# *Supporting Information*

## Metal-free triphenyl phosphite-catalyzed Ritter-type amidation of allylic alcohols

Longzhi Zhu,*[a] Furong Guo,[a] Weiwei Luo,[a] Shuangjiao Xie,[a] Tingyuan Zhu,[a] Zihe Liao,[a] Yu Liu,[a] Biquan Xiong,*[a] Ke-Wen Tang[a] and Renhua Qiu*[b]

[a] Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang 414006, China. Emails: zhulongzhi@hnu.edu.cn (Dr. L. Zhu), xiongbiquan@126.com (Prof. B. Xiong).

[b] Advanced Catalytic Engineering Research Center of the Ministry of Education, State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China. Email: renhuaqiu1@hnu.edu.cn (Prof. R. Qiu)

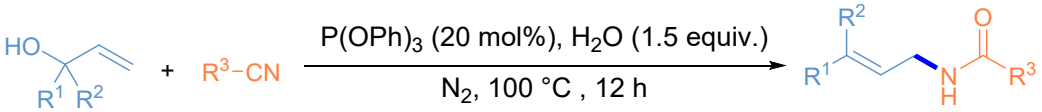
## *Contents*

# 1. General information

## 1.1 General remarks

Unless specifically noted, all reactions were performed in flame-dried glass apparatus under $N_2$ atmosphere with freshly distilled anhydrous solvents. Commercially available reagents and solvents were purchased from Energy chemical, Tansoole, or Bide Pharmatech Ltd., and used without further purification. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Flash column chromatography was performed using 200-300 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates were used. $^{1}H$ (400 MHz), $^{13}C\{^{1}H\}$ (101 MHz), $^{19}F\{^{1}H\}$ (376 MHz) were recorded on a 400 MHz Bruker spectrometer in $CDCl_3$. Spectra were calibrated relative to solvent's residual proton and carbon chemical shift: $CHCl_3$ ($\delta$= 7.26 for $^{1}H$ NMR and $\delta$ = 77.16 for $^{13}C$ NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The electron ionization method was used for HRMS measurements, and the mass analyzer type used for the HRMS measurement is Q Exactive Orbitrap.

## 1.2 General procedure for the Ritter-type amination

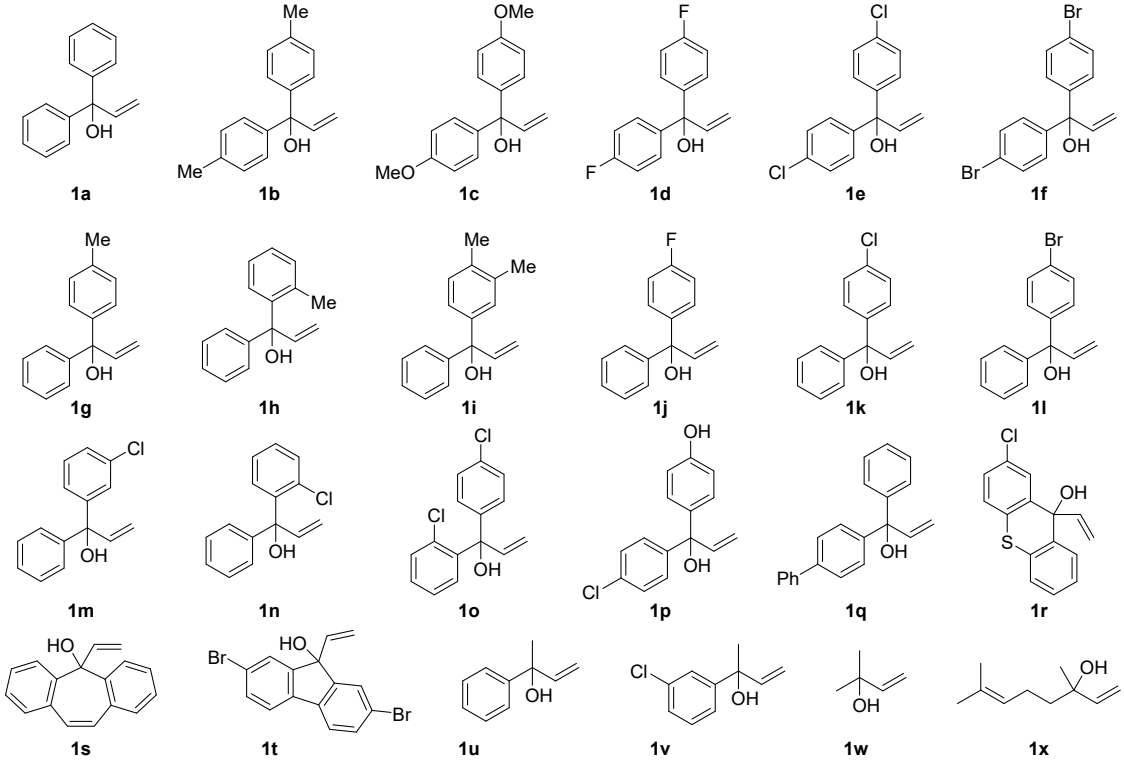



To a Schlenk tube charged with a magnetic stirring bar, the reaction tube was vacuumed with a pump and backfilled with nitrogen for three times. Subsequently, a solution of allylic alcohol **1** (0.10 mmol) in nitrile (3.0 mL) was charged into the reaction vessel under a nitrogen atmosphere, followed by the sequential addition of triphenyl phosphite (0.02 mmol) and $H_2O$ (0.15 mmol). The mixture was allowed to stir at 100 ℃ for 12 hours using an IKA magnetic stirring apparatus with a nine-hole aluminum heating block. After the substrate was completely consumed, the reaction mixture was quenched with water (3.0 mL) and extracted with ethyl acetate (10.0 mL

× 3). The combined organic layer was then washed with saturated sodium chloride solution (10.0 mL) and dried using anhydrous $Na_2SO_4$. Following filtration and concentration in vacuo, the obtained residue was subjected to flash column chromatography with petroleum ether/ethyl acetate (2:1) as an eluent to isolate the pure product.

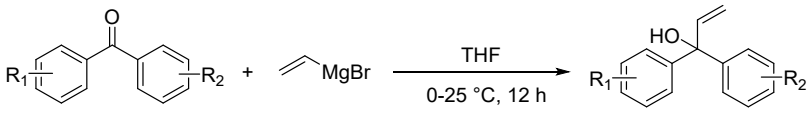
# 2. Preparation of the starting materials

## 2.1 Allylic alcohol compounds list




## 2.2 Preparation of allyl alcohols

The starting materials **1a-1v** were synthesized according to the procedures described below, while compounds **1w** and **1x** were obtained from commercial sources.

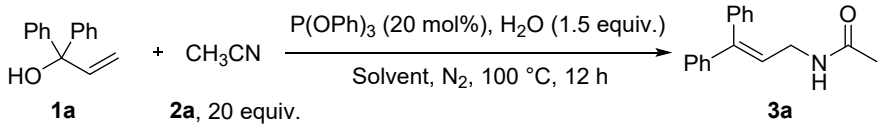



In accordance with the reported protocol,[1, 2] a two-necked flask furnished with a magnetic stirrer was charged with 20 mmol of ketone. The reaction flask was subjected to three vacuum-nitrogen cycles (vacuum pump evacuation followed by $N_2$ backfilling) to ensure inert conditions. Under a sustained nitrogen atmosphere at 0°C, anhydrous tetrahydrofuran (THF, 20 mL) was introduced, and the mixture was stirred

until complete dissolution of the ketone. Subsequently, a vinyl magnesium bromide solution (1 M in THF, 40 mL) was slowly added via syringe over 30 minutes. Upon the completion of the addition of vinyl magnesium bromide, the reaction mixture was continuously stirred at 0 °C for another 30 minutes prior to being allowed to react at ambient temperature for 12 hours. The reaction was terminated by addition of 20 mL of saturated ammonium chloride solution. Subsequently, the reaction products were extracted three times with ethyl acetate (50 mL x 3). The combined organic extracts were then dried with anhydrous $Na_2SO_4$. After filtration, the solvent was removed under reduced pressure with a rotary evaporator. Ultimately, the concentrated residue was subjected to flash column chromatography for separation and purification. Utilizing a mixture of petroleum ether and ethyl acetate in a volume ratio of 10:1 (v:v) as the eluent, the target compound was obtained as a colorless oil.

# 3. Investigation of the reaction solvents

**Table S1**. Investigation of the reaction solvents.[a]




**1a** **2a**, 20 equiv. **3a**

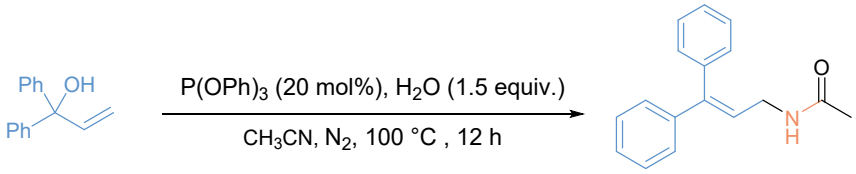
| Entry | Solvent | Temp. | Yield |
|---|---|---|---|
| 1 | THF (1.0 mL) | 100 °C | N.D. |
| 2 | $H_2O$ (1.0 mL) | 100 °C | N.D. |
| 3 | EtOH (1.0 mL) | 100 °C | N.D. |
| 4 | DMSO (1.0 mL) | 100 °C | N.D. |
| 5 | DMF (1.0 mL) | 100 °C | N.D. |
| 6 | Toluene (1.0 mL) | 100 °C | N.D. |
| 7 | EtOAc (1.0 mL) | 100 °C | N.D. |
| 8 | DCE (1.0 mL) | 100 °C | N.D. |
| 9 | 1,4-Dioxane (1.0 mL) | 100 °C | N.D. |
| 10 | HFIP (1.0 mL) | 100 °C | 15% |

[a] Reactions were operated with 1,1-diphenylprop-2-en-1-ol (**1a**, 0.1 mmol), $P(OPh)_3$

(20 mol%), water (1.5 equiv.) and the indicated solvent (1.0 mL) under a nitrogen atmosphere at 100 °C for 12 h; yields were determined by GC analysis, using dodecane as the internal standard. N.D. = not detected.

# 4. Large-scale synthesis and late-stage functionalization

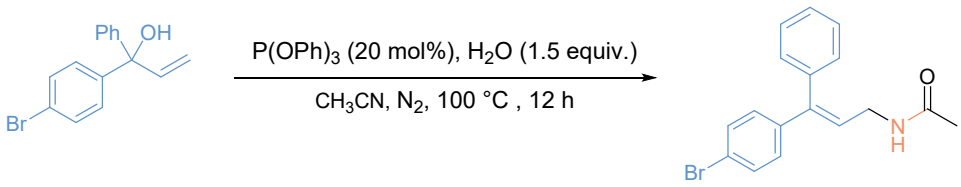
## 4.1 Gram-scale synthesis of 3a and 3l




**1a**, 5 mmol

**3a**, 72% (0.90 g)

In a 500 mL reaction flask equipped with a magnetic stir bar, the reaction flask was vacuumed with a pump and backfilled with nitrogen for three cycles. Subsequently, in the nitrogen atmosphere, diphenyl allyl alcohol (**1a**, 5 mmol, 1.05 g), triphenyl phosphite (1 mmol, 310 mg), water (7.5 mmol, 135 mg) and 150 mL $CH_3CN$ were added. The reaction mixture was vigorously stirred in an oil bath at 100 °C for 12 hours. Upon reaction completion (monitored by TLC), the reaction mixture was concentrated under vacuum. The residue was sequentially washed with brine and extracted three times with ethyl acetate. The recovered MeCN was collected for potential other usage. The combined mixture was concentrated using a rotary vacuum evaporator and separated on a flash silica gel column with a petroleum ether/ethyl acetate eluent (v:v = 2:1) to yield **3a** (0.90 g, 72% yield).



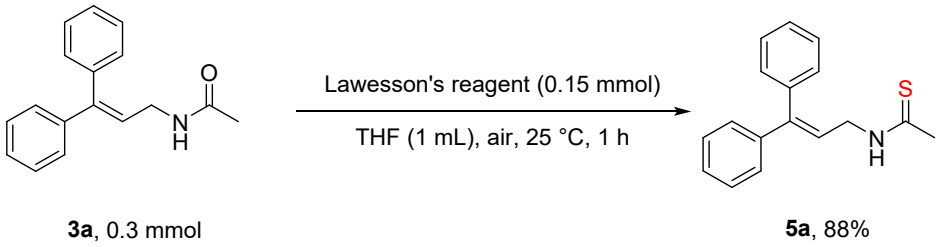

**1l**, 5 mmol

**3l**, 62% (1.02 g)

In a 500 mL reaction flask equipped with a magnetic stir bar, the reaction flask was vacuumed with a pump and backfilled with nitrogen for three cycles. Subsequently, in the nitrogen atmosphere, diphenyl allyl alcohol (**1l**, 5 mmol, 1.45 g),

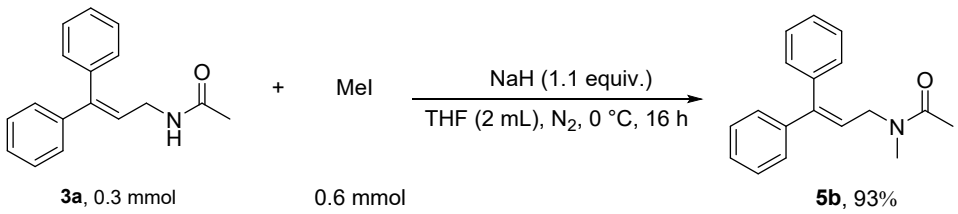
triphenyl phosphite (1 mmol, 310 mg), water (7.5 mmol, 135 mg) and 150 mL $CH_3CN$ were added. The reaction mixture was vigorously stirred in an oil bath at 100 °C for 12 hours. Upon reaction completion (monitored by TLC), the reaction mixture was concentrated under vacuum. The residue was sequentially washed with brine and extracted three times with ethyl acetate. The recovered MeCN was collected for potential other usage. The combined mixture was concentrated using a rotary vacuum evaporator and separated on a flash silica gel column with a petroleum ether/ethyl acetate eluent (v:v = 2:1) to yield **3l** (1.02 g, 62% yield).

### 4.2 Late-stage functionalization of 3a and 3l

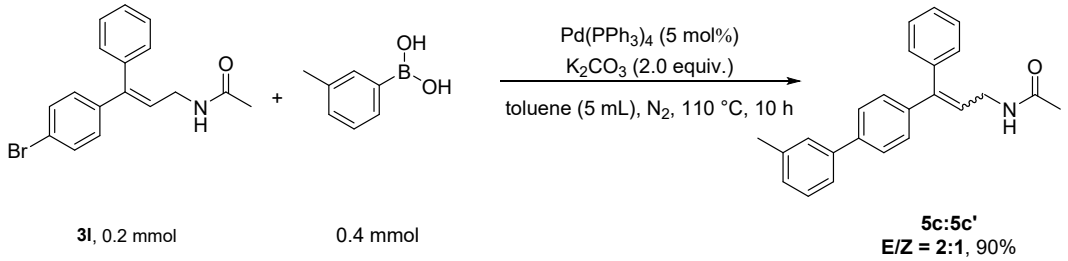



**3a**, 0.3 mmol **5a**, 88%

Compound **5a** was synthesized following a modified synthetic protocol adapted from the literatures.[1, 3] THF (1 mL) as a solvent was added to a 25 mL reaction tube containing Lawesson's reagent (0.15 mmol, 60.7 mg) and **3a** (2.0 eq, 0.3 mmol, 75.3 mg). The reaction was conducted at 25 °C for 1 hours. The obtained mixture was concentrated using a rotary vacuum evaporator and separated on a flash silica gel column with a petroleum ether/ethyl acetate eluent (v:v = 2:1) to yield **5a** (70.5 mg, 0.264 mmol, 88 %) as a yellow solid. mp: 101.7-103.1 ℃. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.34 – 7.26 (m, 3H), 7.19 (dt, J = 5.0, 2.1 Hz, 3H), 7.17 – 7.13 (m, 2H), 7.11 – 7.05 (m, 2H), 6.07 (t, J = 7.0 Hz, 1H), 4.30 – 4.23 (m, 2H), 2.42 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 200.4, 146.1, 141.3, 138.6, 129.6, 128.5, 128.2, 127.8, 127.82, 127.5, 121.8, 45.8, 34.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}NS$ 268.1154; Found 268.1156.

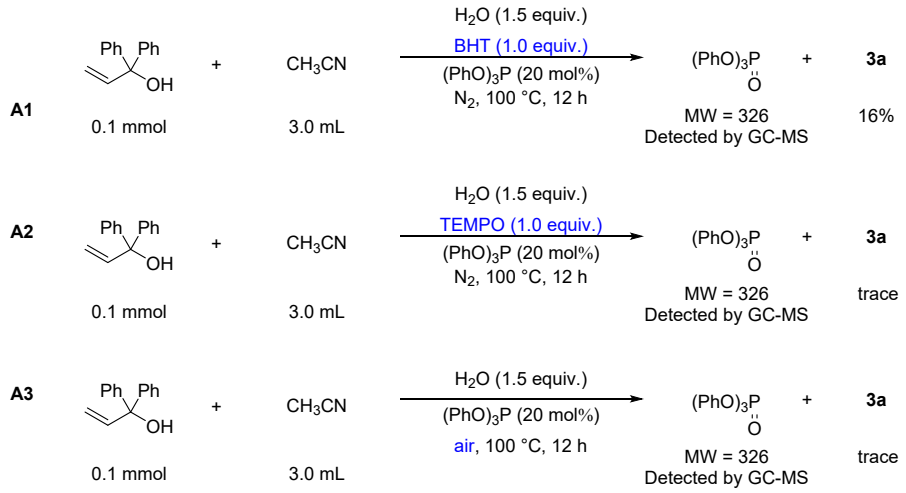



Compound **5b** was synthesized following a modified synthetic protocol adapted from the literature.[4] To a 25 mL round-bottom flask charged with 2 mL of tetrahydrofuran (THF), **3a** (0.3 mmol, 75.3 mg) was added. Subsequently, the reaction mixture was cooled to 0 °C, and sodium hydride, in the form of a 60% wt. oil dispersion (0.33 mmol, 13.2 mg), was introduced. After being stirred for 1 minute, methyl iodide (0.6 mmol, 40 μL) was added dropwise. The reaction was allowed to stir for 16 hours, following which it was quenched with 75 mL of brine and 75 mL of ethyl acetate. The reaction mixture was then transferred to a 250-mL separatory funnel. The organic and aqueous layers were separated, and the aqueous layer was washed three times with 50 mL portions of EtOAc. The combined organic layers were washed once with 50 mL of brine and then dried over anhydrous sodium sulfate. Finally, the combined mixture was concentrated using a rotary vacuum evaporator and purified by flash column chromatography on silica gel, with a petroleum ether/ethyl acetate (v:v = 1:2) eluent. to yield **5b** (74.0 mg, 0.279 mmol, 93 %) as a colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 3H), 7.18 (d, J = 5.0 Hz, 2H), 7.14 (d, J = 9.7 Hz, 3H), 7.11 – 7.03 (m, 2H), 6.03 – 5.84 (m, 1H), 4.00 (d, *J* = 7.0 Hz, 1H), 3.86 (d, *J* = 6.6 Hz, 1H), 2.79 (d, *J* = 17.4 Hz, 3H), 1.93 (d, *J* = 41.7 Hz, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.5, 170.4, 145.3, 144.8, 141.5, 141.1, 139.0, 138.6, 129.8, 129.6, 128.5, 128.4, 128.3, 128.2, 127.9, 127.50, 127.47, 127.4, 127.2, 124.3, 123.2, 49.8, 46.1, 35.5, 33.2, 21.8, 21.4. Known compound. Spectral data were in good agreement with those reported in the literature.[5]




Compound **5c** was synthesized following a modified synthetic protocol adapted from the literature.[6] Under a nitrogen atmosphere, a mixture of **3l** (66.1 mg, 0.20 mmol, E/Z = 2:1) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol) in toluene (5 mL) was charged with $K_2CO_3$ (55.2 mg, 0.4 mmol) and 3-tolylboronic acid (54.4 mg, 0.4 mmol). The reaction mixture was vigorously stirred and heated to 110 °C for 10 h, with reaction progress monitored by TLC and GC-MS. Upon completion, the mixture was allowed to cool to room temperature and filtered through a celite pad. The filter cake was subsequently washed with ethyl acetate (EA). Finally, the combined mixture was concentrated using a rotary vacuum evaporator and purified by flash column chromatography on silica gel, with a petroleum ether/ethyl acetate (v:v = 2:1) eluent. to yield **5c** (61.5 mg, 0.180 mmol, 90 %, E/Z = 2:1) as a white solid. mp: 136.5-138.4 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1.3H), 7.50 (d, *J* = 8.2 Hz, 0.7H), 7.44 – 7.32 (m, 5H), 7.29 (d, *J* = 7.1 Hz, 3H), 7.24 – 7.15 (m, 3H), 6.14 (t, *J* = 7.0 Hz, 0.3H) 6.09 (t, *J* = 7.0 Hz, 0.7H), 5.63 (s, 1H), 4.01 (t, *J* = 6.3 Hz, 1.3H), 3.96 (t, *J* = 6.3 Hz, 0.7H), 2.44 (s, 2H), 2.41 (s, 1H), 1.99 (s, 3H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 170.0, 144.5, 144.4, 141.8, 140.71, 140.7, 140.67, 140.6, 140.5, 139.0, 138.54, 138.5, 137.9, 130.2, 129.8, 128.9, 128.8, 128.6, 128.4, 128.3, 128.2, 128.0, 127.9, 127.83, 127.8, 127.6, 127.2, 127.0, 124.7, 124.4, 124.3, 124.2, 39.22, 39.2, 23.4, 21.71, 21.67. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}NO$ 342.1852; Found 342.1849.

# 5. Investigation of the reaction with radical traps




**Scheme S1**. Standard reaction with the addition of BHT and TEMPO, or under air atmosphere.

To investigate why the addition of radical traps significantly impacts the ionic reaction pathway, detailed analysis of the reaction mixtures using GC-MS and $^{31}P$ NMR spectroscopy revealed two key observations: (i) No detectable radical-adduct fragments were identified with any scavenger; (ii) Multiple intermediates suggest oxidative degradation of the catalyst from triphenyl phosphite to triphenyl phosphate (**Figures S1-S3**). For the 1,1-diphenylethylene system, its elevated electron density at the olefinic moiety renders it an electron-rich entity. Within the proposed reaction pathway, after allylic carbocation formation, this electron-rich system competes with acetonitrile for carbocation capture to produce 1,1,5,5-tetraphenylpenta-1,4-diene (**8b**) (**Scheme S2**), thereby diminishing the yield of **3a**. These findings suggest that the observed yields reduction may primarily stem from unintended catalyst oxidation or competitive side reactions, rather than radical interception.

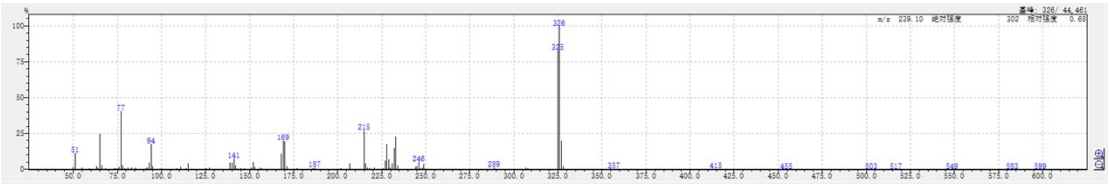


**Figure S1**. GC-MS analysis of the reaction mixture when adding BHT as the radical trap (A1).

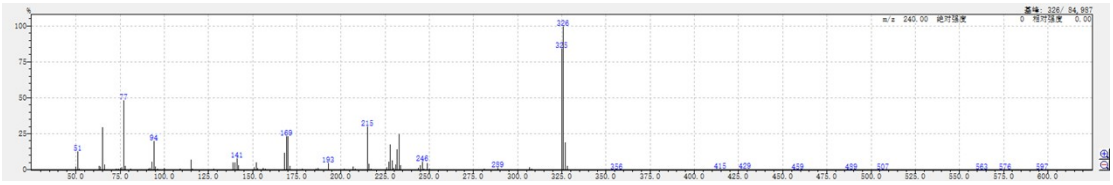


**Figure S2**. GC-MS analysis of the reaction mixture when adding TEMPO as the radical trap (A2).

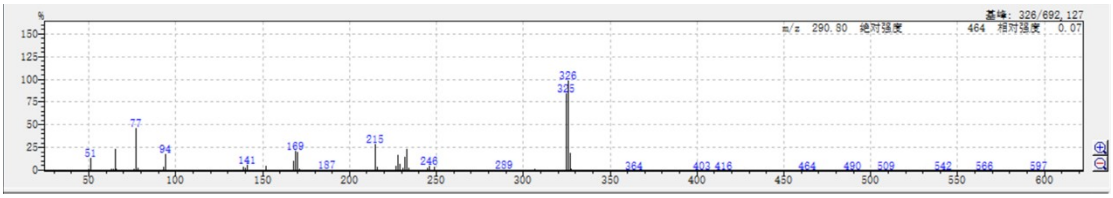
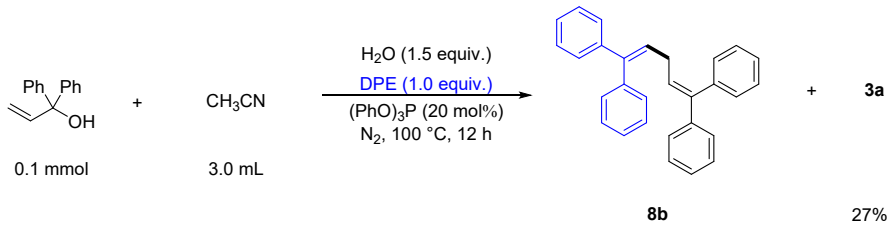


**Figure S3**. GC-MS analysis of the reaction mixture when reacting in air atmosphere (A3).

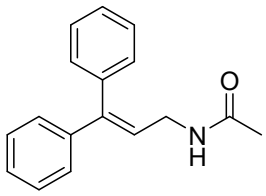



**Scheme S2**. Standard reaction with the addition of DPE.

Here we contrast our findings with prior work (*Green Chem.*, **2024**, *26*, 10886-10892) that shares similar ionic mechanisms but exhibits distinct experimental responses to TEMPO, BHT, and DPE additives. In the previous work, carbocations form via direct protonation and dehydration of allylic alcohols. Critically, BHT/TEMPO addition did not affect this process - unlike our current system where catalyst-dependent carbocation generation is suppressed by BHT/TEMPO-mediated catalyst deactivation, ultimately reducing yields. Similarly, DPE introduction failed to enable competitive formation of 1,1,5,5-tetraphenylpenta-1,4-diene (**8b**) because the thiolate anion's superior nucleophilicity over DPE dominates intermediate capture. This contrasts with this system where DPE competes with weakly nucleophilic nitriles for carbocations, diminishing target product yields. These fundamental differences in catalytic components and possible competition reaction may explain the divergent outcomes.

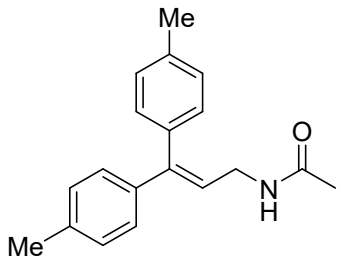
# 6. Analytical data for the compounds

***N-(3,3-diphenylallyl)acetamide (3a)***



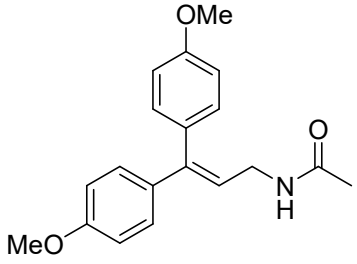
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3a** (22.1 mg, 0.088 mmol, 88%) as a white solid. mp: 123.7-125.1 ℃. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 3H), 7.26 – 7.22 (m, 3H), 7.22 – 7.18 (m, 2H), 7.17 – 7.12 (m, 2H), 6.05 (t, *J* = 7.0 Hz, 1H), 5.97 (s, 1H), 3.95 – 3.88 (m, 2H), 1.94 (s, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.1, 144.5, 141.7, 138.9, 129.7, 128.4, 128.2, 127.6, 127.5, 124.6, 39.1, 23.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{18}NO$ 252.1383; Found 252.1387.

***N-(3,3-di-p-tolylallyl)acetamide (3b)***



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3b** (21.8 mg, 0.078 mmol, 78%) as a white solid. mp: 102.8-103.5 ℃. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 7.07 (d, J = 8.2 Hz, 2H), 7.05 – 7.02 (m, 2H), 6.00 (t, *J* = 7.0 Hz, 1H), 5.62 (s, 1H), 3.93 (dd, *J* = 7.0, 5.6 Hz, 2H), 2.38 (s, 3H), 2.32 (s, 3H), 1.96 (s, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.0, 144.7, 139.1, 137.5, 137.3, 136.1, 129.7, 129.1, 129.0, 127.4, 123.3, 39.2, 23.4, 21.3, 21.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{19}H_{22}NO$ 280.1696; Found 280.1693.

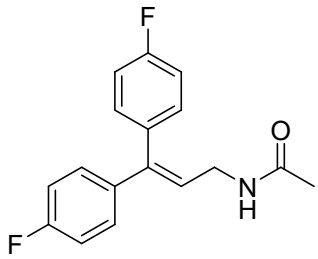
***N-(3,3-bis(4-methoxyphenyl)allyl)acetamide (3c)***



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3c** (21.2 mg, 0.068 mmol, 68%) as a yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.13 (m, 2H), 7.09

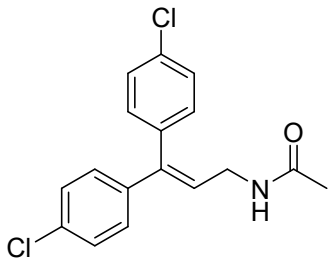
– 7.05 (m, 2H), 6.92 – 6.88 (m, 2H), 6.82 – 6.78 (m, 2H), 5.92 (t, *J* = 7.0 Hz, 1H), 5.55 (s, 1H), 3.96 – 3.92 (m, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 1.97 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.0, 159.3, 159.1, 144.0, 134.7, 132.4, 131.5, 131.0, 128.8, 122.4, 113.8, 113.6, 55.4, 39.2, 23.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{19}H_{22}NO_3$ 312.1594; Found 312.1598

***N-(3,3-bis(4-fluorophenyl)allyl)acetamide (3d)***



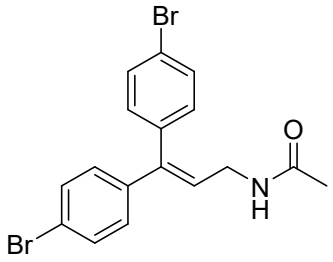

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3d** (24.4 mg, 0.085 mmol, 85%) as a colorless oil. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.14 (m, 2H), 7.13 – 7.05 (m, 4H), 6.99 – 6.93 (m, 2H), 6.00 (t, *J* = 7.0 Hz, 1H), 5.55 (s, 1H), 3.92 (dd, *J* = 7.0, 5.7 Hz, 2H), 1.98 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.0, 162.6 (d, *J* = 247.2 Hz), 162.4 (d, *J* = 247.4 Hz), 142.7, 137.7 (d, *J* = 2.6 Hz), 134.7 (d, *J* = 3.2 Hz), 131.4 (d, *J* = 7.9 Hz), 129.1 (d, *J* = 8.0 Hz), 124.9, 115.6 (d, *J* = 36.7 Hz), 115.4 (d, *J* = 36.7 Hz), 39.1, 23.4. $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -114.0, -114.5 HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{16}F_2NO$ 288.1194; Found 288.1189.

***N-(3,3-bis(4-chlorophenyl)allyl)acetamide (3e)***



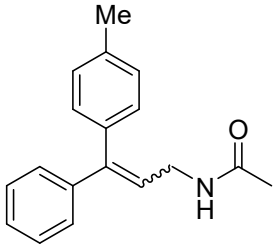

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3e** (26.3 mg, 0.082 mmol, 82%) as a yellow solid. mp: 97.9-99.8 °C. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.26 (d, *J* = 5.4 Hz, 1H), 7.23 (s, 1H), 7.13 – 7.07 (m, 4H), 6.05 (t, *J* = 6.9 Hz, 1H), 5.66 (t, *J* = 5.8 Hz, 1H), 3.93 – 3.89 (m, 2H), 1.98 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.1, 142.4, 139.8, 136.9, 134.0, 133.8, 131.1, 128.9, 128.8, 128.6, 125.8, 39.1, 23.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{16}Cl_2NO$ 320.0603; Found 320.0601.

***N-(3,3-bis(4-bromophenyl)allyl)acetamide (3f)***




According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3f** (33.1 mg, 0.081 mmol, 81%) as a white solid. mp: 127.6-129.3 ℃. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.41 – 7.38 (m, 2H), 7.06 – 7.01 (m, 4H), 6.06 (t, *J* = 6.9 Hz, 1H), 5.56 (s, 1H), 3.91 (dd, *J* = 7.0, 5.6 Hz, 2H), 1.98 (s, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.0, 142.4, 140.2, 137.4, 131.9, 131.6, 131.4, 129.1, 125.9, 122.2, 122.1, 39.1, 23.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{16}Br_2NO$ 407.9593; Found 407.9596.

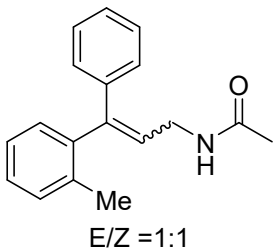
***N-(3-phenyl-3-(p-tolyl)allyl)acetamide (3g)***




E/Z = 1:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3g** (20.7 mg, 0.078 mmol, 78%) as a yellow solid. mp: 100.8-102.5 ℃. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.24 – 7.12 (m, 4H), 7.11 – 7.03 (m, 3H), 6.06 – 6.04 (m, 0.5H), 6.04 – 6.01 (m, 0.5H), 5.51 (s, 1H), 3.97 – 3.94 (m, 1H), 3.94 – 3.90 (m, 1H), 2.38 (s, 1.5H), 2.33 (s, 1.5H), 1.97 (d, *J* = 1.6 Hz, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 169.9, 144.8, 144.7, 141.9, 139.2, 138.9, 137.6, 137.5, 136.0, 129.8, 129.7, 129.2, 129.0, 128.5, 128.3, 127.7, 127.66, 127.6, 127.4, 124.3, 123.6, 39.2, 39.1, 23.4, 21.4, 21.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{18}H_{20}NO$ 266.1539; Found 266.1544.

***N-(3-phenyl-3-(o-tolyl)allyl)acetamide (3h)***

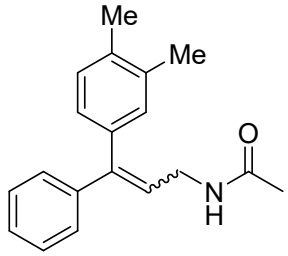



E/Z =1:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3h** (22.0 mg, 0.083 mmol, 83%) as a yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 1.6 Hz, 1H), 7.16 (d, J = 2.4 Hz, 4H), 7.14 – 7.11

(m, 3H), 7.00 (d, J = 6.6 Hz, 1H), 6.13 (t, *J* = 6.9 Hz, 1H), 5.69 (s, 1H), 3.73 (q, *J* = 7.9 Hz, 1H), 3.66 – 3.54 (m, 1H), 1.97 (s, 3H), 1.86 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.1, 143.6, 140.1, 138.2, 136.4, 130.4, 129.7, 128.4, 127.8, 127.6, 126.4, 126.0, 124.3, 39.1, 23.3, 19.7. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{18}H_{20}NO$ 266.1539; Found 266.1544.

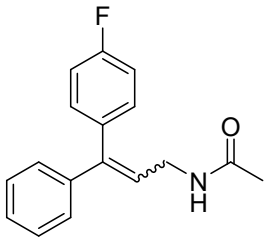
***N-(3-(3,4-dimethylphenyl)-3-phenylallyl)acetamide (3i)***



E/Z = 1.3:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3i** (24.3 mg, 0.087 mmol, 87%) as a yellow oil. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 11.7, 7.3 Hz, 2H), 7.20 (d, *J* = 4.1 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 2H), 7.01 – 6.81 (m, 3H), 5.99 (d, *J* = 6.7 Hz, 0.6H), 5.96 (d, *J* = 6.6 Hz, 0.5H), 5.62 (s, 1H), 3.92 – 3.86 (m, 2H), 2.24 (s, 1.3H), 2.21 (s, 1.3H), 2.19 (s, 1.7H), 2.16 (s, 1.7H), 1.92 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 169.9, 144.9, 144.7, 142.0, 139.3, 139.2, 136.6, 136.4, 136.3, 136.0, 130.9, 129.74, 129.7, 129.6, 128.6, 128.4, 128.2, 127.6, 127.5, 127.2, 125.1, 124.2, 123.5, 39.2, 39.1, 23.4, 19.9, 19.6, 19.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{19}H_{22}NO$ 280.1696; Found 280.1693.

***N-(3-(4-fluorophenyl)-3-phenylallyl)acetamide (3j)***

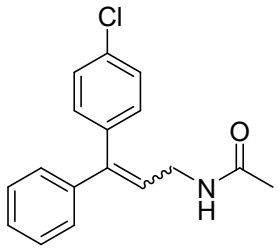


E/Z = 2.3:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3j** (24.2 mg, 0.090 mmol, 90%) as a yellow solid. mp: 98.8-100.4 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 1H), 7.29 – 7.26 (m, 2H), 7.21 – 7.12 (m, 4H), 7.10 – 7.04 (m, 1.4H), 6.98 – 6.92 (m, 0.6H), 6.06 (t, *J* = 7.0 Hz, 0.7H), 6.02(t, *J* = 7.2 Hz, 0.3H), 5.58 (s, 1H), 3.95 – 3.91 (m, 2H), 1.98 (s, 2.1H), 1.97 (s, 0.9 H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.0, 162.5 (d, *J* = 246.8 Hz), 162.3 (d, *J* = 247.0 Hz), 143.7, 141.6, 138.8, 137.8 (d, *J* = 3.4 Hz), 134.9 (d, *J* = 3.6 Hz), 131.5 (d, *J* = 8.0 Hz), 129.7, 129.1 (d, *J* = 8.1 Hz), 128.6, 128.4, 127.9, 127.5,

125.0, 124.5, 115.5 (d, $J$ = 21.4 Hz), 115.2 (d, $J$ = 21.5 Hz), 39.14, 39.1, 23.4. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -114.3, -114.8. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}FNO$ 270.1289; Found 270.1287.

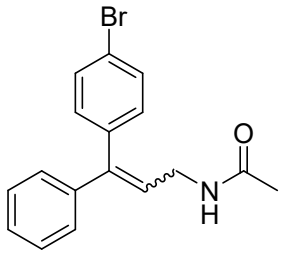
***N-(3-(4-chlorophenyl)-3-phenylallyl)acetamide (3k)***



E/Z = 1:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3k** (24.3 mg, 0.085 mmol, 85%) as a white solid. mp: 89.2-90.7 ℃. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.19 – 7.03 (m, 4H), 7.02 – 6.96 (m, 3H), 6.41 (t, $J$ = 5.7 Hz, 0.5H), 6.36 (t, $J$ = 5.7 Hz, 0.5H), 5.96 (d, $J$ = 7.0 Hz, 0.5H),5.92 (d, $J$= 7.0 Hz, 0.5H) 3.80 (dd, $J$ = 4.6, 2.4 Hz, 1H), 3.78 (dd, $J$ = 4.5, 2.4 Hz, 1H), 1.85 (s, 1.5H), 1.84 (s, 1.5H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 170.2, 143.14, 143.1, 141.2, 140.1, 138.4, 137.3, 133.5, 133.3, 131.1, 129.6, 128.7, 128.6, 128.5, 128.3, 128.26, 127.8, 127.7, 127.3, 125.2, 125.1, 39.02, 39.0, 23.1. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}ClNO$ 286.0993; Found 286.0988.

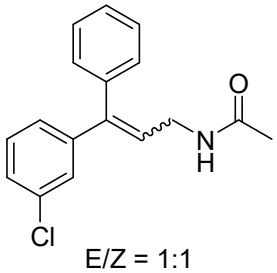
***N-(3-(4-bromophenyl)-3-phenylallyl)acetamideo (3l)***



E/Z = 2:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3l** (26.4 mg, 0.080 mmol, 80%) as a white solid. mp: 110.2-111.1 ℃. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, $J$ = 8.3 Hz, 1H), 7.41 – 7.26 (m, 4H), 7.21 – 7.12 (m, 2H), 7.06 (dd, $J$ = 12.0, 8.5 Hz, 2H), 6.07 (t, $J$ = 7.0 Hz, 1H), 5.59 (s, 1H), 3.93 (t, $J$ = 6.3 Hz, 2H), 1.98 (s, 2H), 1.97 (s, 1H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 170.0, 143.6, 143.5, 141.2, 140.6, 138.5, 137.9, 131.7, 131.5, 131.4, 129.7, 129.1, 128.7, 128.4, 128.0, 127.5, 125.2, 121.9, 121.8, 39.1, 23.4. HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{17}BrNO$ 330.0488; Found 330.0490.

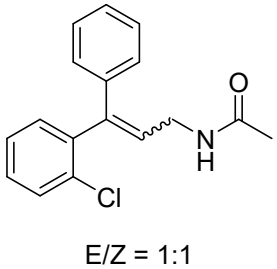
***N-(3-(3-chlorophenyl)-3-phenylallyl)acetamide (3m)***




E/Z = 1:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3m** (17.4 mg, 0.061 mmol, 61%) as a yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 3H), 7.22 – 7.19 (m, 2H), 7.15 – 7.11 (m, 2H), 7.09 – 7.06 (m, 1H), 7.02 – 6.99 (m, 1H), 6.04 – 6.01 (m, 0.6H), 6.00-5.99 (m, 0.4H), 5.48 (s, 1H), 3.90 – 3.86 (m, 1.1H), 3.86 – 3.84 (m, 0.9H), 1.92 (s, 1.6H), 1.91 (s, 1.3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.0, 143.6, 143.5, 143.4, 141.0, 140.9, 138.3, 134.5, 134.3, 129.9, 129.7, 129.5, 128.7, 128.5, 128.1, 128.02, 128.0, 127.96, 127.7, 127.6, 127.4, 125.9, 125.8, 125.4, 39.1, 23.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{17}ClNO$ 286.0993; Found 286.0990.

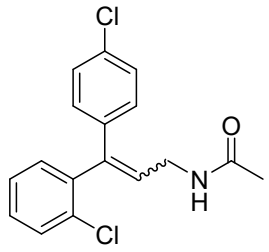
***N-(3-(2-chlorophenyl)-3-phenylallyl)acetamide (3n)***




E/Z = 1:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3n** (15.1 mg, 0.053 mmol, 53%) as a yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 1H), 7.34 – 7.27 (m, 4H), 7.25 – 7.18 (m, 4H), 6.26 (t, *J* = 7.1 Hz, 1H), 5.56 (s, 1H), 4.00 – 3.93 (m, 1H), 3.62 (dd, *J* = 14.3, 8.0 Hz, 1H), 1.96 (s, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.0, 141.7, 139.5, 137.7, 133.5, 131.6, 129.9, 129.3, 128.5, 127.9, 127.2, 126.5, 125.6, 39.2, 23.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{17}ClNO$ 286.0993; Found 286.0987.

***N-(3-(2-chlorophenyl)-3-(4-chlorophenyl)allyl)acetamide (3o)***

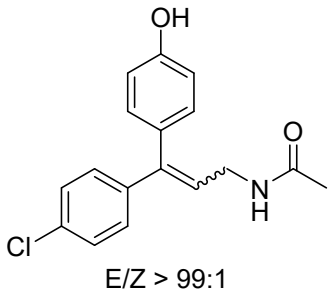



E/Z = 1:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3o** (20.8 mg, 0.065 mmol, 65%) as a yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 1H), 7.33 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.20 – 7.17 (m, 1H), 7.15 – 7.11 (m, 2H), 6.24 (t, *J* =

7.0 Hz, 1H), 5.58 (s, 1H), 3.94 (q, *J* = 7.9 Hz, 1H), 3.59 (d, *J* = 14.2 Hz, 1H), 1.96 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.1, 140.5, 138.1, 137.2, 133.8, 133.5, 131.5, 130.0, 129.6, 128.7, 127.8, 127.3, 126.3, 39.1, 23.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{16}Cl_2NO$ 320.0603; Found 320.0601.

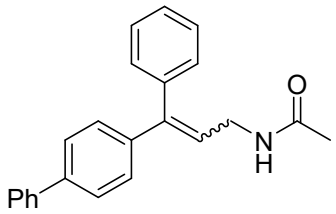
***N-(3-(4-chlorophenyl)-3-(4-hydroxyphenyl)allyl)acetamide (3p)***



E/Z > 99:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3p** (18.1 mg, 0.060 mmol, 60%) as a yellow oil. $^{1}H$ NMR (400 MHz, DMSO-$d_6$) δ 9.53 (s, 1H), 8.01 (t, *J* = 5.5 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.69 (d, *J* = 8.6 Hz, 2H), 5.90 (t, *J* = 7.0 Hz, 1H), 3.62 (t, *J* = 6.1 Hz, 2H), 1.80 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, DMSO-$d_6$) δ 168.9, 157.1, 141.0, 138.0, 132.1, 131.9, 131.3, 128.4, 128.2, 123.7, 115.2, 38.3, 22.6. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{17}ClNO_2$ 302.0942; Found 302.0946.

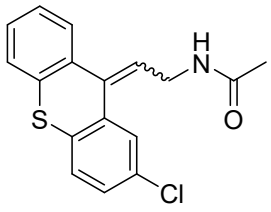
***N-(3-([1,1'-biphenyl]-4-yl)-3-phenylallyl)acetamide (3q)***



E/Z =1.2:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3q** (27.5 mg, 0.084 mmol, 84%) as a white solid. mp: 167.9-169.8 ℃. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 3H), 7.52 – 7.34 (m, 6H), 7.31 – 7.27 (m, 3H), 7.25 – 7.19 (m, 2H), 6.15 (t, *J* = 7.0 Hz, 0.6H), 6.09 (t, *J* = 7.0 Hz, 0.4H), 5.64 (s, 1H), 4.02 (dd, *J* = 7.0, 5.6 Hz, 0.9H), 3.96 (dd, *J* = 7.0, 5.6 Hz, 1.1H), 1.99 (s, 1.4H), 1.98 (s, 1.6H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.0, 144.4, 144.3, 141.7, 140.7, 140.66, 140.6, 140.5, 140.49, 138.9, 138.0, 130.3, 129.8, 128.95, 128.9, 128.6, 128.4, 127.9, 127.8, 127.6, 127.56, 127.5, 127.2, 127.1, 127.0, 124.8, 124.5, 39.2, 39.16, 23.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{23}H_{22}NO$ 328.1696; Found 328.1699.

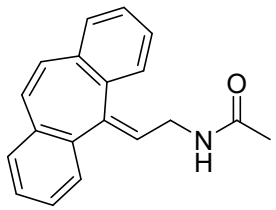
***N-(2-(2-chloro-9H-thioxanthen-9-ylidene)ethyl)acetamide (3r)***



E/Z > 99:1

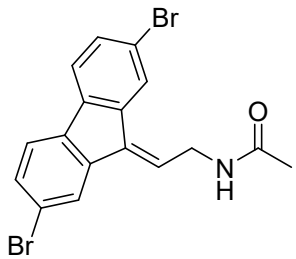
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3r** (24.3 mg, 0.077 mmol, 77%) as a yellow solid. mp: 143.7-144.9 ℃. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.37 (dd, *J* = 7.7, 2.4 Hz, 2H), 7.28 (d, *J* = 1.8 Hz, 2H), 7.26 – 7.21 (m, 2H), 5.86 (t, *J* = 6.7 Hz, 1H), 5.71 (s, 1H), 4.27 (t, *J* = 6.3 Hz, 2H), 1.97 (s, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.1, 137.0, 136.8, 134.2, 132.3, 132.1, 131.2, 128.7, 128.6, 127.9, 127.8, 127.6, 127.5, 126.0, 38.8, 23.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{15}ClNOS$ 316.0557; Found 316.0562.

***N-(2-(5H-dibenzo[a,d][7]annulen-5-ylidene)ethyl)acetamide (3s)***




According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3s** (22.3 mg, 0.081 mmol, 81%) as a yellow solid. mp: 118.3-120.1 ℃. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.34 (m, 2H), 7.34 – 7.31 (m, 2H), 7.29 (dd, *J* = 7.8, 3.9 Hz, 3H), 7.18 (d, *J* = 7.7 Hz, 1H), 6.87 (s, 2H), 5.57 (dd, *J* = 8.9, 4.8 Hz, 1H), 5.43 (s, 1H), 4.33 – 4.26 (m, 1H), 3.63 – 3.56 (m, 1H), 1.91 (s, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 169.9, 144.3, 141.5, 136.2, 134.6, 133.8, 131.3, 131.1, 129.3, 129.03, 129.0 128.9, 128.5, 128.3, 127.7, 127.6, 127.4, 38.4, 23.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{19}H_{18}NO$ 276.1383; Found 276.1387.

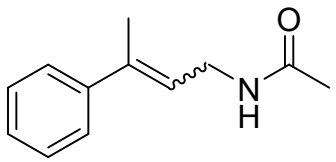
***N-(2-(2,7-dibromo-9H-fluoren-9-ylidene)ethyl)acetamide (3t)***




According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3t** (33.8 mg, 0.083 mmol, 83%) as a white solid. mp: 260.1-261.0 ℃. $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 8.47 (t, *J*

= 5.6 Hz, 1H), 8.08 (s, 1H), 7.93 – 7.89 (m, 2H), 7.84 (d, *J* = 6.7 Hz, 1H), 7.64 (dt, *J* = 8.1, 1.5 Hz, 1H), 7.55 (dt, *J* = 8.1, 1.6 Hz, 1H), 6.96 – 6.92 (m, 1H), 4.45 (t, *J* = 6.0 Hz, 2H), 1.91 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, DMSO-$d_6$) δ 169.5, 140.3, 138.3, 137.8, 136.2, 133.9, 132.8, 131.2, 130.8, 128.0, 123.6, 122.3, 122.1, 121.0, 120.8, 38.1, 22.6. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{17}H_{14}Br_2NO$ 405.9437; Found 405.9436.

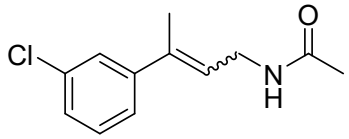
***N-(3-phenylbut-2-en-1-yl)acetamide (3u)***



E/Z > 99:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3u** (15.5 mg, 0.082 mmol, 82%) as a yellow solid. mp: 75.6-77.4 °C. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 6.7 Hz, 1H), 5.92 (s, 1H), 5.78 (t, *J* = 7.0 Hz, 1H), 4.07 (t, *J* = 6.2 Hz, 2H), 2.10 (s, 3H), 2.02 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.2, 142.8, 138.5, 128.4, 127.4, 125.8, 123.4, 38.2, 23.3, 16.1. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{12}H_{16}NO$ 190.1226; Found 190.1223.

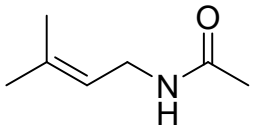
***N-(3-(3-chlorophenyl)but-2-en-1-yl)acetamide (3v)***



E/Z > 99:1

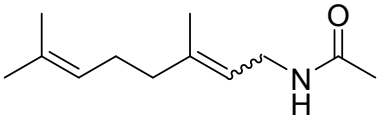
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3v** (19.5 mg, 0.087 mmol, 87%) as a green oil. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.20 (q, *J* = 3.5 Hz, 3H), 6.06 (d, *J* = 12.6 Hz, 1H), 5.74 (t, *J* = 6.8 Hz, 1H), 4.01 (t, *J* = 6.2 Hz, 2H), 2.02 (s, 3H), 1.98 (d, *J* = 1.7 Hz, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.2, 144.6, 137.0, 134.2, 129.6, 127.3, 126.0, 124.7, 123.9, 38.2, 23.3, 16.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{12}H_{15}ClNO$ 224.0837; Found 224.0840.

***N-(3-methylbut-2-en-1-yl)acetamide (3w)***



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3w** (9.5 mg, 0.075 mmol, 75%) as a yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.41 (s, 1H), 5.18 (t, *J* = 6.5 Hz, 1H), 3.82 (t, *J* = 6.2 Hz, 2H), 1.97 (s, 3H), 1.72 (s, 3H), 1.67 (s, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.1, 136.8, 120.0, 37.8, 25.8, 23.4, 18.0. Known compound. Spectral data were in good agreement with those reported in the literature.[7]

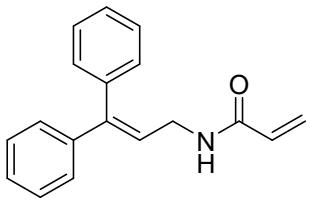
***N-(3,7-dimethylocta-2,6-dien-1-yl)acetamide (3x)***



E/Z > 99:1

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **3x** (14.3 mg, 0.073 mmol, 73%) as a yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 5.55 (s, 1H), 5.17 (t, *J* = 6.4 Hz, 1H), 5.09 – 5.02 (m, 1H), 3.83 (t, *J* = 6.1 Hz, 2H), 2.10 – 1.98 (m, 4H), 1.97 (s, 3H), 1.67 (s, 3H), 1.65 (s, 3H), 1.58 (s, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 170.0, 140.1, 131.9, 123.9, 119.8, 39.6, 37.7, 26.5, 25.8, 23.4, 17.8, 16.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ Calcd for $C_{12}H_{22}NO$ 196.1696; Found 196.1698.

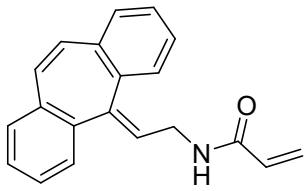
***N-(3,3-diphenylallyl)acrylamide (4a)***



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4a** (22.6 mg, 0.086 mmol, 86%) as a white solid. mp: 109.1-110.8 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.35 (p, *J* = 6.8 Hz, 3H), 7.25 (d, *J* = 6. Hz, 3H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.1 Hz, 2H), 6.27 (d, *J* = 16.9 Hz, 1H), 6.13 – 6.03 (m, 2H), 5.90 (s, 1H), 5.61 (d, *J* = 10.3 Hz, 1H), 4.02 (t, *J* = 6.4 Hz, 2H). $^{13}$C {$^{1}$H} NMR (101 MHz, CDCl3) δ 165.5, 144.8, 141.6, 138.9, 130.8,

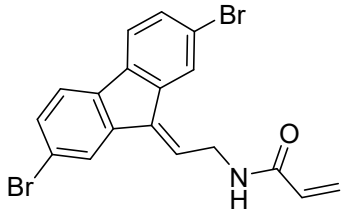
129.8, 128.5, 128.3, 127.7, 127.5, 126.7, 124.3, 39.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}NO$ 264.1383; Found 264.1379.

***N-(2-(5H-dibenzo[a,d][7]annulen-5-ylidene)ethyl)acetamide (4b)***



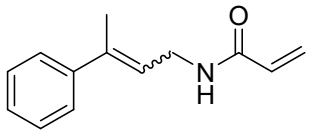
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4b** (22.4 mg, 0.078 mmol, 78%) as a yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 3.9 Hz, 3H), 7.24 – 7.21 (m, 2H), 7.19 (d, J = 7.4 Hz, 2H), 7.12 (d, J = 7.2 Hz, 1H), 6.78 (s, 2H), 6.13 (d, *J* = 17.0 Hz, 1H), 5.91 (dd, *J* = 17.0, 10.3 Hz, 1H), 5.66 (s, 1H), 5.54 – 5.45 (m, 2H), 4.30 – 4.24 (m, 1H), 3.62 – 3.56 (m, 1H). $^{13}$C {$^1$H} NMR (101 MHz, $CDCl_3$) δ 165.4, 144.3, 141.5, 136.1, 134.6, 133.8, 131.3, 131.1, 130.7, 129.1, 129.0, 128.9, 128.87, 128.5, 128.3, 127.7, 127.6, 127.4, 126.6, 38.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}NO$ 288.1383; Found 288.1379.

***N-(2-(2,7-dibromo-9H-fluoren-9-ylidene)ethyl)acrylamide (4c)***



According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4c** (30.2 mg, 0.072 mmol, 72%) as a white solid. mp: 219.7-220.8 °C. $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.75 (t, *J* = 5.2 Hz, 1H), 8.10 (s, 1H), 7.95 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 6.97 (t, *J* = 6.2 Hz, 1H), 6.31 (dd, *J* = 17.1, 10.1 Hz, 1H), 6.17 (dd, *J* = 17.1, 1.9 Hz, 1H), 5.67 (dd, *J* = 10.1, 1.9 Hz, 1H), 4.56 (t, *J* = 5.9 Hz, 2H). $^{13}$C {$^1$H} NMR (101 MHz, DMSO-$d_6$) δ 164.9, 140.3, 138.4, 137.8, 136.3, 133.4, 133.1, 131.5, 131.3, 130.8, 128.1, 125.7, 123.7, 122.3, 122.1, 121.0, 120.8, 38.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}Br_2NO$ 417.9437; Found 417.9440.

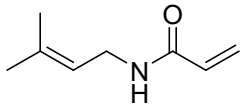
***N-(3-phenylbut-2-en-1-yl)acrylamide (4d)***



E/Z > 99:1

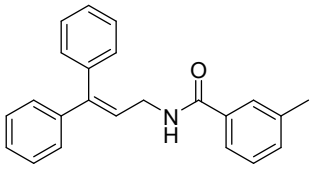
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4d** (14.7 mg, 0.073 mmol, 73%) as a yellow oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.1 Hz, 2H), 7.21 (dd, *J* = 17.4, 6.9 Hz, 3H), 6.23 (d, *J* = 16.9 Hz, 1H), 6.06 (dd, *J* = 17.0, 10.2 Hz, 1H), 5.95 (s, 1H), 5.71 (t, *J* = 6.7 Hz, 1H), 5.56 (d, *J* = 10.2 Hz, 1H), 4.06 (t, *J* = 6.0 Hz, 2H), 2.02 (s, 3H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 165.6, 142.8, 138.8, 130.8, 128.4, 127.4, 126.6, 125.8, 123.1, 38.2, 16.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}NO$ 202.1226; Found 202.1224.

***N-(3-methylbut-2-en-1-yl)acrylamide (4e)***




According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4e** (8.8 mg, 0.063 mmol, 63%) as a colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 6.24 (dd, *J* = 17.0, 1.5 Hz, 1H), 6.09 (dd, *J* = 17.0, 10.2 Hz, 1H), 5.96 (s, 1H), 5.58 (dd, *J* = 10.2, 1.5 Hz, 1H), 5.25 – 5.09 (m, 1H), 3.91 – 3.81 (m, 2H), 1.67 (d, *J* = 16.0 Hz, 6H). $^{13}$C {$^{1}$H} NMR (101 MHz, $CDCl_3$) δ 165.5, 136.6, 131.0, 126.2, 120.0, 37.7, 25.7, 17.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_8H_{14}NO$ 140.1070; Found 140.1067.

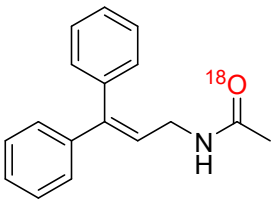
***N-(3,3-diphenylallyl)-3-methylbenzamide (4f)***




According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product **4f** (23.2 mg, 0.071 mmol, 71%) as a colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.53 – 7.50 (m, 1H), 7.44 – 7.32 (m, 4H), 7.31 (d, *J* = 4.8 Hz, 2H), 7.27 (s, 3H), 7.25 – 7.21 (m, 3H), 6.20 (d, *J* = 7.0 Hz, 1H),

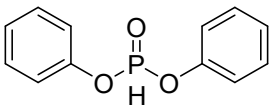
6.15 (s, 1H), 4.18 – 4.14 (m, 2H), 2.39 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 167.6, 145.0, 141.7, 139.1, 138.6, 134.6, 132.3, 129.8, 128.6, 128.57, 128.3, 127.8, 127.6, 124.5, 124.0, 39.5, 21.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}NO$ 328.1696; Found 328.167.

***N-(3,3-diphenylallyl)acetamide-$^{18}O$ (3a')***



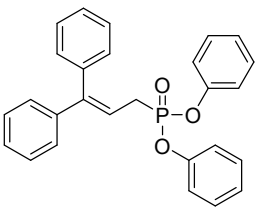

According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 2:1) gave product ***3a'*** (20.3 mg, 0.080 mmol, 80%) as a white solid. mp: 129.1-130.3 ℃. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 3H), 7.26 – 7.23 (m, 3H), 7.20 (dd, J = 7.4, 2.3 Hz, 2H), 7.14 (d, J = 6.4 Hz, 2H), 6.06 (t, *J* = 7.0 Hz, 1H), 5.63 (s, 1H), 3.93 (dd, *J* = 7.0, 5.6 Hz, 2H), 1.96 (s, 3H). $^{13}C$ {$^{1}H$} NMR (101 MHz, $CDCl_3$) δ 170.0, 169.97, 144.7, 141.7, 139.0, 129.8, 128.5, 128.3, 127.7, 127.5, 124.5, 39.1, 23.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}N^{18}O$ 254.1425; Found 254.1423.

***diphenyl phosphonate (6a)***




$^{31}P$ NMR (162 MHz, $CDCl_3$) δ 0.39. Known compound. Spectral data were in good agreement with those reported in the literature.[8]

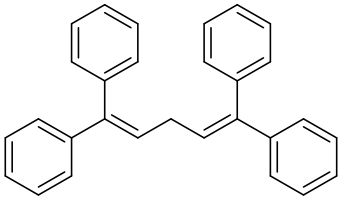
***diphenyl (3,3-diphenylallyl)phosphonate (8a)***




According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 10:1) gave product **8a** as a yellow oil. $^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.3 Hz, 3H), 7.23 (s, 1H), 7.20 (d, *J* = 8.4 Hz, 6H), 7.17 – 7.12 (m, 4H), 7.11 – 7.02 (m, 6H), 6.17 (q, *J* = 7.7 Hz, 1H), 2.99 (dd, *J* = 22.5, 7.8 Hz, 2H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 150.43 (d, *J* = 9.0 Hz), 146.9 (d, *J* = 16.0 Hz), 141.76 (d, *J* = 3.5 Hz), 138.84 (d, *J* = 3.1 Hz), 129.88, 129.85, 128.61, 128.33, 127.80, 127.74, 127.55 (d, *J* = 2.2 Hz), 125.28,

120.62 (d, $J$ = 4.4 Hz), 116.06 (d, $J$ = 11.4 Hz), 28.68 (d, $J$ = 140.4 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 20.73. Known compound. Spectral data were in good agreement with those reported in the literature.[2]

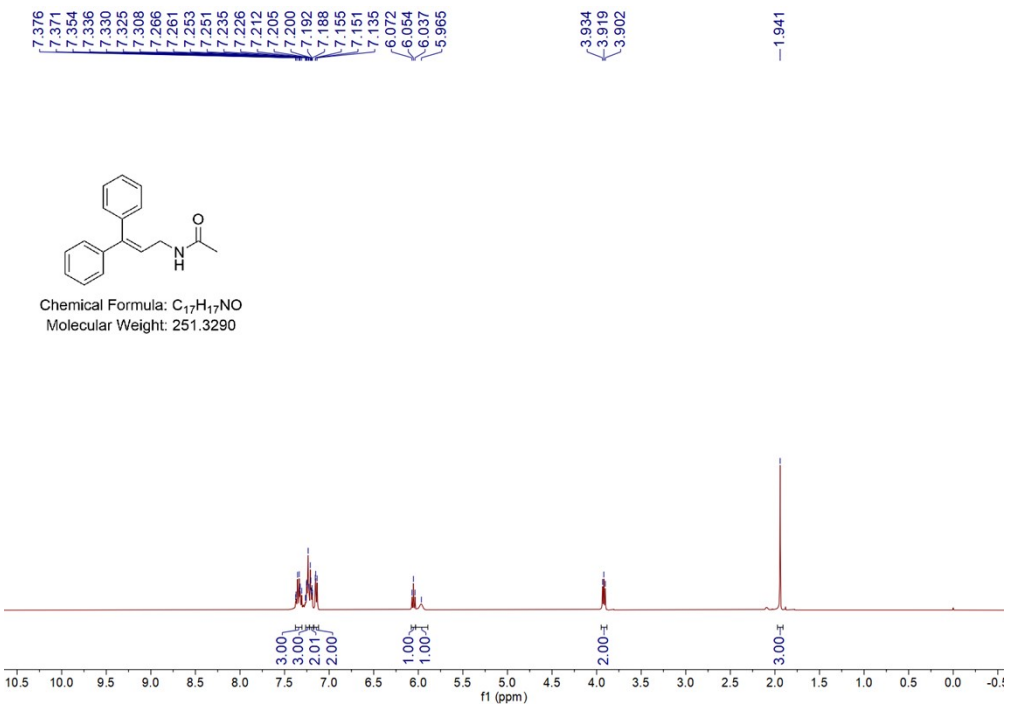
***1,1,5,5-tetraphenylpenta-1,4-diene (8b)***



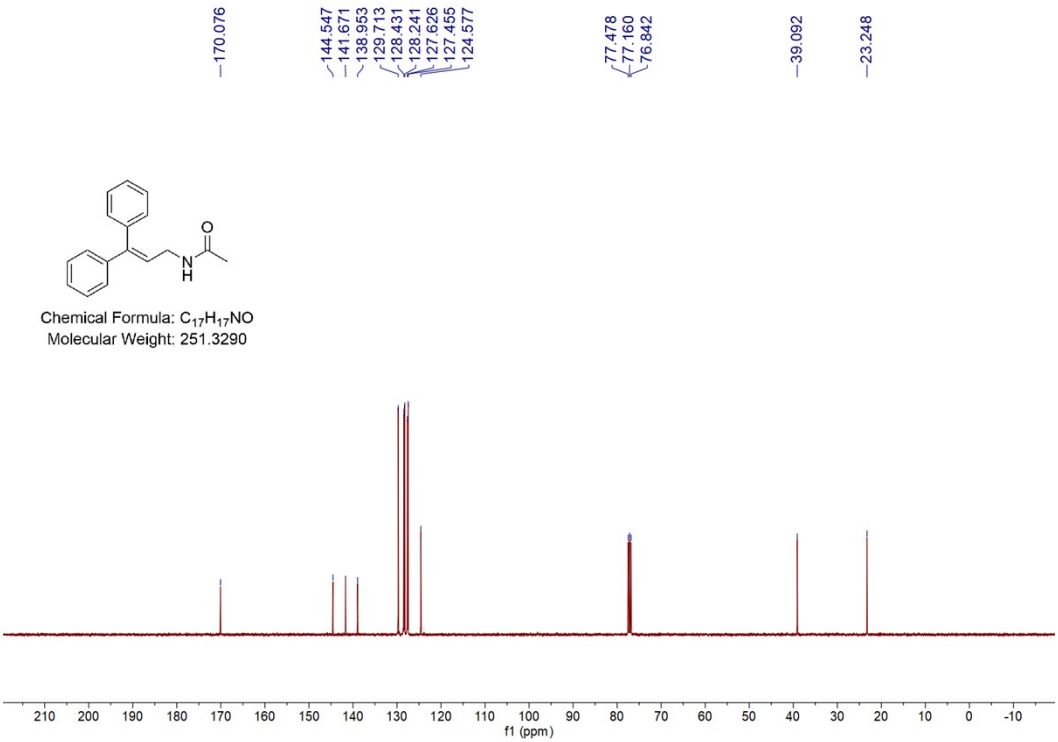
According to the general procedure and work-up, purification by flash column·chromatography·using petroleum·ether/ethyl acetate as eluent (v:v = 50:1) gave product **8b** as a colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 16H), 7.06 (d, $J$ = 7.5 Hz, 4H), 6.03 (t, $J$ = 7.5 Hz, 2H), 2.91 (t, $J$ = 7.5 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 142.8, 142.4, 139.9, 130.0, 128.3, 128.2, 127.5, 127.4, 127.13, 127.10, 30.8. Known compound. Spectral data were in good agreement with those reported in the literature.[9]

# 7. Copies of $^{1}H$, $^{13}C$, $^{31}P$ and $^{19}F$ NMR spectra of isolated compounds

***N-(3,3-diphenylallyl)acetamide(3a)***

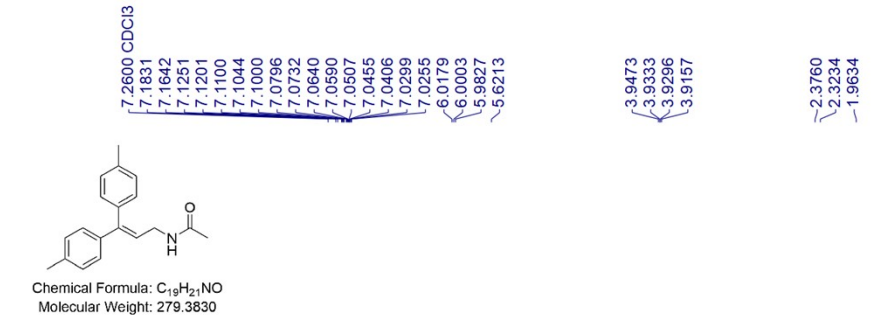


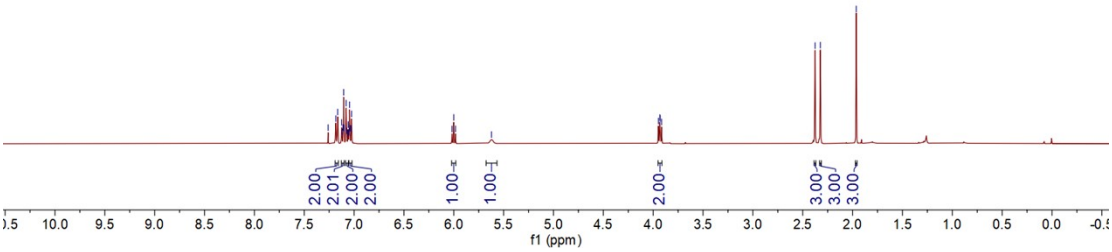

**$^{1}H$ NMR spectrum of 3a, 400 MHz, $CDCl_3$**



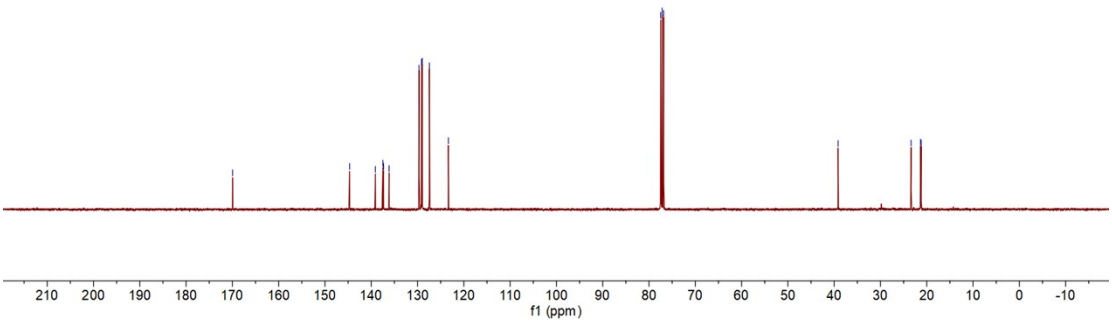

**$^{13}C$ NMR spectrum of 3a, 101 MHz, $CDCl_3$**

## *N-(3,3-di-p-tolylallyl)acetamide (3b)*



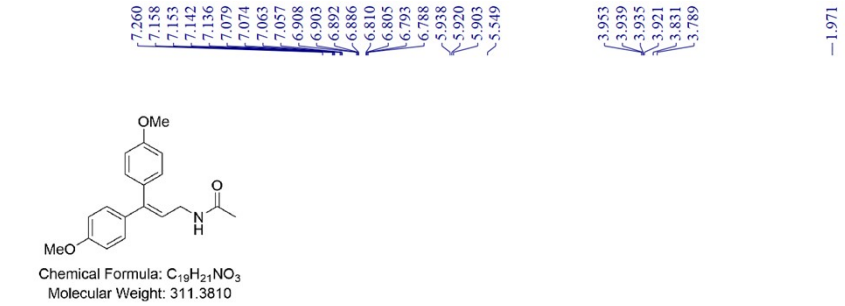




**$^{1}$H NMR spectrum of 3b, 400 MHz, $CDCl_3$**

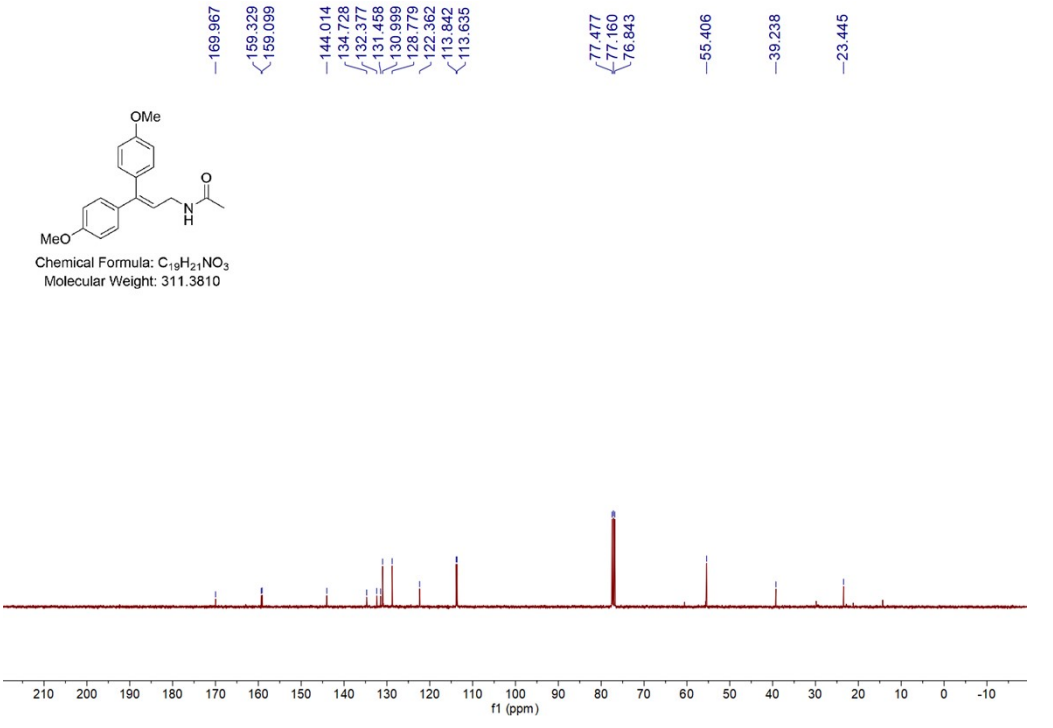




**$^{13}$C NMR spectrum of 3b, 101 MHz, $CDCl_3$**

## *N-(3,3-bis(4-methoxyphenyl)allyl)acetamide (3c)*

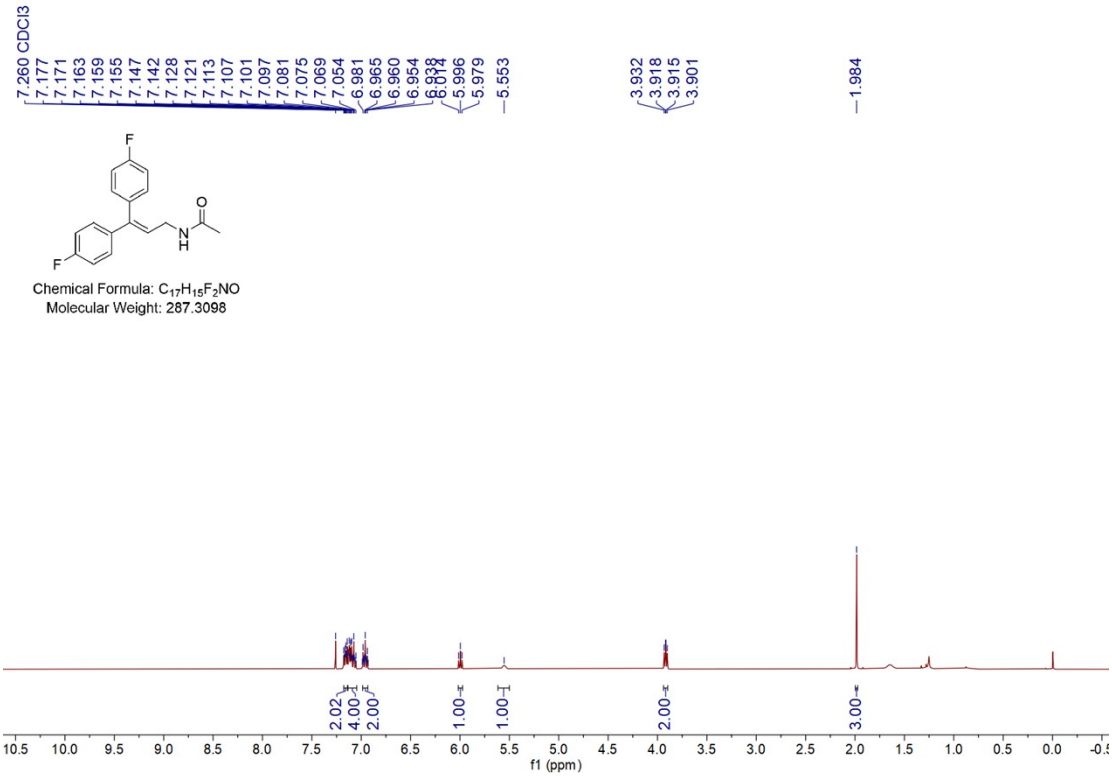



**$^{1}$H NMR spectrum of 3c, 400 MHz, $CDCl_3$**

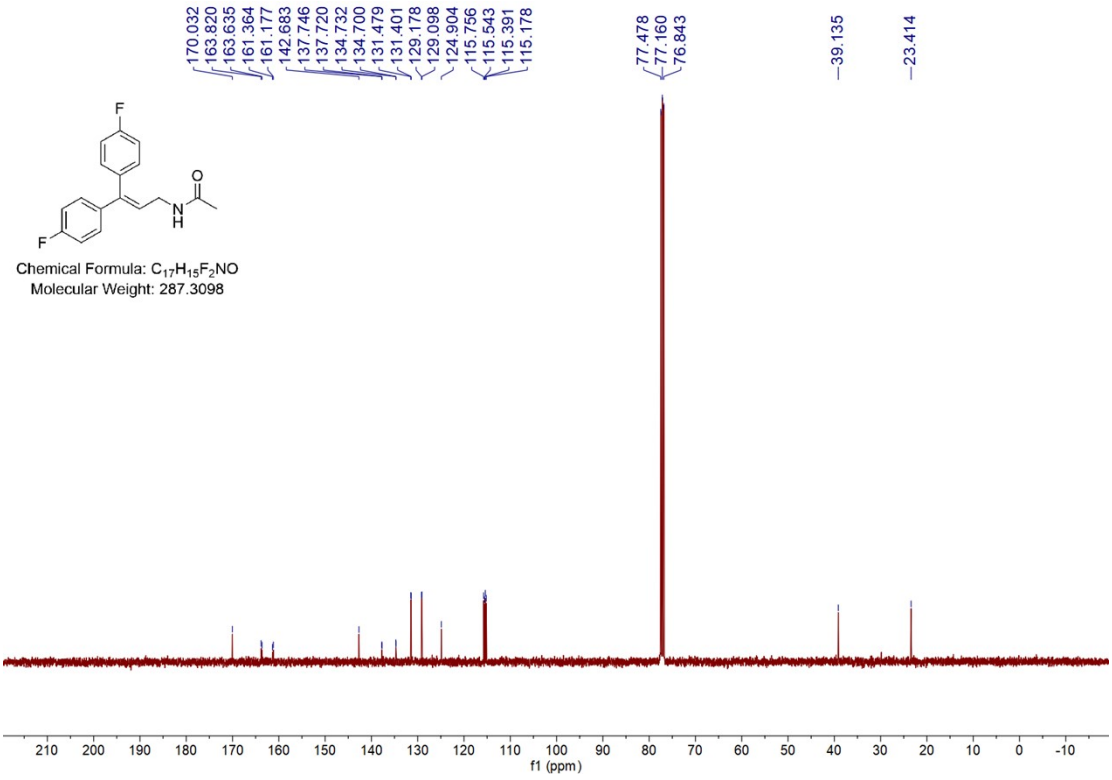



**$^{13}$C NMR spectrum of 3c, 101 MHz, $CDCl_3$**

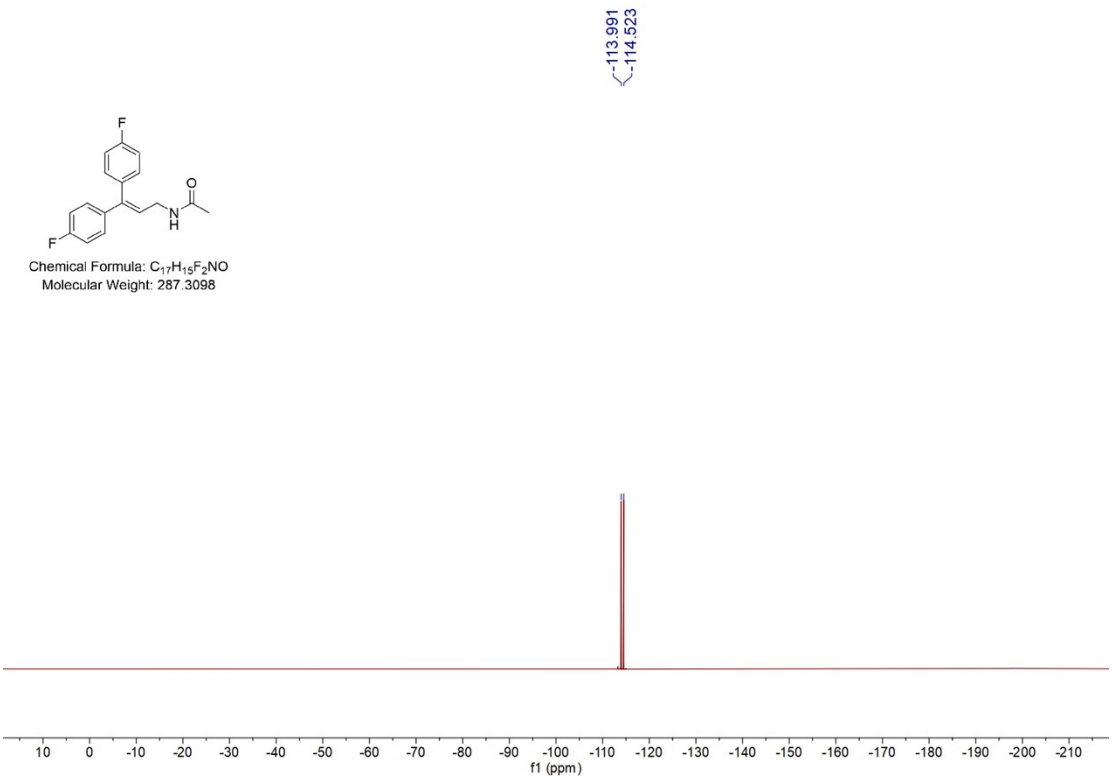
*N-(3,3-bis(4-fluorophenyl)allyl)acetamide (3d)*




**$^{1}$H NMR spectrum of 3d, 400 MHz, $CDCl_3$**

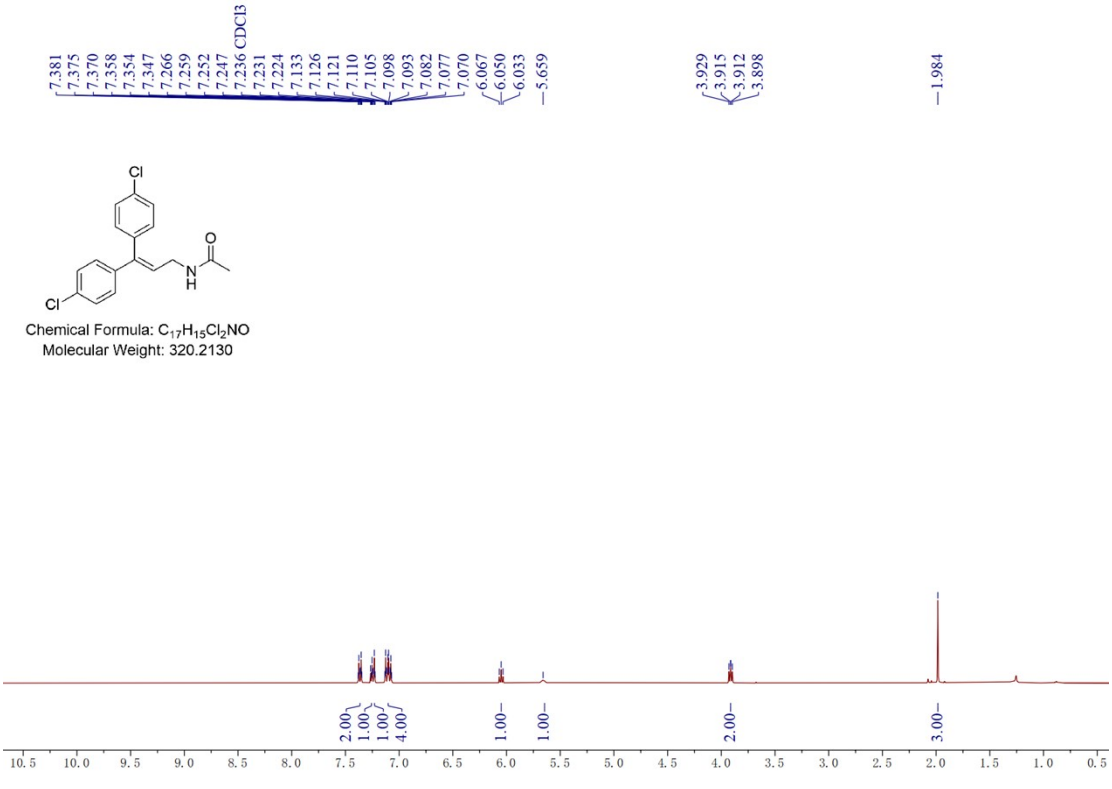



**$^{13}$C NMR spectrum of 3d, 101 MHz, $CDCl_3$**

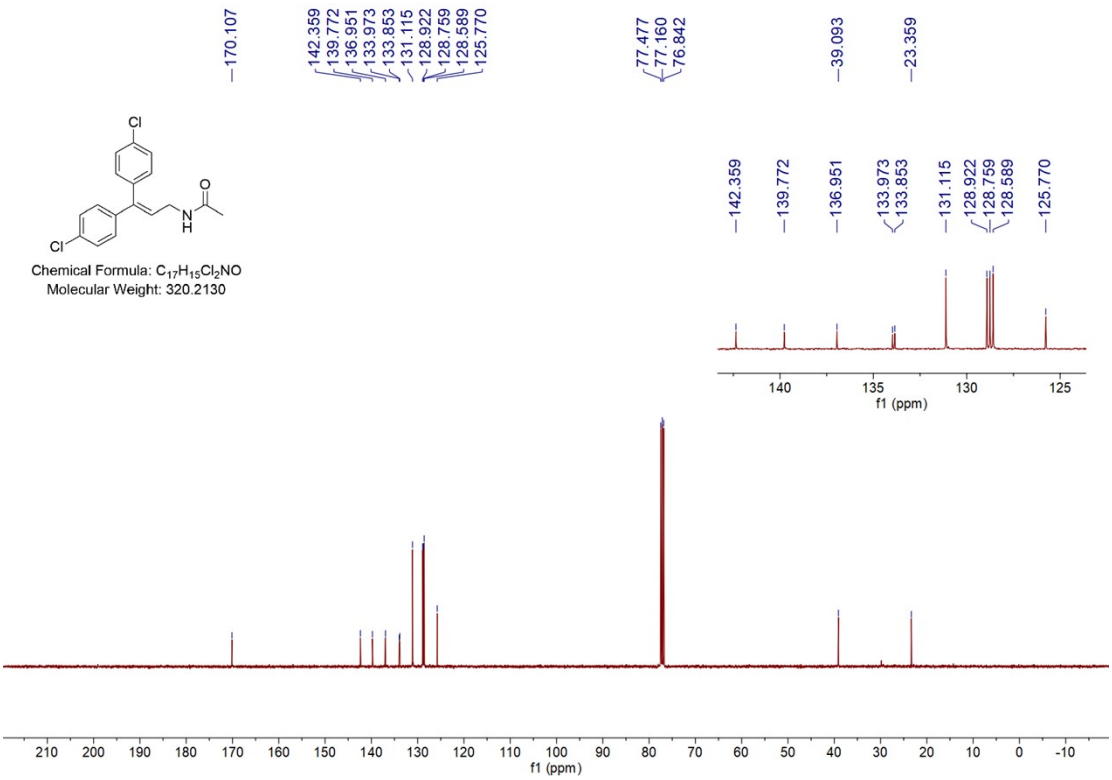



**$^{19}$F NMR spectrum of 3d, 376 MHz, $CDCl_3$**

## *N-(3,3-bis(4-chlorophenyl)allyl)acetamide (3e)*

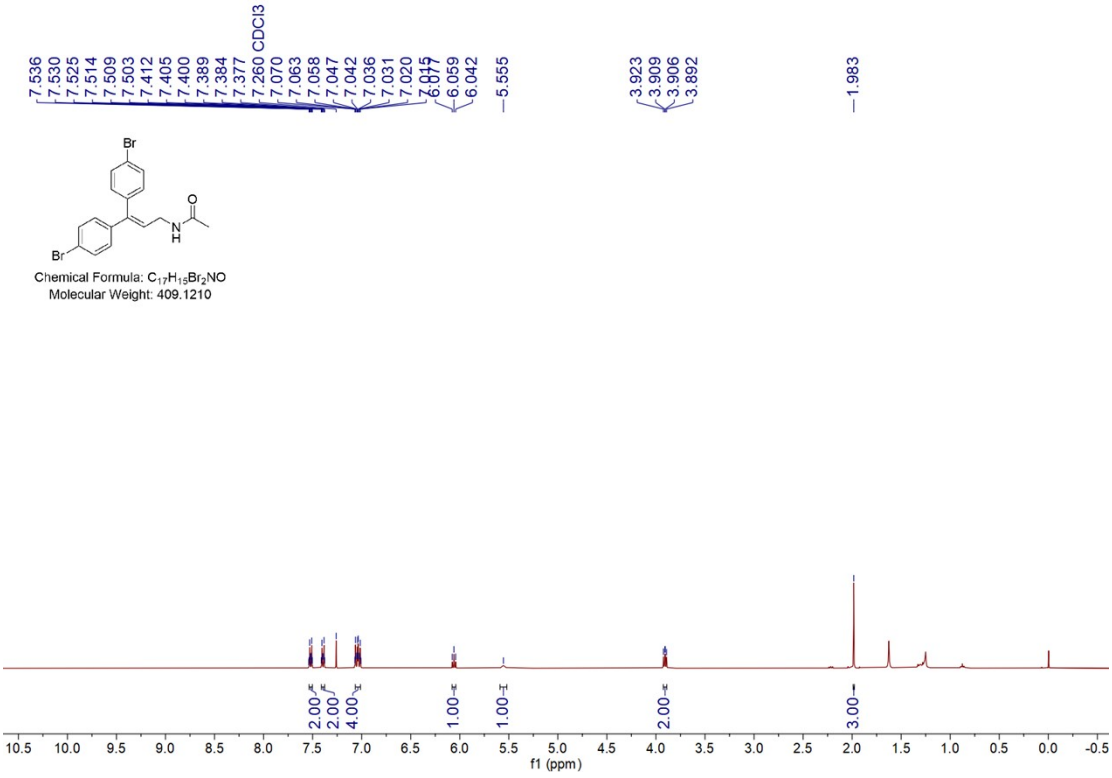



**$^{1}$H NMR spectrum of 3e, 400 MHz, $CDCl_3$**

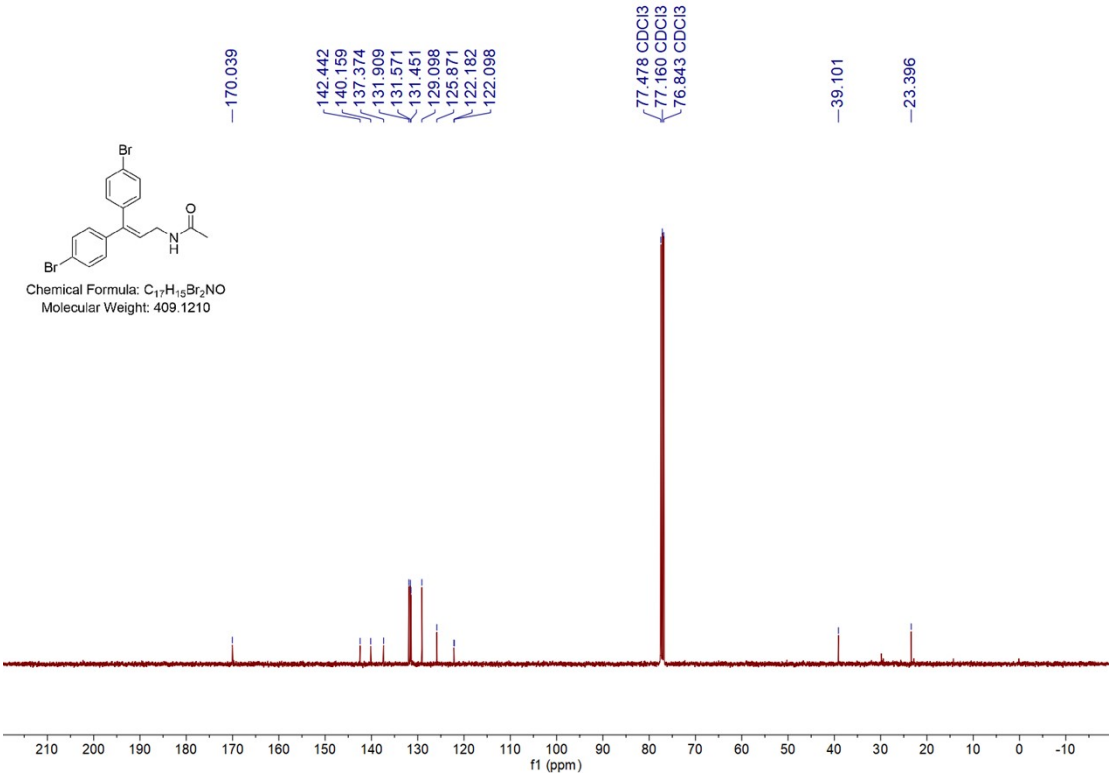



**$^{13}$C NMR spectrum of 3e, 101 MHz, $CDCl_3$**

## *N-(3,3-bis(4-bromophenyl)allyl)acetamide (3f)*

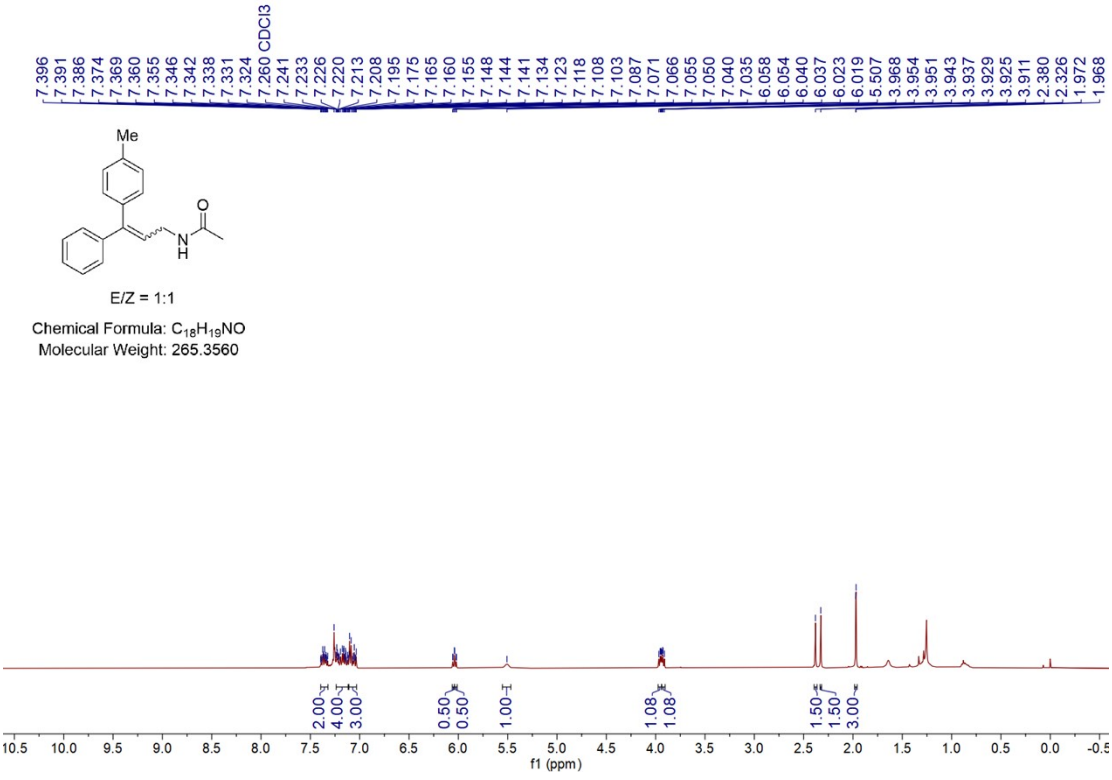



**$^{1}$H NMR spectrum of 3f, 400 MHz, $CDCl_3$**

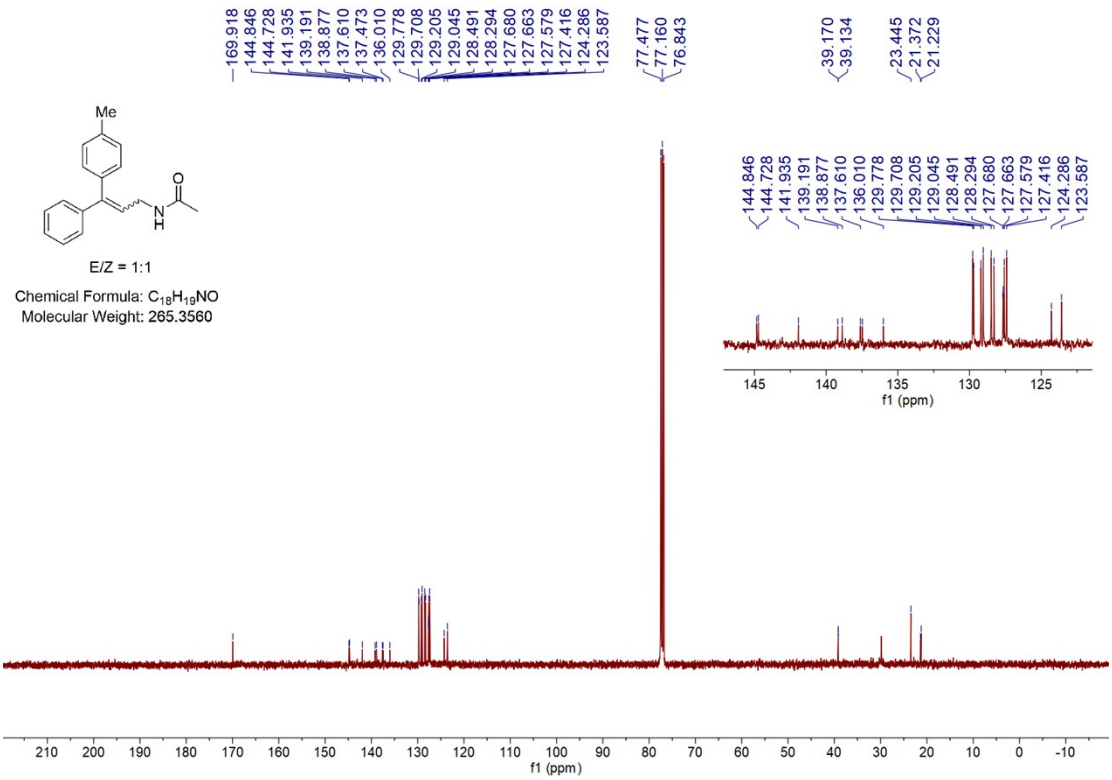



**$^{13}$C NMR spectrum of 3f, 101 MHz, $CDCl_3$**

## *N-(3-phenyl-3-(p-tolyl)allyl)acetamide (3g)*

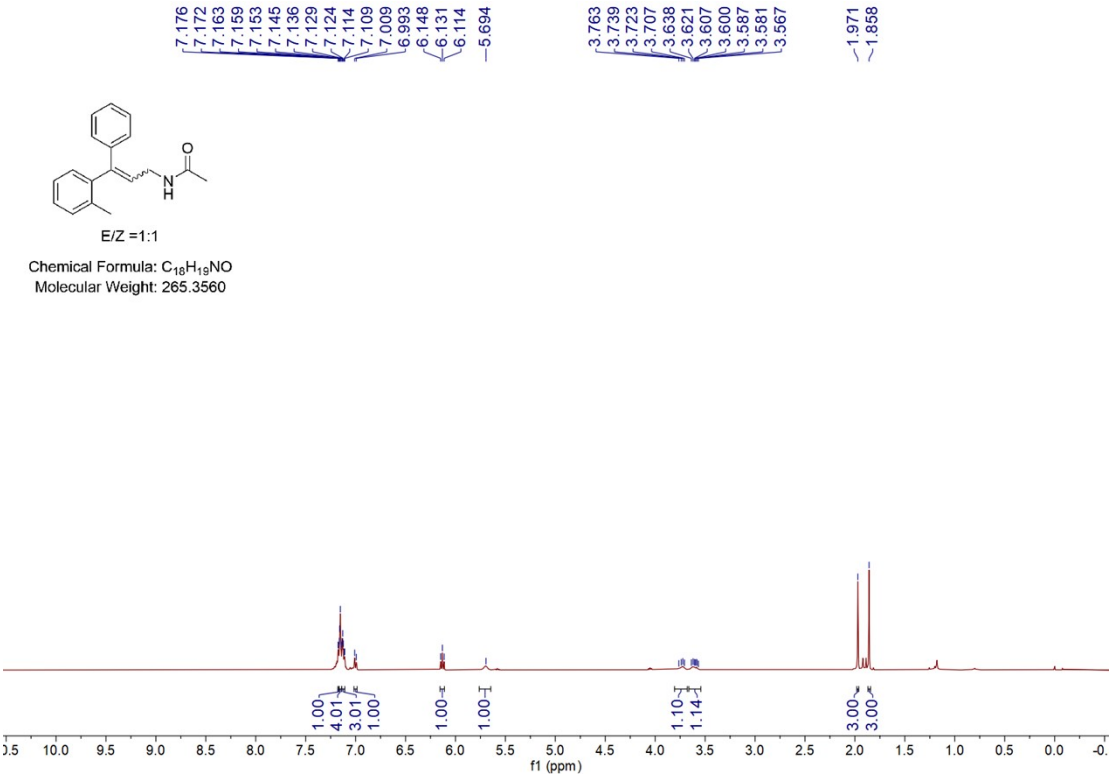



**$^{1}$H NMR spectrum of 3g, 400 MHz, $CDCl_3$**

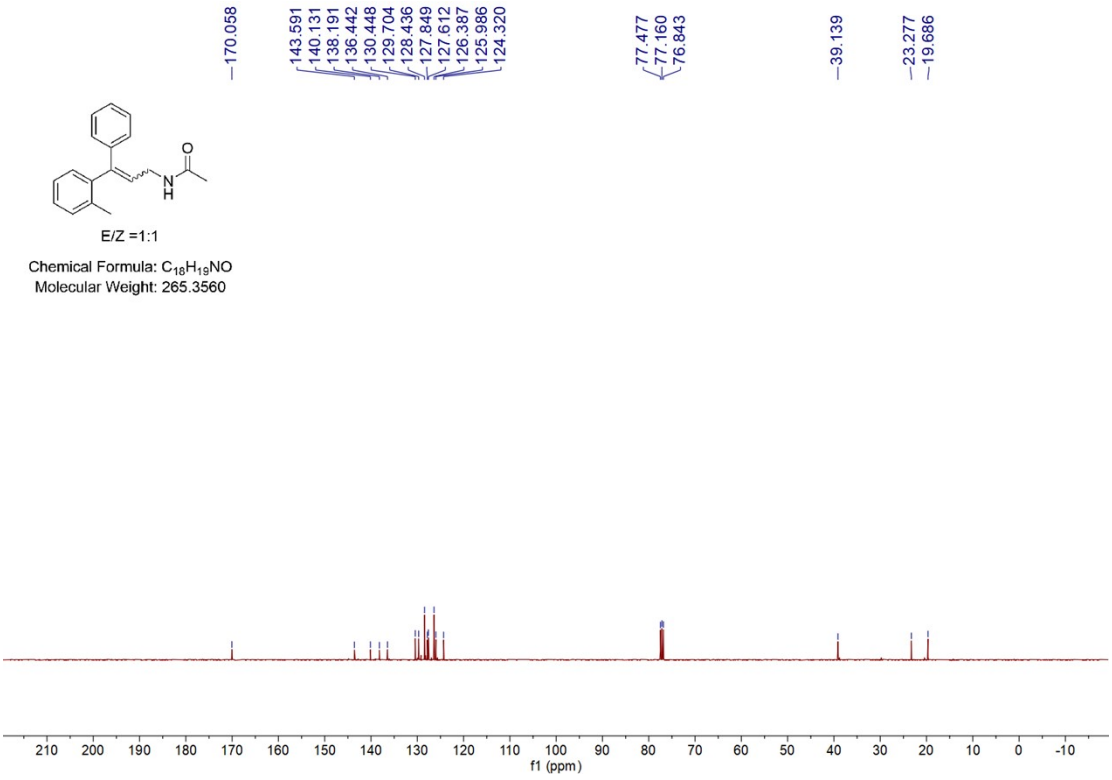



**$^{13}$C NMR spectrum of 3g, 101 MHz, $CDCl_3$**

## *N-(3-phenyl-3-(o-tolyl)allyl)acetamide (3h)*

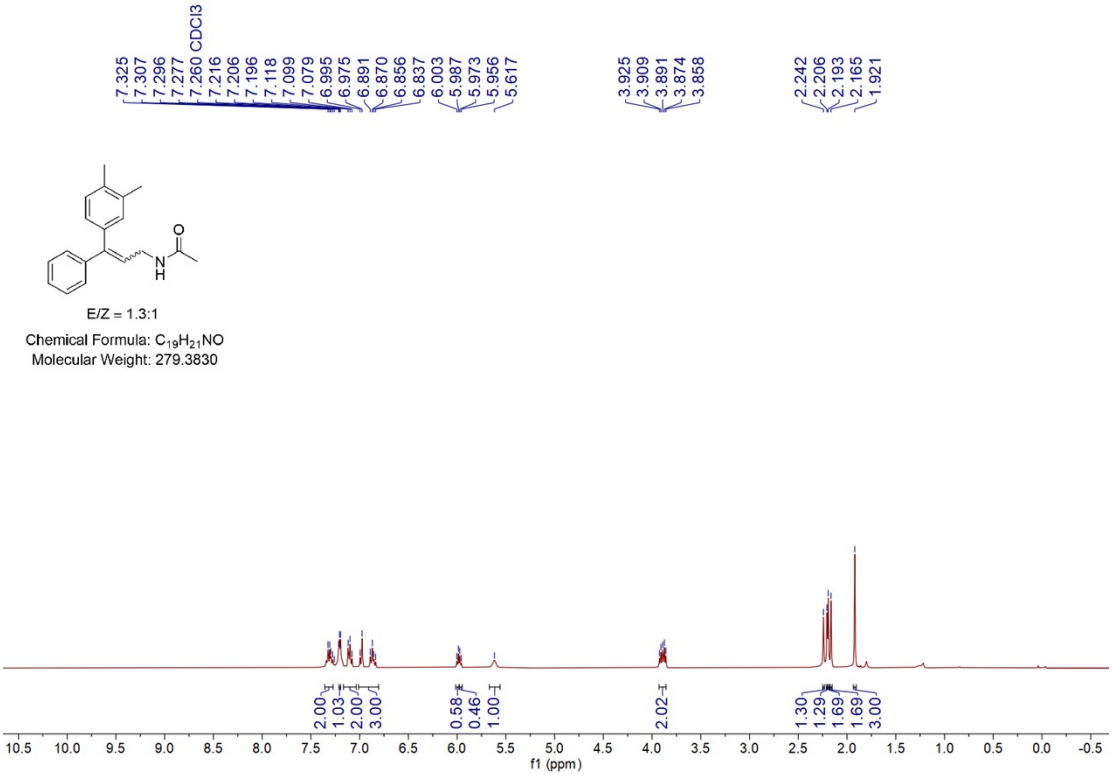



**$^{1}$H NMR spectrum of 3h, 400 MHz, $CDCl_3$**

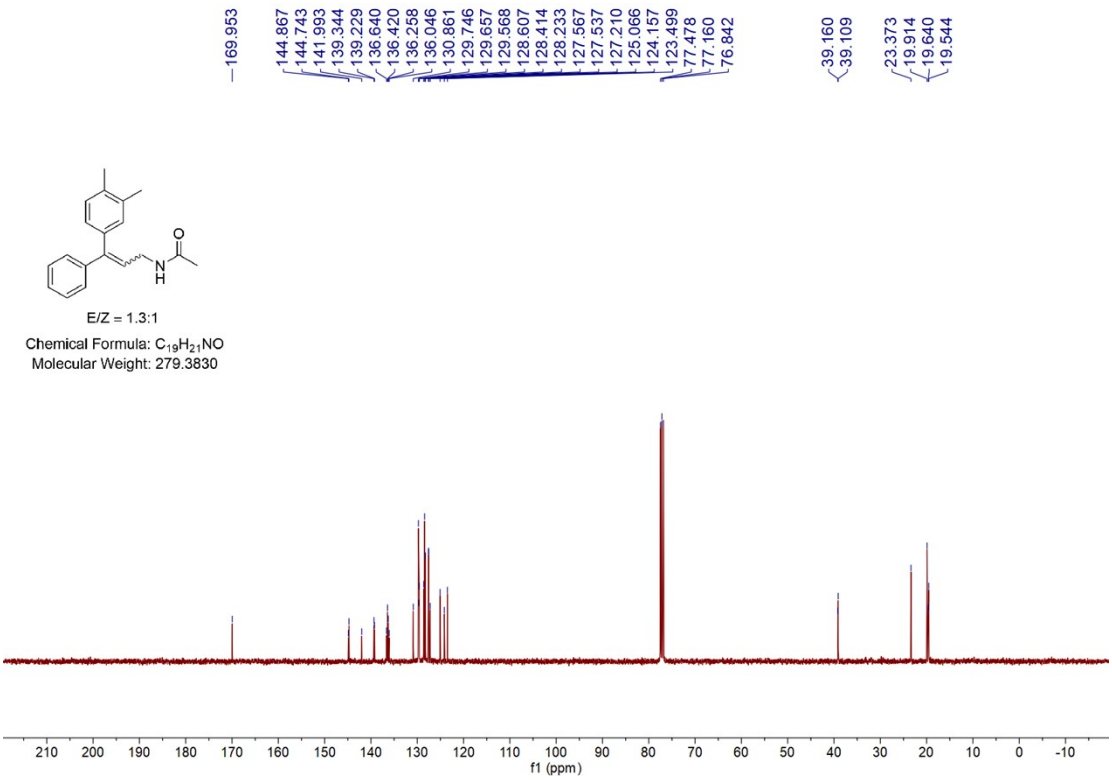



**$^{13}$C NMR spectrum of 3h, 101 MHz, $CDCl_3$**

## *N-(3-(3,4-dimethylphenyl)-3-phenylallyl)acetamide (3i)*

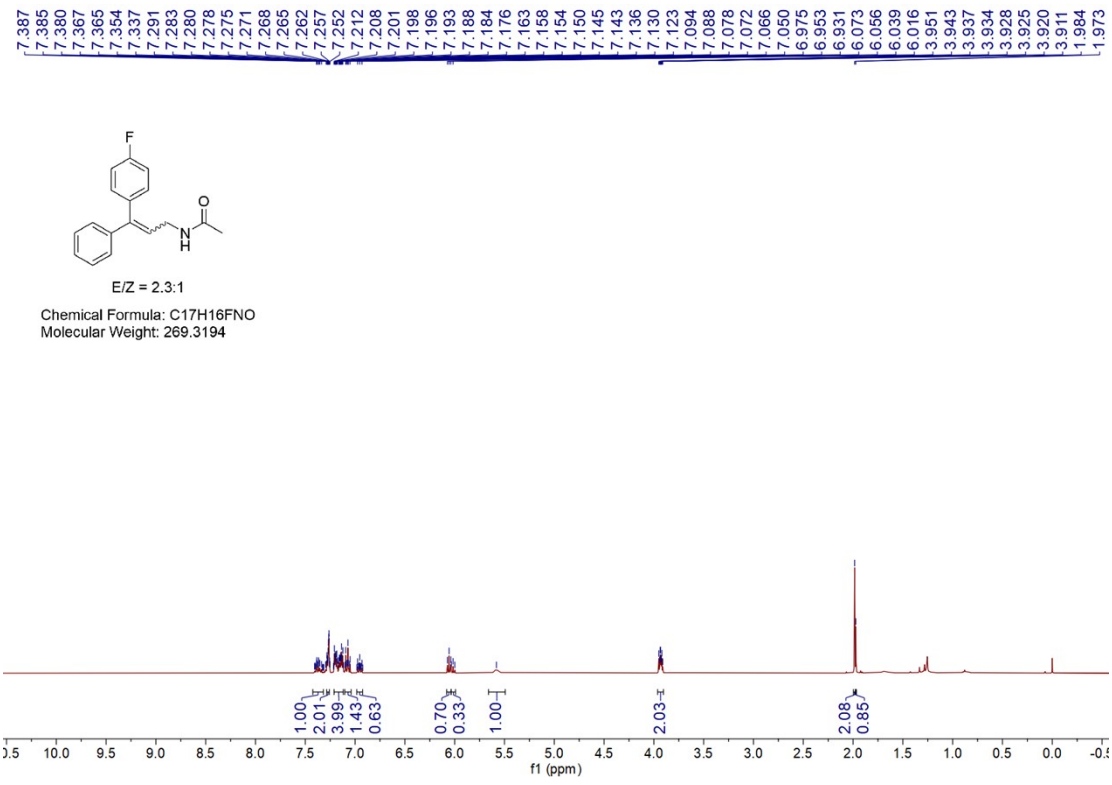



**$^{1}$H NMR spectrum of 3i, 400 MHz, $CDCl_3$**

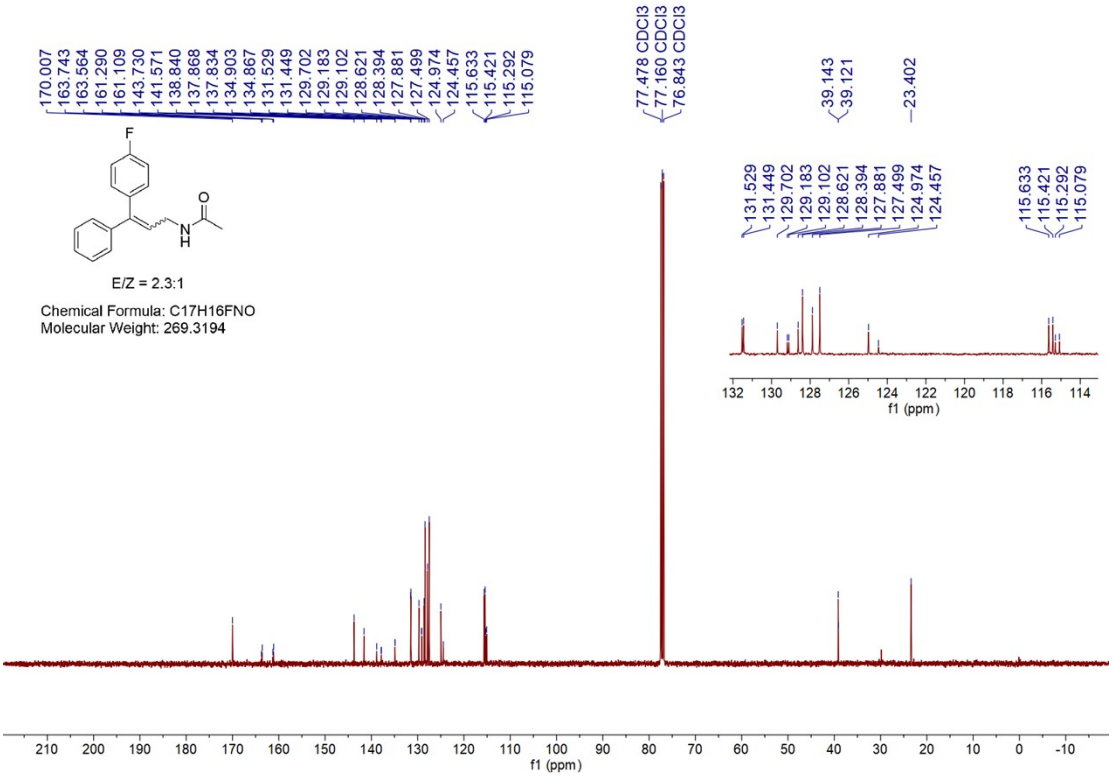



**$^{13}$C NMR spectrum of 3i, 101 MHz, $CDCl_3$**

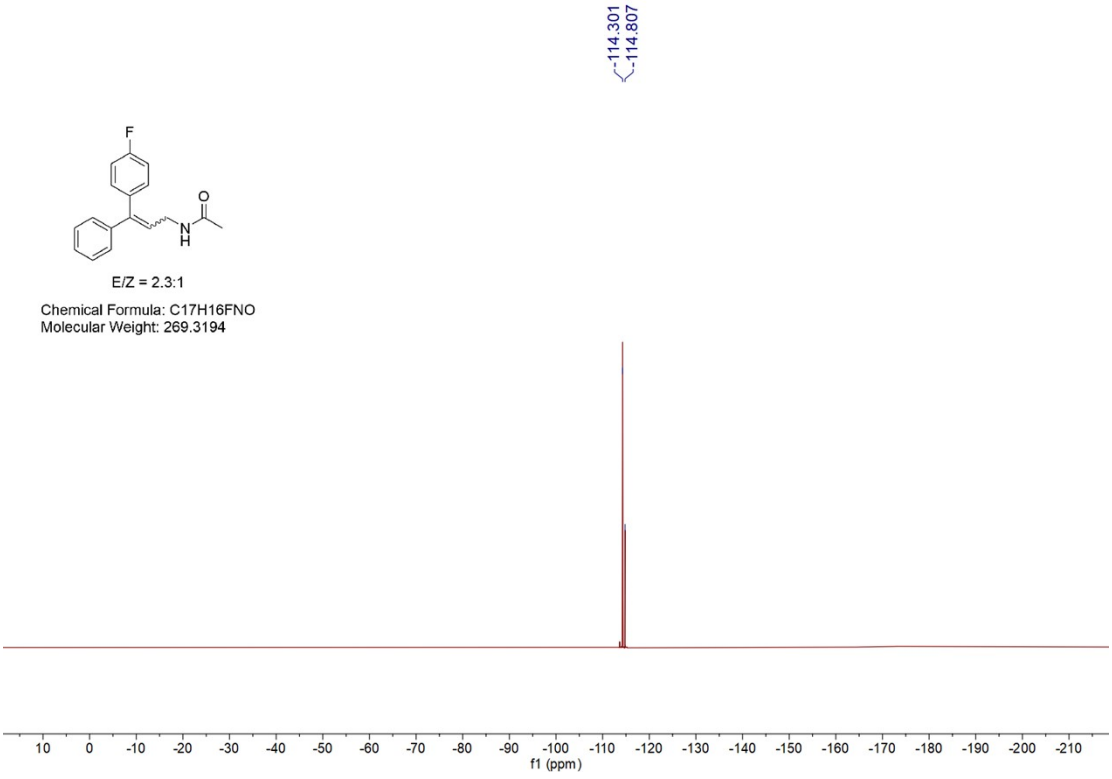
## *N-(3-(4-fluorophenyl)-3-phenylallyl)acetamide (3j)*




**$^{1}$H NMR spectrum of 3j, 400 MHz, $CDCl_3$**

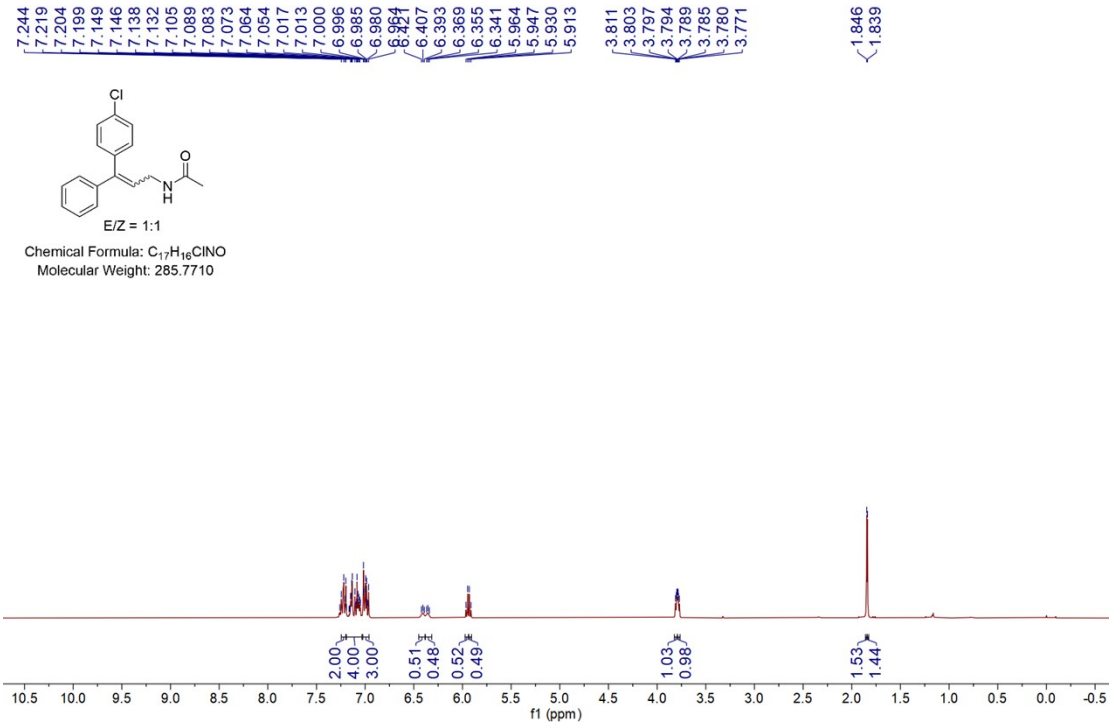



**$^{13}$C NMR spectrum of 3j, 101 MHz, $CDCl_3$**

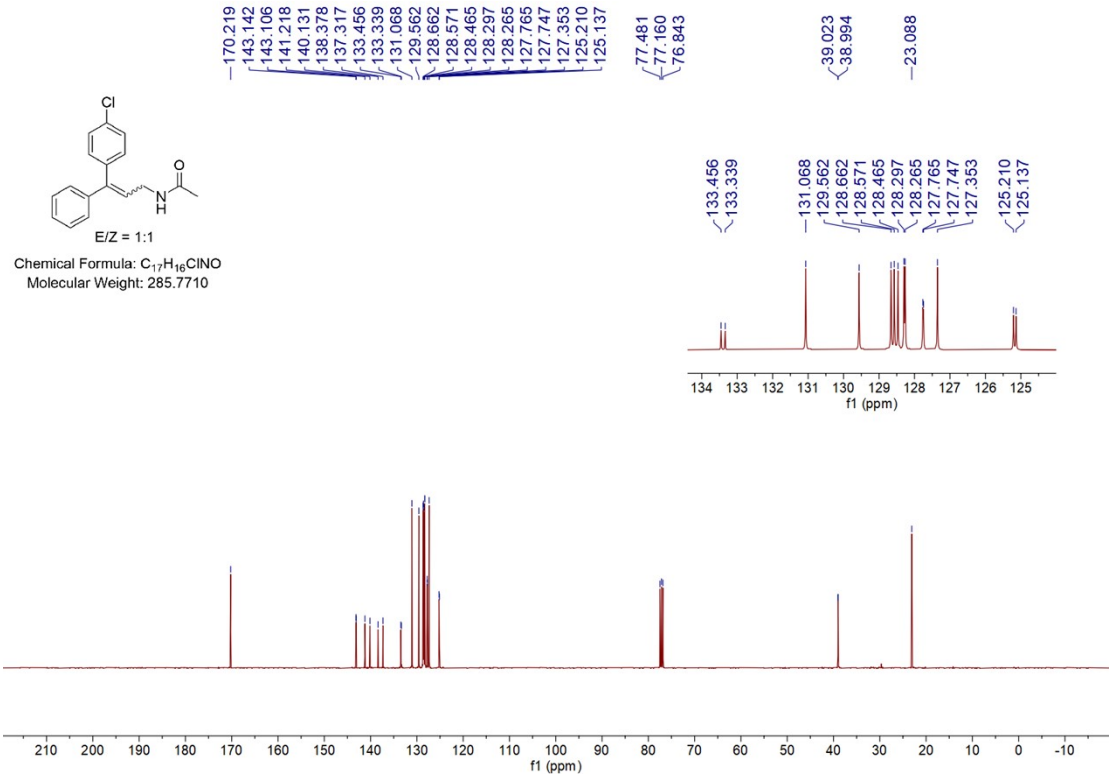



**$^{19}$F NMR spectrum of 3j, 376 MHz, $CDCl_3$**

*N-(3-(4-chlorophenyl)-3-phenylallyl)acetamide (3k)*

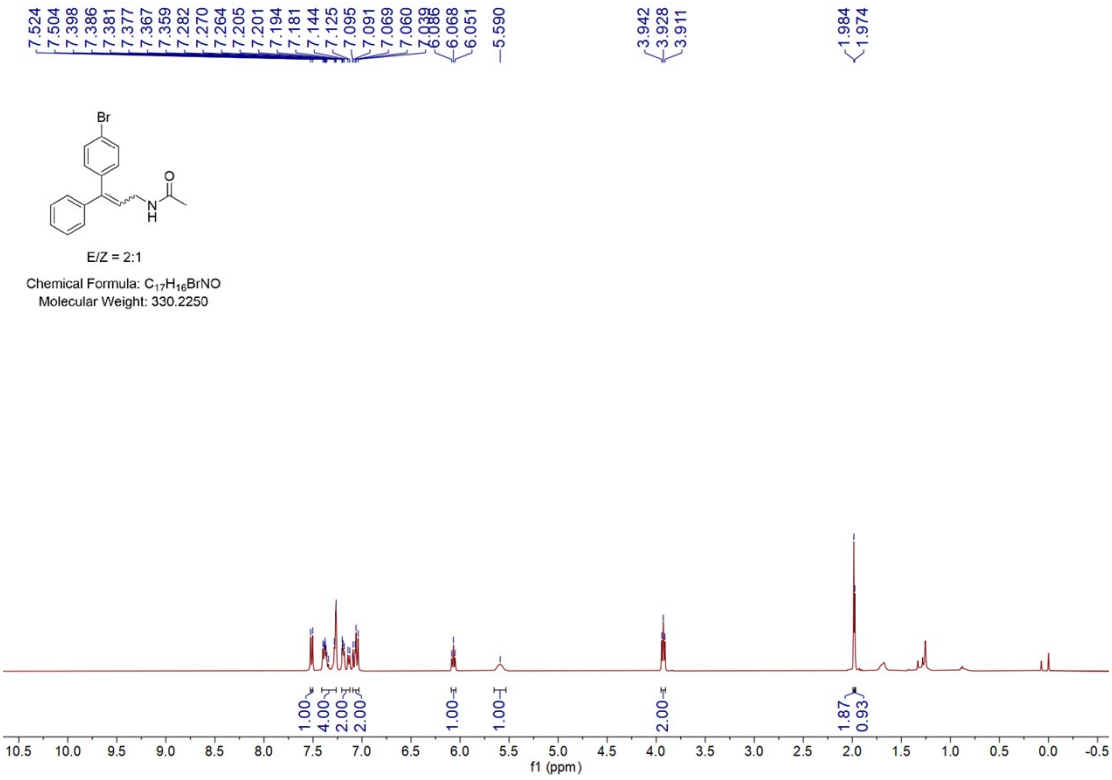



**$^{1}$H NMR spectrum of 3k, 400 MHz, $CDCl_3$**

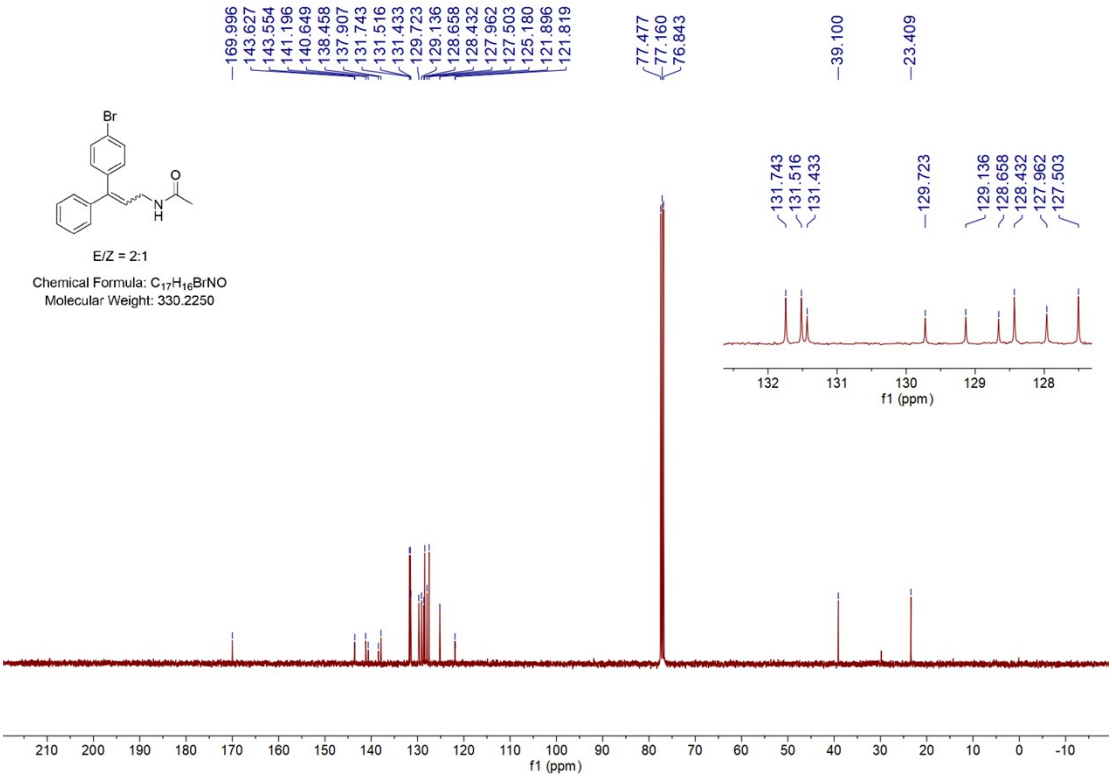



**$^{13}$C NMR spectrum of 3k, 101 MHz, $CDCl_3$**

***N-(3-(4-bromophenyl)-3-phenylallyl)acetamideo (3l)***

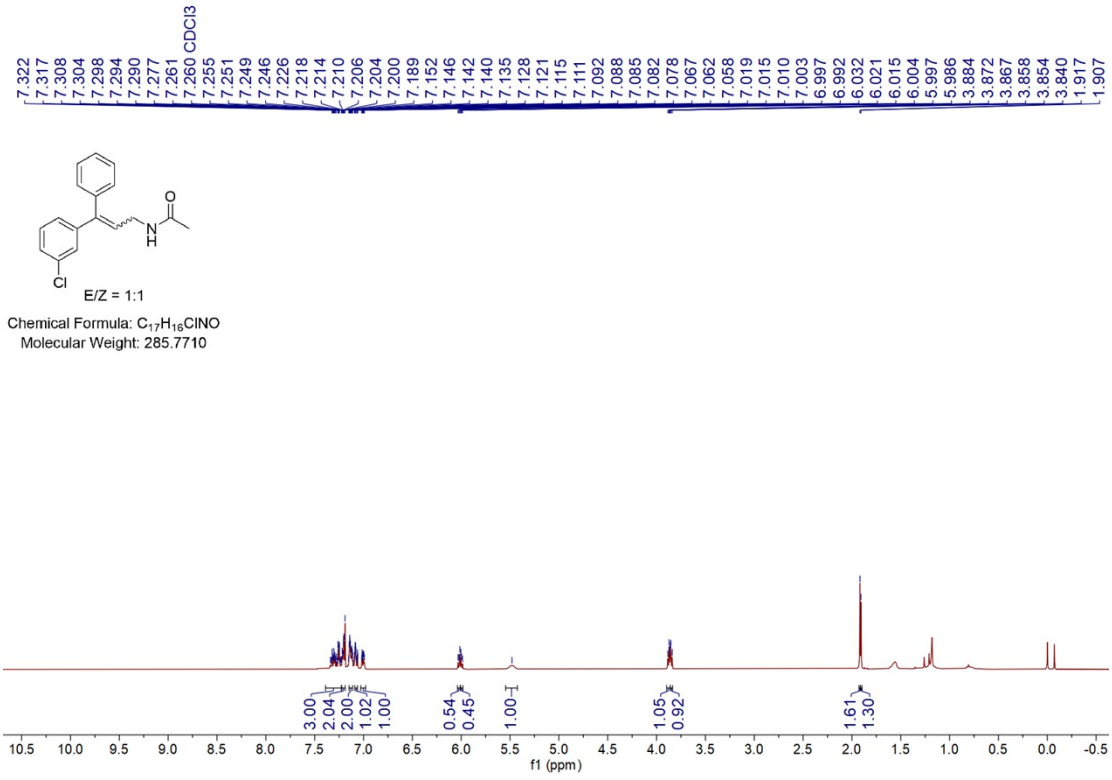



**$^{1}$H NMR spectrum of 3l, 400 MHz, $CDCl_3$**

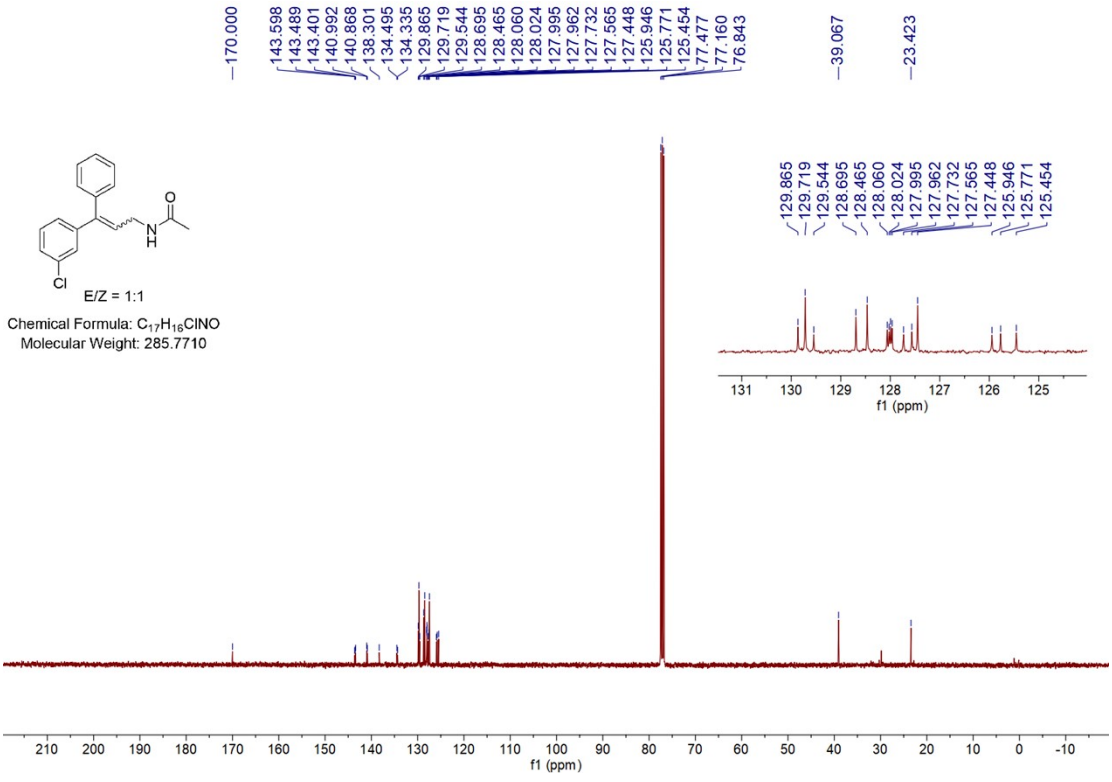



**$^{13}$C NMR spectrum of 3l, 101 MHz, $CDCl_3$**

## *N-(3-(3-chlorophenyl)-3-phenylallyl)acetamide (3m)*

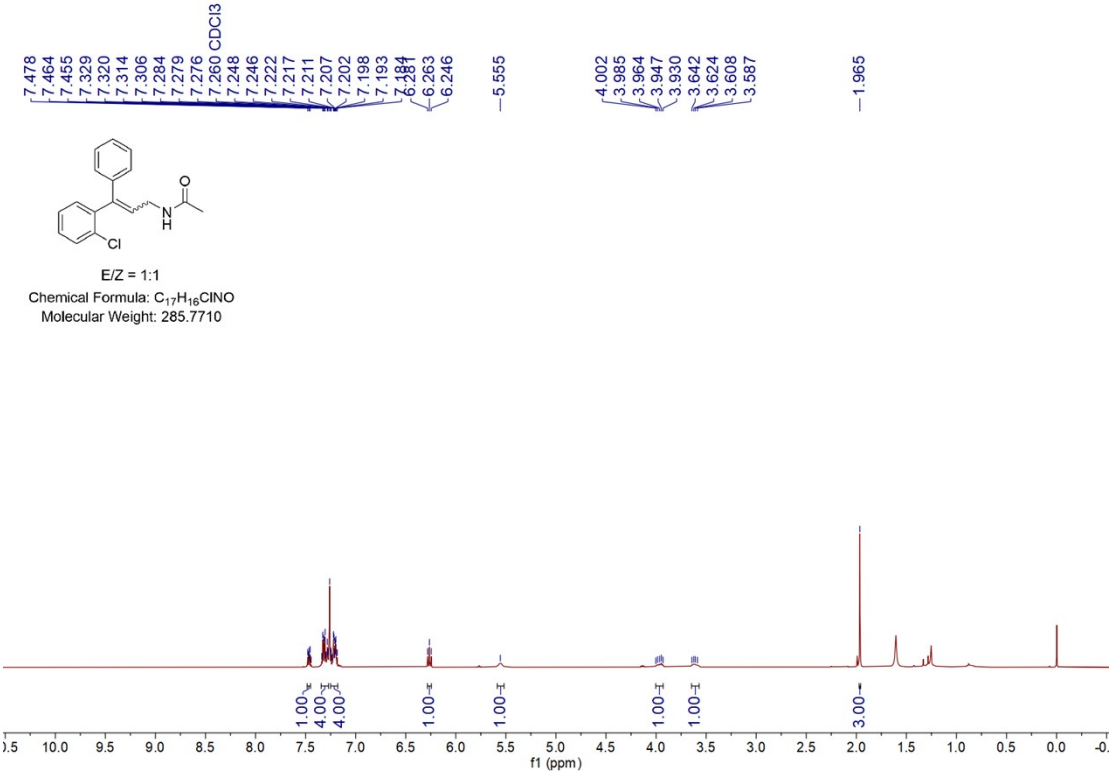



**$^{1}$H NMR spectrum of 3m, 400 MHz, $CDCl_3$**

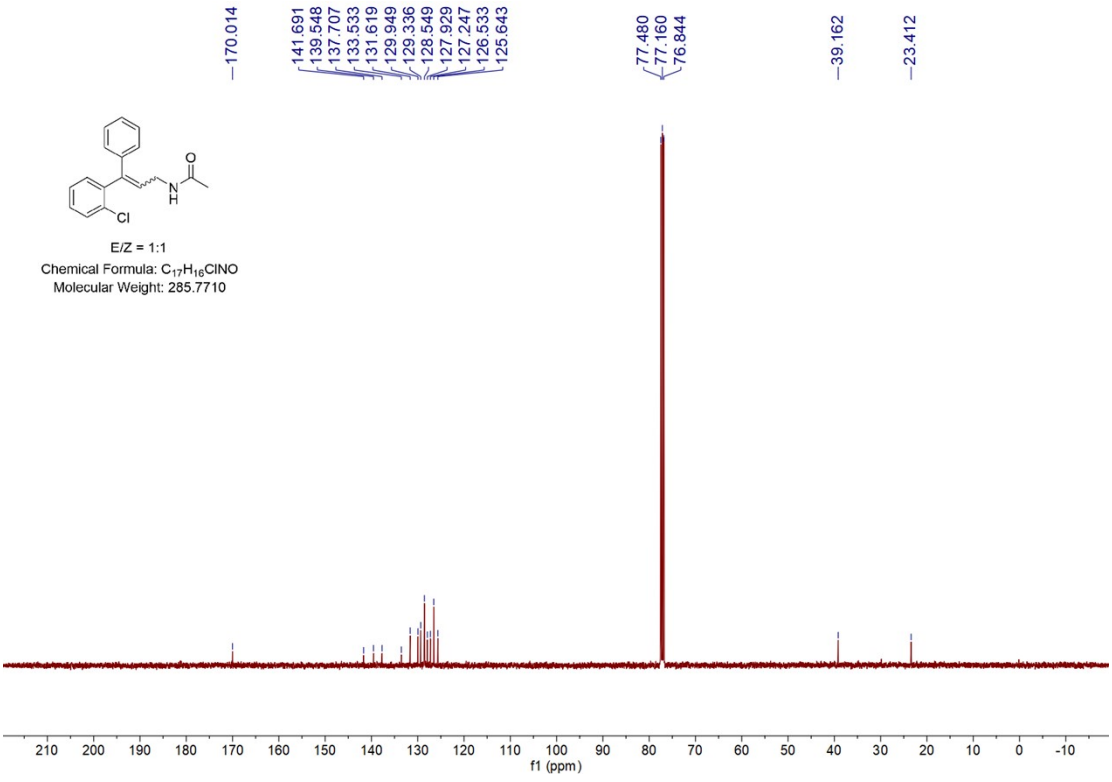



**$^{13}$C NMR spectrum of 3m, 101 MHz, $CDCl_3$**

## *N-(3-(2-chlorophenyl)-3-phenylallyl)acetamide (3n)*

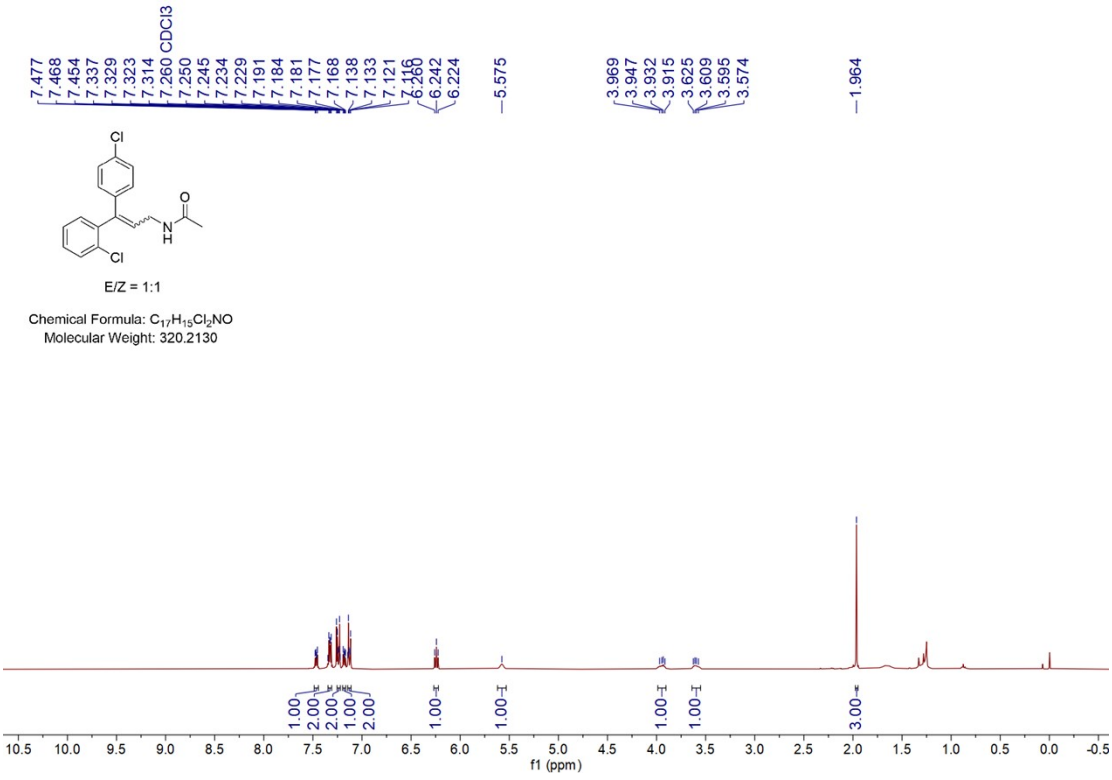



**$^{1}$H NMR spectrum of 3n, 400 MHz, $CDCl_3$**

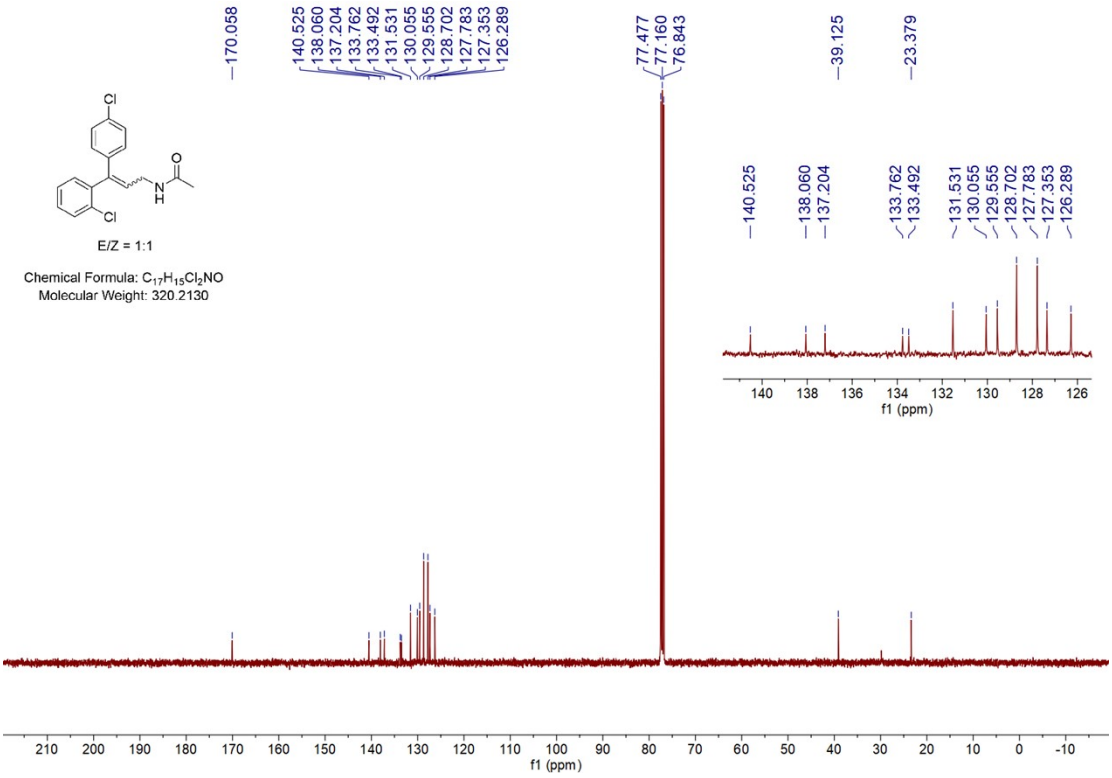



**$^{13}$C NMR spectrum of 3n, 101 MHz, $CDCl_3$**

## *N-(3-(2-chlorophenyl)-3-(4-chlorophenyl)allyl)acetamide (3o)*

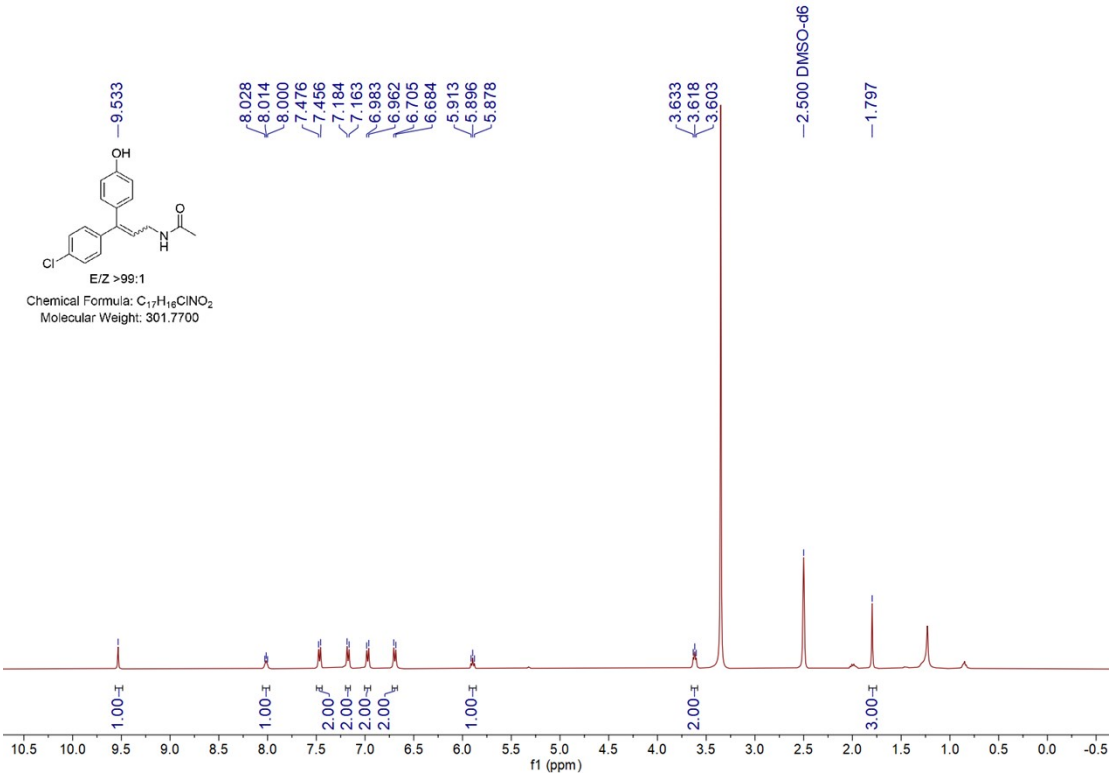



**$^{1}$H NMR spectrum of 3o, 400 MHz, $CDCl_3$**

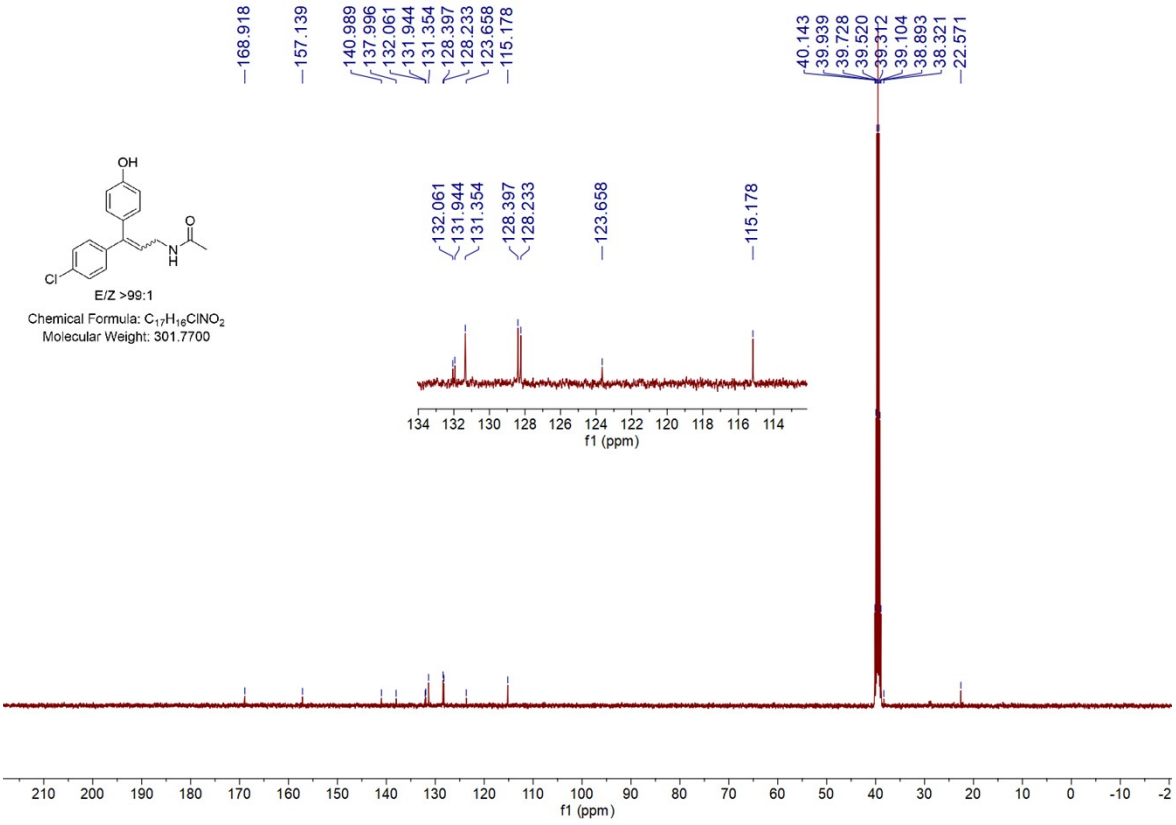



**$^{13}$C NMR spectrum of 3o, 101 MHz, $CDCl_3$**

***N-(3-(4-chlorophenyl)-3-(4-hydroxyphenyl)allyl)acetamide (3p)***

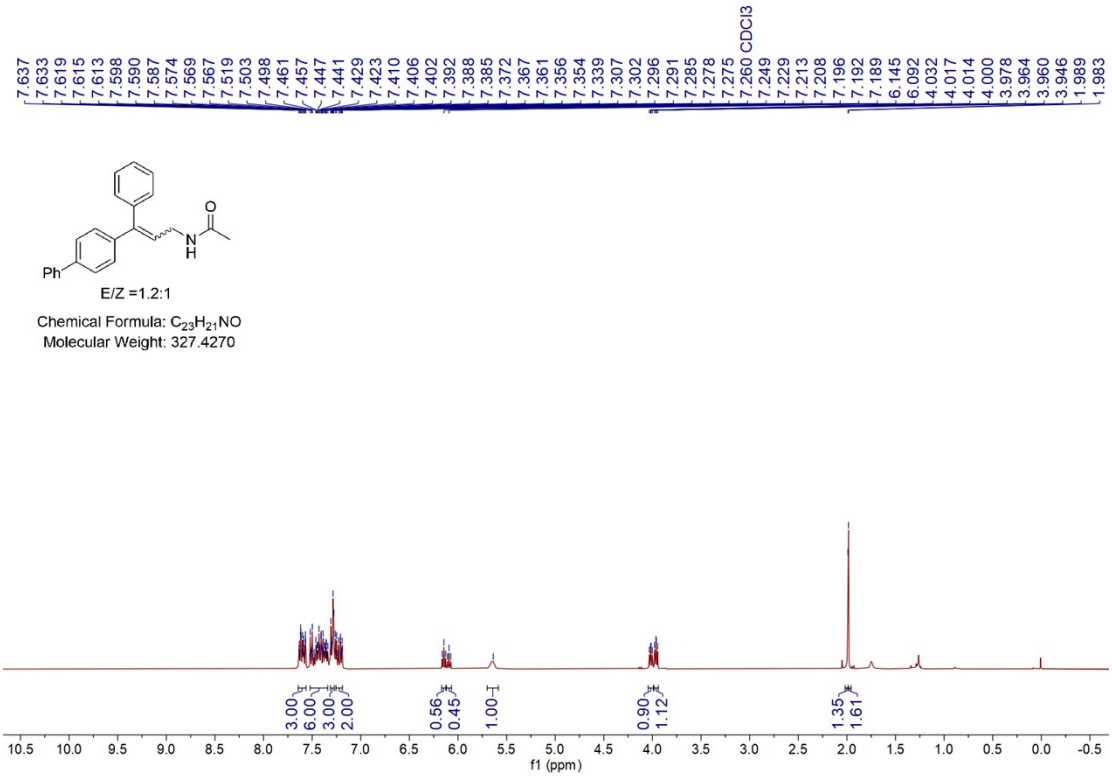



**$^{1}$H NMR spectrum of 3p, 400 MHz, DMSO-$d_6$**

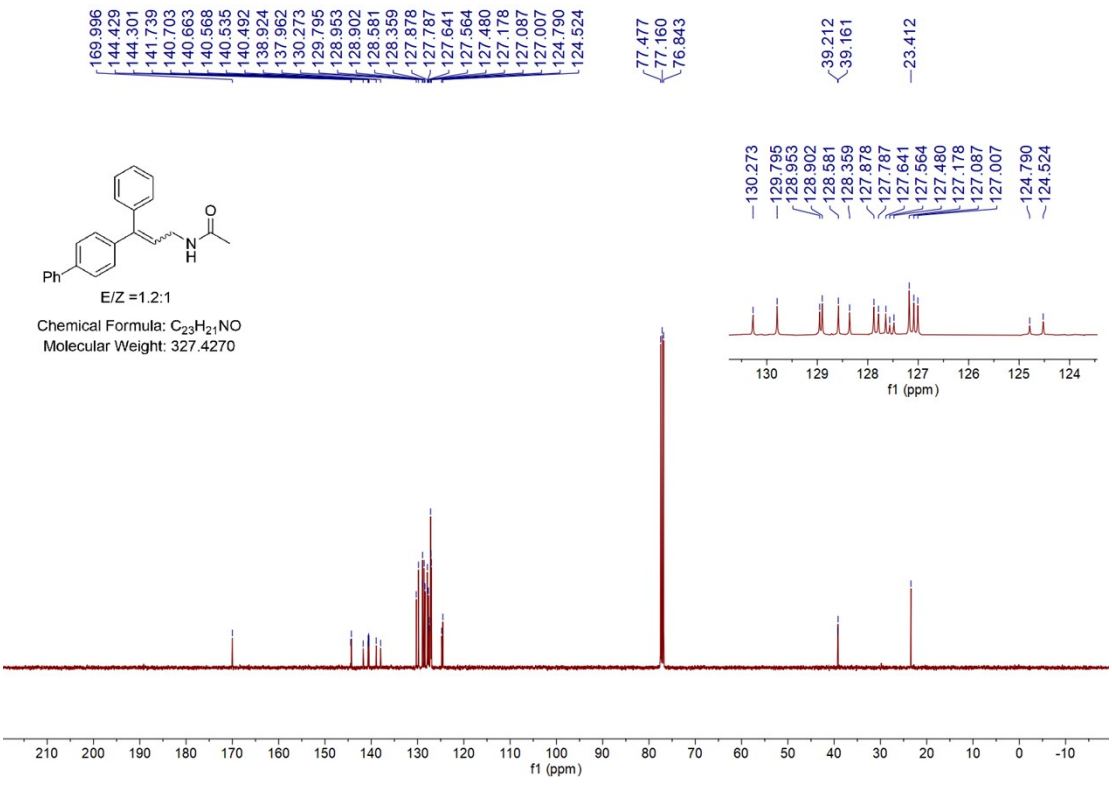



**$^{13}$C NMR spectrum of 3p, 101 MHz, DMSO-$d_6$**

*N-(3-([1,1'-biphenyl]-4-yl)-3-phenylallyl)acetamide (3q)*

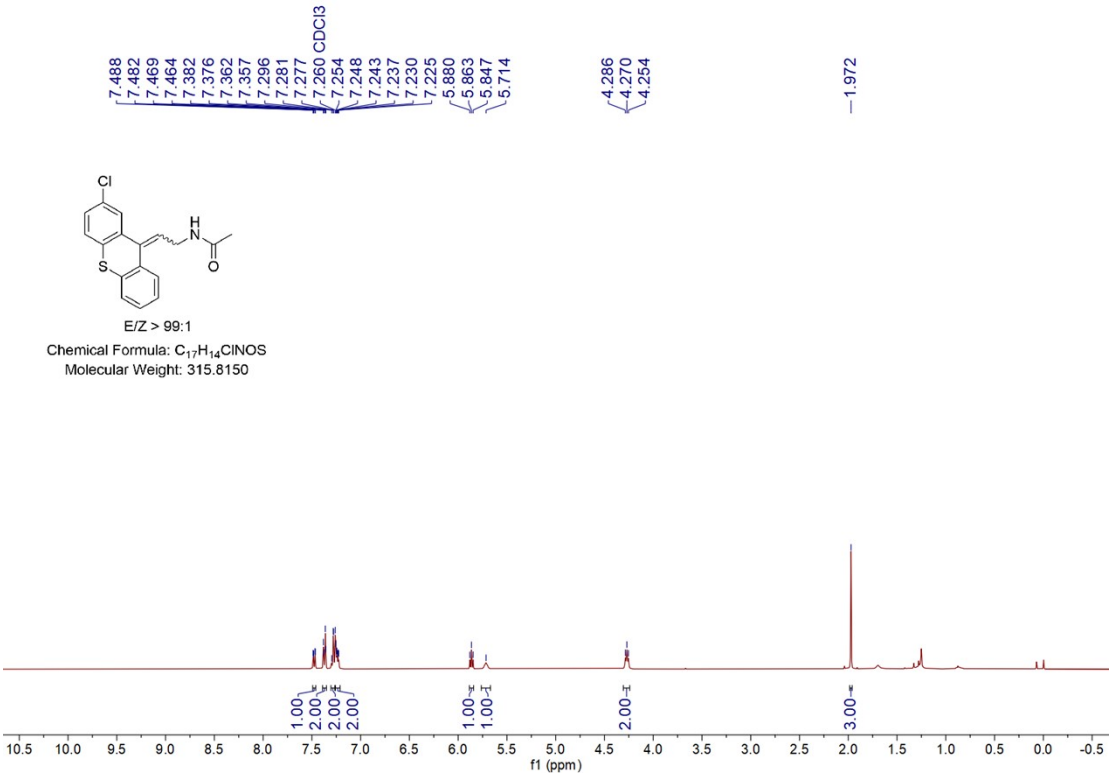



**$^{1}$H NMR spectrum of 3q, 400 MHz, $CDCl_3$**

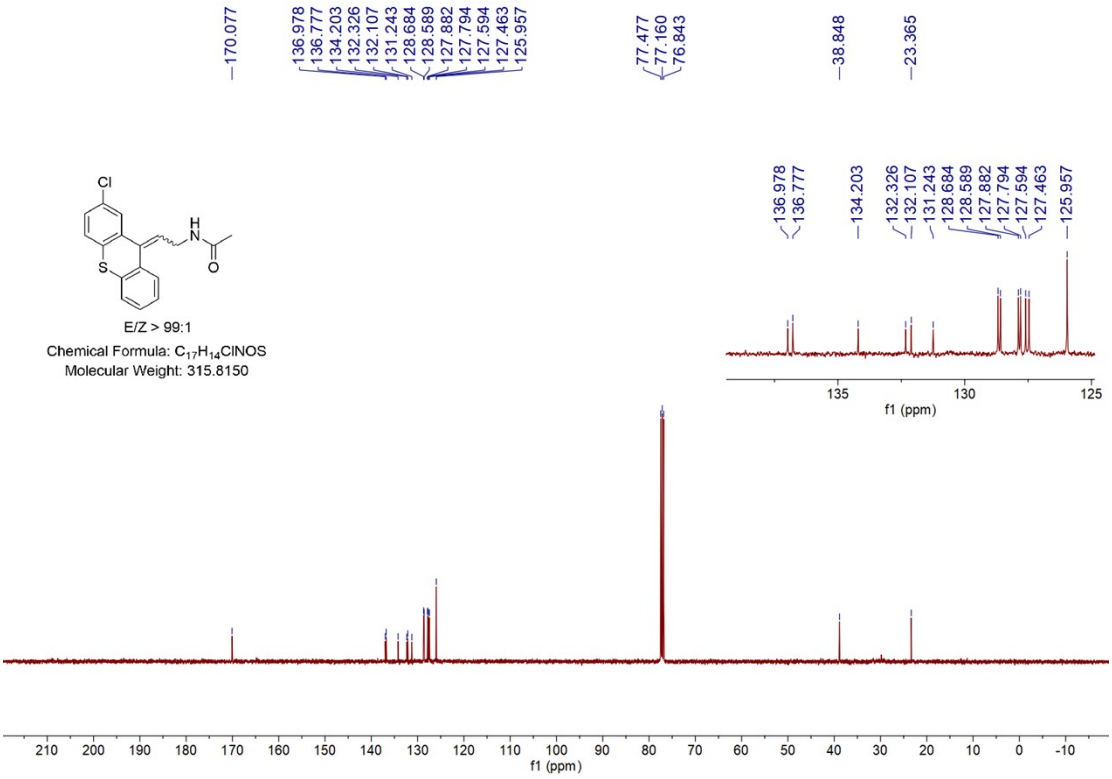



**$^{13}$C NMR spectrum of 3q, 101 MHz, $CDCl_3$**

*N-(2-(2-chloro-9H-thioxanthen-9-ylidene)ethyl)acetamide (3r)*

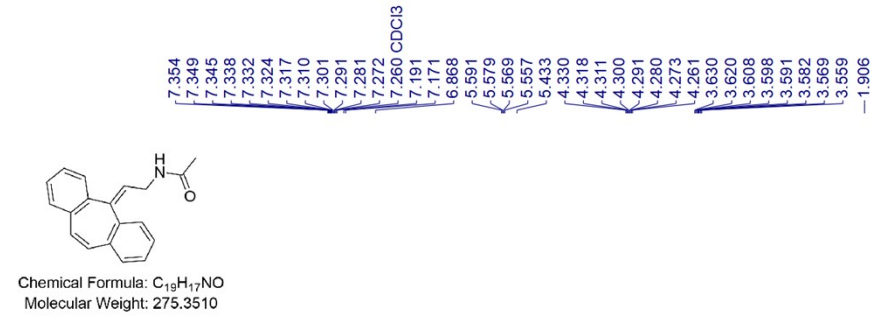


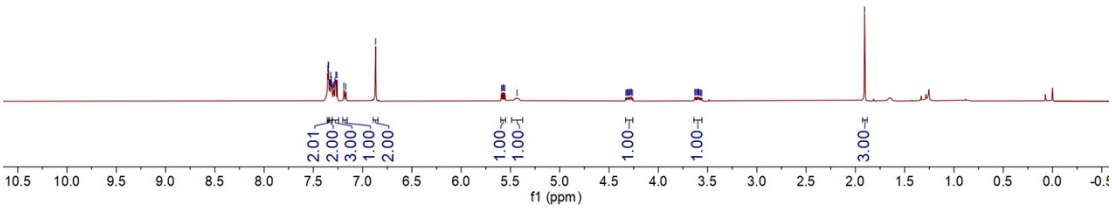

**$^{1}$H NMR spectrum of 3r, 400 MHz, $CDCl_3$**



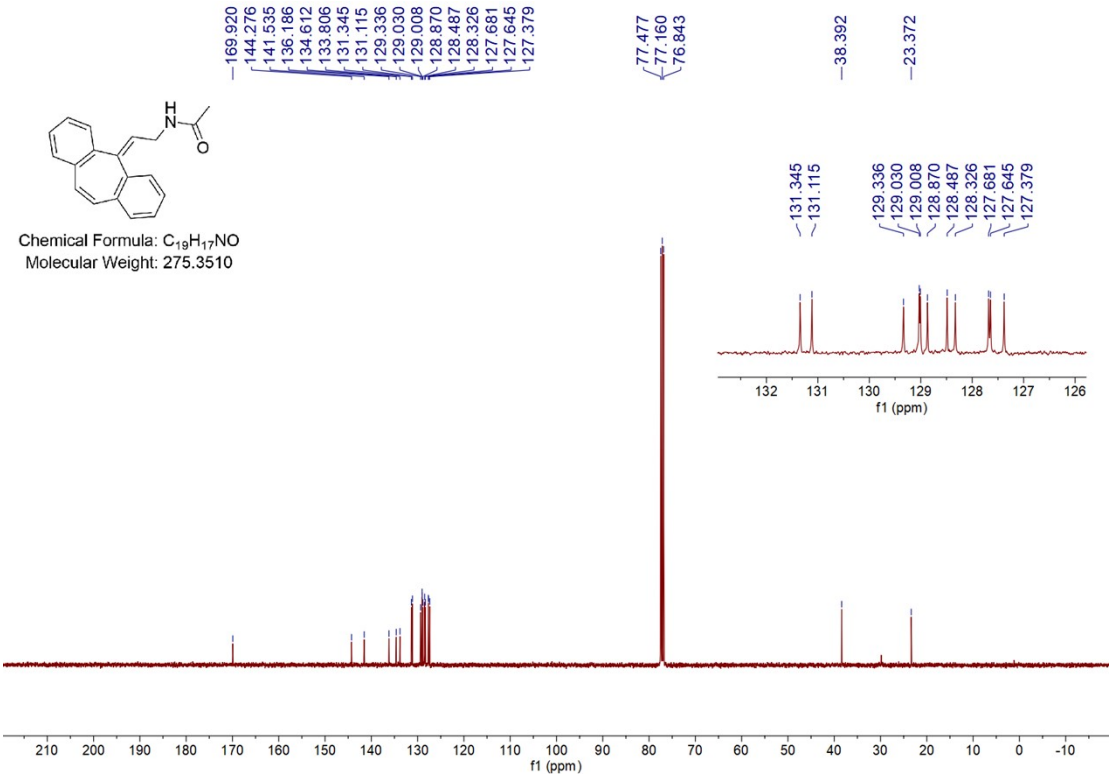

**$^{13}$C NMR spectrum of 3r, 101 MHz, $CDCl_3$**

***N-(2-(5H-dibenzo[a,d][7]annulen-5-ylidene)ethyl)acetamide (3s)***



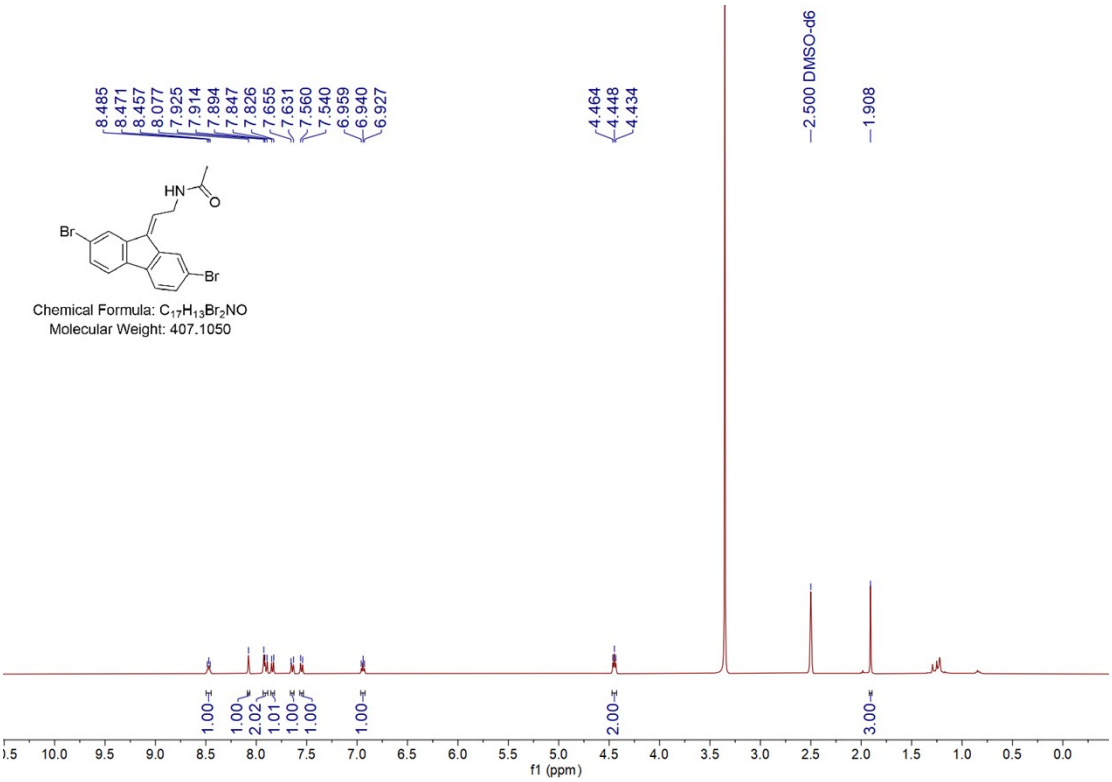




**$^{1}$H NMR spectrum of 3s, 400 MHz, $CDCl_3$**

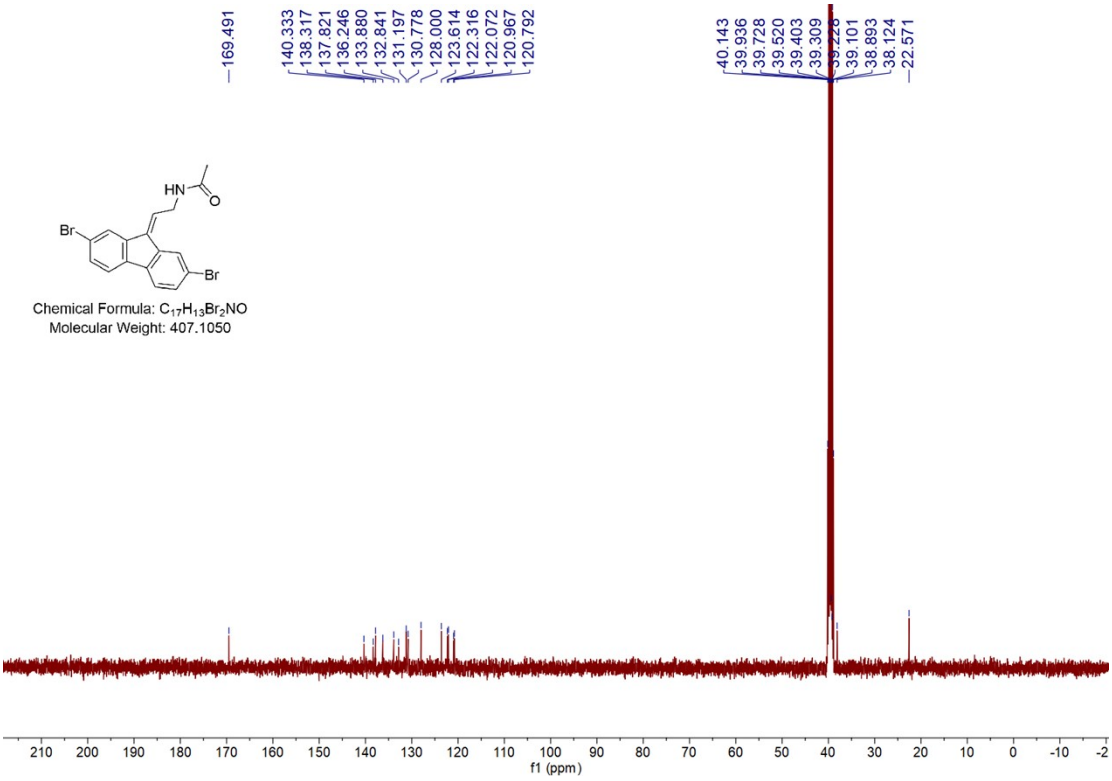



**$^{13}$C NMR spectrum of 3s, 101 MHz, $CDCl_3$**

***N-(2-(2,7-dibromo-9H-fluoren-9-ylidene)ethyl)acetamide (3t)***

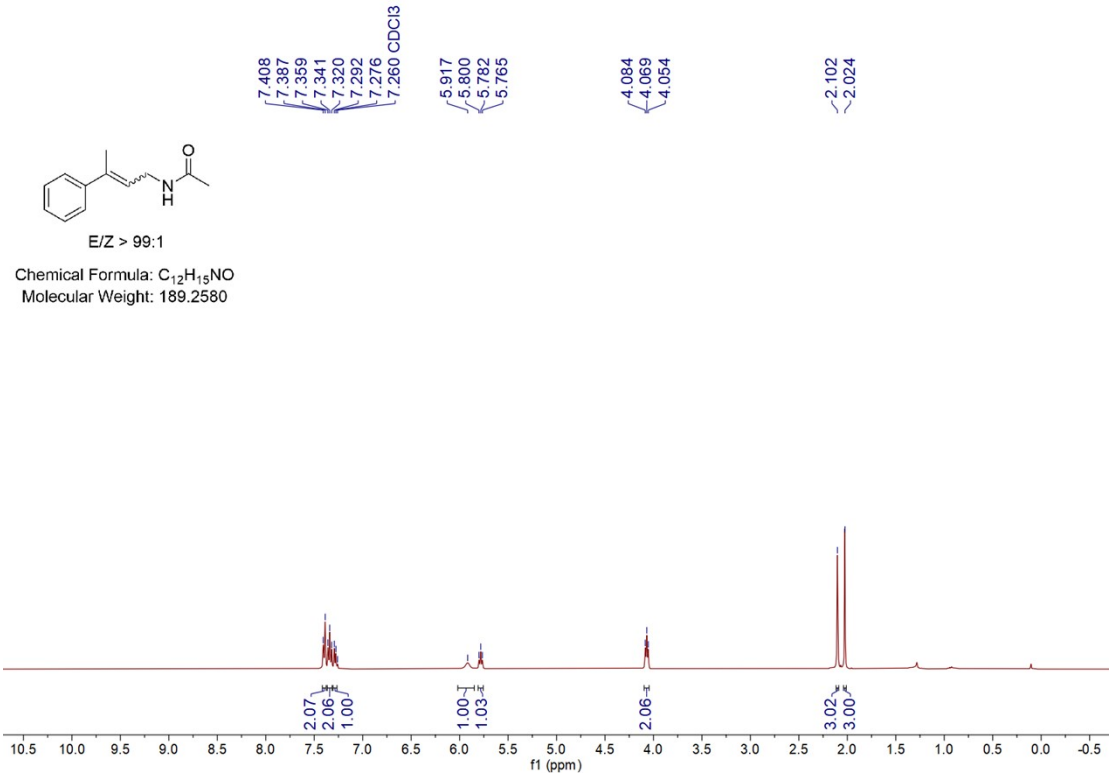



**$^{1}$H NMR spectrum of 3t, 400 MHz, DMSO-$d_6$**

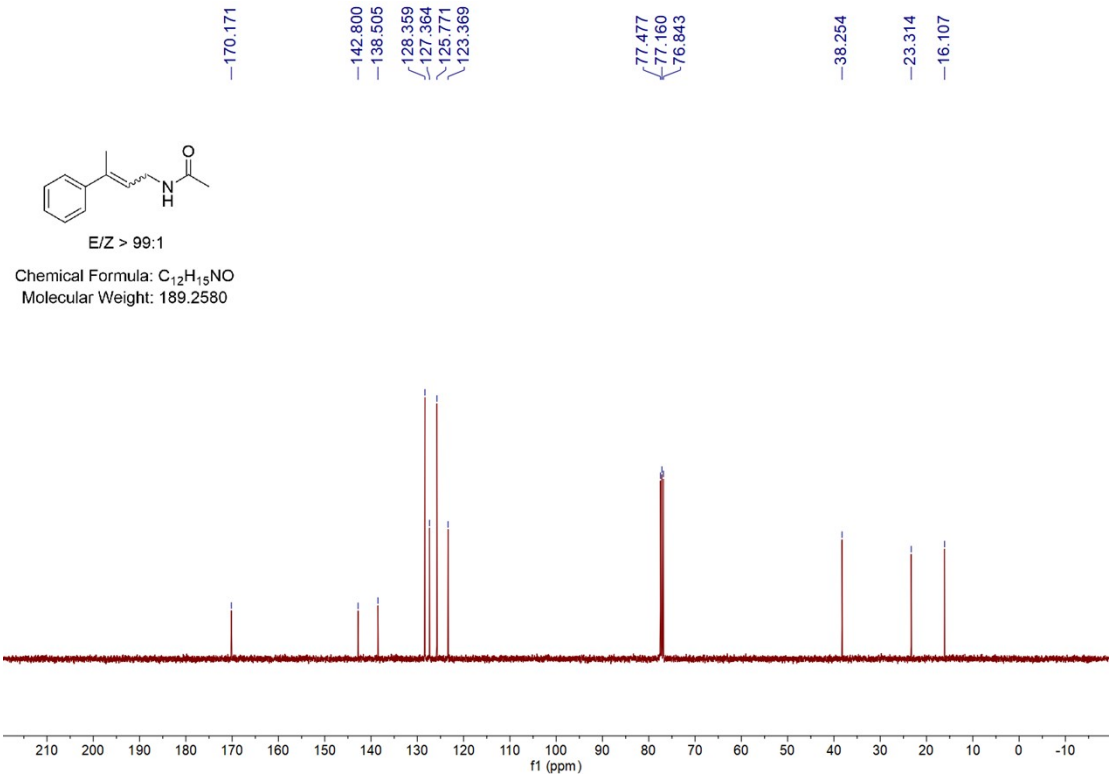



**$^{13}$C NMR spectrum of 3t, 101 MHz, DMSO-$d_6$**

## *N-(3-phenylbut-2-en-1-yl)acetamide (3u)*

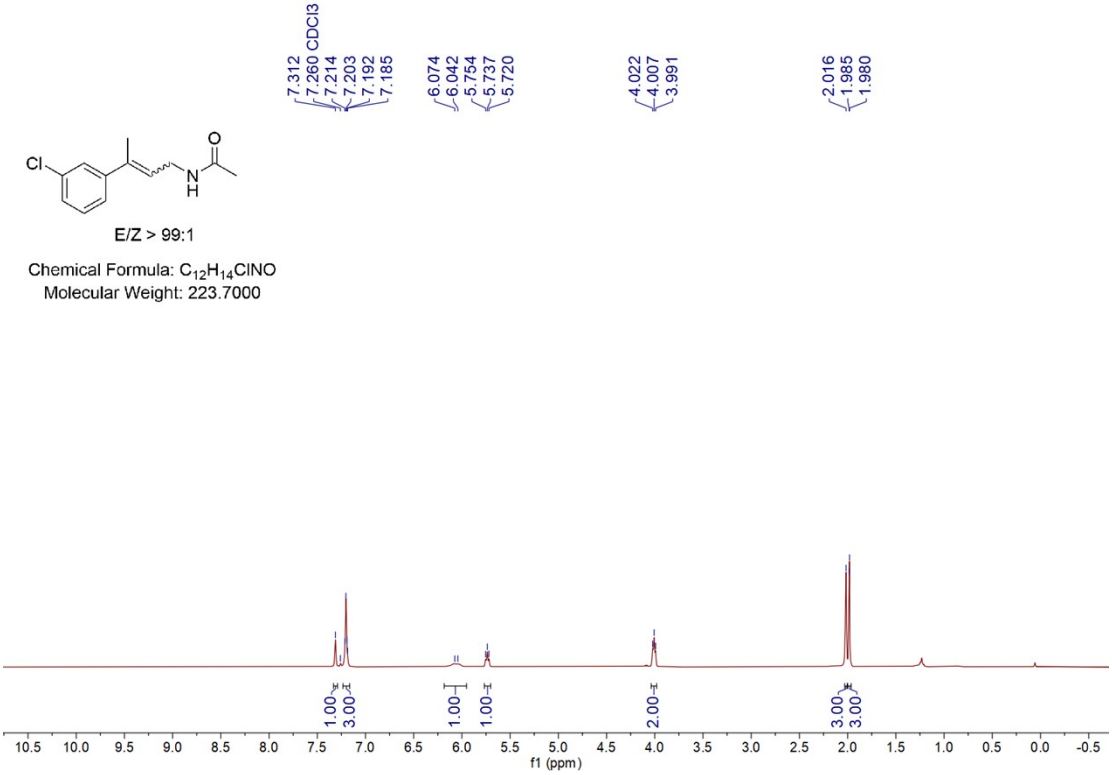



**$^{1}$H NMR spectrum of 3u, 400 MHz, $CDCl_3$**

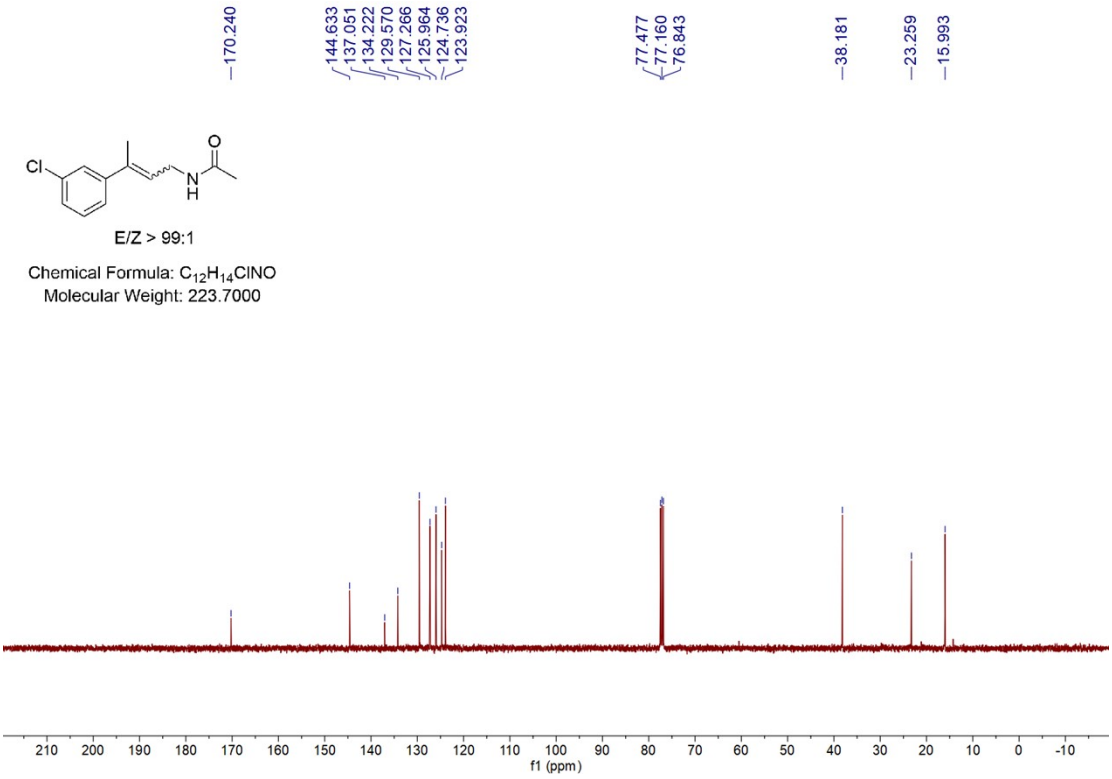



**$^{13}$C NMR spectrum of 3u, 101 MHz, $CDCl_3$**

## *N-(3-(3-chlorophenyl)but-2-en-1-yl)acetamide (3v)*

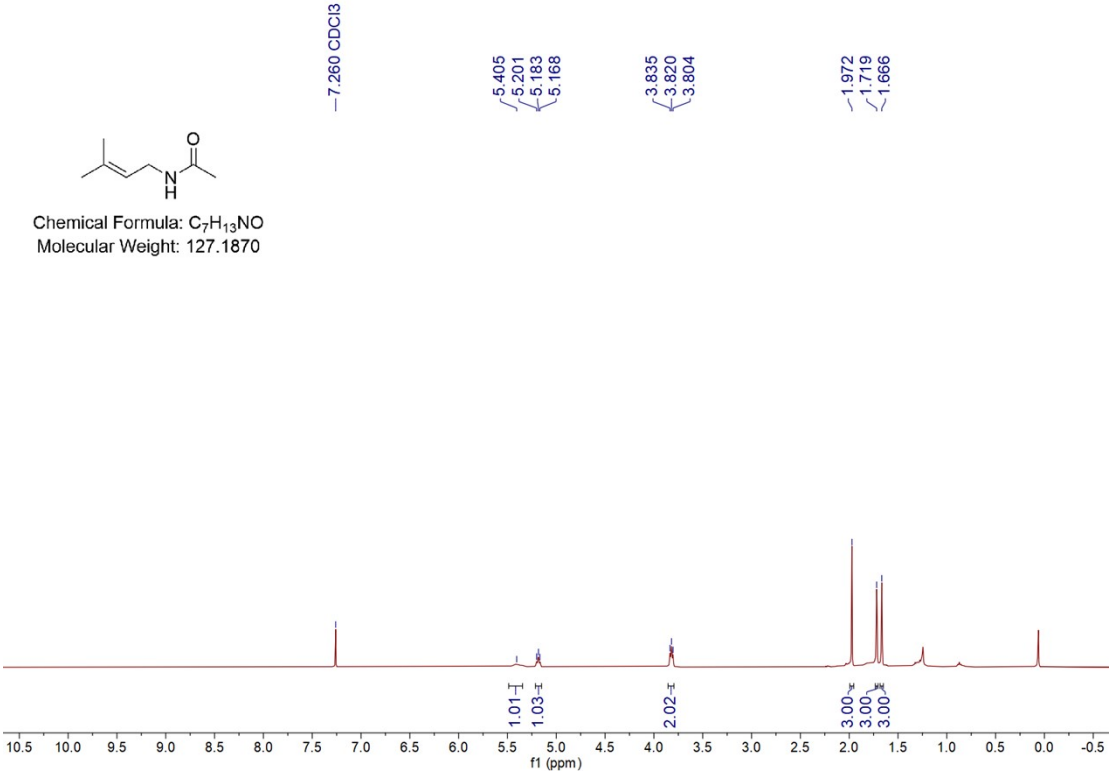



**$^{1}$H NMR spectrum of 3v, 400 MHz, $CDCl_3$**

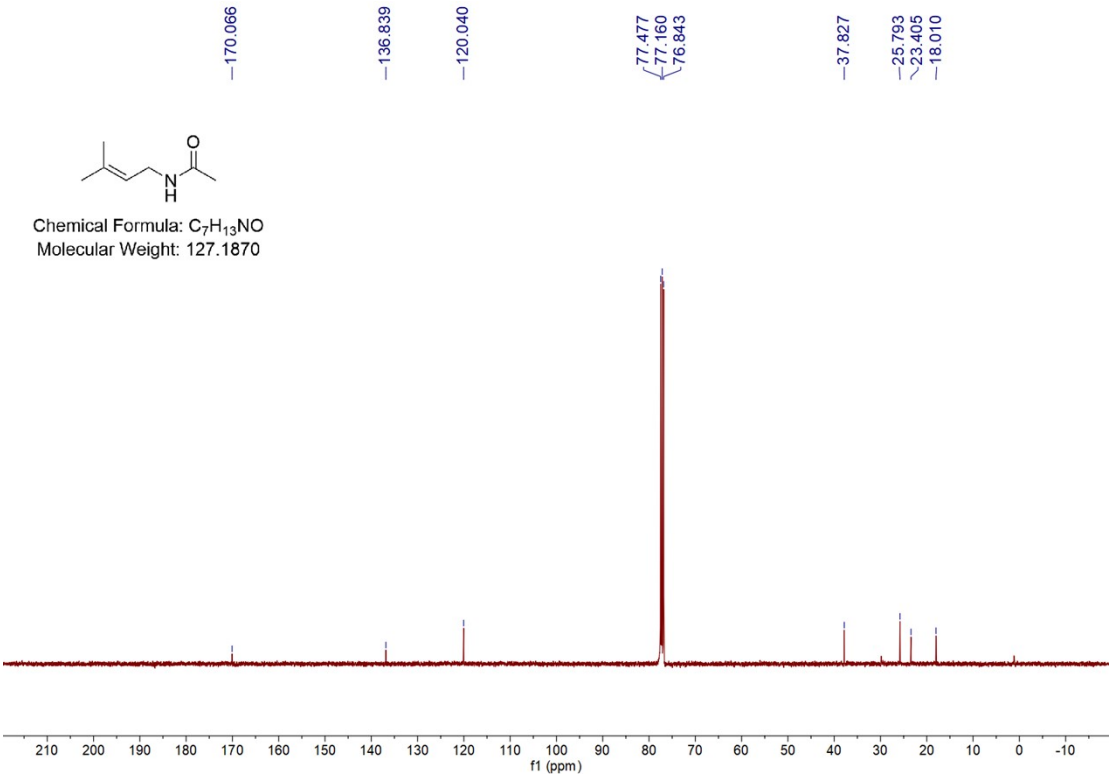



**$^{13}$C NMR spectrum of 3v, 101 MHz, $CDCl_3$**

## *N-(3-methylbut-2-en-1-yl)acetamide (3w)*

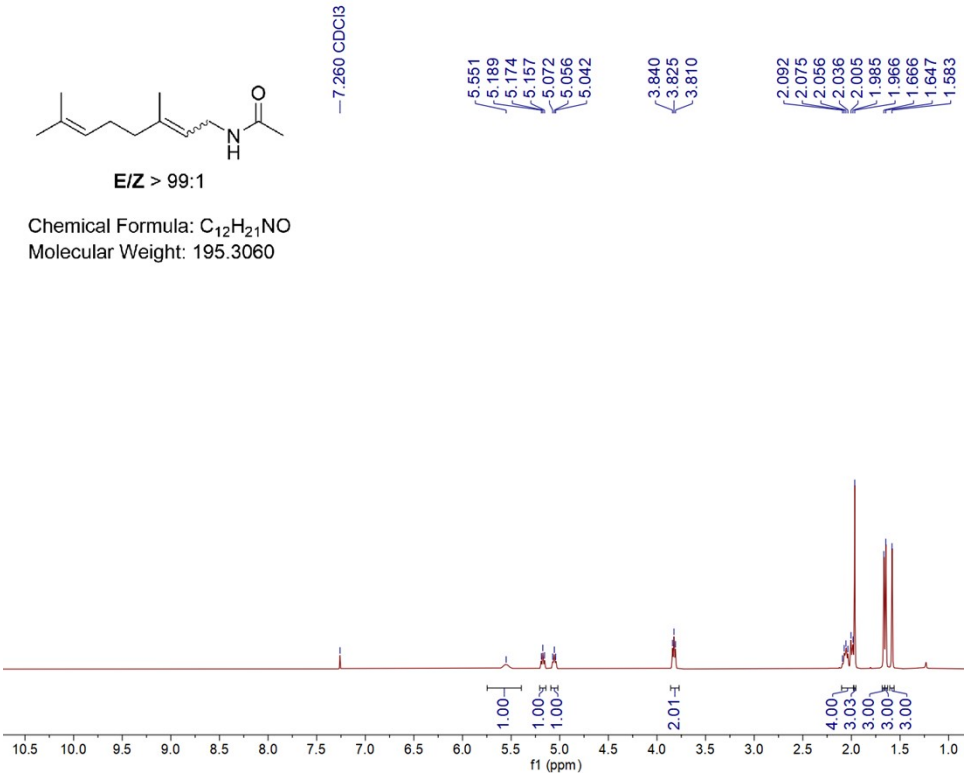



**$^{1}$H NMR spectrum of 3w, 400 MHz, $CDCl_3$**

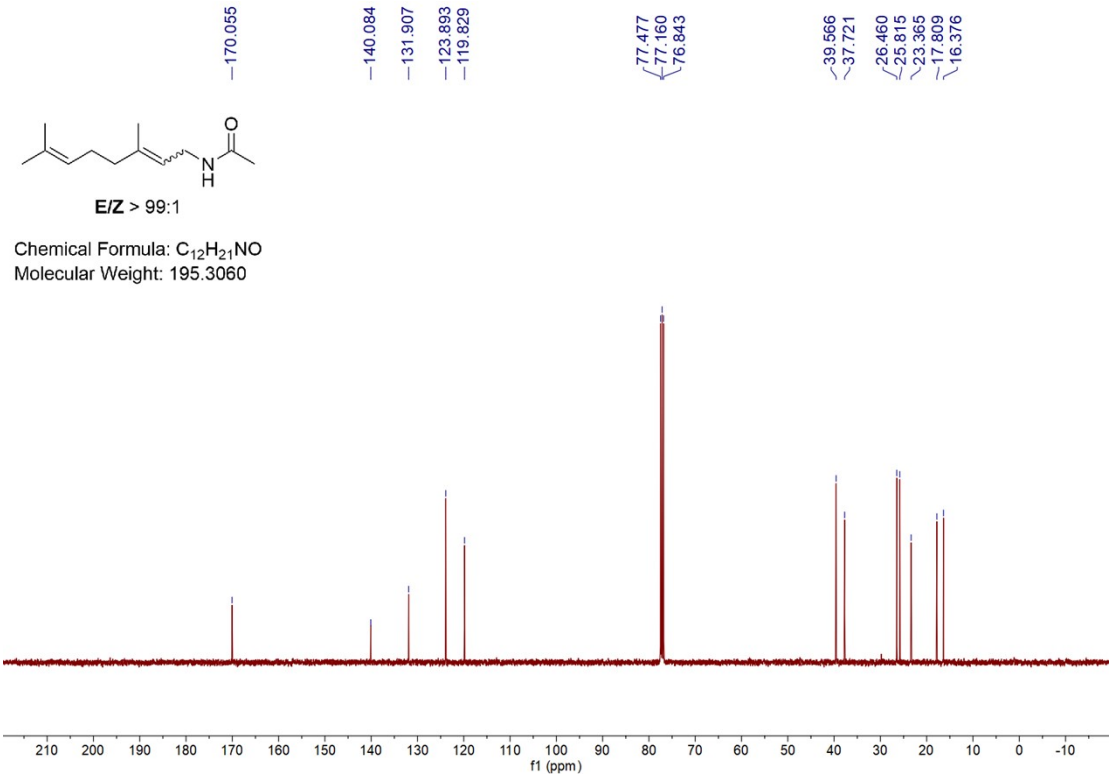



**$^{13}$C NMR spectrum of 3w, 101 MHz, $CDCl_3$**

## *N-(3,7-dimethylocta-2,6-dien-1-yl)acetamide (3x)*

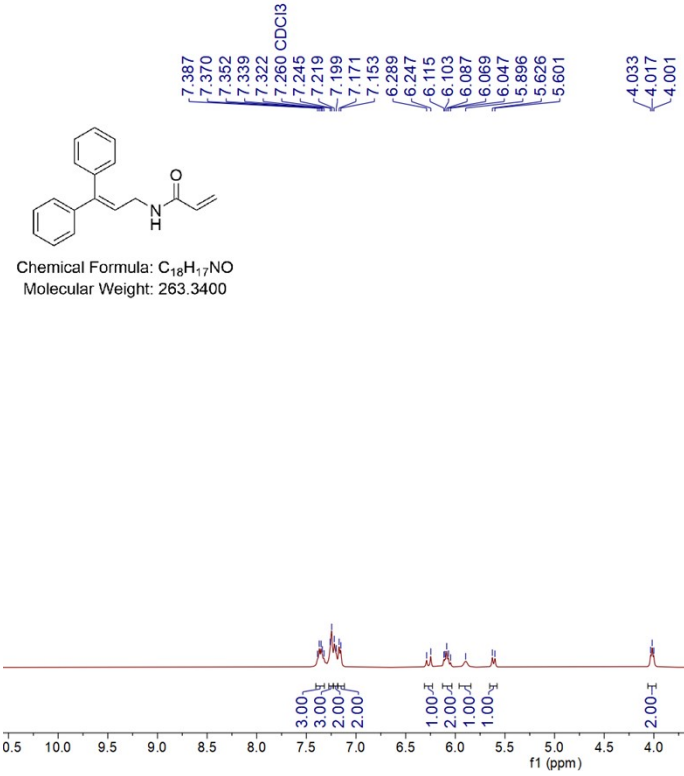



**$^{1}$H NMR spectrum of 3x, 400 MHz, $CDCl_3$**

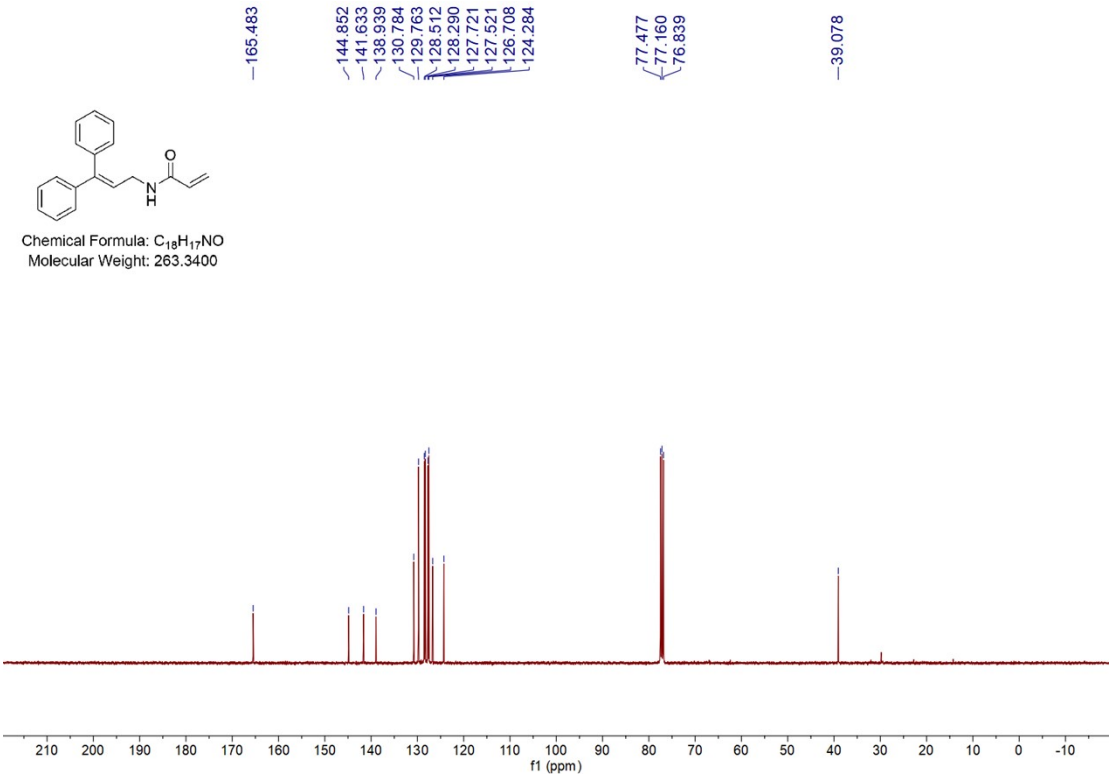



**$^{13}$C NMR spectrum of 3x, 101 MHz, $CDCl_3$**

## *N-(3,3-diphenylallyl)acrylamide (4a)*

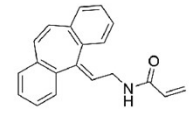



**$^{1}$H NMR spectrum of 4a, 400 MHz, $CDCl_3$**

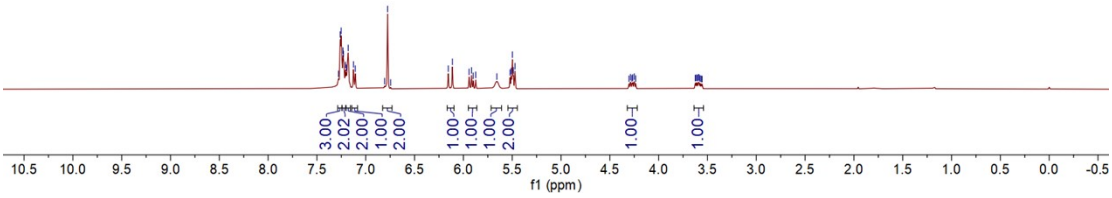



**$^{13}$C NMR spectrum of 4a, 101 MHz, $CDCl_3$**

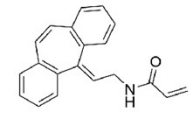
## *N-(2-(5H-dibenzo[a,d][7]annulen-5-ylidene)ethyl)acetamide (4b)*

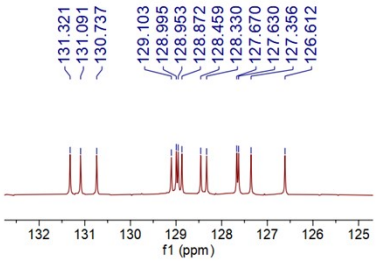
Chemical Formula: $C_{20}H_{17}NO$
Molecular Weight: 287.3620

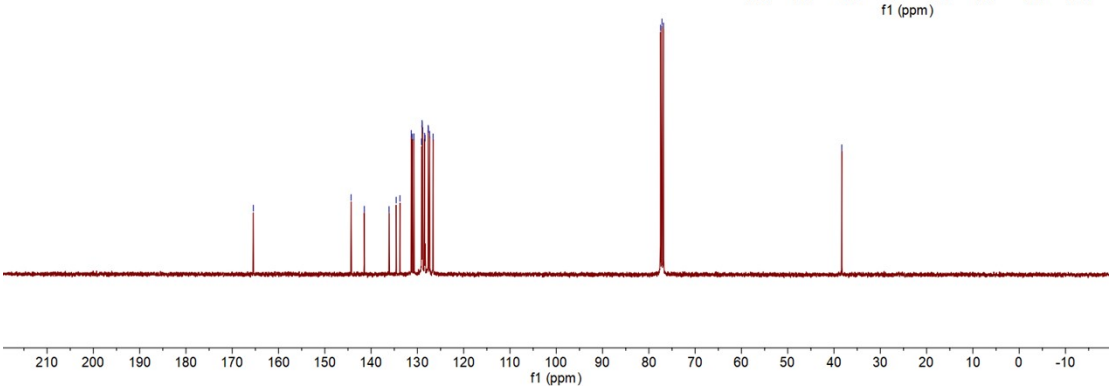



**$^{1}$H NMR spectrum of 4b, 400 MHz, $CDCl_3$**

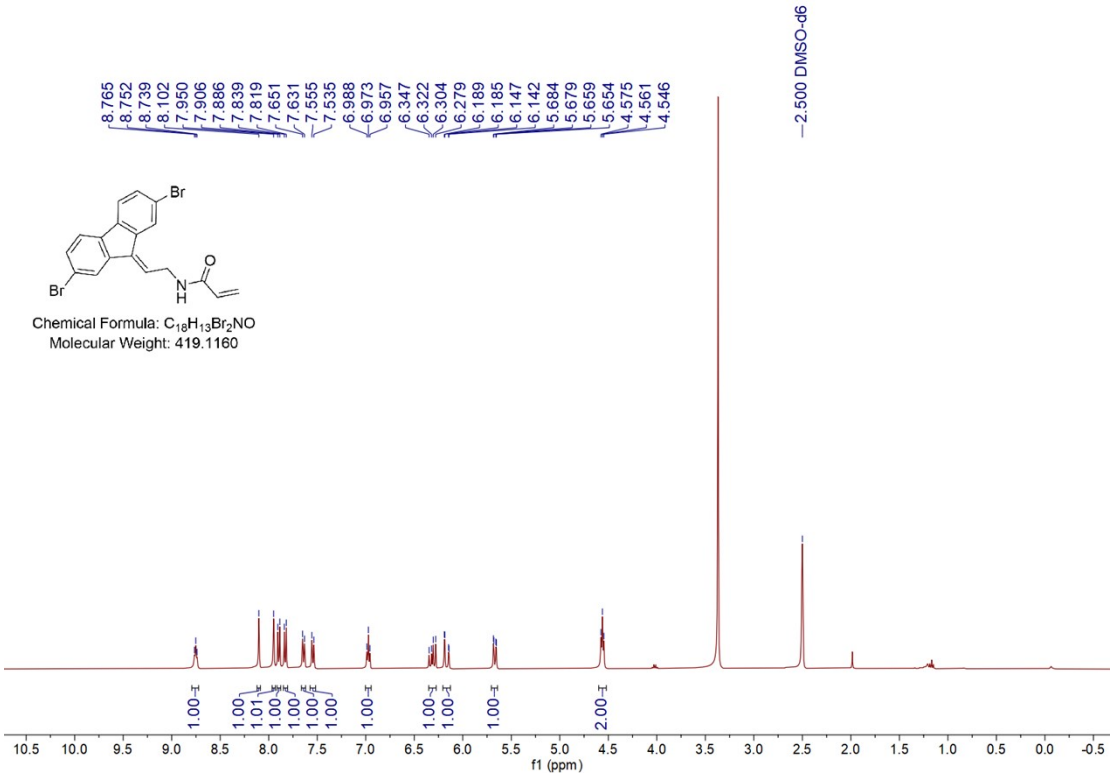
Chemical Formula: $C_{20}H_{17}NO$
Molecular Weight: 287.3620



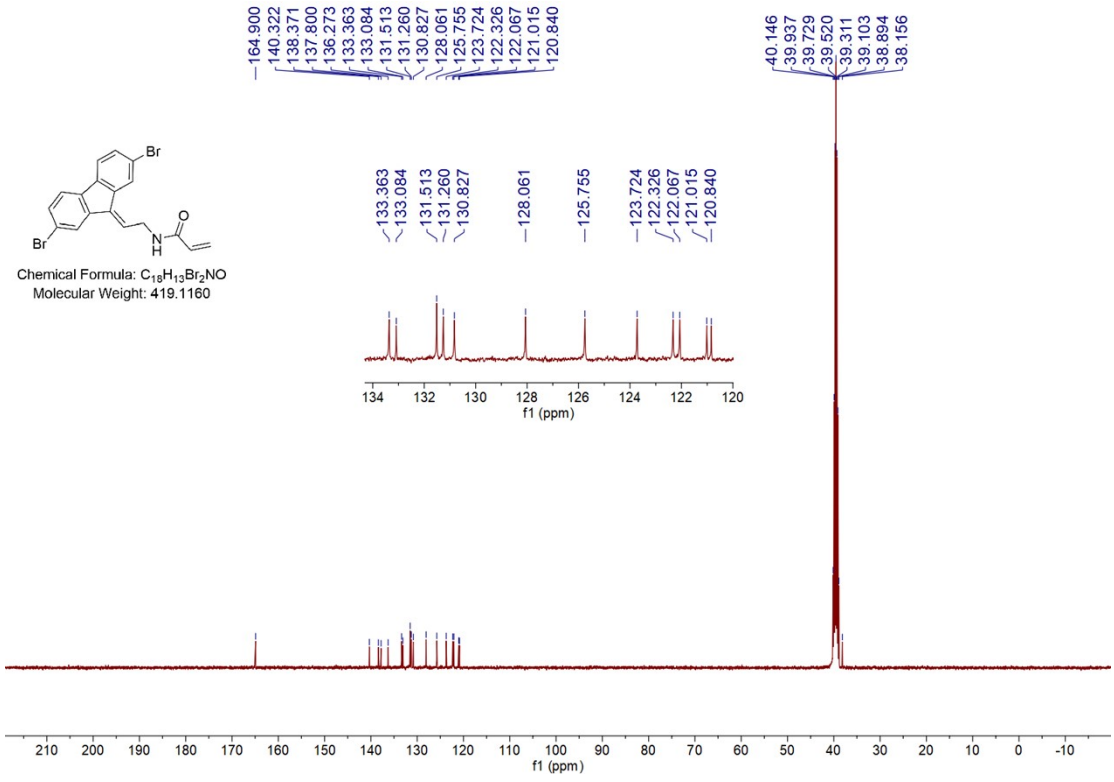




**$^{13}$C NMR spectrum of 4b, 101 MHz, $CDCl_3$**

***N-(2-(2,7-dibromo-9H-fluoren-9-ylidene)ethyl)acrylamide (4c)***

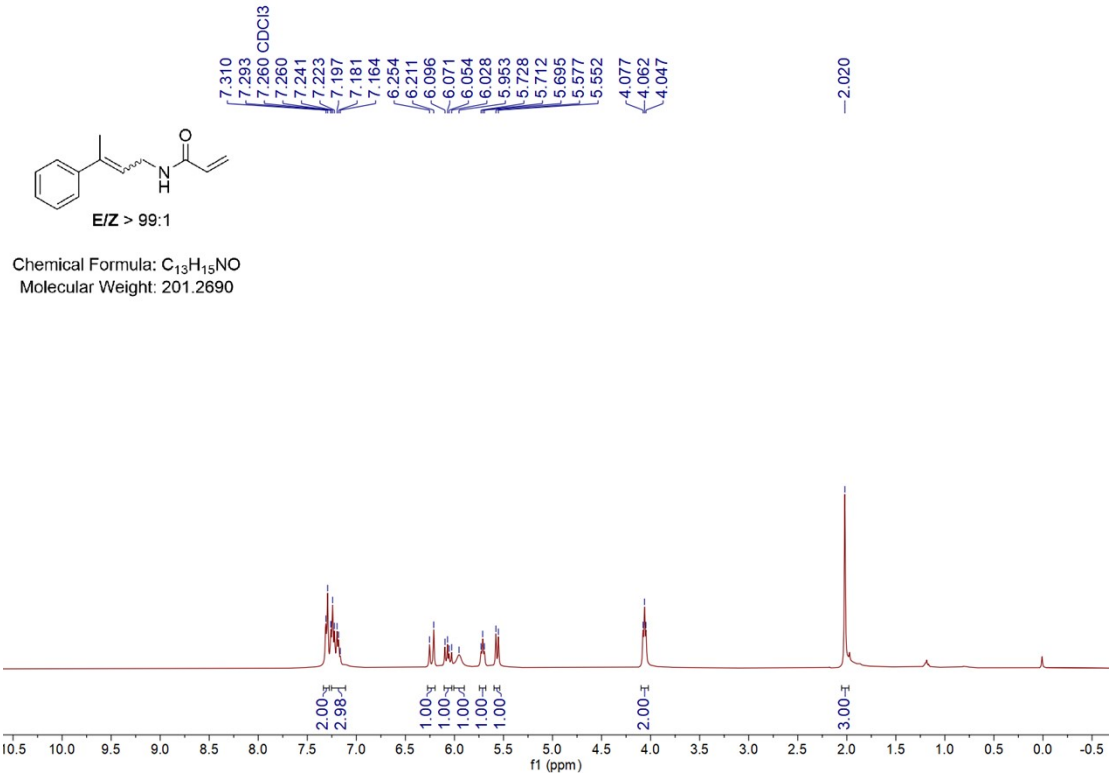



**$^{1}$H NMR spectrum of 4c, 400 MHz, DMSO-$d_6$**

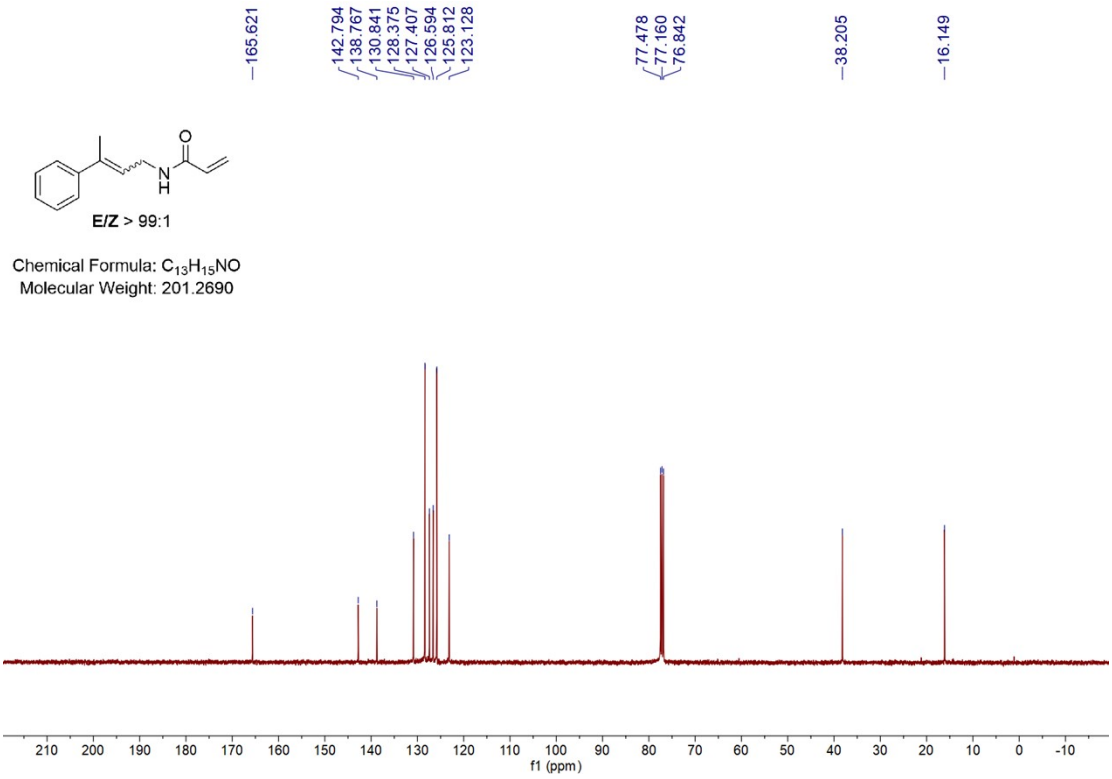



**$^{13}$C NMR spectrum of 4c, 101 MHz, DMSO-$d_6$**

## *N-(3-phenylbut-2-en-1-yl)acrylamide (4d)*

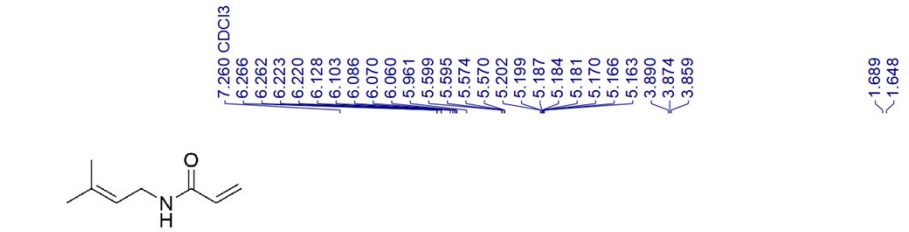



**$^{1}$H NMR spectrum of 4d, 400 MHz, $CDCl_3$**



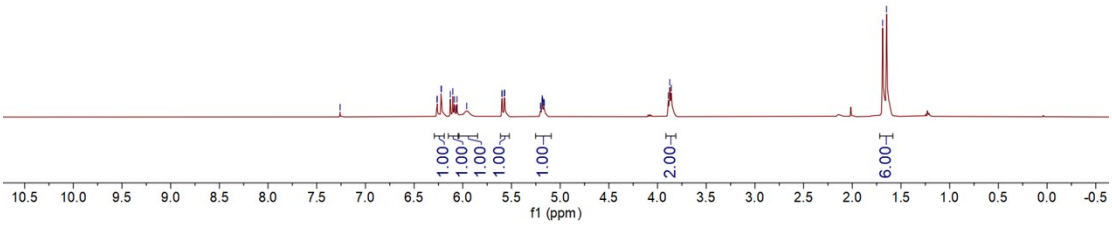

**$^{13}$C NMR spectrum of 4d, 101 MHz, $CDCl_3$**

## *N-(3-methylbut-2-en-1-yl)acrylamide (4e)*

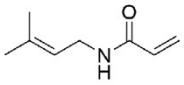




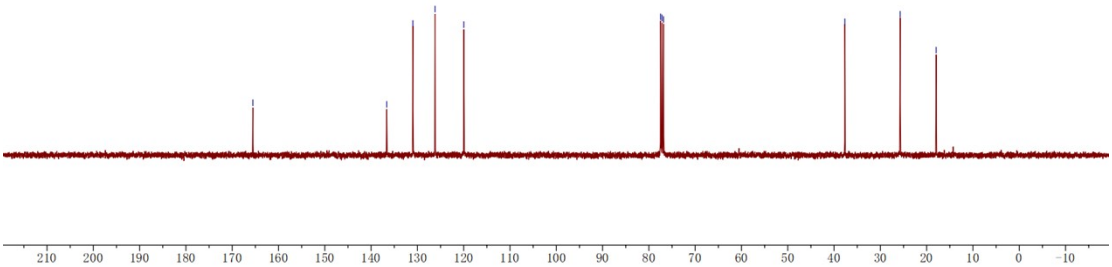

Chemical Formula: $C_8H_{13}NO$
Molecular Weight: 139.1980




**$^{1}$H NMR spectrum of 4e, 400 MHz, $CDCl_3$**

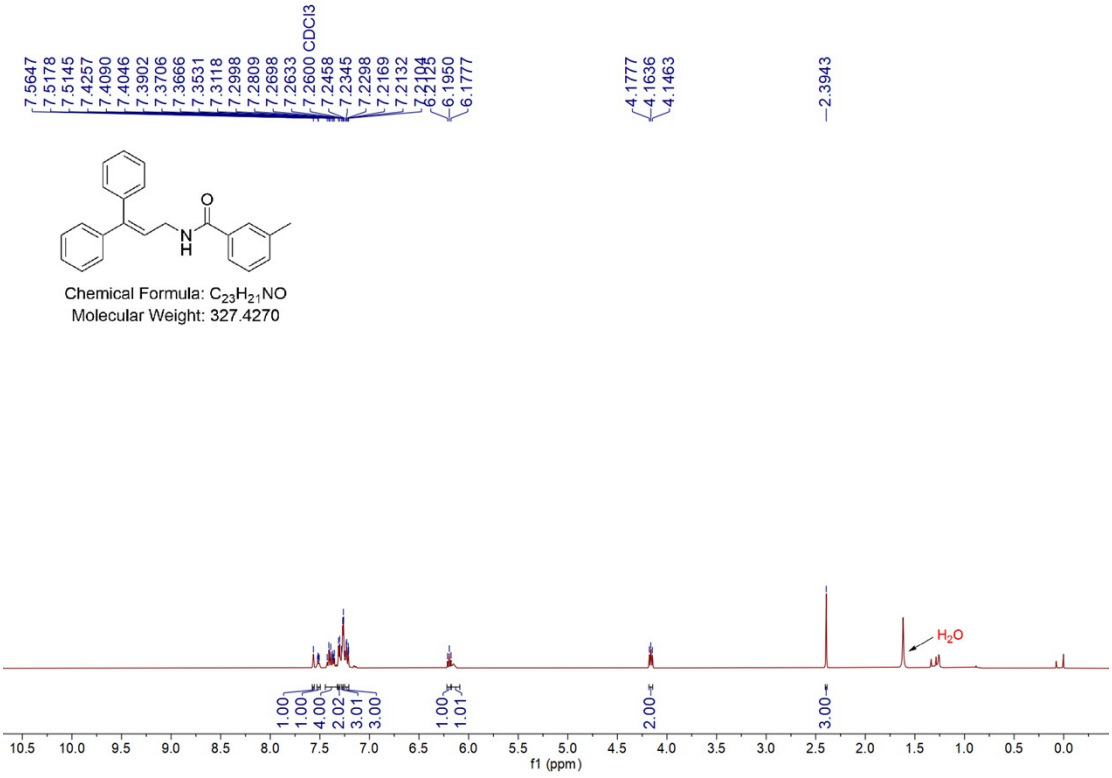



Chemical Formula: $C_8H_{13}NO$
Molecular Weight: 139.1980

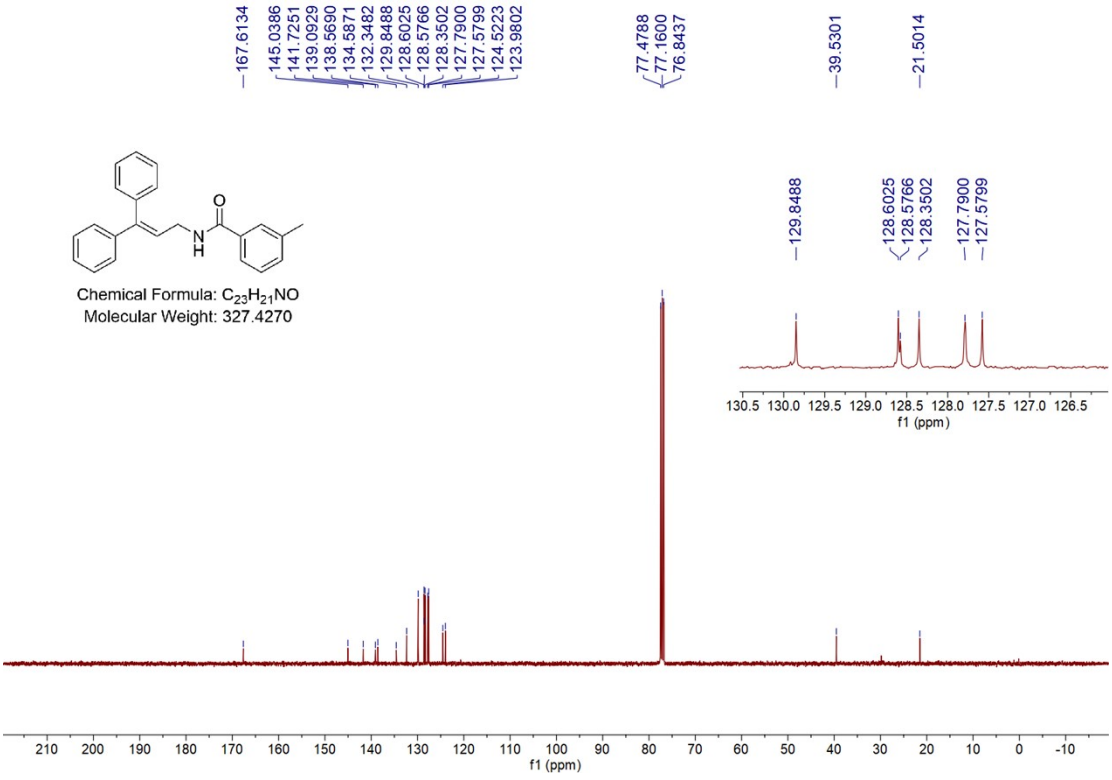



**$^{13}$C NMR spectrum of 4e, 101 MHz, $CDCl_3$**

## *N-(3,3-diphenylallyl)-3-methylbenzamide (4f)*

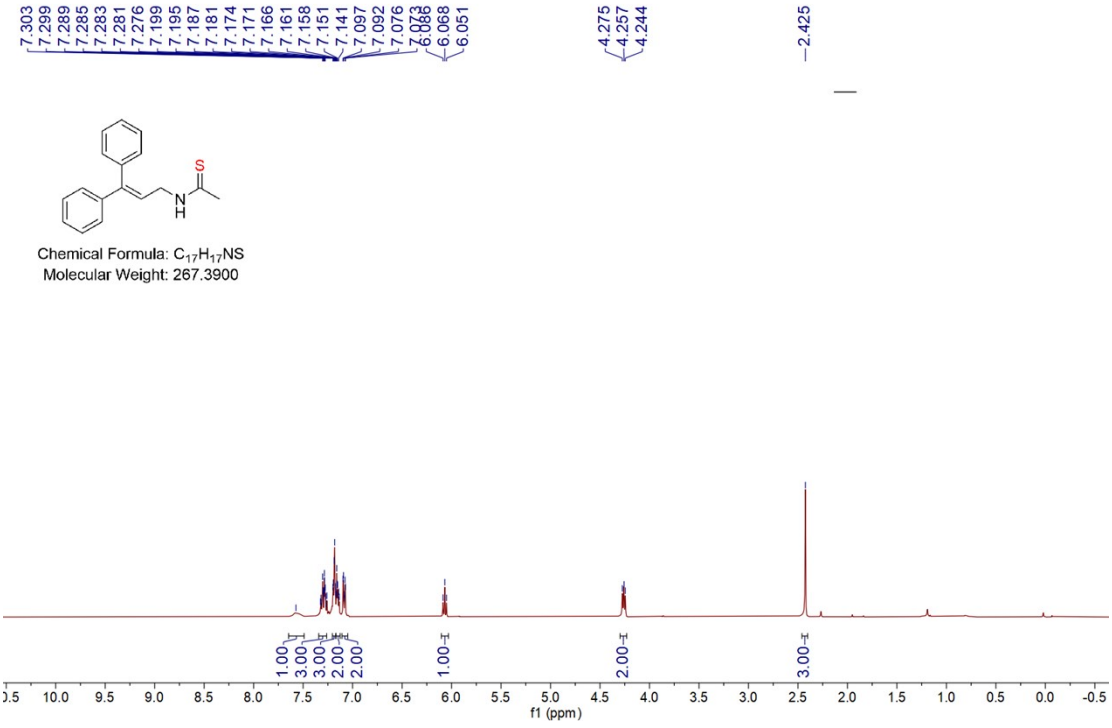



**$^{1}$H NMR spectrum of 5a, 400 MHz, $CDCl_3$**

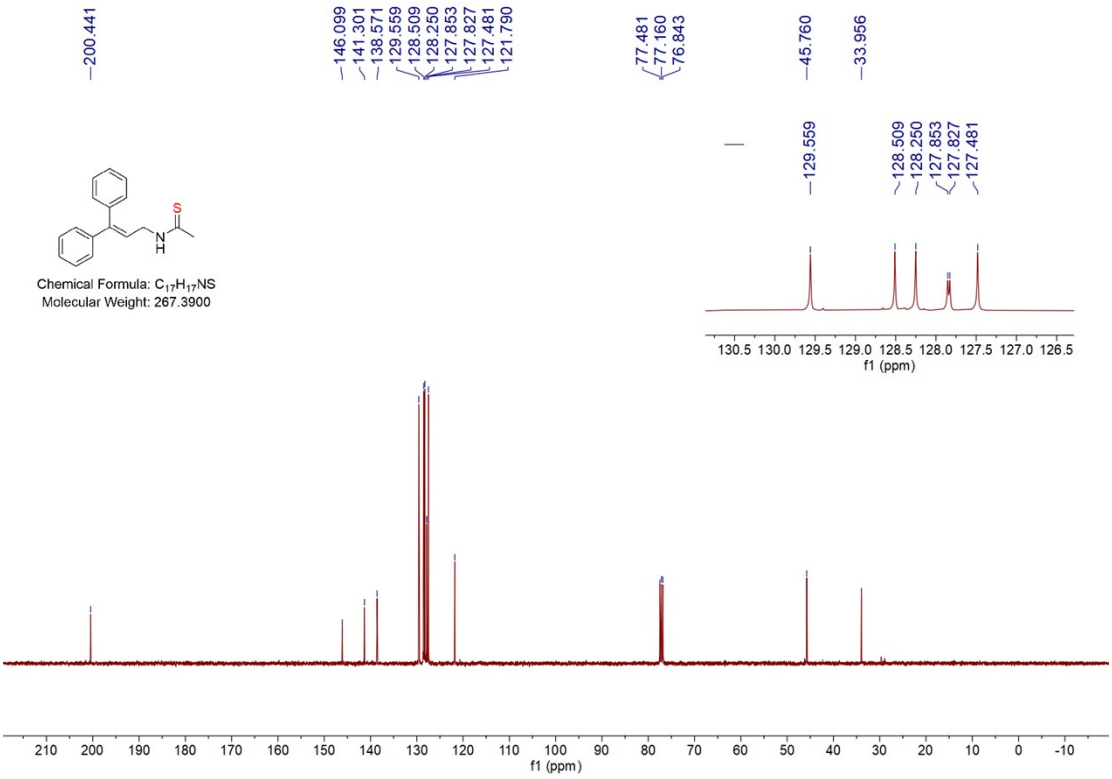



**$^{13}$C NMR spectrum of 5a, 101 MHz, $CDCl_3$**

## *N-(3,3-diphenylallyl)ethanethioamide (5a)*

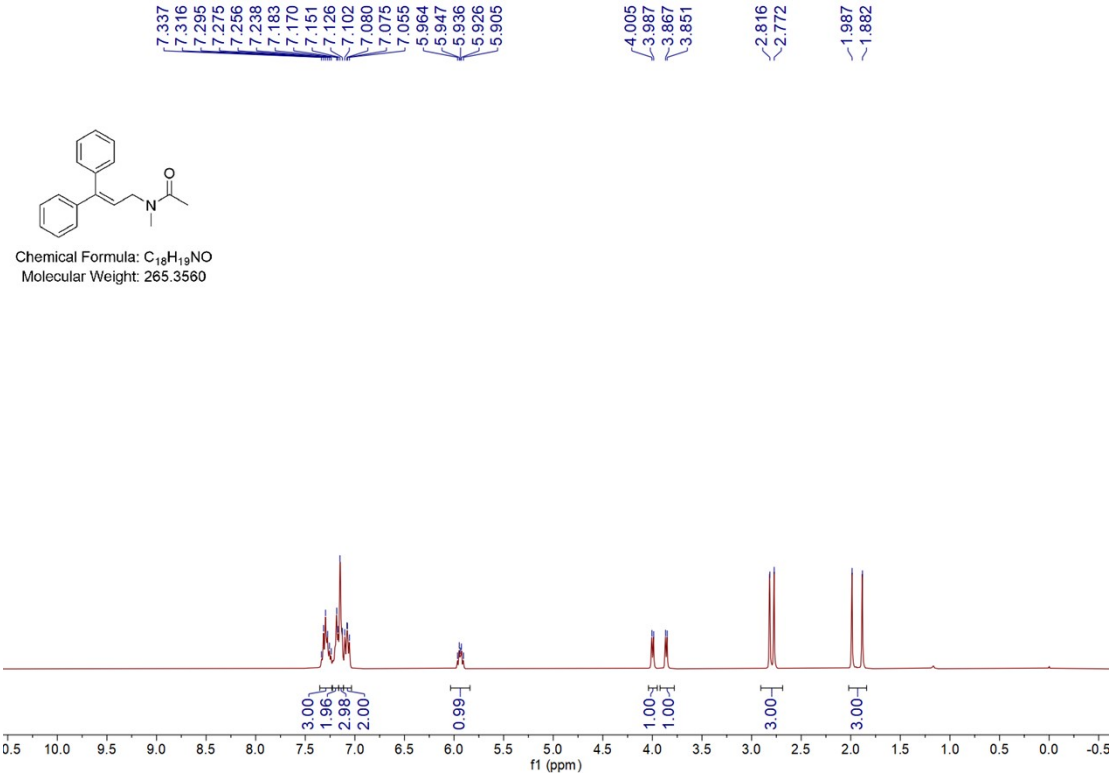



**$^{1}$H NMR spectrum of 5a, 400 MHz, $CDCl_3$**

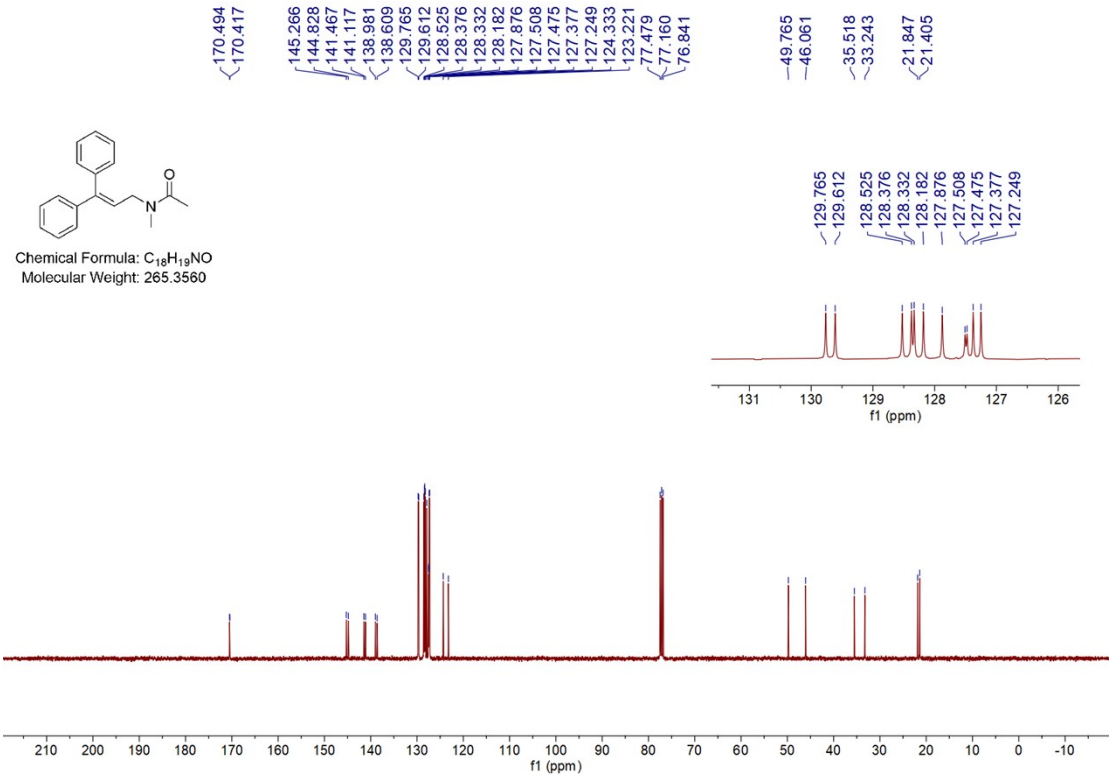



**$^{13}$C NMR spectrum of 5a, 101 MHz, $CDCl_3$**

## *N-(3,3-diphenylallyl)-N-methylacetamide (5b)*

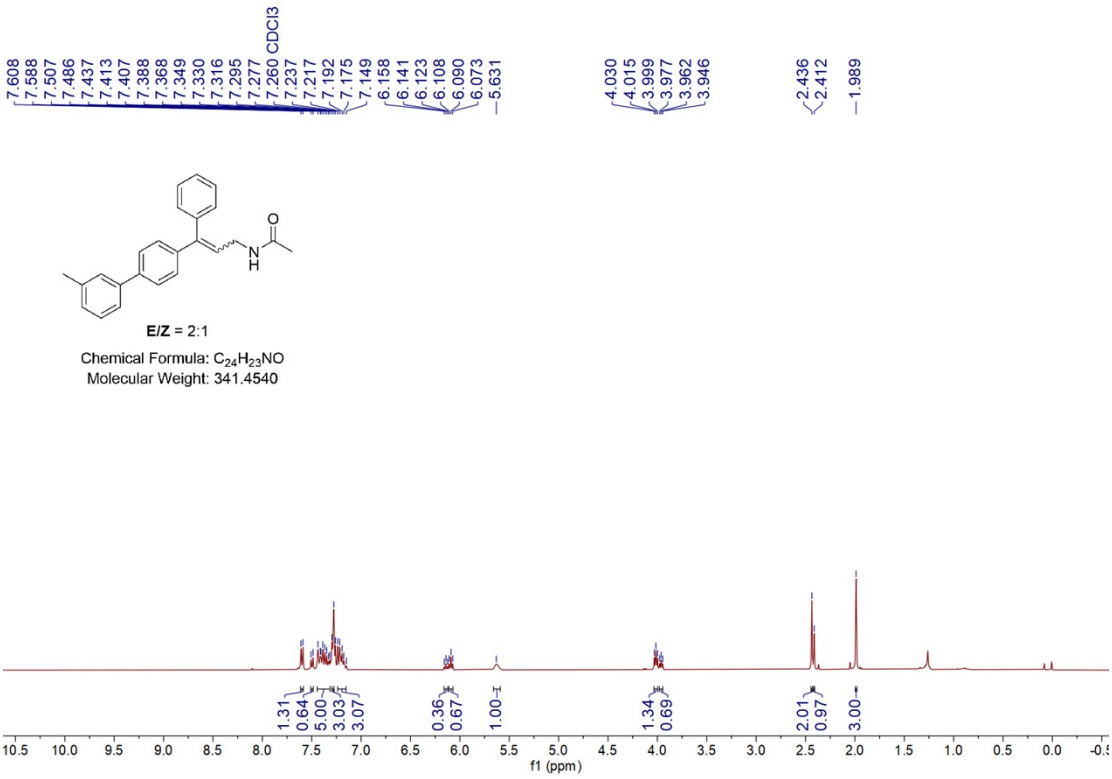



**$^{1}$H NMR spectrum of 5b, 400 MHz, $CDCl_3$**

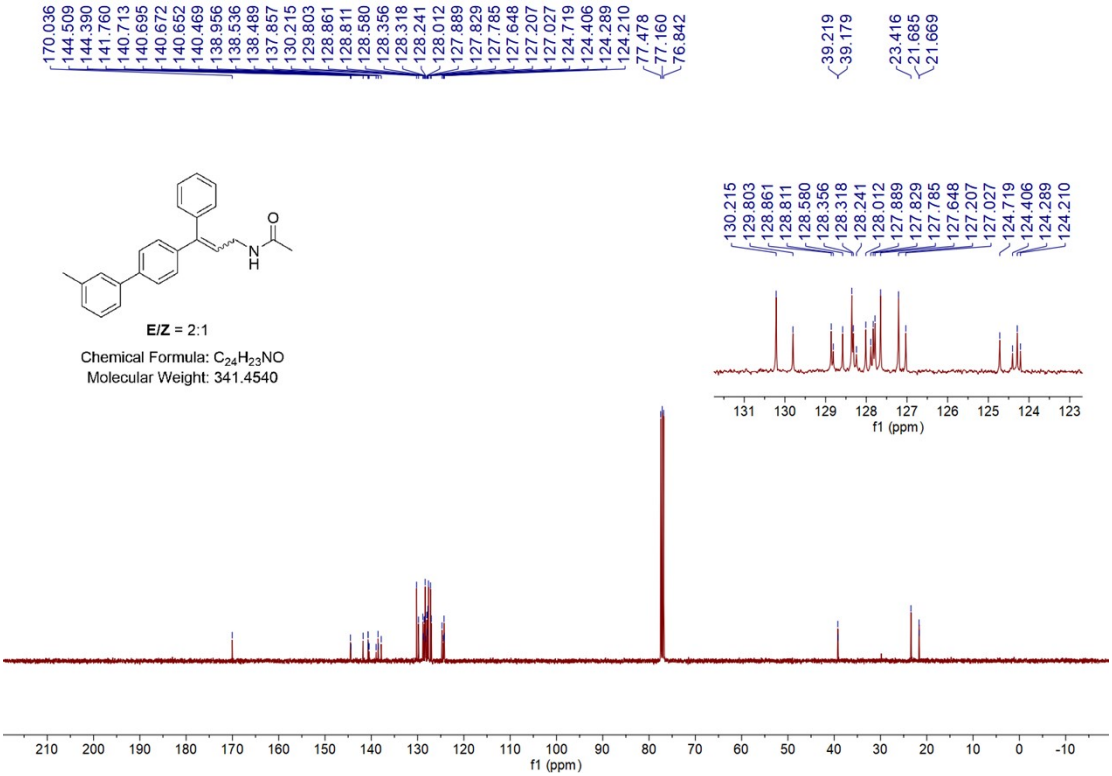



**$^{13}$C NMR spectrum of 5b, 101 MHz, $CDCl_3$**

## *N-(3-(3'-methyl-[1,1'-biphenyl]-4-yl)-3-phenylallyl)acetamide (5c)*

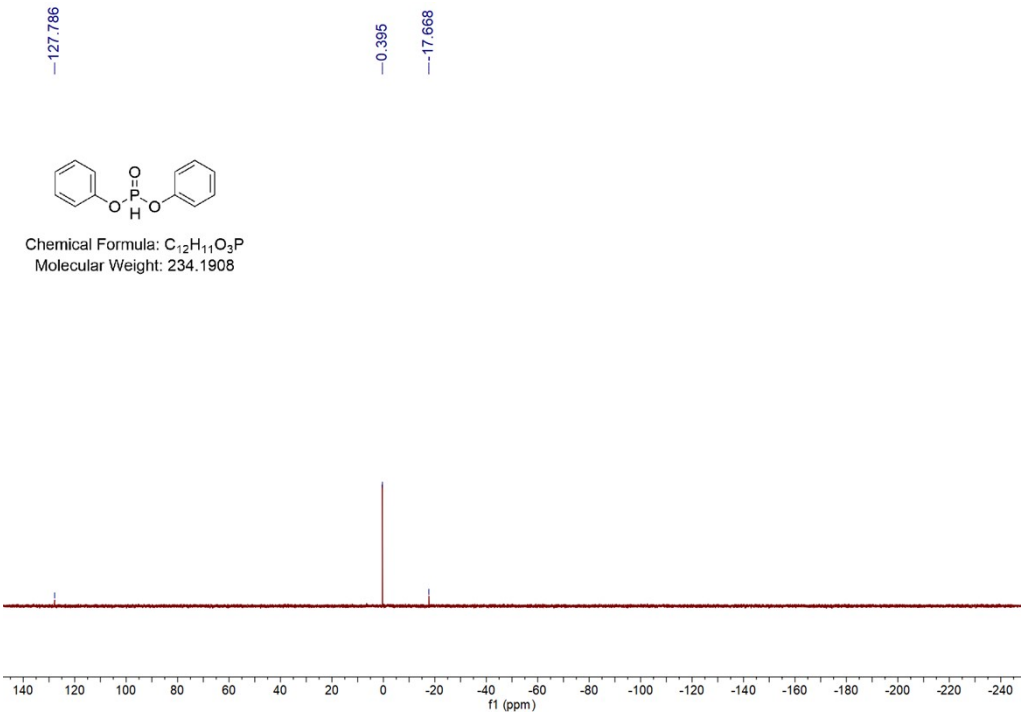



**$^{1}$H NMR spectrum of 5c, 400 MHz, $CDCl_3$**



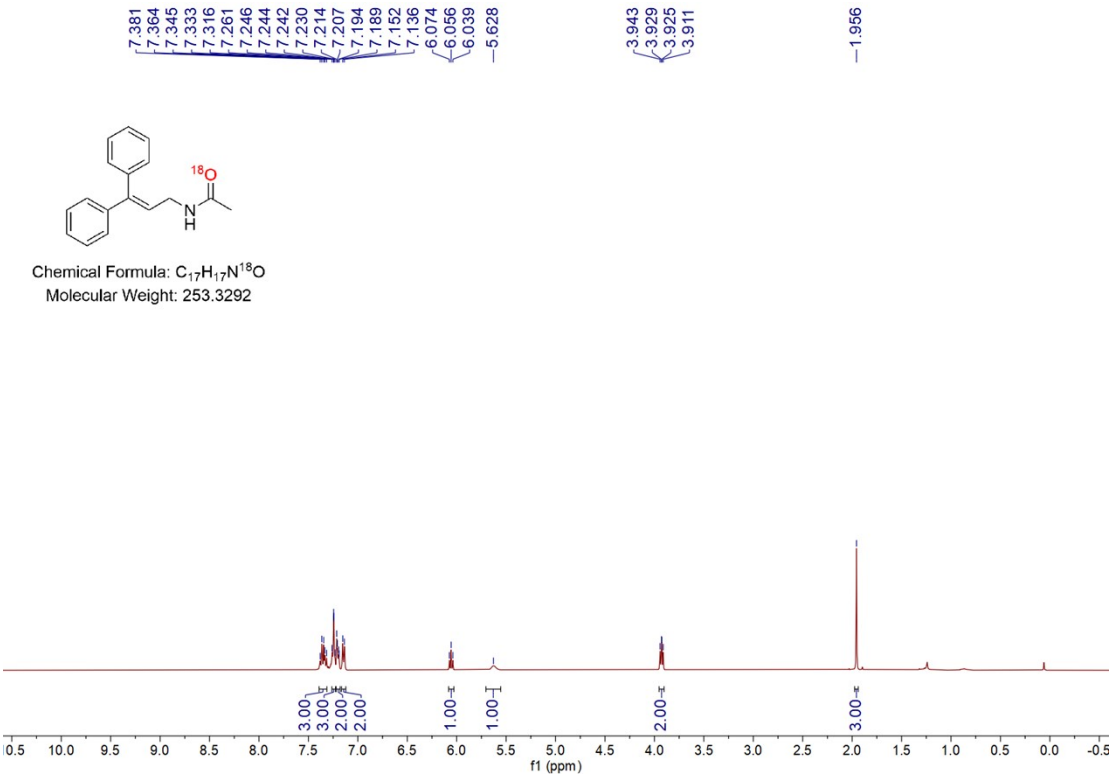

**$^{13}$C NMR spectrum of 5c, 101 MHz, $CDCl_3$**

*diphenyl phosphonate (6a)*

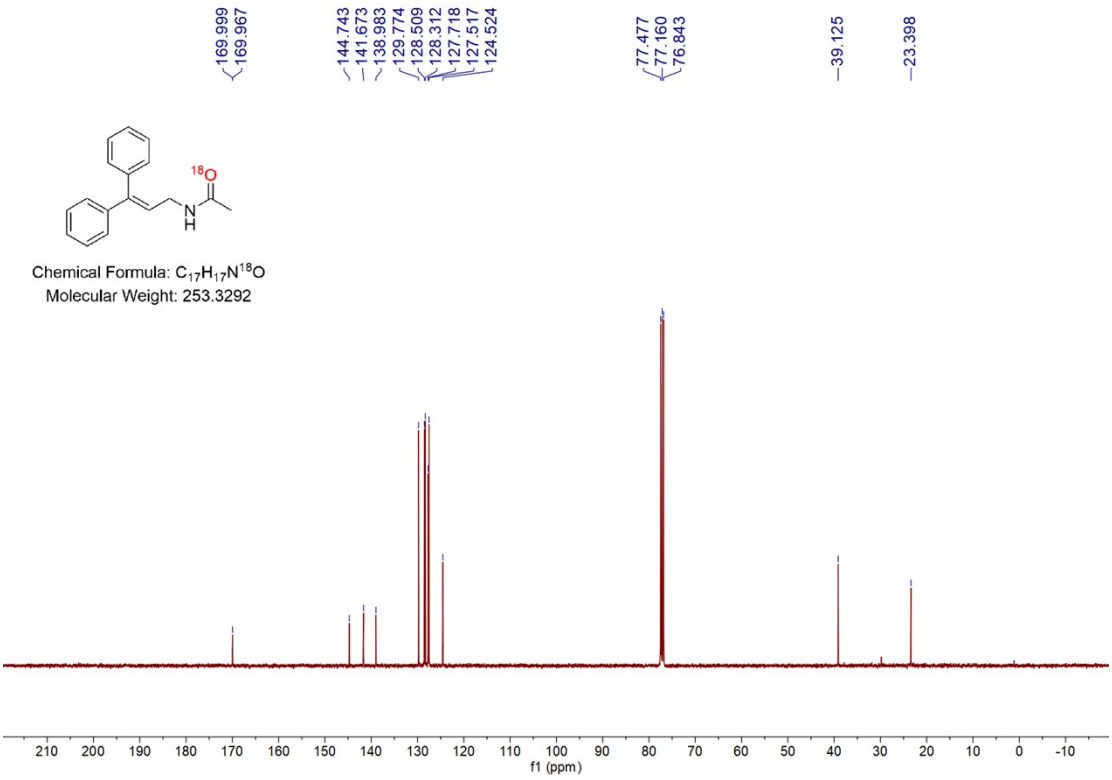



**$^{31}$P NMR spectrum of 6a, 162 MHz, $CDCl_3$ (reaction mixture)**

*N-(3,3-diphenylallyl)acetamide-$^{18}$O (3a')*

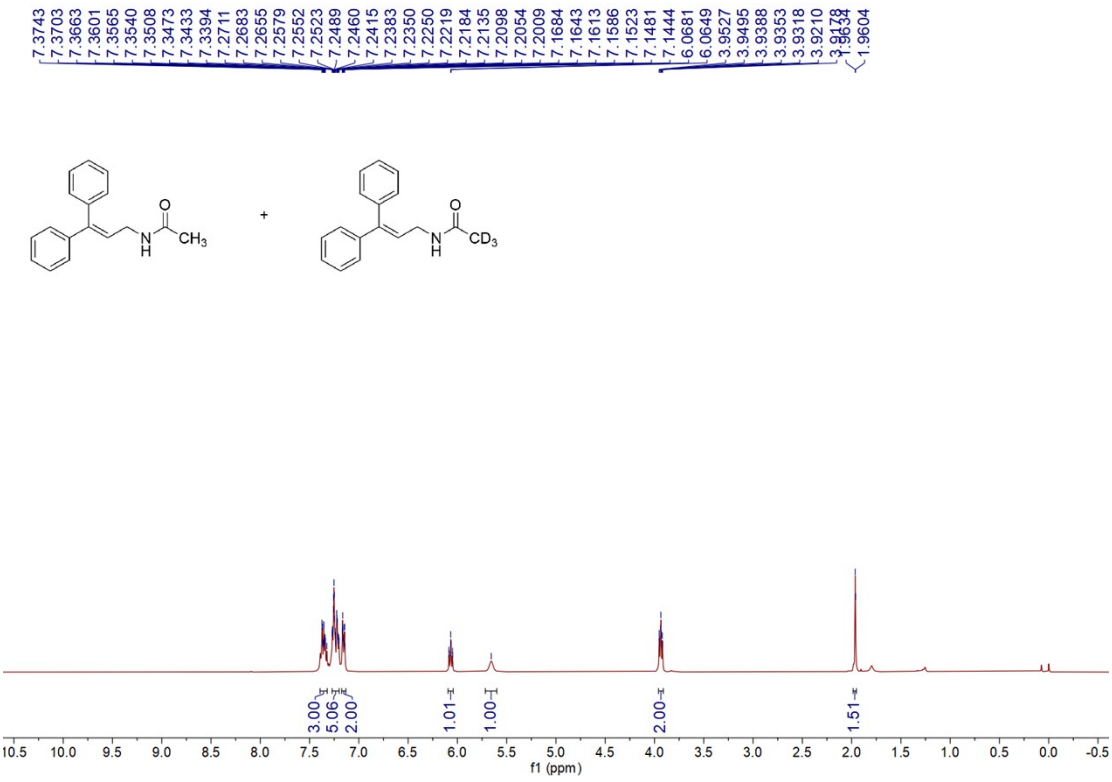



**$^{1}$H NMR spectrum of 3a', 400 MHz, $CDCl_3$**



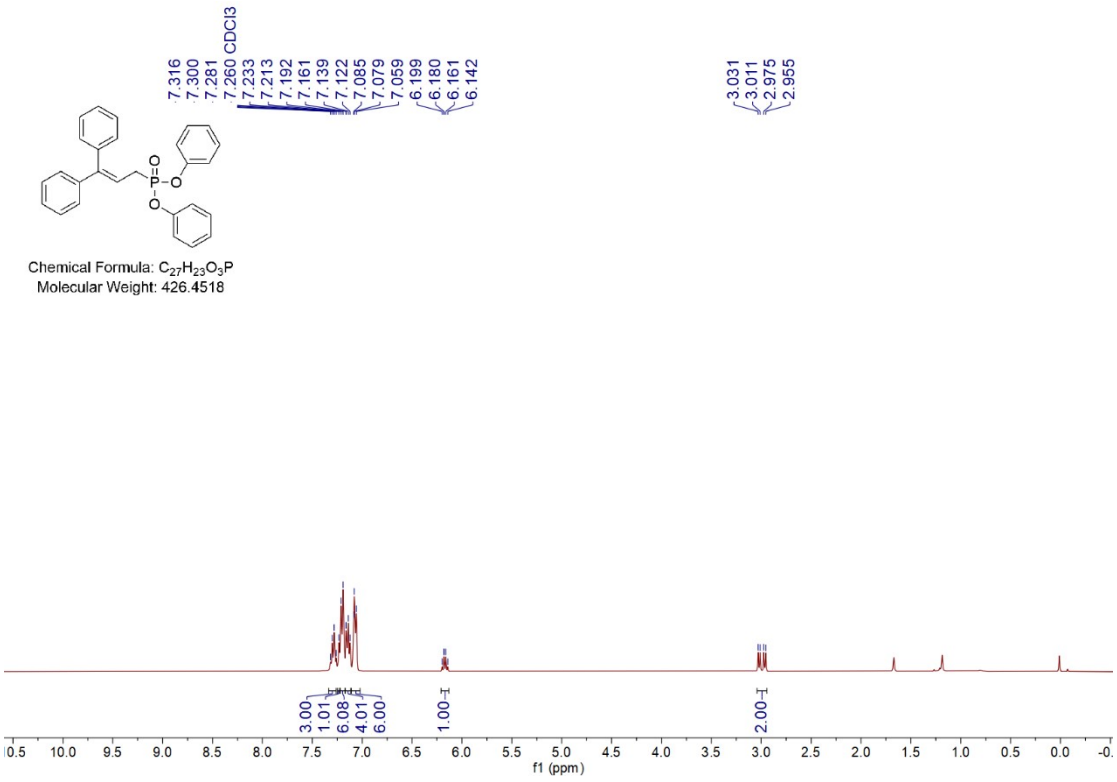

**$^{13}$C NMR spectrum of 3a', 101 MHz, $CDCl_3$**

***Competitive intermolecular reactions between $CH_3CN$ and $CD_3CN$***

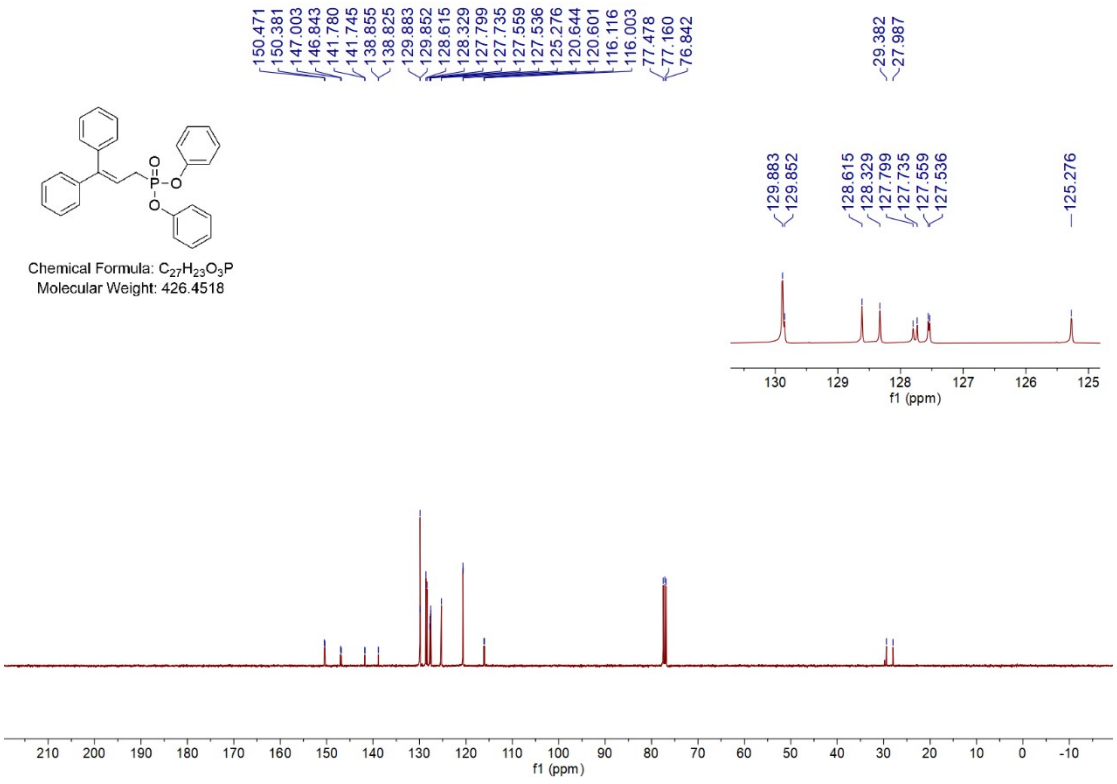



**$^{1}$H NMR spectrum of 3a and 7a, 400 MHz, $CDCl_3$**

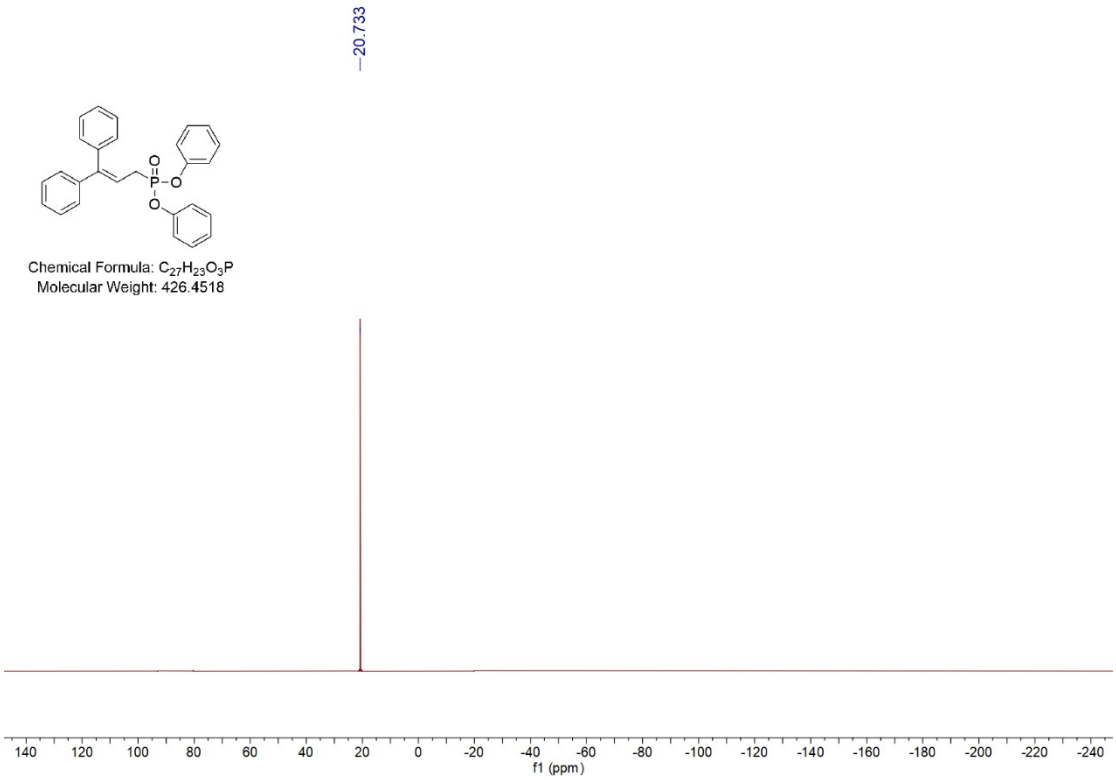
***diphenyl (3,3-diphenylallyl)phosphonate (8a)***




**$^{1}$H NMR spectrum of 8a, 400 MHz, $CDCl_3$**

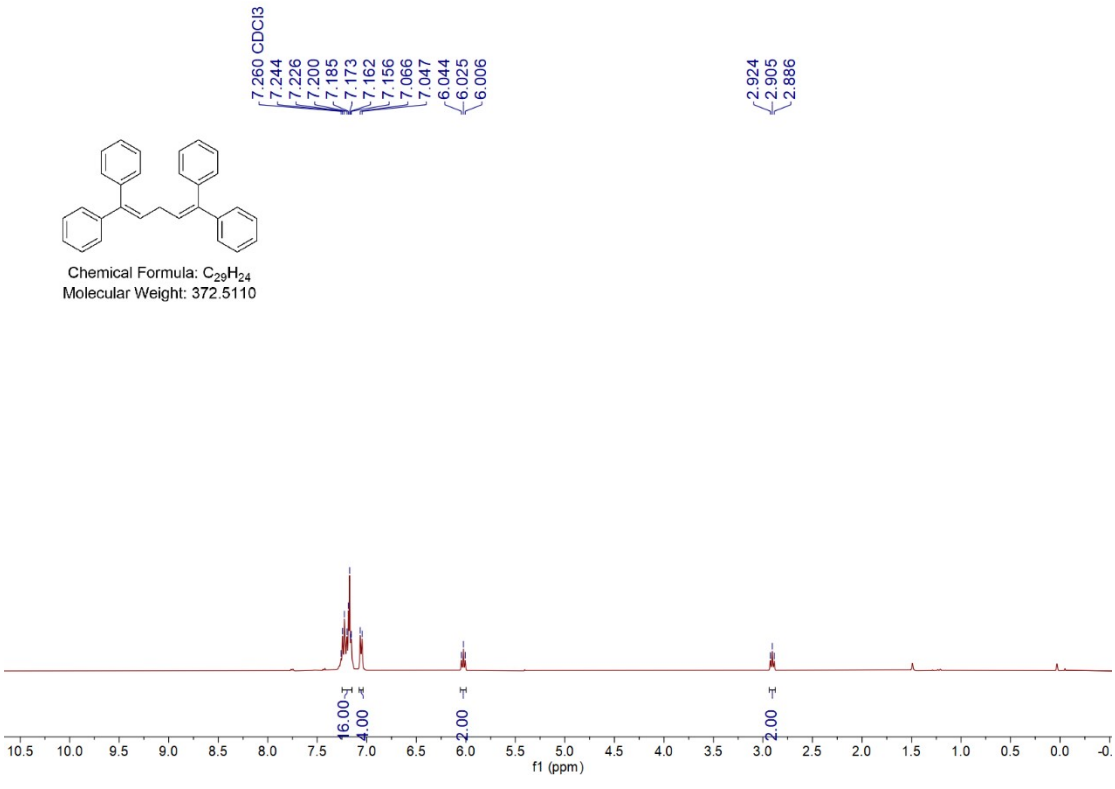



**$^{13}$C NMR spectrum of 8a, 101 MHz, $CDCl_3$**

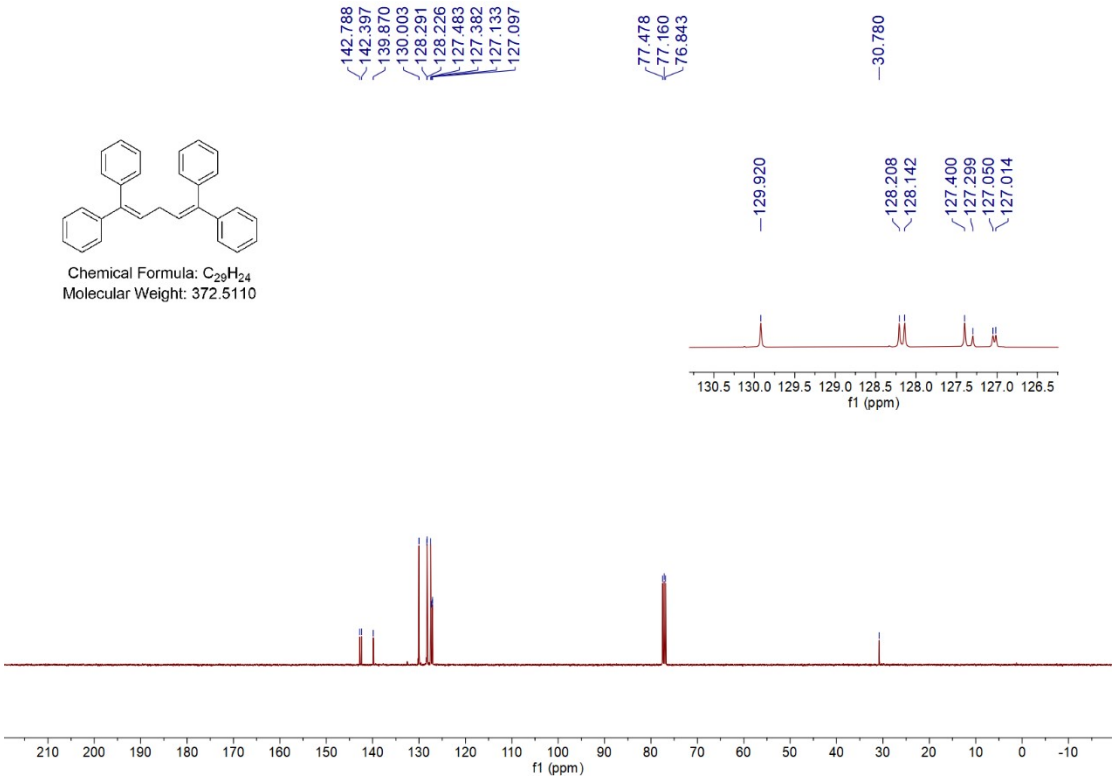



**$^{31}$P NMR spectrum of 8a, 162 MHz, $CDCl_3$**

## *1,1,5,5-tetraphenylpenta-1,4-diene (8b)*




**$^{1}$H NMR spectrum of 8b, 400 MHz, $CDCl_3$**




**$^{13}$C NMR spectrum of 8b, 101 MHz, $CDCl_3$**

# 8. References


1. L. Zhu, W. Luo, F. Guo, L. Chen, Y. Tang, B. Xiong, Y. Liu, K.-W. Tang and R. Qiu, Halide-free and metal-free allylic thiolation/selenation of P(O)H compounds with sulfur/selenium and allylic alcohols, *Green Chem.*, 2024, **26**, 10886-10892.
2. B. Xiong, C. Shi, Y. Ren, W. Xu, Y. Liu, L. Zhu, F. Cao, K.-W. Tang and S.-F. Yin, Zn-Catalyzed Dehydroxylative Phosphorylation of Allylic Alcohols with P(III)-Nucleophiles, *J. Org. Chem.*, 2024, **89**, 3033-3048.
3. X.-L. Wang, J.-X. Chen, X.-S. Jia and L. Yin, Synthesis of α,β-Unsaturated Phosphine Sulfides, *Synthesis*, 2019, **52**, 141-149.
4. K. Saint-Jacques, C. L. Ladd and A. B. Charette, Access to hexahydroazepinone heterocycles via palladium-catalysed C($sp^3$)–H alkenylation/ring-opening of cyclopropanes, *Chem. Commun.*, 2022, **58**, 7550-7553.
5. D.-L. Kong, L. Cheng, H.-R. Wu, Y.-X. Li, D. Wang and L. Liu, A metal-free yne-addition/1,4-aryl migration/decarboxylation cascade reaction of alkynoates with $Csp^3$–H centers, *Org. Biomol. Chem.*, 2016, **14**, 2210-2217.
6. F. Li, Z. Wu and J. Wang, Oxidative Enantioselective α-Fluorination of Aliphatic Aldehydes Enabled by N-Heterocyclic Carbene Catalysis, *Angew. Chem. Int. Ed.*, 2015, **54**, 656-659.
7. X. Xiong, J. Wong and Y.-Y. Yeung, Silver Salt-Mediated Allylation Reactions Using Allyl Bromides, *J. Org. Chem.*, 2021, **86**, 6974-6982.
8. H. C. Fisher, L. Prost and J.-L. Montchamp, Organophosphorus Chemistry without $PCl_3$: A Bridge from Hypophosphorous Acid to *H*-Phosphonate Diesters, *Eur. J. Org. Chem.*, 2013, **2013**, 7973-7978.
9. B. Qian, G. Zhang, Y. Ding and H. Huang, Catalytic cross deoxygenative and dehydrogenative coupling of aldehydes and alkenes: a redox-neutral process to produce skipped dienes, *Chem. Commun.*, 2013, **49**, 9839-9841.