Supporting Information

Nickel-Catalyzed Reductive Aminocarbonylation of Vinyl Triflates with Nitro Compounds for the Synthesis of *α,β*-Unsaturated Amides

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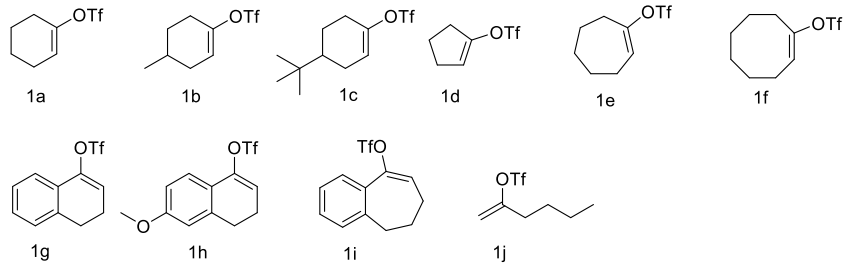
1. General Information

Unless otherwise noted, all reactions were carried out under N_2 atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dry solvents. Column chromatography was performed on silica gel (200-300 meshes) using dichloromethane and ethyl acetate as eluent. NMR spectra were recorded on a Bruker Avance operating at for ^{1}H NMR at 400 MHz, ^{13}C NMR at 101 MHz and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and $CDCl_3$ (^{1}H NMR δ 7.26, ^{13}C NMR δ 77.00) as solvent. All coupling constants (*J*) are reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014C chromatograph equipped with a FID detector. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or Waters TOFMS GCT Premier using EI or ESI ionization. Melting points were measured with WRR digital point apparatus and not corrected.

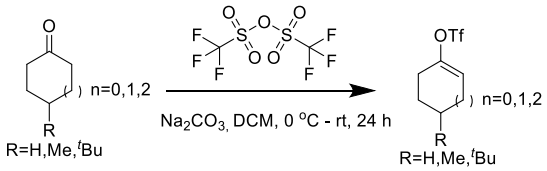
2. General Procedures

2.1 General Procedure for the Synthesis of Vinyl Triflates



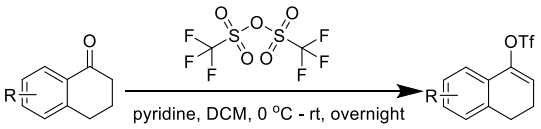
Known compounds **1a**–**1e**[1], **1g**–**1i**[2],**1f**[3] and **1j**[3] were prepared according to the literature procedure. The preparations of new compounds are provided as follows.

Method A:



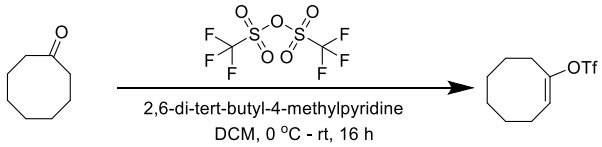
To a solution of ketone (10.0 mmol) in DCM (15 mL) was added anhydrous sodium carbonate (16.0 mmol). To this solution was added Tf_2O (20.0 mmol) in DCM (15 mL) over a period of 10 minutes. The reaction was stirred for an addition 24 h at room temperature. At this time, the reaction mixture was washed with sodium hydrogen carbonate (2 × 50 mL), water (2 × 50 mL), and dried with $MgSO_4$, filtered, and the solvent was removed in vacuum. Resulting **1a**–**1e** were purified by column chromatography.[1]

Method B:



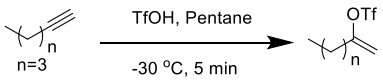
To a solution of 1-tetralone (10.0 mmol) in DCM, Tf_2O (20.0 mmol) and pyridine (100.0 mmol) were sequentially added at 0 ºC. The mixture was allowed to warm to room temperature and stirred ovemight. H_2O was added and the aqueous layer was extracted by DCM 3 times, and the combined organic layer was dried over $MgSO_4$ and concentrated in vacuum. Resulting **1g**–**1i** were purified by column chromatography.[2]

Method C:



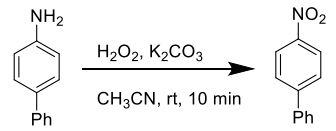
The solution of cyclohexanone (15.0 mmol) in DCM (45 mL) was cooled to 0 °C and then 2,6-di-*tert*-butyl-4-methylpyridine (17.0 mmol) and Tf_2O (18.0 mmol) were added to the reaction mixture. The reaction mixture was warmed to room temperature, stirred overnight, and evaporated to dryness. Petroleum ether was added and the solid pyridinium triflate was filtered off (the free base can be recovered) which was washed with petroleum ether. The combined petroleum ether solution was washed subsequently with cool HCl (1 M) and saturated brine, and dried over Na_2SO_4. Resulting **1f** was purified by column chromatography.[3]

Method D:

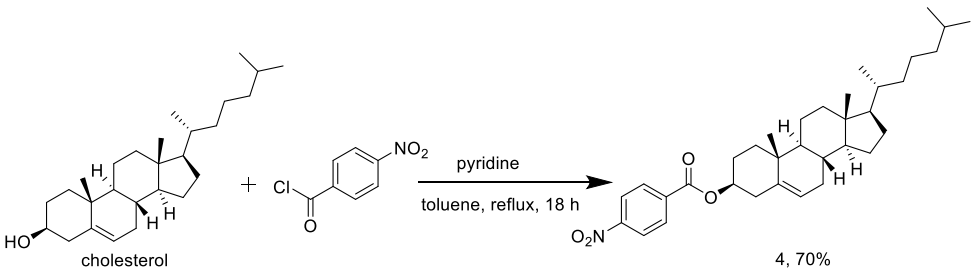


A solution of 1-hexyne (3.4 mL, 18.0 mmol) in pentane (20 mL) was cooled to -30 °C. TfOH (0.9 mL, 10.0 mmol) was added dropwise over 5 min. The cooling bath was removed and the reaction mixture was warmed to 0 °C. Saturated aqueous $NaHCO_3$ was added to the reaction mixture and this mixture was stirred for another 5 min. The organic layer was separated, washed twice with saturated $NaHCO_3$ and dried over K_2CO_3. Resulting **1j** was purified by column chromatography.[3]

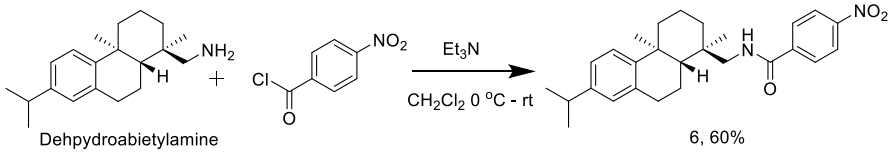
2.2 General Procedure for the Synthesis of Nitroarenes



To a solution of biphenyl-4-amine (1.0 mmol) and potassium carbonate (1.0 mmol) in CH_3CN (3 mL) were added a solution of 50% aqueous H_2O_2 (3.0 mmol) and the mixture was stirred at room temperature for 10–15 min. The mixture was then dried to vacuum and extracted three times with ethyl acetate followed by washing with brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent under vacuum afforded the crude product, which was further purified by column chromatography and afforded the product **2m**.[4]



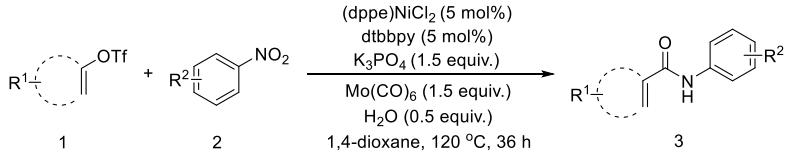
4-Nitrobenzoyl chloride (6.2 mmol, 1.2 g), cholesterol (6.2 mmol, 2.4 g,), and pyridine (6.2 mmol, 0.5 g) were refluxed in toluene (18 mL) for 18 h under a nitrogen atmosphere. After solvent removal, Purification by column chromatography (dichloromethane : ethyl acetate = 3 : 1, volume ratio) afforded **4** as a light yellow solid (2.3 g, 70%).[5]



An oven-dried round-bottom flask was charged under air with dehydroabietylamine (10.0 mmol, 2.9 g), DCM (40 mL), and triethylamine (12.0 mmol, 1.2 g), 4-nitrobenzoyl chloride (11.0 mmol, 2.0 g) was added in slowly and stirred at 0 °C, then stirred the reaction mixture at room temperature until completion (monitored by TLC). The reaction mixture was then diluted with 40 mL of H_2O and extracted three times with 25 mL of DCM. The combined organic phases were dried

over magnesium sulfate, filtered through short celite pad, and concentrated under reduced pressure. Purification by column chromatography (petroleum ether : ethyl acetate = 10 : 1 to 5 : 1, volume ratio) afforded **6** as a bright yellow solid (2.6 g, 60%).[6]

2.3 General Procedure for the synthesis of Products

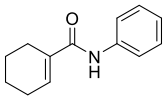


1 2 3

Under nitrogen atmosphere, **1** (0.3 mmol), **2** (1.2 equiv., 0.36 mmol), (dppe)$NiCl_2$ (5 mol %, 7.9 mg), dtbbpy (5 mol %, 4.0 mg), K_3PO_4 (1.5 equiv., 95.1 mg) and $Mo(CO)_6$ (1.5 equiv., 117.9 mg) were added to an oven-dried 15.0 mL In-Ex tube. Then dry 1,4-dioxane (2 mL) and H_2O (0.5 equiv., 2.7 mg) were added to the reaction. The tube was sealed and the mixture was stirred at 120 °C for 36 h. After the reaction was completed, the reaction mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1 to 2 : 1, volume ratio) on silica gel to afford the corresponding product **3aa** to **3ja**, **5** and **7**.

1 mmol scale: Under nitrogen atmosphere, **1a** (1 mmol), **2a** (1.2 equiv.), (dppe)$NiCl_2$ (5 mol %), dtbbpy (5 mol %), K_3PO_4 (1.5 equiv.) and $Mo(CO)_6$ (1.5 equiv.) were added to an oven-dried 15.0 mL In-Ex tube. Then dry 1,4-dioxane (5 mL) and H_2O (0.5 equiv.) were added to the reaction. The tube was sealed and the mixture was stirred at 120 °C for 36 h. After the reaction was completed, the reaction mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 20 : 1 to 2 : 1, volume ratio) on silica gel to afford the corresponding product **3aa** in 81% yield (162.8 mg).

3. Characterization Data of Products



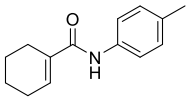
***N*-phenylcyclohex-1-ene-1-carboxamide (3aa)**[7]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.3) to give the titled product **3aa** as a **light yellow** solid (51.8 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 7.9 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 6.81 – 6.68 (m, 1H), 2.44 – 2.33 (m, 2H), 2.28 – 2.16 (m, 2H), 1.75 – 1.60 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 138.1, 134.0, 133.9, 128.7, 123.9, 120.0, 25.3, 24.2, 22.0, 21.3.

M.p. 105.3 – 106.1 °C



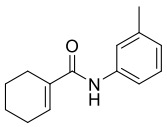
***N*-(*p*-tolyl)cyclohex-1-ene-1-carboxamide (3ab)**[8]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.2) to give the titled product **3ab** as a **light yellow solid** (54.2 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.39 (s, 1H), 7.12 (d, J = 8.3 Hz, 2H), 6.74 – 6.69 (m, 1H), 2.38 – 2.32 (m, 2H), 2.31 (s, 3H), 2.24 – 2.16 (m, 2H), 1.74 – 1.61 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 135.5, 134.0, 133.9, 133.7, 129.4, 120.0, 25.4, 24.3, 22.1, 21.5, 20.8.

M. p. 121.3 – 122.2 °C



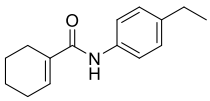
***N*-(*m*-tolyl)cyclohex-1-ene-1-carboxamide** (**3ac**)

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.2) to give the titled product **3ac** as a **light yellow liquid** (29.0 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.40 (s, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.80 – 6.74 (m, 1H), 2.43 – 2.36 (m, 5H), 2.30 – 2.23 (m, 2H), 1.81 – 1.66 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 138.9, 137.9, 134.1, 128.8, 124.9, 120.6, 117.0, 25.5, 24.4, 22.1, 21.5.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{14}H_{18}NO$ 216.1383; Found 216.1390.



***N*-(*p*-ethylphenyl)cyclohex-1-ene-1-carboxamide** (**3ad**)

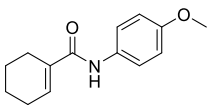
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.2) to give the titled product **3ad** as a **light yellow solid** (55.6 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 2H), 7.40 (s, 1H), 7.15 (d, J = 8.0 Hz, 2H), 6.72 (s, 1H), 2.61 (q, J = 15.0, 7.5 Hz, 2H), 2.40 – 2.31 (m, 2H), 2.26 – 2.18 (m, 2H), 1.75 – 1.62 (m, 4H), 1.21 (t, J = 7.5, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 140.2, 135.7, 134.1, 134.0, 128.3, 120.2, 28.3, 25.5, 24.4, 22.2, 21.5, 15.7.

M.p. 99.6 – 100.4 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{15}H_{20}NO$ 230.1539; Found 230.1548.

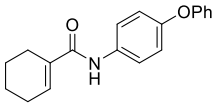


***N*-(*p*-methoxyphenyl)cyclohex-1-ene-1-carboxamide** (**3ae**)[9]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 5 : 1, Rf = 0.2) to give the titled product **3ae** as a **light yellow oil compound** (60.9 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 9.0 Hz, 2H), 7.43 (s, 1H), 6.90 (d, J = 9.0 Hz, 2H), 6.78 – 6.73 (m, 1H), 3.83 (s, 3H), 2.40 – 2.34 (m, 2H), 2.28 – 2.21 (m, 2H), 1.78 – 1.66 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 156.3, 134.0, 133.9, 131.2, 121.9, 114.1, 55.5, 25.5, 24.4, 22.1, 21.5.



***N*-(*p*-phenoxyphenyl)cyclohex-1-ene-1-carboxamide** (**3af**)

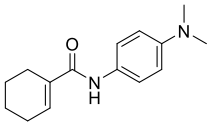
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 5 : 1, Rf = 0.2) to give the titled product **3af** as a **light yellow solid** (50.9 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.49 (m, 2H), 7.45 (s, 1H), 7.31 (t, J = 7.9 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 8.1 Hz, 4H), 6.78 – 6.69 (m, 1H), 2.39 – 2.30 (m, 2H), 2.26 – 2.18 (m, 2H), 1.76 – 1.62 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 157.6, 153.3, 134.2, 133.9, 133.6, 129.7, 122.9, 121.8, 119.6, 118.3, 25.5, 24.3, 22.1, 21.5.

M.p. 112.8 – 114.1 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{19}H_{20}NO_2$ 245.1648; Found 245.1657.



***N*-(*p*-(dimethylamino)phenyl)cyclohex-1-ene-1-carboxamide** (**3ag**)

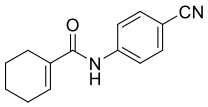
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 5 : 1, Rf = 0.2) to give the titled product **3ag** as a **light yellow solid** (65.9 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, J = 8.6, 4.2 Hz, 2H), 7.28 (s, 1H), 6.77 – 6.67 (m, 3H), 2.93 (d, J = 4.3 Hz, 6H), 2.40 – 2.29 (m, 2H), 2.27 – 2.18 (m, 2H), 1.75 – 1.61 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 147.9, 133.9, 133.6, 127.9, 121.9, 113.1, 41.0 (d, J = 9.8 Hz, 2C), 25.5, 24.4, 22.2, 21.5.

M.p. 179.9 – 182.4 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{15}H_{20}N_2O$ 294.1489; Found 294.1501.



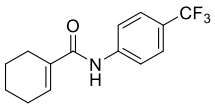
***N*-(*p*-cyanophenyl)cyclohex-1-ene-1-carboxamide** (**3ah**)

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 5 : 1, Rf = 0.2) to give the titled product **3ah** as a **light yellow oil compound** (30.5 mg, 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 3H), 7.59 (d, J = 8.6 Hz, 2H), 6.77 (s, 1H), 2.38 – 2.29 (m, 2H), 2.26 – 2.18 (m, 2H), 1.74 – 1.61 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 142.3, 135.7, 133.7, 133.2, 119.7, 118.9, 106.7, 25.6, 24.3, 22.0, 21.3.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{14}H_{15}N_2O$ 227.1179; Found 227.1185.



***N*-(*p*-(trifluoromethyl)phenyl)cyclohex-1-ene-1-carboxamide** (**3ai**)

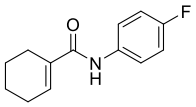
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.2) to give the titled product **3ai** as a **light yellow solid** (50.1 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 9.6 Hz, 2H), 7.61 – 7.53 (m, 3H), 6.76 (m, 1H), 2.39 – 2.30 (m, 2H), 2.26 – 2.19 (m, 2H), 1.75 – 1.62 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 141.2, 135.2, 133.8, 126.2 (q, J = 3.6 Hz, 1C), 125.8 (q, J = 32.8 Hz, 1C), 124.1 (q, J = 271.4 Hz, 1C), 119.5, 25.6, 24.3, 22.1, 21.4.

M.p. 120.2 – 121.9 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{14}H_{15}F_3NO$ 270.1100; Found 270.1107.



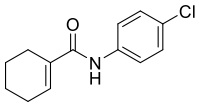
***N*-(*p*-fluorophenyl)cyclohex-1-ene-1-carboxamide** (**3aj**)[10]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 20 : 1, Rf = 0.2) to give the titled product **3aj** as a **light yellow solid** (49.3 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.50 (s, 1H), 7.03 (ddd, J = 12.3, 5.3, 2.8 Hz, 2H), 6.78 – 6.73 (m, 1H), 2.42 – 2.32 (m, 2H), 2.29 – 2.18 (m, 2H), 1.78 – 1.65 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 159.3 (d, J = 243.3 Hz, 1C), 134.4, 134.1 (d, J = 2.6 Hz, 1C), 133.8, 121.9 (d, J = 7.8 Hz, 1C), 115.6 (d, J = 22.4 Hz, 1C), 25.5, 24.4, 22.1, 21.5.

M.p. 105.3 – 106.4 °C



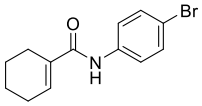
***N*-(*p*-chlorophenyl)cyclohex-1-ene-1-carboxamide** (**3ak**)[7]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 20 : 1, Rf = 0.2) to give the titled product **3ak** as a **light yellow solid** (53.6 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.8 Hz, 2H), 7.47 (s, 1H), 7.31 (d, J = 8.8 Hz, 2H), 6.81 – 6.73 (m, 1H), 2.40 – 2.32 (m, 2H), 2.27 – 2.19 (m, 2H), 1.78 – 1.65 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 136.7, 134.7, 133.8, 129.1, 128.9, 121.3, 25.5, 24.3, 22.1, 21.5.

M.p. 135.3 – 136.1 °C



***N*-(*p*-bromophenyl)cyclohex-1-ene-1-carboxamide** (**3al**)

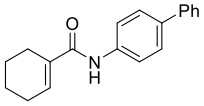
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 20 : 1, Rf = 0.2) to give the titled product **3al** as a **light yellow solid** (41.0 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 5H), 6.80 – 6.75 (m, 1H), 2.42 – 2.33 (m, 2H), 2.31 – 2.21 (m, 2H), 1.81 – 1.65 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 137.2, 134.7, 133.8, 131.9, 121.5, 116.6, 25.5, 24.4, 22.1, 21.5.

M.p. 159.1 – 160.2 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{15}BrNO$ 280.0332; Found 280.0338.



***N*-([1,1'-biphenyl]-4-yl)cyclohex-1-ene-1-carboxamide (3am)**

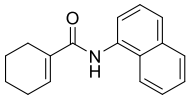
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.2) to give the titled product **3am** as a **light yellow solid** (57.6 mg, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.6 Hz, 2H), 7.64 – 7.58 (m, 4H), 7.52 (s, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 6.83 – 6.76 (m, 1H), 2.46 – 2.37 (m, 2H), 2.30 – 2.24 (m, 2H), 1.82 – 1.67 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 140.6, 137.4, 137.0, 134.4, 134.0, 128.8, 127.6, 127.1, 126.9, 120.3, 25.5, 24.4, 22.2, 21.5.

M.p. 168.1 – 168.7 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{19}H_{20}NO$ 278.1539; Found 278.1556.



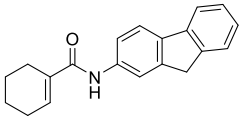
***N*-(naphthalen-1-yl)cyclohex-1-ene-1-carboxamide (3an)**[11]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 5 : 1, Rf = 0.2) to give the titled product **3an** as a **light yellow solid** (56.5 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (sd, J = 4.9 Hz, 1H), 7.98 – 7.83 (m, 3H), 7.74 (sd, J = 5.4 Hz, 1H), 7.60 – 7.50 (m, 3H), 6.93 (s, 1H), 2.58 – 2.44 (m, 2H), 2.37 – 2.28 (m, 2H), 1.87 – 1.71 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 134.7, 134.1, 133.9, 132.6, 128.9, 127.2, 126.3, 125.9, 125.9, 125.6, 120.7, 120.5, 25.6, 24.6, 22.2, 21.5.

M.p. 137.6 – 138.5 °C



***N*-(9*H*-fluoren-2-yl)cyclohex-1-ene-1-carboxamide** (**3ao**)

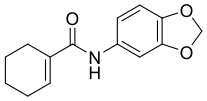
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.2) to give the titled product **3ao** as a **light yellow solid** (53.7 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.78 – 7.71 (m, 2H), 7.55 (d, J = 7.3 Hz, 2H), 7.43 (dd, J = 8.2, 1.9 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.30 (td, J = 7.4, 6.4, 1.0 Hz, 1H), 6.82 – 6.77 (m, 1H), 3.92 (s, 2H), 2.45 – 2.38 (m, 2H), 2.31 – 2.23 (m, 2H), 1.82 – 1.67 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 144.3, 143.2, 141.3, 137.9, 136.9, 134.2, 134.0, 126.7, 126.2, 124.9, 120.1, 119.5, 118.7, 116.9, 37.0, 25.5, 24.4, 22.1, 21.5.

M.p. 178.1 – 180.0 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{20}H_{19}NO$ 290.1539; Found 290.1557.



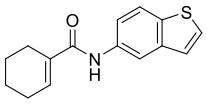
***N*-(benzo[*d*][1,3]dioxol-5-yl)cyclohex-1-ene-1-carboxamide** (**3ap**)

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 5 : 1, Rf = 0.2) to give the titled product **3ap** as a **light yellow oil compound** (47.8 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H), 6.80 (dd, J = 8.3, 2.1 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 6.72 – 6.69 (m, 1H), 5.94 (s, 2H), 2.36 – 2.29 (m, 2H), 2.24 – 2.18 (m, 2H), 1.77 – 1.61 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 147.8, 144.2, 134.2, 133.9, 132.4, 113.2, 108.1, 103.0, 101.3, 25.5, 24.4, 22.1, 21.5.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{14}H_{16}NO_3$ 246.1125; Found 246.1131.



***N*-(benzo[*b*]thiophen-5-yl)cyclohex-1-ene-1-carboxamide** (**3aq**)

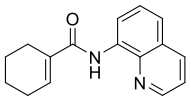
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 5 : 1, Rf = 0.2) to give the titled product **3aq** as a **light yellow solid** (51.7 mg, 67%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 1.9 Hz, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.61 (s, 1H), 7.47 (d, J = 5.4 Hz, 1H), 7.40 (dd, J = 8.6, 2.0 Hz, 1H), 7.31 (d, J = 5.8 Hz, 1H), 6.83 – 6.77 (m, 1H), 2.47 – 2.37 (m, 2H), 2.34 – 2.20 (m, 2H), 1.78 – 1.65 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 140.2, 135.3, 134.8, 134.2, 133.9, 127.4, 123.9, 122.6, 117.8, 114.7, 25.5, 24.4, 22.1, 21.5.

M.p. 123.1 – 124.7 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{15}H_{16}NOS$ 258.0947; Found 258.0963.

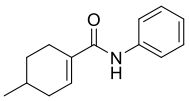


***N*-(quinolin-8-yl)cyclohex-1-ene-1-carboxamide** (**3ar**)[12]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 5 : 1, Rf = 0.2) to give the titled product **3ar** as a **light brown oil compound** (52.2 mg, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 8.90 – 8.82 (m, 2H), 8.18 (dd, J = 8.3, 1.6 Hz, 1H), 7.61 – 7.45 (m, 3H), 7.02 – 6.96 (m, 1H), 2.60 – 2.49 (m, 2H), 2.37 – 2.27 (m, 2H), 1.85 – 1.71 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 148.1, 138.8, 136.4, 134.8, 134.8, 134.2, 128.0, 127.5, 121.5, 121.2, 116.5, 25.7, 24.4, 22.3, 21.6.



4-methyl-*N*-phenylcyclohex-1-ene-1-carboxamide (**3ba**)

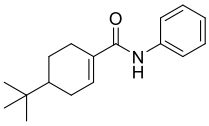
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.3) to give the titled product **3ba** as a **light yellow solid** (56.8 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.6 Hz, 2H), 7.41 (s, 1H), 7.32 (t, J = 7.9 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H), 6.73 – 6.68 (m, 1H), 2.52 – 2.42 (m, 1H), 2.39 – 2.27 (m, 2H), 1.89 – 1.77 (m, 2H), 1.76 – 1.66 (m, 1H), 1.35 – 1.27 (m, 1H), 1.01 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 138.1, 133.9, 133.7, 129.0, 124.1, 120.0, 33.9, 30.3, 27.6, 24.4, 21.4.

M.p. 93.4 – 94.3 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{14}H_{18}NO$ 216.1383; Found 216.1388.



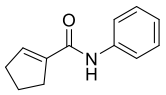
4-(*tert*-butyl)-*N*-phenylcyclohex-1-ene-1-carboxamide (**3ca**)[13]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.3) to give the titled product **3ca** as a **light yellow solid** (63.2 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.6 Hz, 2H), 7.45 (s, 1H), 7.32 (t, J = 7.9 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 6.76 – 6.71 (m, 1H), 2.59 – 2.51 (m, 1H), 2.33 – 2.17 (m, 2H), 2.03 – 1.90 (m, 2H), 1.36 – 1.17 (m, 2H), 0.90 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 138.1, 134.8, 133.9, 129.0, 124.1, 120.0, 43.4, 32.2, 27.3, 27.1, 25.9, 23.7.

M.p. 70.1 – 71.5 °C



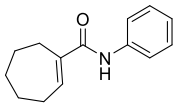
***N*-phenylcyclopent-1-ene-1-carboxamide (3da)**[14]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.3) to give the titled product **3da** as a **light yellow solid** (47.7 mg, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.7 Hz, 2H), 7.40 – 7.29 (m, 3H), 7.10 (t, J = 7.4 Hz, 1H), 6.69 – 6.62 (m, 1H), 2.71 – 2.63 (m, 2H), 2.60 – 2.49 (m, 2H), 2.09 – 1.98 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 139.9, 139.1, 137.9, 129.0, 124.2, 119.9, 33.4, 31.7, 23.4.

M.p. 119.4 – 120.1 °C



***N*-phenylcyclohept-1-ene-1-carboxamide** (3ea)

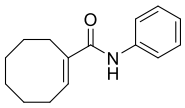
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 20 : 1, Rf = 0.2) to give the titled product **3ea** as a **light yellow solid** (59.3 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.55 (m, 3H), 7.35 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 6.71 (t, J = 6.5 Hz, 1H), 2.61 – 2.54 (m, 2H), 2.38 – 2.28 (m, 2H), 1.87 – 1.79 (m, 2H), 1.67 – 1.57 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 142.1, 138.3, 137.0, 129.0, 124.0, 119.9, 32.1, 28.7, 28.5, 26.5, 26.0.

M.p. 118.6 – 120.2 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{14}H_{18}NO$ 216.1383; Found 216.1392.



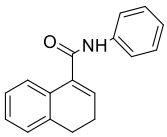
***N*-phenylcyclooct-1-ene-1-carboxamide (3fa)**[14]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 20 : 1, Rf = 0.2) to give the titled product **3fa** as a **light yellow solid** (44.6 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 2H), 7.51 (s, 1H), 7.32 (t, J = 7.8 Hz, 2H), 7.09 (t, J = 7.4 Hz, 1H), 6.61 (t, J = 8.3 Hz, 1H), 2.61 – 2.48 (m, 2H), 2.37 – 2.27 (m, 2H), 1.74 – 1.68 (m, 2H), 1.64 – 1.60 (m, 2H), 1.55 – 1.51 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 138.2, 137.9, 136.0, 129.0, 124.1, 120.0, 29.5, 29.2, 27.1, 26.6, 26.0, 25.6.

M.p. 94.7 – 95.4 °C



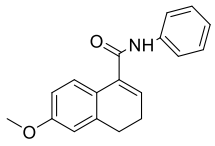
***N*-phenyl-3,4-dihydronaphthalene-1-carboxamide (3ga)**[15]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.2) to give the titled product **3ga** as a **light yellow solid** (60.5 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 3H), 7.48 (p, J = 3.4 Hz, 1H), 7.35 (t, J = 7.9 Hz, 2H), 7.25 – 7.17 (m, 3H), 7.14 (t, J = 7.4 Hz, 1H), 6.66 (t, J = 4.6 Hz, 1H), 2.81 (t, J = 8.0 Hz, 2H), 2.39 (td, J = 8.0, 4.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 137.9, 136.7, 136.4, 132.4, 131.0, 129.1, 128.1, 128.0, 126.9, 125.1, 124.5, 119.9, 27.6, 23.0.

M.p. 168.5 – 169.3 °C



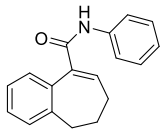
6-methoxy-*N*-phenyl-3,4-dihydronaphthalene-1-carboxamide (**3ha**)[13]

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 5 : 1, Rf = 0.2) to give the titled product **3ha** as a **light yellow solid** (43.5 mg, 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.9 Hz, 2H), 7.54 (s, 1H), 7.43 (d, J = 8.2 Hz, 1H), 7.35 (t, J = 7.9 Hz, 2H), 7.13 (t, J = 7.4 Hz, 1H), 6.77 – 6.72 (m, 2H), 6.54 (t, J = 4.7 Hz, 1H), 3.81 (s, 3H), 2.79 (t, J = 7.9 Hz, 2H), 2.39 (td, J = 7.9, 4.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 159.3, 138.3, 138.0, 136.3, 129.8, 129.1, 126.5, 124.4, 124.0, 119.9, 114.3, 111.4, 55.3, 28.1, 23.0.

M.p. 134.7 – 135.5 °C



***N*-phenyl-6,7-dihydro-5*H*-benzo[7]annulene-9-carboxamide** (**3ia**)

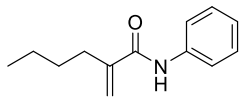
Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.2) to give the titled product **3ia** as a **light yellow solid** (47.3 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.43 – 7.36 (m, 2H), 7.36 – 7.27 (m, 6H), 7.13 – 7.06 (m, 1H), 2.64 (t, J = 7.0 Hz, 2H), 2.18 (p, J = 7.1 Hz, 2H), 2.02 (q, J = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 142.5, 140.0, 138.0, 137.2, 135.1, 129.6, 129.0, 128.5, 128.5, 126.7, 124.3, 119.9, 33.7, 32.0, 25.1.

M.p. 112.4 – 113.5 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{18}H_{18}NO$ 264.1383; Found 264.1399.



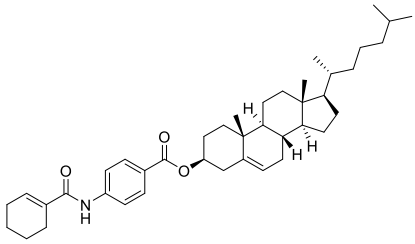
2-methylene-*N*-phenylhexanamide (**3ja**)

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.3) to give the titled product **3ja** and **3ja'** as a **light yellow liquid** (30.5 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 3H), 7.33 (t, J = 7.9 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 5.69 (s, 1H), 5.39 (s, 1H), 2.40 (t, J = 7.5 Hz, 2H), 1.52 – 1.45 (m, 2H), 1.43 – 1.32 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 146.6, 137.9, 129.0, 124.4, 119.9, 117.6, 32.2, 30.3, 22.4, 13.9.

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{13}H_{18}NO$ 204.1383; Found 204.1391.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 4-(cyclohex-1-ene-1-carboxamido)benzoate (**5**)

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 10 : 1, Rf = 0.2) to give the titled product **5** as a **light yellow solid** (110.1 mg, 60%).

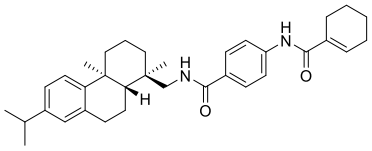
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.7 Hz, 2H), 7.67 (d, J = 8.8 Hz, 2H), 7.57 (s, 1H), 6.83 – 6.76 (m, 1H), 5.45 (d, J = 3.8 Hz, 1H), 4.94 – 4.82 (m, 1H), 2.49 (d, J = 7.7 Hz, 2H), 2.43 – 2.36 (m, 2H), 2.31 – 2.23 (m, 2H), 2.10 – 1.91 (m, 5H), 1.80 – 1.74 (m, 3H), 1.72 – 1.66 (m, 3H), 1.62 – 1.59 (m, 2H), 1.57 – 1.50 (m, 4H), 1.49 (d, J = 4.5 Hz, 1H), 1.41 – 1.35 (m, 3H), 1.25 – 1.13 (m, 7H), 1.10 (s, 3H), 1.07 – 1.03 (m, 2H), 0.96 (d, J = 6.5 Hz, 3H), 0.90 (dd, J = 6.6, 1.7 Hz, 6H), 0.72 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 165.6, 142.1, 139.7, 135.0, 133.9, 130.8, 126.1, 122.7, 118.9, 74.5, 56.7, 56.2, 50.1, 42.4, 39.8, 39.5, 38.3, 37.1, 36.7, 36.2, 35.8,

31.94 (d, *J* = 4.7 Hz, 2C), 28.3, 28.0, 27.9, 25.6, 24.3, 24.3, 23.9, 22.8, 22.6, 22.1, 21.4, 21.1, 19.4, 18.7, 11.9.

M.p. > 254 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{41}H_{59}NO_3$ 614.4568; Found 614.4568.



4-(cyclohex-1-ene-1-carboxamido)-*N*-(((1*R*,4a*S*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)benzamide (**7**)

Upon completion, the mixture was concentrated and purified via flash column chromatography (petroleum ether : ethyl acetate = 2 : 1, Rf = 0.2) to give the titled product **7** as a **bright yellow liquid** (64.5 mg, 42%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 – 7.55 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.88 (s, 1H), 6.79 – 6.68 (m, 1H), 6.11 (t, *J* = 6.2 Hz, 1H), 3.37 (qd, *J* = 13.7, 6.4 Hz, 2H), 2.99 – 2.75 (m, 3H), 2.38 – 2.19 (m, 6H), 2.01 – 1.90 (m, 1H), 1.85 – 1.68 (m, 6H), 1.51 (t, *J* = 12.4 Hz, 2H), 1.39 (td, *J* = 13.2, 3.9 Hz, 2H), 1.23 (d, *J* = 4.1 Hz, 6H), 1.21 (s, 3H), 1.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 166.8, 147.1, 145.7, 141.0, 134.9, 134.8, 133.9, 130.1, 127.9, 127.0, 124.2, 123.9, 119.4, 50.4, 45.9, 38.4, 37.7, 37.6, 36.5, 33.4, 30.5, 25.6, 25.4, 24.3, 24.0, 22.1, 21.4, 19.1, 18.8, 18.7.

M.p. 147.8 – 148.1 °C

HRMS (ESI): $[M+H]^+$ Calcd. for $C_{34}H_{44}N_2O_2$ 513.3476; Found 513.3482.

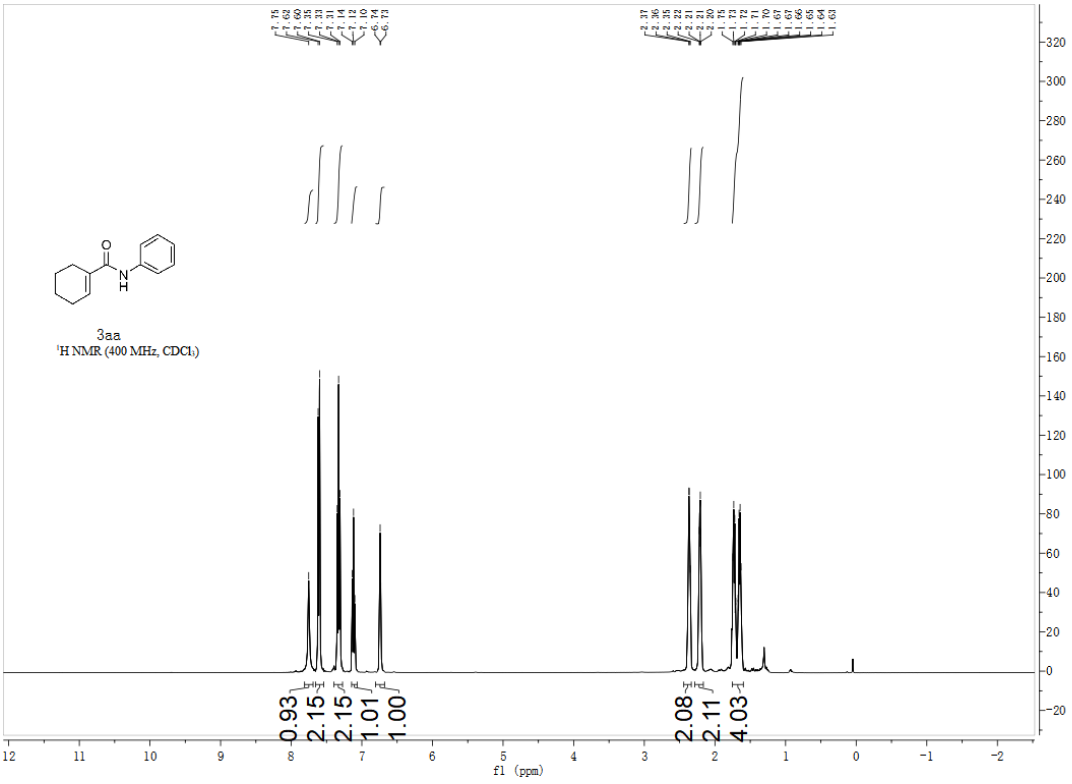
4. Reference

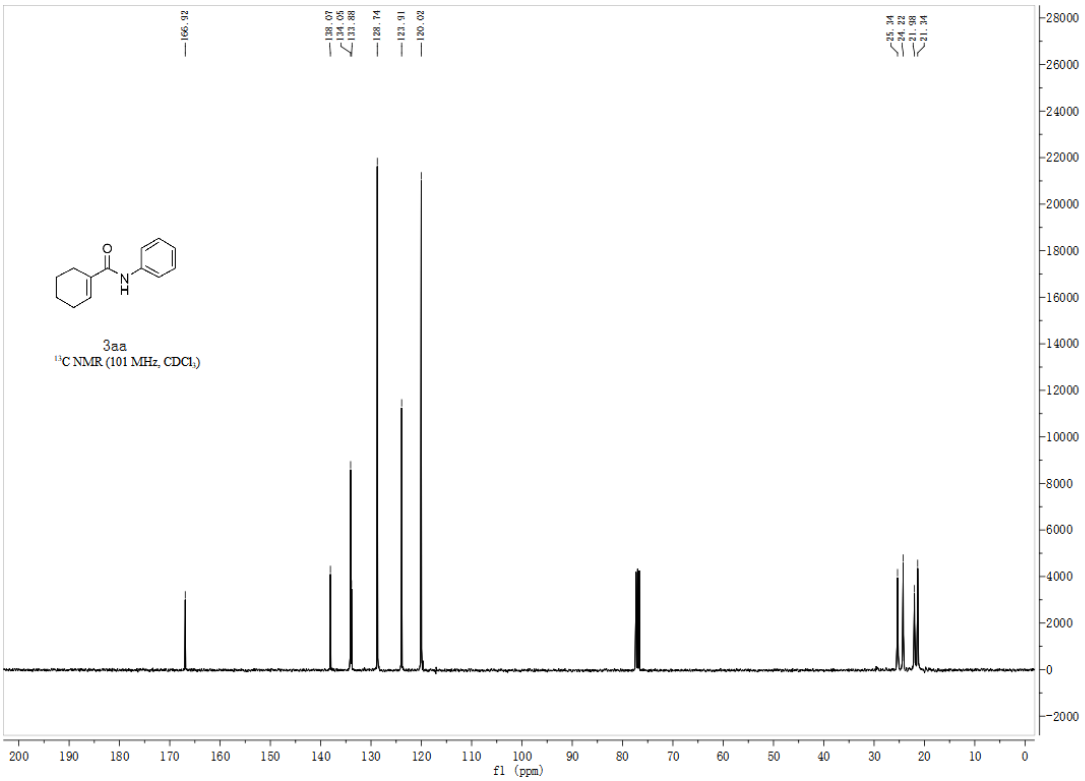
(1) Astrid, M. O.; Daniel, J. W. Multimetallic Ni- and Pd-Catalyzed Cross-Electrophile Couplin g to Form Highly Substituted 1,3-Dienes. *J. Am. Chem. Soc.* **2018**, *140*, 2446−2449.

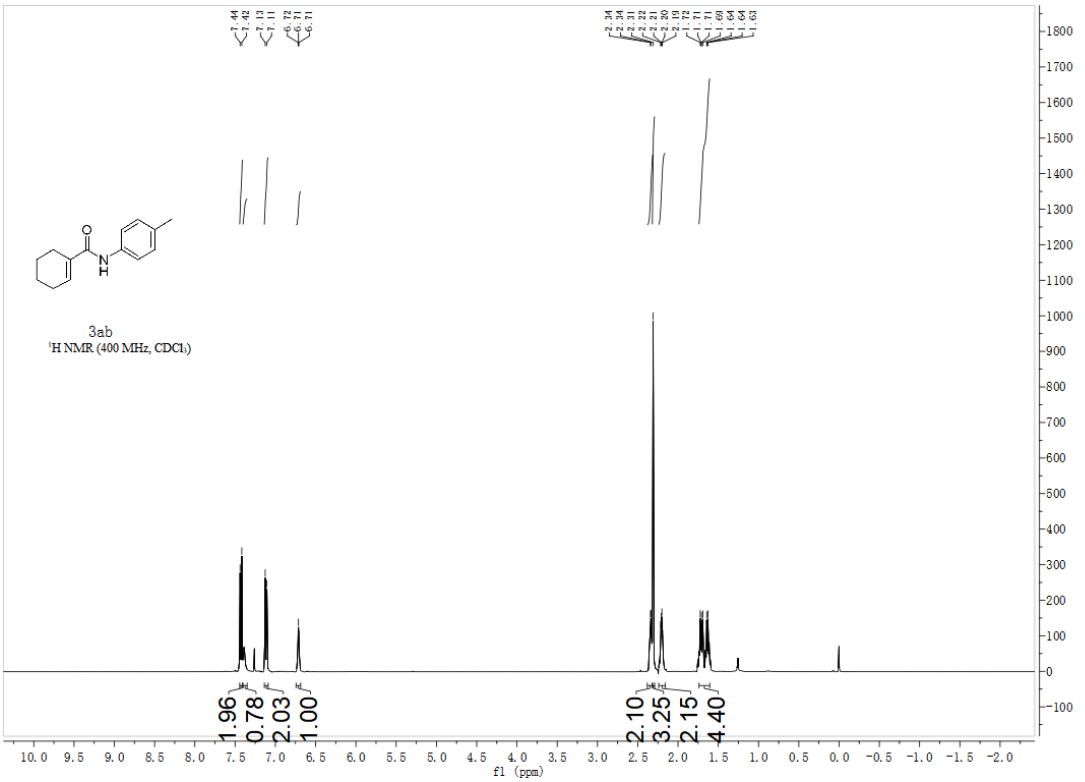
(2) Ping, Y. J.; Zhou, Y.-M.; Wu, L.; Li, Z.-R.; Gu, X.; Wan, X. L.; Xu, Z.-J.; Che, C.-M. F e-BPsalan complexes catalyzed highly enantioselective Diels-Alder reaction of alkylidene β-keto esters. *Org. Chem. Front.* **2021**, *8*, 1910−1917.

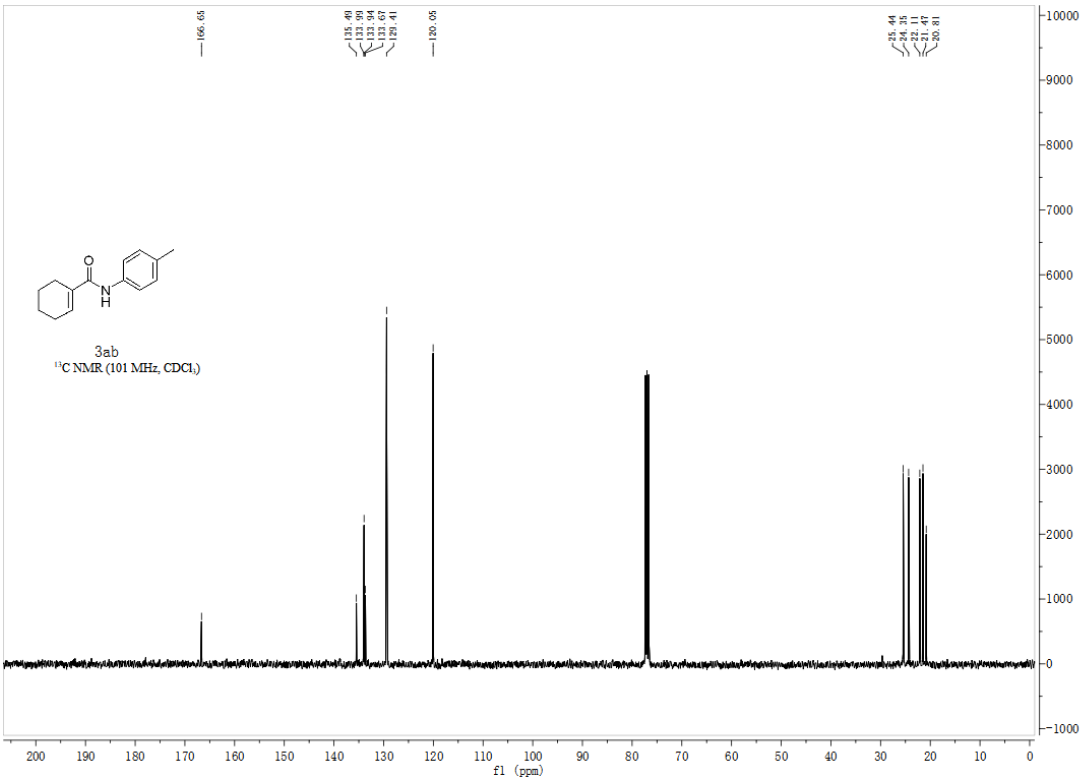
(3) Su, X. L.; Huang, H. G.; Yuan, Y. F.; Li, Y. Radical Desulfur-Fragmentation and Reconstr uction of Enol Triflates: Facile Access to α-Trifluoromethyl Ketones. *Angew. Chem. Int. Ed.* **2 017**, *56*, 1338−1341.
(4) Gupta, S.; Ansari, A.; Sashidhara, K. V. Base promoted peroxide systems for the efficient s ynthesis of Nitroarenes and Benzamides. *Tetrahedron lett.* **2019**, *60*, 151076.
(5) Liu, Y.; Chen, J. M.; Qi, Y. X.; Gao, S.; Balaji, K.; Zhang, Y. H.; Xue, Q. B.; Lu, Z. J. Cross-linked liquid crystalline polybenzoxazines bearing cholesterol-based mesogen side groups. *Polymer* **2018**, *145*, 252−260.
(6) Bao, Z.-P.; Miao, R.-G.; Qi, X.; Wu, X.-F. A Novel Construction of Acetamides from Rho dium-Catalyzed Aminocarbonylation of DMC with Nitro compounds. *Chem. Commun.* **2021**, *57*, 1955−1958.
(7) Zhang, S.; Neumann, H.; Beller, M. Pd-Catalyzed Carbonylation of Vinyl Triflates To Affor d α,β-Unsaturated Aldehydes, Esters, and Amides under Mild Conditions. *Org. Lett.* **2019**, *21*, 3528−3532.
(8) Formentín, P.; Sabater, M. J.; Chrétien, M. N.; García, H.; J Scaiano,. C. Enantioselective photocyclization of p-toluidides of unsaturated carboxylic acids in solution. A mechanistic and preparative study. *J. Chem. Soc., Perkin Trans. 2*, **2002**, 164-167.
(9) Shimazawa, R.; Shirai, R.; Hashimoto, Y.; Iwasaki, S. *Bioorg. Med. Chem. Lett.* **1994**, *4*, 2 377-2382.
(10) Zhu, Y.-Q.; Liu, Y.; Wang, H.; Liu, W.; Li, C.-J. Reaction of alkenecarboxylic acids with isocyanates via rhodium(III)-catalyzed C–H activation: a versatile route to cyclic imides. *Org. Chem. Front.*, **2016**, *3*, 971-974.
(11) Banfi, L.; Riva, R. *Org. Rec.* **2005**, *65*, 1-65.
(12) Tsuzuki, S.; Sakurai, S.; Matsumoto, A.; Kano, T.; Maruoka, K. Ni-Catalyzed C(sp2)–H al kylation of N-quinolylbenzamides using alkylsilyl peroxides as structurally diverse alkyl sources. *Chem. Commun.*, **2021**, *57*, 7942-7945.
(13) Lagerlund, O.; Mantel, M. L. H.; Larhed, M. Aminocarbonylations of alkenyl phosphates, chlorides, bromides, and triflates with Mo(CO)6 as a solid CO source. *Tetrahedron* **2009**, *65*, 7646-7652.
(14) Hell, S. M.; Meyer, C. F.; Misale, A.; Sap, J. B. I.; Christensen, K. E.; Willis, M. C.; Tr abanco, A. A.; Gouverneur, V. Hydrosulfonylation of Alkenes with Sulfonyl Chlorides under V isible Light Activation. *Angew. Chem. Int. Ed.* **2020**, *59*, 11620-11626.
(15) Niestroj, M.; Neumannt, W. P.; Thies, O. A Mild and Effective Synthesis of unsaturated Carboxamides and Sulfonamides by Electrophilic Substitution of Alkenylstannanes with Isocyana tes. *Chem. Ber.* **1994**, *127*, 1131-1136.
(16) Farkas, R.; Molnar, E. A.; Acs, P.; Takacs, A.; Kollar, L. High-yielding synthesis of 1-car boxamido-3,4-dihydronaphthalenes via palladium-catalyzed aminocarbonylation. *Tetrahedron* **2013**, *69*, 500-504.

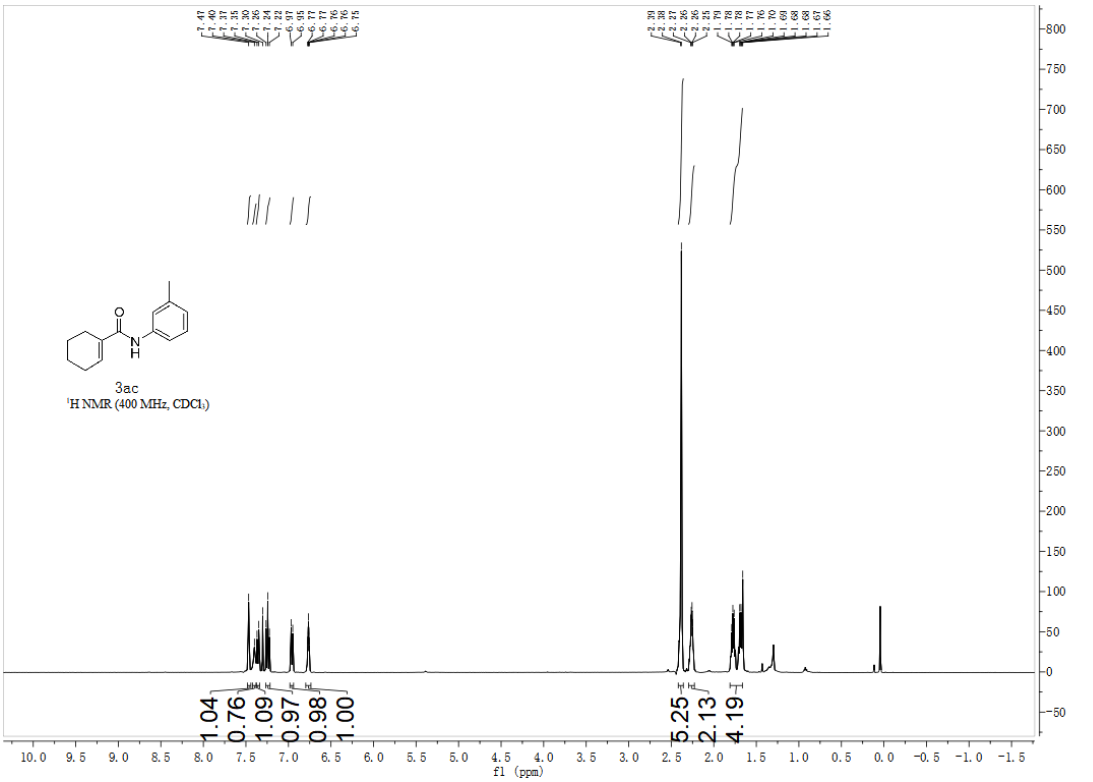
5. Copy of ^{1}H and ^{13}C NMR Spectra of Products

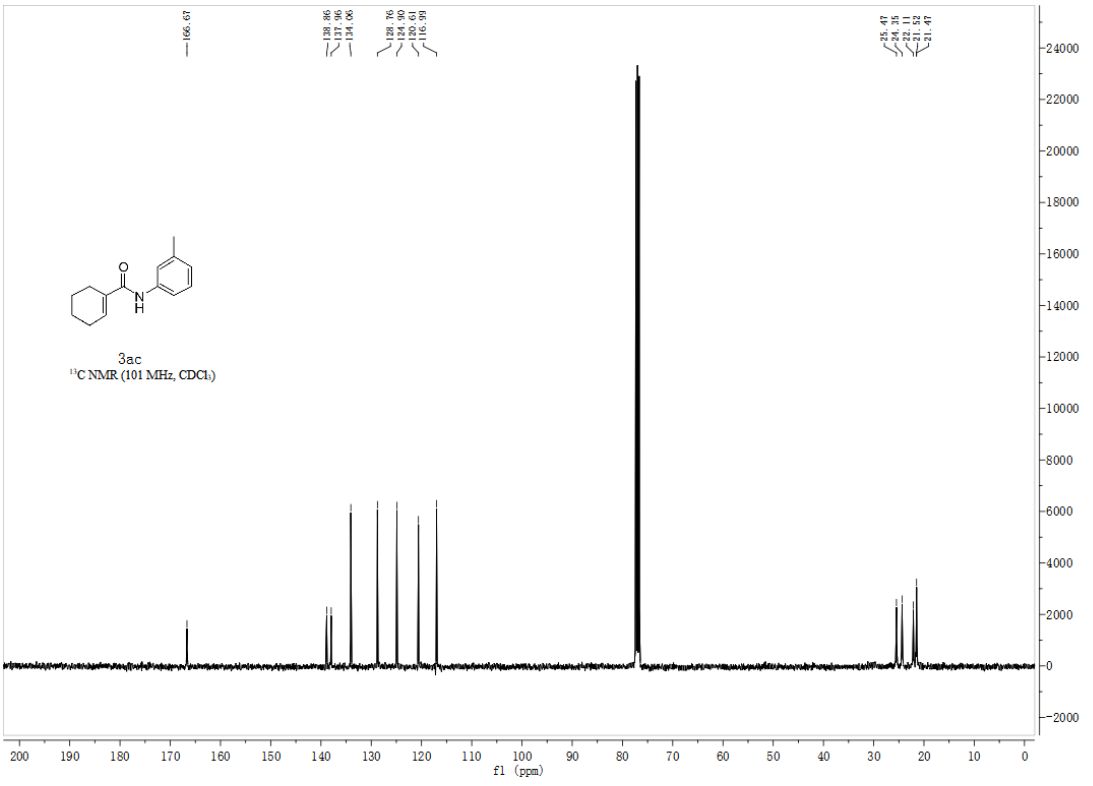


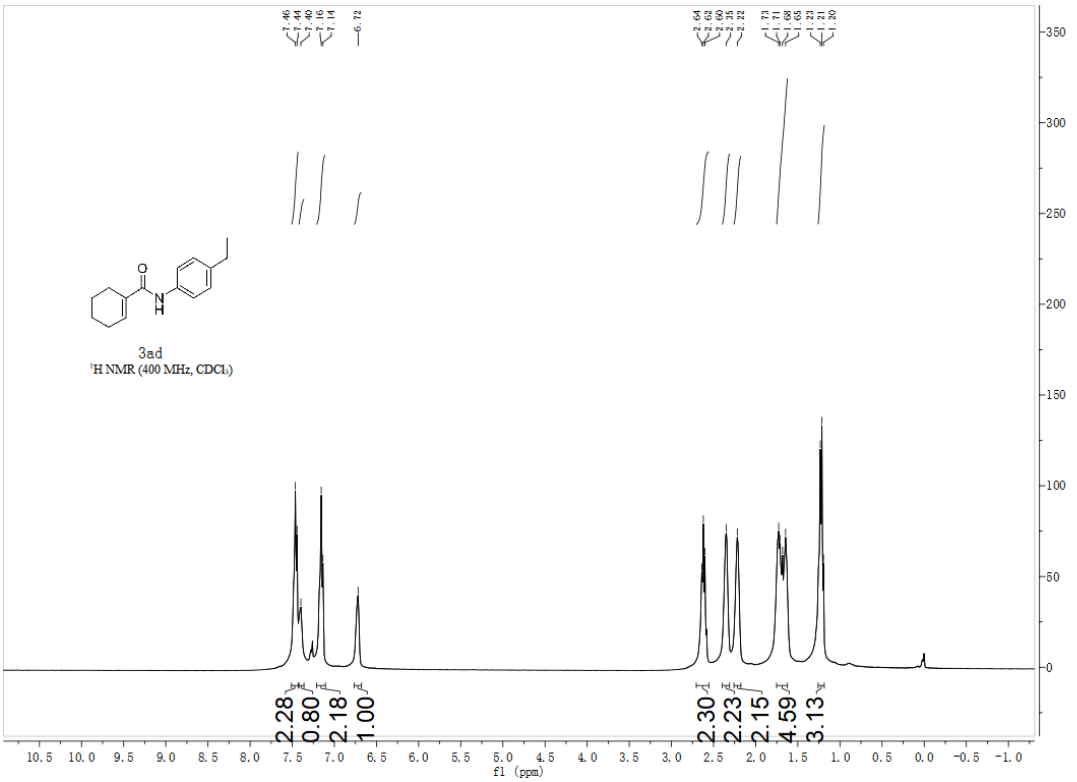


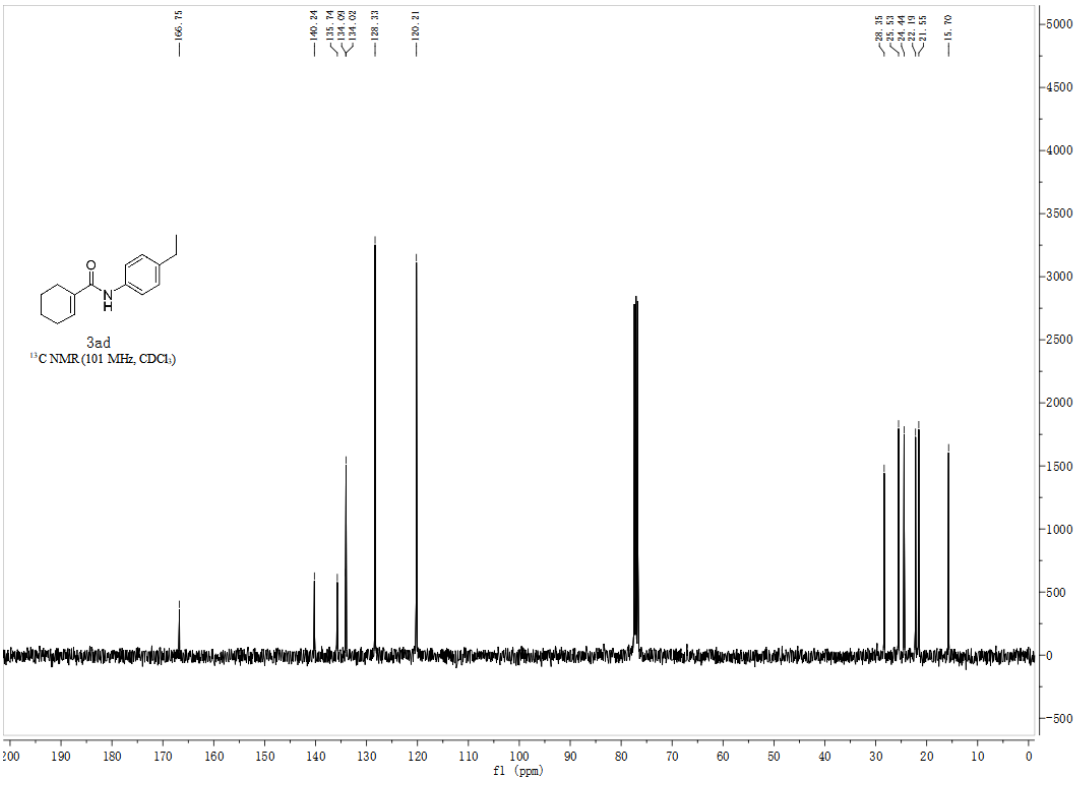

3ab
^{1}H NMR (400 MHz, CDCl$_3$)
7.44
7.42
7.13
7.11
6.72
6.71
6.71
2.34
2.34
2.31
2.31
2.21
2.21
2.20
2.19
2.12
1.71
1.71
1.69
1.64
1.64
1.63
1.96
0.78
2.03
1.00
2.10
3.25
2.15
4.40
f1 (ppm)

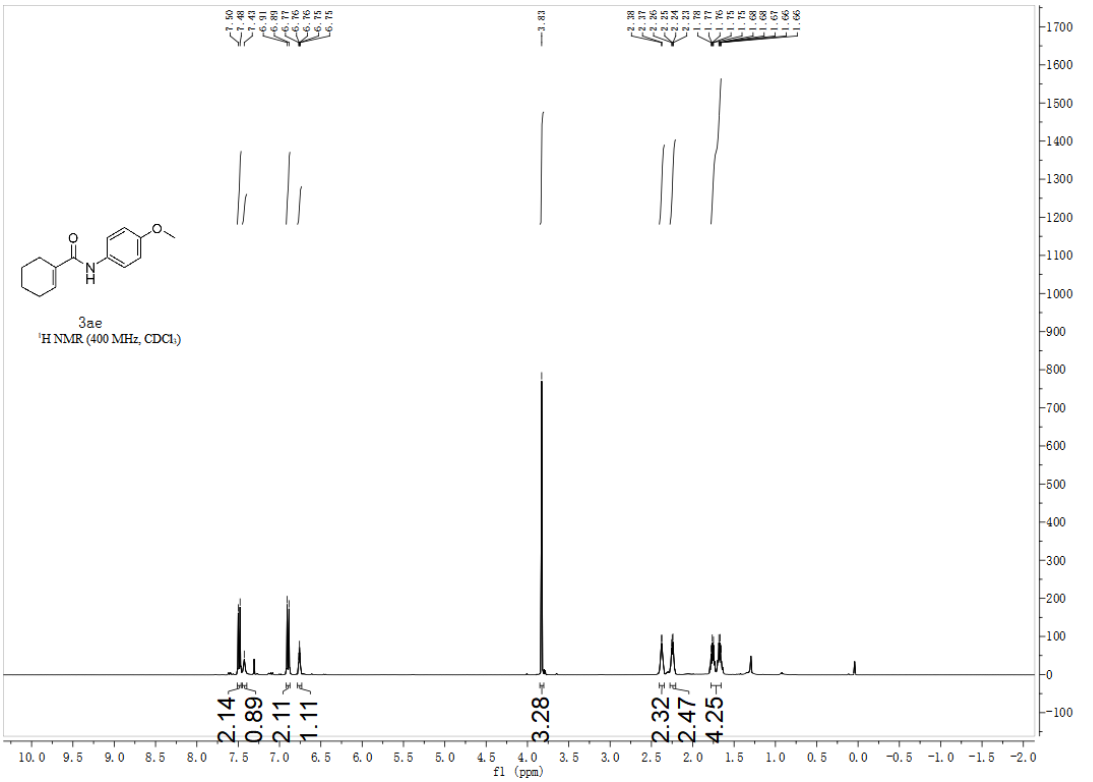

3ab
^{13}C NMR (101 MHz, CDCl$_3$)
166.65
135.49
133.99
133.94
133.67
129.41
120.05
25.44
24.35
22.11
21.47
20.81
f1 (ppm)

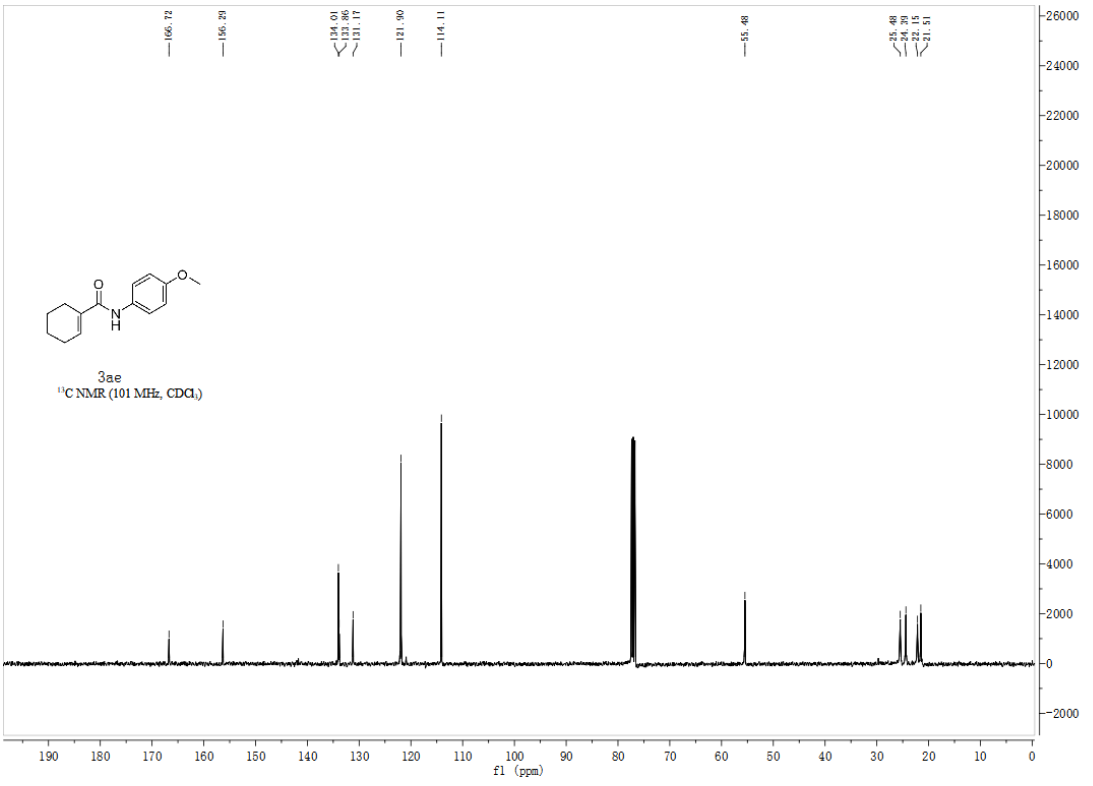

3ac
^{1}H NMR (400 MHz, CDCl$_3$)
1.04
0.76
1.09
0.97
0.98
1.00
5.25
2.13
4.19
f1 (ppm)

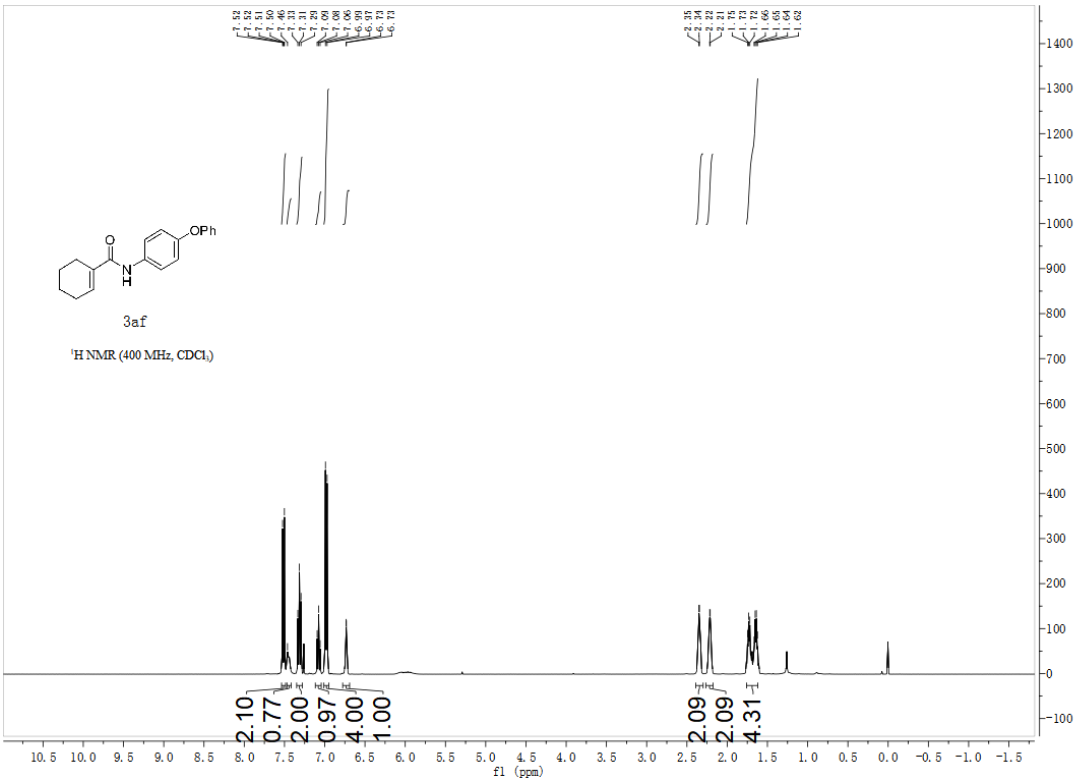

3ac
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

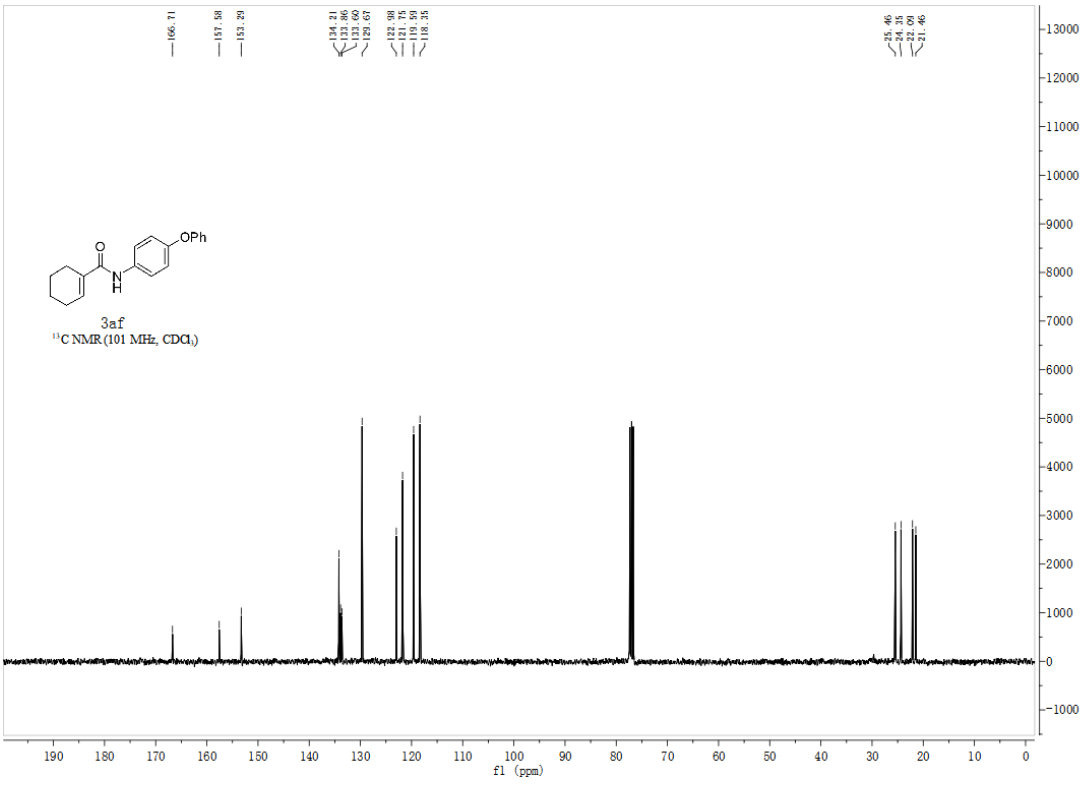

3ad
^{1}H NMR (400 MHz, CDCl$_3$)
7.46
7.44
7.40
7.16
7.14
6.72
2.64
2.62
2.60
2.35
2.22
1.73
1.71
1.68
1.65
1.23
1.21
1.20
2.28
0.80
2.18
1.00
2.30
2.23
2.15
4.59
3.13
f1 (ppm)

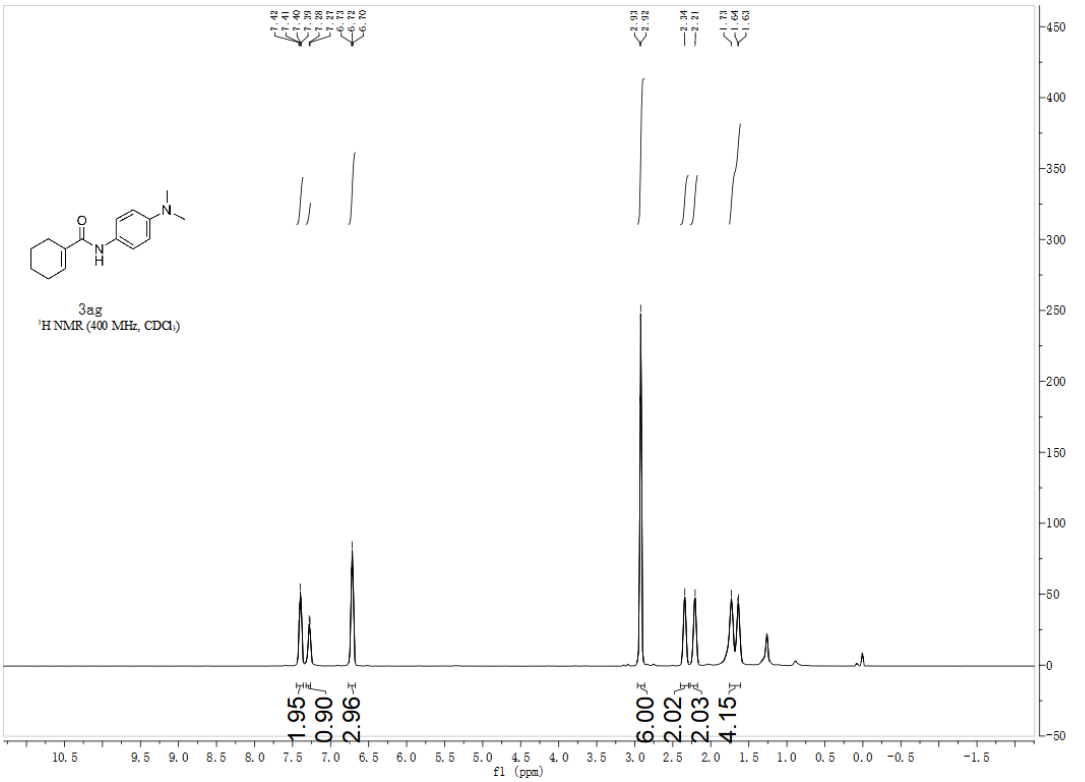

3ad
^{13}C NMR (101 MHz, CDCl$_3$)
166.75
140.24
135.74
134.09
134.02
128.33
120.21
28.35
25.53
24.44
22.19
21.15
15.70
f1 (ppm)

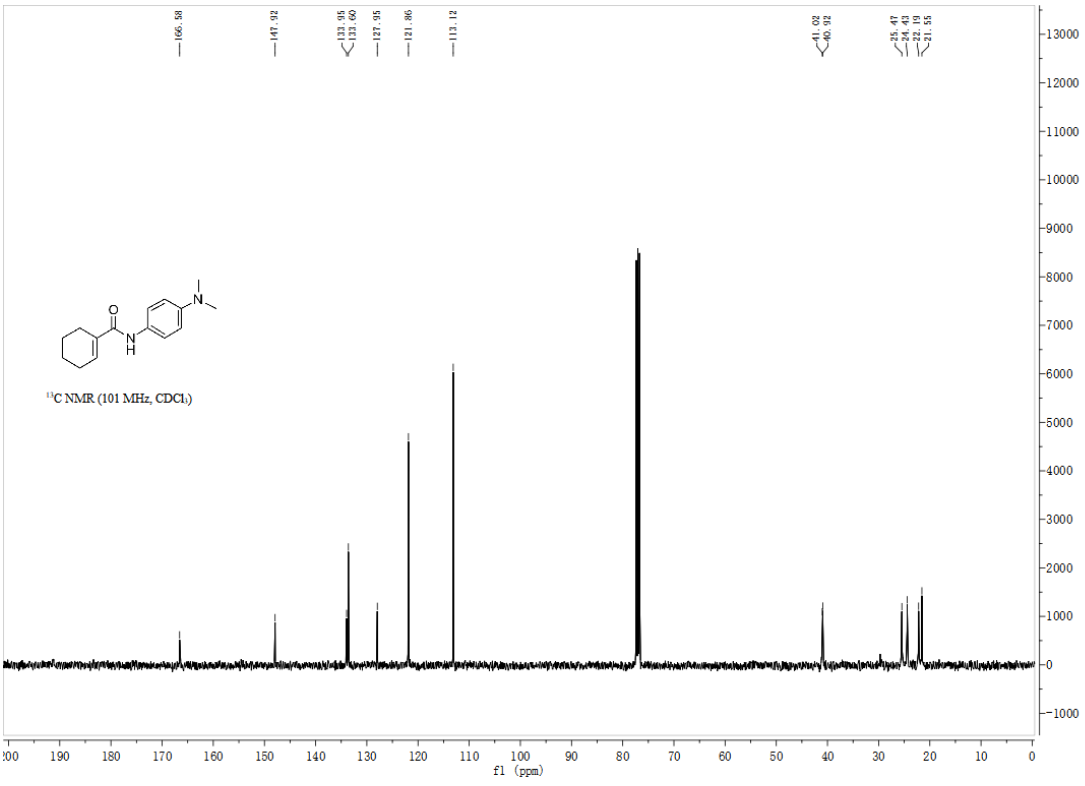

3ae
^{1}H NMR (400 MHz, CDCl$_3$)
7.50
7.48
7.47
7.45
6.91
6.89
6.77
6.76
6.76
6.75
6.75
3.83
2.38
2.37
2.26
2.25
2.24
2.23
1.78
1.77
1.76
1.75
1.75
1.73
1.68
1.68
1.67
1.66
1.66
2.14
0.89
2.11
1.11
3.28
2.32
2.47
4.25
f1 (ppm)

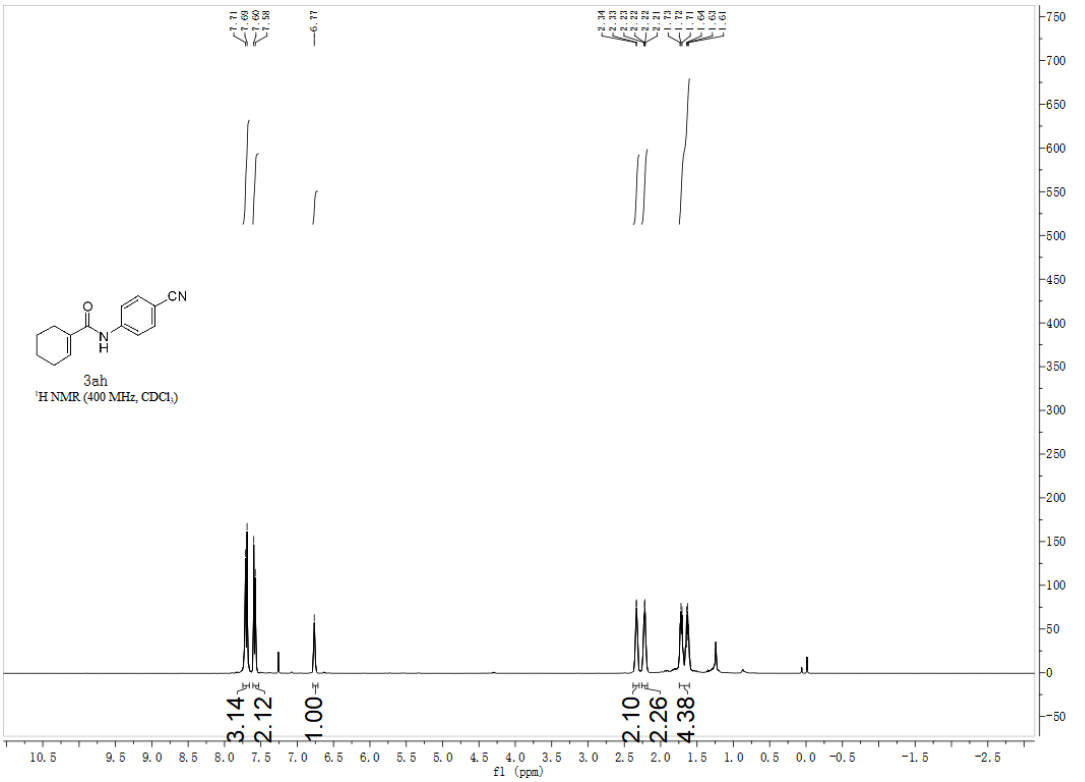

3ae
^{13}C NMR (101 MHz, CDCl$_3$)
166.72
156.29
134.01
133.86
131.17
121.90
114.11
55.48
25.48
24.39
22.15
21.51
f1 (ppm)

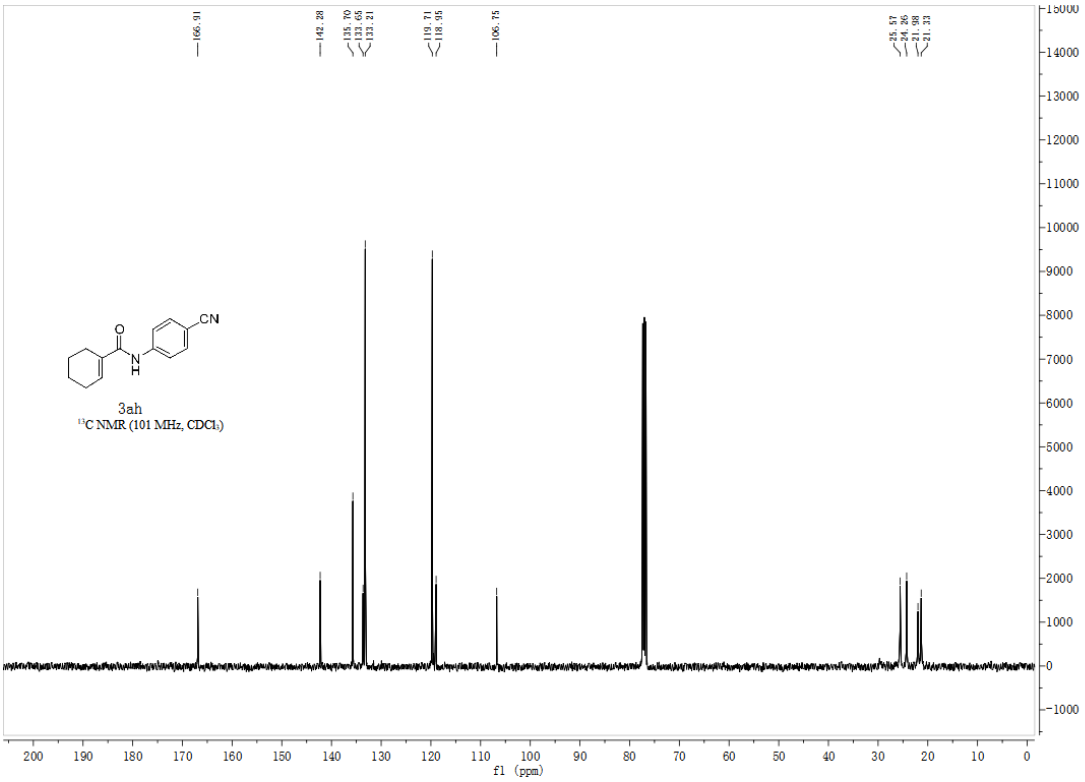

3af
^{1}H NMR (400 MHz, CDCl$_3$)
2.10
0.77
2.00
0.97
4.00
1.00
2.09
2.09
4.31
f1 (ppm)

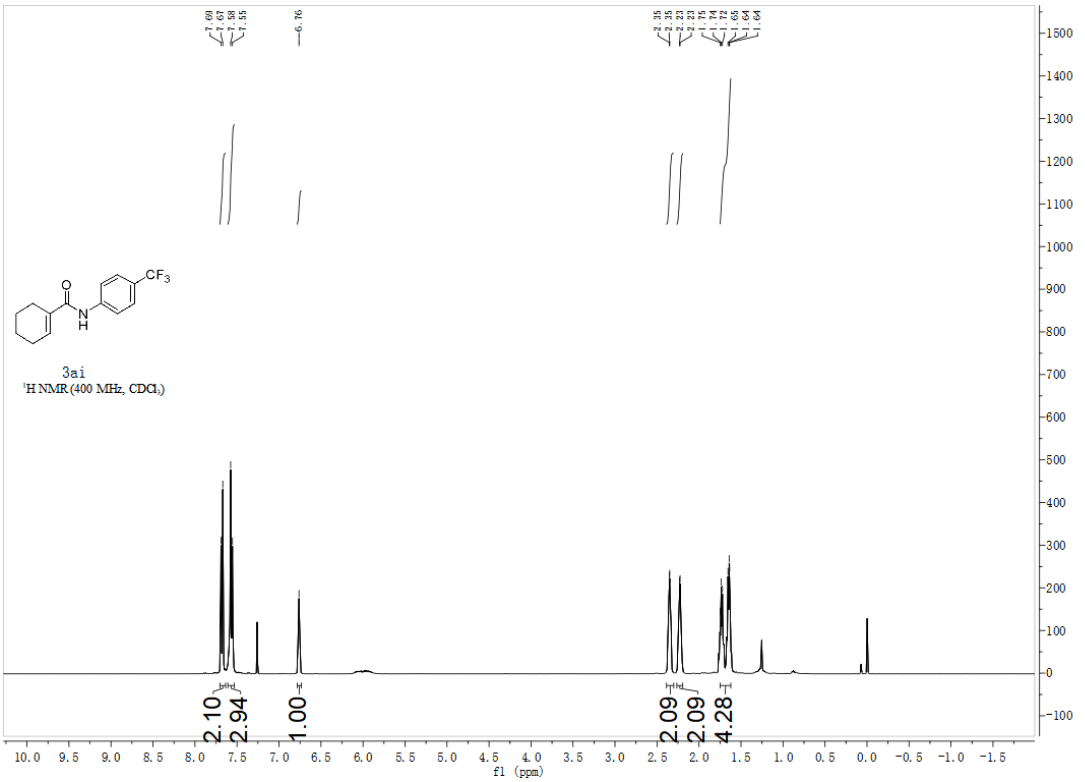

3af
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

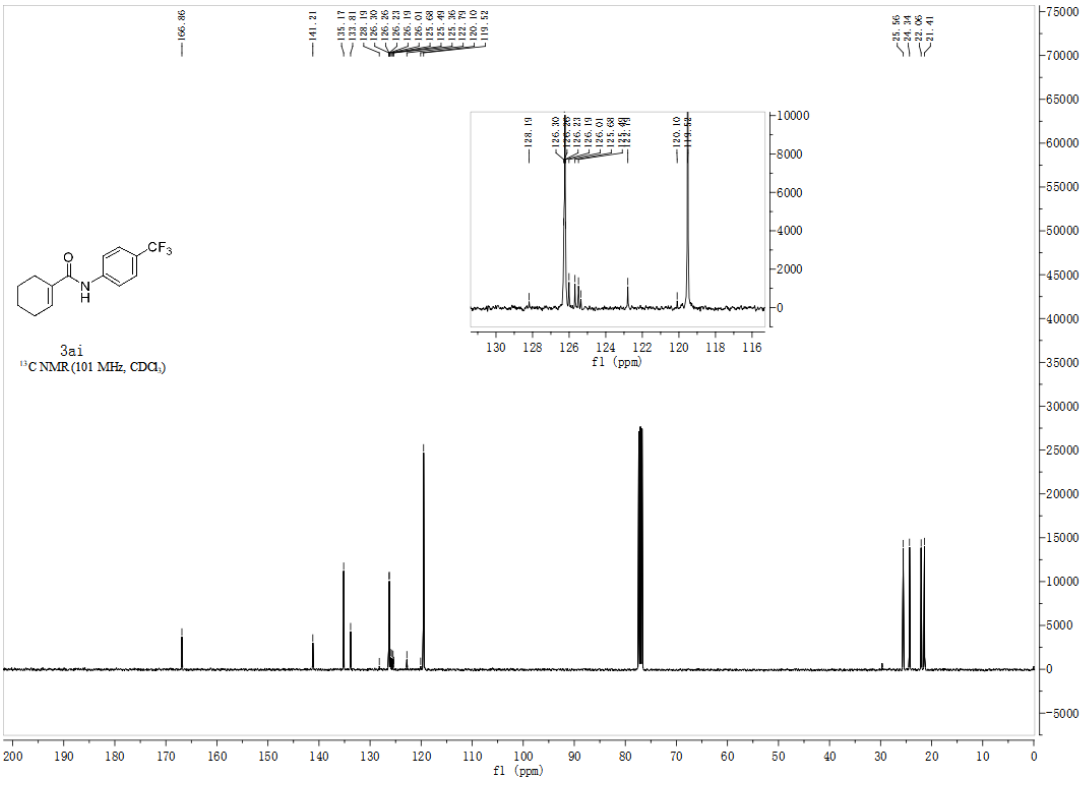

3ag
1H NMR (400 MHz, CDCl3)
1.95
0.90
2.96
6.00
2.02
2.03
4.15
f1 (ppm)

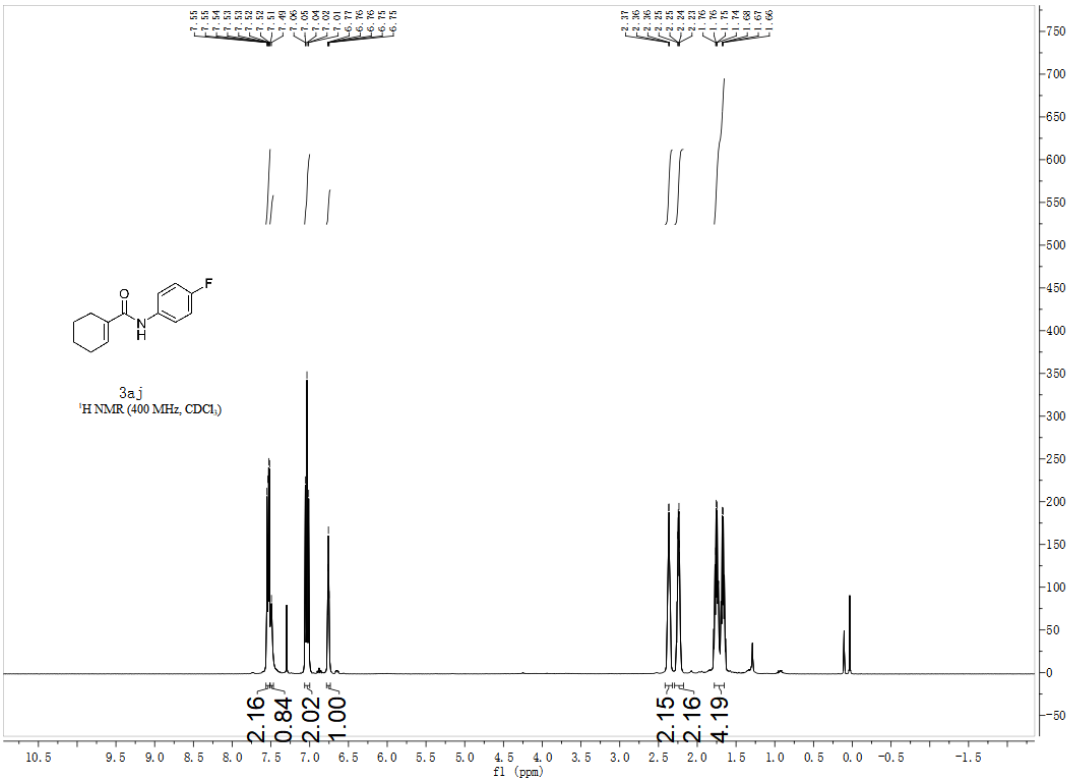

13C NMR (101 MHz, CDCl3)
f1 (ppm)

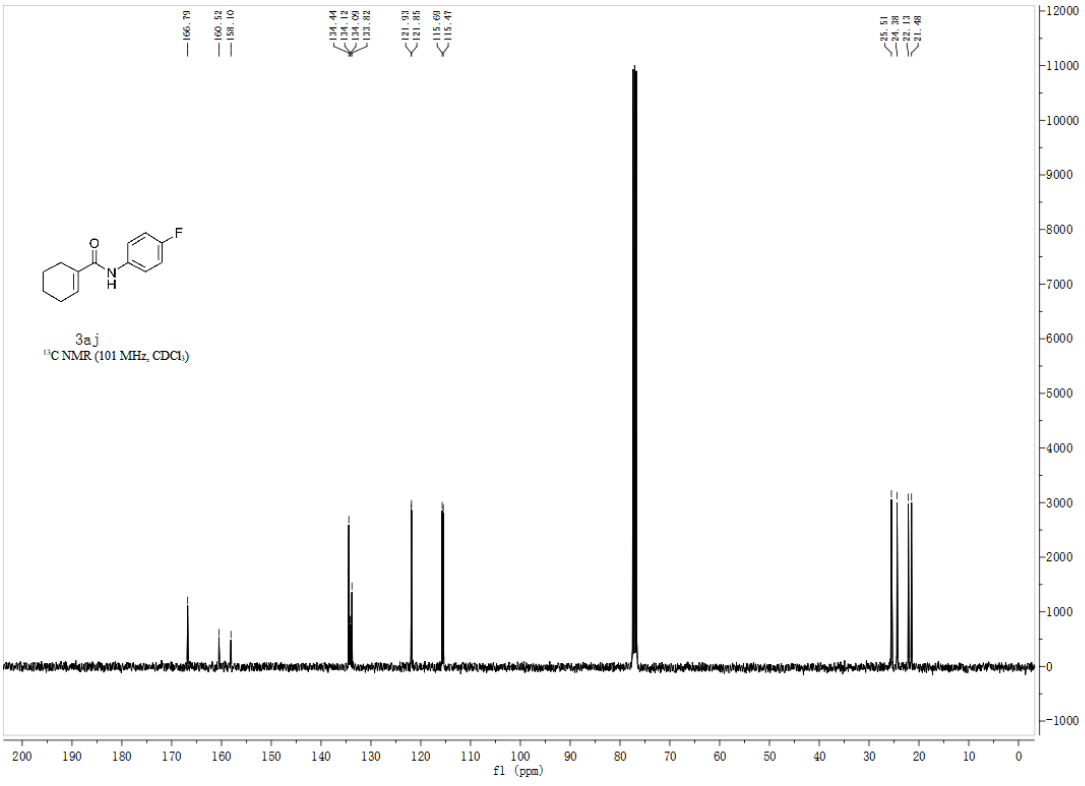

7.71
7.69
7.68
7.58
6.77
2.34
2.33
2.23
2.22
2.22
2.21
1.73
1.72
1.71
1.64
1.63
1.61
CN
O
N
H
3ah
¹H NMR (400 MHz, CDCl₃)
3.14
2.12
1.00
2.10
2.26
4.38
f1 (ppm)

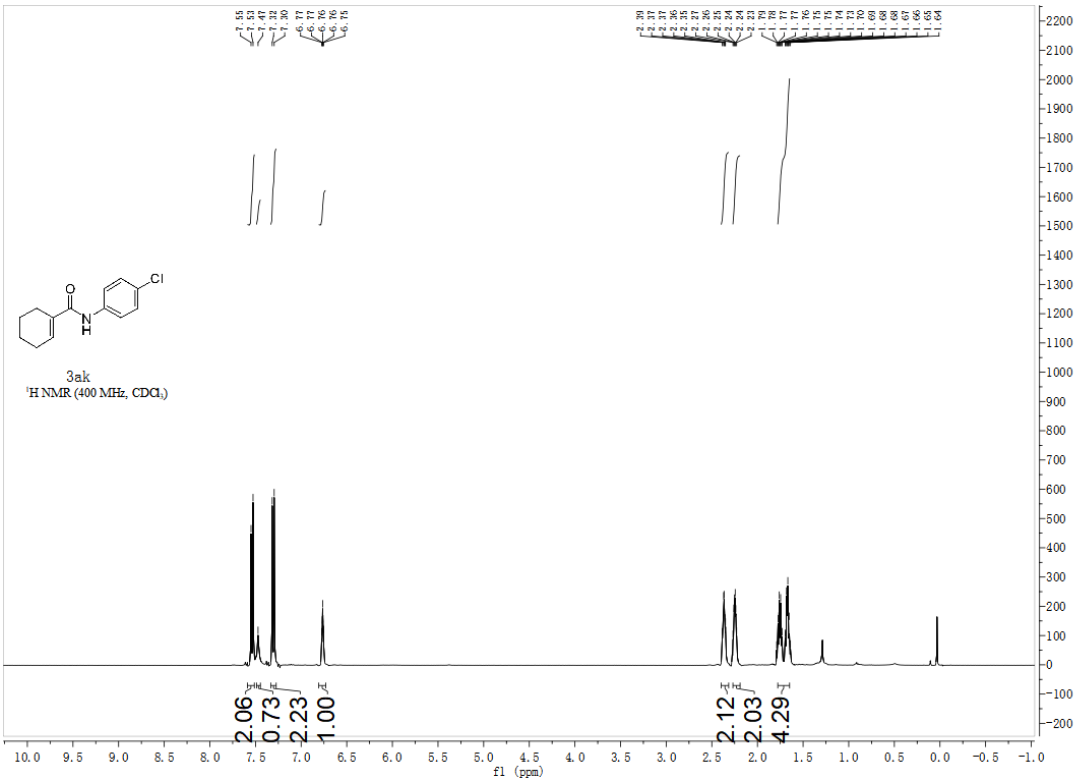

166.91
142.28
135.70
133.65
133.21
119.71
118.95
106.75
25.57
24.26
21.98
21.23
CN
O
N
H
3ah
¹³C NMR (101 MHz, CDCl₃)
f1 (ppm)

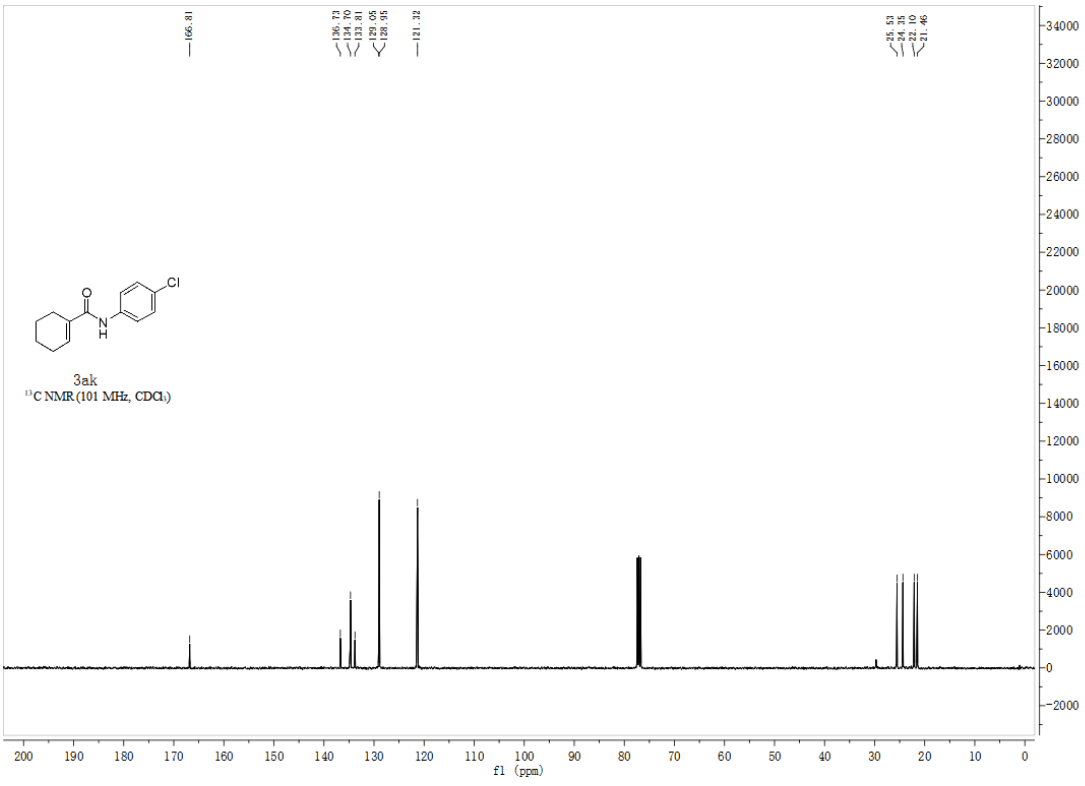

3ai
^{1}H NMR (400 MHz, CDCl$_3$)
2.10
2.94
1.00
2.09
2.09
4.28
f1 (ppm)

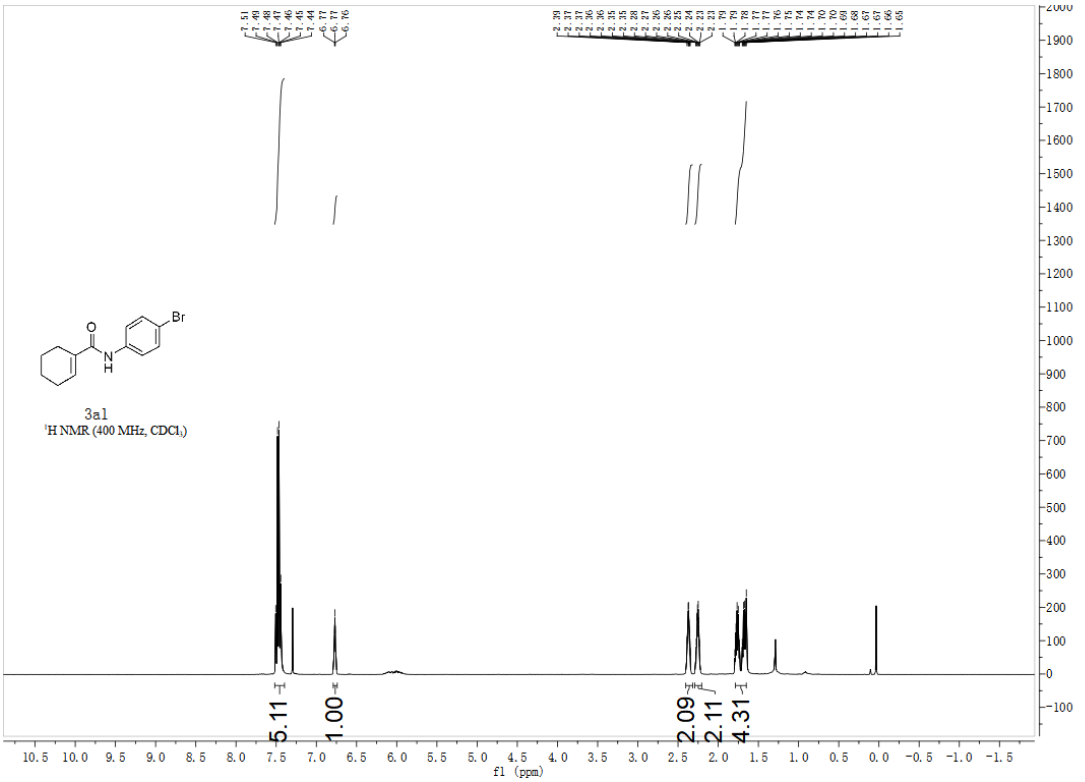

3ai
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

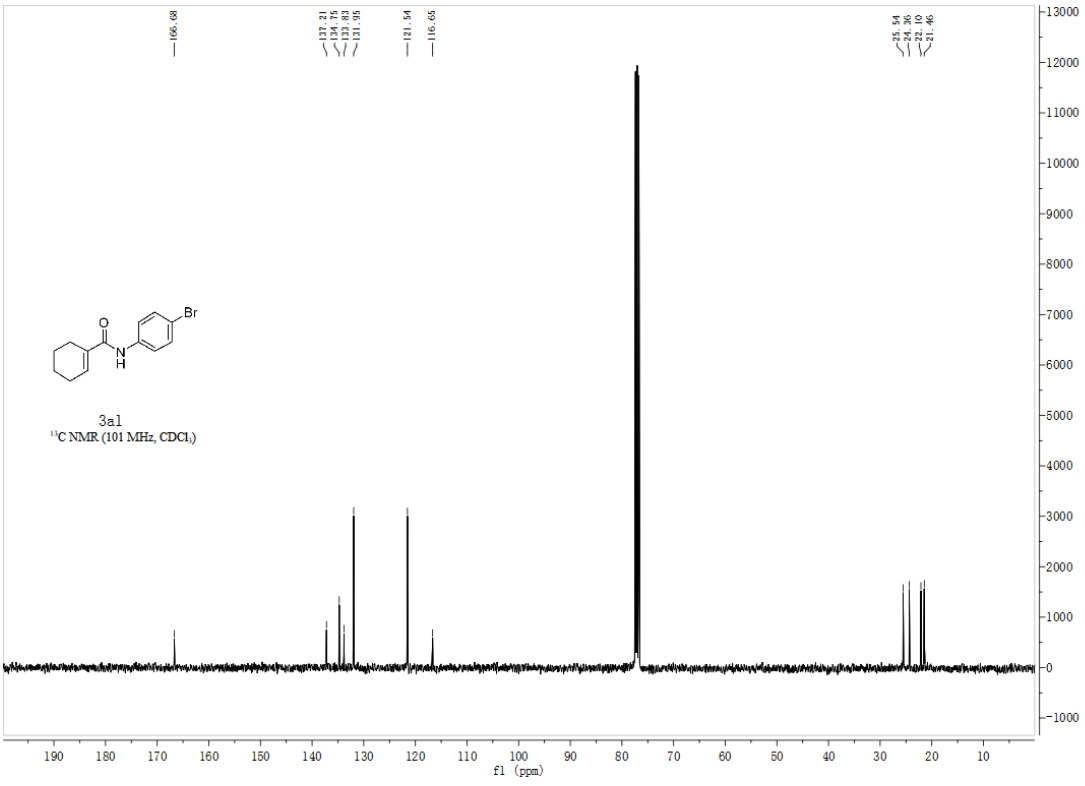

3a,j
1H NMR (400 MHz, CDCl3)
2.16
0.84
2.02
1.00
2.15
2.16
4.19
f1 (ppm)

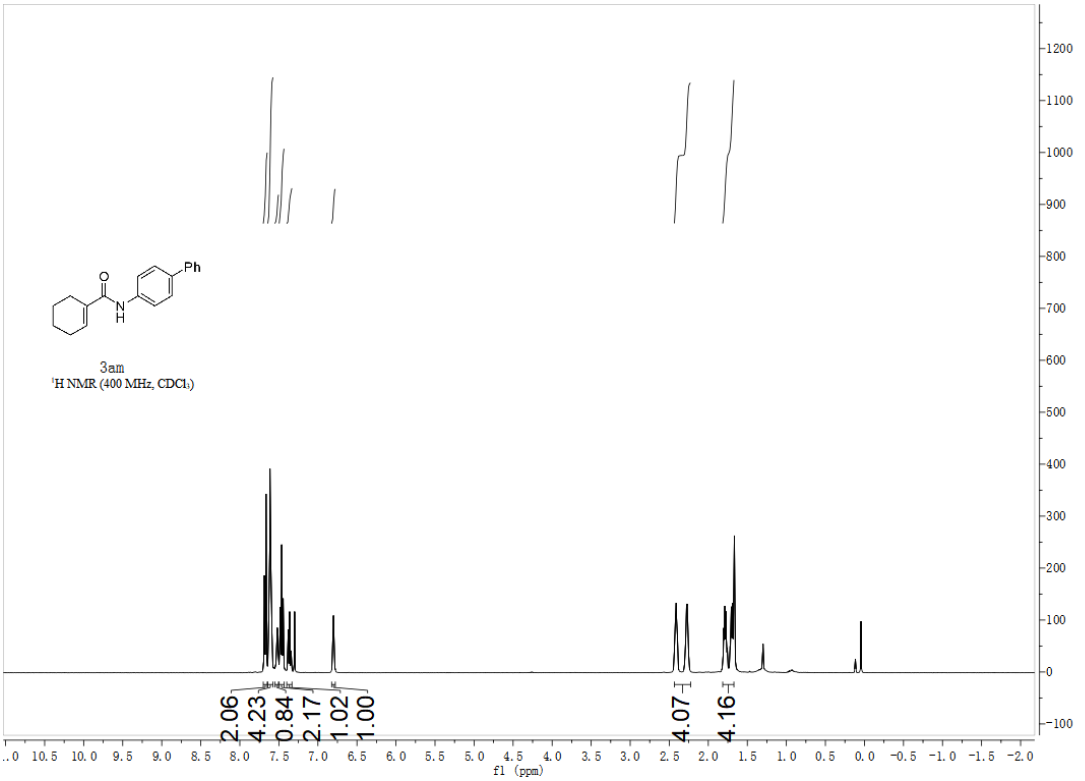

3a,j
13C NMR (101 MHz, CDCl3)
f1 (ppm)

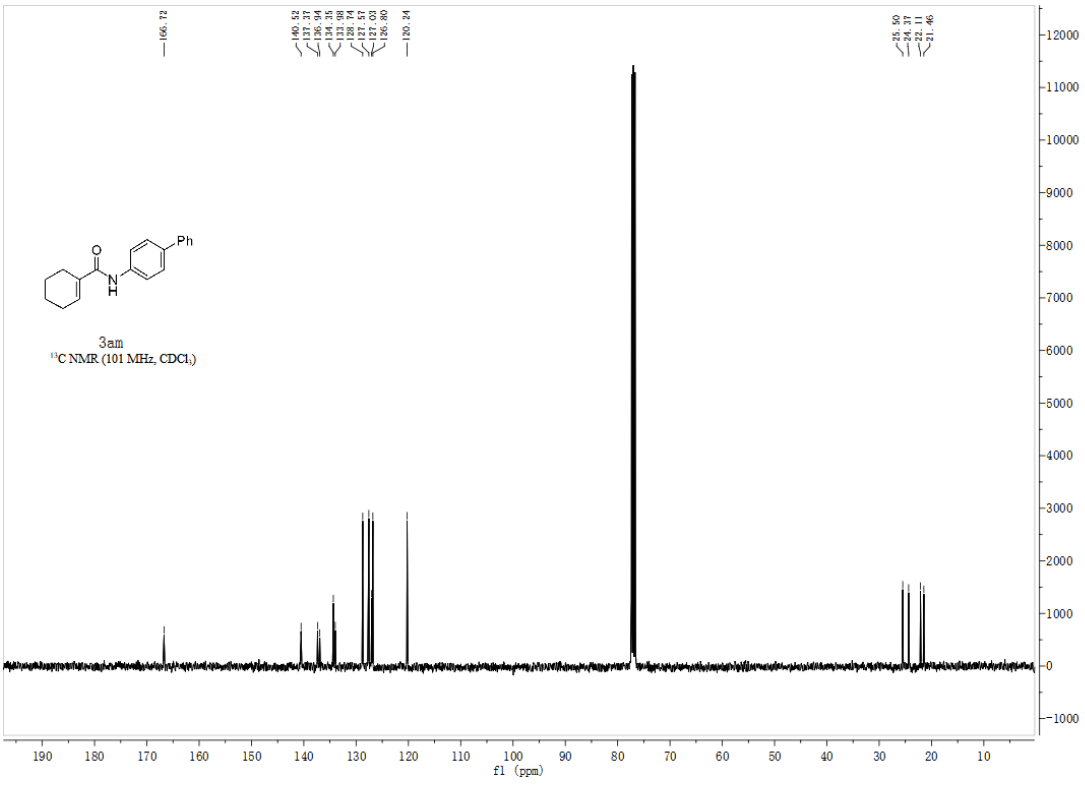

3ak
^{1}H NMR (400 MHz, CDCl$_3$)
2.06
0.73
2.23
1.00
2.12
2.03
4.29
f1 (ppm)

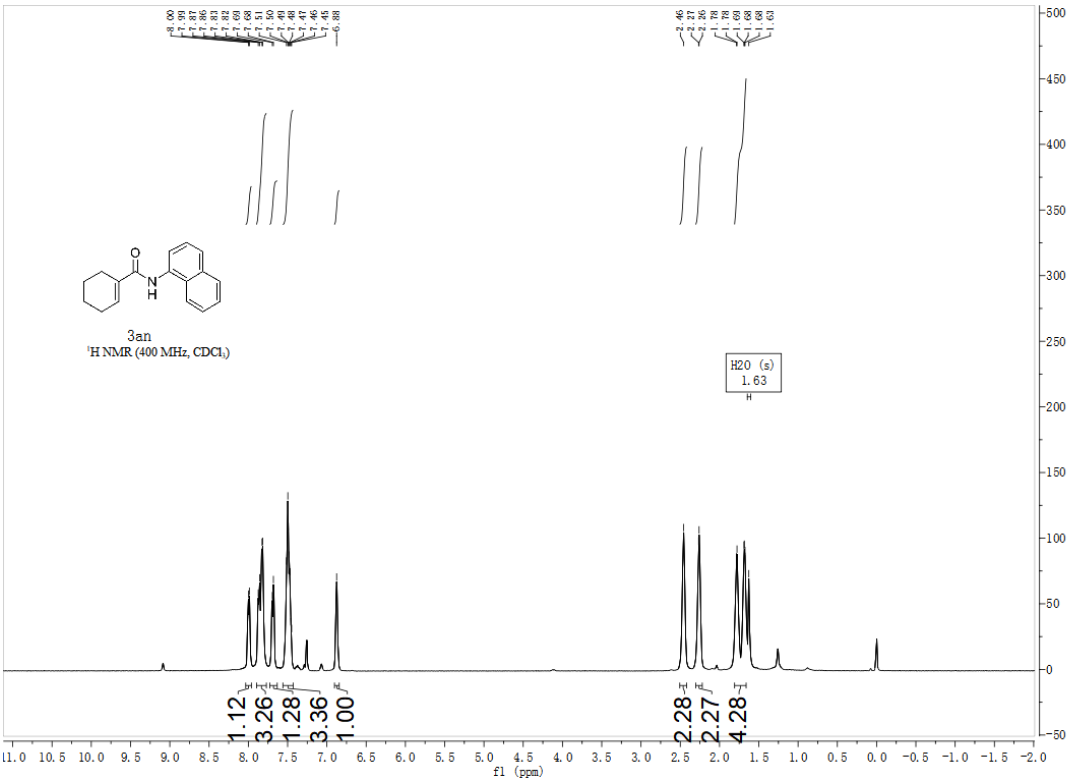

3ak
^{13}C NMR (101 MHz, CDCl$_3$)
166.81
136.73
134.70
133.81
129.05
128.95
121.32
25.53
24.35
22.10
21.46
f1 (ppm)

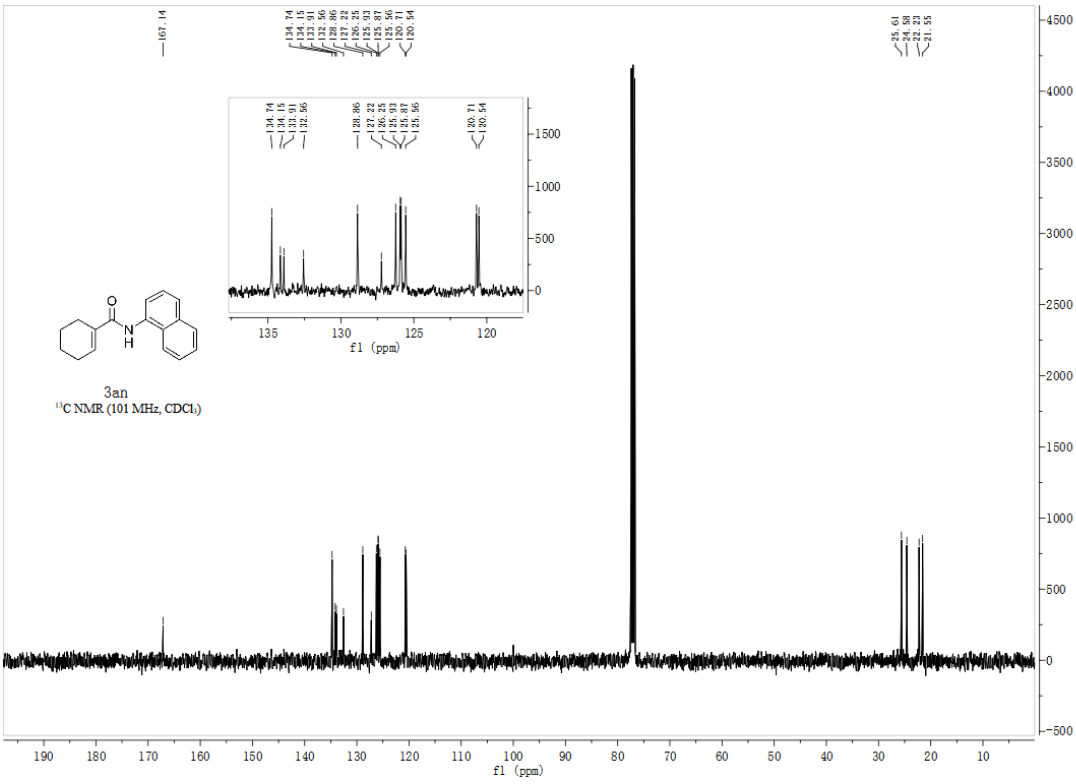

3al
1H NMR (400 MHz, CDCl3)
5.11
1.00
2.09
2.11
4.31
f1 (ppm)

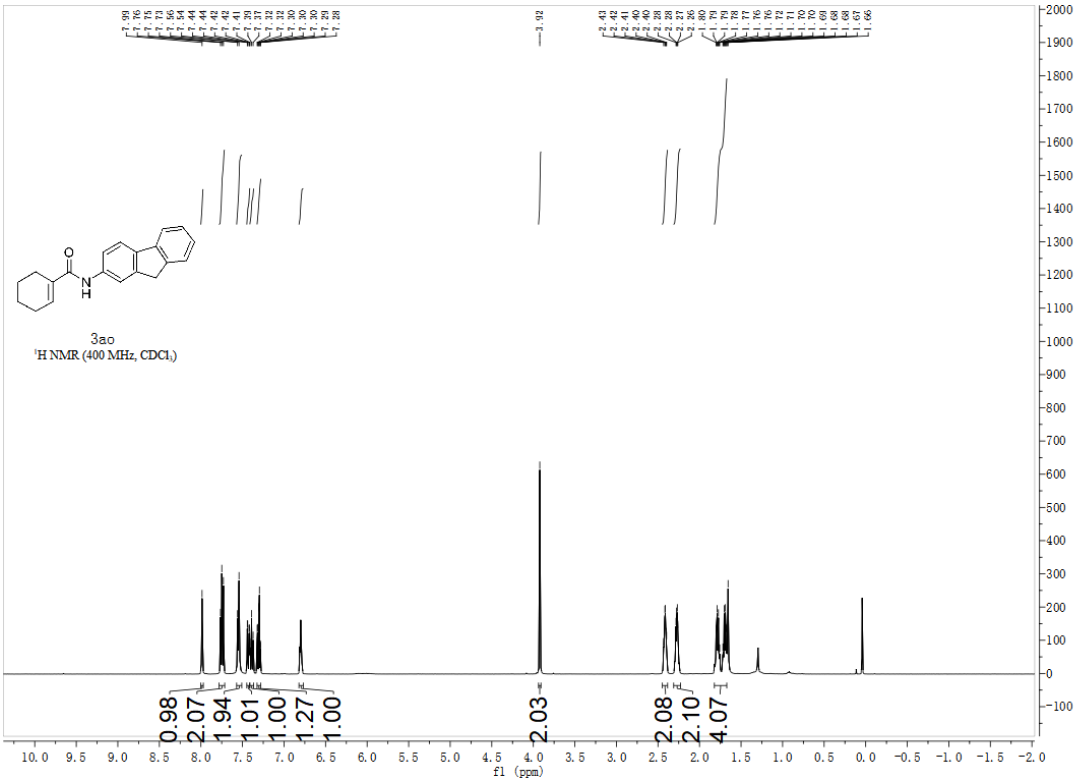

3al
13C NMR (101 MHz, CDCl3)
f1 (ppm)

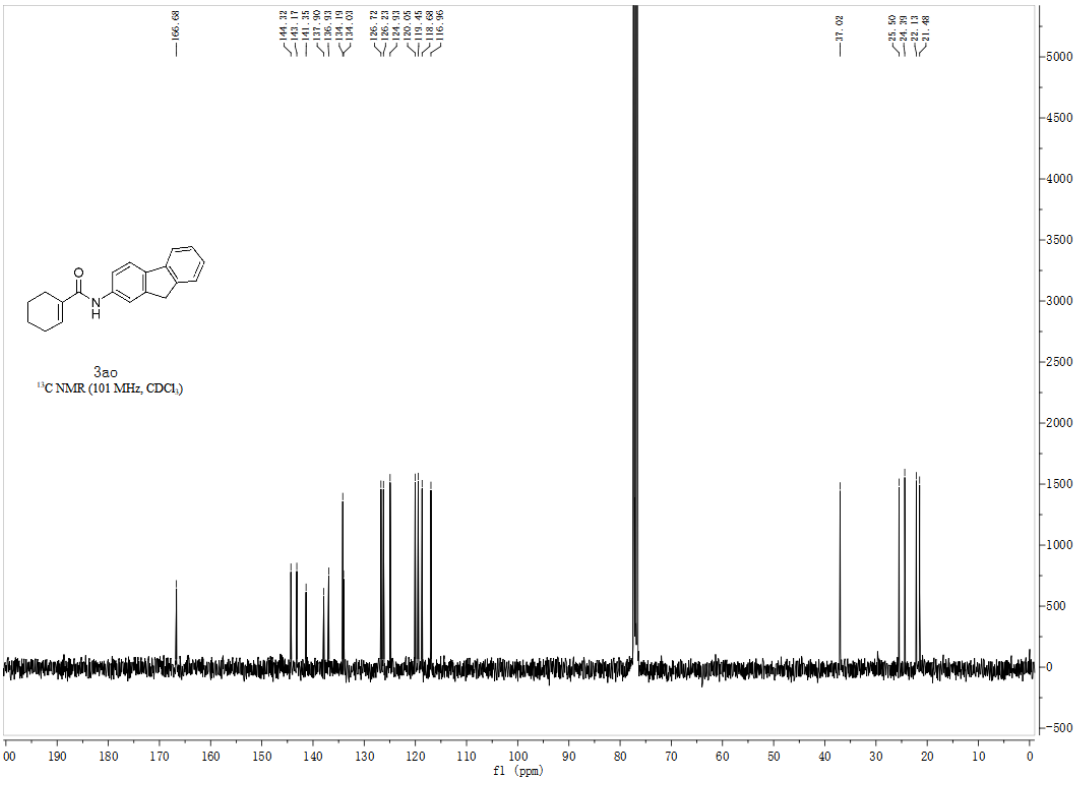

Ph
O
N
H
3am
^{1}H NMR (400 MHz, CDCl$_3$)
2.06
4.23
0.84
2.17
1.02
1.00
4.07
4.16
f1 (ppm)

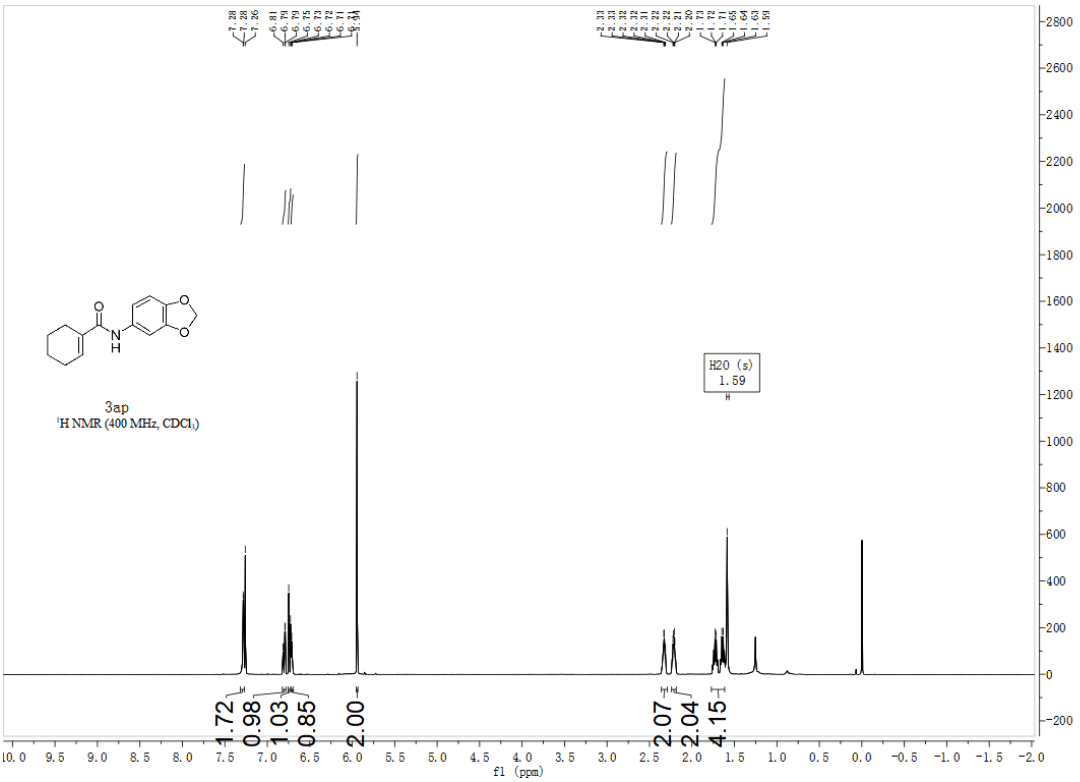

Ph
O
N
H
3am
^{13}C NMR (101 MHz, CDCl$_3$)
166.72
140.52
137.37
136.94
134.35
133.98
129.04
127.57
127.03
126.80
120.24
25.50
24.37
22.11
21.46
f1 (ppm)

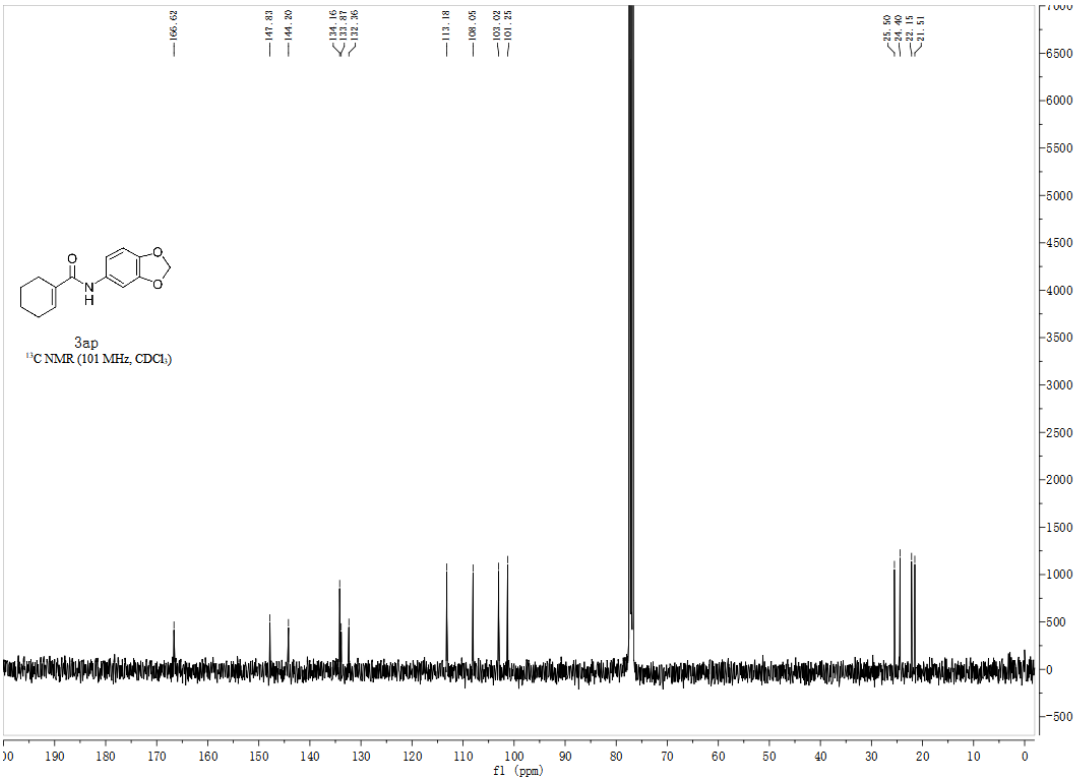

3an
^{1}H NMR (400 MHz, CDCl$_3$)
H2O (s)
1.63
1.12
3.26
1.28
3.36
1.00
2.28
2.27
4.28
f1 (ppm)

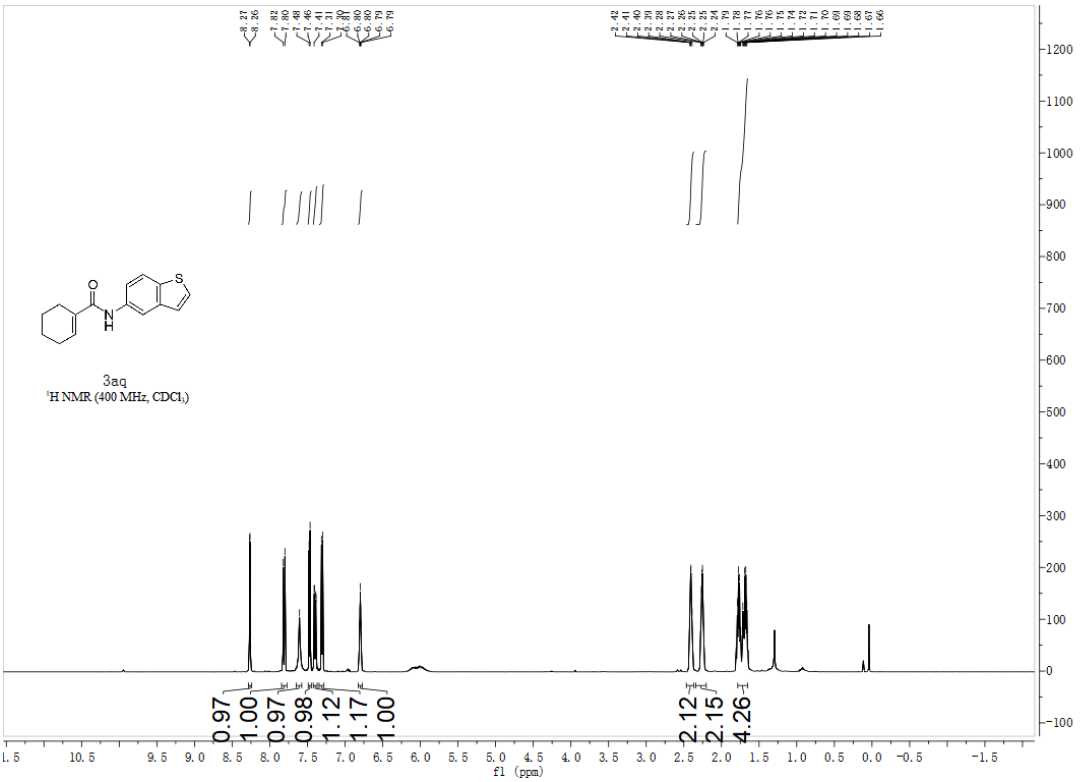

3an
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

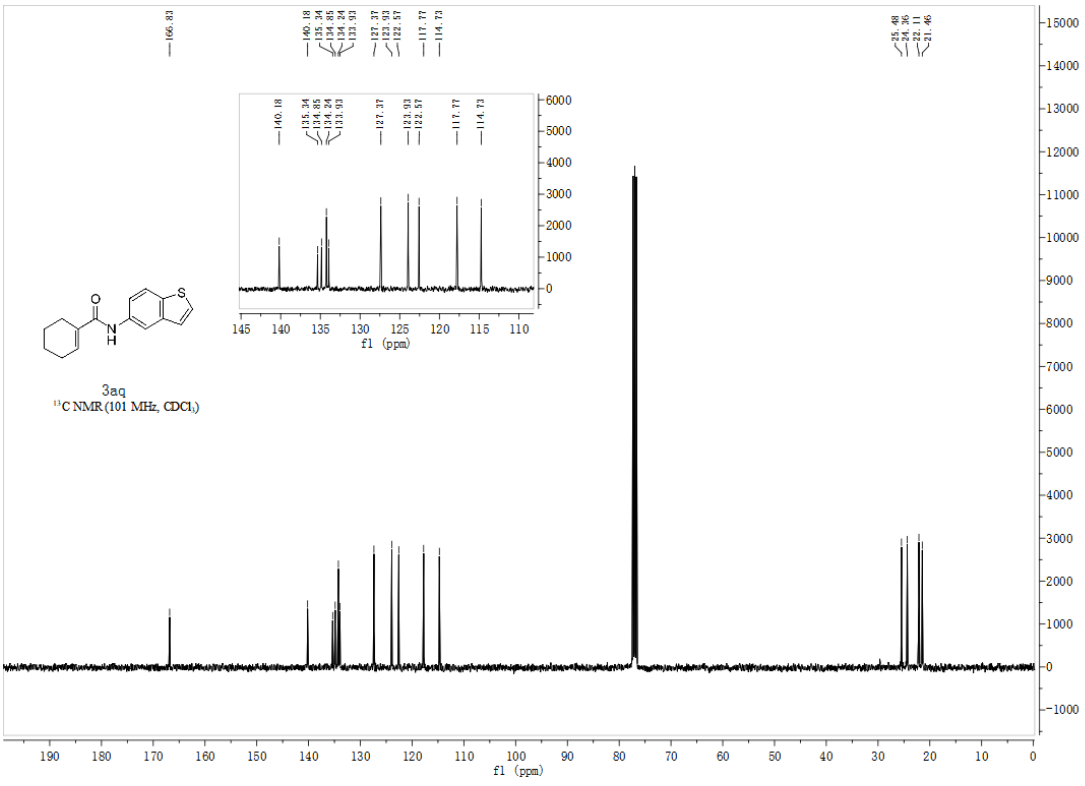

3ao
^{1}H NMR (400 MHz, CDCl$_3$)
0.98
2.07
1.94
1.01
1.00
1.27
1.00
2.03
2.08
2.10
4.07
f1 (ppm)

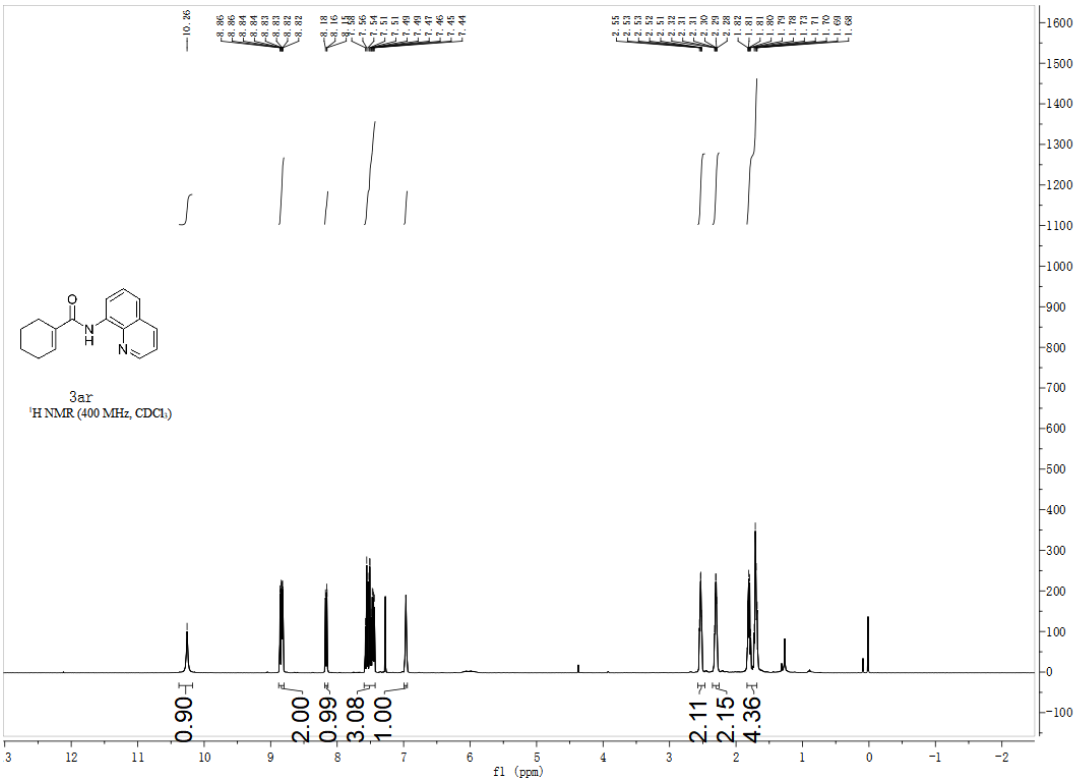

3ao
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

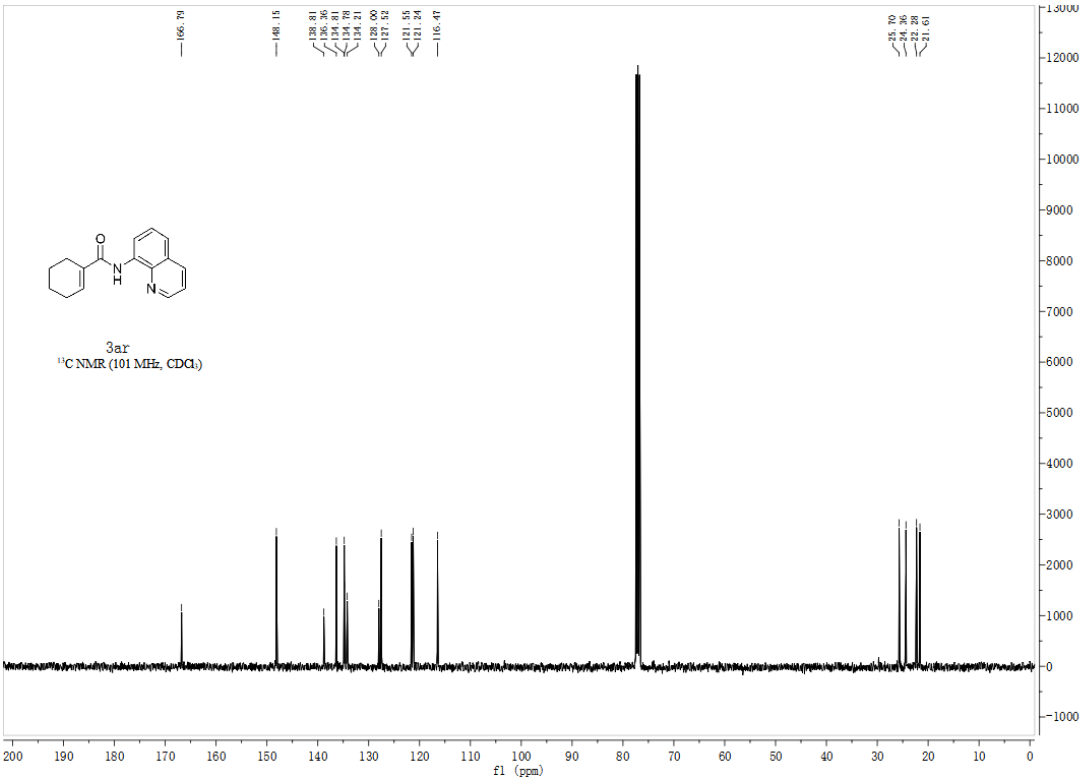

3ap
^{1}H NMR (400 MHz, CDCl$_3$)
H2O (s)
1.59
1.72
0.98
1.03
0.85
2.00
2.07
2.04
4.15
f1 (ppm)

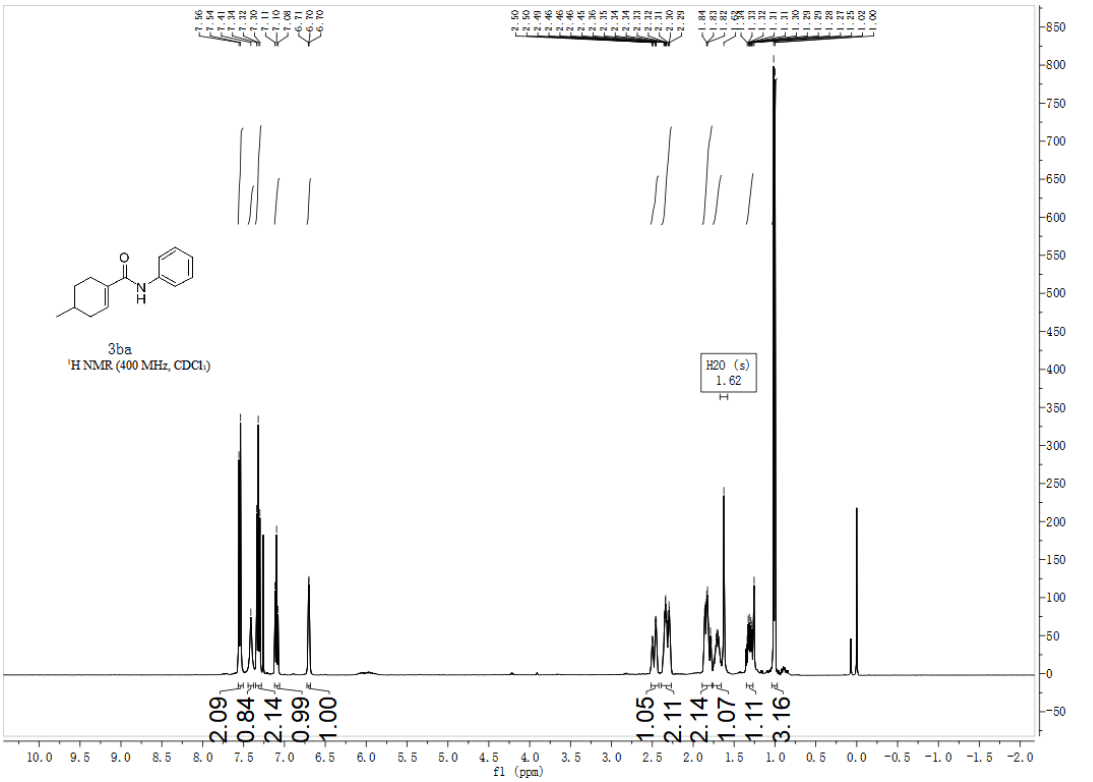

3ap
^{13}C NMR (101 MHz, CDCl$_3$)
166.62
147.83
144.20
134.16
133.87
132.36
113.18
108.05
103.02
101.25
25.50
24.40
21.15
21.51
f1 (ppm)

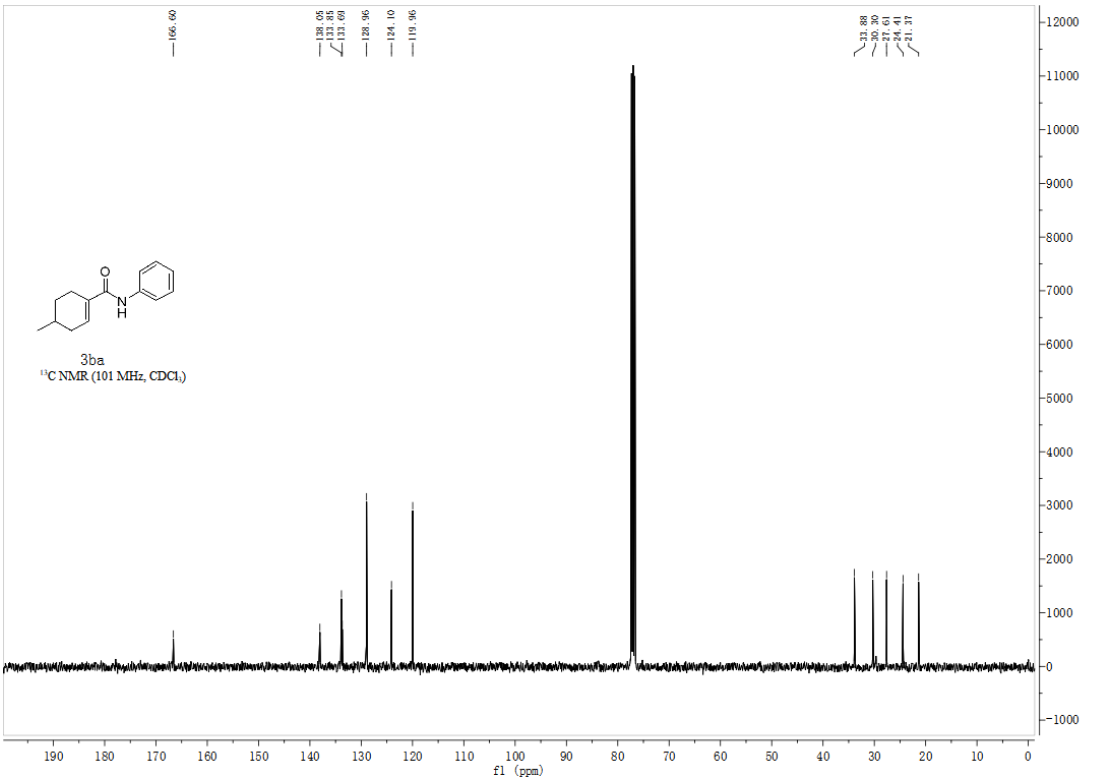

3aq
^{1}H NMR (400 MHz, CDCl$_3$)
0.97
1.00
0.97
0.98
1.12
1.17
1.00
2.12
2.15
4.26
f1 (ppm)

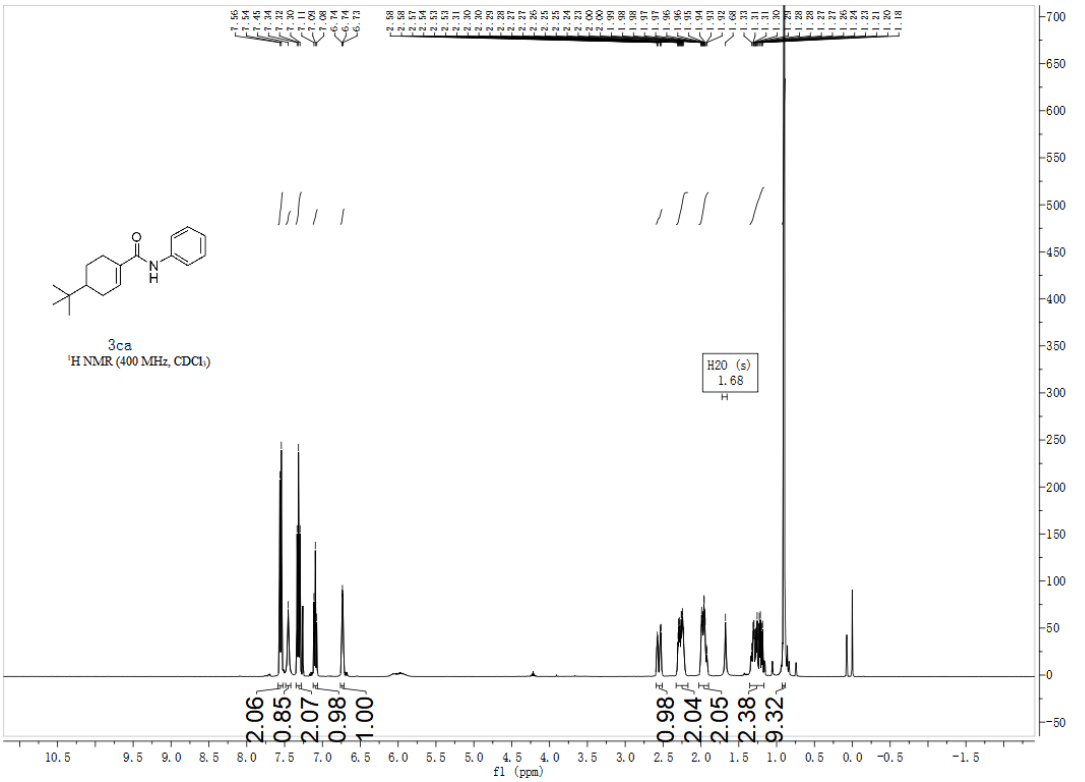

3aq
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

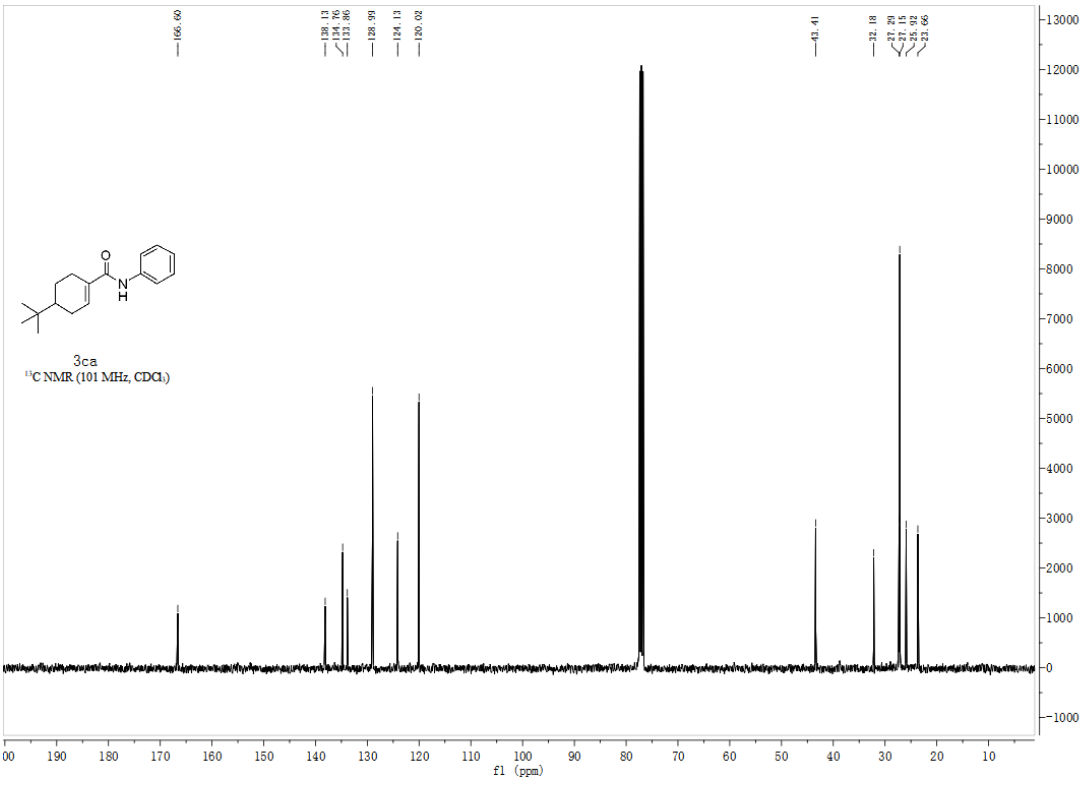

3ar
^{1}H NMR (400 MHz, CDCl$_3$)
0.90
2.00
0.99
3.08
1.00
2.11
2.15
4.36
f1 (ppm)

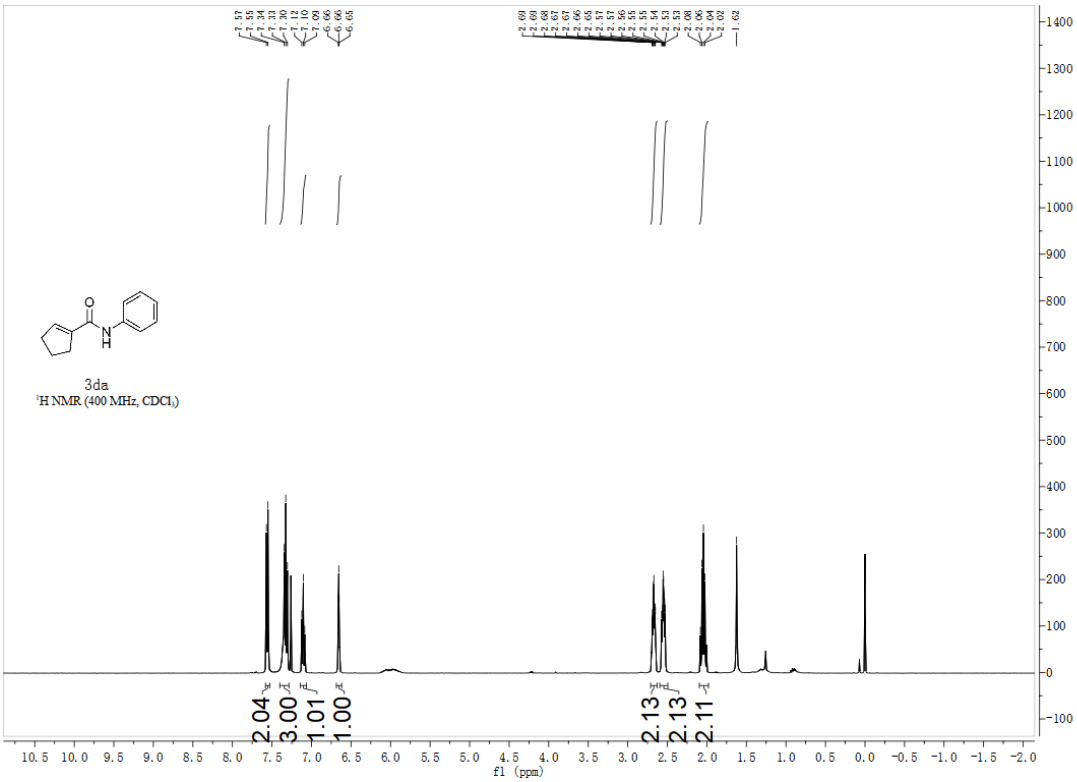

3ar
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

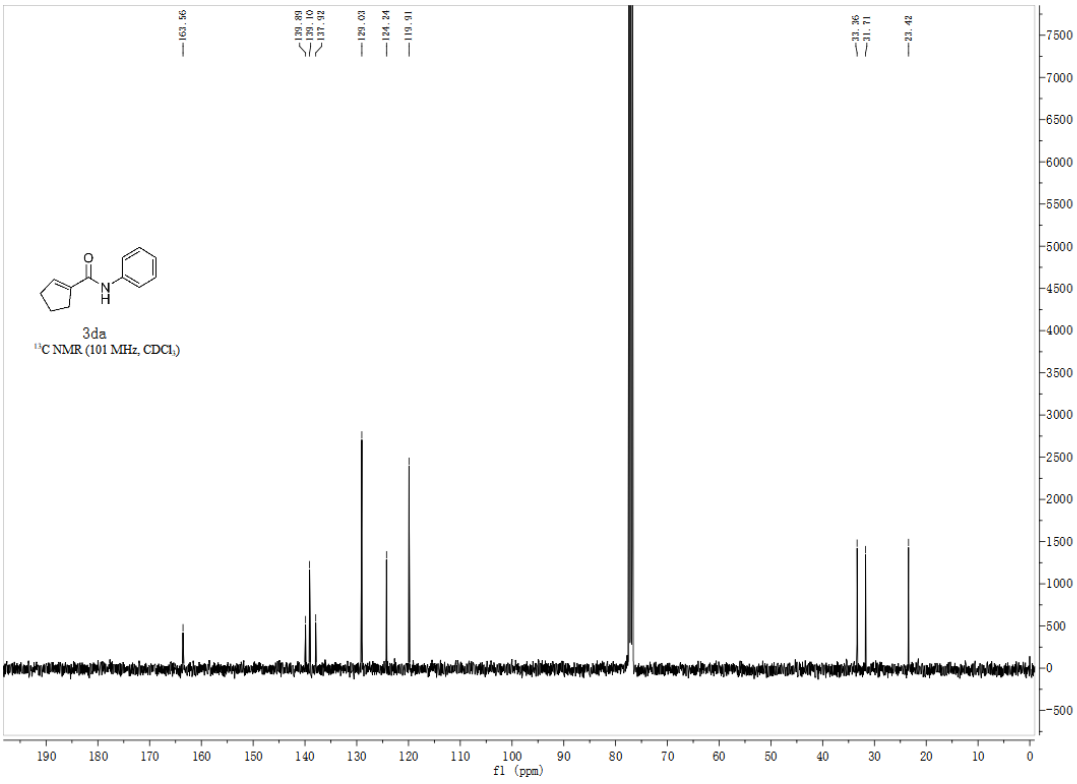

3ba
¹H NMR (400 MHz, CDCl₃)
H20 (s)
1.62
2.09
0.84
2.14
0.99
1.00
1.05
2.11
2.14
1.07
1.11
3.16
f1 (ppm)

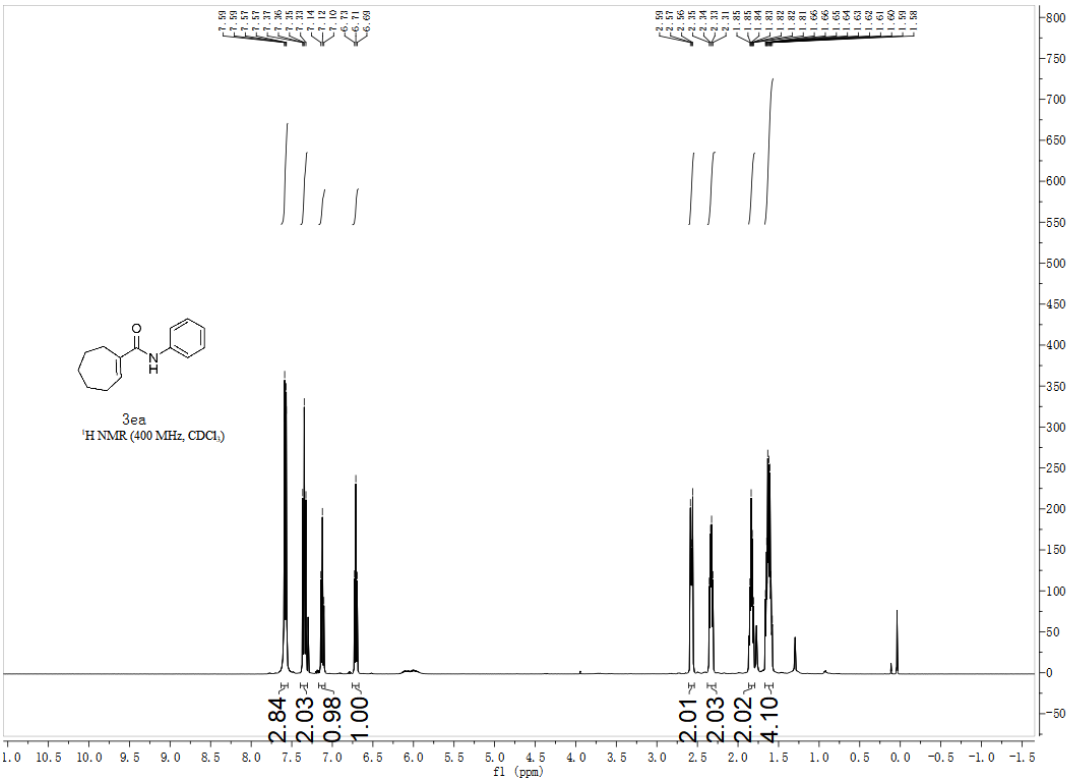

3ba
¹³C NMR (101 MHz, CDCl₃)
166.60
138.05
133.85
133.69
128.96
124.10
119.96
23.88
20.30
27.61
24.41
21.37
f1 (ppm)

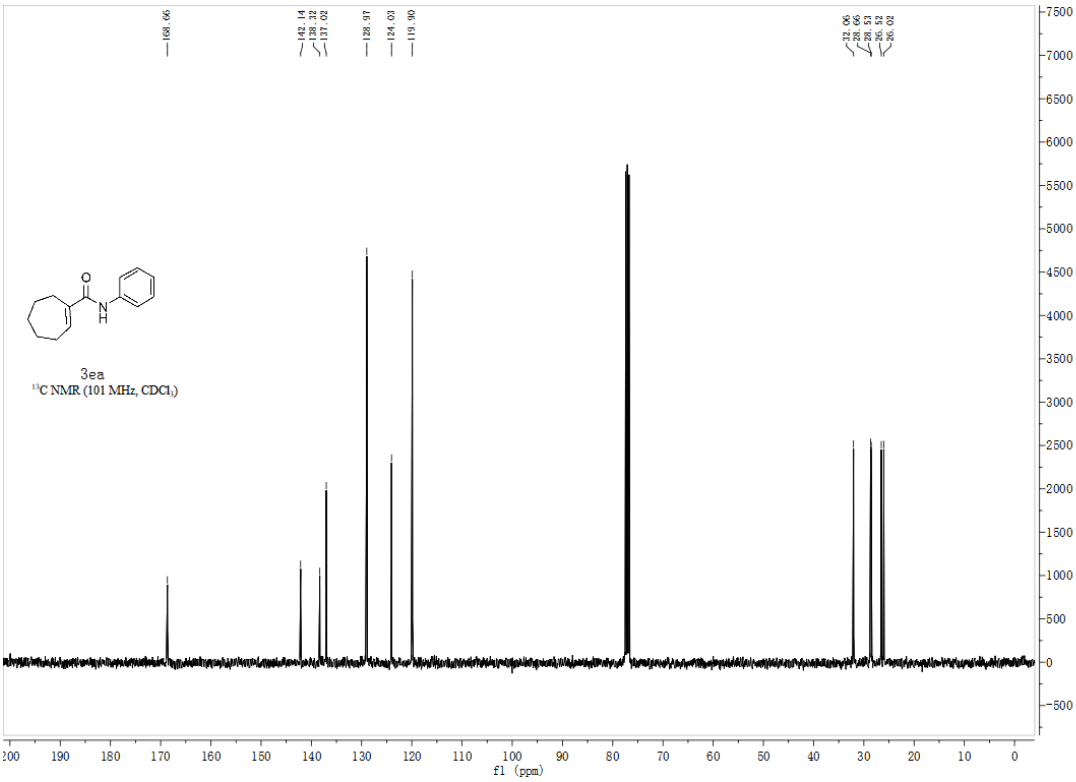

3ca
¹H NMR (400 MHz, CDCl₃)
H20 (s)
1.68
2.06
0.85
2.07
0.98
1.00
0.98
2.04
2.05
2.38
9.32
f1 (ppm)

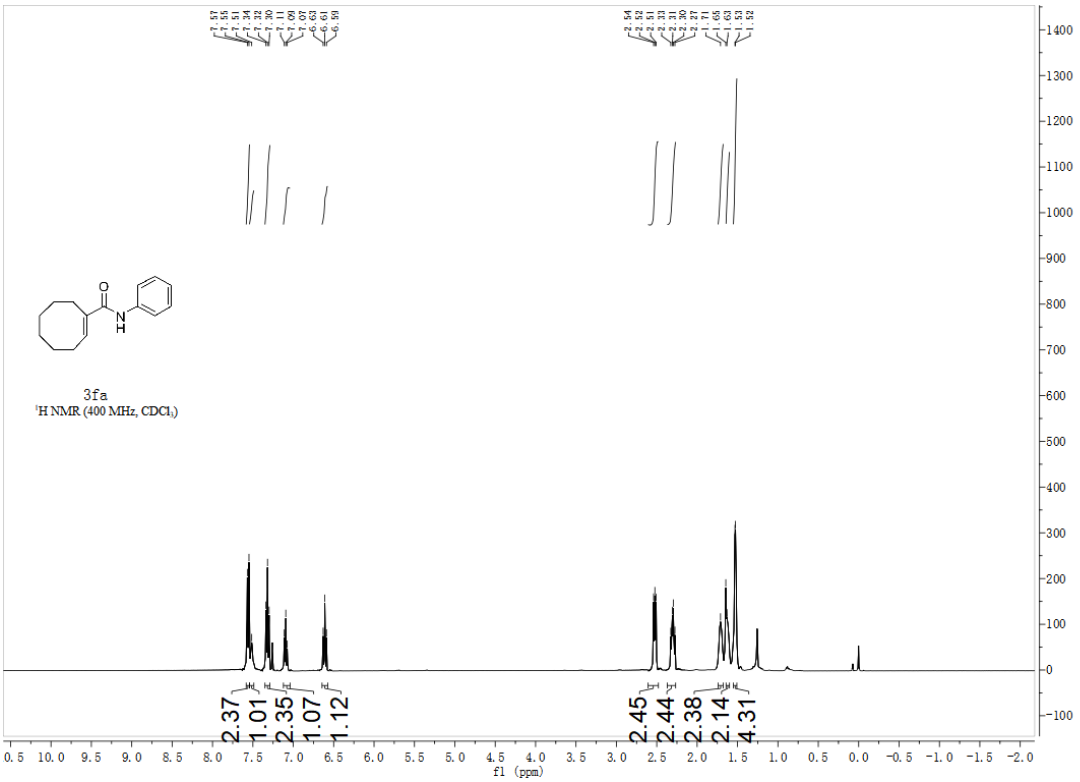

166.60
138.13
134.96
133.86
128.99
124.13
120.02
43.41
32.18
27.29
27.15
25.92
23.66
3ca
¹³C NMR (101 MHz, CDCl₃)
f1 (ppm)

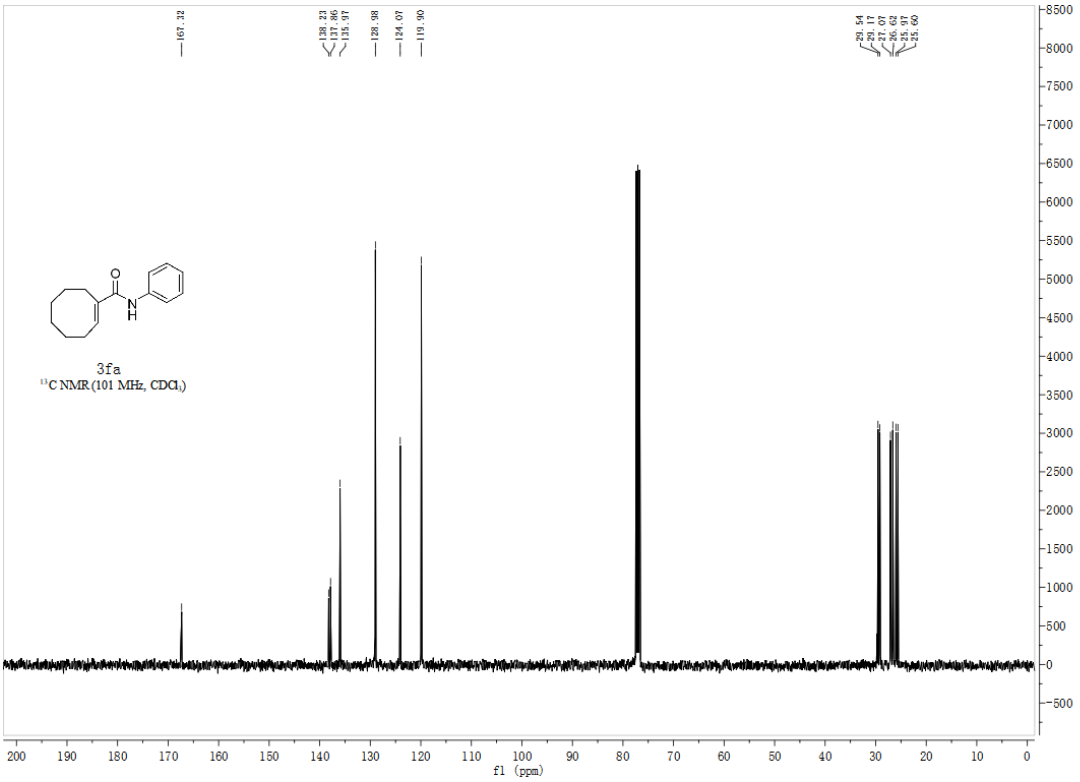

3da
^{1}H NMR (400 MHz, CDCl$_3$)
2.04
3.00
1.01
1.00
2.13
2.13
2.11
f1 (ppm)

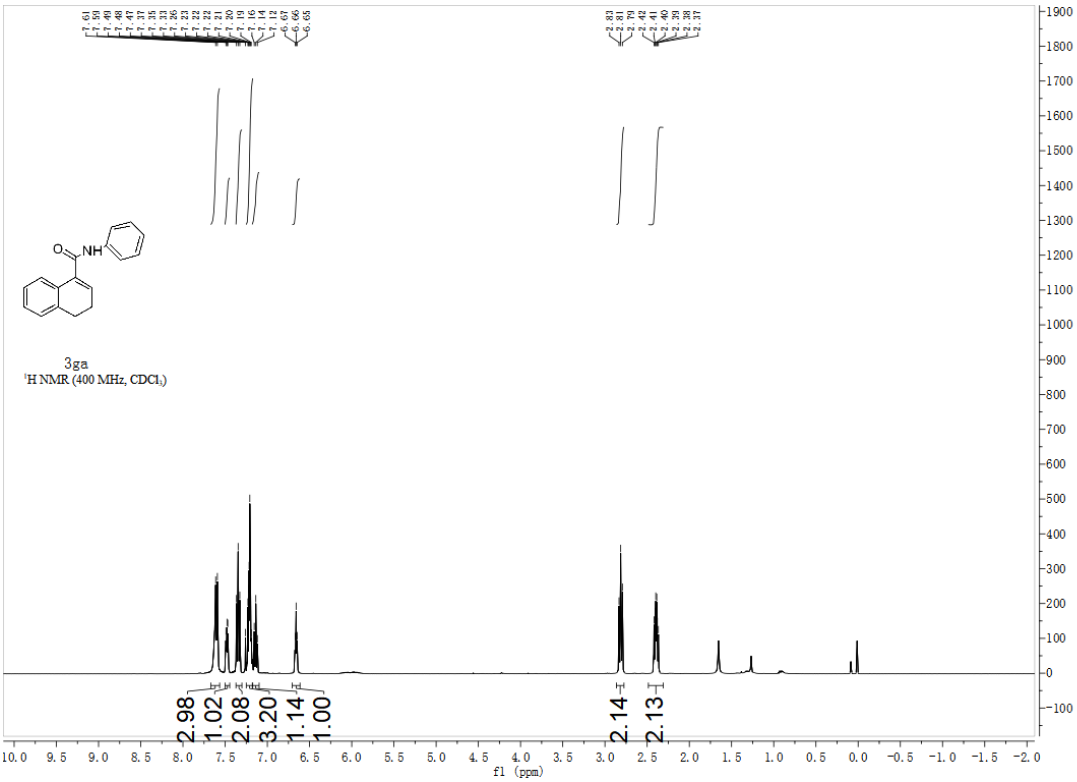

3da
^{13}C NMR (101 MHz, CDCl$_3$)
163.56
139.89
139.10
137.92
129.03
124.24
119.91
33.36
31.71
23.42
f1 (ppm)

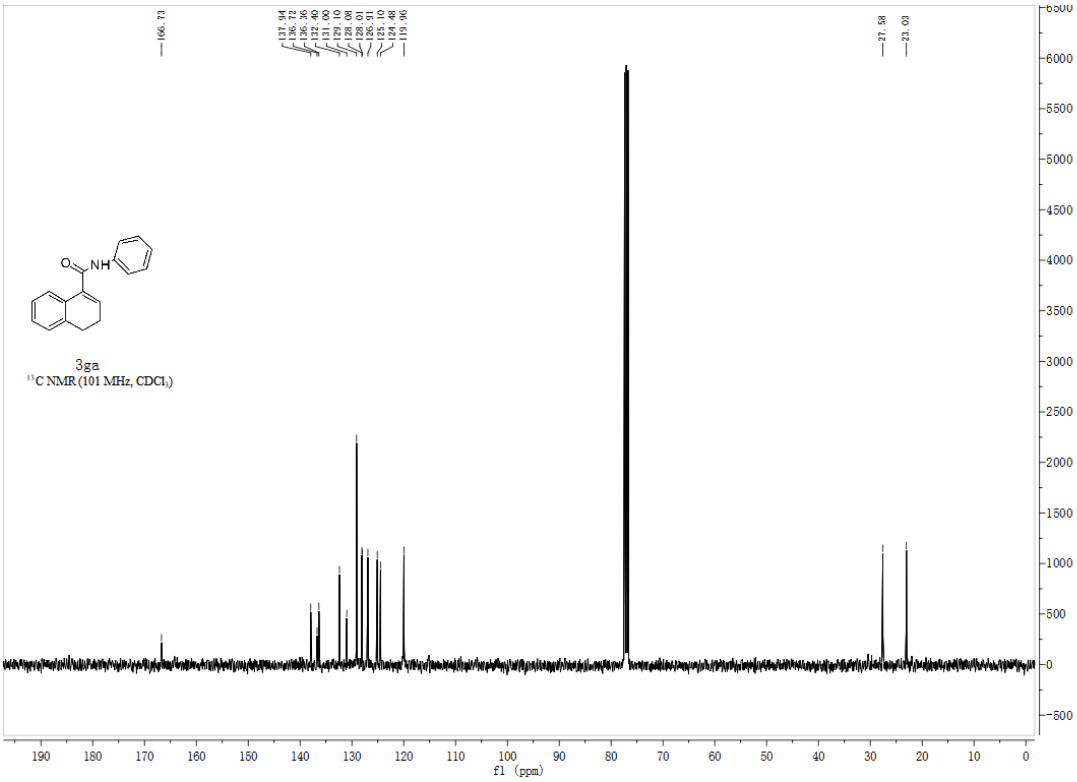

3ea
^{1}H NMR (400 MHz, CDCl$_3$)
2.84
2.03
0.98
1.00
2.01
2.03
2.02
4.10
f1 (ppm)

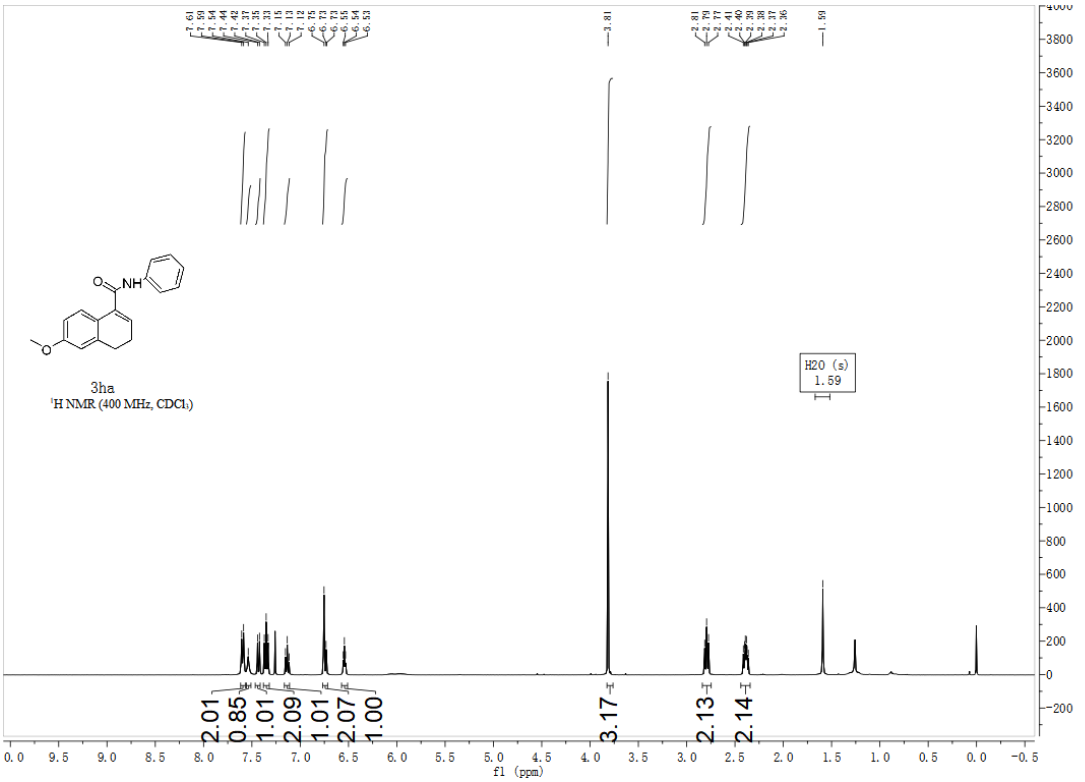

3ea
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

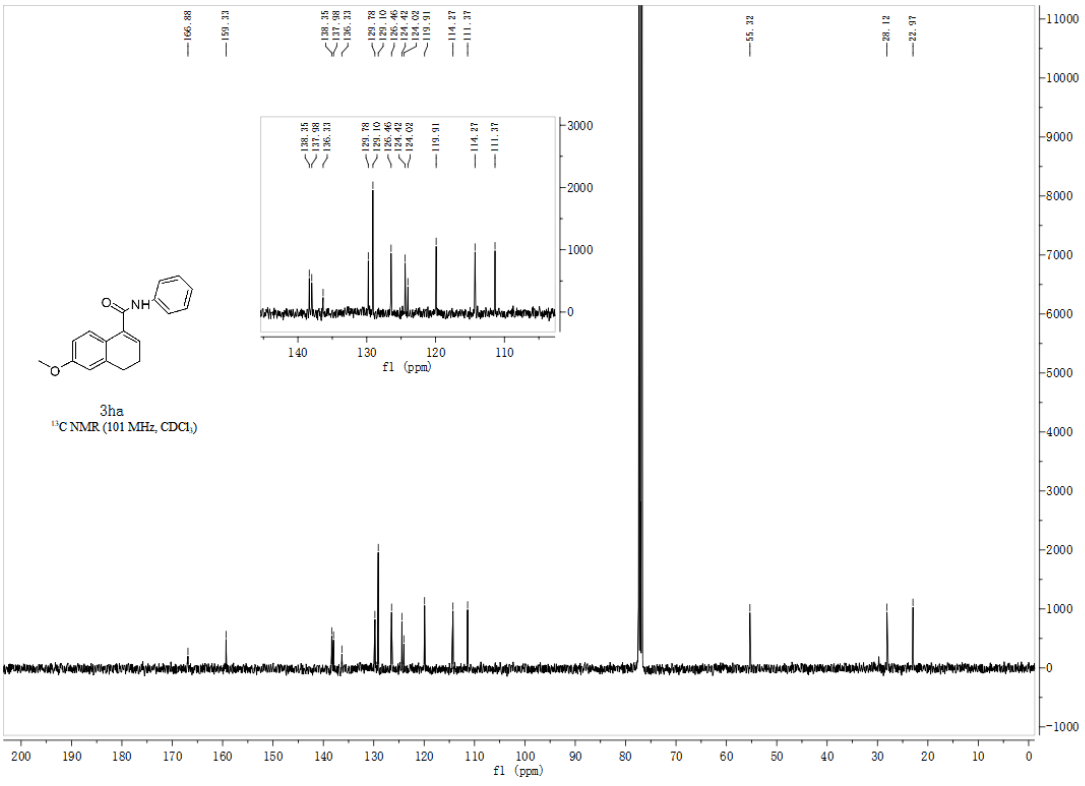

3fa
^{1}H NMR (400 MHz, CDCl$_3$)
2.37
1.01
2.35
1.07
1.12
2.45
2.44
2.38
2.14
4.31
f1 (ppm)

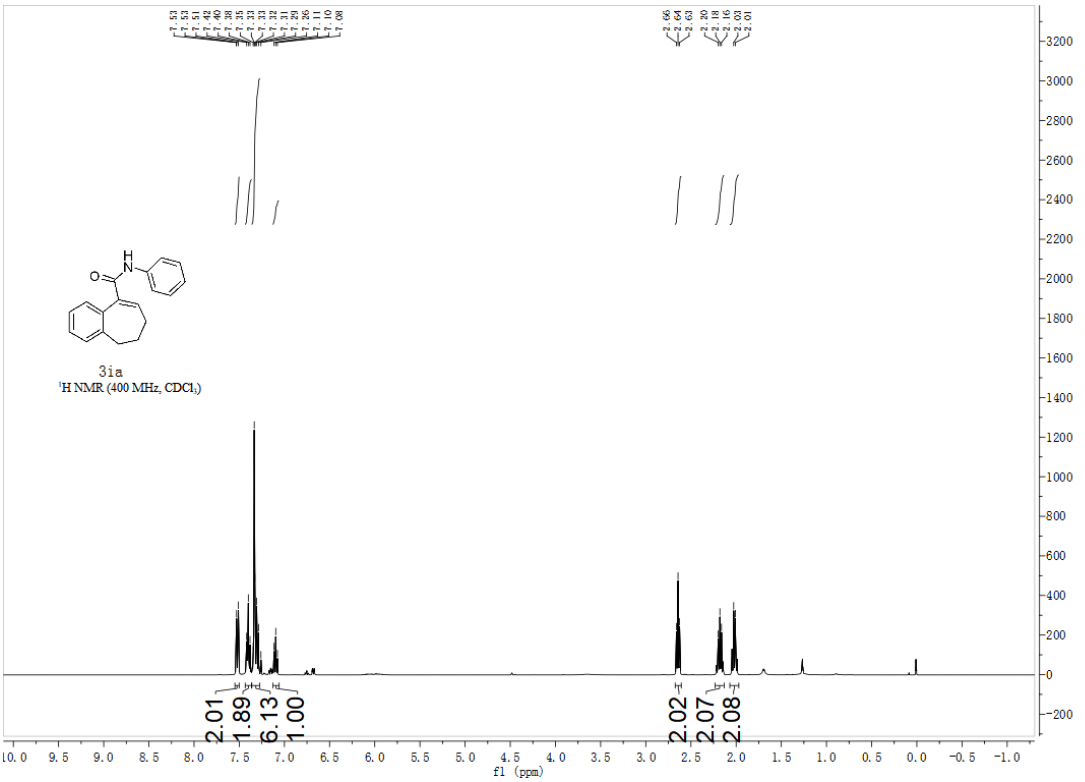

3fa
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

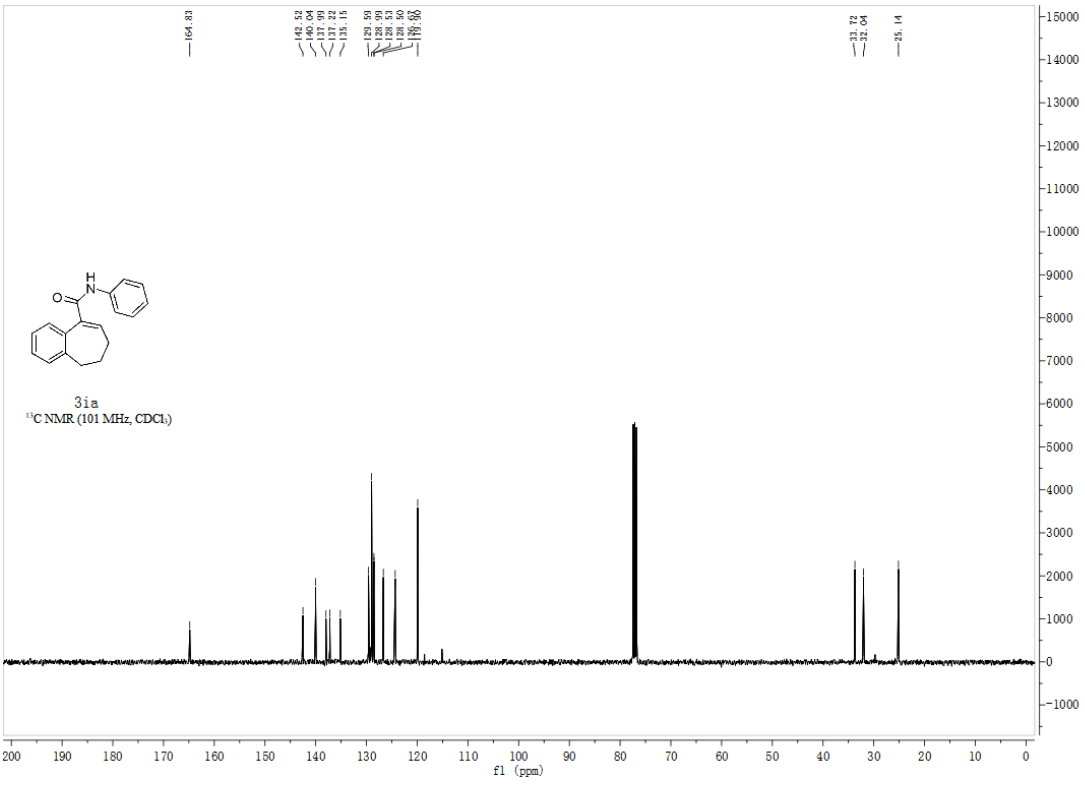

3ga
^{1}H NMR (400 MHz, CDCl$_3$)
2.98
1.02
2.08
3.20
1.14
1.00
2.14
2.13
f1 (ppm)

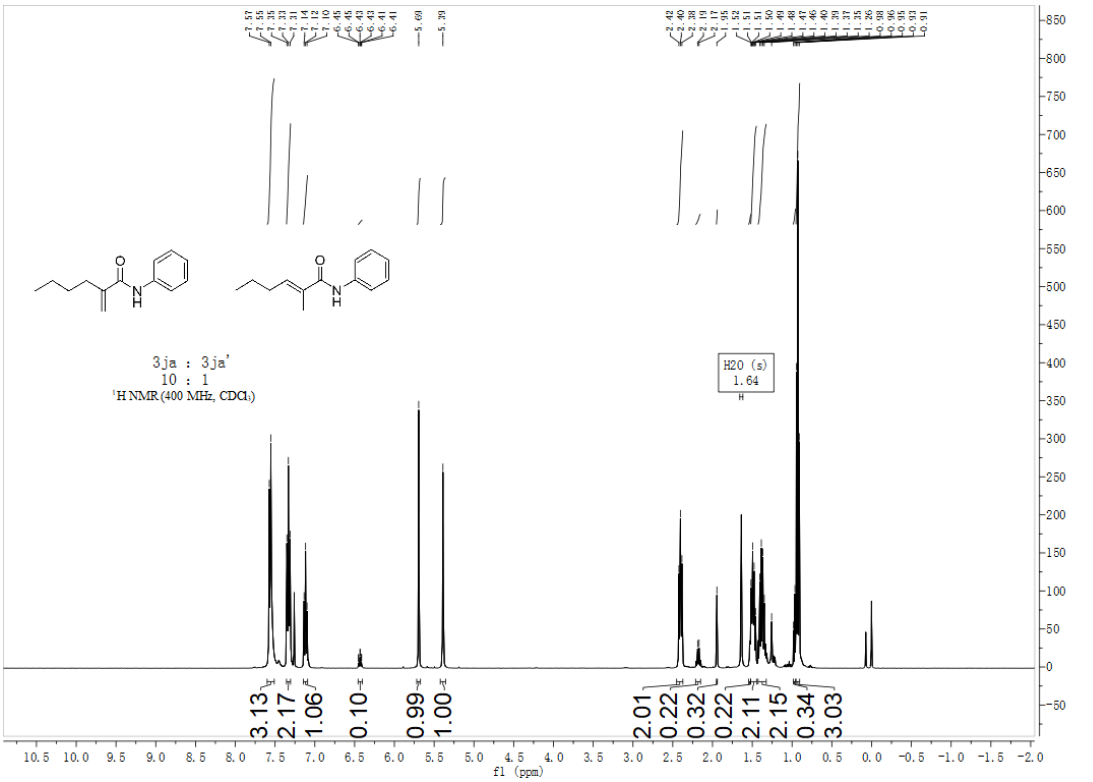

3ga
^{13}C NMR (101 MHz, CDCl$_3$)
166.73
137.94
135.72
135.35
132.40
131.00
129.10
128.08
128.01
126.91
125.10
124.48
121.96
27.58
23.03
f1 (ppm)

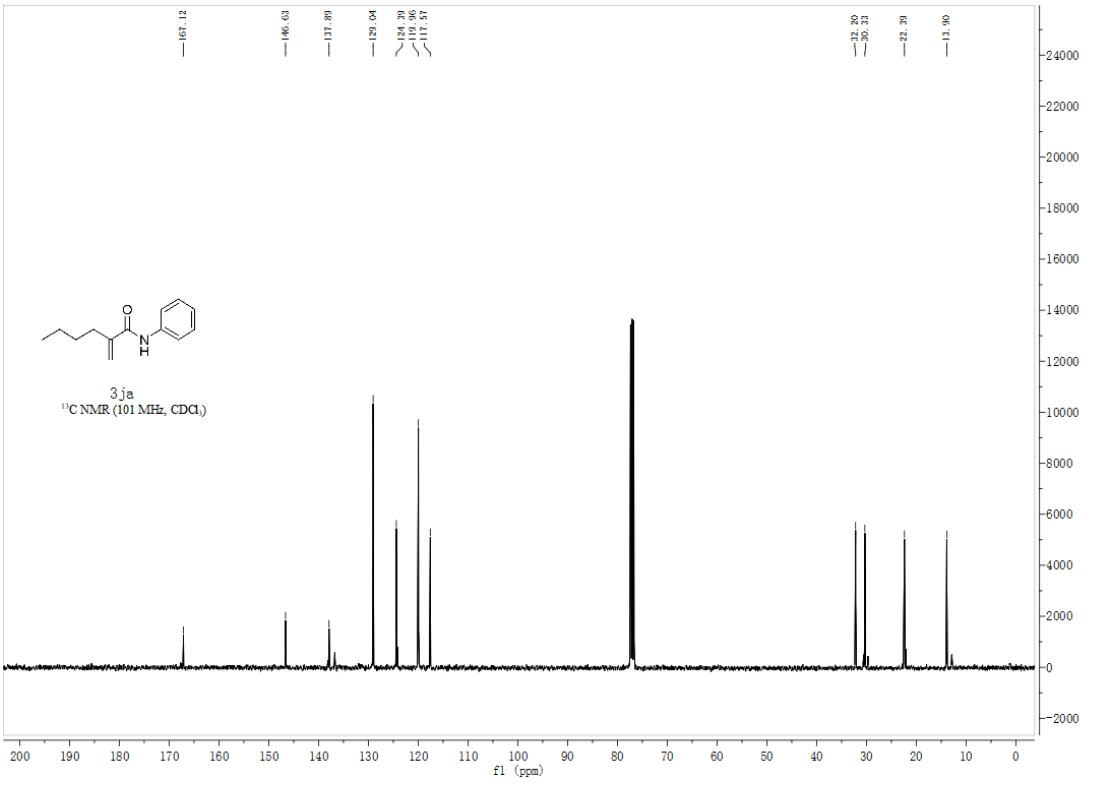

3ha
1H NMR (400 MHz, CDCl3)
H2O (s)
1.59
2.01
0.85
1.01
2.09
1.01
2.07
1.00
3.17
2.13
2.14
f1 (ppm)

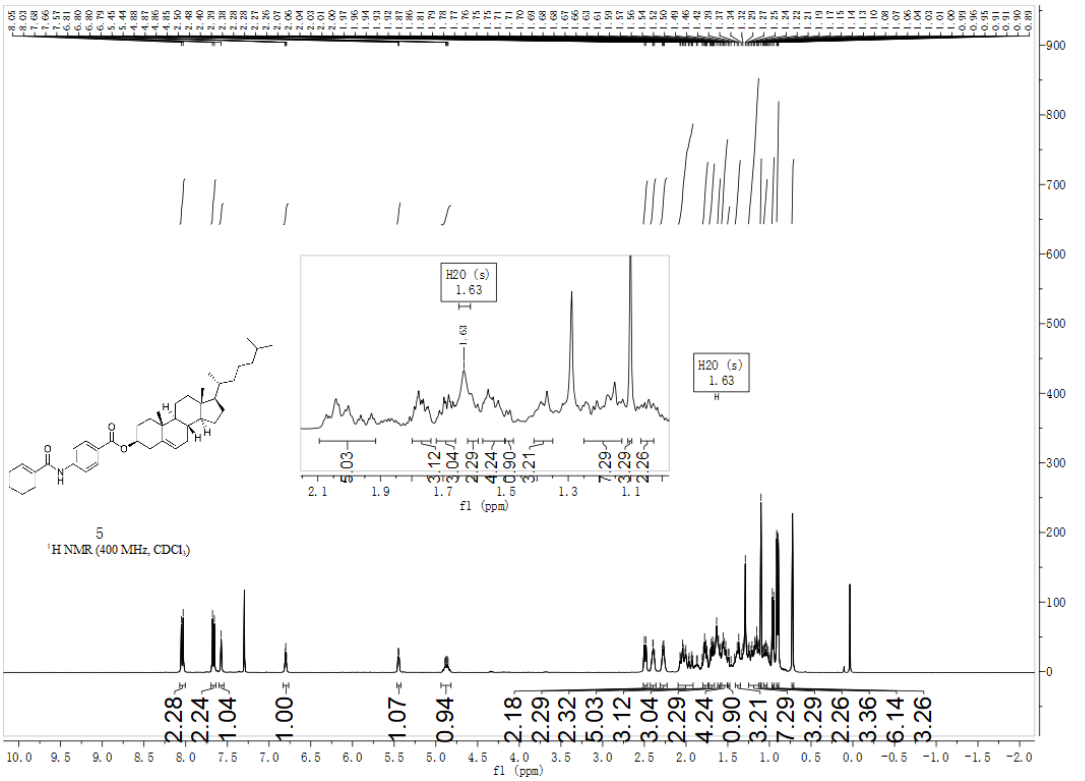

3ha
13C NMR (101 MHz, CDCl3)
166.88
159.33
138.35
137.98
136.33
129.78
129.10
126.46
124.42
124.02
119.91
114.27
111.37
55.32
28.12
22.97
f1 (ppm)

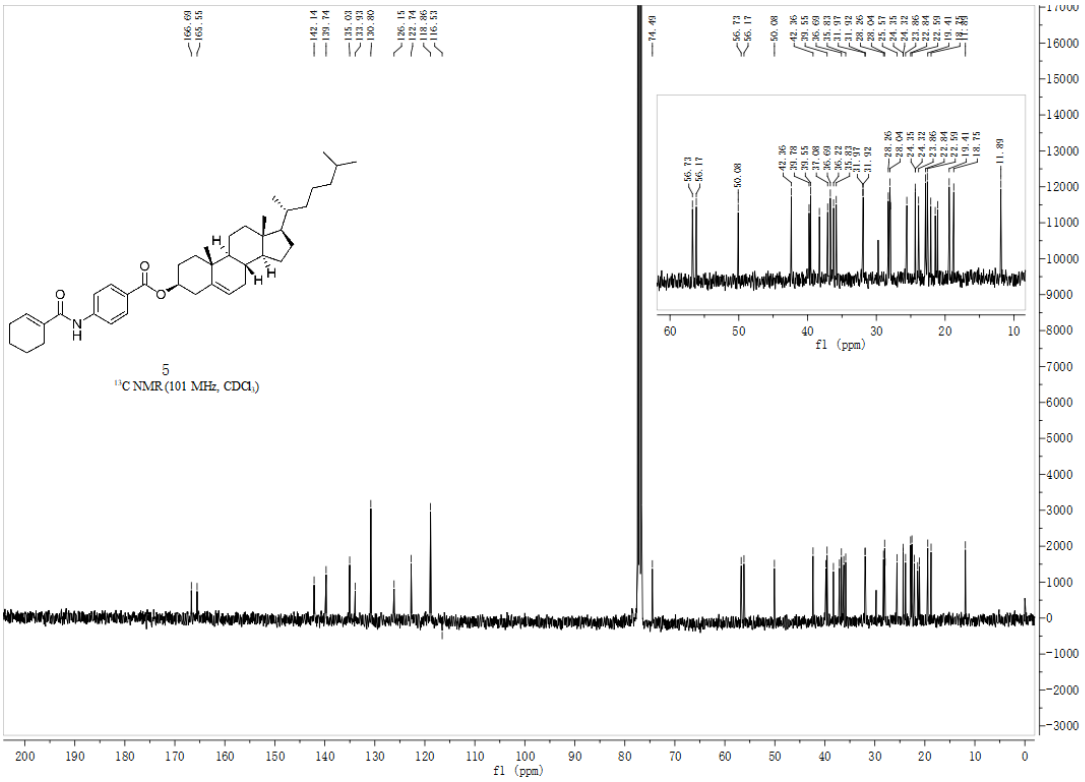

3ia
^{1}H NMR (400 MHz, CDCl$_3$)
2.01
1.89
6.13
1.00
2.02
2.07
2.08
f1 (ppm)

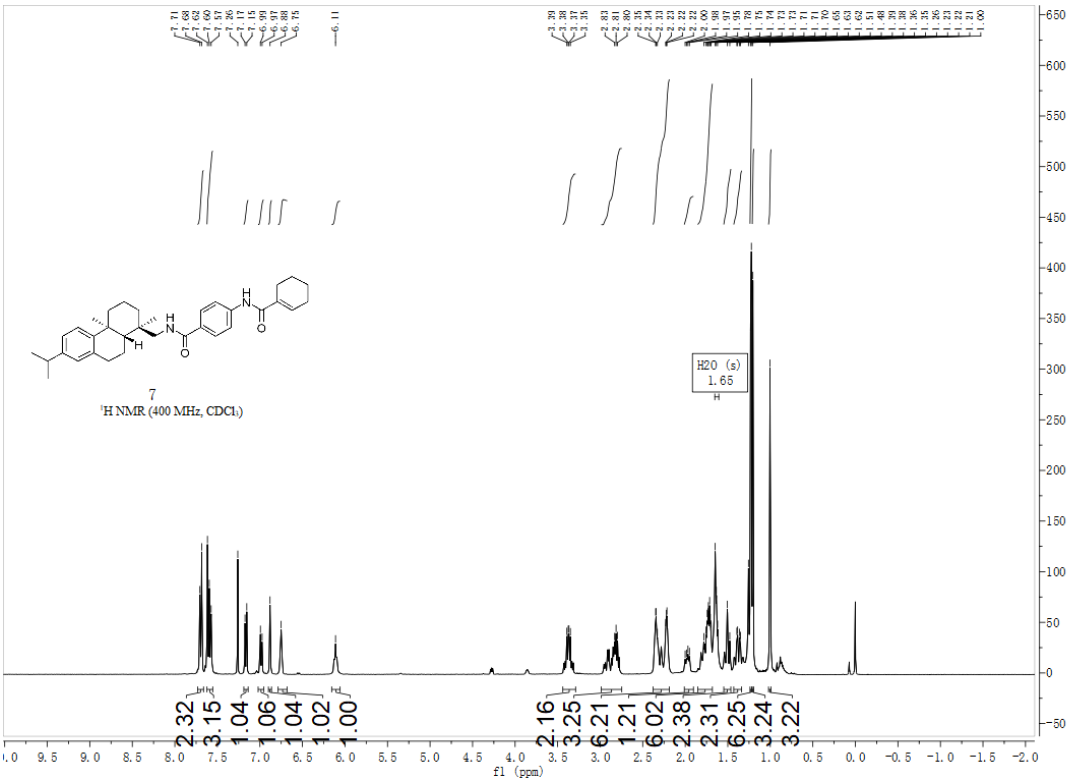

3ia
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)


3ja : 3ja'
10 : 1
^{1}H NMR (400 MHz, CDCl$_3$)
H2O (s)
1.64
3.13
2.17
1.06
0.10
0.99
1.00
2.01
0.22
0.32
0.22
2.11
2.15
0.34
3.03
f1 (ppm)

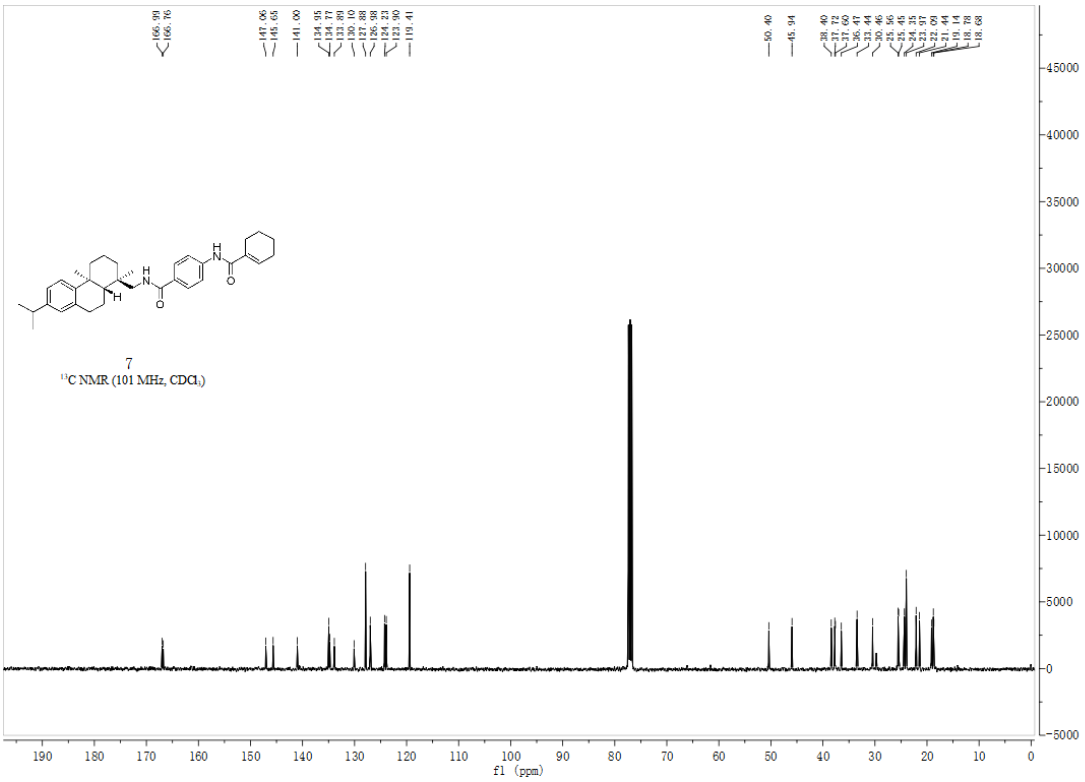

167.12
146.63
137.89
129.04
124.39
119.96
117.57
32.39
26.33
22.39
13.90
3ja
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)


H20 (s)
1.63
5
¹H NMR (400 MHz, CDCl₃)
f1 (ppm)


5
¹³C NMR (101 MHz, CDCl₃)
f1 (ppm)



7
^{1}H NMR (400 MHz, $CDCl_3$)



7
^{13}C NMR (101 MHz, $CDCl_3$)