Supporting Information

Photocatalytic intramolecular C-H amination using *N*-oxyureas as nitrene precursors

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General Information

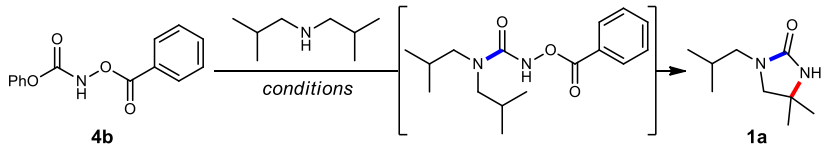
Purification of reaction products was carried out by flash column chromatography using silica gel (40-63 μm), unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on aluminum or glass, cut to size. Visualization was accomplished with UV light followed by staining with a potassium permanganate solution, and heating. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 300 MHz and 400 MHz spectrometers at ambient temperature, unless otherwise indicated. Spectral data was reported in ppm using solvent as the reference ($CDCl_3$ at 7.26 ppm or DMSO-d_6 at 2.50 ppm or CD_3CN at 1.94 ppm for ^{1}H NMR and $CDCl_3$ at 77.0 ppm or DMSO-d_6 at 39.43 for ^{13}C NMR). ^{1}H NMR data was reported as: multiplicity (app = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextuplet, sept = septuplet, m = multiplet), integration and coupling constant(s) in Hz. Infrared (IR) spectra were obtained were recorded on a Attenuated Total Reflectance Fourier transform infrared spectrometer (ATR-FTIR). High-resolution mass spectroscopy (HRMS) was performed on a mass spectrometer with an electron beam of 70ev (EI) or Micromass Q-TOF I - Time of flight Electrospray Ionization mass spectrometer (ESI). Reactions were performed at 0.3 to 1.0 mmol reaction scale. Microwave reactions were conducted on a Biotage Initiator 8 series microwave reactor. Photoredox reactions were conducted using 12V flexible blue LED strip lights or a Kessil 40W Tuna blue LED lamp when specified.

Materials

Unless otherwise noted, all commercially available materials were purchased from commercial sources and used without further purification.

Extended optimization efforts

Table S1. Thermal cascade reaction of **4b**



Entry	Base	Solvent	Temp °C	Time h	%**1a**
1	Et_3N	THF	70	15	0
2	*i*-Pr_2NEt	THF	90	15	0
3	*i*-Pr_2NEt	EtOH	90	15	<10
4	*i*-Pr_2NEt	MeCN	90	15	16
5	Et_3N	MeCN	90	20	23
6	K_2CO_3	MeCN	90	20	11
7	*i*-Pr_2NEt	$(CH_2Cl)_2$	90	15	20
8	Et_3N	$(CH_2Cl)_2$	90	15	35
9	Et_3N	$(CH_2Cl)_2$	90	65	73
10	DMAP	$(CH_2Cl)_2$	90	15	7
11	DABCO	$(CH_2Cl)_2$	90	15	12
12	**TMG**	$(CH_2Cl)_2$	**90**	**15**	**62**
13	Imidazole	$(CH_2Cl)_2$	90	15	6
14	DBU	$(CH_2Cl)_2$	90	15	6
15	Pyridine	$(CH_2Cl)_2$	90	15	5
16	Et_3N	$PHCF_3$	120	15	10
17	Et_3N	$(CH_2Cl)_2$	120	15	45
18	Et_3N	$(CH_2Cl)_2$	150	15	46
19	Imidazole	$(CH_2Cl)_2$	120	15	70
20	Imidazole	$(CH_2Cl)_2$ [Ar]	120	15	65
21	Imidazole	$CDCl_3$	120	15	72
22	Imidazole	$(CH_2Cl)_2$ - sieves	120	15	62
23	Imidazole	$CHCl_3$	120	15	8
24	Imidazole	DMSO	120	15	53
25	Imidazole	DMF	120	15	50

Conditions: phenyl *N*-benzoyloxycarbamate **4b** (1.00 equiv), diisobutylamine (1.00 equiv), base (0.20 equiv) in solvent (0.30 M) stir in oil bath. NMR yields are shown using 1,3,5-trimethoxybenzene as an internal standard.

Scheme S1: Preliminary scope of thermal C-H amination (cascade reaction)

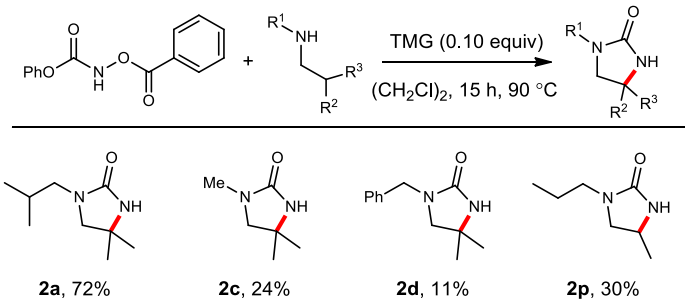
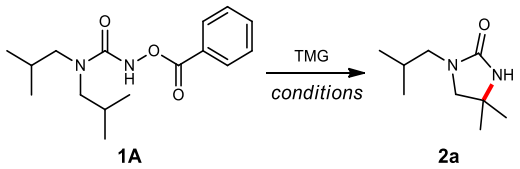


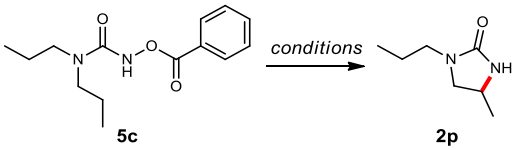
Table S2. Thermal C-H amination of **4b** via microwave irradiation



Entry	Solvent	Temp °C	Time h	%**2a**
1	$(CH_2Cl)_2$	100	1	66
2	$(CH_2Cl)_2$	**100**	**2**	**83**
3	$(CH_2Cl)_2$	150	3	67
4	$CHCl_3$	90	2	0

Conditions: 3-(benzoyloxy)-1,1-diisobutylurea **1A** (1.00 equiv), TMG (0.10 equiv) in solvent (0.30 M) stir under microwave irradiation. NMR yields are shown using 1,3,5-trimethoxybenzene as an internal standard.

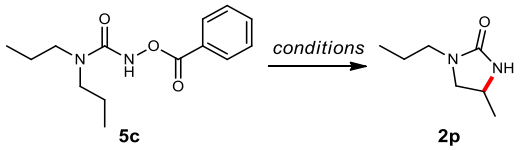
Table S3. Thermal C-H amination of **5c**



Entry	Additive	Solvent	Temp °C	Time h	%**2p**
1	TMG	$(CH_2Cl)_2$	90	15	20
2	TMG	$CHCl_3$	90	15	13
3	TMG	$PHCF_3$	90	15	<10
4	TMG	DMSO	90	15	0
5	TMG	EtOH - sieves	90	15	25
6	TMG	MeCN	90	15	18
7	TMG	Monoglyme	90	15	0
8	TMG	Diglyme	90	15	0
9	TMG	$PhCF_3$	150	15	26
10	TMG	DMSO	150	15	0
11	TMG	DMF	150	15	0
12	**TMG**	**Diglyme**	**150**	**15**	**69**
13	TMG	Dichlorobenzene	150	15	0
14	Benzoic acid	$CHCl_3$	90	15	0
15	Phosphazene	$CHCl_3$	90	15	27
16	AIBN	MeCN	90	15	0
17	-	MeCN	90	15	0
18	-	DMSO	90	15	0
19	-	$PhCF_3$	90	15	0
20	-	EtOH - sieves	90	15	30
21	-	EtOH	90	15	30
22	-	MeOH	90	15	0
23	-	*i*-PrOH	90	15	15
24	-	*t*-BuOH	90	15	0

Conditions: 3-(benzoyloxy)-1,1-dipropylurea **5c** (1.00 equiv), additive (0.10 equiv) in solvent (0.30 M) stir in oil bath. NMR yields are shown using 1,3,5-trimethoxybenzene as an internal standard.

Table S4. Thermal C-H amination of **5c** via microwave irradiation



Entry	Additive (equiv)	Solvent	Temp °C	%**2p**
1	**TMG (0.10)**	$(CH_2Cl)_2$	**120**	**60**
2	DBU (0.10)	$(CH_2Cl)_2$	120	52
3	**Et_3N (0.10)**	$(CH_2Cl)_2$	**120**	**60**
4	*i*-Pr_2NEt (0.10)	$(CH_2Cl)_2$	120	57
5	TMG (0.10)	$(CH_2Cl)_2$	90	14
6	DMAP (0.10)	$(CH_2Cl)_2$	120	14
7	$BF_3.OEt_2$ (1.00)	MeCN	100	0
8	$PhI(OAc)_2$ (1.20)	MeCN	120	0
9	HCl (g) (excess)	MeCN	120	0

Conditions: 3-(benzoyloxy)-1,1-dipropylurea **5c** (1.00 equiv), additive in solvent (0.30 M) stir under microwave irradiation. NMR yields are shown using 1,3,5-trimethoxybenzene as an internal standard.

Scheme S2: Preliminary scope of thermal C-H amination (sequential) via microwave irradiation

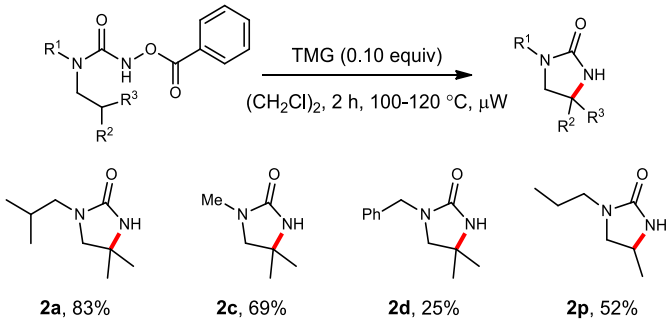
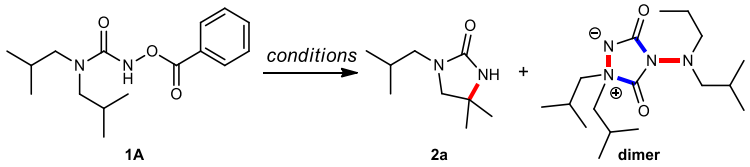


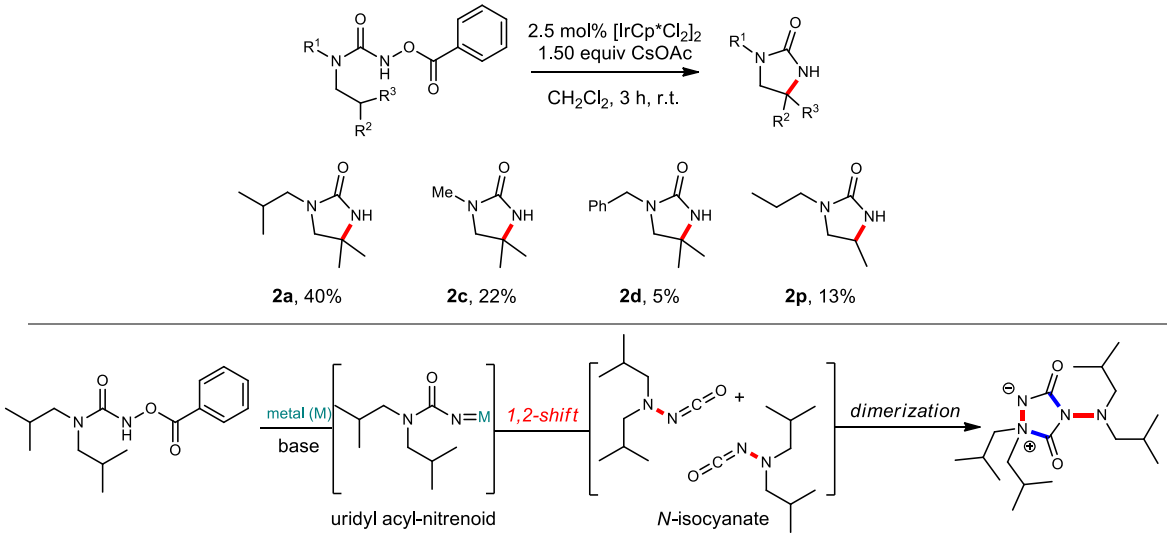
Table S5. Metal catalyzed C-H amination of **1A**



Entry	Metal (mol%)	Base (equiv)	Solvent	Temp °C	Time	%**1A**	%**2a**	%dimer
1	$[IrCp^*Cl_2]_2$ (2.5)	K_2CO_3 (1.5)	CH_2Cl_2	rt	3	0	16	20
2	**$[IrCp^*Cl_2]_2$ (2.5)**	**CsOAc (1.5)**	**CH_2Cl_2**	**rt**	**3**	**0**	**20**	**33**
3	$[IrCp^*Cl_2]_2$ (2.5)	Imidazole (1.5)	CH_2Cl_2	rt	16	100	0	0
4	$[IrCp^*Cl_2]_2$ (2.5)	CsOAc (0.2)	CH_2Cl_2	rt	3	0	17	20
5	$[IrCp^*Cl_2]_2$ (0.5)	CsOAc (0.2)	CH_2Cl_2	rt	3	0	21	15
6	$[IrCp^*Cl_2]_2$ (0.5)	CsOAc (5.0)	CH_2Cl_2	rt	3	0	18	14
7	$[IrCp^*Cl_2]_2$ (0.5)	CsOAc (0.2)	THF	rt	13	72	11	3
8	$[IrCp^*Cl_2]_2$ (0.5)	CsOAc (0.2)	$PhCF_3$	rt	13	0	27	18
9	$[IrCp^*Cl_2]_2$ (0.5)	CsOAc (0.2)	MeCN	rt	13	37	11	6
10	$[IrCp^*Cl_2]_2$ (0.5)	CsOAc (0.2)	DMSO	rt	13	60	0	0
11	$[IrCp^*Cl_2]_2$ (0.5)	KOAc (0.2)	CH_2Cl_2	rt	3	24	21	11
12	$[IrCp^*Cl_2]_2$ (0.5)	NaOAc (0.2)	CH_2Cl_2	rt	3	25	19	10
13	$[IrCp^*Cl_2]_2$ (0.5)	MgO (0.2)	CH_2Cl_2	rt	3	15	7	7
14	$[IrcodCl_2]_2$ (2.5)	CsOAc (1.5)	CH_2Cl_2	rt	16	100	0	0
15	$[IrcodCl_2]_2$ (2.5)	CsOAc (1.5)	MeOH	rt	16	40	24	0
16	$[IrcodCl_2]_2$ (2.5)	CsOAc (0.2)	CH_2Cl_2	rt	16	0	17	20
17	$[RhCp^*Cl_2]_2$ (2.5)	K_2CO_3 (1.5)	MeOH	rt	16	0	5	0
18	$[RhCp^*Cl_2]_2$ (2.5)	CsOAc (1.5)	MeOH	rt	16	0	0	0
19	$[RhCp^*Cl_2]_2$ (2.5)	Cs_2OAc_3 (1.5)	MeOH	rt	16	0	7	0
20	$[RhCp^*Cl_2]_2$ (2.5)	*t*-BuOK (1.5)	MeOH	rt	16	0	13	0
21	$[RhCp^*Cl_2]_2$ (2.5)	*t*-BuOK (1.5)	MeOH	rt	16	0	0	0
22	$[RhCp^*Cl_2]_2$ (2.5)	*t*-BuOK (1.5)	*i*-PrOh	rt	16	0	0	0
23	$[RhOAc]_2$ (5.0)	K_2CO_3 (1.5)	CH_2Cl_2	rt	16	0	10	
24[a]	$[RhOAc]_2$ (5.0)	Imidazole (1.5)	$(CH_2Cl)_2$	90	16		37	
25	$[Rhesp_2]_2$ (5.0)	K_2CO_3 (1.5)	$(CH_2Cl)_2$	rt	16	100	0	0

Conditions: 3-(benzoyloxy)-1,1-diisobutylurea **1A** (1.00 equiv), metal, base in solvent (0.3M) stir at r.t.. [a]Cascade reaction with 80% of SM converted. NMR yield are shown using 1,3,5-trimethoxybenzene as an internal standard.

Scheme S3. Preliminary scope of metal catalyzed C-H amination / mechanism for dimerization



Scheme S4. C-H amination using photocatalytic conditions (initial benzoate precursors)

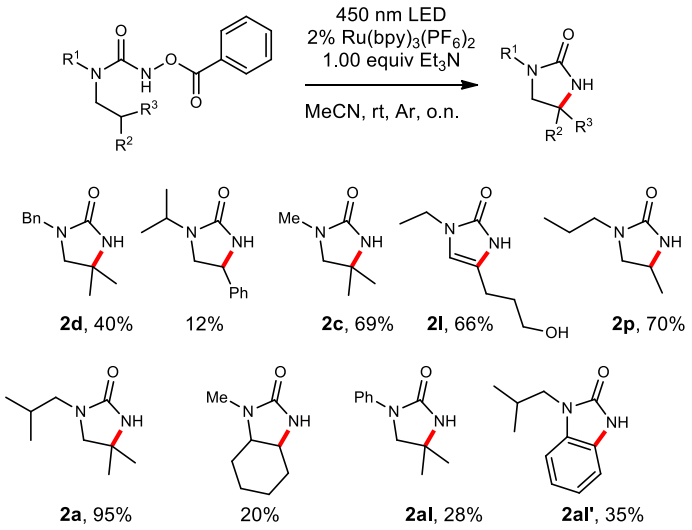
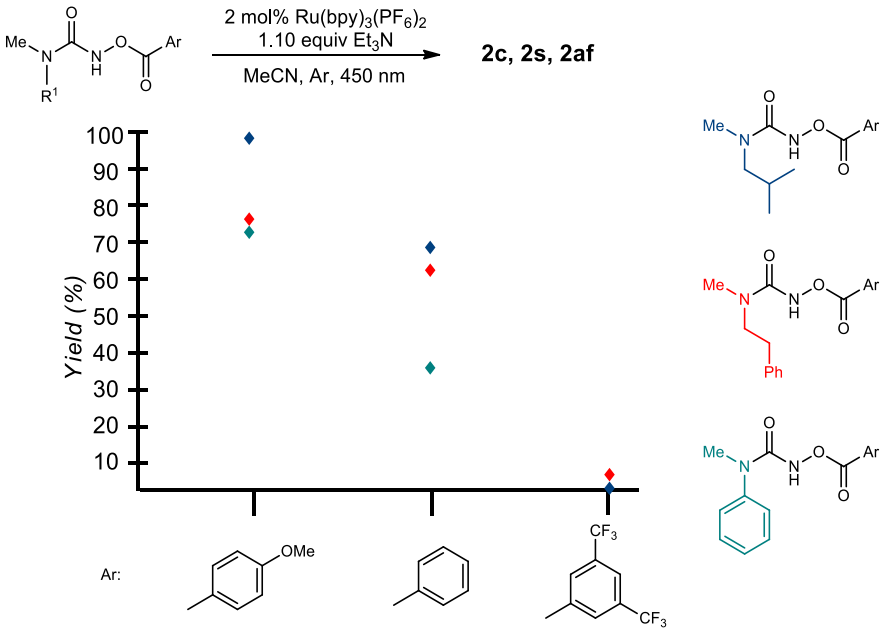


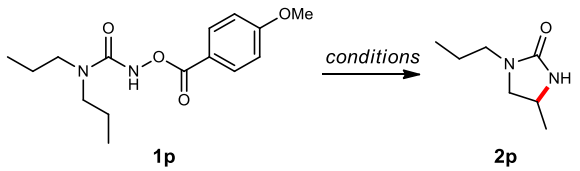
Figure S1. Optimization of the *O*-acyl substituent



In contrast to recent work by Chang,[1] which clearly demonstrated the effectiveness of the 3,5-*bis*-trifluoromethyl group as an activating group for EnT induced triplet nitrene formation of amide and carbamate precursors. In our studies of carbamoyl nitrene precursors, we found this substrate to be completely ineffective. It would decompose rapidly, even under our milder reaction conditions. In contrast, we found that more electron rich precursors were more effective (**Figure S2**). This finding was also inconsistent with *N*-centered radical approaches which rely on an initial SET reduction to generate the radical.[2]

[1] Jung, H.; Keum, H.; Kweon, J.; Chang, S. *J. Am. Chem. Soc.* **2020**. https://doi.org/10.1021/jacs.0c00868.
[2] Ren, X.; Guo, Q.; Chen, J.; Xie, H.; Xu, Q.; Lu, Z. *Chem. Eur. J.* **2016**, *22*, 18695–18699.

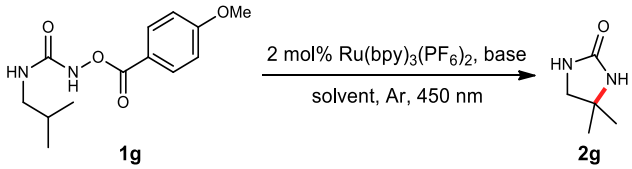
Table S6. Optimization of photocatalytic C-H amination using **1p**



Entry	Photocatalyst	Base	Solvent	%**2p**
1	-	Et_3N	MeCN	0
2	$[Ru(bpy)_3](PF_6)_2$	-	MeCN	0
3	**$[Ru(bpy)_3](PF_6)_2$**	**Et_3N**	**MeCN**	**92**
4	$[Ir(ppy)_2(dtbpy)](PF_6)$	Et_3N	MeCN	40
5	$[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$	Et_3N	MeCN	33
6	$[Ru(bpm)_3]Cl_2$	Et_3N	MeCN	11
7	TPP	Et_3N	MeCN	0
8	$Ir(dFppy)_3$	Et_3N	MeCN	0
9	$[Ru(bpy)_3](PF_6)_2$	Ph_3P	MeCN	17
10	$[Ru(bpy)_3](PF_6)_2$	Et_3N	$PhCF_3$	0
11	$[Ru(bpy)_3](PF_6)_2$	Et_3N	DMSO	57
12	$[Ru(bpy)_3](PF_6)_2$	Et_3N	Dioxane	0
13	$[Ru(bpy)_3](PF_6)_2$	Et_3N	THF	9
14	$[Ru(bpy)_3](PF_6)_2$	Et_3N	$(CH_2Cl)_2$	78
15	$[Ru(bpy)_3](PF_6)_2$	Et_3N	CH_2Cl_2	77

Conditions: 3-(benzoyloxy)-1,1-dipropylurea **1p** (1.00 equiv), photocatalyst (2 mol%), additive (1.10 equiv) in solvent (0.3M) irradiated under inert atmosphere with 450 nm blue LED. [a]BDFE calculated using a reported method.[3]

Table S7. Optimization of photocatalytic C-H amination using **1g**



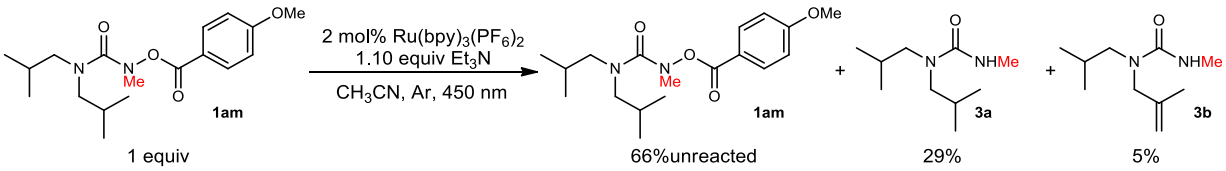
Entry	Base (equiv)	Solvent	Temp °C	%Product
1	Et_3N (1.10 equiv)	MeCN	r.t.	0
2	Phosphate (5 mol%)	CH_2Cl_2	r.t.	18
3	Phosphate (5 mol%)	CH_2Cl_2	40	45
4	Phosphate (5 mol%)	CH_2Cl_2	60	50
5	Phopshate (5 mol%)	CH_2Cl_2	80	17

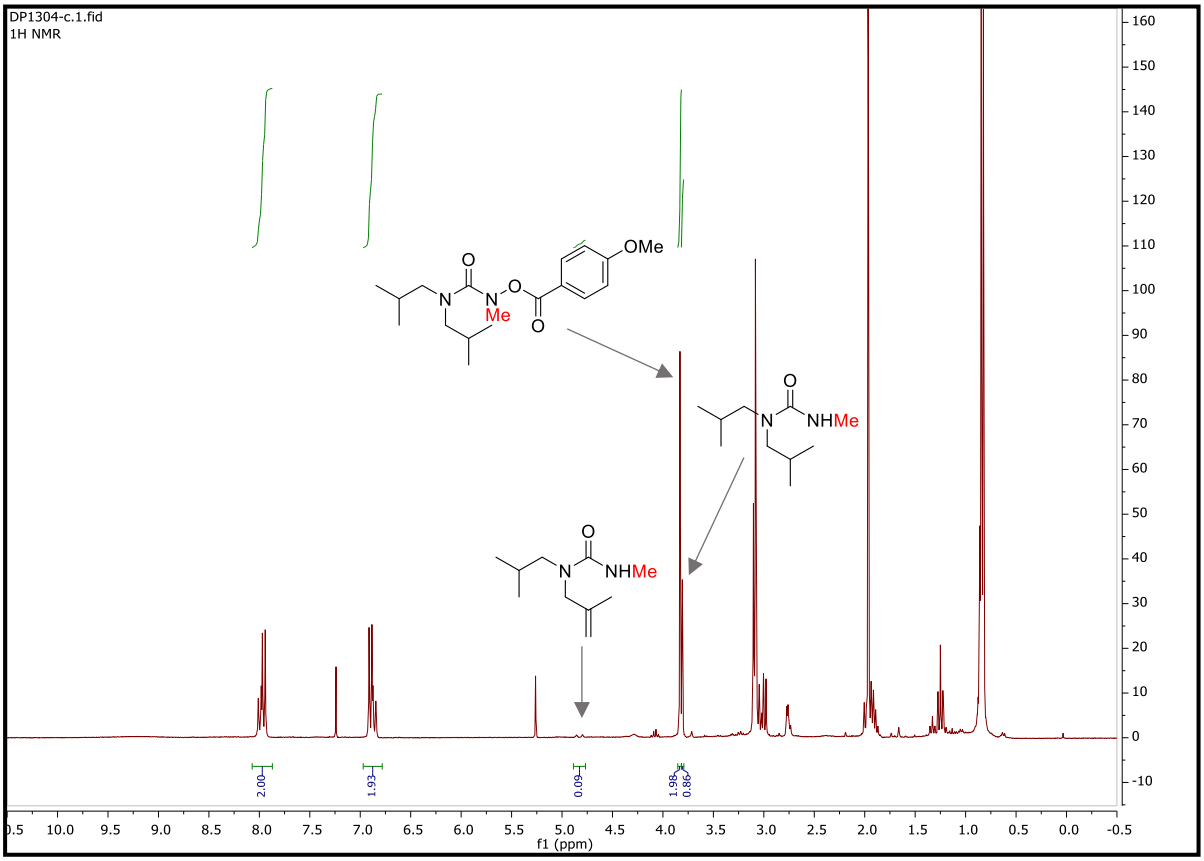
Conditions: 1-isobutyl-3-((4-methoxybenzoyl)oxy)urea **1g** (1.00 equiv), photocatalyst (2 mol%), additive (1.10 equiv) in solvent (0.3M) irradiated under inert atmosphere with 450 nm blue LED.

[3] Choi, G. J.; Knowles, R. R. *J. Am. Chem. Soc.* **2015**, *137*, 9226–9229.

Mechanistic probes of the photocatalytic C-H amination

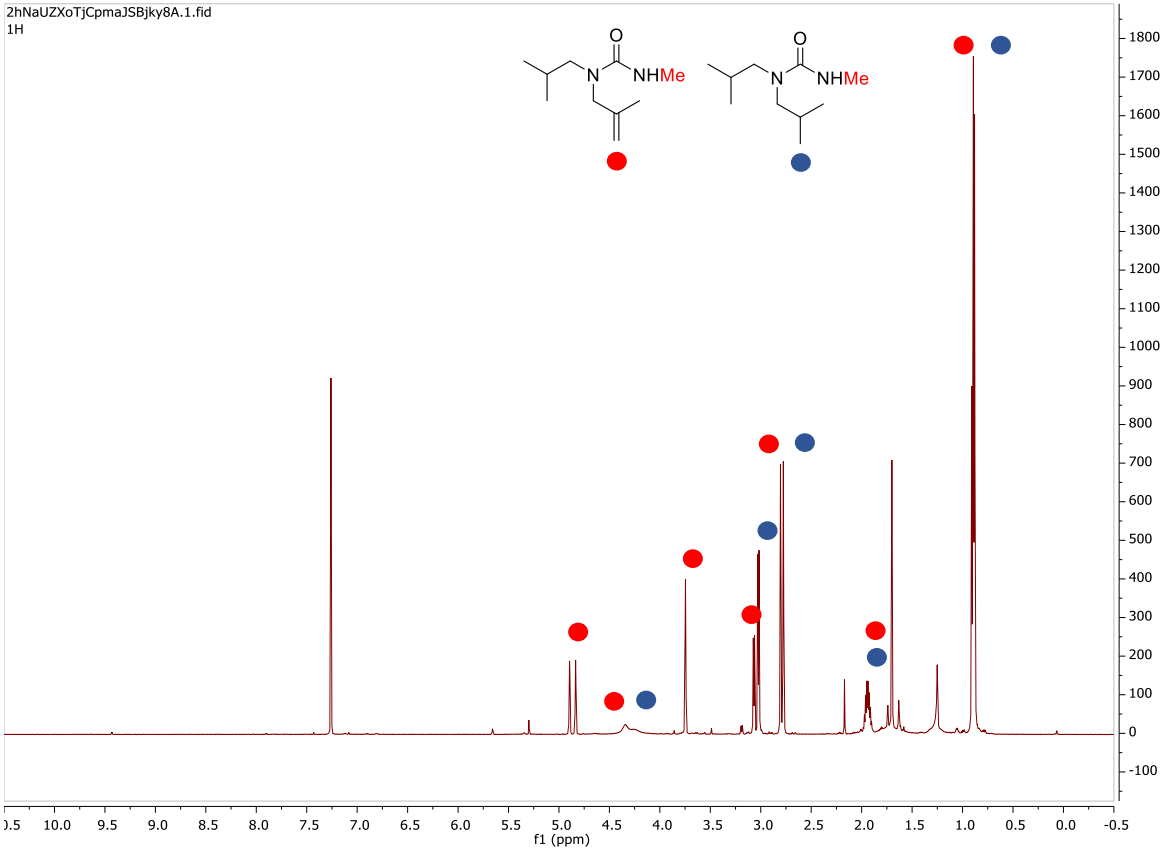
Figure S2. Mixture of urea (**3a** and **3b**) obtained from photocatalytic reaction using **1ar**

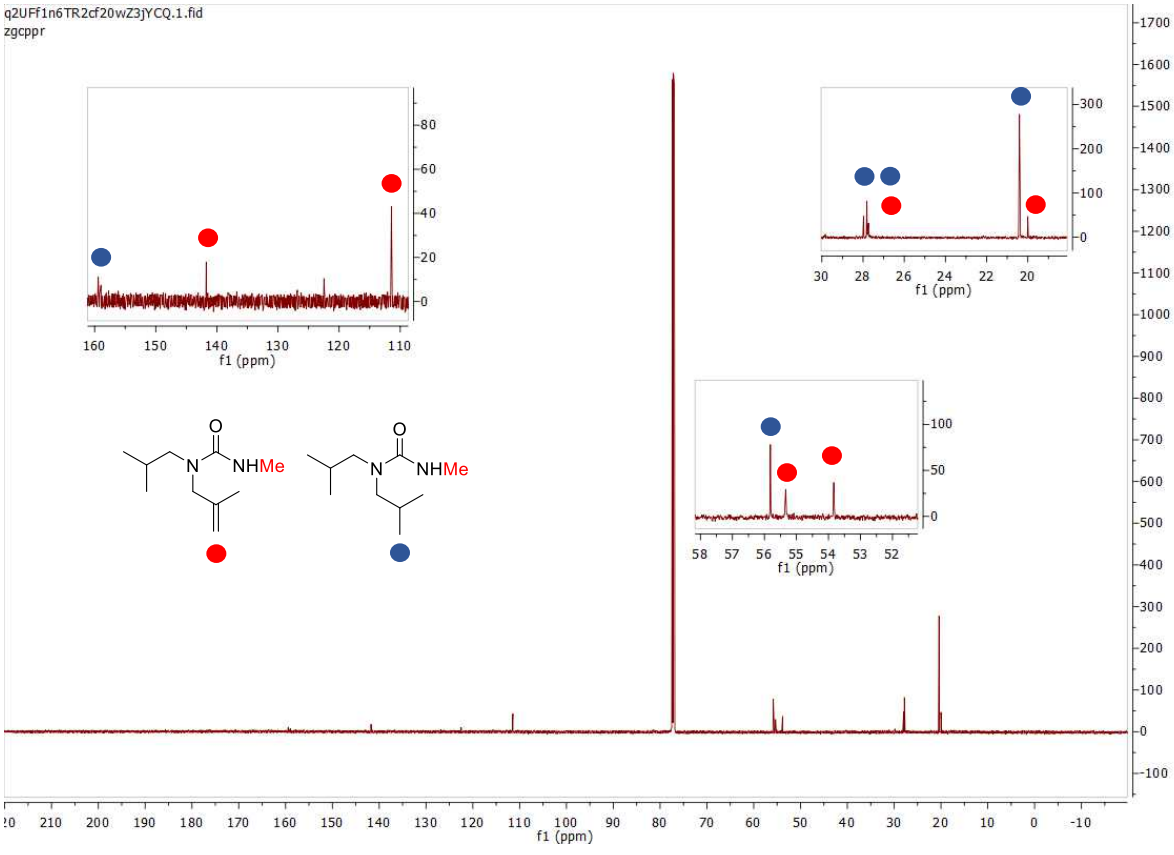




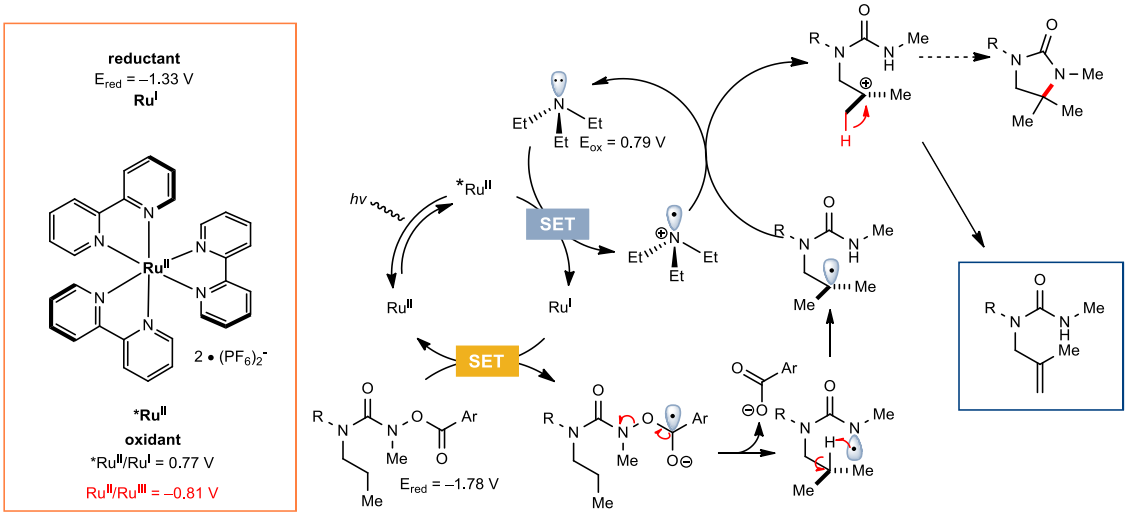
When the *N*-methylated derivative **1am** was subjected to the reaction, we noticed that there was no product formation in the crude NMR. Notably, the reaction was sluggish, even after 72 hours 66% of the starting material remained unreacted. This was accompanied by the observance and isolation of two ureas, **3a** and **3b**, which were obtainable from reduction of the precursor. This indicated to us that the *N*-H was crucial for effective C-H amination. This could be explained by invoking the EnT reaction recently introduced by Chang, which required deprotonation of the hydroxamate precursors for exothermic EnT. This is supported by our own DFT calculations (see below), which clearly demonstrate that EnT to the neutral species is exceptionally endergonic (E_T *neutral* = 74 kcal/mol) whereas EnT to the deprotonated precursor is thermodynamically accessible (E_T *anionic* = 53 kcal/mol). Moreover, the isolation of **3b** is crucial as it clearly showcases that an alternative mechanism involving 1,5-HAT and oxidation of the alkyl-radical followed by carbocation trapping ring-closure is likely not operating in this system (**Scheme S5**).

*NMR of isolated mixture of ureas (**3a** and **3b**)*

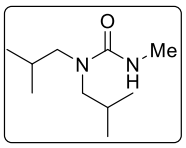




The two ureas were isolated as an inseparable mixture. A genuine sample of **3a** was synthesized to account for its peaks in the NMR mixture. *The peak at 122.5 ppm is an artifact from the NMR.*



Scheme S5. *N*-methylation probe casts doubt on above *N*-centered radical mechanism



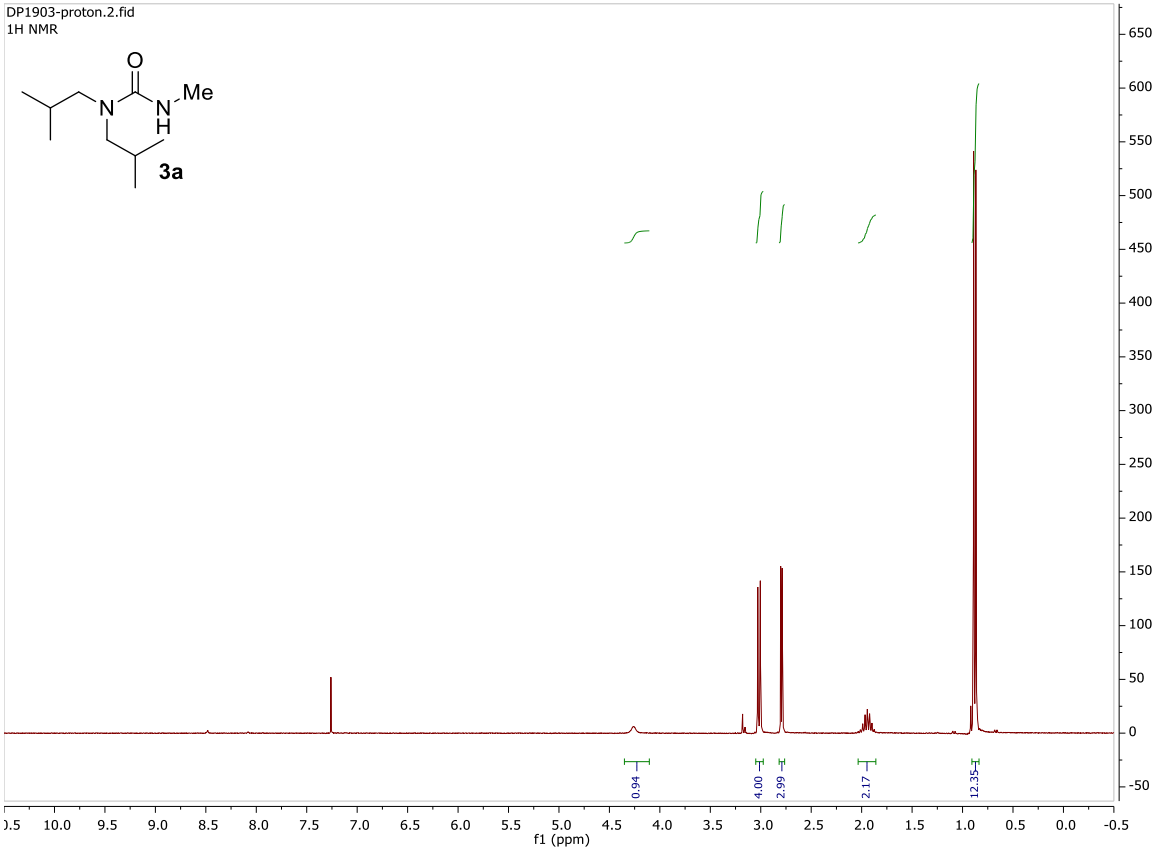
1,1-diisobutyl-3-methylurea (3a): The title compound was synthesized according general procedure **D** using diisobutylamine (0.87 mL, 5.0 mmol), toluene (0.8 M), KOH pellets (0.280 g, 5.00 mmol), and water (2.9 M) at 0 °C. A dripping funnel was affixed on top of the roundbottom flask and this apparatus was purged with argon for 10 minutes. Phosgene (15% in toluene) (8.2 mL, 11.5 mmol) was added to the dripping funnel under inert atmosphere, and was allowed to drip over 1 hour at 0 °C while stirring vigorously. The reaction was allowed to stir for an additional 30 minutes after complete addition of phosgene solution. Upon competition, the crude reaction mixture was bubbled with an argon balloon for 20 minutes in a well ventilated fumehood, to release any excess phosgene gas. The crude reaction mixture was then extracted to remove the aqueous layer, and then the organic phase was washed with brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-diisobutylcarbamoyl chloride which was used in the next step without further purification.
To the crude *N*-diisobutylcarbamoyl chloride was added CH_2Cl_2 (0.3 M) and cooled to 0 °C. To this was added methylamine hydrochloride (0.338 g, 5.00 mmol), and followed immediately by Et_3N (1.39 mL, 10.0 mmol). The reaction was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure which was purified by flash column chromatography (30% EtOAc/Hexanes → 70% EtOAc/Hexanes) to yield a colourless oil (0.507 g, 54% over 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.33-4.20 (br s, 1H), 3.2 (d, J = 7.5 Hz, 2H), 2.79 (d, J = 4.7 Hz, 4H), 2.08-1.78 (m, 2H), 0.88 (d, J = 6.6 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0 (C), 55.7 (CH_2), 27.7 (CH), 27.0 (CH), 20.4 (CH_3).

The title compound has been previously reported.[4]

[4] Snyder, J. K.; Stock, L. M. *J. Org. Chem.* **1980**, *45*, 886-891.


DP1903-proton.2.fid
1H NMR
O
N
N
H
Me
3a
0.94
4.00
2.99
2.17
12.35
f1 (ppm)

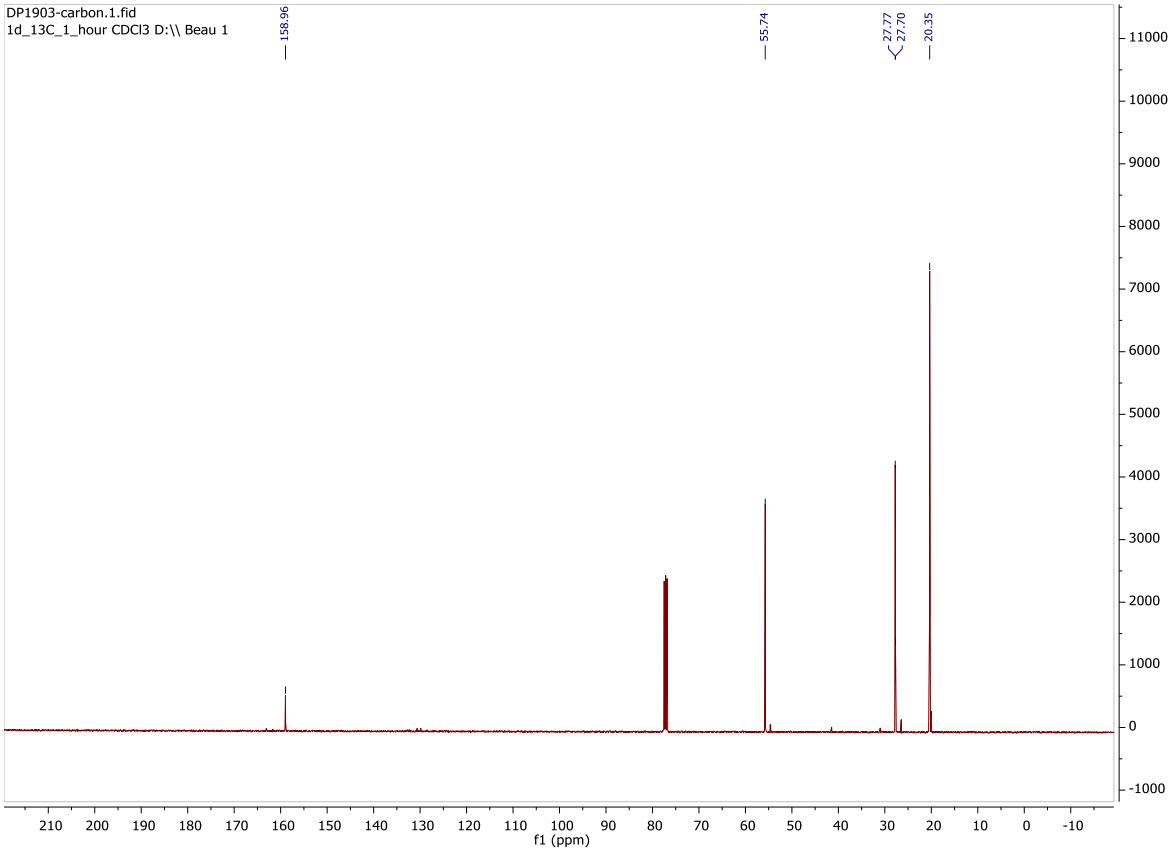
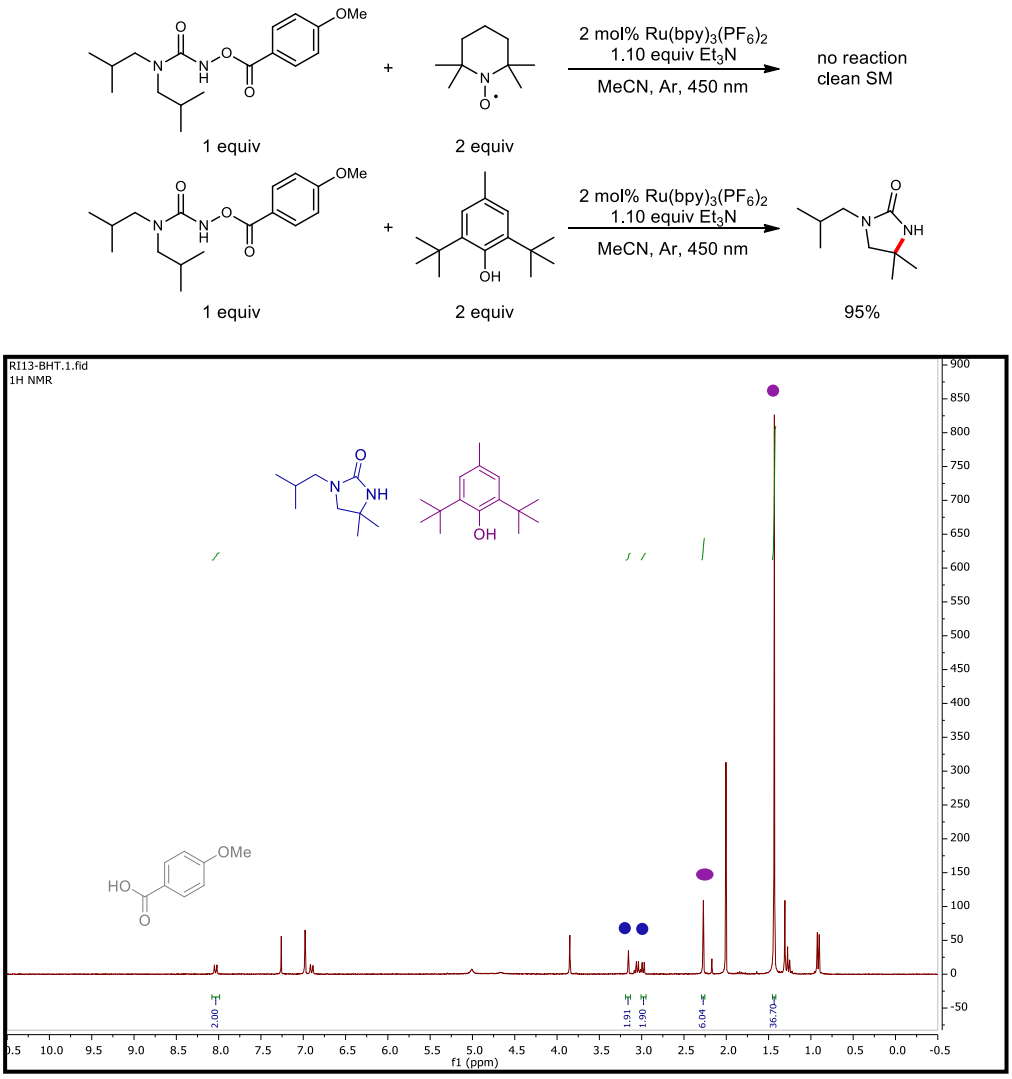

DP1903-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 1
158.96
55.74
27.77
27.70
20.35
f1 (ppm)

Figure S3. Radical trap experiments using BHT

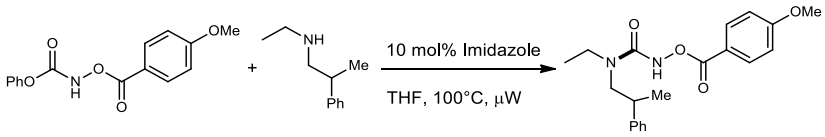


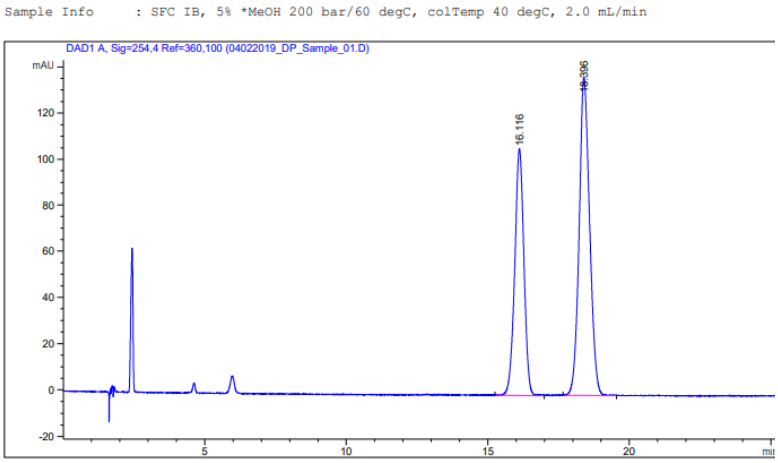
BHT is known to perturb reactions involving 1,5- and 1,6-HAT pathways.[5] Therefore, the fact that BHT had no effect on this reaction was inconsistent with an SET induced radical pathway. However, this finding would fit well within the framework of a triplet nitrene C-H amination. However, TEMPO led to starting material recover. It is possible that TEMPO engaged in redox reactions with the excited photocatalyst, diminishing its ability to engage in productive EnT with the nitrene precursors.

[5] (a) Yuan, W.; Zhou, Z.; Gong, L.; Meggers, E. *Chem. Commun.* **2017**, *53*, 8964-8967. (b) Ma, Z.Y.; Guo, L.-N.; You, Y.; Yang, F.; Hu, M.; Duan, X.-H. *Org. Lett.* **2019**, *21*, 5500-5504. (c) Bao, X.; Wang, Q.; Zhu, J. *Nat. Commun.* **2019**, *10*, 769.

HPLC

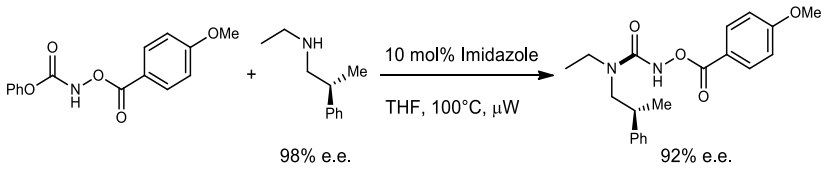
Figure S4. HPLC spectrum of **1k**



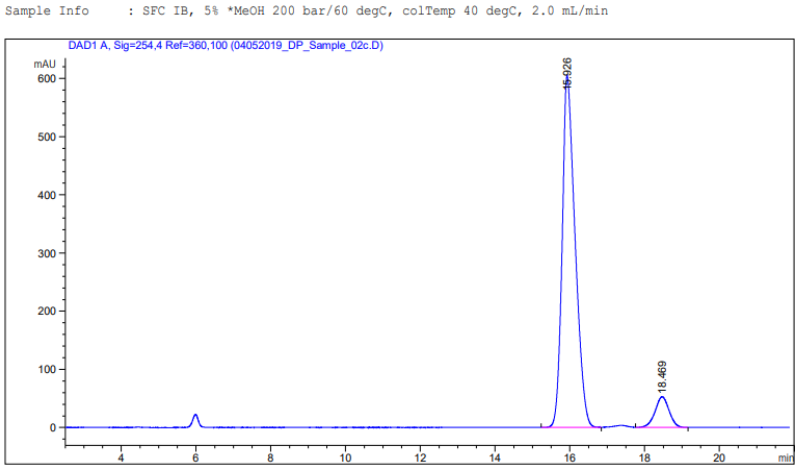


#	Time	Area	Height Width	%
1	16.116	2402.9	106.9	40.4366
2	18.396	3539.2	137.9	59.5634

Figure S5. HPLC spectrum of enantioenriched **1an**

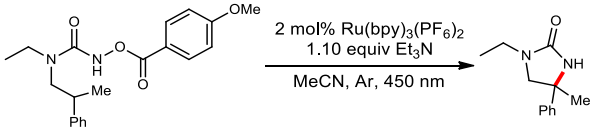


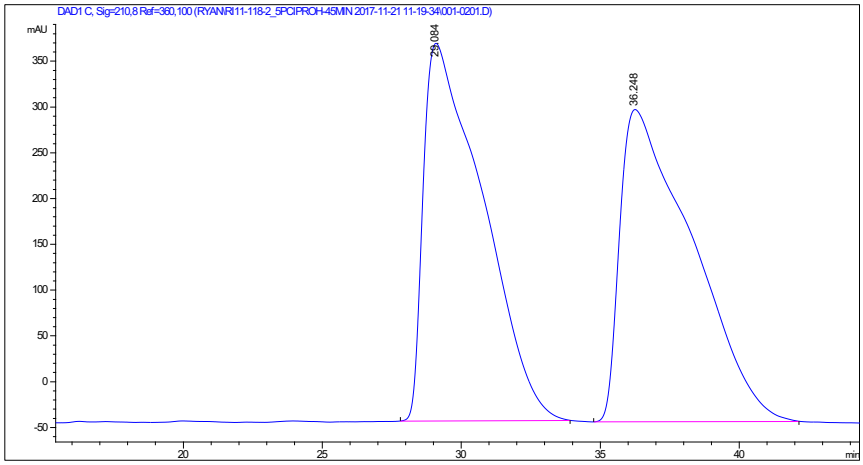
98% e.e. 92% e.e.



#	Time	Area	Height Width	%
1	15.926	14526.3	604.9	91.3709
2	18.469	1371.9	52.9	8.6291

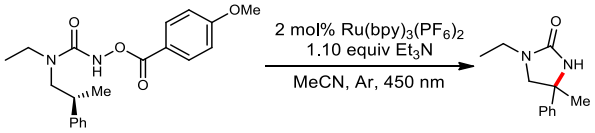
Figure S6. HPLC spectrum of **2k** from photocatalytic C-H amination of **1k**

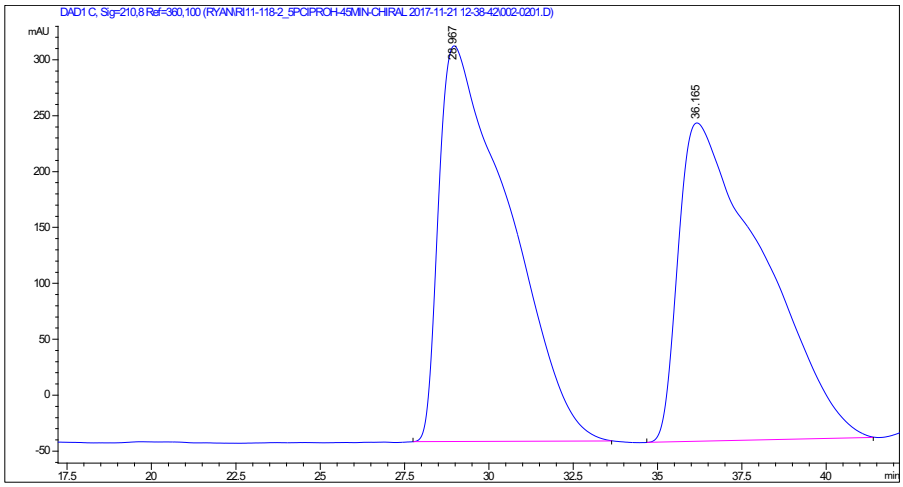




#	Time	Area	Height Width	%
1	29.084	61505.5	412.4	49.893
2	36.248	61769.7	341	50.107

Figure S7. HPLC spectrum of **2k** from photocatalytic C-H amination of enantioenriched **1an**



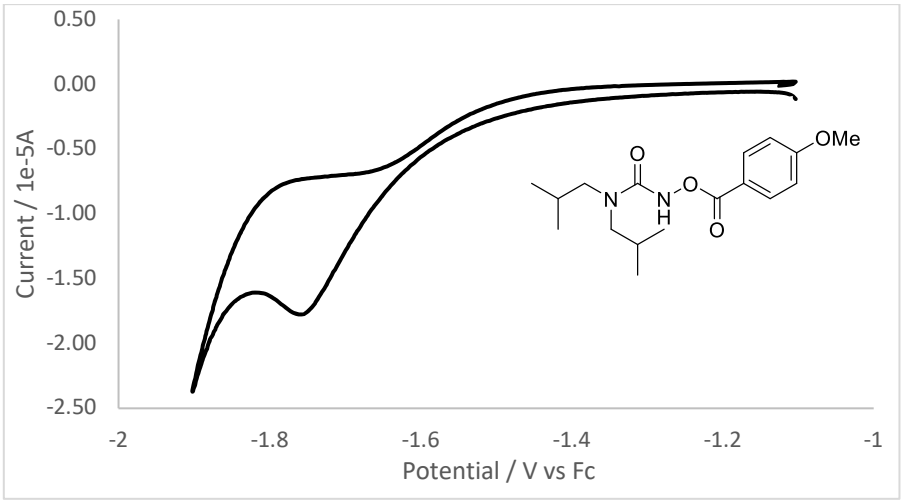


#	Time	Area	Height Width	%
1	28.967	51326.1	354	50.790
2	36.165	49730.3	284.8	49.210

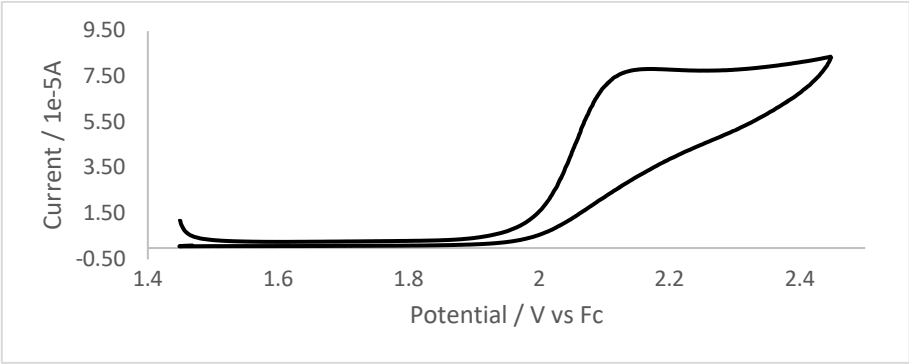
Cyclic voltammetry

Cyclic voltammetry was performed using a Princeton Applied Research Versastat 3 potentiostat employing a glass cell and platinum auxiliary wires for the counter and pseudo-reference electrodes, where a 1.6 mm platinum disk electrode was used for the working electrode. The measurements were carried out in CH_3CN solutions (dried by J. C. Meyer solvent system and stored over molecular sieves) containing 0.1 M tetrabutylammonium hexafluorophosphate (Sigma Aldrich) as supporting electrolyte with a scan rate of 100 mV/s. The experiments were referenced to the Fc/Fc^+ redox couple of ferrocene (Sigma Aldrich).

Figure S9. Cyclic voltammetry of **1a**

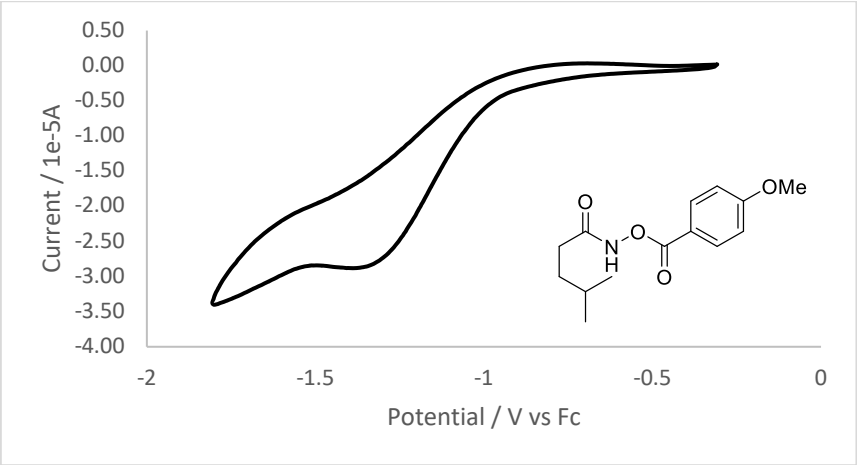


Irreversible reduction at -1.75V vs Fc^+/Fc.

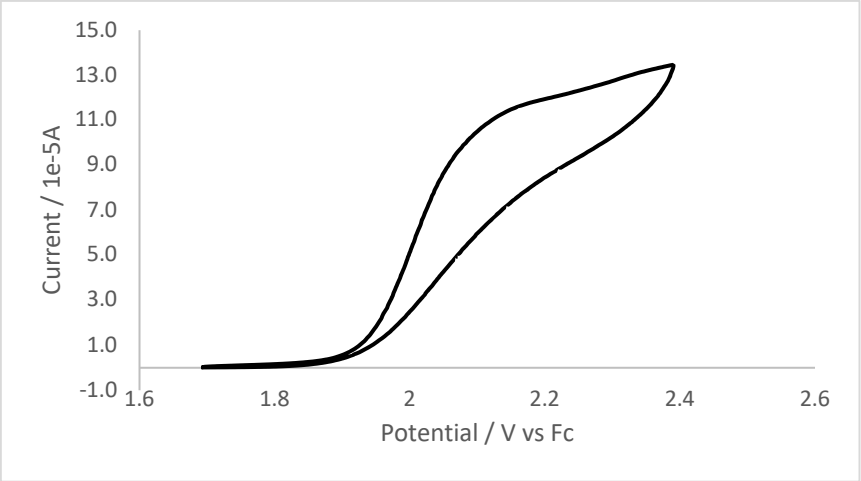


Irreversible oxidation at +2.15V vs Fc^+/Fc.

Figure S10. Cyclic voltammetry of **1h**



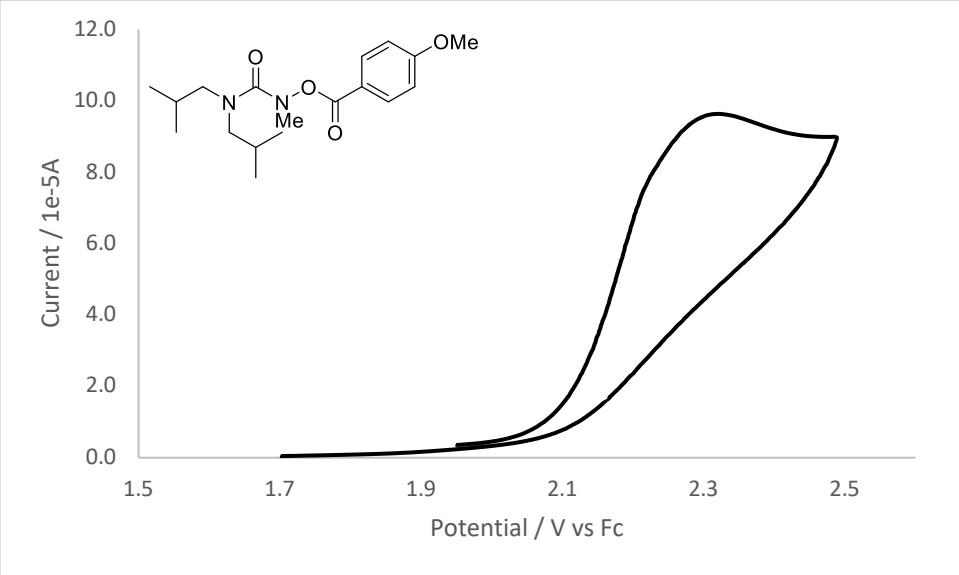
Irreversible reduction at -1.36 vs Fc^{+}/Fc



Irreversible oxidation at +2.13 vs Fc^{+}/Fc

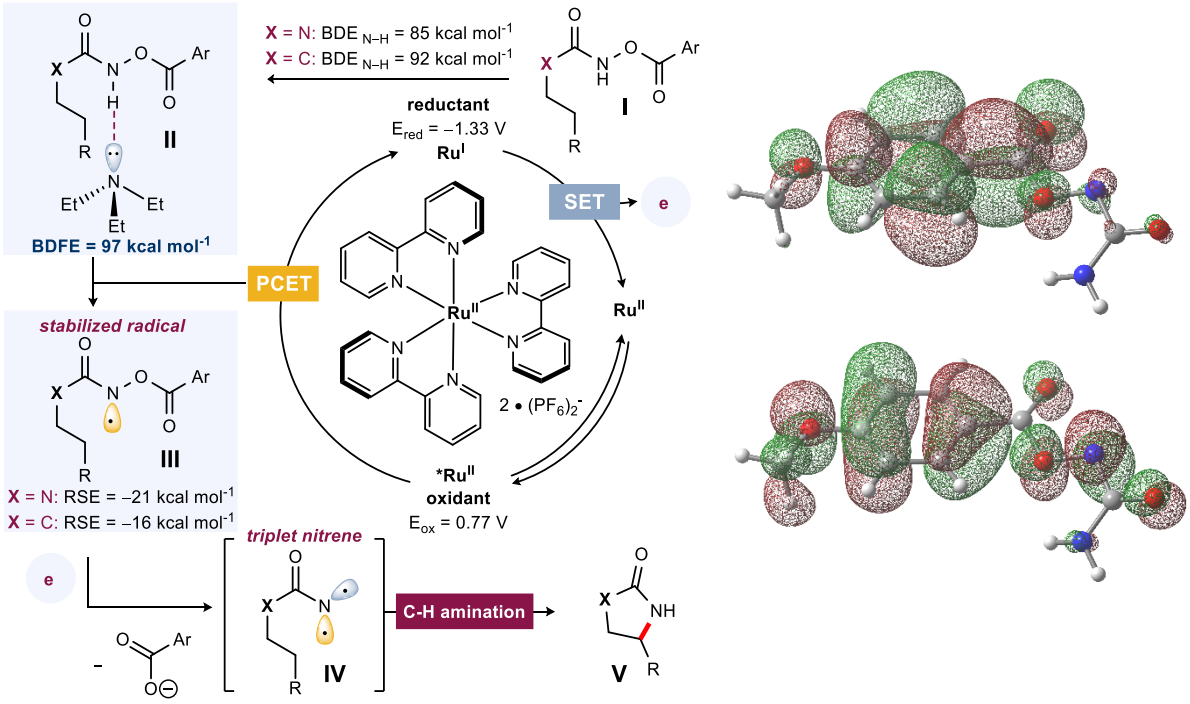
Figure S11. Cyclic voltammetry of **1am**

No reduction was observed at potential -2.3 V vs Fc^{+}/Fc.



Irreversible oxidation at +2.30 vs Fc^{+}/Fc

Alternate mechanism considered: single electron α-elimination



Scheme S6. Alternative mechanism invoking sequential PCET oxidation / reduction

An alternative mechanism (**Scheme S6**) begins with **I** forming H-bonded complex **II**, which undergoes PCET with Ru^{II*} (BDFE = 97 kcal/mol)[6] to produce stabilized radical **III.** A radical stabilization energy (RSE) of –21 kcal/mol was calculated for **III** by DFT using B3LYP 6-311+G(2d,p) indicating a substantial degree of stabilization (persistent radical DPPH = –27 kcal/mol). The PCET is therefore a highly exergonic process (ΔG = –12 kcal/mol) and **III** can then undergo SET reduction by Ru^{I} (E_{red} = –1.33 V). Analysis of the putative *N*-centered radical **III** highlights that SET reduction should be significantly favoured over reduction of **I** ($E_{red(I)}$ = –1.8 V). Visualization of the LUMO by DFT indicates that addition to the carbonyl electrophore would be preferred. Nocera recently calculated the rates of back-electron-transfer (BET)[7] in photochemical PCET reactions of amides. In the proposed mechanism, rapid BET in the presence of a more suitable electrophore should lead to the desired reaction outcome. This not only provides a rationale for the increased rate of conversion observed with the *N*-H vs. *N*-methyl urea precursors, but also justifies the use of *p*-methoxy benzoate precursors to facilitate the careful orchestration of events required to access the triplet nitrene. Reductive N-O bond cleavage from **III** expels the carboxylate via 1-electron α-elimination to provide triplet nitrene **IV** and C-H amination then leads to the products **V**. While to our knowledge such a 1-electron α-elimination process has not been reported, each individual step is well-precedented: 1) PCET is an effective strategy to form amidyl radicals from mildly acidic N-H bonds by an oxidative pathway.[8] 2) Reductive-quenching is efficient to form amidyl radicals by reductive SET-initiated N-O bond cleavage.[9] In this system, the adjacent oxygen atom of the hydroxylamine derivative should facilitate PCET by: 1) lowering the pKa[10] of the N-H bond, and 2) increasing the stability of the generated *N*-radical by a capto-dative effect.[11] In addition, precedent for 1-electron α-elimination emerged during the course of this study,

[6] BDFE were calculated using the formula: Formal BDFE (kcal/mol) = 2.3RTpKa +23.06E + 54.9 (MeCN).

[7] Ruccolo, S.; Qin, Y.; Schnedermann, C.; Nocera, D. G. *J. Am. Chem. Soc.* **2018**, *140*, 14926–14937.

[8] (a) Gentry, E. C.; Knowles, R. R. *Acc. Chem. Res.* **2016**, *49*, 1546-1556. (b) Zheng, S.; Gutiérrez-Bonet, Á.; Molander, G. A. *Chem* **2019**, *5*, 339–352.

[9] Davies, J.; Svejstrup, T. D.; Fernandez Reina, D.; Sheikh, N. S.; Leonori, D. *J. Am. Chem. Soc.* **2016**, *138*, 8092-8095.

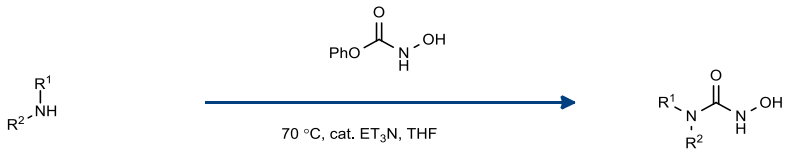
[10] Bordwell, F. G.; Fried, H. E.; Hughes, D. L.; Lynch, T. Y.; Satish, A. V; Whang, Y. E. *J. Org. Chem.* **1990**, *55*, 3330-3336.

[11] Hioe, J.; Šakić, D.; Vrček, V.; Zipse, H. *Org. Biomol. Chem.* **2015**, *13*, 157-169.

with a detailed study on the photogeneration of a Rh_2 nitrenoid from chloramine-T, although synthetic applications were not evaluated.[12]

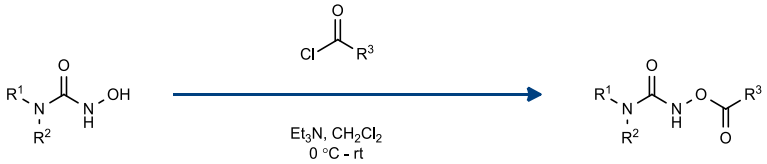
General Procedures

General Procedure A: ***Substitution of N-hydroxycarbamates***[13]



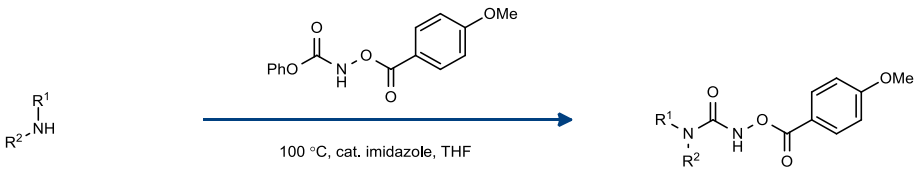
To a 5.0 mL microwave vial charged with a stir bar was added the phenyl *N*-hydroxycarbamate (1.10 equiv.), then THF (0.30 M), to which was added triethylamine (0.20 equiv.) and the corresponding amine (1.00 equiv.). The vial was sealed with a microwave cap and heated for 16 h at 70 °C via conventional (oil bath) heating. Solvent was removed under reduced pressure and the products were then purified by silica gel chromatography to give the corresponding pure hydroxyureas.

General Procedure B: ***Synthesis of N-oxycarbamates***[13]



To a roundbottom flask charged with a stir bar was added *N*-hydroxycarbamate (1.00 equiv.) then CH_2Cl_2 (0.30 M) and allowed to stir at 0 °C. *Hydroxycarbamates are insoluble and will not always dissolve completely before the next step of the reaction* Upon observing most of the hydroxycarbamate dissolve, Et_3N was added (1.00 equiv.) and finally the acyl chloride was added dropwise (1.00 equiv.). The reaction was allowed to warm gradually to room temperature. Upon completion, H_2O was added and the reaction mixture was extracted with CH_2Cl_2. The organic layer was recollected and washed with a saturated $NaHCO_3$ solution, and then the organic phase was recollected and washed with brine. The organic phase was dried over Na_2SO_4 (stirring for 15 minutes). Solids were filtered and the filtrate was collected and concentrated under reduced pressure to give the corresponding pure acyloxycarbamates.

General Procedure C: ***Substitution of N-acyloxycarbamates***[13]

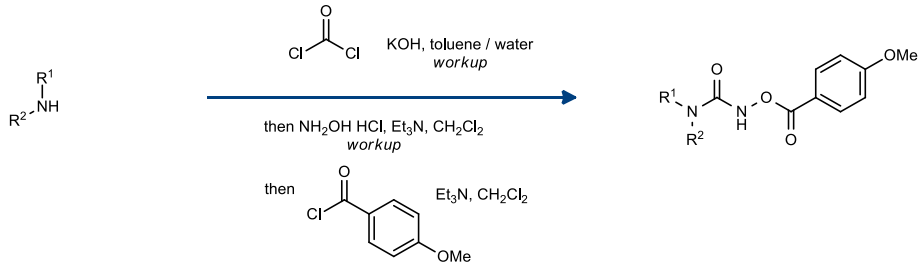


To a 5 mL microwave vial charged with a stir bar was added the phenyl *N*-acyloxycarbamate (1.00 equiv.), then THF (0.2 M), to which was added the corresponding amine (1.05 equiv.) and then imidazole (0.10 equiv.). The vial was sealed with a microwave cap and heated for 1-3 hours at 100 ºC

[12] Das, A.; Maher, A. G.; Telser, J.; Powers, D. C. *J. Am. Chem. Soc.* **2018**, *140*, 10412-10415.
[13] Allen, M. A.; Ivanovich, R. A.; Polat, D. E.; Beauchemin, A. M. *Org. Lett*. **2017**, *19*, 6574.

via microwave irradiation. The reaction mixture was diluted with EtOAc and transferred to a separatory funnel, then washed twice with 1 M NaOH and once with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the corresponding pure acyloxyureas. In some cases, a higher degree of purity was needed after the extraction and the products could be recrystallized or purified by silica gel chromatography.

General Procedure D: ***Synthesis of N-oxyureas via carbamoyl chloride formation***

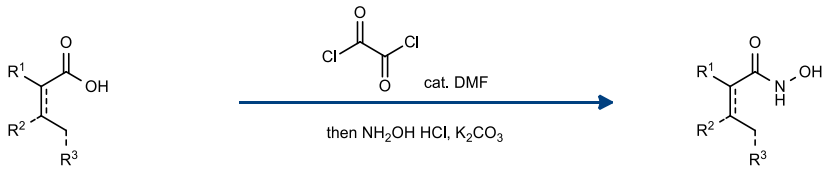


To a clean 50 mL round bottom flask charged with a stir bar was added the amine (1.00 equiv.) then PhMe (0.8 M) to which was added KOH pellets (1.00 equiv.) and water (2.9 M). A dripping funnel was affixed on top of the roundbottom flask and this apparatus was purged with argon for 10 minutes at 0 °C. Phosgene (15% in toluene) (2.30 equiv.) was added to the dripping funnel under inert atmosphere, and was allowed to drip over 1 hour at 0 °C while stirring vigorously. The reaction was allowed to stir for an additional 30 minutes after complete addition of phosgene solution. Upon competition, the crude reaction mixture was bubbled with an argon balloon for 20 minutes in a well ventilated fumehood, to release any excess phosgene gas. The crude reaction mixture was then extracted to remove the aqueous layer, and then the organic phase was washed with brine (5 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude carbamoyl chloride which was used in the next step without further purification.

To the crude carbamoyl chloride was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added hydroxylamine hydrochloride (1.00 equiv.), and followed immediately by Et_3N (2.00 equiv.). The reaction was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-hydroxyurea, which could be used in the next step without further purification.

To the crude *N*-hydroxyurea was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (1.00 equiv.) followed immediately by addition of *p*-methoxybenzoylchloride (1.00 equiv.). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-oxyurea which was be recrystallized or purified by silica gel chromatography.

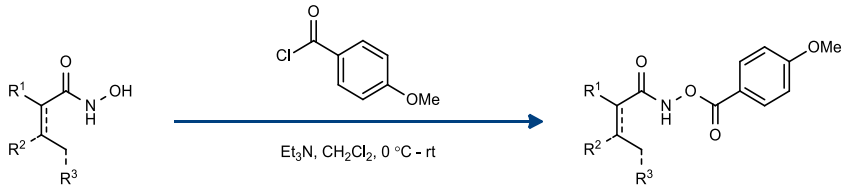
General Procedure E: ***Synthesis of hydroxamic acids***[14]



To a clean 50 mL round bottom flask charged with a stir bar was added the carboxylic acid (1.00 equiv.), then CH_2Cl_2 (0.07 M) and cooled to 0 °C. To this was added oxalyl chloride (2.00 equiv.) and DMF (2 drops) and the reaction was allowed to stir for an additional 2.5 to 4 hours at room temperature. Upon completion, the crude reaction was evaporated under reduced pressure to provide the crude hydroxamic acid which was used in the next step without further purification.

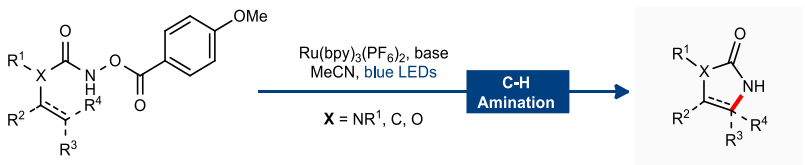
To a clean 50 mL round bottom flask charged with a stir bar was added the hydroxylamine hydrochloride (1.20 equiv.), then a 2:1 mixture of EtOAc and H_2O (0.08 M) and cooled to 0 °C. To this was added K_2CO_3 (2.00 equiv.) and the crude hydroxamic acid was added dropwise. The reaction was allowed to stir for 12 hours at room temperature. Upon completion, the reaction was separated and extracted twice with EtOAc (20 mL x2). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-oxyurea which was be recrystallized or purified by silica gel chromatography.

General Procedure F: ***Synthesis of N-p-methoxybenzoylhydroxamic acid***



To a clean 50 mL round bottom flask charged with a stir bar was added the pure hydroxamic acid (1.00 equiv.), then CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (1.00 equiv.) followed immediately by portionwise addition of *p*-methoxybenzoylchloride (1.00 equiv.). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x2), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N-p*-methoxybenzoylhydroxamic acid which was be recrystallized or purified by silica gel chromatography.

General Procedure G: ***Photoinduced C-H amination of N-oxyureas.***



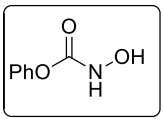
To a 8 mL Kimax glass vial charged with a stir bar was added the *N*-oxyurea (1.00 equiv.), then MeCN (0.2m), to which was added tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (2 mol%), and then

[14] Hong, S.Y.; Park. Y.; Hwang, Y.; Kim. Y. B.; Baik, M.-H.; Chang, S. *Science* **2018**, *359*, 1016.

base triethylamine (1.10 equiv.) or tetrabutylammonium dibutylphosphate (5 mol%). The vial was closed with Teflon screw cap and was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by silica gel chromatography.

Characterization Data

Synthesis of phenyl N-hydroxycarbamate



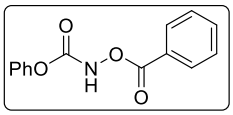
Phenyl *N*-hydroxycarbamate (4a): The title compound was synthesized according to a literature procedure.[13]

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.43-10.15 (br s, 1 H), 9.11-9.03 (br s, 1H), 7.45-7.33 (m, 2H), 7.26-7.17 (m, 1H), 7.14-7.06 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): 155.5 (C), 150.7 (C), 129.4 (CH), 125.1 (CH), 121.6 (CH).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.

Synthesis of N-acyloxycarbamates

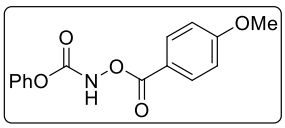


Phenyl *N*-benzoyloxycarbamate (4b): The title compound was synthesized according to a literature procedure.[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (br s, 1H), 8.11 (d, *J* = 7.9 Hz, 2H), 7.66-7.61 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.39-7.34 (m, 2H), 7.25-7.16 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7 (C), 154.7 (C), 150.1 (C), 134.3 (CH), 129.9 (CH), 129.4 (CH), 128.7 (CH), 126.4 (C), 126.1 (CH), 121.2 (CH).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.



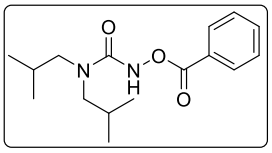
Phenyl (4-methoxybenzoyl)oxycarbamate (4c): The title compound was synthesized according to a literature procedure.[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.82 (br s, 1H), 8.10 (d, *J* = 8.9 Hz, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.28-7.20 (m, 3H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5 (C), 164.6 (C), 154.9 (C), 150.3 (C), 132.3 (CH), 129.6 (CH), 126.2 (CH), 121.3 (CH), 118.6 (C), 114.2 (CH), 55.6 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.

Synthesis of N-oxyureas

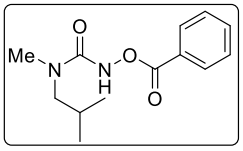


3-(Benzoyloxy)-1,1-diisobutylurea (1a): The title compound was synthesized according to a literature procedure.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (br s, 1H), 8.11 (dd, *J* = 8.4, 1.1 Hz, 2H), 7.62-7.58 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 3.14 (d, *J* = 7.6 Hz, 4H), 2.16-1.97 (m, 2H), 0.95 (d, *J* = 6.7 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3 (C), 158.1 (C), 134.1 (C), 130.0 (CH), 128.7 (CH), 127.3 (CH), 55.1 (CH_2), 27.3 (CH), 20.3 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.



3-(Benzoyloxy)-1-isobutyl-1-methylurea (1b): The title compound was synthesized according to general procedure **C** using phenyl benzoyloxycarbamate (1.29 g, 5.00 mmol), and *N*-methylisobutylamine (0.60 mL, 5.0 mmol) and imidazole (0.034 g, 0.50 mmol) in THF (16.7 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (30% EtOAc/Et_2O) to yield the title compound as a colourless oil (1.05 g, 84%).

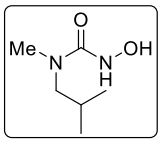
TLC R_f: 0.30 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54-8.43 (br s., 1H), 8.17-8.10 (m, 2H), 7.67-7.58 (m, 1H), 7.53-7.44 (m, 2H), 3.17 (d, *J* = 7.7 Hz, 2H), 3.02 (s, 3H), 2.04-1.97 (m, 1H), 0.96 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0 (C), 157.9 (C), 134.0 (CH), 129.9 (CH), 128.6 (CH), 127.1 (C), 56.6 (CH_2), 34.6 (CH), 27.2 (CH), 20.0 (CH).

IR (FTIR): 3269, 2657, 1747, 167, 1489, 1243 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{13}H_{18}N_2O_3Na$ $[M+Na]^+$: 273.1317. Found: 273.1302.



1-Isobutyl-1-methyl-3-hydroxyurea (4d): The title compound was synthesized according to general procedure **A** using phenyl *N*-hydroxycarbamate (0.841 g, 5.50 mmol), and *N*-methylisobutylamine (0.436 g, 5.00 mmol) and Et_3N (0.14 mL, 1.0 mmol) in THF (16.6 mL, 0.30 M). The vial was sealed with a microwave cap and heated for 16 h at 70 °C via an oil bath heating. The reaction mixture was concentrated under reduced pressure and isolated using flash chromatography (2% MeOH/CH_2Cl_2). The title compound was obtained as an amorphous white solid (0.530 g, 73%).

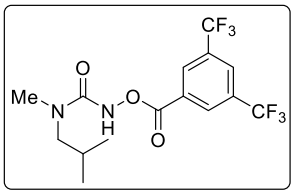
TLC R_f: 0.12 in 2% MeOH/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-6.95 (br s, 1H), 6.86-6.77 (br s, 1H), 3.09 (d, *J* = 7.6 Hz, 2H), 2.89 (s, 3H), 2.02-1.86 (m, 1H), 0.90 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (C), 56.2 (CH_2), 34.1 (CH_3), 27.2 (CH), 19.9 (CH_3).

IR (FTIR): 3220, 2956, 1615, 1521, 1386, 1287, 1108 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_6H_{14}N_2O_2$ $[M]^+$: 146.1055. Found: 146.1040.



3-((3,5-Bistrifuoromethylbenzoyl)oxy)-1-isobutyl-1-methylurea (1c): The title compound was synthesized according to general procedure **C** using the pure 1-isobutyl-1-methyl-3-hydoxyurea (0.530 g, 3.60 mmol) was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (0.50 mL, 3.60 mmol) followed immediately by dropwise addition of 3,5-bis(trifluoromethyl)benzoyl chloride (0.65 mL, 3.60 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude which was purified by flash column chromatography (20% EtOAc/Hexanes). The title compound was obtained as an amorphous white solid (0.831 g, 60%).

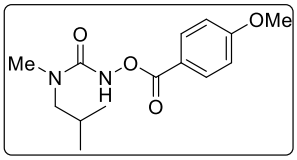
TLC R_f: 0.94 in 2% MeOH/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58-8.56 (br s, 2H), 8.43-8.41 (br s, 1H), 8.14-8.11 (br s, 1H), 3.17 (d, *J* = 7.4 Hz, 2H), 3.03 (s, 3H), 2.07-1.95 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7 (C), 157.3 (C), 132.5 (C, q, *J* = 23 Hz), 130.0 (CH, m), 129.5 (C), 127.3 (CH, m), 122.6 (C, d, *J* = 203 Hz), 56.6 (CH_2), 34.6 (CH), 27.1 (CH), 19.9 (CH_3).

IR (FTIR): 2697, 1767, 1664, 1221, 1127, 697 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{15}H_{16}N_2O_3F_6Na$ $[M+Na]^+$: 409.0963. Found: 409.0983.



1-Isobutyl-3-((4-methoxybenzoyl)oxy)-1-methylurea (1d): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N*-methyl-isobutylamine (0.262 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (10% EtOAc/Hexanes → 33% EtOAc/Hexanes) to yield the title compound as an amorphous white solid (0.800 g, 95%).

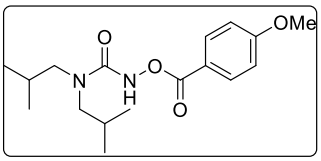
TLC R_f: 0.36 in 40% EtOAc/Hexanes.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50-8.37 (br s, 1H), 8.12-7.99 (m, 2H), 7.04-6.86 (m, 2H), 3.85 (s, 3H), 3.14 (d, *J* = 10.7 Hz, 2H), 2.98 (s, 3H), 1.98 (dquintet, *J* = 13.8, 6.9 Hz, 1H), 0.93 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9 (C), 164.3 (C), 158.1 (C), 132.2 (CH), 119.5 (C), 114.1 (CH), 56.7 (CH_3) 55.6 (CH_3), 51.4 (CH_2), 34.9 (CH_2), 27.4 (CH), 20.1 (CH_3).

IR (FTIR): 3158, 3005, 2959, 1751, 1663, 1604, 1507, 1315, 1249, 1159 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{14}H_{20}N_2O_4Na$ $[M+Na]^+$: 303.1315. Found: 303.1325.



1-Diisobutyl-3-((4-methoxybenzoyl)oxy)urea (1a'): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and N,N-diisobutylamine (0.388 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (20% EtOAc/hexanes) to yield the title compound as an amorphous off-white solid (0.940 g, 97%).

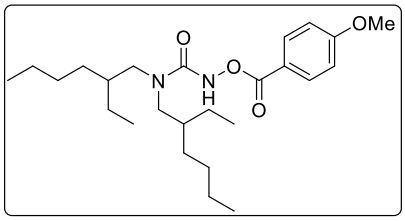
TLC R_f: 0.28 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (br s, 1H), 8.07-8.04 (m, 2H), 6.93-6.90 (m, 2H), 3.84 (s, 3H), 3.12 (d, J = 7.6 Hz, 4H), 2.04 (dquintet, J = 13.7, 6.9 Hz, 2H), 0.93 (d, J = 6.7 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0 (C), 164.3 (C), 158.3 (C), 132.2 (CH), 119.5 (C), 114.1 (CH), 55.5 (CH_3), 55.0 (CH_2), 27.2 (CH), 20.2 (CH_3).

IR (FTIR): 3186, 2954, 2870, 1748, 1655, 1605, 1509, 1484, 1316, 1242 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{17}H_{26}N_2O_4Na$ $[M+Na]^+$: 345.1785. Found: 345.1799.



3-((4-Methoxybenzoyl)oxy)-1,1-bis(2-methylhexyl)urea (1b'): The title compound was synthesized according to a modified general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.639 g, 3.00 mmol), and bis(2-ethylhexyl)amine (0.640 g, 2.65 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (10% EtOAc/hexanes) to yield the title compound as an amorphous off-white solid (0.917 g, 85%).

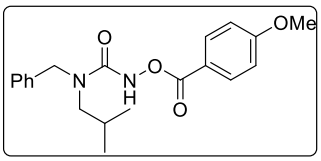
TLC R_f: 0.40 in 10% EtOAc/Hexanes.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.21-10.18 (br s, 1H), 7.99-7.91 (m, 2H), 7.14-7.04 (m, 2H), 3.86 (s, 3H), 3.21-3.01 (m, 4H), 1.76-1.58 (m, 2H), 1.36-1.12 (m, 16H), 0.94-0.76 (m, 12H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 165.5 (C), 163.4 (C), 158.4 (C), 131.9 (CH), 120.4 (C), 114.7 (CH), 56.1 (CH), 49.5 (CH_2), 49.5 (CH_2), 37.1 (CH), 30.2 (CH_2), 28.6 (CH_2), 23.6 (CH_2), 23.0 (CH_2), 14.4 (CH_3), 11.0 (CH_3).

IR (FTIR): 3177, 2959, 2925, 1756, 1658, 1509, 1241 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{25}H_{42}N_2O_4Na$ $[M+Na]^+$: 457.3043. Found: 457.3058.



1-Benzyl-1-isobutyl-3-((4-methoxybenzoyl)oxy)urea (1d'): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and benzyl-2-methylpropan-1-amine (0.490 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (20% EtOAc/hexanes) to yield the title compound as an amorphous off-white solid (0.930 g, 87%).

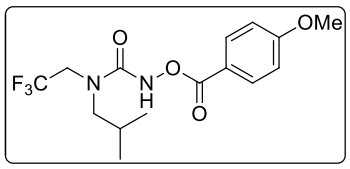
TLC R_f: 0.28 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (br s, 1H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.40-7.30 (m, 6H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.59 (s, 2H), 3.86 (s, 3H), 3.17 (d, *J* = 7.5 Hz, 2H), 2.07 (dquintet, *J* = 13.7, 6.9 Hz, 1H), 0.97 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7 (C), 164.2 (C), 158.5 (C), 136.5 (C), 132.1 (CH), 129.0 (CH), 127.8 (CH), 127.1, (CH), 119.4 (C), 113.9 (CH), 55.5 (CH_3), 54.6 (CH_2), 27.4 (CH), 20.2 (CH_3).

IR (FTIR): 3116, 2959, 2840, 1751, 1647, 1603, 1509, 1419, 1315, 1238 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{20}H_{24}N_2O_4Na$ $[M+Na]^+$: 379.1628. Found: 379.1634.



1-Isobutyl-3-((4-methoxybenzoyl)oxy)-1-(2,2,2-trifluoroethyl)urea (1e): The title compound was synthesized according to general procedure **D** using *N*-propylaniline (1.55 g, 10.0 mmol), toluene (0.8 M), KOH pellets (0.561 g, 10.0 mmol), and water (2.9 M) at 0 °C. A dripping funnel was affixed on top of the roundbottom flask and this apparatus was purged with argon for 10 minutes. Phosgene (15% in toluene) (16.4 mL, 23 mmol) was added to the dripping funnel under inert atmosphere, and was allowed to drip over 1 hour at 0 °C while stirring vigorously. The reaction was allowed to stir for an additional 30 minutes after complete addition of phosgene solution. Upon competition, the crude reaction mixture was bubbled with an argon balloon for 20 minutes in a well ventilated fumehood, to release any excess phosgene gas. The crude reaction mixture was then extracted to remove the aqueous layer, and then the organic phase was washed with brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude isobutyl(2,2,2-trifluoroethyl)carbamic chloride which was used in the next step without further purification.

To the crude isobutyl(2,2,2-trifluoroethyl)carbamic chloride was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added hydroxylamine hydrochloride (0.691 g, 10.0 mmol), and followed immediately by Et_3N (2.79 mL, 20.0 mmol). The reaction was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude N-propylanilinehydroxyurea, which could be used in the next step without further purification.

To the crude 3-hydroxy-1-isobutyl-1-(2,2,2-trifluoroethyl)urea was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (1.39 mL, 10.0 mmol) followed immediately by addition of p-methoxybenzoylchloride (1.70 g, 10.0 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and

then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude 1-isobutyl-3-((4-methoxybenzoyl)oxy)-1-(2,2,2-trifluoroethyl)urea which was purified by recrystallization with Et_2O to yield a white crystalline solid (2.43 g, 70% over 3 steps).

TLC R_f: 0.57 in 33% EtOAc/Hexanes.

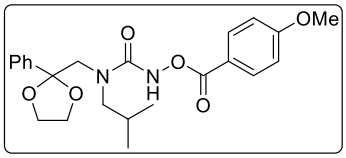
M.p.: 105.8-106.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (br s, 1H), 8.07 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 4.01 (q, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.26 (d, *J* = 7.7 Hz, 2H), 2.13 (dsept, *J* = 13.7, 6.9 Hz, 1H), 0.99 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4 (C), 164.4 (C), 158.1 (C), 132.2 (CH), 124.5 (q, *J* = 278 Hz, C), 118.9 (C), 114.0 (CH), 55.5 (CH_3), 55.3 (CH_2), 48.1 (q, *J* = 34 Hz, CH_2), 27.1 (CH), 19.9 (CH_3).

IR (FTIR): 3144, 2971, 2889, 2360, 1749, 1660, 1606, 1249, 1160, 1143 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{15}H_{19}F_3N_2O_4Na$ $[M+Na]^+$: 371.1188. Found: 371.1195.



1-Isobutyl-1-(2-phenyl-1,3-dioxolan-2-yl)isobutyl-3-((4-methoxybenzoyl)oxy)urea (1f): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.574 g, 2.00 mmol), and isobutylamine (0.470 g, 2.00 mmol) and imidazole (0.014 g, 0.20 mmol) in THF (6.6 mL, 0.20 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. The reaction mixture was concentrated under reduced pressure and isolated using flash chromatography (10% EtOAc/Hexanes). The title compound was obtained as an amorphous pale orange solid (0.770 g, 90%).

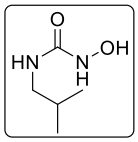
TLC R_f: 0.24 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.28-10-21 (br s, 1H), 8.16-8.07 (m, 2H), 7.58-7.51 (m, 2H), 7.45-7.32 (m, 3H), 7.00-6.90 (m, 2H), 4.30-4.23 (m, 2H), 3.96-3.85 (m, 5H), 3.75-3.65 (br s, 2H), 3.33-3.21 (d, *J*= 6.9 Hz, 2H), 2.18-2.01 (m, 1H), 0.88 (d, *J*= 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8 (C), 163.9 (C), 159.5 (C), 139.9 (C), 132.0 (CH), 128.8 (CH), 128.5 (CH), 125.7 (CH), 119.9 (C), 113.8 (CH), 110.6 (C), 65.4 (CH_2), 56.7 (CH_2), 55.4 (CH), 54.0 (CH_2), 26.8 (CH), 20.1 (CH_3).

IR (FTIR): 3221, 2941, 1740, 1691, 1468, 1257 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{23}H_{28}N_2O_6Na$ $[M+Na]^+$: 451.1845. Found: 451.1825.



1-Isobutyl-3-hydroxyurea (4.5): The title compound was synthesized according to a modified general procedure **A** using phenyl *N*-hydroxycarbamate (0.765 g, 5.00 mmol), and *N*-isobutylamine (2.48 mL, 25.0 mmol) and Et_3N (0.14 mL, 1.0 mmol) in THF (16.6 mL, 0.30 M). The vial was sealed with a microwave cap and heated for 16 h at 70 °C via an oil bath heating. The reaction mixture was concentrated under reduced pressure and isolated using flash chromatography (5% MeOH/CH_2Cl_2 then 7% MeOH/CH_2Cl_2). The title compound was obtained as an amorphous white solid (0.380 g, 58%).

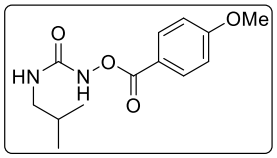
TLC R_f: 0.28 in 10% MeOH/CH_2Cl_2.

^{1}H NMR (300 MHz, DMSO-d_6): δ 8.52 (d, *J*= 1.2 Hz, 1H), 8.21 (br s, 1H), 6.61 (t, *J*= 6.2 Hz, 1H), 2.86 (t, *J*= 6.9 Hz, 2H), 1.78-1.65 (m, 1H), 0.82 (d, *J*= 6.7 Hz, 6H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 162.0 (C), 46.7 (CH_2), 28.9 (CH), 20.4 (CH_3).

IR (FTIR): 3389, 3123, 2955, 2871, 1617, 1549, 1424 cm^{-1}.

HRMS (EI) m/z: Despite multiple attempts to obtain an accurate mass using both ESI and EI, one could not be obtained for this compound. However, this product was a precursor to **1g**, for which all characterization was obtained, thereby clearly demonstrating this to be the desired product.



3-((4-Methoxybenzoyl)oxy)-1-isobutylurea (1g): The title compound was synthesized according to general procedure **B** using the pure 1-isobutyl-3-hydroxyurea (0.330 g, 2.50 mmol) was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (0.35 mL, 0.40 mmol) mmol) followed immediately by addition of p-methoxybenzoylchloride (0.427 g, 2.50 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated vacuo and purified by recrystallization with Et_2O to yield a white crystalline solid (0.548 g, 82%).

TLC R_f: 0.21 in 2% MeOH/CH_2Cl_2.

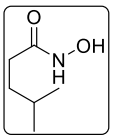
M.p.: 139.7-140.5 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.68-9.60 (br s, 1H), 7.98 (d, *J*= 8.9 Hz, 2H), 7.09 (d, *J*= 8.9 Hz, 2H), 7.04 (t, *J*= 6.0 Hz, 1H), 3.84 (s, 3H), 2.86 (t, *J*= 6.4 Hz, 2H), 1.80-1.63 (m, 1H), 0.81 (d, *J*= 6.7 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 165.5 (C), 164.1 (C), 159.3 (C), 132.2 (CH), 120.2 (C), 114.7 (CH), 56.1 (CH), 47.0 (CH_2), 28.8 (CH), 20.4 (CH_3).

IR (FTIR): 3304, 2959, 1748, 1663, 1571, 1510, 1249 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{13}H_{18}N_2O_4Na$ $[M+Na]^+$: 289.1165. Found: 289.1176.

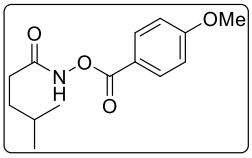


***N*-Hydroxy-4-methylpentanamide (6a):** The title compound was synthesized according to general procedure **E** using 4-methylpentanoyl chloride (1.35 g, 10.0 mmol) and hydroxylamine hydrochloride (0.694 g, 10.0 mmol) and $NaHCO_3$ (1.85 g, 22.0 mmol) in 2 : 1 CH_2Cl_2 : H_2O (0.30 M). Upon completion, the reaction mixture was concentrated in vacuo and isolated using flash chromatography (50% EtOAc/ Hexanes) to yield the title compound as a white solid (1.13 g, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (br s, 2H), 2.18-2.13 (m, 2H), 1.62-1.49 (m, 3H), 0.90 (d, *J* = 6.2 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 172.1 (C), 34.2 (CH_2), 31.0 (CH_2), 27.7 (CH), 22.2 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[15]



***N*-((4-Methoxybenzoyl)oxy)-4-methylpentanamide (1h):** The title compound was synthesized according to general procedure **F** using *N*-hydroxy-4-methylpentanamide (0.656 g, 5.00 mmol) and 4-methoxybenzoyl chloride (0.853 g, 5.00 mmol) and triethylamine (0.70 mL, 5.0 mmol) in CH_2Cl_2 (0.30 M). Upon completion the reaction mixture was extracted with saturated $NaHCO_3$ three times (10 mL x 3) followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (20.0 mL). The filtrate was collected, and concentrated in vacuo and isolated using flash chromatography (50% EtOAc/Hexanes) to yield the title compound as a white solid (1.12 g, 82% yield).

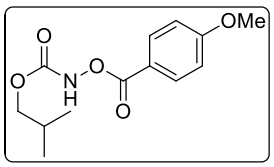
TLC R_f: 0.71 in 50% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.11 (br s, 1H), 8.03 (d, *J*= 9.0 Hz, 2H), 6.93 (d, *J*= 9.0 Hz, 2H), 3.85 (s, 3H), 2.30 (t, *J*= 7.4 Hz, 2H), 1.67-1.57 (m, 4H), 0.90 (d, *J*= 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (C), 164.8 (C), 164.4 (C), 132.2 (CH), 118.9 (C), 114.0 (CH), 55.5 (CH_3), 33.9 (CH_2), 31.2 (CH_2) 27.7 (CH), 22.2 (CH_3).

IR (FTIR): 3147, 2959, 1759, 1657, 1603, 1509, 1248, 1167, 1024 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{14}H_{19}NO_4Na$ $[M+Na]^+$: 288.1210. Found: 288.1212.



Isobutyl (4-methoxybenzoyl)oxycarbamate (1i): Isobutyl hydroxycarbamate was synthesized according to general procedure **A** using isobutyl chloroformate (1.30 mL, 10.0 mmol) and hydroxylamine hydrochloride (0.694 g, 10.0 mmol) and $NaHCO_3$ (1.85 mL, 22.0 mmol) in 2 : 1 CH_2Cl_2 : H_2O (0.30 M). Upon completion, the reaction mixture was concentrated in vacuo to provide the crude isobutyl hydroxycarbamate which was used in the next step without further purification.

The title compound was synthesized according to general procedure **B** using the crude isobutyl hydroxycarbamate (0.666 g, 5.00 mmol) to this was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (0.70 mL, 5.0 mmol) followed immediately by addition of *p*-methoxybenzoylchloride (0.853 g, 5.00 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion the reaction mixture was extracted with saturated $NaHCO_3$ three times (10 mL x 3) followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (20.0 mL). The filtrate was collected, and concentrated in vacuo and isolated using flash chromatography (15% EtOAc/Hexanes) to yield the title compound as a clear oil (1.17 g, 88% yield).

TLC R_f: 0.70 in 33% EtOAc/Hexanes.

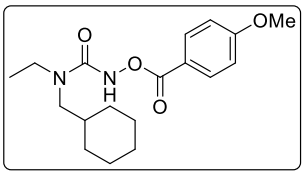
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (br s, 1H), 8.04 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.98 (d, *J* = 6.6 Hz, 2H), 3.86 (s, 3H), 1.96 (dquintet, *J* = 13.4, 6.7 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 6H).

[15] Dube, P.; Nathel, N. F. F.; Vetelino, M.; Couturier, M.; Aboussafy, C. L.; Pichette, S.; Jorgensen, M. L.; Hardink, M. *Org. Lett.* **2009**, *11*, 5622.

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7 (C), 164.4 (C), 157.0 (C), 132.2 (CH), 118.9 (C), 114.1 (CH), 72.7 (CH_2), 55.6 (CH_3), 27.9 (CH), 18.9 (CH_3)

IR (FTIR): 3147, 2960, 1759, 1656, 1603, 1509, 1459, 1248, 1167 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{13}H_{17}NO_5Na$ $[M+Na]^+$: 290.1005. Found: 290.1004.



3-((4-Methoxybenzoyl)oxy)-1-cyclohexylmethyl-1-ethylurea (1j): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.861 g, 3.00 mmol), and *N*-(cyclohexylmethyl)-*N*-ethylamine (0.555 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (15.0 mL, 0.20 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was diluted with EtOAc (20 mL) and washed three times using 1 M NaOH (2.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated vacuo and isolated using silica plug (15% EtOAc/Hexanes → 50% EtOAc/Hexanes) to yield the title compound as a colourless oil (0.653 g, 54%).

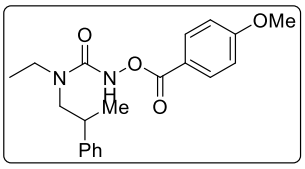
TLC R_f: 0.30 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.21-10.14 (br s, 1H), 8.00-7.91 (m, 2H), 7.14-7.05 (m, 2H), 3.85 (s, 3H), 3.25 (q, *J*= 7.0 Hz, 2H), 3.05 (d, *J*= 6.9 Hz, 2H), 1.74-1.45 (m, 6H), 1.27-1.12 (m, 3H), 1.08 (t, *J*= 7.0 Hz, 3H), 0.98-0.80 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 165.2 (C), 163.6 (C), 157.2 (C), 131.4 (CH), 119.8 (C), 114.3 (CH), 55.6 (CH), 51.4 (CH_2), 41.2 (CH_2), 36.2 (CH), 30.2 (CH_2), 26.1 (CH_2), 25.4 (CH_2), 13.0 (CH_3).

IR (FTIR): 3251, 2923, 2850, 1741, 1660, 1604, 1248, 1164 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{21}H_{34}N_2O_4Na$ $[M+Na]^+$: 401.2417. Found: 401.2423.



1-Ethyl-3-((4-methoxybenzoyl)oxy)-1-(2-phenylpropyl)urea (1k): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N*-ethyl-2-phenylpropan-1-amine (0.490 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (15.0 mL, 0.20 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was diluted with EtOAc (20 mL) and washed three times using 1 M NaOH (2.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated vacuo and isolated using silica plug (20% EtOAc/Hexanes → 40% EtOAc/Hexanes) to yield the title compound as a colourless oil (0.919 g, 86%).

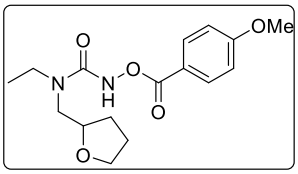
TLC R_f: 0.19 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (br s, 1H), 8.11-7.99 (m, 2H), 7.35-7.27 (m, 2H), 7.27-7.17 (m, 3H), 6.98-6.86 (m, 2H), 3.85 (s, 3H), 3.58 (dd, *J* = 6.4, 13.6 Hz, 1H), 3.27-3.11 (m, 3H), 2.96 (qd, *J* = 7.2, 14.6 Hz, 1H), 1.35-1.27 (m, 3H), 1.18-1.03 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4 (C), 164.2 (C), 157.7 (C), 144.0 (C), 132.1 (CH), 128.8 (CH), 127.3 (CH), 126.8 (CH), 119.4 (C), 113.9 (CH), 55.5 (CH_3), 54.6 (CH_2), 42.6 (CH_2), 38.8 (CH), 18.6 (CH_3), 12.9 (CH_3).

IR (FTIR): 3216, 2966, 1747, 1668, 1604, 1509, 1454, 1245, 1167 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{20}H_{24}N_2O_4Na$ $[M+Na]^+$: 379.1628. Found: 379.1634.



1-Ethyl-3-((4-methoxybenzoyl)oxy)-1-((tetrahydrofuran-2-yl)methyl)urea (1l): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N*-((tetrahydrofuran-2-yl)methyl)ethanamine (0.388 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (20% EtOAc/Hexanes) to yield the title compound as a clear oil (0.580 g, 59%).

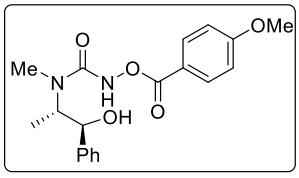
TLC R_f: 0.34 in 50% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (br s, 1H), 8.05 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 4.10-4.02 (m, 2H), 3.86-3.81 (m, 4H), 3.50-3.26 (m, 4H), 2.02-1.90 (m, 3H), 1.63-1.58 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2 (C), 164.0 (C), 156.0 (C), 132.1 (CH), 120.1 (C), 113.9 (CH), 79.5 (CH), 68.6 (CH_2), 55.5 (CH_3), 54.6 (CH_2), 43.8 (CH_2), 28.8 (CH_2), 26.1 (CH_2), 13.0 (CH_3).

IR (FTIR): 3192, 2962, 1685, 1604, 1566, 1245, 1067 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{16}H_{22}N_2O_5Na$ $[M+Na]^+$: 345.1421. Found: 345.1426.



1-(2-Hydroxy-2-phenylethyl)-3-((4-methoxybenzoyl)oxy)-1-methylurea (1m): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.861 g, 3.00 mmol), and (−)-(1*R*,2*S*)-ephedrine (0.495 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (15.0 mL, 0.20 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was diluted with EtOAc (20 mL) and washed three times using 1 M NaOH (2.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated vacuo and isolated using flash chromatography (20% EtOAc/Hexanes → 50% EtOAc/Hexanes) to yield the title compound as a colourless oil (1.16 g, 97%).

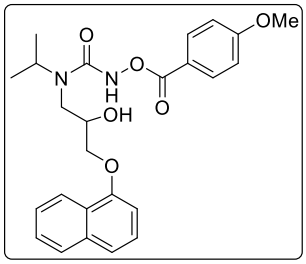
TLC R_f: 0.30 in 20% EtOAc/Hexanes.

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.53-8.83 (br s, 1H), 8.10-8.01 (m, 2H), 7.43-7.25 (m, 5H), 6.98-6.89 (m, 2H), 4.84 (d, *J* = 3.2 Hz, 1H), 4.36 (qd, *J* = 6.8, 3.0 Hz, 1H), 3.86 (s, 3H), 3.62-3.01 (br s, 1H), 2.51 (s, 3H), 1.20 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (C), 164.2 (C), 159.5 (C), 132.2 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 126.6 (CH), 119.6 (CH), 119.8 (C), 114.3 (CH), 77.7 (CH), 57.5 (CH), 55.6 (CH), 30.7 (CH), 13.4 (CH_3).

IR (FTIR): 3251, 2923, 2850, 1741, 1660, 1604, 1248, 1164 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{21}H_{34}N_2O_4Na$ $[M+Na]^+$: 401.2417. Found: 401.2423.



1-(2-Hydroxy-3-(naphthalen-1-yloxy)propyl)-1-isopropyl-3-((4-methoxybenzoyl)oxy)urea (1n): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.861 g, 3.00 mmol), and propranolol (0.778 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (12.0 mL, 0.25 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was concentrated in vacuo and isolated using flash chromatography (40% Et_2O/Toluene) to yield the title compound as a white solid (0.855 g, 60%).

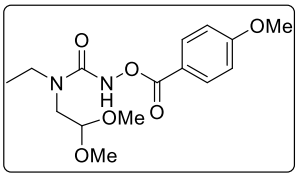
TLC R_f: 0.22 in 20% Et_2O/Toluene.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.85-9.73 (br s, 1H), 8.26-8.16 (m, 2H), 8.12-8.03 (m, 2H), 7.87-7.78 (m, 1H), 7.56-7.44 (m, 3H), 7.42-7.34 (m, 1H), 6.97-6.90 (m, 2H), 6.86-6.80 (m, 1H), 4.57-4.36 (m, 2H), 4.17 (qd, *J* = 9.5, 6.0 Hz, 2H), 3.86 (s, 3H), 3.68 (dd, *J* = 15.8, 9.0 Hz, 1H), 3.52 (dd, *J* = 15.7, 2.2 Hz, 1H), 1.28 (app dd, *J* = 24.1, 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7 (C), 164.1 (C), 159.7 (C), 153.8 (C), 134.6 (C), 132.2 (CH), 127.8 (CH), 126.7 (CH), 125.9 (CH), 125.6 (CH), 125.5 (C), 121.6 (CH), 121.2 (CH), 119.7 (C), 114.0 (CH), 105.7 (CH), 72.4 (CH), 69.9 (CH_2), 55.6 (CH_3), 47.8 (CH), 45.6 (CH_2), 21.2 (CH), 20.0 (CH_3).

IR (FTIR): 3205, 2973, 1742, 1633, 1604, 1509, 1249 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{25}H_{28}N_2O_6Na$ $[M+Na]^+$: 475.1845. Found: 475.1823.



1-(2,2-Dimethoxyethyl)-1-ethyl-3-((4-methoxybenzoyl)oxy)urea (1o): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N*-ethyl-2,2-dimethoxyethanamine (0.399 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (30% EtOAc/Hexanes → 40% EtOAc/Hexanes) to yield the title compound as a clear oil (0.979 g, 99%).

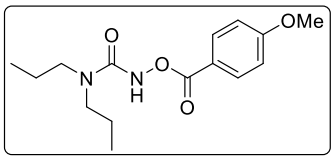
TLC R_f: 0.40 in 40% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.63 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 2H), 6.93-6.90 (m, 2H), 4.46 (t, *J* = 5.3 Hz, 1H), 3.84 (s, 3H), 3.50 (s, 6H), 3.36-3.45 (m, 4H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3 (C), 163.9 (C), 158.6 (C), 132.0 (CH), 119.8 (C), 113.9 (CH), 104.4 (CH), 55.6 (CH_3), 55.5 (CH_3), 49.4 (CH_2), 43.3 (CH_2), 13.4 (CH_3).

IR (FTIR): 3216, 2943, 1740, 1686, 1466, 1247, 1169, 1068 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{15}H_{22}N_2O_6Na$ $[M+Na]^+$: 349.1370. Found: 349.1376.

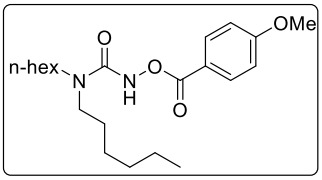


3-((4-Methoxybenzoyl)oxy)-1,1-dipropylurea (1p): The title compound was synthesized according to a literature procedure.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 8.07-8.04 (m, 2H), 6.93-6.91 (m, 2H), 3.23 (t, *J* = 7.6 Hz, 4H), 1.64 (ap sext, 7.5 Hz, 4H), 0.92 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0 (C), 164.3 (C), 157.8 (C), 132.2 (CH), 119.5 (C), 114.1 (CH), 55.6 (CH_3), 49.1 (CH_2), 21.6 (CH_2), 11.4 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.



1,1-Dihexyl-3-((4-methoxybenzoyl)oxy)urea (1q): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N,N*-dihexylamine (0.555 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was diluted with EtOAc (20 mL) and washed three times using 1 M NaOH (2.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated in vacuo and isolated using silica column chromatography (10% EtOAc/Hexanes → 20% EtOAc/Hexanes) to yield the title compound as a colourless oil (0.840 g, 74%).

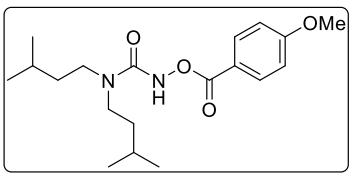
TLC R_f: 0.24 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (br s, 1H), 8.06 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 3.24 (t, *J* = 7.7 Hz, 4H), 1.62-1.58 (m, 4H), 1.32-1.27 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0 (C), 164.3 (C), 157.7 (C), 132.2 (CH), 119.5 (C), 114.0 (CH), 55.6 (CH_3), 47.5 (CH_2), 31.7 (CH_2), 28.3 (CH_2), 26.7 (CH_2), 22.7 (CH_2), 14.2 (CH_3).

IR (FTIR): 3156, 2955, 2930, 2856, 1753, 1652, 1509, 1486, 1264 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{21}H_{34}N_2O_4Na$ $[M+Na]^+$: 401.2411. Found: 401.2416.



1,1-Diisopentyl-3-((4-methoxybenzoyl)oxy)urea (1r): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N,N*-diisopentylamine (0.472 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was diluted with EtOAc (20 mL) and washed three times using 1 M NaOH (2.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated in vacuo

and isolated using silica column chromatography (15% EtOAc/Hexanes → 30% EtOAc/Hexanes) to yield the title compound as a colourless oil (0.800 g, 79%).

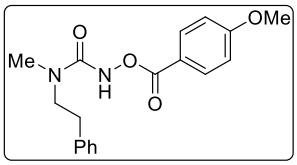
TLC R_f: 0.38 in 33% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (br s, 1H), 8.06 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 3.26 (t, *J* = 7.9 Hz, 4H), 1.63-1.54 (m, 2H), 1.54-1.47 (m, 4H), 0.93 (d, *J* = 6.5 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0 (C), 164.3 (C), 157.5 (C), 132.2 (CH), 119.5 (C), 114.1 (CH), 55.6 (CH_3), 45.8 (CH_2), 37.1 (CH_2), 26.2 (CH), 22.6 (CH_3).

IR (FTIR): 3263, 2953, 2868, 1745, 1655, 1604, 1510, 1249, 1166 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{19}H_{30}N_2O_4Na$ $[M+Na]^+$: 373.2098. Found: 373.2103.



3-((4-Methoxybenzoyl)oxy)-1-methyl-1-phenethylurea (1s): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N*-methyl-2-phenylethanamine (0.406 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (30% EtOAc/Hexanes → 40% EtOAc/Hexanes) to yield the title compound as an amorphous off-white solid (0.896 g, 91%).

TLC R_f: 0.22 in 33% EtOAc/Hexanes.

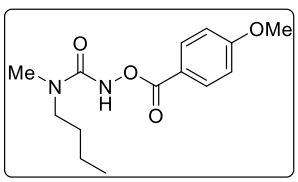
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (br s, 1H), 8.07 (d, *J* = 9.0 Hz, 2H), 7.34-7.21 (m, 5H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.56 (t, *J* = 7.4 Hz, 2H), 2.93-2.89 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (C), 164.3 (C), 157.9 (C), 138.7 (C), 132.2 (CH), 129.0 (CH), 128.9 (CH), 126.7 (CH), 119.4 (C), 114.0 (CH), 55.6 (CH_3), 51.4 (CH_2), 34.9 (CH_3), 34.3 (CH_2).

IR (FTIR): 3302, 3065, 2972, 2934, 1737, 1702, 1602, 1508, 1456 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{18}H_{20}N_2O_4Na$ $[M+Na]^+$: 351.1315. Found: 351.1321.

3-((4-Methoxybenzoyl)oxy)-1-butyl-1-methylurea (1t): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.861 g, 3.00 mmol), and *N*-methylbutylamine (0.262 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (15.0 mL, 0.20 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was diluted with EtOAc (20 mL) and washed three times using 1 M NaOH (2.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated in vacuo and isolated using flash chromatography (25% EtOAc/Hexanes) to yield the title compound as a yellow oil (0.466 g, 55%).



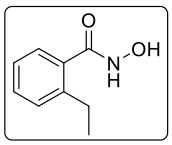
TLC R_f: 0.16 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45-8.42 (br s, 1H), 8.12-8.06 (m, 2H), 6.98-6.92 (m, 2H), 3.88 (s, 3H), 3.37-3.30 (m, 2H), 3.00 (s, 3H), 1.66-1.54 (m, 2H), 1.43-1.30 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (C), 164.1 (C), 157.8 (C), 132.0 (CH), 119.3 (C), 113.9 (CH), 55.4 (CH), 48.8 (CH_2), 33.9 (CH_3), 29.7 (CH_2), 19.9 (CH_2), 13.8 (CH_3).

IR (FTIR): 3213, 2956, 2870, 1752, 1649, 1503, 1244, 1074 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{14}H_{20}N_2O_4Na$ $[M+Na]^+$: 303.1321. Found: 303.1298.

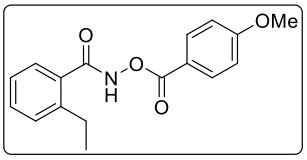


2-Ethyl-*N*-hydroxybenzamide (6b): The title compound was synthesized according to a literature procedure.[14]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.87-8.09 (br s, 2H), 7.47-7.38 (m, 1H), 7.38-7.29 (m, 2H), 7.26-7.19 (m, 1H), 2.81 (q, *J*= 7.4 Hz, 2H), 1.24 (t, *J*= 7.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.8 (C), 143.3 (C), 131.3 (C), 131.0 (CH), 129.6 (CH), 127.3 (CH), 125.8 (CH), 26.2 (CH_2), 15.7 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.



2-Ethyl-*N*-((4-methoxybenzoyl)oxy)benzamide (1u): The title compound was synthesized according to the general procedure **F** using 2-ethyl-*N*-hydroxybenzamide (0.520 g, 3.15 mmol), CH_2Cl_2 (0.30 M) at 0 °C. To this was added Et_3N (0.42 mL, 3.0 mmol) followed immediately by portionwise addition of *p*-methoxybenzoylchloride (0.516 g, 3.00 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x2), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure and the crude product isolated using flash column chromatography (20 % EtOAc/Hexanes) to yield the title compound as an amorphous white solid (0.592 g, 67%).

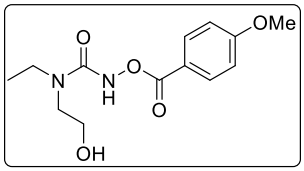
TLC R_f: 0.21 in 20% EtOAc/Hexanes.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.36-9.27 (br s, 1H), 8.15-8.07 (m, 2H), 7.55 (dd, *J*= 7.6, 1.2 Hz, 1H), 7.48-7.42 (m, 1H), 7.36-7.30 (m, 1H), 7.29-7.22 (m, 1H), 7.00-6.94 (m, 2H), 3.90 (s, 3H), 2.87 (q, *J*= 7.5 Hz, 2H), 1.28 (t, *J*= 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9 (C), 164.5 (C), 143.9 (C), 132.3 (CH), 131.4 (CH), 131.3 (C), 127.7 (CH), 125.8 (CH), 118.6 (CH), 114.1 (CH), 55.6 (CH), 26.3 (CH_2), 16.0 (CH_3).

IR (FTIR): 3138, 2957, 1751, 1653, 1505, 1252 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{17}H_{17}NO_4Na$ $[M+Na]^+$: 322.1056. Found: 322.1056.



1-Ethyl-1-(2-hydroxyethyl)-3-((4-methoxybenzoyl)oxy)urea (1v): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and 2-(ethylamino)ethanol (0.267 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was concentrated in vacuo and isolated using silica column chromatography (50% EtOAc/Hexanes → 40% EtOAc/DCM) to yield the title compound as a white solid (0.788 g, 93%).

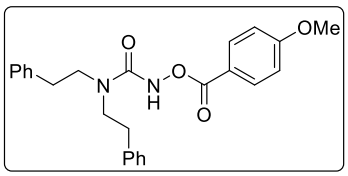
TLC R_f: 0.20 in 40% EtOAc/DCM.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (br s, 1H), 8.04 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H), 3.81 (t, *J* = 4.8 Hz, 2H), 3.45 (t, *J* = 4.8 Hz, 2H), 3.37 (q, *J* = 7.1 Hz, 2H), 3.14 (br s, 1H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7 (C), 164.1 (C), 159.1 (C), 132.1 (CH), 119.6 (C), 113.9 (CH), 62.2 (CH_2), 55.6 (CH_3), 48.8 (CH_2), 42.7 (CH_2), 13.2 (CH_3).

IR (FTIR): 3404, 3181, 2864, 1720, 1678, 1600, 1514, 1475, 1325, 1262, 1246, 1172 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{13}H_{18}N_2O_5Na$ $[M+Na]^+$: 305.1108. Found: 305.1113.



3-((4-Methoxybenzoyl)oxy)-1,1-diphenethylurea (1w): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N,N*-diphenethylamine (0.676 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was concentrated in vacuo and isolated using silica column chromatography (20% EtOAc/Hexanes) to yield the title compound as a white solid (0.880 g, 70%).

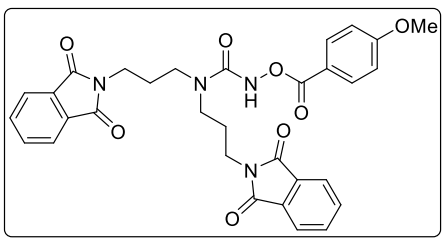
TLC R_f: 0.31 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (br s, 1H), 8.09-8.06 (m, 2H), 7.35-7.19 (m, 10H), 6.96-6.93 (m, 2H), 3.87 (s, 3H), 3.43 (t, *J* = 7.5 Hz, 4H), 2.89 (t, *J* = 7.4 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5 (C), 164.3 (C), 157.7 (C), 138.7 (C), 132.2 (CH), 128.93 (CH), 128.90 (CH), 126.8 (CH), 119.4 (C), 114.1 (CH), 55.6 (CH_3), 50.1 (CH_2), 34.7 (CH_2).

IR (FTIR): 3209, 2931, 1744, 1673, 1604, 1475, 1247, 1166 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{25}H_{26}N_2O_4Na$$[M+Na]^+$: 441.1785. Found: 441.1790.



1,1-Bis(3-(1,3-dioxoisoindolin-2-yl)propyl)-3-((4-methoxybenzoyl)oxy)urea (1x): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N,N*-diphenethylamine (1.17 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction

was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was concentrated in vacuo and isolated using silica column chromatography (gradient: 50% EtOAc/Hexanes → 100% EtOAc) to yield the title compound as a white foam (1.45 g, 83%).

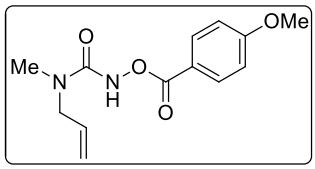
TLC R_f: 0.75 in 100% EtOAc.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (br s, 1H), 8.04 (d, *J* = 9.0 Hz, 2H), 7.84-7.78 (m, 4H), 7.73-7.67 (m, 4H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 3.76 (t, *J* = 6.8 Hz, 4H), 3.42 (t, *J* = 7.3 Hz, 4H), 2.02 (quintet, *J* = 7.1 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4 (C), 166.5 (C), 164.1 (C), 157.9 (C), 134.0 (CH), 132.0 (CH), 123.3 (CH), 119.3 (C), 113.9 (CH), 55.5 (CH), 44.8 (CH_2), 35.5 (CH_2), 27.4 (CH_2).

IR (FTIR): 2939, 1694, 1604, 1389, 1244, 1167, 1025 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{31}H_{28}N_4O_8Na$ $[M+Na]^+$: 607.1805. Found: 607.1791.



1-Allyl-3-((4-methoxybenzoyl)oxy)-1-methylurea (1y): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.511 g, 1.78 mmol), and *N*-methylallylamine (0.17 mL, 1.78 mmol) and imidazole (0.012 g, 0.18 mmol) in THF (9.0 mL, 0.20 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was diluted with EtOAc (20 mL) and washed three times using 1 M NaOH (2.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated in vacuo and isolated using silica plug (20% EtOAc/Hexanes) to yield the title compound as a colourless oil (0.376 g, 80%).

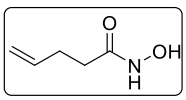
TLC R_f: 0.11 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46-8.43 (br s, 1H), 8.11-8.05 (m, 2H), 6.99-6.93 (m, 2H), 5.93-5.78 (m, 1H), 5.35-5.26 (m, 2H), 3.97 (dt, *J*= 5.3, 1.6 Hz, 2H), 3.88 (s, 3H), 3.01 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (C), 164.2 (C), 157.0 (C), 132.3 (CH), 132.1 (CH), 119.3 (C), 117.5 (CH_2), 114.0 (CH), 55.5 (CH), 51.3 (CH_2), 34.2 (CH).

IR (FTIR): 3184, 3010, 1744, 1651, 1506, 1238 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{13}H_{16}N_2O_4Na$ $[M+Na]^+$: 287.1008. Found: 287.1014.

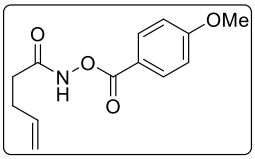


***N*-Hydroxypent-4-enamide (6c)**: The title compound was synthesized according to a literature procedure. [16]

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.46-10.25 (br s, 1H), 878-8.57 (br s, 1H), 5.78 (ddt, *J*= 17.0, 10.4, 6.4 Hz, 1H), 5.08-4.91 (m, 2H), 2.29-.217 (m, 2H), 2.08-1.97 (m, 2H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 168.4 (C), 137.5 (CH), 115.2 (CH_2), 31.5 (CH_2), 29.0 (CH_2).

[16] Hong, S. Y.; Chang, S. *J. Am. Chem. Soc.* **2019**, 141, 10399.



***N*-((4-Methoxybenzoyl)oxy)pent-4-enamide (1z):** The title compound was synthesized according to general procedure **C** using *N*-hydroxypent-4-enamide (1.15 g, 10.0 mmol), and *p*-methoxybenzoyl chloride (1.71 g, 10.0 mmol), and Et_3N (1.39 mL, 10.0 mmol) in CH_2Cl_2 (0.30 M) at 0 °C to rt. Upon completion the reaction was extracted three times using sat. $NaHCO_3$ (10.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (50.0 mL). The filtrate was collected, concentrated in vacuo to yield the title compound as a white solid (2.49 g, 99%).

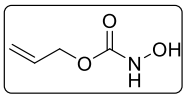
TLC R_f: 0.27 in 33% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.85 (ddt, *J* = 17.0, 10.4, 6.5 Hz, 1H), 5.13-5.03 (m, 2H), 3.87 (s, 3H), 2.48-2.41 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7 (C), 164.4 (C), 136.4 (CH), 132.2 (CH), 131.7 (CH), 118.7 (C), 116.1 (CH_2), 114.1 (C), 55.6 (CH_3), 32.4 (CH_2), 28.9 (CH_2).

IR (FTIR): 3186, 2971, 2840, 1759, 1663, 1604, 1506, 1419, 1248, 1168 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{13}H_{15}NO_4Na$ $[M+Na]^+$: 272.0897. Found: 272.0899.



Allylhydroxycarbamate (6d): The title compound was synthesized according to a literature procedure.[17]

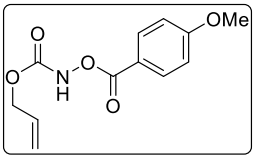
TLC R_f: 0.27 in 2% MeOH/CH_2Cl_2.

^{1}H NMR (300 MHz, DMSO-d_6): δ 9.69-9.57 (br s, 1H), 8.73-8.70 (br s, 1H), 5.95-5.85 (m, 1H), 5.31-5.16 (m, 2H), 4.50 (dt, *J*= 5.3, 1.5 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5 (C), 133.5 (CH), 117.2 (CH_2), 64.4 (CH_2).

IR (FTIR): 3272, 2947, 1699, 1456, 1260, 1110 cm^{-1}.

HRMS (ESI) m/z: Despite multiple attempts to obtain an accurate mass using both ESI and EI, one could not be obtained for this compound. However, this product was a precursor to **1ae**, for which all characterization was obtained, thereby clearly demonstrating this to be the desired product.



Allyl (4-methoxybenzoyl)oxycarbamate (1aa): The title compound was synthesized according to general procedure **C** using allyl hydroxycarbamate (1.17 g, 10.0 mmol), and *p*-methoxybenzoyl chloride (1.71 g, 10.0 mmol), and Et_3N (1.39 mL, 10.0 mmol) in CH_2Cl_2 (0.30 M) at 0 °C to rt. Upon completion the reaction was extracted three times using sat. $NaHCO_3$ (10.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (50.0 mL). The filtrate was collected, concentrated in vacuo and isolated using silica gel column chromatography (solvent system) to yield the title compound as a white solid (2.20 g, 88%).

TLC R_f: 0.54 in 33% EtOAc/Hexanes.

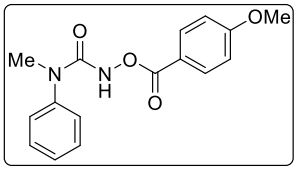
[17] Donohoe, T. J.; Chughtai, M. J.; Klauber, D. J.; Griffin, D.; Campbell, A. D. *J. Am. Chem. Soc.* **2006**, *128*, 2514.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 8.06-7.98 (m, *J* = 9.0 Hz, 2H), 6.97-6.88 (m, *J* = 9.0 Hz, 2H), 5.97-5.85 (m, 1H), 5.37-5.19 (m, 2H), 4.68 (td, *J* = 1.4, 5.7 Hz, 2H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5 (C), 164.4 (C), 156.4 (C), 132.1 (CH), 131.4 (CH), 118.9 (CH_2), 118.8 (C), 114.0 (CH), 67.1 (CH_2), 55.5 (CH).

IR (FTIR): 3199, 2953, 2844, 1754, 1718, 1602, 1492, 1238 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{12}H_{13}NO_5Na$ $[M+Na]^+$: 274.0696. Found: 274.0691.



3-((4-Methoxybenzoyl)oxy)-1-methyl-1-phenylurea (1ab): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N*-methyl aniline (0.325 mL, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (30% EtOAc/hexanes) to yield the title compound as an amorphous off-white solid (0.896 g, 91%).

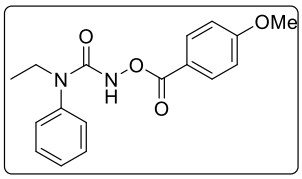
TLC R_f: 0.22 in 33% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (br s, 1H), 8.03-7.99 (m, 2H), 7.49-7.36 (m, 5H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 3.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (C), 164.3 (C), 157.2 (C), 141.5 (C), 132.2 (CH), 130.4 (CH), 128.5 (CH), 127.2, (CH), 119.4 (C), 114.0 (CH), 55.6 (CH_3), 38.0 (CH_3).

IR (FTIR): 3307, 2936, 1693, 1596, 1453, 1249 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{16}H_{16}N_2O_4Na$ $[M+Na]^+$ 323.1011. Found: 323.1108.



3-((4-Methoxybenzoyl)oxy)-1-ethyl-1-phenylurea (1ac): The title compound was synthesized according general procedure **D** using *N*-ethylaniline (1.26 mL, 10.0 mmol), toluene (0.8 M), KOH pellets (0.561 g, 10.0 mmol), and water (2.9 M) at 0 °C. A dripping funnel was affixed on top of the roundbottom flask and this apparatus was purged with argon for 10 minutes. Phosgene (15% in toluene) (16.4 mL, 23.0 mmol) was added to the dripping funnel under inert atmosphere, and was allowed to drip over 1 hour at 0 °C while stirring vigorously. The reaction was allowed to stir for an additional 30 minutes after complete addition of phosgene solution. Upon competition, the crude reaction mixture was bubbled with an argon balloon for 20 minutes in a well ventilated fumehood, to release any excess phosgene gas. The crude reaction mixture was then extracted to remove the aqueous layer, and then the organic phase was washed with brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-ethylanilinecarbamoyl chloride which was used in the next step without further purification.

To the crude *N*-ethylanilinecarbamoyl chloride was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added hydroxylamine hydrochloride (0.695 g, 10.0 mmol), and followed immediately by Et_3N (2.79 mL, 20.0 mmol). The reaction was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (10 mL x1), and then brine (10 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-ethylanilinehydroxyurea, which could be used in the next step without further purification.

To the crude *N*-ethylanilinehydroxyurea (1.53 g, 8.53 mmol) was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (1.19 mL, 8.53 mmol) followed immediately by dropwise addition of *p*-methoxybenzoylchloride (1.45 g, 8.53 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (10 mL x1), and then brine (10 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude 3-((4-methoxybenzoyl)oxy)-1-ethyl-1-phenylurea which was purified by flash column chromatography (10 % Et_2O/Toluene) to yield a colourless oil (1.93 g, 62% over 3 steps).

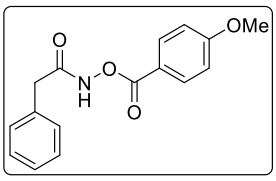
TLC R_f: 0.23 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.00 (m, 2H), 7.97-7.95 (br s, 1H), 7.53-7.46 (m, 2H), 7.44-7.37 (m, 3H), 6.96-6.90 (m, 2H), 3.86 (s, 3H), 3.77 (q, *J*= 7.2 Hz, 2H), 1.17 (t, *J*= 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4 (C), 164.1 (C), 156.6 (C), 138.5 (C), 132.0 (CH), 130.2 (CH), 128.4 (CH), 119.2 (C), 113.9 (CH), 55.5 (CH), 45.0 (CH_2), 13.3 (CH_3).

IR (FTIR): 3302, 2972, 1737, 1701, 1602, 1508, 1646, 1168 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{17}H_{18}N_2O_4Na$ $[M+Na]^+$: 337.1165. Found: 337.1194.



***N*-((4-Methoxybenzoyl)oxy)-2-phenylacetamide (1ad):** *N*-hydroxy-2-phenylacetamide was synthesized according to general procedure **A** using phenylacetyl chloride (1.55 g, 10.0 mmol) and hydroxylamine hydrochloride (0.695 g, 10.0 mmol) and $NaHCO_3$ (1.85 g, 22.0 mmol) in 2 : 1 CH_2Cl_2 : H_2O (0.30 M). The reaction allowed to stir at room temperature overnight; the following day a substantial amount of white solid had precipitated out of solution. The white solid was collected over a fritted funnel and used directly in the subsequent step without further purification.

The title compound was synthesized using the general procedure **B** using the crude hydroxamic acid was dissolved in CH_2Cl_2 (0.30 M, sparingly soluble). To the crude solution of phenylacetyl hydroxamic acid was added 4-methoxybenzoyl chloride (1.71 g, 10.0 mmol) and triethylamine (1.39 mL, 10.0 mmol). Upon completion the reaction mixture was extracted with saturated $NaHCO_3$ three times (10 mL x 3) followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (20 mL). The filtrate was collected, and concentrated in vacuo and isolated using flash chromatography (50% EtOAc/Hexanes) to yield the title compound as a white solid (2.51 g, 88% yield over two steps).

TLC R_f: 0.57 in 50% EtOAc/Hexanes.

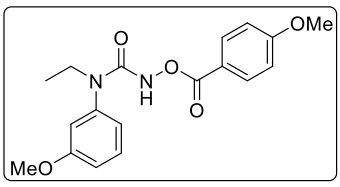
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.94 (br s, 1H), 8.04-8.01 (m, 2H), 7.41-7.31 (m, 5H), 6.94 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.73 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 (C), 164.7 (C), 164.6 (C), 133.2 (C), 132.3 (CH), 129.5 (CH), 129.2 (CH), 127.8 (CH), 118.7 (C), 114.2 (CH), 55.7 (CH), 41.9 (CH_2)

IR (FTIR): 3162, 2963, 1753, 1669, 1600, 1501, 12050, 1025 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{16}H_{15}NO_4Na$ $[M+Na]^+$: 308.0899. Found: 308.0897.

1-Ethyl-3-((4-methoxybenzoyl)oxy)-1-(3-methoxyphenyl)urea (1ae): The title compound was synthesized according general procedure **D** using *N*-ethyl-3-methoxyaniline (1.51 g, 10.0 mmol),



toluene (0.8 M), KOH pellets (0.561 g, 10.0 mmol), and water (2.9 M) at 0 °C. A dripping funnel was affixed on top of the roundbottom flask and this apparatus was purged with argon for 10 minutes. Phosgene (15% in toluene) (16.4 mL, 23.0 mmol) was added to the dripping funnel under inert atmosphere, and was allowed to drip over 1 hour at 0 °C while stirring vigorously. The reaction was allowed to stir for an additional 30 minutes after complete addition of phosgene solution. Upon competition, the crude reaction mixture was bubbled with an argon balloon for 20 minutes in a well ventilated fumehood, to release any excess phosgene gas. The crude reaction mixture was then extracted to remove the aqueous layer, and then the organic phase was washed with brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-ethyl(3-methoxyphenyl)carbamic chloride which was used in the next step without further purification.

To the crude ethyl(3-methoxyphenyl)carbamic chloride was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added hydroxylamine hydrochloride (0.695 g, 10.0 mmol), and followed immediately by Et_3N (2.79 mL, 20.0 mmol). The reaction was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (10 mL x1), and then brine (10 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude 1-ethyl-3-hydroxy-1-(3-methoxyphenyl)urea, which could be used in the next step without further purification.
To the crude 1-ethyl-3-hydroxy-1-(3-methoxyphenyl)urea was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (1.39 mL, 10.0 mmol) followed immediately by addition of *p*-methoxybenzoylchloride (1.70 g, 10.0 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (10 mL x1), and then brine (10 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude 1-ethyl-3-((4-methoxybenzoyl)oxy)-1-(3-methoxyphenyl)urea which was purified by flash column chromatography (20 % EtOAc/Hexanes) to yield a light pink solid (2.60 g, 76% over 3 steps).

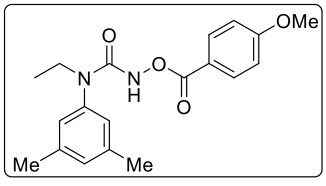
TLC R_f: 0.15 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (br s, 1H), 8.00 (d, *J* = 8.6 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 6.97-6.89 (m, 5H), 3.84 (s, 3H), 3.82 (s, 3H), 3.73 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6 (C), 164.3 (C), 161.0 (C), 156.8 (C), 140.8 (C), 132.2 (CH), 131.0 (CH), 120.5 (CH), 119.4 (C), 114.5 (CH), 114.04 (CH), 113.94 (CH), 55.6 (CH_3), 45.2 (CH_2), 13.5 (CH_3).

IR (FTIR): 3294, 2940, 2842, 2360, 1748, 1701, 1601, 1446, 1286, 1246, 1209, 1172 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{18}H_{20}N_2O_5Na$ $[M+Na]^+$: 367.1291. Found: 367.1270.



1-(3,5-Dimethylphenyl)-1-ethyl-3-((4-methoxybenzoyl)oxy)urea (1af): The title compound was synthesized according to general procedure **D** using *N*-ethyl-3,5-dimethylaniline (1.49 g, 10.0 mmol), toluene (0.8 M), KOH pellets (0.561 g, 10.0 mmol), and water (2.9 M) at 0 °C. A dripping funnel was affixed on top of the roundbottom flask and

this apparatus was purged with argon for 10 minutes. Phosgene (15% in toluene) (16.4 mL, 23.0 mmol) was added to the dripping funnel under inert atmosphere, and was allowed to drip over 1 hour at 0 °C while stirring vigorously. The reaction was allowed to stir for an additional 30 minutes after complete addition of phosgene solution. Upon competition, the crude reaction mixture was bubbled with an argon balloon for 20 minutes in a well ventilated fumehood, to release any excess phosgene gas. The crude reaction mixture was then extracted to remove the aqueous layer, and then the organic phase was washed with brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude (3,5-dimethylphenyl)(ethyl)carbamic chloride which was used in the next step without further purification.
To the crude (3,5-dimethylphenyl)(ethyl)carbamic chloride was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added hydroxylamine hydrochloride (0.695 g, 10.0 mmol), and followed immediately by Et_3N (2.79 mL, 20.0 mmol). The reaction was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (10 mL x1), and then brine (10 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude 1-(3,5-dimethylphenyl)-1-ethyl-3-hydroxyurea, which could be used in the next step without further purification.
To the crude 1-(3,5-dimethylphenyl)-1-ethyl-3-hydroxyurea was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (1.39 mL, 10.0 mmol) followed immediately by dropwise addition of *p*-methoxybenzoylchloride (1.70 g, 10.0 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (10 mL x1), and then brine (10 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude 1-(3,5-dimethylphenyl)-1-ethyl-3-((4-methoxybenzoyl)oxy)urea which was purified by flash column chromatography (20% EtOAc/Hexanes → 40% EtOAc/Hexanes) to yield a colourless oil (2.74 g, 80% over 3 steps).

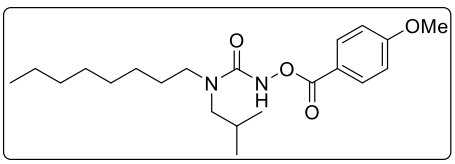
TLC R_f: 0.21 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02-7.98 (m, 2H), 7.97 (br s, 1H), 7.00 (d, *J* = 0.6 Hz, 1H), 6.96 (d, *J* = 0.5 Hz, 2H), 6.91-6.88 (m, 2H), 3.83 (d, *J* = 3.6 Hz, 3H), 3.70 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 6H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5 (C), 164.1 (C), 156.7 (C), 140.0 (C), 139.3 (C), 132.1 (CH), 130.3 (CH), 125.8 (CH), 119.3 (C), 113.9 (CH), 55.5 (CH_3), 45.0 (CH_2), 21.2 (CH_3), 13.4 (CH_3).

IR (FTIR): 2970, 1744, 1695, 1602, 1510, 1454, 1310, 1245, 1167, 1062 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{19}H_{22}N_2O_4Na$ $[M+Na]^+$: 365.1458. Found: 365.1477.



3-((4-Methoxybenzoyl)oxy)-1-isobutyl-1-octylurea (1ag): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.861 g, 3.00 mmol), and *N*-isobutyloctylamine (0.555 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (15.0 mL, 0.20 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was diluted with EtOAc (20 mL) and washed three times using 1 M NaOH (2.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over

Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated in vacuo and isolated using silica plug (20% EtOAc/Hexanes) to yield the title compound as a colourless oil (0.957 g, 84%).

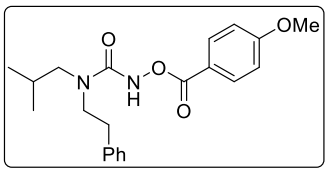
TLC R_f: 0.54 in 20% EtOAc/Hexanes.

^{1}H NMR (300 MHz, DMSO-d_6): δ 10.21-10.13 (br s, 1H), 8.01-7.91 (m, 2H) 7.15-7.03 (m, 2H), 3.85 (s, 3H), 3.23-3.14 (m, 2H), 3.03 (d, *J*= 7.4 Hz, 2H), 2.01-1.84 (m, 1H), 1.57-1.45 (m, 2H), 1.32-1.18 (m, 10H), 0.89-0.81 (m, 9H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 165.2 (C), 163.5 (C), 157.4 (C), 131.4 (CH), 119.8 (C), 114.3 (CH), 55.6 (CH), 53.0 (CH_2), 46.4 (CH_2), 31.2 (CH_2), 28.8 (CH_2), 28.7 (CH_2), 27.4 (CH_2), 26.7 (CH), 26.2 (CH_2), 22.1 (CH_2), 19.8 (CH), 13.9 (CH_3).

IR (FTIR): 3230, 2924, 2854, 1750, 1669, 1605, 1510, 1248 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{21}H_{34}N_2O_4Na$ $[M+Na]^+$: 401.2417. Found: 401.2423.



1-Isobutyl-3-((4-methoxybenzoyl)oxy)-1-phenethylurea (1ah): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and 2-(ethylamino)ethanol (0.532 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was concentrated in vacuo and isolated using silica column chromatography (10% EtOAc/Hexanes → 30% EtOAc/Hexanes) to yield the title compound as a white solid (1.06 g, 95%).

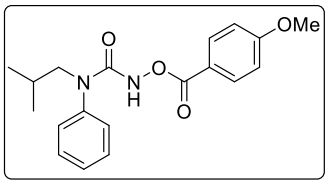
TLC R_f: 0.80 in 40% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (br s, 1H), 8.06 (d, *J* = 9.0 Hz, 2H), 7.38-7.15 (m, 5H), 6.92 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H), 3.50 (t, *J* = 7.7 Hz, 2H), 3.00 (d, *J* = 7.6 Hz, 2H), 2.92 (t, *J* = 7.7 Hz, 2H), 1.99 (dsextet, *J* = 13.7, 6.9 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7 (C), 164.2 (C), 157.8 (C), 138.7 (C), 132.1 (CH), 128.8 (CH), 128.7 (CH), 126.6 (CH), 119.3 (C), 113.9 (CH), 55.5 (CH), 55.1 (CH_2), 50.0 (CH_2), 34.2 (CH_2), 27.6 (CH), 20.1 (CH_3).

IR (FTIR): 3181, 2957, 1744, 1649, 1603, 1509, 1244, 1168 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{21}H_{26}N_2O_4Na$ $[M+Na]^+$: 393.1784. Found: 393.1790.



3-((4-Methoxybenzoyl)oxy)-1-isobutyl-1-phenylurea (1ai): The title compound was synthesized according to general procedure **D** using *N*-isobutylaniline (1.07 g, 7.20 mmol), toluene (0.8 M), KOH pellets (0.389 g, 7.20 mmol), and water (2.9 M) at 0 °C. A dripping funnel was affixed on top of the roundbottom flask and this apparatus was purged with argon for 10 minutes. Phosgene (15% in toluene) (11.8 mL, 23.0 mmol) was added to the dripping funnel under inert atmosphere, and was allowed to drip over 1 hour at 0 °C while stirring vigorously. The reaction was allowed to stir for an additional 30 minutes after complete addition of phosgene solution. Upon competition, the crude reaction mixture was bubbled with an argon balloon for 20 minutes in a well ventilated fumehood, to release any excess phosgene gas. The crude reaction mixture was then

extracted to remove the aqueous layer, and then the organic phase was washed with brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-isobutylanilinecarbamoyl chloride which was used in the next step without further purification.
To the crude *N*-isobutylanilinecarbamoyl chloride was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added hydroxylamine hydrochloride (0.500 g, 7.20 mmol), and followed immediately by Et_3N (1.00 mL, 14.4 mmol). The reaction was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (10 mL x1), and then brine (10 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-isobutylanilinehydroxyurea, which could be used in the next step without further purification.
To the crude *N*-isobutylanilinehydroxyurea (1.38 g, 6.63 mmol) was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (0.92 mL, 6.63 mmol) followed immediately by dropwise addition of *p*-methoxybenzoylchloride (1.13 g, 6.63 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude 3-((4-methoxybenzoyl)oxy)-1-isobutyl-1-phenylurea which was purified by recrystallization with Et_2O to yield a white crystalline solid (1.23 g, 36% over 3 steps).

TLC R_f: 0.34 in 20% EtOAc/Hexanes.

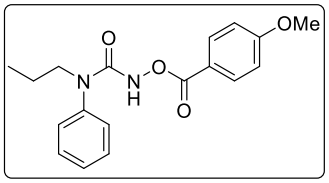
M.p.: 137.0-137.7°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.00 (m, 2H), 7.98-7.96 (br s, 1H), 7.53-7.46 (m, 2H), 7.45-7.37 (m, 3H), 6.96-6.90 (m, 2H), 3.87 (s, 3H), 3.57 (d, *J*= 7.4 Hz, 2H), 1.87-1.75 (m, 1H), 0.95 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5 (C), 164.1 (C), 157.3 (C), 140.0 (C), 132.1 (CH), 130.2 (CH), 128.5 (CH), 128.2 (CH), 119.2 (C), 113.9 (CH), 57.2 (CH_2), 55.5 (CH), 26.9 (CH), 19.9 (CH).

IR (FTIR): 2960, 1741, 1709, 1604, 1490, 1246, 1173, 1053 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{19}H_{22}N_2O_4Na$ $[M+Na]^+$: 365.1478. Found: 365.1501.



3-((4-Methoxybenzoyl)oxy)-1-phenyl-1-propylurea (1aj): The title compound was synthesized according to general procedure **D** using *N*-propylaniline (0.812 g, 6.00 mmol), toluene (0.8 M), KOH pellets (0.336 g, 6.00 mmol), and water (2.9 M) at 0 °C. A dripping funnel was affixed on top of the roundbottom flask and this apparatus was purged with argon for 10 minutes. Phosgene (15% in toluene) (9.8 mL, 14 mmol) was added to the dripping funnel under inert atmosphere, and was allowed to drip over 1 hour at 0 °C while stirring vigorously. The reaction was allowed to stir for an additional 30 minutes after complete addition of phosgene solution. Upon competition, the crude reaction mixture was bubbled with an argon balloon for 20 minutes in a well ventilated fumehood, to release any excess phosgene gas. The crude reaction mixture was then extracted to remove the aqueous layer, and then the organic phase was washed with brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-propylanilinecarbamoyl chloride which was used in the next step without further purification.
To the crude *N*-propylanilinecarbamoyl chloride was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added hydroxylamine hydrochloride (0.417 g, 6.00 mmol), and followed immediately by Et_3N (1.67 mL, 12.0 mmol). The reaction was allowed to warm to room temperature and stir overnight. Upon

completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N*-propylanilinehydroxyurea, which could be used in the next step without further purification.
To the crude *N*-propylanilinehydroxyurea (0.927 g, 5.45 mmol) was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (0.76 mL, 5.45 mmol) followed immediately by dropwise addition of *p*-methoxybenzoylchloride (1.06 g, 5.45 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude 3-((4-methoxybenzoyl)oxy)-1-phenyl-1-propylurea which was purified by recrystallization with Et_2O to yield a white crystalline solid (0.935 g, 48% over 3 steps).

TLC R_f: 0.40 in 20% EtOAc/Hexanes.

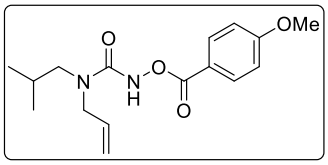
M.p.: 118.3-119.4°C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-7.99 (m, 2H), 7.98-7.95 (br s, 1H), 7.54-7.46 (m, 2H), 7.45-7.37 (m, 3H), 6.97-6.89 (m, 2H), 3.87 (s, 3H), 3.71-3.66 (m, 2H), 1.59 (dq, *J*= 14.9, 7.5 Hz, 2H), 0.93 (t, *J*= 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5 (C), 164.2 (C), 156.9 (C), 139.7 (C), 132.1 (CH), 130.2 (CH), 128.6 (CH), 128.3 (CH), 119.2 (C), 113.9 (CH), 55.5 (CH), 51.7 (CH_2), 21.2 (CH_2), 11.0 (CH_3).

IR (FTIR): 3291, 2913, 1748, 1716, 1605, 1490, 1247, 1175 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{18}H_{20}N_2O_4Na$ $[M+Na]^+$: 351.1321. Found: 351.1347.



1-Allyl-1-isobutyl-3-((4-methoxybenzoyl)oxy)urea (1ak): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N*-isobutylprop-2-en-1-amine (0.340 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was concentrated in vacuo and isolated using silica column chromatography (10% EtOAc/Hexanes → 20% EtOAc/Hexanes) to yield the title compound as a white solid (0.919 g, 95%).

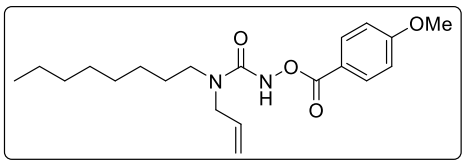
TLC R_f: 0.22 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (br s, 1H), 8.08-8.05 (m, 2H), 6.95-6.92 (m, 2H), 5.92-5.81 (m, 1H), 5.37-5.30 (m, 2H), 3.95 (td, *J* = 3.4, 1.7 Hz, 2H), 3.86 (d, *J* = 5.3 Hz, 3H), 3.16 (d, *J* = 7.5 Hz, 2H), 1.98 (dsextet, *J* = 13.7, 6.8 Hz, 1H), 0.95 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7 (C), 164.2 (C), 158.2 (C), 132.7 (CH), 132.1 (CH), 119.3 (C), 117.5 (CH_2), 113.9 (CH), 55.5 (CH_3), 55.1 (CH_2), 49.9 (CH_2), 27.5 (CH), 20.1 (CH_3).

IR (FTIR): 3277, 2953, 1739, 1685, 1463, 1253, 1024 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{16}H_{22}N_2O_4Na$ $[M+Na]^+$: 329.1491. Found: 329.1477.



1-Allyl-3-((4-methoxybenzoyl)oxy)-1-octylurea (1al): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and *N*-allyloctan-1-amine (0.508 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was concentrated in vacuo and isolated using silica column chromatography (10% EtOAc/Hexanes → 20% EtOAc/Hexanes) to yield the title compound as a white solid (0.870 g, 80%).

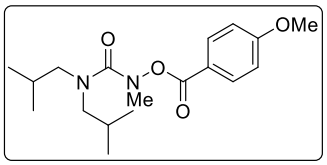
TLC R_f: 0.28 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$):) δ 8.47 (s, 1H), 8.05 (d, *J* = 9.0 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 5.85 (ddt, *J* = 17.3, 10.3, 5.2 Hz, 1H), 5.35-5.27 (m, 2H), 3.92 (dt, *J* = 5.2, 1.6 Hz, 2H), 3.84 (s, 3H), 3.30 (t, *J* = 7.6 Hz, 2H), 1.60 (s, 3H), 1.28-1.25 (m, 11H), 0.85 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7 (C), 164.2 (C), 157.8 (C), 132.9 (CH), 132.1 (CH), 119.3 (C), 117.4 (CH_2), 113.9 (CH), 55.5 (CH_3), 49.5 (CH_2), 47.8 (CH_2), 31.8 (CH_2), 29.34 (CH_2), 29.22 (CH_2), 28.2 (CH_2), 26.9 (CH_2), 22.6 (CH_2), 14.1 (CH_3).

IR (FTIR): 3270, 2922, 2854, 1737, 1692, 1601, 163, 1251 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{20}H_{30}N_2O_4Na$ $[M+Na]^+$: 385.2099. Found: 385.2103.



3-((4-Methoxybenzoyl)oxy)-1,1-diisobutyl-3-methylurea (1am): The title compound was synthesized according to general procedure **D** using *N*,*N*-diisobutylamine (1.75 mL, 10.0 mmol), toluene (0.8 M), NaOH pellets (0.400 g, 10.0 mmol), and water (2.9 M) at 0 °C. A dripping funnel was affixed on top of the roundbottom flask and this apparatus was purged with argon for 10 minutes. Phosgene (15% in toluene) (16.4 mL, 23.0 mmol) was added to the dripping funnel under inert atmosphere, and was allowed to drip over 1 hour at 0 °C while stirring vigorously. The reaction was allowed to stir for an additional 30 minutes after complete addition of phosgene solution. Upon competition, the crude reaction mixture was bubbled with an argon balloon for 20 minutes in a well ventilated fumehood, to release any excess phosgene gas. The crude reaction mixture was then extracted to remove the aqueous layer, and then the organic phase was washed with brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N,N*-diisobutylaminecarbamoyl chloride which was used in the next step without further purification.
To the crude *N,N*-diisobutylaminecarbamoyl chloride was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added hydroxylamine hydrochloride (0.835 g, 10.0 mmol), and followed immediately by Et_3N (2.79 mL, 20.0 mmol). The reaction was allowed to warm to room temperature and stir overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (10 mL x1), and then brine (10 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude *N,N*-diisobutylaminehydroxyurea, which could be used in the next step without further purification.
To the crude *N,N*-diisobutylaminehydroxyurea (1.77 g, 8.80 mmol) was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (1.23 mL, 8.80 mmol) followed immediately by dropwise addition of *p*-methoxybenzoylchloride (1.19 mL, 8.80 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide

the crude 3-((4-methoxybenzoyl)oxy)-1,1-diisobutyl-3-methylurea which was purified by flash column chromatography (10 % EtOAc/Hexanes) to yield a colourless oil (0.760 g, 23% over 3 steps).

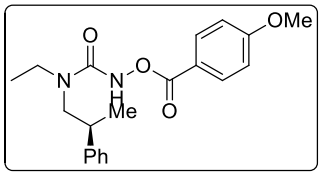
TLC R_f: 0.65 in 20% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-7.97 (m, 2H), 6.98-6.90 (m, 2H), 3.88 (s, 3H), 3.17-3.09 (m, 7H), 1.98 (dt, *J*= 13.8, 7 Hz, 2H), 0.88 (d, *J*= 6.9 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0 (C), 163.9 (C), 163.3 (C), 131.7 (CH), 120.3 (C), 113.9 (CH), 55.5 (CH), 54.6 (CH_2), 40.1 (CH), 26.4 (CH), 20.0 (CH_3).

IR (FTIR): 2655, 1692, 1622, 1534, 1332, 1261 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{18}H_{28}N_2O_4Na$ $[M+Na]^+$: 359.1947. Found: 359.1957.



1-Ethyl-3-((4-methoxybenzoyl)oxy)-1-(2-phenylpropyl)urea (1an): The title compound was synthesized according to general procedure **C** using phenyl (4-methoxybenzoyl)oxycarbamate (0.862 g, 3.00 mmol), and (S)-*N*-ethyl-2-phenylpropan-1-amine (0.490 g, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (15.0 mL, 0.20 M). The reaction was heated under microwave irradiation for 2 h at 100 °C. Upon completion, the reaction mixture was diluted with EtOAc (20 mL) and washed three times using 1 M NaOH (2.0 mL x 3), followed by a single brine wash (10 mL x 1). The organic phase was collected and dried over Na_2SO_4 (stirring for 15 min). The solids were filtered over a frit and rinsed with CH_2Cl_2 (5.0 mL). The filtrate was collected, concentrated vacuo and isolated using silica plug (20% EtOAc/Hexanes → 40% EtOAc/Hexanes) to yield the title compound as a (0.950 g, 89%).

TLC R_f: 0.19 in 20% EtOAc/Hexanes.

$[\alpha]_D^{26°C}$: +45.5 (C= 0.1 M in CH_2Cl_2).

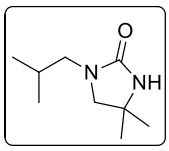
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (br s, 1H), 8.11-7.99 (m, 2H), 7.35-7.27 (m, 2H), 7.27-7.17 (m, 3H), 6.98-6.86 (m, 2H), 3.85 (s, 3H), 3.58 (dd, *J* = 6.4, 13.6 Hz, 1H), 3.27-3.11 (m, 3H), 2.96 (qd, *J* = 7.2, 14.6 Hz, 1H), 1.35-1.27 (m, 3H), 1.18-1.03 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4 (C), 164.2 (C), 157.7 (C), 144.0 (C), 132.1 (CH), 128.8 (CH), 127.3 (CH), 126.8 (CH), 119.4 (C), 113.9 (CH), 55.5 (CH_3), 54.6 (CH_2), 42.6 (CH_2), 38.8 (CH), 18.6 (CH_3), 12.9 (CH_3).

IR (FTIR): 3216, 2966, 1747, 1668, 1604, 1509, 1454, 1245, 1167 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{20}H_{24}N_2O_4Na$ $[M+Na]^+$: 379.1628. Found: 379.1634.

Synthesis of imidazolidin-2-one via photoinduced C-H amination



1-Isobutyl-4,4-dimethylimidazolidin-2-one (2a): The title compound was synthesized according to general procedure **G** using 1,1-diisobutyl-3-((4-methoxybenzoyl)oxy)urea (0.161 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The

vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.080 g, 95%).

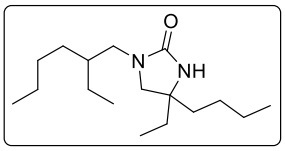
TLC R_f: 0.30 in 50% EtOAc/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.34 (br. s, 1H), 3.14 (s, 2H), 2.96 (d, *J* = 7.5 Hz, 2H), 1.89-1.76 (m, 1H), 1.29 (s, 6H), 0.90 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4 (C), 58.7 (CH_2), 52.1 (C), 50.9 (CH_2), 28.6 (CH_3), 27.1 (CH), 20.1 (CH_3).

IR (FTIR): 3208, 3074, 2955, 2871, 1683, 1488, 1448, 1295, 1240 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_9H_{18}N_2O$ $[M]^+$: 170.1419. Found: 170.1407.



4-Butyl-4-methyl-1-(2-ethylhexyl)imidazolidin-2-one1-isobutyl-4,4-dimethylimidazolidin-2-one (2b): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1,1-bis(2-ethylhexyl)urea (0.196 g, 0.450 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (60% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.095 g, 75% as a 1:1 diastereoisomers mixt).

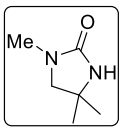
TLC R_f: 0.21 in 2% MeOH/CH_2Cl_2.

^{1}H NMR (300 MHz, DMSO-d_6): δ 6.37-6.34 (br s, 1H), 3.02-2.99 (m, 2H), 2.91-2.86 (m, 2H), 1.51-1.33 (m, 5H), 1.32-1.11 (m, 14H), 0.91-0.75 (m, 14H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 160.6 (C), 56.0 (C), 56.0 (C), 54.0 (CH_2), 53.9 (CH_2), 46.2 (CH_2), 38.7 (CH_2), 38.7 (CH_2), 37.0 (CH_2), 36.9 (CH), 31.8 (CH_2), 31.8 (CH_2), 30.1 (CH_2), 28.2 (CH_2), 28.1 (CH_2), 25.3 (CH_2), 23.5 (CH_2), 23.5 (CH_2), 22.7 (CH_2), 22.6 (CH_2), 22.6 (CH_2), 22.5 (CH_2), 14.0 (CH), 13.9 (CH), 10.5 (CH_3), 10.5 (CH_3), 7.7 (CH_3), 7.7 (CH_3).

IR (FTIR): 3196, 3069, 2967, 2893, 1685, 1441, 1118 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{15}H_{30}N_2O$ $[M]^+$: 282.2671. Found: 282.2655.



1,4,4-Trimethylimidazolidin-2-one (2c): The title compound was synthesized according to general procedure **G** using 1-isobutyl-3-((4-methoxybenzoyl)oxy)-1-methylurea (0.140 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial

with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.060 g, 93%).

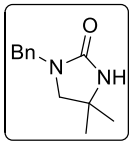
TLC R_f: 0.16 in 50% EtOAc/CH_2Cl_2.

^{1}H NMR (300 MHz, $CDCl_3$): δ 4.57 (br. s, 1H), 3.13 (s, 2H), 2.77 (s, 3H), 1.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (C), 60.7 (CH_2), 51.9 (C), 30.6 (CH_3), 28.6 (CH_3).

IR (FTIR): 3540, 3475, 3224, 2955, 2927, 2846, 1673, 1502, 1446, 1405, 1305 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_6H_{12}N_2O$ $[M]^+$: 128.0950. Found: 128.0945.



1-Benzyl-4,4-dimethylimidazolidin-2-one (2d): The title compound was synthesized according to general procedure **G** using 1-benzyl-1-isobutyl-3-((4-methoxybenzoyl)oxy)urea (0.190 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.051 g, 50%).

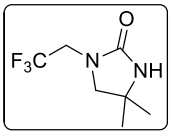
TLC R_f: 0.35 in 50% EtOAc/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.23 (m, 5H), 4.50 (br s, 1H), 4.35 (s, 2H), 3.00 (s, 2H), 1.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9 (C), 137.2 (C), 128.6 (CH), 128.0 (CH), 127.4 (CH), 57.4 (CH_2), 52.0 (C), 47.4 (CH_2), 28.5 (CH_3).

IR (FTIR): 3201, 3069, 2962, 2861, 1688, 1492, 1437, 1363, 1299 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{12}H_{16}N_2$ $[M]^+$: 204.1263. Found: 204.1252.



4,4-Dimethyl-1-(2,2,2-trifluoroethyl)imidazolidin-2-one (2e): The title compound was synthesized according to general procedure **G** using 1-isobutyl-3-((4-methoxybenzoyl)oxy)-1-(2,2,2-trifluoroethyl)urea (0.174 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic

acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (30% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.092 g, 94%).

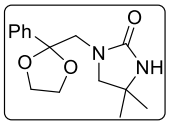
TLC R_f: 0.45 in 50% EtOAc/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.87 (br s, 1H), 3.78 (q, J = 9.1 Hz, 2H), 3.30 (s, 2H), 1.32 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3 (C), 124.7 (q, J = 278 Hz, C), 59.0 (CH_2), 52.5 (C), 45.4 (q, J = 34 Hz, CH_2), 28.4 (CH_3).

IR (FTIR): 3223, 3082, 2976, 1697, 1446, 1416, 1313, 1265, 1221, 1149 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_7H_{11}N_2OF_3$ $[M]^+$: 196.0823. Found: 196.0807.



4,4-Dimethyl-1-((2-phenyl-1,3-dioxolan-2-yl)methyl)imidazolidin-2-one (2f): The title compound was synthesized according to general procedure **G** using 1-isobutyl-1-(2-phenyl-1,3-dioxolan-2-yl)isobutyl-3-((4-methoxybenzoyl)oxy)urea (0.214 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.118 g, 86%).

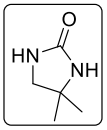
TLC R_f: 0.13 in 2% MeOH/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.46 (m, 2H), 7.41-7.30 (m, 3H), 4.19-4.10 (br s, 1H), 4.09-4.00 (m, 2H), 3.91-3.79 (m, 2H), 3.58 (s, 2H), 3.23 (s, 2H), 1.20 (s, 6H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 160.8 (C), 140.3 (C), 128.3 (CH), 128. (CH), 109.7 (C), 64.7 (CH_2), 59.6 (CH_2), 51.8 (C), 50.5 (CH_2), 28.3 (CH_3).

IR (FTIR): 3197, 3070, 2967, 2893, 1685, 1442, 1243, 1023 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{15}H_{20}N_2O_3Na$ $[M+Na]^+$: 299.1372. Found: 299.1394.

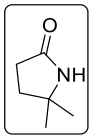


4,4-Dimethylimidazolidin-2-one (2g): The title compound was synthesized according to a modified general procedure **G** using 1-isobutyl-3-((4-methoxybenzoyl)oxy)urea (0.133 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), tetrabutylammonium dibutyl phosphate (0.026 g, 5 mol%) in CH_2Cl_2 (5.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and heated in a water bath at 60 ºC overnight. Upon completion, the reaction was diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (5% MeOH/CH_2Cl_2 + 1% Et_3N) to yield a clear oil (0.013 g, 22%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.94-4.62 (br s, 2H), 3.23 (s, 2H), 1.31 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9 (C), 55.3 (C), 54.0 (CH_2), 28.4 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[18]

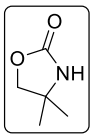


5,5-Dimethylpyrrolidin-2-one (2h): The title compound was synthesized according to general procedure **G** using *N*-((4-methoxybenzoyl)oxy)-4-methylpentanamide (0.265 g, 1.00 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.017 g, 2 mol%), triethylamine (0.026 g, 5 mol%) in CH_2Cl_2 (5.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2 → 100% EtOAc) to yield a clear oil (0.088 g, 78%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.09 (s, 1H), 2.41 (dd, *J* = 8.4, 7.6 Hz, 2H), 1.93 (t, *J* = 8.0 Hz, 2H), 1.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1 (C), 56.7 (C), 35.5 (CH_2), 30.8 (CH_2), 29.3 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[14]

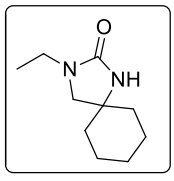


4,4-Dimethyloxazolidin-2-one (2i): The title compound was synthesized according to general procedure **G** using isobutyl ((4-methoxybenzoyl)oxy)carbamate (0.134 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), tetrabutylammonium dibutyl phosphate (0.011 g, 5 mol%) in CH_2Cl_2 (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (20% EtOAc/CH_2Cl_2 → 100% EtOAc) to yield a clear oil (0.014 g, 24%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.21-5.00 (br s, 1H), 4.09 (s, 2H), 1.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3 (C), 77.1 (C), 55.4 (CH_2), 27.7 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[14]



3-Ethyl-1,3-diazaspiro[4.5]decan-2-one (2j): The title compound was synthesized according to general procedure **G** using 3-((4-Methoxybenzoyl)oxy)-1-cyclohexylmethyl-1-ethylurea (0.167 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.22 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir

[18] Leung, M.-K.; Lai, J.-L.; Lau, K.-H.; Yu, H.-H.; Hsiao, H.-J. *J. Org. Chem.* **1996**, *61*, 4175.

overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (40% EtOAc/Hexanes) to yield an amorphous white solid (0.080 g, 88%).

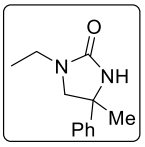
TLC R_f: 0.39 in 2% MeOH/CH_2Cl_2.

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.65-6.60 (br s, 1H), 3.08-3.01 (m, 4H), 1.62-1.21 (m, 10H), 0.97 (t, *J*= 7.2 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 159.9 (C), 54.5 (CH_2), 53.6 (C), 37.3 (CH_2), 37.1 (CH_2), 24.9 (CH_2), 22.1 (CH_2), 12.6 (CH_3).

IR (FTIR): 3202, 2926, 2853, 1677, 1489, 1330, 1258, 1198 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{10}H_{18}N_2O$ $[M]^+$: 182.1419. Found: 182.1413.



1-Ethyl-4-methyl-4-phenylimidazolidin-2-one (2k): The title compound was synthesized according to general procedure **G** using 1-ethyl-3-((4-methoxybenzoyl)oxy)-1-(2-phenylpropyl)urea (0.163 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.079 g, 77%).

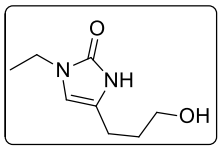
TLC R_f: 0.42 in 30% EtOAc/CH_2Cl_2

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.27 (m, 5H), 4.69-4.68 (m, 1H), 3.45 (q, *J* = 10.0 Hz, 2H), 3.39-3.17 (m, 2H), 1.68 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8 (C), 145.9 (C), 128.8 (CH), 127.4 (CH), 124.9 (CH), 58.9 (CH_2), 57.2 (C), 37.9 (CH_2), 28.6 (CH_3), 12.8 (CH_3).

IR (FTIR): 3194, 3069, 2969, 2925, 2854, 1679, 1493, 1444, 1299, 1283, 1089 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{12}H_{16}N_2O$ $[M]^+$: 204.1263. Found: 204.1237.



1-Ethyl-4-(3-hydroxypropyl)-1*H*-imidazol-2(3*H*)-one (2l): The title compound was synthesized according to general procedure **G** using 1-ethyl-3-((4-methoxybenzoyl)oxy)-1-((tetrahydrofuran-2-yl)methyl)urea (0.161 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate

(3 x 2 mL) to remove the benzoic acid. The majority of the product was found to dissolve in the aqueous phase, and so the aqueous phase was collected, and concentrated under reduced pressure. The combined organic and aqueous phases were purified by column chromatography (50% EtOAc/CH_2Cl_2 → 5% MeOH/CH_2Cl_2) to yield an amorphous white solid (0.079 g, 93%).

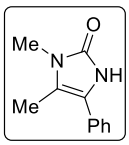
TLC R_f: 0.06 in 50% EtOAc/CH_2Cl_2; 0.53 in 10% MeOH/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.63 (s, 1H), 5.91 (br. s, 1H), 3.74 (s, 1H), 3.68-3.56 (m, 4H), 2.50 (t, *J* = 6.9 Hz, 2H), 1.81-1.72 (m, 2H), 1.27-1.20 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2 (C), 122.6 (C), 106.3 (CH), 60.9 (CH_2), 37.8 (CH_2), 31.8 (CH_2), 21.7 (CH_2), 14.9 (CH_3).

IR (FTIR): 3271, 2962, 1683, 1428, 1351, 1242, 1047 cm^{-1}.

HRMS (EI) m/z: Despite multiple attempts to obtain an accurate mass using both ESI and EI, one could not be obtained for this compound. However, C^{13} peaks at 122.6 and 106.3 ppm align with known structures and provides solid evidence for structural assignment. Moreover, this product is formed in analogy to **2m**, **2n** and **2x**.

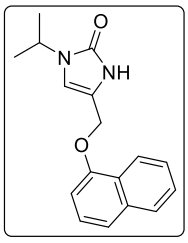


1,5-Dimethyl-4-phenyl-1H-imidazol-2(3H)-one (2m): The title compound was synthesized according to general procedure **G** using 1-(2-hydroxy-2-phenylethyl)-3-((4-methoxybenzoyl)oxy)-1-methylurea (0.167 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the product precipitated from solution and was collected by filtration to yield an amorphous white solid (0.047 g, 50%) the filtrate was evaporated to reveal product in solution which could be purified by silica column chromatography (50% EtOAc/CH_2Cl_2 → 5% CH_3OH/ CH_2Cl_2) (0.020 g, 18%). The combined isolated yield is therefore 0.067 g, 71%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.32 (d, *J* = 39.5 Hz, 6H), 3.24 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.4 (C), 131.0 (C), 129.1 (CH), 127.0 (CH), 126.5 (CH), 117.7 (C), 116.4 (C), 27.2 (CH_3), 9.8 (CH_3)

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[19]



1-Ethyl-4-((naphthalen-1-yloxy)methyl)-1H-imidazol-2(3H)-one (2n): The title compound was synthesized according to general procedure **G** using 1-(2-hydroxy-3-(naphthalen-1-yloxy)propyl)-1-isopropyl-3-((4-methoxybenzoyl)oxy)urea (0.158 g, 0.350 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.006 g, 2 mol%), triethylamine (0.039 g, 0.385 mmol) in MeCN (1.75 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the product precipitated from solution and was collected by filtration to yield an amorphous white solid (0.035 g, 35%).

[19] Holzmann, G.; Krieg, B.; Lautenschläger, H.; Konieczny, P. *J. Heterocycl. Chem.* **1979**, *16*, 983-985.

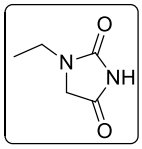
TLC R_f: 0.07 in 50% EtOAc/CH_2Cl_2; 0.45 in 5% MeOH/CH_2Cl_2.

^{1}H NMR (600 MHz, DMSO-d_6): δ 10.36-10.35 (m, 1H), 8.17-8.15 (m, 1H), 7.88-7.86 (m, 1H), 7.54-7.43 (m, 5H), 7.09-7.08 (m, 1H), 6.78-6.78 (m, 1H), 4.92 (d, *J* = 5.4 Hz, 2H), 4.19 (dt, *J* = 0.8, 0.4 Hz, 1H), 1.25-1.21 (m, 6H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 154.0 (C), 153.4 (C), 134.5 (C), 127.9 (CH), 127.0 (CH), 126.6 (CH), 125.7 (CH), 125.5 (C), 122.3 (CH), 120.7 (CH), 116.7 (C), 108.8 (CH), 106.2 (CH), 62.1 (CH_2), 43.7 (CH), 22.3 (CH_3).

IR (FTIR): 3292, 3227, 2952, 2878, 1681, 1577, 1491, 1453, 1394 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{17}H_{18}N_2O_2$ $[M]^+$: 282.1368. Found: 282.1378.

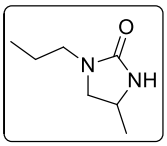


1-Ethylimidazolidine-2,4-dione (2o): The title compound was synthesized according to general procedure **G** using 1-(2,2-dimethoxyethyl)-1-ethyl-3-((4-methoxybenzoyl)oxy)urea (0.148 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure and then purified by column chromatography (50% EtOAc/CH_2Cl_2 → 5% CH_3OH/ CH_2Cl_2) to yield an amorphous white solid (0.055 g, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 3.91 (s, 2H), 3.43 (q, *J* = 7.3 Hz, 2H), 1.19 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4 (C), 156.0 (C), 50.2 (CH_2), 37.2 (CH_2), 12.9 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[20]



4-Methyl-1-propylimidazolidin-2-one (2p): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1,1-dipropylurea (0.147 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.059 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.065 g, 92%).

TLC R_f: 0.15 in 2% MeOH/CH_2Cl_2.

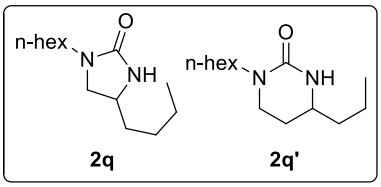
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13-4.23 (br s, 1H), 3.84-3.68 (m, 1H), 3.50 (t, *J*= 8.5 Hz, 1H), 3.25 – 3.01 (m, 2H), 2.94 (dd, *J* =8.5, 6.3 Hz, 1H), 1.50 (h, *J* =7.4 Hz, 1H), 1.22 (d, *J*= 6.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

[20] Sigachev, A. S.; Kravchenko, A. N.; Belyakov, P. A.; Lebedev, O. V.; Makhova N. N. *Russ. Chem. Bull.* **2006**, *55*, 865-872.

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (C), 52.3 (CH), 45.6 (CH_2), 45.0 (CH_2), 21.6 (CH_2), 20.9 (CH_3), 11.3 (CH_3).

IR (FTIR): 3327, 2973, 2866, 1666, 1381, 1045 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_7H_{14}N_2$ $[M]^+$: 142.1106. Found: 142.1124.



1-Hexyl-4-butyl-imidazol-2-one (2q) and 1-hexyl-4-propyltetrahydropyrimidin-2(1H)-one (2q'): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1,1-dihexylurea (0.189 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.059 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compounds were purified by column chromatography (97:2:1 CH_2Cl_2/iPrOH/AcOH) to yield an inseparable mixture as a colourless oil (0.051 g, 72%).

TLC R_f: 0.18 in 2% MeOH/CH_2Cl_2.

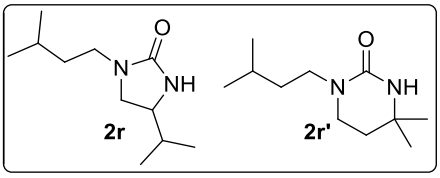
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.50-6.40 (br s, 1H), 6.08-5.99 (br s, 1H), 3.53-3.26 (m, 3H), 3.21-2.90 (m, 3H), 2.89-2.83 (m, 1H), 1.47-1.14 (m, 1H), 0.90-0.81 (m, 8H).

Compound **2q**: **^{13}C NMR (100 MHz, DMSO-d_6):** δ 161.3 (C), 49.9 (CH2), 49.1 (CH), 42.5 (CH_2), 35.3 (CH_2), 30.9 (CH_2), 27.0 (CH_2), 25.9 (CH_2), 22.1 (CH_2), 22.0 (CH_2), 22.0 (CH_2), 13.9 (CH_3), 13.9 (CH_3).

Compound **2q'**: **^{13}C NMR (100 MHz, DMSO-d_6):** δ 155.1 (C), 49.8 (CH), 46.2 (CH_2), 43.3 (CH_2), 37.8 (CH_2), 31.1 (CH_2), 28.1 (CH_2), 27.3 (CH_2), 27.1 (CH_2), 26.0 (CH_2), 18.0 (CH_2), 14.0 (CH_3).
(one carbon is missing due to overlap with compound A).

IR (FTIR): 3213, 2956, 2923, 2856, 1687, 1449, 1261 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{13}H_{26}N_2O$ $[M]^+$: 226.2045. Found: 226.2030.



1-Isopentyl-4-isopropylimidazolidin-2-one (2r) and 1-isopentyl-4-isopropylimidazolidin-2-one (2r'): The title compound was synthesized according to general procedure **G** using 1,1-diisopentyl-3-((4-methoxybenzoyl)oxy)urea (0.175 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with

Na_2SO_4, filtered, and concentrated under reduced pressure. The title compounds were purified by column chromatography (96:3:1 CH_2Cl_2/iPrOH/AcOH) to yield an inseparable mixture as a colourless oil (0.078 g, 79%).

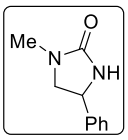
TLC R_f: 0.51 in 50% EtOAc/CH2Cl_2.

^{1}H NMR (300 MHz, DMSO-d_6): δ 6.55-6.50 (br s, 1H), 6.08-6.02 (br s, 1H), 3.29-2.88 (m, 10H), 1.66-1.58 (m, 2H), .56-1.41 (m, 4H), 1.38-1.22 (m, 6H), 1.09 (s, 6H), 0.91-0.77 (m, 27H).

^{13}C (100 MHz, DMSO-d_6): δ 161.4 (C), 154.7 (C), 54.9 (CH), 49.3 (C), 47.8 (CH2), 44.4 (CH2), 41.5 (CH2), 40.8 (CH2), 36.0 (CH2), 35.9 (CH2), 34.3 (CH2), 32.7 (CH), 29.0 (CH), 25.4 (CH), 25.2 (CH), 22.5 (CH), 22.4 (CH), 22.3 (CH), 18.2 (CH_3), 17.7 (CH_3).

IR (FTIR): 3210, 2956, 2870, 1685, 1644, 1459, 1261 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{11}H_{22}N_2O$ $[M]^+$: 198.1732. Found: 198.1716.



1-Methyl-4-phenylimidazolidin-2-one (2s): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1-methyl-1-phenethylurea (0.164 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (40% EtOAc/Hexanes → 100% EtOAc) to yield a white solid (0.067 g, 75%).

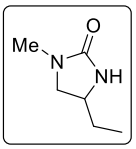
TLC R_f: 0.29 in 50% EtOAc/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.27 (m, 5H), 4.77 (br. s, 1H), 4.72 (ddd, *J* = 8.8, 7.4, 1.5 Hz, 1H), 3.76 (t, *J* = 8.8 Hz, 1H), 3.20 (dd, *J* = 8.8, 7.4 Hz, 1H), 2.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3 (C), 141.7 (C), 129.0 (CH), 128.3 (CH), 126.2 (CH), 56.2 (CH_2), 53.8 (CH), 30.7 (CH_3).

IR (FTIR): 3198, 3083, 2919, 2852, 1681, 1500, 1440, 1403, 1252 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{10}H_{12}N_2O$ $[M]^+$: 176.0950. Found: 176.0974.



1-Methyl-4-ethyl-imidazol-2-one (2t): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1-butyl-1-methylurea (0.140 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered,

and concentrated under reduced pressure. The title compound was purified by column chromatography (96:3:1 CH_2Cl_2/iPrOH/AcOH) to yield an amorphous white solid (0.032 g, 50%).

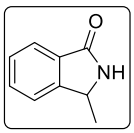
TLC R_f: 0.36 in 2% MeOH/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.64-4.28 (br s, 1H), 3.64-3.46 (m, 2H), 3.03 (dd, *J* = 8, 6.1 Hz, 1H), 2.78 (s, 3H), 1.61-1.56 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (C), 52.9 (CH_2), 51.1 (CH), 30.5 (CH), 28.6 (CH_2), 9.6 (CH_3).

IR (FTIR): 3203, 2960, 1683, 1507, 1311, 161, 1231 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_6H_{12}N_2O$ $[M]^+$: 128.0950. Found: 128.0946.

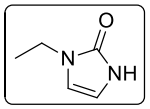


3-Methylisoindolin-1-one (2u): The title compound was synthesized according to general procedure **G** using 2-ethyl-N-((4-methoxybenzoyl)oxy)benzamide (0.150 g, 0.50 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), tetrabutylammonium dibutyl phosphate (0.011 g, 5 mol%) in CH_2Cl_2 (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.048 g, 65%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.58 (td, *J* = 7.5, 1.2 Hz, 1H), 7.52 – 7.40 (m, 2H), 6.73-6.57 (br s, 1H), 4.70 (q, J = 6.7 Hz, 1H), 1.51 (d, J = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7 (C), 149.0 (C), 132.1 (CH), 131.6 (C), 128.3 (CH), 124.0 (CH), 122.3 (CH), 52.6 (CH), 20.5 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[14]



1-Ethyl-1*H*-imidazol-2(3*H*)-one (2v): The title compound was synthesized according to general procedure **G** using 1-ethyl-1-(2-hydroxyethyl)-3-((4-methoxybenzoyl)oxy)urea (0.141 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2 → 5% MeOH/CH_2Cl_2) to yield a white solid (0.028 g, 50%).

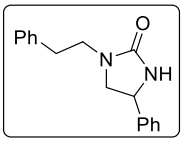
TLC R_f: 0.07 in 50% EtOAc/CH_2Cl_2; 0.45 in 5% MeOH/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 6.29 (t, *J* = 2.6 Hz, 1H), 6.20 (t, *J* = 2.5 Hz, 1H), 3.67 (q, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3 (C), 110.8 (CH), 108.0 (CH), 37.9 (CH_2), 14.8 (CH_3).

IR (FTIR): 3200, 2929, 1663, 1455, 1258, 1088 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_5H_8N_2O$ $[M]^+$: 112.0637. Found: 112.0618.



Phenethyl-4-phenylimidazolidin-2-one (2w): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1,1-diphenethylurea (0.209 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (40% EtOAc/Hexanes) to yield a white solid (0.100 g, 75%).

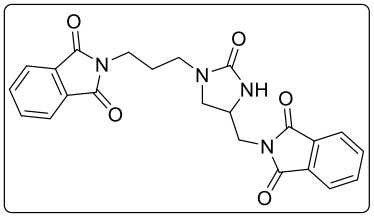
TLC R_f: 0.50 in 50% EtOAc/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.19 (m, 10H), 4.73 (br. s, 1H), 4.68 (ddd, *J* = 8.8, 7.1, 1.4 Hz, 1H), 3.68 (t, J = 8.8 Hz, 1H), 3.56-3.43 (m, 2H), 3.14 (dd, *J* = 8.8, 7.1 Hz, 1H), 2.85 (t, *J* = 7.1 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7 (C), 141.7 (C), 139.0 (C), 129.0 (CH), 128.9 (C), 128.6 (CH), 128.3 (CH), 126.5 (CH), 126.2 (CH), 54.2 (CH_2), 53.9 (CH), 44.9 (CH_2), 34.5 (CH_2).

IR (FTIR): 3216, 3083, 3028, 2917, 2854, 1680, 1490, 1452, 1360, 1318, 1255 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{17}H_{18}N_2O$ $[M]^+$: 266.1419. Found: 233.1431.



2-(3-(4-((1,3-Dioxoisoindolin-2-yl)methyl)-2-oxoimidazolidin-1-yl)propyl)isoindoline-1,3-dione (2x): The title compound was synthesized according to general procedure **G** using 1,1-bis(3-(1,3-dioxoisoindolin-2-yl)propyl)-3-((4-methoxybenzoyl)oxy)urea (0.292 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2 → 100% EtOAc) to yield a white solid (0.078 g, 36%).

TLC R_f: 0.16 in 50% EtOAc/CH_2Cl_2.

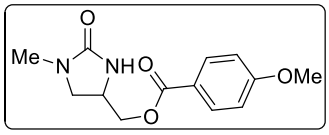
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (ddd, *J* = 13.4, 5.5, 3.0 Hz, 4H), 7.70 (ddd, *J* = 14.6, 5.5, 3.0 Hz, 4H), 4.74 (s, 1H), 3.98 (dq, *J* = 9.0, 4.8 Hz, 1H), 3.90 (dd, *J* = 14.0, 5.8 Hz, 1H), 3.78 (dd, *J* = 14.0, 4.7 Hz, 1H), 3.68 (td, *J* = 7.3, 3.2 Hz, 2H), 3.56 (t, *J* = 8.8 Hz, 1H), 3.34 (dd, *J* = 9.0, 5.6 Hz, 1H), 3.25-3.12 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5 (C), 138.2 (C), 161.1 (C), 134.3 (CH), 133.9 (CH), 131.1 (C), 131.7 (C), 123.6 (CH), 123.2 (CH), 49.3 (CH), 48.6 (CH_2), 41.1 (CH_2), 40.9 (CH_2), 35.4 (CH2), 26.6 (CH_2).

IR (FTIR): 3200, 2864, 1693, 1387, 1258, 1027 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{23}H_{20}N_4O_5Na$ $[M+Na]^+$: 455.1325. Found: 455.1331.

Aziridination



(1-Methyl-2-oxoimidazolidin-4-yl)methyl 4-methoxybenzoate (2y): The title compound was synthesized according to general procedure **G** using 1-allyl-3-((4-methoxybenzoyl)oxy)-1-methylurea (0.132 g, 0.50 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.057 g, 0.55 mmol) in CH_2Cl_2 (5.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL). The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2 → 30% EtOAc/CH_2Cl_2) to yield a white solid (0.089 g, 66%).

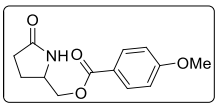
TLC R_f: 0.51 in 2% MeOH/CH_2Cl_2

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.94 (m, 2H), 6.97-6.91 (m, 2H), 4.68-4.58 (br s, 1H), 4.41-4.35 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.26-4.20 (dd, *J* = 11.2, 7.1 Hz, 1H), 4.09-4.00 (m, 1H), 3.88 (s, 3H), 3.62 (t, *J* = 9.0 Hz, 3H), 3.26 (dd, *J* = 9.0, 5.5 Hz, 1H), 2.79 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (C), 163.7 (C), 161.5 (C), 131.7 (CH), 121.8 (C), 113.8 (CH), 66.2 (CH_2), 55.5 (CH), 49.8 (CH_2), 48.4 (CH), 30.5 (CH_3).

IR (FTIR): 3200, 2942, 2866, 1699, 1600, 1444, 1252 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{11}H_{14}N_2O_2Na$ $[M+Na]^+$: 287.1008. Found: 287.1003.



(5-Oxopyrrolidin-2-yl)methyl 4-methoxybenzoate (2z): The title compound was synthesized according to general procedure **G** using *N*-((4-methoxybenzoyl)oxy)pent-4-enamide (0.249 g, 1.00 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.017 g, 2 mol%), tetrabutylammonium dibutyl phosphate (0.022 g, 5 mol%) in CH_2Cl_2 (5.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL). The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2 → 100% EtOAc) to yield a white solid (0.169 g, 68%).

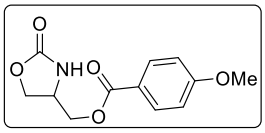
TLC R_f: 0.12 in 50% EtOAc/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.12 (br s, 1H), 4.40 (dd, *J* = 11.2, 3.7 Hz, 1H), 4.11 (dd, *J* = 11.2, 7.2 Hz, 1H), 4.04-3.98 (m, 1H), 3.84 (s, 3H), 2.45-2.26 (m, 3H), 1.95-1.86 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 177.9 (C), 166.0 (C), 163.7 (C), 131.7 (CH), 121.8 (C), 113.8 (CH), 67.2 (CH_2), 55.5 (CH_3), 53.0 (CH), 29.5 (CH_2), 23.4 (CH_2).

IR (FTIR): 3168, 3079, 2965, 2841, 1680, 1605, 1511, 1461, 1383, 1252 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{13}H_{15}NO_4Na$ $[M+Na]^+$: 272.0899. Found: 272.0904.



(2-Oxooxazolidin-4-yl)methyl 4-methoxybenzoate (2aa): The title compound was synthesized according to general procedure **G** using allyl (4-methoxybenzoyl)oxycarbamate (0.126 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.057 g, 0.55 mmol) in CH_2Cl_2 (5.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL). The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2 → 100% EtOAc) to yield a white solid (0.065 g, 52%).

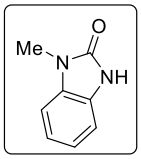
TLC R_f: 0.32 in 50% EtOAc/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.79 (br s, 1H), 4.59-4.55 (m, 1H), 4.44-4.41 (m, 1H), 4.31-4.22 (m, 3H), 3.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1 (C), 164.0 (C), 159.4 (C), 132.0 (CH), 121.5 (C), 114.0 (CH), 67.2 (CH_2), 65.3 (CH_2), 55.6 (CH_3), 51.5 (CH).

IR (FTIR): 3277, 2941, 2840, 1750, 1706, 1603, 1580, 1511, 1417, 1281, 1251 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{12}H_{13}NO_5$ $[M]^+$: 251.0794. Found: 251.0799.

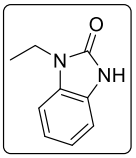


1-Methyl-1H-benzo[d]imidazol-2(3H)-one (2ab): The title compound was synthesized following general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1-methyl-1-phenylurea (0.240 g, 0.800 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.014 g, 2 mol%), triethylamine (0.089 g, 0.88 mmol) in MeCN (4.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (10% EtOAc/Hexanes → 50% EtOAc/Hexanes) to yield a white solid (0.085 g, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.11-7.05 (m, 3H), 6.98-6.95 (m, 1H), 3.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0 (C), 131.1 (C), 128.0 (C), 121.8 (CH), 121.5 (CH), 109.7 (CH), 107.8 (CH), 27.0 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[21]

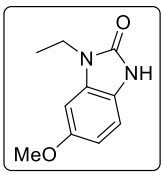


1-Ethyl-1,3-dihydro-benzoimidazol-2-one (2ac): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1-ethyl-1-phenylurea (0.157 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (50% EtOAc/CH_2Cl_2) to yield an amorphous white solid (0.039 g, 48%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.49-10.20 (br s, 1H), 7.19-6.96 (m, 4H), 3.98 (q, *J*= 7.2 Hz, 2H), 1.38 (t, *J*= 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5 (C), 130.0 (C), 128.1 (C), 121.4 (CH), 121.2 (CH), 109.7 (CH), 107.7 (CH), 35.6 (CH_2), 13.6 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[22]



1-Ethyl-5-methoxy-1H-benzo[d]imidazol-2(3H)-one (2af): The title compound was synthesized according to general procedure **G** using 1-ethyl-3-((4-methoxybenzoyl)oxy)-1-(3-methoxyphenyl)urea (0.276 g, 0.800 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.014 g, 2 mol%), triethylamine (0.089 g, 0.88 mmol) in MeCN (4.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (40% EtOAc/CH_2Cl_2) to yield a white solid (0.143 g, 93%).

TLC R_f: 0.33 in 50% EtOAc/CH_2Cl_2.

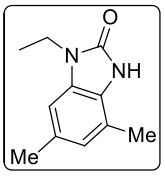
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.57 (d, *J* = 0.3 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.61 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9 (C), 155.5 (C), 131.1 (C), 122.2 (C), 109.9 (CH), 106.7 (CH), 95.3 (CH), 56.1 (CH_3), 35.8 (CH_2), 13.7 (CH_3).

IR (FTIR): 2978, 2934, 1681, 1629, 1609, 1493, 1447, 1396, 1223, 1081 cm^{-1}.

[21] Ando,K.; Kobayashi, T.; Uchida, N. *Org. Lett.* **2015**, *17*, 2554–2557.
[22] Peng, L.; Zhiming, W.; Xianming, H. *Eur. J. Org. Chem.* **2012**, *10*, 1994 – 2000.

HRMS (EI) m/z: Exact mass calcd for $C_{10}H_{12}N_2O_2$ $[M]^+$: 192.0899. Found: 192.0876.



1-Ethyl-4,6-dimethyl-1H-benzo[d]imidazol-2(3H)-one (2ag): The title compound was synthesized according to general procedure **G** using 1-(3,5-dimethylphenyl)-1-ethyl-3-((4-methoxybenzoyl)oxy)urea (0.273 g, 0.80 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.014 g, 2 mol%), triethylamine (0.089 g, 0.88 mmol) in MeCN (4.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the product precipitated out of solution and was collected over a fritted funnel (0.128 g, 84%).

TLC R_f: 0.42 in 50% EtOAc/CH_2Cl_2.

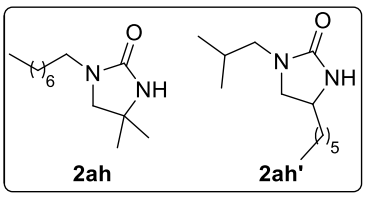
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (br s, 1H), 6.68 (s, 1H), 6.65 (s, 1H), 3.90 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7 (C), 130.8 (C), 129.8 (C), 125.0 (C), 123.3 (CH), 119.1 (C), 105.9 (CH), 35.6 (CH_2), 21.5 (CH_3), 16.2 (CH_3), 13.7 (CH_3).

IR (FTIR): 2978, 1687, 1459, 1396, 1280 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{11}H_{14}N_2O$ $[M]^+$: 190.1106. Found: 190.1120.

Site competition experiments



1-Octyl-4,4-dimethylimidazolidin-2-one (2ah) and 4-hexyl-1-isobutylimidazolidin-2-one (2ah'): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1-isobutyl-1-octylurea (0.189 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.057 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (30% EtOAc/Hexanes) to yield a colourless oil (0.077 g, 68%).

TLC R_f: 0.48 in 50% EtOAc/CH_2Cl_2.

1-Octyl-4,4-dimethylimidazolidin-2-one (2ah):

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.36-6.33 (br s, 1H), 3.03-2.97 (m, 4H), 1.42-1.35 (m, 3H, 2aj and 2aj'), 1.30-1.18 (m, 13H, 2aj and 2aj'), 1.15 (s, 6H), 0.85 (app t, *J*= 6.9 Hz, 4H, 2aj and 2aj'), 0.81 (app dd, *J*= 6.6, 2.4 Hz, 2H, 2aj and 2aj').

^{13}C NMR (100 MHz, DMSO-d_6): δ 160.3 (C), 57.1 (CH_2), 51.1 (C), 42.2 (CH_2), 31.2 (CH_2), 28.6 (CH_2), 28.6 (CH), 28.0 (CH), 27.0 (CH_2), 26.1 (CH_2), 22.1 (CH_2), 13.9 (CH_3).

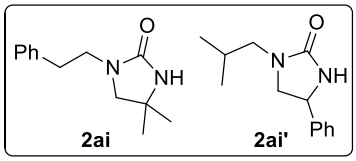
4-Hexyl-1-isobutylimidazolidin-2-one (2ah'):

^{1}H NMR (400 MHz, DMSO-d_6): δ 6.46-6.44 (br s, 1H), 3.52-3.46 (m, 1H), 3.43-3.38 (m, 2H), 2.89-2.85 (m, 1H), 2.83-2.74 (m, 2H), 1.81-1.71 (m, 1H), 1.42-1.35 (m, 3H, , 2aj and 2aj'), 1.30-1.18 (m, 13H, , 2aj and 2aj'), 0.85 (app t, *J*= 6.9 Hz, 4H, , 2aj and 2aj'), 0.81 (app dd, *J*= 6.6, 2.4 Hz, 2H, , 2aj and 2aj').

^{13}C NMR (100 MHz, DMSO-d_6): δ 161.4, 50.6, 50.3, 49.1, 35.7, 26.4, 24.7, 22.0, 20.0, 19.9, 13.9 (one carbon is missing due to overlap).

IR (FTIR): 3202, 2917, 2852, 1686, 1457, 1303, 1240 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{13}H_{26}N_2O$ $[M]^+$: 226.2045. Found: 226.2020.



4,4-Dimethyl-1-phenethylimidazolidin-2-one (2ai) and 1-Isobutyl-4-phenylimidazolidin-2-one (2ai'): The title compound was synthesized according to general procedure **G** using 1-isobutyl-3-((4-methoxybenzoyl)oxy)-1-phenethylurea (0.185 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.056 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was purified by column chromatography (gradient 20% EtOAc/Hexanes → 40% EtOAc/Hexanes) to yield a white solid (0.037 g, 37%).

4,4-Dimethyl-1-phenethylimidazolidin-2-one (2ai): as an amorphous white solid (0.037 g, 37%).

TLC R_f: 0.13 in 30% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.19 (m, 5H), 4.31 (s, 1H), 3.44 (dd, *J* = 7.9, 6.8 Hz, 2H), 3.02 (s, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 1.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9 (C), 139.3 (C), 128.9 (CH), 128.6 (CH), 126.5 (CH), 58.6 (CH_2), 52.1 (C), 44.8 (CH_2), 34.6 (CH_2), 28.5 (CH_3).

IR (FTIR): 3202, 3069, 2967, 2956, 2857, 1683, 1489, 1452, 1365, 1302 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{13}H_{18}N_2O$ $[M]^+$: 218.1419. Found: 218.1396.

1-Isobutyl-4-phenylimidazolidin-2-one (2ai'): as amorphous white solid (0.059 g, 50%).

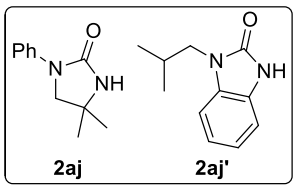
TLC R_f: 0.28 in 30% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.29 (m, 5H), 4.77-4.73 (m, 2H), 3.79 (t, *J* = 9.0 Hz, 1H), 3.22 (dd, *J* = 8.8, 7.3 Hz, 1H), 3.09-2.95 (m, 2H), 1.82 (dquintet, *J* = 13.7, 6.9 Hz, 1H), 0.91 (dd, *J* = 6.7, 4.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (C), 141.9 (C), 129.1 (CH), 128.3 (CH), 126.2 (CH), 54.4 (CH_2), 54.0 (CH), 51.2 (CH_2), 27.1 (CH), 20.16 (CH_3).

IR (FTIR): 3200, 3082, 2953, 1682, 1491, 1449, 1255 cm^{-1}.

HRMS (EI) m/z: Exact mass calcd for $C_{13}H_{18}N_2O$ $[M]^+$: 218.1419. Found: 218.1404.



4,4-Dimethyl-1-phenylimidazolidin-2-one (2aj) and 1-isobutyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2aj'): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1-isobutyl-1-phenylurea (0.171 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%), triethylamine (0.057 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compounds were purified by column chromatography (10% EtOAc/CH_2Cl_2 → 20% EtOAc/CH_2Cl_2).

4,4-Dimethyl-1-phenyl-2-imidazolidinone (2aj): as a white solid (0.039 g, 41%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.51 (m, 2H), 7.39-7.30 (m, 2H), 7.10-7.02 (m, 1H), 4.61-5.43 (br s, 1H), 3.66 (s, 2H), 1.41 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2 (C), 140.2 (C), 128.8 (CH), 122.5 (CH), 117.7 (CH), 58.2 (CH_2), 51.3 (C), 28.6 (CH_3).

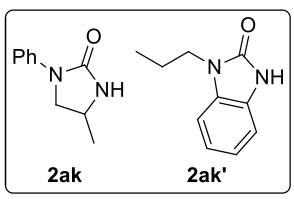
The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[23]

1-Isobutyl-1,3-dihydro-benzoimidazol-2-one (2aj'): as a pink solid (0.033 g, 35%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.92-8.83 (br s, 1H), 7.13-7.05 (m, 3H), 7.02-6.97 (m, 1H), 3.70 (d, *J* = 7.5 Hz, 2H), 2.33-2.17 (m, 1H), 1.00 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8 (C), 130.8 (C), 127.9 (C), 121.3 (CH), 121.1 (CH), 109.5 (CH), 108.1 (CH), 48.3 (CH_2), 27.9 (CH), 20.1 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports. [24]



4-Methyl-1-phenylimidazolidin-2-one (2ak) and 1-propyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2ak'): The title compound was synthesized according to general procedure **G** using 3-((4-methoxybenzoyl)oxy)-1-phenyl-1-propylurea (0.164 g, 0.500 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.009 g, 2 mol%),

[23] Kim, T. H.; Lee, G.-J. *J. Org. Chem.* **1999**, *64*, 2941-2943.
[24] Vernin, G.; Domlog, H.; Siv, C.; Metzger, J., El-Shafei, A. K. *J. Heterocycl. Chem.* **1981**, *18*, 85-89.

triethylamine (0.057 g, 0.55 mmol) in MeCN (2.5 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compounds were purified by column chromatography (10% EtOAc/CH_2Cl_2 → 20% EtOAc/CH_2Cl_2).

4-Methyl-1-phenylimidazolidin-2-one (2ak): as a yellow solid (0.009 g, 10%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.51 (m, 2H), 7.39-7.31 (m, 2H), 7.10-7.02 (m, 1H), 4.87-4.79 (br s, 1H), 4.08-3.90 (m, 2H), 3.50 (dd, *J* = 8.3, 7.7 Hz, 1H), 1.36 (d, *J* = 5.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8 (C), 140.1 (C), 128.8 (CH), 122.7 (CH), 117.8 (CH), 52.5 (CH_2), 44.8 (CH), 21.7 (CH_3).

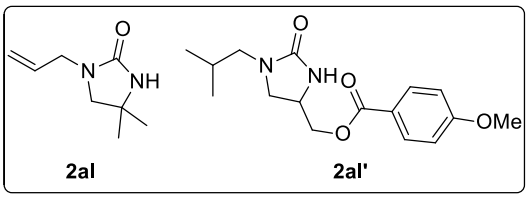
The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports. [25]

1-Propyl-1,3-dihydro-2H-benzo[d]imidazol-2-one (2ak'): as a yellow solid (0.056 g, 63%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.69-10.36 (br s, 1H), 7.20-6.97 (m, 4H), 3.93-3.84 (m, 2H), 1.83 (apt sxt, *J* = 7.4 Hz, 2H), 1.01 (t, *J* = 7.4 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8 (C), 130.4 (C), 128.0 (C), 121.3 (CH), 121.1 (CH), 109.7 (CH), 107.9 (CH), 42.4 (CH_2), 21.7 (CH_2), 11.3 (CH).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[26]



1-Allyl-4,4-dimethylimidazolidin-2-one (2al) and (1-isobutyl-2-oxoimidazolidin-4-yl)methyl 4-methoxybenzoate (2al'): The title compound was synthesized according to general procedure **G** using 1-allyl-1-isobutyl-3-((4-methoxybenzoyl)oxy)urea (0.306 g, 1.00 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.017 g, 2 mol%), triethylamine (0.111 g, 0.55 mmol) in MeCN (5.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compounds were isolated as a mixture by column chromatography (20% EtOAc/CH_2Cl_2 → 40% EtOAc/CH_2Cl_2), white solid (59%, 1 : 2 (**2al** : **2al'**)).

[25] Kim, T. H.; Lee, G.-J. *J. Org. Chem.* **1999**, *64*, 2941-2943.

[26] Tapia, I.; Alonso-Cires, L.; López-Tudanca, P. L.; Mosquera, R.; Labeaga, L.; Innerárity, A.; Orjales, A. *J. Med. Chem.* **1999**, *42*, 2870-2880.

TLC R_f: 0.30 in 50% EtOAc/CH_2Cl_2.

1-Allyl-4,4-dimethylimidazolidin-2-one (2al):

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 (ddt, *J* = 17.1, 10.2, 6.0 Hz, 1H), 5.19-5.12 (m, 2H), 4.50 (br s, 1H), 3.76 (dt, *J* = 6.0, 1.4 Hz, 2H), 3.09 (s, 2H), 1.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7 (C), 133.5 (CH), 117.4 (CH_2), 57.7 (CH_2), 52.0 (C), 46.1 (CH_2), 28.5 (CH_3).

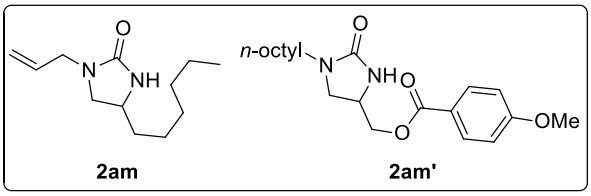
The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.[27]

1-Isobutyl-2-oxoimidazolidin-4-yl)methyl 4-methoxybenzoate (2al'):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 5.07 (br s, 1H), 4.33 (dd, *J* = 11.1, 4.9 Hz, 1H), 4.19 (dd, *J* = 11.1, 7.0 Hz, 1H), 4.05-3.98 (m, 1H), 3.84 (s, 3H), 3.57 (t, *J* = 9.1 Hz, 1H), 3.22 (dd, *J* = 9.2, 5.3 Hz, 1H), 2.97 (qd, *J* = 12.5, 7.5 Hz, 2H), 1.84 (tt, *J* = 13.8, 6.9 Hz, 1H), 0.88 (dd, *J* = 6.7, 3.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0 (C), 163.7 (C), 161.7 (C), 131.8 (CH), 121.9 (C), 113.8 (CH), 66.4 (CH_2), 55.5 (CH_3), 51.0 (CH_2), 48.6 (CH), 48.0 (CH_2), 26.9 (CH), 20.0 (CH_3).

IR (FTIR): 3210, 2950, 1681, 1604, 1450, 1254, 1113 cm^{-1}.



1-Allyl-4-hexylimidazolidin-2-one (2am) and (1-octyl-2-oxoimidazolidin-4-yl)methyl 4-methoxybenzoate (2am'): The title compounds were synthesized according to general procedure **G** using 1-allyl-3-((4-methoxybenzoyl)oxy)-1-octylurea (0.362 g, 1.00 mmol), tris(2,2′-bipyridine)ruthenium(II) hexafluorophosphate (0.017 g, 2 mol%), triethylamine (0.111 g, 0.55 mmol) in MeCN (5.0 mL, 0.2 M) in a 8 mL Kimax glass vial with a Teflon screw cap and a stir bar. The vial was placed in an ice bath and purged with Argon for 10 min. The vial was positioned between 2 and 4 cm form the light source (blue LED strips) and allowed to stir overnight at ambient temperature. Upon completion, the reaction was concentrated under reduced pressure, diluted in CH_2Cl_2 (5.0 mL) and extracted three times with sodium bicarbonate (3 x 2 mL) to remove the benzoic acid. The organic phase was collected, dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The title compounds co-eluted upon flash column chromatography (20% EtOAc/CH_2Cl_2 → 40% EtOAc/CH_2Cl_2), (0.175 g, 48% yield) white solid (10 : 1 (**2am** : **2am'**)).

TLC R_f = 0.41 in 100% EtOAc.

1-Allyl-4-hexylimidazolidin-2-one (2am):

^{1}H NMR (400 MHz, $CDCl_3$): (300 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 17.1, 10.1, 6.0 Hz, 1H), 5.20-5.13 (m, 2H), 4.45 (br s, 1H), 3.82-3.69 (m, 2H), 3.63-3.61 (m, 1H), 3.01-2.94 (m, 1H), 1.53-1.44 (m, 10H), 0.90-0.88 (m, 3H).

[27] Kim, T. H.; Lee, G.-J. *J. Org. Chem.* **1999**, *64*, 2941-2943.

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3 (C), 133.4 (CH), 117.5 (CH_2), 50.5 (CH_2), 50.1 (CH), 46.2 (CH_2), 36.0 (CH_2), 31.6 (CH_2), 29.1 (CH_2), 25.5 (CH_2), 22.5 (CH_2), 14.1 (CH_3).

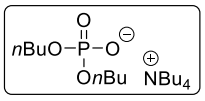
(1-Octyl-2-oxoimidazolidin-4-yl)methyl 4-methoxybenzoate (2am'):

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 4.67 (br s, 1H), 4.33 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.20 (dd, *J* = 11.1, 6.9 Hz, 1H), 4.03-3.99 (m, 1H), 3.85 (s, 3H), 3.58 (t, *J* = 9.0 Hz, 1H), 3.45 (s,), 3.24-3.12 (m, 3H), 1.29-1.23 (m, 12H), 0.87-0.84 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0 (C), 163.7 (C), 161.4 (C), 131.8 (CH), 121.8 (C), 113.8 (CH), 66.3 (CH_2), 55.5 (CH_3), 48.6 (CH), 47.4 (CH_2), 43.4 (CH_2), 31.8 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 27.6 (CH_2), 26.8 (CH_2), 22.6 (CH_2), 14.1 (CH_3).

IR (FTIR): 3205, 2920, 2855, 1681, 1605, 1455, 1255, 1118 cm^{-1}.

Synthesis of tetrabutylammonium dibutyl phosphate base



Tetrabutylammonium dibutyl phosphate (7a): The title compound was synthesized according to a literature procedure.[28]

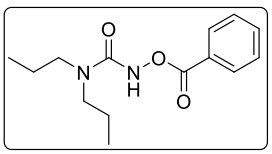
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81 (q, *J*= 6.6 Hz, 4H), 3.44-3.31 (m, 8H), 1.75-1.52 (m, 12H), 1.51-1.29 (m, 12H), 0.99 (t, *J*= 7.3 12H), 0.89 (t, *J*= 7.3 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 64.7 (CH_2), 59.0 (CH_2), 33.3 (CH_2), 24.3 (CH_2), 19.0 (CH_2), 19.3 (CH_2), 14.0 (CH_3), 13.8 (CH_3).

^{31}P NMR (121 MHz, CDCl3): δ -2.26 (s).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.

Synthesis of benzoyl N-oxyureas for initial reaction screening

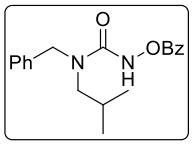


3-(Benzoyloxy)-1,1-dipropylurea (5a): The title compound was synthesized according to a literature procedure.[13]

[28] Zhu, Q.; Graff, D. E.; Knowles, R. R. *J. Am. Chem. Soc.* **2018**, *140*, 741.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (br s, 1H), 8.12-8.08 (m, 2H), 7.62-7.56 (m, 1H), 7.44 (tt, *J* = 7.5, 1.3 Hz, 2H), 3.24 (t, *J* = 7.6 Hz, 4H), 1.64 (ap sext, *J* = 7.5 Hz, 4H), 0.92 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2 (C), 157.6 (C), 134.0 (C), 129.9 (CH), 128.6 (CH), 127.3 (C), 49.0 (CH_2), 21.4 (CH_2), 11.3 (CH_3).



3-(Benzoyloxy)-1-benzyl-1-isobutylurea (5b): The title compound was synthesized according to general procedure **C** using phenyl benzoyloxycarbamate (0.630 g, 2.45 mmol), and *N*-benzyl-2-methylpropan-1-amine (0.400 g, 2.45 mmol) and imidazole (0.017 g, 0.25 mol) in THF (10.0 mL, 0.30 M). The reaction was heated under microwave irradiation for 4 h at 100 °C. Upon completion, the reaction mixture was concentrated under reduced pressure. The crude mixture was dissolved in hexanes and then recrystallized in Et_2O/hexanes. The solid was then filtered and washed with hexanes to give pure product. The title compound was obtained as a crystalline white solid (0.763 g, 78%).

M.p.: 140.1-140.4 °C.

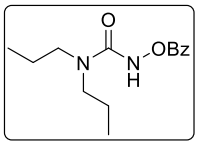
TLC R_f: 0.55 in 25% EtOAc/Hexanes.

^{1}H NMR (300 MHz; $CDCl_3$): δ 8.50-8.40 (1H, br. s.), 8.18-8.08 (2H, m), 7.67-7.57 (1H, m), 7.53-7.27 (7H, m), 4.61 (2H, s), 3.20 (2H, d, *J*=6 Hz), 2.09 (1H, sept, *J*=6 Hz), 0.99 (6H, d, *J*=6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0 (C), 158.3 (C), 136.4 (C), 134.0 (CH), 129.9 (CH), 128.9 (CH), 128.6 (CH), 127.8 (CH), 127.1 (CH), 127.0 (C), 54.6 (CH2), 50.6 (CH2), 27.3 (CH), 20.2 (CH_3).

IR (FTIR): 3106, 2955, 1756, 1645, 1495, 1232 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{19}H_{22}N_2O_3Na$ $[M+Na]^+$: 349.1528. Found: 349.1515.

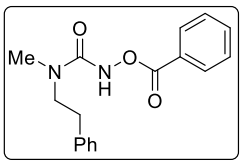


3-(Benzoyloxy)-1,1-dipropylurea (5c): The title compound was synthesized according to a literature procedure.[13]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (br s, 1H), 8.12-8.08 (m, 2H), 7.62-7.56 (m, 1H), 7.44 (tt, *J* = 7.5, 1.3 Hz, 2H), 3.24 (t, *J* = 7.6 Hz, 4H), 1.64 (ap sext, *J* = 7.5 Hz, 4H), 0.92 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2 (C), 157.6 (C), 134.0 (C), 129.9 (CH), 128.6 (CH), 127.3 (C), 49.0 (CH_2), 21.4 (CH_2), 11.3 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.



3-(Benzoyloxy)-1-methyl-1-phenethylurea (5d): The title compound was synthesized according to general procedure **C** using phenyl benzoyloxycarbamate (0.772 g, 3.00 mmol), and *N*-methyl-2-phenylethanamine (0.406 mg, 3.00 mmol) and imidazole (0.020 g, 0.30 mmol) in THF (16.7 mL, 0.30 M). The reaction was heated under microwave irradiation for 2 h at 100 °C Solvent was removed under reduced pressure and the crude product isolated using flash chromatography (20% EtOAc/Hexanes) to yield the title compound as a colourless oil (0.841 g, 95%).

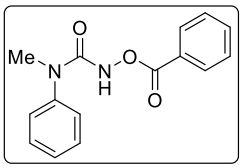
TLC R_f: 0.35 in 33% EtOAc/Hexanes.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.11-8.08 (m, 2H), 7.63-7.57 (m, 1H), 7.48-7.43 (m, 2H), 7.33-7.28 (m, 2H), 7.23-7.19 (m, 3H), 3.56 (t, *J* = 7.4 Hz, 2H), 2.92-2.88 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9 (C), 157.7 (C), 138.7 (C), 134.1 (C), 130.1 (CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 127.3 (C), 126.8 (CH), 51.5 (CH2), 34.9 (CH_3), 34.3 (CH_2).

IR (FTIR): 3257, 3071, 3027, 2948, 1750, 1672, 1485, 1253, 1079 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{17}H_{18}N_2O_3Na$ $[M+Na]^+$: 321.1210. Found: 321.1215.

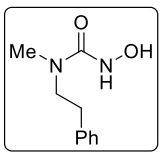


3-(Benzoyloxy)-1-methyl-1-phenylurea (5e): The title compound was synthesized according to a literature procedure.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (br s, 1H), 8.07-8.04 (m, 2H), 7.62-7.57 (m, 1H), 7.51-7.35 (m, 7H), 3.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8 (C), 157.1 (C), 141.4 (C), 134.0 (C), 130.4 (CH), 130.0 (CH), 128.7 (CH), 128.6 (CH), 127.2 (CH), 127.1 (CH), 38.0 (CH_3).

The ^{1}H NMR and ^{13}C NMR is in agreement with previous reports.



1-Methyl-1-phenethyl-3-hydroxyurea (6e): The title compound was synthesized according to general procedure **C** using phenyl *N*-hydroxycarbamate (0.337 g, 2.20 mmol), and *N*-methyl-*N*-phenethylamine (0.270 g, 2.20 mmol) and Et_3N (0.6 mL, 0.4 mmol) in THF (6.0 mL, 0.30 M). The vial was sealed with a microwave cap and heated for 16 h at 70 °C via an oil bath heating. The reaction mixture was concentrated under reduced pressure and isolated using flash chromatography (1% MeOH/CH_2Cl_2 → 5% MeOH/CH_2Cl_2). The title compound was obtained as an amorphous white solid (0.321 g, 83%).

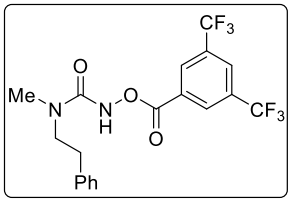
TLC R_f: 0.15 in 2% MeOH/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.30 (m, 2H), 7.29-7.23 (m, 1H), 7.22-7.18 (m, 2H), 6.43-6.38 (br s, 1H), 6.30-6.23 (br s, 1H), 3.52 (t, *J* = 7.1 Hz, 2H), 2.90-2.83 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (C), 138.5 (C), 128.9 (CH), 128.8 (CH), 126.9 (CH), 50.6 (CH_2), 34.1 (CH_2), 33.9 (CH_3).

IR (FTIR): 3326, 3023, 2924, 1645, 1491, 1390, 1296 cm^{-1}.

HRMS (ESI) m/z: Exact mass calcd for $C_{10}H_{14}N_2O_2Na$ $[M+Na]^+$: 217.0948. Found: 217.0926.



3-((3,5-Bistrifuoromethylbenzoyl)oxy)-1-methyl-1-phenethylurea (5f): The title compound was synthesized according to the general procedure **B** using the pure 1-methyl-1-phenethyl-3-hydroxyurea (0.321 g, 1.66 mmol) was added CH_2Cl_2 (0.30 M) and cooled to 0 °C. To this was added Et_3N (0.23 mL, 1.66 mmol) followed immediately by dropwise addition of 3,5-bis(trifluoromethyl)benzoyl chloride (0.30 mL, 1.66 mmol). The reaction was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was extracted with $NaHCO_3$ (5.0 mL x1), and then brine (5.0 mL x1). The organic phase was collected and dried with Na_2SO_4. The solids were filtered over a cotton plug, and the filtrate was evaporated under reduced pressure to provide the crude which was purified by flash column chromatography (20% EtOAc/Hexanes). The title compound was obtained as an amorphous white solid (0.370 g, 46%).

TLC R_f: 0.97 in 2% MeOH/CH_2Cl_2.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56-8.53 (br s, 2H), 8.14-8.11 (br s, 1H), 8.10-8.06 (br s, 1H), 7.38-7.32 (m, 2H), 7.30-7.23 (m, 3H), 3.60 (t, *J* = 7.2 Hz, 2H), 2.96-2.89 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 164.3 (C), 157.0 (C), 138.4 (C), 132.5 (C, q, *J*= 26 Hz), 130.0 (CH), 129.5 (C), 128.9 (CH), 128.8 (CH), 127.3 (CH, m), 126.8 (CH), 122.7 (C, d, *J*= 203 Hz), 51.3 (CH_2), 34.7 (CH), 34.1 (CH_2).

IR (FTIR): 3208, 1774, 1670, 1497, 1279, 1121 cm^{-1}.

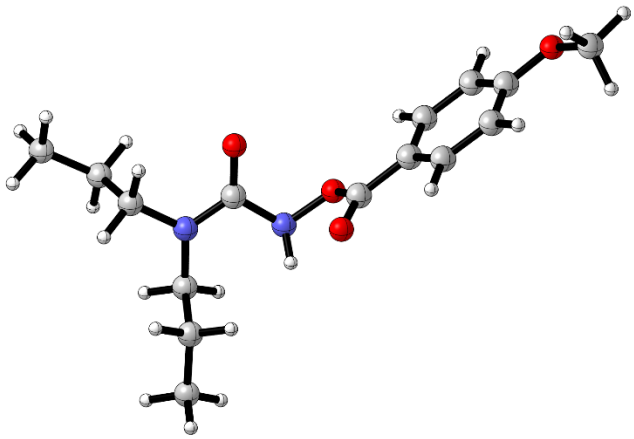
HRMS (ESI) m/z: Exact mass calcd for $C_9H_{16}F_6N_2O_3Na$ $[M+Na]^+$: 457.0963. Found: 457.0954.

Computational Details/DFT Calculations

Density functional theory (DFT) calculations have been performed using WebMO (G09). Optimized molecular geometries were calculated using the B3LYP[29] exchange-correlation functional. The 6-311+G(2d,p) basis set was used for calculations. Vibrational frequency calculations were performed to ensure that the stationary points and to calculate vibrational zero point energy. The unscaled frequencies were used for calculating enthalpies and BDEs (at 298 K and 1 atm).

Ultimately DFT data are inconsistent with an EnT process affording triplet nitrenes from the neutral precursor. Combined with ^{1}H-NMR studies, which indicated that deprotonation of the substrate does not occur with Et_3N, we conclude that EnT to the anionic precursor is also unlikely in this system. Moreover, even if the precursor could be deprotonated, the triplet transfer from $Ru(bpy)_3$ to the anionic substrate is still expected to be slow, given the endothermicity of the process. On the other hand, DFT lends some support to the PCET oxidation pathway, given the downhill formation of the capto-dative N-centered radical.

([29]) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.



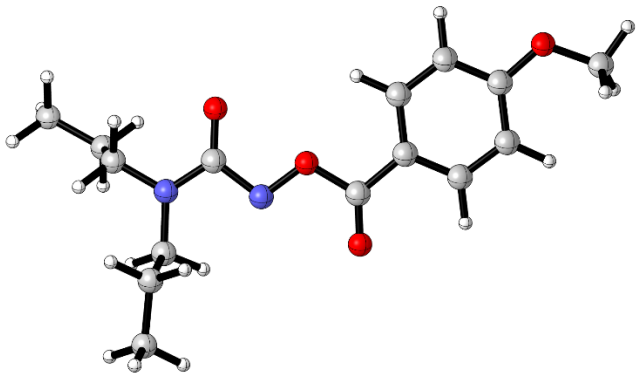
Vibrational frequency of 1p

Quantity	Value
Job History	20370,20385,37254,37256,40582
Route	#N B3LYP/6-311+G(2d,p) FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=Conne
Stoichiometry	$C_{15}H_{22}N_2O_4$
Symmetry	C1
Basis	6-311+G(2d,p)
RB3LYP Energy	-995.546488834 Hartree
ZPE	0.359200 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-995.164753 Hartree
Enthalpy	-995.163809 Hartree
Free Energy	-995.242439 Hartree
C_v	81.842 cal/mol-K
Entropy	165.491 cal/mol-K
Dipole Moment	3.1563 Debye
Server	10.72.192.49 (10221)
CPU time	96457.7 sec

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.432224
3	6	0	1.183856	0.000000	2.085138
4	6	0	2.433916	0.001153	1.456067
5	6	0	3.585120	0.001332	2.228635
6	6	0	3.519575	-0.000618	3.623707
7	6	0	2.260242	-0.001332	4.244469
8	6	0	1.108261	-0.000827	3.485685
9	1	0	0.132897	0.000084	3.955443
10	1	0	2.187256	0.000507	5.323079
11	6	0	4.781127	0.006717	4.380493
12	8	0	5.896918	0.050575	3.913319
13	8	0	4.566769	-0.082665	5.736446
14	7	0	5.738994	-0.024985	6.519091
15	6	0	6.109635	1.327536	6.813344
16	8	0	5.374201	2.265570	6.533386
17	7	0	7.286710	1.440592	7.471586
18	6	0	8.107298	0.297135	7.888463
19	1	0	8.564971	0.561239	8.844482
20	1	0	7.455273	-0.554478	8.087730
21	6	0	9.202361	-0.085642	6.886945
22	6	0	10.056578	-1.247440	7.395331
23	1	0	10.830572	-1.508891	6.671335
24	1	0	10.552125	-0.991239	8.335581
25	1	0	9.448750	-2.139028	7.570814
26	1	0	8.749588	-0.351457	5.926531
27	1	0	9.834914	0.786040	6.696256

28	6	0	7.754372	2.783462	7.833989
29	1	0	8.845564	2.775186	7.779251
30	1	0	7.393986	3.482671	7.080371
31	6	0	7.300322	3.232989	9.224962
32	6	0	7.838154	4.619893	9.579063
33	1	0	7.503627	4.927736	10.571774
34	1	0	8.931601	4.633687	9.577120
35	1	0	7.494507	5.372096	8.863826
36	1	0	6.207430	3.235682	9.255078
37	1	0	7.635539	2.505619	9.970688
38	1	0	6.465460	-0.532652	6.019176
39	1	0	4.554037	0.002910	1.746703
40	1	0	2.517199	0.002177	0.379126
41	1	0	-1.046656	-0.000115	-0.292206
42	1	0	0.489787	0.894243	-0.390436
43	1	0	0.489964	-0.894242	-0.390303



Vibrational frequency of 1p radical

Quantity	Value
Job History	20370,20385,37254,37256,37262,37918,37924,40580
Route	#N B3LYP/6-311+G(2d,p) FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=Conne
Stoichiometry	$C_{15}H_{21}N_2O_4$(2)
Symmetry	C1
Basis	6-311+G(2d,p)
UB3LYP Energy	-994.897469537 Hartree
ZPE	0.345825 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-994.529155 Hartree
Enthalpy	-994.528211 Hartree
Free Energy	-994.607363 Hartree
C_v	81.219 cal/mol-K
Entropy	166.590 cal/mol-K
Dipole Moment	2.1669 Debye
Server	10.72.192.49 (8931)
CPU time	196664.1 sec

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.433319
3	6	0	1.180029	0.000000	2.087334
4	6	0	2.432270	-0.000042	1.459080
5	6	0	3.581012	0.000109	2.231527
6	6	0	3.513957	0.000449	3.628938
7	6	0	2.251920	0.000141	4.248712
8	6	0	1.102275	0.000029	3.488243
9	1	0	0.126073	-0.000077	3.955997
10	1	0	2.177308	-0.000396	5.326875
11	6	0	4.773627	0.000731	4.376796
12	8	0	5.887718	0.000080	3.930605
13	8	0	4.518235	0.001432	5.766537
14	7	0	5.636782	0.004070	6.523536
15	6	0	5.225394	-0.011077	7.889625
16	8	0	4.057880	-0.067216	8.268736
17	7	0	6.299620	0.044579	8.719248
18	6	0	7.699296	0.112199	8.270771
19	1	0	8.294802	-0.410877	9.022457
20	1	0	7.803498	-0.436386	7.338025
21	6	0	8.210684	1.545103	8.101867
22	6	0	9.693195	1.579160	7.729952
23	1	0	10.039733	2.607003	7.606027
24	1	0	10.307106	1.111617	8.504498
25	1	0	9.879097	1.049666	6.791727
26	1	0	7.616680	2.038248	7.327299

27	1	0	8.047615	2.102393	9.029053
28	6	0	6.051758	0.065835	10.162910
29	1	0	6.848302	0.653788	10.623421
30	1	0	5.108061	0.581604	10.338005
31	6	0	6.005606	-1.335205	10.782879
32	6	0	5.766103	-1.280142	12.291890
33	1	0	5.739741	-2.284855	12.718416
34	1	0	6.558452	-0.723387	12.799526
35	1	0	4.814797	-0.794375	12.524707
36	1	0	5.212278	-1.909157	10.297508
37	1	0	6.946560	-1.853296	10.574884
38	1	0	4.550552	0.000008	1.750804
39	1	0	2.516054	-0.000131	0.382245
40	1	0	-1.046705	0.000533	-0.291425
41	1	0	0.490416	0.894223	-0.389182
42	1	0	0.489496	-0.894740	-0.389198

Vibrational frequency of H-atom

Quantity	Value
Job History	20371,20372
Route	#N B3LYP/6-311+G(2d,p) OPT FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=C
Stoichiometry	H(2)
Symmetry	OH
Basis	6-311+G(2d,p)
UB3LYP Energy	-0.502177020841 Hartree
ZPE	0.000000 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-0.500761 Hartree
Enthalpy	-0.499817 Hartree
Free Energy	-0.512831 Hartree
C_v	2.981 cal/mol-K
Entropy	27.392 cal/mol-K
Dipole Moment	0.0000 Debye
Server	10.72.192.49 (31757)
CPU time	1.4 sec

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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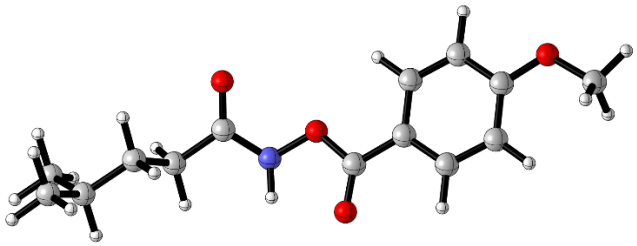

Vibrational frequency of 1h

Quantity	Value
Job History	20370,23453,23465,23475,43197,43199,43200
Route	#N B3LYP/6-311+G(2d,p) FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=Conne
Stoichiometry	$C_{14}H_{19}NO_4$
Symmetry	C1
Basis	6-311+G(2d,p)
RB3LYP Energy	-900.848191837 Hartree
ZPE	0.313090 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-900.515112 Hartree
Enthalpy	-900.514168 Hartree
Free Energy	-900.587179 Hartree
C_v	73.106 cal/mol-K
Entropy	153.663 cal/mol-K
Dipole Moment	5.0929 Debye
Server	General (68310)
CPU time	47443.4 sec

Input orientation:

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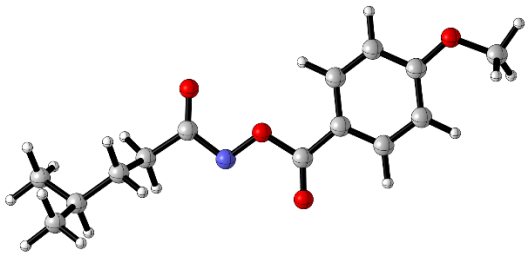
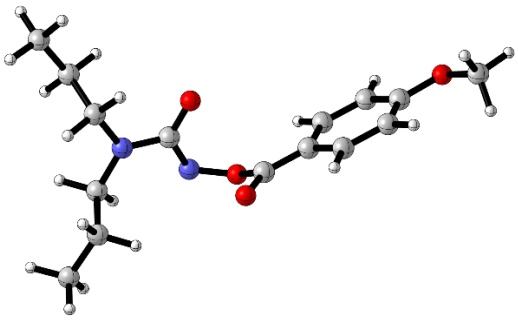
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.432488
3	6	0	1.183246	0.000000	2.084958
4	6	0	2.433339	-0.000998	1.455466
5	6	0	3.584850	0.000545	2.227149
6	6	0	3.518197	0.002396	3.622355
7	6	0	2.259107	0.001652	4.244269
8	6	0	1.107581	0.000830	3.485905
9	1	0	0.132244	0.001129	3.955581
10	1	0	2.186121	0.003003	5.323061
11	6	0	4.777573	0.012235	4.377362
12	8	0	5.898884	0.018895	3.913350
13	8	0	4.565548	0.009506	5.730537
14	7	0	5.761918	-0.016691	6.465634
15	6	0	5.737598	0.640001	7.670672
16	8	0	4.708463	1.038367	8.190357
17	6	0	7.104442	0.743914	8.317405
18	1	0	7.865008	0.266773	7.694283
19	1	0	7.048533	0.176776	9.249499
20	6	0	7.480931	2.207841	8.595924
21	6	0	8.866346	2.391900	9.238061
22	6	0	9.217220	3.882917	9.306828
23	1	0	10.216273	4.032273	9.723774
24	1	0	9.193432	4.343815	8.315987
25	1	0	8.506826	4.420260	9.943071
26	6	0	8.962656	1.750791	10.627580

27	1	0	9.952101	1.917582	11.060609
28	1	0	8.223786	2.186300	11.307994
29	1	0	8.796896	0.671832	10.598722
30	1	0	9.603455	1.904233	8.587801
31	1	0	7.456505	2.762005	7.651985
32	1	0	6.718836	2.654983	9.241476
33	1	0	6.567514	0.030681	5.846898
34	1	0	4.553641	0.000885	1.744967
35	1	0	2.516132	-0.002115	0.378450
36	1	0	-1.046614	-0.001082	-0.292134
37	1	0	0.489258	0.894823	-0.389817
38	1	0	0.490999	-0.893881	-0.389454



Vibrational frequency of 1h radical

Quantity	Value
Job History	20370,23453,23465,23475,43197,43199
Route	#N B3LYP/6-311+G(2d,p) FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=Conne
Stoichiometry	$C_{14}H_{18}NO_4$(2)
Symmetry	C1
Basis	6-311+G(2d,p)
UB3LYP Energy	-900.18925328 Hartree
ZPE	0.299774 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-899.869514 Hartree
Enthalpy	-899.868570 Hartree
Free Energy	-899.942308 Hartree
C_v	72.402 cal/mol-K
Entropy	155.196 cal/mol-K
Dipole Moment	4.9703 Debye
Server	General (68314)
CPU time	138251.9 sec

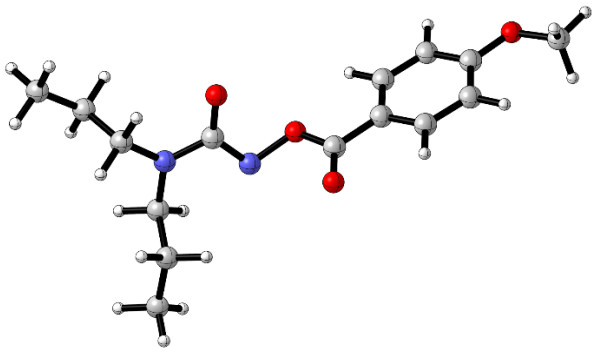


Vibrational frequency of anionic 1p (triplet)

Quantity	Value
Job History	20370,20385,37254,37256,40582,43019,43020
Route	#N B3LYP/6-311+G(2d,p) FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=Conne
Stoichiometry	$C_{15}H_{21}N_2O_4$(1-,3)
Symmetry	C1
Basis	6-311+G(2d,p)
UB3LYP Energy	-994.974027916 Hartree
ZPE	0.341705 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-994.609506 Hartree
Enthalpy	-994.608561 Hartree
Free Energy	-994.687569 Hartree
C_v	83.224 cal/mol-K
Entropy	166.286 cal/mol-K
Dipole Moment	8.1645 Debye
Server	General (67416)
CPU time	172639.6 sec

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.420378
3	6	0	1.225533	0.000000	2.062304
4	6	0	2.469280	0.000479	1.421119
5	6	0	3.642919	-0.000588	2.160257
6	6	0	3.631793	-0.001551	3.593625
7	6	0	2.339968	-0.005045	4.216482
8	6	0	1.184496	-0.001859	3.470272
9	1	0	0.217364	-0.000929	3.961681
10	1	0	2.270869	-0.005158	5.296346
11	6	0	4.848408	0.013788	4.296652
12	8	0	6.028770	0.043437	3.905808
13	8	0	4.647484	-0.201347	5.773641
14	7	0	5.393370	0.468680	6.662058
15	6	0	5.771025	1.787333	6.277628
16	8	0	5.053174	2.512801	5.586500
17	7	0	6.922369	2.205208	6.866145
18	6	0	7.774887	1.347822	7.695737
19	1	0	8.182560	1.972893	8.495102
20	1	0	7.153627	0.587423	8.165783
21	6	0	8.919198	0.680846	6.926767
22	6	0	9.820781	-0.139594	7.850241
23	1	0	10.628445	-0.614700	7.289638
24	1	0	10.275366	0.488626	8.621394
25	1	0	9.256634	-0.929038	8.354529
26	1	0	8.496072	0.039428	6.149381
27	1	0	9.511310	1.446417	6.416206

28	6	0	7.343315	3.593182	6.667764
29	1	0	8.435577	3.613071	6.679063
30	1	0	7.018221	3.910776	5.677052
31	6	0	6.791582	4.551822	7.727859
32	6	0	7.277432	5.985243	7.510770
33	1	0	6.875032	6.656025	8.272746
34	1	0	8.368456	6.045486	7.557005
35	1	0	6.964786	6.365255	6.534236
36	1	0	5.699372	4.517452	7.697953
37	1	0	7.092506	4.204811	8.721242
38	1	0	4.595405	0.001528	1.645579
39	1	0	2.534652	0.001799	0.340683
40	1	0	-1.045121	0.000739	-0.303846
41	1	0	0.492981	0.891299	-0.400936
42	1	0	0.491691	-0.892029	-0.401027



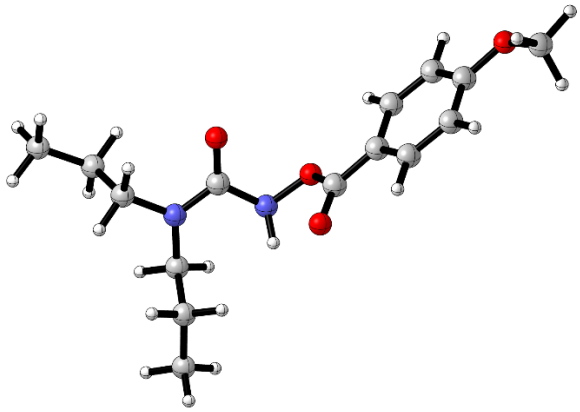
Vibrational frequency of anionic 1p (singlet)

Quantity	Value
Job History	20370,20385,37254,37256,40582,43019
Route	#N B3LYP/6-311+G(2d,p) FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=Conne
Stoichiometry	$C_{15}H_{21}N_2O_4(1-)$
Symmetry	C1
Basis	6-311+G(2d,p)
RB3LYP Energy	-995.061093687 Hartree
ZPE	0.344749 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-994.693880 Hartree
Enthalpy	-994.692936 Hartree
Free Energy	-994.772062 Hartree
C_v	81.054 cal/mol-K
Entropy	166.534 cal/mol-K
Dipole Moment	6.1381 Debye
Server	General (67415)
CPU time	57784.6 sec

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.429579
3	6	0	1.193395	0.000000	2.079474
4	6	0	2.438607	-0.001272	1.446001
5	6	0	3.596413	-0.003518	2.215222
6	6	0	3.545116	-0.001282	3.608358
7	6	0	2.288144	0.002276	4.230191
8	6	0	1.127967	0.001261	3.478645
9	1	0	0.155783	0.000614	3.956061
10	1	0	2.224446	0.002283	5.309582
11	6	0	4.827985	-0.007007	4.373619
12	8	0	5.918917	-0.105368	3.835797
13	8	0	4.617541	0.100680	5.683493
14	7	0	5.785415	-0.084789	6.543622
15	6	0	6.091123	1.109692	7.087416
16	8	0	5.592991	2.232155	6.808632
17	7	0	7.083996	1.030095	8.072871
18	6	0	7.731178	-0.224666	8.431400
19	1	0	8.048944	-0.151385	9.477738
20	1	0	6.991795	-1.024706	8.379711
21	6	0	8.944140	-0.596679	7.567180
22	6	0	9.602193	-1.899484	8.023811
23	1	0	10.463654	-2.150393	7.400409
24	1	0	9.951809	-1.826671	9.058075
25	1	0	8.900168	-2.736882	7.971156
26	1	0	8.619192	-0.685348	6.527711

27	1	0	9.677122	0.216243	7.602062
28	6	0	7.663274	2.254310	8.605278
29	1	0	8.751248	2.130740	8.665631
30	1	0	7.467954	3.060267	7.898422
31	6	0	7.128008	2.651589	9.987315
32	6	0	7.800695	3.912991	10.530447
33	1	0	7.407480	4.182677	11.513369
34	1	0	8.880993	3.773052	10.632426
35	1	0	7.639937	4.765119	9.863504
36	1	0	6.047389	2.805377	9.913457
37	1	0	7.278954	1.823171	10.687660
38	1	0	4.562959	-0.006631	1.728251
39	1	0	2.516791	-0.001050	0.368387
40	1	0	-1.046342	0.000235	-0.294727
41	1	0	0.490583	0.893603	-0.392484
42	1	0	0.490249	-0.893632	-0.392994



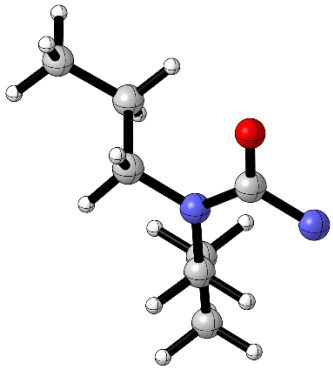
Vibrational frequency of neutral 1p (triplet)

Quantity	Value
Job History	20370,20385,37254,37256,40582,41038
Route	#N B3LYP/6-311+G(2d,p) FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=Conne
Stoichiometry	$C_{15}H_{22}N_2O_4$(3)
Symmetry	C1
Basis	6-311+G(2d,p)
UB3LYP Energy	-995.430848351 Hartree
ZPE	0.354867 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-995.052591 Hartree
Enthalpy	-995.051647 Hartree
Free Energy	-995.133360 Hartree
C_v	84.460 cal/mol-K
Entropy	171.981 cal/mol-K
Dipole Moment	4.5586 Debye
Server	10.72.192.49 (27526)
CPU time	137523.1 sec

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.436900
3	6	0	1.166266	0.000000	2.100749
4	6	0	2.461378	0.005115	1.509784
5	6	0	3.569028	-0.000460	2.295943
6	6	0	3.449079	-0.021306	3.769763
7	6	0	2.120582	-0.011091	4.350101
8	6	0	1.031883	-0.002317	3.550334
9	1	0	0.030354	0.004056	3.962299
10	1	0	2.010879	-0.011265	5.424540
11	6	0	4.640415	-0.052328	4.551526
12	8	0	5.795718	-0.059294	4.117061
13	8	0	4.385191	-0.116292	5.927892
14	7	0	5.541363	-0.013103	6.720695
15	6	0	5.864064	1.346022	7.026460
16	8	0	5.098636	2.264610	6.759079
17	7	0	7.039155	1.495478	7.685278
18	6	0	7.899255	0.378127	8.091807
19	1	0	8.358193	0.655194	9.043628
20	1	0	7.276751	-0.494299	8.295757
21	6	0	8.996322	0.030478	7.079531
22	6	0	9.895550	-1.099988	7.580933
23	1	0	10.669438	-1.337723	6.848651
24	1	0	10.393130	-0.824100	8.514581
25	1	0	9.320534	-2.011179	7.766427
26	1	0	8.542618	-0.253192	6.124661
27	1	0	9.596297	0.923146	6.880353

28	6	0	7.460378	2.849767	8.059204
29	1	0	8.551306	2.879811	8.004535
30	1	0	7.076090	3.543169	7.312022
31	6	0	6.992029	3.272412	9.454051
32	6	0	7.480538	4.674737	9.818800
33	1	0	7.137340	4.962681	10.814545
34	1	0	8.572842	4.727651	9.814904
35	1	0	7.108916	5.419892	9.110188
36	1	0	5.899752	3.235938	9.484443
37	1	0	7.353248	2.551392	10.193822
38	1	0	6.292577	-0.489910	6.226318
39	1	0	4.559526	0.006211	1.866185
40	1	0	2.569699	0.015607	0.433697
41	1	0	-1.046159	-0.003428	-0.290631
42	1	0	0.490562	0.896900	-0.379926
43	1	0	0.496673	-0.893641	-0.379849

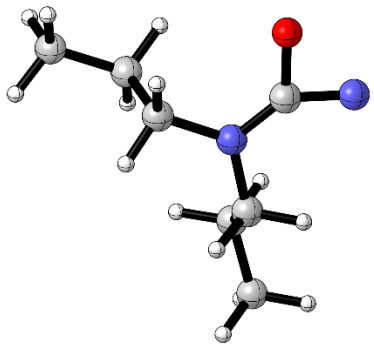


Vibrational frequency of nitrene 1p (triplet)

Quantity	Value
Job History	20370,20382,20416,37250,37252,40581
Route	#N B3LYP/6-311+G(2d,p) FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=Conne
Stoichiometry	$C_7H_{14}N_2O(3)$
Symmetry	C1
Basis	6-311+G(2d,p)
UB3LYP Energy	-459.965682017 Hartree
ZPE	0.206760 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-459.746817 Hartree
Enthalpy	-459.745872 Hartree
Free Energy	-459.798765 Hartree
C_v	42.509 cal/mol-K
Entropy	111.322 cal/mol-K
Dipole Moment	6.9519 Debye
Server	10.72.192.49 (9017)
CPU time	8678.3 sec

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	7	0	0.000000	0.000000	1.468465
3	6	0	1.145661	0.000000	2.181806
4	7	0	2.352798	0.059300	1.497850
5	8	0	1.222740	-0.049254	3.421474
6	6	0	-1.271939	-0.081637	2.194852
7	6	0	-1.739250	1.249206	2.797444
8	6	0	-3.046827	1.079813	3.571886
9	1	0	-3.373004	2.032427	3.993667
10	1	0	-3.846953	0.709902	2.925146
11	1	0	-2.929283	0.372255	4.396797
12	1	0	-0.959848	1.631707	3.459886
13	1	0	-1.870488	1.983650	1.999354
14	1	0	-2.016280	-0.465075	1.495448
15	1	0	-1.150136	-0.817936	2.992649
16	6	0	-0.483845	1.309907	-0.625523
17	6	0	-0.438238	1.247577	-2.152846
18	1	0	-0.786135	2.185740	-2.588891
19	1	0	0.578516	1.068560	-2.512060
20	1	0	-1.074680	0.445561	-2.535754
21	1	0	-1.504859	1.521799	-0.298124
22	1	0	0.143554	2.128639	-0.262033
23	1	0	1.015018	-0.215869	-0.335465
24	1	0	-0.630951	-0.831314	-0.327450



Vibrational frequency of nitrene 1p (singlet)

Quantity	Value
Job History	20370,20382,20416,37250,37252,40581,40847,42883,42886
Route	#N B3LYP/6-311+G(2d,p) FREQ SCRF=(PCM,Solvent=Acetonitrile) Geom=Conne
Stoichiometry	$C_7H_{14}N_2O$
Symmetry	C1
Basis	6-311+G(2d,p)
RB3LYP Energy	-459.951776226 Hartree
ZPE	0.207153 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-459.732259 Hartree
Enthalpy	-459.731315 Hartree
Free Energy	-459.784642 Hartree
C_v	42.649 cal/mol-K
Entropy	112.237 cal/mol-K
Dipole Moment	7.4145 Debye
Server	General (66802)
CPU time	3396.1 sec

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	7	0	0.000000	0.000000	1.471179
3	6	0	1.153932	0.000000	2.103188
4	7	0	2.422072	0.038088	1.899005
5	8	0	1.445369	-0.059049	3.376245
6	6	0	-1.249390	-0.105714	2.245158
7	6	0	-1.798805	1.230541	2.749653
8	6	0	-3.084161	1.037103	3.555337
9	1	0	-3.465538	1.995015	3.913537
10	1	0	-3.866084	0.572542	2.948692
11	1	0	-2.913474	0.398888	4.426410
12	1	0	-1.039661	1.715119	3.369685
13	1	0	-1.986407	1.894905	1.903053
14	1	0	-1.975466	-0.601775	1.598385
15	1	0	-1.065283	-0.772674	3.090245
16	6	0	-0.456683	1.314364	-0.632464
17	6	0	-0.374801	1.256610	-2.158511
18	1	0	-0.708375	2.197121	-2.600564
19	1	0	0.649631	1.074242	-2.493637
20	1	0	-1.004815	0.458065	-2.559168
21	1	0	-1.484051	1.530568	-0.329074
22	1	0	0.166132	2.128714	-0.251845
23	1	0	1.017006	-0.234178	-0.323152
24	1	0	-0.637527	-0.824471	-0.330241

*BDE calculation for carbamoyl precursor **1p***

BDE = [ΔH(radical) + ΔH(hydrogen)] – ΔH(precursor)

BDE = [-994.528211+ (-0.499817)]– (-995.163809)

BDE = 0.135781 Hartree

BDE = 85.2 kcal/mol

BDE for the urea derived substrates was calculated to be 85.2 kcal/mol

*BDE calculation for amide precursor **1h***

BDE = [ΔH(radical) + ΔH(hydrogen)] – ΔH(precursor)

BDE = [-899.868570 + (-0.499817)]– (-900.514168)

BDE = 0.145781 Hartree

BDE = 91.5 kcal/mol

BDE for the amide derived substrates was calculated to be 91.5 kcal/mol

*E_T calculation from neutral **1p***

$E_T = T^1 - S^0$

E_T = -995.133360– -995.242439

$E_T = 0.109079$

E_T = 68.4 kcal/mol

Energy transfer (EnT) to the neutral urea precursor was calculated to be 68.4 kcal/mol

*E_T calculation from anionic **1p***

$E_T = T^1 - S^0$

E_T = -994.687569 – -994.772062

$E_T = 0.084493$

E_T = 53.0 kcal/mol

Energy transfer (EnT) to the neutral urea precursor was calculated to be 53.0 kcal/mol

Triplet vs singlet nitrene energy from **1p**

$\Delta G = T^1 - S^0$

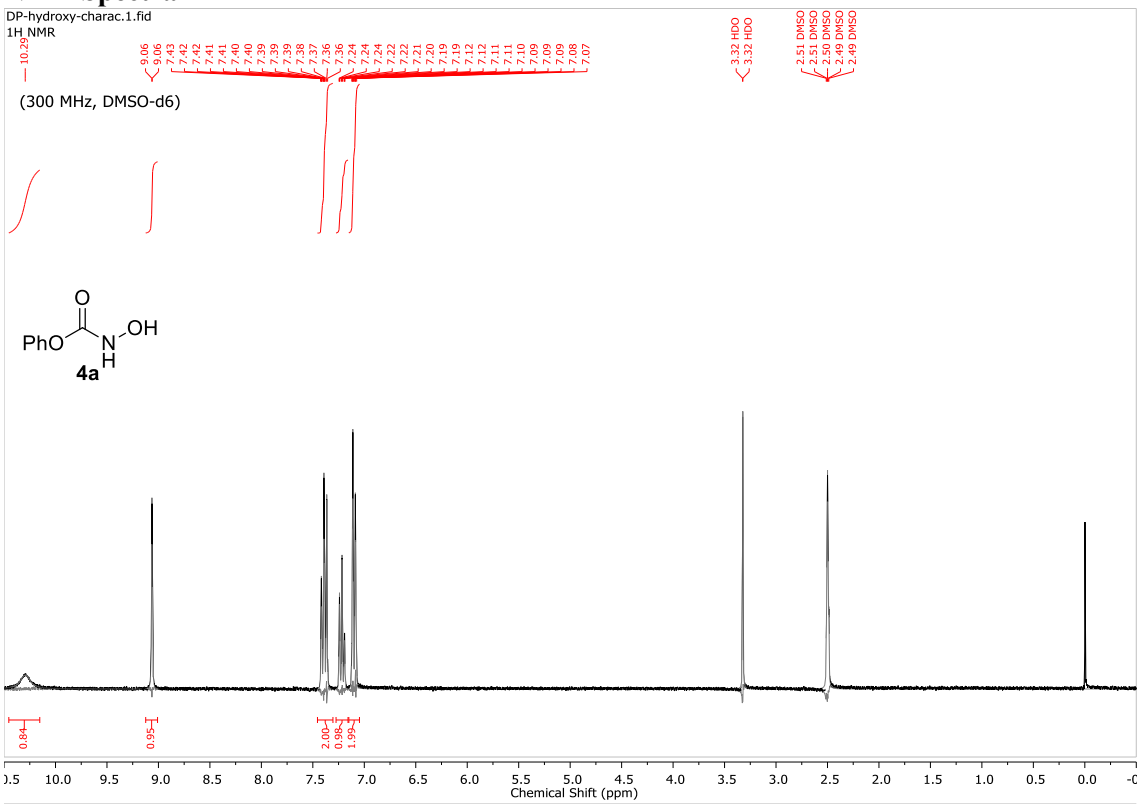
ΔG = -459.798765 – (-459.784642)

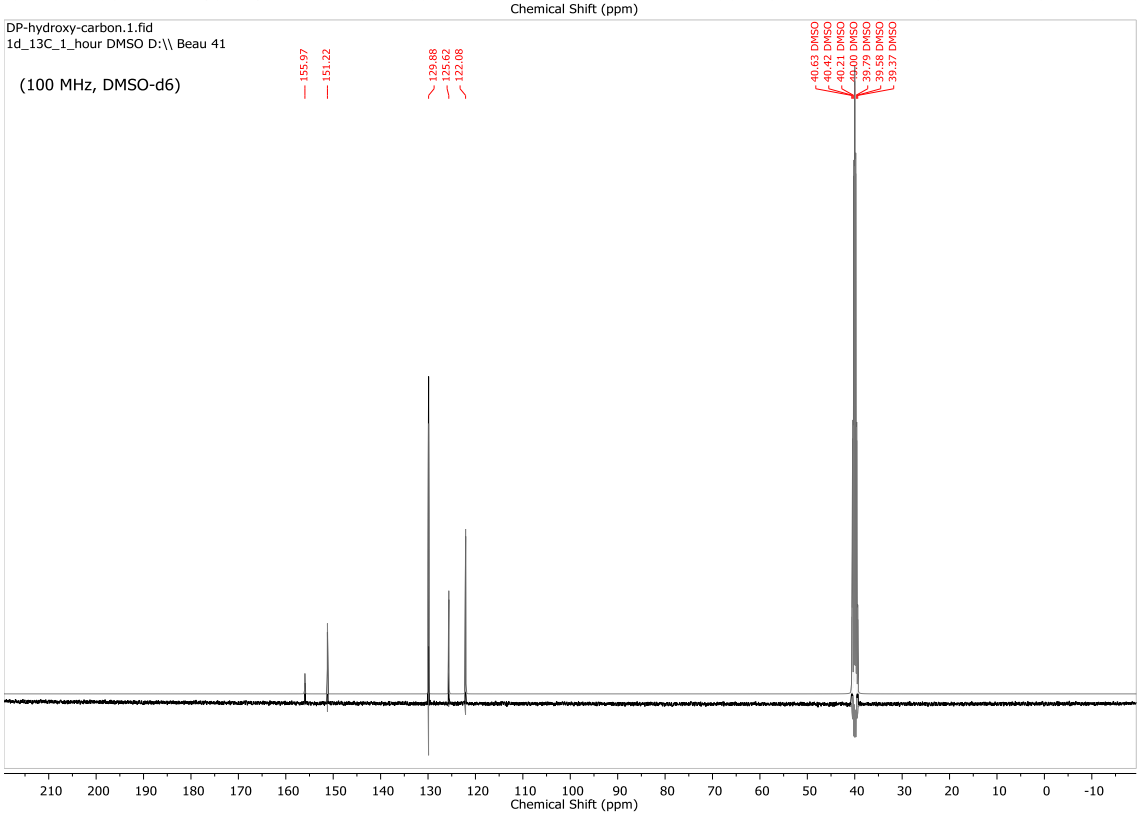
ΔG = -0.014123

ΔG = -8.9 kcal/mol

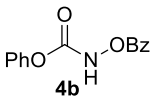
Triplet nitrene was calculated to be 8.9 kcal/mol lower in energy to the singlet nitrene

NMR Spectra


DP-hydroxy-charac.1.fid
1H NMR
(300 MHz, DMSO-d6)
10.29
9.06
9.06
7.43
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.24
7.24
7.24
7.22
7.22
7.21
7.20
7.19
7.19
7.12
7.12
7.11
7.11
7.10
7.09
7.09
7.09
7.08
7.07
3.32 HDO
3.32 HDO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
PhO
O
N
H
OH
4a
0.84
0.95
2.00
0.98
1.99
Chemical Shift (ppm)

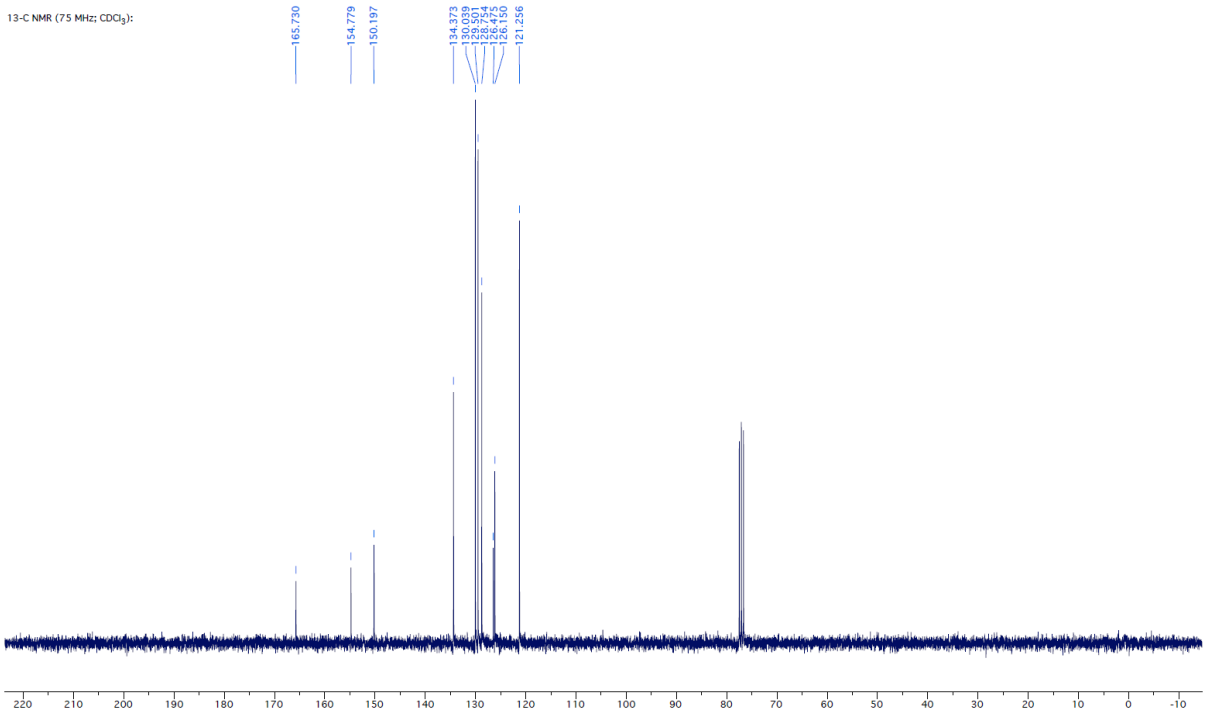

DP-hydroxy-carbon.1.fid
1d_13C_1_hour DMSO D:\\ Beau 41
(100 MHz, DMSO-d6)
155.97
151.22
129.88
125.62
122.08
40.63 DMSO
40.42 DMSO
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.37 DMSO
Chemical Shift (ppm)

1-H NMR (300 MHz; $CDCl_3$):

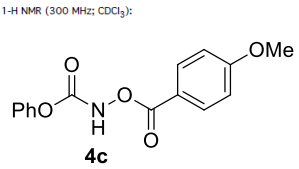


4b

13-C NMR (75 MHz; $CDCl_3$):

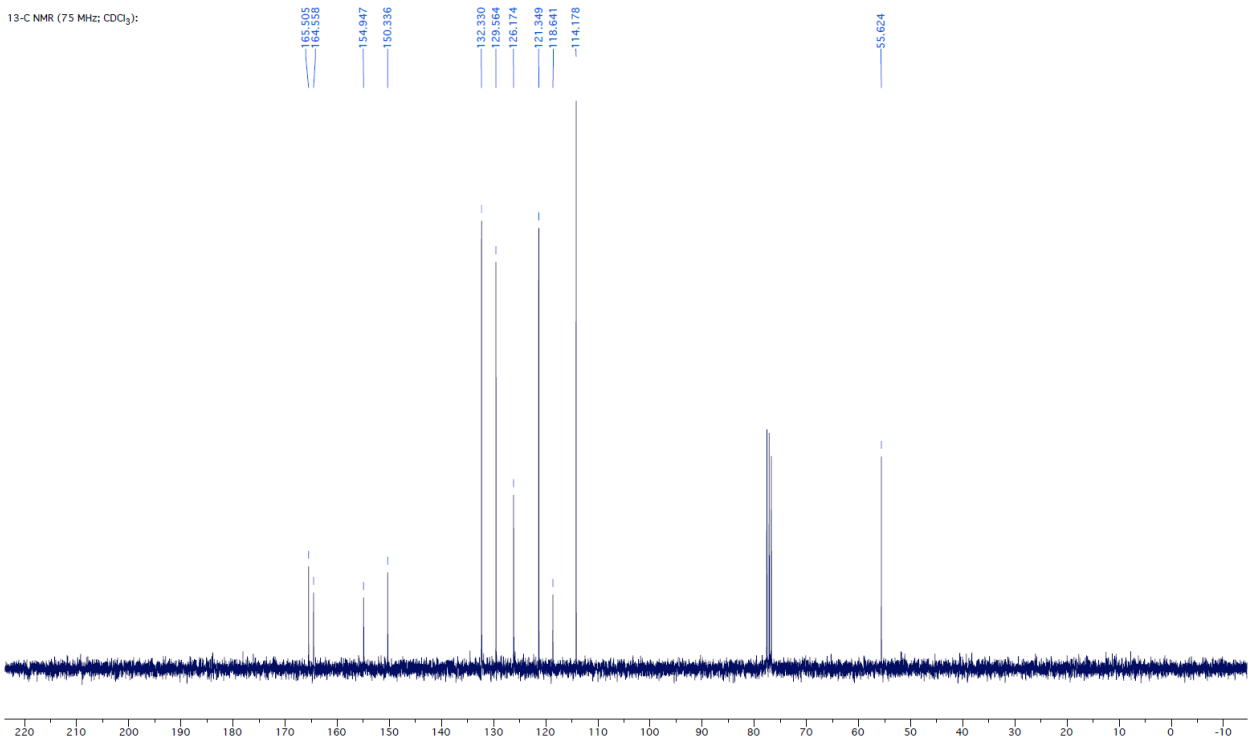


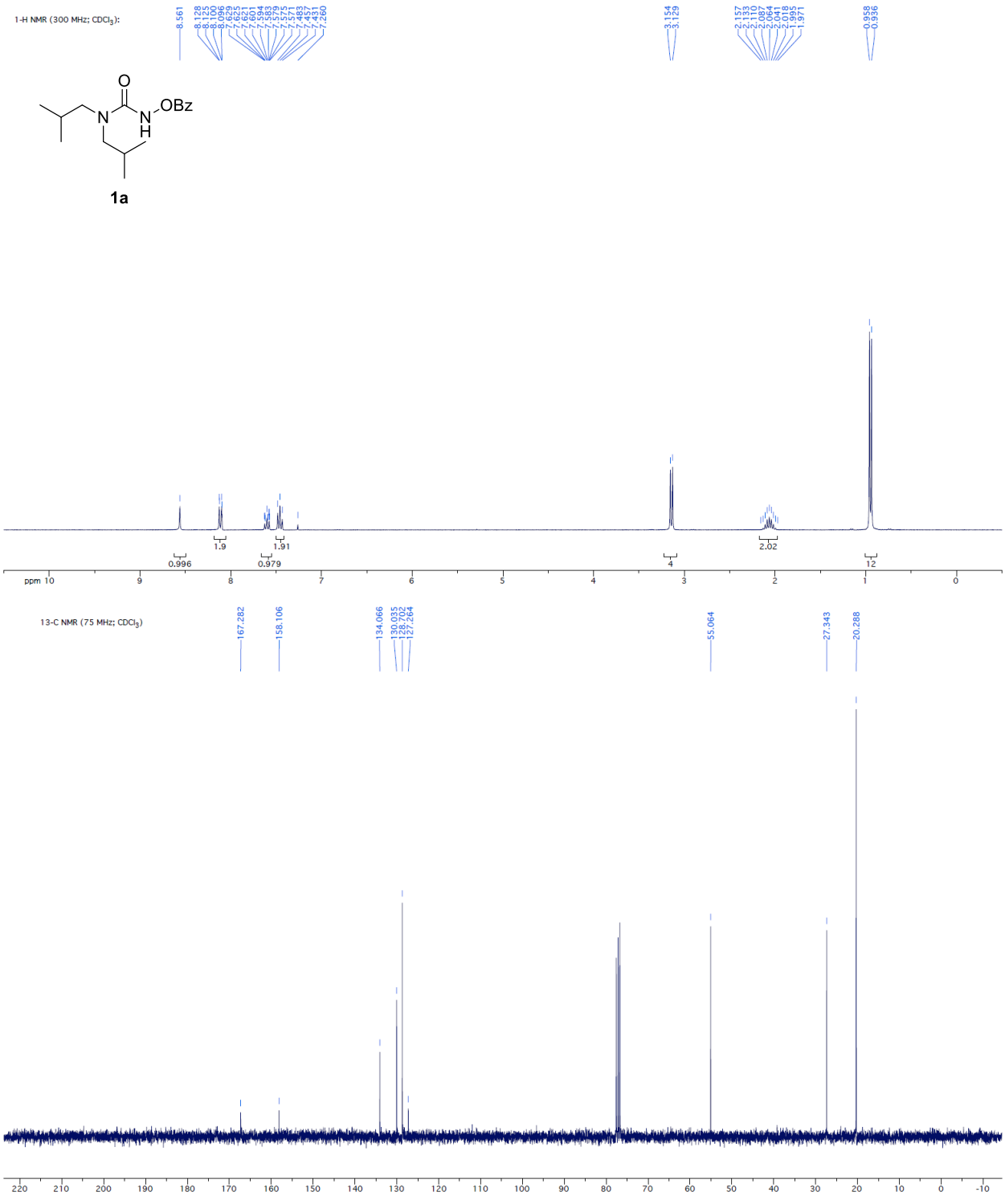
1-H NMR (300 MHz; $CDCl_3$):

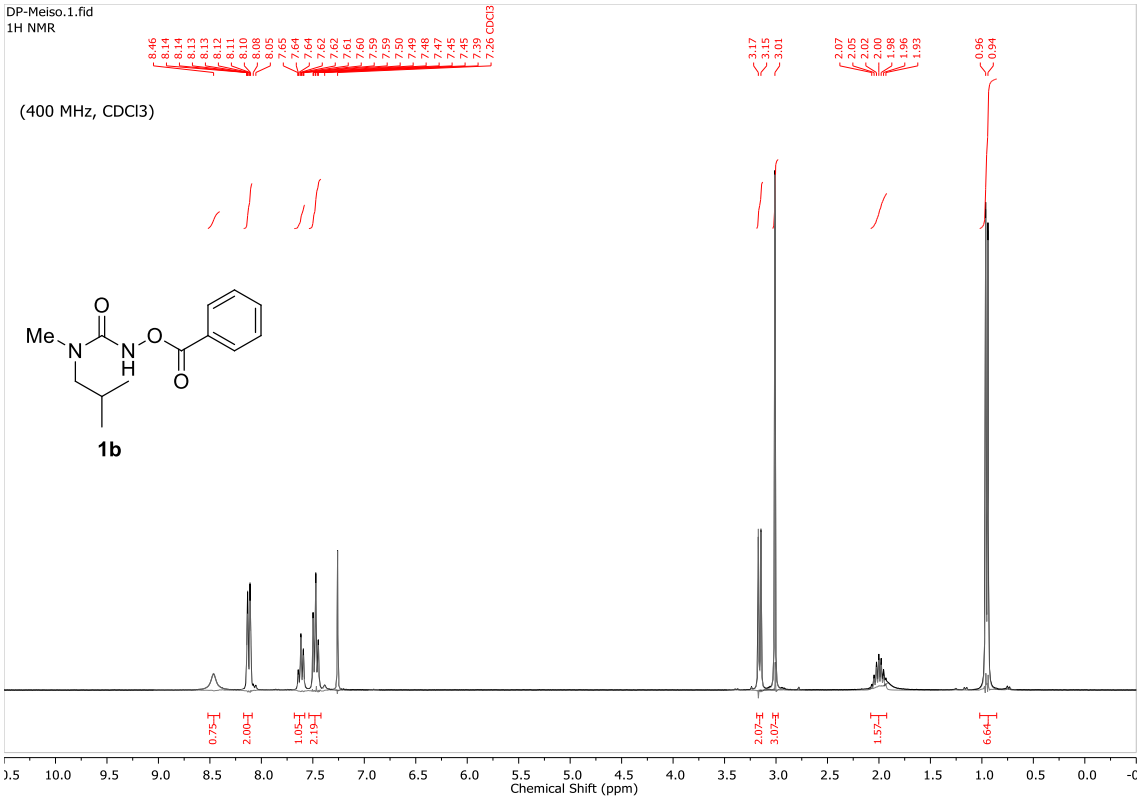


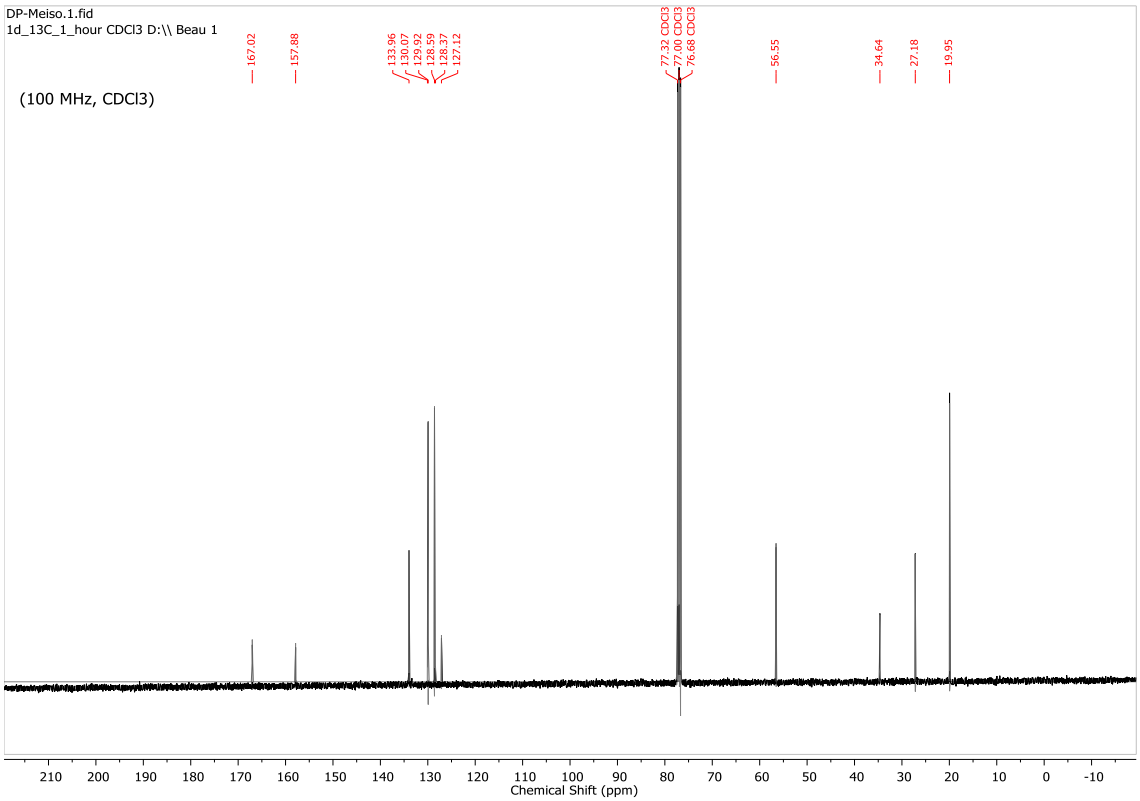
4c

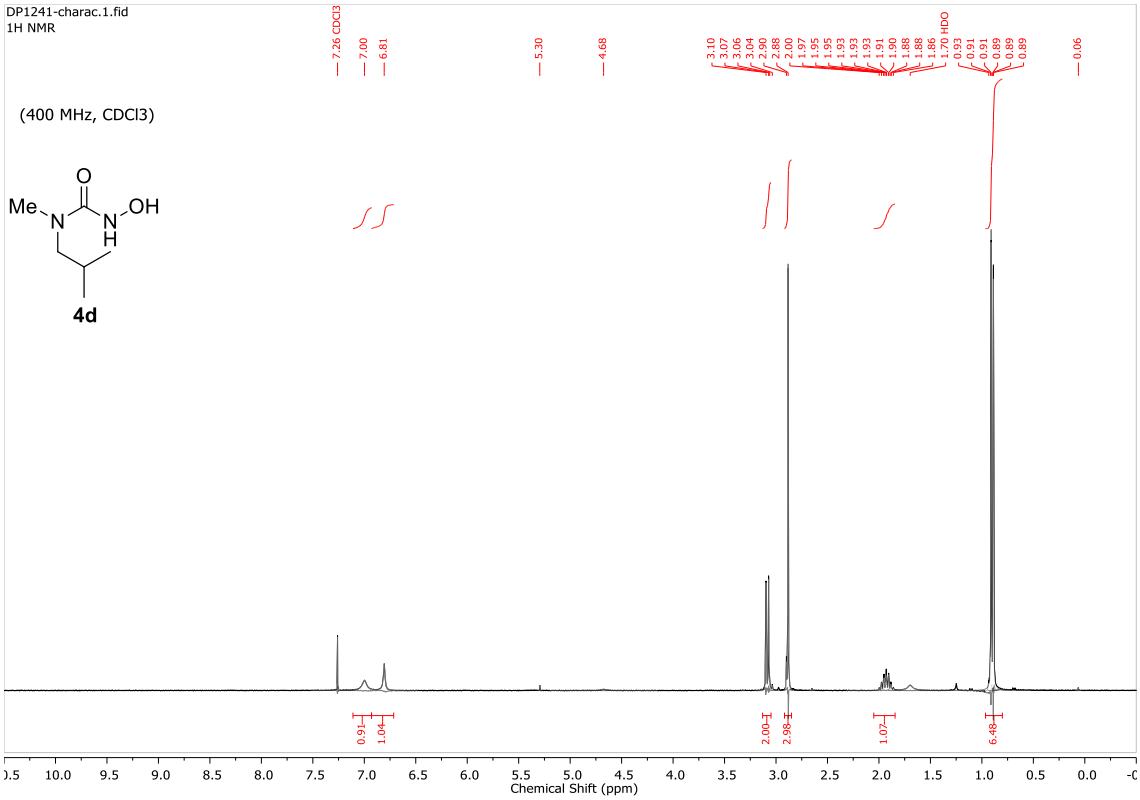
13-C NMR (75 MHz; $CDCl_3$):

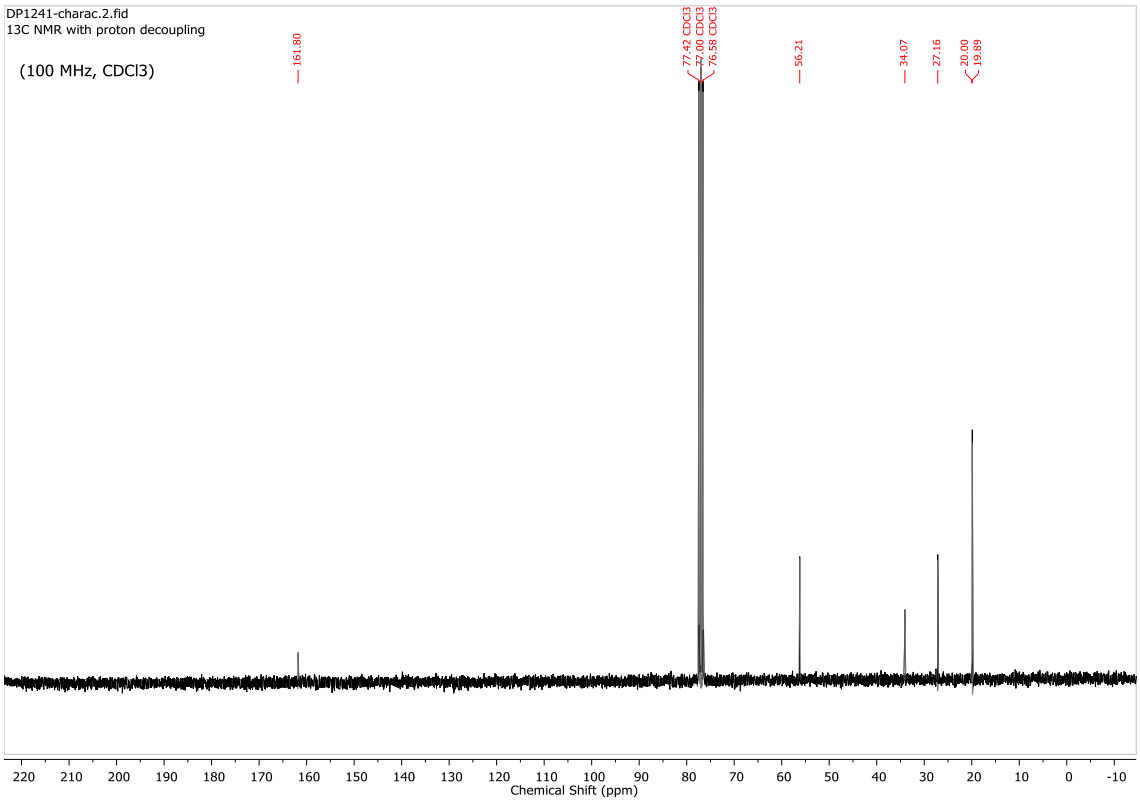


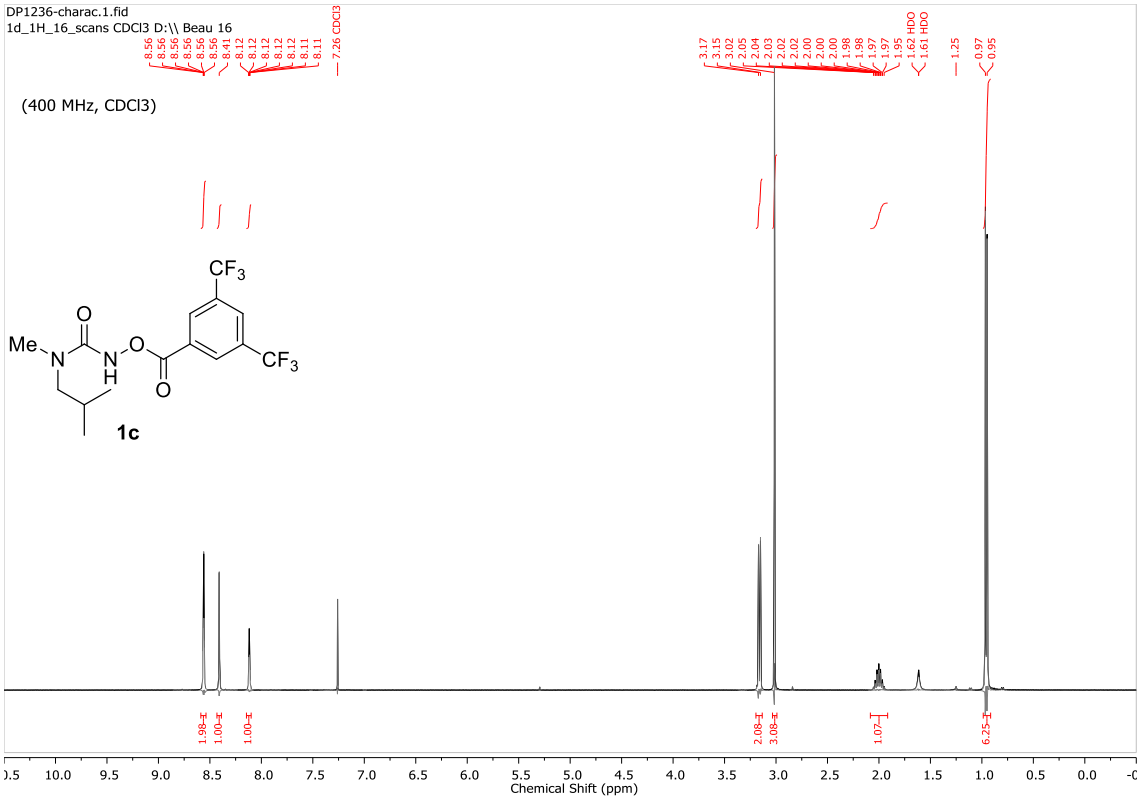

1-H NMR (300 MHz; CDCl3):
8.561
8.128
8.125
8.100
8.096
8.029
7.625
7.621
7.601
7.594
7.583
7.579
7.575
7.571
7.483
7.457
7.431
7.260
3.154
3.129
2.157
2.133
2.110
2.087
2.064
2.041
2.018
1.995
1.971
0.958
0.936
O
N
N
H
OBz
1a
0.996
1.9
0.979
1.91
4
2.02
12
ppm 10
13-C NMR (75 MHz; CDCl3)
167.282
158.106
134.066
130.035
128.702
127.264
55.064
27.343
20.288

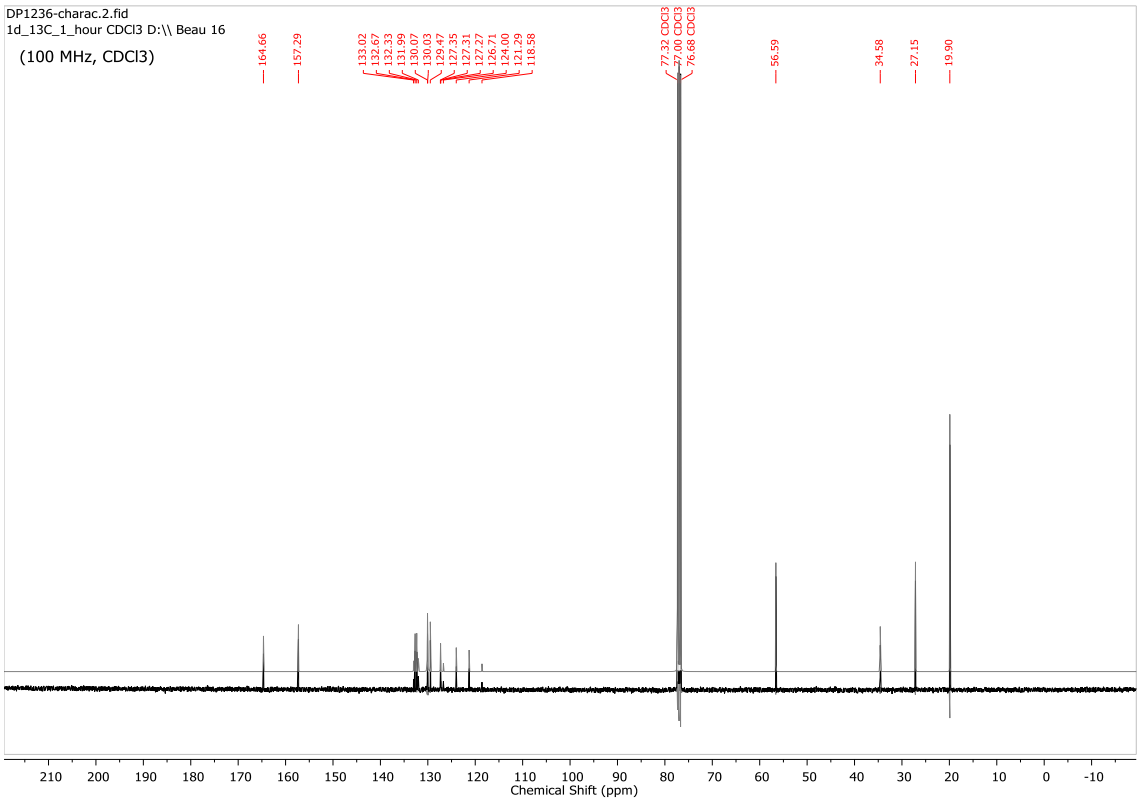

DP-Meiso.1.fid
1H NMR
(400 MHz, CDCl3)
Me
N
O
N
H
O
O
1b
Chemical Shift (ppm)

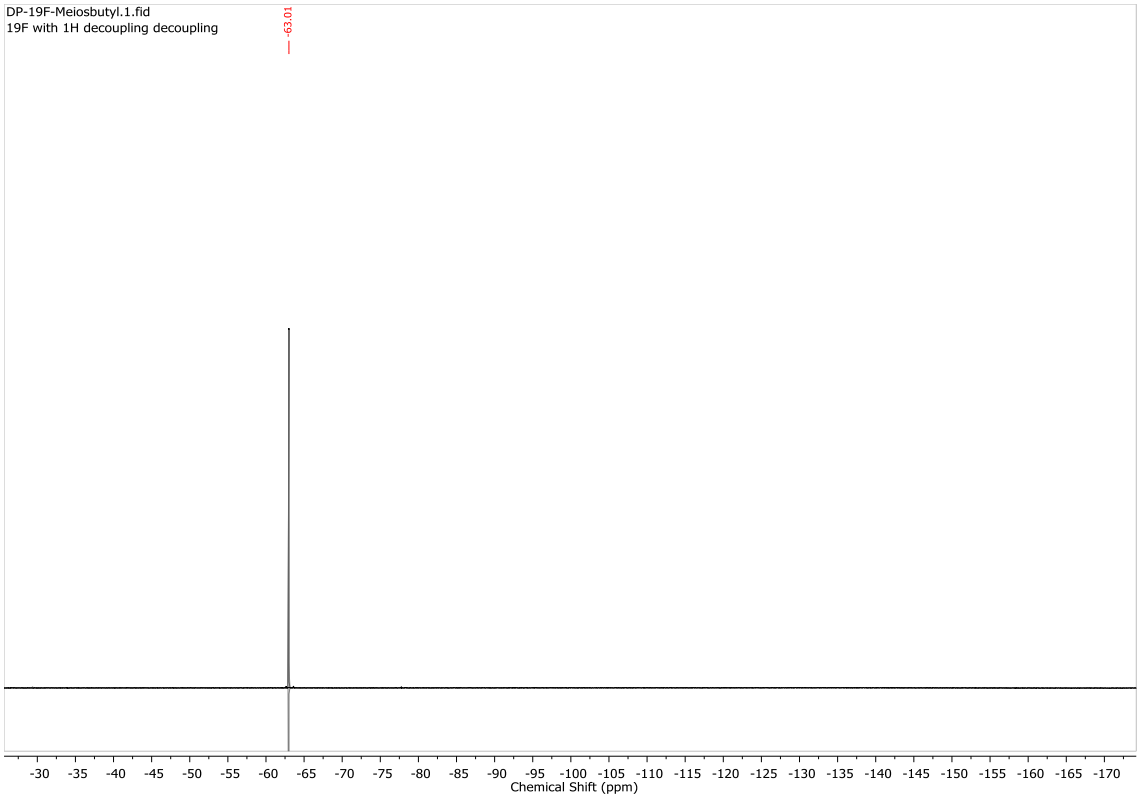

DP-Meiso.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 1
(100 MHz, CDCl3)
Chemical Shift (ppm)


DP1241-charac.1.fid
1H NMR
(400 MHz, CDCl3)
Me
N
O
N
OH
H
4d
7.26 CDCl3
7.00
6.81
5.30
4.68
1.70 HDO
0.06
0.91
1.04
2.00
2.98
1.07
6.48
Chemical Shift (ppm)

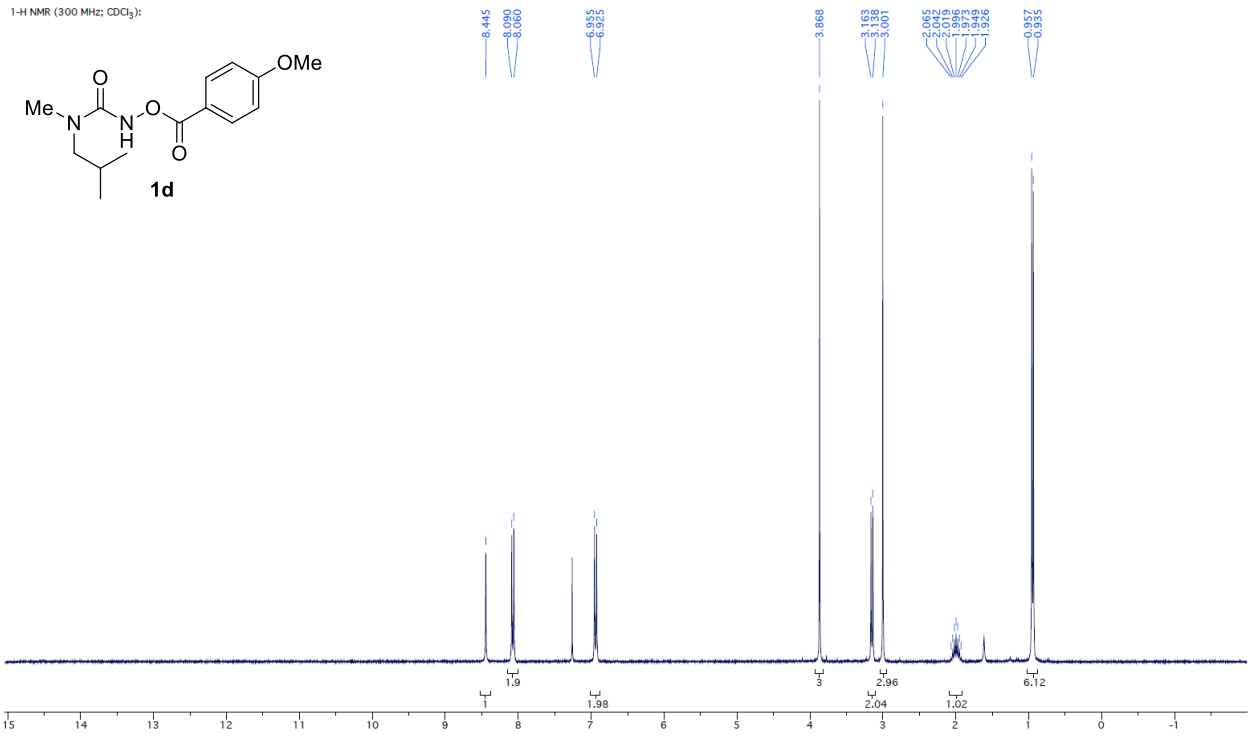

DP1241-charac.2.fid
13C NMR with proton decoupling
(100 MHz, CDCl3)
161.80
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
56.21
34.07
27.16
20.00
19.89
Chemical Shift (ppm)


DP1236-charac.1.fid
1d_1H_16_scans CDCl3 D:\\ Beau 16
(400 MHz, CDCl3)
Me
N
O
N
H
O
O
CF3
CF3
1c
Chemical Shift (ppm)


DP1236-charac.2.fid
1d_13C_1_hour CDCl3 D:\\ Beau 16
(100 MHz, CDCl3)
Chemical Shift (ppm)

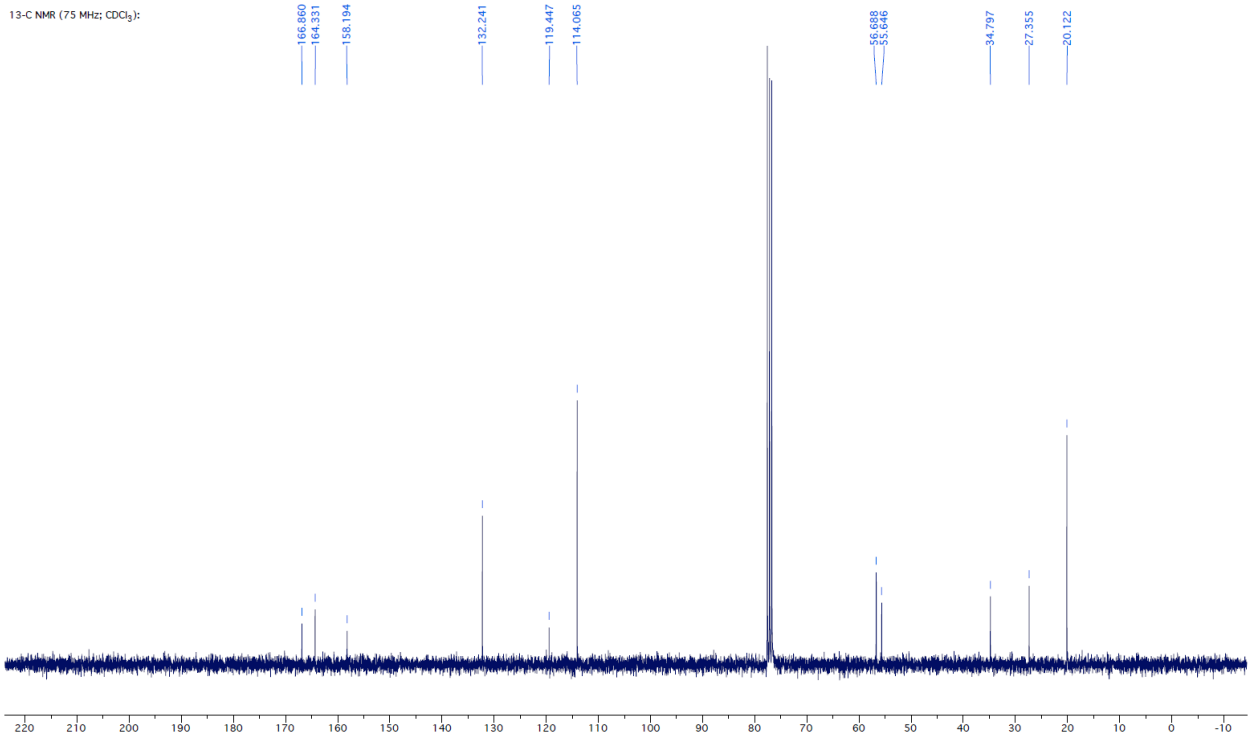

DP-19F-Meiosbutyl.1.fid
19F with 1H decoupling decoupling
-63.01
-30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170
Chemical Shift (ppm)

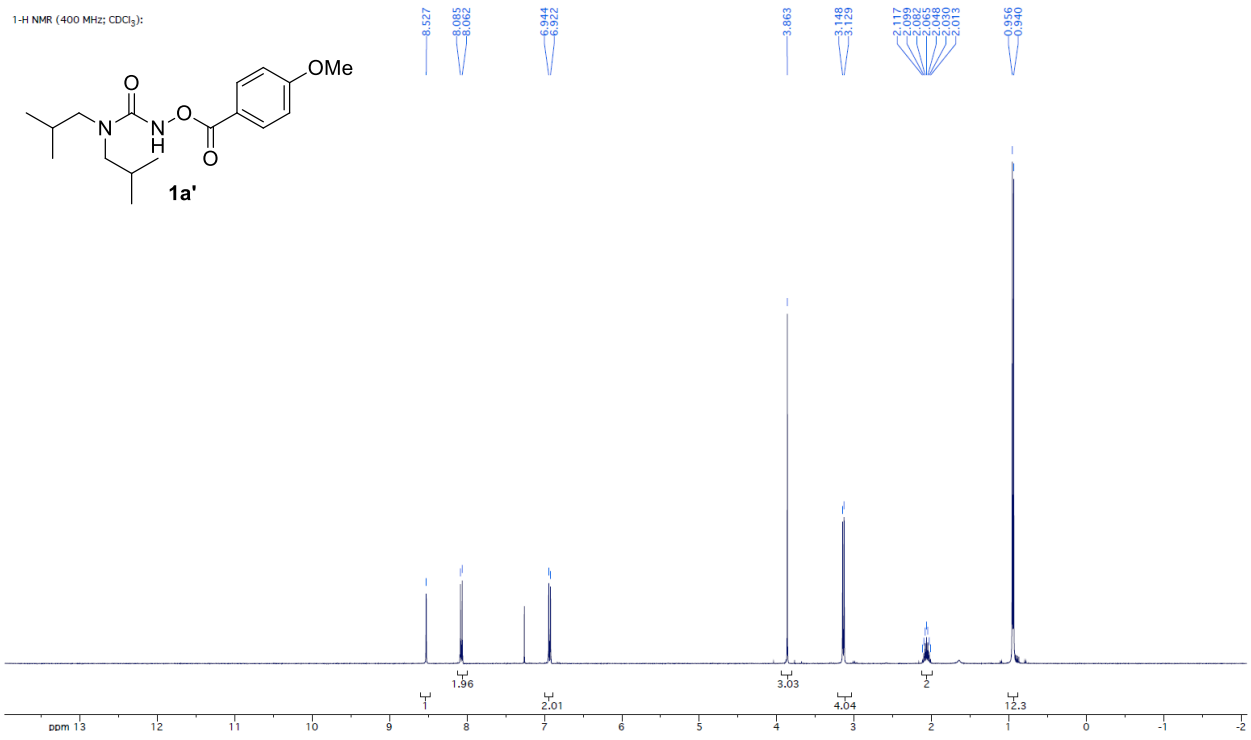
1-H NMR (300 MHz; $CDCl_3$):

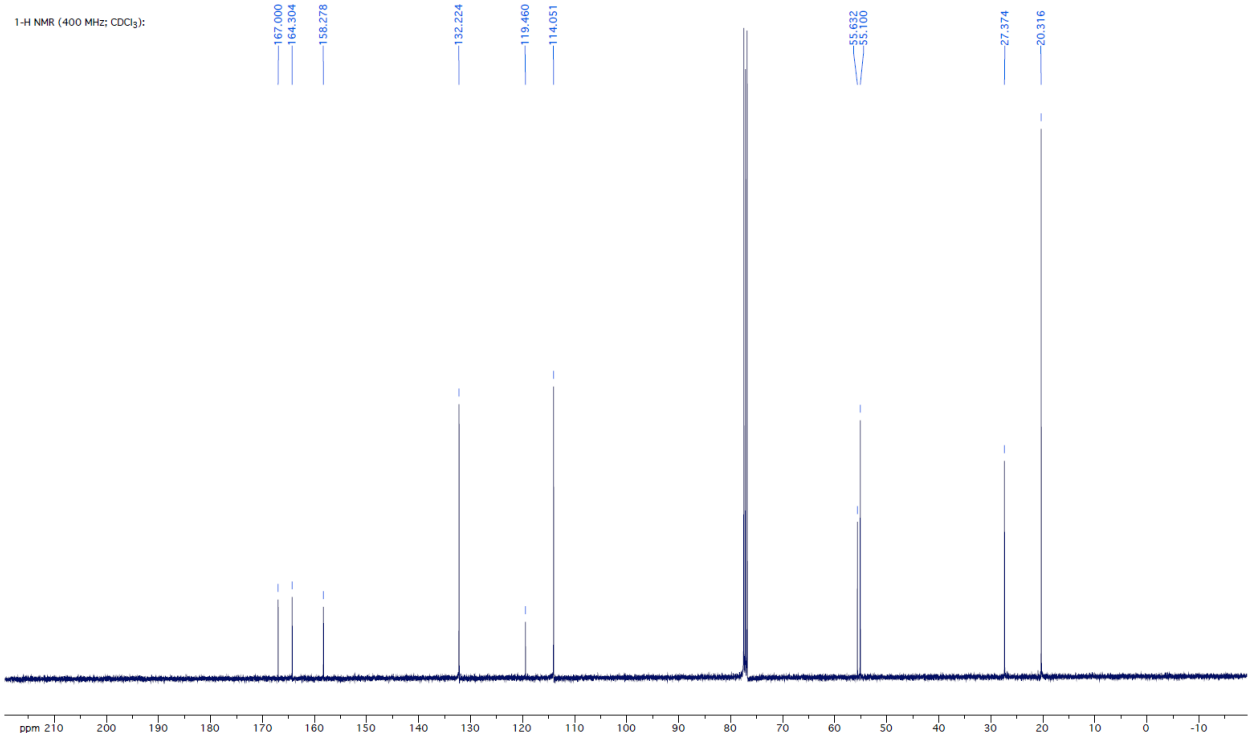


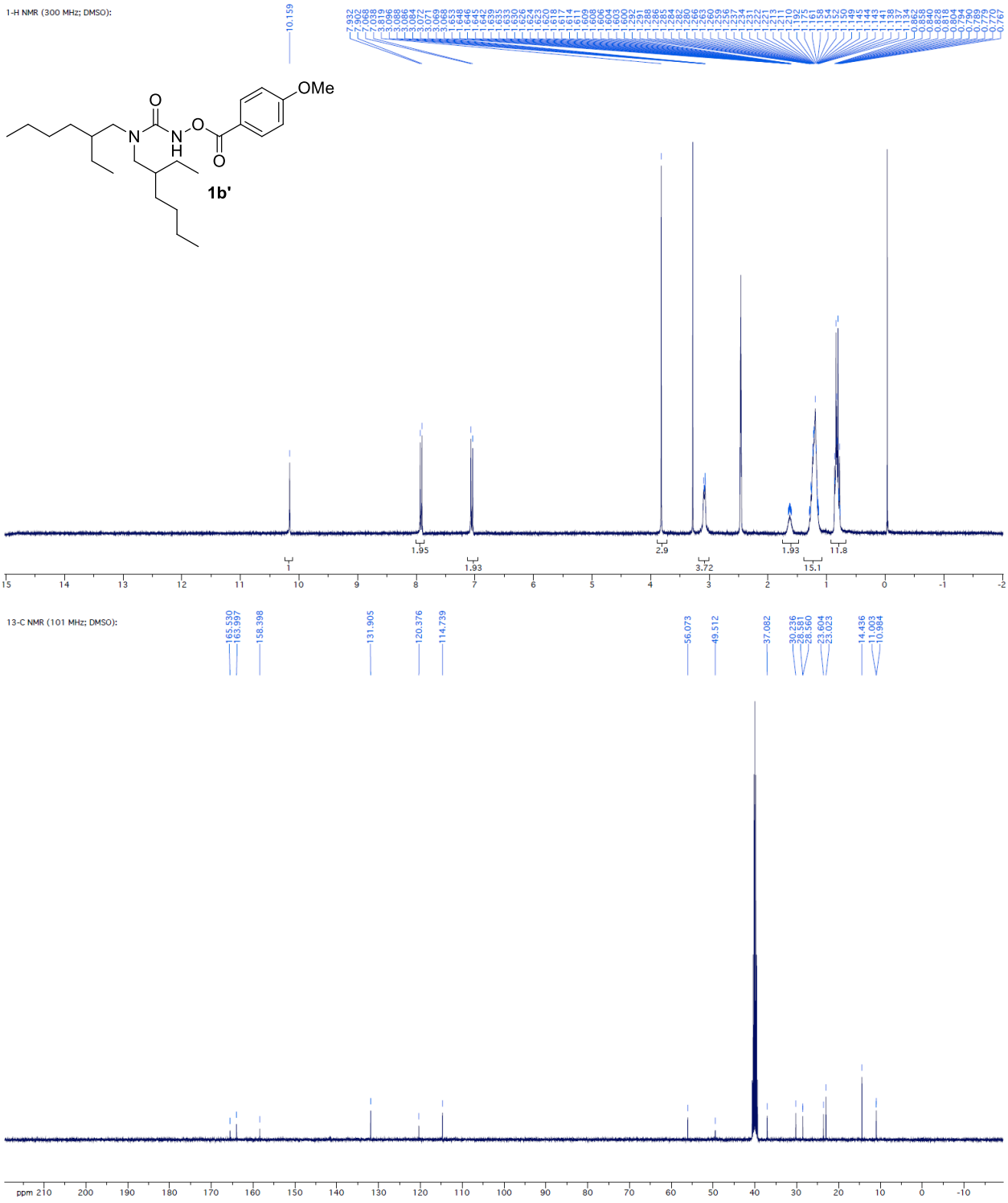
1d

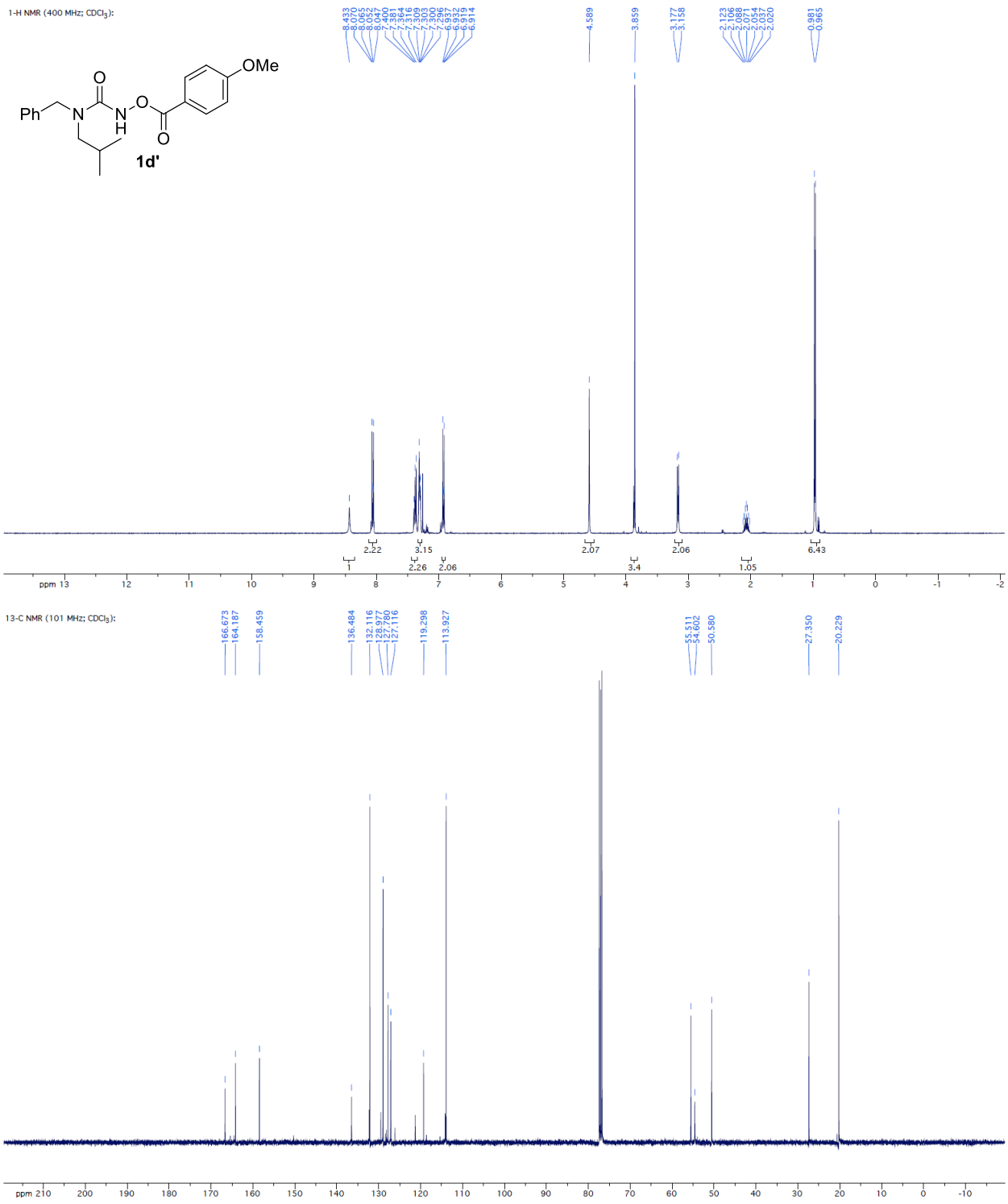
13-C NMR (75 MHz; $CDCl_3$):

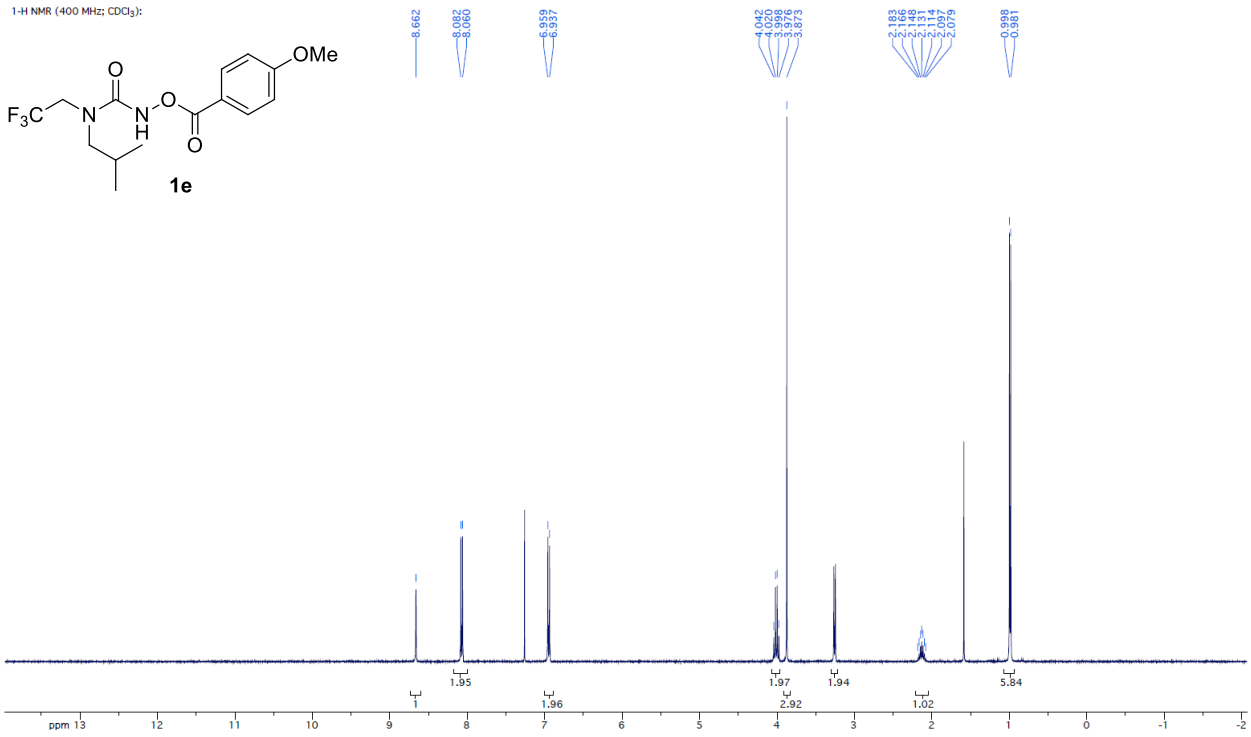


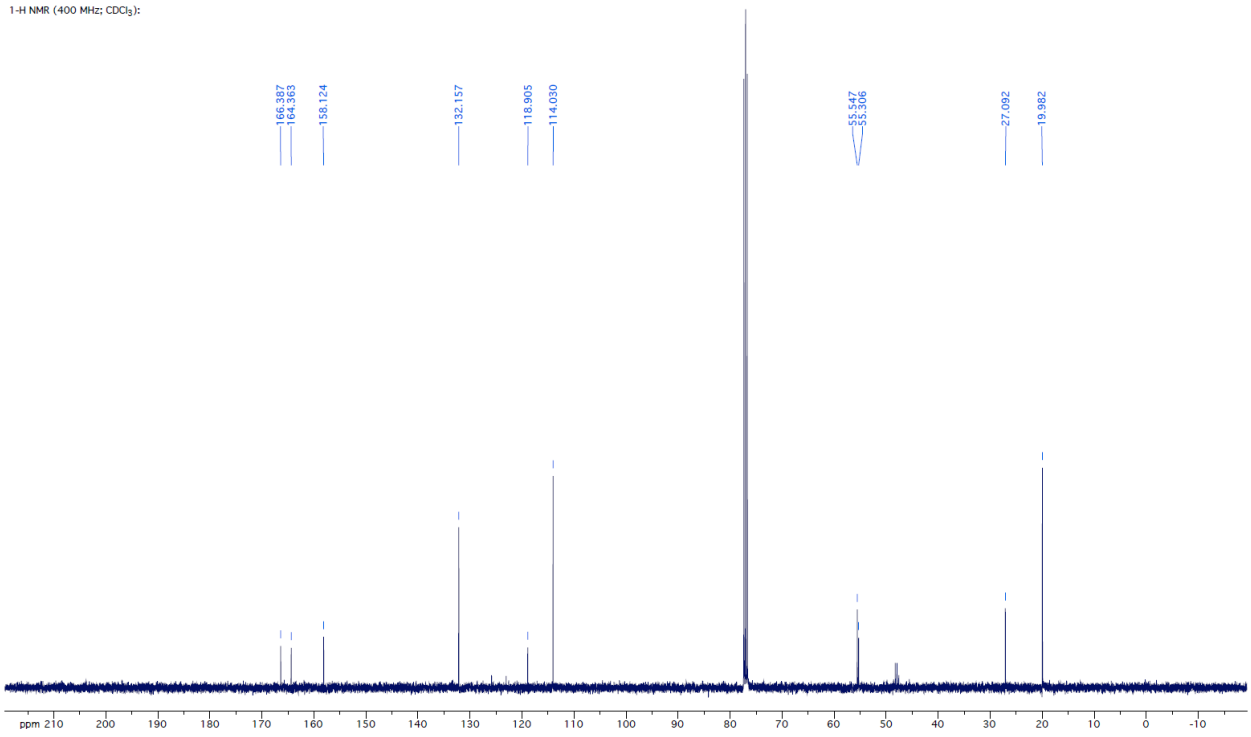

1-H NMR (400 MHz; CDCl3):
8.527
8.085
8.062
6.944
6.922
3.863
3.148
3.129
2.117
2.099
2.082
2.065
2.048
2.030
2.013
0.956
0.940
OMe
O
N
N
H
O
O
1a'
1.96
2.01
3.03
4.04
2
12.3
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2


1-H NMR (400 MHz; CDCl3):
167.000
164.304
158.278
132.224
119.460
114.051
55.632
55.100
27.374
20.316
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

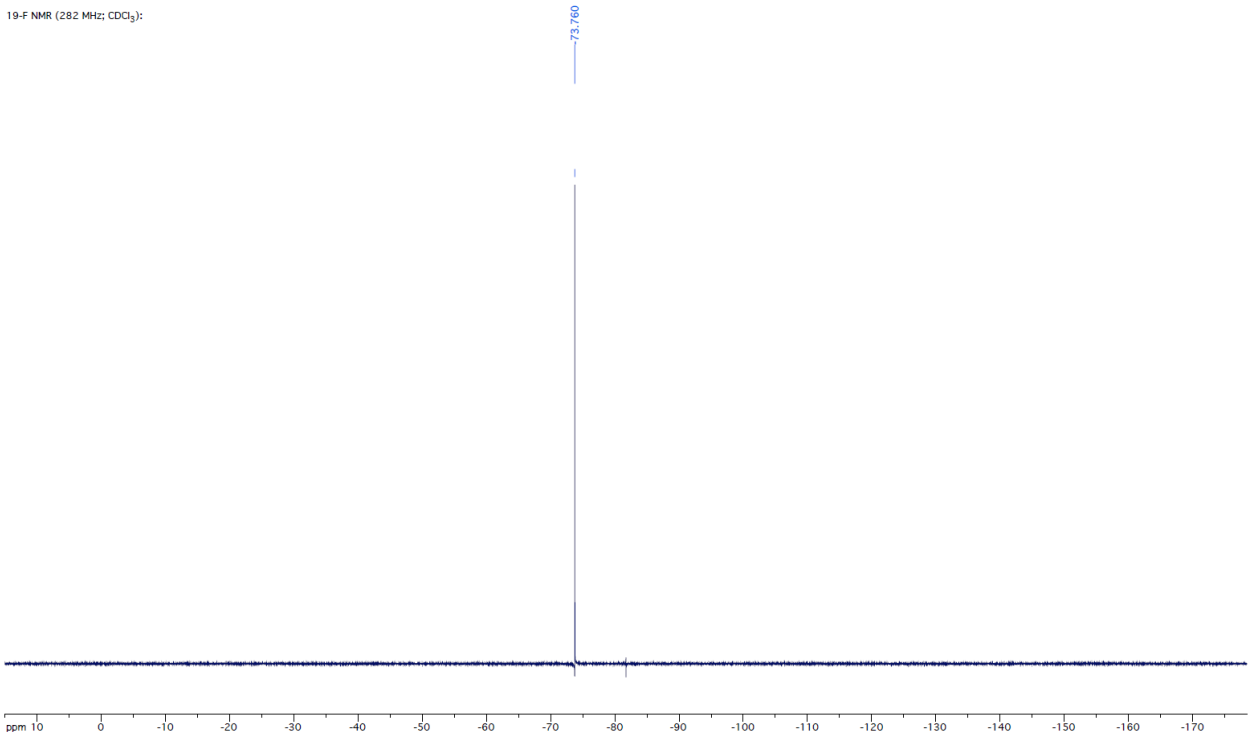

1-H NMR (300 MHz; DMSO):
OMe
1b'
13-C NMR (101 MHz; DMSO):
ppm

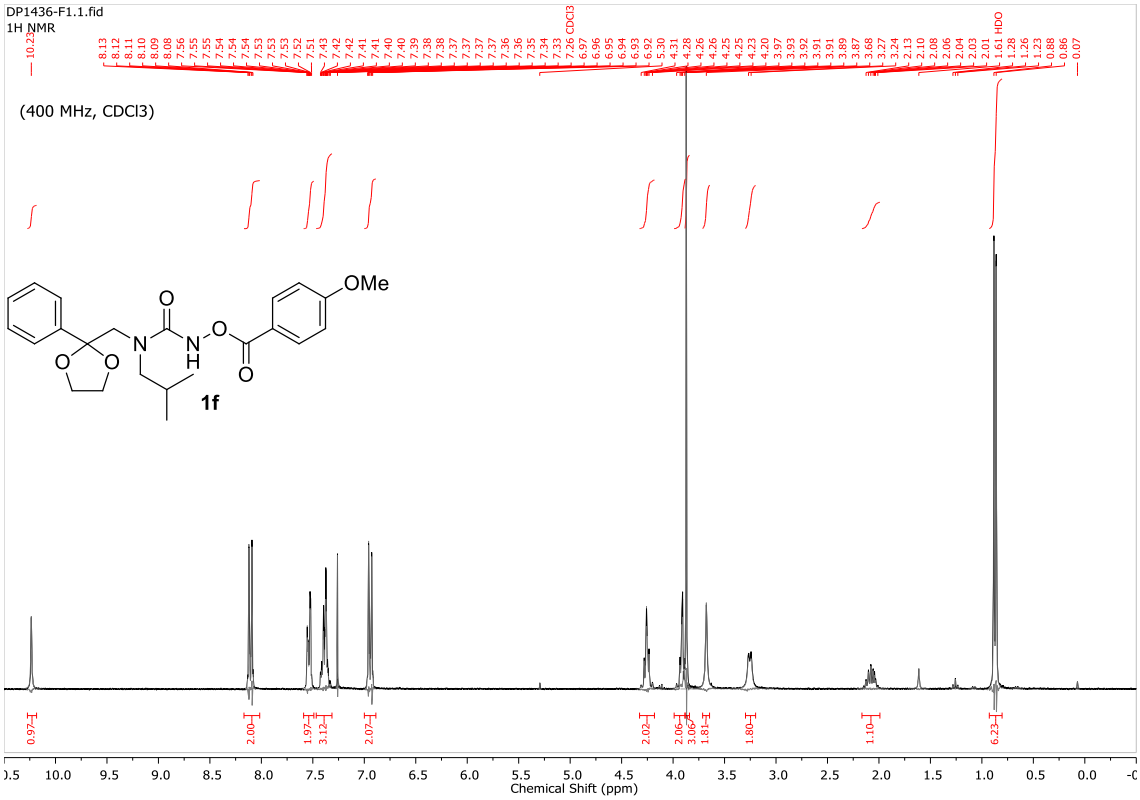

1-H NMR (400 MHz; CDCl3):
OMe
Ph
N
O
N
H
O
O
1d'
13-C NMR (101 MHz; CDCl3):

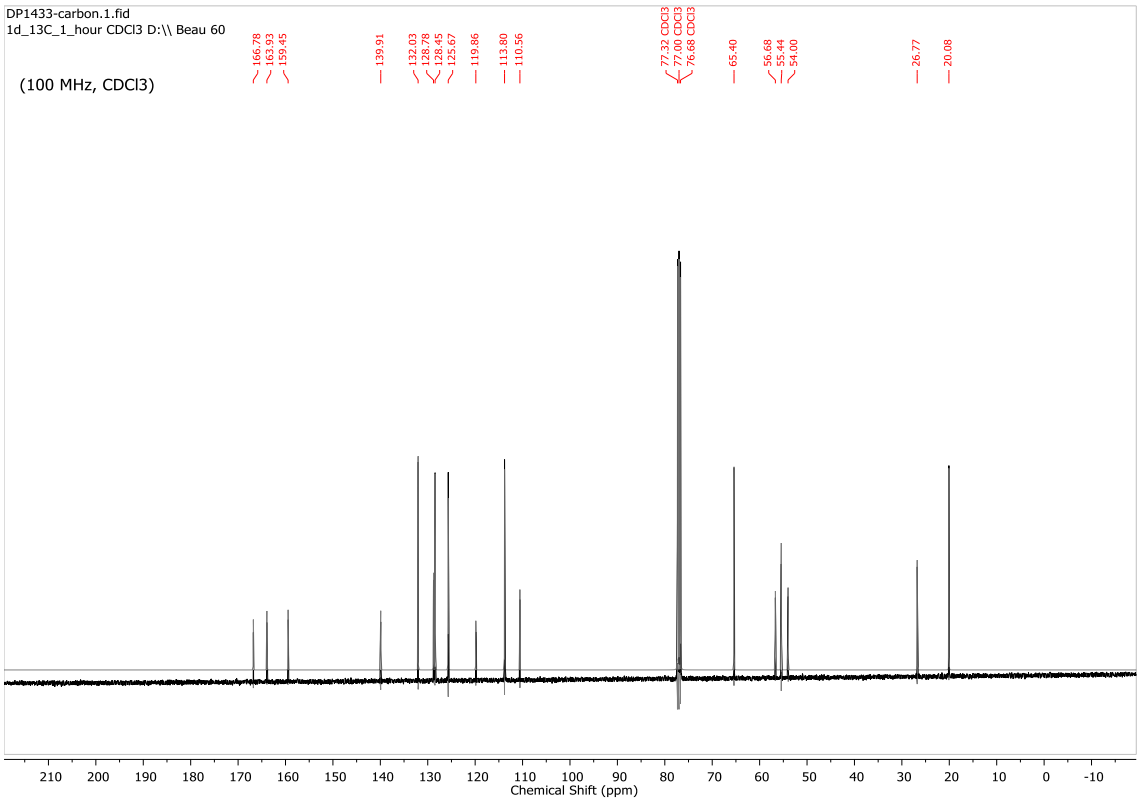

1-H NMR (400 MHz; CDCl3):
8.662
8.082
8.060
6.959
6.937
4.042
4.020
3.998
3.976
3.873
2.183
2.166
2.148
2.131
2.114
2.097
2.079
0.998
0.981
OMe
O
F3C
N
N
H
O
O
1e
1.95
1.96
2.92
1.97
1.94
1.02
5.84
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2

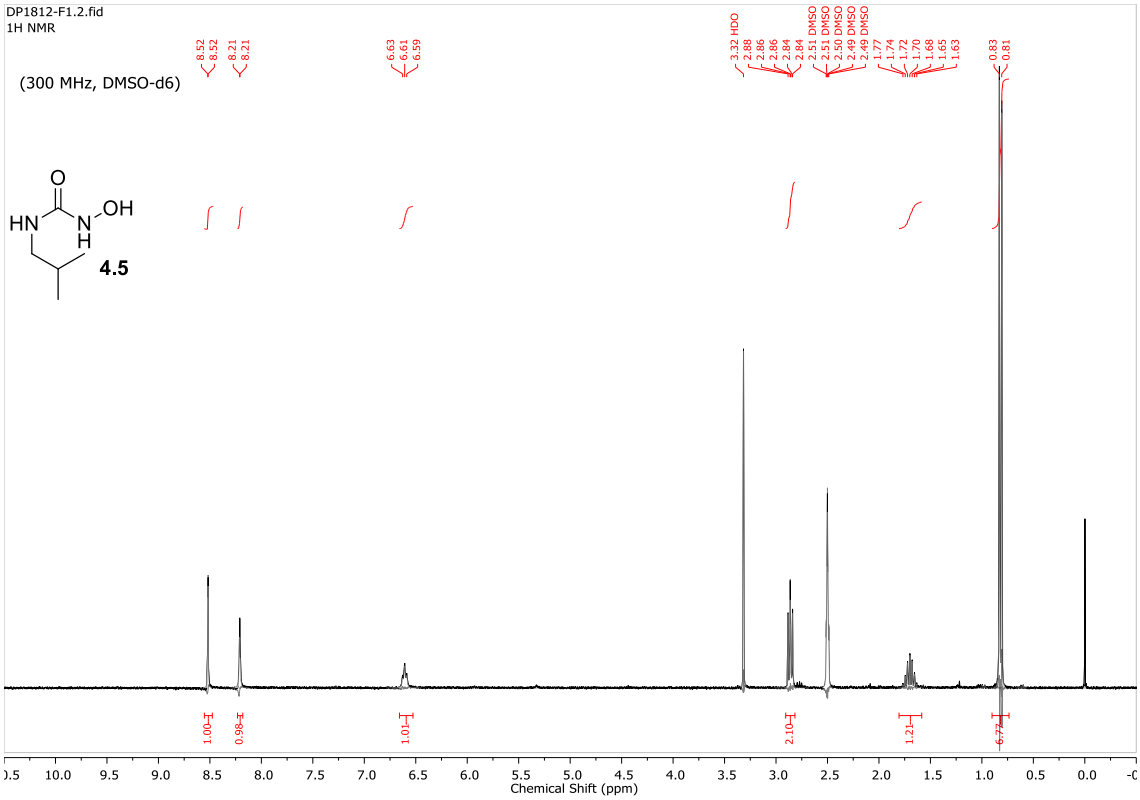

1-H NMR (400 MHz; CDCl3):
166.387
164.363
158.124
132.157
118.905
114.030
55.547
55.306
27.092
19.982
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

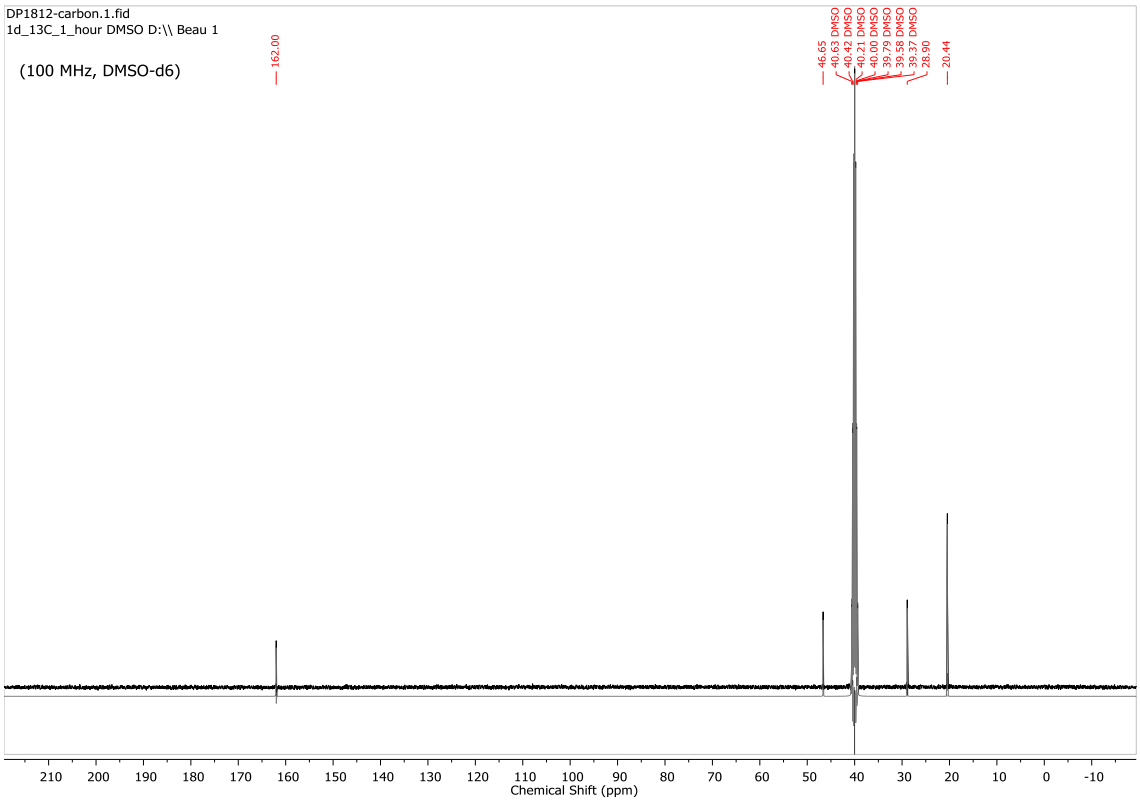
19-F NMR (282 MHz; $CDCl_3$):

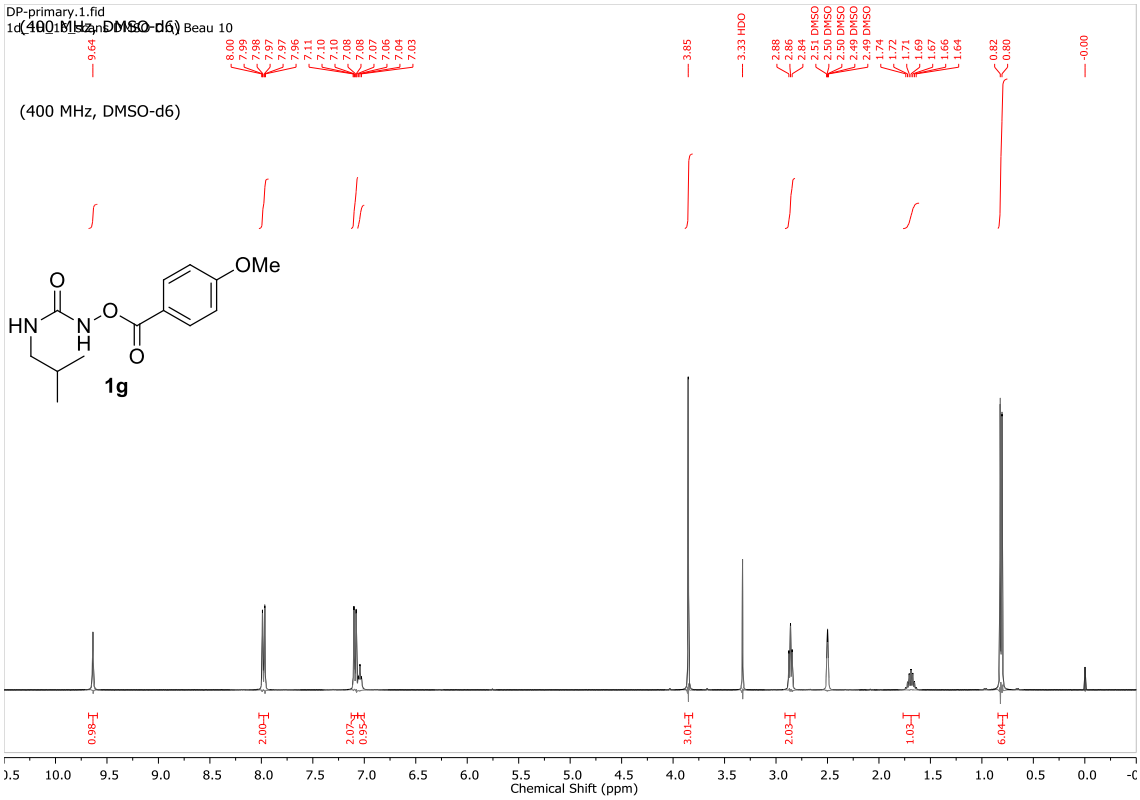


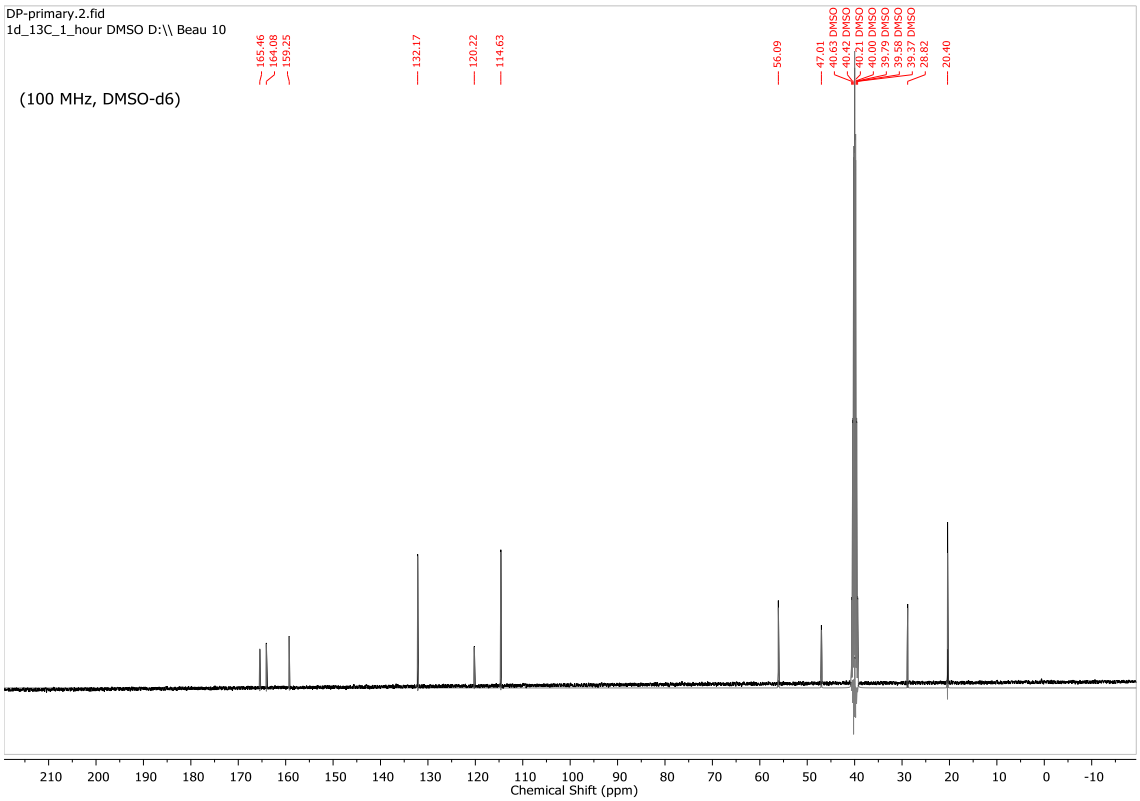

DP1436-F1.1.fid
1H NMR
(400 MHz, CDCl3)
OMe
1f
Chemical Shift (ppm)


DP1433-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 60
(100 MHz, CDCl3)
Chemical Shift (ppm)

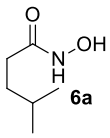

DP1812-F1.2.fid
1H NMR
(300 MHz, DMSO-d6)
4.5
Chemical Shift (ppm)


DP1812-carbon.1.fid
1d_13C_1_hour DMSO D:\\ Beau 1
(100 MHz, DMSO-d6)
Chemical Shift (ppm)


DP-primary.1.fid
1d_1H_1_hour DMSO D:\\ Beau 10
(400 MHz, DMSO-d6)
OMe
HN
N
H
O
O
O
1g
Chemical Shift (ppm)

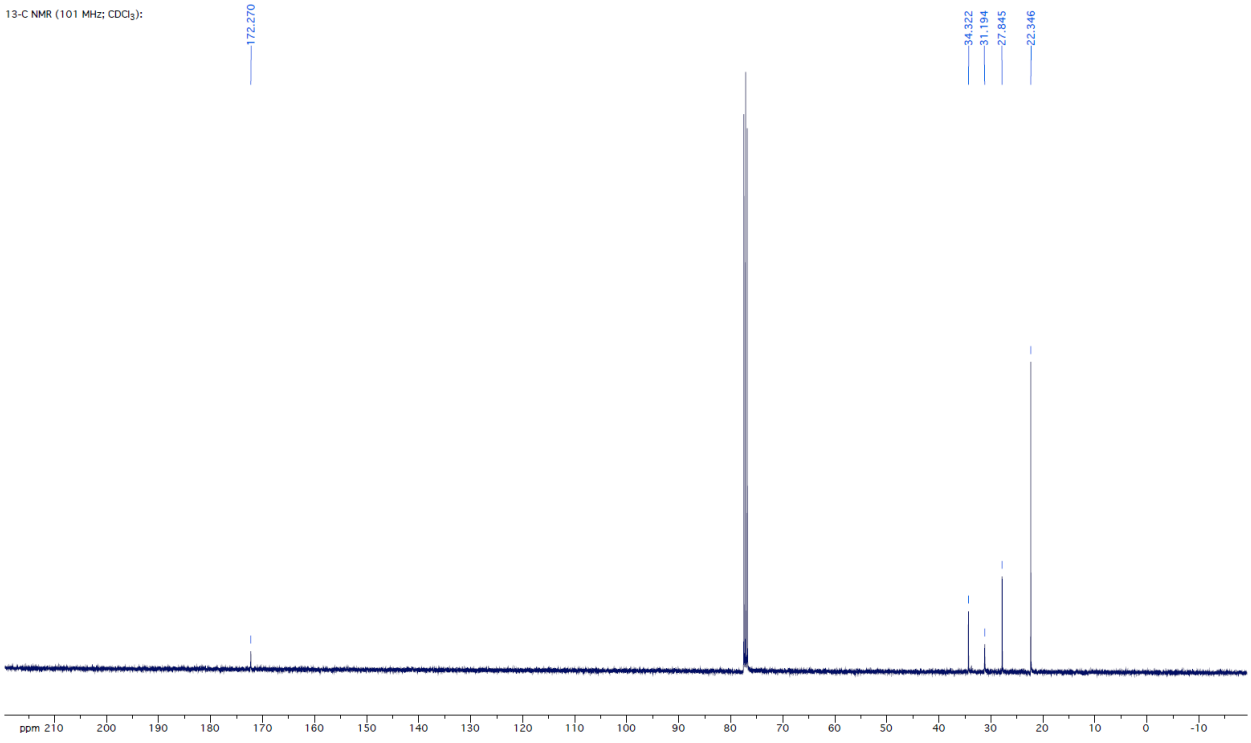

DP-primary.2.fid
1d_13C_1_hour DMSO D:\\ Beau 10
(100 MHz, DMSO-d6)
Chemical Shift (ppm)

1-H NMR (400 MHz; $CDCl_3$):

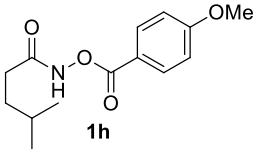


6a

13-C NMR (101 MHz; $CDCl_3$):

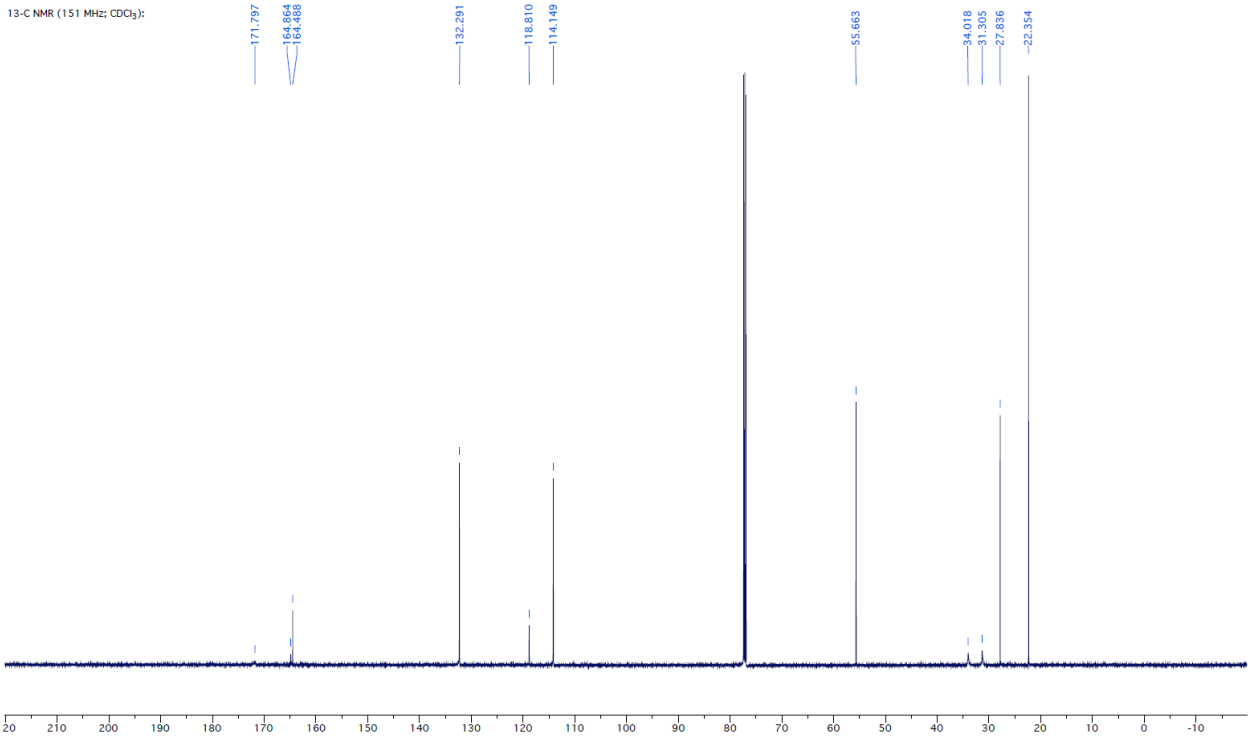


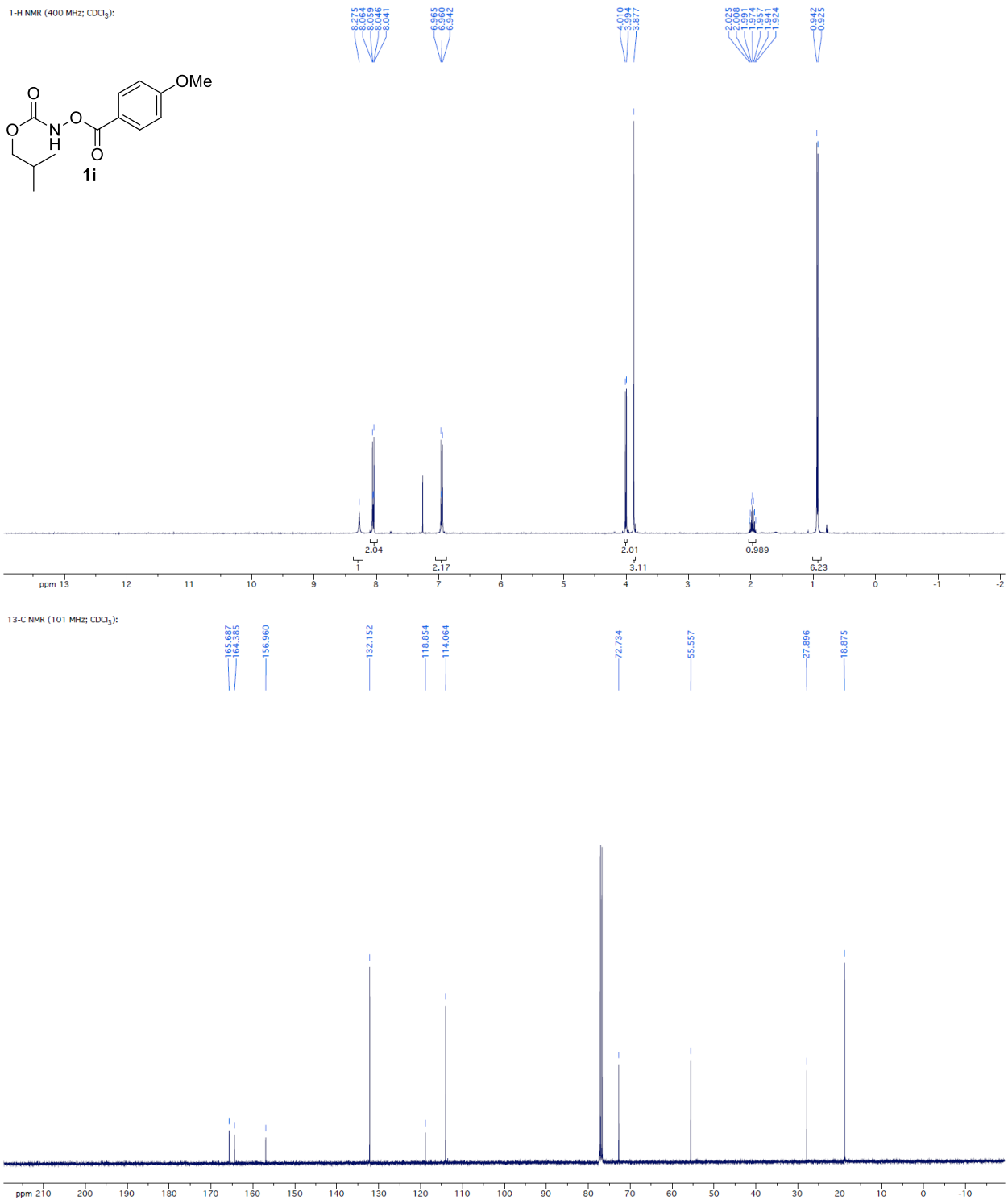
1-H NMR (300 MHz; $CDCl_3$):

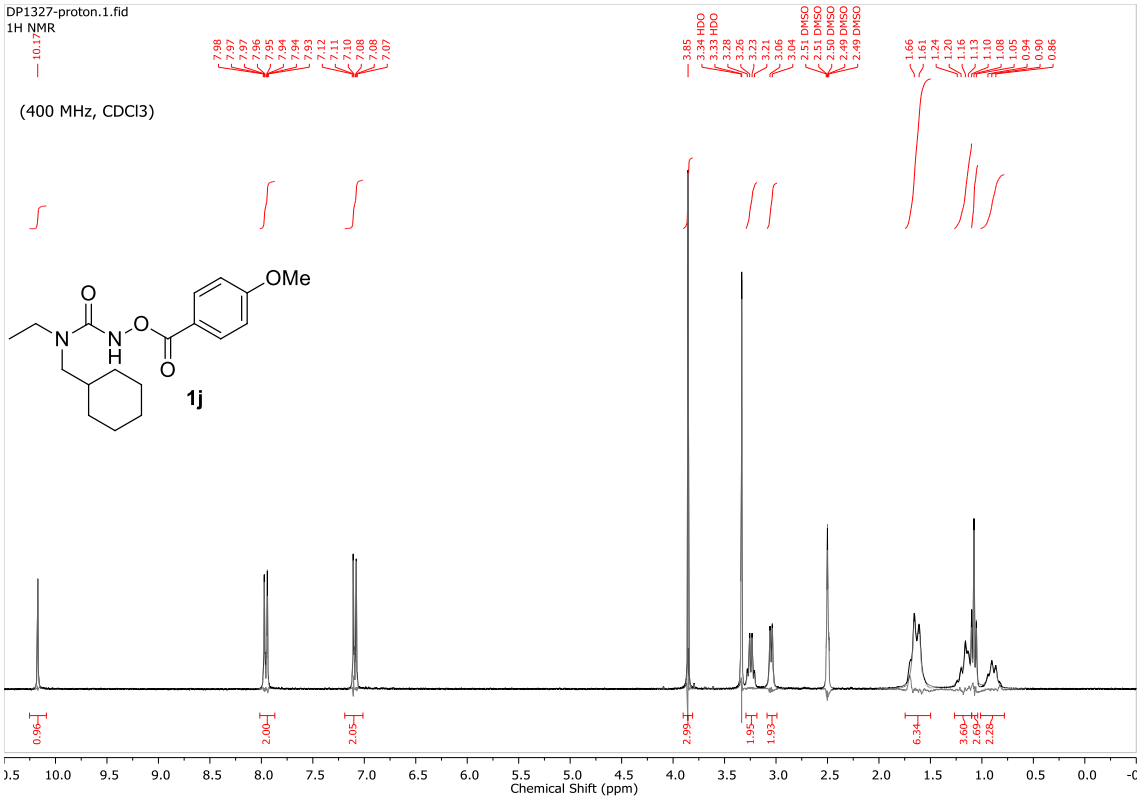


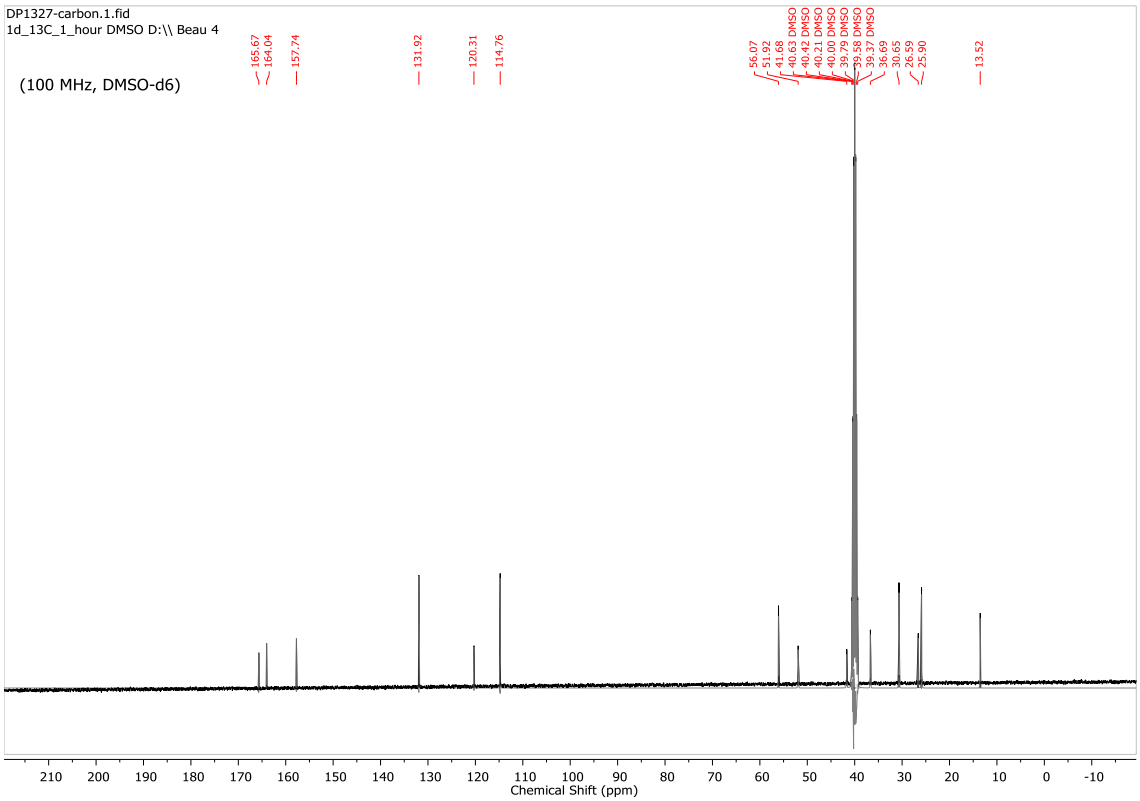
1h

13-C NMR (151 MHz; $CDCl_3$):

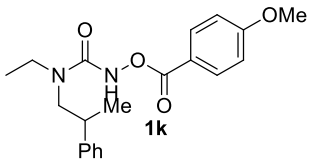



1-H NMR (400 MHz; CDCl3):
8.275
8.064
8.059
8.046
8.041
6.965
6.960
6.942
4.010
3.994
3.977
2.025
2.008
1.991
1.974
1.957
1.941
1.924
0.942
0.925
OMe
O
O
N
H
O
O
1i
2.04
2.17
2.01
3.11
0.989
6.23
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
13-C NMR (101 MHz; CDCl3):
165.687
164.385
156.960
132.152
118.854
114.064
72.734
55.557
27.896
18.875
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


DP1327-proton.1.fid
1H NMR
(400 MHz, CDCl3)
OMe
1j
Chemical Shift (ppm)

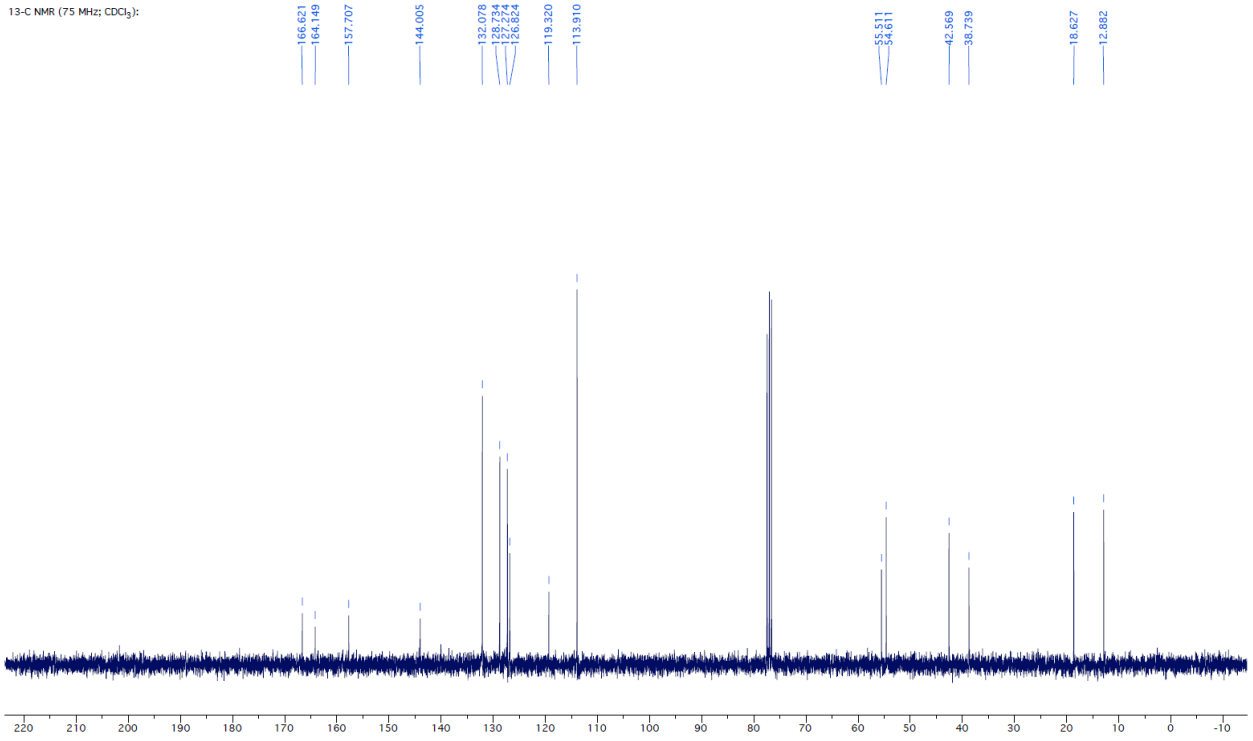

DP1327-carbon.1.fid
1d_13C_1_hour DMSO D:\\ Beau 4
(100 MHz, DMSO-d6)
Chemical Shift (ppm)

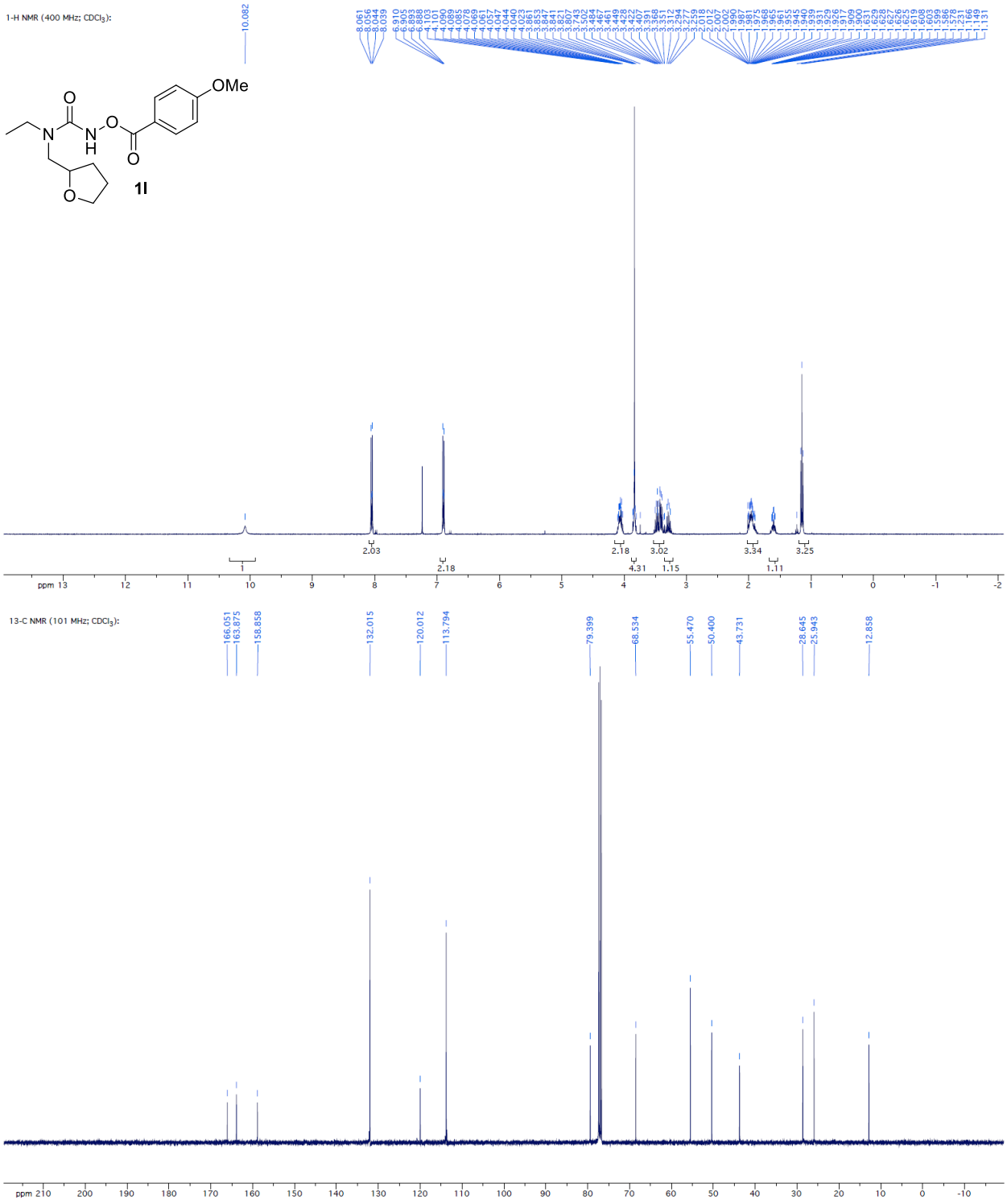
1-H NMR (300 MHz; $CDCl_3$):



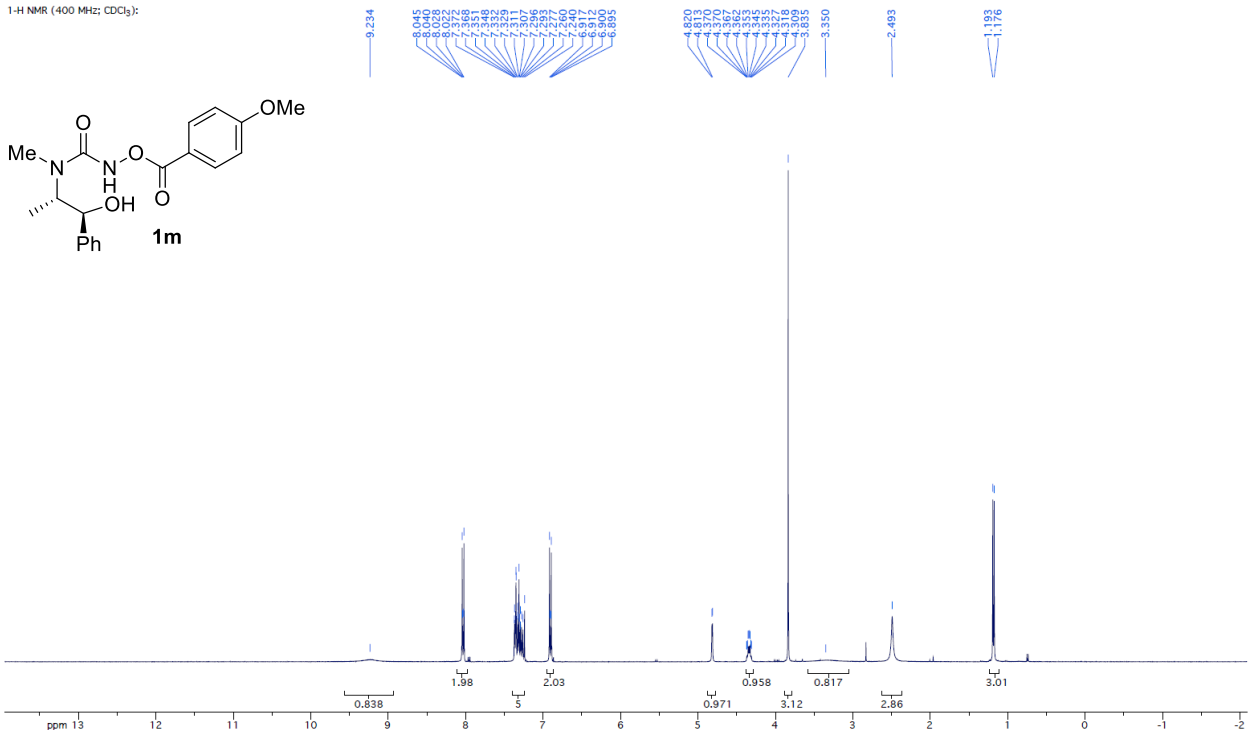
1k

13-C NMR (75 MHz; $CDCl_3$):



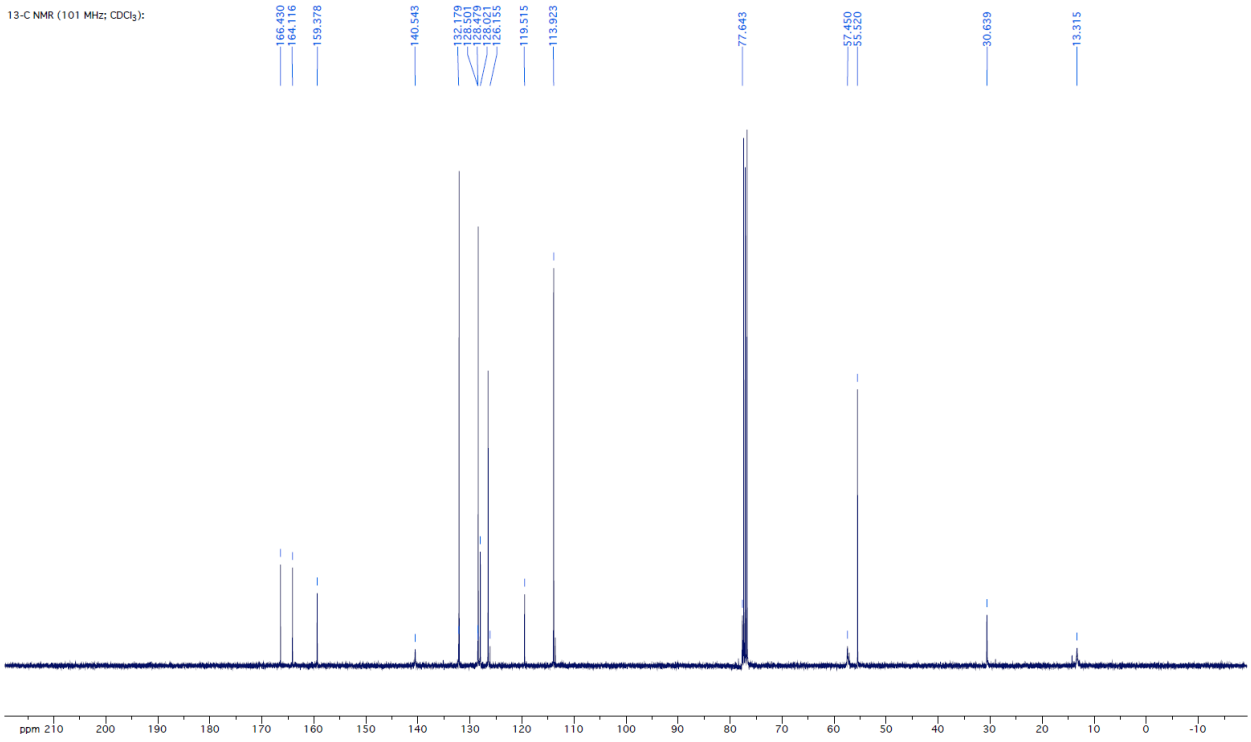

1-H NMR (400 MHz; CDCl3):
10.082
OMe
O
N
N
H
O
O
O
1l
2.03
2.18
2.18
4.31
3.02
1.15
3.34
1.11
3.25
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
13-C NMR (101 MHz; CDCl3):
166.051
163.875
158.858
132.015
120.012
113.794
79.399
68.534
55.470
50.400
43.731
28.645
25.943
12.858
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

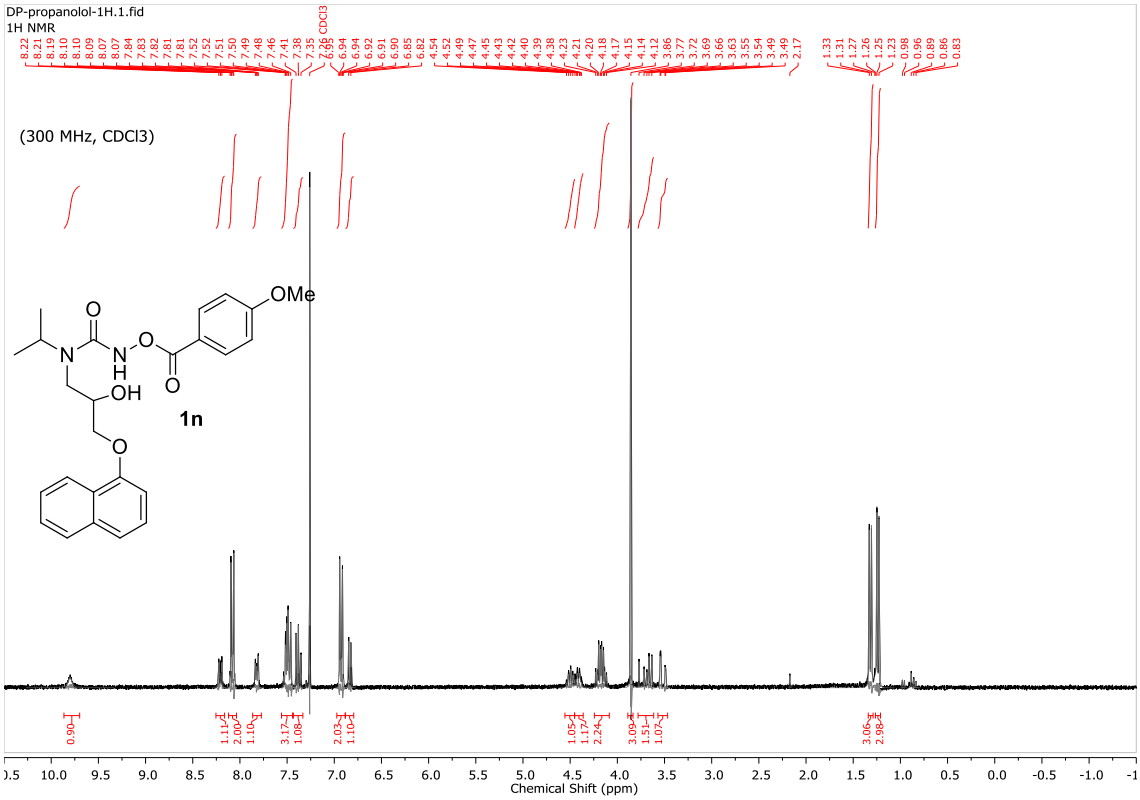
1-H NMR (400 MHz; $CDCl_3$):

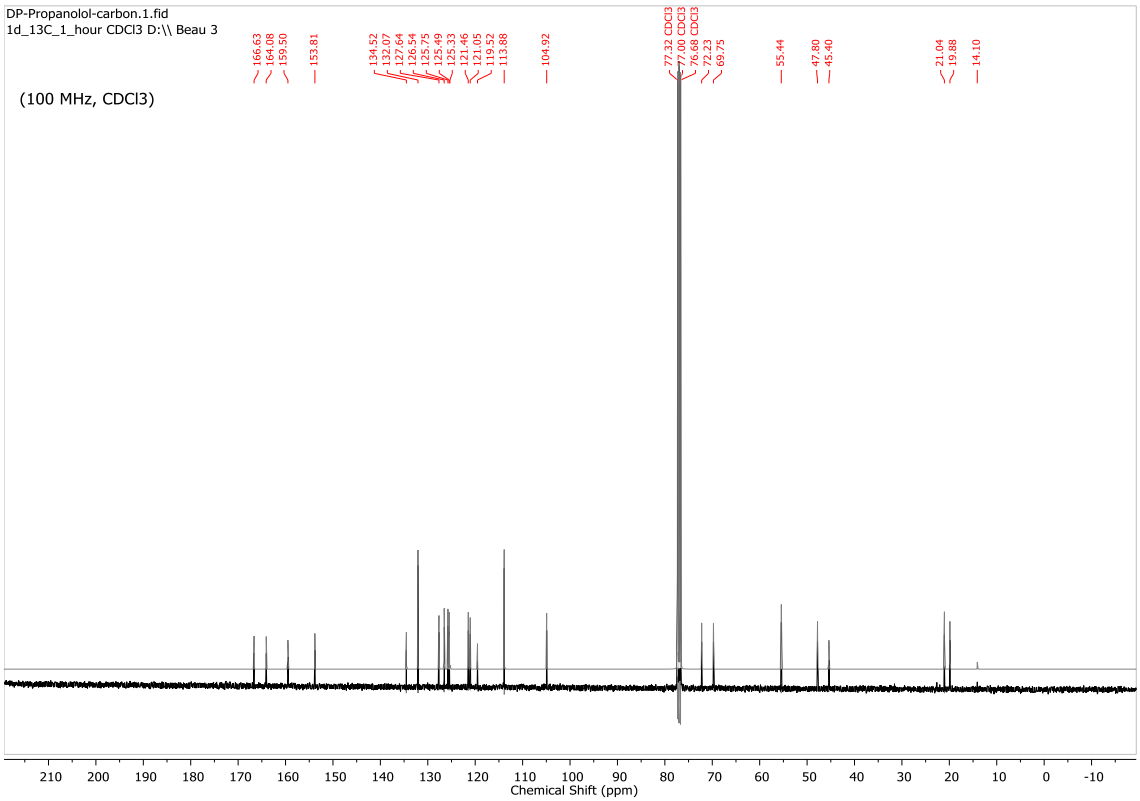


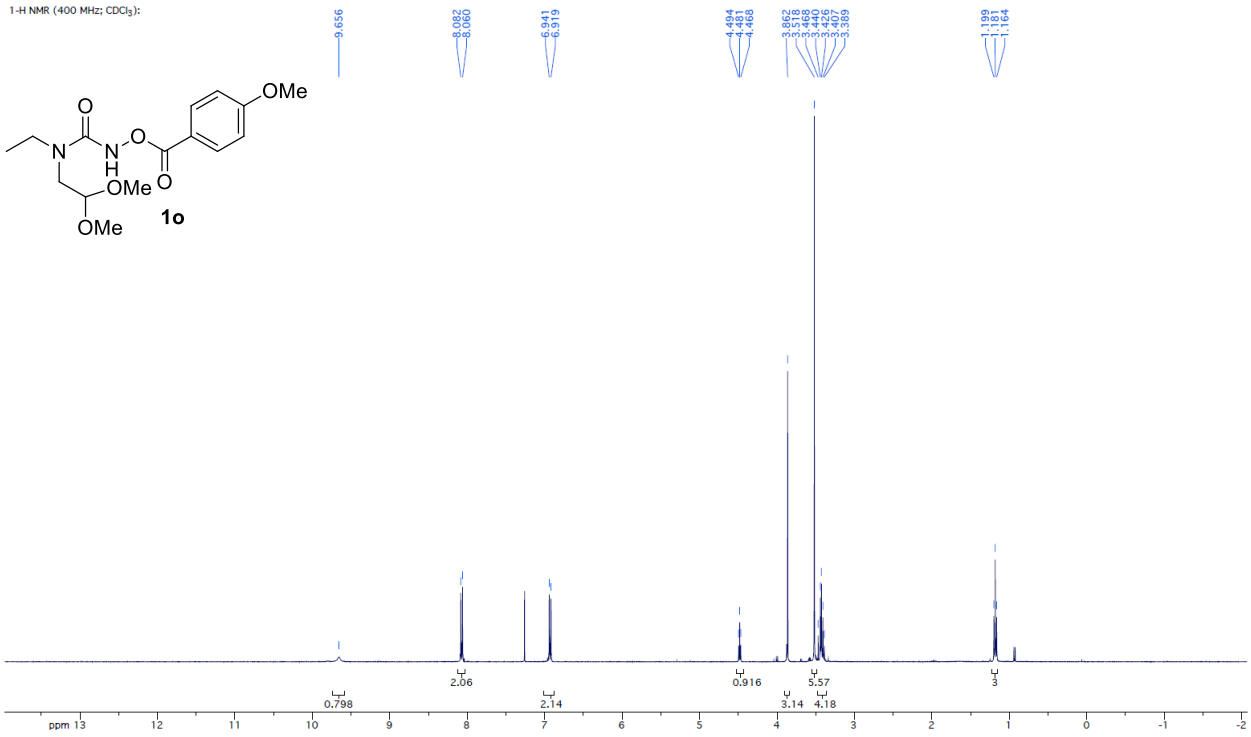
1m

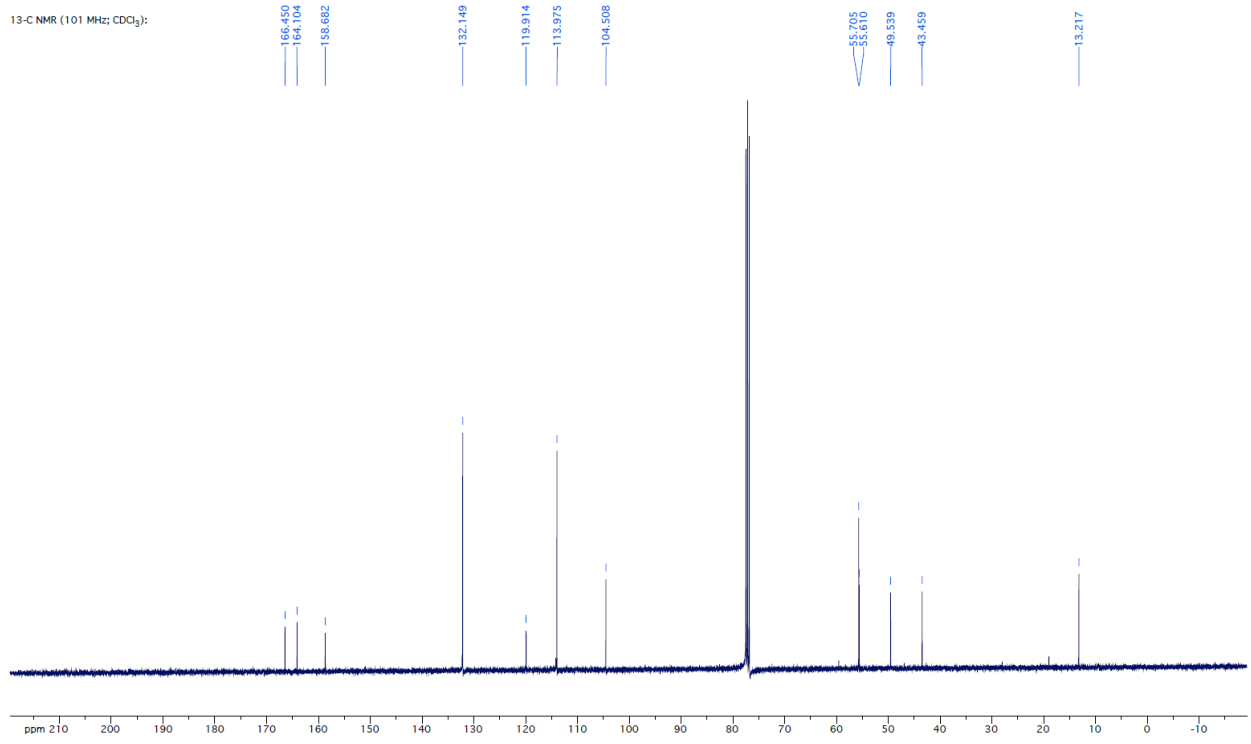
13-C NMR (101 MHz; $CDCl_3$):

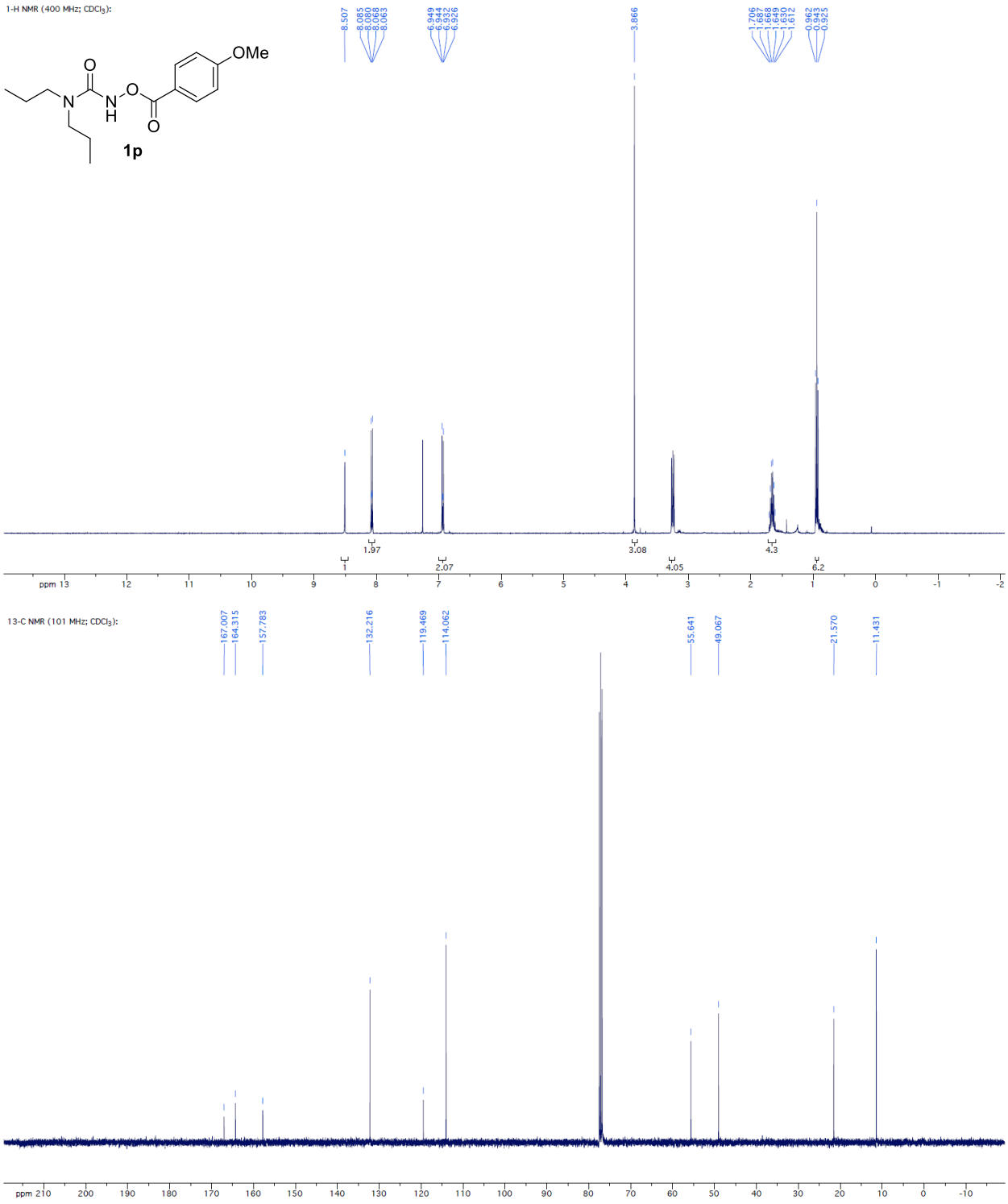


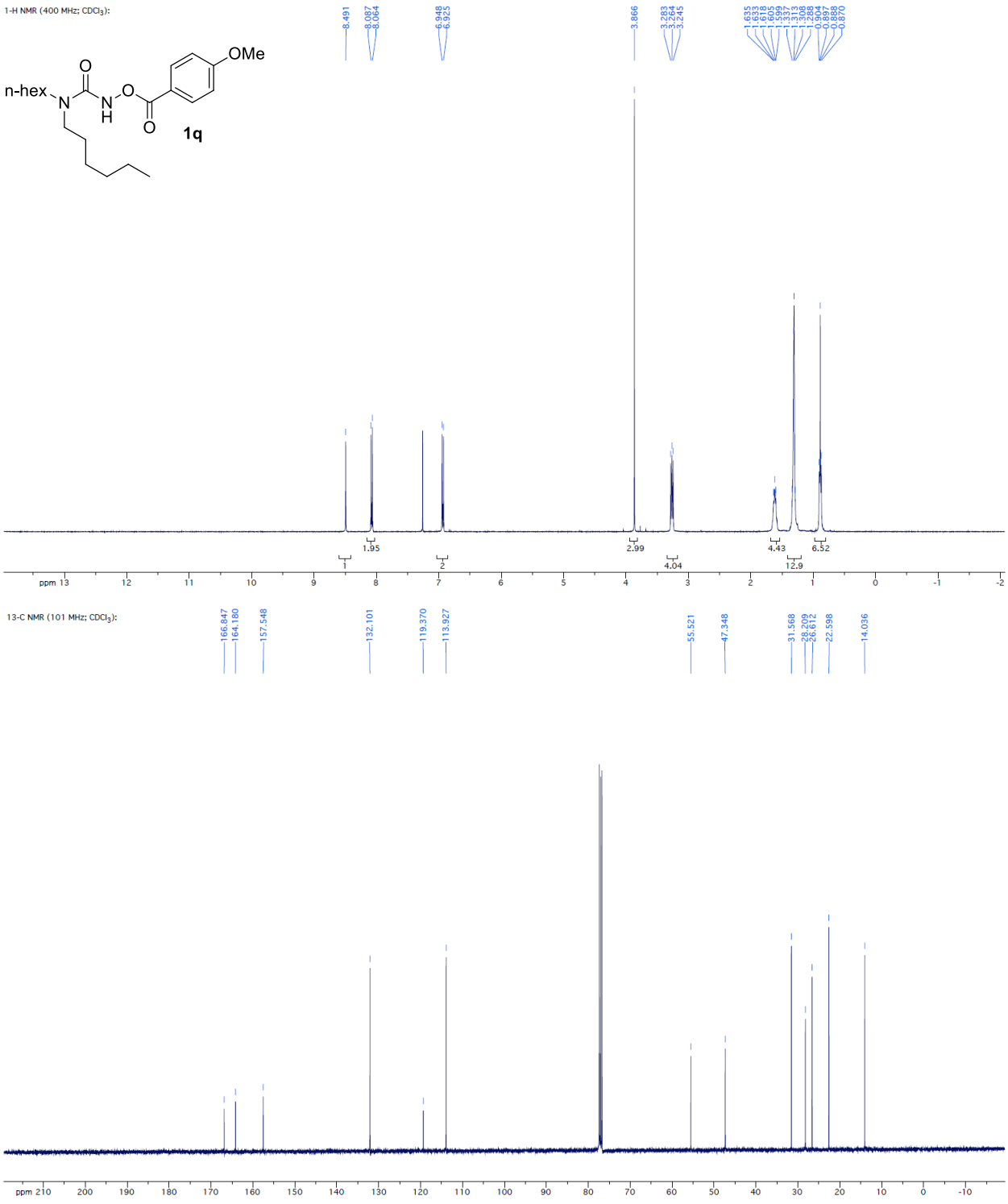

DP-propanolol-1H.1.fid
1H NMR
(300 MHz, CDCl3)
OMe
1n
Chemical Shift (ppm)

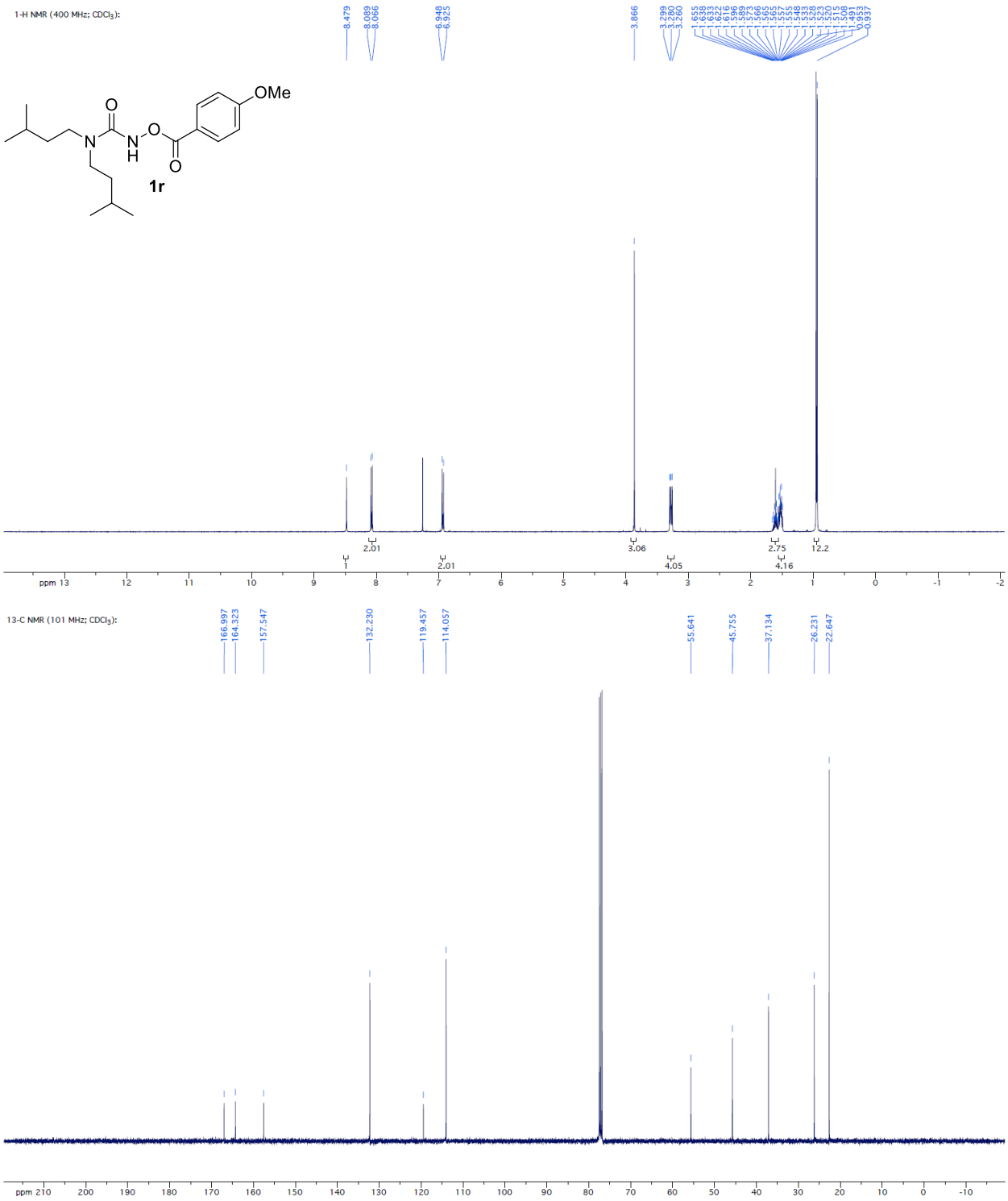

DP-Propanolol-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 3
(100 MHz, CDCl3)
Chemical Shift (ppm)

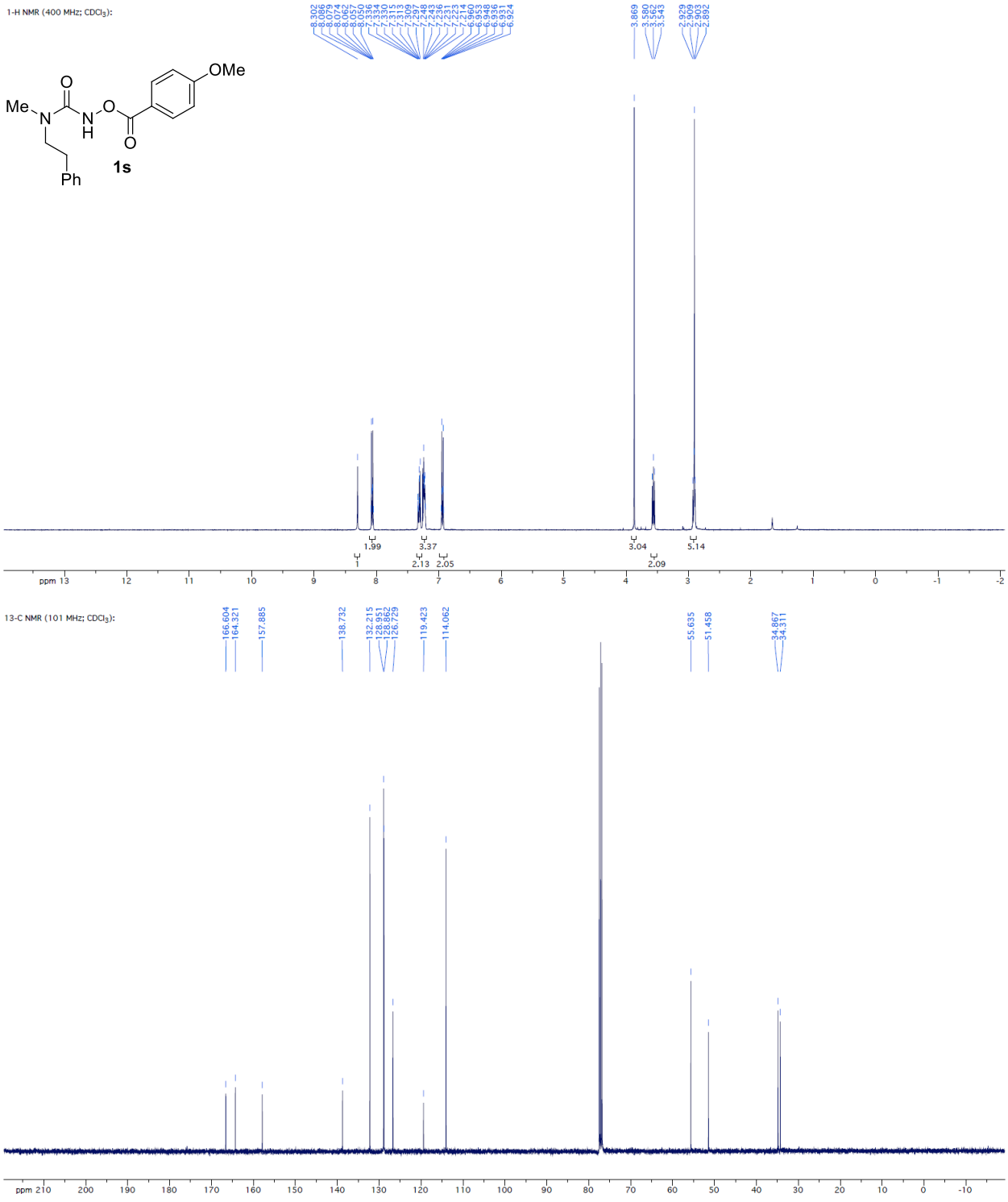

1-H NMR (400 MHz; CDCl3):
9.656
8.082
8.060
6.941
6.919
4.494
4.481
4.468
3.862
3.518
3.468
3.440
3.426
3.407
3.389
1.199
1.181
1.164
OMe
O
N
N
H
O
O
OMe
OMe
1o
2.06
0.798
2.14
0.916
3.14
5.57
4.18
3
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2

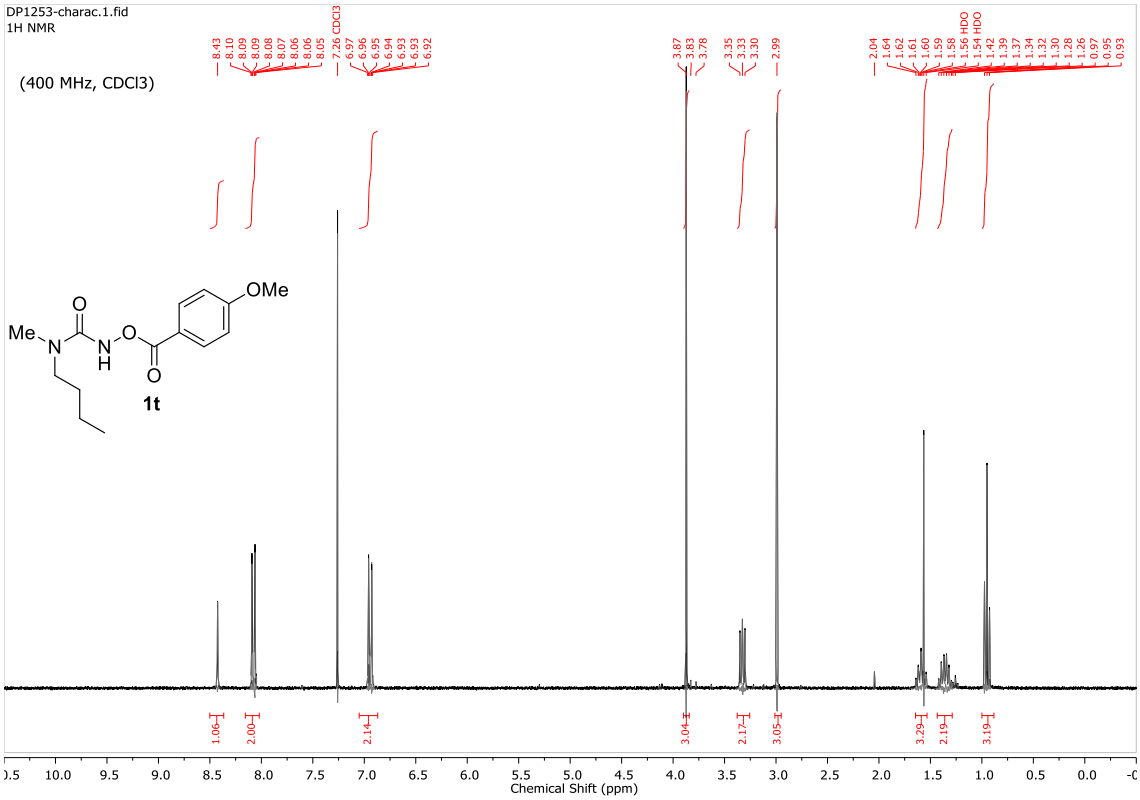

13-C NMR (101 MHz; CDCl3):
166.450
164.104
158.682
132.149
119.914
113.975
104.508
55.705
55.610
49.539
43.459
13.217
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

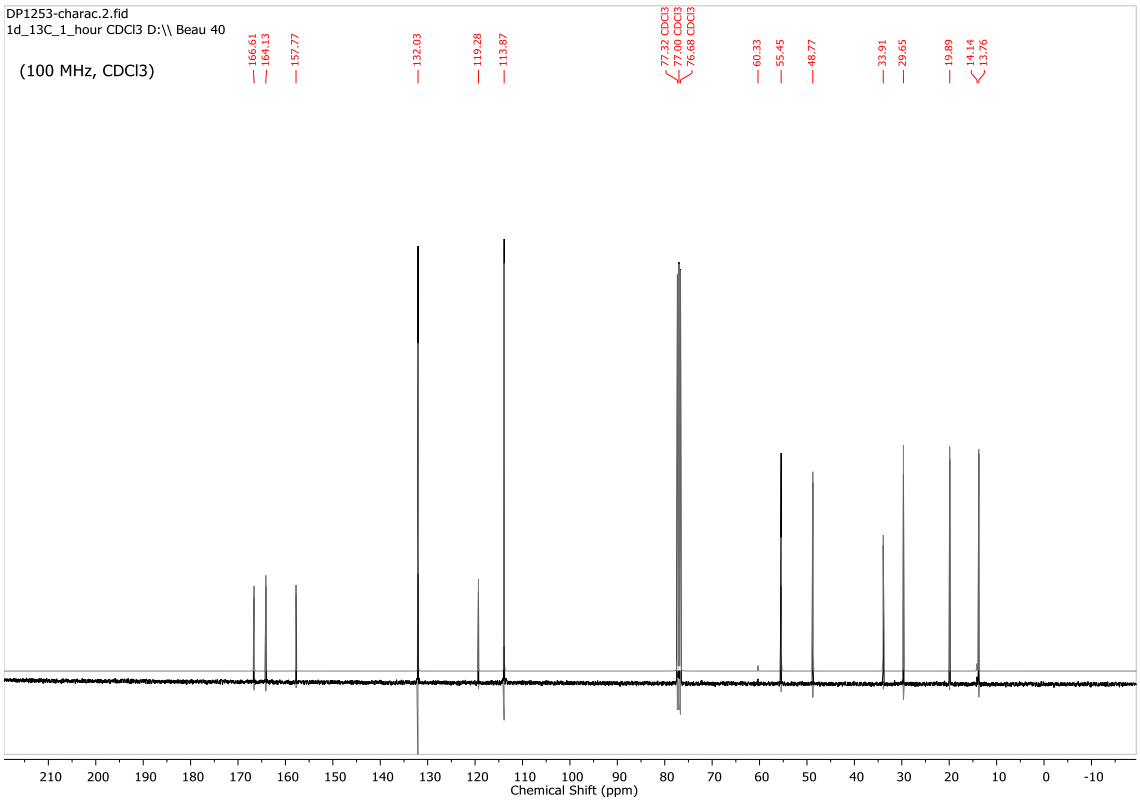

1-H NMR (400 MHz; CDCl3):
OMe
1p
8.507
8.085
8.080
8.065
8.063
6.949
6.944
6.932
6.926
3.866
1.706
1.687
1.668
1.649
1.630
1.612
0.962
0.943
0.925
1.97
2.07
3.08
4.05
4.3
6.2
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
13-C NMR (101 MHz; CDCl3):
167.007
164.315
157.783
132.216
119.469
114.062
55.641
49.067
21.570
11.431
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


1-H NMR (400 MHz; CDCl3):
n-hex
N
O
N
H
O
O
OMe
1q
8.491
8.087
8.064
6.948
6.925
3.866
3.283
3.264
3.245
1.635
1.633
1.618
1.605
1.599
1.337
1.313
1.308
1.288
0.897
0.894
0.888
0.870
1.95
2.99
4.43
6.52
4.04
12.9
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
13-C NMR (101 MHz; CDCl3):
166.847
164.180
157.548
132.101
119.370
113.927
55.521
47.348
31.568
28.209
26.612
22.598
14.036
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

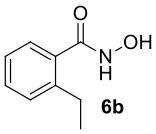

1-H NMR (400 MHz; CDCl3):
8.479
8.089
8.066
6.948
6.925
3.866
3.299
3.280
3.260
OMe
O
N
O
N
H
O
O
1r
2.01
2.01
1
3.06
4.05
2.75
4.16
12.2
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
13-C NMR (101 MHz; CDCl3):
166.997
164.323
157.547
132.230
119.457
114.057
55.641
45.755
37.134
26.231
22.647
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


1-H NMR (400 MHz; CDCl3):
OMe
Me
N
O
N
H
O
O
Ph
1s
13-C NMR (101 MHz; CDCl3):


DP1253-charac.1.fid
1H NMR
(400 MHz, CDCl3)
Me
N
O
N
H
O
O
OMe
1t
Chemical Shift (ppm)

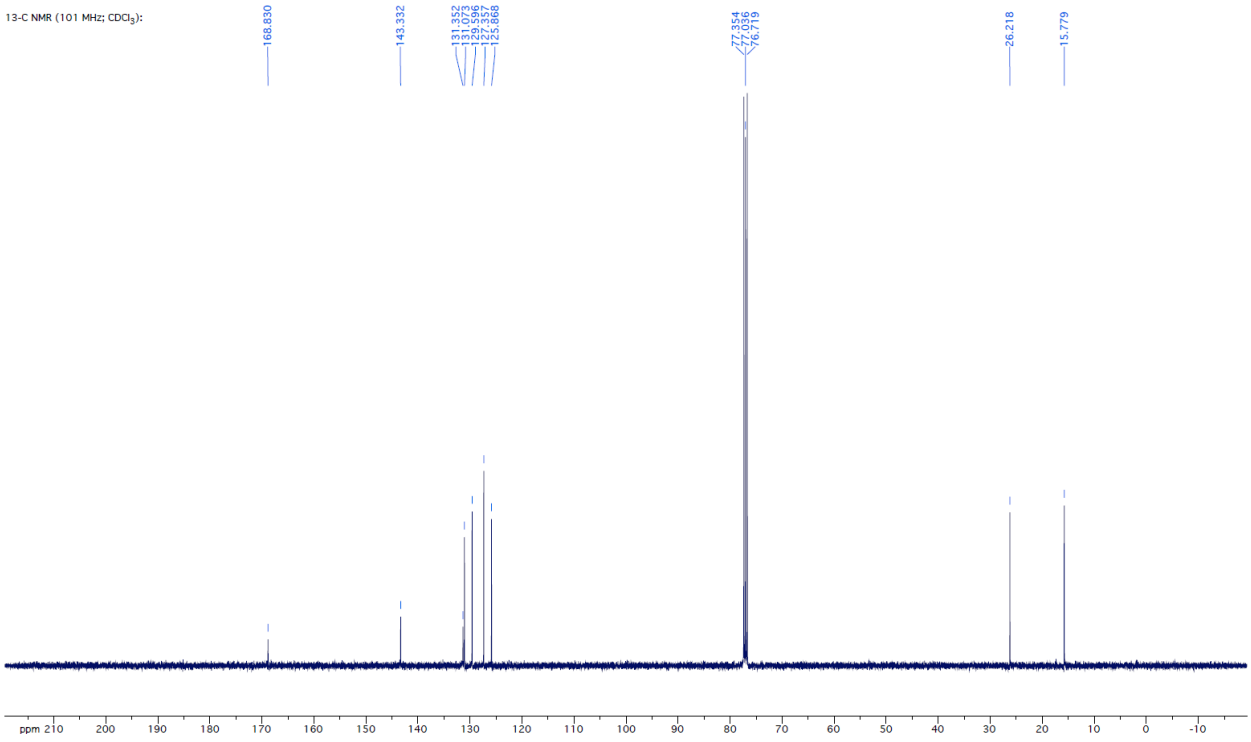

DP1253-charac.2.fid
1d_13C_1_hour CDCl3 D:\\ Beau 40
(100 MHz, CDCl3)
Chemical Shift (ppm)

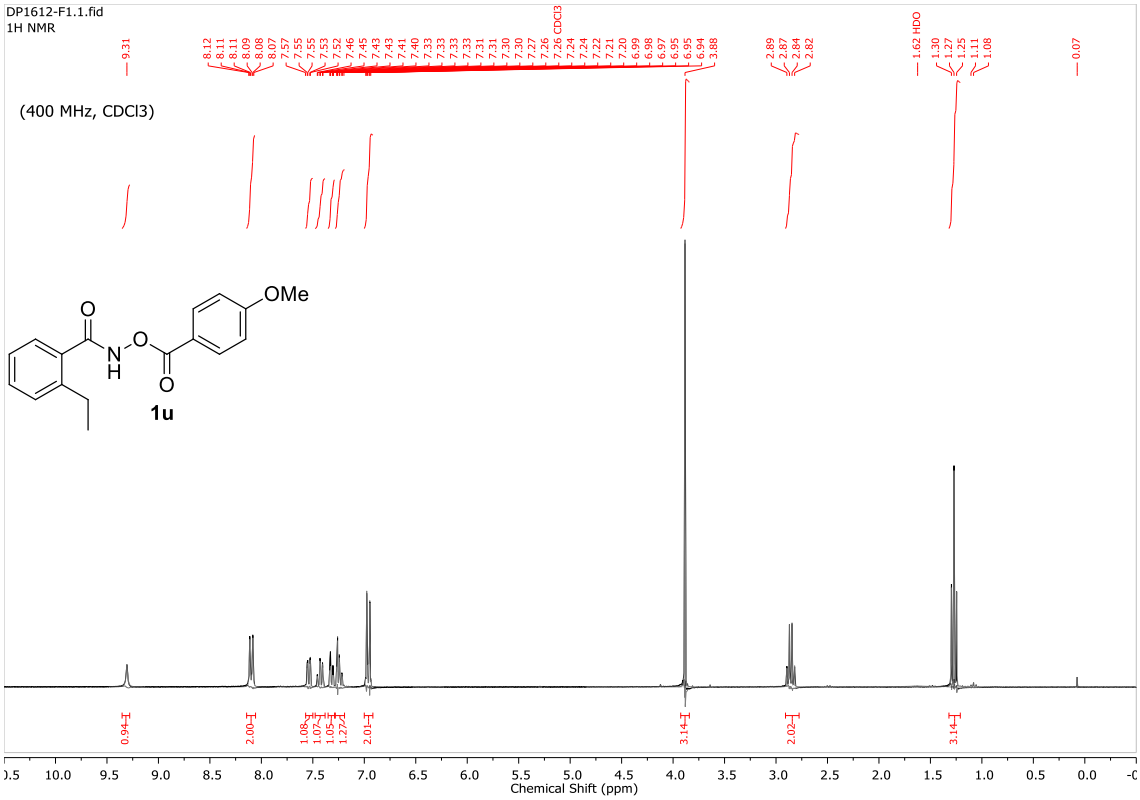
1-H NMR (300 MHz; $CDCl_3$):

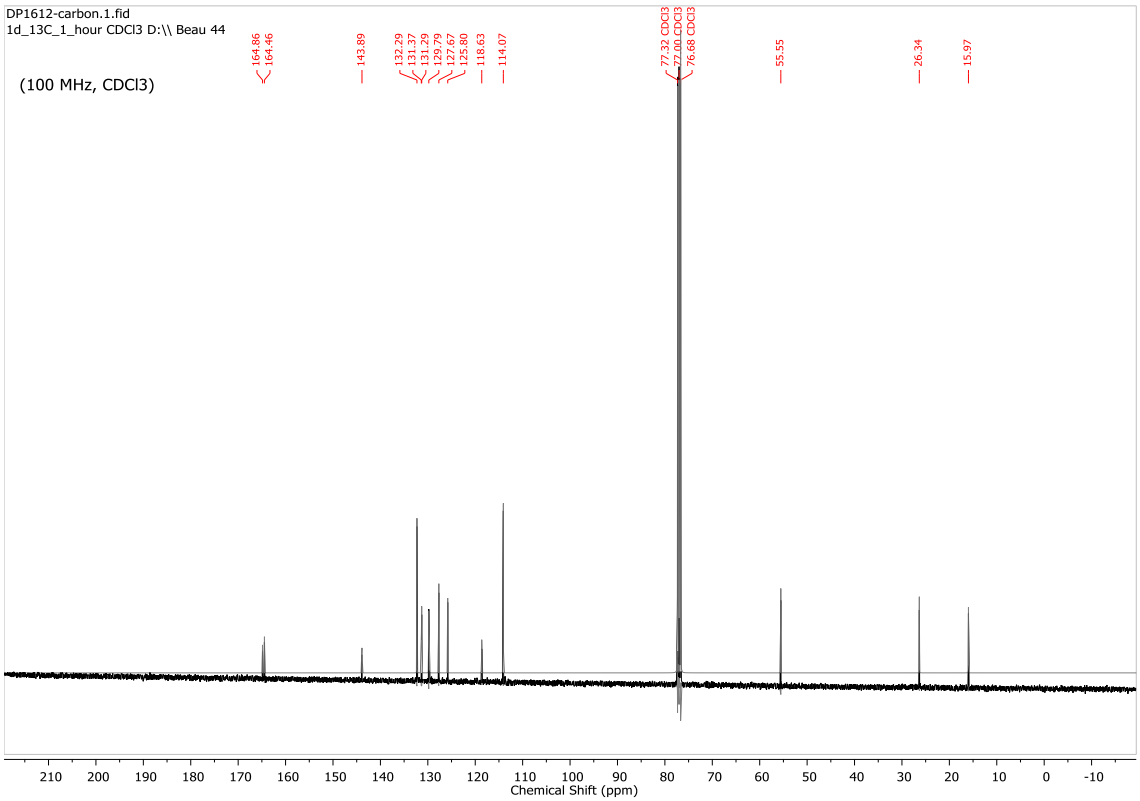


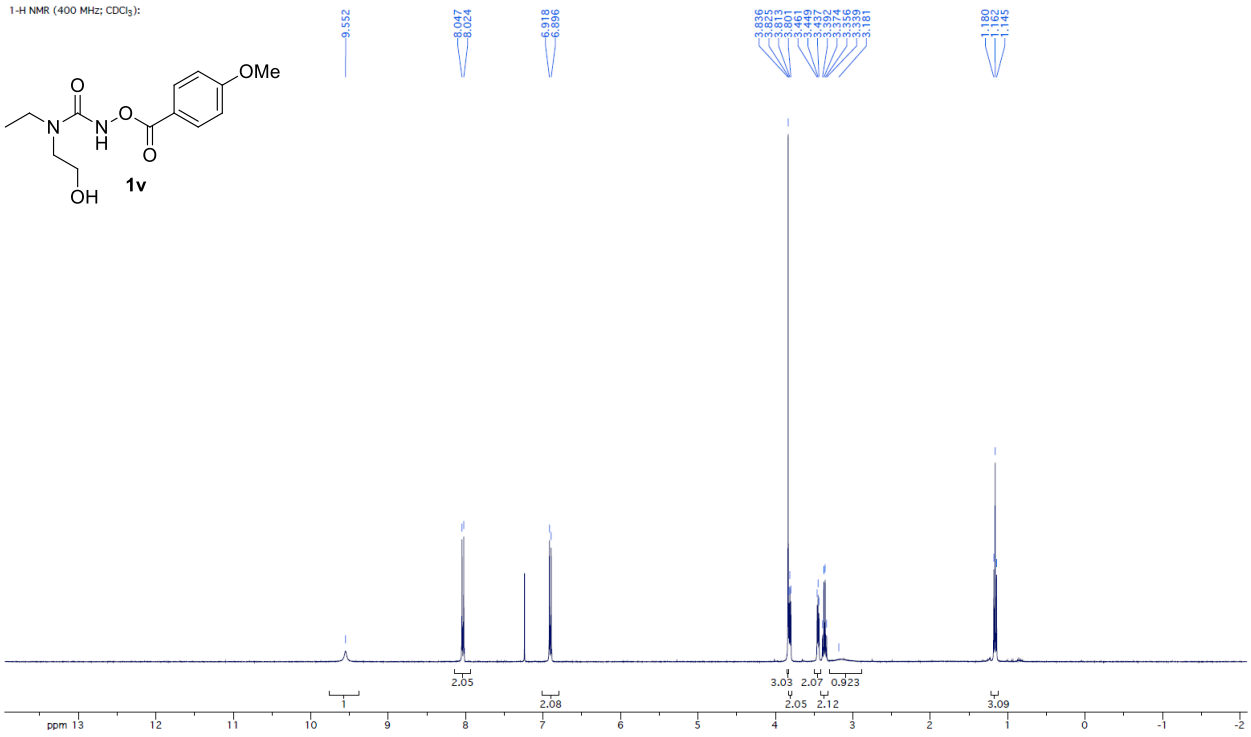
6b

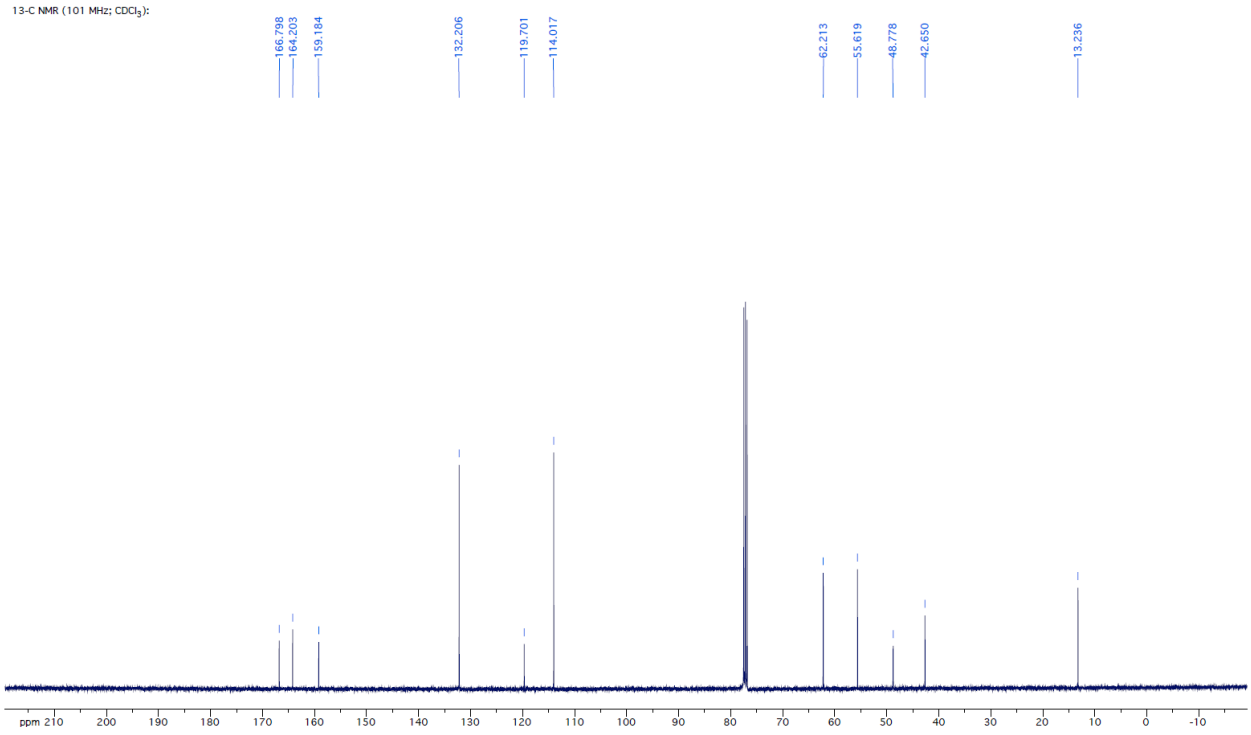
13-C NMR (101 MHz; $CDCl_3$):



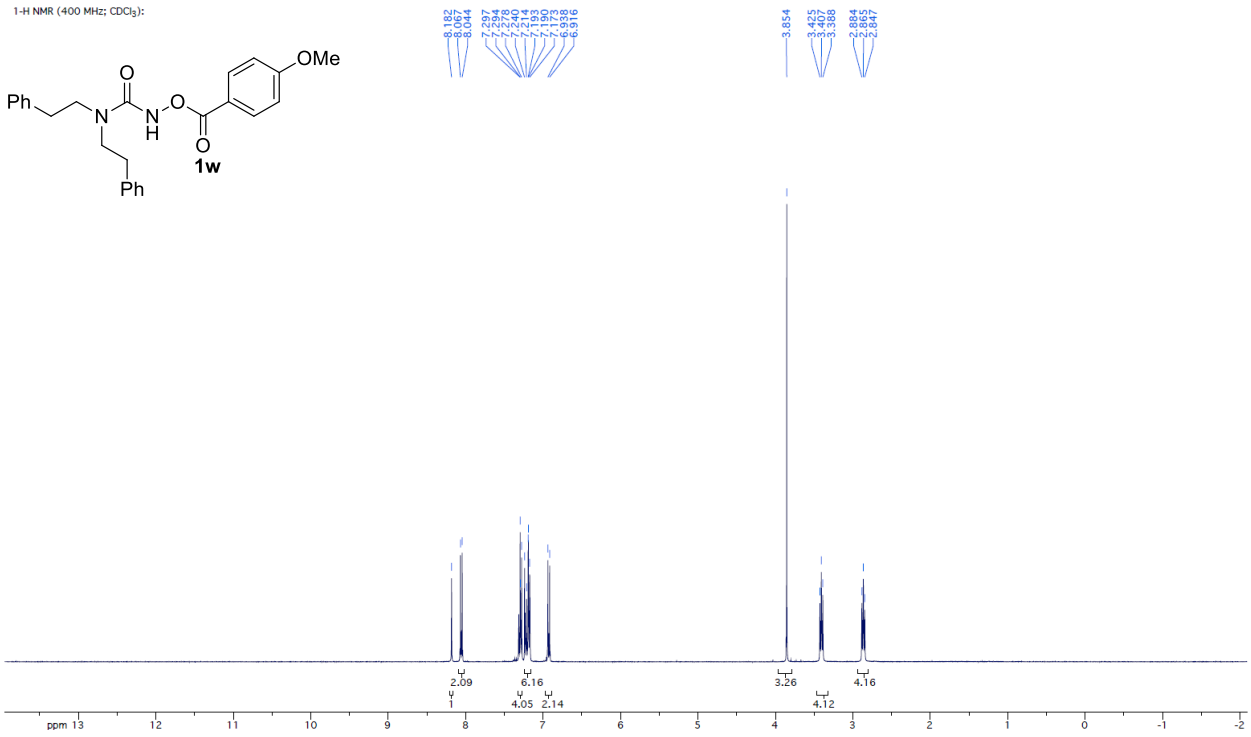

DP1612-F1.1.fid
1H NMR
(400 MHz, CDCl3)
OMe
O
N
H
O
O
1u
Chemical Shift (ppm)


DP1612-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 44
(100 MHz, CDCl3)
Chemical Shift (ppm)

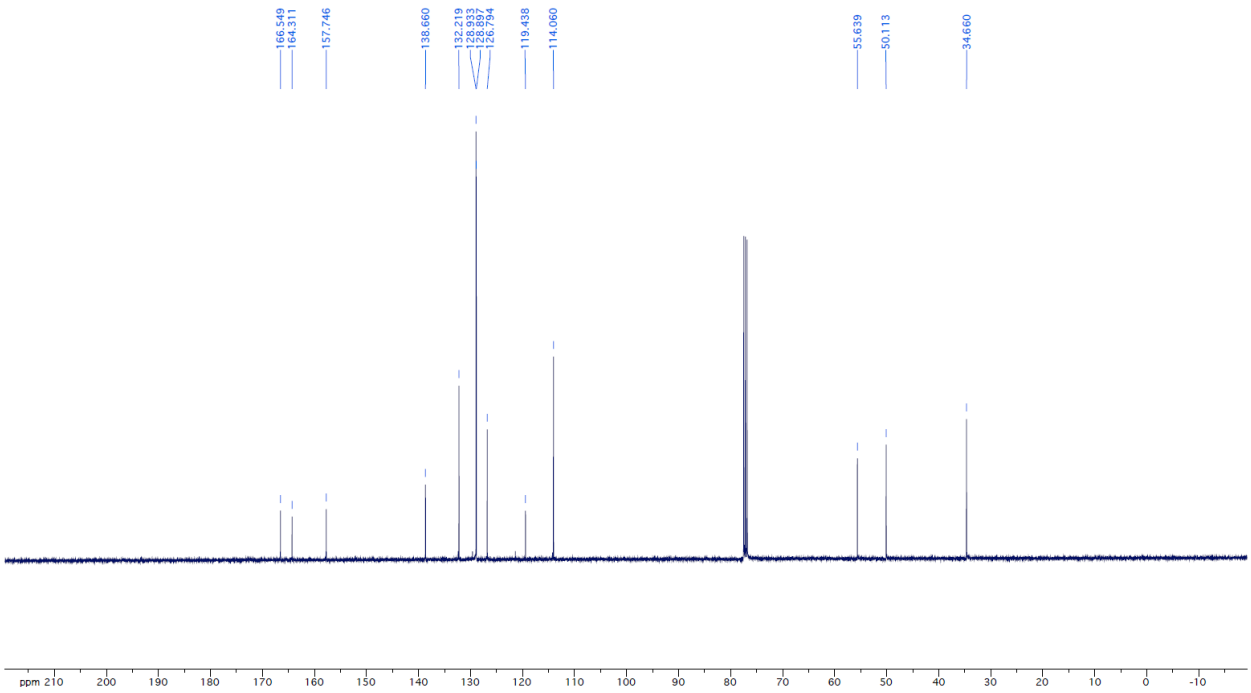

1-H NMR (400 MHz; CDCl3):
9.552
8.047
8.024
6.918
6.896
3.836
3.825
3.813
3.801
3.461
3.449
3.437
3.392
3.374
3.356
3.339
3.181
1.180
1.162
1.145
OMe
O
N
O
N
H
O
OH
1v
2.05
1
2.08
3.03
2.05
2.07
2.12
0.923
3.09
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2

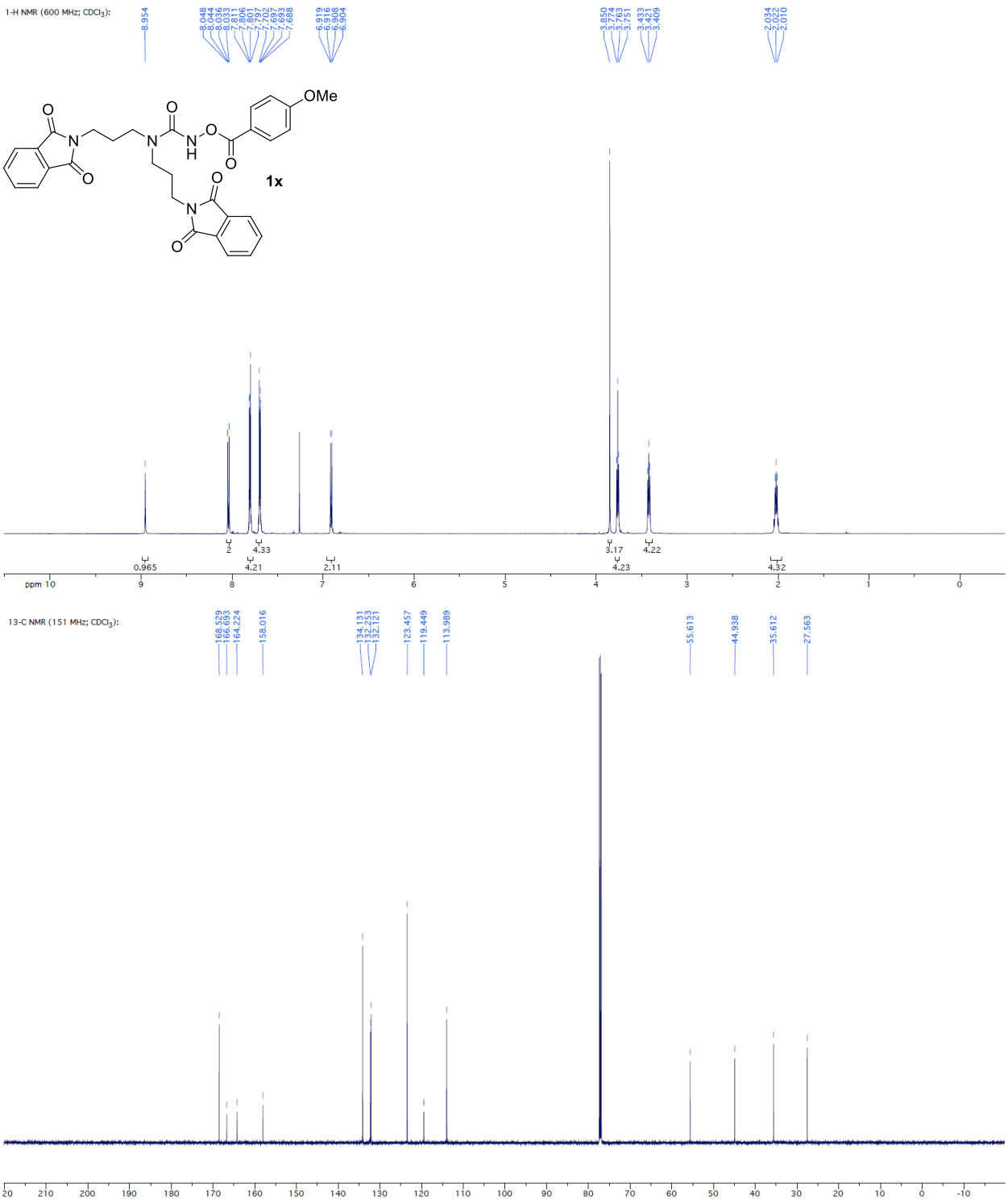

13-C NMR (101 MHz; CDCl3):
166.798
164.203
159.184
132.206
119.701
114.017
62.213
55.619
48.778
42.650
13.236
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

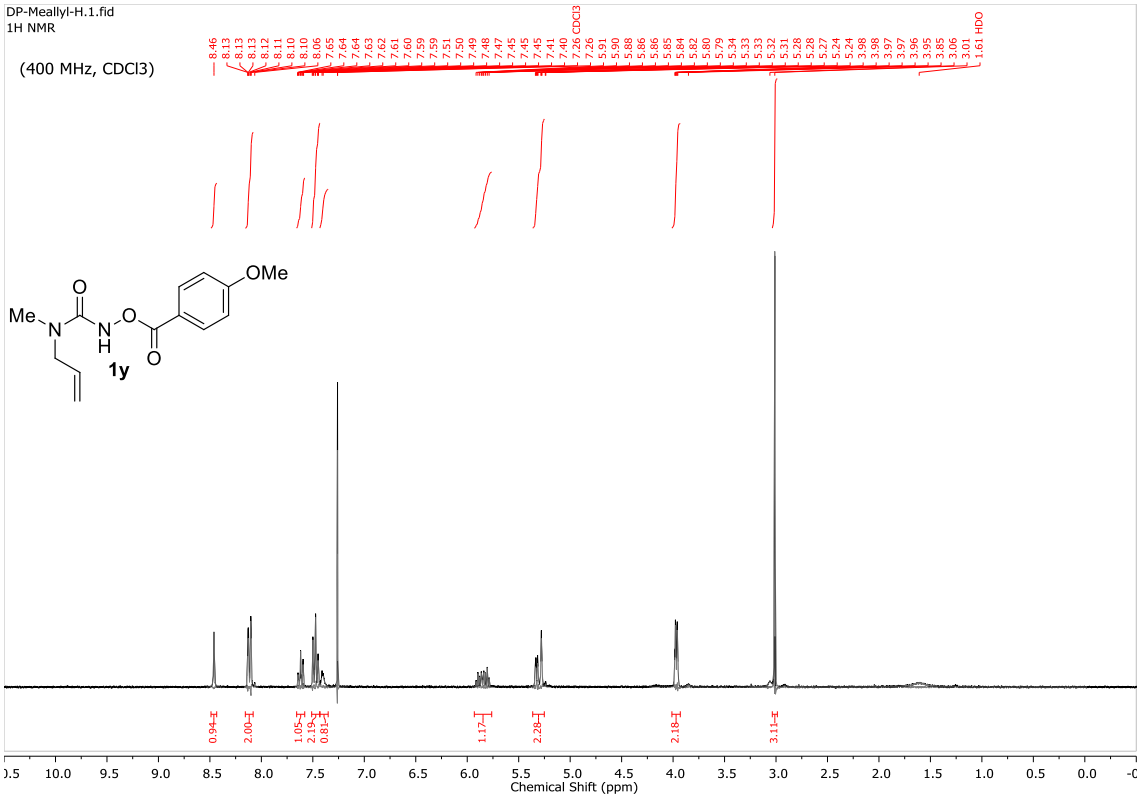
1-H NMR (400 MHz; $CDCl_3$):

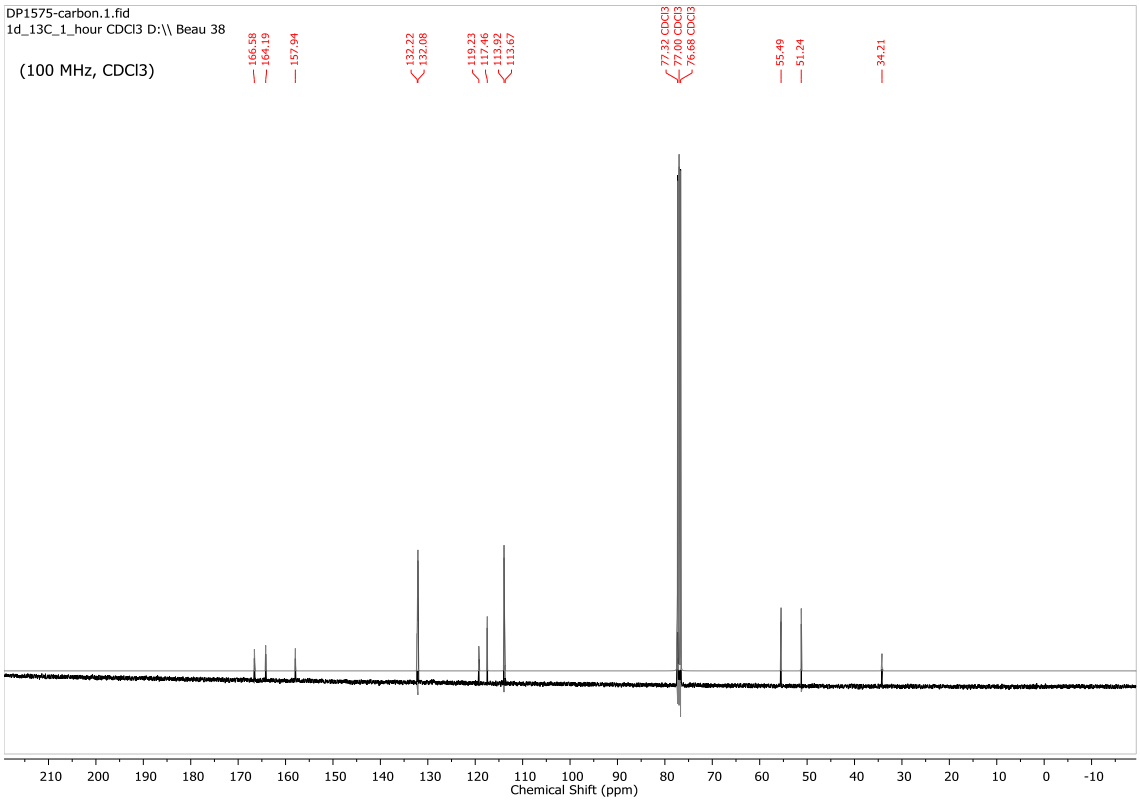


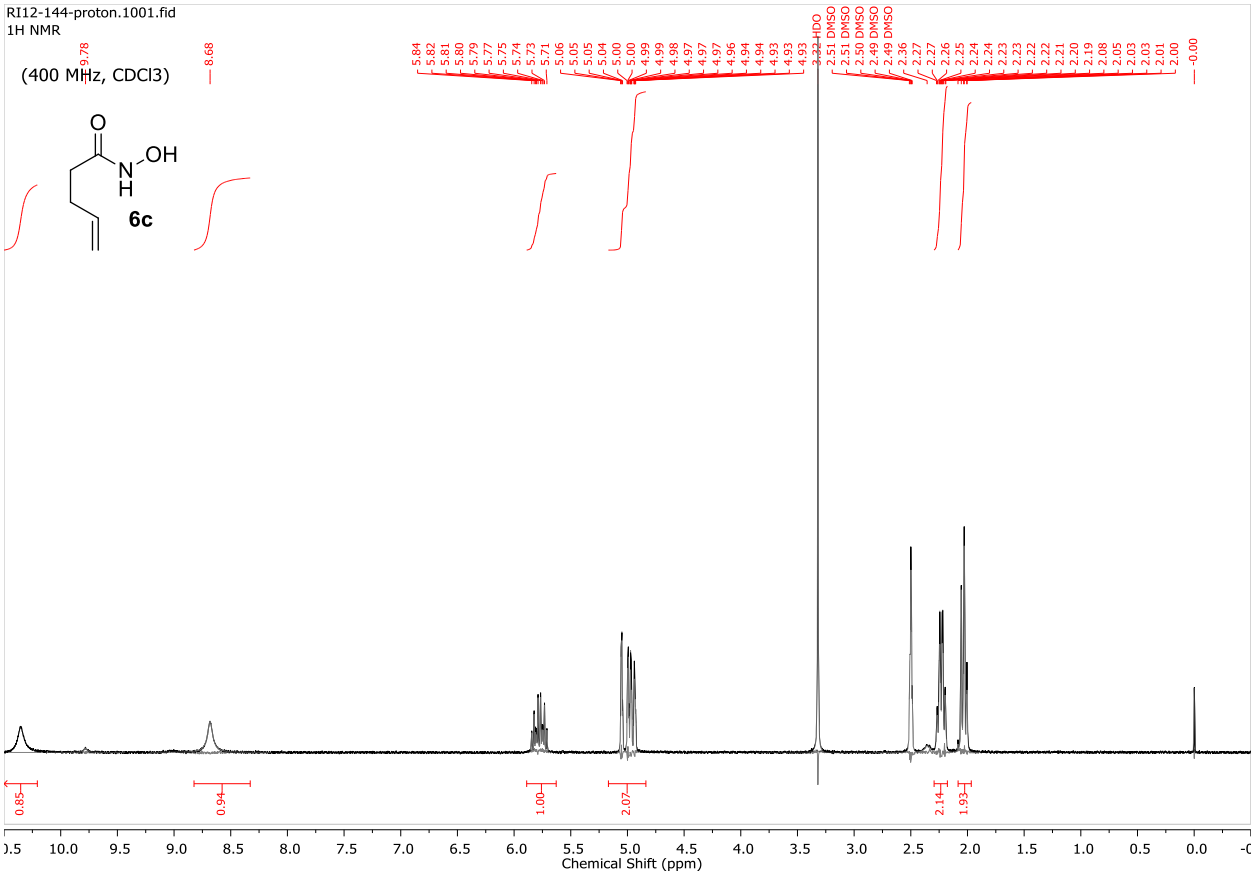
13-C NMR (101 MHz; $CDCl_3$):

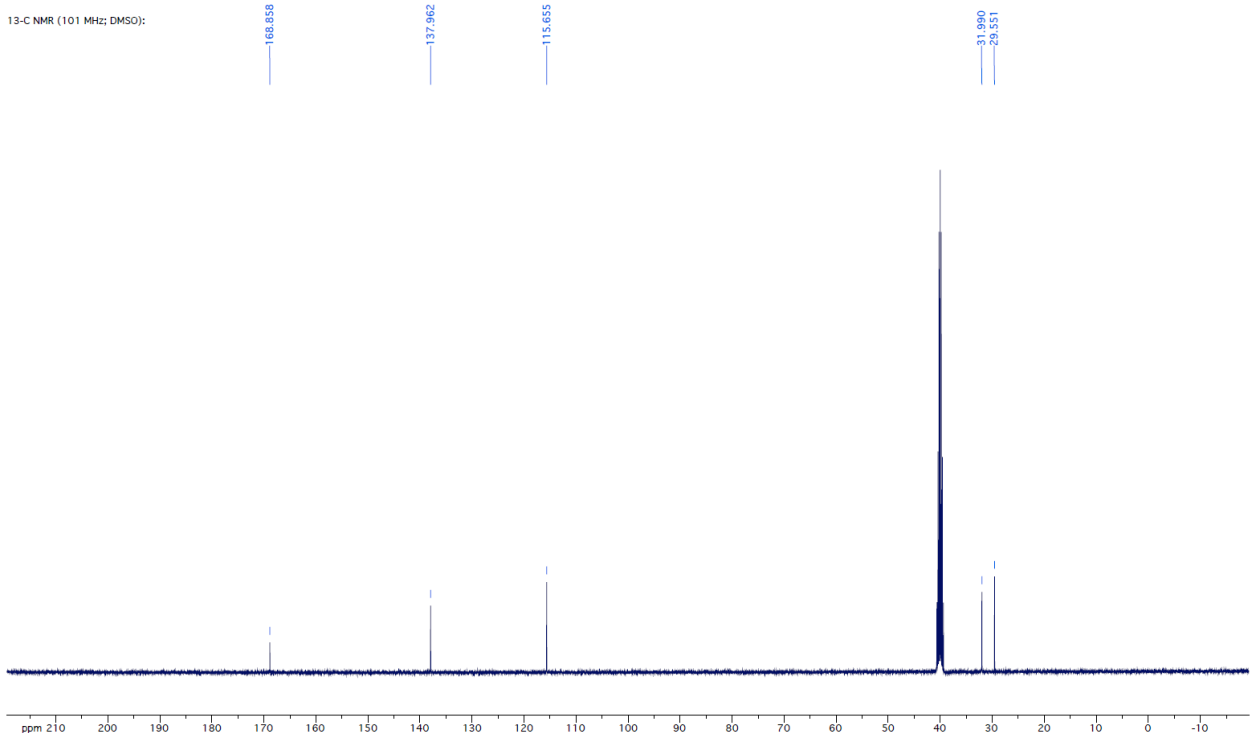


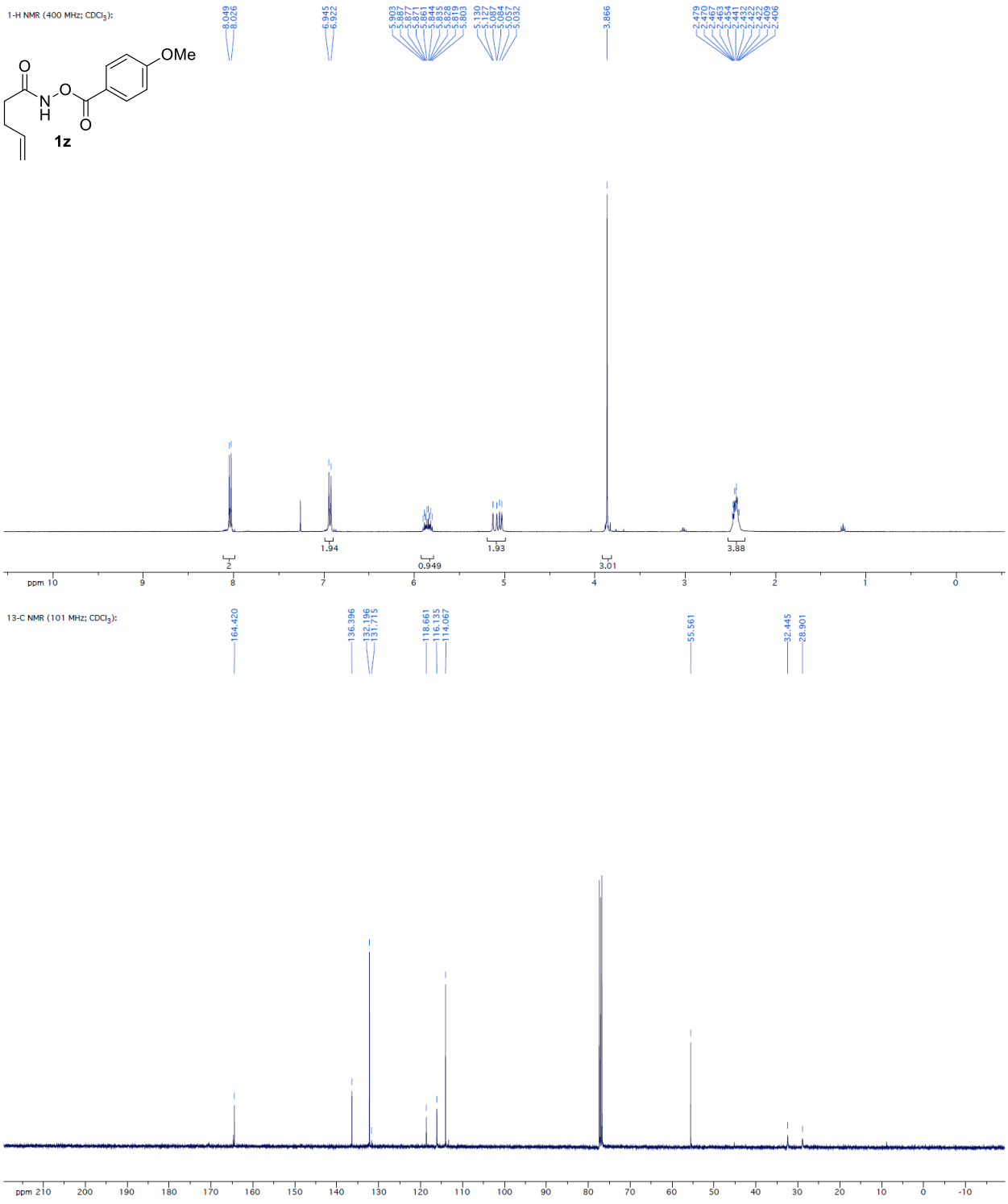

1-H NMR (600 MHz; CDCl3):
8.954
8.048
8.044
8.036
8.033
7.811
7.806
7.801
7.797
7.792
7.697
7.693
7.688
6.919
6.916
6.908
6.904
3.850
3.774
3.763
3.751
3.433
3.421
3.409
2.034
2.022
2.010
OMe
1x
0.965
2
4.33
4.21
2.11
3.17
4.23
4.22
4.32
ppm 10
13-C NMR (151 MHz; CDCl3):
168.529
166.693
164.224
158.016
134.131
132.253
132.121
123.457
119.449
113.989
55.613
44.938
35.612
27.563

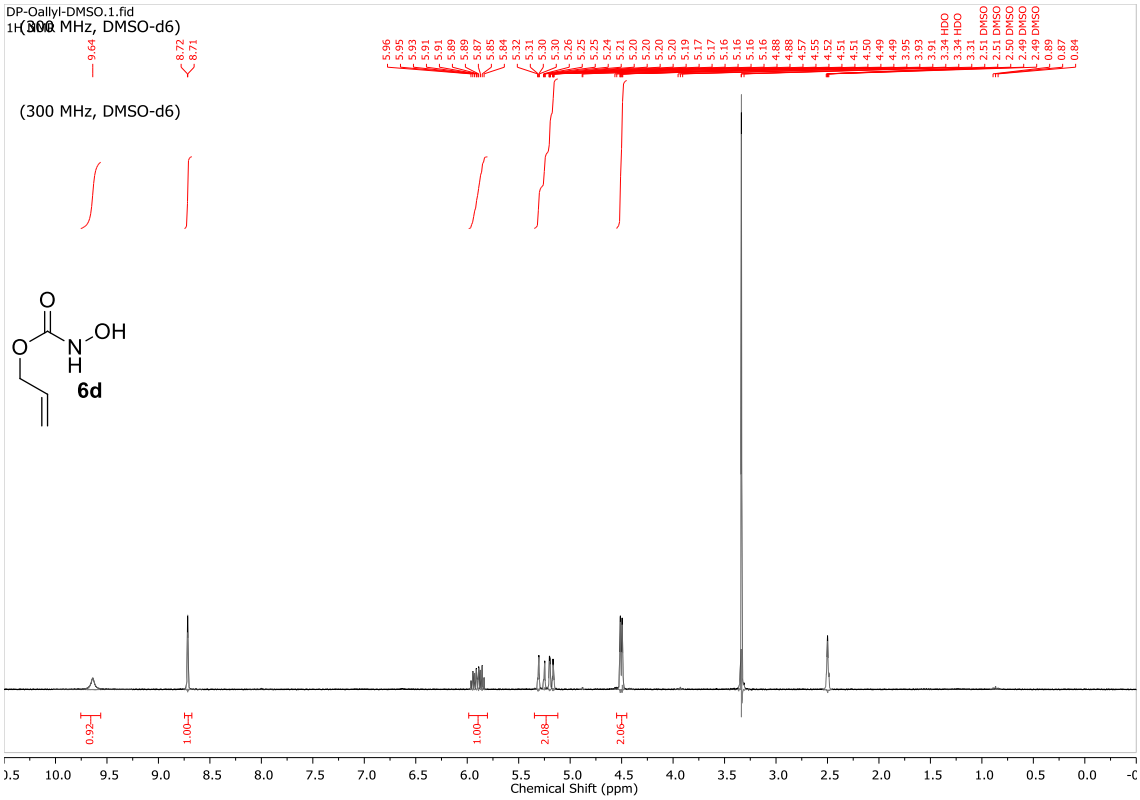

DP-Meallyl-H.1.fid
1H NMR
(400 MHz, CDCl3)
OMe
Me
N
O
N
H
O
O
1y
Chemical Shift (ppm)

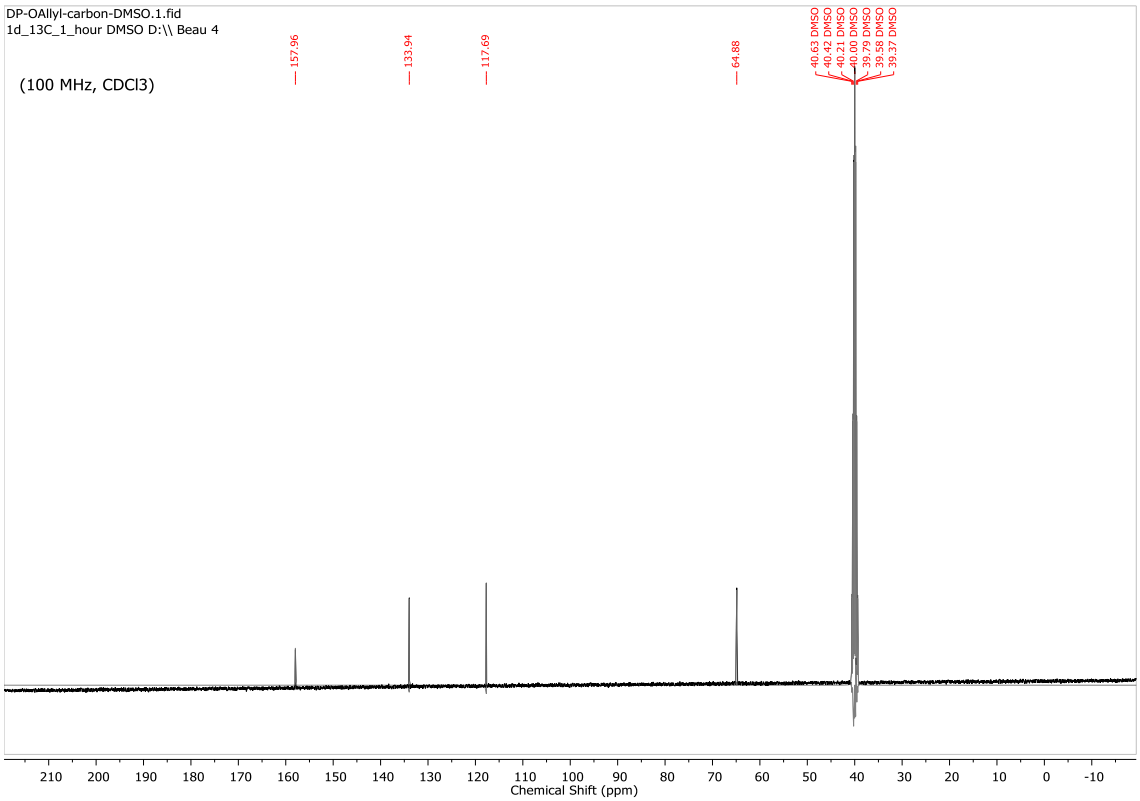

DP1575-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 38
(100 MHz, CDCl3)
Chemical Shift (ppm)

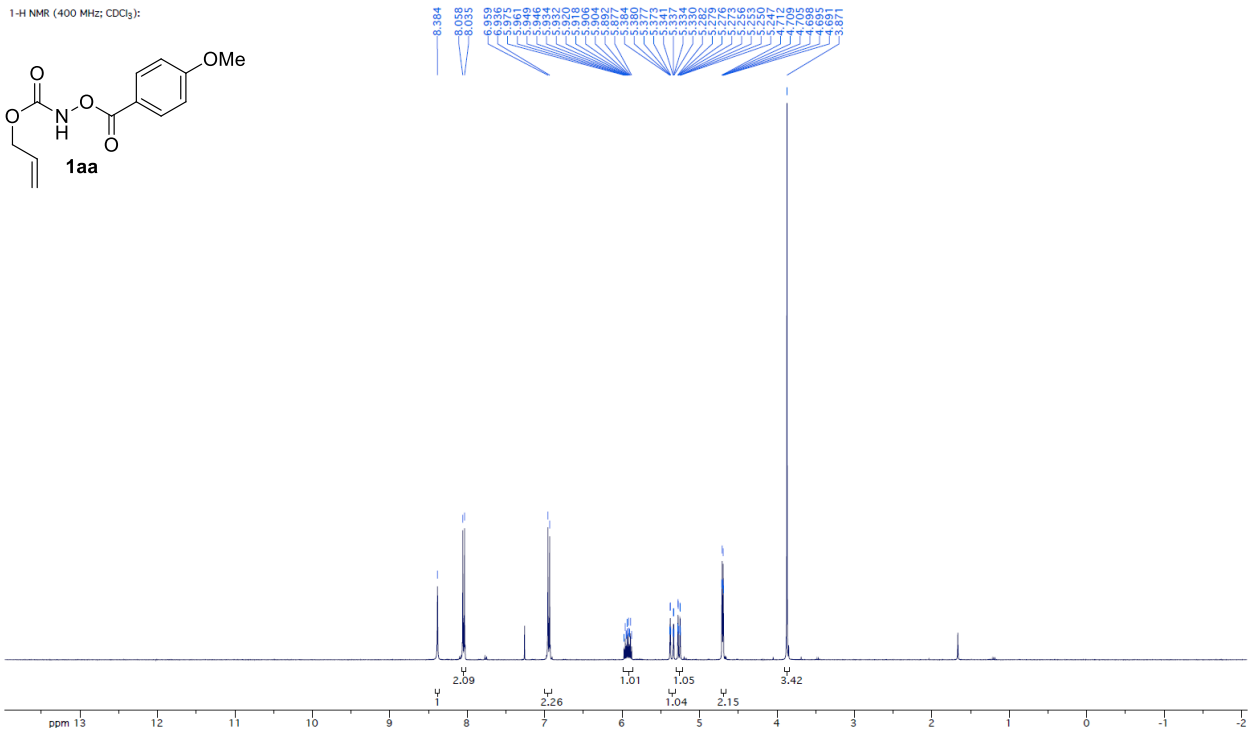

RI12-144-proton.1001.fid
1H NMR
(400 MHz, CDCl3)
9.78
8.68
O
N
OH
H
6c
5.84
5.82
5.81
5.80
5.79
5.77
5.75
5.74
5.73
5.71
5.06
5.05
5.05
5.04
5.00
5.00
4.99
4.99
4.98
4.97
4.97
4.97
4.96
4.94
4.94
4.93
4.93
3.32 HDO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.49 DMSO
2.49 DMSO
2.36
2.27
2.27
2.26
2.25
2.24
2.24
2.23
2.23
2.22
2.22
2.21
2.20
2.19
2.08
2.05
2.03
2.03
2.01
2.00
-0.00
0.85
0.94
1.00
2.07
2.14
1.93
Chemical Shift (ppm)

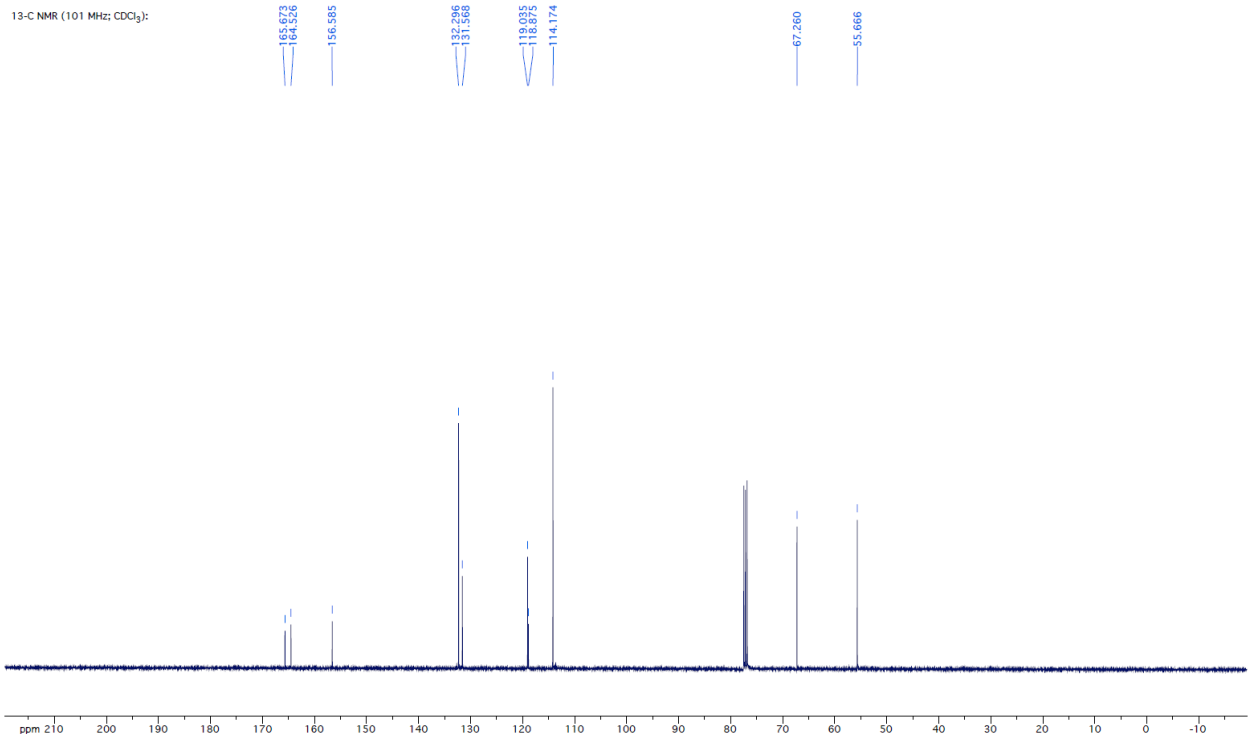

13-C NMR (101 MHz; DMSO):
168.858
137.962
115.655
31.990
29.551
ppm

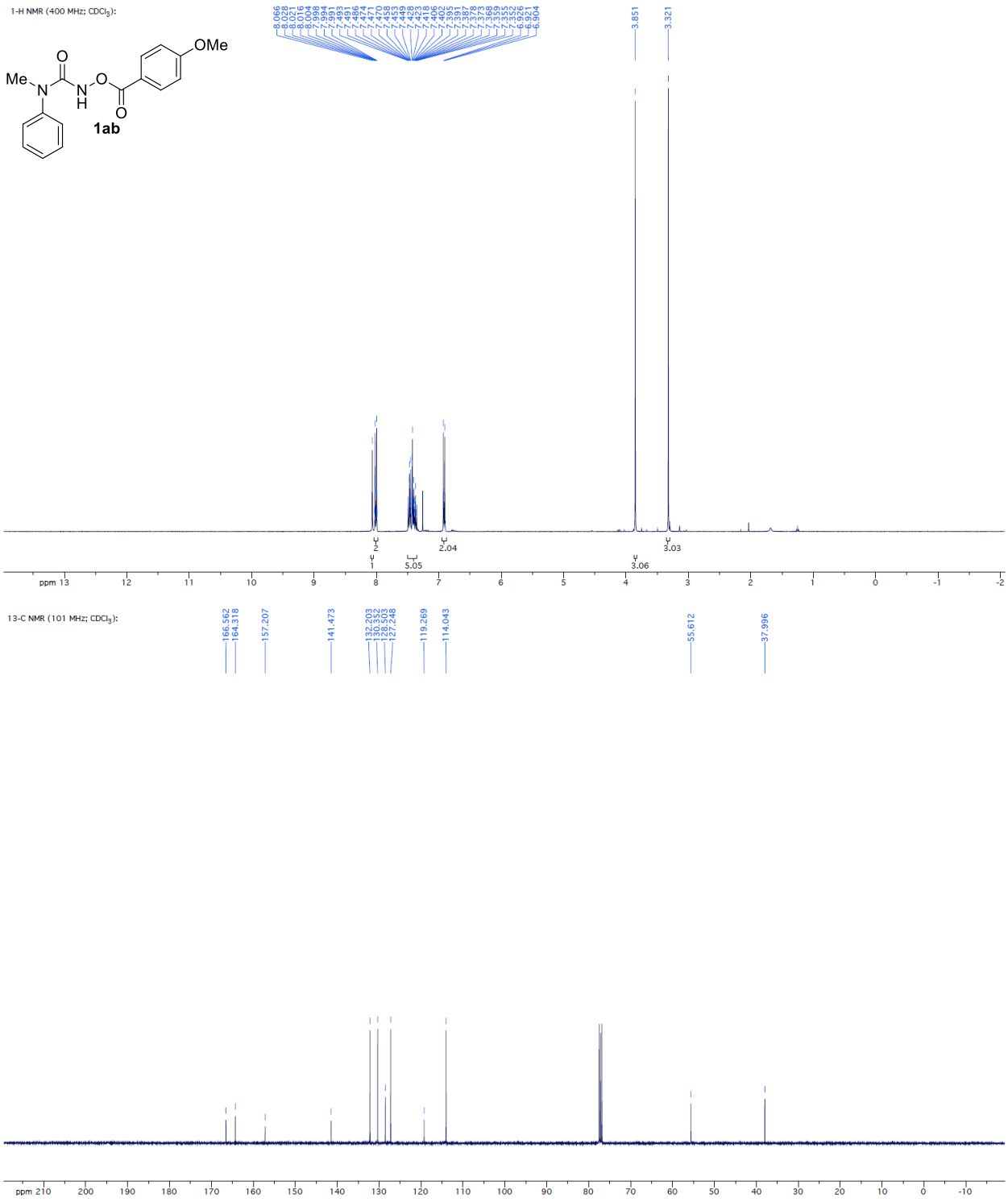

1-H NMR (400 MHz; CDCl3):
OMe
O
N
H
O
O
1z
8.049
8.026
6.945
6.922
5.903
5.897
5.877
5.871
5.861
5.844
5.835
5.828
5.819
5.803
5.130
5.127
5.087
5.084
5.057
5.032
3.866
2.479
2.470
2.467
2.463
2.454
2.441
2.432
2.422
2.412
2.409
2.406
1.94
0.949
1.93
3.01
3.88
2
ppm 10
9
8
7
6
5
4
3
2
1
0
13-C NMR (101 MHz; CDCl3):
164.420
136.396
132.196
131.715
118.661
116.135
114.067
55.561
32.445
28.901
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

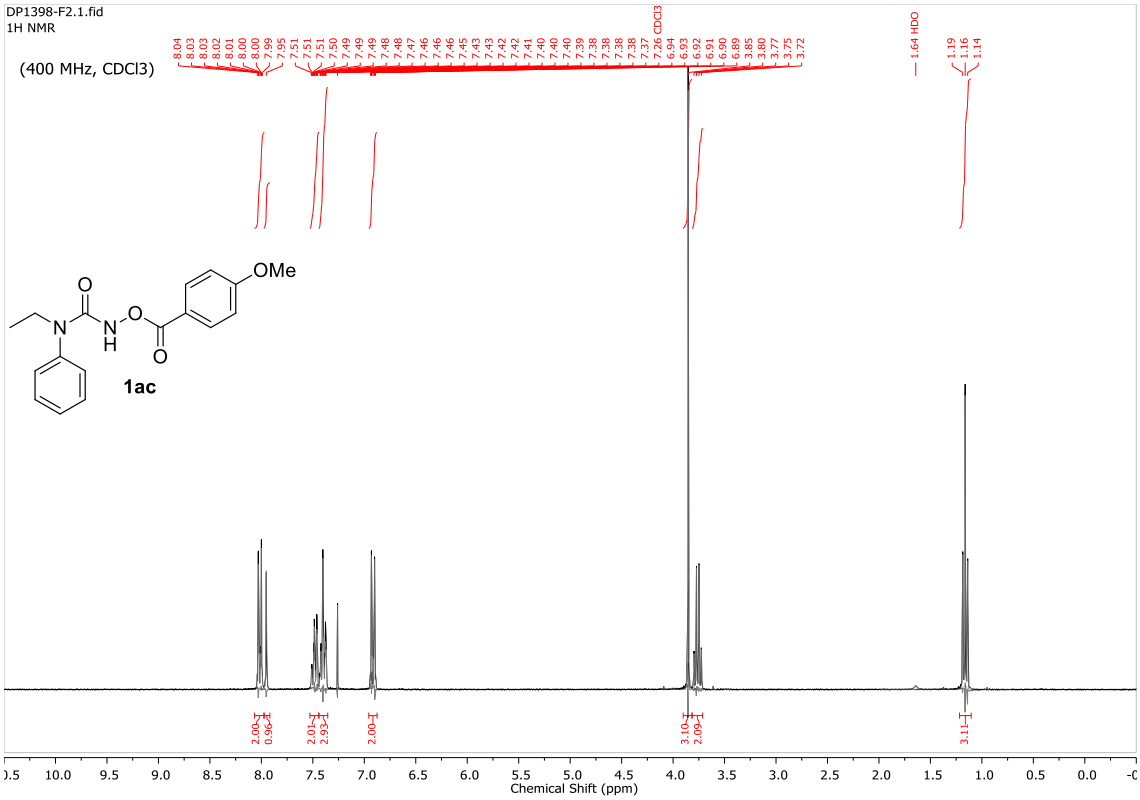

DP-Oallyl-DMSO.1.fid
1H (300 MHz, DMSO-d6)
(300 MHz, DMSO-d6)
6d
Chemical Shift (ppm)

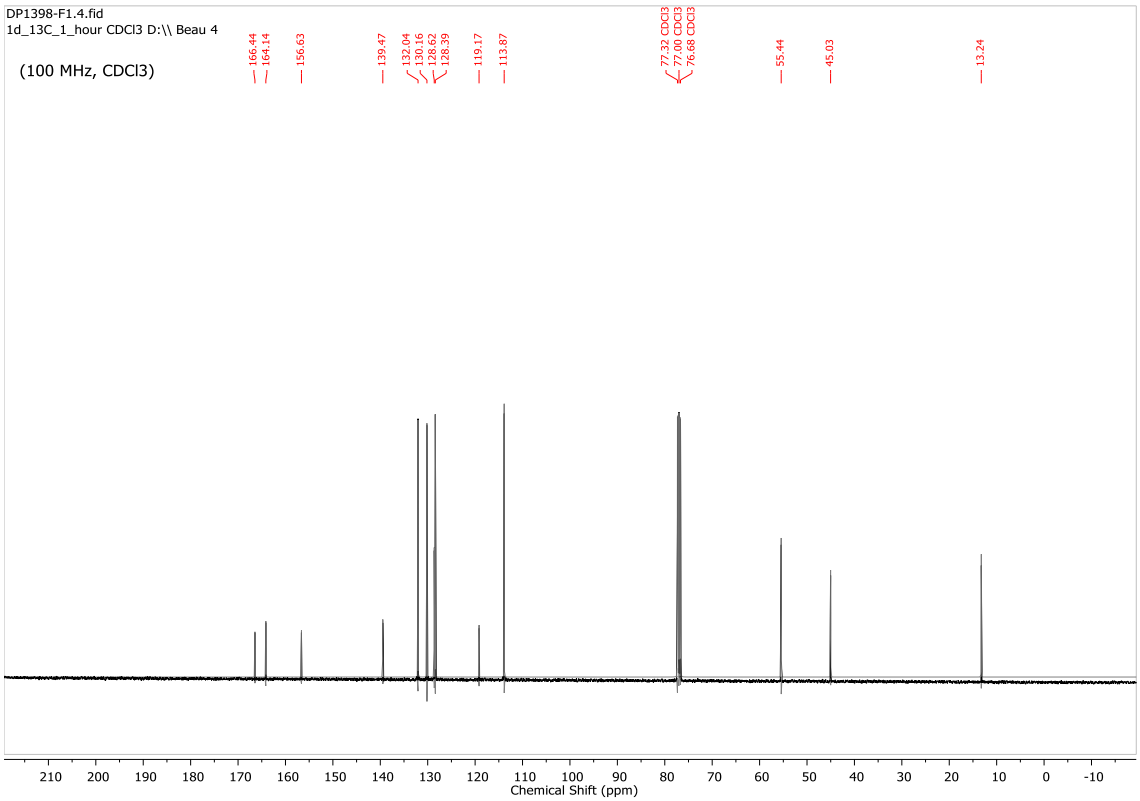

DP-OAllyl-carbon-DMSO.1.fid
1d_13C_1_hour DMSO D:\\ Beau 4
(100 MHz, CDCl3)
Chemical Shift (ppm)

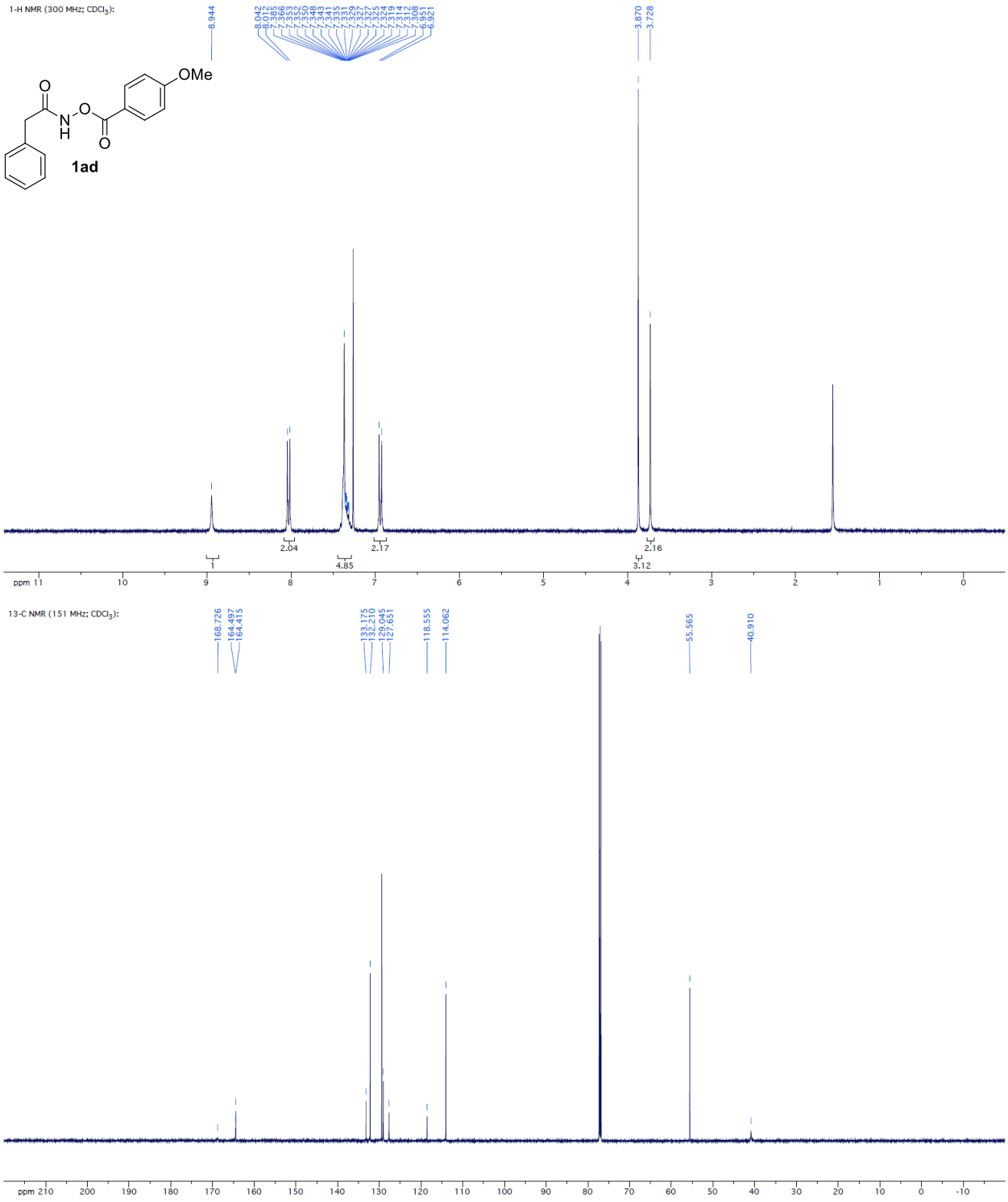

1-H NMR (400 MHz; CDCl3):
OMe
1aa
8.384
8.058
8.035
6.959
6.956
6.937
5.961
5.949
5.946
5.934
5.932
5.920
5.918
5.906
5.904
5.892
5.877
5.384
5.380
5.377
5.373
5.341
5.337
5.334
5.330
5.280
5.279
5.276
5.256
5.253
5.250
5.247
4.712
4.709
4.698
4.695
4.691
3.871
2.09
1.01
1.05
3.42
1
2.26
1.04
2.15
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2

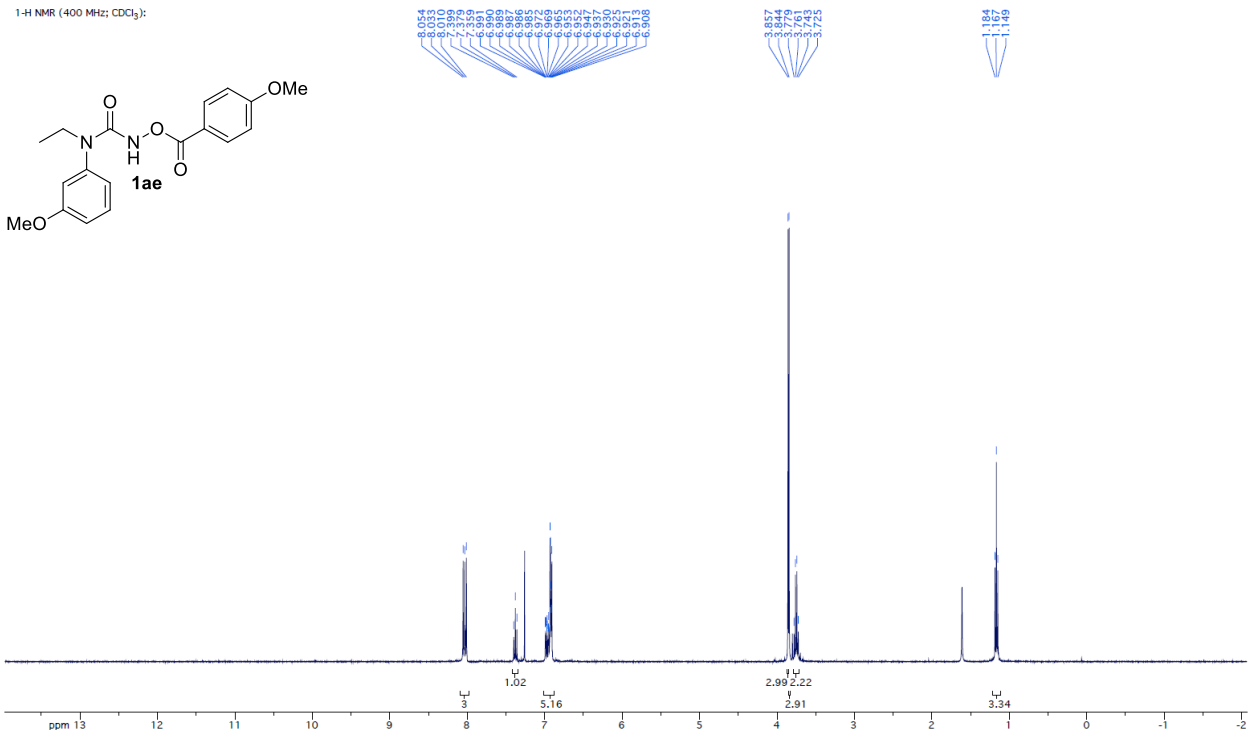

13-C NMR (101 MHz; CDCl3):
165.673
164.526
156.585
132.286
131.588
119.035
118.875
114.174
67.260
55.666
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

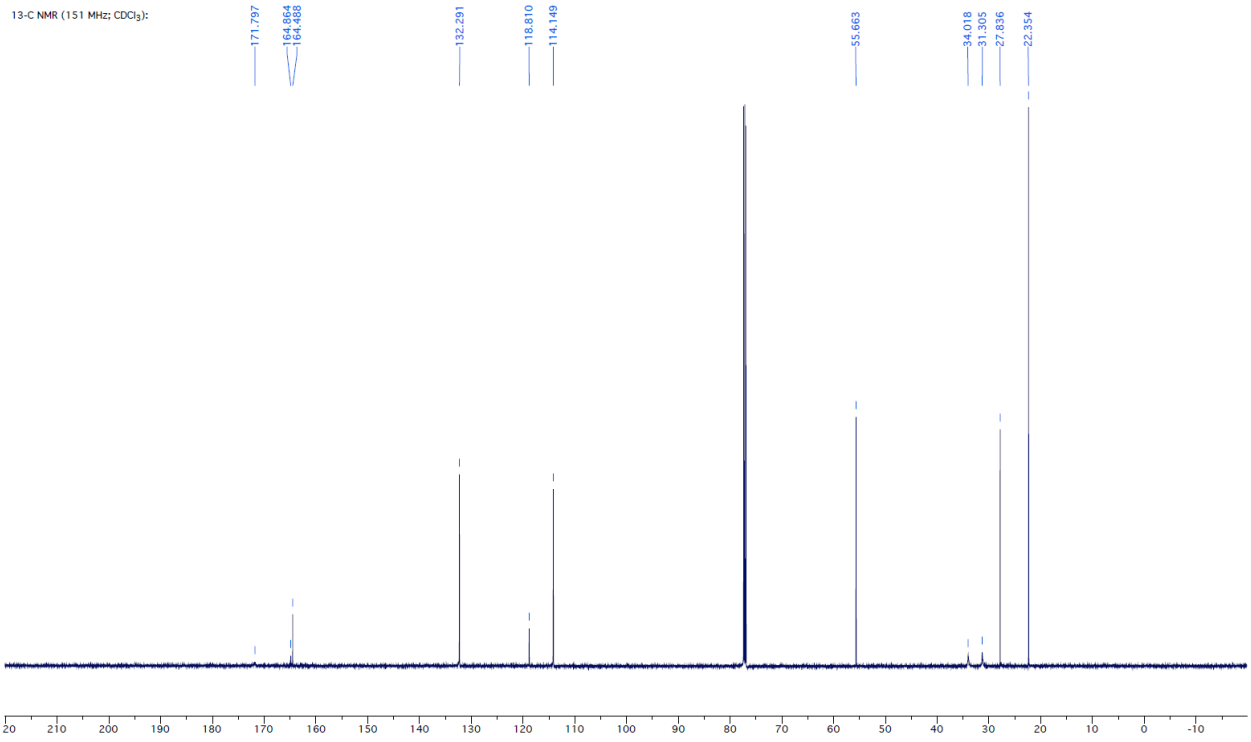

1-H NMR (400 MHz; CDCl3):
Me
N
O
N
H
O
O
OMe
1ab
8.066
8.058
8.021
8.016
8.004
7.998
7.994
7.991
7.493
7.491
7.486
7.474
7.471
7.470
7.456
7.453
7.449
7.428
7.423
7.418
7.406
7.402
7.395
7.391
7.387
7.378
7.373
7.368
7.359
7.355
7.352
6.926
6.921
6.904
3.851
3.321
2.02
1
2.04
5.05
3.06
3.03
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
13-C NMR (101 MHz; CDCl3):
166.562
164.318
157.207
141.473
132.203
129.372
128.503
127.248
119.269
114.043
55.612
37.996
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

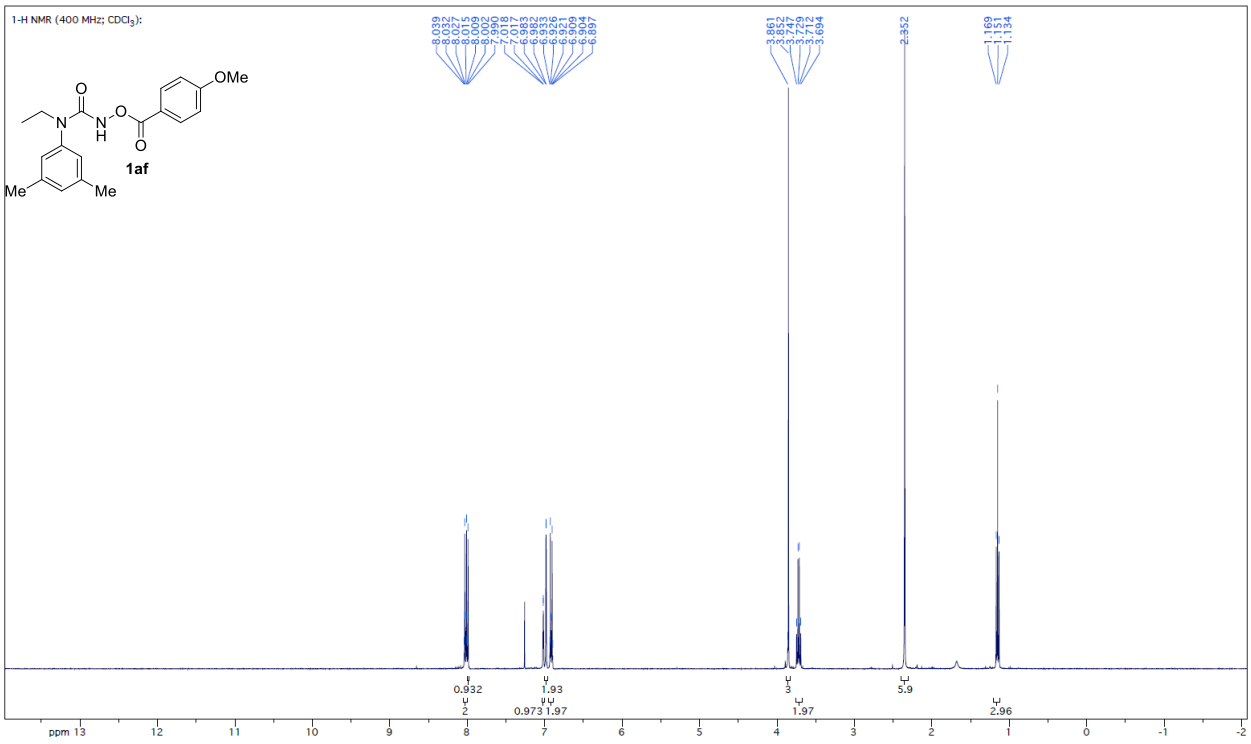

DP1398-F2.1.fid
1H NMR
(400 MHz, CDCl3)
OMe
1ac
Chemical Shift (ppm)

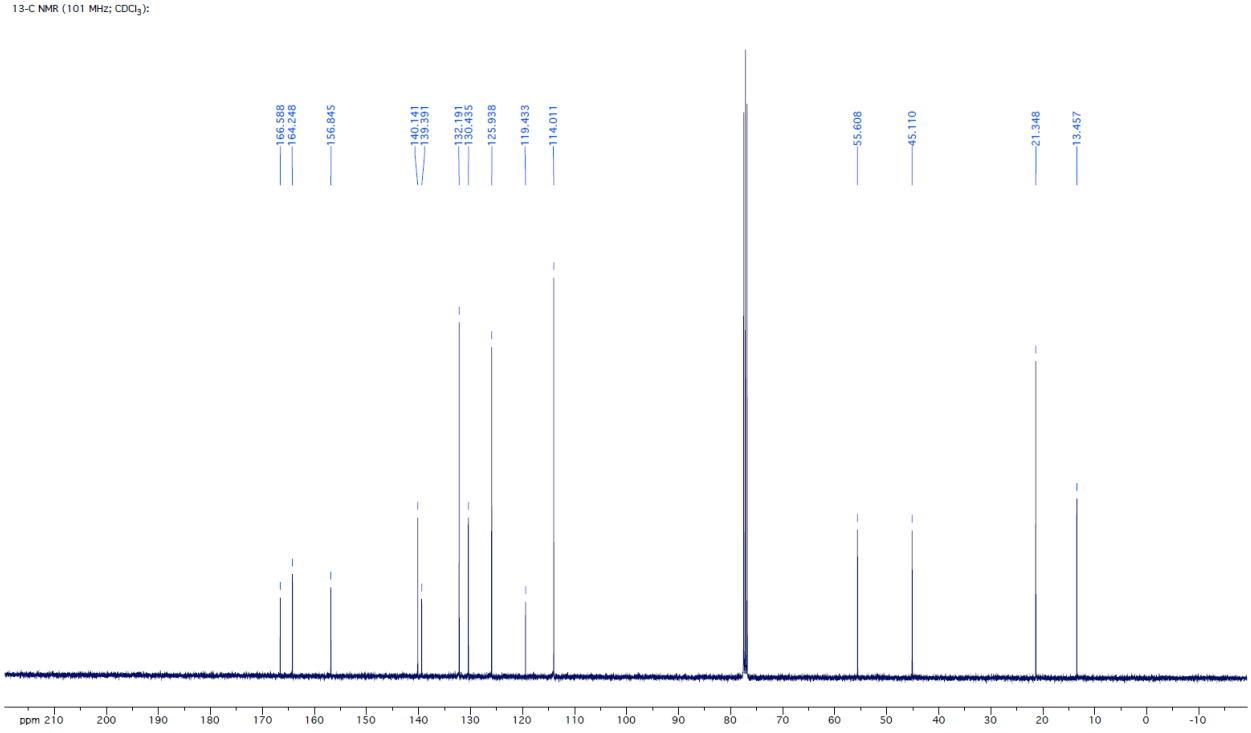

DP1398-F1.4.fid
1d_13C_1_hour CDCl3 D:\\ Beau 4
(100 MHz, CDCl3)
Chemical Shift (ppm)

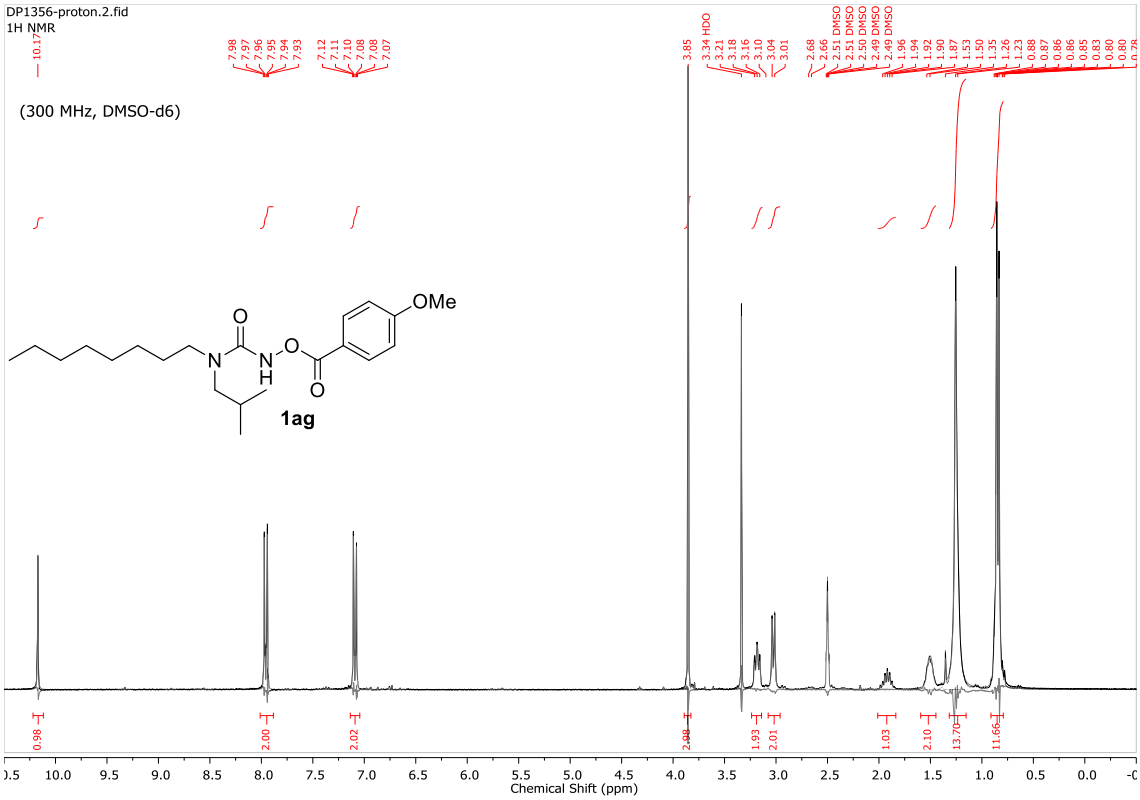

1-H NMR (300 MHz; CDCl3):
8.944
8.042
8.012
8.005
7.366
7.353
7.350
7.348
7.343
7.341
7.335
7.331
7.329
7.327
7.325
7.324
7.319
7.314
7.312
7.308
6.921
6.921
3.870
3.728
OMe
O
N
H
O
O
1ad
2.04
4.85
2.17
3.12
2.16
ppm 11
10
9
8
7
6
5
4
3
2
1
0
13-C NMR (151 MHz; CDCl3):
168.726
164.497
164.415
133.175
132.210
129.045
127.651
118.555
114.062
55.565
40.910
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

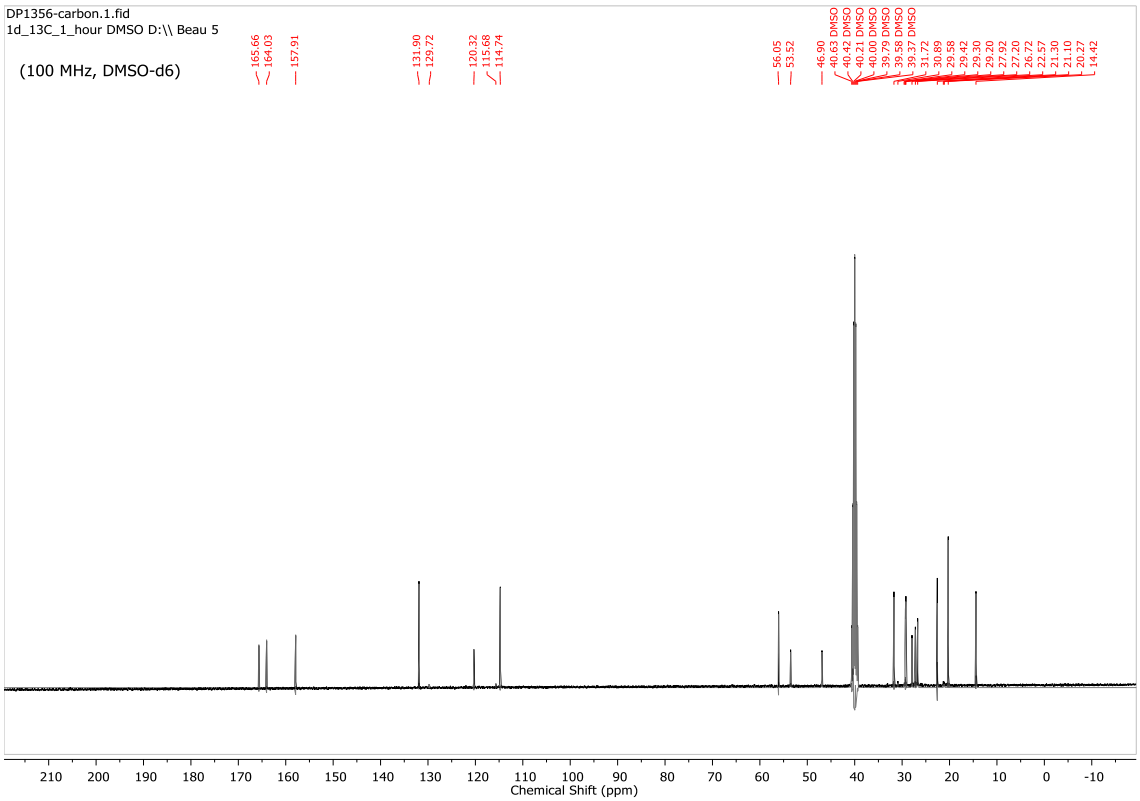

1-H NMR (400 MHz; CDCl3):
OMe
MeO
1ae
ppm


13-C NMR (151 MHz; CDCl3):

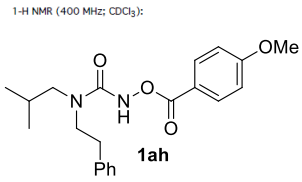

1-H NMR (400 MHz; CDCl3):
OMe
1af
Me
Me
8.039
8.032
8.027
8.015
8.009
8.002
7.990
7.018
7.017
6.983
6.982
6.933
6.926
6.921
6.909
6.904
6.897
3.861
3.852
3.847
3.729
3.712
3.694
2.352
1.169
1.151
1.134
0.932
1.93
3.
1.97
5.9
2.96
0.973 1.97
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2


13-C NMR (101 MHz; CDCl3):
166.588
164.248
156.845
140.141
139.391
132.191
130.435
125.938
119.433
114.011
55.608
45.110
21.348
13.457
ppm 210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


DP1356-proton.2.fid
1H NMR
(300 MHz, DMSO-d6)
OMe
1ag
Chemical Shift (ppm)

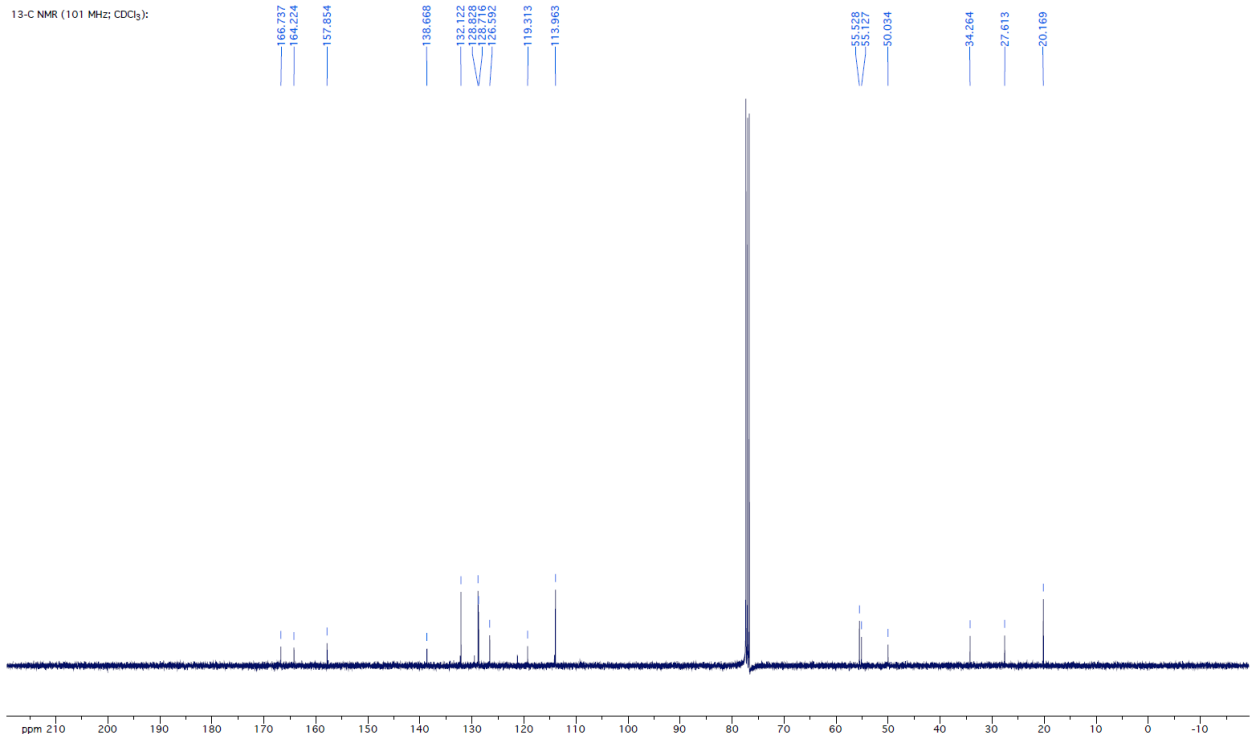

DP1356-carbon.1.fid
1d_13C_1_hour DMSO D:\\ Beau 5
(100 MHz, DMSO-d6)
Chemical Shift (ppm)

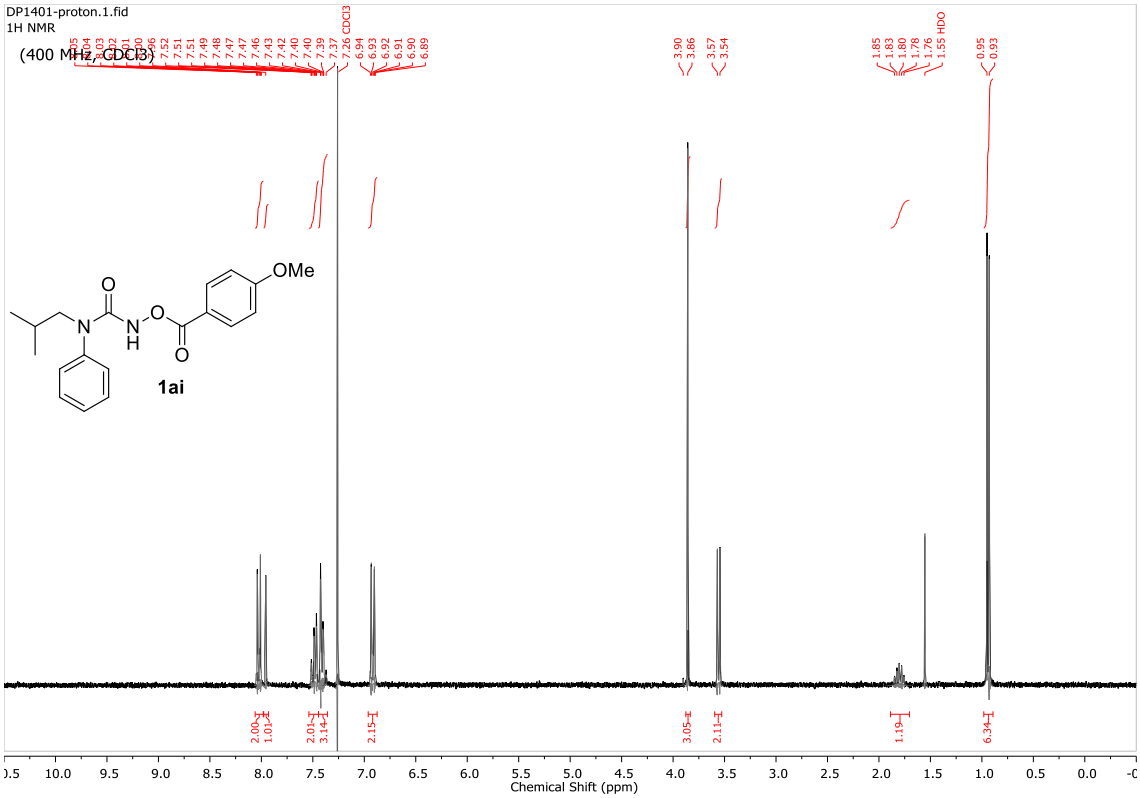
1-H NMR (400 MHz; $CDCl_3$):

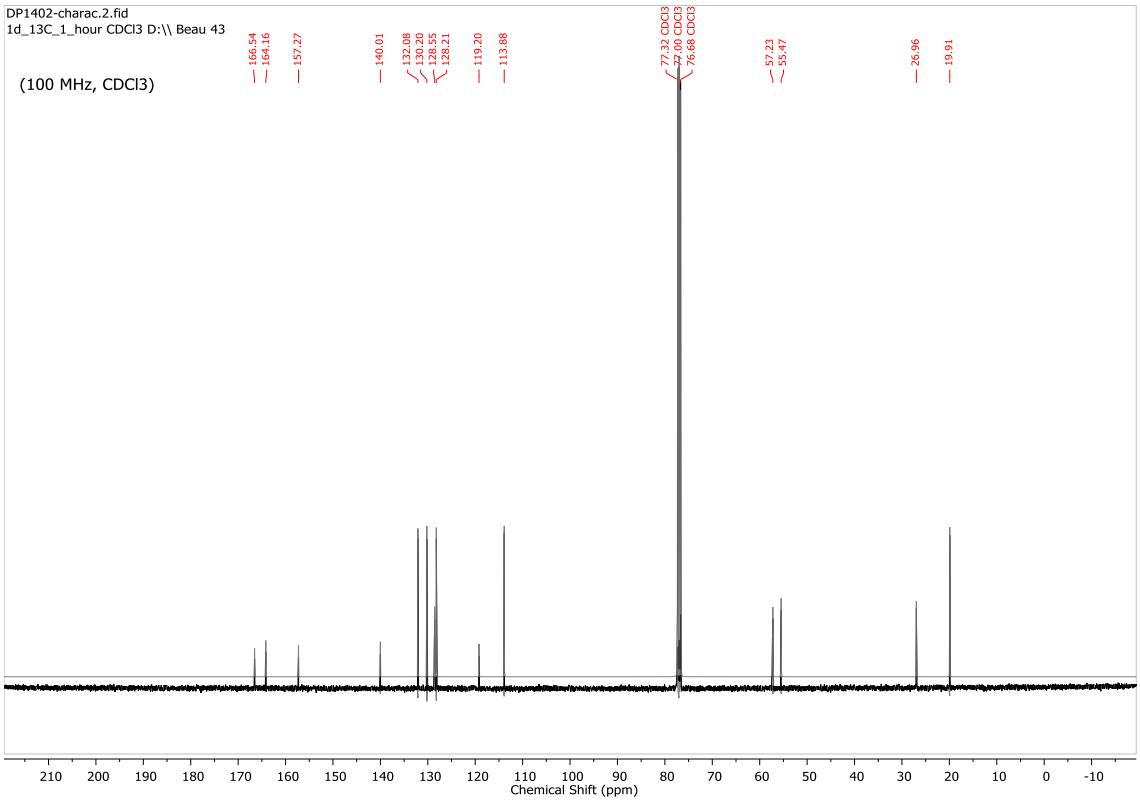


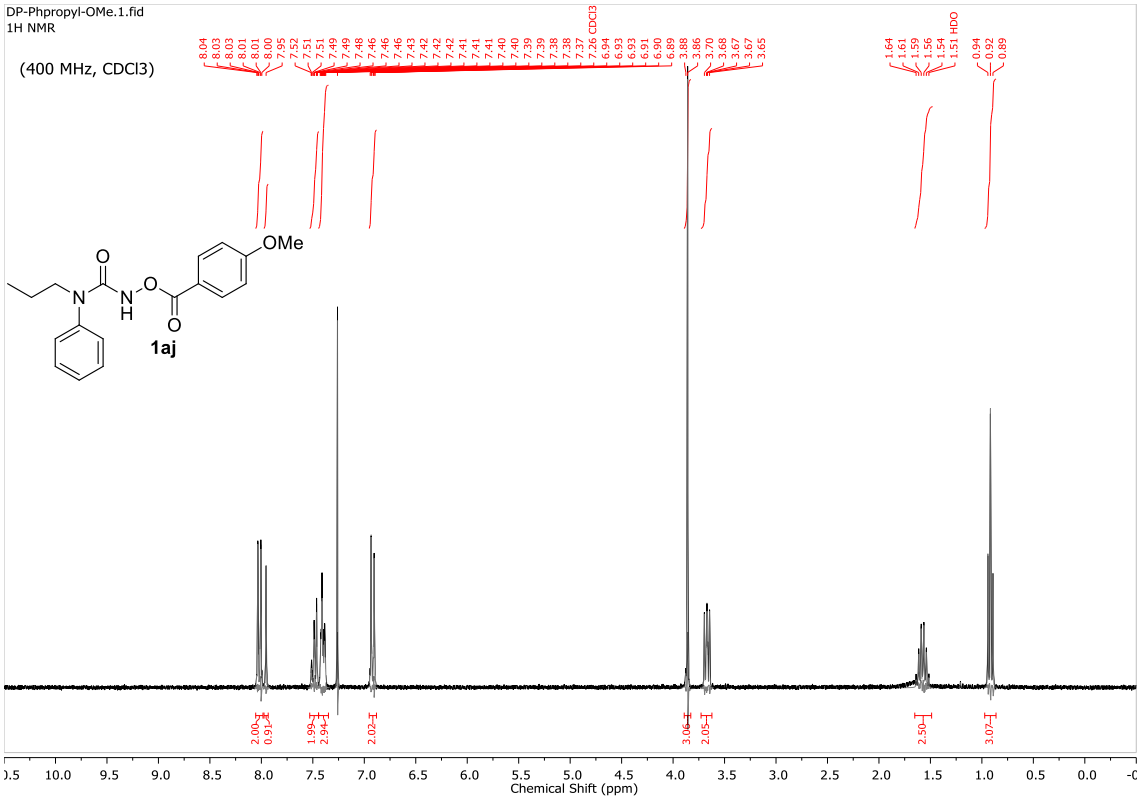
1ah

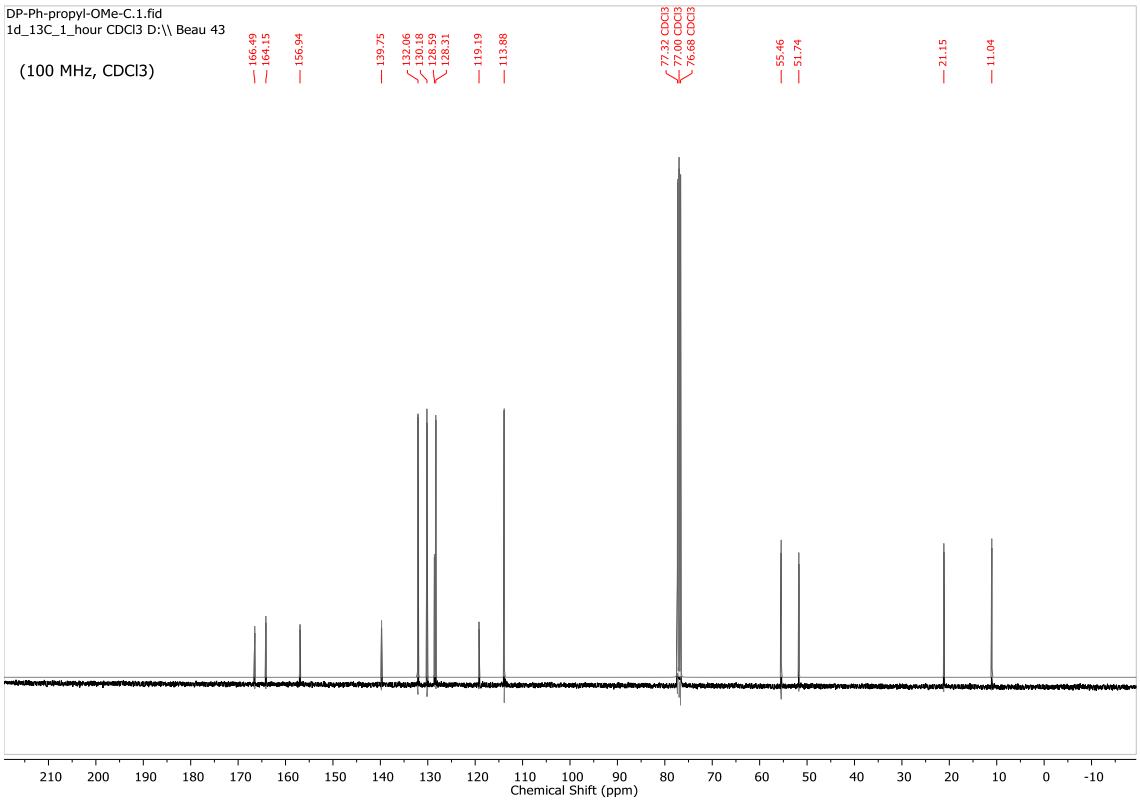
13-C NMR (101 MHz; $CDCl_3$):



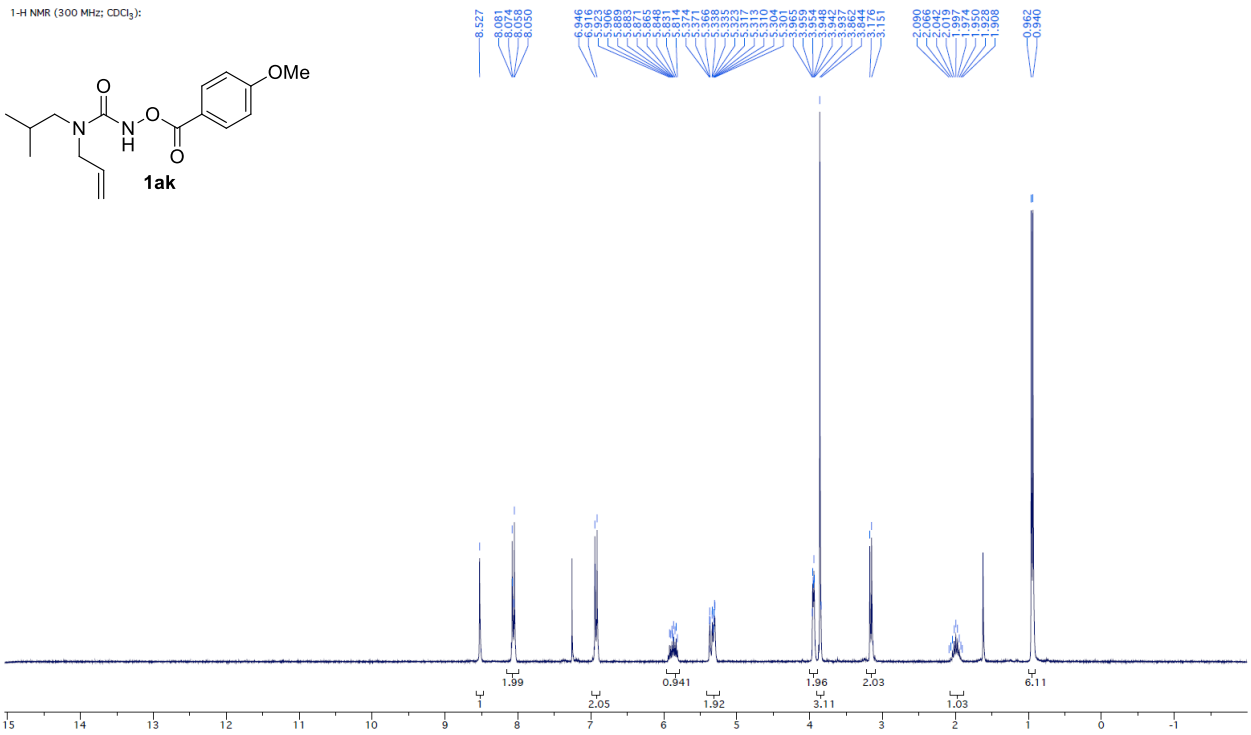

DP1401-proton.1.fid
1H NMR
(400 MHz, CDCl3)
7.26 CDCl3
3.90
3.86
3.57
3.54
1.85
1.83
1.80
1.78
1.76
1.55 HDO
0.95
0.93
OMe
1ai
Chemical Shift (ppm)


DP1402-charac.2.fid
1d_13C_1_hour CDCl3 D:\\ Beau 43
(100 MHz, CDCl3)
166.54
164.16
157.27
140.01
132.08
130.20
128.55
128.21
119.20
113.88
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
57.23
55.47
26.96
19.91
Chemical Shift (ppm)

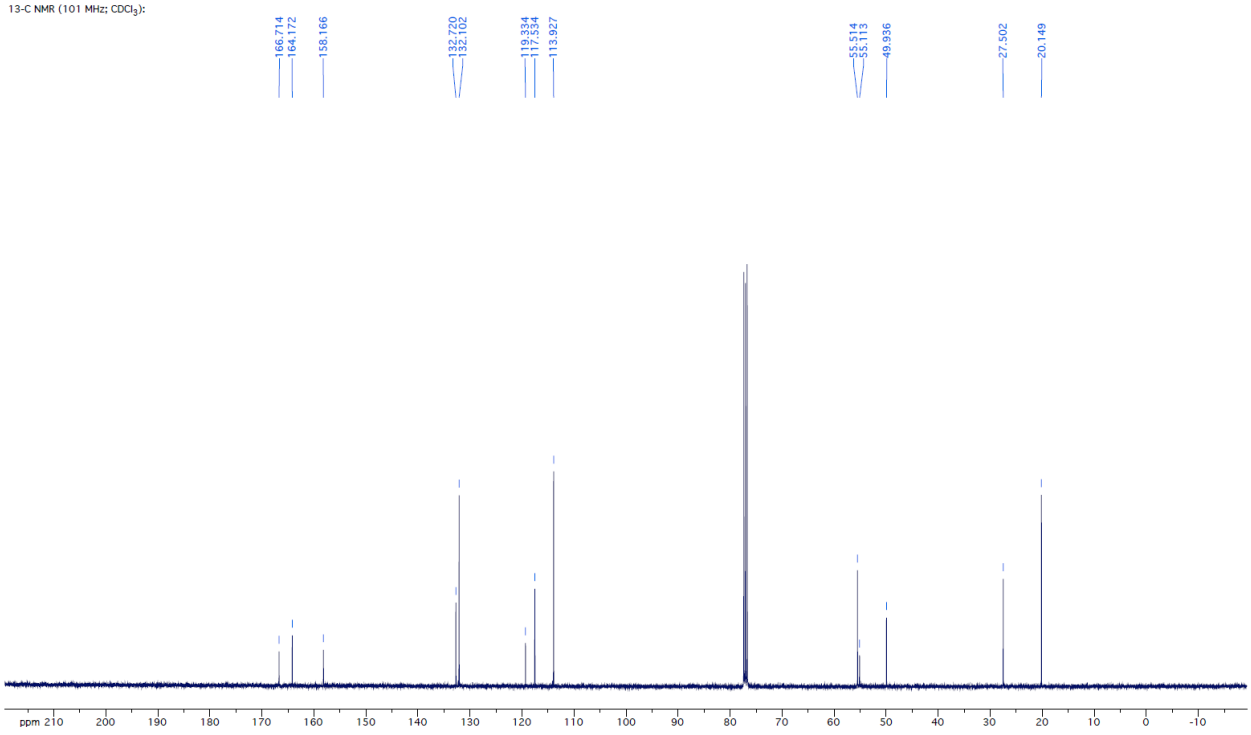

DP-Phpropyl-OMe.1.fid
1H NMR
(400 MHz, CDCl3)
OMe
1aj
Chemical Shift (ppm)


DP-Ph-propyl-OMe-C.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 43
(100 MHz, CDCl3)
Chemical Shift (ppm)

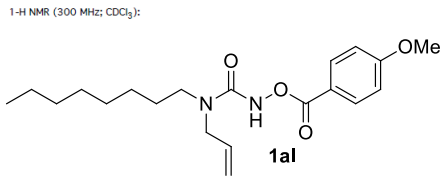
1-H NMR (300 MHz; $CDCl_3$):



13-C NMR (101 MHz; $CDCl_3$):

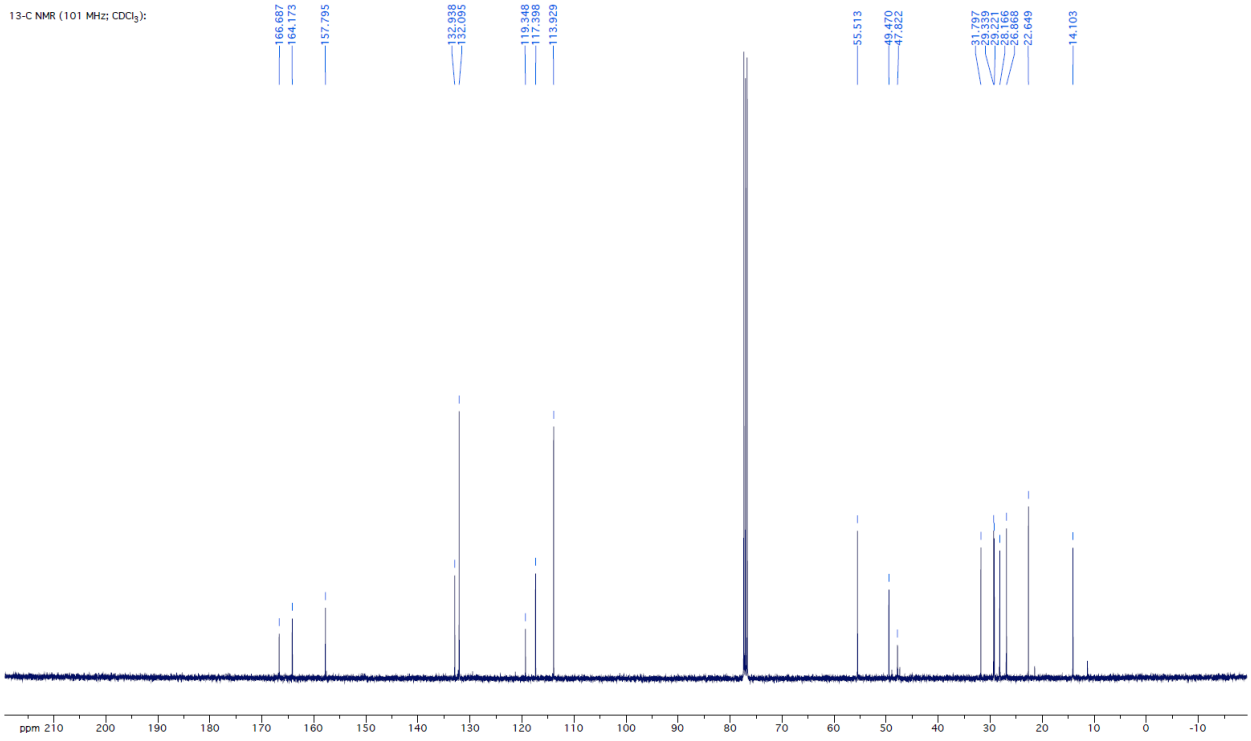


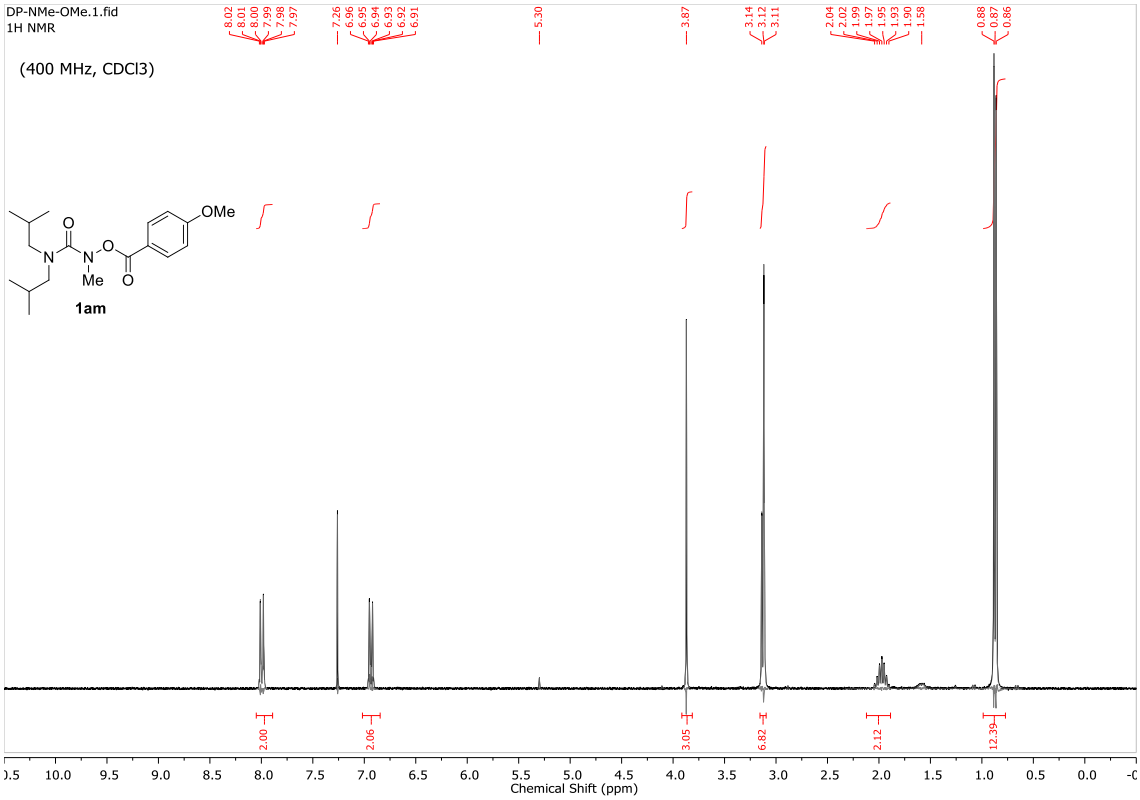
1-H NMR (300 MHz; $CDCl_3$):

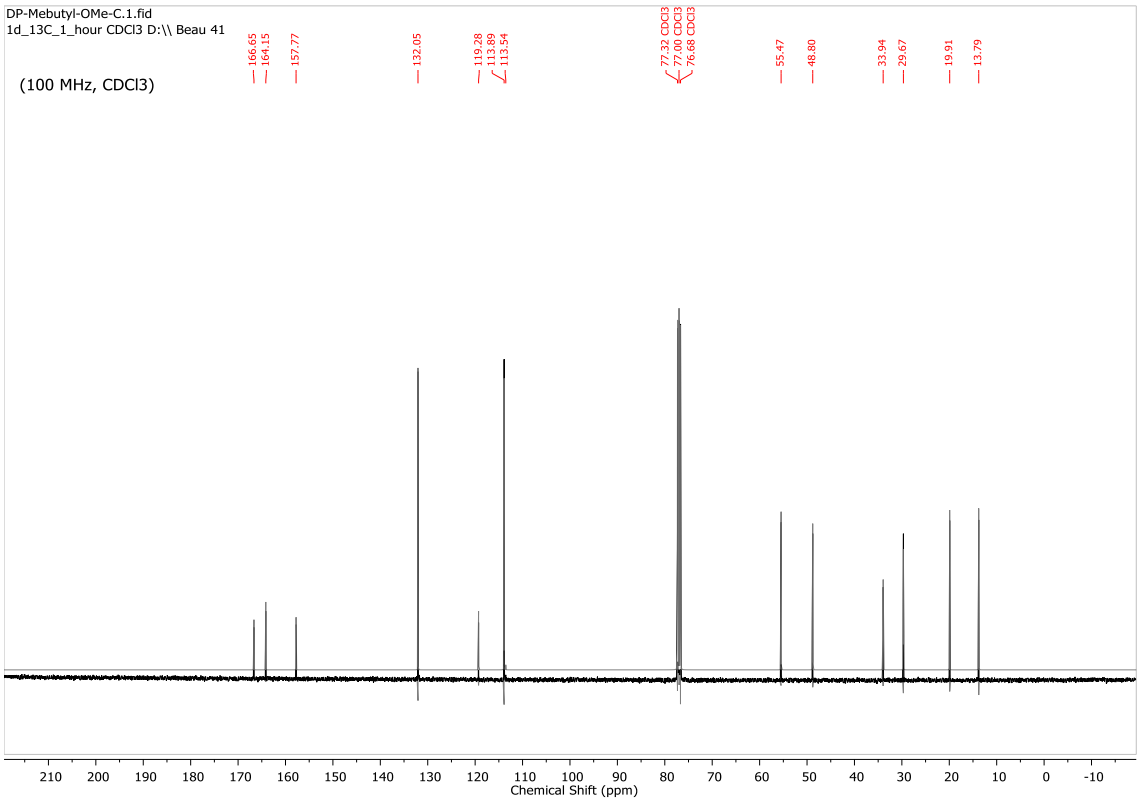


1al

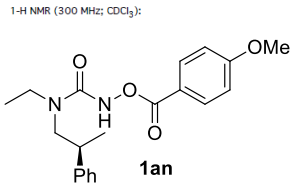
13-C NMR (101 MHz; $CDCl_3$):




DP-NMe-OMe.1.fid
1H NMR
(400 MHz, CDCl3)
OMe
N
O
N
O
Me
O
1am
8.02
8.01
8.00
7.99
7.98
7.97
7.26
6.96
6.95
6.94
6.93
6.92
6.91
5.30
3.87
3.14
3.12
3.11
2.04
2.02
1.99
1.97
1.95
1.93
1.90
1.58
0.88
0.87
0.86
2.00
2.06
3.05
6.82
2.12
12.39
Chemical Shift (ppm)

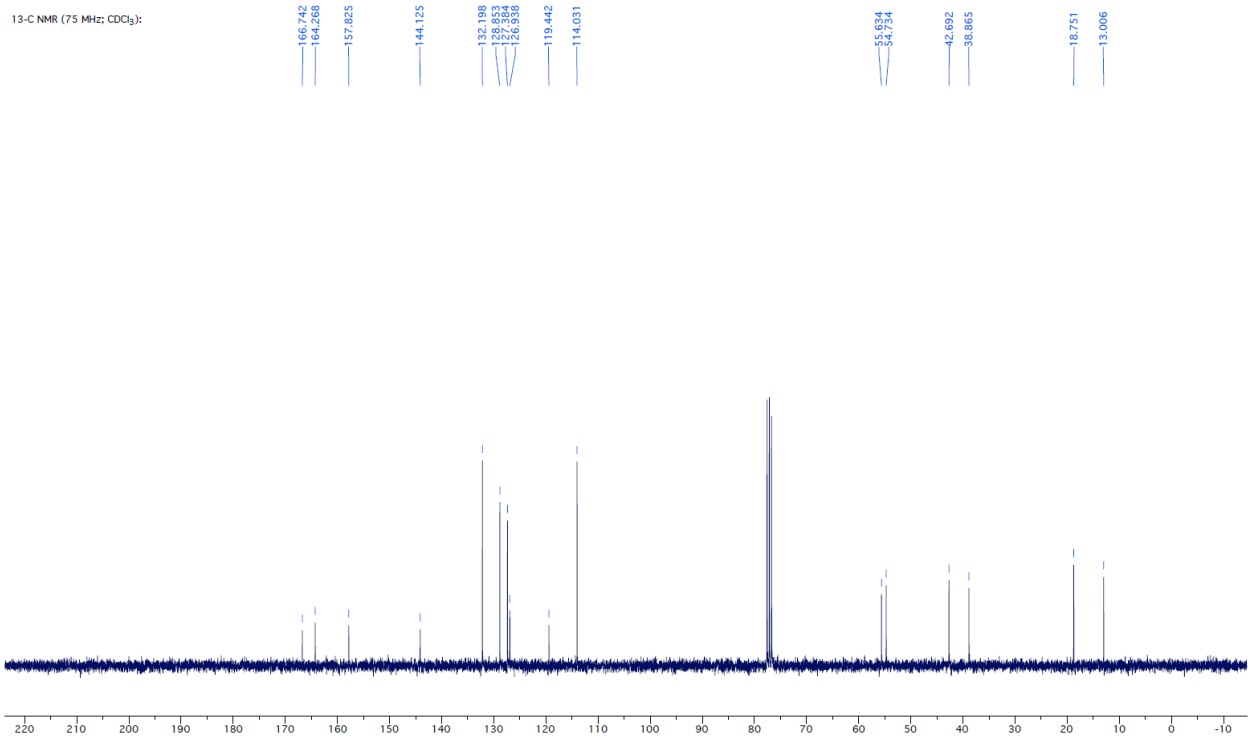

DP-Mebutyl-OMe-C.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 41
(100 MHz, CDCl3)
166.65
164.15
157.77
132.05
119.28
113.89
113.54
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.47
48.80
33.94
29.67
19.91
13.79
Chemical Shift (ppm)

1-H NMR (300 MHz; $CDCl_3$):

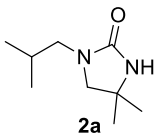


1an

13-C NMR (75 MHz; $CDCl_3$):

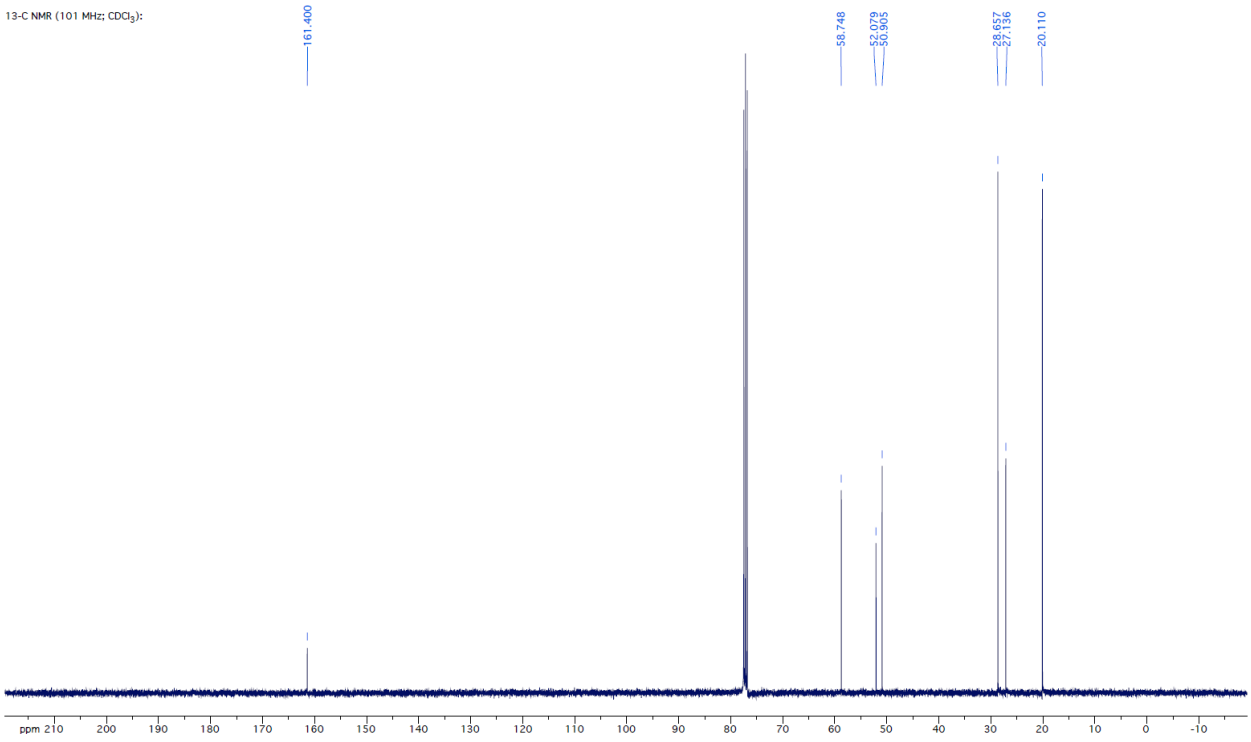


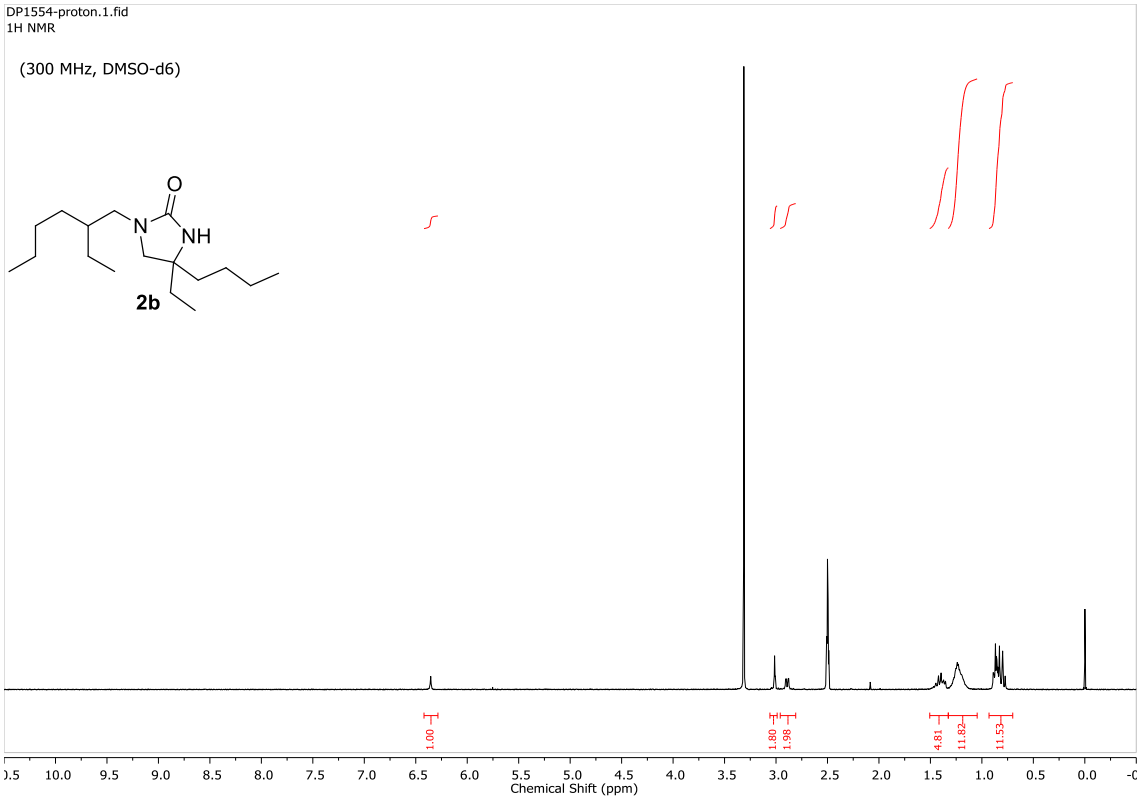
1-H NMR (400 MHz; $CDCl_3$):

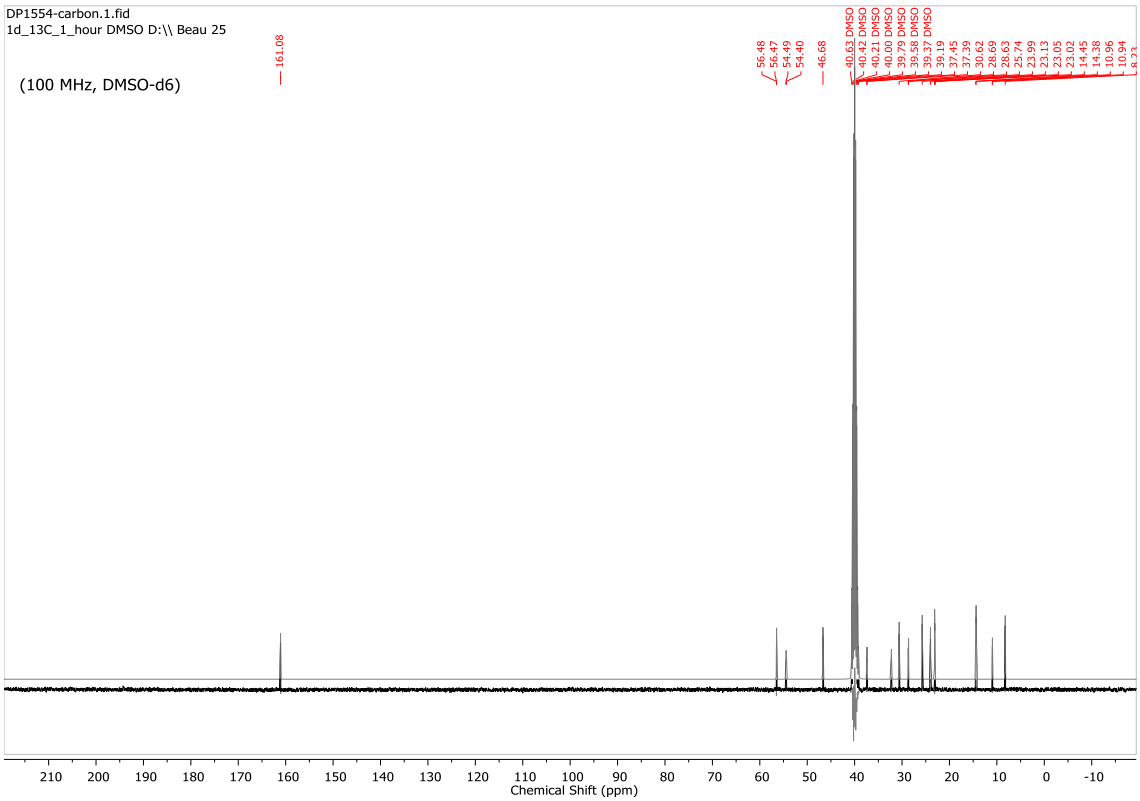


2a

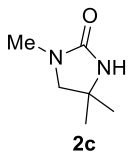
13-C NMR (101 MHz; $CDCl_3$):




DP1554-proton.1.fid
1H NMR
(300 MHz, DMSO-d6)
O
N
NH
2b
1.00
1.80
1.98
4.81
11.82
11.53
Chemical Shift (ppm)

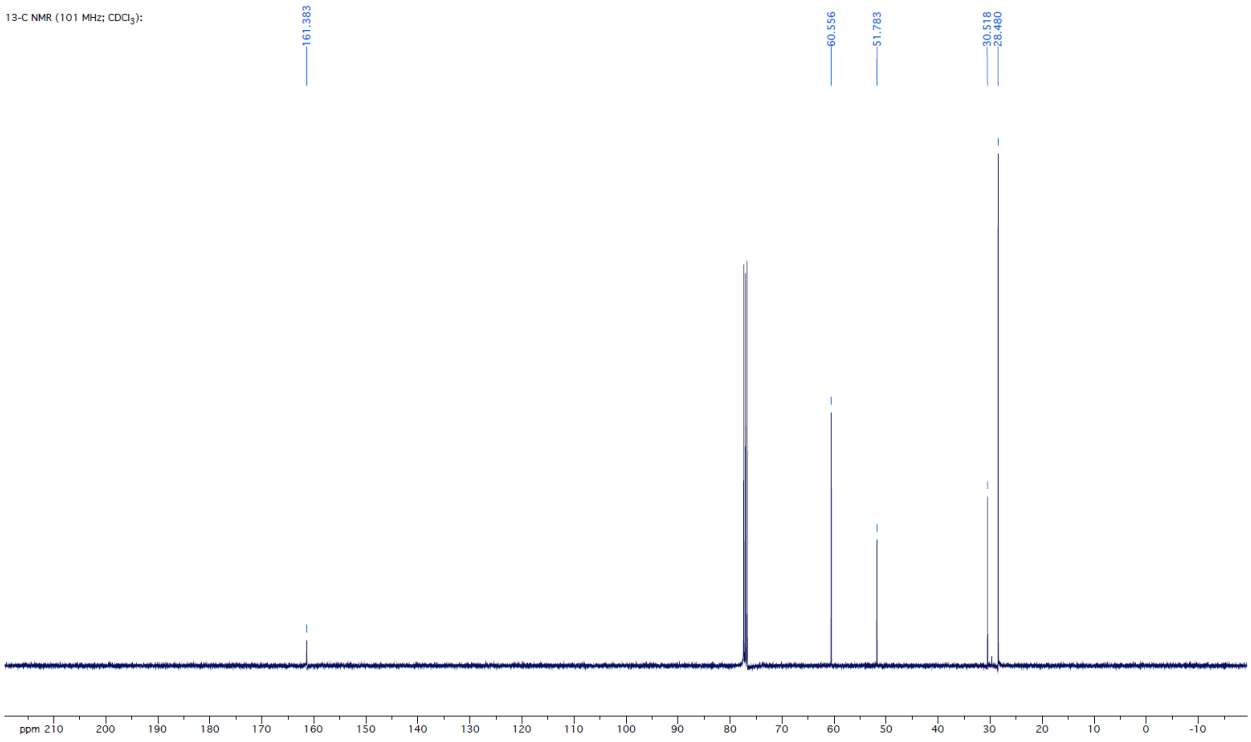

DP1554-carbon.1.fid
1d_13C_1_hour DMSO D:\\ Beau 25
(100 MHz, DMSO-d6)
161.08
56.48
56.47
54.49
54.40
46.68
40.63 DMSO
40.42 DMSO
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.37 DMSO
39.19
37.45
37.39
30.62
28.69
28.63
25.74
23.99
23.13
23.05
23.02
14.45
14.38
10.96
10.94
Chemical Shift (ppm)

1-H NMR (400 MHz; $CDCl_3$):

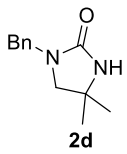


2c

13-C NMR (101 MHz; $CDCl_3$):

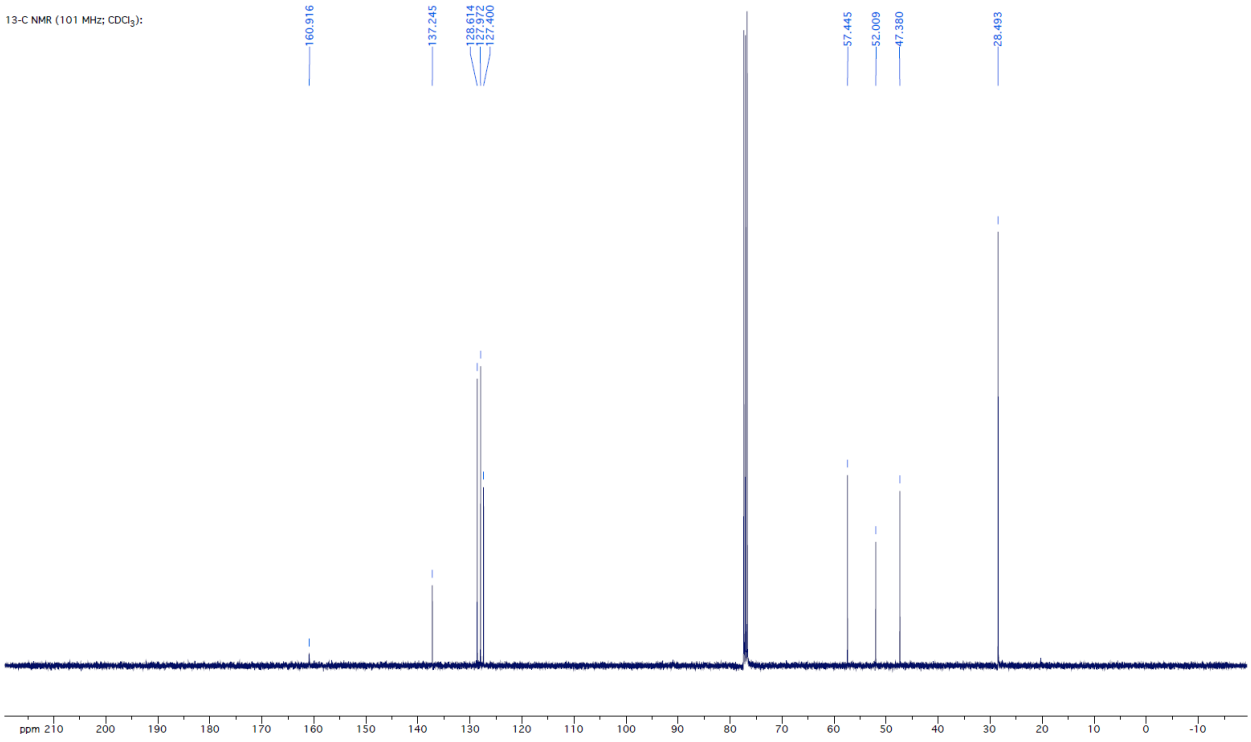


1-H NMR (400 MHz; $CDCl_3$):

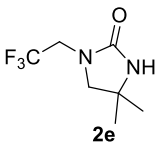


2d

13-C NMR (101 MHz; $CDCl_3$):

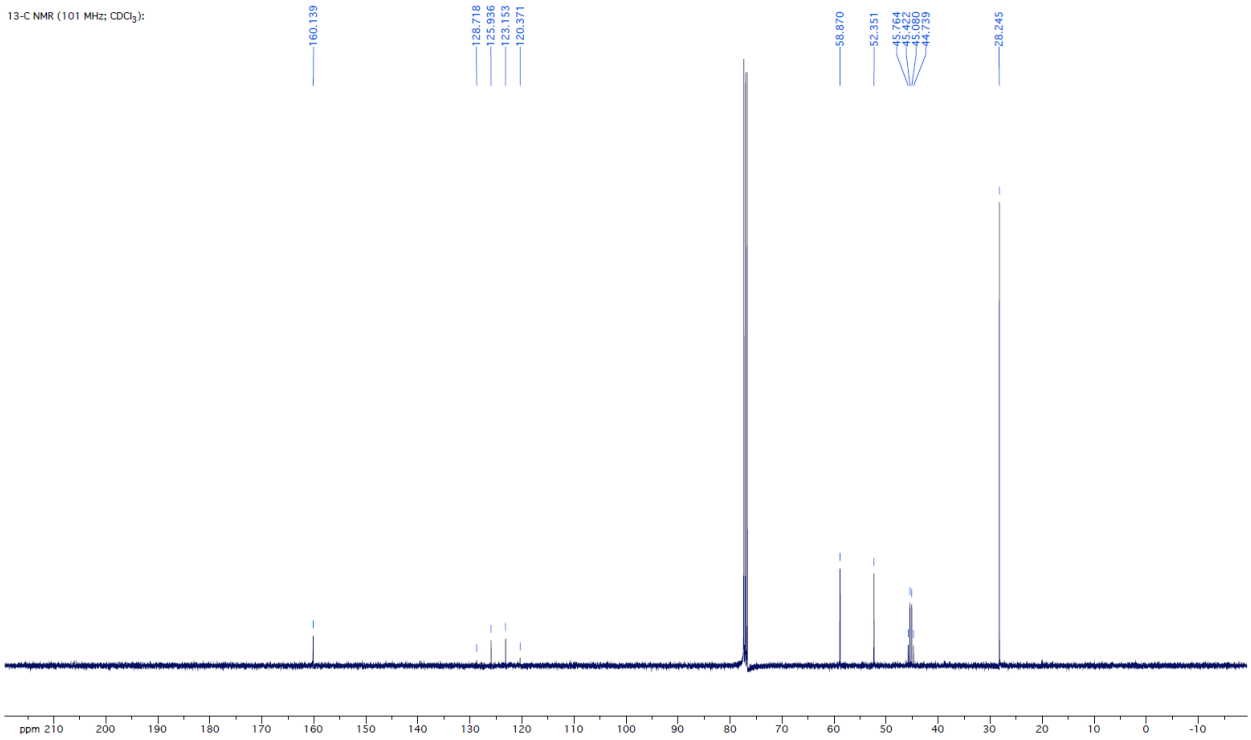


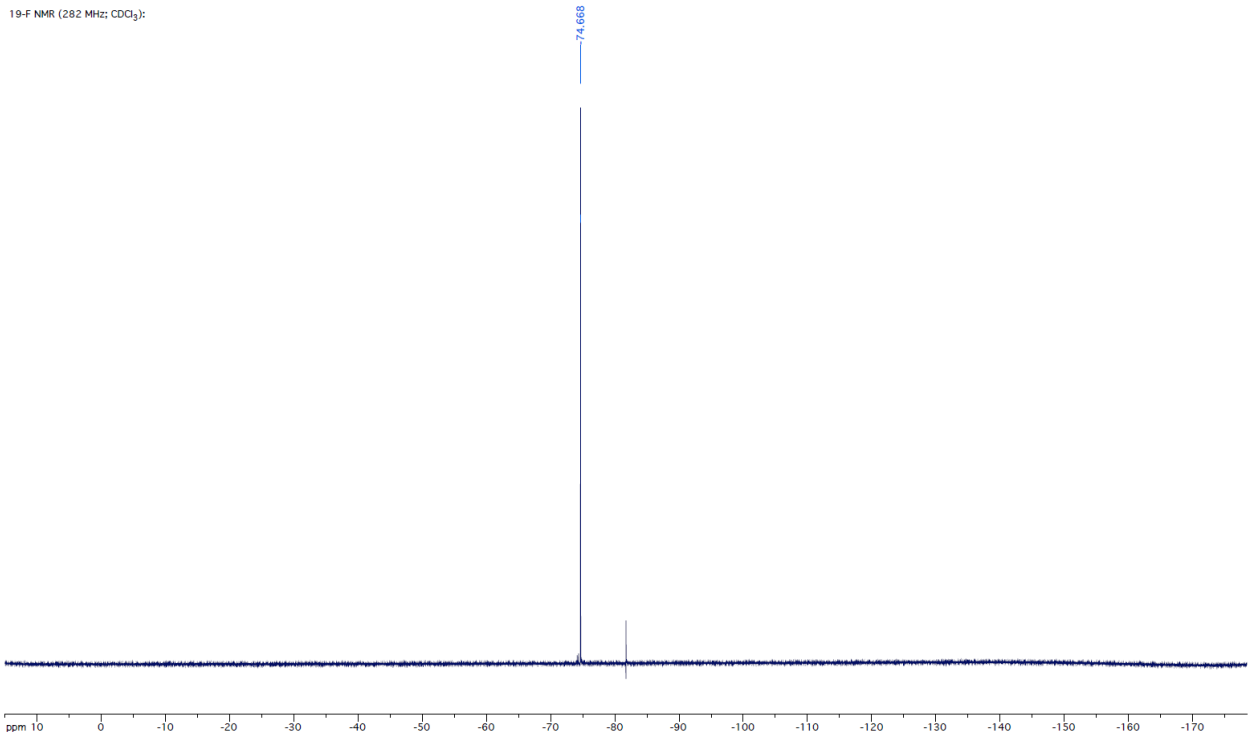
1-H NMR (400 MHz; $CDCl_3$):

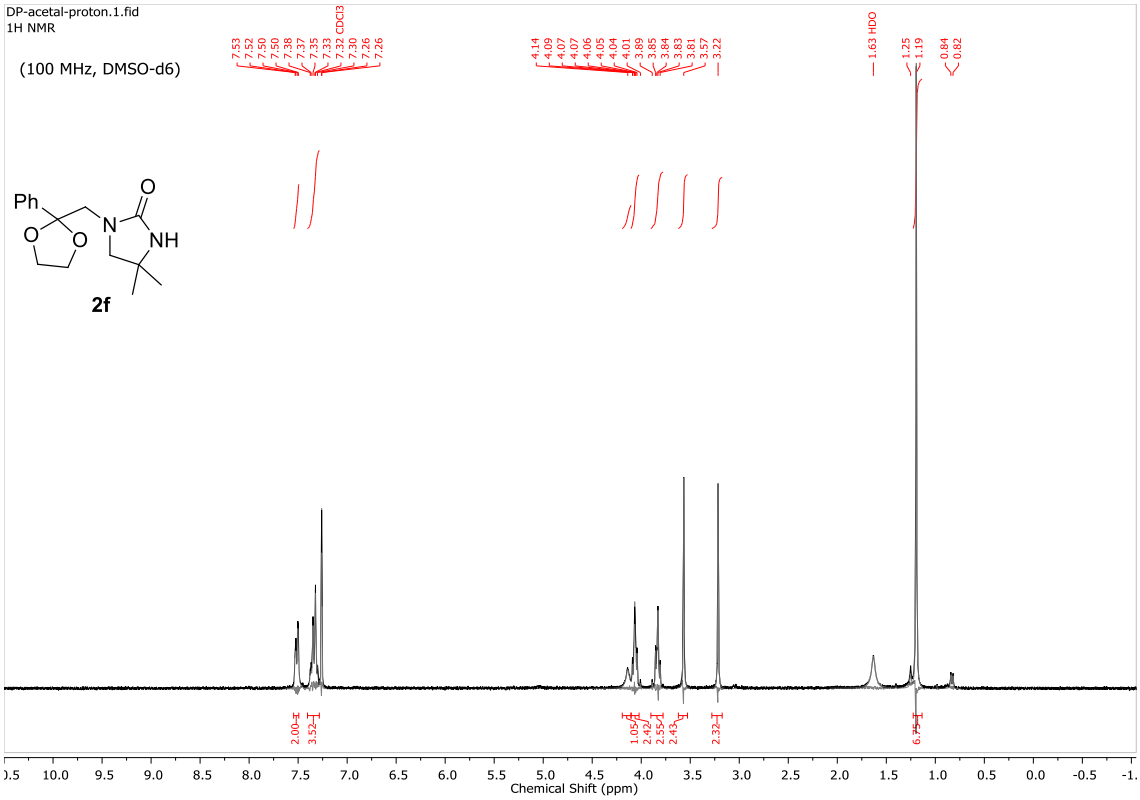


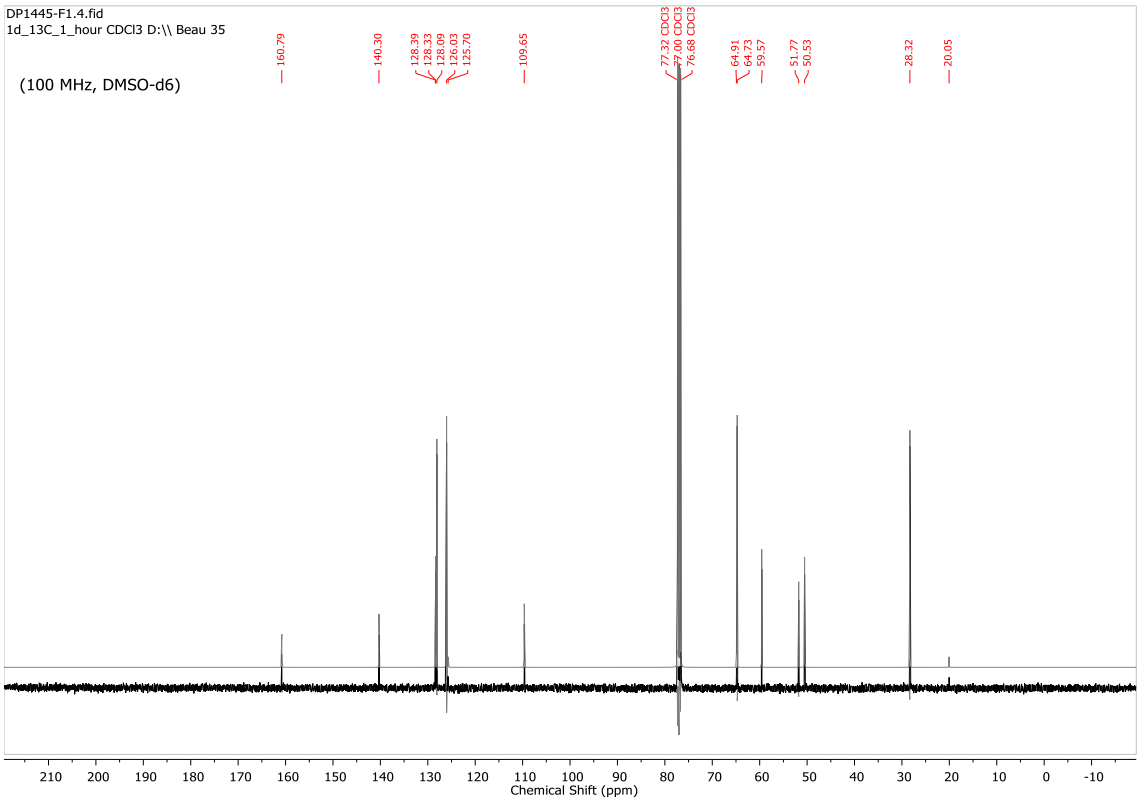
2e

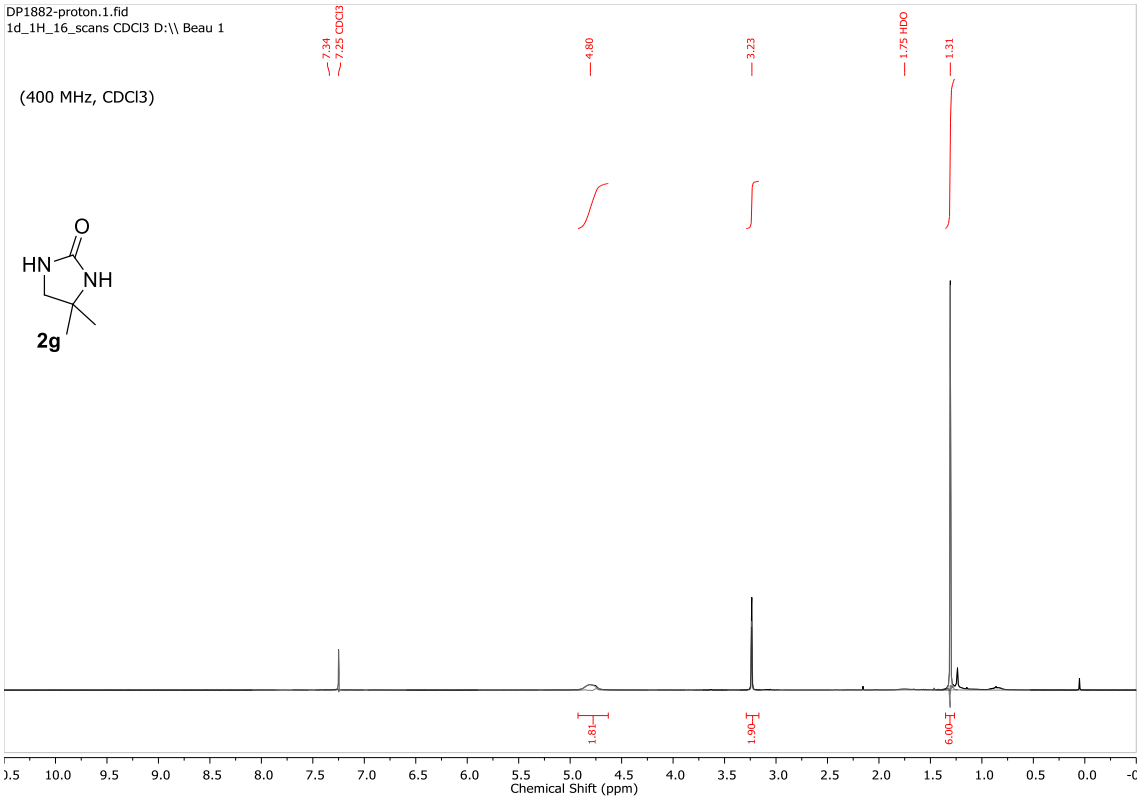
13-C NMR (101 MHz; $CDCl_3$):

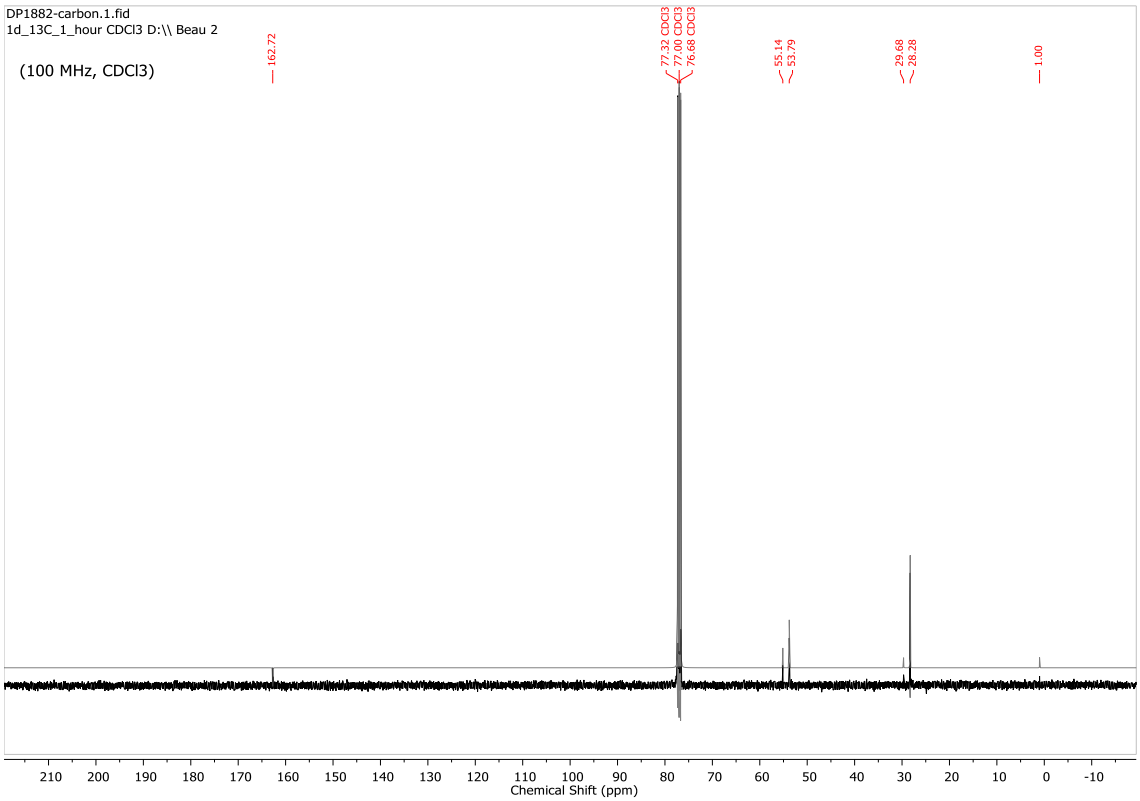



19-F NMR (282 MHz; $CDCl_3$):
-74.668
ppm 10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170

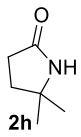

DP-acetal-proton.1.fid
1H NMR
(100 MHz, DMSO-d6)
Ph
O
O
O
N
NH
2f
Chemical Shift (ppm)


DP1445-F1.4.fid
1d_13C_1_hour CDCl3 D:\\ Beau 35
(100 MHz, DMSO-d6)
Chemical Shift (ppm)


DP1882-proton.1.fid
1d_1H_16_scans CDCl3 D:\\ Beau 1
(400 MHz, CDCl3)
7.34
7.25 CDCl3
4.80
3.23
1.75 HDO
1.31
O
HN
NH
2g
1.81
1.90
6.00
Chemical Shift (ppm)

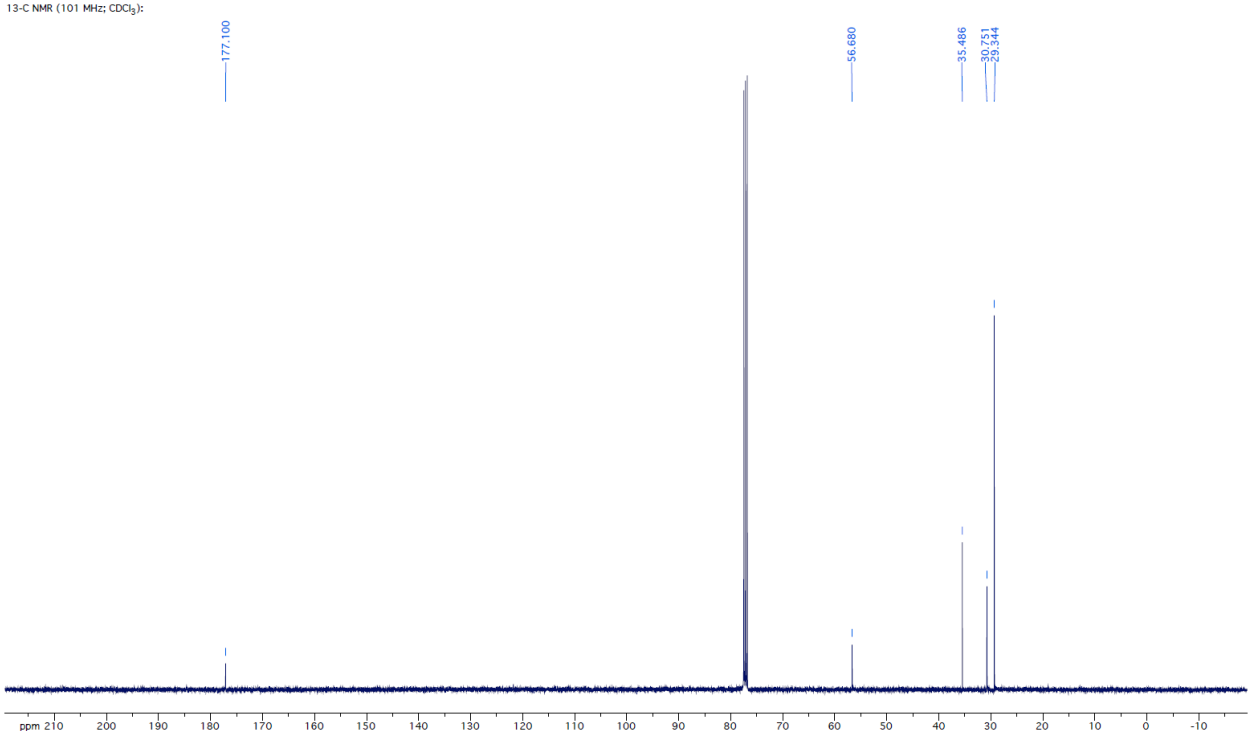

DP1882-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 2
(100 MHz, CDCl3)
162.72
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
55.14
53.79
29.68
28.28
1.00
Chemical Shift (ppm)

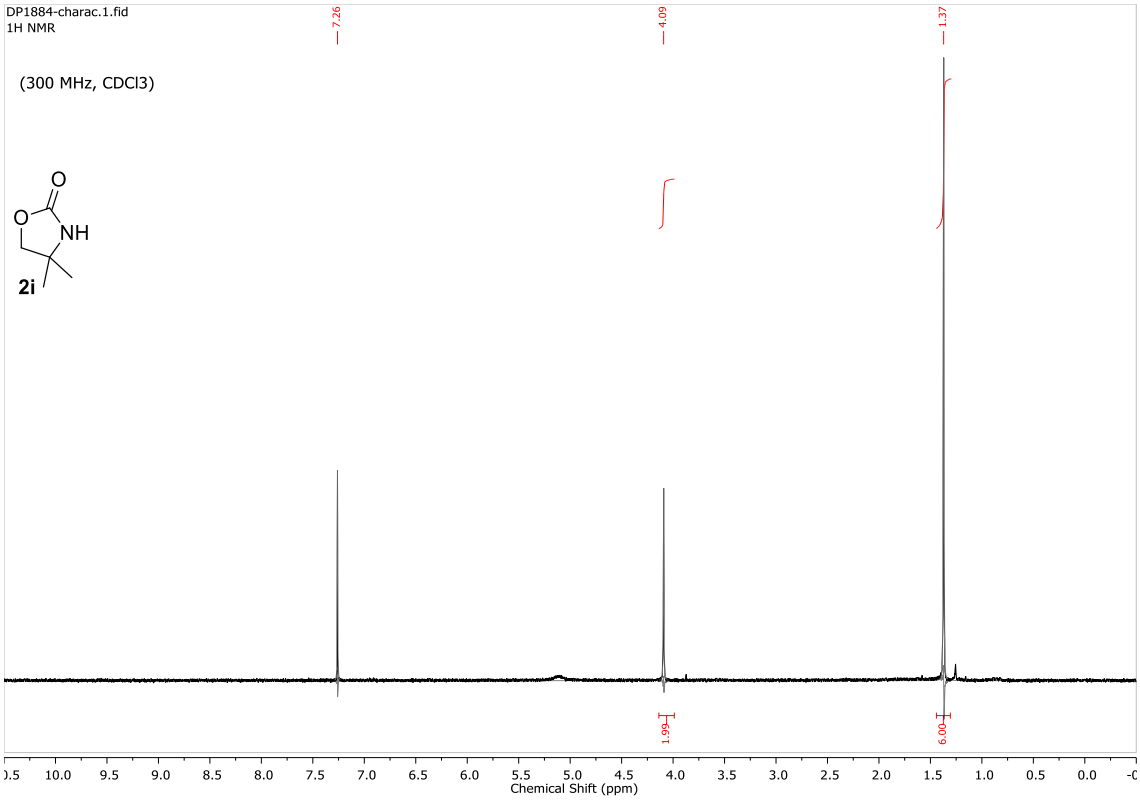
1-H NMR (400 MHz; $CDCl_3$):

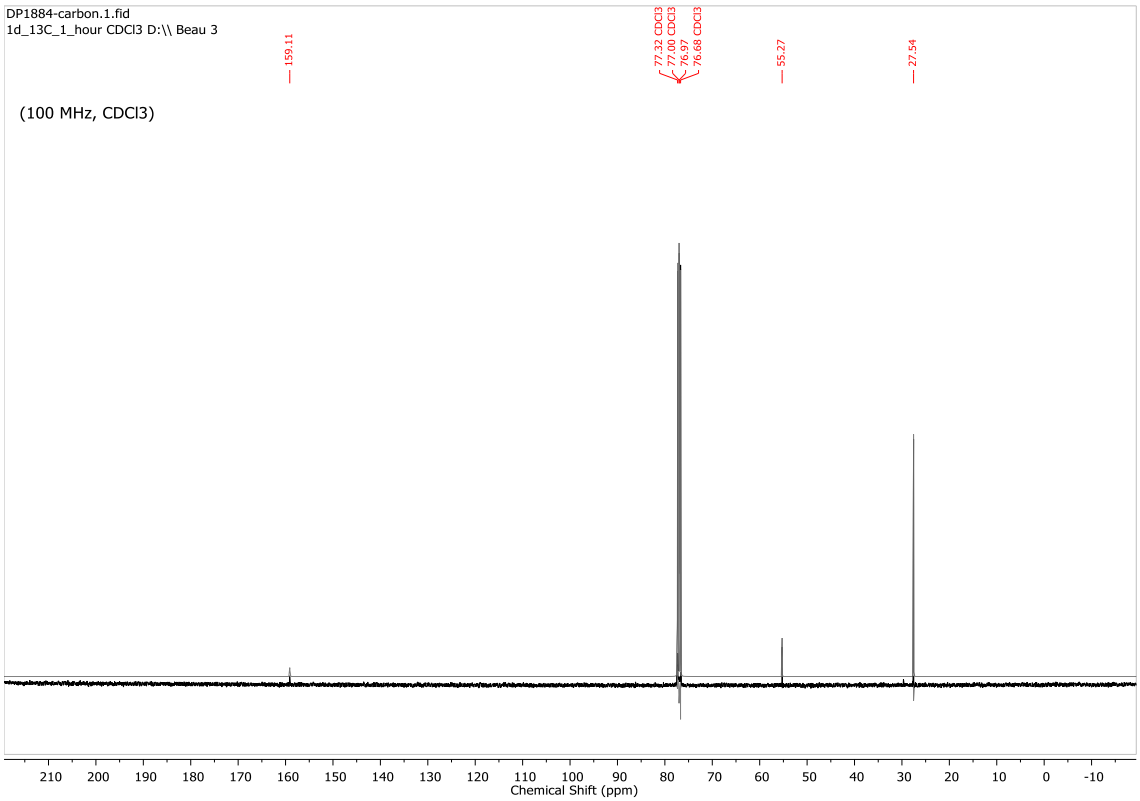


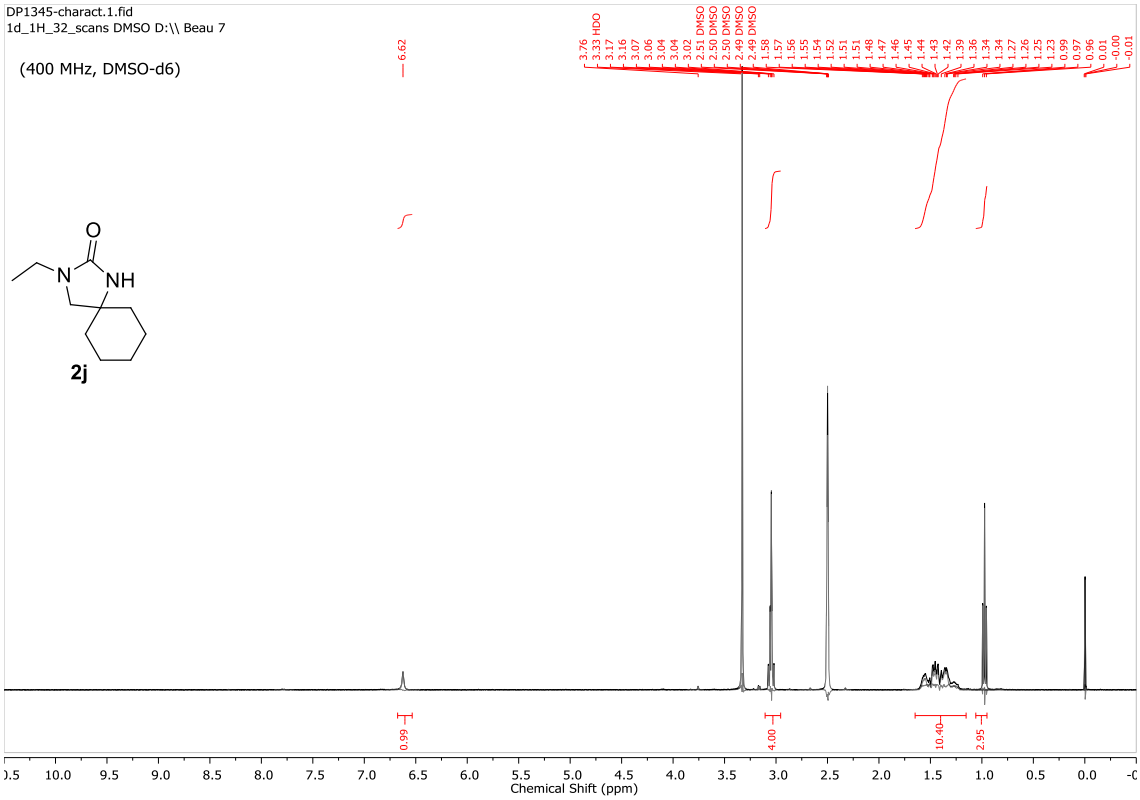
2h

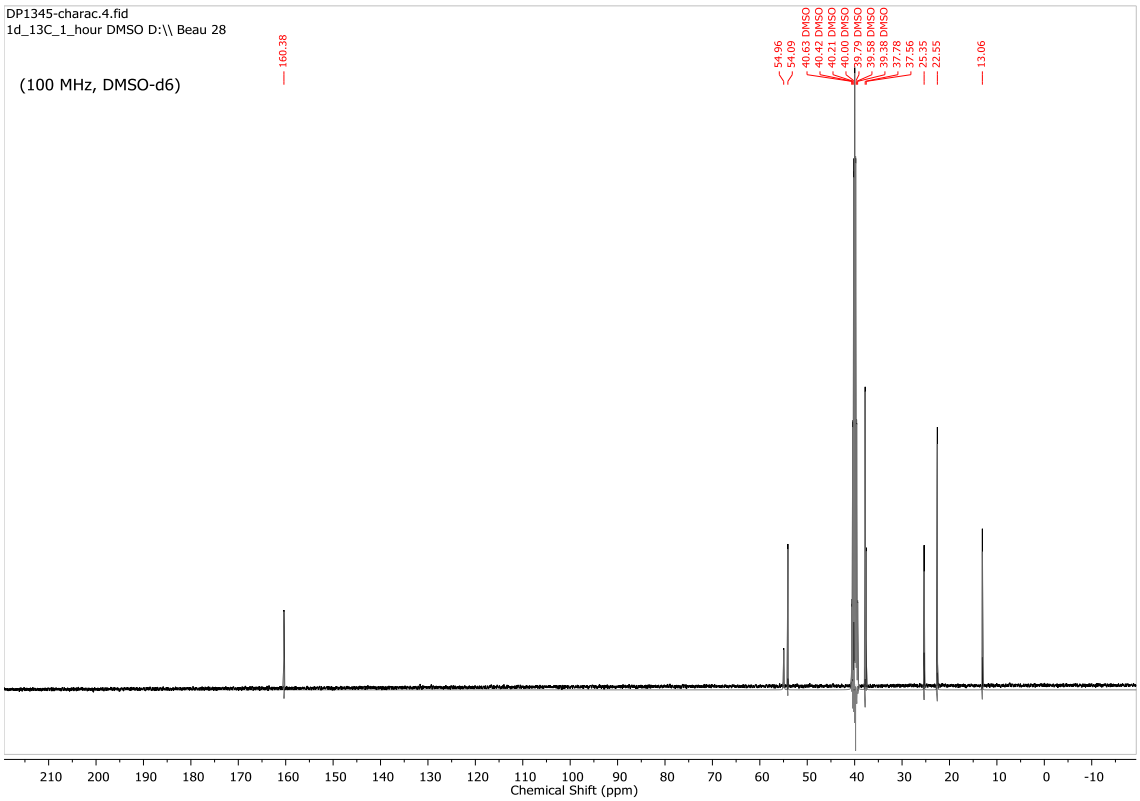
13-C NMR (101 MHz; $CDCl_3$):



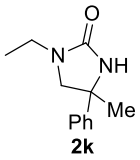

DP1884-charac.1.fid
1H NMR
(300 MHz, CDCl3)
7.26
4.09
1.37
O
O
NH
2i
1.99
6.00
Chemical Shift (ppm)


DP1884-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 3
(100 MHz, CDCl3)
159.11
77.32 CDCl3
77.00 CDCl3
76.97
76.68 CDCl3
55.27
27.54
Chemical Shift (ppm)


DP1345-charact.1.fid
1d_1H_32_scans DMSO D:\\ Beau 7
(400 MHz, DMSO-d6)
2j
Chemical Shift (ppm)

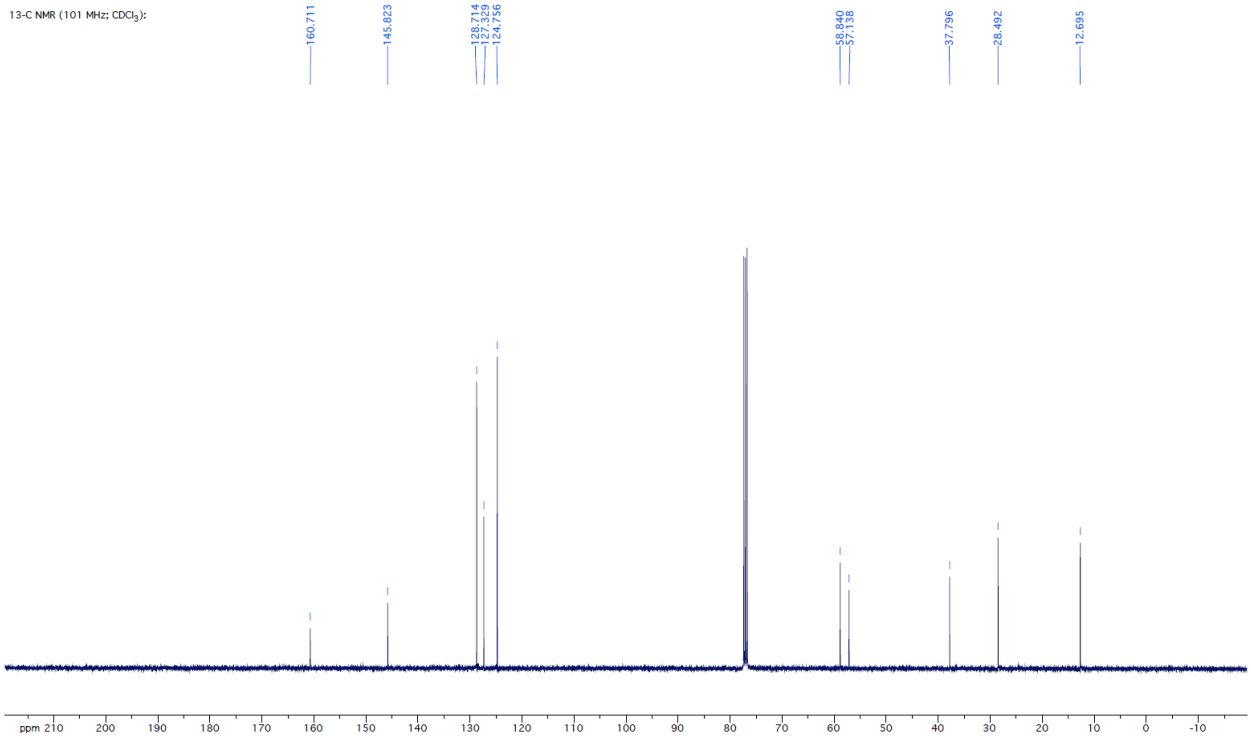

DP1345-charac.4.fid
1d_13C_1_hour DMSO D:\\ Beau 28
(100 MHz, DMSO-d6)
Chemical Shift (ppm)

1-H NMR (400 MHz; $CDCl_3$):

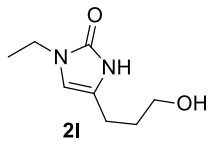


2k

13-C NMR (101 MHz; $CDCl_3$):

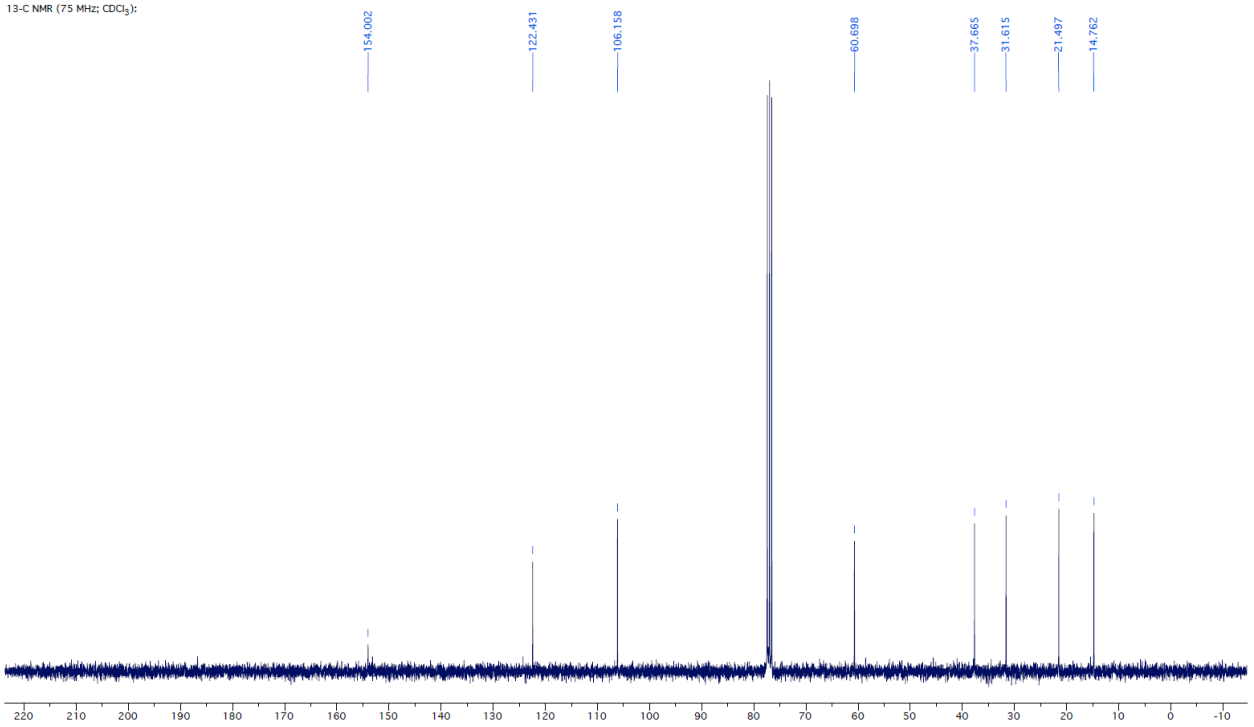


1-H NMR (300 MHz; $CDCl_3$):

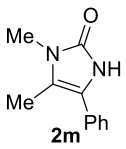


2l

13-C NMR (75 MHz; $CDCl_3$):

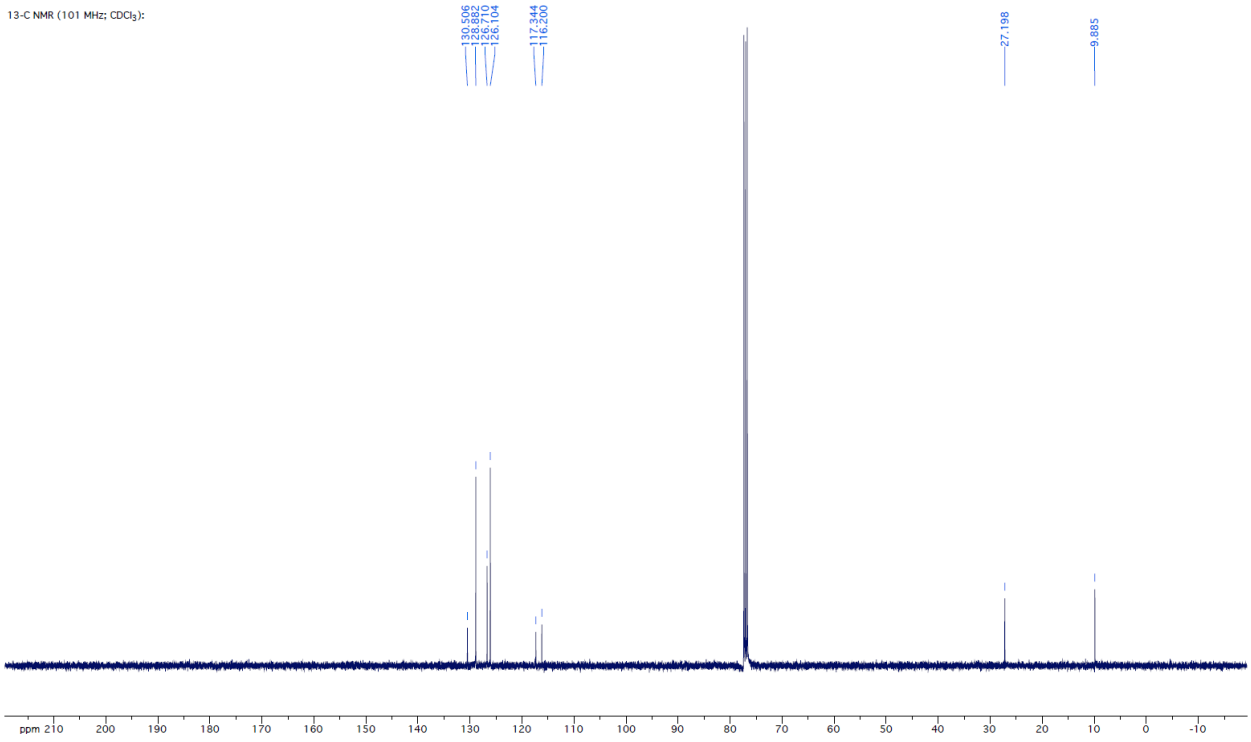


1-H NMR (400 MHz; $CDCl_3$):

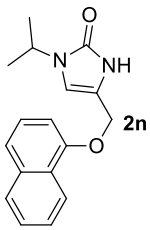


2m

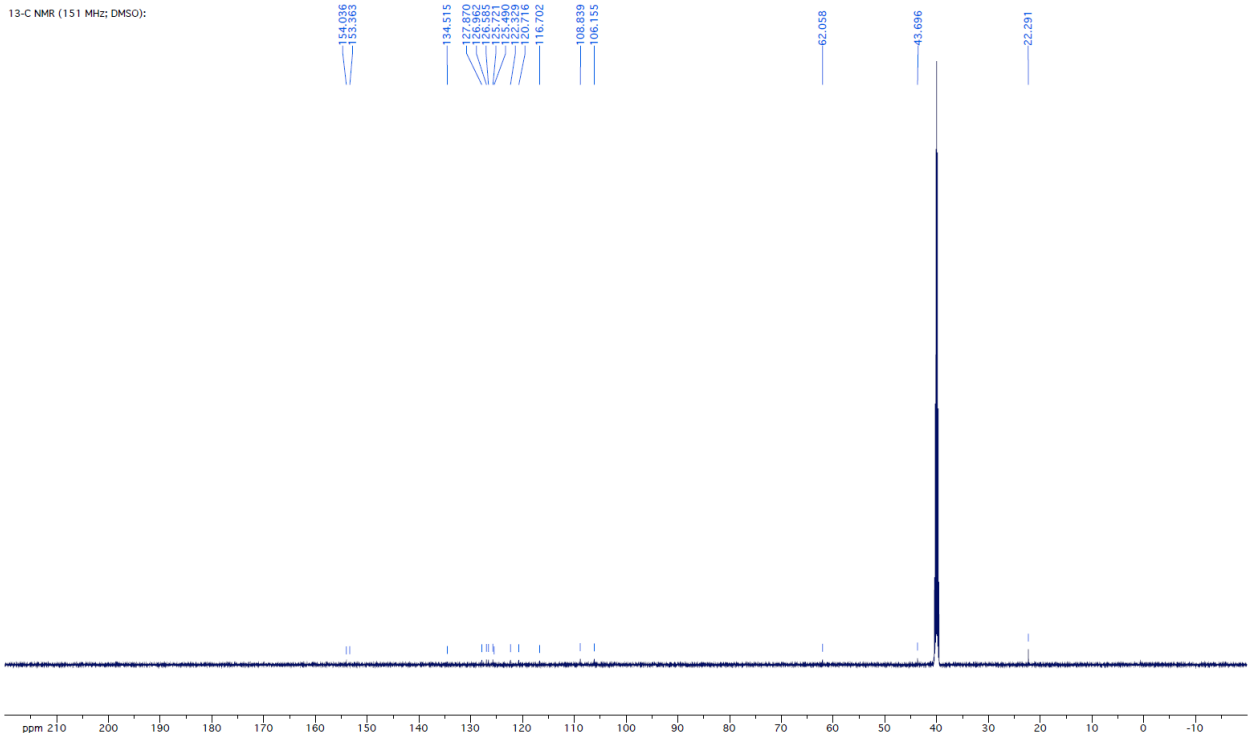
13-C NMR (101 MHz; $CDCl_3$):



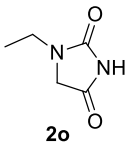
1-H NMR (600 MHz; DMSO):



13-C NMR (151 MHz; DMSO):

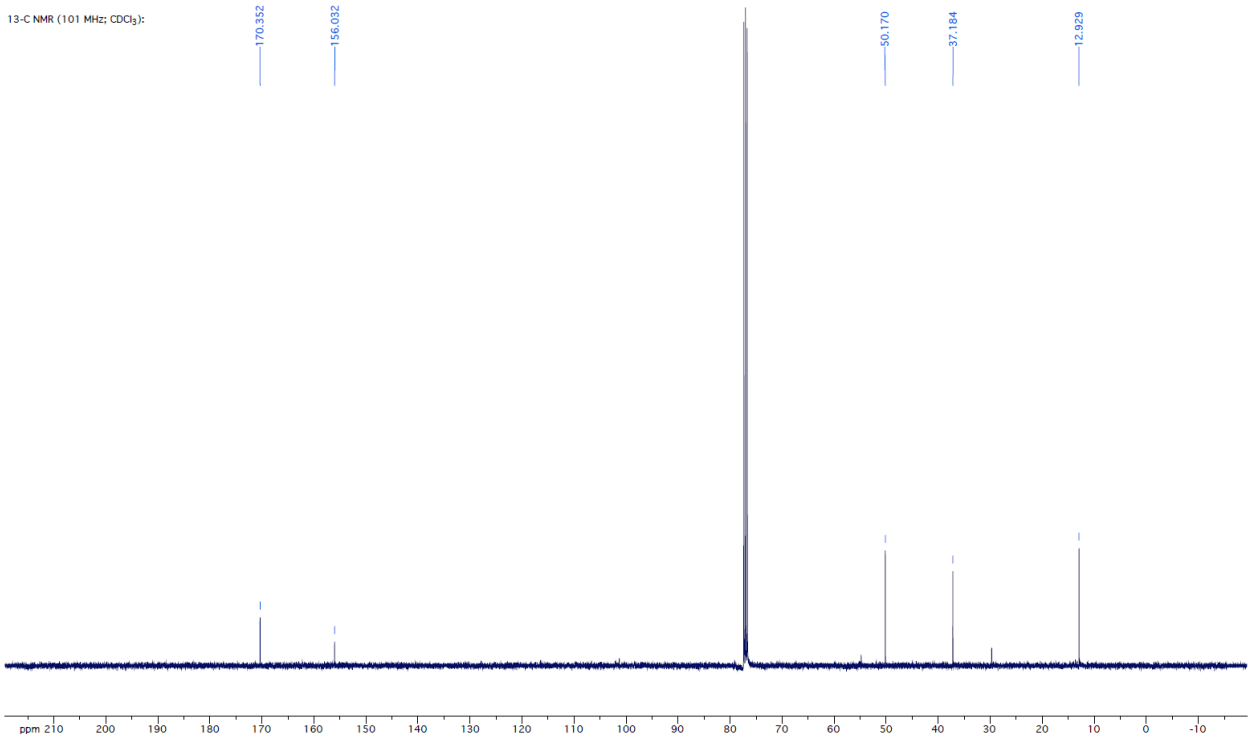


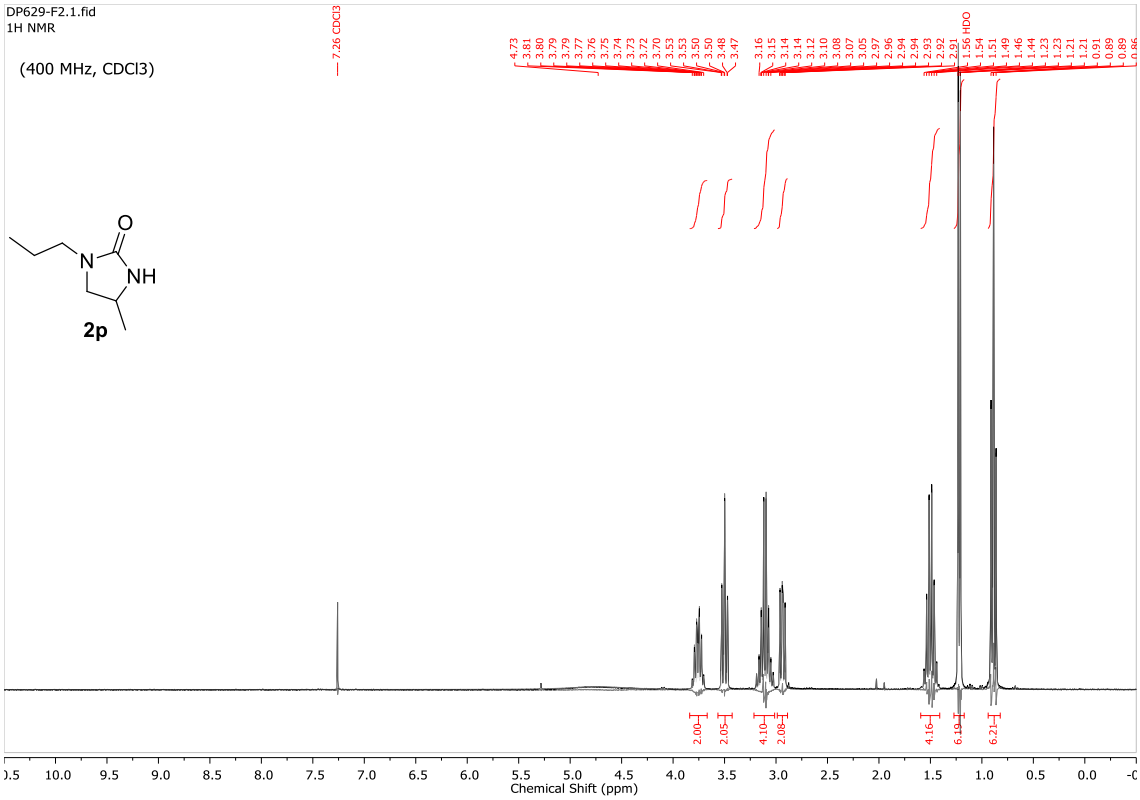
1-H NMR (400 MHz; $CDCl_3$):

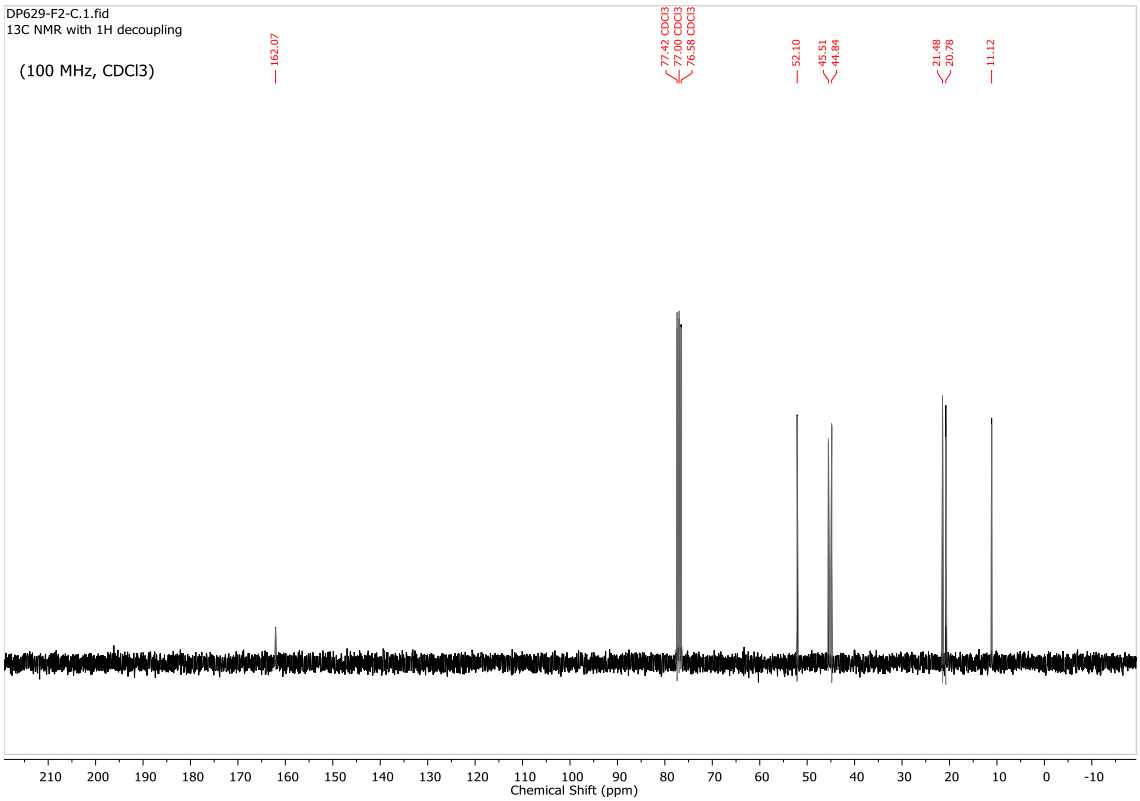


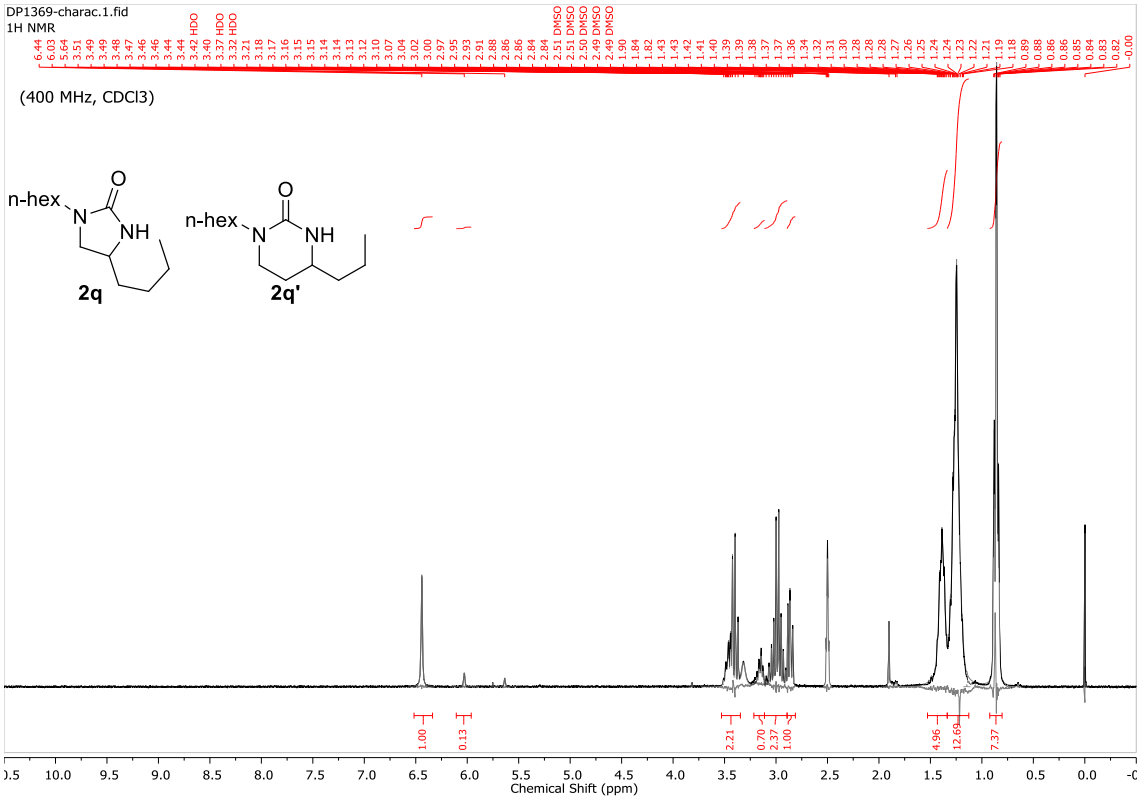
2o

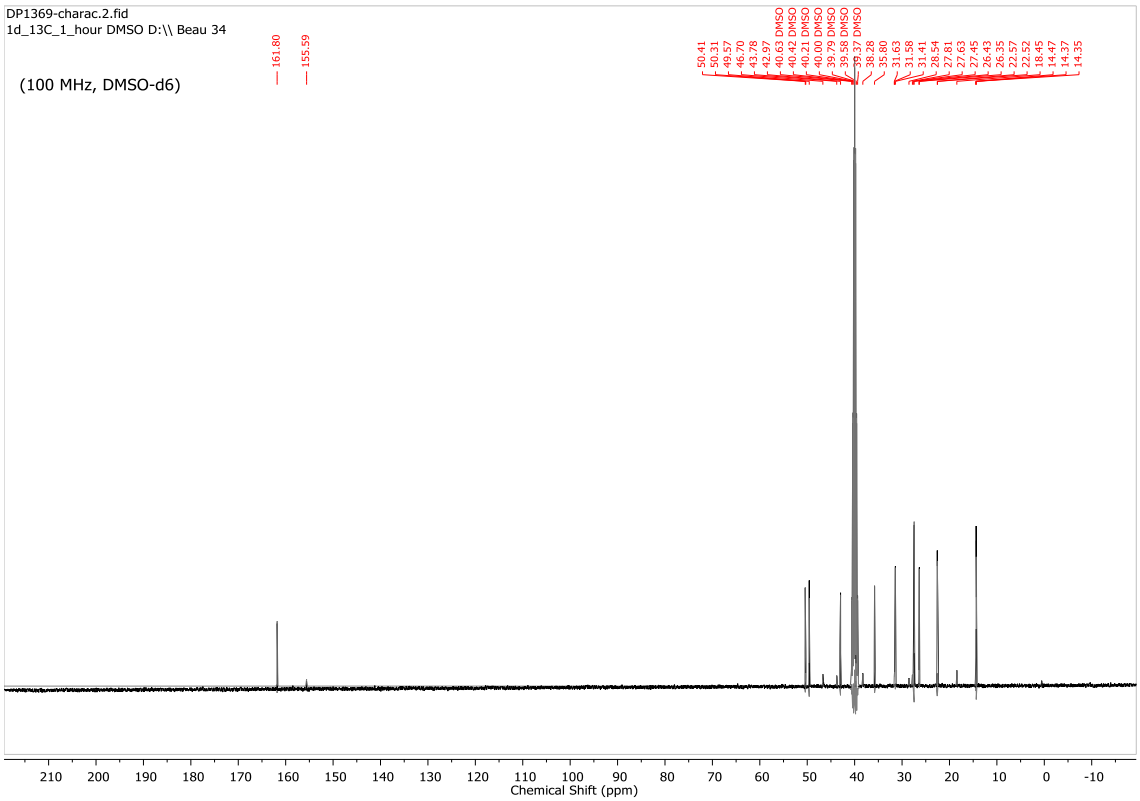
13-C NMR (101 MHz; $CDCl_3$):

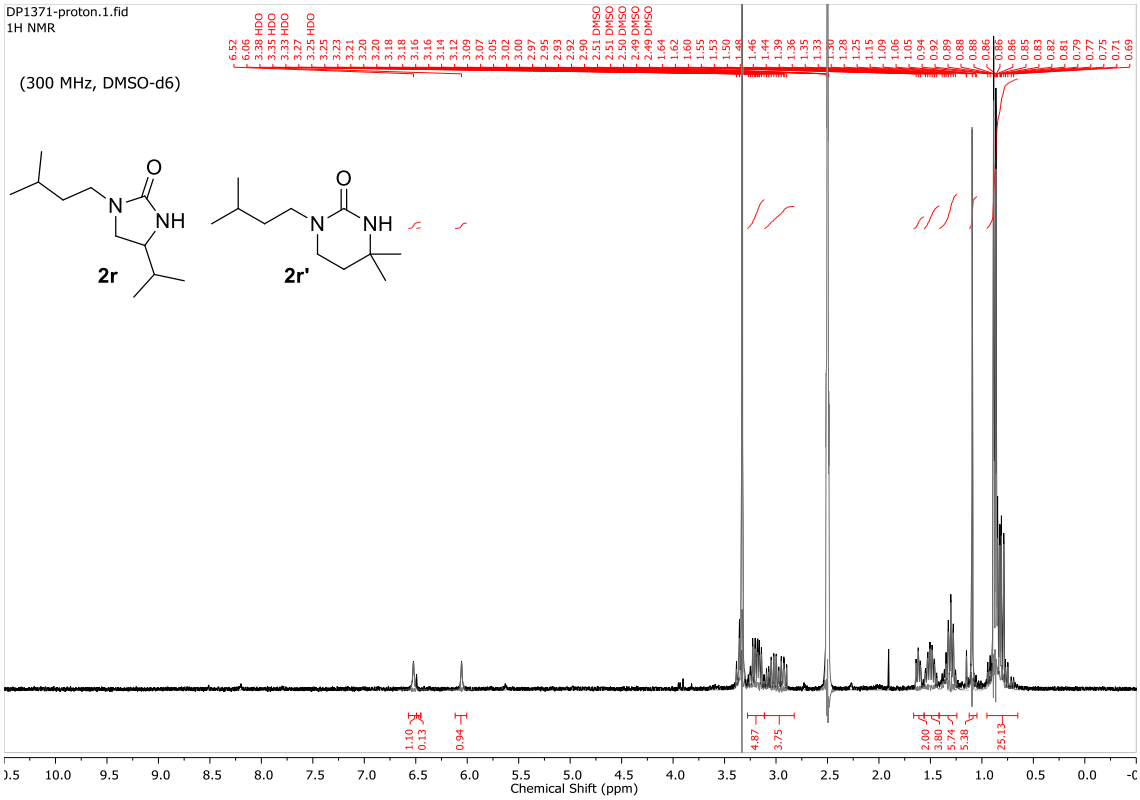


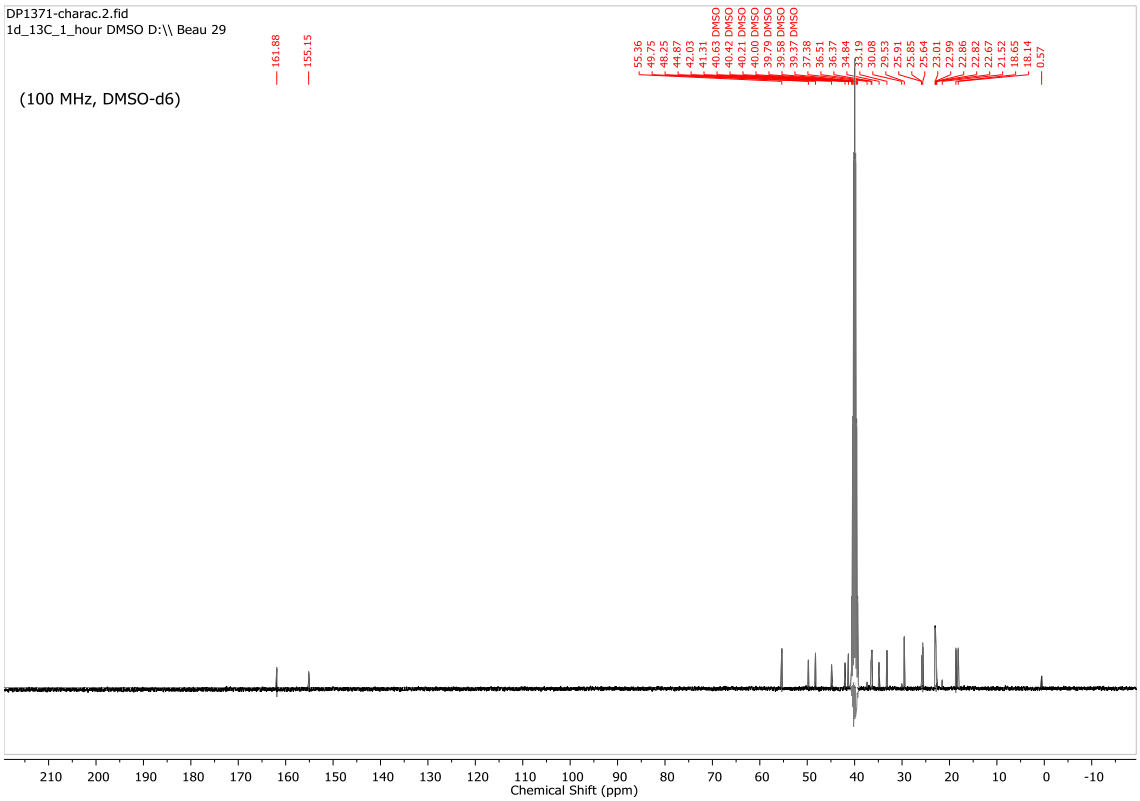

DP629-F2.1.fid
1H NMR
(400 MHz, CDCl3)
7.26 CDCl3
1.56 HDO
2p
2.00
2.05
4.10
2.08
4.16
6.19
6.21
Chemical Shift (ppm)


DP629-F2-C.1.fid
13C NMR with 1H decoupling
(100 MHz, CDCl3)
162.07
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
52.10
45.51
44.84
21.48
20.78
11.12
Chemical Shift (ppm)

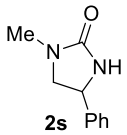

DP1369-charac.1.fid
1H NMR
(400 MHz, CDCl3)
n-hex
N
O
NH
2q
n-hex
N
O
NH
2q'
Chemical Shift (ppm)


DP1369-charac.2.fid
1d_13C_1_hour DMSO D:\\ Beau 34
(100 MHz, DMSO-d6)
161.80
155.59
Chemical Shift (ppm)


DP1371-proton.1.fid
1H NMR
(300 MHz, DMSO-d6)
2r
2r'
Chemical Shift (ppm)

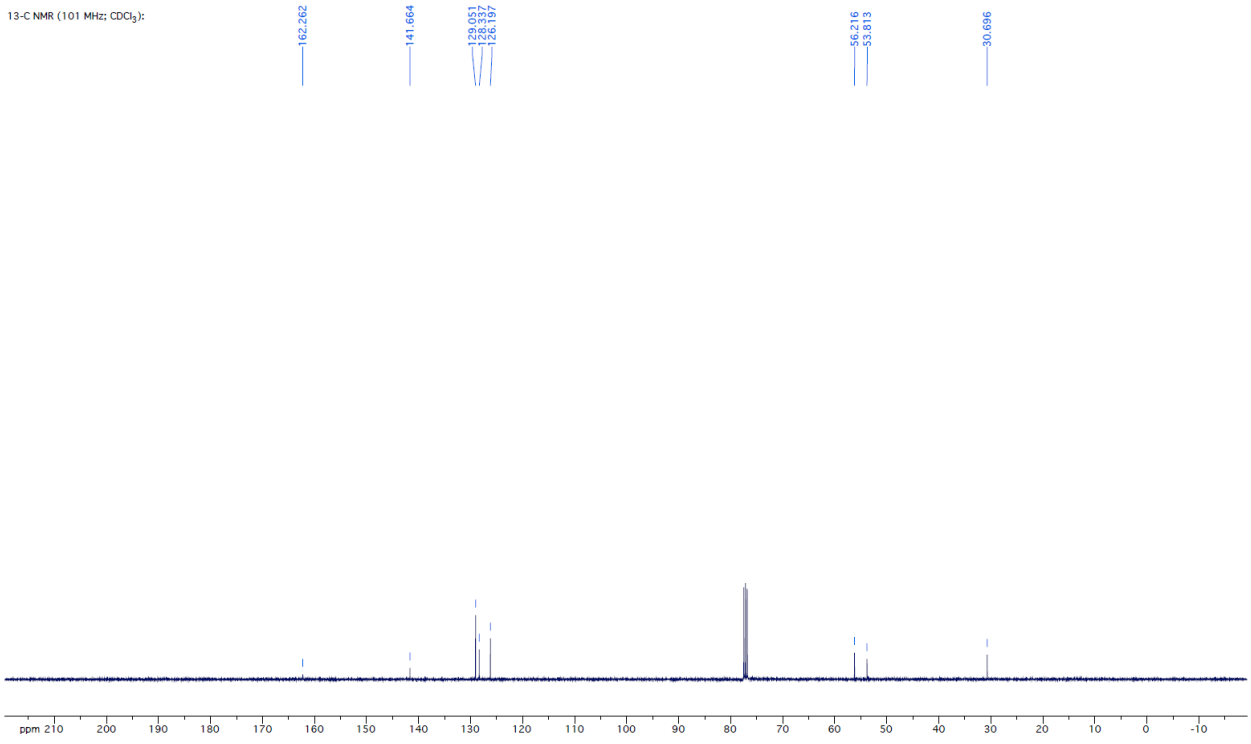

DP1371-charac.2.fid
1d_13C_1_hour DMSO D:\\ Beau 29
(100 MHz, DMSO-d6)
Chemical Shift (ppm)

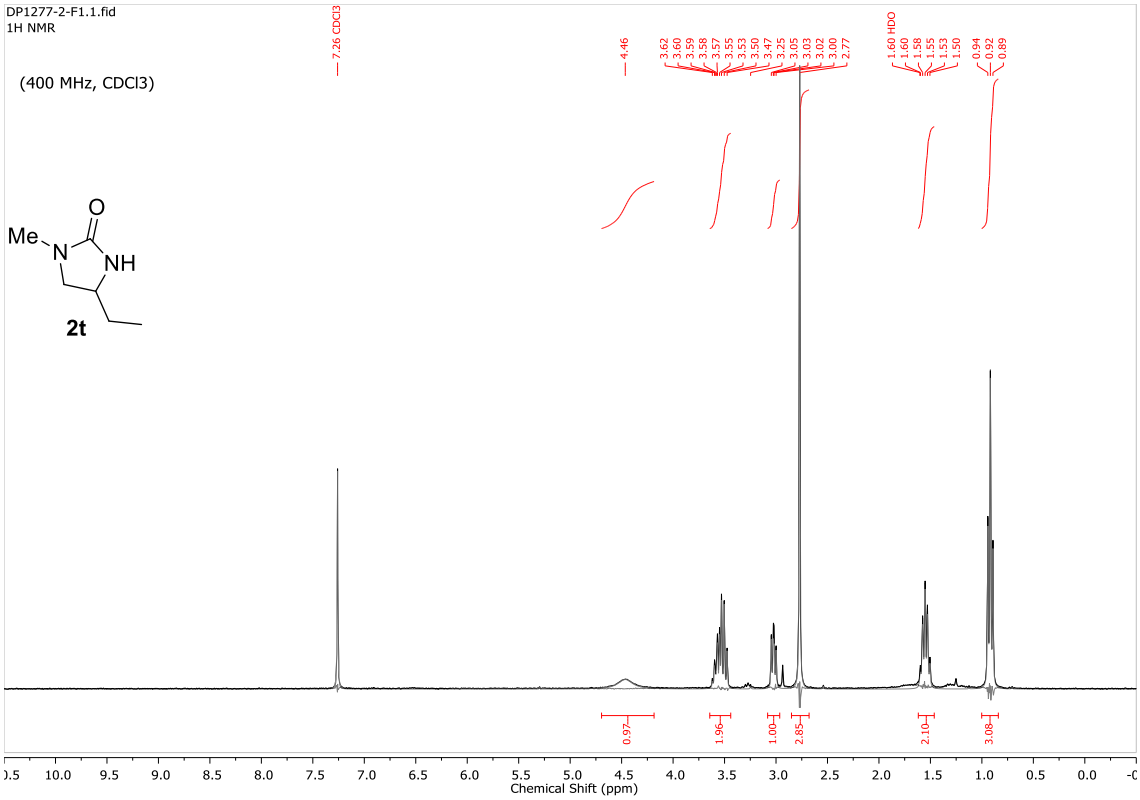
1-H NMR (400 MHz; $CDCl_3$):

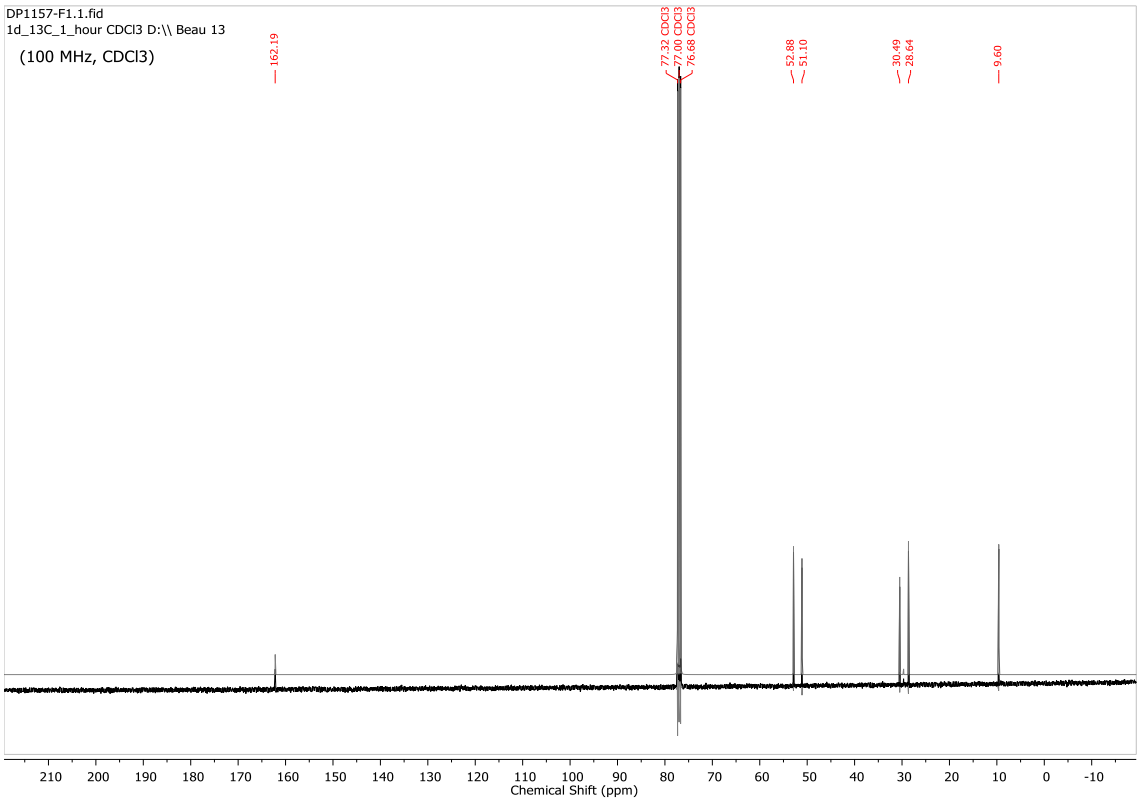


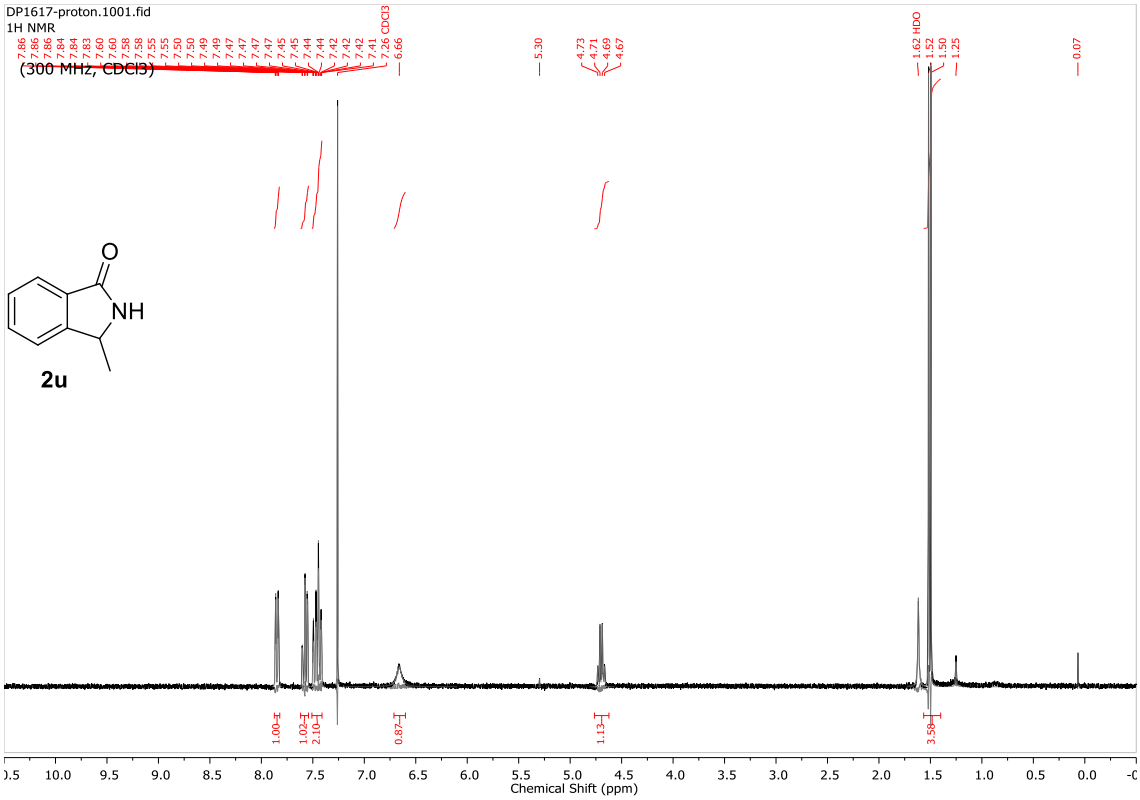
2s

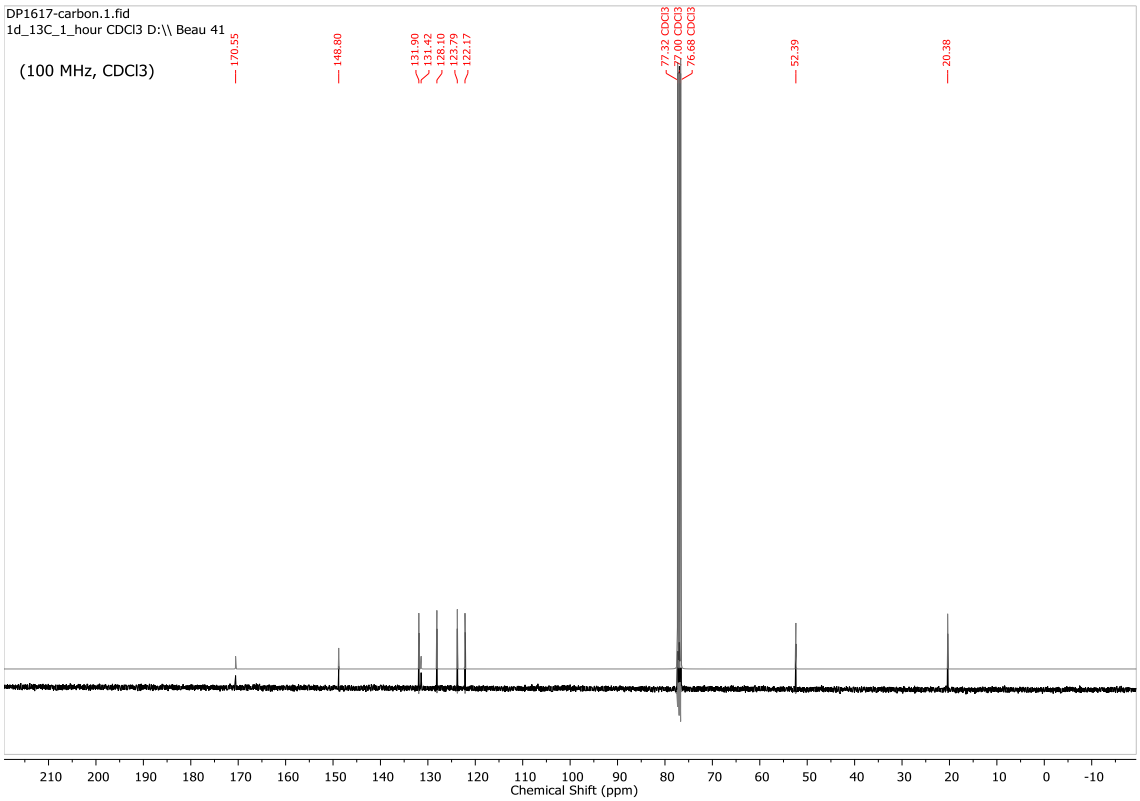
13-C NMR (101 MHz; $CDCl_3$):



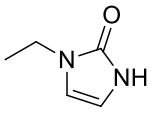

DP1277-2-F1.1.fid
1H NMR
(400 MHz, CDCl3)
Me
N
O
NH
2t
7.26 CDCl3
4.46
3.62
3.60
3.59
3.58
3.57
3.55
3.53
3.50
3.47
3.25
3.05
3.03
3.02
3.00
2.77
1.60 HDO
1.60
1.60
1.58
1.55
1.53
1.50
0.94
0.92
0.89
0.97
1.96
1.00
2.85
2.10
3.08
Chemical Shift (ppm)


DP1157-F1.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 13
(100 MHz, CDCl3)
162.19
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
52.88
51.10
30.49
28.64
9.60
Chemical Shift (ppm)


DP1617-proton.1001.fid
1H NMR
(300 MHz, CDCl3)
7.86 7.86 7.86 7.84 7.84 7.84 7.83 7.60 7.60 7.58 7.58 7.55 7.55 7.50 7.50 7.49 7.49 7.47 7.47 7.47 7.47 7.45 7.45 7.44 7.44 7.42 7.42 7.42 7.42 7.41 7.26 CDCl3 6.66
5.30
4.73 4.71 4.69 4.67
1.62 HDO 1.52 1.50 1.25
0.07
O
NH
2u
1.00 1.02 2.10 0.87 1.13 3.58
Chemical Shift (ppm)

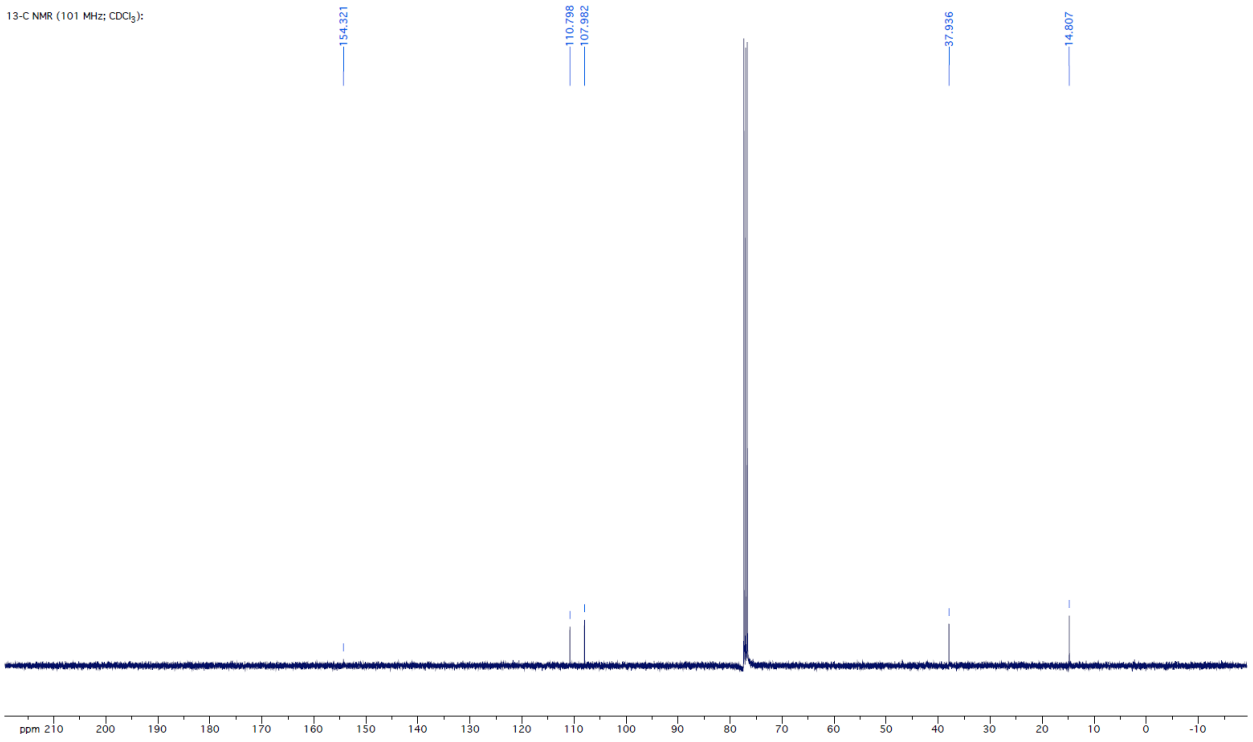

DP1617-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 41
(100 MHz, CDCl3)
170.55
148.80
131.90 131.42 128.10 123.79 122.17
77.32 CDCl3 77.00 CDCl3 76.68 CDCl3
52.39
20.38
Chemical Shift (ppm)

1-H NMR (300 MHz; $CDCl_3$):

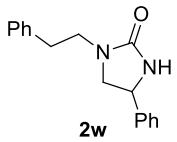


2v

13-C NMR (101 MHz; $CDCl_3$):

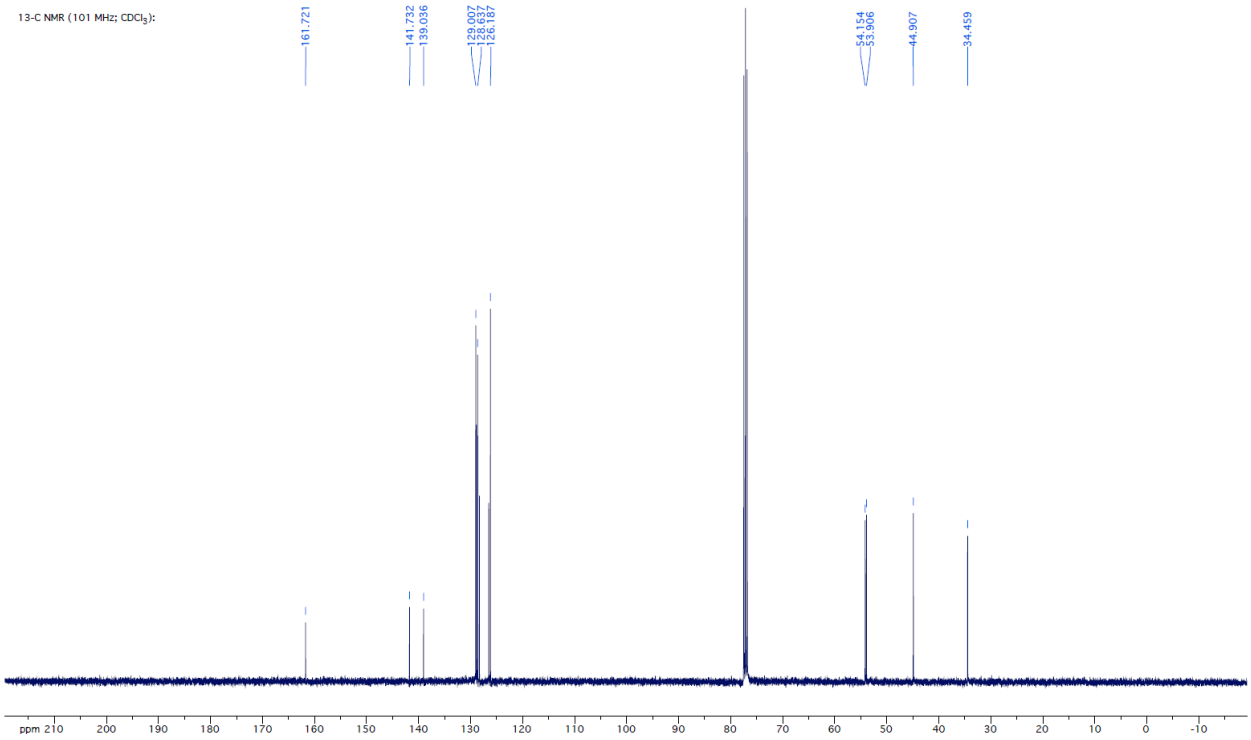


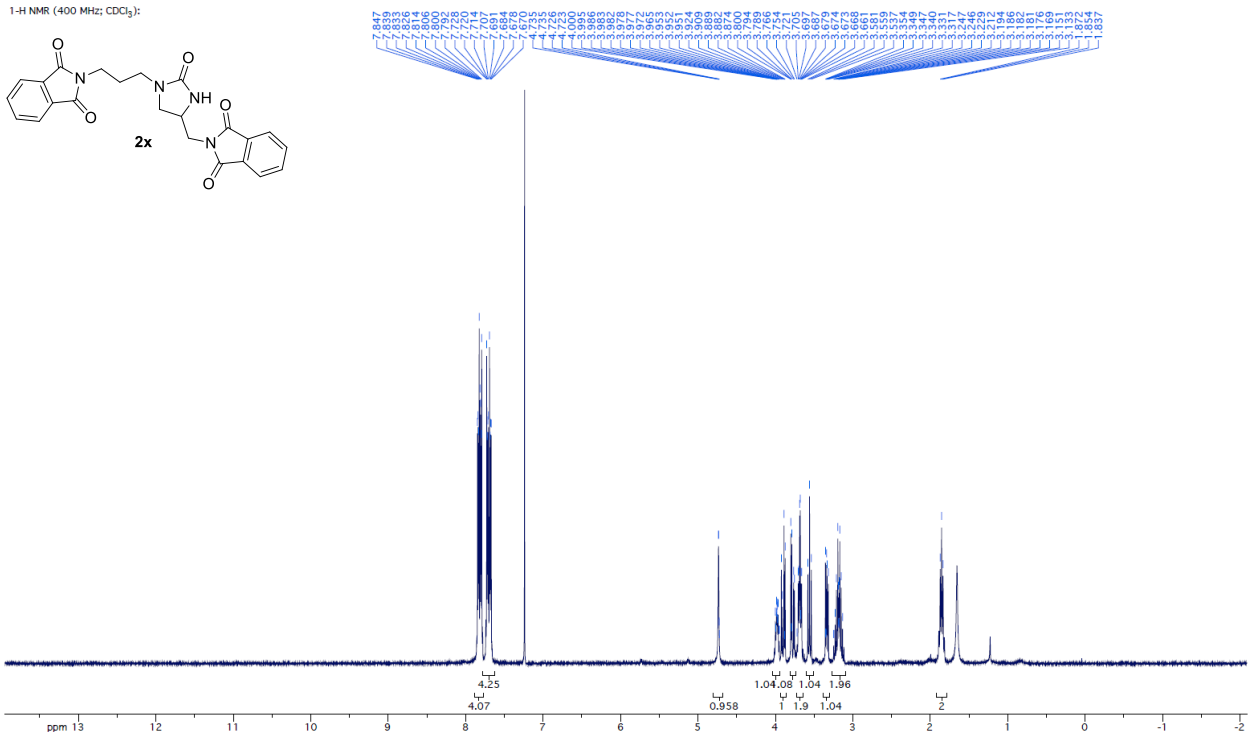
1-H NMR (400 MHz; $CDCl_3$):

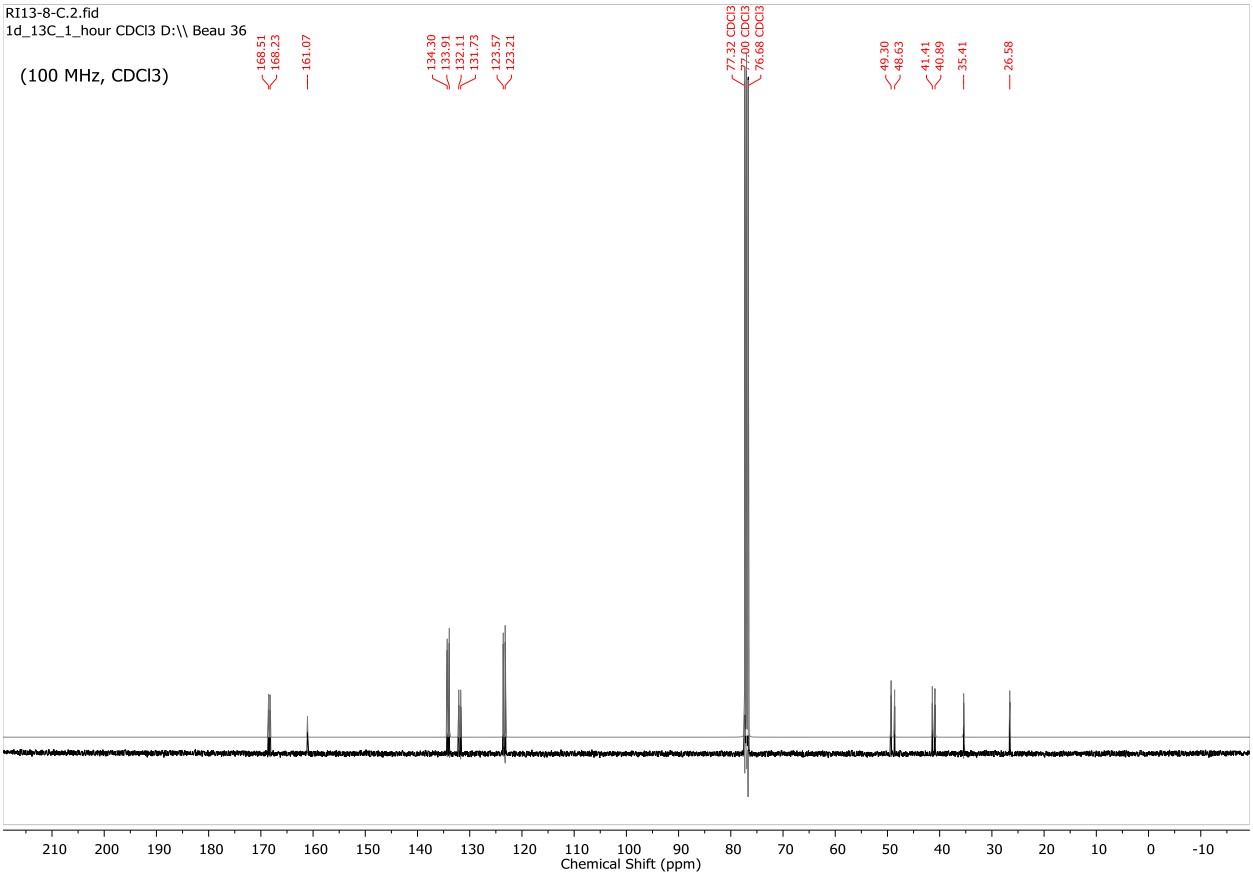


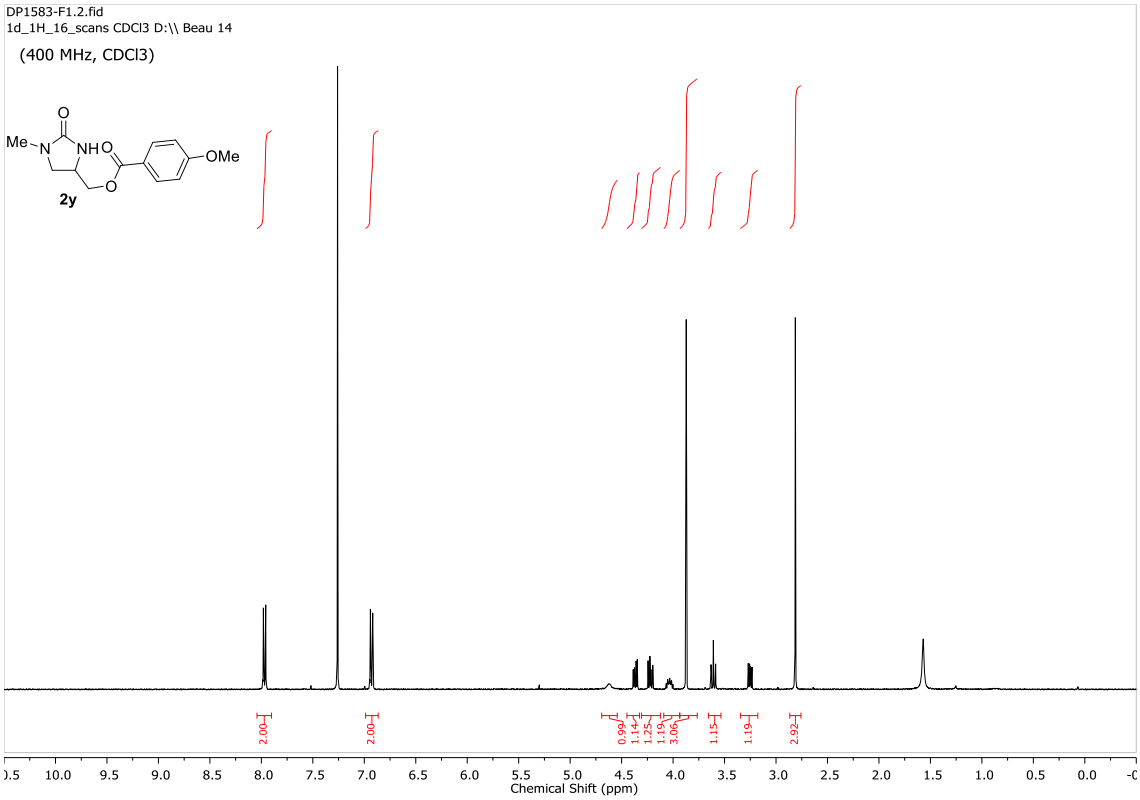
2w

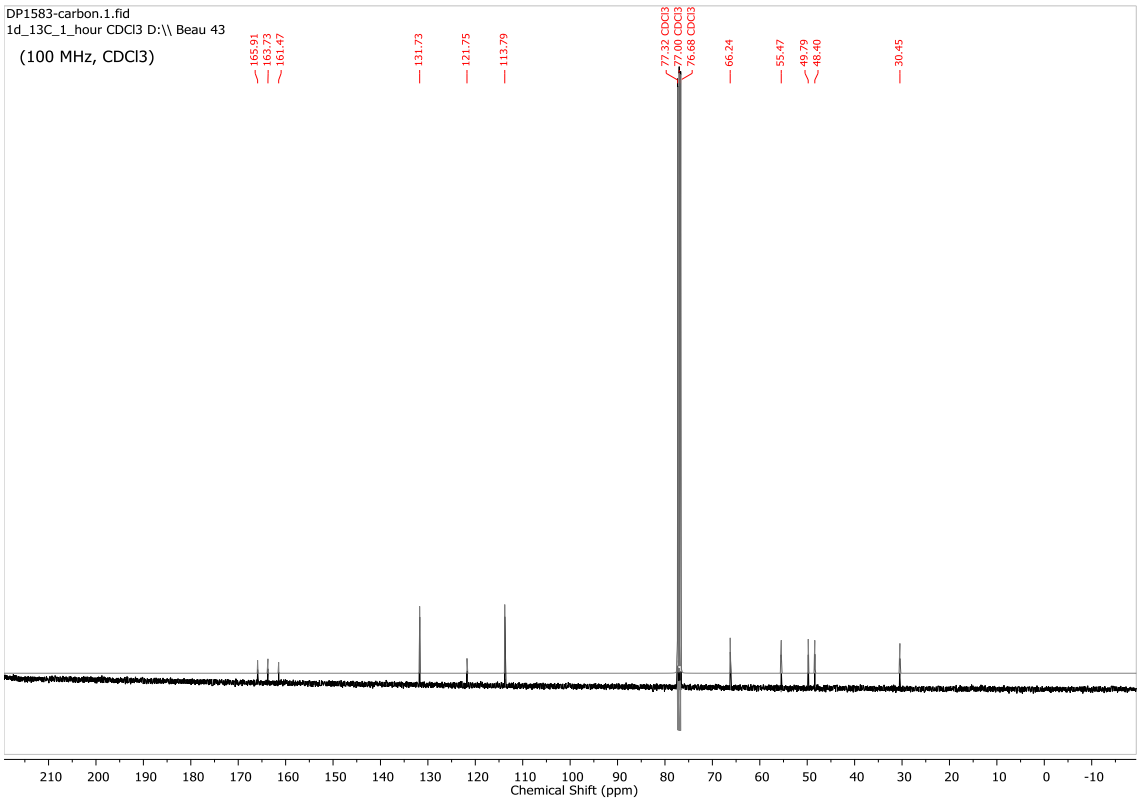
13-C NMR (101 MHz; $CDCl_3$):



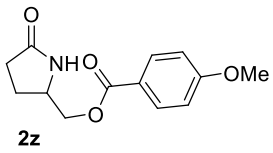

1-H NMR (400 MHz; CDCl3):
2x
4.25
4.07
0.958
1.04
1.08
1
1.04
1.9
1.96
1.04
2
ppm 13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2


RI13-8-C.2.fid
1d_13C_1_hour CDCl3 D:\\ Beau 36
(100 MHz, CDCl3)
168.51
168.23
161.07
134.30
133.91
132.11
131.73
123.57
123.21
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
49.30
48.63
41.41
40.89
35.41
26.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)


DP1583-F1.2.fid
1d_1H_16_scans CDCl3 D:\\ Beau 14
(400 MHz, CDCl3)
Me
N
NH
O
O
O
OMe
2y
2.00
2.00
0.99
1.14
1.25
1.19
3.06
1.15
1.19
2.92
Chemical Shift (ppm)

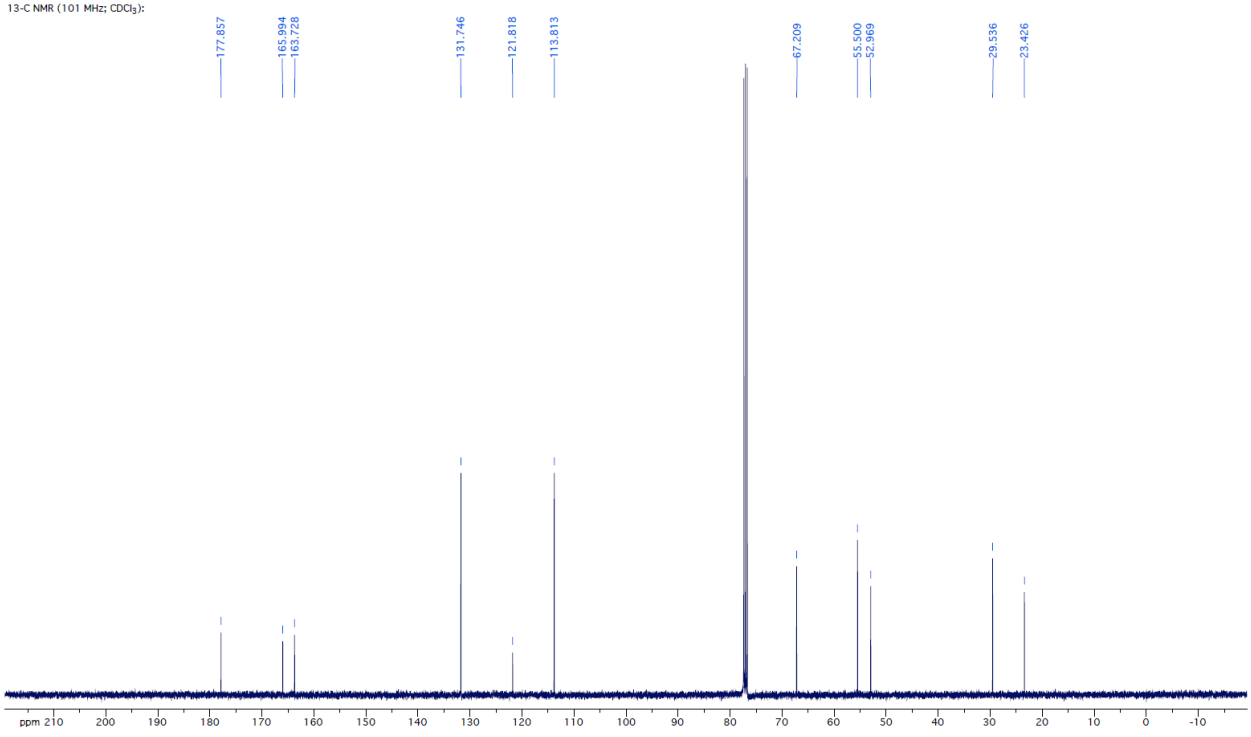

DP1583-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 43
(100 MHz, CDCl3)
165.91
163.73
161.47
131.73
121.75
113.79
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
66.24
55.47
49.79
48.40
30.45
Chemical Shift (ppm)

1-H NMR (400 MHz; $CDCl_3$):

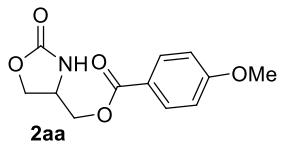


2z

13-C NMR (101 MHz; $CDCl_3$):

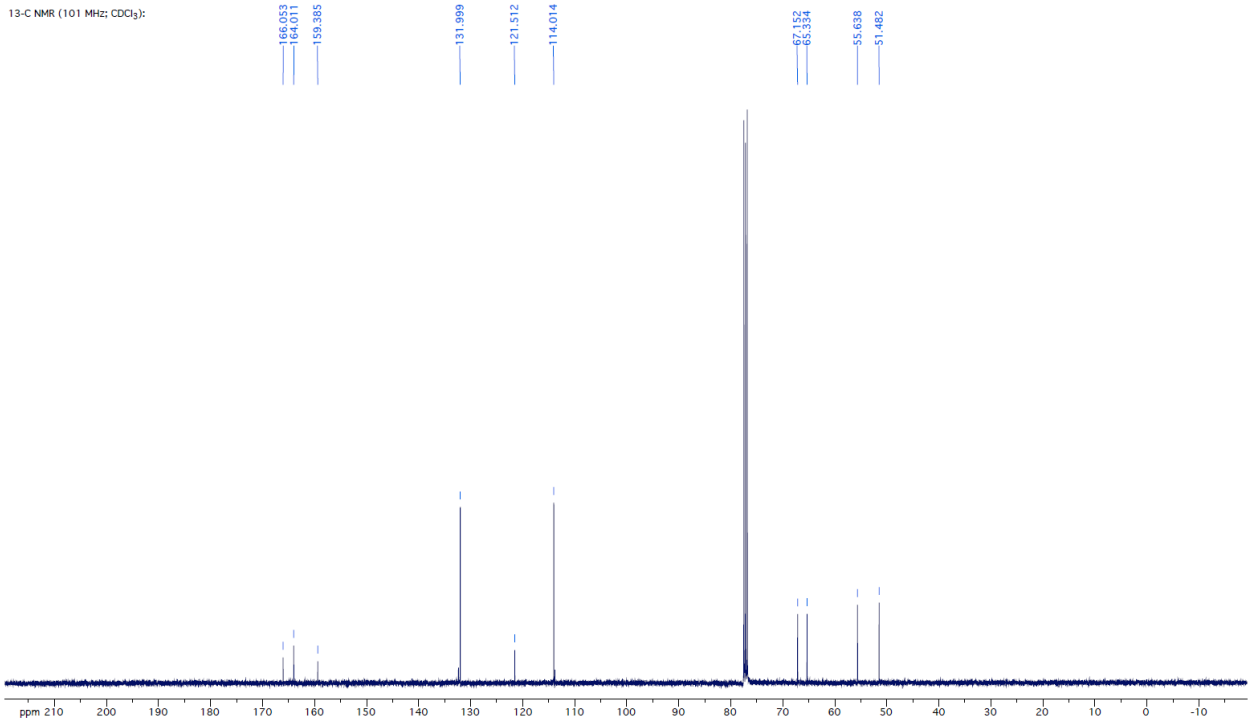


1-H NMR (400 MHz; $CDCl_3$):

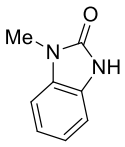


2aa

13-C NMR (101 MHz; $CDCl_3$):

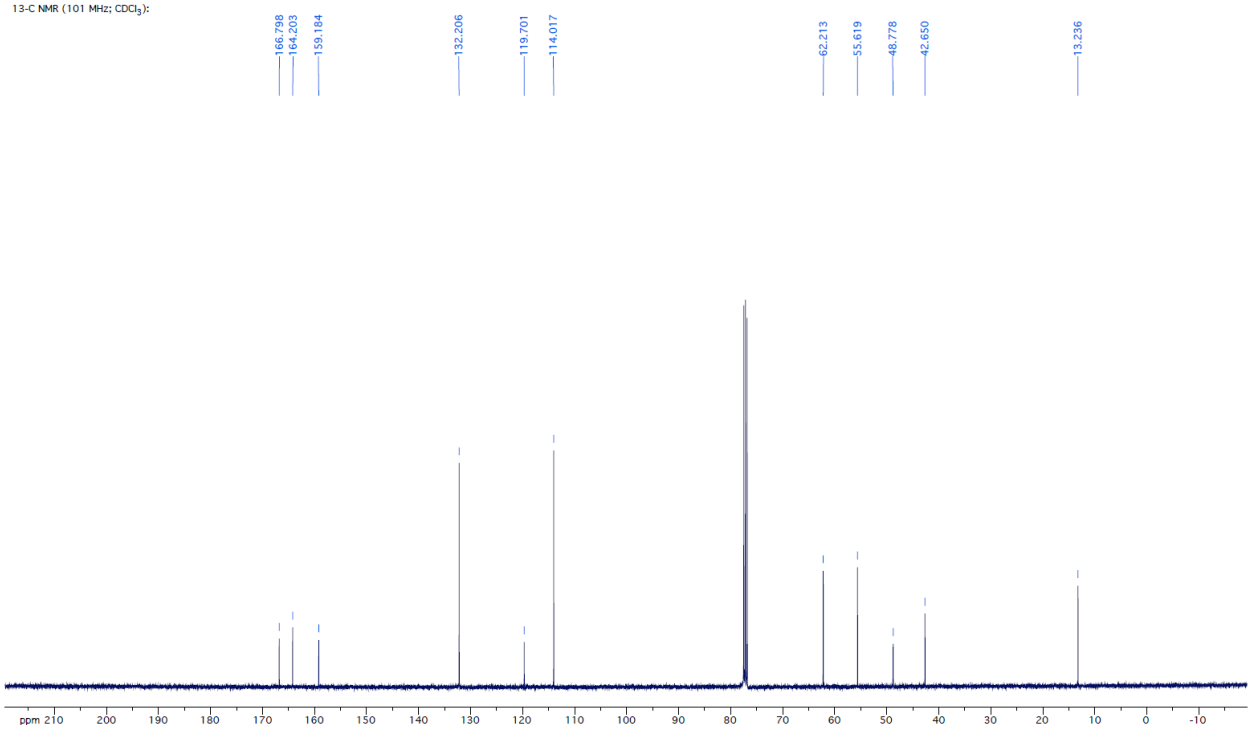


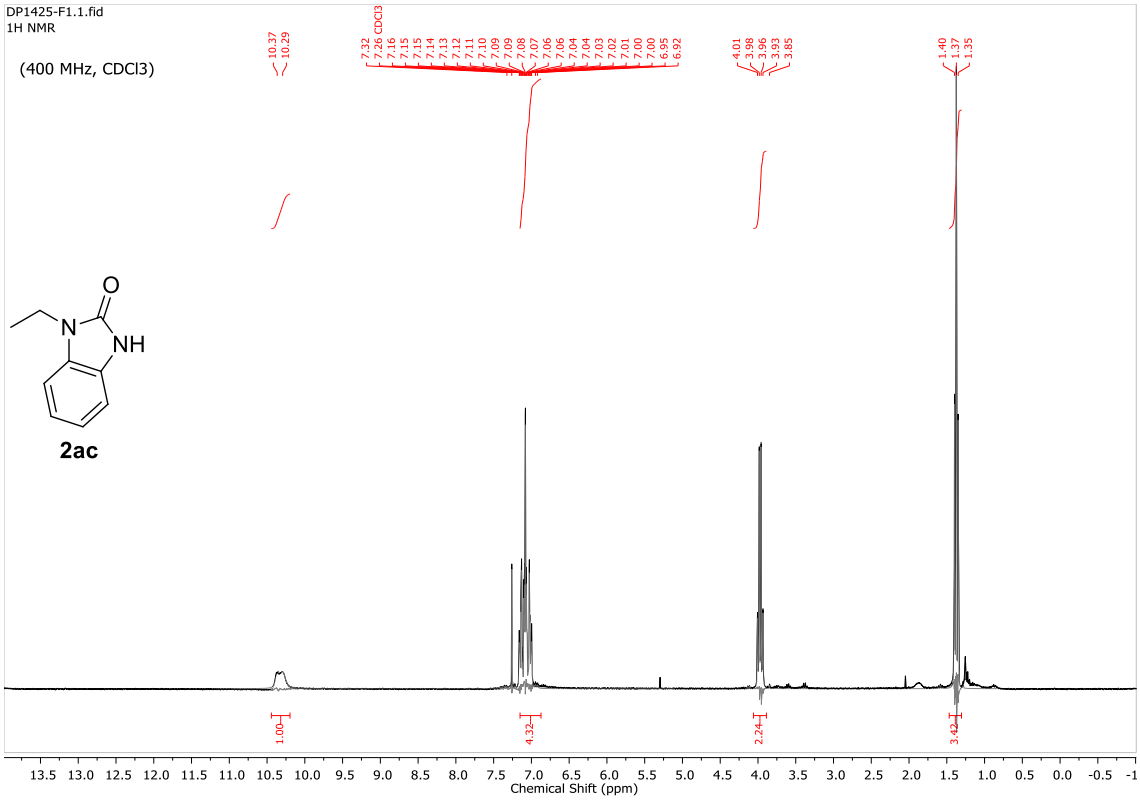
1-H NMR (400 MHz; $CDCl_3$):

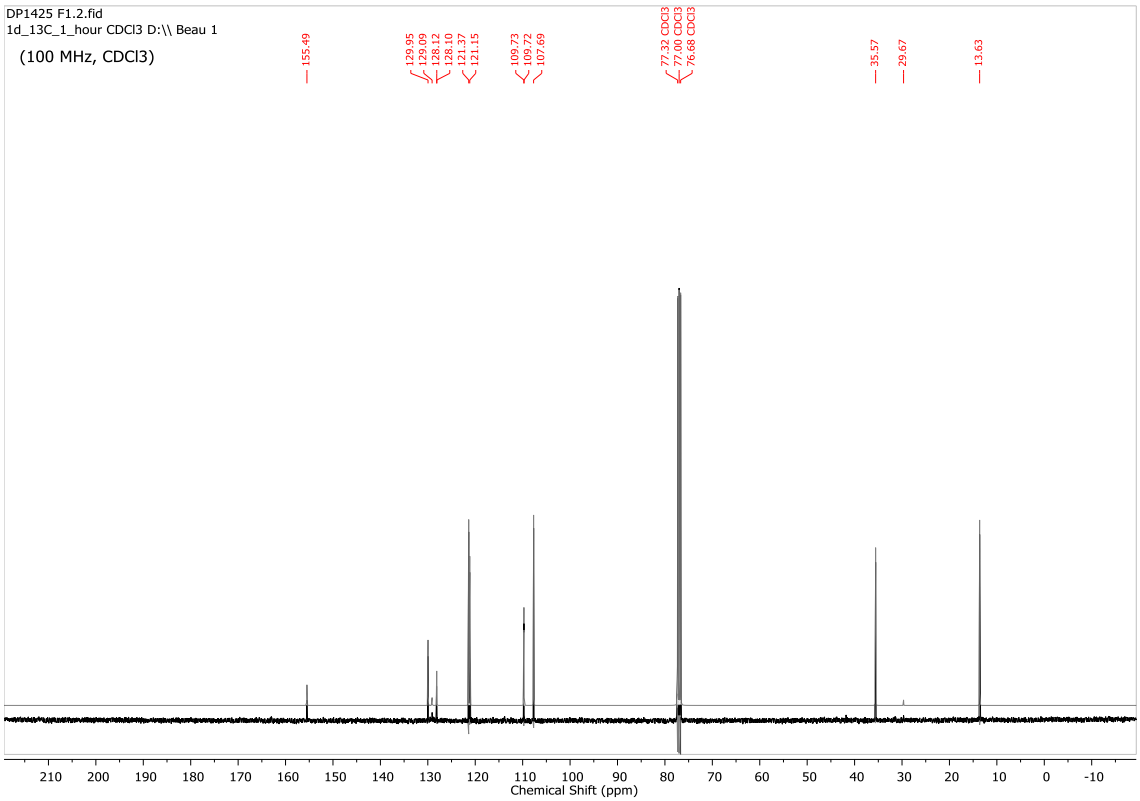


2ab

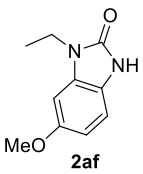
13-C NMR (101 MHz; $CDCl_3$):




DP1425-F1.1.fid
1H NMR
(400 MHz, CDCl3)
10.37
10.29
7.32
7.26 CDCl3
7.16
7.15
7.15
7.14
7.13
7.12
7.11
7.10
7.09
7.09
7.08
7.07
7.06
7.06
7.04
7.04
7.03
7.02
7.01
7.00
7.00
6.95
6.92
4.01
3.98
3.96
3.93
3.85
1.40
1.37
1.35
O
N
NH
2ac
1.00
4.32
2.24
3.42
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
Chemical Shift (ppm)

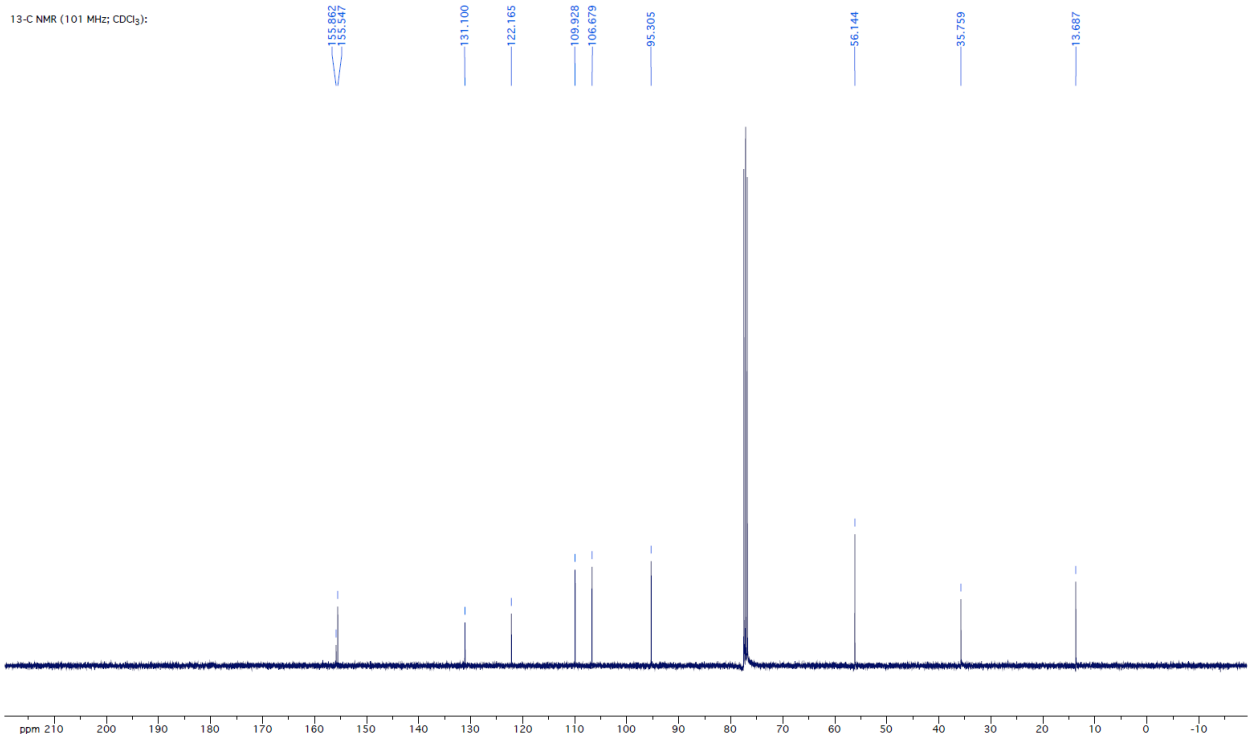

DP1425 F1.2.fid
1d_13C_1_hour CDCl3 D:\\ Beau 1
(100 MHz, CDCl3)
155.49
129.95
129.09
128.12
128.10
121.37
121.15
109.73
109.72
107.69
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
35.57
29.67
13.63
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

1-H NMR (400 MHz; $CDCl_3$):

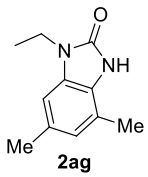


2af

13-C NMR (101 MHz; $CDCl_3$):

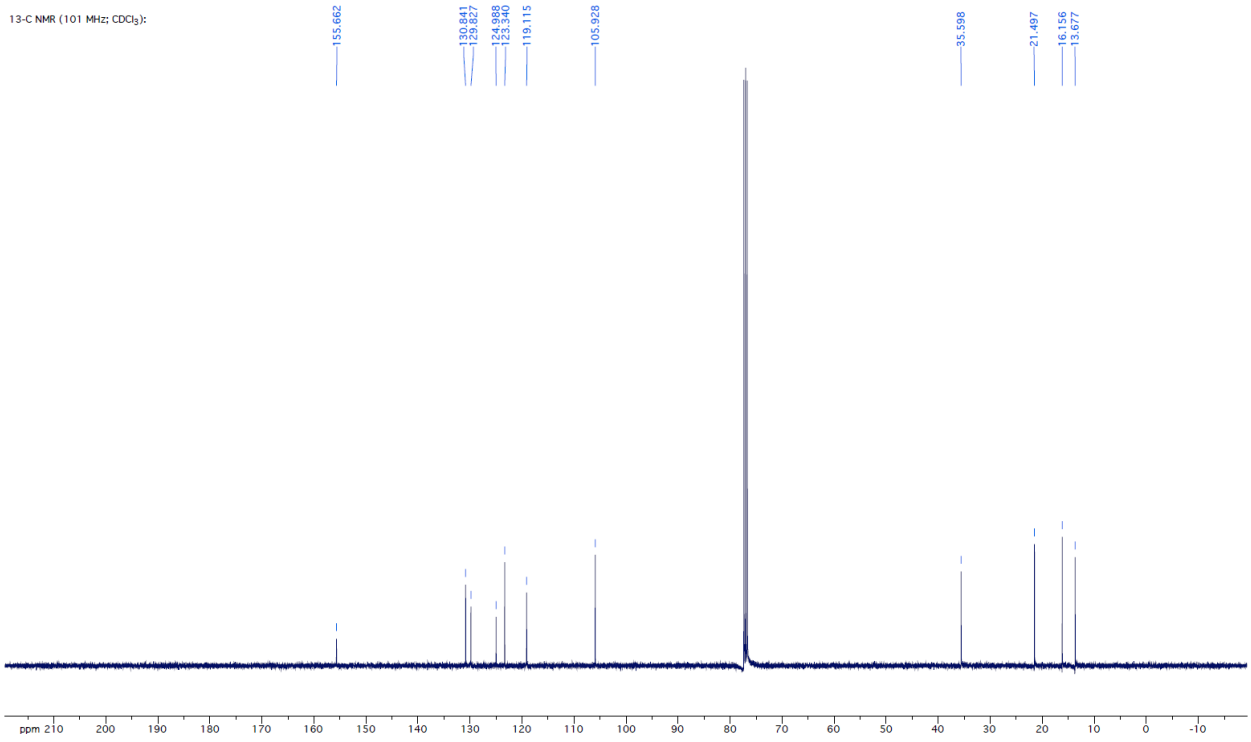


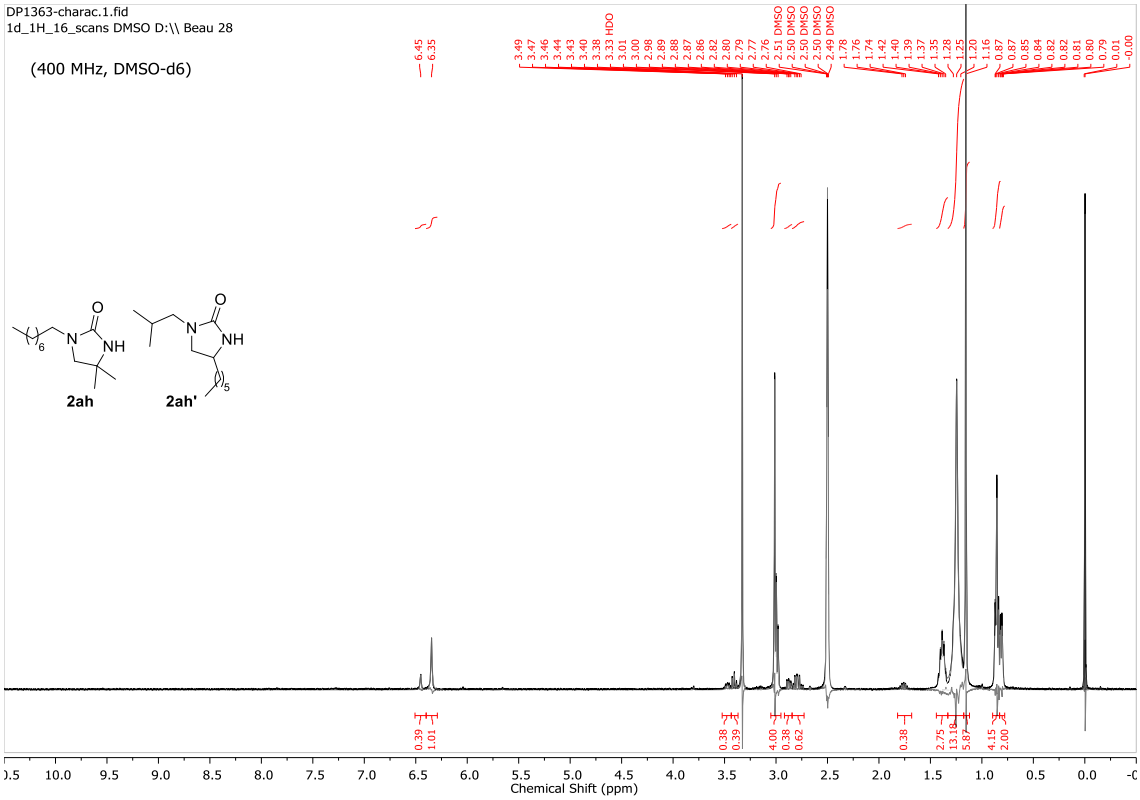
1-H NMR (400 MHz; $CDCl_3$):

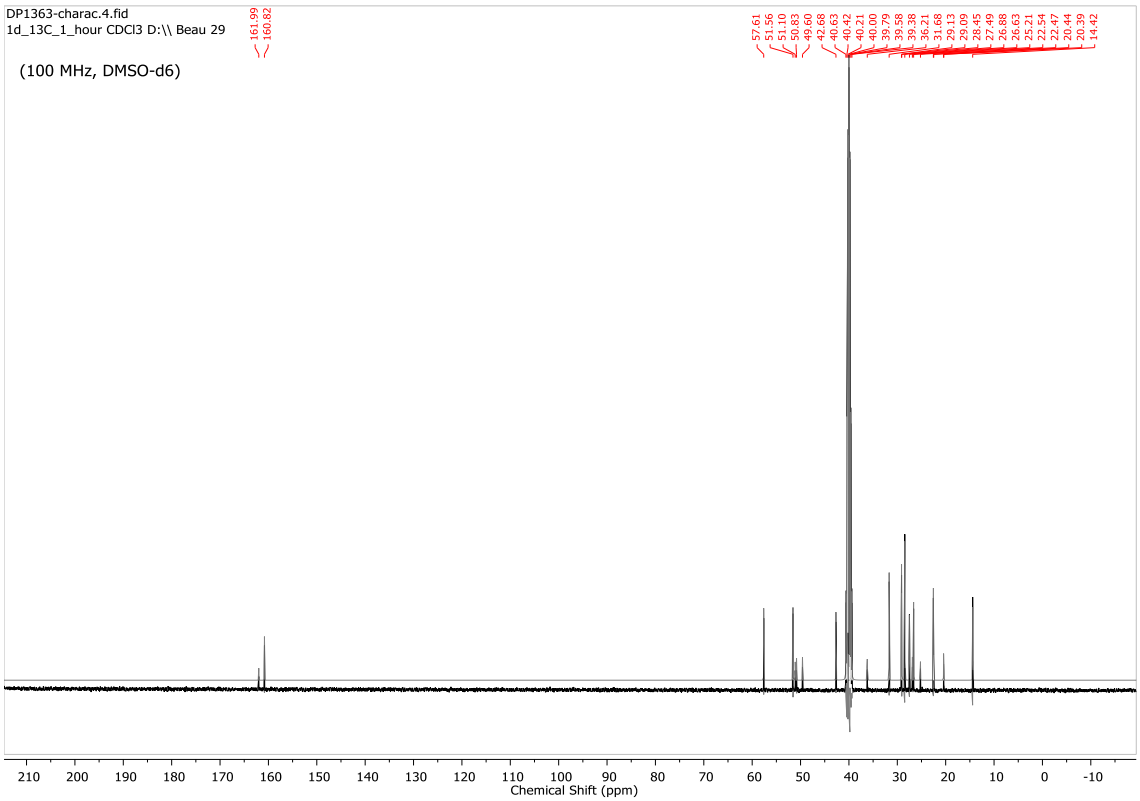


2ag

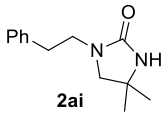
13-C NMR (101 MHz; $CDCl_3$):




DP1363-charac.1.fid
1d_1H_16_scans DMSO D:\\ Beau 28
(400 MHz, DMSO-d6)
2ah
2ah'
Chemical Shift (ppm)

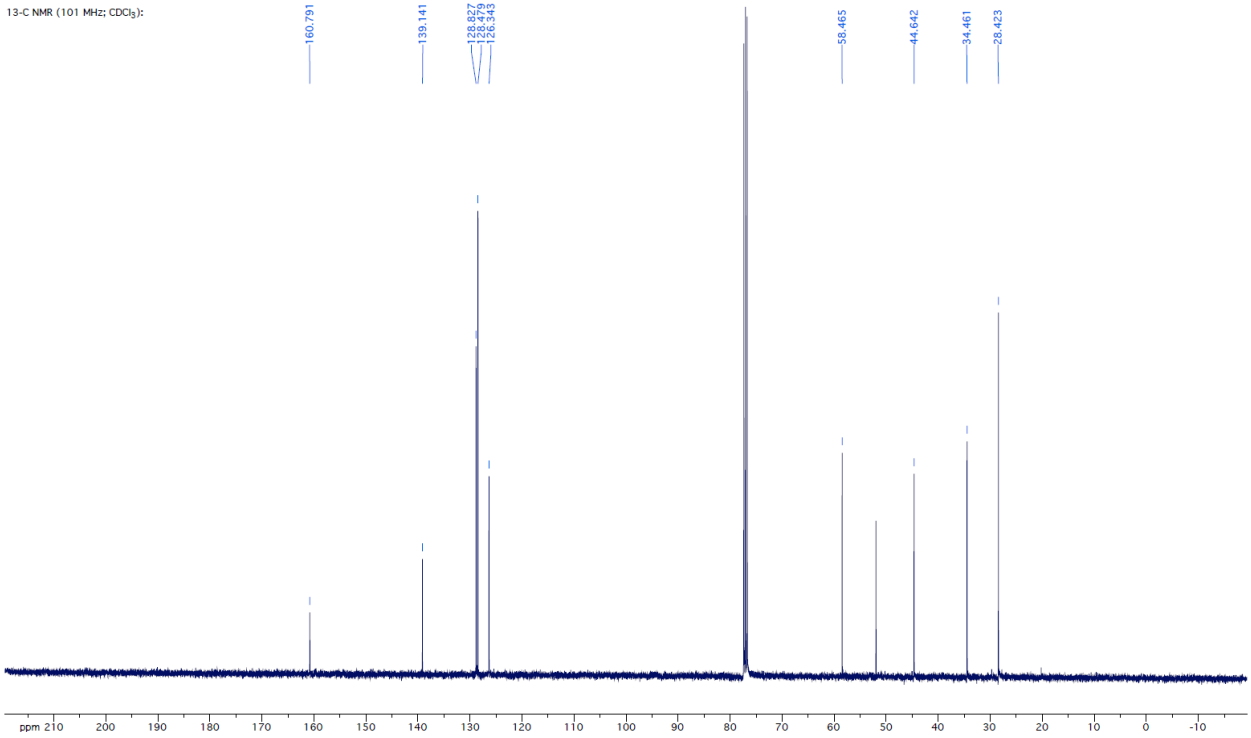

DP1363-charac.4.fid
1d_13C_1_hour CDCl3 D:\\ Beau 29
(100 MHz, DMSO-d6)
Chemical Shift (ppm)

1-H NMR (400 MHz; $CDCl_3$):

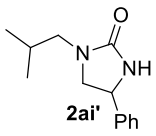


2ai

13-C NMR (101 MHz; $CDCl_3$):

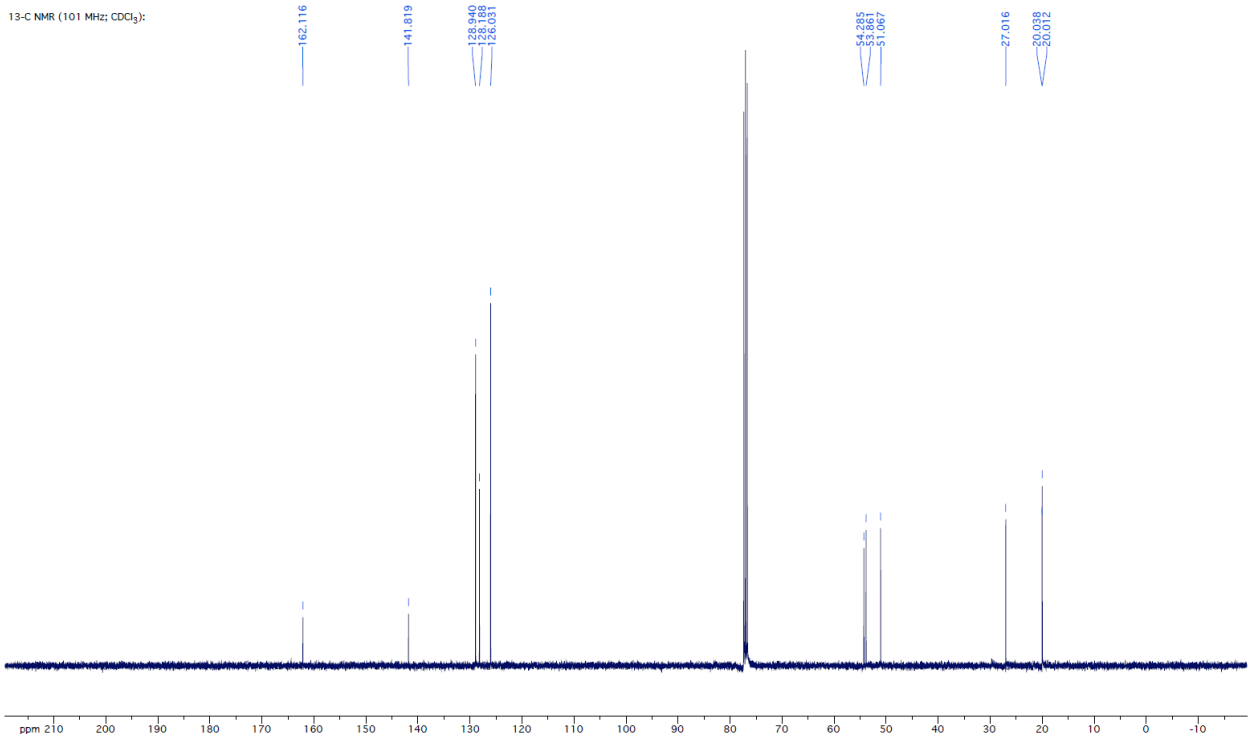


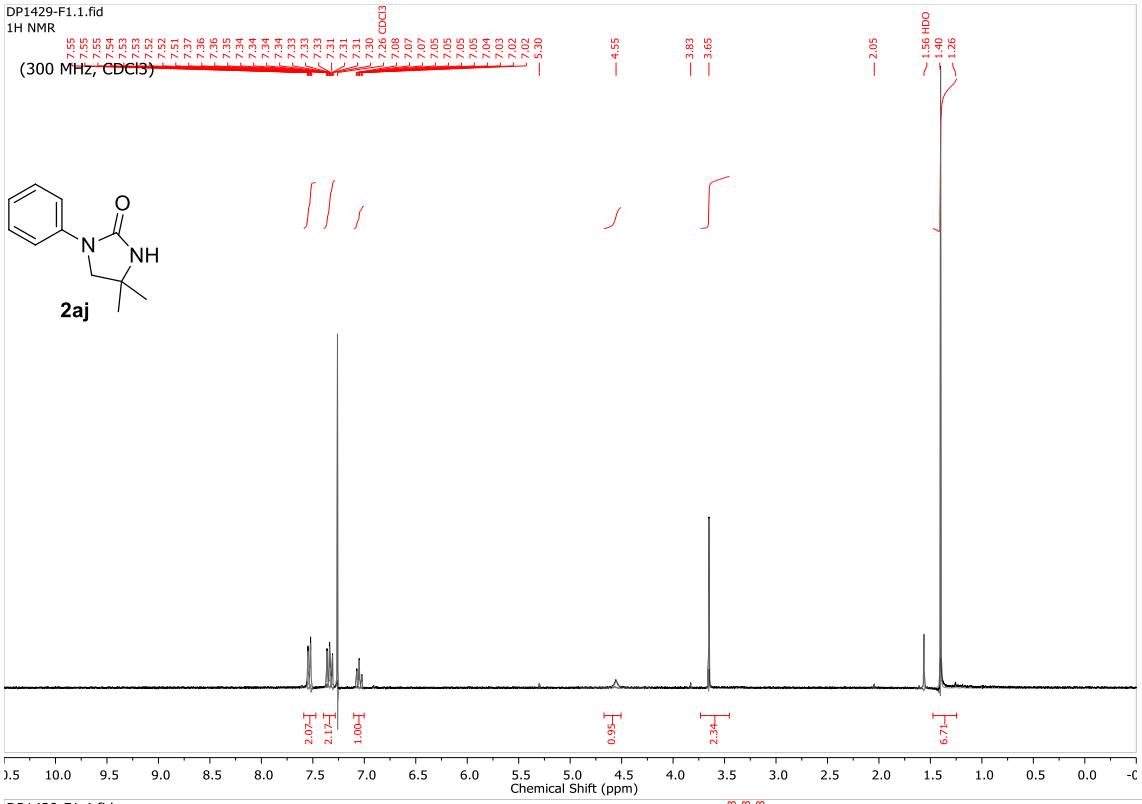
1-H NMR (400 MHz; $CDCl_3$):

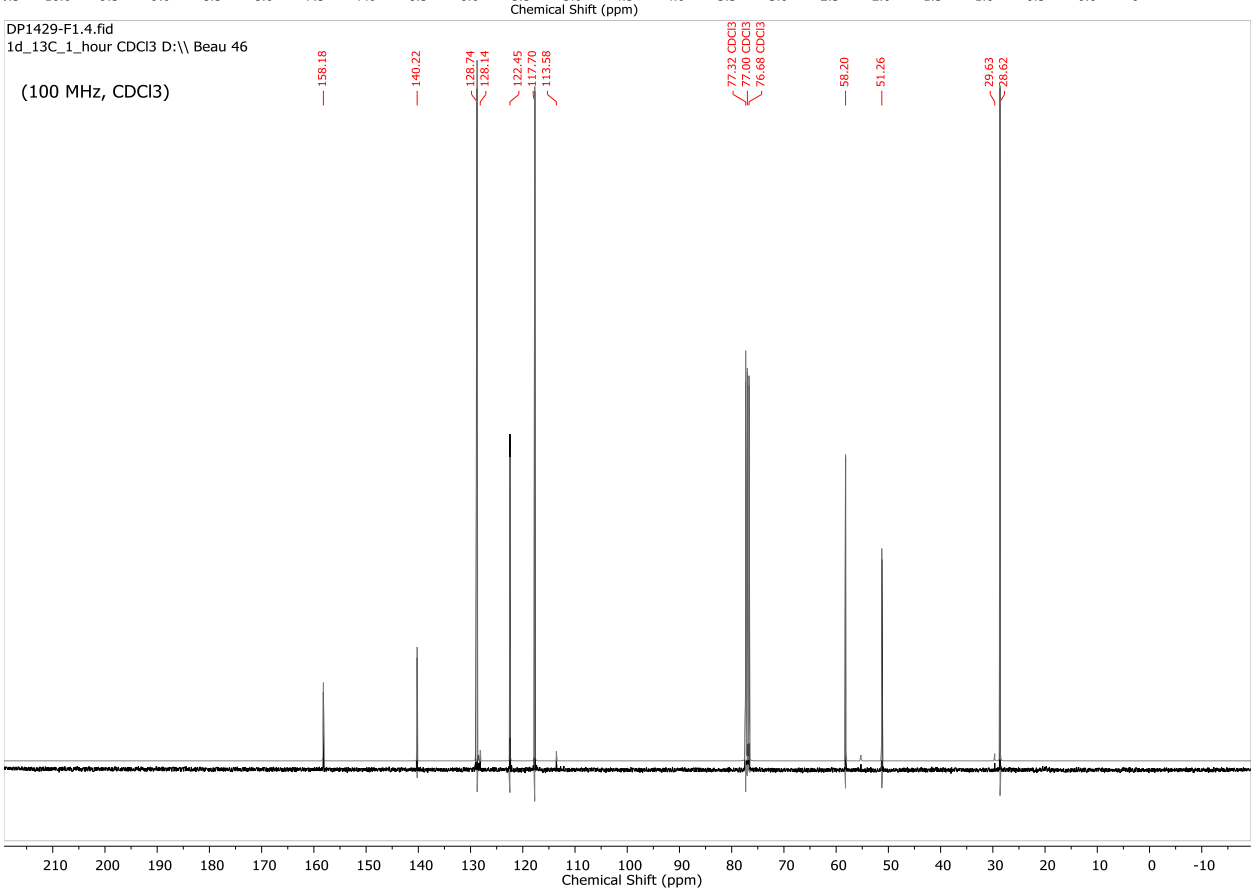


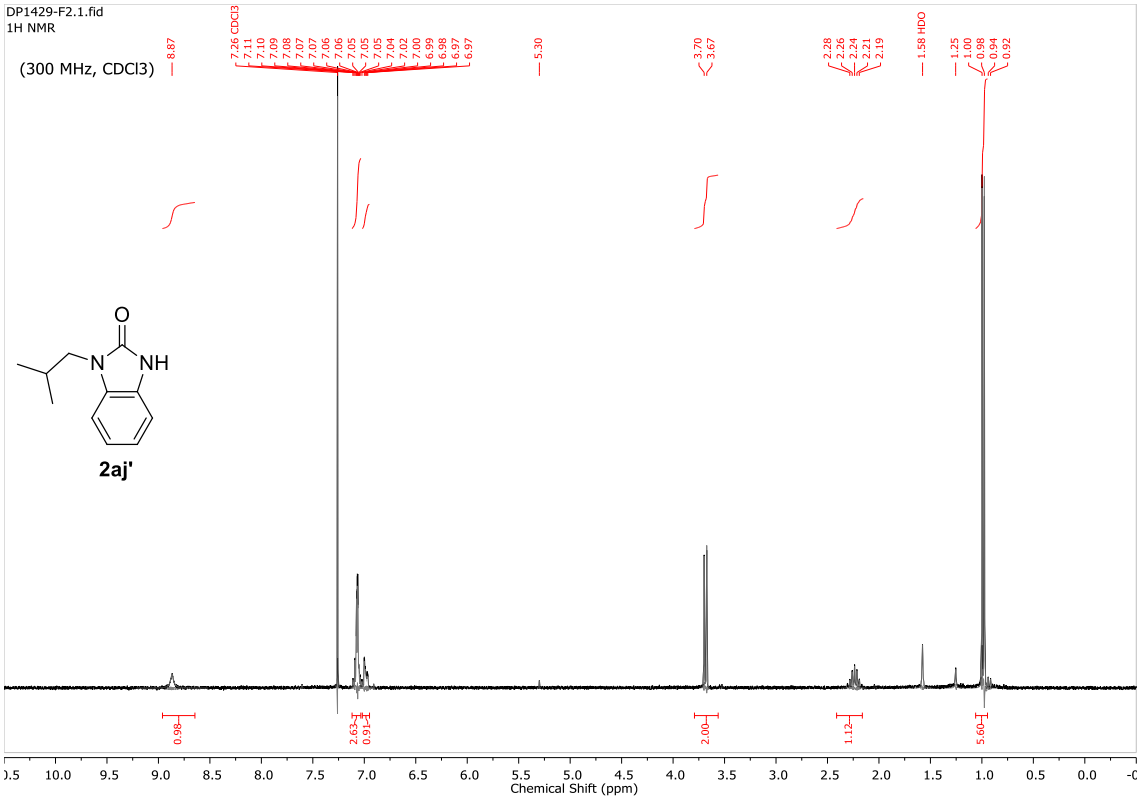
2ai'

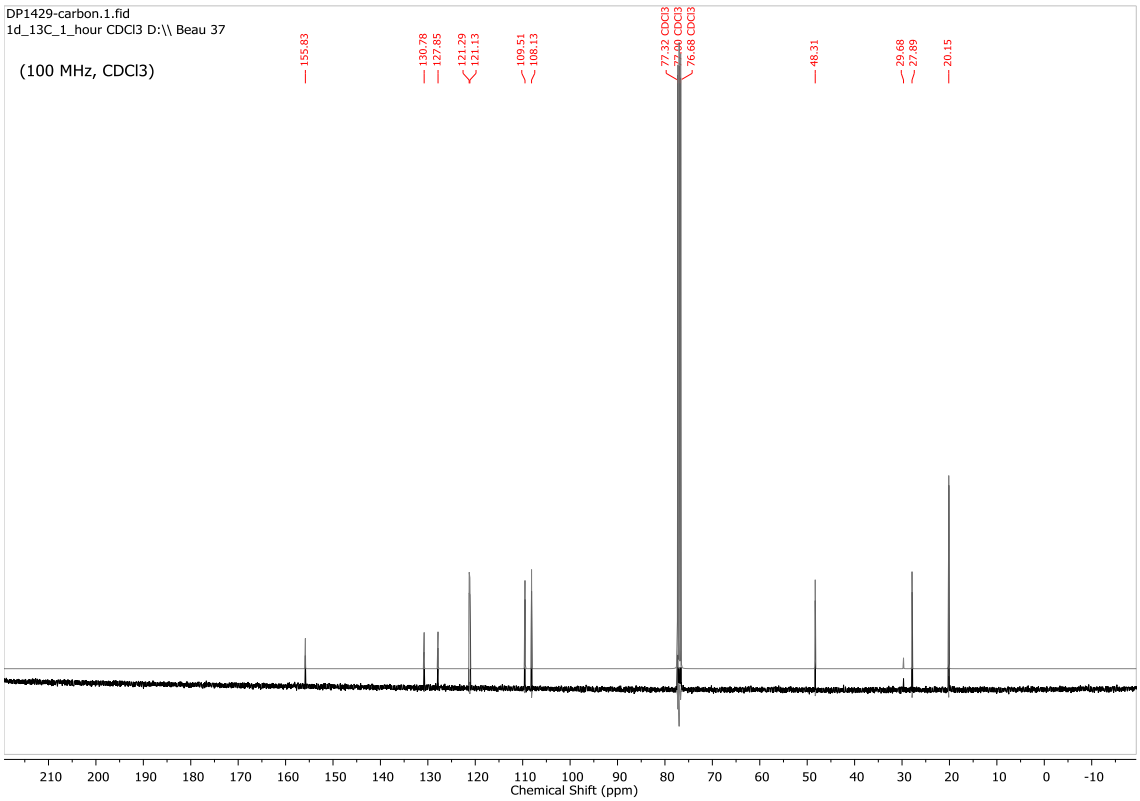
13-C NMR (101 MHz; $CDCl_3$):

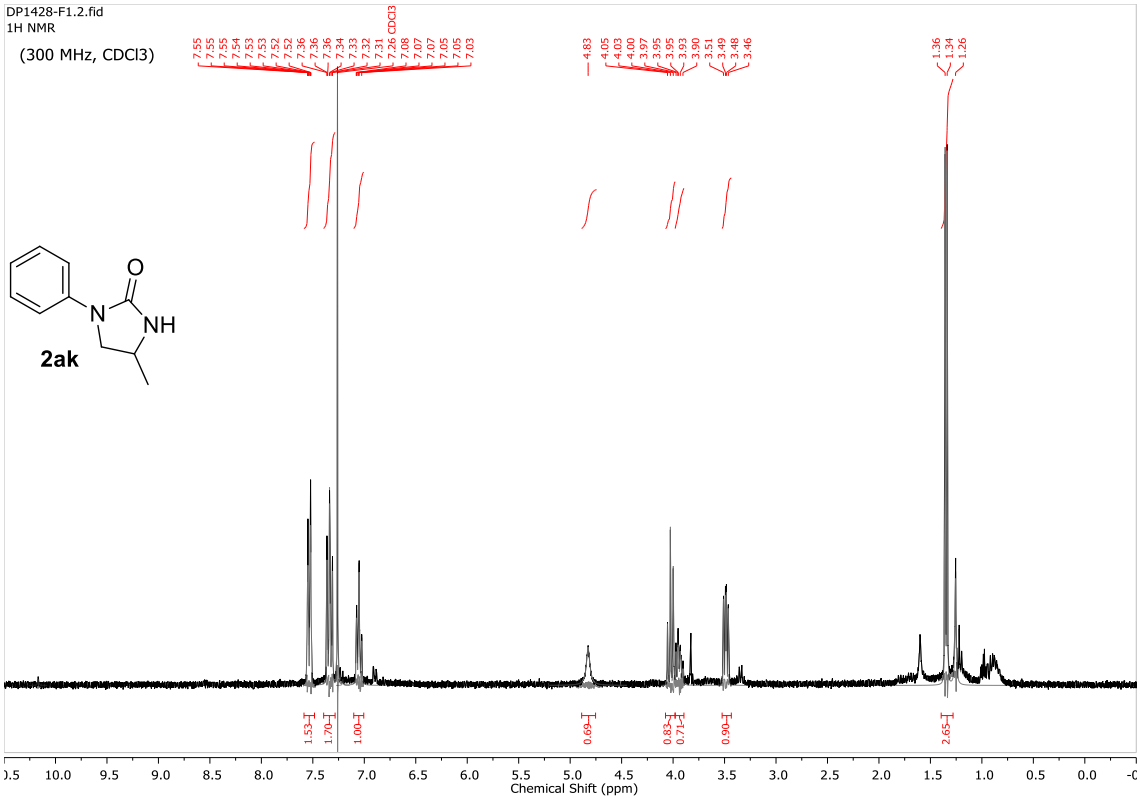


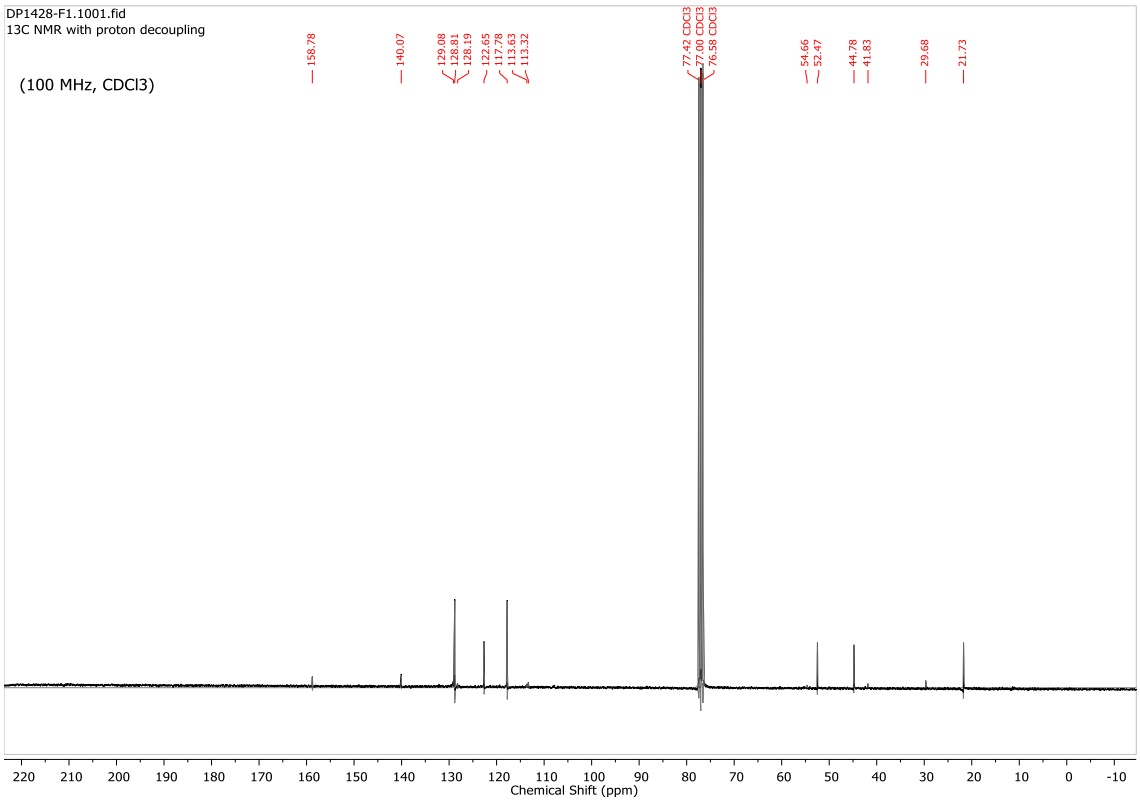

DP1429-F1.1.fid
1H NMR
(300 MHz, CDCl3)
2aj
Chemical Shift (ppm)

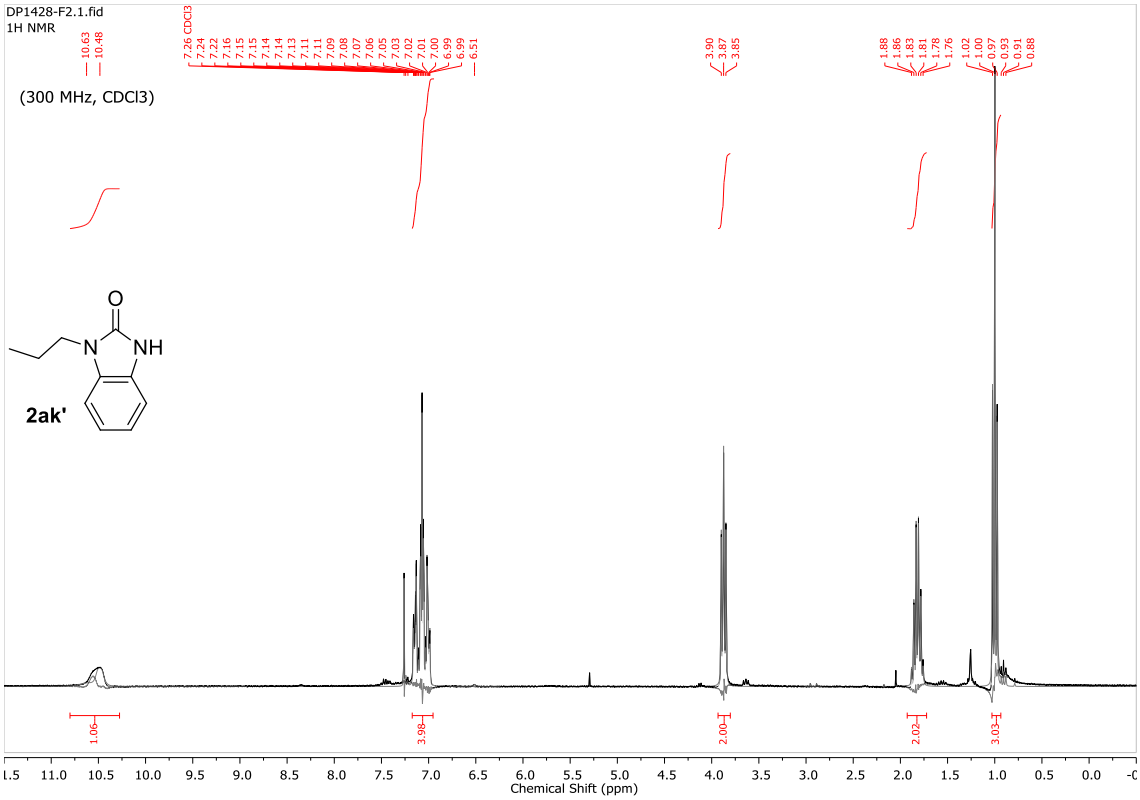

DP1429-F1.4.fid
1d_13C_1_hour CDCl3 D:\\ Beau 46
(100 MHz, CDCl3)
Chemical Shift (ppm)

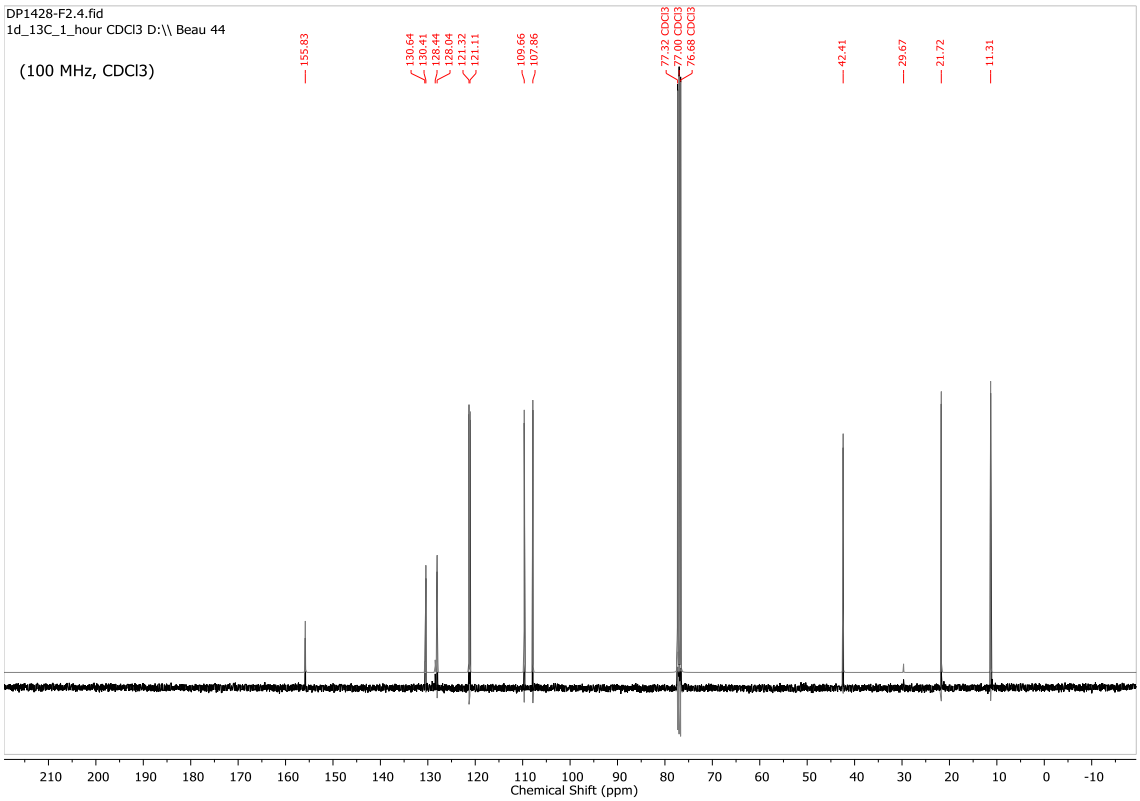

DP1429-F2.1.fid
1H NMR
(300 MHz, CDCl3)
2aj'
Chemical Shift (ppm)


DP1429-carbon.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 37
(100 MHz, CDCl3)
Chemical Shift (ppm)

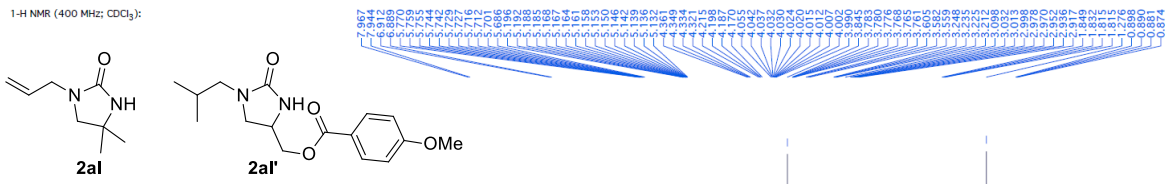

DP1428-F1.2.fid
1H NMR
(300 MHz, CDCl3)
2ak
Chemical Shift (ppm)


DP1428-F1.1001.fid
13C NMR with proton decoupling
(100 MHz, CDCl3)
Chemical Shift (ppm)


DP1428-F2.1.fid
1H NMR
(300 MHz, CDCl3)
2ak'
Chemical Shift (ppm)

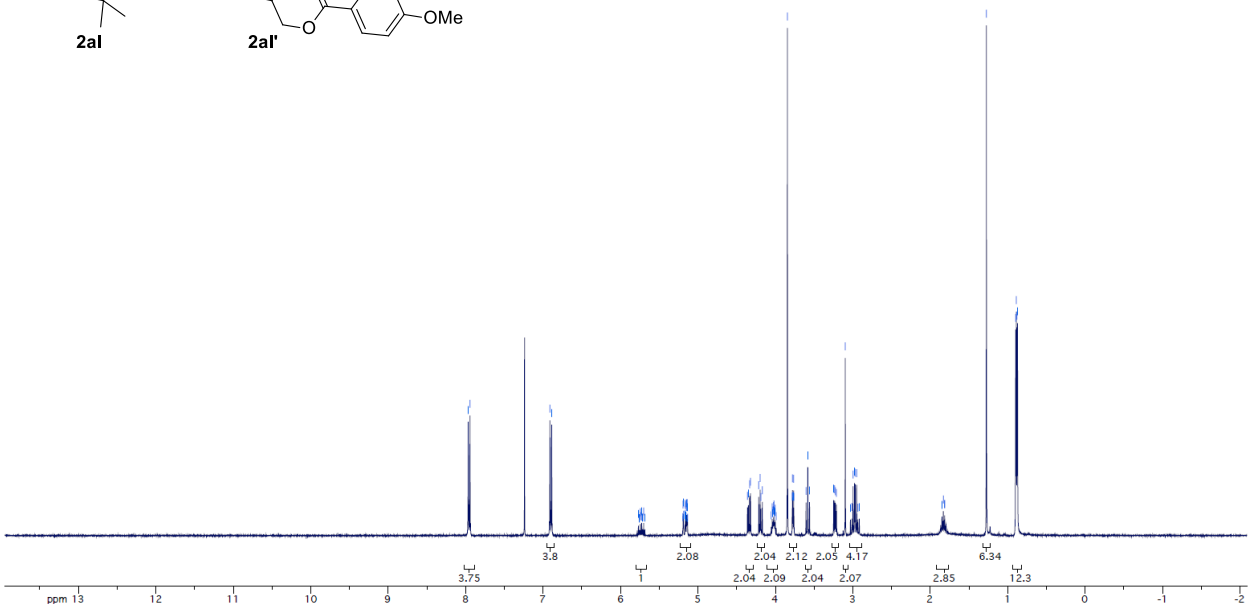

DP1428-F2.4.fid
1d_13C_1_hour CDCl3 D:\\ Beau 44
(100 MHz, CDCl3)
Chemical Shift (ppm)

1-H NMR (400 MHz; $CDCl_3$):

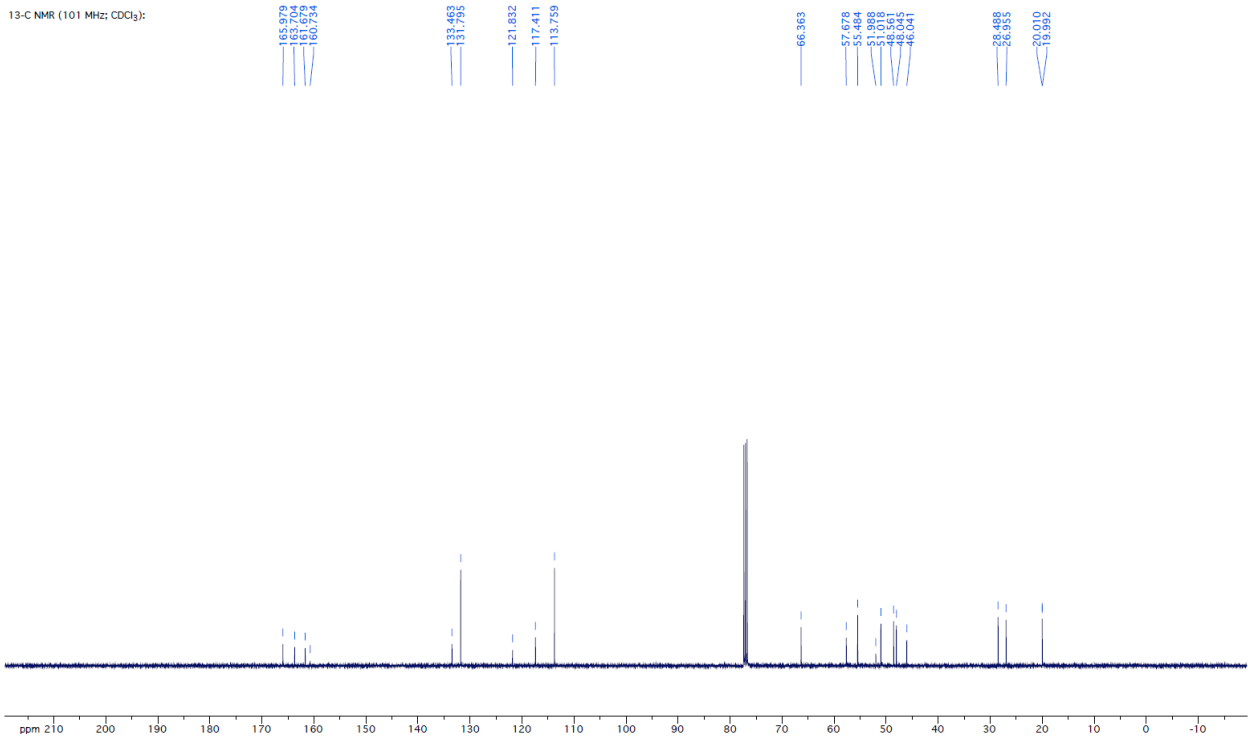


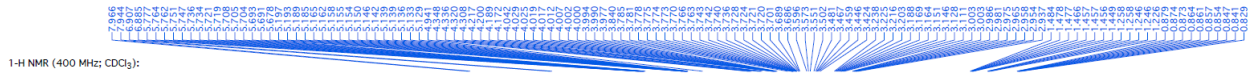
2al

2al'

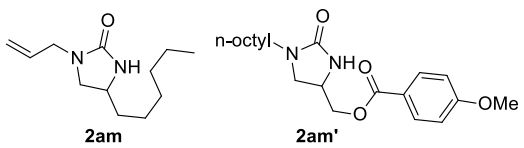


13-C NMR (101 MHz; $CDCl_3$):

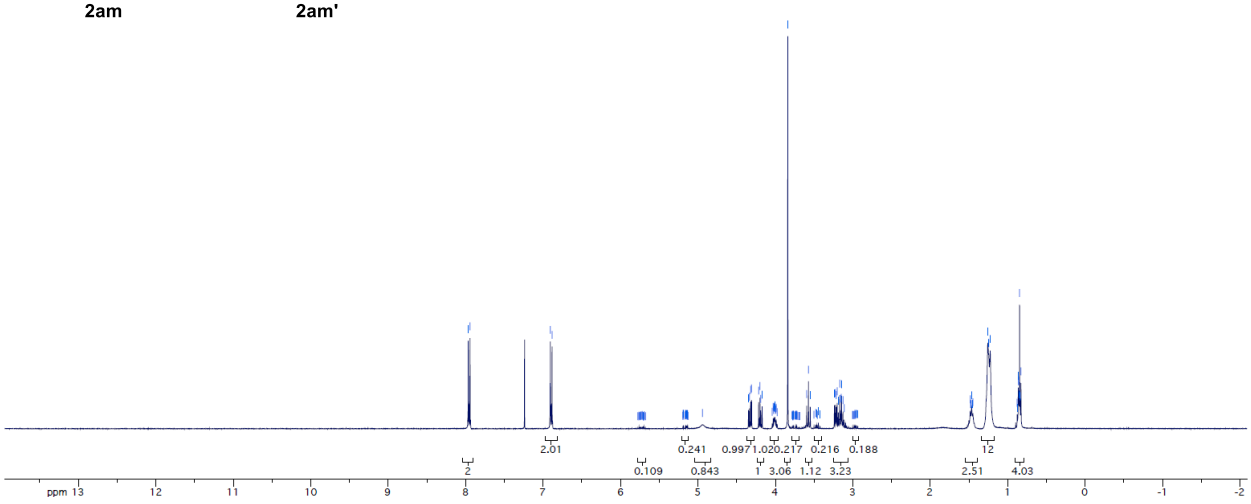




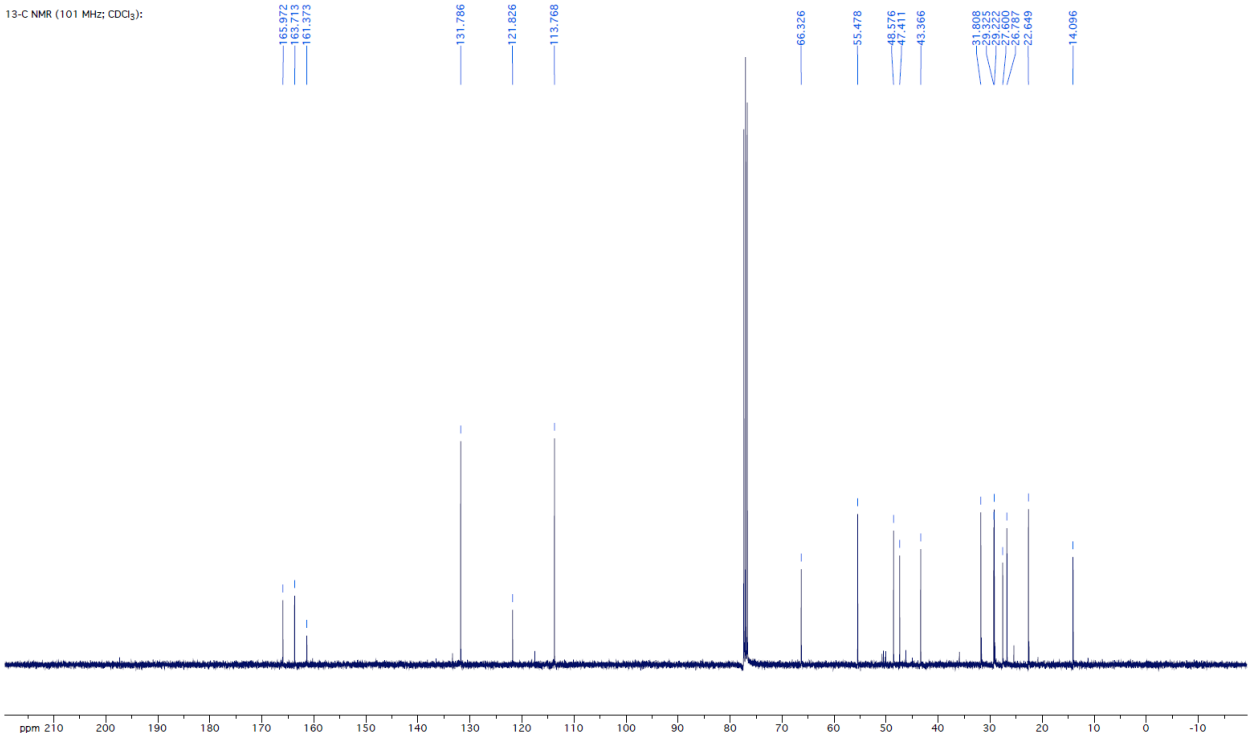
1-H NMR (400 MHz; $CDCl_3$):

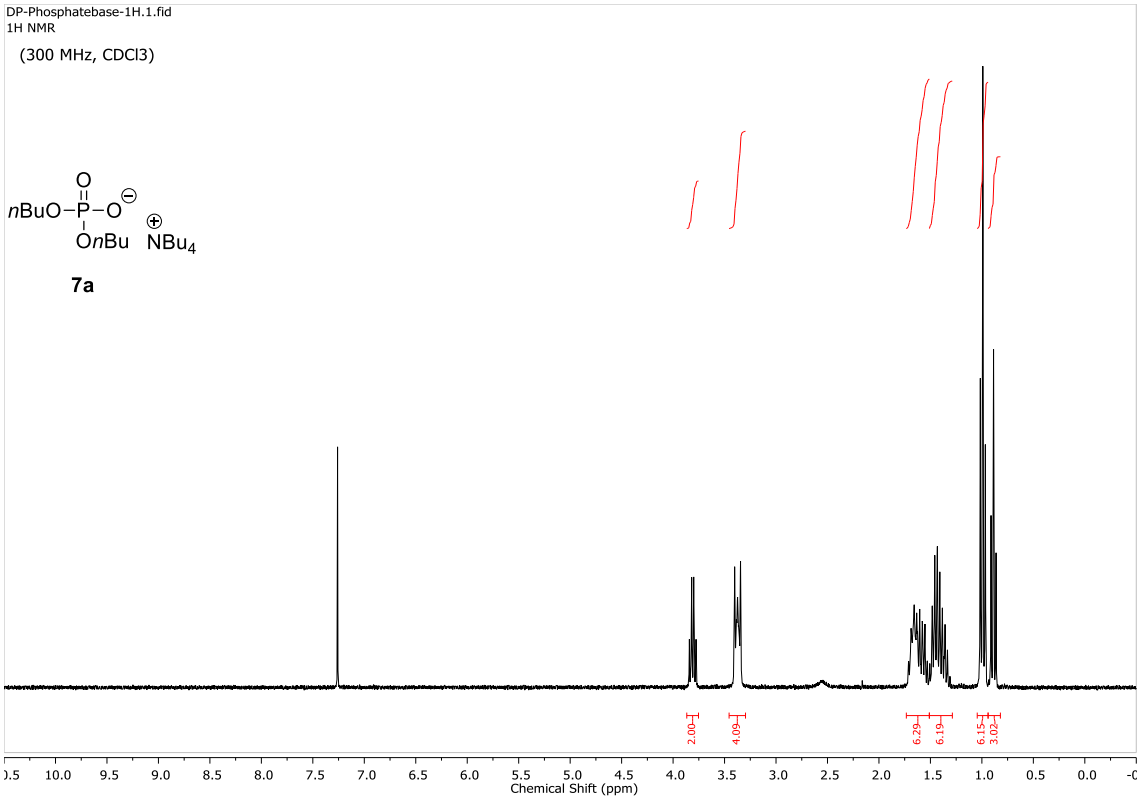


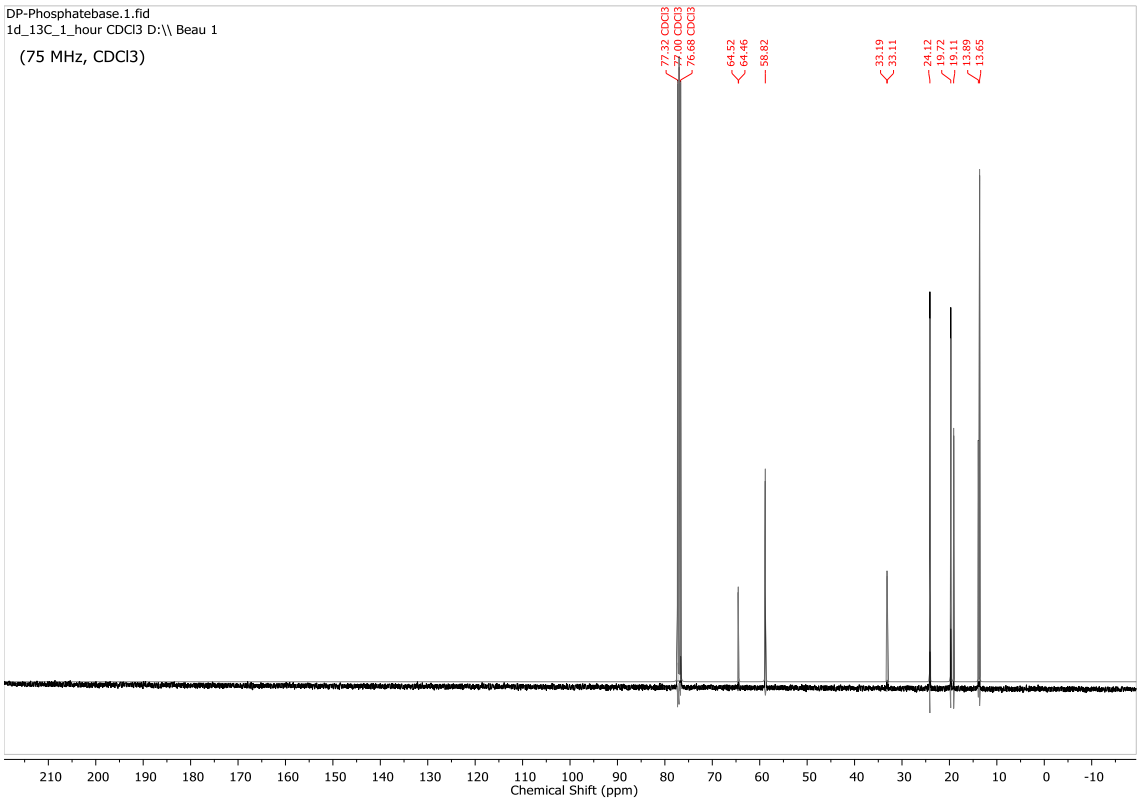
2am **2am'**

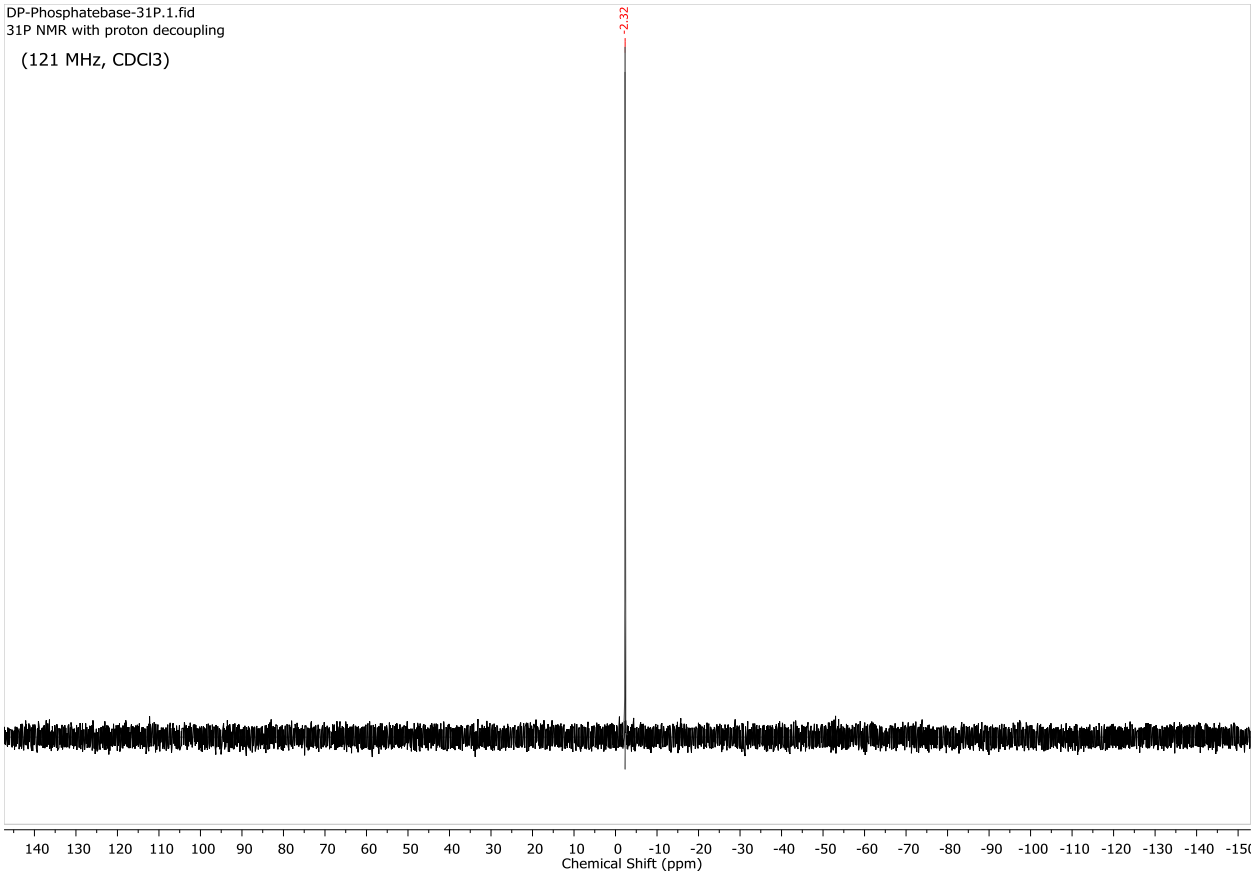


13-C NMR (101 MHz; $CDCl_3$):

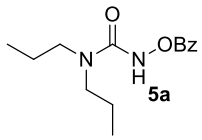



DP-Phosphatebase-1H.1.fid
1H NMR
(300 MHz, CDCl3)
nBuO–P–O
OnBu NBu4
7a
2.00
4.09
6.29
6.19
6.15
3.02
Chemical Shift (ppm)

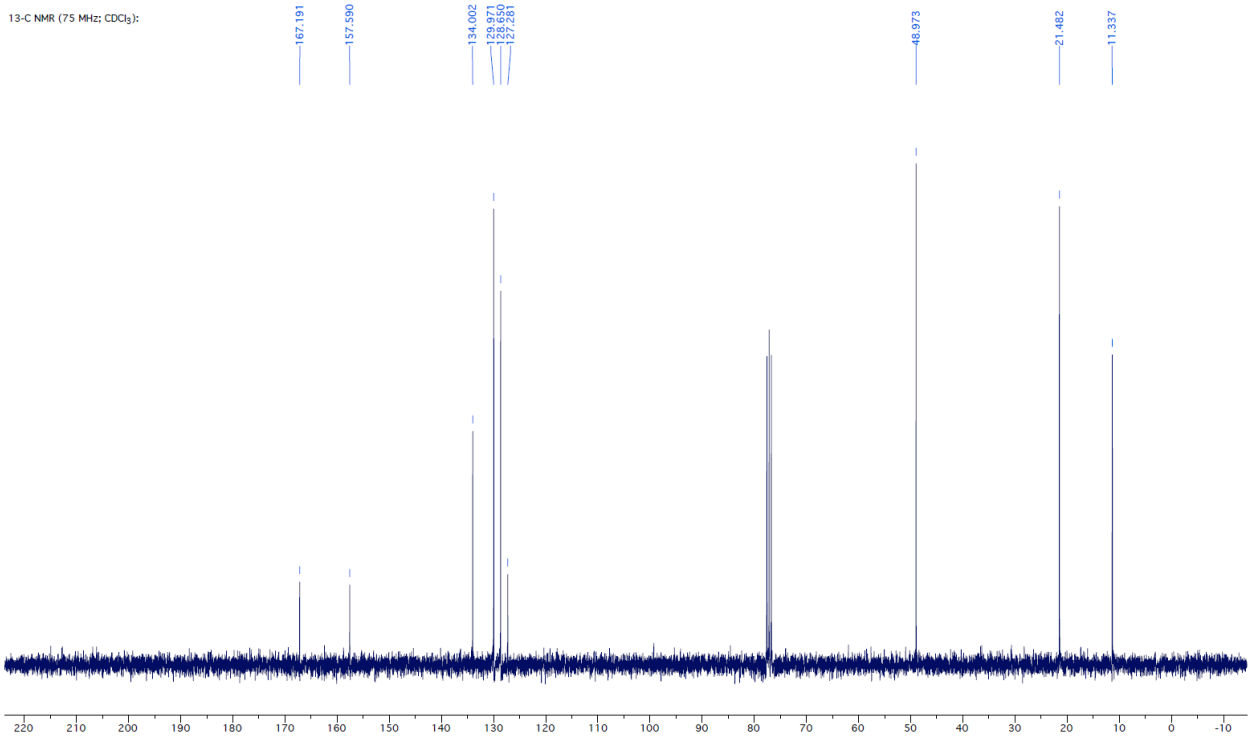

DP-Phosphatebase.1.fid
1d_13C_1_hour CDCl3 D:\\ Beau 1
(75 MHz, CDCl3)
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
64.52
64.46
58.82
33.19
33.11
24.12
19.72
19.11
13.89
13.65
Chemical Shift (ppm)

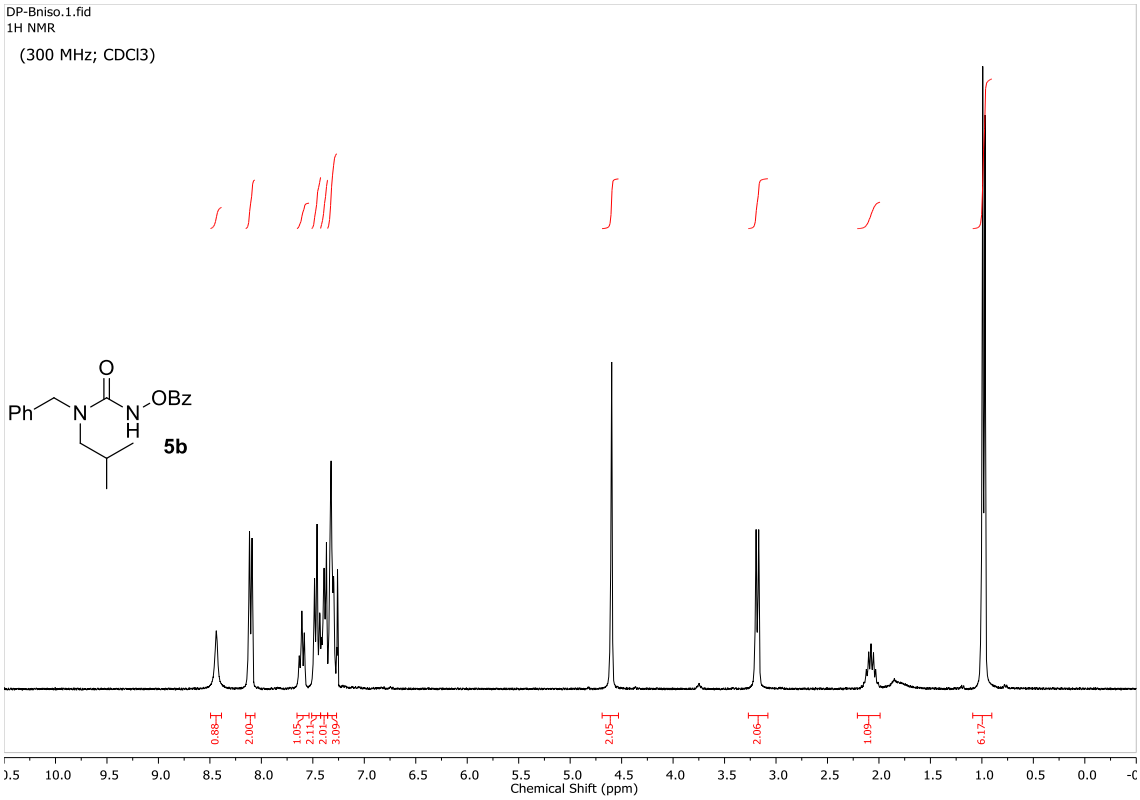

DP-Phosphatebase-31P.1.fid
31P NMR with proton decoupling
(121 MHz, CDCl3)
-2.32
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140
Chemical Shift (ppm)

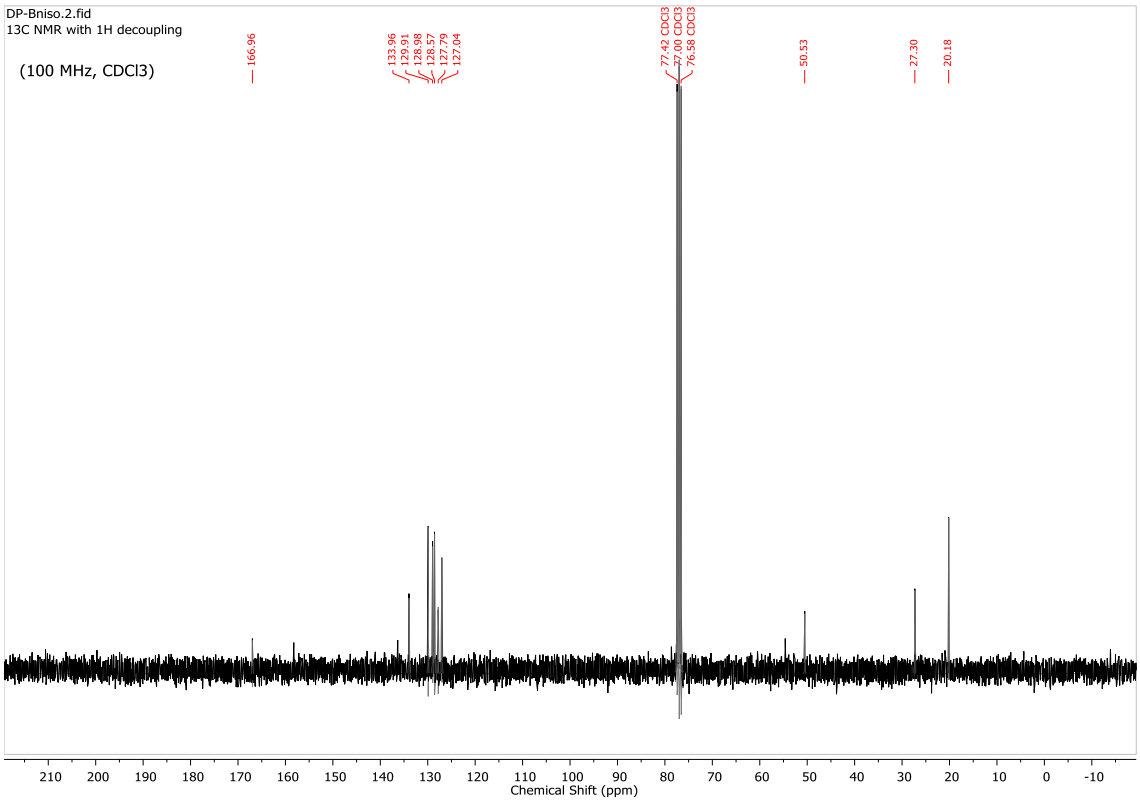
1-H NMR (300 MHz; $CDCl_3$):



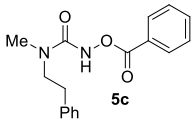
13-C NMR (75 MHz; $CDCl_3$):




DP-Bniso.1.fid
1H NMR
(300 MHz; CDCl3)
Ph
N
O
N
H
OBz
5b
0.88
2.00
1.05
2.11
2.01
3.09
2.05
2.06
1.09
6.17
Chemical Shift (ppm)

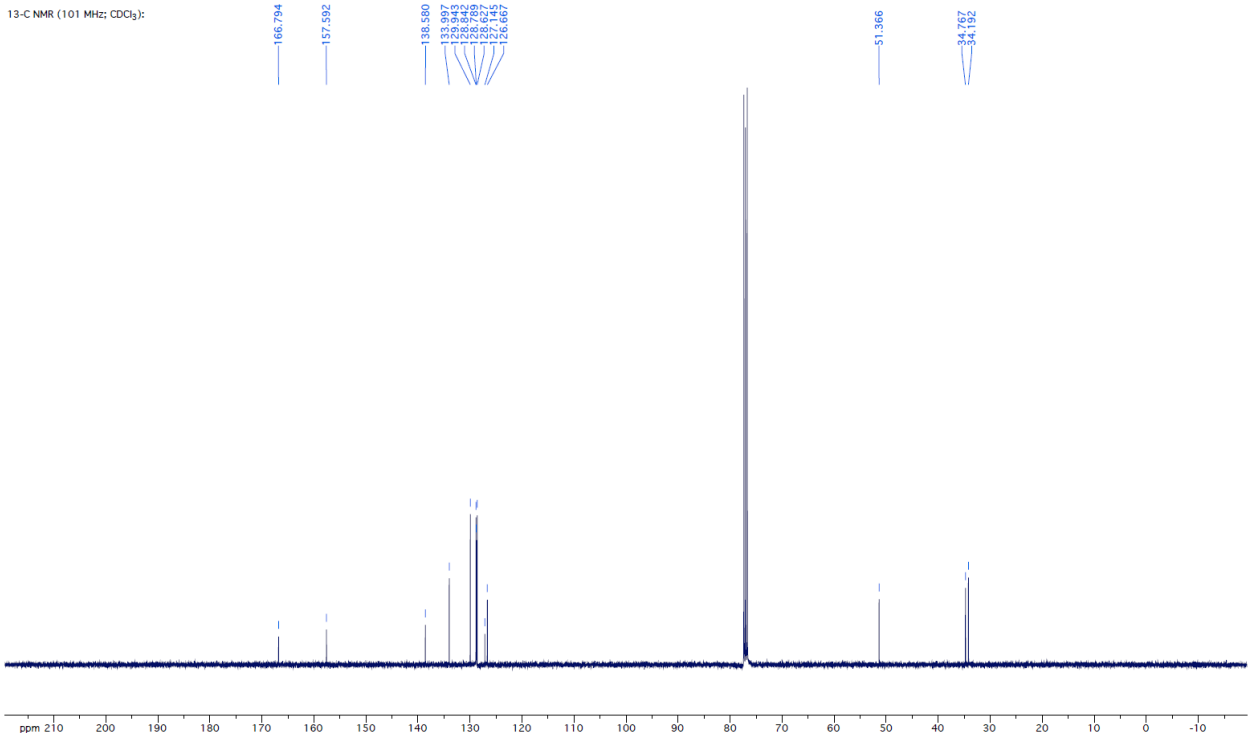

DP-Bniso.2.fid
13C NMR with 1H decoupling
(100 MHz, CDCl3)
166.96
133.96
129.91
128.98
128.57
127.79
127.04
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
50.53
27.30
20.18
Chemical Shift (ppm)

1-H NMR (400 MHz; $CDCl_3$):

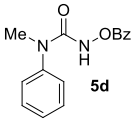


5c

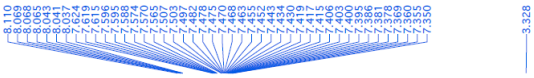
13-C NMR (101 MHz; $CDCl_3$):

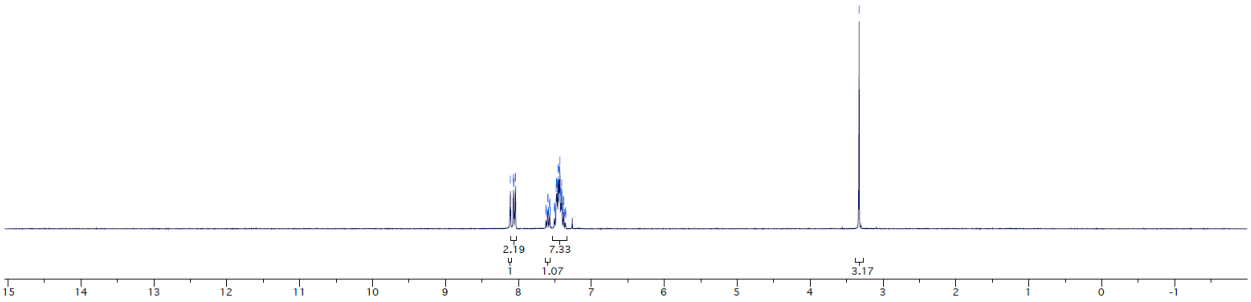


1-H NMR (300 MHz; $CDCl_3$):

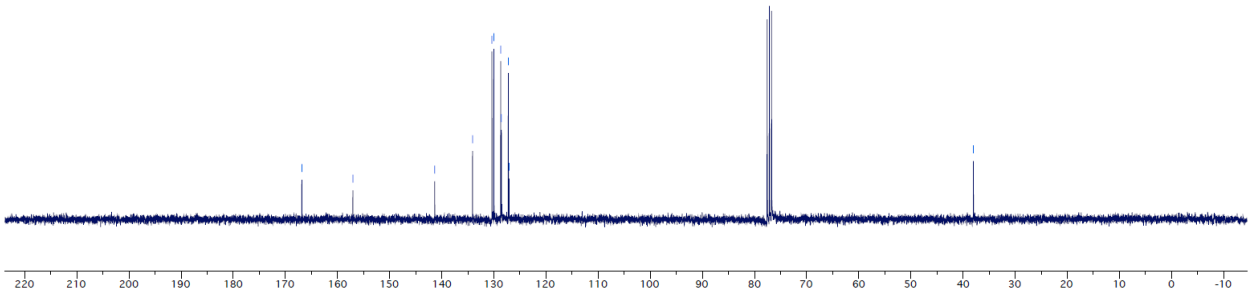


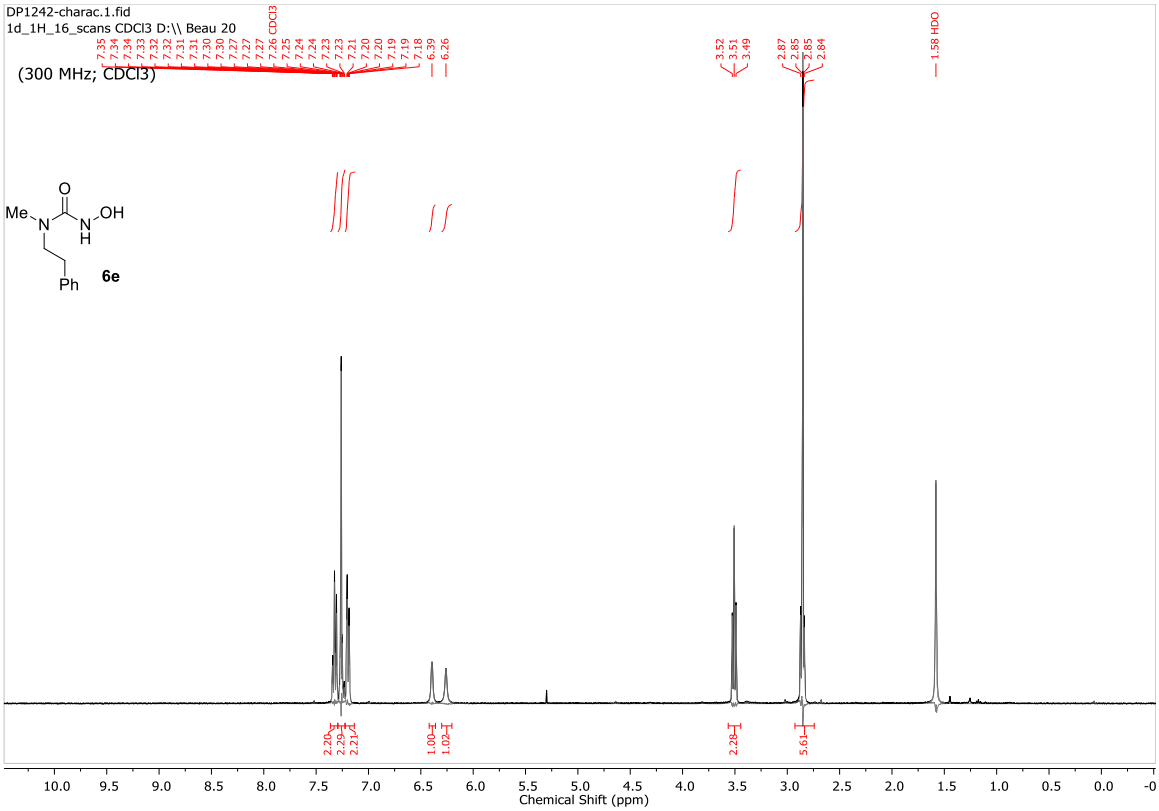
5d

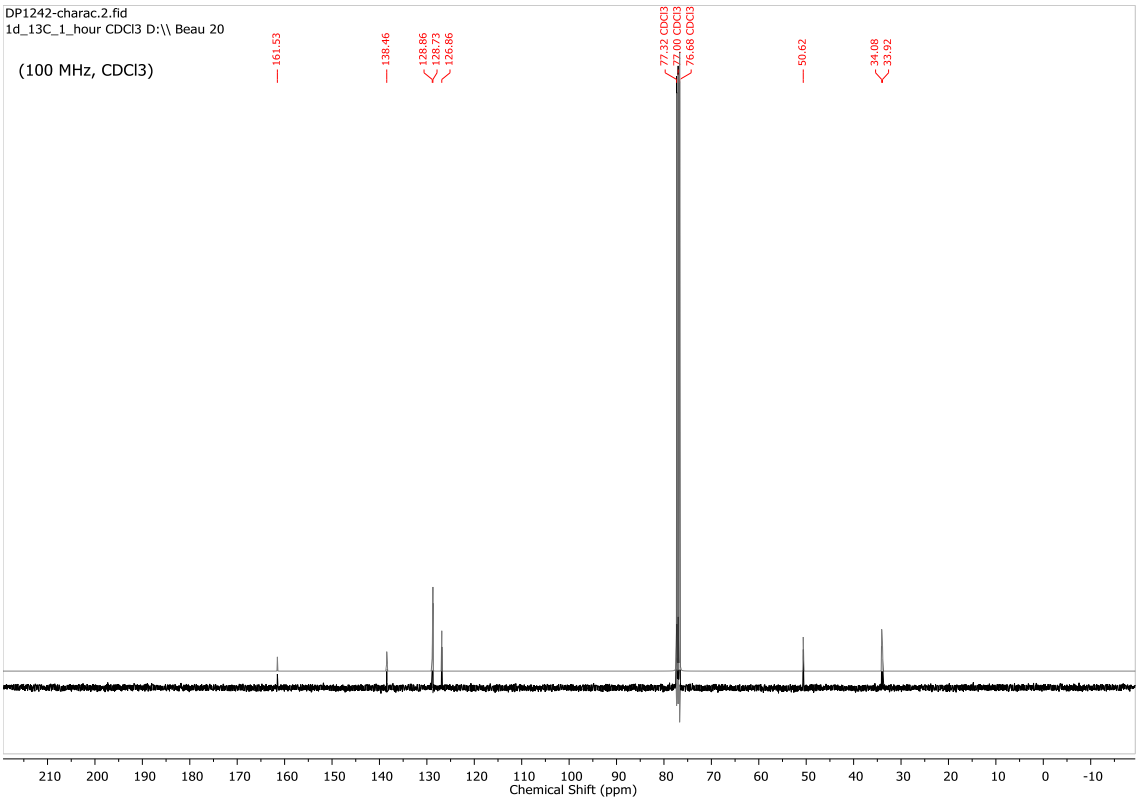


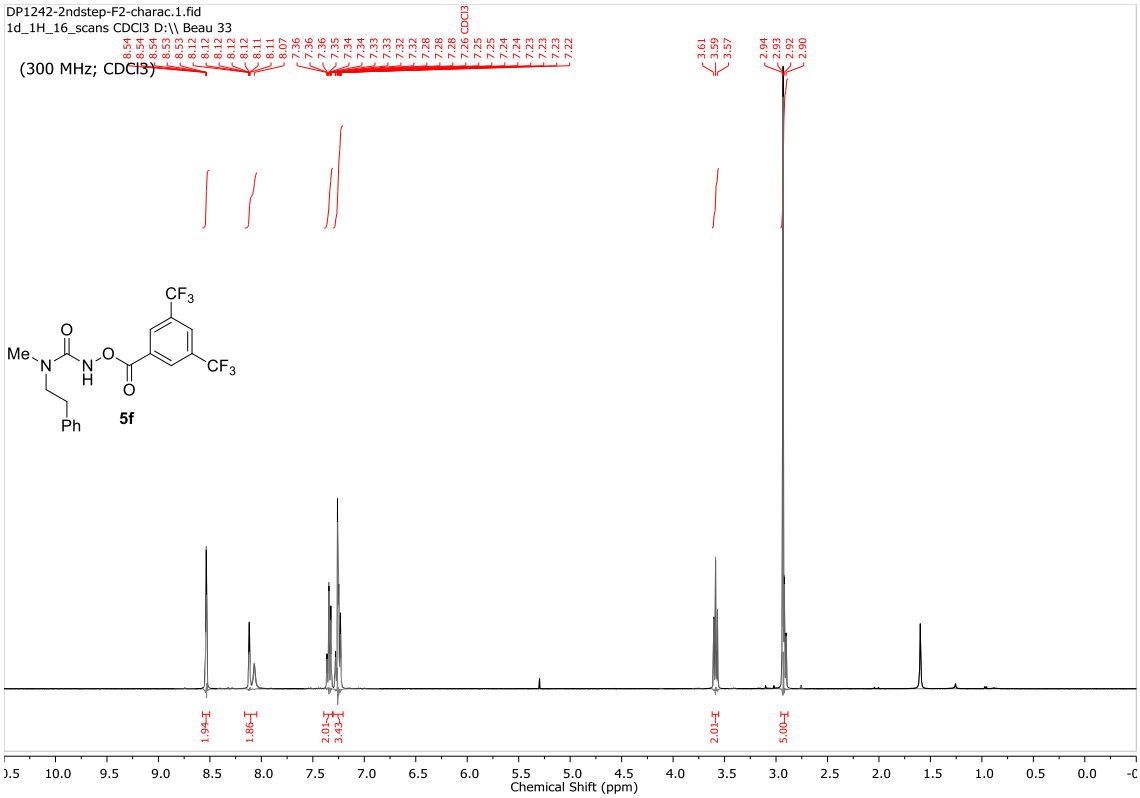


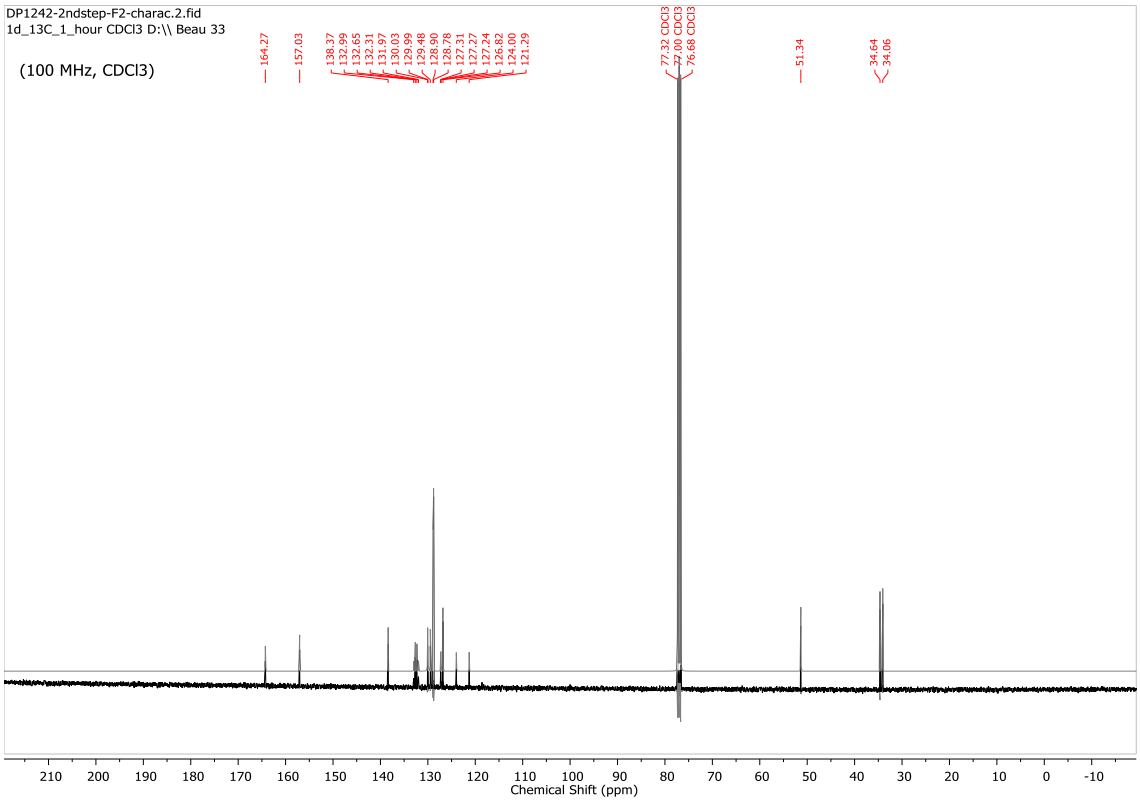
13-C NMR (75 MHz; $CDCl_3$):

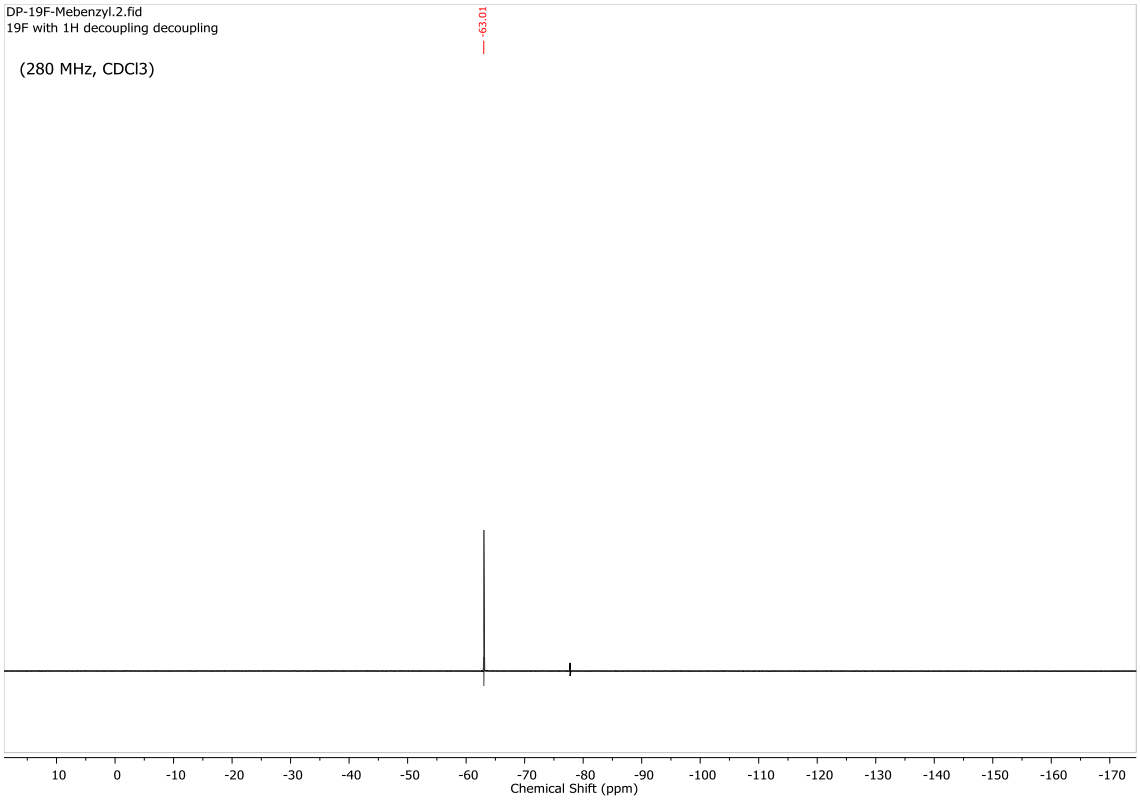



DP1242-charac.1.fid
1d_1H_16_scans CDCl3 D:\\ Beau 20
(300 MHz; CDCl3)
Me
N
O
N
H
OH
Ph
6e
CDCl3
1.58 HDO
Chemical Shift (ppm)


DP1242-charac.2.fid
1d_13C_1_hour CDCl3 D:\\ Beau 20
(100 MHz, CDCl3)
161.53
138.46
128.86
128.73
126.86
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
50.62
34.08
33.92
Chemical Shift (ppm)


DP1242-2ndstep-F2-charac.1.fid
1d_1H_16_scans CDCl3 D:\\ Beau 33
(300 MHz; CDCl3)
Me
N
O
N
H
O
O
CF3
CF3
Ph
5f
Chemical Shift (ppm)


DP1242-2ndstep-F2-charac.2.fid
1d_13C_1_hour CDCl3 D:\\ Beau 33
(100 MHz, CDCl3)
Chemical Shift (ppm)


DP-19F-Mebenzyl.2.fid
19F with 1H decoupling decoupling
(280 MHz, CDCl3)
-63.01
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
Chemical Shift (ppm)