

Supporting Information

Decatungstate-Photocatalyzed Radical Addition of C(sp³)-H to Azauracils

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1. General Information

1.1 Materials and instruments

All the chemicals were purchased from commercial suppliers, all commercially available reagents were directly used without further purification. Reactions were monitored by Thin Layer Chromatography (TLC) using UV light (254/365 nm) for detection. Products were purified by column chromatography, which was carried out on 200-300 mesh of silica gel purchased. All the ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on Bruker Avance 400 MHz spectrometer and Bruker Avance 600 MHz spectrometer. Proton chemical shifts δ were given in ppm using tetramethylsilane as an internal standard. All NMR spectra were recorded in CDCl_3 at room temperature ($20 \pm 3^\circ\text{C}$). High-resolution mass spectra (HRMS) were taken with a 3000-mass spectrometer, using Waters Q-ToF MS/MS system with the ESI technique. EPR spectra were recorded at room temperature using a Bruker EPR E580-10/12 spectrometer.

1.2 The spectrum of the lamp and the light irradiation instrument

Photochemical reaction was carried out under light irradiation by a purple LED at 25°C . RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system. Eight 10 W purple LEDs were equipped in this Photo reactor. Eight 10 W purple LEDs were equipped in this Photo reactor. The reaction vessel is a borosilicate glass test tube and the distance between it and the lamp is 15 mm, no filter applied.

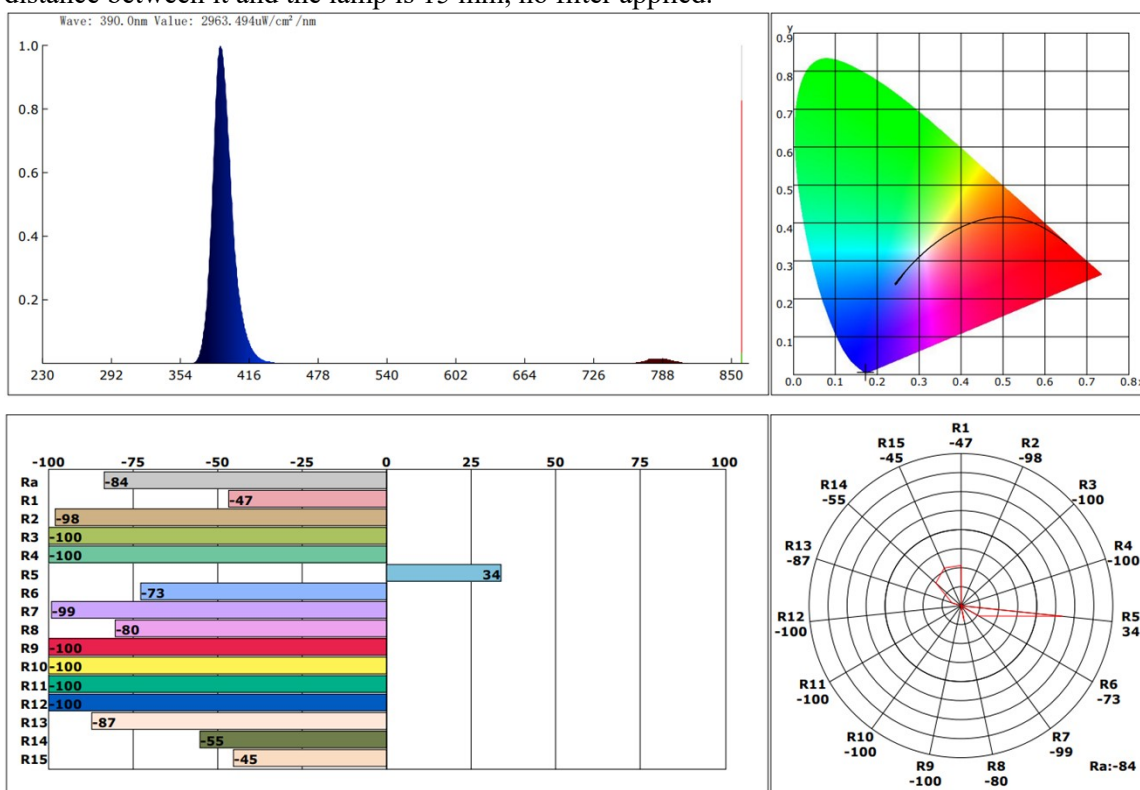


Figure S1. The spectrum of our lamp (390 nm LED)



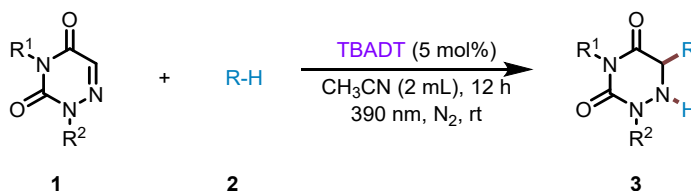
Figure S2. Photograph of photocatalytic reactor

2. Experimental procedures

2.1 Preparation of photocatalyst tetrabutylammonium decatungstate (TBADT)

The photocatalyst was synthesized according to the literature report.¹ To a 2 L beaker wrapped in aluminum foil for insulation and equipped with a 4" Teflon stir bar were added tetrabutylammonium bromide (4.80 g, 14.9 mmol, 0.49 equiv.) and deionized water (1600 mL). In a separate 4 L beaker wrapped in aluminum foil for insulation and equipped with a 4" Teflon stir bar were added Na₂WO₄•2H₂O (10 g, 30.3 mmol, 1.00 equiv.) and deionized water (1600 mL). Both solutions were rapidly stirred and heated to 90 °C. When both solutions reached 90 °C, concentrated HCl was added to each solution until pH stabilized at 2. At this point, the acidified solutions were combined in the 4 L beaker, and the resultant suspension was stirred at 90 °C for an additional 30 minutes. The reaction mixture was cooled to room temperature, then filtered through a pad of silica gel. The solids were washed with water and left to dry under vacuum. When the silica-supported solids were dry, the receiving flask was exchanged, and the pad was washed with 3 x 200 mL dichloromethane. The filtrate was collected and solvent was removed. The residue was thoroughly dried under vacuum to afford TBADT. Isolated as pale yellow crystals (82% yield). UV-Vis and CV characterization are consistent with literature data.¹

2.2 General experimental procedures for the hydroalkylation of 1,2,4-triazine-3,5(2*H*, 4*H*)-diones



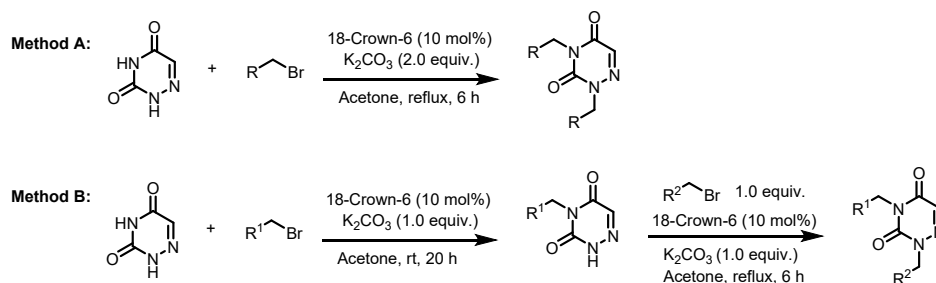
Scheme S1. General experimental procedures for the hydroalkylation of 1,2,4-triazine-3,5(2*H*, 4*H*)-diones

1,2,4-Triazine-3,5(2*H*, 4*H*)-diones **1** (0.2 mmol, 1.0 equiv.), alkanes **2** (2.0 mmol, 10.0 equiv.), TBADT (5 mol%) and CH₃CN (2.0 mL) were sequentially added into a 25 mL Schlenk tube equipped with a teflon coated magnetic stirring bar. The tube was sealed with a rubber stopper and the reacting mixture was degassed three times using the freeze-pump-thaw method and then back-filled with nitrogen gas. Then the reaction tube was exposed to 10 W purple LED (390 nm)

irradiation and stirred at room temperature. After 12 hours, the solvent was evaporated under vacuum, all the crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate as an eluting solvent to give the desired products **3**.

2.3 General procedure for the preparation of 1,2,4-triazine-3,5(2*H*, 4*H*)-diones

The substrates of various 1,2,4-triazine-3,5(2*H*, 4*H*)-diones involved in Scheme 2-3 were synthesized according to procedures described in the previous literature,² and the spectral characteristics data were consistent with those reported previously in the literature.³



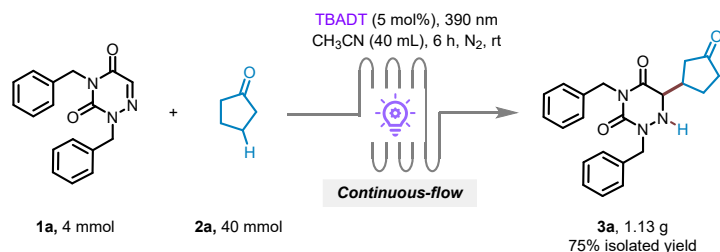
Scheme S2. General procedure for the preparation of 2,4-dibenzyl-triazin-3,5(2*H*,4*H*)-diones **3**

Method A: A solution of 1,2,4-triazine-3,5(2*H*,4*H*)-dione (5 mmol, 1.0 equiv.) in dry acetone (30 mL) was mixed with anhydrous potassium carbonate (10 mmol, 2.0 equiv.) and a catalytic amount of 18-crown-6-ether (0.5 mmol, 10 mol%). Then benzyl bromide (10 mmol, 2.0 equiv.) was added and the mixture refluxed for 6 h (monitored by TLC). The solvent was evaporated to afford crude products and the crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate as eluting solvent to give the desired products.

Method B: A solution of 1,2,4-triazine-3,5(2*H*,4*H*)-diones (5 mmol, 1.0 equiv.) in dry acetone (25 mL) was mixed with anhydrous potassium carbonate (5mmol, 1.0 equiv.) and a catalytic amount of 18-crown-6-ether (0.5 mmol, 10 mol%). Benzyl bromide in dry acetone (15 mL), which was added to the flask five times, each time with 3 mL drop by drop in 20 min for 2 h, stirred at room temperature for a total of 20 h (monitored by TLC). The solvent was evaporated to afford a crude product and the crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate as eluting solvent to give the desired products 4-benzyl-1,2,4-triazin-3,5(2*H*,4*H*)-diones.

Then, a solution of 4-benzyl-1,2,4-triazin-3,5(2*H*,4*H*)-dione (1.0 equiv.) in dry acetone (30 mL) was mixed with anhydrous potassium carbonate (1.0 equiv.) and a catalytic amount of 18-crown-6-ether (10 mol%). Then benzyl bromide (1.0 equiv.) was added and the mixture refluxed for 6 h (monitored by TLC). The solvent was evaporated to afford a crude product and the crude products were purified by silica gel chromatography using petroleum ether/ethyl acetate as eluting solvent to give the desired products **3**.

2.4 Gram-scale reaction by continuous flow



Scheme S3. Gram-scale reaction by continuous flow

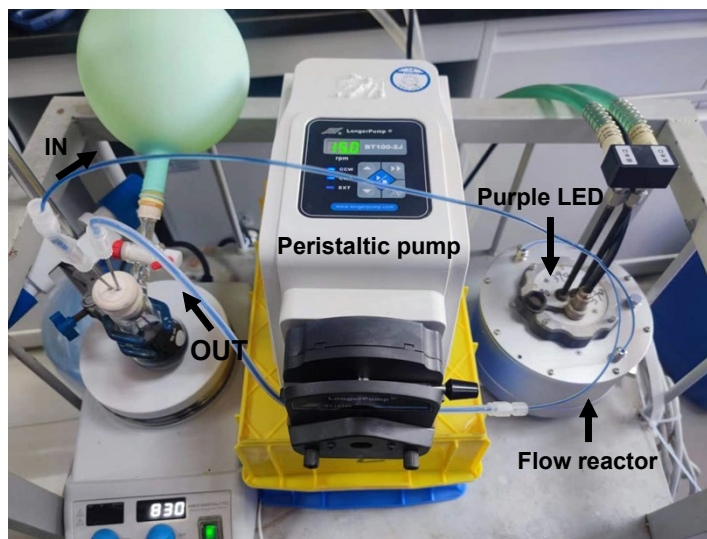
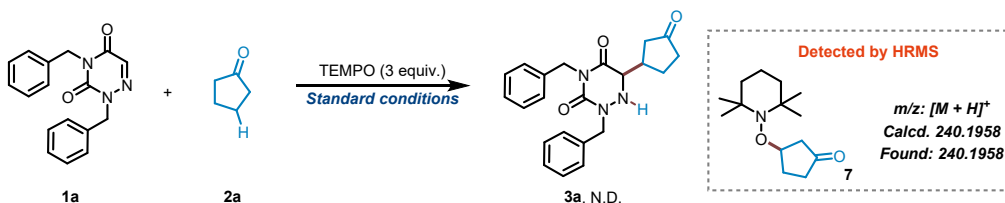


Figure S3. The continuous-flow instrument

The gram-scale synthesis of **3a** by continuous-flow: **1a** (4 mmol, 1 equiv.), **2a** (40 mmol, 10 equiv.), TBADT (5 mol%) and CH₃CN (40 mL) were sequentially added into the reaction flask. Then a continuous-flow instrument was connected, and the reaction system was replaced with an N₂ atmosphere. The reaction system was pushed into the continuous-flow instrument by a peristaltic pump and reacted under purple LED (390 nm, 8 × 10 W) irradiation for 6 h. The isolated yield of **3a** (75%, 1.13 g) was given. PFA tubing, ID = 1 mm, volume = 10 mL, flow rate (5.0 mL/min).

2.5 Investigation of the mechanism

TEMPO was used as a radical scavenger



Scheme S4. TEMPO was used as a radical scavenger

*N*₂,*N*₄-dibenzyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione **1a** (0.2 mmol, 1.0 equiv.), cyclopentanone **2a** (2.0 mmol, 10.0 equiv.), TBADT (5 mol%), TEMPO (2,2,6,6-tetramethyl-1-piperidine-1-oxyl, 3.0

equiv.) and CH₃CN (2.0 mL) were sequentially added into a 25 mL Schlenk tube equipped with a teflon coated magnetic stirring bar. The tube was sealed with a rubber stopper and the reacting mixture degassed three times using the freeze-pump-thaw method and then back-filled with nitrogen gas. Then the reaction tube was exposed to 10 W purple LED (390 nm) irradiation and stirred at room temperature for 12 hours. As it can be seen, the reaction was completely suppressed, reminding of a radical-involved process. The adduct **7** were detected by high-resolution mass spectrometry (HRMS) as shown in Figure S4.

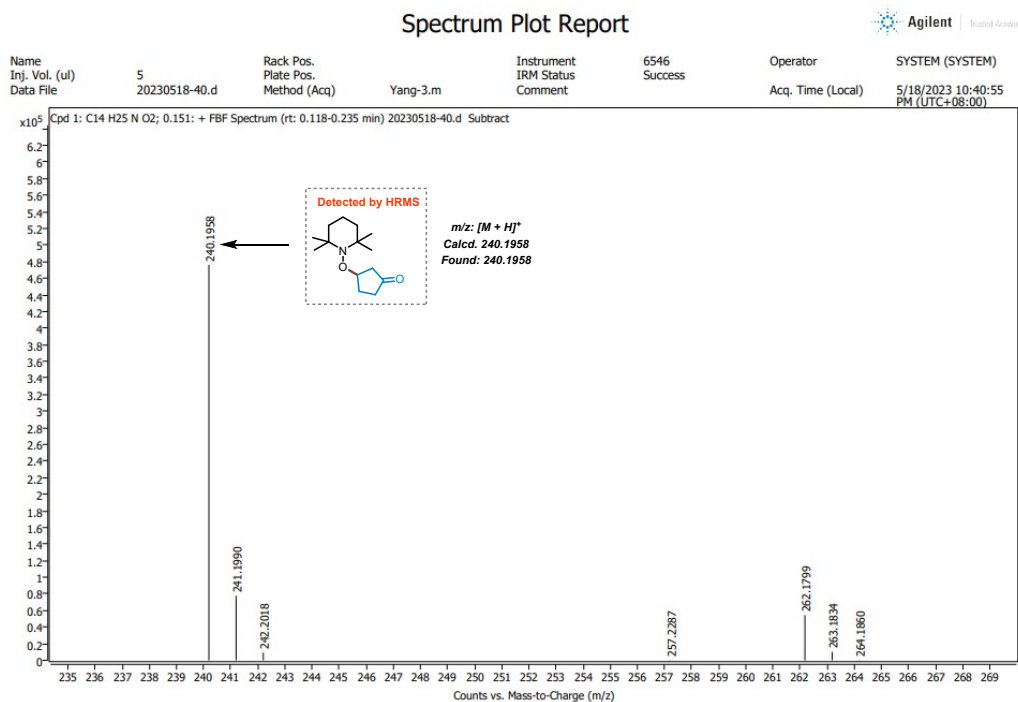
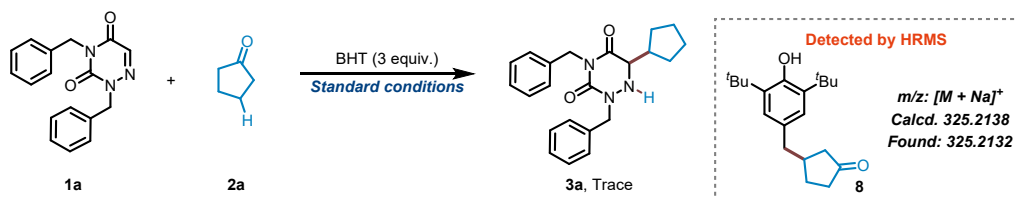


Figure S4. HRMS of the reaction when TEMPO was used as a radical scavenger

2,6-Di-*tert*-butyl-4-methylphenol was used as a radical scavenger



Scheme S5. BHT was used as a radical scavenger

*N*₂,*N*₄-dibenzyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione **1a** (0.2 mmol, 1.0 equiv.), cyclopentanone **2a** (2.0 mmol, 10.0 equiv.), TBADT (5 mol%), BHT (2,6-di-*tert*-butyl-4-methylphenol, 3.0 equiv.) and CH₃CN (2.0 mL) were sequentially added into a 25 mL Schlenk tube equipped with a teflon coated magnetic stirring bar. The tube was sealed with a rubber stopper and the reacting mixture degassed three times using the freeze-pump-thaw method and then back-filled with nitrogen gas. Then the reaction tube was exposed to 10 W purple LED (390 nm) irradiation and stirred at room temperature for 12 hours. As it can be seen, the reaction was completely suppressed, reminding of

a radical-involved process. The adduct **8** was detected by high-resolution mass spectrometry (HRMS) as shown in Figure S5.

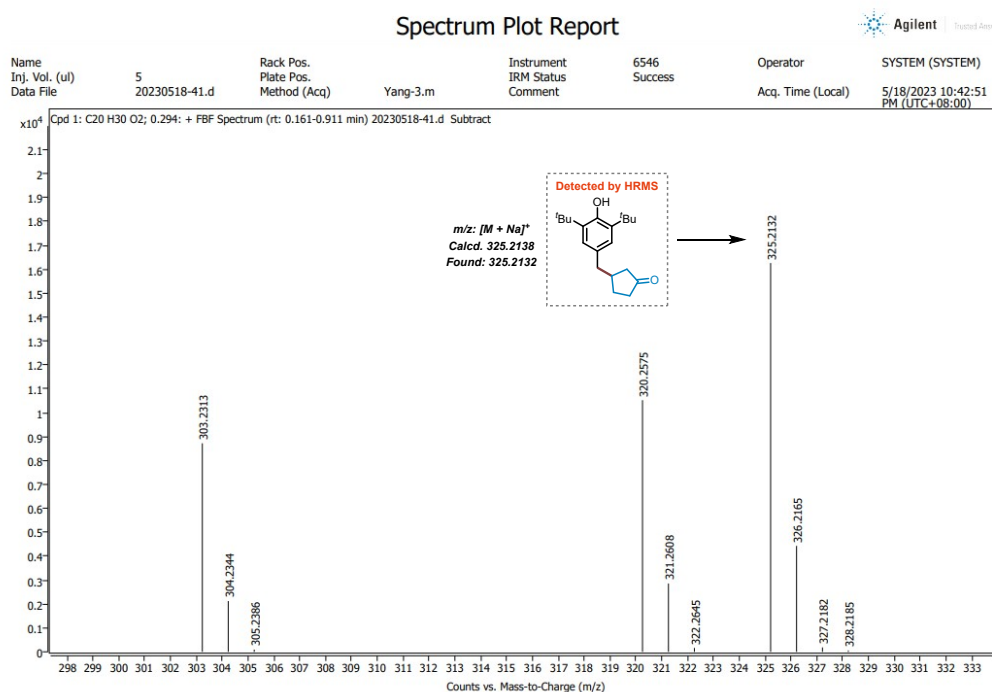
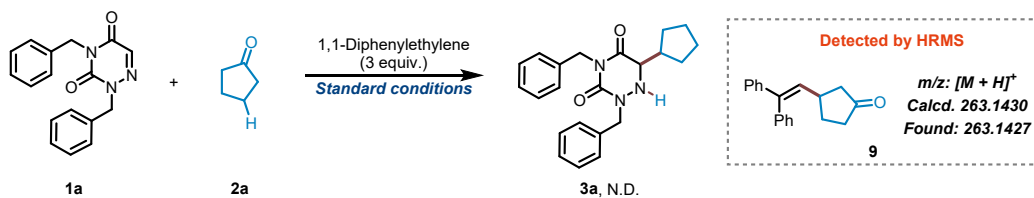


Figure S5. HRMS of the reaction when BHT was used as a radical scavenger

1,1-Diphenylethylene was used as a radical scavenger



Scheme S6. 1,1-diphenylethylene was used as a radical scavenger

*N*₂,*N*₄-dibenzyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione **1a** (0.2 mmol, 1.0 equiv.), cyclopentanone **2a** (2.0 mmol, 10.0 equiv.), TBADT (5 mol%), 1,1-diphenylethylene (3.0 equiv.), and CH₃CN (2.0 mL) were sequentially added into a 25 mL Schlenk tube equipped with a Teflon-coated magnetic stirring bar. The tube was sealed with a rubber stopper and the reacting mixture was degassed three times using the freeze-pump-thaw method and then back-filled with nitrogen gas. Then the reaction tube was exposed to 10 W purple LED (390 nm) irradiation and stirred at room temperature for 12 hours. As it can be seen, the reaction was completely suppressed, reminding of a radical-involved process. The adduct **9** was detected by high-resolution mass spectrometry (HRMS) as shown in Figure S6.

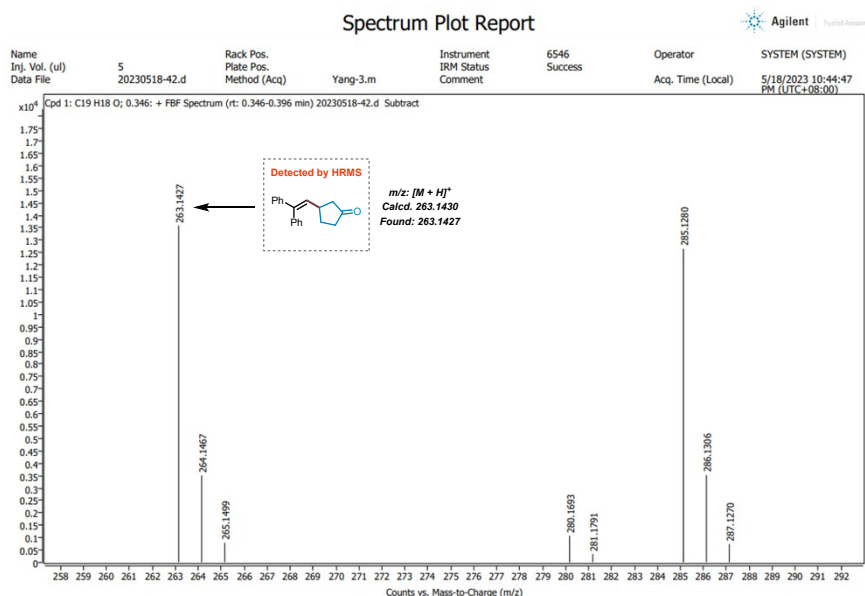
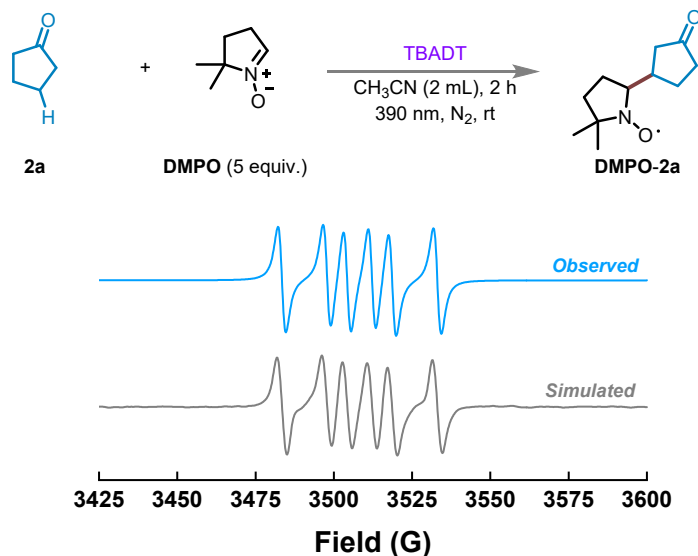


Figure S6. HRMS of the reaction when 1,1-diphenylethylene was used as a radical scavenger
EPR experiment

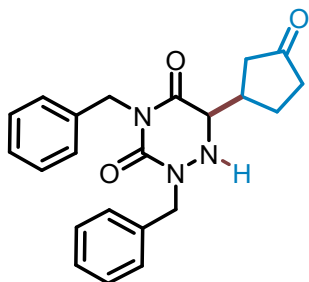
Cyclopentanone **2a** (2 mmol), TBADT (33.0 mg), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 5.0 equiv.), and CH₃CN (2.0 mL) were added into a 25 mL Schlenk tube equipped with a Teflon coated magnetic stirring bar. The tube was sealed with a rubber stopper and the reacting mixture was degassed three times using the freeze-pump-thaw method and then back-filled with nitrogen gas. Then the reaction tube was exposed to 10 W purple LED (390 nm) irradiation and stirred at room temperature. After 2 hours, the EPR experiment was conducted. EPR spectra were recorded at room temperature using a Bruker EPR E580-10/12 spectrometer.



Scheme S7 EPR experiment

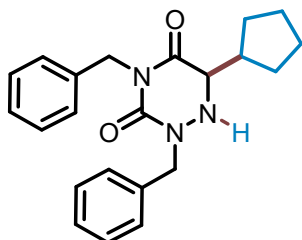
3. Characterization Data for Products

2,4-dibenzyl-6-(3-oxocyclopentyl)-1,2,4-triazinane-3,5-dione (3a)



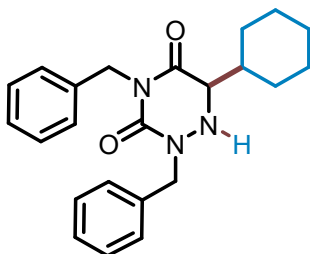
Purification by flash column chromatography (PE:EA, v/v = 3:1) to provide **3a**. Yellow oil (64.1 mg, 85% yield, dr = 1:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.18 (m, 10H), 5.00 – 4.86 (m, 2H), 4.70 – 4.54 (m, 2H), 4.47 (d, *J* = 5.8 Hz, 0.5H), 4.43 (d, *J* = 6.6 Hz, 0.5H), 3.28 – 3.16 (m, 1H), 2.38 – 2.26 (m, 1H), 2.24 – 1.63 (m, 5H), 1.56 – 1.20 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 217.24, 217.20, 169.7, 169.4, 152.83, 152.77, 137.4, 137.3, 136.4, 136.2, 129.1, 128.71, 128.69, 128.5, 128.2, 128.1, 127.6, 62.2, 62.0, 53.13, 53.11, 43.67, 43.65, 42.1, 41.5, 37.9, 37.8, 35.44, 35.39, 26.3, 25.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₄N₃O₃⁺, 378.1812; Found: 378.1813.

2,4-dibenzyl-6-cyclopentyl-1,2,4-triazinane-3,5-dione (3b)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3b**. White oil (60.0 mg, 83% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.16 (m, 10H), 4.93 (dd, *J* = 30.4, 14.2 Hz, 2H), 4.62 (dd, *J* = 118.3, 14.3 Hz, 2H), 4.26 (d, *J* = 5.9 Hz, 1H), 3.13 (dd, *J* = 9.3, 5.8 Hz, 1H), 2.11 – 2.00 (m, 1H), 1.78 – 1.20 (m, 8H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.7, 153.1, 137.7, 136.5, 129.0, 128.7, 128.6, 128.4, 127.9, 127.4, 62.7, 53.3, 43.6, 38.3, 29.9, 29.0, 25.3, 24.8. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₆N₃O₂⁺, 364.2020; Found: 364.2022.

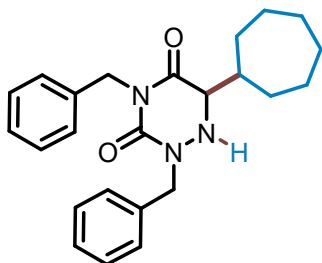
2,4-dibenzyl-6-cyclohexyl-1,2,4-triazinane-3,5-dione (3c)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3c**. Colorless oil (64.1

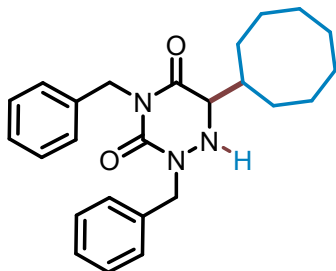
mg, 85% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.18 (m, 10H), 4.94 (dd, *J* = 35.0, 14.1 Hz, 2H), 4.62 (dd, *J* = 86.9, 14.3 Hz, 2H), 4.19 (s, 1H), 3.11 (d, *J* = 7.2 Hz, 1H), 1.75 – 0.94 (m, 10H), 0.90 – 0.74 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.1, 153.1, 137.6, 136.5, 129.0, 128.7, 128.6, 128.4, 127.9, 127.5, 63.7, 53.3, 43.6, 36.2, 29.6, 29.3, 26.1, 25.92, 25.85. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₃H₂₈N₃O₂⁺, 378.2176; Found: 378.2177.

2,4-dibenzyl-6-cycloheptyl-1,2,4-triazinane-3,5-dione (3d)



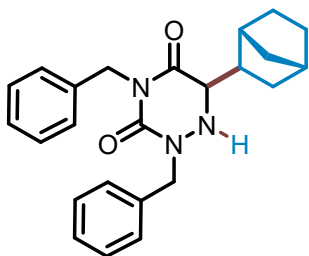
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3d**. Colorless oil (61.0 mg, 78% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.21 (m, 10H), 4.95 (dd, *J* = 31.2, 14.1 Hz, 2H), 4.63 (dd, *J* = 151.2, 14.3 Hz, 2H), 4.14 (d, *J* = 6.8 Hz, 1H), 3.17 (t, *J* = 6.4 Hz, 1H), 2.00 – 1.91 (m, 1H), 1.66 – 1.24 (m, 12H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.5, 153.2, 137.6, 136.5, 128.9, 128.7, 128.6, 128.4, 127.9, 127.4, 64.2, 53.3, 43.7, 37.6, 31.2, 29.7, 28.5, 27.7, 26.5, 26.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₄H₃₀N₃O₂⁺, 392.2333; Found: 392.2335.

2,4-dibenzyl-6-cyclooctyl-1,2,4-triazinane-3,5-dione (3e)



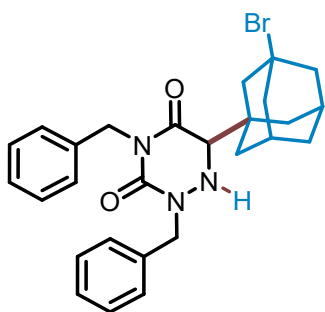
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3e**. Colorless oil (58.3 mg, 72% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.25 (m, 10H), 4.95 (dd, *J* = 29.1, 14.1 Hz, 2H), 4.65 (dd, *J* = 172.0, 14.3 Hz, 2H), 4.13 (d, *J* = 7.9 Hz, 1H), 3.18 (t, *J* = 7.5 Hz, 1H), 2.08 – 2.01 (m, 1H), 1.64 – 1.31 (m, 14H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.6, 153.3, 137.6, 136.4, 128.9, 128.68, 128.66, 128.4, 127.9, 127.4, 64.5, 53.4, 43.7, 35.7, 29.7, 28.1, 26.8, 26.4, 26.29, 26.26, 24.8. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₅H₃₂N₃O₂⁺, 406.2489; Found: 406.2494.

2,4-dibenzyl-6-bicyclo[2.2.1]heptan-2-yl-1,2,4-triazinane-3,5-dione (3f)



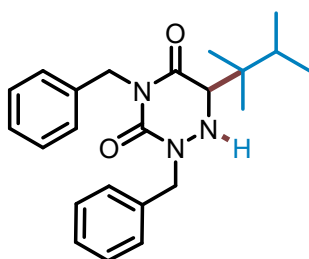
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3f**. Colorless oil (36.6 mg, 47% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.21 (m, 10H), 5.06 – 4.76 (m, 3H), 4.52 – 4.16 (m, 2H), 3.01 (dd, J = 10.5, 4.9 Hz, 0.5H), 2.94 (dd, J = 11.0, 4.1 Hz, 0.5H), 2.36 – 2.15 (m, 2H), 1.56 – 0.90 (m, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.6, 170.2, 153.0, 137.6, 136.4, 129.1, 129.0, 128.7, 128.6, 128.4, 127.9, 127.4, 62.3, 62.1, 53.5, 53.3, 43.62, 43.56, 40.7, 40.2, 38.3, 38.2, 36.8, 36.6, 35.7, 35.6, 35.1, 33.7, 29.7, 29.6, 28.7, 28.6. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_2^+$, 390.2176; Found: 390.2171.

2,4-dibenzyl-6-(3-bromoadamantan-1-yl)-1,2,4-triazinane-3,5-dione (3g)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3g**. Colorless oil (61.9 mg, 61% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.26 (m, 10H), 4.97 – 4.94 (m, 2H), 4.65 (dd, J = 208.1, 14.1 Hz, 2H), 4.15 (dd, J = 6.2, 1.7 Hz, 1H), 2.97 (d, J = 6.1 Hz, 1H), 2.25 – 2.04 (m, 8H), 1.66 – 1.50 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 152.8, 137.4, 135.9, 129.2, 129.1, 128.8, 128.4, 128.2, 127.6, 66.2, 64.6, 53.2, 50.6, 48.3, 48.2, 43.7, 40.9, 37.7, 37.0, 34.5, 32.0, 31.9. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{27}\text{H}_{31}\text{BrN}_3\text{O}_2^+$, 508.1594; Found: 508.1594.

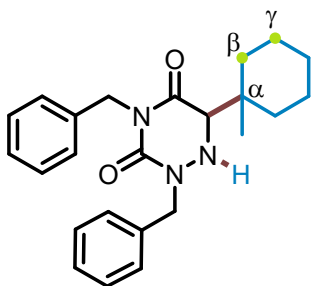
2,4-dibenzyl-6-(2,3-dimethylbutan-2-yl)-1,2,4-triazinane-3,5-dione (3h)



Purification by flash column chromatography (PE:EA, v/v = 6:1) to provide **3h**. Colorless oil (20.0

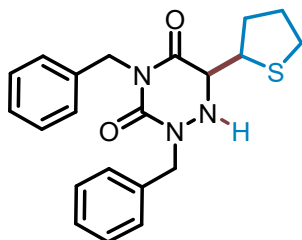
mg, 26% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.22 (m, 10H), 5.12 – 4.91 (m, 3H), 4.31 (d, *J* = 14.3 Hz, 1H), 4.04 (d, *J* = 7.7 Hz, 1H), 3.37 (d, *J* = 7.8 Hz, 1H), 2.08 – 1.98 (m, 1H), 0.91 (s, 3H), 0.85 (s, 3H), 0.81 (d, *J* = 6.9 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.2, 153.4, 137.8, 136.3, 129.2, 128.9, 128.6, 128.3, 127.8, 127.3, 64.0, 53.0, 43.7, 39.2, 32.9, 20.9, 19.8, 17.0, 16.9. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₃H₂₉N₃O₂Na⁺, 402.2152; Found: 402.2151.

2,4-dibenzyl-6-(1-methylcyclohexyl)-1,2,4-triazinane-3,5-dione + **2,4-dibenzyl-6-(2-methylcyclohexyl)-1,2,4-triazinane-3,5-dione** + **2,4-dibenzyl-6-(3-methylcyclohexyl)-1,2,4-triazinane-3,5-dione (3iα+3iβ+3iγ)**



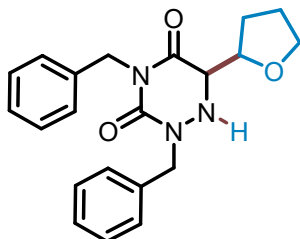
Purification by flash column chromatography (PE:EA, v/v = 6:1) to provide **3i**. Colorless oil (30.0 mg, 38% yield). Major (α):minor (β+γ) = 2.3:1. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.13 (m, 10H), 5.18 – 3.89 (m, 5H), 3.60 (dd, *J* = 12.5, 3.1 Hz, 0.2H), 3.45 – 3.35 (m, 0.1H), 3.30 (d, *J* = 6.9 Hz, 0.7H, **3iα**), 1.74 – 1.10 (m, 10H), 0.94 (s, 2.1H, **3iα**), 0.77 (d, *J* = 6.6 Hz, 0.3H), 0.67 (d, *J* = 6.4 Hz, 0.6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.7, 169.7, 153.6, 153.3, 137.8, 137.7, 136.7, 136.3, 128.9, 128.84, 128.78, 128.7, 128.59, 128.55, 128.4, 128.3, 127.82, 127.76, 127.3, 65.1, 59.8, 53.1, 53.0, 43.62, 43.60, 43.4, 37.0, 35.5, 35.32, 35.25, 32.7, 26.39, 26.37, 26.2, 25.9, 21.6, 21.5, 19.4. HRMS (ESI-TOF) *m/z*: [M + K]⁺ Calcd for C₂₄H₂₉N₃O₂K⁺, 430.1891; Found: 430.1889.

2,4-dibenzyl-6-(tetrahydrothiophen-2-yl)-1,2,4-triazinane-3,5-dione (3j)



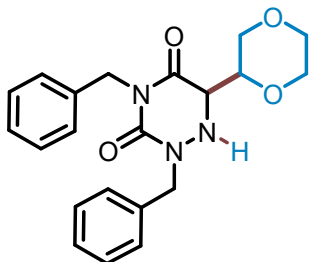
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3j**. Colorless oil (33.5 mg, 44% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.22 (m, 10H), 4.95 (dd, *J* = 37.0, 14.2 Hz, 2H), 4.85 – 4.44 (m, 3H), 4.06 – 4.02 (m, 1H), 3.43 (dd, *J* = 11.0, 4.9 Hz, 1H), 2.80 – 2.71 (m, 2H), 2.17 – 1.83 (m, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.8, 153.0, 137.3, 136.5, 128.9, 128.7, 128.6, 128.5, 127.9, 127.5, 62.3, 53.3, 46.0, 43.8, 33.3, 32.8, 31.5. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₁H₂₃N₃O₂SNa⁺, 404.1403; Found: 404.1398.

92,4-dibenzyl-6-(tetrahydrofuran-2-yl)-1,2,4-triazinane-3,5-dione (3k)



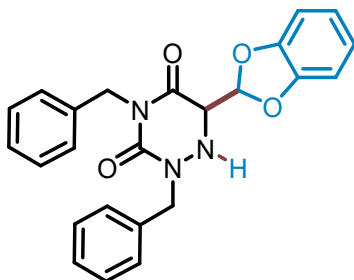
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3k**. Colorless oil (53.3 mg, 73% yield, dr = 1.9:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.20 (m, 10H), 5.04 – 4.89 (m, 2H), 4.82 – 3.93 (m, 4H), 3.87 – 3.53 (m, 2H), 3.47 (dd, *J* = 6.2, 3.8 Hz, 0.35H), 3.35 (dd, *J* = 12.0, 2.4 Hz, 0.65H), 2.06 – 1.65 (m, 4H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.8, 169.2, 153.3, 137.5, 137.4, 136.6, 136.5, 128.9, 128.783, 128.777, 128.66, 128.61, 128.57, 128.43, 128.35, 127.9, 127.8, 127.4, 127.3, 78.7, 75.3, 69.2, 69.1, 61.3, 61.1, 53.6, 53.3, 43.9, 43.8, 29.2, 27.6, 26.2, 25.1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₄N₃O₃⁺, 366.1812; Found: 366.1813.

2,4-dibenzyl-6-(1,4-dioxan-2-yl)-1,2,4-triazinane-3,5-dione (3l)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3l**. Colorless oil (59.5 mg, 78% yield, dr = 1:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.17 (m, 10H), 5.06 – 4.85 (m, 2H), 4.74 – 4.45 (m, 3H), 4.17 (d, *J* = 10.4 Hz, 0.5H), 3.72 – 3.35 (m, 7H), 3.20 (d, *J* = 11.4 Hz, 0.5H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.0, 168.2, 153.1, 152.8, 137.4, 137.3, 136.6, 136.3, 129.1, 128.8, 128.7, 128.6, 128.5, 128.44, 128.38, 128.0, 127.9, 127.5, 127.4, 74.4, 72.0, 67.8, 67.7, 67.1, 66.3, 66.2, 66.1, 59.2, 58.8, 53.4, 53.2, 44.0, 43.8. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₁H₂₃N₃O₄Na⁺, 404.1581; Found: 404.1571.

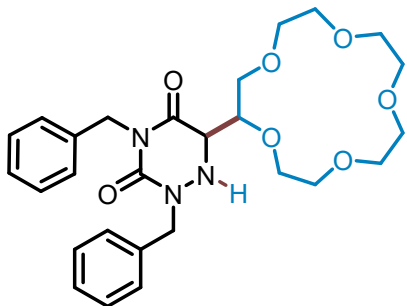
6-(benzo[d][1,3]dioxol-2-yl)-2,4-dibenzyl-1,2,4-triazinane-3,5-dione (3m)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3m**. Colorless oil (63.9

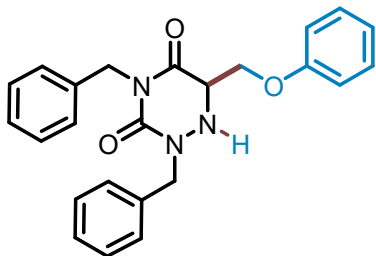
mg, 77% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 (d, *J* = 7.1 Hz, 2H), 7.25 – 7.15 (m, 8H), 6.82 – 6.73 (m, 4H), 6.36 (d, *J* = 1.9 Hz, 1H), 4.82 (dd, *J* = 43.1, 14.3 Hz, 2H), 4.57 (dd, *J* = 134.0, 14.4 Hz, 2H), 4.07 (d, *J* = 14.4 Hz, 1H), 3.82 (dd, *J* = 8.3, 1.9 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.9, 152.5, 147.3, 146.8, 137.1, 134.0, 129.0, 128.70, 128.69, 128.6, 128.0, 127.6, 122.2, 122.0, 108.8, 108.7, 107.9, 60.8, 53.3, 43.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₄H₂₂N₃O₄⁺, 416.1605; Found: 416.1605.

2,4-dibenzyl-6-(1,4,7,10,13-pentaoxacyclopentadecan-2-yl)-1,2,4-triazinane-3,5-dione (3n)



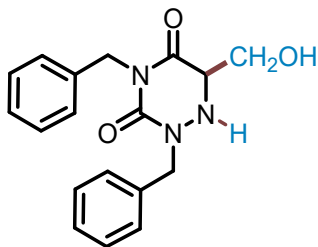
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3n**. Colorless oil (72.0 mg, 68% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.23 (m, 10H), 4.99 (dd, *J* = 29.1, 14.3 Hz, 2H), 4.64 (dd, *J* = 93.3, 14.4 Hz, 2H), 4.43 (d, *J* = 12.9 Hz, 1H), 4.34 – 4.29 (m, 1H), 4.04 (dd, *J* = 9.3, 5.9 Hz, 1H), 3.68 (s, 15H), 3.51 – 3.44 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.7, 153.4, 137.5, 136.8, 128.7, 128.52, 128.45, 128.4, 127.7, 127.3, 76.4, 72.3, 71.2, 71.0, 70.8, 70.6, 70.5, 70.2, 70.1, 69.3, 59.7, 53.1, 43.6. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₇H₃₆N₃O₇⁺, 514.2548; Found: 514.2531.

2,4-dibenzyl-6-(phenoxymethyl)-1,2,4-triazinane-3,5-dione (3o)



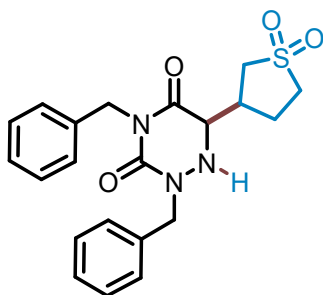
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3o**. Yellow oil (34.5 mg, 43% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.39 (m, 2H), 7.34 – 7.20 (m, 10H), 6.98 – 6.91 (m, 1H), 6.81 – 6.74 (m, 2H), 5.00 (dd, *J* = 38.3, 14.3 Hz, 2H), 4.71 – 4.55 (m, 3H), 4.40 (dd, *J* = 9.5, 3.9 Hz, 1H), 4.10 (dd, *J* = 9.6, 3.0 Hz, 1H), 3.75 – 3.71 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.1, 158.0, 153.3, 137.3, 136.5, 129.6, 128.781, 128.780, 128.7, 128.5, 127.9, 127.6, 121.7, 114.7, 65.2, 58.7, 53.4, 43.9. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₄H₂₄N₃O₃⁺, 402.1812; Found: 402.1814.

2,4-dibenzyl-6-(hydroxymethyl)-1,2,4-triazinane-3,5-dione (3p)



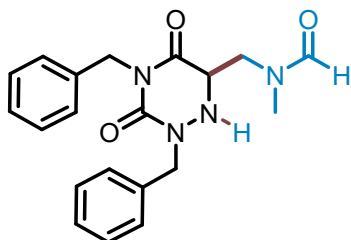
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3p**. Colorless oil (46.8 mg, 72% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.22 (m, 10H), 4.97 – 4.90 (m, 2H), 4.78 – 4.47 (m, 3H), 3.91 (dd, J = 11.7, 4.7 Hz, 1H), 3.64 (dd, J = 11.7, 3.5 Hz, 1H), 3.49 – 3.44 (m, 1H), 2.38 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 153.0, 137.2, 136.4, 128.8, 128.7, 128.6, 128.5, 128.1, 127.6, 60.2, 59.3, 53.1, 43.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_3\text{O}_3^+$, 326.1499; Found: 326.1498.

2,4-dibenzyl-6-(1,1-dioxotetrahydrothiophen-3-yl)-1,2,4-triazinane-3,5-dione (3q)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3q**. Colorless oil (59.5 mg, 72% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.28 (m, 10H), 4.98 (s, 2H), 4.86 – 4.37 (m, 3H), 3.40 (dd, J = 9.4, 5.8 Hz, 0.5H), 3.33 (dd, J = 9.6, 6.6 Hz, 0.5H), 3.20 – 2.75 (m, 3H), 2.71 – 2.44 (m, 2H), 2.22 – 2.07 (m, 1H), 1.93 – 1.67 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 168.2, 152.5, 152.4, 137.03, 136.98, 136.2, 135.9, 129.17, 129.15, 128.94, 128.86, 128.8, 128.62, 128.60, 128.5, 128.3, 127.82, 127.79, 60.9, 60.7, 53.34, 53.27, 53.0, 52.9, 51.1, 50.9, 43.81, 43.80, 34.61, 34.57, 25.8, 25.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_4\text{S}^+$, 414.1482; Found: 414.1480.

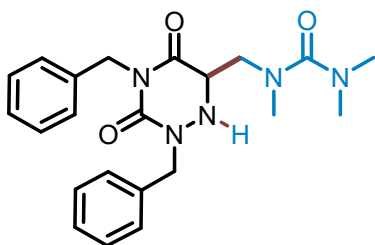
N-((2,4-dibenzyl-3,5-dioxo-1,2,4-triazinan-6-yl)methyl)-N-methylformamide (3r)



Purification by flash column chromatography (PE:EA, v/v = 4:1) to provide **3r**. Colorless oil (57.1 mg, 78% yield, dr = 1.2:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 0.55H), 7.63 (s, 0.45H),

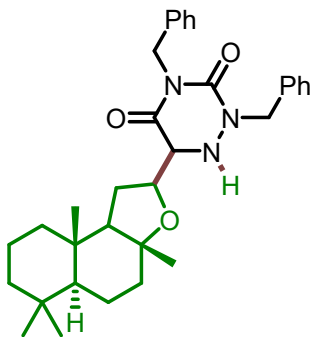
7.37 – 7.22 (m, 10H), 4.95 – 4.72 (m, 3H), 4.48 – 4.39 (m, 2H), 3.71 – 3.33 (m, 3H), 2.74 (s, 1.65H), 2.70 (s, 1.35H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.3, 168.9, 163.3, 163.1, 153.02, 152.99, 137.2, 137.1, 136.4, 136.0, 129.0, 128.9, 128.81, 128.79, 128.7, 128.6, 128.53, 128.48, 128.2, 127.9, 127.7, 127.6, 57.2, 56.4, 53.1, 53.0, 47.3, 43.74, 43.68, 42.2, 34.9, 30.1. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₀H₂₂N₄O₃Na⁺, 389.1584; Found: 389.1569.

1-((2,4-dibenzyl-3,5-dioxo-1,2,4-triazinan-6-yl)methyl)-1,3,3-trimethylurea (3s)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3s**. Colorless oil (66.3 mg, 81% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.20 (m, 10H), 4.92 (dd, *J* = 17.0, 14.3 Hz, 2H), 4.85 – 4.38 (m, 3H), 3.69 (dd, *J* = 8.4, 6.2 Hz, 1H), 3.54 – 3.41 (m, 2H), 2.70 – 2.62 (m, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.9, 165.1, 153.1, 137.4, 136.5, 128.9, 128.63, 128.58, 128.4, 127.9, 127.4, 57.0, 53.1, 47.8, 43.6, 38.5, 37.8. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₈N₅O₃⁺, 410.2187; Found: 410.2188.

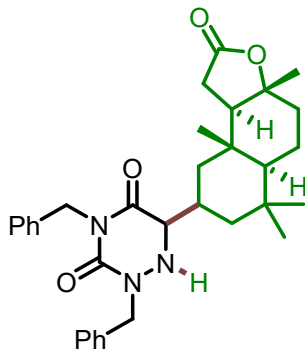
2,4-dibenzyl-6-((3aR,5aS,9aS)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan-2-yl)-1,2,4-triazinane-3,5-dione (3t)



Purification by flash column chromatography (PE:EA, v/v = 3:1) to provide **3t**. Colorless oil (88.5 mg, 84% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.20 (m, 10H), 5.02 – 4.90 (m, 2H), 4.81 – 3.98 (m, 4H), 3.47 – 3.22 (m, 1H), 1.93 – 0.71 (m, 26H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 169.6, 169.34, 169.33, 169.2, 153.5, 153.3, 153.1, 137.7, 137.6, 137.5, 137.4, 136.8, 136.6, 136.5, 129.19, 129.16, 129.0, 128.9, 128.8, 128.7, 128.52, 128.47, 128.4, 128.30, 128.25, 127.9, 127.8, 127.7, 127.6, 127.3, 127.2, 82.4, 82.0, 81.82, 81.80, 75.7, 74.5, 72.3, 62.7, 62.4, 62.2, 60.7, 60.5, 60.3, 58.4, 57.6, 57.2, 57.1, 56.7, 53.7, 53.5, 53.3, 52.9, 44.1, 44.0, 43.7, 43.4, 42.6, 42.52, 42.47, 42.41, 40.5, 40.4, 40.20, 40.16, 40.11, 39.8, 39.5, 39.1, 36.41, 36.37, 36.1, 33.6, 33.5, 33.4, 33.1, 33.0, 27.2, 26.5, 26.4, 26.2, 24.5, 24.3, 21.2, 21.13, 21.09, 21.03, 20.97, 18.42, 18.40, 18.3, 15.8,

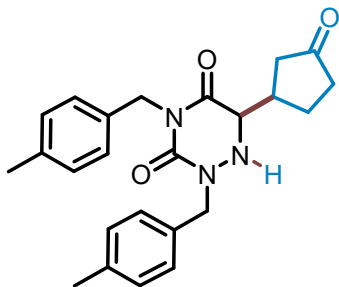
15.6, 14.8. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{33}H_{44}N_3O_3^+$, 530.3377; Found: 530.3384.

2,4-dibenzyl-6-((3aR,5aS,9aS,9bR)-3a,6,6,9a-tetramethyl-2-oxododecahydronaphtho[2,1-b]furan-8-yl)-1,2,4-triazinane-3,5-dione (3u)



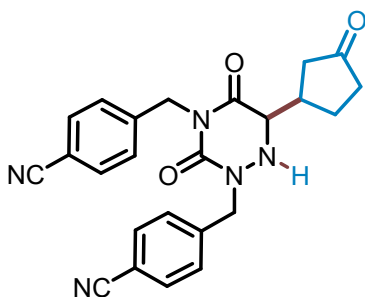
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3u**. Colorless oil (47.3 mg, 44% yield, dr = 1:1). 1H NMR (400 MHz, Chloroform- d) δ 7.46 – 7.21 (m, 10H), 5.03 – 4.85 (m, 2.5H), 4.74 (d, J = 14.2 Hz, 0.5H), 4.54 (d, J = 14.3 Hz, 0.5H), 4.43 (d, J = 14.3 Hz, 0.5H), 4.24 (d, J = 7.0 Hz, 1H), 3.19 (t, J = 6.7 Hz, 0.5H), 3.14 (t, J = 6.8 Hz, 0.5H), 2.34 – 2.14 (m, 2H), 2.13 – 1.97 (m, 2H), 1.91 – 1.74 (m, 2H), 1.69 – 1.51 (m, 2H), 1.48 – 1.11 (m, 7H), 0.97 – 0.58 (m, 10H). ^{13}C NMR (101 MHz, Chloroform- d) δ 176.1, 176.0, 169.7, 169.6, 153.2, 153.1, 137.52, 137.50, 136.33, 136.31, 129.1, 128.9, 128.8, 128.70, 128.65, 128.4, 128.3, 128.00, 127.95, 127.5, 85.9, 85.8, 63.47, 63.45, 58.9, 58.8, 56.4, 56.3, 53.49, 53.46, 45.1, 44.6, 43.8, 42.4, 41.5, 38.6, 36.4, 36.3, 33.59, 33.56, 32.99, 32.95, 28.9, 28.57, 28.55, 21.5, 21.2, 20.9, 20.4, 15.5, 15.2. HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $C_{33}H_{41}N_3O_4Na^+$, 566.2989; Found: 566.2991.

2,4-bis(4-methylbenzyl)-6-(3-oxocyclopentyl)-1,2,4-triazinane-3,5-dione (3v)



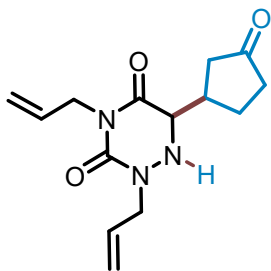
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3v**. White oil (47.3 mg, 58% yield, dr = 1:1). 1H NMR (400 MHz, Chloroform- d) δ 7.31 – 7.28 (m, 2H), 7.25 – 7.20 (m, 2H), 7.16 – 7.09 (m, 4H), 4.99 – 4.86 (m, 2H), 4.68 – 4.55 (m, 2H), 4.27 (d, J = 6.0 Hz, 0.5H), 4.23 (d, J = 7.0 Hz, 0.5H), 3.31 – 3.28 (m, 0.5H), 3.27 – 3.24 (m, 0.5H), 2.51 – 1.77 (m, 13H). ^{13}C NMR (101 MHz, Chloroform- d) δ 217.09, 217.07, 169.6, 169.3, 152.8, 152.7, 138.1, 137.9, 137.4, 134.4, 134.3, 133.2, 133.0, 129.4, 129.3, 129.2, 129.1, 128.9, 62.3, 62.0, 52.82, 52.81, 43.43, 43.40, 42.2, 41.5, 38.0, 37.9, 35.6, 35.5, 26.4, 26.0, 21.2, 21.1. HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{24}H_{28}N_3O_3^+$, 406.2125; Found: 406.2126.

4,4'-((3,5-dioxo-6-(3-oxocyclopentyl)-1,2,4-triazinane-2,4-diyl)bis(methylene))dibenzonitrile (3w)



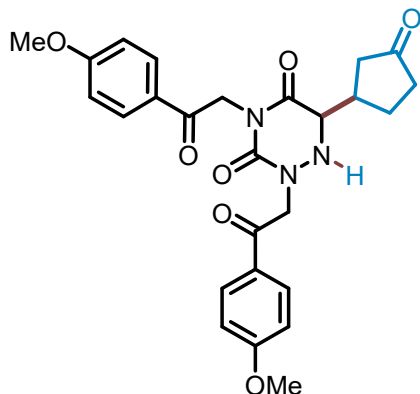
Purification by flash column chromatography (PE:EA, v/v = 1:2) to provide **3w**. White oil (80.0 mg, 93% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.57 (m, 2H), 7.54 – 7.46 (m, 6H), 5.13 – 4.97 (m, 2H), 4.87 – 4.54 (m, 3H), 3.47 – 3.42 (m, 0.5H), 3.41 – 3.38 (m, 0.5H), 2.59 – 2.45 (m, 1H), 2.40 – 2.02 (m, 5H), 1.89 – 1.63 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 216.72, 216.66, 169.6, 169.3, 152.93, 152.87, 142.40, 142.38, 141.5, 141.4, 132.49, 132.47, 132.3, 129.72, 129.69, 129.5, 118.6, 118.4, 111.89, 111.87, 111.21, 111.19, 62.1, 62.0, 53.11, 53.05, 43.5, 41.9, 41.6, 37.9, 37.7, 35.4, 35.3, 26.2, 26.1. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{21}\text{N}_5\text{O}_3\text{Na}^+$, 450.1537; Found: 450.1531.

2,4-diallyl-6-(3-oxocyclopentyl)-1,2,4-triazinane-3,5-dione (3x)



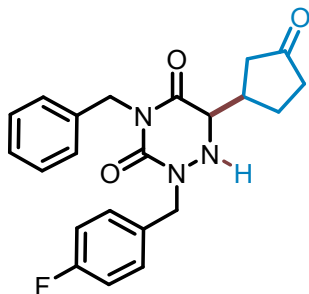
Purification by flash column chromatography (PE:EA, v/v = 1:2) to provide **3x**. Colorless oil (41.6 mg, 75% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 5.94 – 5.74 (m, 2H), 5.31 – 5.14 (m, 4H), 4.74 (d, J = 6.1 Hz, 0.5H), 4.66 (d, J = 7.0 Hz, 0.5H), 4.40 – 4.30 (m, 2H), 4.23 – 3.98 (m, 2H), 3.47 – 3.39 (m, 1H), 2.69 – 2.56 (m, 1H), 2.52 – 2.13 (m, 5H), 1.99 – 1.88 (m, 0.5H), 1.87 – 1.74 (m, 0.5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 217.3, 217.2, 169.7, 169.4, 152.4, 152.3, 132.40, 132.35, 131.8, 131.7, 119.2, 119.1, 117.63, 117.58, 62.3, 62.0, 52.2, 42.48, 42.45, 42.4, 41.6, 38.1, 37.8, 35.4, 35.3, 26.4, 26.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{20}\text{N}_3\text{O}_3^+$, 278.1499; Found: 278.1497.

2,4-bis(2-(4-methoxyphenyl)-2-oxoethyl)-6-(3-oxocyclopentyl)-1,2,4-triazinane-3,5-dione (3y)



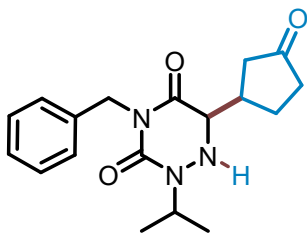
Purification by flash column chromatography (PE:EA, v/v = 1:2) to provide **3y**. White oil (81.8 mg, 83% yield, dr = 1:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.90 (m, 4H), 6.99 – 6.92 (m, 4H), 5.39 – 5.16 (m, 4H), 4.73 (d, *J* = 17.5 Hz, 0.5H), 4.62 (d, *J* = 17.5 Hz, 0.5H), 3.88 – 3.86 (m, 6H), 3.75 – 3.60 (m, 1H), 3.33 – 2.66 (m, 1H), 2.47 – 1.85 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 217.60, 217.55, 192.4, 192.3, 190.33, 190.27, 170.5, 170.2, 164.31, 164.27, 164.2, 164.0, 153.9, 153.7, 130.5, 130.41, 130.39, 127.7, 127.5, 127.38, 127.35, 114.2, 114.11, 114.08, 114.0, 62.3, 62.0, 55.90, 55.88, 55.6, 55.5, 46.3, 46.2, 42.5, 41.6, 38.4, 38.1, 37.4, 36.8, 35.90, 35.86, 27.3, 26.4. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₆H₂₈N₃O₇⁺, 494.1922; Found: 494.1922.

4-benzyl-2-(4-fluorobenzyl)-6-(3-oxocyclopentyl)-1,2,4-triazinane-3,5-dione (3z)



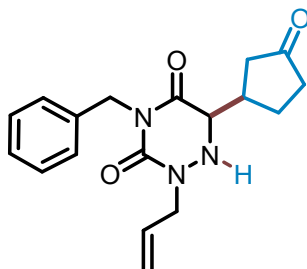
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3z**. Colorless oil (56.9 mg, 72% yield, dr = 1:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 7H), 7.05 – 6.98 (m, 2H), 5.01 – 4.90 (m, 2H), 4.71 – 4.48 (m, 2H), 4.36 (d, *J* = 6.4 Hz, 0.5H), 4.31 (d, *J* = 7.1 Hz, 0.5H), 3.33 – 3.26 (m, 1H), 2.48 – 2.35 (m, 1H), 2.21 – 1.57 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 216.94, 216.88, 169.51, 169.2, 162.59 (d, *J* = 247.2 Hz), 162.58 (d, *J* = 247.3 Hz), 152.81, 152.75, 137.24, 137.20, 132.1 (d, *J* = 3.3 Hz), 132.0 (d, *J* = 3.3 Hz), 130.90 (d, *J* = 8.2 Hz), 130.87 (d, *J* = 8.1 Hz), 128.779, 128.778, 128.5, 127.7, 115.64 (d, *J* = 21.5 Hz), 115.60 (d, *J* = 21.4 Hz), 62.2, 62.0, 52.5, 52.4, 43.72, 43.69, 42.1, 41.5, 37.9, 37.8, 35.44, 35.41, 26.3, 26.0. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -113.52, -113.63. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₂H₂₃FN₃O₃⁺, 396.1718; Found: 396.1715.

4-benzyl-2-isopropyl-6-(3-oxocyclopentyl)-1,2,4-triazinane-3,5-dione (3aa)



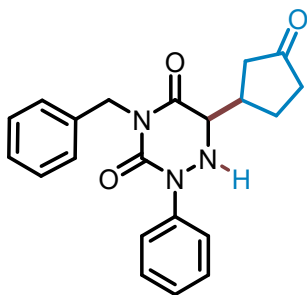
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3aa**. Colorless oil (49.4 mg, 75% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.36 (m, 2H), 7.31 – 7.24 (m, 3H), 4.98 – 4.89 (m, 2H), 4.62 – 4.51 (m, 1H), 4.04 (d, $J = 7.7$ Hz, 0.5H), 3.95 (d, $J = 9.3$ Hz, 0.5H), 3.42 – 3.31 (m, 1H), 2.67 – 2.57 (m, 1H), 2.40 – 1.83 (m, 6H), 1.20 – 1.14 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 217.3, 217.1, 169.7, 169.4, 152.5, 152.3, 137.44, 137.42, 128.80, 128.78, 128.5, 127.6, 62.5, 62.2, 48.03, 47.95, 43.7, 43.6, 42.4, 41.7, 38.0, 37.8, 35.2, 35.1, 26.3, 26.2, 19.6, 19.43, 19.41, 19.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{N}_3\text{O}_3^+$, 330.1812; Found: 330.1812.

2-allyl-4-benzyl-6-(3-oxocyclopentyl)-1,2,4-triazinane-3,5-dione (3ab)



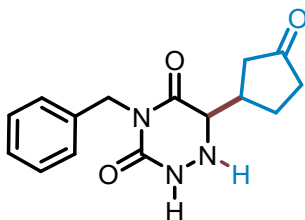
Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3ab**. White oil (28.1 mg, 43% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.27 (m, 5H), 5.91 – 5.76 (m, 1H), 5.30 – 5.20 (m, 2H), 4.97 – 4.89 (m, 2H), 4.45 (d, $J = 6.1$ Hz, 0.5H), 4.39 (d, $J = 7.1$ Hz, 0.5H), 4.23 – 4.16 (m, 1H), 4.10 – 3.95 (m, 1H), 3.45 – 3.37 (m, 1H), 2.65 – 2.52 (m, 1H), 2.32 – 1.70 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 217.1, 217.0, 169.7, 169.4, 152.6, 152.5, 137.29, 137.26, 131.7, 131.6, 129.1, 128.8, 128.5, 127.7, 119.4, 119.2, 62.4, 62.1, 52.4, 43.63, 43.60, 42.4, 41.5, 38.1, 37.8, 35.37, 35.35, 26.4, 26.1. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{22}\text{N}_3\text{O}_3^+$, 328.1656; Found: 328.1654.

4-benzyl-6-(3-oxocyclopentyl)-2-phenyl-1,2,4-triazinane-3,5-dione (3ac)



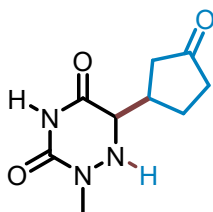
Purification by flash column chromatography (PE:EA, v/v = 1:2) to provide **3ac**. White oil (49.5 mg, 68% yield, dr = 1.5:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.56 (m, 2H), 7.43 – 7.40 (m, 2H), 7.35 – 7.27 (m, 5H), 7.17 – 7.12 (m, 1H), 5.03 – 4.98 (m, 2H), 4.86 (d, *J* = 6.1 Hz, 0.6H), 4.80 (d, *J* = 7.2 Hz, 0.4H), 3.60 – 3.51 (m, 1H), 2.70 – 2.59 (m, 1H), 2.35 – 1.88 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 216.92, 216.89, 169.9, 169.7, 151.6, 151.5, 141.2, 141.1, 137.13, 137.11, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 127.8, 125.44, 125.41, 121.3, 121.2, 62.6, 62.4, 43.71, 43.67, 42.4, 41.6, 38.1, 37.8, 35.6, 35.5, 26.5, 26.2. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₂₁H₂₂N₃O₃⁺, 364.1656; Found: 364.1655.

4-benzyl-6-(3-oxocyclopentyl)-1,2,4-triazinane-3,5-dione (3ad)



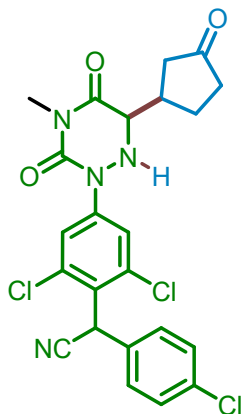
Purification by flash column chromatography (PE:EA, v/v = 1:2) to provide **3ad**. White oil (40.8 mg, 71% yield, dr = 1:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.34 – 7.25 (m, 5H), 4.90 (d, *J* = 4.2 Hz, 2H), 4.45 (d, *J* = 5.6 Hz, 0.5H), 4.39 (d, *J* = 6.7 Hz, 0.5H), 3.41 – 3.32 (m, 1H), 2.68 – 2.56 (m, 1H), 2.35 – 2.10 (m, 5H), 1.85 – 1.70 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 217.6, 217.5, 169.9, 169.6, 154.4, 154.3, 137.1, 137.0, 128.6, 128.5, 127.7, 62.0, 61.8, 43.02, 43.00, 42.2, 41.7, 38.1, 37.8, 35.41, 35.37, 26.3, 26.2. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₁₅H₁₈N₃O₃⁺, 288.1343; Found: 288.1340.

2-methyl-6-(3-oxocyclopentyl)-1,2,4-triazinane-3,5-dione (3ae)



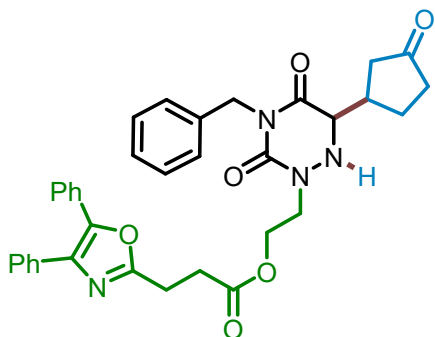
Purification by flash column chromatography (PE:EA, v/v = 1:2) to provide **3ae**. Yellow oil (35.5 mg, 84% yield, dr = 1:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 (s, 1H), 4.44 (d, *J* = 6.4 Hz, 0.5H), 4.37 (d, *J* = 7.4 Hz, 0.5H), 3.50 – 3.42 (m, 1H), 3.18 (s, 1.5H), 3.16 (s, 1.5H), 2.77 – 2.66 (m, 1H), 2.38 – 1.95 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 217.4, 217.3, 170.4, 170.1, 154.7, 154.6, 62.0, 61.8, 42.2, 41.8, 38.1, 37.9, 35.6, 26.74, 26.70, 26.34, 26.26. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for C₉H₁₄N₃O₃⁺, 212.1030; Found: 212.1028.

2-(4-chlorophenyl)-2-(2,6-dichloro-4-(4-methyl-3,5-dioxo-6-(3-oxocyclopentyl)-1,2,4-triazinane-2-yl)phenyl)acetonitrile (3af)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3af**. White oil (67.5 mg, 67% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.89 (m, 2H), 7.34 – 7.24 (m, 4H), 6.12 (s, 0.5H), 6.11 (s, 0.5H), 5.15 (d, J = 5.3 Hz, 0.5H), 5.08 (d, J = 7.4 Hz, 0.5H), 3.68 – 3.63 (m, 1H), 3.23 (s, 1.5H), 3.21 (s, 1.5H), 2.71 – 2.60 (m, 1H), 2.48 – 2.10 (m, 5H), 1.98 – 1.80 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 216.8, 216.6, 169.9, 169.6, 151.7, 151.63, 151.57, 143.0, 135.7, 134.1, 131.2, 131.14, 131.10, 129.11, 129.09, 128.2, 126.32, 126.29, 126.28, 120.2, 116.79, 116.76, 62.38, 62.35, 62.3, 42.3, 41.7, 38.2, 37.8, 36.8, 35.6, 27.61, 27.58, 26.6, 26.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{19}\text{Cl}_3\text{N}_4\text{O}_3\text{Na}^+$, 527.0415; Found: 527.0406.

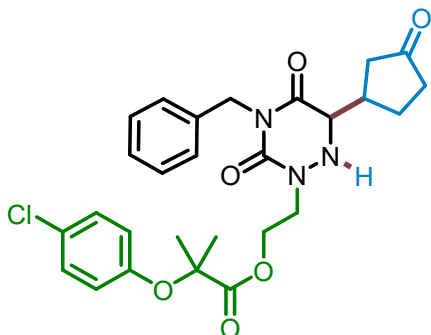
2-(4-benzyl-3,5-dioxo-6-(3-oxocyclopentyl)-1,2,4-triazinan-2-yl)ethyl 3-(4,5-diphenyloxazol-2-yl)propanoate (3ag)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3ag**. Colorless oil (72.8 mg, 60% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.53 (m, 4H), 7.37 – 7.31 (m, 8H), 7.27 – 7.18 (m, 3H), 5.07 – 4.86 (m, 3H), 4.46 – 4.39 (m, 1H), 4.31 – 4.26 (m, 0.5H), 4.23 – 4.19 (m, 0.5H), 4.12 – 4.00 (m, 1H), 3.57 – 3.51 (m, 0.5H), 3.44 – 3.38 (m, 0.5H), 3.19 (dd, J = 8.7, 7.0 Hz, 0.5H), 3.09 (dd, J = 9.4, 6.1 Hz, 0.5H), 2.96 – 2.91 (m, 2H), 2.73 – 2.65 (m, 2H), 2.54 – 2.47 (m, 1H), 2.35 – 2.04 (m, 5H), 1.83 – 1.65 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 217.1, 172.3, 172.2, 169.8, 169.5, 161.59, 161.58, 153.2, 153.1, 145.5, 137.32, 137.29, 135.00, 134.99, 132.3, 128.73, 128.70, 128.61, 128.60, 128.6, 128.44, 128.43, 128.25, 128.24, 128.04, 128.01, 127.5, 126.33, 126.32, 61.84, 61.75, 60.73, 60.67, 48.32, 48.28, 43.43, 43.38, 42.3, 41.6, 38.0, 37.8, 35.4, 31.2, 31.1, 26.4, 26.1, 23.3. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for

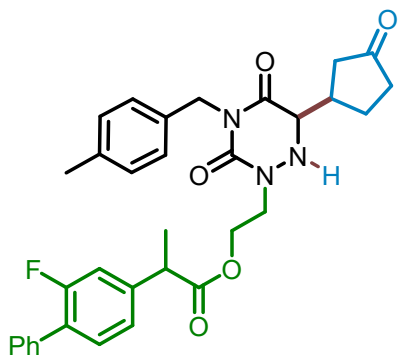
C₃₅H₃₄N₄O₆Na⁺, 629.2371; Found: 629.2369.

2-(4-benzyl-3,5-dioxo-6-(3-oxocyclopentyl)-1,2,4-triazinan-2-yl)ethyl 2-(4-chlorophenoxy)-2-methylpropanoate (3ah)



Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3ah**. Colorless oil (68.5 mg, 65% yield, dr = 1:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.33 (m, 2H), 7.31 – 7.21 (m, 3H), 7.17 – 7.12 (m, 2H), 6.70 – 6.64 (m, 2H), 4.94 – 4.82 (m, 2H), 4.49 – 4.28 (m, 3H), 4.01 – 3.91 (m, 1H), 3.66 – 3.60 (m, 0.5H), 3.56 – 3.50 (m, 0.5H), 3.37 – 3.20 (m, 1H), 2.53 – 2.44 (m, 1H), 2.38 – 2.06 (m, 5H), 1.83 – 1.66 (m, 1H), 1.49 – 1.47 (m, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 216.98, 216.95, 174.3, 174.2, 169.5, 169.3, 153.8, 152.9, 152.8, 137.19, 137.16, 129.3, 128.6, 128.5, 127.6, 127.27, 127.26, 120.04, 120.00, 79.33, 79.31, 62.0, 61.8, 61.7, 61.6, 48.33, 48.27, 43.7, 43.6, 42.2, 41.6, 38.0, 37.8, 35.4, 35.3, 26.3, 26.2, 25.2, 25.14, 25.10, 25.05. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₇H₃₀ClN₃O₆Na⁺, 550.1715; Found: 550.1713.

2-(4-(4-methylbenzyl)-3,5-dioxo-6-(3-oxocyclopentyl)-1,2,4-triazinan-2-yl)ethyl 2-(2-fluoro-1,1'-biphenyl)-4-ylpropanoate (3ai)

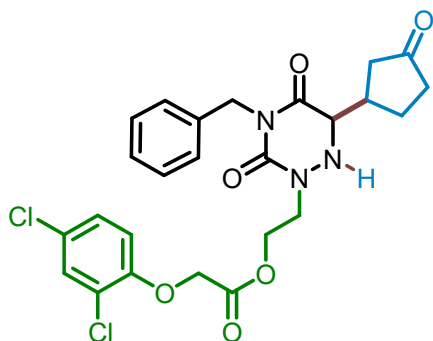


Purification by flash column chromatography (PE:EA, v/v = 2:1) to provide **3ai**. Colorless oil (45.9 mg, 40% yield, dr = 1:1:1:1). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.25 (m, 4H), 7.12 – 7.00 (m, 4H), 4.92 – 4.78 (m, 2H), 4.50 – 4.17 (m, 3H), 4.01 – 3.91 (m, 1H), 3.65 – 3.46 (m, 2H), 3.34 – 3.24 (m, 0.5H), 3.24 – 3.16 (m, 0.5H), 2.52 – 2.41 (m, 1H), 2.33 – 2.03 (m, 8H), 1.78 – 1.59 (m, 1H), 1.46 – 1.39 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 216.87, 216.85, 174.4, 174.33, 174.26, 174.1, 169.6, 169.5, 169.3, 159.6 (d, *J* = 248.9 Hz), 153.1, 153.03, 152.99, 152.94, 141.44 (d, *J* = 7.6 Hz), 141.39 (d, *J* = 7.7 Hz), 141.3 (d,

$J = 7.5$ Hz), 137.3, 135.1, 130.8 (d, $J = 3.8$ Hz), 129.2, 128.92, 128.88, 128.79, 128.78, 128.52, 128.51, 127.8, 123.6 (d, $J = 2.3$ Hz), 123.5 (d, $J = 2.9$ Hz), 115.38 (d, $J = 23.6$ Hz), 115.36 (d, $J = 23.6$ Hz), 115.29 (d, $J = 23.6$ Hz), 115.27 (d, $J = 23.6$ Hz), 62.1, 62.0, 61.9, 61.1, 61.0, 48.5, 48.4, 48.2, 45.0, 44.9, 43.4, 43.3, 42.2, 42.1, 41.7, 41.6, 37.99, 37.96, 37.79, 37.76, 35.41, 35.38, 35.37, 35.3, 26.4, 26.3, 26.2, 26.14, 21.13, 18.1, 18.0. ^{19}F NMR (376 MHz, Chloroform- d) δ -116.99, -117.01, -117.07, -117.09. HRMS (ESI-TOF) m/z : $[\text{M} + \text{NH}_4]^+$ Calcd for $\text{C}_{33}\text{H}_{38}\text{FN}_4\text{O}_5^+$, 589.2821; Found: 589.2867.

2-(4-benzyl-3,5-dioxo-6-(3-oxocyclopentyl)-1,2,4-triazinan-2-yl)ethyl
dichlorophenoxy)acetate (3aj)

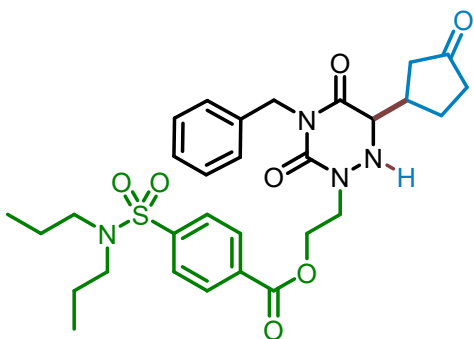
2-(2,4-



Purification by flash column chromatography (PE:EA, v/v = 1:1) to provide **3aj**. White oil (60.8 mg, 57% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform- d) δ 7.40 – 7.12 (m, 7H), 6.71 (d, $J = 8.8$ Hz, 1H), 4.94 – 4.86 (m, 2H), 4.75 (d, $J = 6.6$ Hz, 0.5H), 4.68 (d, $J = 7.8$ Hz, 0.5H), 4.58 – 4.47 (m, 1H), 4.48 (s, 1H), 4.47 (s, 1H), 4.42 – 4.34 (m, 0.5H), 4.34 – 4.25 (m, 0.5H), 4.04 – 3.94 (m, 1H), 3.64 – 3.58 (m, 0.5H), 3.56 – 3.46 (m, 0.5H), 3.48 – 3.35 (m, 1H), 2.65 – 2.52 (m, 1H), 2.44 – 2.08 (m, 5H), 1.92 – 1.70 (m, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 216.9, 169.6, 169.3, 168.7, 168.6, 153.2, 153.14, 152.11, 137.14, 137.12, 130.30, 130.29, 128.5, 128.4, 127.7, 127.6, 127.2, 127.1, 123.9, 114.6, 66.1, 66.0, 62.2, 62.0, 61.59, 61.56, 48.5, 48.4, 43.63, 43.59, 42.2, 41.6, 38.0, 37.8, 35.5, 35.4, 26.3, 26.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{25}\text{Cl}_2\text{N}_3\text{O}_6\text{Na}^+$, 556.1013; Found: 556.1011.

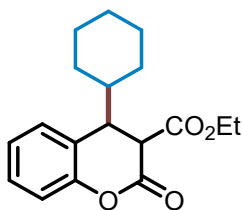
2-(4-benzyl-3,5-dioxo-6-(3-oxocyclopentyl)-1,2,4-triazinan-2-yl)ethyl
dipropylsulfamoyl)benzoate (3ak)

4-(N,N-



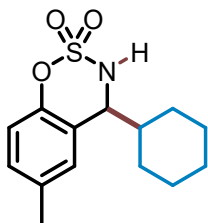
Purification by flash column chromatography (PE:EA, v/v = 1:1) to provide **3ak**. Colorless oil (62.2 mg, 52% yield, dr = 1:1). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 2H), 7.84 – 7.80 (m, 2H), 7.26 – 7.17 (m, 5H), 4.92 – 4.81 (m, 3H), 4.69 – 4.62 (m, 1H), 4.54 – 4.49 (m, 0.5H), 4.47 – 4.42 (m, 0.5H), 4.18 – 4.07 (m, 1H), 3.80 – 3.74 (m, 0.5H), 3.70 – 3.64 (m, 0.5H), 3.53 – 3.44 (m, 1H), 3.11 – 3.06 (m, 4H), 2.67 – 2.58 (m, 1H), 2.40 – 2.11 (m, 5H), 1.92 – 1.79 (m, 1H), 1.58 – 1.52 (m, 4H), 0.88 (d, J = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 216.91, 216.88, 169.7, 169.4, 165.7, 165.6, 153.2, 153.1, 144.5, 144.4, 137.1, 137.0, 132.79, 132.78, 130.3, 128.4, 128.3, 127.5, 127.0, 62.1, 62.0, 61.69, 61.65, 50.0, 48.5, 48.4, 43.6, 43.5, 42.2, 41.6, 38.0, 37.8, 35.44, 35.40, 31.6, 26.3, 26.2, 22.6, 22.0, 14.1, 11.2. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{30}\text{H}_{38}\text{N}_4\text{O}_7\text{Na}^+$, 621.2353; Found: 621.2317.

4-cyclohexyl-3-((ethylperoxy)-12-methyl)chroman-2-one (6a)⁴



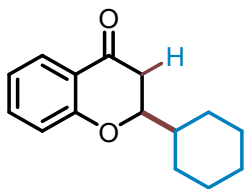
Purification by flash column chromatography (PE:EA, v/v = 20:1) to provide **6a**. Colorless oil (46.4 mg, 77% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.23 – 7.16 (m, 1H), 7.08 – 6.98 (m, 3H), 4.04 – 3.85 (m, 3H), 3.04 (dd, J = 8.1, 1.5 Hz, 1H), 1.83 – 0.88 (m, 14H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.6, 165.1, 151.0, 129.8, 128.7, 124.3, 123.2, 116.9, 62.1, 49.8, 46.1, 41.2, 30.5, 30.0, 26.1, 26.0, 25.9, 13.7.

4-cyclohexyl-6-methyl-3,4-dihydrobenzo[e][1,2,3]oxathiazine 2,2-dioxide (6b)



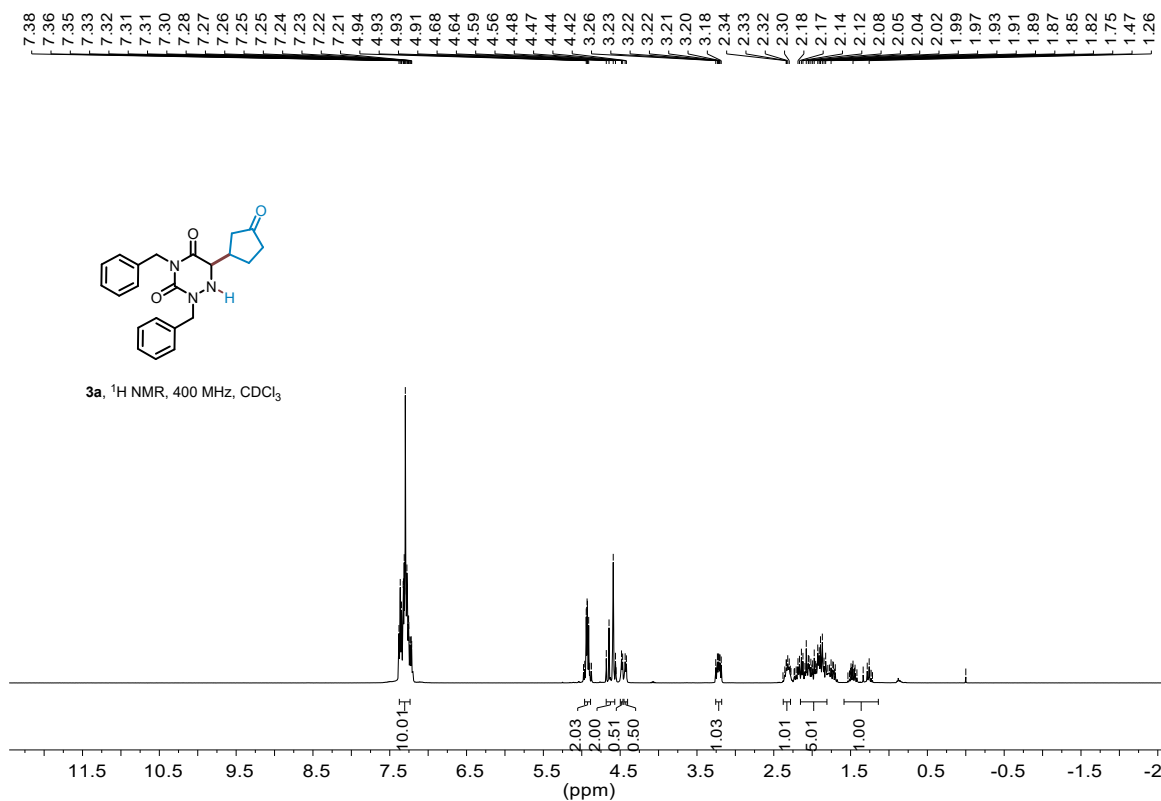
Purification by flash column chromatography (PE:EA, v/v = 30:1) to provide **6b**. White solid (26.4 mg, 47% yield), mp 112 – 113 °C. ^1H NMR (600 MHz, Chloroform-*d*) δ 7.08 (d, J = 8.3 Hz, 1H), 6.99 (s, 1H), 6.89 (d, J = 8.3 Hz, 1H), 4.63 – 4.55 (m, 2H), 2.34 (s, 3H), 2.23 – 2.17 (m, 1H), 1.89 – 1.58 (m, 5H), 1.45 – 1.13 (m, 4H), 0.96 – 0.90 (m, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 149.9, 135.1, 129.8, 126.5, 121.7, 118.7, 62.0, 40.3, 30.0, 26.4, 26.09, 26.07, 21.0. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{SNa}^+$, 304.0978; Found: 304.1013.

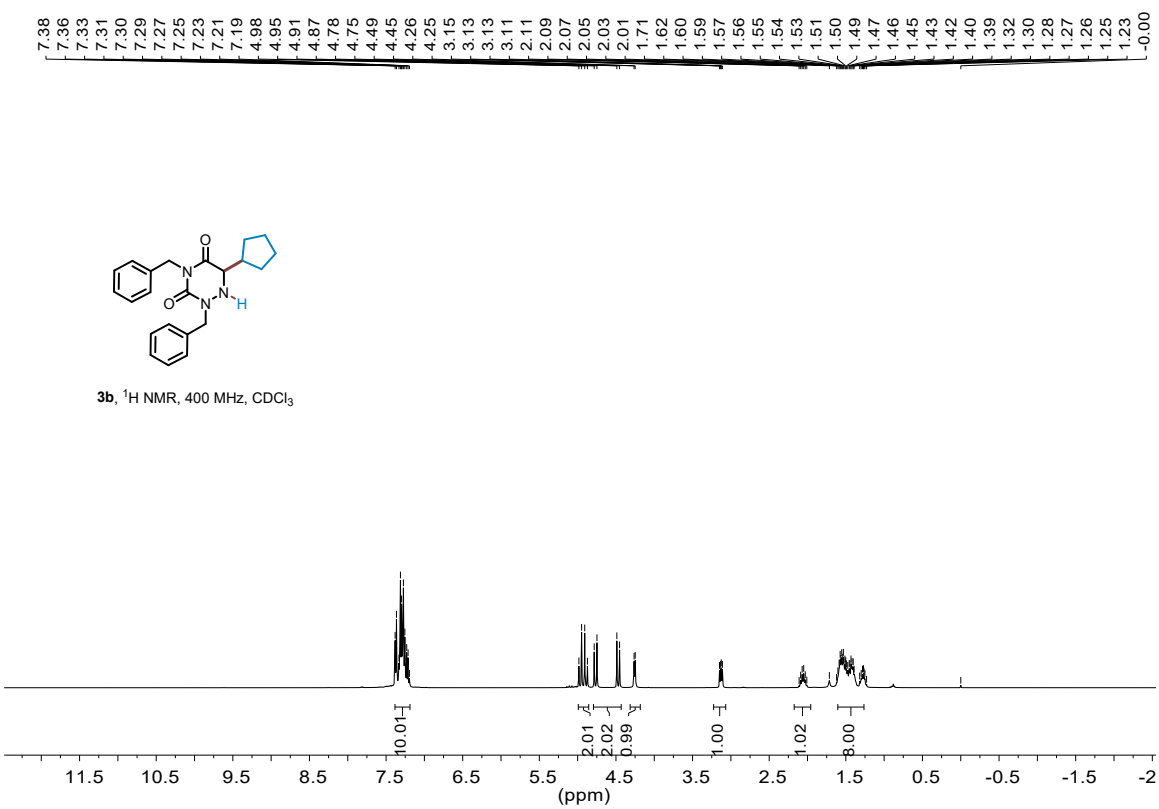
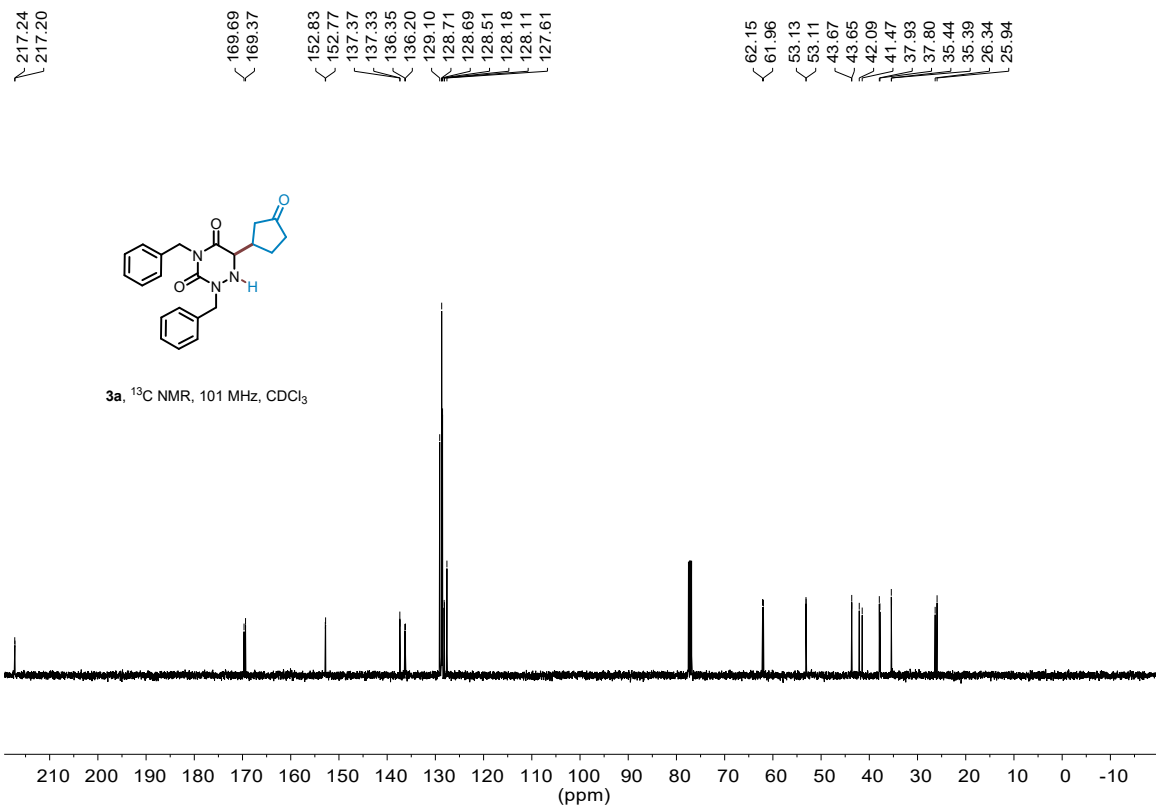
2-cyclohexylchroman-4-one (6c)⁵

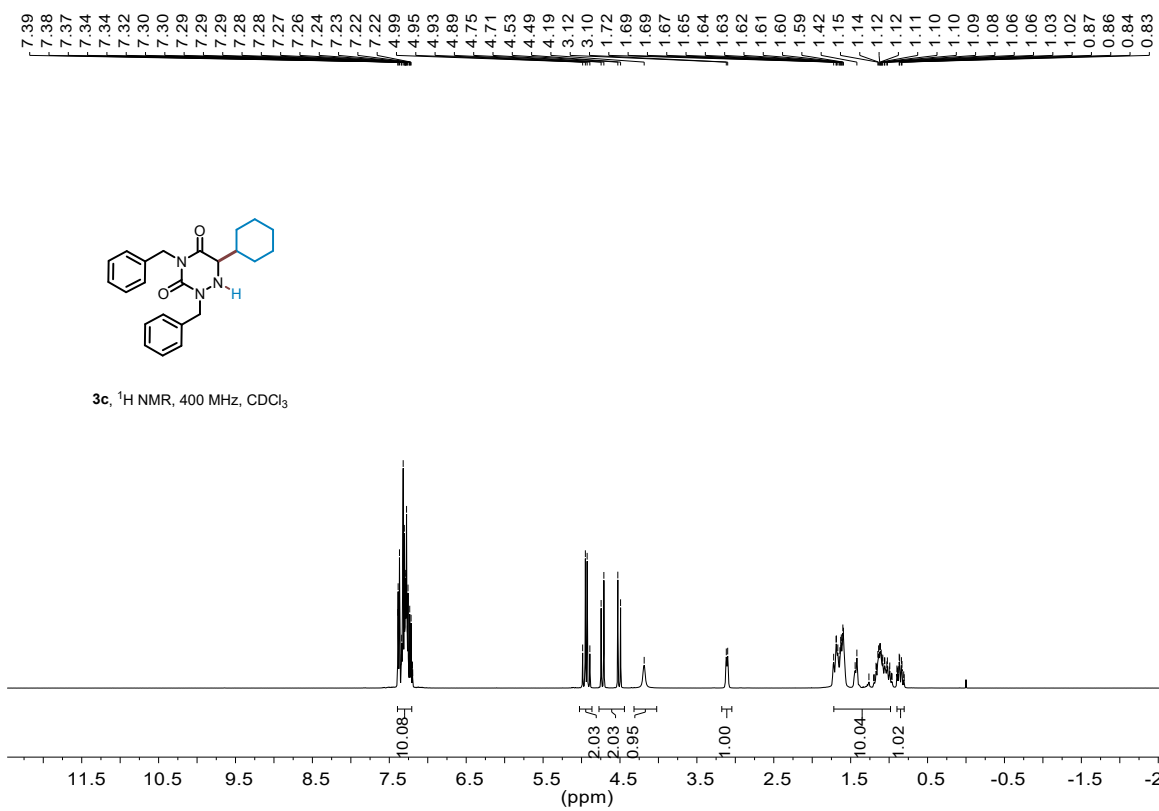
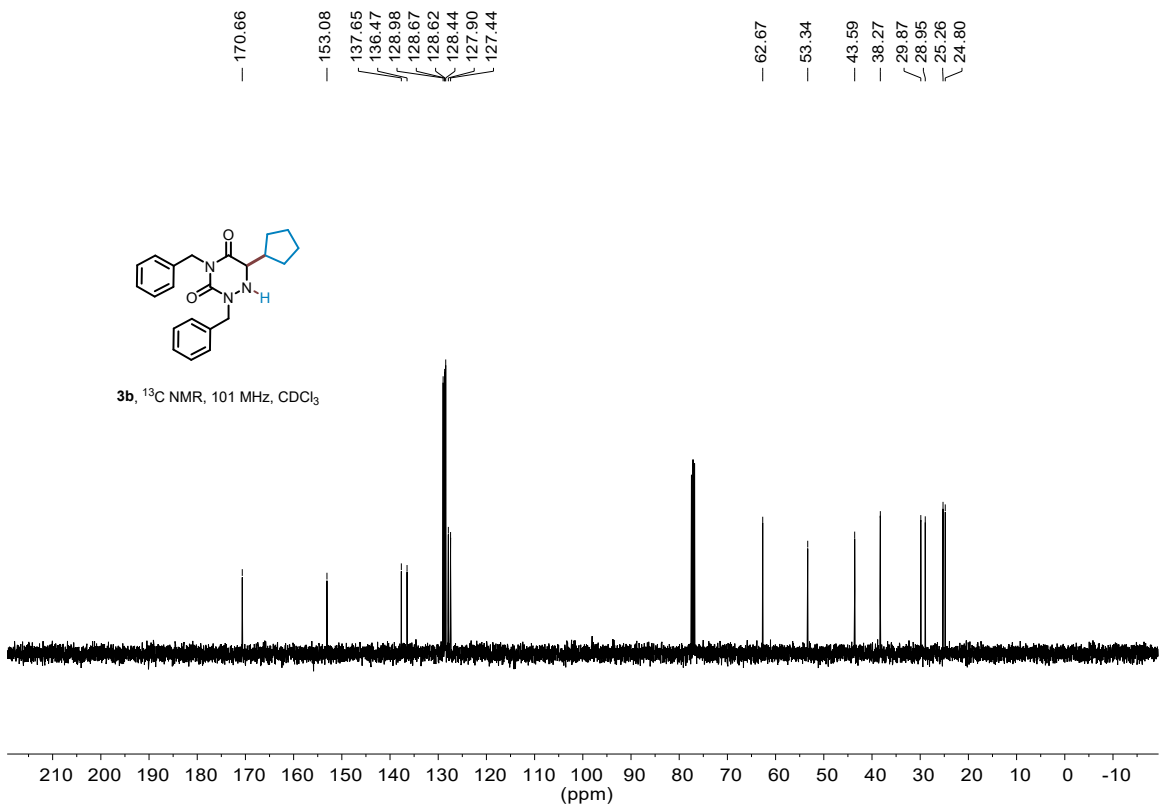


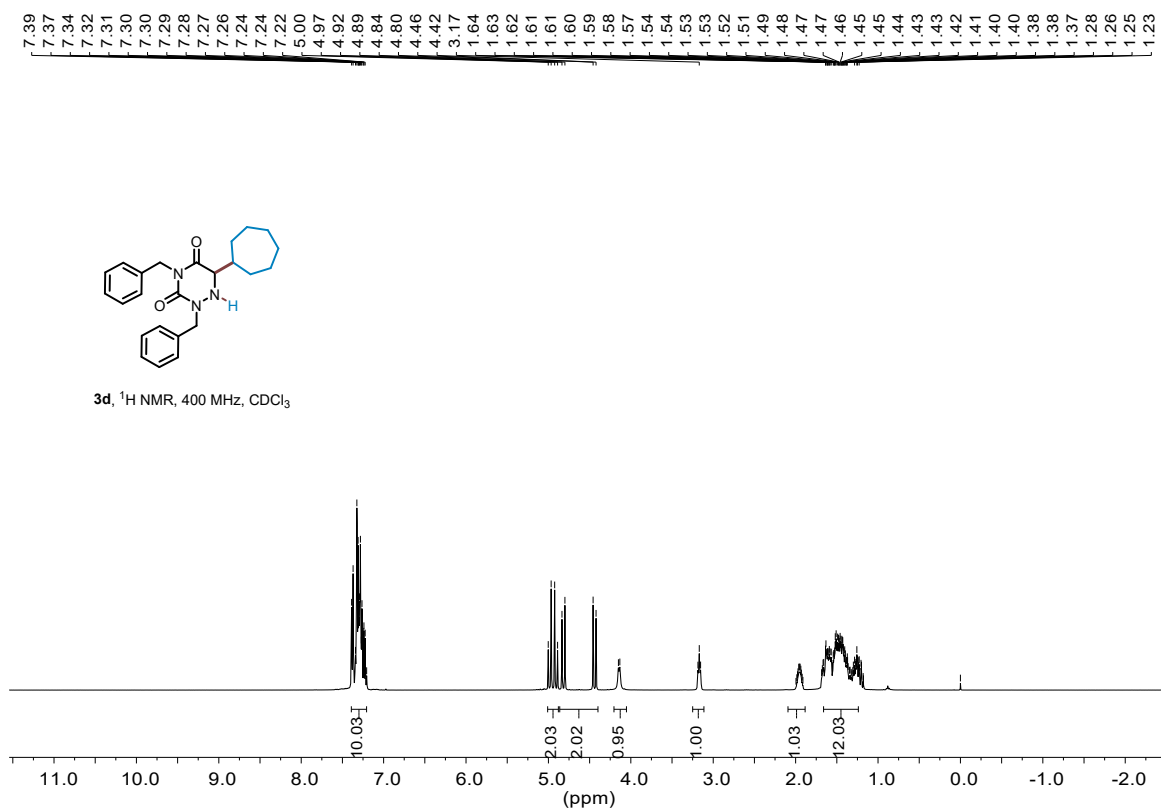
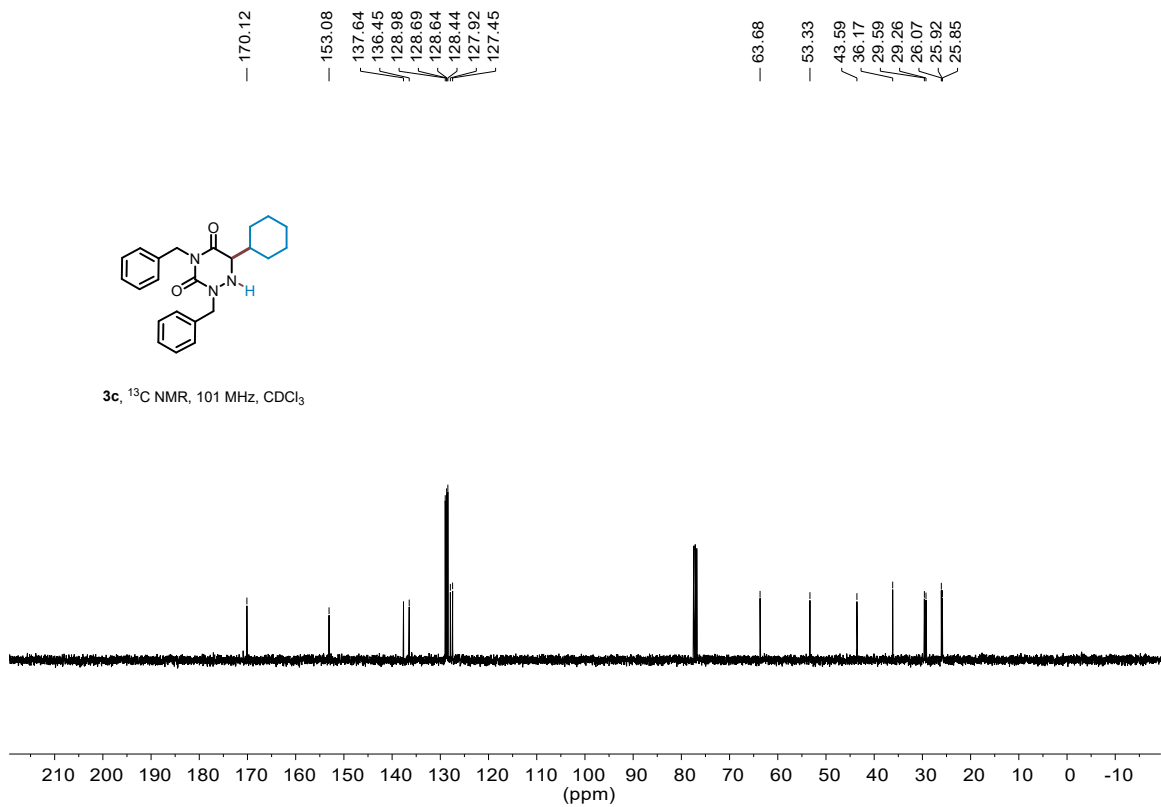
Purification by flash column chromatography (PE:EA, v/v = 20:1) to provide **6c**. Colorless oil (24.9 mg, 54% yield). ^1H NMR (600 MHz, Chloroform-*d*) δ 7.86 (dd, $J = 7.8, 1.6$ Hz, 1H), 7.47 – 7.44 (m, 1H), 7.04 – 6.92 (m, 2H), 4.22 – 7.18 (m, 1H), 2.77 – 2.63 (m, 2H), 1.99 (d, $J = 12.7$ Hz, 1H), 1.85 – 1.69 (m, 5H), 1.36 – 1.09 (m, 5H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.1, 161.9, 135.9, 126.9, 121.0, 117.9, 82.0, 41.8, 40.3, 28.3, 28.2, 26.3, 26.0, 25.9.

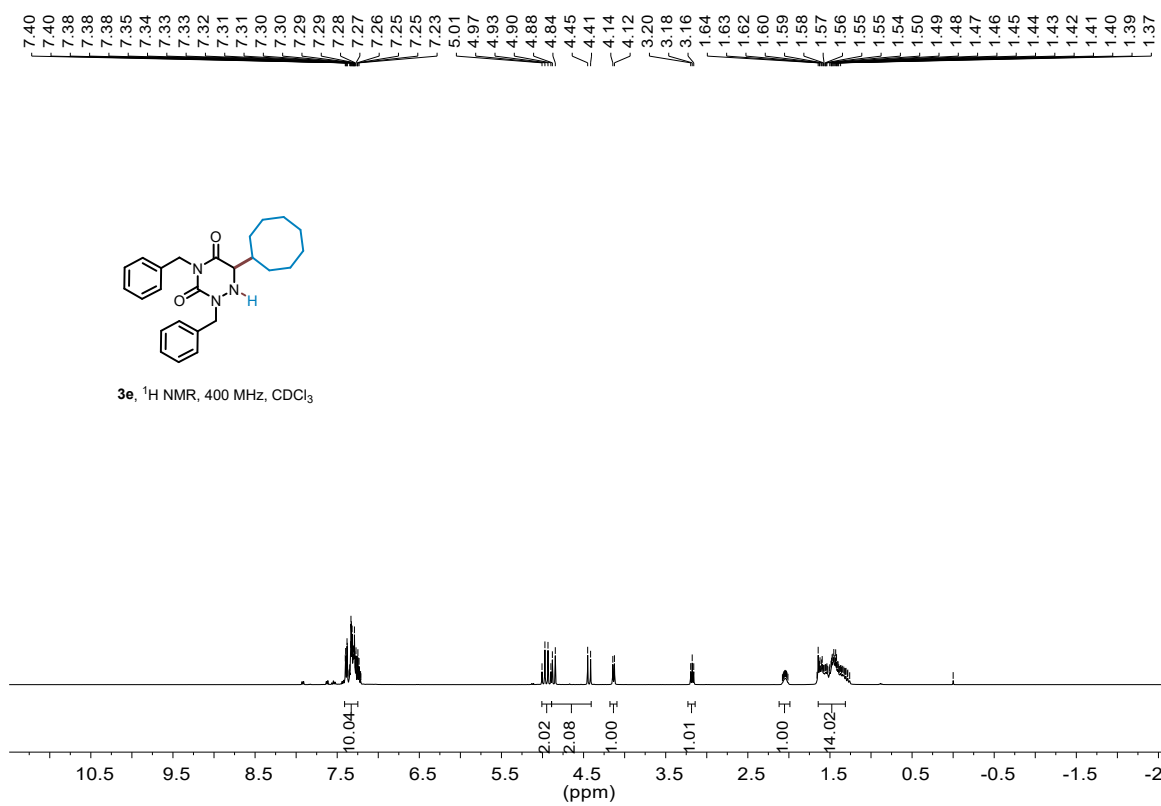
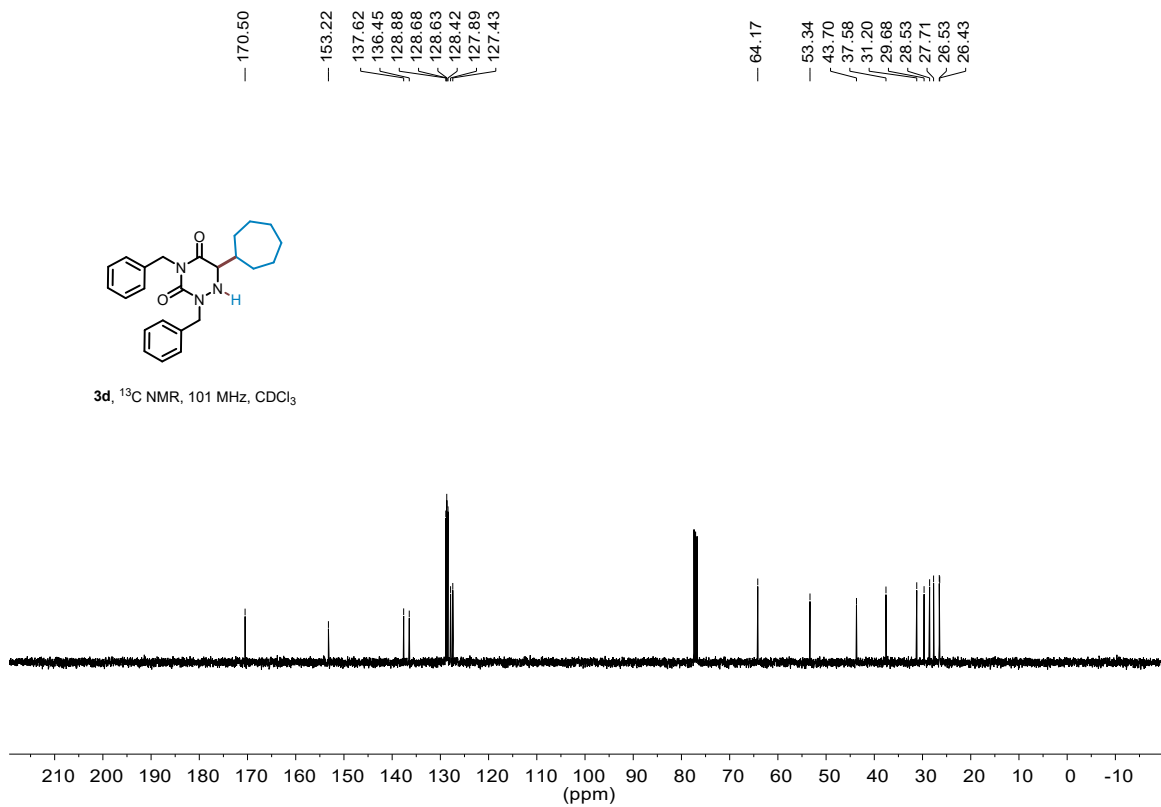
4. NMR Copies of Products

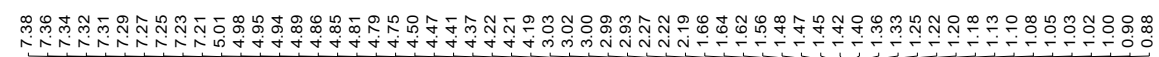
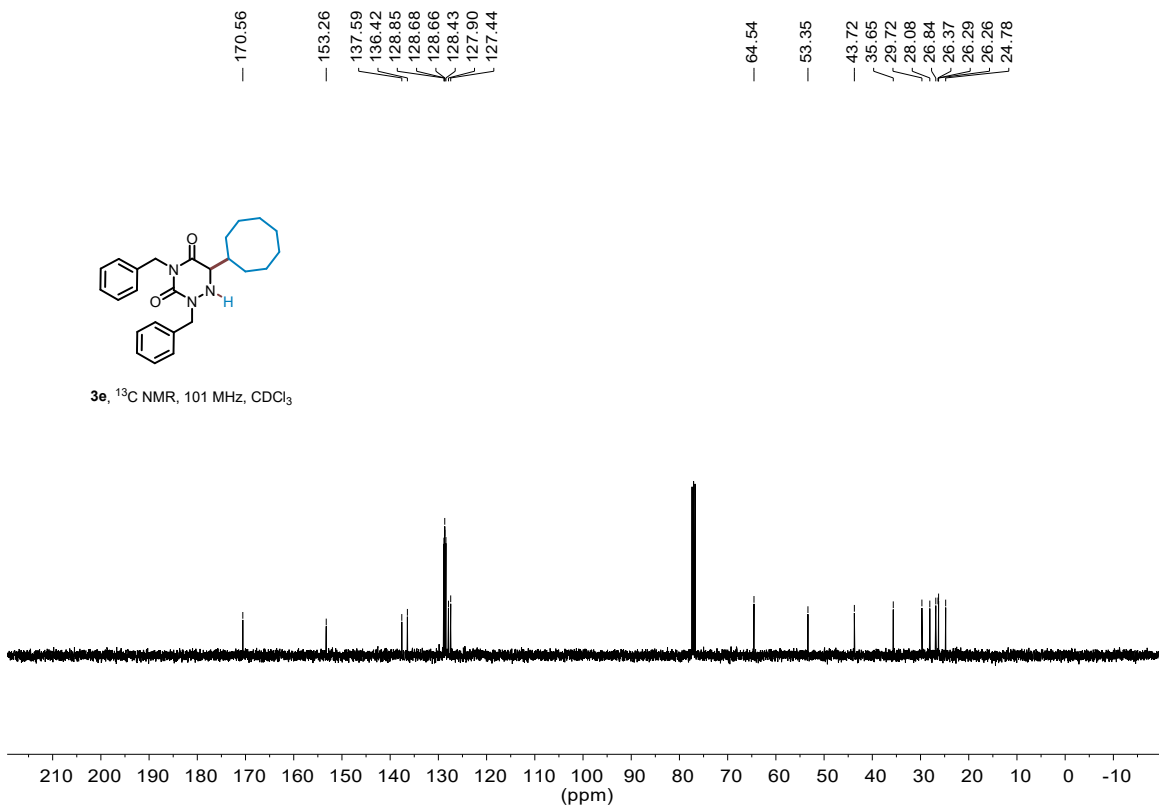




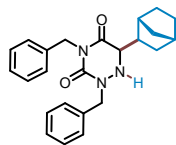




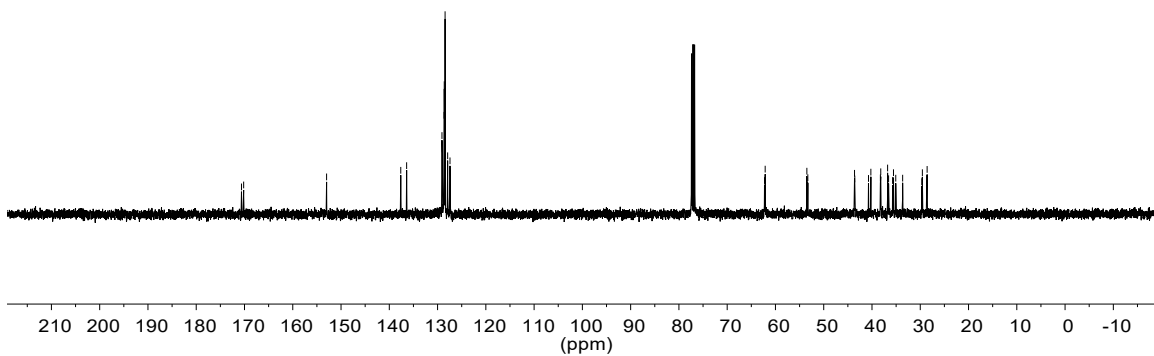




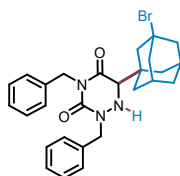
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137.63
136.41
129.09
129.02
128.66
128.62
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127.91
127.43
62.27
62.13
53.49
53.29
43.62
43.56
40.72
40.23
38.26
38.18
36.76
36.56
35.73
35.55
35.08
33.65
29.68
29.56
28.65
28.58



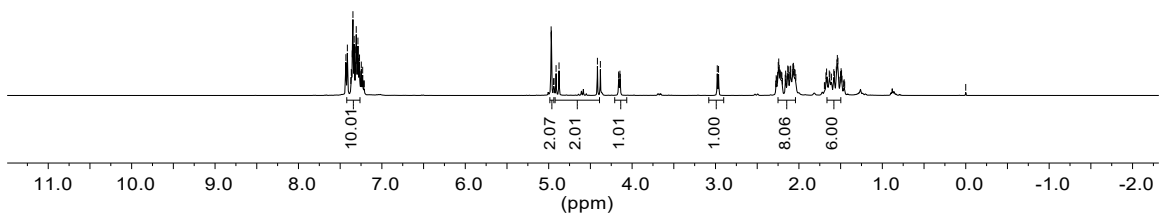
3f, ^{13}C NMR, 101 MHz, CDCl_3

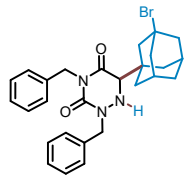


7.44
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1.49

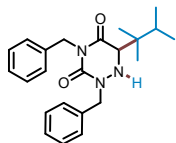
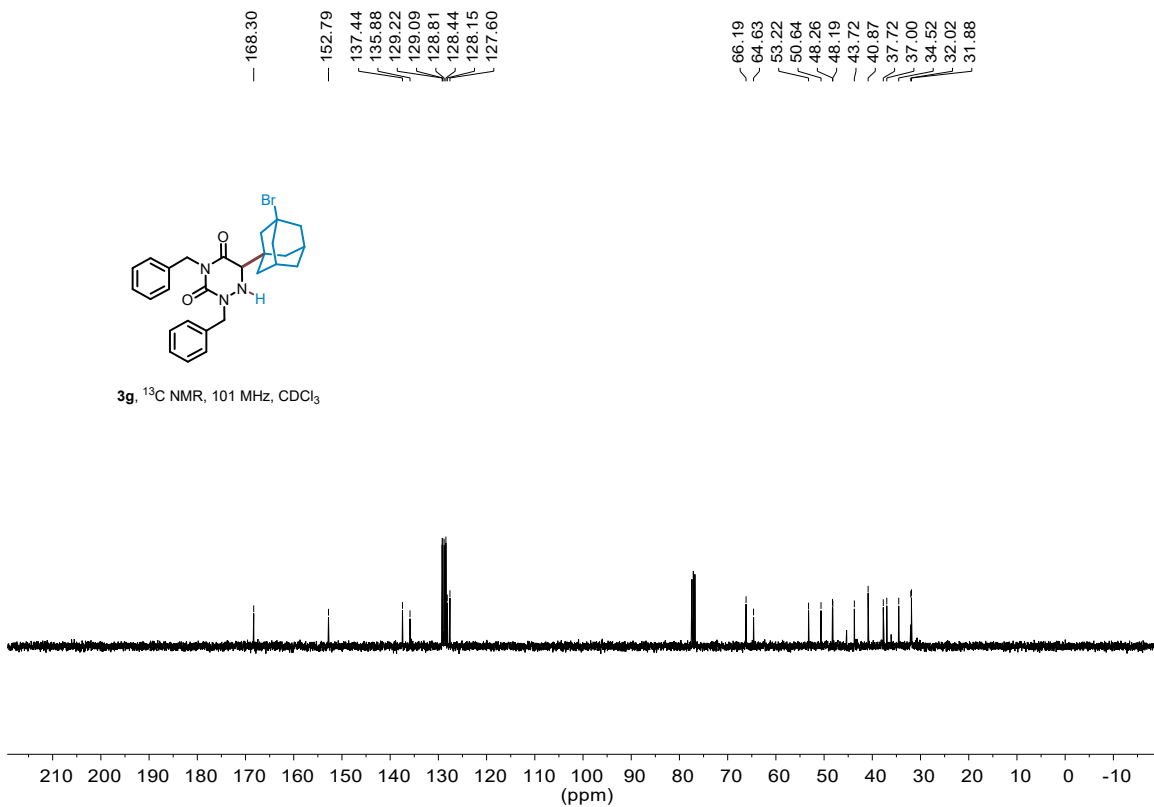


3g, ^1H NMR, 400 MHz, CDCl_3

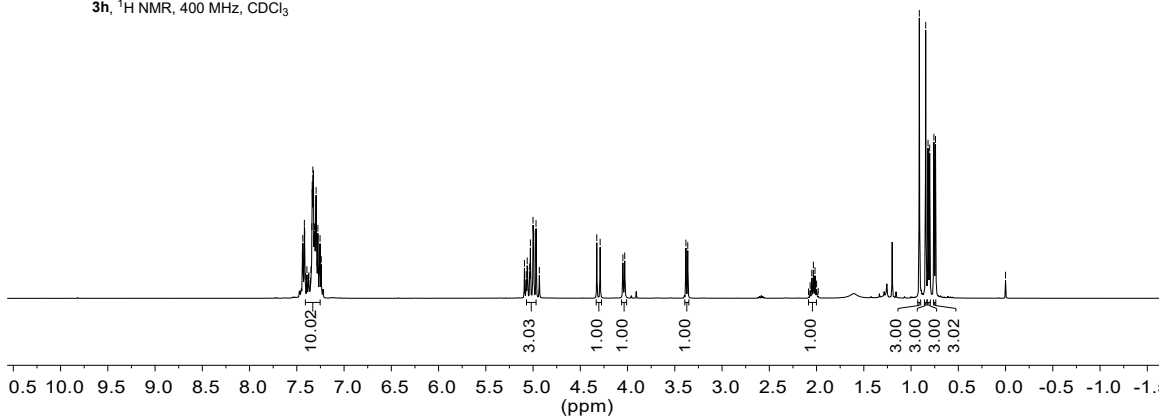


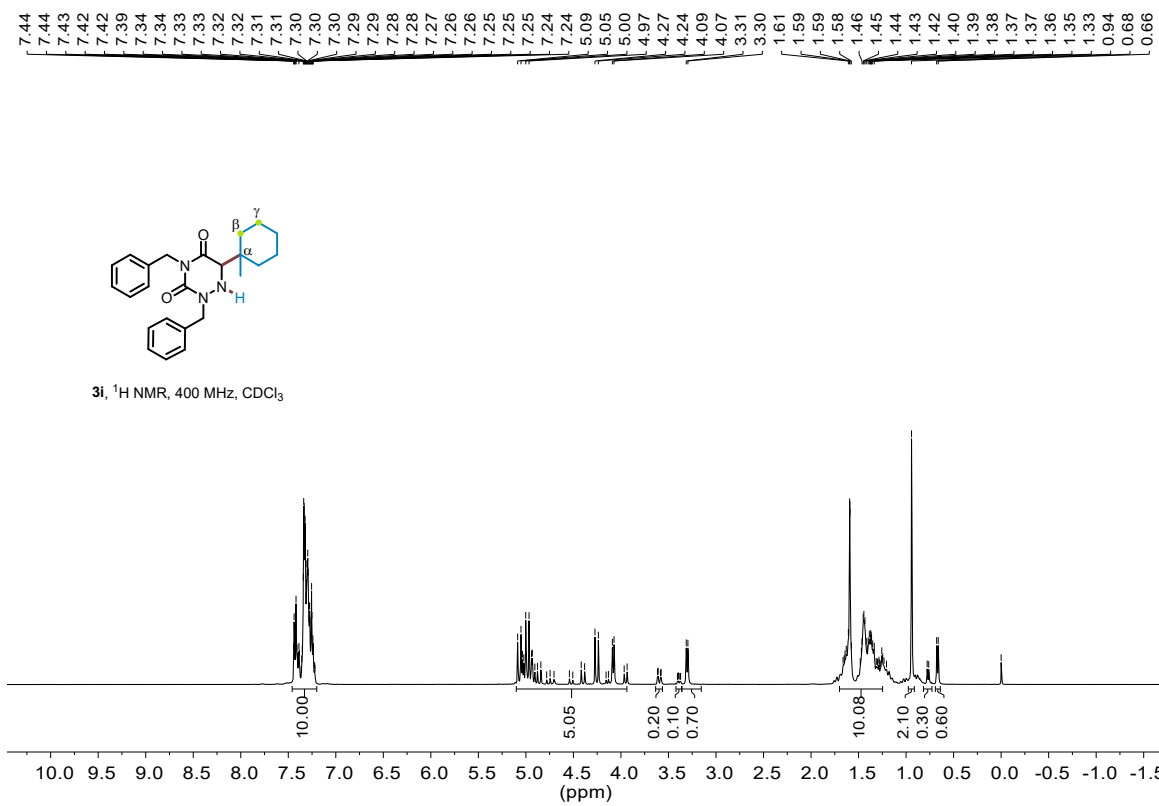
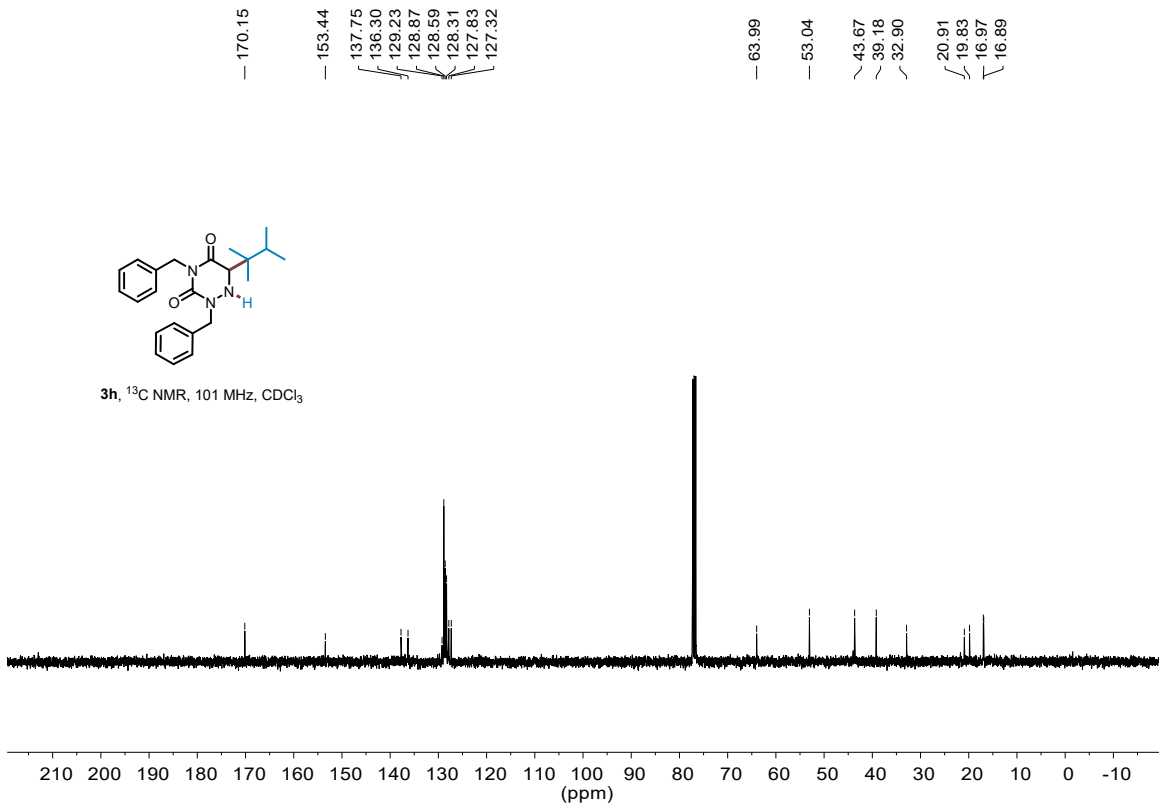


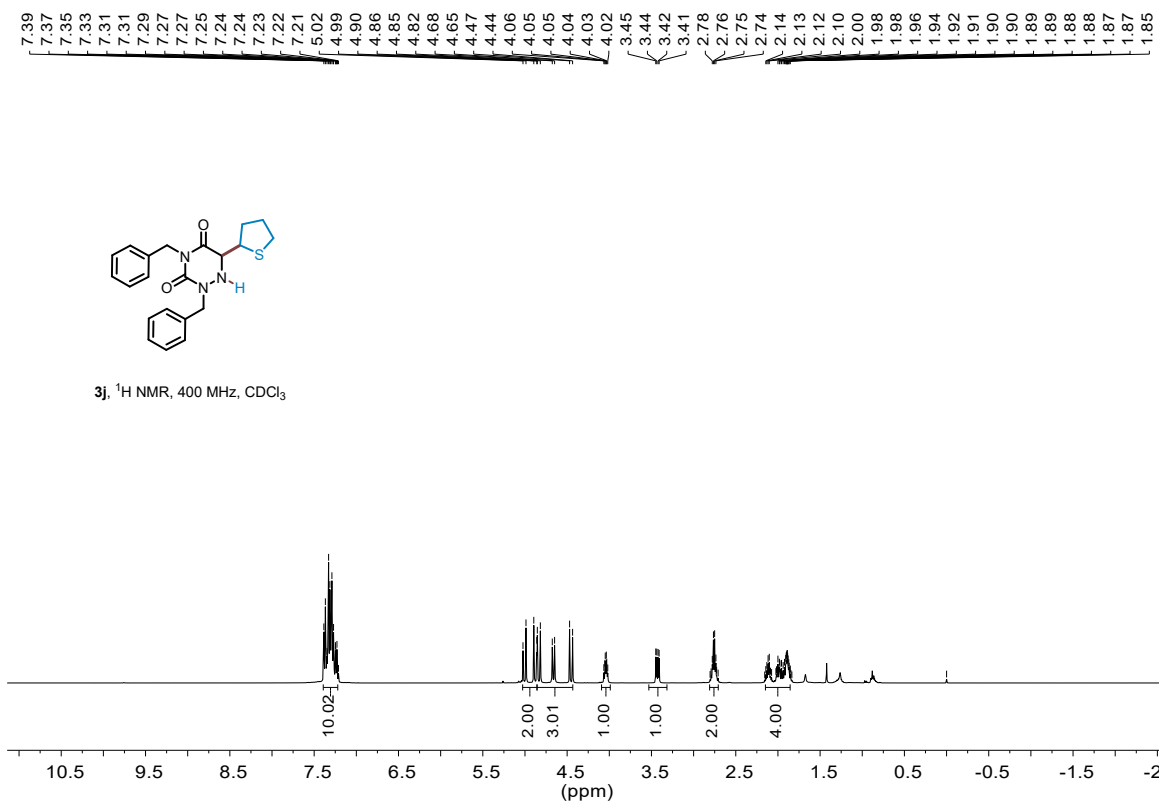
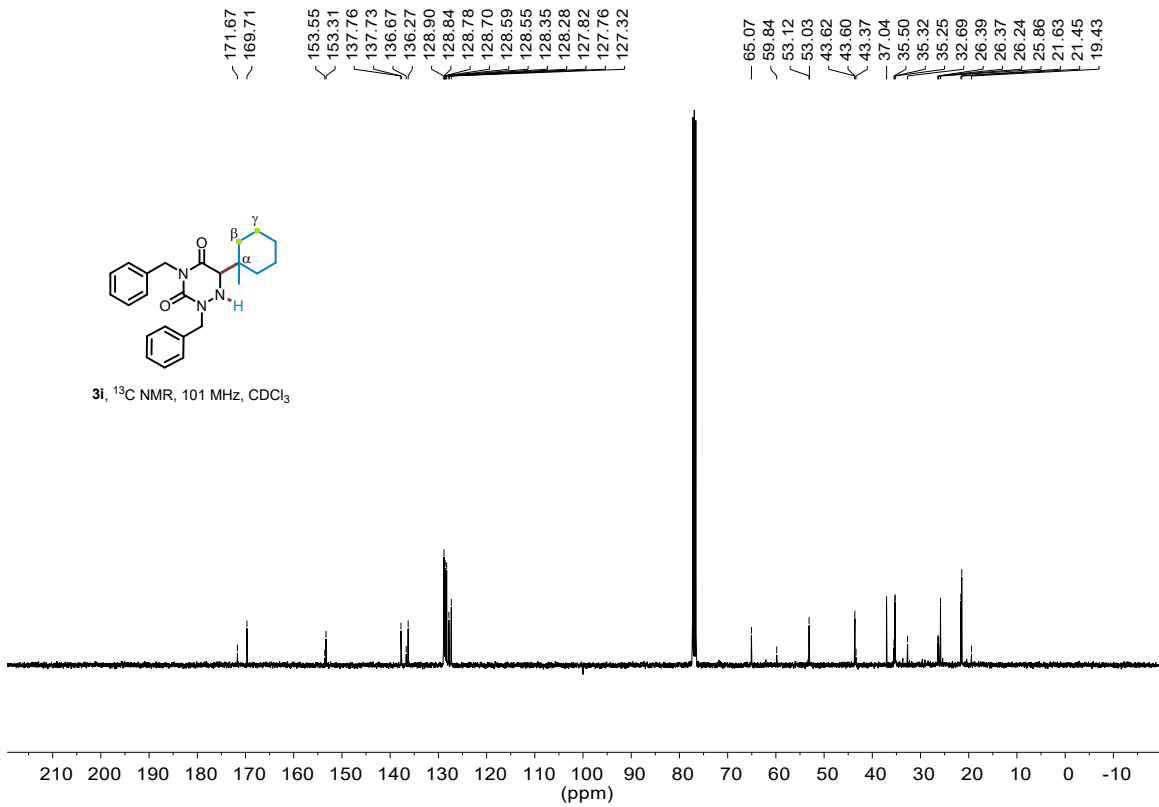
3g, ^{13}C NMR, 101 MHz, CDCl_3



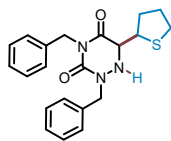
3h, ^1H NMR, 400 MHz, CDCl_3



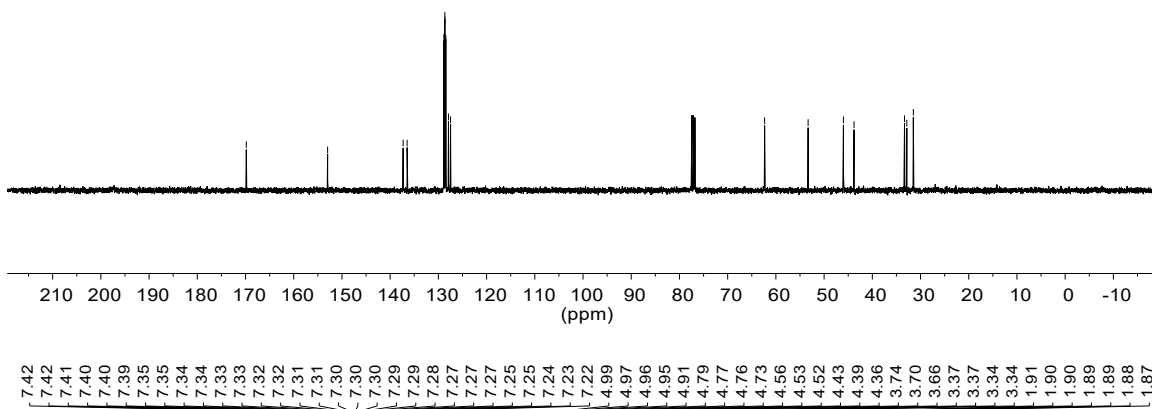




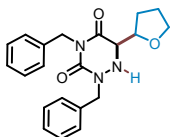
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 — 152.97
 137.31
 136.48
 128.86
 128.66
 128.64
 128.46
 127.90
 127.48
 — 62.34
 53.31
 45.99
 43.79
 33.32
 32.84
 31.49



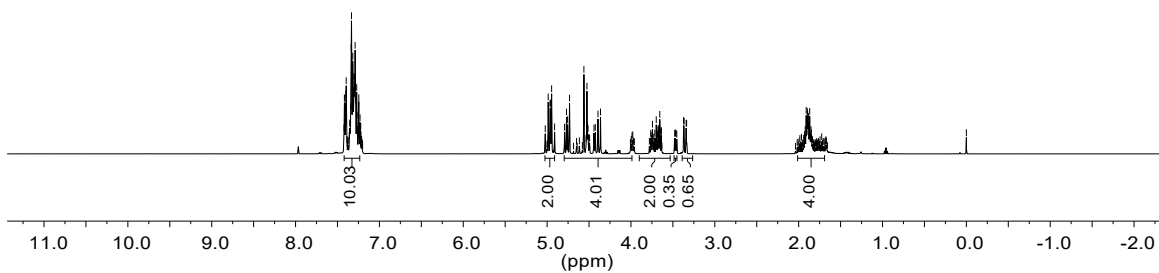
3j, ^{13}C NMR, 101 MHz, CDCl_3



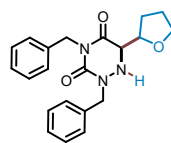
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1.87



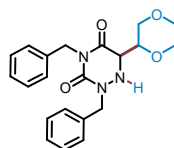
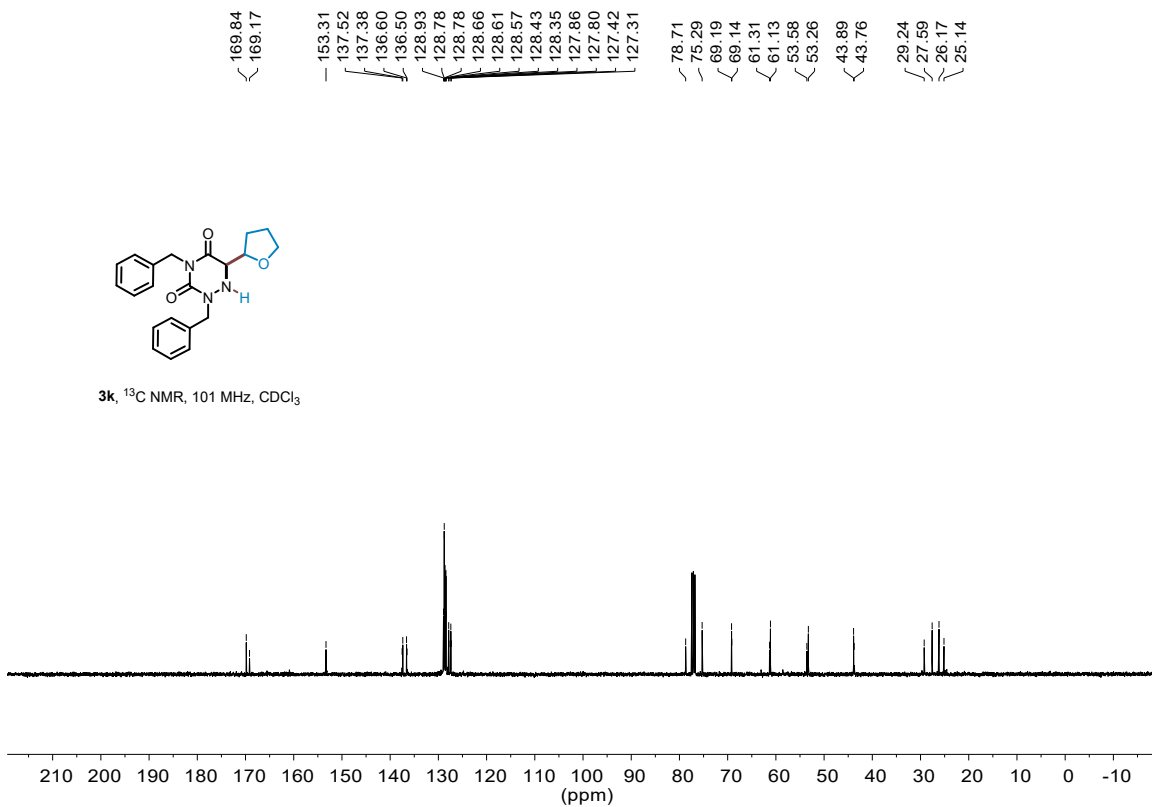
3k, ^1H NMR, 400 MHz, CDCl_3



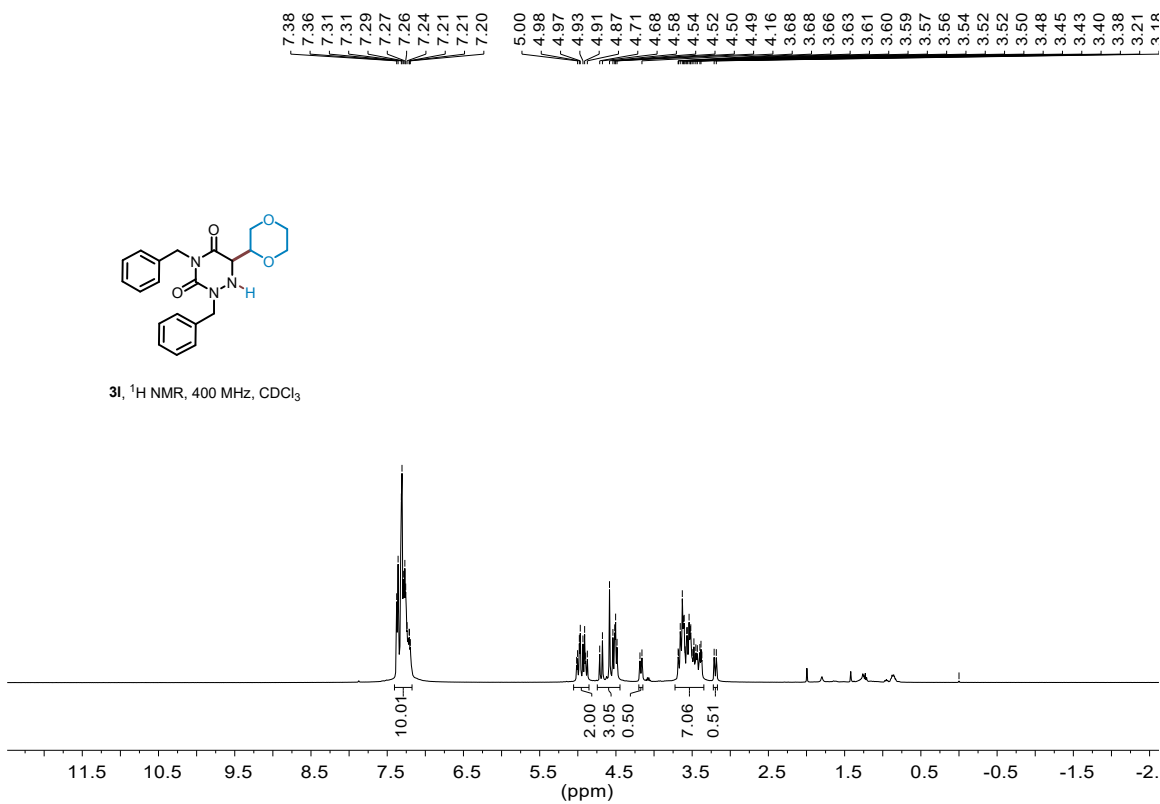
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4.0
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1.0
0.0
-1.0
-2.0



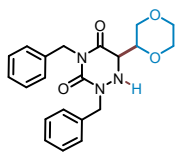
3k, ^{13}C NMR, 101 MHz, CDCl_3



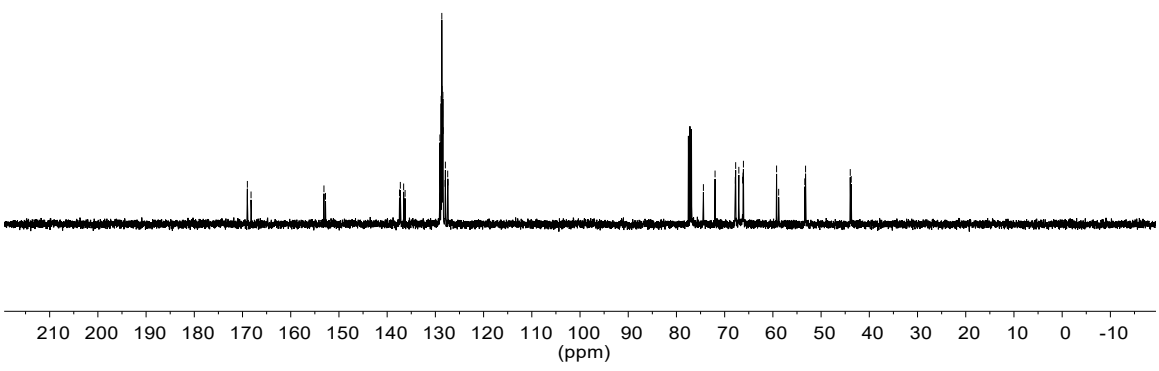
3l, ^1H NMR, 400 MHz, CDCl_3



168.99
168.23
153.11
152.79
137.44
137.27
136.58
136.28
129.06
128.81
128.67
128.61
128.50
128.44
128.38
127.98
127.92
127.45
127.38
74.41
71.99
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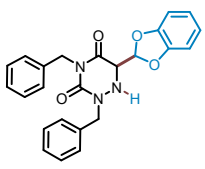


3l, ¹³C NMR, 101 MHz, CDCl₃

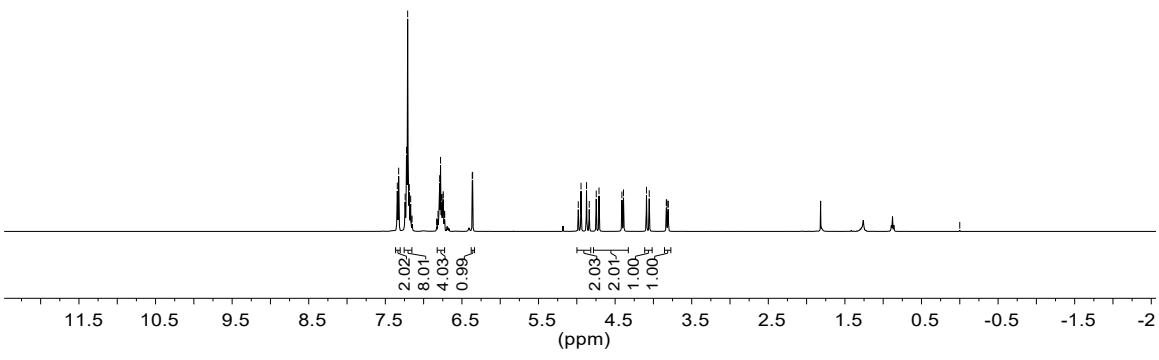


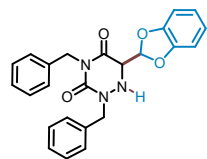
7.34
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3.83
3.83
3.81
3.81

-0.00



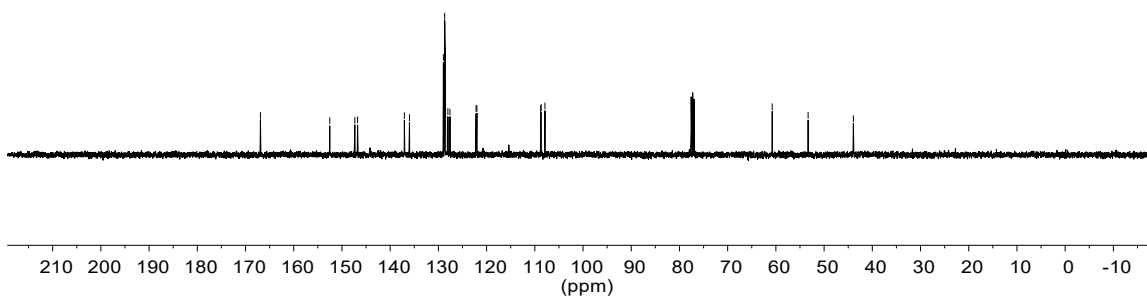
3m, ¹H NMR, 400 MHz, CDCl₃



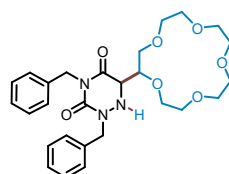


3m, ^{13}C NMR, 101 MHz, CDCl_3

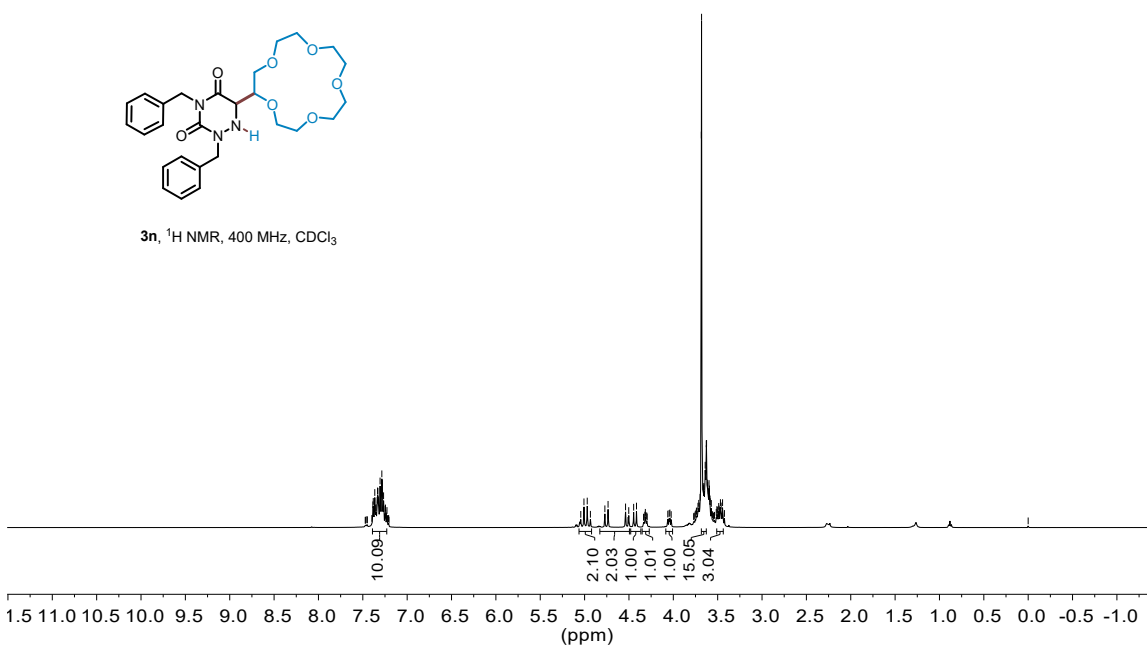
- 166.9063
- 152.5282
- 147.3222
- 146.7590
- 137.0497
- 135.9923
- 128.9603
- 128.6987
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- 128.5488
- 128.0278
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- 122.0115
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- 108.6889
- 107.8971
- 60.7543
- 53.3139
- 43.9270

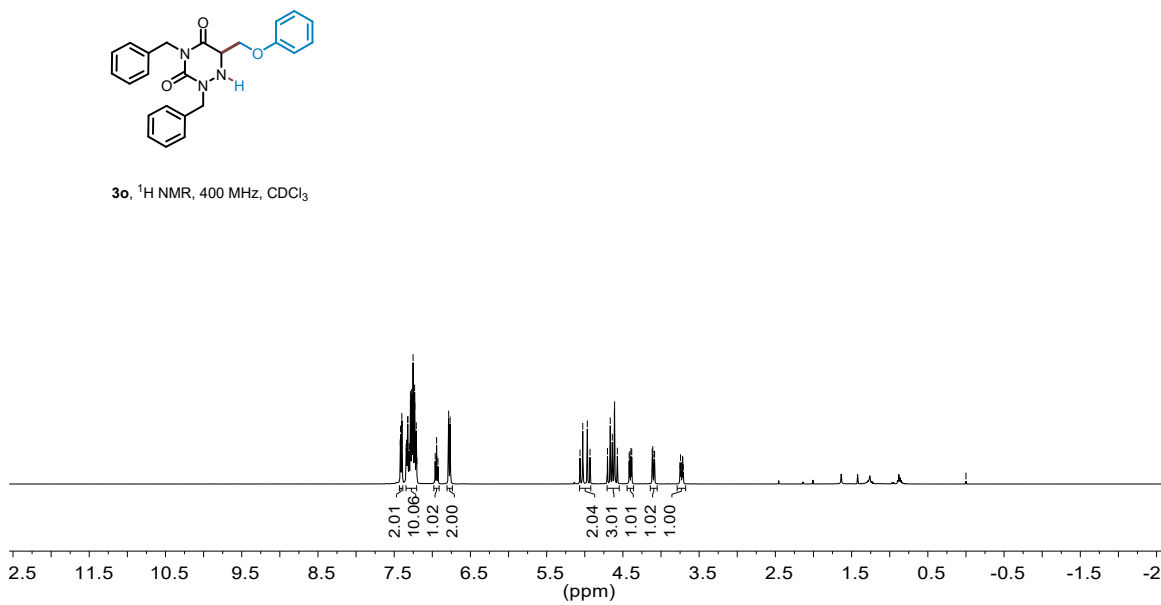
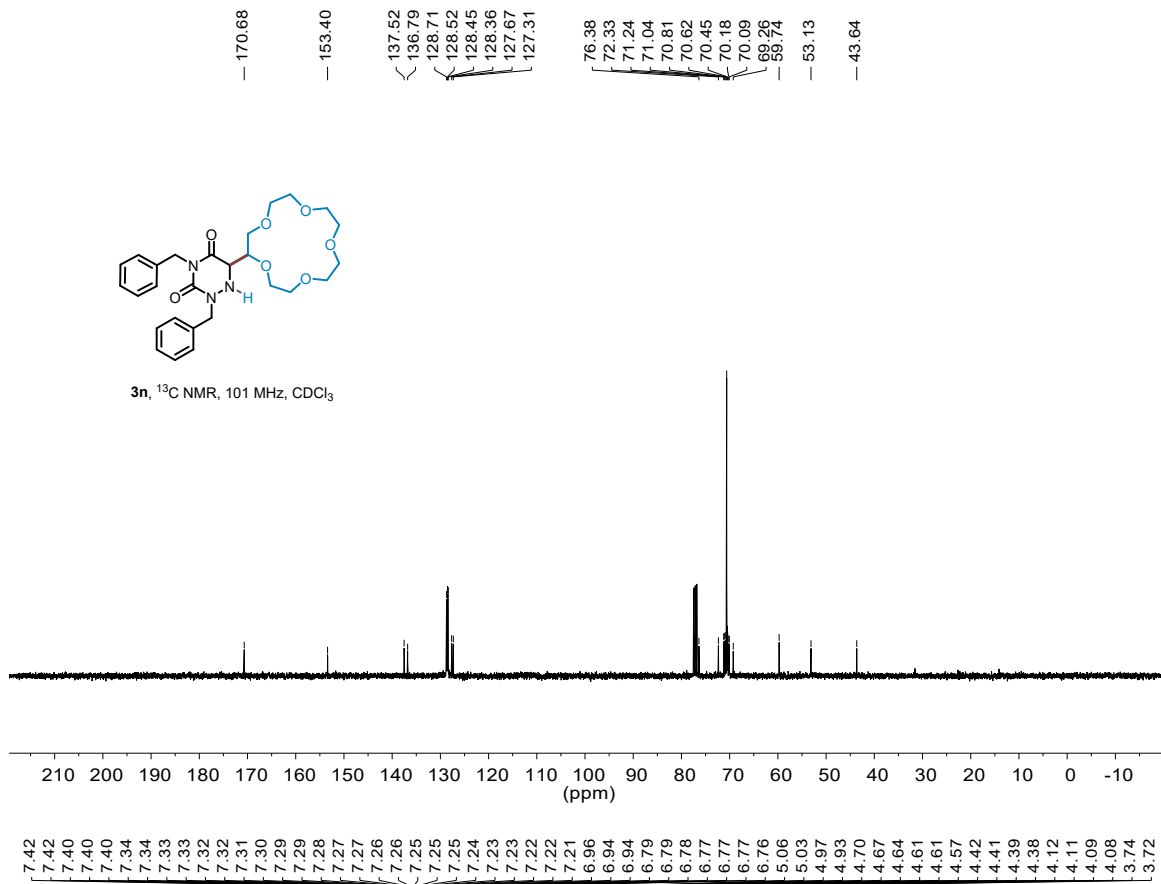


- 7.39
- 7.38
- 7.37
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- 7.24
- 7.23
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- 3.46
- 3.44

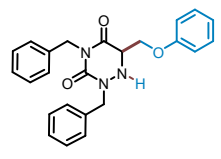


3n, ^1H NMR, 400 MHz, CDCl_3

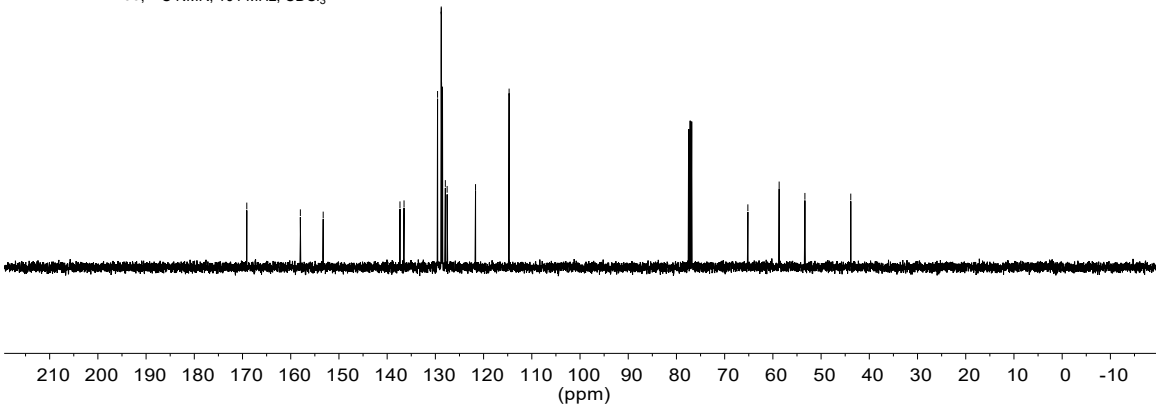




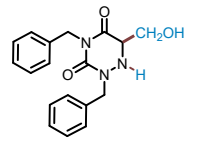
— 169.11
 — 158.00
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 127.93
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 121.67
 114.71
 65.19
 58.70
 53.36
 43.85



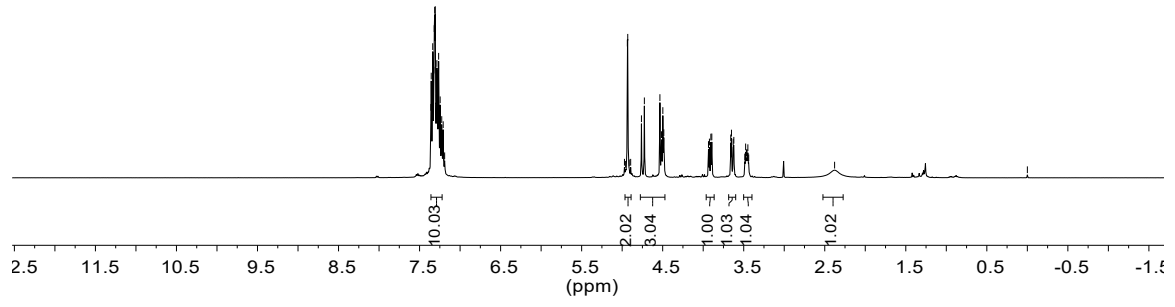
3o, ¹³C NMR, 101 MHz, CDCl₃

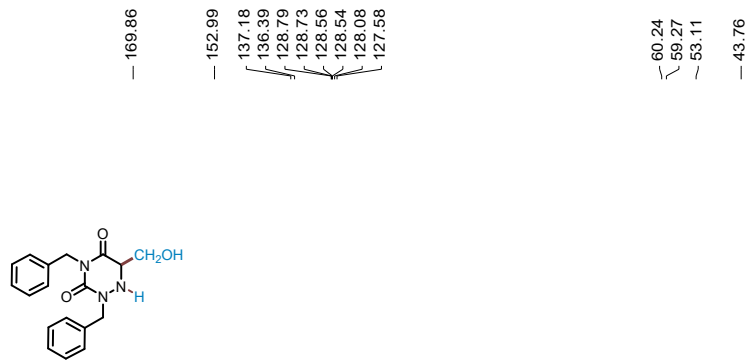


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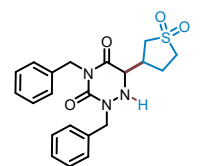
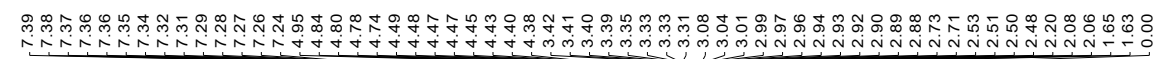
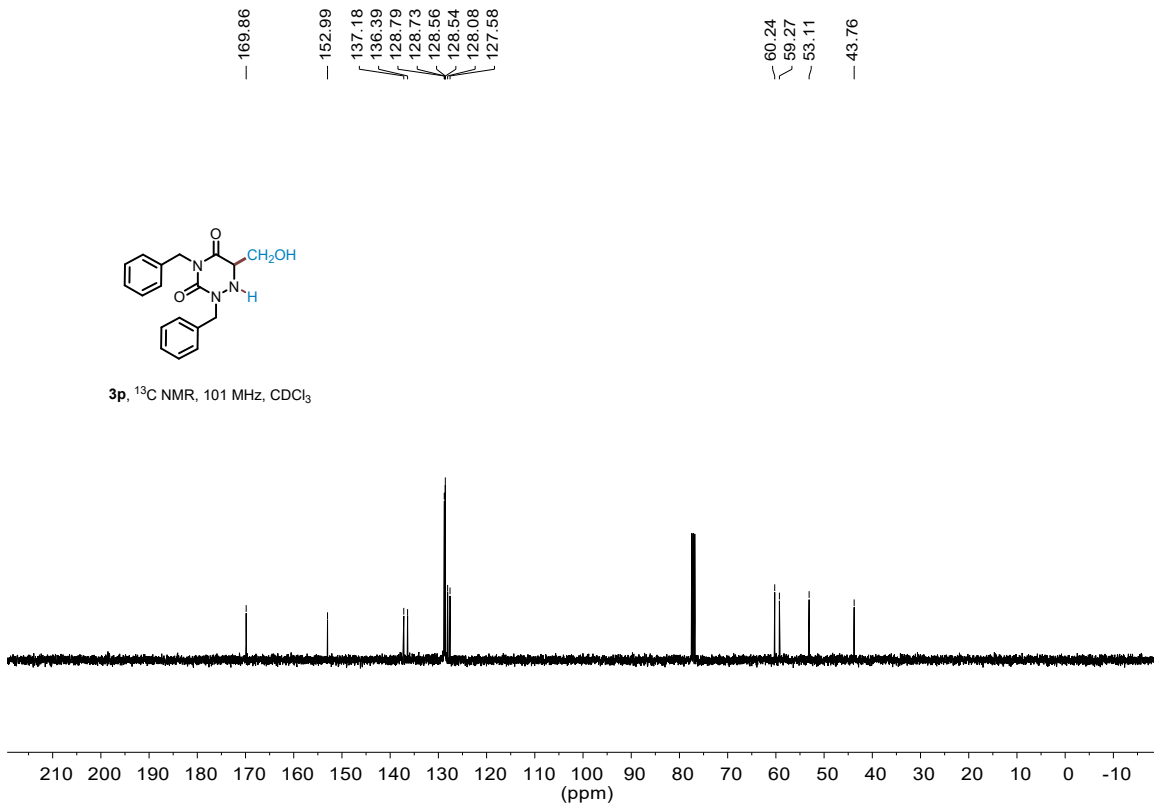


3p, ¹H NMR, 400 MHz, CDCl₃

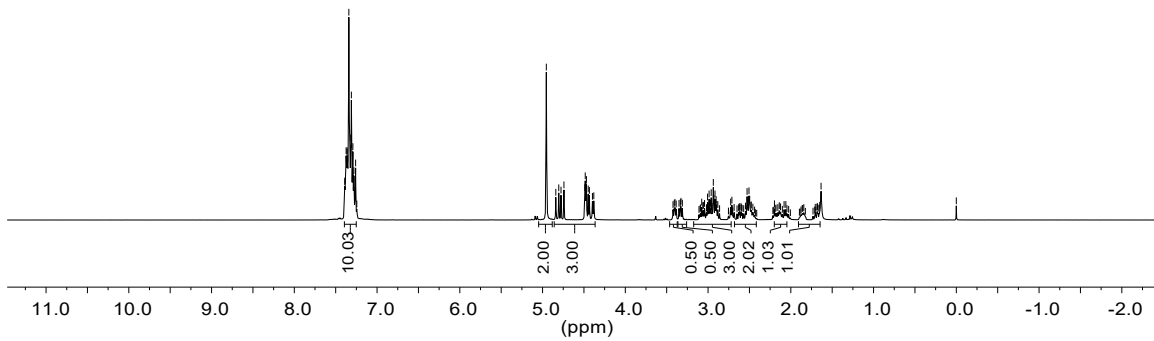


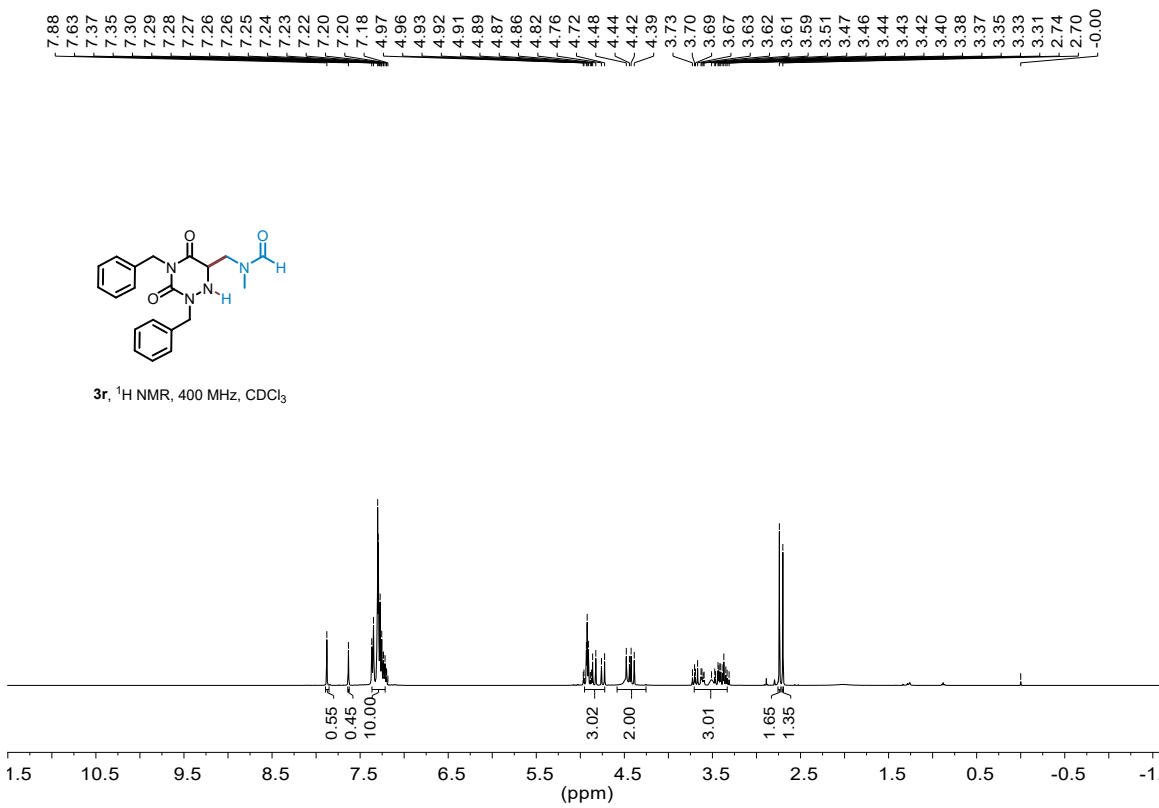
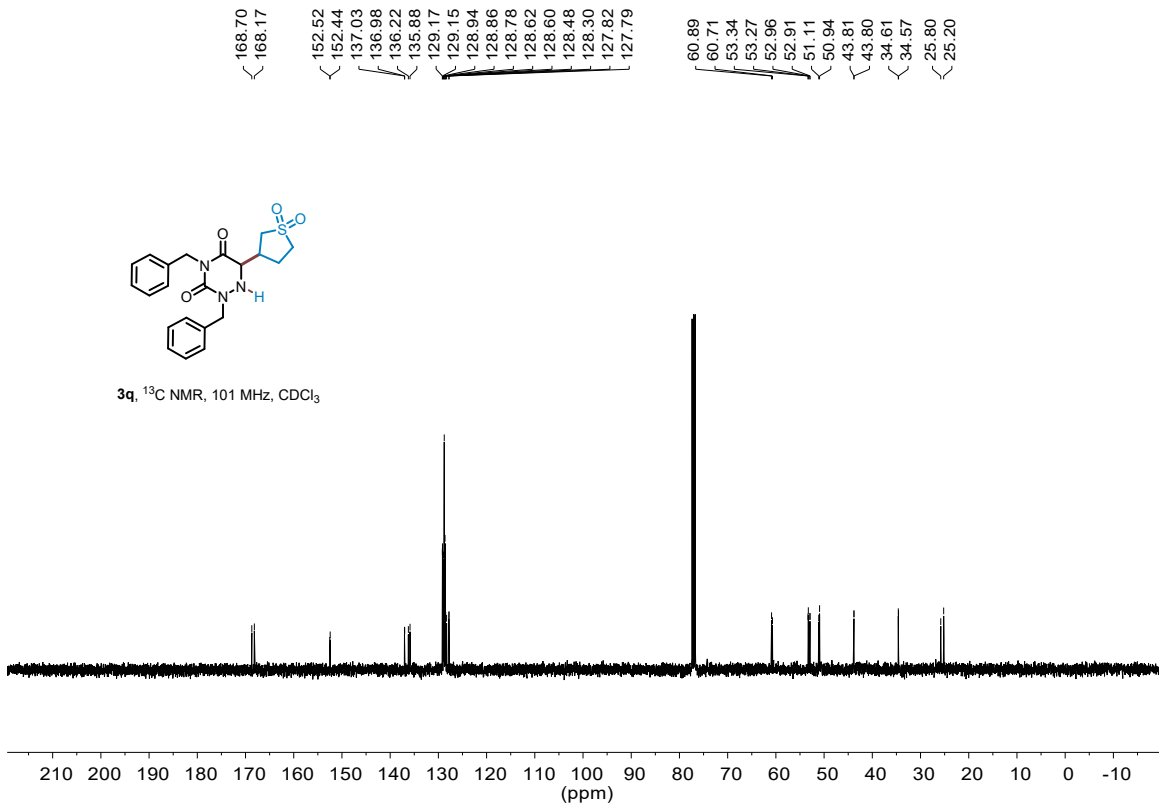


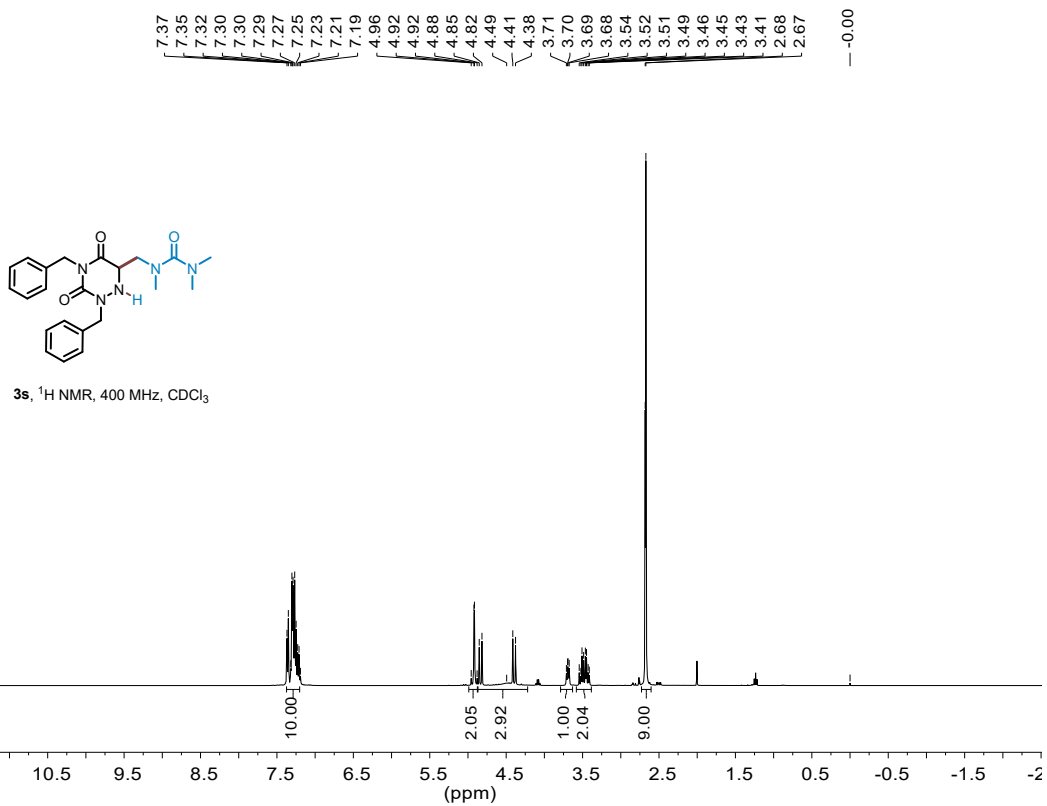
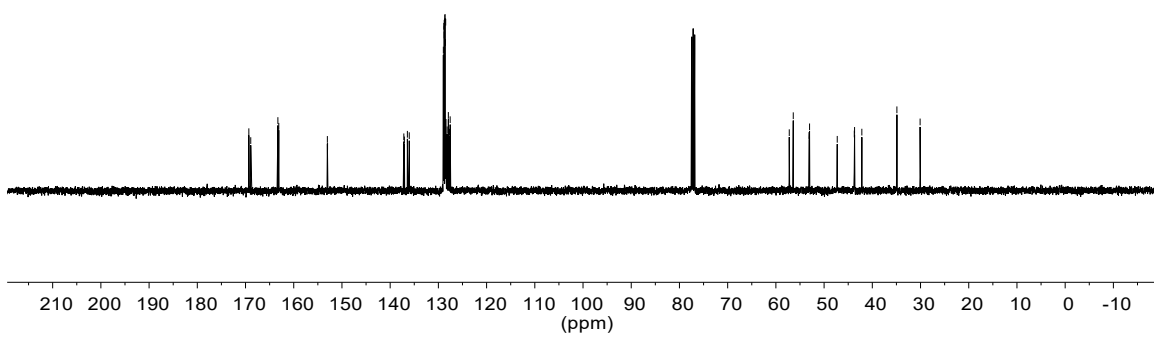
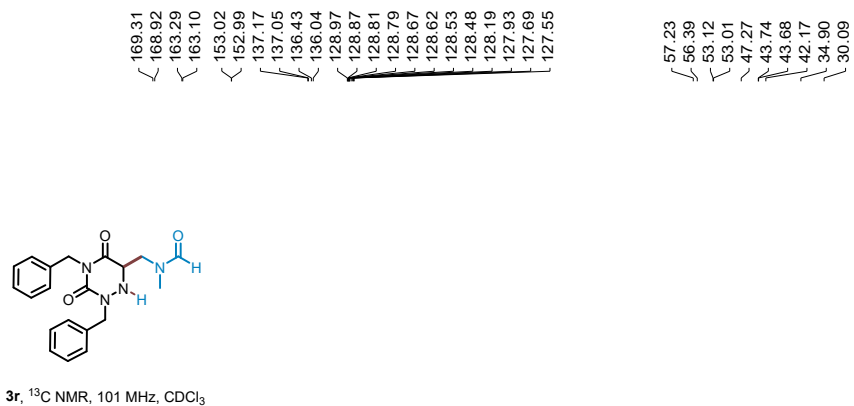
3p, ¹³C NMR, 101 MHz, CDCl₃

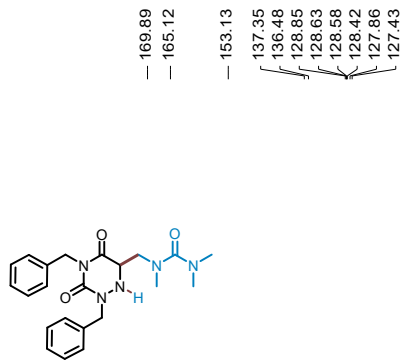


3q, ¹H NMR, 400 MHz, CDCl₃

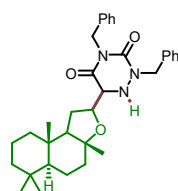
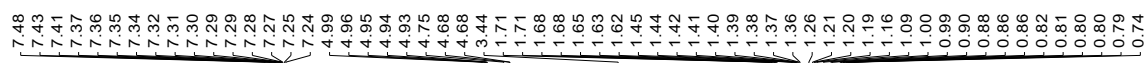
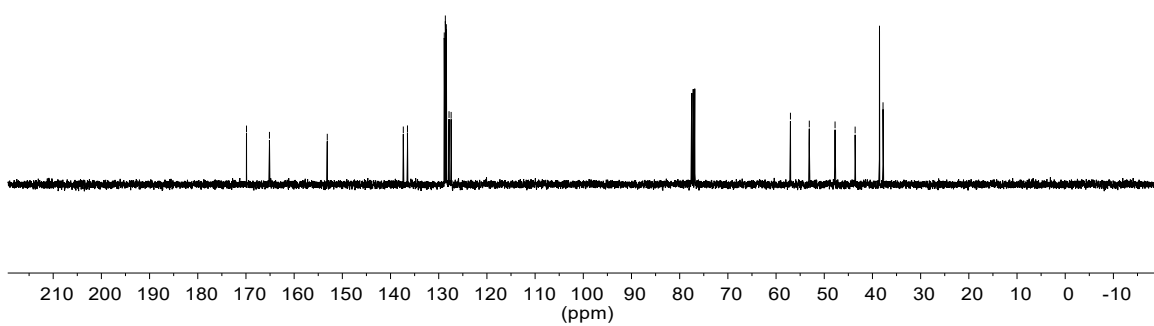




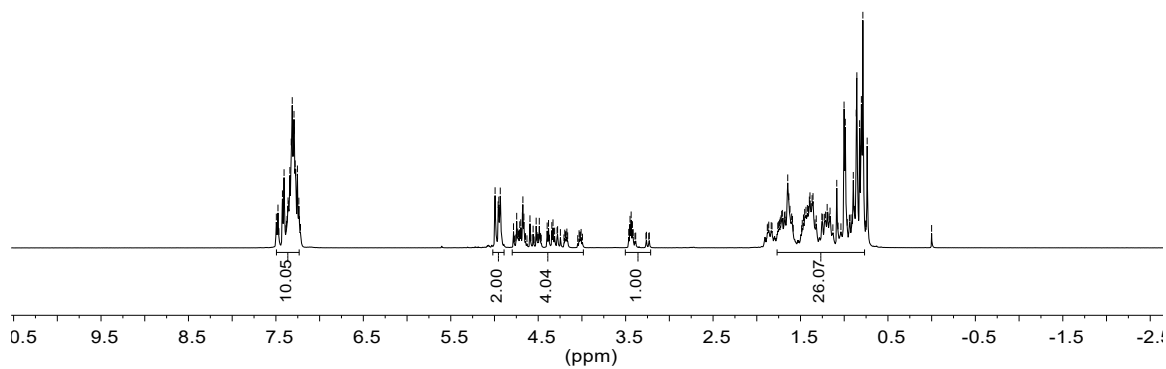


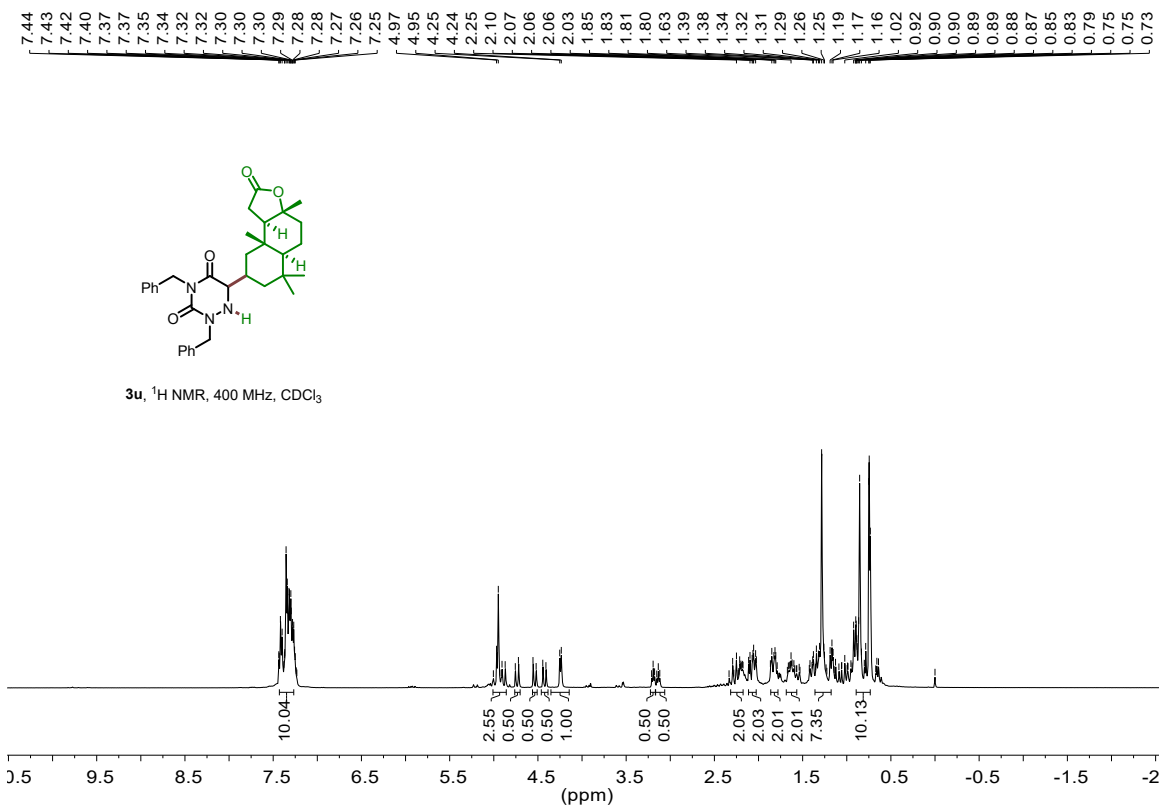
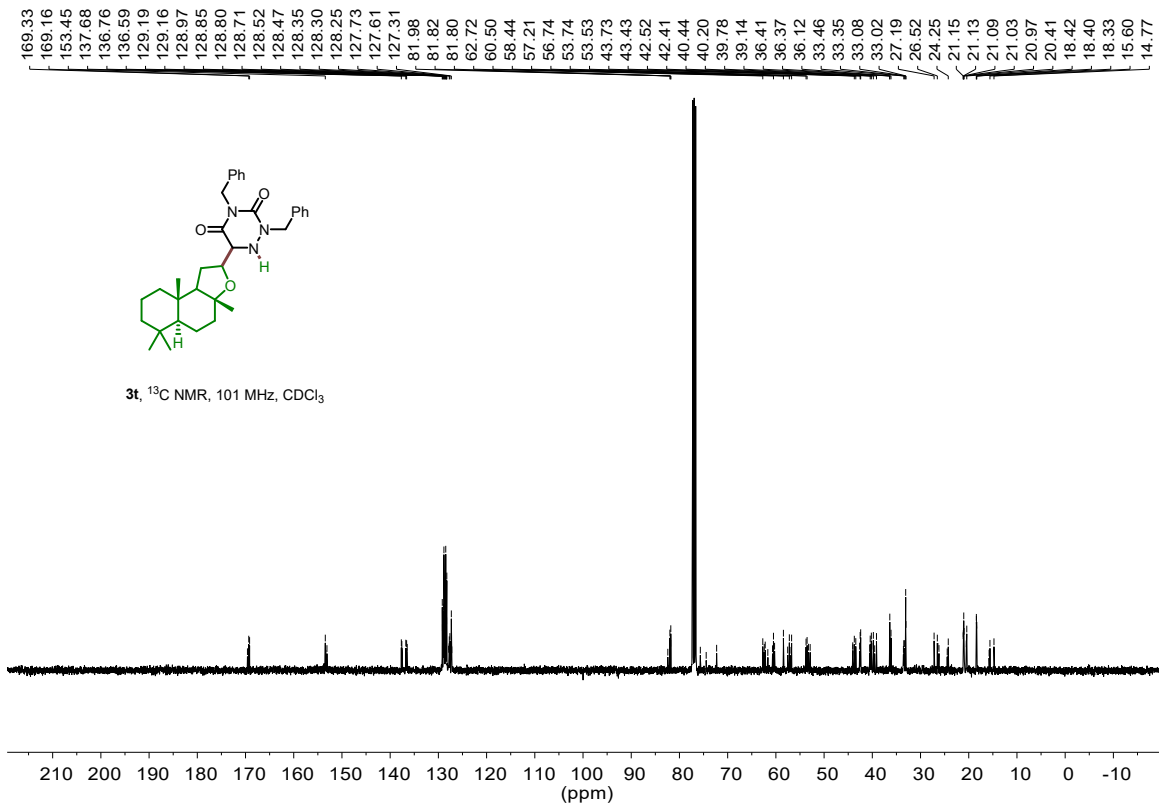


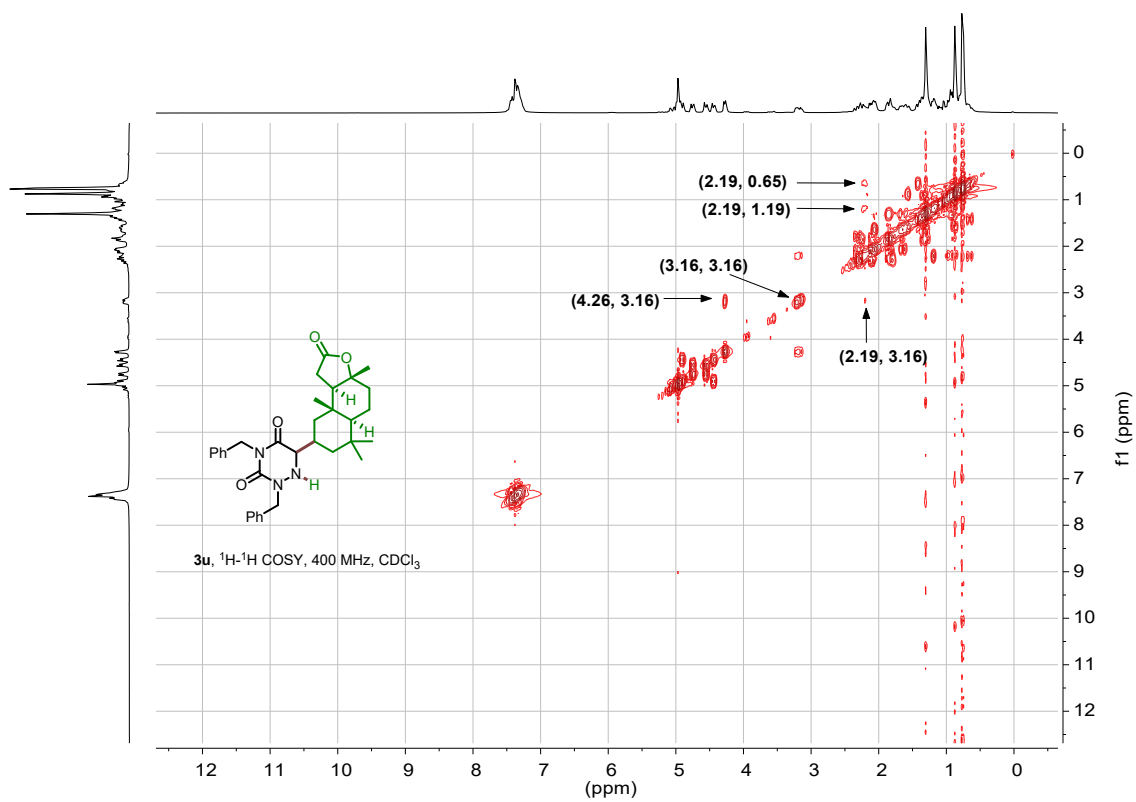
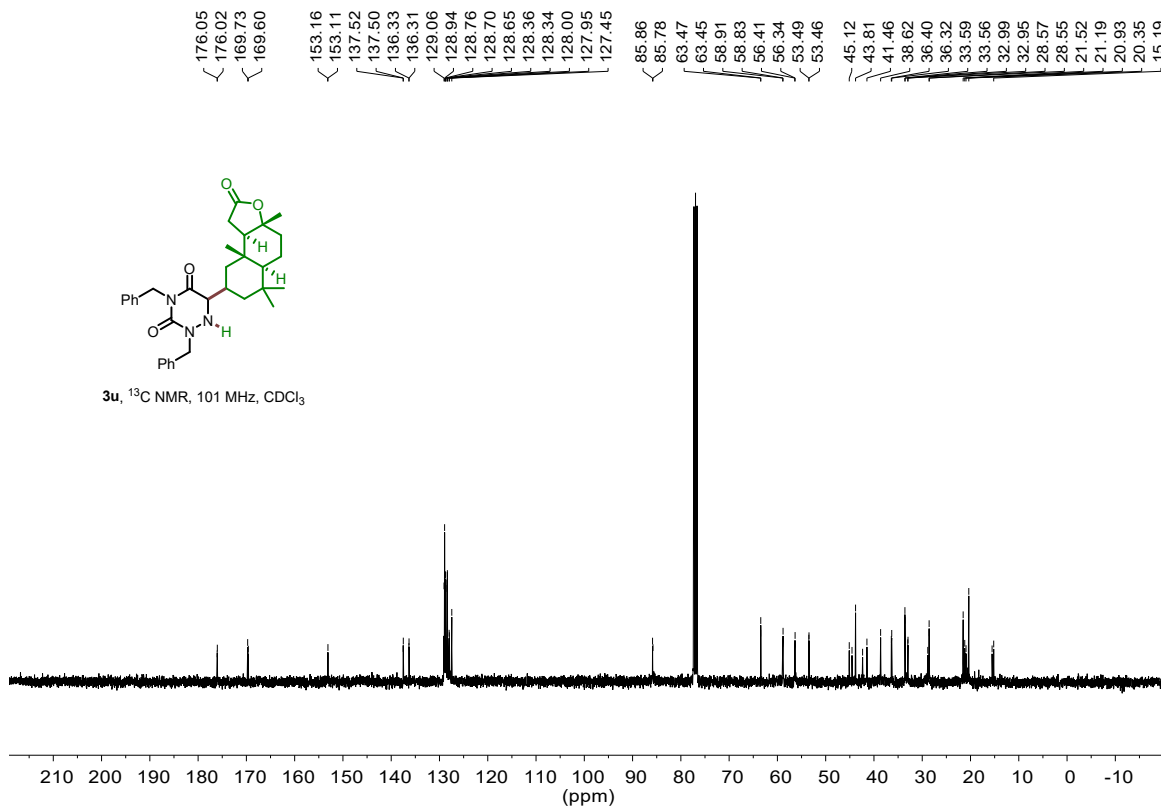
3s, ^{13}C NMR, 101 MHz, CDCl_3

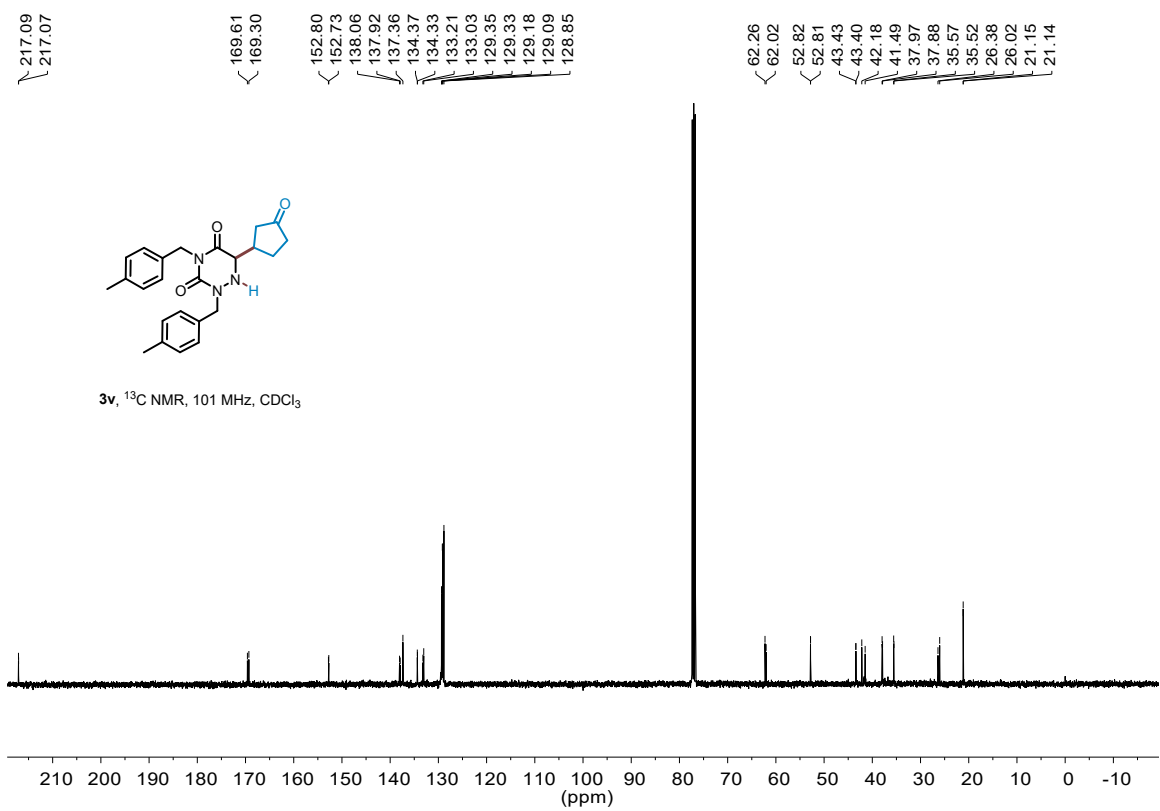
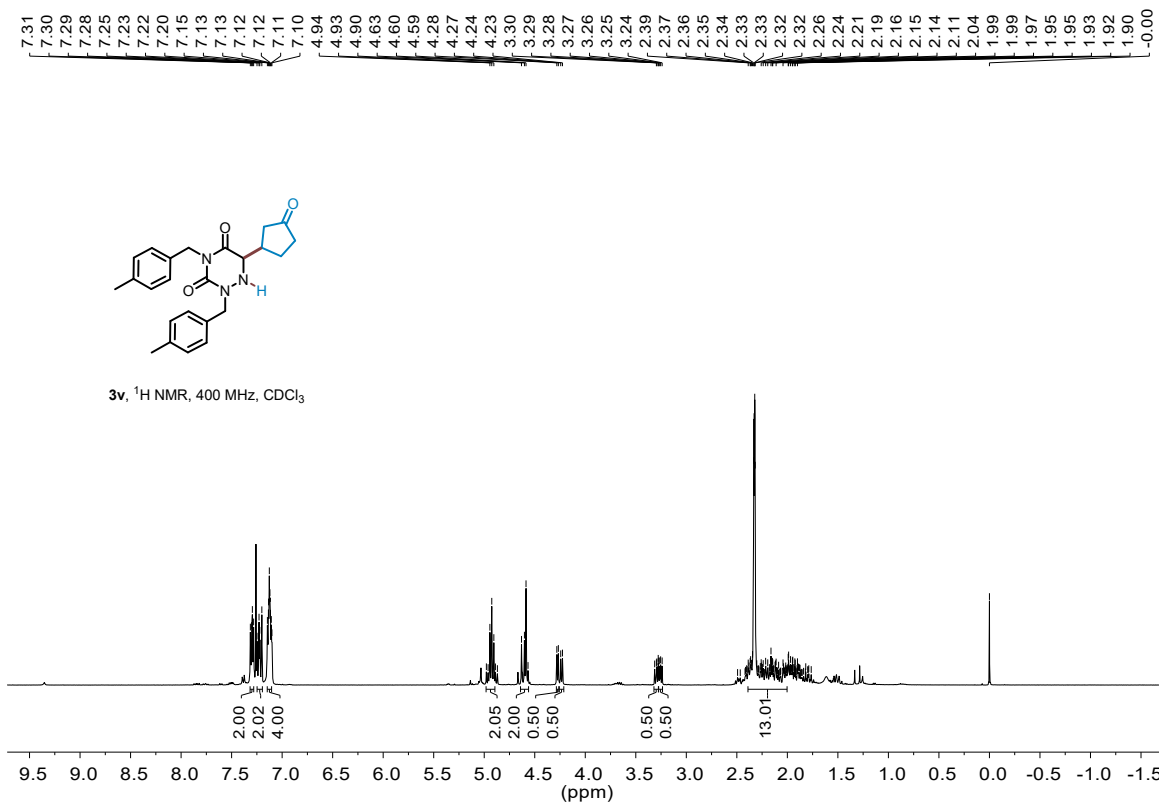


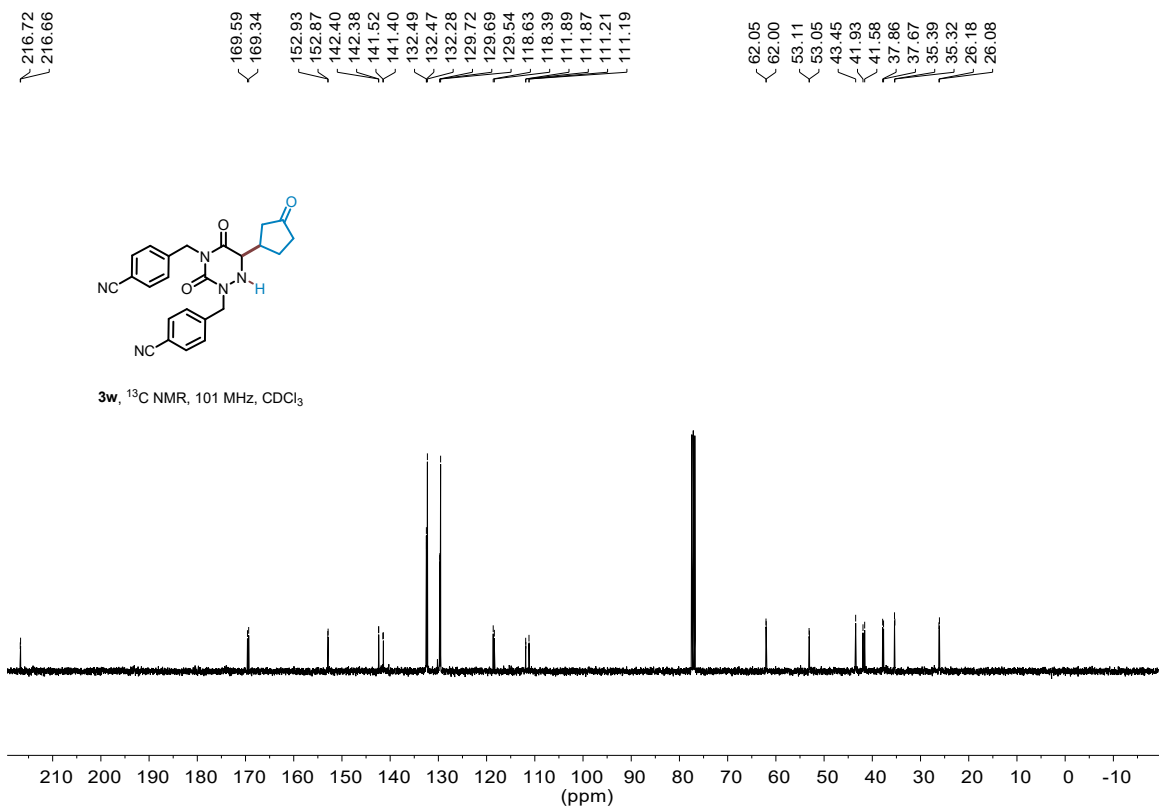
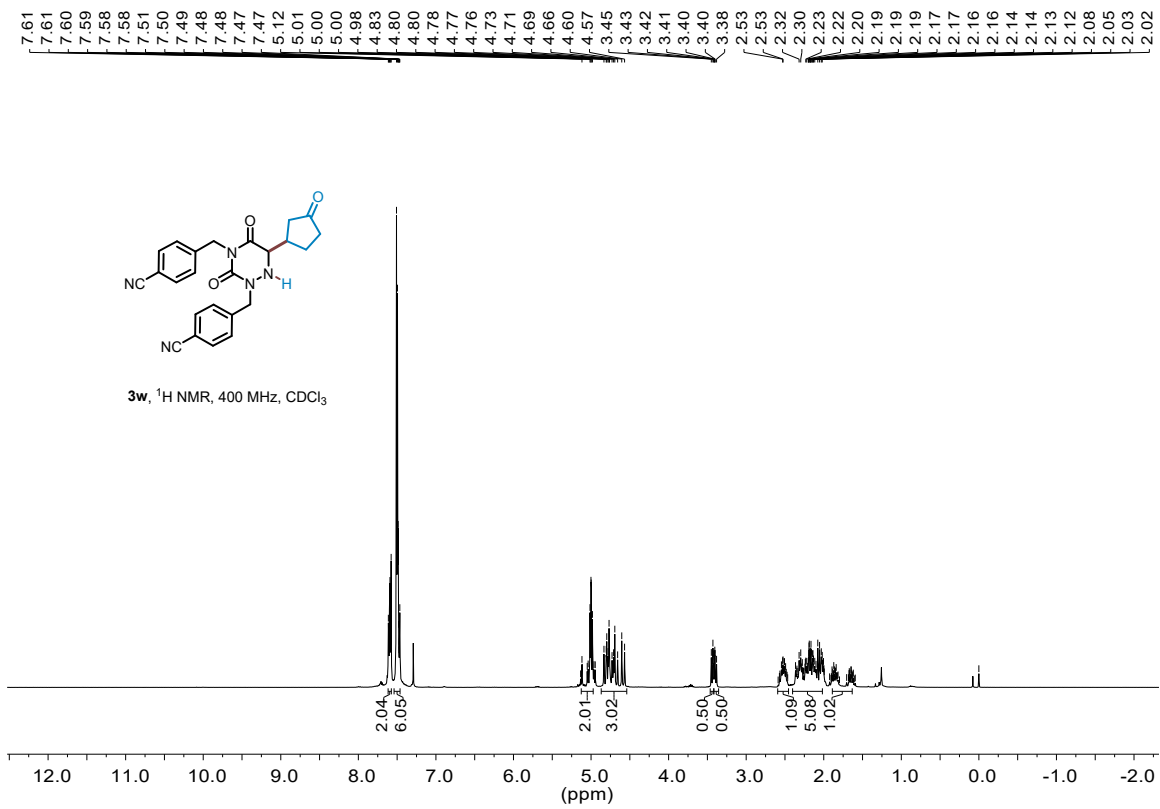
3t, ^1H NMR, 400 MHz, CDCl_3

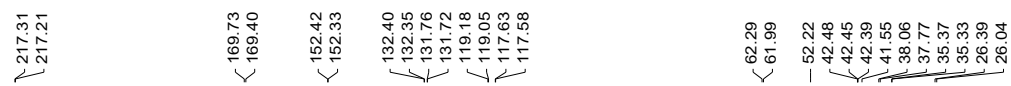
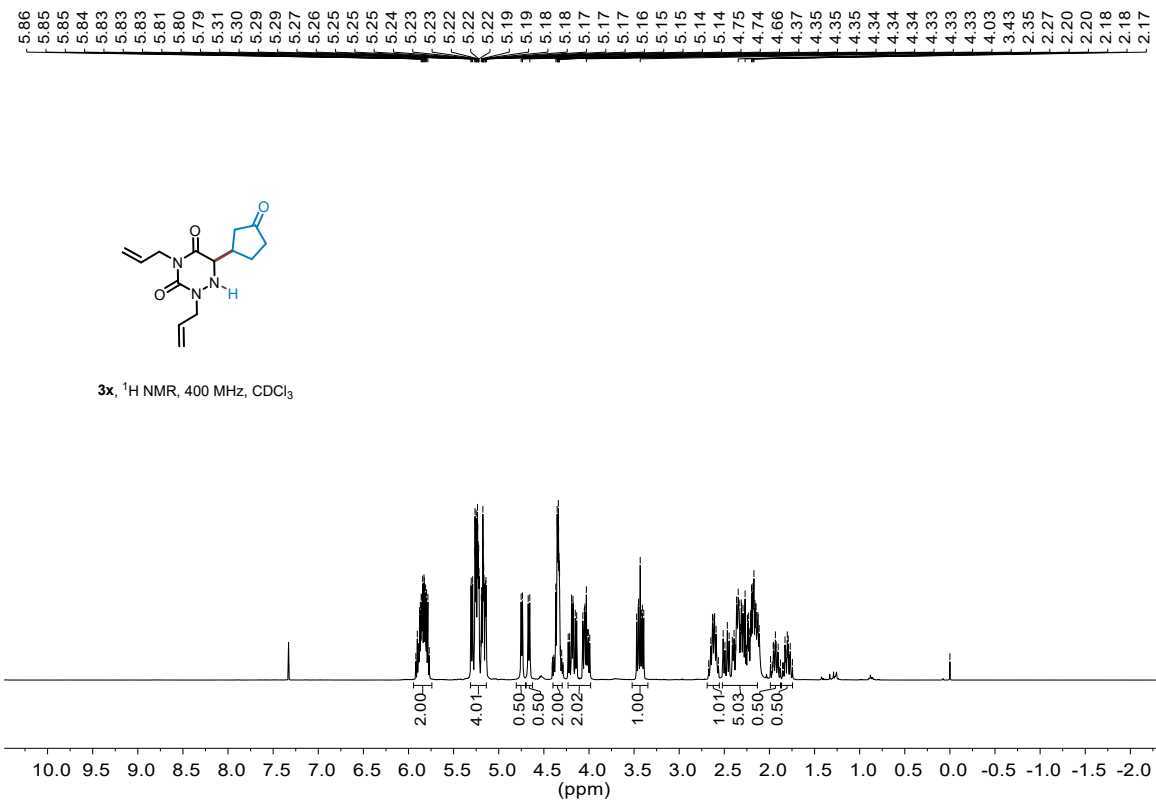


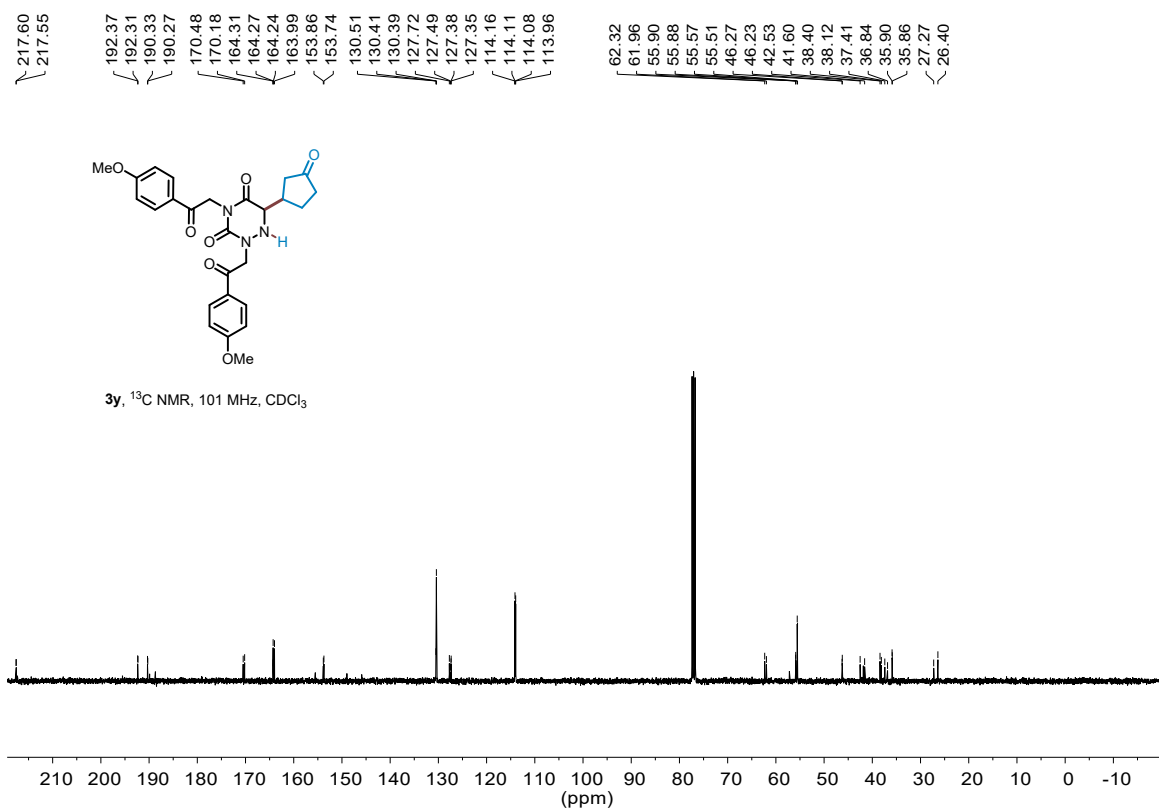
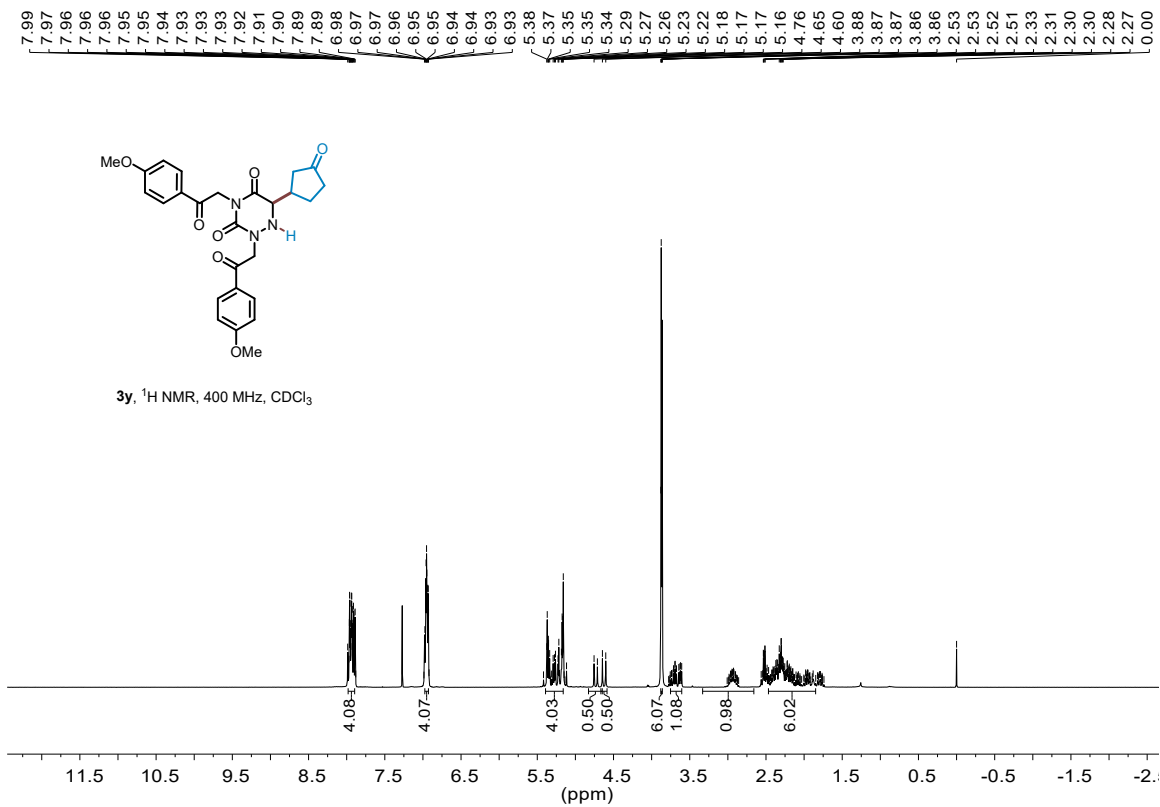


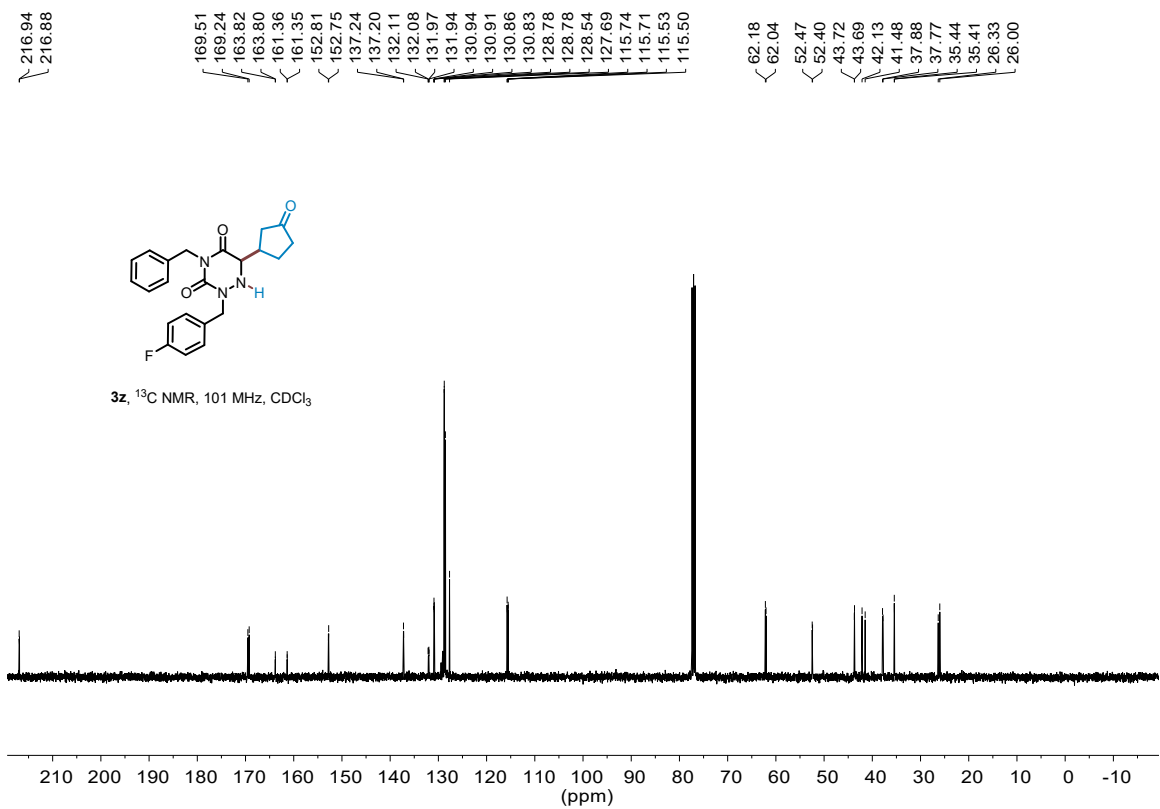
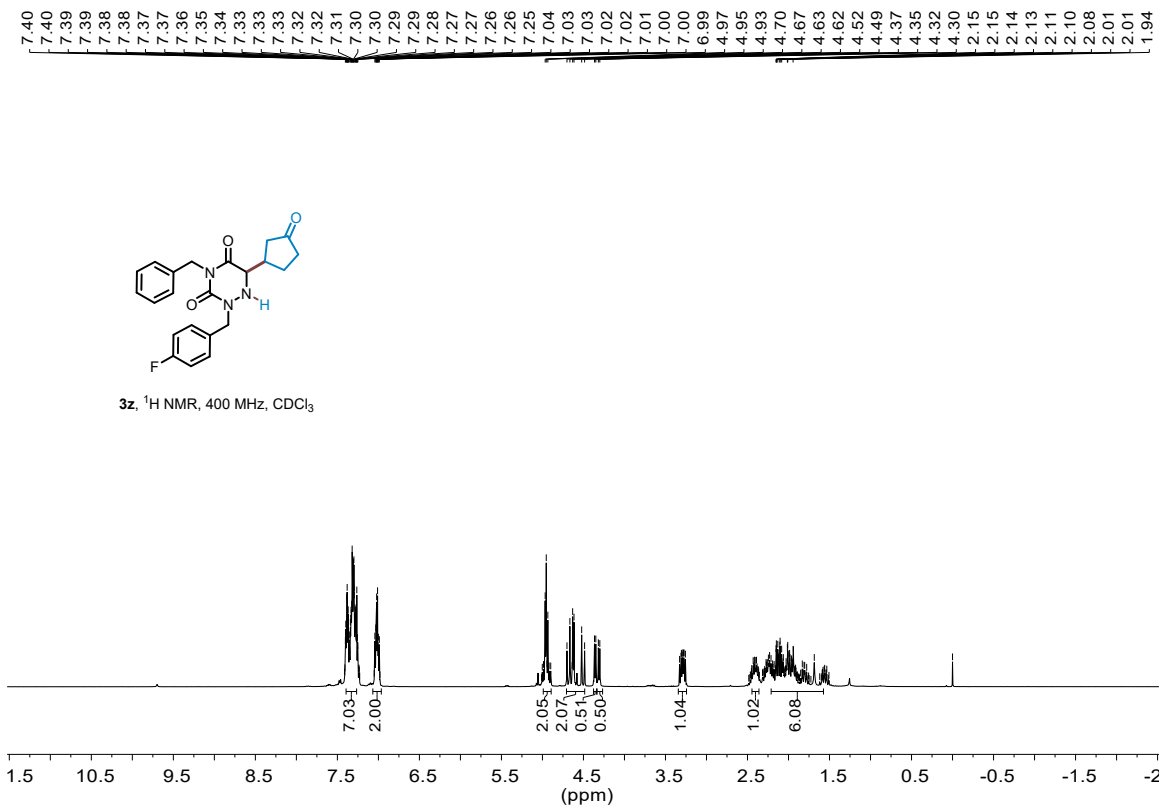


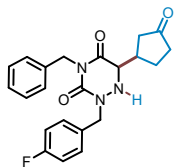




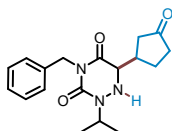
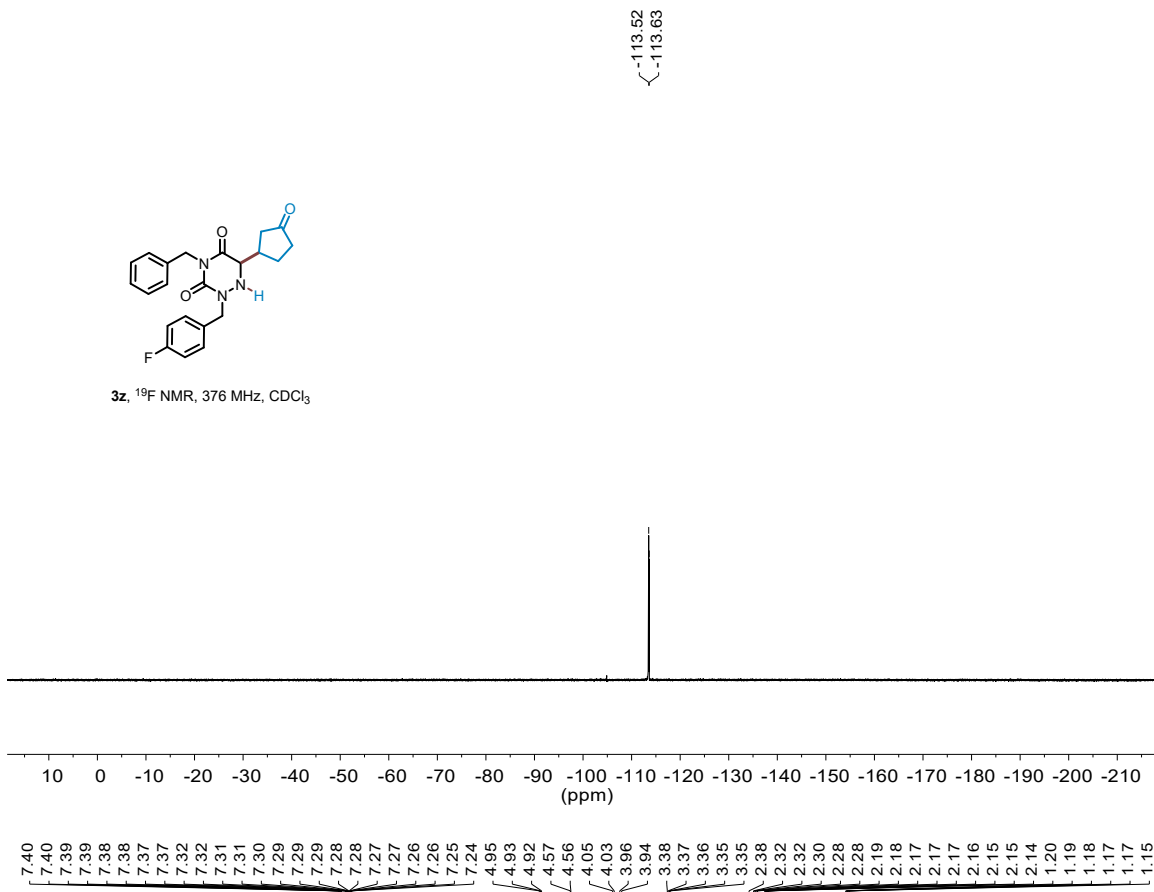




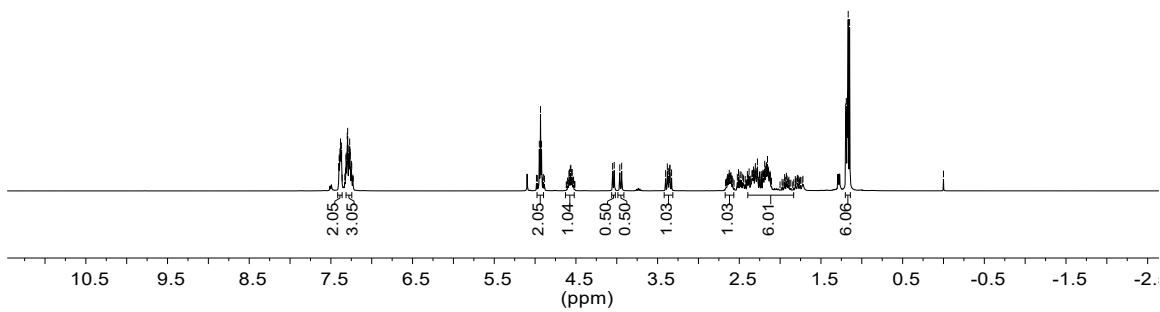


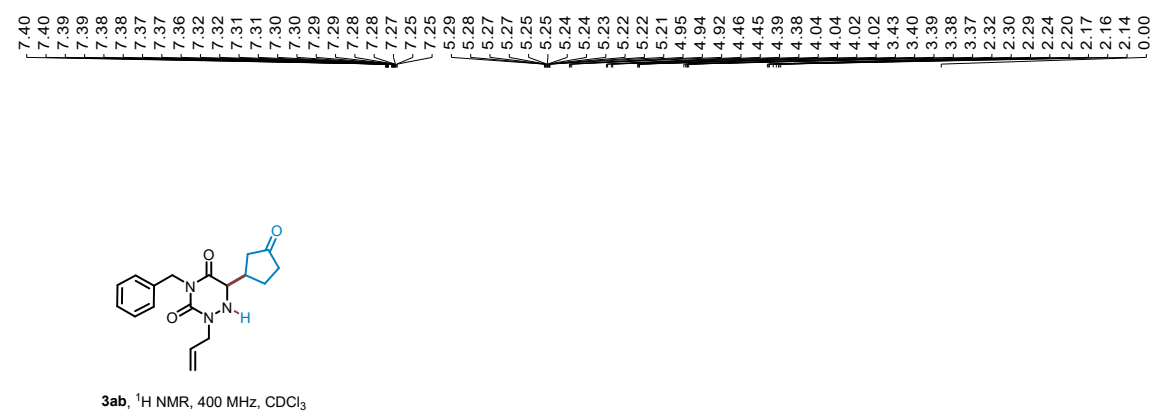
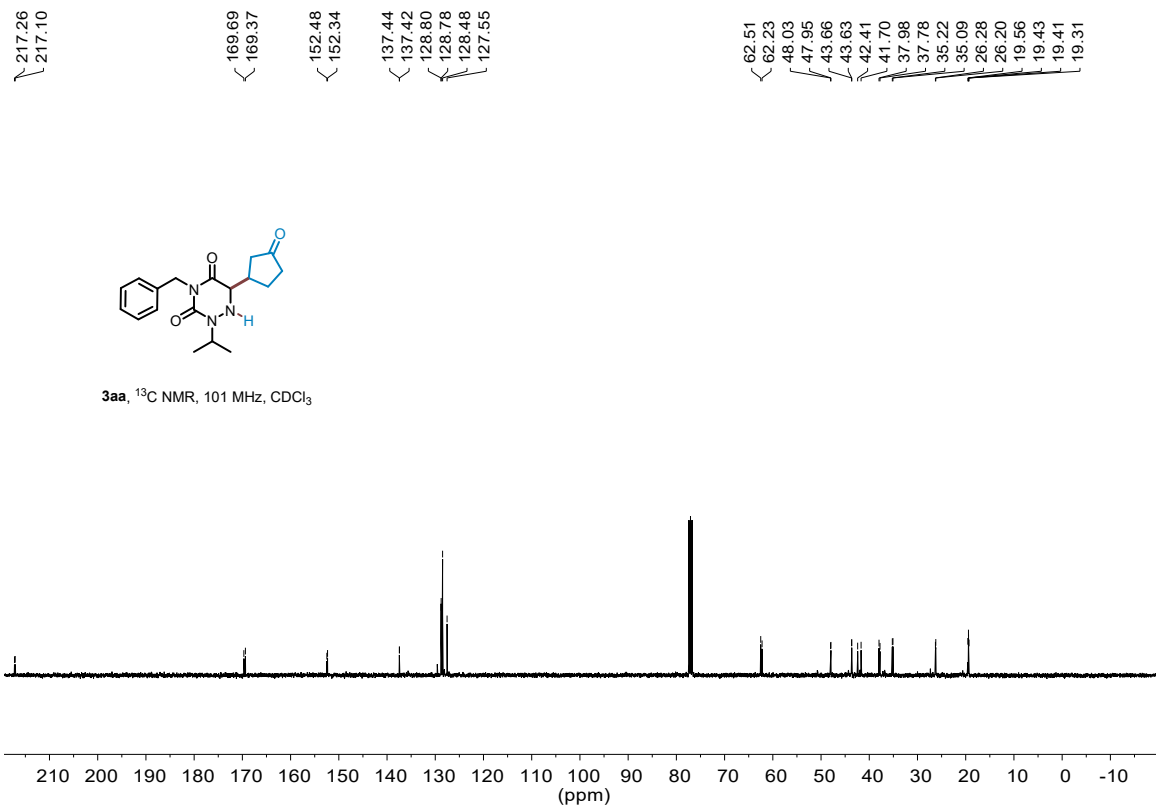


3z, ^{19}F NMR, 376 MHz, CDCl_3



3aa, ^1H NMR, 400 MHz, CDCl_3

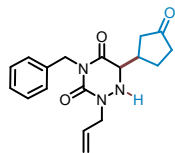




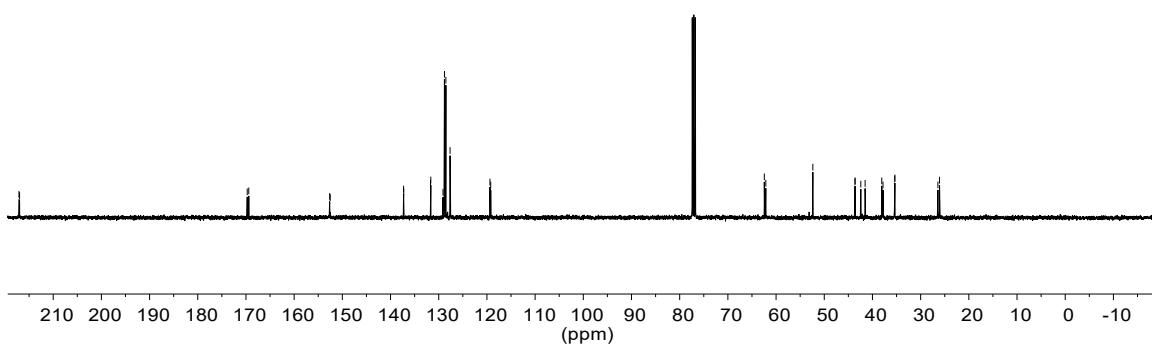
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216.98

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137.26
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128.52
127.65
119.37
119.21

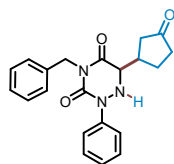
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26.42
26.08



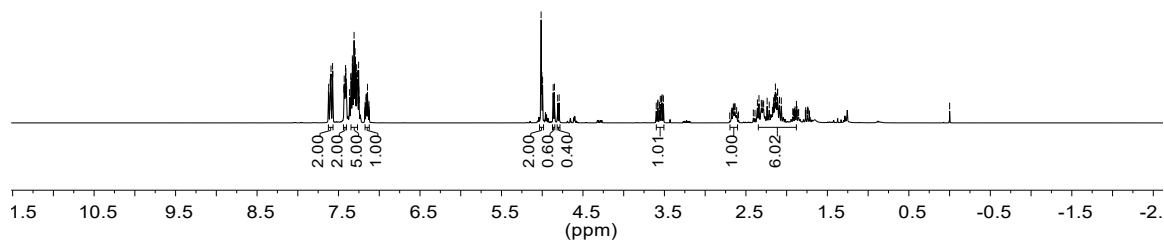
3ab, ^{13}C NMR, 101 MHz, CDCl_3

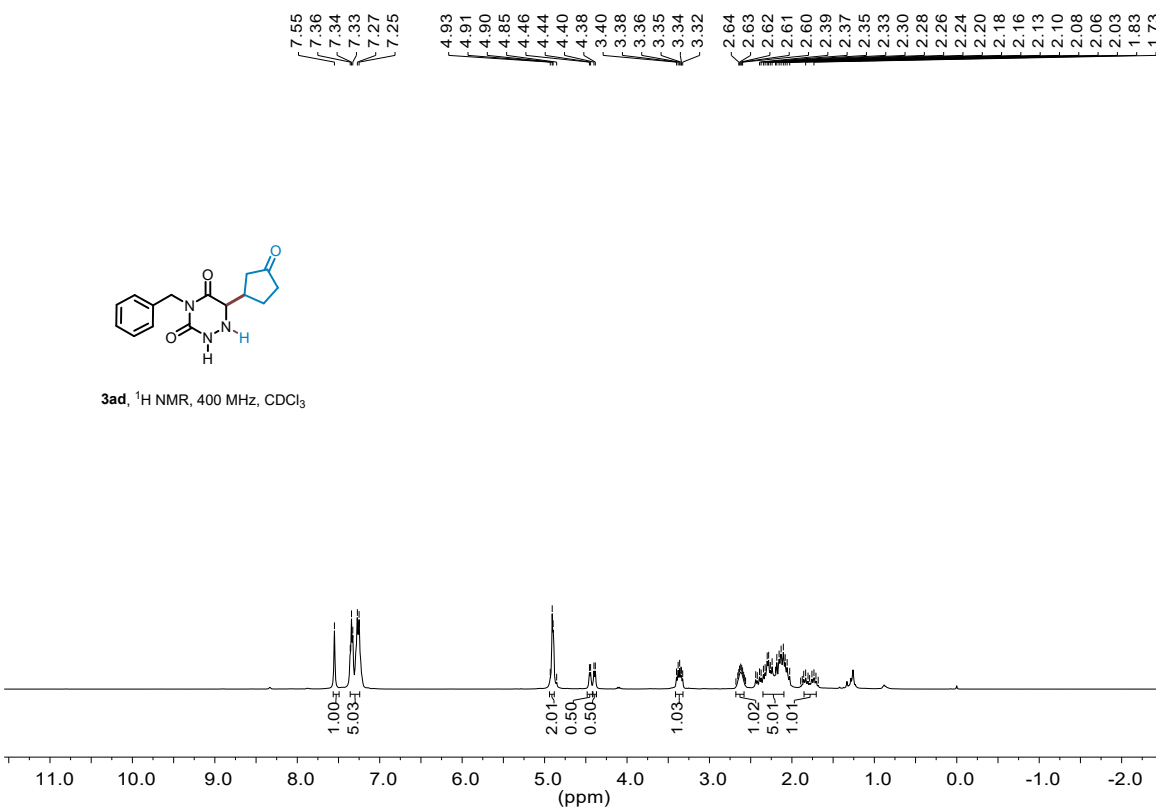
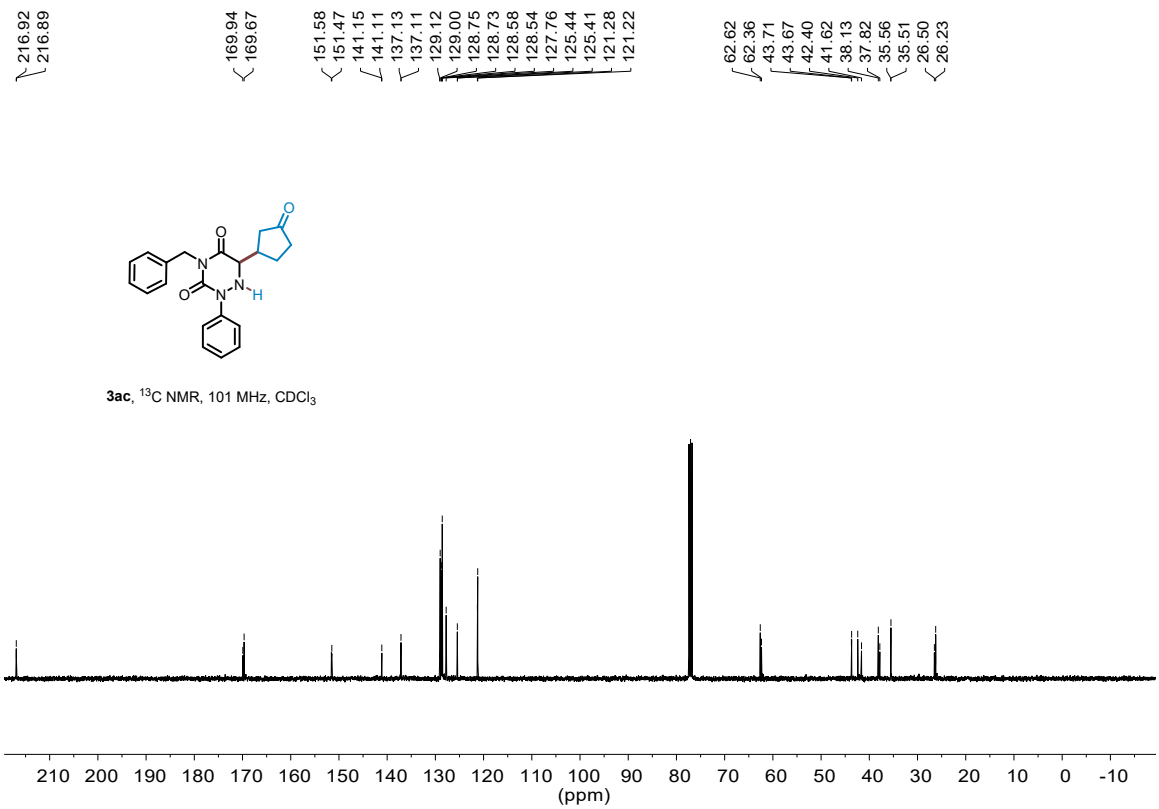


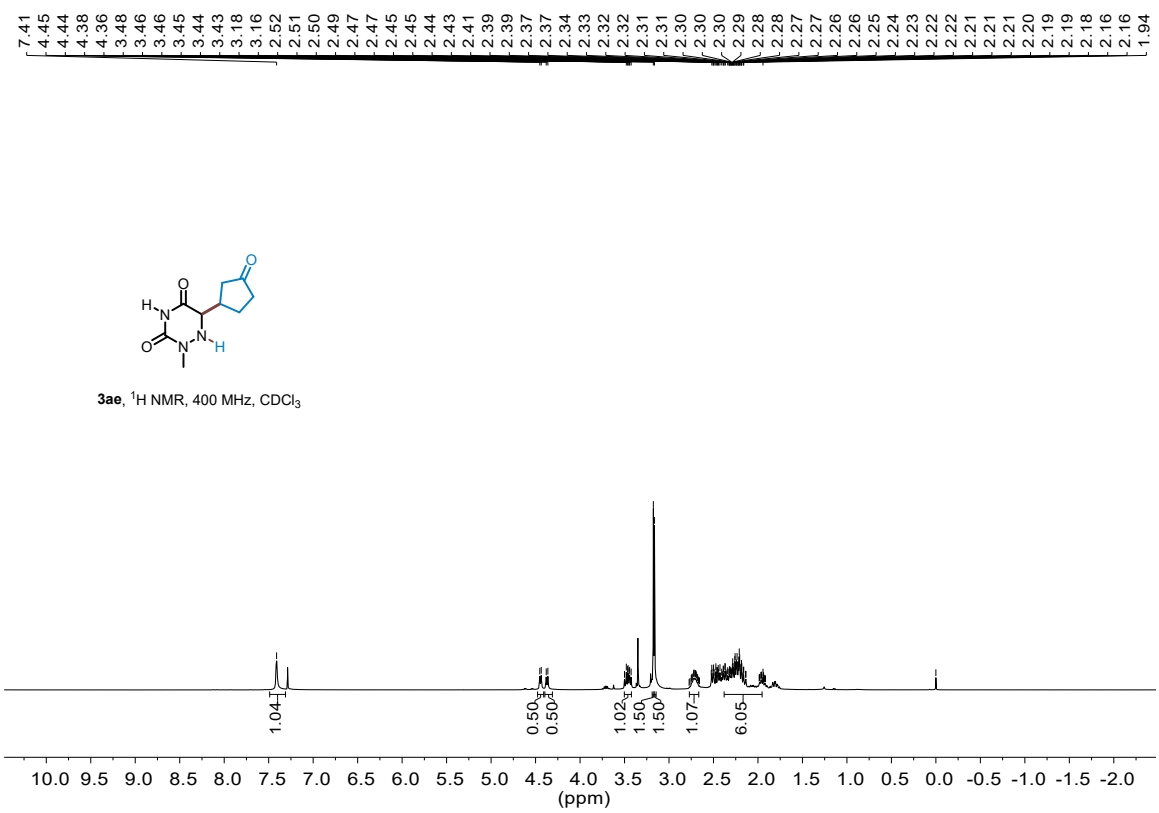
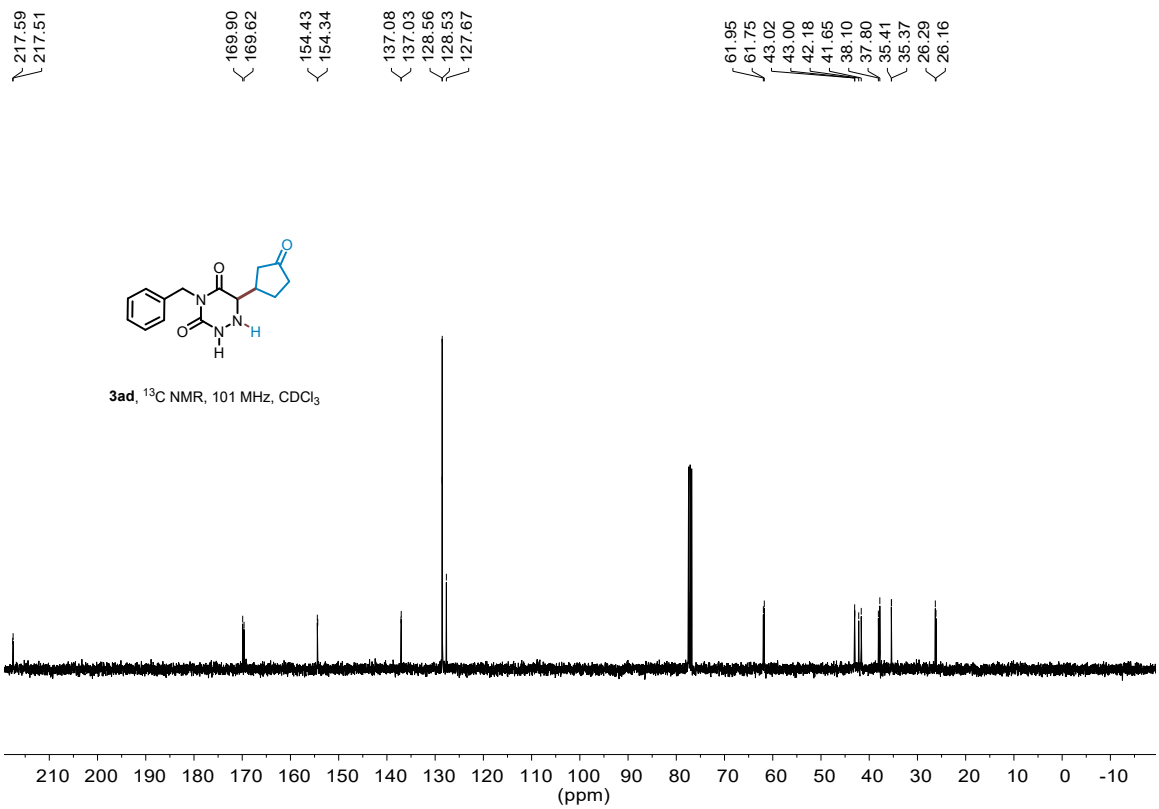
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7.14
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5.01
5.00
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4.85
4.81
4.81
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2.11
2.11

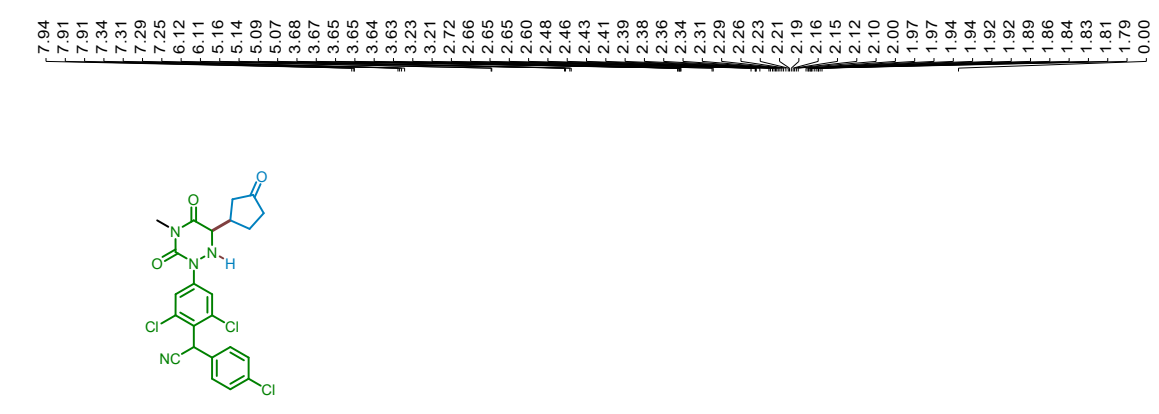
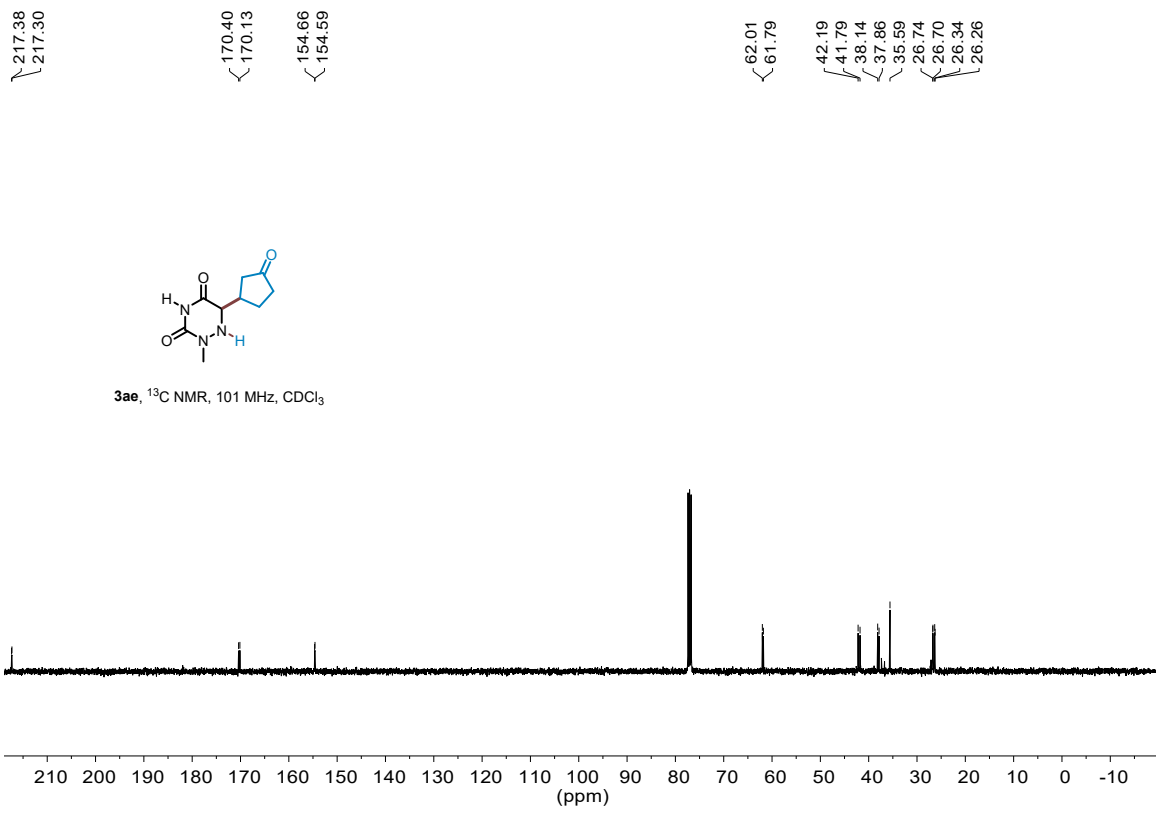


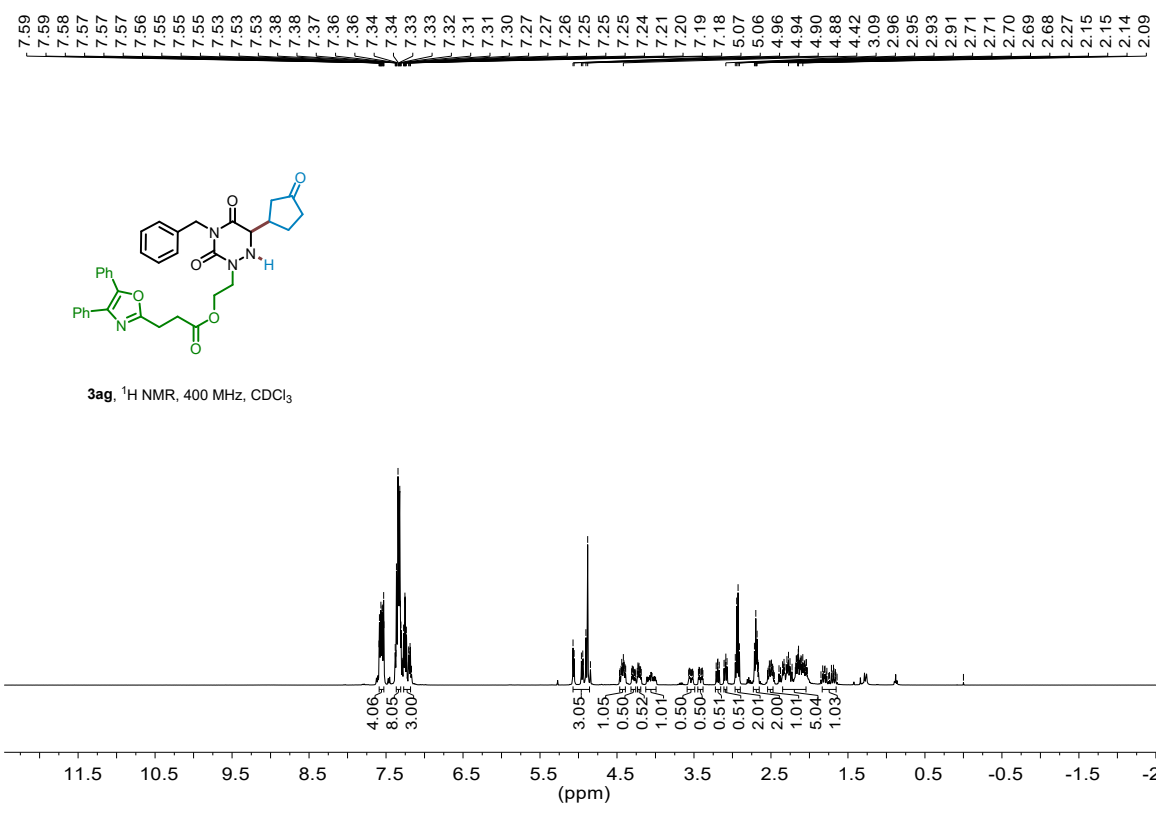
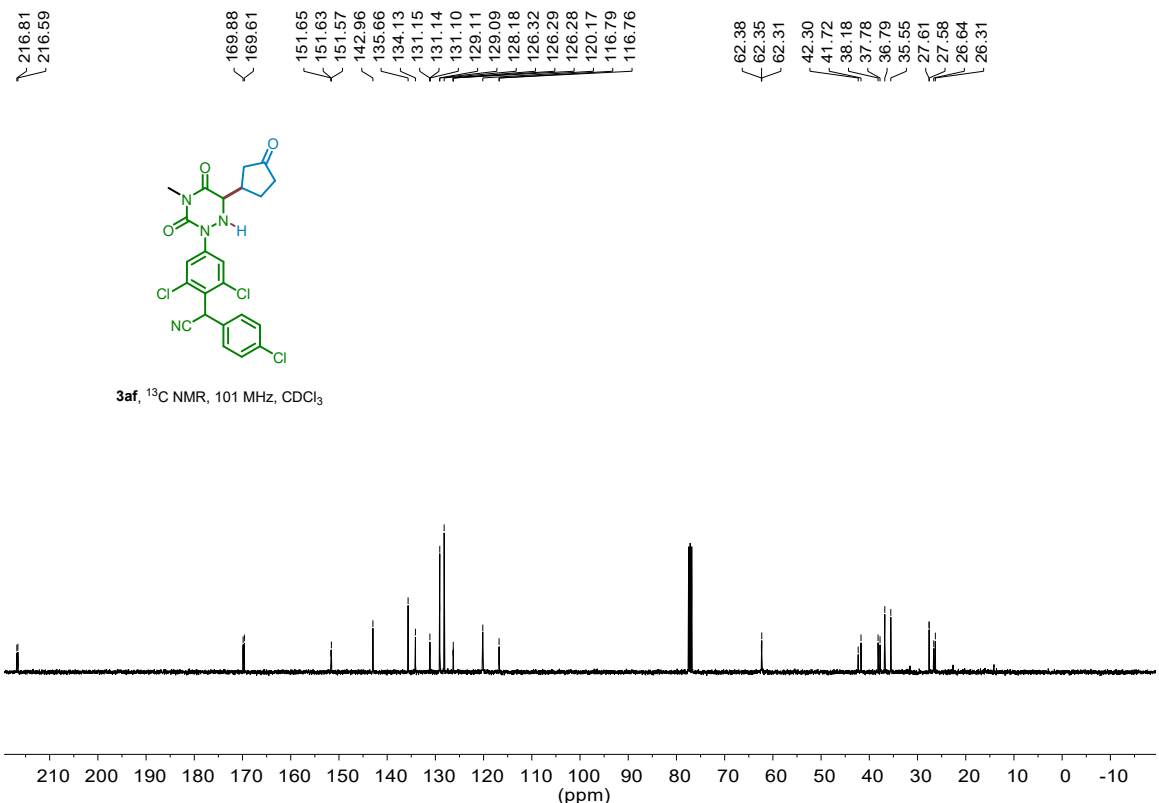
3ac, ^1H NMR, 400 MHz, CDCl_3



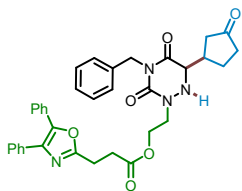




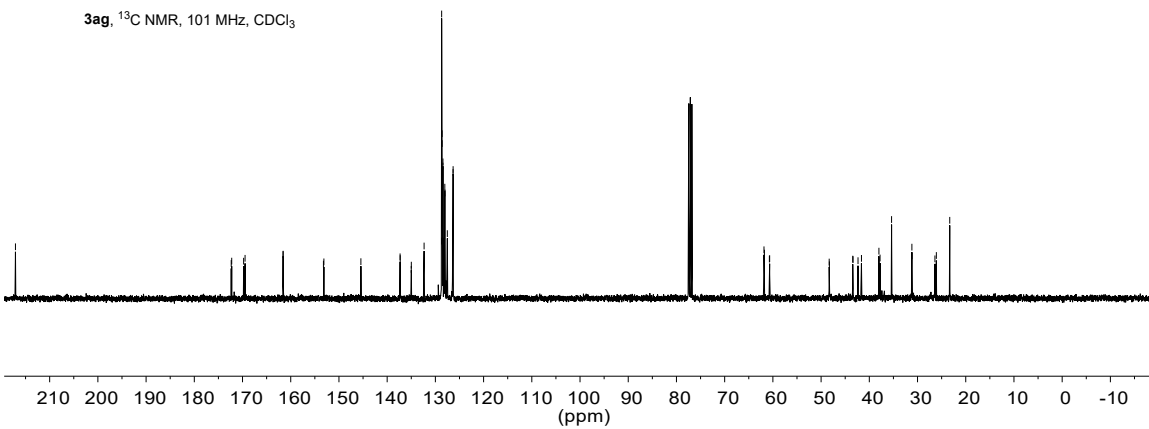




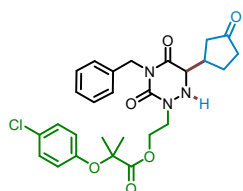
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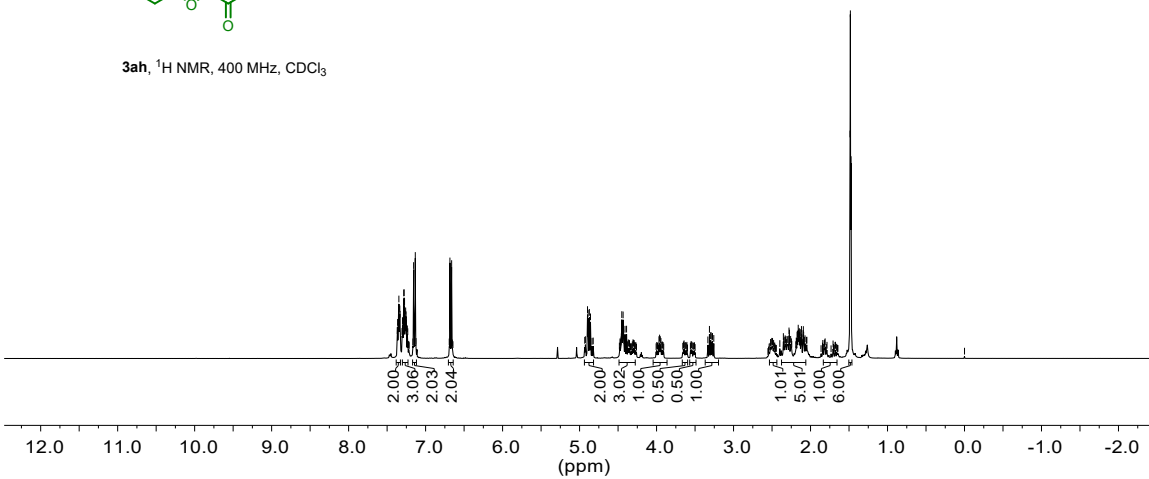
3ag, ^{13}C NMR, 101 MHz, CDCl_3

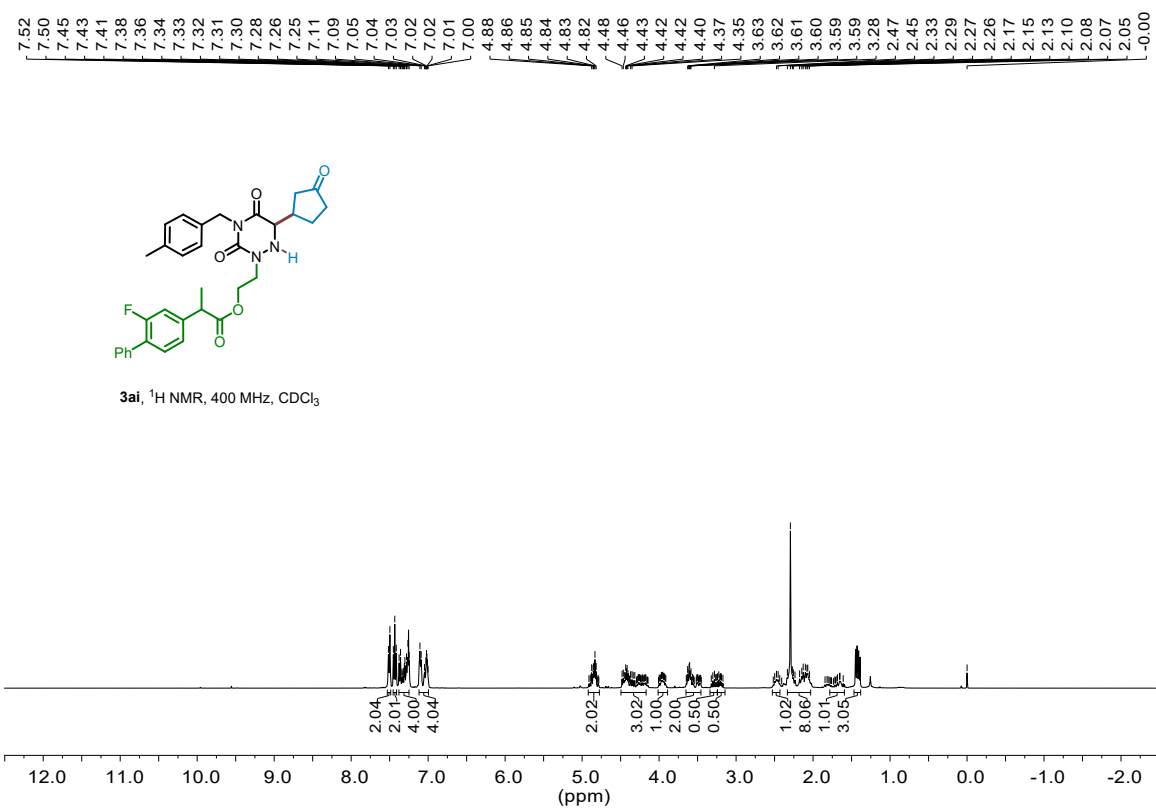
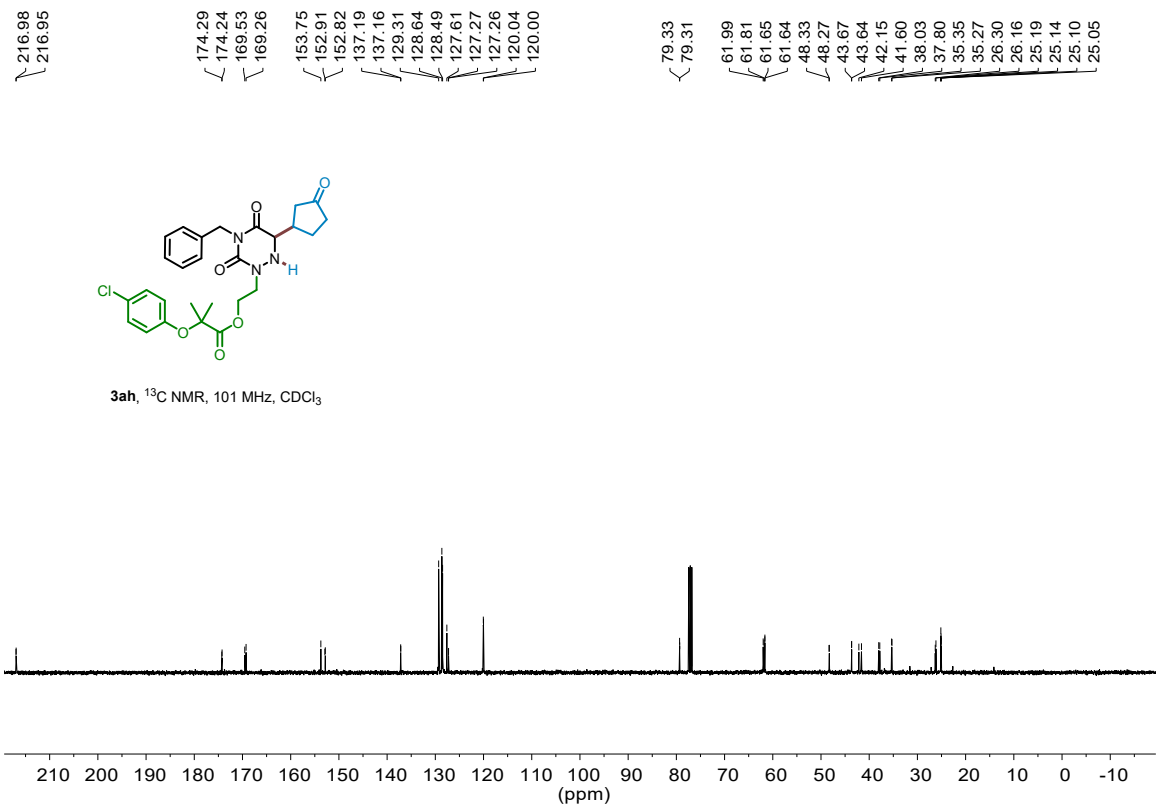


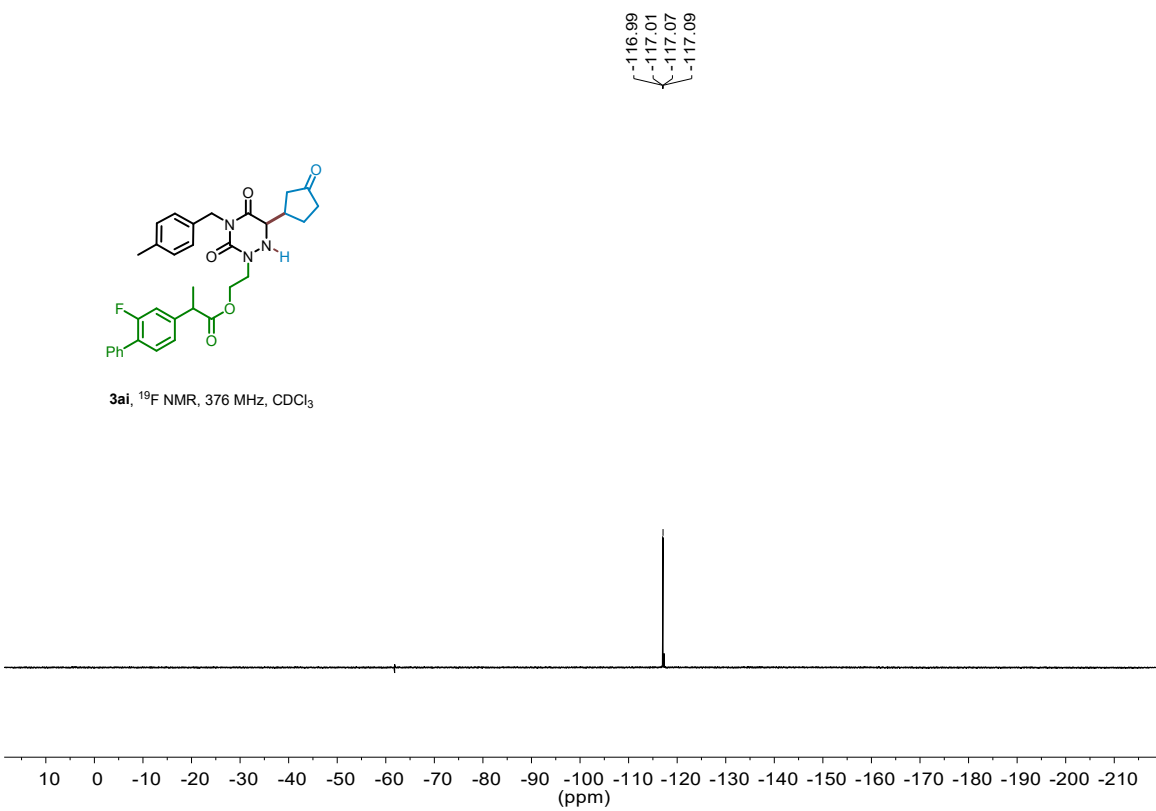
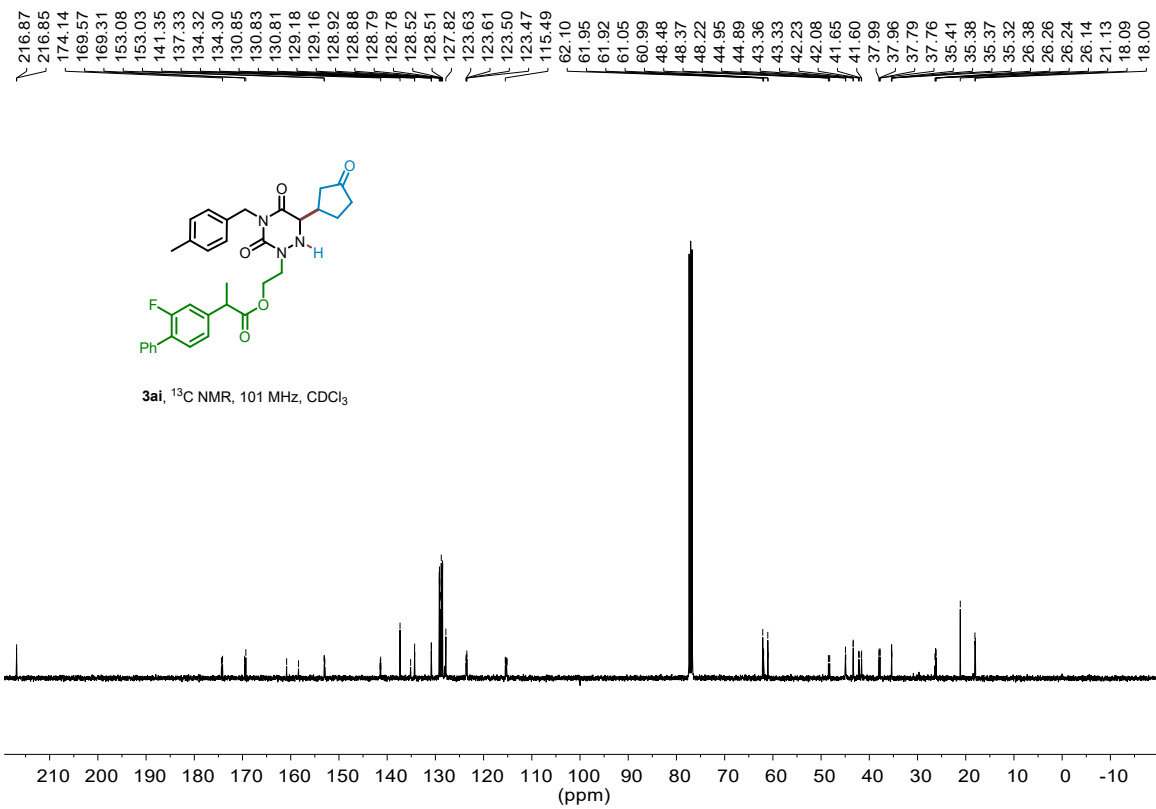
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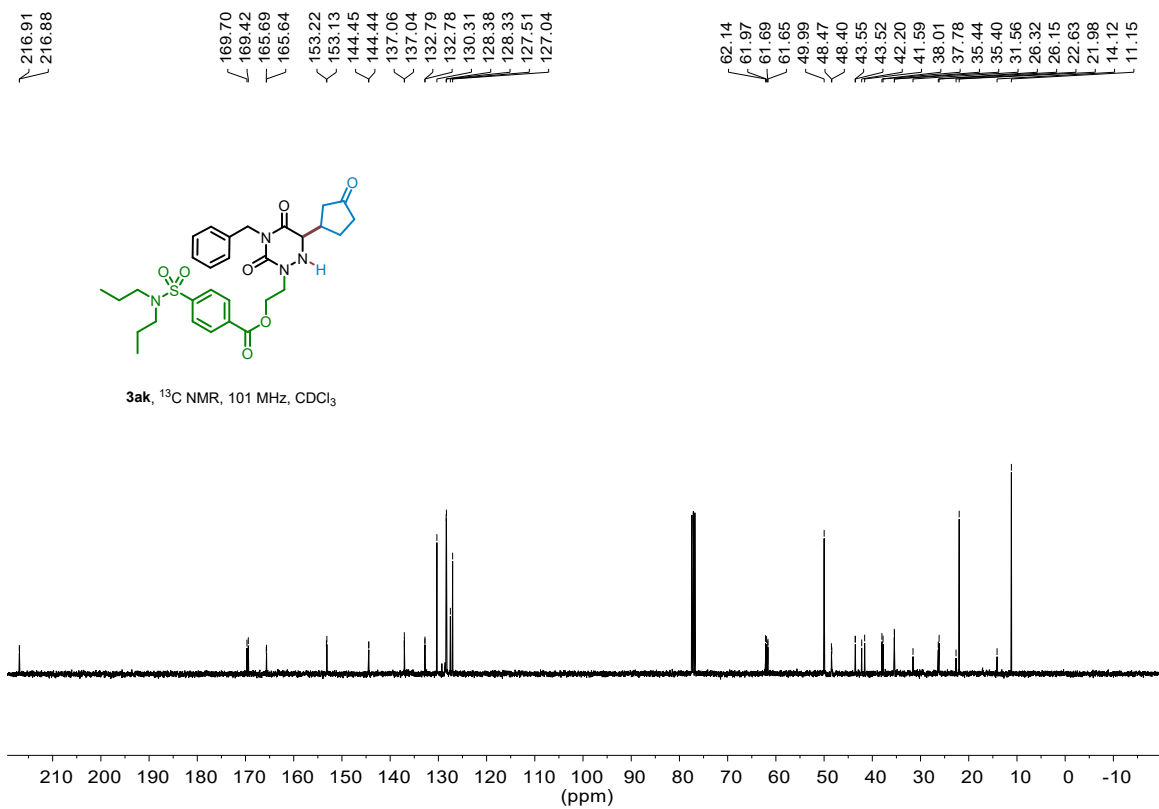
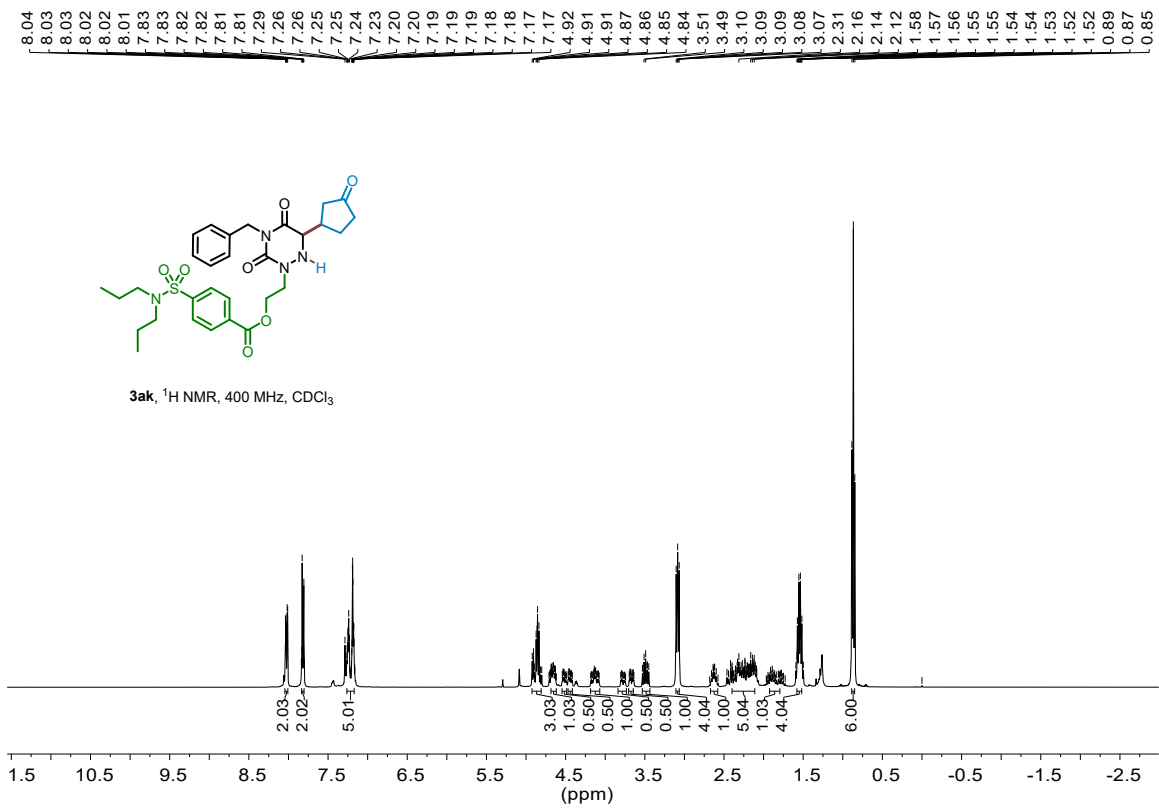


3ah, ^1H NMR, 400 MHz, CDCl_3

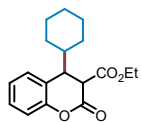




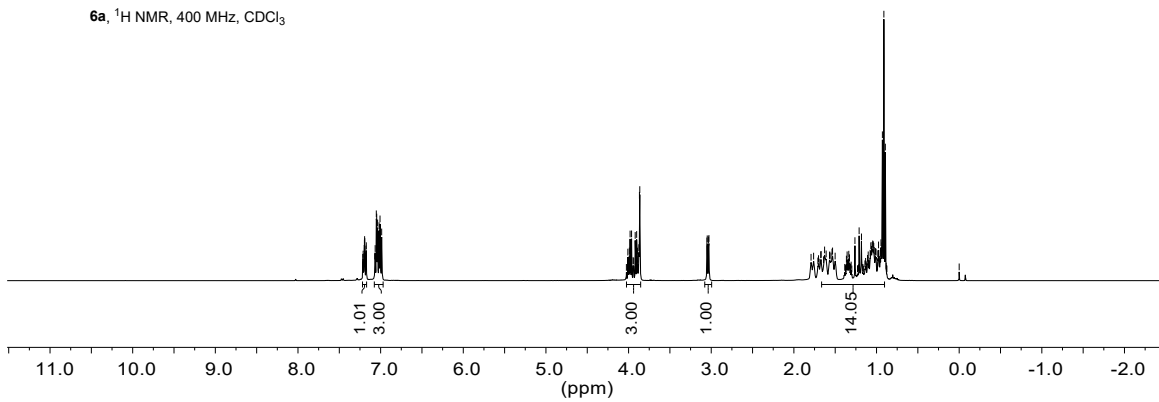




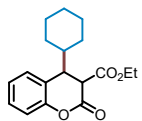
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7.01
7.01
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3.89
3.88
3.87
3.86
3.05
3.05
3.03
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1.67
1.63
1.61
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1.26
1.21
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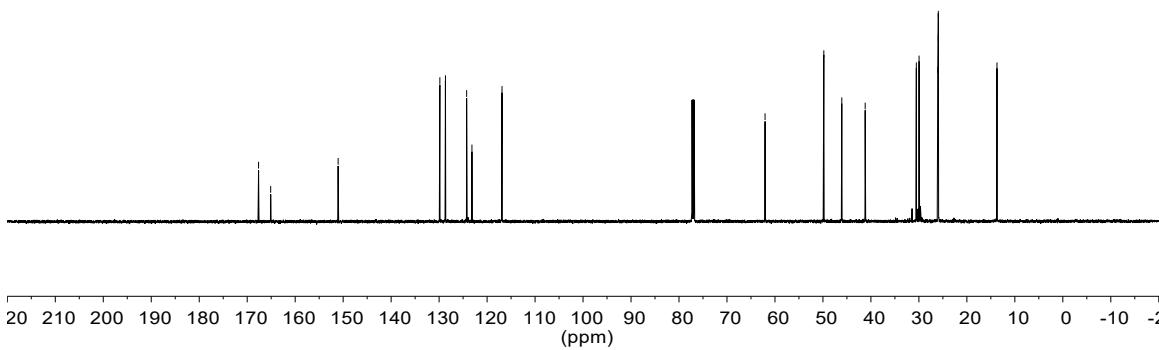
6a, ¹H NMR, 400 MHz, CDCl₃

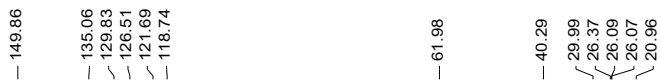
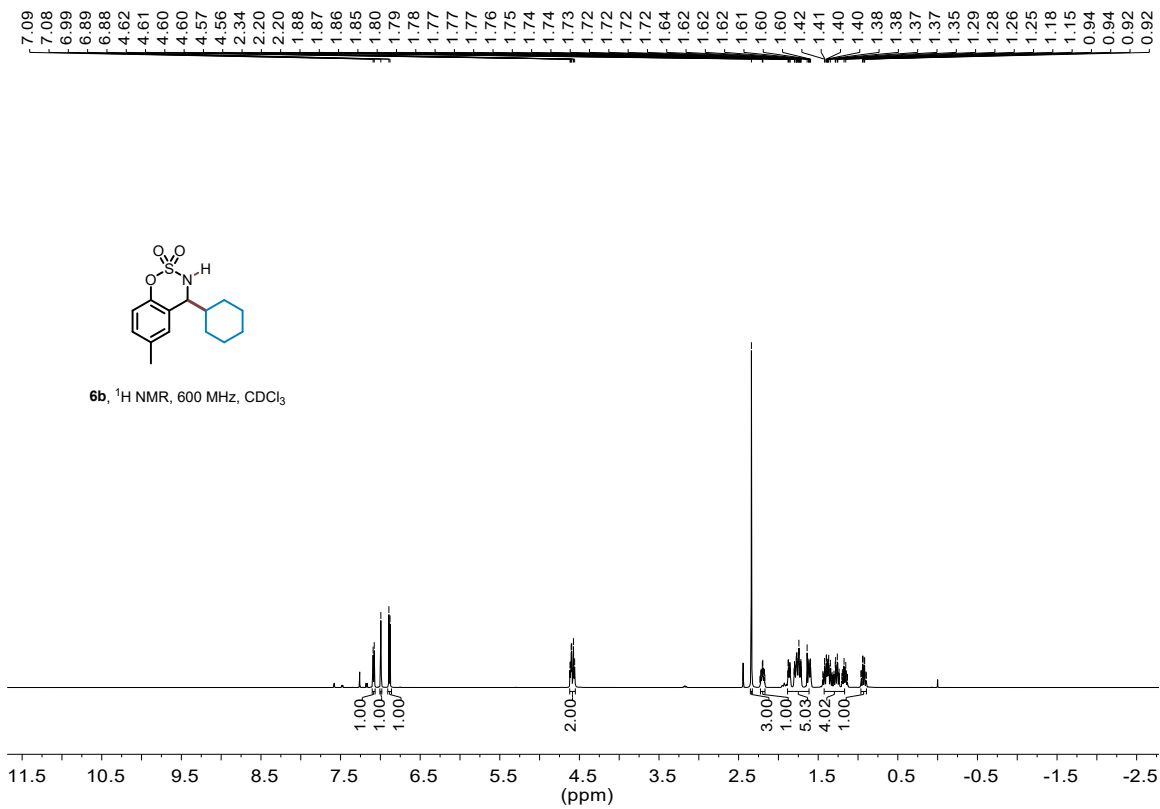


167.63
165.10
151.05
129.84
128.68
124.26
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41.20
30.53
29.96
26.06
25.96
25.95
13.72

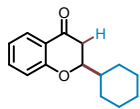


6a, ¹³C NMR, 151 MHz, CDCl₃

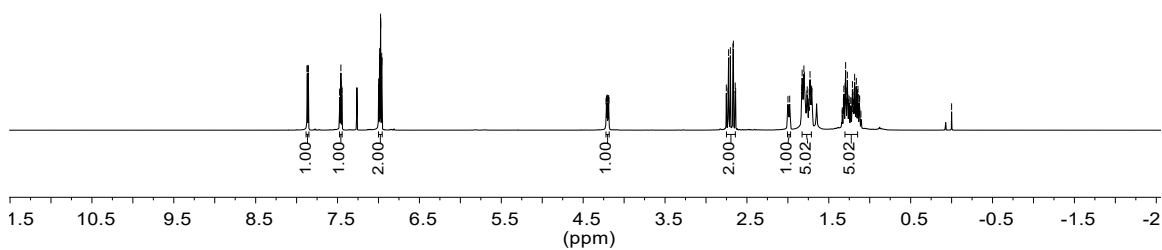




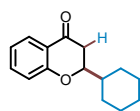
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1.14



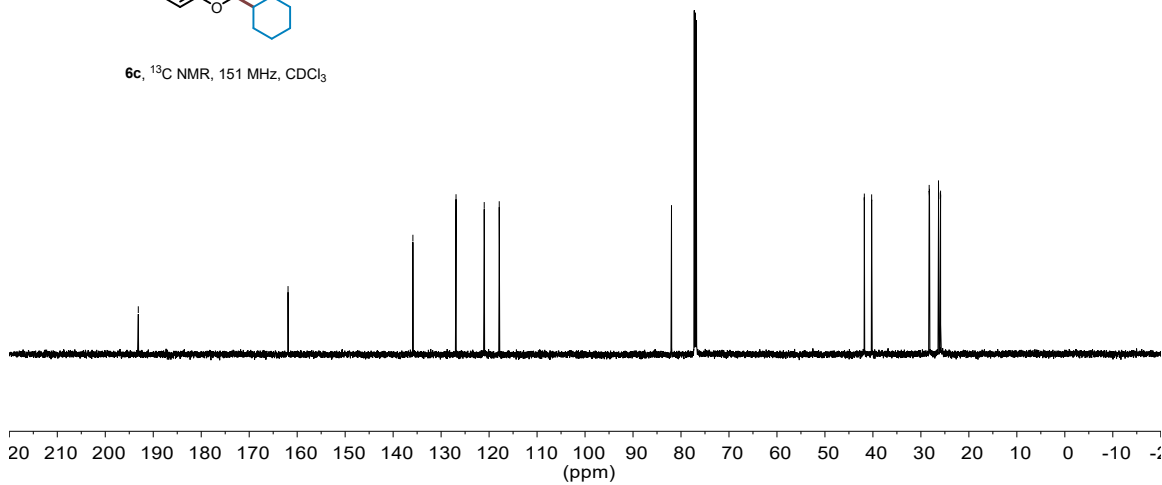
6c, ¹H NMR, 600 MHz, CDCl₃



193.12
161.90
135.88
126.89
121.01
117.88
81.98
41.79
40.27
28.27
28.21
26.33
25.96
25.90



6c, ¹³C NMR, 151 MHz, CDCl₃



5. Reference

1. L. Qiao, X. Fu, Y. Si, X. Chen, L. Qu and B. Yu, Switchable arylation and diarylation of allyl sulfones with aldehydes enabled by decatungstate photocatalysis, *Green Chem.*, 2022, **24**, 5614-5619.
2. L.-C. Hwang, S.-Y. Yang, C.-L. Chuang and G.-H. Lee, An Optimized Synthesis, Molecular Structure and Characterization of Benzylic Derivatives of 1,2,4-Triazin-3,5(2*H*,4*H*)-dione, *Molecules*, 2017, **22**, 1924.
3. (a) P. Ghosh, N. Y. Kwon, S. Kim, S. Han, S. H. Lee, W. An, N. K. Mishra, S. B. Han and I. S. Kim, C–H Methylation of Iminoamido Heterocycles with Sulfur Ylides**, *Angew. Chem. Int. Ed.*, 2021, **60**, 191-196; (b) H.-Y. Zhang, J. Chen, C.-C. Lu, Y.-P. Han, Y. Zhang and J. Zhao, Visible-Light-Induced C(sp²)–C(sp³) Cross-Dehydrogenative-Coupling Reaction of *N*-Heterocycles with *N*-Alkyl-*N*-methylanilines under Mild Conditions, *J. Org. Chem.*, 2021, **86**, 11723-11735.
4. S. Singh, K. N. Tripathi and R. P. Singh, Redox activated amines in the organophotoinduced alkylation of coumarins, *Org. Biomol. Chem.*, 2022, **20**, 5716-5720.
5. J. R. Zimmerman, M. Manpadi and R. Spatney, Tin-free radical reactions under minimal solvent conditions for the synthesis of substituted chromones and coumarins, *Green Chem.*, 2011, **13**, 3103-3106.