

## Supporting Information

# Selective synthesis of acylated caprolactam via sequential Michael addition/palladium-catalyzed *alpha*-arylation of ketone

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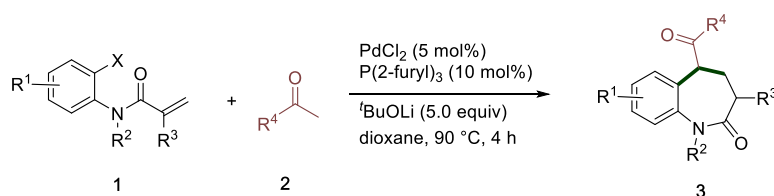
## 1. General considerations

All reactions were carried out under a nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Solvents were purified and dried according to standard methods prior to use. For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90) are used.  $^1\text{H}$  NMR spectra were recorded on a Bruker advance III 400 MHz in  $\text{CDCl}_3$  and  $^{13}\text{C}$  NMR spectra were recorded on 101 MHz in  $\text{CDCl}_3$  using TMS as internal standard, Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for  $^{13}\text{C}$  NMR is reported in terms of chemical shift ( $\delta$ , ppm). High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II.

## 2. Preparation of substrates

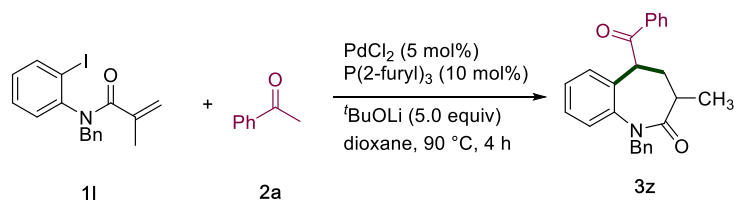
Substrates **1** were synthesized according to literatures.<sup>1</sup> Methyl ketones **2** were purchased from commercial suppliers.

## 3. Experiment procedure



**1** (0.2 mmol), **2** (0.3 mmol),  $\text{PdCl}_2$  (5 mol%),  $\text{P}(2\text{-furyl})_3$  (10 mol%),  $^t\text{BuOLi}$  (1.0 mmol), were added to a sealed tube, dioxane (2.0 mL) were added via syringe. The mixture was flushed with  $\text{N}_2$  and stirred at room temperature for 10 min firstly, and then was heated at 90 °C about for 4 h until completion (monitored by TLC). After cooling at room temperature, the reaction mixture was filtered through Celite. The solvent in the filtrate was evaporated under reduced pressure. The residue was purified through silica gel chromatography to afford the products **3**.

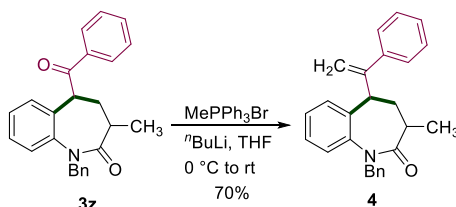
## 4. Gram-scale reaction of **3z**



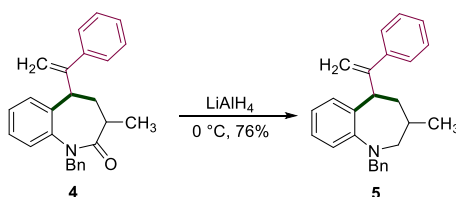
**1l** (3.0 mmol, 1.13 g), **2a** (4.5 mmol, 0.54 g),  $\text{PdCl}_2$  (5 mol%),  $\text{P}(2\text{-furyl})_3$  (10 mol%),  $^t\text{BuOLi}$  (15 mmol), were added to a sealed tube, dioxane (30.0 mL) were added via syringe. The mixture was flushed with  $\text{N}_2$  and stirred at room temperature for 10 min firstly, and then was heated at 90 °C about for 4 h until completion (monitored by TLC). After cooling at room temperature, the mixture was diluted with water and extracted with DCM,

dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by silica gel chromatography to afford the product **3z** (0.71 g, 64% yield).

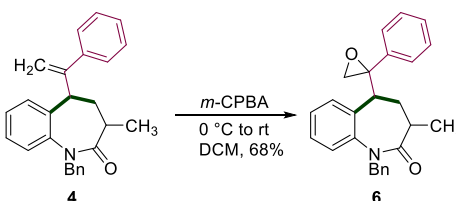
## 5. Synthetic transformations



0.1 mL of <sup>n</sup>BuLi (2.5 M, 0.23 mmol) was added dropwise to a solution of methyltriphenylphosphonium bromide (80.4 mg, 0.23 mmol) in 2.0 mL of THF at 0 °C. The reaction was stirred for about 15 min and then **3z** (74 mg, 0.2 mmol) in 2.0 mL of THF was added. After an additional 15 min, the ice bath was removed and the reaction was allowed to room temperature for 12 h. The reaction mixture was diluted with water (3.0 mL) and extracted with EtOAc (3.0 mL). The combined organic layers were washed with brine, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by a silica gel column chromatography (petroleum ether/ethyl acetate = 20:1, v/v) to afford **4** (51.5 mg, 70% yield) as a pale yellow solid.

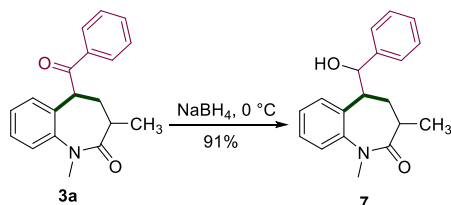


To a solution of **4** (0.2 mmol) in 2.0 mL of THF was added a solution of LiAlH<sub>4</sub> (3.0 equiv.) at 0 °C. The ice bath was removed and the reaction was allowed to rt stir for about 3 h. The reaction mixture was diluted with ice water (5.0 mL) and extracted with EtOAc (10 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was purified by a silica gel column chromatography to afford **5** with 76% yield as colorless oil.

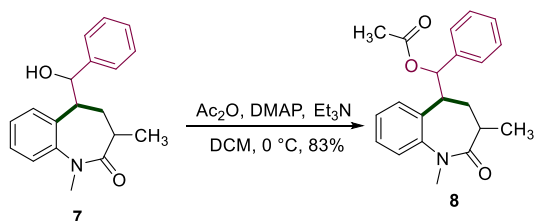


To a solution of **4** (0.2 mmol,) in DCM (2.0 mL) was added *m*CPBA (0.4 mmol, 69.0 mg, 2.0 equiv.) at 0 °C under air. Then the reaction mixture was allowed to room temperature, and stirred for 12 h. The reaction mixture was filtered through Celite. The solvent in the filtrate was evaporated under reduced pressure, and the crude product was purified by flash chromatography (Hexane/EtOAc = 10:1) to afford the pure epoxide product **6** in 68%

yield as a pale yellow solid.

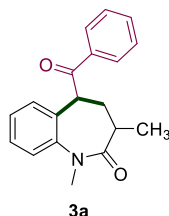


To a solution of **3a** (0.2 mmol, 1.0 equiv.) in THF (2.0 mL) was added  $\text{NaBH}_4$  (0.6 mmol, 3.0 equiv.) at  $0\text{ }^\circ\text{C}$  under air. Then the reaction mixture was allowed to warm stirred for 2 h at room temperature. The reaction mixture was filtered through Celite. The solvent in the filtrate was evaporated under reduced pressure, and the crude product was purified by flash chromatography (Hexane/EtOAc = 5:1) to afford the pure epoxide product **7** as a pale yellow solid.



To a solution of alcohol **7** (0.2 mmol),  $\text{Et}_3\text{N}$  (0.4 mmol, 2.0 equiv.), DMAP (0.02 mmol, 0.1 equiv.) in 2 mL  $\text{CH}_2\text{Cl}_2$  was added acetic acid anhydride (0.3 mmol, 1.5 equiv.) at  $0\text{ }^\circ\text{C}$  under argon atmosphere. After stirring at room temperature for 1 hour, the reaction mixture was quenched with saturated aq.  $\text{NH}_4\text{Cl}$  and separated layers. The aqueous layer is extracted with 2 x 5 mL  $\text{CH}_2\text{Cl}_2$ , then 5 mL brine, then dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuo. The crude product was purified by flash chromatography (Hexane/EtOAc = 10:1) to afford the pure epoxide product **8** as a pale yellow solid.

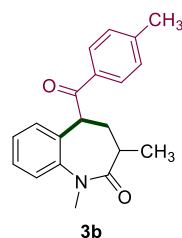
## 6. Spectra data



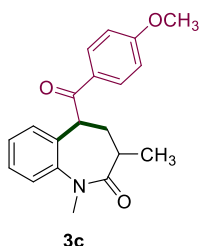
**5-benzoyl-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3a):** 42 mg; 72% yield; pale yellow solid; mp =  $137\text{--}139\text{ }^\circ\text{C}$ ;  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.84-7.74 (m, 2H), 7.54-7.47 (m, 1H), 7.38 (t,  $J = 7.7\text{ Hz}$ , 2H), 7.32-7.25 (m, 2H), 7.05 (td,  $J = 7.3, 1.7\text{ Hz}$ , 1H), 6.85 (dd,  $J = 7.7, 1.4\text{ Hz}$ , 1H), 4.78 (dd,  $J = 12.5, 6.4\text{ Hz}$ , 1H), 3.52 (s, 3H), 2.71 (td,  $J = 12.8, 7.6\text{ Hz}$ , 1H), 2.53-2.35 (m, 1H), 1.95 (ddd,  $J = 13.2, 11.8, 6.4\text{ Hz}$ , 1H), 1.15 (d,  $J = 6.6\text{ Hz}$ , 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  198.9, 175.2, 142.4, 136.1, 133.9,



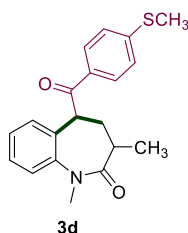
133.2, 128.6, 128.6, 128.2, 126.9, 126.4, 122.9, 46.3, 39.6, 35.2, 35.0, 15.6. **HRMS** (ESI) calcd for  $C_{19}H_{20}NO_2$   $[M+H]^+$  : 294.1489, found: 294.1491.



**1,3-dimethyl-5-(4-methylbenzoyl)-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3b):** 42 mg; 69% yield; yellow oil;  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.65-7.56 (m, 2H), 7.23-7.18 (m, 2H), 7.10 (d,  $J$  = 8.0 Hz, 2H), 6.97 (td,  $J$  = 7.4, 1.7 Hz, 1H), 6.77 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 4.68 (dd,  $J$  = 12.5, 6.4 Hz, 1H), 3.44 (s, 3H), 2.62 (td,  $J$  = 12.8, 7.6 Hz, 1H), 2.35 (dt,  $J$  = 11.7, 6.8 Hz, 1H), 2.28 (s, 3H), 1.86 (ddd,  $J$  = 13.1, 11.8, 6.4 Hz, 1H), 1.08 (d,  $J$  = 6.5 Hz, 3H).  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.5, 175.3, 144.2, 142.4, 134.1, 133.6, 129.3, 128.8, 128.1, 127.0, 126.4, 122.9, 46.2, 39.6, 35.3, 35.0, 21.6, 15.6. **HRMS** (ESI) calcd for  $C_{20}H_{21}NNO_2$   $[M+Na]^+$  : 330.1465, found: 330.1466.

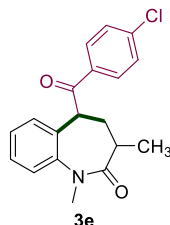


**5-(4-methoxybenzoyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3c):** 52 mg; 80% yield; pale yellow solid; mp = 104-106 °C;  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.71-7.67 (m, 2H), 7.26-7.16 (m, 2H), 6.97 (td,  $J$  = 7.4, 1.7 Hz, 1H), 6.81-6.75 (m, 3H), 4.65 (dd,  $J$  = 12.5, 6.4 Hz, 1H), 3.75 (s, 3H), 3.44 (s, 3H), 2.62 (td,  $J$  = 12.9, 7.6 Hz, 1H), 2.41-2.27 (m, 1H), 1.85 (ddd,  $J$  = 13.2, 11.8, 6.4 Hz, 1H), 1.07 (d,  $J$  = 6.5 Hz, 3H).  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  197.3, 175.3, 163.5, 142.4, 134.2, 130.9, 129.1, 128.1, 127.0, 126.4, 122.9, 113.8, 55.4, 46.0, 39.7, 35.3, 35.0, 15.6. **HRMS** (ESI) calcd for  $C_{20}H_{21}NaNO_3$   $[M+Na]^+$  : 346.1414, found: 346.1414.



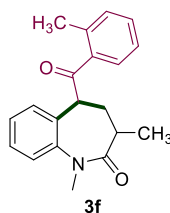
**1,3-dimethyl-5-(4-(methylthio)benzoyl)-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3d):** 45 mg; 66% yield; colorless oil;  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.65-7.57 (m, 2H), 7.26-7.15 (m, 2H), 7.11-7.05 (m, 2H), 6.96 (td,  $J$  = 7.4, 1.7 Hz, 1H), 6.79-6.72 (m, 1H), 4.64 (dd,  $J$  = 12.5, 6.3 Hz, 1H), 3.44 (s, 3H), 2.62 (td,  $J$  = 12.9, 7.6 Hz, 1H), 2.39 (s, 3H), 2.34 (dt,  $J$  =

11.8, 6.8 Hz, 1H), 1.85 (ddd,  $J = 13.1, 11.8, 6.4$  Hz, 1H), 1.07 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  197.8, 175.2, 146.3, 142.4, 134.0, 132.2, 129.0, 128.1, 126.9, 126.4, 124.8, 122.9, 46.1, 39.5, 35.2, 35.0, 15.6, 14.5. **HRMS** (ESI) calcd for  $\text{C}_{20}\text{H}_{21}\text{NaNO}_2\text{S}$   $[\text{M}+\text{Na}]^+$  : 362.1185, found: 362.1189.



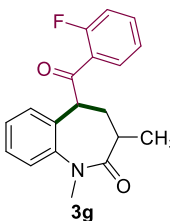
**5-(4-chlorobenzoyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3e):**

46 mg; 70% yield; colorless oil;  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.67-7.62 (m, 2H), 7.30-7.18 (m, 4H), 6.98 (td,  $J = 7.4, 1.6$  Hz, 1H), 6.72 (dd,  $J = 7.8, 1.4$  Hz, 1H), 4.63 (dd,  $J = 12.5, 6.3$  Hz, 1H), 3.44 (s, 3H), 2.61 (td,  $J = 12.9, 7.6$  Hz, 1H), 2.41-2.26 (m, 1H), 1.86 (ddd,  $J = 13.1, 11.8, 6.3$  Hz, 1H), 1.07 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  197.8, 175.1, 142.4, 139.7, 134.3, 133.6, 130.02, 129.0, 128.3, 126.8, 126.5, 123.0, 46.4, 39.5, 35.3, 35.0, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{18}\text{NaNO}_2\text{Cl}$   $[\text{M}+\text{Na}]^+$  : 350.0918, found: 350.0920.



**1,3-dimethyl-5-(2-methylbenzoyl)-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3f):**

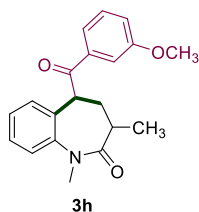
47 mg; 76% yield; pale yellow oil;  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.31 (dd,  $J = 7.9, 1.4$  Hz, 1H), 7.24 (qd,  $J = 7.6, 1.5$  Hz, 2H), 7.17 (dd,  $J = 8.0, 1.5$  Hz, 2H), 7.02 (qd,  $J = 7.3, 1.4$  Hz, 2H), 6.92 (dd,  $J = 7.8, 1.5$  Hz, 1H), 4.63 (dd,  $J = 12.6, 6.3$  Hz, 1H), 3.39 (s, 3H), 2.57 (dd,  $J = 12.8, 7.6$  Hz, 1H), 2.52 (s, 3H), 2.40-2.29 (m, 1H), 1.89 (ddd,  $J = 12.9, 11.7, 6.4$  Hz, 1H), 1.06 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  202.3, 175.1, 142.5, 139.2, 136.8, 133.9, 132.3, 131.7, 129.2, 128.1, 126.5, 126.4, 125.7, 123.0, 48.4, 40.4, 35.2, 35.0, 21.8, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{20}\text{H}_{21}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 330.1465, found: 330.1482.



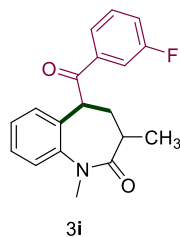
**5-(2-fluorobenzoyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3g):**

39 mg; 63% yield; yellow oil;  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.93 (td,  $J = 7.7, 1.9$  Hz, 1H), 7.41 (dddd,  $J = 8.5, 7.0, 5.0, 1.9$  Hz, 1H), 7.26-7.14 (m, 3H), 6.97 (td,  $J = 7.5, 1.6$  Hz, 1H), 6.88 (ddd,  $J = 11.5, 8.3, 1.1$  Hz, 1H), 6.73 (dd,  $J = 7.7, 1.4$  Hz, 1H), 4.62 (dd,  $J = 12.6, 6.1$  Hz, 1H),

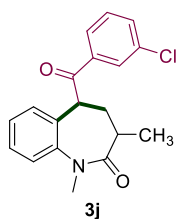
3.39 (s, 3H), 2.53 (tdd,  $J = 12.8, 7.6, 2.5$  Hz, 1H), 2.38-2.25 (m, 1H), 1.93 (ddd,  $J = 13.0, 11.7, 6.2$  Hz, 1H), 1.07 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  196.7, 175.1, 143.1, 135.1, 135.0, 133.7, 131.0, 131.0, 128.0, 126.3, 125.8, 124.6, 124.6, 123.1, 117.0, 116.7, 51.0, 50.9, 39.6, 35.1, 35.0, 15.6.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -108.8. HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{18}\text{NaNO}_2\text{F}$   $[\text{M}+\text{Na}]^+$  : 334.1214, found: 334.1217.



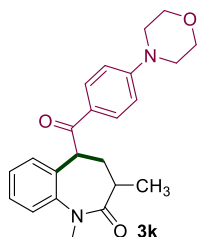
**5-(3-methoxybenzoyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3h):** 50 mg; 78% yield; yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 (q,  $J = 1.3$  Hz, 1H), 7.28-7.12 (m, 4H), 6.98 (dtd,  $J = 7.0, 3.5, 1.5$  Hz, 2H), 6.77 (dd,  $J = 7.7, 1.4$  Hz, 1H), 4.69 (dd,  $J = 12.5, 6.3$  Hz, 1H), 3.72 (s, 3H), 3.44 (s, 3H), 2.62 (td,  $J = 12.8, 7.6$  Hz, 1H), 2.42-2.27 (m, 1H), 1.86 (ddd,  $J = 13.2, 11.8, 6.4$  Hz, 1H), 1.07 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.7, 175.2, 159.7, 142.3, 137.4, 134.0, 129.6, 128.2, 126.9, 126.5, 122.9, 121.3, 119.7, 112.8, 55.3, 46.5, 39.6, 35.2, 35.0, 15.6. HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{21}\text{NaNO}_3$   $[\text{M}+\text{Na}]^+$  : 346.1414, found: 346.1413.



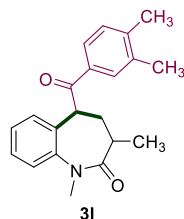
**5-(3-fluorobenzoyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3i):** 32 mg; 52% yield; yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.43 (dd,  $J = 9.3, 2.3$  Hz, 2H), 7.30-7.20 (m, 3H), 7.17-7.08 (m, 1H), 6.99 (td,  $J = 7.4, 1.6$  Hz, 1H), 6.73 (dd,  $J = 7.8, 1.4$  Hz, 1H), 4.65 (dd,  $J = 12.5, 6.3$  Hz, 1H), 3.45 (s, 3H), 2.61 (td,  $J = 12.8, 7.6$  Hz, 1H), 2.40-2.27 (m, 1H), 1.87 (ddd,  $J = 13.3, 11.8, 6.3$  Hz, 1H), 1.08 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  197.7, 175.1, 142.4, 133.5, 130.4, 130.3, 128.4, 126.8, 126.5, 124.4, 124.4, 123.1, 120.4, 120.2, 115.4, 115.2, 46.6, 39.5, 35.3, 35.0, 15.6.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -111.4. HRMS (ESI) calcd for  $\text{C}_{19}\text{H}_{18}\text{NaNFO}_2$   $[\text{M}+\text{Na}]^+$  : 334.1214, found: 334.1210.



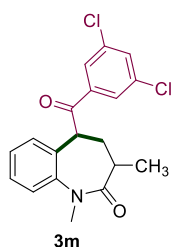
**5-(3-chlorobenzoyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3j)** : 39 mg; 59% yield; yellow oil;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.76 (t,  $J$  = 1.9 Hz, 1H), 7.50 (dt,  $J$  = 7.8, 1.3 Hz, 1H), 7.41 (ddd,  $J$  = 8.0, 2.2, 1.0 Hz, 1H), 7.27-7.19 (m, 3H), 6.99 (td,  $J$  = 7.5, 1.6 Hz, 1H), 6.73 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 4.65 (dd,  $J$  = 12.5, 6.3 Hz, 1H), 3.45 (s, 3H), 2.61 (td,  $J$  = 12.9, 7.6 Hz, 1H), 2.41-2.28 (m, 1H), 1.87 (ddd,  $J$  = 13.2, 11.8, 6.3 Hz, 1H), 1.08 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  197.7, 175.1, 142.4, 137.6, 135.1, 133.4, 133.2, 130.0, 128.7, 128.4, 126.8, 126.7, 126.6, 123.1, 46.6, 39.5, 35.3, 35.0, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{18}\text{NaNO}_2\text{Cl}$   $[\text{M}+\text{Na}]^+$  : 350.0918, found: 350.0917.



**1,3-dimethyl-5-(4-morpholinobenzoyl)-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3k)**: 51 mg; 68% yield; pale yellow oil;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.71-7.58 (m, 2H), 7.26-7.15 (m, 2H), 6.96 (td,  $J$  = 7.4, 1.7 Hz, 1H), 6.81 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 6.76-6.63 (m, 2H), 4.63 (dd,  $J$  = 12.5, 6.4 Hz, 1H), 3.80-3.66 (m, 4H), 3.43 (s, 3H), 3.19 (dd,  $J$  = 6.0, 3.9 Hz, 4H), 2.62 (td,  $J$  = 12.9, 7.6 Hz, 1H), 2.34 (dt,  $J$  = 11.7, 6.8 Hz, 1H), 1.83 (ddd,  $J$  = 13.1, 11.8, 6.4 Hz, 1H), 1.06 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  196.8, 175.3, 154.1, 142.3, 134.5, 130.7, 127.9, 127.0, 126.7, 126.4, 122.8, 113.1, 66.4, 47.1, 45.6, 39.7, 35.2, 35.0, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{23}\text{H}_{26}\text{NaN}_2\text{O}_3$   $[\text{M}+\text{Na}]^+$  : 401.1836, found: 401.1809.

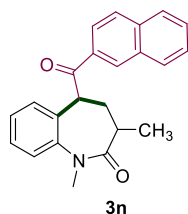


**5-(3,4-dimethylbenzoyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3l)**: 44 mg; 69% yield; pale yellow solid; mp = 112-114 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.58 (d,  $J$  = 2.0 Hz, 1H), 7.35 (dd,  $J$  = 7.9, 2.0 Hz, 1H), 7.28-7.14 (m, 2H), 7.05-6.89 (m, 2H), 6.78 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 4.69 (dd,  $J$  = 12.6, 6.4 Hz, 1H), 3.44 (s, 3H), 2.61 (td,  $J$  = 12.9, 7.6 Hz, 1H), 2.44-2.27 (m, 1H), 2.18 (d,  $J$  = 4.6 Hz, 6H), 1.85 (ddd,  $J$  = 13.1, 11.8, 6.4 Hz, 1H), 1.07 (d,  $J$  = 6.6 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  198.8, 175.3, 143.0, 142.4, 137.0, 134.2, 134.0, 129.8, 129.6, 128.0, 126.9, 126.4, 126.4, 122.9, 46.1, 39.7, 35.2, 35.0, 20.0, 19.8, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{21}\text{H}_{23}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 344.1621, found: 344.1621.

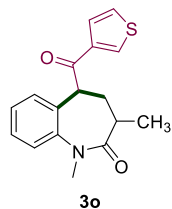


**5-(3,5-dichlorobenzoyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one**

**(3m):** 39 mg; 54% yield; pale yellow solid; mp = 107-109 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.54 (d,  $J$  = 1.8 Hz, 2H), 7.41 (t,  $J$  = 1.9 Hz, 1H), 7.28 (td,  $J$  = 7.6, 1.5 Hz, 1H), 7.22 (dd,  $J$  = 8.1, 1.5 Hz, 1H), 7.01 (td,  $J$  = 7.5, 1.5 Hz, 1H), 6.69 (dd,  $J$  = 7.7, 1.4 Hz, 1H), 4.59 (dd,  $J$  = 12.4, 6.3 Hz, 1H), 3.44 (s, 3H), 2.59 (td,  $J$  = 12.8, 7.6 Hz, 1H), 2.43-2.26 (m, 1H), 1.86 (ddd,  $J$  = 13.1, 11.8, 6.3 Hz, 1H), 1.07 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  196.6, 175.0, 142.4, 138.5, 135.6, 133.0, 132.8, 128.7, 127.0, 126.6, 126.5, 123.2, 46.6, 39.5, 35.2, 35.0, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{17}\text{NaNO}_2\text{Cl}_2$   $[\text{M}+\text{Na}]^+$  : 384.0529, found: 384.0529.



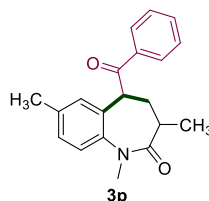
**5-(2-naphthoyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3n):** 42 mg; 61% yield; yellow solid; mp = 116-118 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.23-8.18 (m, 1H), 7.80-7.71 (m, 4H), 7.44 (dddd,  $J$  = 26.6, 8.1, 6.9, 1.3 Hz, 2H), 7.23-7.18 (m, 2H), 6.93 (ddd,  $J$  = 7.7, 5.3, 3.5 Hz, 1H), 6.84-6.77 (m, 1H), 4.86 (dd,  $J$  = 12.5, 6.3 Hz, 1H), 3.49 (s, 3H), 2.68 (td,  $J$  = 12.8, 7.6 Hz, 1H), 2.47-2.32 (m, 1H), 1.92 (ddd,  $J$  = 13.0, 11.8, 6.4 Hz, 1H), 1.09 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  198.9, 175.3, 142.4, 135.5, 134.0, 133.4, 132.3, 130.4, 129.6, 128.6, 128.5, 128.2, 127.7, 127.0, 126.8, 126.5, 124.1, 123.0, 46.4, 39.7, 35.3, 35.1, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{23}\text{H}_{21}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 366.1465, found: 366.1465.



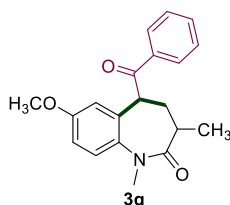
**1,3-dimethyl-5-(thiophene-3-carbonyl)-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one**

**(3o):** 34 mg; 57% yield; yellow oil;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.76 (dd,  $J$  = 2.9, 1.3 Hz, 1H), 7.32 (dd,  $J$  = 5.1, 1.3 Hz, 1H), 7.24 (td,  $J$  = 7.6, 1.5 Hz, 1H), 7.22-7.14 (m, 2H), 7.00 (td,  $J$  = 7.5, 1.5 Hz, 1H), 6.84 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 4.53 (dd,  $J$  = 12.6, 6.4 Hz, 1H), 3.42 (s, 3H), 2.58 (td,  $J$  = 12.9, 7.6 Hz, 1H), 2.42-2.27 (m, 1H), 1.91-1.83 (m, 1H), 1.06 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  193.1, 175.2, 142.5, 141.5, 133.8, 133.0, 128.2,

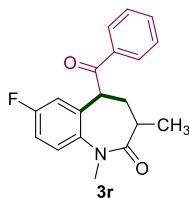
127.1, 126.8, 126.4, 122.9, 48.0, 39.3, 35.2, 35.0, 15.6. **HRMS** (ESI) calcd for  $C_{17}H_{17}NaNO_2S$   $[M+Na]^+$  : 322.0872, found: 322.0872.



**5-benzoyl-1,3,7-trimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3p):** 37 mg; 60% yield; yellow solid; mp = 150-151 °C;  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.77-7.68 (m, 2H), 7.50-7.40 (m, 1H), 7.32 (t,  $J$  = 7.7 Hz, 2H), 7.11-7.01 (m, 2H), 6.61-6.53 (m, 1H), 4.68 (dd,  $J$  = 12.5, 6.3 Hz, 1H), 3.42 (s, 3H), 2.61 (td,  $J$  = 12.8, 7.6 Hz, 1H), 2.35 (dt,  $J$  = 11.7, 6.8 Hz, 1H), 2.11 (s, 3H), 1.84 (ddd,  $J$  = 13.1, 11.8, 6.3 Hz, 1H), 1.07 (d,  $J$  = 6.5 Hz, 3H).  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.2, 175.3, 139.8, 136.4, 136.2, 133.6, 133.3, 128.8, 128.7, 128.6, 127.3, 122.8, 46.3, 39.7, 35.3, 35.0, 21.0, 15.6. **HRMS** (ESI) calcd for  $C_{20}H_{21}NaNO_2$   $[M+Na]^+$  : 330.1465, found: 330.1468.

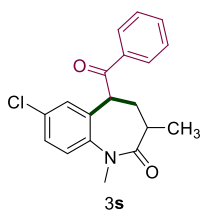


**5-benzoyl-7-methoxy-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3q):** 35 mg; 54% yield; colorless oil;  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.72 (dt,  $J$  = 8.2, 1.0 Hz, 2H), 7.44 (td,  $J$  = 7.4, 1.3 Hz, 1H), 7.31 (t,  $J$  = 7.6 Hz, 2H), 7.12 (d,  $J$  = 8.7 Hz, 1H), 6.75 (dd,  $J$  = 8.8, 2.9 Hz, 1H), 6.31 (d,  $J$  = 2.8 Hz, 1H), 4.67 (dd,  $J$  = 12.5, 6.3 Hz, 1H), 3.56 (d,  $J$  = 1.0 Hz, 3H), 3.41 (s, 3H), 2.60 (td,  $J$  = 12.8, 7.6 Hz, 1H), 2.43-2.28 (m, 1H), 1.85 (ddd,  $J$  = 13.5, 11.8, 6.3 Hz, 1H), 1.07 (d,  $J$  = 6.8 Hz, 3H).  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.0, 175.3, 157.6, 136.2, 135.3, 135.1, 133.3, 128.7, 128.6, 124.1, 113.1, 112.4, 55.4, 46.4, 39.5, 35.3, 34.9, 15.6. **HRMS** (ESI) calcd for  $C_{20}H_{21}NaNO_3$   $[M+Na]^+$  : 346.1414, found: 346.1414.

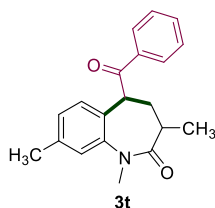


**5-benzoyl-7-fluoro-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3r):** 37 mg; 59% yield; yellow oil;  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.75-7.67 (m, 2H), 7.49-7.43 (m, 1H), 7.33 (t,  $J$  = 7.8 Hz, 2H), 7.18 (dt,  $J$  = 8.8, 4.1 Hz, 1H), 6.93 (ddd,  $J$  = 8.7, 7.8, 2.9 Hz, 1H), 6.53 (dd,  $J$  = 9.1, 2.9 Hz, 1H), 4.69 (dd,  $J$  = 12.5, 6.4 Hz, 1H), 3.42 (s, 3H), 2.61 (td,  $J$  = 12.9, 7.6 Hz, 1H), 2.41-2.24 (m, 1H), 1.86 (ddd,  $J$  = 13.2, 11.8, 6.4 Hz, 1H), 1.07 (d,  $J$  = 6.5 Hz, 3H).  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.3, 175.0, 138.5, 138.4, 135.9, 135.8, 135.8, 133.5, 128.8, 128.6, 124.6, 124.5, 115.1, 114.9, 114.1, 113.9, 46.1, 46.1, 39.5, 35.4, 34.9,

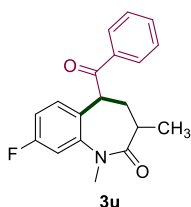
15.5.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -113.9. **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{18}\text{NNaFO}_2$   $[\text{M}+\text{Na}]^+$  : 334.1214, found: 334.1208.



**5-benzoyl-7-chloro-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3s):** 33 mg; 51% yield; yellow solid; mp = 153-154 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.76-7.68 (m, 2H), 7.53-7.44 (m, 1H), 7.34 (t,  $J$  = 7.8 Hz, 2H), 7.24 – 7.19 (m, 1H), 7.14 (d,  $J$  = 8.6 Hz, 1H), 6.80 (d,  $J$  = 2.3 Hz, 1H), 4.69 (dd,  $J$  = 12.5, 6.4 Hz, 1H), 3.42 (s, 3H), 2.62 (td,  $J$  = 12.9, 7.6 Hz, 1H), 2.35 (dt,  $J$  = 11.8, 6.7 Hz, 1H), 1.87 (ddd,  $J$  = 13.1, 11.8, 6.4 Hz, 1H), 1.08 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.3, 174.9, 141.0, 135.9, 135.5, 133.6, 131.9, 128.8, 128.6, 128.3, 126.9, 124.2, 46.0, 39.6, 35.3, 35.0, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{18}\text{NaNClO}_2$   $[\text{M}+\text{Na}]^+$  : 350.0918, found: 350.0925.

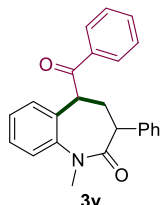


**5-benzoyl-1,3,8-trimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3t):** 42 mg, 68% yield, yellow solid; mp = 168-169 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.77-7.65 (m, 2H), 7.49-7.39 (m, 1H), 7.29 (t,  $J$  = 7.8 Hz, 2H), 7.01 (d,  $J$  = 1.8 Hz, 1H), 6.77 (dd,  $J$  = 7.4, 1.4 Hz, 1H), 6.63 (d,  $J$  = 7.9 Hz, 1H), 4.65 (dd,  $J$  = 12.5, 6.3 Hz, 1H), 3.43 (s, 3H), 2.60 (td,  $J$  = 12.8, 7.6 Hz, 1H), 2.41-2.29 (m, 1H), 2.25 (s, 3H), 1.84 (ddd,  $J$  = 13.1, 11.8, 6.3 Hz, 1H), 1.07 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.1, 175.3, 142.2, 138.2, 136.1, 133.2, 130.9, 128.6, 128.6, 127.2, 126.7, 123.6, 46.1, 39.6, 35.2, 35.0, 21.1, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{20}\text{H}_{21}\text{NNaO}_2$   $[\text{M}+\text{Na}]^+$  : 330.1465, found: 330.1476.

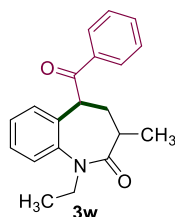


**5-benzoyl-8-fluoro-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3u):** 39 mg; 62% yield; yellow solid; mp = 121-123 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.75-7.67 (m, 2H), 7.50-7.40 (m, 1H), 7.32 (t,  $J$  = 7.8 Hz, 2H), 6.93 (dd,  $J$  = 9.5, 2.5 Hz, 1H), 6.79-6.64 (m, 2H), 4.65 (dd,  $J$  = 12.6, 6.3 Hz, 1H), 3.43 (s, 3H), 2.62 (td,  $J$  = 12.9, 7.6 Hz, 1H), 2.44-2.27 (m, 1H), 1.86 (ddd,  $J$  = 13.2, 11.8, 6.3 Hz, 1H), 1.09 (d,  $J$  = 6.5 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,

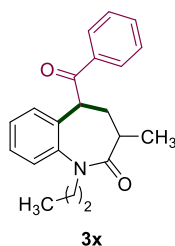
Chloroform-*d*)  $\delta$  198.7, 175.1, 143.9, 143.8, 135.9, 133.5, 129.7, 129.6, 128.7, 128.6, 128.2, 128.1, 113.4, 113.2, 110.6, 110.3, 45.8, 39.7, 35.2, 15.6.  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -112.6 (td,  $J = 9.0, 6.5$  Hz). **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{18}\text{NaNO}_2\text{F}$   $[\text{M}+\text{Na}]^+$  : 334.1214, found: 334.1207.



**5-benzoyl-1-methyl-3-phenyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3v):** 38 mg; 53% yield; yellow solid; mp = 140-142 °C;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.79-7.72 (m, 2H), 7.44 (t,  $J = 7.4$  Hz, 1H), 7.34-7.27 (m, 4H), 7.23-7.16 (m, 5H), 7.02 (ddd,  $J = 8.6, 6.4, 2.3$  Hz, 1H), 6.88-6.77 (m, 1H), 4.87 (dd,  $J = 12.5, 6.3$  Hz, 1H), 3.54 (dd,  $J = 12.4, 7.5$  Hz, 1H), 3.46 (s, 3H), 2.89-2.74 (m, 1H), 2.49 (td,  $J = 12.9, 6.3$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  198.5, 173.0, 142.5, 137.9, 136.0, 133.5, 133.3, 129.5, 128.7, 128.6, 128.5, 128.0, 127.2, 127.1, 126.8, 123.1, 46.7, 46.5, 39.1, 35.5. **HRMS** (ESI) calcd for  $\text{C}_{24}\text{H}_{21}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 378.1465, found: 378.1468.



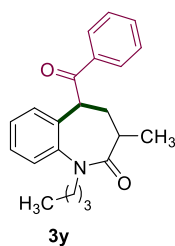
**5-benzoyl-1-ethyl-3-methyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3w):** 40 mg; 65% yield; yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.75-7.69 (m, 2H), 7.47-7.39 (m, 1H), 7.29 (t,  $J = 7.8$  Hz, 2H), 7.25-7.20 (m, 2H), 6.98 (ddd,  $J = 7.7, 6.1, 2.5$  Hz, 1H), 6.82-6.75 (m, 1H), 4.70 (dd,  $J = 12.6, 6.3$  Hz, 1H), 4.47 (dq,  $J = 14.2, 7.2$  Hz, 1H), 3.54 (dq,  $J = 13.9, 7.0$  Hz, 1H), 2.60 (td,  $J = 12.9, 7.6$  Hz, 1H), 2.40-2.24 (m, 1H), 1.87 (ddd,  $J = 13.2, 11.8, 6.4$  Hz, 1H), 1.26 (t,  $J = 7.1$  Hz, 3H), 1.06 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  199.1, 174.5, 140.8, 136.2, 135.0, 133.2, 128.6, 128.5, 128.2, 126.9, 126.6, 123.5, 46.5, 42.4, 39.7, 35.0, 15.6, 14.0. **HRMS** (ESI) calcd for  $\text{C}_{20}\text{H}_{21}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 330.1465, found: 330.1465.



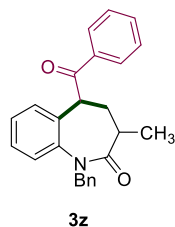
**5-benzoyl-1-ethyl-3-methyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3x):** 44 mg; 69% yield; yellow oil;  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.74-7.69 (m, 2H), 7.45-7.38 (m,



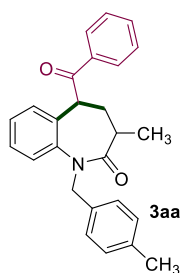
1H), 7.29 (dd,  $J = 8.4, 7.2$  Hz, 2H), 7.24-7.21 (m, 2H), 6.97 (dt,  $J = 7.7, 4.3$  Hz, 1H), 6.76 (d,  $J = 7.7$  Hz, 1H), 4.70 (dd,  $J = 12.5, 6.3$  Hz, 1H), 4.31 (ddd,  $J = 13.5, 10.3, 6.0$  Hz, 1H), 3.43 (ddd,  $J = 13.4, 10.1, 5.0$  Hz, 1H), 2.60 (td,  $J = 12.9, 7.5$  Hz, 1H), 2.37-2.24 (m, 1H), 1.86 (ddd,  $J = 13.2, 11.8, 6.4$  Hz, 1H), 1.74 (dddd,  $J = 13.3, 10.1, 7.5, 6.0$  Hz, 1H), 1.68-1.53 (m, 1H), 1.05 (d,  $J = 6.5$  Hz, 3H), 0.94 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  199.1, 174.6, 141.1, 136.2, 134.8, 133.2, 128.6, 128.5, 128.2, 126.9, 126.5, 123.3, 49.4, 46.5, 39.6, 35.0, 22.1, 15.6, 11.7. **HRMS** (ESI) calcd for  $\text{C}_{21}\text{H}_{23}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 344.1621, found: 344.1620.



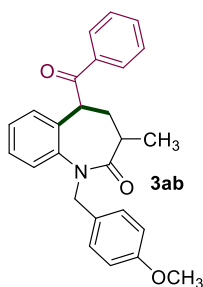
**5-benzoyl-1-ethyl-3-methyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3y):** 47 mg; 70% yield; yellow solid; mp = 105-107 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.77-7.70 (m, 2H), 7.46-7.39 (m, 1H), 7.29 (t,  $J = 7.8$  Hz, 2H), 7.25-7.20 (m, 2H), 6.97 (ddd,  $J = 7.7, 5.0, 3.7$  Hz, 1H), 6.81-6.74 (m, 1H), 4.71 (dd,  $J = 12.5, 6.3$  Hz, 1H), 4.41 (ddd,  $J = 13.5, 9.9, 6.2$  Hz, 1H), 3.44 (ddd,  $J = 13.5, 9.8, 5.0$  Hz, 1H), 2.60 (td,  $J = 12.9, 7.5$  Hz, 1H), 2.37-2.24 (m, 1H), 1.86 (ddd,  $J = 13.1, 11.8, 6.4$  Hz, 1H), 1.69 (dddd,  $J = 12.8, 9.7, 6.2, 3.6$  Hz, 1H), 1.62-1.49 (m, 1H), 1.45-1.28 (m, 2H), 1.06 (d,  $J = 6.5$  Hz, 3H), 0.89 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  199.1, 174.6, 141.0, 136.2, 134.8, 133.2, 128.5, 128.2, 126.9, 126.5, 123.3, 47.4, 46.5, 39.7, 35.0, 31.1, 20.5, 15.6, 13.9. **HRMS** (ESI) calcd for  $\text{C}_{22}\text{H}_{25}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 358.1778, found: 358.1770.



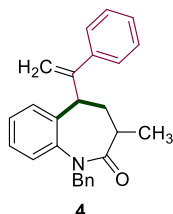
**5-benzoyl-1-benzyl-3-methyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3z):** 52 mg; 71% yield; yellow solid; mp = 135-137 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.37 (dd,  $J = 8.1, 1.3$  Hz, 1H), 7.33 (dt,  $J = 7.0, 1.5$  Hz, 2H), 7.29 (dt,  $J = 7.3, 1.4$  Hz, 1H), 7.27-7.20 (m, 4H), 7.04 (t,  $J = 7.8$  Hz, 2H), 7.00-6.94 (m, 2H), 6.91 (td,  $J = 7.6, 1.3$  Hz, 1H), 6.58 (dd,  $J = 7.8, 1.5$  Hz, 1H), 5.89 (d,  $J = 14.1$  Hz, 1H), 4.35 (d,  $J = 14.1$  Hz, 1H), 4.30 (dd,  $J = 12.5, 6.4$  Hz, 1H), 2.57 (td,  $J = 12.9, 7.5$  Hz, 1H), 2.41-2.28 (m, 1H), 1.84 (ddd,  $J = 13.2, 11.8, 6.4$  Hz, 1H), 1.10 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  198.9, 174.8, 140.2, 137.9, 135.6, 135.1, 132.8, 129.4, 128.8, 128.5, 128.4, 128.0, 127.8, 127.1, 126.7, 123.7, 50.3, 45.9, 39.7, 34.8, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{25}\text{H}_{23}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 392.1621, found: 392.1598.



**5-benzoyl-3-methyl-1-(4-methylbenzyl)-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3aa):** 55 mg; 72% yield; yellow solid; mp = 160-162 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.37 (dd,  $J = 8.0, 1.3$  Hz, 1H), 7.31 (tt,  $J = 7.0, 1.8$  Hz, 1H), 7.26-7.20 (m, 3H), 7.05-6.96 (m, 6H), 6.90 (td,  $J = 7.6, 1.3$  Hz, 1H), 6.56 (dd,  $J = 7.8, 1.4$  Hz, 1H), 5.87 (d,  $J = 14.1$  Hz, 1H), 4.33-4.23 (m, 2H), 2.56 (td,  $J = 12.9, 7.5$  Hz, 1H), 2.40-2.27 (m, 1H), 2.24 (s, 3H), 1.85 (ddd,  $J = 13.2, 11.8, 6.4$  Hz, 1H), 1.10 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  198.9, 174.8, 140.2, 137.3, 135.6, 135.3, 135.0, 132.8, 129.5, 129.3, 128.6, 128.3, 128.0, 127.1, 126.6, 123.8, 50.1, 46.1, 39.7, 34.8, 21.3, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{26}\text{H}_{25}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 406.1778, found: 406.1754.

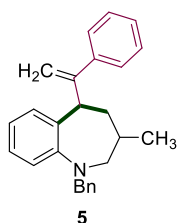


**5-benzoyl-1-(4-methoxybenzyl)-3-methyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (3ab):** 55 mg; 69% yield; yellow solid; mp = 105-107 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.37 (dd,  $J = 8.1, 1.3$  Hz, 1H), 7.31 (tt,  $J = 7.4, 1.3$  Hz, 1H), 7.28-7.21 (m, 3H), 7.05 (t,  $J = 7.9$  Hz, 2H), 6.99-6.87 (m, 3H), 6.78-6.70 (m, 2H), 6.58 (dd,  $J = 7.7, 1.5$  Hz, 1H), 5.88 (d,  $J = 14.1$  Hz, 1H), 4.33-4.19 (m, 2H), 3.66 (s, 3H), 2.56 (td,  $J = 12.9, 7.5$  Hz, 1H), 2.39-2.26 (m, 1H), 1.83 (ddd,  $J = 13.1, 11.7, 6.4$  Hz, 1H), 1.10 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  198.9, 174.7, 159.1, 140.1, 135.6, 135.2, 132.9, 130.7, 130.1, 128.6, 128.3, 128.0, 127.0, 126.7, 123.9, 114.1, 55.0, 49.6, 45.9, 39.8, 34.7, 15.6. **HRMS** (ESI) calcd for  $\text{C}_{26}\text{H}_{25}\text{NaNO}_3$   $[\text{M}+\text{Na}]^+$  : 422.1727, found: 422.1731.

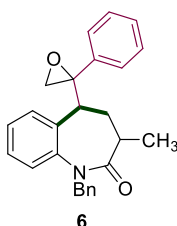


**1-benzyl-3-methyl-5-(1-phenylvinyl)-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (4):** 51 mg; 70% yield; pale yellow solid; mp = 141-143 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.34 (dd,  $J = 7.5, 2.1$  Hz, 2H), 7.30-7.23 (m, 4H), 7.21-7.17 (m, 1H), 7.10-7.05 (m, 1H), 7.02-6.95 (m, 4H), 6.71-6.66 (m, 2H), 5.72-5.65 (m, 2H), 5.26 (d,  $J = 1.6$  Hz, 1H), 4.55 (d,  $J =$

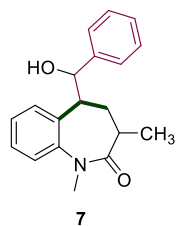
14.3 Hz, 1H), 3.91 (dd,  $J = 13.0, 5.9$  Hz, 1H), 2.51-2.40 (m, 1H), 2.26 (td,  $J = 12.7, 7.6$  Hz, 1H), 2.11 (td,  $J = 12.1, 6.0$  Hz, 1H), 1.20 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  175.1, 147.3, 141.0, 140.9, 137.9, 137.5, 129.1, 128.6, 128.1, 127.6, 127.4, 127.2, 127.0, 126.3, 125.9, 122.8, 115.0, 50.7, 43.3, 41.2, 35.5, 16.0. **HRMS** (ESI) calcd for  $\text{C}_{26}\text{H}_{25}\text{NaNO}$   $[\text{M}+\text{Na}]^+$  : 390.1828, found: 390.1812.



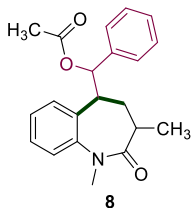
**1-benzyl-3-methyl-5-(1-phenylvinyl)-2,3,4,5-tetrahydro-1H-benzo[b]azepine (3z):** 54 mg; 76% yield; colorless oil;  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.54-7.48 (m, 2H), 7.33 (q,  $J = 3.8, 2.8$  Hz, 6H), 7.29-7.23 (m, 3H), 7.07 (dd,  $J = 7.4, 1.8$  Hz, 1H), 6.95 (ddd,  $J = 8.6, 7.4, 1.8$  Hz, 1H), 6.57 (td,  $J = 7.3, 1.1$  Hz, 1H), 6.41 (d,  $J = 8.3$  Hz, 1H), 6.33 (dd,  $J = 7.1, 1.7$  Hz, 1H), 4.72 (d,  $J = 17.6$  Hz, 1H), 4.51 (d,  $J = 17.6$  Hz, 1H), 3.64 (dq,  $J = 4.3, 2.1$  Hz, 1H), 3.48 (dd,  $J = 7.2, 1.3$  Hz, 1H), 2.85-2.68 (m, 2H), 1.57-1.48 (m, 2H), 0.93 (d,  $J = 6.9$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  146.9, 146.0, 139.9, 139.6, 128.7, 128.6, 128.4, 127.9, 127.9, 127.3, 126.8, 126.1, 125.6, 118.9, 116.5, 115.1, 62.7, 58.3, 44.7, 39.1, 34.0, 23.3. **HRMS** (ESI) calcd for  $\text{C}_{26}\text{H}_{27}\text{NaN}$   $[\text{M}+\text{Na}]^+$  : 376.2036, found: 376.2021.



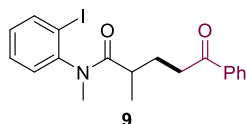
**1-benzyl-3-methyl-5-(2-phenyloxiran-2-yl)-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (6):** 52 mg; 68% yield; pale yellow solid; mp = 153-155 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.37 (dd,  $J = 8.0, 1.5$  Hz, 1H), 7.34-7.23 (m, 6H), 7.20-7.10 (m, 5H), 7.03 (dd,  $J = 8.5, 7.0$  Hz, 2H), 6.77-6.66 (m, 2H), 5.70 (d,  $J = 14.3$  Hz, 1H), 4.53 (d,  $J = 14.4$  Hz, 1H), 3.63 (dd,  $J = 13.0, 6.8$  Hz, 1H), 3.32 (d,  $J = 4.8$  Hz, 1H), 3.16 (d,  $J = 4.8$  Hz, 1H), 2.35 (dt,  $J = 12.0, 6.7$  Hz, 1H), 2.05 (ddd,  $J = 13.1, 12.1, 6.9$  Hz, 1H), 1.60 (td,  $J = 13.1, 7.3$  Hz, 1H), 1.14 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform- $d$ )  $\delta$  174.7, 140.9, 139.5, 137.5, 136.5, 128.8, 128.6, 128.2, 127.6, 127.6, 127.3, 126.6, 126.5, 126.0, 123.6, 57.6, 52.5, 50.6, 40.0, 39.4, 34.9, 15.8. **HRMS** (ESI) calcd for  $\text{C}_{26}\text{H}_{25}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 406.1778, found: 406.1791.



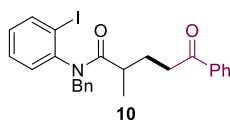
**5-(hydroxy(phenyl)methyl)-1,3-dimethyl-1,3,4,5-tetrahydro-2H-benzo[b]azepin-2-one (7):** 54 mg; 91% yield; pale yellow solid; mp = 218-219 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.51 (dd,  $J = 7.1, 2.2$  Hz, 1H), 7.33-7.21 (m, 7H), 7.12 (dd,  $J = 7.4, 1.9$  Hz, 1H), 4.96 (d,  $J = 9.9$  Hz, 1H), 3.29 (s, 3H), 3.12 (ddd,  $J = 12.9, 10.0, 6.6$  Hz, 1H), 2.29 (s, 1H), 2.17 (dt,  $J = 11.9, 6.7$  Hz, 1H), 1.48 (td,  $J = 12.9, 7.3$  Hz, 1H), 1.13 (dt,  $J = 12.5, 6.2$  Hz, 1H), 0.80 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  174.9, 143.7, 141.9, 135.5, 128.7, 128.4, 127.3, 127.0, 126.2, 125.7, 122.8, 74.9, 45.1, 41.9, 35.4, 35.1, 15.5. **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{21}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 318.1465, found: 318.1465.



**1,3-dimethyl-2-oxo-2,3,4,5-tetrahydro-1H-benzo[b]azepin-5-yl(phenyl)methyl acetate (8):** 56 mg; 83% yield; pale yellow solid; mp = 190-192 °C;  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.42-7.30 (m, 6H), 7.26-7.20 (m, 3H), 6.13 (d,  $J = 10.8$  Hz, 1H), 3.43 (s, 4H), 2.27 (dt,  $J = 11.9, 6.7$  Hz, 1H), 1.56 (td,  $J = 13.0, 7.3$  Hz, 1H), 1.29-1.24 (m, 1H), 0.90 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  174.7, 170.3, 143.2, 138.1, 135.1, 128.6, 128.5, 127.4, 127.3, 126.2, 124.7, 122.8, 75.5, 42.5, 41.5, 35.3, 35.1, 21.1, 15.5. **HRMS** (ESI) calcd for  $\text{C}_{21}\text{H}_{23}\text{NaNO}_3$   $[\text{M}+\text{Na}]^+$  : 360.1570, found: 360.1563.



**N-(2-iodophenyl)-N,2-dimethyl-5-oxo-5-phenylpentanamide (9):** 76 mg; 90% yield; yellow oil; Two sets of signals were observed due to the existence of rotamers.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  7.86 (ddt,  $J = 16.8, 7.9, 1.1$  Hz, 6H), 7.50-7.42 (m, 2H), 7.41-7.33 (m, 5H), 7.22 (dtd,  $J = 7.6, 3.6, 1.5$  Hz, 2H), 7.11 (dd,  $J = 7.8, 1.6$  Hz, 1H), 6.99 (dtd,  $J = 15.9, 7.6, 1.6$  Hz, 2H), 3.13-3.00 (m, 7H), 2.97-2.75 (m, 3H), 2.23 (q,  $J = 6.7$  Hz, 1H), 2.17-2.03 (m, 2H), 1.93-1.80 (m, 1H), 1.80-1.61 (m, 2H), 1.10 (d,  $J = 6.7$  Hz, 3H), 1.00 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz, Chloroform-*d*)  $\delta$  199.9, 175.9, 175.8, 145.6, 140.2, 140.2, 136.8, 132.9, 132.8, 129.8, 129.7, 129.7, 129.7, 129.2, 129.0, 128.5, 128.4, 128.1, 127.9, 99.6, 37.3, 36.9, 36.2, 36.1, 36.0, 35.5, 28.3, 28.2, 18.8, 17.6. **HRMS** (ESI) calcd for  $\text{C}_{19}\text{H}_{20}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 444.0431, found: 444.0432.



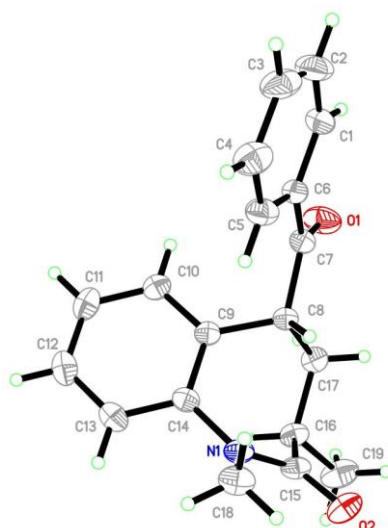
**N-benzyl-N-(2-iodophenyl)-2-methyl-5-oxo-5-phenylpentanamide (10):** 87 mg; 88% yield; yellow oil; Two sets of signals were observed due to the existence of rotamers.  $^1\text{H NMR}$  (400 MHz, Chloroform-*d*)  $\delta$  8.01-7.95 (m, 2H), 7.93 (ddd,  $J = 7.9, 2.7, 1.5$  Hz, 2H),

7.87-7.81 (m, 2H), 7.58-7.51 (m, 2H), 7.48-7.41 (m, 4H), 7.28-7.16 (m, 12H), 7.11-6.98 (m, 3H), 6.71 (dd,  $J = 7.8, 1.6$  Hz, 1H), 6.57 (dd,  $J = 7.7, 1.7$  Hz, 1H), 5.77 (dd,  $J = 14.2, 2.2$  Hz, 2H), 3.86 (dd,  $J = 14.3, 1.7$  Hz, 2H), 3.20 (ddd,  $J = 17.0, 9.6, 4.9$  Hz, 1H), 3.01 (ddd,  $J = 17.0, 9.0, 5.9$  Hz, 1H), 2.85 (t,  $J = 7.4$  Hz, 2H), 2.31-2.15 (m, 3H), 1.94 (dq,  $J = 14.0, 7.0$  Hz, 2H), 1.87-1.75 (m, 2H), 1.22 (d,  $J = 6.6$  Hz, 3H), 1.07 (d,  $J = 6.3$  Hz, 3H).  **$^{13}\text{C}$  NMR** (101 MHz, Chloroform- $d$ )  $\delta$  200.0, 199.4, 175.8, 175.7, 143.6, 143.3, 140.2, 140.2, 137.1, 136.8, 133.0, 132.8, 131.0, 130.8, 129.9, 129.7, 129.3, 129.2, 128.9, 128.9, 128.5, 128.4, 128.4, 128.3, 128.1, 127.9, 127.5, 127.4, 51.6, 51.4, 37.4, 37.1, 36.2, 35.5, 28.7, 28.1, 18.9, 17.6. **HRMS** (ESI) calcd for  $\text{C}_{25}\text{H}_{24}\text{NaNO}_2$   $[\text{M}+\text{Na}]^+$  : 520.0744, found: 520.0746.

## 7. References

(1) (a) Liu, X.; Ma, X.; Huang, Y.; Gu, Z. *Org. Lett.* **2013**, *15*, 4814. (b) Wei, W.; Wen, J.; Yang, D.; Guo, M.; Tian, L.; You, J.; Wang, H. *RSC Adv.* **2014**, *4*, 48535. (c) Tang, X.; Thomason, C. S.; Dolbier, W. R. *Org. Lett.* **2014**, *16*, 4594.

## 8. Crystallographic data of 3a

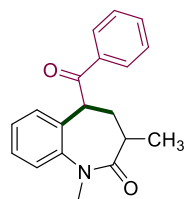


Structure of 3a CCDC: 2016010

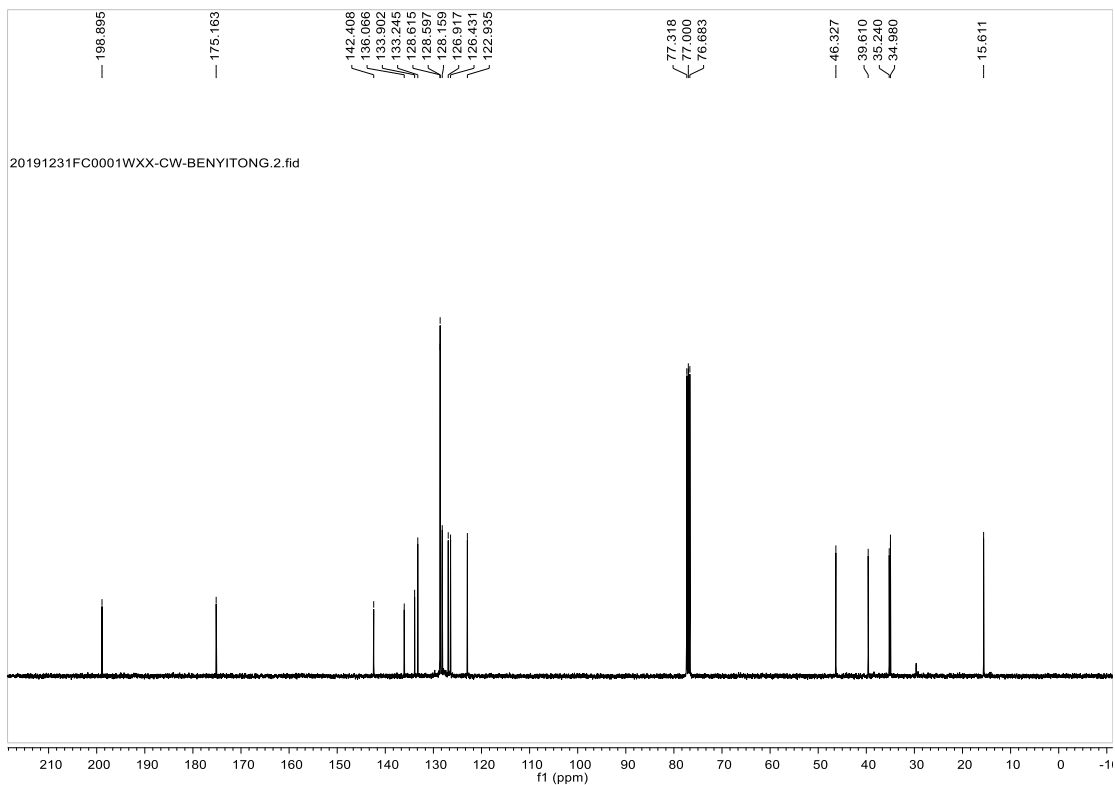
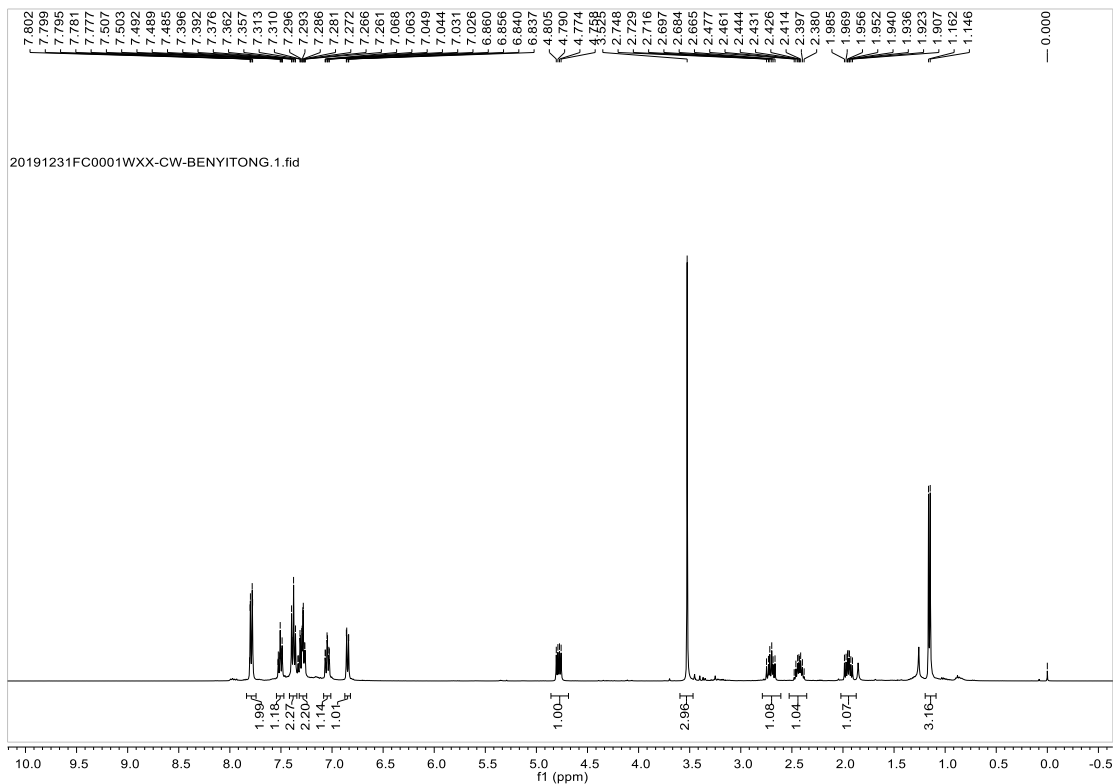
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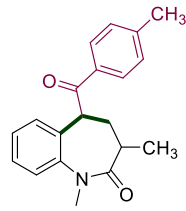
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	alpha=90	beta=90 gamma=90
Temperature:	293 K	
	Calculated	Reported
Volume	3113.32(8)	3113.31(8)
Space group	p b c a	p b c a
Hall group	-p 2ac 2ab	-p 2ac 2ab
Moiety formula	C19 H19 N O2	
Sum formula	C19 H19 N O2	C19 H19 N O2
Mr	293.35	293.35
Dx,g cm <sup>-3</sup>	1.252	1.252
Z	8	8
Mu (mm <sup>-1</sup> )	0.643	0.643
F000	1248.0	1248.0
F000'	1251.61	
h,k,lmax	18,13,21	18,13,21
Nref	2788	2789
Tmin,Tmax	0.926, 0.932	0.889, 1.000
Tmin'	0.926	
Correction method = # Reported T Limits: Tmin = 0.889 Tmax = 1.000		
AbsCorr = MULTI-SCAN		
Data completeness = 1.000	Theta (max) = 67.214	
R (reflections) = 0.0416(2352)	wR2 (reflections) = 0.1129(2789)	
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## 9. NMR spectra

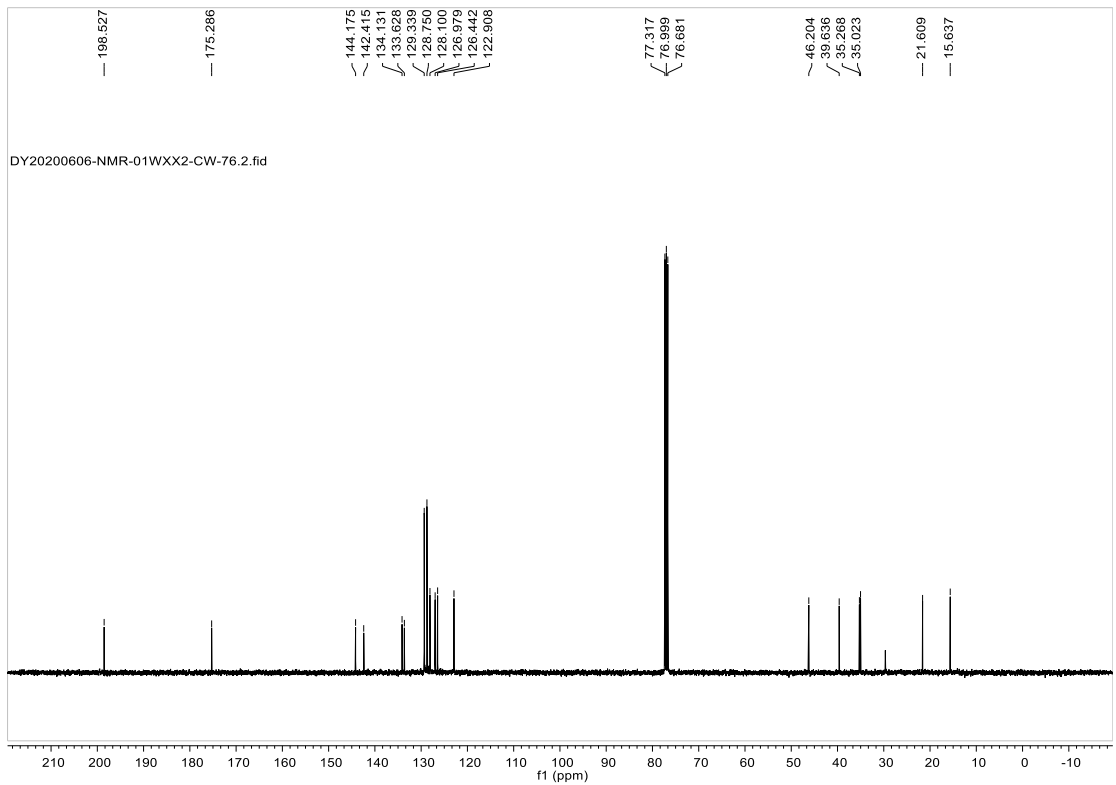
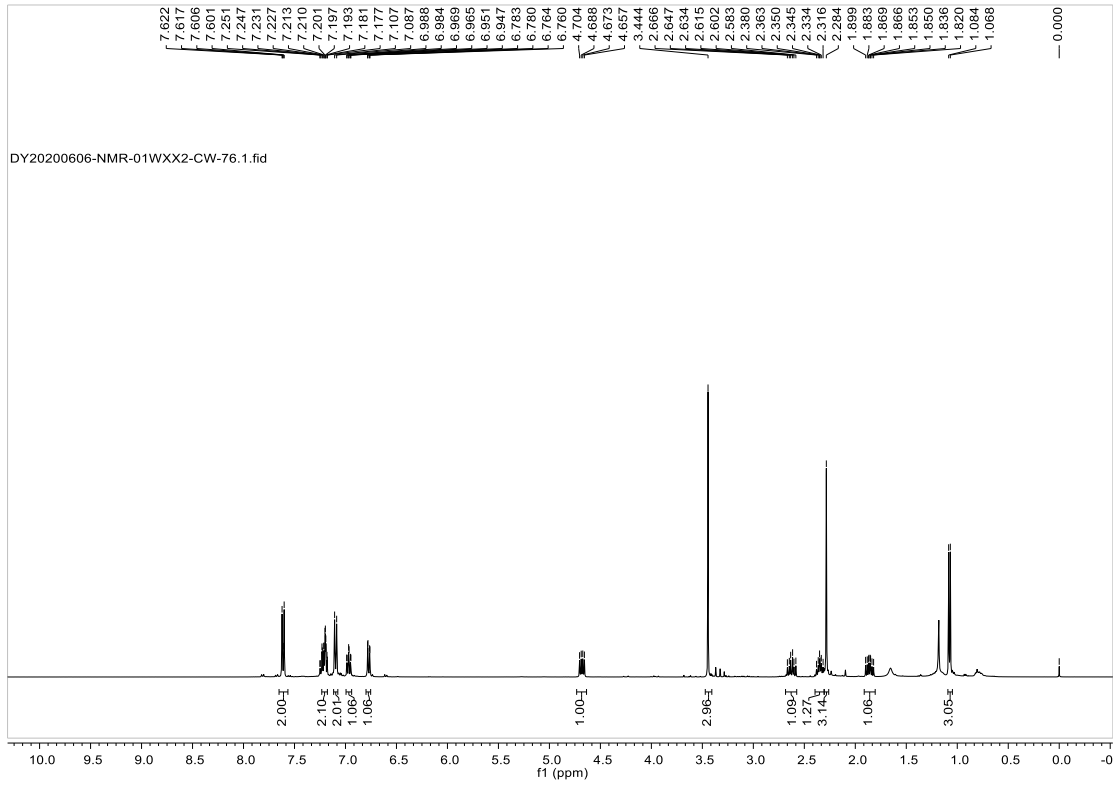


3a

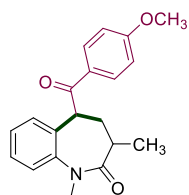




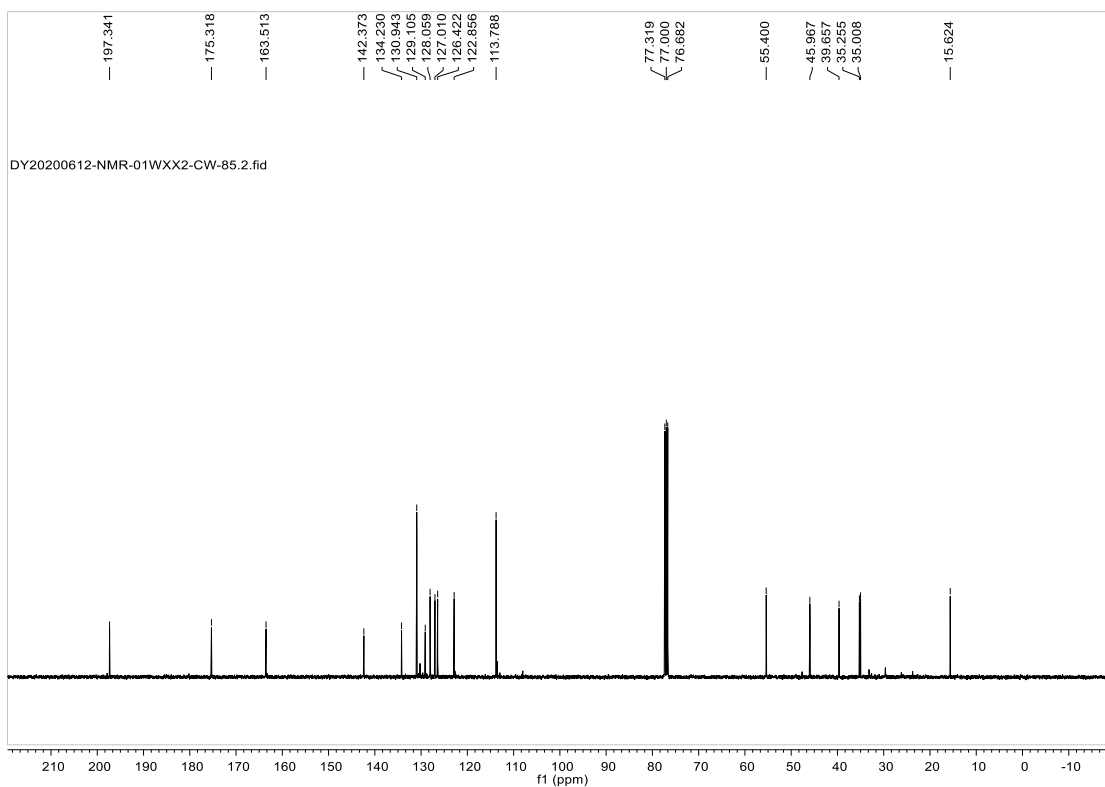
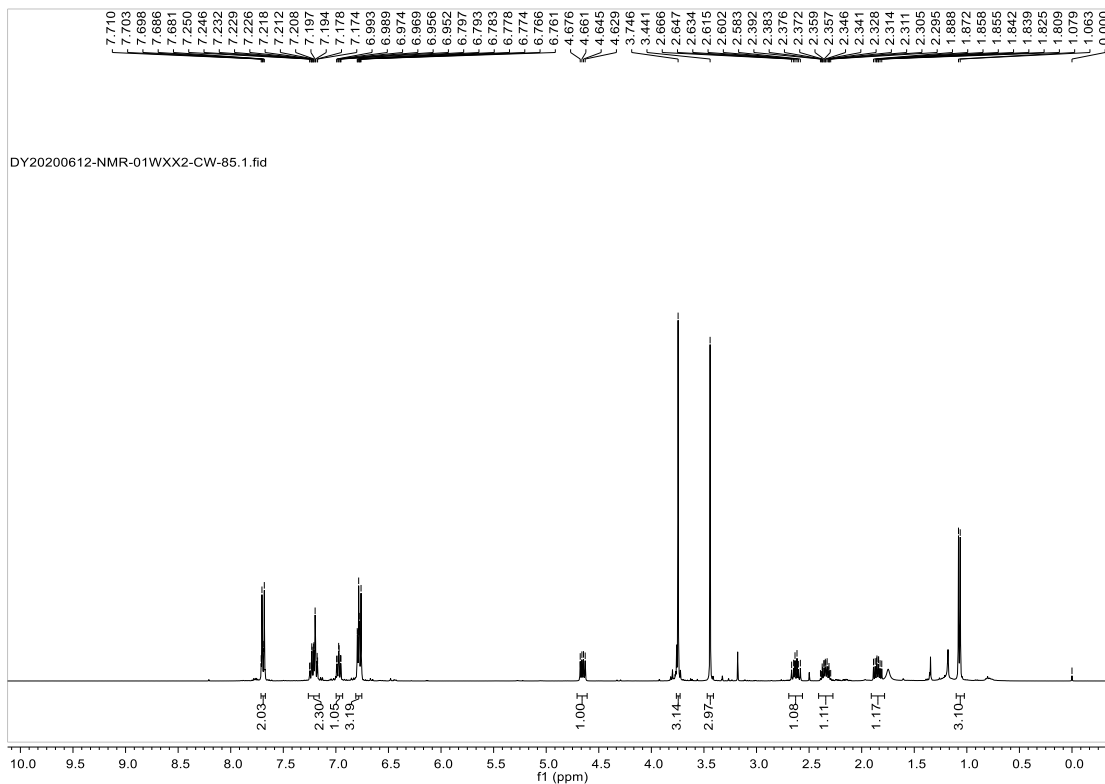
**3b**

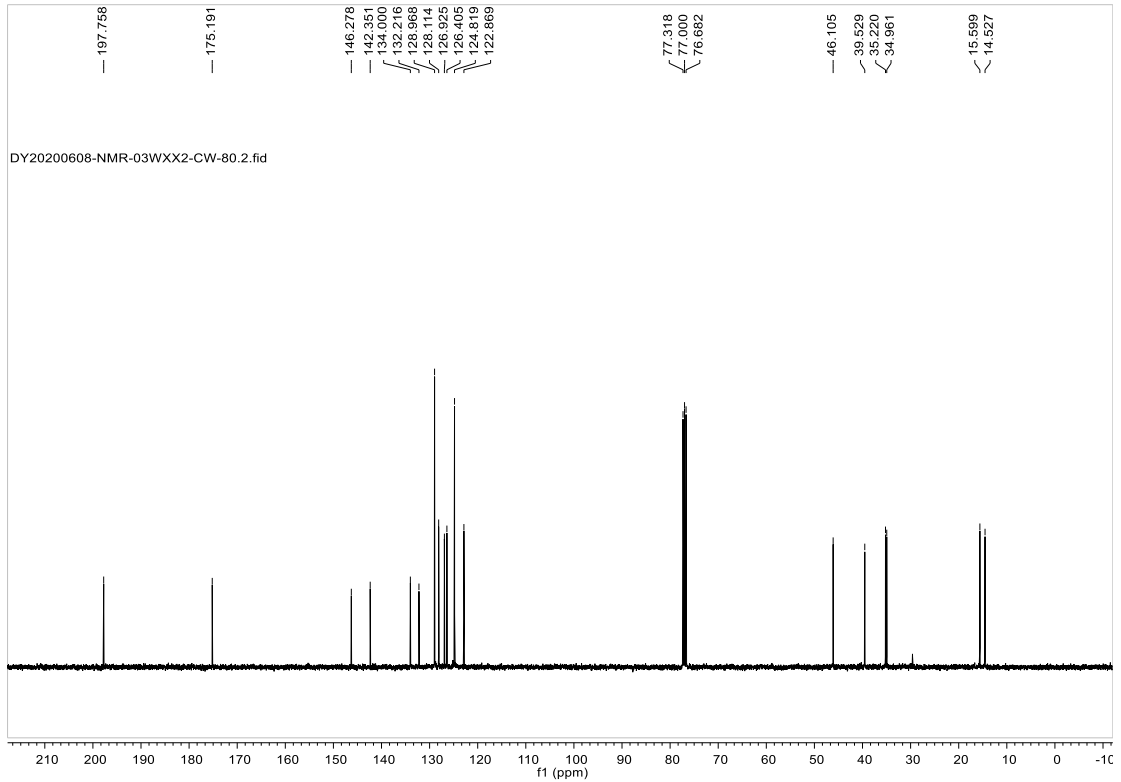
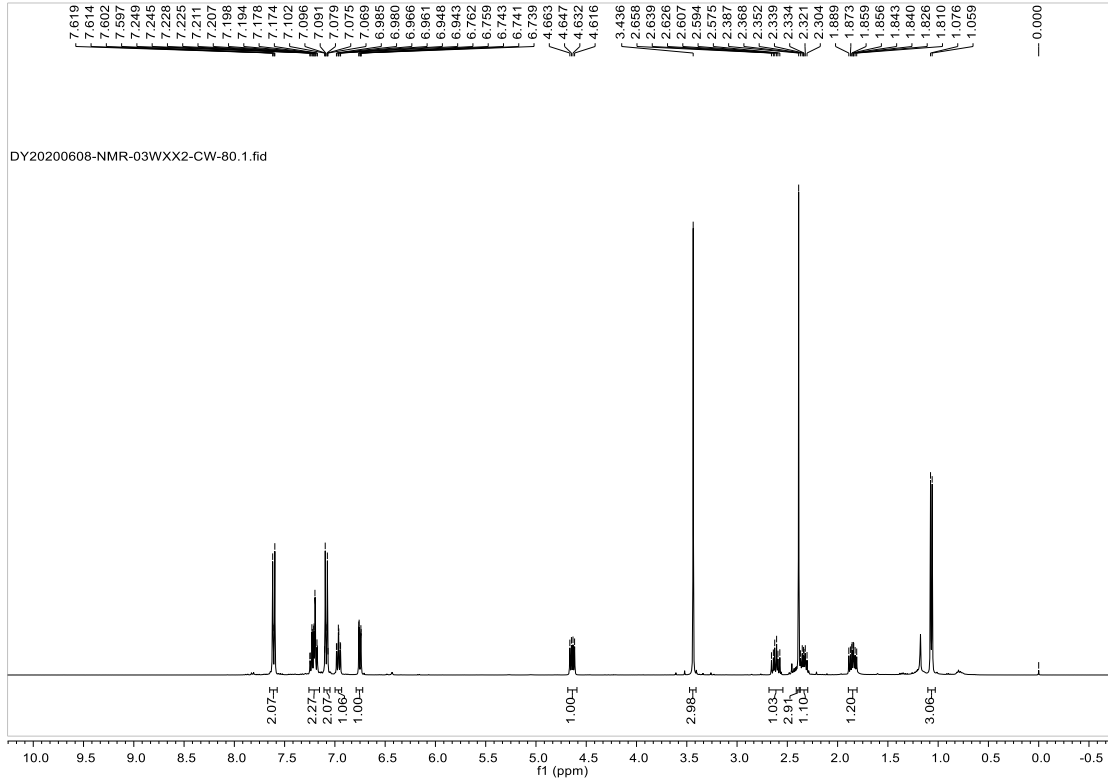
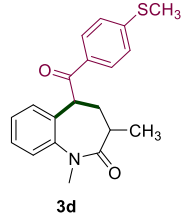


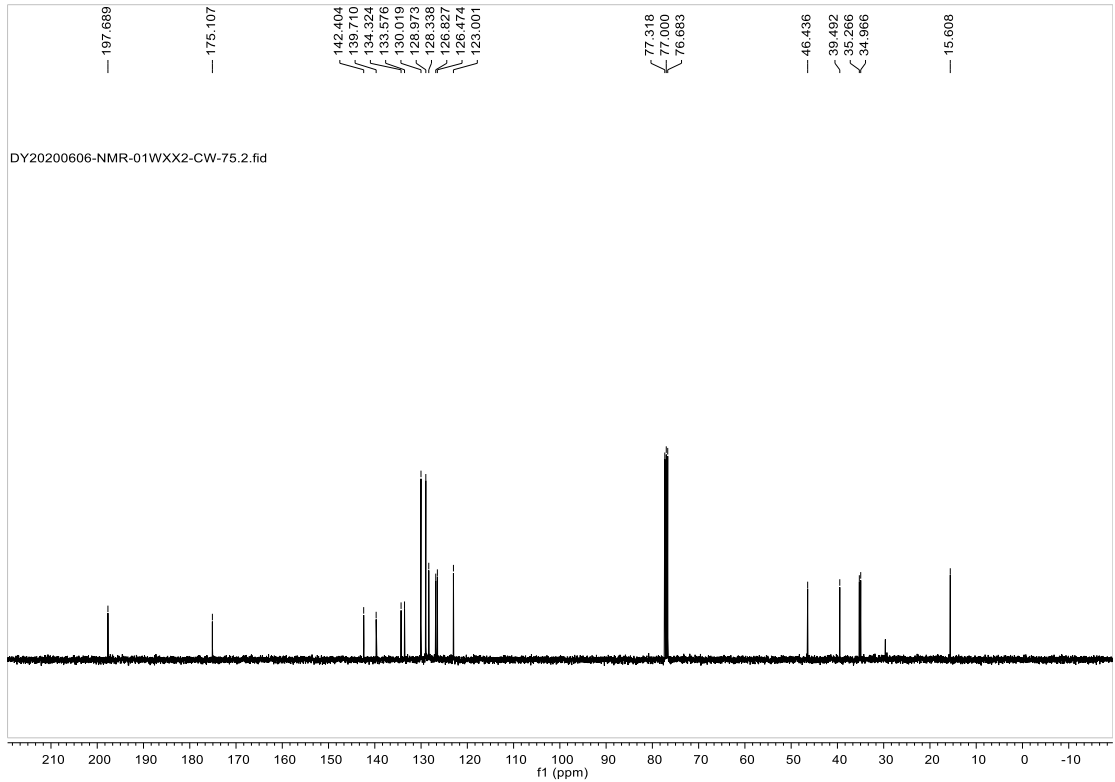
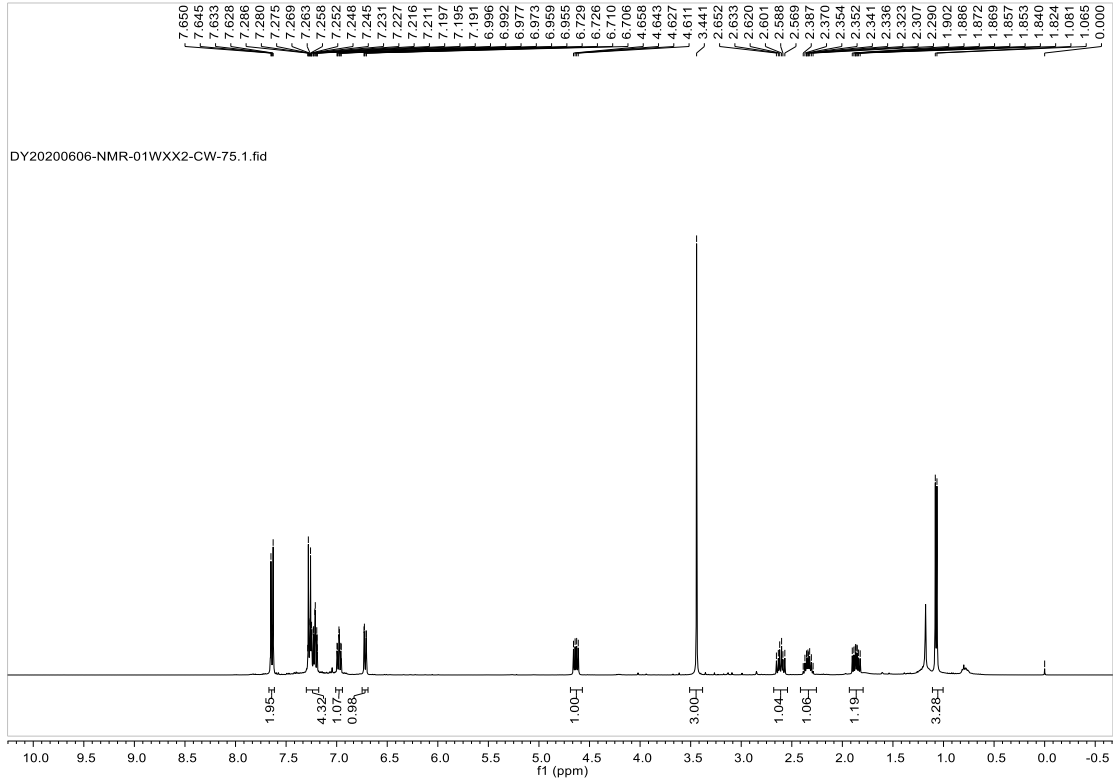
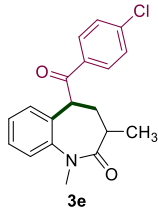


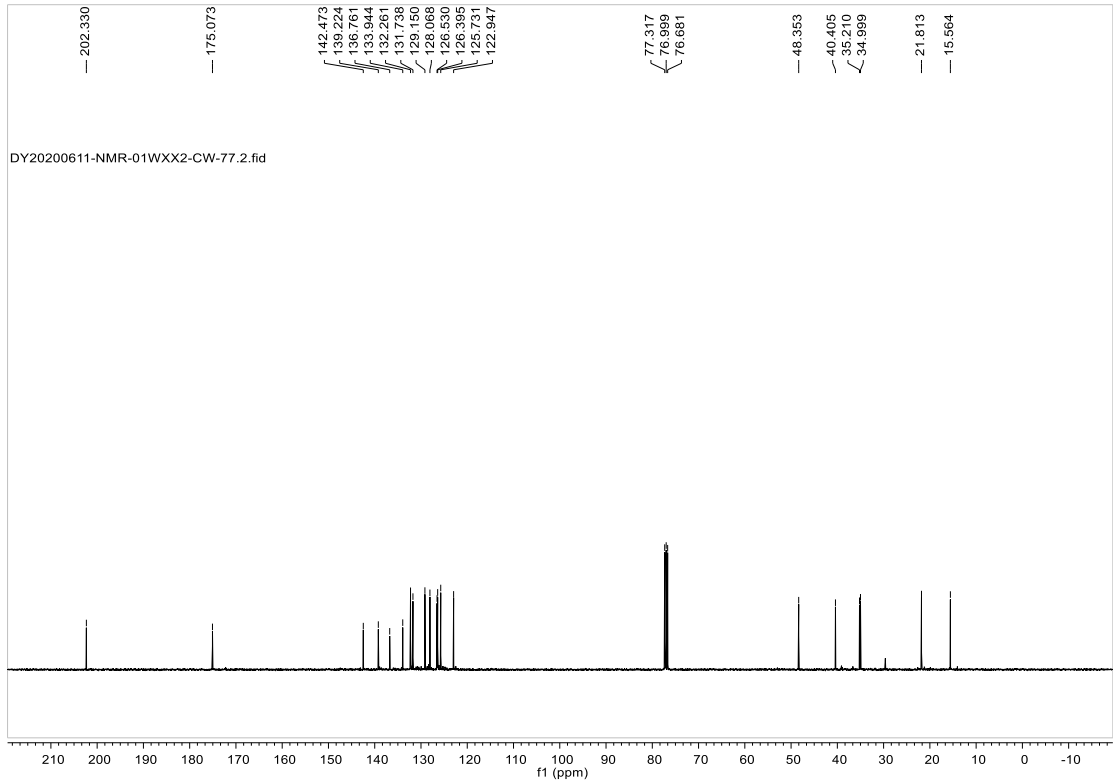
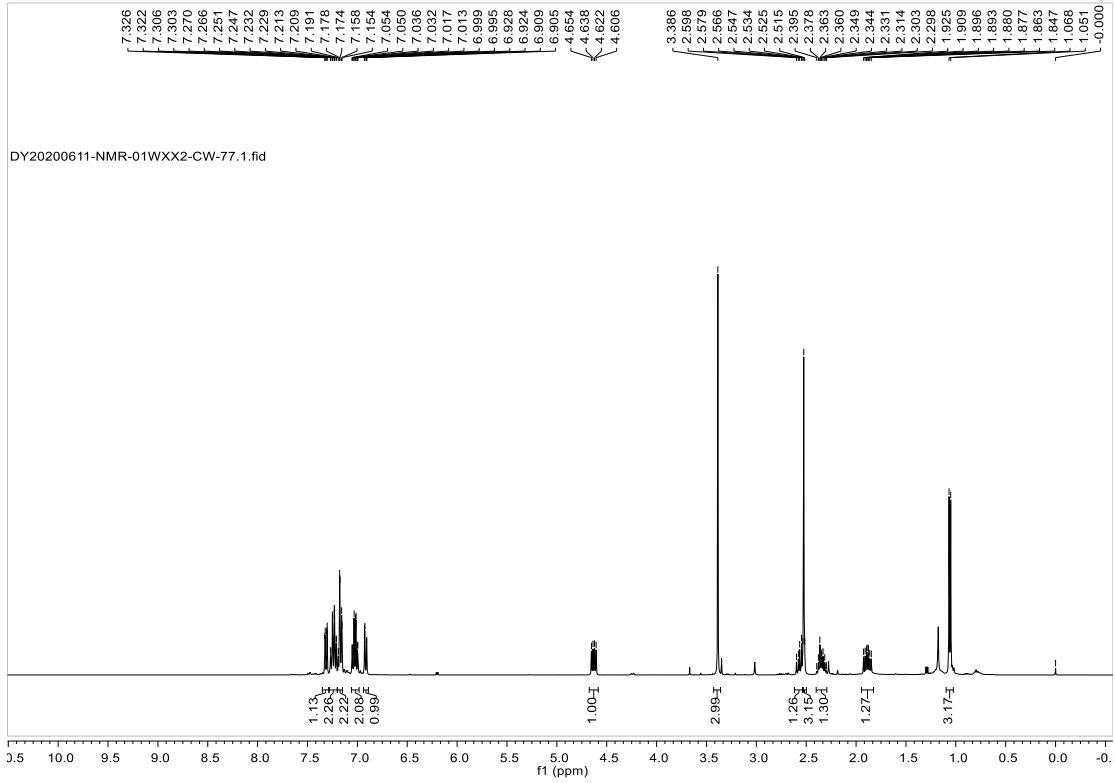
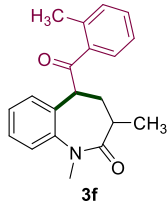


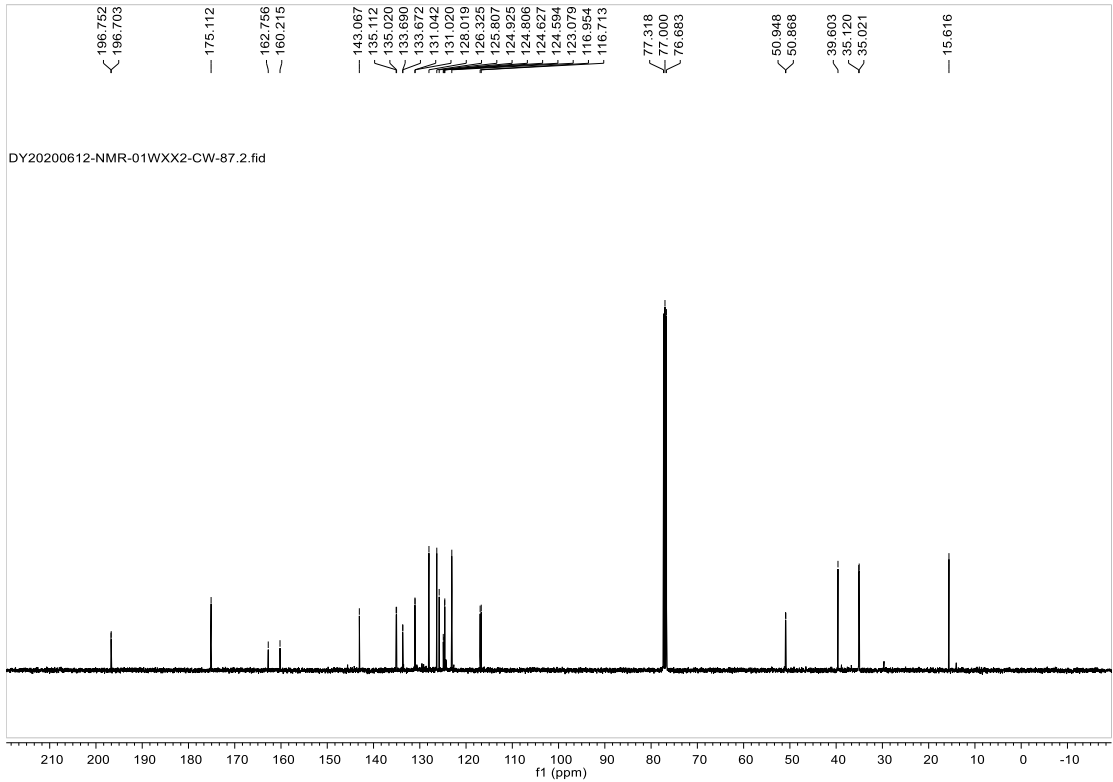
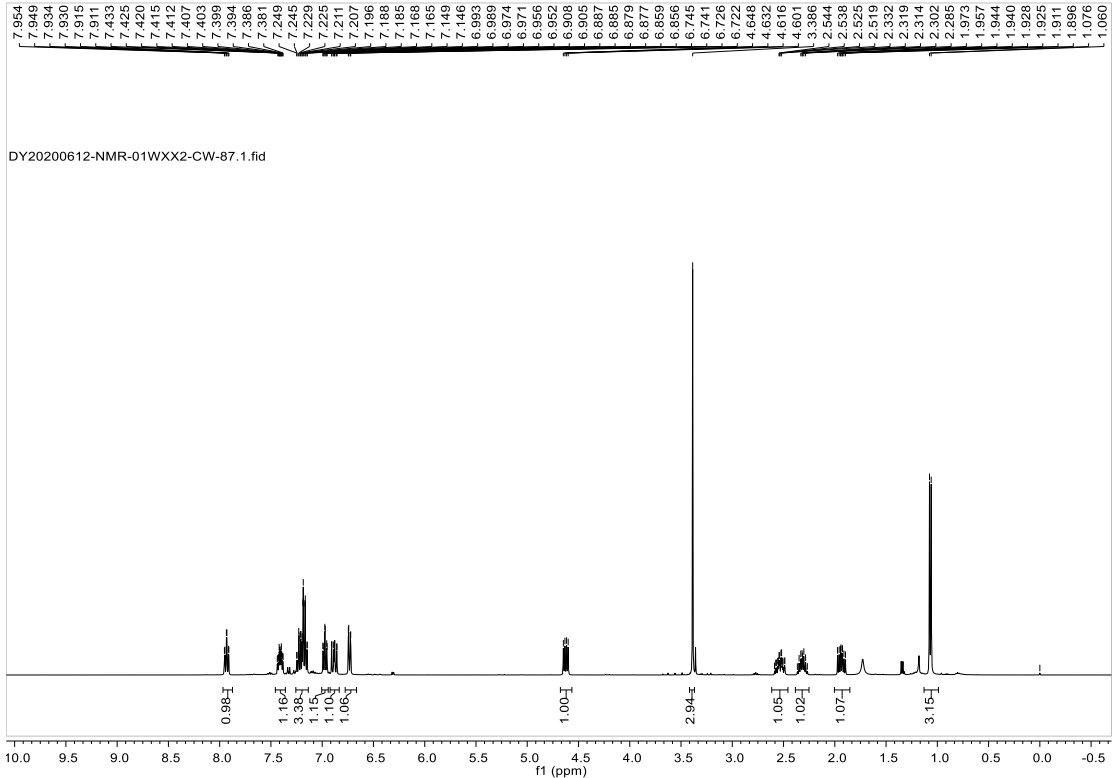
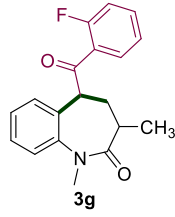
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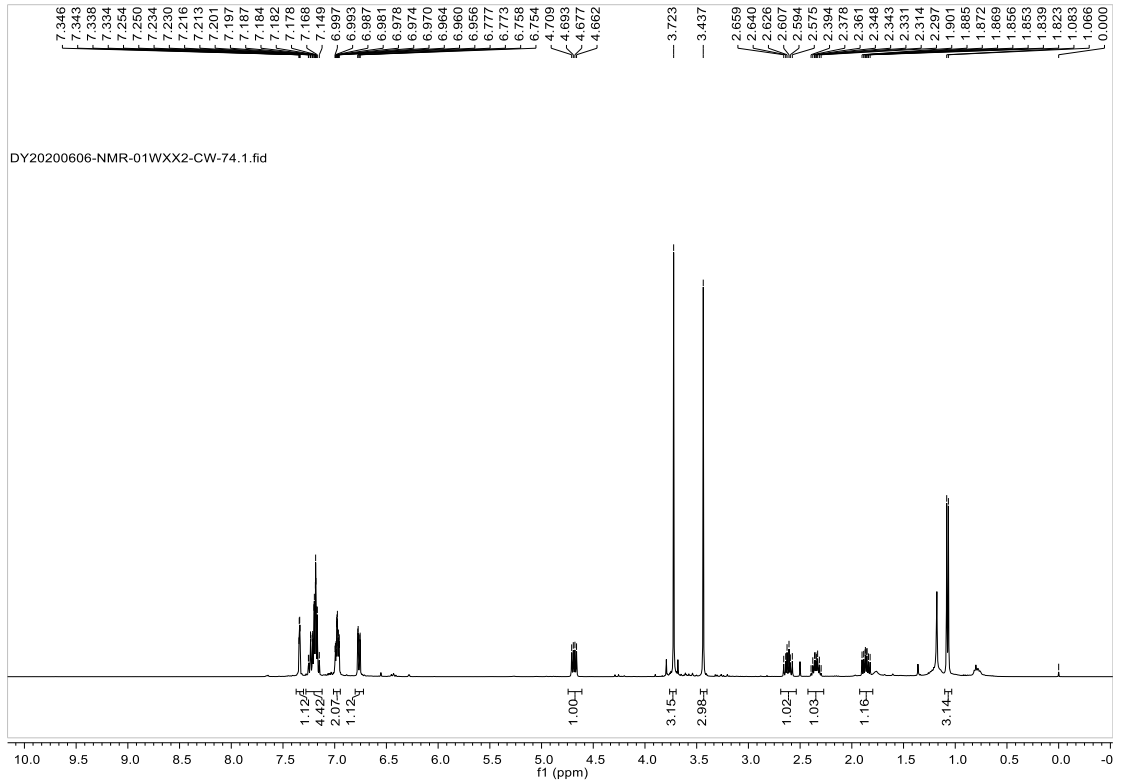
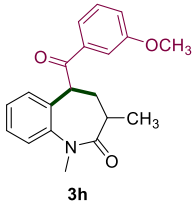
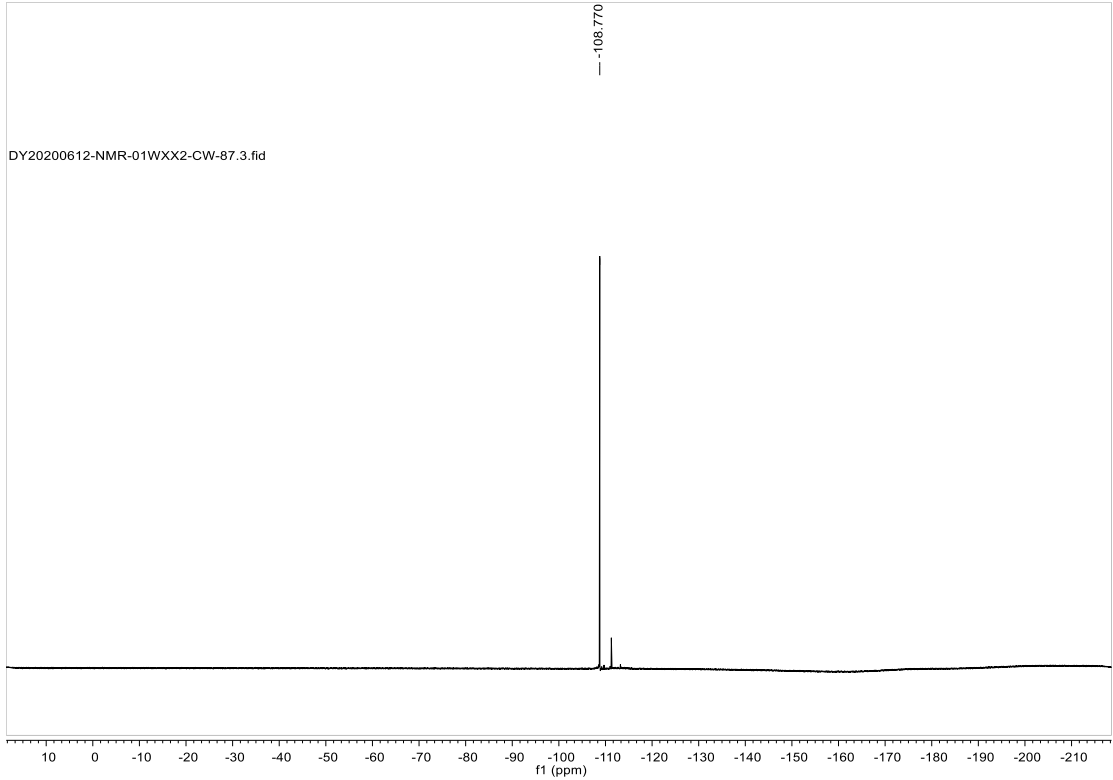


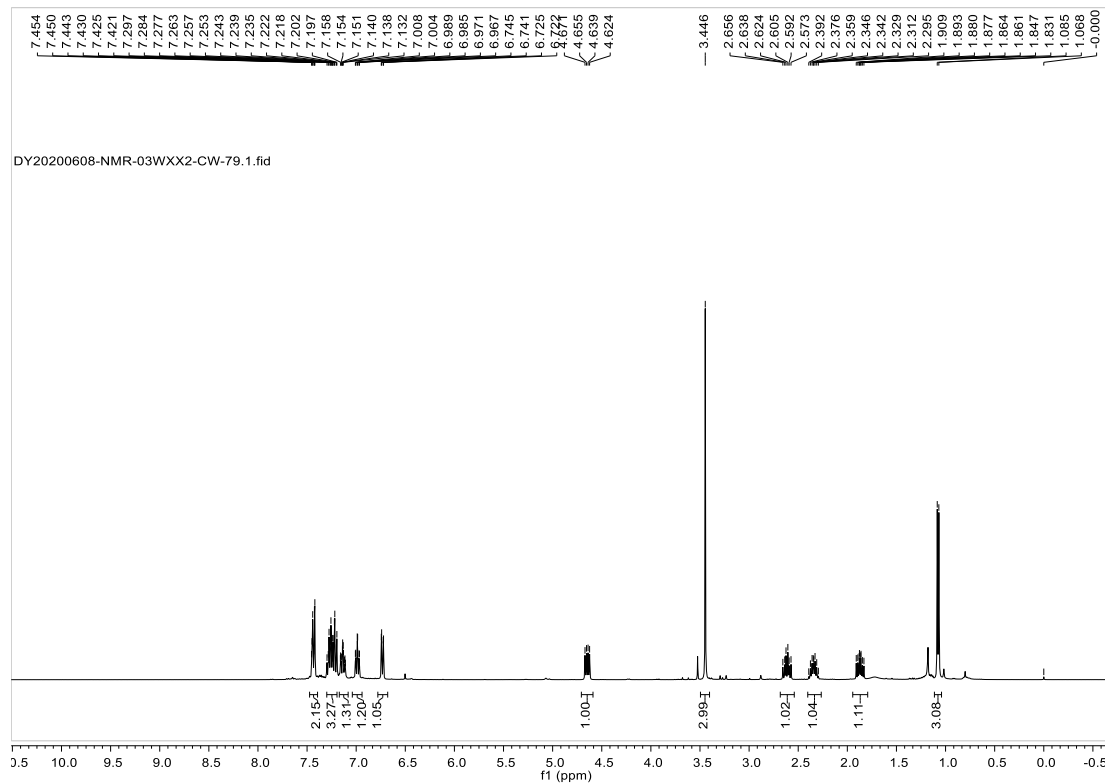
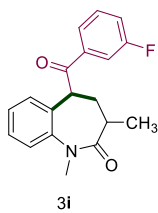
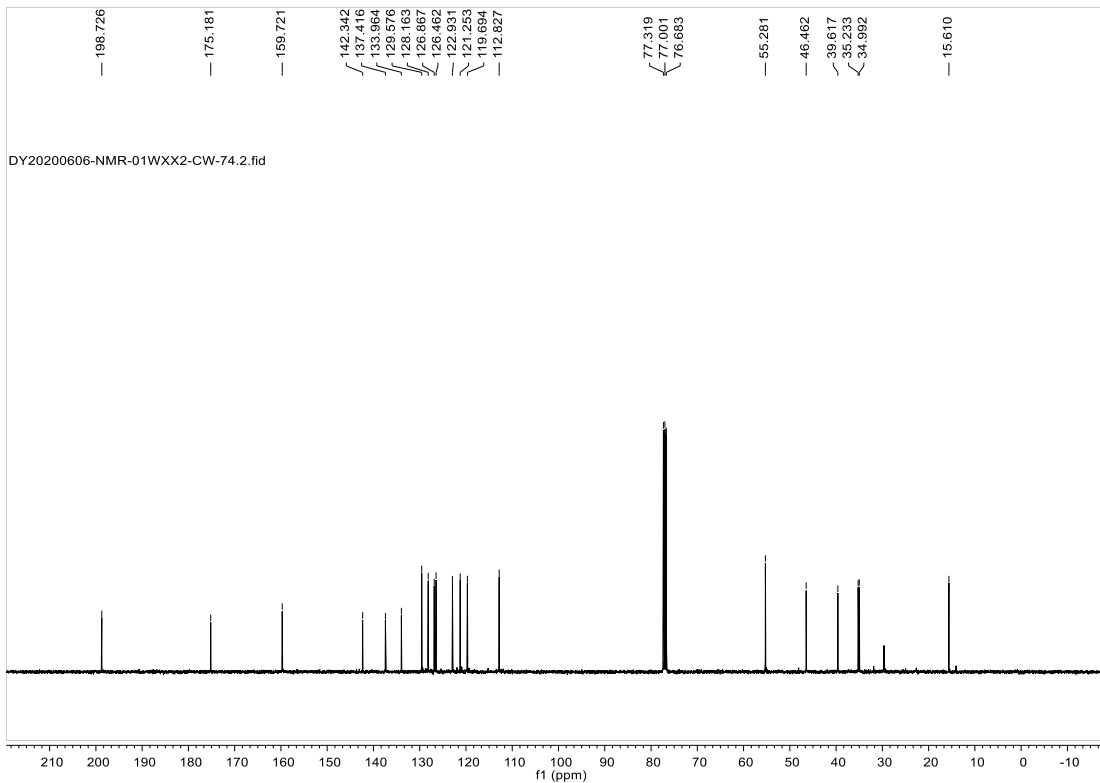


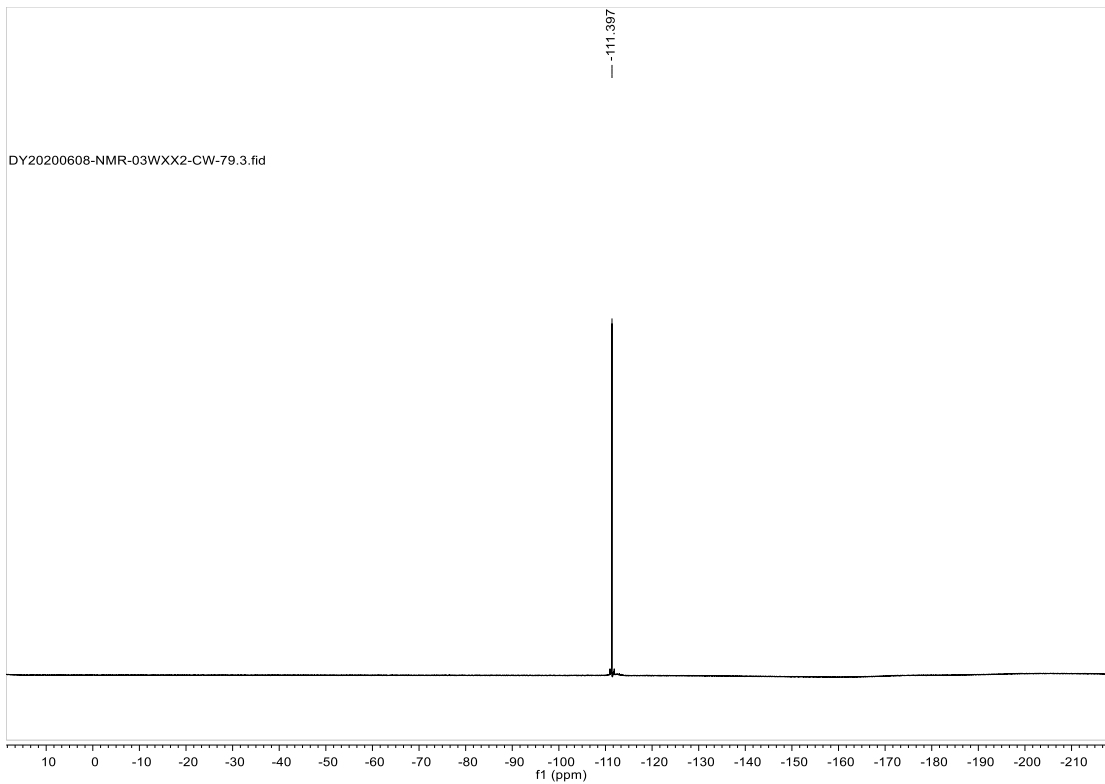
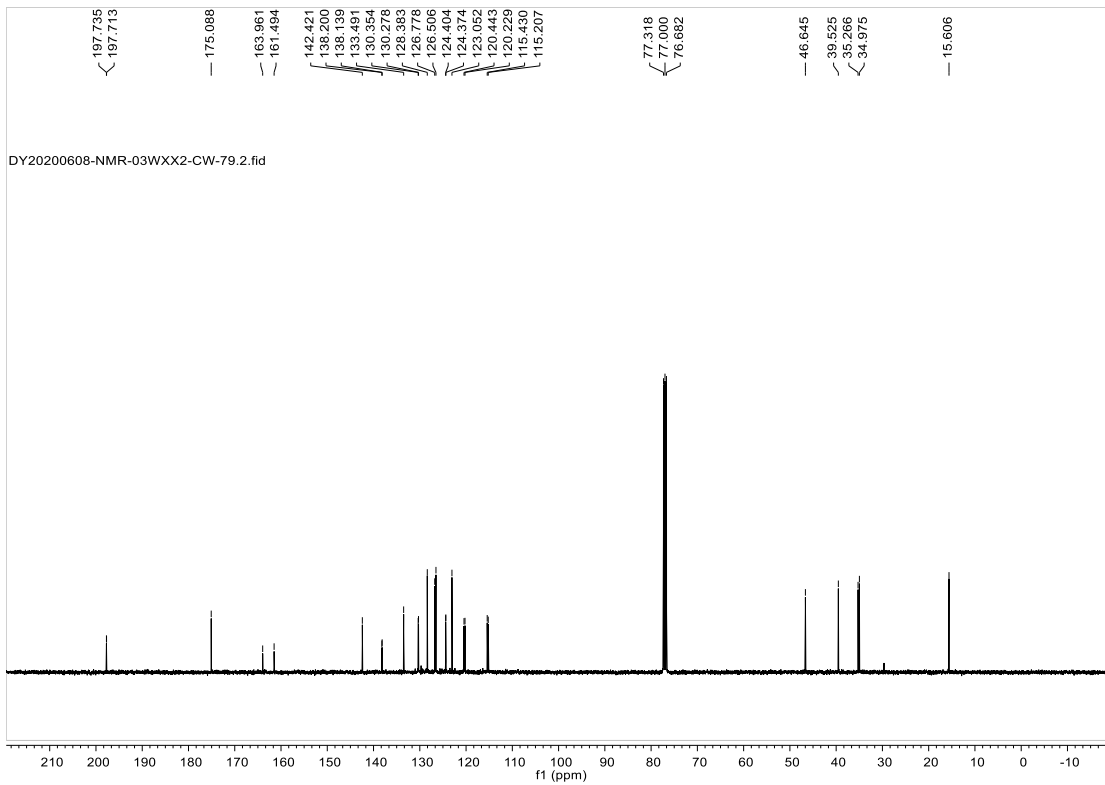






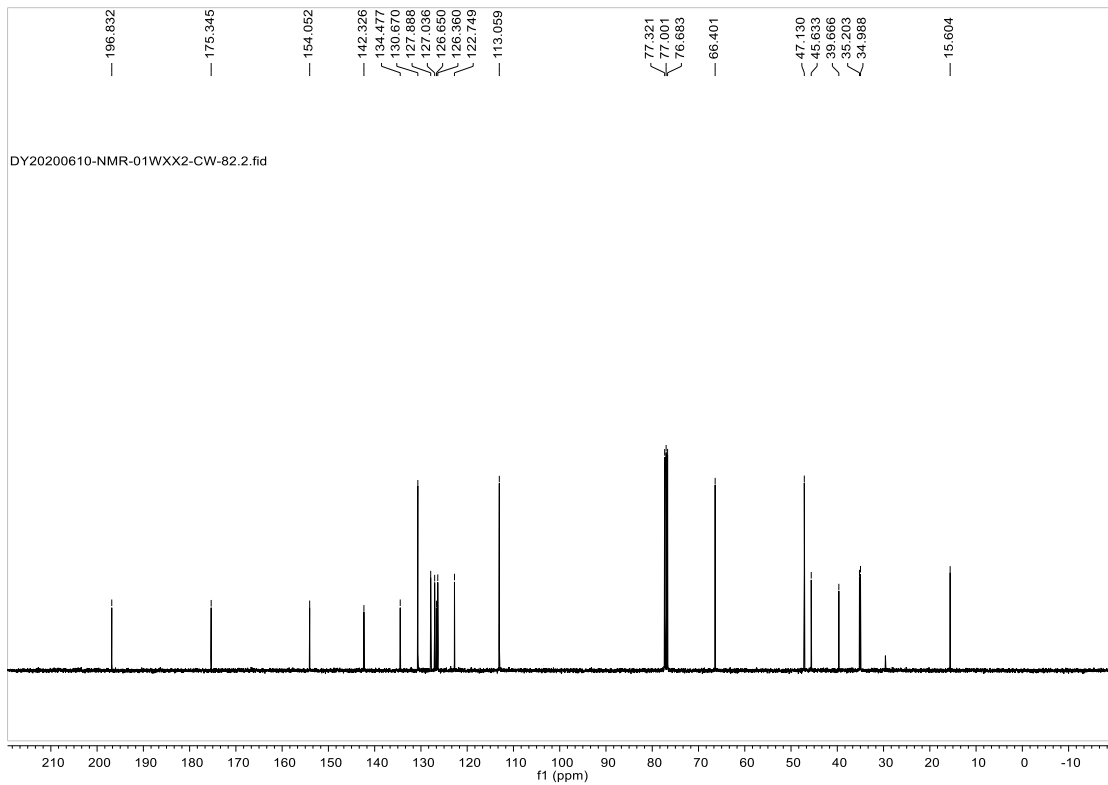
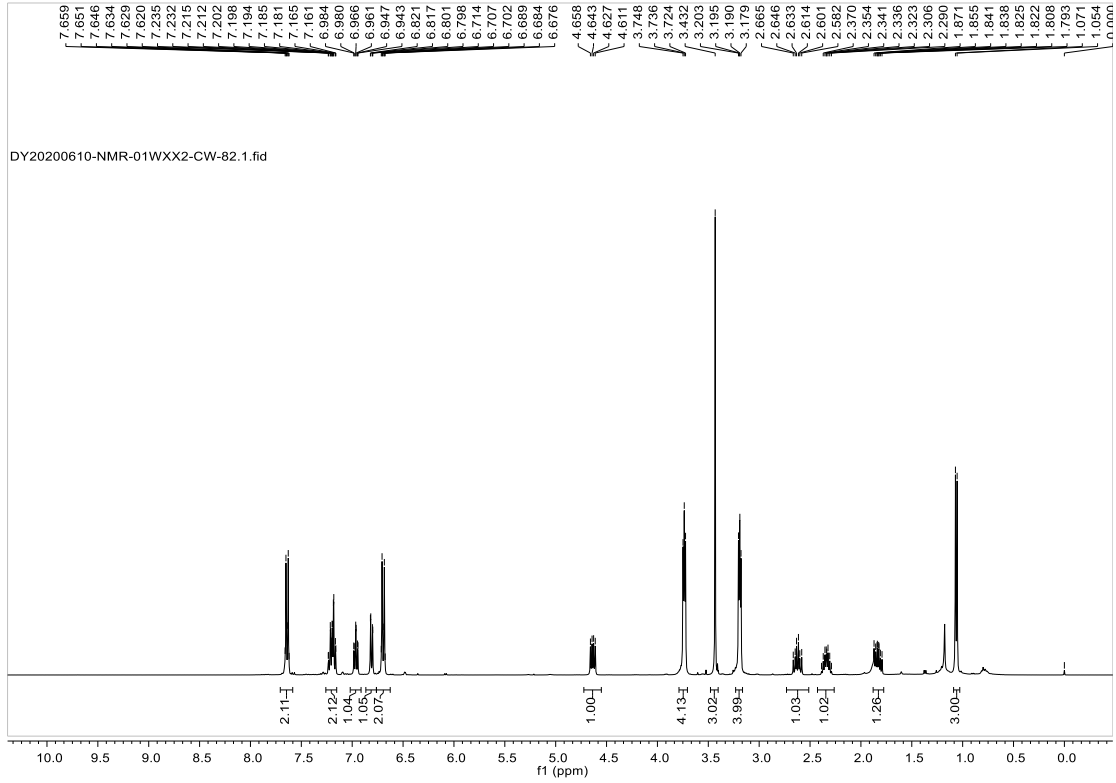
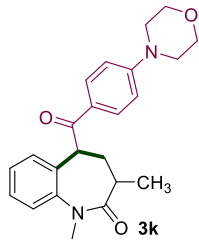


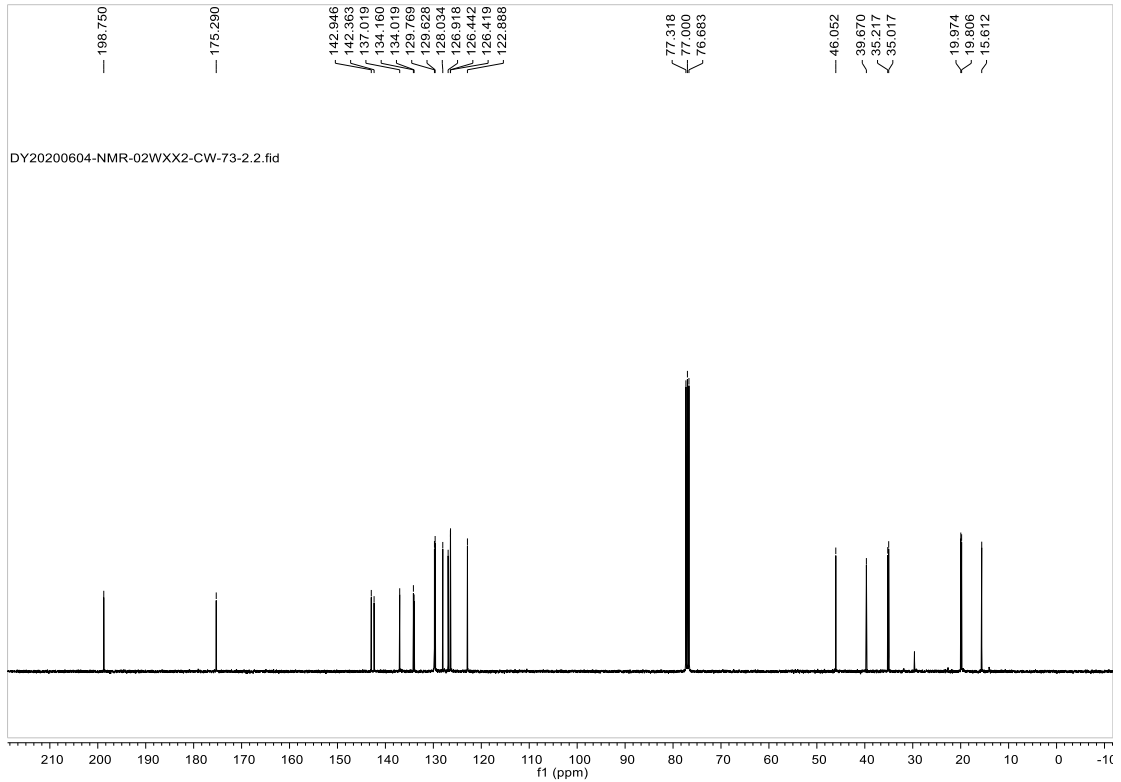
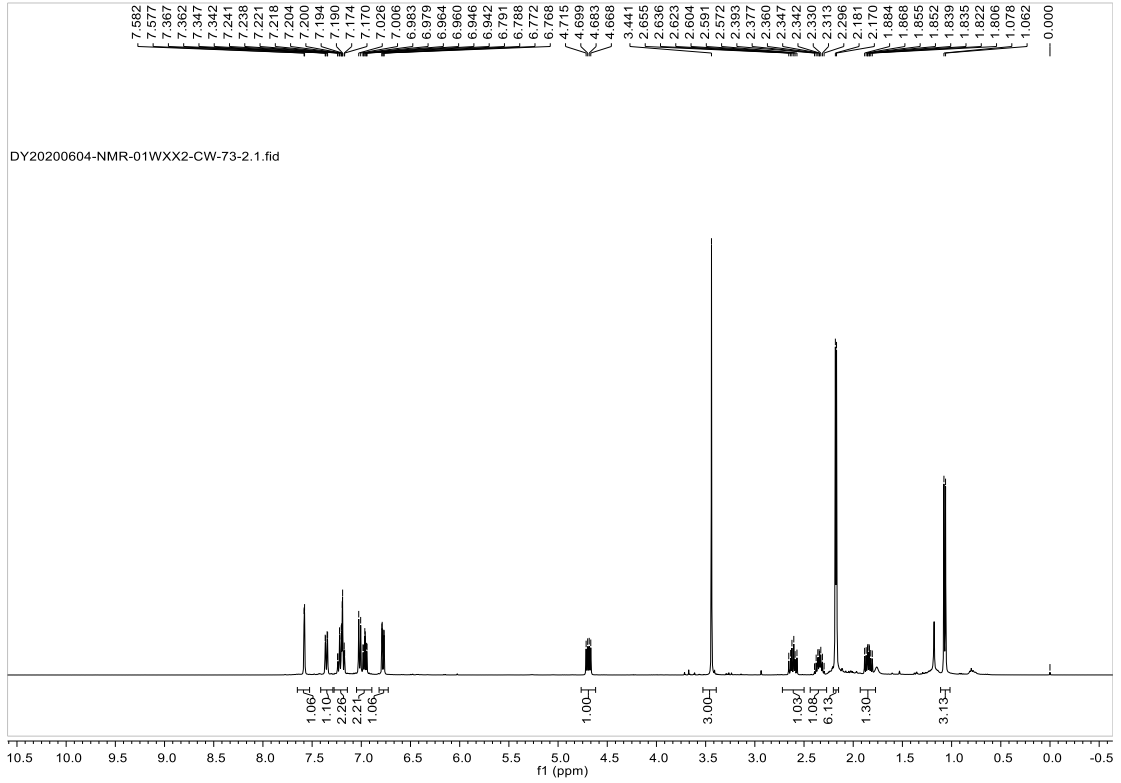
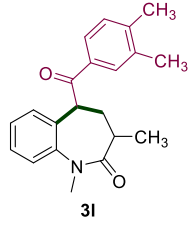


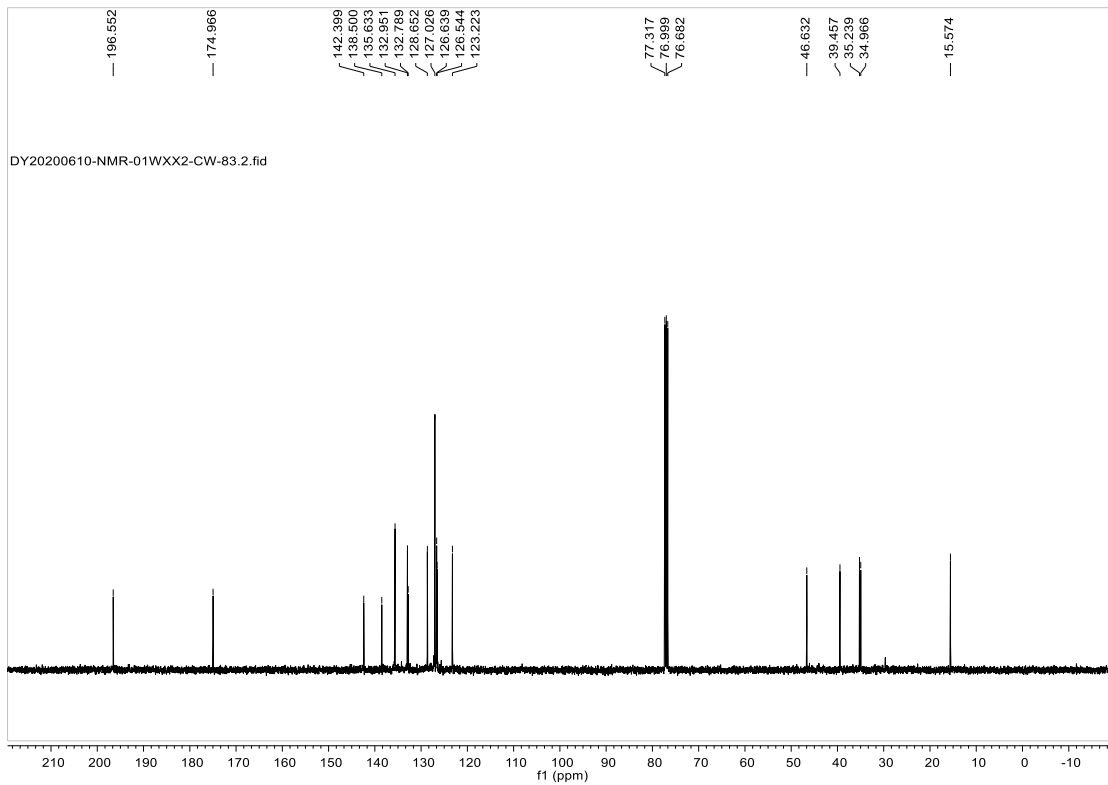
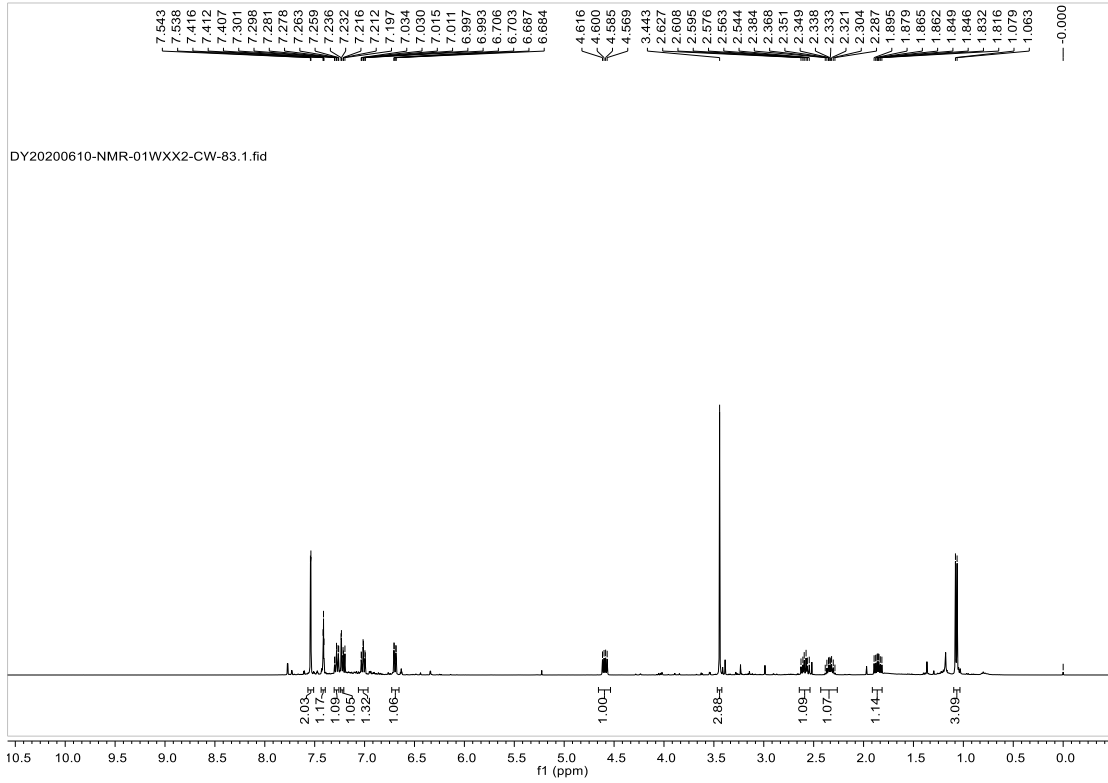
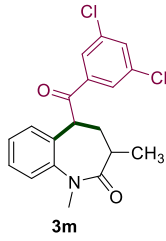


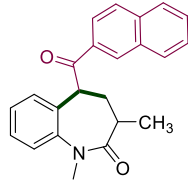




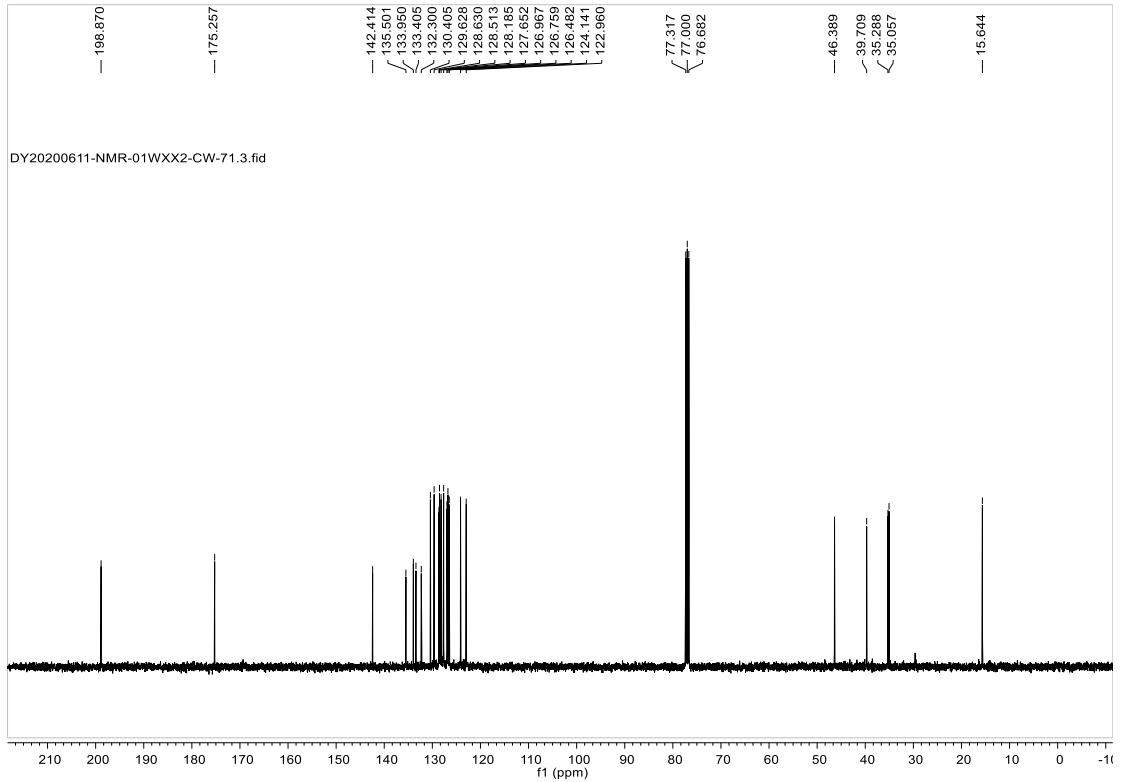
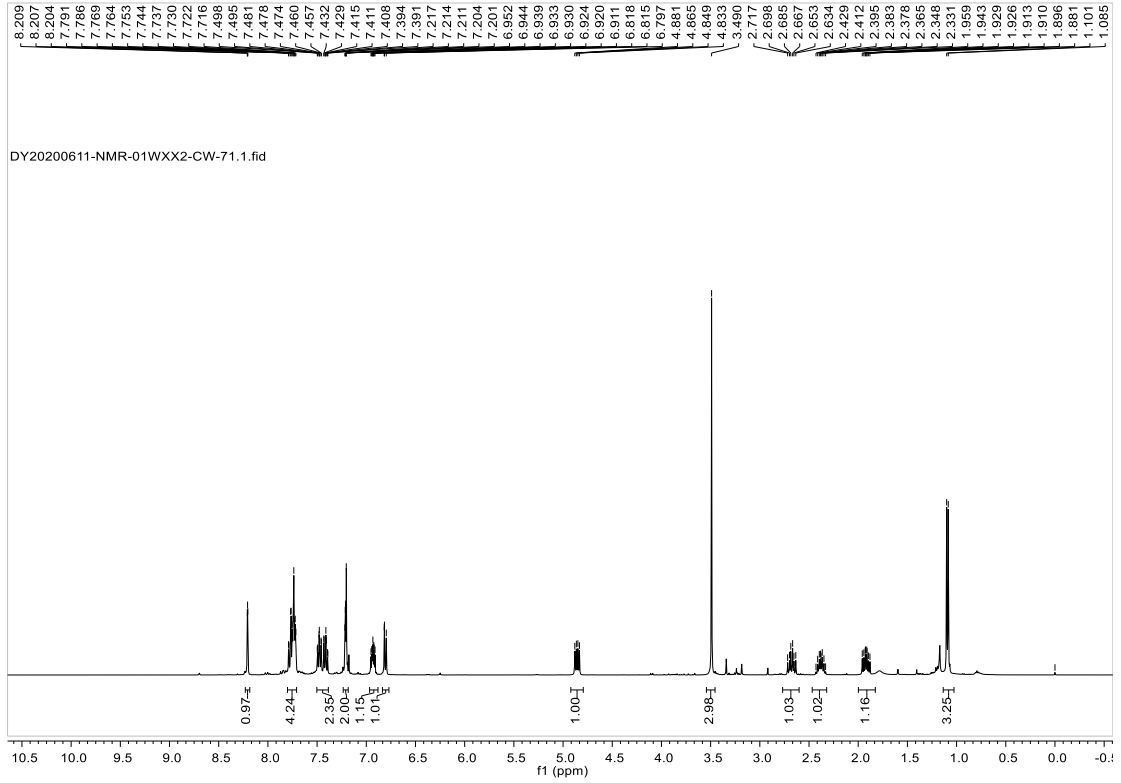


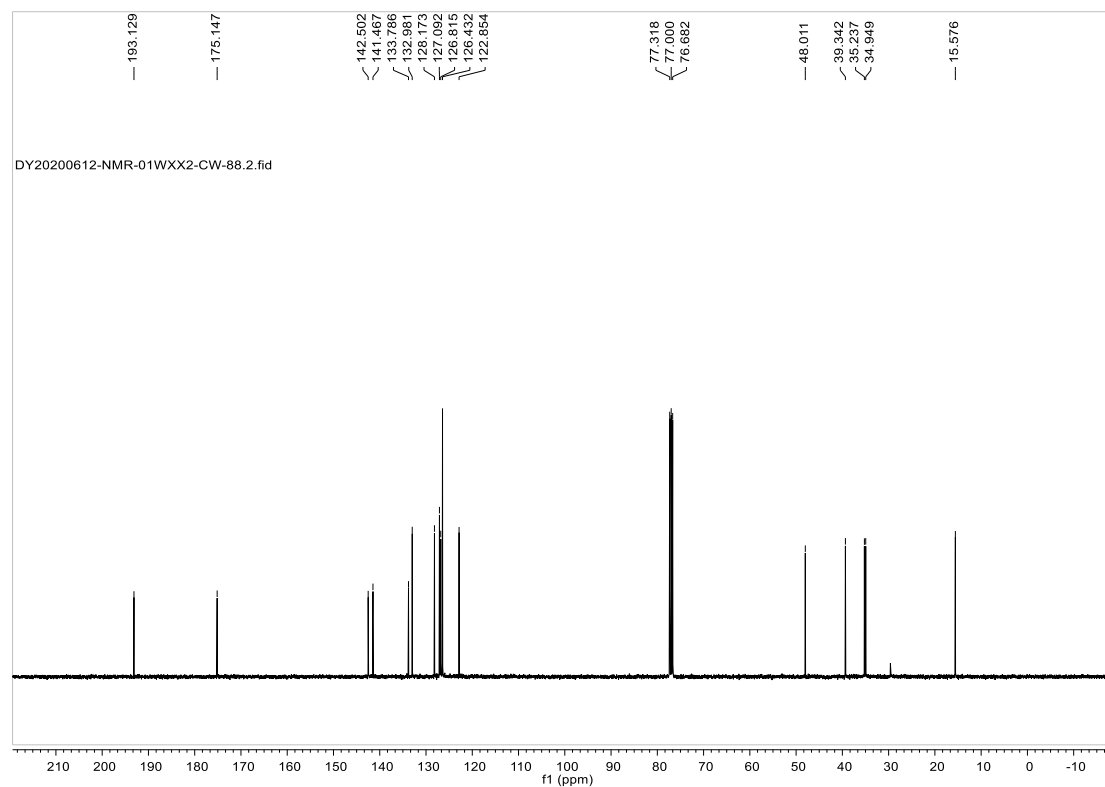
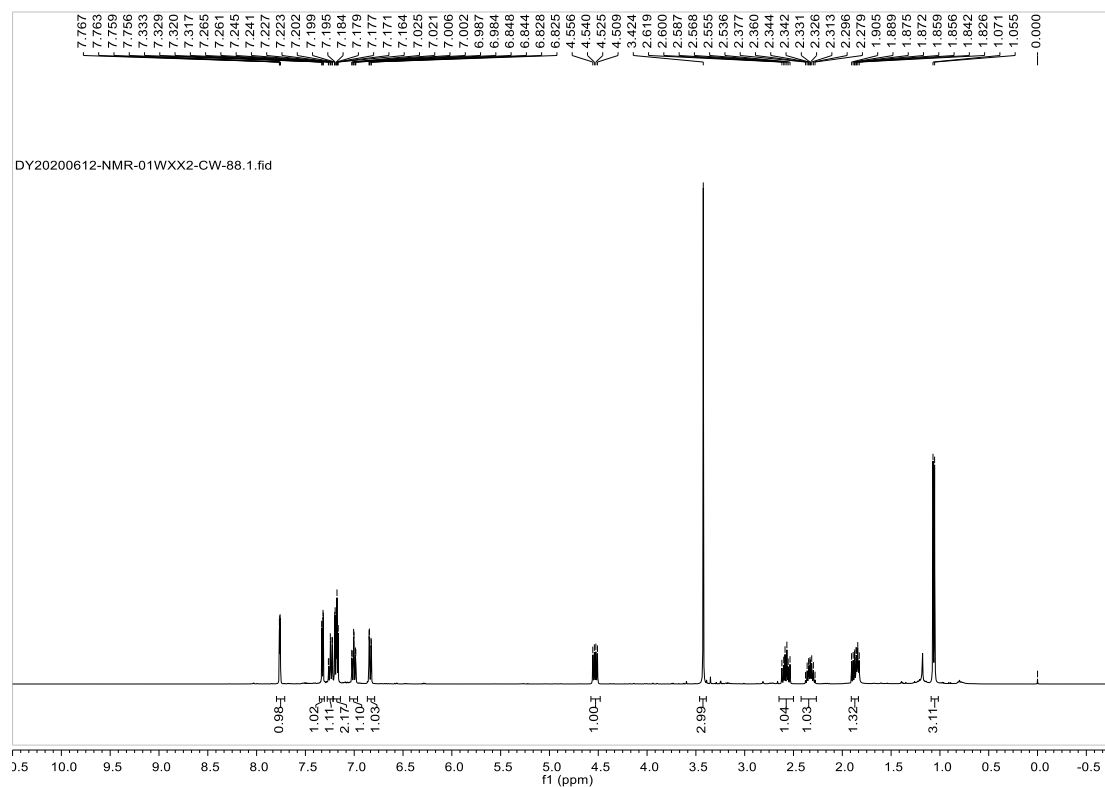
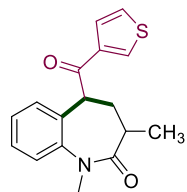


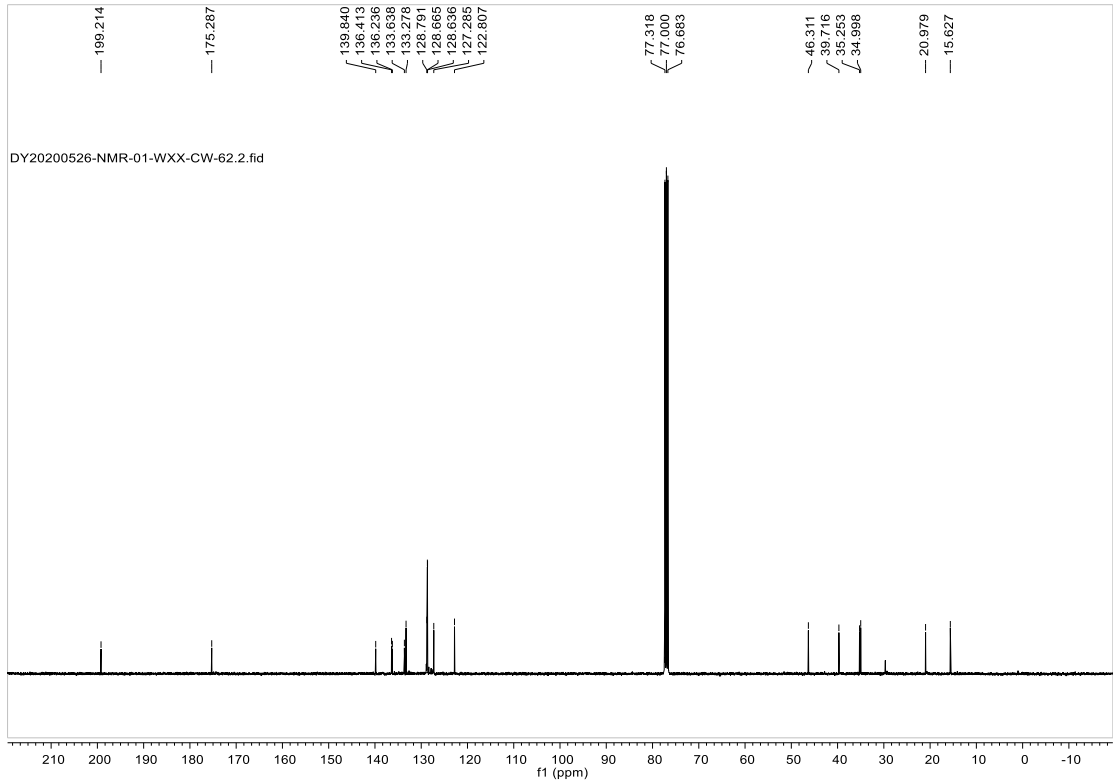
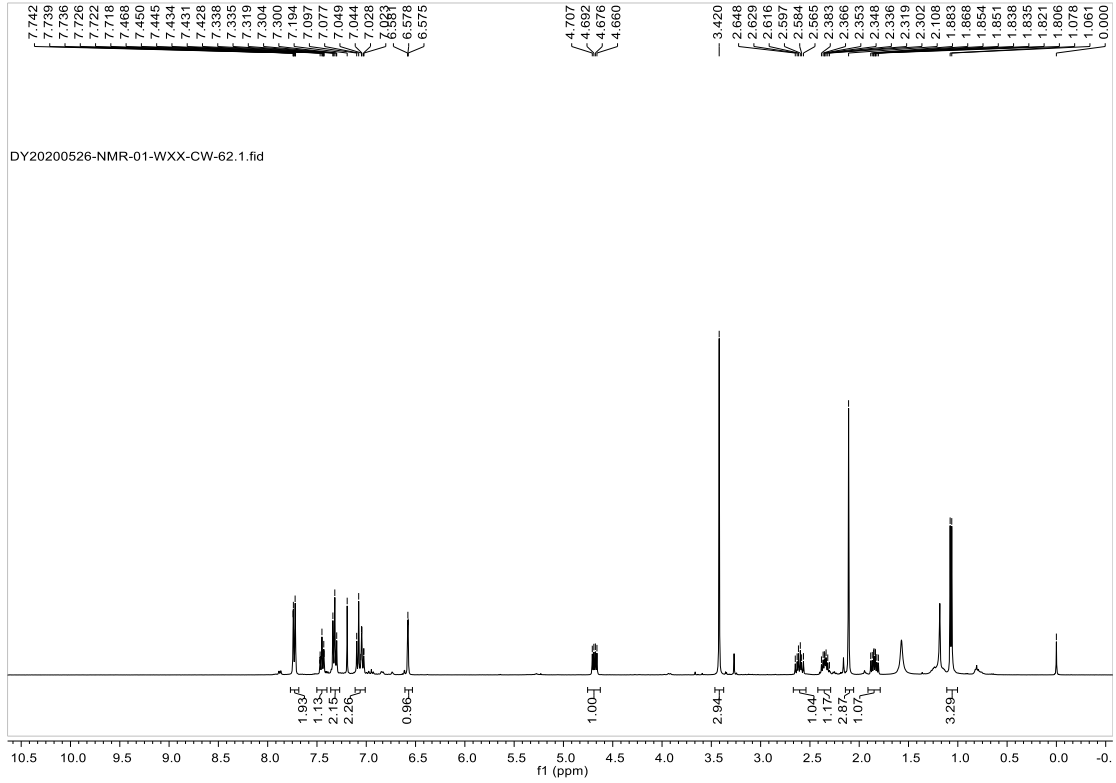
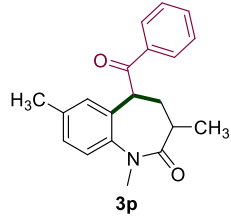


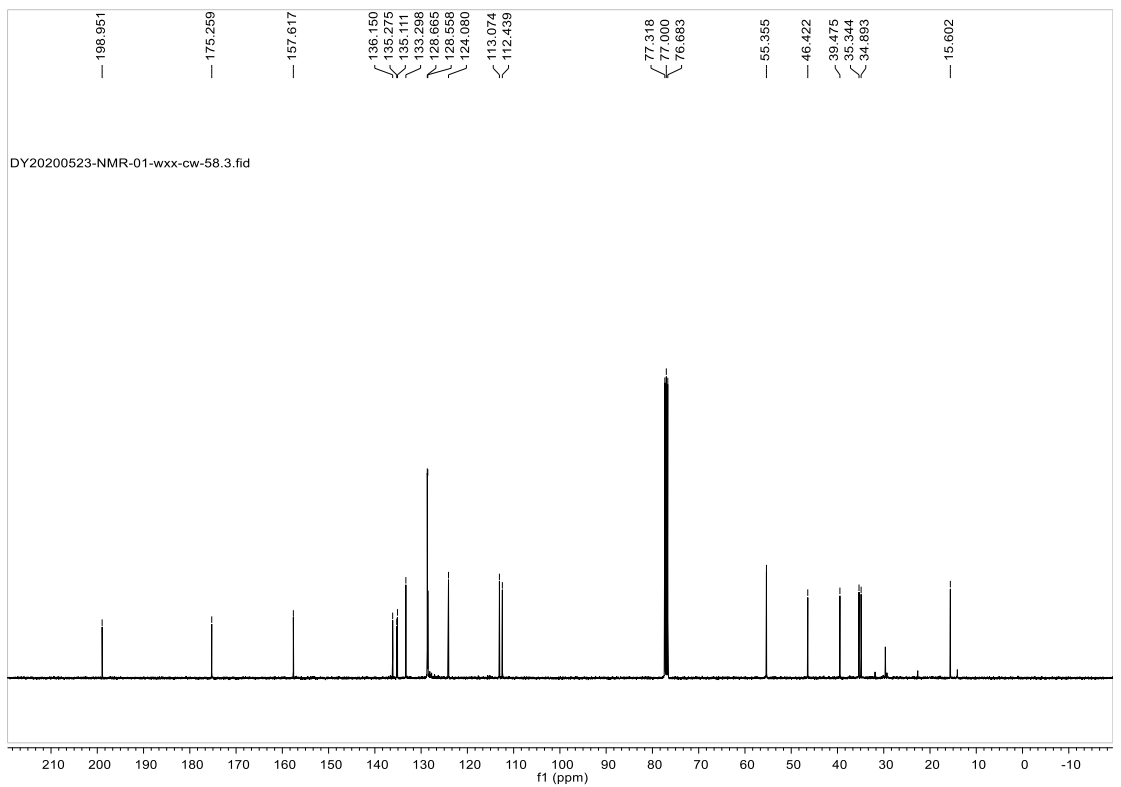
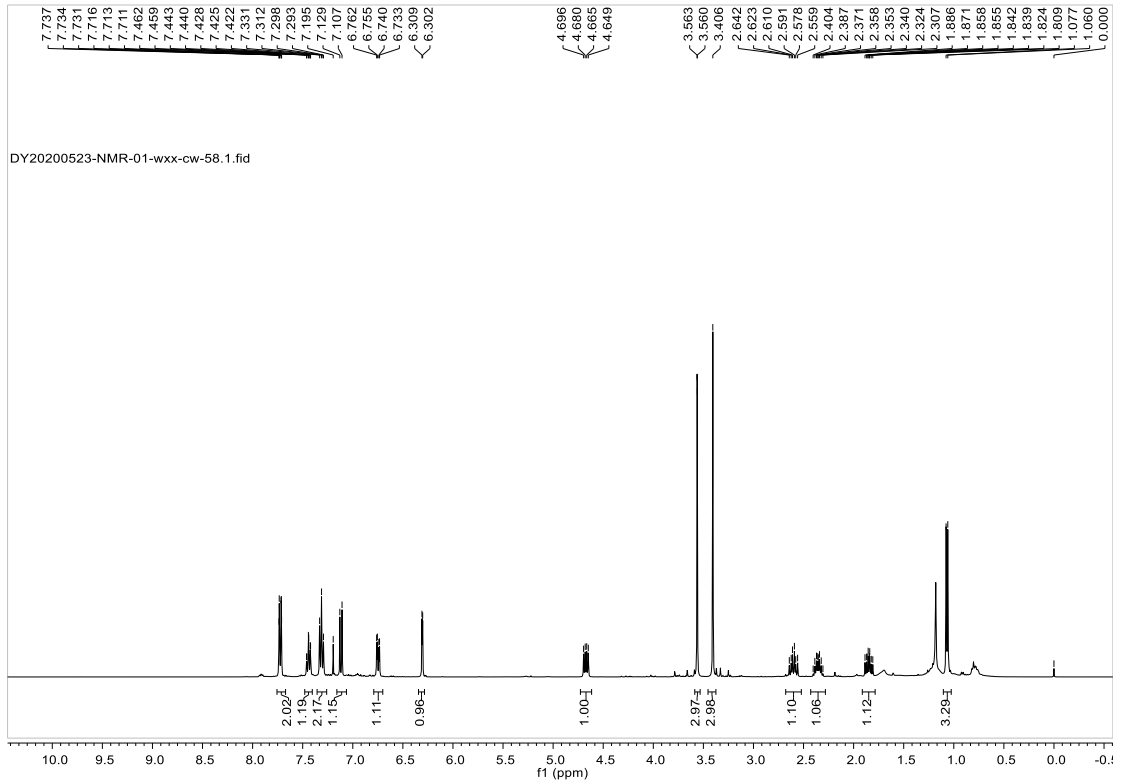
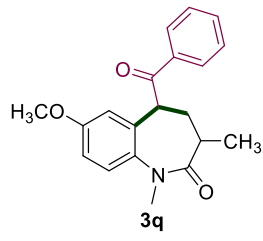


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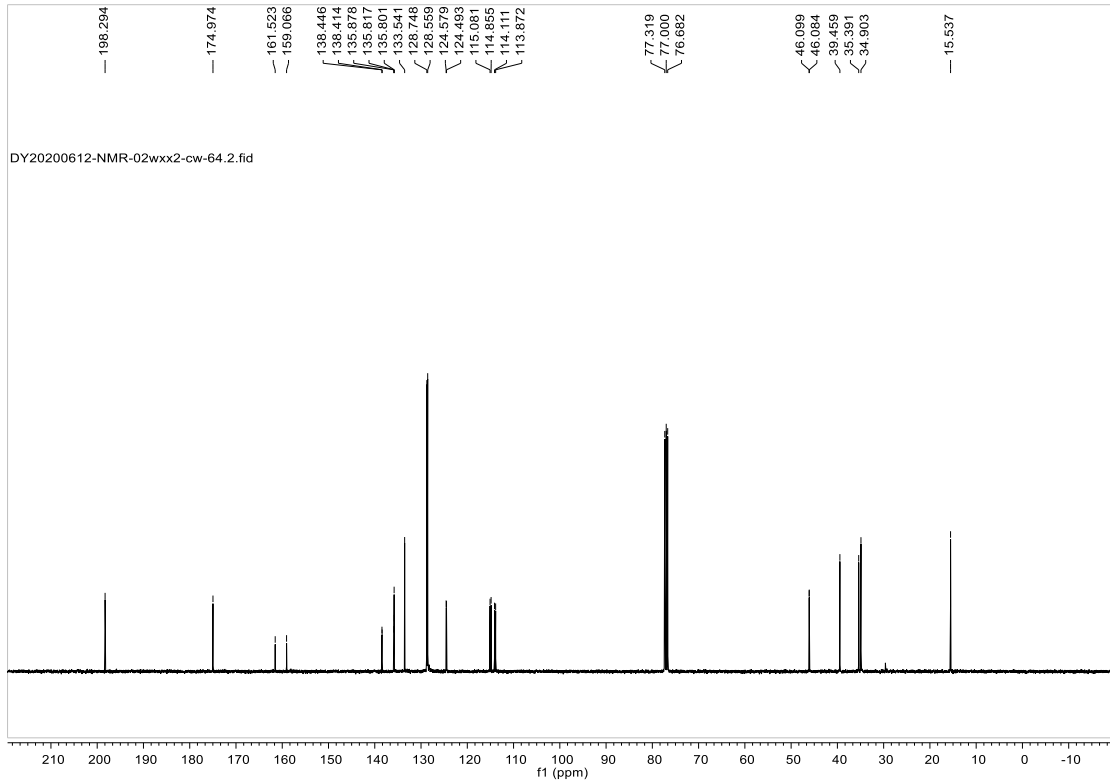
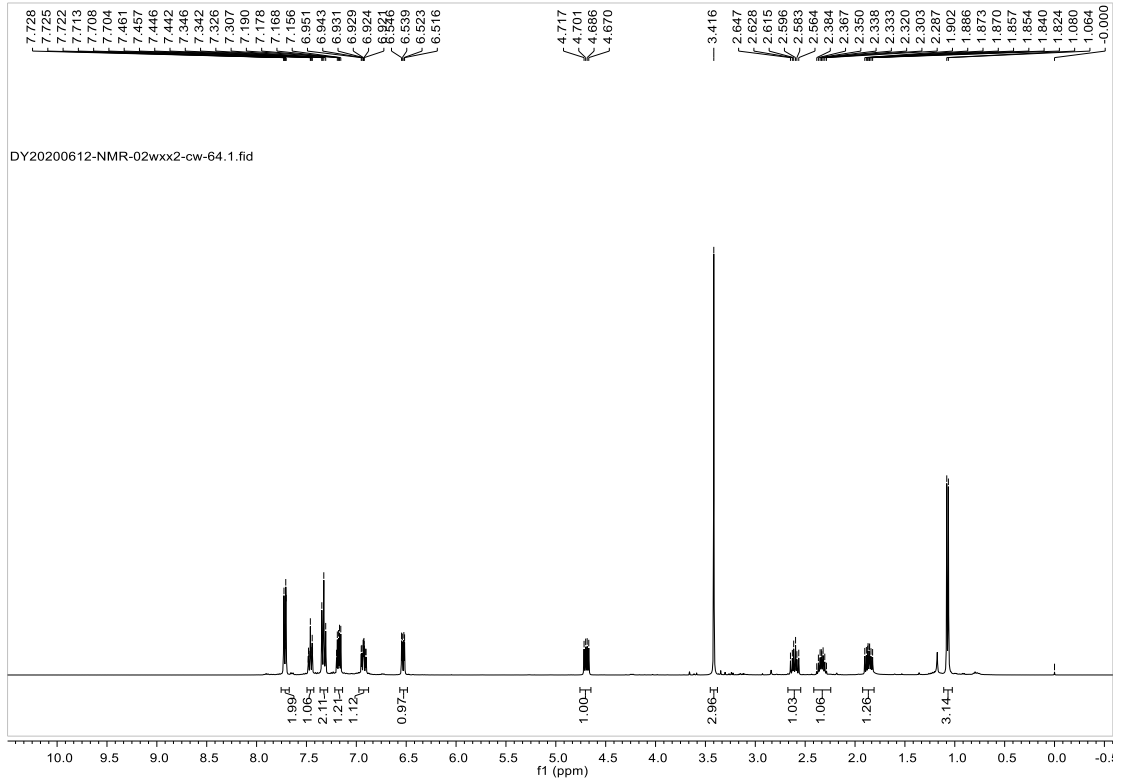
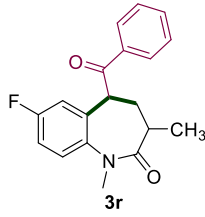


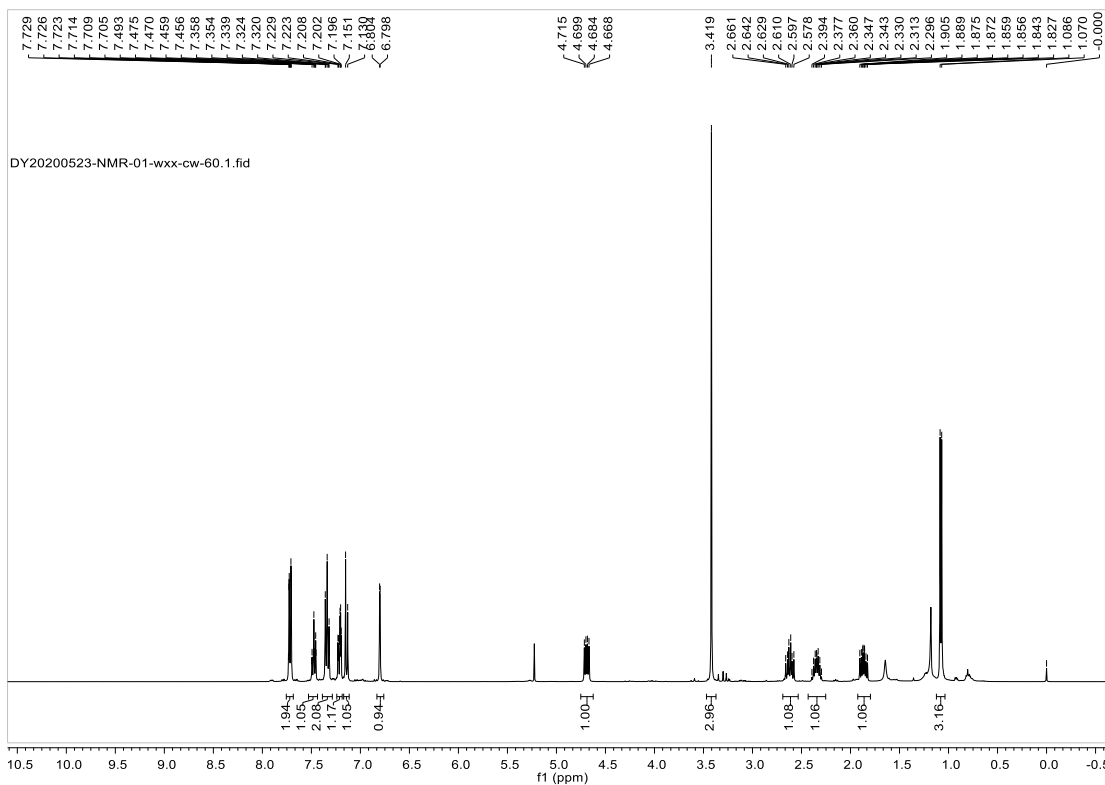
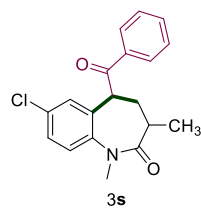
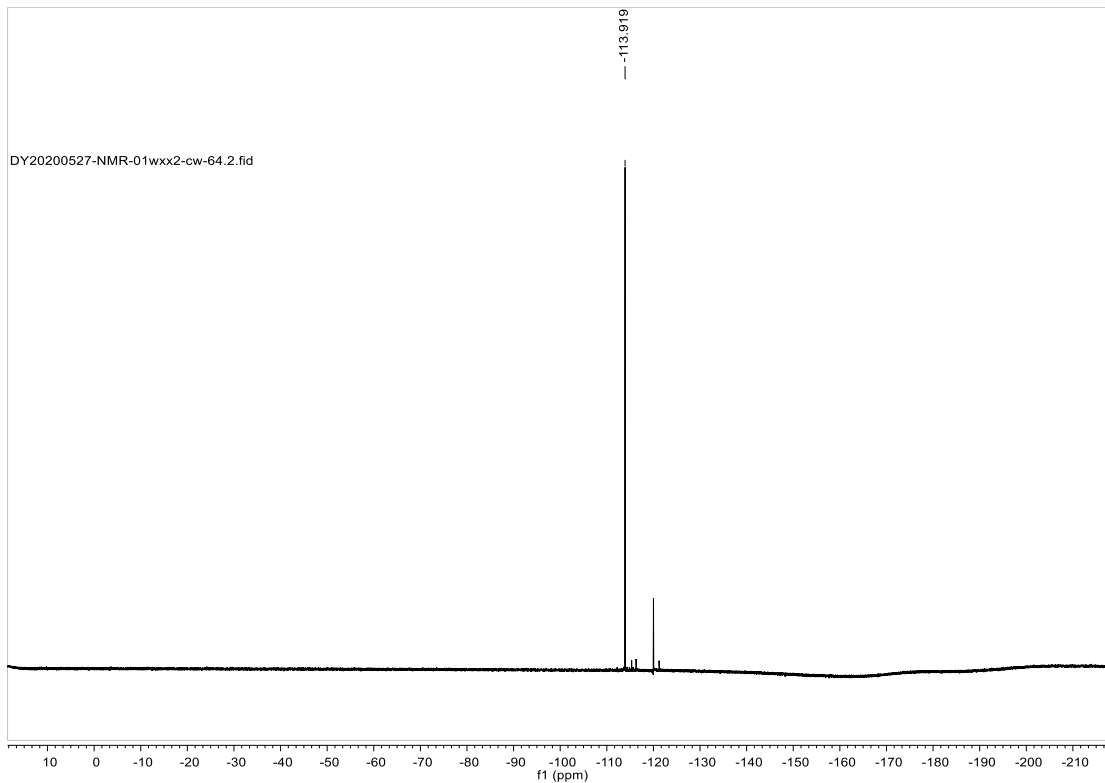


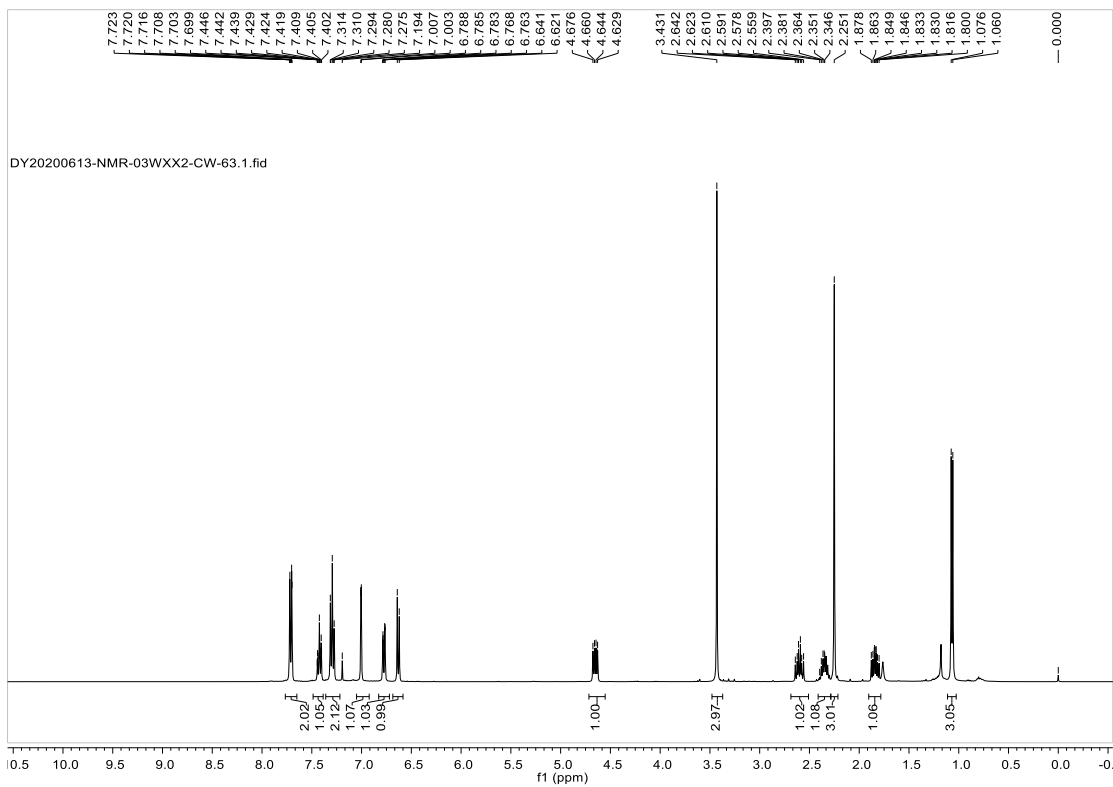
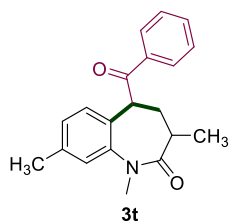
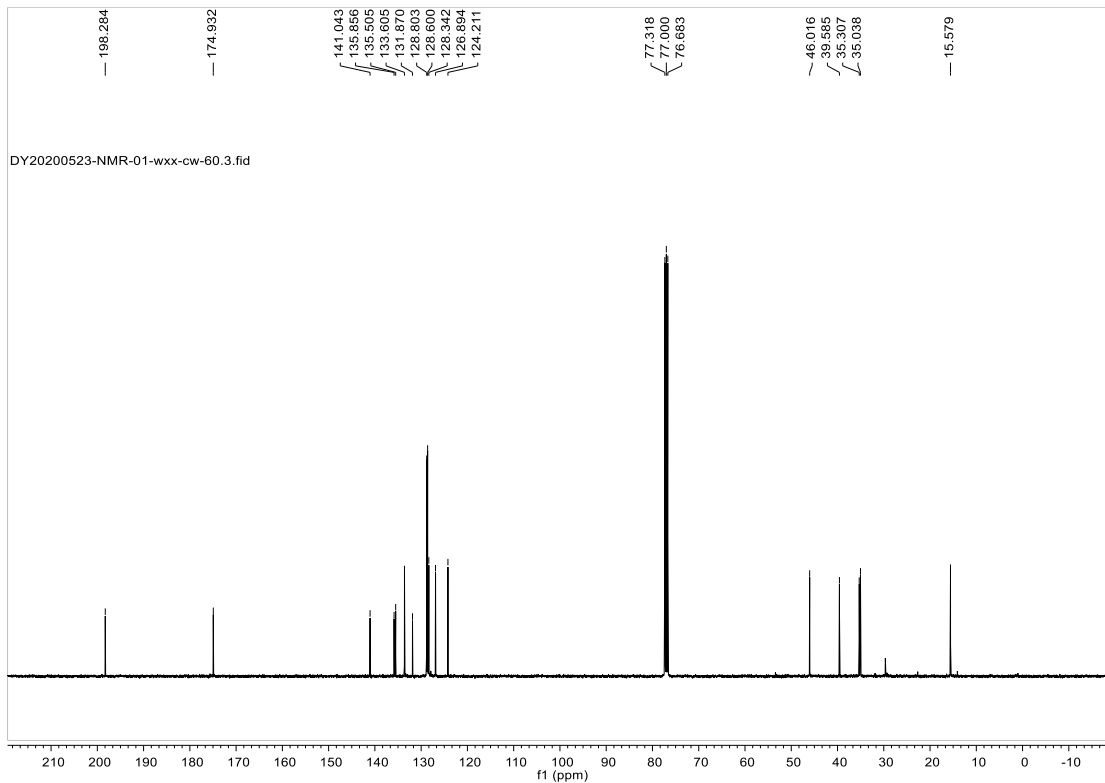


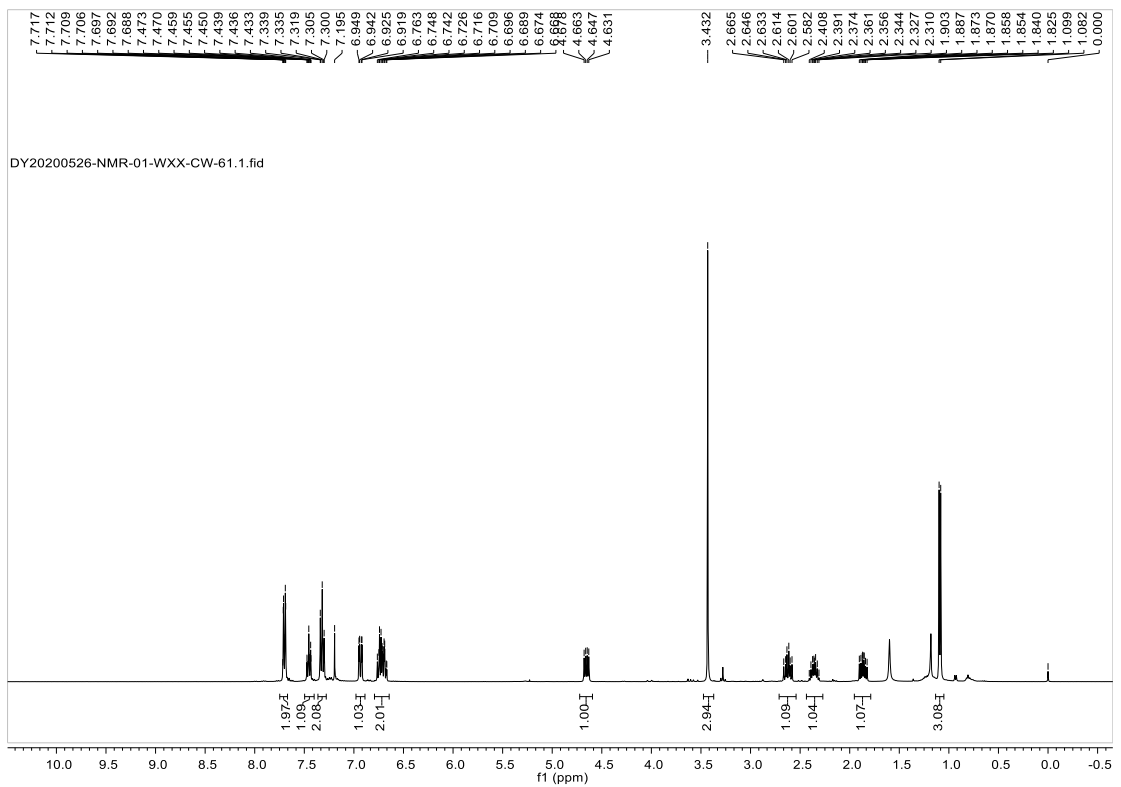
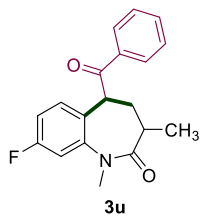
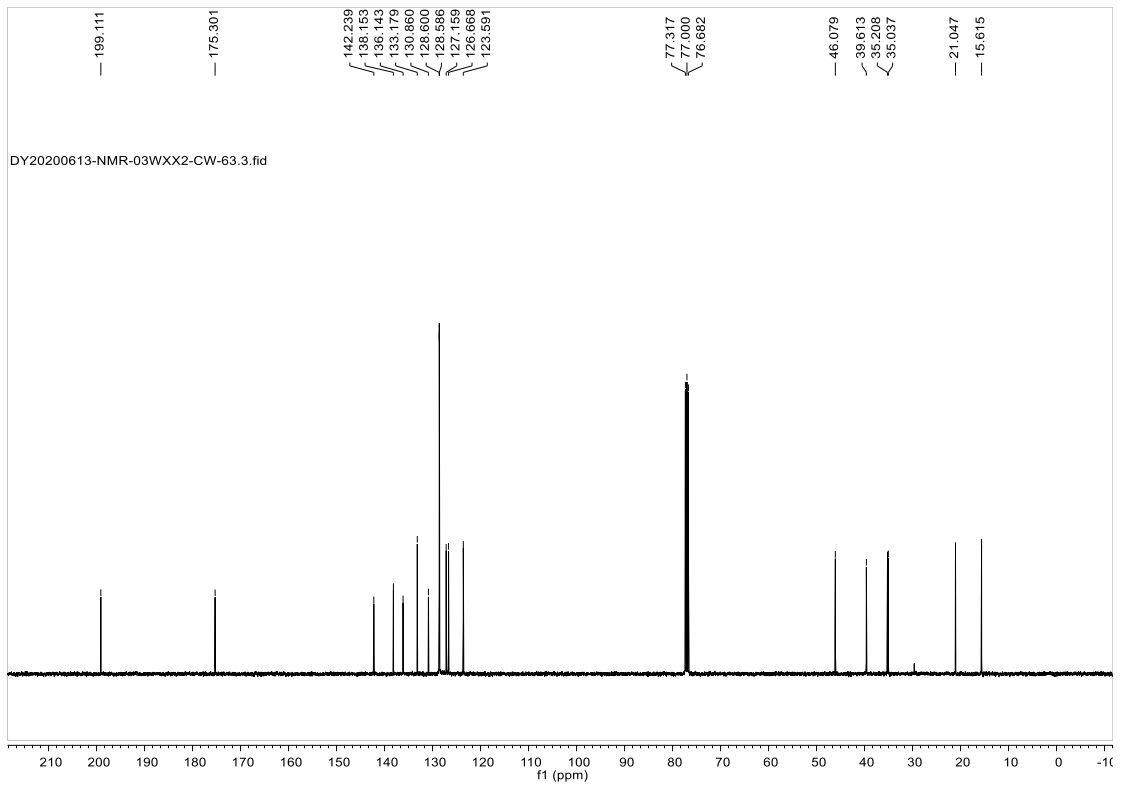


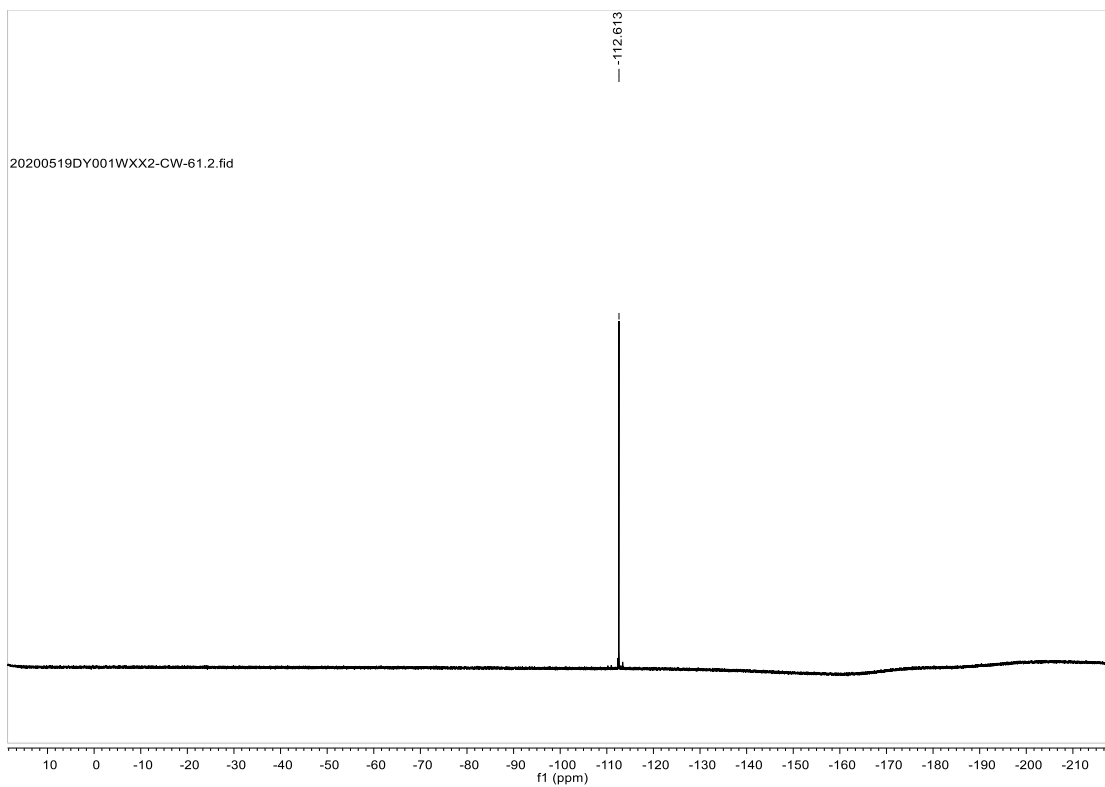
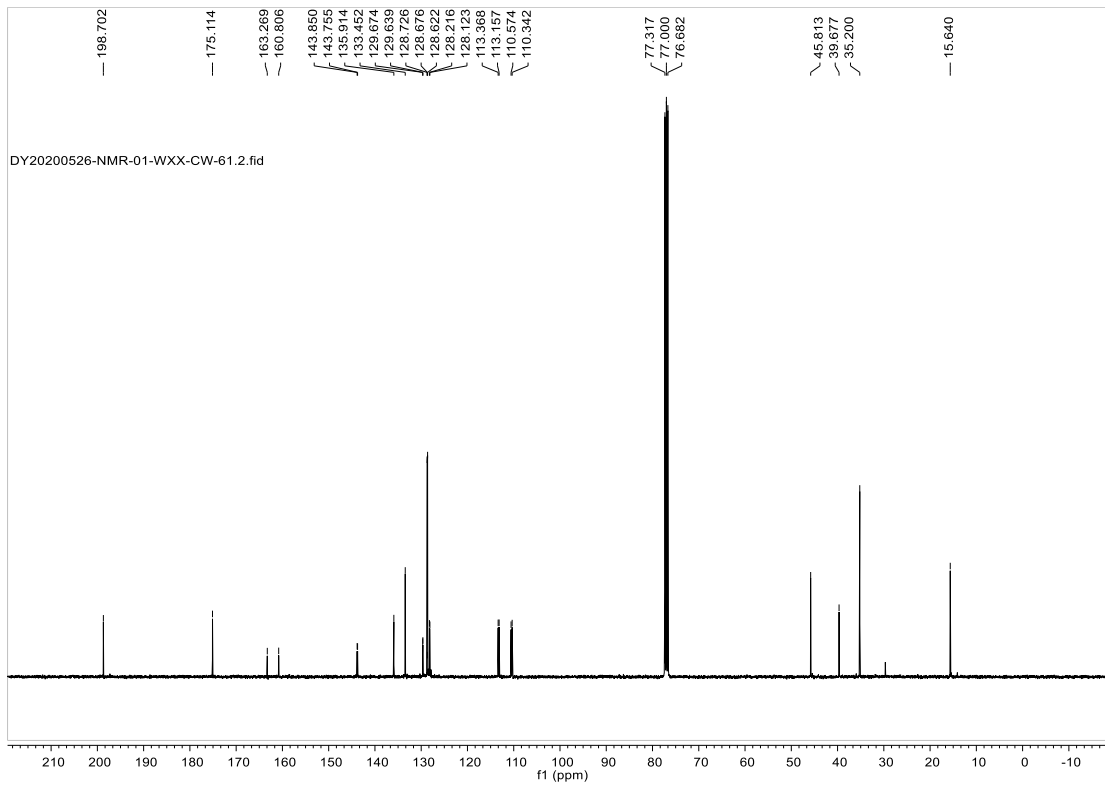


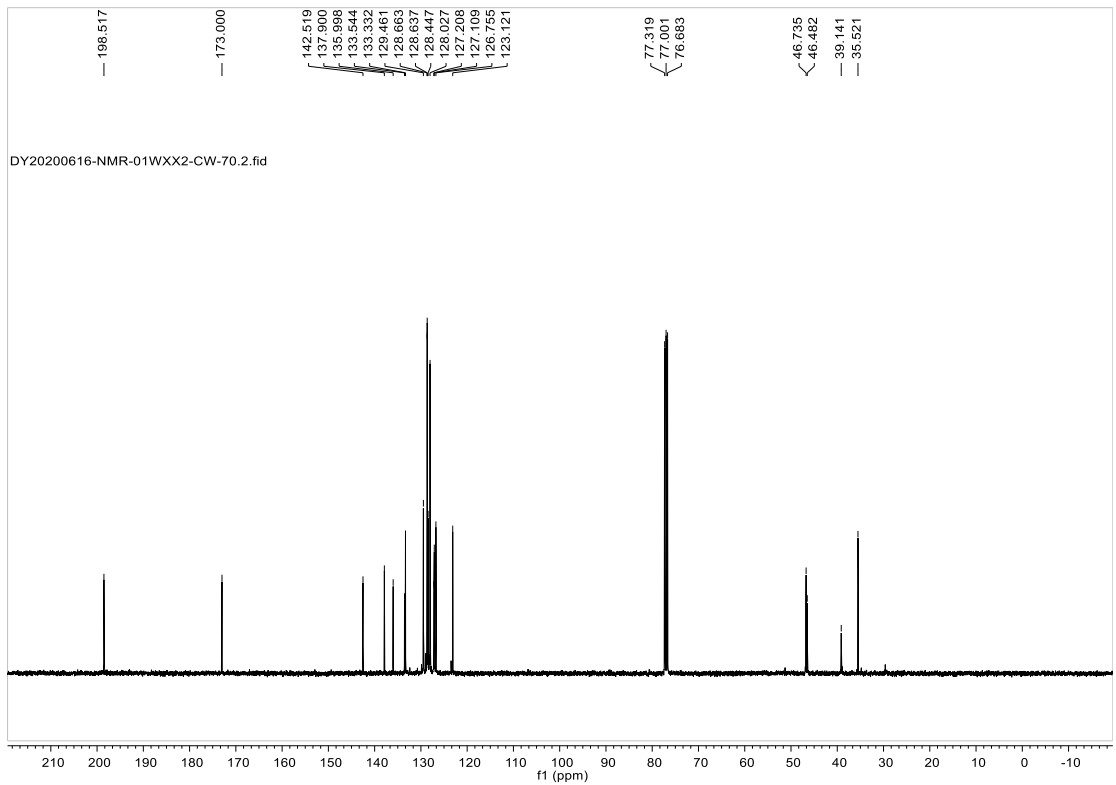
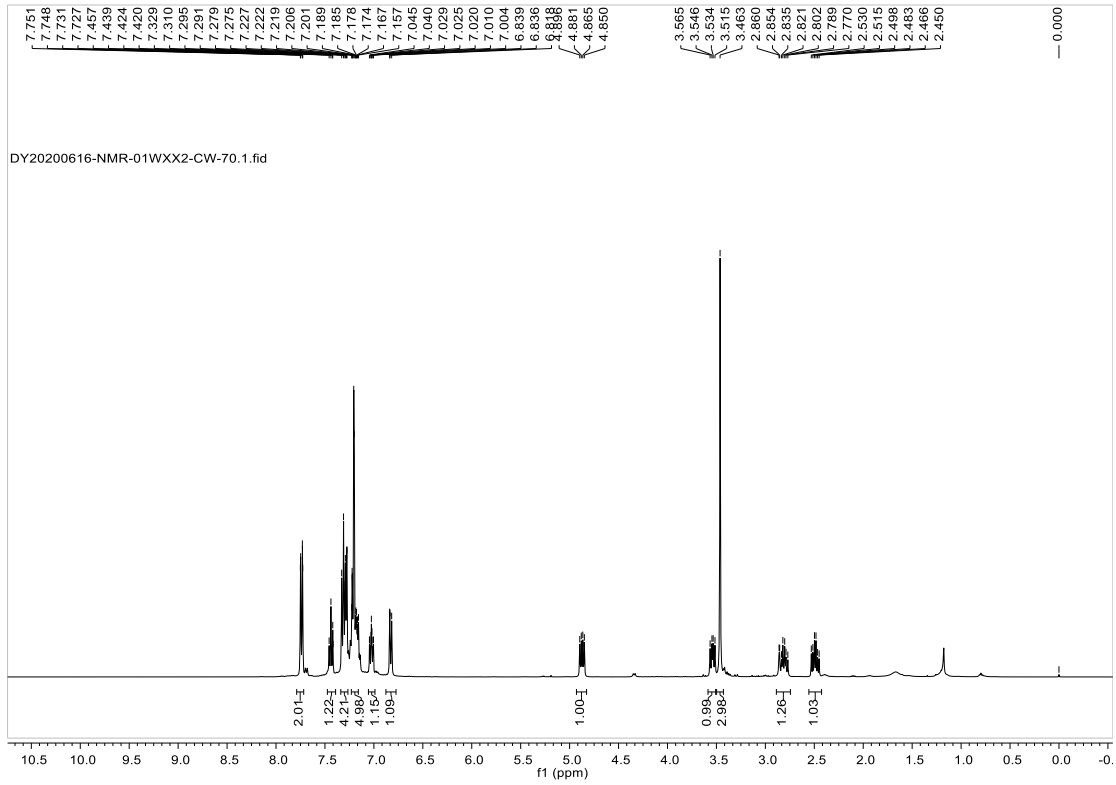
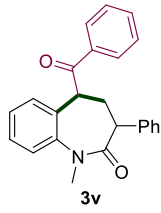


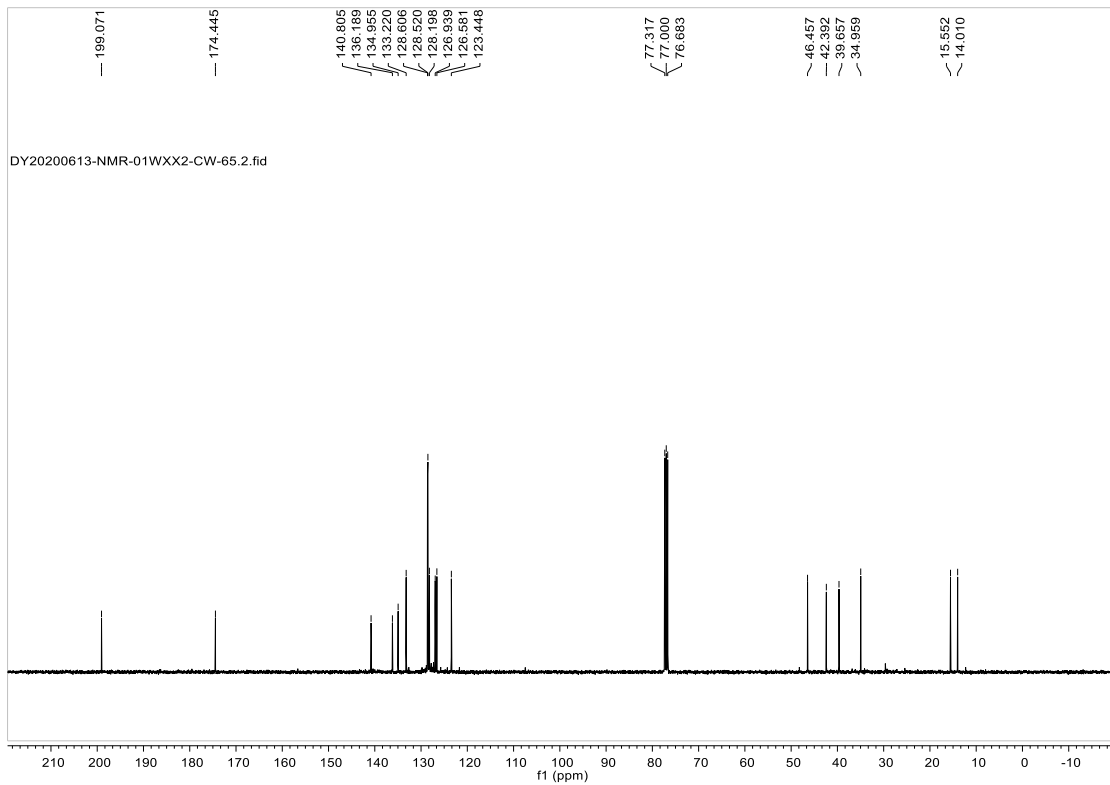
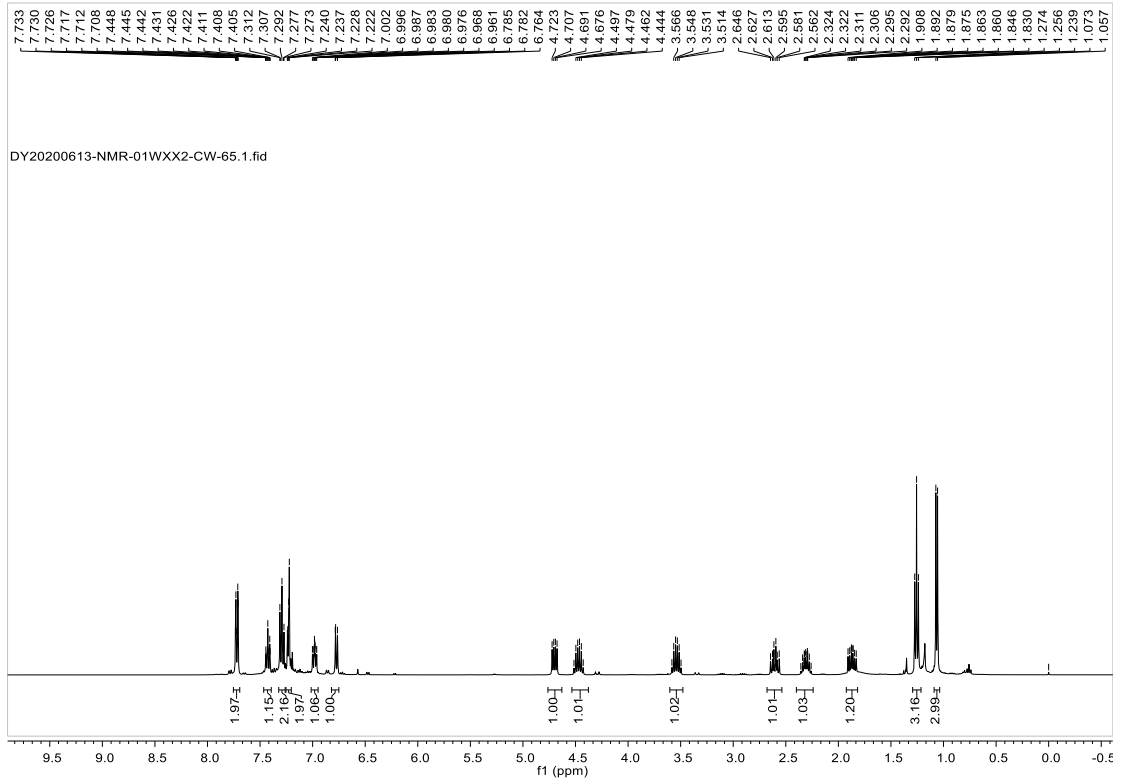
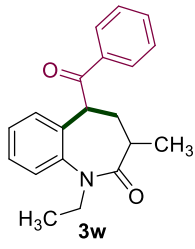


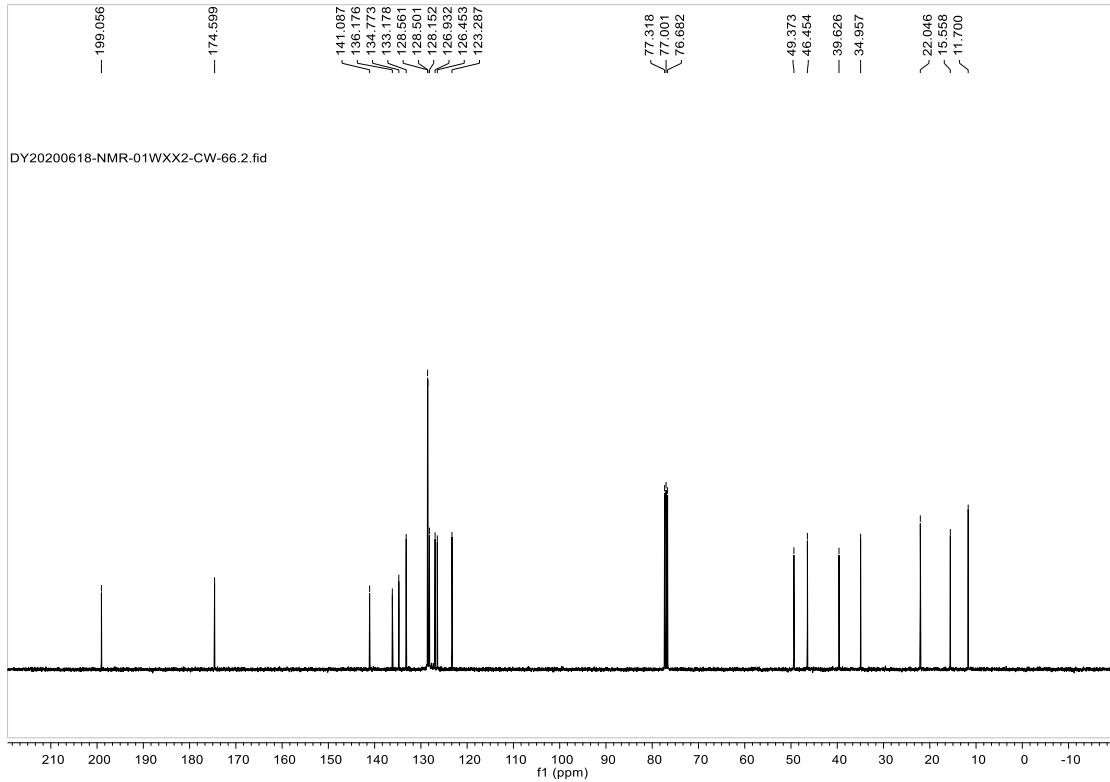
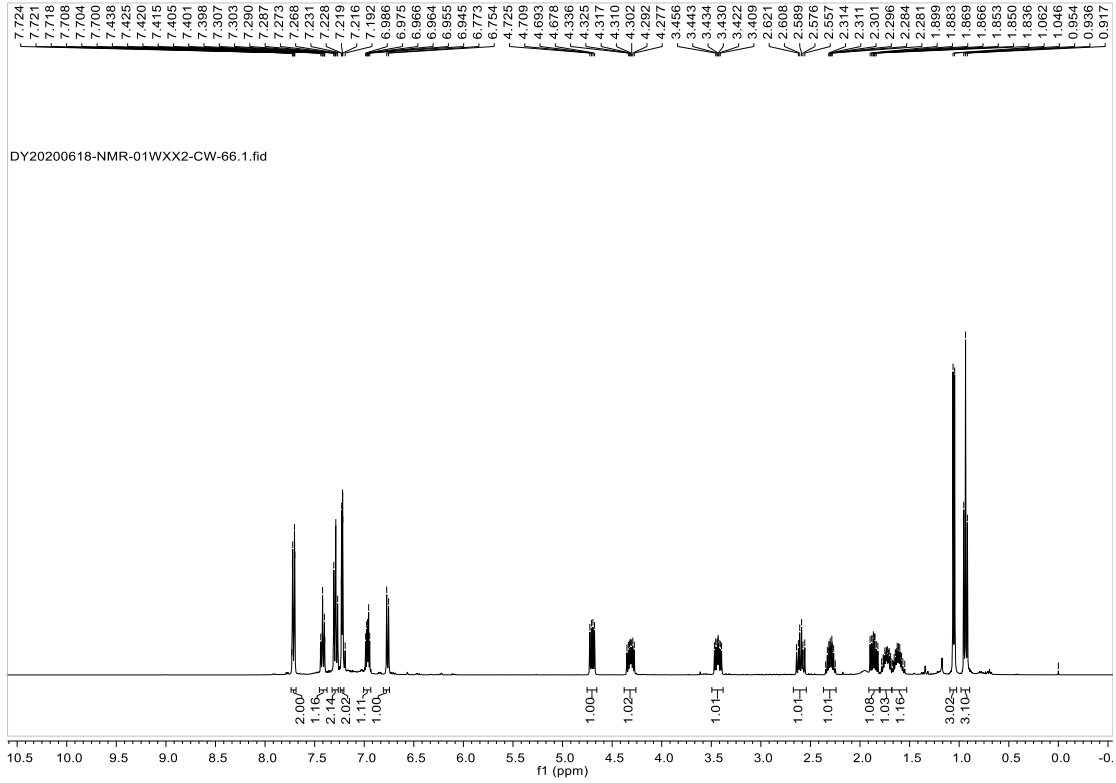
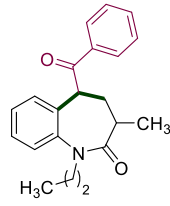




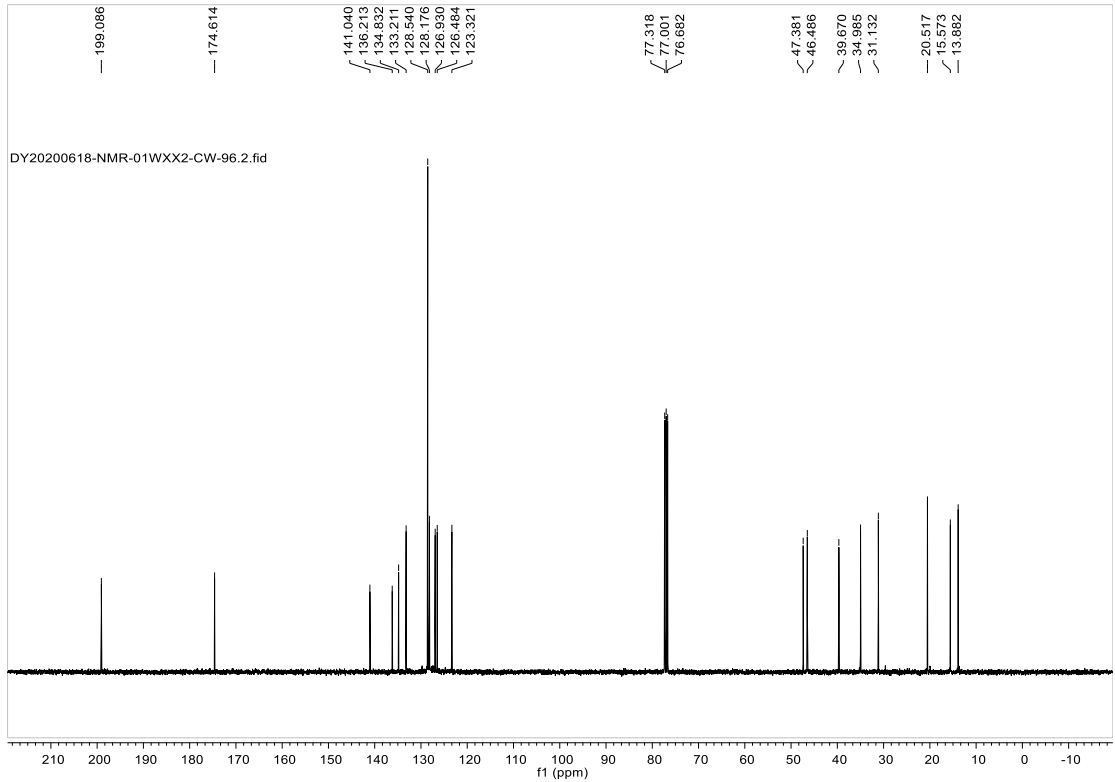
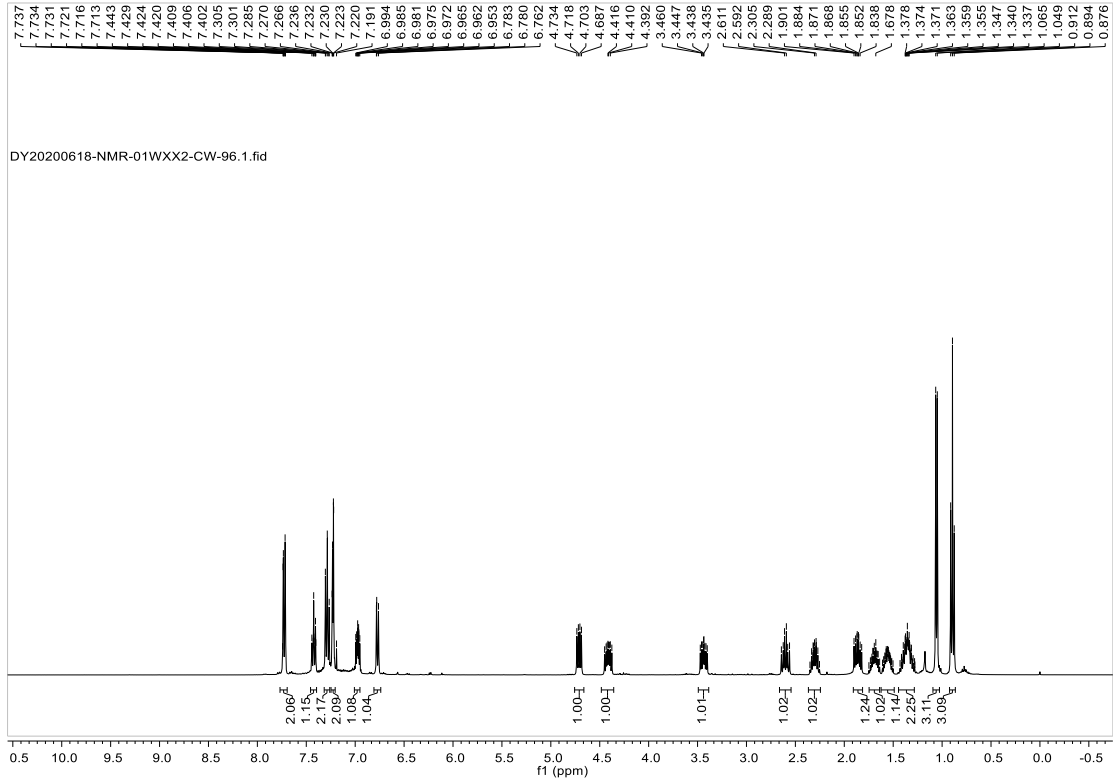
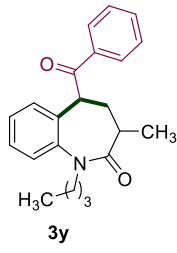


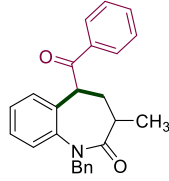












3z

