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Electrochemical C-H functionalization reaction of *N*-heterocycles with alkyl iodides

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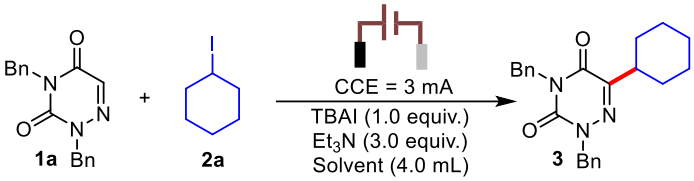
1. General Information

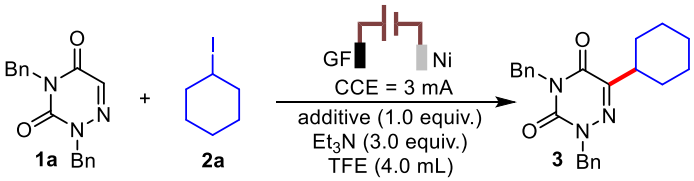
Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich, Alfa Aesar, Fluorochem and Carl Roth. Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F254 indicator, visualized by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume. ^{1}H NMR and ^{13}C NMR were recorded on a Varian AV600/AV400, an Agilent DD2 400 NMR spectrometer, or a Brucker 500 MHz NMR spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (J) are in Hertz (Hz). HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization or on a Finnigan MAT 95 using EI ionization at 70 eV of an Agilent 6500 Q-TOF spectrometer.

2. Optimization Tables for Alkylation of Aza-Uracil.



Entry	Electrode	Solvent	Time(h)	Yield of 3 [%]
1	GF(+) and GF(-)	MeCN	30	13
2	GF(+) and Pt(-)	MeCN	30	-
3	GF(+) and Ni(-)	MeCN	30	33
4	GF(+) and Ni(-)	DCM	30	61
5	GF(+) and Ni(-)	1,4-Dioxane	24	-
6	GF(+) and Ni(-)	DMF	24	traces
7	GF(+) and Ni(-)	THF	20	31
8	GF(+) and Ni(-)	HFIP	31	77
9	GF(+) and Ni(-)	TFE	30	86
10	GF(+) and Ni(-)	MeOH	17	18

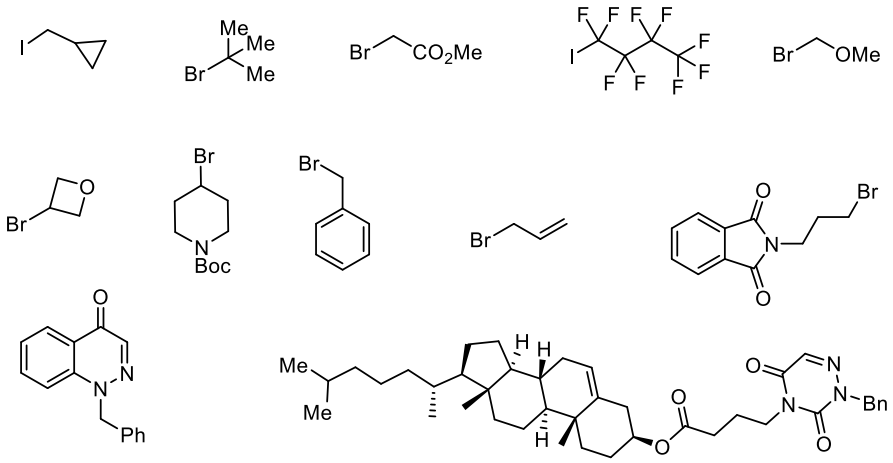
Reaction conditions: 1 (0.2 mmol), 2 (2.0 equiv.), TBAI (1.0 equiv.) and Et_3N (3.0 equiv.) in solvent (4.0 mL) at CCE of 3 mA.



Entry	Additive	Time(h)	Yield[%]
1	$^{n}Bu_4NPF_6$	50	13
2	$^{n}Bu_{44}ClO_4$	30	90
3	$^{n}Bu_4NBr$	30	69
4[a]	$^{n}Bu_4NClO_4$	42	53
5[b]	$^{n}Bu_4NClO_4$	42	82
6[c]	$^{n}Bu_4NClO_4$	42	69
7[d]	$^{n}Bu_4NClO_4$	22	93

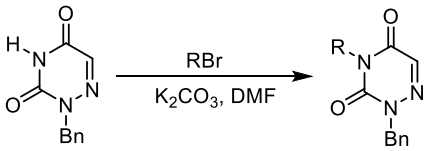
Reaction conditions: **1a** (0.2 mmol), **2a** (2.0 equiv.), additive (1.0 equiv.) and Et_3N (3.0 equiv.) in TFE (4.0 mL) at 6 mA constant current using graphite anode and nickel foam as cathode. [a]DIPEA was used instead of Et_3N. [b]Et_3N (1.0 equiv.) was used. [c]**2a** (1.0 equiv.) was used. [d]CCE at 6 mA.

3. Incompatible Substrates



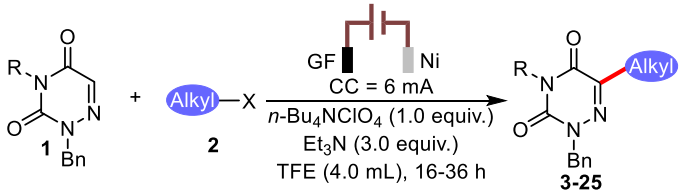
4. Experimental Procedures and Spectroscopic Data

General Procedure for the Synthesis of alkylated Aza-Uracils – GP1



According to a reported procedure,[1] alkyl bromide (2.0 mmol, 1.0 equiv.) was added dropwise to a stirring solution of *N*-1-benzyl-6-azauracils (2.0 mmol, 1.0 equiv.), K_2CO_3 (2.0 mmol, 1.0 equiv.) in DMF (20 mL). The reaction mixture was allowed to stir at room temperature for 16 h. Then, the mixture was quenched with saturated Na_2CO_3 solution and extracted with DCM for three times. The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude products were purified through silica gel column chromatography using *n*-hexane : ethyl acetate as eluent to afford the corresponding alkylated azauracils.

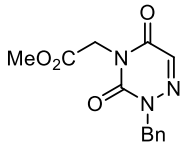
General Procedure for Electro-catalysed Alkylation of Heterocycles-GP2



A dry 10 mL vial equipped with a teflon-coated magnetic stir bar was charged with heterocycle substrate **1** (0.2 mmol) and tetrabutylammonium perchlorate (0.2 mmol) followed by addition of trifluoroethanol (4.0 mL). Then alkyl halide **2** (2.0 equiv.) and triethylamine (3.0 equiv.) was added sequentially and electrolyzed at a constant current of 6 mA. After complete conversion of the substrate **1** (indicated by TLC), the electrodes were taken out and washed twice by sonicating in dichloromethane for 5 min. The solvents were combined and concentrated on a rotatory evaporator. The crude mixture was then purified *via* silica gel column chromatography

using a mixture of *n*-hexane : ethyl acetate as eluent to provide the pure alkylated products **3-25**.

Methyl 2-(2-benzyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)acetate (1b)



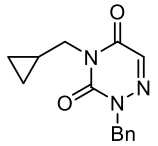
The title compound **1b** was synthesized according to the general procedure (GP-1) using *N*-1-benzyl-6-azauracils (2.0 mmol), methyl bromoacetate (2.0 mmol) and K_2CO_3 (2.0 mmol) in DMF at room temperature. The product was obtained after silica column chromatography (*n*-hexane : ethyl acetate 4 : 1) as a white solid (75%, 412 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 3H), 7.33 - 7.28 (m, 3H), 5.09 (s, 2H), 4.69 (s, 2H), 3.78 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.8, 155.9, 148.9, 135.2, 135.2, 129.3, 128.8, 128.3, 52.9, 52.7, 44.1.

HRMS (ESI, m/z) calcd for $C_{13}H_{11}N_3O_4Na$ $[M+Na]^+$: 298.0804, found; 298.0811.

2-Benzyl-4-(cyclopropylmethyl)-1,2,4-triazine-3,5(2*H*,4*H*)-dione (1c)



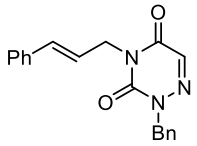
The title compound **1c** was synthesized according to the general procedure (GP-1) using *N*-1-benzyl-6-azauracils (2.0 mmol), (bromomethyl)cyclopropane (2.0 mmol) and K_2CO_3 (2.0 mmol) in DMF at room temperature. The product was obtained after silica column chromatography (*n*-hexane : ethyl acetate 4 : 1) as a white solid (60%, 309 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.40 (s, 1H), 7.35 – 7.29 (m, 3H), 5.10 (s, 2H), 3.82 (d, J = 7.0 Hz, 2H), 1.28 – 1.23 (m, 1H), 0.58 – 0.53 (m, 2H), 0.40 – 0.37 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 148.9, 135.6, 134.2, 129.6, 128.7, 128.2, 56.82, 44.0, 10.1, 3.7.

HRMS (ESI, m/z) calcd for $C_{14}H_{15}N_3O_2Na$ $[M+Na]^+$: 280.1062, found; 280.1057.

2-Benzyl-4-cinnamyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (1d)



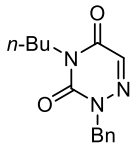
The title compound **1d** was synthesized according to the general procedure (GP-1) using *N*-1-benzyl-6-azauracils (2.0 mmol), cinnamyl bromide (2.0 mmol) and K_2CO_3 (2.0 mmol) in DMF

at room temperature. The product was obtained after silica column chromatography (*n*-hexane : ethyl acetate 4 : 1) as a white solid (81%, 517 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.41 (s, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.31 – 7.24 (m, 6H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.33 – 6.21 (m, 1H), 5.08 (s, 2H), 4.69 (d, *J* = 6.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.1, 148.6, 136.1, 135.5, 135.2, 134.7, 129.6, 128.7, 128.3, 128.3, 126.8, 122.1, 54.1, 44.1.

2-Benzyl-4-butyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (1e)



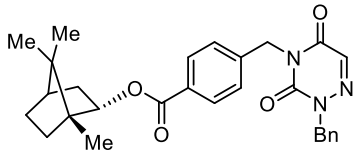
The title compound **1e** was synthesized according to the general procedure (GP-1) using *N*-1-benzyl-6-azauracils (2.0 mmol), 1-bromobutane (2.0 mmol) and K_2CO_3 (2.0 mmol) in DMF at room temperature. The product was obtained after silica column chromatography (*n*-hexane : ethyl acetate 4 : 1) as a white solid (80%, 415 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 7.39 (s, 1H), 7.33 – 7.27 (m, 3H), 5.08 (s, 2H), 3.95 (t, 2H), 1.74 – 1.69 (m, 2H), 1.39 – 1.33 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.0, 148.7, 135.6, 134.1, 129.4, 128.6, 128.1, 51.7, 43.9, 30.2, 19.7, 13.7.

HRMS (ESI) m/z calcd for $C_{14}H_{17}N_3O_2Na$ $[M+Na]^+$: 282.1213; Found: 282.1213.

(1*R*,2*R*,4*R*)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-((2-benzyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)methyl)benzoate (1f)



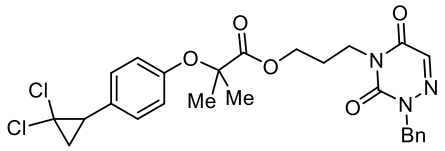
The title compound **1f** was synthesized according to the general procedure (GP-1) using *N*-1-benzyl-6-azauracils (2.0 mmol), (1*R*,2*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(bromomethyl)benzoate (2.0 mmol) and K_2CO_3 (2.0 mmol) in DMF at room temperature. The product was obtained after silica column chromatography (*n*-hexane : ethyl acetate 4 : 1) as a white solid (62%, 614 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 2H), 7.45 (dd, *J* = 8.0, 6.0 Hz, 4H), 7.41 (s, 1H), 7.34 – 7.26 (m, 3H), 5.14 (s, 2H), 5.13 – 5.08 (m, 1H), 5.06 (s, 2H), 2.51 – 2.42 (m, 1H), 2.10 (ddd, *J* = 13.5, 9.4, 4.4 Hz, 1H), 1.80 (ddt, *J* = 12.0, 8.0, 3.9 Hz, 1H), 1.73 (t, *J* = 4.5 Hz, 1H), 1.43 – 1.37 (m, 1H), 1.32 – 1.27 (m, 1H), 1.09 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.96 (s, 3H), 0.91 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 155.9, 148.8, 140.2, 135.4, 134.9, 131.0, 130.14, 129.5, 128.7, 128.6, 128.3, 80.8, 55.2, 49.2, 48.0, 45.1, 44.1, 37.0, 28.2, 27.5, 19.8, 19.0, 13.7.

HRMS (ESI, m/z) calcd for $C_{28}H_{31}N_3O_4Na$ $[M+Na]^+$: 496.2212, found; 496.2202.

3-(2-benzyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)propyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (1g)



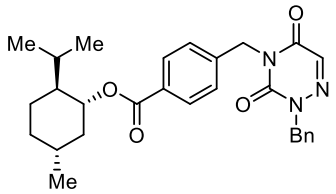
The title compound **1g** was synthesized according to the general procedure (GP-1) using *N*-1-benzyl-6-azauracils (1.0 mmol), 2-bromoethyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (1.0 mmol) and K_2CO_3 (1.0 mmol) in DMF at room temperature. The product was obtained after silica column chromatography (*n*-hexane : ethyl acetate 4 : 1) as a white solid (75%, 415 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.45 (m, 2H), 7.34 – 7.28 (m, 3H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.04 (s, 2H), 4.21 (t, *J* = 6.1 Hz, 2H), 3.92 – 3.89 (m, 2H), 2.83 – 2.80 (m, 1H), 2.07 – 2.03 (m, 2H), 1.93 – 1.90 (m, 1H), 1.76 – 1.74 (m, 1H), 1.59 (s, 7H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 155.9, 155.0, 148.7, 135.5, 134.5, 129.8, 129.5, 128.7, 128.3, 118.7, 79.2, 62.6, 60.9, 48.9, 44.0, 34.9, 27.3, 25.9, 25.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{27}N_3O_5Cl_2Na$: 554.1220; Found: 554.1220.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-((2-benzyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)methyl)benzoate (1h)



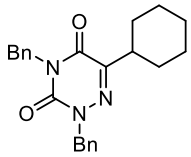
The title compound **1h** was synthesized according to the general procedure (GP-1) using *N*-1-benzyl-6-azauracils (1.0 mmol), (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-(bromomethyl)benzoate (1.0 mmol) and K_2CO_3 (1.0 mmol) in DMF at room temperature. The product was obtained after silica column chromatography (*n*-hexane : ethyl acetate 4 : 1) as a white solid (80%, 398 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.47 – 7.40 (m, 5H), 7.33 – 7.27 (m, 3H), 5.14 (s, 2H), 5.07 (s, 2H), 4.95 – 4.90 (m, 1H), 2.13 – 2.09 (m, 1H), 1.95 – 1.91 (m, 1H), 1.74 – 1.72 (m, 2H), 1.58 – 1.52 (m, 2H), 1.17 – 1.06 (m, 2H), 0.93 – 0.90 (m, 7H), 0.78 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 155.9, 148.8, 140.1, 135.4, 134.9, 130.9, 130.2, 129.5, 128.7, 128.6, 128.3, 75.1, 55.2, 47.4, 44.1, 41.0, 34.4, 31.5, 26.6, 23.7, 22.1, 20.9, 16.6.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{33}N_3O_4Na$: 498.2363; Found: 498.2363.

2,4-Dibenzyl-6-cyclohexyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (3)

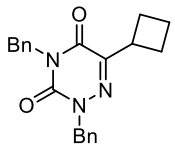


The title compound **6** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (76%, 57.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 2H), 7.42 – 7.39 (m, 2H), 7.37 – 7.27 (m, 6H), 5.08 (d, J = 3.0 Hz, 4H), 2.90 – 2.84 (m, 1H), 1.88 – 1.71(m, 5H), 1.42 – 1.15 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 149.1, 149.0, 136.0, 135.9, 129.6, 128.9, 128.8, 128.6, 128.2, 128.1, 55.4, 44.3, 38.6, 30.6, 26.3, 26.1.

2,4-Dibenzyl-6-cyclobutyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (4)

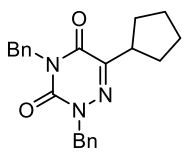


The title compound **6** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (43%, 30.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.44 – 7.40 (m, 2H), 7.37 – 7.25 (m, 6H), 5.10 (s, 2H), 5.05 (s, 2H), 3.64 (p, J = 8.3 Hz, 1H), 2.27 – 2.18 (m, 4H), 2.07 – 1.95 (m, 1H), 1.88 – 1.79 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 149.1, 147.5, 136.0, 135.9, 129.6, 128.9, 128.8, 128.7, 128.3, 128.1, 55.4, 44.2, 35.3, 26.4, 18.4.

2,4-Dibenzyl-6-cyclopentyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (5)

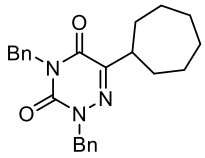


The title compound **5** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (63%, 45.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.45 (m, 2H), 7.40 – 7.37 (m, 2H), 7.35 – 7.24 (m, 6H), 5.06 (d, *J* = 2.1 Hz, 4H), 3.29 – 3.22 (m, 1H), 1.95 – 1.90 (m, 2H), 1.70 – 1.60 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 149.1, 148.4, 136.0, 135.9, 129.6, 128.9, 128.7, 128.6, 128.2, 128.1, 55.3, 44.2, 40.2, 30.5, 25.4.

2,4-Dibenzyl-6-cycloheptyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (6)

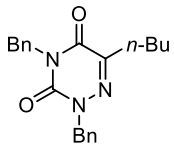


The title compound **7** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (62%, 48.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.34 – 7.31 (m, 2H), 7.29 – 7.18 (m, 6H), 4.99 (s, 4H), 3.01 – 2.94 (m, 1H), 1.81 – 1.76 (m, 2H), 1.70 – 1.63 (m, 2H), 1.59 – 1.42 (m, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 150.1, 149.0, 136.0, 135.9, 129.5, 128.8, 128.7, 128.6, 128.2, 128.1, 55.3, 44.3, 39.9, 32.3, 28.2, 26.7.

2,4-Dibenzyl-6-butyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (7)

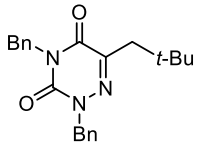


The title compound **8** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (61%, 42.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.33 – 7.31 (m, 2H), 7.28 – 7.17 (m, 6H), 5.00 (s, 4H), 2.52 (t, *J* = 7.4 Hz, 2H), 1.52 (p, *J* = 7.4 Hz, 2H), 1.29 (h, *J* = 7.3 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.2, 149.1, 145.9, 136.1, 135.5, 129.6, 128.8, 128.8, 128.7, 128.3, 128.1, 55.3, 44.3, 30.1, 28.4, 22.4, 13.9.

2,4-Dibenzyl-6-neopentyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (8)

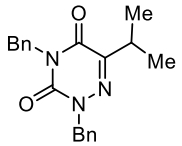


The title compound **9** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (14%, 10.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.40 – 7.28 (m, 8H), 5.09 (s, 4H), 2.54 (s, 2H), 0.93 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7, 149.0, 144.6, 135.9, 129.4, 128.9, 128.8, 128.7, 128.3, 128.1, 55.4, 44.2, 42.0, 32.5, 29.6.

2,4-Dibenzyl-6-isopropyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (9)

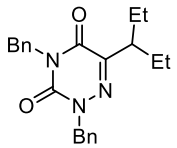


The title compound **10** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (73%, 48.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.38 (m, 2H), 7.33 – 7.31 (m, 2H), 7.27 – 7.18 (m, 6H), 4.99 (d, J = 2.5 Hz, 4H), 3.09 (p, J = 6.8 Hz, 1H), 1.11 (d, J = 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 149.6, 149.0, 136.0, 135.9, 129.6, 128.9, 128.8, 128.6, 128.24, 128.1, 55.3, 44.2, 29.3, 20.1.

2,4-Dibenzyl-6-(pentan-3-yl)-1,2,4-triazine-3,5(2*H*,4*H*)-dione (10)

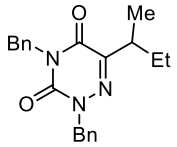


The title compound **11** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (51%, 37.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 2H), 7.39 – 7.37 (m, 2H), 7.35 – 7.26 (m, 6H), 5.08 (d, J = 5.0 Hz, 4H), 2.91 – 2.84 (m, 1H), 1.74 – 1.53 (m, 4H), 0.81 (t, J = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 148.9, 147.9, 136.0, 136.0, 129.4, 128.8, 128.7, 128.2, 128.0, 55.3, 44.3, 42.4, 25.0, 11.6.

2,4-Dibenzyl-6-(sec-butyl)-1,2,4-triazine-3,5(2*H*,4*H*)-dione (11)

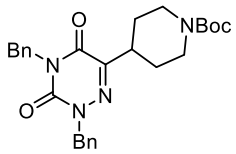


The title compound **11** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (77%, 53.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.45 (m, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.26 (m, 6H), 5.11 – 5.03 (m, 4H), 2.99 (q, *J* = 7.0 Hz, 1H), 1.73 (dp, *J* = 14.0, 7.0 Hz, 1H), 1.46 (dp, *J* = 14.5, 7.0 Hz, 1H), 1.15 (d, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 149.0, 149.0, 136.0, 136.0, 129.5, 128.8, 128.8, 128.7, 128.2, 128.1, 55.4, 44.3, 35.7, 27.3, 17.6, 11.8.

***tert*-Butyl 4-(2,4-dibenzyl-3,5-dioxo-2,3,4,5-tetrahydro-1,2,4-triazin-6-yl)piperidine-1-carboxylate (12)**

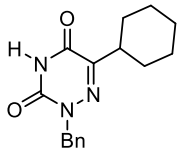


The title compound **12** was synthesized according to the general procedure (GP2) at 3 mA current, and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a white solid (64%, 61mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 2H), 7.42 – 7.37 (m, 2H), 7.37 – 7.26 (m, 6H), 5.07 (s, 4H), 4.49 – 3.92 (m, 2H), 3.00 (tt, *J* = 11.5, 3.3 Hz, 1H), 2.84 – 2.81 (m, 2H), 1.87 – 1.81 (m, 2H), 1.59 – 1.51 (m, 2H), 1.47 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.7, 154.9, 148.8, 147.2, 135.9, 135.7, 129.6, 128.9, 128.84, 128.7, 128.4, 128.2, 79.7, 55.5, 44.4, 36.9, 29.4, 28.6.

2-Benzyl-6-cyclohexyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (13)

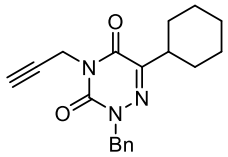


The title compound **13** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (68%, 38.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.49 – 7.45 (m, 2H), 7.32 – 7.24 (m, 3H), 5.07 (s, 2H), 2.88 – 2.81 (m, 1H), 1.86 – 1.69 (m, 5H), 1.35 – 1.24 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0, 135.7, 129.6, 128.7, 128.2, 43.7, 38.5, 30.5, 26.2, 26.1.

2-Benzyl-6-cyclohexyl-4-(prop-2-yn-1-yl)-1,2,4-triazine-3,5(2*H*,4*H*)-dione (14)

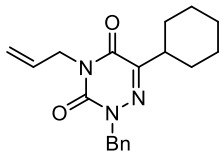


The title compound **14** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (29%, 18.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.34 – 7.28 (m, 3H), 5.09 (s, 2H), 4.70 (d, *J* = 2.5 Hz, 2H), 2.89 – 2.86 (m, 1H), 2.33 (t, *J* = 2.5 Hz, 1H), 1.88 – 1.79 (m, 5H), 1.43 – 1.31 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 149.8, 148.6, 135.7, 129.8, 129.8, 128.7, 128.2, 77.3, 73.3, 44.4, 41.6, 38.7, 30.5, 26.2, 26.1.

4-Allyl-2-benzyl-6-cyclohexyl-1,2,4-triazine-3,5(2*H*,4H)-dione (15)

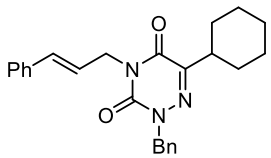


The title compound **15** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (35%, 22.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.49 (m, 2H), 7.33 – 7.26 (m, 3H), 5.97 – 5.90 (m, 1H), 5.27 – 5.23 (m, 2H), 5.09 (s, 2H), 4.53 (d, *J* = 5.0 Hz, 2H), 2.90 – 2.85 (m, 1H), 1.86 – 1.79 (m, 4H), 1.73 – 1.70 (m, 1H), 1.39 – 1.34 (m, 4H), 1.26 – 1.20 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 149.1, 148.9, 136.0, 131.8, 129.6, 128.7, 128.1, 118.9, 54.1, 44.2, 38.6, 30.5, 26.2, 26.1.

2-Benzyl-4-cinnamyl-6-cyclohexyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (16)



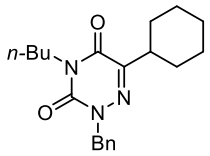
The title compound **16** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (76%, 61.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.37 – 7.23 (m, 8H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.32 – 6.25 (m, 1H), 5.08 (s, 2H), 4.67 (d, *J* = 7.0 Hz, 2H), 2.89 – 2.85 (m, 1H), 1.86 – 1.69 (m, 5H), 1.41 – 1.30 (m, 4H), 1.25 – 1.19 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 149.2, 148.9, 136.4, 136.0, 134.6, 129.7, 128.7, 128.7, 128.1, 126.7, 122.8, 53.8, 44.3, 38.7, 30.5, 26.3, 26.1.

HRMS (EI, m/z) calcd for $C_{25}H_{27}N_3O_2$ $[M]^+$: 401.2103, found; 401.2098.

2-Benzyl-4-butyl-6-cyclohexyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (17)



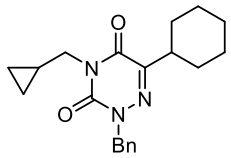
The title compound **17** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (57%, 38.9 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.48 (m, 2H), 7.32 – 7.26 (m, 3H), 5.09 (s, 2H), 3.93 (t, *J* = 7.0 Hz, 2H), 2.90 – 2.85 (m, 1H), 1.86 – 1.80 (m, 4H), 1.73 – 1.68 (m, 3H), 1.39 – 1.33 (m, 6H), 1.26 – 1.20 (m, 1H), 0.94 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 149.0, 148.6, 136.1, 129.6, 128.6, 128.1, 51.4, 44.2, 38.5, 30.6, 30.3, 26.3, 26.1, 19.8, 13.8.

HRMS (EI, m/z) calcd for $C_{20}H_{27}N_3O_2$ $[M]^+$: 341.2103, found; 341.2098.

2-Benzyl-6-cyclohexyl-4-(cyclopropylmethyl)-1,2,4-triazine-3,5(2*H*,4*H*)-dione (18)



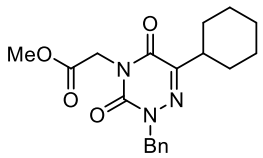
The title compound **18** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (62%, 42.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.32 – 7.24 (m, 3H), 5.08 (s, 2H), 3.78 (d, *J* = 7.0 Hz, 2H), 2.89 – 2.83 (m, 1H), 1.87 – 1.69 (m, 5H), 1.38 – 1.31 (m, 4H), 1.24 – 1.19 (m, 2H), 0.51 – 0.48 (m, 2H), 0.38 – 0.34 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 149.1, 148.6, 136.1, 129.7, 128.6, 128.1, 56.4, 44.2, 38.4, 30.6, 26.3, 26.1, 10.1, 3.6.

HRMS (EI, m/z) calcd for $C_{20}H_{25}N_3O_2$ $[M]^+$: 339.1947, found; 339.1941.

Methyl 2-(2-benzyl-6-cyclohexyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)acetate (19)



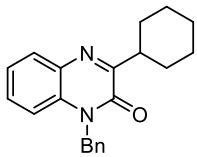
The title compound **19** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (94%, 67.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.43 (m, 2H), 7.31 – 7.25 (m, 3H), 5.07 (s, 2H), 4.65 (s, 2H), 3.76 (s, 3H), 2.89 – 2.82 (m, 1H), 1.86 – 1.67 (m, 5H), 1.36– 1.24 (m, 5H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 155.7, 149.7, 149.2, 135.7, 129.4, 128.7, 128.1, 52.8, 52.7, 44.3, 38.6, 30.4, 26.2, 26.0.

HRMS (EI, m/z) calcd for $C_{19}H_{23}N_3O_4$ $[M]^+$: 357.1688, found; 357.1682.

1-Benzyl-3-cyclohexylquinoxalin-2(1*H*)-one (20)

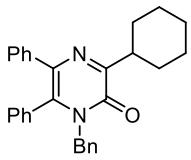


The title compound **20** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (76%, 48.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.31 – 7.22 (m, 7H), 5.47 (s, 2H), 3.39 (tt, *J* = 12.5, 3.0 Hz, 1H), 2.00 (d, *J* = 10.0 Hz, 2H), 1.89 – 1.85 (m, 2H), 1.76 (d, *J* = 13.0 Hz, 1H), 1.65 – 1.55 (m, 2H), 1.52 – 1.41 (m, 2H), 1.33 (tt, *J* = 12.5, 3.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 154.7, 135.6, 133.3, 132.3, 130.0, 129.5, 129.0, 127.7, 127.1, 123.6, 114.4, 46.1, 41.0, 30.7, 26.5, 26.3.

1-Benzyl-3-cyclohexyl-5,6-diphenylpyrazin-2(1*H*)-one (21)

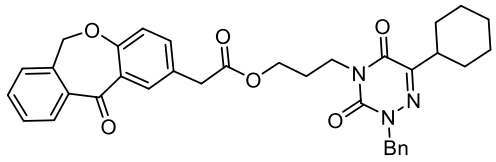


The title compound **21** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (40%, 33.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.40 (m, 6H), 7.36 – 7.34 (m, 1H), 7.30 – 7.26 (m, 6H), 5.53 (s, 2H), 3.16 (tt, *J* = 12.0, 3.5 Hz, 1H), 1.98 (d, *J* = 12.0 Hz, 2H), 1.90 – 1.87 (m, 2H), 1.79 – 1.74 (m, 3H), 1.49 – 1.42 (m, 2H), 1.36 – 1.31 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.2, 148.6, 145.2, 143.5, 139.4, 139.1, 137.6, 130.0, 130.0, 128.6, 128.1, 128.1, 127.9, 127.6, 67.8, 39.9, 30.8, 26.6, 26.3.

3-(2-Benzyl-6-cyclohexyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)propyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate (22)



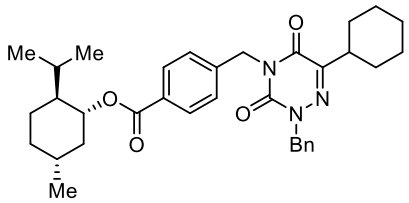
The title compound **22** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (34%, 40.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.47 – 7.24 (m, 8H), 7.01 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.16 (s, 2H), 5.05 (s, 2H), 4.15 – 4.12 (m, 2H), 4.03 – 3.99 (m, 2H), 3.58 (s, 2H), 2.86 – 2.81 (m, 1H), 2.09 – 2.05 (m, 2H), 1.82 – 1.74 (m, 4H), 1.69 – 1.62 (m, 2H), 1.34 – 1.24 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 190.9, 171.4, 160.6, 155.7, 149.1 149.0, 140.6, 136.5, 135.9, 135.7, 132.9, 132.6, 129.7, 129.6, 129.4, 128.7, 128.1, 127.9, 127.8, 125.3, 121.2, 73.7, 62.2, 48.5, 44.3, 40.2, 38.5, 30.5, 27.4, 26.2, 26.1.

HRMS (ESI, m/z) calcd for $C_{35}H_{35}N_3O_6Na$ $[M+Na]^+$: 616.2424, found; 616.2423.

(1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl 4-((2-benzyl-6-cyclohexyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)methyl)benzoate (23)



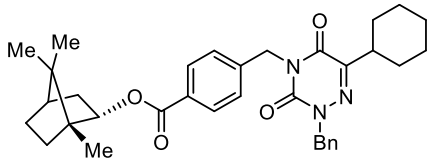
The title compound **23** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (37%, 41.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.48 – 7.43 (m, 4H), 7.33 – 7.27 (m, 3H), 5.12 (d, *J* = 3.0 Hz, 2H), 5.06 (s, 2H), 4.95 – 4.89 (m, 1H), 2.89 – 2.84 (m, 1H), 2.11 (d, *J* = 11.0 Hz, 1H), 1.96 – 1.90 (m, 1H), 1.87 – 1.80 (m, 4H), 1.74 – 1.70 (m, 3H), 1.60 – 1.51 (m, 3H), 1.37 – 1.34 (m, 5H), 1.15 – 1.07 (m, 2H), 0.92 (t, *J* = 7.0 Hz, 6H), 0.78 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 155.7, 149.5, 149.0, 140.7, 135.9, 130.8, 130.1, 129.6, 128.7, 128.6, 128.2, 75.1, 55.0, 47.4, 44.4, 41.1, 38.6, 34.5, 31.6, 30.6, 26.7, 26.2, 26.1, 23.8, 22.2, 20.9, 16.7.

HRMS (ESI, m/z) calcd for $C_{34}H_{43}N_3O_4Na$ $[M+Na]^+$: 580.3151, found; 580.3143.

(1R,2S,4R)-4,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-((2-benzyl-6-cyclohexyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)methyl)benzoate (24)



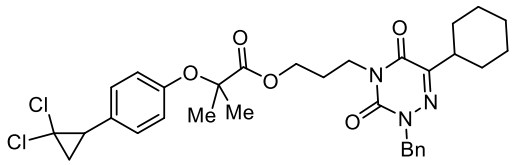
The title compound **24** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (41%, 45.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.46 – 7.43 (m, 4H), 7.31 – 7.24 (m, 3H), 5.11 – 5.07 (m, 3H), 5.05 (s, 2H), 2.88 – 2.83 (m, 1H), 2.49 – 2.41 (m, 1H), 2.13 – 2.06 (m, 1H), 1.86 – 1.78 (m, 5H), 1.76 – 1.69 (m, 2H), 1.41 – 1.31 (m, 5H), 1.28 – 1.24 (m, 2H), 1.08 (dd, *J* = 14.0, 3.0 Hz, 1H), 0.95 (s, 3H), 0.89 (d, *J* = 5.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 155.7, 149.5, 149.0, 140.8, 135.9, 130.8, 130.1, 129.6, 128.7, 128.6, 128.2, 80.8, 55.0, 49.2, 48.0, 45.1, 44.3, 38.6, 37.0, 30.6, 28.2, 27.5, 26.2, 26.09, 19.85, 19.05, 13.73.

HRMS (ESI, m/z) calcd for $C_{34}H_{41}N_3O_4Na$ $[M+Na]^+$: 578.2995, found; 579.2986.

3-(2-Benzyl-6-cyclohexyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)propyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (25)



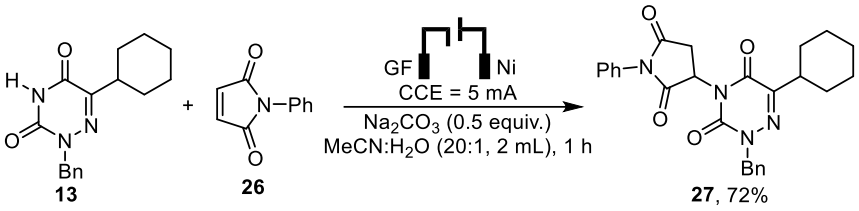
The title compound **25** was synthesized according to the general procedure (GP2), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20 : 1) as a colourless solid (58%, 61.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.31 – 7.25 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 11.0 Hz, 2H), 5.04 (s, 2H), 4.19 (t, *J* = 6.0 Hz, 2H), 3.88 (t, *J* = 7.0 Hz, 2H), 2.86 – 2.77 (m, 2H), 2.03 (p, *J* = 6.5 Hz, 2H), 1.90 (dd, *J* = 11.0, 7.0 Hz, 1H), 1.84 – 1.71 (m, 6H), 1.58 (s, 6H), 1.36 – 1.24 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 155.7, 155.0, 149.1, 148.9, 135.9, 129.8, 129.6, 128.7, 128.3, 128.1, 118.8, 79.3, 62.7, 61.0, 48.3, 44.2, 38.5, 34.9, 30.5, 27.4, 26.2, 26.1, 25.9, 25.6, 25.5.

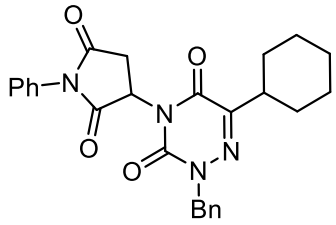
HRMS (ESI, m/z) calcd for $C_{32}H_{37}Cl_2N_3O_5Na$ $[M+Na]^+$: 636.2008, found; 636.1998.

Procedure for the electro-catalysed N-alkylation reaction



To a 10 mL test tube equipped with a magnetic stir bar was added 2-Benzyl-6-cyclohexyl-1,2,4-triazine-3,5(2*H*,4*H*)-dione (**13**) (0.029 g, 0.1 mmol), *N*-phenylmaleimide (0.1 mmol, 1.0 equiv.), Na_2CO_3 (0.05 mmol, 0.5 equiv.) and MeCN:H_2O (20:1, 2.0 mL). The reaction mixture was subjected to constant current electrolysis at 5 mA for 1 hour using graphite (anode) and nickel (cathode) electrodes. The solvent was evaporated on rotatory evaporator and the product was purified by silica gel column chromatography using *n*-hexane : EtOAc (10:1) as eluent to yield **27** as a white solid (32.9 mg, 72%).

2-Benzyl-6-cyclohexyl-4-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-1,2,4-triazine-3,5(2*H*,4*H*)-dione (27)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 4H), 7.45 – 7.42 (m, 1H), 7.35 – 7.29 (m, 5H), 5.62 (s, 1H), 5.12 – 5.07 (m, 2H), 3.31 (dd, *J* = 18.0, 9.5 Hz, 1H), 3.10 (dd, *J* = 18.0, 5.5 Hz, 1H), 2.91 – 2.86 (m, 1H), 1.88 (t, *J* = 14.0 Hz, 2H), 1.82 – 1.79 (m, 2H), 1.74 – 1.71 (m, 1H), 1.38 – 1.26 (m, 5H).

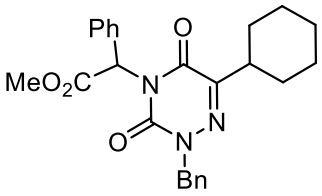
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 172.2, 155.3, 151.0, 148.9, 135.3, 131.6, 129.7, 129.5, 129.2, 128.8, 128.4, 126.6, 44.6, 38.8, 34.1, 30.4, 30.4, 26.1, 26.0.

HRMS (EI, m/z) calcd for $C_{26}H_{26}N_4O_4$ $[M]^+$: 458.1954, found; 458.1948.

Procedure for the photochemical N-H insertion reaction

Prepared according to the literature report.[2] To a 10 mL test tube equipped with a magnetic stir bar was added substrate **13** (0.029 g, 0.1 mmol) and DCM (2.0 mL). Then, phenyl diazoester **28** (0.035 g, 0.2 mmol, 2.0 equiv.), was added and the resulting mixture was irradiated with a 12 W (440 nm) blue LEDs at a distance of ca. 1.5 cm (with cooling by the fan) for 2 h. After finishing the reaction, the product was purified by silica gel column chromatography using *n*-hexane : EtOAc (20:1 to 10:1) as eluent to yield **29** as a colourless wax (29.1 mg, 67%).

Methyl 2-(2-benzyl-6-cyclohexyl-3,5-dioxo-2,5-dihydro-1,2,4-triazin-4(3*H*)-yl)-2-phenylacetate (29)

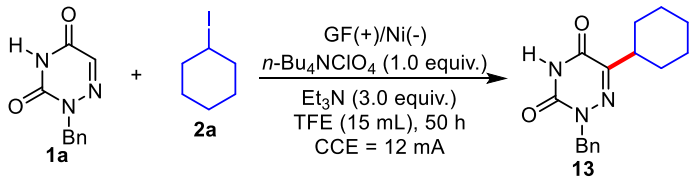


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 4H), 7.39 – 7.38 (m, 3H), 7.33 – 7.28 (m, 3H), 6.40 (s, 1H), 5.08 (s, 2H), 3.77 (s, 3H), 2.83 (t, *J* = 11.5 Hz, 1H), 1.91 (d, *J* = 12.5 Hz, 1H), 1.73 (q, *J* = 17.0 Hz, 4H), 1.40 – 1.14 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.2, 155.4, 149.3, 149.0, 135.7, 133.4, 130.3, 129.6, 129.2, 128.7, 128.6, 128.2, 64.5, 53.0, 44.5, 38.6, 30.6, 30.3, 26.1, 26.1, 26.1.

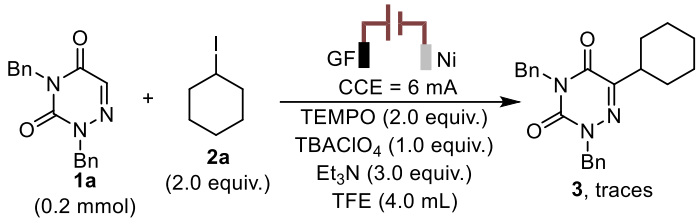
HRMS (ESI, m/z) calcd for $C_{25}H_{27}N_3O_4Na$ $[M+Na]^+$: 456.1899, found; 456.1891.

Procedure for scale up reaction



A dry 50 mL RB equipped with a teflon-coated magnetic stir bar was charged with azauracil **1a** (2.0 mmol) and tetrabutylammonium perchlorate (2.0 mmol) followed by addition of trifluoroethanol (15 mL). Then alkyl iodide **2a** (2.0 equiv.) and triethylamine (3.0 equiv.) was added sequentially and electrolyzed at a constant current of 12 mA. After complete conversion (in 50 hours) of the substrate **1a** (indicated by TLC), the electrodes were taken out and washed twice by sonicating in dichloromethane for 5 min. The solvents were combined and concentrated on a rotatory evaporator. The crude mixture was then purified *via* silica gel column chromatography using a mixture of *n*-hexane : ethyl acetate as eluent to provide the product **13** (308.2 mg, 54%).

5. Radical Quenching Experiment

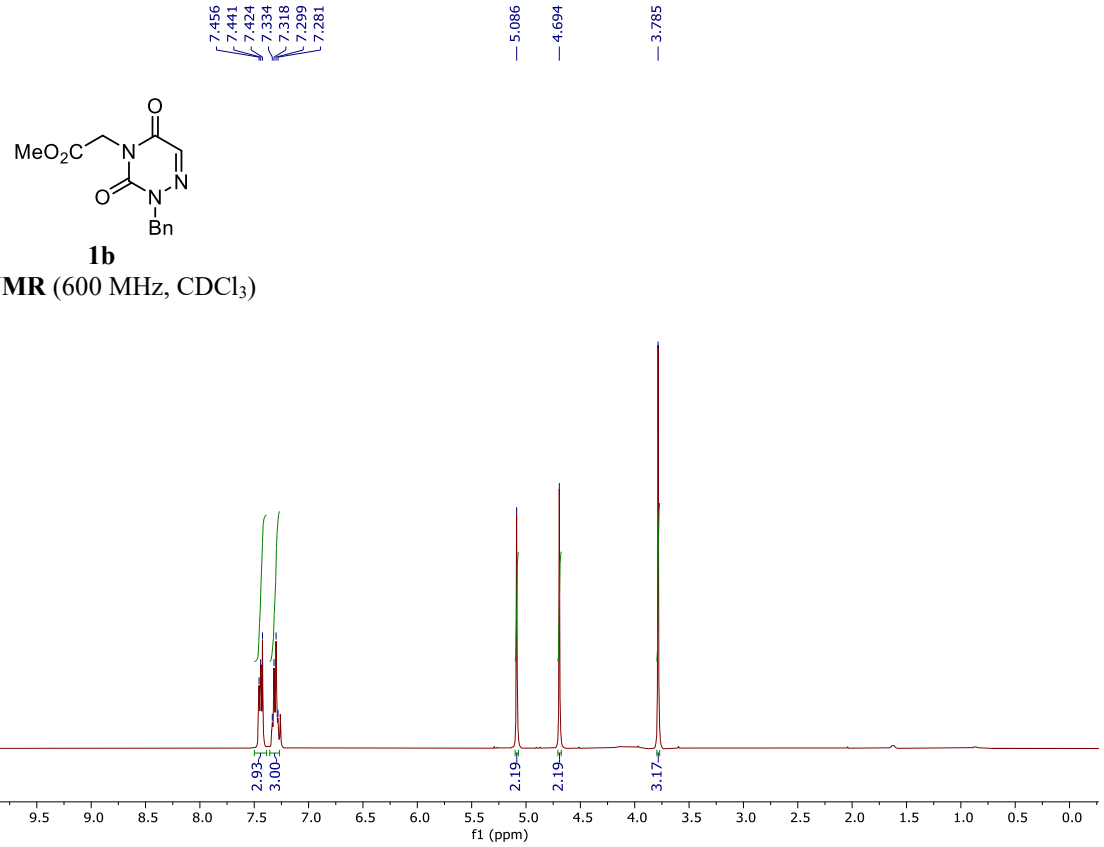


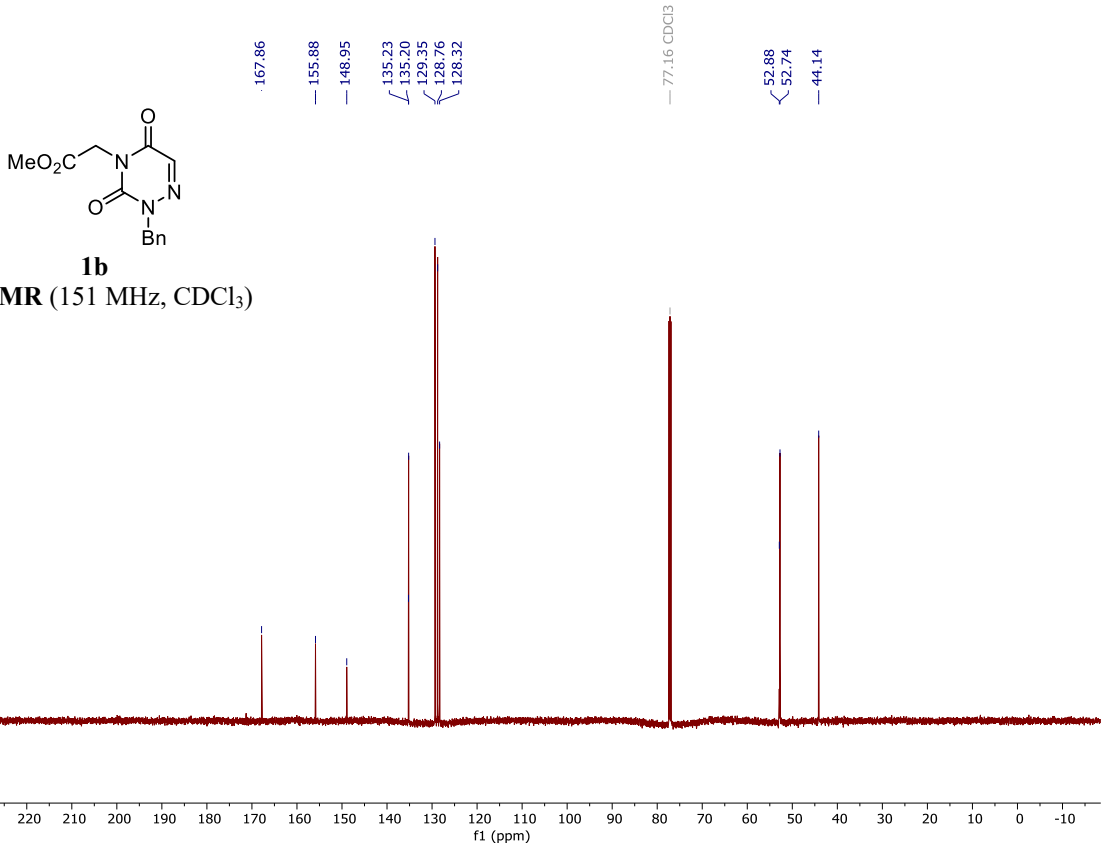
A dry 10 mL vial equipped with a teflon-coated magnetic stir bar was charged with azauracil **1a** (0.2 mmol), TEMPO (0.4 mmol, 2.0 equiv.) and tetrabutylammonium perchlorate (0.2 mmol, 1.0 equiv.) followed by addition of trifluoroethanol (4.0 mL). Then alkyl iodide **2a** (2.0 equiv.) and triethylamine (3.0 equiv.) was added sequentially and electrolyzed at a constant current of 6 mA. After electrolysing the reaction for 22 hours the product was formed only in trace amount.

6. References

1. (a) K. Sun, A. Shi, Y. Liu, X. Chen, P. Xiang, X. Wang, L. Qua, B. Yu, *Chem. Sci.,* 2022, **13**, 5659; (b) R. K. Samanta, P. Meher and S. Murarka, *J. Org. Chem.,* 2022, **87**, 10947.
2. S. K. Hota and S. Murarka, *Chem. Asian J.,* 2024, **19**, e202301027.

7. NMR Spectra



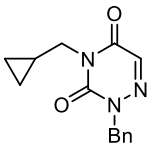


1b

^{1}H NMR (600 MHz, $CDCl_3$)

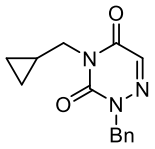
1b

^{13}C NMR (151 MHz, $CDCl_3$)



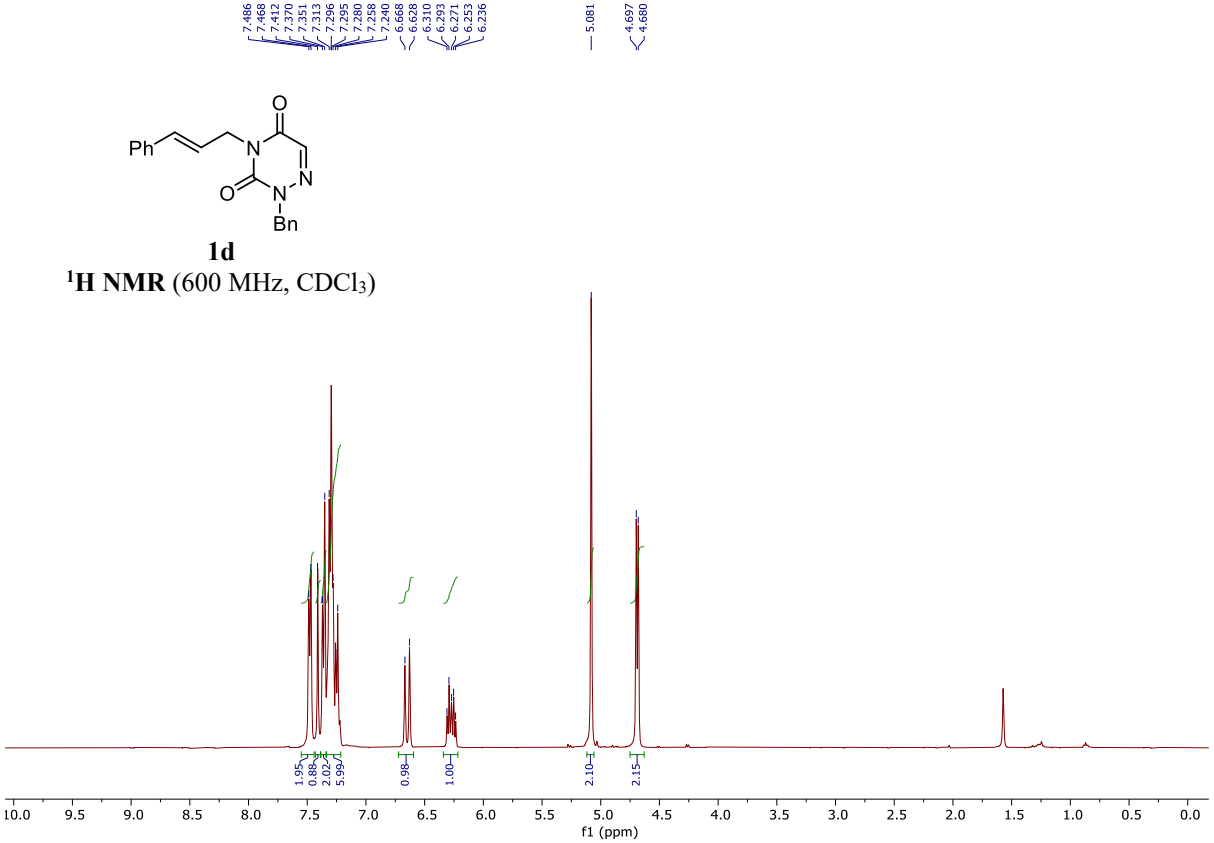
1c

^{1}H NMR (600 MHz, $CDCl_3$)



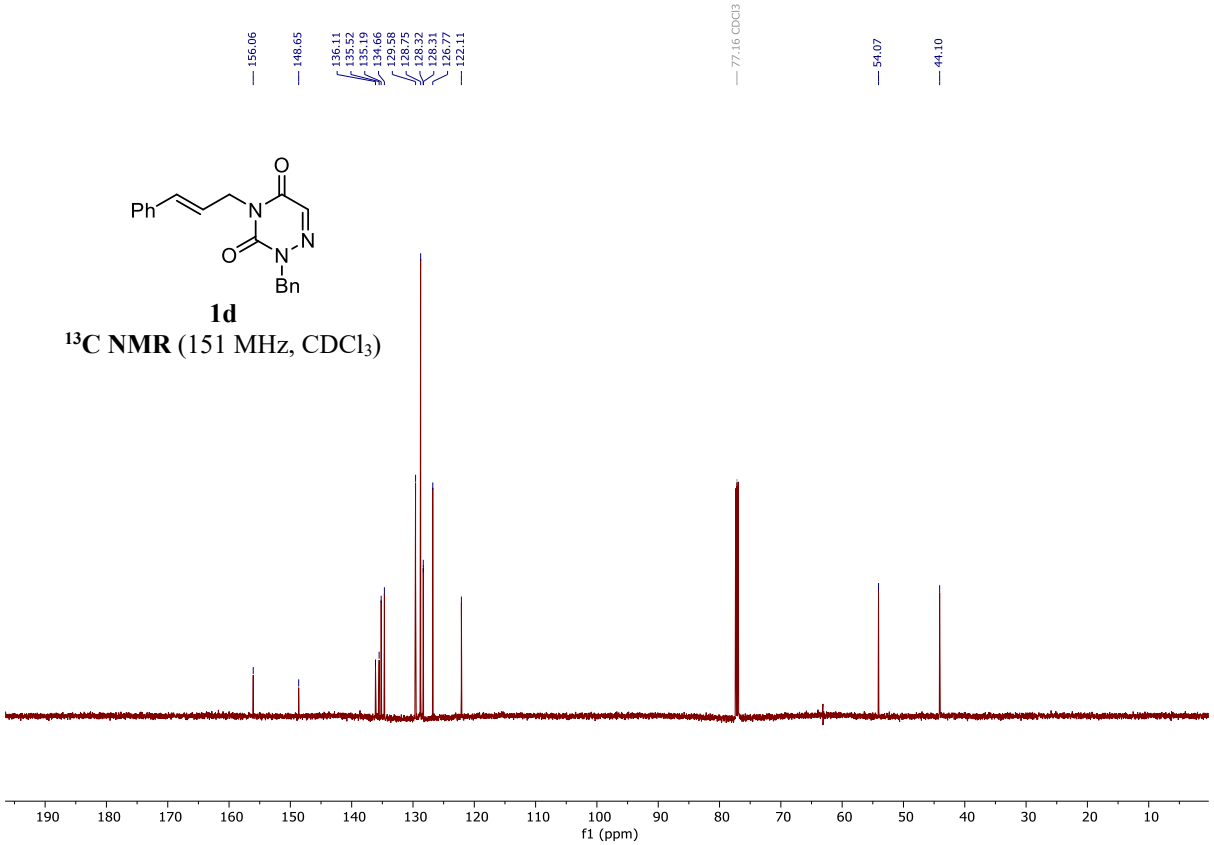
1c

^{13}C NMR (151 MHz, $CDCl_3$)



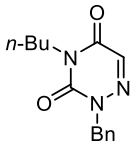
1d

^{1}H NMR (600 MHz, $CDCl_3$)



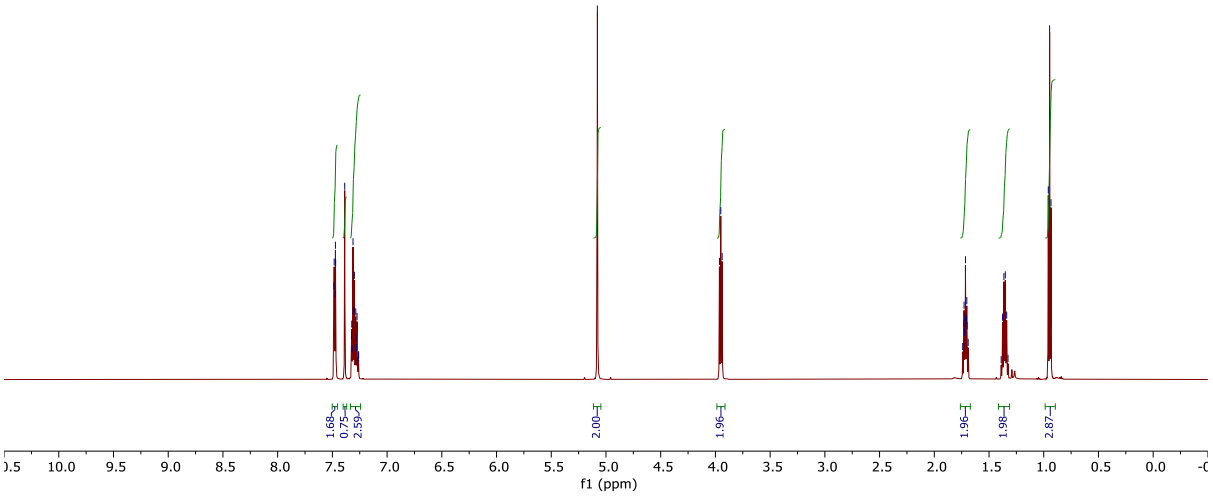
1d

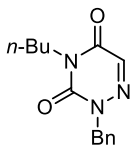
^{13}C NMR (151 MHz, $CDCl_3$)



1e

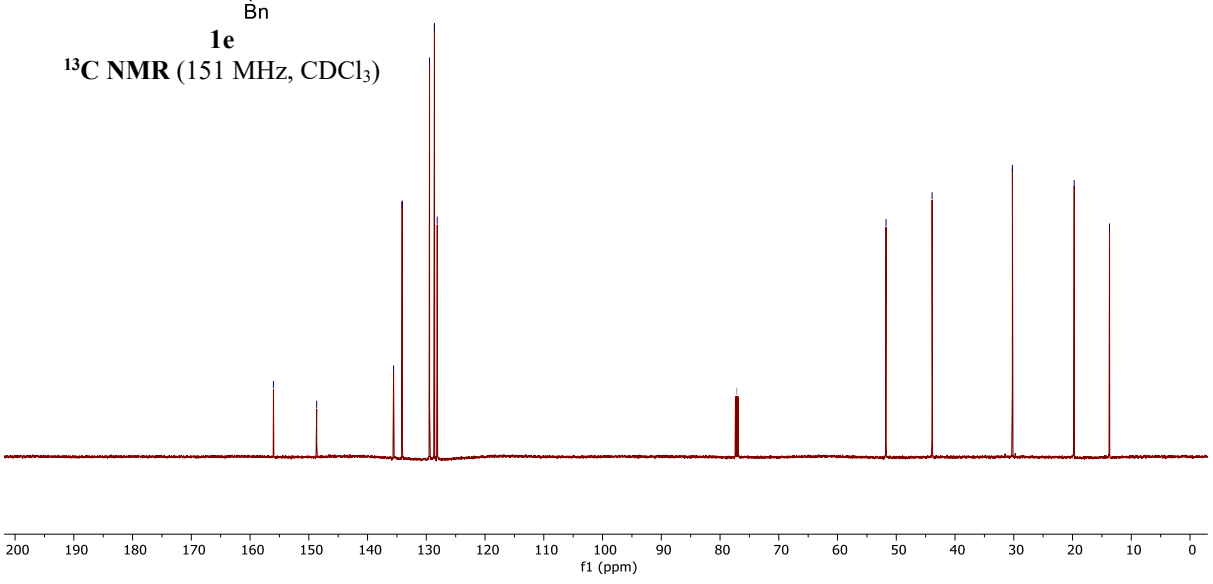
^{1}H NMR (600 MHz, $CDCl_3$)

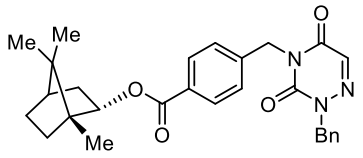




1e

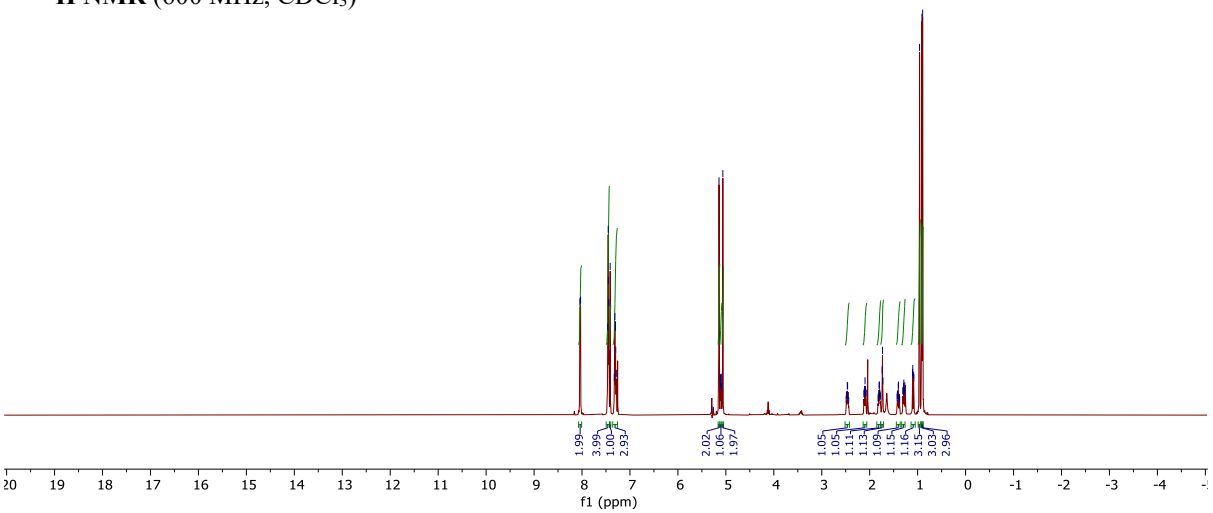
^{13}C NMR (151 MHz, $CDCl_3$)

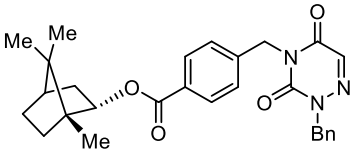




1f

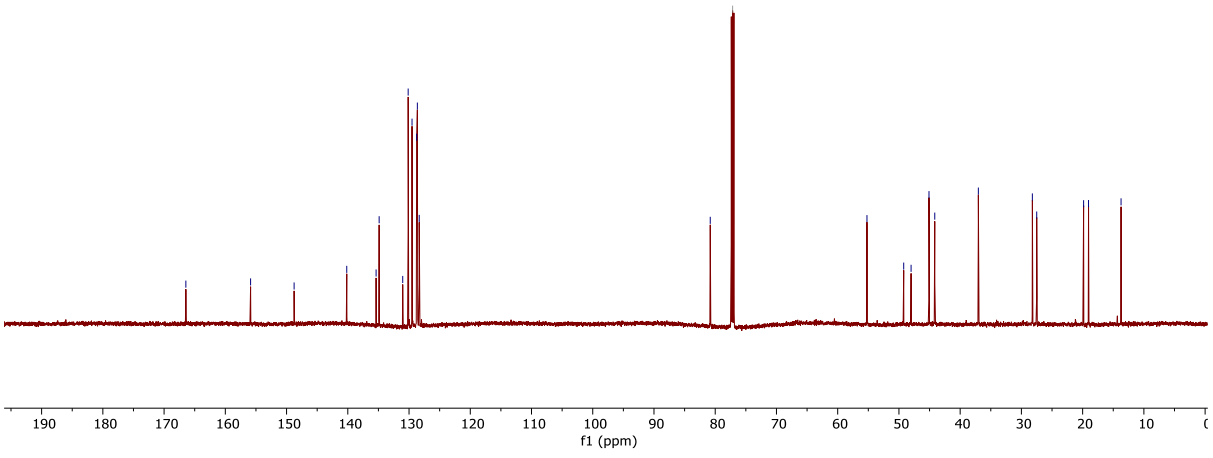
^{1}H NMR (600 MHz, $CDCl_3$)

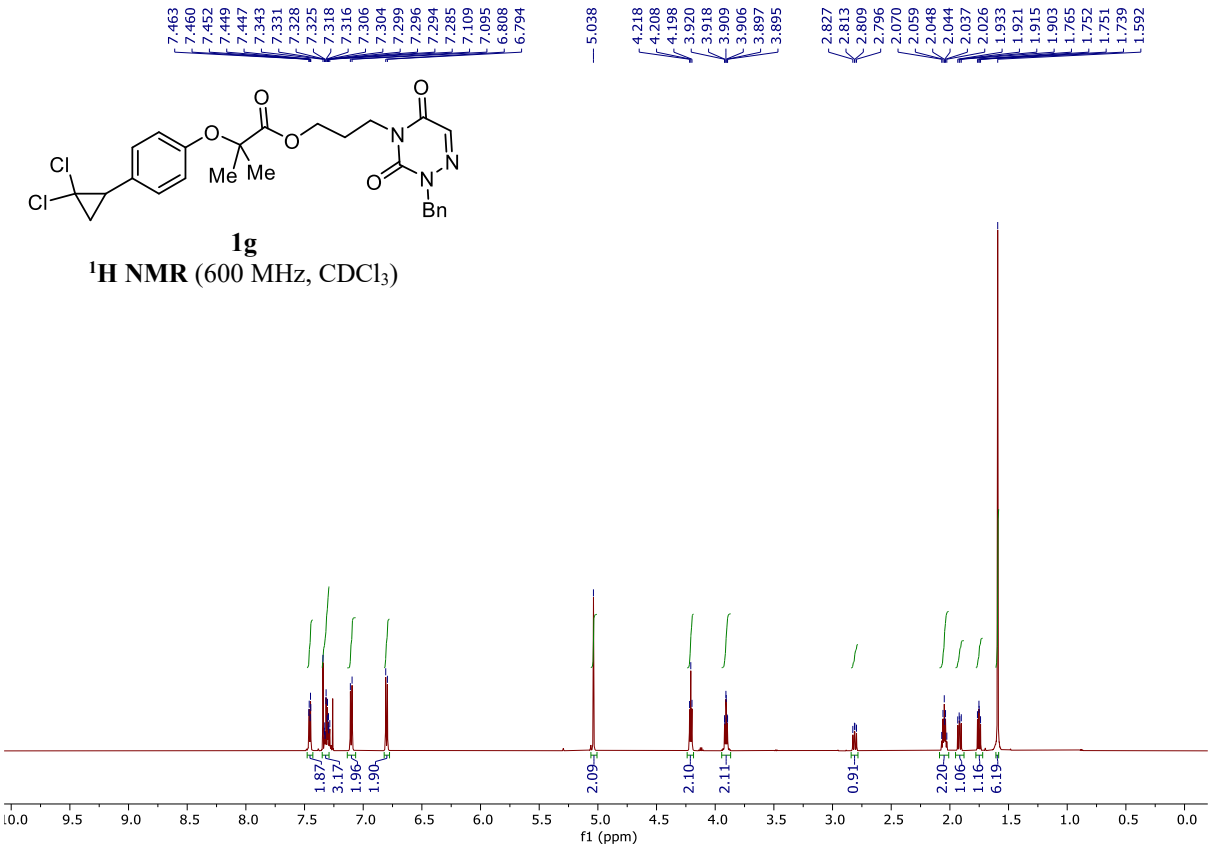




1f

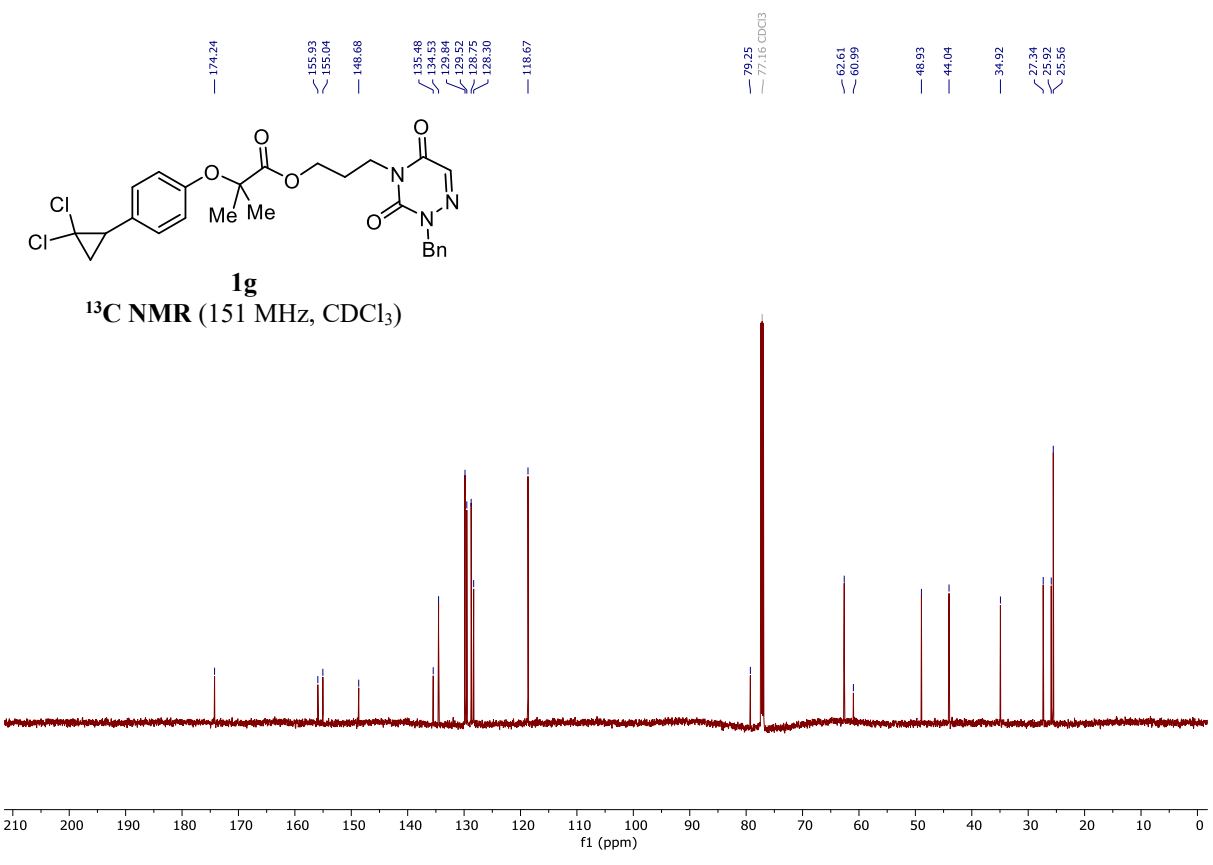
^{13}C NMR (151 MHz, $CDCl_3$)





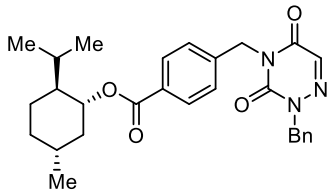
1g

^{1}H NMR (600 MHz, $CDCl_3$)



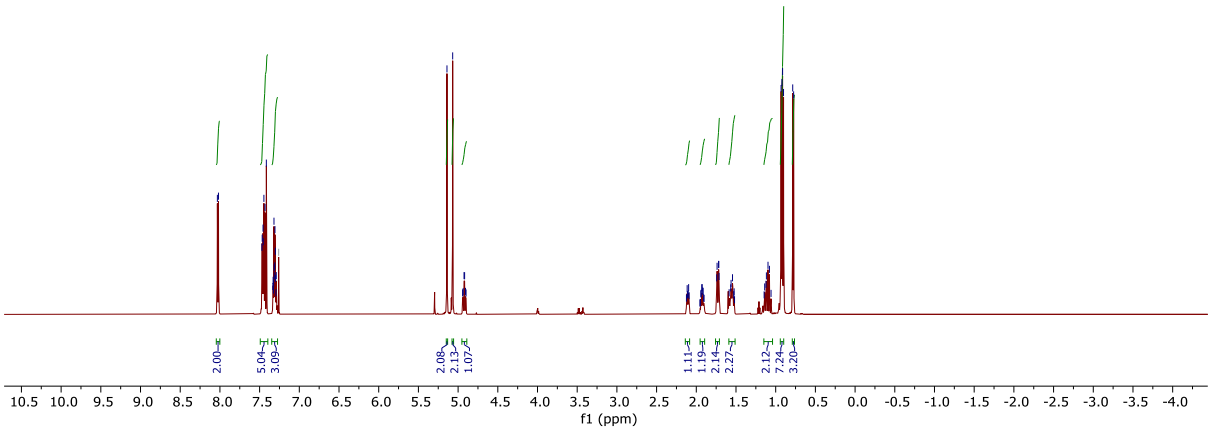
1g

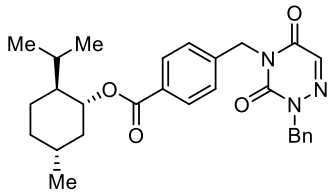
^{13}C NMR (151 MHz, $CDCl_3$)



1h

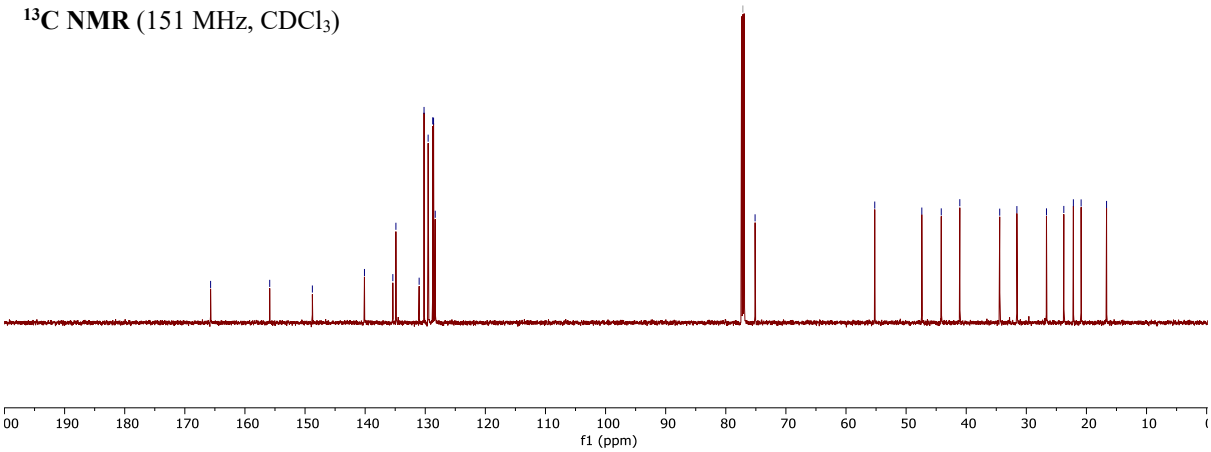
^{1}H NMR (600 MHz, $CDCl_3$)

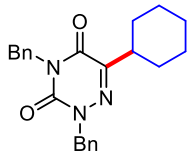




1h

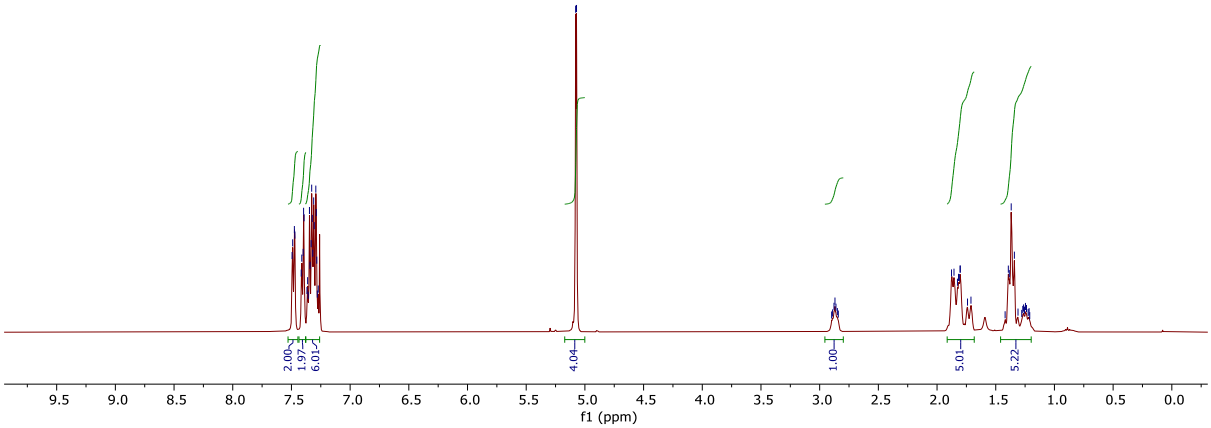
^{13}C NMR (151 MHz, $CDCl_3$)

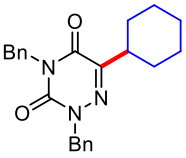




3

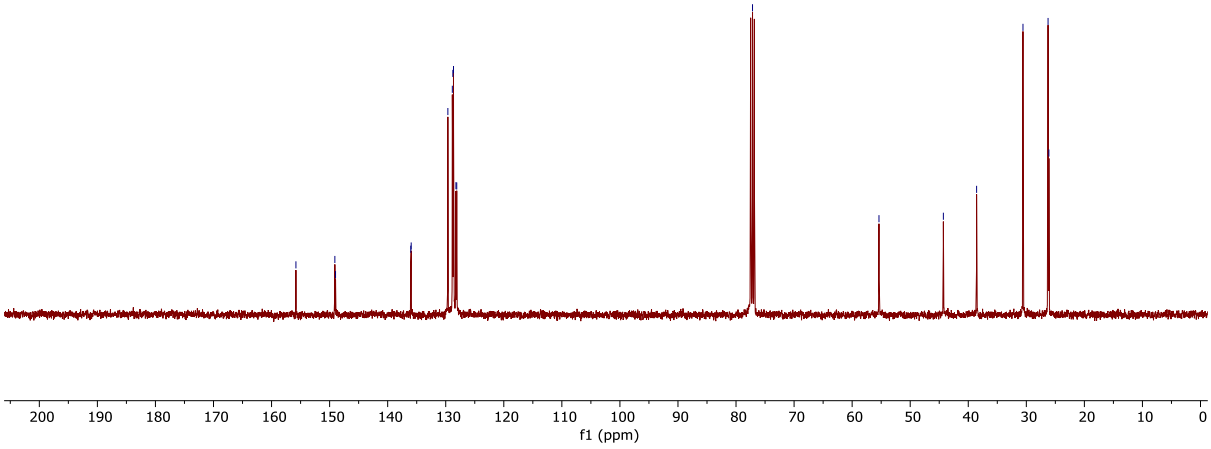
^{1}H NMR (400 MHz, $CDCl_3$)

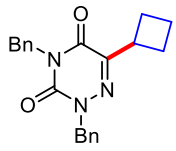




4

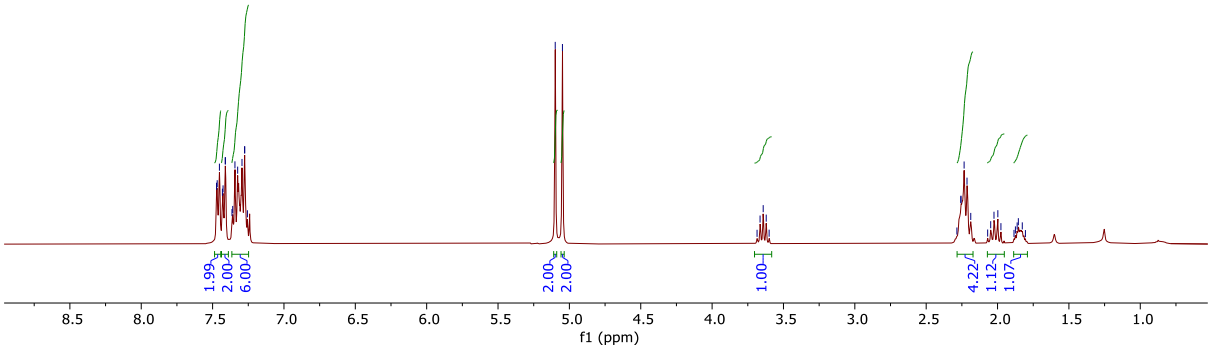
^{13}C NMR (101 MHz, $CDCl_3$)

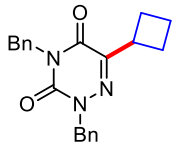




4

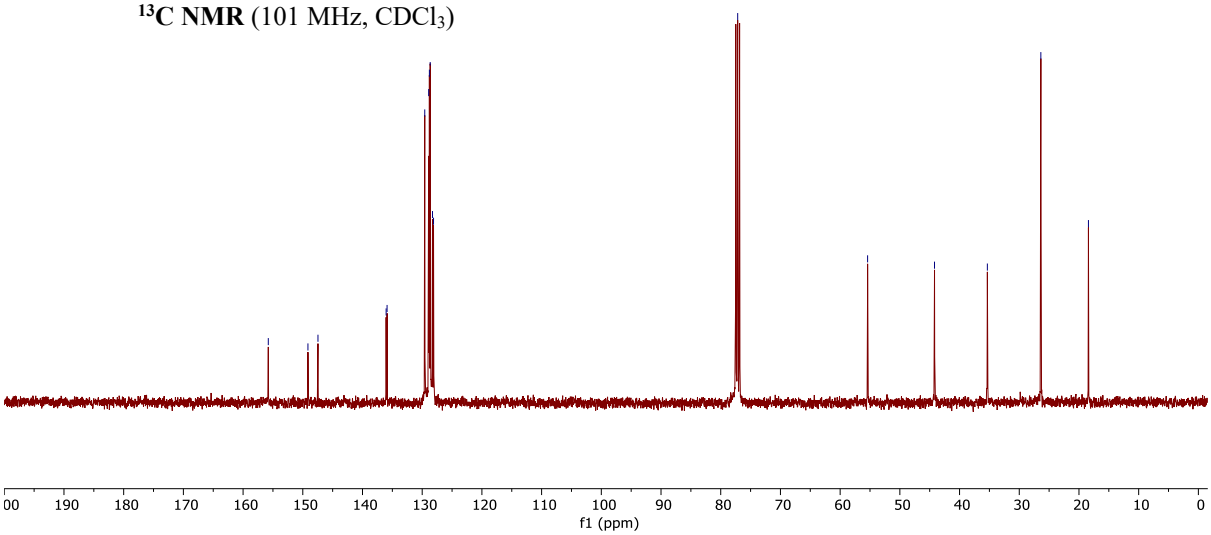
^{1}H NMR (400 MHz, $CDCl_3$)

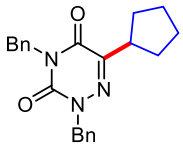




4

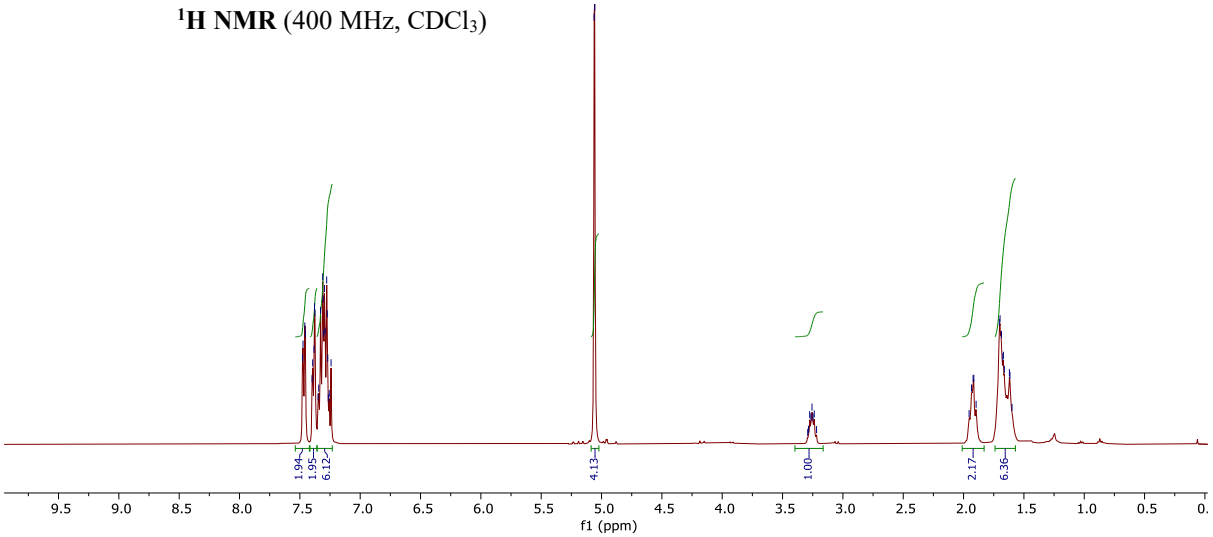
^{13}C NMR (101 MHz, $CDCl_3$)

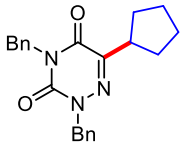




5

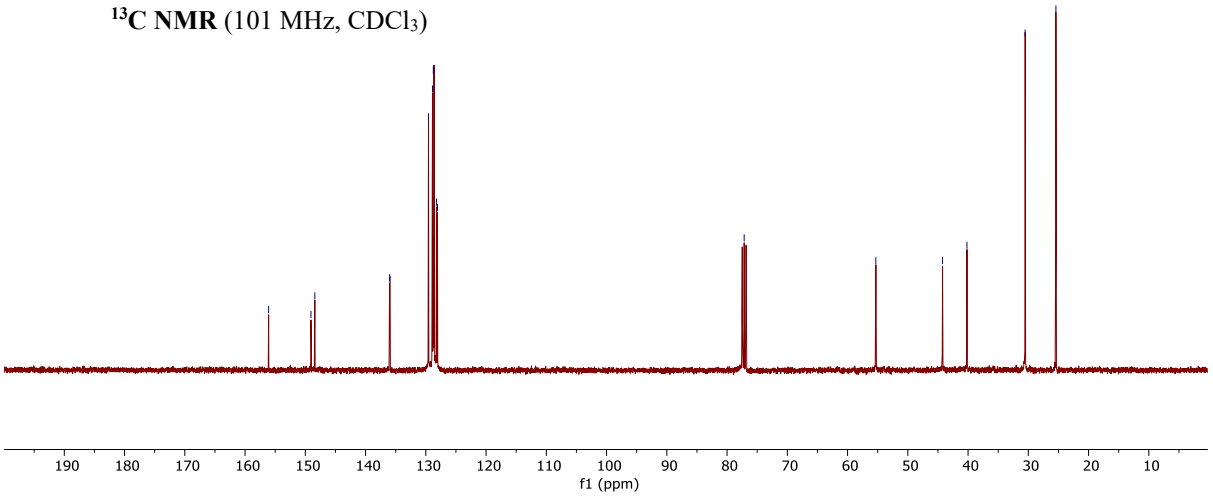
^{1}H NMR (400 MHz, $CDCl_3$)

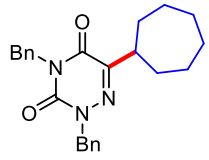




5

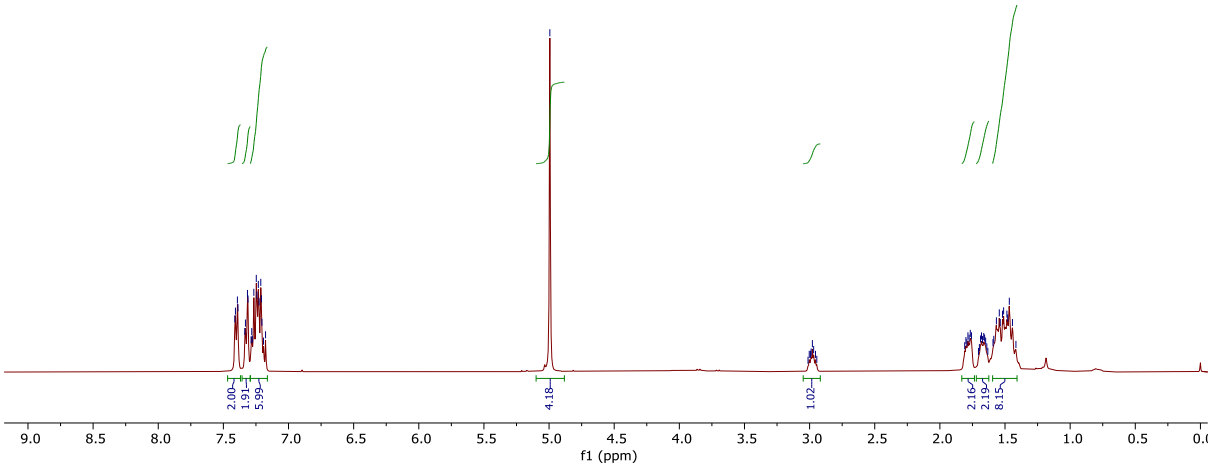
^{13}C NMR (101 MHz, $CDCl_3$)

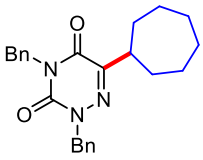




6

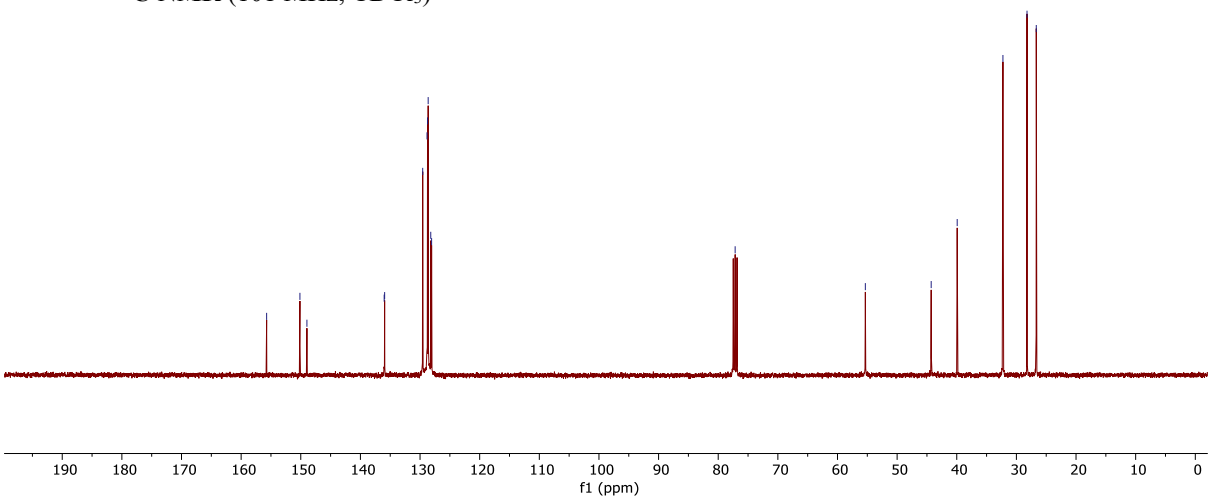
^{1}H NMR (400 MHz, $CDCl_3$)

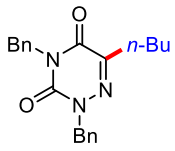




6

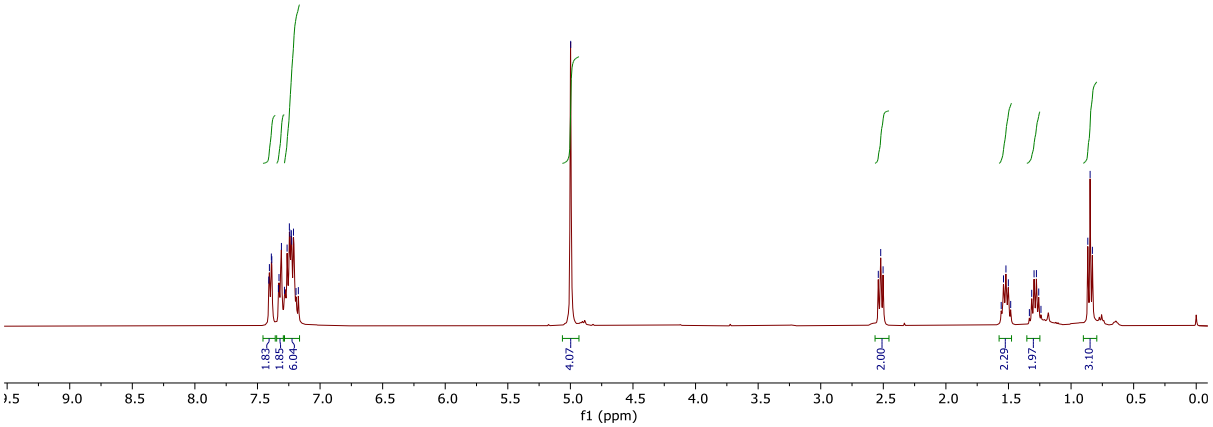
^{13}C NMR (101 MHz, $CDCl_3$)

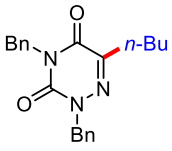




7

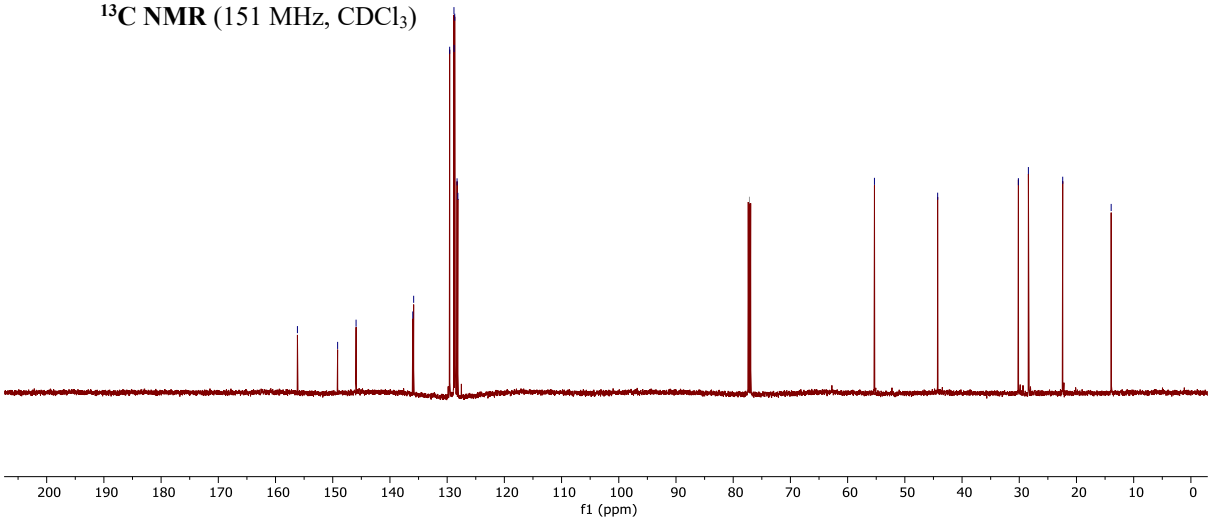
^{1}H NMR (400 MHz, $CDCl_3$)

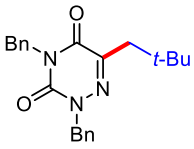




7

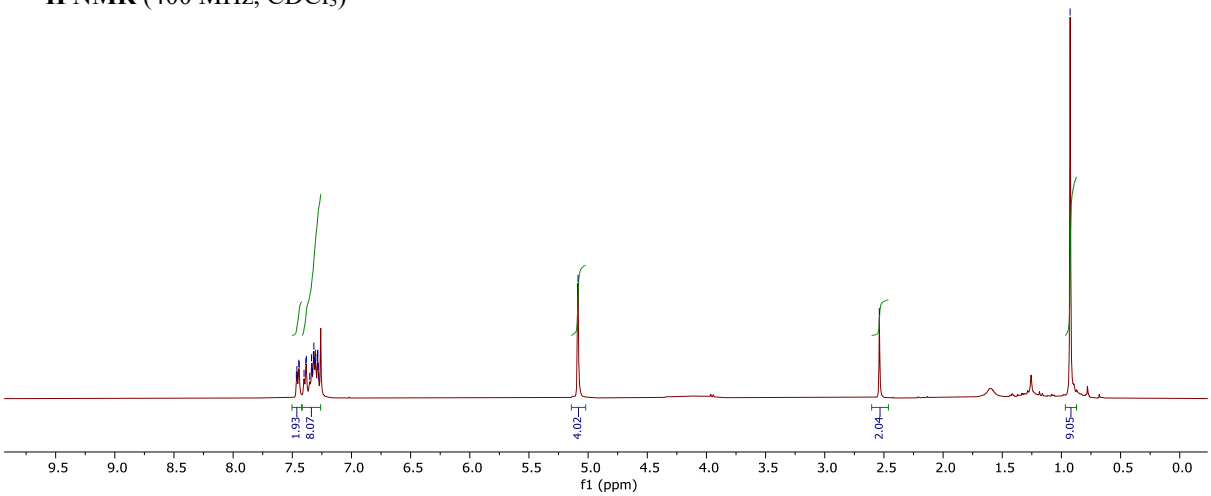
^{13}C NMR (151 MHz, $CDCl_3$)

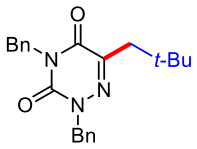




8

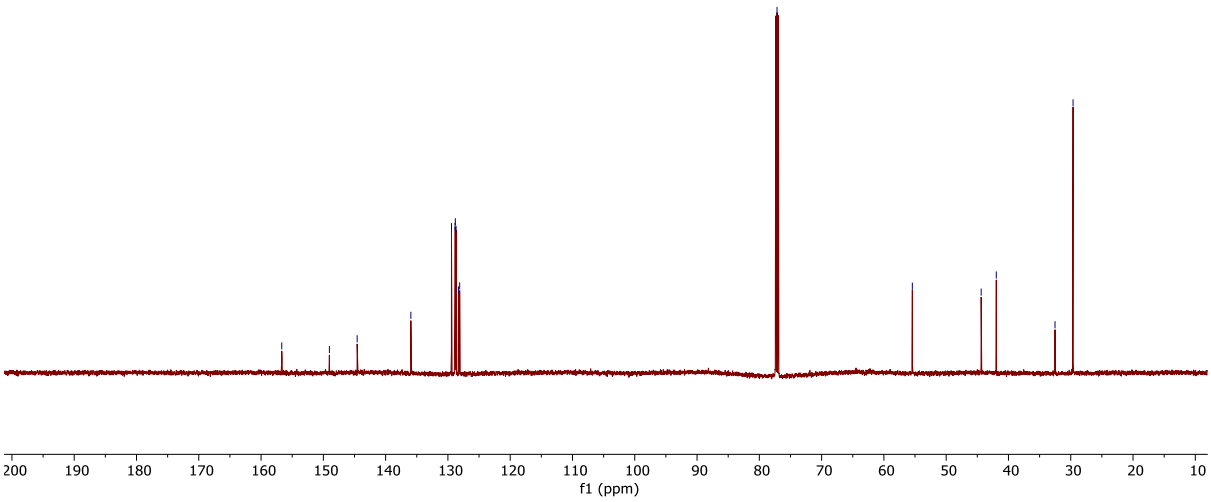
^{1}H NMR (400 MHz, $CDCl_3$)

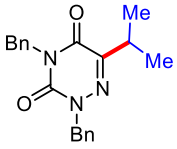




8

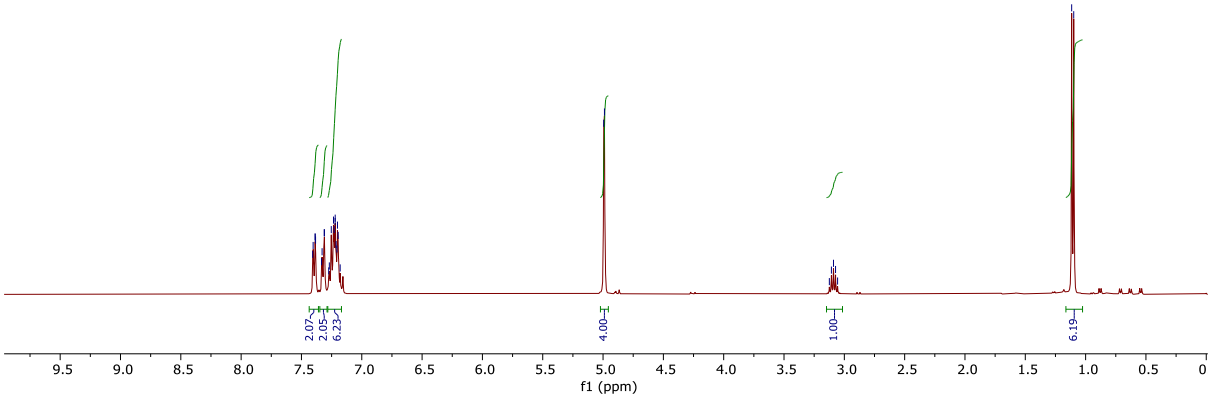
^{13}C NMR (151 MHz, $CDCl_3$)

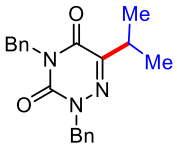




9

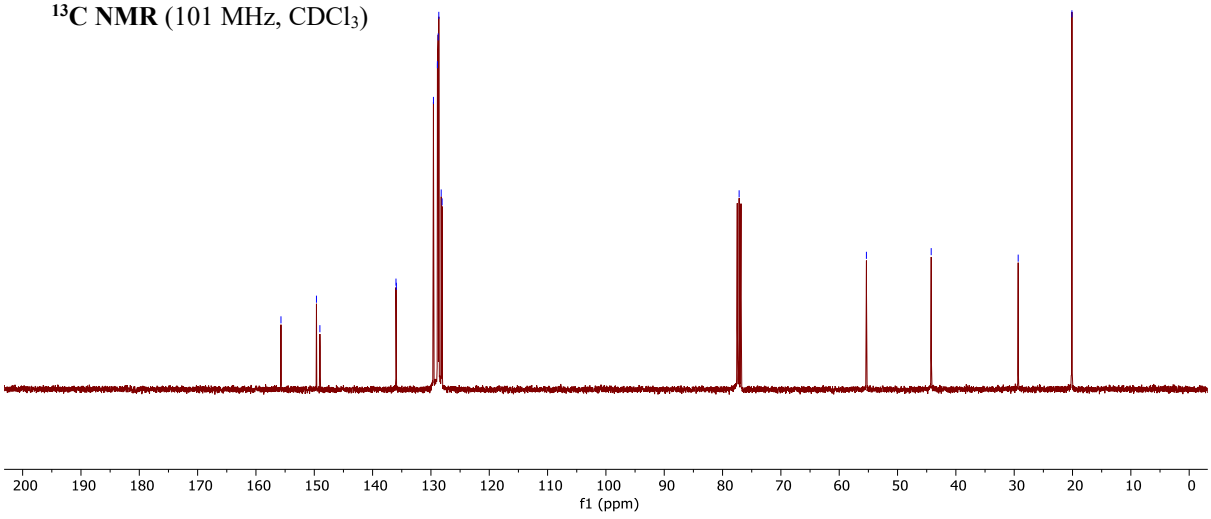
^{1}H NMR (400 MHz, $CDCl_3$)

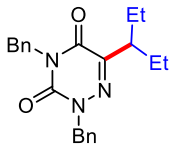




9

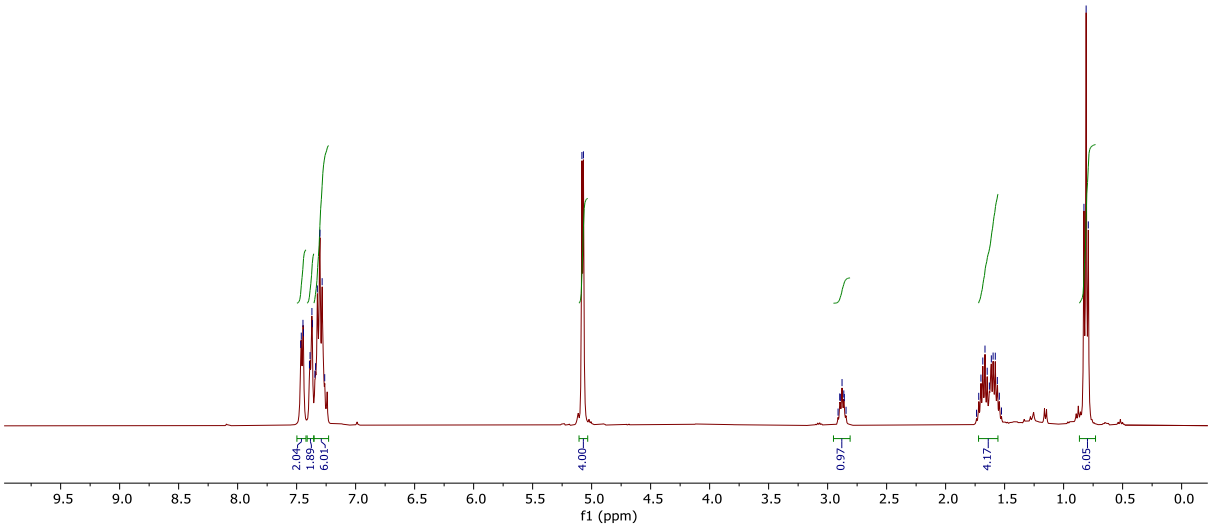
^{13}C NMR (101 MHz, $CDCl_3$)

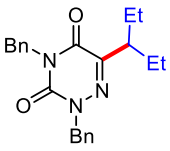




10

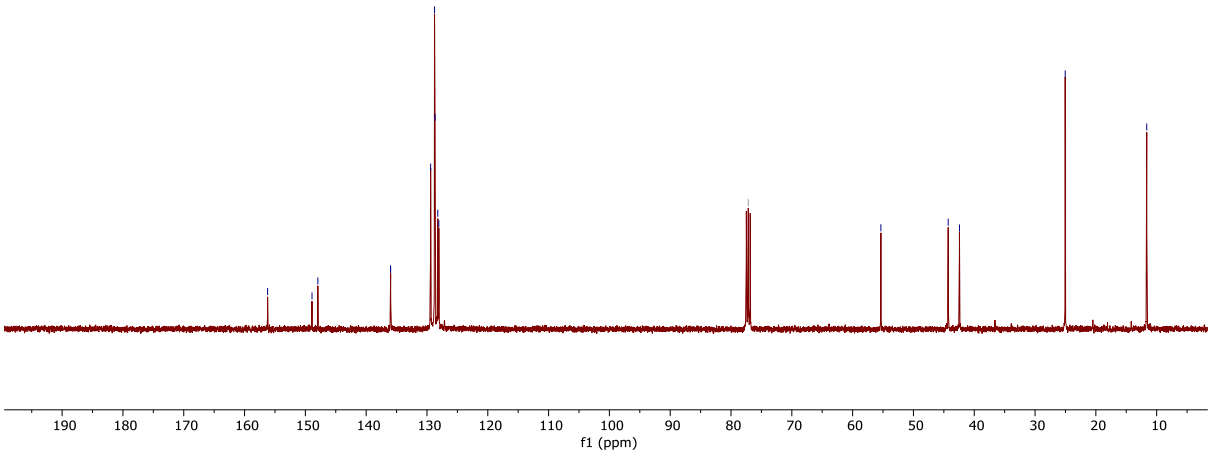
^{1}H NMR (400 MHz, $CDCl_3$)

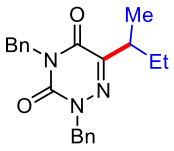




10

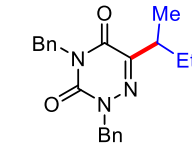
^{13}C NMR (101 MHz, $CDCl_3$)





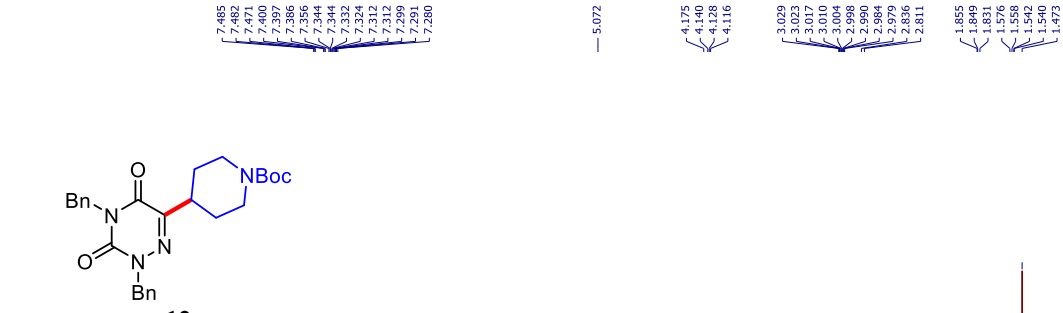
11

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



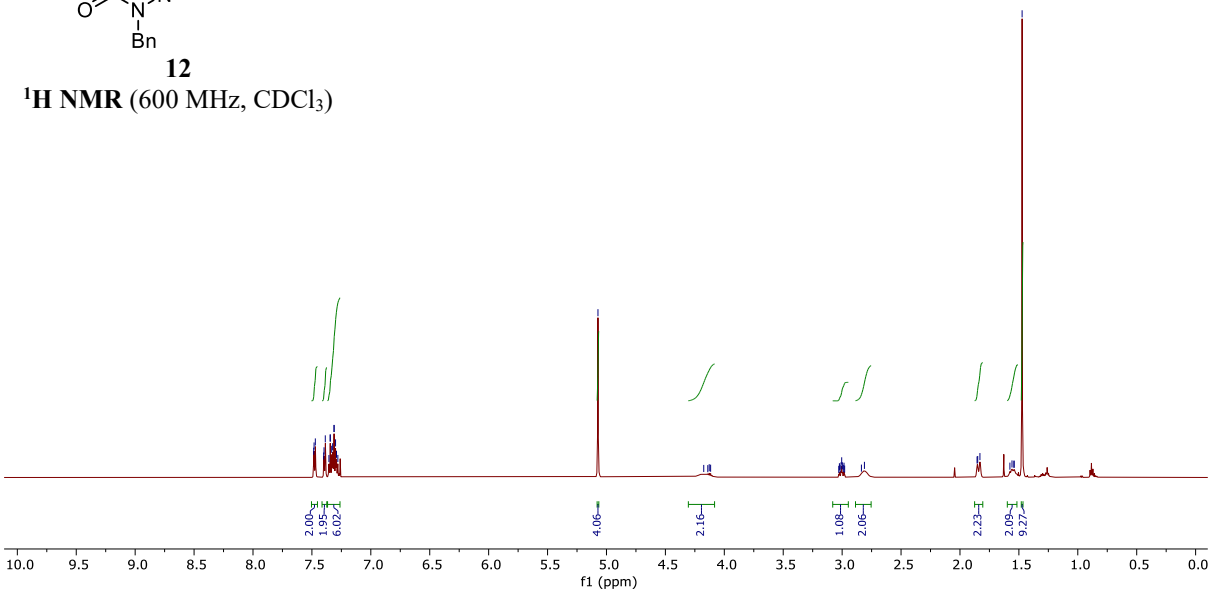
11

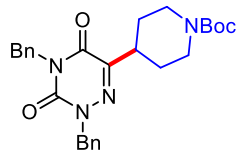
^{13}C NMR (101 MHz, $CDCl_3$)



12

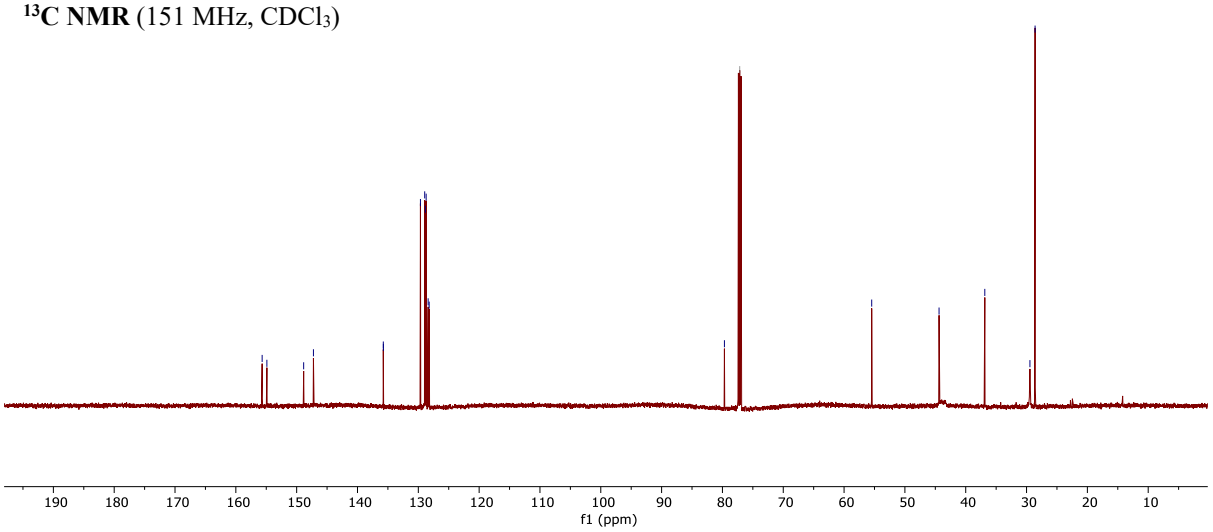
^{1}H NMR (600 MHz, $CDCl_3$)

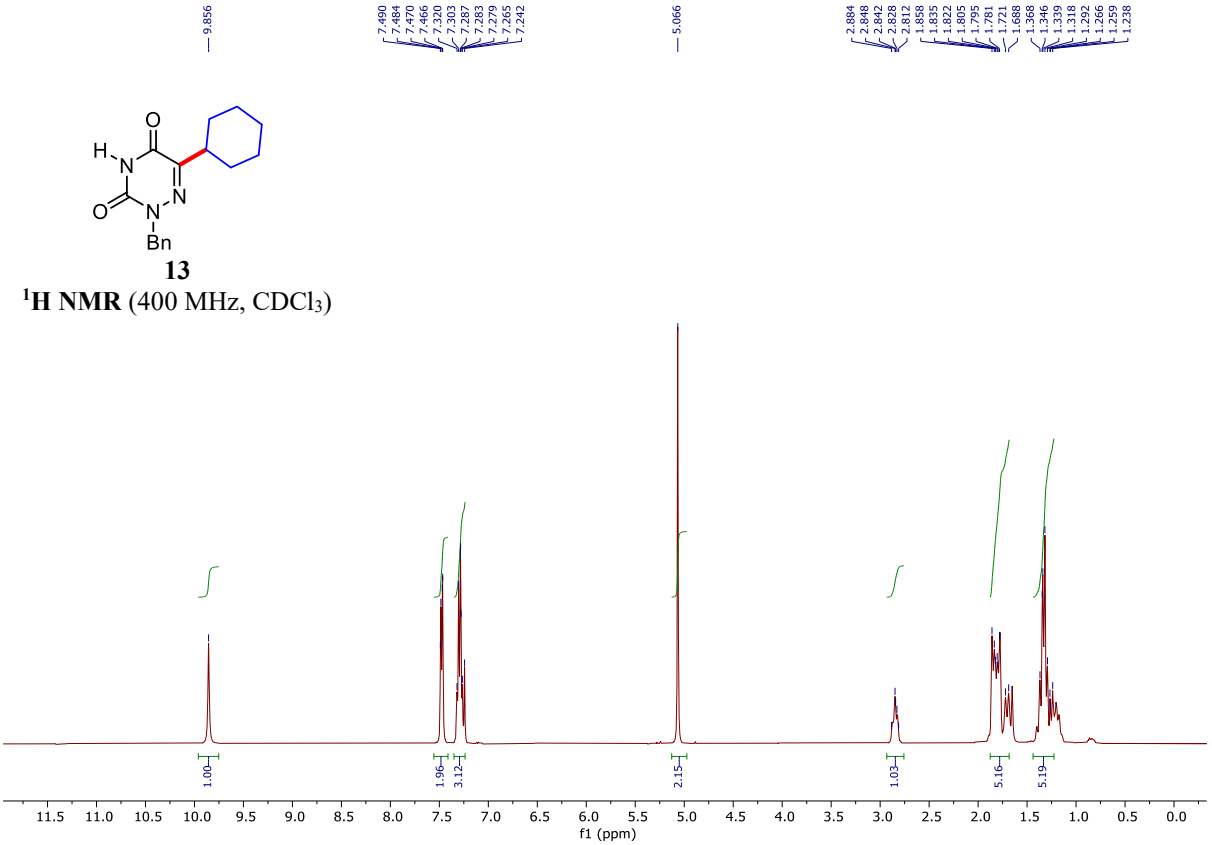




12

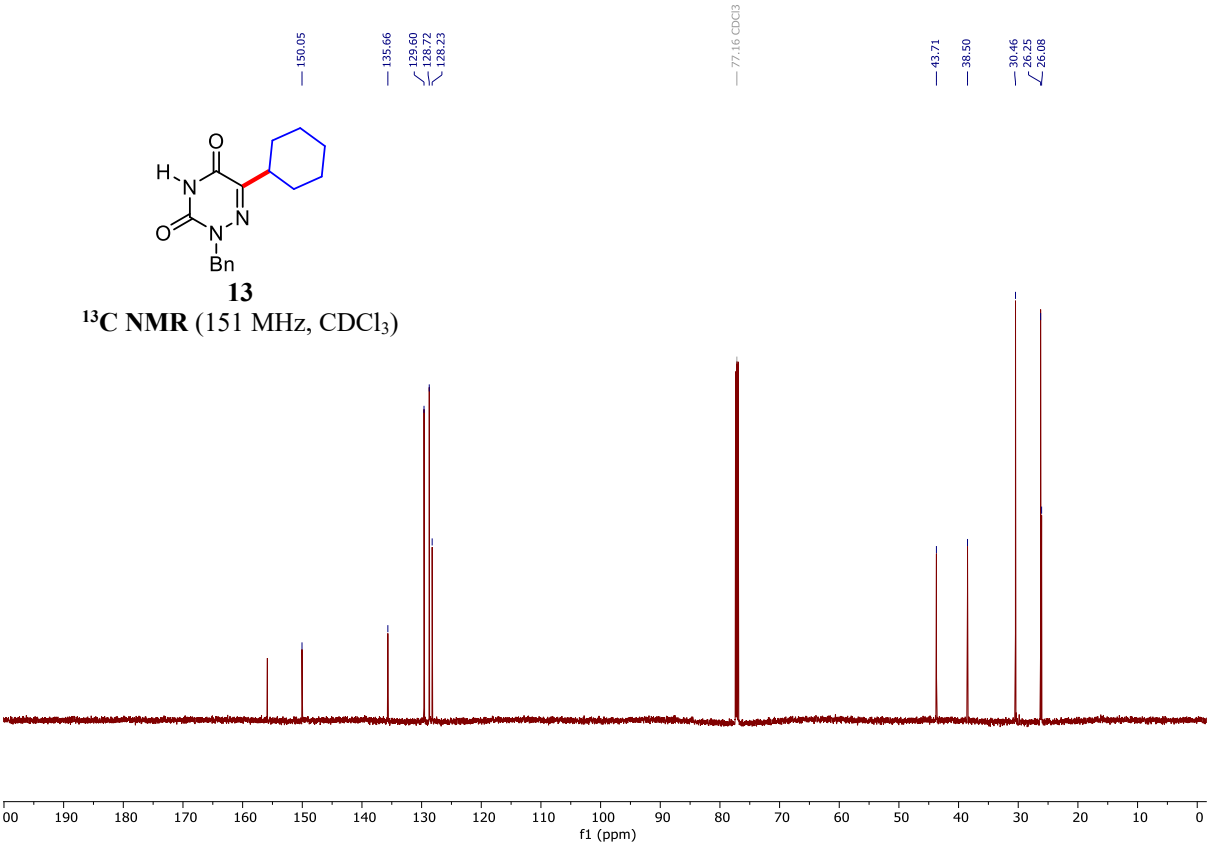
^{13}C NMR (151 MHz, $CDCl_3$)





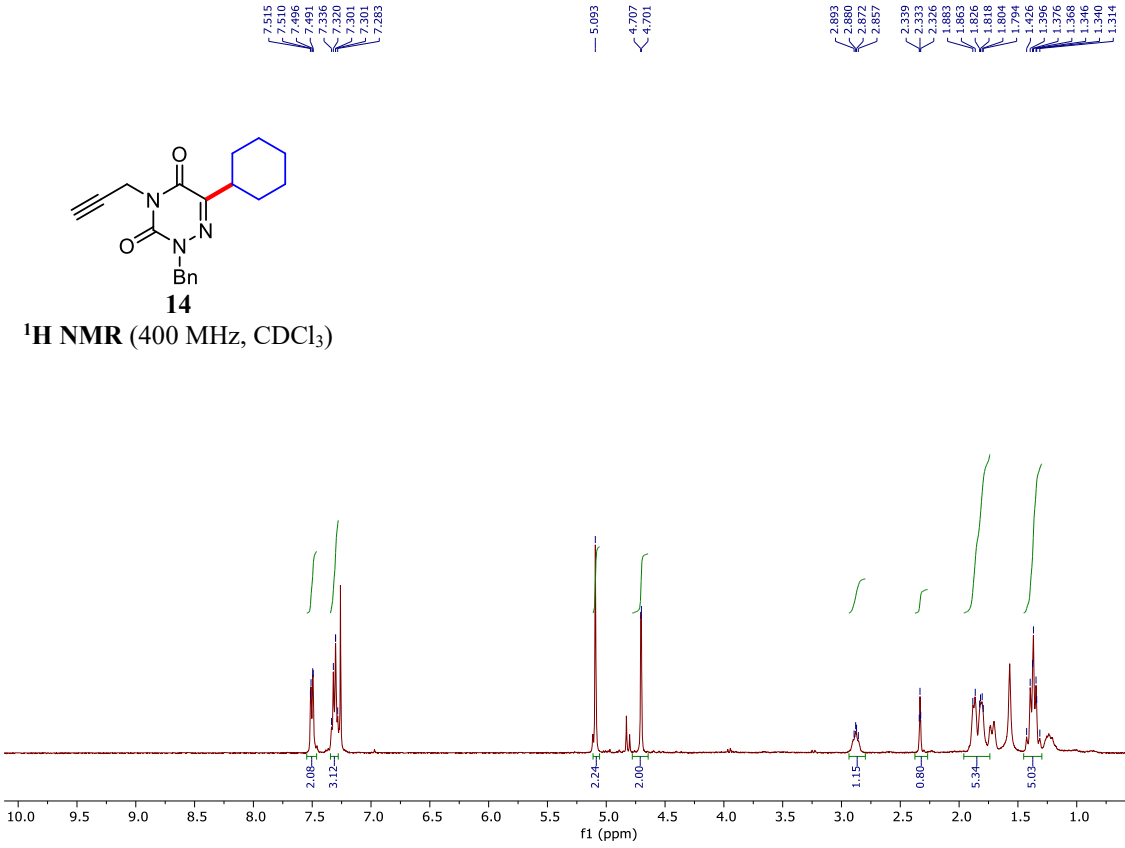
13

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



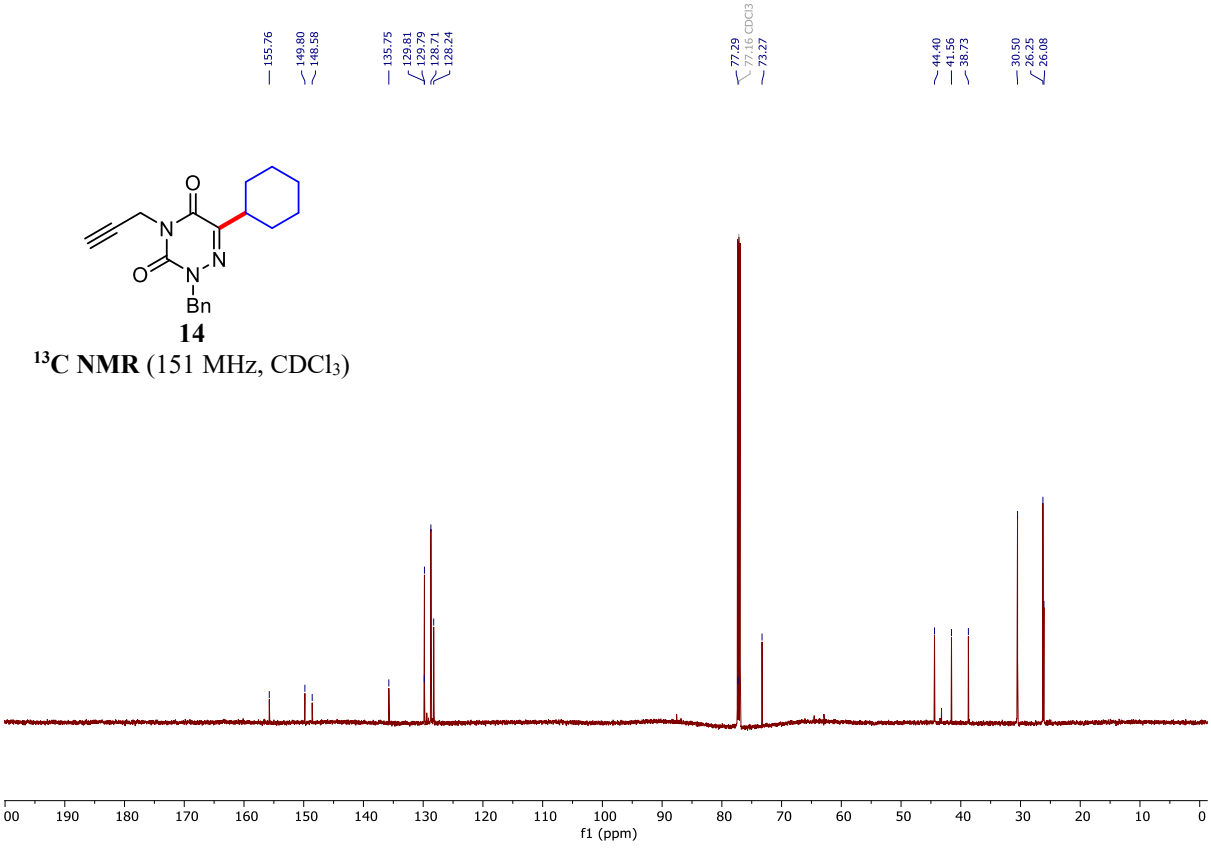
13

^{13}C NMR (151 MHz, $CDCl_3$)



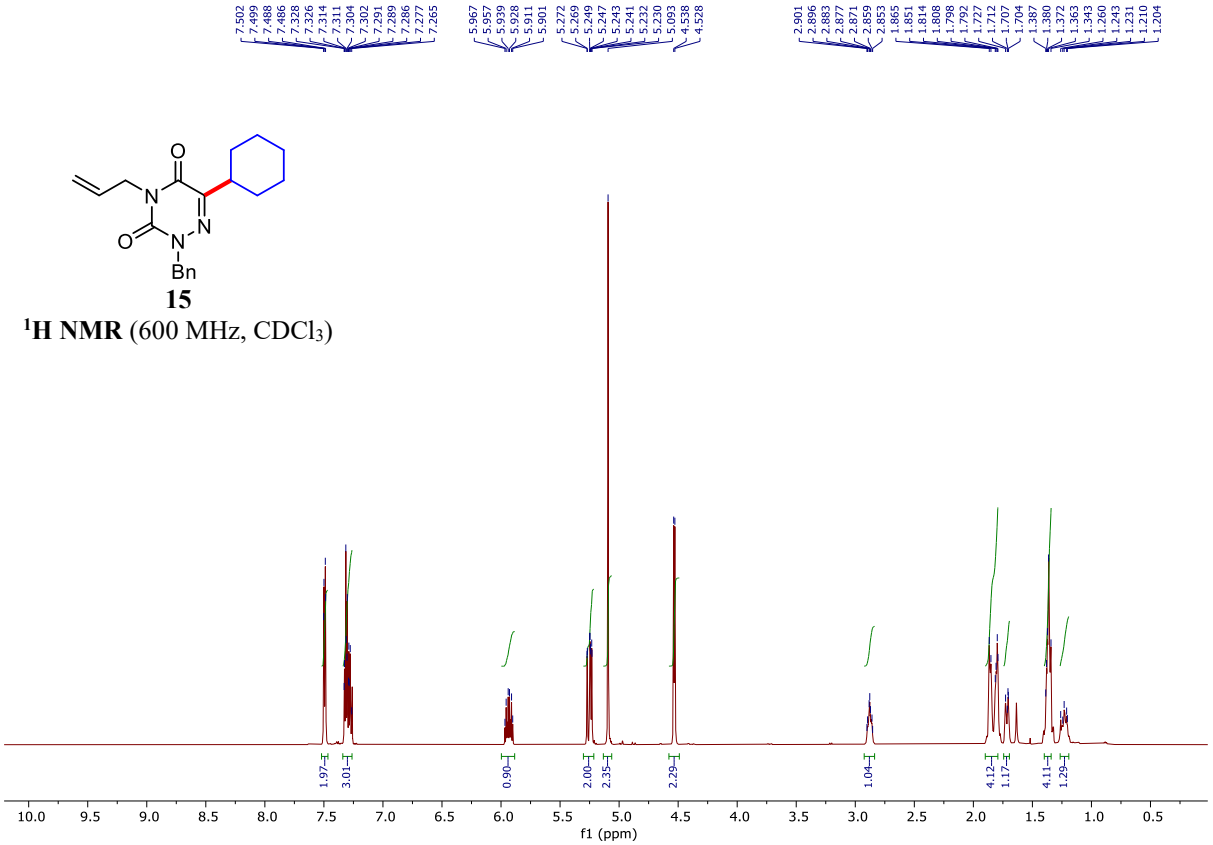
14

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



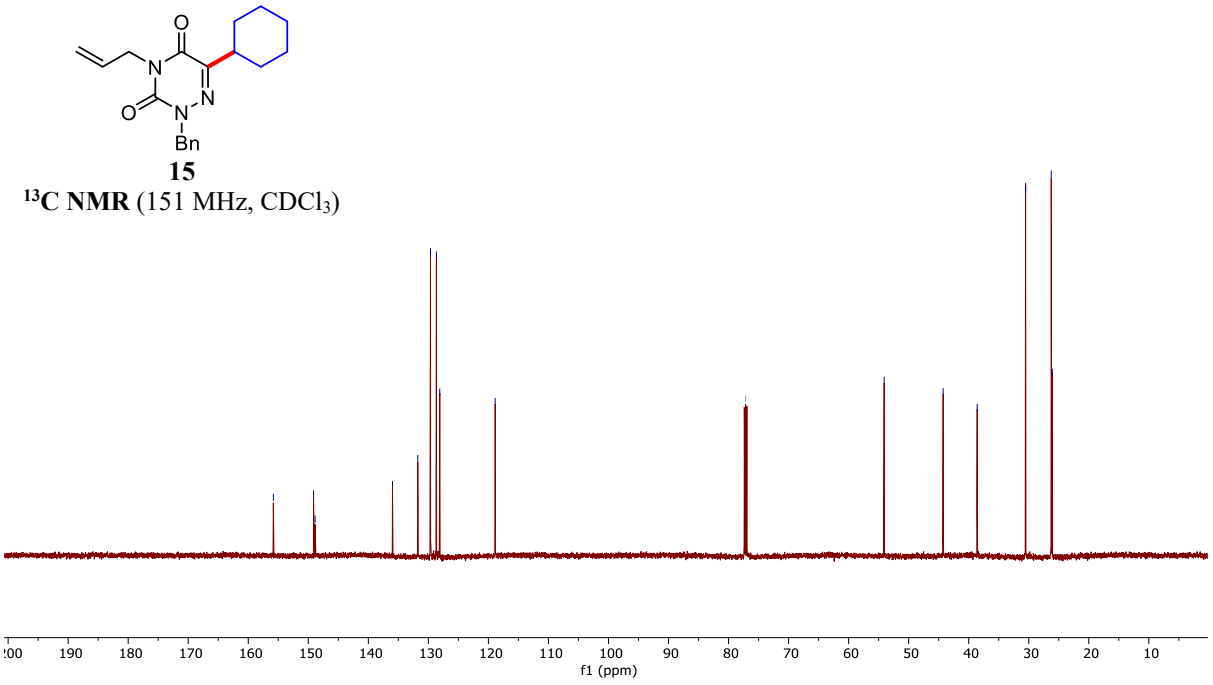
14

^{13}C NMR (151 MHz, $CDCl_3$)



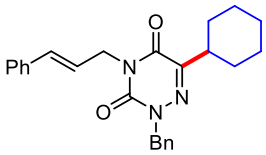
15

^{1}H NMR (600 MHz, $CDCl_3$)



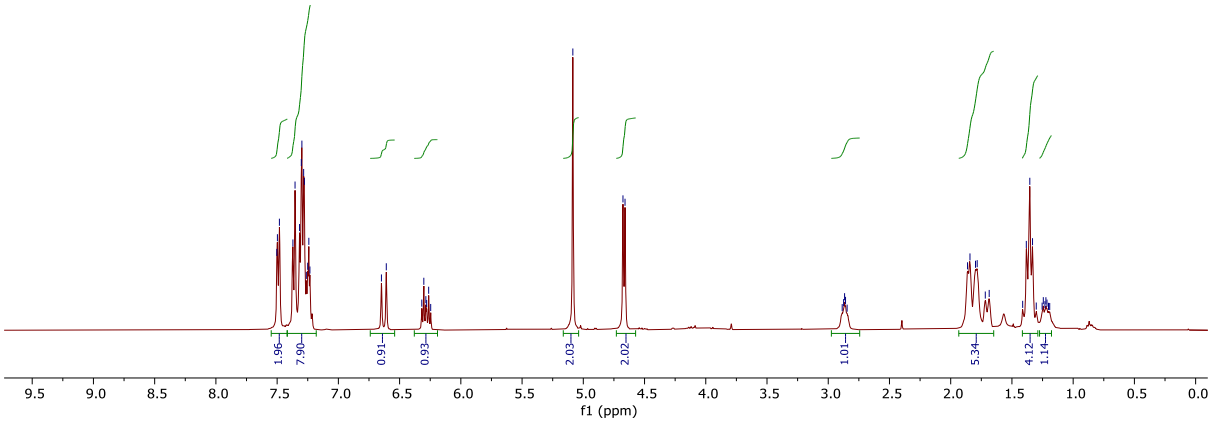
15

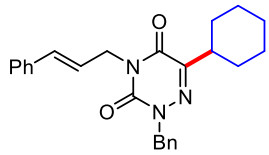
^{13}C NMR (151 MHz, $CDCl_3$)



16

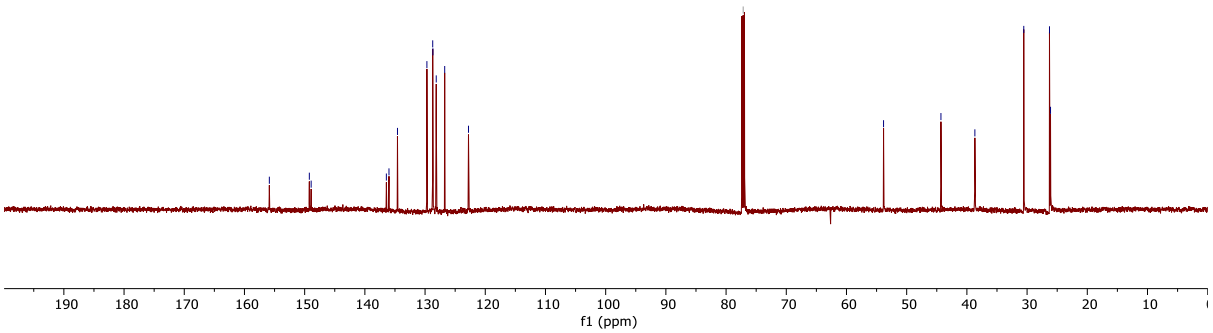
^{1}H NMR (400 MHz, $CDCl_3$)

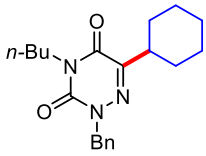




16

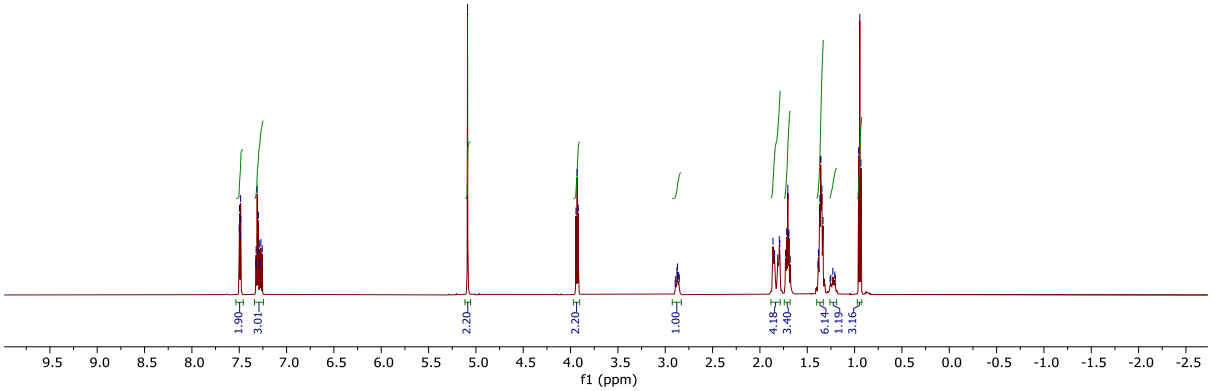
^{13}C NMR (151 MHz, $CDCl_3$)

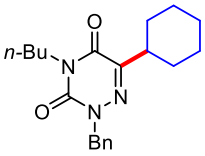




17

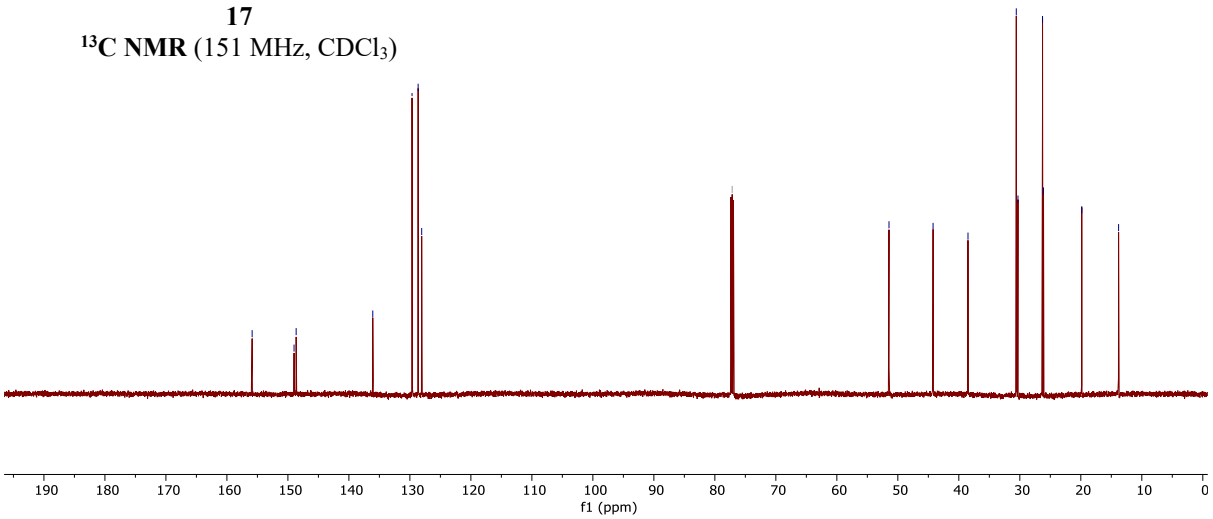
^{1}H NMR (400 MHz, $CDCl_3$)

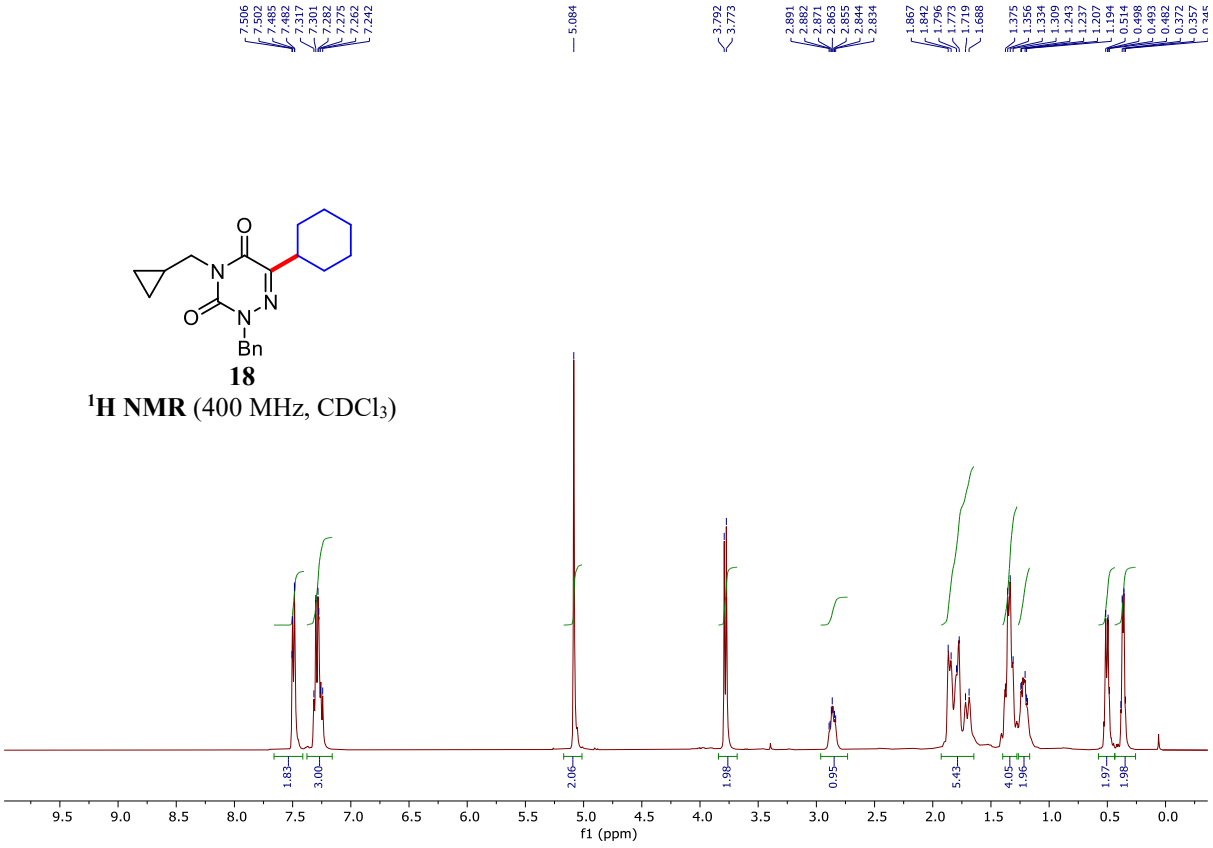




17

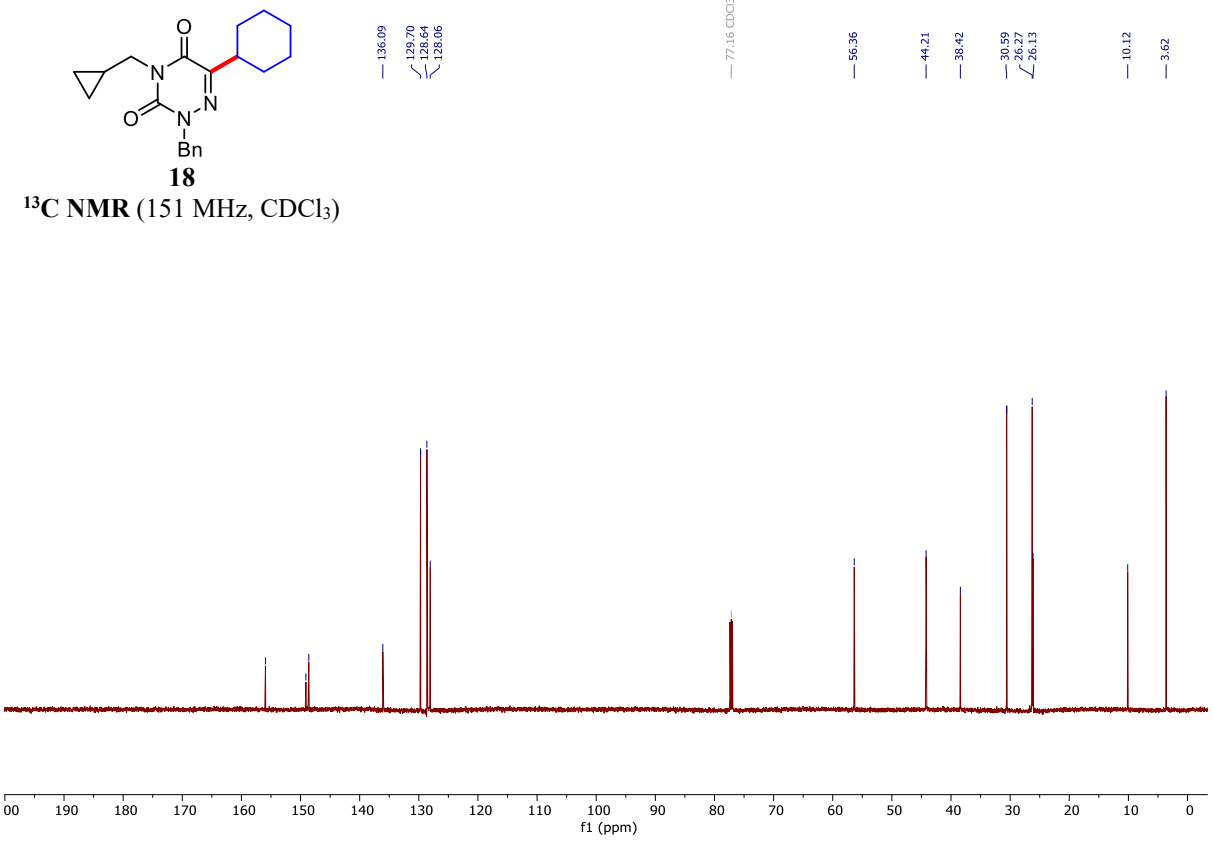
^{13}C NMR (151 MHz, $CDCl_3$)





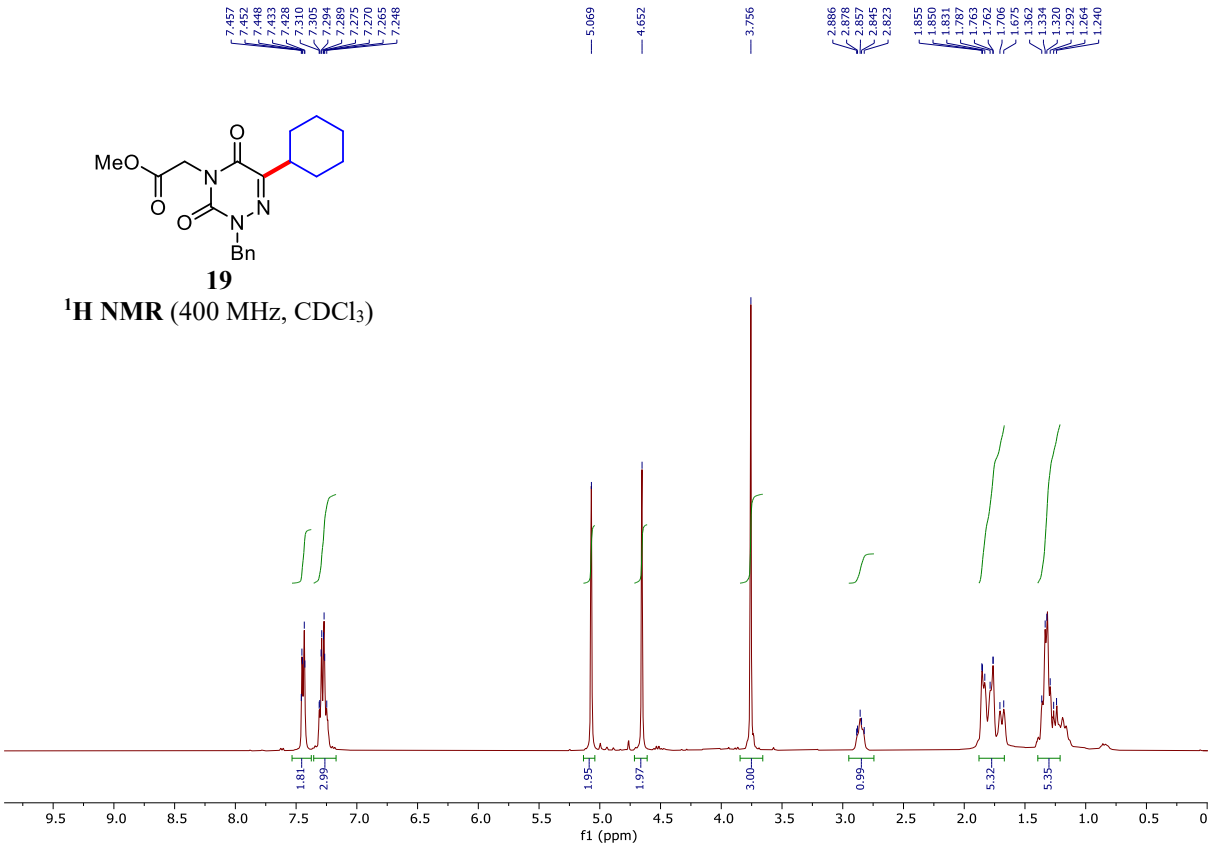
18

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



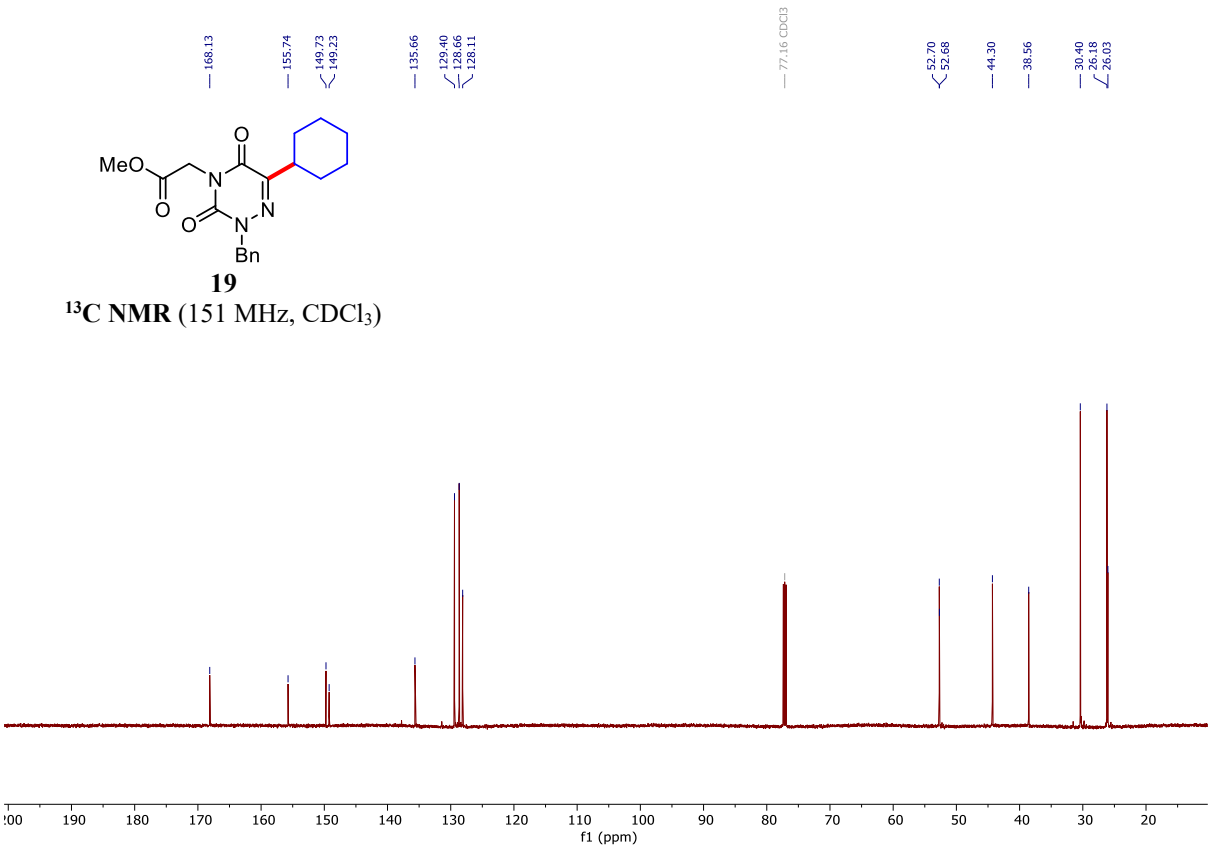
18

^{13}C NMR (151 MHz, $CDCl_3$)



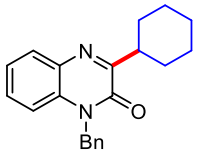
19

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



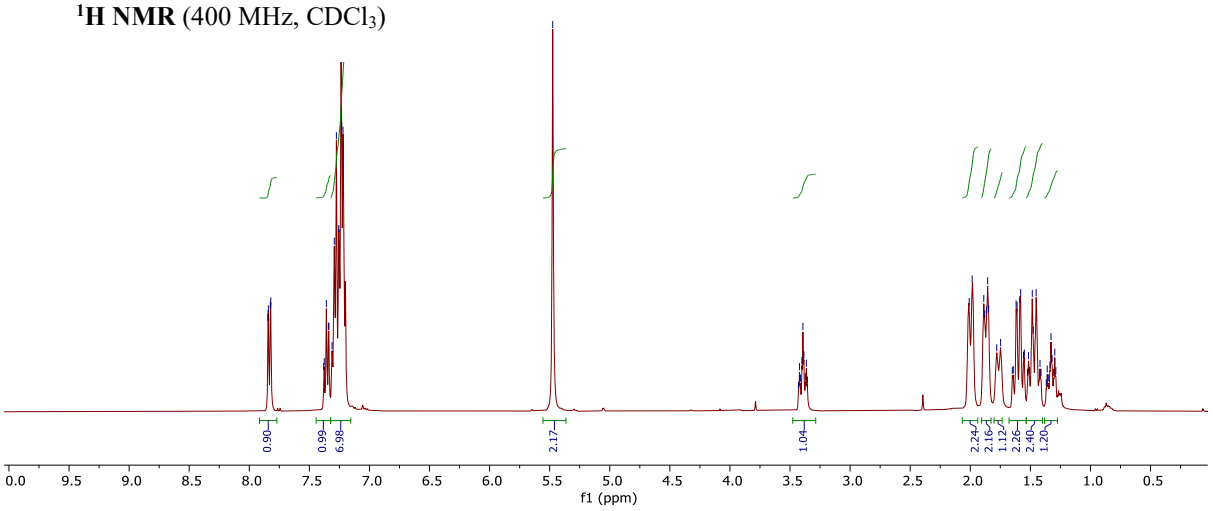
19

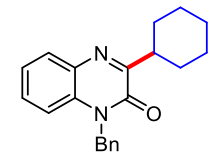
^{13}C NMR (151 MHz, $CDCl_3$)



20

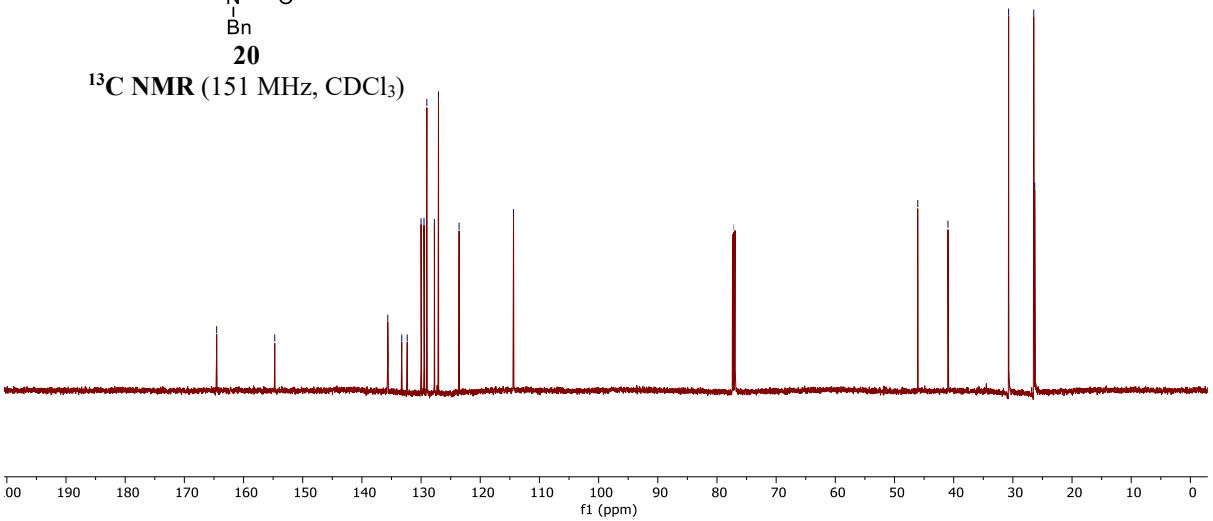
^{1}H NMR (400 MHz, $CDCl_3$)

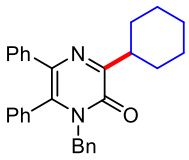




20

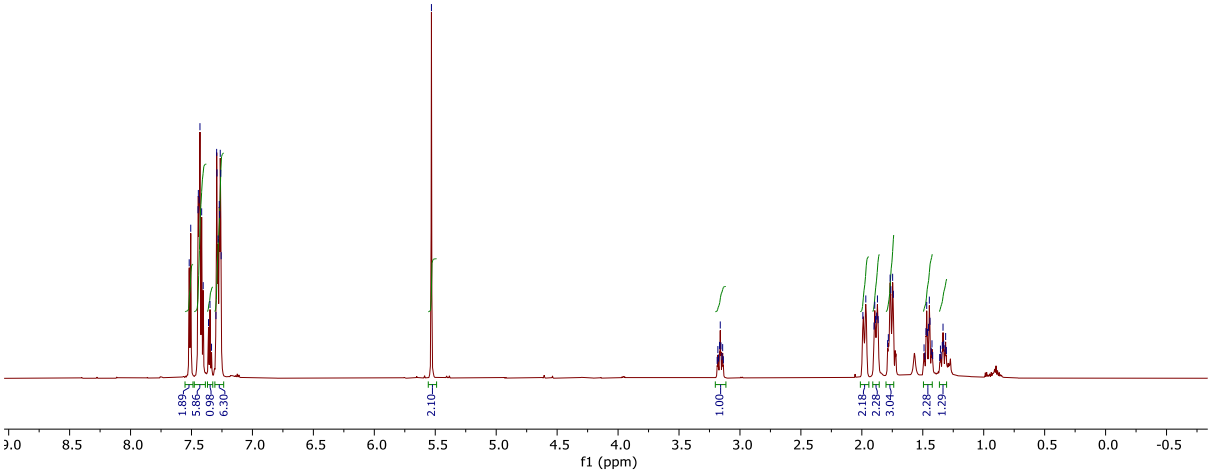
^{13}C NMR (151 MHz, $CDCl_3$)





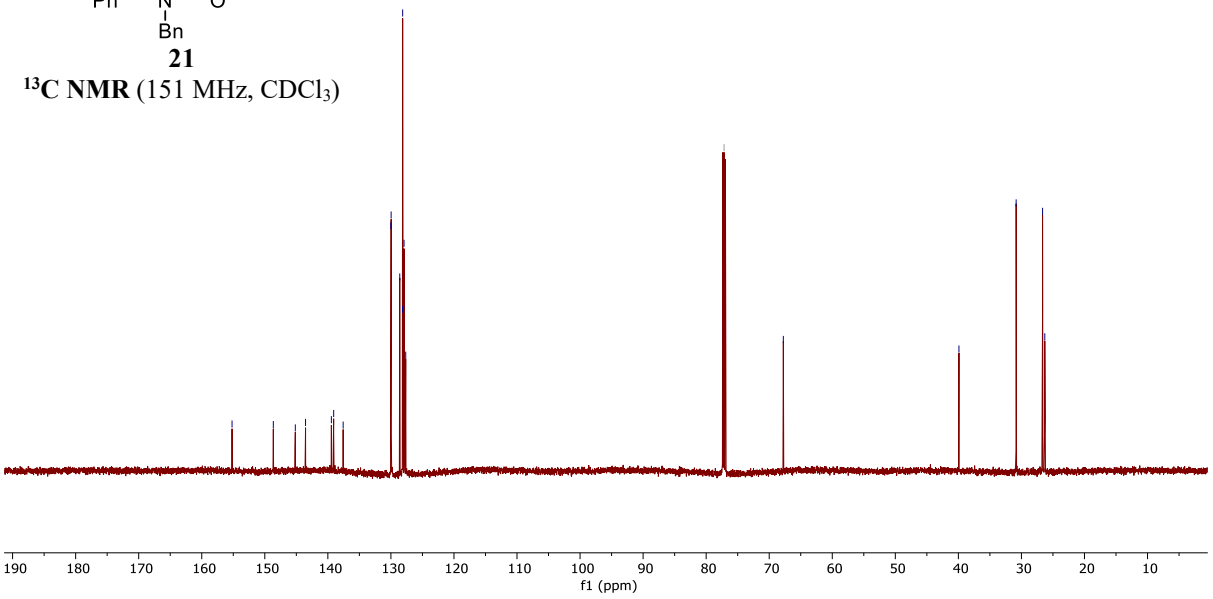
21

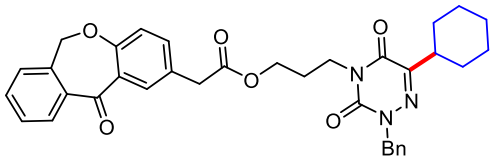
^{1}H NMR (600 MHz, $CDCl_3$)



21

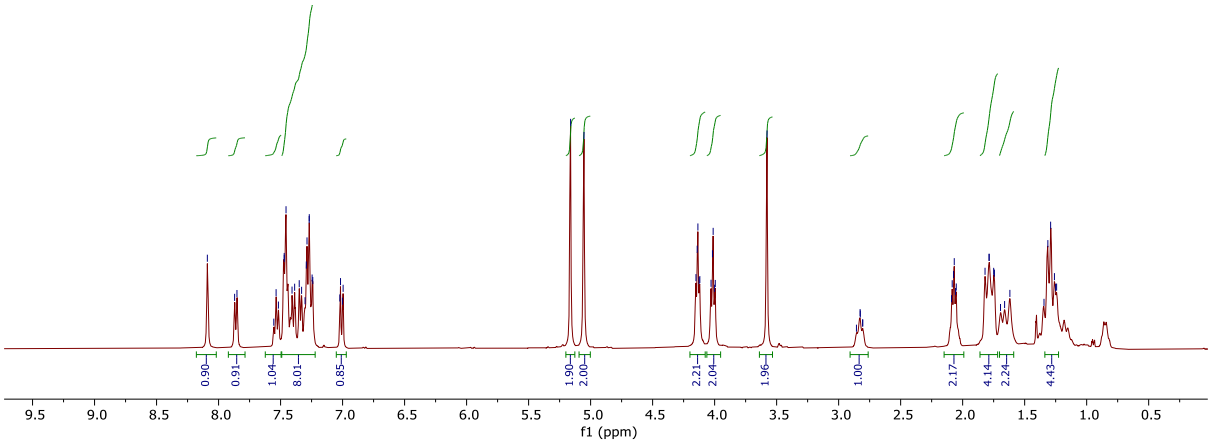
^{13}C NMR (151 MHz, $CDCl_3$)

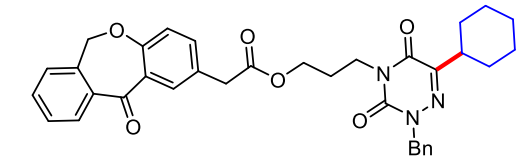




22

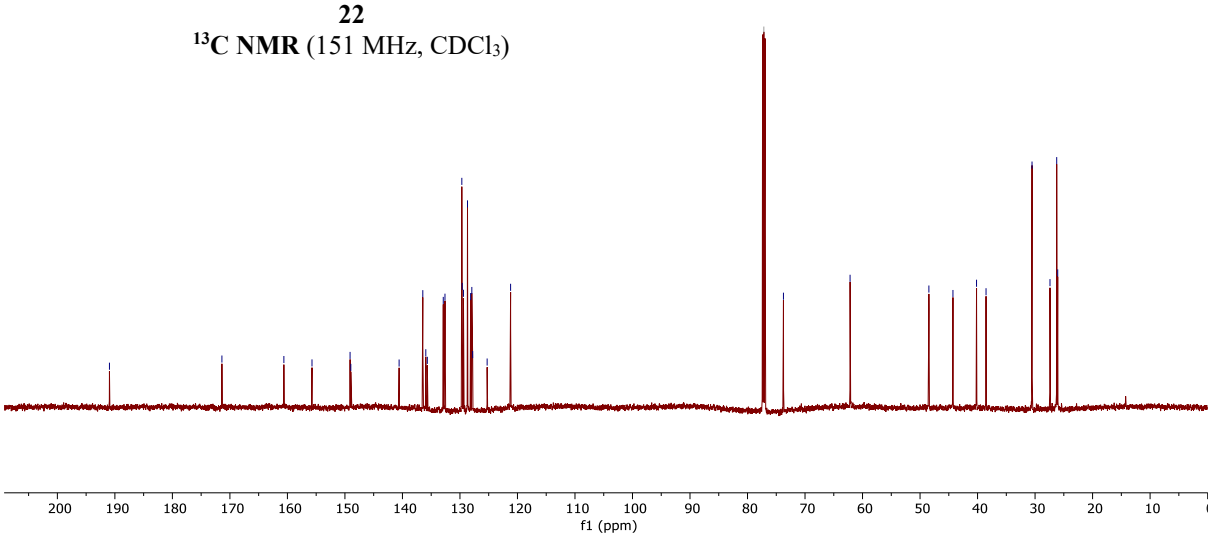
^{1}H NMR (400 MHz, $CDCl_3$)

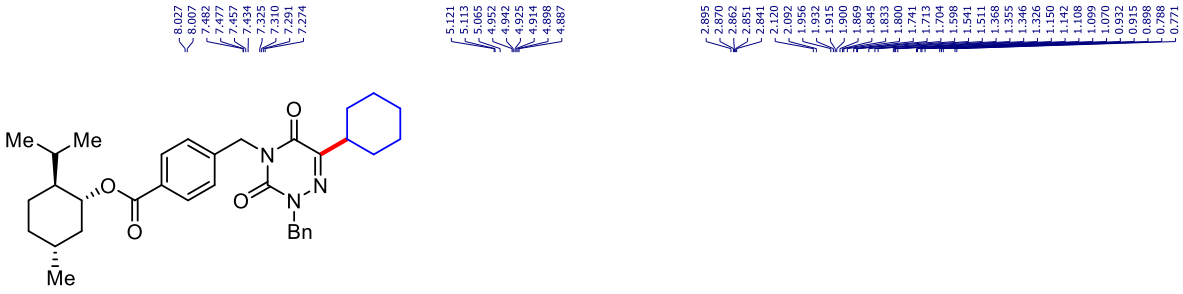




22

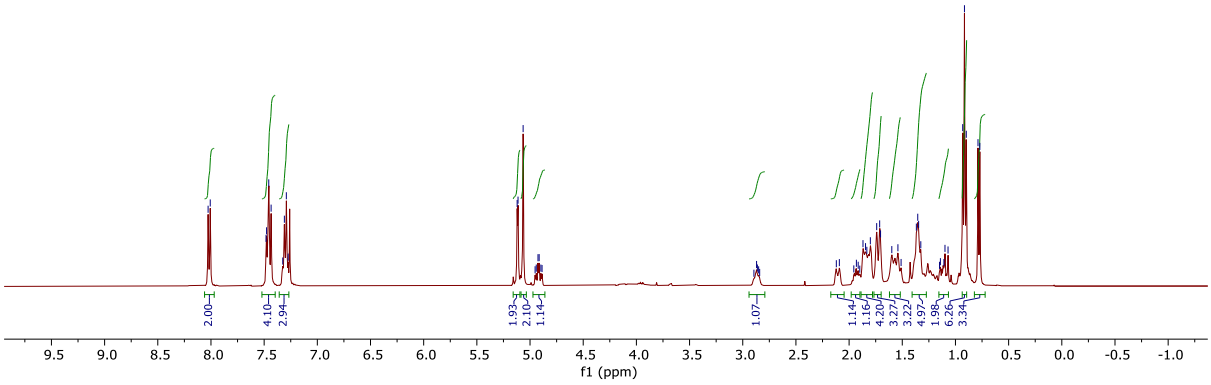
^{13}C NMR (151 MHz, $CDCl_3$)

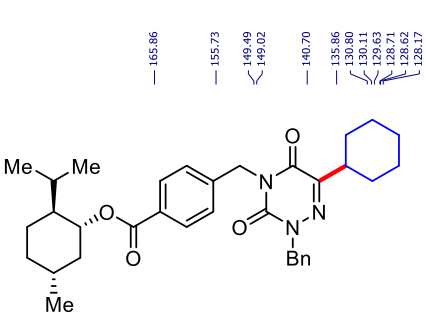




23

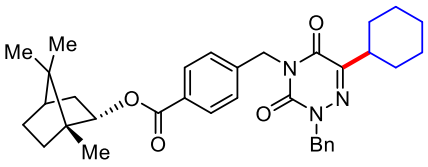
^{1}H NMR (400 MHz, $CDCl_3$)





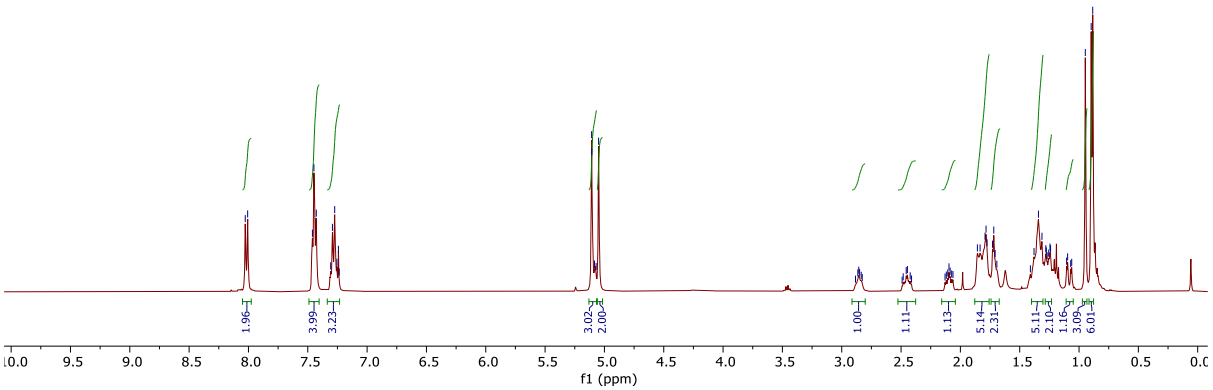
23

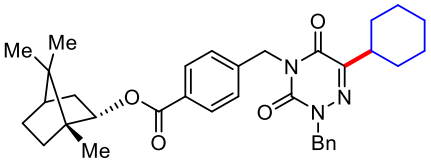
^{13}C NMR (101 MHz, $CDCl_3$)



24

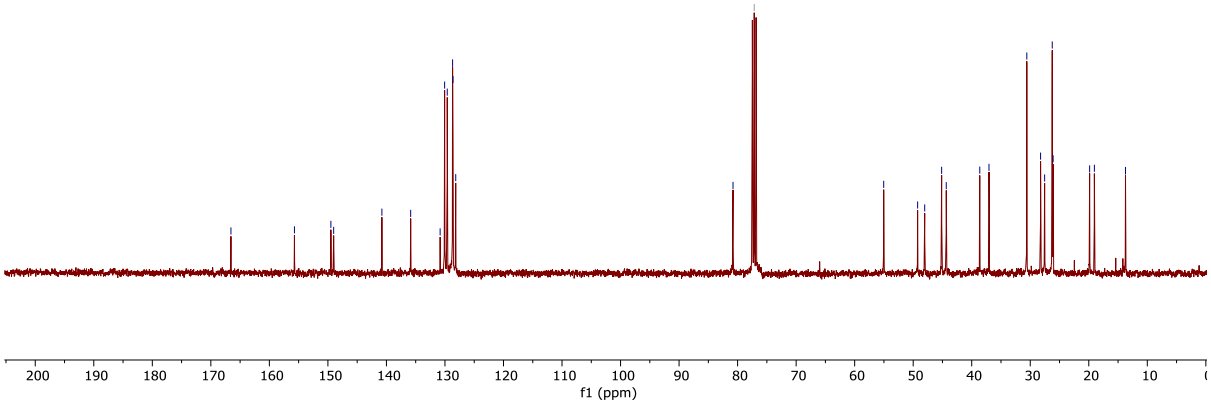
^{1}H NMR (400 MHz, $CDCl_3$)

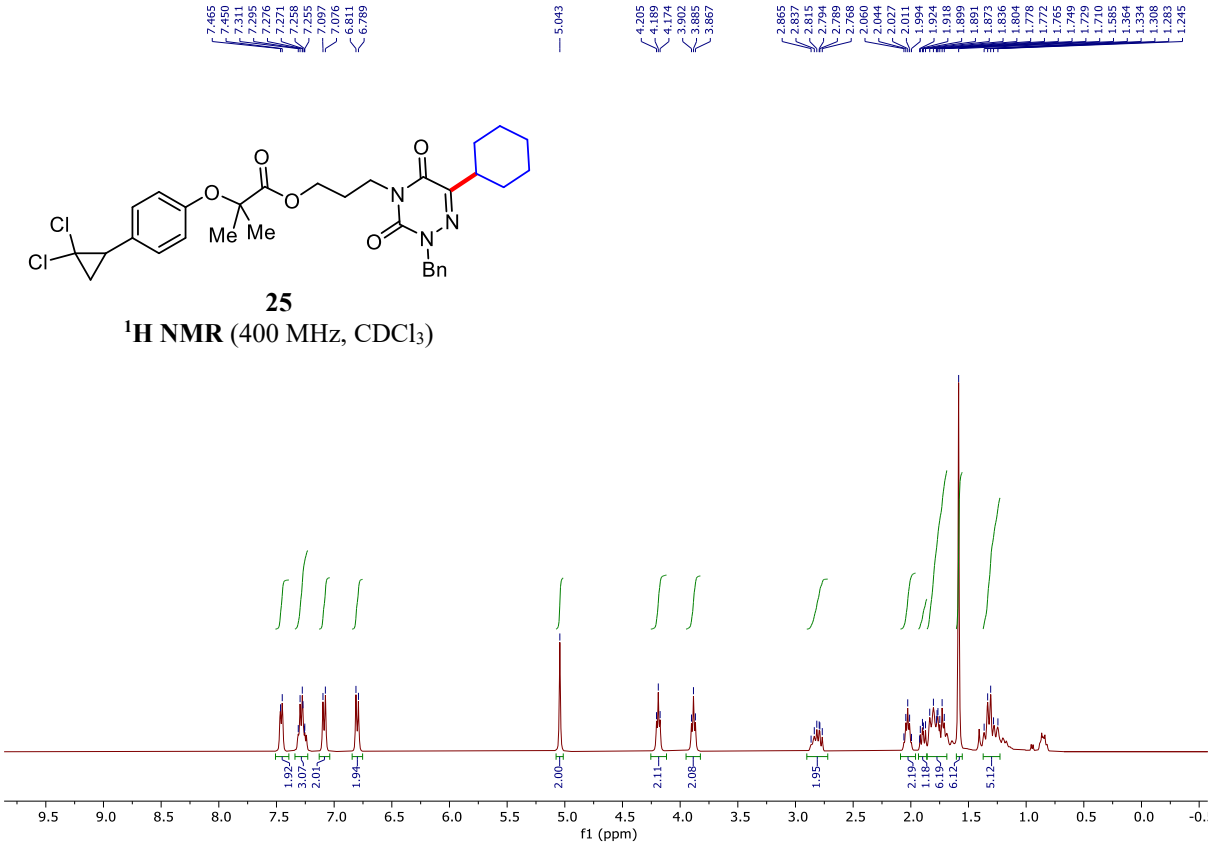




24

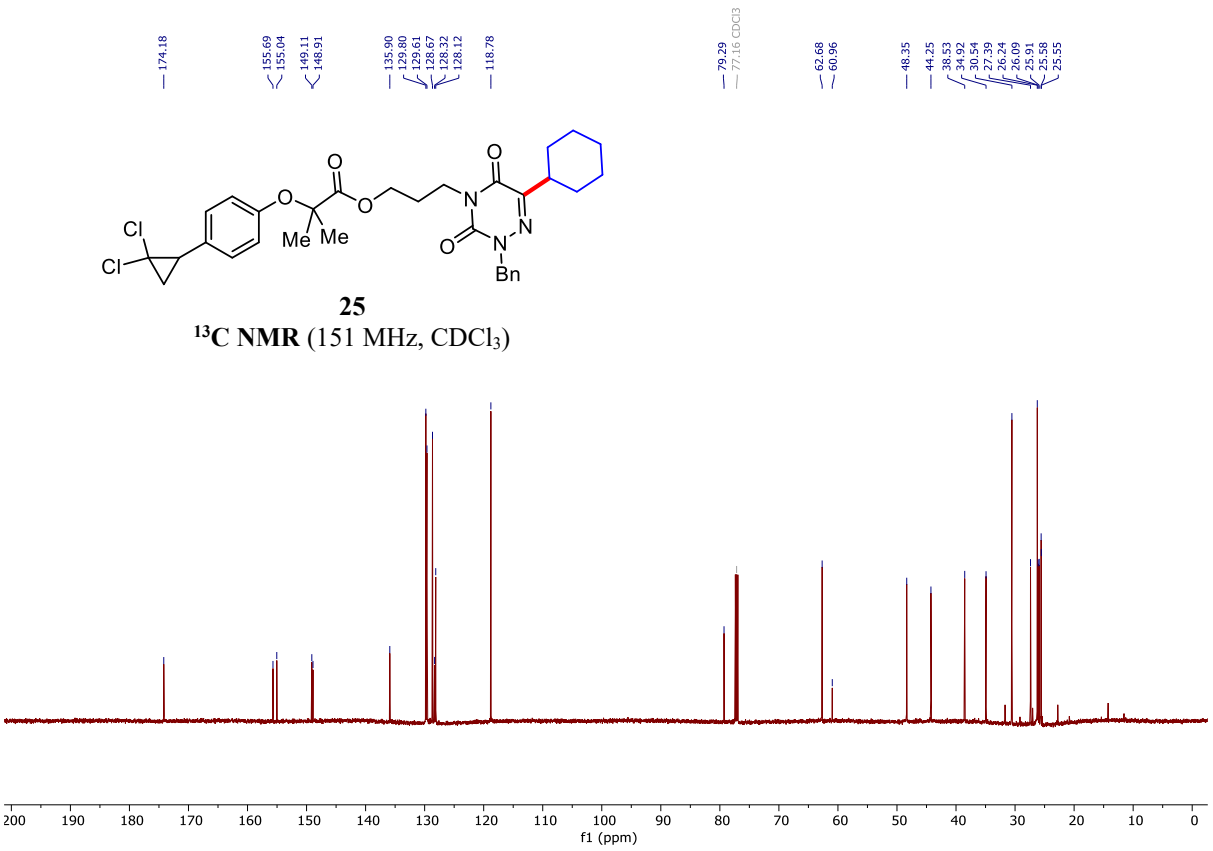
^{13}C NMR (101 MHz, $CDCl_3$)





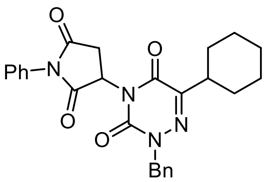
25

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



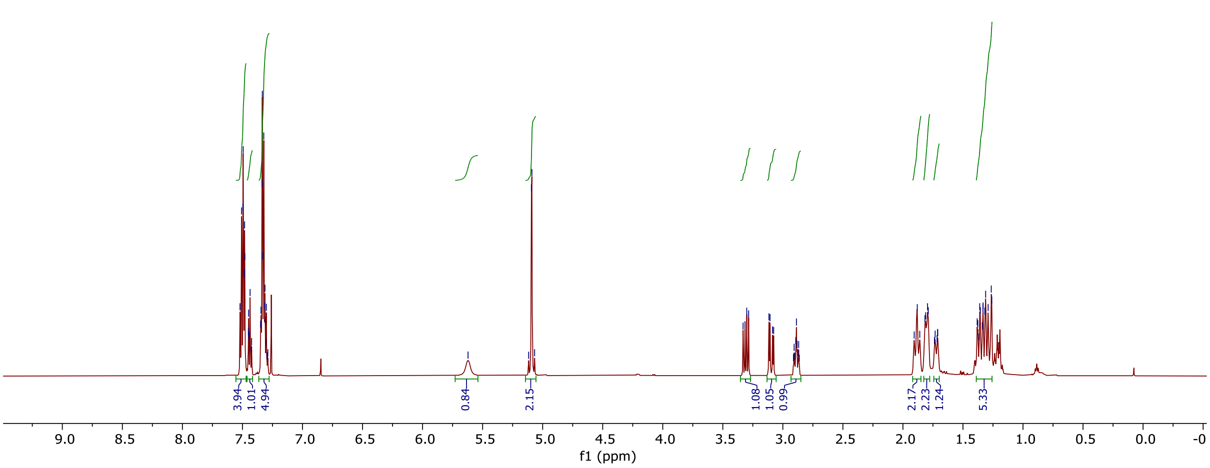
25

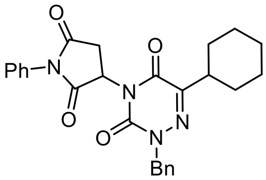
^{13}C NMR (151 MHz, $CDCl_3$)



27

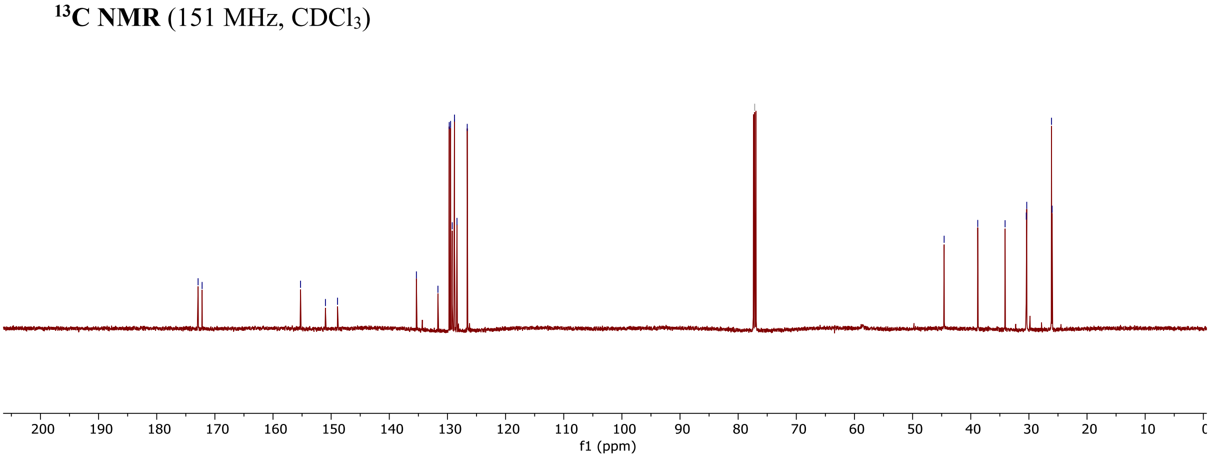
[1]H NMR (600 MHz, $CDCl_3$)

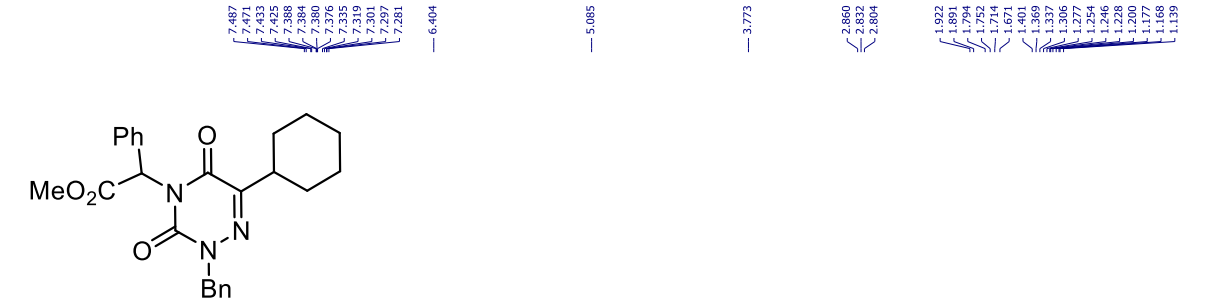




27

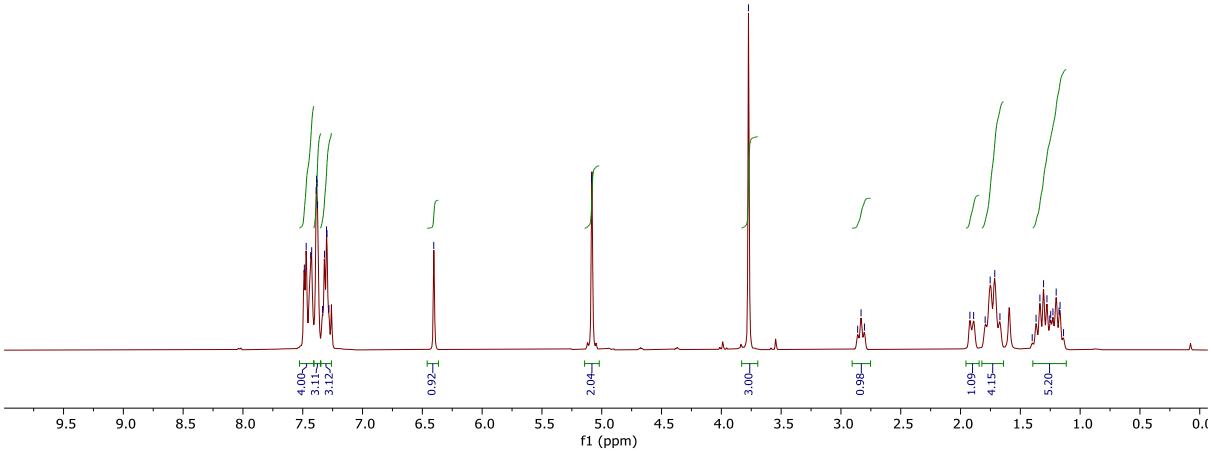
[13]C NMR (151 MHz, $CDCl_3$)

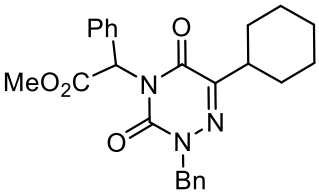




29

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





29

^{13}C NMR (151 MHz, $CDCl_3$)