Supplementary Information (SI) for Chemical Communications.
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Supplementary Information

Direct C-H Amidation of 1,3-Azoles: Light-Mediated, Photosensitiser-Free *vs.* Thermal

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1. General Experimental

Reagents were purchased from commercially available sources. All solvents employed were obtained from commercial sources. All thermal reactions were heated using aluminium heating blocks. All light mediated reactions were carried out in the Penn M2 photoreactor (Figure 1). The Penn M2 photoreactor from Sigma-Aldrich (Z744035) has a 360-degree reflective environment and offers control of defined parameters: reaction wavelength (365 nm, 420 nm or 450 nm), temperature, light-intensity, fan speed and stirring. Temperature monitoring confirms that the reaction was approximately 25 °C throughout a reaction. ^{1}H, ^{13}C and ^{19}F Nuclear Magnetic Resonances were recorded on Bruker® AV300 or AV400 (^{1}H NMR at 300 MHz or 400 MHz respectively, ^{13}C NMR at 75 MHz or 100 MHz respectively and ^{19}F NMR at 376 MHz) spectrometers with chemical shifts given in parts per million (ppm), employing DMSO-d_6, methanol-d_4 or chloroform-*d* as the solvent with residual $(CHD_2)CD_3SO$ ($\delta = 2.50$), CHD_2OD ($\delta = 3.31$) or $CHCl_3$ ($\delta = 7.26$) as a standard reference peak, respectively. ^{13}C Nuclear Magnetic Resonances were recorded with total proton decoupling. The chemical shifts are reported relative to chloroform-*d* ($\delta = 77.16$), methanol-d_4 ($\delta = 49.00$) or DMSO-d_6 ($\delta = 39.52$) as standard reference peaks. *J* values are given in Hz and br, s, d, t, q, quin, sextuplet, sept, multiplet respectively, or a combination of these. High resolution mass spectrometric (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units. High-Resolution Mass Spectra were recorded using a micrOTOF instrument under ESI conditions by the analytical services at the University of Edinburgh. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neatly to a diamond/ZnSe plate. Column chromatography was carried out using Matrix silica gel 60 from Fluorochem. TLC was performed using Merck silica gel 60 F254 and visualised by UV (254 nm) and/or stained using aqueous acidic $KMnO_4$. Non anhydrous DMSO was used in all reactions unless otherwise stated (approx. 4.3% water by volume). "Ad" abbreviation in structures refers to 1-adamantyl.

Figure 1: *Penn M2 Photoreactor*

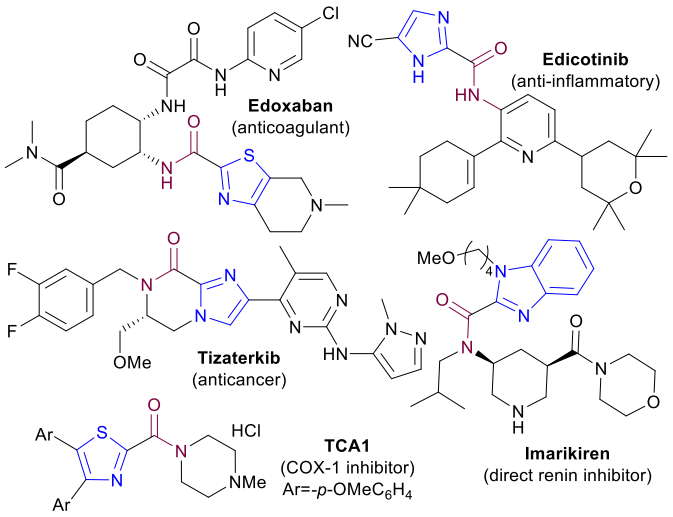
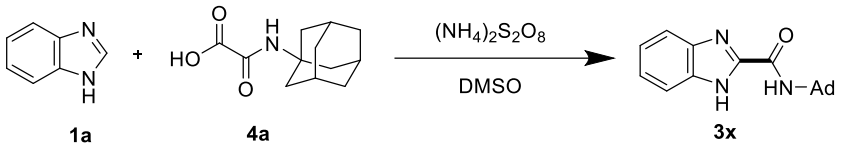


Figure 2: *Examples of Biologically Active 1,3-Azole-2-carboxamides*

2. Reaction Optimisation

2.1 Thermal Reaction Optimisation

Table 1 Benzimidazole Optimisation – Thermal

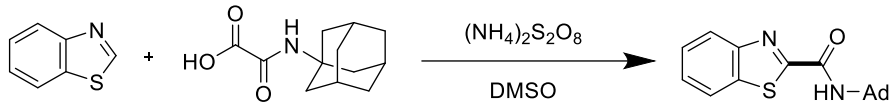


1a 4a 3x

Entry	Conc. (M)	Temp. (°C)	Equiv. of Acid	Equiv. of $(NH_4)_2S_2O_8$	Reaction Time (h)	**1a** (%)[a]	**3x** (%)[a]
1	0.3	50	2	3	24	0	52 (50)[b]
2	0.3	40	2	3	24	0	28
3	0.3	60	2	3	24	0	53
4	0.3	50	2	3	6	0	38
5	0.3	40	2	3	6	0	43
6	0.3	50	1.1	3	24	0	15
7	0.3	50	3	3	24	0	11
8	0.3	50	5	3	24	0	15
9	0.15	50	2	3	24	0	30
10	**0.5**	**50**	**2**	**3**	**24**	**0**	**70 (70)[b]**
11	0.5	50	2	2	24	0	25
12	0.5	50	2	4	24	0	15
13	0.5	50	2	5	24	0	25
14	0.5	50	2	6	24	0	29
15	0.5	50	2	3	2	0	28
16	0.5	50	2	3	4	0	37
17	0.5	50	2	3	6	0	39
18	0.5	50	2	3	72	0	40[c]
19	0.5	40	2	3	24	0	25
20	0.4	50	2	3	24	0	50
21	0.6	50	2	3	24	10	15

[a]Yield determined by ^{1}H NMR analysis of the crude mixture after aq. workup, using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yields in parenthesis. [c]From ^{1}H NMR analysis of the crude, the reduction in yield is most likely due to instability of reaction products under extended reaction times, as the rest of the material is a complex mixture. We do not see any evidence of the desired product amidating further.

Table 2 Benzothiazole Optimisation – Thermal

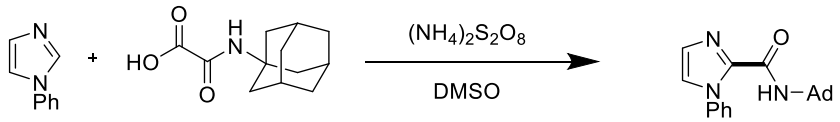


1b **4a** **3a**

Entry	Conc. (M)	Temp. (°C)	Equiv. of Acid	Equiv. of $(NH_4)_2S_2O_8$	Reaction Time (h)	**1b** (%)[a]	**3a** (%)[a]
1	0.3	50	2	3	24	8	82
2	0.5	50	2	3	24	-	-
3	0.15	50	2	3	24	10	75
4	0.2	50	2	3	24	5	81
5	0.4	50	2	3	24	3	86 (70)[b]
6	0.6	50	2	3	24	53	33
7	**0.35**	**50**	**2**	**3**	**24**	**-**	**(80)[b]**
8	0.3	50	2	3	24	4	84[c]

[a]Yield determined by ^{1}H NMR analysis of the crude mixture after aq. workup, using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yields in parenthesis. [c]In the dark.

Table 3 1-Phenylimidazole Optimisation -Thermal

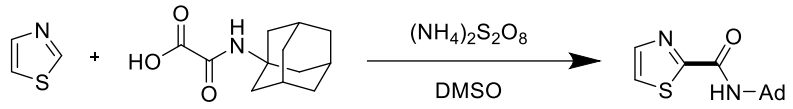


1c **4a** **3ad**

Entry	Conc. (M)	Temp. (°C)	Equiv. of Acid	Equiv. of $(NH_4)_2S_2O_8$	Reaction Time (h)	**1c** (%)[a]	**3ad** (%)[a]
1	0.4	50	2	3	24	35	55
2	0.3	50	2	3	24	11	75 (69)[b]
3	0.5	50	2	3	24	45	42
4	**0.2**	**50**	**2**	**3**	**24**	**0**	**83 (81)[b]**

Unsubstituted imidazole (with no substituent on *N*) is not a suitable substrate and no product was observed. [a]Yield determined by ^{1}H NMR analysis of the crude mixture after aq. workup, using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yields in parenthesis.

Table 4 Thiazole Optimisation -Thermal



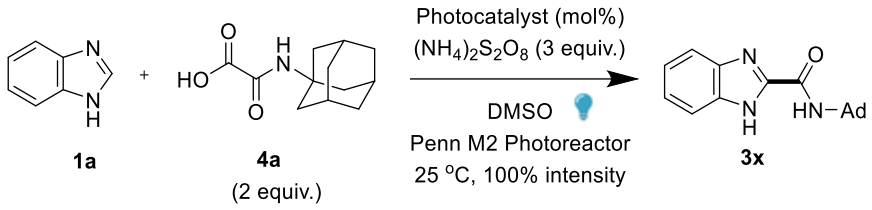
1d **4a** **3j**

Entry	Conc. (M)	Temp. (°C)	Equiv. of Acid	Equiv. of $(NH_4)_2S_2O_8$	Reaction Time (h)	**1d** (%)[a]	**3j** (%)[a]
1	0.5	50	2	3	24	12	68
2	0.3	50	2	3	24	3	52
3	**0.4**	**50**	**2**	**3**	**24**	**0**	**75 (72)[b]**
4	0.6	50	2	3	24	12	48

[a]Yield determined by ^{1}H NMR analysis of the crude mixture after aq. workup, using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yields in parenthesis.

2.2 Light-Mediated Reaction Optimisation

Table 5 Benzimidazole Optimisation – Light-Mediated

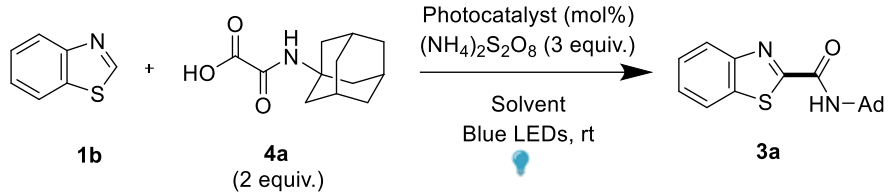


1a **4a** (2 equiv.) **3x**

Entry	Photocatalyst	mol%	Solvent Concentration (M)	Wavelength (nm)	Time (h)	**1a** (%)[a]	**3x** (%)[a]
1	-	-	0.5	450	24	46	49
2	Ir cat.	1.5	0.5	450	24	38	45
3	-	-	0.5	420	24	Complex mixture	Complex mixture
4	**-**	**-**	**0.5**	**420**	**3**	**10**	**67 (67)[b]**
5	Ir cat.	1.5	0.5	420	3	9	38
6	-	-	0.5	365	24		59
7	Ir cat.	1.5	0.5	365	24		65

[a]Yield determined by ^{1}H NMR analysis of the crude mixture after aq. workup, using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yields in parenthesis.
Nb: Equivalents of **1a** and **4a** were previously optimised under thermal conditions.
Ir cat. = $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$

Table 6 Benzothiazole Optimisation – Light-Mediated

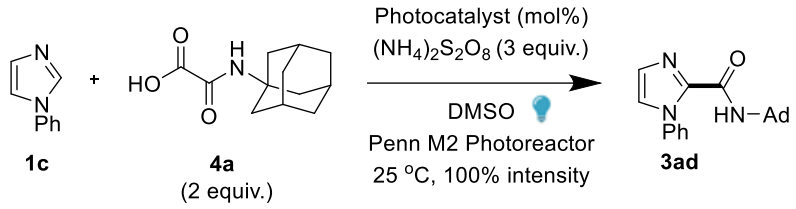


1b + **4a** (2 equiv.) → **3a**

Entry	Photocat.	mol%	Solvent	Conc. (M)	Light Source	Wavelength (nm)	Time (h)	**1b** (%)[a]	**3a** (%)[a]
1	Ir cat.	1.0	DMSO	0.30	SynLED	465-470	24	0	71
2	Ir cat.	1.0	DMSO	0.40	SynLED	465-470	24	0	73
3	Ir cat.	1.0	DMSO	0.50	SynLED	465-470	24	0	54
4	Ir cat.	1.0	DMSO	0.35	SynLED	465-470	24	3	82
5	Ir cat.	1.0	DMSO	0.35	Penn Reactor	450	24	0	80
6	Ir cat.	1.5	DMSO	0.35	SynLED	465-470	24	0	85
7	Ir cat.	2.0	DMSO	0.35	SynLED	465-470	24	2	62
8	4-CzIPN	1.0	DMSO	0.35	SynLED	465-470	24	66	41
9	4-CzIPN	2.0	DMSO	0.35	SynLED	465-470	24	70	18
10	Fukuzumi	0.75	DMSO	0.35	SynLED	465-470	24	20	73
11	Fukuzumi	1.0	DMSO	0.35	SynLED	465-470	24	17	70
12	Fukuzumi	1.25	DMSO	0.35	SynLED	465-470	24	28	64
13	Fukuzumi	1.5	DMSO	0.35	SynLED	465-470	24	57	33
15	-	-	DMSO	0.35	SynLED	465-470	24	0	85
16	-	-	DMSO	0.35	Penn Reactor	450	24	0	85
17[c]	-	-	DMSO	0.35	Penn Reactor	450	24	0	71
18[d]	-	-	DMSO	0.35	-	-	24	43	45
19[d]	Ir cat.	1.0	DMSO	0.35	-	-	24	34	54
20	-	-	MeCN	0.35	Penn Reactor	450	24	70	20
21	-	-	H_2O	0.35	Penn Reactor	450	24	44	32
22	-	-	MeOH	0.35	Penn Reactor	450	24	Mess	Mess
23	-	-	Acetone	0.35	Penn Reactor	450	24	83	17
24	-	-	DCM	0.35	Penn Reactor	450	24	30	69
25[d]	-	-	DCM	0.35	-	-	24	90	Trace
26	-	-	DMSO	0.35	Penn Reactor	365	24	0	82
27	-	-	DMSO	0.35	Penn Reactor	365	6	1	81
28	-	-	DMSO	0.35	Penn Reactor	365	4	1	82
29	-	-	DMSO	0.35	Penn Reactor	365	3	1	82
30	-	-	DMSO	0.35	Penn Reactor	365	2	2	82
31	-	-	DMSO	0.35	Penn Reactor	365	1	10	80
32	-	-	DMSO	0.35	Penn Reactor	420	24	0	80
33	**-**	**-**	**DMSO**	**0.35**	**Penn Reactor**	**420**	**3**	**0**	**85 (84)[b]**
34	-	-	DMSO	0.35	Penn Reactor	450	3	0	74
35[d]	-	-	DMSO	0.35	Penn Reactor	-	3	-	-[e]
36[f]	-	-	DMSO	0.35	Penn Reactor	420	3	-	-[e]

[a]Yield determined by ^{1}H NMR analysis of the crude mixture after aq. workup, using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yields in parenthesis. [c]Reaction under 50% light intensity. [d]Reaction conducted in the dark. [e]No reaction. [f]No persulfate. *Nb:* Equivalents of **1b** and **4a** were previously optimised under thermal conditions. Ir cat = $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$ Fukuzumi = $[Mes–Acr]^+[ClO_4]^-$

Table 7 1-Phenylimidazole Optimisation – Light-Mediated

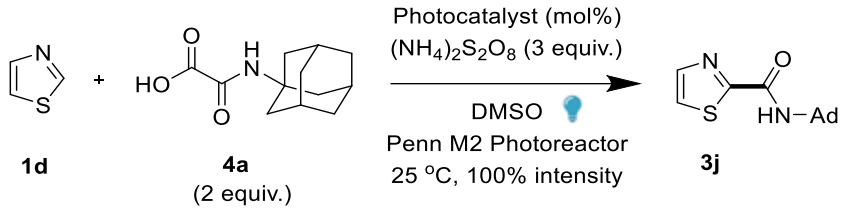


1c + **4a** (2 equiv.) → **3ad**

Entry	Photocatalyst	mol%	Concentration (M)	Wavelength (nm)	Time (h)	**1c** (%)[a]	**3ad** (%)[a]
1	-	-	0.2	450	24	0	79
2	Ir cat.	1.5	0.2	450	24	0	73
3	-	-	0.2	420	3	50	50
4	-	-	0.2	420	4	29	61
5	-	-	0.2	420	5	17	73
6	**-**	**-**	**0.2**	**420**	**6**	**0**	**81(81)[b]**
7	-	-	0.2	420	16	0	81
8	-	-	0.2	420	24	0	80
9	Ir cat.	1.5	0.2	420	3	0	79

[a]Yield determined by ^{1}H NMR analysis of the crude mixture after aq. workup, using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yields in parenthesis. *Nb:* Equivalents of **1c** and **4a** were previously optimised under thermal conditions. Ir cat = $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$

Table 8 Thiazole Optimisation – Light-Mediated



1d **4a** (2 equiv.) **3j**

Entry	Photocatalyst	mol%	Concentration (M)	Wavelength (nm)	Time (h)	**1d** (%)[a]	**3j** (%)[a]
1	-	-	0.2	450	24	7	73
2	-	-	0.4	450	24	0	88
3	Ir cat.	1.5	0.4	450	24	3	77
4	-	-	0.4	420	24	0	77
5	**-**	**-**	**0.4**	**420**	**3**	**0**	**Quant. (82)[b]**

[a]Yield determined by ^{1}H NMR analysis of the crude mixture after aq. workup, using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yields in parenthesis. *Nb:* Equivalents of **1d** and **4a** were previously optimised under thermal conditions. Ir cat. = $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$

The difference in temperature and time (Conditions A: 50 °C for 24 h *vs.* Conditions B: 25 °C and 1-6 h) and thus the difference in the mildness of the reaction conditions tend to account for the majority of cases where there may be discrepancies in yields between the two Conditions. For example, reactions that could potentially suffer from competitive side reactions generally give better yields under the milder light-mediated conditions B (e.g. **3p**, **3q, 3ak**), whereas reactions that tend to react sluggishly generally give better results under the thermal conditions A, where the conditions are harsher, and the reaction can be pushed further if necessary (e.g. **3an**, **3bi, 3al, 3m**). The two conditions are thus complementary.

A crucial point to note is that the optimised concentrations were different for each class of 1,3-azole studied: benzothiazoles: 0.35 M, thiazoles: 0.4 M; benzimidazoles: 0.5 M; imidazoles: 0.2 M. The concentrations quoted are with respect to the limiting reagent, **1**.

3. UV-vis Absorption Studies

UV-vis absorption spectra of individual reactants and/or mixtures of reactants in DMSO were recorded on a Shimadzu UV-2550 spectrophotometer. Since there was no absorption at 420 nm (reaction irradiation wavelength) at low concentration of 0.001 M (Figure 3), the UV-vis studies were subsequently carried out at the corresponding reaction concentrations instead for each class of azole (Figures 4-7). Persulfate refers to $(NH_4)_2S_2O_8$. Baseline correction was carried out to ensure that baselines are at zero.

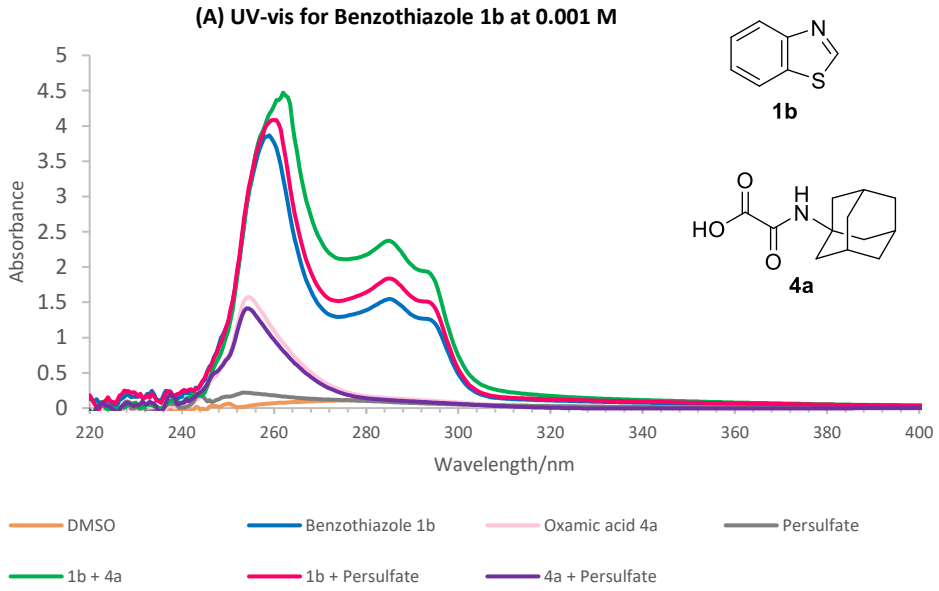


*Figure 3: UV-Vis absorption studies for benzothiazole (**1b**) and its mixtures in DMSO at diluted concentration (0.001 M).*

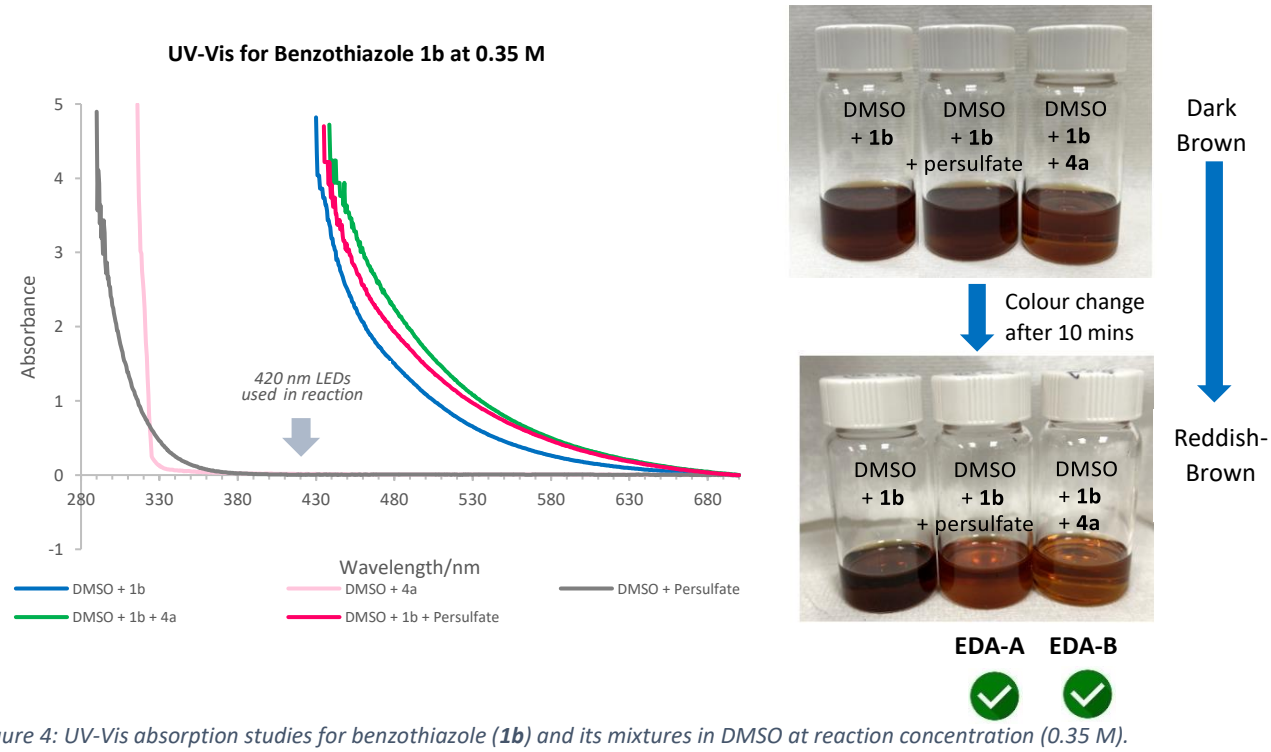


*Figure 4: UV-Vis absorption studies for benzothiazole (**1b**) and its mixtures in DMSO at reaction concentration (0.35 M).*

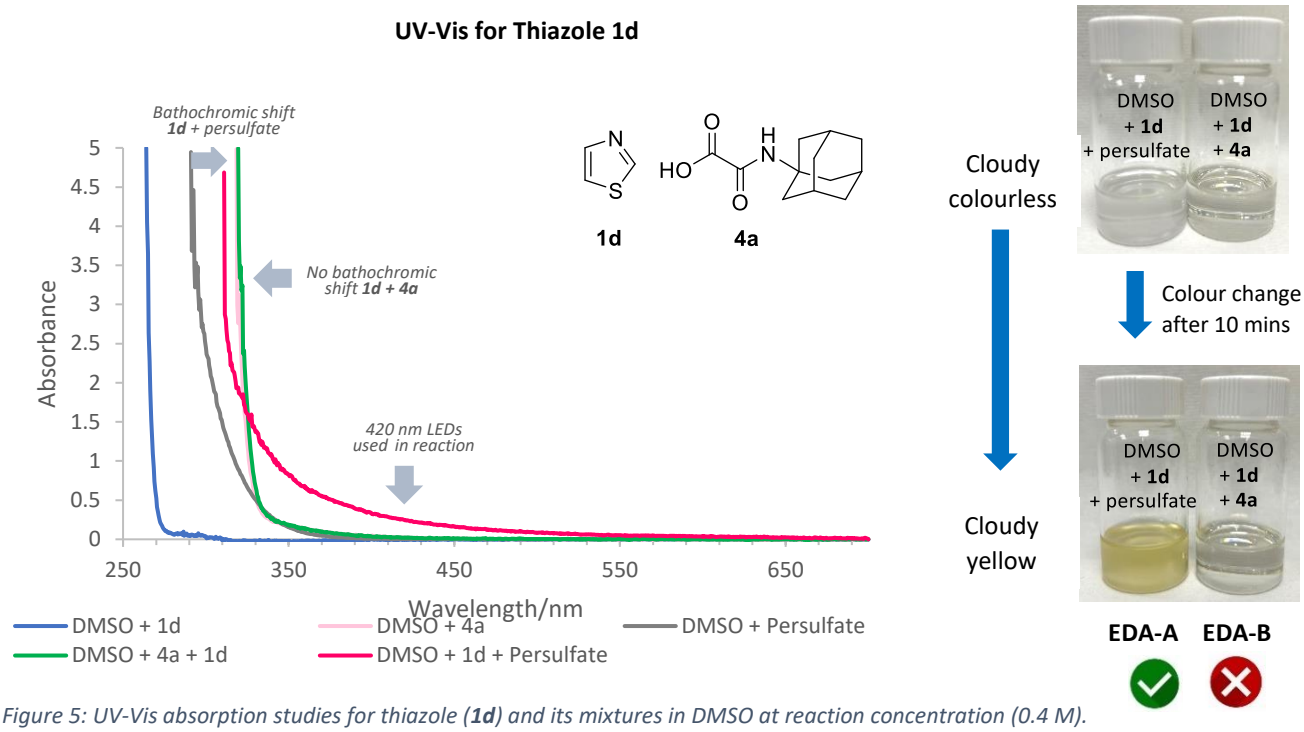


*Figure 5: UV-Vis absorption studies for thiazole (**1d**) and its mixtures in DMSO at reaction concentration (0.4 M).*

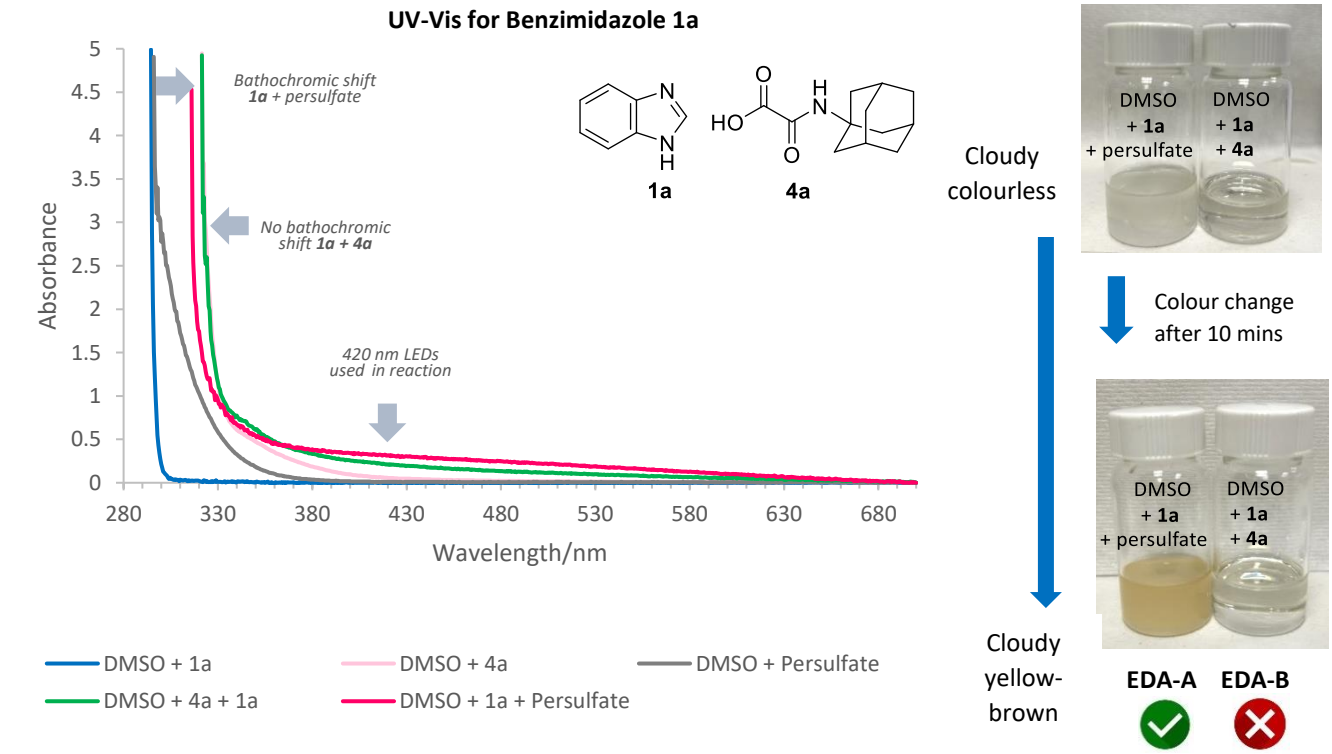


*Figure 6: UV-Vis absorption studies for benzimidazole (**1a**) and its mixtures in DMSO at reaction concentration (0.5 M).*

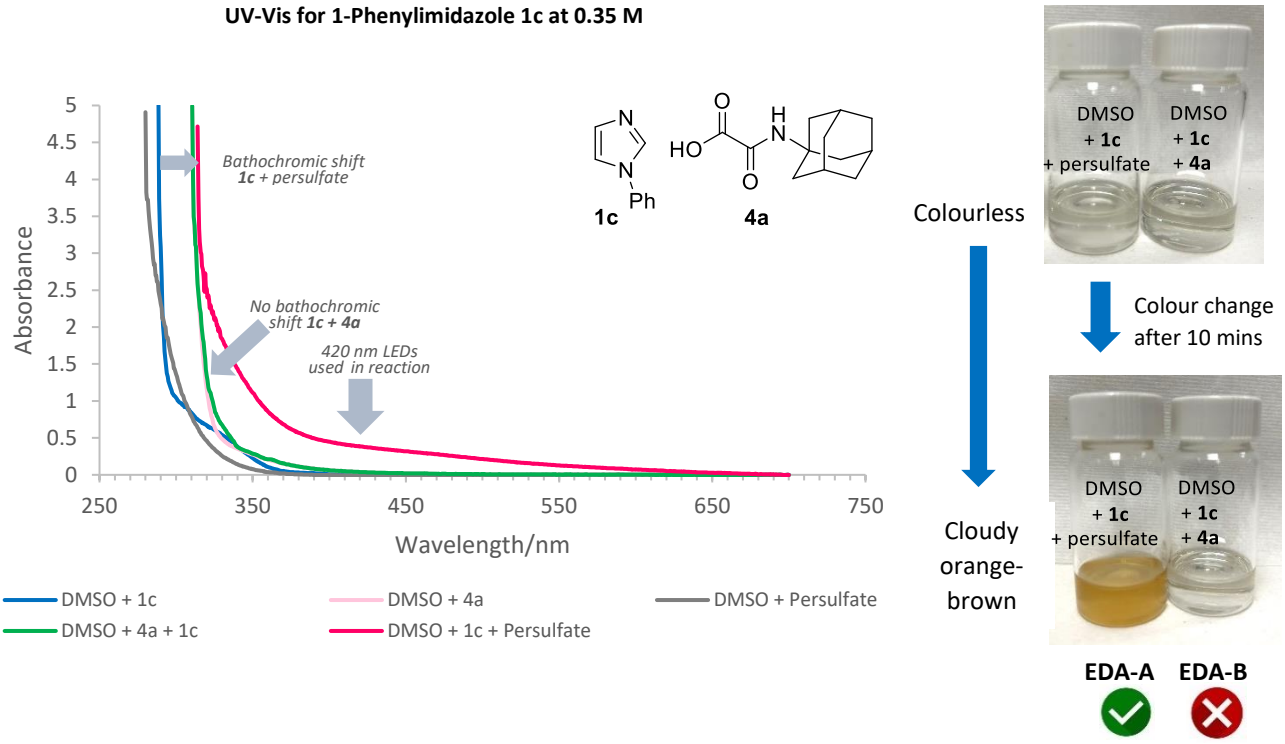


*Figure 7: UV-Vis absorption studies for 1-phenylimidazole (**1c**) and its mixtures in DMSO at reaction concentration (0.2 M).*

At reaction concentration of 0.35 M, benzothiazole **1b** itself absorbed at 420 nm (Figure 4). Both combinations of (**1b** + persulfate = **EDA-A**) and (**1b** + **4a** = **EDA-B**) absorbed at approx. 420 nm, showed increased absorption, displayed a bathochromic shift and a colour change from dark brown to reddish brown. These results indicate two possible EDAs: **EDA-A** and **EDA-B** (Figure 4) with benzothiazole **1b**. However, benzothiazole **1b** turns out to be an exception. Similar UV-vis studies with thiazole **1d** (Figure 5), 1-phenylimidazole **1c** (Figure 7) and benzimidazole **1a** (Figure 6), show that these 1,3-azoles do not absorb at around 420 nm at their respective reaction concentrations and only showed significant increased absorption, bathochromic shift and colour change for the combination of (azole **1** + persulfate = **EDA-A**). Therefore, only **EDA-A** (**1** + persulfate) is observed across all four 1,3-azoles studied, which indicates that any *general* mechanism for 1,3-azoles likely proceeds *via* light absorption by **EDA-A**.

4. Stoichiometry of the EDA complexes in solution

The Job's method of continuous variations was performed to establish the molar donor/acceptor ratio of EDA complexes in solution.[1] A Job's plot was constructed in order to evaluate the stoichiometry of the EDA complexes between each individual azole and persulfate. The absorption at 420 nm of DMSO solutions with different donor/acceptor ratios but constant concentrations of the two components was measured. Two standard solutions were prepared. Solution A: azole in DMSO (c = X M) and solution B: persulfate in DMSO (c = X M). Using solutions A and B, 6 samples were prepared with differing ratios of azole:persulfate and the absorbance of these 6 samples at 420 nm was recorded. The absorbance values were plotted against the molar fraction (%) of azole (Figures 8 - 11). Since maximum absorptions are *not* at 1:1 ratio, this implies that the mechanism does not proceed *via* a SET from donor to acceptor of the EDA. Instead, we propose that excitation of **EDA-A** allows for homolytic decomposition of persulfate. Note that persulfate itself does not absorb at 420 nm but **EDA-A** does. Photodecomposition of persulfate itself is slow requires excitation at 280 nm (UV-light) for homolytic decomposition.[2]

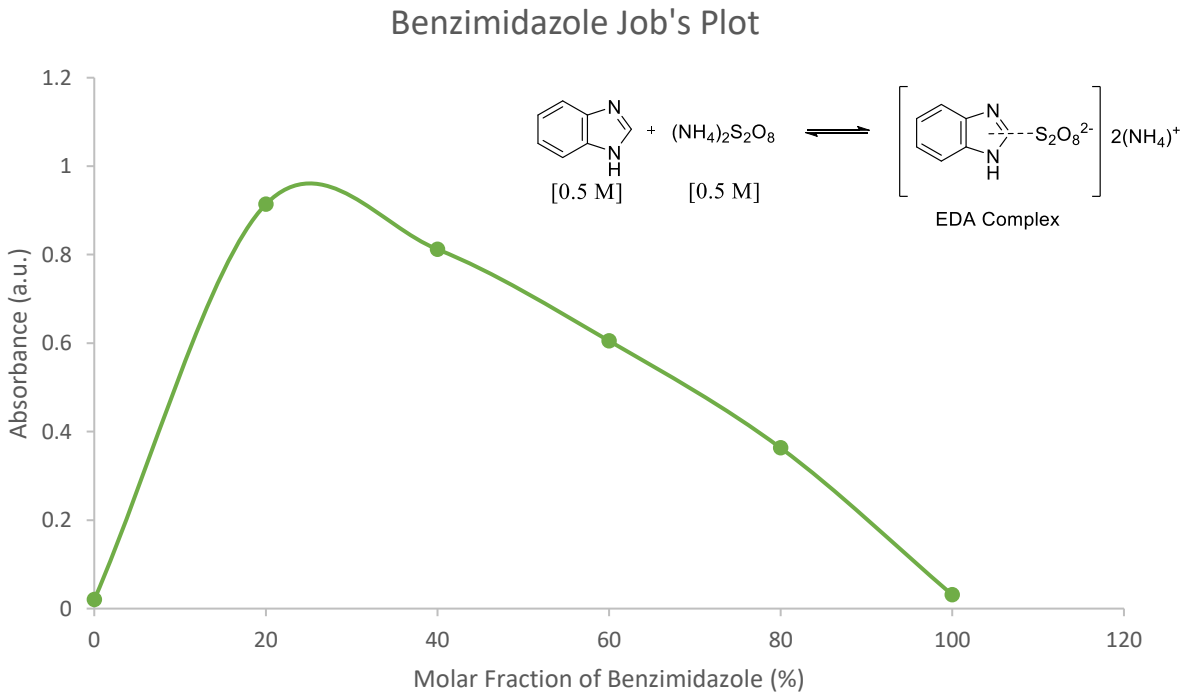


Figure 8: Benzimidazole Job's Plot

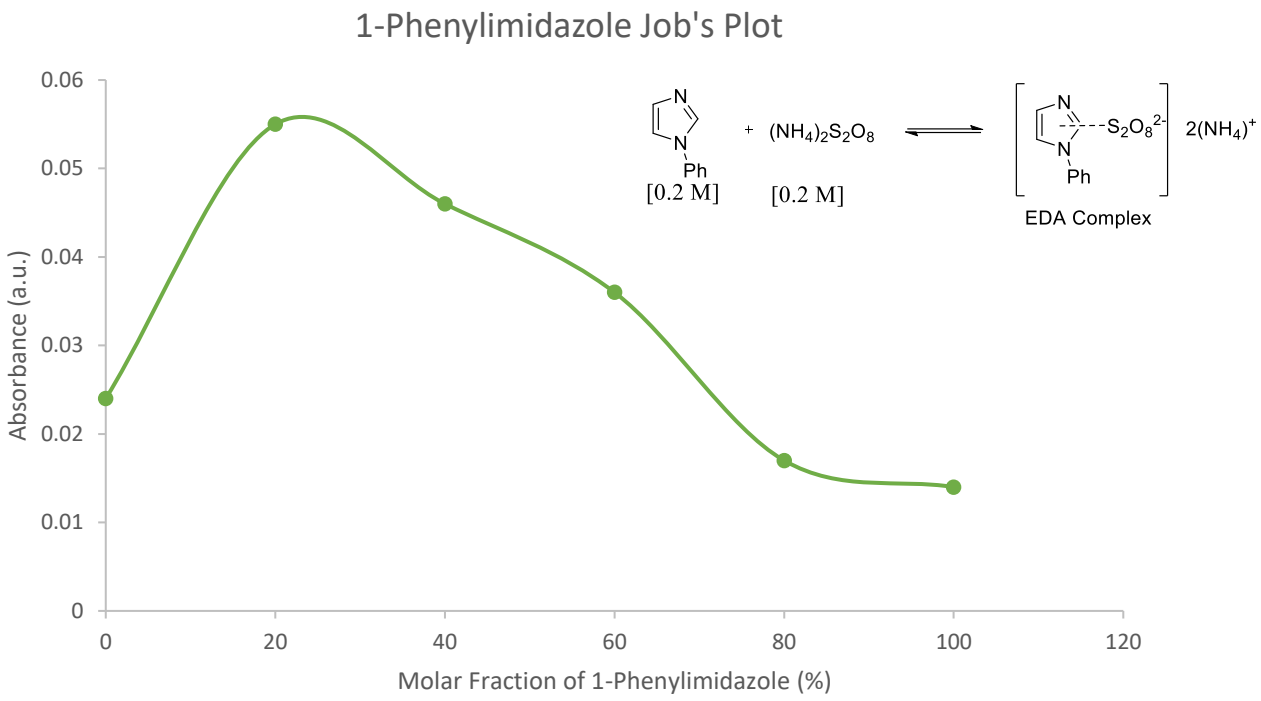


Figure 9: 1-Phenylimidazole Job's Plot

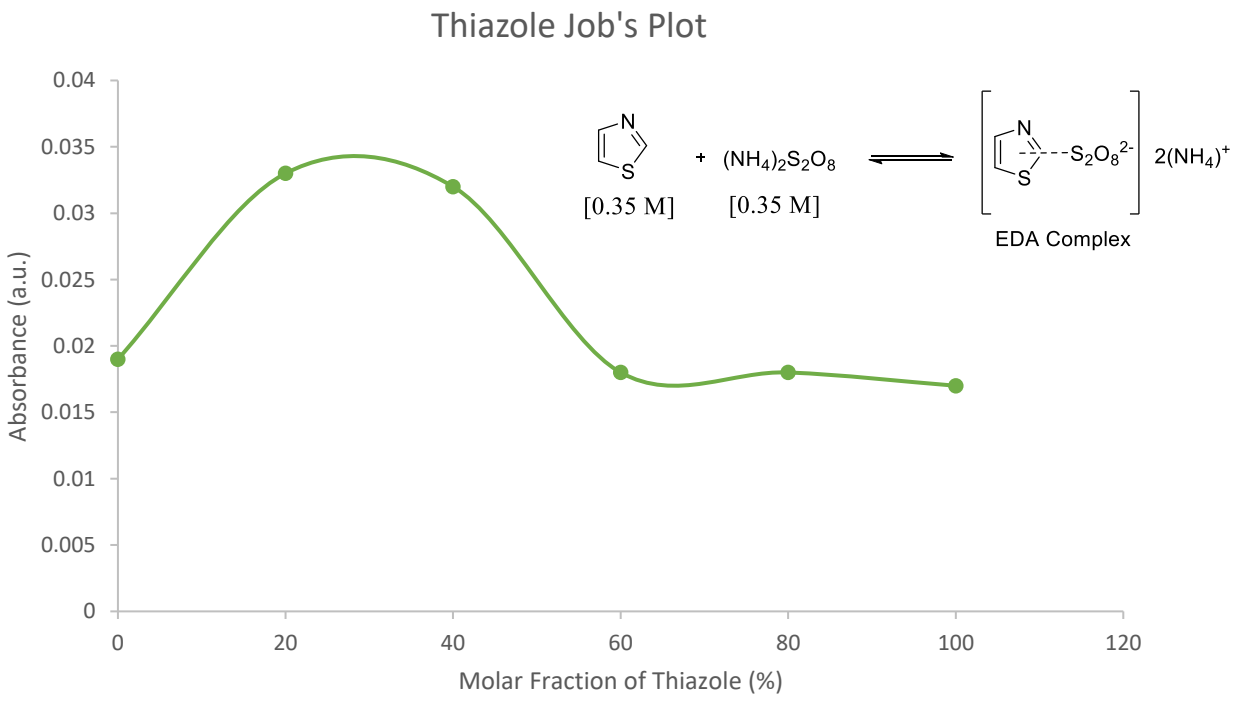


Figure 10: Thiazole Job's Plot

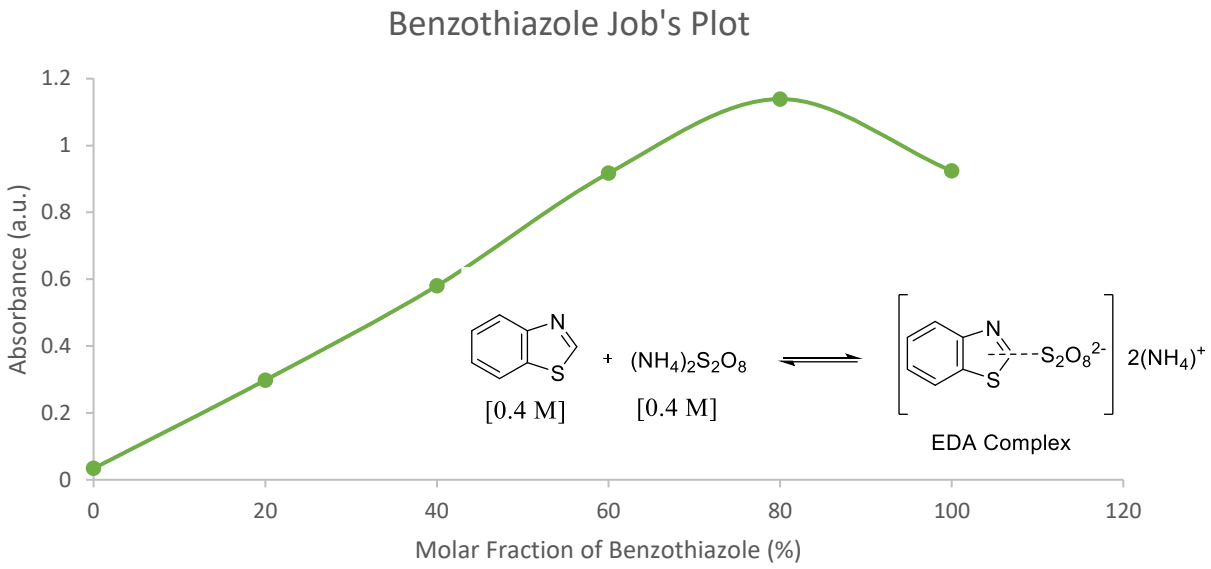
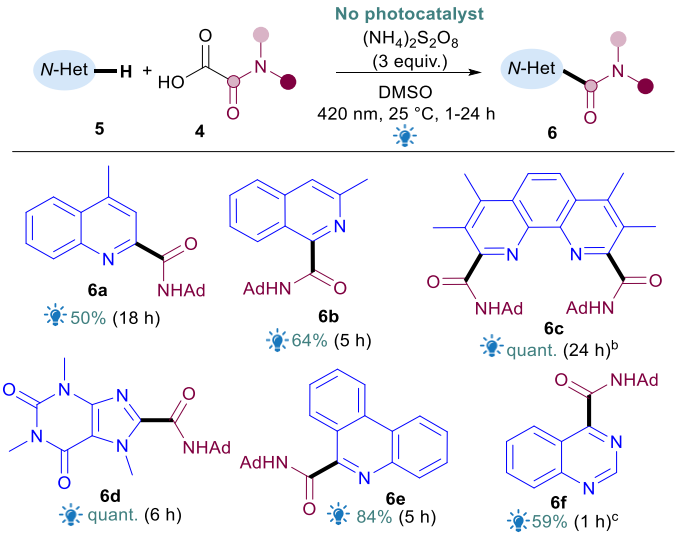


Figure 11: Benzothiazole Job's Plot

5. Light-Mediated Reactions with Other *N*-Heterocycles

We decided to ascertain whether the photocatalyst-free light mediated methodology could be applied more generally to other *N*-heterocycle motifs beyond azoles. If so, our discovery would be of significance as it means that photocatalysts/photosensitisers are generally not required for light-mediated direct Minisci amidations. To this end, several different classes of *N*-heterocycles were evaluated using the photosensitiser-free light mediated reactions (Scheme 1). Previously, Minisci amidations with oxamic acids on these substrate classes required an oxidant with either heat (with[38] or without[15a, 15b, 15d] silver catalyst) or an added photocatalyst with light[3-9] to proceed well. To our delight, all *N*-heterocycles tested in Table 6, including a quinoline (**6a**, 50%), an isoquinoline (**6b**, 64%) a phenanthroline (**6c**, quant.), a xanthine (**6d**, quant.), a phenanthridine (**6e**, 84%) and a quinazoline (**6f**, 59%) proceeded to form the amidation products smoothly under photocatalyst-free light mediated reactions. Our discovery allows for milder room temperature reactions, often shorter reaction times as well as cost and atom economy benefits associated with not requiring an added metal catalyst, photocatalyst or photosensitiser.

Scheme 1 Ascertaining that the photosensitiser/photocatalyst-free light-mediated methodology is generally applicable to *N*-heterocycles beyond 1,3-azoles[a]



[a]Isolated yields reported unless otherwise stated. Ad = 1-Adamantyl. 2 equiv. of **4** unless otherwise stated. [b]5 equiv. of **4**, 6 equiv. of $(NH_4)_2S_2O_8$. [c]1.5 equiv. of **4**.

6. Quantum Yield Determination

General Information:

The following procedure was adapted from the literature.[10] Samples were irradiated using Penn M2 Photoreactor at 420 nm with 100% light intensity, fan speed = 6800 rpm, 25 ^{o}C and 750 rpm stir speed.

Photon flux measurements:

A) Potassium ferrioxalate trihydrate preparation

To a warm, stirred aqueous solution of potassium oxalate monohydrate (12 g, 65.1 mmol, 3.3 eq.) in DI water (20 mL) at 70 °C was added an aqueous solution of iron (III) chloride (3.2 g, 19.7 mmol, 1.0 eq.) in DI water (8 mL). The reaction was then cooled to rt and further cooled to 0 °C to precipitate a light green solid. This solid was then recrystallised three more times with water and left to air-dry overnight. Caution: potassium ferrioxalate trihydrate is sensitive to light and should be kept in the dark as much as possible.

B) 1,10-Phenanthroline buffer preparation

An aqueous solution in DI water of sodium acetate (4.92 g, 60.0 mmol), 1,10-phenanthroline (100 mg, 0.555 mmol) and concentrated sulfuric acid (1 mL) was prepared using a 100 mL volumetric flask.

C) Determination of photon flux

A 0.15 M aqueous solution of potassium ferrioxalate trihydrate (1.47 g, 3.00 mmol) in DI water (20 mL) was prepared using a 20 mL volumetric flask. 1.0 mL of the prepared solution was transferred to a 2 mL vial and irradiated for 20 seconds. The vial was then returned to darkness. 0.5 mL of the irradiated solution was transferred to a 25 mL volumetric flask, and 5 mL of the 1,10-phenanthroline buffer was added and diluted to the mark with DI water. A stirrer bar was added and the solution was stirred for 20 minutes at room temperature. 250 μL was transferred to a quartz cuvette along with DI water (2.5 mL). Using the Shimadzu UV-2550 spectrophotometer, the average absorbance after 10 s was 0.18 and after 20 s was 0.329. Substitution of these absorbances through the Beer-Lambert law permits the back-calculation of the Fe(II) concentration present in the stock solutions; noting the path length of the cuvette was 1 cm.

D) Calculating photon flux

Step 1: Concentration of the Fe(II) in the cuvette:

The photolysis gives a ligated Fe^{2+} complex that displays a characteristic absorbance peak at 510 nm. (ε = 11110 $L^{-1}cm^{-1}mol^{-1}$). The concentration of Fe^{2+} in the cuvette can be calculated using the Beer-Lambert Law:

$$A = \varepsilon l C$$

Where ε is molar absorptivity, l is path length, and C is concentration.

Calculation for 10 seconds:

$$\mathrm{A} = \varepsilon \mathrm{l} \mathrm{c}_1$$

$$\mathrm{c}_1 = \frac{\mathrm{A}}{\varepsilon \mathrm{l}}$$

$$\mathrm{c}_1 = \frac{0.18}{11{,}110\ \mathrm{L\ mol^{-1}\ cm^{-1}} \times 1\ \mathrm{cm}}$$

$$\mathrm{c}_1 = 1.62 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$$

Calculation for 20 seconds:

$$\mathrm{A} = \varepsilon \mathrm{l} \mathrm{c}_1$$

$$\mathrm{c}_1 = \frac{\mathrm{A}}{\varepsilon \mathrm{l}}$$

$$\mathrm{c}_1 = \frac{0.329}{11{,}110\ \mathrm{M^{-1} cm^{-1}} \times 1\ \mathrm{cm}}$$

$$\mathrm{c}_1 = 2.96 \times 10^{-5}\ \mathrm{mol\ L^{-1}}$$

Step 2: Concentration of Fe(II) upon irradiation:

From the cuvette concentration calculated above, the concentration of Fe(II) in the vial after photolysis can be found using the dilution equation (two times):

$$C_1V_1 = C_2V_2$$

Calculation for 10 seconds:

$$\mathrm{c}_1\mathrm{v}_1 = \mathrm{c}_2\mathrm{v}_2\ (1.2)$$

$$c_2 = \frac{c_1 v_1}{v_2}$$

$$c_2 = \frac{1.62 \times 10^{-5}\ \text{mol L}^{-1} \times 2.75 \times 10^{-3}\ \text{L}}{0.25 \times 10^{-3}\ \text{L}}$$

$$c_2 = 1.782 \times 10^{-4}\ \text{mol L}^{-1}$$

$$c_2 v_2 = c_3 v_3\ (1.3)$$

$$c_3 = \frac{1.782 \times 10^{-4}\ \text{mol L}^{-1} \times 25 \times 10^{-3}\ \text{L}}{0.5 \times 10^{-3}\ \text{L}}$$

$$\mathbf{c_3 = 8.91 \times 10^{-3}\ mol\ L^{-1}}$$

Calculation for 20 seconds:

$$c_1 v_1 = c_2 v_2\ (1.2)$$

$$c_2 = \frac{c_1 v_1}{v_2}$$

$$c_2 = \frac{2.96 \times 10^{-5}\ \text{mol L}^{-1} \times 2.75 \times 10^{-3}\ \text{L}}{0.25 \times 10^{-3}\ \text{L}}$$

$$c_2 = 3.256 \times 10^{-4}\ \text{mol L}^{-1}$$

$$c_2 v_2 = c_3 v_3\ (1.3)$$

$$c_3 = \frac{3.256 \times 10^{-4}\ \text{mol L}^{-1} \times 25 \times 10^{-3}\ \text{L}}{0.5 \times 10^{-3}\ \text{L}}$$

$$\mathbf{c_3 = 16.28 \times 10^{-3}\ mol\ L^{-1}}$$

Step 3: Photon flux

The moles of incident photons can be approximated using the absolute quantum yield of Fe(II), previously found to be $\Phi_{Fe(II),\ 457.9\ nm} = 0.85$.[11] Dividing the moles of photons by the time irradiated then gives the photon flux in the units photons per second. Independent trials with irradiation times of 10 s and 20 s gave an average photon flux of 1.003 x 10^{-6} mol s^{-1} (std. dev. = 0.063 x 10^{-6}).

Calculation for 10 seconds:

$$\text{moles of incident photons} = \frac{c_{\text{sample}} v_{\text{reaction}}}{\Phi_{Fe(II),457.9\,nm}}$$

$$\text{moles of incident photons} = \frac{(8.91 \times 10^{-3}\ \text{mol L}^{-1}) \times (1.0 \times 10^{-3}\ \text{L})}{0.85}$$

$$\text{moles of incident photons} = 1.048 \times 10^{-5}\ \text{mol}$$

$$\text{photon flux} = \frac{1.048 \times 10^{-5}}{10\ \text{s}}$$

$$\text{photon flux} = 1.048 \times 10^{-6}\ \text{mol s}^{-1}$$

Calculation for 20 seconds:

$$\text{moles of incident photons} = \frac{\text{C}_{\text{sample}}\text{V}_{\text{reaction}}}{\Phi_{Fe(II),457.9\,nm}}$$

$$\text{moles of incident photons} = \frac{(16.28 \times 10^{-3}\ \text{mol L}^{-1}) \times (1.0 \times 10^{-3}\ \text{L})}{0.85}$$

$$\text{moles of incident photons} = 1.915 \times 10^{-5}\ \text{mol}$$

$$\text{photon flux} = \frac{1.915 \times 10^{-5}}{20\ \text{s}}$$

$$\text{photon flux} = 9.576 \times 10^{-7}\ \text{mol s}^{-1}$$

E) Determining quantum yield

The quantum yield (Φ) of a reaction can be obtained by stopping the reaction at varying degrees of conversion using the following relationship:

$$\Phi_{\text{R}} = \frac{\text{moles of product}}{\text{moles of incident photons}}$$

NMR yield = 50%, reaction time 3 h (10,800 s)

$$\Phi_{\text{R}} = \frac{\text{moles of product}}{\text{moles of incident photons}}$$

$$\Phi_{\text{R}} = \frac{\text{moles of product}}{\text{photon flux} \times \text{reaction time}}$$

$$\Phi_{\text{R}} = \frac{1.75 \times 10^{-4}\ \text{mol}}{1.003 \times 10^{-6}\ \text{mol s}^{-1} \times 10{,}800\ \text{s}}$$

$$\Phi_{\text{R}} = 0.016$$

NMR yield = 61%, reaction time 4 h (14,400 s)

$$\Phi_{\text{R}} = \frac{\text{moles of product}}{\text{moles of incident photons}}$$

$$\Phi_R = \frac{\text{moles of product}}{\text{photon flux } \times \text{reaction time}}$$

$$\Phi_R = \frac{2.14 \times 10^{-4}\ \text{mol}}{1.003 \times 10^{-6}\ \text{mol s}^{-1}\ \times 14{,}400\ \text{s}}$$

$$\Phi_R = 0.015$$

NMR yield = 73%, reaction time 5 h (18,000 s)

$$\Phi_R = \frac{\text{moles of product}}{\text{moles of incident photons}}$$

$$\Phi_R = \frac{\text{moles of product}}{\text{photon flux } \times \text{reaction time}}$$

$$\Phi_R = \frac{2.56 \times 10^{-4}\ \text{mol}}{1.003 \times 10^{-6}\ \text{mol s}^{-1}\ \times 18{,}000\ \text{s}}$$

$$\Phi_R = 0.014$$

NMR yield = 81%, reaction time 6 h (21,600 s)

$$\Phi_R = \frac{\text{moles of product}}{\text{moles of incident photons}}$$

$$\Phi_R = \frac{\text{moles of product}}{\text{photon flux } \times \text{reaction time}}$$

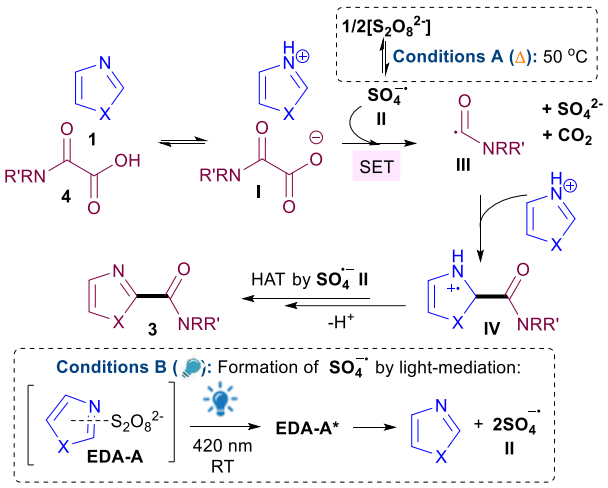
$$\Phi_R = \frac{2.56 \times 10^{-4}\ \text{mol}}{3.95 \times 10^{-7}\ \text{mol s}^{-1}\ \times 21{,}600\ \text{s}}$$

$$\Phi_R = 0.012$$

The average quantum yield (Φ) under Conditions B is 0.014 (std. dev. 0.0017), implying that a radical chain propagation mechanism does not occur.[12]

7. Discussion on Electronic Trends

In a typical Minisci reaction with pyridine-type heterocycles, the electron-withdrawing substituents are seen to enhance reactivity, presumably due to the higher reactivity of the protonated heterocycle towards nucleophilic radicals.[13] However, for benzothiazoles and thiazoles under our conditions, the opposite trend is observed, where electron-rich substituents generally resulted in better yields. This observation was initially puzzling, and one possible explanation is that it reflects the expected trend in pK_aH values of the (benzo)thiazole substrates 1.[14, 15] In our proposed mechanism (Scheme 2), the 1,3-azole 1 needs to be sufficiently basic to deprotonate oxamic acid 4 for the dual purpose of forming the carboxylate I for subsequent SET, but also for the crucial activation of the heterocycle towards nucleophilic radical addition *via* protonation. Therefore, if electron-withdrawing substituents on 1,3-azole 1 reduces its basicity sufficiently to disfavour the deprotonation 1+4→I, reaction may be impeded (e.g. 3s-u). For example, thiazole has a pK_aH of 2.53 (in H_2O) whereas imidazole has a pK_aH of 7,[14, 15] and the predicted pK_aH of oxamic acid 4 is between 1.60-2.49 (ACD/Chemaxon). Therefore, electron-withdrawing groups, and thereby reduced basicity, can potentially hinder reactivity with the less basic thiazole (e.g. 3s-u) but not the more basic imidazole (e.g. 3aj-3am). Following this argument, oxazole (pK_aH of 0.8)[13] and benzoxazole (ACD calculated pK_aH of 1.2±0.1) will likely not be suitable substrates in this reaction as they are not sufficiently basic to deprotonate oxamic acid 4. Indeed, attempts to amidate benzoxazole using 4a under both thermal and light-mediated conditions failed to produce any desired product, thereby corroborating our theory.



Scheme 2 Proposed Mechanisms

8. General Procedures

2.1 General Procedure for Oxamic Acid Synthesis:

General Procedure A: Ethyl oxalyl chloride (11 mmol, 1.1 equiv.) was added dropwise to a solution of the desired amine (10 mmol, 1 equiv.) and triethylamine (11 mmol, 1.1 equiv.) at 0 ^{o}C. The reaction mixture was then allowed to warm to room temperature and stirred at room temperature for 3 h. 1 M HCl (aq.) (20 mL) was then added and the organic phase separated. The aqueous phase was then extracted with CH_2Cl_2 (3 x 30 mL) and the organic phases combined, washed with brine (70 mL), dried over Na_2SO_4 and the solvent removed *in vacuo*. The oily residue was then carried through to the next step without further purification. 1 M NaOH (aq.) (50 mL, 50 mmol, 5 equiv.) was added and the mixture stirred overnight at 30 ^{o}C or starting material consumption was monitored *via* TLC. The mixture was then acidified with 1 M HCl (aq.) and the product extracted with CH_2Cl_2 (3 x 30 mL). The organic phases were then combined, washed with brine (80 mL), and dried over Na_2SO_4, filtered, the solvent was then removed *in vacuo* to afford the product.

2.2 General Procedures for Thermal Amidation Reaction:

General Procedure B (for benzimidazoles): A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Benzimidazole (0.35 mmol, 1 equiv.), oxamic acid (0.70 mmol, 2 equiv.) and ammonium persulfate (1.05 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. The DMSO (0.7 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and stirred at 40 – 70 ^{o}C for 24 h. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product.

General Procedure C (for imidazoles): A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Imidazole (0.35 mmol, 1 equiv.), oxamic acid (0.70 mmol, 2 equiv.) and ammonium persulfate (1.05 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. The DMSO

(1.75 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and stirred at 40 – 70 ^{o}C for 24 h. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product.

General Procedure D (for benzothiazoles): A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Benzothiazole (0.35 mmol, 1 equiv.), oxamic acid (0.70 mmol, 2 equiv.) and ammonium persulfate (1.05 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. The DMSO (1.0 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and stirred at 40 – 70 ^{o}C for 24 h. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product.

General Procedure E (for thiazoles): A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Thiazole (0.35 mmol, 1 equiv.), oxamic acid (0.70 mmol, 2 equiv.) and ammonium persulfate (1.05 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. The DMSO (0.875 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and stirred at 40 – 70 ^{o}C for 6 – 24 h. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product.

2.3 General Procedures for Light-Mediated Amidation Reaction:

General Procedure F (for benzimidazoles): A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Benzimidazole (0.35 mmol, 1 equiv.), oxamic acid (0.70 mmol, 2 equiv.) and ammonium persulfate (1.05 mmol, 3 equiv.) were added

quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. The DMSO (0.7 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 3 h at 25 ^{o}C with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product.

General Procedure G (for imidazoles): A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Imidazole (0.35 mmol, 1 equiv.), oxamic acid (0.70 mmol, 2 equiv.) and ammonium persulfate (1.05 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. The DMSO (1.75 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 6 h at 25 ^{o}C with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product.

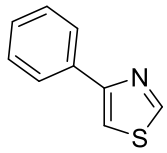
General Procedure H (for benzothiazoles): A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Benzothiazole (0.35 mmol, 1 equiv.), oxamic acid (0.70 mmol, 2 equiv.) and ammonium persulfate (1.05 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. The DMSO (1.0 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 3 h at 25 ^{o}C with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product.

General Procedure I (for thiazoles): A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Thiazole (0.35 mmol, 1 equiv.), oxamic acid (0.70 mmol, 2 equiv.) and ammonium persulfate (1.05 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. The DMSO (0.875 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 3 h at 25 ^{o}C with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the crude product.

9. Product Characterisation

Starting Materials

4-Phenylthiazole (SI1)

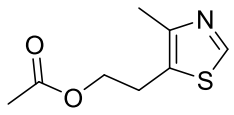


SI1

4-Bromothiazole (430.3 mg, 2.67 mmol, 1 equiv.), phenylboronic acid (488.1 mg, 4.005 mmol, 1.5 equiv.), potassium carbonate (737.0 mg, 5.34 mmol, 2 equiv.) and tetrakis(triphenylphosphine)palladium(0) (205.8 mg, 0.178 mmol, 6.67 mol%) were slurried in a 1,4-dioxane:H_2O (3:1) mixture and purged with argon for 5 minutes. The reaction mixture was then heated to 100 °C and left with continuous stirring for 18 h. After 18 h, the reaction was allowed to cool to room temperature, diluted in ethyl acetate (15 ml), the pH adjusted to pH 14 with NaOH (1M) and the organic phase collected. The aqueous was extracted with ethyl acetate (2x10 ml), the organic layers combined, washed with brine (50 ml), dried over sodium sulfate, filtered and the solvent removed in *vacuo* to afford 4-phenylthiazole **SI1** as a colourless oil (226.0 mg, 1.415 mmol, 53%).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.88 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.97 – 7.91 (m, 2H, 2xAr-H), 7.54 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.49 – 7.40 (m, 2H, Ar-H), 7.35 (tt, J = 14.5, 6.5, 1.5 Hz, 1H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6 (C), 152.9 (CH), 134.4 (C), 129.0 (CH), 128.4 (CH), 126.6 (CH), 112.7 (CH). ν_{max}/cm^{-1} 3113, 3072, 3028, 1602, 1579, 1520, 1475, 1445, 1416, 1322, 1296, 1277, 1177. Data consistent with literature.[16]

2-(4-Methylthiazol-5-yl)ethyl acetate (SI2)



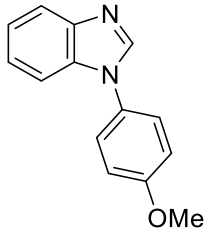
SI2

2-(4-Methylthiazol-5-yl)ethan-1-ol (505.6 mg, 3.5 mmol, 1 equiv.), 4-(dimethylamino)pyridine (22.6 mg 0.175 mmol, 0.05 equiv.) and triethylamine (0.54 ml, 3.85 mmol, 1.1 equiv.) were dissolved in dichloromethane and allowed to cool to 0 °C. Acetic anhydride (0.36 ml, 3.85 mmol, 1.1 equiv.) was then added dropwise with continuous stirring. The reaction was then allowed to warm to room temperature and left with continuous stirring

for 18 h. After 18 h, the reaction was diluted in dichloromethane (10 ml), washed with HCl (1M) (20 ml) and the organic phase collected. The aqueous was then extracted with dichloromethane (3x10 ml), the organic phases combined, washed with brine (70 ml), dried over sodium sulfate, filtered and the solvent removed in *vacuo* to afford 2-(4-methylthiazol-5-yl)ethyl acetate **SI2** as an orange oil (427.3 mg, 2.31 mmol, 66%).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.57 (s, 1H, Ar-H), 4.20 (t, *J* = 6.5 Hz, 2H, CH_2), 3.06 (t, *J* = 6.5 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3), 2.02 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8 (C), 150.0 (C), 149.9 (CH), 126.8 (C), 64.1 (CH_2), 25.8 (CH_2), 20.9 (CH_3), 14.9 (CH_3). ν_{max}/cm^{-1} 3080, 2955, 2926, 1736, 1544, 1414, 1380, 1363, 1309, 1222, 1156, 1096, 1044. Data consistent with literature.[17]

1-(4-Methoxyphenyl)-1*H*-benzo[*d*]imidazole (SI3)



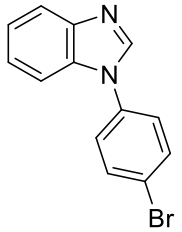
SI3

Benzimidazole (476.1 mg, 4.0 mmol, 1 equiv.), (4-methoxyphenyl)boronic acid (733.2 mg, 4.8 mmol, 1.2 equiv.) and $CuCl_2.2H_2O$ (54.2 mg, 0.32 mmol, 8 mol%) were dissolved in methanol (32 ml), heated to 40 °C and left with continuous stirring for 5 h. After 5 h, the reaction was allowed to cool to room temperature, washed with saturated sodium bicarbonate (30 ml) and the organic layer collected. The aqueous was then extracted with dichloromethane (3x10 ml), the organic layers combined, washed with brine (50 ml), dried over sodium sulfate, filtered and the solvent removed in *vacuo* to afford the crude product. The crude was then purified via column chromatography (60:40, hexane:ethyl acetate) to afford 1-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole **SI3** as a colourless oil (139.4 mg, 0.64 mmol, 16%).

R_f = 0.15 (60:40, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.06 (s, 1H, Ar-H), 7.91 – 7.85 (m, 1H, Ar-H), 7.47 – 7.43 (m, 1H, Ar-H), 7.41 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 7.35 – 7.29 (m, 2H, 2xAr-H), 7.07 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 3.89 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5 (C), 143.8 (C), 142.6 (C), 134.4 (C), 129.2 (CH), 125.9 (CH), 123.7 (CH), 122.8 (CH), 120.6 (CH), 115.3 (CH), 110.5 (CH), 55.8 (CH_3). ν_{max}/cm^{-1} 3628, 3367,

3054, 3004, 2958, 2837, 1613, 1513, 1489, 1456, 1373, 1344, 1320. Data consistent with literature.[18]

1-(4-Bromophenyl)-1*H*-benzo[*d*]imidazole (SI4)

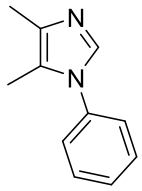


SI4

Benzimidazole (473.4 mg, 4.0 mmol, 1 equiv.), (4-bromophenyl)boronic acid (965.0 mg, 4.8 mmol, 1.2 equiv.) and $CuCl_2.2H_2O$ (55.9 mg, 0.32 mmol, 8 mol%) were dissolved in methanol (32 ml), heated to 40 °C and left with continuous stirring for 5 h. After 5 h, the reaction was allowed to cool to room temperature, washed with saturated sodium bicarbonate (30 ml) and the organic layer collected. The aqueous was then extracted with dichloromethane (3x10 ml), the organic layers combined, washed with brine (50 ml), dried over sodium sulfate, filtered and the solvent removed in *vacuo* to afford the crude product. The crude was then purified *via* column chromatography (60:40, hexane:ethyl acetate) to afford 1-(4-bromophenyl)-1*H*-benzo[*d*]imidazole **SI4** as a colourless oil (930.6 mg, 3.40 mmol, 85%).

R_f = 0.30 (60:40, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.12 (s, 1H, Ar-H), 7.95 – 7.87 (m, 1H, Ar-H), 7.72 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 7.52 – 7.47 (m, 1H, Ar-H), 7.41 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 7.38 – 7.34 (m, 2H, 2xAr-H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.7 (C), 135.5 (C), 135.2 (C), 133.5 (C), 130.9 (CH), 125.8 (CH), 124.5 (CH), 123.6 (CH), 122.2 (CH), 120.7 (CH), 110.6 (CH). ν_{max}/cm^{-1} 3085, 3055, 1613, 1585, 1559, 1533, 1495, 1453, 1438, 1409, 1376, 1343, 1326, 1311, 1294, 1285, 1273. Data consistent with literature.[18]

4,5-Dimethyl-1-phenyl-1*H*-imidazole (SI5)



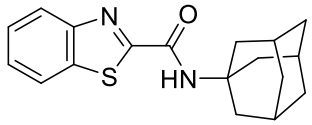
SI5

2,3-Butanedione (0.88 ml, 10.0 mmol, 1 equiv.), aniline (1.1 ml, 12.0 mmol, 1.2 equiv.), paraformaldehyde (300.9 mg, 10.0 mmol, 1 equiv.), acetic acid (0.57 ml, 10.0 mmol, 1 equiv.) and ammonium acetate (788.5 mg, 10.0 mmol, 1 equiv.) were dissolved in a chloroform:H_2O, 40:1 (20:0.5 ml) mixture, heated to reflux and left with continuous stirring for 4 h. After 4 h, the reaction was allowed to cool to room temperature and the reaction mixture concentrated in *vacuo*. The oily residue was then diluted in ethyl acetate (20 ml) and in an ice-bath, 40% potassium hydroxide was added to adjust the pH to pH 14. The organic layer was then collected, the aqueous extracted with ethyl acetate (3x20 ml), the organic layers combined, washed with water (80 ml), washed with brine (80 ml), dried over sodium sulfate, filtered and the solvent removed in *vacuo* to afford the crude product. The crude was then purified *via* column chromatography (20:80, hexane:ethyl acetate) to afford 4,5-dimethyl-1-phenyl-1*H*-imidazole **SI5** as a brown oil (712.2 mg, mmol, 41%).

R_f = 0.13 (20:80, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.52 – 7.36 (m, 4H, 4xAr-H), 7.29 – 7.23 (m, 2H, 2xAr-H), 2.23 (d, *J* = 1.0 Hz, 3H, CH_3), 2.09 (d, *J* = 1.0 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2 (C), 135.3 (C), 134.7 (CH), 129.6 (CH), 128.1 (CH), 125.7 (CH), 123.0 (C), 13.0 (CH_3), 9.3 (CH_3). ν_{max}/cm^{-1} 3381, 3061, 2906, 2848, 2248, 1684, 1598, 1524, 1498, 1481, 1447, 1393, 1358, 1343, 1311, 1293, 1276, 1259. Data consistent with literature.[19]

Benzothiazole Scope

***N*-(Adamantan-1-yl)benzo[*d*]thiazole-2-carboxamide (3a)**



3a

Thermal: General procedure D was followed: benzothiazole (49.0 mg, 0.362 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.9 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)benzo[*d*]thiazole-2-carboxamide **3a** as a white solid (86.9 mg, 0.278 mmol, 77%).

Light Mediated: General procedure H was followed: benzothiazole (47.4 mg, 0.351 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)benzo[*d*]thiazole-2-carboxamide **3a** as a white solid (91.5 mg, 0.293 mmol, 83%).

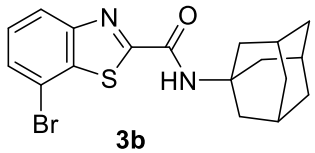
1 g Scale Thermal Reaction: benzothiazole (1.0053 g, 7.437 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (3.3065 g, 14.8 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (5.0692 g, 22.2 mmol, 3 equiv.) in DMSO (21 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)benzo[*d*]thiazole-2-carboxamide **3a** as a white solid (1.864 g, 5.994 mmol, 81%).

0.7 g Scale Light-Mediated Reaction: benzothiazole (0.7098 g, 5.251 mmol, 1 equiv.), 2-(adamantan-1-yl-amino)-2-oxoacetic acid (2.342 g, 10.48 mmol, 2 equiv.) and ammonium persulfate (3.595 g, 15.75 mmol, 3 equiv.) in DMSO (0.35 M) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (98:2, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)benzo[*d*]thiazole-2-carboxamide **3a** as a white solid (1.099 g, 3.520 mmol, 67%).

R_f = 0.09 (95:5, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.04 (ddd, *J* = 8.0, 1.5, 1.0 Hz, 1H, Ar-H), 7.95 (ddd, *J* = 8.0, 1.5, 1.0 Hz, 1H, Ar-H), 7.53 (dt, *J* = 8.0, 1.5 Hz, 1H, Ar-H), 7.46 (dt, *J* = 8.0, 1.5 Hz, 1H, Ar-H), 7.20 (s, 1H, N-H), 2.21 – 2.12 (m, 9H, 3xCH and 3xCH_2), 1.79 – 1.68 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9 (C), 158.9 (C),

153.1 (C), 137.4 (C), 126.8 (CH), 126.6 (CH), 124.2 (CH), 122.5 (CH), 52.9 (C), 41.6 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3395, 2901, 2847, 1676, 1652, 1524, 1490, 1456, 1436, 1359, 1242, 1145. M.P. = 158 - 161 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{21}N_2O_1S_1$, 313.1369; found 313.1373.

***N*-(Adamantan-1-yl)-7-bromobenzo[*d*]thiazole-2-carboxamide (3b)**



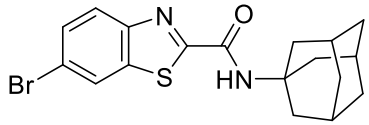
3b

Thermal: General procedure D was followed: 7-bromobenzothiazole (76.0 mg, 0.355 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.3 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 ºC for 24 h. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-7-bromobenzo[*d*]thiazole-2-carboxamide **3b** as a white solid (104.7 mg, 0.266 mmol, 75%).

Light Mediated: General procedure H was followed: 7-bromobenzothiazole (75.0 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.8 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.0 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 ºC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-7-bromobenzo[*d*]thiazole-2-carboxamide **3a** as a white solid (117.0 mg, 0.300 mmol, 86%).

R_f = 0.20 (95:5, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-H), 7.60 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-H), 7.41 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.14 (s, 1H, N-H), 2.21 – 2.12 (m, 9H, 3xCH and 3xCH_2), 1.77 – 1.70 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3 (C), 158.5 (C), 152.7 (C), 140.4 (C), 129.4 (CH), 127.9 (CH), 123.1 (CH), 114.8 (C), 53.0 (C), 41.6 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3375, 2906, 2849, 1673, 1652, 1527, 1475, 1449, 1361, 1317, 1297, 1244, 1139. M.P. = 206 - 209 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{20}{}^{79}Br_1N_2O_1S_1$, 391.0474; found 391.0482.

***N*-(Adamantan-1-yl)-6-bromobenzo[*d*]thiazole-2-carboxamide (3c)**



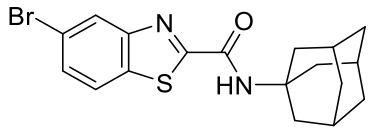
3c

Thermal: General procedure D was followed: 6-bromobenzothiazole (76.5 mg, 0.357 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.5 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (238.3 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (93:7, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-6-bromobenzo[*d*]thiazole-2-carboxamide **3c** as a white solid (90.1 mg, 0.231 mmol, 65%).

Light Mediated: General procedure H was followed: 6-bromobenzothiazole (74.9 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-6-bromobenzo[*d*]thiazole-2-carboxamide **3a** as a white solid (105.0 mg, 0.268 mmol, 77%).

R_f = 0.24 (93:7, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 2.0, 0.5 Hz, 1H, Ar-H), 7.89 (dd, *J* = 9.0, 0.5 Hz, 1H, Ar-H), 7.63 (dd, *J* = 9.0, 2.0 Hz, 1H, Ar-H), 7.14 (s, 1H, N-H), 2.21 – 2.10 (m, 9H, 3xCH and 3xCH_2), 1.79 – 1.69 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5 (C), 158.5 (C), 151.9 (C), 139.0 (C), 130.5 (CH), 125.3 (CH), 125.1 (CH), 120.6 (C), 53.0 (C), 41.6 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3386, 3090, 2907, 2887, 2850, 1677, 1672, 1652, 1635, 1581, 1524, 1489, 1451, 1350, 1344, 1156, 1102. M.P. = 227 - 230 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{20}{}^{79}Br_1N_2O_1S_1$, 391.0474; found 391.0466.

***N*-(Adamantan-1-yl)-5-bromobenzo[*d*]thiazole-2-carboxamide (3d)**



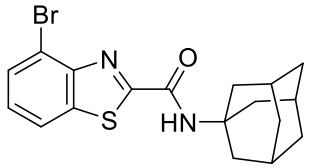
3d

Thermal: General procedure D was followed: 5-bromobenzothiazole (75.8 mg, 0.354 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.2 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (93:7, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-5-bromobenzo[*d*]thiazole-2-carboxamide **3d** as a white solid (87.0 mg, 0.224 mmol, 63%).

Light Mediated: General procedure H was followed: 5-bromobenzothiazole (74.9 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.9 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (93:7, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-5-bromobenzo[*d*]thiazole-2-carboxamide **3d** as a white solid (114.0 mg, 0.291 mmol, 83%).

R_f = 0.24 (93:7, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 2.0, 0.5 Hz, 1H, Ar-H), 7.81 (dd, *J* = 9.0, 0.5 Hz, 1H, Ar-H), 7.57 (dd, *J* = 9.0, 2.0 Hz, 1H, Ar-H), 7.15 (s, 1H, N-H), 2.20 – 2.13 (m, 9H, 3xCH and 3xCH_2), 1.80 – 1.68 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6 (C), 158.4 (C), 154.2 (C), 136.2 (C), 129.8 (CH), 127.0 (CH), 123.6 (CH), 120.4 (C), 53.0 (C), 41.6 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3379, 3091, 2909, 2887, 2849, 1678, 1672, 1581, 1540, 1524, 1489, 1451, 1360, 1312, 1192, 1101. M.P. = 214 - 217 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{20}{}^{79}Br_1N_2O_1S_1$, 391.0474; found 391.0481.

***N*-(Adamantan-1-yl)-4-bromobenzo[*d*]thiazole-2-carboxamide (3e)**



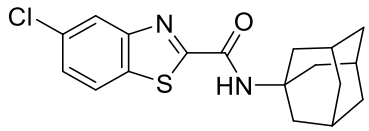
3e

Thermal: General procedure D was followed: 4-bromobenzothiazole (75.5 mg, 0.353 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (238.4 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (93:7, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-bromobenzo[*d*]thiazole-2-carboxamide **3e** as a white solid (106.0 mg, 0.271 mmol, 77%).

Light Mediated: General procedure H was followed: 4-bromobenzothiazole (74.9 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.5 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (93:7, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-bromobenzo[*d*]thiazole-2-carboxamide **3e** as a white solid (101.0 mg, 0.258 mmol, 74%).

R_f = 0.13 (93:7, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-H), 7.73 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-H), 7.32 (t, *J* = 8.0 Hz, 1H, Ar-H), 7.23 (s, 1H, N-H), 2.23 – 2.12 (m, 9H, 3xCH and 3xCH_2), 1.81 – 1.67 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6 (C), 158.4 (C), 151.3 (C), 138.3 (C), 130.3 (CH), 127.4 (CH), 121.7 (CH), 117.8 (C), 53.0 (C), 41.5 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3395, 2903, 2887, 2848, 1673, 1652, 1538, 1530, 1486, 1451, 1360, 1243, 1205, 1096. M.P. = 189 - 191 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{20}{}^{79}Br_1N_2O_1S_1$, 391.0474; found 391.0458.

***N*-(Adamantan-1-yl)-5-chlorobenzo[*d*]thiazole-2-carboxamide (3f)**



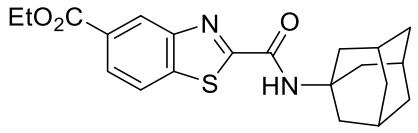
3f

Thermal: General procedure D was followed: 5-chlorobenzothiazole (61.2 mg, 0.361 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.7 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-5-chlorobenzo[*d*]thiazole-2-carboxamide **3f** as a white solid (84.8 mg, 0.245 mmol, 68%).

Light Mediated: General procedure H was followed: 5-chlorobenzothiazole (59.4 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-5-chlorobenzo[*d*]thiazole-2-carboxamide **3f** as a white solid (88.9 mg, 0.256 mmol, 73%).

R_f = 0.12 (95:5, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 2.0 Hz, 1H, Ar-H), 7.87 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.44 (dd, *J* = 9.0, 2.0 Hz, 1H, Ar-H), 7.15 (s, 1H, N-H), 2.20 – 2.12 (m, 9H, 3xCH and 3xCH_2), 1.77 – 1.71 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8 (C), 158.4 (C), 153.8 (C), 135.6 (C), 132.9 (C), 127.2 (CH), 123.9 (CH), 123.3 (CH), 53.0 (C), 41.6 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3382, 3092, 2910, 2886, 2852, 1680, 1652, 1590, 1521, 1489, 1453, 1436, 1361, 1242, 1193, 1157, 1102, 1083, 813. M.P. = 217 - 220 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{18}H_{20}{}^{35}Cl_1N_2O_1S_1$, 347.0979; found 347.0976.

Ethyl-2-((adamantan-1-yl)carbamoyl)benzo[*d*]thiazole-5-carboxylate (3g)



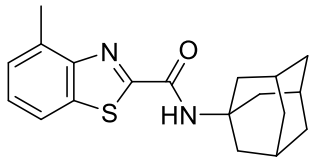
3g

Thermal: General procedure D was followed: ethyl-benzothiazole-5-carboxylate (73.7 mg, 0.356 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.6 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.0 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford ethyl-2-((adamantan-1-yl)carbamoyl)benzo[*d*]thiazole-5-carboxylate **3g** as a white solid (71.6 mg, 0.186 mmol, 52%).

Light Mediated: General procedure H was followed: ethyl-benzothiazole-5-carboxylate (72.5 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.8 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford ethyl-2-((adamantan-1-yl)carbamoyl)benzo[*d*]thiazole-5-carboxylate **3g** as a white solid (70.4 mg, 0.183 mmol, 52%).

R_f = 0.35 (90:10, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.74 (dd, *J* = 2.0, 1.0 Hz, 1H, Ar-H), 8.14 (dd, *J* = 9.0, 2.0 Hz, 1H, Ar-H), 8.00 (dd, *J* = 9.0, 1.0 Hz, 1H, Ar-H), 7.19 (s, 1H, N-H), 4.44 (q, *J* = 7.0 Hz, 2H, CH_2), 2.21 – 2.13 (m, 9H, 3xCH and 3xCH_2), 1.78 – 1.71 (m, 6H, 3xCH_2), 1.44 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4 (C), 166.2 (C), 158.4 (C), 152.9 (C), 141.8 (C), 129.6 (C), 127.0 (CH), 125.9 (CH), 122.4 (CH), 61.5 (CH_2), 53.0 (C), 41.6 (CH_2), 36.4 (CH_2), 29.6 (CH), 14.5 (CH_3). ν_{max}/cm^{-1} 3392, 2906, 2848, 2359, 1708, 1674, 1527, 1489, 1479, 1469, 1456, 1345, 1326, 1313, 1299, 1285, 1246, 1225, 1208, 1151, 1142, 1045, 1024. M.P. = 111 - 114 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{25}N_2O_3S_1$, 385.1580; found 385.1583.

***N*-(Adamantan-1-yl)-4-methylbenzo[*d*]thiazole-2-carboxamide (3h)**



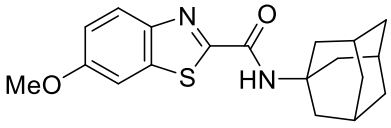
3h

Thermal: General procedure D was followed: 4-methylbenzothiazole (54.0 mg, 0.362 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (238.9 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (97:3, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-methylbenzo[*d*]thiazole-2-carboxamide **3h** as a colourless oil (82.5 mg, 0.252 mmol, 70%).

Light Mediated: General procedure H was followed: 4-methylbenzothiazole (52.2 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (97:3, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-methylbenzo[*d*]thiazole-2-carboxamide **3h** as a colourless oil (97.8 mg, 0.300 mmol, 86%).

R_f = 0.08 (97:3, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.76 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H, Ar-H), 7.38 – 7.29 (m, 2H, 2xAr-H), 7.22 (s, 1H, N-H), 2.75 (s, 3H, CH_3), 2.24 – 2.11 (m, 9H, 3xCH and 3xCH_2), 1.82 – 1.67 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (C), 159.1 (C), 152.6 (C), 137.4 (C), 134.4 (C), 127.1 (CH), 126.6 (CH), 119.9 (CH), 52.8 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH), 18.3 (CH_3). ν_{max}/cm^{-1} 3379, 2906, 2846, 1667, 1514, 1485, 1452, 1357, 1342, 1313, 1296, 1281, 1239, 1134, 1099. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{19}H_{23}N_2O_1S_1$, 327.1526; found 327.1528.

***N*-(Adamantan-1-yl)-6-methoxybenzo[*d*]thiazole-2-carboxamide (3i)**



3i

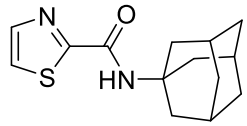
Thermal: General procedure D was followed: 6-methoxybenzothiazole (57.6 mg, 0.349 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.1 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.1 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-6-methoxybenzo[*d*]thiazole-2-carboxamide **3i** as a white solid (108.8 mg, 0.319 mmol, 91%).

Light Mediated: General procedure H was followed: 6-methoxybenzothiazole (57.8 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-6-methoxybenzo[*d*]thiazole-2-carboxamide **3i** as a white solid (119.0 mg, 0.347 mmol, 99%).

R_f = 0.40 (80:20, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 9.0 Hz, 1H, Ar-H), 7.36 (d, *J* = 2.5 Hz, 1H, Ar-H), 7.12 (dd, *J* = 9.0, 2.5 Hz, 2H, Ar-H and N-H), 3.89 (s, 3H, CH_3), 2.19 – 2.11 (m, 9H, 3xCH), 1.80 – 1.67 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2 (C), 159.1 (C), 158.9 (C), 147.6 (C), 139.0 (C), 124.8 (CH), 117.1 (CH), 104.1 (CH), 55.9 (CH_3), 52.8 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3392, 3113, 2901, 2892, 2847, 1668, 1652, 1602, 1555, 1519, 1492, 1462, 1456, 1449, 1359, 1310, 1285, 1259, 1244, 1225, 1151, 1119, 1094, 1074, 1045, 1024. M.P. = 157 - 160 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{19}H_{23}N_2O_2S_1$, 343.1475; found 343.1472.

Thiazole Scope

***N*-(Adamantan-1-yl)thiazole-2-carboxamide (3j)**



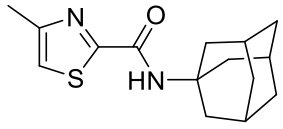
3j

Thermal: General procedure E was followed: thiazole (29.5 mg, 0.347 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)thiazole-2-carboxamide **3j** as a white solid (66.4 mg, 0.252 mmol, 73%).

Light Mediated: General procedure I was followed: thiazole (30.0 mg, 0.352 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.5 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)thiazole-2-carboxamide **3a** as a white solid (74.5 mg, 0.284 mmol, 81%).

R_f = 0.29 (90:10, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.52 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.02 (s, 1H, N-H), 2.15 – 2.12 (m, 9H, 3xCH and 3xCH_2), 1.76 – 1.69 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9 (C), 158.5 (C), 143.3 (CH), 124.4 (CH), 52.6 (C), 41.7 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3382, 3081, 2909, 2852, 2360, 1669, 1524, 1485, 1476, 1456, 1436, 1395, 1356, 1316, 1253, 1169, 1154, 1101, 1073. M.P. = 130 - 133 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{19}N_2S_1O_1$, 263.1213; found 263.1204.

***N*-(Adamantan-1-yl)-4-methylthiazole-2-carboxamide (3k)**



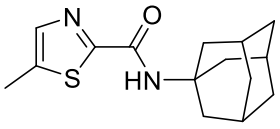
3k

Thermal: General procedure E was followed: 4-methyl-1,3-thiazole (34.7 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (158.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (242.0 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) at 50 ºC for 24 h. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-methylthiazole-2-carboxamide **3k** as a white solid (76.9 mg, 0.278 mmol, 79%).

Light Mediated: General procedure I was followed: 4-methyl-1,3-thiazole (34.8 mg, 0.351 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.1 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 ºC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-methylthiazole-2-carboxamide **3k** as a white solid (85.8 mg, 0.310 mmol, 88%).

R_f = 0.27 (90:10, hexane:ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.06 (q, *J* = 1.0 Hz, 1H, Ar-H), 6.98 (s, 1H, N-H), 2.45 (d, *J* = 1.0 Hz, 3H, CH_3), 2.17 – 2.10 (m, 9H, 3xCH and 3xCH_2), 1.77 – 1.67 (m, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7 (C), 158.7 (C), 153.7 (C), 119.2 (CH), 52.5 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH), 17.2 (CH_3). ν_{max}/cm^{-1} 3377, 2930, 2913, 2848, 1666, 1518, 1440, 1359, 1320, 1317, 1298, 1282, 1140, 1108, 1101. M.P. = 116-119˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{21}N_2O_1S_1$, 277.1369; found 277.1363.

***N*-(Adamantan-1-yl)-5-methylthiazole-2-carboxamide (3l)**



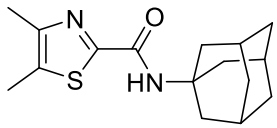
3l

Thermal: General procedure E was followed: 5-methyl-1,3-thiazole (34.3 mg, 0.346 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.6 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (238.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) at 50 ºC for 24 h. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-5-methylthiazole-2-carboxamide **3l** as a white solid (81.0 mg, 0.293 mmol, 85%).

Light Mediated: General procedure I was followed: 5-methyl-1,3-thiazole (35.4 mg, 0.357 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 ºC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-5-methylthiazole-2-carboxamide **3l** as a white solid (91.6 mg, 0.331 mmol, 93%).

R_f = 0.24 (90:10, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.44 (q, *J* = 1.0 Hz, 1H, Ar-H), 6.92 (s, 1H, N-H), 2.50 (d, *J* = 1.0 Hz, 3H, CH_3), 2.11 (app. s, 9H, 3xCH and 3xCH_2), 1.73 – 1.68 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 (C), 158.8 (C), 141.2 (CH), 139.9 (C), 52.5 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH), 12.5 (CH_3). ν_{max}/cm^{-1} 3387, 2908, 2848, 1663, 1512, 1454, 1416, 1361, 1343, 1299, 1246, 1188, 1153, 1101. M.P. = 106-109 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{21}N_2O_1S_1$, 277.1369; found 277.1373.

***N*-(Adamantan-1-yl)-4,5-dimethylthiazole-2-carboxamide (3m)**



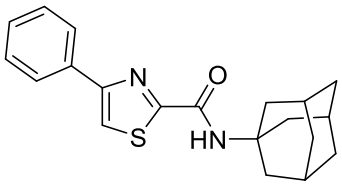
3m

Thermal: General procedure E was followed: 4,5-dimethyl-1,3-thiazole (42.8 mg, 0.378 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (158.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (238.8 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) at 70 ^oC for 24 h. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4,5-dimethylthiazole-2-carboxamide **3m** as a white solid (50.4 mg, 0.174 mmol, 46%).

Light Mediated: General procedure I was followed: 4,5-dimethyl-1,3-thiazole (39.8 mg, 0.352 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4,5-dimethylthiazole-2-carboxamide **3m** as a white solid (42.7 mg, 0.147 mmol, 42%).

R_f = 0.08 (95:5, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 6.91 (s, 1H, N-H), 2.38 (d, *J* = 1.0 Hz, 3H, CH_3), 2.32 (d, *J* = 1.0 Hz, 3H, CH_3), 2.15 – 2.09 (m, 9H, 3xCH and 3xCH_2), 1.74 – 1.67 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3 (C), 158.9 (C), 149.5 (C), 132.9 (C), 52.4 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH), 14.9 (CH_3), 12.0 (CH_3). ν_{max}/cm^{-1} 3395, 2914, 2850, 1672, 1510, 1443, 1357, 1344, 1298, 1246, 1154, 1108. M.P. = 125 - 128 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{16}H_{23}N_2O_1S_1$, 291.1526; found 291.1532.

***N*-(Adamantan-1-yl)-4-phenylthiazole-2-carboxamide (3n)**

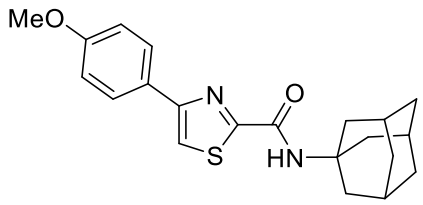


3n

Light Mediated: General procedure I was followed: 4-phenyl-1,3-thiazole (56.4 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (97:3, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-phenylthiazole-2-carboxamide **3n** as a white solid (54.5 mg, 0.161 mmol, 46%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H, 2xAr-H), 7.65 (s, 1H, Ar-H), 7.48 – 7.41 (m, 2H, 2xAr-H), 7.36 (tt, *J* = 7.0, 1.5 Hz, 1H, Ar-H), 7.12 (br. s, 1H, N-H), 2.16 (app. s, 9H, 3xCH and 3xCH_2), 1.74 (app. s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4 (C), 158.5 (C), 156.2 (C), 133.9 (C), 129.0 (CH), 128.7 (CH), 126.5 (CH), 118.1 (CH), 52.6 (C), 41.7 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3379, 3087, 2914, 2850, 1664, 1531, 1481, 1440, 1360, 1345, 1303, 1250, 1156, 1103, 1077. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{23}N_2O_1S_1$, 339.1526; found 339.1522.

***N*-(Adamantan-1-yl)-4-(4-methoxyphenyl)thiazole-2-carboxamide (3o)**



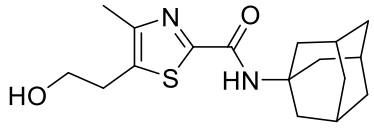
3o

Thermal: General procedure E was followed: 4-(4-methoxyphenyl)-1,3-thiazole (66.4 mg, 0.349 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (4:5.7:0.3, hexane:DCM:MeCN) to afford *N*-(adamantan-1-yl)-4-(4-methoxyphenyl)thiazole-2-carboxamide **3o** as an off-white solid (66.3 mg, 0.174 mmol, 52%).

Light Mediated: General procedure I was followed: 4-(4-methoxyphenyl)-1,3-thiazole (67.0 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.5 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.8 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (97:3, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-(4-methoxyphenyl)thiazole-2-carboxamide **3o** as an off-white solid (77.2 mg, 0.209 mmol, 60%).

R_f = 0.51 (4:5.7:0.3, hexane:DCM:MeCN). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 7.52 (s, 1H, Ar-H), 7.11 (s, 1H, N-H), 6.97 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 3.86 (s, 3H, CH_3), 2.21 – 2.11 (m, 9H, 3xCH and 3xCH_2), 1.81 – 1.67 (m, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2 (C), 160.1 (C), 158.6 (C), 156.0 (C), 127.8 (CH), 126.9 (C), 116.5 (CH), 114.4 (CH), 55.5 (CH_3), 52.6 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3384, 3092, 2905, 2849, 2248, 2034, 1668, 1611, 1580, 1527, 1482. M.P. = 183 – 186 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{24}N_2O_2S$, 369.1631; found 369.1635.

***N*-(Adamantan-1-yl)-5-(2-hydroxyethyl)-4-methylthiazole-2-carboxamide (3p)**

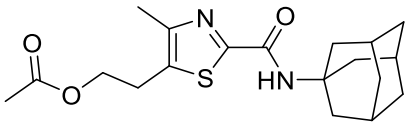


3p

Light Mediated: General procedure I was followed: 2-(4-methyl-1,3-thiazol-5yl)ethanol (50.5 mg, 0.353 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (50:50, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-5-(2-hydroxyethyl)-4-methylthiazole-2-carboxamide **3p** as a colourless oil (62.7 mg, 0.196 mmol, 55%).

^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.95 (br. s, 1H, N-H), 3.82 (t, *J* = 5.0 Hz, 2H, CH_2), 2.99 (t, *J* = 6.0 Hz, 2H, CH_2), 2.59 (br. s, 1H, O-H), 2.35 (s, 3H, CH_3), 2.09 (app. s, 9H, 3xCH and 3xCH_2), 1.69 (app. s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1 (C), 158.9 (C), 150.0 (C), 134.9 (C), 62.7 (CH), 52.4 (C), 41.6 (CH_2), 36.4 (CH_2), 30.2 (CH_2), 29.5 (CH), 15.1 (CH_3). ν_{max}/cm^{-1} 3378, 2905, 2849, 1657, 1519, 1477, 1451, 1436, 1378, 1359, 1345, 1302, 1284, 1253, 1189, 1156, 1103, 1051. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{17}H_{25}N_2O_2S_1$, 321.1631; found 321.1634.

2-(2-((Adamantan-1-yl)carbamoyl)-4-methylthiazol-5-yl)ethyl acetate (3q)



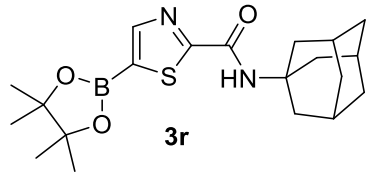
3q

Thermal: General procedure E was followed: 2-(4-methylthiazol-5-yl)ethyl acetate (68.3 mg, 0.369 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (159.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.2 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford 2-(2-((adamantan-1-yl)carbamoyl)-4-methylthiazol-5-yl)ethyl acetate **3q** as a colourless oil (70.7 mg, 0.195 mmol, 53%).

Light Mediated: General procedure I was followed: 2-(4-methylthiazol-5-yl)ethyl acetate (68.2 mg, 0.368 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.5 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.8 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford 2-(2-((adamantan-1-yl)carbamoyl)-4-methylthiazol-5-yl)ethyl acetate **3q** as a colourless oil (106.0 mg, 0.294 mmol, 79%).

R_f = 0.26 (80:20, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 6.93 (s, 1H, N-H), 4.23 (t, *J* = 6.5 Hz, 2H, CH_2), 3.08 (t, *J* = 6.5 Hz, 2H, CH_2), 2.36 (s, 3H, CH_3), 2.15 – 2.09 (m, 9H, 3xCH and 3xCH_2), 2.06 (s, 3H, CH_3), 1.71 (s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9 (C), 161.8 (C), 158.7 (C), 150.3 (C), 133.5 (C), 63.8 (CH_2), 52.5 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH), 26.4 (CH_2), 21.0 (CH_3), 15.1 (CH_3). ν_{max}/cm^{-1} 3383, 2911, 2852, 2253, 1738, 1665, 1519, 1453, 1441, 1360, 1346, 1241, 1158, 1104, 1047, 904. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd. for $C_{19}H_{27}N_2O_3S_1$, 363.1737; found 363.1745.

***N*-(Adamantan-1-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole-2-carboxamide (3r)**



3r

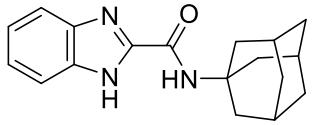
Thermal: General procedure E was followed: 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole (74.3 mg, 0.352 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (158.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) at 50 ^oC for 24 h. The crude product was triturated with water to afford *N*-(adamantan-1-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole-2-carboxamide **3r** as an off-white solid (68.2 mg, 0.176 mmol, 50%).

Light Mediated: General procedure I was followed: 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole (74.0 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.8 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was triturated with water to afford *N*-(adamantan-1-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiazole-2-carboxamide **3r** as an off-white solid (56.6 mg, 0.146 mmol, 42%).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.16 (s, 1H, Ar-H), 7.07 (s, 1H, N-H), 2.13 (s, 9H, 3xCH and 3xCH_2), 1.71 (s, 6H, 3xCH_2), 1.35 (s, 12H, 4xCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6 (C), 158.4 (C), 151.9 (CH), plus one overlapping (C) peak at either 158.5 or 151.9, 84.9 (C), 52.6 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH), 24.9 (CH_3). ^{11}B NMR (128 MHz, Chloroform-*d*) δ 28.94 (br. S, BPin). ν_{max}/cm^{-1} 3383, 2979, 2908, 2851, 2249, 1702, 1671, 1522, 1520, 1456, 1418, 1381, 1373, 1329, 1311, 1285, 1273, 1188, 1167, 1140. M.P. = 152 – 155 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{29}B_1N_2O_3S_1$, 389.2068; found 389.2060.

Benzimidazole Scope

***N*-(Adamantan-1-yl)-1*H*-benzo[*d*]imidazole-2-carboxamide (3x)**



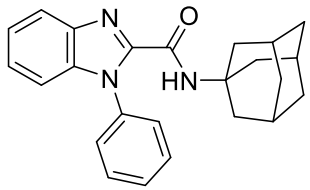
3x

Thermal: General procedure B was followed: benzimidazole (42.0 mg, 0.356 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.1 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.5 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (85:15, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1*H*-benzo[*d*]imidazole-2-carboxamide **3x** as a white solid (72.6 mg, 0.246 mmol, 69%).

Light Mediated: General procedure F was followed: benzimidazole (41.6 mg, 0.352 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO:H_2O (0.7 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (85:15, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1*H*-benzo[*d*]imidazole-2-carboxamide **3x** as a white solid (70.1 mg, 0.237 mmol, 67%).

R_f = 0.19 (85:15, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 11.06 (s, 1H, NH), 7.79 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.58 (d, *J* = 7.5 Hz, 1H, Ar-H), 7.40 – 7.28 (m, 3H, 2xAr-H and NH), 2.25 – 2.12 (m, 9H, 3xCH and 3xCH_2), 1.77 (app. s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.2 (C), 146.0 (C), 143.0 (C), 134.1 (C), 124.9 (CH), 123.5 (CH), 120.6 (CH), 112.2 (CH), 52.9 (C), 41.6 (CH_2), 36.3 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3381, 3178, 2903, 2849, 1664, 1542, 1495. M.p. = 268 – 271 ^oC. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}N_3OH$ 296.1757; Found 296.1747.

***N*-(Adamantan-1-yl)-1-phenyl-1*H*-benzo[*d*]imidazole-2-carboxamide (3y)**



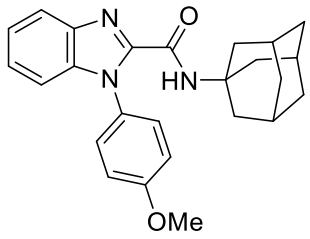
3y

Thermal: General procedure B was followed: 1-phenyl-1*H*-benzimidazole (69.3 mg, 0.357 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.7 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(-adamantan-1-yl)-1-phenyl-1*H*-benzo[*d*]imidazole-2-carboxamide **3y** as a white solid (115.4 mg, 0.311 mmol, 87%).

Light Mediated: General procedure F was followed: 1-phenyl-1*H*-benzimidazole (40.5 mg, 0.209 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (93.9 mg, 0.42 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (143.9 mg, 0.63 mmol, 3 equiv.) in DMSO (0.45 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(-adamantan-1-yl)-1-phenyl-1*H*-benzo[*d*]imidazole-2-carboxamide **3y** as a white solid (65.0 mg, 0.175 mmol, 84%).

R_f = 0.22 (90:10, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.84 – 7.80 (m, 1H, Ar-H), 7.58 – 7.49 (m, 3H, 3xAr-H), 7.43 (s, 1H, NH), 7.40 – 7.35 (m, 2H, 2xAr-H), 7.34 – 7.26 (m, 2H, 2xAr-H), 7.14 – 7.08 (m, 1H, Ar-H), 2.15 – 2.05 (m, 9H, 3xCH and 3xCH_2), 1.69 (s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6 (C), 144.9 (C), 141.1 (C), 138.3 (C), 137.1 (C), 129.4 (CH), 128.9 (CH), 127.2 (CH), 125.0 (CH), 123.9 (CH), 120.5 (CH), 111.6 (CH), 52.6 (C), 41.6 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3381, 2911, 2846, 1684, 1593, 1524, 1498. M.p. = 171 – 174 ^oC. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{25}N_3OH$ 372.2070; Found 372.2072.

***N*-(Adamantan-1-yl)-1-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole-2-carboxamide (3z)**



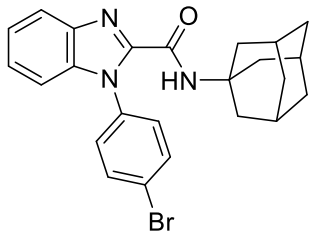
3z

Thermal: General procedure B was followed: 1-(4-methoxyphenyl)-1*H*-benzimidazole (46.1 mg, 0.206 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (89.1 mg, 0.40 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (138.0 mg, 0.60 mmol, 3 equiv.) in DMSO (0.4 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(-adamantan-1-yl)-1-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole-2-carboxamide **3z** as a white solid (17.7 mg, 0.044 mmol, 21%).

Light Mediated: General procedure F was followed: 1-(4-methoxyphenyl)-1*H*-benzimidazole (38.3 mg, 0.171 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (76.8 mg, 0.336 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (116.6 mg, 115.01 mmol, 3 equiv.) in DMSO (0.34 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(-adamantan-1-yl)-1-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole-2-carboxamide **3z** as a colourless oil (61.9 mg, 0.154 mmol, 90%).

R_f = 0.21 (90:10, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.80 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H, Ar-H), 7.44 (s, 1H, N-H), 7.38 – 7.26 (m, 4H, 4xAr-H), 7.11 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H, Ar-H), 7.03 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 3.88 (s, 3H, CH_3), 2.15 – 2.05 (m, 9H, 3xCH and 3xCH_2), 1.75 – 1.62 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, CDCl3) δ 159.7 (C), 157.6 (C), 144.9 (C), 140.9 (C), 138.6 (C), 129.7 (C), 128.3 (CH), 124.9 (CH), 123.8 (CH), 120.4 (CH), 114.6 (CH), 111.7 (CH), 55.6 (C), 52.6 (CH_3), 41.6 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3375, 2906, 2849, 2245, 1682, 1511, 1449, 1401. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}N_3O_2$ 402.2176; Found 402.2184.

***N*-(Adamantan-1-yl)-1-(4-bromophenyl)-1*H*-benzo[*d*]imidazole-2-carboxamide (3aa)**



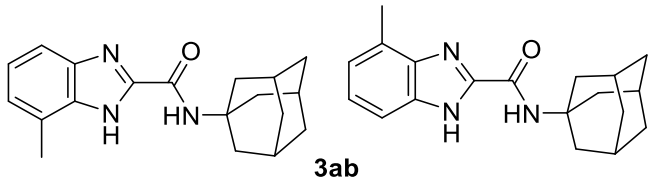
3aa

Thermal: General procedure B was followed: 1-(4-bromophenyl)-1*H*-benzimidazole (96.5 mg, 0.353 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.1 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (241.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-(4-bromophenyl)-1*H*-benzo[*d*]imidazole-2-carboxamide **3aa** as a colourless oil (45.9 mg, 0.102 mmol, 29%).

Light Mediated: General procedure F was followed: 1-(4-bromophenyl)-1*H*-benzimidazole (95.4 mg, 0.349 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.8 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.5 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(-adamantan-1-yl)-1-(4-bromophenyl)-1*H*-benzo[*d*]imidazole-2-carboxamide **3aa** as a colourless oil (95.3 mg, 0.212 mmol, 61%).

R_f = 0.21 (95:5, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.82 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H, Ar-H), 7.66 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 7.44 (s, 1H, N-H), 7.40 – 7.29 (m, 2H, 2xAr-H), 7.28 – 7.24 (m, 2H, 2xAr-H), 7.10 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H, Ar-H), 2.11 (app. s, 9H, 3xCH and 3xCH_2), 1.69 (app. s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5 (C), 144.6 (C), 141.1 (C), 138.0 (C), 136.1 (C), 132.7 (CH), 128.9 (CH), 125.3 (C), 124.1 (CH), 122.9 (CH), 120.7 (CH), 111.4 (CH), 52.7 (C), 41.6 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3375, 3066, 2906, 2849, 2247, 1682, 1524, 1489, 1447. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{24}Br^{79}N_3O$ 450.1180; Found 450.1176.

***N*-(Adamantan-1-yl)-4(7)-methyl-1*H*-benzo[*d*]imidazole-2-carboxamide (3ab)**



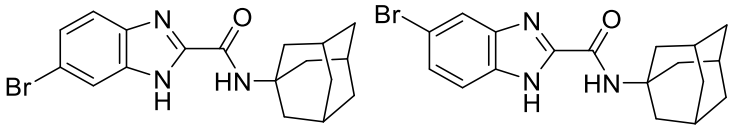
3ab

Thermal: General procedure B was followed: 4(7)-methyl-1*H*-benzimidazole (47.8 mg, 0.362 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (238.9 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford a mixture of 1:0.8, *N*-(adamantan-1-yl)-4(7)-methyl-1*H*-benzo[*d*]imidazole-2-carboxamide isomers **3ab** as a white solid (39.8 mg, 0.129 mmol, 36%).
[Note that doubling the eq. of persulfate and **4a** at 70 °C led to <5% yield.]

Light Mediated: General procedure F was followed: 4(7)-methyl-1*H*-benzimidazole (47.5 mg, 0.359 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.8 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford a mixture of 1:0.8, *N*-(adamantan-1-yl)-4(7)-methyl-1*H*-benzo[*d*]imidazole-2-carboxamide isomers **3ab** as a white solid (39.8 mg, 0.129 mmol, 36%).

R_f = 0.23 (90:10, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 11.82 (s, 1H, N-H_{major}), 10.90 (s, 1H, N-H_{minor}), 7.61 (dd, *J* = 8.0, 1.0 Hz, 1H, Ar-H_{minor}), 7.48 (s, 1H, N-H_{major}), 7.42 (dt, *J* = 8.0, 1.0 Hz, 1H, Ar-H_{major}), 7.37 (s, 1H, N-H_{minor}), 7.26 – 7.19 (m, 2H, 2xAr-H_{major}), 7.13 – 7.09 (m, 2H, Ar-H_{minor}), 2.67 (s, 3H, $CH_{3\ major}$), 2.56 (s, 3H, $CH_{3\ minor}$), 2.28 – 2.23 (m, 6H, 3xCH_{major} and 3xCH_{minor}), 2.22 – 2.10 (m, 12H, 3x$CH_{2\ major}$ and 3x$CH_{2\ minor}$), 1.80 – 1.72 (m, 12H, 3x$CH_{2\ major}$ and 3x$CH_{2\ minor}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.8 (C_{major}), 158.5 (C_{minor}), 145.9 (C_{minor}), 145.4 (C_{major}), 142.72 (C_{minor}), 142.68 (C_{major}), 134.3 (C_{major}), 134.1 (C_{minor}), 130.8 (C_{major}), 125.3 (CH_{minor}), 124.6 (CH_{major}), 123.6 (CH_{minor}), 123.3 (CH_{major}), 122.3 (C_{minor}), 118.0 (CH_{minor}), 109.7 (CH_{major}), 52.9 (C_{minor}), 52.8 (C_{major}), 41.7 ($CH_{2\ major\ and\ minor}$), 36.5 ($CH_{2\ major}$), 36.4 ($CH_{2\ minor}$), 29.62 ($CH_{major}$), 29.59 ($CH_{minor}$), 17.4 ($CH_{3\ minor}$), 16.8 ($CH_{3\ major}$). ν_{max}/cm^{-1} 3368, 3205, 2906, 2850, 1652, 1549, 1514, 1438. M.p. = 243 – 246 °C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{23}N_3O$ 310.1914; Found 310.1921.

***N*-(Adamantan-1-yl)-6(5)-bromo-1*H*-benzo[*d*]imidazole-2-carboxamide (3ac)**



3ac

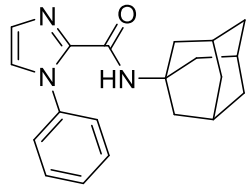
Thermal: General procedure B was followed: 6(5)-bromo-1*H*-benzimidazole (69.5 mg, 0.353 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.9 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford a mixture of 1:0.75, *N*-(adamantan-1-yl)-6(5)-bromo-1*H*-benzo[*d*]imidazole-2-carboxamide isomers **3ac** as a white solid (31.2 mg, 0.083 mmol, 24%).

Light Mediated: General procedure F was followed: 6(5)-bromo-1*H*-benzimidazole (70.0 mg, 0.355 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.9 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.4 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford a mixture of 1:0.75, *N*-(adamantan-1-yl)-6(5)-bromo-1*H*-benzo[*d*]imidazole-2-carboxamide isomers **3ac** as a white solid (18.0 mg, 0.048 mmol, 14%).

R_f = 0.23 (90:10, hexane:ethyl acetate). ^1H NMR (400 MHz, Toluene-d_8, 75 ^oC) δ 10.79 (s, 1H, N-H_{major}), 10.40 (s, 1H, N-H_{minor}), 7.99 (d, *J* = 2.0 Hz, 1H, Ar-H_{minor}), 7.50 (d, *J* = 9.0 Hz, 1H, Ar-H_{minor}), 7.44 (d, *J* = 2.0 Hz, 1H, Ar-H_{major}), 7.29 (s, 1H, N-H_{major}), 7.24 (dd, *J* = 9.0, 2.0 Hz, 1H, Ar-H_{minor}), 7.24 (dd, *J* = 9.0, 2.0 Hz, 1H, Ar-H_{major}), 6.92 (d, *J* = 9.0 Hz, 1H, Ar-H_{major}), 2.06 (t, *J* = 3.5 Hz, 12H, 3x$CH_{2\ major}$ and 3x$CH_{2\ minor}$), 1.96 (s, 6H, 3xCH_{major} and 3xCH_{minor}), 1.67 – 1.54 (m, 12H, 3x$CH_{2\ major}$ and 3x$CH_{2\ minor}$). ^{13}C NMR (101 MHz, Tol) δ 144.9 (C $_{major\ and\ minor}$), 142.5 (C $_{major\ and\ minor}$), 126.7 (CH_{major}), 123.8 (CH_{minor}), 122.2 (C $_{major\ and\ minor}$), 118.1 ($CH_{major\ and\ minor}$), 116.3 (C $_{major\ and\ minor}$), 115.8 (CH $_{major\ and\ minor}$), 113.6 ($C_{major\ and\ minor}$), 52.5 (C $_{major}$), 52.4 (C $_{minor}$), 41.53 ($CH_{2\ major}$), 41.49 ($CH_{2\ minor}$), 36.6 ($CH_{2\ major}$), 36.5 ($CH_{2\ minor}$), 29.9 ($CH_{major\ and\ minor}$). ν_{max}/cm^{-1} 3377, 3290, 3181, 2903, 2847, 1739, 1662, 1549, 1486. M.P. = 287 – 290 ^oC. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}{}^{79}BrN_3O$ 374.0863; Found 374.0861.

Imidazole Scope

***N*-(Adamantan-1-yl)-1-phenyl-1*H*-imidazole-2-carboxamide (3ad)**



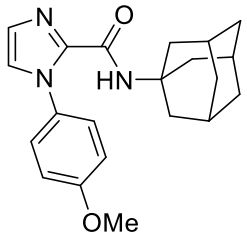
3ad

Thermal: General procedure C was followed: 1-phenyl-1*H*-imidazole (50.7 mg, 0.352 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.3 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-phenyl-1*H*-imidazole-2-carboxamide **3ad** as a white solid (90.7 mg, 0.282 mmol, 80%).

Light Mediated: General procedure G was followed: 1-phenyl-1*H*-imidazole (50.6 mg, 0.351 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.5 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 6 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-phenyl-1*H*-imidazole-2-carboxamide **3ad** as a white solid (91.0 mg, 0.283 mmol, 81%).

R_f = 0.32 (80:20, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.48 – 7.40 (m, 3H, 3xAr-H), 7.37 – 7.31 (m, 2H, 2xAr-H), 7.15 (s, 1H, N-H), 7.08 (d, *J* = 1.0 Hz, 1H, Ar-H), 7.06 (d, *J* = 1.0 Hz, 1H, Ar-H), 2.08 – 2.03 (m, 9H, 3xCH and 3xCH_2), 1.67 (s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2 (C), 140.4 (C), 138.7 (C), 128.9 (CH), 128.7 (CH), 127.7 (CH), 126.1 (2xCH), 126.0 (CH), 52.1 (C), 41.7 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3373, 3114, 2902, 2850, 1677, 1652, 1641, 1597, 1530, 1492, 1476, 1455, 1450, 1436, 1408, 1311, 1304, 1292, 1274, 1238, 1151, 1114. M.P. = 139 - 142 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{24}N_3O_1$, 322.1914; found 322.1914.

***N*-(Adamantan-1-yl)-1-(4-methoxyphenyl)-1*H*-imidazole-2-carboxamide (3ae)**



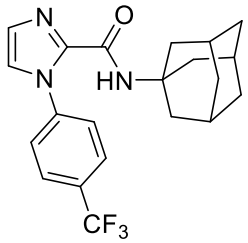
3ae

Thermal: General procedure C was followed: 1-(4-methoxyphenyl)-1*H*-imidazole (65.3 mg, 0.375 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.1 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.8 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ºC for 24 h. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-(4-methoxyphenyl)-1*H*-imidazole-2-carboxamide **3ae** as a white solid (93.1 mg, 0.265 mmol, 71%).

Light Mediated: General procedure G was followed: 1-(4-methoxyphenyl)-1*H*-imidazole (62.1 mg, 0.356 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (235.4 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 6 h at 25 ºC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-(4-methoxyphenyl)-1*H*-imidazole-2-carboxamide **3ae** as a white solid (111.8 mg, 0.318 mmol, 89%).

R_f = 0.35 (70:30, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 7.15 (s, 1H, N-H), 7.06 (d, *J* = 1.0 Hz, 1H, Ar-H), 7.03 (d, *J* = 1.0 Hz, 1H, Ar-H), 6.93 (d, *J* = 9.0 Hz, 2H, 2xAr-H), 3.83 (s, 3H, CH_3), 2.06 (app. s, 9H, 3xCH and 3xCH_2), 1.66 (app. s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6 (C), 157.3 (C), 140.5 (C), 131.6 (C), 127.5 (CH), 127.2 (CH), 126.3 (CH), 114.1 (CH), 55.6 (CH_3), 52.1 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3380, 2905, 2848, 2245, 1677, 1611, 1589, 1531, 1511, 1495, 1452, 1359, 1344, 1296. M.p. = 155 – 158 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{25}N_3O_2$, 352.2020; found 352.2025.

***N*-(Adamantan-1-yl)-1-(4-(trifluoromethyl)phenyl)-1*H*-imidazole-2-carboxamide (3af)**



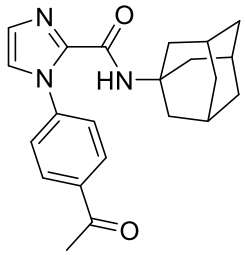
3af

Thermal: General procedure C was followed: 1-(4-(trifluoromethyl)phenyl)-1*H*-imidazole (74.9 mg, 0.353 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.2 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-(4-(trifluoromethyl)phenyl)-1*H*-imidazole-2-carboxamide **3af** as a white solid (125.8 mg, 0.323 mmol, 92%).

Light Mediated: General procedure G was followed: 1-(4-(trifluoromethyl)phenyl)-1*H*-imidazole (79.0 mg, 0.372 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (155.8 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (242.7 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 6 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-(4-(trifluoromethyl)phenyl)-1*H*-imidazole-2-carboxamide **3af** as a white solid (118.4 mg, 0.304 mmol, 82%).

R_f = 0.23 (80:20, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.74 – 7.68 (m, 2H, 2xAr-H), 7.51 – 7.45 (m, 2H, 2xAr-H), 7.17 (s, 1H, N-H), 7.12 (d, *J* = 1.0 Hz, 1H, Ar-H), 7.06 (d, *J* = 1.0 Hz, 1H, Ar-H), 2.11 – 2.04 (m, 9H, 3xCH and 3xCH_2), 1.71 – 1.65 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1 (C), 141.6 (C), 140.4 (C), 130.5 (CH), 126.91 (q, J = 274.0 Hz, CF_3), plus an overlapping CH at 126.7 or 128.3, 126.7 (CH), 126.20 (q, *J* = 4.0 Hz, CH), 52.3 (C), 41.7 (CH_2), 36.4 (CH_2), 29.6 (CH). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.59 (s, CF_3). ν_{max}/cm^{-1} 3386, 2910, 2850, 1677, 1614, 1511, 1495, 1453, 1414. M.p. = 151 – 154 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{22}F_3N_3O$, 390.1788; found 390.1796.

1-(4-Acetylphenyl)-*N*-(adamantan-1-yl)-1*H*-imidazole-2-carboxamide (3ag)



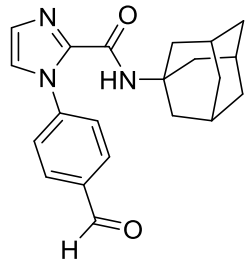
3ag

Thermal: General procedure C was followed: 1-(4-(1*H*-imidazol-1-yl)phenyl)ethan-1-one (65.4 mg, 0.351 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.3 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford 1-(4-acetylphenyl)-*N*-(adamantan-1-yl)-1*H*-imidazole-2-carboxamide **3ag** as a colourless oil (109.2 mg, 0.300 mmol, 86%).

Light Mediated: General procedure G was followed: 1-(4-(1*H*-imidazol-1-yl)phenyl)ethan-1-one (65.1 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.7 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (244.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 6 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford 1-(4-acetylphenyl)-*N*-(adamantan-1-yl)-1*H*-imidazole-2-carboxamide **3ag** as a colourless oil (91.9 mg, 0.253 mmol, 72%).

R_f = 0.21 (70:30, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.5 Hz, 2H, 2xAr-H), 7.45 (d, *J* = 8.5 Hz, 2H, 2xAr-H), 7.15 (s, 1H, N-H), 7.12 (d, *J* = 1.0 Hz, 1H, Ar-H), 7.08 (d, *J* = 1.0 Hz, 1H, Ar-H), 2.63 (s, 3H, CH_3), 2.06 (app. s, 9H, 3xCH and 3xCH_2), 1.67 (app. s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.0 (C), 157.1 (C), 142.5 (C), 140.4 (C), 137.0 (C), 129.1 (CH), 128.3 (CH), 126.4 (CH), 125.5 (CH), 52.3 (C), 41.7 (CH_2), 36.4 (CH_2), 29.6 (CH), 26.8 (CH_3). ν_{max}/cm^{-1} 3375, 3112, 2906, 2850, 2246, 1677, 1603, 1582, 1532, 1509, 1498, 1450, 1415, 1358, 1345. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{25}N_3O_2$, 364.2020; found 364.2031.

***N*-(Adamantan-1-yl)-1-(4-formylphenyl)-1*H*-imidazole-2-carboxamide (3ah)**



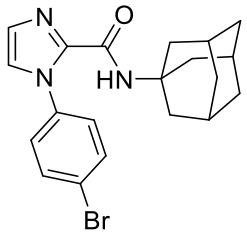
3ah

Thermal: General procedure C was followed: 4-(1*H*-imidazol-1-yl)benzaldehyde (58.5 mg, 0.340 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.4 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-(4-formylphenyl)-1*H*-imidazole-2-carboxamide **3ah** as a colourless oil (69.3 mg, 0.198 mmol, 58%).

Light Mediated: General procedure G was followed: 4-(1*H*-imidazol-1-yl)benzaldehyde (62.4 mg, 0.362 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (158.8 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (237.2 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 6 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-(4-formylphenyl)-1*H*-imidazole-2-carboxamide **3ah** as a colourless oil (83.2 mg, 0.238 mmol, 66%).

R_f = 0.24 (70:30, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 10.06 (s, 1H, C(O)H), 7.97 (d, *J* = 8.5 Hz, 2H, 2xAr-H), 7.53 (d, *J* = 8.5 Hz, 2H, 2xAr-H), 7.15 (s, 1H, N-H), 7.13 (d, *J* = 1.0 Hz, 1H, Ar-H), 7.09 (d, *J* = 1.0 Hz, 1H, Ar-H), 2.06 (app. s, 9H, 3xCH and 3xCH_2), 1.67 (app. s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1 (C), 157.0 (C), 143.6 (C), 140.4 (C), 136.2 (C), 130.4 (CH), 128.4 (CH), 127.0 (CH), 125.5 (CH), 52.3 (C), 41.6 (CH_2), 36.4 (CH_2), 29.5 (CH). ν_{max}/cm^{-1} 3378, 3112, 2906, 2849, 2734, 2247, 1703, 1674, 1604, 1585, 1532, 1511, 1498, 1449, 1408, 1359. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{23}N_3O_2$, 350.1863; found 350.1863.

***N*-(Adamantan-1-yl)-1-(4-bromophenyl)-1*H*-imidazole-2-carboxamide (3ai)**



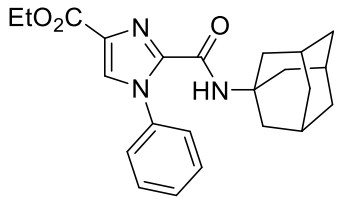
3ai

Thermal: General procedure C was followed: 1-(4-bromophenyl)-1*H*-imidazole (79.4 mg, 0.356 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.1 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.8 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-(4-bromophenyl)-1*H*-imidazole-2-carboxamide **3ai** as a white solid (111.6 mg, 0.279 mmol, 78%).

Light Mediated: General procedure G was followed: 1-(4-bromophenyl)-1*H*-imidazole (79.1 mg, 0.355 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.4 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 6 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-(4-bromophenyl)-1*H*-imidazole-2-carboxamide **3ai** as a white solid (139.7 mg, 0.349 mmol, 98%).

R_f = 0.25 (80:20, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.5 Hz, 2H, 2xAr-H), 7.22 (d, *J* = 8.5 Hz, 2H, 2xAr-H), 7.15 (s, 1H, N-H), 7.09 (d, *J* = 1.0 Hz, 1H, Ar-H), 7.03 (d, *J* = 1.0 Hz, 1H, Ar-H), 2.06 (app. s, 9H, 3xCH and 3xCH_2), 1.67 (app. s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.1 (C), 140.3 (C), 137.7 (C), 132.1 (CH), 128.1 (CH), 127.8 (CH), 125.8 (CH), 122.7 (C), 52.3 (C), 41.7 (CH_2), 36.4 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3375, 3137, 2908, 2847, 2245, 1676, 1524, 1500, 1489, 1447, 1409, 1359, 1345. M.p. = 166 – 169 ^oC. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{22}{}^{79}BrN_3O$, 400.1019; found 400.1023.

Ethyl-2-((adamantan-1-yl)carbamoyl)-1-phenyl-1*H*-imidazole-4-carboxylate (3aj)



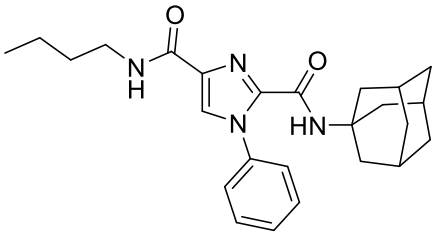
3aj

Thermal: General procedure C was followed: ethyl-1-phenyl-1*H*-imidazole-4-carboxylate (77.4 mg, 0.358 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.9 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford ethyl-2-((adamantan-1-yl)carbamoyl)-1-phenyl-1*H*-imidazole-4-carboxylate **3aj** as a colourless oil (113.7 mg, 0.289 mmol, 81%).

Light Mediated: General procedure G was followed: ethyl-1-phenyl-1*H*-imidazole-4-carboxylate (76.2 mg, 0.352 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.1 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (235.3 mg, 1.05 mmol, 3 equiv.) in DMSO:H_2O (1.75 mL) irradiated with 420 nm light for 6 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford ethyl-2-((adamantan-1-yl)carbamoyl)-1-phenyl-1*H*-imidazole-4-carboxylate **3aj** as a colourless oil (98.0 mg, 0.249 mmol, 71%).

R_f = 0.26 (70:30, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.68 (s, 1H, Ar-H), 7.49 – 7.43 (m, 3H, 3xAr-H), 7.36 – 7.31 (m, 2H, 2xAr-H), 7.17 (s, 1H, N-H), 4.40 (q, *J* = 7.0 Hz, 2H, CH_3), 2.06 (app. s, 9H, 3xCH and 3xCH_2), 1.66 (app. s, 6H, 3xCH_2), 1.39 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5 (C), 156.6 (C), 141.1 (C), 138.1 (C), 132.0 (C), 130.8 (CH), 129.2 (CH), 129.1 (CH), 125.9 (CH), 61.1 (CH_2), 52.6 (C), 41.5 (CH_2), 36.4 (CH_2), 29.6 (CH), 14.5 (CH_3). ν_{max}/cm^{-1} 3384, 3218, 3066, 2907, 2850, 2247, 2160, 1733, 1682, 1598, 1525, 1498, 1455, 1415, 1390. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{27}N_3O_3$, 394.2125; found 394.2123.

N^2-(Adamantan-1-yl)-N^4-butyl-1-phenyl-1*H*-imidazole-2,4-dicarboxamide (3ak)

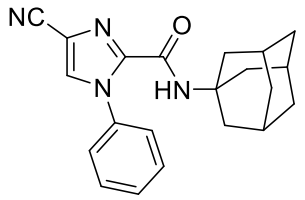


3ak

Light Mediated: General procedure G was followed: *N*-butyl-1-phenyl-1*H*-imidazole-4-carboxamide (32.9 mg, 0.135 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (60.3 mg, 0.27 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (92.5 mg, 0.405 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 1 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, petroleum ether 40/60:ethyl acetate) to afford N^2-(Adamantan-1-yl)-N^4-butyl-1-phenyl-1*H*-imidazole-2,4-dicarboxamide **3ak** as a colourless oil (30.5 mg, 0.073 mmol, 54%).

R_f = 0.25 (70:30, petroleum ether 40/60:ethyl acetate). ^1H NMR (400 MHz, Chloroform-*d*) δ 10.65 (s, 1H, NH), 7.67 (t, *J* = 5.5 Hz, 1H, NH), 7.47 – 7.42 (m, 4H, Ar-H), 7.29 – 7.27 (m, 2H, Ar-H), 3.46 (td, *J* = 7.0, 5.5 Hz, 2H, CH_2), 2.10 (d, *J* = 3.0 Hz, 6H, 3xCH_2), 2.04 (app. s, 3H, 3xCH), 1.72 – 1.60 (m, 8H, 4xCH_2), 1.50 – 1.38 (m, 2H, CH_2), 0.97 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8 (C), 157.1 (C), 138.7 (CH), 137.9 (C), 134.6 (C), 130.1 (C), 129.1 (CH), 128.8 (CH), 125.9 (CH), 52.3 (C), 41.3 (CH_2), 39.3 (CH_2), 36.6 (CH_2), 31.7 (CH_2), 29.6 (CH), 20.3 (CH_2), 13.9 (CH_3). ν_{max}/cm^{-1} 3394, 3221, 2907, 2850, 1963, 1885, 1672, 1642, 1592, 1549, 1498, 1456, 1381. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{25}H_{32}N_4O_2$, 421.2598; found 421.2592.

***N*-(Adamantan-1-yl)-4-cyano-1-phenyl-1*H*-imidazole-2-carboxamide (3al)**



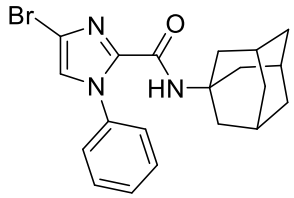
3al

Thermal: General procedure C was followed: 1-phenyl-1*H*-imidazole-4-carbonitrile (59.2 mg, 0.35 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (80:20, petroleum ether 40/60:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-cyano-1-phenyl-1*H*-imidazole-2-carboxamide **3al** as a white solid (67.8 mg, 0.196 mmol, 56%).

Light Mediated: General procedure G was followed: 1-phenyl-1*H*-imidazole-4-carbonitrile (59.2 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 6 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, petroleum ether 40/60:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-cyano-1-phenyl-1*H*-imidazole-2-carboxamide **3al** as a white solid (36.9 mg, 0.105 mmol, 30%).

R_f = 0.20 (80:20, petroleum ether 40/60:ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (s, 1H, Ar-H), 7.54 – 7.49 (m, 3H, Ar-H), 7.35 – 7.30 (m, 2H, Ar-H), 5.98 (s, 1H, NH), 2.08 (t, *J* = 3.0 Hz, 3H, 3xCH), 2.03 (d, *J* = 3.0 Hz, 6H, 3xCH_2), 1.67 (t, *J* = 3.0 Hz, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.4 (C), 140.7 (CH), 135.41 (C), 135.35 (C), 130.0 (CH), 129.8 (CH), 125.6 (CH), 115.5 (C), 114.3 (C), 53.8 (C), 41.5 (CH_2), 36.3 (CH_2), 29.5 (CH). ν_{max}/cm^{-1} 3248, 3218, 3129, 3037, 2914, 2889, 2854, 2238, 1671, 1595, 1557, 1498, 1456, 1387. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{22}N_4O$, 347.1866; found 347.1867. M.p. = 251 – 254 °C.

***N*-(Adamantan-1-yl)-4-bromo-1-phenyl-1*H*-imidazole-2-carboxamide (3am)**



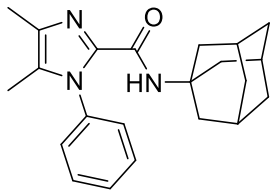
3am

Thermal: General procedure C was followed: 4-bromo-1-phenyl-1*H*-imidazole (78.1 mg, 0.35 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (80:20, petroleum ether 40/60:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-bromo-1-phenyl-1*H*-imidazole-2-carboxamide **3am** as a colourless oil (71.0 mg, 0.179 mmol, 51%).

Light Mediated: General procedure G was followed: 4-bromo-1-phenyl-1*H*-imidazole (78.1 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 6 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, petroleum ether 40/60:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-bromo-1-phenyl-1*H*-imidazole-2-carboxamide **3am** as a colourless oil (43.3 mg, 0.109 mmol, 31%).

R_f = 0.22 (80:20, petroleum ether 40/60:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.47 – 7.42 (m, 3H, Ar-H), 7.35 – 7.29 (m, 2H, Ar-H), 7.03 (s, 1H, Ar-H), 7.02 (s, 1H, NH), 2.05 (app. s, 9H, 3xCH and 3xCH_2), 1.66 (app. s, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1 (C), 139.9 (C), 137.8 (C), 129.2 (CH), 129.1 (CH), 126.0 (CH), 125.1 (CH), 114.5 (C), 52.5 (C), 41.6 (CH_2), 36.4 (CH_2), 29.5 (CH). ν_{max}/cm^{-1} 3386, 3144, 2906, 2849, 2248, 1888, 1682, 1597, 1527, 1497, 1456, 1436, 1408, 1359, 1344. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{22}N_3O^{79}Br$, 400.1019; found 400.1023.

***N*-(Adamantan-1-yl)-4,5-dimethyl-1-phenyl-1*H*-imidazole-2-carboxamide (3an)**

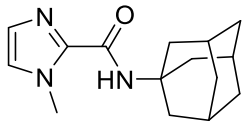


3an

Thermal: General procedure C was followed: 4,5-dimethyl-1-phenyl-1*H*-imidazole (60.7 mg, 0.352 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.8 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (241.6 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4,5-dimethyl-1-phenyl-1*H*-imidazole-2-carboxamide **3an** as a yellow oil (52.3 mg, 0.150 mmol, 43%).

R_f = 0.20 (80:20, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.51 – 7.41 (m, 3H, 3xAr-H), 7.21 – 7.16 (m, 2H, 2xAr-H), 7.02 (s, 1H, N-H), 2.21 (d, *J* = 0.5 Hz, 3H, CH_3), 2.06 – 2.02 (m, 9H, 3xCH and 3xCH_2), 1.88 (d, *J* = 0.5 Hz, 3H, CH_3), 1.64 (app. s, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5 (C), 138.8 (C), 138.1 (C), 133.1 (C), 129.1 (C), 128.9 (CH), 128.6 (CH), 127.2 (CH), 51.9 (C), 41.7 (CH_2), 36.5 (CH_2), 29.6 (CH), 12.8 (CH_3), 9.4 (CH_3). ν_{max}/cm^{-1} 3382, 2907, 2849, 2244, 1734, 1674, 1590, 1522, 1499, 1453, 1435, 1418, 1359, 1344, 1304. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{27}N_3O$, 350.2227; found 350.2226.

***N*-(Adamantan-1-yl)-1-methyl-1*H*-imidazole-2-carboxamide (3ao)**



3ao

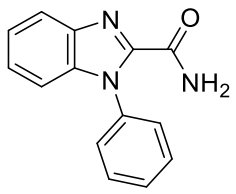
Thermal: General procedure C was followed: 1-methylimidazole (29.7 mg, 0.362 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.9 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.2 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-methyl-1*H*-imidazole-2-carboxamide **3ao** as a colourless oil (29.8 mg, 0.115 mmol, 32%).

Light Mediated: General procedure G was followed: 1-methylimidazole (32.1 mg, 0.391 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (158.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.4 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) irradiated with 420 nm light for 6 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1-methyl-1*H*-imidazole-2-carboxamide **3ao** as a colourless oil (25.4 mg, 0.098 mmol, 25%).

R_f = 0.20 (80:20, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.15 (s, 1H, N-H), 6.95 (d, *J* = 1.0 Hz, 1H, Ar-H), 6.91 (d, *J* = 1.0 Hz, 1H, Ar-H), 4.03 (s, 3H, CH_3), 2.14 – 2.09 (m, 9H, 3xCH and 3xCH_2), 1.71 (app. s, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7 (C), 139.9 (C), 127.2 (CH), 125.6 (CH), 52.1 (C), 41.8 (CH_2), 36.5 (CH_2), 35.9 (CH_3), 29.6 (CH). ν_{max}/cm^{-1} 3395, 3095, 2906, 2850, 2358, 2247, 1736, 1671, 1604, 1532, 1500, 1471, 1456, 1417, 1406, 1359, 1344, 1310, 1297. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{15}H_{21}N_3O$, 260.1757; found 260.1756.

Oxamic Acid Scope

1-Phenyl-1*H*-benzo[*d*]imidazole-2-carboxamide (3ap)



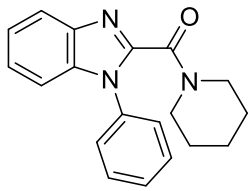
3ap

Thermal: General procedure B was followed: 1-phenyl-1*H*-benzimidazole (68.1 mg, 0.351 mmol, 1 equiv.), oxamic acid (62.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.3 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (100% ethyl acetate) to afford 1-phenyl-1*H*-benzo[*d*]imidazole-2-carboxamide **3ap** as a white solid (41.6 mg, 0.175 mmol, 50%).

Light Mediated: General procedure F was followed: 1-phenyl-1*H*-benzimidazole (68.9 mg, 0.355 mmol, 1 equiv.), oxamic acid (64.6 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (241.1 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (100% ethyl acetate) to afford 1-phenyl-1*H*-benzo[*d*]imidazole-2-carboxamide **3ap** as a white solid (30.9 mg, 0.130 mmol, 37%).

R_f = 0.74 (100% ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.87 – 7.83 (m, 1H, Ar-H), 7.59 – 7.50 (m, 3H, 3xAr-H), 7.50 – 7.43 (m, 1H, N*H*H), 7.43 – 7.31 (m, 4H, 4xAr-H), 7.20 – 7.15 (m, 1H, Ar-H), 5.57 (s, 1H, NH*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4 (C), 143.2 (C), 141.3 (C), 138.2 (C), 136.7 (C), 129.4 (CH), 129.1 (CH), 127.3 (CH), 125.6 (CH), 124.1 (CH), 120.9 (CH), 111.8 (CH). ν_{max}/cm^{-1} 3456, 3306, 3162, 3068, 2782, 2247, 1687, 1595, 1492, 1447, 1425. M.p. = 195 – 198 °C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{11}N_3O$ 238.0975; Found 238.0967.

(1-Phenyl-1*H*-benzo[*d*]imidazol-2-yl)(piperidin-1-yl)methanone (3aq)



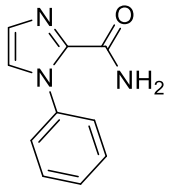
3aq

Thermal: General procedure B was followed: 1-phenyl-1*H*-benzimidazole (70.5 mg, 0.363 mmol, 1 equiv.), 2-oxo-2-(piperidin-1-yl)acetic acid (111.6 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (241.9 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (50:50, hexane:ethyl acetate) to afford (1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)(piperidin-1-yl)methanone **3aq** as a colourless oil (71.8 mg, 0.233 mmol, 64%).

Light Mediated: General procedure F was followed: 1-phenyl-1*H*-benzimidazole (70.2 mg, 0.362 mmol, 1 equiv.), 2-oxo-2-(piperidin-1-yl)acetic acid (112.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.8 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (50:50, hexane:ethyl acetate) to afford (1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)(piperidin-1-yl)methanone **3aq** as a colourless oil (77.2 mg, 0.254 mmol, 70%).

R_f = 0.28 (50:50, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 1H, Ar-H), 7.59 – 7.44 (m, 5H, 5xAr-H), 7.39 – 7.30 (m, 3H, 3xAr-H), 3.65 – 3.58 (m, 2H, CH_2), 3.45 – 3.38 (m, 2H, CH_2), 1.65 – 1.47 (m, 4H, 2xCH_2), 1.43 – 1.34 (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2 (C), 146.6 (C), 142.3 (C), 135.8 (C), 135.1 (C), 129.9 (CH), 128.8 (CH), 126.1 (CH), 124.5 (CH), 123.4 (CH), 120.9 (CH), 110.9 (CH), 48.0 (CH_2), 43.0 (CH_2), 26.5 (CH_2), 25.5 (CH_2), 24.5 (CH_2). ν_{max}/cm^{-1} 3053, 2938, 2856, 1641, 1596, 1516, 1497, 1435, 1384. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}N_3O$ 306.1601; Found 306.1610.

1-Phenyl-1*H*-imidazole-2-carboxamide (3ar)



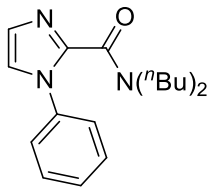
3ar

Thermal: General procedure C was followed: 1-phenyl-1*H*-imidazole (51.5 mg, 0.357 mmol, 1 equiv.), oxamic acid (63.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (10:90, hexane:ethyl acetate) to afford 1-phenyl-1*H*-imidazole-2-carboxamide **3ar** as a white solid (51.5 mg, 0.275 mmol, 77%).

Light Mediated: General procedure G was followed: 1-phenyl-1*H*-imidazole (50.8 mg, 0.352 mmol, 1 equiv.), oxamic acid (64.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.0 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) irradiated with 420 nm light for 6 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (10:90, hexane:ethyl acetate) to afford 1-phenyl-1*H*-imidazole-2-carboxamide **3ar** as a white solid (39.9 mg, 0.213 mmol, 61%).

R_f = 0.34 (10:90, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.50 – 7.41 (m, 3H, 3xAr-H), 7.39 – 7.32 (m, 2H, 2xAr-H), 7.15 (dd, *J* = 5.0, 1.0 Hz, 3H, 2xAr-H and N*H*H), 5.29 (s, 1H, NH*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9 (C), 138.9 (C), 138.4 (C), 129.0 (CH), 128.9 (CH), 128.6 (CH), 126.5 (CH), 126.1 (CH). ν_{max}/cm^{-1} 3387, 3142, 3106, 3015, 2990, 1695, 1662, 1629, 1596, 1494. M.p. = 180 °C decomposed. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_9N_3O$ 188.0818; Found 188.0818.

***N*,*N*-Dibutyl-1-phenyl-1*H*-imidazole-2-carboxamide (3as)**



3as

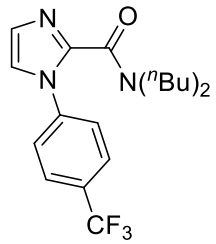
Thermal: General procedure C was followed: 1-phenyl-1*H*-imidazole (50.4 mg, 0.350 mmol, 1 equiv.), 2-(dibutylamino)-2-oxoacetic acid (144.6 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$

(240.2 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*,*N*-dibutyl-1-phenyl-1*H*-imidazole-2-carboxamide **3as** as a colourless oil (34.7 mg, 0.116 mmol, 33%).

Light Mediated: General procedure G was followed: 1-phenyl-1*H*-imidazole (53.3 mg, 0.370 mmol, 1 equiv.), 2-(dibutylamino)-2-oxoacetic acid (143.9 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.4 mg, 1.05 mmol, 3 equiv.) in DMSO (0.7 mL) irradiated with 420 nm light for 6 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*,*N*-dibutyl-1-phenyl-1*H*-imidazole-2-carboxamide **3as** as a colourless oil (31.5 mg, 0.105 mmol, 28%).

R_f = 0.18 (70:30, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47 – 7.37 (m, 3H, 3xAr-H), 7.37 – 7.31 (m, 2H, 2xAr-H), 7.15 (d, *J* = 1.0 Hz, 1H, Ar-H), 7.12 (d, *J* = 1.0 Hz, 1H, Ar-H), 3.48 – 3.34 (m, 4H, 2xCH_2), 1.56 – 1.43 (m, 4H, 2xCH_2), 1.35 – 1.13 (m, 4H, 2xCH_2), 0.92 – 0.80 (m, 6H, 2xCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.3 (C), 141.5 (C), 137.9 (C), 129.4 (CH), 128.44 (CH), 128.36 (CH), 124.8 (CH), 121.7 (CH), 48.6 (CH_2), 45.4 (CH_2), 31.1 (CH_2), 29.5 (CH_2), 20.3 (CH_2), 20.1 (CH_2), 14.0 (CH_3), 13.8 (CH_3). ν_{max}/cm^{-1} 3110, 3063, 2957, 2930, 2872, 1634, 1599, 1520, 1498, 1481, 1456. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{25}N_3O$ 300.2070; Found 300.2076.

***N*,*N*-Dibutyl-1-(4-(trifluoromethyl)phenyl)-1H-imidazole-2-carboxamide (3at)**

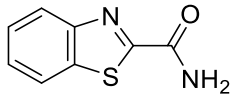


3at

Thermal: General procedure C was followed: 1-(4-trifluoromethyl)phenyl-1*H*-imidazole (75.3 mg, 0.355 mmol, 1 equiv.), 2-(dibutylamino)-2-oxoacetic acid (146.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (241.1 mg, 1.05 mmol, 3 equiv.) in DMSO (1.75 mL) at 50 °C for 24 h. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*,*N*-dibutyl-1-(4-(trifluoromethyl)phenyl)-1H-imidazole-2-carboxamide **3at** as a colourless oil (65.0 mg, 0.177 mmol, 50%).

R_f = 0.35 (70:30, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.0 Hz, 2H, 2xAr-H), 7.46 (d, *J* = 8.0 Hz, 2H, 2xAr-H), 7.19 (d, *J* = 1.5 Hz, 1H, Ar-H), 7.13 (d, *J* = 1.5 Hz, 1H, Ar-H), 3.61 – 3.53 (m, 2H, CH_2), 3.44 – 3.36 (m, 2H, CH_2), 1.61 – 1.47 (m, 4H, 2xCH_2), 1.36 – 1.16 (m, 4H, 2xCH_2), 0.93 – 0.83 (m, 6H, 2xCH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6 (C), 141.2 (C), 140.9 (C), 130.4 (q, *J* = 33.0 Hz, C), 128.9 (CH), 126.7 (q, *J* = 4.0 Hz, CH), 125.2 (CH), 123.7 (q, *J* = 272.0 Hz, CF_3), 122.0 (CH), 48.7 (CH_2), 45.6 (CH_2), 31.2 (CH_2), 29.5 (CH_2), 20.3 (CH_2), 20.1 (CH_2), 14.0 (CH_3), 1j3.8 (CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.59 (s, CF_3). ν_{max}/cm^{-1} 2959, 2933, 2875, 1634, 1519, 1456, 1432, 1398, 1380, 1323. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}F_3N_3O$ 368.1957; Found 368.1944.

Benzo[*d*]thiazole-2-carboxamide (3au)

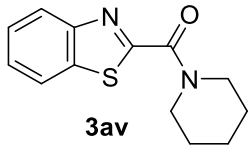


3au

Light Mediated: General procedure H was followed: benzothiazole (47.0 mg, 0.348 mmol, 1 equiv.), oxamic acid (62.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford benzo[*d*]thiazole-2-carboxamide **3au** as a white solid (30.9 mg, 0.173 mmol, 50%).

R_f = 0.34 (10:90, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.10 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H, Ar-H), 7.99 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H, Ar-H), 7.61 – 7.48 (m, 2H, 2xAr-H), 7.31 (s, 1H, N*H*H), 5.70 (s, 1H, NH*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (C), 161.9 (C), 153.1 (C), 137.6 (C), 127.14 (CH), 127.07 (CH), 124.7 (CH), 122.6 (CH).ν_{max}/cm^{-1} 3347, 3279, 3230, 3180, 3064, 2915, 2848, 1696, 1662, 1620, 1508, 1406. M.p. = 233 – 236 °C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_8H_9N_2OS$ 1179.0274; Found 179.0273.

Benzo[*d*]thiazol-2-yl(piperidin-1-yl)methanone (3av)



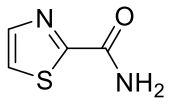
3av

Thermal: General procedure D was followed: benzothiazole (49.0 mg, 0.362 mmol, 1 equiv.), 2-oxo-2-(piperidin-1-yl)acetic acid (111.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.8 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (93:7, hexane:ethyl acetate) to afford benzo[*d*]thiazol-2-yl(piperidin-1-yl)methanone **3av** as a colourless oil (44.6 mg, 0.181 mmol, 50%).

Light Mediated: General procedure H was followed: benzothiazole (49.2 mg, 0.364 mmol, 1 equiv.), 2-oxo-2-(piperidin-1-yl)acetic acid (110.5 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.9 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (93:7, hexane:ethyl acetate) to afford benzo[*d*]thiazol-2-yl(piperidin-1-yl)methanone **3av** as a colourless oil (40.5 mg, 0.164 mmol, 45%).

R_f = 0.10 (93:7, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 8.08 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H, Ar-H), 7.95 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H, Ar-H), 7.56 – 7.43 (m, 2H, 2xAr-H), 4.29 – 4.21 (m, 2H, CH_2), 3.82 – 3.72 (m, 2H, CH_2), 1.78 – 1.66 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1 (C), 160.1 (C), 153.2 (C), 136.3 (C), 126.6 (CH), 126.5 (CH), 124.7 (CH), 121.9 (CH), 47.8 (CH_2), 44.9 (CH_2), 26.9 (CH_2), 25.9 (CH_2), 24.7 (CH_2). ν_{max}/cm^{-1} 3058, 3034, 2997, 2940, 2856, 1612, 1554, 1502, 1454, 1432, 1441. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}N_2OS$ 247.0900; Found 247.0908.

Thiazole-2-carboxamide (3aw)



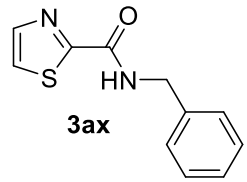
3aw

Thermal: General procedure E was followed: thiazole (32.5 mg, 0.382 mmol, 1 equiv.), oxamic acid (63.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.0 mg, 1.05 mmol, 3 equiv.) in DMSO (0.87 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford thiazole-2-carboxamide **3aw** as a colourless oil (19.6 mg, 0.153 mmol, 40%).

Light Mediated: General procedure I was followed: thiazole (31.9 mg, 0.375 mmol, 1 equiv.), oxamic acid (62.5 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (241.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (60:40, hexane:ethyl acetate) to afford thiazole-2-carboxamide **3aw** as a colourless oil (24.2 mg, 0.189 mmol, 50%).

R_f = 0.22 (60:40, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.61 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.16 (s, 1H, N*H*H), 5.84 (s, 1H, NH*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1 (C), 161.5 (C), 143.9 (CH), 125.4 (CH). ν_{max}/cm^{-1} 3337, 3174, 3099, 1698, 1686, 1616, 1495, 1432, 1379, 1322. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_4H_4N_2OS$ 150.9937; Found 150.9942.

***N*-Benzylthiazole-2-carboxamide (3ax)**

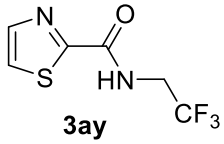


3ax

Light Mediated: General procedure I was followed: thiazole (29.0 mg, 0.341 mmol, 1 equiv.), 2-(benzylamino)-2-oxoacetic acid (127.5 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.3 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-benzylthiazole-2-carboxamide **3ax** as a white solid (56.2 mg, 0.257 mmol, 75%).

R_f = 0.33 (80:20, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.60 (d, *J* = 3.0 Hz, 2H, Ar-H and NH), 7.40 – 7.37 (m, 4H, 4xAr-H), 7.36 – 7.29 (m, 1H, Ar-H), 4.68 (d, *J* = 6.0 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9 (C), 159.5 (C), 143.6 (CH), 137.7 (C), 129.0 (CH), 128.1 (CH), 127.9 (CH), 124.8 (CH), 43.8 (CH_2). ν_{max}/cm^{-1} 3317, 3115, 3086, 3026, 2926, 1656, 1528, 1495, 1484, 1455, 1431. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{10}N_2OS$ 219.0587; Found 219.0596.

***N*-(2,2,2-Trifluoroethyl)thiazole-2-carboxamide (3ay)**

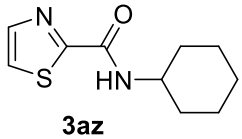


3ay

Light Mediated: General procedure I was followed: thiazole (29.8 mg, 0.350 mmol, 1 equiv.), 2-oxo-2-((2,2,2-trifluoroethyl)amino)acetic acid (120.7 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.9 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(2,2,2-trifluoroethyl)thiazole-2-carboxamide **3ay** as a white solid (52.6 mg, 0.250 mmol, 71%).

R_f = 0.28 (80:20, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.64 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.58 (s, 1H, N-H), 4.11 (qd, *J* = 9.0, 7.0 Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2 (C), 159.8 (C), 143.9 (CH), 125.6 (CH), 124.3 (q, J = 280.0 Hz, CF_3), 41.0 (q, *J* = 35.0 Hz, CH_2). ^{19}F NMR (282 MHz, Chloroform-*d*) δ -72.28 (t, *J* = 9.0 Hz, CF_3). ν_{max}/cm^{-1} 3301, 3116, 2954, 1668, 1538, 1488, 1425, 1405, 1394. M.P. = 100 – 103 °C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_6H_5F_3N_2OS$ 211.0147; Found 211.0148.

***N*-Cyclohexylthiazole-2-carboxamide (3az)**



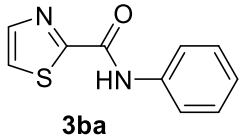
3az

Light Mediated: General procedure I was followed: thiazole (31.6 mg, 0.371 mmol, 1 equiv.), 2-(cyclcohexylamino)-2-oxoacetic acid (122.2 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.1 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-cyclohexylthiazole-2-carboxamide **3az** as a colourless oil (69.7 mg, 0.331 mmol, 89%).

R_f = 0.30 (80:20, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.54 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.14 (s, 1H, N-H), 4.02 – 3.87 (m, 1H, CH), 2.07 – 1.96 (m, 2H, CH_2), 1.82 – 1.71 (m, 2H, CH_2), 1.70 – 1.59 (m, 2H, CH_2), 1.50 – 1.14 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7 (C), 158.6 (C), 143.4 (CH), 124.5 (CH), 48.7

(CH), 33.1 (CH_2), 25.6 (CH_2), 24.9 (CH_2). ν_{max}/cm^{-1} 3396, 3300, 3081, 2929, 2853, 1652, 1524, 1484, 1464, 1450, 1401, 1370. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_{14}N_2OS$ 211.0900; Found 211.0897.

***N*-Phenylthiazole-2-carboxamide (3ba)**

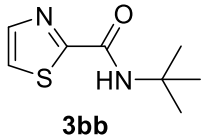


3ba

Light Mediated: General procedure I was followed: thiazole (30.9 mg, 0.363 mmol, 1 equiv.), 2-oxo-2-(phenylamino)acetic acid (115.6 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.2 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-phenylthiazole-2-carboxamide **3ba** as a colourless oil (35.5 mg, 0.174 mmol, 48%).

R_f = 0.24 (90:10, hexane:ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.10 (s, 1H, N-H), 7.92 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.71 (dd, *J* = 9.0, 1.0 Hz, 2H, 2xAr-H), 7.64 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.39 (ddt, *J* = 9.0, 7.0, 2.0 Hz, 2H, 2xAr-H), 7.17 (tt, *J* = 7.0, 1.0 Hz, 1H, Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2 (C), 157.3 (C), 143.6 (CH), 137.3 (C), 129.4 (CH), 125.4 (CH), 124.9 (CH), 119.9 (CH). ν_{max}/cm^{-1} 3360, 3290, 3114, 3084, 3059, 1668, 1596, 15271501, 1495, 1484, 1443, 1394. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{10}H_8N_2OS$ 205.0430; Found 205.0438.

***N*-(Tert-butyl)thiazole-2-carboxamide (3bb)**

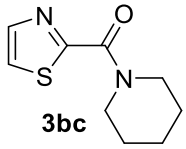


3bb

Light Mediated: General procedure I was followed: thiazole (33.1 mg, 0.389 mmol, 1 equiv.), 2-(tert-butylamino)-2-oxoacetic acid (102.6 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.8 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(tert-butyl)thiazole-2-carboxamide **3bb** as a colourless oil (52.3 mg, 0.284 mmol, 73%).

R_f = 0.28 (90:10, hexane:ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.52 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.14 (s, 1H, N-H), 1.48 (s, 9H, 3xCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7 (C), 158.8 (C), 143.3 (CH), 124.4 (CH), 51.9 (C), 28.9 (CH_3). ν_{max}/cm^{-1} 3394, 3320, 3083, 2968, 2933, 1670, 1522, 1485, 1394, 1365. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_8H_{12}N_2OS$ 185.0743; Found 185.0743.

Piperidin-1-yl(thiazol-2-yl)methanone (3bc)



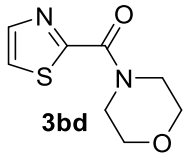
3bc

Thermal: General procedure E was followed: thiazole (29.2 mg, 0.343 mmol, 1 equiv.), 2-oxo-2-(piperidin-1-yl)acetic acid (110.9 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) at 50 ºC for 24 h. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford piperidin-1-yl(thiazol-2-yl)methanone **3bc** as a colourless oil (45.3 mg, 0.231 mmol, 67%).

Light Mediated: General procedure I was followed: thiazole (30.2 mg, 0.355 mmol, 1 equiv.), 2-oxo-2-(piperidin-1-yl)acetic acid (111.3 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.2 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 ºC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford piperidin-1-yl(thiazol-2-yl)methanone **3bc** as a colourless oil (46.8 mg, 0.238 mmol, 67%).

R_f = 0.18 (90:10, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.52 (d, *J* = 3.0 Hz, 1H, Ar-H), 4.27 (app. s, 2H, CH_2), 3.76 (app. s, 2H, CH_2), 1.77 – 1.65 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7 (C), 159.5 (C), 143.1 (CH), 123.7 (CH), 47.7 (CH_2), 44.8 (CH_2), 26.9 (CH_2), 26.0 (CH_2), 24.8 (CH_2). ν_{max}/cm^{-1} 3080, 3036, 2997, 2936, 2855, 1609, 1493, 1442, 1399, 1370, 1351. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_9H_{12}N_2OS$ 197.0743; Found 197.0745.

Morpholino(thiazol-2-yl)methanone (3bd)

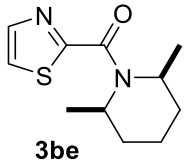


3bd

Light Mediated: General procedure I was followed: thiazole (29.9 mg, 0.351 mmol, 1 equiv.), 2-morpholino-2-oxoacetic acid (113.5 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (238.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford morpholino(thiazol-2-yl)methanone **3bd** as a colourless oil (40.8 mg, 0.206 mmol, 59%).

R_f = 0.27 (70:30, hexane:ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.54 (d, *J* = 3.0 Hz, 1H, Ar-H), 4.47 (t, *J* = 5.0 Hz, 2H, CH_2), 3.84 – 3.74 (m, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1 (C), 159.3 (C), 143.3 (CH), 124.4 (CH), 67.3 (CH_2), 67.1 (CH_2), 47.2 (CH_2), 43.9 (CH_2). ν_{max}/cm^{-1} 3083, 3028, 2965, 2902, 2855, 1616, 1493, 1436, 1397, 1363. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_8H_{10}N_2O_2S$ 199.0536; Found 199.0535.

((2R,6S)-2,6-Dimethylpiperidin-1-yl)(thiazol-2-yl)methanone (3be)



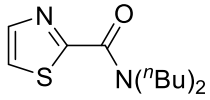
3be

Light Mediated: General procedure I was followed: thiazole (29.7 mg, 0.349 mmol, 1 equiv.), 2-((2R,6S)-2,6-dimethylpiperidin-1-yl)-2-oxoacetic acid (131.5 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.1 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford ((2R,6S)-2,6-dimethylpiperidin-1-yl)(thiazol-2-yl)methanone **3be** as a colourless oil (39.8 mg, 0.177 mmol, 51%).

R_f = 0.25 (90:10, hexane:ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.48 (d, *J* = 3.0 Hz, 1H, Ar-H), 5.35 (app. s, 1H, CH), 5.02 (app. s, 1H, CH), 1.90 (qt, *J* = 13.0, 3.5 Hz, 1H, C*H*H), 1.80 – 1.69 (m, 2H, CH_2), 1.65 (d, *J* = 13.5 Hz, 2H, CH_2), 1.54 (dt, *J* = 13.0, 3.5 Hz, 1H, CH*H*), 1.37 (s, 3H, CH_3), 1.35 (s, 3H, CH_3). ^{13}C NMR (101

MHz, $CDCl_3$) δ 166.3 (C), 160.6 (C), 143.1 (CH), 123.5 (CH), 47.8 (CH), 30.4 (CH_2), 21.5 (CH_3), 14.2 (CH_2). ν_{max}/cm^{-1} 3082, 2969, 2935, 2869, 1605, 1489, 1466, 1424, 1370. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{11}H_{16}N_2OS$ 225.1056; Found 225.1065.

***N*,*N*-Dibutylthiazole-2-carboxamide (3bf)**



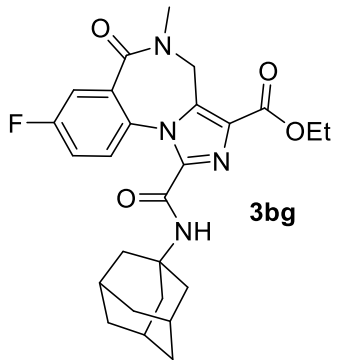
3bf

Light Mediated: General procedure I was followed: thiazole (28.8 mg, 0.338 mmol, 1 equiv.), 2-(dibutylamino)-2-oxoacetic acid (142.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.6 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*,*N*-dibutylthiazole-2-carboxamide **3bf** as a colourless oil (41.7 mg, 0.173 mmol, 51%).

R_f = 0.14 (95:5, hexane:ethyl acetate). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 3.0 Hz, 1H, Ar-H), 7.49 (d, *J* = 3.0 Hz, 1H, Ar-H), 4.00 (t, *J* = 7.0 Hz, 2H, CH_2), 3.49 (t, *J* = 7.0 Hz, 2H, CH_2), 1.70 – 1.59 (m, 4H, 2xCH_2), 1.44 – 1.25 (m, 4H, 2xCH_2), 0.96 (t, *J* = 7.0 Hz, 3H, CH_3), 0.91 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1 (C), 160.5 (C), 143.3 (CH), 123.8 (CH), 48.5 (CH_2), 47.8 (CH_2), 31.4 (CH_2), 29.8 (CH_2), 20.5 (CH_2), 20.0 (CH_2), 14.0 (CH_3), 13.9 (CH_3). ν_{max}/cm^{-1} 3081, 2957, 2931, 2872, 1616, 1495, 1464, 1456, 1429, 1400, 1377. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{20}N_2OS$ 241.1369; Found 241.1370.

Late-Stage Applications

Ethyl-1-((adamantan-1-yl)carbamoyl)-8-fluoro-5-methyl-6-oxo-5,6-dihydro-4*H*-benzo[*f*]imidazo[1,5][1,4]diazepine-3-carboxylate (3bg)

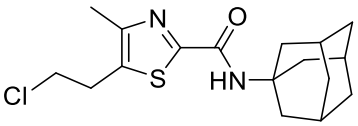


3bg

Thermal: General procedure C was followed: flumazenil (32.9 mg, 0.108 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (46.5 mg, 0.20 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (70.3 mg, 0.30 mmol, 3 equiv.) in DMSO (0.5 mL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (30:70, hexane:ethyl acetate) to afford ethyl-1-((adamantan-1-yl)carbamoyl)-8-fluoro-5-methyl-6-oxo-5,6-dihydro-4*H*-benzo[*f*]imidazo[1,5][1,4]diazepine-3-carboxylate **3bg** as a colourless oil (47.4 mg, 0.0986 mmol, 91%).

R_f = 0.39 (30:70, hexane:ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.5, 3.0 Hz, 1H, Ar-H), 7.54 (dd, *J* = 8.5, 4.5 Hz, 1H, Ar-H), 7.26 (ddd, *J* = 16.5, 7.5, 3.0 Hz, 1H, Ar-H), 7.16 (s, 1H, N-H), 5.12 (d, *J* = 16.0 Hz, 1H, C*H*H), 4.54 – 4.39 (m, 2H, CH_2), 4.19 (d, *J* = 16.0 Hz, 1H, CH*H*), 3.19 (s, 3H, CH_3), 2.09 (app. s, 9H, 3xCH and 3xCH_2), 1.69 (app. s, 6H, 3xCH_2), 1.46 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8 (C), 162.7 (C), 162.27 (d, *J* = 251.0 Hz, C), 156.1 (C), 140.2 (C), 140.0 (C), 131.98 (d, *J* = 7.9 Hz, C), 129.64 (d, *J* = 8.5 Hz, CH), 128.51 (d, *J* = 3.0 Hz), 126.7 (C), 118.33 (d, *J* = 23.0 Hz), 116.79 (d, *J* = 25.0 Hz), 61.5 (CH_2), 52.9 (C), 42.9 (CH_2), 41.5 (CH_2), 36.4 (CH_2), 35.3 (CH_3), 29.6 (CH), 14.5 (CH_3). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.96 (ddd, *J* = 16.0, 7.5, 5.0 Hz). ν_{max}/cm^{-1} 3385, 3224, 3074, 2907, 2851, 2249, 1729, 1671, 1652, 1578, 1527, 1484, 1456, 1436. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{29}FN_4O_4$ 481.2246; Found 481.2234.

***N*-(Adamantan-1-yl)-5-(2-chloroethyl)-4-methylthiazole-2-carboxamide (3bh)**



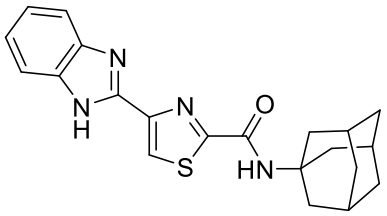
3bh

Thermal: General procedure E was followed: clomethiazole (56.4 mg, 0.349 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (158.1 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.7 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875nmL) at 50 ^oC for 24 h. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-5-(2-chloroethyl)-4-methylthiazole-2-carboxamide **3bh** as a white solid (60.6 mg, 0.179 mmol, 51%).

Light Mediated: General procedure I was followed: clomethiazole (60.3 mg, 0.373 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (157.9 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (241.1 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-5-(2-chloroethyl)-4-methylthiazole-2-carboxamide **3bh** as a white solid (59.8 mg, 0.176 mmol, 47%).

R_f = 0.31 (80:20, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 6.93 (s, 1H, N-H), 3.67 (t, *J* = 7.0 Hz, 2H, CH_2), 3.22 (t, *J* = 7.0 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3), 2.12 (s, 9H, 3xCH and 3xCH_2), 1.74 – 1.68 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0 (C), 158.6 (C), 150.7 (C), 133.7 (C), 52.5 (C), 44.3 (CH_2), 41.7 (CH_2), 36.5 (CH_2), 30.3 (CH_2), 29.6 (CH), 15.2 (CH_3). ν_{max}/cm^{-1} 3481, 3375, 3284, 2911, 2849, 1670, 1639, 1514, 1454, 1431. M.p. 104 – 107 ^oC. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{23}{}^{35}ClN_2OS$ 339.1292; Found 339.1301.

***N*-(Adamantan-1-yl)-4-(1*H*-benzo[*d*]imidazol-2-yl)thiazole-2-carboxamide (3bi)**



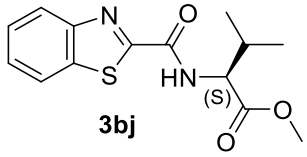
3bi

Thermal: General procedure E was followed: 2-(4-thiazole)benzimidazole (70.3 mg, 0.349 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (312.4 mg, 1.40 mmol, 4 equiv.) and $(NH_4)_2S_2O_8$ (240.0 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) at 60 °C for 24 h. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-(1*H*-benzo[*d*]imidazol-2-yl)thiazole-2-carboxamide **3bi** as a white solid (65.7 mg, 0.174 mmol, 50%).

Light Mediated: General procedure I was followed: 2-(4-thiazole)benzimidazole (70.4 mg, 0.350 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (156.4 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (239.7 mg, 1.05 mmol, 3 equiv.) in DMSO (0.875 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (70:30, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-(1*H*-benzo[*d*]imidazol-2-yl)thiazole-2-carboxamide **3bi** as a white solid (46.9 mg, 0.124 mmol, 35%).

R_f = 0.20 (70:30, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 12.46 (s, 1H, N-H), 10.33 (s, 1H, N-H), 8.79 (s, 1H, Ar-H), 7.80 – 7.73 (m, 1H, Ar-H), 7.57 – 7.50 (m, 1H, Ar-H), 7.41 – 7.31 (m, 2H, 2xAr-H), 2.34 (app. d, *J* = 3.0 Hz, 6H, 3xCH_2), 2.17 (s, 3H, 3xCH), 1.85 – 1.70 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7 (C), 155.1 (CH), 147.2 (C), 142.6 (C), 141.4 (C), 139.3 (C), 132.5 (C), 124.9 (CH), 123.4 (CH), 119.6 (CH), 111.5 (CH), 53.6 (C), 41.4 (CH_2), 36.7 (CH_2), 29.7 (CH). ν_{max}/cm^{-1} 3395, 2903, 2848, 1671, 1652, 1616, 1538, 1486, 1451, 1419, 1409, 1360, 1346, 1318, 1300, 1243, 1205, 1190, 1098, 1068, 1012. M.p. = 286 - 289 ˚C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{22}N_4O_1S_1$, 379.1587; found 379.1597.

Methyl(benzo[*d*]thiazole-2-carbonyl)-*L*-valinate (3bj)



3bj

Light Mediated: General procedure H was followed: benzothiazole (47.9 mg, 0.354 mmol, 1 equiv.), (s)-2-((1-methoxy-3-methyl-1-oxobutan-2-yl)amino)-2-oxoacetic acid (142.9 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (241.9 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford methyl(benzo[*d*]thiazole-2-carbonyl)-*L*-valinate **3bj** as a colourless oil (53.2 mg, 0.182 mmol, 51%).

R_f = 0.23 (90:10, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.12 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H, Ar-H), 7.97 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H, Ar-H), 7.89 (d, *J* = 9.0 Hz, 1H, N-H), 7.56 (ddd, *J* = 15.0, 7.0, 1.5 Hz, 1H, Ar-H), 7.49 (ddd, *J* = 15.0, 7.0, 1.5 Hz, 1H, Ar-H), 4.75 (dd, *J* = 9.0, 5.0 Hz, 1H, CH), 3.80 (s, 3H, CH_3), 2.34 (pd, *J* = 7.0, 5.0 Hz, 1H, CH), 1.06 (d, *J* = 7.0 Hz, 3H, CH_3), 1.03 (d, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9 (C), 163.2 (C), 160.0 (C), 153.1 (C), 137.4 (C), 127.0 (CH), 126.9 (CH), 124.7 (CH), 122.5 (CH), 57.8 (CH), 52.5 (CH_3), 31.8 (CH), 19.3 (CH_3), 18.1 (CH_3). ν_{max}/cm^{-1} 3397, 3066, 2963, 2874, 1739, 1677, 1595, 1520, 1458, 1436, 1391. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{14}H_{16}N_2O_3S_1$, 293.0954; found 293.0961. $[\alpha]_D^{23.4}$ +56 (c 0.5, $CHCl_3$). HPLC (CHIRALPAK OD-H, hexane/2-propanol: 92:8, flow rate: 1.0 mL min^{-1}, detection UV 254nm, 25 °C) tR of major isomer: 12.217 min.

CSP-HPLC traces overleaf:

Racemic sample:

Area % Report

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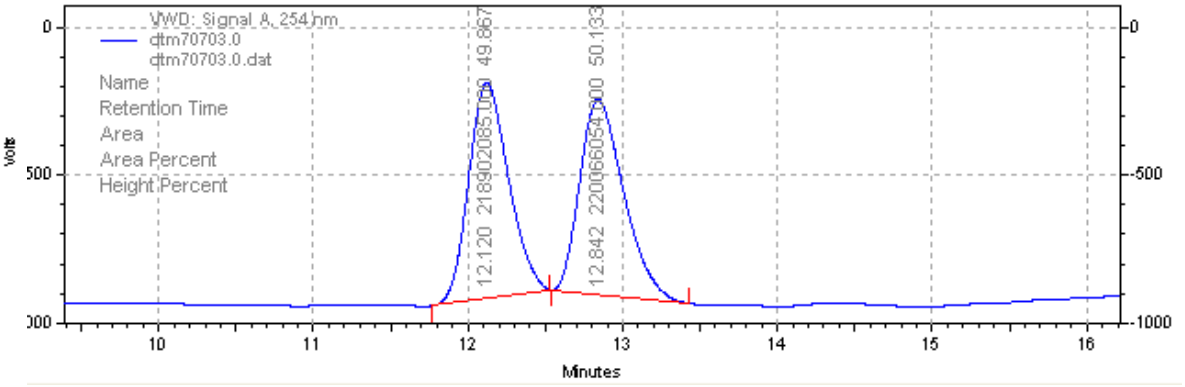

VWD: Signal A, 254 nm Results

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12.842	220066054	50.13	11099611	47.55
Totals	438968139	100.00	23342514	100.00

3bj:

Area % Report

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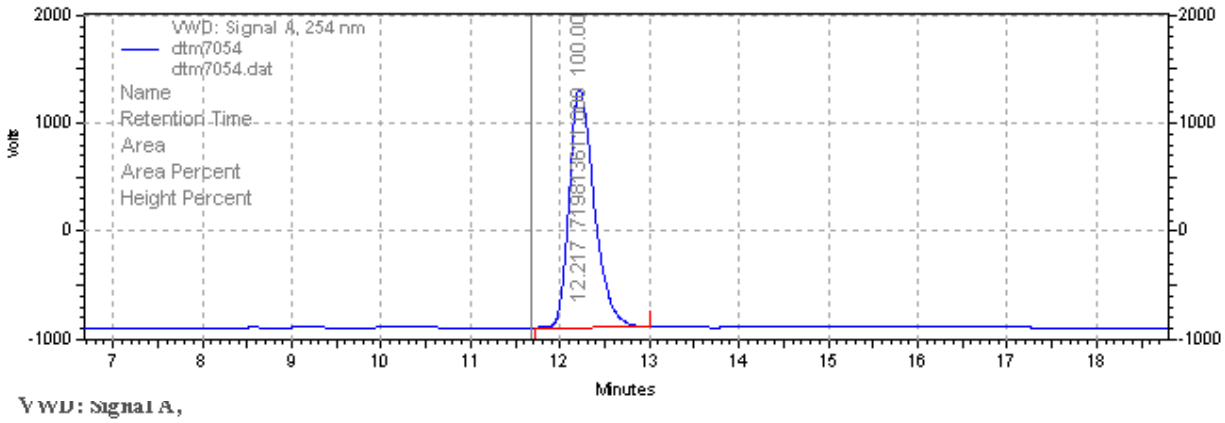

VWD: Signal A, 254 nm Results

Retention Time	Area	Area %	Height	Height %
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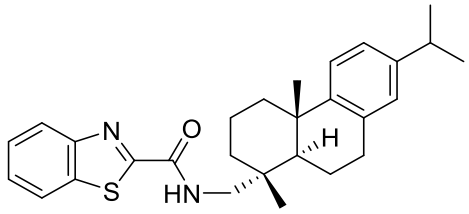
Totals	719813611	100.00	36942588	100.00

***N*-(((1R,4aS,10aR)-7-Isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)benzo[*d*]thiazole-2-carboxamide (3bk)**



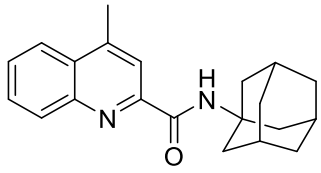
3bk

Light Mediated: General procedure H was followed: benzothiazole (50.5 mg, 0.373 mmol, 1 equiv.), 2-((((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)amino)-2-oxoacetic acid (251.0 mg, 0.70 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (240.7 mg, 1.05 mmol, 3 equiv.) in DMSO (1 mL) irradiated with 420 nm light for 3 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)benzo[*d*]thiazole-2-carboxamide **3bk** as a white solid (71.3 mg, 0.160 mmol, 43%).

R_f = 0.13 (95:5, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.06 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H, Ar-H), 7.96 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H, Ar-H), 7.57 – 7.43 (m, 3H, 2xAr-H and N-H), 7.17 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.99 (dd, *J* = 8.0, 2.0 Hz, 1H, Ar-H), 6.90 (d, *J* = 1.5 Hz, 1H, Ar-H), 3.52 (dd, *J* = 13.5, 7.0 Hz, 1H, C*H*H), 3.33 (dd, *J* = 13.5, 7.0 Hz, 1H, CH*H*), 3.02 – 2.75 (m, 3H, CH and CH_2), 2.31 (dd, *J* = 14.0, 4.0 Hz, 1H, C*H*H), 2.07 – 1.96 (m, 1H, CH*H*), 1.91 – 1.66 (m, 3H, CH_2 and C*H*H), 1.60 – 1.53 (m, 2H, CH and CH*H*), 1.44 (tdd, *J* = 12.5, 8.0, 4.0 Hz, 2H, CH_2), 1.25 (s, 3H, CH_3), 1.21 (d, *J* = 7.0 Hz, 6H, 2xCH_3), 1.05 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2 (C), 160.2 (C), 153.0 (C), 147.1 (C), 145.8 (C), 137.3 (C), 134.9 (C), 127.1 (CH), 126.9 (CH), 126.7 (CH), 124.5 (CH), 124.4 (CH), 124.0 (CH), 122.5 (CH), 50.5 (CH_2), 45.7 (CH), 38.4 (CH_2), 38.1 (C), 37.7 (C), 36.5 (CH_2), 33.6 (CH), 30.5 (CH_2), 25.6 (CH_3), 24.1 (CH_3), 19.3 (CH_2), 19.0 (CH_3), 18.8 (CH_2). ν_{max}/cm^{-1} 3409, 3314, 3050, 2957, 2925, 2867, 1677, 1616, 1531, 1507, 1384, 1361, 1319. M.p. = 181 – 184 °C. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{34}N_2OS$, 447.2465; found 447.2469. $[\alpha]_D^{23.3}$ -32 (c 0.5, $CHCl_3$).

Light-Mediated Results with Other *N*-Heterocycles

***N*-(Adamantan-1-yl)-4-methylquinoline-2-carboxamide (6a)**

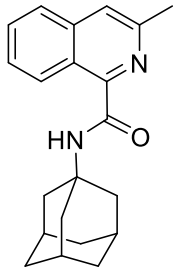


6a

Light Mediated - A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Lepidine (23.4 mg, 0.163 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (67.7 mg, 0.30 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (103.1 mg, 0.45 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. DMSO (0.5 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 18 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give the crude product. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-4-methylquinoline-2-carboxamide **6a** as a white solid (26.3 mg, 0.0821 mmol, 50%).

R_f = 0.38 (90:10, hexane:ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.07 (m, 3H, NH and 2xAr-H), 8.03 (dd, *J* = 8.5, 1.5 Hz, 1H, Ar-H), 7.74 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H, Ar-H), 7.61 (ddd, *J* = 8.0, 7.0, 1.5 Hz, 1H, Ar-H), 2.76 (s, 3H, CH_3), 2.24 – 2.20 (m, 6H, 3xCH_2), 2.19 – 2.13 (m, 3H, 3xCH), 1.82 – 1.71 (m, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 (C), 150.6 (C), 146.4 (C), 146.0 (C), 130.4 (CH), 129.7 (CH), 129.3 (C), 127.5 (CH), 124.0 (CH), 119.3 (CH), 51.8 (C), 41.7 (CH_2), 36.6 (CH_2), 29.7 (CH), 19.1 (CH_3). ν_{max}/cm^{-1} 3364, 3067, 2906, 2849, 2247, 1674, 1616, 1596, 1560, 1525, 1505, 1451, 1412, 1359. M.p. = 118 – 121 °C. Data consistent with literature.[9]

***N*-(Adamantan-1-yl)-3-methylisoquinoline-1-carboxamide (6b)**

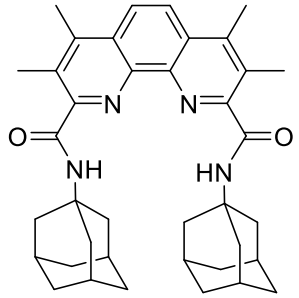


6b

Light-Mediated - A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. 3-Methylisoquinoline (23.3 mg, 0.163 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (68.2 mg, 0.30 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (101.2 mg, 0.45 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. DMSO (0.5 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 5 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give the crude product. The crude product was then purified *via* column chromatography (95:5, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-3-methylisoquinoline-1-carboxamide **6b** as a white solid (33.6 mg, 0.105 mmol, 64%).

R_f = 0.15 (95:5, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 9.56 (dq, *J* = 8.5, 1.0 Hz, 1H, Ar-H), 8.12 (s, 1H, NH), 7.74 – 7.69 (m, 1H, Ar-H), 7.66 – 7.52 (m, 3H, 3xAr-H), 2.68 (d, *J* = 1.0 Hz, 3H, CH_3), 2.26 – 2.21 (m, 6H, 3xCH_2), 2.19 – 2.12 (m, 3H, 3xCH), 1.84 – 1.68 (m, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5 (C), 148.9 (C), 148.5 (C), 138.5 (C), 130.3 (CH), 128.2 (CH), 127.5 (CH), 126.3 (CH), 125.4 (CH), 122.3 (CH), 51.9 (C), 41.7 (CH_2), 36.7 (CH_2), 29.7 (CH), 24.1 (CH_3). ν_{max}/cm^{-1} 3350, 3051, 2905, 2848, 2247, 1669, 1625, 1590, 1557, 1512, 1454, 1404, 1378. M.p. = 145 – 148 ^oC. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{24}N_2O$, 321.1961; found 321.1968.

***N*,*N*-Di(adamantan-1-yl)-3,4,7,8-tetramethyl-1,10-phenanthroline-2,9-dicarboxamide (6c)**

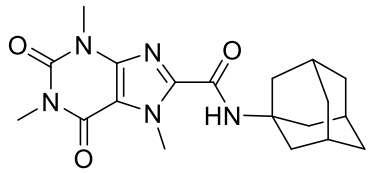


6c

Light-Mediated - A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. 3,4,7,8-Tetramethyl-1,10-phenanthroline (29.1 mg, 0.123 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (136.8 mg, 0.60 mmol, 5 equiv.) and $(NH_4)_2S_2O_8$ (166.2 mg, 0.72 mmol, 6 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. DMSO (1.2 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 24 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with water (5 mL) and filtered. The filter cake was then washed with water (15 mL), methanol (10 mL) and diethyl ether (10 mL) to afford *N*,*N*-di(adamantan-1-yl)-3,4,7,8-tetramethyl-1,10-phenanthroline-2,9-dicarboxamide **6c** as an off-white solid (73.0 mg, 0.123 mmol, quant.).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 2H, Ar-H), 7.93 (s, 2H, Ar-H), 2.83 (s, 6H, 2xCH_3), 2.73 (s, 6H, 2xCH_3), 2.30 (d, *J* = 3.0 Hz, 12H, 6xCH_2), 2.17 (s, 6H, 6xCH), 1.81 – 1.73 (m, 12H, 6xCH_2). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8 (C), 150.5 (C), 144.6 (C), 142.3 (C), 131.3 (C), 128.2 (C), 123.3 (CH), 52.1 (C), 41.8 (CH_2), 36.7 (CH_2), 29.7 (CH), 16.4 (CH_3), 15.1 (CH_3). ν_{max}/cm^{-1} 3352, 2904, 2851, 1671, 1516, 1487, 1358. M.p. = >300 ^oC. Data consistent with literature.[5]

***N*-(Adamantan-1-yl)-1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purine-8-carboxamide (6d)**

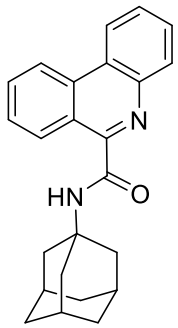


6d

Light-Mediated - A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Caffeine (38.5 mg, 0.199 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (91.1 mg, 0.40 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (138.9 mg, 0.60 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. The DMSO (1.3 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 6 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give the crude product. The crude product was then purified *via* column chromatography (80:20, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)-1,3,7-trimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1*H*-purine-8-carboxamide **6d** as a white solid (75.3 mg, 0.199 mmol, quant.).

R_f = 0.15 (80:20, hexane:ethyl acetate). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.16 (s, 1H, N-H), 4.38 (s, 3H, CH_3), 3.56 (s, 3H, CH_3), 3.40 (s, 3H, CH_3), 2.13 (app. s, 9H, 3xCH_2 and 3xCH), 1.76 – 1.70 (m, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3 (C), 155.7 (C), 151.7 (C), 146.1 (C), 141.8 (C), 110.2 (C), 52.8 (C), 41.6 (CH_2), 36.4 (CH_2), 34.8 (CH_3), 29.9 (CH_3), 29.5 (CH), 28.2 (CH_3). ν_{max}/cm^{-1} 3382, 2950, 2904, 2850, 2253, 1714, 1677, 1654, 1595, 1525. M.p. = 280 – 283 °C. Data consistent with literature.[6]

***N*-(Adamantan-1-yl)phenanthridine-6-carboxamide (6e)**

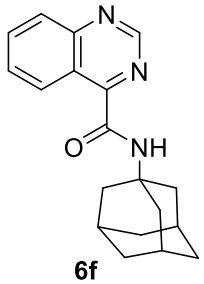


6e

Light-Mediated - A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Phenanthridine (29.1 mg , 0.162 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (68.4 mg, 0.30 mmol, 2 equiv.) and $(NH_4)_2S_2O_8$ (103.0 mg, 0.45 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. DMSO (0.5 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 5 h at 25 ^oC with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give the crude product. The crude product was then purified *via* column chromatography (90:10, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)phenanthridine-6-carboxamide **6e** as a white solid (48.5 mg, 0.136 mmol, 84%).

R_f = 0.37 (90:10, hexane:ethyl acetate). ^1H NMR (300 MHz, Chloroform-*d*) δ 9.60 (dd, *J* = 8.5, 1.5 Hz, 1H, Ar-H), 8.63 (dt, *J* = 8.5, 1.0, 0.5 Hz, 1H, Ar-H), 8.60 – 8.55 (m, 1H, Ar-H), 8.19 – 8.13 (m, 1H, Ar-H), 7.96 (s, 1H, NH), 7.85 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H, Ar-H), 7.79 – 7.68 (m, 3H, 3xAr-H), 2.31 – 2.26 (m, 6H, 3xCH_2), 2.22 – 2.16 (m, 3H, 3xCH), 1.86 – 1.71 (m, 6H, 3xCH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4 (C), 150.5 (C), 141.9 (C), 133.9 (C), 130.9 (CH), 130.5 (CH), 129.3 (CH), 128.9 (CH), 128.3 (CH), 127.9 (CH), 125.5 (C), 124.4 (C), 122.2 (CH), 121.9 (CH), 52.2 (C), 41.6 (CH_2), 36.6 (CH_2), 29.7 (CH). ν_{max}/cm^{-1} 3304, 3055, 2895, 2882, 2857, 2841, 1659, 1613, 1569, 1535, 1524, 1488, 1460, 1447, 1359. M.p. = 176 – 179 ^oC. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{24}N_2O$, 357.1961; found 357.1970.

***N*-(Adamantan-1-yl)quinazoline-4-carboxamide (6f)**



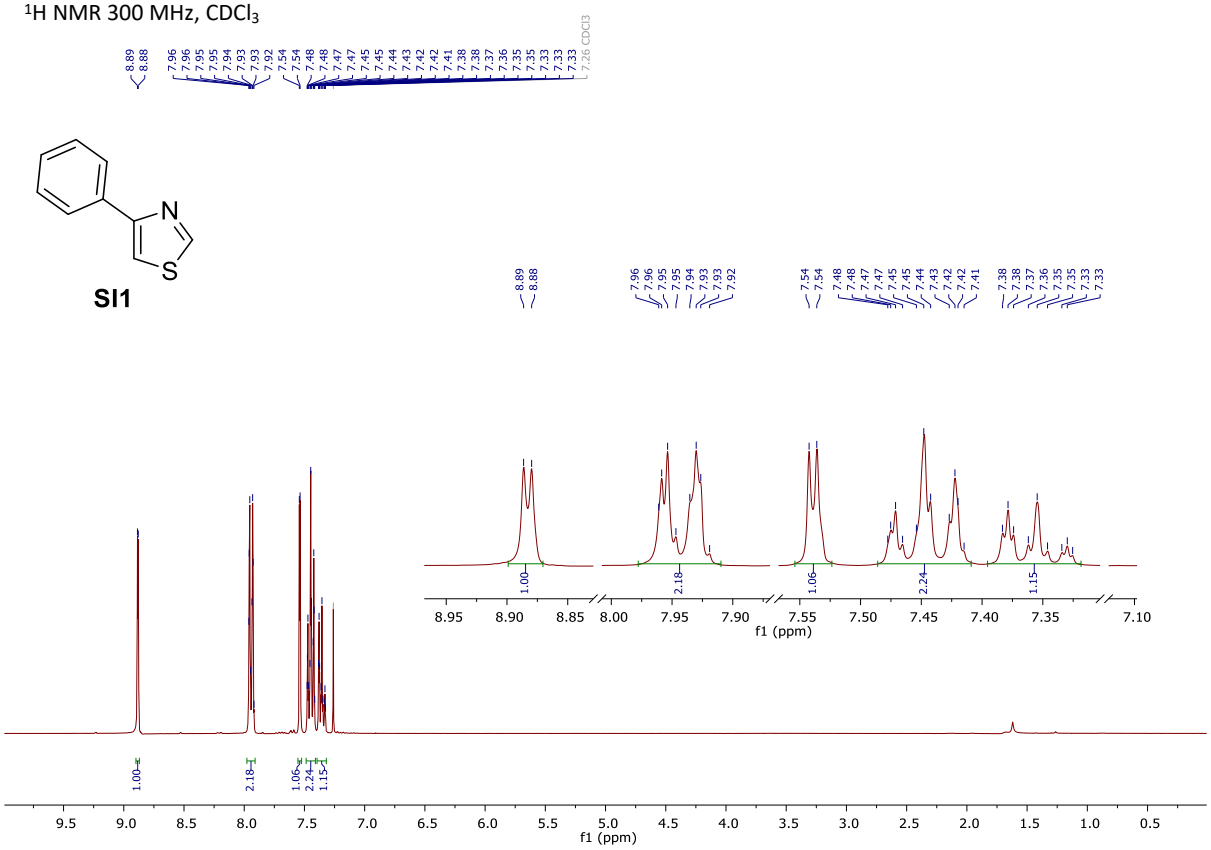
6f

Light-Mediated - A 4 mL vial equipped with a stirrer bar was purged with argon for 30 seconds, then sealed tightly. Quinazoline (20.6 mg, 0.158 mmol, 1 equiv.), 2-((adamantan-1-yl)amino)-2-oxoacetic acid (51.6 mg, 0.225 mmol, 1.5 equiv.) and $(NH_4)_2S_2O_8$ (102.4 mg, 0.45 mmol, 3 equiv.) were added quickly to the 4 mL screw top vial equipped with a magnetic stirrer bar, and then resealed. Separately, a Schlenk tube containing DMSO was purged with argon balloon for 10-15 mins. DMSO (0.5 mL) was added to the 4 mL vial, and argon was blown into the opening for approx. 30 seconds. The vial was quickly sealed tight and irradiated with 420 nm light for 1 h at 25 °C with 100% intensity of light using a Penn M2 photoreactor. The reaction mixture was then diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ solution (80 mL). The aqueous phase was then extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were then washed with brine (80 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give the crude product. The crude product was then purified *via* column chromatography (85:15, hexane:ethyl acetate) to afford *N*-(adamantan-1-yl)quinazoline-4-carboxamide **6f** as a colourless oil (28.8 mg, 0.094 mmol, 59%).

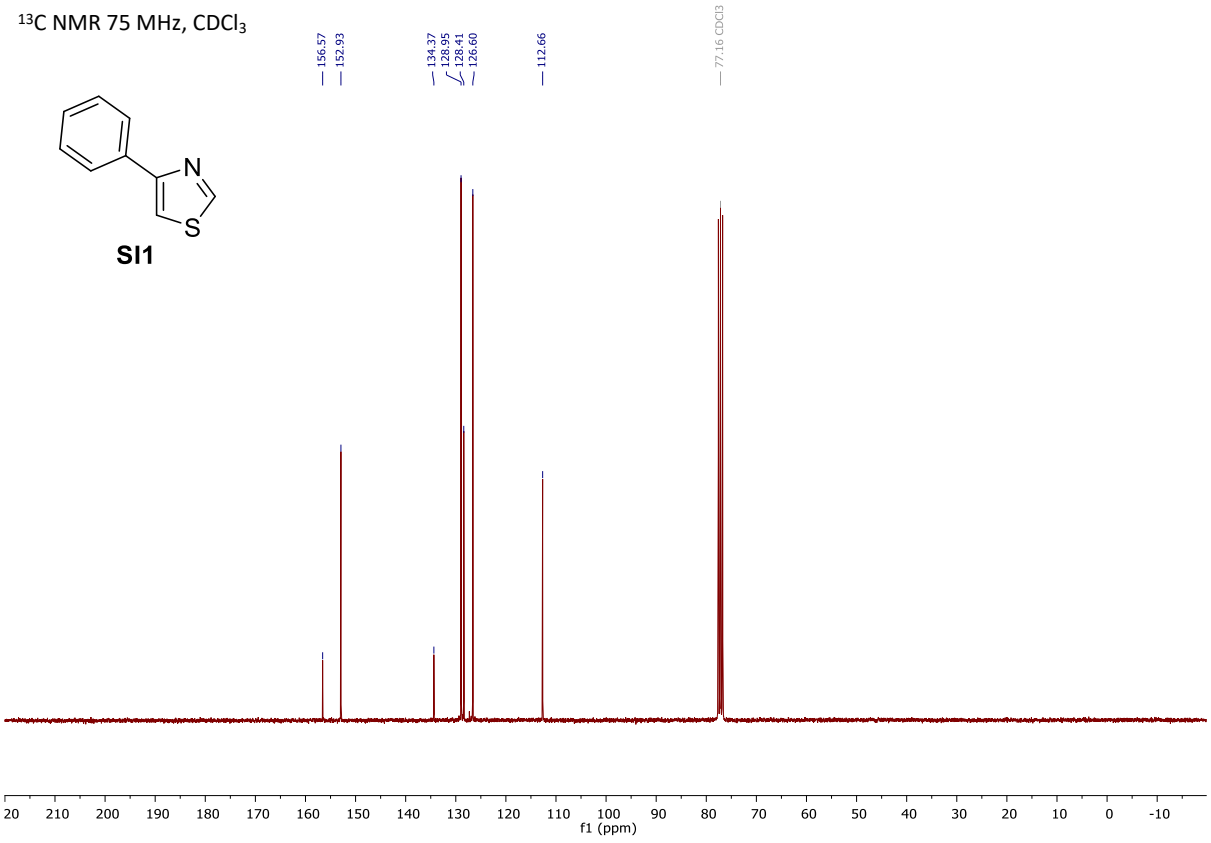
R_f = 0.21 (85:15, hexane:ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.50 (ddd, *J* = 8.5, 1.5, 0.5 Hz, 1H, Ar-H), 9.27 (s, 1H, Ar-H), 8.06 (d, *J* = 8.5 Hz, 1H, Ar-H), 8.00 (s, 1H, NH), 7.93 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H, Ar-H), 7.70 (ddd, *J* = 8.5, 7.0, 1.5 Hz, 1H, Ar-H), 2.21 (app. s, 6H, 3xCH_2), 2.19 – 2.15 (m, 3H, 3xCH), 1.82 – 1.71 (m, 6H, 3xCH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 (C), 156.2 (C), 153.0 (CH), 152.6 (C), 134.5 (CH), 129.0 (CH), 128.7 (CH), 128.1 (CH), 122.8 (C), 52.4 (C), 41.5 (CH_2), 36.5 (CH_2), 29.6 (CH). ν_{max}/cm^{-1} 3364, 3115, 3042, 2905, 2848, 2680, 1675, 1613, 1552, 1514, 1486, 1454, 1405, 1376, 1359, 1344. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd. for $C_{19}H_{21}N_3O$, 308.1757; found 308.1768.

10. NMR Spectra

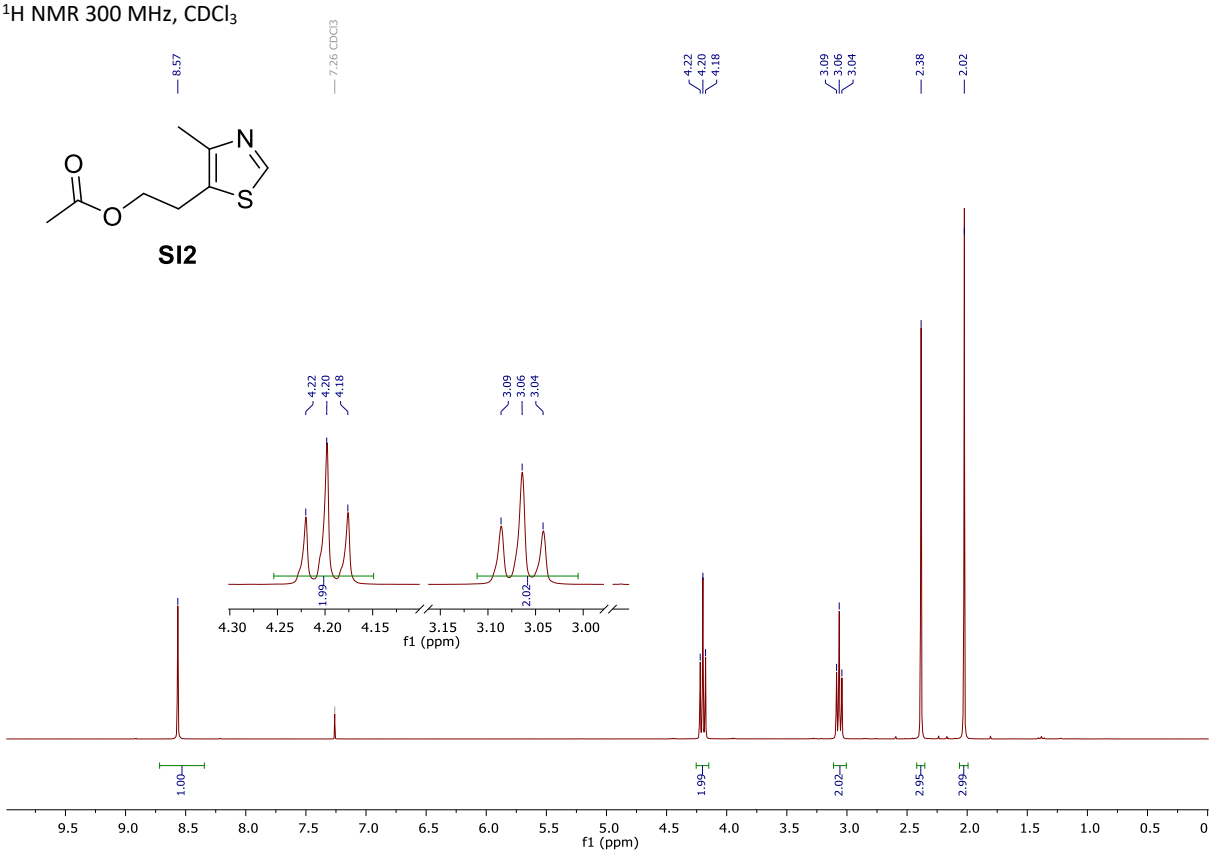
^{1}H NMR 300 MHz, $CDCl_3$



^{13}C NMR 75 MHz, $CDCl_3$

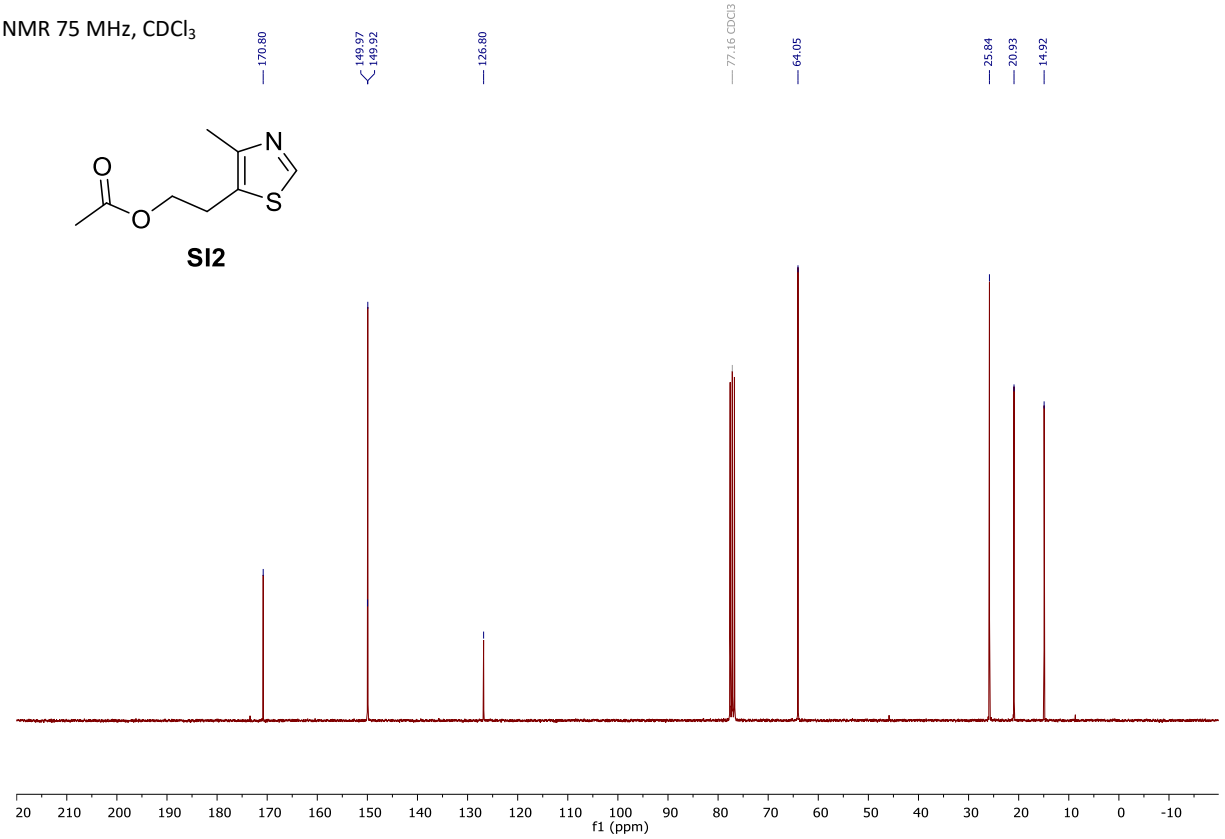


^{1}H NMR 300 MHz, $CDCl_3$



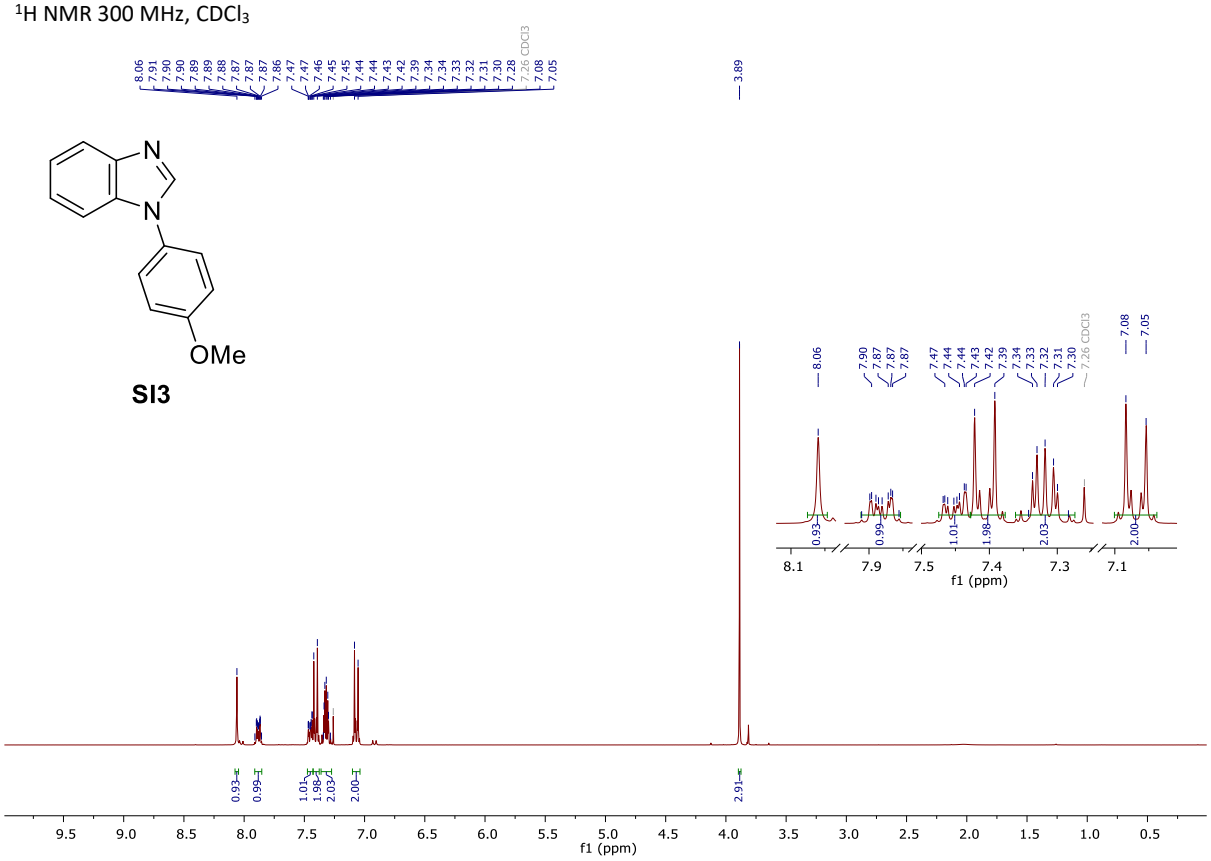
SI2

^{13}C NMR 75 MHz, $CDCl_3$

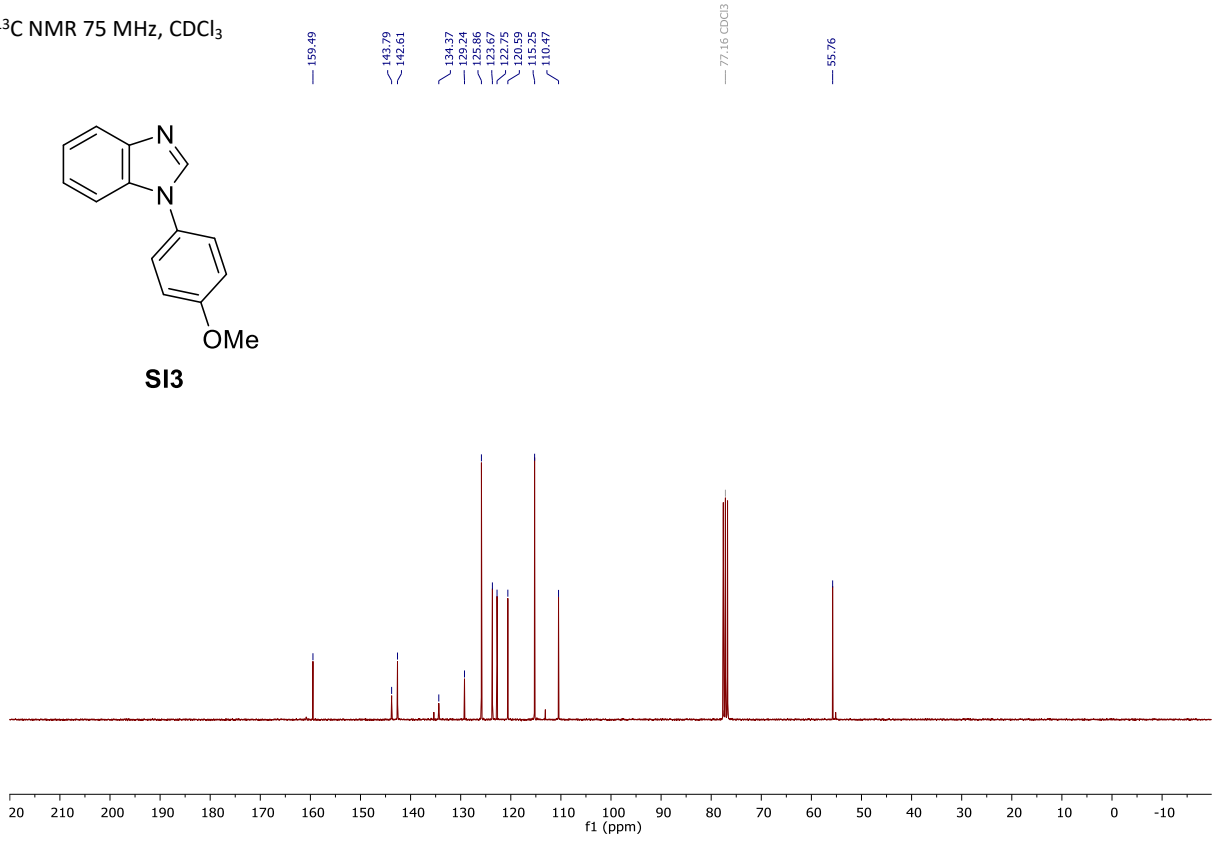


SI2

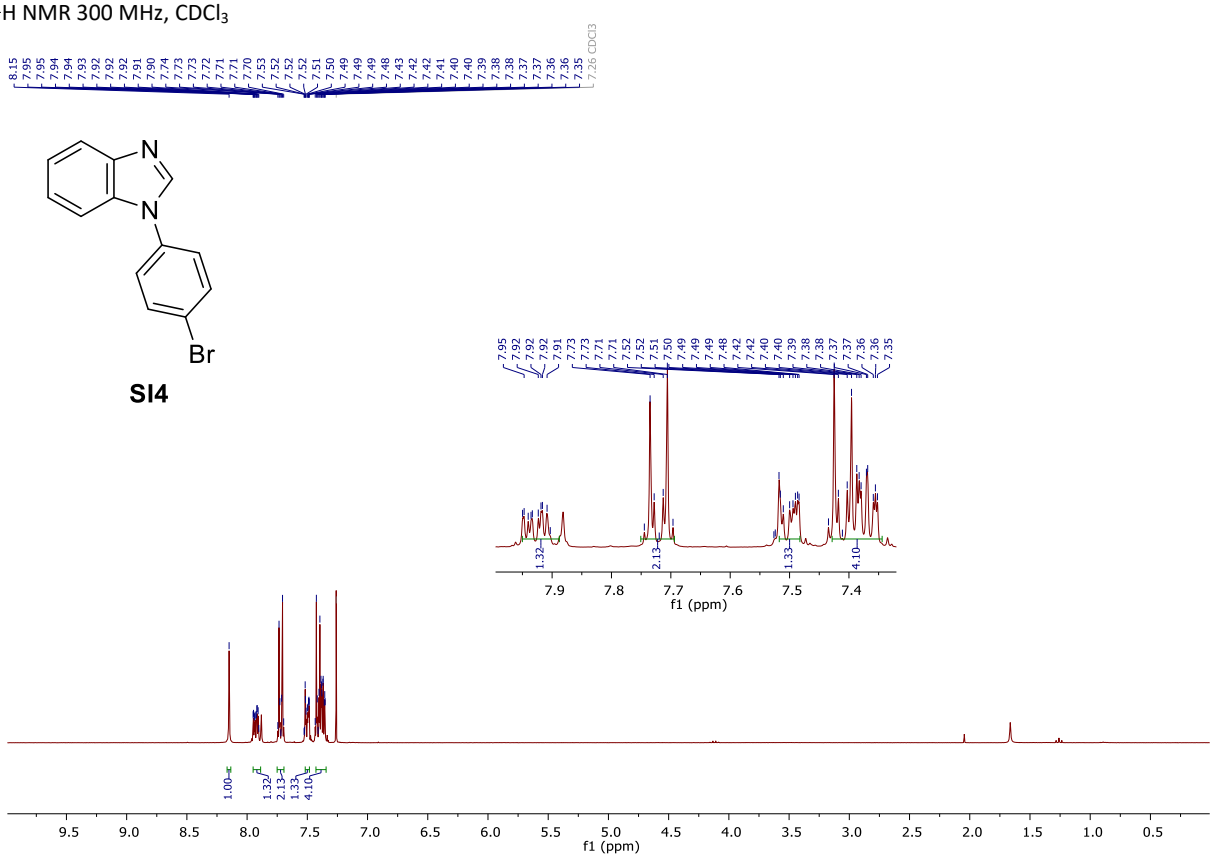
^{1}H NMR 300 MHz, $CDCl_3$



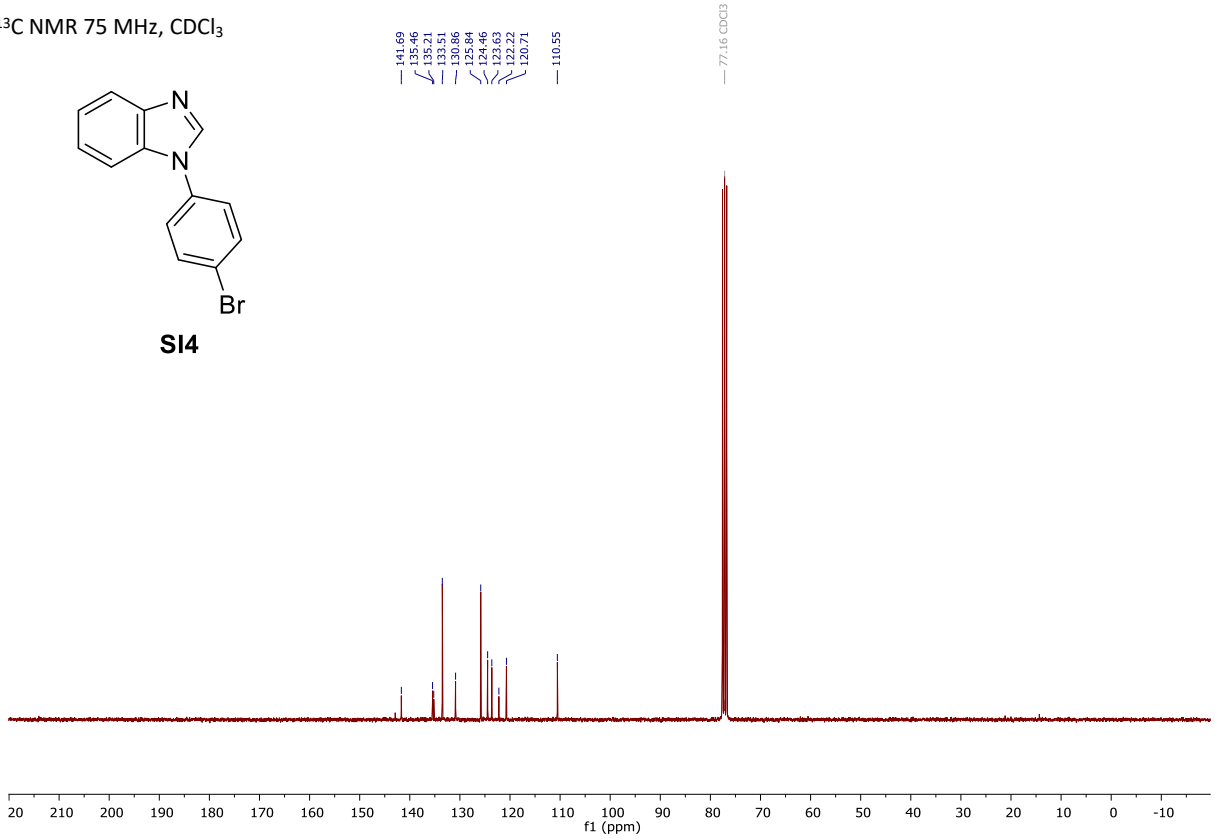
^{13}C NMR 75 MHz, $CDCl_3$



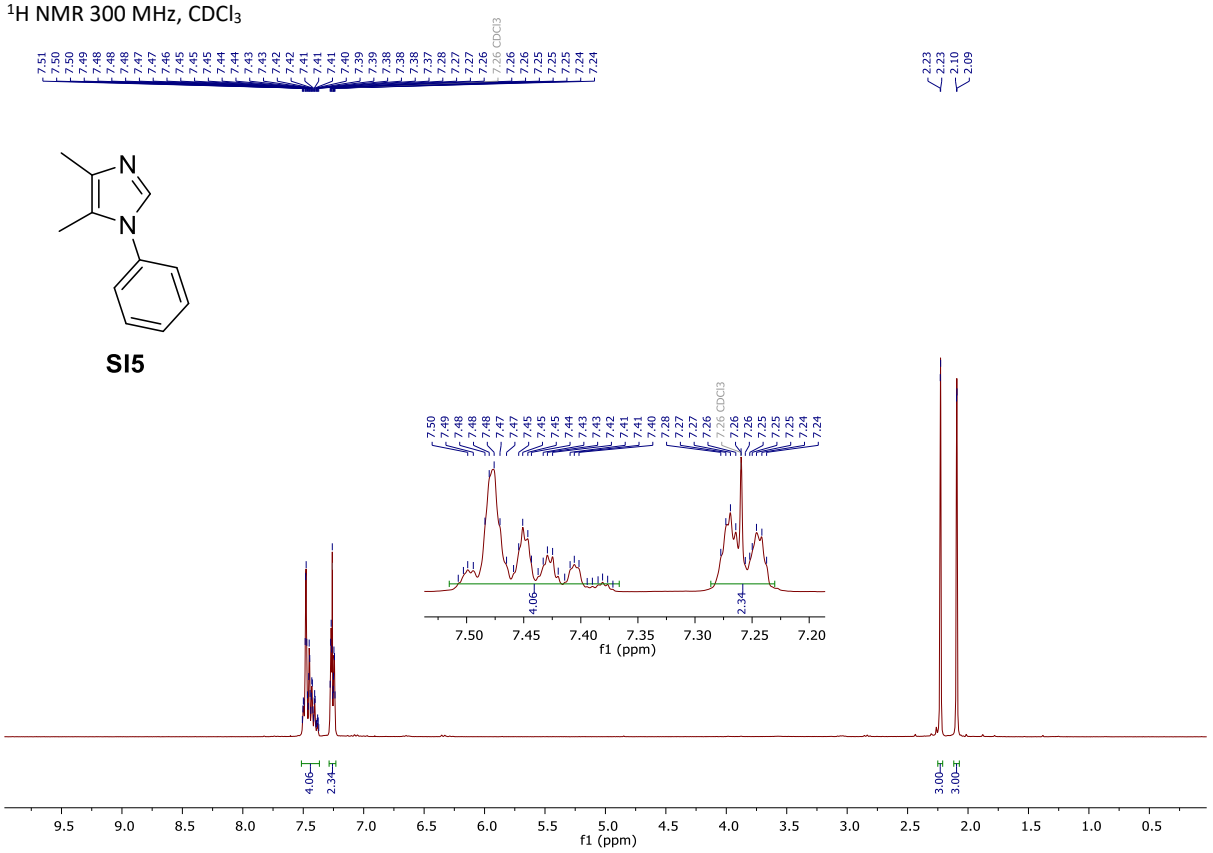
^{1}H NMR 300 MHz, $CDCl_3$



^{13}C NMR 75 MHz, $CDCl_3$

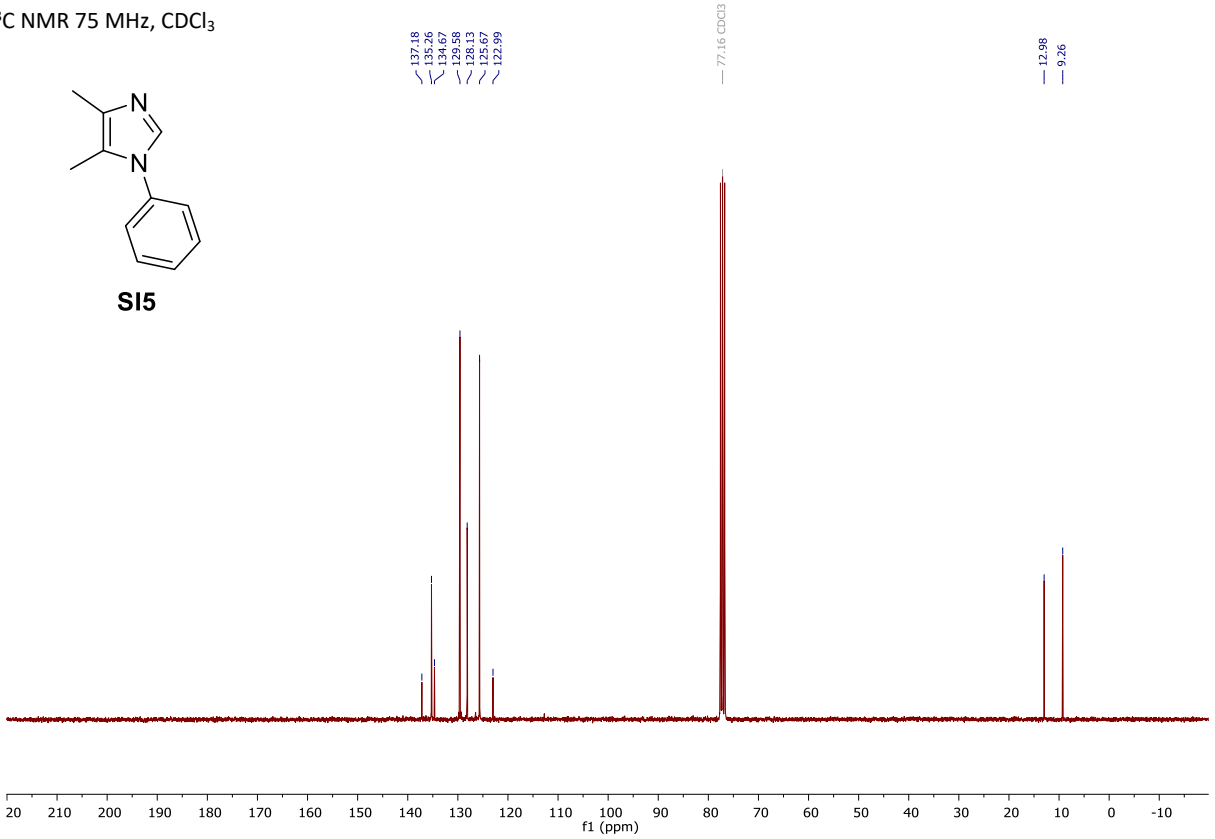


^{1}H NMR 300 MHz, $CDCl_3$



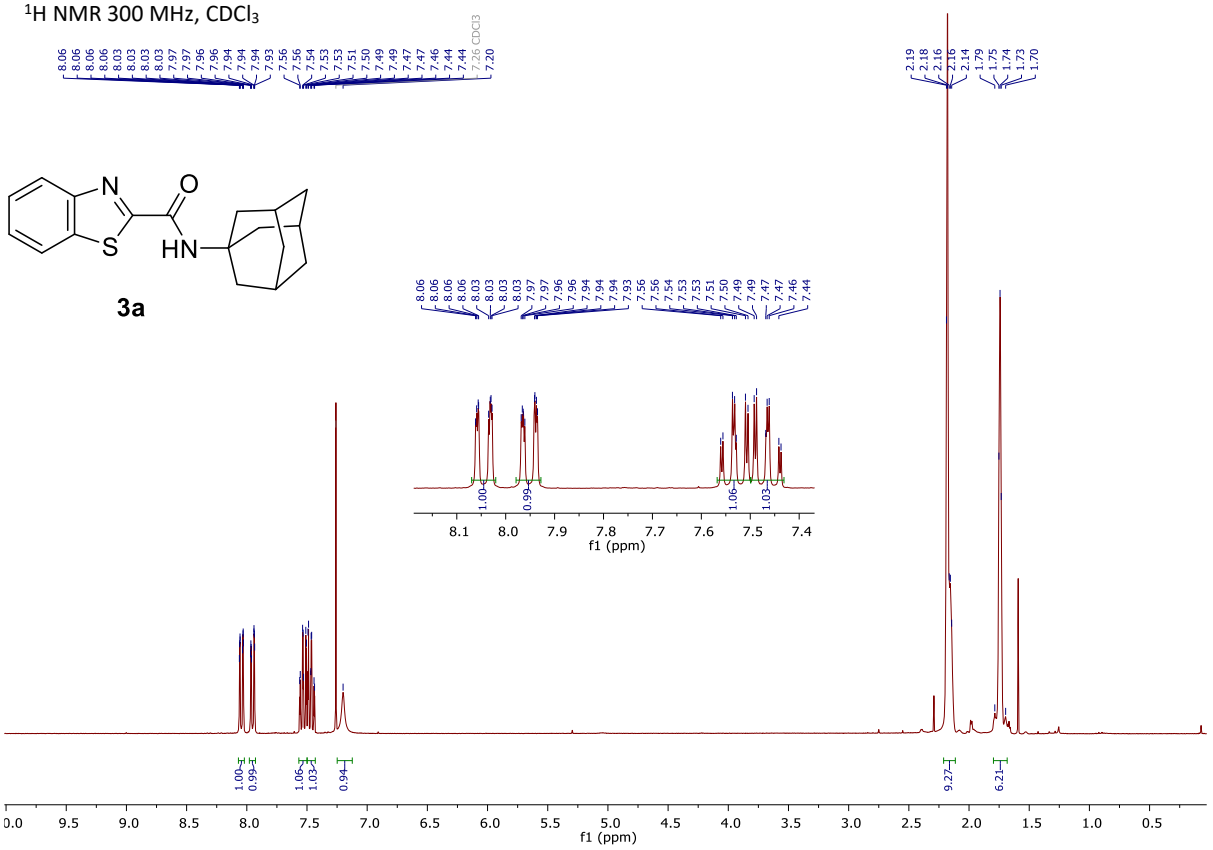
SI5

^{13}C NMR 75 MHz, $CDCl_3$

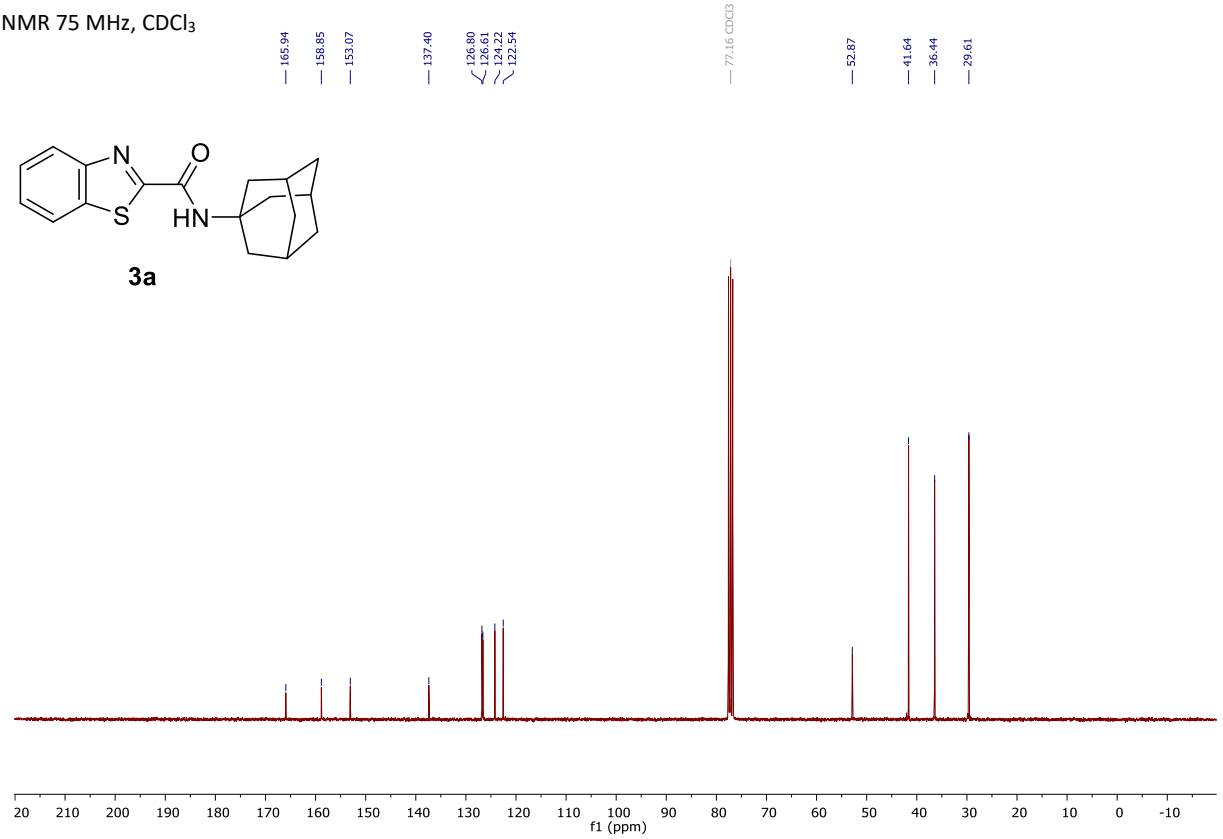


SI5

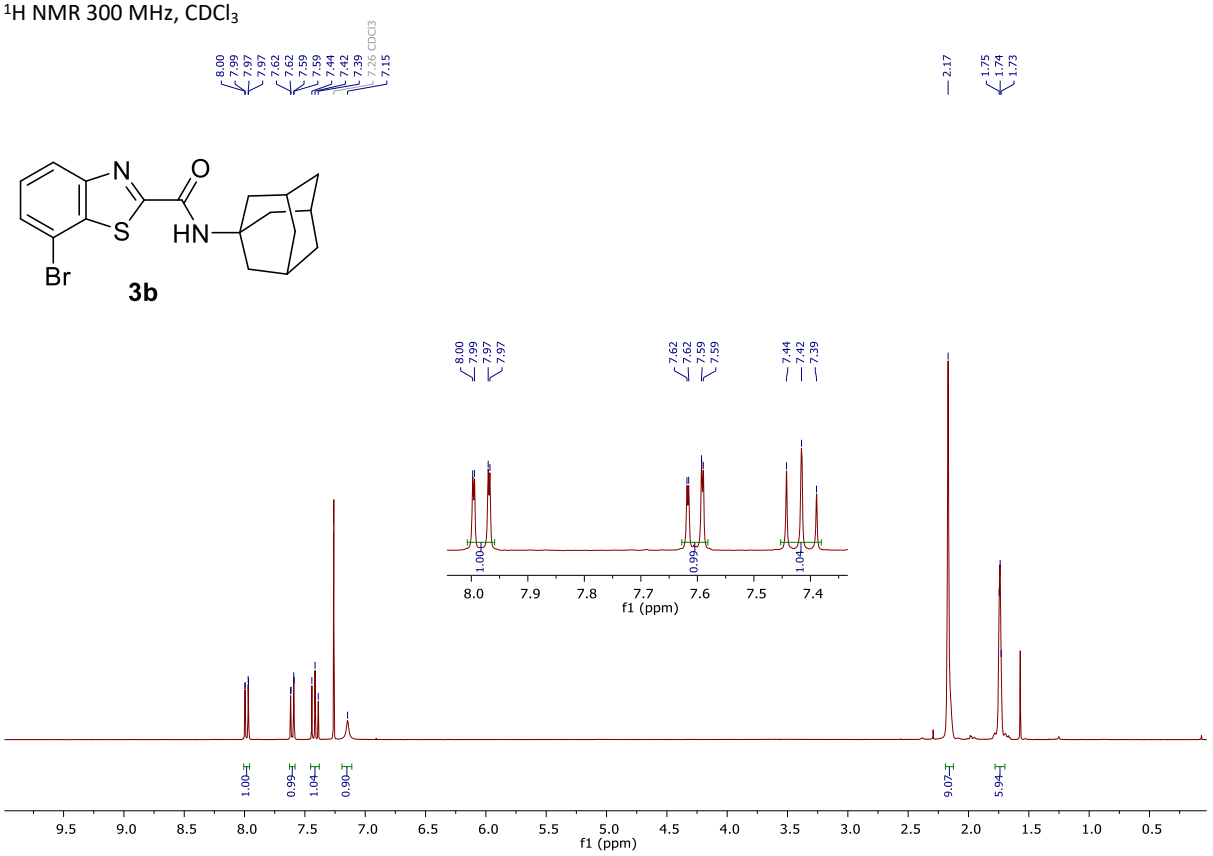
^{1}H NMR 300 MHz, $CDCl_3$



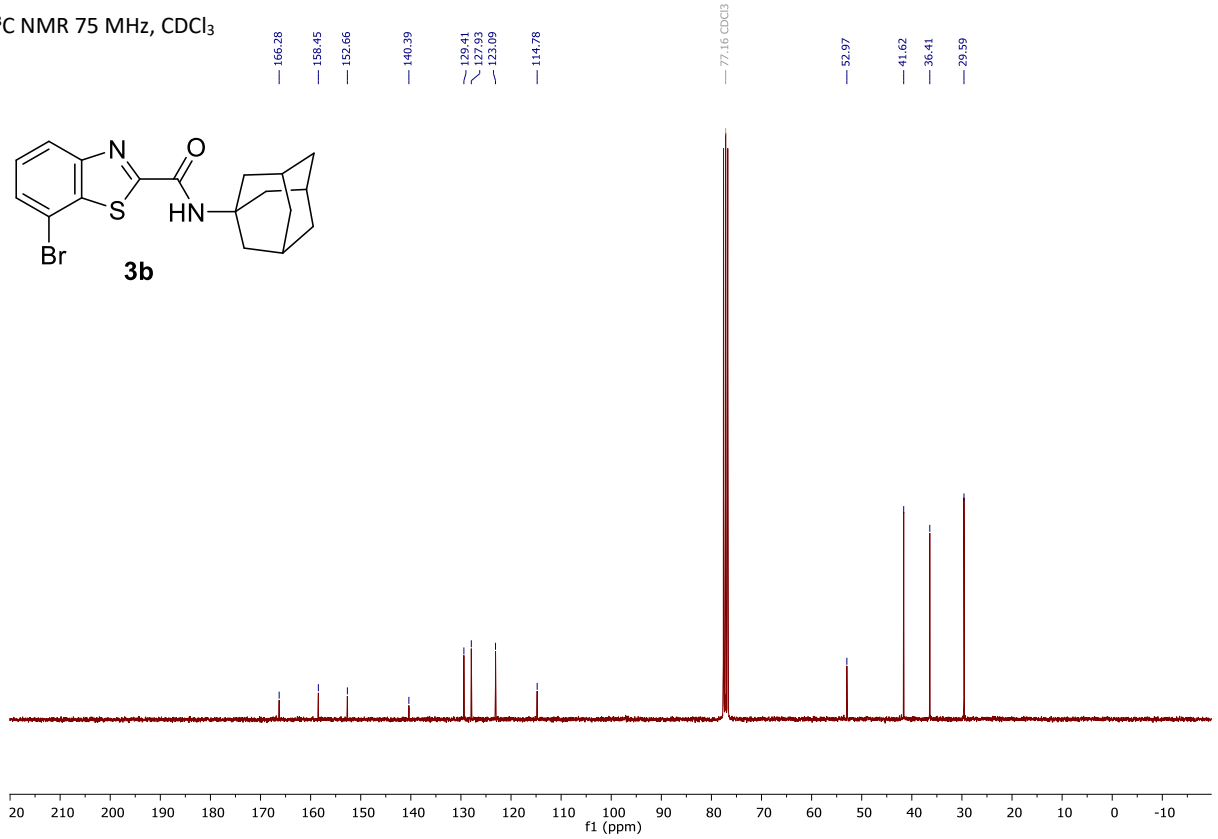
^{13}C NMR 75 MHz, $CDCl_3$



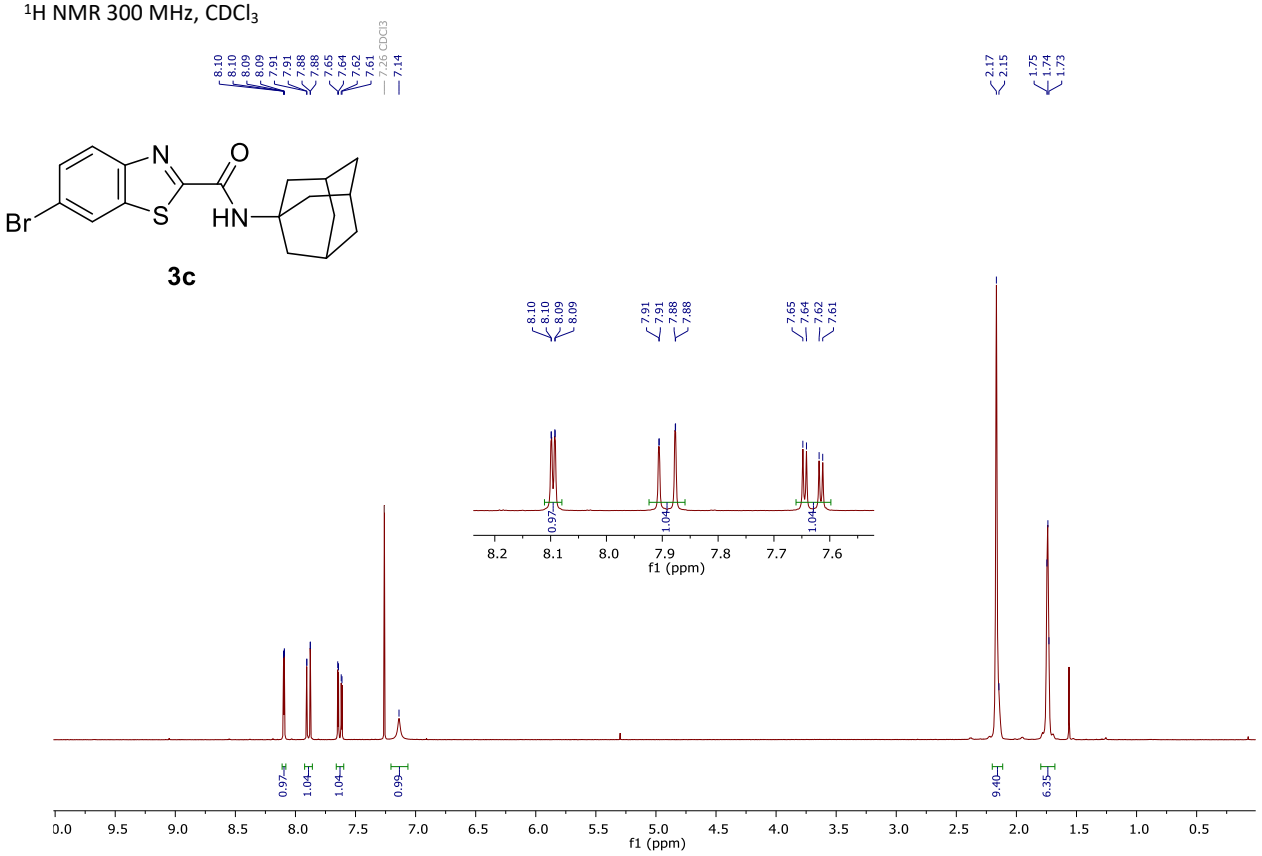
^{1}H NMR 300 MHz, $CDCl_3$



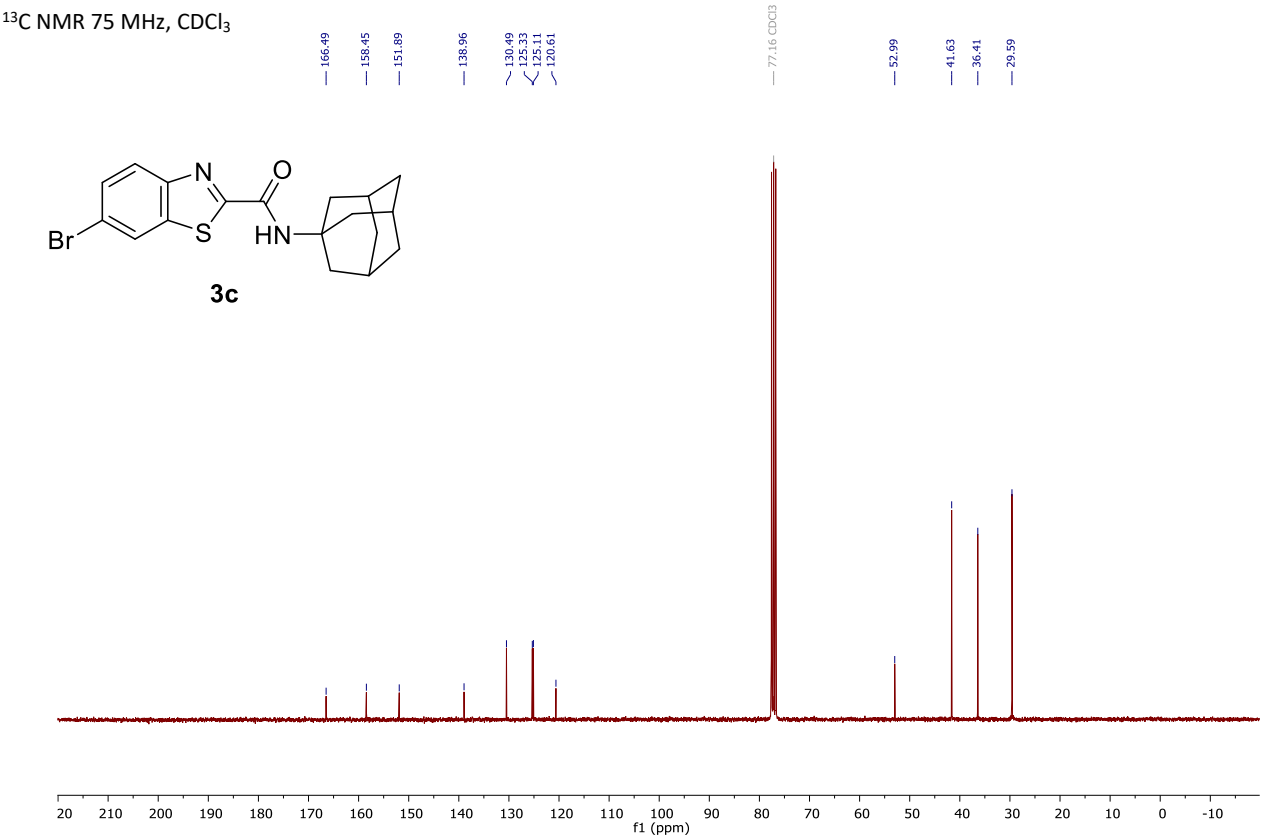
^{13}C NMR 75 MHz, $CDCl_3$



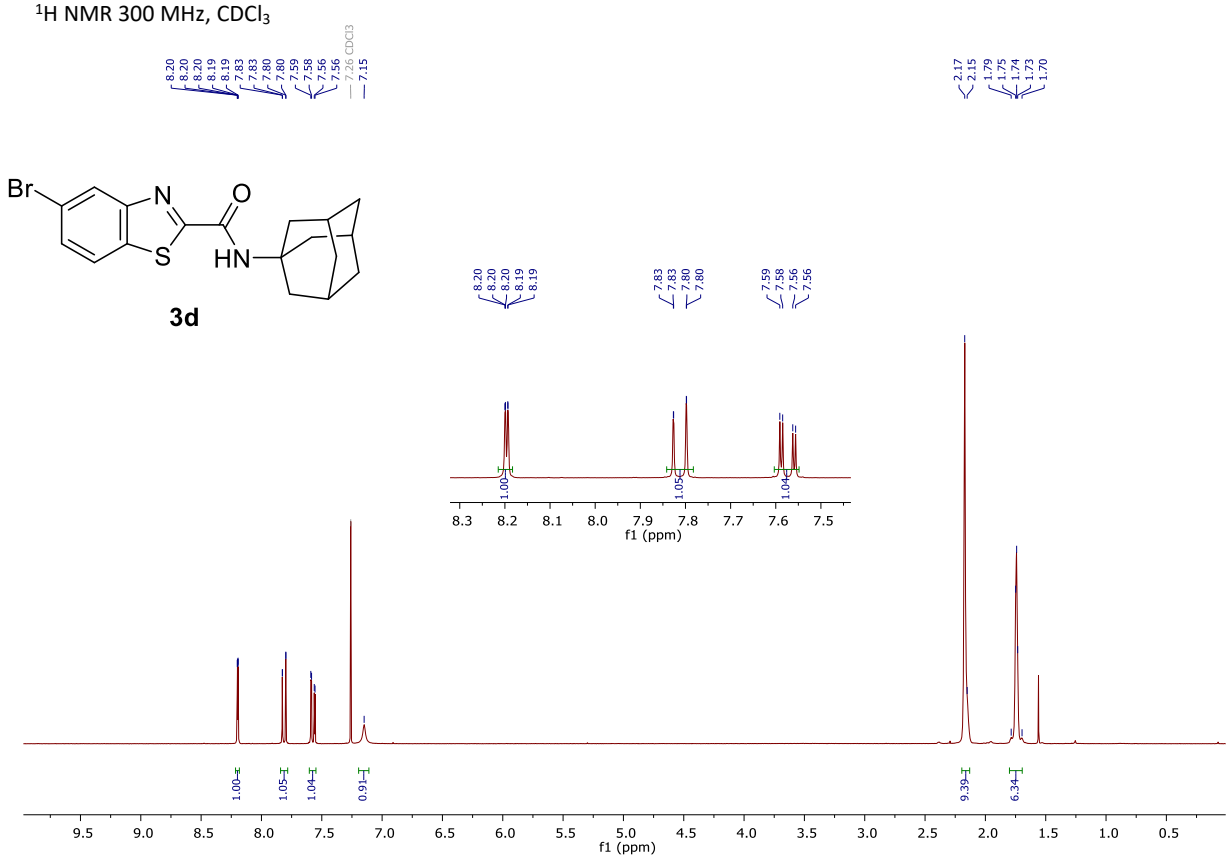
^{1}H NMR 300 MHz, $CDCl_3$



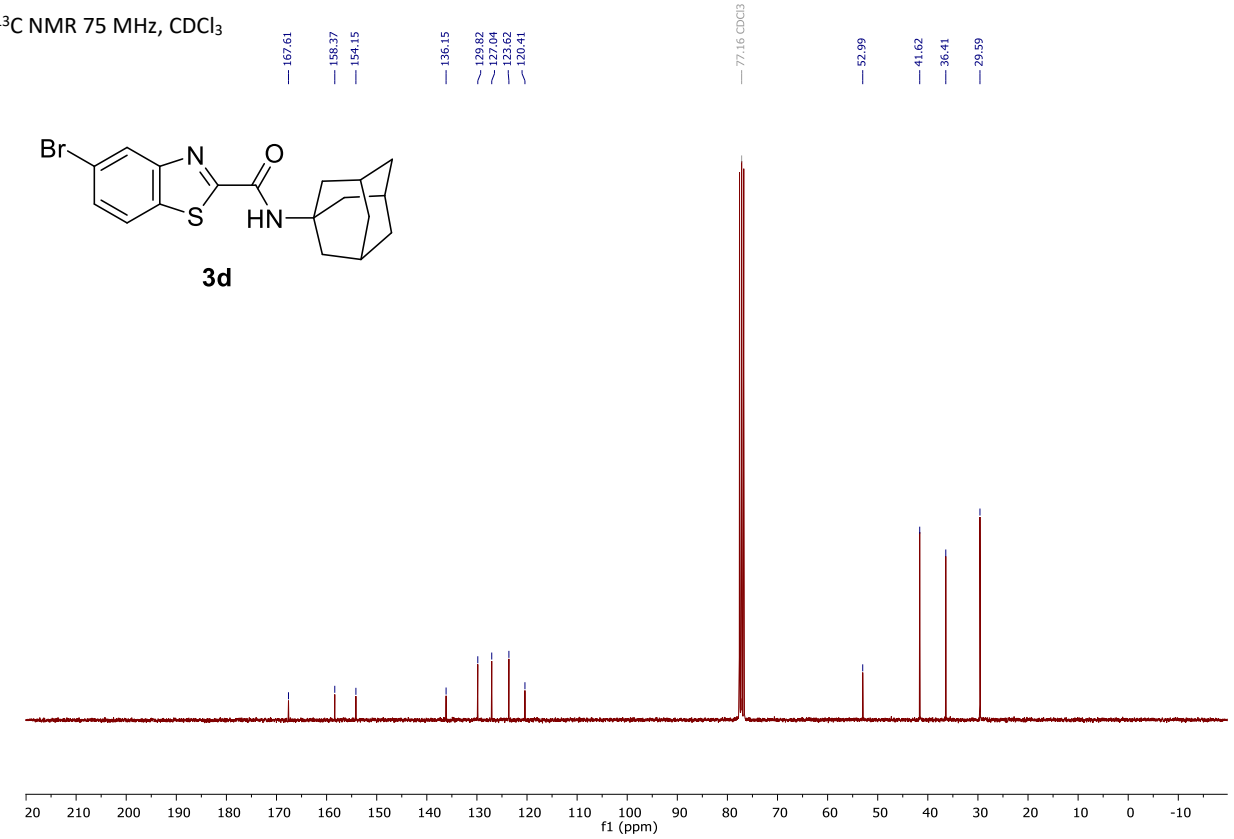
^{13}C NMR 75 MHz, $CDCl_3$



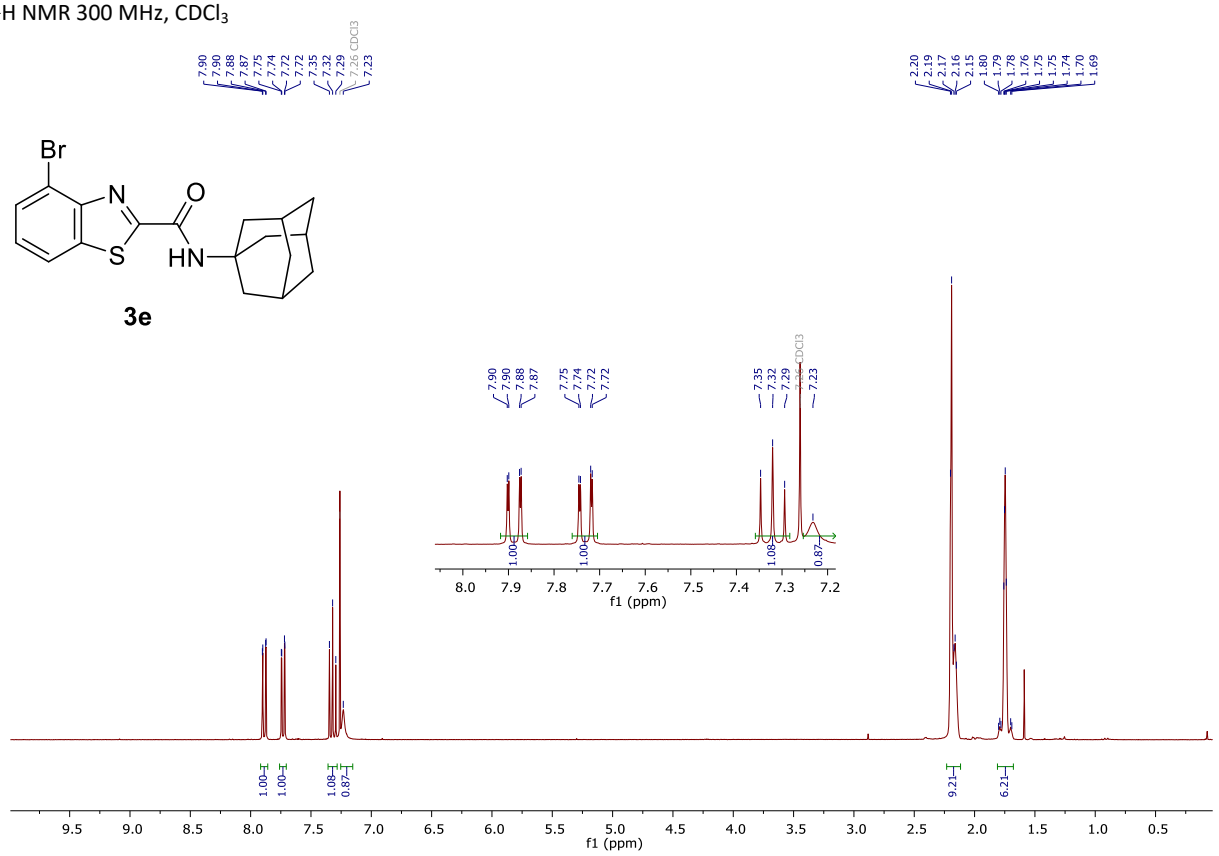
^{1}H NMR 300 MHz, $CDCl_3$



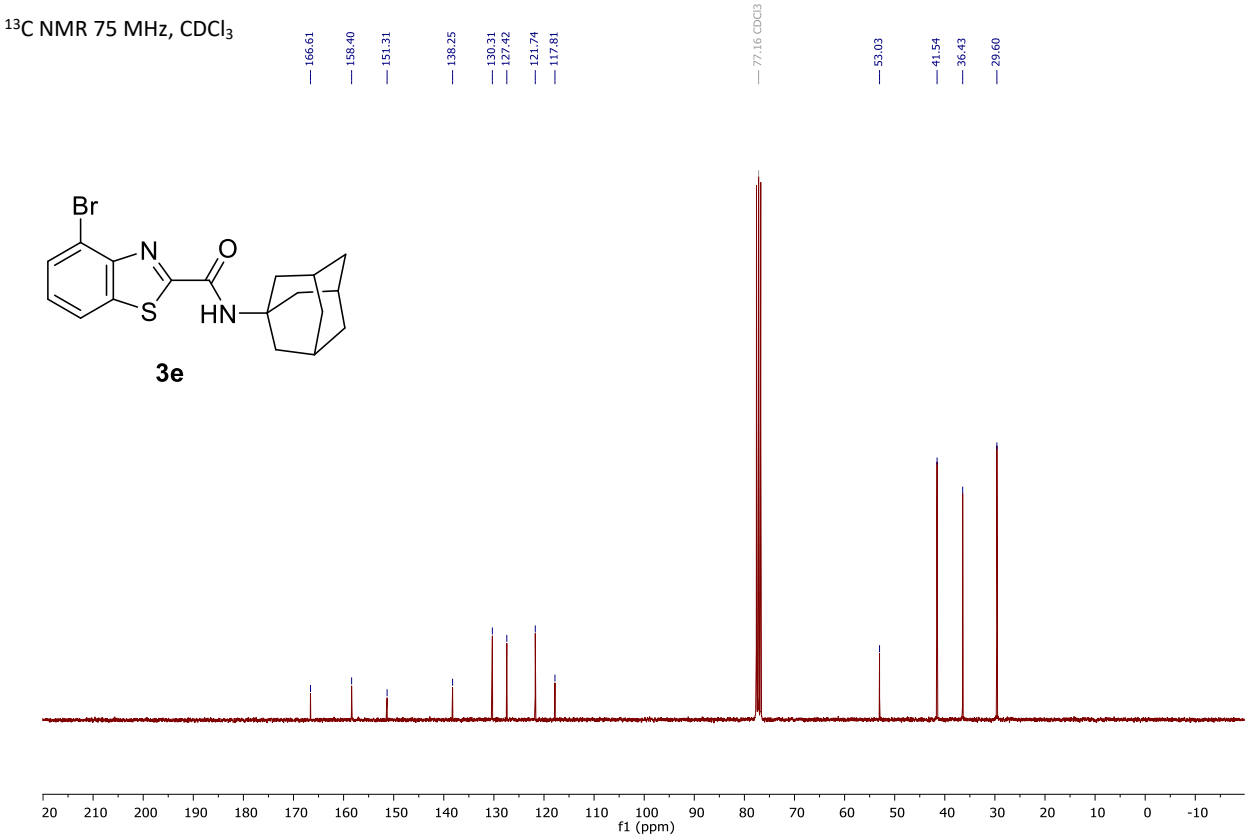
^{13}C NMR 75 MHz, $CDCl_3$



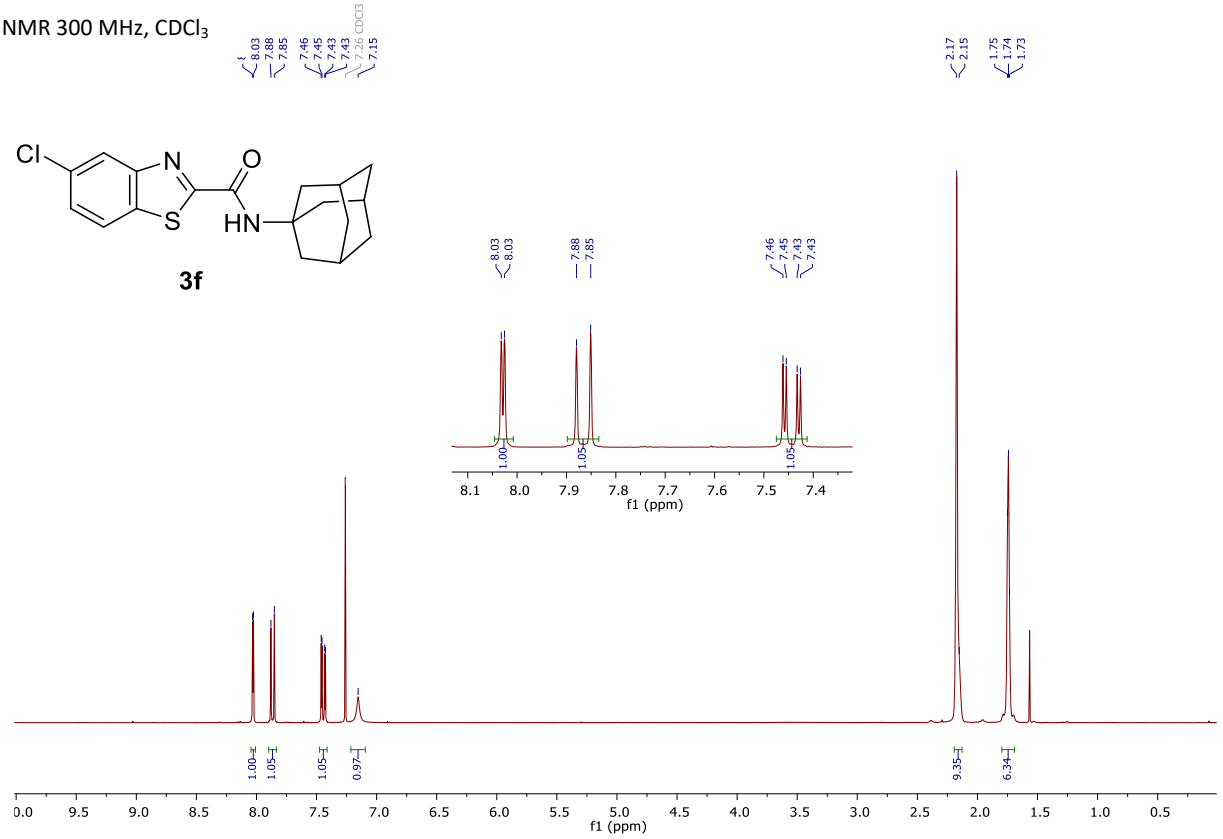
^{1}H NMR 300 MHz, $CDCl_3$



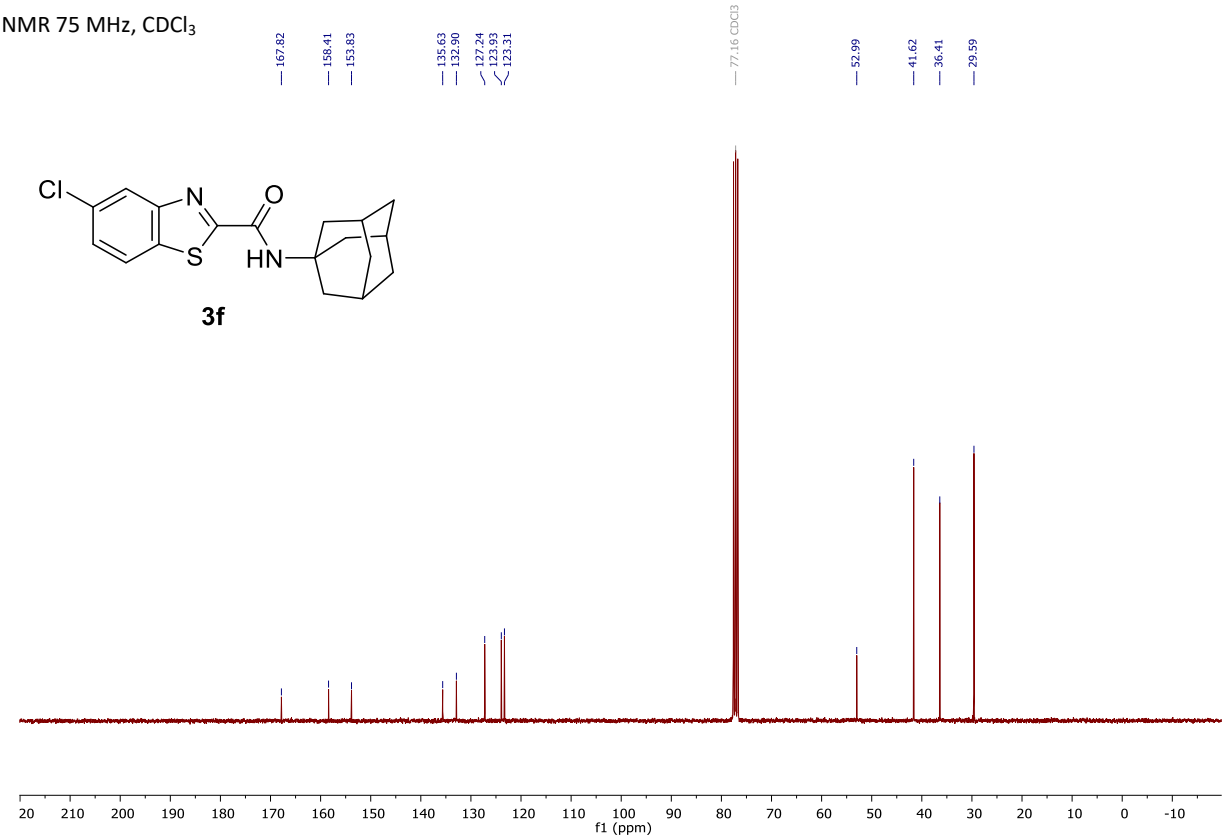
^{13}C NMR 75 MHz, $CDCl_3$



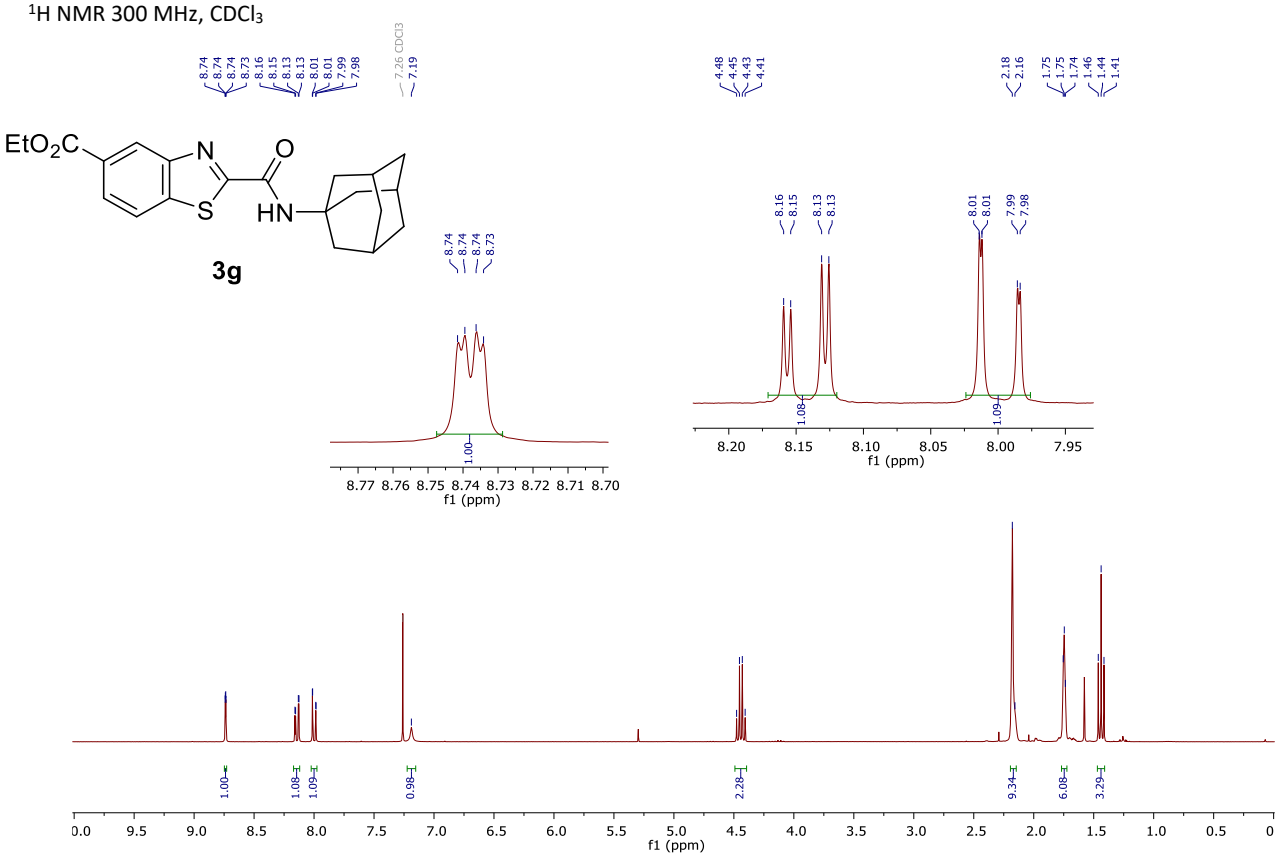
^{1}H NMR 300 MHz, $CDCl_3$



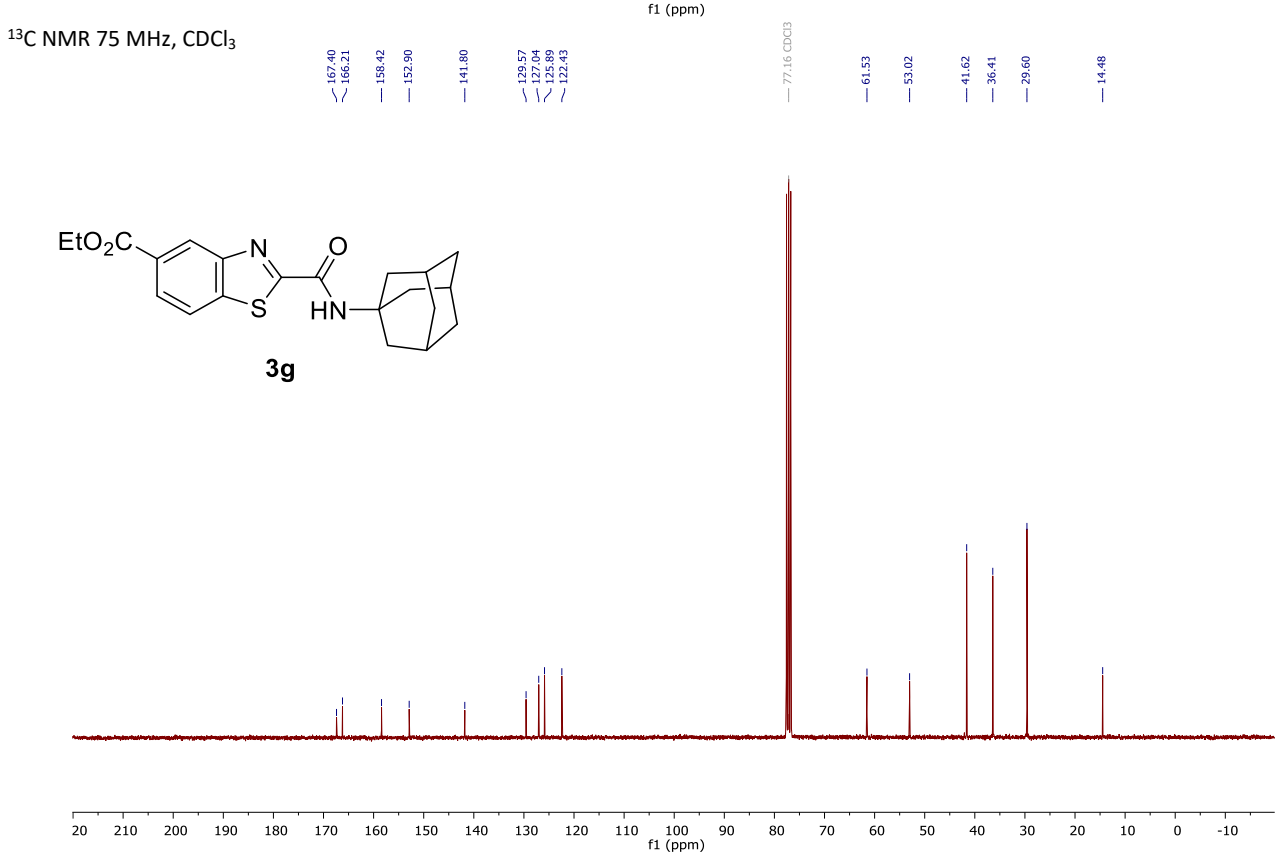
^{13}C NMR 75 MHz, $CDCl_3$



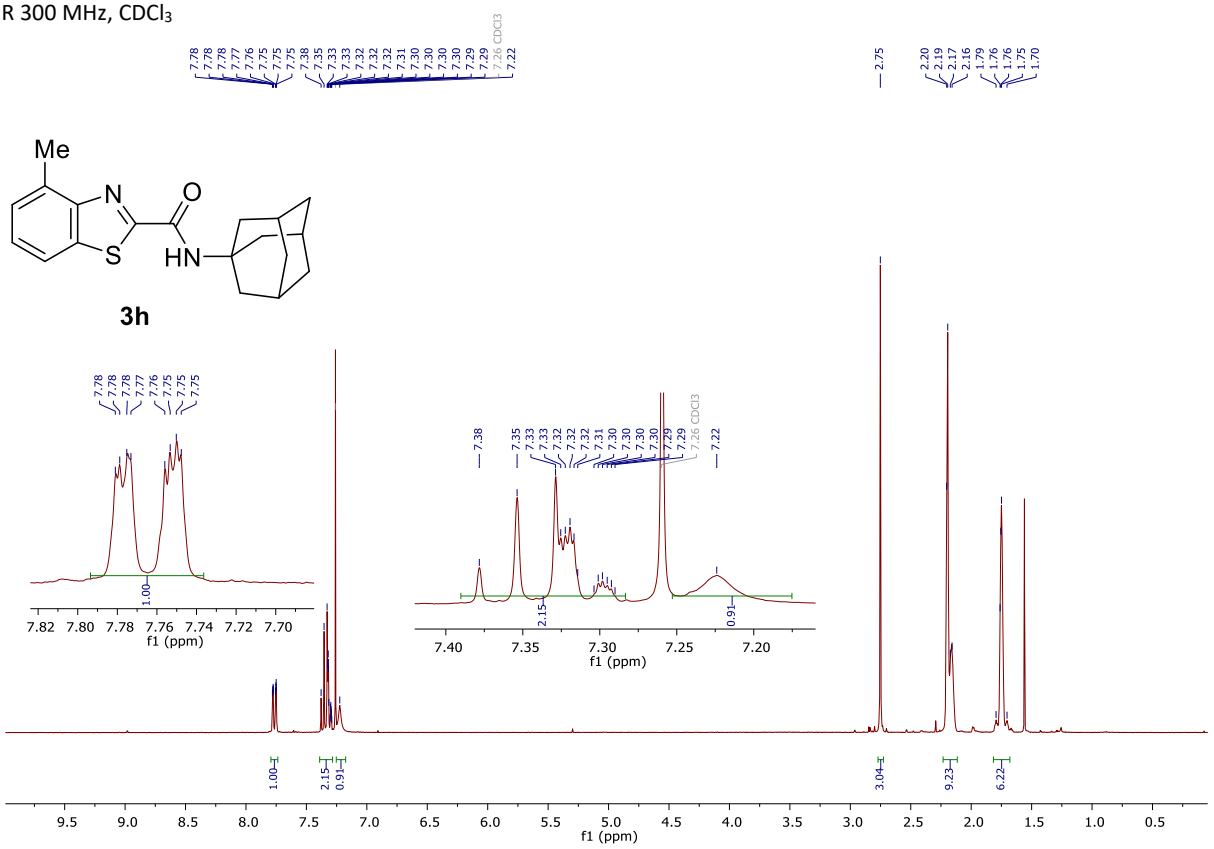
^{1}H NMR 300 MHz, $CDCl_3$



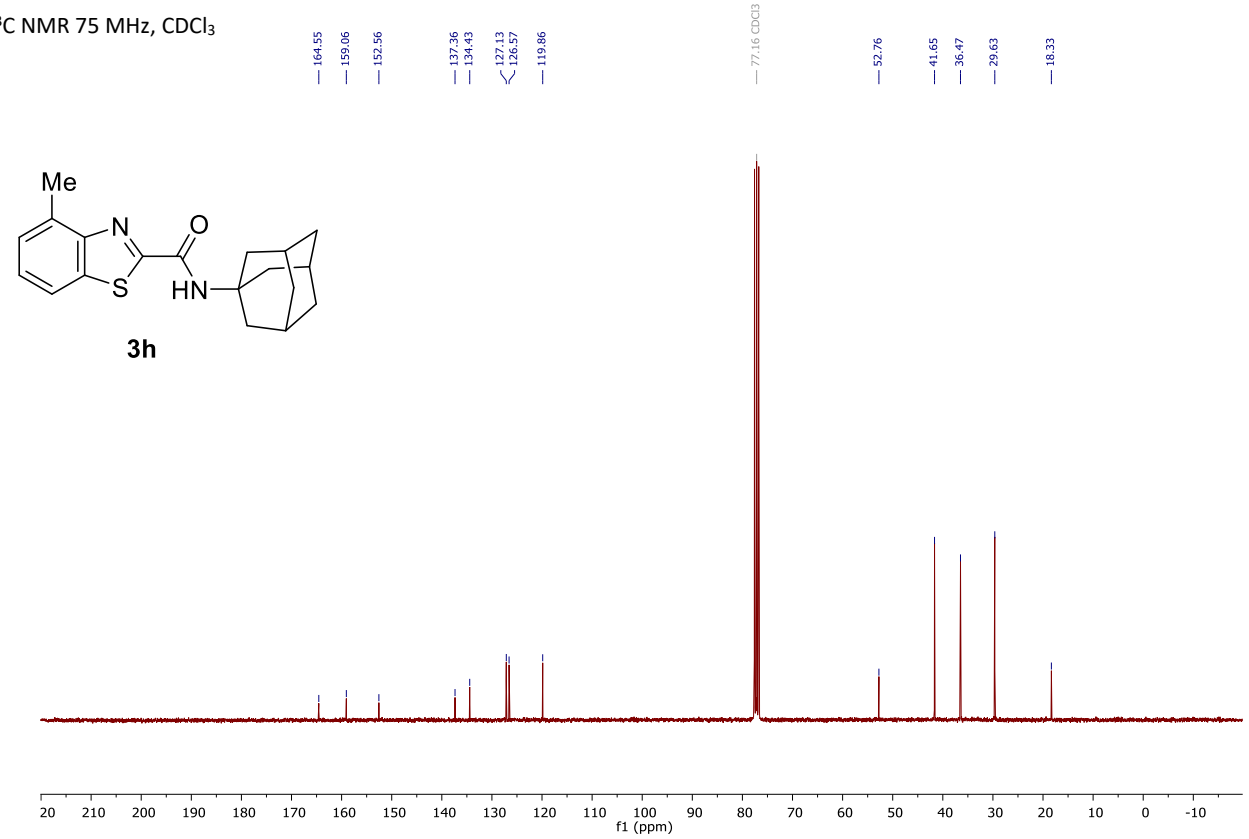
^{13}C NMR 75 MHz, $CDCl_3$



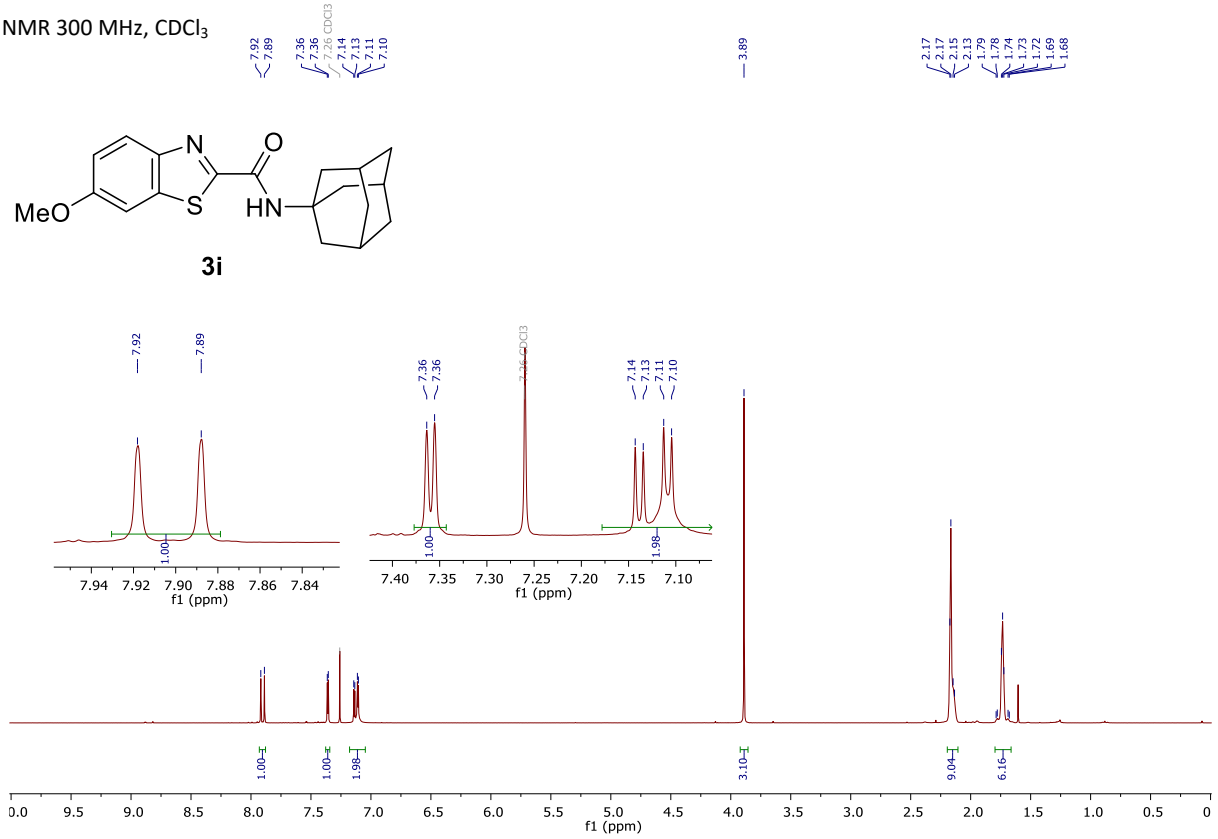
^{1}H NMR 300 MHz, $CDCl_3$



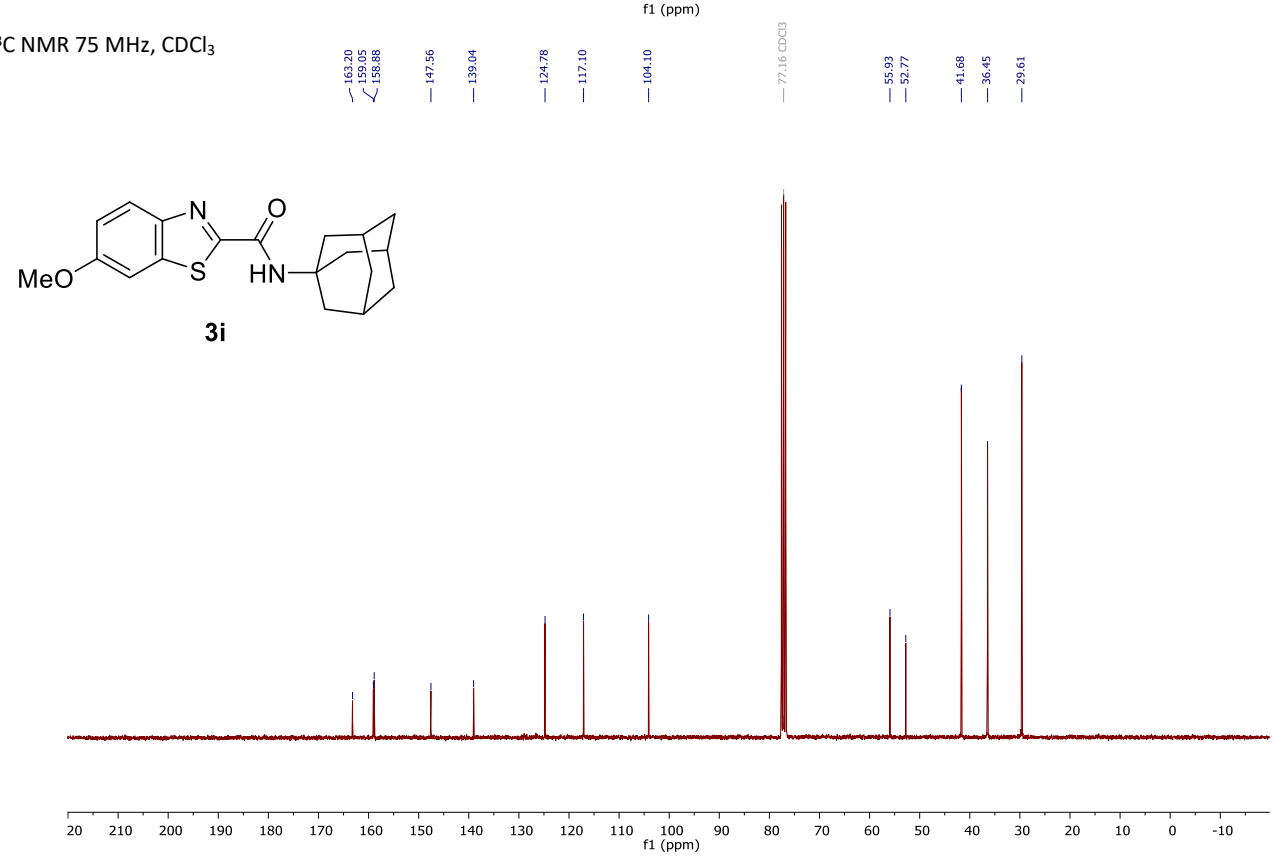
^{13}C NMR 75 MHz, $CDCl_3$



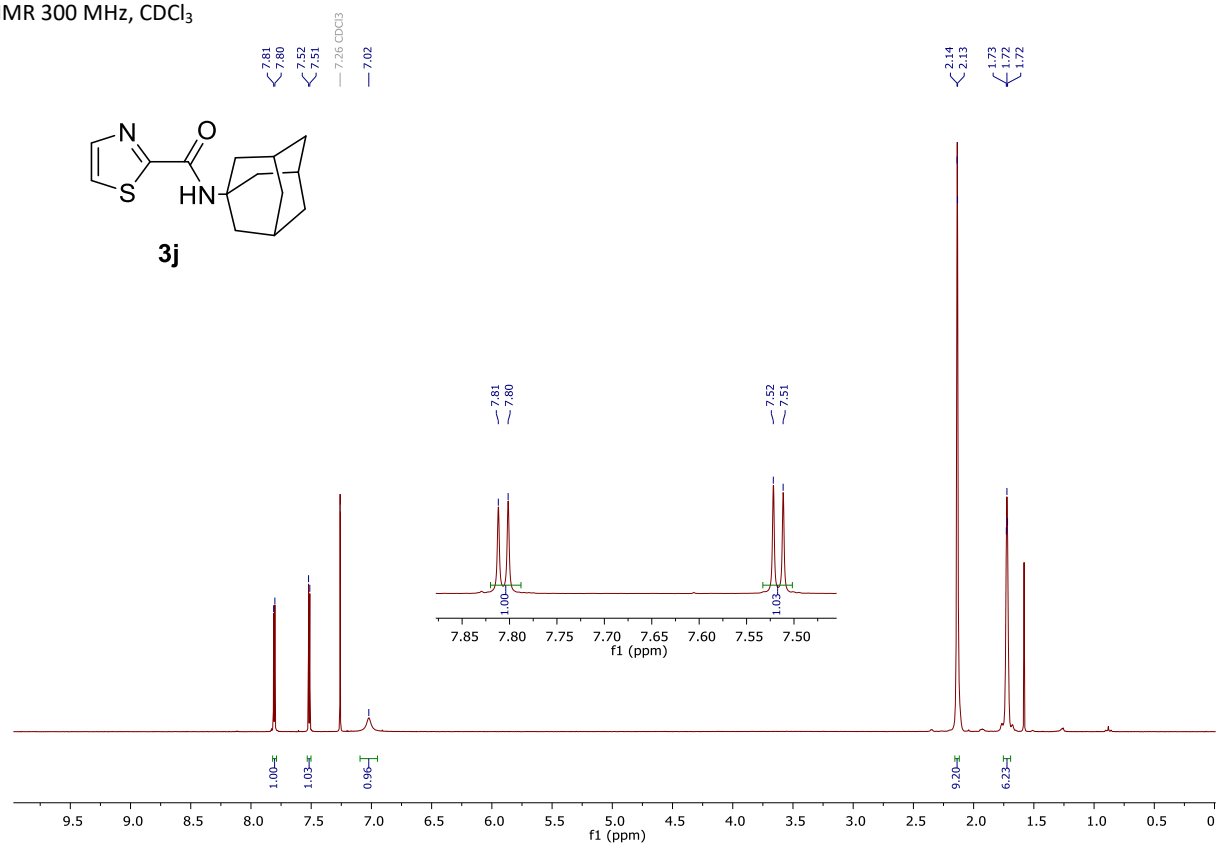
^{1}H NMR 300 MHz, $CDCl_3$



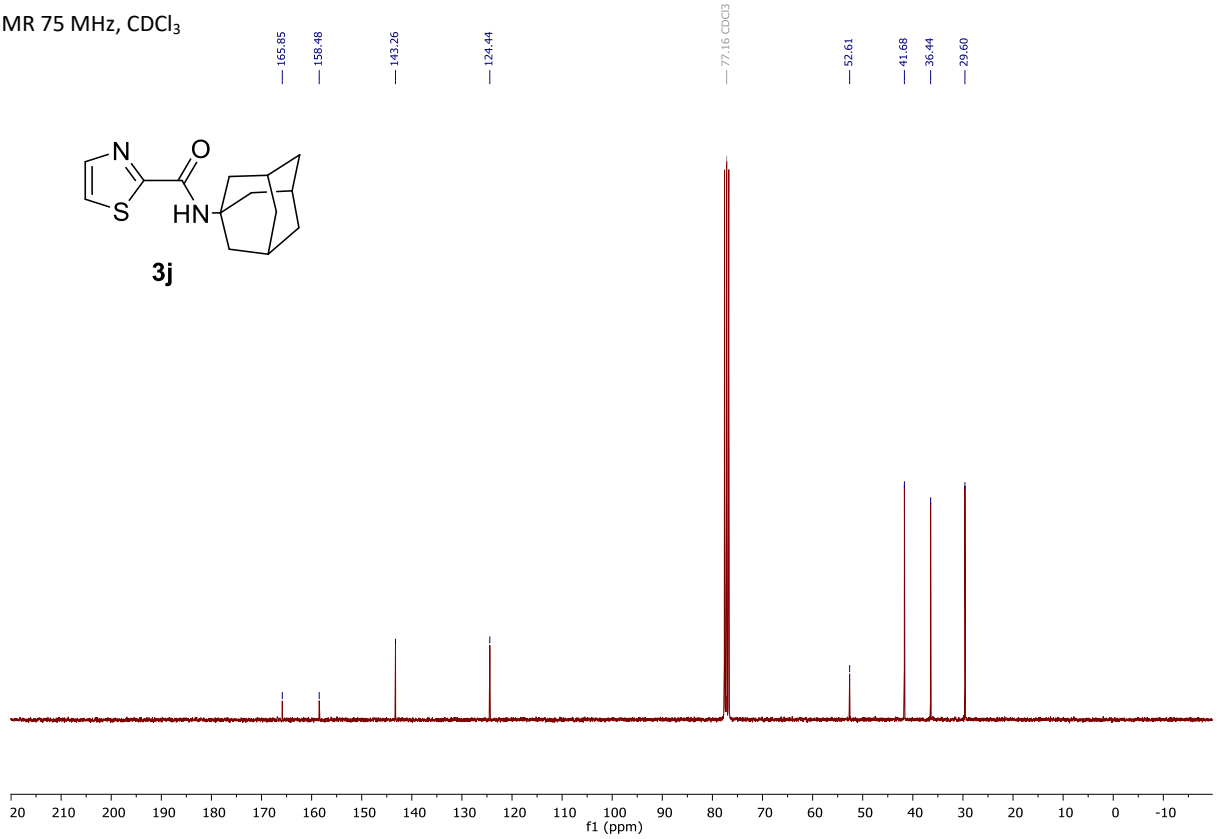
^{13}C NMR 75 MHz, $CDCl_3$



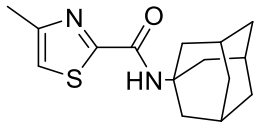
^{1}H NMR 300 MHz, $CDCl_3$



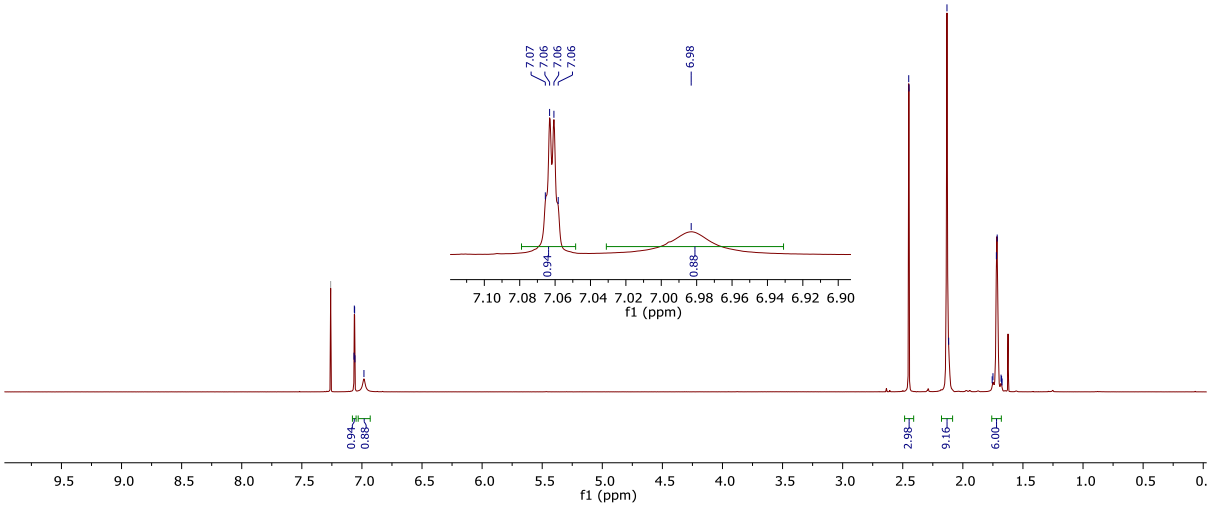
^{13}C NMR 75 MHz, $CDCl_3$



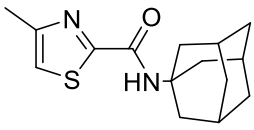
^{1}H NMR 400 MHz, $CDCl_3$



3k

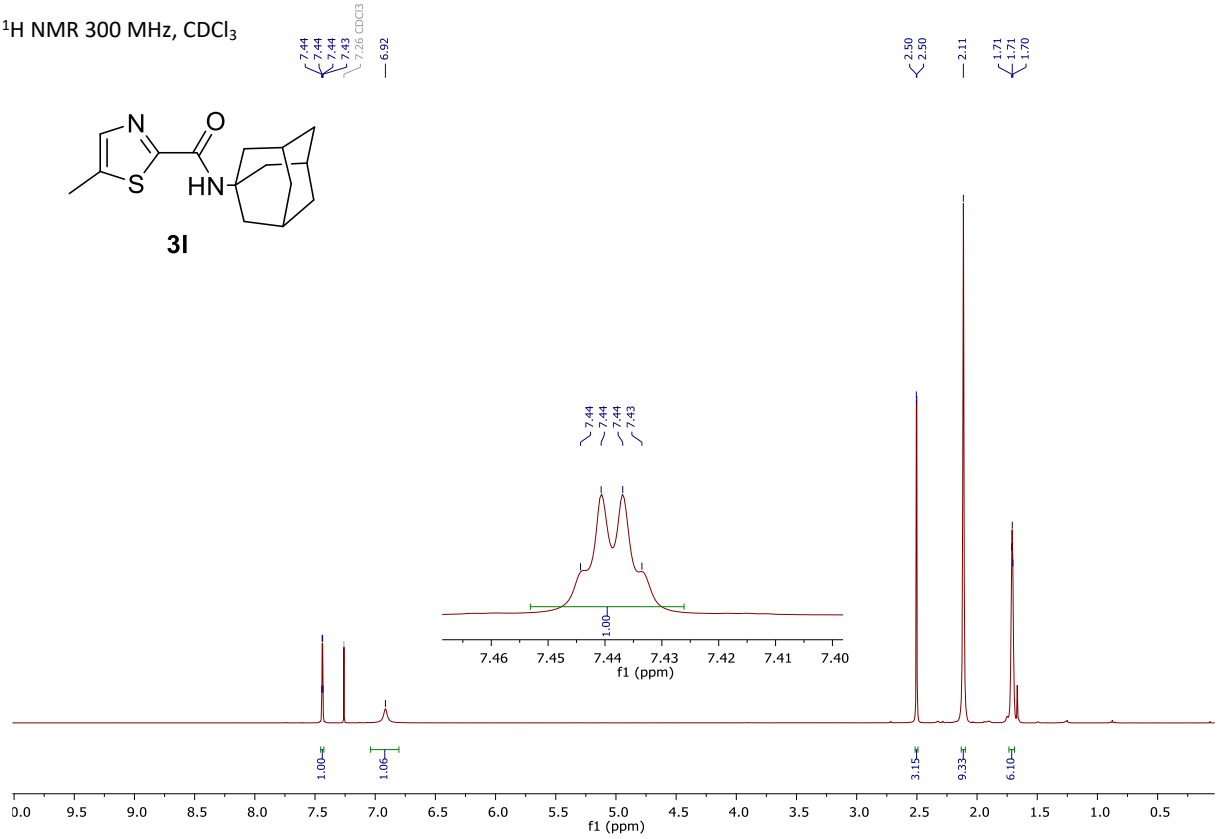


^{13}C NMR 101 MHz, $CDCl_3$

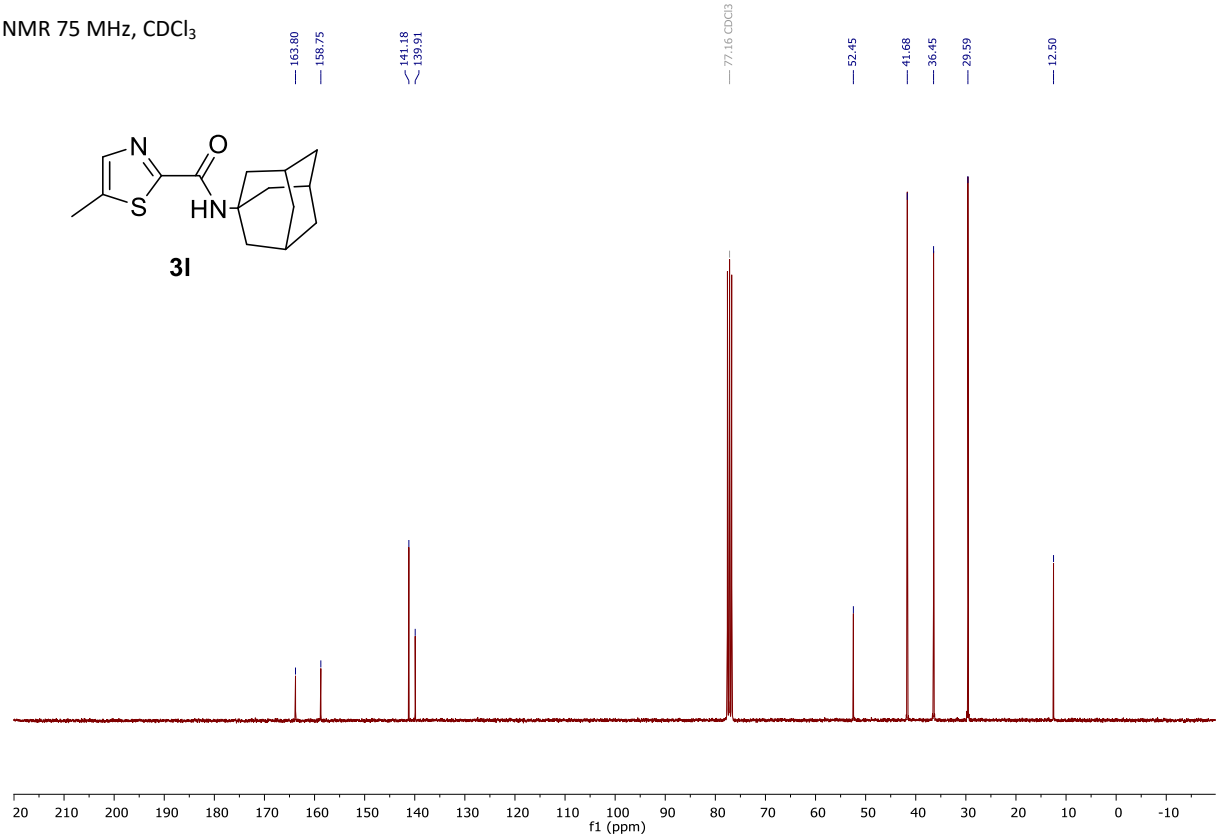


3k

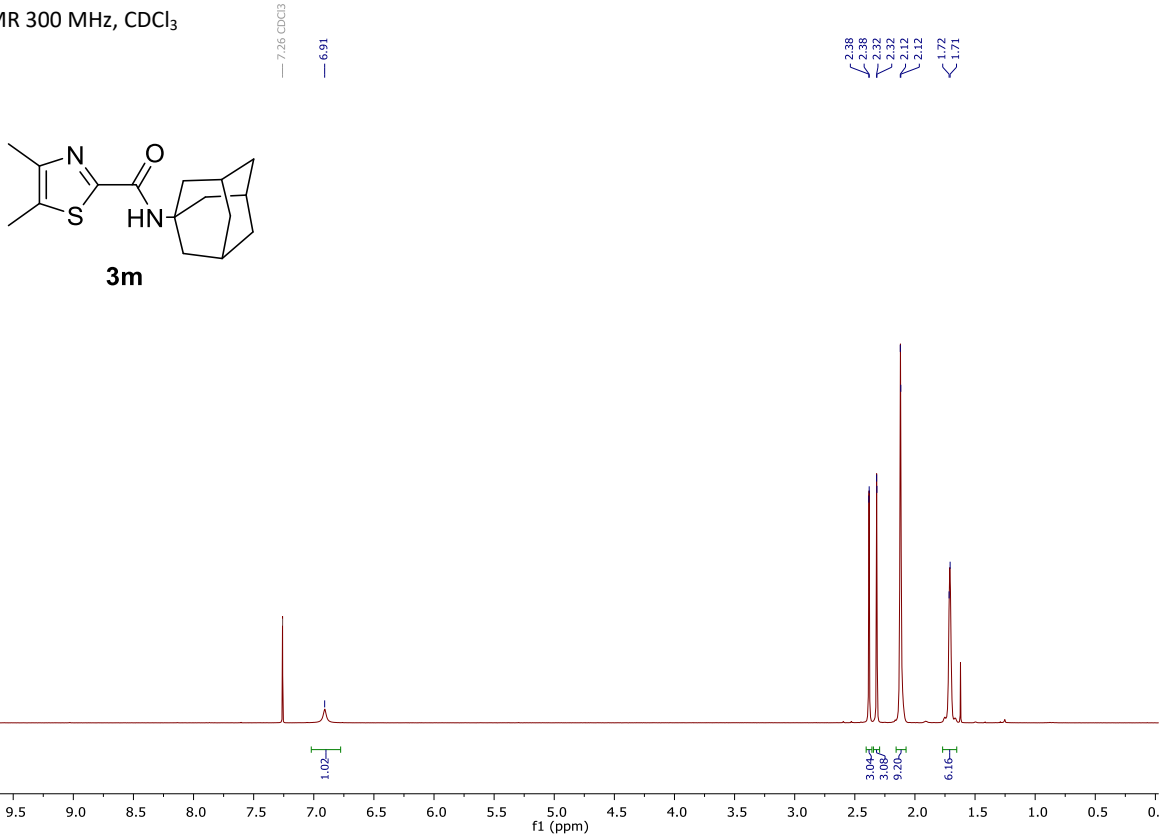
^{1}H NMR 300 MHz, $CDCl_3$



^{13}C NMR 75 MHz, $CDCl_3$

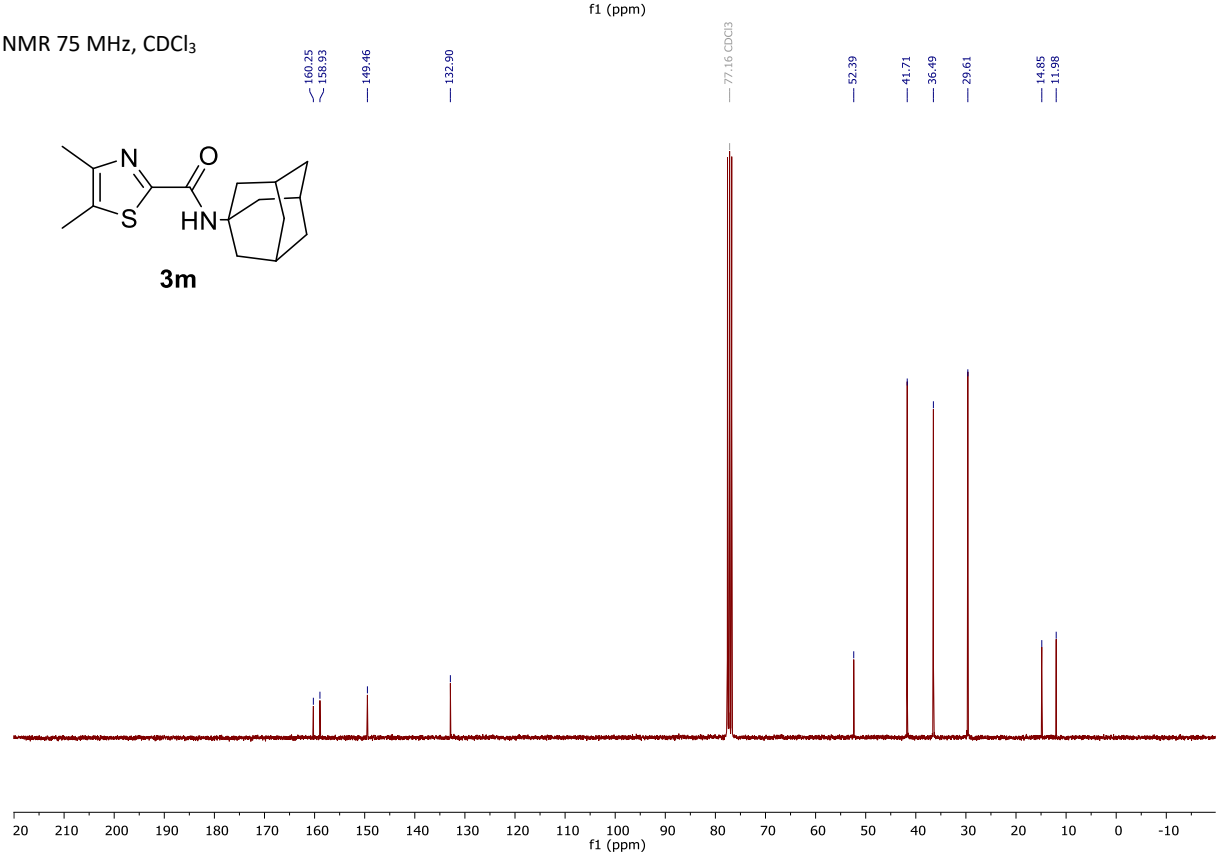


^{1}H NMR 300 MHz, $CDCl_3$



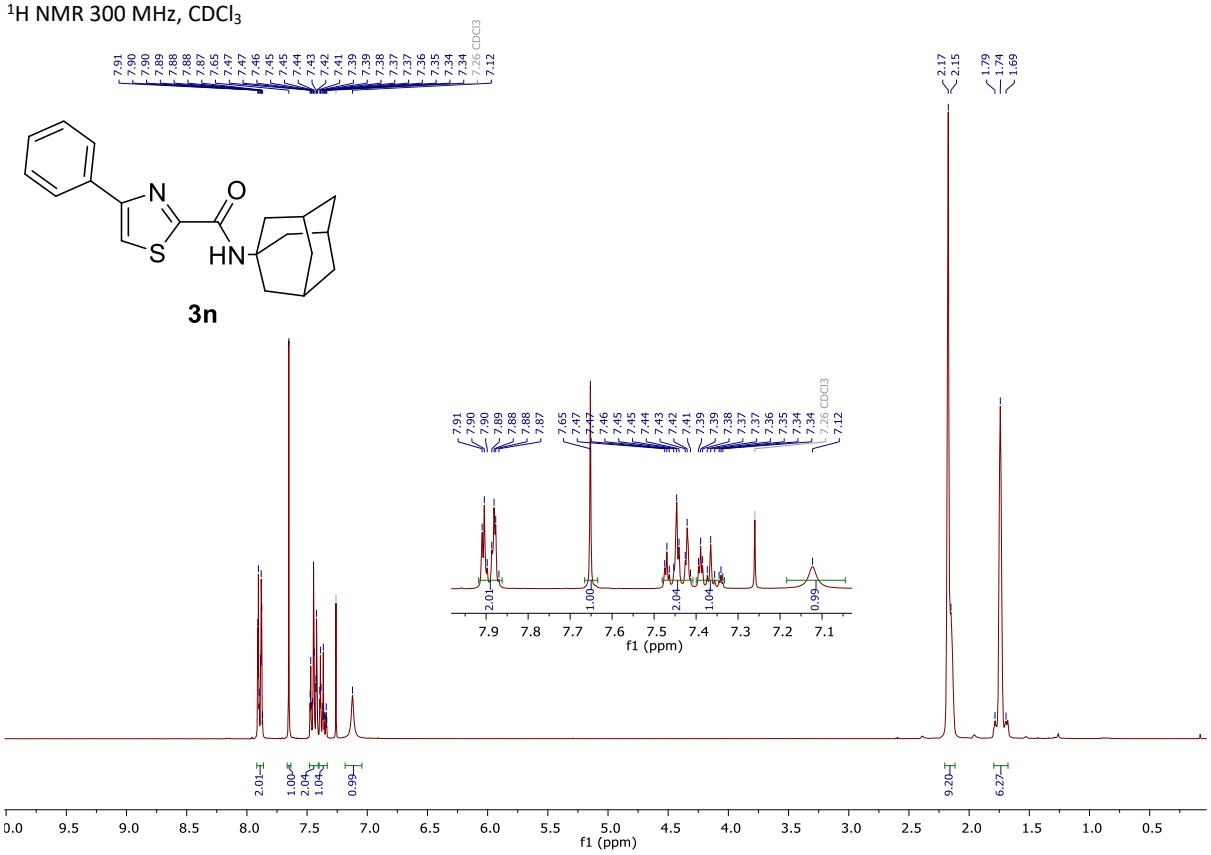
3m

^{13}C NMR 75 MHz, $CDCl_3$

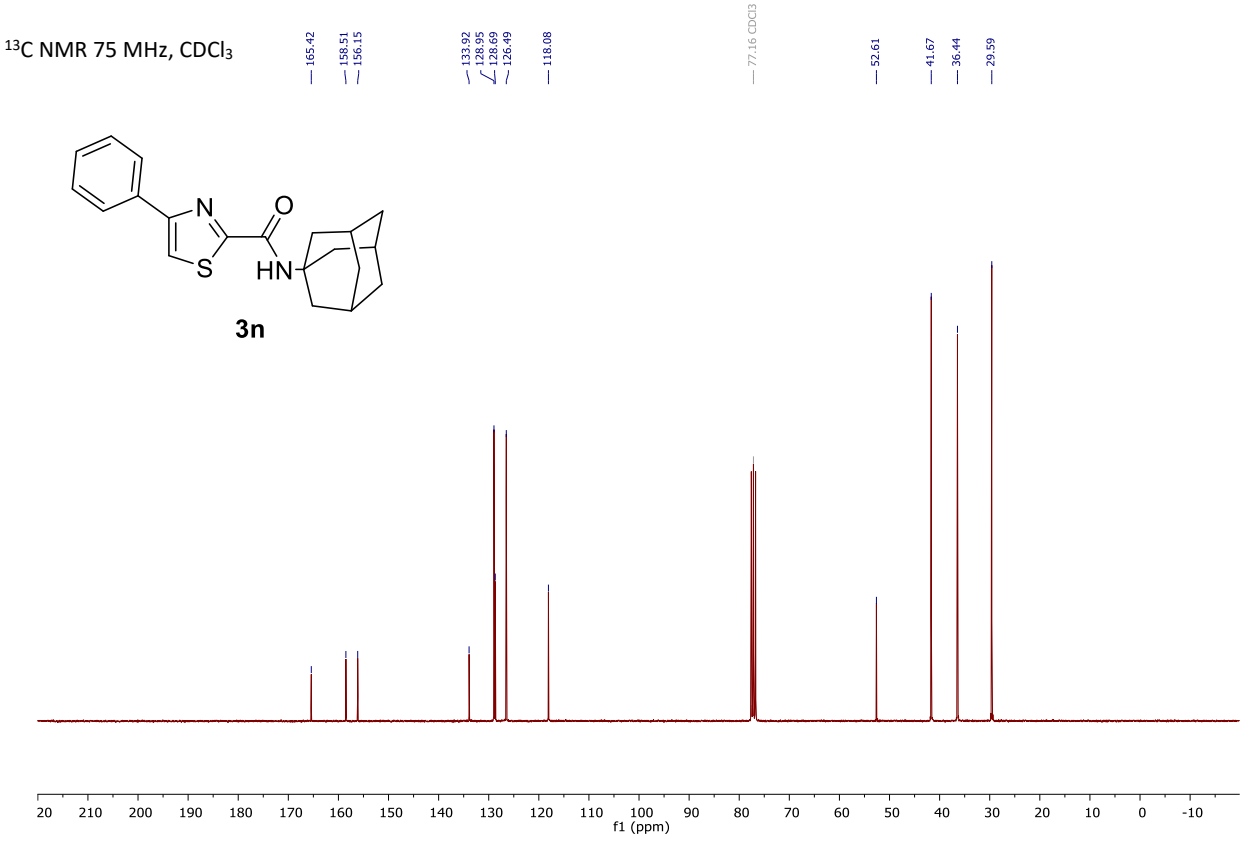


3m

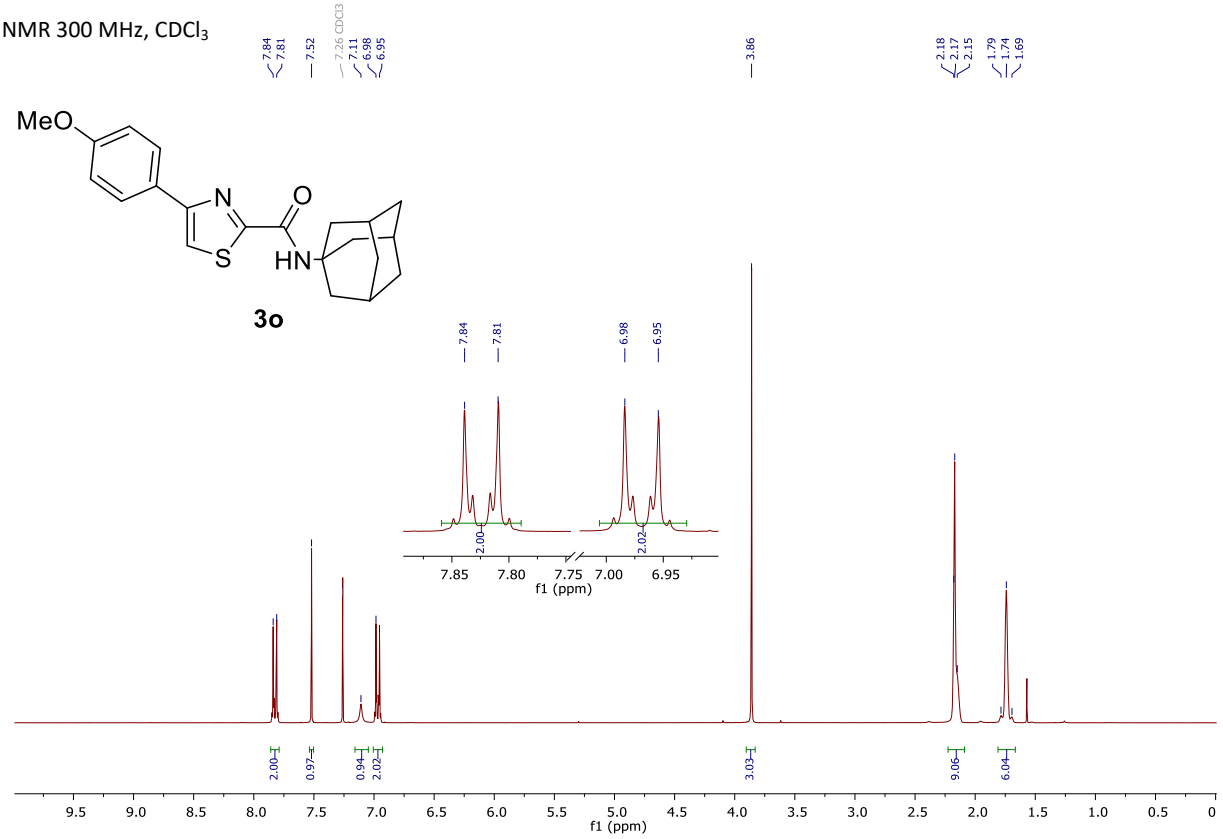
^{1}H NMR 300 MHz, $CDCl_3$



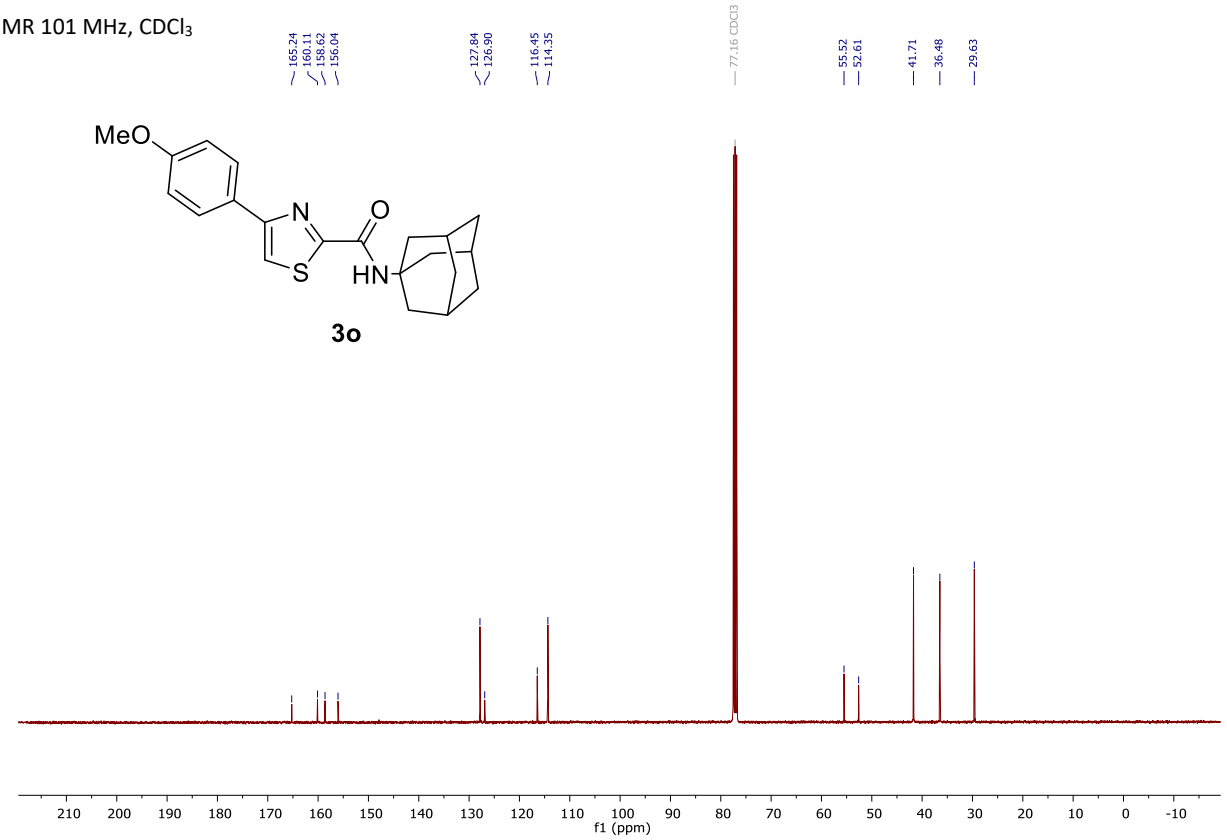
^{13}C NMR 75 MHz, $CDCl_3$



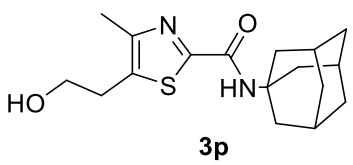
^{1}H NMR 300 MHz, $CDCl_3$



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

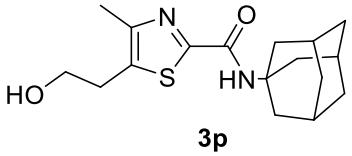


^{1}H NMR 300 MHz, $CDCl_3$



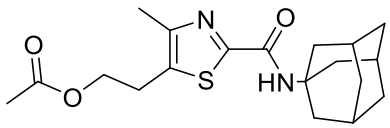
3p

^{13}C NMR 75 MHz, $CDCl_3$



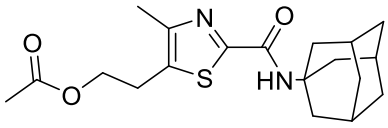
3p

^{1}H NMR 300 MHz, $CDCl_3$



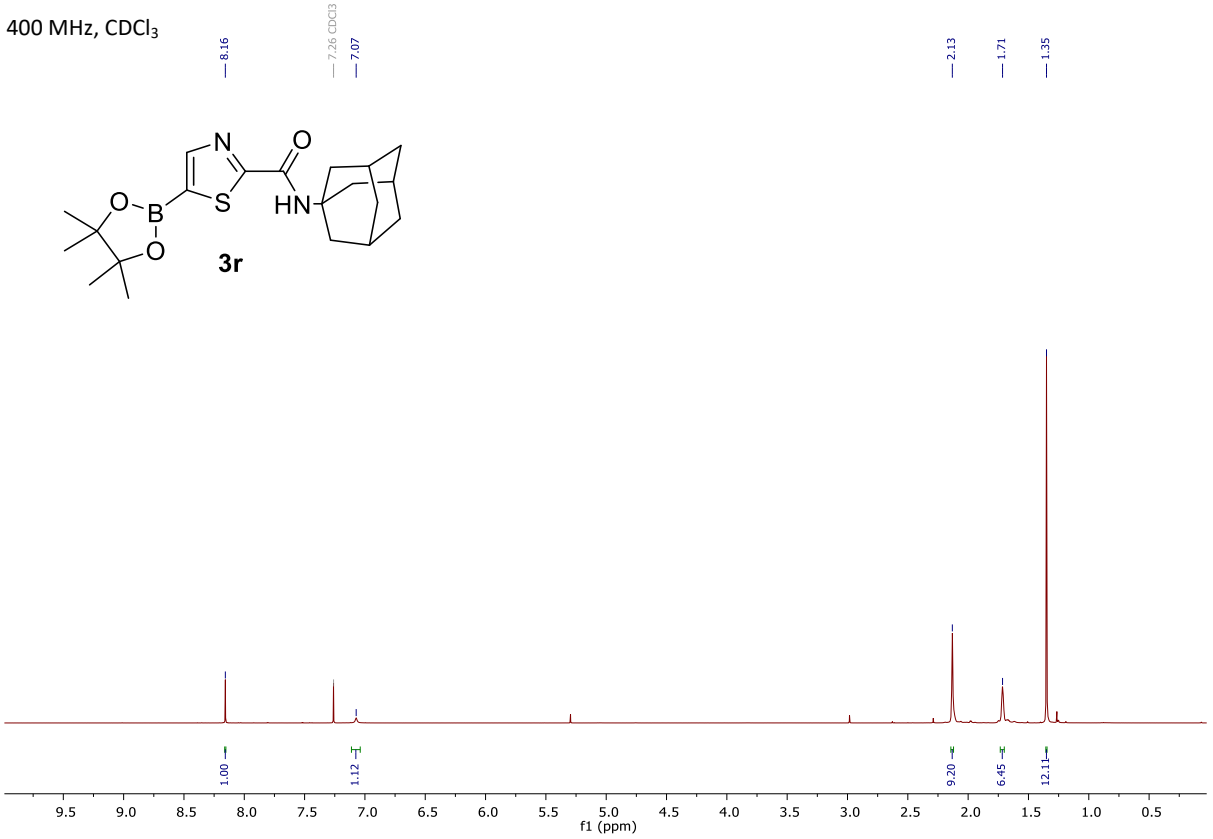
3q

^{13}C NMR 75 MHz, $CDCl_3$

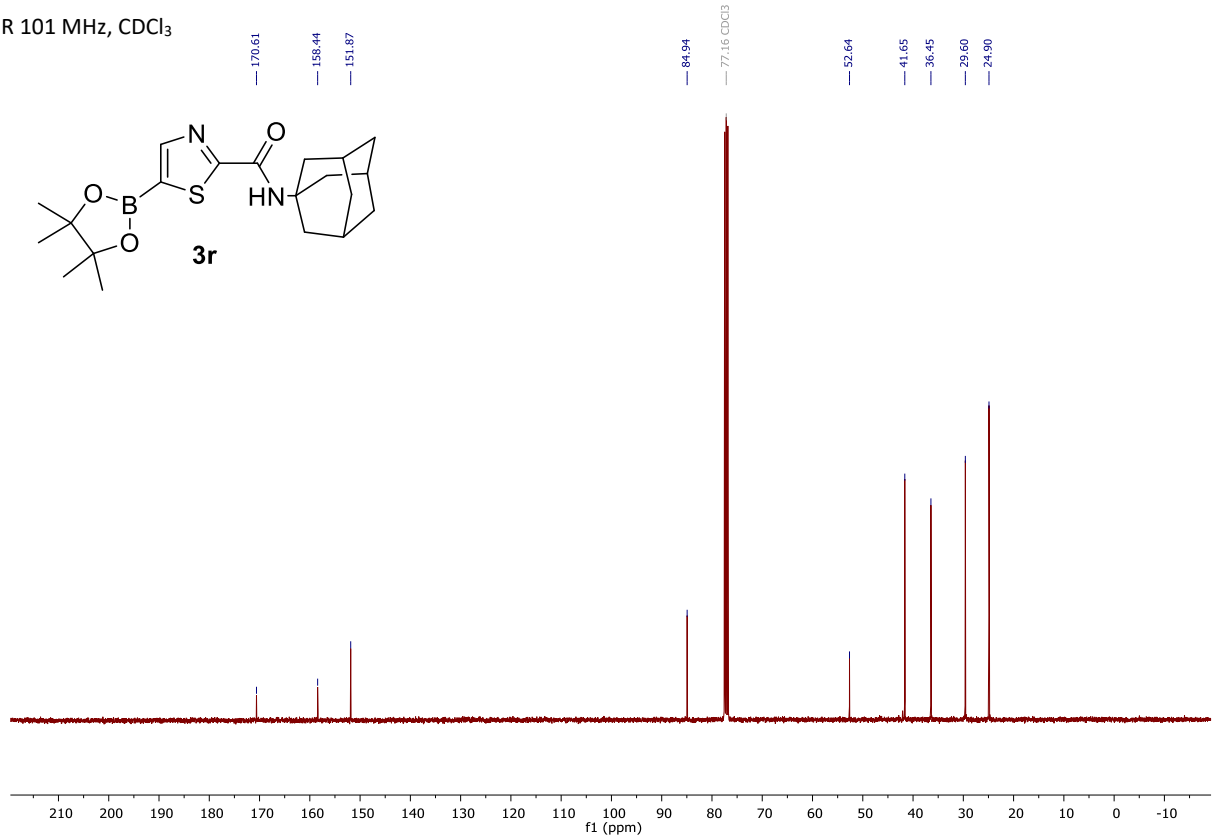


3q

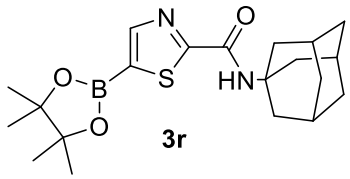
^{1}H NMR 400 MHz, $CDCl_3$



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

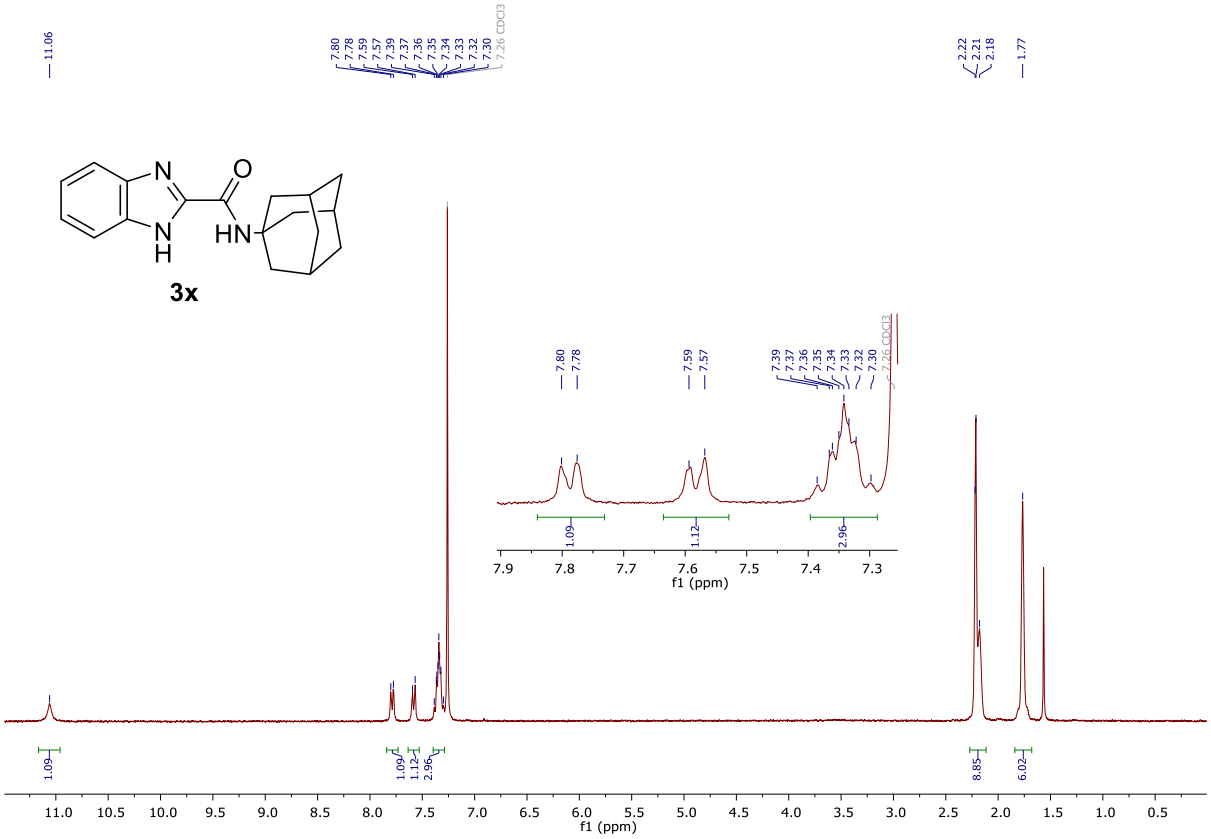


^{11}B NMR 96 MHz, $CDCl_3$

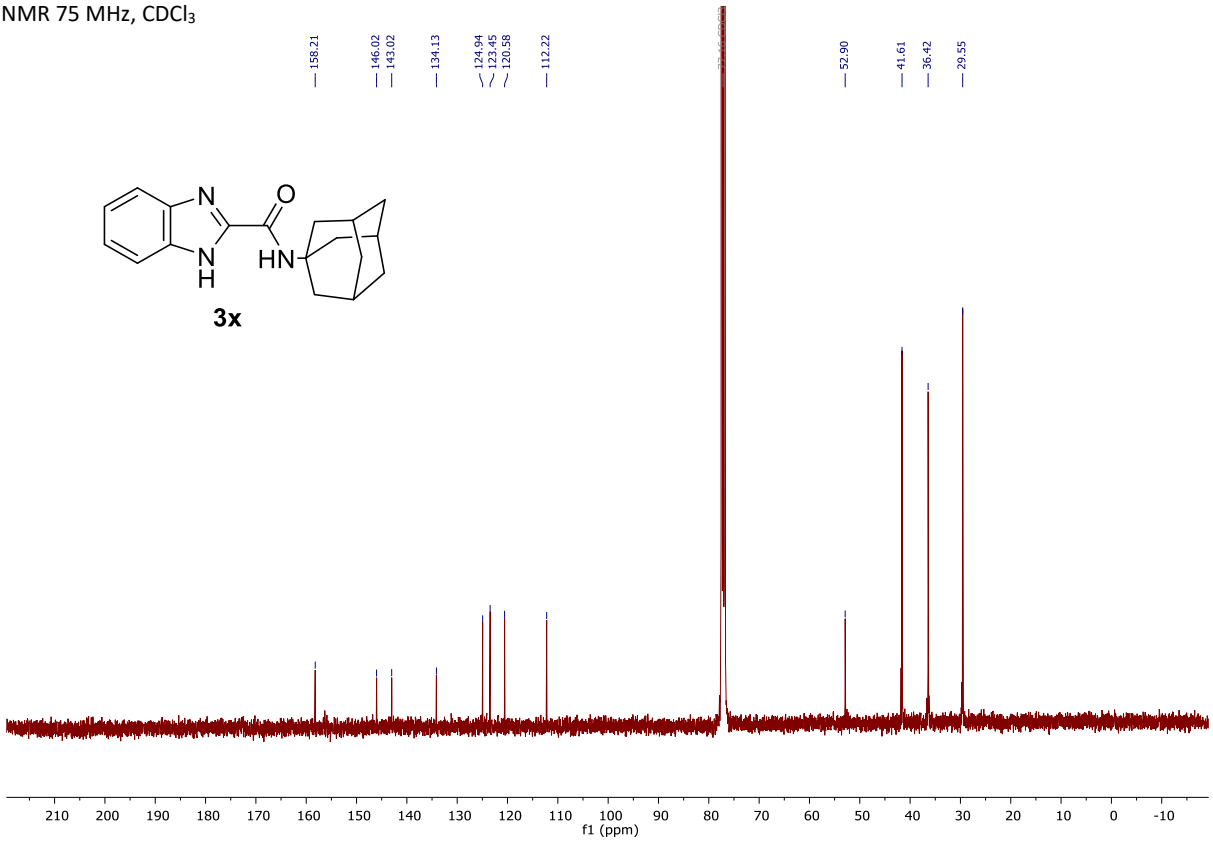


3r

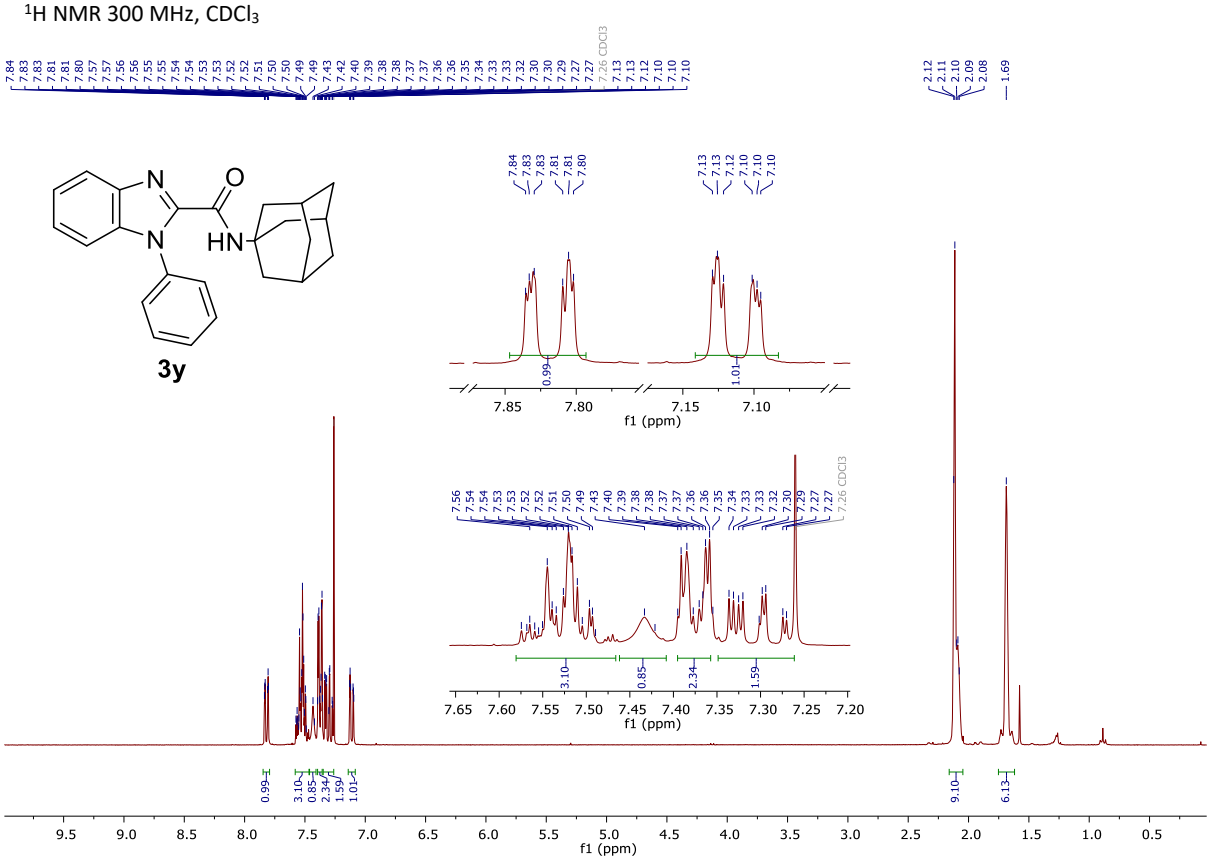
^{1}H NMR 300 MHz, $CDCl_3$



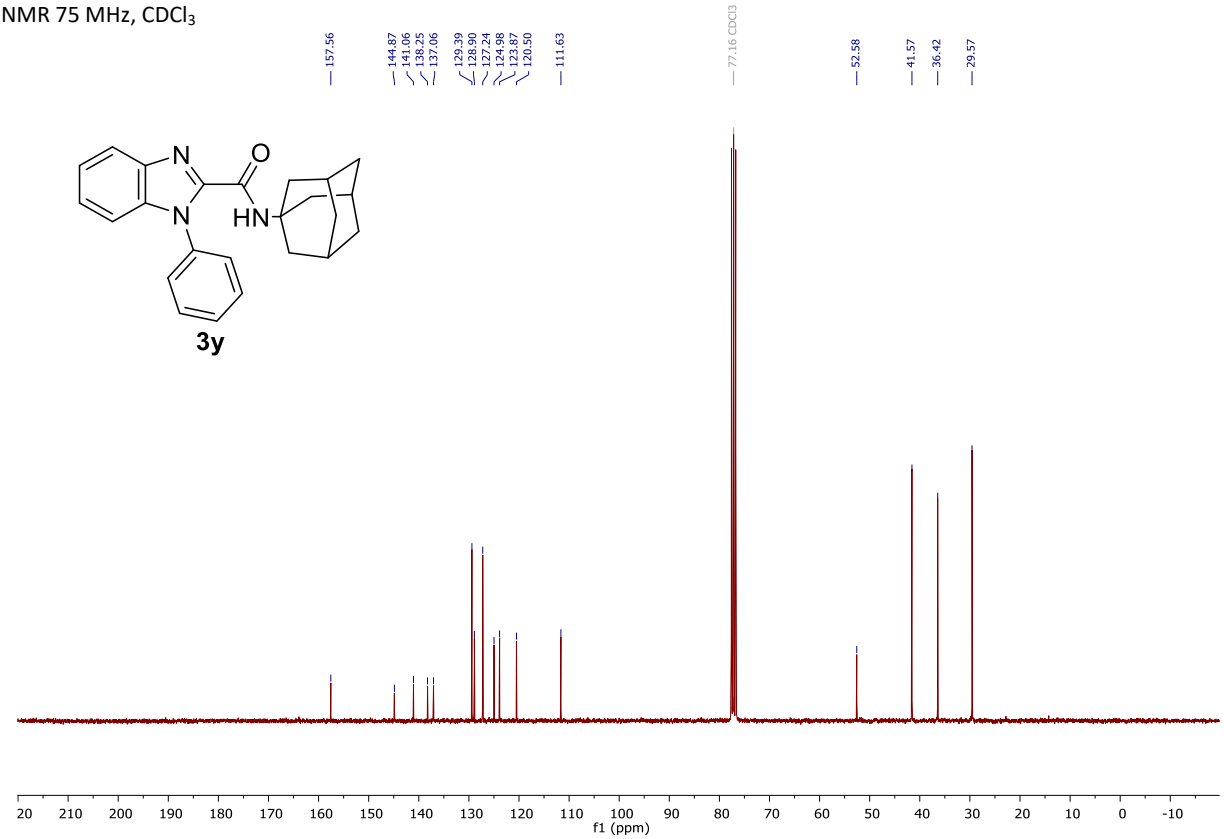
^{13}C NMR 75 MHz, $CDCl_3$



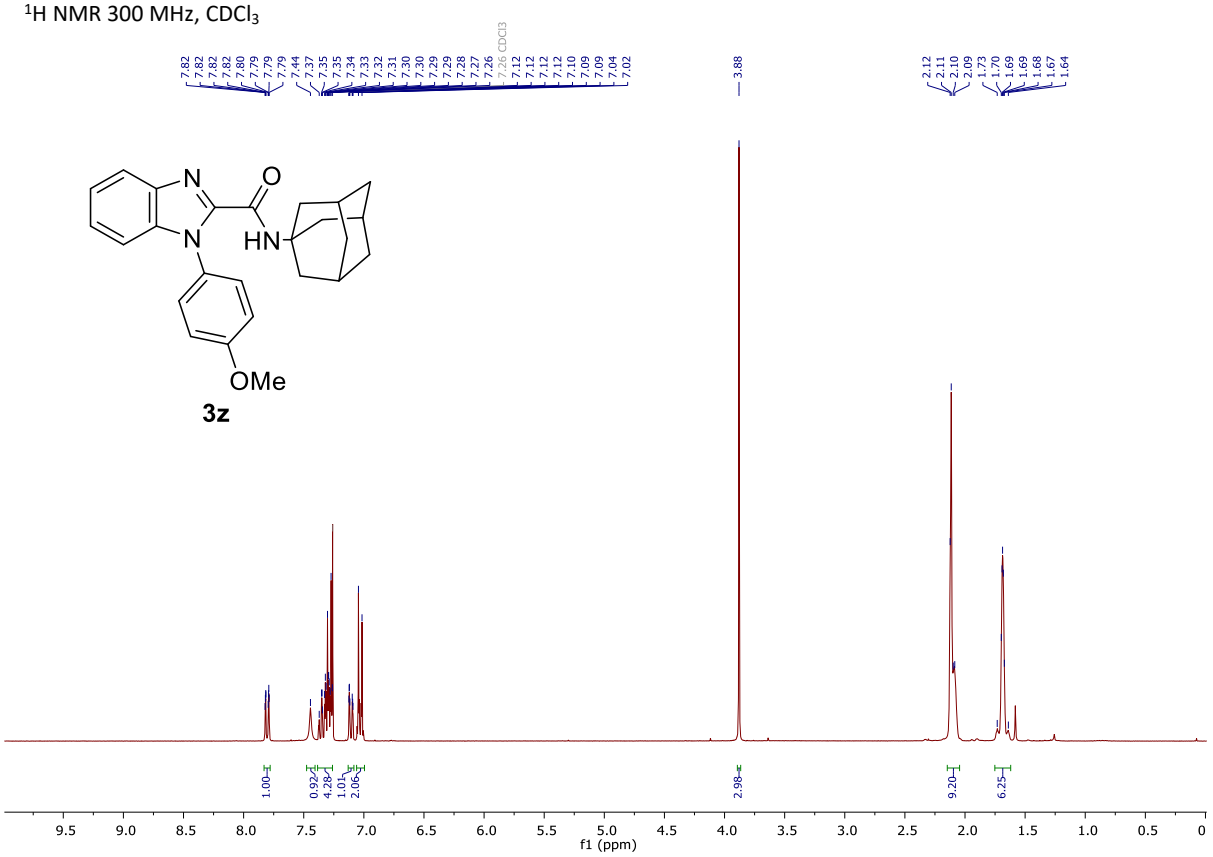
^{1}H NMR 300 MHz, $CDCl_3$



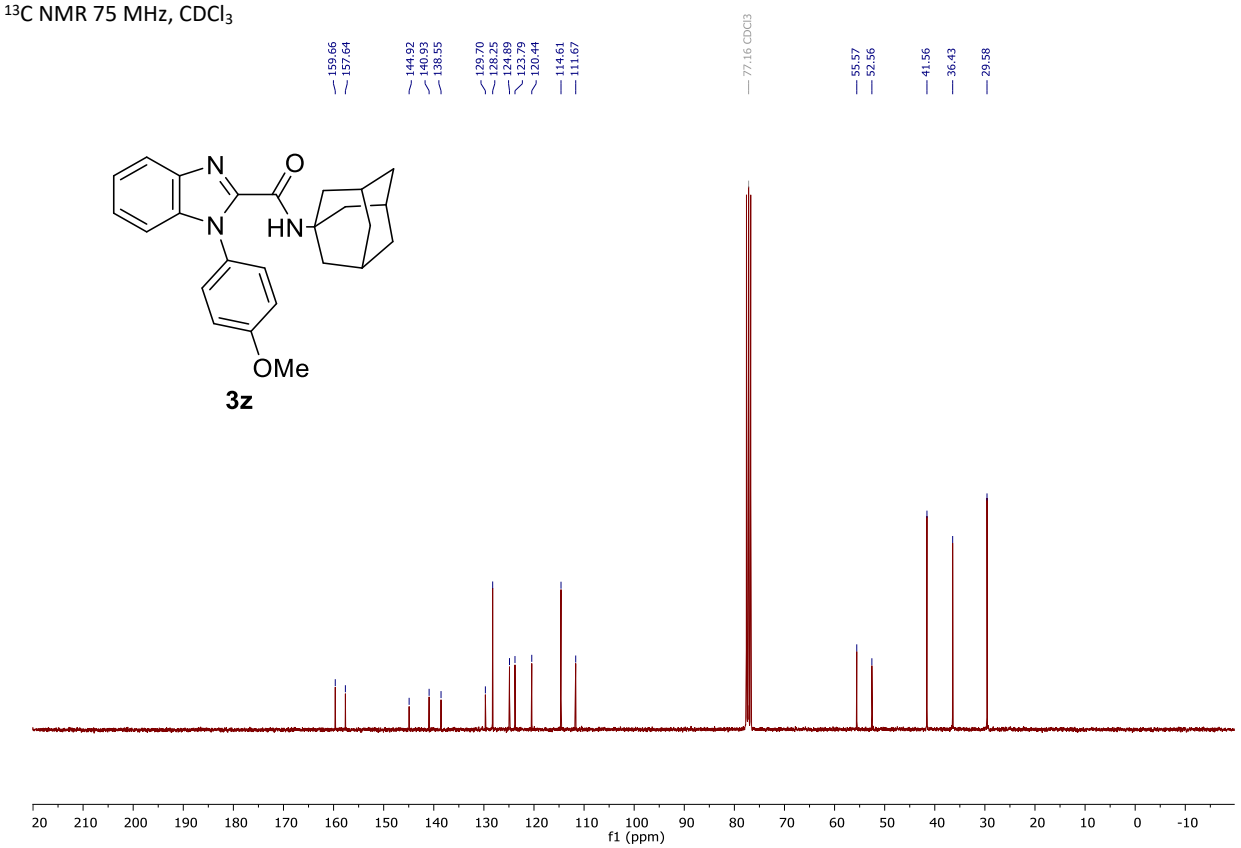
^{13}C NMR 75 MHz, $CDCl_3$



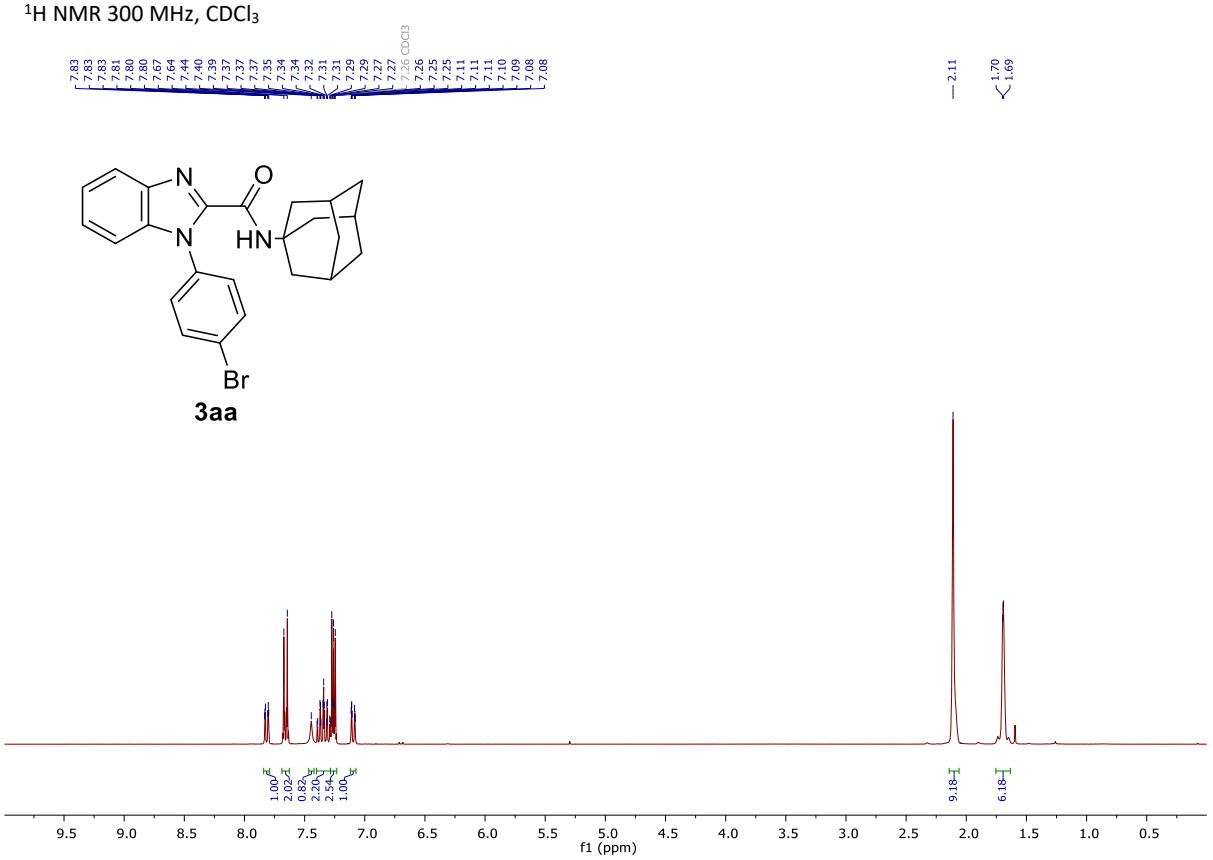
^{1}H NMR 300 MHz, $CDCl_3$



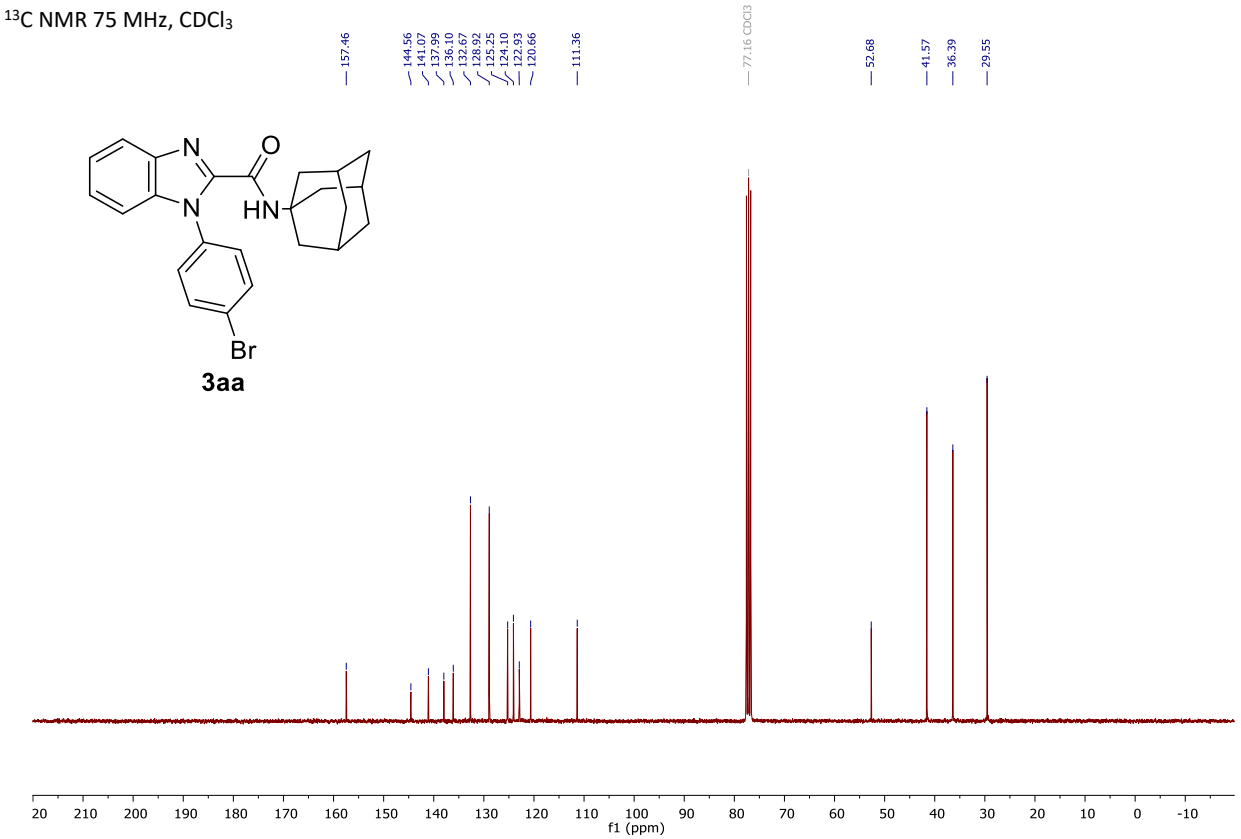
^{13}C NMR 75 MHz, $CDCl_3$



^{1}H NMR 300 MHz, $CDCl_3$

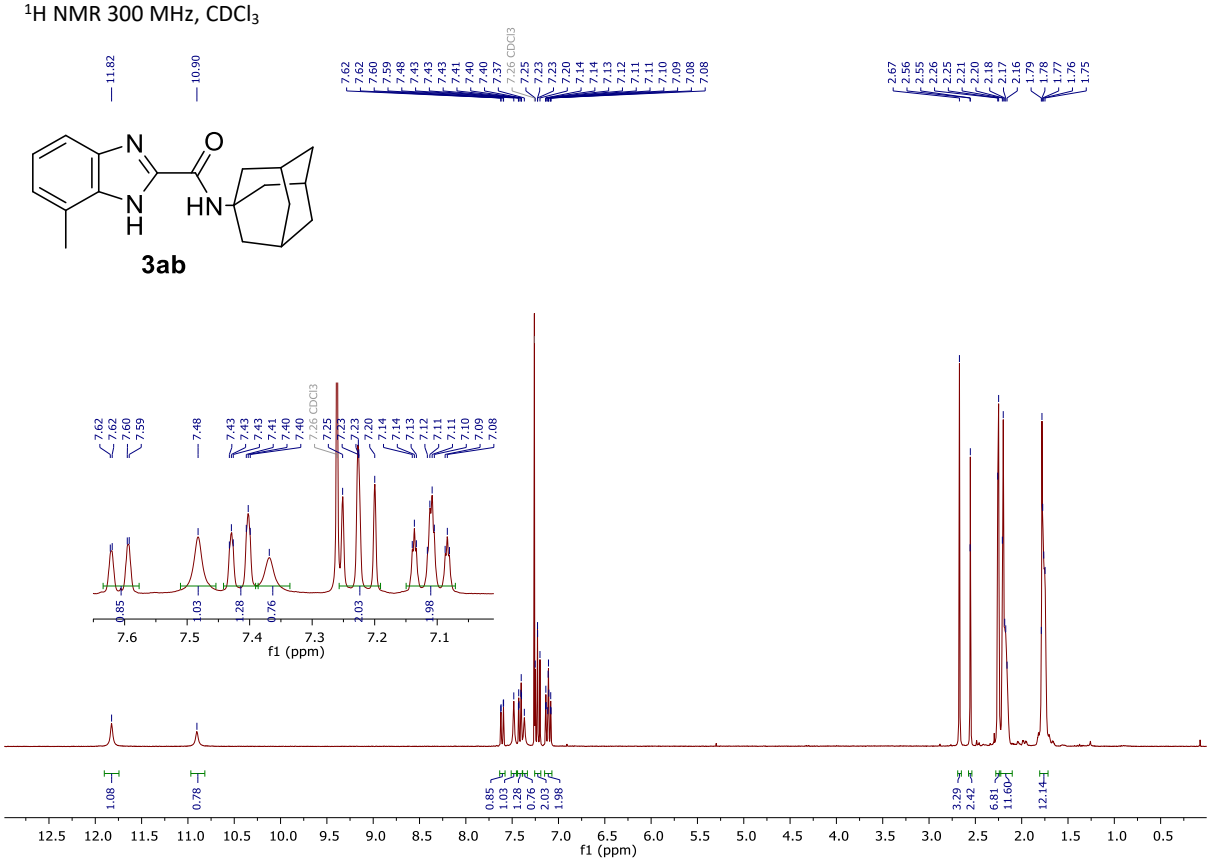


^{13}C NMR 75 MHz, $CDCl_3$

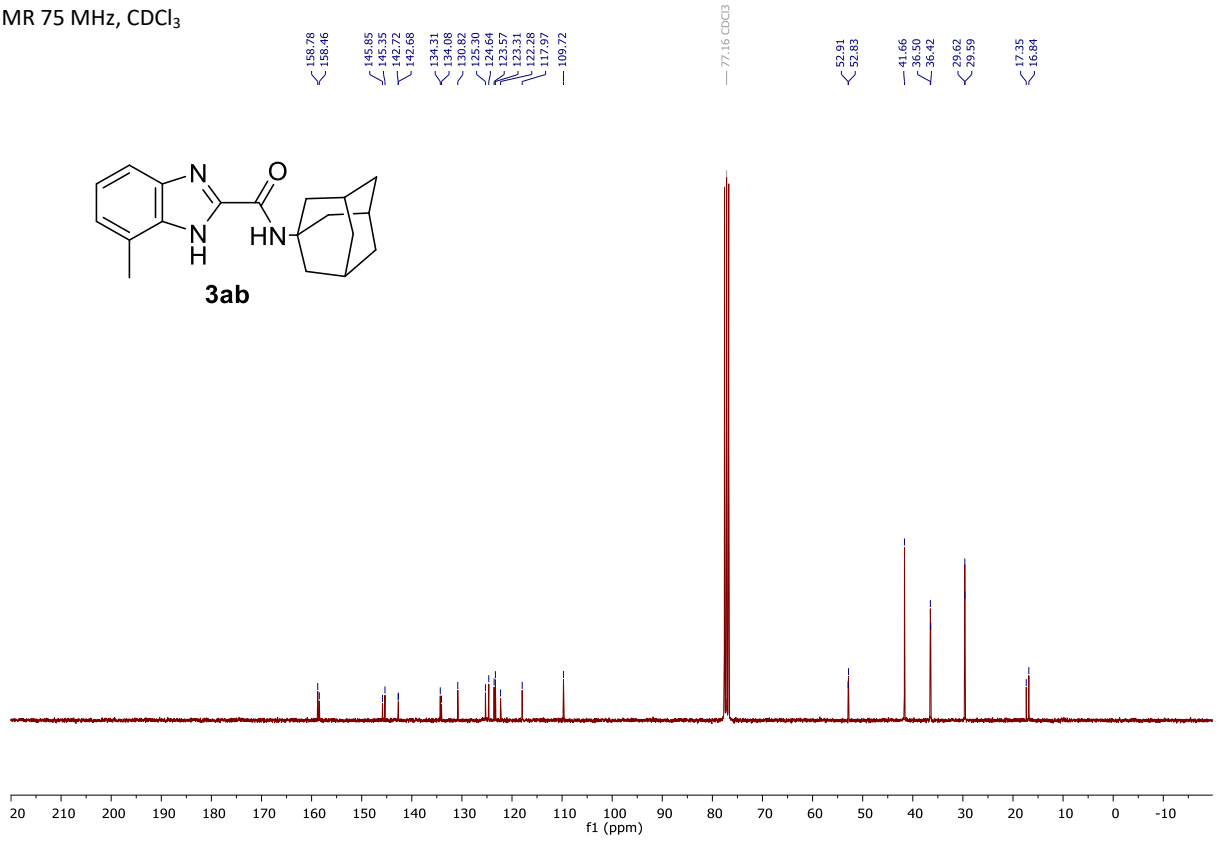


(Mixture of 4/7-isomers)

^{1}H NMR 300 MHz, $CDCl_3$

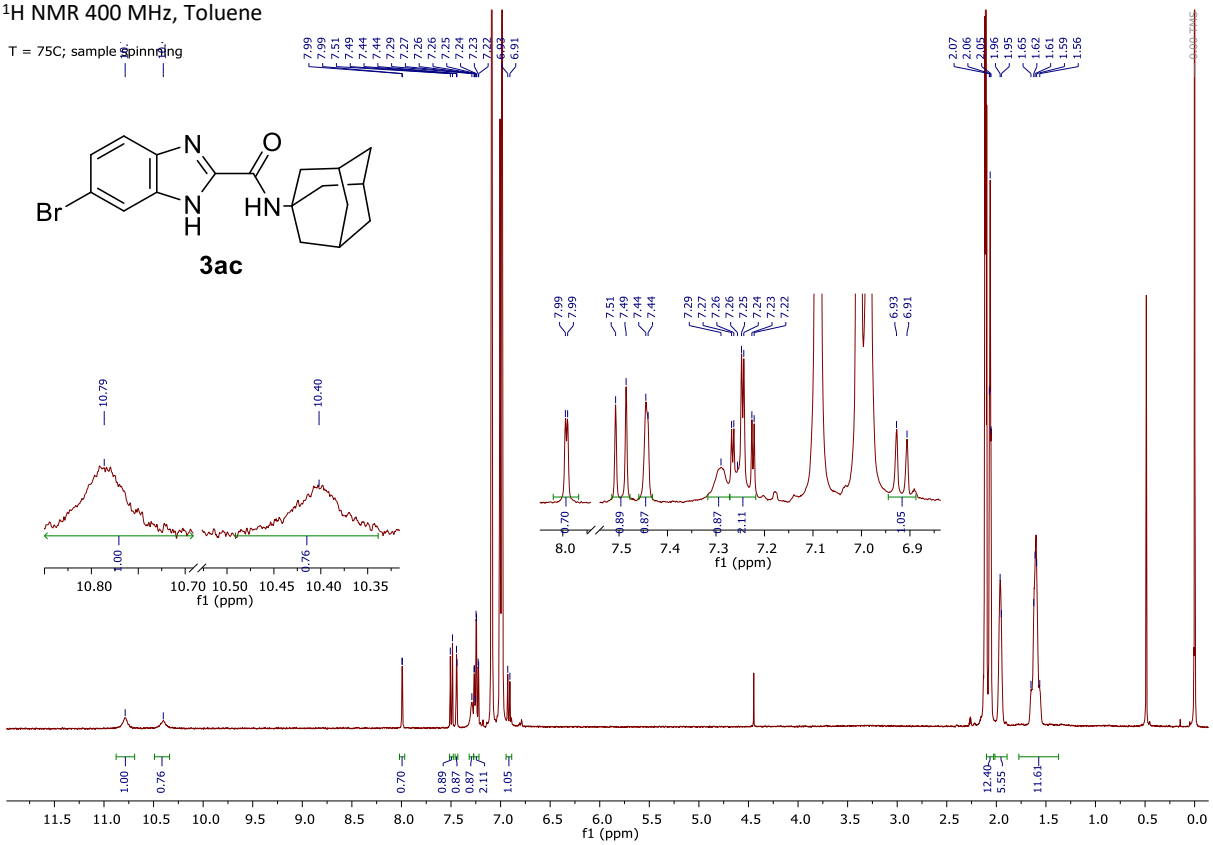


^{13}C NMR 75 MHz, $CDCl_3$

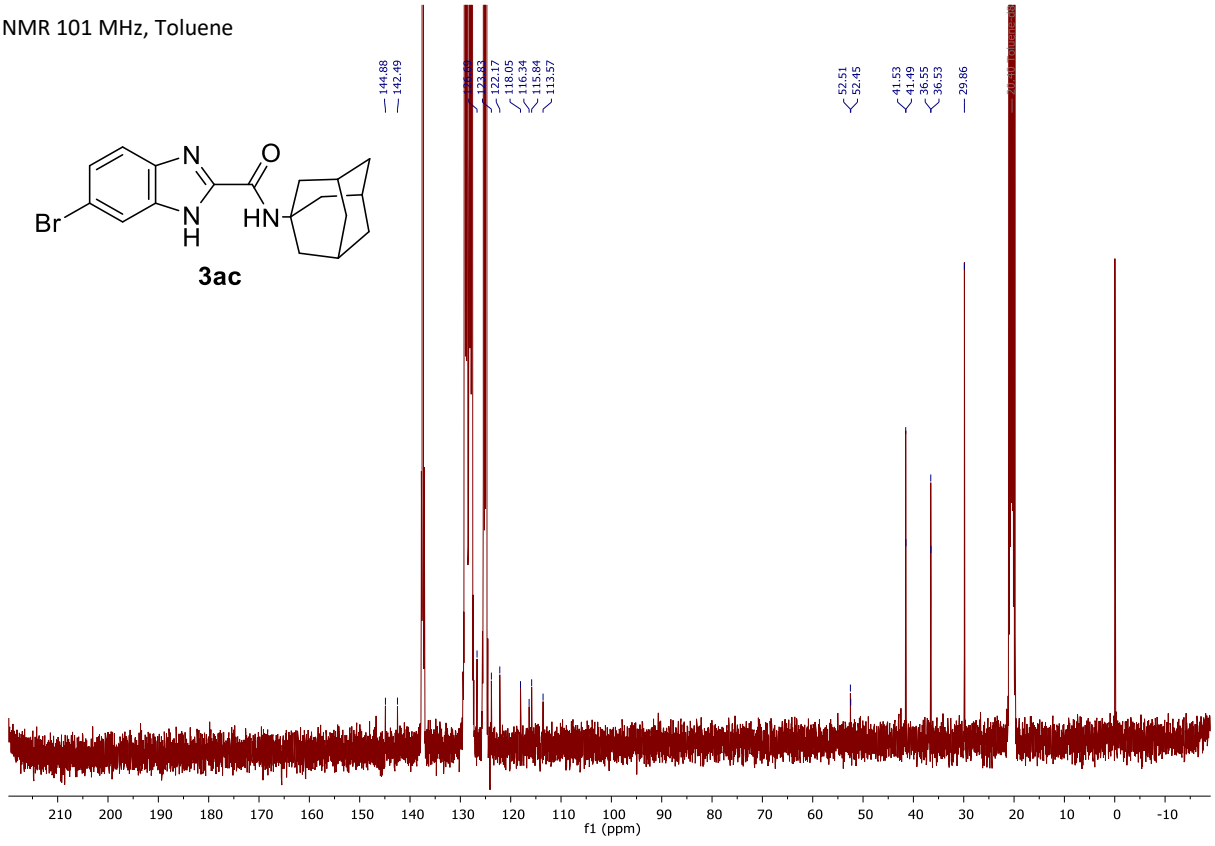


(Mixture of 5/6-isomers)

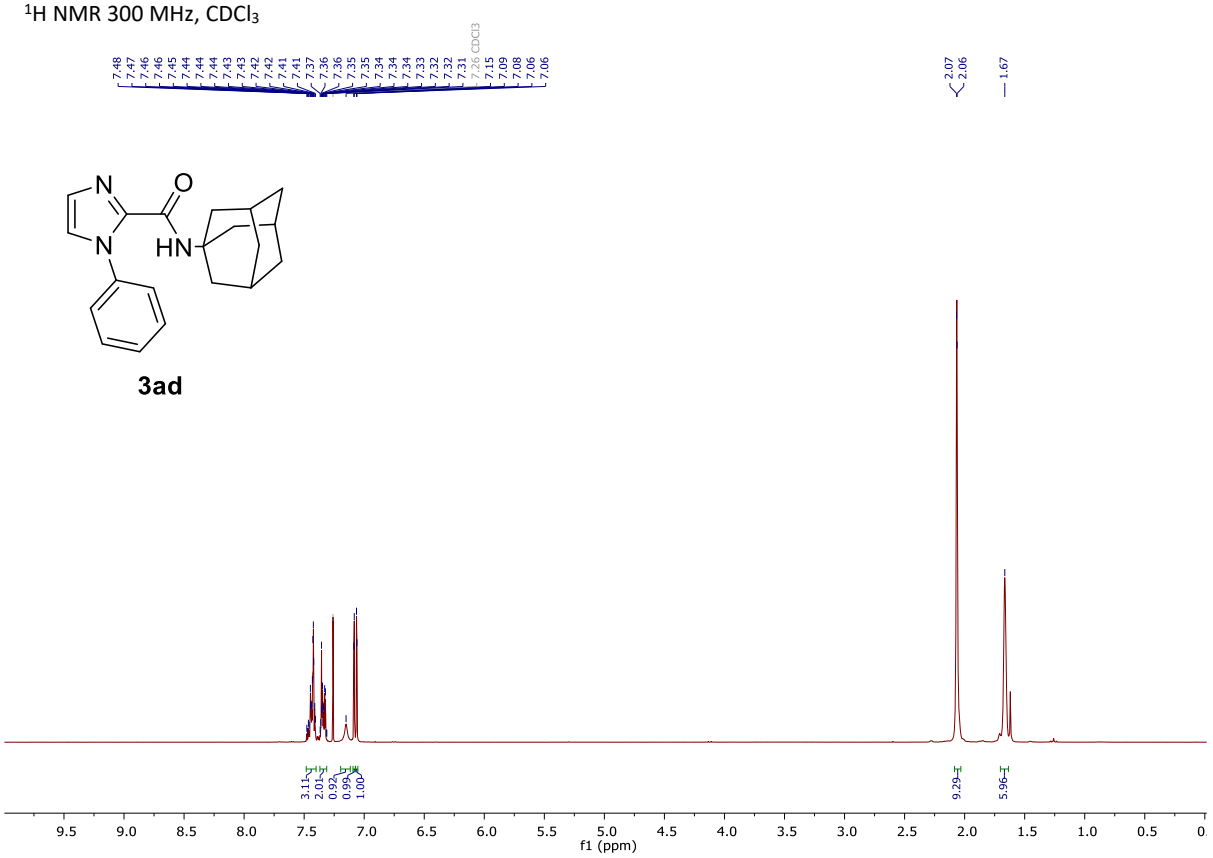
^{1}H NMR 400 MHz, Toluene



^{13}C NMR 101 MHz, Toluene

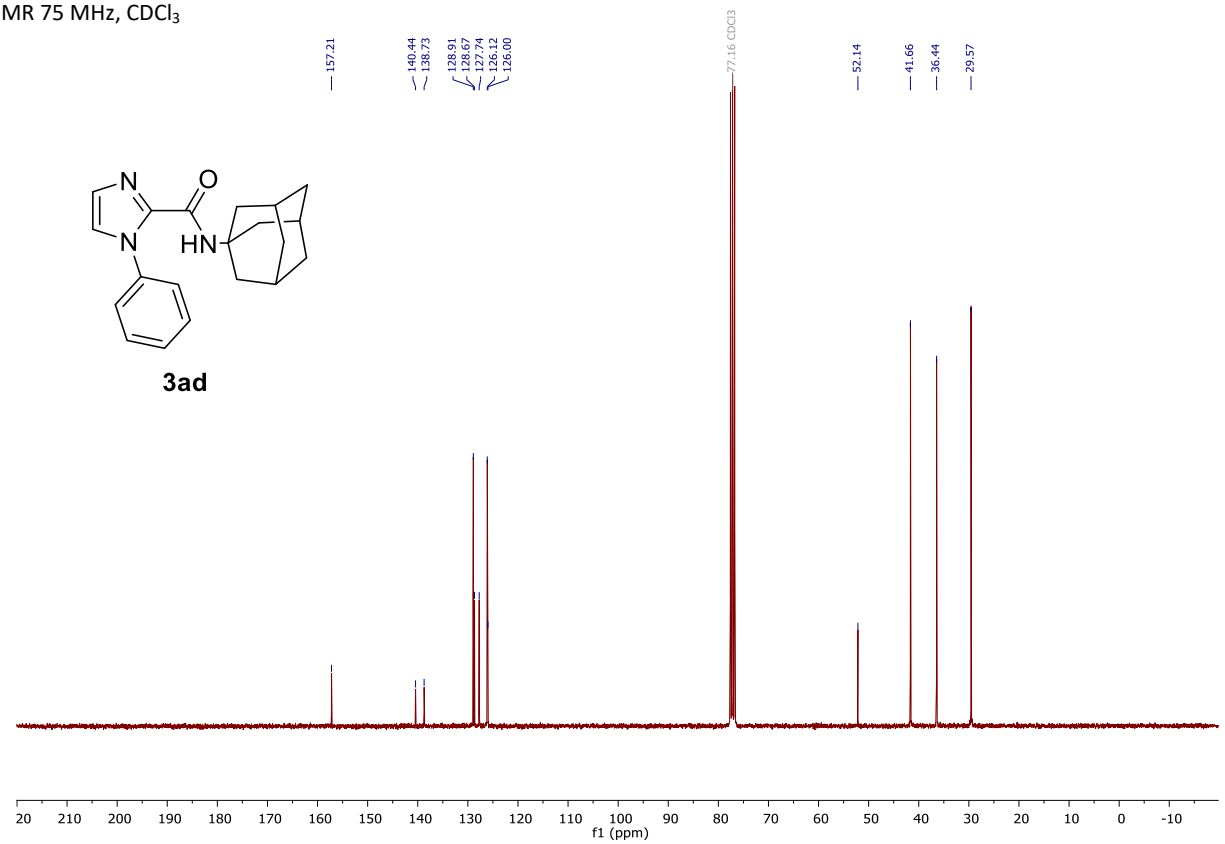


^{1}H NMR 300 MHz, $CDCl_3$



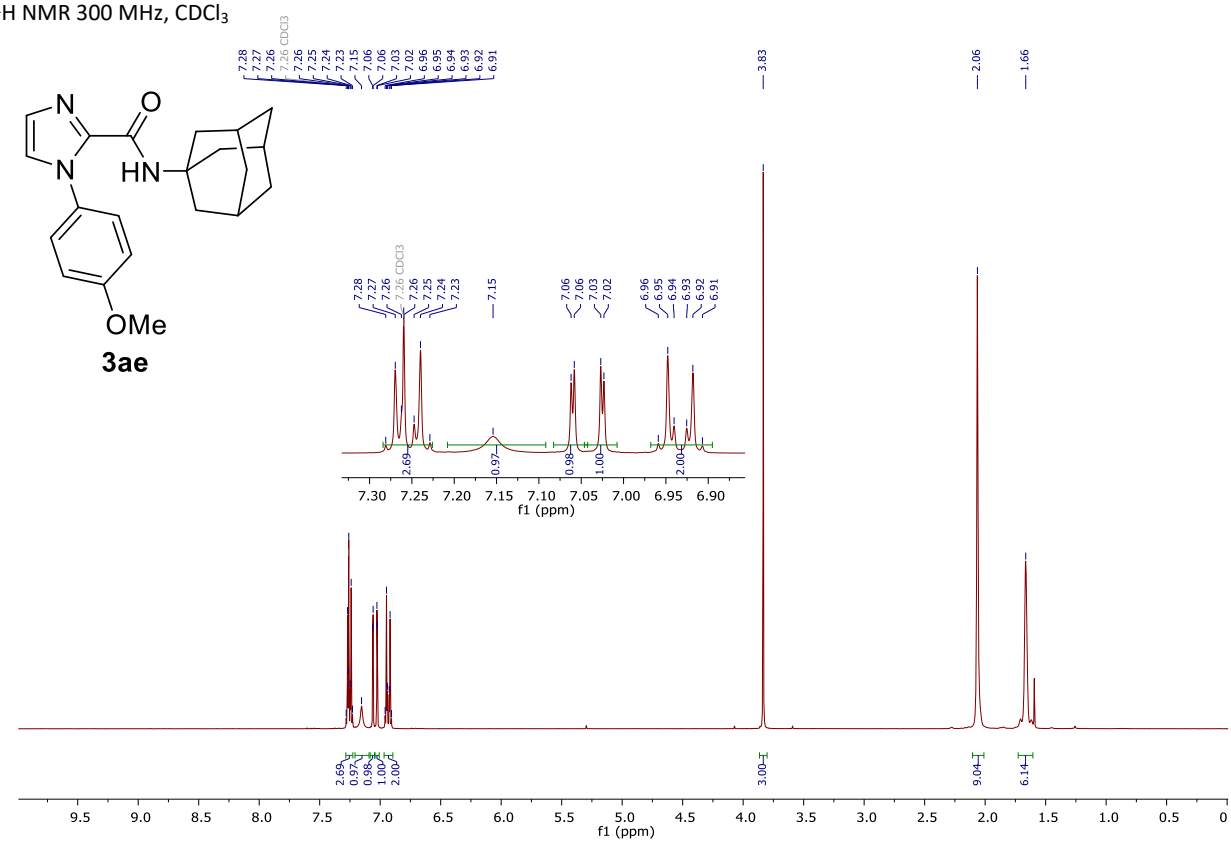
3ad

^{13}C NMR 75 MHz, $CDCl_3$

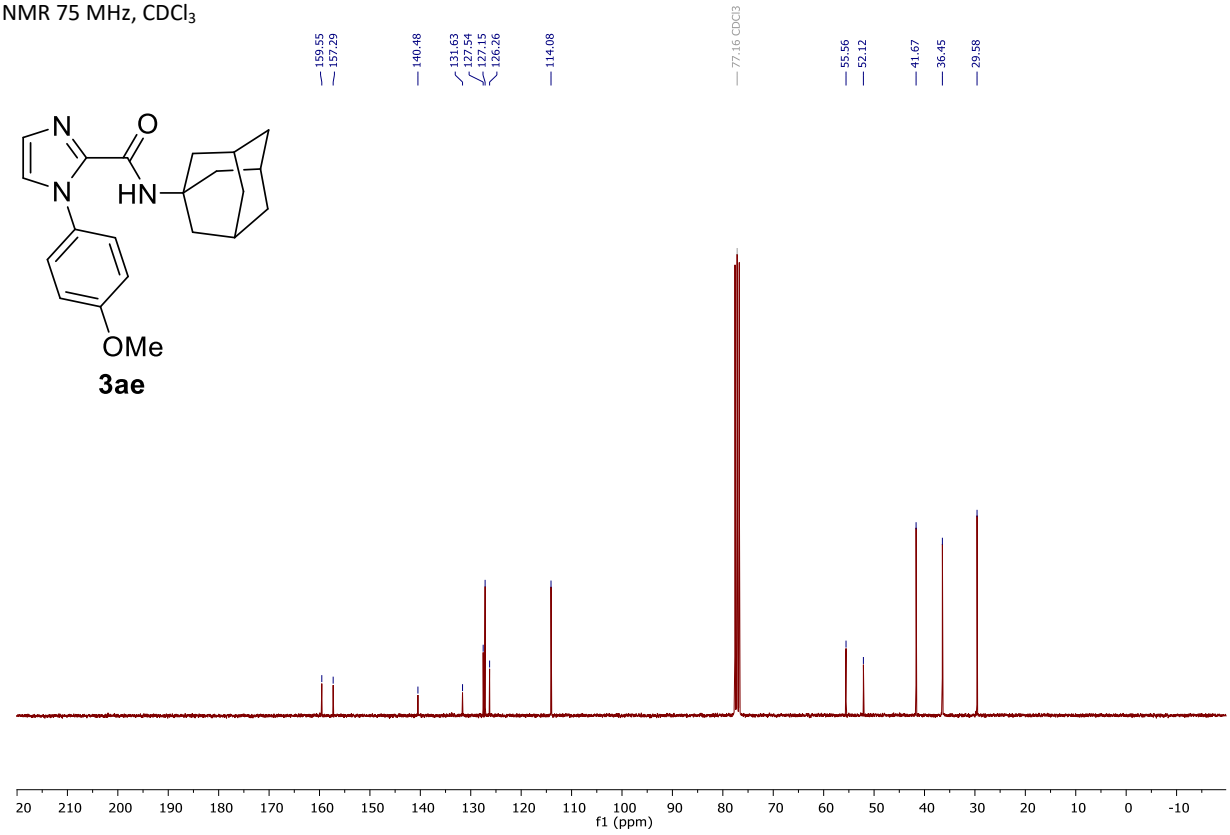


3ad

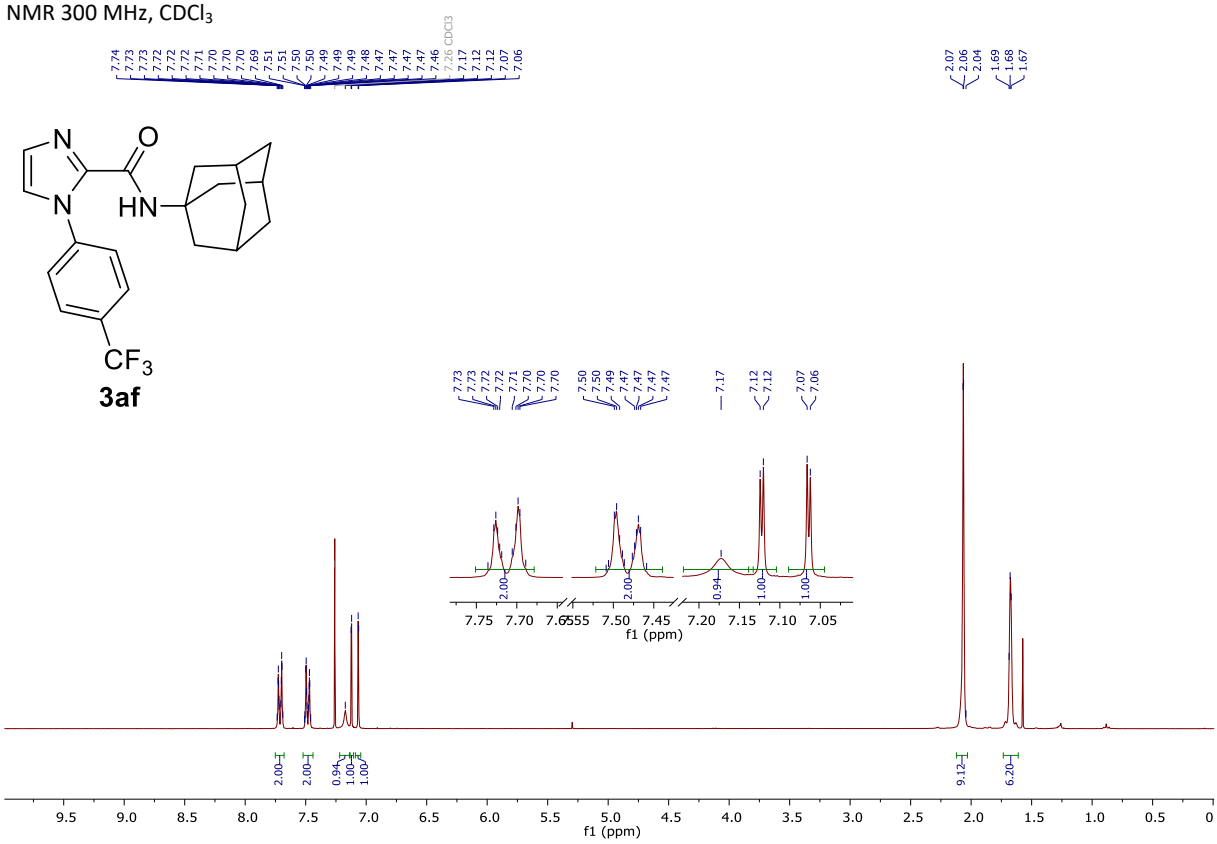
^{1}H NMR 300 MHz, $CDCl_3$



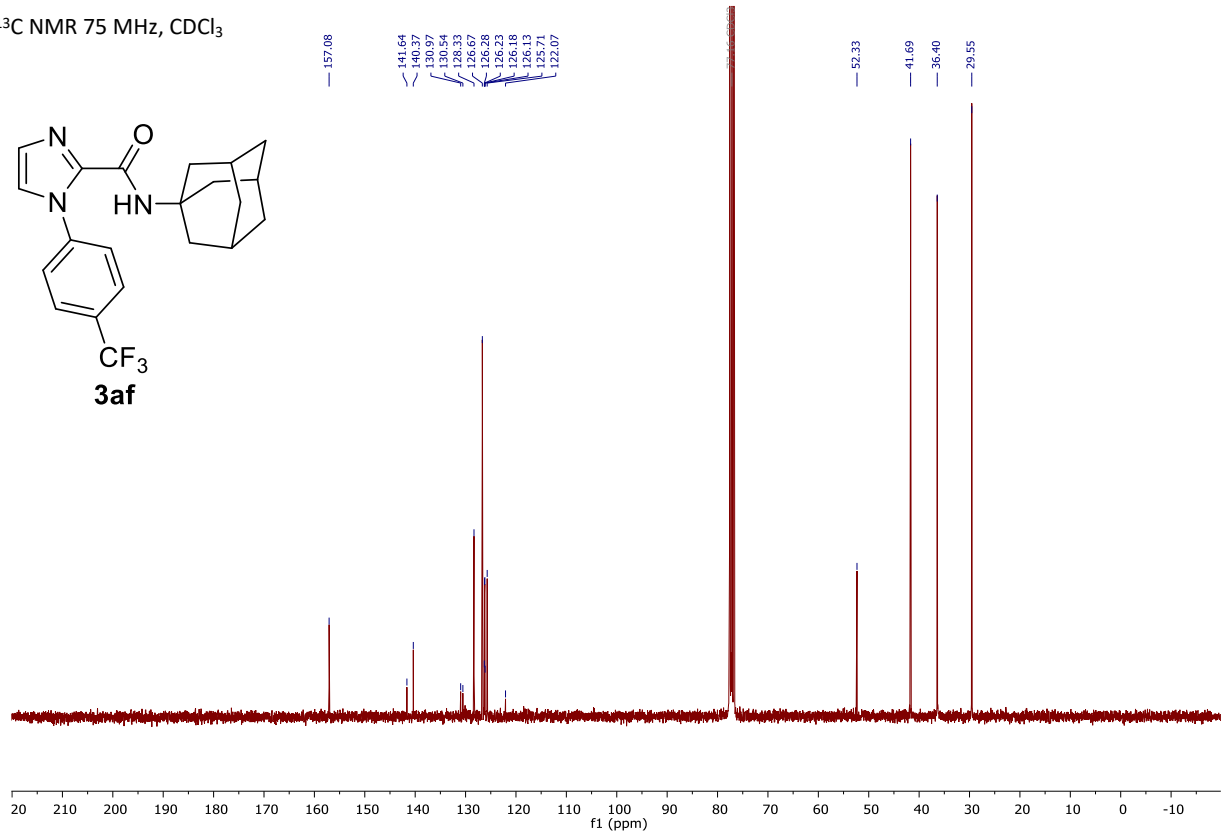
^{13}C NMR 75 MHz, $CDCl_3$



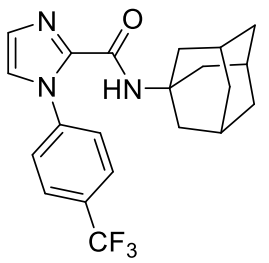
^{1}H NMR 300 MHz, $CDCl_3$



^{13}C NMR 75 MHz, $CDCl_3$

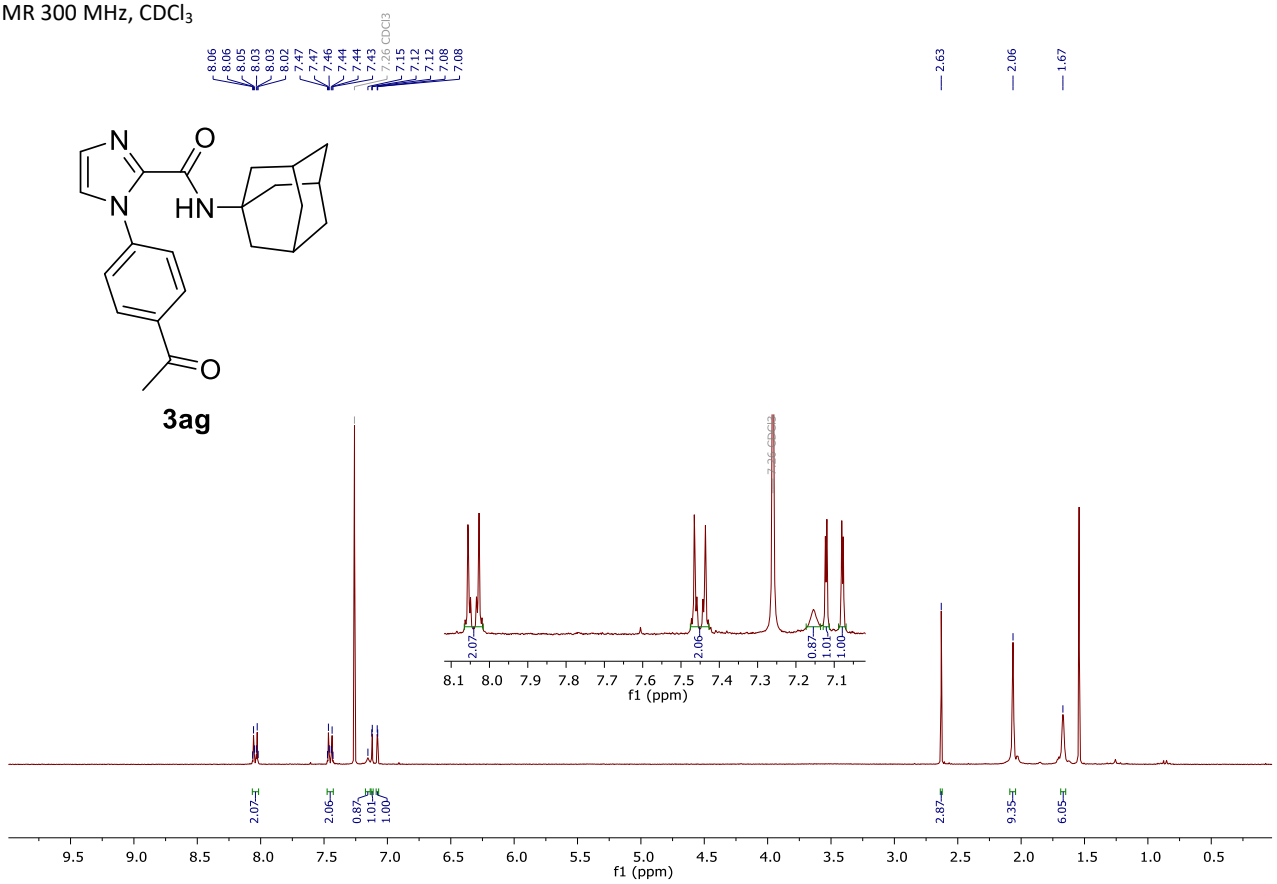


^{19}F NMR 282 MHz, $CDCl_3$

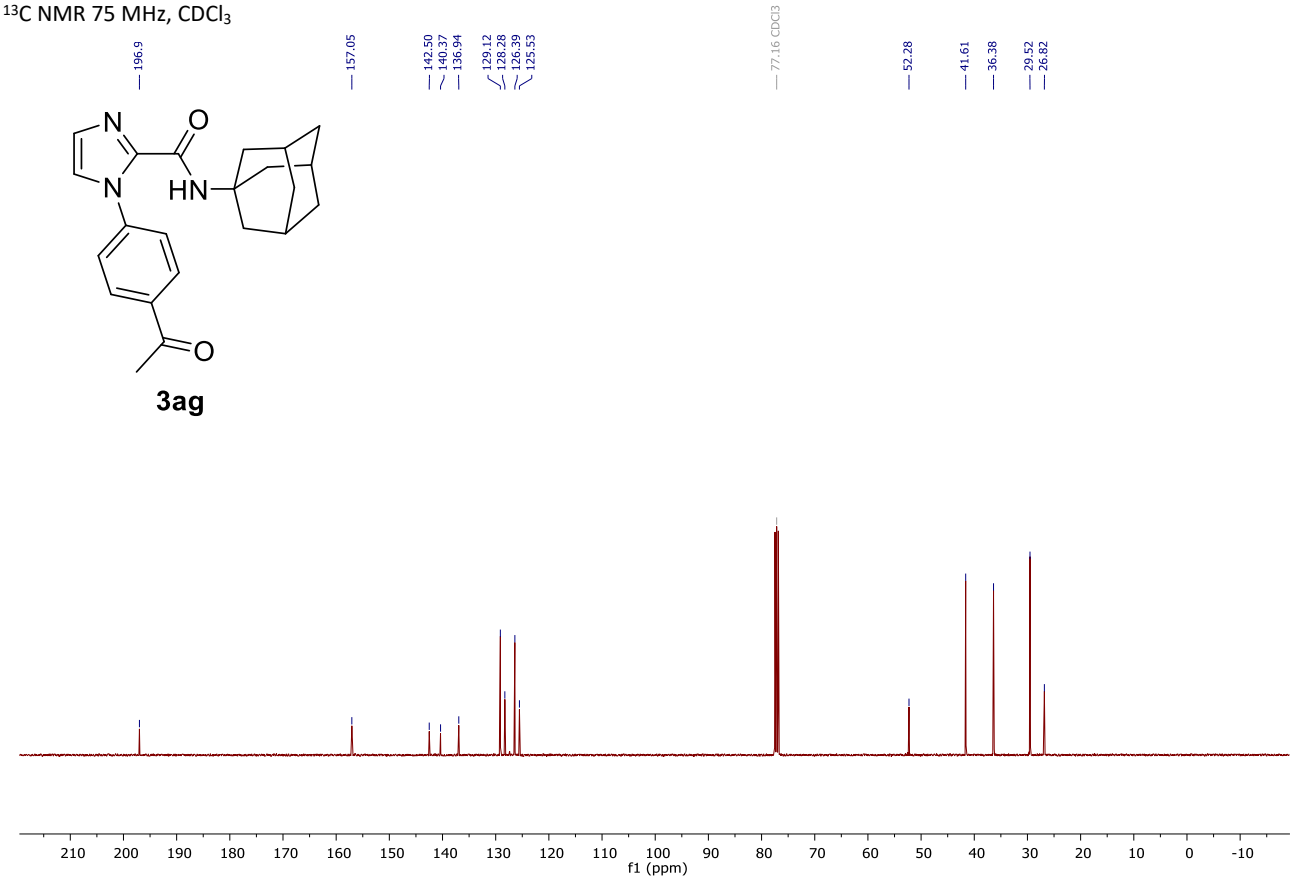


3af

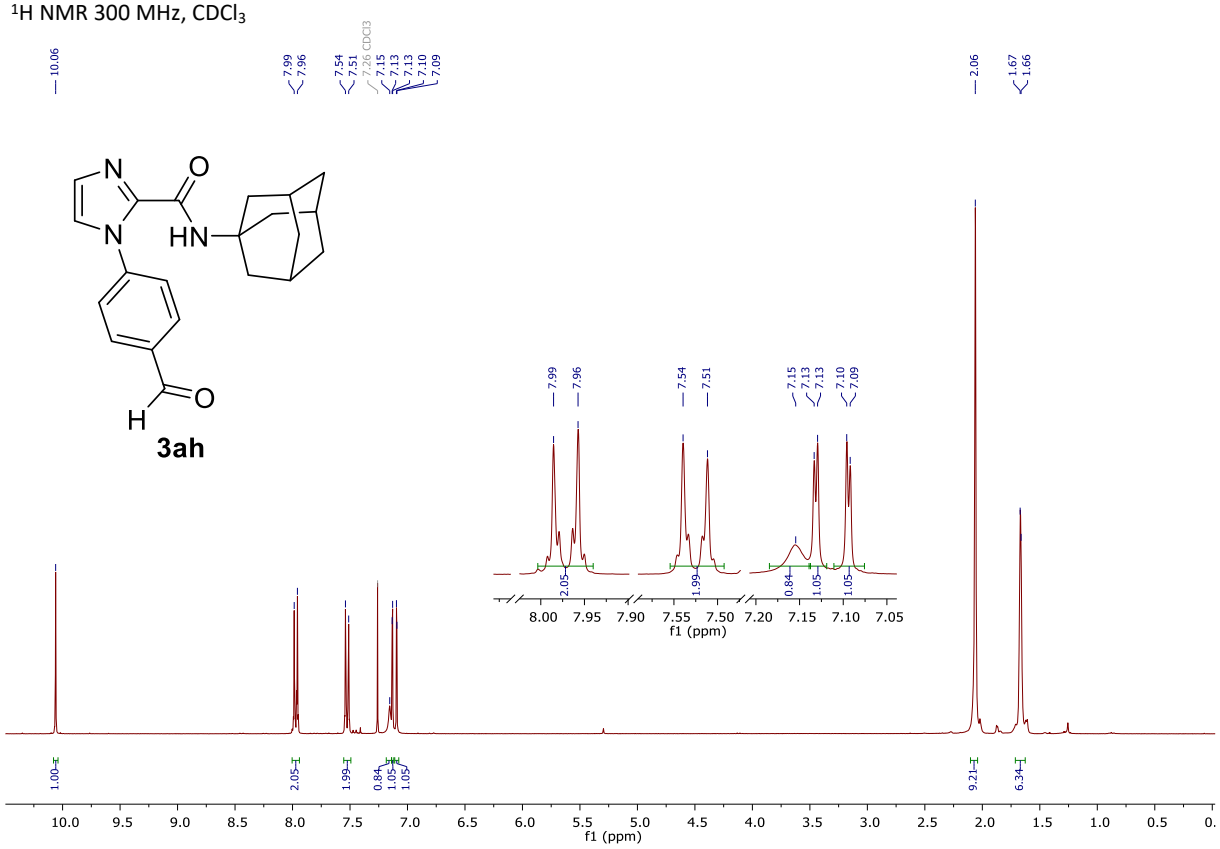
^{1}H NMR 300 MHz, $CDCl_3$



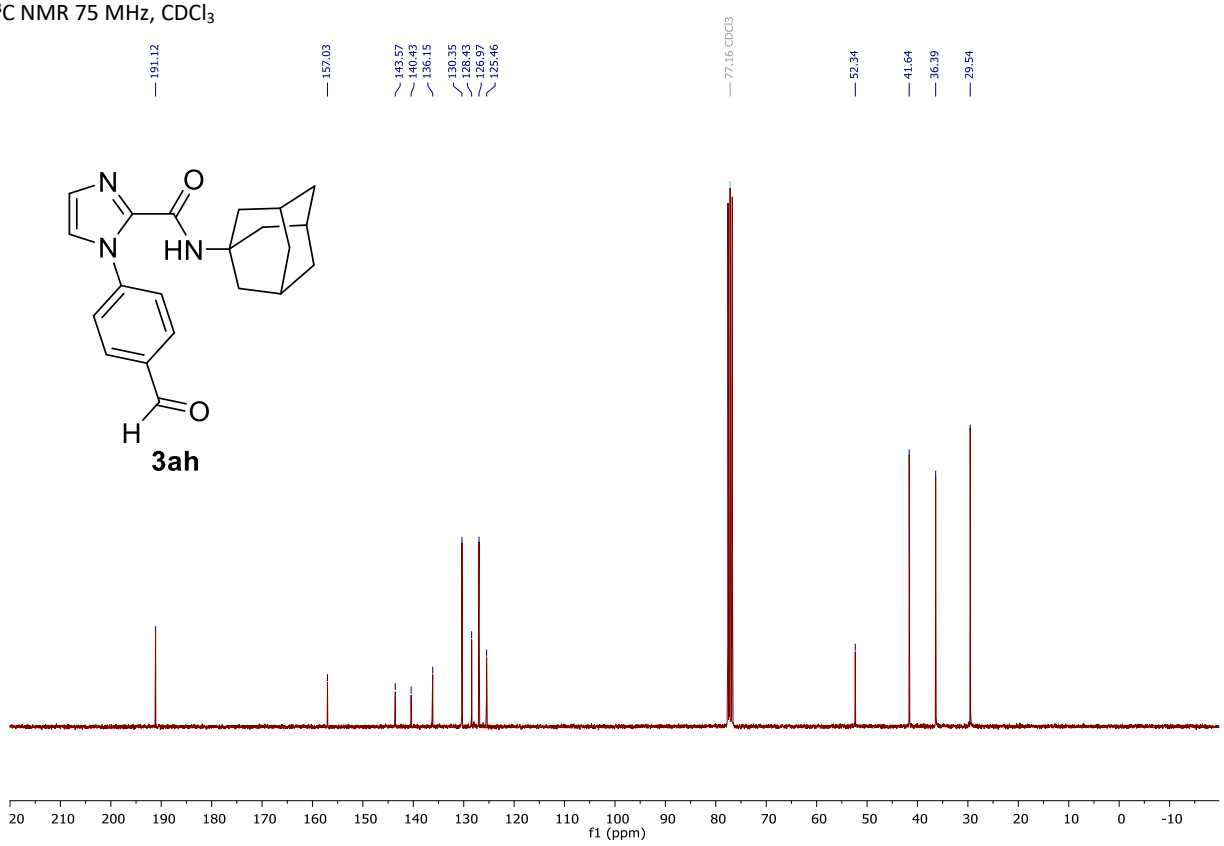
^{13}C NMR 75 MHz, $CDCl_3$



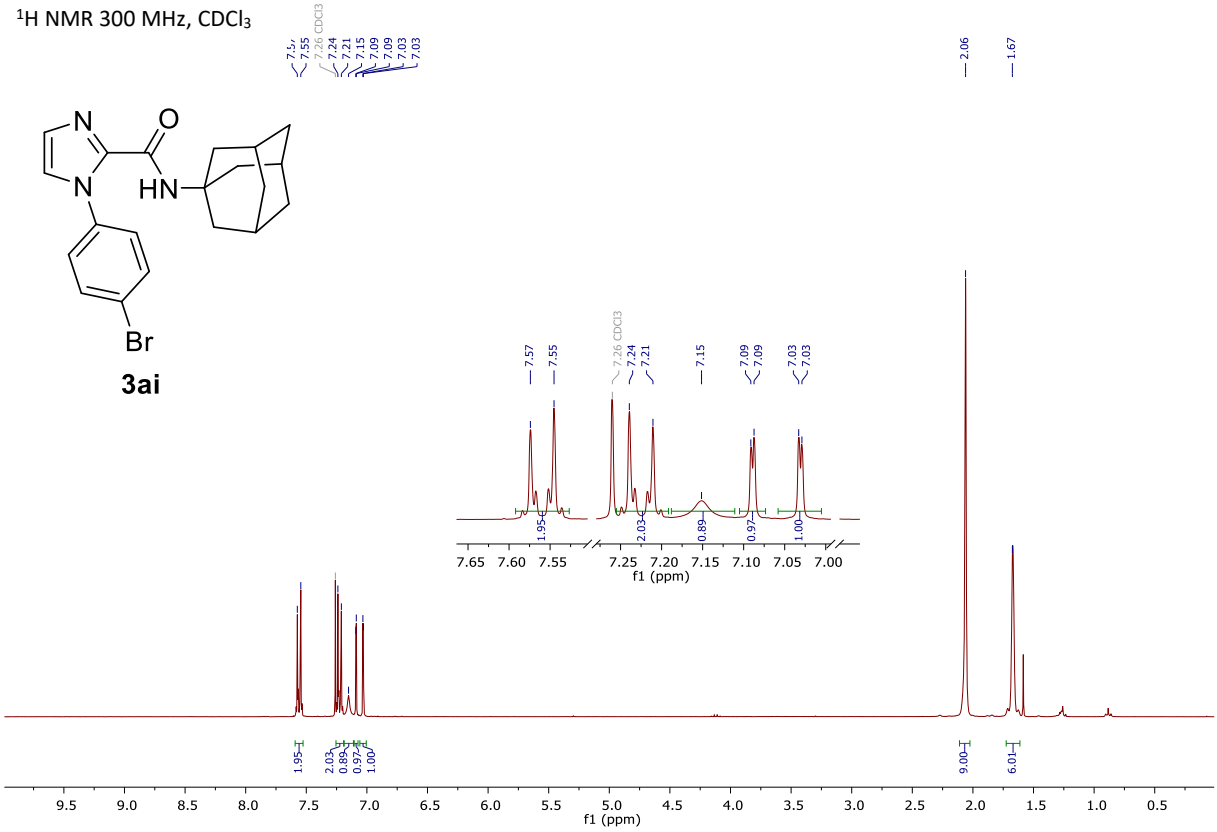
^{1}H NMR 300 MHz, $CDCl_3$



^{13}C NMR 75 MHz, $CDCl_3$

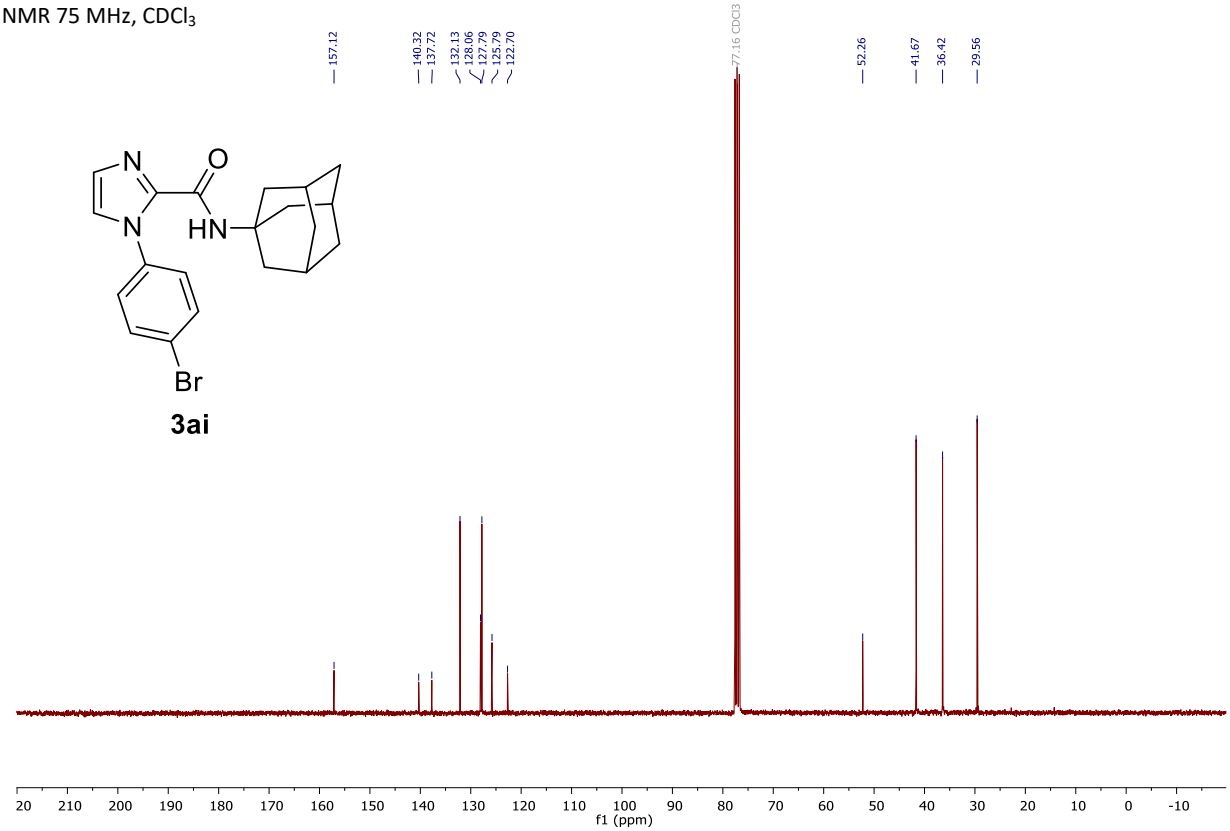


^{1}H NMR 300 MHz, $CDCl_3$



3ai

^{13}C NMR 75 MHz, $CDCl_3$



3ai

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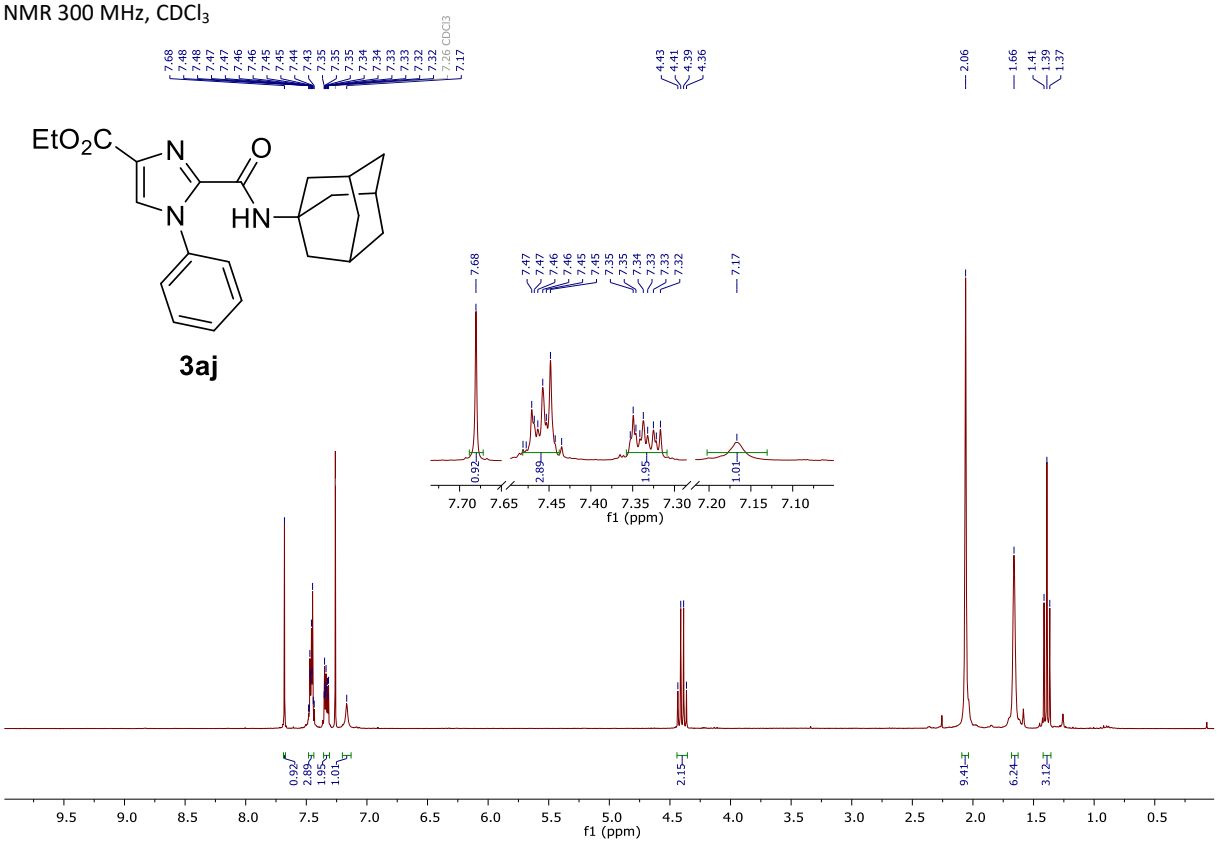

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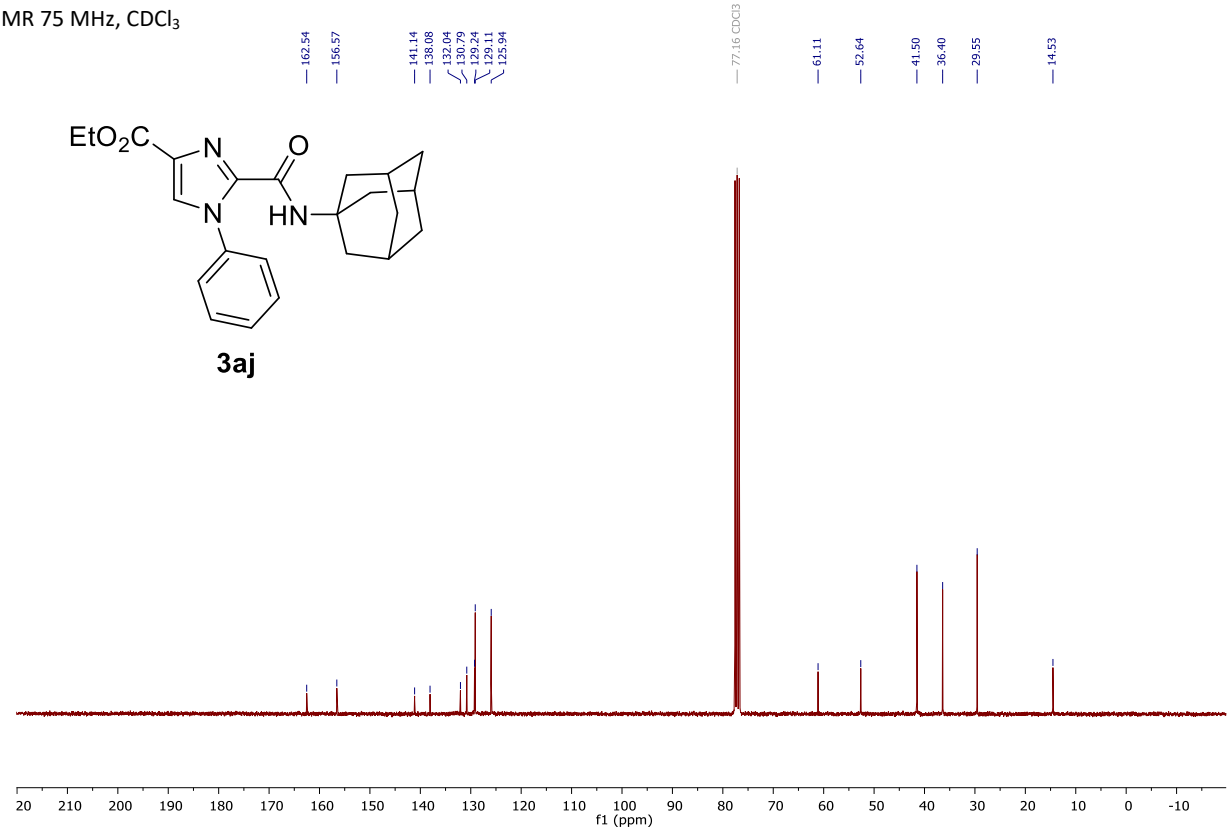

^{1}H NMR 400 MHz, $CDCl_3$

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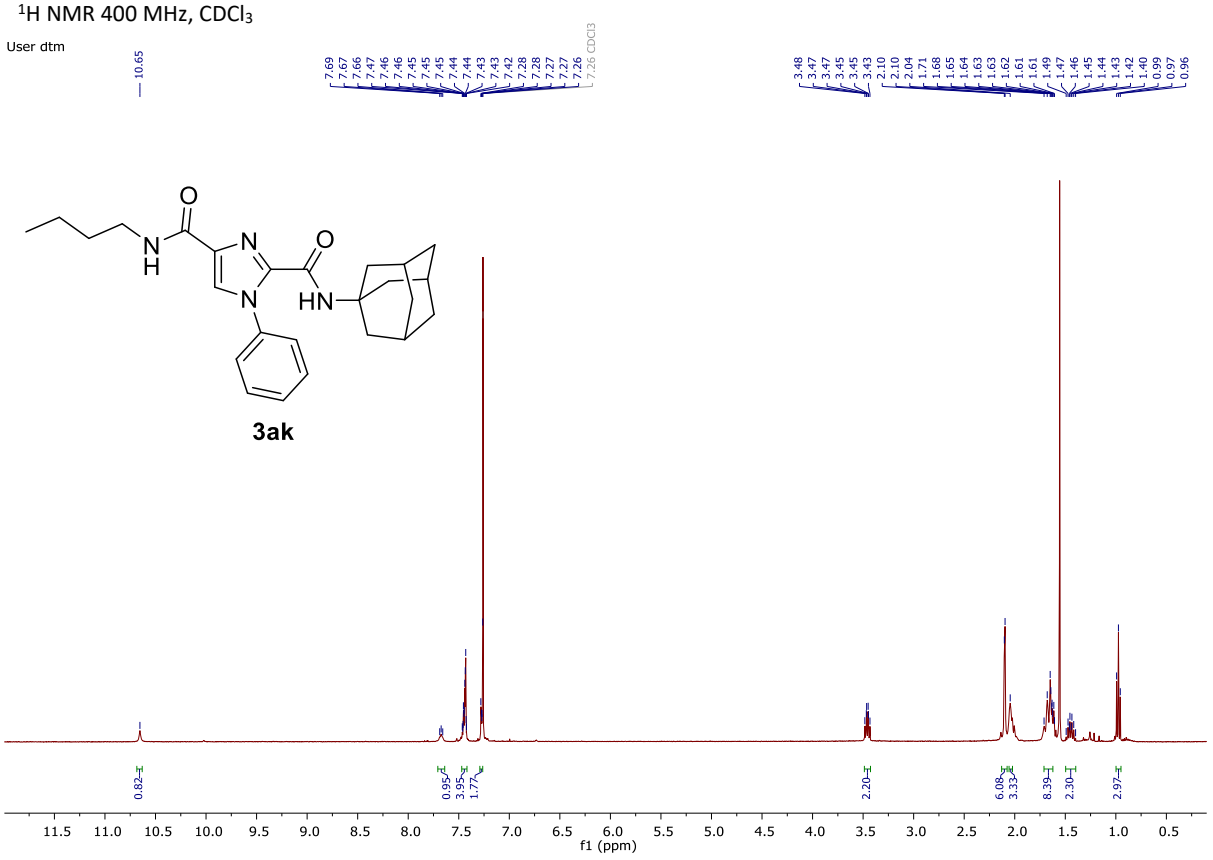

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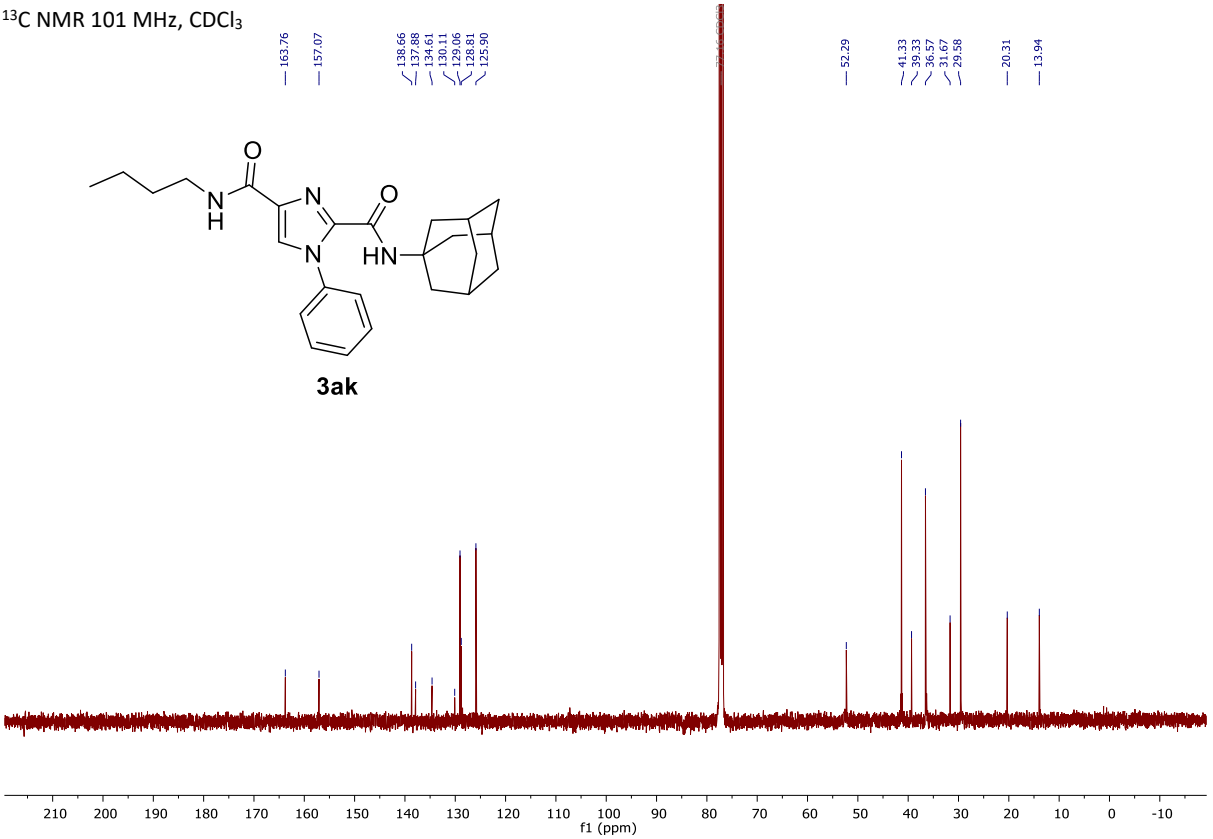
^{13}C NMR 101 MHz, $CDCl_3$



3ak

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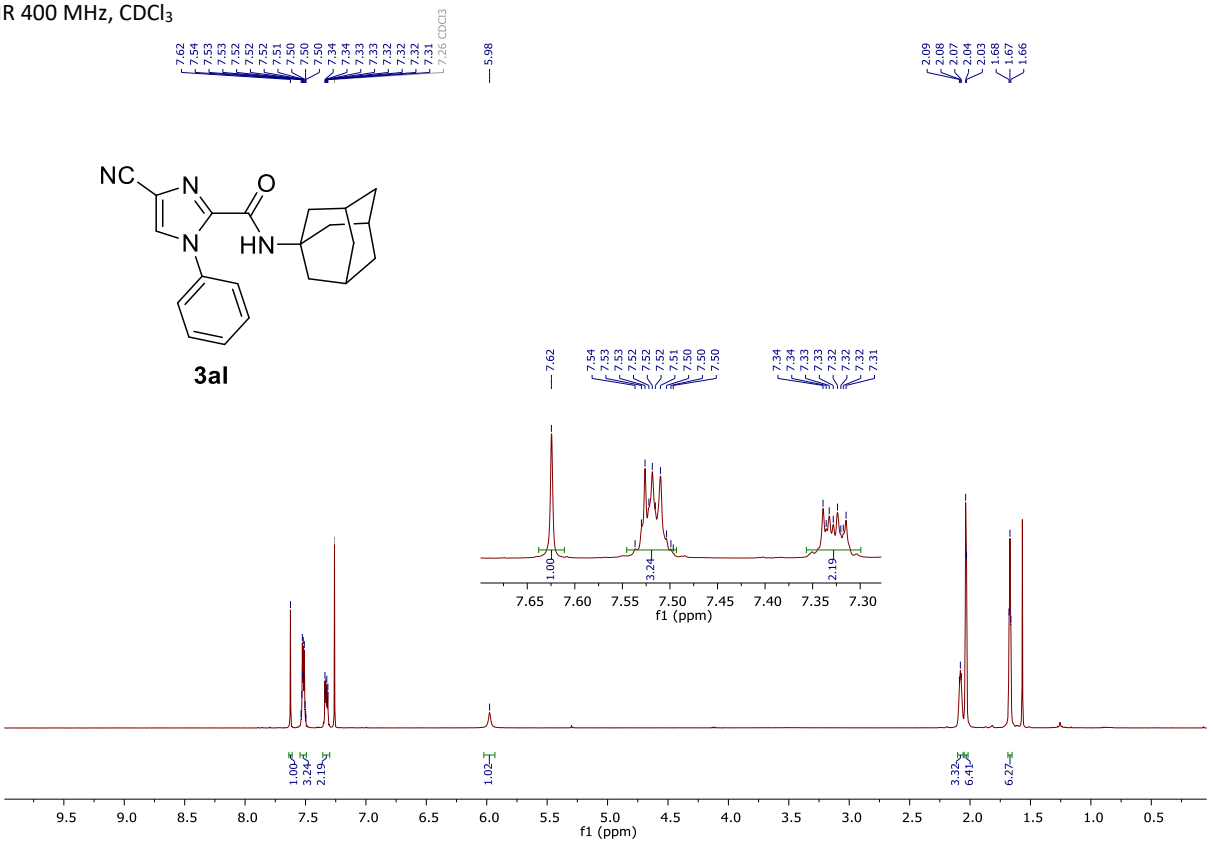

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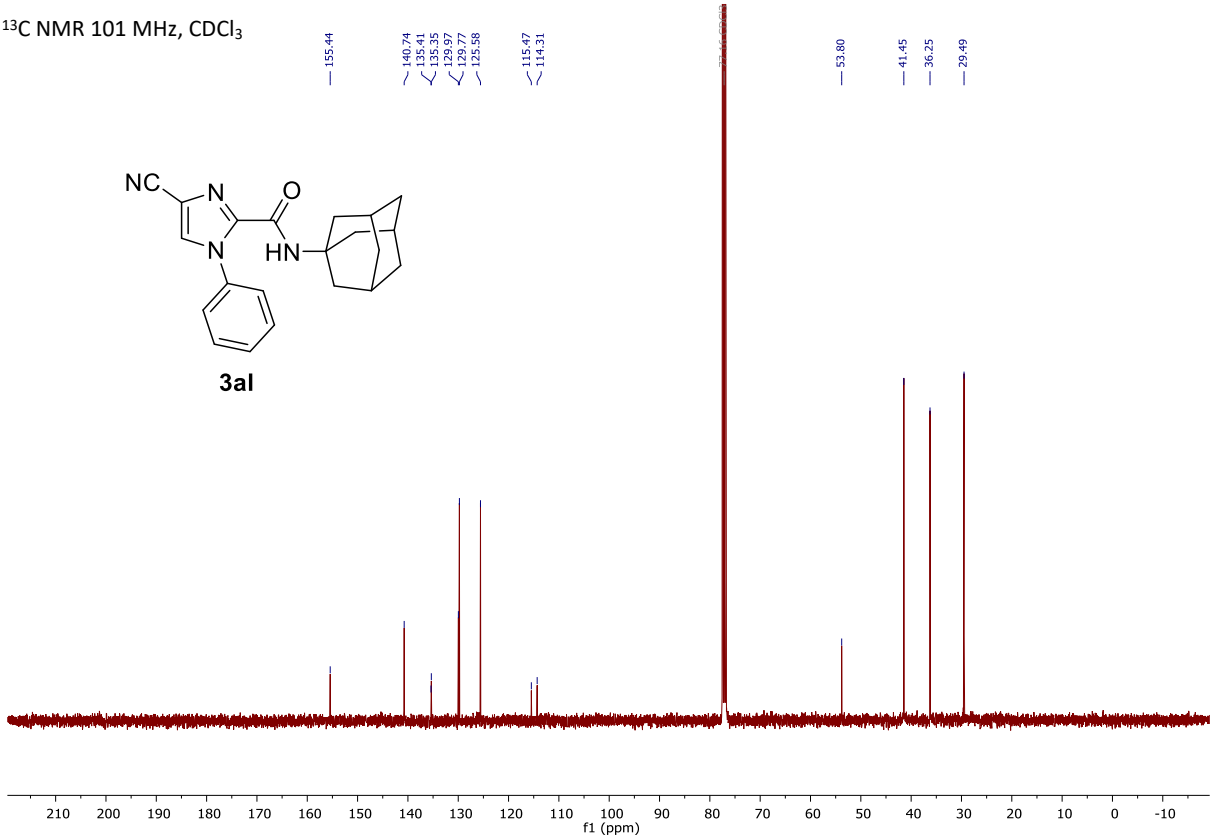

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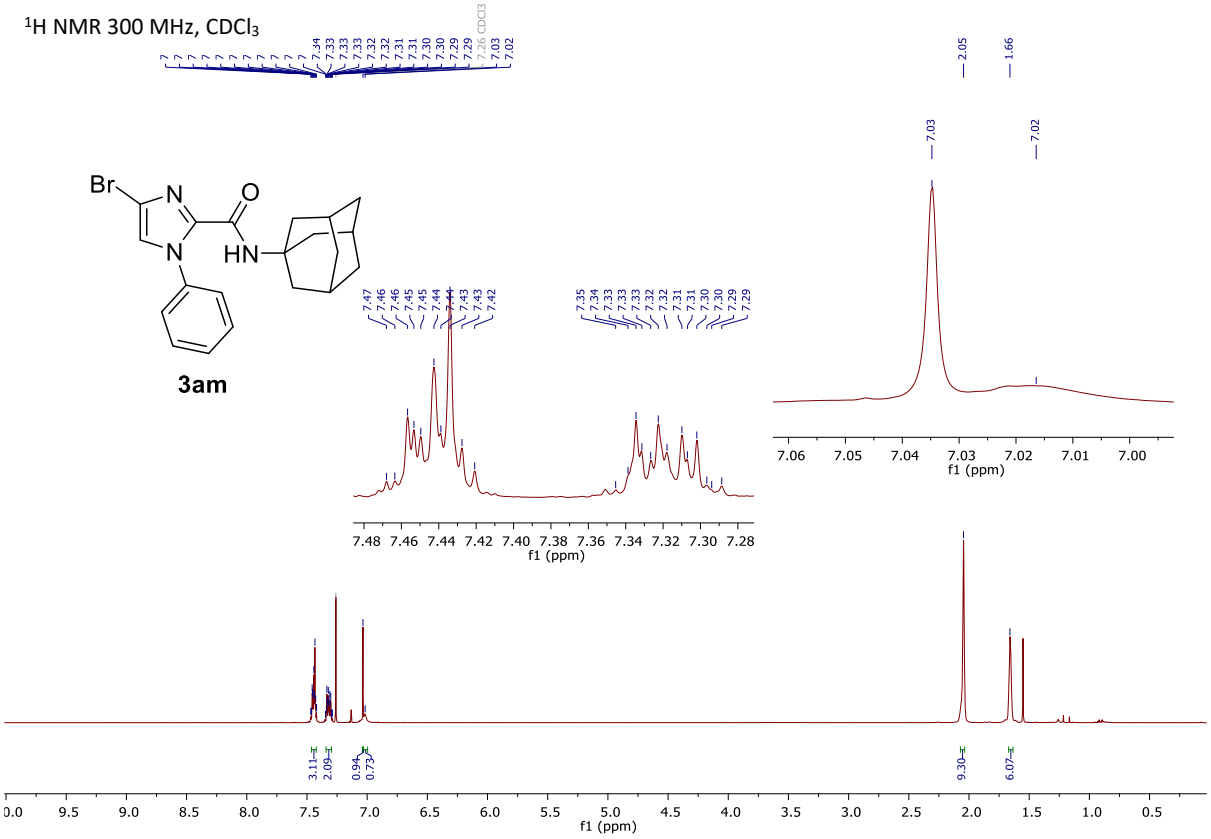

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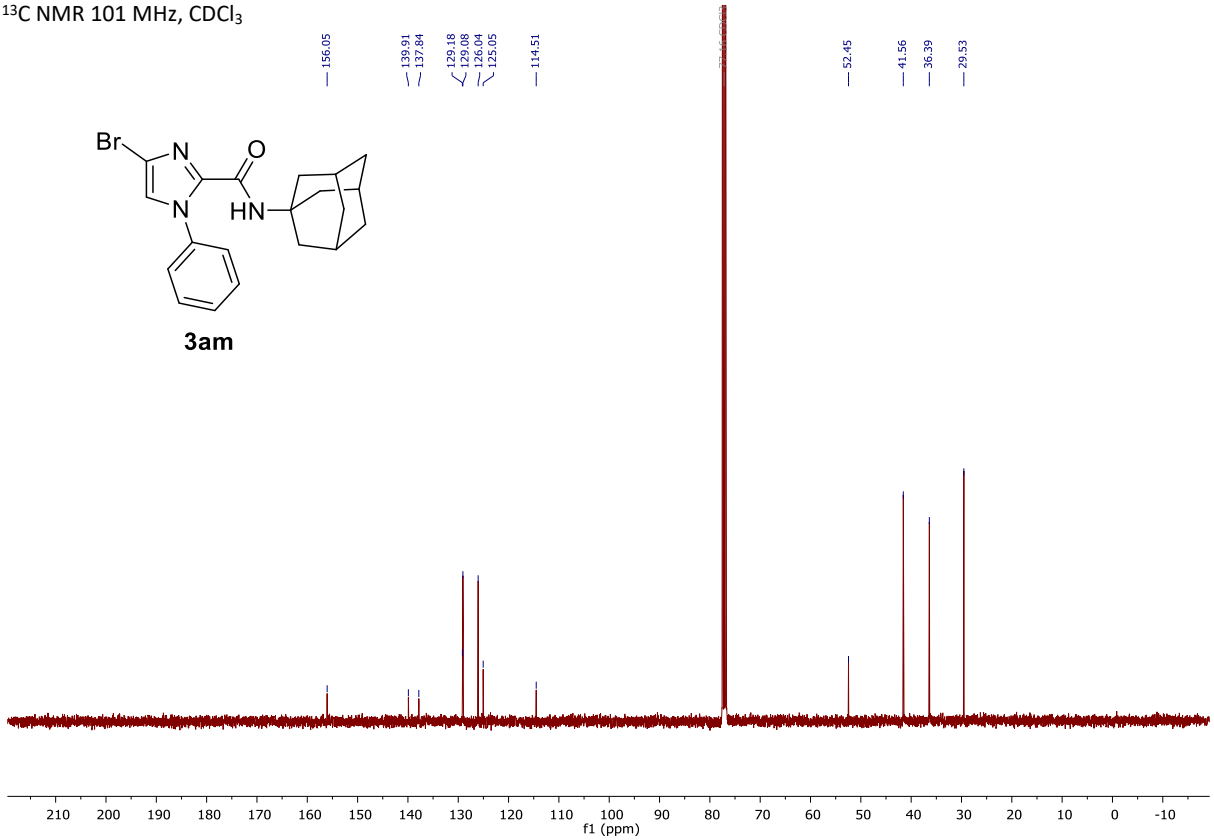

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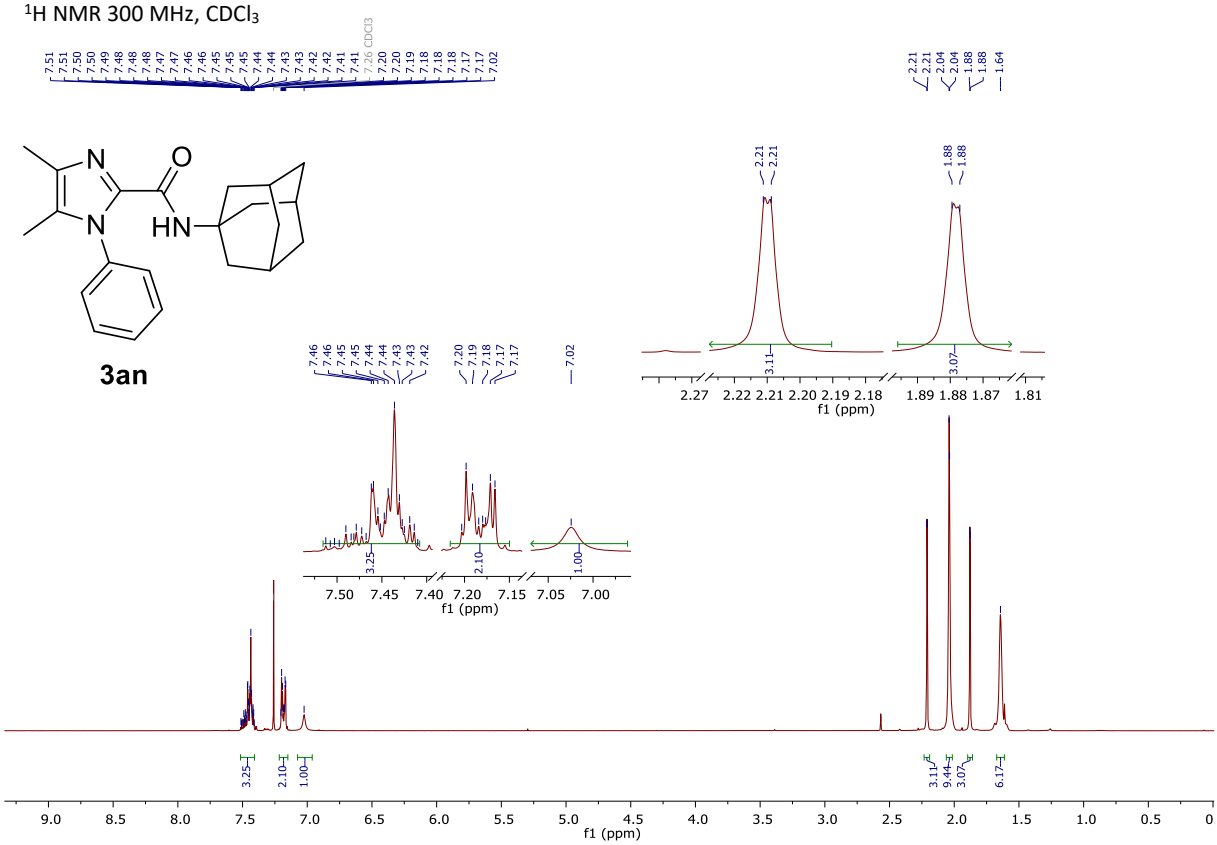
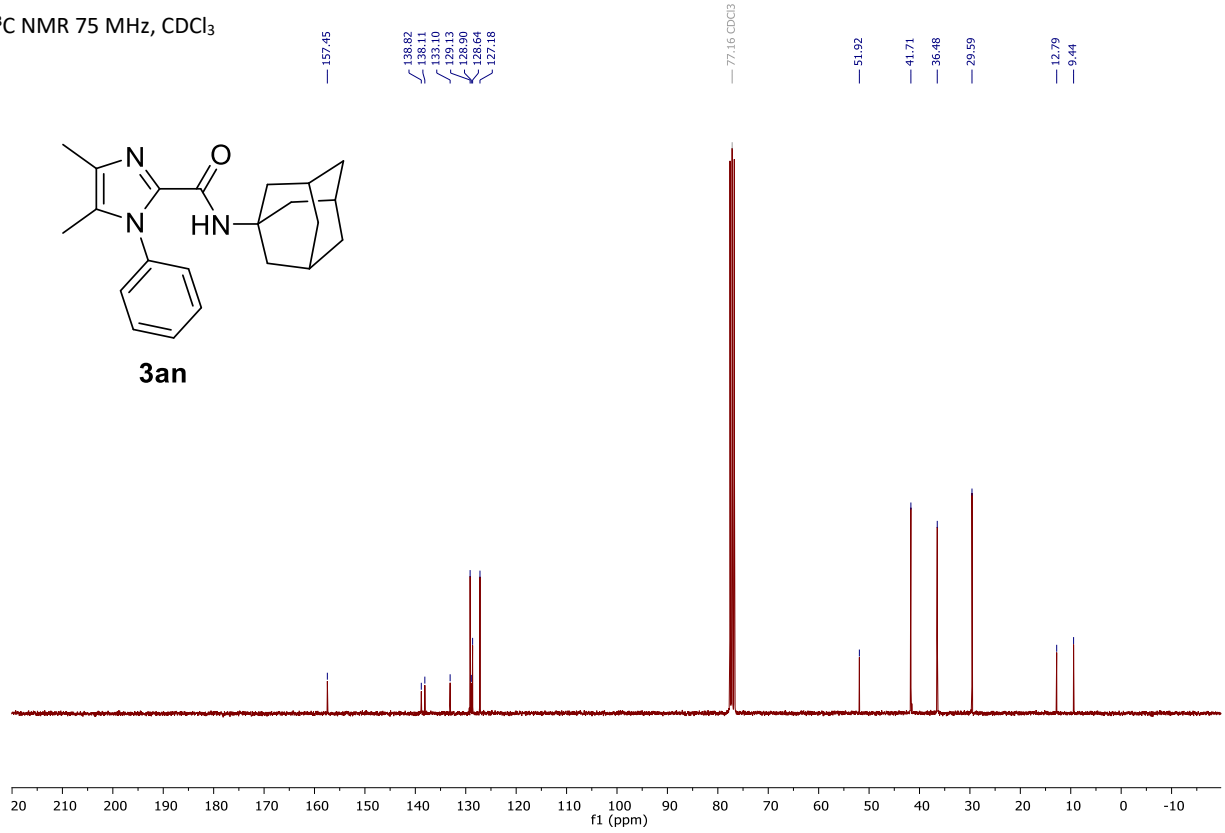


^{13}C NMR 75 MHz, $CDCl_3$



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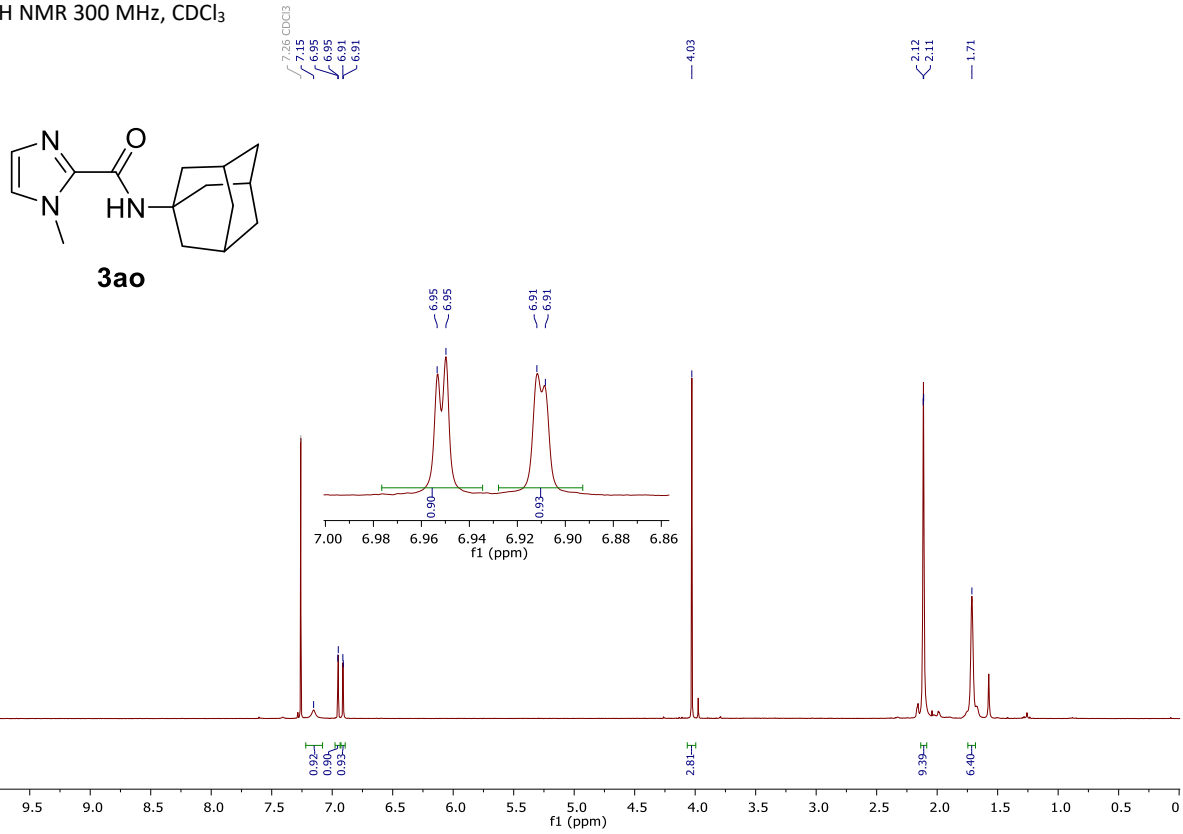

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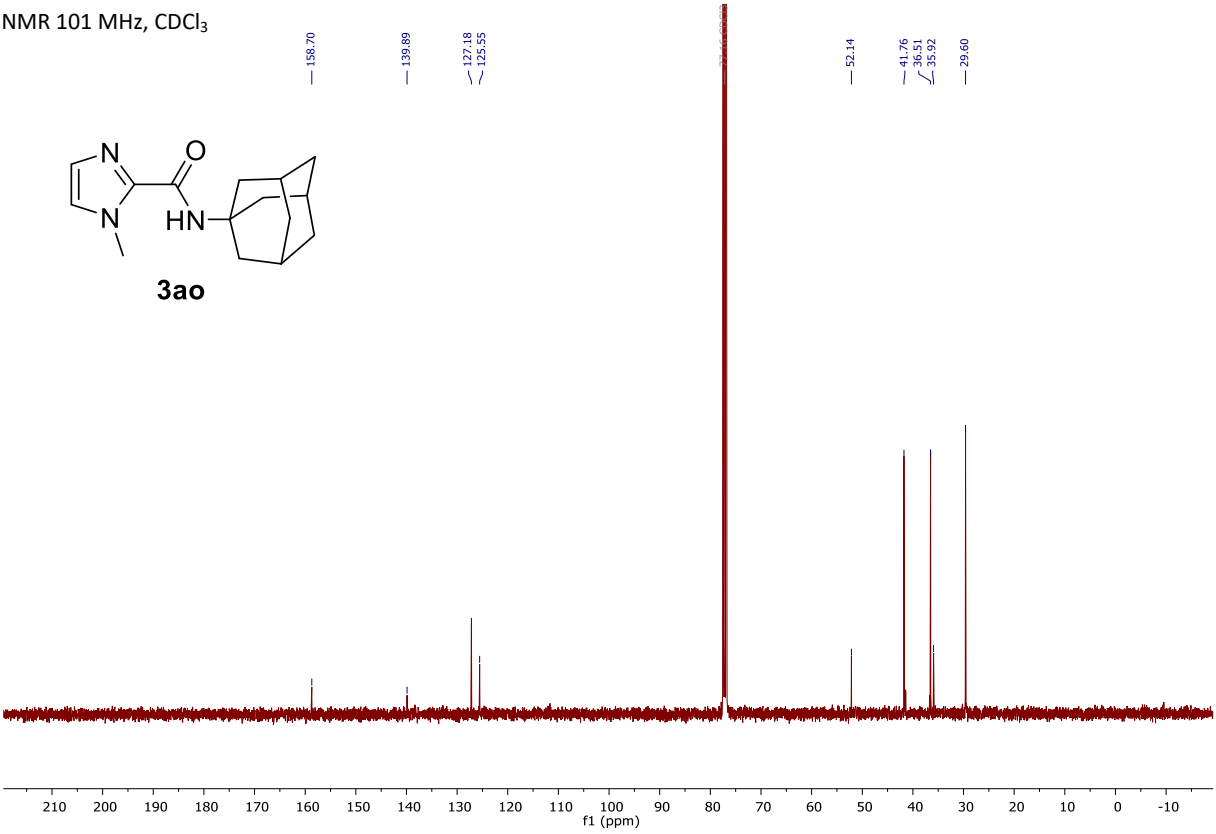

3ao

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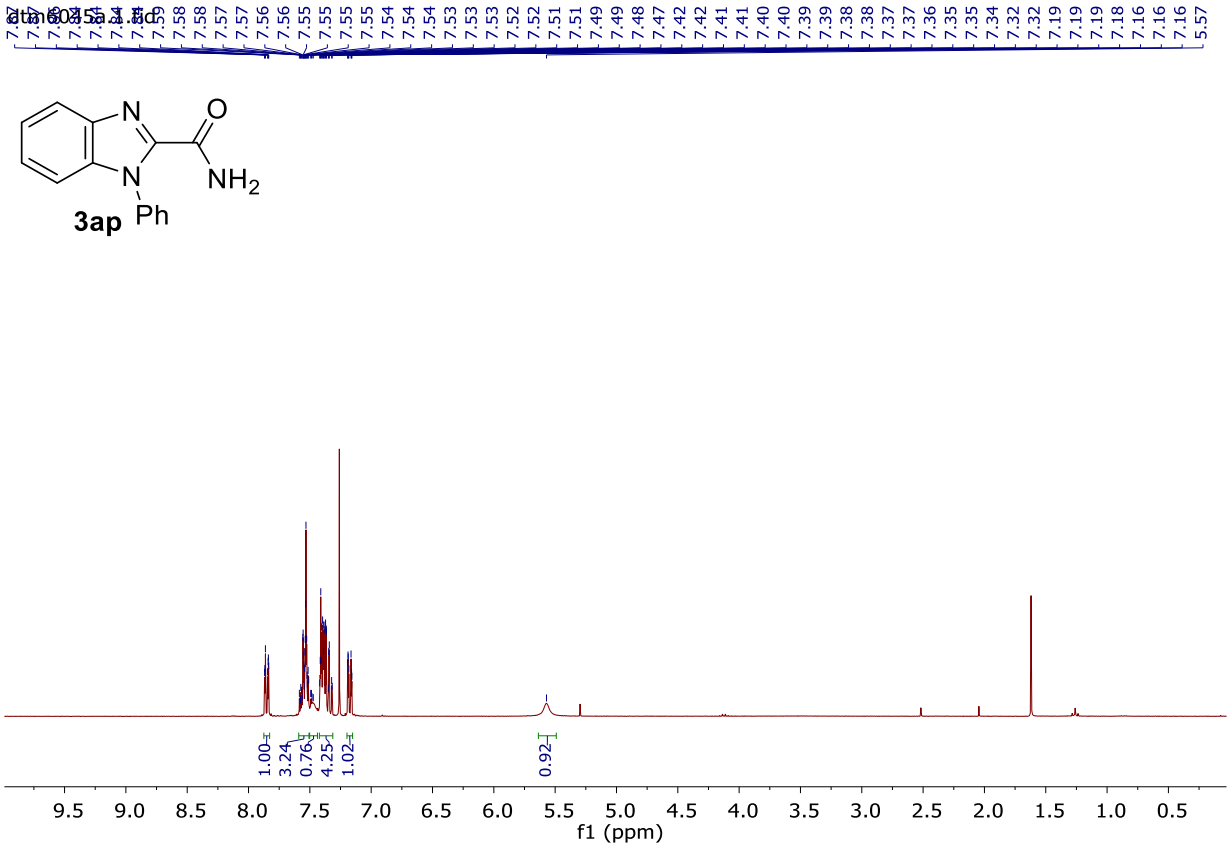

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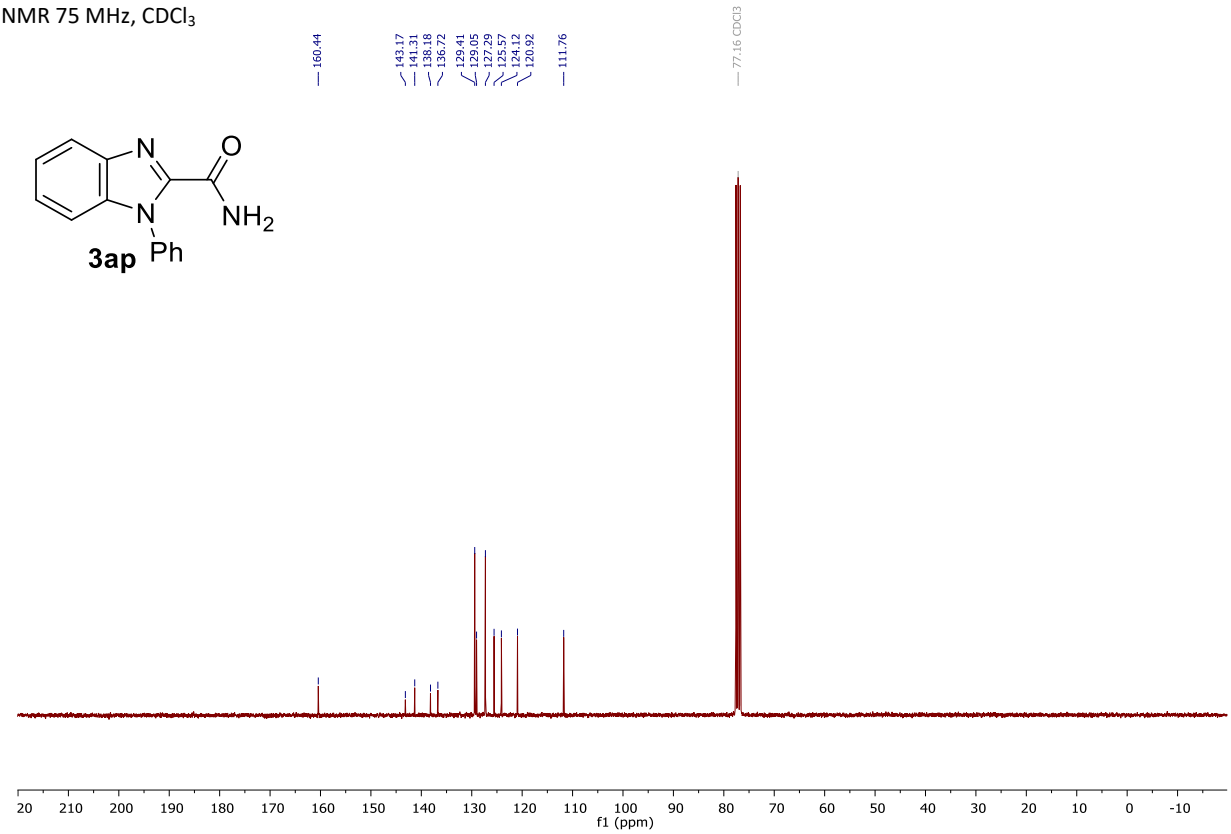

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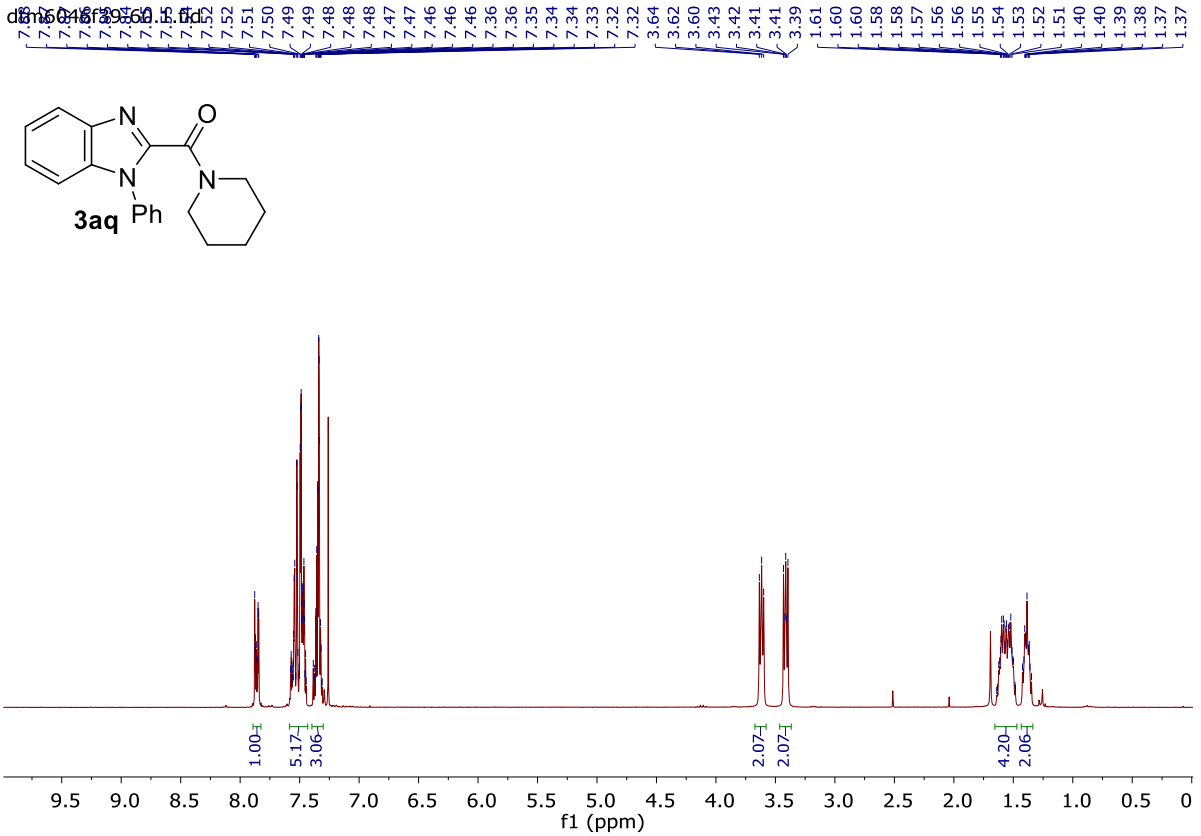

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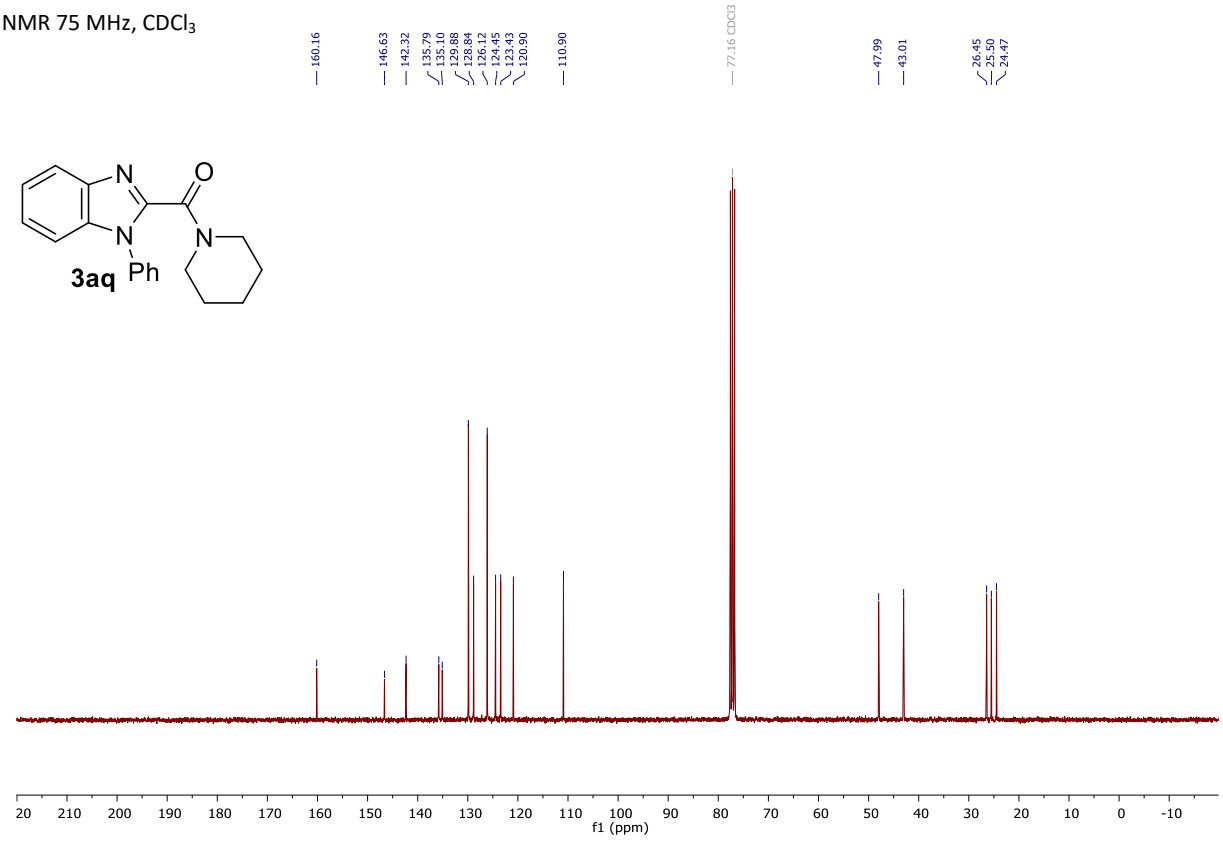

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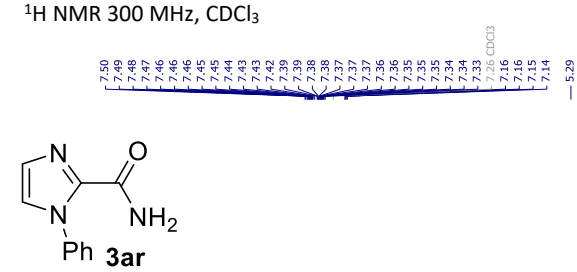

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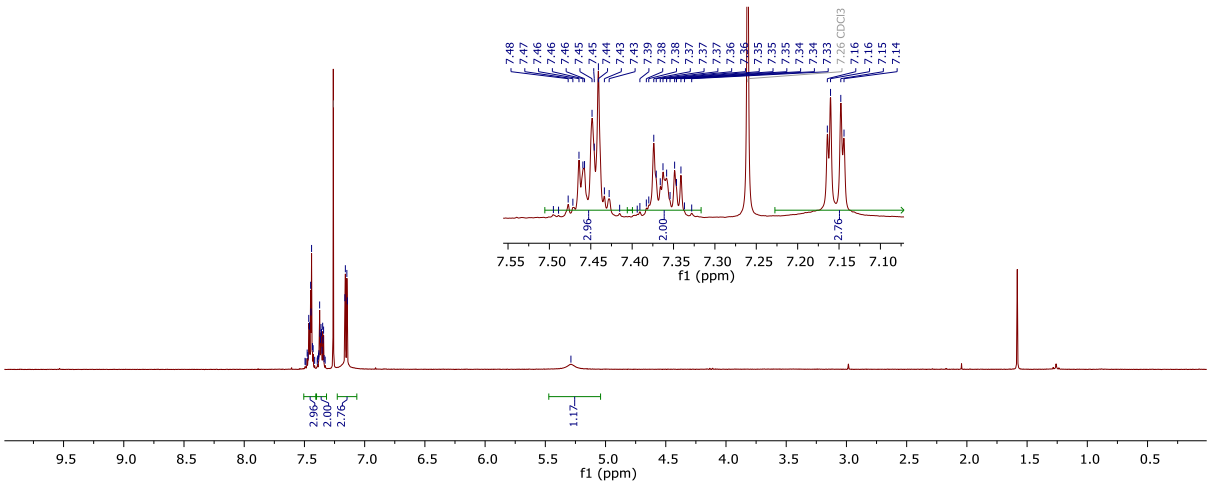

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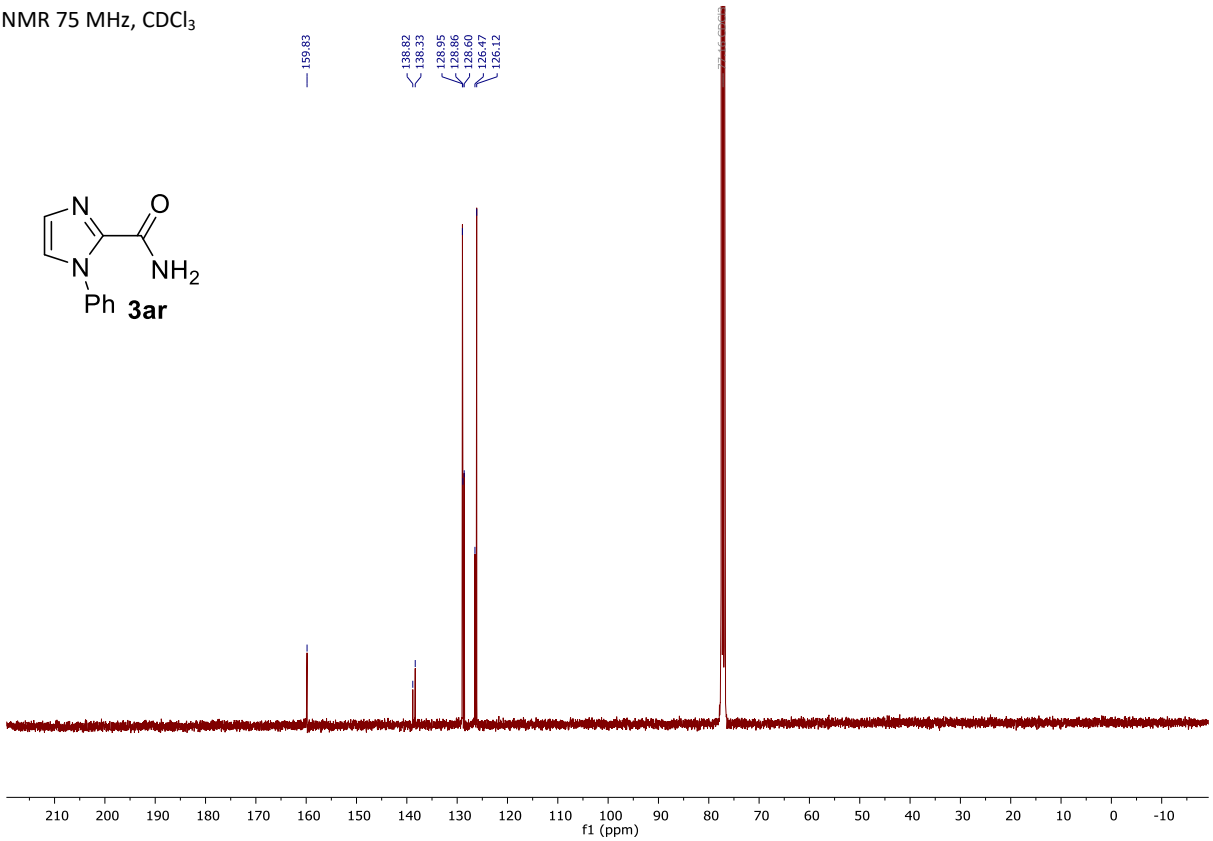

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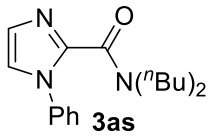

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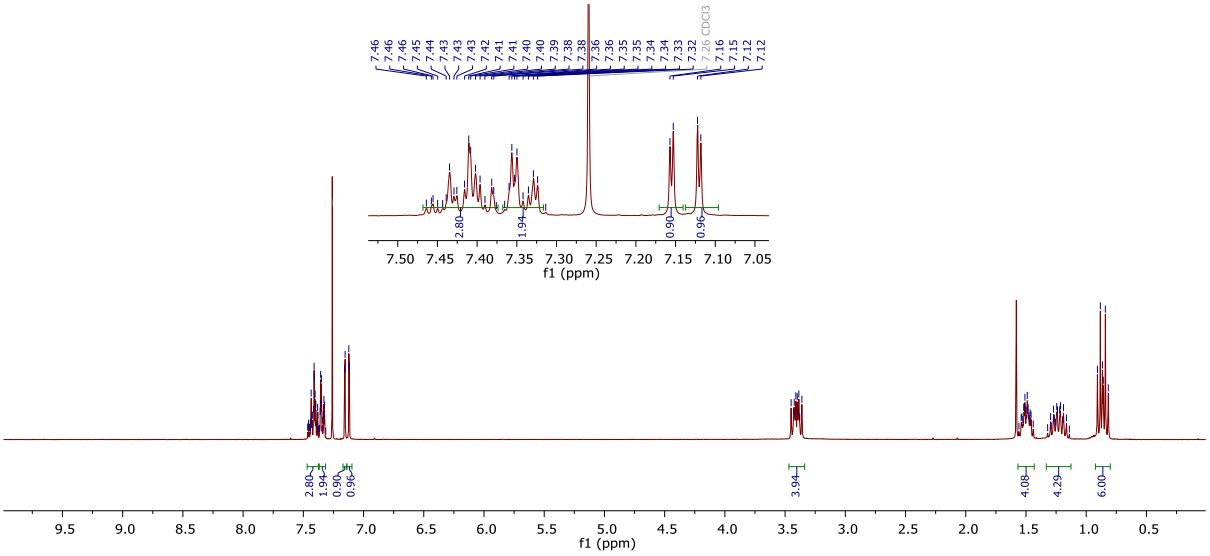

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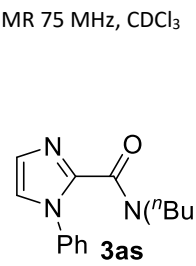

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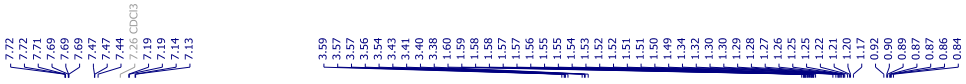

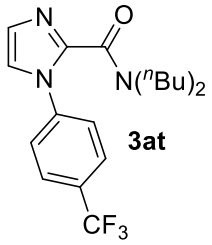

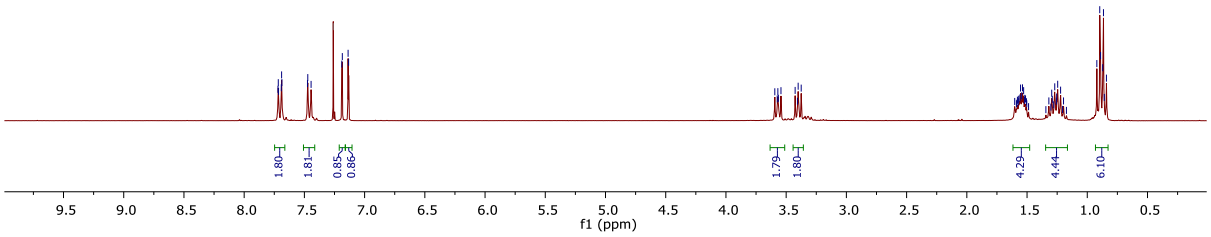

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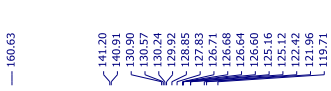
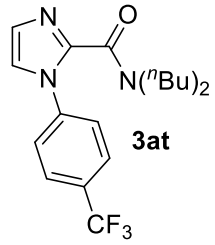
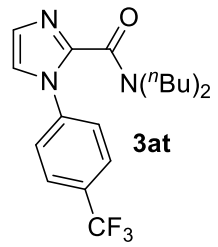


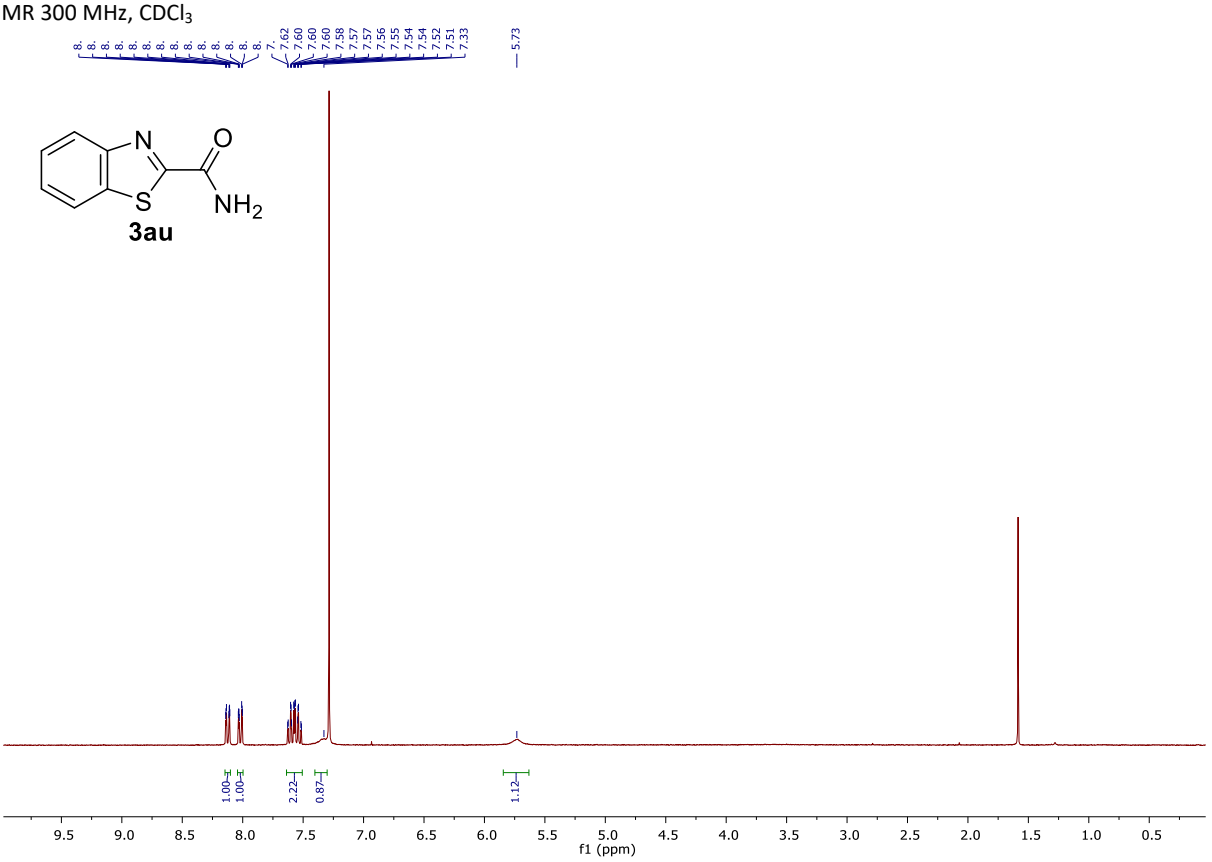


^{19}F NMR 282 MHz, $CDCl_3$

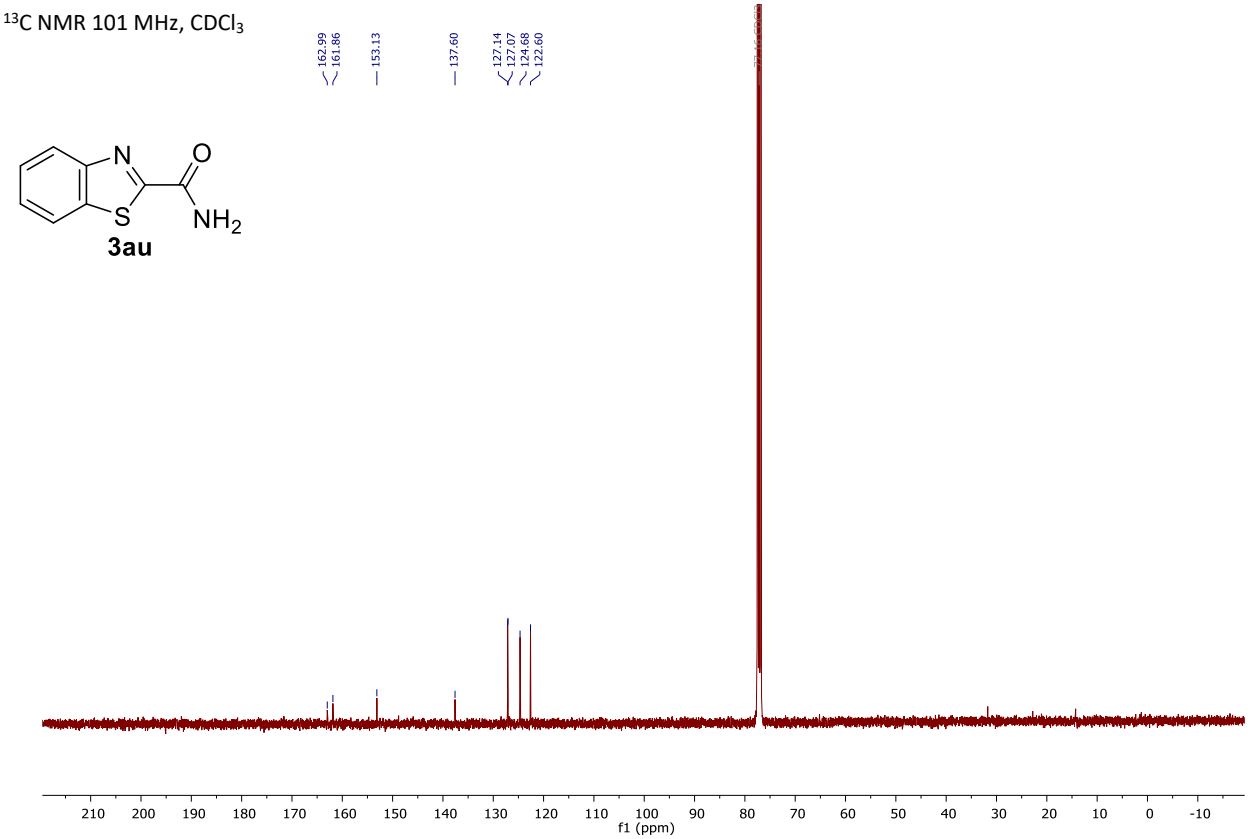


3at

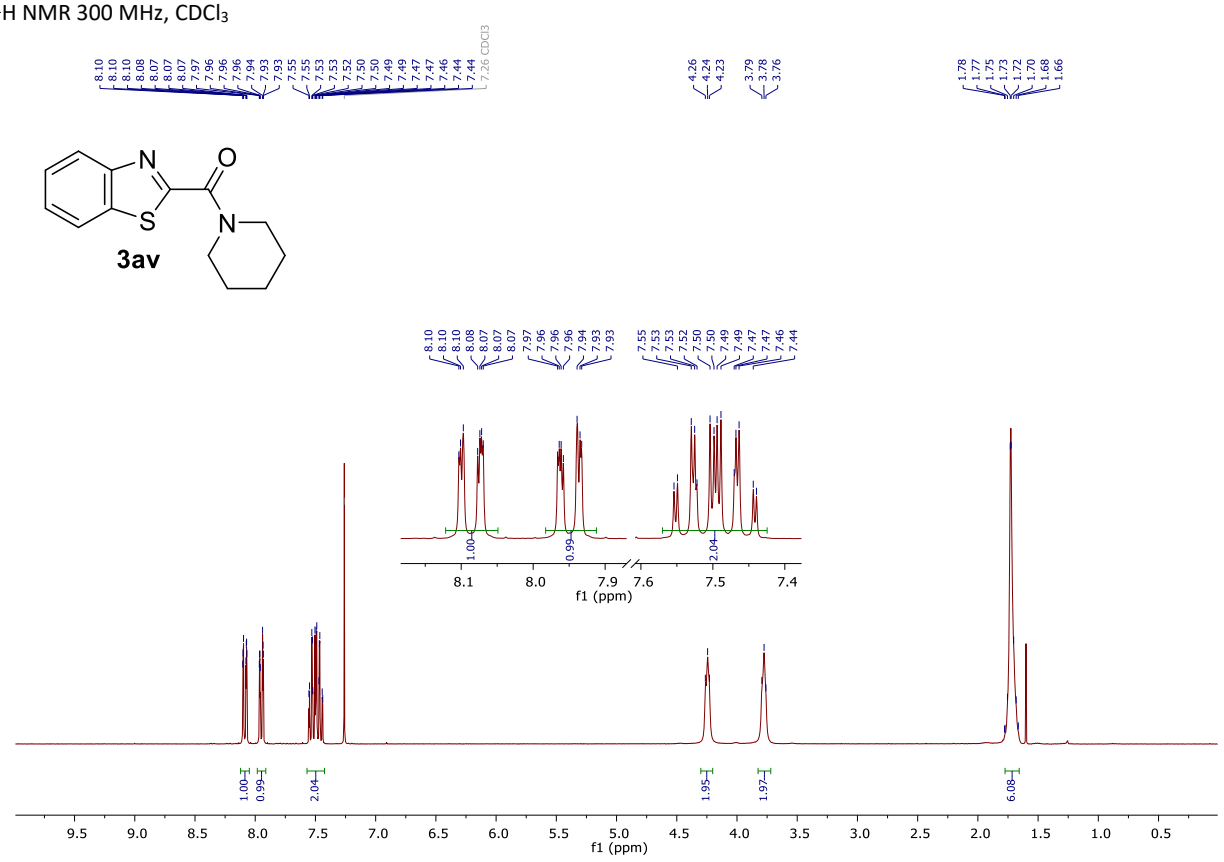
^{1}H NMR 300 MHz, $CDCl_3$



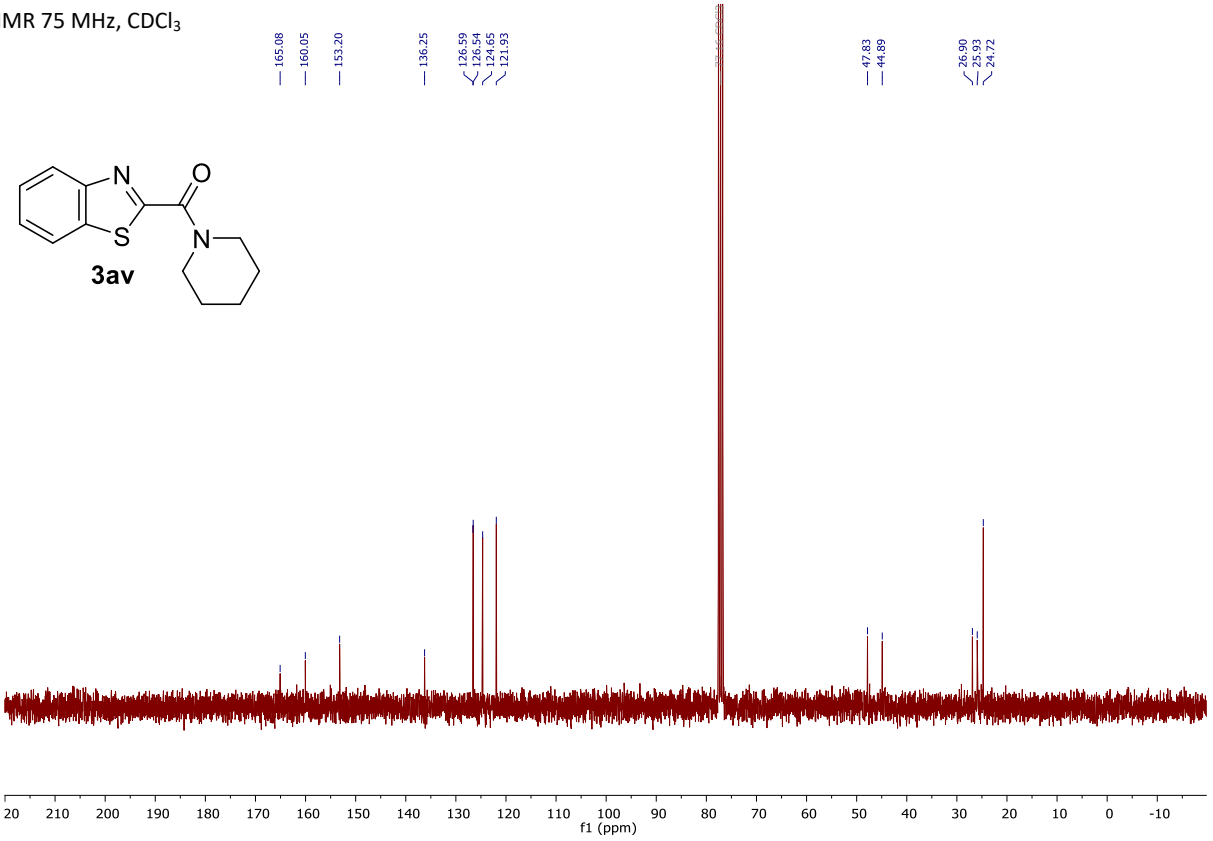
^{13}C NMR 101 MHz, $CDCl_3$



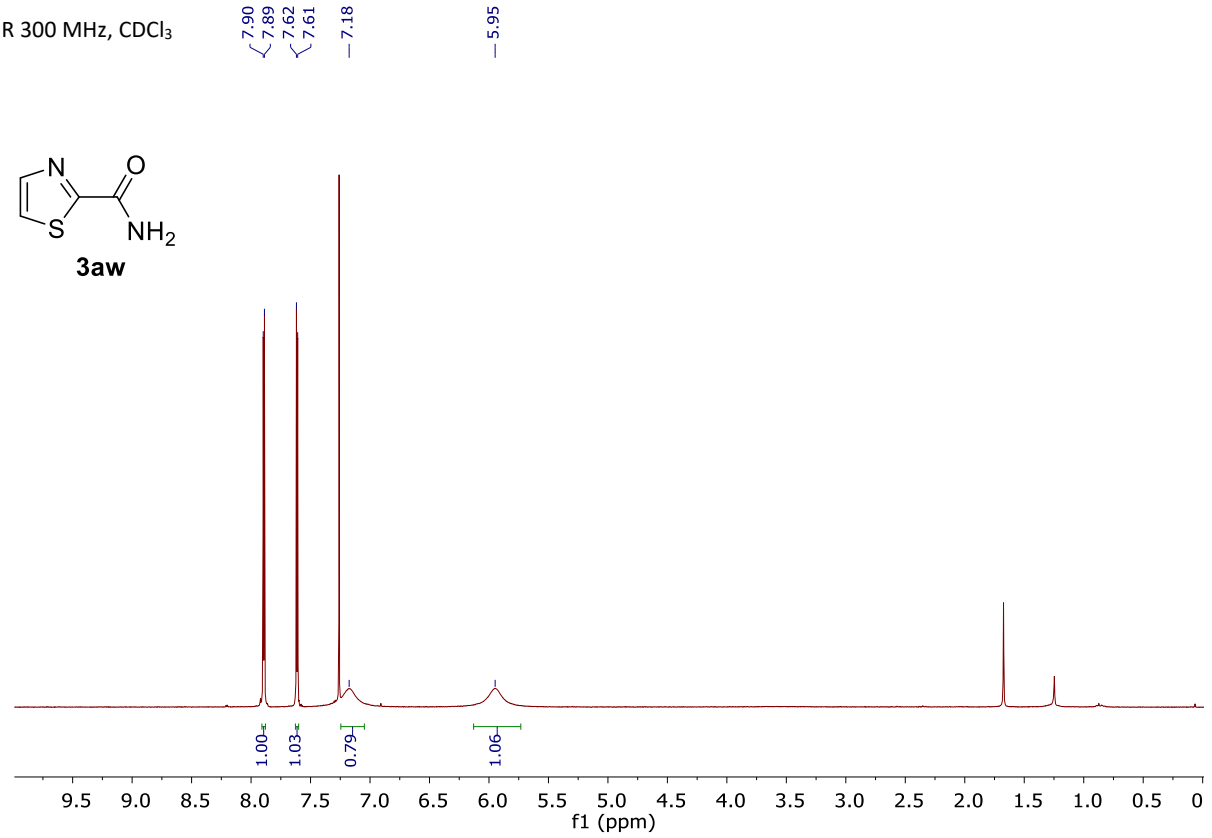
^{1}H NMR 300 MHz, $CDCl_3$



^{13}C NMR 75 MHz, $CDCl_3$



^{1}H NMR 300 MHz, $CDCl_3$



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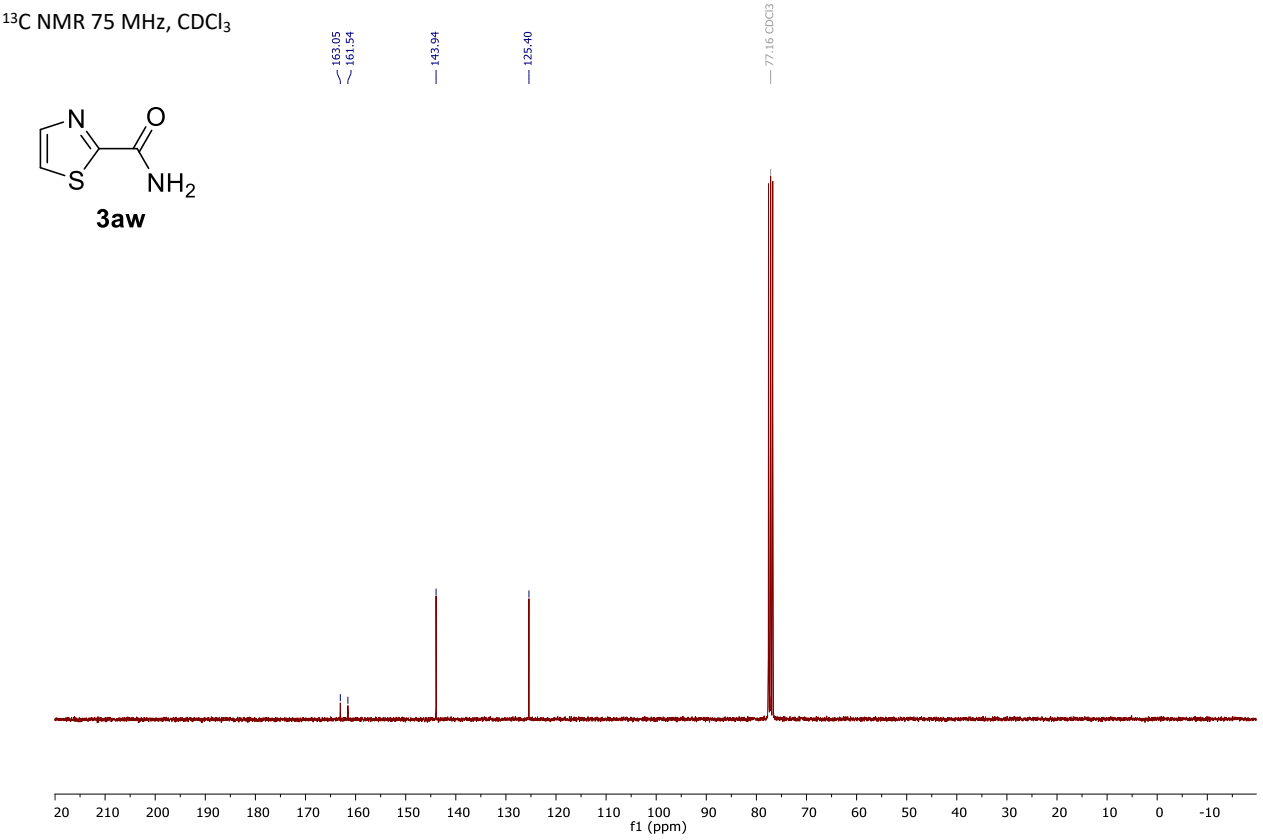
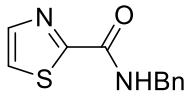
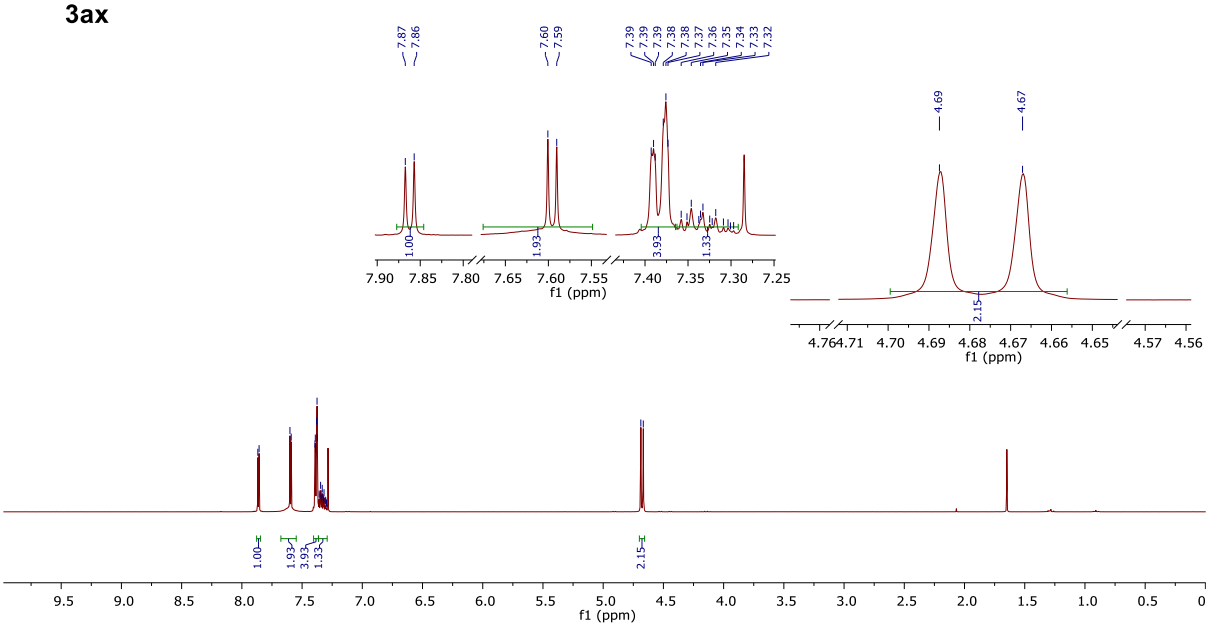


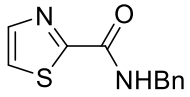
^{1}H NMR 300 MHz, $CDCl_3$



3ax



^{13}C NMR 75 MHz, $CDCl_3$



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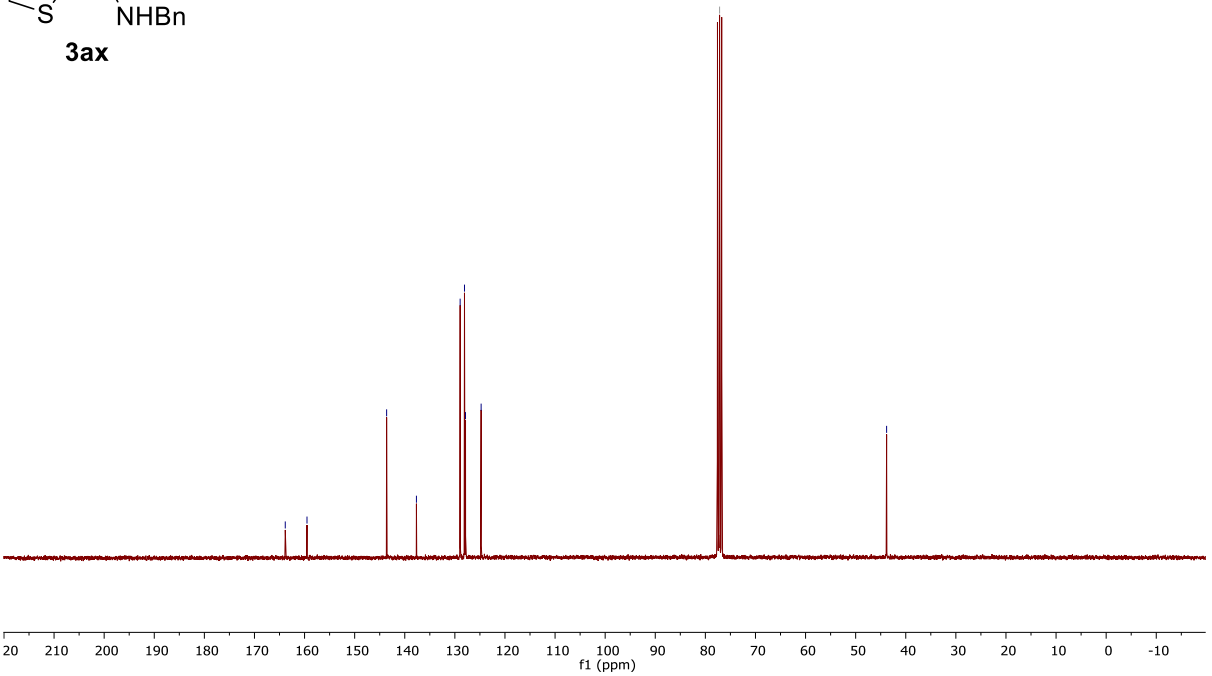

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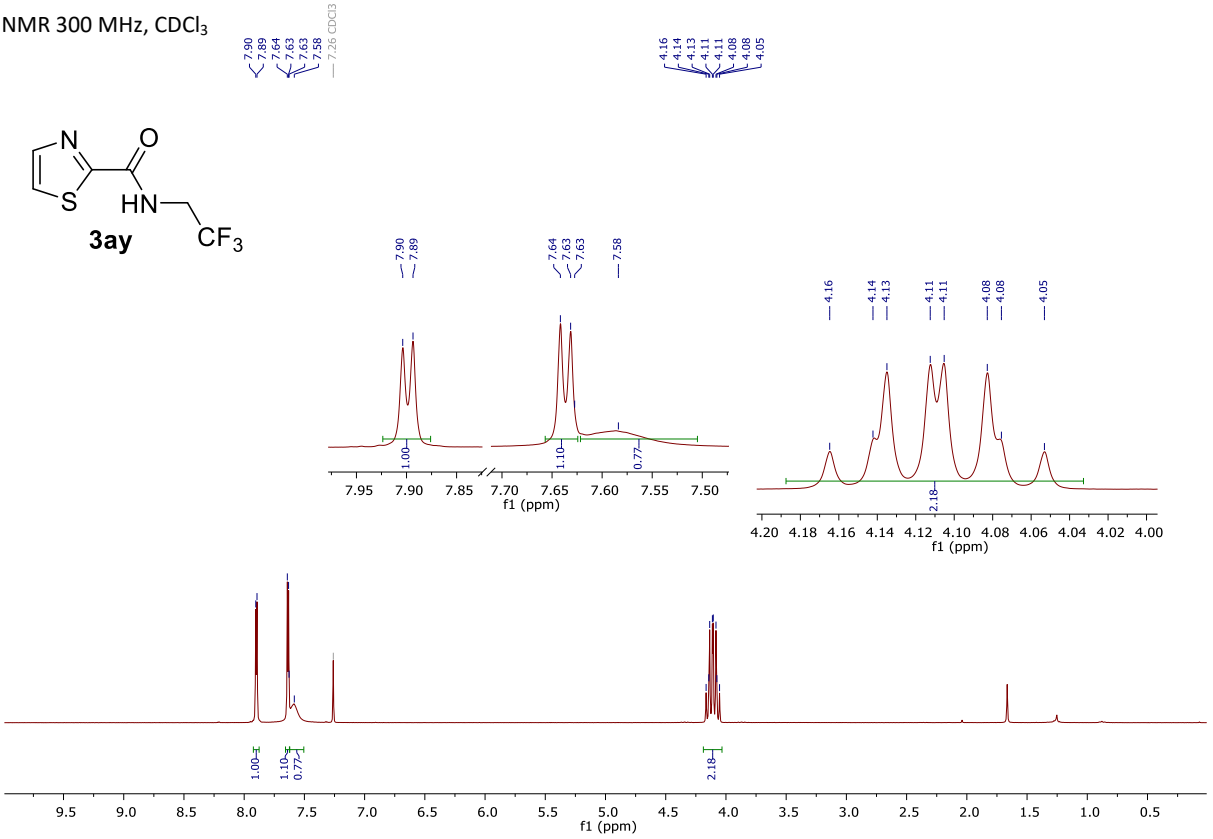

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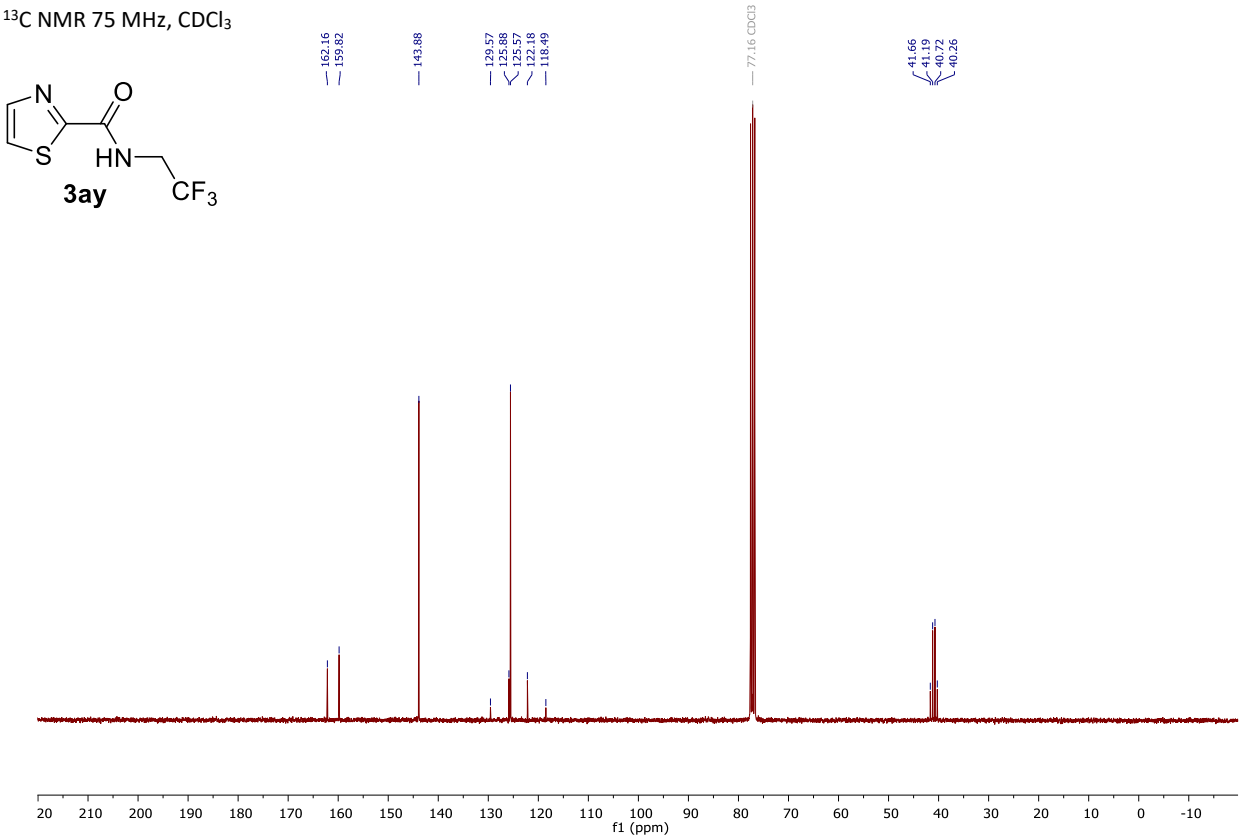
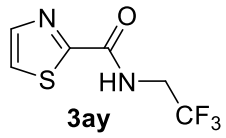


^{19}F NMR 282 MHz, $CDCl_3$



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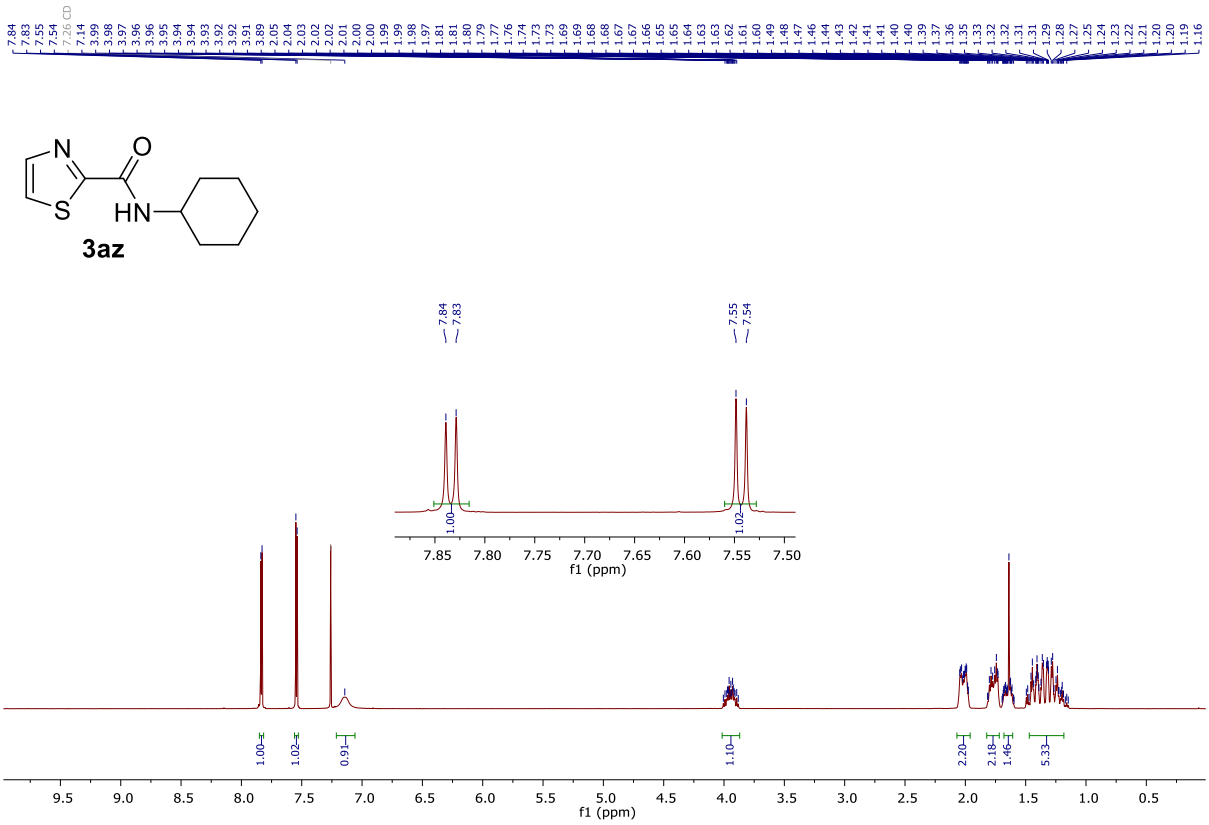

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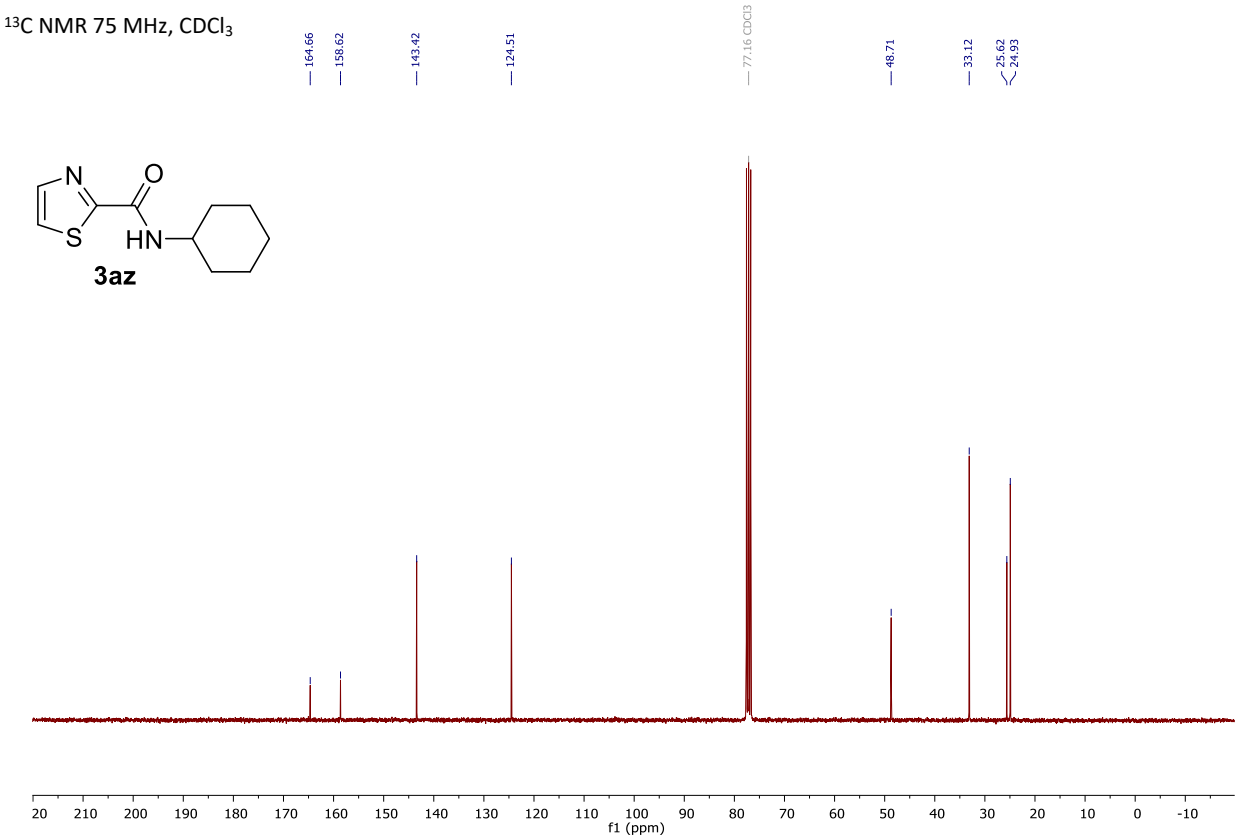

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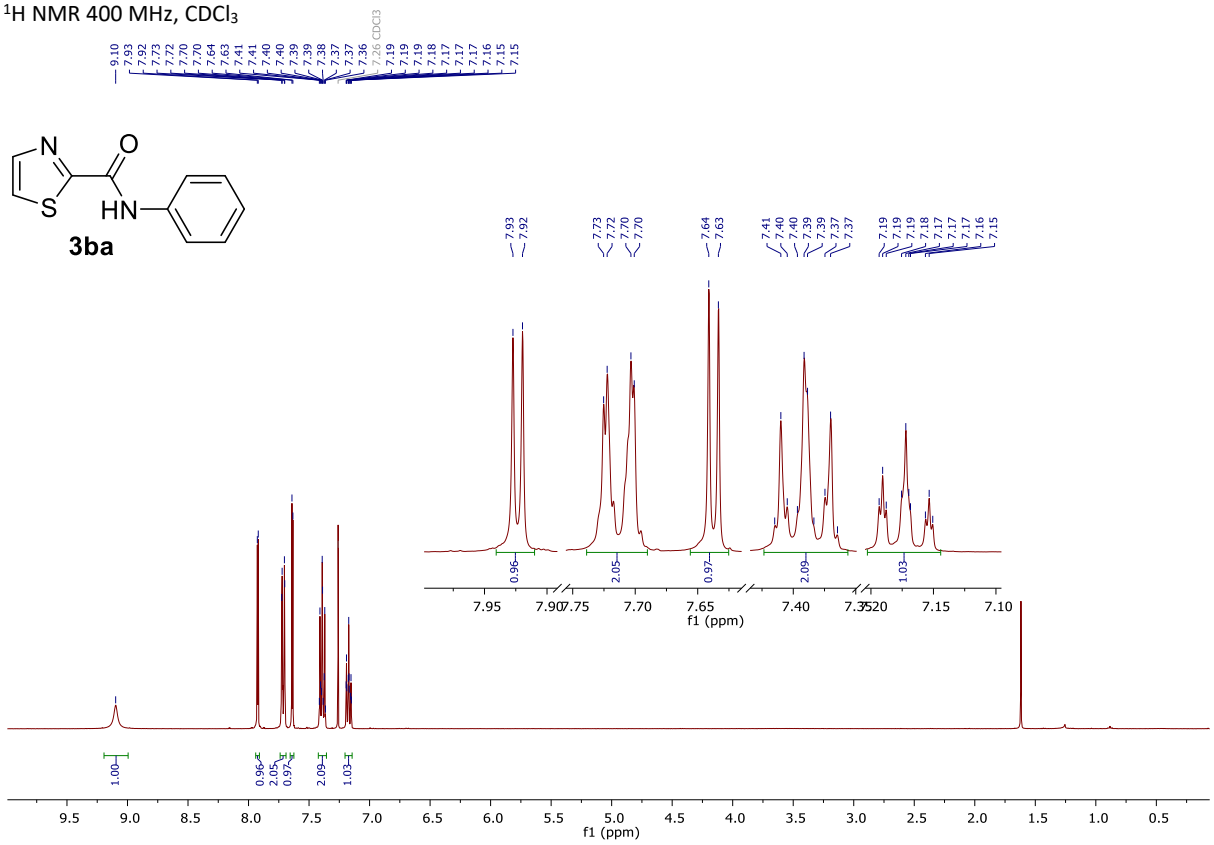
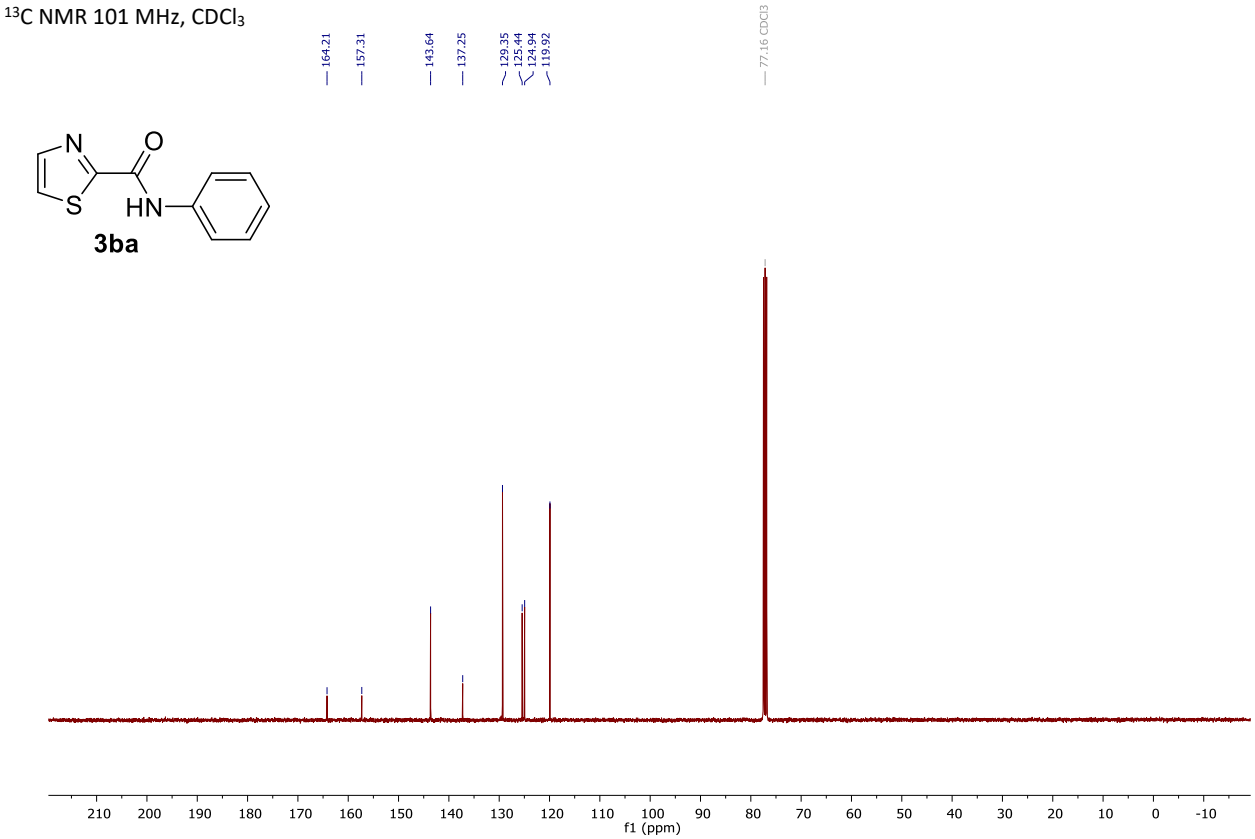


^{13}C NMR 101 MHz, $CDCl_3$



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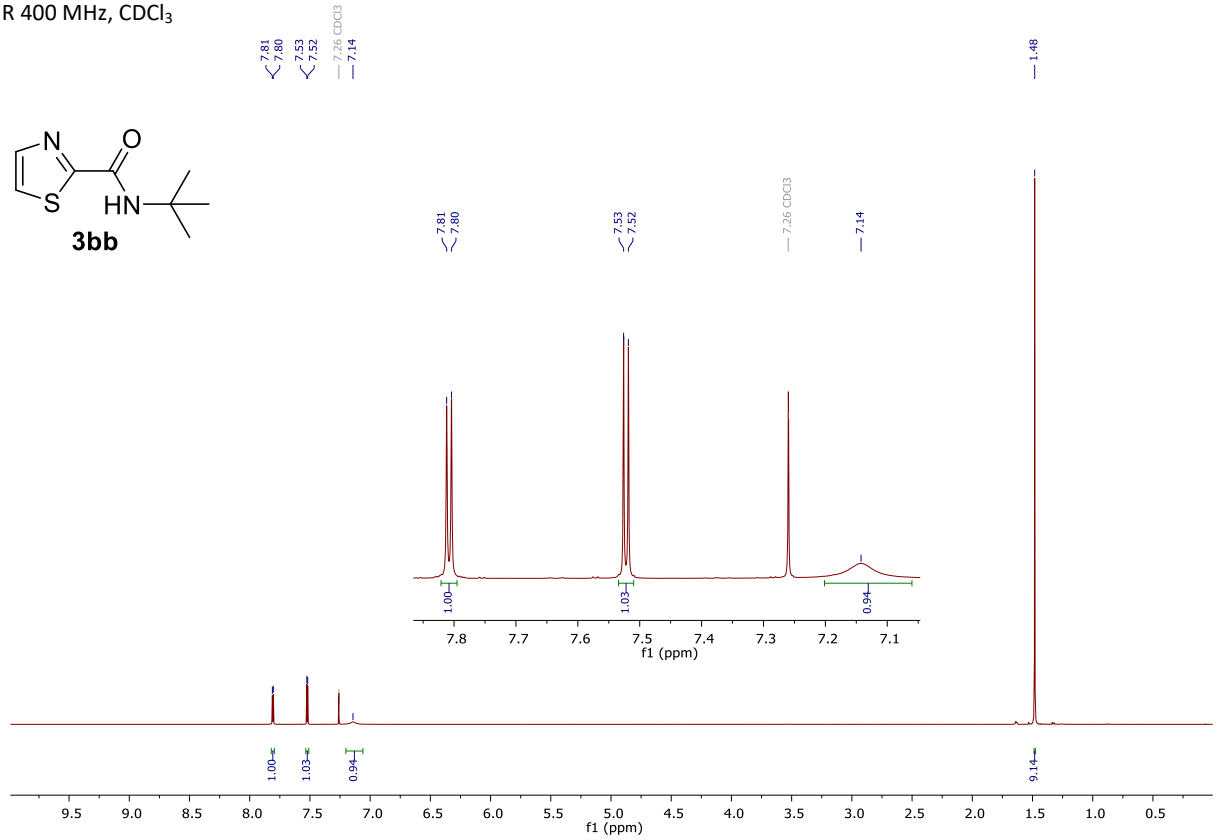

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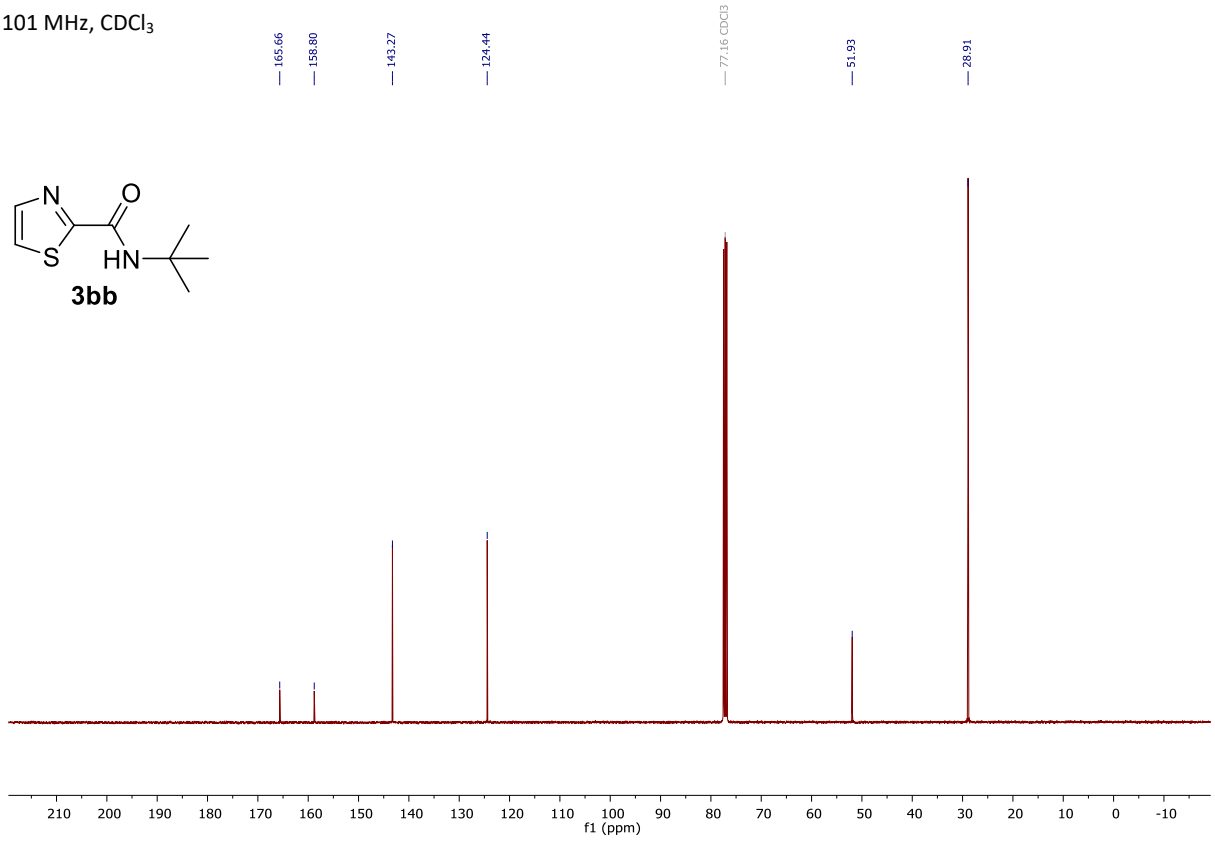

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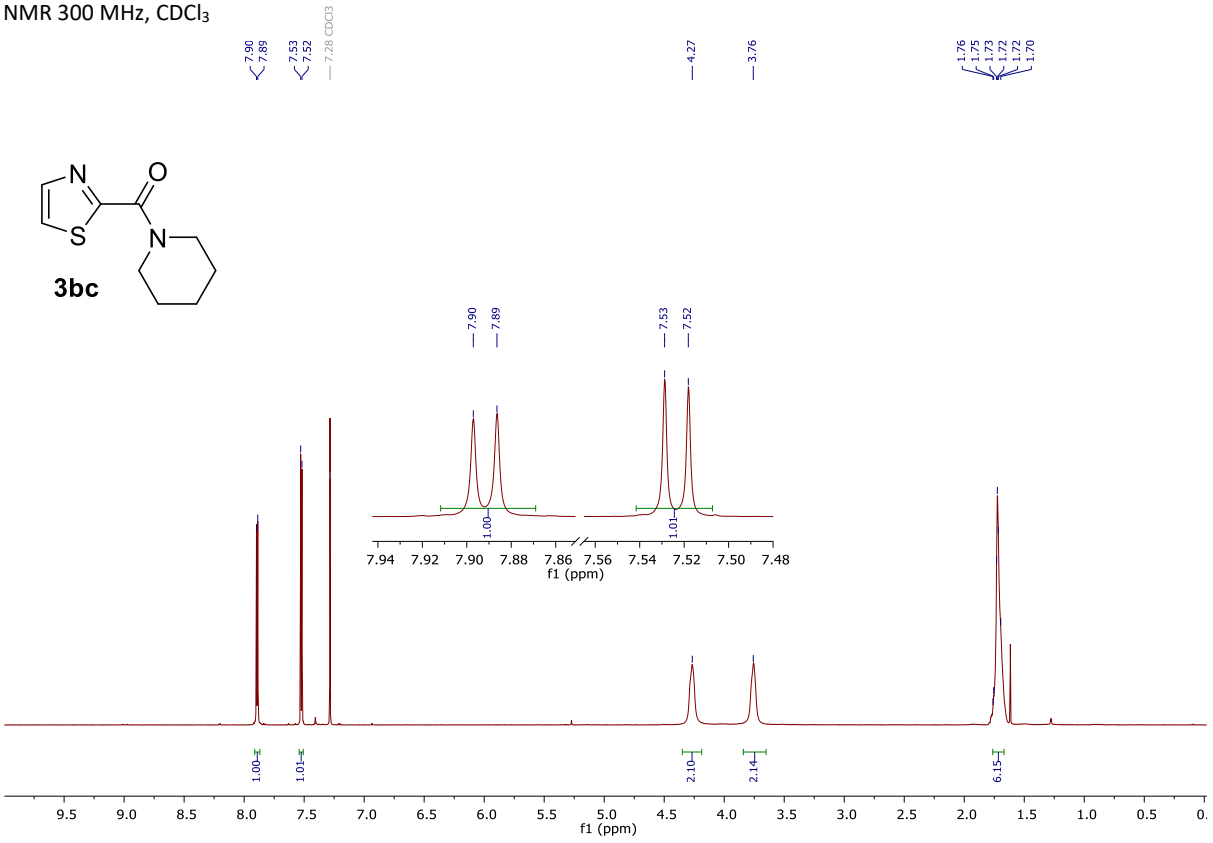

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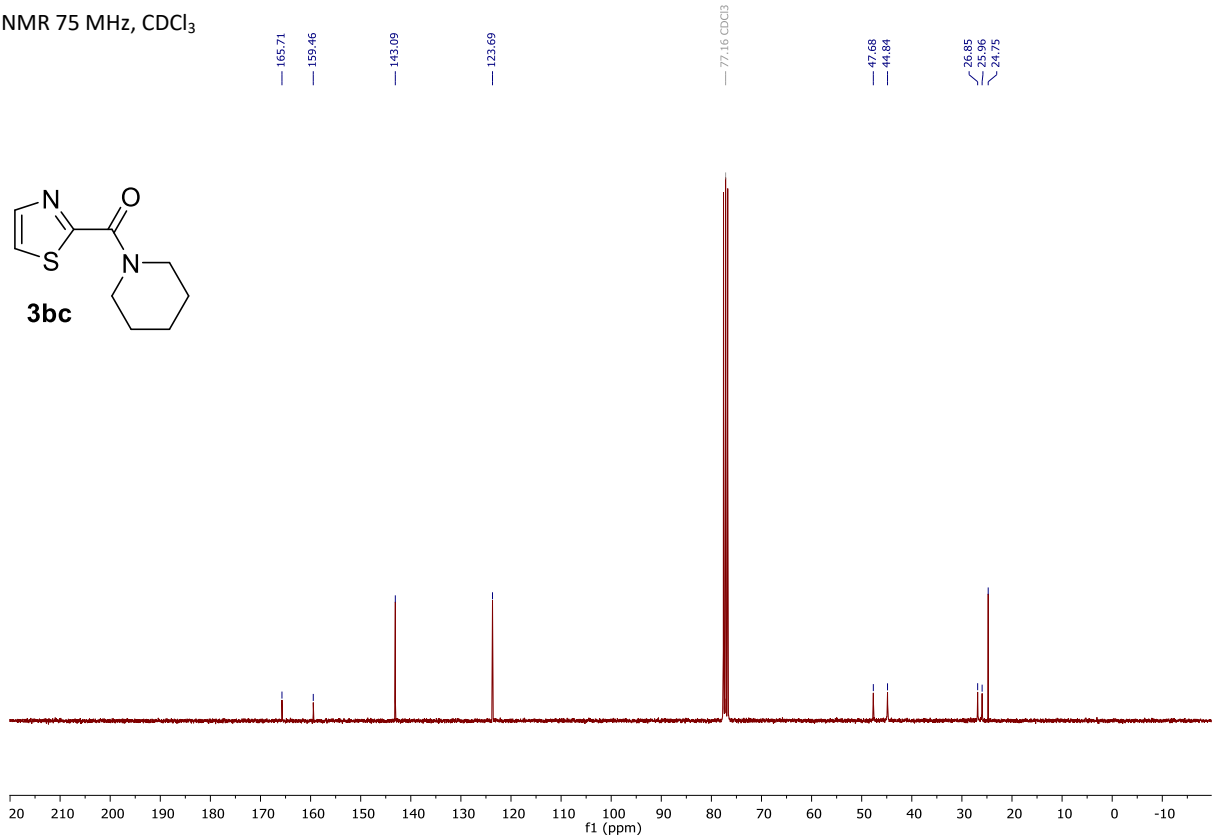

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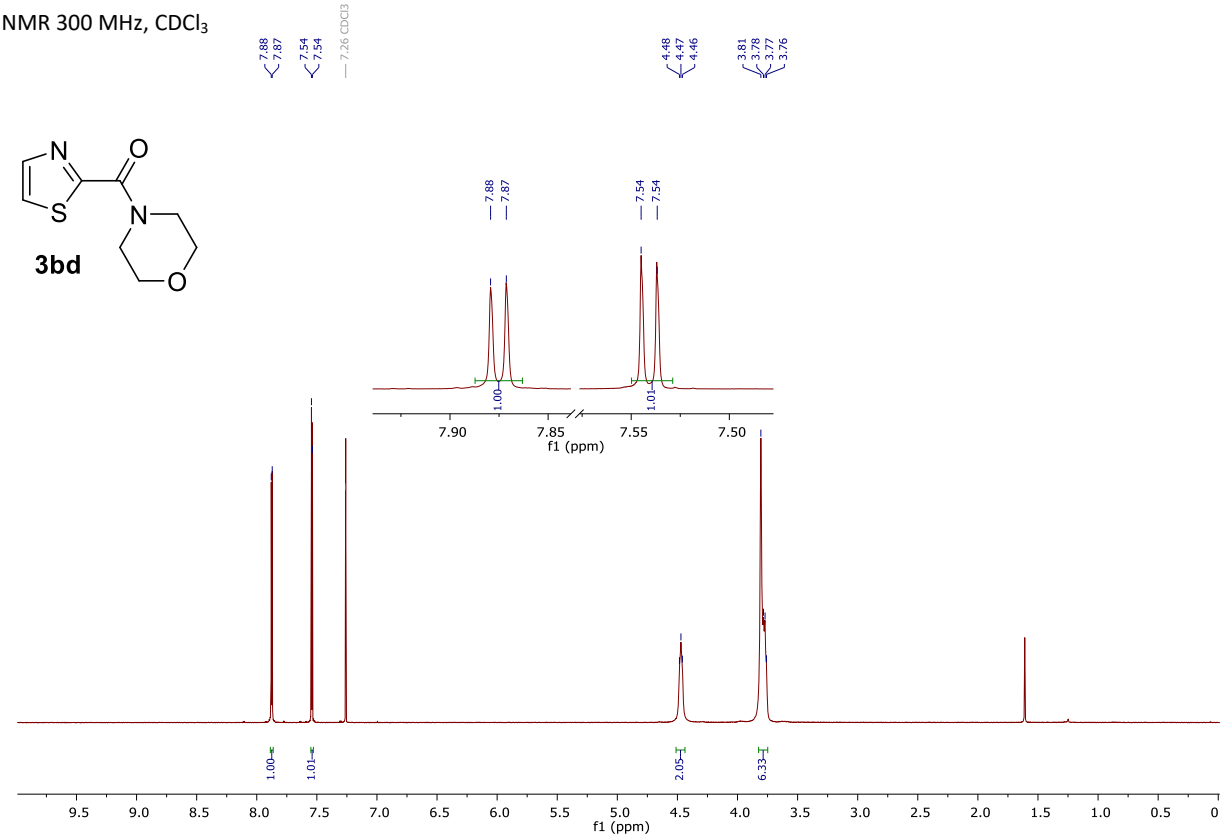

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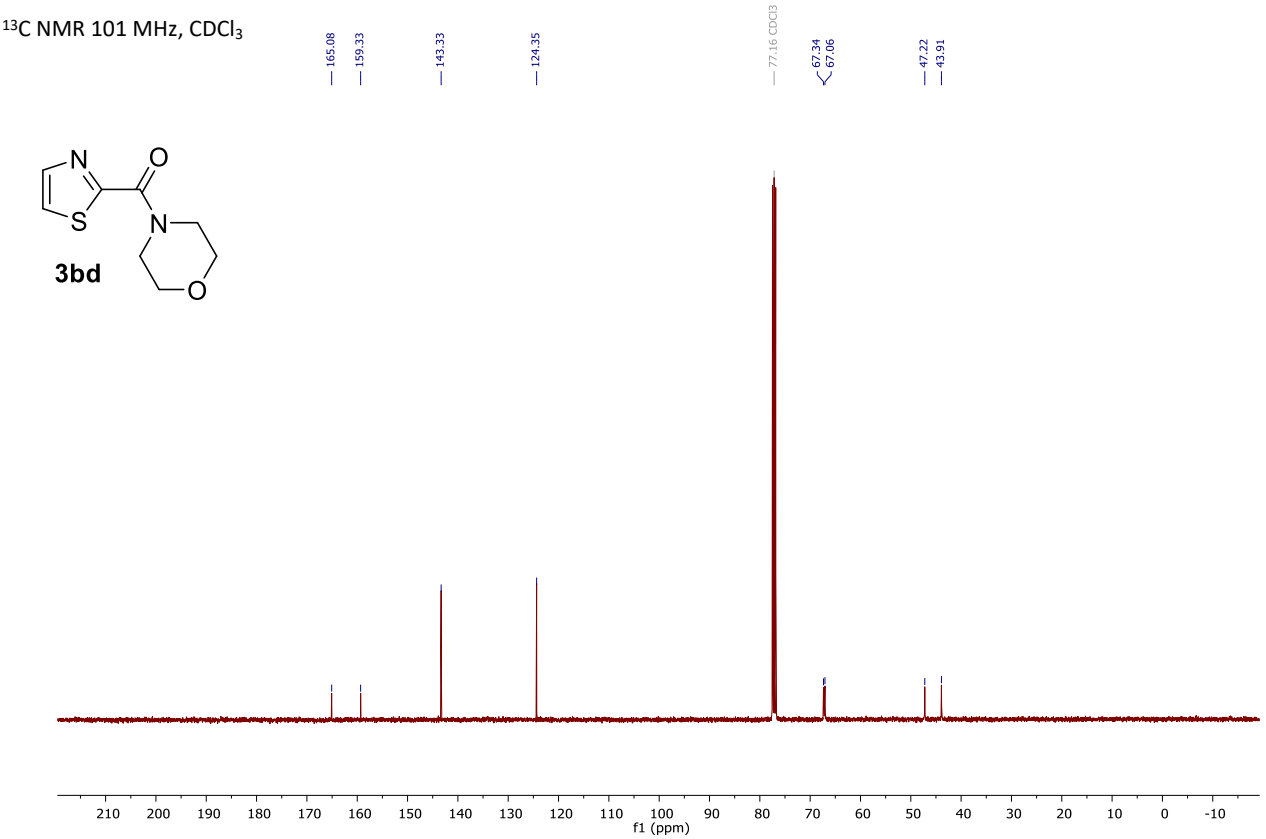
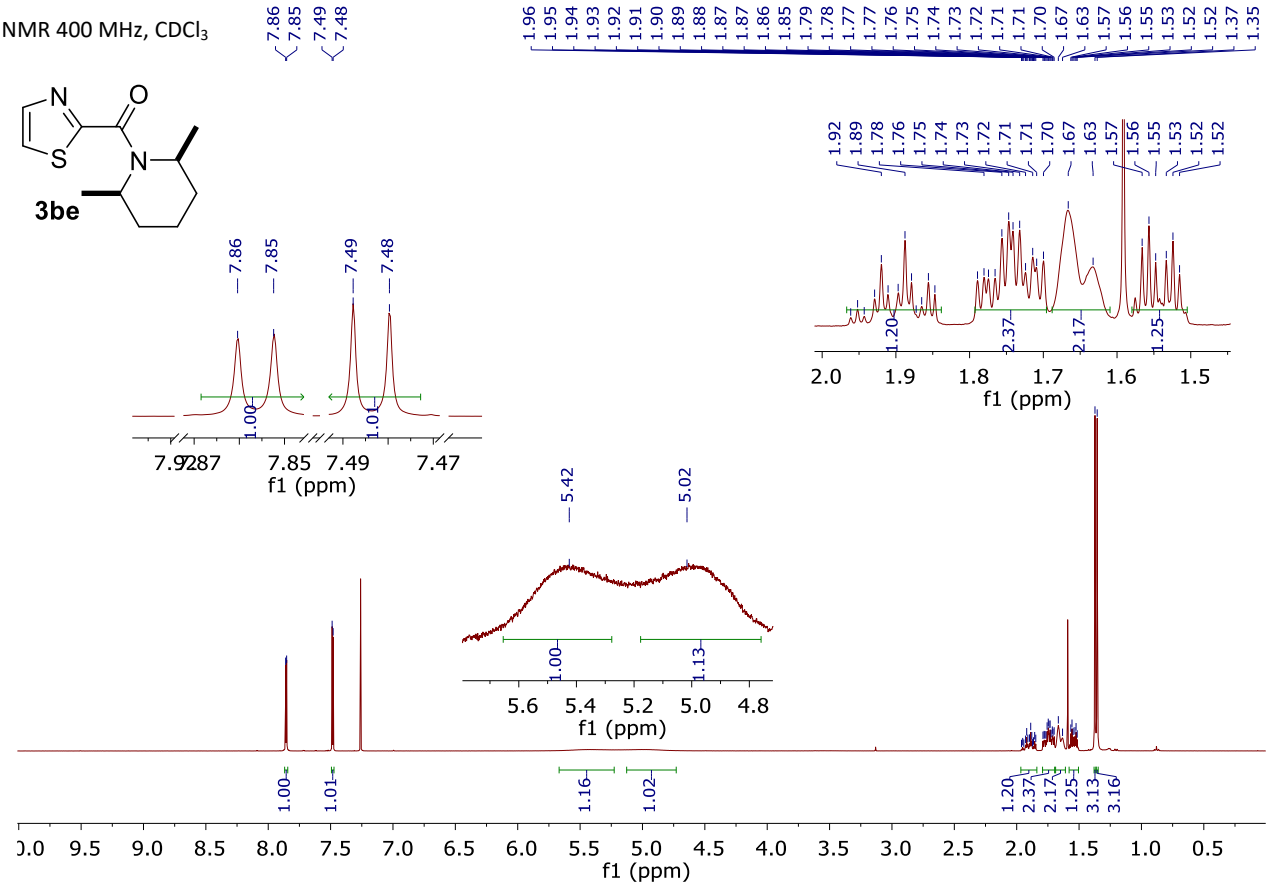
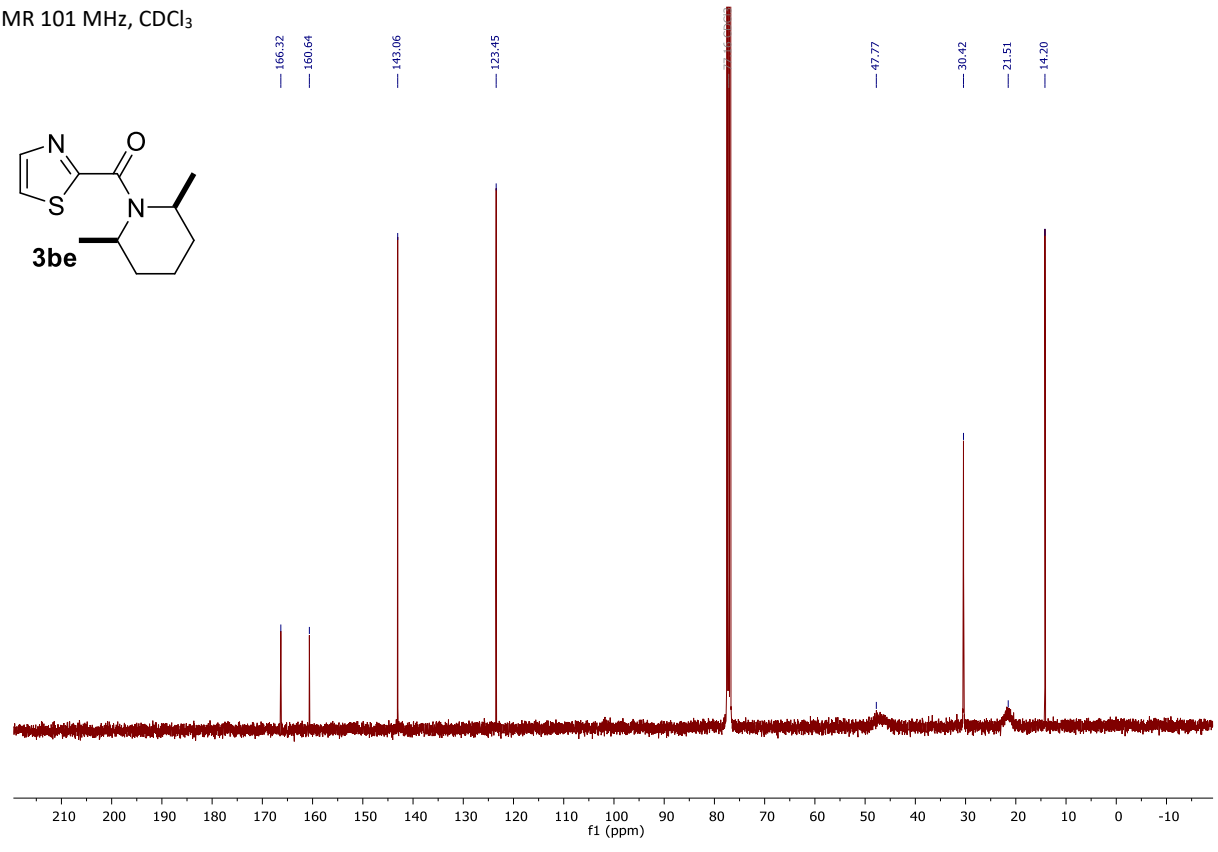


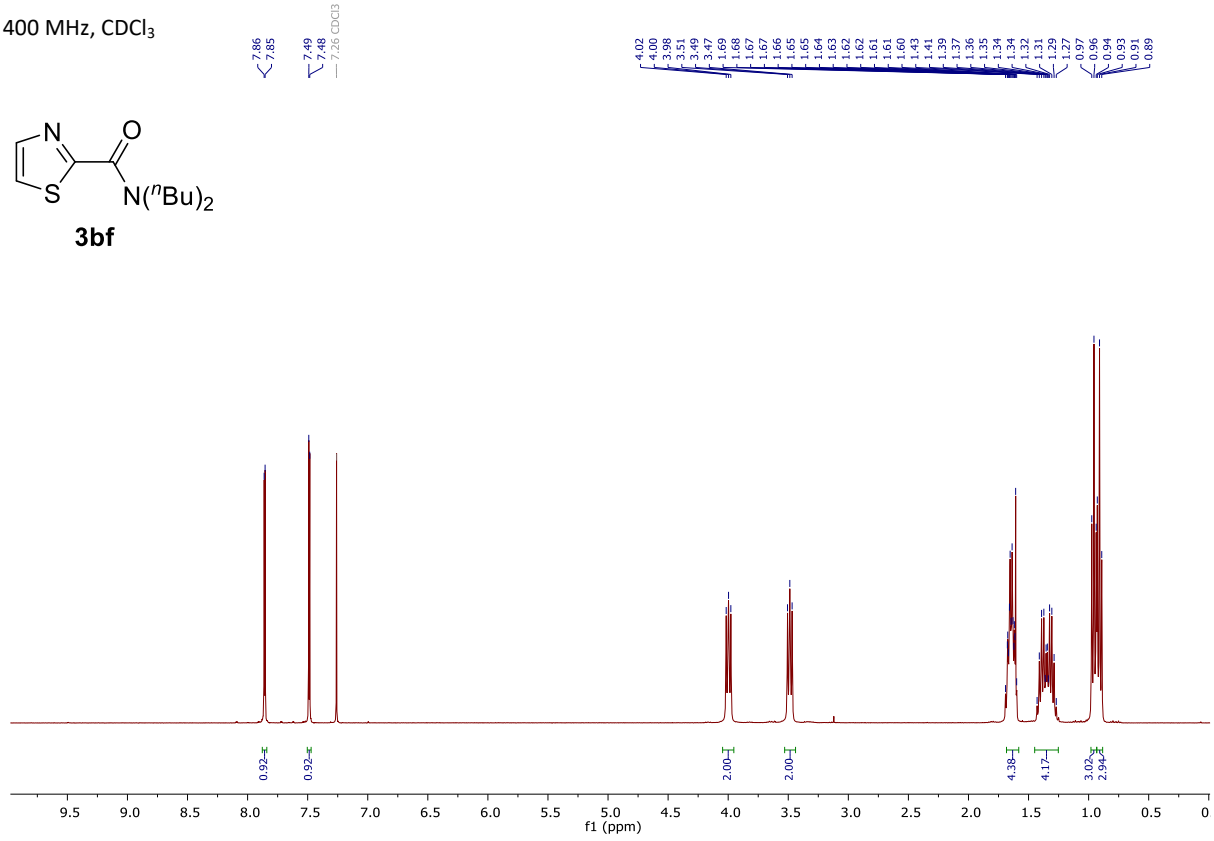
^{1}H NMR 400 MHz, $CDCl_3$



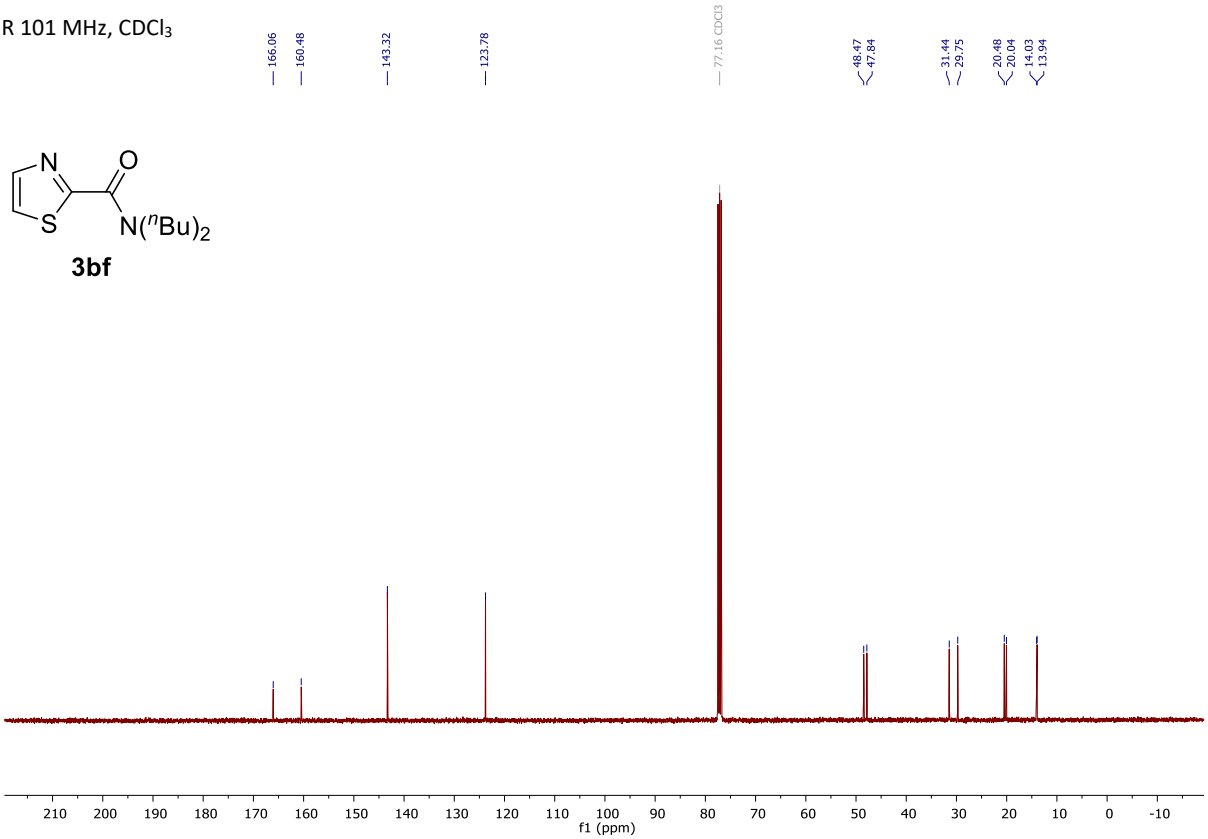
^{13}C NMR 101 MHz, $CDCl_3$



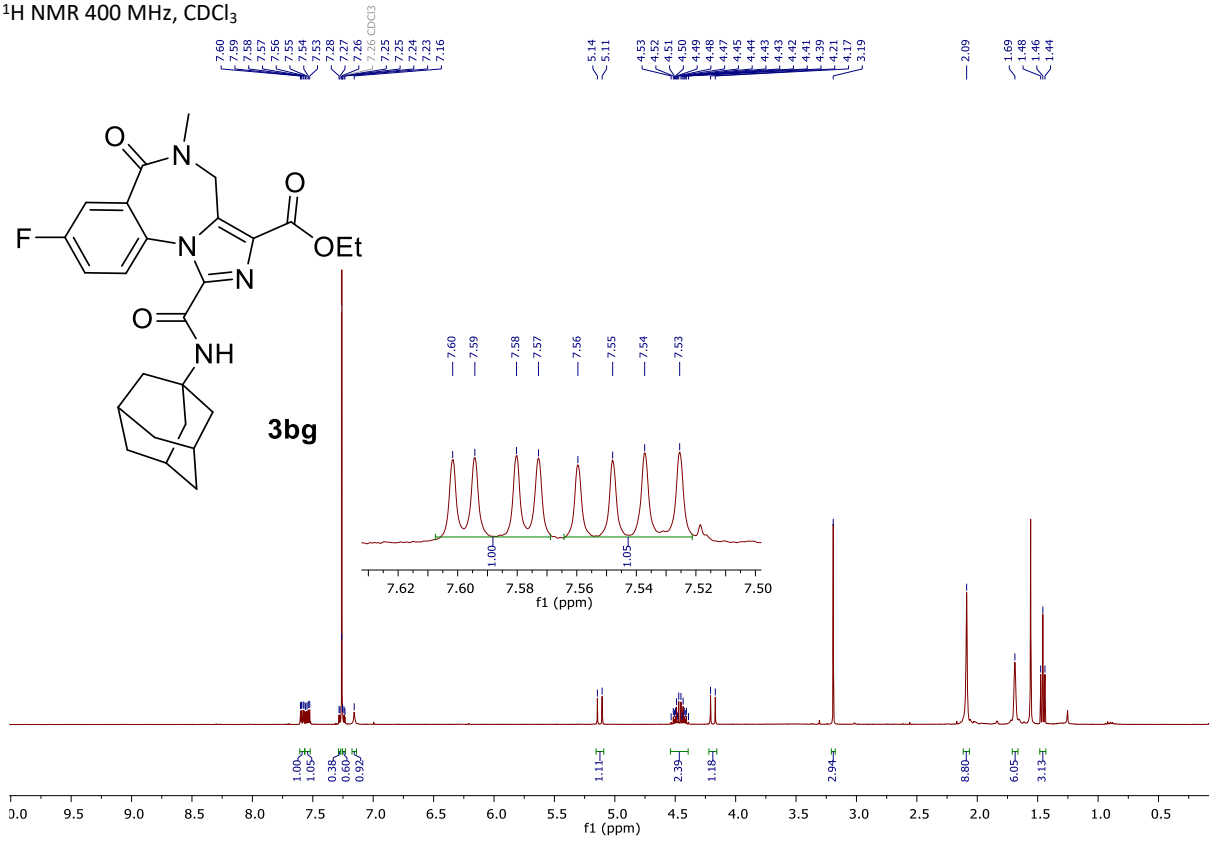
^{1}H NMR 400 MHz, $CDCl_3$



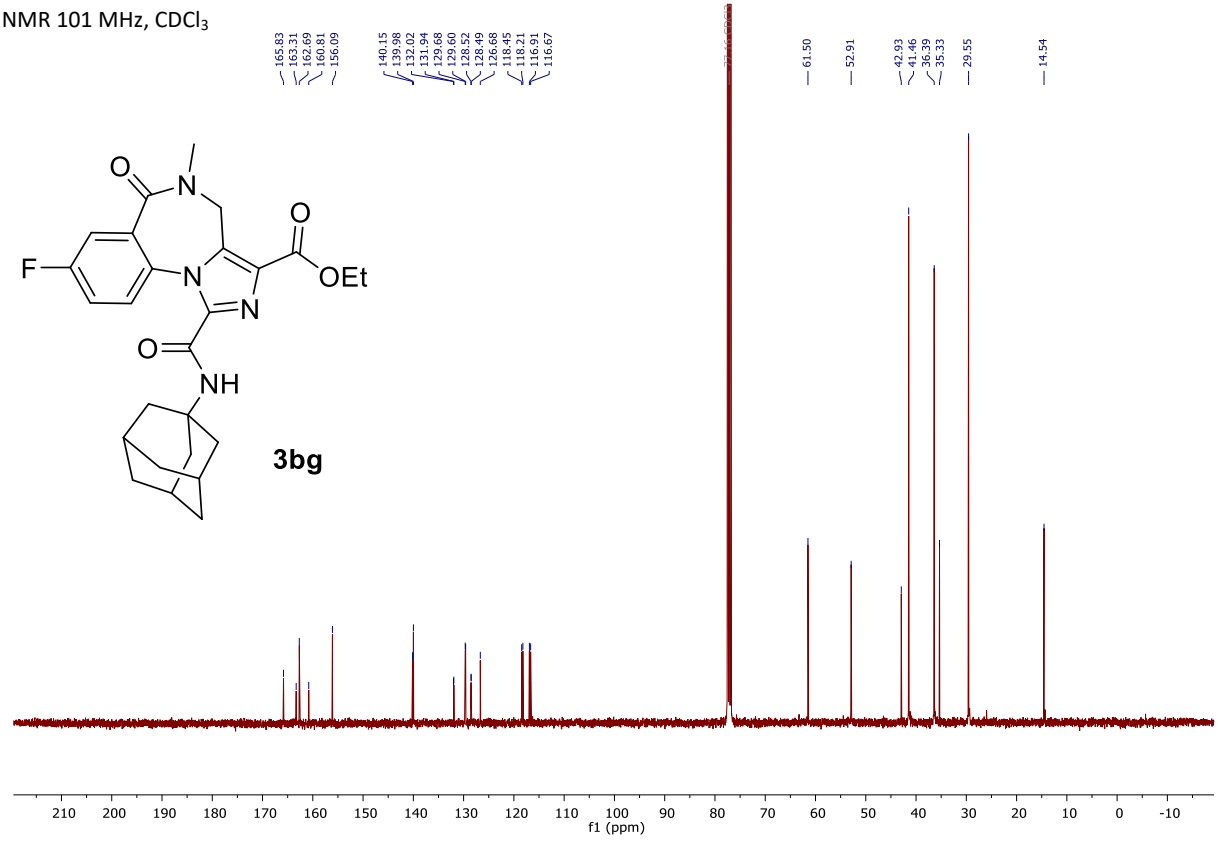
^{13}C NMR 101 MHz, $CDCl_3$



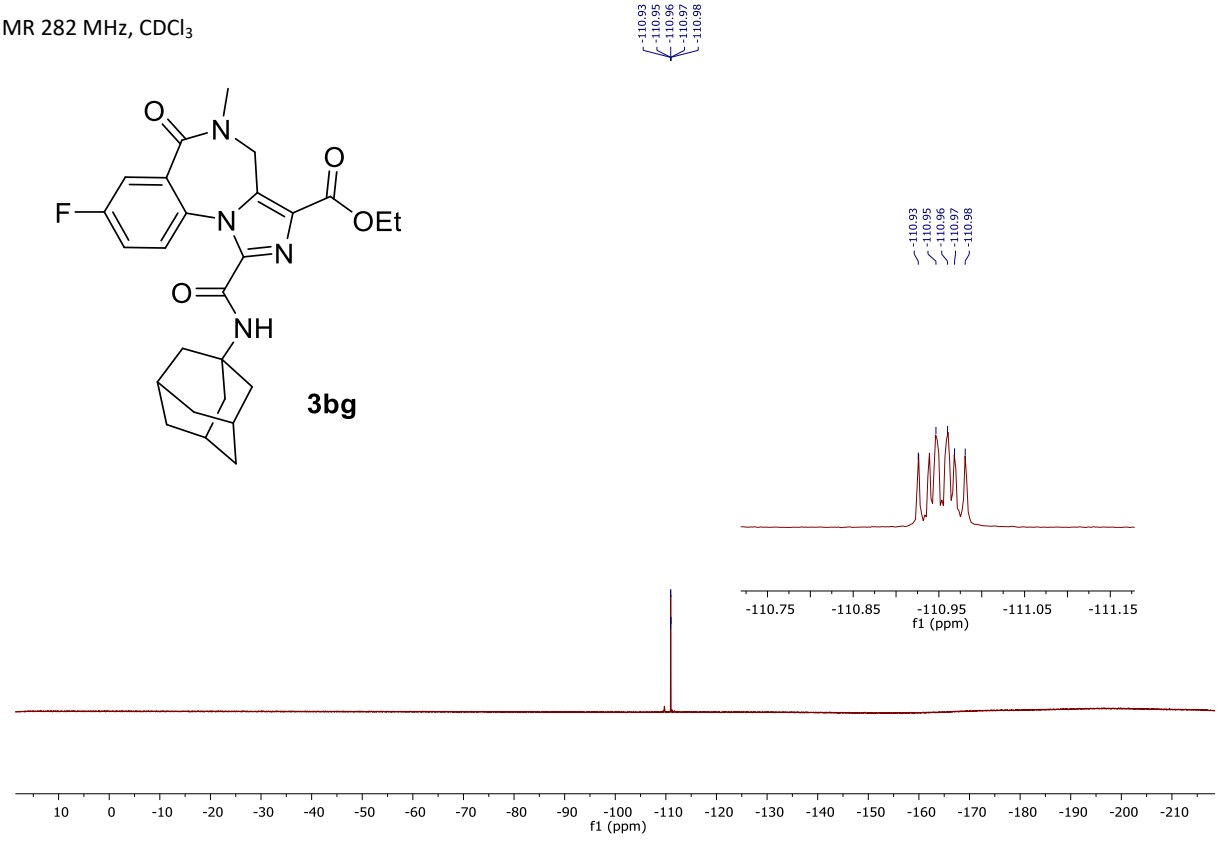
^{1}H NMR 400 MHz, $CDCl_3$



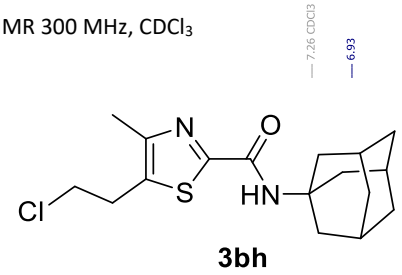
^{13}C NMR 101 MHz, $CDCl_3$



^{19}F NMR 282 MHz, $CDCl_3$

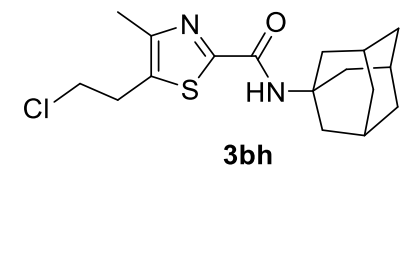


^{1}H NMR 300 MHz, $CDCl_3$



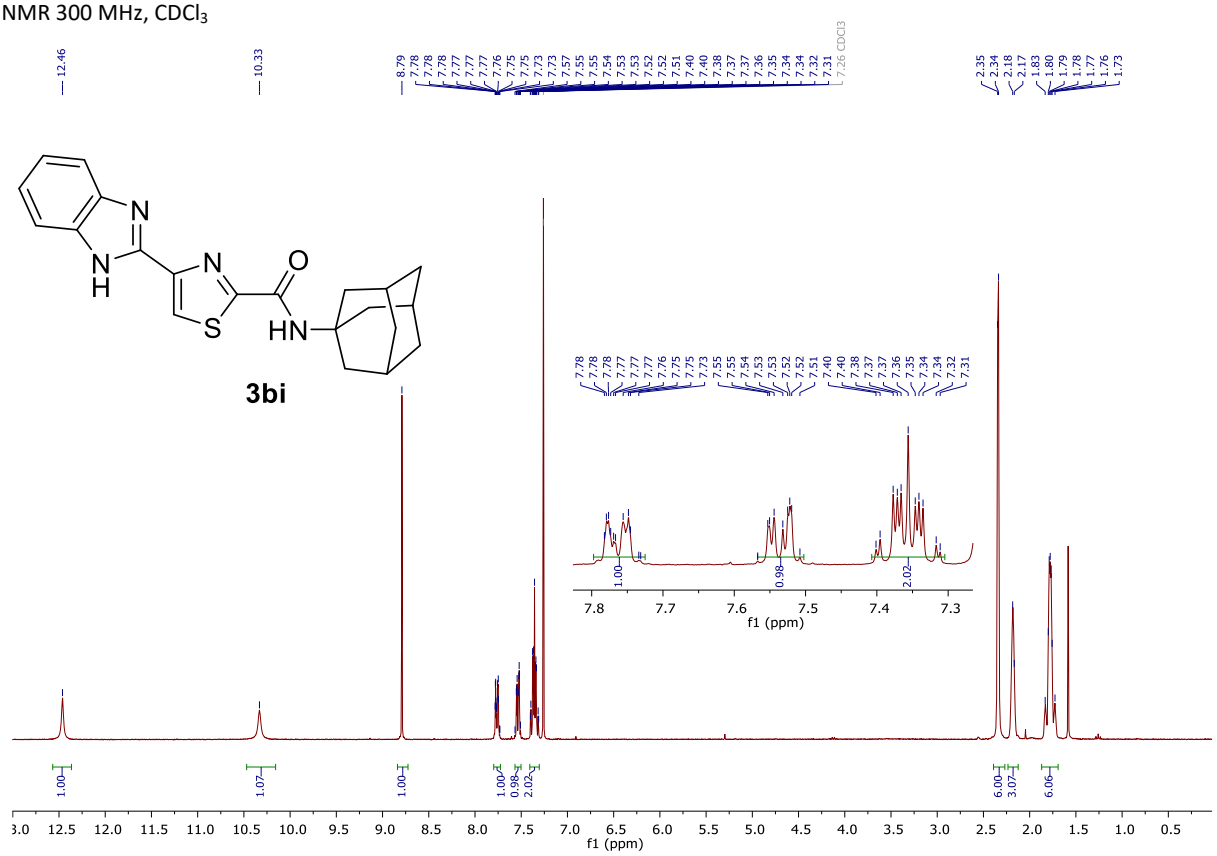
3bh

^{13}C NMR 75 MHz, $CDCl_3$

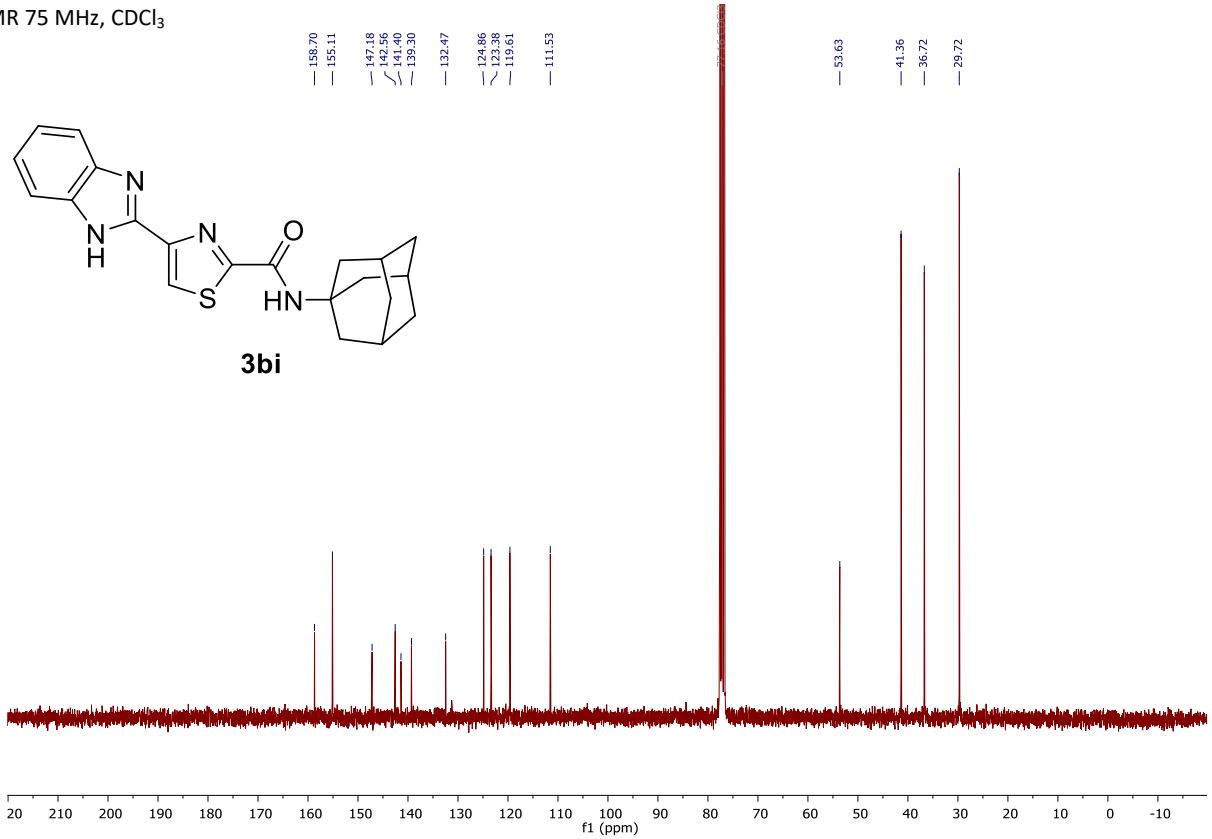


3bh

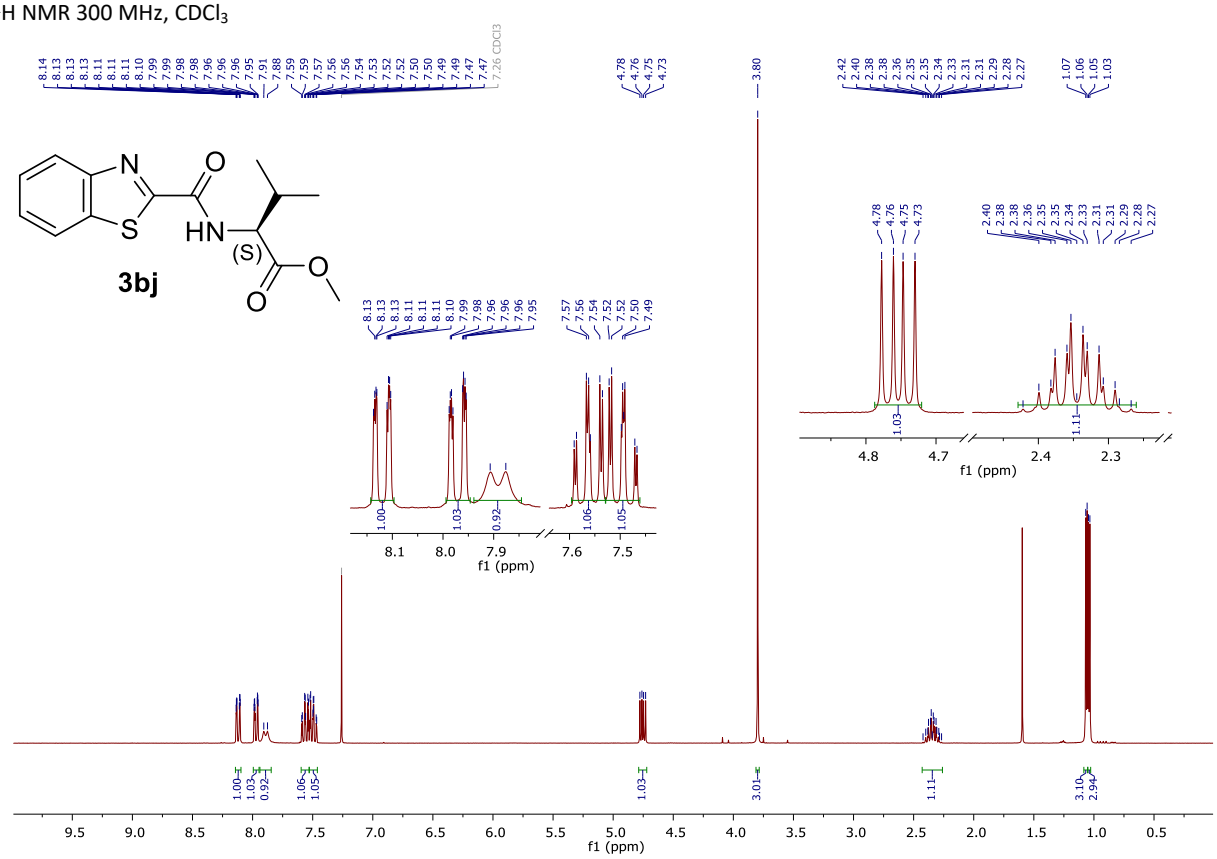
^{1}H NMR 300 MHz, $CDCl_3$



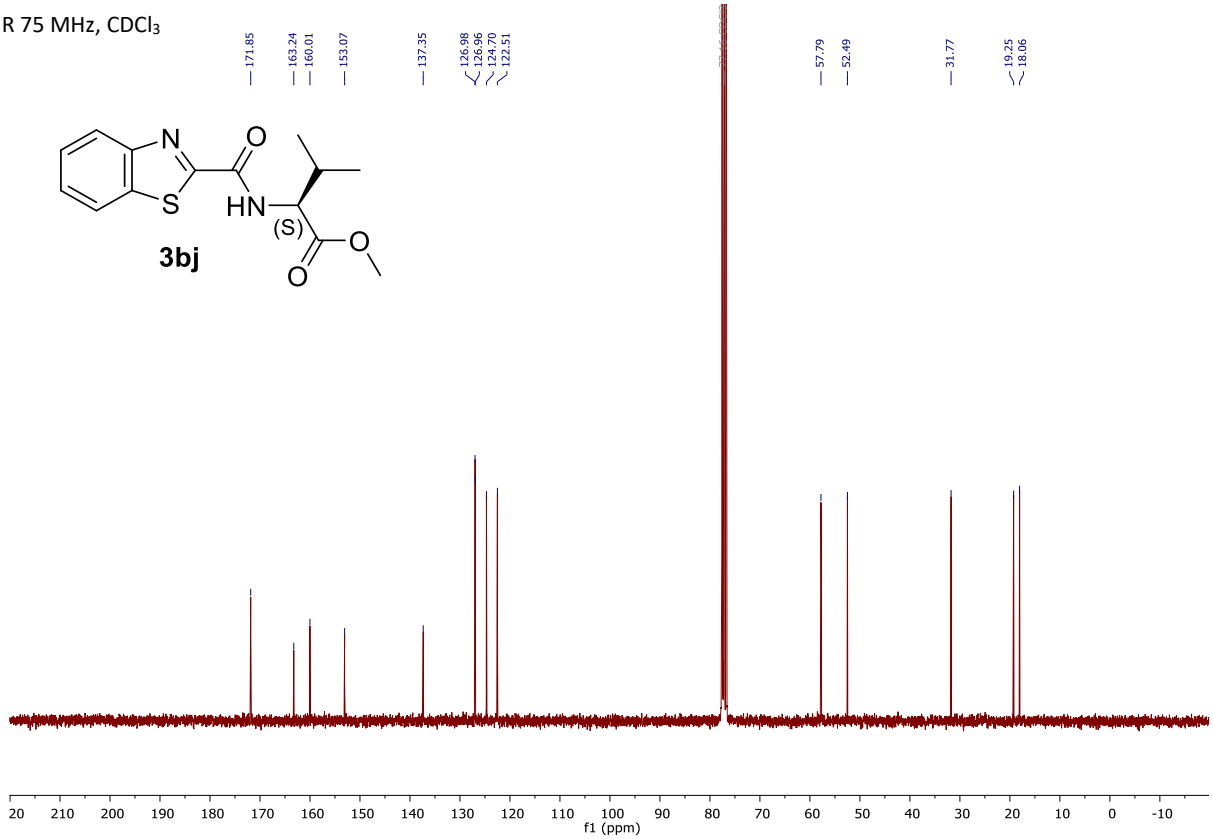
^{13}C NMR 75 MHz, $CDCl_3$



^{1}H NMR 300 MHz, $CDCl_3$



^{13}C NMR 75 MHz, $CDCl_3$



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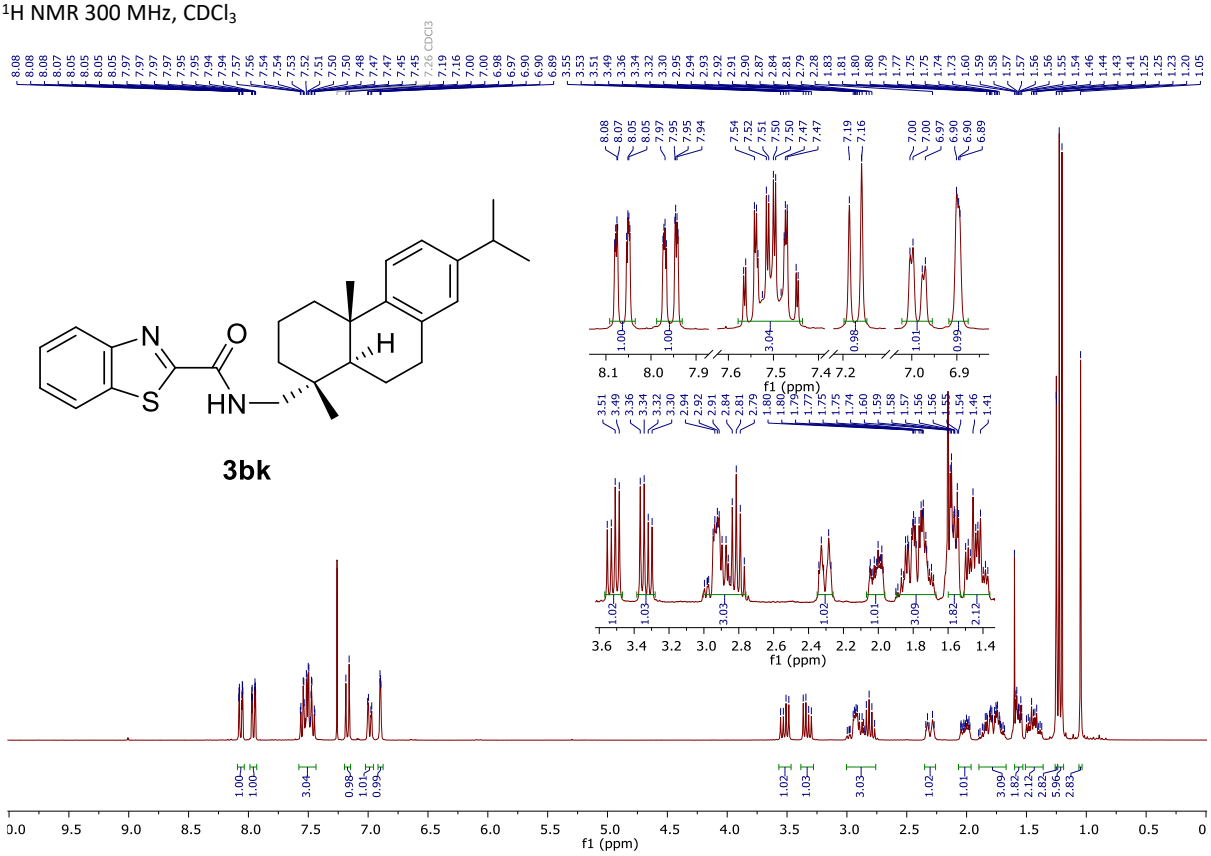
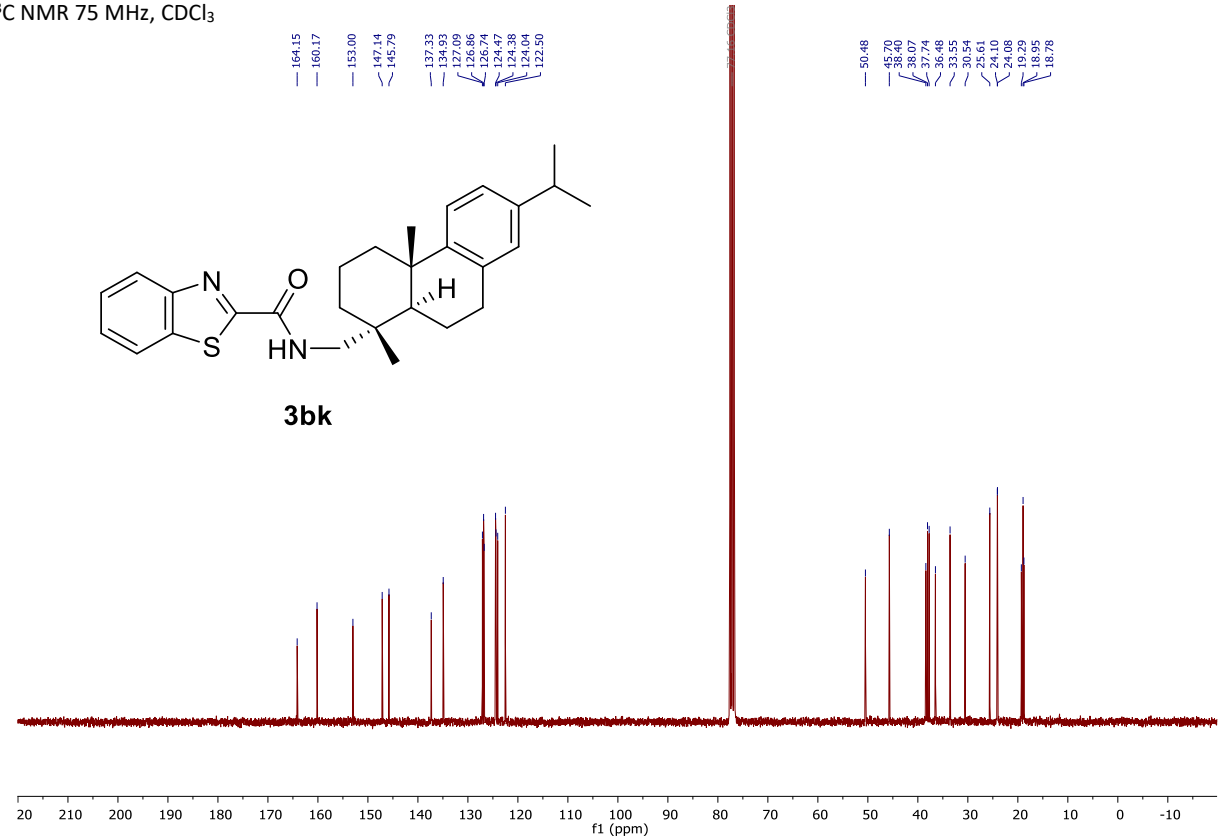
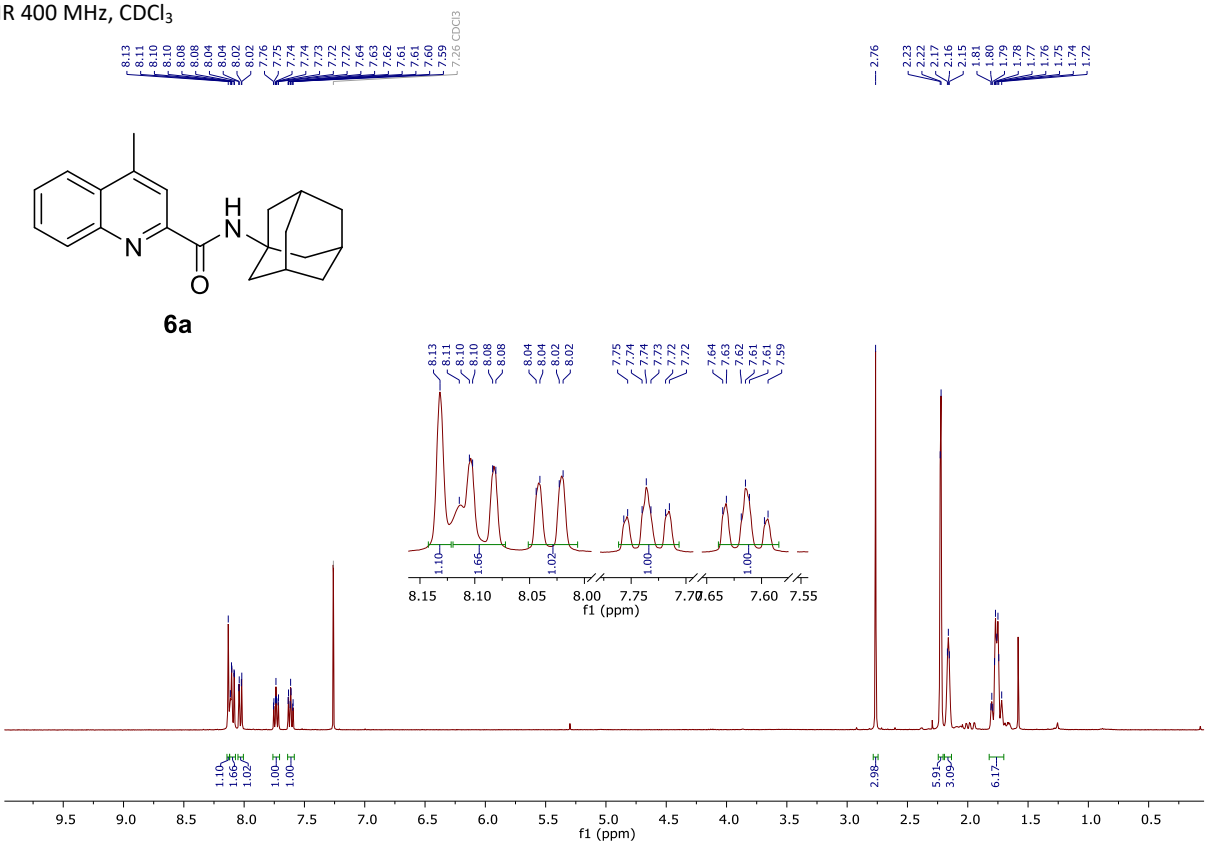


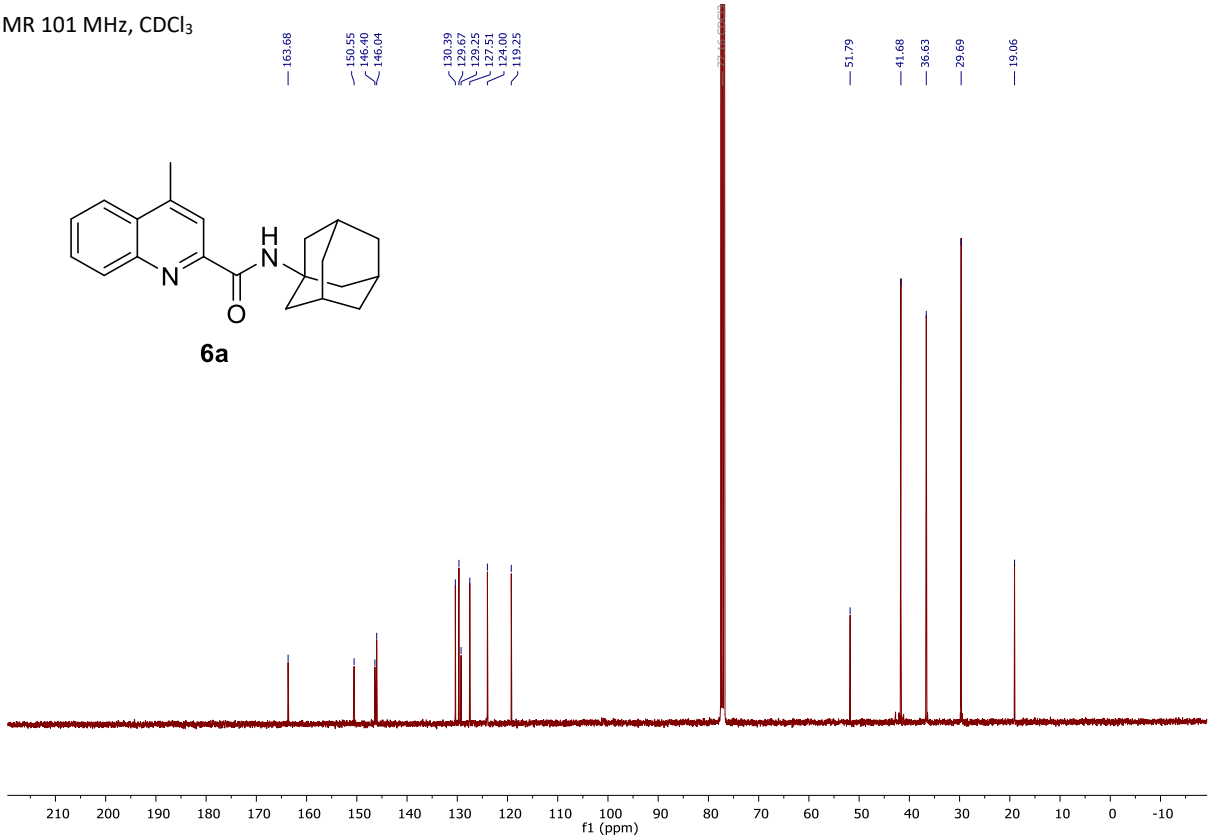
^{13}C NMR 75 MHz, $CDCl_3$



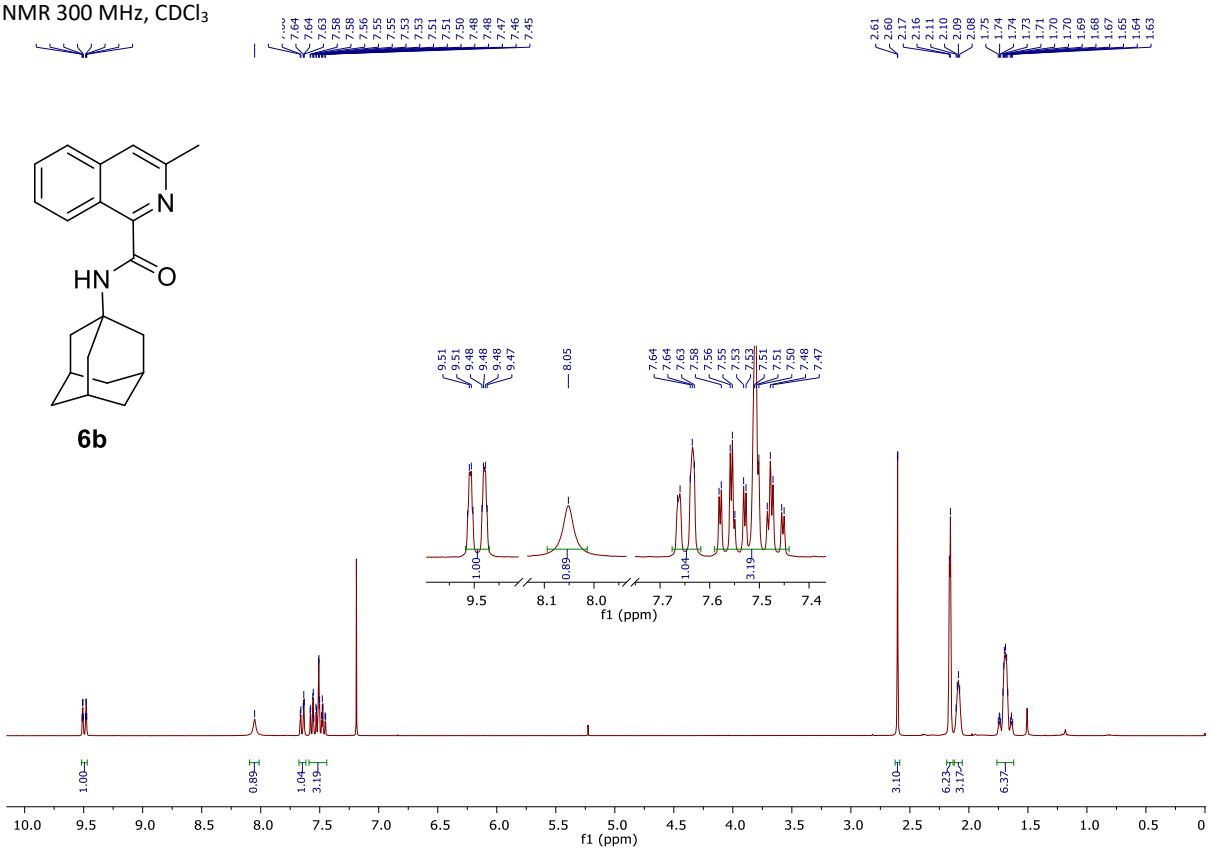
^{1}H NMR 400 MHz, $CDCl_3$



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



^{1}H NMR 300 MHz, $CDCl_3$



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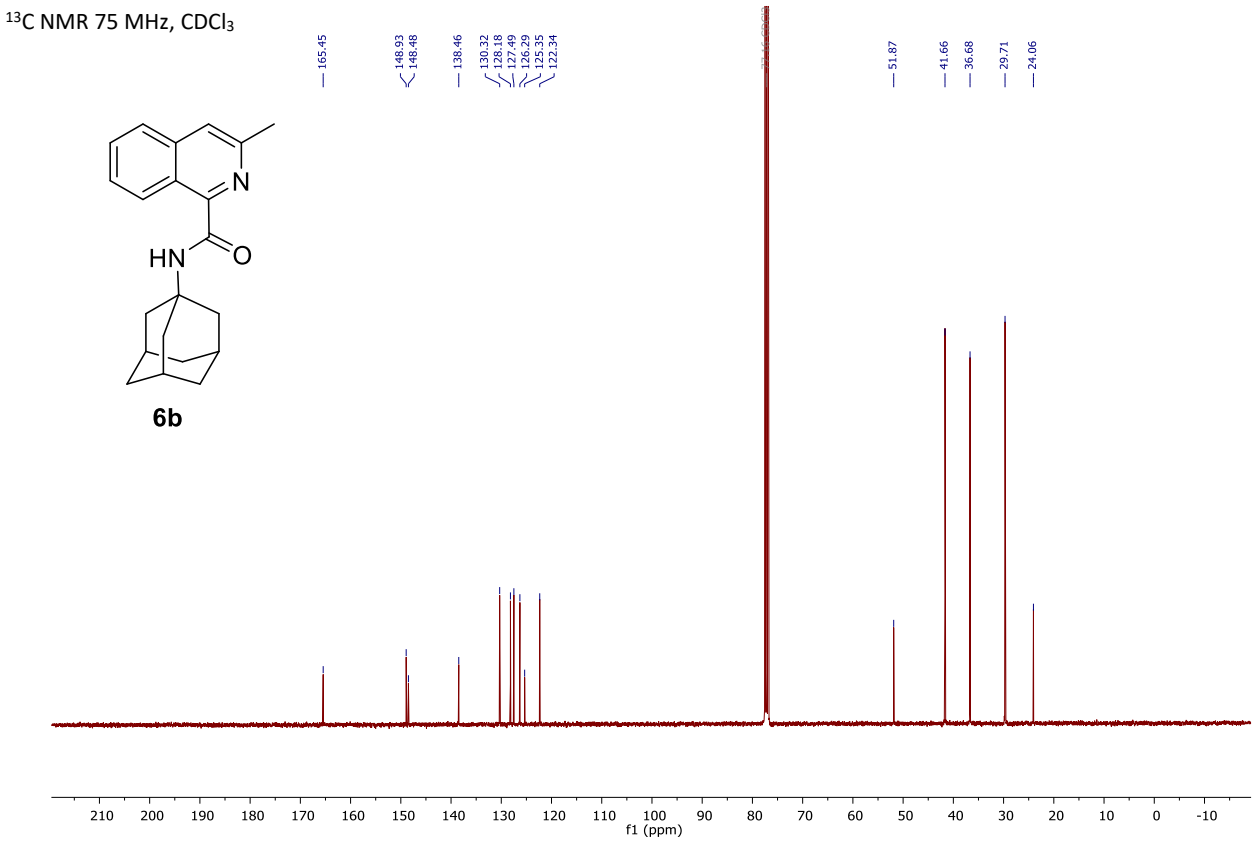

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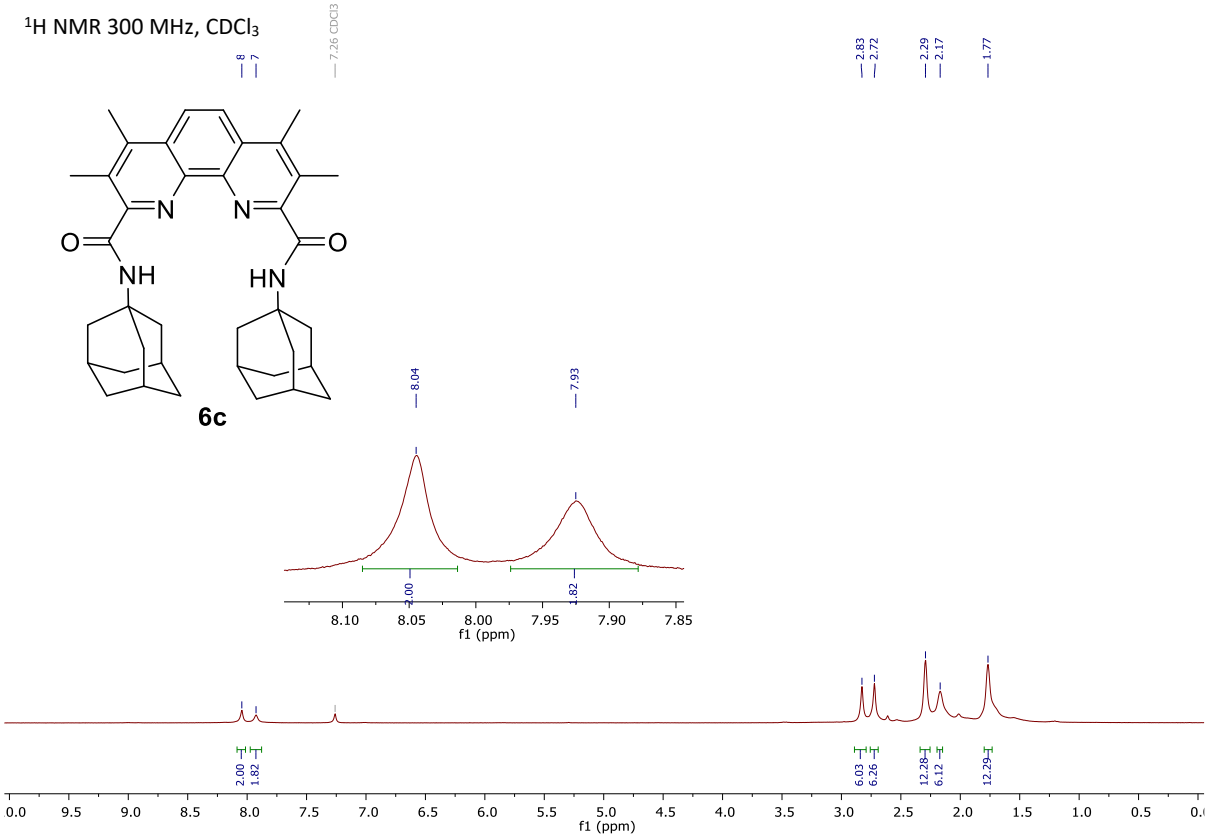

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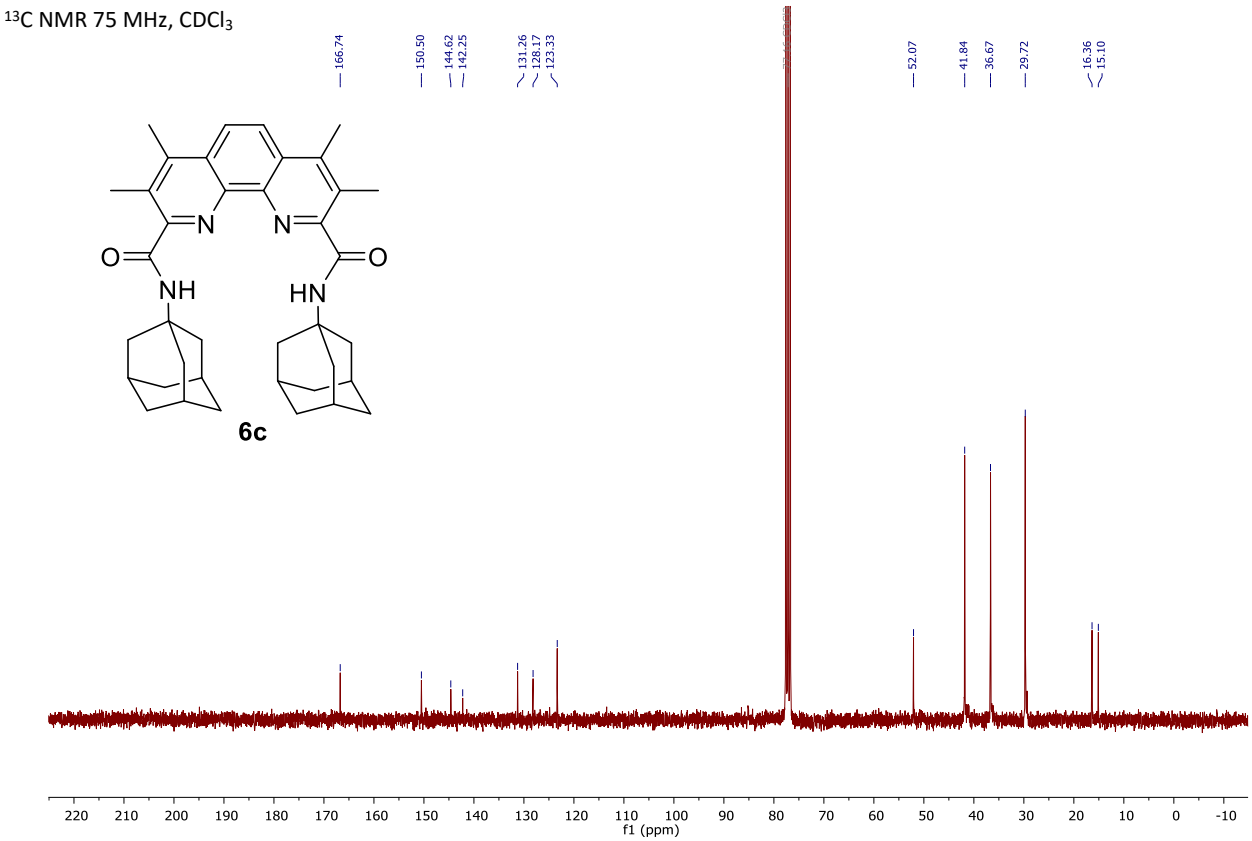
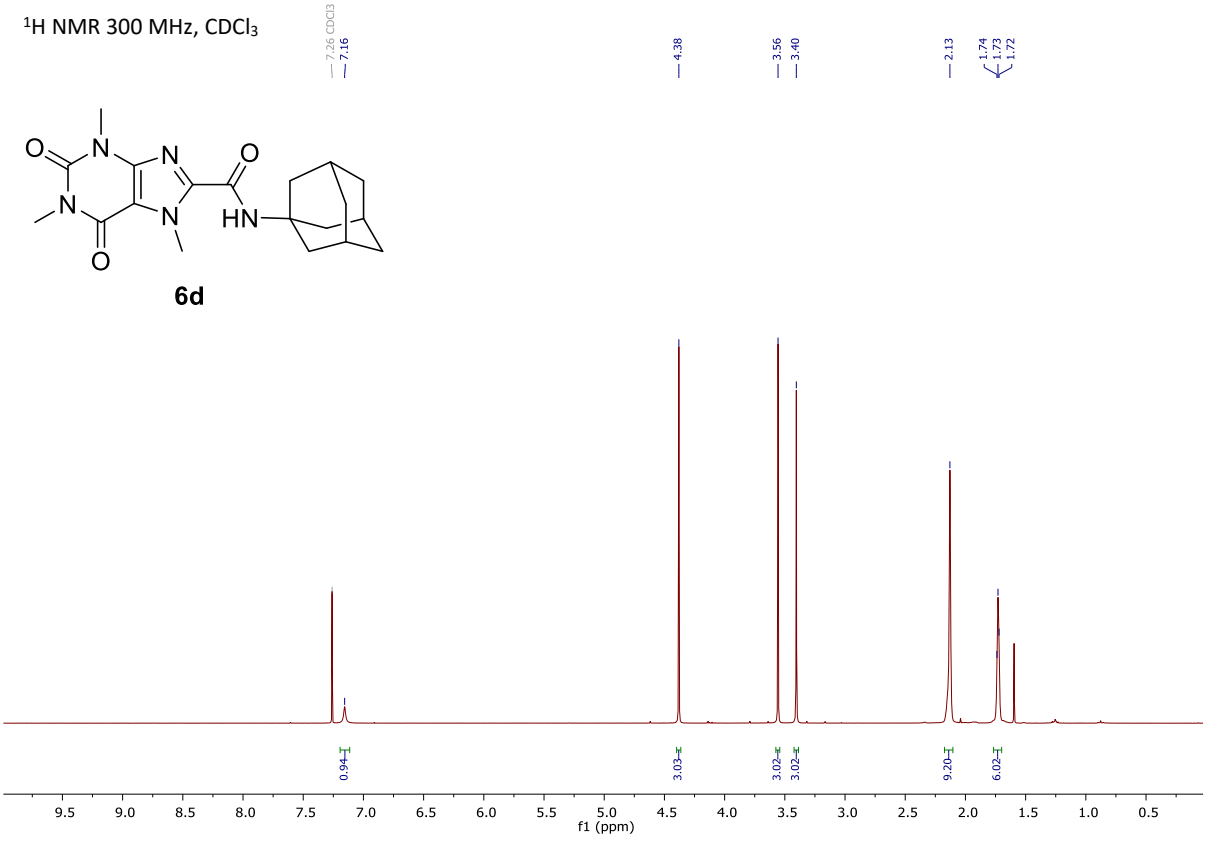
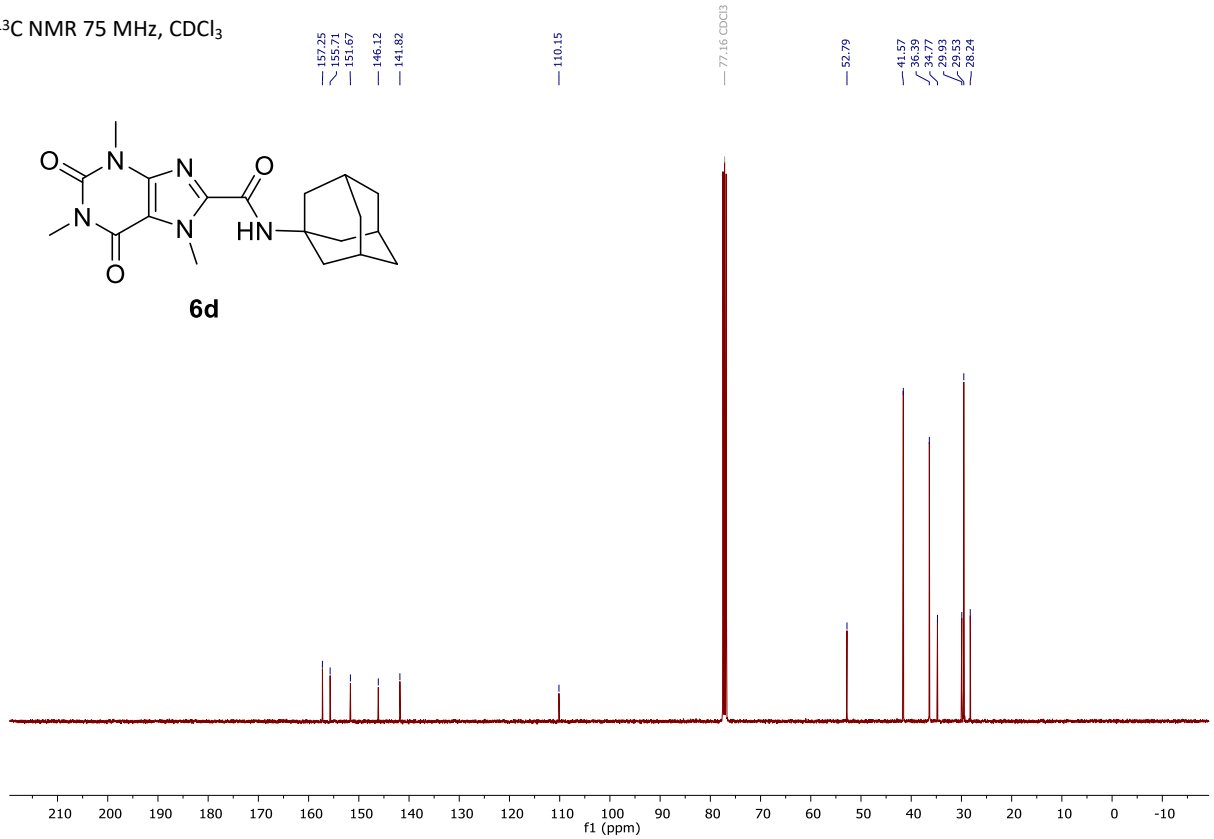


^{1}H NMR 300 MHz, $CDCl_3$



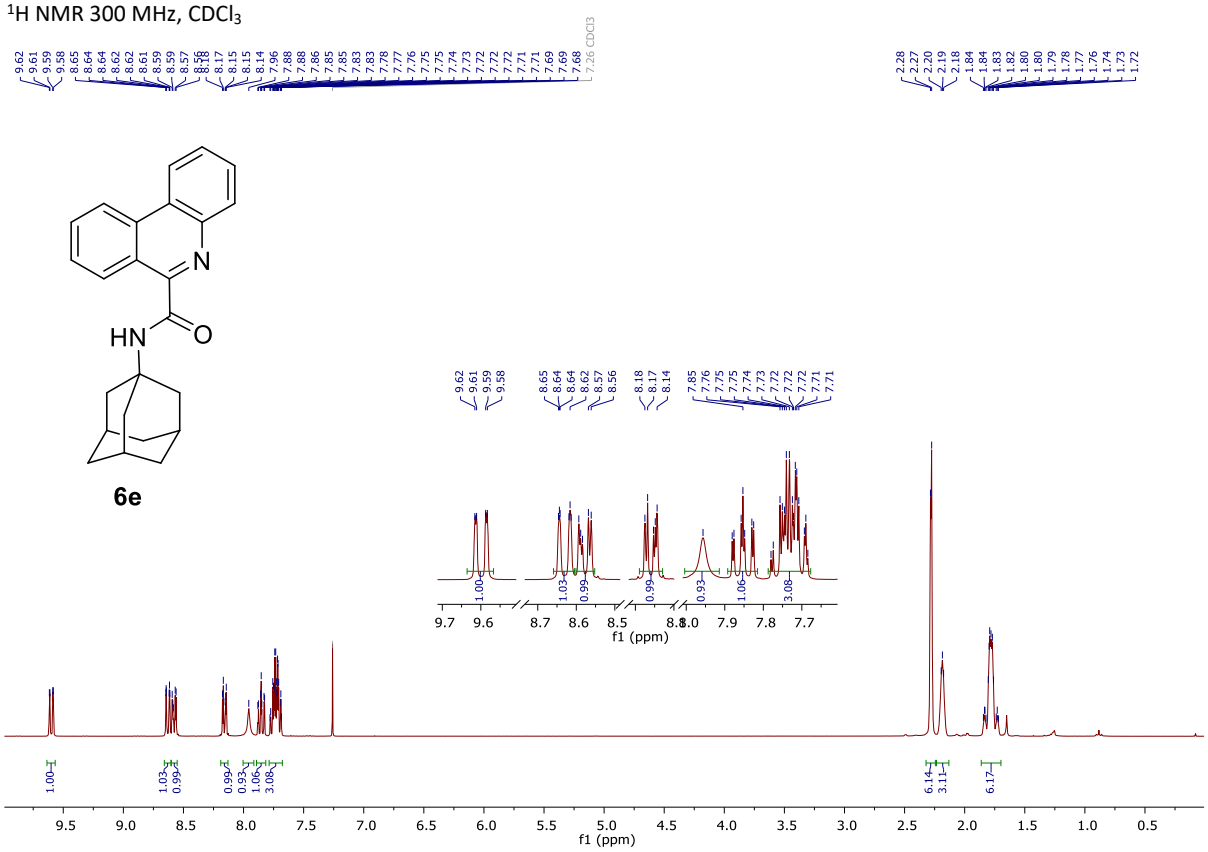
6d

^{13}C NMR 75 MHz, $CDCl_3$

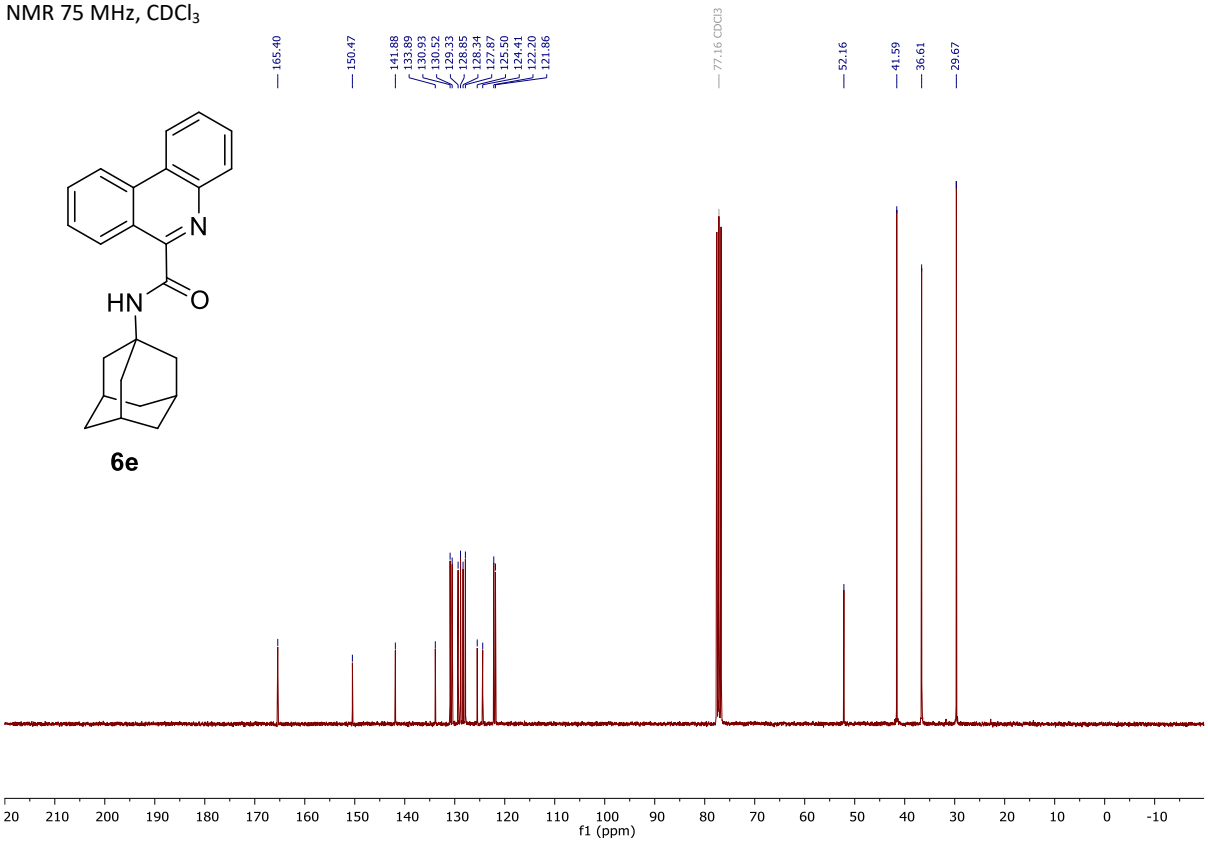


6d

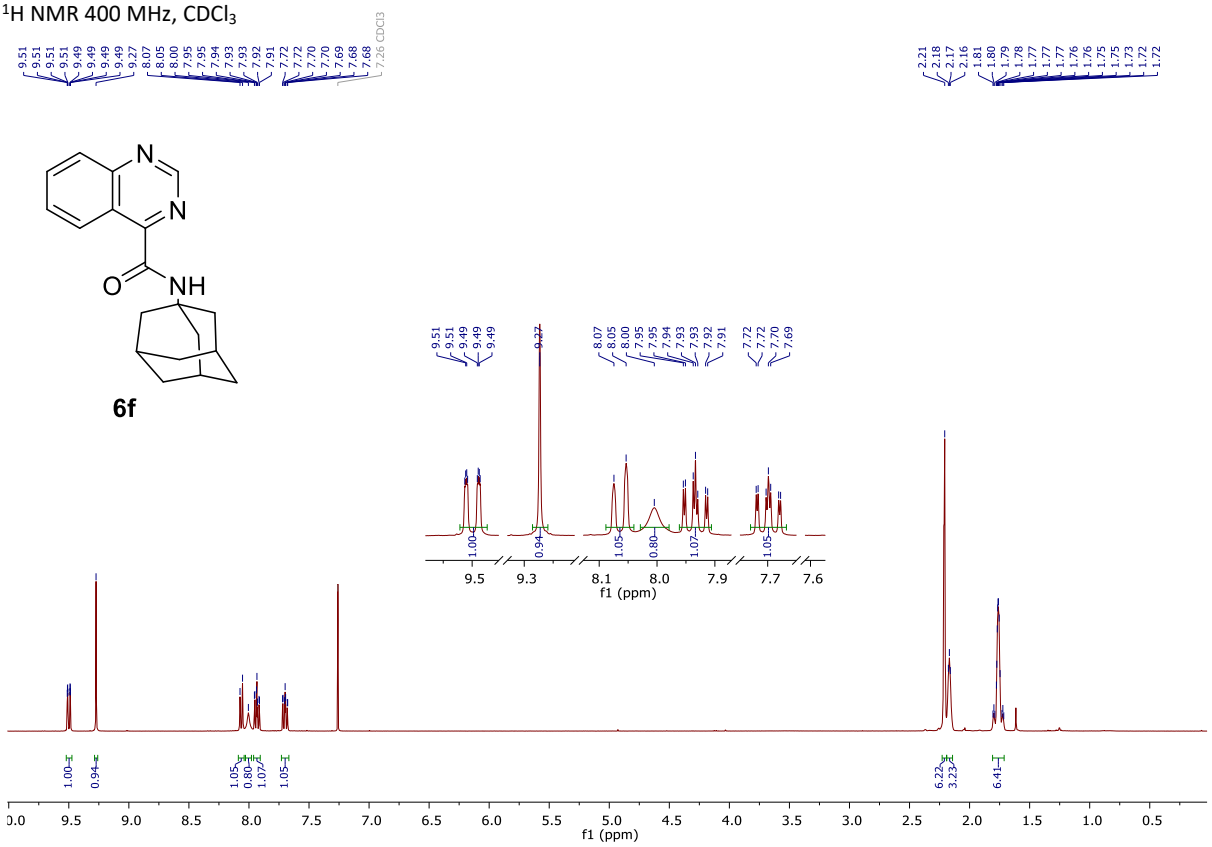
^{1}H NMR 300 MHz, $CDCl_3$



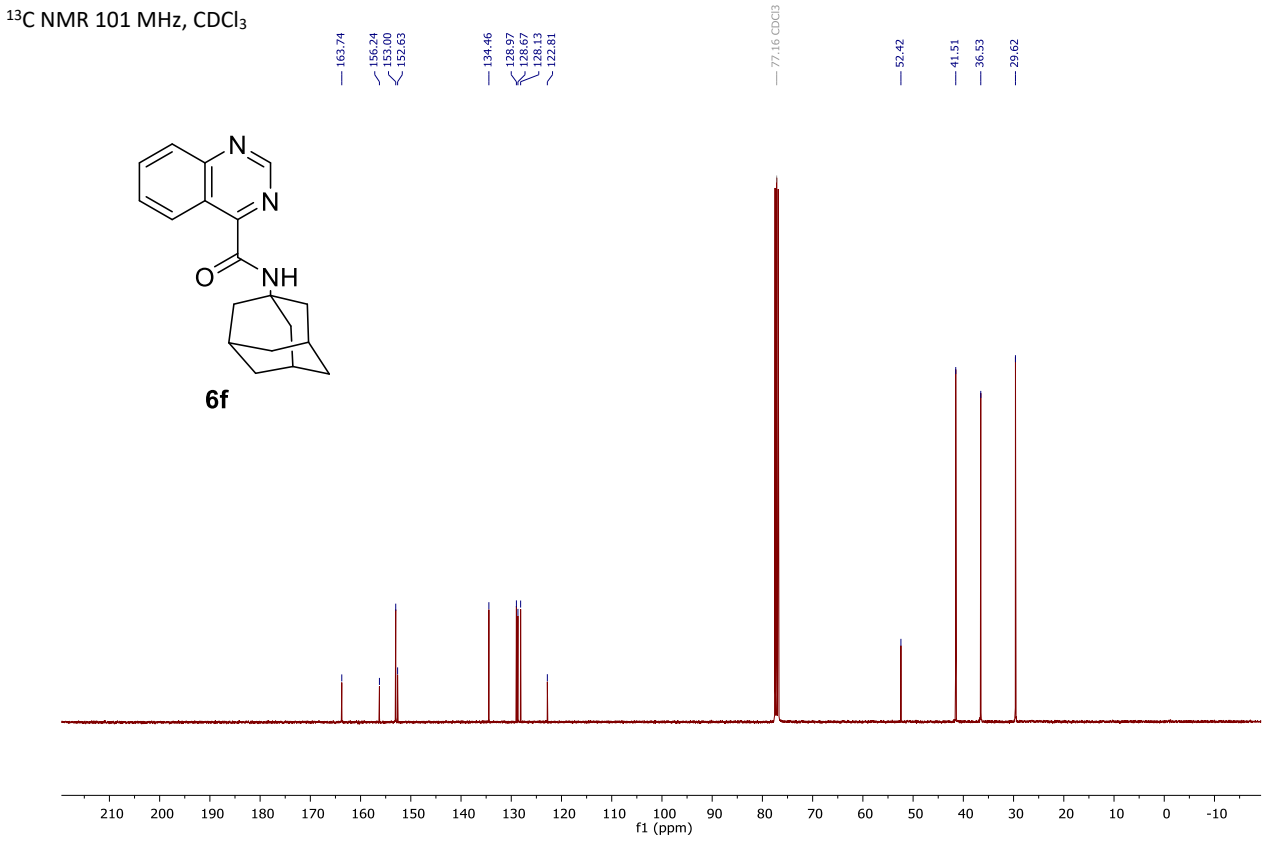
^{13}C NMR 75 MHz, $CDCl_3$



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



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



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