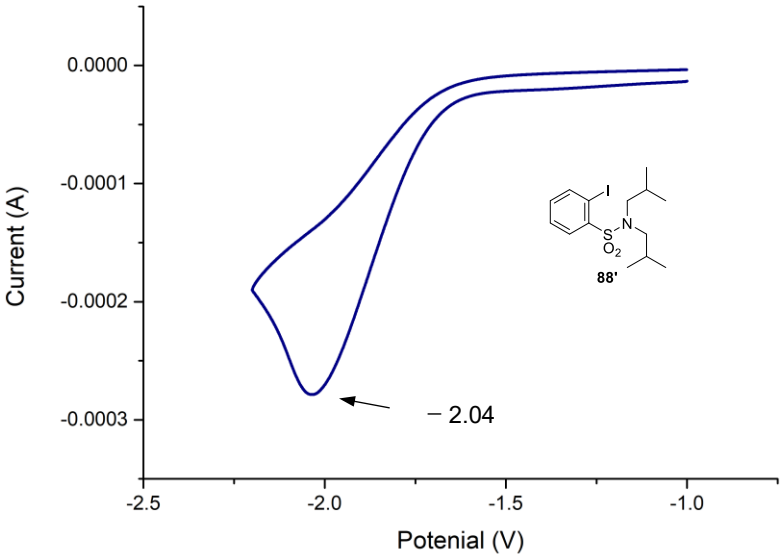


Figure S4. The cyclic voltammetry experiment of amide **88'** (0.01 M) and nBu$_4$NPF$_6$ (0.1 M) in CH$_3$CN with a sweep rate of 100 mV/s under anhydrous and anaerobic conditions. The redox potentials of **88'** was $E_{\mathrm{p}}^{\mathrm{red}} = -2.04$ V vs SCE.

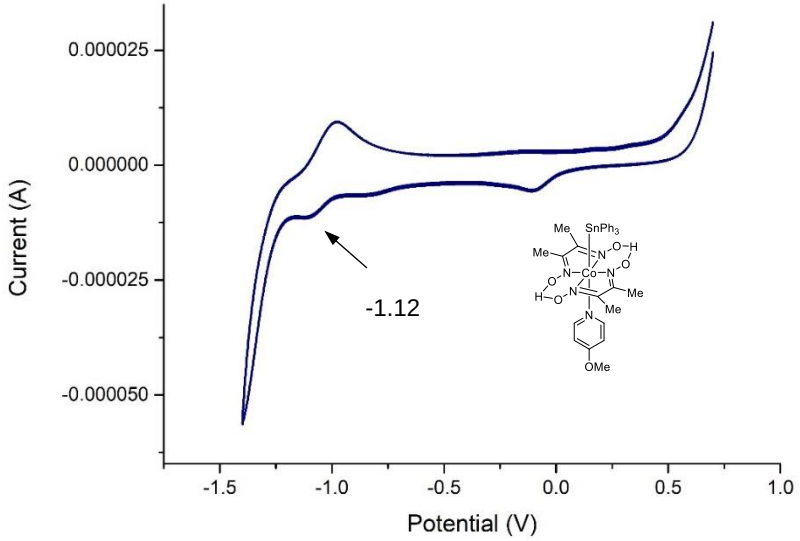


Figure S5. The cyclic voltammetry experiment of $Co(dmgH)_2(4\text{-OMe-Py})SnPh_3$ (0.001 M) and nBu$_4$NPF$_6$ (0.01 M) in CH_3CN with a sweep rate of 100 mV/s under anhydrous and anaerobic conditions. The redox potentials of $Co(dmgH)_2(4\text{-OMe-Py})SnPh_3$ was $E_p^{red}(Co^{II/I}) = -1.12V$ vs SCE.[7]

8. UV-Vis Absorption Spectra[8]

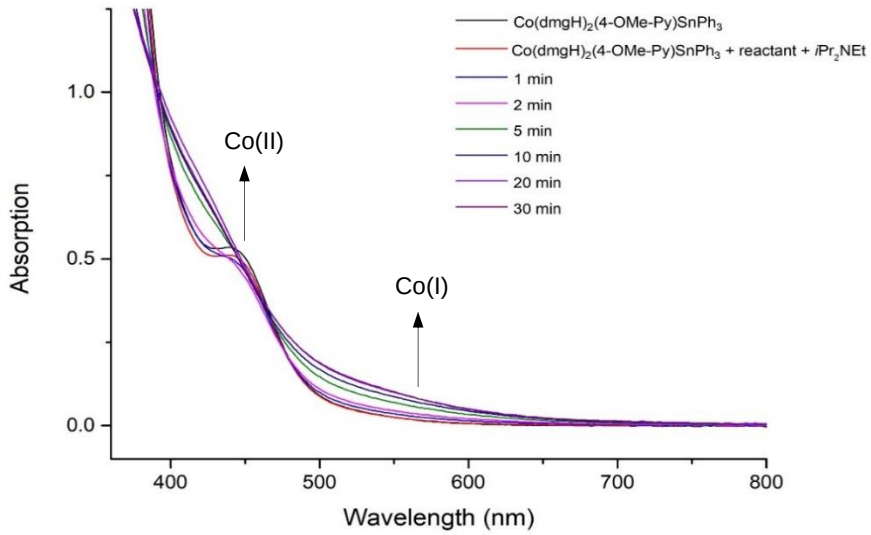
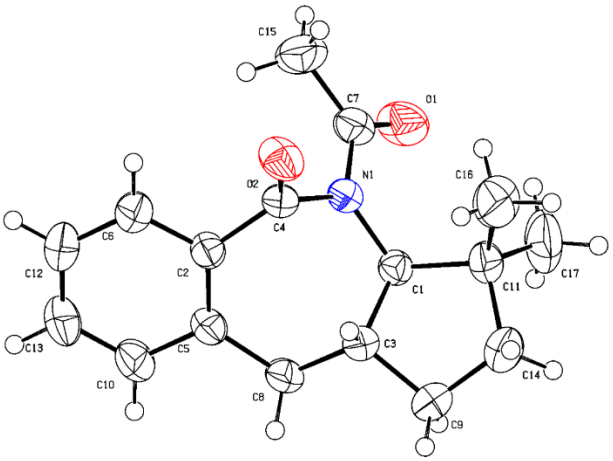
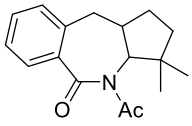


Figure S6. UV-Vis absorption spectra: (a) a solution of $Co(dmgH)_2(4\text{-OMe-Py})SnPh_3$ (3.0×10^{-4} M) in acetone under argon atmosphere; (b) a solution of $Co(dmgH)_2(4\text{-OMe-Py})SnPh_3$ (3.0×10^{-4} M), N-(2-iodophenyl)-N-methylcyclohexanecarboxamide **1'** (2.0×10^{-3} M) and iPr$_2$NEt (6.0×10^{-3} M) in acetone was irradiated with blue LEDs for 0 s, 1 min, 2 min, 5 min, 10 min, 20 min and 30 min under argon atmosphere.

9. X-Ray Crystallographic Data

X-ray crystallographic data of product **80**





CCDC 2117638

Bond precision:	C-C = 0.0019 A		Wavelength=1.54184
Cell:	a=8.1149(2)	b=9.1915(3)	c=10.8628(4)
	alpha=68.232(3)	beta=78.440(2)	gamma=81.264(2)
Temperature:	301 K		
	Calculated		Reported
Volume	734.51(4)		734.51(4)
Space group	P -1		P -1
Hall group	-P 1		-P 1
Moiety formula	C17 H21 N O2		C17 H21 N O2
Sum formula	C17 H21 N O2		C17 H21 N O2
Mr	271.35		271.35
Dx,g cm-3	1.227		1.227
Z	2		2
Mu (mm-1)	0.633		0.633
F000	292.0		292.0
F000'	292.83		
h,k,lmax	10,11,13		10,11,13
Nref	3120		2912
Tmin,Tmax	0.892,0.927		0.853,1.000
Tmin'	0.892		

Correction method= # Reported T Limits: Tmin=0.853 Tmax=1.000

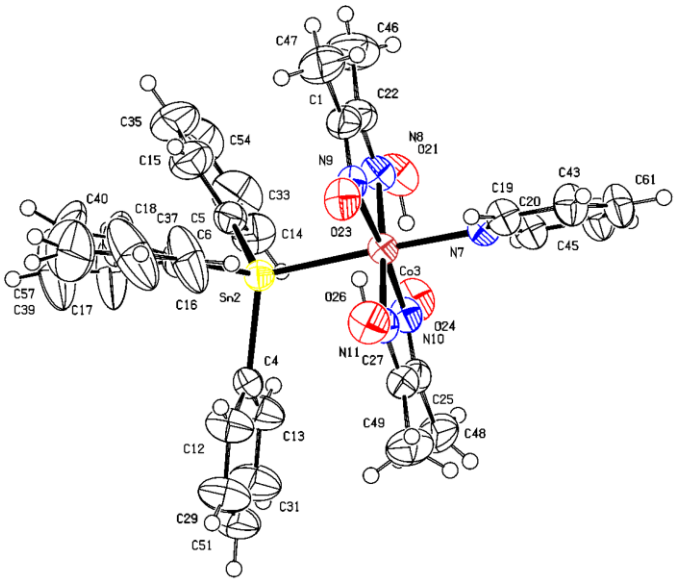
AbsCorr = MULTI-SCAN

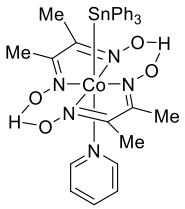
Data completeness= 0.933 Theta(max)= 77.395

R(reflections)= 0.0418(2697) wR2(reflections)= 0.1156(2912)

S = 1.059 Npar= 184

X-ray crystallographic data of Catalyst **I**





CCDC 2142047

Bond precision:	C-C = 0.0050 A		Wavelength=0.71073
Cell:	a=15.0187(7)	b=14.1539(5)	c=30.0583(11)
	alpha=90	beta=90	gamma=90
Temperature:	275 K		
	Calculated		Reported
Volume	6389.6(4)		6389.6(4)
Space group	P b c a		P b c a
Hall group	-P 2ac 2ab		-P 2ac 2ab
Moiety formula	C31 H34 Co N5 O4 Sn		C31 H34 Co N5 O4 Sn
Sum formula	C31 H34 Co N5 O4 Sn		C31 H32 Co N5 O4 Sn
Mr	718.27		716.23
Dx,g cm-3	1.493		1.489
Z	8		8
Mu (mm-1)	1.343		1.343
F000	2912.0		2896.0
F000'	2910.47		
h,k,lmax	21,20,43		21,17,40
Nref	10110		8171
Tmin,Tmax	0.829,0.851		0.121,1.000
Tmin'	0.829		

Correction method= # Reported T Limits: Tmin=0.121 Tmax=1.000

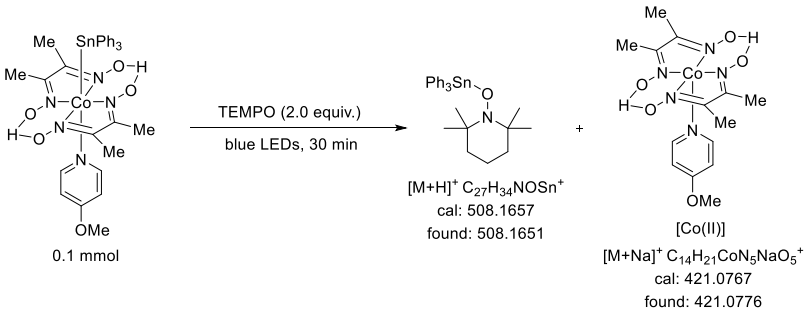
AbsCorr = MULTI-SCAN

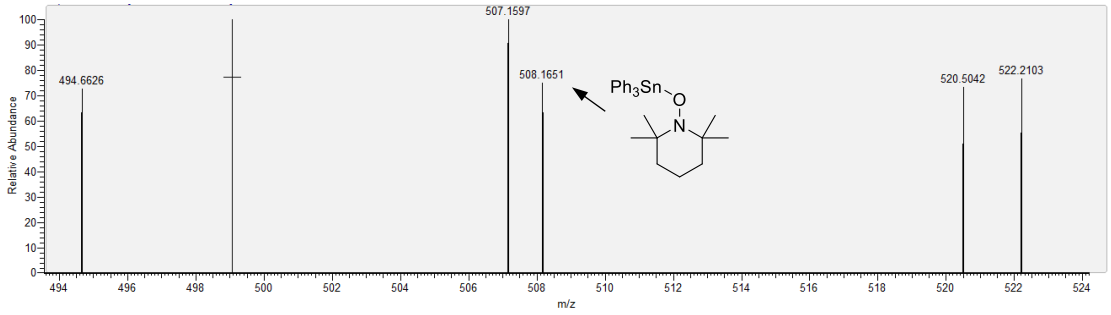
Data completeness= 0.808 Theta(max)= 30.911

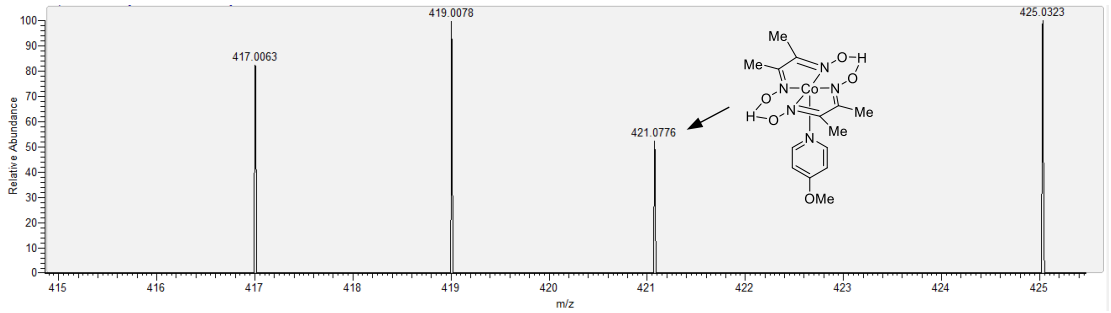
R(reflections)= 0.0363(5195) wR2(reflections)= 0.0861(8171)

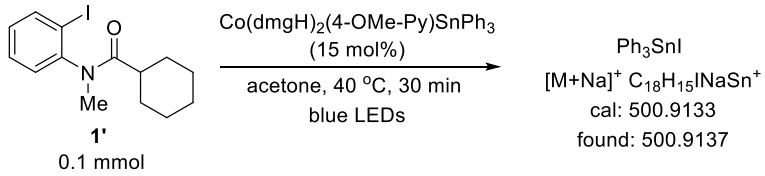
S = 1.035 Npar= 410

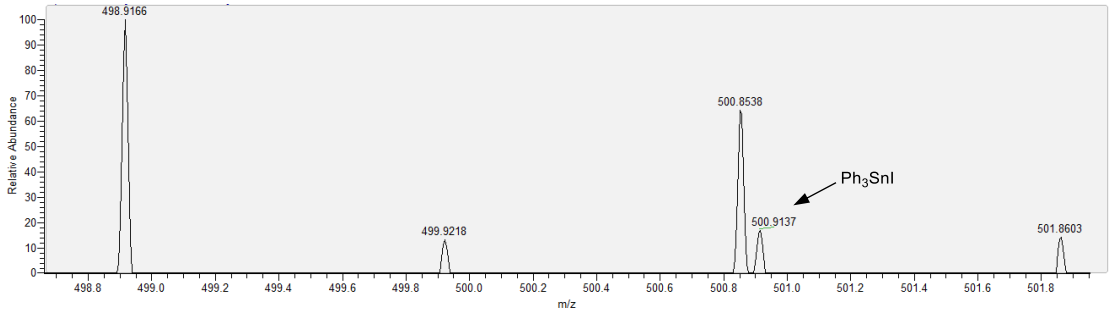
10. Control Experiments

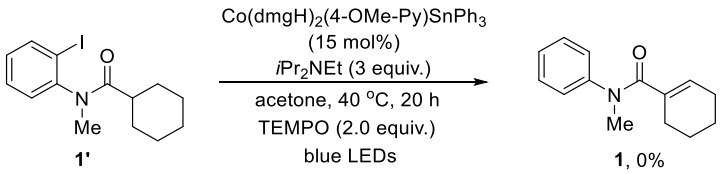




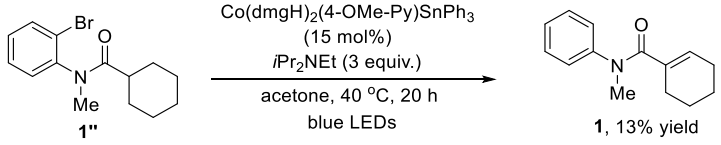




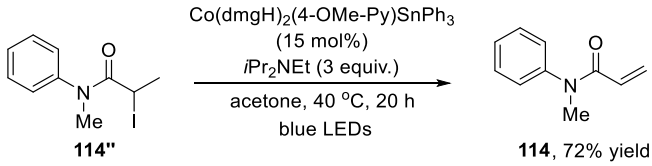




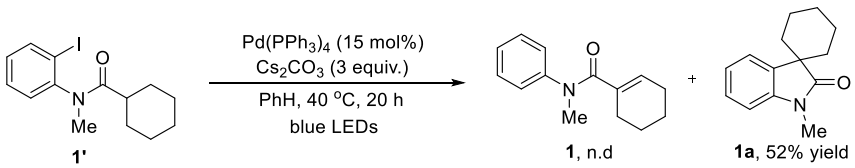
A solution of **1'** (0.1 mmol), $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (15 mol %), *i*Pr_2NEt (0.3 mmol) and TEMPO (0.2 mmol) in acetone (2 mL) was irradiated with 18 W blue LEDs for 20 hours under argon atmosphere at 40 ℃. After reaction, GC-MS showed that no product was obtained.



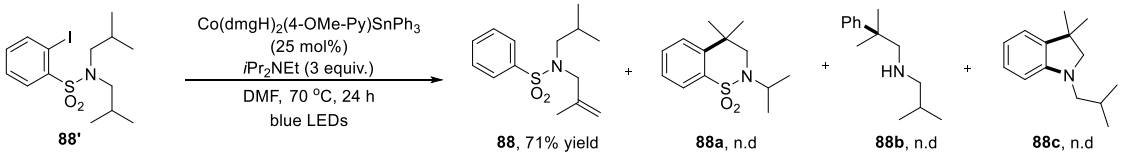
A solution of **1"** (0.1 mmol), $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (15 mol %), *i*Pr_2NEt (0.3 mmol) and TEMPO (0.2 mmol) in acetone (2 mL) was irradiated with 18 W blue LEDs for 20 hours under argon atmosphere at 40 ℃. After reaction, the residue was purified by flash chromatography on silica gel to get the product **1**. The result shown that the substitution of aryliodide for arylbromide derivatives lead a significant drop in yield.



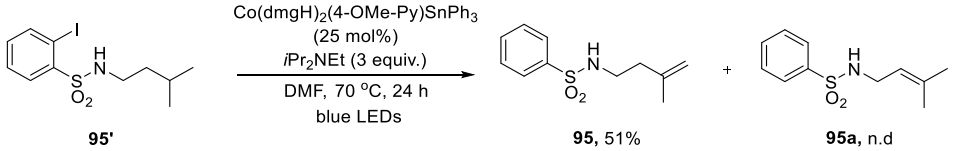
A solution of **114"** (0.1 mmol), $Co(dmgH)_2$(4-OMe-Py)$SnPh_3$ (15 mol %), *i*Pr_2NEt (0.3 mmol) in acetone (2 mL) was irradiated with 18 W blue LEDs for 20 hours under argon atmosphere at 40 ℃. ^1H NMR analysis showed that the product **114** could be also obtained.



A solution of **1'** (0.1 mmol), $Pd(PPh_3)_4$ (15 mol %), Cs_2CO_3 (0.3 mmol) in benzene (2 mL) was irradiated with 18 W blue LEDs for 20 hours under argon atmosphere at 40 ℃. After reaction, ^1H NMR analysis showed that only **1a** was obtained[9], **1** was not detected.

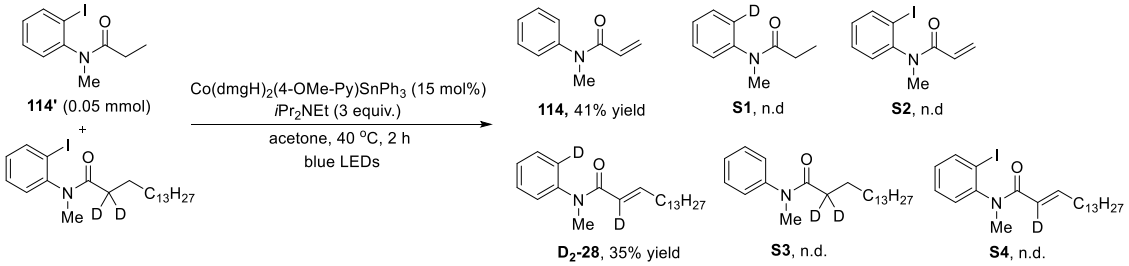


A solution of **88'** (0.1 mmol), $Co(dmgH)_2(4\text{-}OMe\text{-}Py)SnPh_3$ (25 mol %), $i Pr_2NEt$ (0.3 mmol) in DMF (2 mL) was irradiated with 18 W blue LEDs for 24 hours under argon atmosphere at 70 °C. The cyclization byproduct **88a** and Smiles rearrangement byproducts **88b** and **88c** were not detected by ^1H NMR analysis.

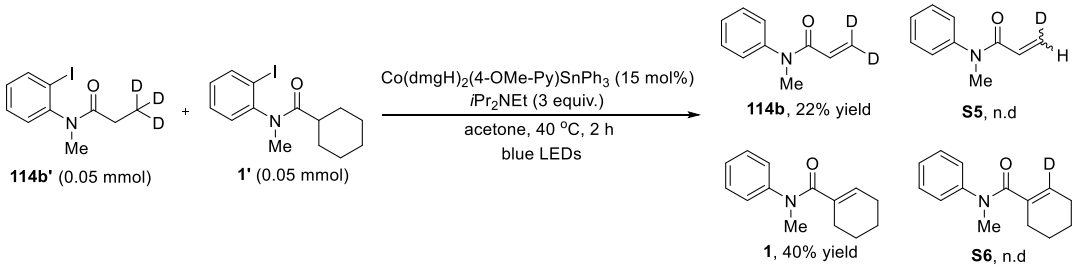


A solution of **95'** (0.1 mmol), $Co(dmgH)_2(4\text{-}OMe\text{-}Py)SnPh_3$ (25 mol %), $i Pr_2NEt$ (0.3 mmol) in DMF (2 mL) was irradiated with 18 W blue LEDs for 24 hours under argon atmosphere at 70 °C. The double bond isomerization **95a** was not detected by ^1H NMR analysis.

11. Isotope Labeling Crossover Experiment

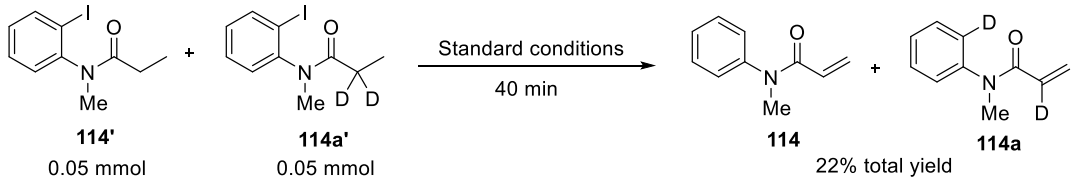


The solution of **114'** (0.05 mmol) and **D_2-28'** (0.05 mmol), Co(dmgH)$_2$(4-OMe-Py)SnPh$_3$ (15 mol %) and *i*Pr$_2$NEt (0.3 mmol) in acetone (2 mL) was irradiated with 18 W blue LEDs for 2 h under argon atmosphere at 40 ℃. After reaction, ^{1}H NMR and HRMS analysis showed that only compound **114** and **D_2-28** were afforded. The result suggested that the intermolecular HAT process was unlikely.

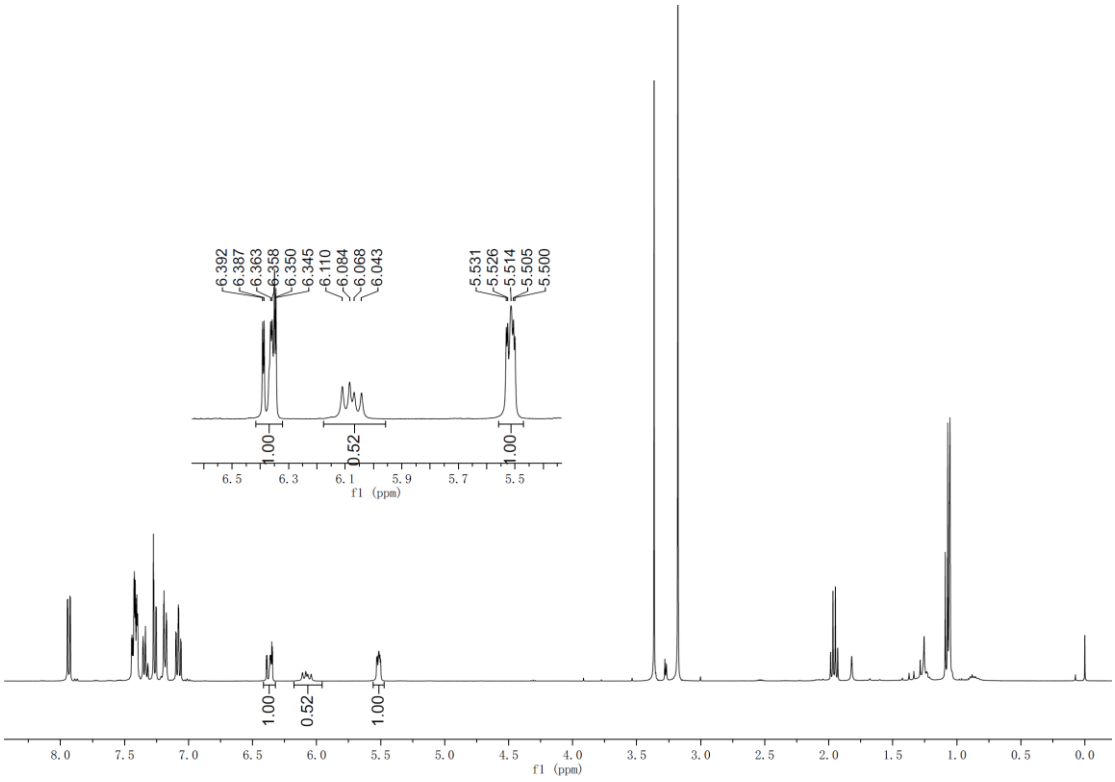


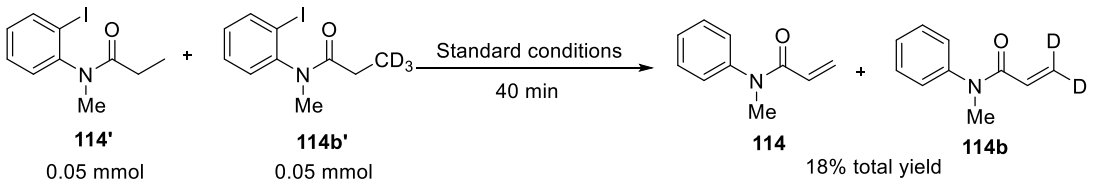
The solution of **114b'** (0.05 mmol) and **1'** (0.05 mmol), Co(dmgH)$_2$(4-OMe-Py)SnPh$_3$ (15 mol %) and *i*Pr$_2$NEt (0.3 mmol) in acetone (2 mL) was irradiated with 18 W blue LEDs for 2 h under argon atmosphere at 40 ℃. After reaction, ^{1}H NMR and HRMS showed that only compound **114b** and **1** were afforded. The result suggested that the β-position H/D exchange through reversible addition of Co(III)−H/D across the double bond to produce **S5** and **S6** was unlikely in this reaction conditions.

12. Competition KIE Experiments

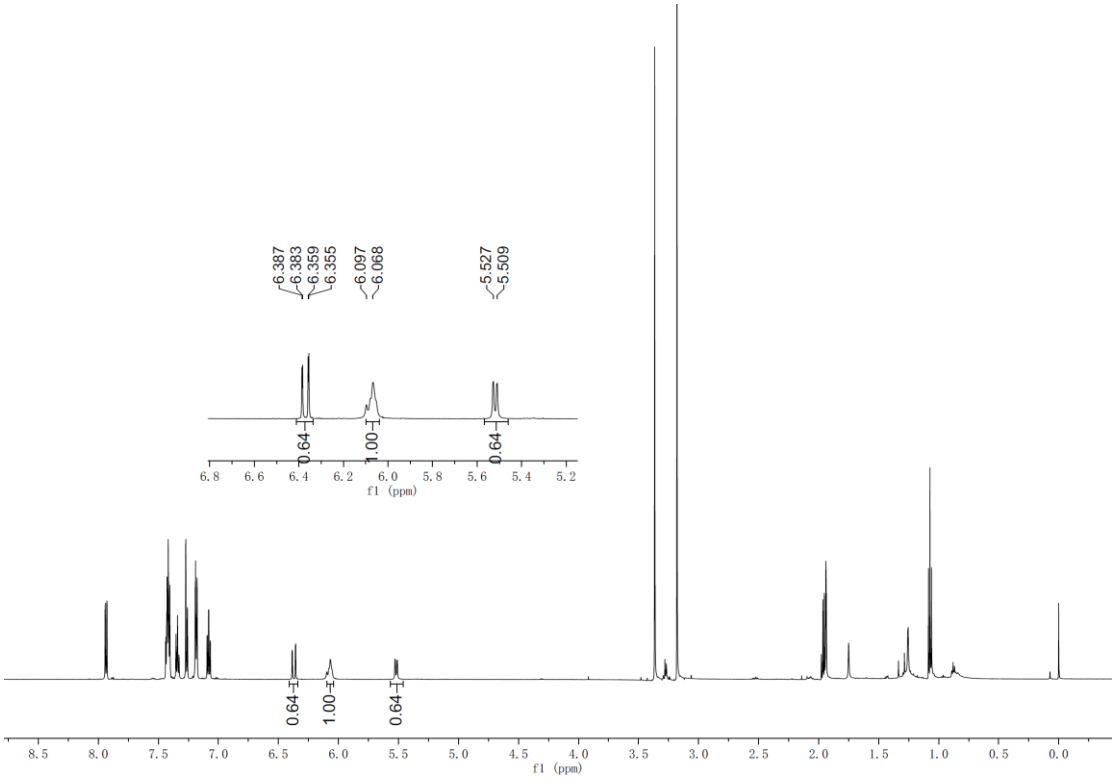


The solution of **114'** (0.05 mmol) and **114a'** (0.05 mmol), $Co(dmgH)_2(4\text{-}OMe\text{-}Py)SnPh_3$ (15 mol %) and iPr$_2$NEt (0.3 mmol) in acetone (2 mL) was irradiated with 18 W blue LEDs for 40 min under argon atmosphere at 40 ℃. After reaction, upon removal of solvent under vacuum, the residue was purified by flash chromatography on silica gel to get the crude products, which subsequently detected by ^{1}H NMR analysis. The KIE value is 1.08.





The solution of **114'** (0.05 mmol) and **114b'** (0.05 mmol), $Co(dmgH)_2(4\text{-}OMe\text{-}Py)SnPh_3$ (15 mol %) and *i*Pr_2NEt (0.3 mmol) in acetone (2 mL) was irradiated with 18 W blue LEDs for 40 min under argon atmosphere at 40 ℃. After reaction, upon removal of solvent under vacuum, the residue was purified by flash chromatography on silica gel to get the crude products, which subsequently detected by ^1H NMR analysis. The KIE value is 1.78.



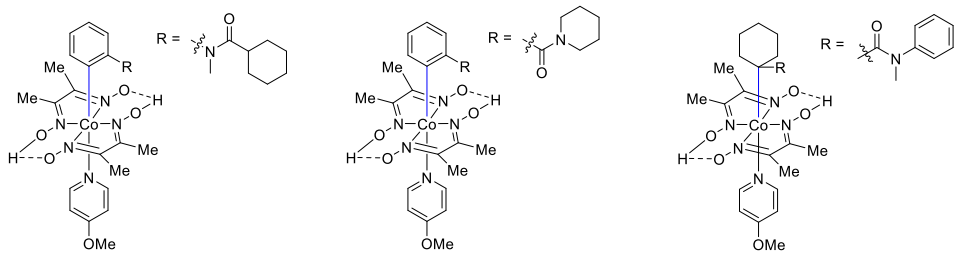
13. Supplementary Experiments

1. Computational experiment

Calculation details

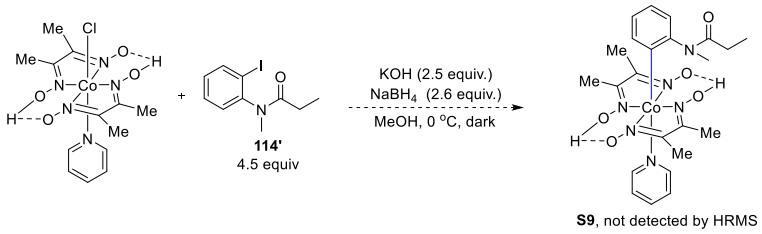
All the calculations were performed with the Gaussian 16 program package using the default conditions implemented in it. For geometry optimization and frequency analysis we adopted the B3LYP-D3BJ with the def2-SVP basis set. To refine the calculated energy, single point calculations were performed using the larger basis set def2-TZVP based on these optimized structures. Solvent effect was modeled in these optimization and single point calculations by employing SMD continuum solvation model, taking acetone as the solvent for each reaction.

Determination the BDE of Co-C bond



S7-1, BDE (Co-C) = 47.5 kcal/mol　　**S7-2**, BDE (Co-C) = 42.7 kcal/mol　　**S8**, BDE (Co-C) = 22.4 kcal/mol

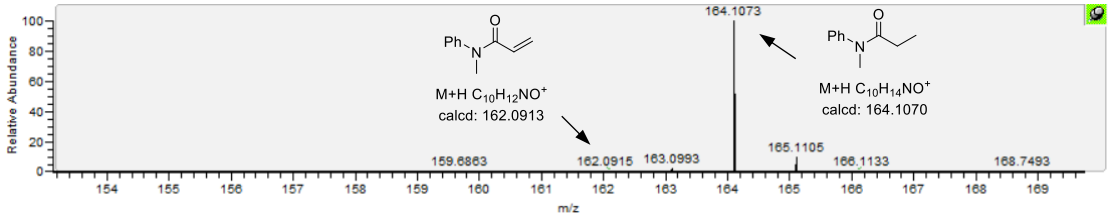
2. Synthesis of aryl cobaloxime intermediates[10]



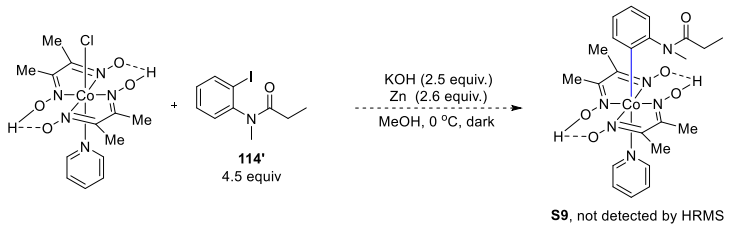
S9, not detected by HRMS

To a solution of KOH (70 mg, 1.25 mmol, 2.5 equiv.) in MeOH (10 mL) was added $Co(dmgH)_2PyCl$ (200 mg, 0.5 mmol, 1.0 equiv.). The solution was cooled to 0 °C and degassed via passing argon through the solution via needle for 15 minutes. $NaBH_4$ (49 mg, 1.3 mmol, 2.6 equiv.) was then added, the reaction was stirred for 5 minutes and aryl iodide **114'** (0.30 mL, 2.25 mmol, 4.5 equiv.) was added. The reaction was stirred for 30 minutes, H_2O (20 mL) was added, the mixture was extracted by CH_2Cl_2. HRMS showed that no aryl cobaloxime **S9** was detected, and only reduction and dehydrogenation products of **114'** could be detected. It is likely that aryl iodide **114'** was

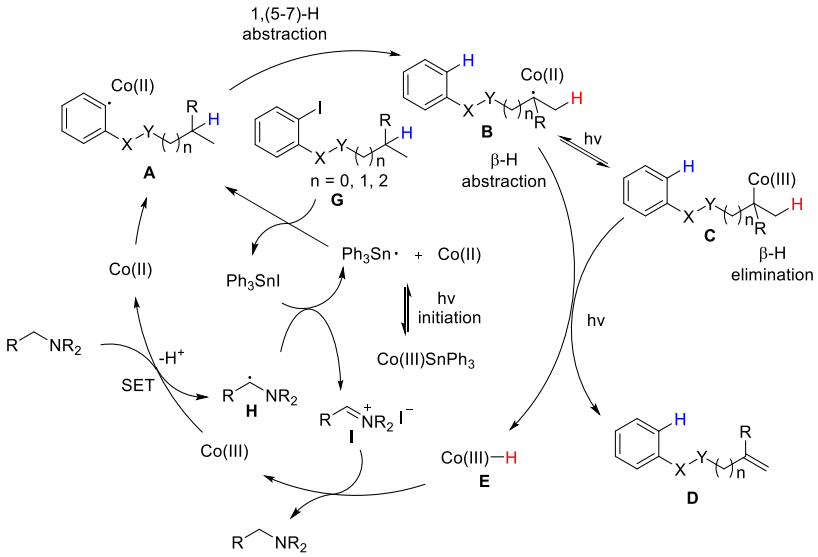
reduced by Co(I) species via single electron transfer. Subsequently, aryl radical undergoes a fast 1,5-HAT to produce alkyl radical.



The same result was afforded using Zn as reduction.



An alternative mechanism



Another path based on aminoalkyl radicals as halogen-atom transfer agents might be also possible in the presence of amine base such as *i*Pr_2NEt or NEt_3. An alpha aminyl radical intermediate **H** generated from photooxidation by cobalt (III) performs halogen atom transfer (XAT) from Ph_3SnI. The fast and irreversible dissociation of the resulting alpha-iodoamine into the iminium iodide **I** provides the thermodynamic driving force to the process. Subsequently, iminium iodide **I** might be reduced by Co(III)-H to regenerate amine base. Next, the generated triphenyltin radical performs secondary halogen atom transfer (XAT) from aryl iodide **G** to produce aryl radical.

Reference

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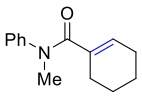
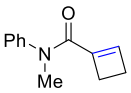
14. Characterization of Products

N-methyl-N-phenylcyclohex-1-ene-1-carboxamide (1)



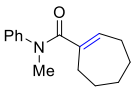
Colorless oil; 20.7 mg, 96% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.35-7.33 (m, 2H), 7.26-7.18 (m, 1H), 7.14-7.11 (m, 2H), 5.91-5.74 (m, 1H), 3.34 (s, 3H), 1.98-1.80 (m, 4H), 1.49-1.34 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.6, 144.9, 134.5, 132.5, 128.9, 126.4, 126.3, 37.6, 25.9, 24.8, 21.9, 21.3; HRMS (ESI) for $C_{14}H_{18}NO$ $[M+H]^+$ calcd 216.1383, found 216.1382.

N-methyl-N-phenylcyclobut-1-ene-1-carboxamide (2)



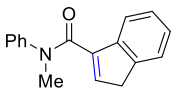
Colorless oil; 11.6 mg, 62% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.42-7.33 (m, 3H), 7.23 (d, *J* = 7.1 Hz, 2H), 5.70 (s, 1H), 3.31 (s, 3H), 2.22 (s, 2H), 2.17 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 162.7, 143.6, 143.3, 141.2, 129.4, 127.9, 127.8, 37.7, 30.9, 26.7; HRMS (ESI) for $C_{12}H_{14}NO$ $[M+H]^+$ calcd 188.1070, found 188.1069.

N-methyl-N-phenylcyclohept-1-ene-1-carboxamide (3)



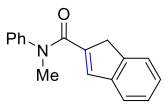
Colorless oil; 20.5 mg, 89% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.34 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 6.07 (t, *J* = 6.4 Hz, 1H), 3.33 (s, 3H), 2.12-2.05 (m, 2H), 2.02 (dd, *J* = 10.7, 6.2 Hz, 2H), 1.58-1.53 (m, 2H), 1.34-1.25 (m, 2H), 1.24-1.20 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 173.8, 144.8, 140.6, 137.1, 129.0, 127.0, 126.5, 37.6, 31.8, 30.8, 28.6, 26.0, 25.7; HRMS (ESI) for $C_{15}H_{20}NO$ $[M+H]^+$ calcd 230.1539, found 230.1539.

N-methyl-N-phenyl-1H-indene-3-carboxamide (4)



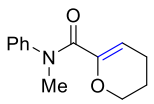
Colorless oil; 22.5 mg, 90% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.68 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.26-7.21 (m, 2H), 7.21-7.11 (m, 4H), 6.09 (s, 1H), 3.50 (s, 3H), 3.22 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.6, 144.5, 142.7, 142.5, 139.2, 136.5, 129.1, 126.8, 126.5, 126.4, 125.2, 123.5, 121.5, 38.5, 37.6; HRMS (ESI) for $C_{17}H_{16}NO$ $[M+H]^+$ calcd 250.1226, found 250.1228.

N-methyl-N-phenyl-1H-indene-2-carboxamide (5)



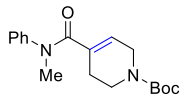
White solid; 24.0 mg, 96% yield, reaction time 20 h; mp 78-80 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.44-7.33 (m, 4H), 7.29-7.19 (m, 5H), 6.66 (s, 1H), 3.47 (s, 3H), 3.43 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.4, 144.8, 143.7, 143.0, 140.7, 138.1, 129.5, 127.4, 127.2, 126.42, 126.38, 123.7, 122.5, 40.1, 38.5; HRMS (ESI) for $C_{17}H_{16}NO$ $[M+H]^+$ calcd 250.1226, found 250.1229.

N-methyl-N-phenyl-3,4-dihydro-2H-pyran-6-carboxamide (6)



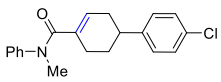
Colorless oil; 18.7 mg, 86% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.37-7.31 (m, 2H), 7.25-7.20 (m, 1H), 7.20-7.14 (m, 2H), 5.40 (t, *J* = 4.0 Hz, 1H), 3.49 (t, *J* = 5.0 Hz, 2H), 3.33 (s, 3H), 2.00 (dt, *J* = 6.4, 4.1 Hz, 2H), 1.70-1.56 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 165.9, 148.4, 144.9, 128.8, 126.4, 125.5, 106.9, 65.6, 37.9, 21.5, 20.0; HRMS (ESI) for $C_{13}H_{16}NO_2$ $[M+H]^+$ calcd 218.1176, found 218.1170.

tert-butyl 4-(methyl(phenyl)carbamoyl)-3,6-dihydropyridine-1(2H)-carboxylate (7)



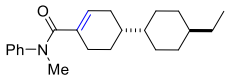
Colorless oil; 28.8 mg, 91% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.37-7.32 (m, 2H), 7.27-7.22 (m, 1H), 7.13-7.07 (m, 2H), 5.88-5.86 (m, 1H), 3.78 (dd, *J* = 5.7, 2.8 Hz, 2H), 3.35 (s, 3H), 3.28 (t, *J* = 5.6 Hz, 2H), 2.02-1.99 (m, 2H), 1.41 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 170.6, 154.6, 144.5, 129.3, 127.0, 126.5, 79.7, 37.9, 28.4, 28.3, 26.30, 26.27; HRMS (ESI) for $C_{18}H_{24}N_2NaO_3$ $[M+Na]^+$ calcd 339.1679, found 339.1682.

4'-chloro-N-methyl-N-phenyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-carboxamide (8)



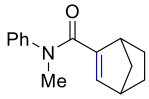
White solid; 31.0 mg, 95% yield, reaction time 20 h; mp 70-72 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.38-7.34 (m, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.17-7.11 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.91 (d, *J* = 1.9 Hz, 1H), 3.35 (s, 3H), 2.62-2.50 (m, 1H), 2.21 (dt, *J* = 18.4, 4.1 Hz, 1H), 2.14-2.02 (m, 2H), 2.01-1.89 (m, 1H), 1.84-1.73 (m, 1H), 1.58-1.47 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.1, 144.9, 144.5, 134.6, 131.6, 131.5, 129.1, 128.4, 128.1, 126.7, 126.4, 38.2, 37.7, 32.6, 29.1, 26.1; HRMS (ESI) for $C_{20}H_{21}ClNO$ $[M+H]^+$ calcd 326.1306, found 326.1306.

(1R*,1'r*,4'R*)-4'-ethyl-N-methyl-N-phenyl-[1,1'-bi(cyclohexan)]-3-ene-4-carboxamide (9)



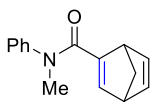
White solid; 29.9 mg, 92% yield, reaction time 20 h; mp 67-69 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.33 (t, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 5.84 (s, 1H), 3.33 (s, 3H), 2.09-1.81 (m, 3H), 1.75-1.58 (m, 6H), 1.20-0.99 (m, 5H), 0.93-0.73 (m, 8H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.5, 145.0, 134.5, 132.7, 129.0, 126.44, 126.37, 42.0, 39.5, 38.1, 37.6, 32.9, 29.9, 29.8, 28.9, 26.5, 25.5, 11.4; HRMS (ESI) for $C_{22}H_{32}NO$ $[M+H]^+$ calcd 326.2478, found 326.2479.

N-methyl-N-phenylbicyclo[2.2.1]hept-2-ene-2-carboxamide (10)



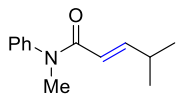
Colorless oil; 18.3 mg, 81% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.35 (t, *J* = 7.7 Hz, 2H), 7.29-7.25 (m, 1H), 7.15 (d, *J* = 7.7 Hz, 2H), 5.66 (d, *J* = 3.0 Hz, 1H), 3.33 (s, 3H), 2.96 (s, 1H), 2.73 (s, 1H), 1.64-1.52 (m, 2H), 1.22-1.16 (m, 1H), 1.16-1.08 (m, 1H), 0.98 (d, *J* = 8.3 Hz, 1H), 0.95-0.88 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.8, 144.8, 142.9, 141.8, 129.1, 127.2, 127.0, 47.3, 44.2, 43.3, 37.8, 24.8; HRMS (ESI) for $C_{15}H_{18}NO$ $[M+H]^+$ calcd 228.1383, found 228.1381.

N-methyl-N-phenylbicyclo[2.2.1]hepta-2,5-diene-2-carboxamide (11)



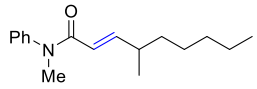
Colorless oil; 15.7 mg, 70% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.36 (t, *J* = 7.5 Hz, 2H), 7.31-7.26 (m, 1H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.55 (d, *J* = 3.1 Hz, 1H), 6.53-6.45 (m, 1H), 6.42-6.36 (m, 1H), 3.45 (d, *J* = 10.7 Hz, 2H), 3.34 (s, 3H), 1.87 (d, *J* = 6.2 Hz, 1H), 1.82 (d, *J* = 6.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 167.0, 152.2, 149.3, 144.2, 143.2, 140.6, 129.3, 127.3, 127.1, 72.7, 52.4, 50.9, 38.0; HRMS (ESI) for $C_{15}H_{16}NO$ $[M+H]^+$ calcd 226.1226, found 226.1225.

(E)-N,4-dimethyl-N-phenylpent-2-enamide (12)



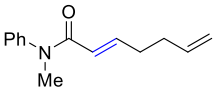
Colorless oil; 19.0 mg, 93% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.41 (t, *J* = 7.5 Hz, 2H), 7.35-7.31 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 6.87 (dd, *J* = 15.2, 7.1 Hz, 1H), 5.69 (d, *J* = 15.2 Hz, 1H), 3.35 (s, 3H), 2.30 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.4, 152.1, 143.7, 129.4, 127.3, 127.2, 118.5, 37.3, 30.9, 21.4; HRMS (ESI) for $C_{13}H_{18}NO$ $[M+H]^+$ calcd 204.1383, found 204.1382.

(E)-N,4-dimethyl-N-phenylnon-2-enamide (13)



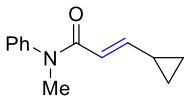
Colorless oil; 22.6 mg, 87% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.40 (t, *J* = 7.5 Hz, 2H), 7.34-7.30 (m, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 6.77 (dd, *J* = 15.2, 8.3 Hz, 1H), 5.68 (d, *J* = 15.2 Hz, 1H), 3.34 (s, 3H), 2.09 (m, 1H), 1.26-1.16 (m, 8H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.4, 151.2, 143.8, 129.3, 127.2, 119.7, 37.3, 36.5, 36.1, 31.7, 26.8, 22.5, 19.7, 14.0; HRMS (ESI) for $C_{17}H_{26}NO$ $[M+H]^+$ calcd 260.2009, found 260.2010.

(E)-N-methyl-N-phenylhepta-2,6-dienamide (14)



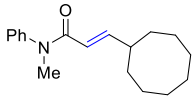
Colorless oil; 17.4 mg, 81% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.42 (t, *J* = 7.5 Hz, 2H), 7.35-7.31 (m, 1H), 7.20-7.13 (m, 2H), 6.91 (dt, *J* = 15.0, 6.6 Hz, 1H), 5.77-5.68 (m, 2H), 5.01-4.88 (m, 2H), 3.34 (s, 3H), 2.19-2.06 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.0, 144.9, 143.6, 137.3, 129.4, 127.33, 127.26, 121.7, 115.1, 37.3, 32.2, 31.4; HRMS (ESI) for $C_{14}H_{17}NNaO$ $[M+Na]^+$ calcd 238.1202 , found 238.1200.

(E)-3-cyclopropyl-N-methyl-N-phenylacrylamide (15)



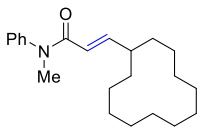
White solid; 18.3 mg, 91% yield, reaction time 20 h; mp = 52-54 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.44-7.40 (m, 2H), 7.36-7.28 (m, 1H), 7.23-7.13 (m, 2H), 6.35 (dd, *J* = 14.9, 10.2 Hz, 1H), 5.83 (d, *J* = 14.9 Hz, 1H), 3.33 (s, 3H), 1.41-1.28 (m, 1H), 0.86-0.74 (m, 2H), 0.58-0.49 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.0, 150.6, 143.7, 129.4, 127.3, 127.2, 118.2, 37.2, 14.3, 8.1; HRMS (ESI) for $C_{13}H_{16}NO$ $[M+H]^+$ calcd 202.1226, found 202.1228.

(E)-3-cyclooctyl-N-methyl-N-phenylacrylamide (16)



Colorless oil; 23.1 mg, 85% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.43-7.39 (m, 2H), 7.36-7.27 (m, 1H), 7.21-7.13 (m, 2H), 6.88 (dd, *J* = 15.2, 7.7 Hz, 1H), 5.66 (d, *J* = 15.2 Hz, 1H), 3.34 (s, 3H), 2.22-2.20 (m, 1H), 1.60-1.35 (m, 14H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.6, 151.9, 143.8, 129.4, 127.24, 127.21 118.5, 40.6, 37.3, 30.6, 27.2, 25.7, 24.7; HRMS (ESI) for $C_{18}H_{26}NO$ $[M+H]^+$ calcd 272.2009, found 272.2011.

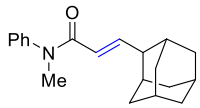
(E)-3-cyclododecyl-N-methyl-N-phenylacrylamide (17)



Colorless oil; 20.9 mg, 64% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.42-7.37 (m, 2H), 7.35-7.28 (m, 1H), 7.18-7.16 (m, 2H), 6.78 (dd, *J* = 15.2, 8.2 Hz, 1H), 5.66 (d, *J* = 15.2 Hz, 1H), 3.33 (s, 3H), 2.19-2.07 (m, 1H), 1.46-1.37 (m, 2H), 1.45-1.15 (m, 20H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.5, 150.9, 143.8, 129.4, 127.2, 120.0, 37.3, 37.0, 29.0, 23.63, 23.60, 23.3, 22.1; HRMS (ESI)

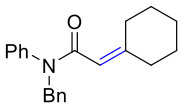
for $C_{22}H_{34}NO$ $[M+H]^+$ calcd 328.2635, found 328.2631.

(E)-3-adamantan-2-yl)-N-methyl-N-phenylacrylamide (18)



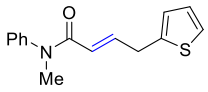
White solid; 19.3 mg, 65% yield, reaction time 20 h; mp = 113-115 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ (ppm) = 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.10 (dd, *J* = 15.4, 6.5 Hz, 1H), 5.72 (d, *J* = 15.3 Hz, 1H), 3.33 (s, 3H), 2.35 (d, *J* = 4.3 Hz, 1H), 1.84-1.81 (m, 3H), 1.78-1.75 (m, 3H), 1.72 (s, 2H), 1.67-1.64 (m, 4H), 1.45 (d, *J* = 12.6 Hz, 2H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 166.6, 149.8, 143.9, 129.4, 127.32, 127.26, 120.7, 46.7, 38.4, 37.8, 37.4, 32.4, 32.1, 27.9, 27.7; HRMS (ESI) for $C_{20}H_{26}NO$ $[M+H]^+$ calcd 296.2009, found 296.2015.

N-benzyl-2-cyclohexylidene-N-phenylacetamide (19)



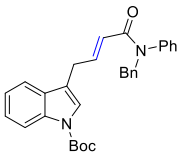
White solid; 22.7 mg, 74% yield, reaction time 20 h; mp = 59-61℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.30-7.21 (m, 8H), 7.01 (d, *J* = 7.2 Hz, 2H), 5.40 (s, 1H), 4.95 (s, 2H), 2.81-2.69 (m, 2H), 1.96 (t, *J* = 5.2 Hz, 2H), 1.62-1.57 (m, 2H), 1.57-1.46 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 167.1, 157.1, 142.7, 137.9, 129.0, 128.4, 128.2, 128.0, 127.1, 127.0, 115.1, 52.5, 37.7, 30.1, 28.4, 27.7, 26.2; HRMS (ESI) for $C_{21}H_{24}NO$ $[M+H]^+$ calcd 306.1852, found 306.1855.

(E)-N-methyl-N-phenyl-4-(thiophen-2-yl)but-2-enamide (20)



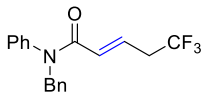
Colorless oil; 21.9 mg, 85% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.45-7.36 (m, 2H), 7.36-7.28 (m, 1H), 7.18-7.16 (m, 2H), 7.10 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.01 (dt, *J* = 15.0, 6.9 Hz, 1H), 6.87 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.78-6.67 (m, 1H), 5.83 (d, *J* = 15.0 Hz, 1H), 3.56 (d, *J* = 6.9 Hz, 2H), 3.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 165.7, 143.5, 142.3, 140.7, 129.5, 127.4, 127.2, 126.8, 125.1, 123.9, 123.0, 37.3, 32.3; HRMS (ESI) for $C_{15}H_{16}NOS$ $[M+H]^+$ calcd 258.0947, found 258.0949.

tert-butyl (E)-3-(4-(benzyl(phenyl)amino)-4-oxobut-2-en-1-yl)-1H-indole-1-carboxylate (21)



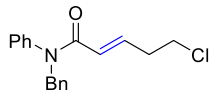
Colorless oil; 37.8 mg, 81% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 8.09 (d, *J* = 6.8 Hz, 1H), 7.34-7.28 (m, 3H), 7.25-7.12 (m, 10H), 6.98-6.86 (m, 2H), 5.80 (d, *J* = 15.1 Hz, 1H), 4.95 (s, 2H), 3.43 (d, *J* = 6.7 Hz, 2H), 1.65 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 165.6, 149.6, 142.7, 141.8, 137.4, 135.5, 130.0, 129.2, 128.6, 128.2, 127.5, 127.2, 124.3, 123.2, 123.1, 122.3, 118.9, 117.2, 115.2, 83.4, 53.0, 28.2, 27.9; HRMS (ESI) for $C_{30}H_{31}N_2O_3$ $[M+H]^+$ calcd 467.2329, found 467.2333.

(E)-N-benzyl-5,5,5-trifluoro-N-phenylpent-2-enamide (22)



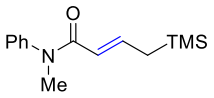
White solid; 23.3 mg, 73% yield, reaction time 20 h; mp = 65-67℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.38-7.31 (m, 3H), 7.31-7.19 (m, 5H), 6.99 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.88-6.80 (m, 1H), 5.92 (d, *J* = 15.2 Hz, 1H), 4.97 (s, 2H), 2.88-2.76 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 164.5, 141.5, 137.1, 132.2 (q, *J* = 4.0 Hz), 129.5, 128.7, 128.4, 128.3, 128.0, 127.8, 127.4, 125.2 (q, *J* = 275.0 Hz), 53.2, 36.7 (q, *J* = 30.3 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) = -65.6; HRMS (ESI) for $C_{18}H_{17}F_3NO$ $[M+H]^+$ calcd 320.1257, found 320.1259.

(E)-N-benzyl-5-chloro-N-phenylpent-2-enamide (23)



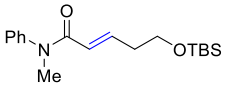
Colorless oil; 13.2 mg, 44% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.36-7.28 (m, 3H), 7.28-7.19 (m, 5H), 7.04-6.96 (m, 2H), 6.96-6.84 (m, 1H), 5.80 (d, *J* = 15.2 Hz, 1H), 4.97 (s, 2H), 3.49 (t, *J* = 6.8 Hz, 2H), 2.51 (qd, *J* = 6.9, 1.1 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 165.4, 141.8, 141.0, 137.4, 129.4, 128.7, 128.4, 128.3, 127.8, 127.3, 124.2, 53.1, 42.5, 35.2; HRMS (ESI) for $C_{18}H_{19}ClNO$ $[M+H]^+$ calcd 300.1150, found 300.1151.

(E)-N-methyl-N-phenyl-4-(trimethylsilyl)but-2-enamide (24)



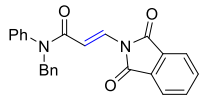
Colorless oil; 19.5 mg, 79% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.40-7.36 (m, 2H), 7.32-7.27 (m, 1H), 7.17-7.15 (m, 2H), 6.96 (dt, *J* = 15.0, 8.9 Hz, 1H), 5.54 (d, *J* = 15.0 Hz, 1H), 3.32 (s, 3H), 1.55 (dd, *J* = 8.8, 0.9 Hz, 2H), -0.04 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.5, 144.1, 144.0, 129.4, 127.4, 127.2, 119.6, 37.2, 24.6, -1.9; HRMS (ESI) for $C_{14}H_{22}NOSi$ $[M+H]^+$ calcd 248.1465, found 248.1467.

(E)-5-((tert-butyldimethylsilyl)oxy)-N-methyl-N-phenylpent-2-enamide (25)



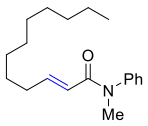
Colorless oil; 24.1 mg, 75% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.38 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.19-7.12 (m, 2H), 6.91-6.83 (m, 1H), 5.78 (d, *J* = 15.2 Hz, 1H), 3.60 (t, *J* = 6.5 Hz, 2H), 3.32 (s, 3H), 2.28-2.20 (m, 2H), 0.83 (s, 9H), -0.02 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 165.9, 143.7, 142.4, 129.4, 127.33, 127.28, 123.0, 61.7, 37.3, 35.8, 25.8, 18.2, -5.4; HRMS (ESI) for $C_{18}H_{30}NO_2Si$ $[M+H]^+$ calcd 320.2040, found 320.2044.

(E)-N-benzyl-3-(1,3-dioxoisoindolin-2-yl)-N-phenylacrylamide (26)



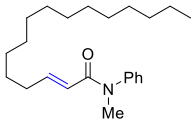
White solid; 22.6 mg, 59% yield, reaction time 30 h; mp = 154-156 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 8.00 (d, *J* = 14.2 Hz, 1H), 7.85-7.82 (m, 2H), 7.79-7.70 (m, 2H), 7.42-7.32 (m, 3H), 7.30-7.22 (m, 5H), 7.12-6.98 (m, 2H), 6.90 (d, *J* = 14.2 Hz, 1H), 5.03 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.1, 165.6, 141.8, 137.5, 134.9, 131.4, 129.5, 129.2, 128.7, 128.4, 128.3, 128.0, 127.3, 124.0, 109.5, 53.2; HRMS (ESI) for $C_{24}H_{19}N_2O_3$ $[M+H]^+$ calcd 383.1390, found 383.1392.

(E)-N-methyl-N-phenyldodec-2-enamide (27)



Colorless oil; 25.9 mg, 90% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.41 (t, *J* = 7.5 Hz, 2H), 7.34-7.30 (m, 1H), 7.20-7.15 (m, 2H), 6.96-6.82 (m, 1H), 5.72 (d, *J* = 15.1 Hz, 1H), 3.34 (s, 3H), 2.07-2.01 (m, 2H), 1.30-1.16 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.2, 146.0, 143.7, 129.4, 127.2, 121.2, 37.3, 32.1, 31.8, 29.4, 29.3, 29.2, 29.0, 28.2, 22.6, 14.0; HRMS (ESI) for $C_{19}H_{30}NO$ $[M+H]^+$ calcd 288.2322, found 288.2323.

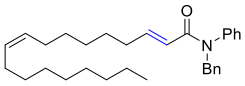
(E)-N-methyl-N-phenylhexadec-2-enamide (28)



Colorless oil; 29.5 mg, 86% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.43-7.38 (m, 2H), 7.34-7.30 (m, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 6.98-6.80 (m, 1H), 5.72 (d, *J* = 15.1 Hz, 1H), 3.34 (s, 3H), 2.06-2.01 (m, 2H), 1.33-1.21 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm)

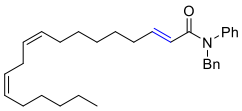
= 166.2, 146.1, 143.7, 129.4, 127.3, 121.3, 37.3, 32.1, 31.8, 29.60, 29.58, 29.55, 29.5, 29.3, 29.0, 28.2, 22.6, 14.1; HRMS (ESI) for $C_{23}H_{38}NO$ $[M+H]^+$ calcd 344.2948, found 344.2948.

(2E,9Z)-N-benzyl-N-phenyloctadeca-2,9-dienamide (29)



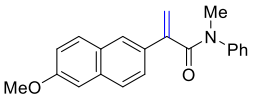
Colorless oil; 31.2 mg, 70% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.34-7.29 (m, 3H), 7.28-7.22 (m, 5H), 7.04-6.94 (m, 3H), 5.70 (d, *J* = 15.1 Hz, 1H), 5.37-5.29 (m, 2H), 4.98 (s, 2H), 2.09-1.95 (m, 6H), 1.34-1.24 (m, 18H), 0.89 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.1, 146.7, 142.2, 137.6, 130.1, 129.5, 129.3, 128.6, 128.4, 128.3, 127.6, 127.2, 121.4, 53.1, 32.2, 31.9, 29.7, 29.5, 29.4, 29.3, 28.1, 27.2, 27.0, 22.7, 14.1; HRMS (ESI) for $C_{31}H_{44}NO$ $[M+H]^+$ calcd 446.3417, found 446.3418.

(2E,9Z,12Z)-N-benzyl-N-phenyloctadeca-2,9,12-trienamide (30)



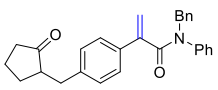
Colorless oil; 25.6 mg, 58% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.33-7.27 (m, 3H), 7.27-7.18 (m, 5H), 7.04-6.92 (m, 3H), 5.69 (d, *J* = 15.1 Hz, 1H), 5.42-5.24 (m, 4H), 4.96 (s, 2H), 2.75 (t, *J* = 5.9 Hz, 2H), 2.07-1.98 (m, 6H), 1.36-1.23 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 165.9, 146.5, 142.1, 137.5, 130.1, 129.7, 129.2, 128.5, 128.2, 128.0, 127.7, 127.5, 127.1, 121.4, 53.0, 32.1, 31.4, 29.3, 29.2, 28.6, 28.1, 27.1, 27.0, 25.5, 22.5, 14.0; HRMS (ESI) for $C_{31}H_{42}NO$ $[M+H]^+$ calcd 444.3261, found 444.3260.

2-(6-methoxynaphthalen-2-yl)-N-methyl-N-phenylacrylamide (31)



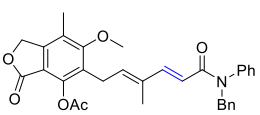
White solid; 15.8 mg, 50% yield, reaction time 20 h; mp = 120-122 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.77-7.67 (m, 3H), 7.54 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.46-7.38 (m, 2H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.22 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.18-7.13 (m, 2H), 6.38-6.23 (m, 2H), 5.55 (dd, *J* = 9.8, 2.5 Hz, 1H), 3.94 (s, 3H), 2.95 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.0, 158.1, 141.0, 139.7, 133.8, 131.7, 129.6, 129.2, 128.5, 127.7, 127.5, 127.1, 126.7, 119.3, 105.6, 55.4, 36.6; HRMS (ESI) for $C_{21}H_{20}NO_2$ $[M+H]^+$ calcd 318.1489, found 318.1492.

N-benzyl-2-(4-((2-oxocyclopentyl)methyl)phenyl)-N-phenylacrylamide (32)



Colorless oil; 27.0 mg, 66% yield, reaction time 20 h; **^{1}H NMR (600 MHz, $CDCl_3$)** δ (ppm) = 7.29-7.23 (m, 5H), 7.09-7.00 (m, 7H), 6.74 (brs, 2H), 5.43 (s, 1H), 5.31 (s, 1H), 5.01 (s, 2H), 3.08 (dd, *J* = 13.7, 3.1 Hz, 1H), 2.50 (dd, *J* = 13.5, 9.6 Hz, 1H), 2.36-2.31(m, 2H), 2.11-1.99 (m, 2H), 1.99-1.88 (m, 1H), 1.80-1.65 (m, 1H), 1.53-1.48 (m, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 219.8, 170.5, 145.3, 142.2, 139.8, 137.4, 134.9, 128.8, 128.7, 128.6, 128.4, 128.1, 127.4, 127.0, 126.2, 117.2, 53.0, 50.8, 38.1, 35.2, 29.0, 20.5; HRMS (ESI) for $C_{28}H_{28}NO_2$ $[M+H]^+$ calcd 410.2115, found 410.2116.

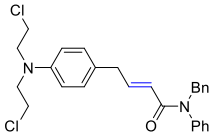
5-((2E,4E)-6-(benzyl(phenyl)amino)-3-methyl-6-oxohexa-2,4-dien-1-yl)-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-4-yl acetate (33)



Colorless oil; 40.2 mg, 76% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.34-7.22 (m, 9H), 7.02 (d, *J* = 7.3 Hz, 2H), 5.79-5.71 (m, 2H), 5.14 (s, 2H), 4.98 (s, 2H), 3.75 (s, 3H), 3.48 (d, *J* = 7.0 Hz, 2H), 2.35 (s,

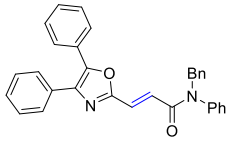
3H), 2.21 (s, 3H), 1.63 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 168.7, 168.1, 166.3, 162.6, 146.6, 146.3, 145.8, 142.2, 137.6, 136.2, 133.5, 129.3, 128.5, 128.28, 128.25, 127.7, 127.6, 127.2, 123.0, 117.3, 113.6, 68.3, 61.2, 53.1, 24.2, 20.4, 12.3, 11.8; HRMS (ESI) for $C_{32}H_{32}NO_6$ $[M+H]^+$ calcd 526.2224, found 526.2229.

(E)-N-benzyl-4-(4-(bis(2-chloroethyl)amino)phenyl)-N-phenylbut-2-enamide (34)



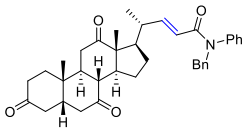
Colorless oil; 24.3 mg, 52% yield, reaction time 20 h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.32-7.19 (m, 8H), 7.08-6.93 (m, 5H), 6.58 (d, *J* = 8.6 Hz, 2H), 5.68 (d, *J* = 15.0 Hz, 1H), 4.95 (s, 2H), 3.68 (t, *J* = 6.9 Hz, 4H), 3.58 (t, *J* = 6.7 Hz, 4H), 3.27 (d, *J* = 6.8 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 165.8, 144.8, 144.5, 142.1, 137.5, 129.8, 129.3, 128.6, 128.34, 128.30, 127.5, 127.3, 127.2, 122.3, 112.3, 53.5, 53.0, 40.4, 37.4; HRMS (ESI) for $C_{27}H_{29}Cl_2N_2O$ $[M+H]^+$ calcd 467.1651, found 467.1655.

(E)-N-benzyl-3-(4,5-diphenyloxazol-2-yl)-N-phenylacrylamide (35)



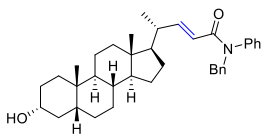
Colorless oil; 19.7 mg, 43% yield, reaction time 36 h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.61-7.56 (m, 3H), 7.51-7.47 (m, 2H), 7.41-7.29 (m, 10H), 7.29-7.23 (m, 4H), 7.10-7.02 (m, 2H), 6.77 (d, *J* = 15.5 Hz, 1H), 5.05 (s, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 164.7, 158.3, 146.4, 141.5, 137.6, 137.1, 131.9, 129.6, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.5, 126.6, 126.5, 125.4, 53.5; HRMS (ESI) for $C_{31}H_{25}N_2O_2$ $[M+H]^+$ calcd 457.1911, found 457.1916.

(R,E)-N-benzyl-4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-N-phenylpent-2-enamide (36)



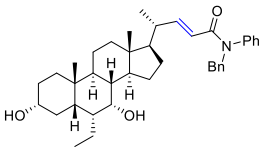
White solid; 36.9 mg, 65% yield, reaction time 24 h; mp = 184-186 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.34-7.28 (m, 3H), 7.27-7.17 (m, 5H), 7.00 (d, *J* = 7.0 Hz, 2H), 6.88 (dd, *J* = 15.1, 8.3 Hz, 1H), 5.65 (d, *J* = 15.1 Hz, 1H), 4.96 (dd, *J* = 31.3, 14.4 Hz, 2H), 2.94-2.74 (m, 3H), 2.35-2.18 (m, 6H), 2.17-1.90 (m, 6H), 1.87-1.76 (m, 2H), 1.60 (td, *J* = 14.0, 5.4 Hz, 1H), 1.38 (s, 3H), 1.20-1.17 (m, 2H), 0.99 (s, 3H), 0.92 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 211.5, 208.9, 208.5, 166.0, 150.6, 142.1, 137.5, 129.2, 128.6, 128.2, 127.5, 127.1, 120.2, 56.6, 53.0, 50.9, 48.7, 46.7, 45.1, 44.8, 42.6, 39.5, 38.4, 36.4, 35.8, 35.1, 26.6, 24.8, 21.8, 20.1, 12.2; HRMS (ESI) for $C_{37}H_{44}NO_4$ $[M+H]^+$ calcd 566.3265, found 566.3268.

(R,E)-N-benzyl-4-((3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-N-phenylpent-2-enamide (37)



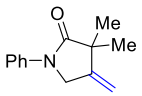
White solid; 43.8 mg, 81% yield, reaction time 24 h; mp = 74-76 °C; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.34-7.19 (m, 8H), 7.00 (d, *J* = 6.8 Hz, 2H), 6.80 (dd, *J* = 15.1, 9.2 Hz, 1H), 5.59 (d, *J* = 15.1 Hz, 1H), 4.96 (q, *J* = 14.4 Hz, 2H), 3.68-3.54 (m, 1H), 2.08-2.01 (m, 1H), 1.89-1.64 (m, 7H), 1.56-1.46 (m, 2H), 1.40-1.01 (m, 15H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.90 (s, 3H), 0.58 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 166.4, 152.0, 142.2, 137.6, 129.2, 128.6, 128.3, 127.5, 127.2, 119.2, 71.7, 56.3, 55.1, 53.0, 42.9, 42.0, 40.4, 39.9, 39.8, 36.4, 35.8, 35.3, 34.5, 30.5, 28.2, 27.1, 26.3, 24.2, 23.3, 20.7, 19.3, 12.2; HRMS (ESI) for $C_{37}H_{50}NO_2$ $[M+H]^+$ calcd 540.3836, found 540.3841.

(R,E)-N-benzyl-4-((3R,5S,6R,7R,8S,9S,10S,13R,14S,17R)-6-ethyl-3,7-dihydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-N-phenylpent-2-enamide (38)



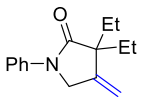
White solid; 43.2 mg, 74% yield, reaction time 24 h; mp = 96-98 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.33-7.20 (m, 8H), 7.00 (d, *J* = 6.7 Hz, 2H), 6.80 (dd, *J* = 15.1, 9.2 Hz, 1H), 5.60 (d, *J* = 15.1 Hz, 1H), 4.96 (dd, *J* = 32.2, 14.4 Hz, 2H), 3.68 (s, 1H), 3.47-3.31 (m, 1H), 2.10-2.02 (m, 1H), 1.90-1.10 (m, 24H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.91-0.87 (m, 6H), 0.60 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.4, 151.9, 142.3, 137.7, 129.3, 128.7, 128.33, 128.30, 127.5, 127.2, 119.3, 72.3, 70.8, 55.0, 53.1, 50.3, 45.2, 42.9, 41.2, 40.0, 39.8, 39.4, 35.54, 35.50, 34.0, 33.3, 30.6, 28.1, 23.7, 23.1, 22.2, 20.7, 19.4, 12.0, 11.6; HRMS (ESI) for $C_{39}H_{54}NO_3$ $[M+H]^+$ calcd 584.4098, found 584.4106.

3,3-dimethyl-4-methylene-1-phenylpyrrolidin-2-one (39)



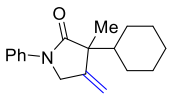
Colorless oil; 9.8 mg, 49% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.71 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.40-7.35 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.14 (t, *J* = 2.0 Hz, 1H), 5.12 (t, *J* = 2.3 Hz, 1H), 4.44 (t, *J* = 2.1 Hz, 2H), 1.34 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.6, 147.6, 139.1, 128.9, 124.4, 119.6, 106.9, 51.3, 45.8, 25.1; HRMS (ESI) for $C_{13}H_{16}NO$ $[M+H]^+$ calcd 202.1226, found 202.1228.

3,3-diethyl-4-methylene-1-phenylpyrrolidin-2-one (40)



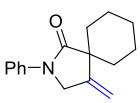
Colorless oil; 12.8 mg, 56% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.72 (d, *J* = 7.8 Hz, 2H), 7.40-7.36 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.33 (t, *J* = 2.1 Hz, 1H), 5.05 (t, *J* = 2.5 Hz, 1H), 4.39 (t, *J* = 2.3 Hz, 2H), 1.91 (dq, *J* = 14.6, 7.3 Hz, 2H), 1.56 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 176.7, 143.5, 138.9, 128.8, 124.5, 119.8, 107.9, 55.8, 52.8, 32.0, 8.9; HRMS (ESI) for $C_{15}H_{20}NO$ $[M+H]^+$ calcd 230.1539, found 230.1542.

3-cyclohexyl-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (41)



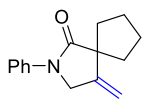
Colorless oil; 8.7 mg, 32% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.71 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.47-7.33 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.24 (t, *J* = 2.0 Hz, 1H), 5.07 (t, *J* = 2.3 Hz, 1H), 4.44-4.27 (m, 2H), 1.88-1.71 (m, 2H), 1.71-1.60 (m, 4H), 1.31 (s, 3H), 1.26-1.17 (m, 2H), 1.15-1.03 (m, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.6, 145.3, 138.9, 128.9, 124.5, 119.8, 109.0, 53.01, 52.96, 46.6, 28.2, 26.6, 26.5, 26.3, 21.5; HRMS (ESI) for $C_{18}H_{24}NO$ $[M+H]^+$ calcd 270.1852, found 270.1855.

4-methylene-2-phenyl-2-azaspiro[4.5]decan-1-one (42)



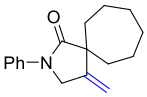
White solid; 12.3 mg, 51% yield, reaction time 24 h; mp = 62-64 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.69 (d, *J* = 7.8 Hz, 2H), 7.41-7.33 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.27 (t, *J* = 2.2 Hz, 1H), 5.15 (t, *J* = 1.9 Hz, 1H), 4.37 (t, *J* = 2.0 Hz, 2H), 1.97-1.85 (m, 4H), 1.66-1.52 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 177.2, 147.4, 139.2, 128.8, 124.3, 119.6, 108.2, 51.4, 48.3, 33.3, 25.3, 21.5; HRMS (ESI) for $C_{16}H_{20}NO$ $[M+H]^+$ calcd 242.1539, found 242.1542.

4-methylene-2-phenyl-2-azaspiro[4.4]nonan-1-one (43)



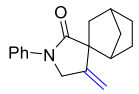
Colorless oil; 9.3 mg, 41% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.71 (dd, *J* = 8.7, 1.0 Hz, 2H), 7.46-7.32 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 5.09-5.06 (m, 2H), 4.42 (t, *J* = 2.1 Hz, 2H), 2.23-2.10 (m, 2H), 1.97-1.87 (m, 2H), 1.87-1.73 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 178.2, 148.8, 139.3, 128.9, 124.3, 119.5, 106.4, 56.2, 51.9, 38.3, 26.3; HRMS (ESI) for $C_{15}H_{18}NO$ $[M+H]^+$ calcd 228.1383, found 228.1386.

4-methylene-2-phenyl-2-azaspiro[4.6]undecan-1-one (44)



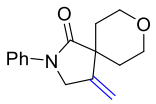
White solid; 12.1 mg, 47% yield, reaction time 24 h; mp = 85-87 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.76-7.63 (m, 2H), 7.39-7.34 (m, 2H), 7.19-7.07 (m, 1H), 5.19 (t, *J* = 2.2 Hz, 1H), 5.10 (t, *J* = 1.9 Hz, 1H), 4.37 (t, *J* = 2.1 Hz, 2H), 2.06 (dd, *J* = 14.6, 8.9 Hz, 2H), 1.96-1.77 (m, 2H), 1.74-1.52 (m, 8H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 178.7, 148.5, 139.3, 128.8, 124.3, 119.6, 107.2, 51.7, 51.5, 36.6, 31.4, 23.7; HRMS (ESI) for $C_{17}H_{22}NO$ $[M+H]^+$ calcd 256.1696, found 256.1697.

4'-methylene-1'-phenylspiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-2'-one (45)



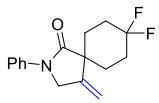
White solid; 8.3 mg, 33% yield, reaction time 24 h; mp = 79-81 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.74-7.69 (m, 2H), 7.39-7.34 (m, 2H), 7.16-7.09 (m, 1H), 5.10 (dd, *J* = 2.1, 1.2 Hz, 1H), 5.00 (dd, *J* = 2.5, 1.0 Hz, 1H), 4.54 (dt, *J* = 12.7, 2.5 Hz, 1H), 4.19 (d, *J* = 12.7 Hz, 1H), 2.37-2.33 (m, 1H), 2.24 (d, *J* = 3.2 Hz, 1H), 1.89-1.80 (m, 2H), 1.74-1.64 (m, 2H), 1.59-1.50 (m, 2H), 1.35-1.27 (m, 1H), 1.26-1.20 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 175.4, 147.7, 139.5, 128.8, 124.0, 119.1, 107.3, 57.1, 52.0, 46.8, 37.7, 37.6, 36.7, 28.3, 24.4; HRMS (ESI) for $C_{17}H_{20}NO$ $[M+H]^+$ calcd 254.1539, found 254.1542.

4-methylene-2-phenyl-8-oxa-2-azaspiro[4.5]decan-1-one (46)



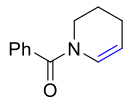
Colorless oil; 12.2 mg, 50% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.71-7.64 (m, 2H), 7.43-7.34 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 5.28 (t, *J* = 2.1 Hz, 1H), 5.23 (t, *J* = 1.8 Hz, 1H), 4.43 (t, *J* = 2.1 Hz, 2H), 4.23-4.16 (m, 2H), 3.83 (dt, *J* = 11.5, 4.6 Hz, 2H), 1.97 (dt, *J* = 13.6, 3.8 Hz, 2H), 1.81-1.74 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 176.1, 146.4, 138.8, 128.9, 124.6, 119.8, 108.6, 63.5, 51.2, 45.2, 33.6; HRMS (ESI) for $C_{15}H_{18}NO_2$ $[M+H]^+$ calcd 244.1332, found 244.1335.

8,8-difluoro-4-methylene-2-phenyl-2-azaspiro[4.5]decan-1-one (47)



Colorless oil; 12.5 mg, 45% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.72-7.60 (m, 2H), 7.45-7.32 (m, 2H), 7.21-7.09 (m, 1H), 5.24-5.16 (m, 2H), 4.44 (t, *J* = 2.2 Hz, 2H), 2.71-2.50 (m, 2H), 2.10-1.94 (m, 4H), 1.94-1.80 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 175.6, 145.8 (d, *J* = 1.8 Hz), 138.8, 129.0, 124.8, 123.3 (t, *J* = 237.0 Hz), 119.9, 108.3, 51.3, 46.0, 31.4 (dd, *J* = 8.9, 1.8 Hz), 29.9 (t, *J* = 24.5 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) = -93.4, -94.1, -101.0, -101.6; HRMS (ESI) for $C_{16}H_{18}F_2NO$ $[M+H]^+$ calcd 278.1351, found 278.1353.

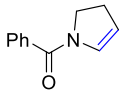
(3,4-dihydropyridin-1(2H)-yl)(phenyl)methanone (48)



Colorless oil; 17.7 mg, 95% yield, a mixture of rotamers, reaction time 16 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.53-7.36 (m, 5H), 7.28-6.43 (m, 1H), 5.23-4.83 (m, 1H), 3.84-3.55 (m, 2H), 2.17-2.03 (m, 2H), 1.96-1.78 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)**

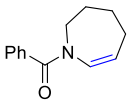
δ (ppm) = 169.1, 134.9, 130.0, 128.2, 128.0, 127.3, 107.4, 40.9, 21.7, 21.5; HRMS (ESI) for $C_{12}H_{14}NO$ $[M+H]^+$ calcd 188.1070, found 188.1072.

(2,3-dihydro-1H-pyrrol-1-yl)(phenyl)methanone (49)



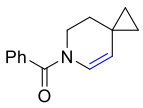
Colorless oil; 15.6 mg, 90% yield, a mixture of rotamers, reaction time 16 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.52-7.50 (m, 2H), 7.44-7.38 (m, 3H), 7.10-6.49 (m, 1H), 5.37-5.16 (m, 1H), 4.05-3.80 (m, 2H), 2.73-2.68 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.8, 135.7, 130.6, 130.2, 128.3, 127.6, 111.6, 45.5, 28.3; HRMS (ESI) for $C_{11}H_{12}NO$ $[M+H]^+$ calcd 174.0913, found 174.0916.

phenyl(2,3,4,5-tetrahydro-1H-azepin-1-yl)methanone (50)



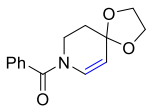
Colorless oil; 17.7 mg, 88% yield, a mixture of rotamers, reaction time 16 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.62-7.31 (m, 5H), 7.01-6.17 (m, 1H), 5.31-5.03 (m, 1H), 3.97-3.55 (m, 2H), 2.35-2.17 (m, 2H), 1.97-1.71 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 169.7, 136.0, 132.8, 130.0, 128.2, 128.0, 116.6, 46.0, 27.8, 26.5, 24.7; HRMS (ESI) for $C_{13}H_{16}NO$ $[M+H]^+$ calcd 202.1226, found 202.1228.

phenyl(6-azaspiro[2.5]oct-4-en-6-yl)methanone (51)



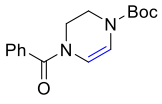
Colorless oil; 19.8 mg, 93% yield, a mixture of rotamers, reaction time 16 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.59-7.33 (m, 5H), 7.32-6.43 (m, 1H), 4.72-4.31 (m, 1H), 3.96-3.66 (m, 2H), 1.82-1.64 (m, 2H), 0.71-0.59 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 168.9, 135.1, 130.1, 128.2, 128.1, 126.5, 115.5, 40.7, 32.0, 16.3, 14.8; HRMS (ESI) for $C_{14}H_{16}NO$ $[M+H]^+$ calcd 214.1226, found 214.1230.

phenyl(1,4-dioxa-8-azaspiro[4.5]dec-6-en-8-yl)methanone (52)



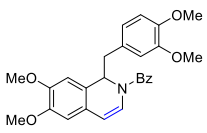
Colorless oil; 20.3 mg, 83% yield, a mixture of rotamers, reaction time 16 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.50-6.64 (m, 6H), 5.27-4.81 (m, 1H), 4.11-3.61 (m, 6H), 2.19-1.80 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 169.5, 134.2, 131.0, 130.6, 128.4, 128.1, 106.8, 103.3, 64.5, 40.1, 32.5; HRMS (ESI) for $C_{14}H_{16}NO_3$ $[M+H]^+$ calcd 246.1125, found 246.1127.

tert-butyl 4-benzoyl-3,4-dihydropyrazine-1(2H)-carboxylate (53)



Colorless oil; 24.5 mg, 85% yield, a mixture of rotamers, reaction time 16 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.54-7.44 (m, 5H), 6.74-5.8 (m, 2H), 3.93-3.65 (m, 4H), 1.50 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 167.6, 151.1, 134.1, 130.5, 128.29, 128.26, 109.6, 109.2, 108.7, 81.4, 42.0, 40.7, 39.4, 28.1; HRMS (ESI) for $C_{16}H_{21}N_2O_3$ $[M+H]^+$ calcd 289.1547, found 289.1548.

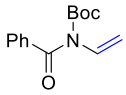
(1-(3,4-dimethoxybenzyl)-6,7-dimethoxyisoquinolin-2(1H)-yl)(phenyl)methanone (54)



Colorless oil; 28.2 mg, 63% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.52-7.41 (m, 5H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.64 (s, 1H), 6.60 (s, 1H), 6.49 (d, *J* = 7.9 Hz, 1H), 6.39 (d, *J* = 7.6 Hz, 1H), 6.02 (s, 1H), 5.79-5.68 (m, 2H), 3.88 (s, 3H), 3.85 (s, 3H), 3.79 (s, 3H), 3.58 (s, 3H), 3.02 (dd, *J* = 12.5, 4.7 Hz, 1H), 2.92-2.86 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 168.8, 148.5, 148.2, 147.6,

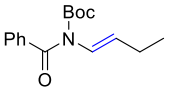
147.3, 134.6, 130.6, 130.0, 128.6, 128.3, 124.9, 124.4, 122.8, 122.3, 113.1, 111.0, 110.8, 109.2, 107.8, 56.4, 55.9, 55.8, 55.74, 55.73, 39.6; HRMS (ESI) for $C_{27}H_{28}NO_5$ $[M+H]^+$ calcd 446.1962, found 446.1965.

tert-butyl benzoyl(vinyl)carbamate (55)



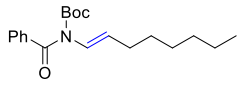
Colorless oil; 18.8 mg, 76% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.71-7.68 (m, 2H), 7.62-7.51 (m, 1H), 7.47-7.38 (m, 2H), 6.87 (dd, *J* = 16.1, 9.4 Hz, 1H), 5.09 (dd, *J* = 16.1, 0.8 Hz, 1H), 4.78 (dd, *J* = 9.4, 0.8 Hz, 1H), 1.19 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 171.7, 151.7, 136.2, 132.4, 130.4, 128.5, 101.1, 83.7, 27.4; HRMS (ESI) for $C_{14}H_{18}NO_3$ $[M+H]^+$ calcd 248.1281, found 248.1276.

tert-butyl (E)-benzoyl(but-1-en-1-yl)carbamate (56)



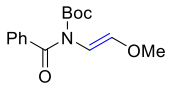
Colorless oil; 17.4 mg, 63% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.66 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 6.49 (d, *J* = 14.3 Hz, 1H), 5.71-5.58 (m, 1H), 2.16-2.09 (m, 2H), 1.19 (s, 9H), 1.03 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.2, 152.3, 136.7, 132.0, 128.3, 128.2, 124.1, 123.9, 83.4, 27.4, 23.6, 13.7; HRMS (ESI) for $C_{16}H_{21}NNaO_3$ $[M+Na]^+$ calcd 298.1414, found 298.1412.

tert-butyl (E)-benzoyl(oct-1-en-1-yl)carbamate (57)



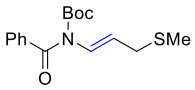
Colorless oil; 15.0 mg, 45% yield, reaction time 32 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.66 (d, *J* = 7.6 Hz, 2H), 7.54-7.50 (m, 1H), 7.44-7.38 (m, 2H), 6.48 (d, *J* = 14.3 Hz, 1H), 5.63-5.55 (m, 1H), 2.09 (q, *J* = 7.2 Hz, 2H), 1.39-1.34 (m, 2H), 1.31-1.25 (m, 6H), 1.21 (s, 9H), 0.88 (t, *J* = 6.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.1, 152.3, 136.6, 132.0, 128.32, 128.27, 124.5, 122.9, 83.3, 31.7, 30.3, 29.3, 28.7, 27.4, 22.6, 14.1; HRMS (ESI) for $C_{20}H_{30}NO_3$ $[M+H]^+$ calcd 332.2220, found 332.2225.

tert-butyl (E)-benzoyl(2-methoxyvinyl)carbamate (58)



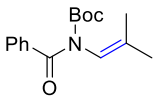
Colorless oil; 13.1 mg, 47% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.72-7.63 (m, 2H), 7.52-7.47 (m, 1H), 7.43-7.35 (m, 2H), 5.93 (d, *J* = 4.5 Hz, 1H), 5.51 (d, *J* = 4.5 Hz, 1H), 3.61 (s, 3H), 1.20 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 171.8, 152.4, 142.5, 136.9, 131.4, 128.1, 128.0, 105.1, 83.0, 60.2, 27.4; HRMS (ESI) for $C_{15}H_{19}NNaO_4$ $[M+Na]^+$ calcd 300.1206, found 300.1201.

tert-butyl (E)-benzoyl(3-(methylthio)prop-1-en-1-yl)carbamate (59)



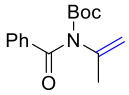
Colorless oil; 16.0 mg, 52% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.73-7.62 (m, 2H), 7.57-7.51 (m, 1H), 7.46-7.40 (m, 2H), 6.62 (dt, *J* = 14.3, 1.1 Hz, 1H), 5.61 (dt, *J* = 14.3, 7.7 Hz, 1H), 3.17 (dd, *J* = 7.7, 1.1 Hz, 2H), 2.07 (s, 3H), 1.20 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 171.8, 152.0, 136.2, 132.3, 128.4, 128.3, 126.4, 116.4, 83.8, 34.1, 27.4, 14.3; HRMS (ESI) for $C_{16}H_{21}NNaO_3S$ $[M+Na]^+$ calcd 330.1134, found 330.1135.

tert-butyl benzoyl(2-methylprop-1-en-1-yl)carbamate (60)



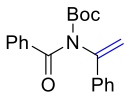
Colorless oil; 13.7 mg, 50% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.69-7.61 (m, 2H), 7.52-7.48 (m, 1H), 7.43-7.39 (m, 2H), 6.01-5.92 (m, 1H), 1.82 (d, *J* = 1.2 Hz, 3H), 1.60 (d, *J* = 1.1 Hz, 3H), 1.20 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.2, 152.9, 137.1, 133.6, 131.4, 128.1, 127.9, 120.1, 83.1, 27.4, 22.3, 17.9; HRMS (ESI) for $C_{16}H_{22}NO_3$ $[M+H]^+$ calcd 276.1594, found 276.1592.

tert-butyl benzoyl(prop-1-en-2-yl)carbamate (61)



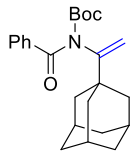
White solid; 20.7 mg, 79% yield, reaction time 24 h; mp = 53-55 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.64-7.61 (m, 2H), 7.54-7.47 (m, 1H), 7.44-7.40 (m, 2H), 5.21 (d, *J* = 1.2 Hz, 1H), 5.01 (s, 1H), 2.06 (s, 3H), 1.23 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.3, 152.4, 142.2, 137.0, 131.5, 128.2, 127.8, 114.6, 83.1, 27.4, 20.8; HRMS (ESI) for $C_{15}H_{20}NO_3$ $[M+H]^+$ calcd 262.1438, found 262.1440.

tert-butyl benzoyl(1-phenylvinyl)carbamate (62)



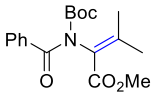
White solid; 19.7 mg, 61% yield, reaction time 24 h; mp = 56-58 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.80-7.70 (m, 2H), 7.57-7.49 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.39-7.29 (m, 3H), 5.72 (s, 1H), 5.26 (s, 1H), 1.15 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.6, 152.8, 145.0, 137.1, 136.3, 131.8, 128.6, 128.5, 128.3, 128.1, 125.7, 113.7, 83.3, 27.3; HRMS (ESI) for $C_{20}H_{22}NO_3$ $[M+H]^+$ calcd 324.1594, found 324.1595.

tert-butyl (1-(adamantan-1-yl)vinyl)(benzoyl)carbamate (63)



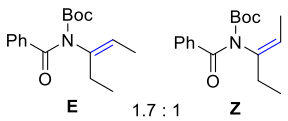
White solid; 15.6 mg, 41% yield, reaction time 24 h; mp = 112-114 °C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ (ppm) = 7.69 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.40 (s, 1H), 5.10 (s, 1H), 2.02 (s, 3H), 1.84 (s, 6H), 1.69 (q, *J* = 12.1 Hz, 6H), 1.21 (s, 9H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 172.6, 154.6, 153.9, 137.3, 131.4, 128.2, 128.1, 114.5, 82.9, 41.5, 39.6, 36.7, 28.5, 27.5; HRMS (ESI) for $C_{24}H_{32}NO_3$ $[M+H]^+$ calcd 382.2377, found 382.2378.

methyl 2-(N-(tert-butoxycarbonyl)benzamido)-3-methylbut-2-enoate (64)



White solid; 10.6 mg, 32% yield, reaction time 32 h; mp = 76-78 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.72-7.63 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 3.75 (s, 3H), 2.34 (s, 3H), 1.92 (s, 3H), 1.20 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 171.9, 164.5, 152.6, 152.4, 137.0, 131.3, 128.1, 127.9, 124.0, 83.2, 51.8, 27.4, 22.8, 21.7; HRMS (ESI) for $C_{18}H_{24}NO_5$ $[M+H]^+$ calcd 334.1649, found 334.1651.

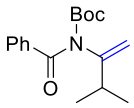
tert-butyl benzoyl(pent-2-en-3-yl)carbamate (65)



Colorless oil; 18.6 mg, 64% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** (major *E*-isomer) δ (ppm) = 7.64-7.39 (m, 5H), 5.60 (qd, *J* = 6.8, 1.6 Hz, 1H), 2.31 (qd, *J* = 7.2, 1.6 Hz, 2H), 1.62 (dt, *J* = 6.8, 1.4 Hz, 3H), 1.22 (s, 9H), 1.12 (t, *J* = 7.4 Hz, 3H); **^{1}H NMR (400 MHz, $CDCl_3$)** (minor *Z*-isomer) δ (ppm) = 7.64-7.39 (m, 5H), 5.50 (q, *J* = 7.0 Hz, 1H), 2.39 (q, *J* = 7.6 Hz, 2H), 1.77 (d, *J* = 7.0 Hz, 3H), 1.19 (s, 9H), 1.11 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** (*E*- and *Z*-isomers) δ (ppm) = 172.7, 171.6, 153.6, 152.7, 139.4, 139.2, 137.6, 137.3, 131.20, 131.18, 128.14, 128.11, 127.7, 127.6, 124.4, 121.5, 82.9, 82.8, 27.8, 27.4, 22.8, 13.0, 12.5, 11.7; HRMS (ESI) for

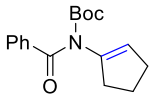
$C_{17}H_{24}NO_3$ $[M+H]^+$ calcd 290.1751, found 290.1752.

tert-butyl benzoyl(3-methylbut-1-en-2-yl)carbamate (66)



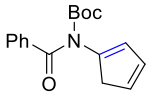
Colorless oil; 19.7 mg, 68% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.64-7.61 (m, 2H), 7.54-7.47 (m, 1H), 7.44-7.40 (m, 2H), 5.28 (s, 1H), 5.06 (s, 1H), 2.61-2.54 (m, 1H), 1.22 (s, 9H), 1.19 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.3, 153.3, 151.9, 137.3, 131.4, 128.2, 127.7, 112.2, 83.0, 32.8, 27.4, 21.0; HRMS (ESI) for $C_{17}H_{23}NNaO_3$ $[M+Na]^+$ calcd 312.1570, found 312.1569.

tert-butyl benzoyl(cyclopent-1-en-1-yl)carbamate (67)



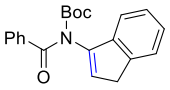
White solid; 21.6 mg, 75% yield, reaction time 24 h; mp = 57-59 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.69-7.60 (m, 2H), 7.55-7.46 (m, 1H), 7.46-7.37 (m, 2H), 5.65-5.62 (m, 1H), 2.61-2.49 (m, 2H), 2.49-2.37 (m, 2H), 2.07-1.94 (m, 2H), 1.23 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.1, 152.4, 139.5, 136.8, 131.7, 128.2, 128.0, 125.6, 83.0, 32.1, 30.4, 27.4, 22.2; HRMS (ESI) for $C_{17}H_{22}NO_3$ $[M+H]^+$ calcd 288.1594, found 288.1598.

tert-butyl benzoyl(cyclopenta-1,3-dien-1-yl)carbamate (68)



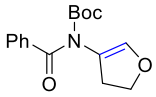
White solid; 15.5 mg, 54% yield, reaction time 24 h; mp = 37-39 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.74-7.67 (m, 2H), 7.55-7.48 (m, 1H), 7.46-7.38 (m, 2H), 6.54-6.45 (m, 2H), 6.19-6.17 (m, 1H), 3.10 (dd, *J* = 2.8, 1.3 Hz, 2H), 1.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.1, 152.5, 141.3, 136.5, 133.5, 131.9, 131.6, 128.31, 128.26, 123.9, 83.4, 39.8, 27.5; HRMS (ESI) for $C_{17}H_{20}NO_3$ $[M+H]^+$ calcd 286.1438, found 286.1437.

tert-butyl benzoyl(1H-inden-3-yl)carbamate (69)



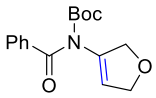
White solid; 16.0 mg, 48% yield, reaction time 24 h; mp = 71-73 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.81-7.72 (m, 2H), 7.54-7.50 (m, 1H), 7.49-7.39 (m, 3H), 7.32-7.20 (m, 3H), 6.43 (t, *J* = 2.1 Hz, 1H), 3.48 (d, *J* = 2.1 Hz, 2H), 1.26 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 171.9, 152.5, 142.6, 140.8, 140.2, 136.4, 131.9, 129.4, 128.27, 128.25, 126.2, 125.4, 124.2, 118.6, 83.6, 36.4, 27.4; HRMS (ESI) for $C_{21}H_{21}NNaO_3$ $[M+Na]^+$ calcd 358.1414, found 358.1410.

tert-butyl benzoyl(4,5-dihydrofuran-3-yl)carbamate (major-70)



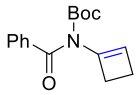
Colorless oil; 13.3 mg, 46% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.64-7.61 (m, 2H), 7.55-7.48 (m, 1H), 7.44-7.40 (m, 2H), 6.52 (t, *J* = 2.0 Hz, 1H), 4.52 (t, *J* = 9.6 Hz, 2H), 2.89 (td, *J* = 9.7, 2.0 Hz, 2H), 1.24 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.4, 152.6, 143.3, 136.7, 131.7, 128.2, 127.9, 116.0, 83.4, 70.4 30.1, 27.5; HRMS (ESI) for $C_{16}H_{20}NO_4$ $[M+H]^+$ calcd 290.1387, found 290.1389.

tert-butyl benzoyl(2,5-dihydrofuran-3-yl)carbamate (minor-70)



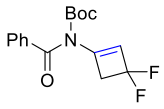
Colorless oil; 8.1 mg, 28% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.74-7.66 (m, 2H), 7.5-7.54 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.88-5.77 (m, 1H), 4.83-4.71 (m, 4H), 1.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 171.5, 151.6, 135.9, 134.5, 132.5, 128.5, 128.4, 115.8, 84.0, 74.4, 72.7, 27.4; HRMS (ESI) for $C_{16}H_{20}NO_4$ $[M+H]^+$ calcd 290.1387, found 290.1386.

tert-butyl benzoyl(cyclobut-1-en-1-yl)carbamate (71)



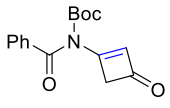
White solid; 14.3 mg, 52% yield, reaction time 24 h; mp = 48-50 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.72-7.64 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.55 (s, 1H), 2.94-2.87 (m, 2H), 2.41-2.33 (m, 2H), 1.20 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 171.0, 151.4, 136.4, 134.8, 132.2, 128.34, 128.25, 115.2, 83.5, 32.2, 27.4, 24.7; HRMS (ESI) for $C_{16}H_{20}NO_3$ $[M+H]^+$ calcd 274.1438, found 274.1436.

tert-butyl benzoyl(3,3-difluorocyclobut-1-en-1-yl)carbamate (72)



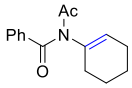
White solid; 13.2 mg, 43% yield, reaction time 24 h; mp = 44-46 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.75-7.72 (m, 2H), 7.67-7.57 (m, 1H), 7.53-7.43 (m, 2H), 5.61 (t, *J* = 1.6 Hz, 1H), 3.37 (t, *J* = 2.4 Hz, 2H), 1.21 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 169.9, 150.3, 142.4 (t, *J* = 25.0 Hz), 134.9, 133.3, 128.7, 128.6, 117.3 (t, *J* = 268.0 Hz), 109.7 (t, *J* = 26.0 Hz), 85.2, 46.6 (t, *J* = 25.0 Hz), 27.3; **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) = -102.1; HRMS (ESI) for $C_{16}H_{17}F_2NNaO_3$ $[M+Na]^+$ calcd 332.1069, found 332.1070.

tert-butyl benzoyl(3-oxocyclobut-1-en-1-yl)carbamate (73)



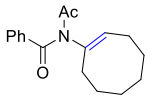
White solid; 8.6 mg, 30% yield, reaction time 32 h; mp = 53-55 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.87-7.76 (m, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 5.64 (s, 1H), 3.50 (s, 2H), 1.26 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 185.3, 169.1, 161.2, 149.5, 134.1 133.7, 129.1, 129.0, 117.9, 86.1, 50.1, 27.4; HRMS (ESI) for $C_{16}H_{18}NO_4$ $[M+H]^+$ calcd 288.1230, found 288.1227.

N-acetyl-N-(cyclohex-1-en-1-yl)benzamide (74)



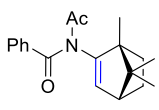
Colorless oil; 14.3 mg, 59% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.62-7.59 (m, 2H), 7.52-7.46 (m, 1H), 7.42-7.38 (m, 2H), 5.55-5.49 (m, 1H), 2.38 (s, 3H), 2.24-2.20 (m, 2H), 2.03-1.97 (m, 2H), 1.69-1.63 (m, 2H), 1.53-1.47 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 173.14, 173.11, 137.0, 135.9, 131.7, 129.6, 128.2, 128.0, 28.4, 25.2, 24.9, 22.5, 21.2; HRMS (ESI) for $C_{15}H_{18}NO_2$ $[M+H]^+$ calcd 244.1332, found 244.1333.

(E)-N-acetyl-N-(cyclooct-1-en-1-yl)benzamide (75)



Colorless oil; 12.4 mg, 46% yield, reaction time 24 h; **^{1}H NMR (600 MHz, $CDCl_3$)** δ (ppm) = 7.65 (d, *J* = 8.1 Hz, 2H), 7.51-7.48 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 5.59 (t, *J* = 8.4 Hz, 1H), 2.35-2.32 (m, 2H), 2.31 (s, 3H), 2.14-2.10 (m, 2H), 1.70-1.68 (m, 2H), 1.56-1.51 (m, 6H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 173.6, 173.4, 139.1, 136.0, 131.9, 131.8, 128.5, 128.4, 32.0, 28.7, 28.5, 26.1, 25.9, 25.2, 25.1; HRMS (ESI) for $C_{17}H_{22}NO_2$ $[M+H]^+$ calcd 272.1645, found 272.1646.

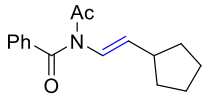
N-acetyl-N-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)benzamide (76)



White solid; 12.4 mg, 42% yield, reaction time 24 h; mp = 76-78 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.78-7.66 (m, 2H), 7.55-7.46 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 5.88 (d, *J* = 3.5 Hz, 1H), 2.41 (t, *J* = 3.6 Hz, 1H), 2.26 (s, 3H), 1.92-1.85 (m, 1H), 1.56-1.49 (m, 1H), 1.42-1.35 (m, 1H), 1.09-1.02 (m, 1H), 0.90 (s, 3H), 0.76 (s, 3H), 0.74 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 174.1, 173.5, 144.0, 135.3, 132.7, 132.5, 129.3, 128.5, 56.8,

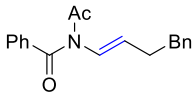
56.0, 51.1, 31.0, 24.8, 24.7, 19.9, 19.0, 11.2; HRMS (ESI) for $C_{19}H_{24}NO_2$ $[M+H]^+$ calcd 298.1802, found 298.1804.

(E)-N-acetyl-N-(2-cyclopentylvinyl)benzamide (77)



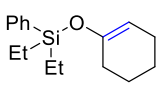
Colorless oil; 19.3 mg, 75% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.73-7.64 (m, 2H), 7.55-7.48 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 6.50 (dd, *J* = 14.2, 0.7 Hz, 1H), 4.96 (dd, *J* = 14.2, 8.4 Hz, 1H), 2.40-2.31 (m, 1H), 2.38 (s, 3H), 1.60-1.52 (m, 2H), 1.49-1.40 (m, 4H), 0.95-0.84 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.6, 171.5, 134.1, 134.0, 132.5, 129.8, 128.4, 124.3, 40.7, 32.4, 24.8, 24.4; HRMS (ESI) for $C_{16}H_{20}NO_2$ $[M+H]^+$ calcd 258.1489, found 258.1493.

(E)-N-acetyl-N-(4-phenylbut-1-en-1-yl)benzamide (78)



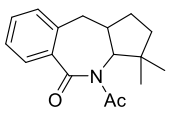
Colorless oil; 23.8 mg, 81% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.72-7.69 (m, 2H), 7.58-7.51 (m, 1H), 7.47-7.41 (m, 2H), 7.22-7.11 (m, 3H), 6.94-6.86 (m, 2H), 6.62 (dt, *J* = 14.2, 1.1 Hz, 1H), 5.06 (dt, *J* = 14.3, 7.2 Hz, 1H), 2.40 (t, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 2.28-2.22 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 172.5, 171.2, 140.8, 133.6, 132.9, 130.0, 128.5, 128.23, 128.17, 127.2, 126.3, 125.9, 35.1, 31.8, 24.2; HRMS (ESI) for $C_{19}H_{20}NO_2$ $[M+H]^+$ calcd 294.1489, found 294.1490.

(cyclohex-1-en-1-yloxy)diethyl(phenyl)silane (79)



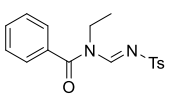
Colorless oil; 18.2 mg, 70% yield, reaction time 16 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.60-7.56 (m, 2H), 7.39-7.34 (m, 3H), 4.88-4.85 (m, 1H), 2.05-1.99 (m, 2H), 1.99-1.92 (m, 2H), 1.66-1.59 (m, 2H), 1.51-1.44 (m, 2H), 1.03-1.00 (m, 2H), 0.99-0.88 (m, 8H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 150.4, 136.4, 133.9, 129.4, 127.7, 104.2, 29.8, 23.8, 23.2, 22.3, 6.7, 5.5; HRMS (ESI) for $C_{16}H_{24}NaOSi$ $[M+Na]^+$ calcd 283.1489, found 283.1501.

4-acetyl-3,3-dimethyl-2,3,3a,4,10,10a-hexahydrobenzo[e]cyclopenta[b]azepin-5(1H)-one (80)



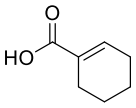
White solid; 14.5 mg, 53% yield, reaction time 36 h; mp = 89-91 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.94 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32-7.26 (m, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 4.07 (d, *J* = 12.4 Hz, 1H), 3.11-2.95 (m, 2H), 2.56-2.46 (m, 1H), 2.02 (s, 3H), 1.91-1.81 (m, 1H), 1.74-1.55 (m, 3H), 1.26 (s, 3H), 0.97 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 176.7, 168.4, 142.6, 135.0, 132.23, 132.21, 130.4, 126.3, 71.3, 43.2, 42.4, 39.7, 38.0, 30.3, 27.8, 24.9, 23.3; HRMS (ESI) for $C_{17}H_{22}NO_2$ $[M+H]^+$ calcd 272.1645, found 272.1643.

(E)-N-ethyl-N-((tosylimino)methyl)benzamide (82)



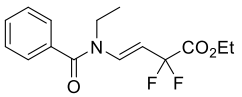
White solid; 21.5 mg, 65% yield in two steps, reaction time 40 h; mp = 117-119 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 8.88 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.65-7.59 (m, 1H), 7.55-7.48 (m, 4H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 171.6, 159.1, 144.0, 136.7, 132.8, 132.2, 129.7, 129.2, 128.9, 127.2, 39.2, 21.6, 12.6; HRMS (ESI) for $C_{17}H_{19}N_2O_3S$ $[M+H]^+$ calcd 331.1111, found 331.1112.

cyclohex-1-ene-1-carboxylic acid (83)



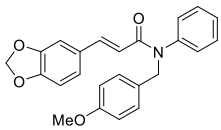
White solid; 4.3 mg, 34% yield (69% yield brsm), reaction time 72 h; mp = 35-37 °C; **^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =** 11.76 (br, 1H), 7.18-7.07 (m, 1H), 2.28-2.18 (m, 4H), 1.71-1.57 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 173.3, 142.5, 129.7, 25.9, 23.7, 21.9, 21.3; HRMS (ESI) for $C_7H_{11}O_2$ $[M+H]^+$ calcd 127.0754, found 127.0752.

ethyl (E)-4-(N-ethylbenzamido)-2,2-difluorobut-3-enoate (81a)



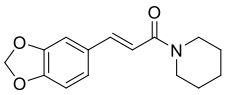
Colorless oil; 17.2 mg, 58% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.53-7.47 (m, 1H), 7.46 (m, 4H), 7.46-7.44 (m, 1H), 5.24-5.14 (m, 1H), 4.31-4.25 (m, 2H), 3.86-3.80 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 170.8, 163.9 (t, *J* = 35.5 Hz), 135.5, 134.0, 131.0, 128.7, 128.0, 113.0 (t, *J* = 246.0 Hz), 99.1 (t, *J* = 27.0 Hz), 63.0, 38.8, 13.9, 11.7; **^{19}F NMR (376 MHz, $CDCl_3$)** δ (ppm) = -99.5; HRMS (ESI) for $C_{15}H_{18}F_2NO_3$ $[M+H]^+$ calcd 298.1249, found 298.1255.

(E)-3-(benzo[d][1,3]dioxol-5-yl)-N-(4-methoxybenzyl)-N-phenylacrylamide (86)



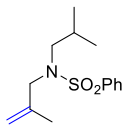
Colorless oil; 29.2 mg, 75% yield, reaction time 20 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.63 (d, *J* = 15.4 Hz, 1H), 7.38-7.30 (m, 3H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.04-7.01 (m, 2H), 6.85 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.81-6.76 (m, 2H), 6.73-6.71 (m, 2H), 6.12 (d, *J* = 15.5 Hz, 1H), 5.92 (s, 2H), 4.95 (s, 2H), 3.77 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.0, 158.8, 148.9, 148.0, 142.0, 141.8, 130.1, 129.7, 129.6, 129.4, 128.5, 127.8, 124.0, 116.9, 113.7, 108.4, 106.3, 101.3, 55.2, 52.6; HRMS (ESI) for $C_{24}H_{22}NO_4$ $[M+H]^+$ calcd 388.1543, found 388.1544.

(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(piperidin-1-yl)prop-2-en-1-one (87)



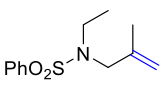
White solid; 12.5 mg, 48% yield, reaction time 4 h; mp = 79-81 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.56 (d, *J* = 15.3 Hz, 1H), 7.03 (d, *J* = 1.5 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 15.3 Hz, 1H), 5.99 (s, 2H), 3.61 (d, *J* = 31.6 Hz, 4H), 1.71-1.64 (m, 2H), 1.63-1.57 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 165.4, 148.8, 148.1, 141.9, 129.9, 123.5, 115.7, 108.4, 106.3, 101.3, 46.9, 43.3, 26.7, 25.6, 24.6; HRMS (ESI) for $C_{15}H_{18}NO_3$ $[M+H]^+$ calcd 260.1281, found 260.1285.

N-isobutyl-N-(2-methylallyl)benzenesulfonamide (88)



Colorless oil; 19.1 mg, 71% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.82 (d, *J* = 7.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.52-7.48 (m, 2H), 4.87 (s, 1H), 4.84 (s, 1H), 3.70 (s, 2H), 2.89 (d, *J* = 7.5 Hz, 2H), 1.95-1.84 (m, 1H), 1.66 (s, 3H), 0.84 (d, *J* = 6.7 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.9, 140.0, 132.3, 128.9, 127.2, 114.5, 56.0, 55.4, 27.0, 20.1, 20.0; HRMS (ESI) for $C_{14}H_{22}NO_2S$ $[M+H]^+$ calcd 268.1366, found 268.1367.

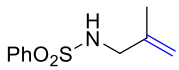
N-ethyl-N-(2-methylallyl)benzenesulfonamide (89)



Colorless oil; 13.0 mg, 54% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.82 (dd, *J* = 8.5, 1.1 Hz, 2H), 7.59-7.53 (m, 1H), 7.53-7.45 (m, 2H), 4.91 (s, 2H), 3.72 (s, 2H), 3.20 (q, *J* = 7.2 Hz, 2H), 1.73 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H);

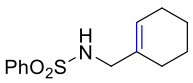
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 140.6, 140.2, 132.3, 128.9, 126.9, 114.2, 53.6, 42.1, 19.6, 13.1; HRMS (ESI) for $C_{12}H_{18}NO_2S$ $[M+H]^+$ calcd 240.1053, found 240.1055.

N-(2-methylallyl)benzenesulfonamide (90)



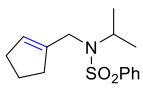
Colorless oil; 9.8 mg, 46% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.92-7.84 (m, 2H), 7.61-7.57 (m, 1H), 7.54-7.50 (m, 2H), 4.86 (s, 1H), 4.83 (s, 1H), 4.53 (brs, 1H), 3.51 (d, J = 6.4 Hz, 2H), 1.68 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.4, 140.0, 132.7, 129.1, 127.1, 112.9, 49.1, 20.1; HRMS (ESI) for $C_{10}H_{14}NO_2S$ $[M+H]^+$ calcd 212.0740, found 212.0739.

N-(cyclohex-1-en-1-ylmethyl)benzenesulfonamide (91)



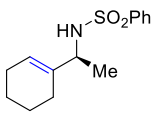
Colorless oil; 12.8 mg, 51% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.90-7.81 (m, 2H), 7.60-7.55 (m, 1H), 7.54-7.48 (m, 2H), 5.54 (s, 1H), 4.40 (t, J = 5.6 Hz, 1H), 3.46 (d, J = 6.0 Hz, 2H), 1.94-1.88 (m, 2H), 1.87-1.82 (m, 2H), 1.54-1.43 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.2, 132.7, 132.5, 129.0, 127.1, 125.5, 49.7, 26.1, 24.9, 22.3, 22.0; HRMS (ESI) for $C_{13}H_{17}NNaO_2S$ $[M+Na]^+$ calcd 274.0872, found 274.0874.

N-(cyclopent-1-en-1-ylmethyl)-N-isopropylbenzenesulfonamide (92)



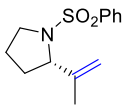
Colorless oil; 16.0 mg, 57% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.80 (d, J = 8.1 Hz, 2H), 7.58-7.43 (m, 3H), 5.58 (s, 1H), 4.16-4.09 (m, 1H), 3.86 (s, 2H), 2.30-2.27 (m, 4H), 1.93-1.71 (m, 2H), 1.06 (d, J = 6.8 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 141.9, 141.4, 132.1, 128.8, 128.0, 126.9, 49.9, 43.4, 33.2, 32.4, 23.4, 20.9; HRMS (ESI) for $C_{15}H_{21}NNaO_2S$ $[M+Na]^+$ calcd 302.1185, found 302.1188.

(S)-N-(1-(cyclohex-1-en-1-yl)ethyl)benzenesulfonamide (93)



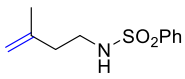
Colorless oil; 9.5 mg, 36% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.87-7.80 (m, 2H), 7.55-7.45 (m, 3H), 5.44 (s, 1H), 4.66-4.62 (m, 1H), 3.90-3.83 (m, 1H), 1.84-1.70 (m, 3H), 1.61-1.54 (m, 1H), 1.47-1.40 (m, 1H), 1.37-1.29 (m, 2H), 1.19-1.11 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 141.1, 136.6, 132.2, 128.7, 127.3, 124.1, 55.6, 24.8, 23.4, 22.1, 22.0, 20.5; HRMS (ESI) for $C_{14}H_{19}NNaO_2S$ $[M+Na]^+$ calcd 288.1029, found 288.1030.

(S)-1-(phenylsulfonyl)-2-(prop-1-en-2-yl)pyrrolidine (94)



White solid; 20.2 mg, 80% yield, reaction time 24 h; mp = 76-78 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.88-7.80 (m, 2H), 7.61-7.58 (m, 1H), 7.55-7.50 (m, 2H), 5.00 (s, 1H), 4.87 (s, 1H), 4.07 (t, J = 6.3 Hz, 1H), 3.51-3.45 (m, 1H), 3.34-3.28 (m, 1H), 1.86-1.76 (m, 1H), 1.73 (s, 3H), 1.71-1.67 (m, 2H), 1.60-1.51 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 144.9, 137.9, 132.5, 128.9, 127.5, 111.9, 65.0, 49.2, 31.4, 24.0, 18.6; HRMS (ESI) for $C_{13}H_{18}NO_2S$ $[M+H]^+$ calcd 252.1053, found 252.1057.

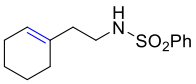
N-(3-methylbut-3-en-1-yl)benzenesulfonamide (95)



Colorless oil; 11.6 mg, 51% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.93-7.84 (m, 2H), 7.61-7.55 (m, 1H), 7.55-7.47 (m, 2H), 4.99

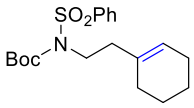
(brs, 1H), 4.77 (s, 1H), 4.63 (s, 1H), 3.15-2.99 (m, 2H), 2.15 (t, *J* = 6.9 Hz, 2H), 1.59 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 141.3, 139.7, 132.5, 129.0, 126.9, 112.9, 40.6, 37.1, 21.6; HRMS (ESI) for $C_{11}H_{16}NO_2S$ $[M+H]^+$ calcd 226.0896, found 226.0899.

N-(2-(cyclohex-1-en-1-yl)ethyl)benzenesulfonamide (96)



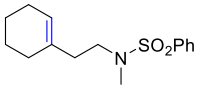
White solid; 11.7 mg, 44% yield, reaction time 24 h; mp = 36-38 ℃; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.89-7.86 (m, 2H), 7.60-7.56 (m, 1H), 7.54-7.49 (m, 2H), 5.37 (s, 1H), 4.70-4.56 (m, 1H), 3.02 (dd, *J* = 12.5, 6.5 Hz, 2H), 2.06 (t, *J* = 6.5 Hz, 2H), 1.94 (s, 2H), 1.72-1.69 (m, 2H), 1.56-1.48 (m, 4H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 139.8, 133.3, 132.5, 129.0, 127.0, 124.7, 40.5, 37.3, 27.4, 25.1, 22.6, 22.1; HRMS (ESI) for $C_{14}H_{19}NNaO_2S$ $[M+Na]^+$ calcd 288.1029, found 288.1028.

tert-butyl (2-(cyclohex-1-en-1-yl)ethyl)(phenylsulfonyl)carbamate (97)



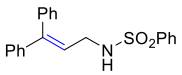
Colorless oil; 19.1 mg, 52% yield, reaction time 24 h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.92-7.89 (m, 2H), 7.62-7.57 (m, 1H), 7.53-7.48 (m, 2H), 5.52 (s, 1H), 3.92-3.88 (m, 2H), 2.42-2.29 (m, 2H), 2.06-1.92 (m, 4H), 1.66-1.52 (m, 4H), 1.32 (s, 9H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 150.8, 140.6, 134.1, 133.0, 128.6, 127.7, 124.0, 84.1, 46.1, 38.5, 28.2, 27.8, 25.3, 22.8, 22.2; HRMS (ESI) for $C_{19}H_{28}NO_4S$ $[M+H]^+$ calcd 366.1734, found 366.1738.

N-(2-(cyclohex-1-en-1-yl)ethyl)-N-methylbenzenesulfonamide (98)



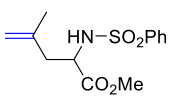
Colorless oil; 17.6 mg, 63% yield, reaction time 24 h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.80-7.77 (m, 2H), 7.61-7.55 (m, 1H), 7.54-7.50 (m, 2H), 5.43 (s, 1H), 3.13-3.03 (m, 2H), 2.74 (s, 3H), 2.15 (t, *J* = 7.6 Hz, 2H), 1.97-1.92 (m, 4H), 1.65-1.47 (m, 4H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 137.8, 134.1, 132.4, 128.9, 127.2, 123.5, 48.7, 36.2, 34.6, 28.0, 25.1, 22.7, 22.2; HRMS (ESI) for $C_{15}H_{22}NO_2S$ $[M+H]^+$ calcd 280.1366, found 280.1369.

N-(3,3-diphenylallyl)benzenesulfonamide (99)



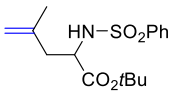
Colorless oil; 31.5 mg, 90% yield, reaction time 24 h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.87-7.75 (m, 2H), 7.57-7.50 (m, 1H), 7.47-7.43 (m, 2H), 7.33-7.26 (m, 3H), 7.26-7.19 (m, 3H), 7.12-6.98 (m, 4H), 5.92 (t, *J* = 7.1 Hz, 1H), 4.84-4.78 (m, 1H), 3.67 (dd, *J* = 7.0, 6.1 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 145.5, 141.2, 140.0, 138.4, 132.6, 129.4, 129.1, 128.4, 128.1, 127.8, 127.7, 127.4, 127.0, 123.0, 42.4; HRMS (ESI) for $C_{21}H_{19}NNaO_2S$ $[M+Na]^+$ calcd 372.1029, found 372.1030.

methyl 4-methyl-2-(phenylsulfonamido)pent-4-enoate (100)



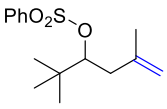
Colorless oil; 16.4 mg, 58% yield, reaction time 24 h; **^{1}H NMR (400 MHz, CDCl$_3$)** δ (ppm) = 7.86-7.82 (m, 2H), 7.60-7.55 (m, 1H), 7.53-7.48 (m, 2H), 5.08 (d, *J* = 8.7 Hz, 1H), 4.85-4.82 (m, 1H), 4.73 (s, 1H), 4.12-4.05 (m, 1H), 3.48 (s, 3H), 2.46-2.32 (m, 2H), 1.64 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ (ppm) = 171.8, 139.6, 139.4, 132.8, 129.0, 127.2, 115.4, 54.2, 52.3, 41.5, 21.7; HRMS (ESI) for $C_{13}H_{17}NNaO_4S$ $[M+Na]^+$ calcd 306.0770, found 306.0768.

tert-butyl 4-methyl-2-(phenylsulfonamido)pent-4-enoate (101)



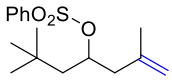
White solid; 14.1 mg, 43% yield, reaction time 24 h; mp = 67-69 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.87-7.82 (m, 2H), 7.58-7.53 (m, 1H), 7.52-7.46 (m, 2H), 5.07 (d, *J* = 9.1 Hz, 1H), 4.83 (s, 1H), 4.74 (s, 1H), 3.99-3.92 (m, 1H), 2.44-2.30 (m, 2H), 1.70 (s, 3H), 1.25 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 170.4, 140.0, 139.8, 132.7, 129.0, 127.3, 115.1, 82.6, 54.7, 42.1, 27.7, 21.9; HRMS (ESI) for $C_{16}H_{23}NNaO_4S$ $[M+Na]^+$ calcd 348.1240, found 348.1238.

2,2,5-trimethylhex-5-en-3-yl benzenesulfonate (102)



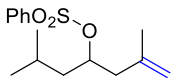
Colorless oil; 20.6 mg, 73% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.95-7.76 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 4.68 (dd, *J* = 8.3, 3.7 Hz, 1H), 4.52 (s, 1H), 4.50 (s, 1H), 2.35-2.19 (m, 2H), 1.66 (s, 3H), 0.95 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.7, 138.3, 133.0, 128.6, 127.5, 114.4, 90.5, 39.5, 35.5, 26.1, 21.9; HRMS (ESI) for $C_{15}H_{23}O_3S$ $[M+H]^+$ calcd 283.1362, found 283.1360.

2,6,6-trimethylhept-1-en-4-yl benzenesulfonate (103)



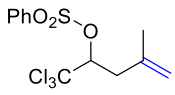
Colorless oil; 20.4 mg, 69% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.92 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 4.97-4.84 (m, 1H), 4.76 (s, 1H), 4.68 (s, 1H), 2.41-2.36 (m, 1H), 2.27-2.21 (m, 1H), 1.65 (s, 3H), 1.61-1.46 (m, 2H), 0.89 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.5, 138.0, 133.5, 129.0, 127.7, 114.6, 80.5, 47.0, 44.7, 29.8, 29.7, 22.4; HRMS (ESI) for $C_{16}H_{24}NaO_3S$ $[M+Na]^+$ calcd 319.1338, found 319.1337.

2,6-dimethylhept-1-en-4-yl benzenesulfonate (104)



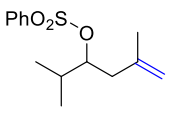
Colorless oil; 18.5 mg, 65% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.94-7.91 (m, 2H), 7.66-7.62 (m, 1H), 7.57-7.50 (m, 2H), 4.78-4.71 (m, 2H), 4.67 (d, *J* = 0.8 Hz, 1H), 2.38 (dd, *J* = 13.9, 5.6 Hz, 1H), 2.26 (dd, *J* = 13.9, 7.2 Hz, 1H), 1.64 (s, 3H), 1.60-1.52 (m, 2H), 1.38-1.29 (m, 1H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.76 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.4, 137.5, 133.5, 129.0, 127.8, 114.5, 81.0, 43.5, 43.1, 24.1, 23.0, 22.4, 21.6; HRMS (ESI) for $C_{15}H_{22}NaO_3S$ $[M+Na]^+$ calcd 305.1182, found 305.1183.

1,1,1-trichloro-4-methylpent-4-en-2-yl benzenesulfonate (105)



Colorless oil; 15.7 mg, 46% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.95-7.87 (m, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 5.26 (dd, *J* = 9.1, 2.3 Hz, 1H), 4.69 (s, 2H), 2.86 (d, *J* = 14.7 Hz, 1H), 2.58 (dd, *J* = 14.7, 9.1 Hz, 1H), 1.76 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 137.9, 137.3, 133.8, 128.8 127.9, 116.5, 98.8, 87.5, 40.2, 21.9; HRMS (ESI) for $C_{12}H_{14}Cl_3O_3S$ $[M+H]^+$ calcd 342.9724, found 342.9727.

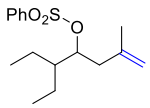
2,5-dimethylhex-5-en-3-yl benzenesulfonate (106)



Colorless oil; 16.3 mg, 61% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.92-7.89 (m, 2H), 7.66-7.59 (m, 1H), 7.56-7.48 (m, 2H), 4.70-4.68 (m, 1H), 4.67-4.65 (m, 1H), 4.65-4.60 (m, 1H), 2.28 (d, *J* = 6.7 Hz, 2H), 2.02-1.93 (m, 1H), 1.61 (s, 3H), 0.90-0.86 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.4, 137.5, 133.4,

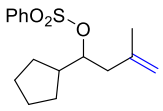
128.9, 127.7, 114.4, 86.7, 39.3, 30.9, 22.2, 18.0, 16.7; HRMS (ESI) for $C_{14}H_{21}O_3S$ $[M+H]^+$ calcd 269.1206, found 269.1205.

5-ethyl-2-methylhept-1-en-4-yl benzenesulfonate (107)



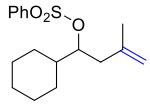
Colorless oil; 20.1 mg, 68% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.97-7.82 (m, 2H), 7.65-7.56 (m, 1H), 7.54-7.49 (m, 2H), 4.87-4.81 (m, 1H), 4.70 (s, 1H), 4.68 (s, 1H), 2.35-2.21 (m, 2H), 1.61 (s, 3H), 1.44-1.20 (m, 5H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.5, 137.7, 133.3, 128.9, 127.6, 114.3, 83.8, 44.4, 38.9, 22.0, 21.9, 21.7, 11.9, 11.8; HRMS (ESI) for $C_{16}H_{25}O_3S$ $[M+H]^+$ calcd 297.1519, found 297.1515.

1-cyclopentyl-3-methylbut-3-en-1-yl benzenesulfonate (108)



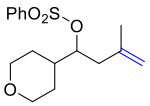
Colorless oil; 17.7 mg, 60% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.91 (d, *J* = 7.6 Hz, 2H), 7.68-7.57 (m, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 4.78-4.71 (m, 1H), 4.70 (s, 1H), 4.66 (s, 1H), 2.33 (d, *J* = 6.4 Hz, 2H), 2.16-2.09 (m, 1H), 1.66 (s, 3H), 1.65-1.40 (m, 6H), 1.32-1.19 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.4, 137.7, 133.3, 128.9, 127.6, 114.4, 85.8, 42.8, 41.9, 28.7, 27.6, 25.4, 25.1, 22.5; HRMS (ESI) for $C_{16}H_{23}O_3S$ $[M+H]^+$ calcd 295.1362, found 295.1359.

1-cyclohexyl-3-methylbut-3-en-1-yl benzenesulfonate (109)



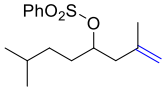
Colorless oil; 13.4 mg, 43% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.95-7.85 (m, 2H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 4.68 (s, 1H), 4.65 (s, 1H), 4.63-4.58 (m, 1H), 2.30-2.27 (m, 2H), 1.72-1.68 (m, 3H), 1.65-1.55 (m, 3H), 1.61 (s, 3H), 1.19-0.97 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.5, 137.7, 133.3, 128.9, 127.7, 114.3, 86.5, 40.9, 39.5, 28.6, 27.3, 26.2, 25.98, 25.96, 22.3; HRMS (ESI) for $C_{17}H_{24}NaO_3S$ $[M+Na]^+$ calcd 331.1338, found 331.1340.

3-methyl-1-(tetrahydro-2H-pyran-4-yl)but-3-en-1-yl benzenesulfonate (110)



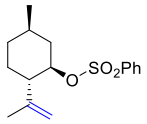
Colorless oil; 12.5 mg, 40% yield, reaction time 24 h; **^{1}H NMR (600 MHz, $CDCl_3$)** δ (ppm) = 7.86 (d, *J* = 8.2 Hz, 2H), 7.61-7.58 (m, 1H), 7.50-7.47 (m, 2H), 4.66 (s, 1H), 4.62 (s, 1H), 4.59-4.55 (m, 1H), 3.90 (t, *J* = 12.6 Hz, 2H), 3.25 (t, *J* = 11.9 Hz, 2H), 2.32-2.24 (m, 2H), 1.86-1.82 (m, 1H), 1.59 (s, 3H), 1.54 (d, *J* = 13.1 Hz, 1H), 1.43-1.31 (m, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 139.9, 137.2, 133.4, 128.9, 127.6, 114.6, 84.8, 67.5, 67.3, 39.4, 38.2, 28.5, 27.2, 22.2; HRMS (ESI) for $C_{16}H_{23}O_4S$ $[M+H]^+$ calcd 311.1312, found 311.1310.

2,7-dimethyloct-1-en-4-yl benzenesulfonate (111)



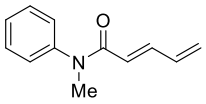
Colorless oil; 14.6 mg, 49% yield, reaction time 24 h; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.93-7.90 (m, 2H), 7.66-7.60 (m, 1H), 7.56-7.50 (m, 2H), 4.76-4.72 (m, 1H), 4.71-4.63 (m, 2H), 2.37-2.32 (m, 1H), 2.29-2.23 (m, 1H), 1.65-1.54 (m, 5H), 1.45-1.37 (m, 1H), 1.18-1.02 (m, 2H), 0.79 (d, *J* = 6.6 Hz, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 140.3, 137.6, 133.4, 129.0, 127.8, 114.5, 82.9, 42.9, 33.5, 31.8, 27.7, 22.5, 22.4, 22.2; HRMS (ESI) for $C_{16}H_{25}O_3S$ $[M+H]^+$ calcd 297.1519, found 297.1520.

(1R,2S,5R)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl benzenesulfonate (112)



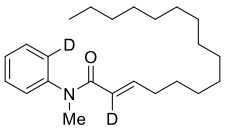
White solid; 24.1 mg, 82% yield, reaction time 24 h; mp = 82-84 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.94-7.80 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 4.66 (s, 1H), 4.59 (s, 1H), 4.47 (td, *J* = 10.8, 4.5 Hz, 1H), 2.24 (d, *J* = 12.3 Hz, 1H), 2.18-2.08 (m, 1H), 1.69-1.59 (m, 2H), 1.55-1.46 (m, 1H), 1.41 (s, 3H), 1.35-1.22 (m, 2H), 0.97-0.85 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 144.8, 137.6, 133.2, 128.8, 127.7, 112.9, 83.4, 50.7, 41.7, 33.6, 31.5, 30.3, 21.8, 19.2; HRMS (ESI) for $C_{16}H_{23}O_3S$ $[M+H]^+$ calcd 295.1362, found 295.1361.

(E)-N-methyl-N-phenylpenta-2,4-dienamide (113)



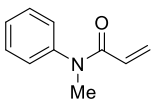
White solid; 10.3 mg, 55% yield, reaction time 20 h; mp = 72-74 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.45-7.38 (m, 2H), 7.37-7.31 (m, 1H), 7.27-7.23 (m, 1H), 7.20-7.16 (m, 2H), 6.26 (dt, *J* = 16.9, 10.5 Hz, 1H), 5.84 (d, *J* = 15.0 Hz, 1H), 5.53 (d, *J* = 16.9 Hz, 1H), 5.34 (d, *J* = 10.0 Hz, 1H), 3.36 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.1, 143.6, 142.0, 135.1, 129.6, 127.5, 127.3, 124.0, 122.6, 37.5; HRMS (ESI) for $C_{12}H_{14}NO$ $[M+H]^+$ calcd 188.1070, found 188.1073.

(E)-N-methyl-N-(phenyl-2-d)hexadec-2-enamide-2-d (D_2-28)



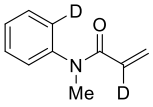
White solid; 28.0 mg, 81% yield, reaction time 20 h; mp = 33-35 ℃; **^{1}H NMR (400 MHz, $CDCl_3$)** δ (ppm) = 7.44-7.37 (m, 2H), 7.32 (t, *J* = 7.1 Hz, 1H), 7.19-7.16 (m, 1H), 6.91-6.87 (m, 1H), 3.34 (s, 3H), 2.06-2.01 (m, 2H), 1.34-1.19 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ (ppm) = 166.3, 146.0, 143.8 (d, *J* = 6.0 Hz), 129.4, 129.3, 127.3, 121.0 (t, *J* = 24.5 Hz), 37.3, 32.1, 31.9, 29.64, 29.61, 29.59, 29.52, 29.33, 29.32, 29.06, 28.23, 22.7, 14.1; HRMS (ESI) for $C_{23}H_{36}D_2NO$ $[M+H]^+$ calcd 346.3073, found 346.3069.

N-methyl-N-phenylacrylamide (114)



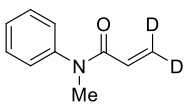
White solid; mp = 73-75 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ (ppm) = 7.43-7.40 (m, 2H), 7.35-7.32 (m, 1H), 7.18 (d, *J* = 7.1 Hz, 2H), 6.37 (d, *J* = 11.2, 1H), 6.15-5.99 (m, 1H), 5.51 (d, *J* = 6.8 Hz, 1H), 3.36 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 165.6, 143.3, 129.5, 128.4, 127.5, 127.22, 127.17, 37.3; HRMS (ESI) for $C_{10}H_{12}NO$ $[M+H]^+$ calcd 162.0913, found 162.0916.

N-methyl-N-(phenyl-2-d)acrylamide-2-d (114a)



White solid; mp = 68-70 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ (ppm) = 7.43-7.40 (m, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.36 (s, 1H), 5.52 (s, 1H), 3.36 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 165.7, 143.4, 129.6, 129.5, 128.3 (t, *J* = 16.5 Hz), 127.6, 127.3, 37.4; HRMS (ESI) for $C_{10}H_{10}D_2NO$ $[M+H]^+$ calcd 164.1039, found 164.1040.

N-methyl-N-phenylacrylamide-3,3-d2 (114b)

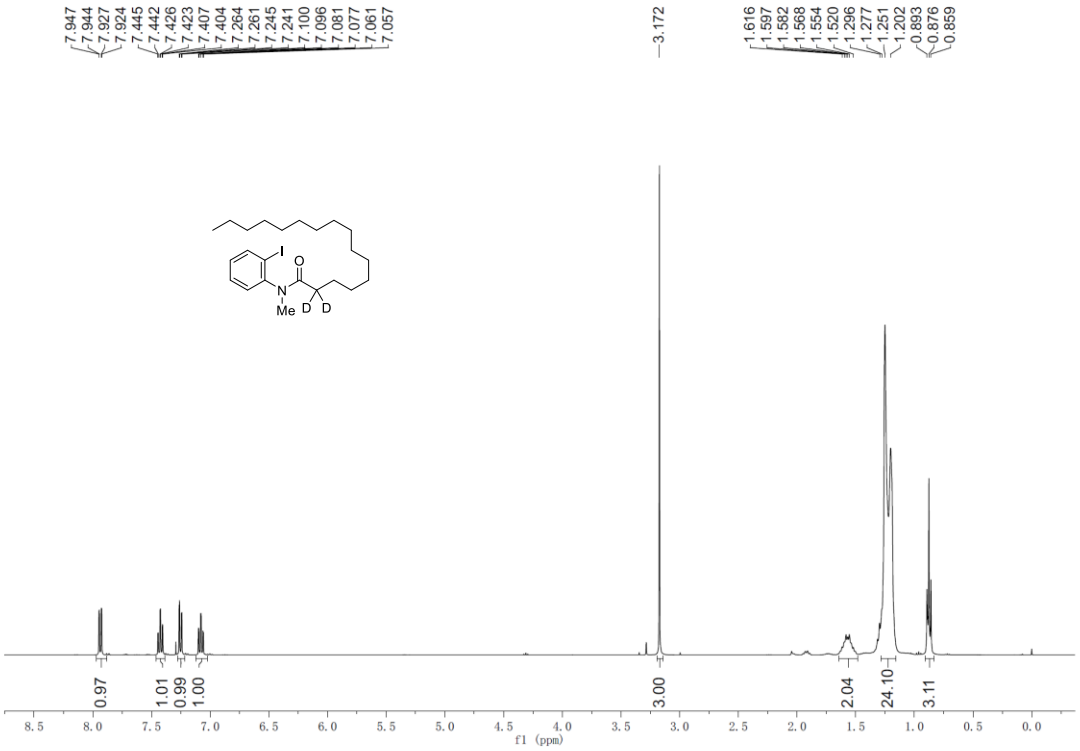


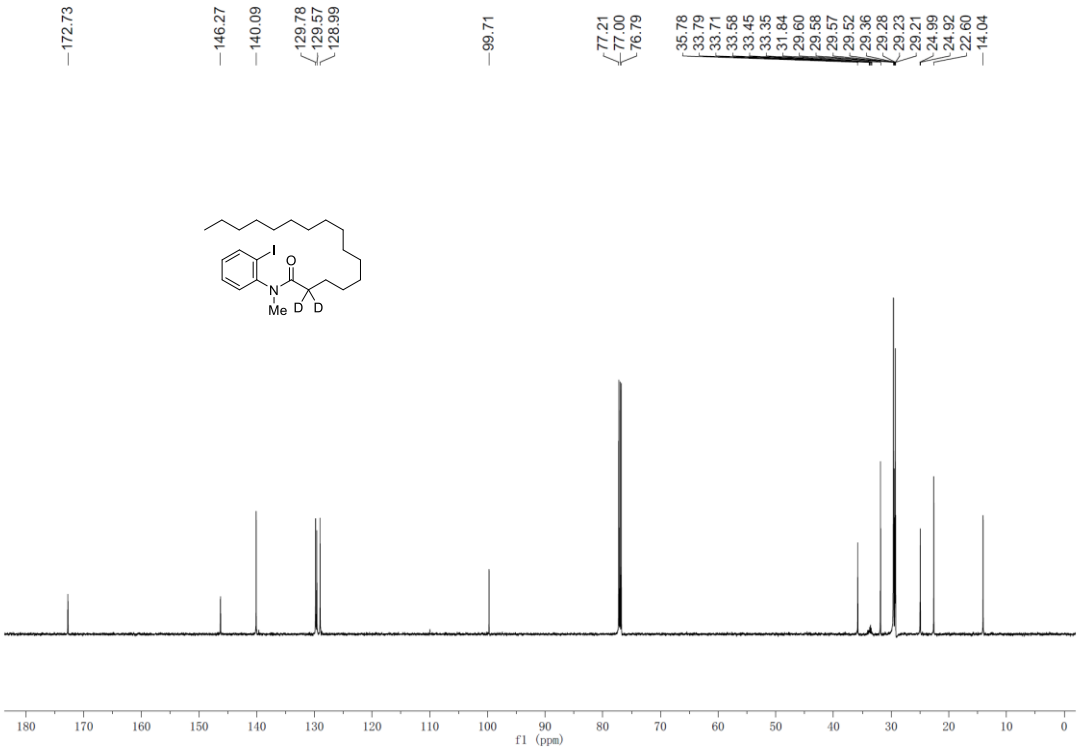
White solid; mp = 74-76 ℃; **^{1}H NMR (600 MHz, $CDCl_3$)** δ (ppm) = 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 2H), 6.06 (s, 1H), 3.36 (s, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ (ppm) = 165.7, 143.4, 129.6, 128.3, 127.6, 127.3, 127.1-126.5 (m), 37.4; HRMS (ESI) for $C_{10}H_{10}D_2NO$ $[M+H]^+$ calcd 164.1039, found

164.1041.

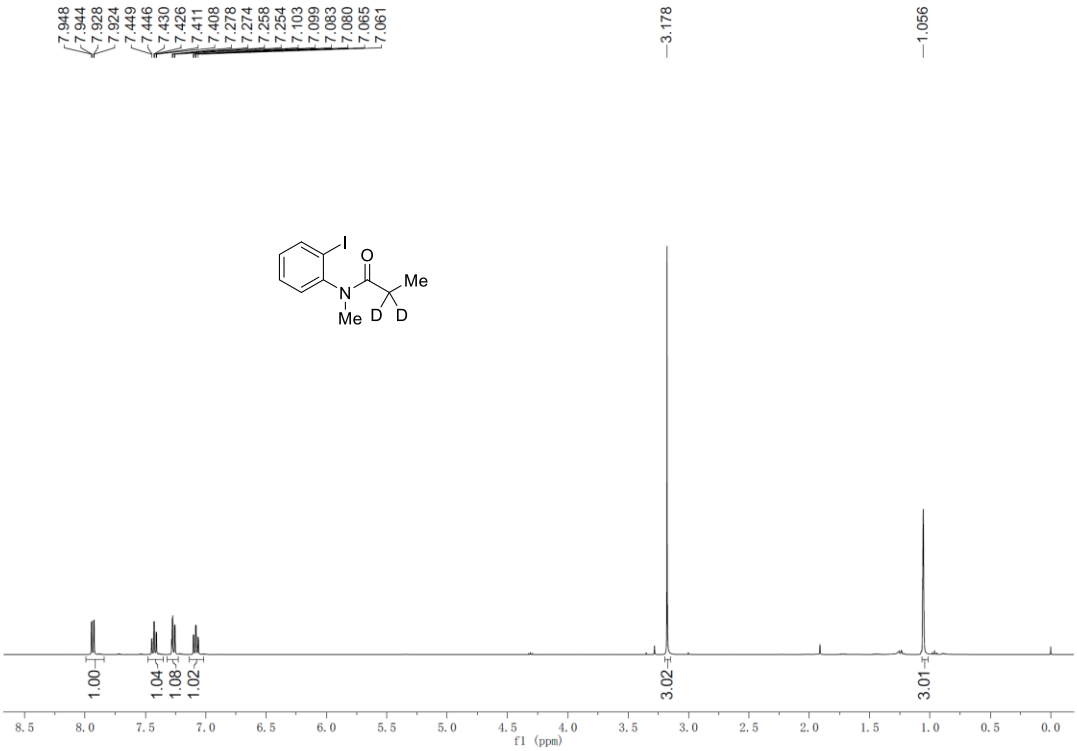
15. NMR Spectra of Compounds

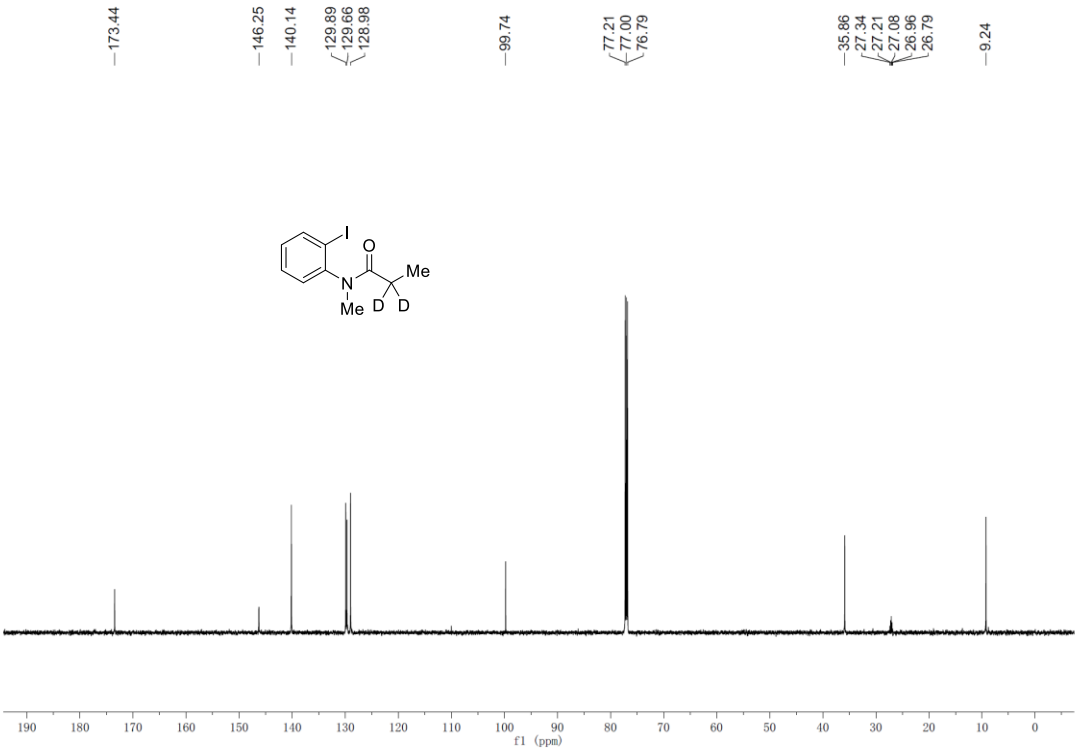
N-(2-iodophenyl)-N-methylhexadecanamide-2,2-d2 (D_2-28')



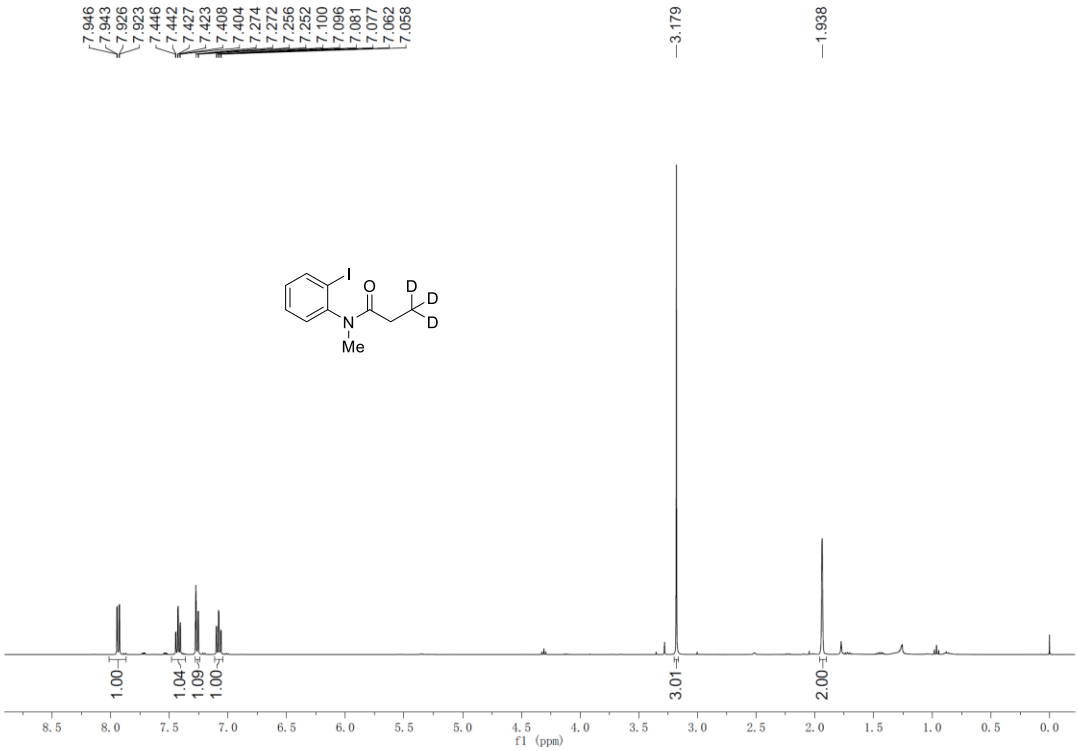


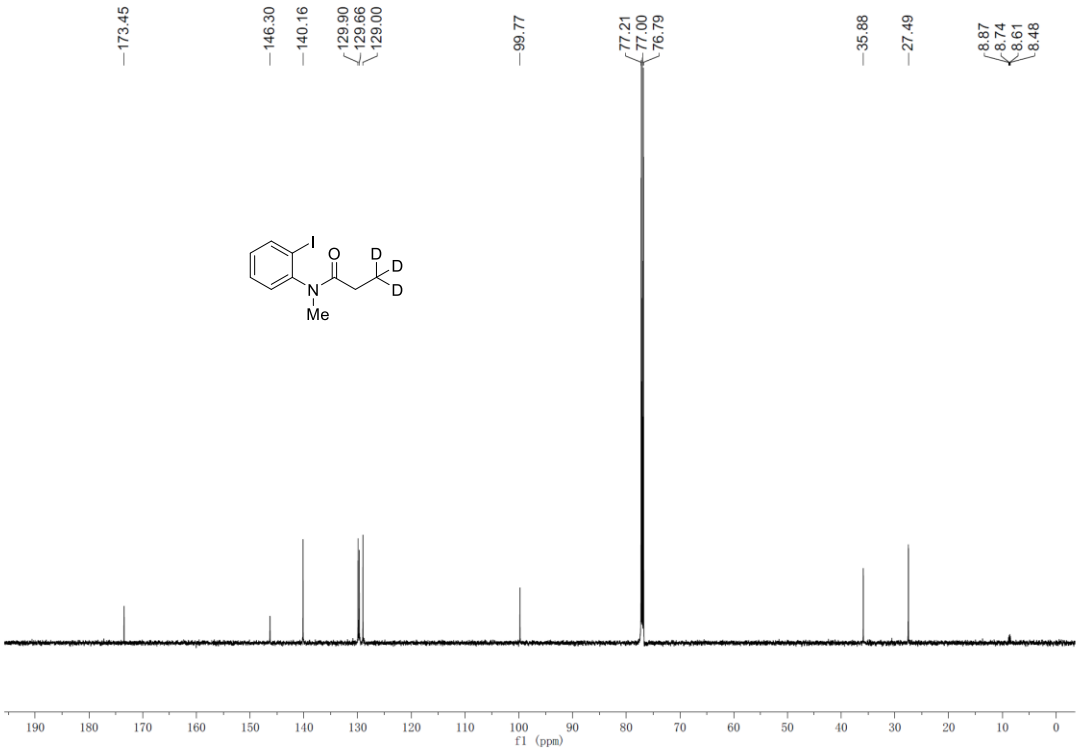
N-(2-iodophenyl)-N-methylpropanamide-2,2-d2 (114a')



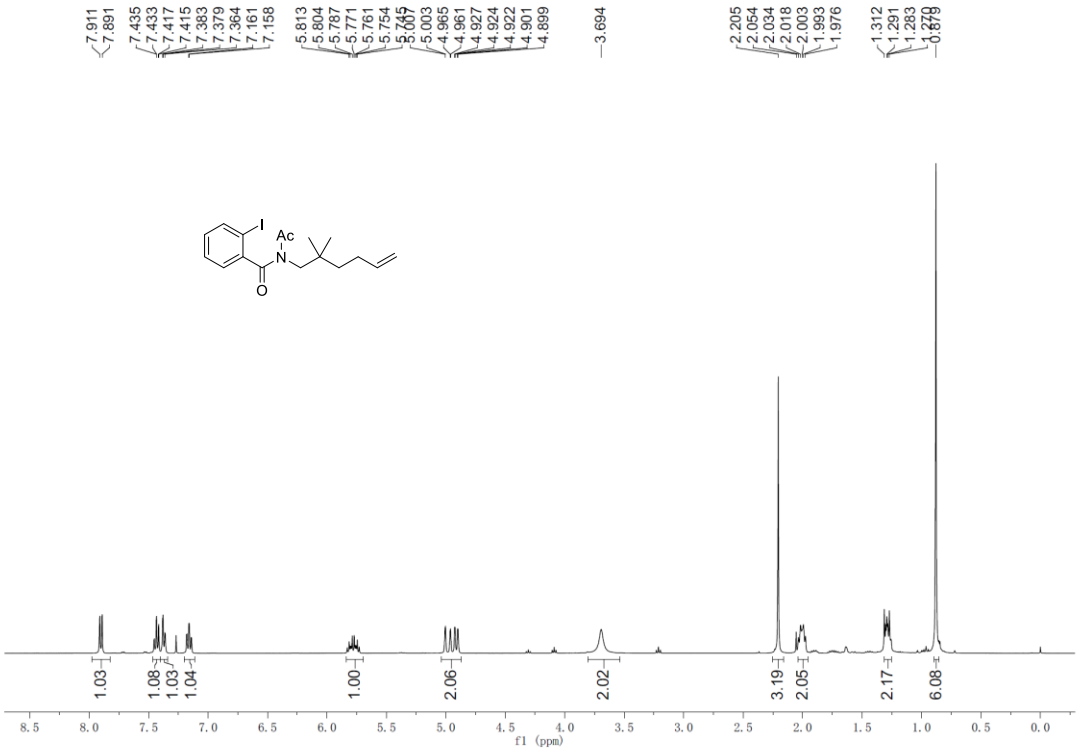


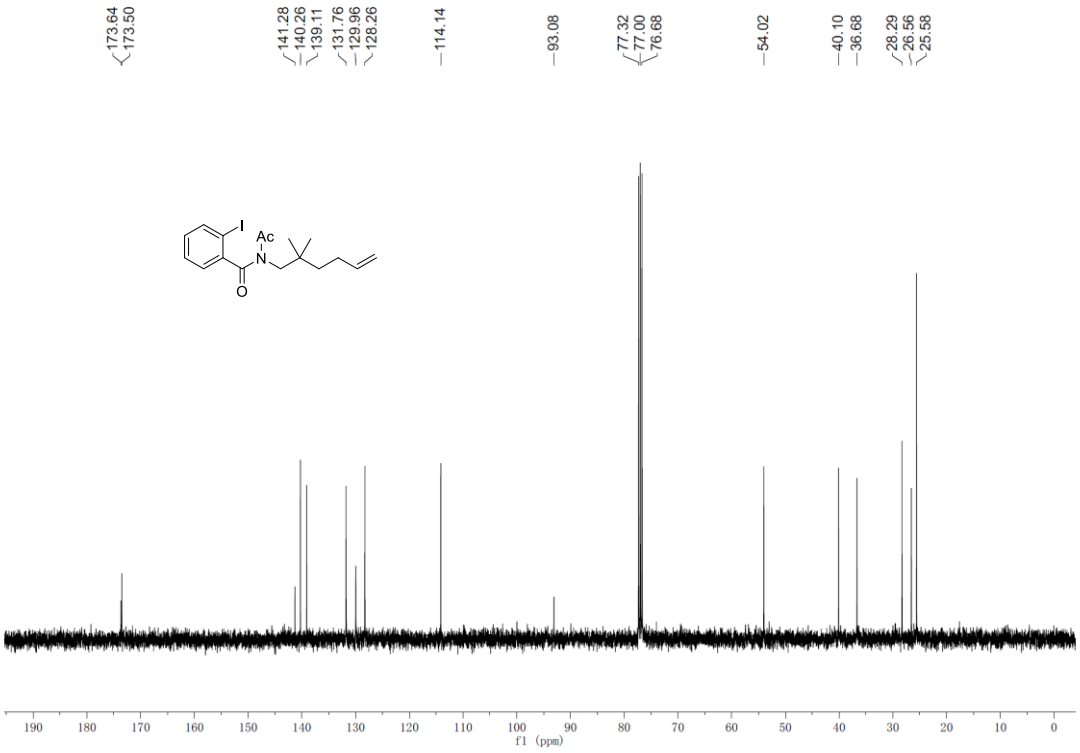
N-(2-iodophenyl)-N-methylpropanamide-3,3,3-d3 (114b')



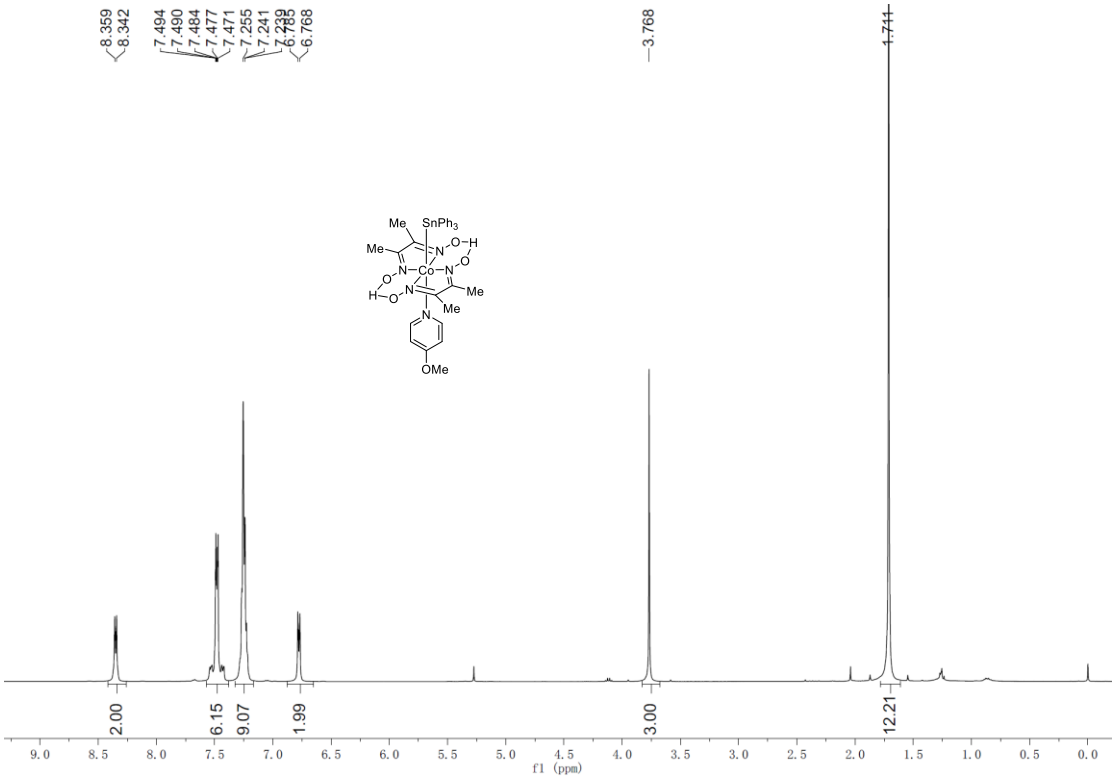


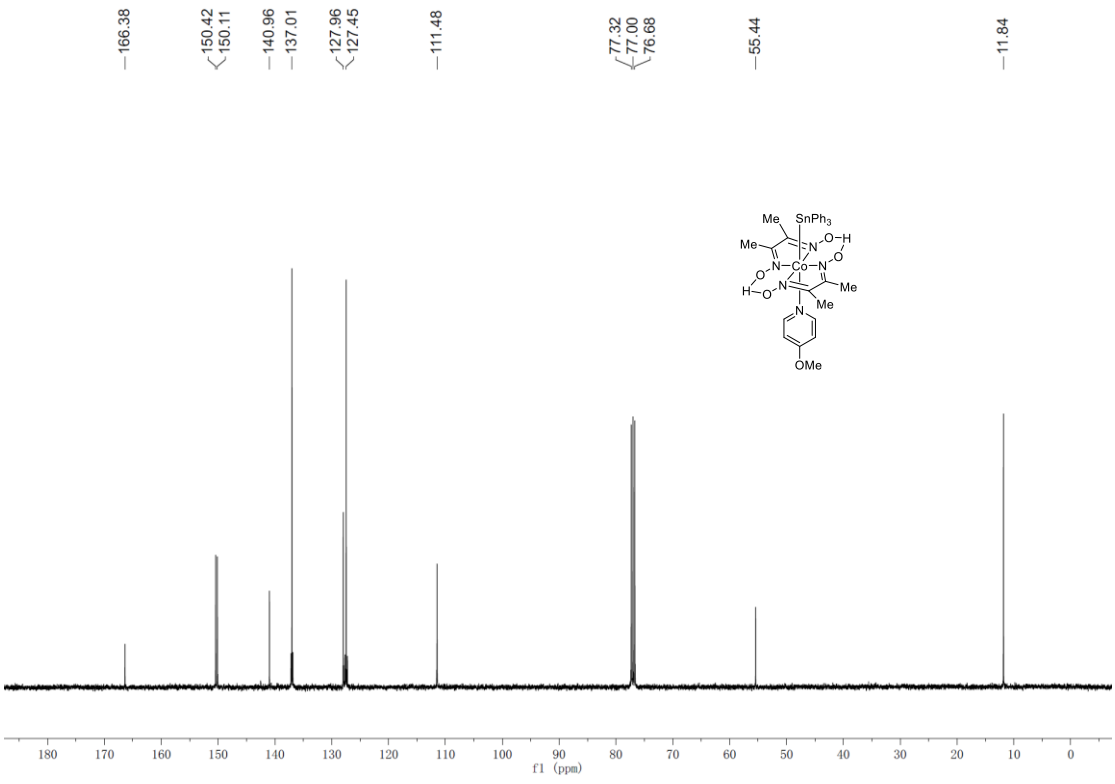
N-acetyl-N-(2,2-dimethylhex-5-en-1-yl)-2-iodobenzamide (80')



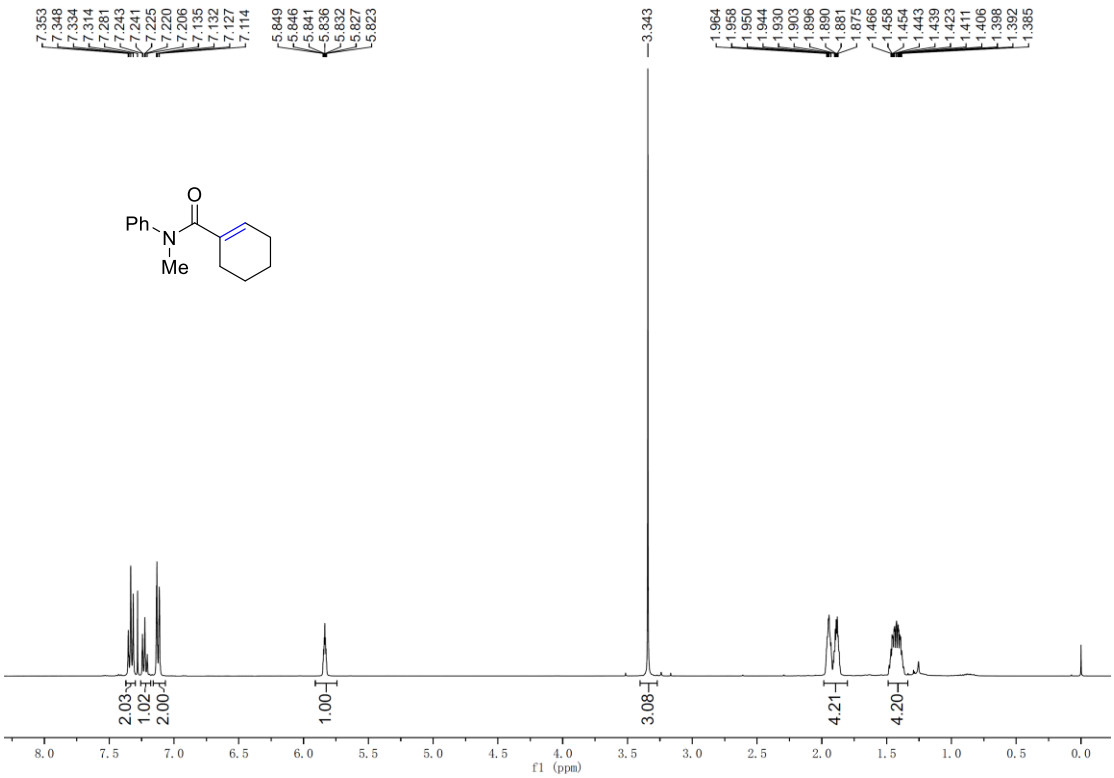


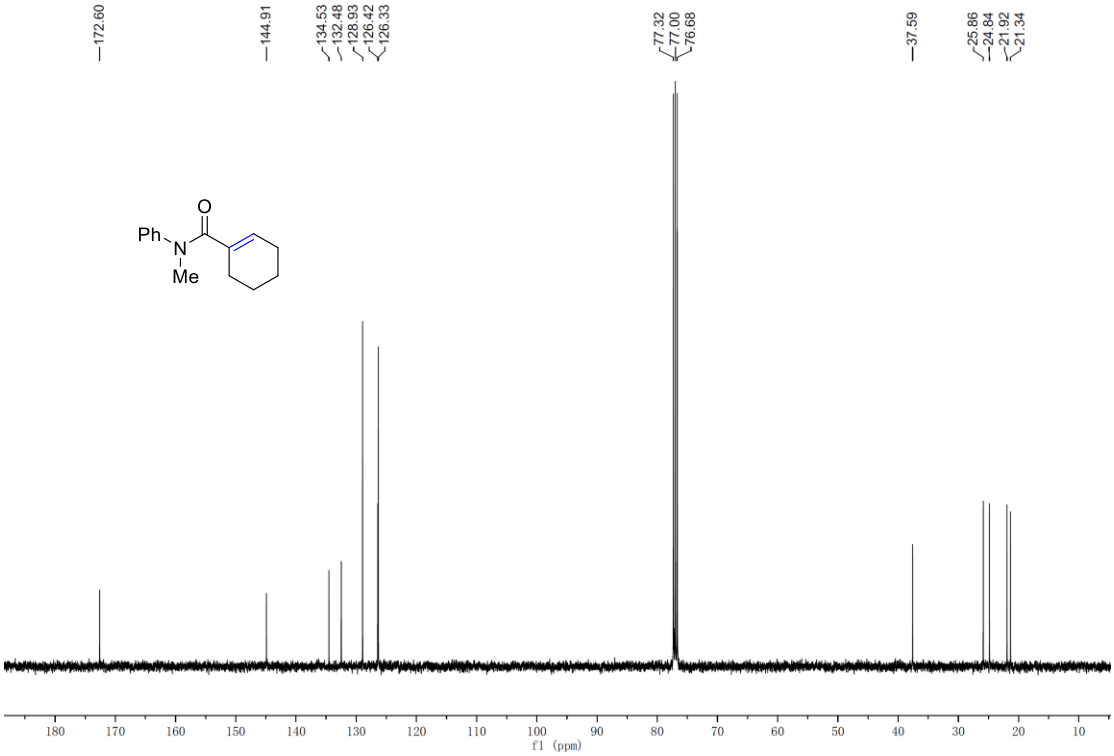
$Co(dmgH)_2(4\text{-}OMe\text{-}Py)SnPh_3$ (III)



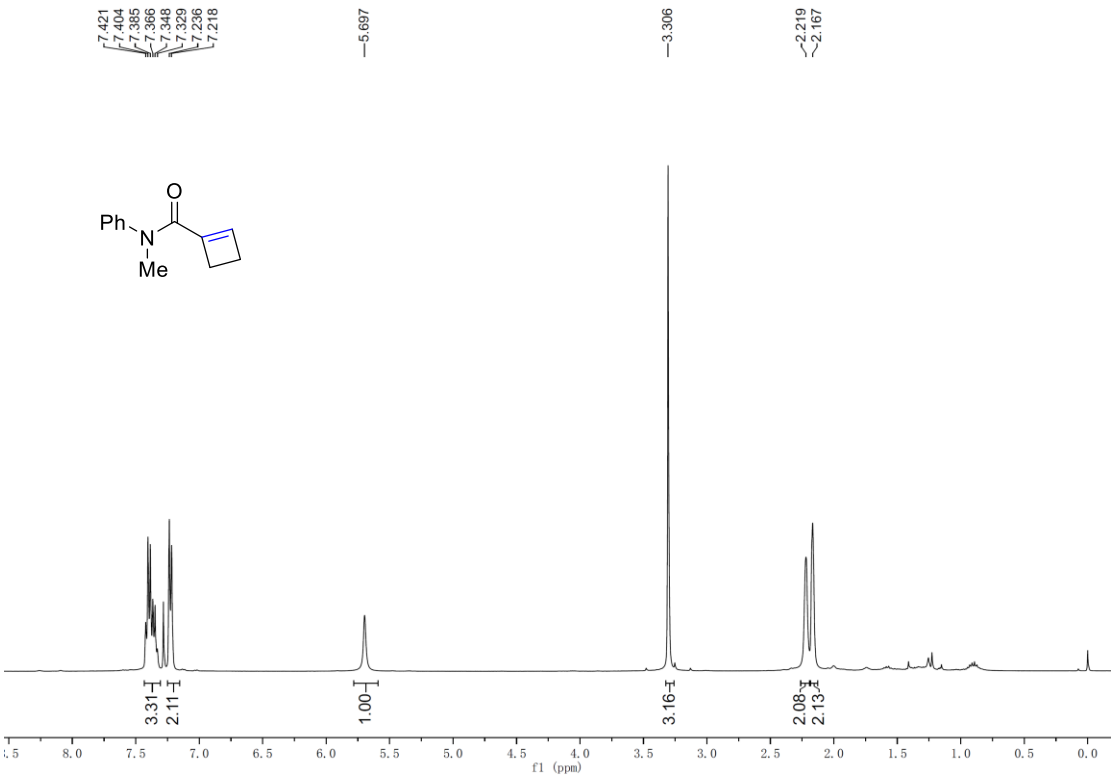


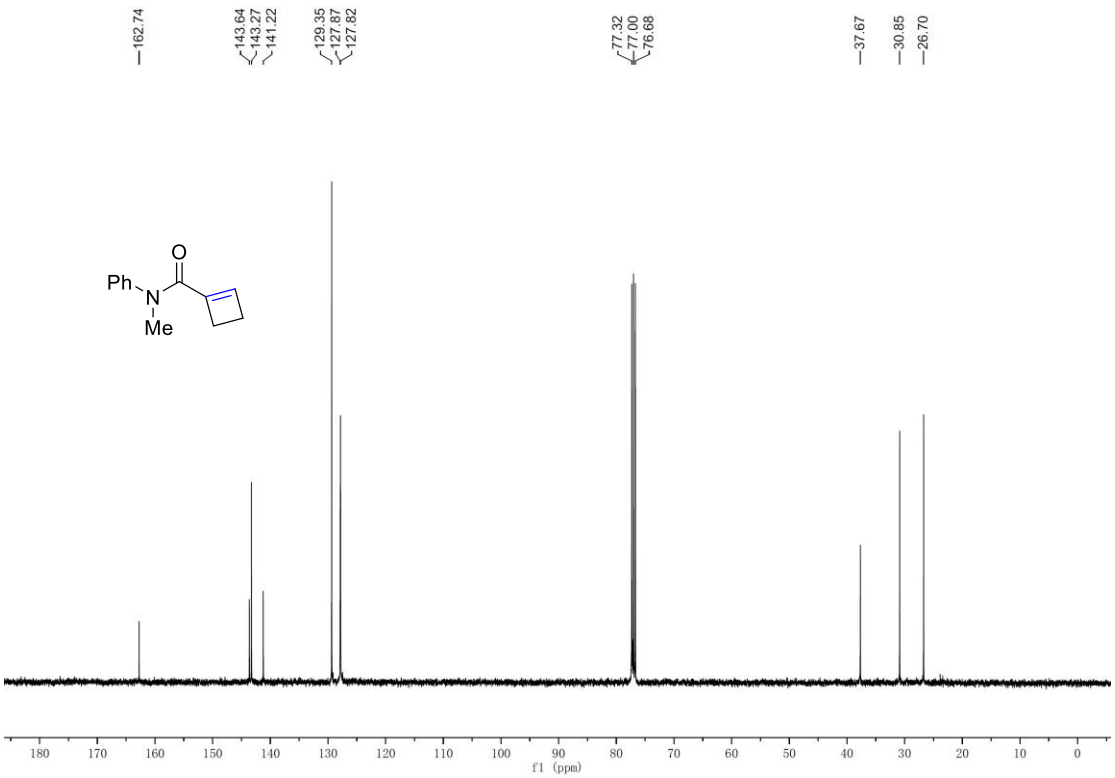
N-methyl-N-phenylcyclohex-1-ene-1-carboxamide (1)



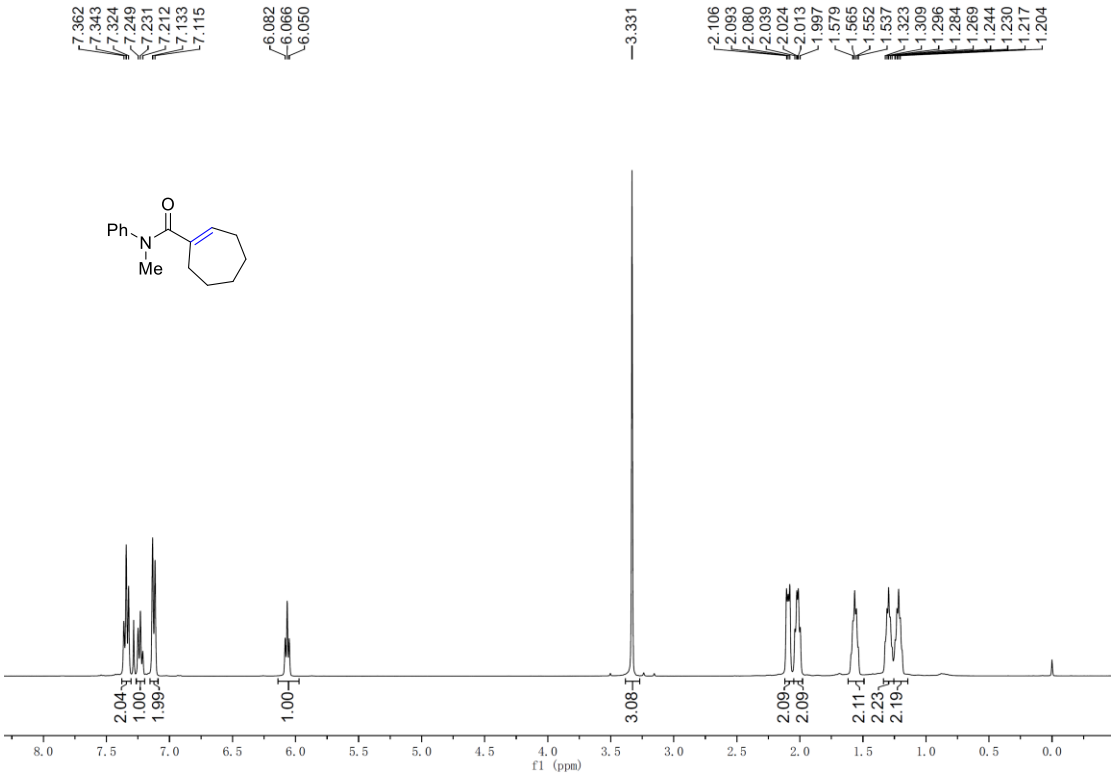


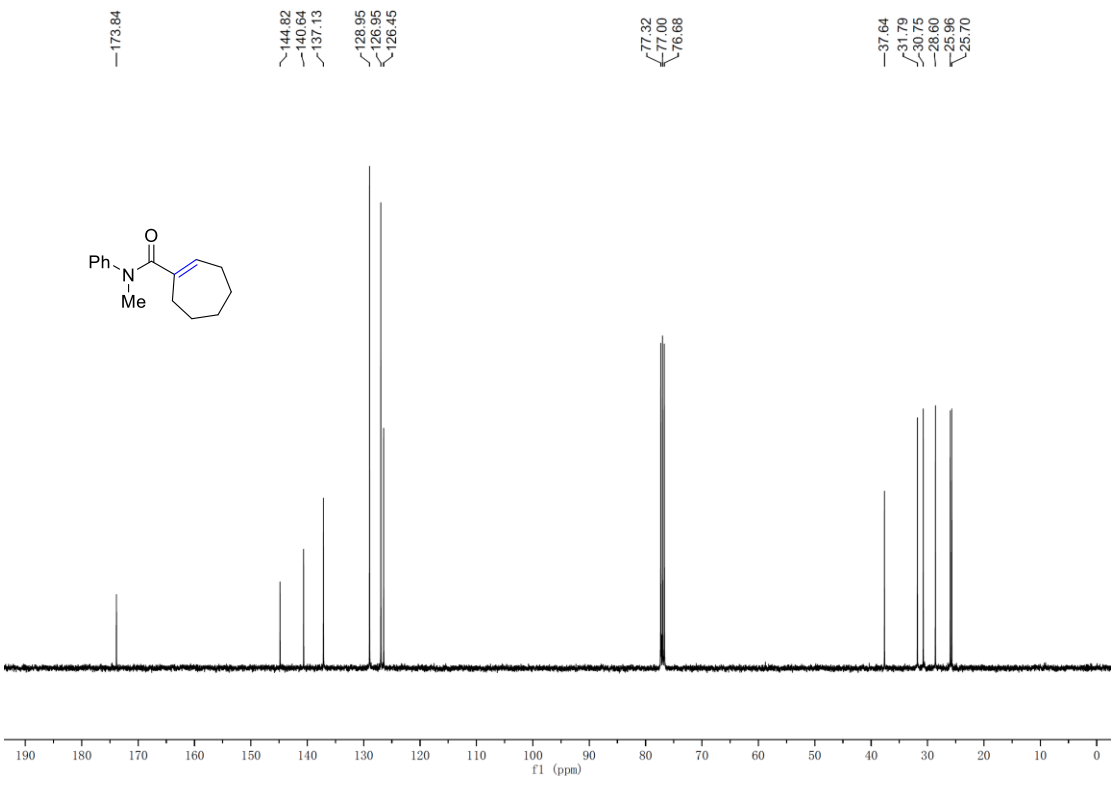
N-methyl-N-phenylcyclobut-1-ene-1-carboxamide (2)



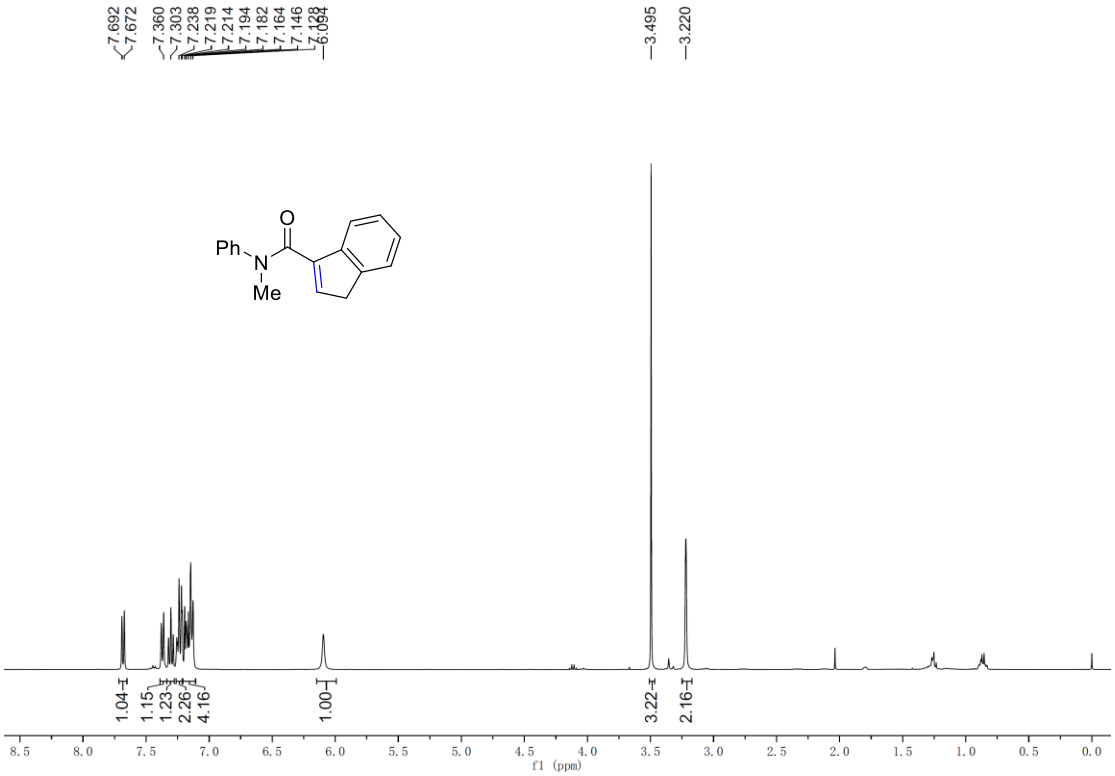


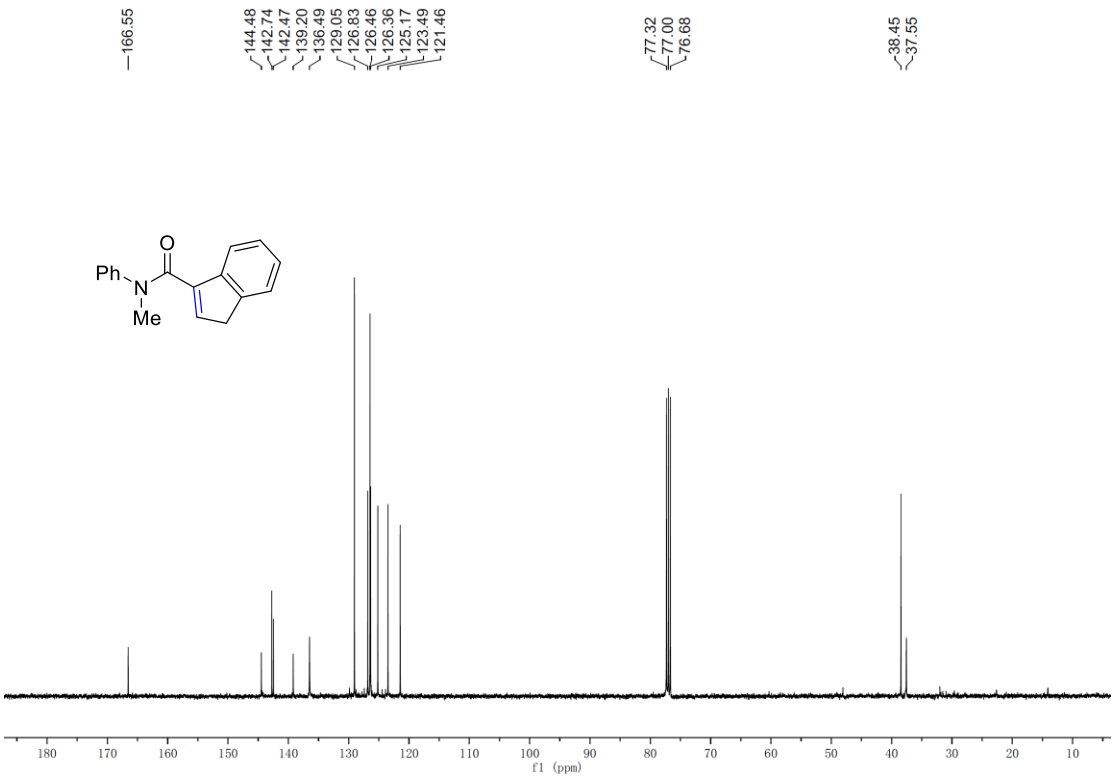
N-methyl-N-phenylcyclohept-1-ene-1-carboxamide (3)



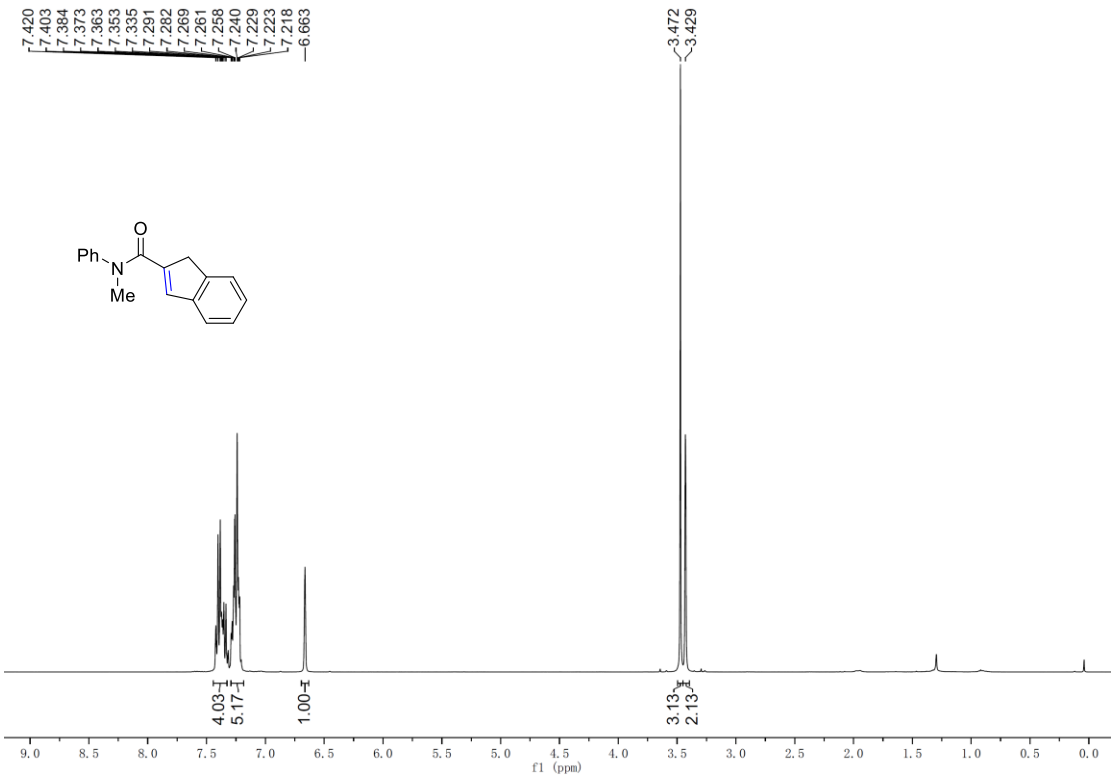


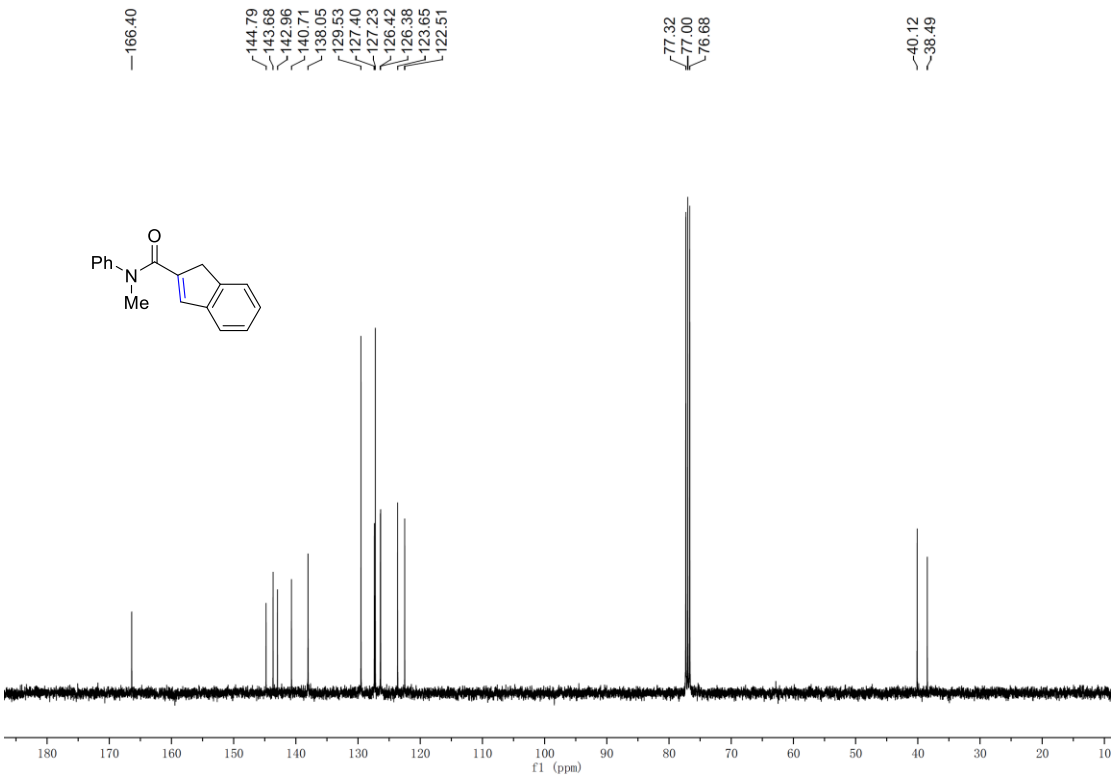
N-methyl-N-phenyl-1H-indene-3-carboxamide (4)



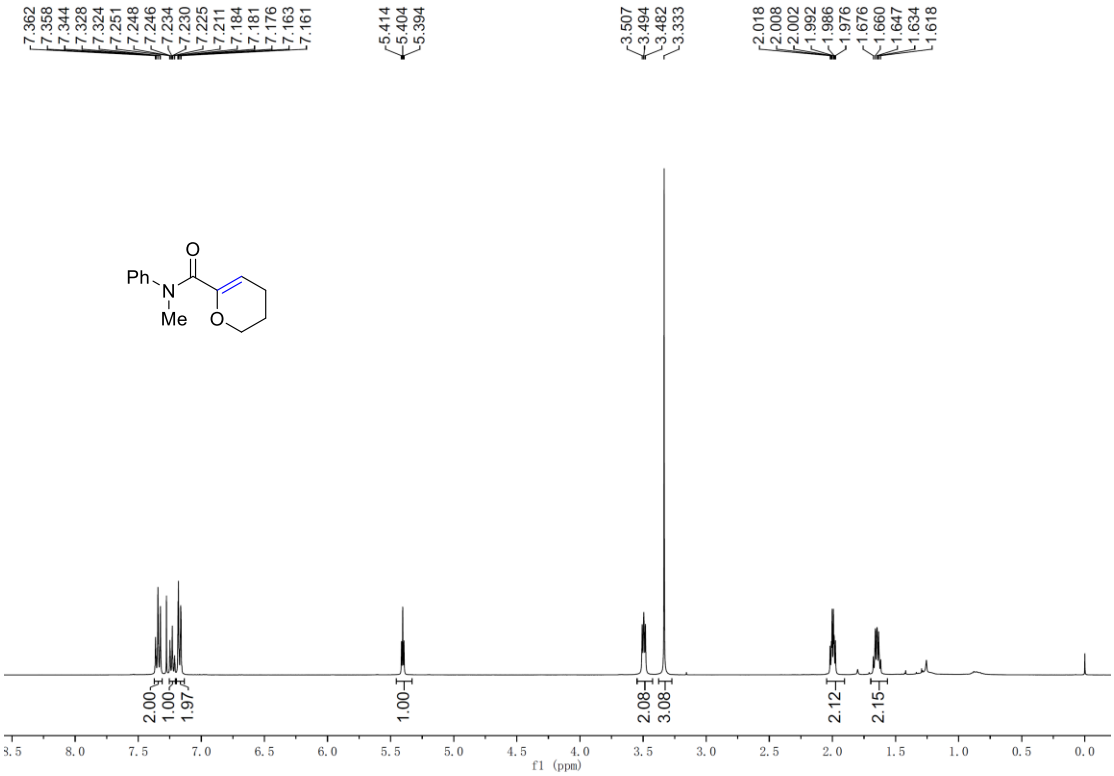


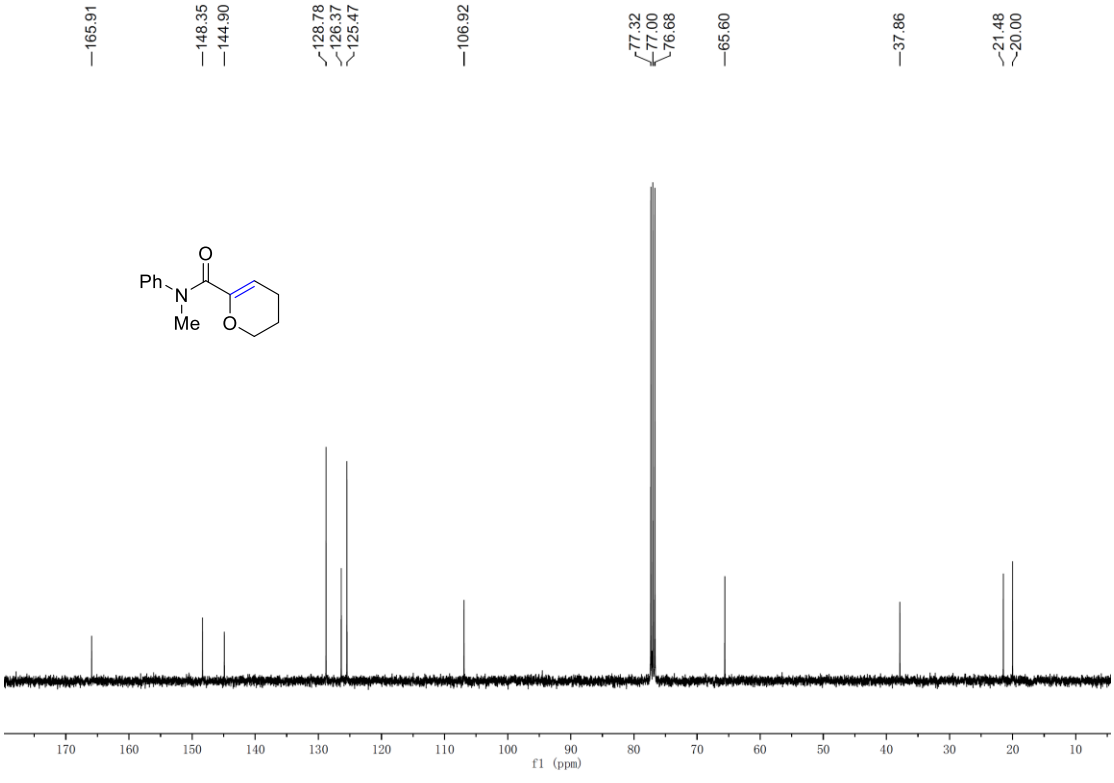
N-methyl-N-phenyl-1H-indene-2-carboxamide (5)



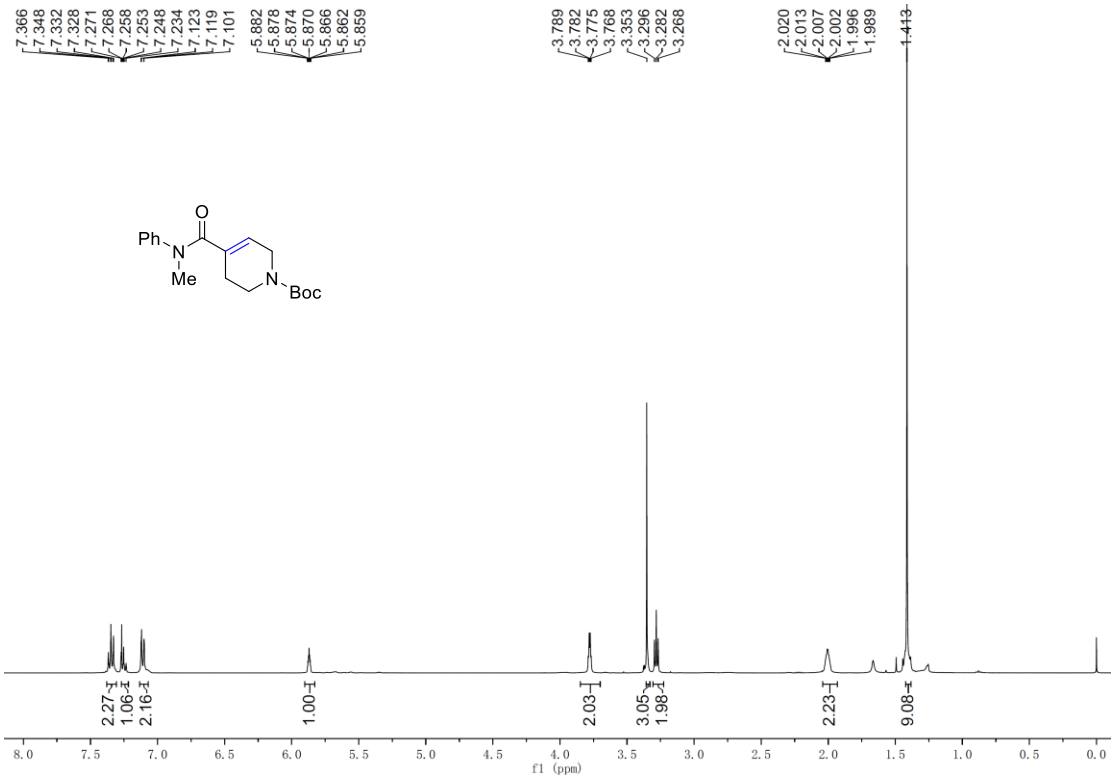


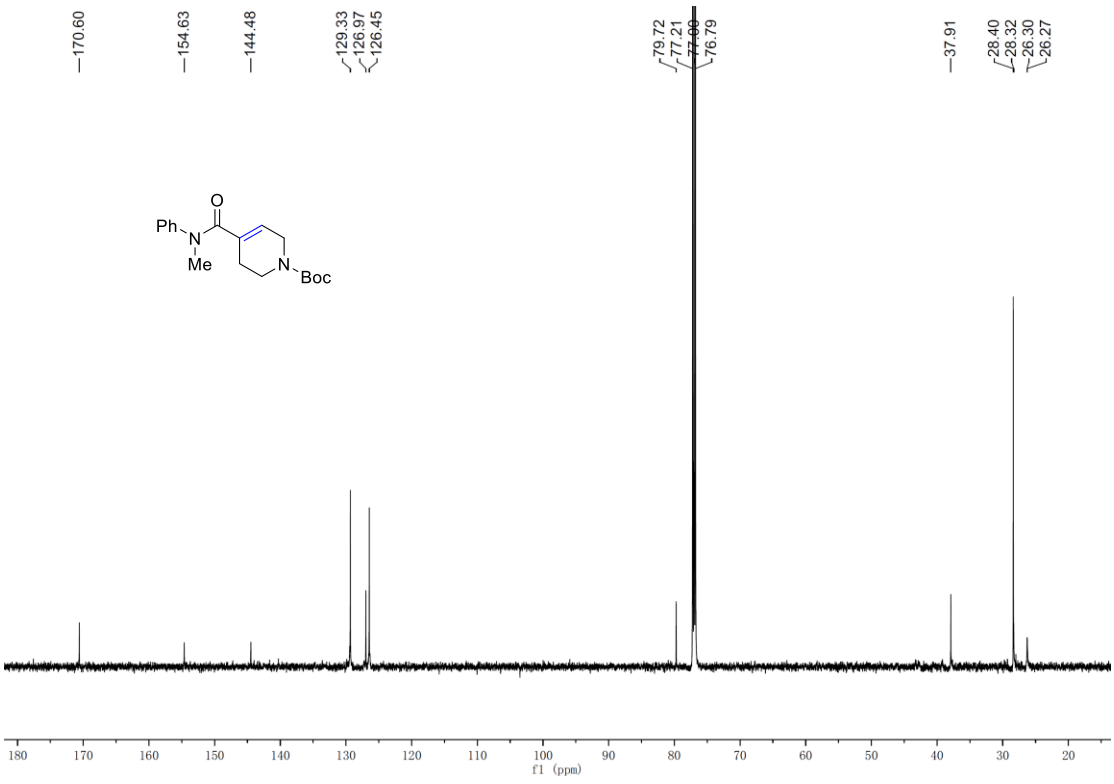
N-methyl-N-phenyl-3,4-dihydro-2H-pyran-6-carboxamide (6)



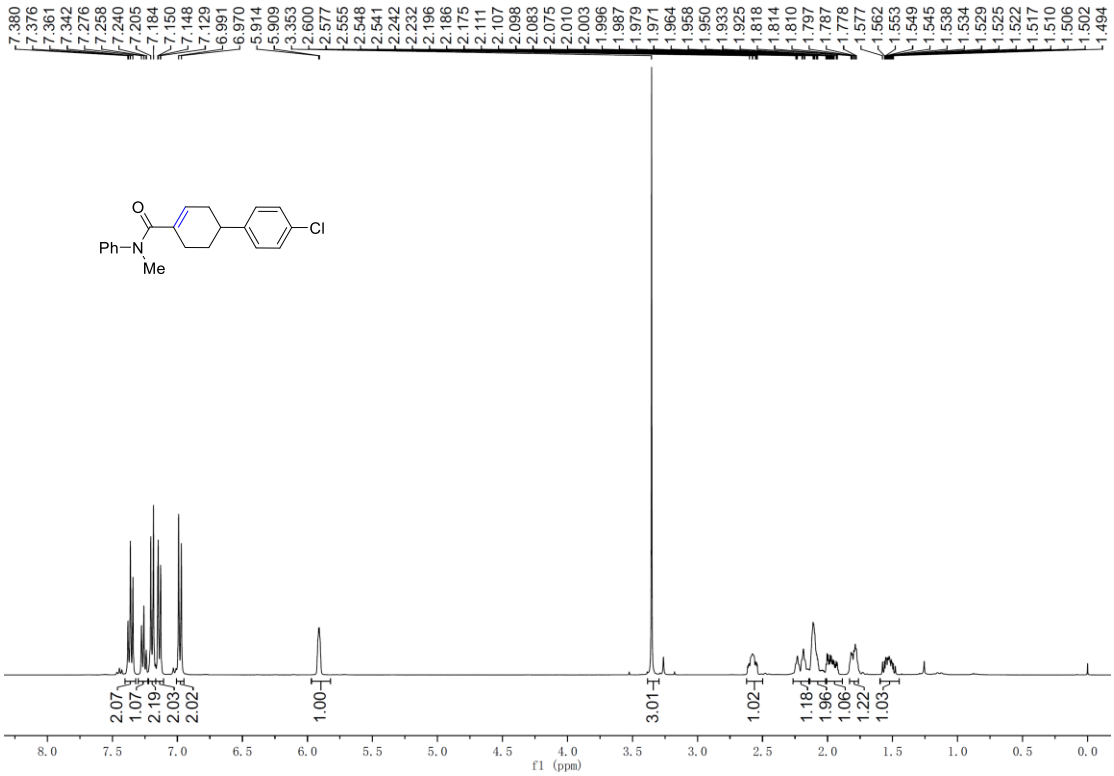


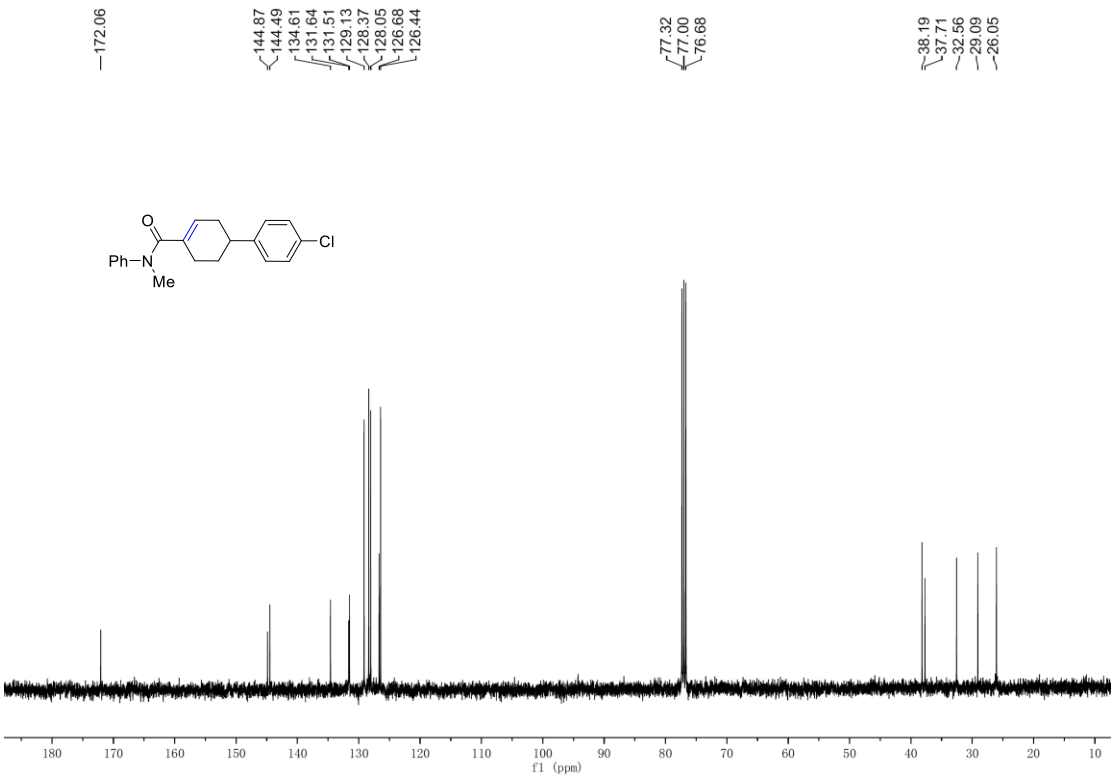
tert-butyl 4-(methyl(phenyl)carbamoyl)-3,6-dihydropyridine-1(2H)-carboxylate (7)



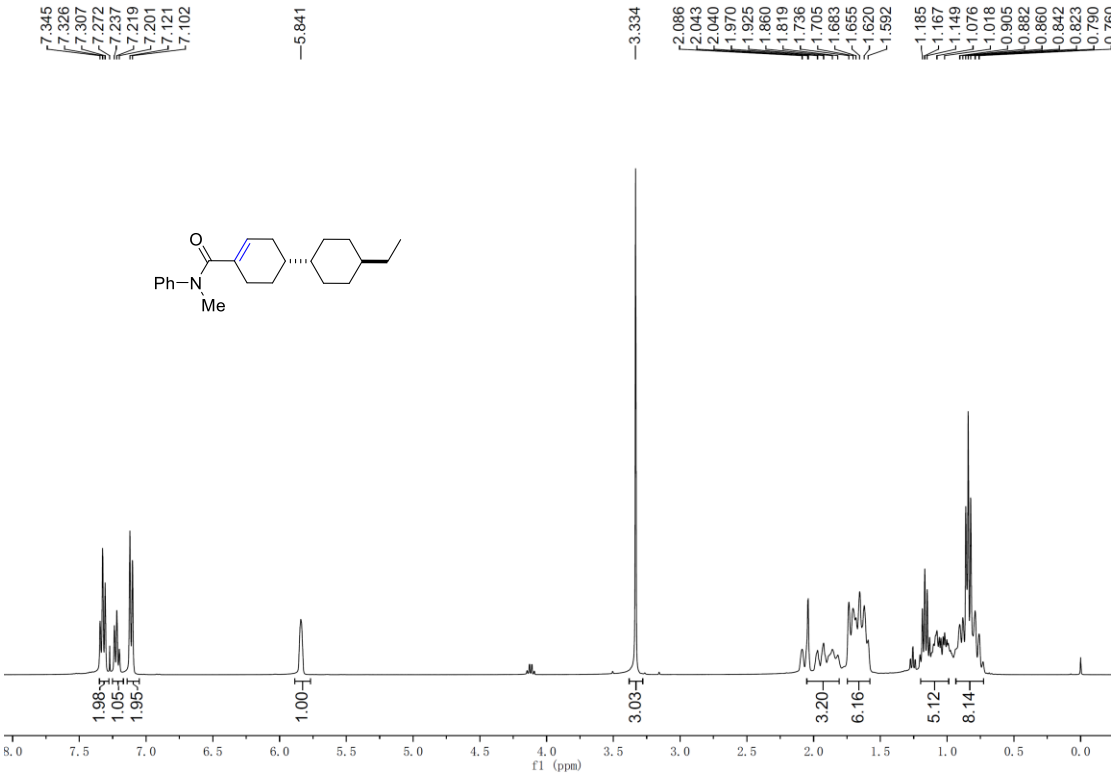


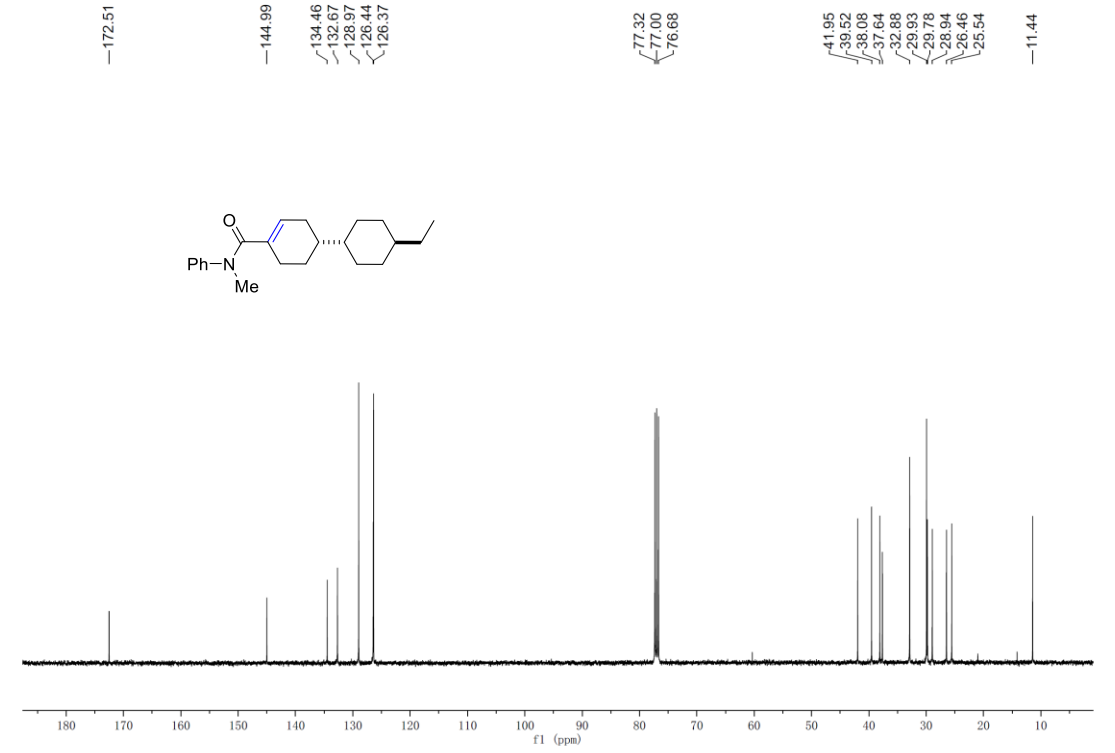
4'-chloro-N-methyl-N-phenyl-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-carboxamide (8)



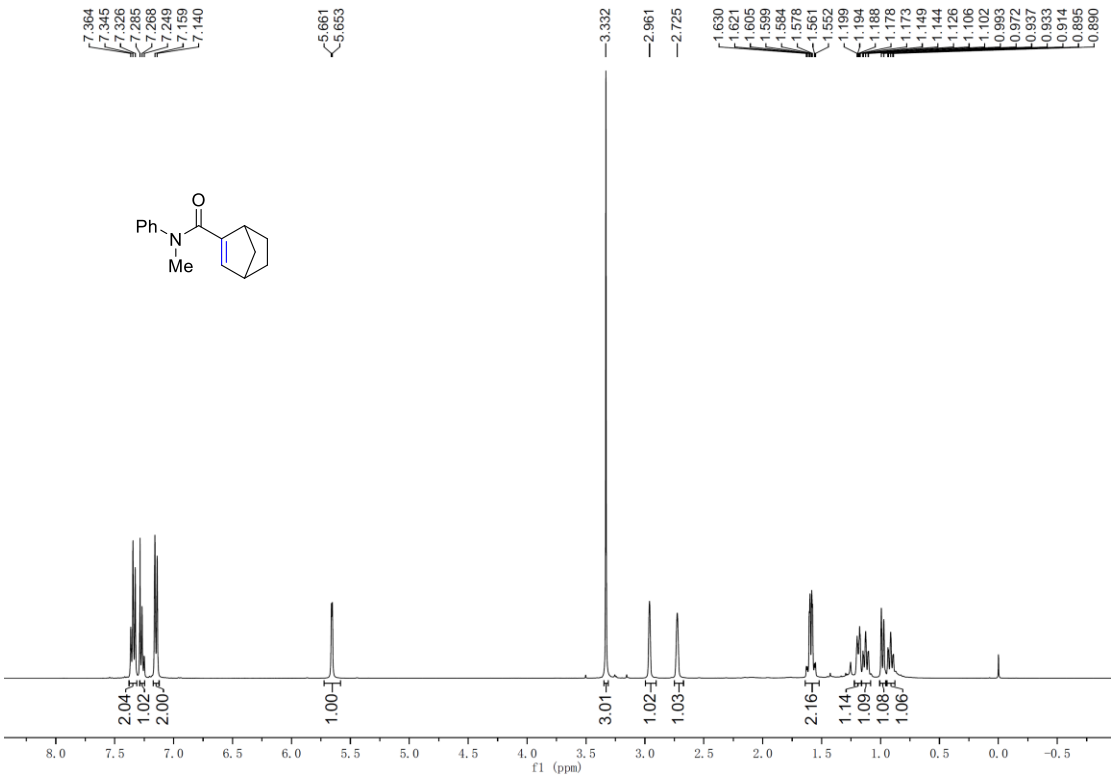


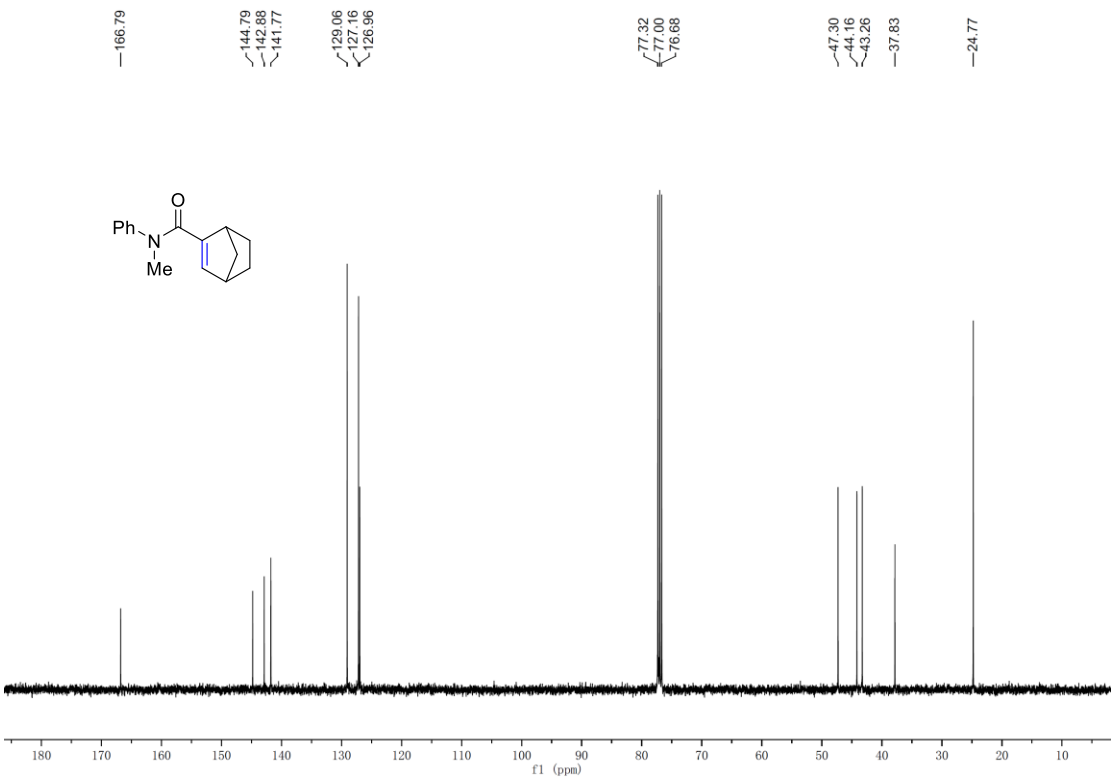
(1R*,1'r*,4'R*)-4'-ethyl-N-methyl-N-phenyl-[1,1'-bi(cyclohexan)]-3-ene-4-carboxamide (9)



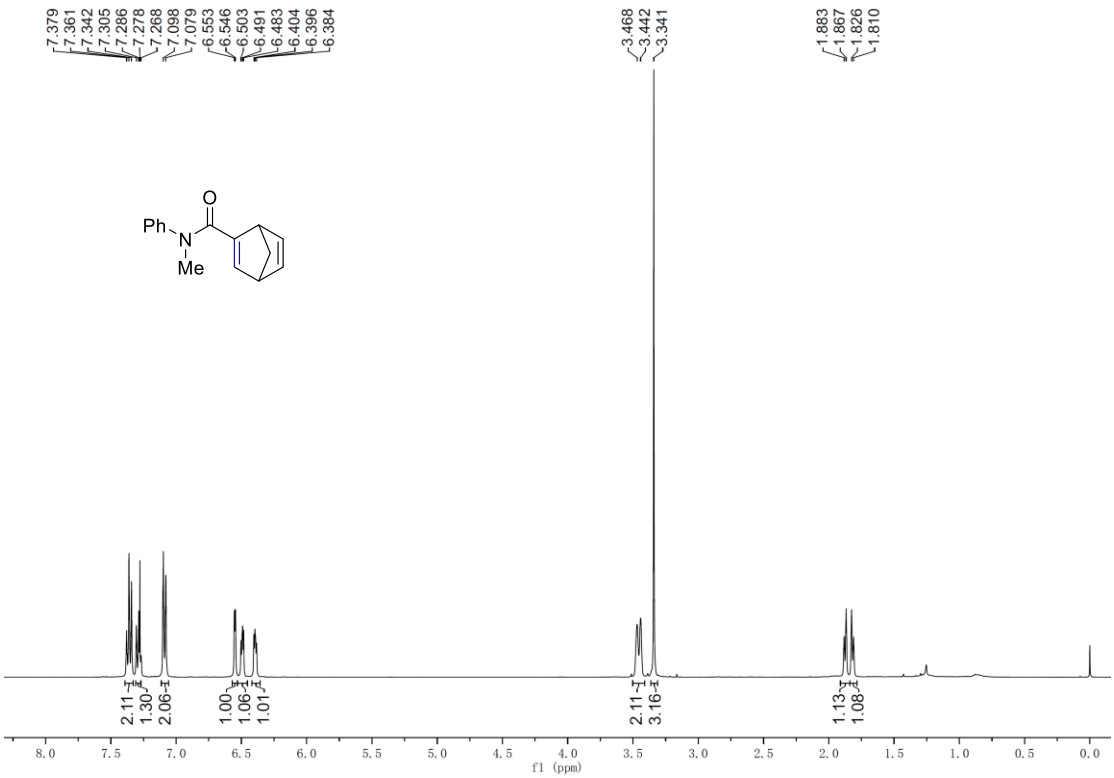


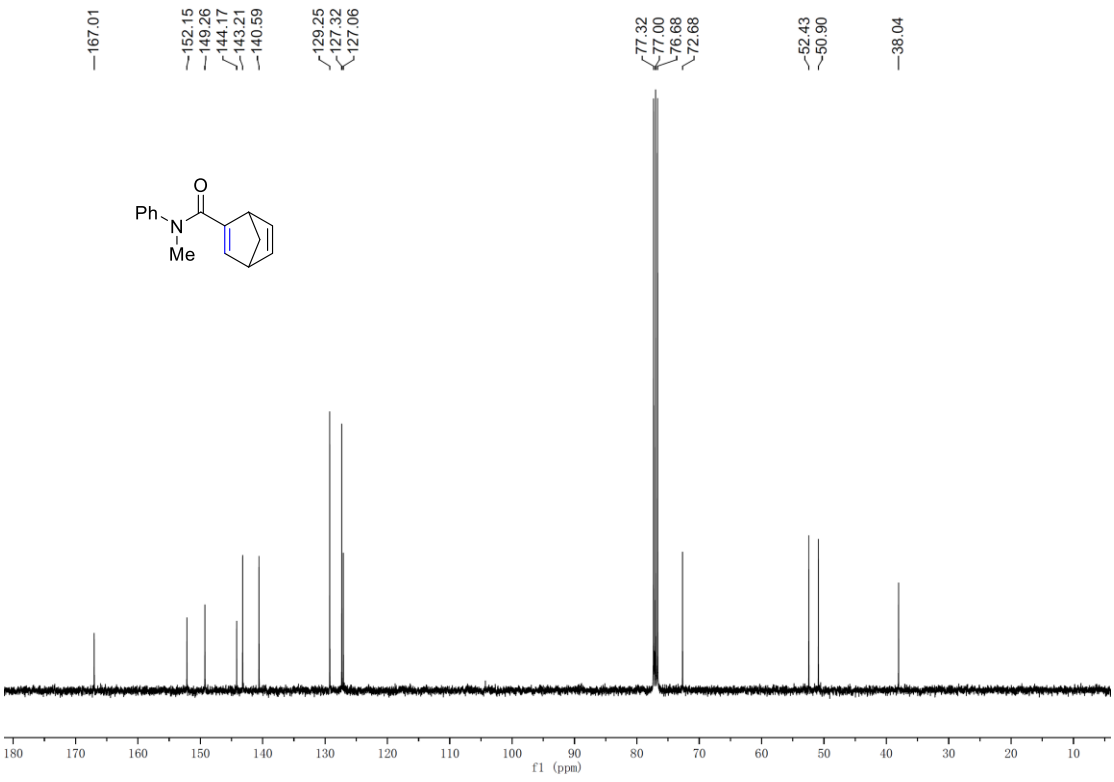
N-methyl-N-phenylbicyclo[2.2.1]hept-2-ene-2-carboxamide (10)



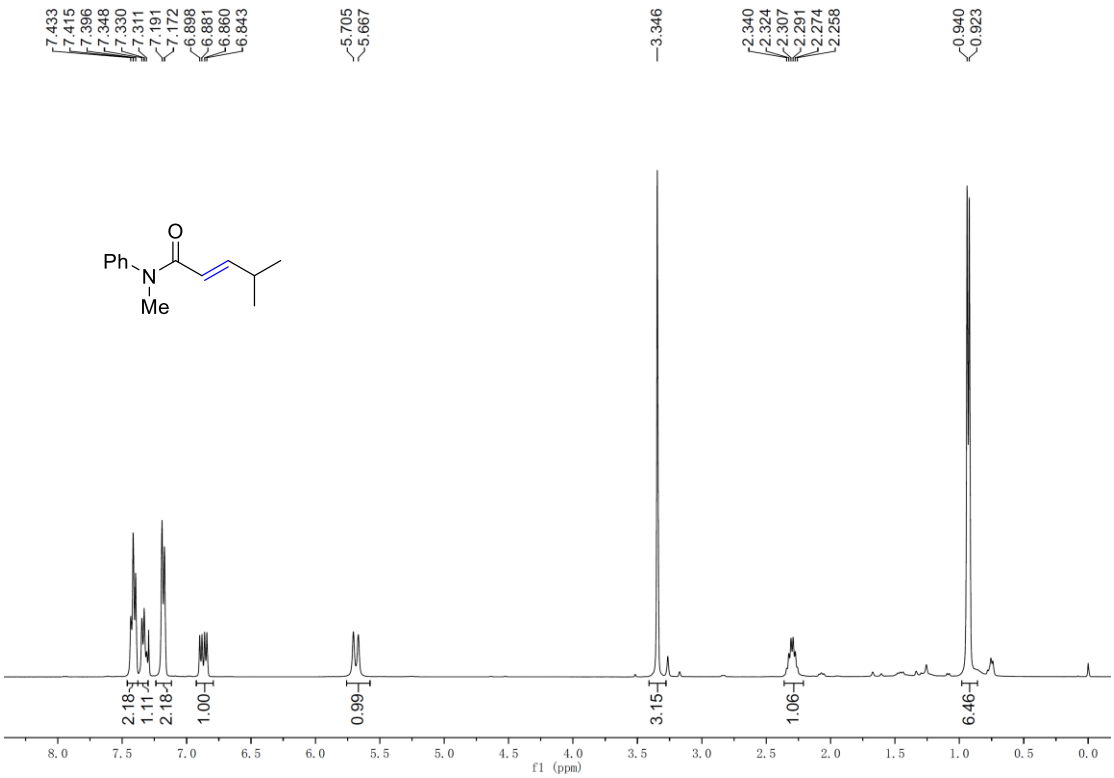


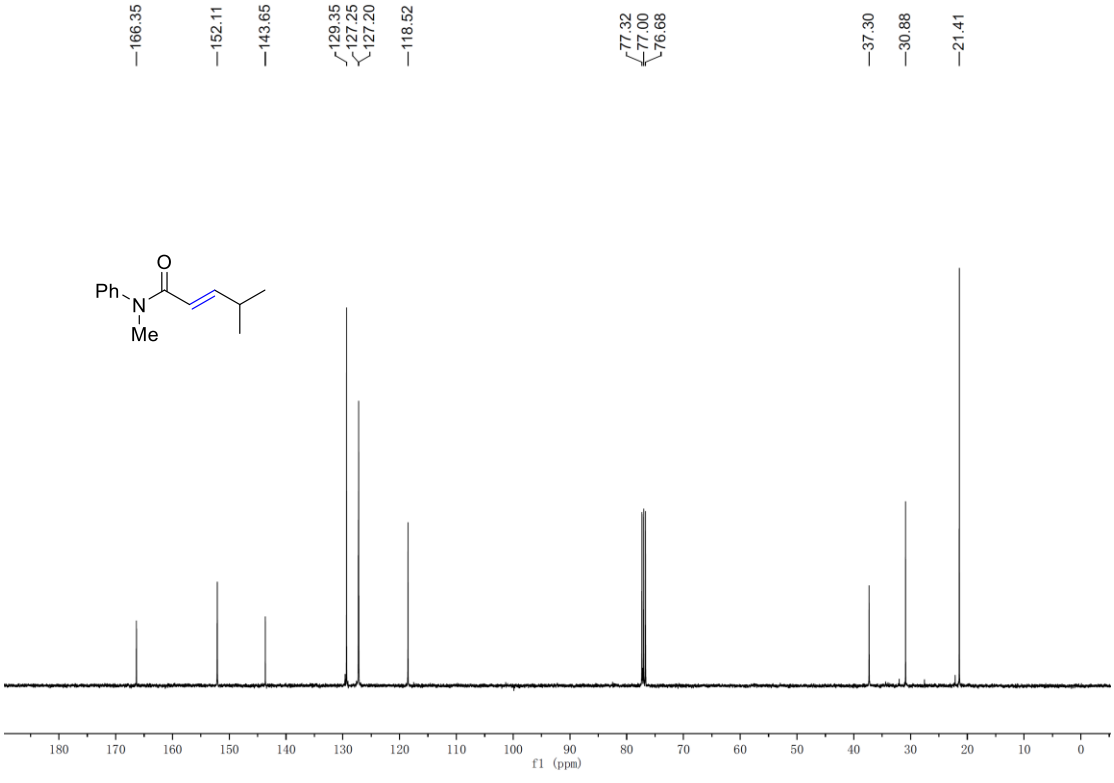
N-methyl-N-phenylbicyclo[2.2.1]hepta-2,5-diene-2-carboxamide (11)



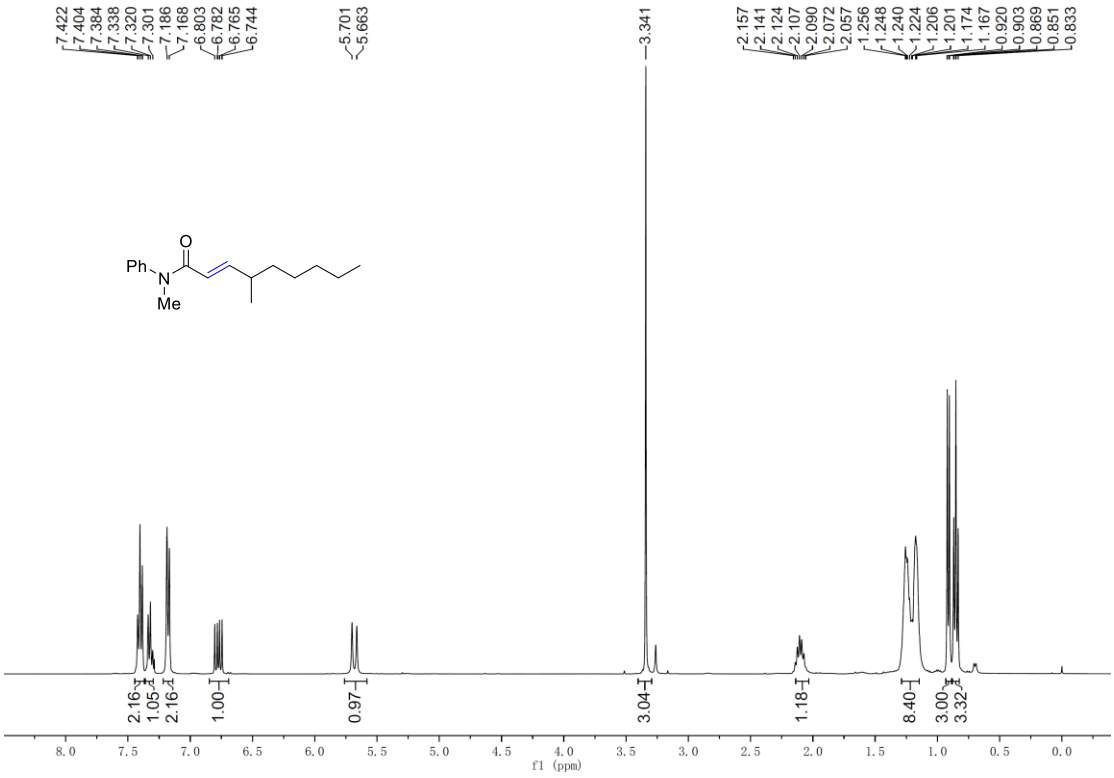


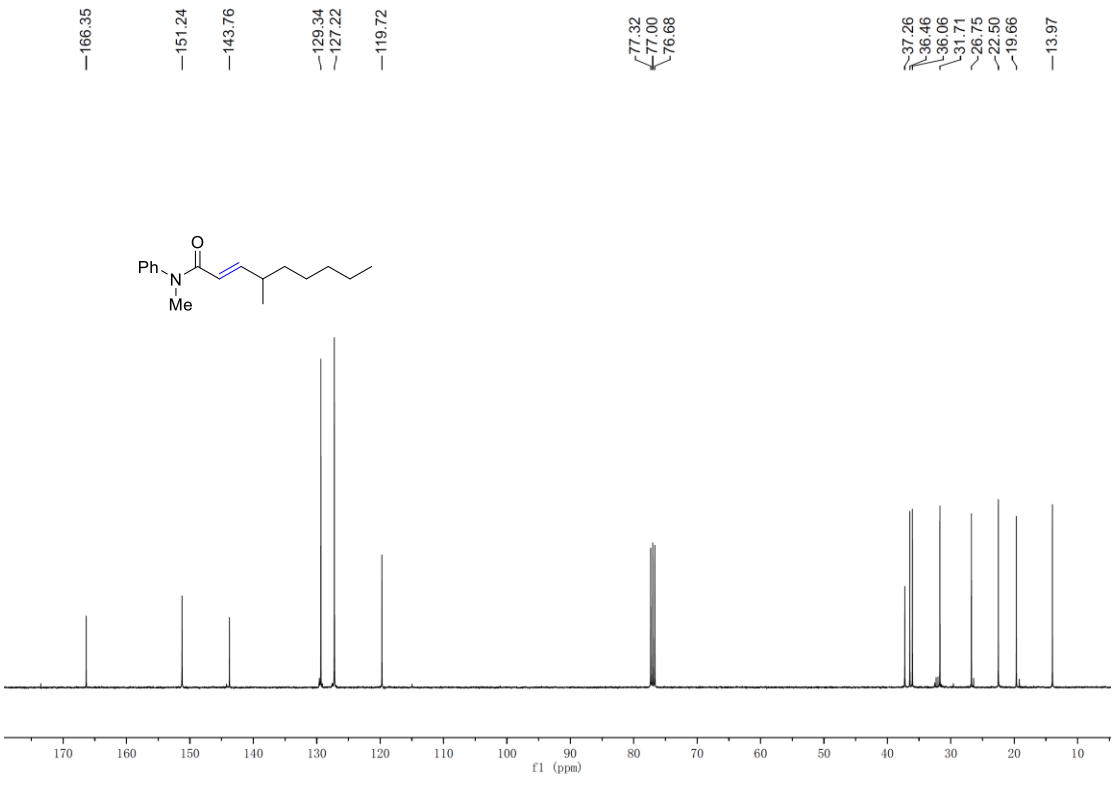
(E)-N,4-dimethyl-N-phenylpent-2-enamide (12)



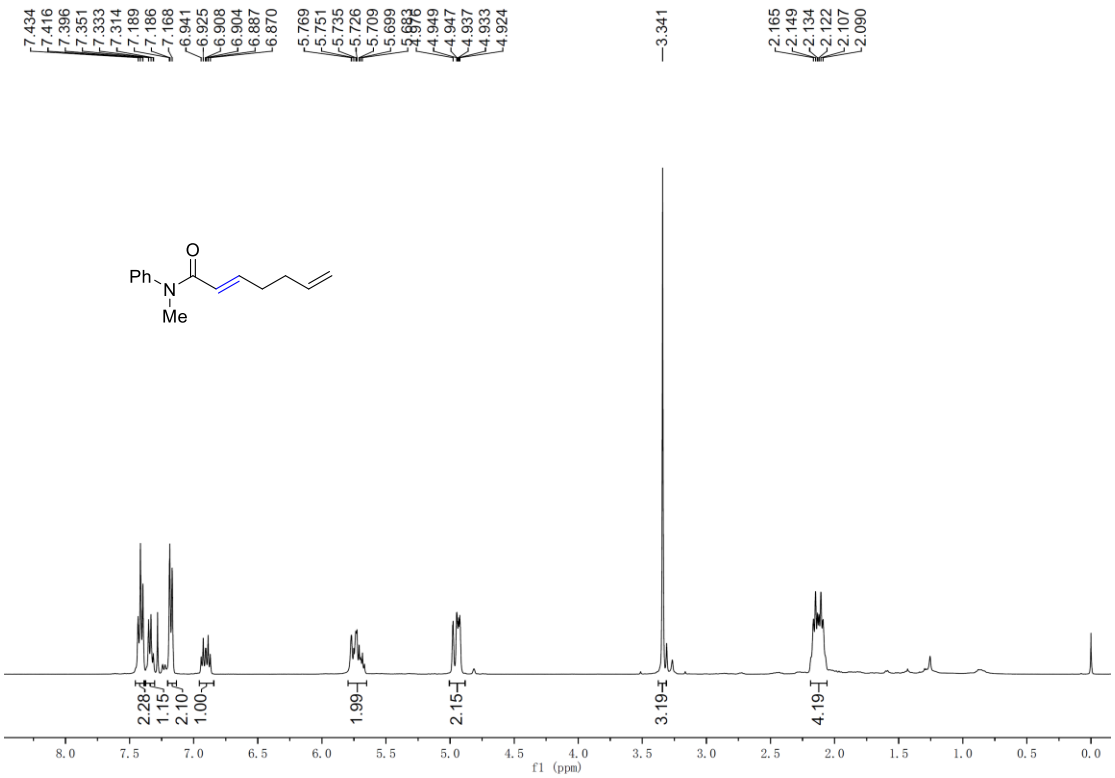


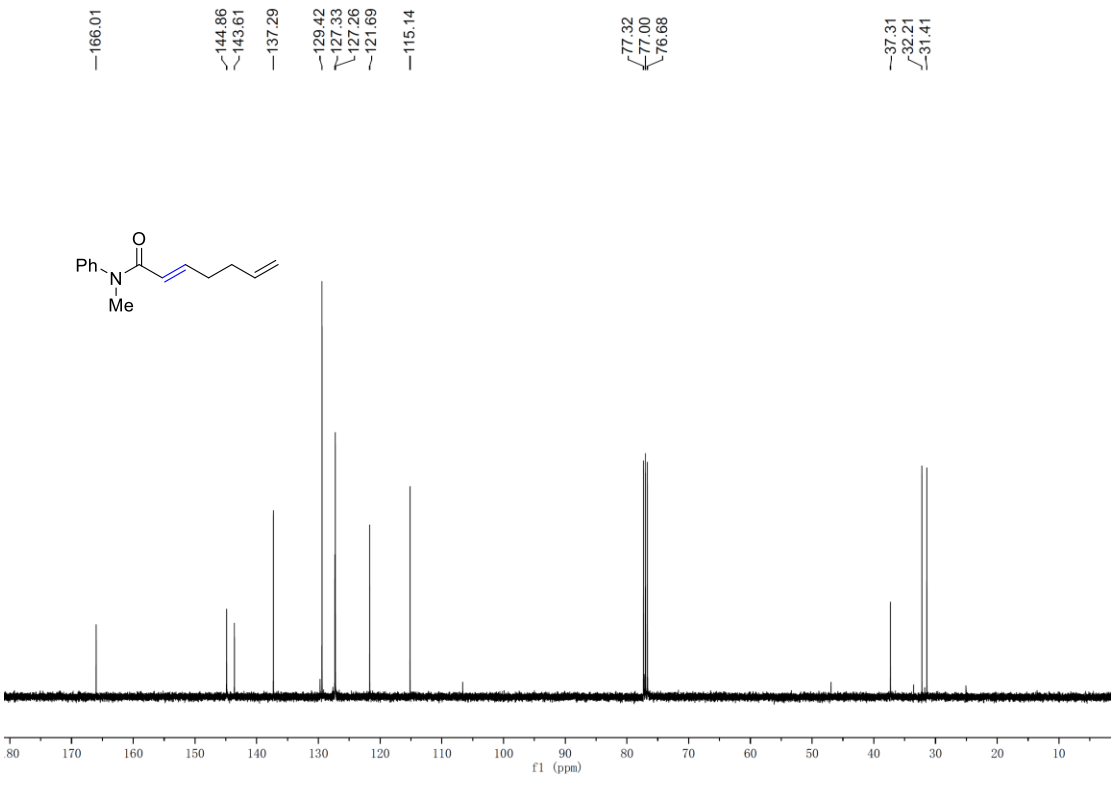
(E)-N,4-dimethyl-N-phenylnon-2-enamide (13)



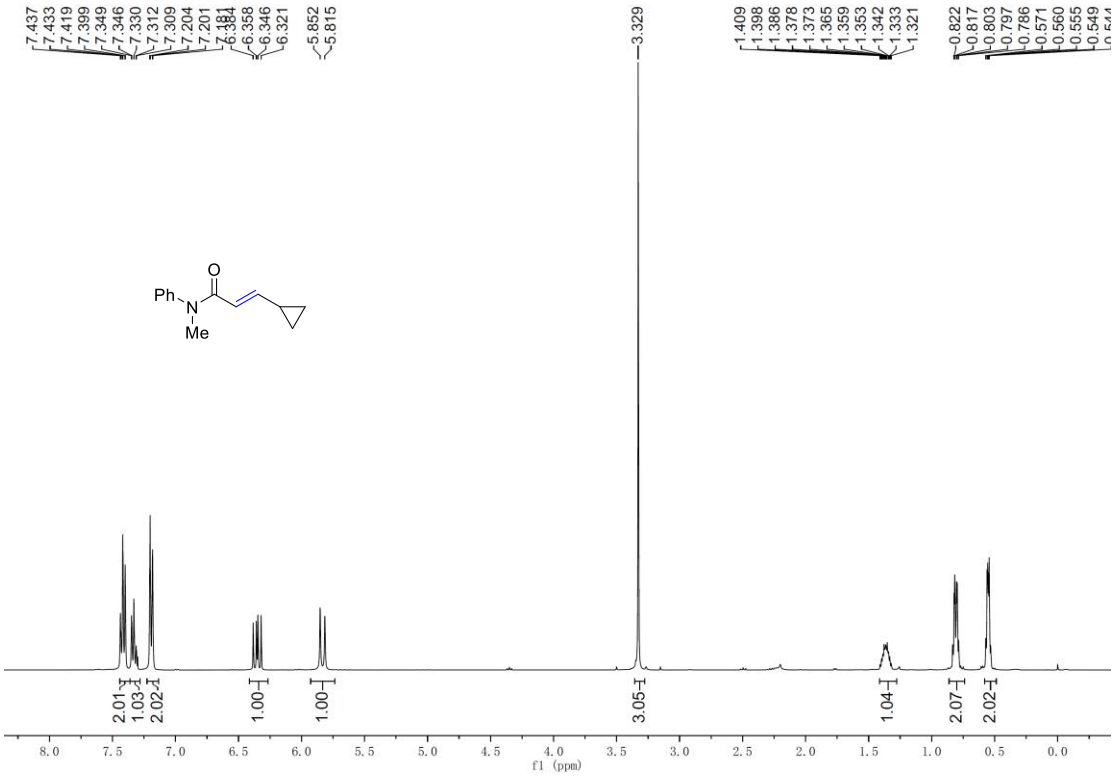


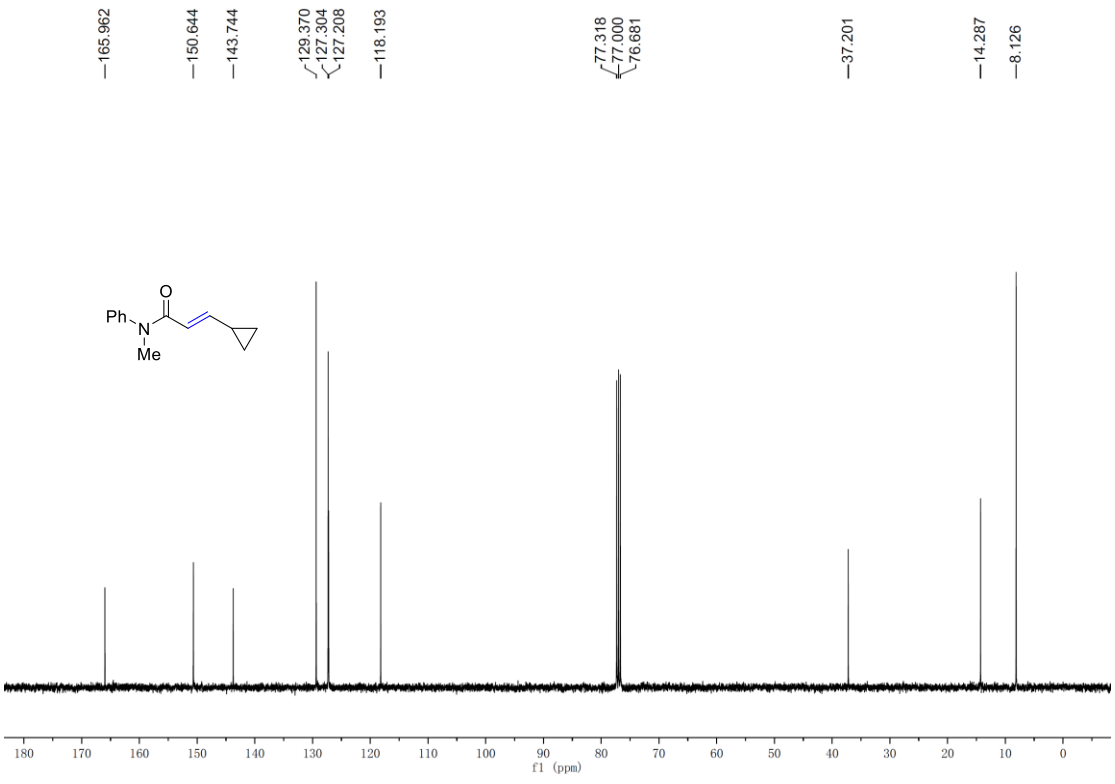
(E)-N-methyl-N-phenylhepta-2,6-dienamide (14)



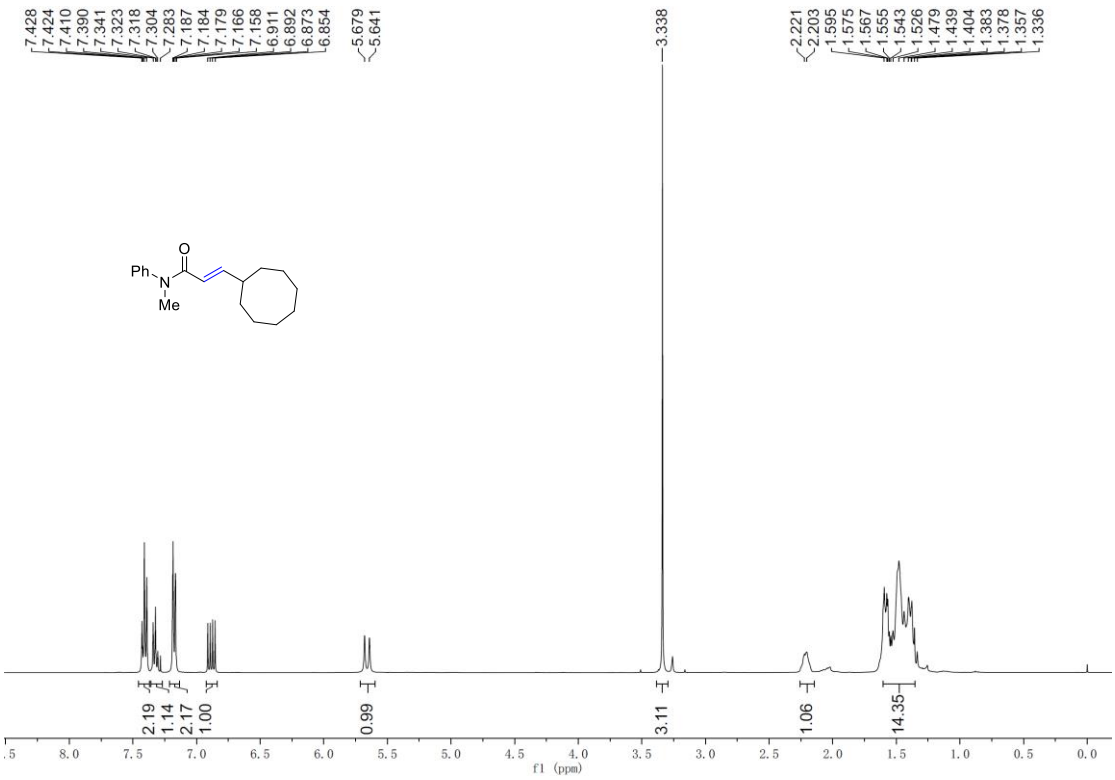


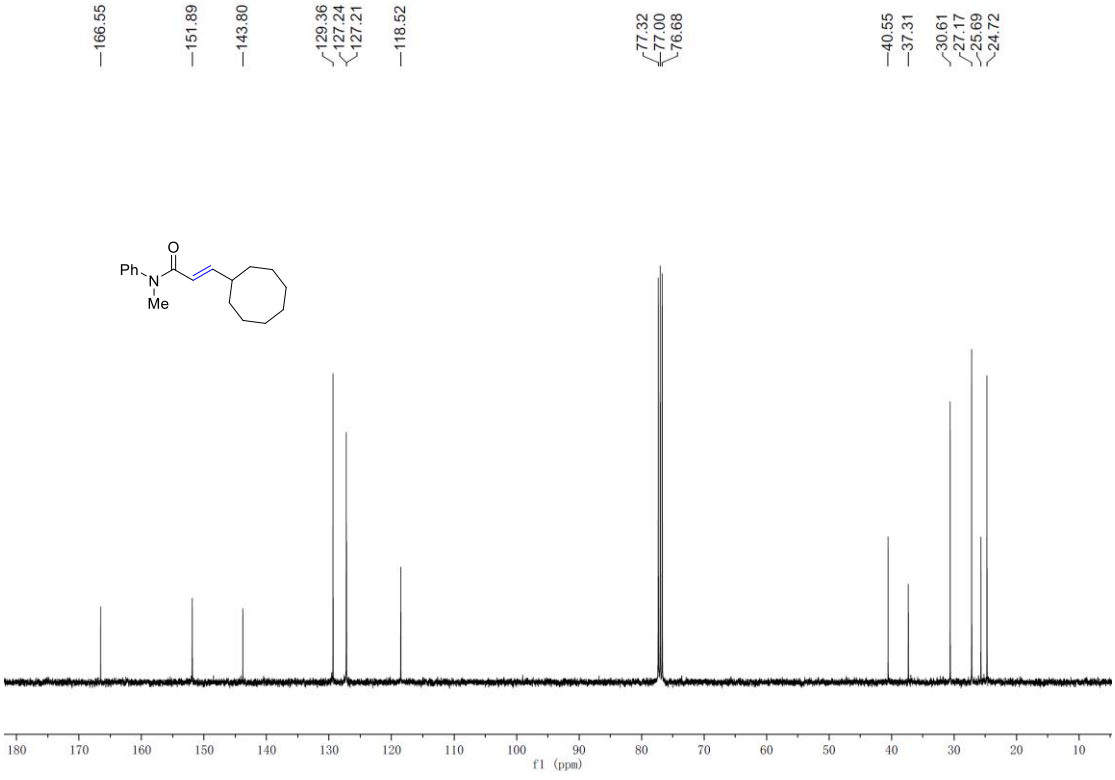
(E)-3-cyclopropyl-N-methyl-N-phenylacrylamide (15)



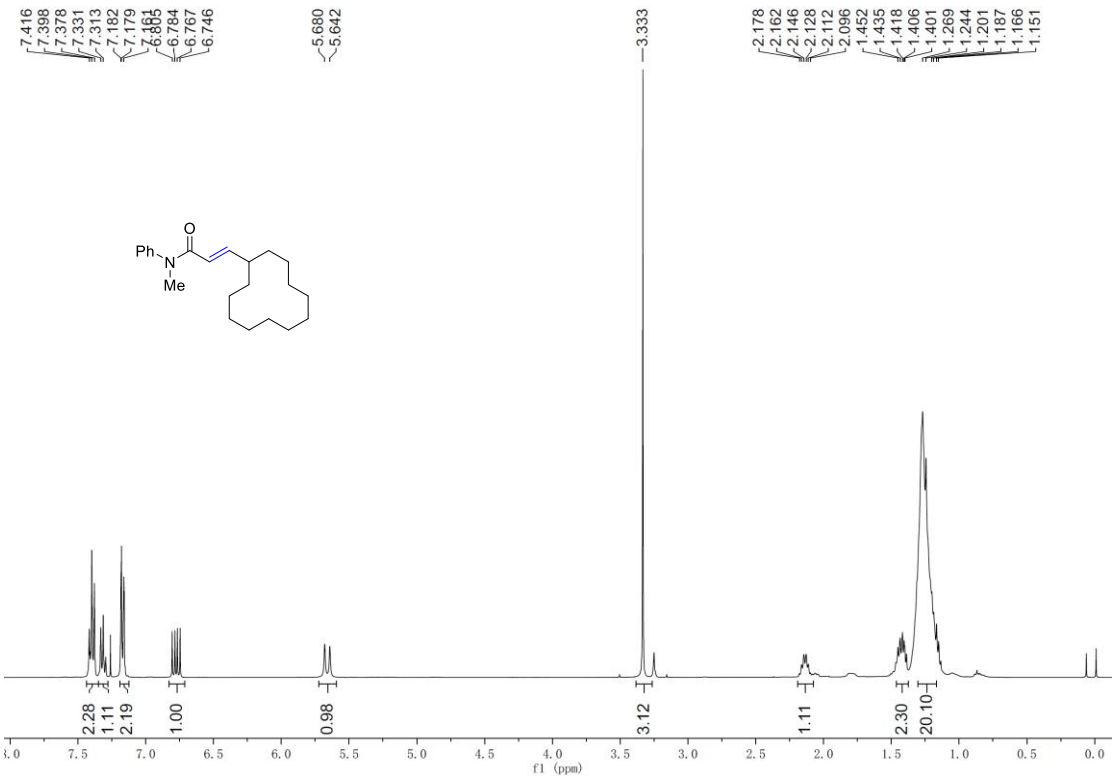


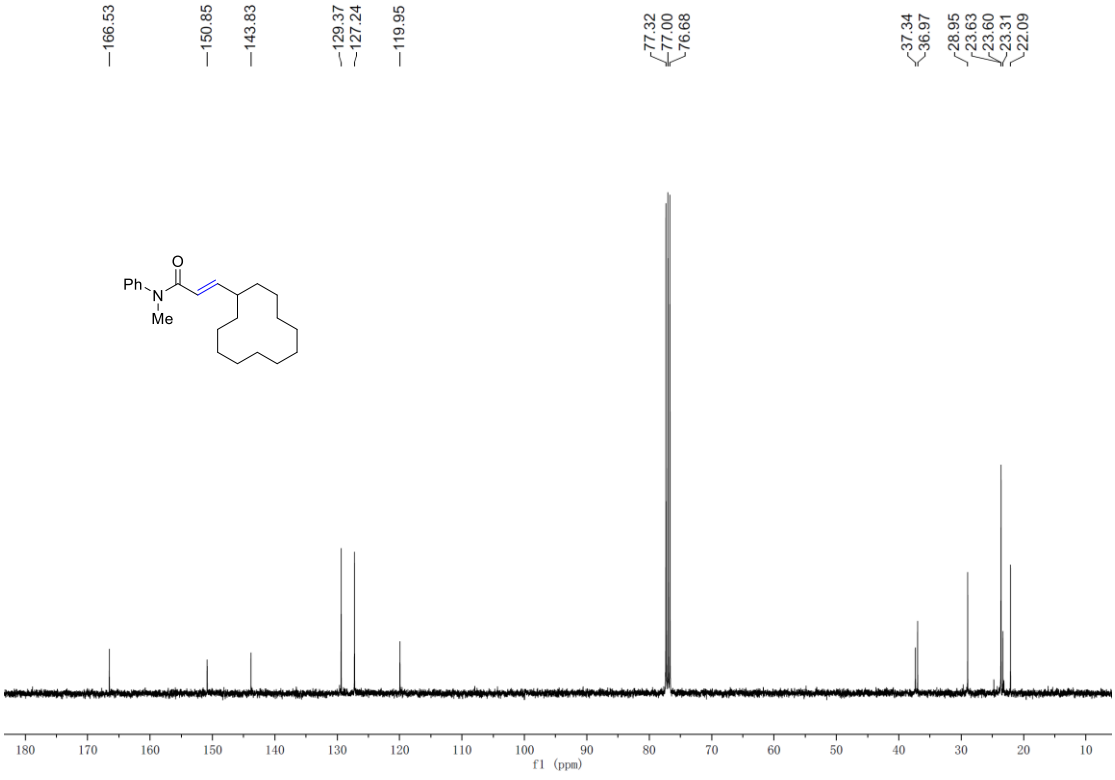
(E)-3-cyclooctyl-N-methyl-N-phenylacrylamide (16)



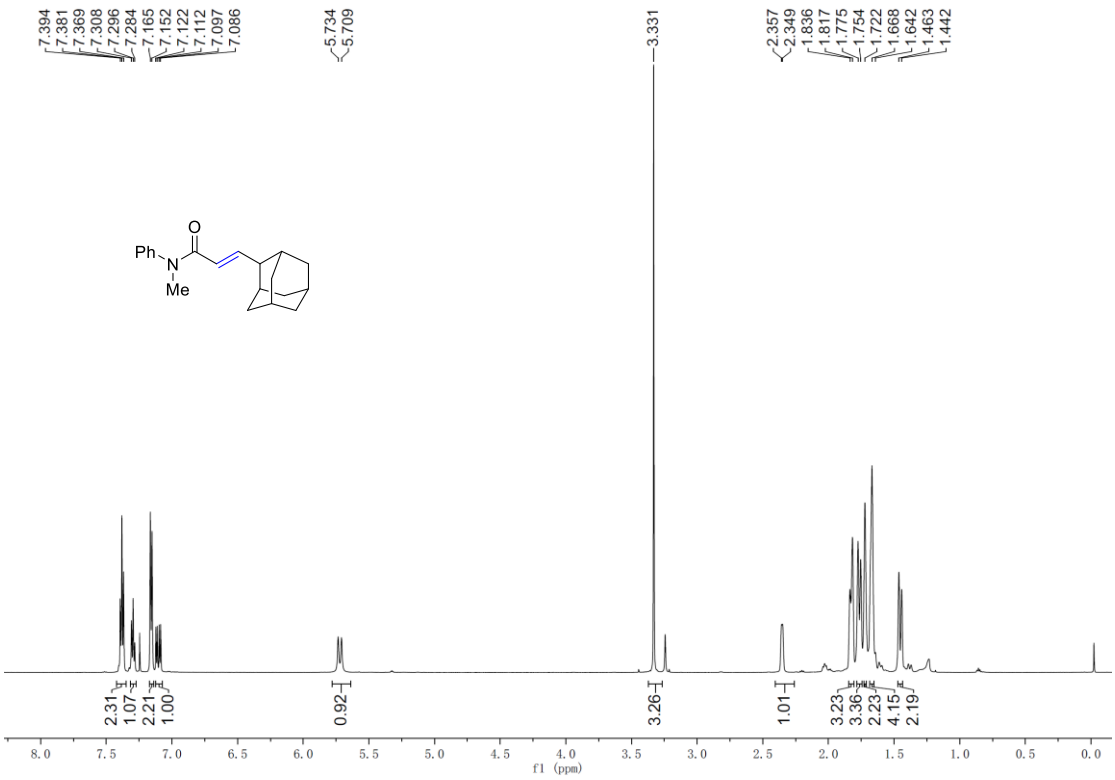


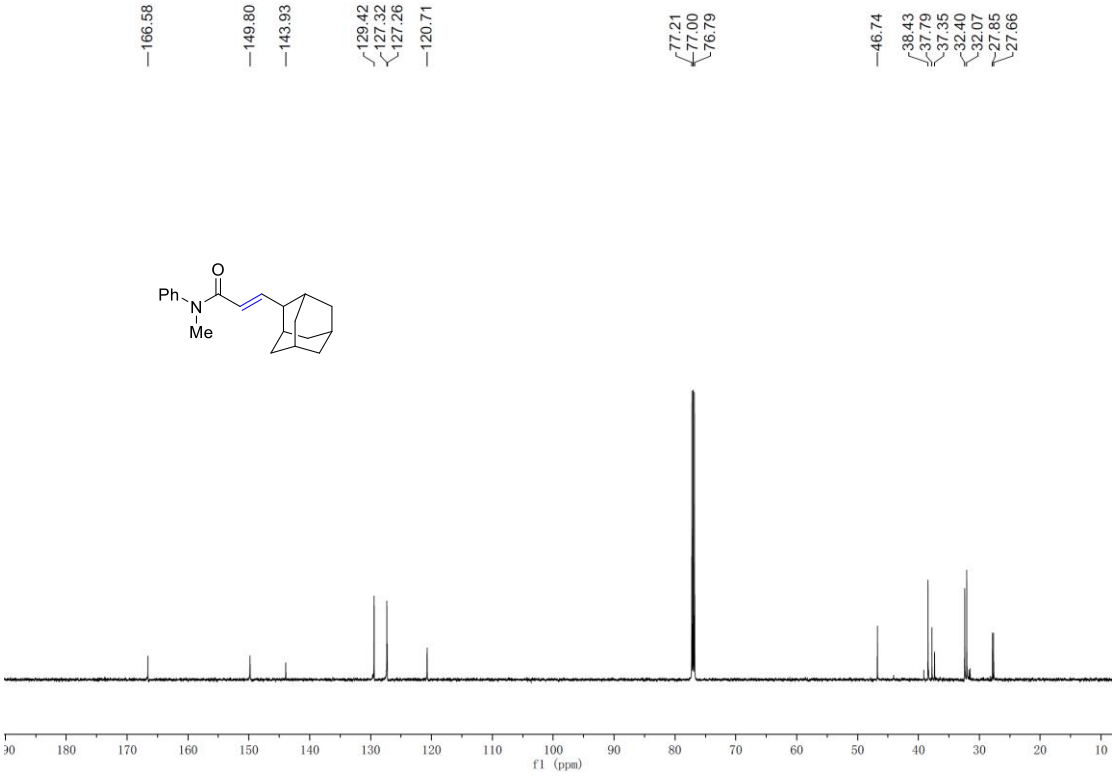
(E)-3-cyclododecyl-N-methyl-N-phenylacrylamide (17)



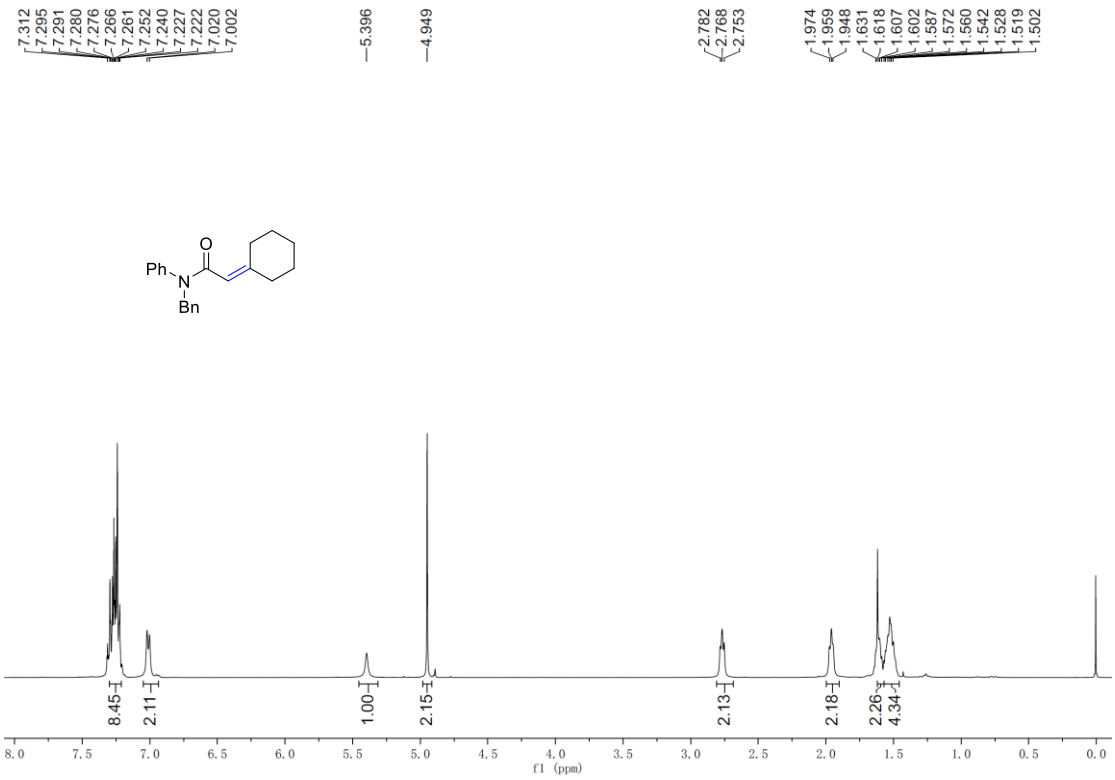


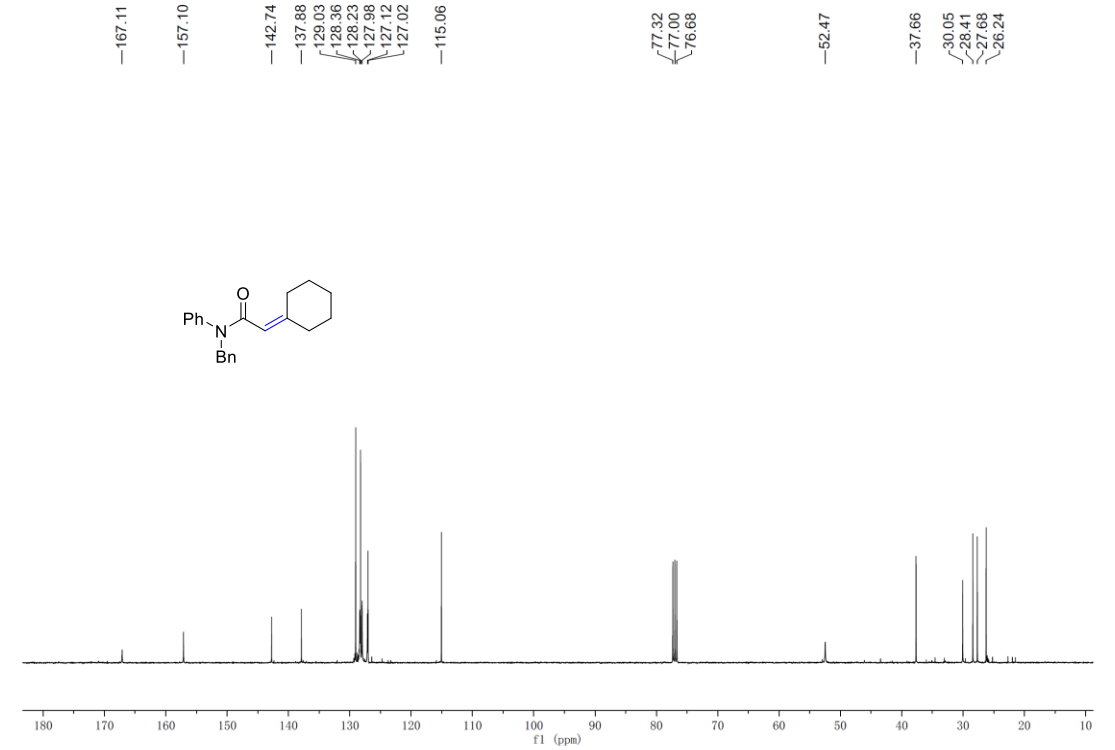
(E)-3-adamantan-2-yl)-N-methyl-N-phenylacrylamide (18)



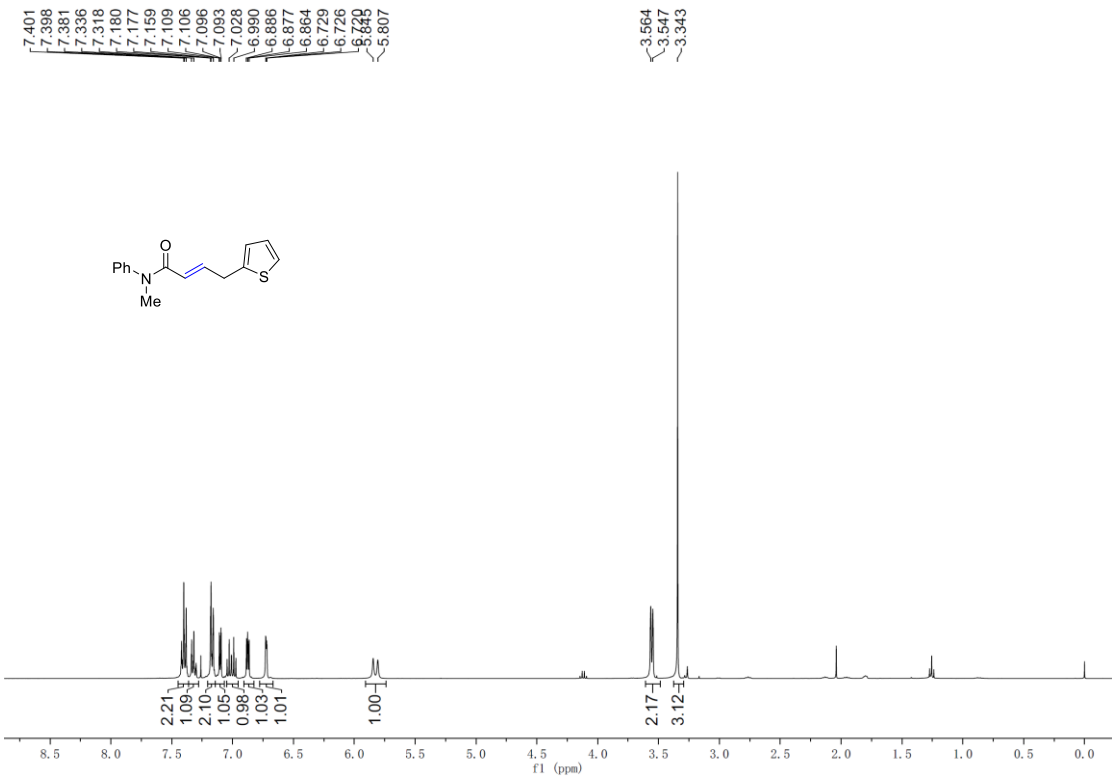


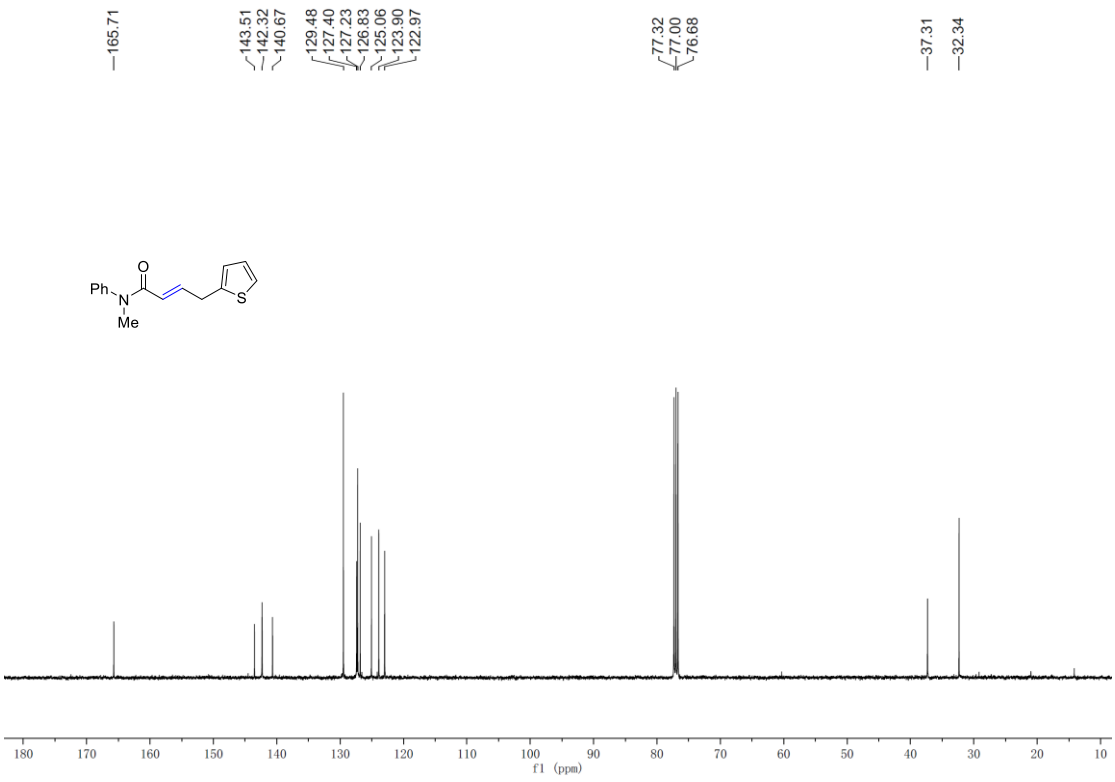
N-benzyl-2-cyclohexylidene-N-phenylacetamide (19)



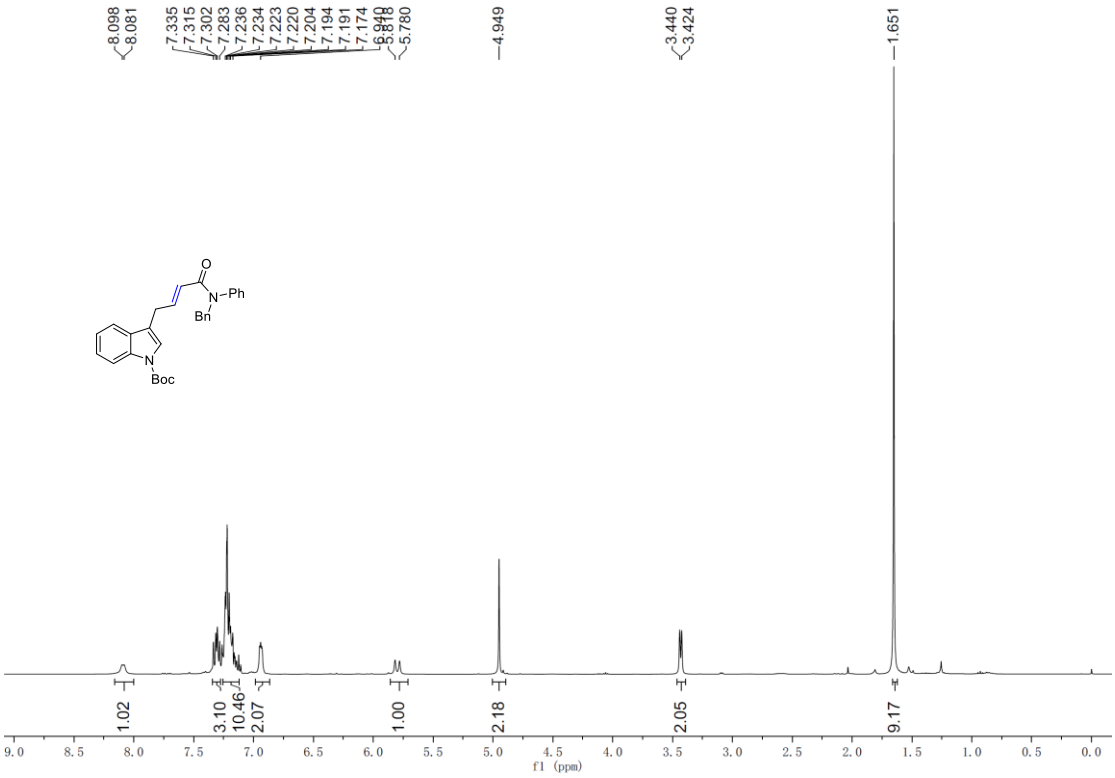


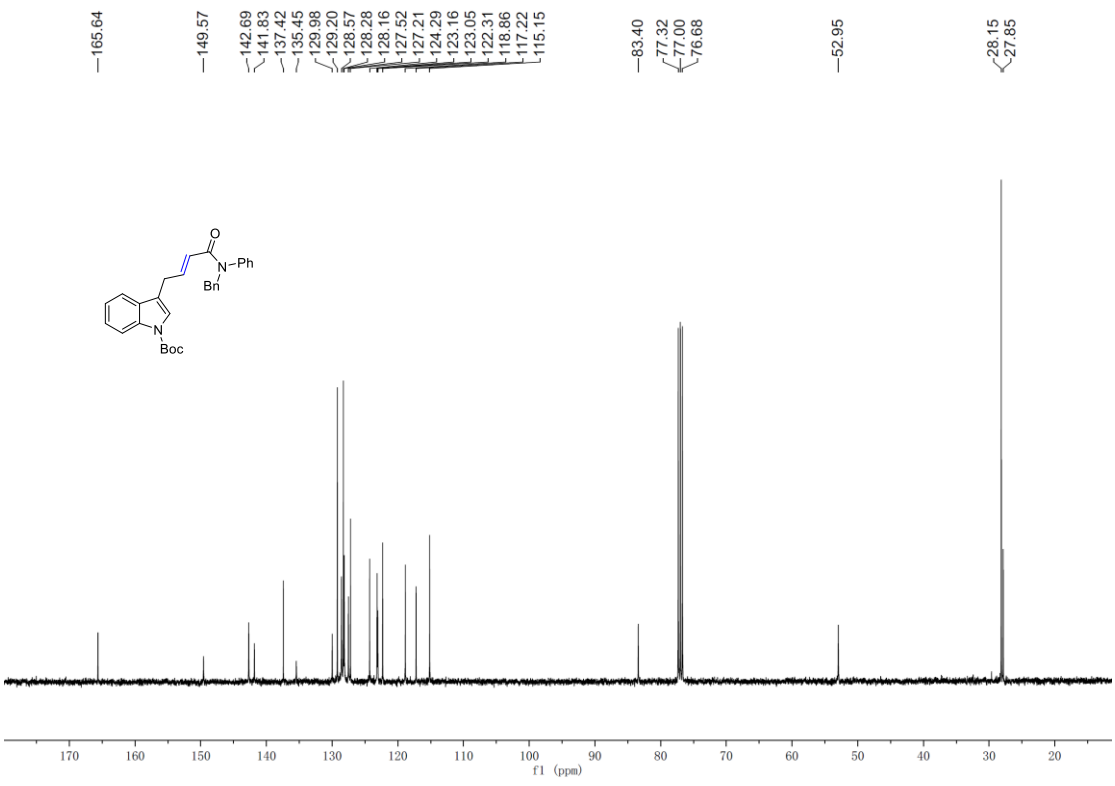
(E)-N-methyl-N-phenyl-4-(thiophen-2-yl)but-2-enamide (20)



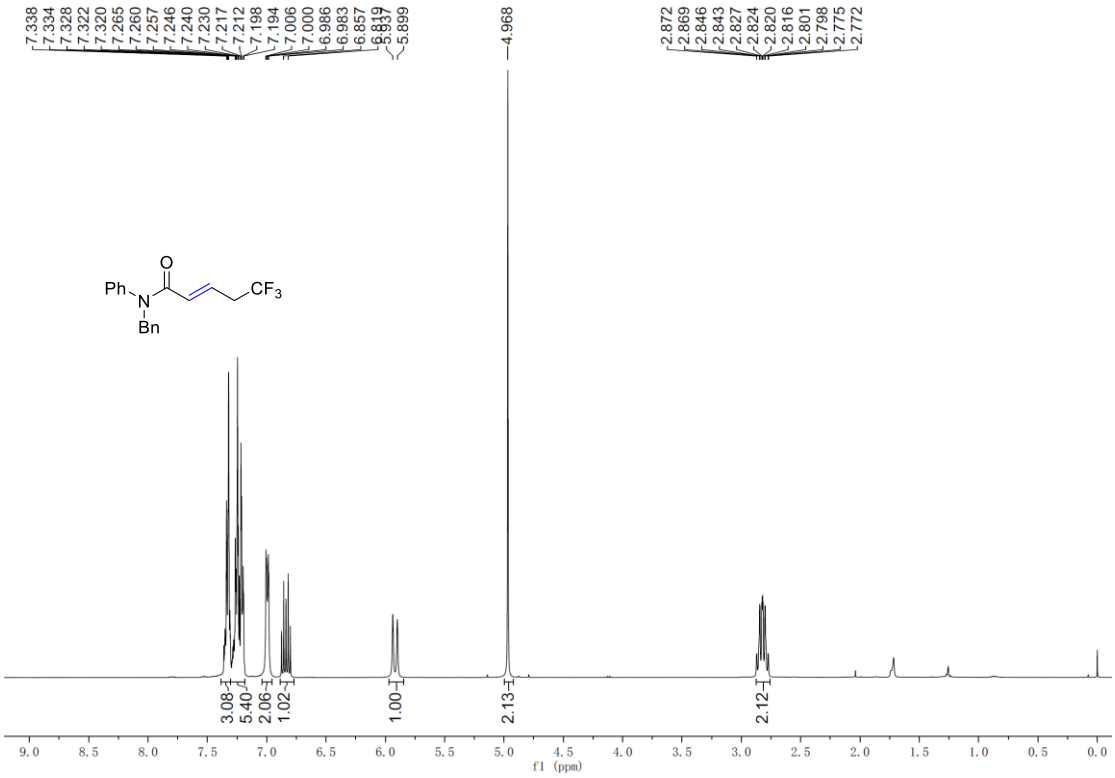


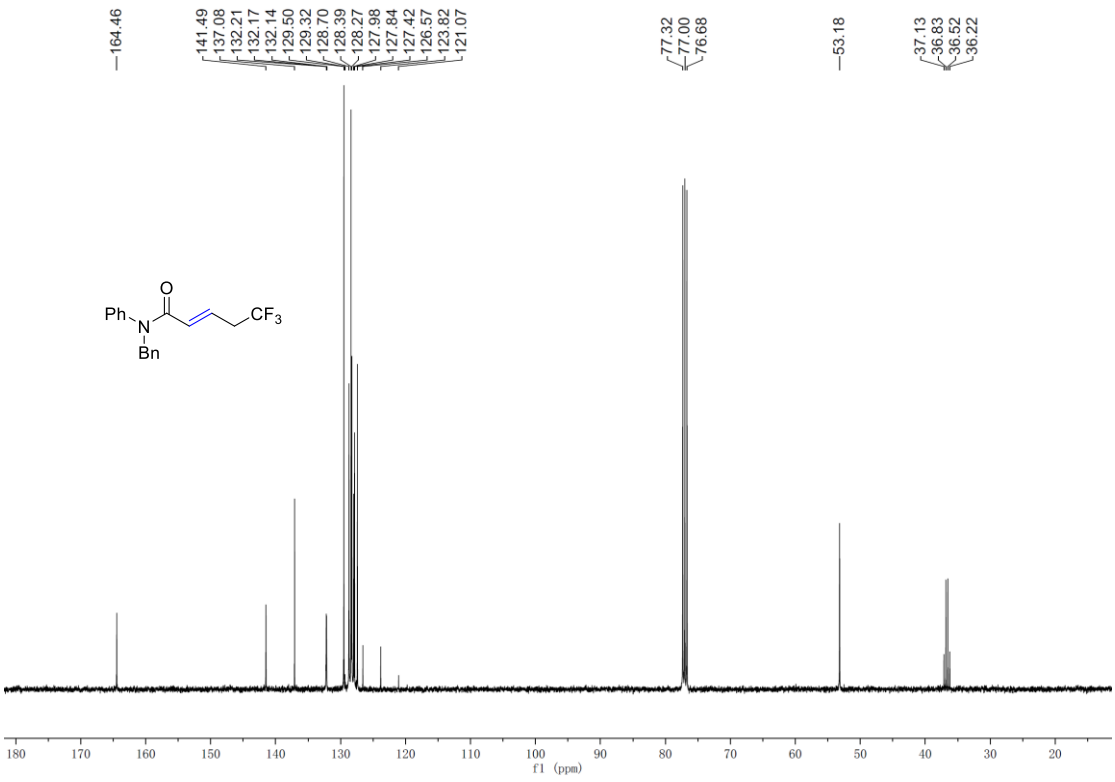
tert-butyl (E)-3-(4-(benzyl(phenyl)amino)-4-oxobut-2-en-1-yl)-1H-indole-1-carboxylate (21)

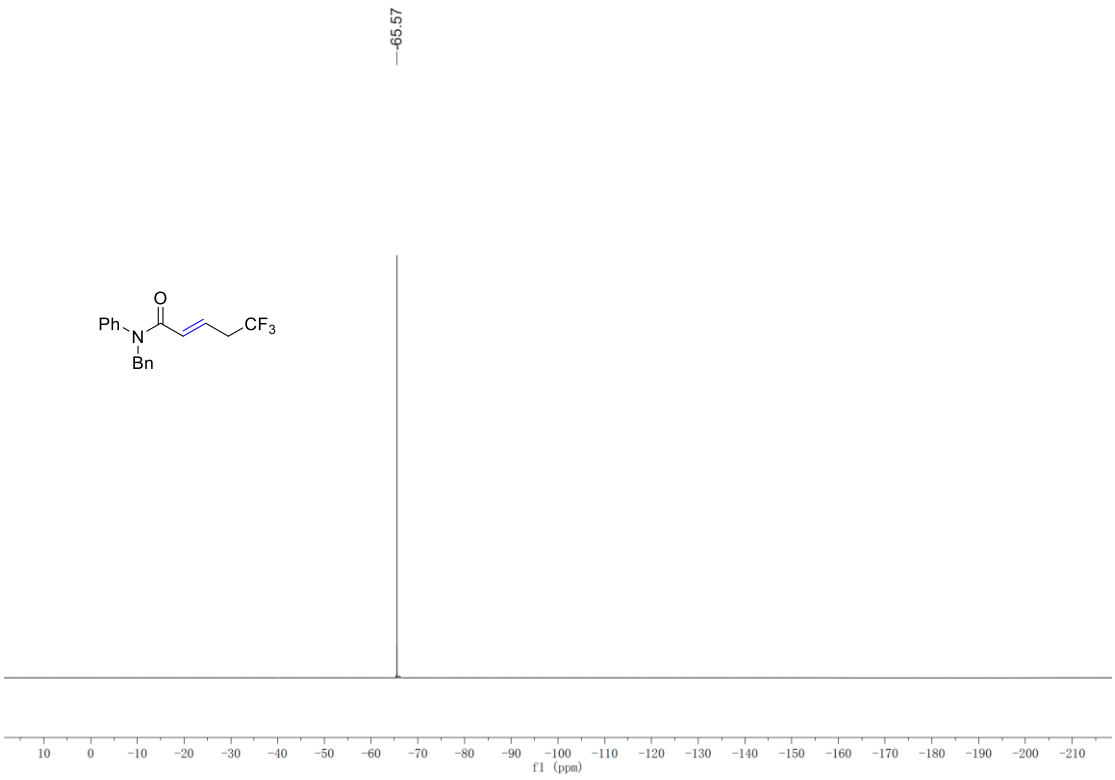




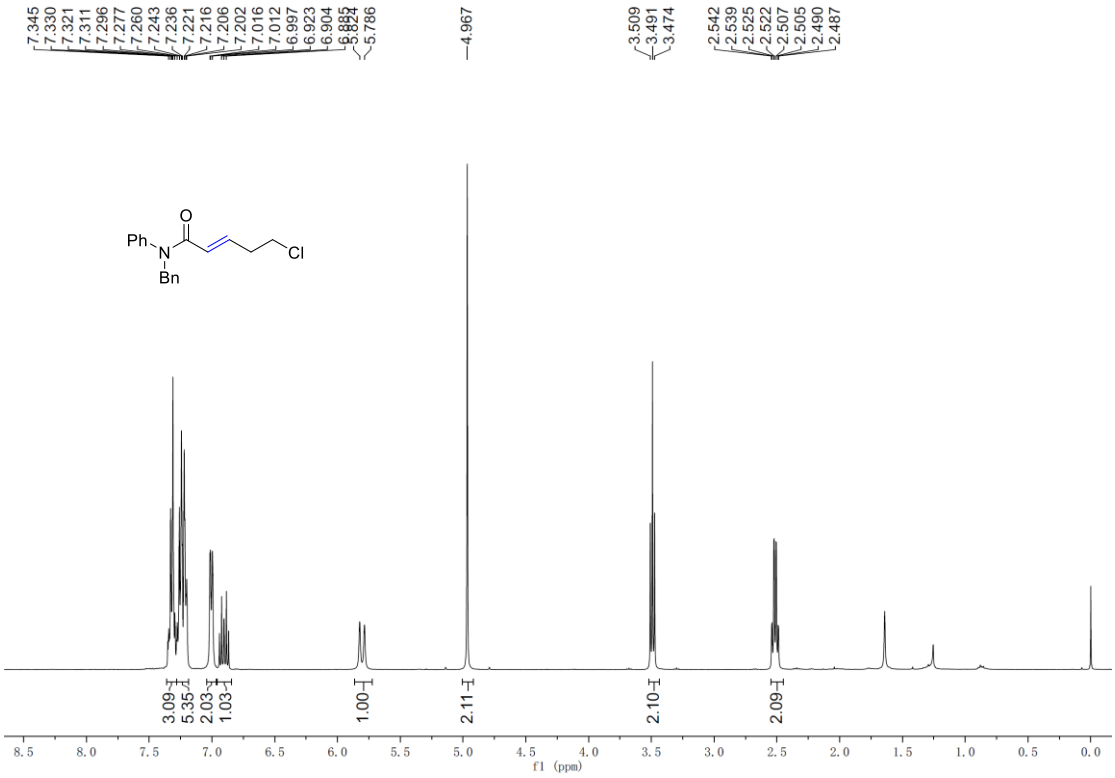
(E)-N-benzyl-5,5,5-trifluoro-N-phenylpent-2-enamide (22)

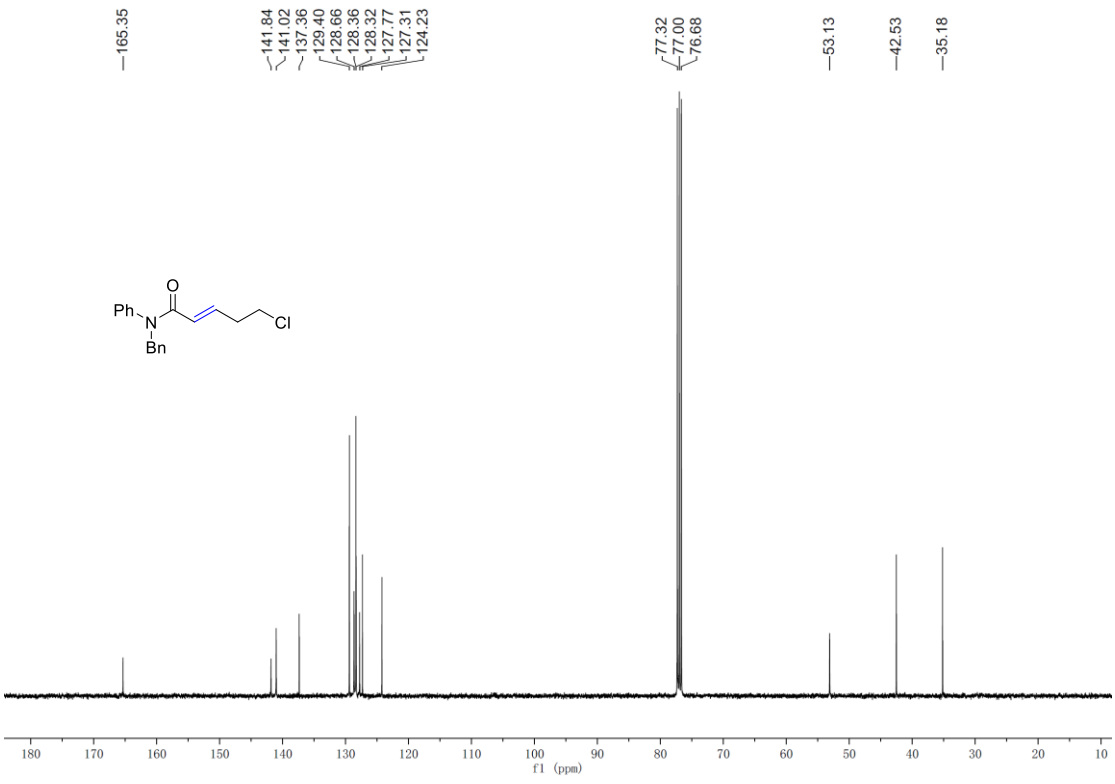




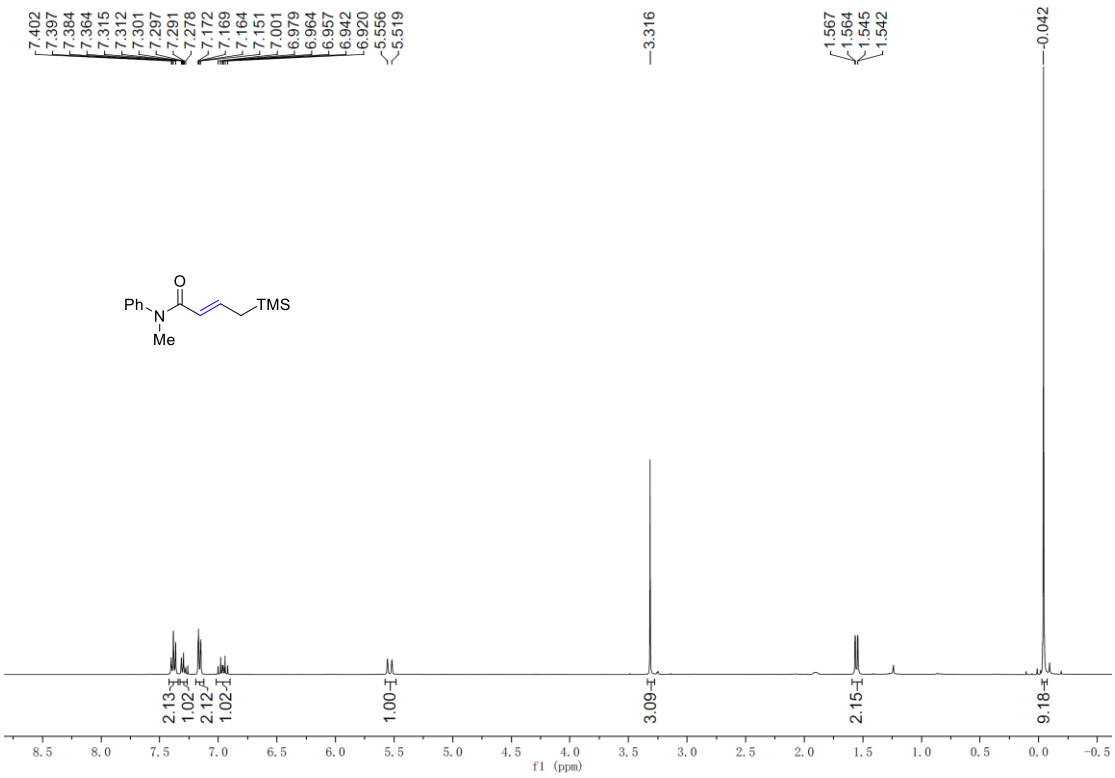

-65.57
Ph
N
Bn
O
CF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

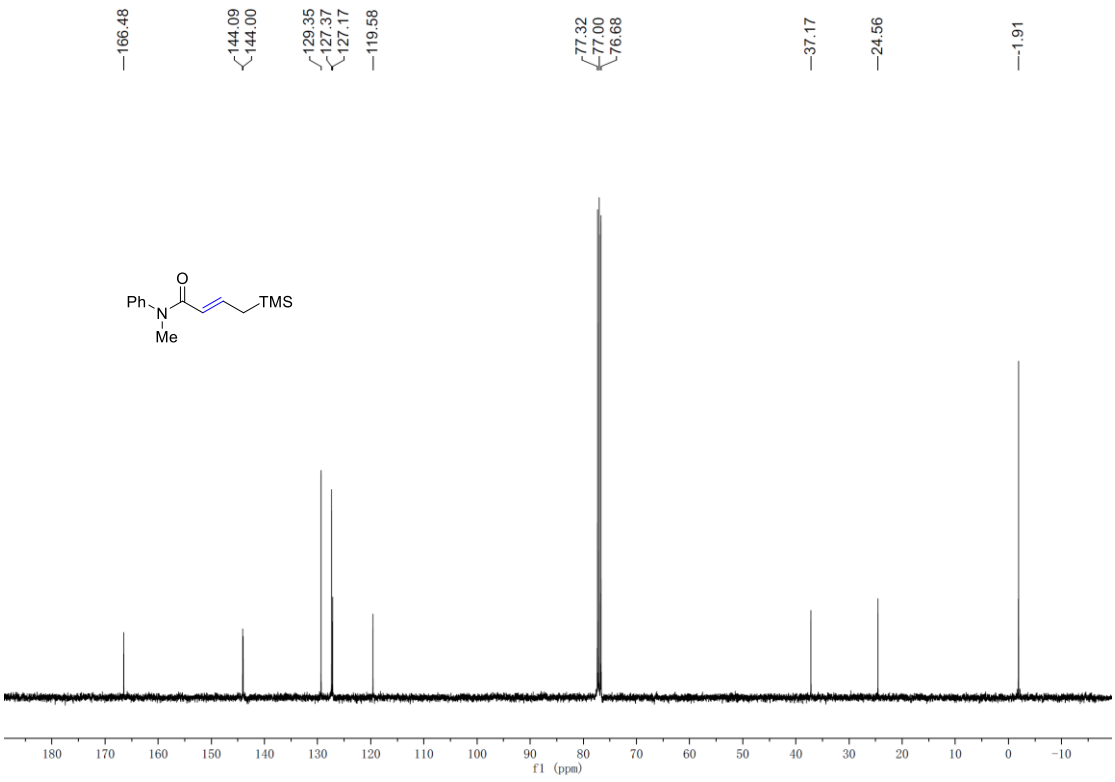
(E)-N-benzyl-5-chloro-N-phenylpent-2-enamide (23)



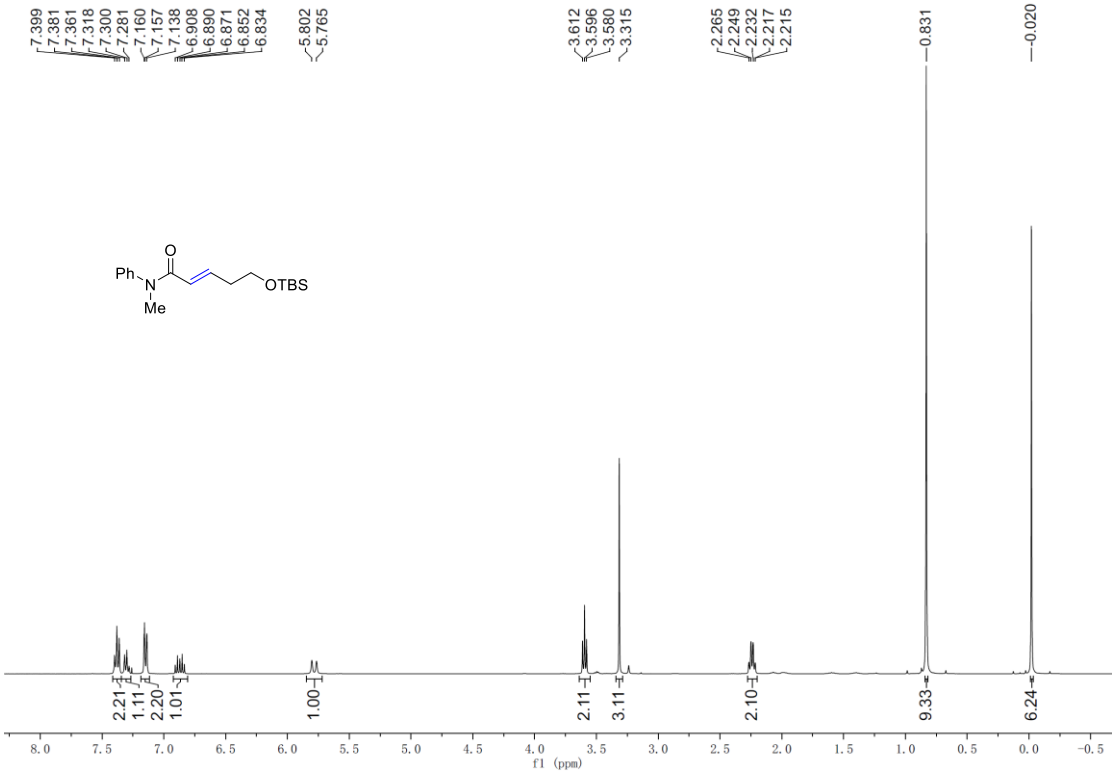


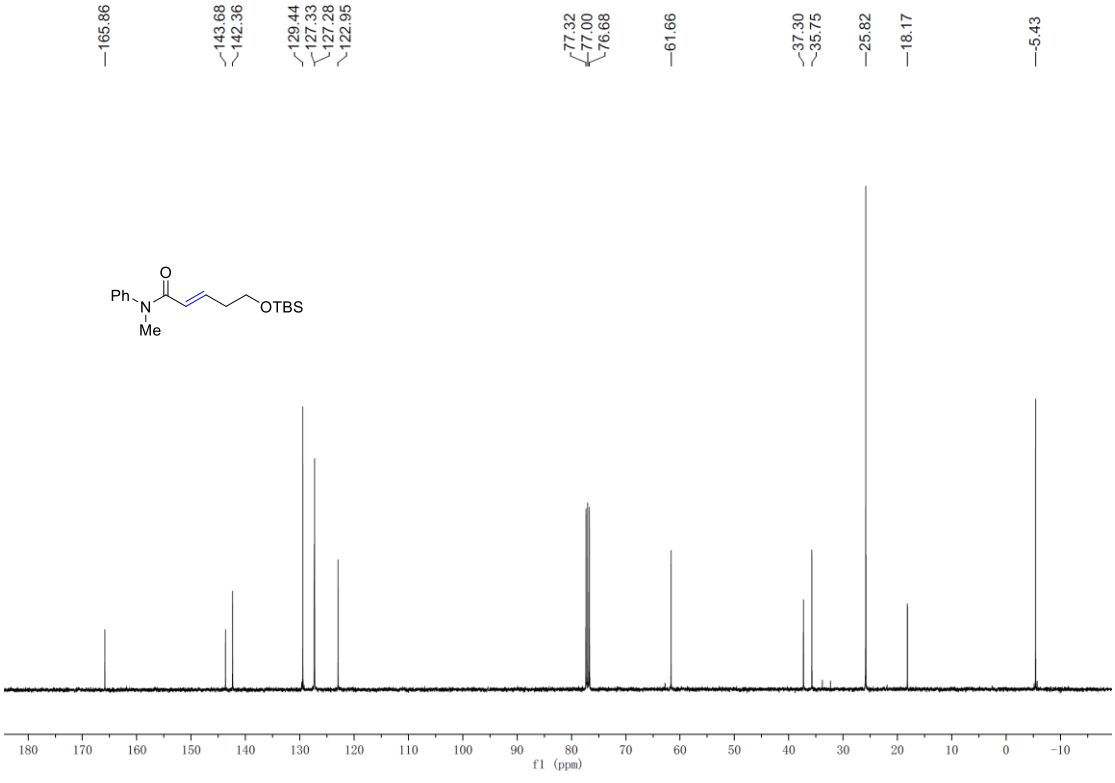
(E)-N-methyl-N-phenyl-4-(trimethylsilyl)but-2-enamide (24)



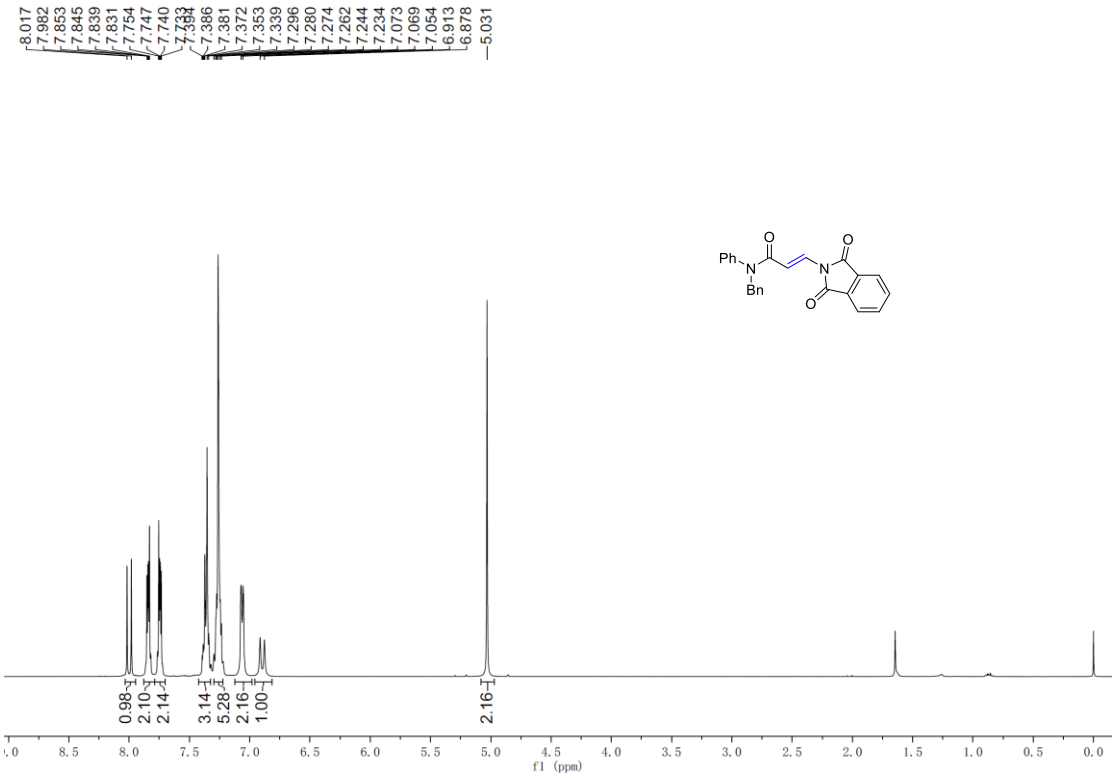


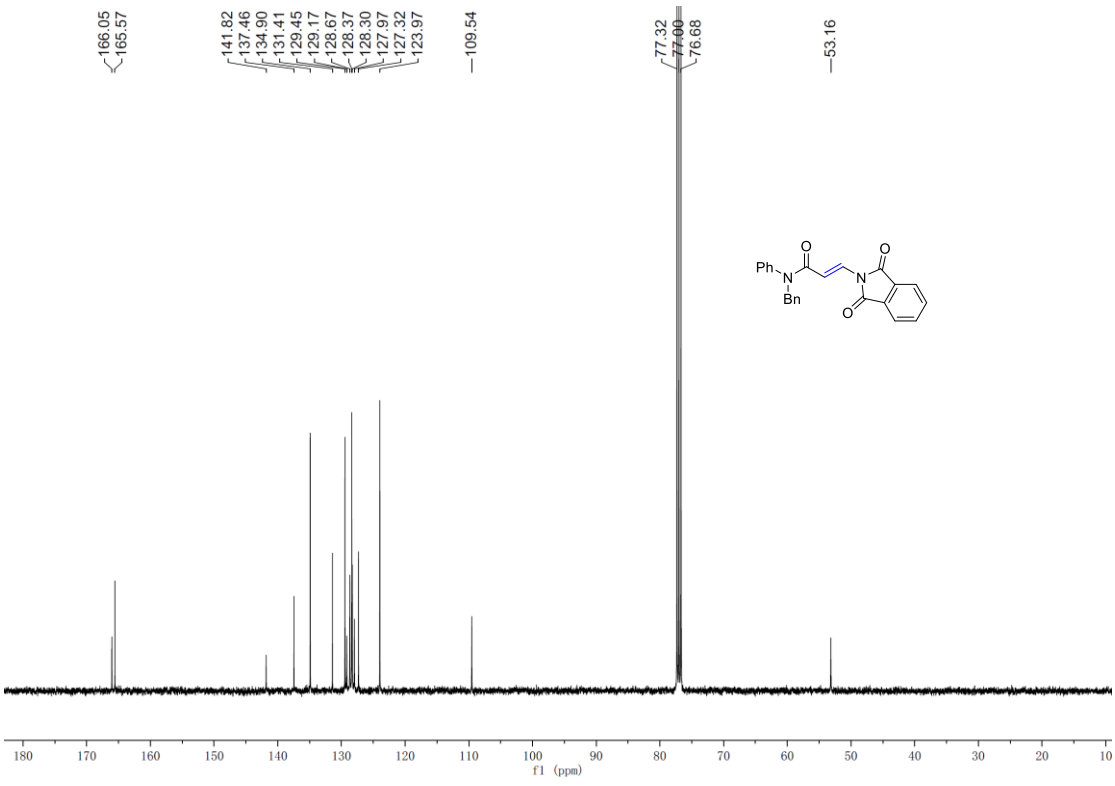
(E)-5-((tert-butyldimethylsilyl)oxy)-N-methyl-N-phenylpent-2-enamide (25)



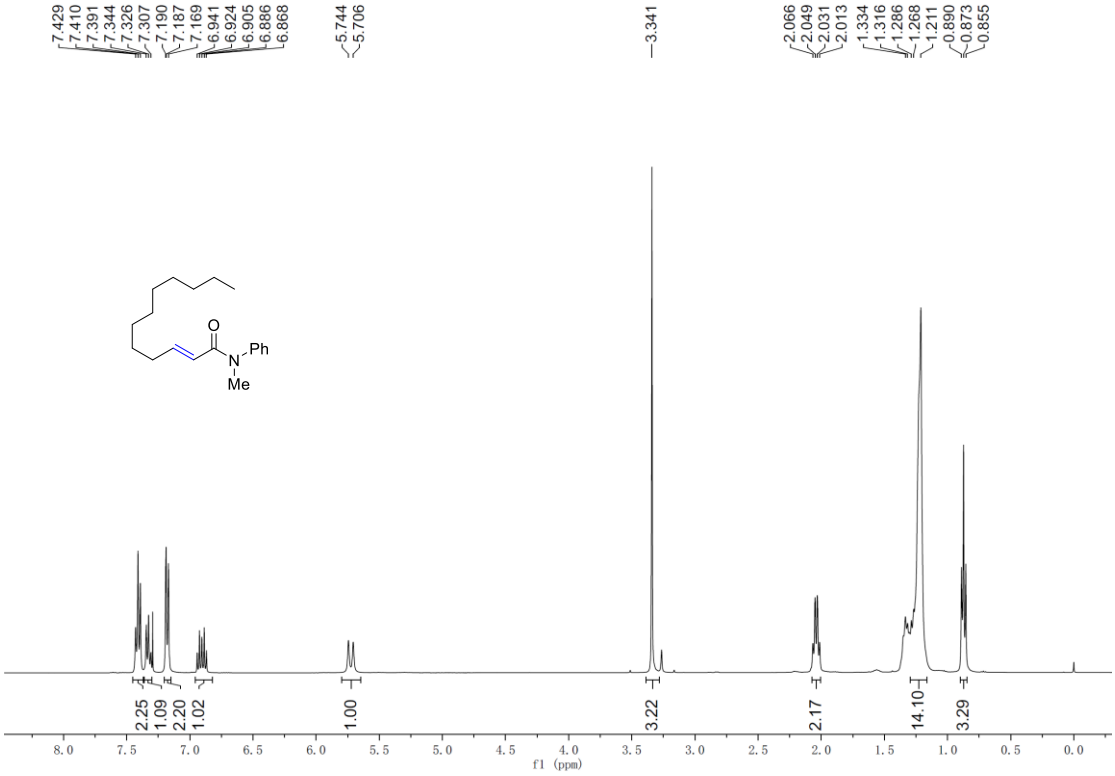


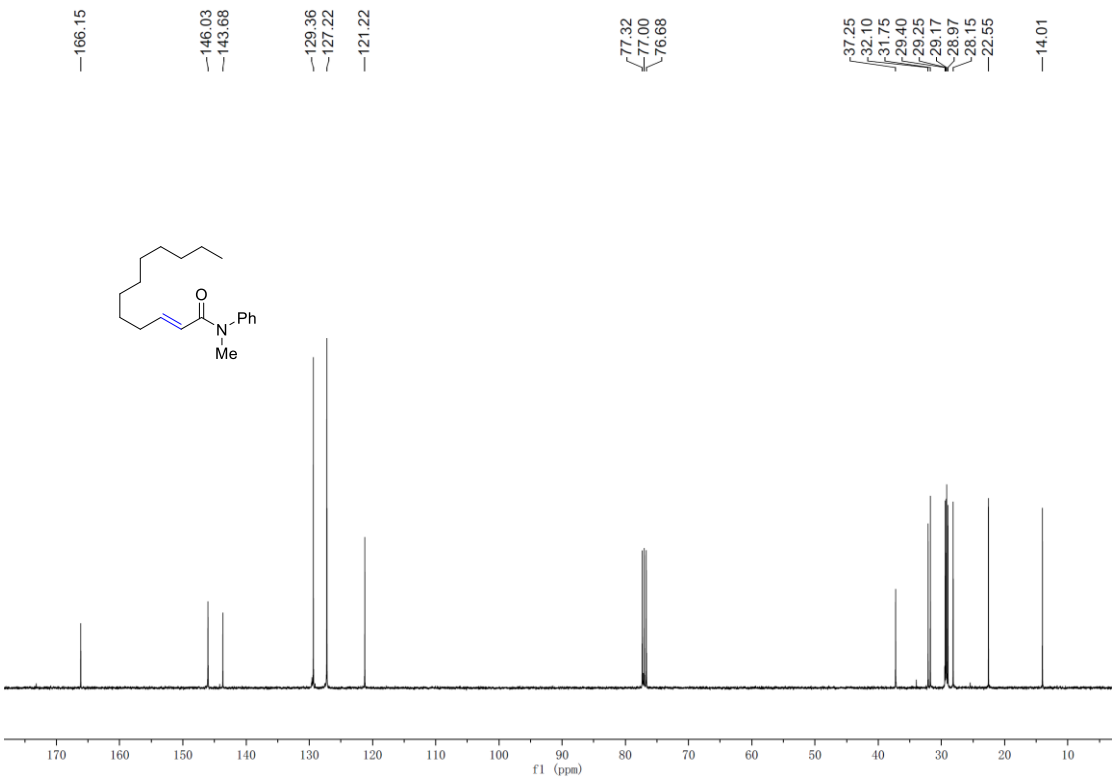
(E)-N-benzyl-3-(1,3-dioxoisoindolin-2-yl)-N-phenylacrylamide (26)



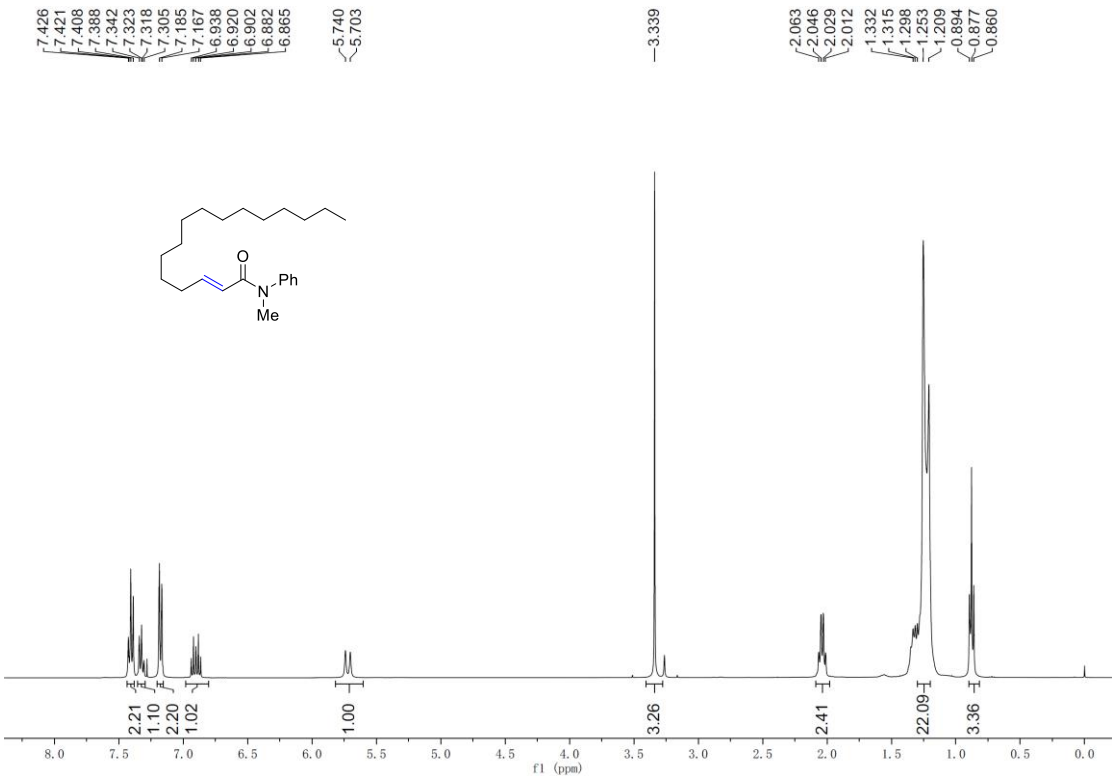


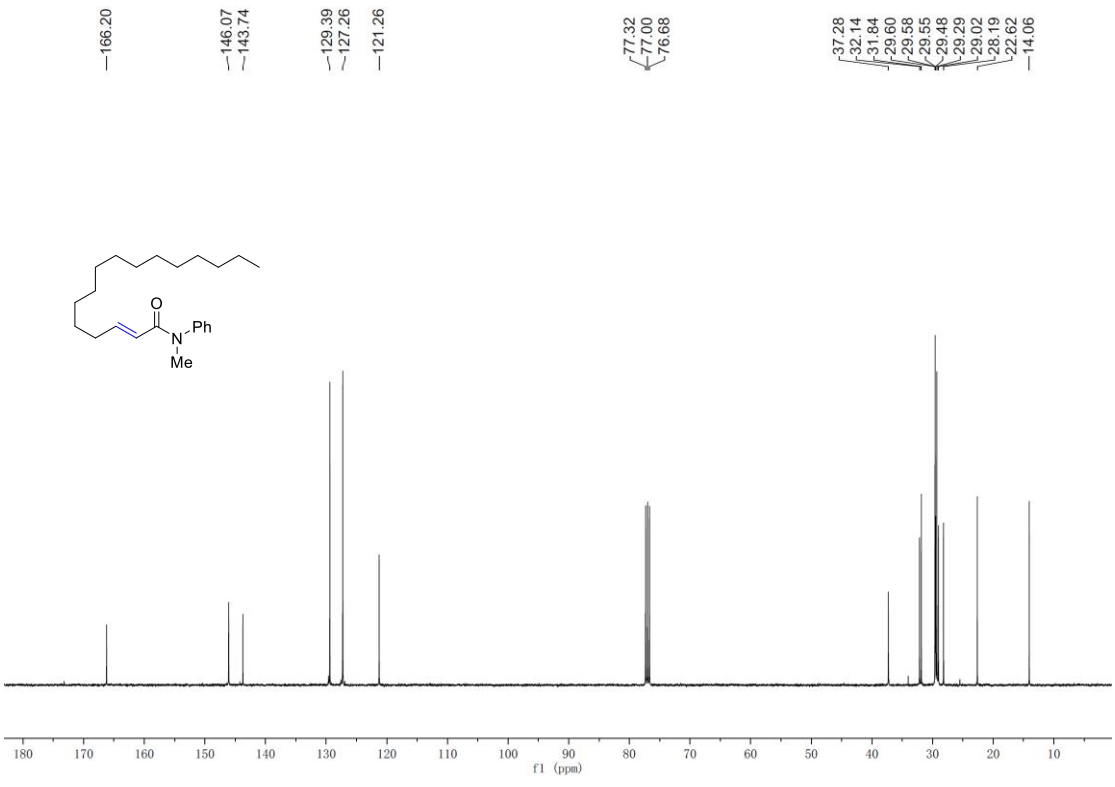
(E)-N-methyl-N-phenyldodec-2-enamide (27)



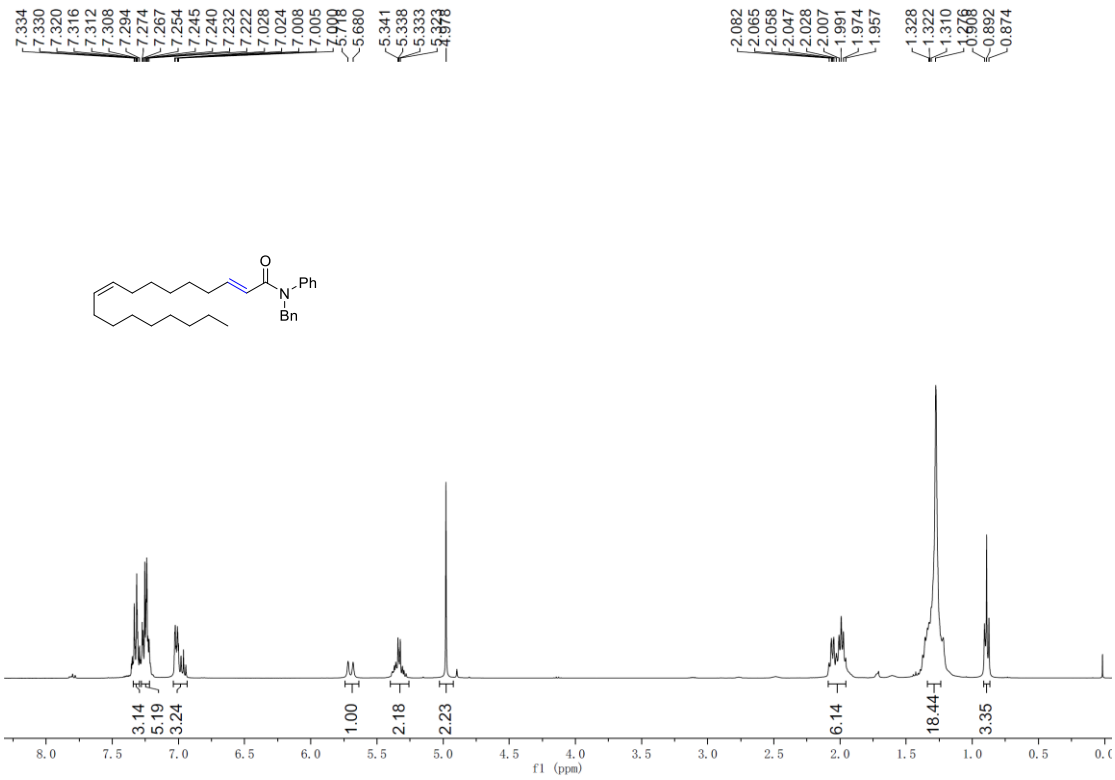


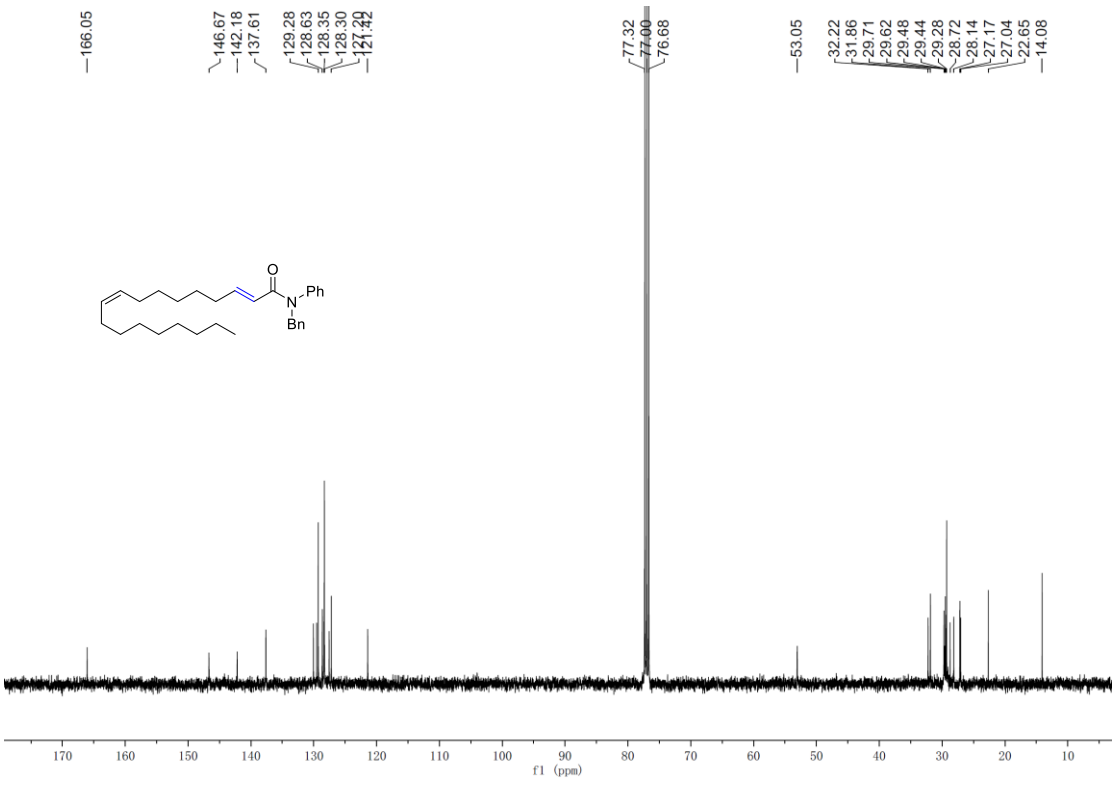
(E)-N-methyl-N-phenylhexadec-2-enamide (28)



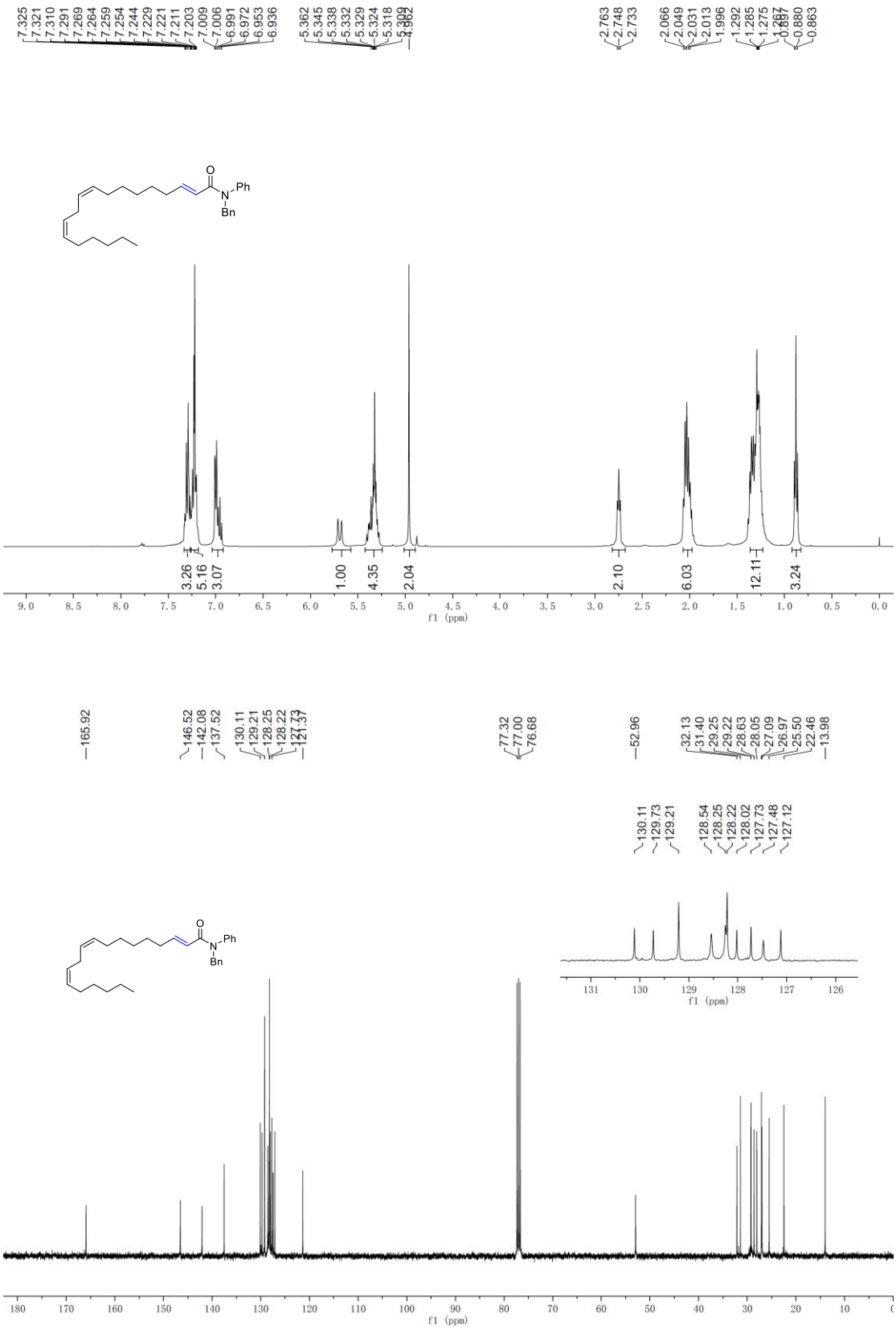


(2E,9Z)-N-benzyl-N-phenyloctadeca-2,9-dienamide (29)

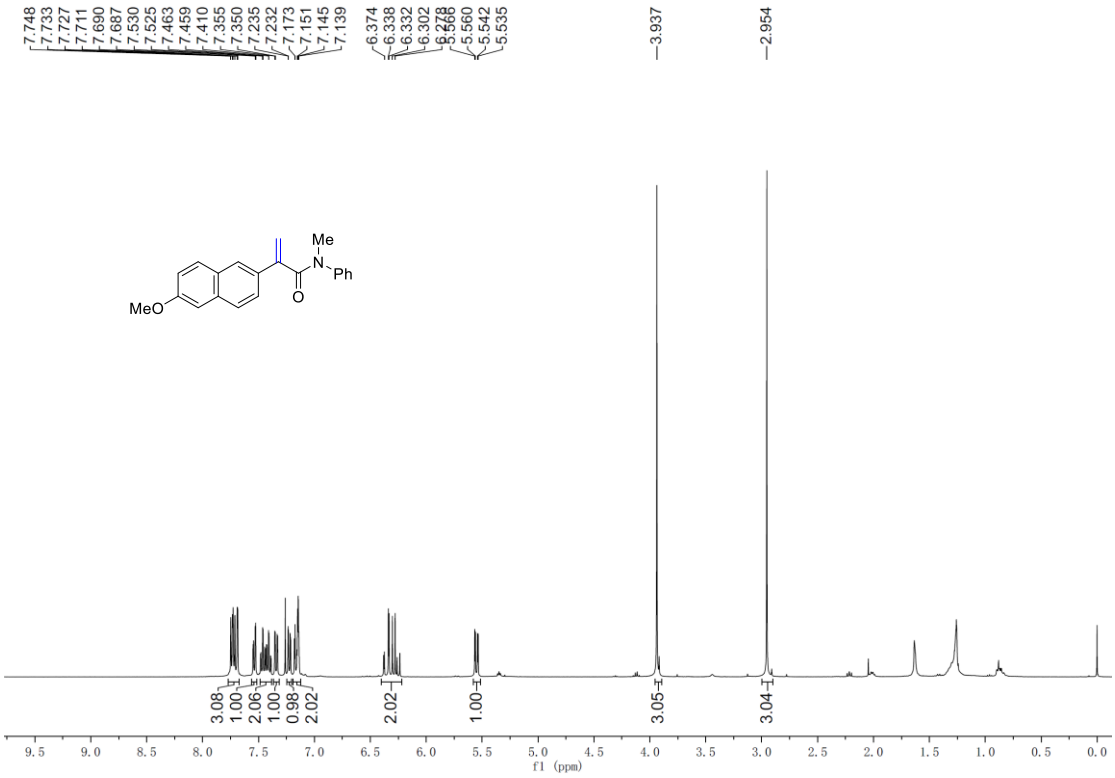


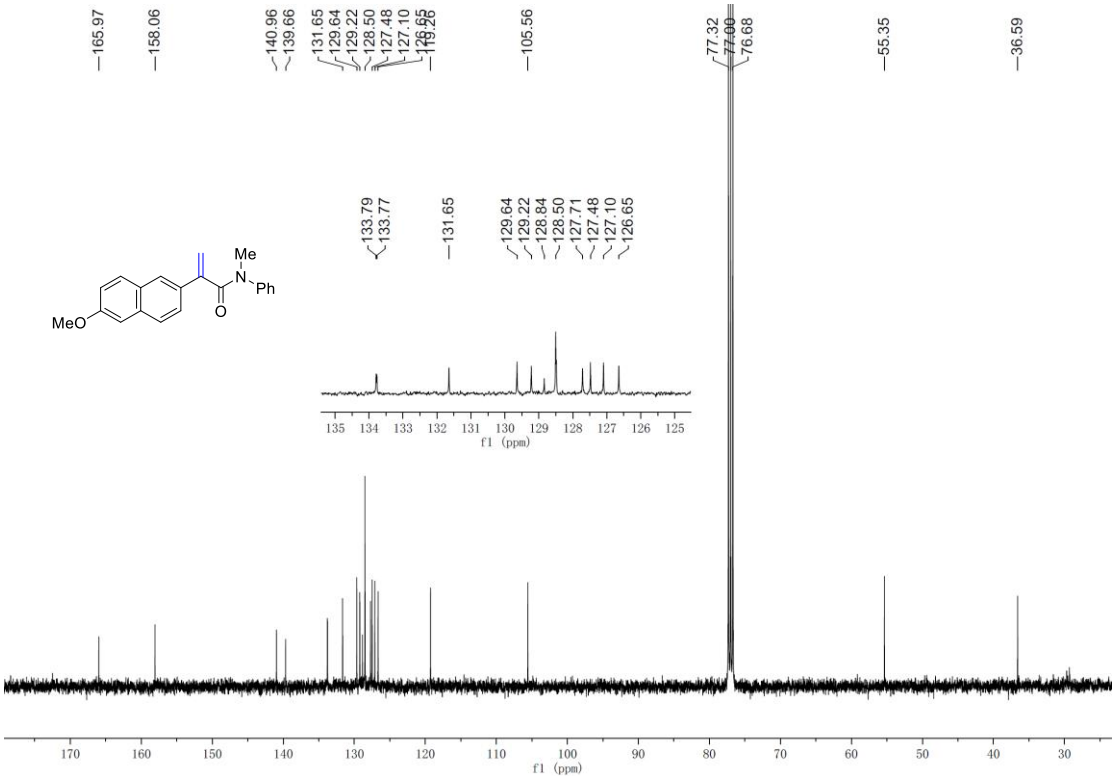


(2E,9Z,12Z)-N-benzyl-N-phenyloctadeca-2,9,12-trienamide (30)

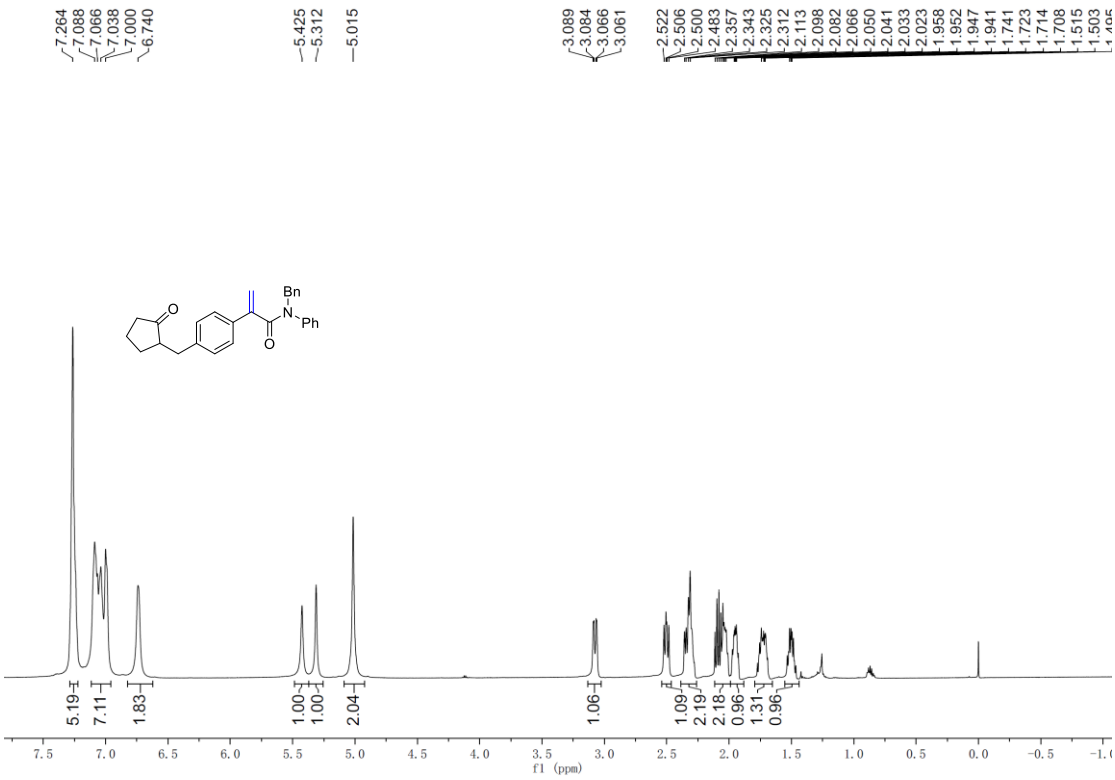


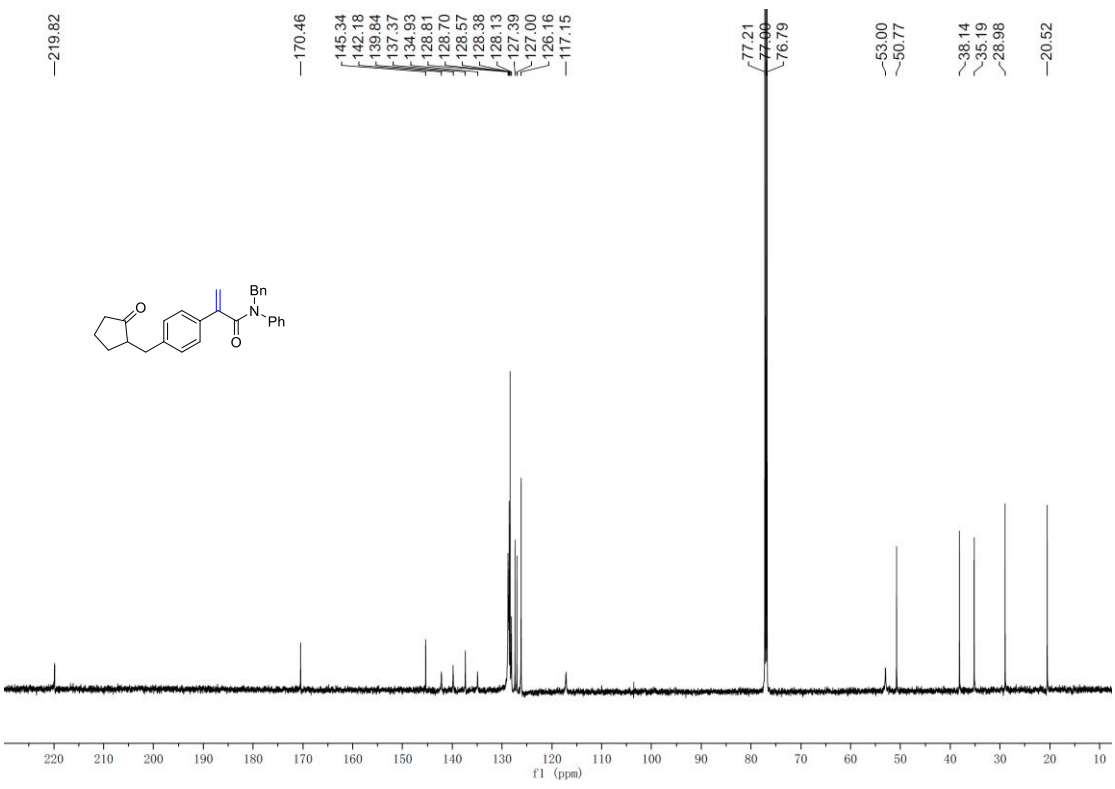
2-(6-methoxynaphthalen-2-yl)-N-methyl-N-phenylacrylamide (31)



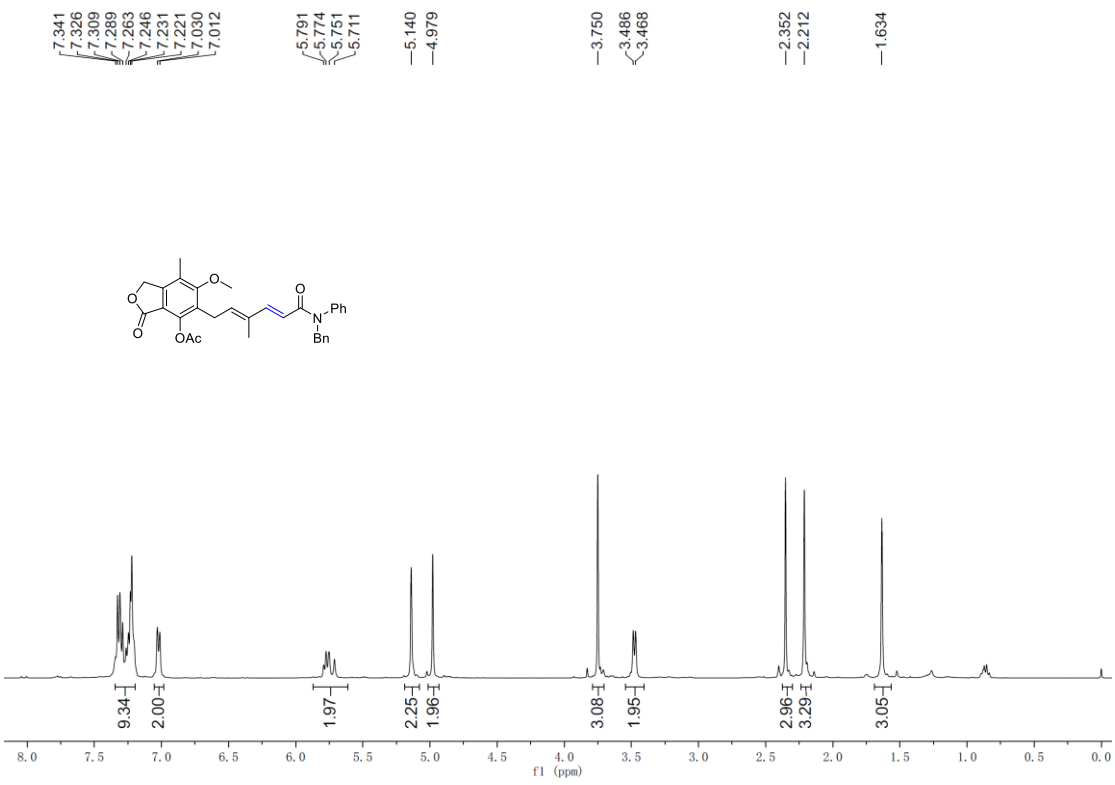


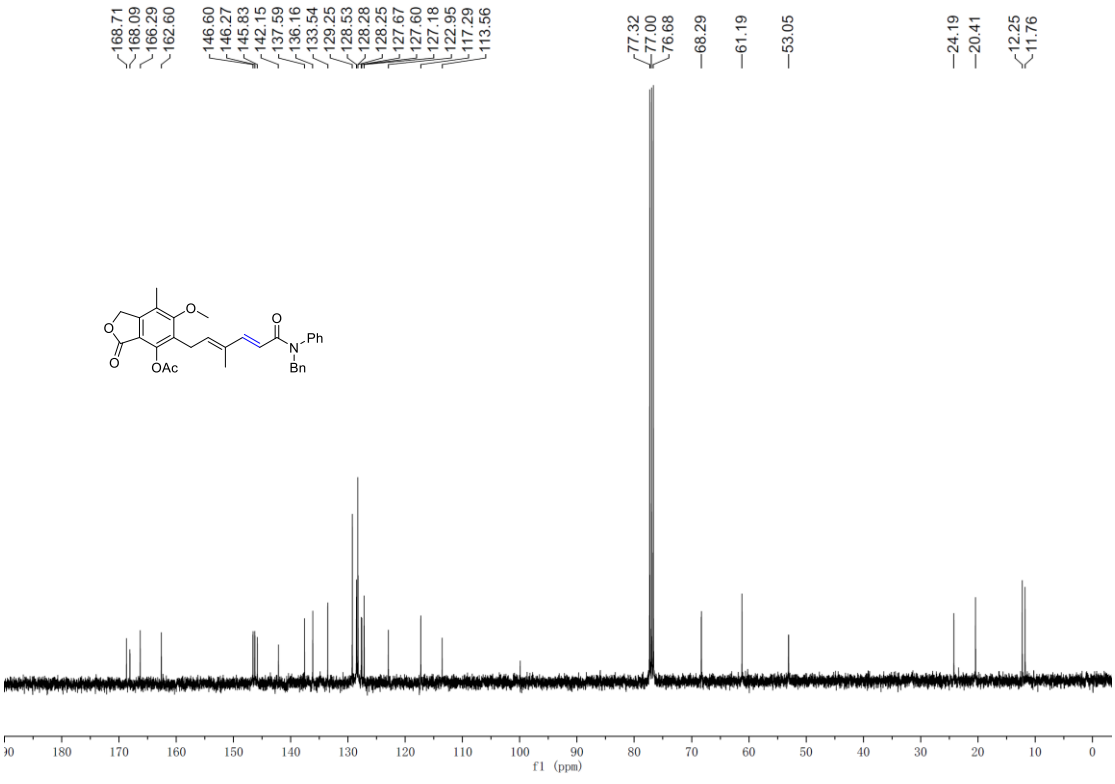
N-benzyl-2-(4-((2-oxocyclopentyl)methyl)phenyl)-N-phenylacrylamide (32)



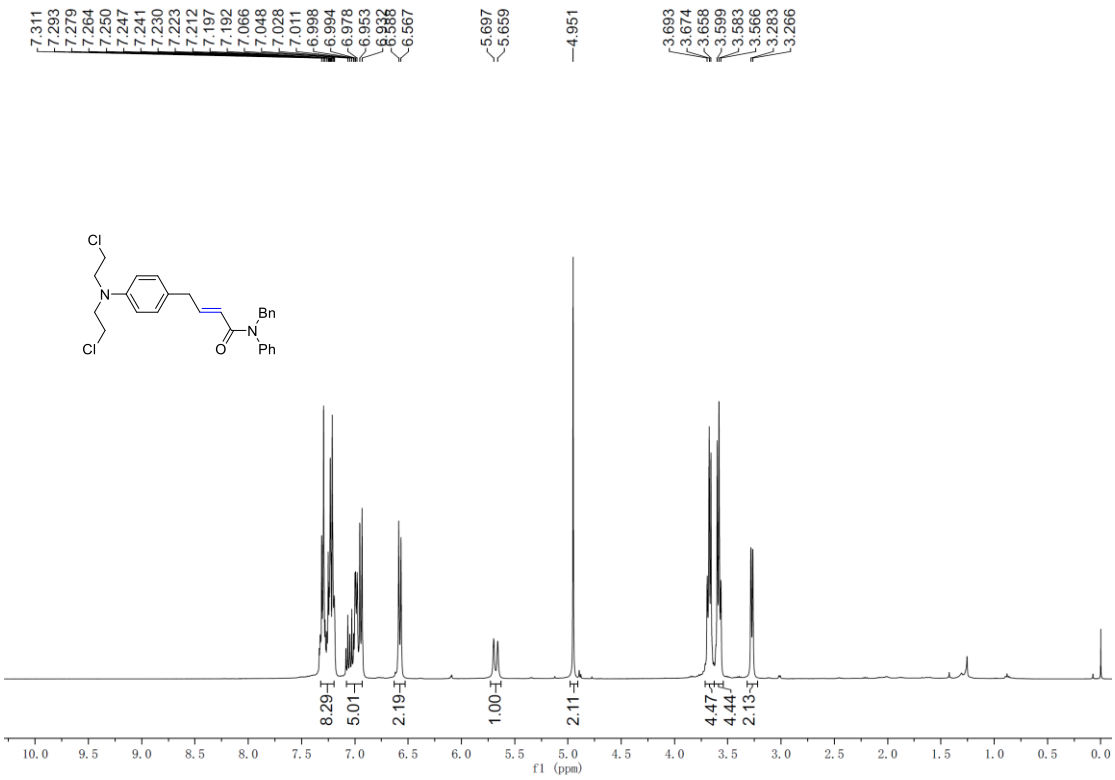


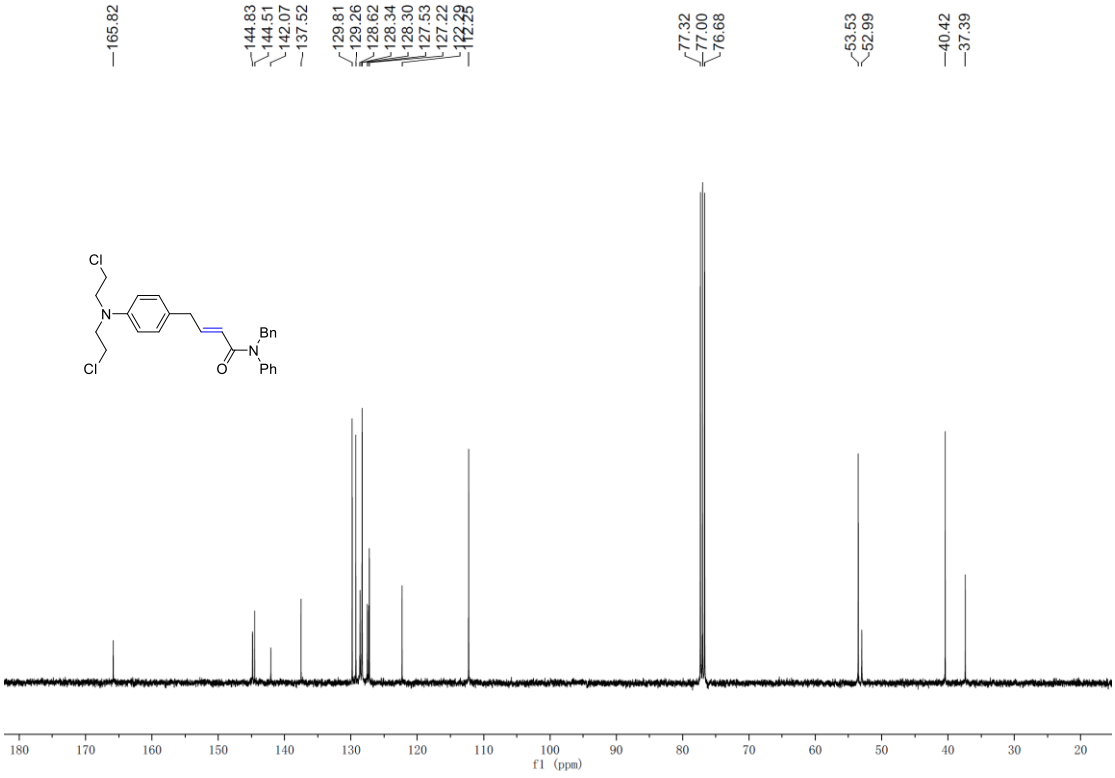
5-((2E,4E)-6-(benzyl(phenyl)amino)-3-methyl-6-oxohexa-2,4-dien-1-yl)-6-methoxy-7-methyl-3-oxo-1,3-dihydroisobenzofuran-4-yl acetate (33)



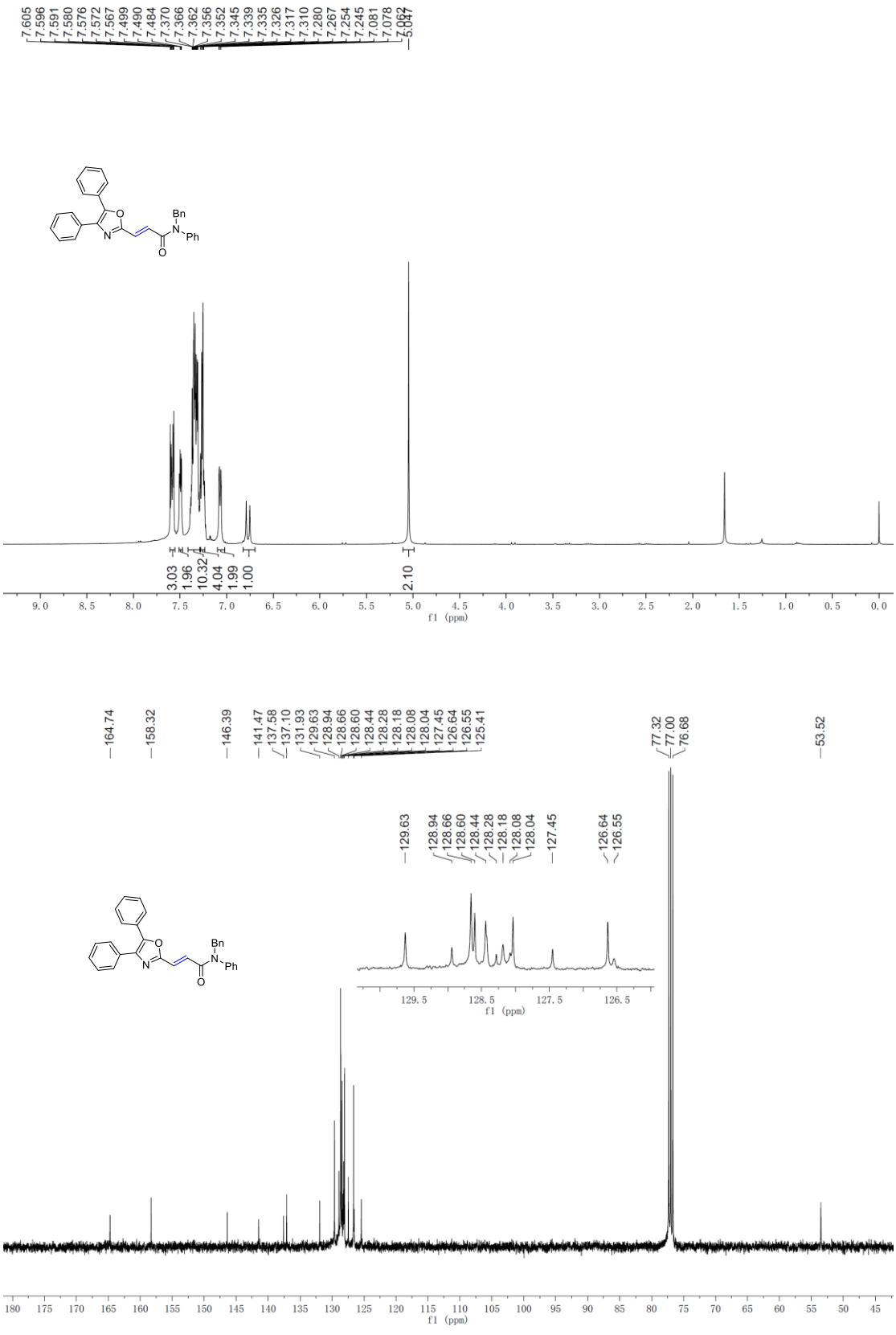


(E)-N-benzyl-4-(4-(bis(2-chloroethyl)amino)phenyl)-N-phenylbut-2-enamide (34)

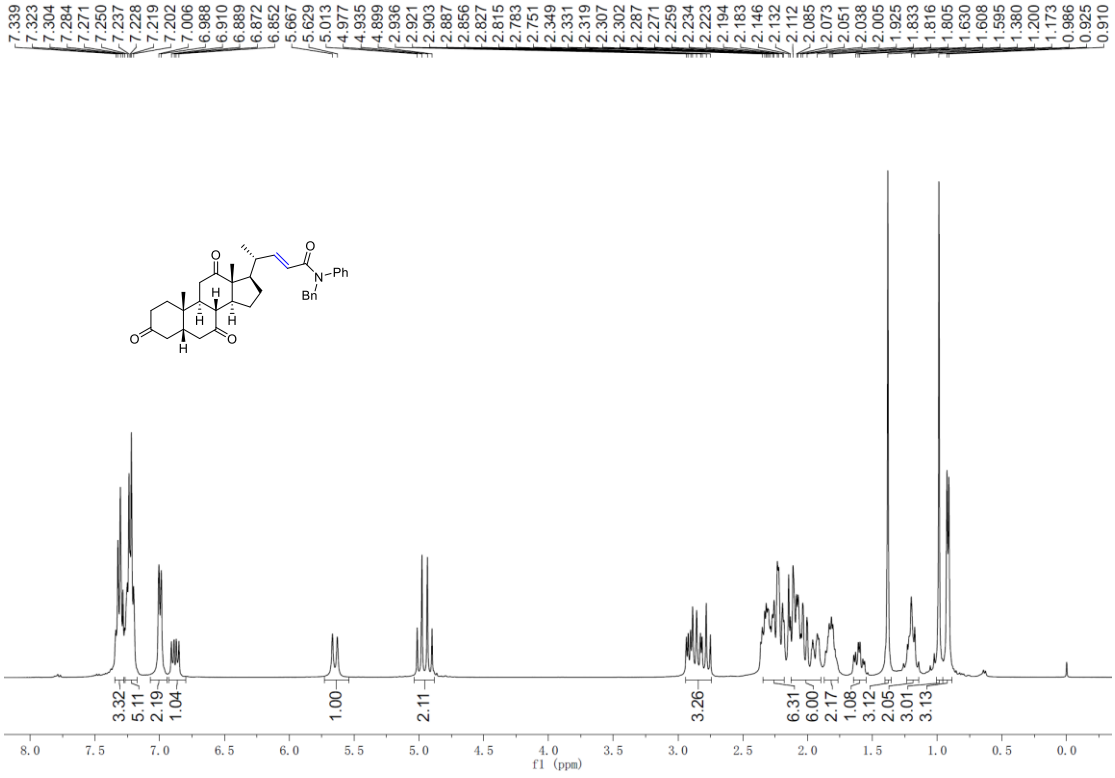


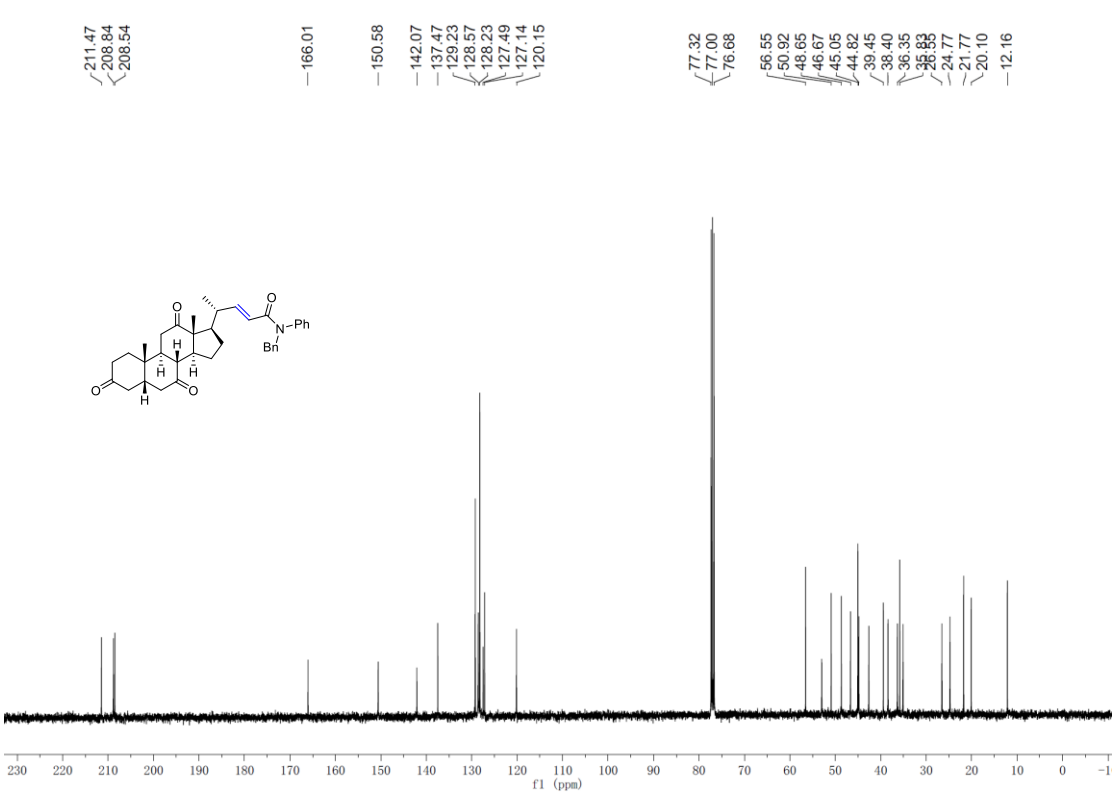


(E)-N-benzyl-3-(4,5-diphenyloxazol-2-yl)-N-phenylacrylamide (35)

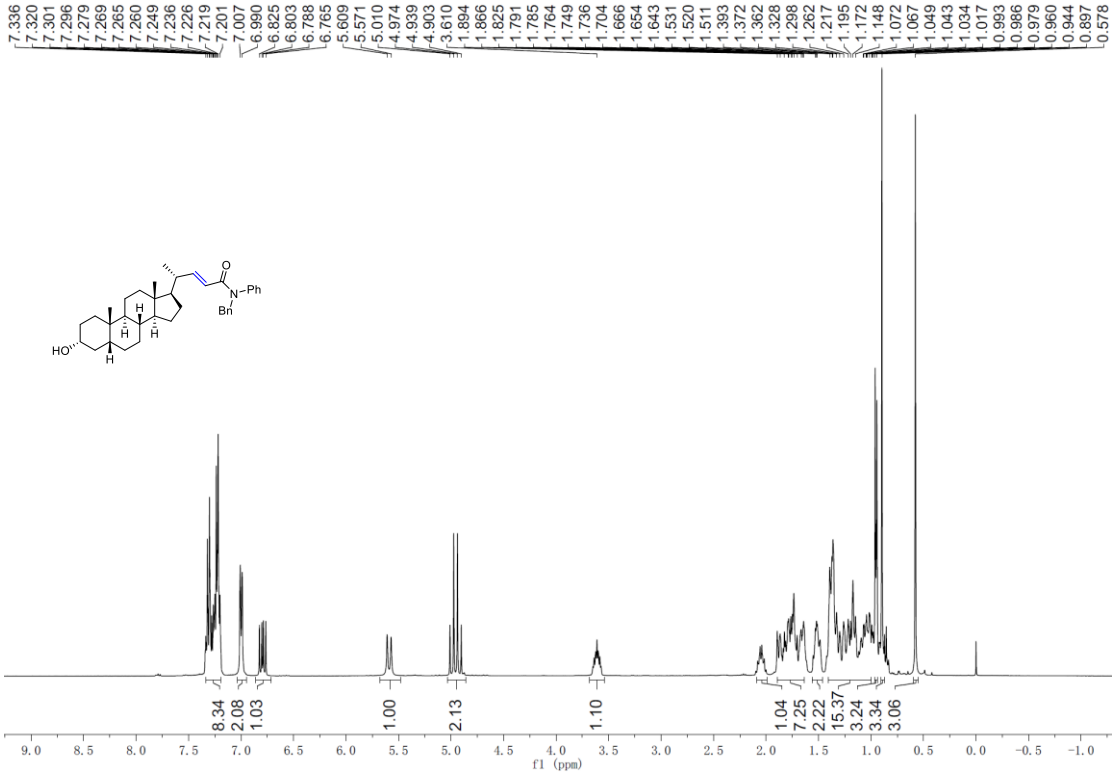


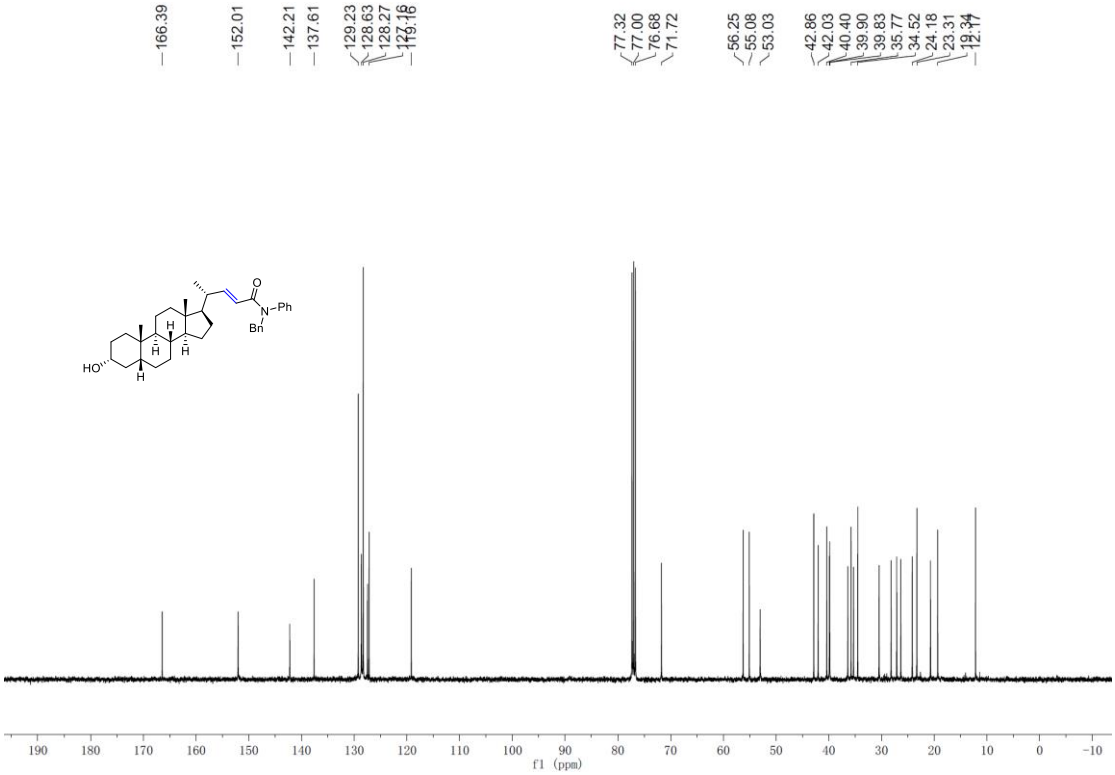
(R,E)-N-benzyl-4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-N-phenylpent-2-enamide (36)



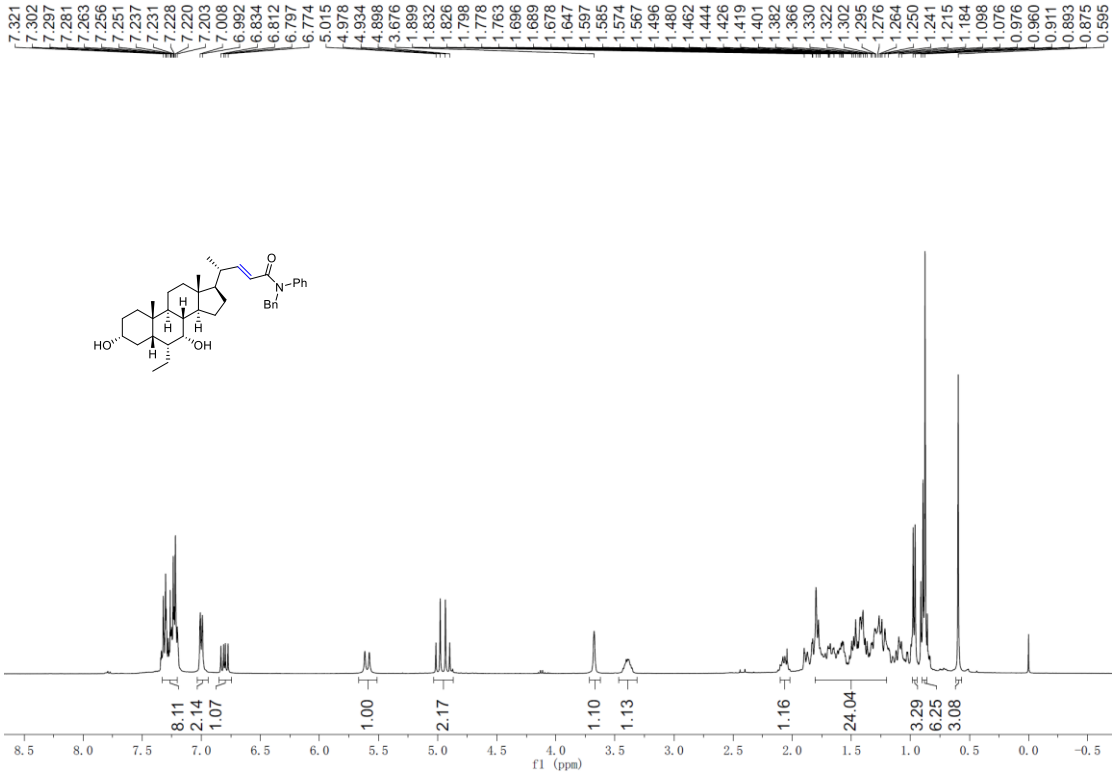


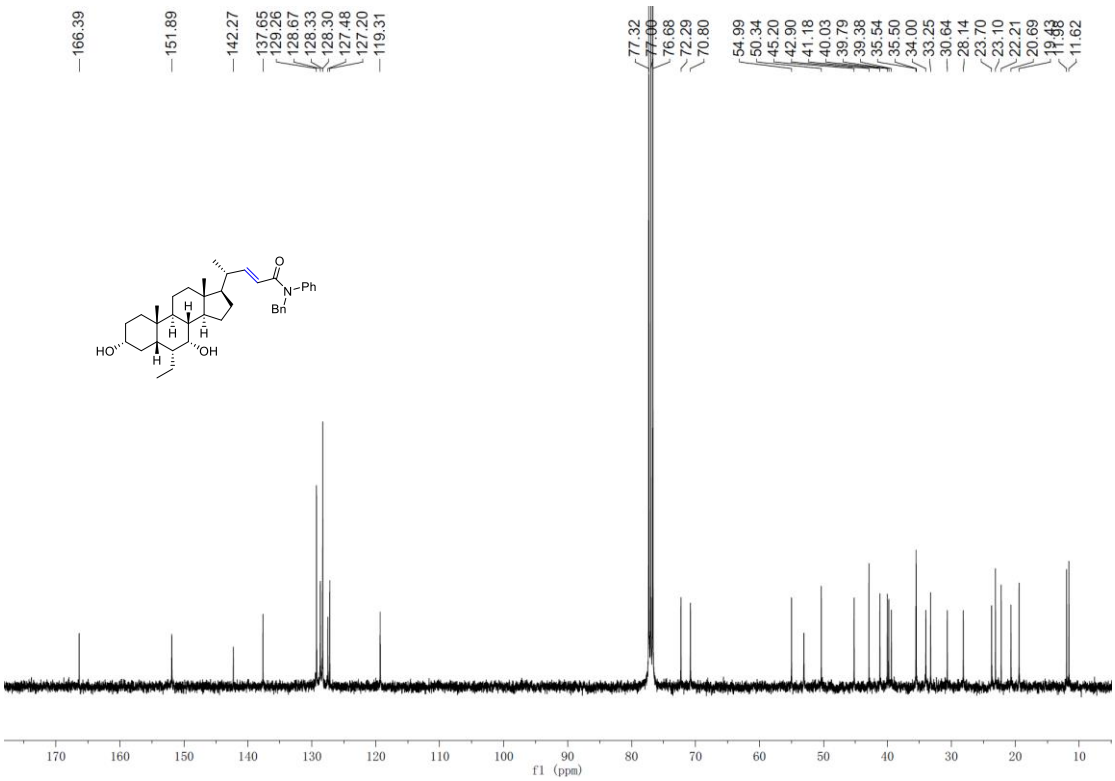
(R,E)-N-benzyl-4-((3R,5R,8R,9S,10S,13R,14S,17R)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-N-phenylpent-2-enamide (37)



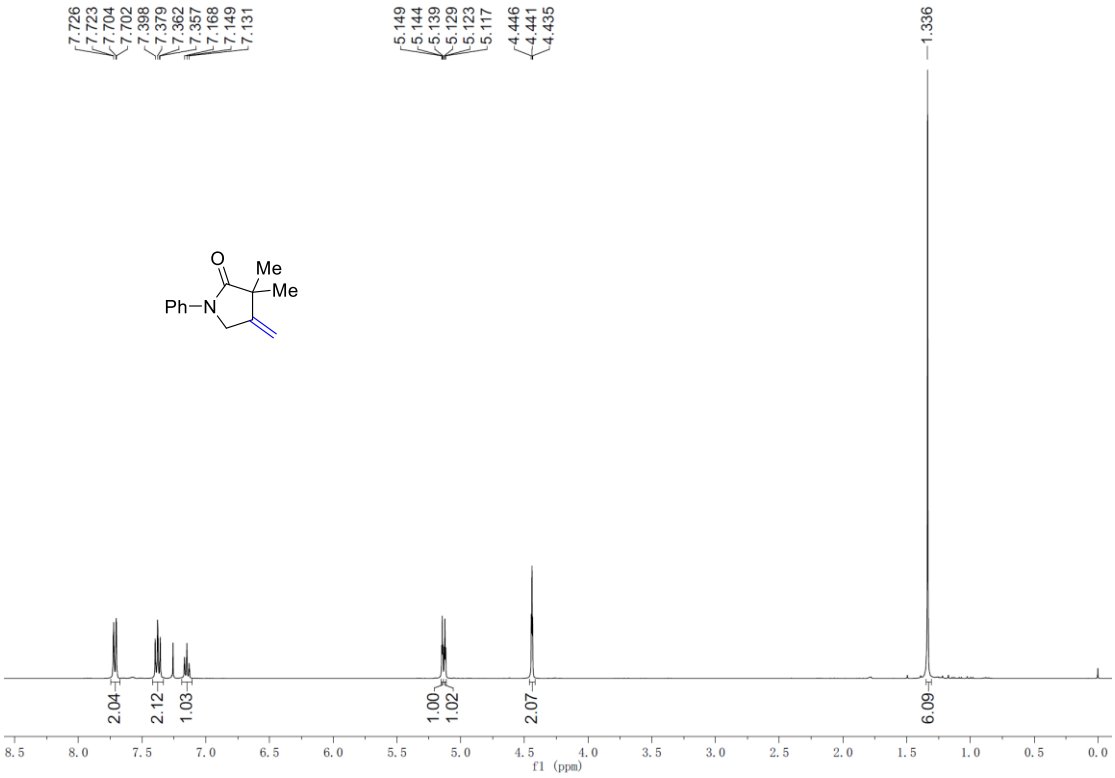


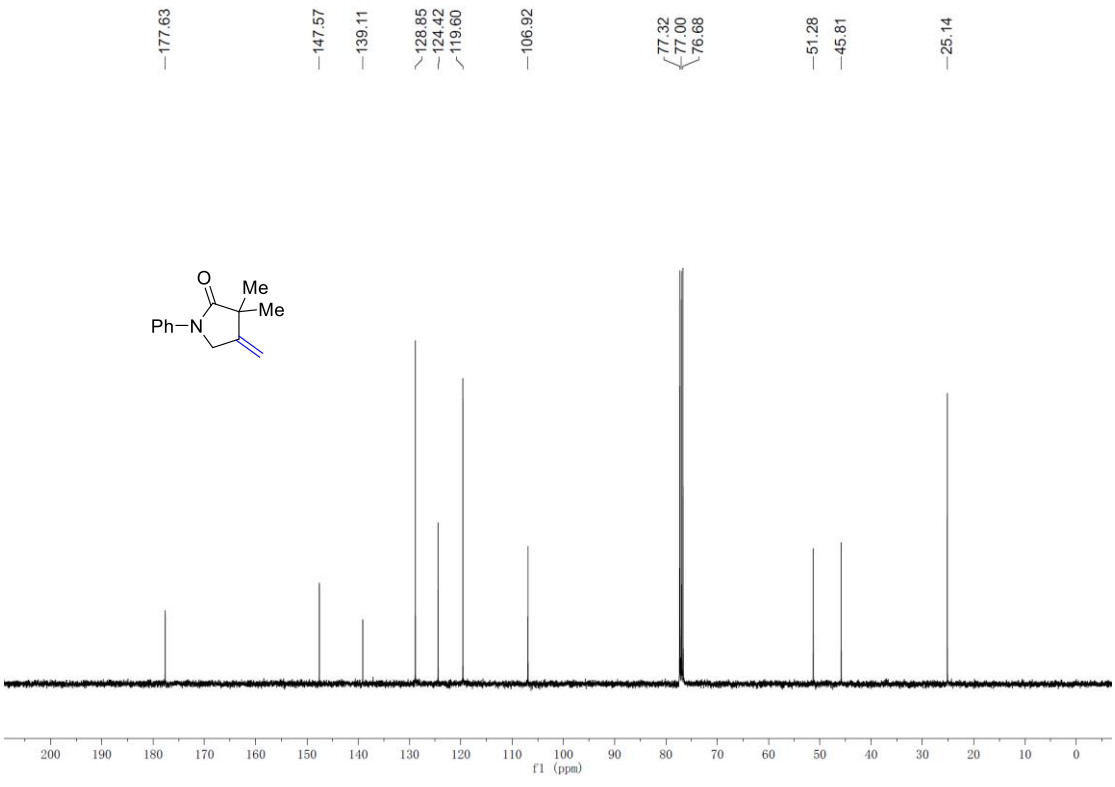
(R,E)-N-benzyl-4-((3R,5S,6R,7R,8S,9S,10S,13R,14S,17R)-6-ethyl-3,7-dihydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-N-phenylpent-2-enamide (38)



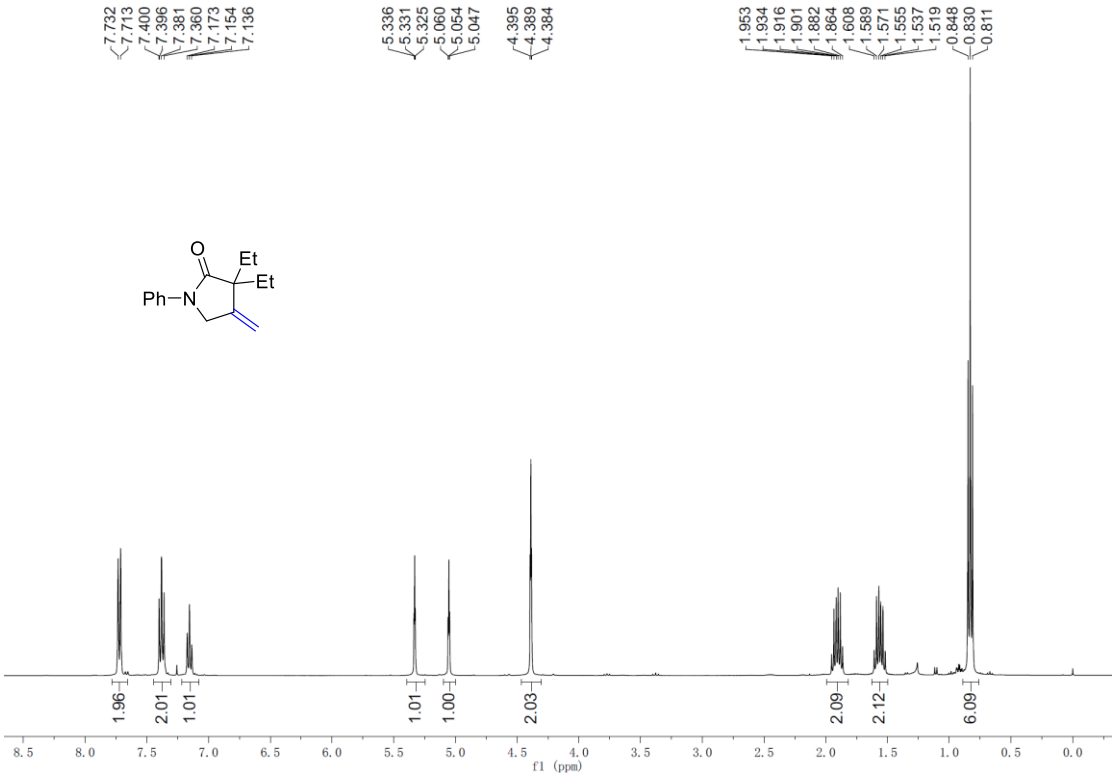


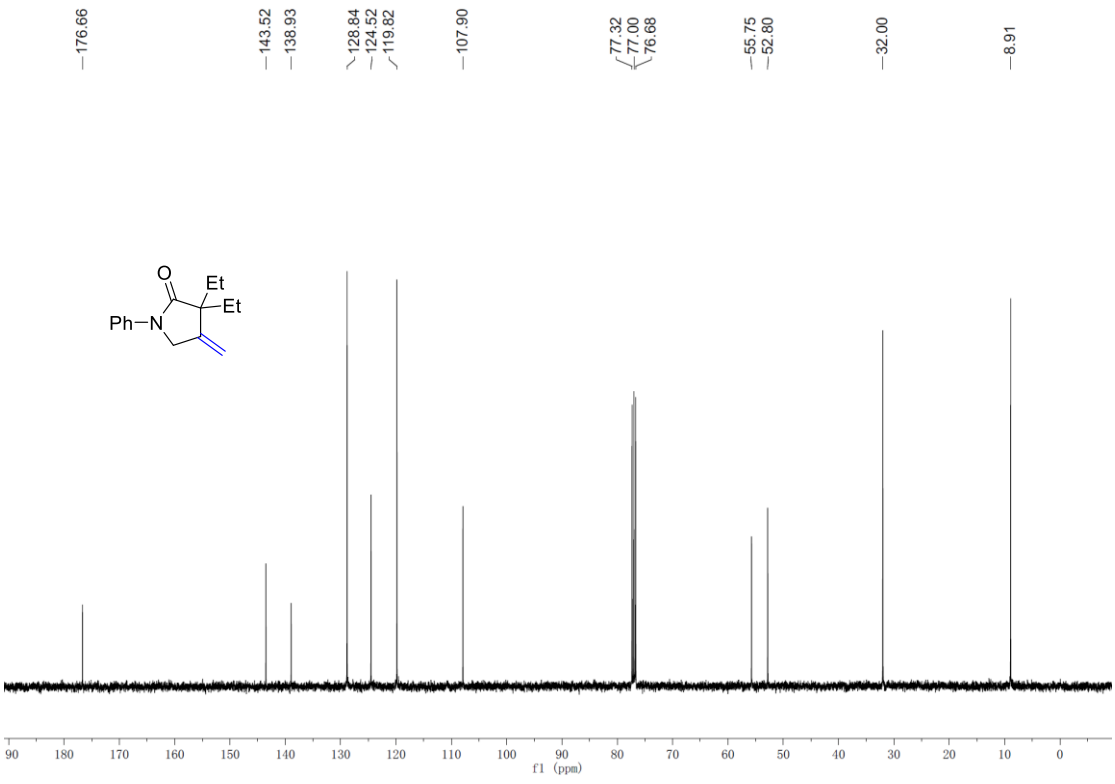
3,3-dimethyl-4-methylene-1-phenylpyrrolidin-2-one (39)



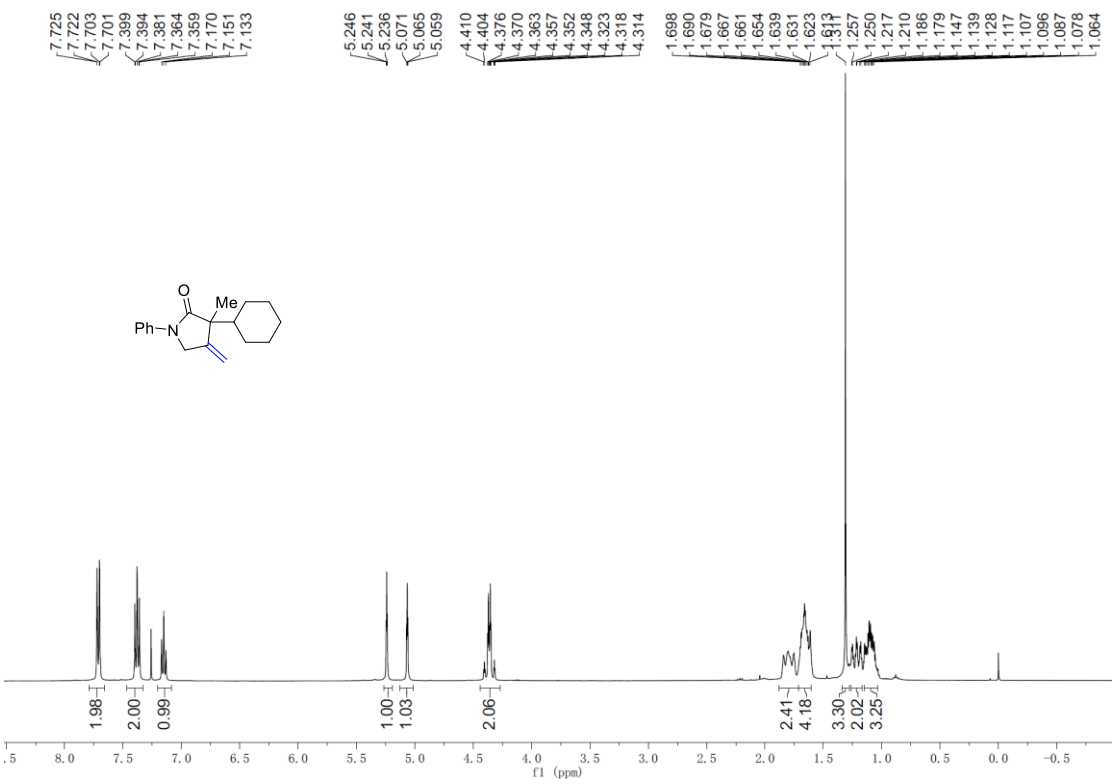


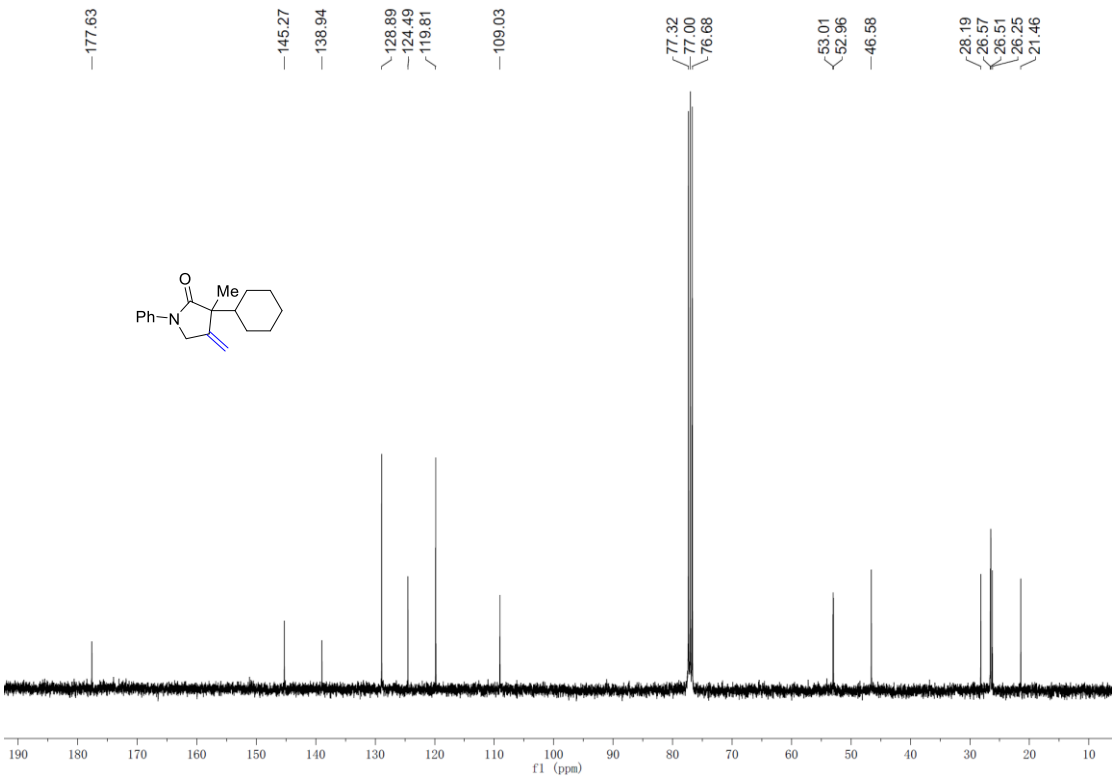
3,3-diethyl-4-methylene-1-phenylpyrrolidin-2-one (40)



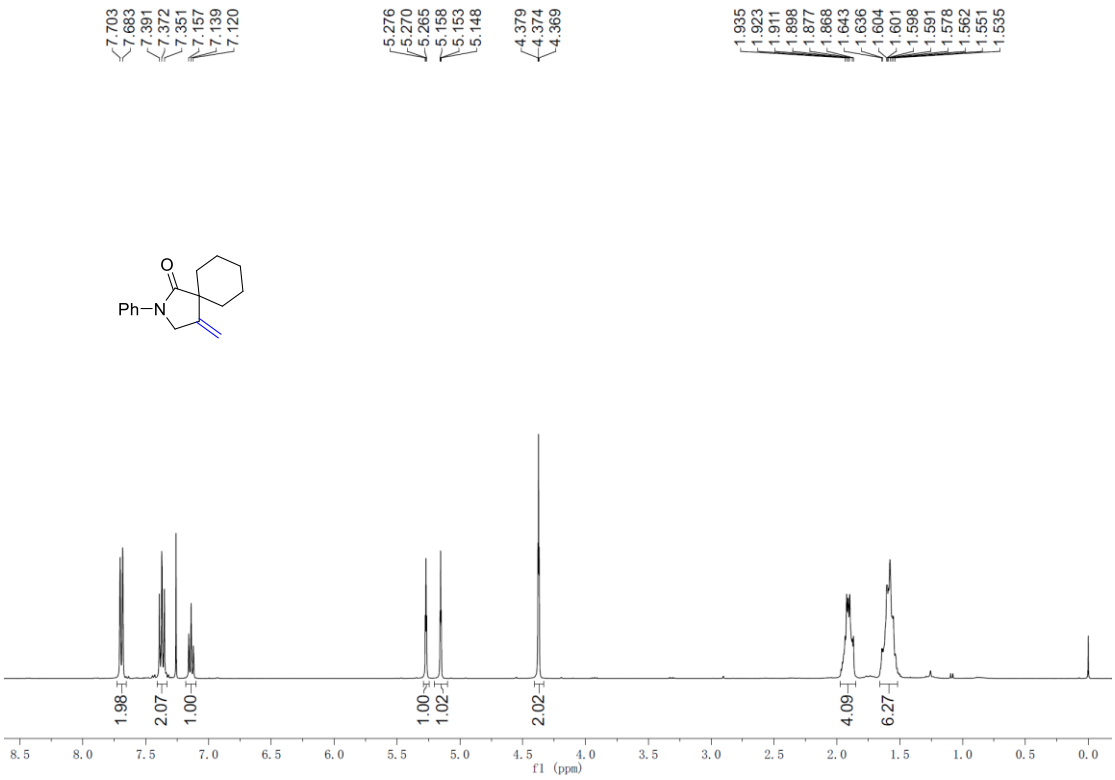


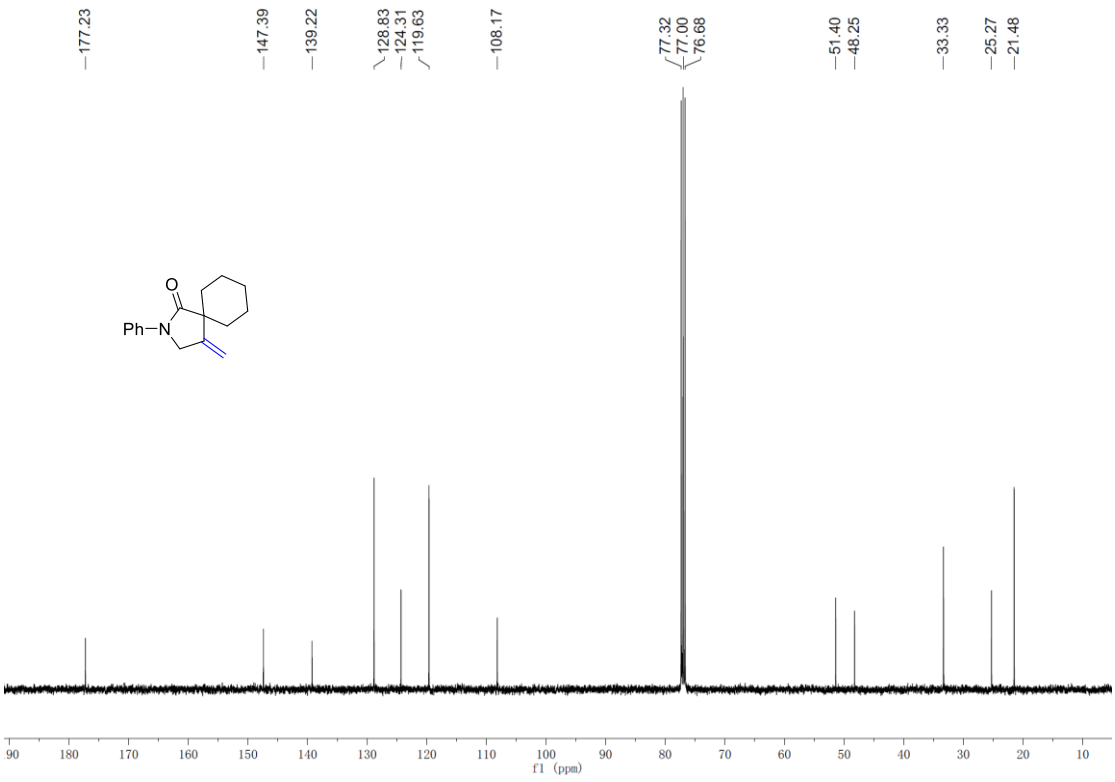
3-cyclohexyl-3-methyl-4-methylene-1-phenylpyrrolidin-2-one (41)



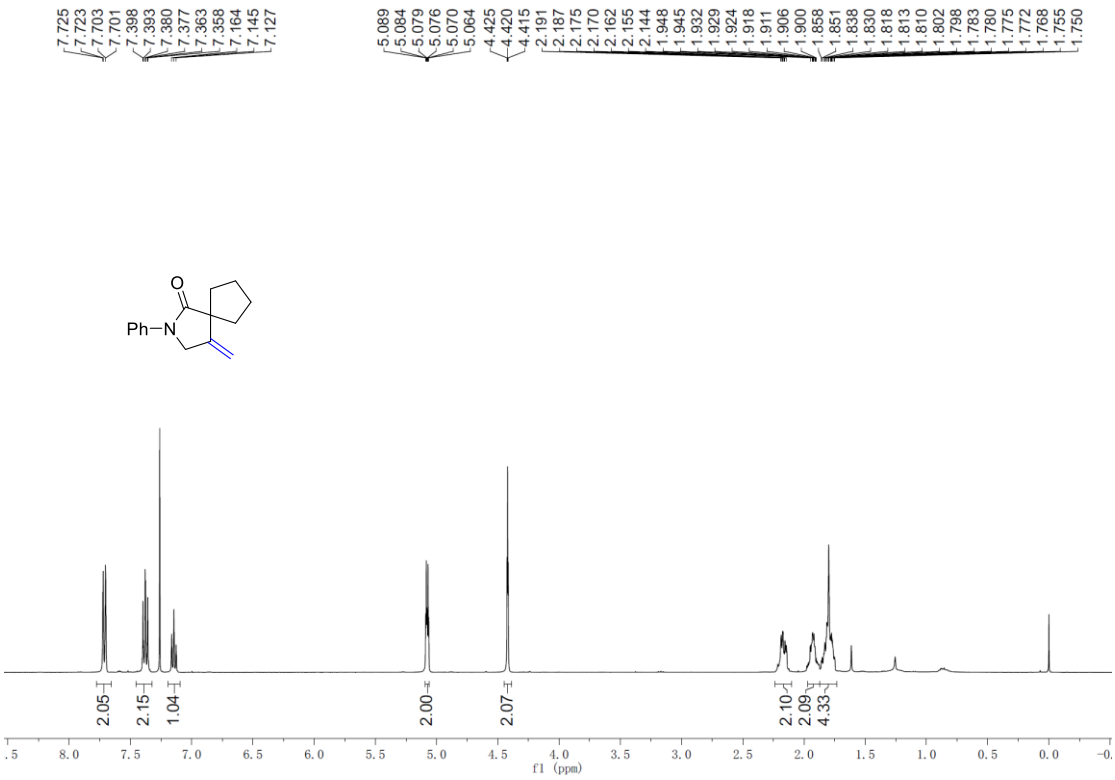


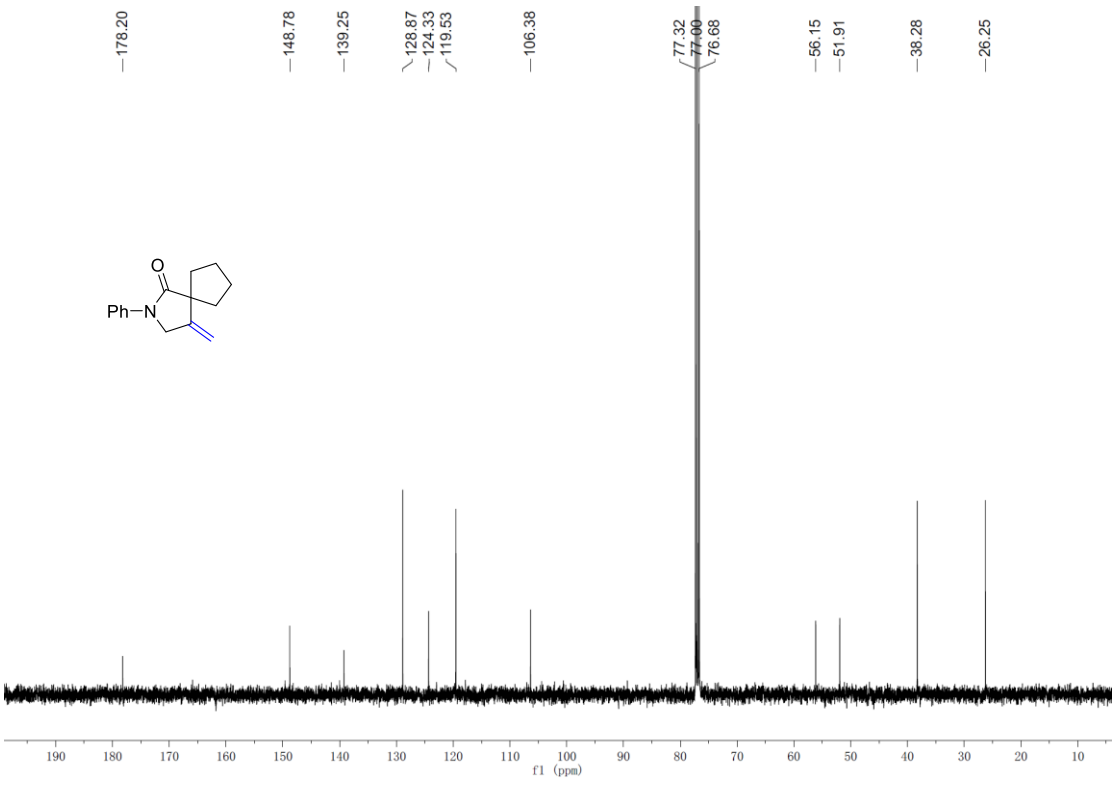
4-methylene-2-phenyl-2-azaspiro[4.5]decan-1-one (42)



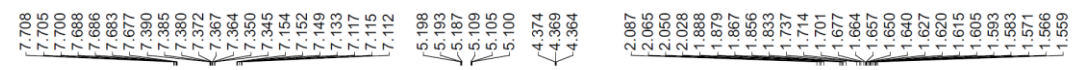


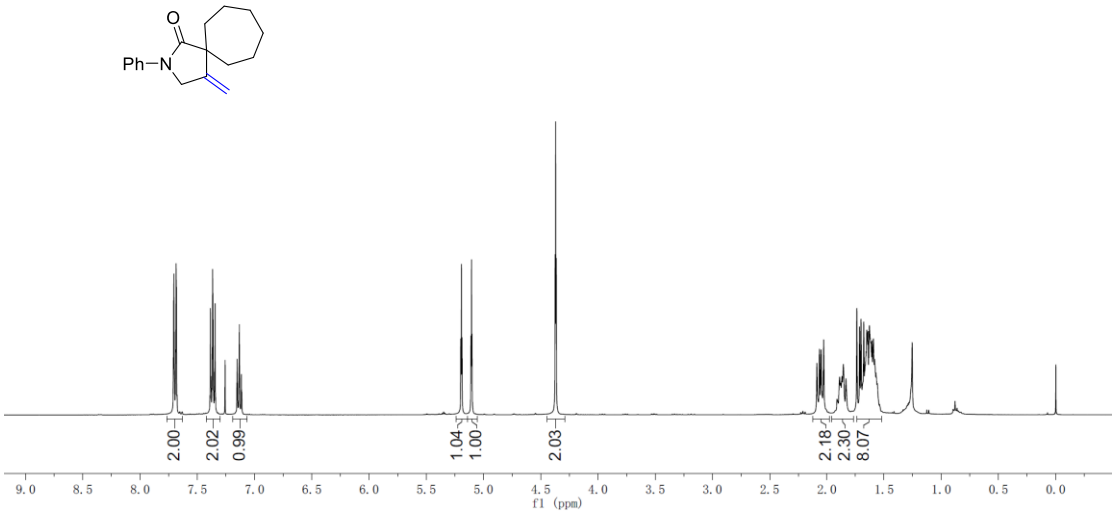
4-methylene-2-phenyl-2-azaspiro[4.4]nonan-1-one (43)

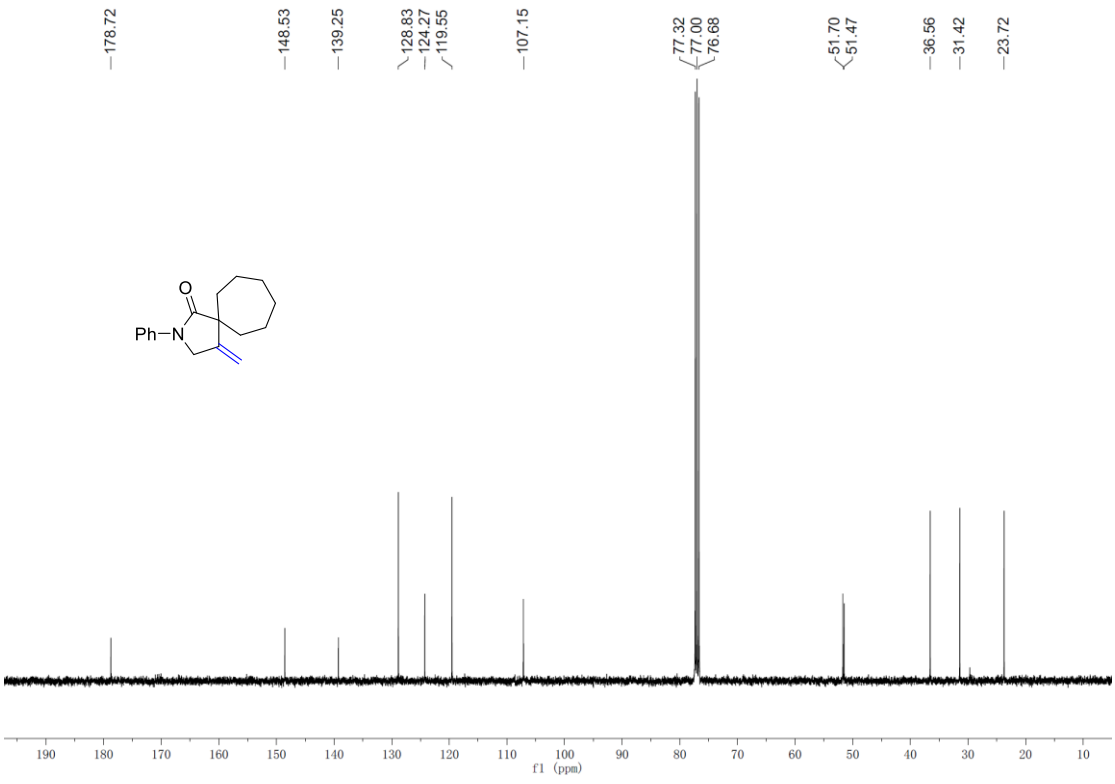




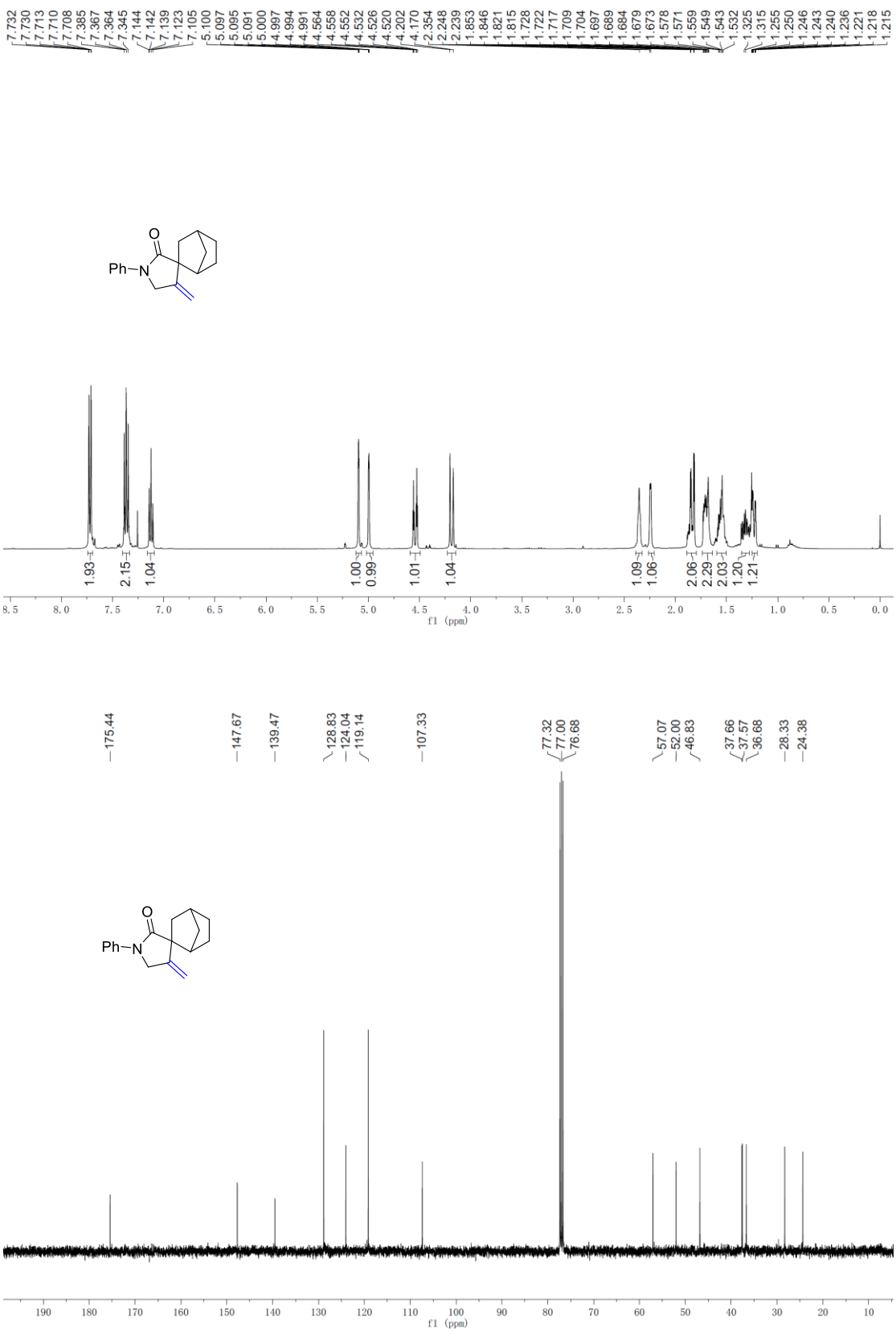
4-methylene-2-phenyl-2-azaspiro[4.6]undecan-1-one (44)



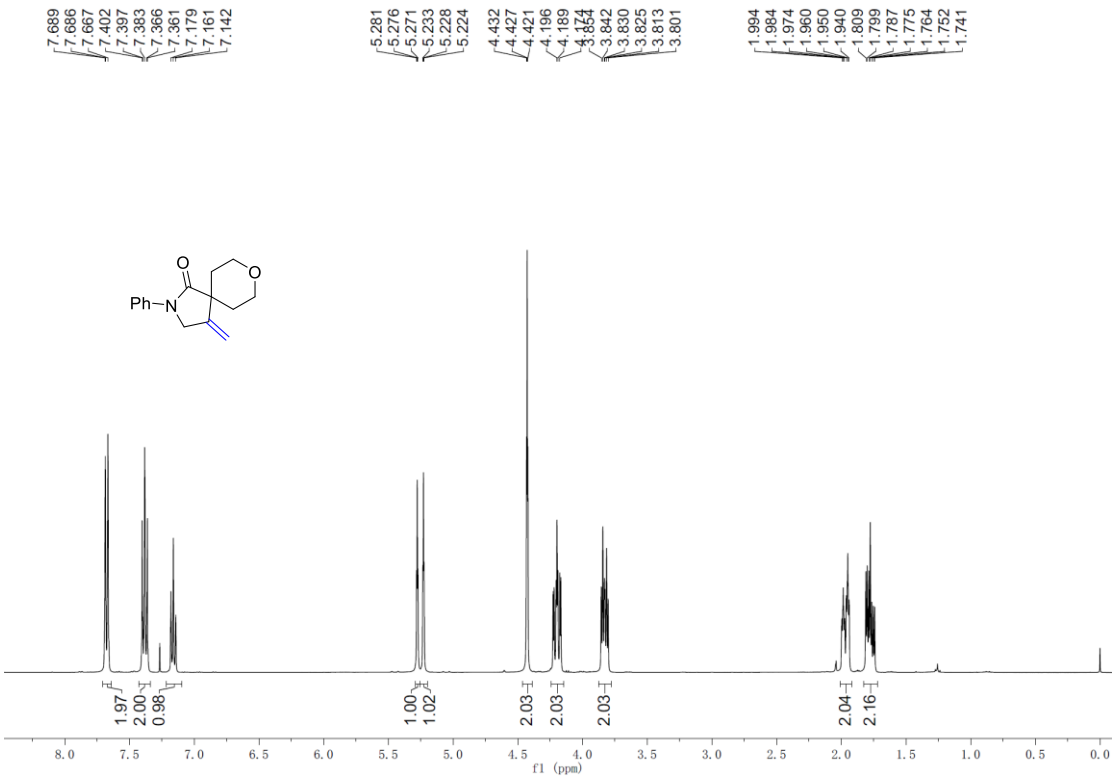


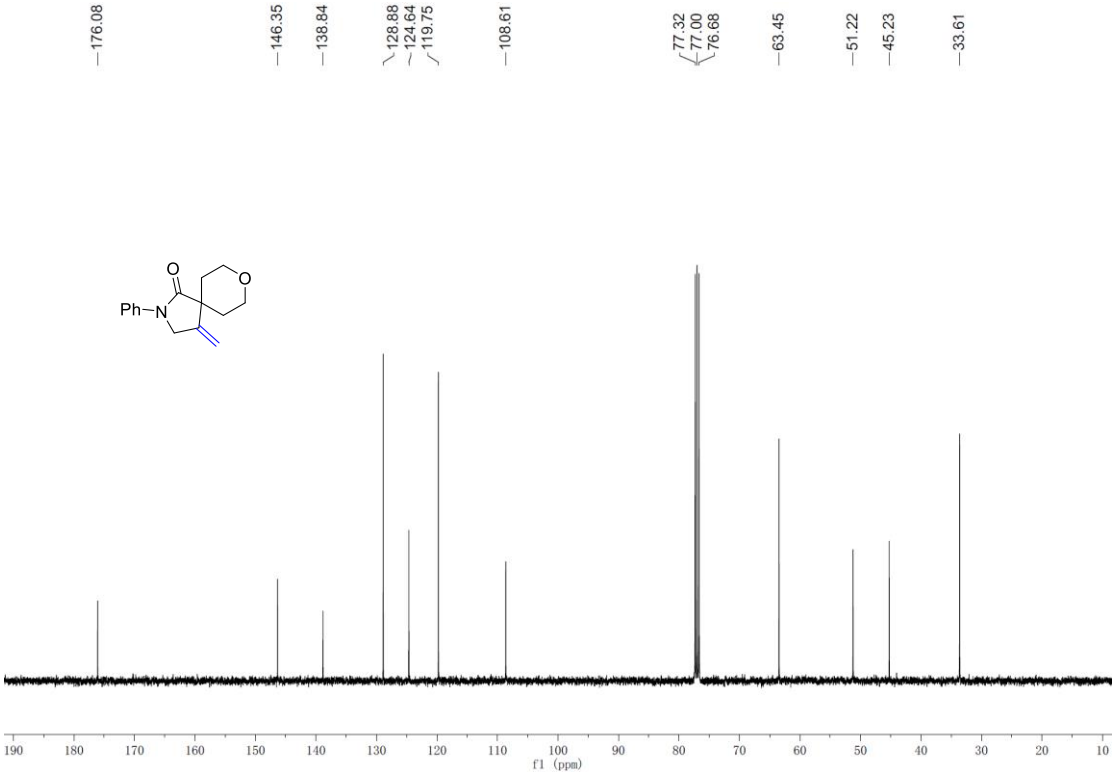


4'-methylene-1'-phenylspiro[bicyclo[2.2.1]heptane-2,3'-pyrrolidin]-2'-one (45)

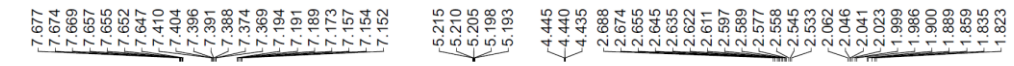


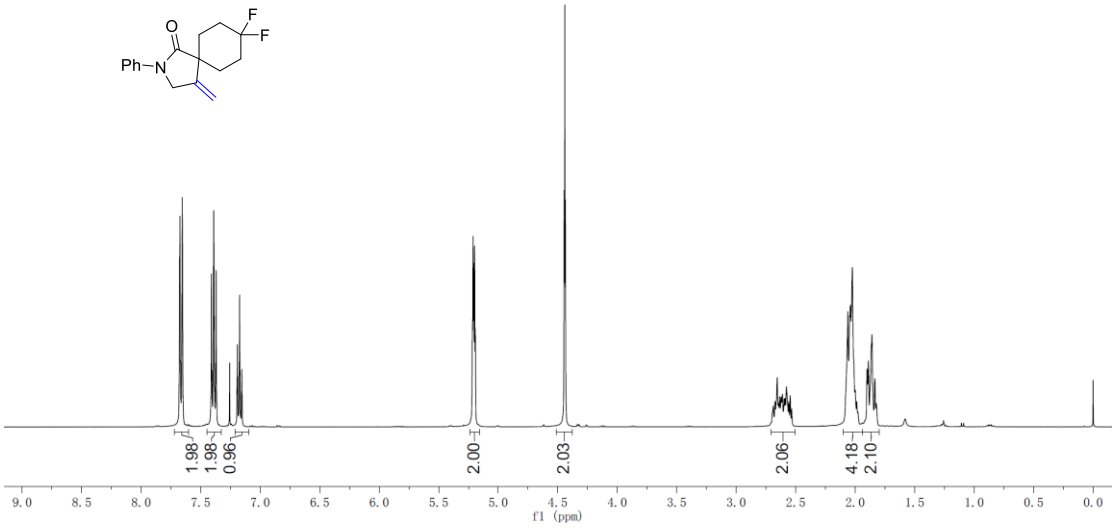
4-methylene-2-phenyl-8-oxa-2-azaspiro[4.5]decan-1-one (46)

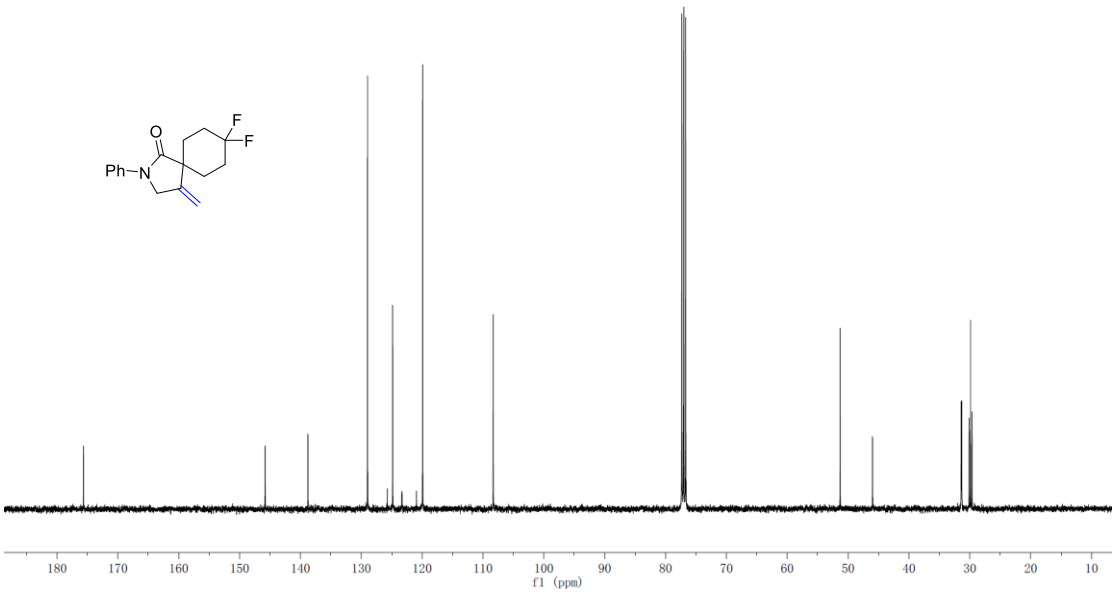


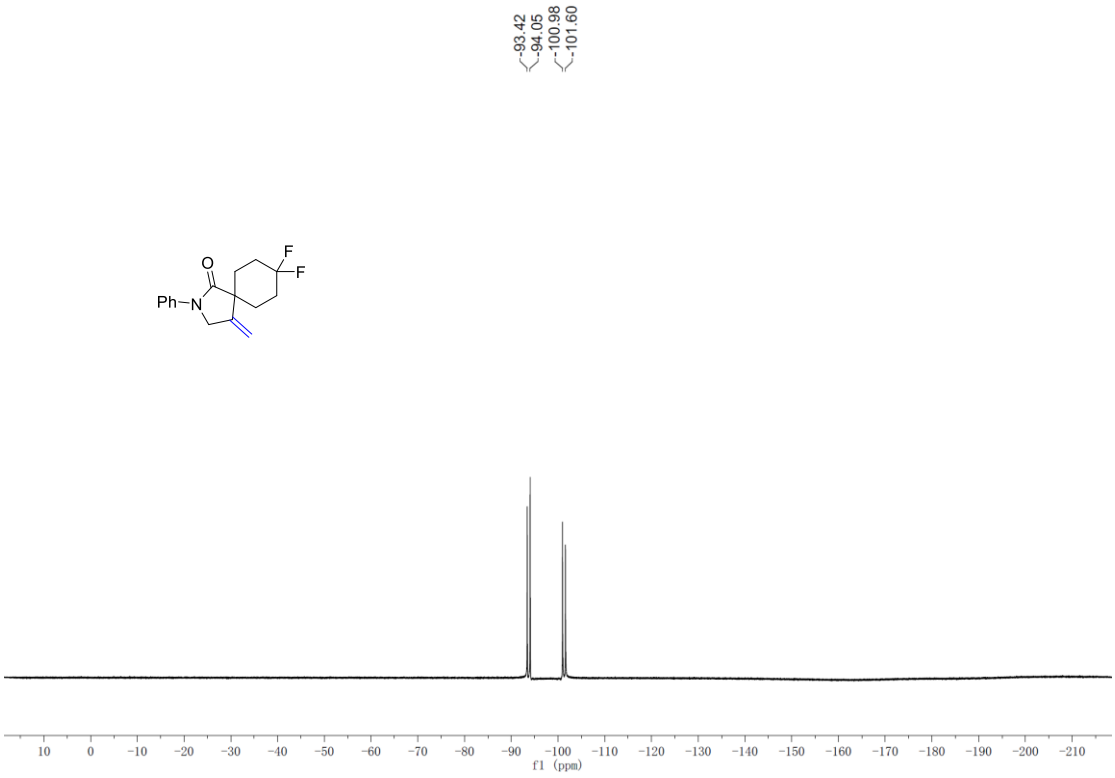


8,8-difluoro-4-methylene-2-phenyl-2-azaspiro[4.5]decan-1-one (47)

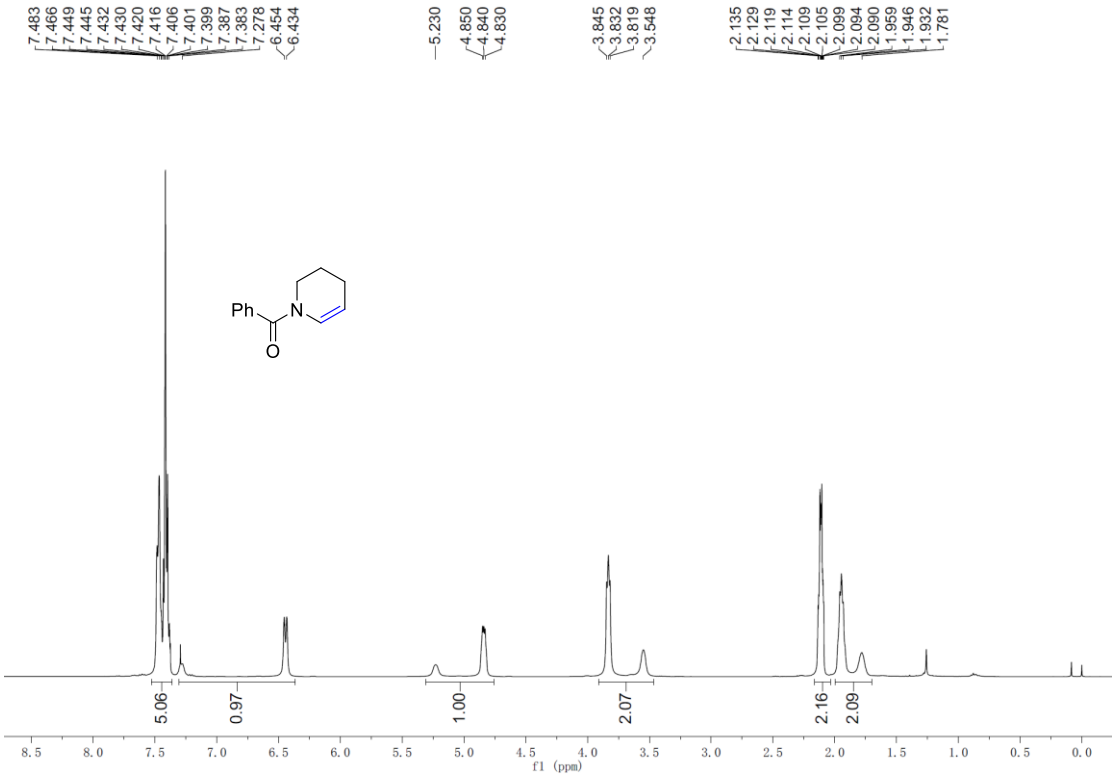


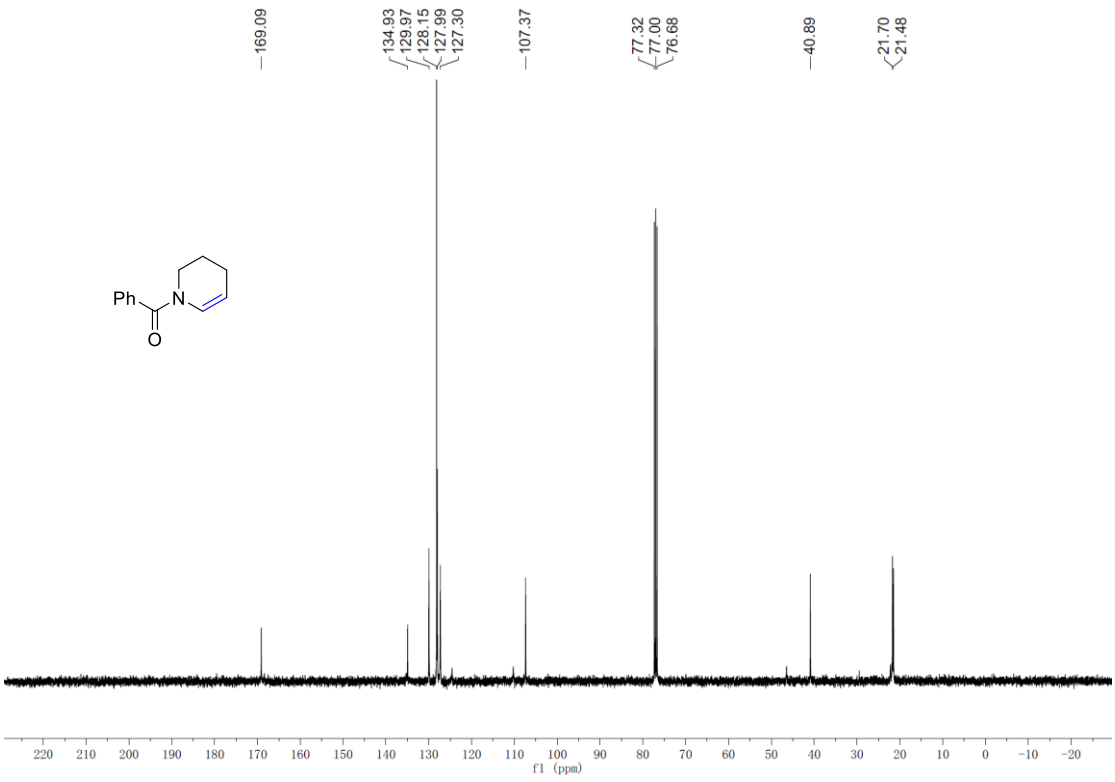




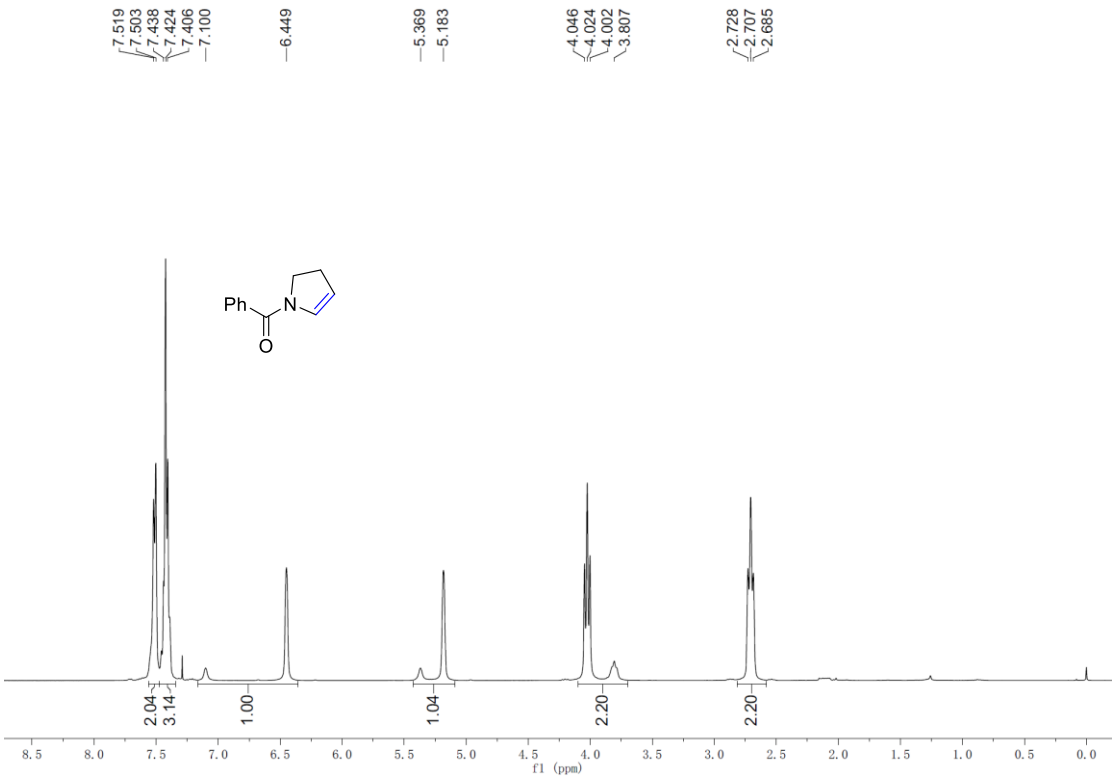

-93.42
-94.05
-100.98
-101.60
O
F
F
Ph–N
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

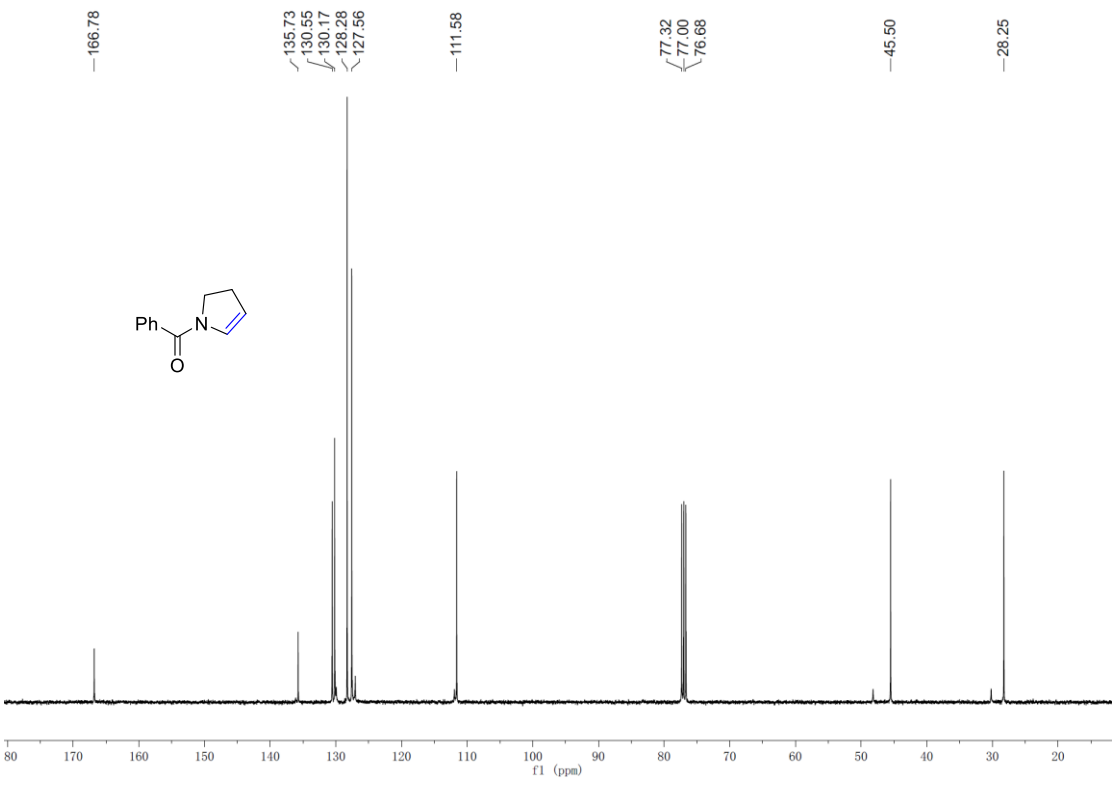
(3,4-dihydropyridin-1(2H)-yl)(phenyl)methanone (48)



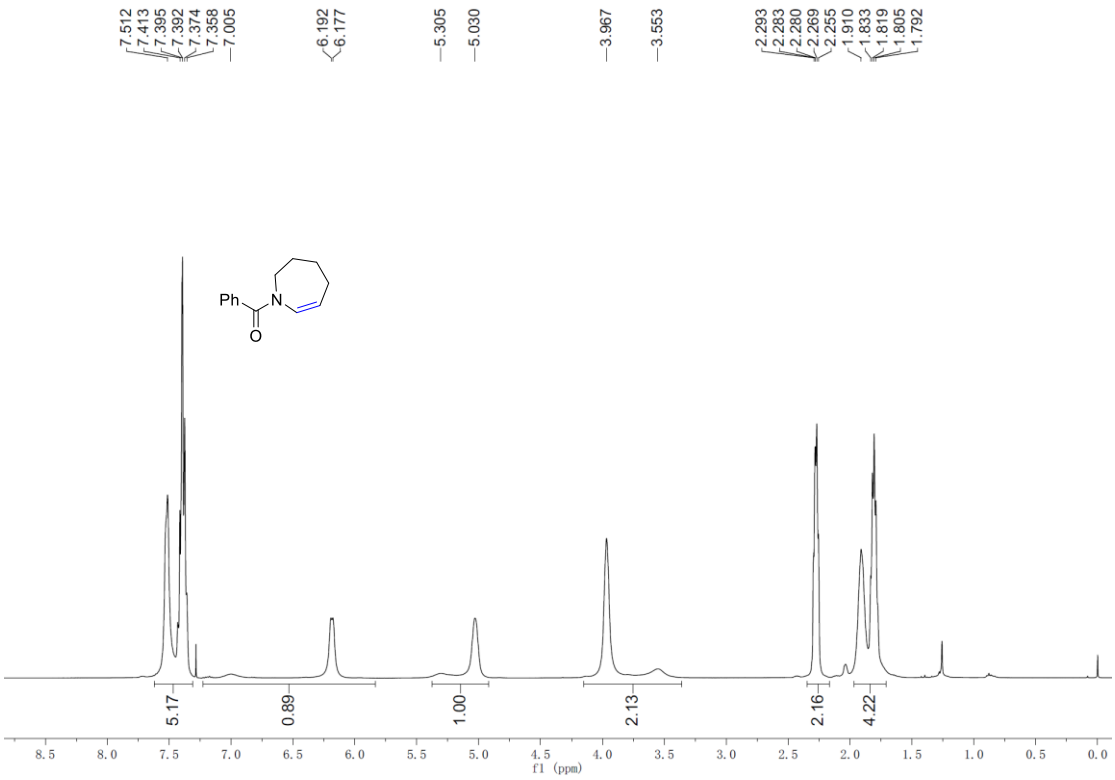


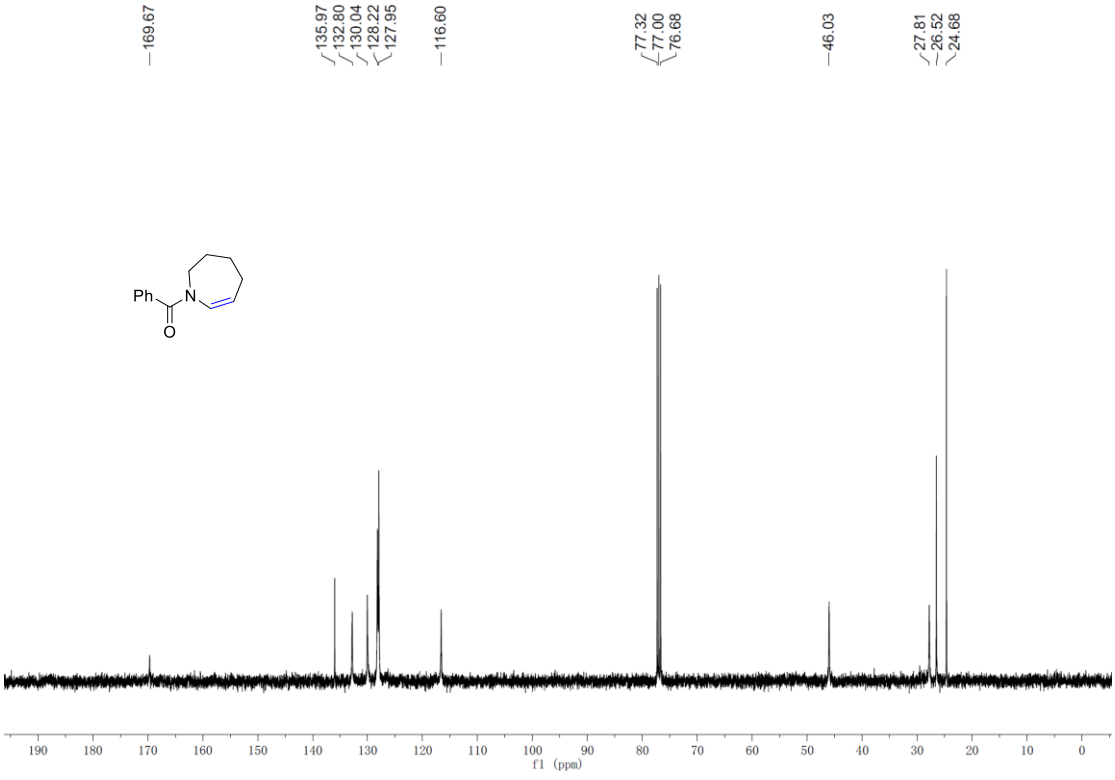
(2,3-dihydro-1H-pyrrol-1-yl)(phenyl)methanone (49)



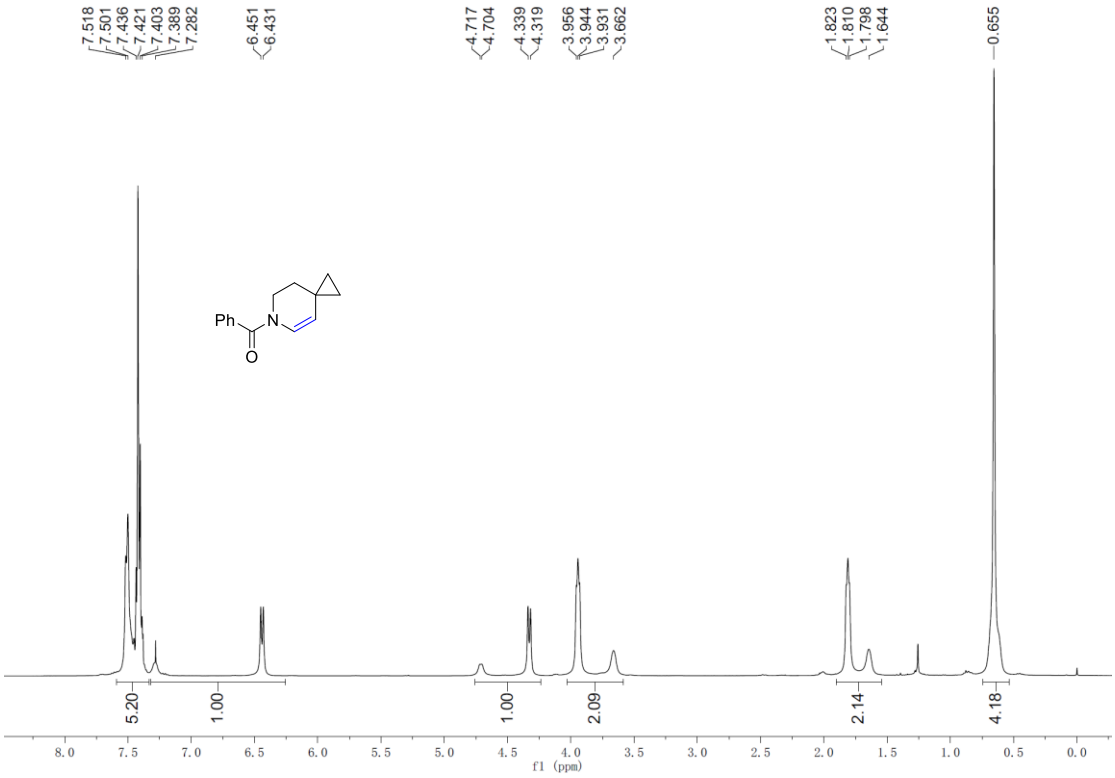


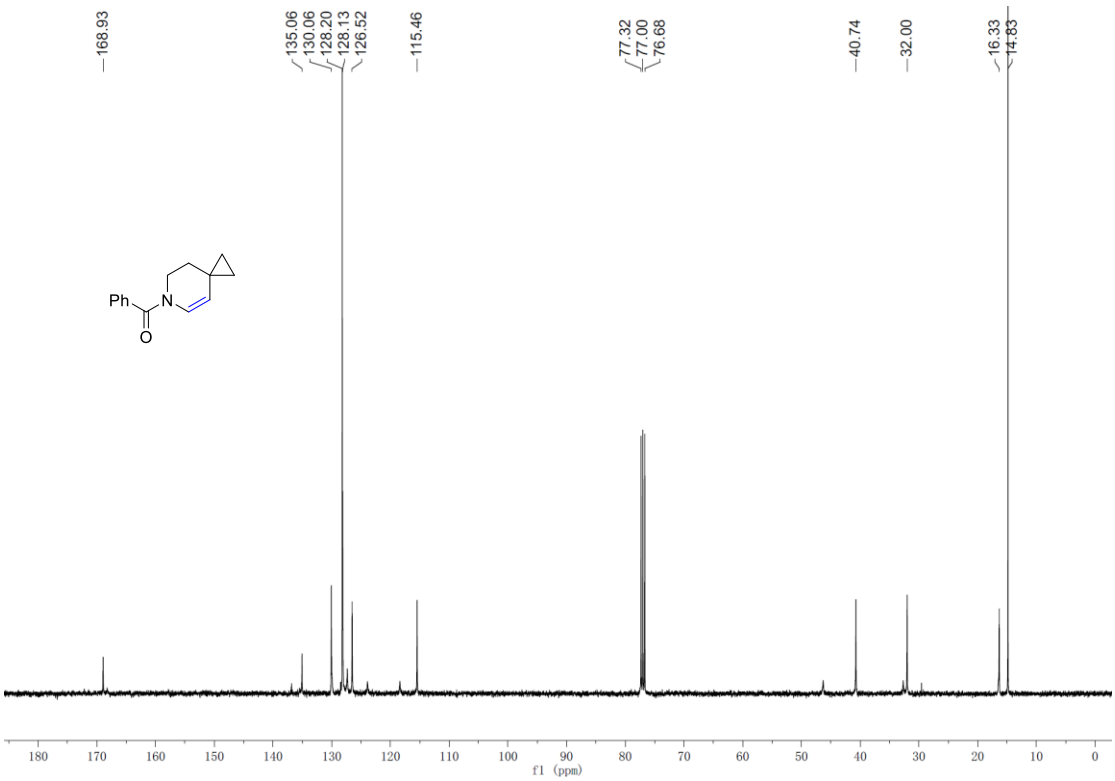
phenyl(2,3,4,5-tetrahydro-1H-azepin-1-yl)methanone (50)



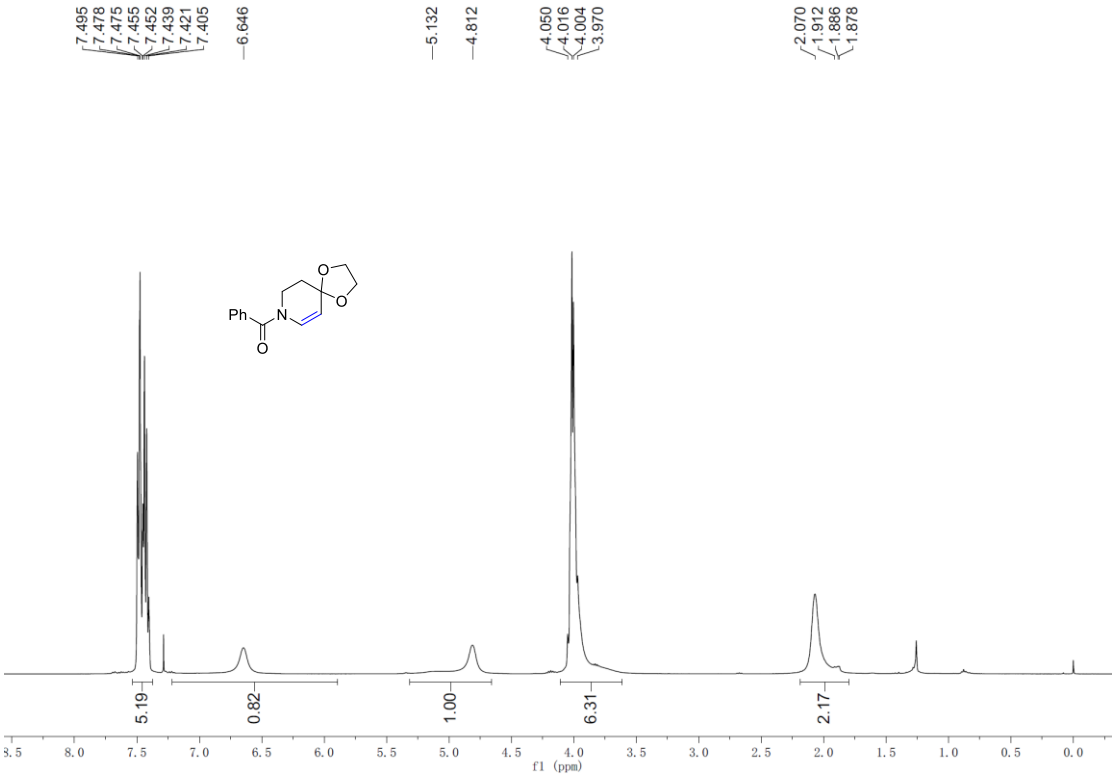


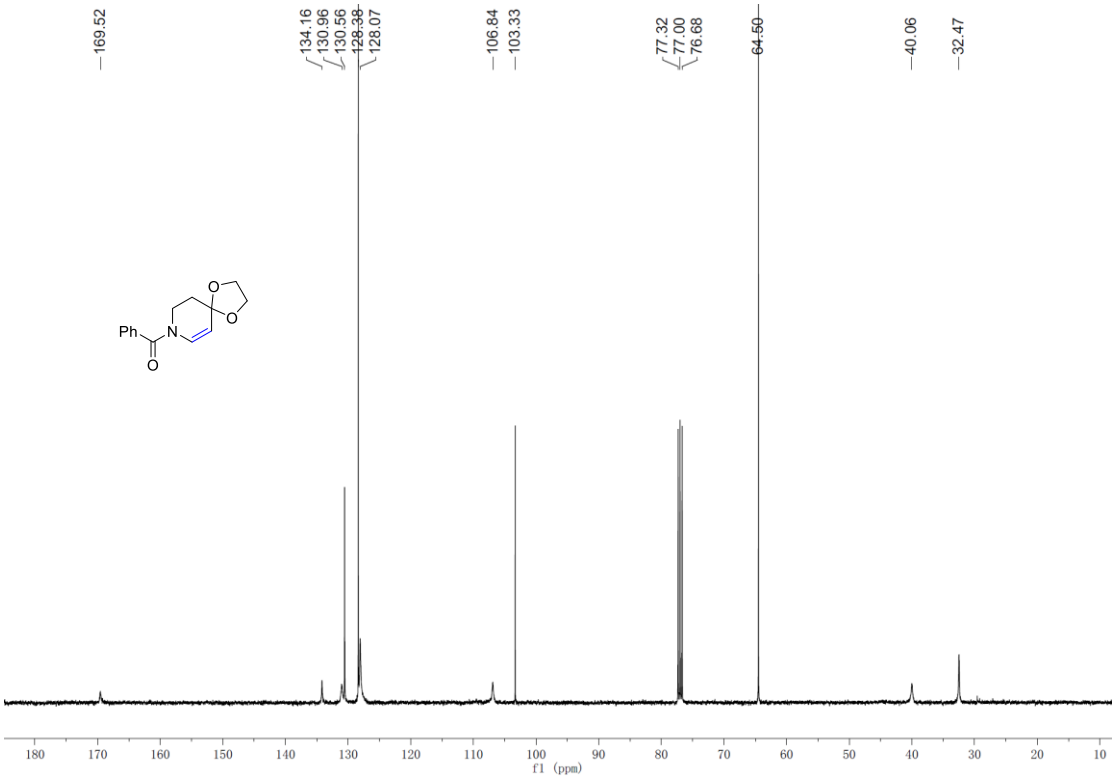
phenyl(6-azaspiro[2.5]oct-4-en-6-yl)methanone (51)



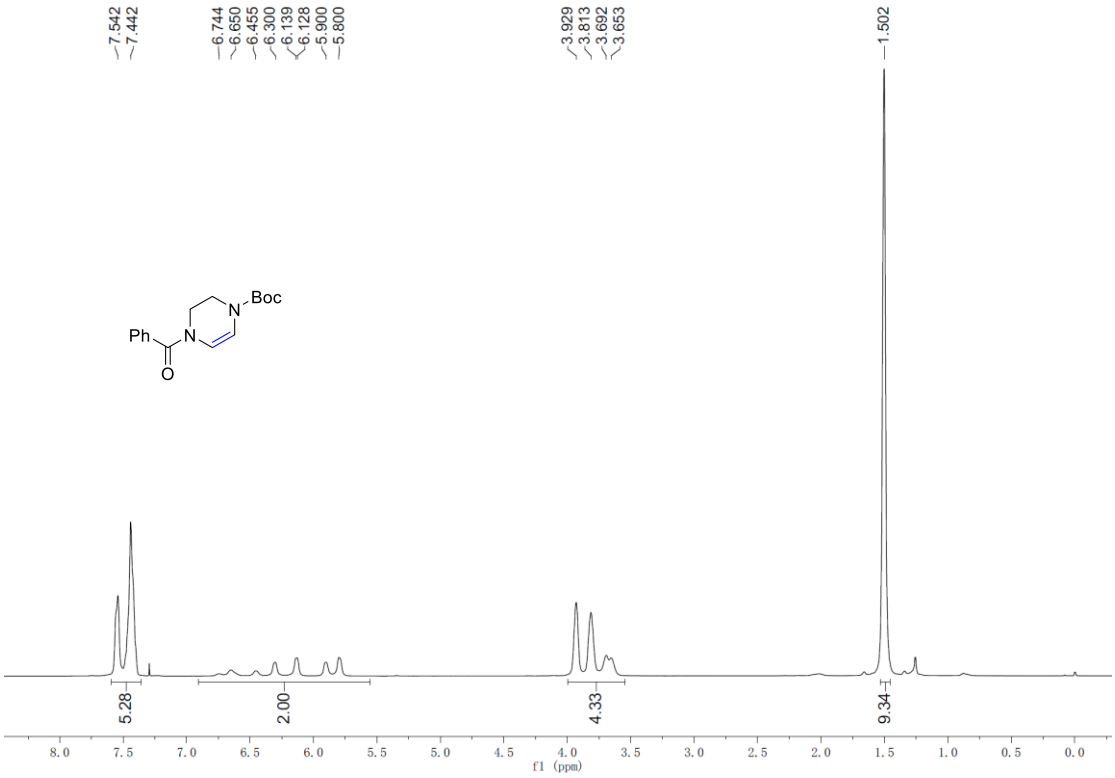


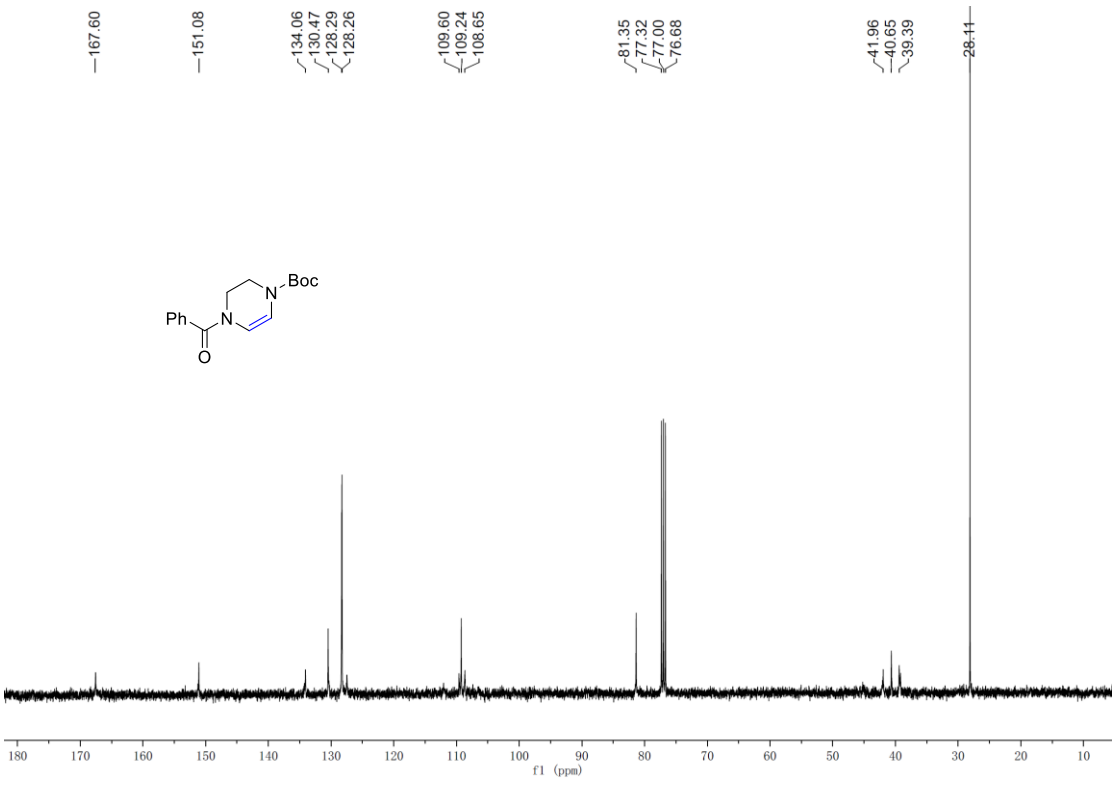
phenyl(1,4-dioxa-8-azaspiro[4.5]dec-6-en-8-yl)methanone (52)



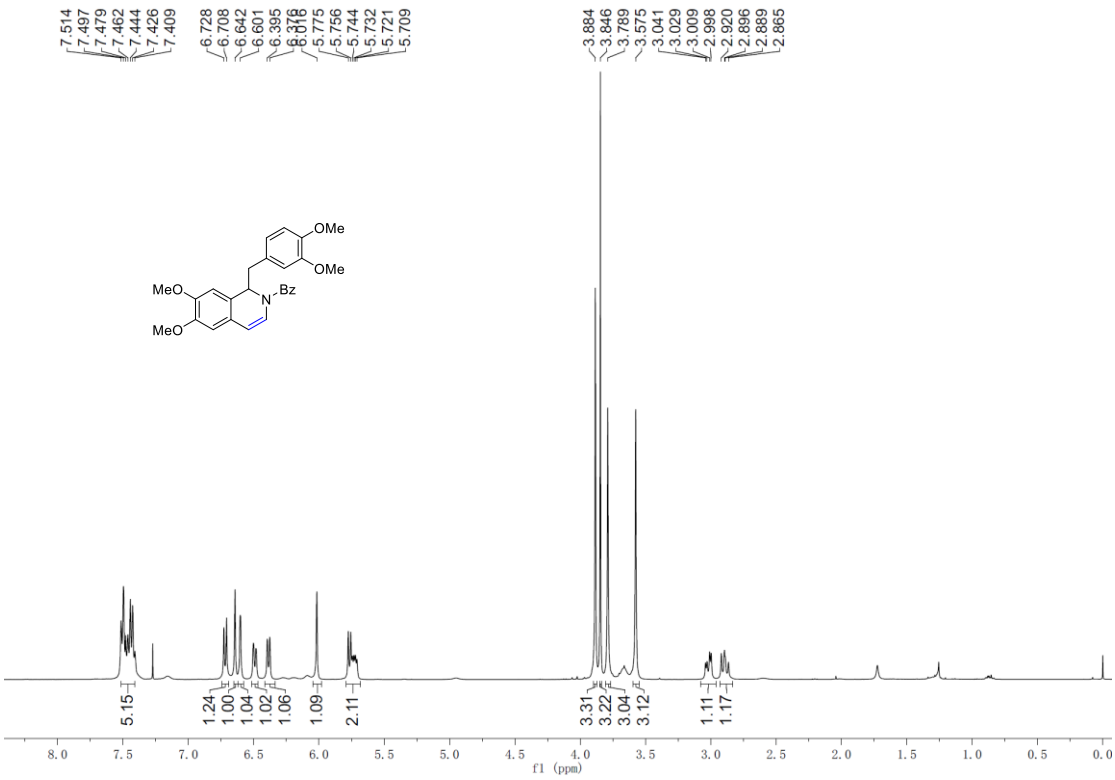


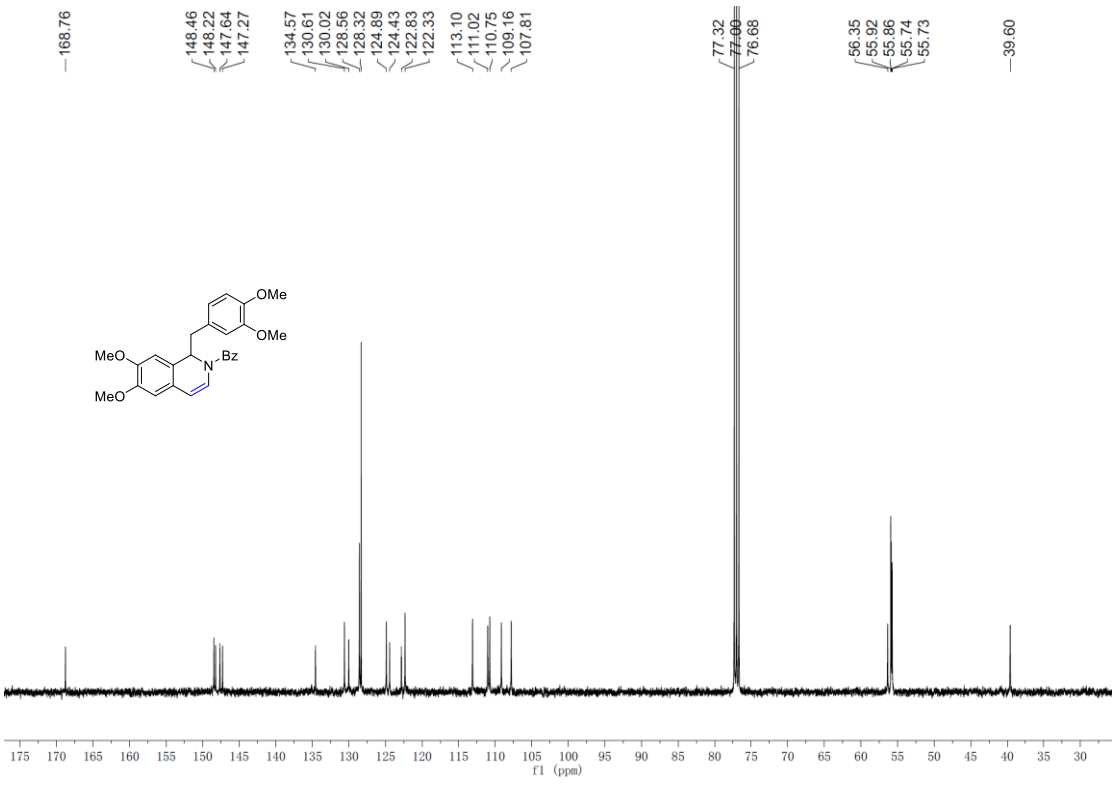
tert-butyl 4-benzoyl-3,4-dihydropyrazine-1(2H)-carboxylate (53)



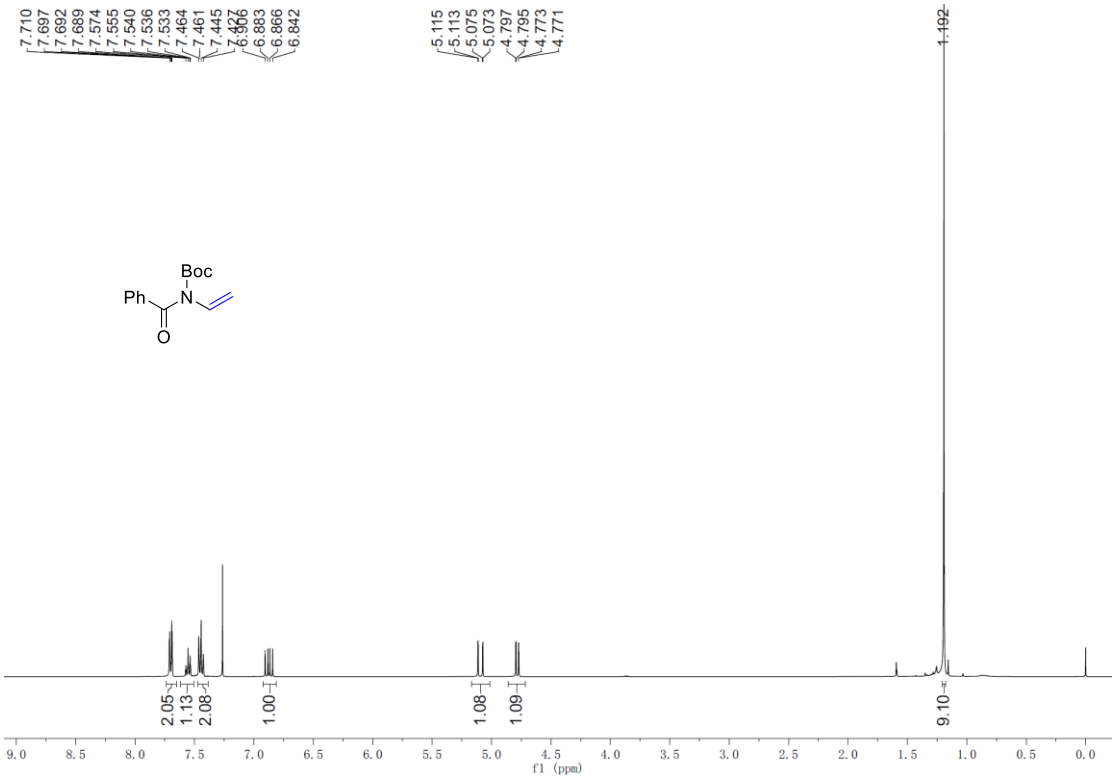


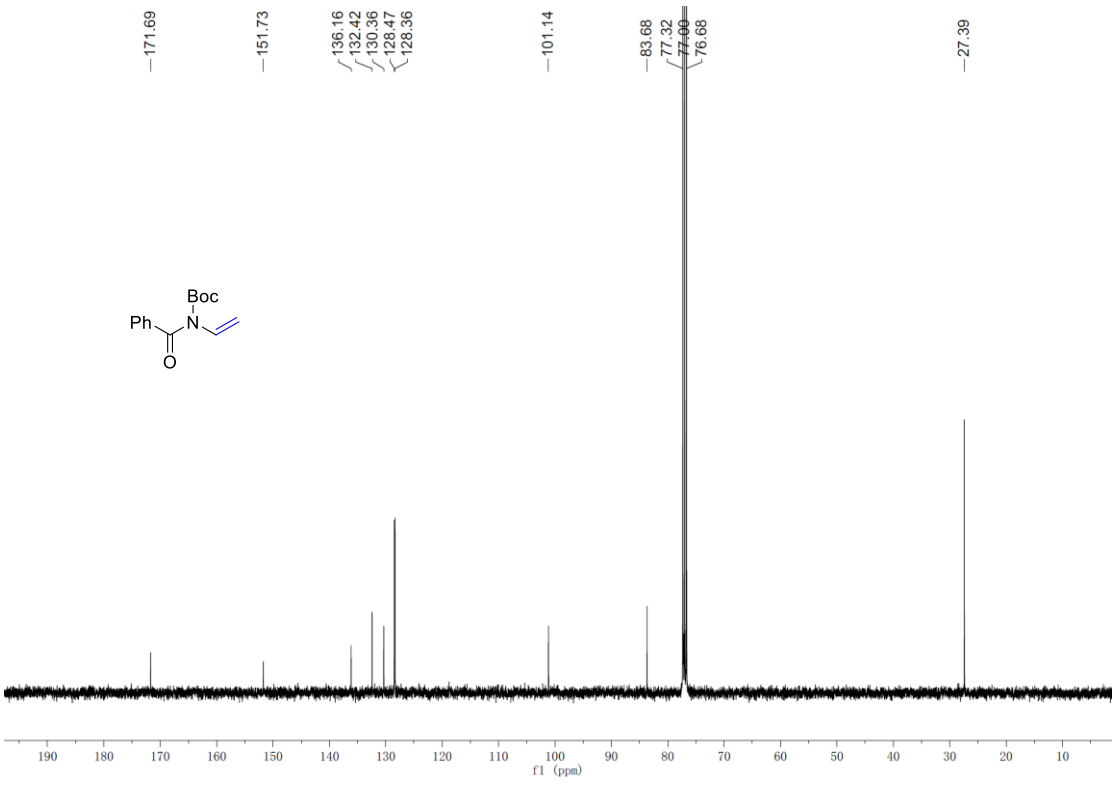
(1-(3,4-dimethoxybenzyl)-6,7-dimethoxyisoquinolin-2(1H)-yl)(phenyl)methanone (54)



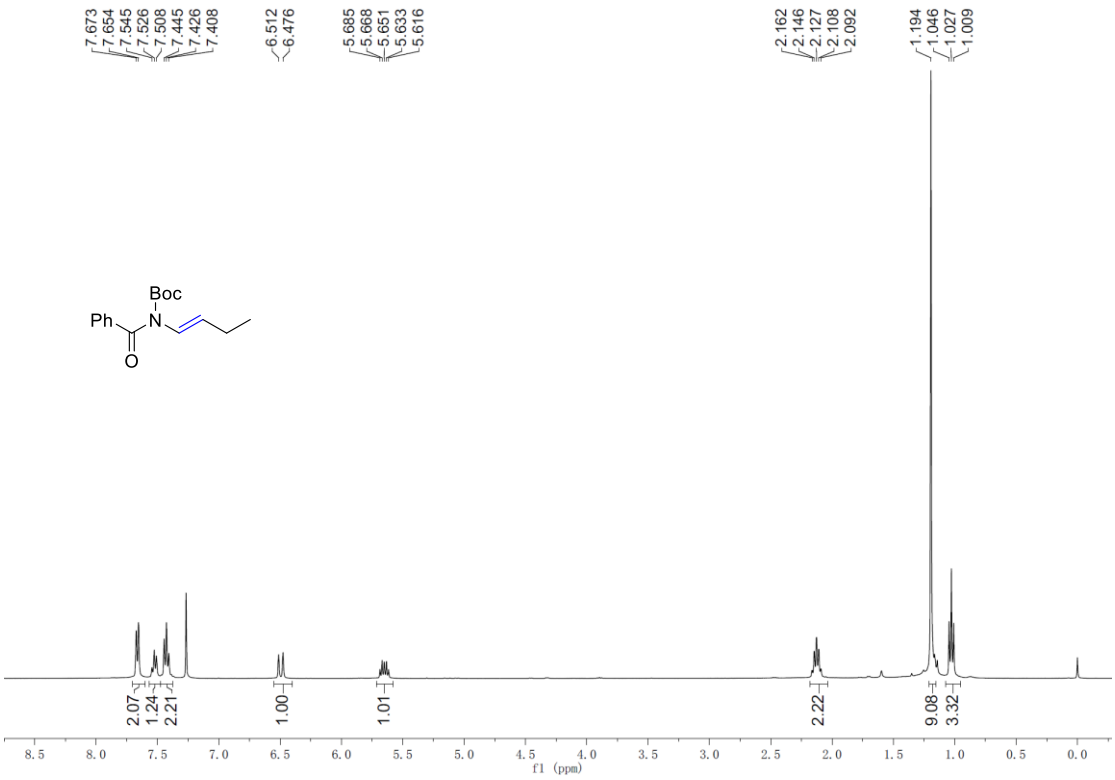


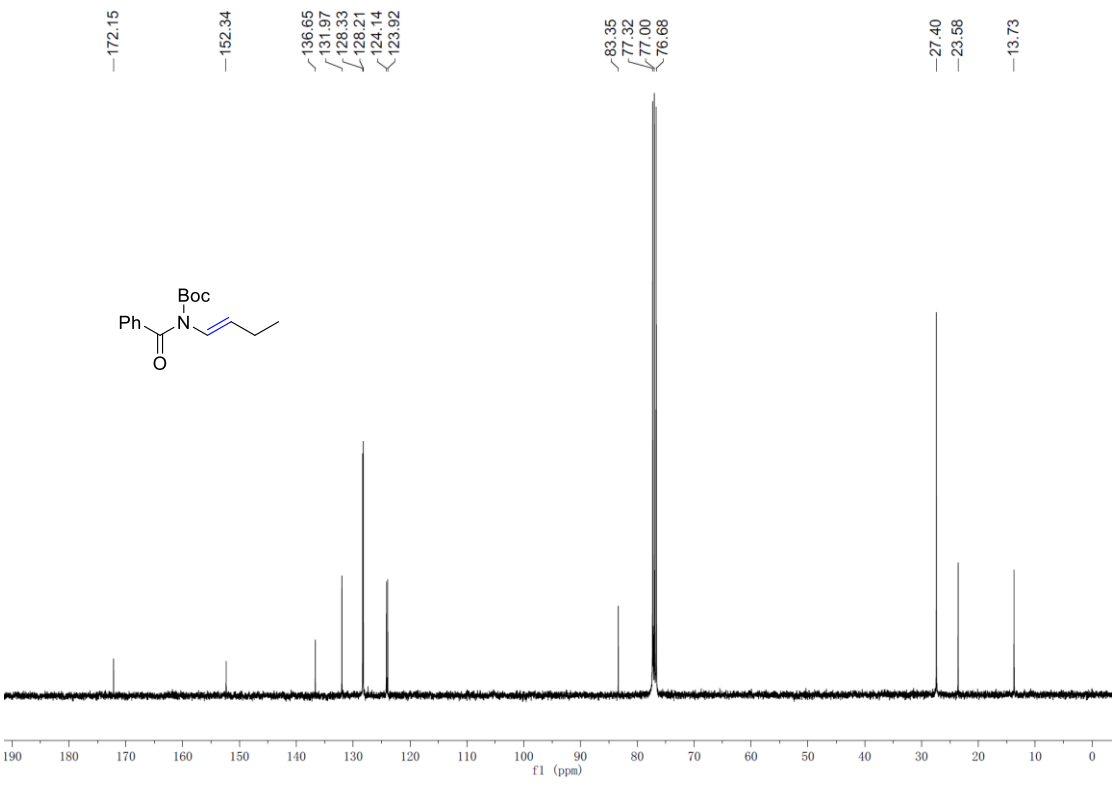
tert-butyl benzoyl(vinyl)carbamate (55)



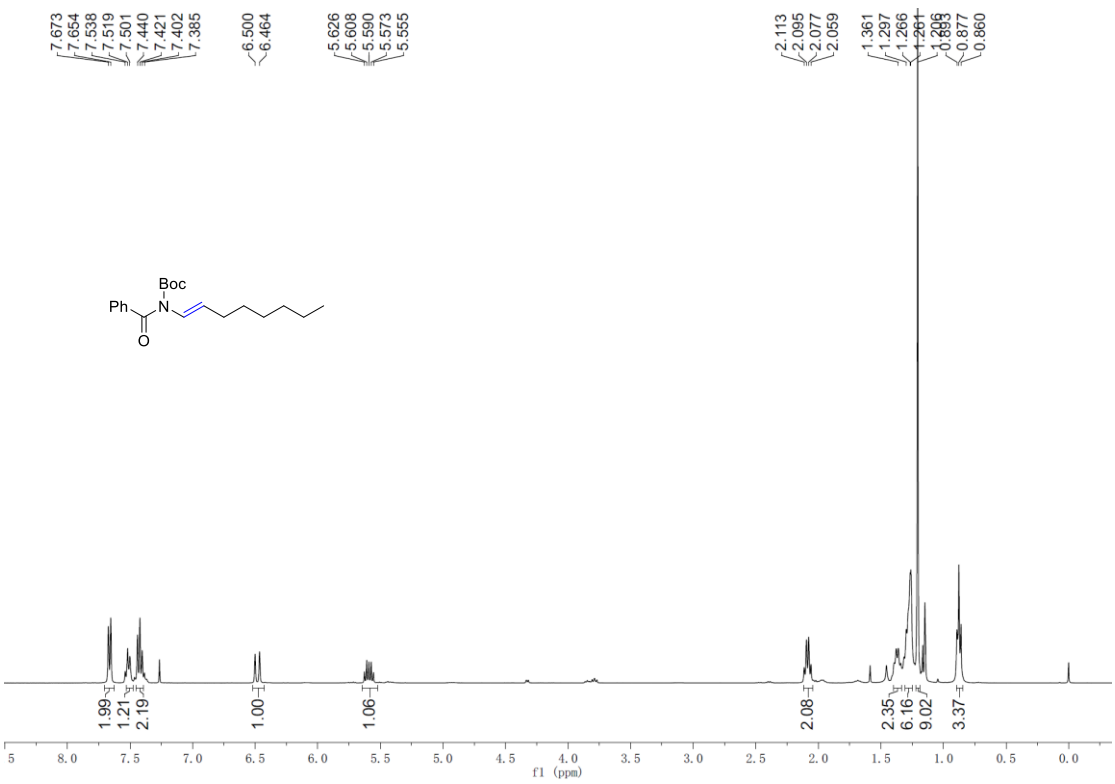


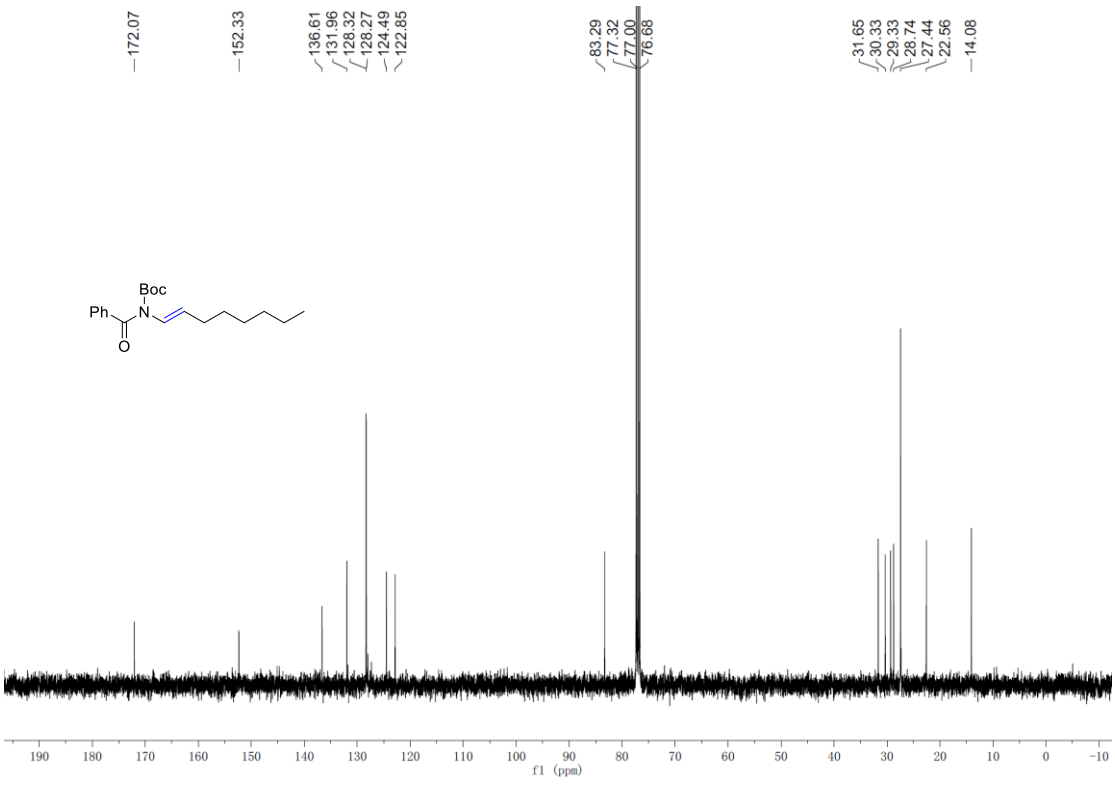
tert-butyl (E)-benzoyl(but-1-en-1-yl)carbamate (56)



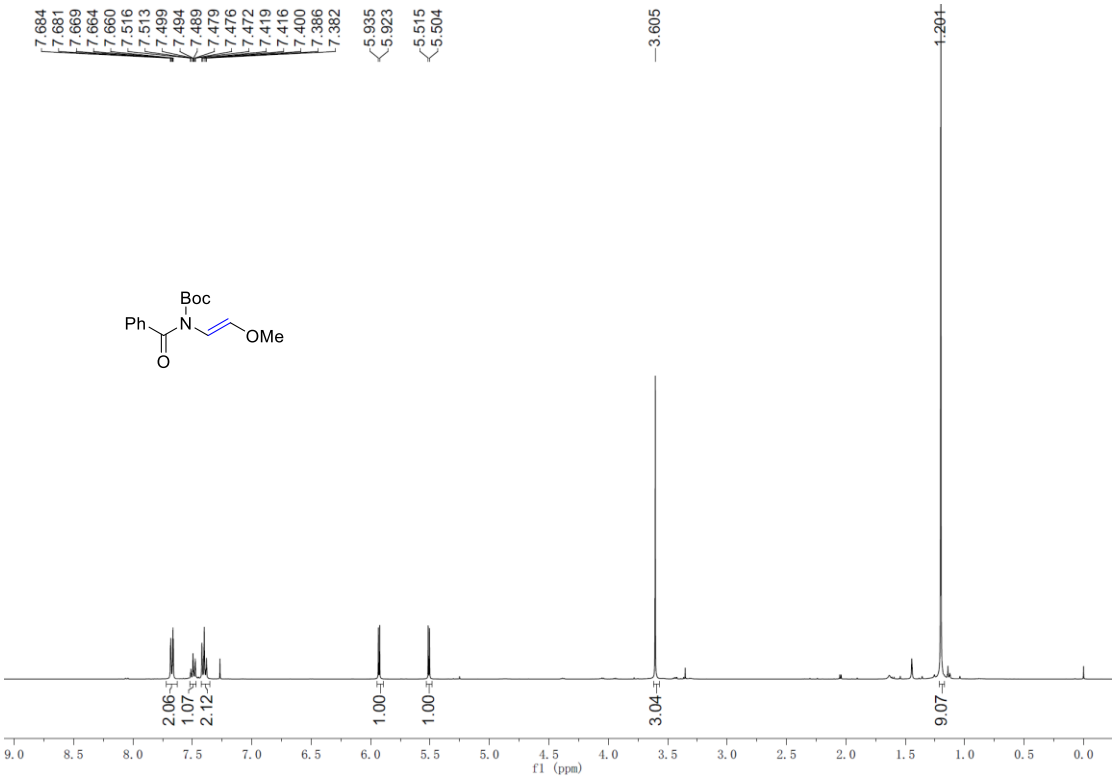


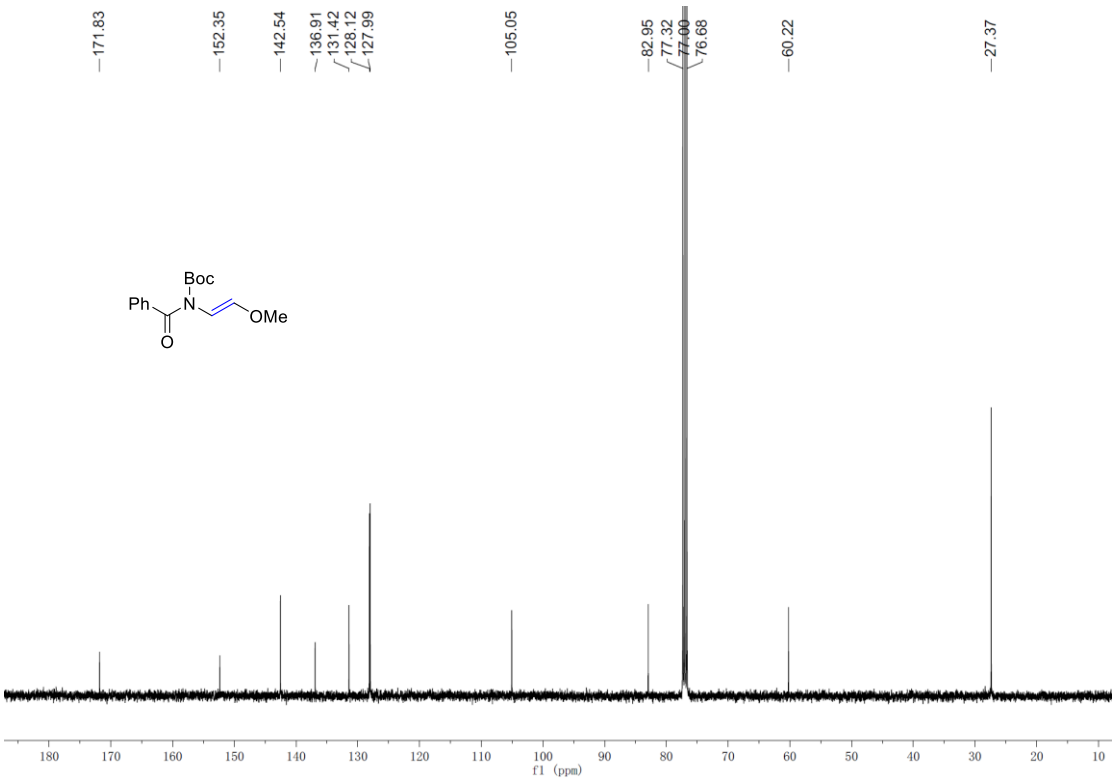
tert-butyl (E)-benzoyl(oct-1-en-1-yl)carbamate (57)



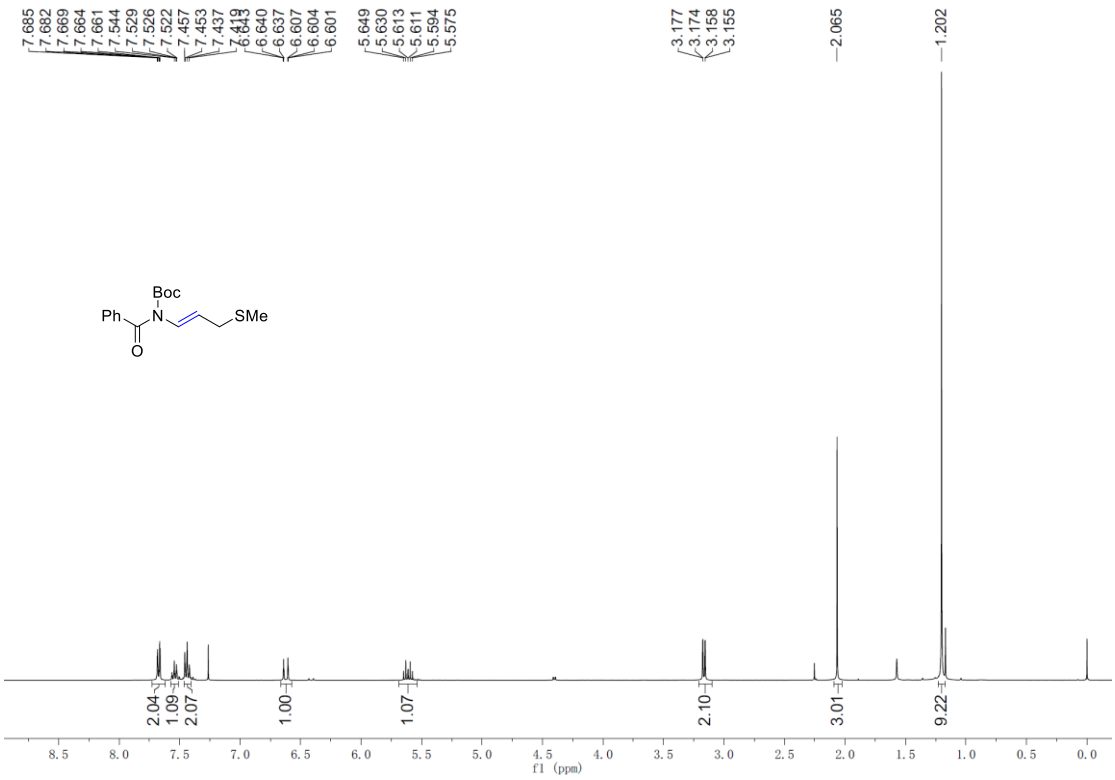


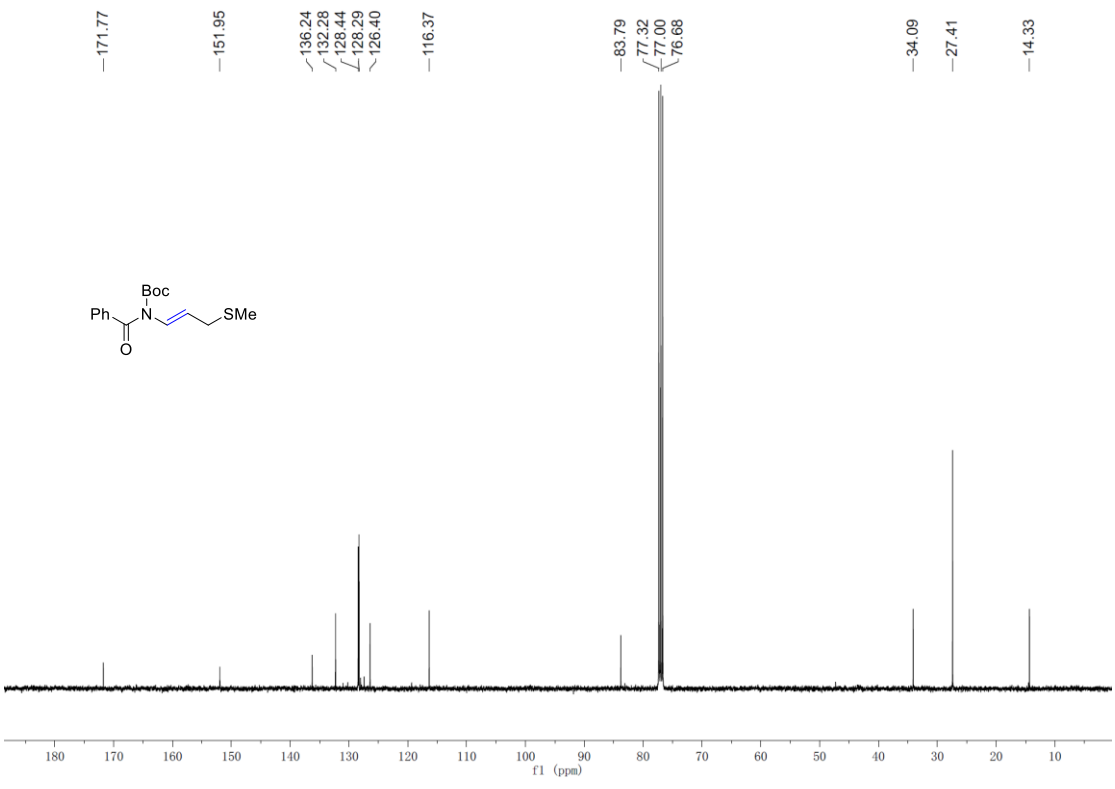
tert-butyl (E)-benzoyl(2-methoxyvinyl)carbamate (58)



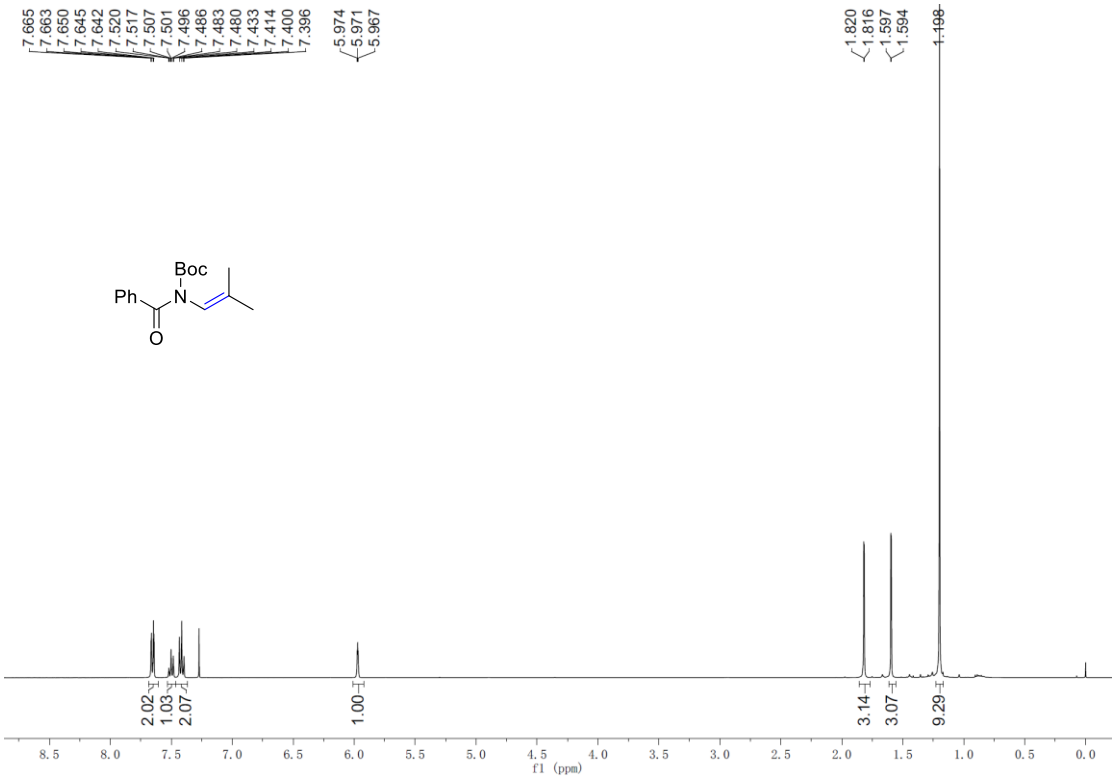


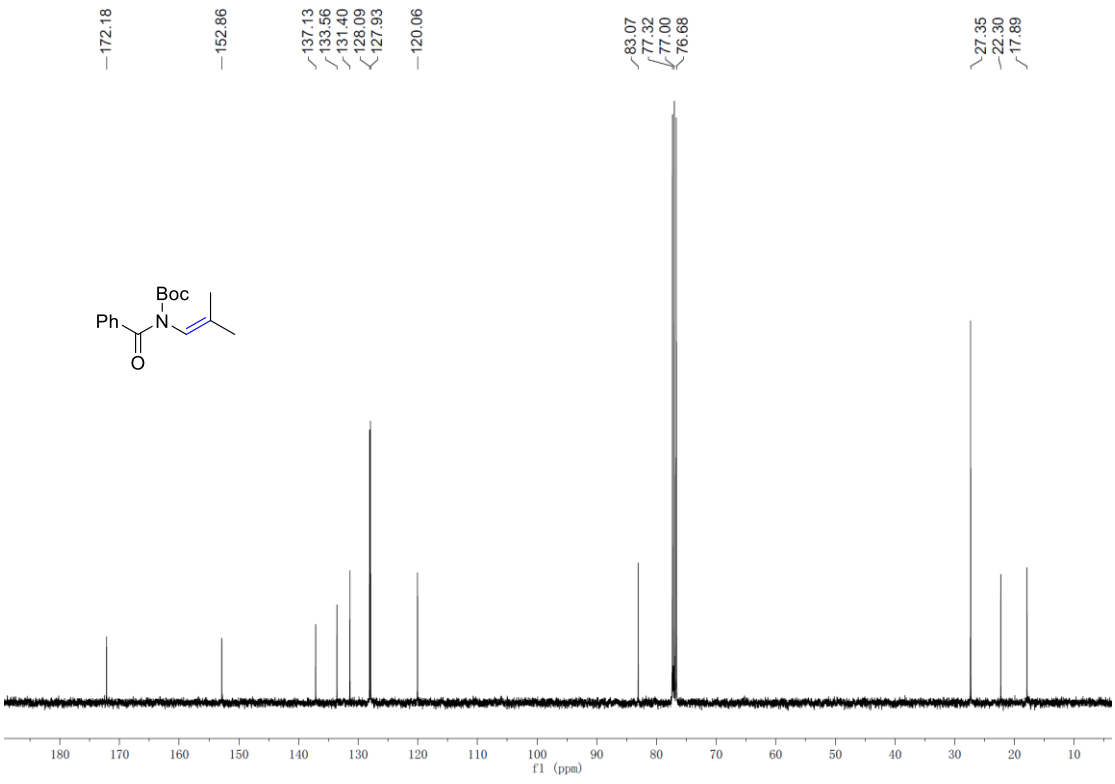
tert-butyl (E)-benzoyl(3-(methylthio)prop-1-en-1-yl)carbamate (59)



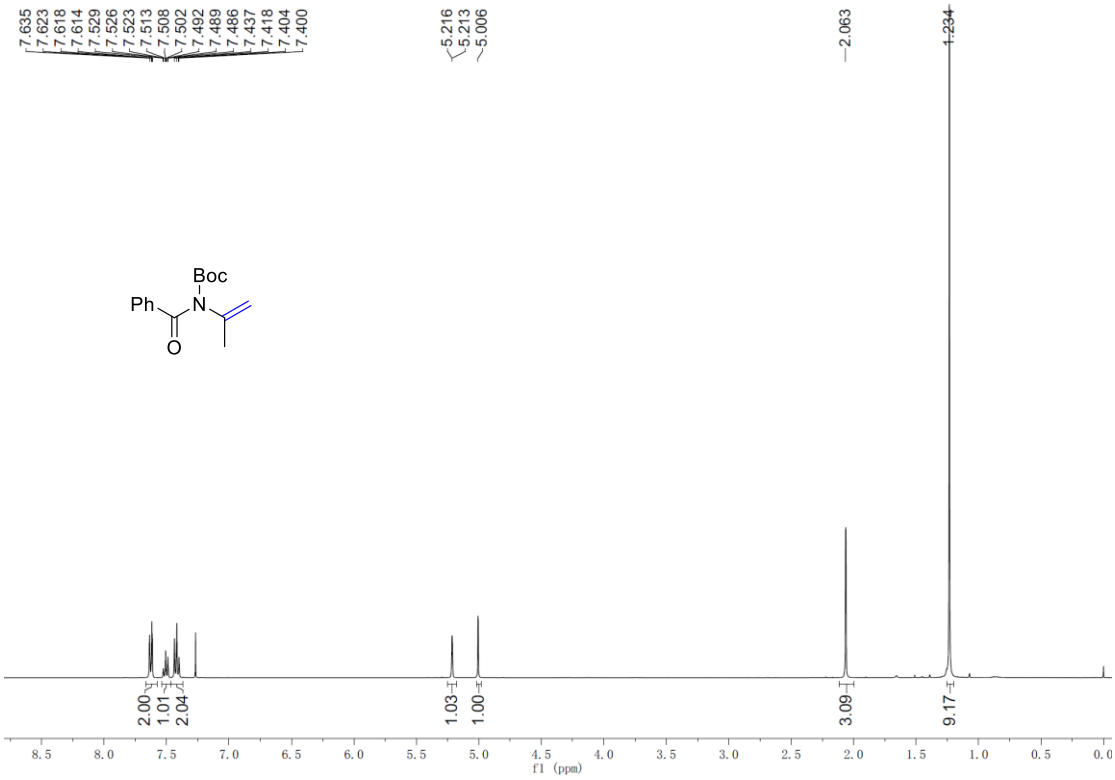


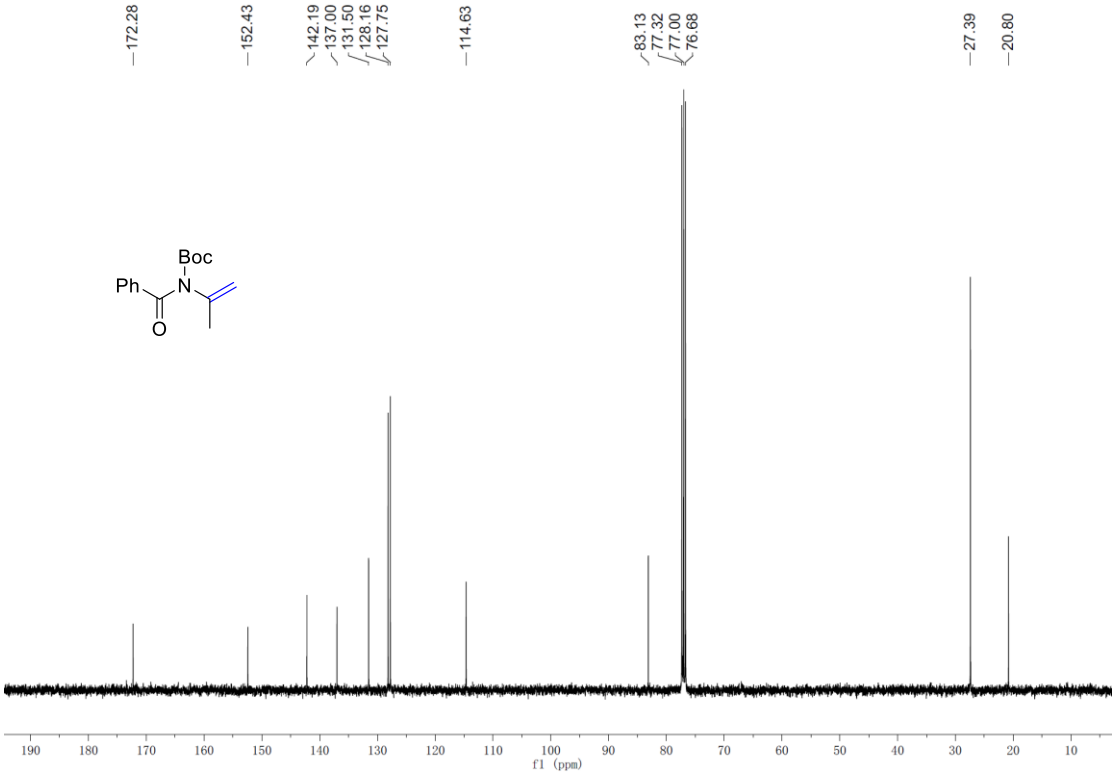
tert-butyl benzoyl(2-methylprop-1-en-1-yl)carbamate (60)



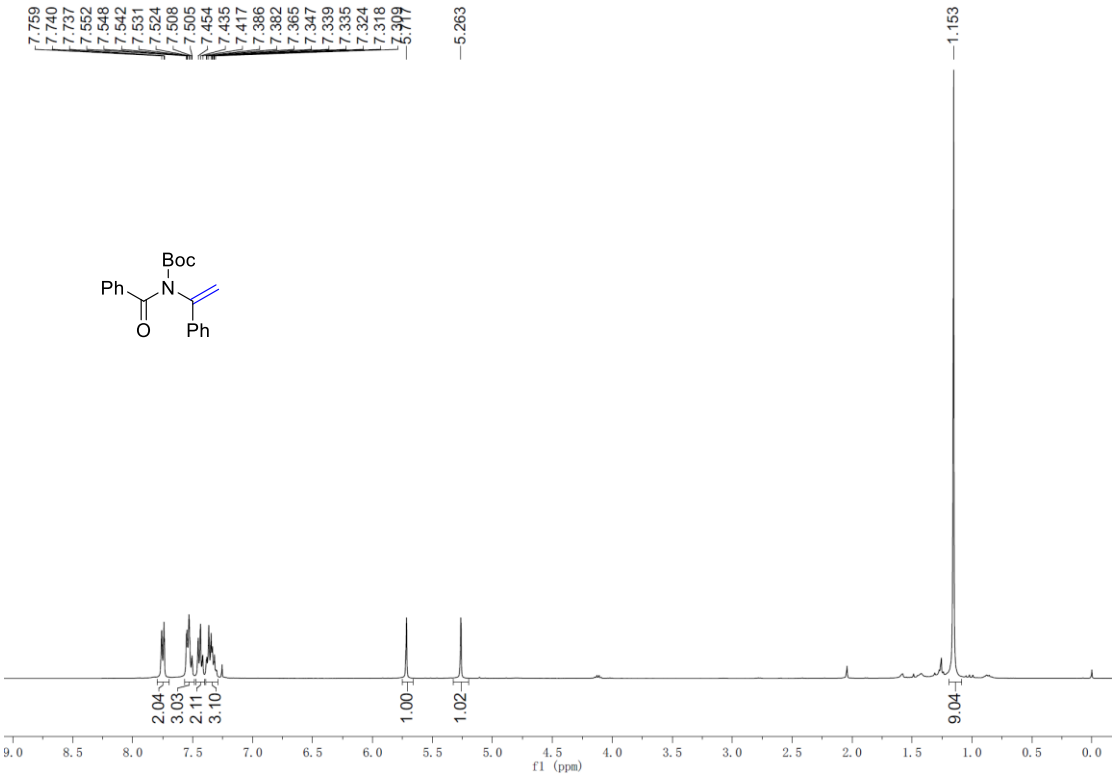


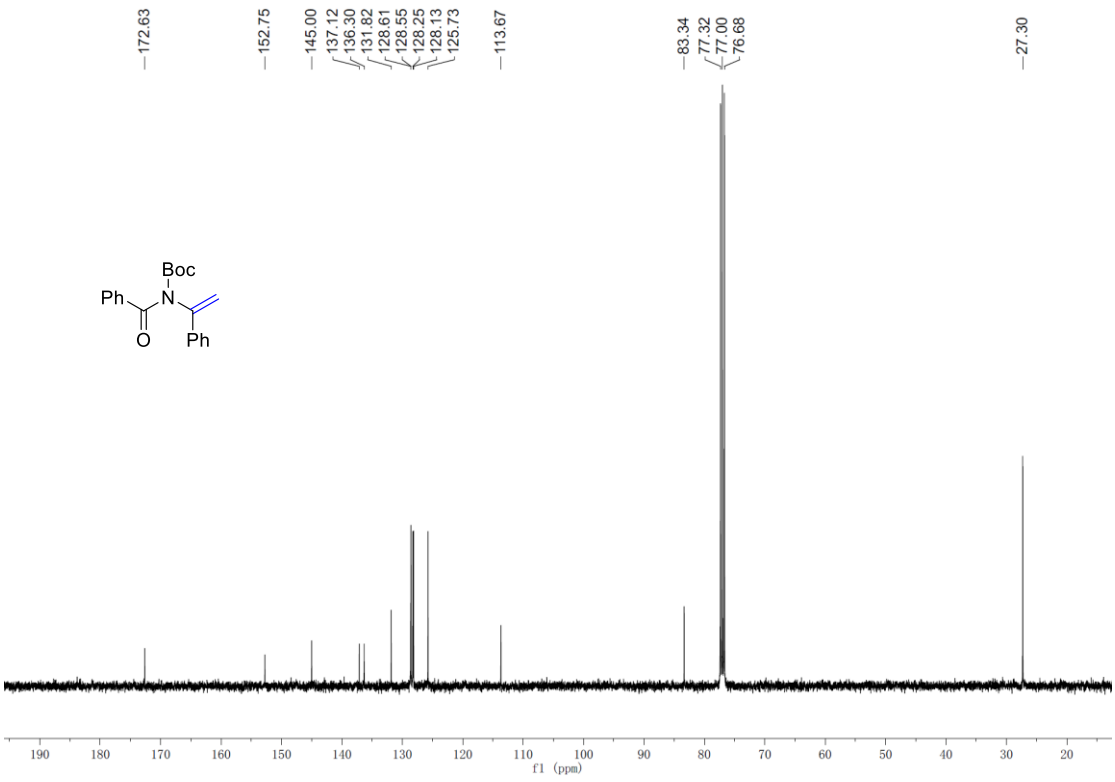
tert-butyl benzoyl(prop-1-en-2-yl)carbamate (61)



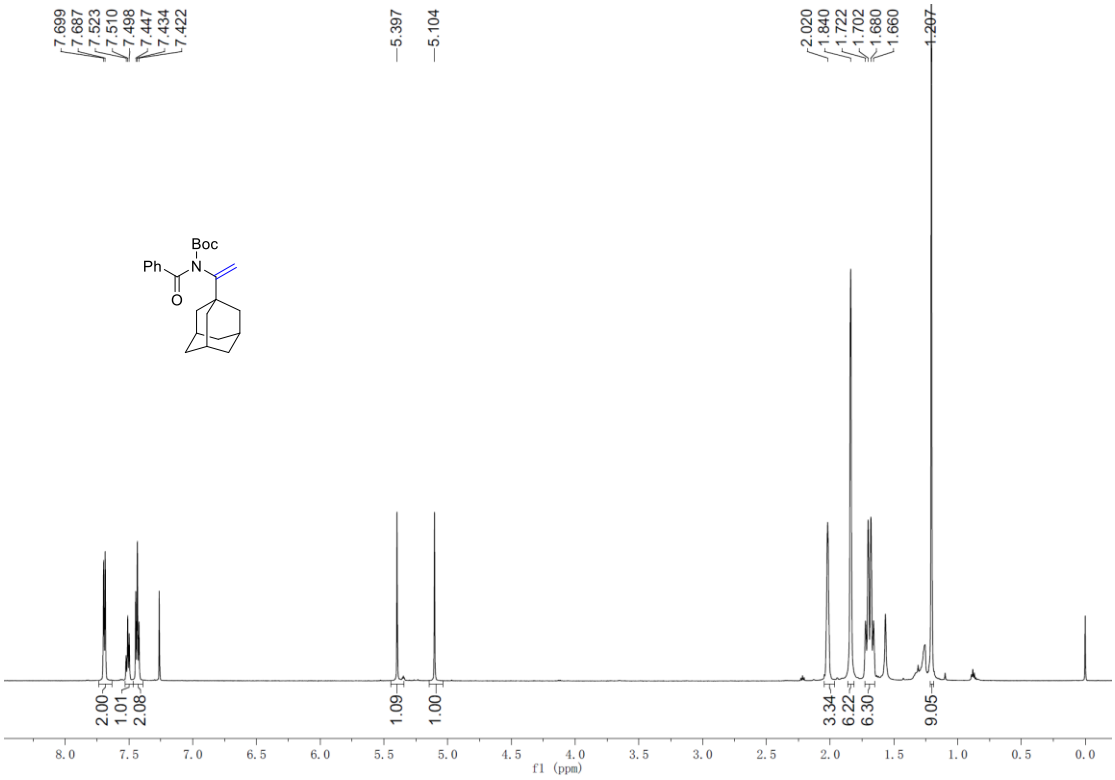


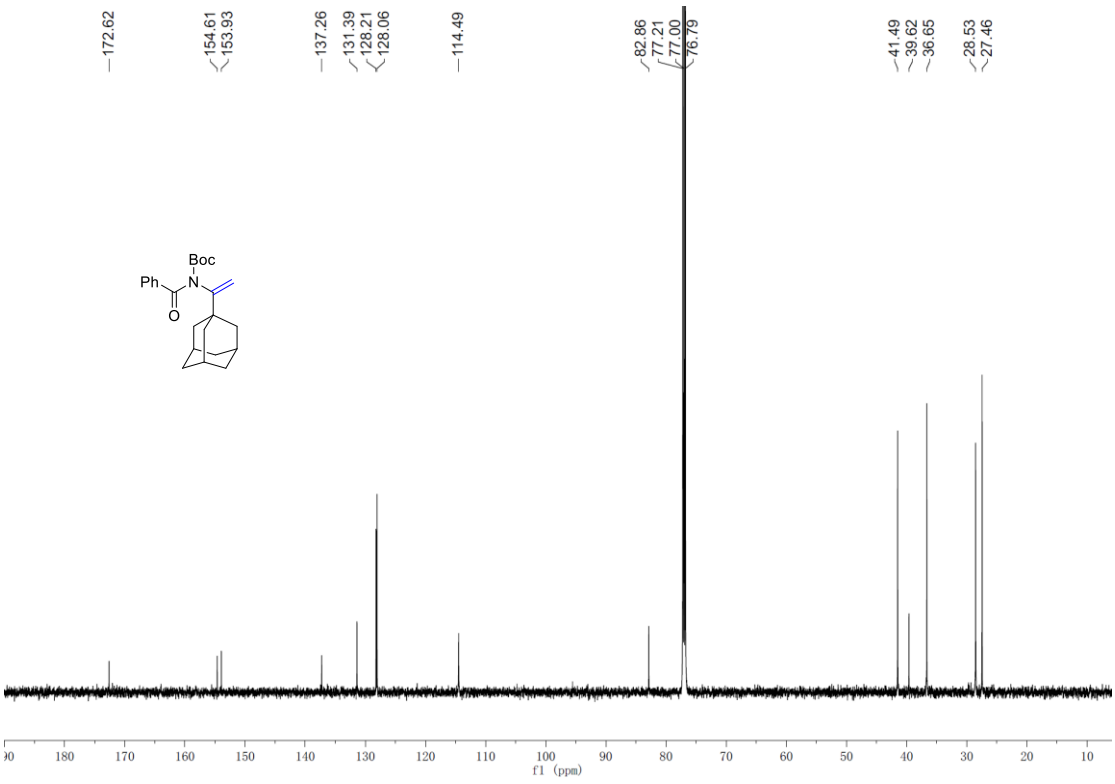
tert-butyl benzoyl(1-phenylvinyl)carbamate (62)



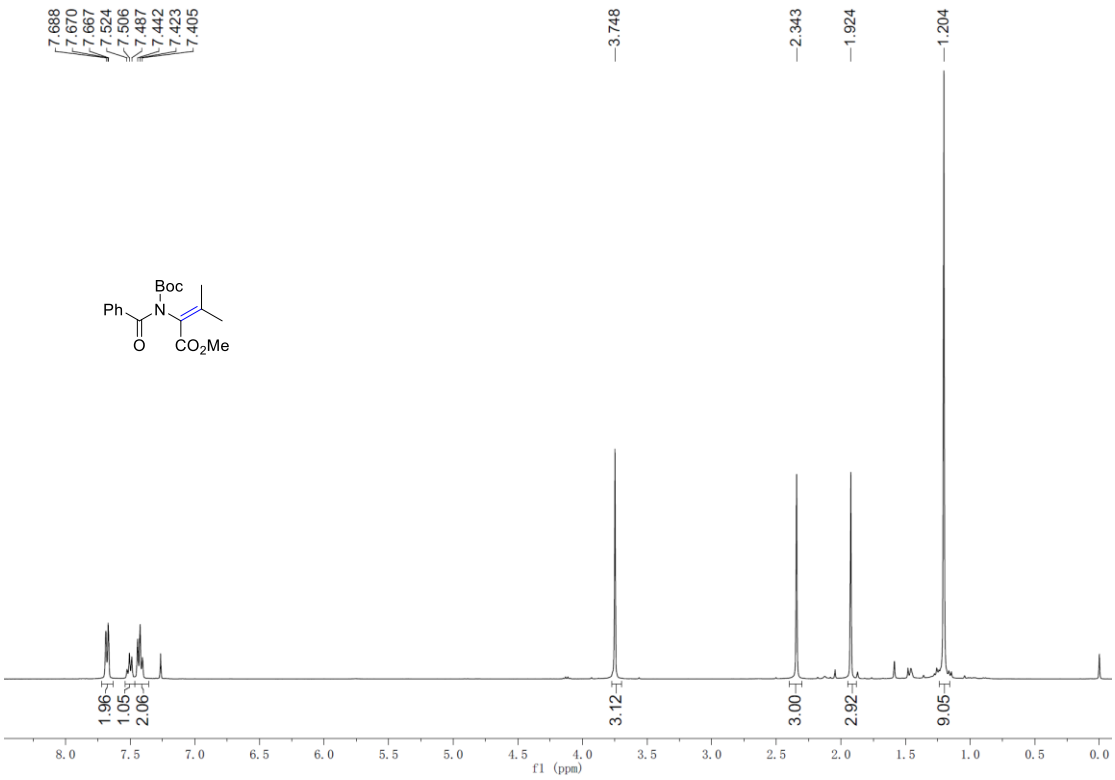


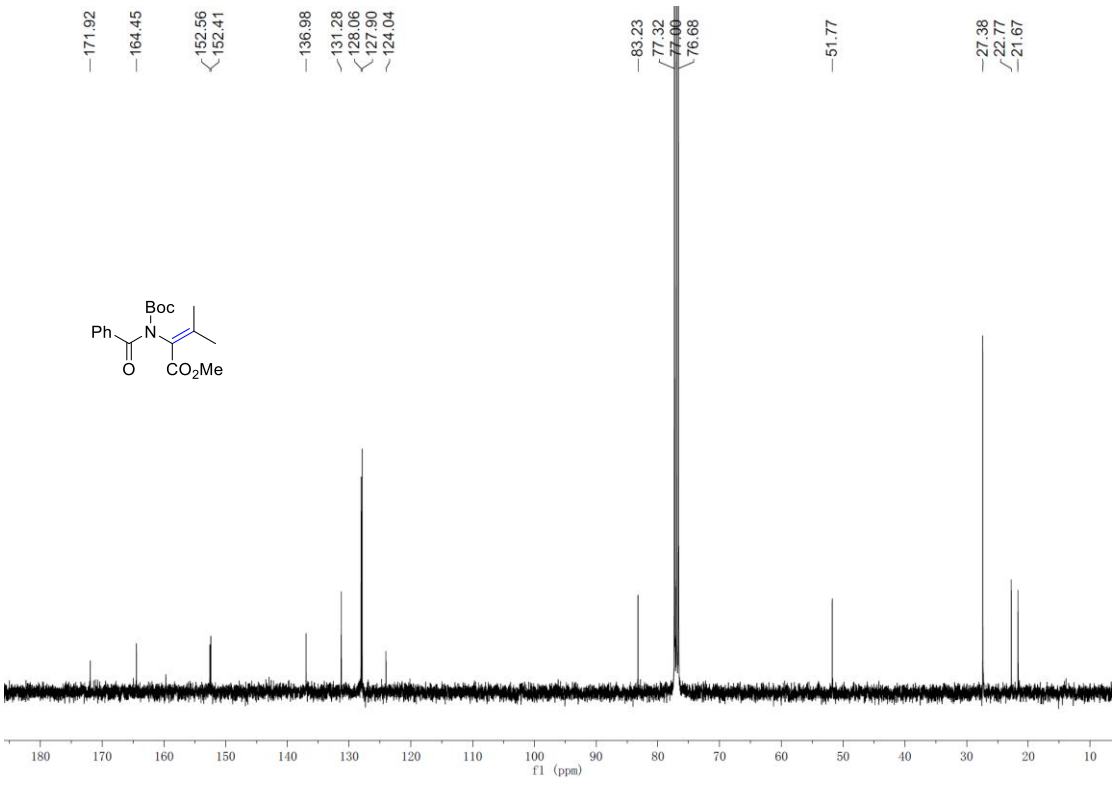
tert-butyl (1-(adamantan-1-yl)vinyl)(benzoyl)carbamate (63)



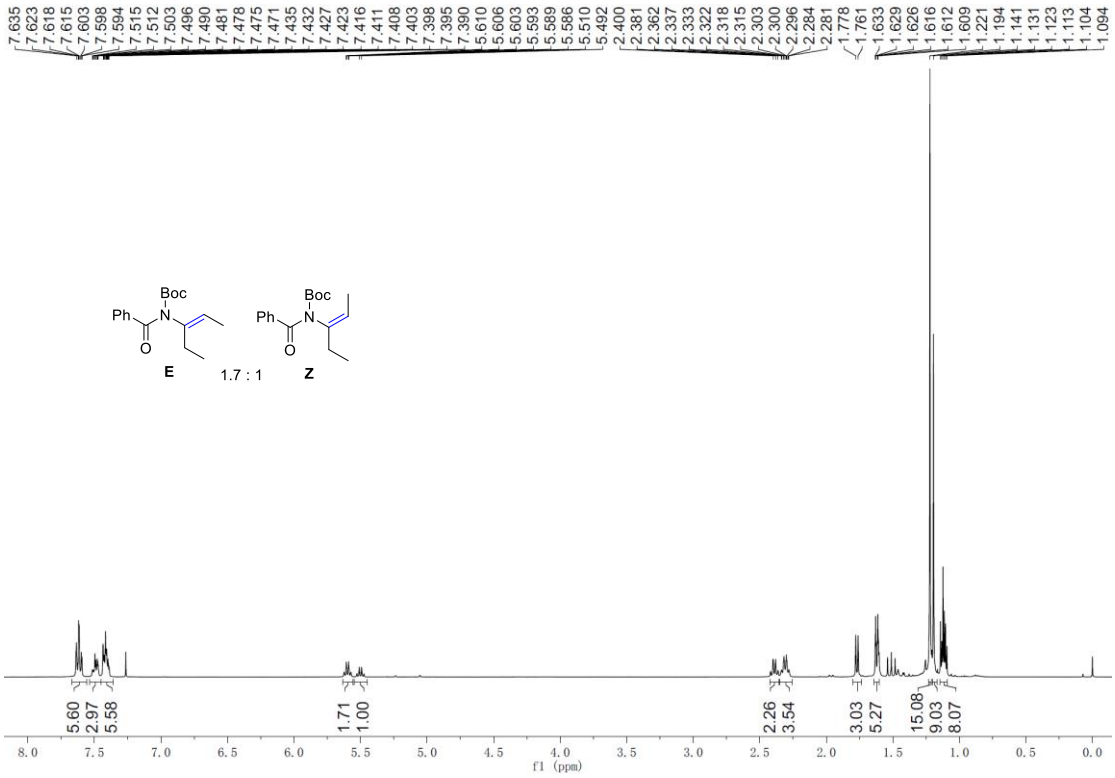


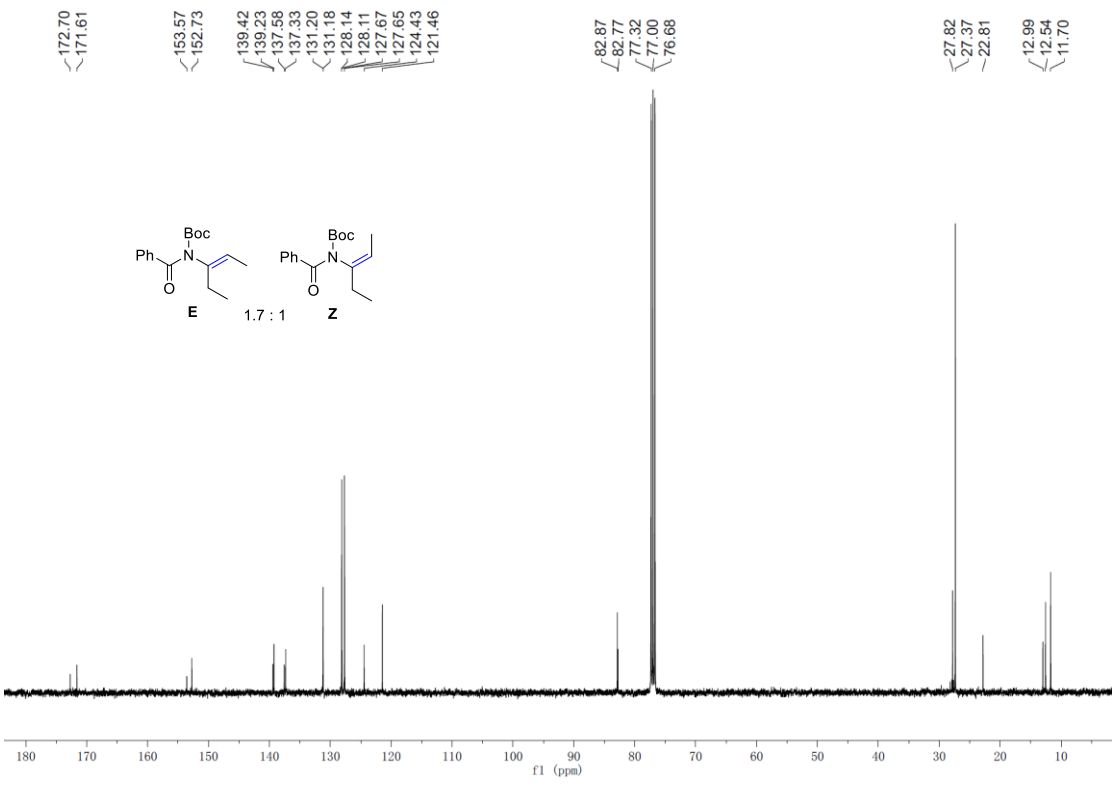
methyl 2-(N-(tert-butoxycarbonyl)benzamido)-3-methylbut-2-enoate (64)



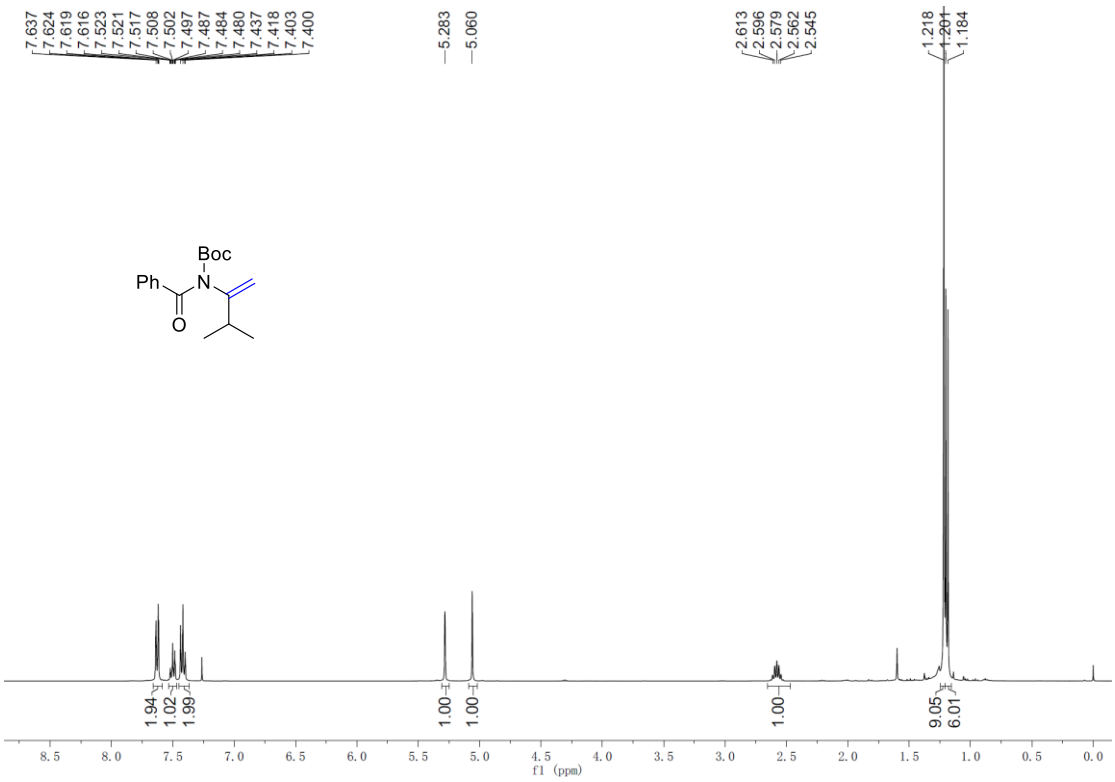


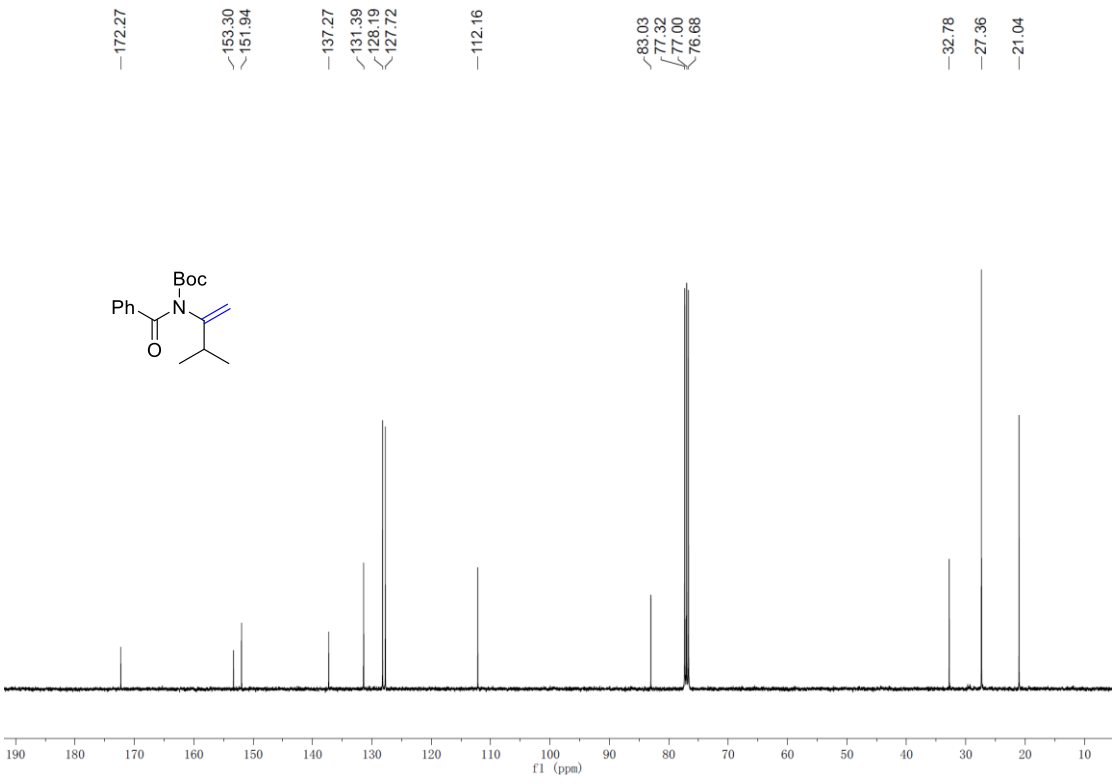
tert-butyl benzoyl(pent-2-en-3-yl)carbamate (65)



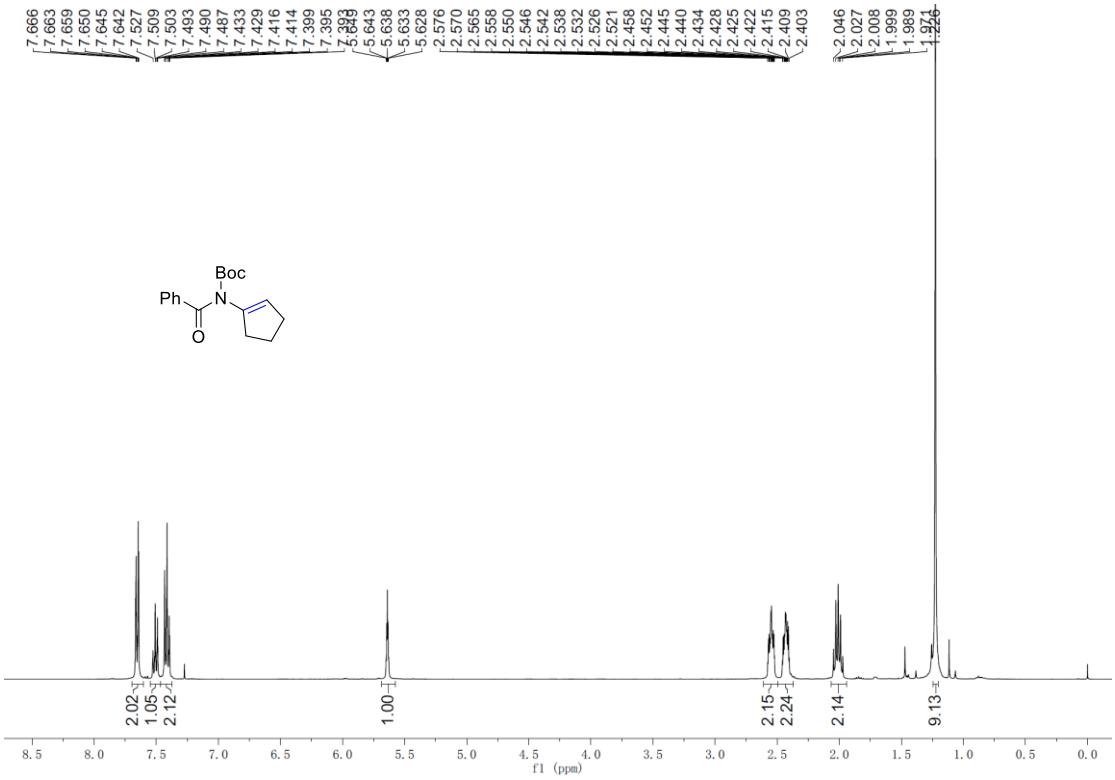


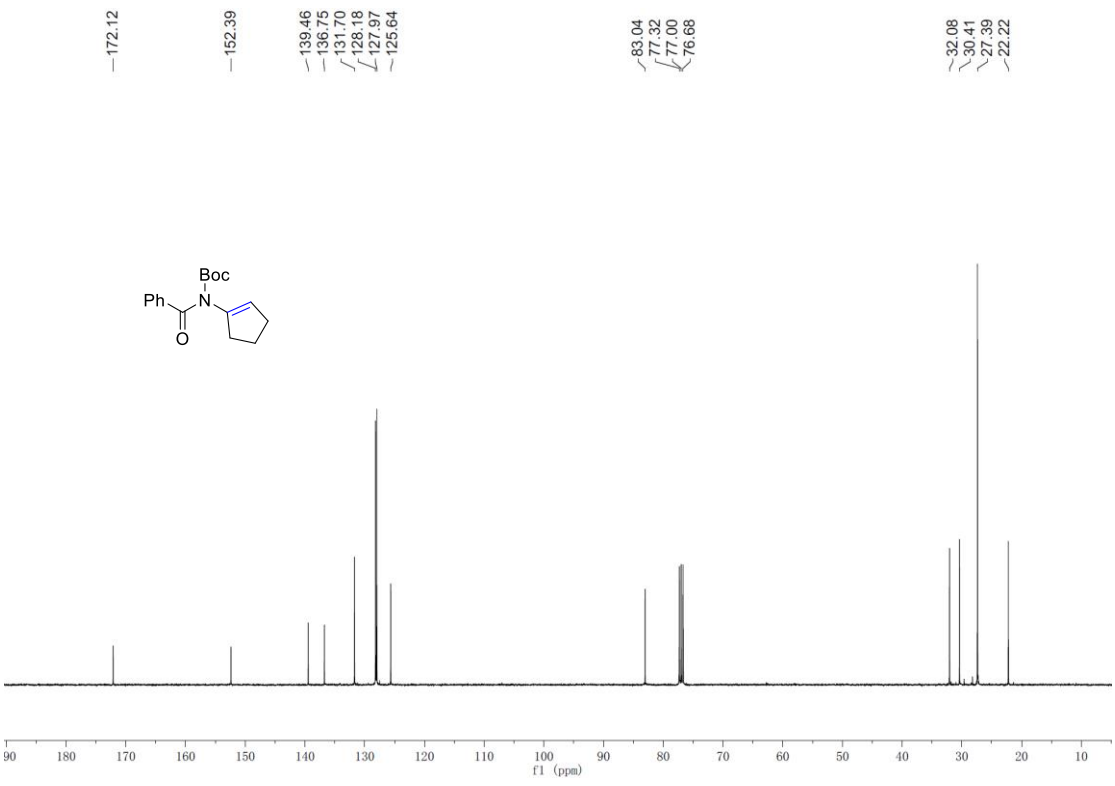
tert-butyl benzoyl(3-methylbut-1-en-2-yl)carbamate (66)



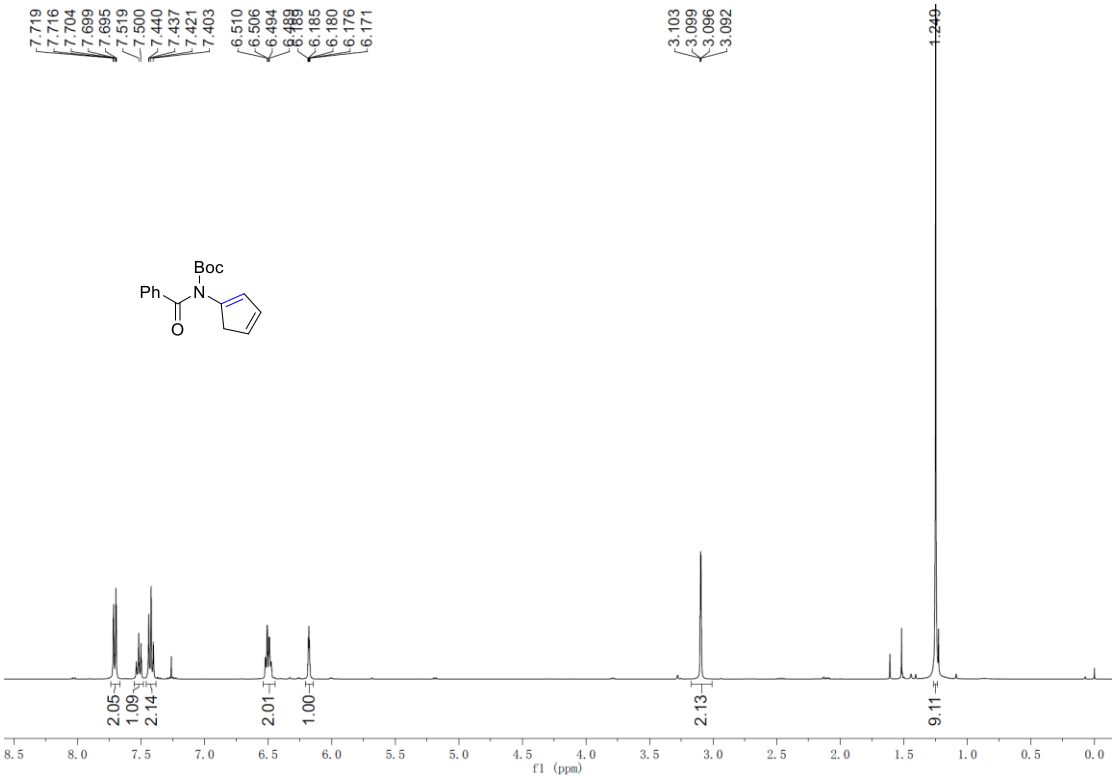


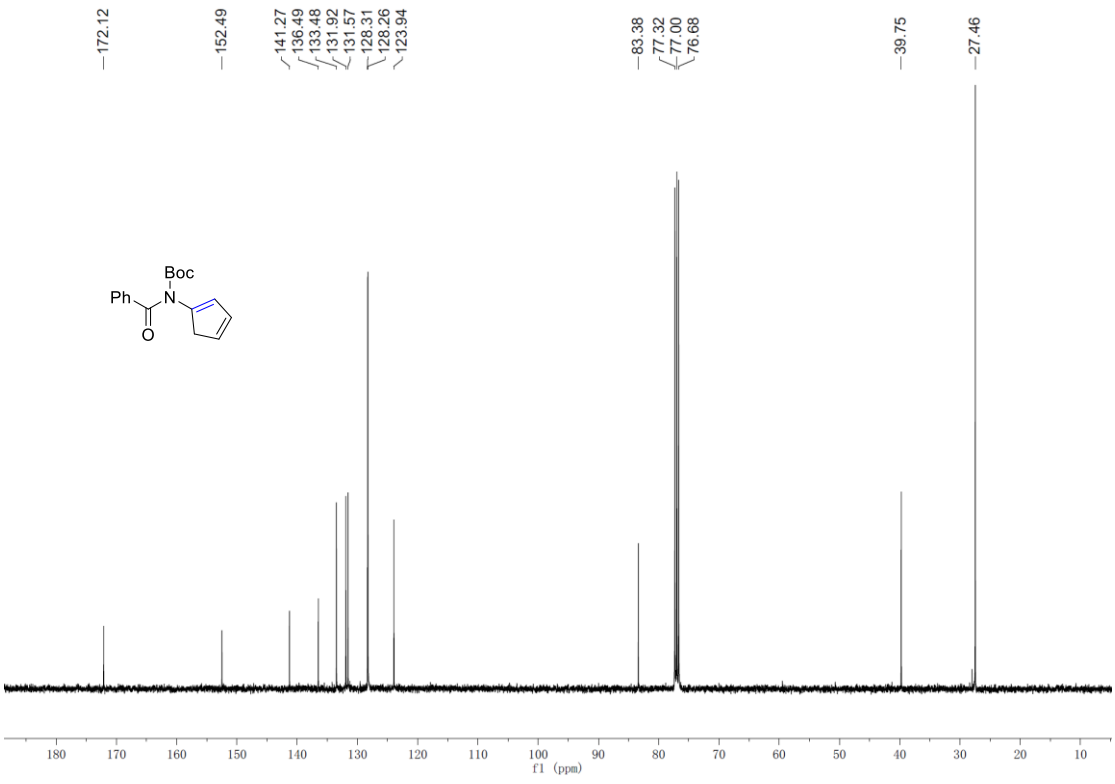
tert-butyl benzoyl(cyclopent-1-en-1-yl)carbamate (67)



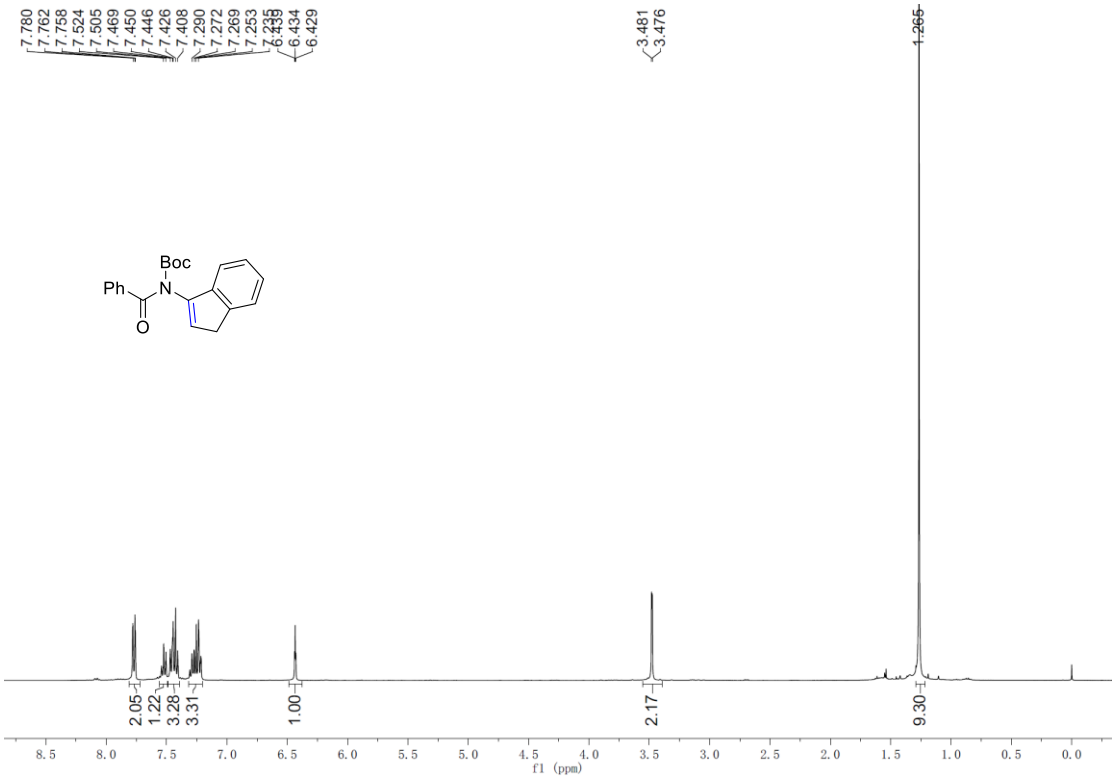


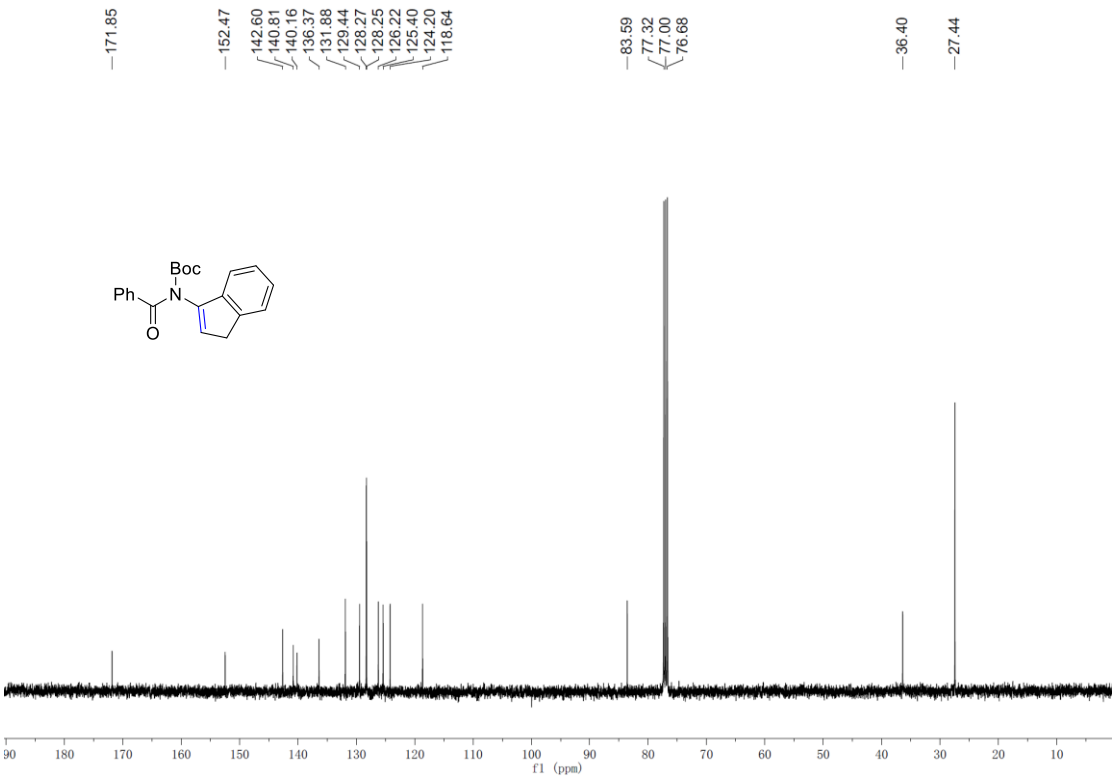
tert-butyl benzoyl(cyclopenta-1,3-dien-1-yl)carbamate (68)



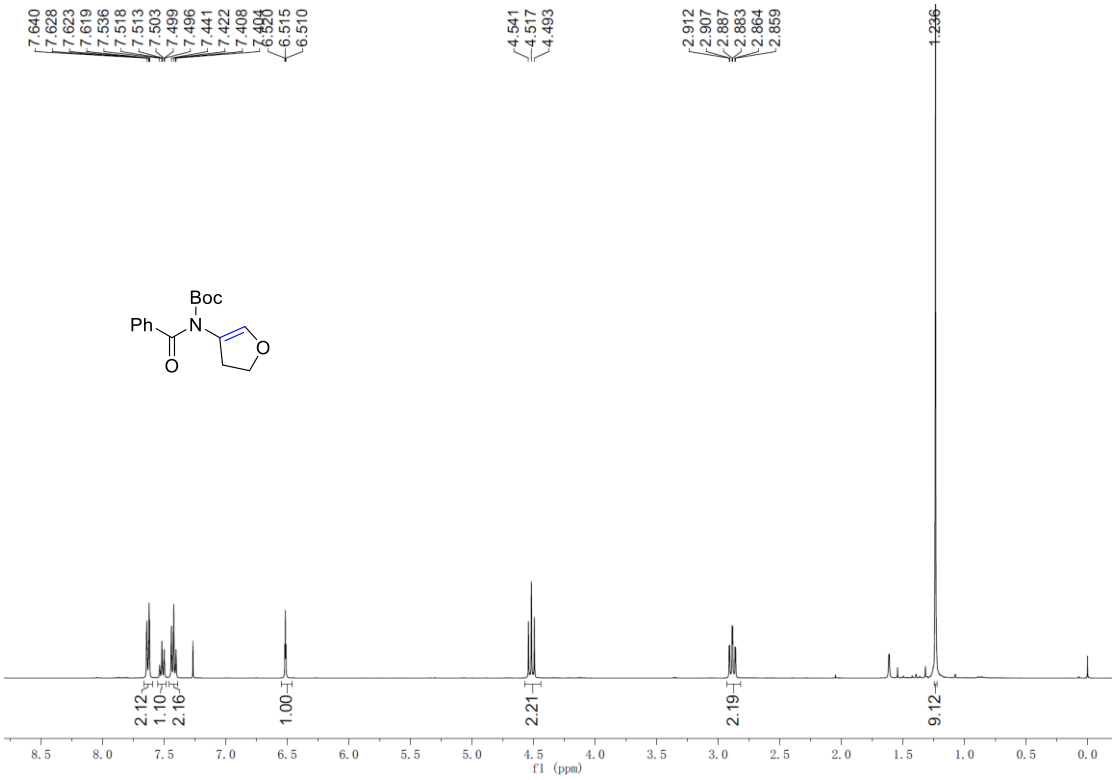


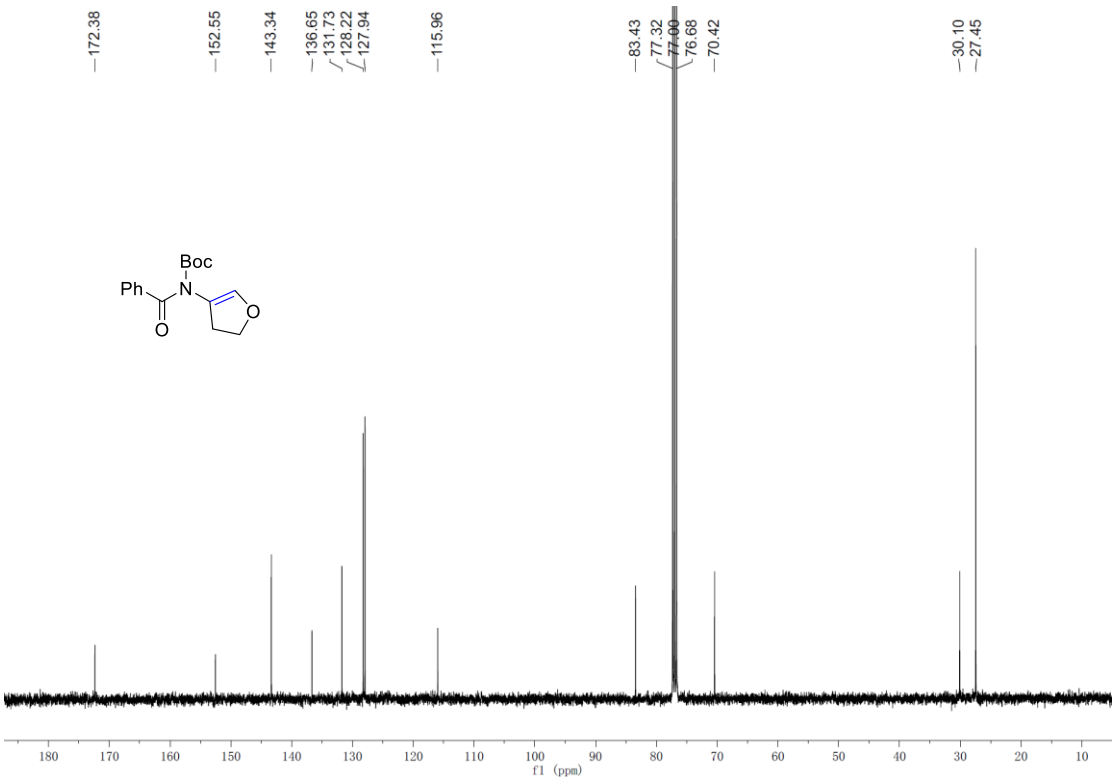
tert-butyl benzoyl(1H-inden-3-yl)carbamate (69)



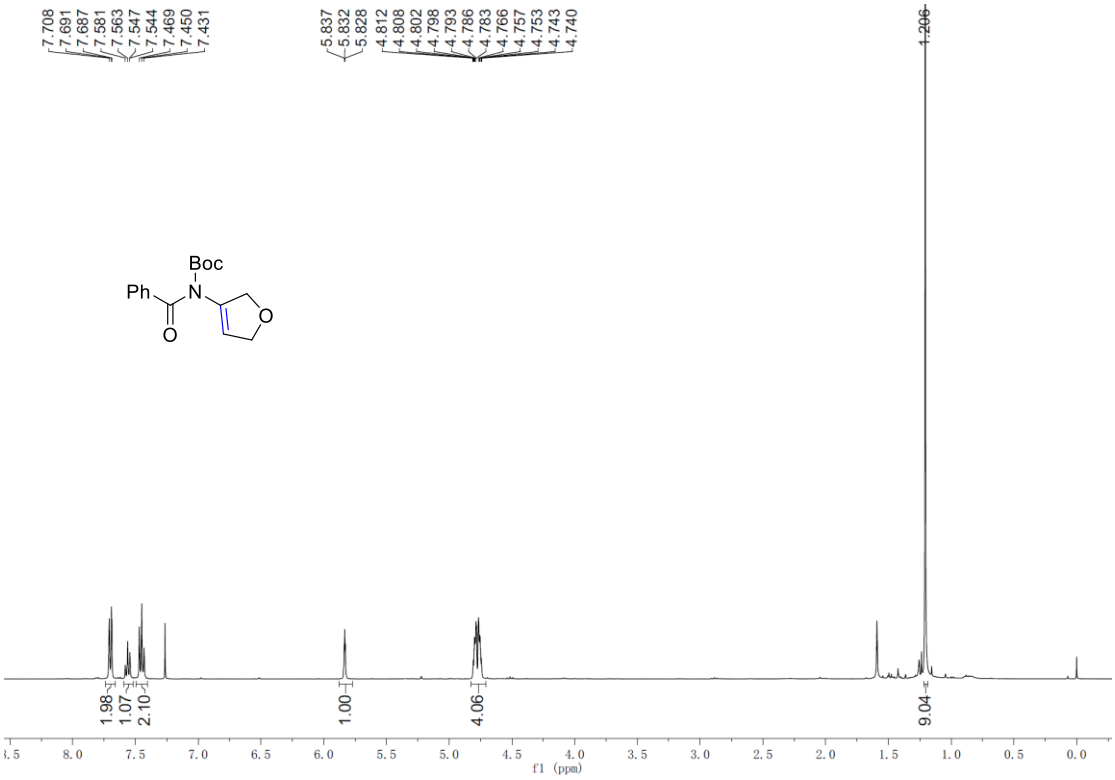


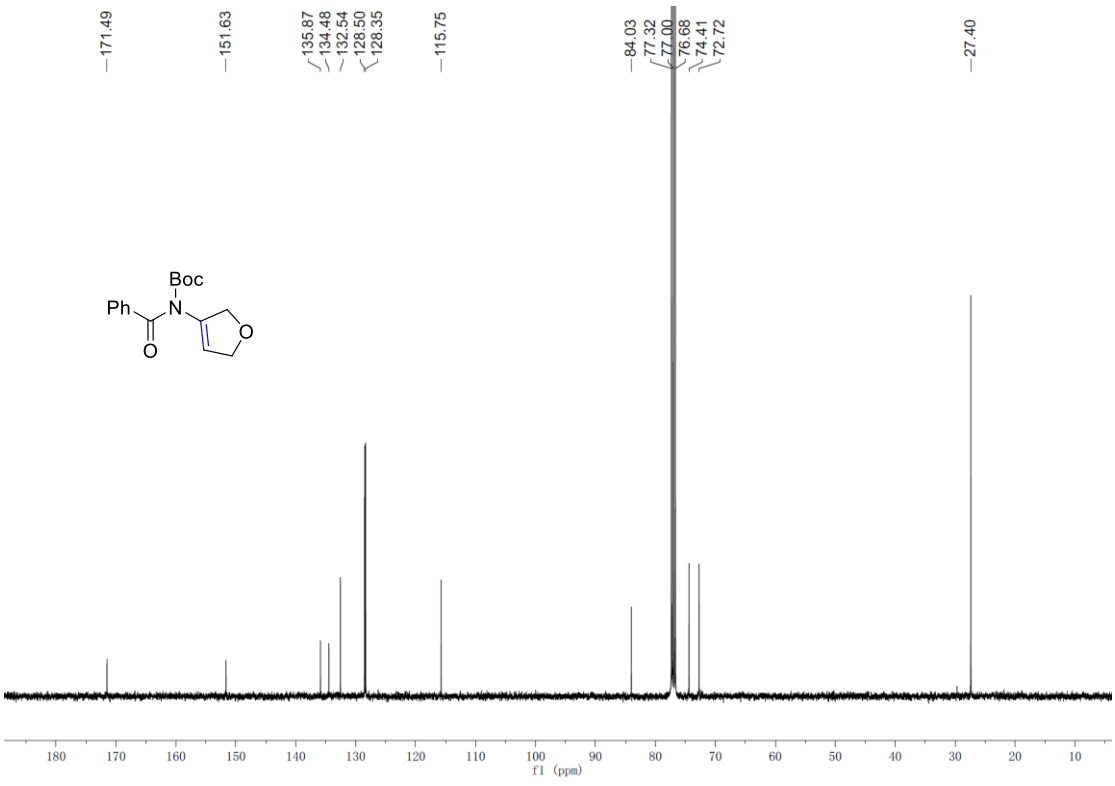
tert-butyl benzoyl(4,5-dihydrofuran-3-yl)carbamate (major-70)



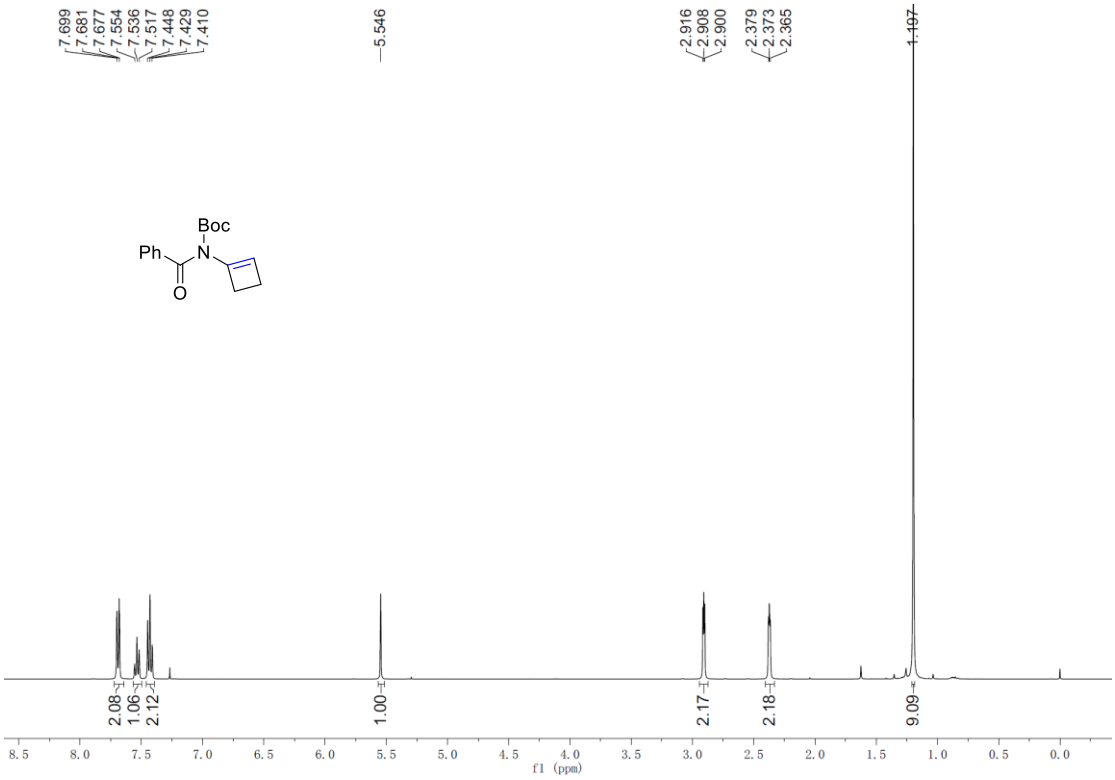


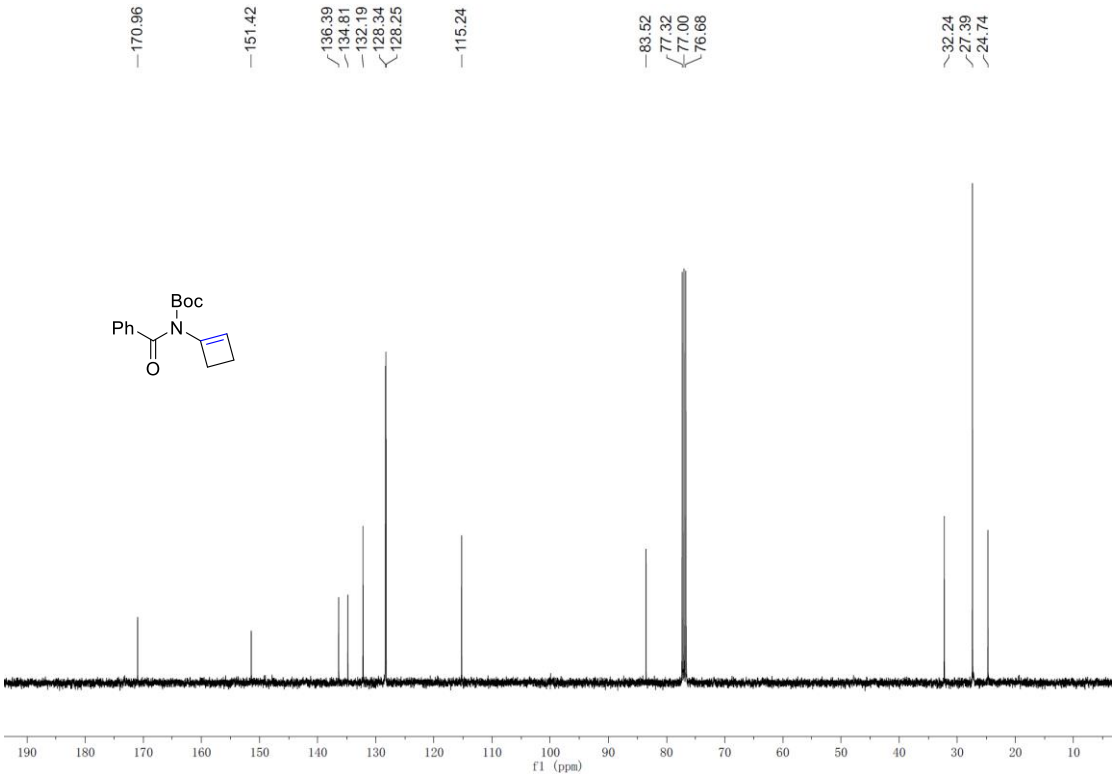
tert-butyl benzoyl(2,5-dihydrofuran-3-yl)carbamate (minor-70)



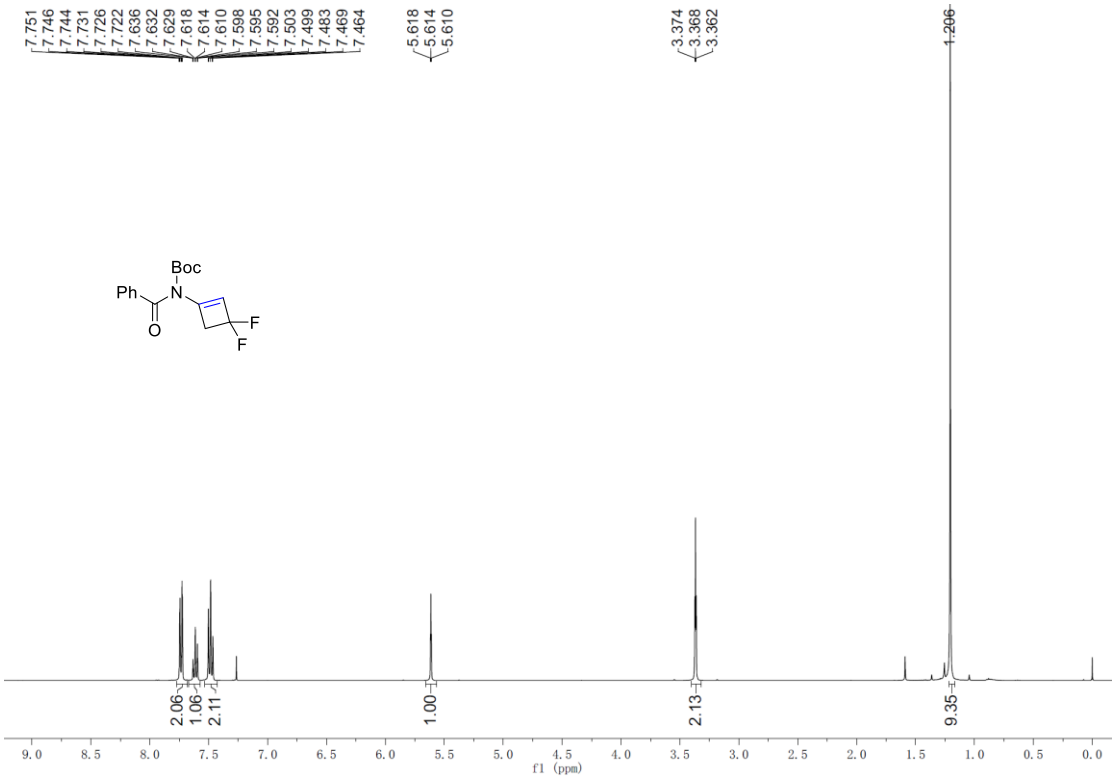


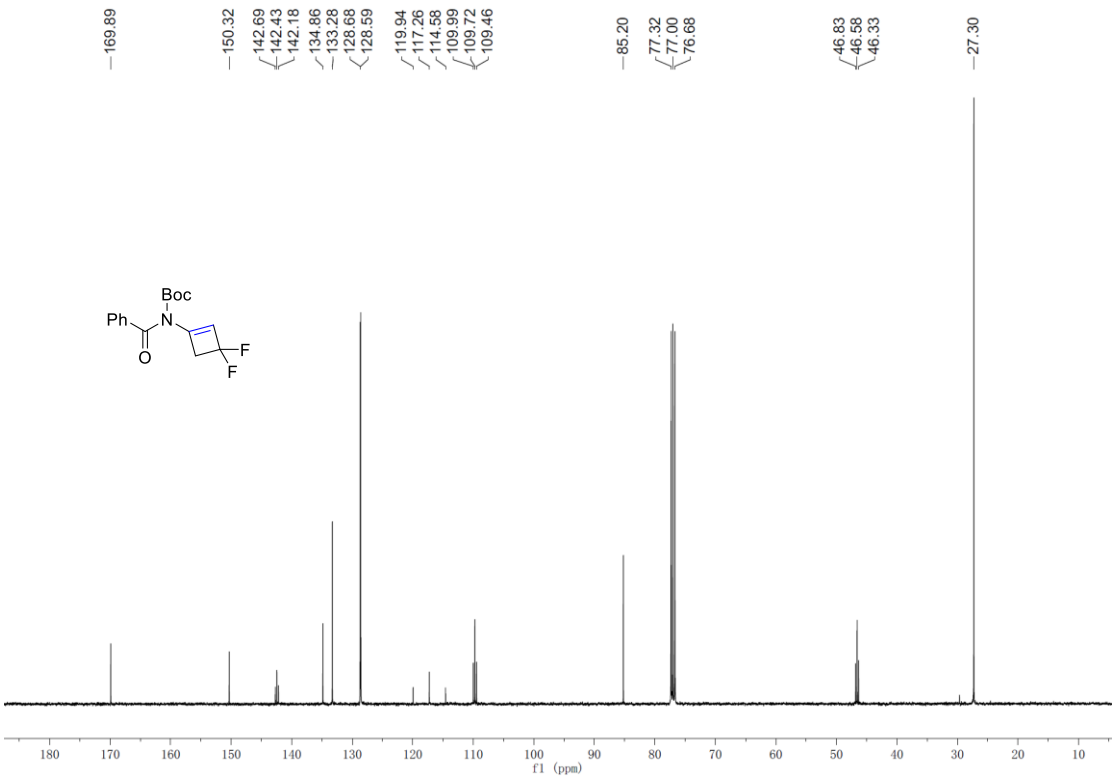
tert-butyl benzoyl(cyclobut-1-en-1-yl)carbamate (71)

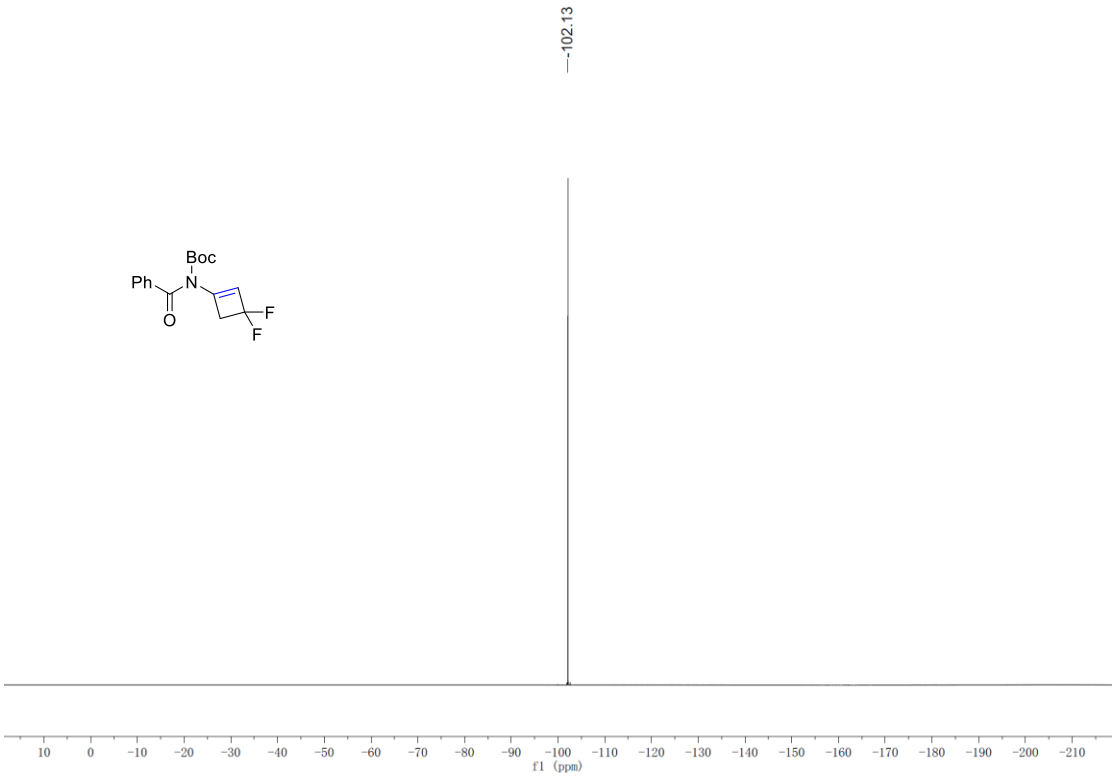




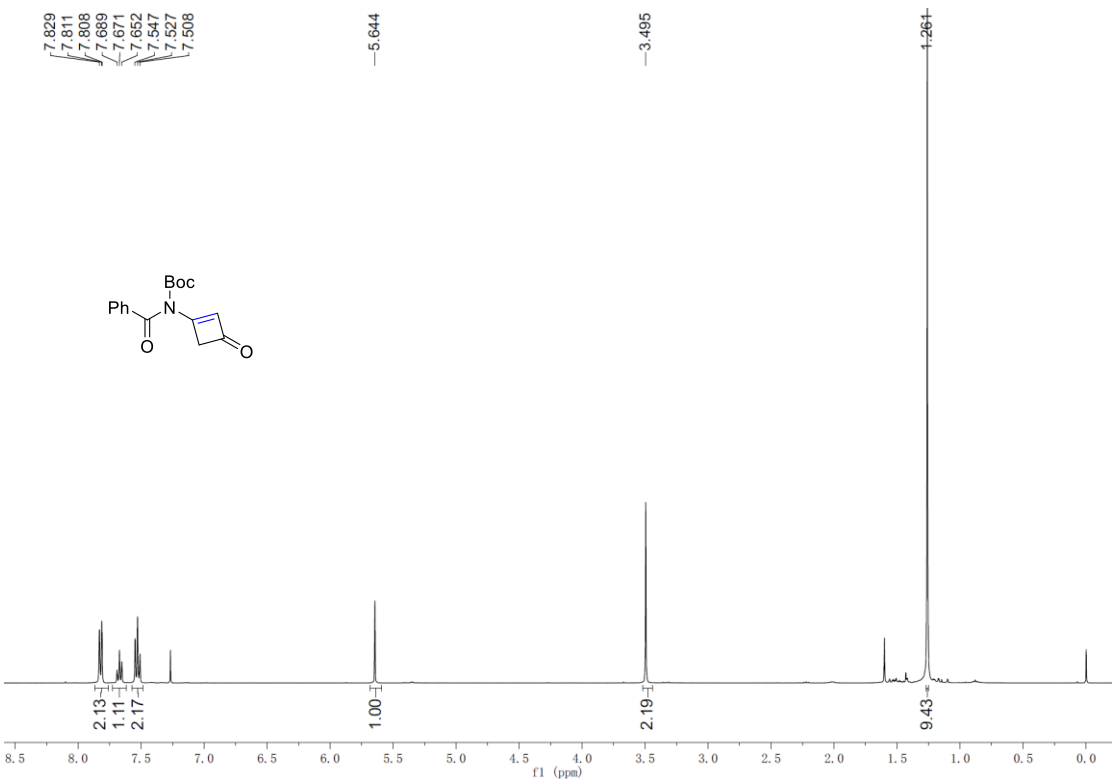
tert-butyl benzoyl(3,3-difluorocyclobut-1-en-1-yl)carbamate (72)

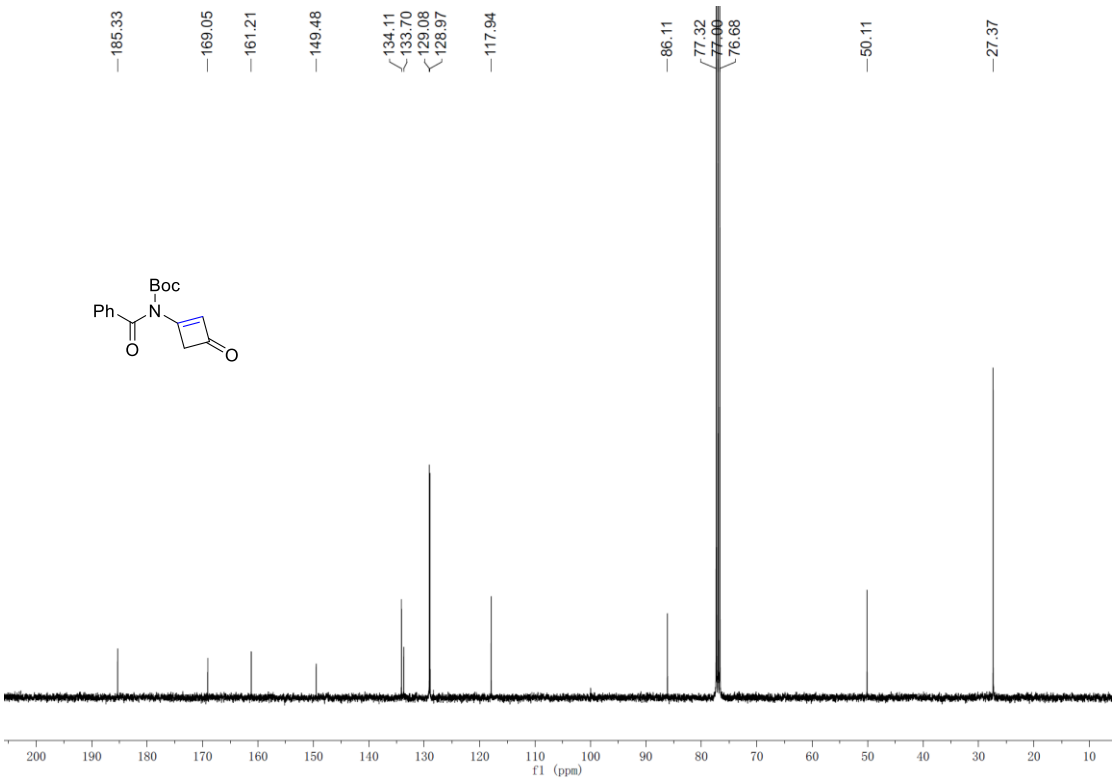




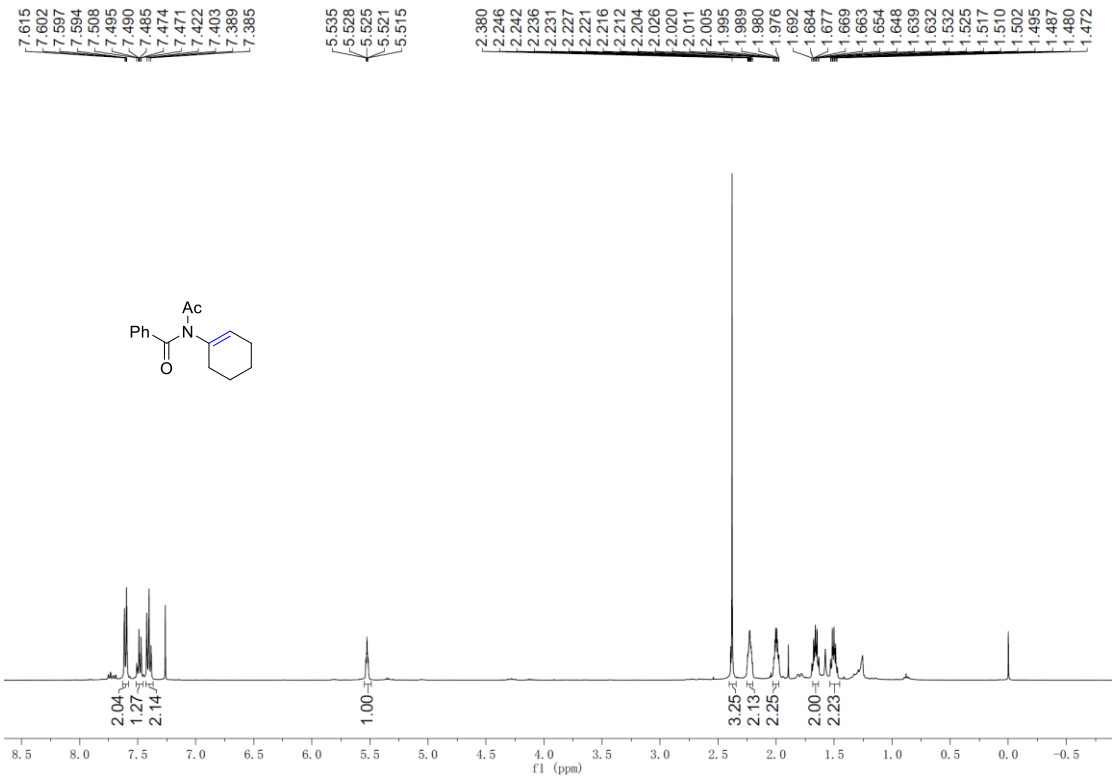

-102.13
Boc
Ph
N
O
F
F
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

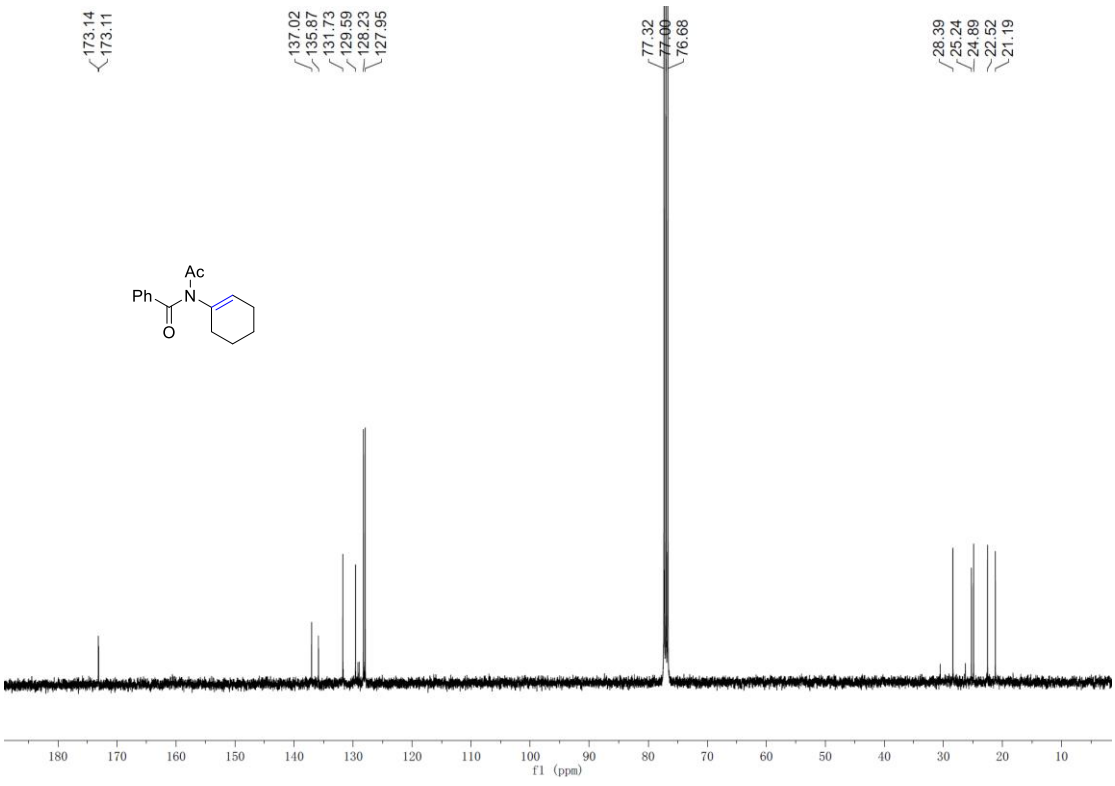
tert-butyl benzoyl(3-oxocyclobut-1-en-1-yl)carbamate (73)



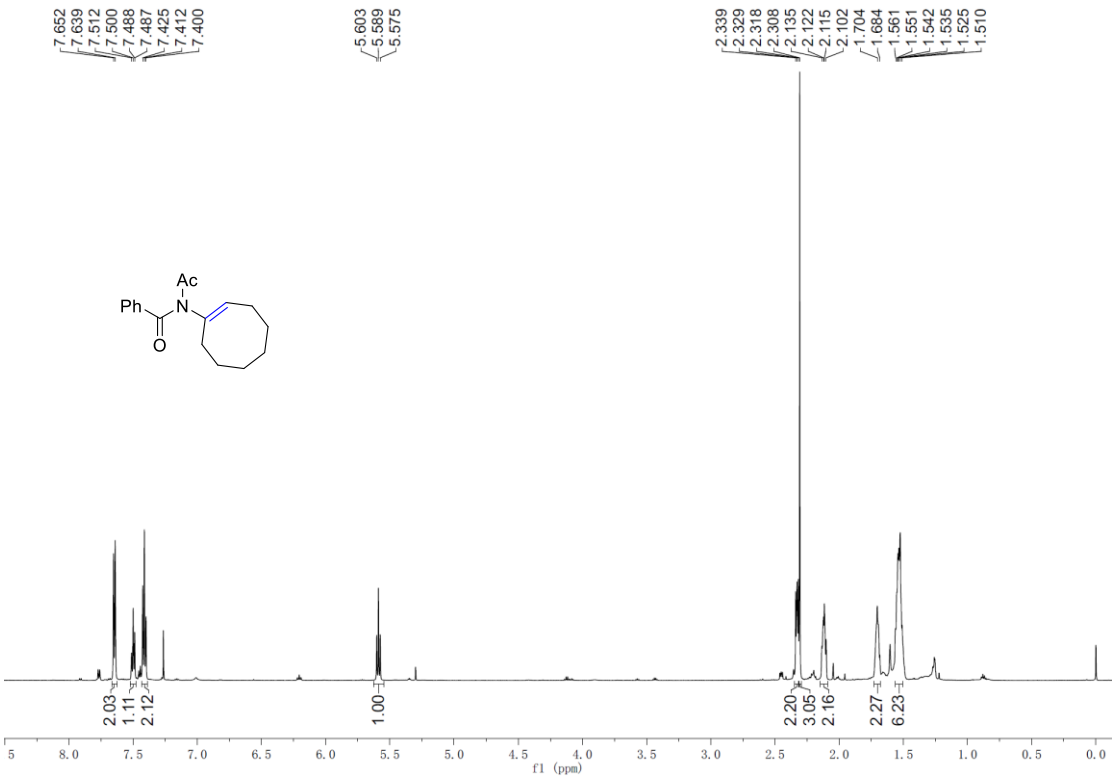


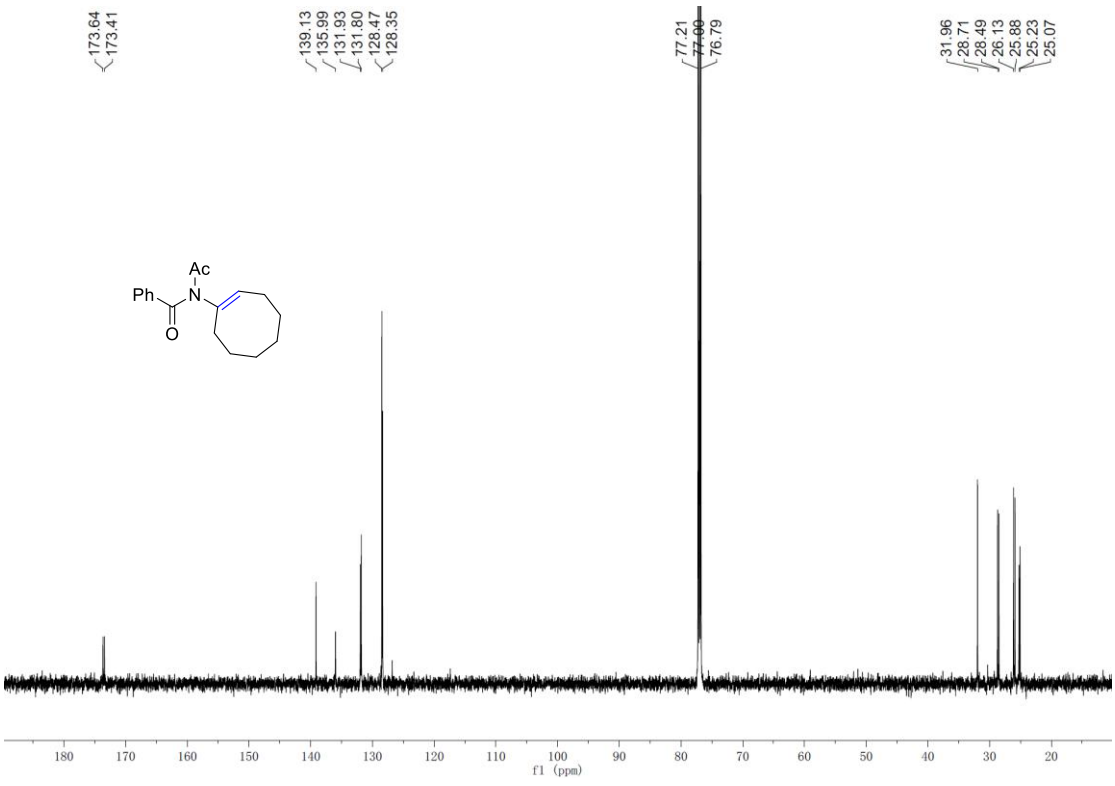
N-acetyl-N-(cyclohex-1-en-1-yl)benzamide (74)



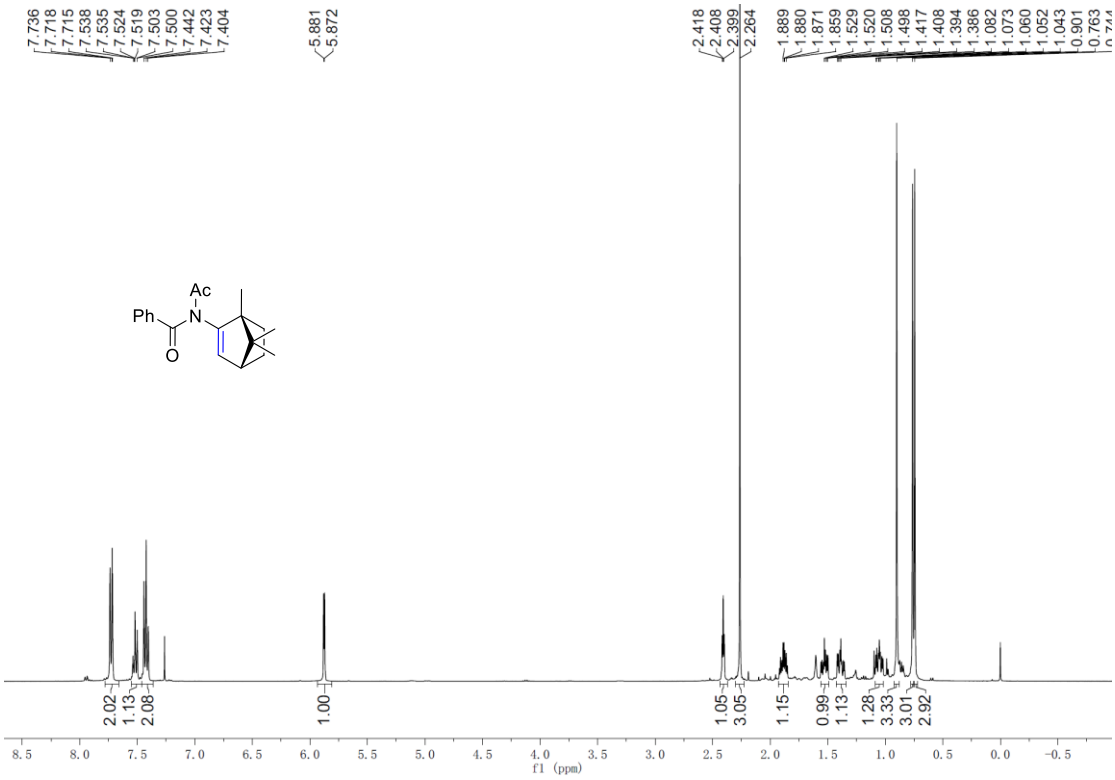


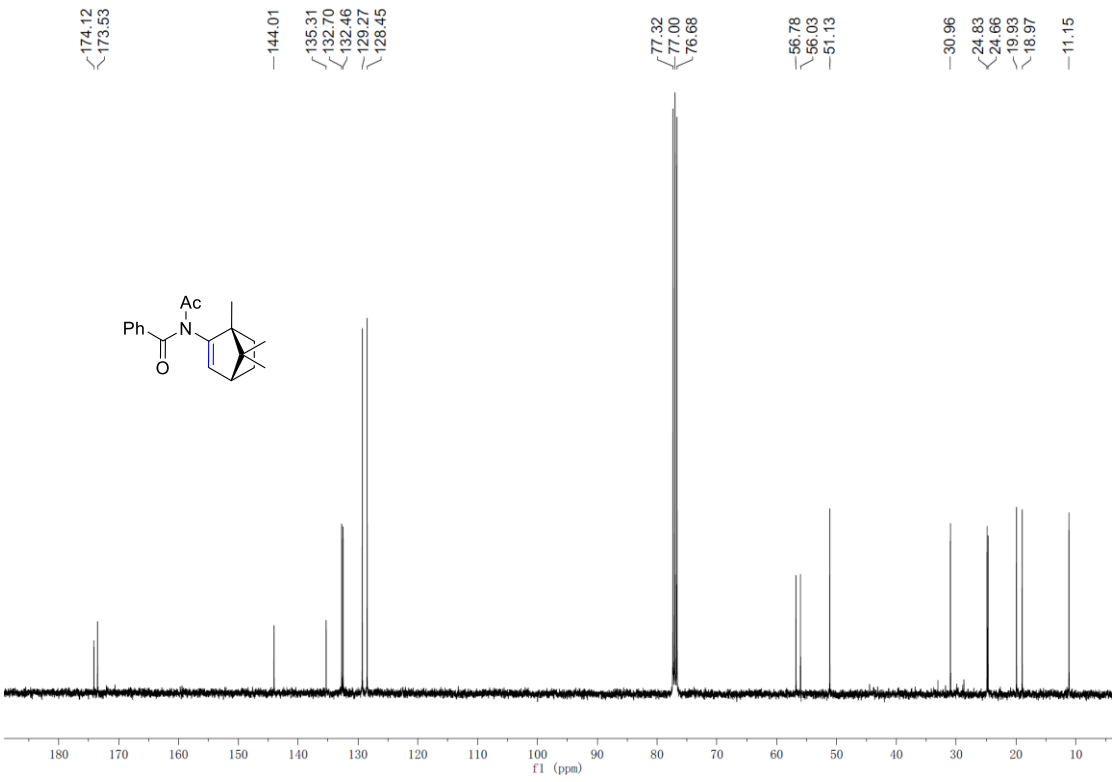
(E)-N-acetyl-N-(cyclooct-1-en-1-yl)benzamide (75)



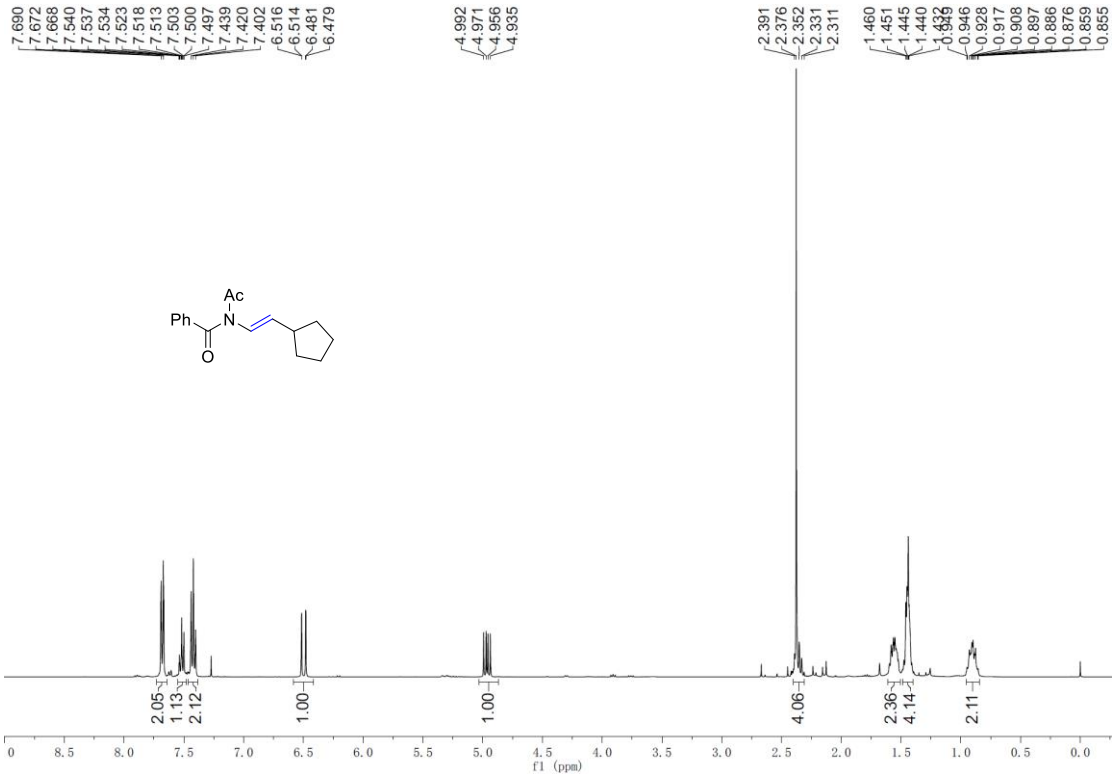


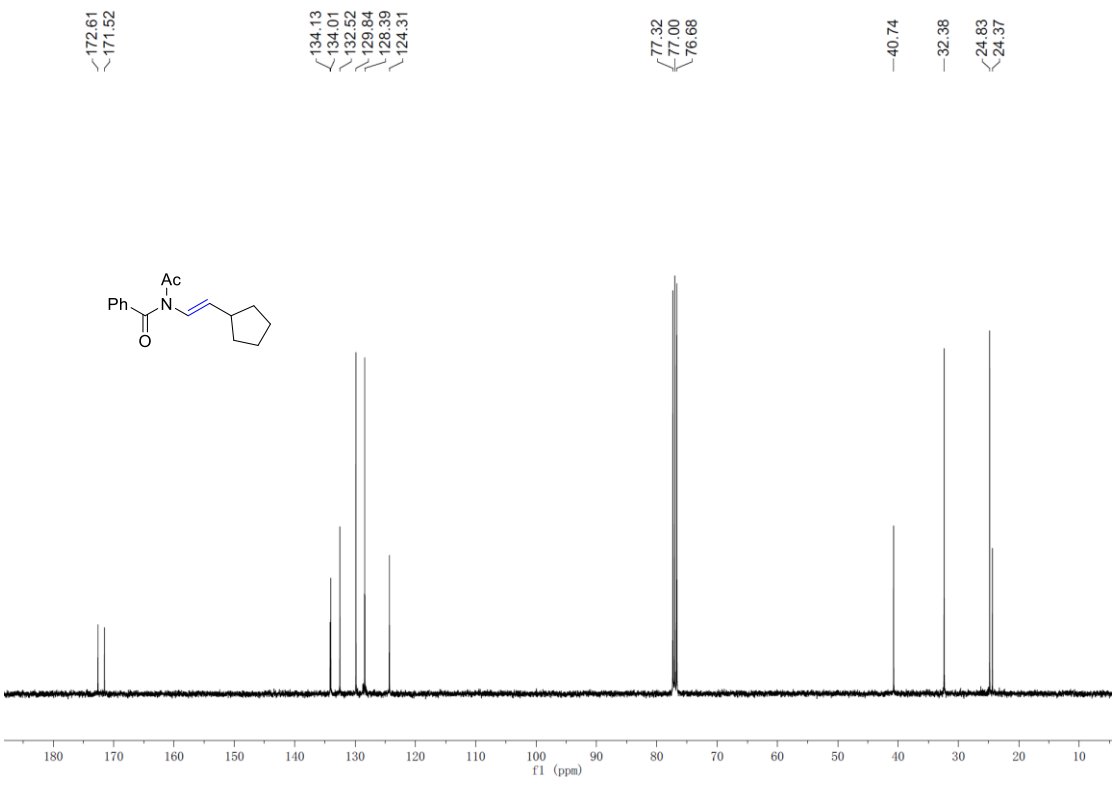
N-acetyl-N-((1R,4R)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl)benzamide (76)



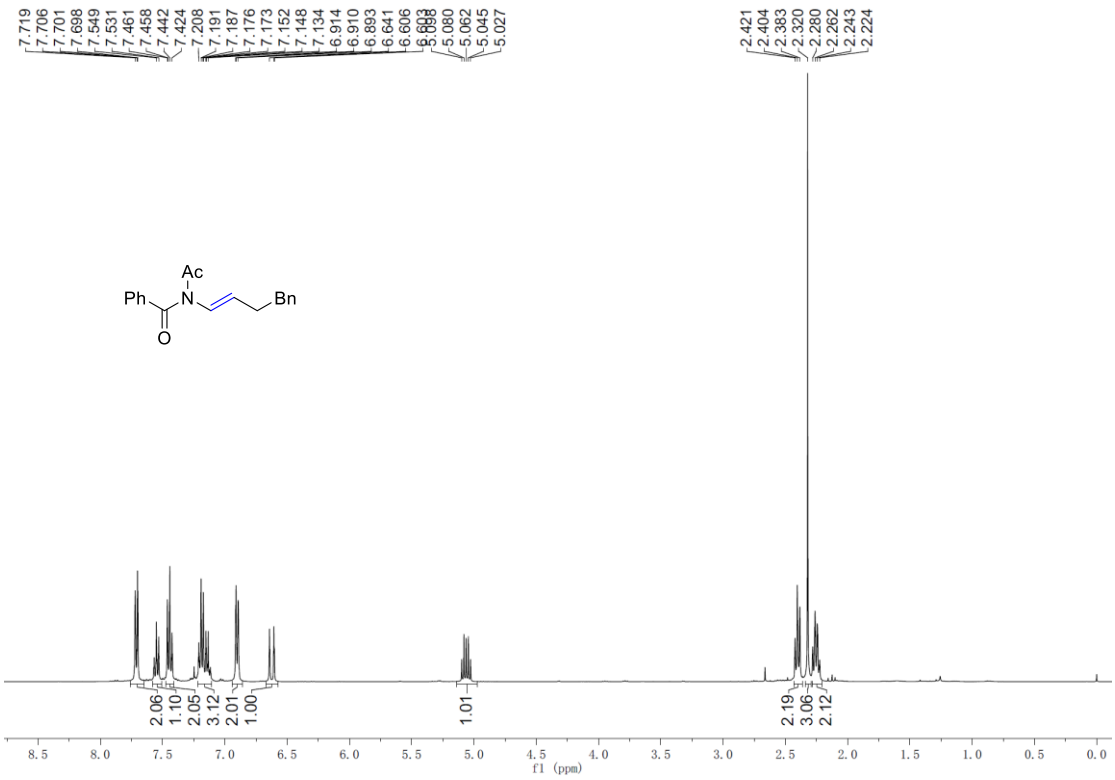


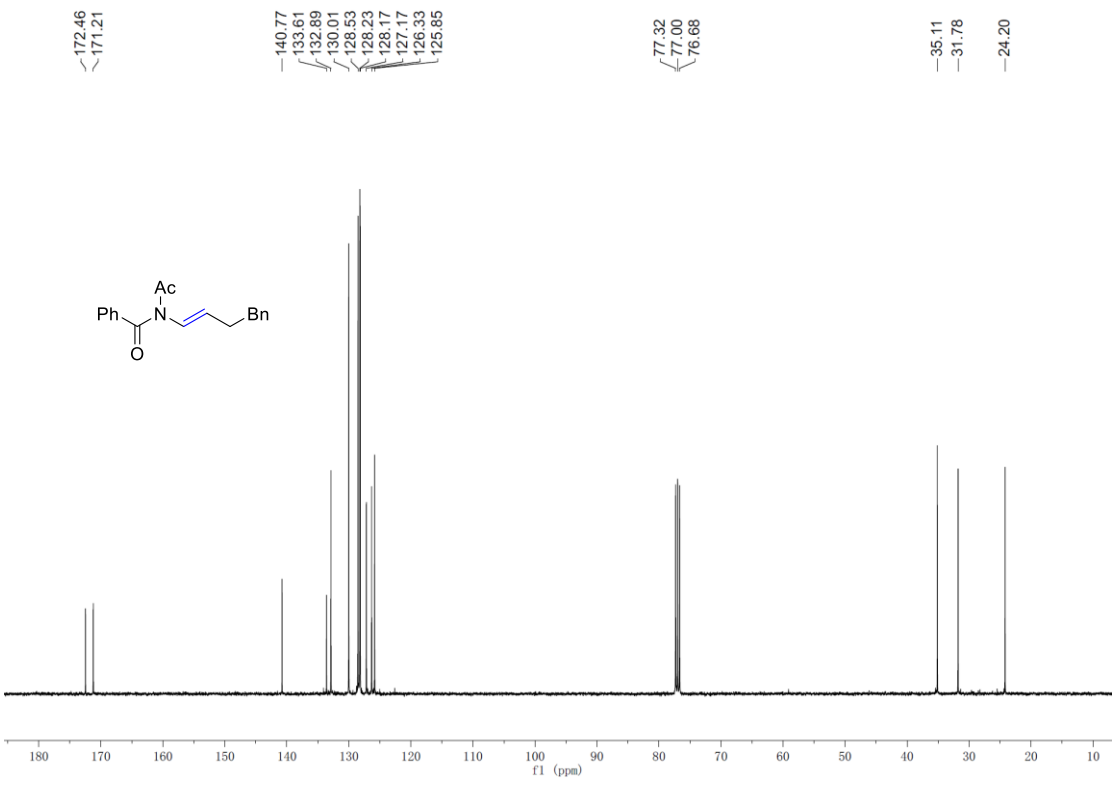
(E)-N-acetyl-N-(2-cyclopentylvinyl)benzamide (77)



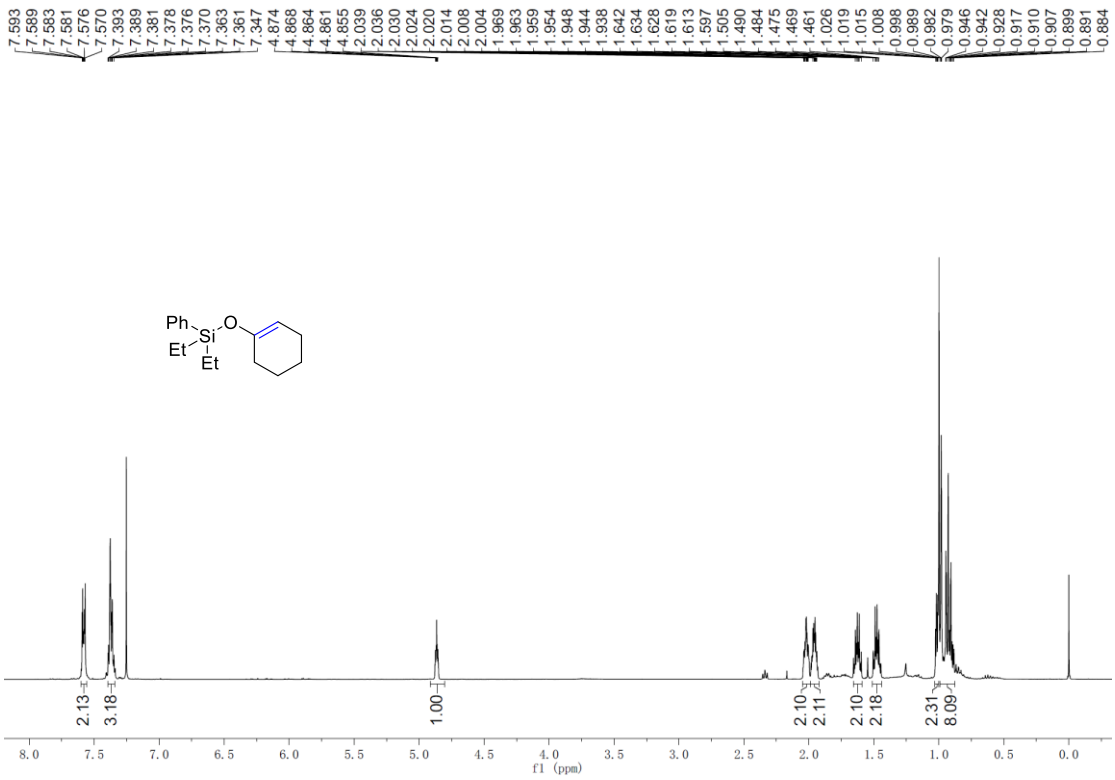


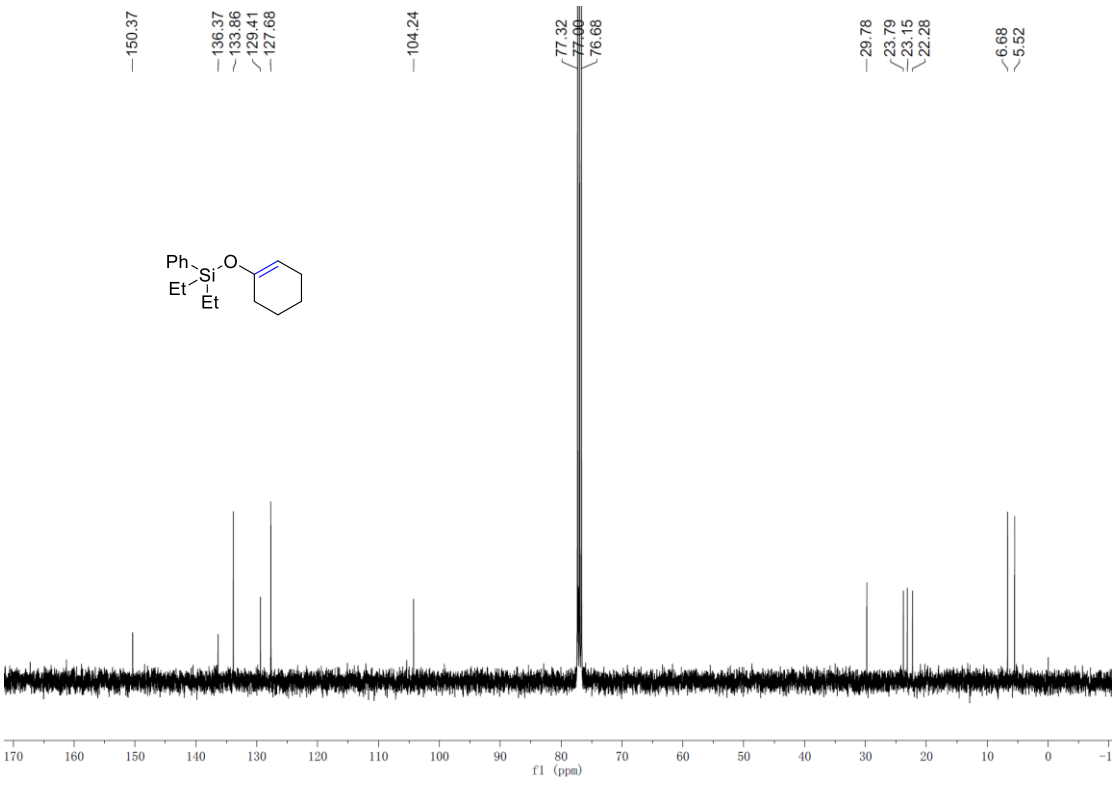
(E)-N-acetyl-N-(4-phenylbut-1-en-1-yl)benzamide (78)



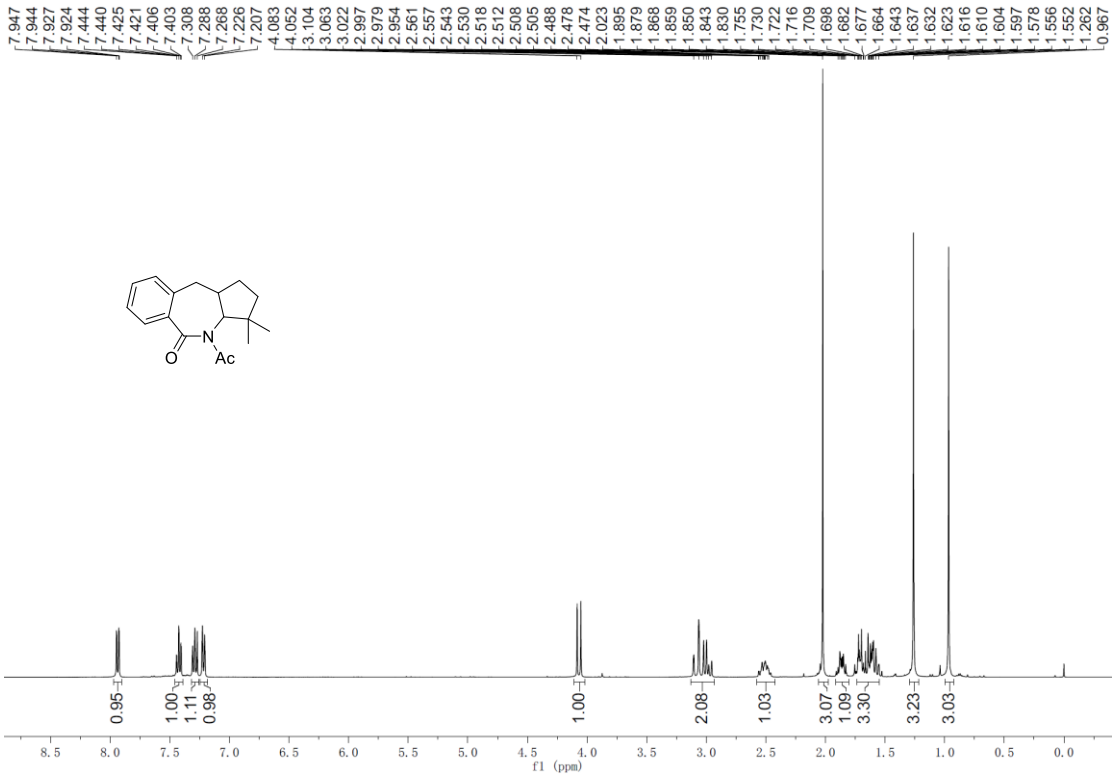


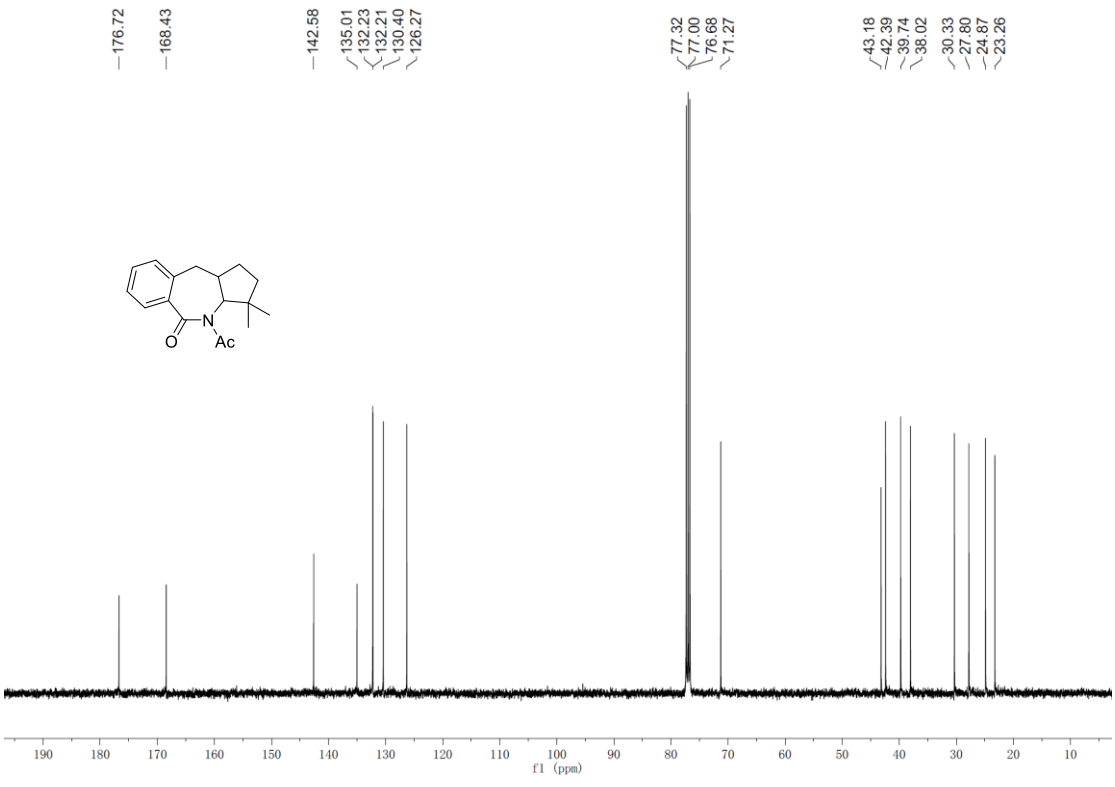
(cyclohex-1-en-1-yloxy)diethyl(phenyl)silane (79)



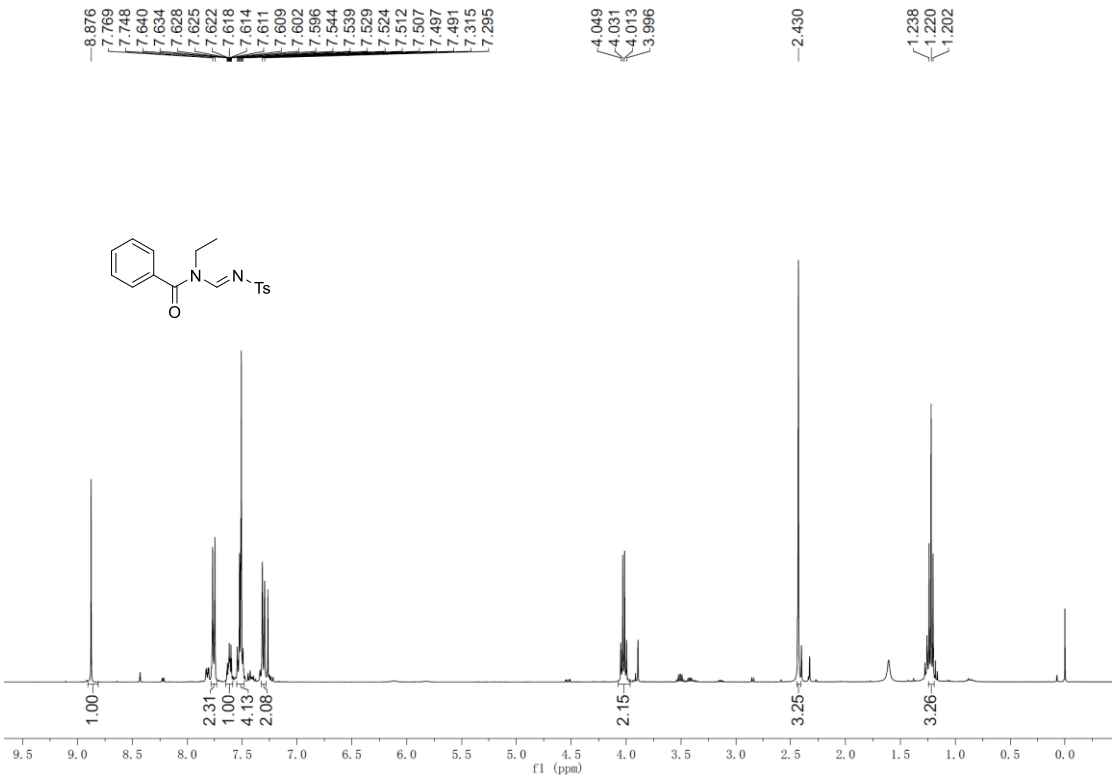


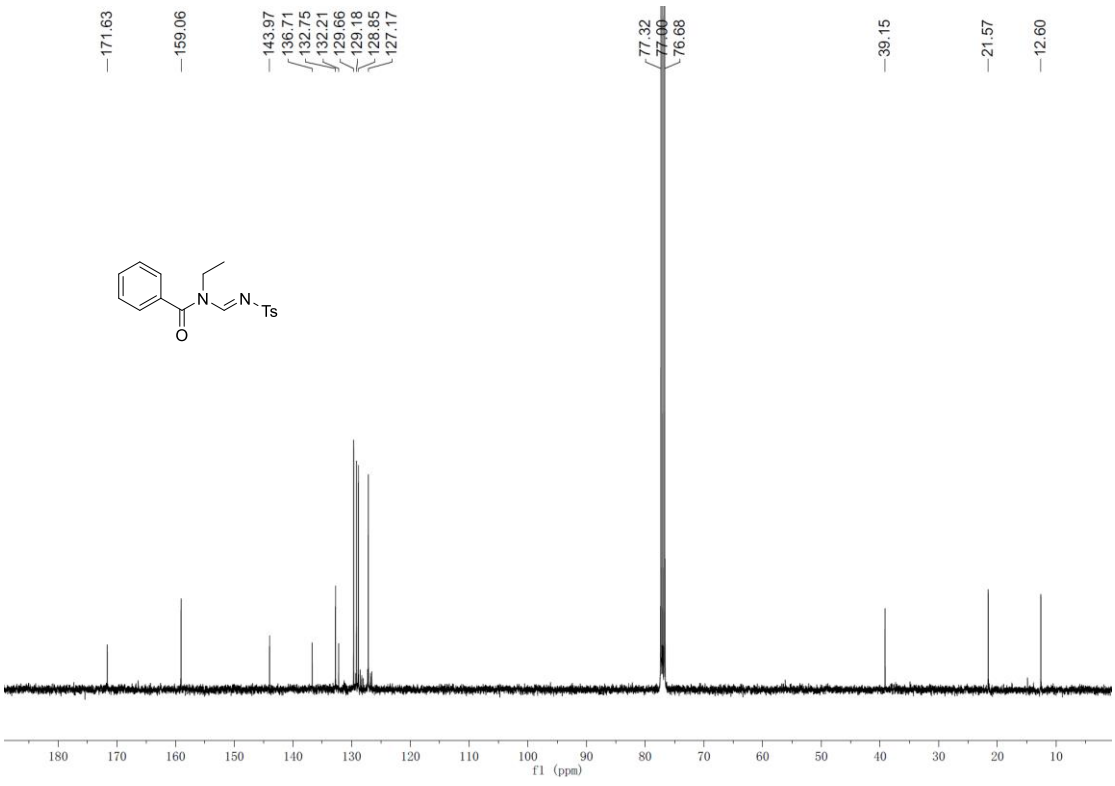
4-acetyl-3,3-dimethyl-2,3,3a,4,10,10a-hexahydrobenzo[e]cyclopenta[b]azepin-5(1H)-one (80)



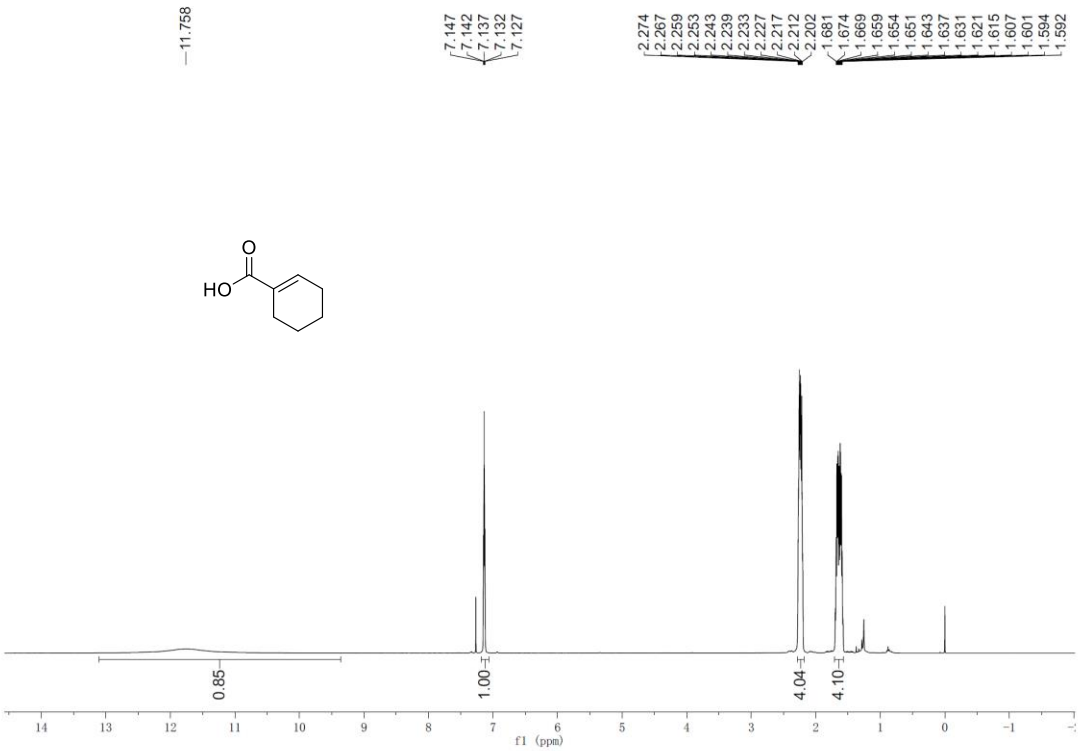


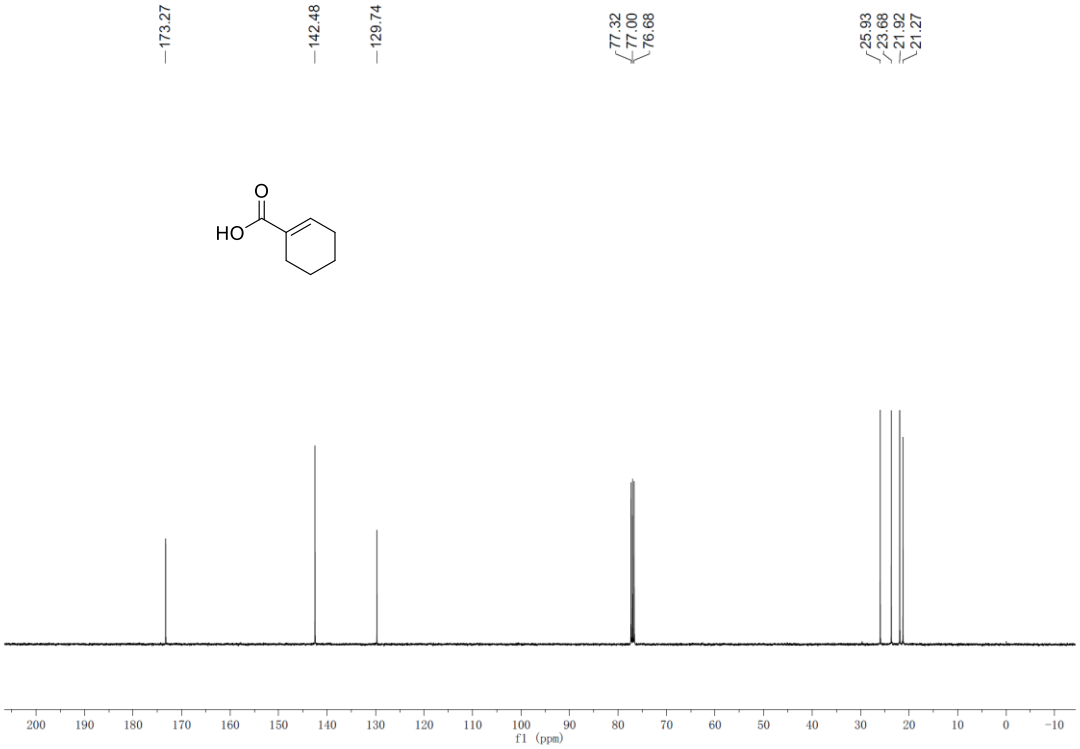
(E)-N-ethyl-N-((tosylimino)methyl)benzamide (82)



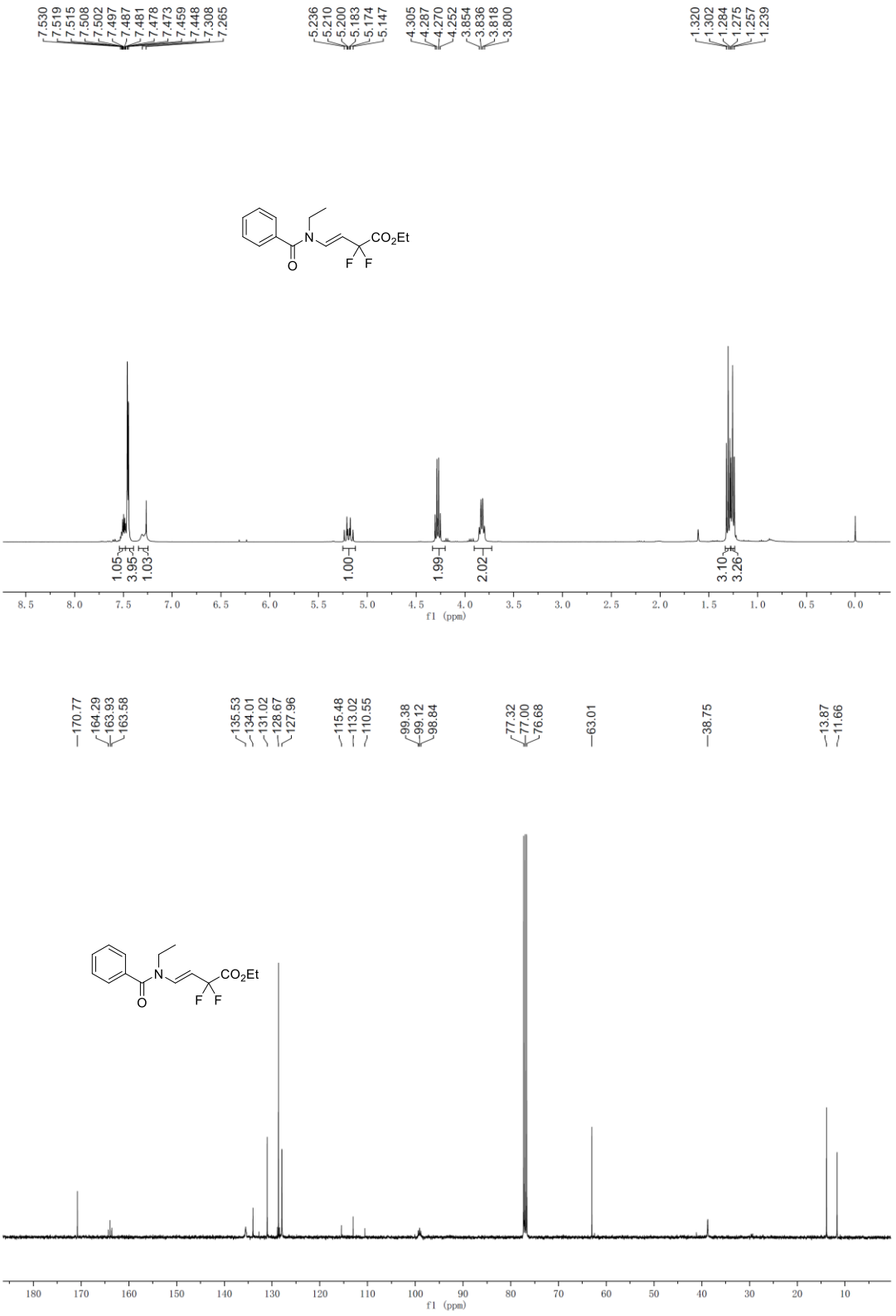


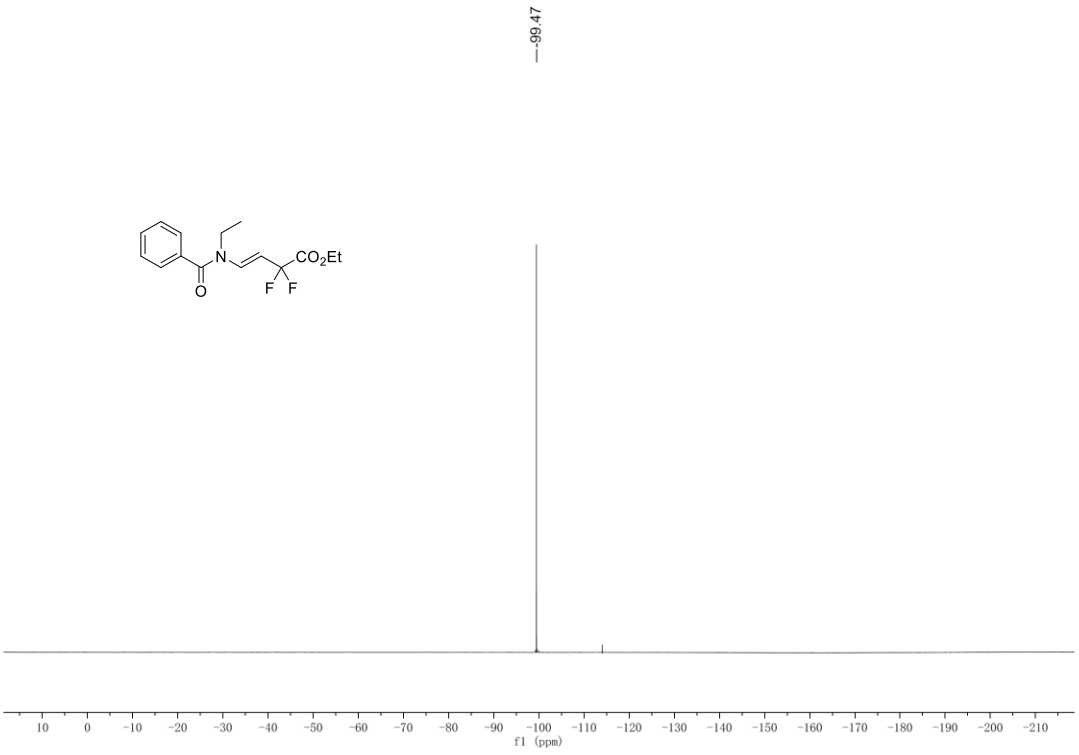
cyclohex-1-ene-1-carboxylic acid (83)



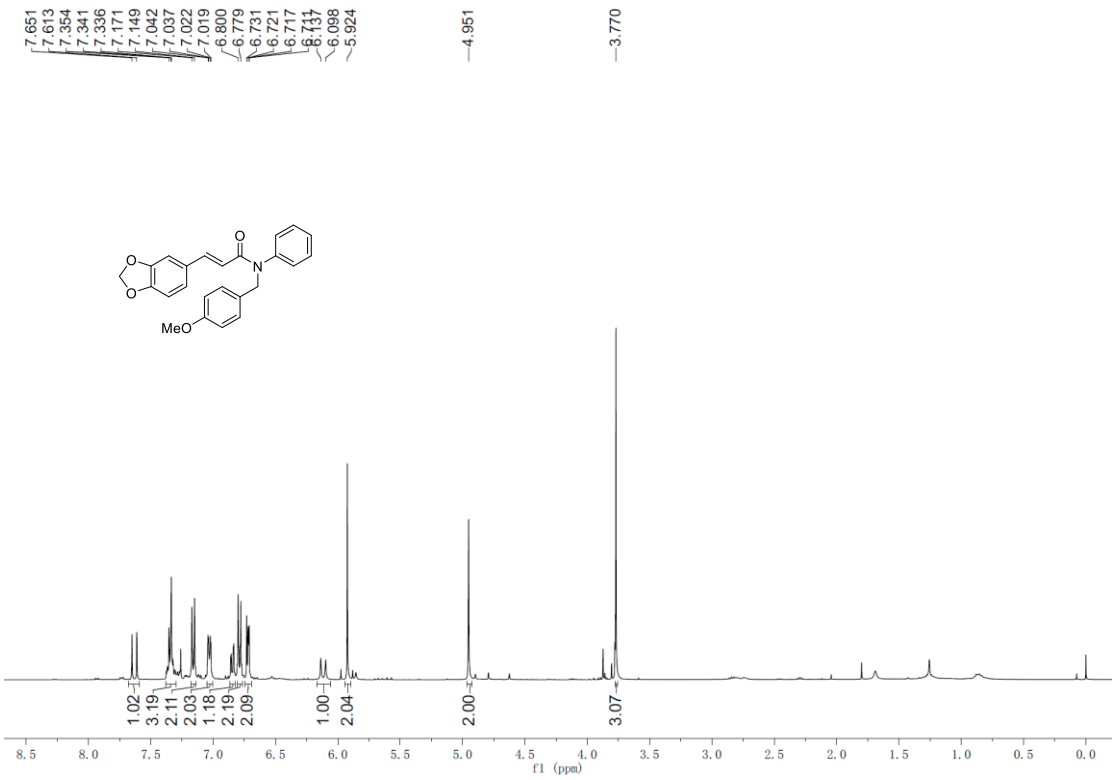


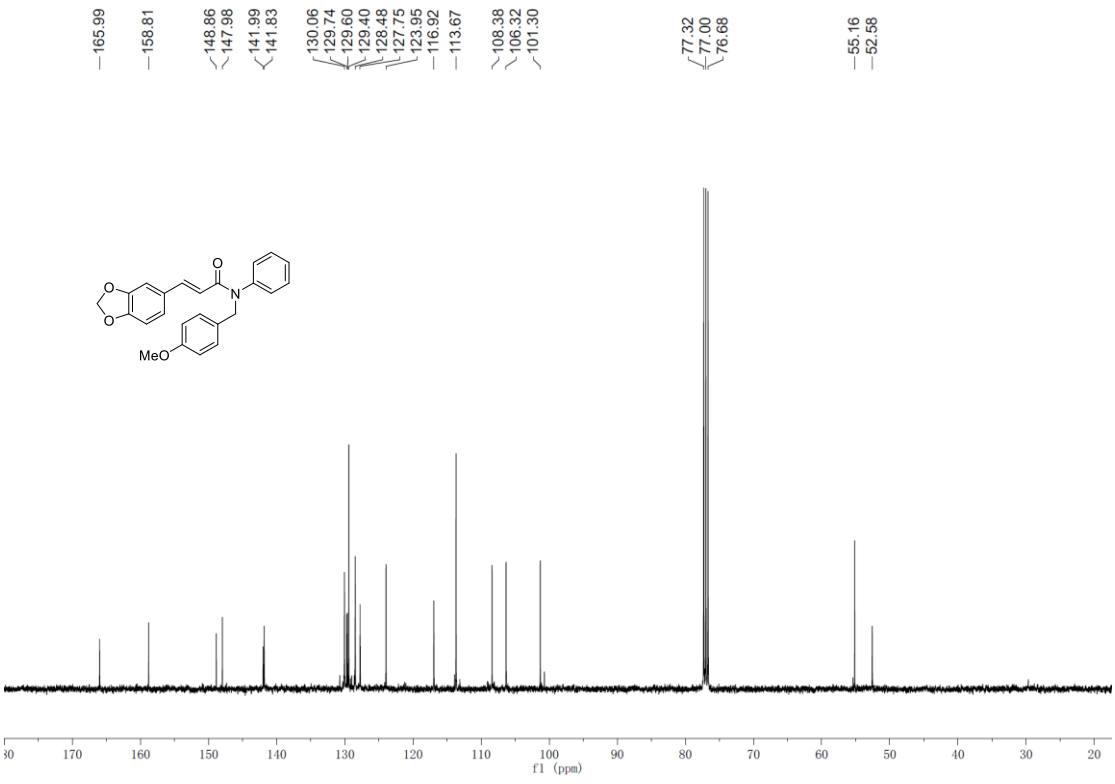
ethyl (E)-4-(N-ethylbenzamido)-2,2-difluorobut-3-enoate (81a)



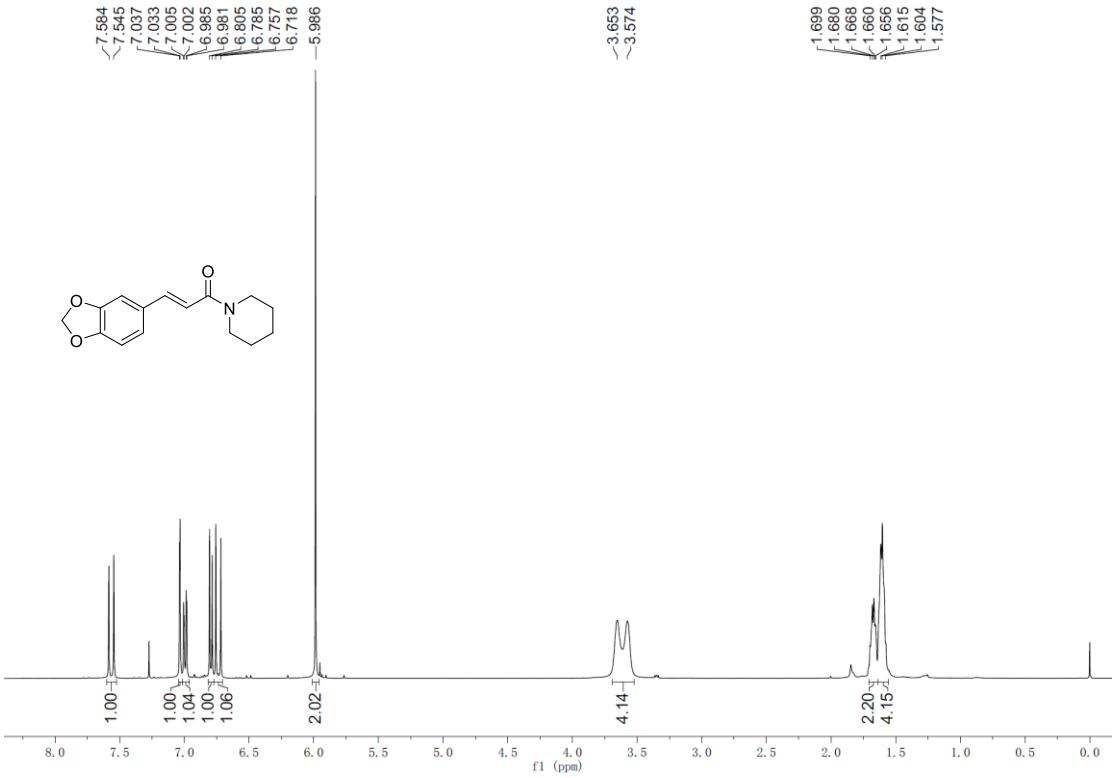

-99.47
N
O
F F
CO2Et
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

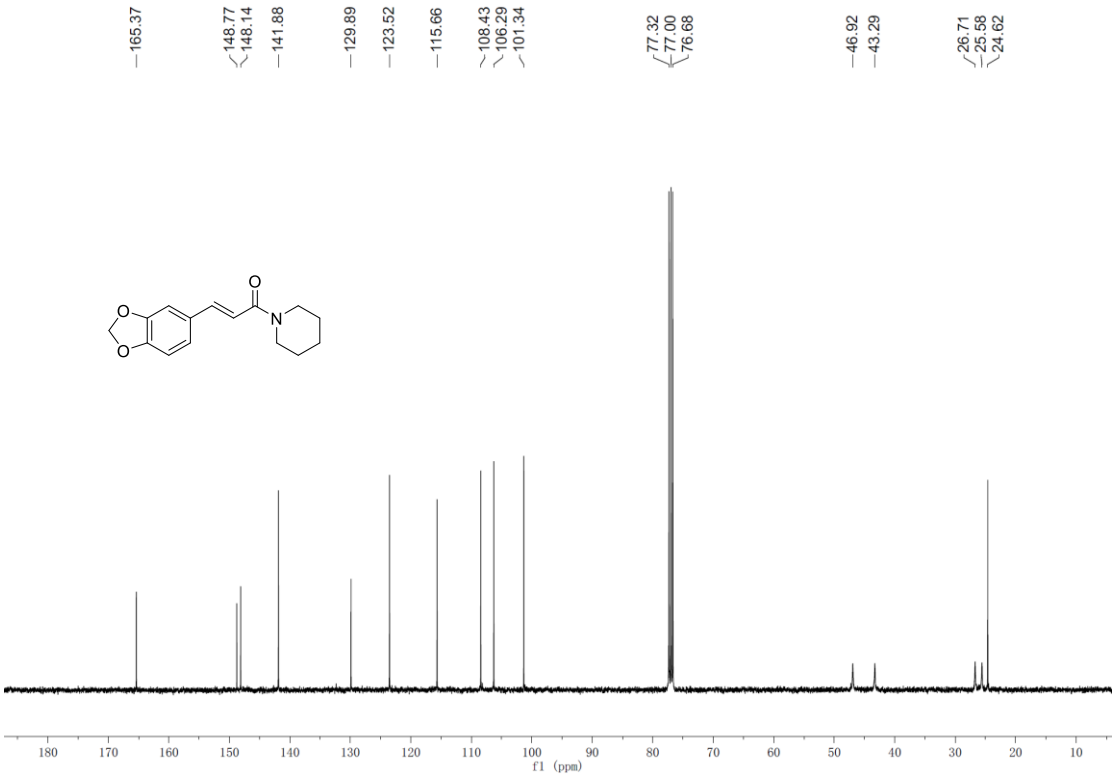
(E)-3-(benzo[d][1,3]dioxol-5-yl)-N-(4-methoxybenzyl)-N-phenylacrylamide (86)



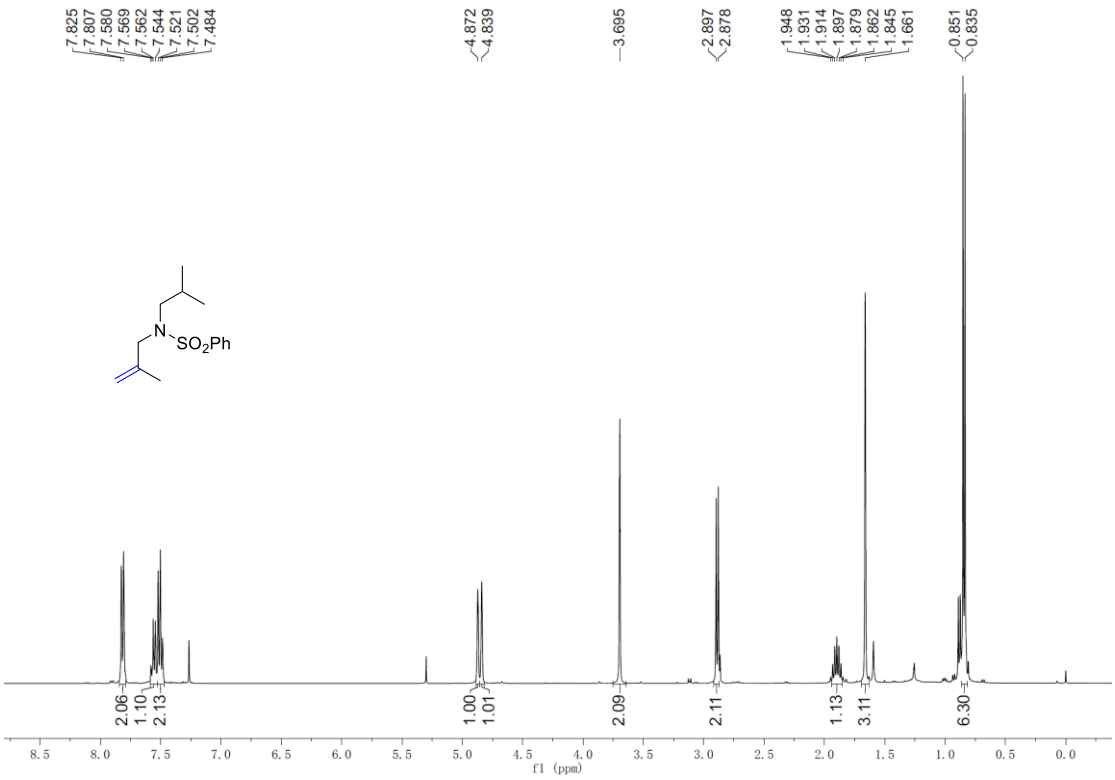


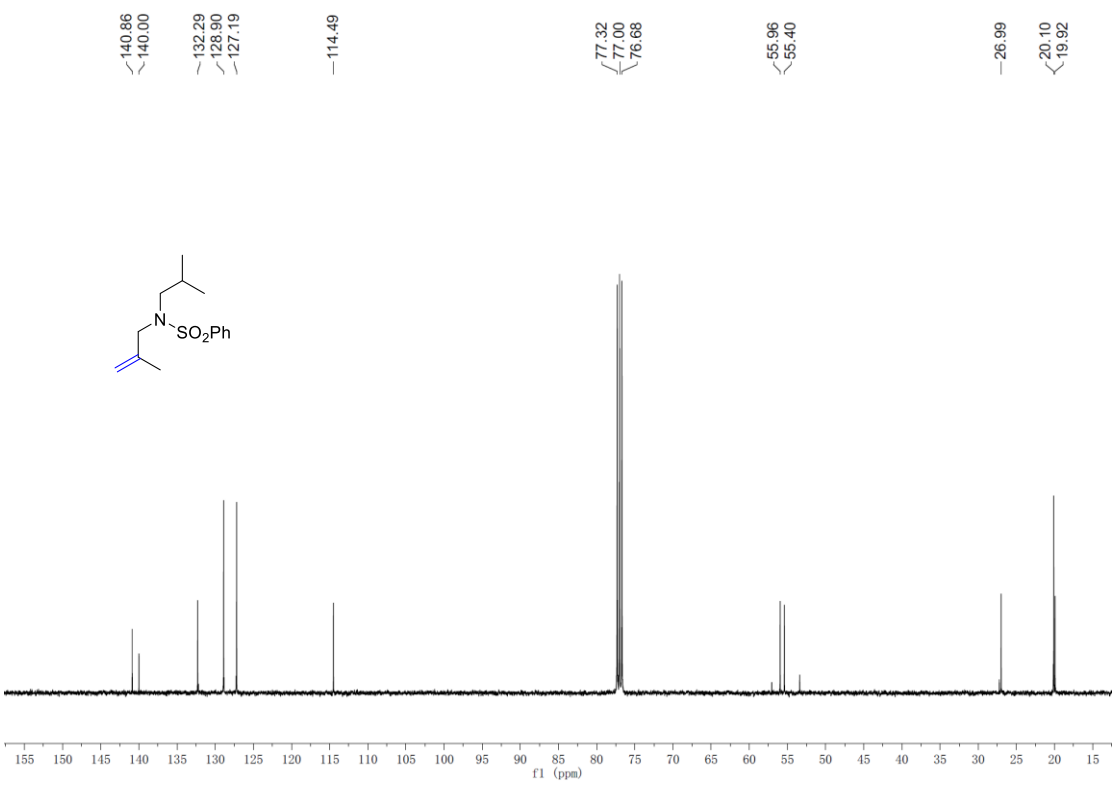
(E)-3-(benzo[d][1,3]dioxol-5-yl)-1-(piperidin-1-yl)prop-2-en-1-one (87)



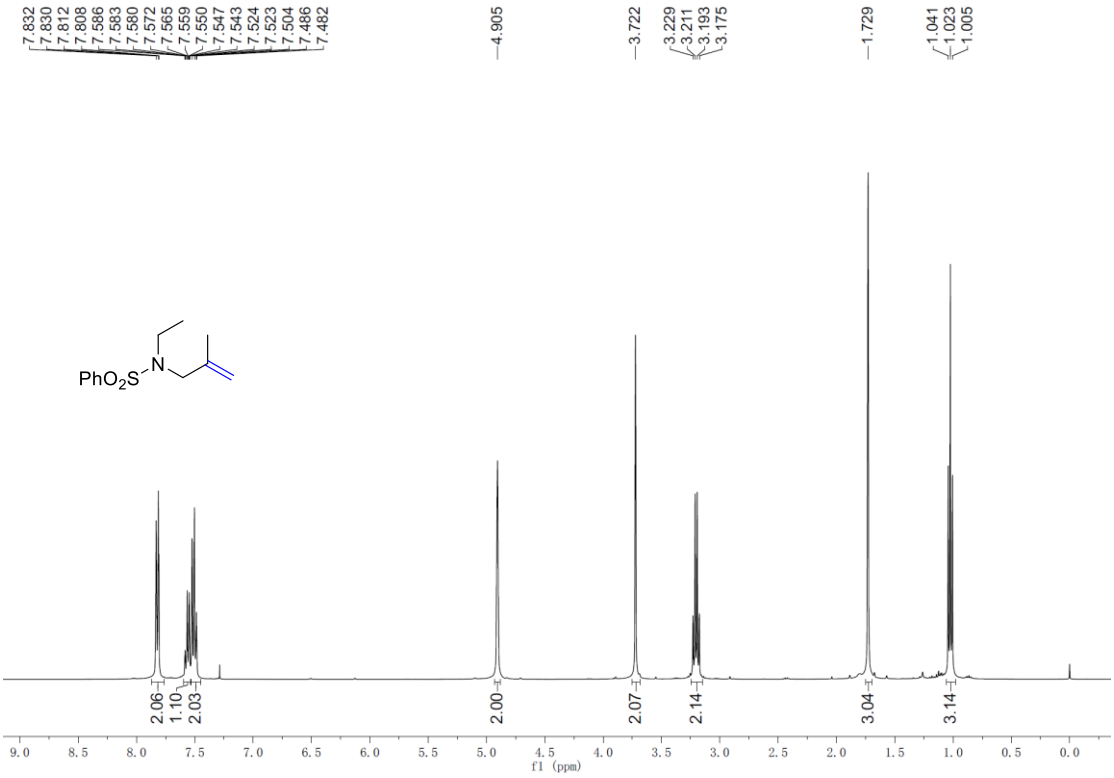


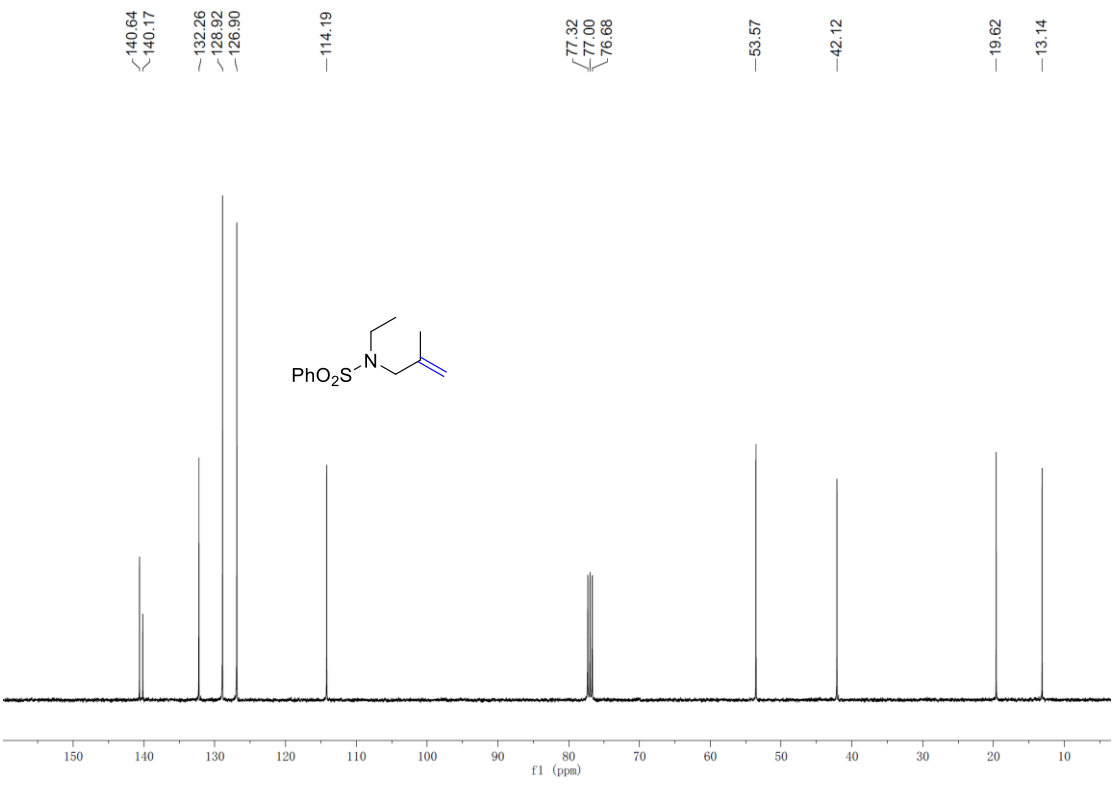
N-isobutyl-N-(2-methylallyl)benzenesulfonamide (88)



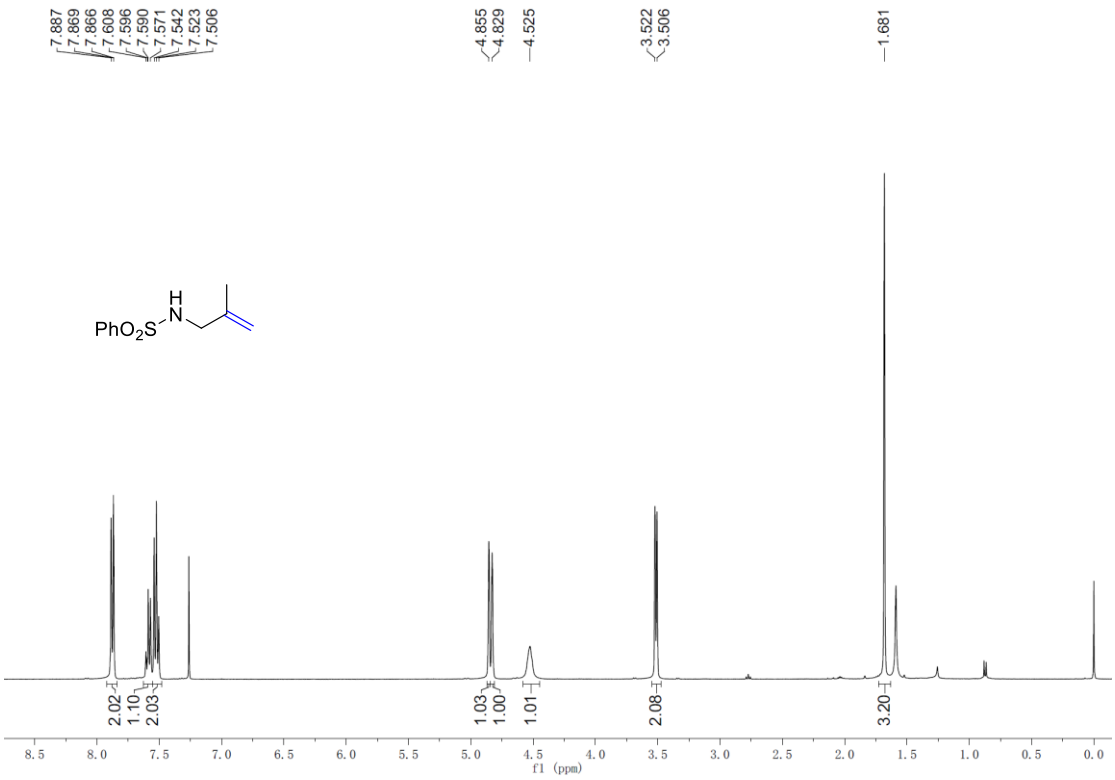


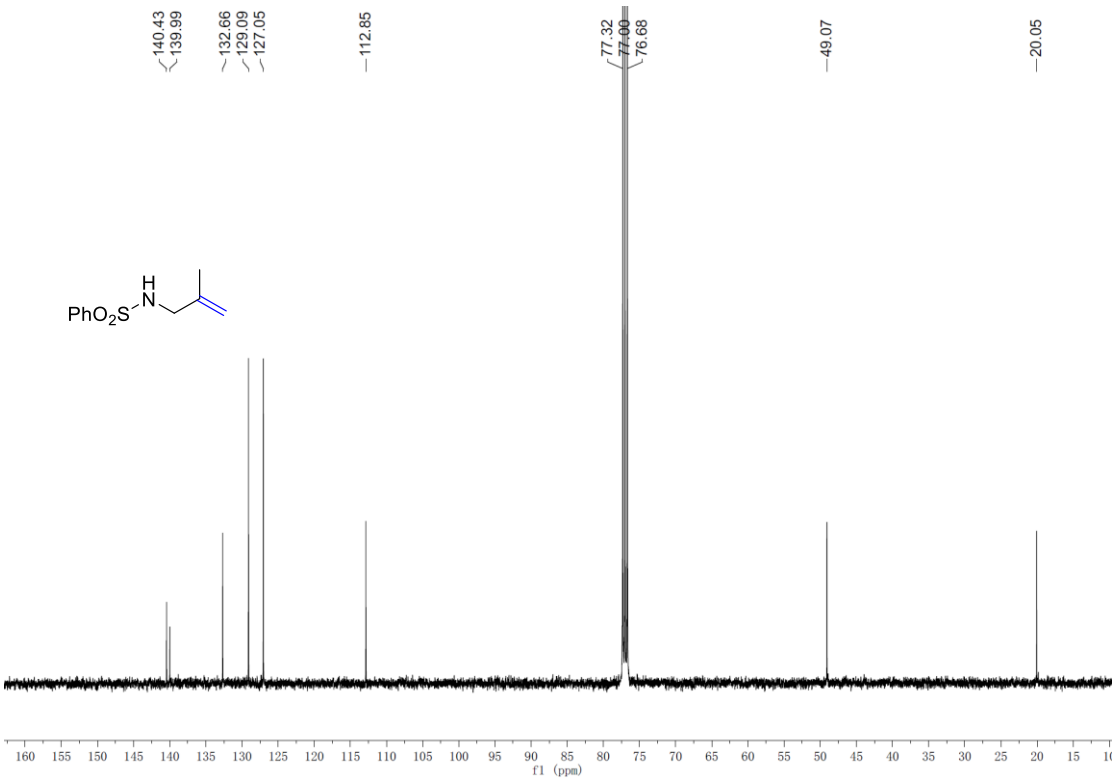
N-ethyl-N-(2-methylallyl)benzenesulfonamide (89)



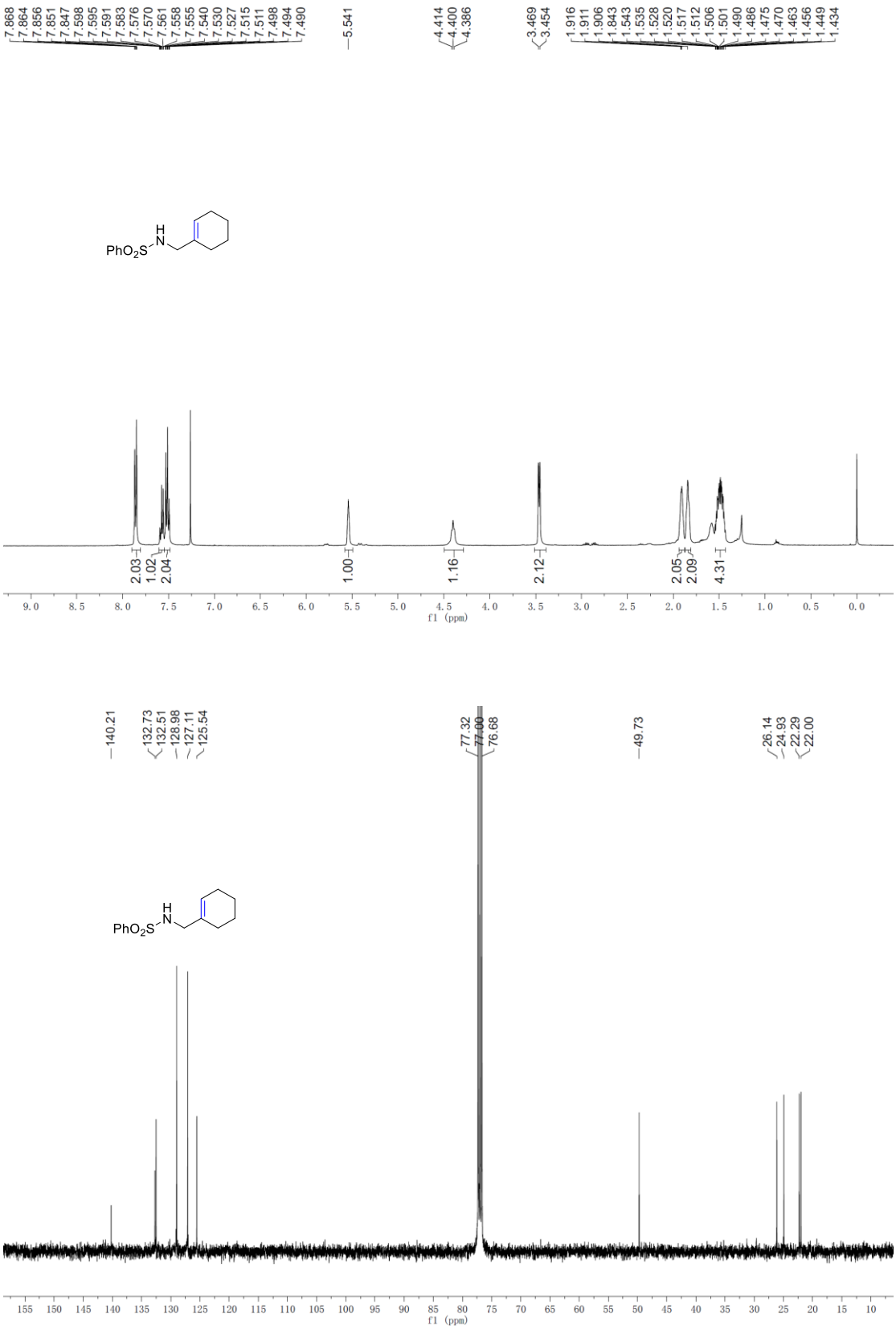


N-(2-methylallyl)benzenesulfonamide (90)

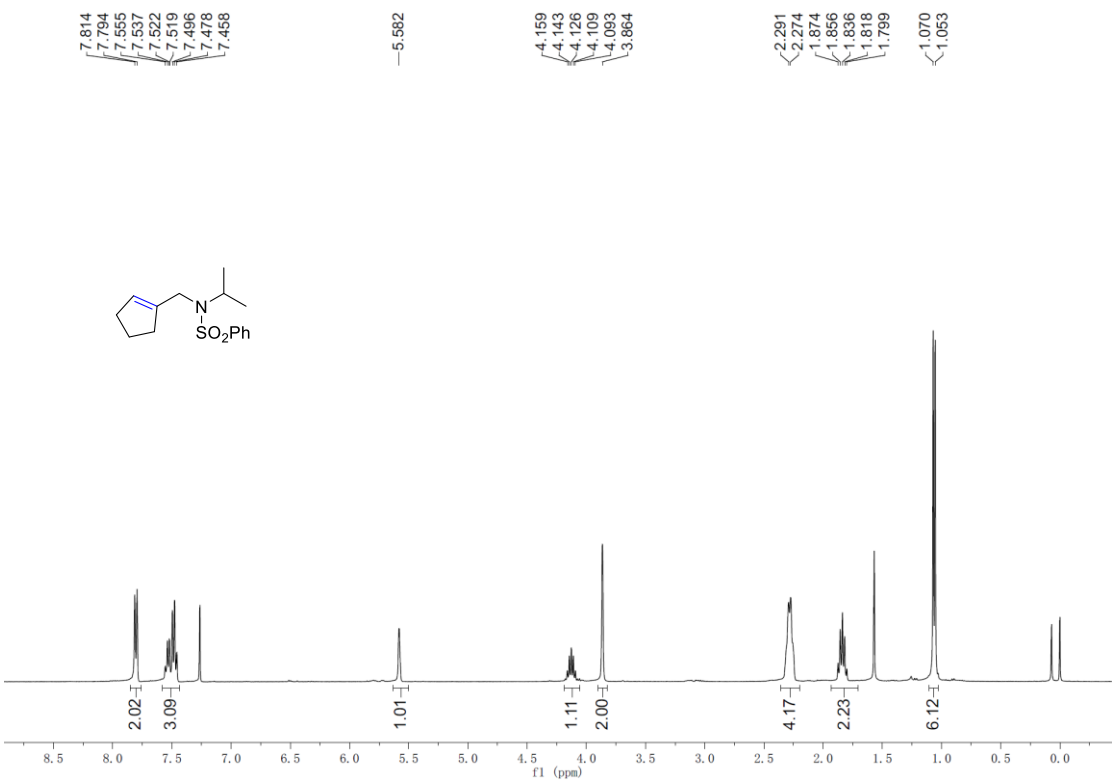


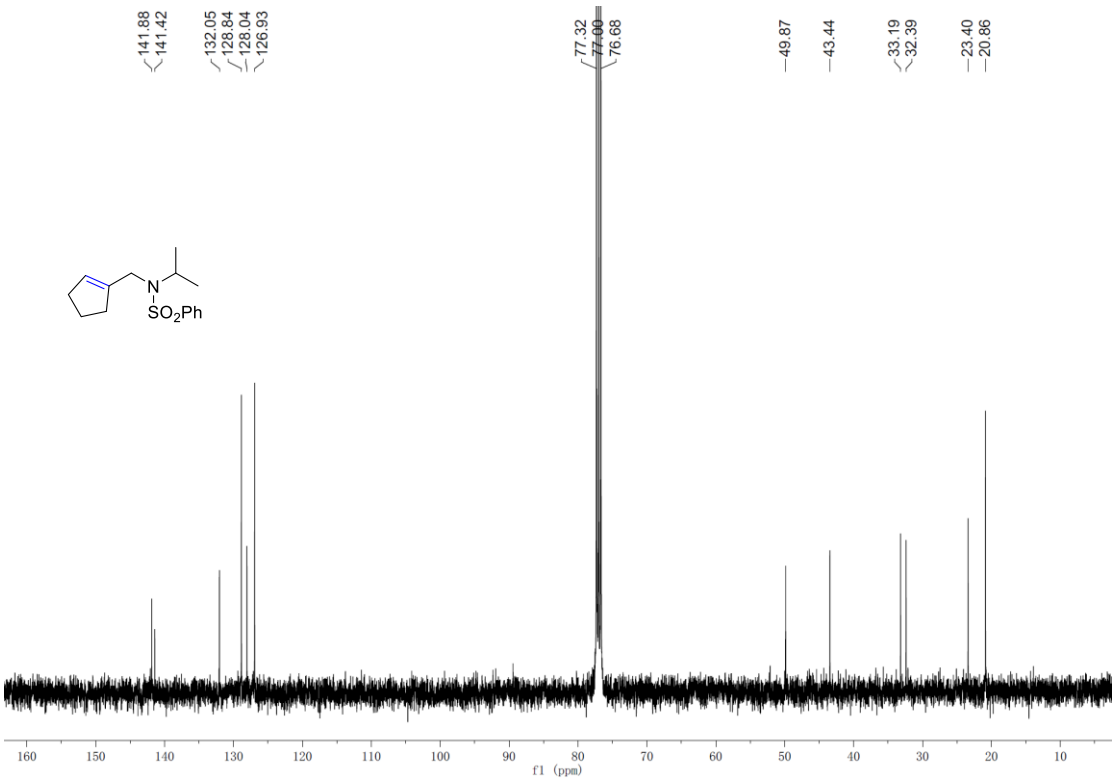


N-(cyclohex-1-en-1-ylmethyl)benzenesulfonamide (91)

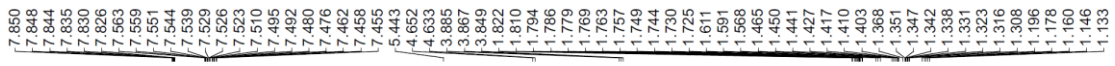


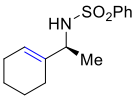
N-(cyclopent-1-en-1-ylmethyl)-N-isopropylbenzenesulfonamide (92)

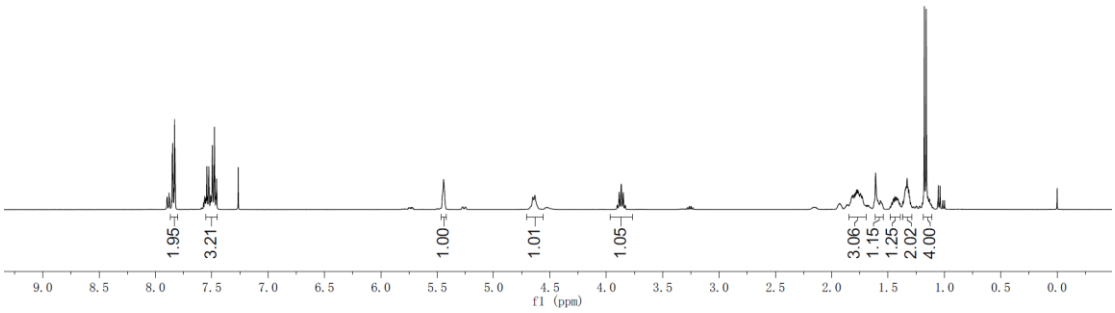


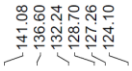


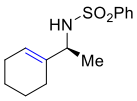
(S)-N-(1-(cyclohex-1-en-1-yl)ethyl)benzenesulfonamide (93)

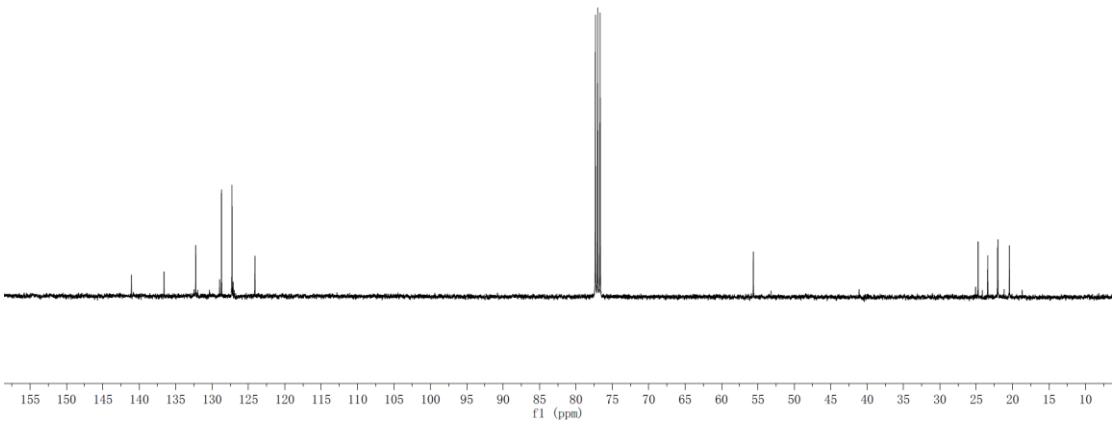




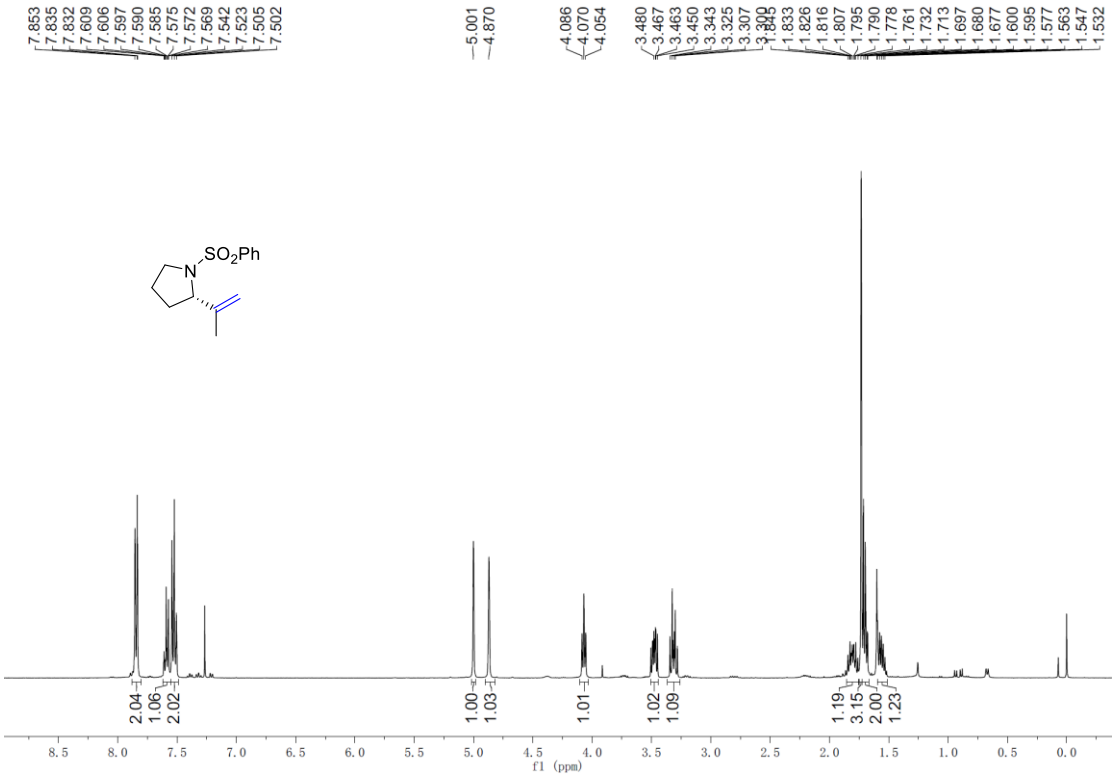


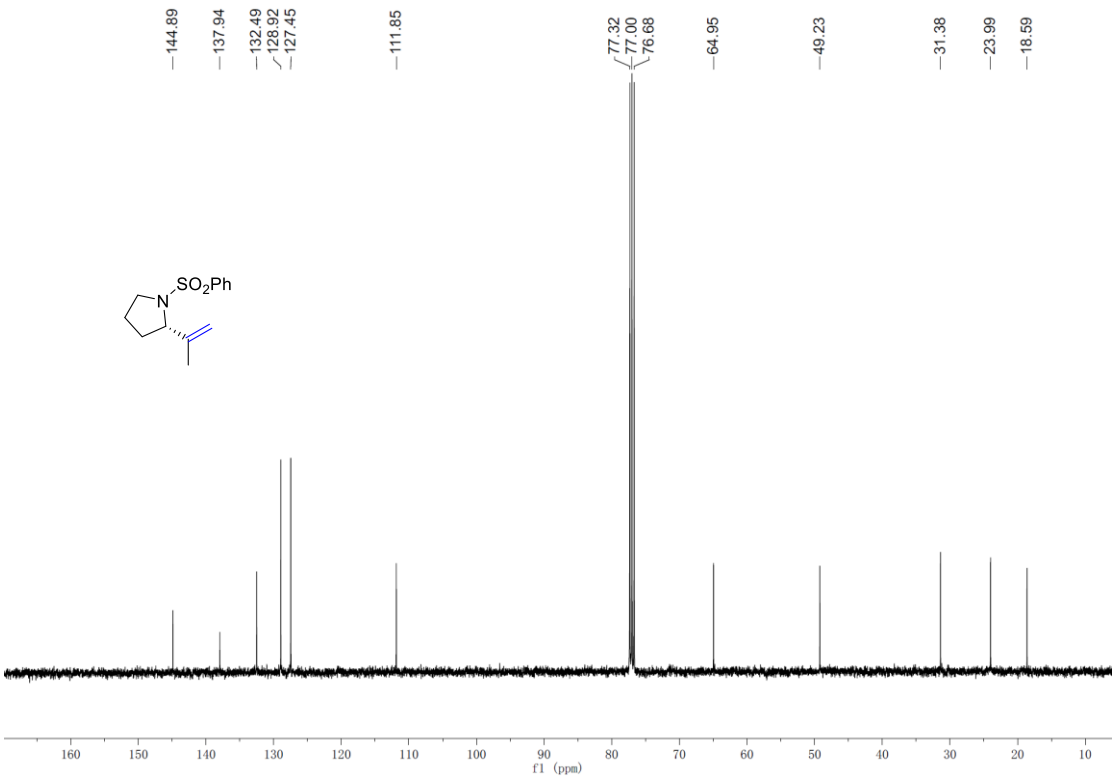




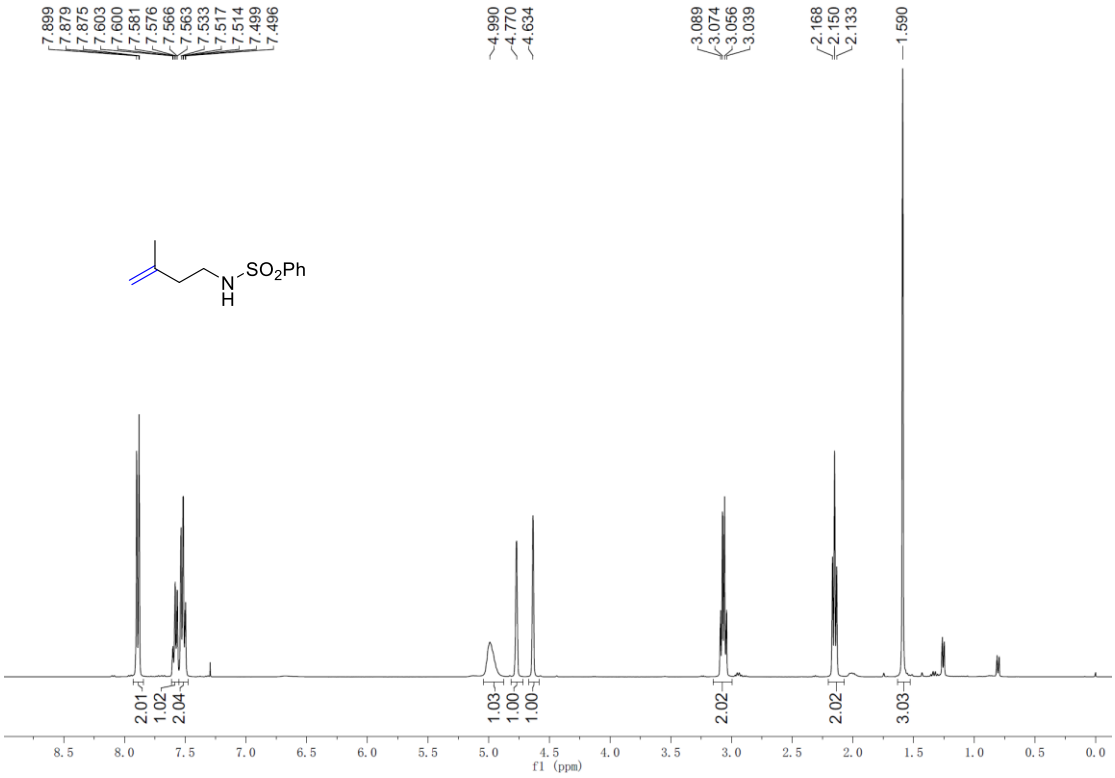


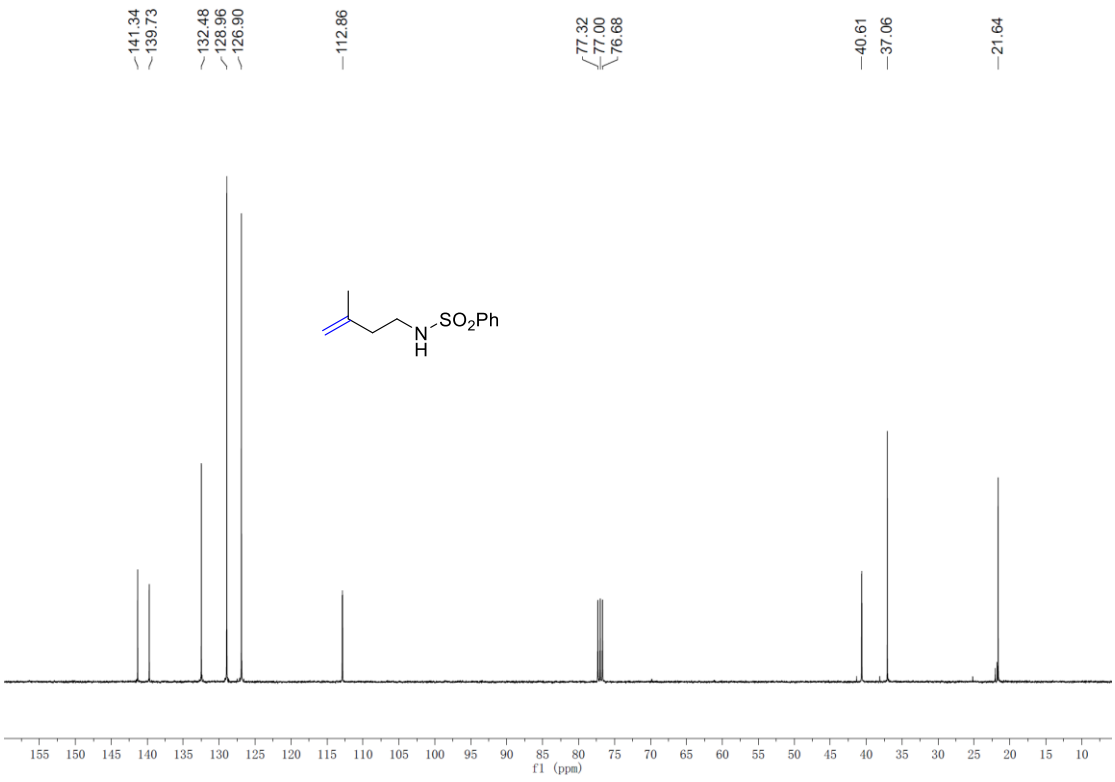
(S)-1-(phenylsulfonyl)-2-(prop-1-en-2-yl)pyrrolidine (94)



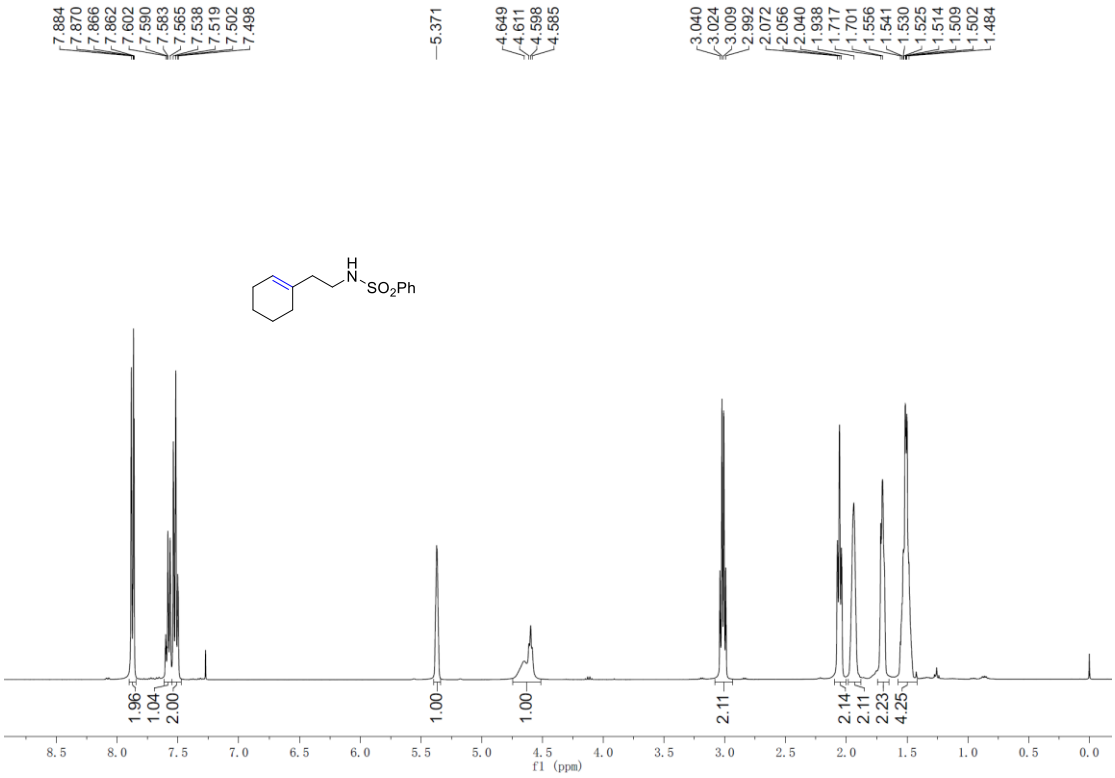


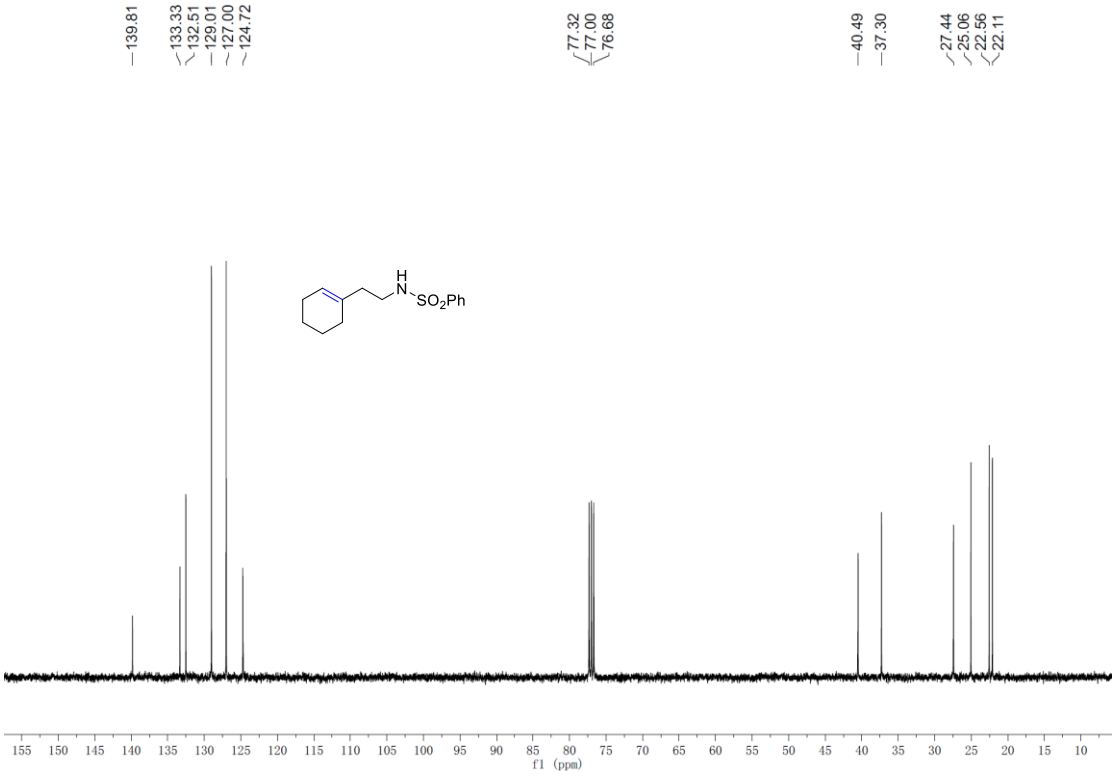
N-(3-methylbut-3-en-1-yl)benzenesulfonamide (95)



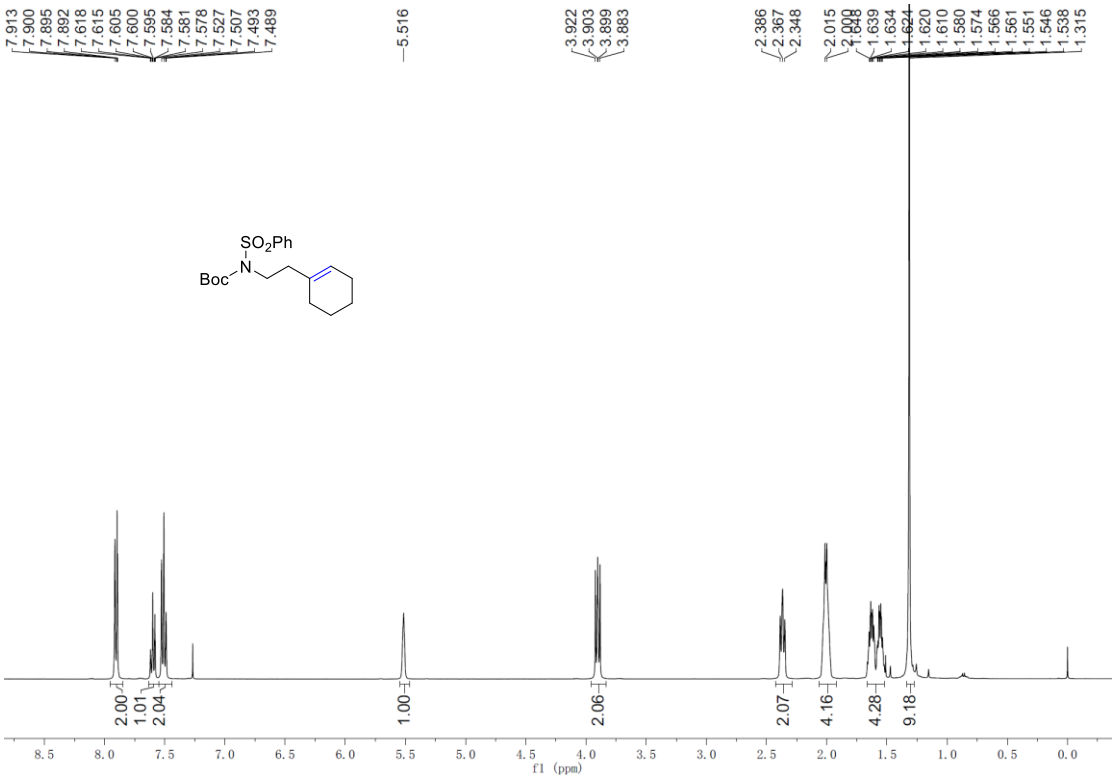


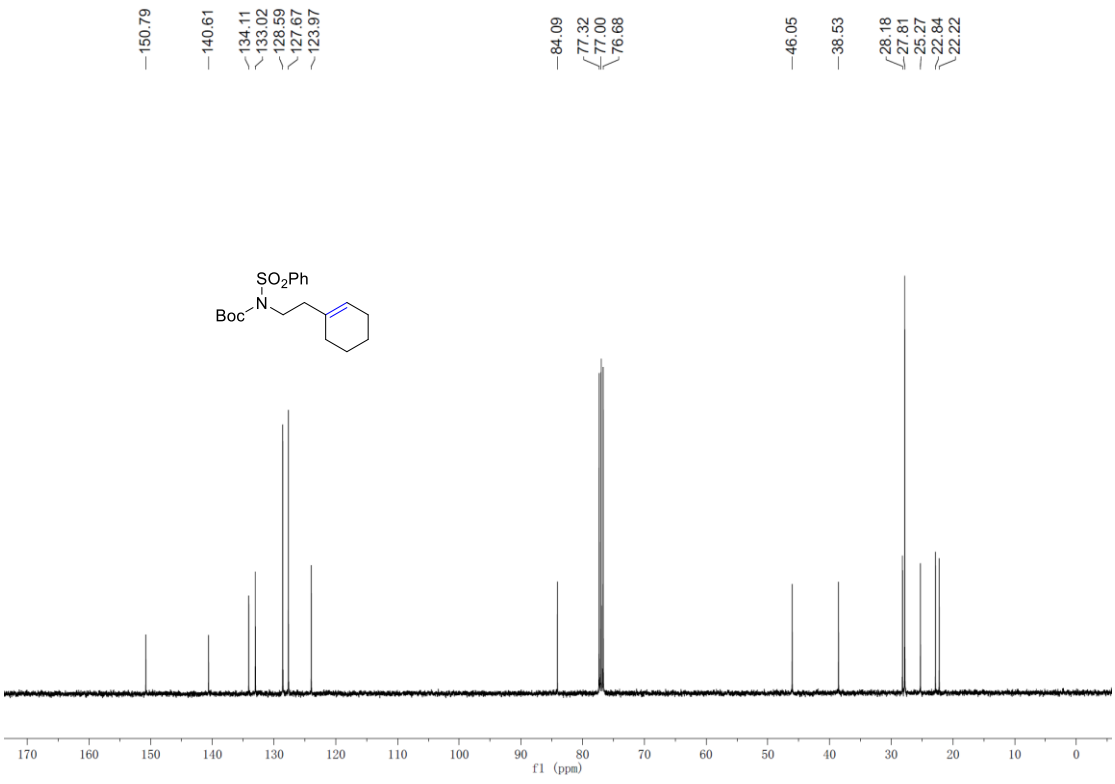
N-(2-(cyclohex-1-en-1-yl)ethyl)benzenesulfonamide (96)



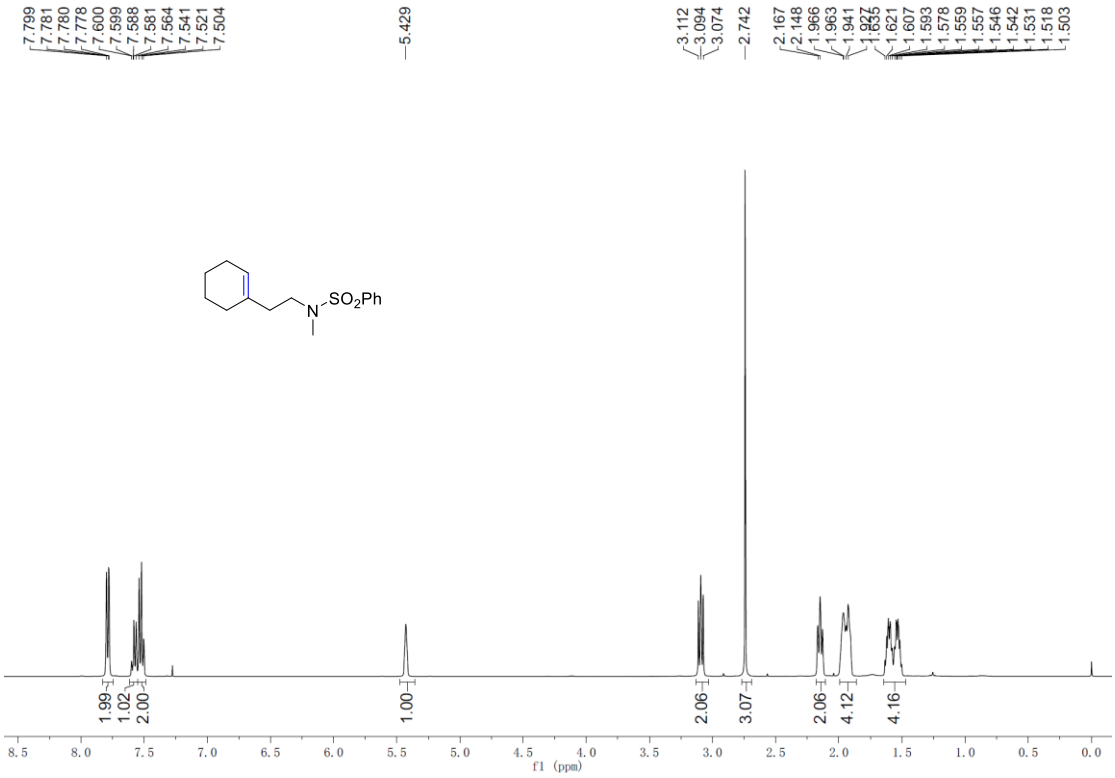


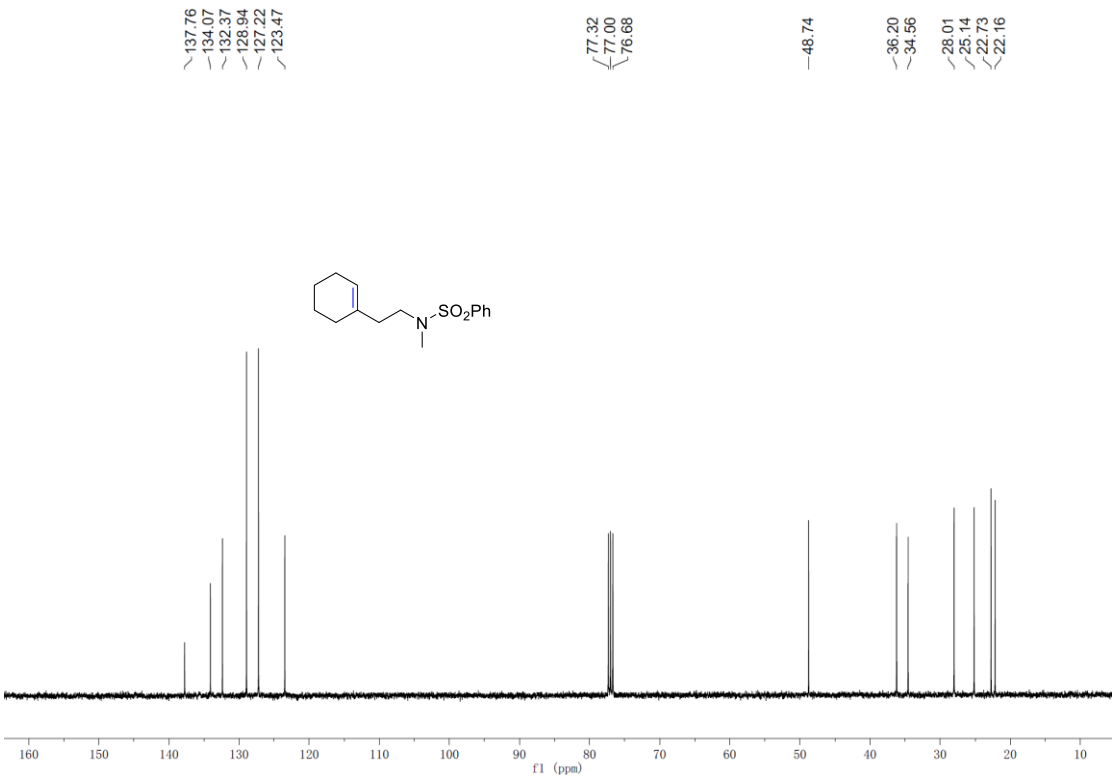
tert-butyl (2-(cyclohex-1-en-1-yl)ethyl)(phenylsulfonyl)carbamate (97)



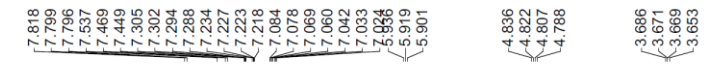


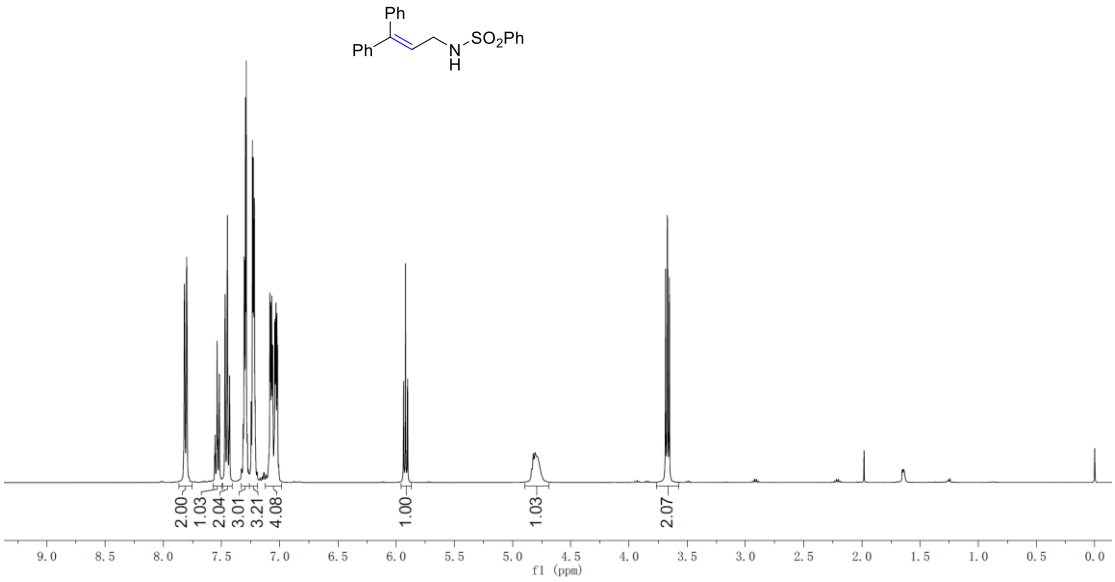
N-(2-(cyclohex-1-en-1-yl)ethyl)-N-methylbenzenesulfonamide (98)

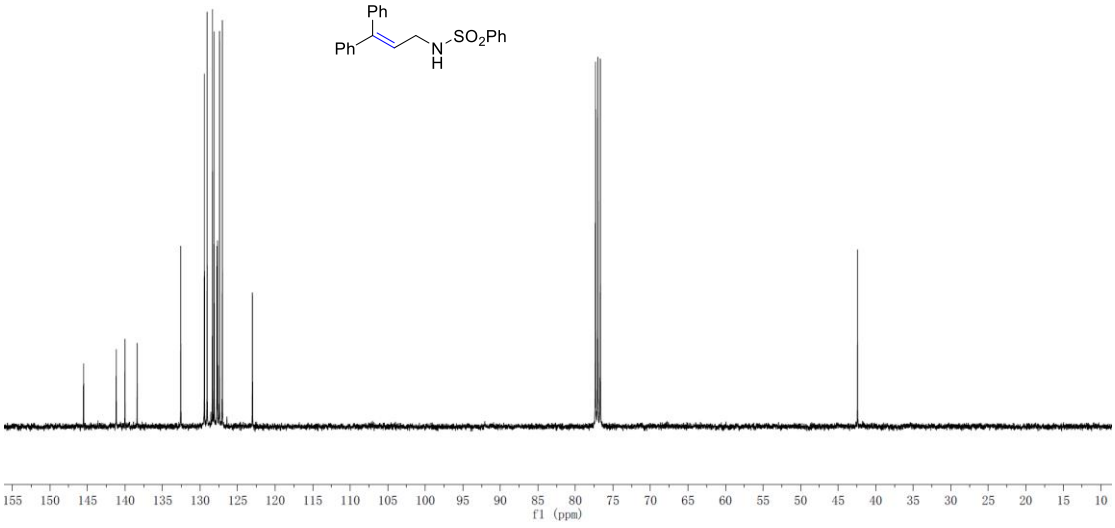




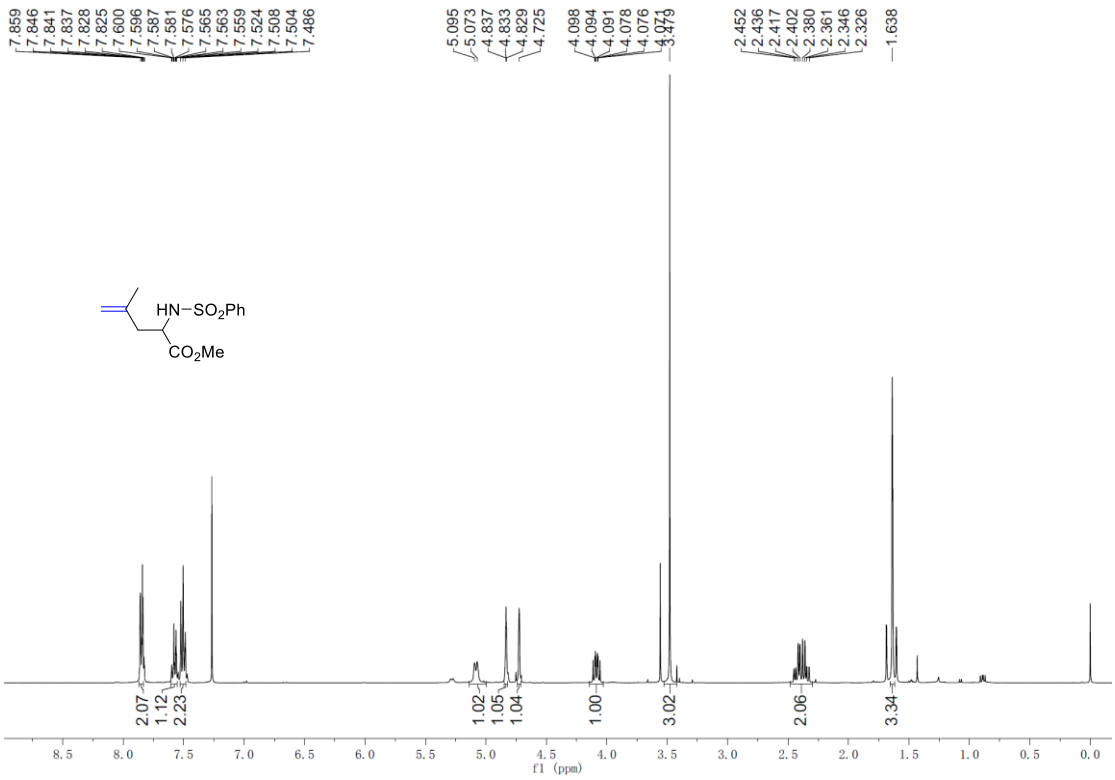
N-(3,3-diphenylallyl)benzenesulfonamide (99)

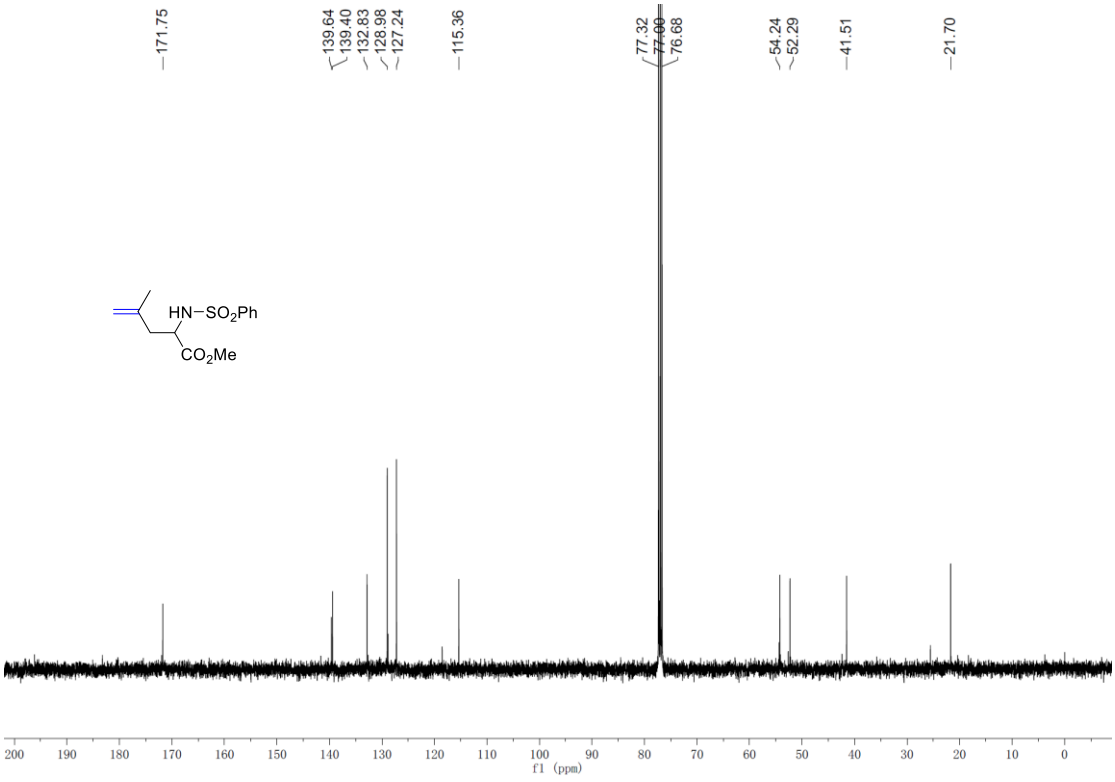




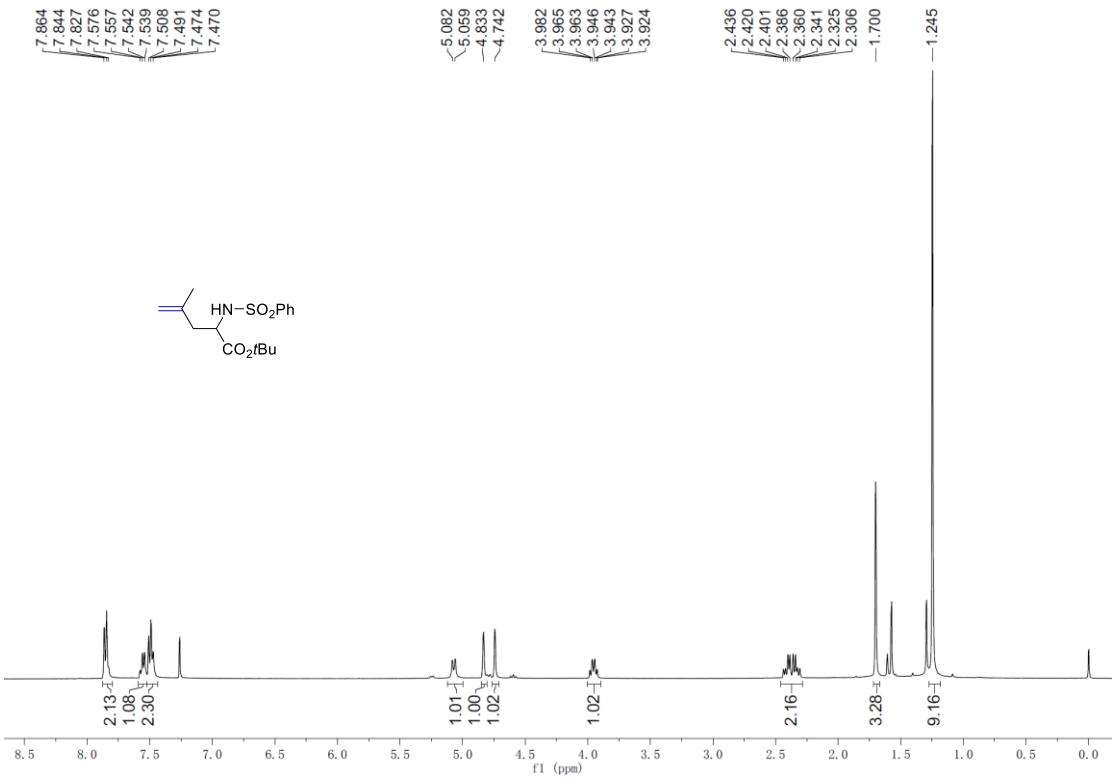


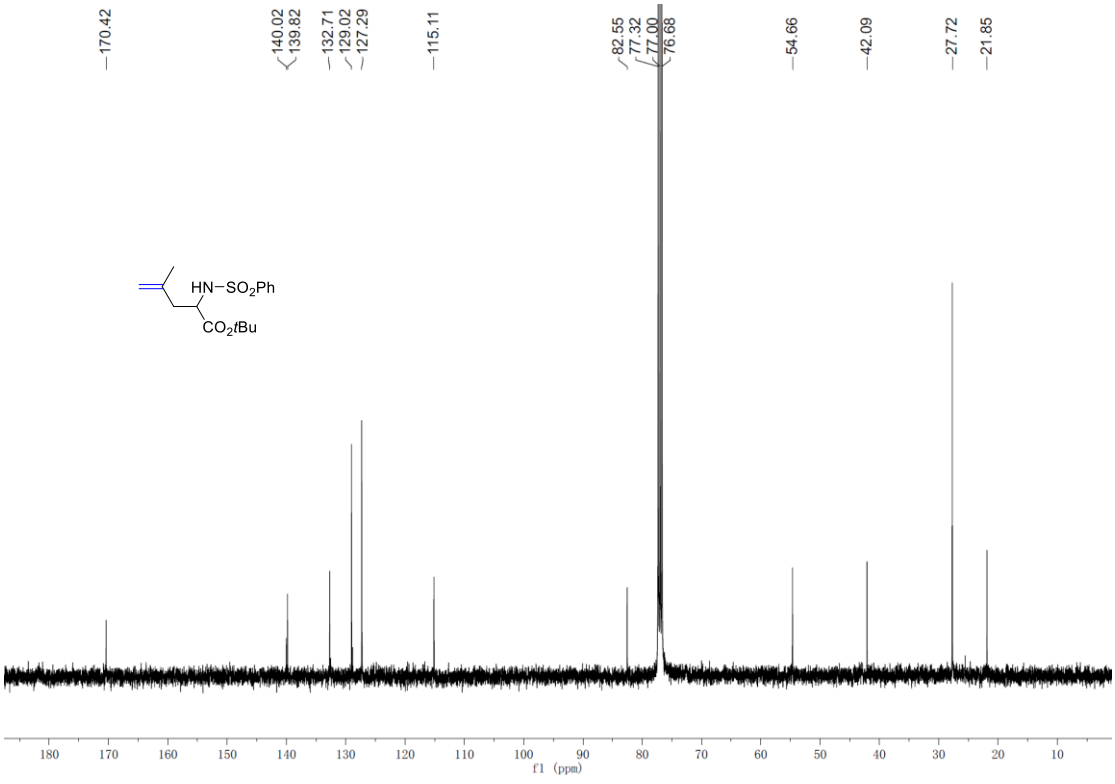
methyl 4-methyl-2-(phenylsulfonamido)pent-4-enoate (100)



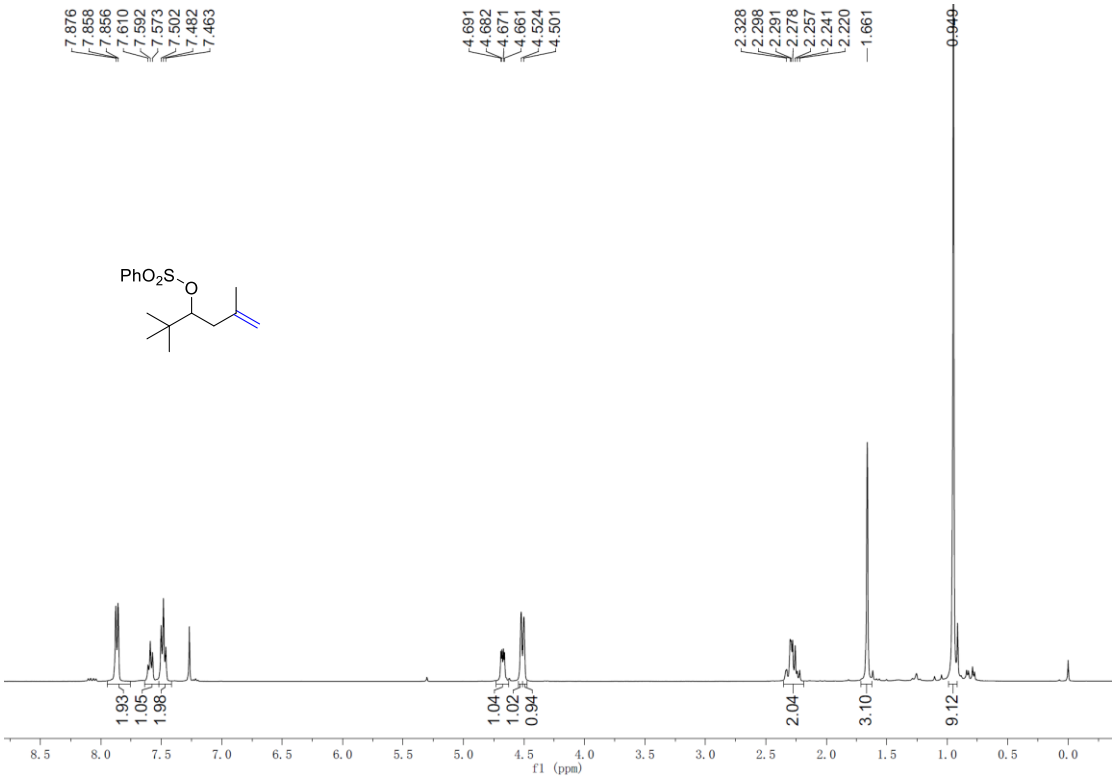


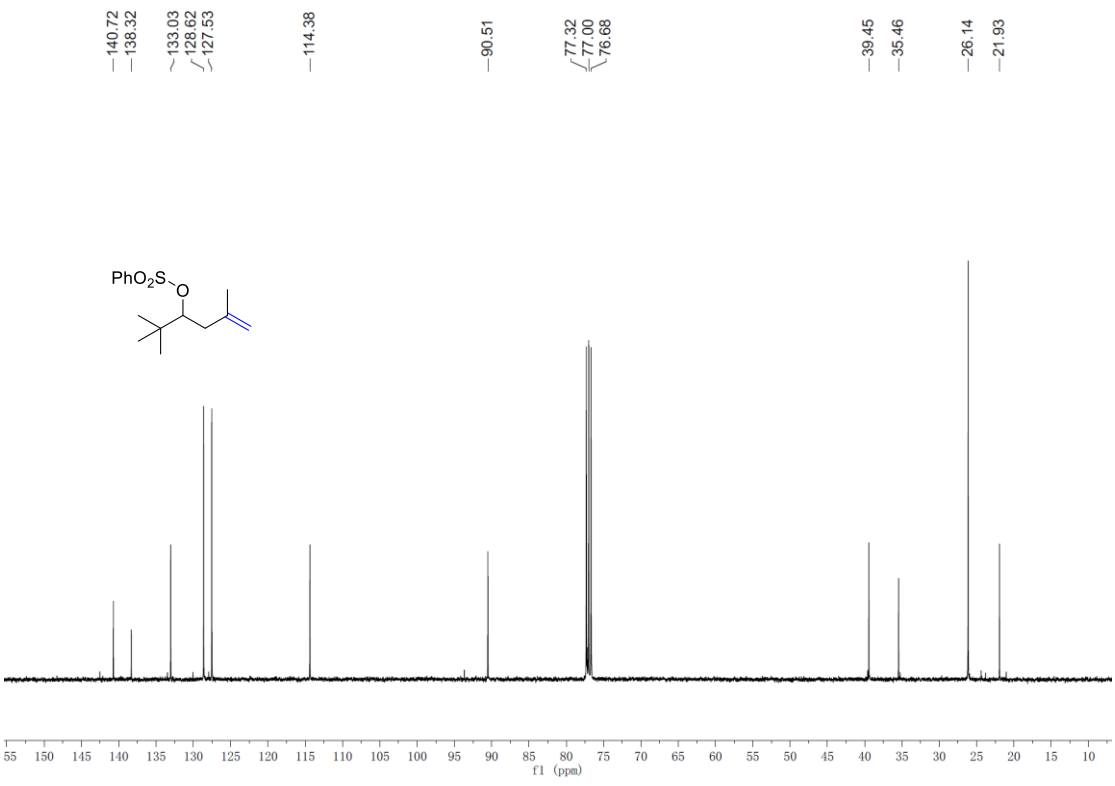
tert-butyl 4-methyl-2-(phenylsulfonamido)pent-4-enoate (101)



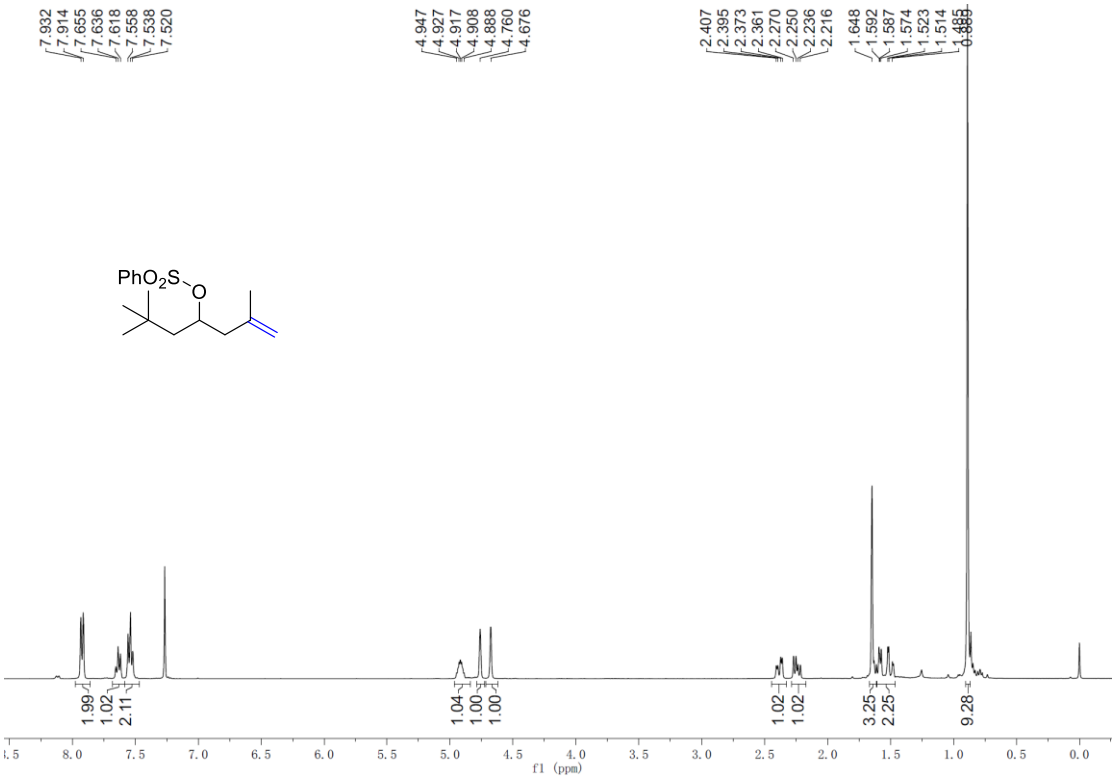


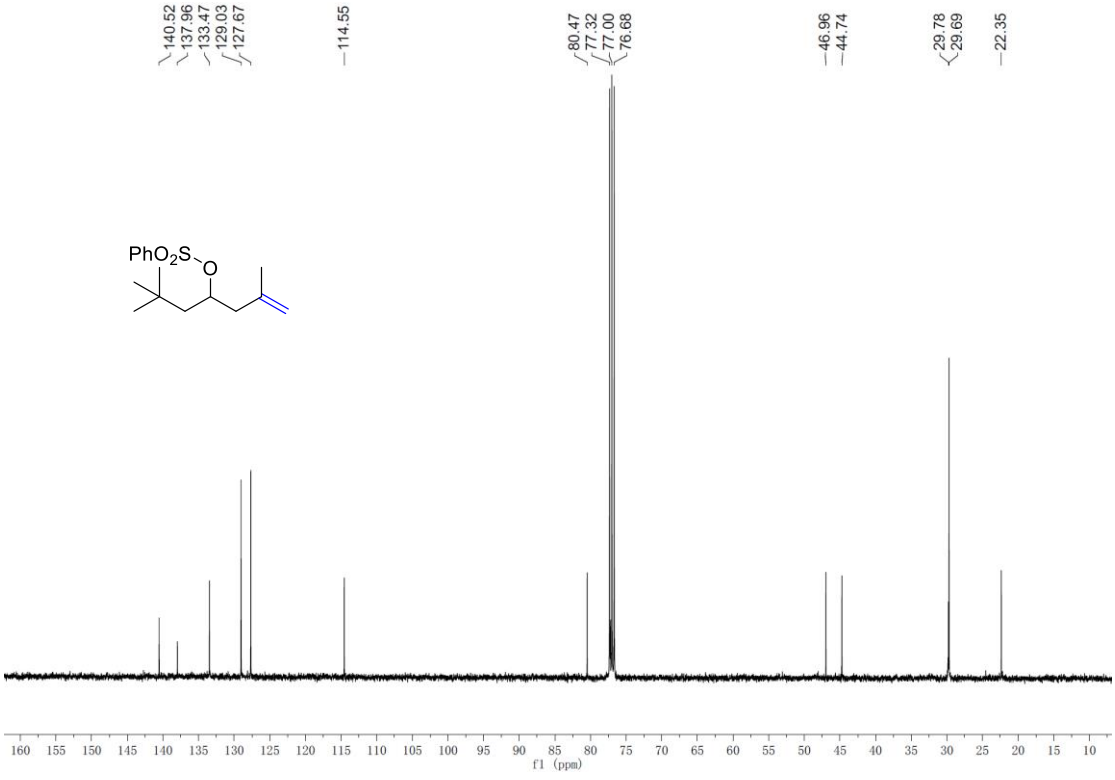
2,2,5-trimethylhex-5-en-3-yl benzenesulfonate (102)



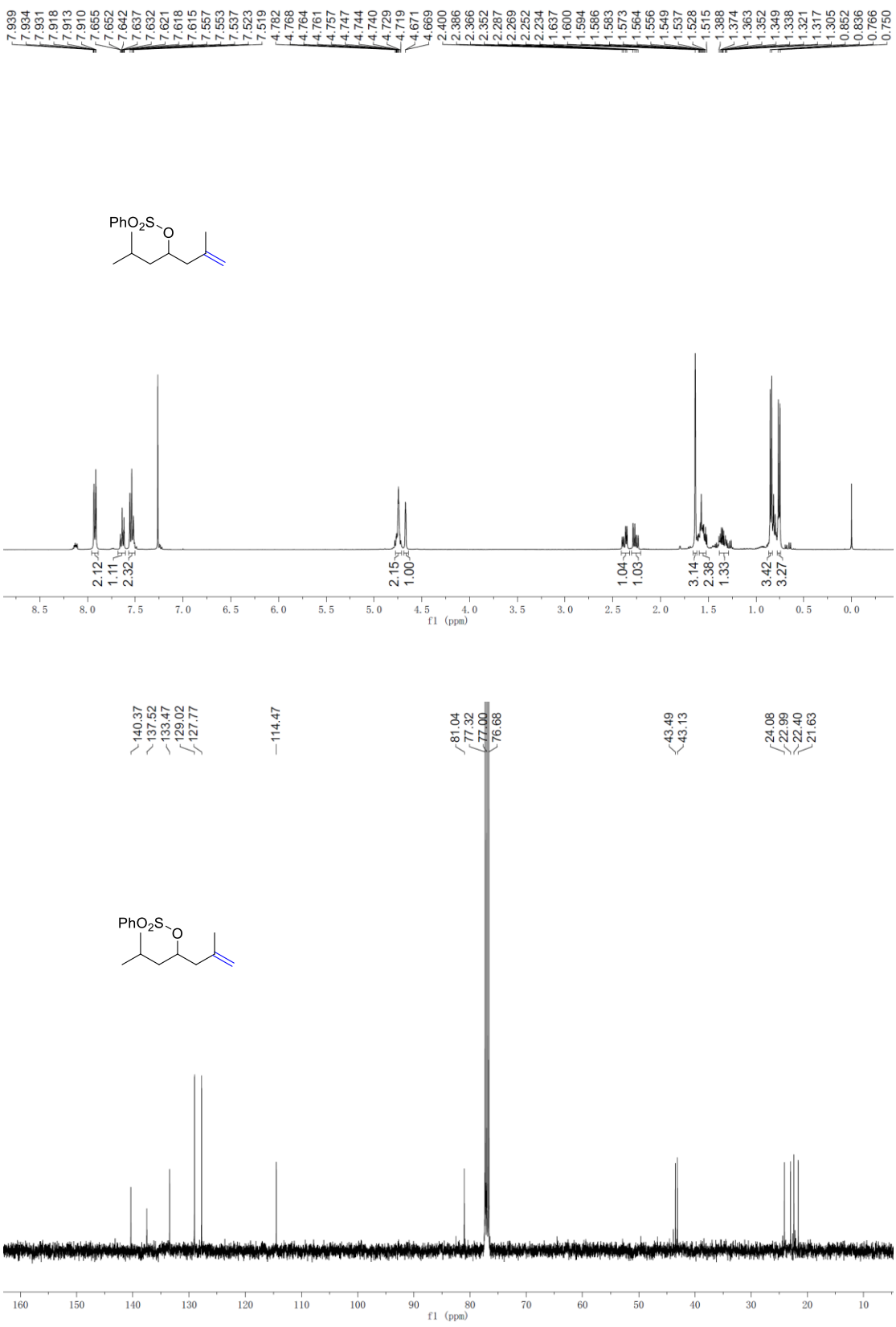


2,6,6-trimethylhept-1-en-4-yl benzenesulfonate (103)

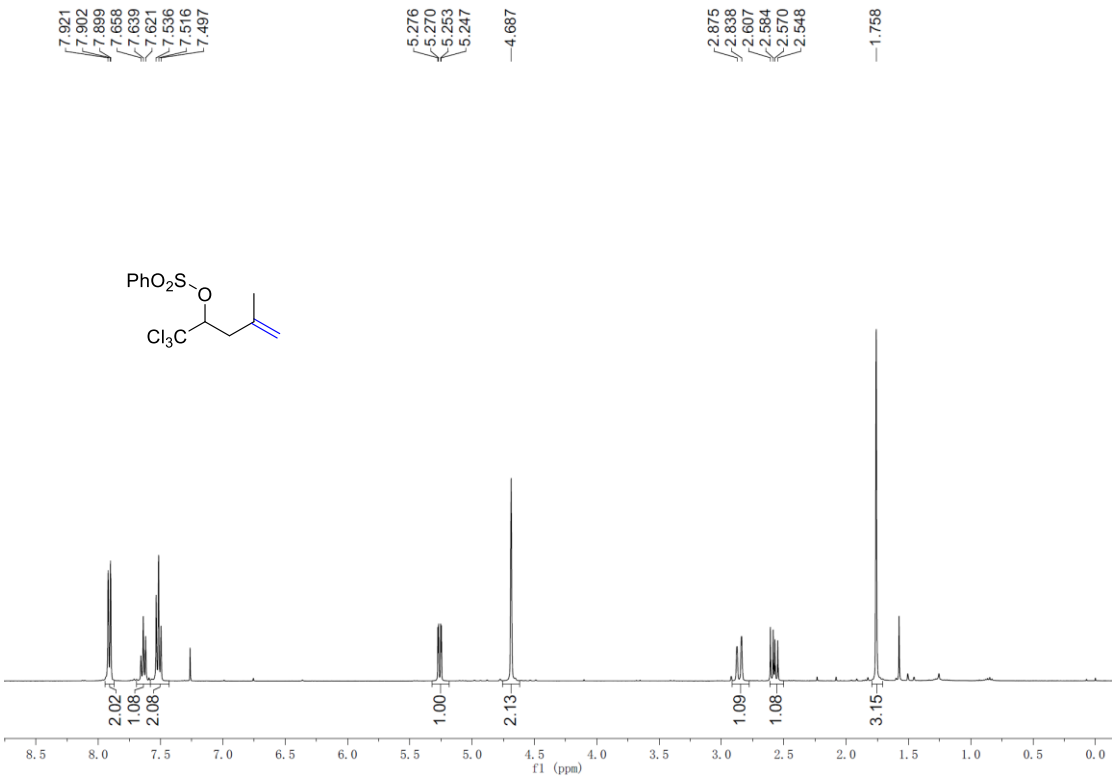


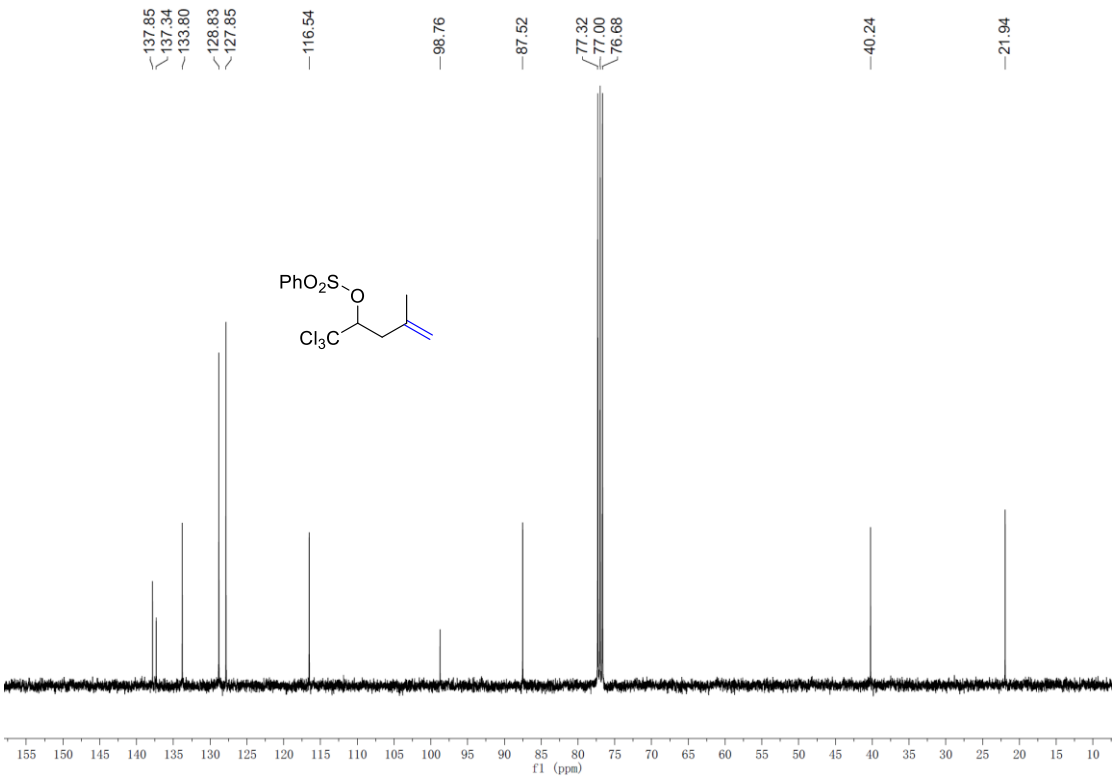


2,6-dimethylhept-1-en-4-yl benzenesulfonate (104)

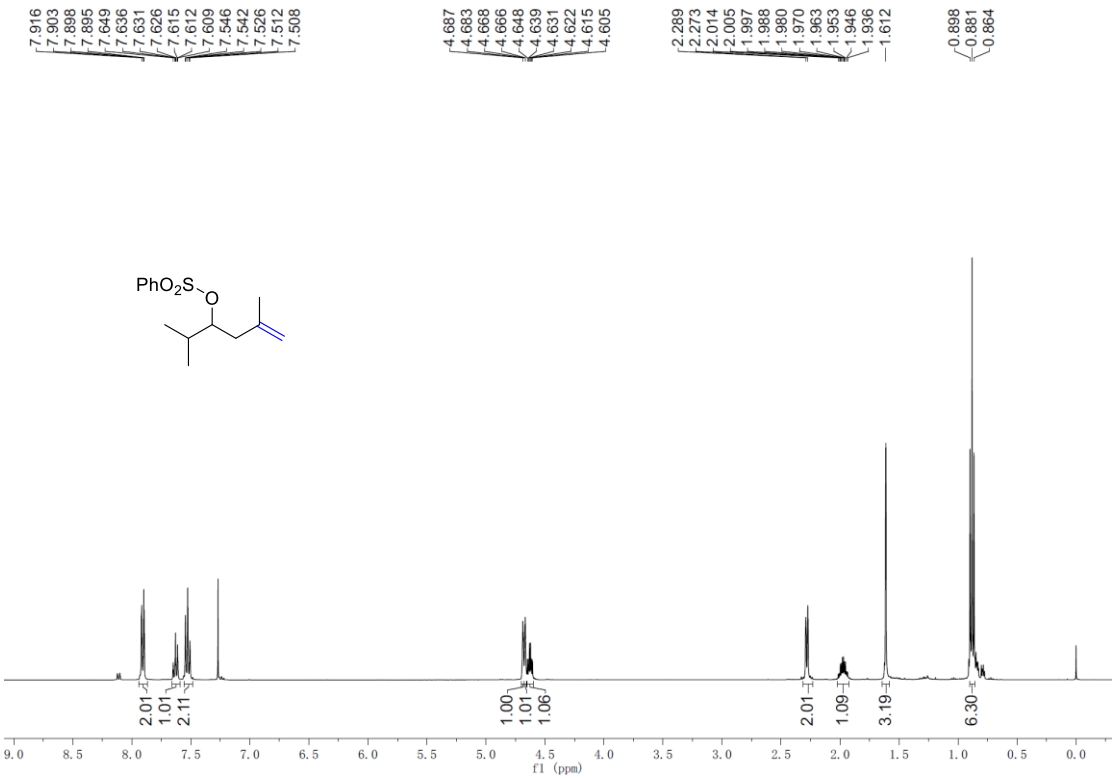


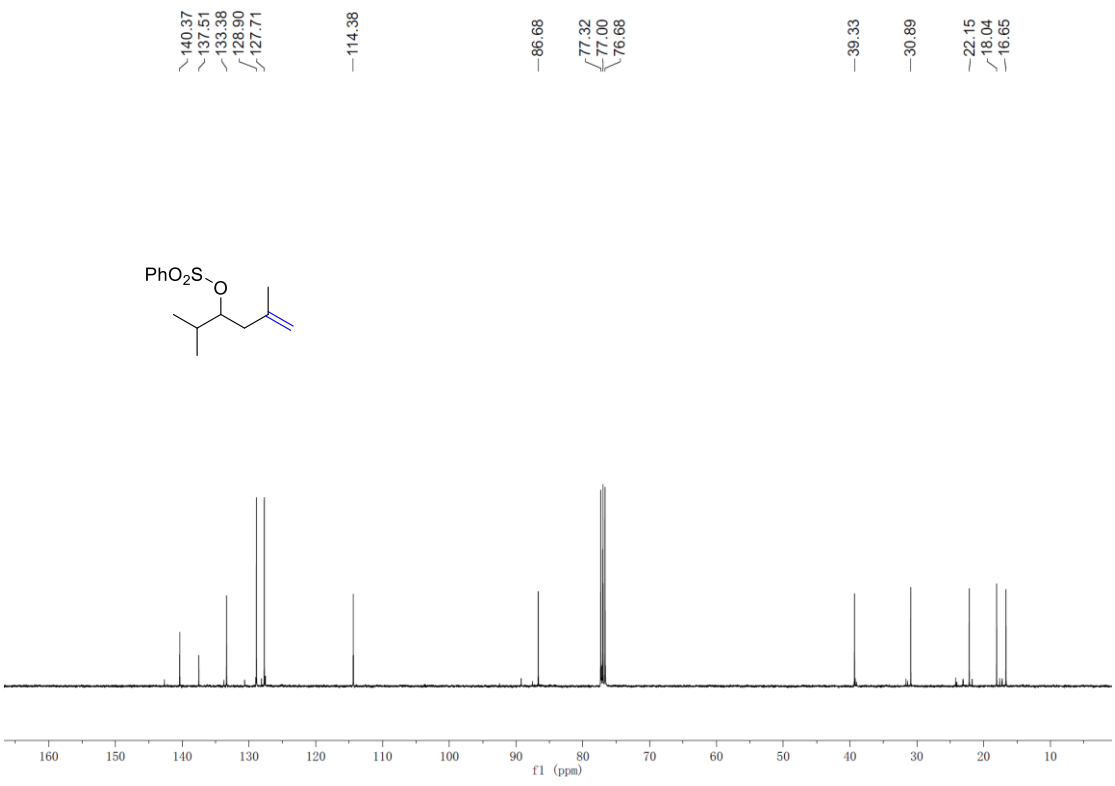
1,1,1-trichloro-4-methylpent-4-en-2-yl benzenesulfonate (105)



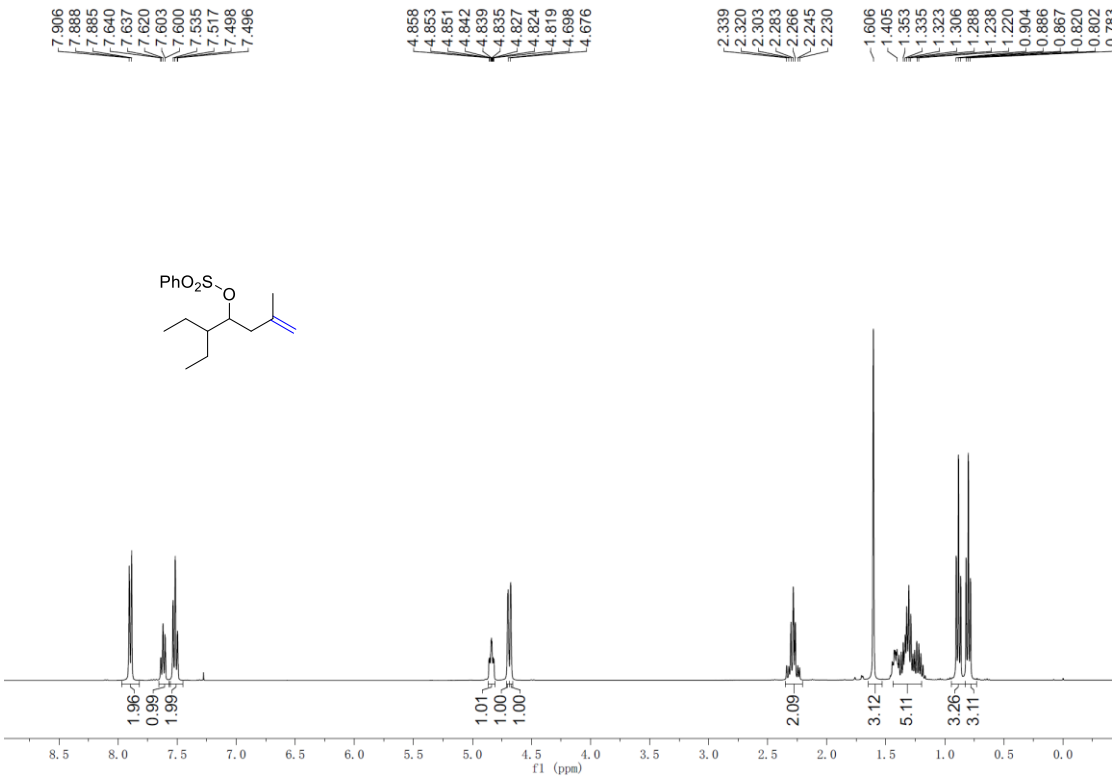


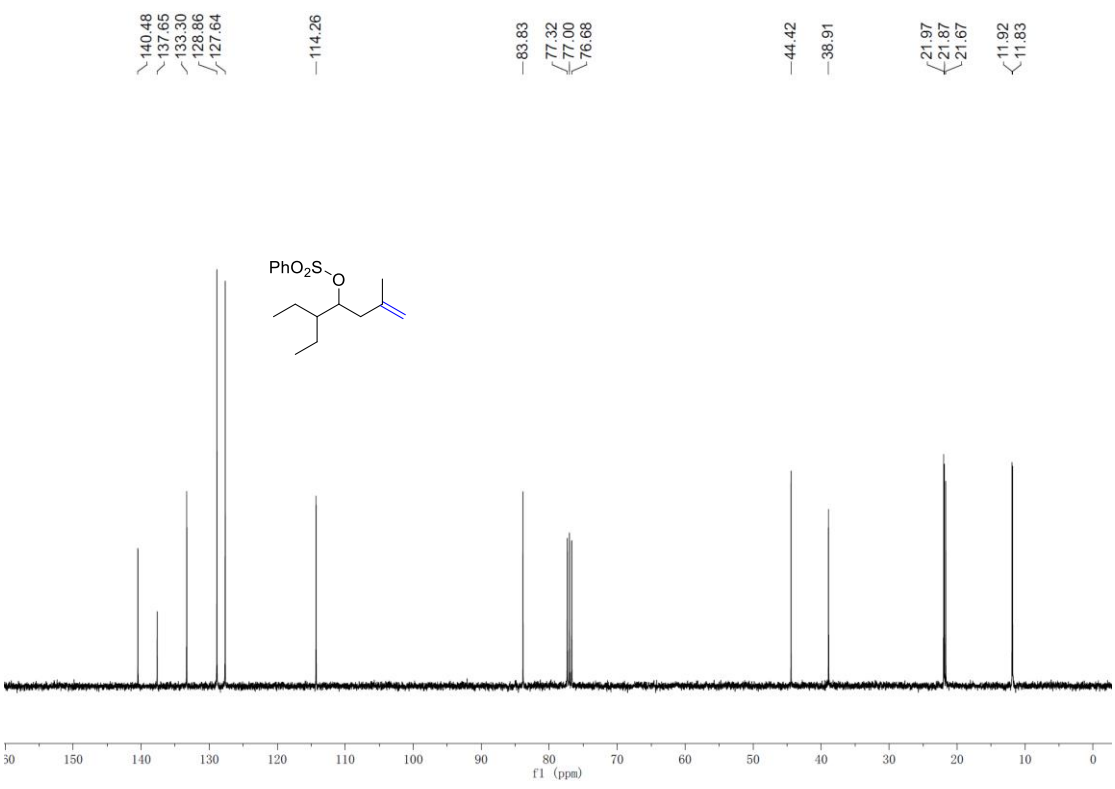
2,5-dimethylhex-5-en-3-yl benzenesulfonate (106)



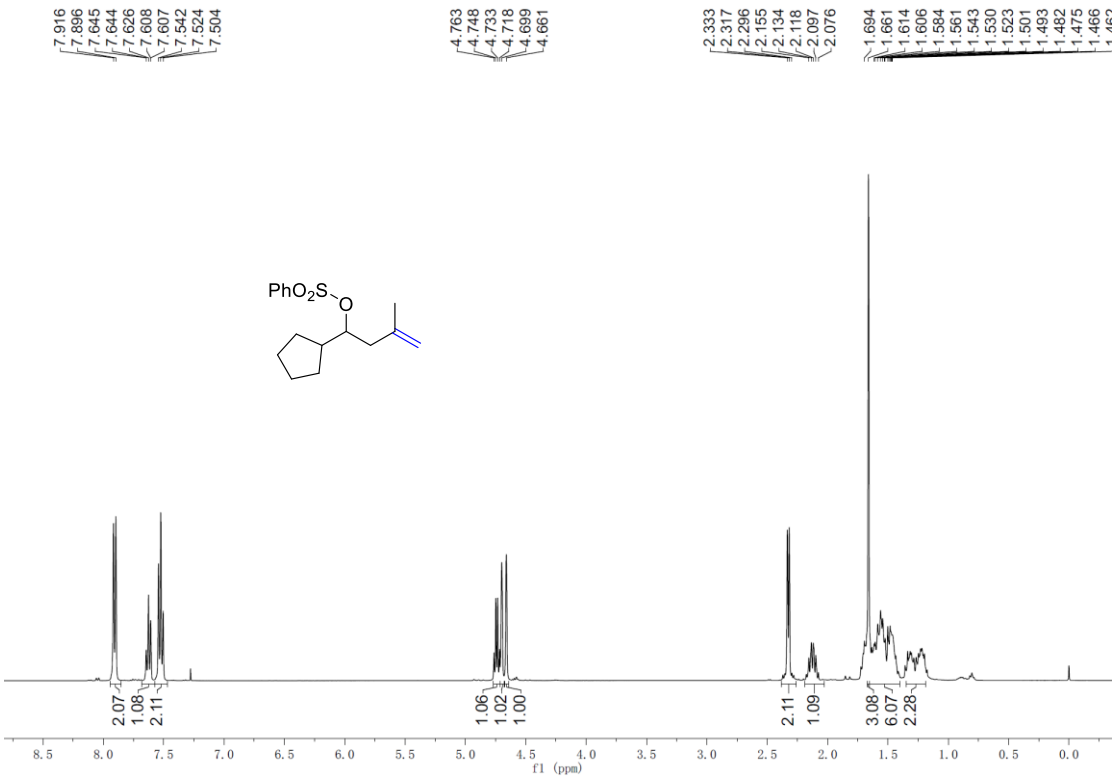


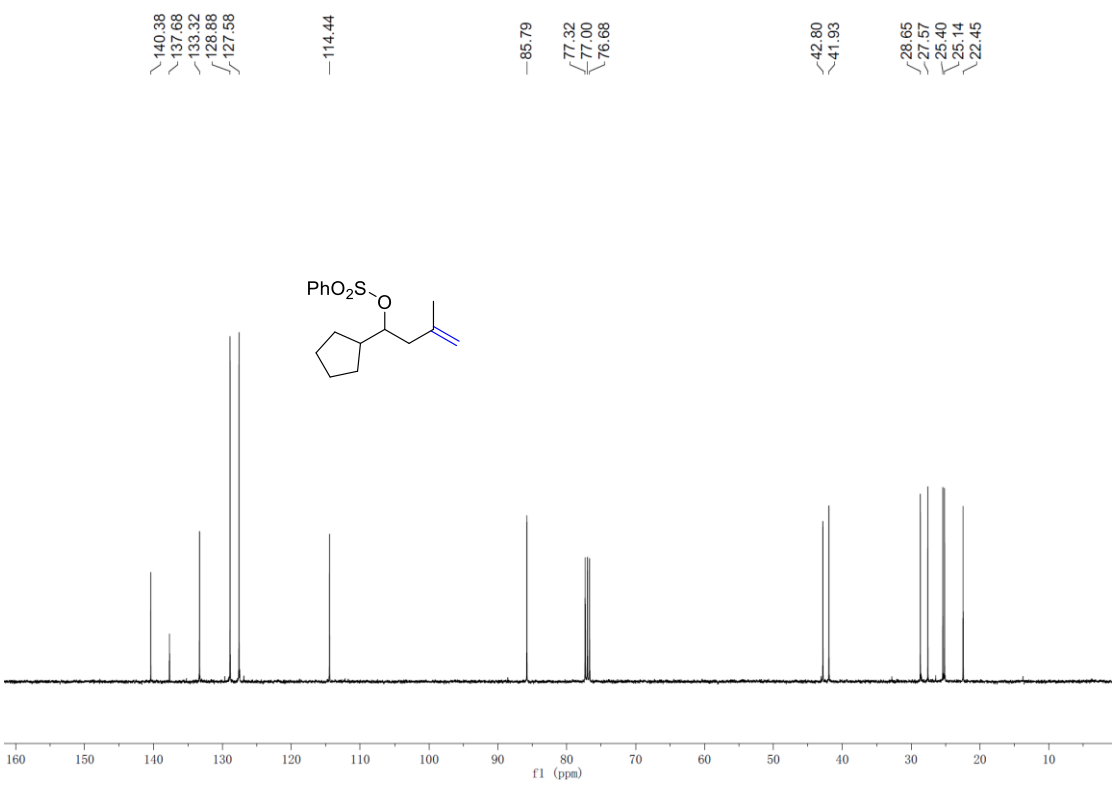
5-ethyl-2-methylhept-1-en-4-yl benzenesulfonate (107)



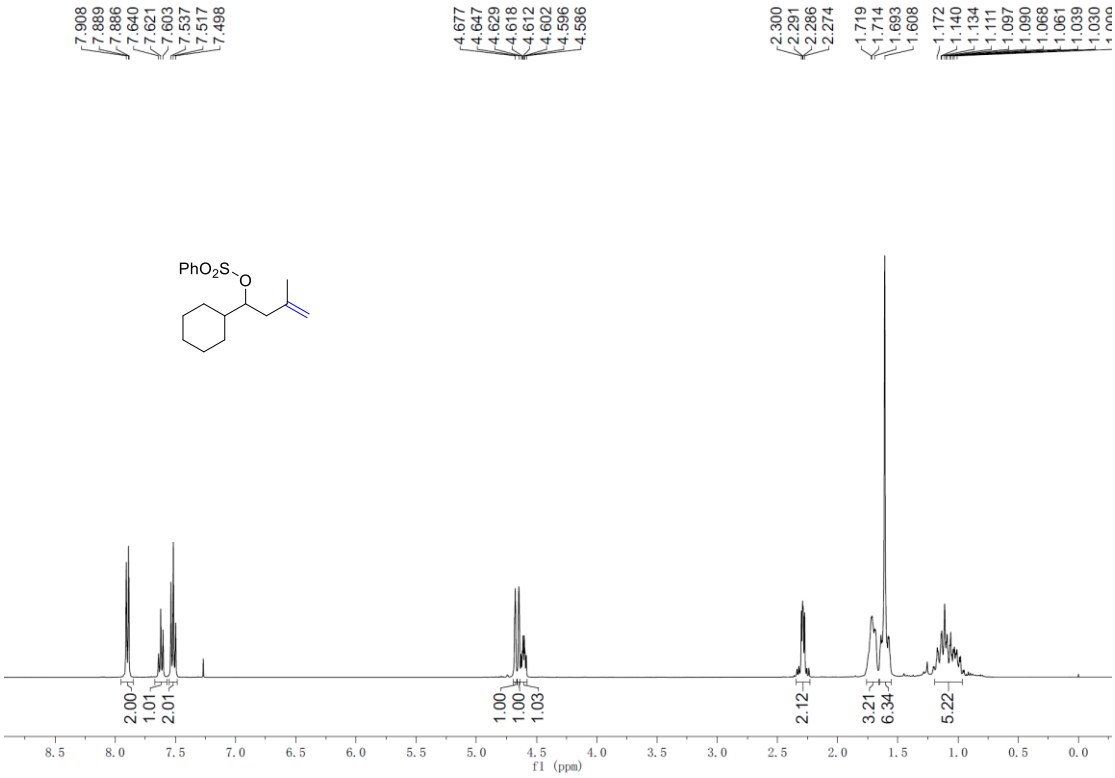


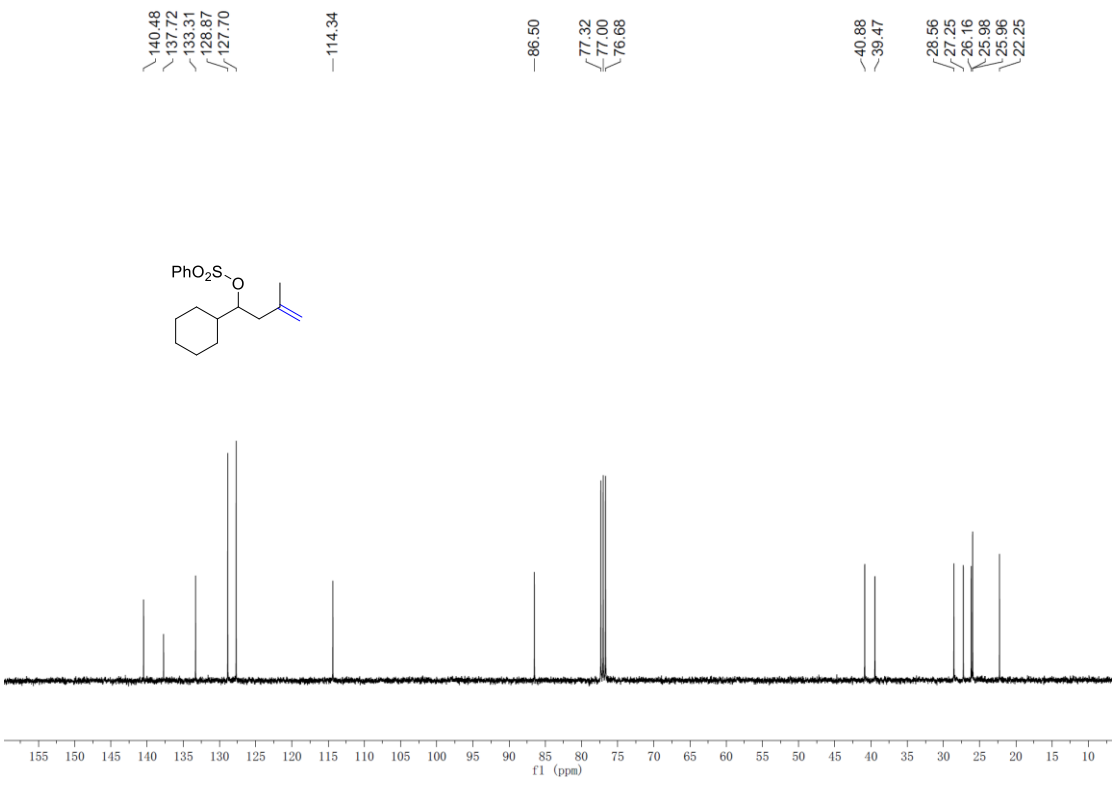
1-cyclopentyl-3-methylbut-3-en-1-yl benzenesulfonate (108)



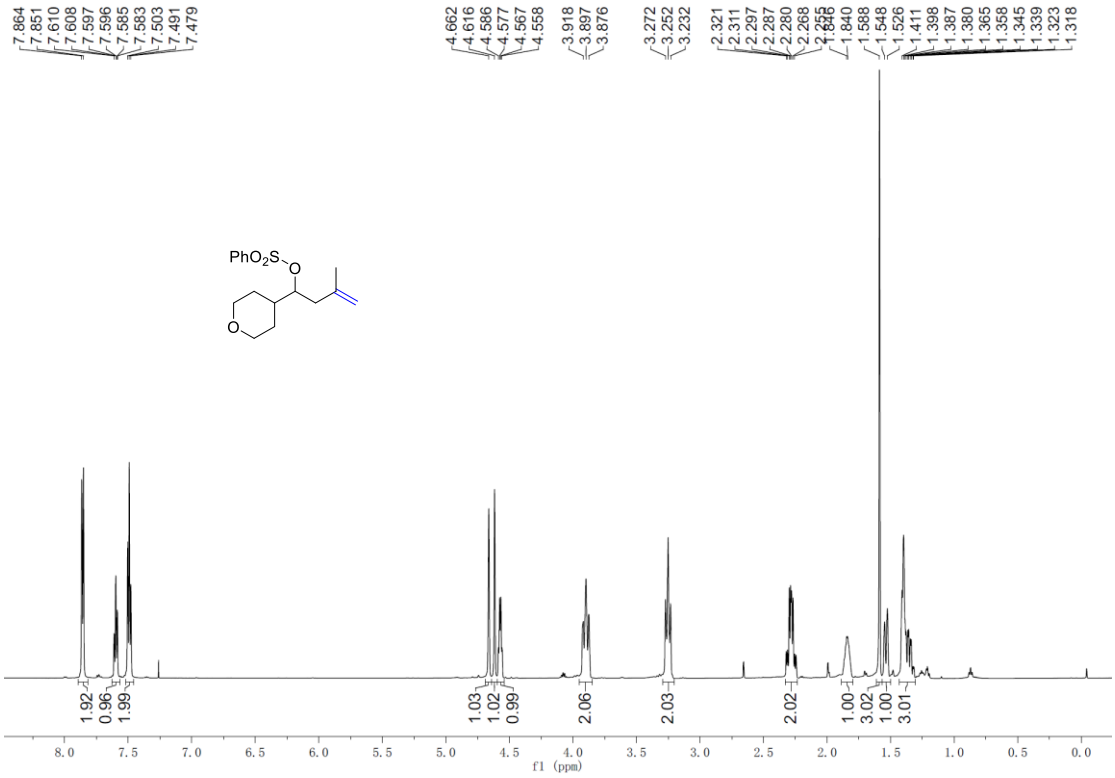


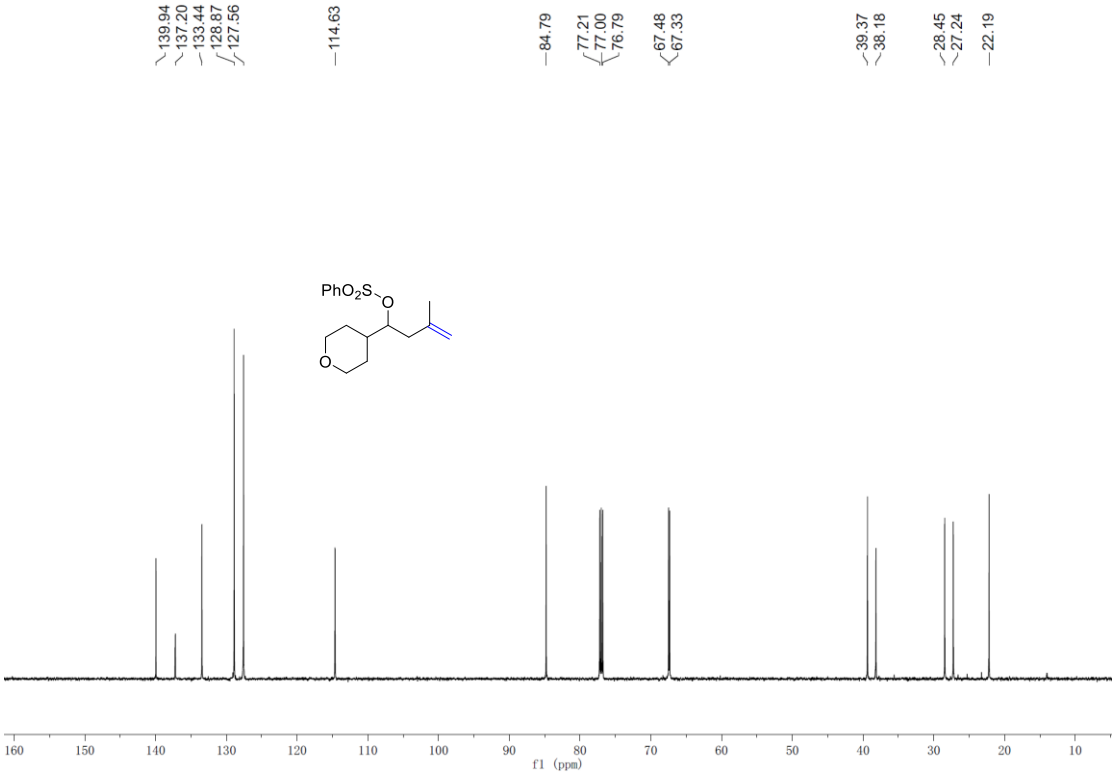
1-cyclohexyl-3-methylbut-3-en-1-yl benzenesulfonate (109)



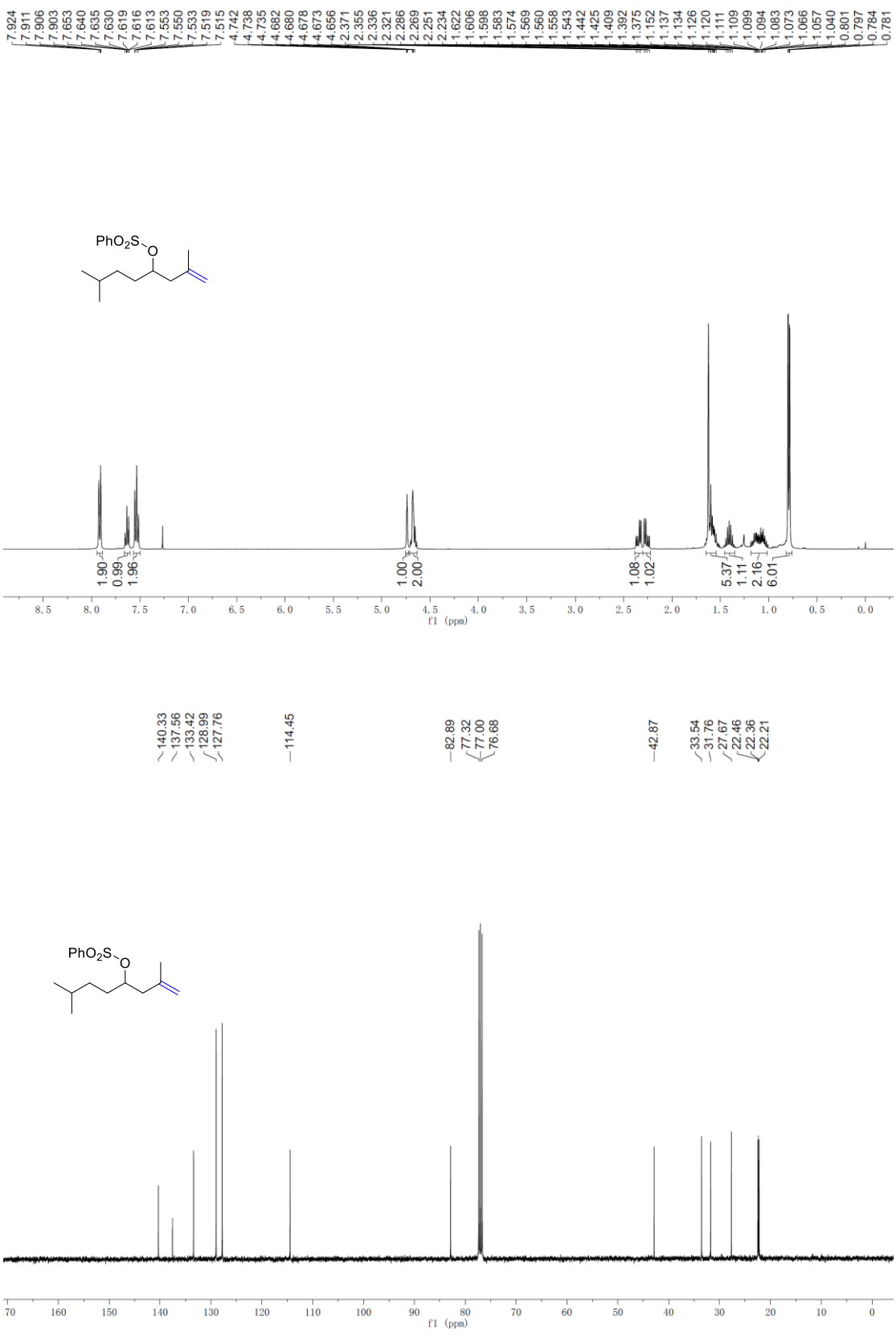


3-methyl-1-(tetrahydro-2H-pyran-4-yl)but-3-en-1-yl benzenesulfonate (110)

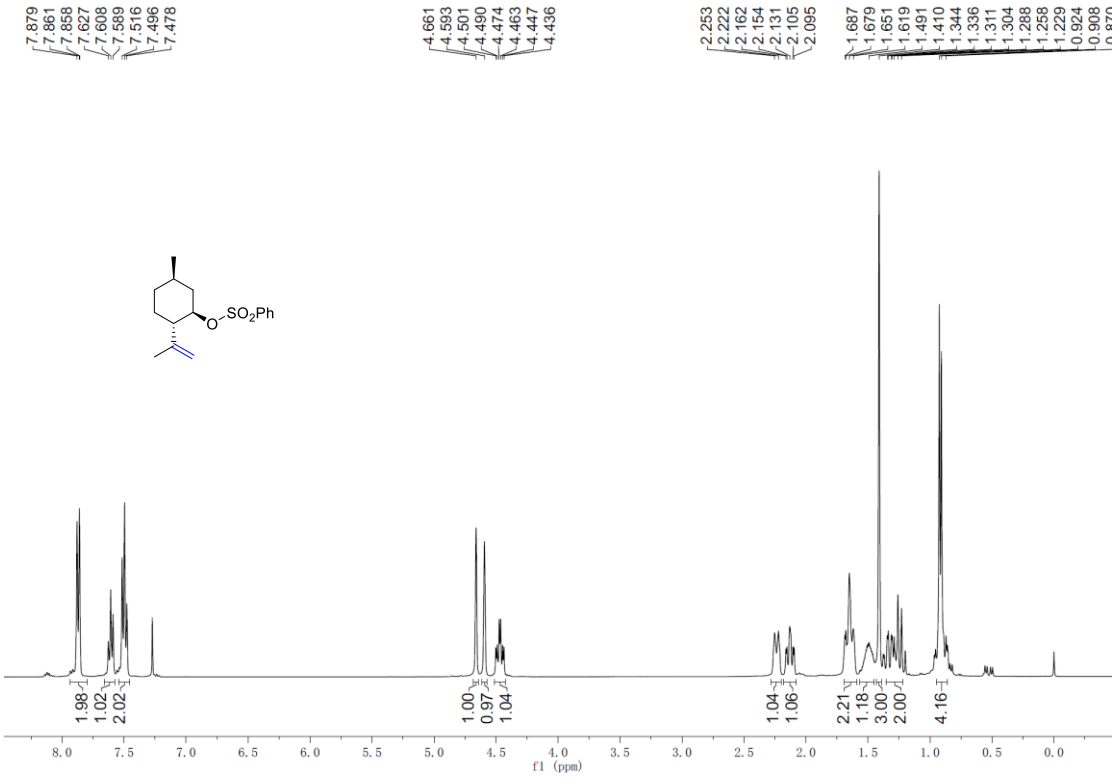


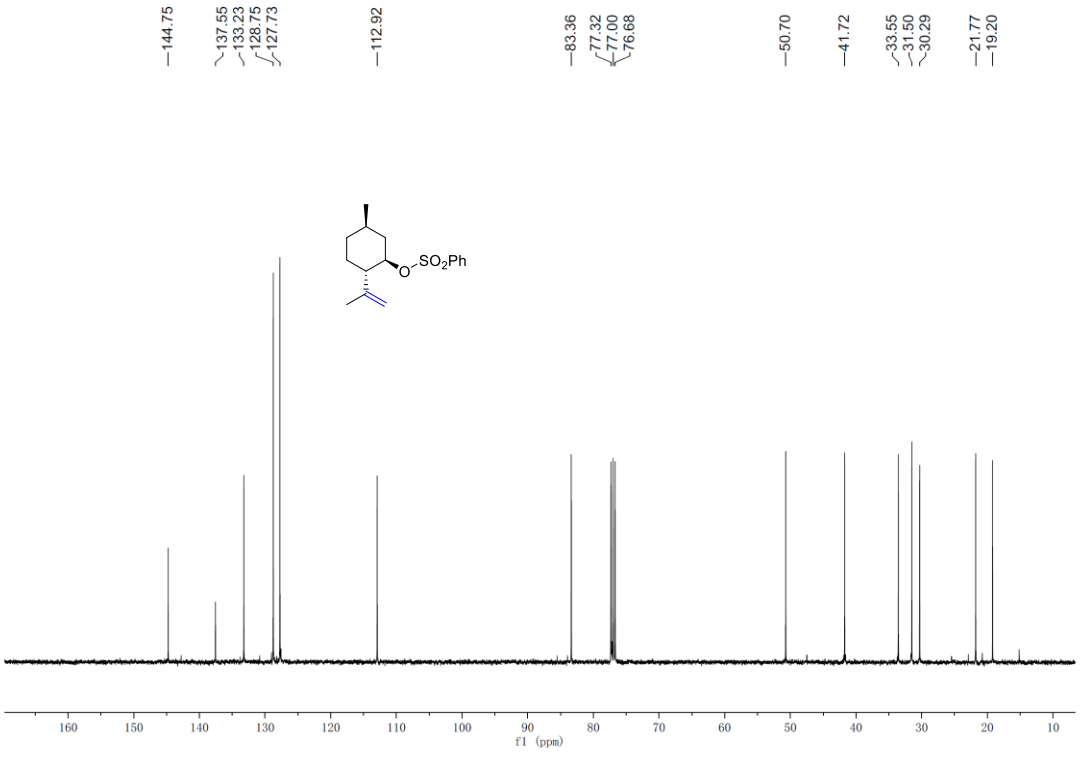


2,7-dimethyloct-1-en-4-yl benzenesulfonate (111)

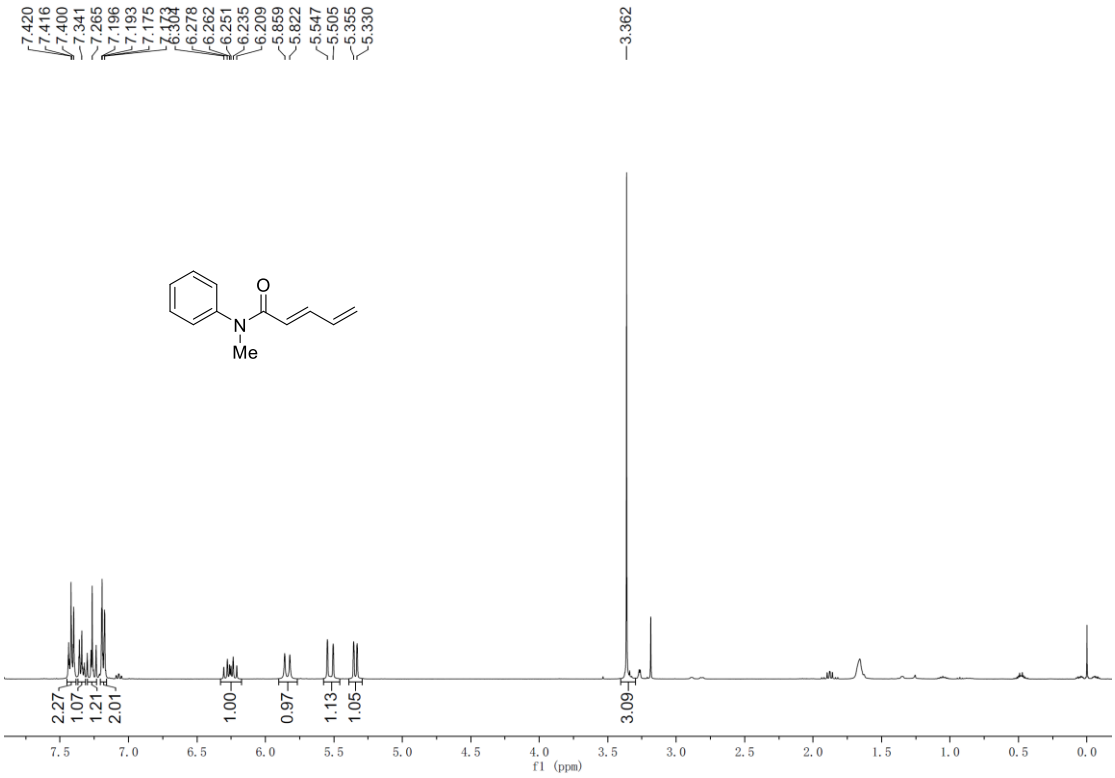


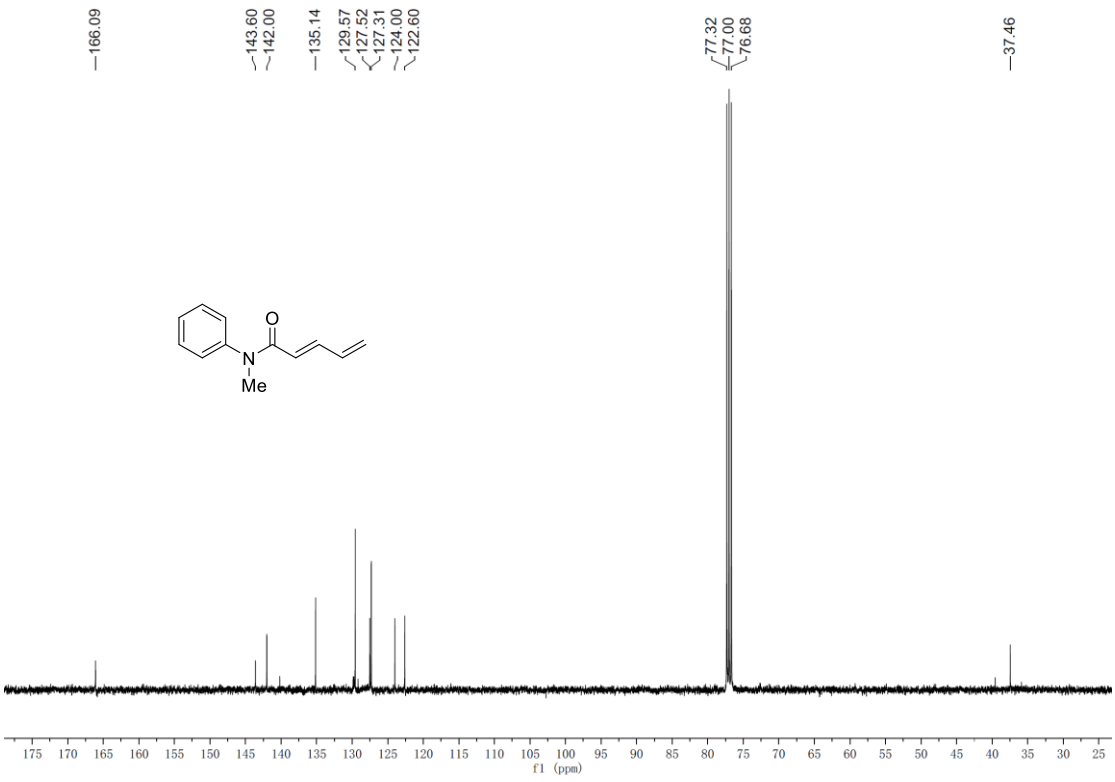
(1R,2S,5R)-5-methyl-2-(prop-1-en-2-yl)cyclohexyl benzenesulfonate (112)



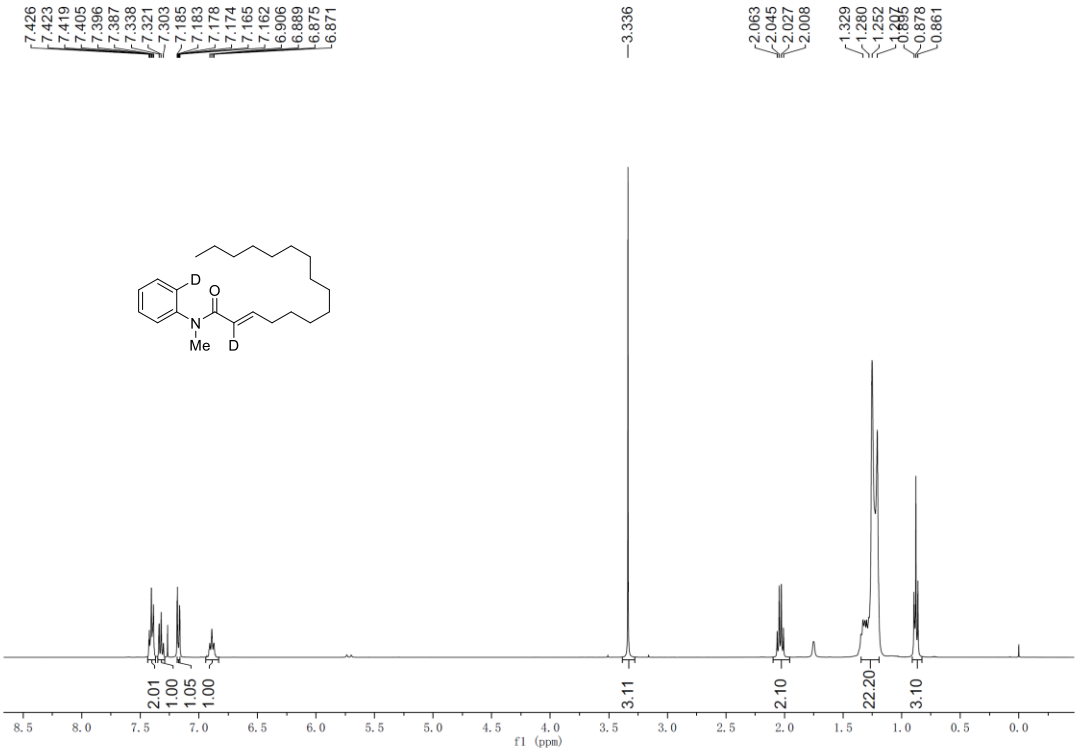


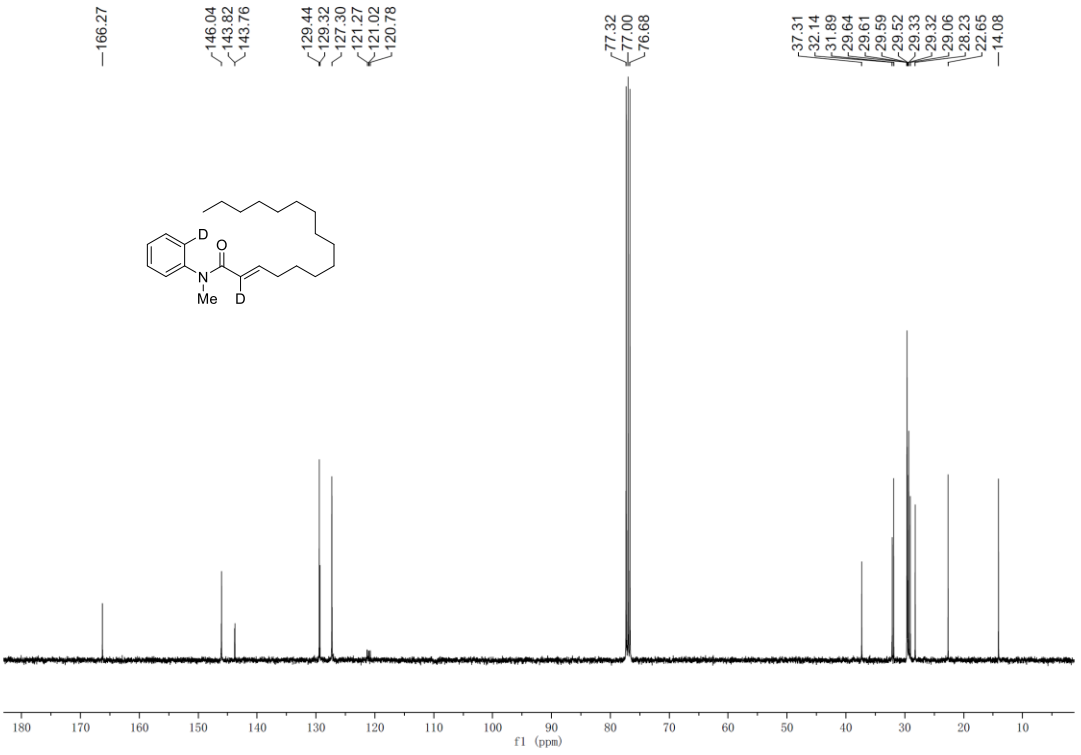
(E)-N-methyl-N-phenylpenta-2,4-dienamide (113)



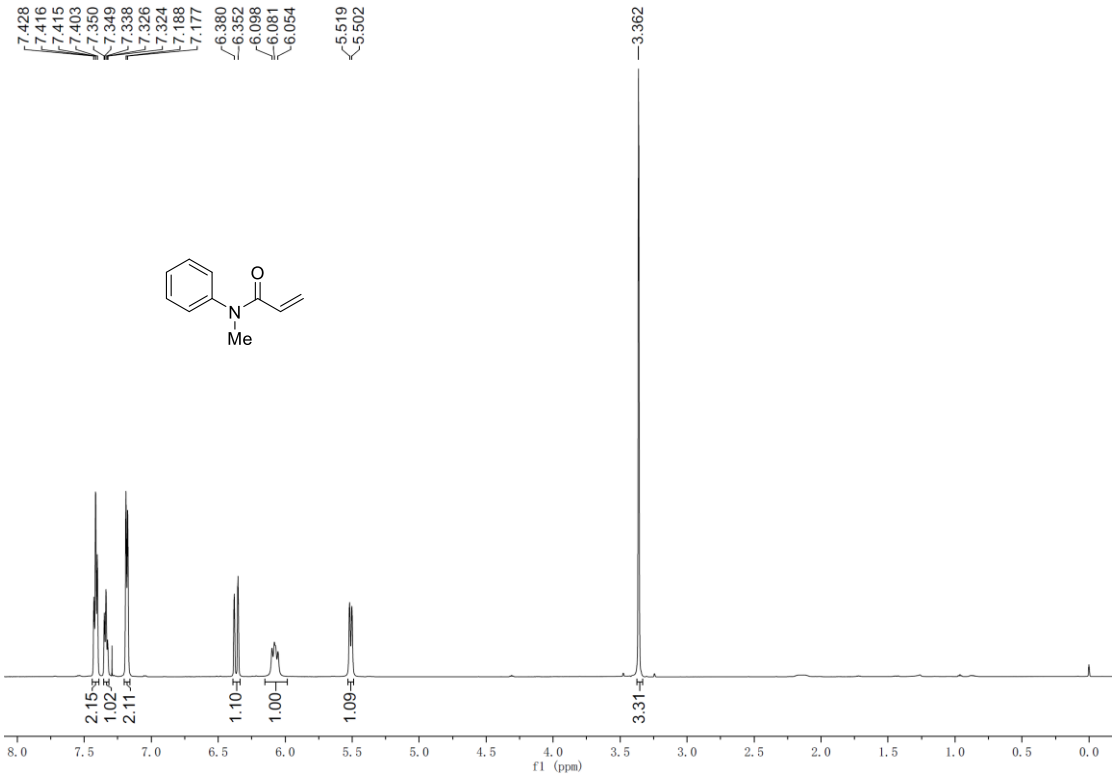


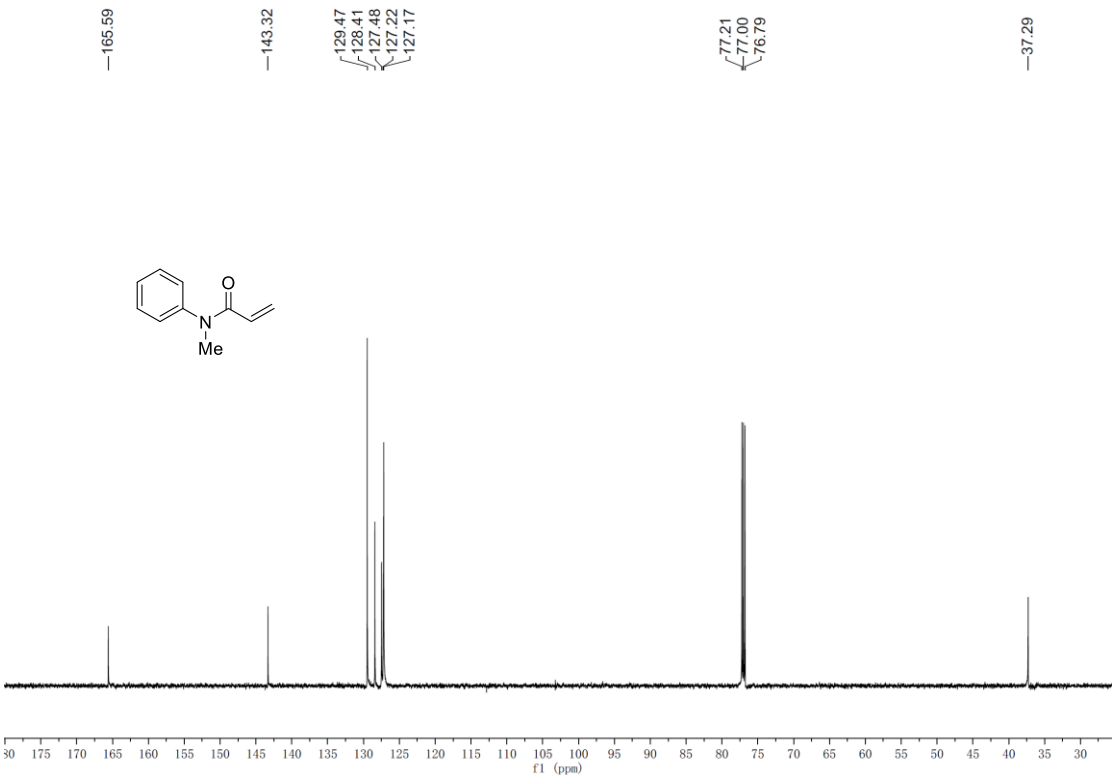
(E)-N-methyl-N-(phenyl-2-d)hexadec-2-enamide-2-d (D_2-28)



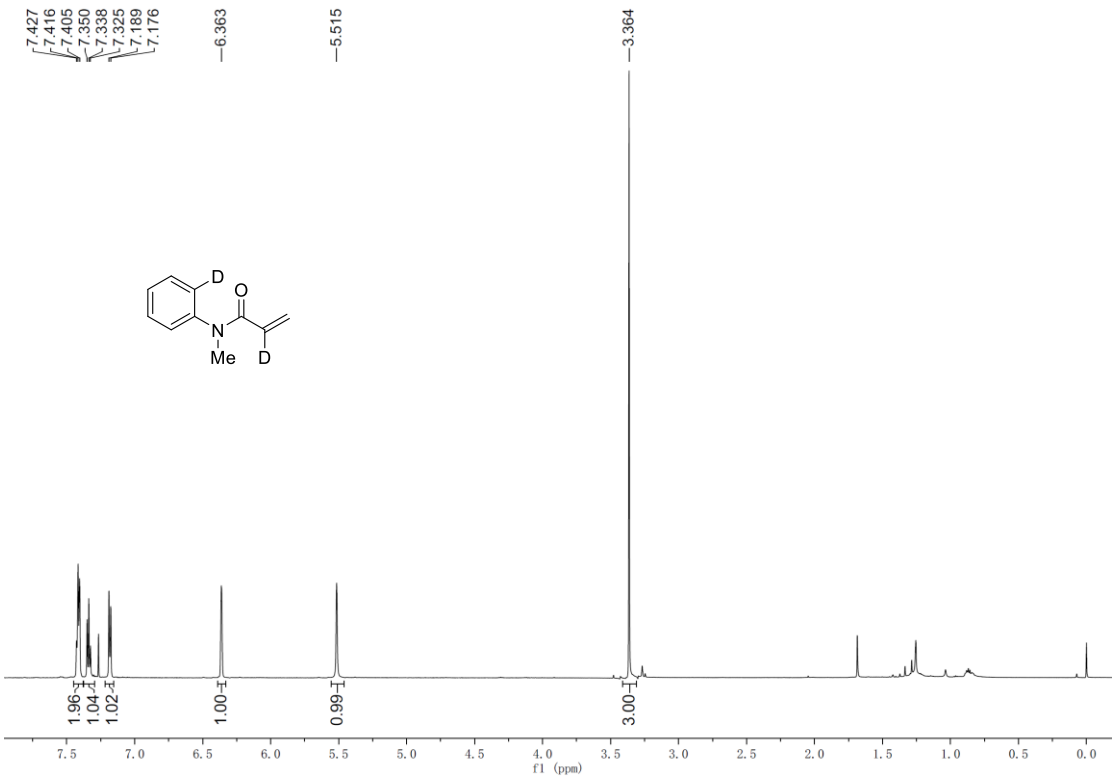


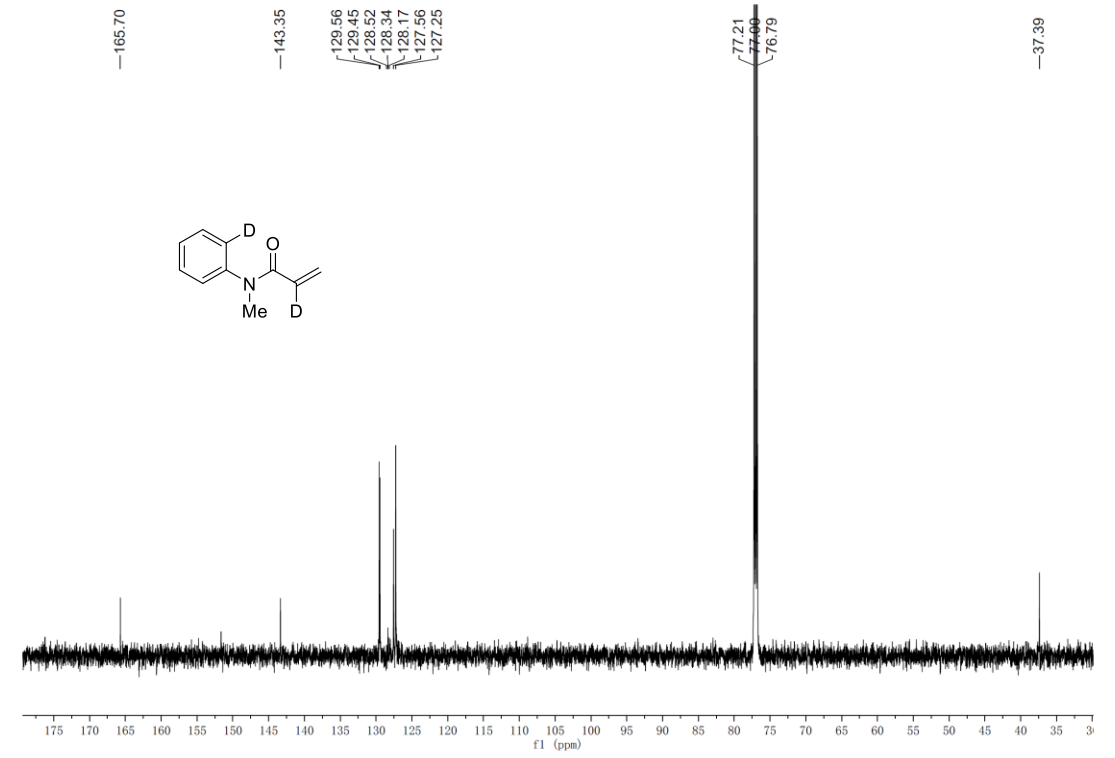
N-methyl-N-phenylacrylamide (114)





N-methyl-N-(phenyl-2-d)acrylamide-2-d (114a)





N-methyl-N-phenylacrylamide-3,3-d2 (114b)