SUPPORTING INFORMATION

Low-Valent Tungsten Catalysis Enables Site-Selective Isomerization–Hydroboration of Unactivated Alkenes

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GENERAL INFORMATION

General Safety Considerations:

$W(CO)_6$ and other $M(CO)_x$ complexes used in this study can decompose to give off free CO, so all reactions run with $M(CO)_x$ complexes should be handled with the same precautions as those using gaseous CO, while taking into account any potential hazards introduced by the metal carbonyl species themselves.

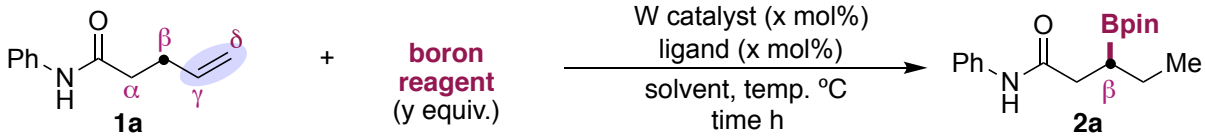
All sealed reactions were allowed to cool to room temperature before being carefully opened in a well ventilated fumehood as gas build-up (H_2 and/or CO) is commonly observed.

Reagents. All materials were used as received from commercial sources without further purification. $W(CO)_6$ was purchased from Strem Chemicals 99.9% purity (Lot 31679900). $W(MeCN)_3(CO)_3$ was purchased from MilliporeSigma (Lot MKCH4360). HBpin was ordered from MilliporeSigma and stored in the glovebox freezer in between uses. THF was purchased from MilliporeSigma in 100-mL Sure/Seal bottles and used as received.

Analytical methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX instrument equipped with a 5 mm DCH cryoprobe (600 MHz and 151 MHz, respectively) and also on Bruker 300 MHz, Bruker 400 MHz and Bruker 500 MHz instruments at 20 °C. ^1H spectra were reported relative to residual solvent signals unless otherwise stated. ^{13}C NMR spectra were calibrated to residual solvent signals. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, hept = heptet and m = multiplet. ^{11}B NMR and ^{19}F NMR were obtained with ^1H decoupling unless otherwise indicated. Coupling constants, *J*, are reported in Hertz. Gas chromatographic analyses were performed on Hewlett-Packard 6890 gas chromatography instrument with a FID detector. Flash chromatography was performed with EM Science silica gel 60 (230–400 mesh). Thin layer chromatography was used to monitor reaction progress and analyze fractions from column chromatography. For this purpose TLC Silica gel 60 F254 aluminum sheets from Merck were used. and visualization was achieved using UV irradiation and/or staining with potassium permanganate or cerium molybdate solution. High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization (positive mode) time of flight experiments.

REACTION INFORMATION

Reaction optimization



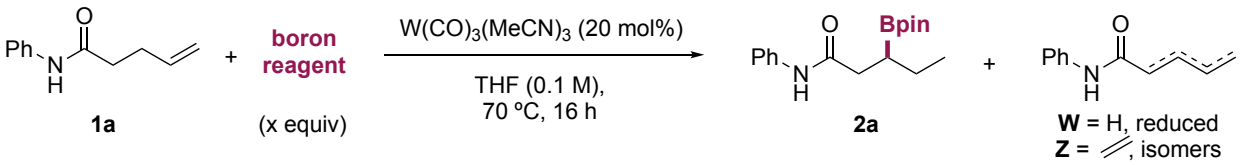
General Procedure. To a 6-mL vial equipped with a Teflon®-coated magnetic stir bar, **1a** (17.5 mg, 0.100 mmol) was added, and the vial was then pumped into an argon-filled glovebox. The appropriate tungsten catalyst (specified amount) was added followed by ligand (if applicable) and solvent. The boron reagent was added, and the vial was sealed, removed from the glovebox, and heated in a preheated oil bath for the specified amount of time.

For reactions with HBpin: The reaction vessel was allowed to cool to room temperature and was vented in the fumehood. A ~5-μL aliquot was diluted in EtOAc and analyzed by GCMS or LCMS.

For reactions with HBcat: The reaction vessel was allowed to cool to room temperature, and a solution of pinacol (47mg, 0.400 mmol) in NEt_3 (55 μL, 0.400 mmol) was added. The resulting mixture was stirred at room temperature for 3 h, at which point a ~5-μL aliquot was diluted in EtOAc and analyzed by GCMS or LCMS.

Analysis of crude reactions: The LCMS and GCMS methods used for analysis were able to separate the γ-, δ-, and β-boryl products. The regioisomeric ratio (r.r.) was calculated by their relative integration. Isomerized alkene starting material peaks showed significant overlap with each other and could not be separated, however, the reduced alkane byproduct was separable from this mixture.

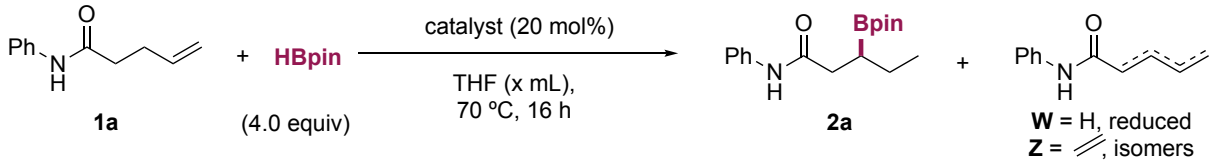
Table S1. Screening of boron reagents.



Entry	Boron reagent	Conv. (%)	2a (%)	W (%)	Z (%)
1	HBcat (3.0 equiv)	100	65	16	16
2	HBcat (4.0 equiv)	100	74	13	13
3	HBcat (5.0 equiv)	100	75	13	12
4	HBcat (3.0 equiv), rt	52	32	16	2
5	HBpin (2.0 equiv)	40	18	22	0
6	HBpin (3.0 equiv)	49	28	21	0
7	HBpin (4.0 equiv)	82	42	40	0
8	HBpin (5.0 equiv)	100	43	46	0
9	HBpin (3.0 equiv), rt	25	10	16	0
10	HBdan (3.0 equiv)	21	0	15	5

Reaction conditions: **1a** (0.1 mmol), boron reagent (x equiv), $W(CO)_3(MeCN)_3$ (20 mol%), THF (1.0 mL), 70 °C, 16 h. Conversion and yields using LC-MS with 1,3,5-trimethoxybenzene as an internal standard. Bcat was converted to Bpin with pinacol and NEt_3. Entry 10, HBdan, no boron containing products were observed.

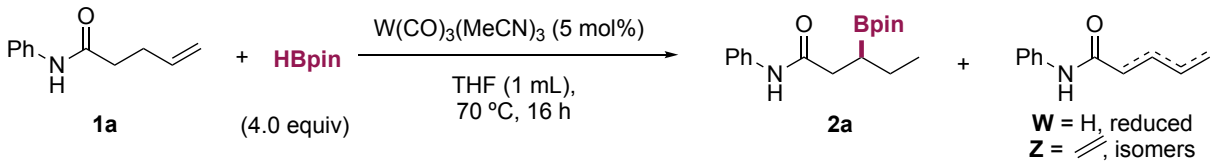
Table S2. Screening of precatalysts and solvent concentration.



Entry	catalyst (solvent volume)	Conv. (%)	2a (%)	W (%)	Z (%)
1	$W(CO)_4(MeCN)_2$ (0.5 mL)	72	48	12	11
2	$W(CO)_4(MeCN)_2$ (1.0 mL)	100	56	13	13
3	$W(CO)_4(MeCN)_2$ (1.5 mL)	100	56	14	13
4	$W(CO)_3(MeCN)_3$ (0.5 mL)	100	76	10	10
5	$W(CO)_3(MeCN)_3$ (1.5 mL)	100	61	22	13
6	5 mol% $W(CO)_3(MeCN)_3$ (1.0 mL)	100	76	10	11
7	$Mo(CO)_3(PrCN)_3$ (1.0 mL)	100	46	18	9
8	$W(CO)_3(PrCN)_3$ (1.0 mL)	100	51	17	11

Reaction conditions: **1a** (0.1 mmol), HBpin (4.0 equiv), $W(CO)_3(MeCN)_3$ (20 mol%), 70 °C, 16 h. Conversion and yields using LC-MS with 1,3,5-trimethoxybenzene as an internal standard. Bcat was converted to Bpin with pinacol and NEt_3.

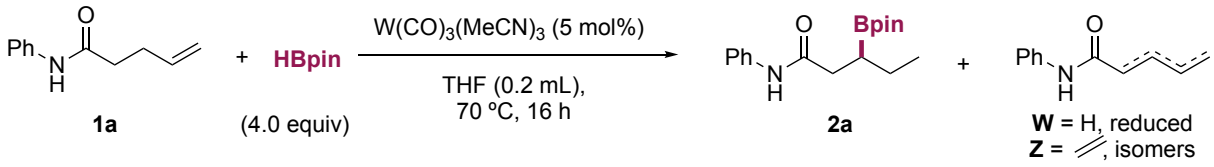
Table S3. Screening of solvent and solvent concentration.



Entry	Deviation from standard conditions	Conv. (%)	2a (%)	W (%)	Z (%)
1	None	95	41	42	3
2	THF (2.0 mL)	94	25	68	3
3	THF (0.5 mL)	100	65	32	1
4	HBpin (2 equiv) and 100 °C	50	12	30	6
5	Dioxane (1.0 mL)	30	3	25	3
6	2-Me-THF (1.0 mL)	20	1	0	11

Reaction conditions: **1a** (0.1 mmol), HBpin (4.0 equiv), $W(CO)_3(MeCN)_3$ (5 mol%), THF (1.0 mL), 70 °C, 16 h. Conversion and yields using LC-MS with 1,3,5-trimethoxybenzene as an internal standard.

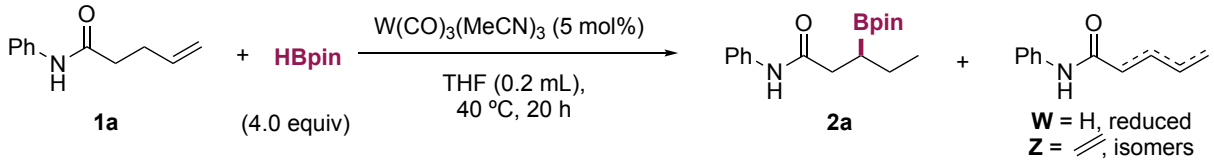
Table S4. Screening of HBpin addition method and temperature.



Entry	Deviation from standard conditions	Conv. (%)	2a (%)	W (%)	Z (%)
1	HBpin (2 equiv at start + 2 equiv 2 h later)	71	31	20	25
2	HBpin (Syringe pump addition over 2 h)	89	46	23	14
3	THF (0.1 mL)	100	79	20	0
4	50 °C	50	12	30	6
5	40 °C	94	90	4	0
6	30 °C	68	42	2	20
7	30 °C using 10% W	76	58	2	15
8	50 °C and 3 equiv of HBpin	98	72	9	9

Reaction conditions: **1a** (0.1 mmol), HBpin (4.0 equiv), $W(CO)_3(MeCN)_3$ (5 mol%), THF (0.2 mL), 70 °C, 16 h. Conversion and yields using LC-MS with 1,3,5-trimethoxybenzene as an internal standard.

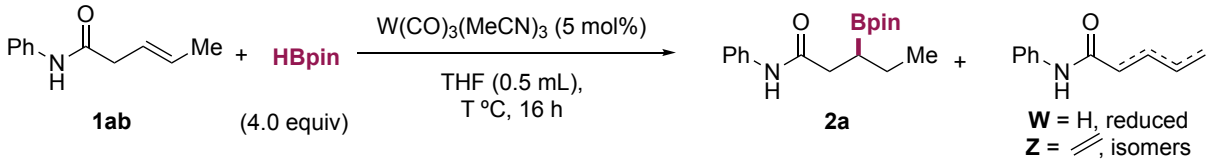
Table S5. Concentration, time, and temperature screening.



Entry	Deviation from standard conditions	Conv. (%)	2a (%)	W (%)	Z (%)
1	none	95	90	4	0
2	24 h	95	90	4	0
3	$W(CO)_3(MeCN)_3$ (7.5 mol%)	100	79	20	0
4	45 °C	96	76	16	0
5	**1a** (0.2 mmol) in THF (0.3 mL)	100	93	3	0
6	No W catalyst	20	0	5	0

Reaction conditions: **1a** (0.1 mmol), HBpin (4.0 equiv), $W(CO)_3(MeCN)_3$ (5 mol%), THF (0.2 mL), 40 °C, 16 h. Conversion and yields using LC-MS with 1,3,5-trimethoxybenzene as an internal standard..

Table S6. Control reactions with **1ab**.

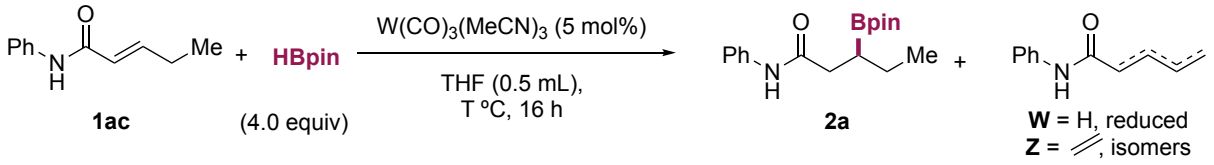


1ab **2a**

Entry	Temperature and catalyst	Conv. (%)	2a (%)	W (%)	Z (%)
1	40 °C	100	70	12	26
2	40 °C, No $W(CO)_3(MeCN)_3$	5	0	0	0

Reaction conditions: **1ab** (0.1 mmol), HBpin (4.0 equiv), $W(CO)_3(MeCN)_3$ (5 mol%), THF (0.5 mL), T °C, 16 h. Conversion and yields using LC-MS with 1,3,5-trimethoxybenzene as an internal standard.

Table S7. Control reactions with **1ac**.

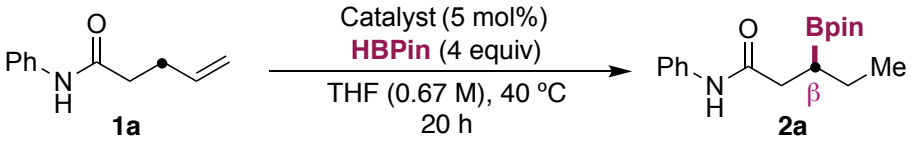


1ac **2a**

Entry	Temperature and catalyst	Conv. (%)	2a (%)	W (%)	Z (%)
1	40 °C	10	0	10	83
2	70 °C	100	0	96	2
3	40 °C, No $W(CO)_3(MeCN)_3$	5	0	5	85
4	70 °C, No $W(CO)_3(MeCN)_3$	100	0	95	2

Reaction conditions: **1ac** (0.1 mmol), HBpin (4.0 equiv), $W(CO)_3(MeCN)_3$ (5 mol%), THF (0.5 mL), T °C, 16 h. Conversion and yields using LC-MS with 1,3,5-trimethoxybenzene as an internal standard.

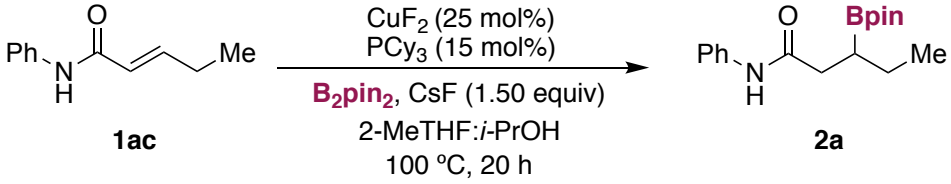
Table S8. Screening of different low-valent transition metals.



Entry	Catalyst	**2a** (%)	**2a** (r.r.)
1	$W(MeCN)_3(CO)_3$	93	>50:1
2	$Cr(CO)_6$	nd	—
3	$Fe_2(CO)_9$	6	3:1
4	$Mo(PrCN)_3(CO)_3$	8	>50:1
5	$Ru_3(CO)_{10}$	4	1:2
6	$Ni(COD)_2$	nd	—
7	$Pd(PPh_3)_4$	nd	—

Reaction conditions: **1a** (0.1 mmol), HBpin (4.0 equiv), catlayst (5 mol%), THF (0.2 mL), 40 °C, 20h. Yields and r.r. determined by GC-MS with 1,3,5-trimethoxybenzene as an internal standard.

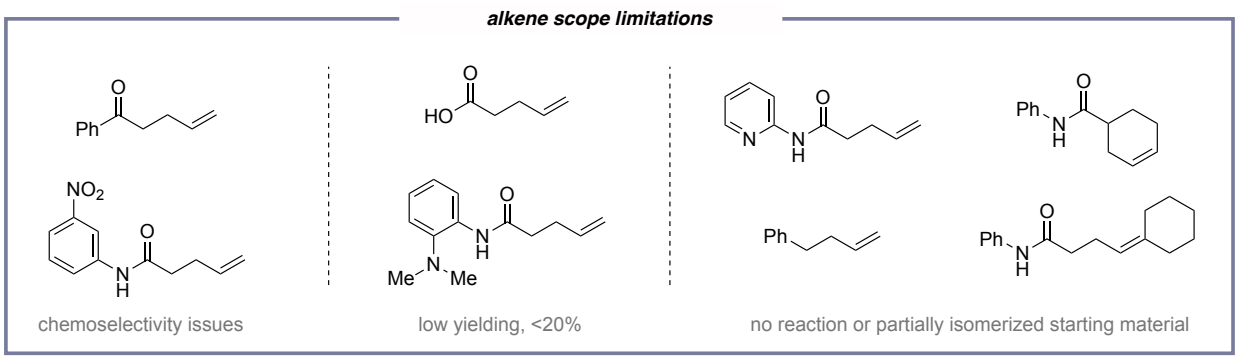
Table S9. Control reactions to determine the necessity of CuF_2 additives and potential reaction mechanism.



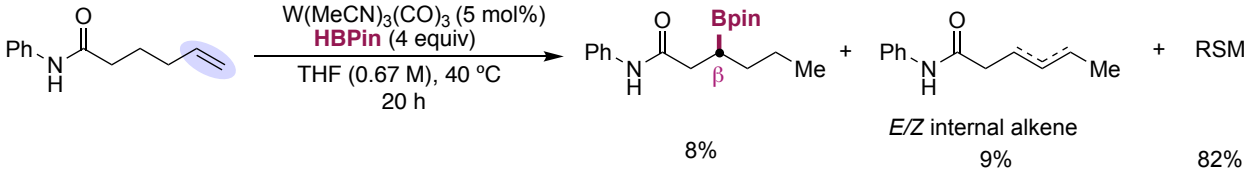
Entry	Deviation from conditions	**2a** (%)	**1ac** (%)
1	none	93	0
2	no CuF_2	66	0
3	no PCy_3	75	0
4	no CuF_2, no PCy_3	25	30

Reaction conditions: **1ac** (0.1 mmol), B_2Pin_2 and CsF (1.5 equiv), CuF_2 (25 mol%), PCy_3 (15 mol%), 2-MeTHF (1.0 mL), 2-PrOH (2 equiv) 100 °C, 20h. Yields determined using ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard.

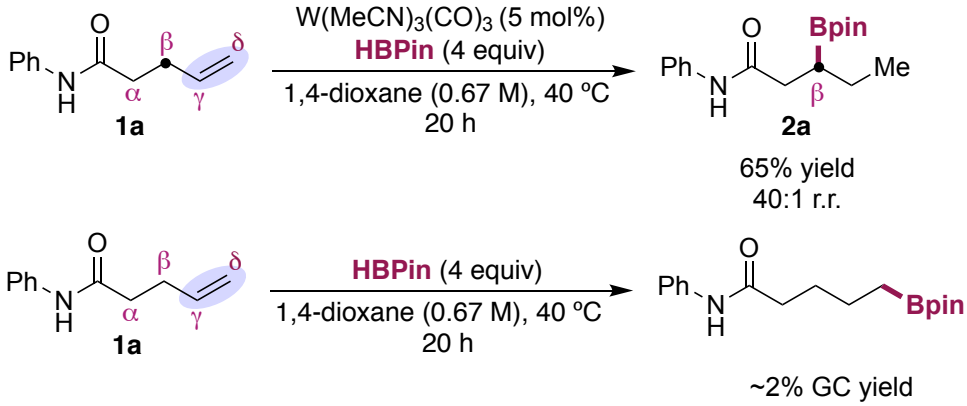
Table S10. Limitations in alkene scope with brief explanation of reaction outcome.



Scheme S1. δ,ε-Unsaturated amide under the optimized reaction conditions.

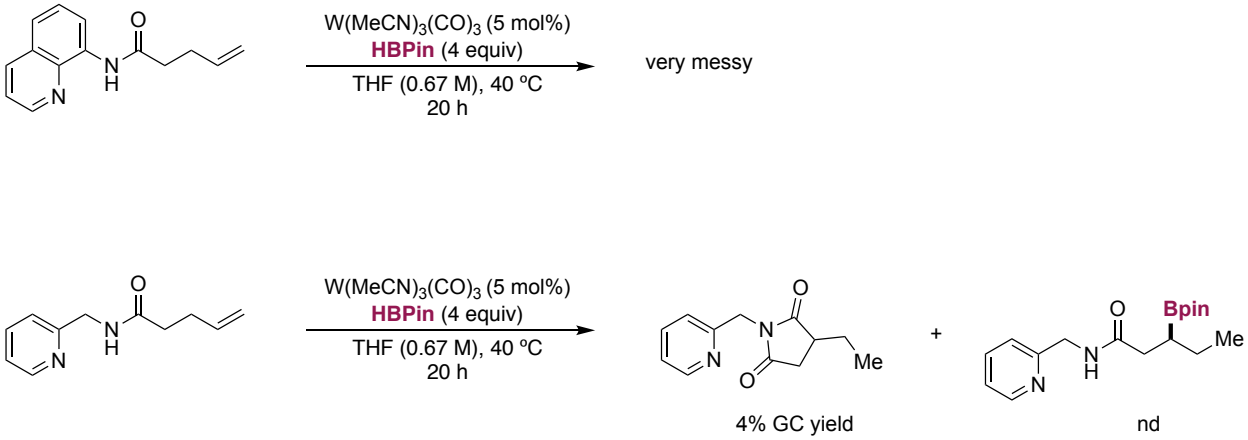


Scheme S2. Rationale for loss of regioselectivity when using dioxane as solvent.

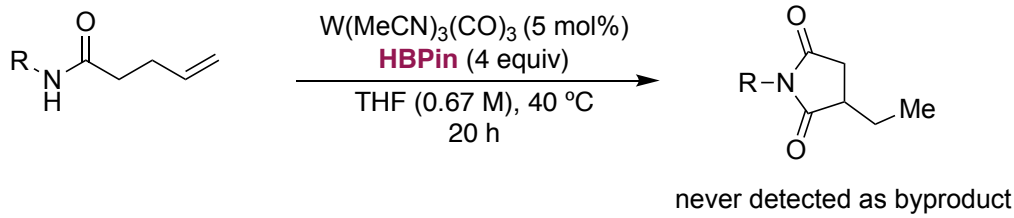


Discussion: With 1,4-dioxane as solvent, approximately the same amount of anti-Markovnikov product is observed in the presence or absence of the W catalyst. Therefore, the decrease in regioselectivity in 1,4-dioxane as solvent is attributed to a non-W-catalyzed pathway that is promoted by 1,4-dioxane.

Scheme S3. Attempted experiments with substrates bearing bidentate directing groups.

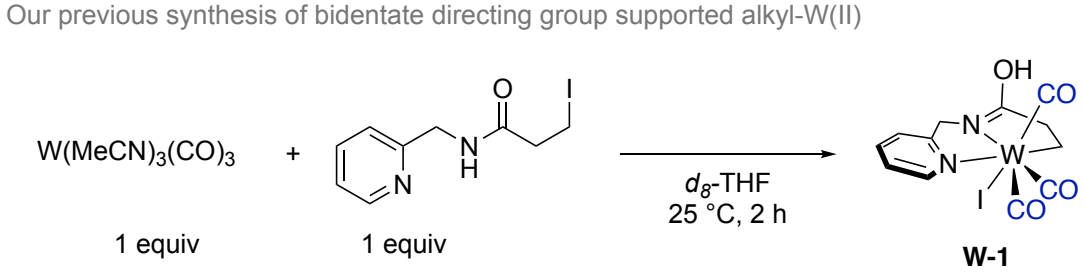


Discussion: These bidentate directing groups were unable to give any detectable hydroboration products. While the 8-aminoquinoline (top) directing group gave a messy GCMS and LCMS trace (>10 peaks), the NH-Pic directing group (bottom) gave the isomerization/hydrocarbonylation product as the exclusive product. In this case, consumption of a CO ligand from $W(MeCN)_3(CO)_3$ would likely result in an unstable $W(L)_4(CO)_2$ which is predicted to rapidly decompose.

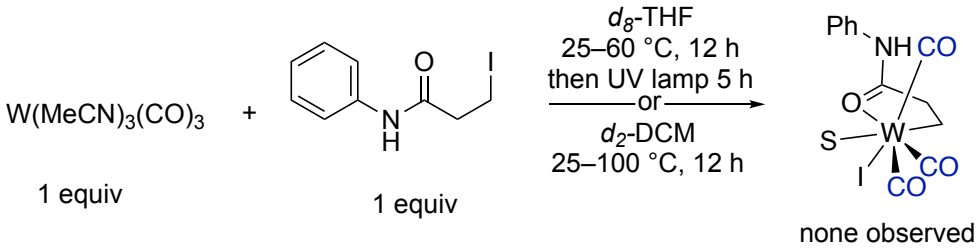


The hydrocarbonylation product shown above is observed with substrate bearing the specific NH-Pic bidentate directing group (Scheme S3). Other classes of bidentate directing groups, as well as the monodentate directing groups used in this study, did not give any hydrocarbonylation products. The identity of the precatalyst also did not affect whether or not hydrocarbonylation took place. For further studies on tungsten catalyzed hydrocarbonylation, see reference S1.

Scheme S4. Attempted synthesis putative alkyl–W intermediates.

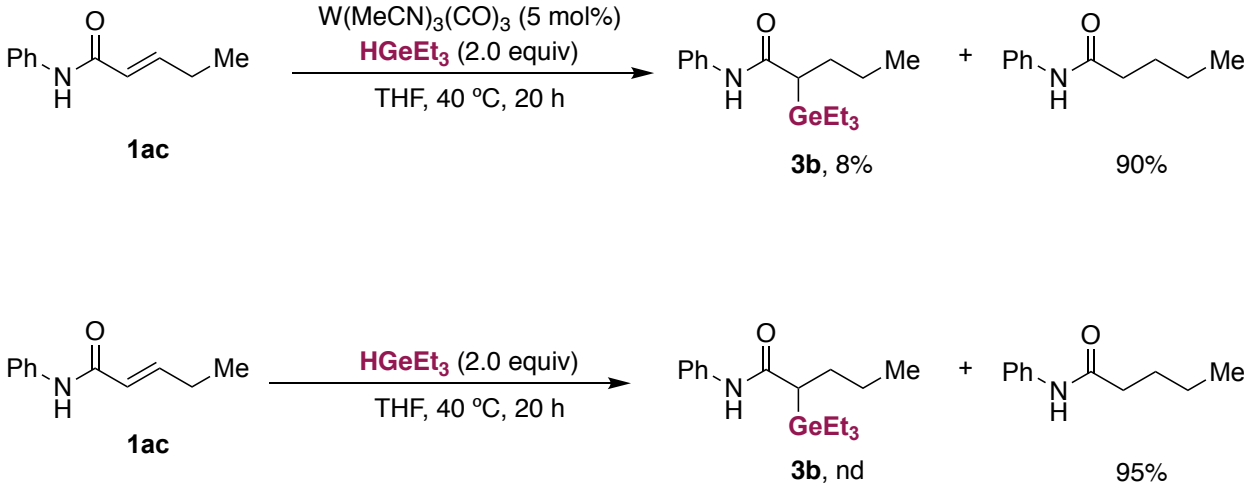


Attempted synthesis of mono-dentate alkyl-W(II)



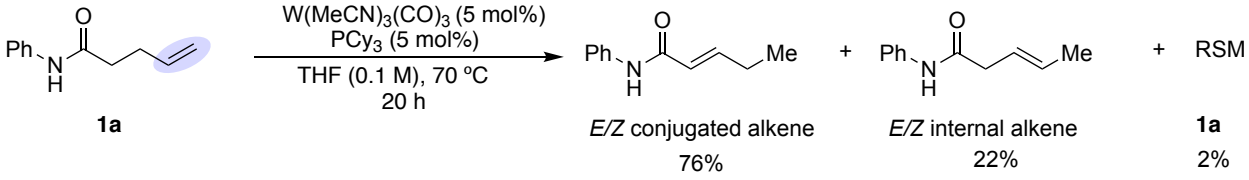
Discussion: As neither of the bidentate directing groups tested in Scheme S3 provided the desired hydroboration product under standard catalytic conditions, alkyl–W(II) complexes supported by these directing groups, as previously prepared by our group,[1] were deemed not to be appropriate organometallic model complexes for this catalytic system. Thus, mechanistic studied with these complexes were not pursued. Attempts to synthesize an alkyl–W(II) model complex using a monodentate amide directing group were unsuccessful.

Scheme S5. Control reactions for hydrogermylation reaction to provide product 3b.



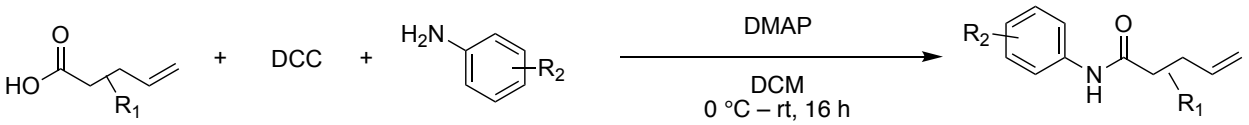
Discussion: These data shown above demonstrate that the hydrogermanylation reaction is tungsten-catalyzed and that it likely proceeds through intermediacy of the α,β-unsaturated alkene **1ac**. A non-catalyzed 1,4-reduction accounts for the main byproduct and explains why a lower yield is obtained when starting from **1ac.**

Scheme S6. Control experiment showing the role of PCy_3.

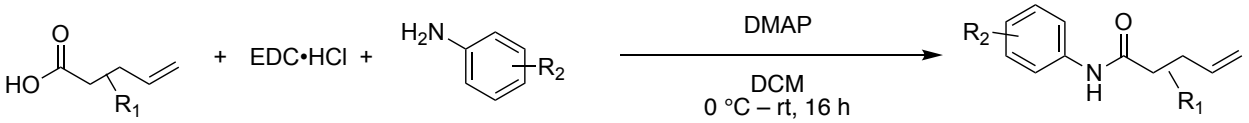


Characterization of New Compounds

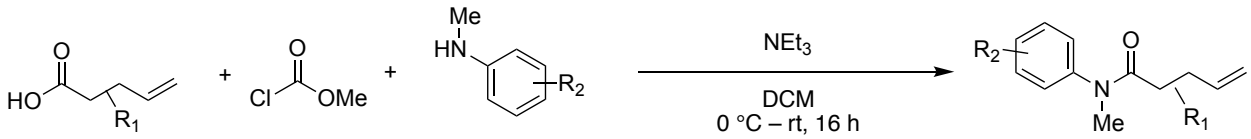
Synthesis of Starting Materials



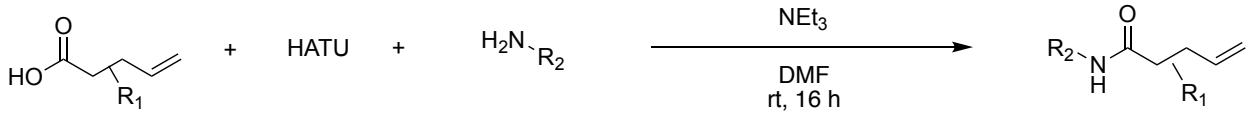
General Procedure A: a solution of the corresponding acid (1.0 equiv), primary amine (1.1 equiv) and DMAP (10 mol%) in DCM (0.33 M) was cooled to 0 ºC. Subsequently, DCC (1.5 equiv) was added to the reaction, and the bath was removed, leaving the reaction stirring overnight. HCl (1 M) was then added (×2), and the mixture was shaken vigorously. The organic layer was then washed with $NaHCO_3$ sat. and brine (×3). Finally, the organic phase was dried over $MgSO_4$, and the solvent was evaporated with a rotavap. Flash silica column chromatography was performed with a mixture of hexane/EtOAc as eluent.



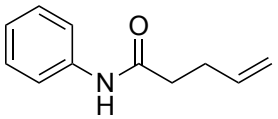
General Procedure B: A round-bottomed flask was charged with DCM (25 mL, 0.4 M), EDC-HCl (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride, 13 mmol, 1.3 equiv), and DMAP (14 mmol, 1.4 equiv). The reaction flask was cooled to 0 °C in an ice bath, and the carboxylic acid (10 mmol, 1.0 equiv) was added. After stirring for 5 min, the substituted aniline (12 mmol, 1.2 equiv) was added. The ice bath was then removed, and the reaction was allowed to stir for 16 hours at room temperature. Then, the reaction was quenched with 1M HCl (25 mL), and the organic layer was separated. The aqueous layer was then extracted with DCM (2 × 25 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated. The crude product was purified by flash silica column chromatography was performed with a mixture of hexane/EtOAc as eluent.



General Procedure C: A solution of the corresponding acid (1.0 equiv) and Et_3N (4.2 equiv) in THF (0.4 M) was cooled to 0 ºC. Then, $ClCO_2Me$ (1 equiv) was added dropwise, and the resulting mixture was stirred for 10 min at 0 ºC. Subsequently, a solution of the secondary amine in THF (3 M) was added to the reaction mixture. The solution was stirred for 60 min at 0 ºC, at which point the reaction was filtered to remove the precipitate that had formed. The filtrate was concentrated under vacuum, and flash silica column chromatography was performed with a mixture of hexane/EtOAc as eluent.

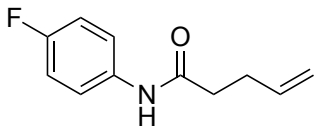


General Procedure D: HATU (1.2 equiv) was added to a solution of the corresponding acid (1.0 equiv), primary amine (1.2 equiv), and Et_3N (2.4 equiv) in DMF (0.2 M). The reaction was left to stir overnight. Then, it was quenched with 1 M NaOH, and the resulting mixture was extracted with DCM. Finally, the organic phase was dried over $MgSO_4$, and the solvent was evaporated with a rotavap. Flash silica column chromatography was performed with a mixture of hexane/EtOAc as eluent.



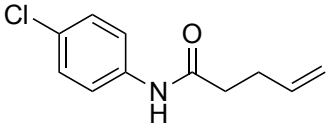
1a

***N*-(Phenyl)pent-4-enamide (1a):** Following General Procedure A, 4-pentenoic acid (0.5 mL, 4.89 mmol), aniline (0.39 mL, 5.38 mmol), DMAP (61 mg, 0.48 mmol), and DCC (1.03 g, 7.34 mmol) in DCM (15 mL) were used, affording the product as a white solid (658 mg, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.53–7.44 (m, 2H), 7.38–7.27 (m, 2H), 7.21 (s, 1H), 7.14–7.08 (m, 1H), 5.89 (ddt, *J* = 16.8, 10.9, 6.0 Hz, 1H), 5.27–4.96 (m, 2H), 2.54–2.40 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.4, 137.8, 136.9, 129.0, 124.3, 119.8, 116.0, 36.9, 29.4 ppm. Spectroscopic data for **1a** match those previously reported in the literature.[2]



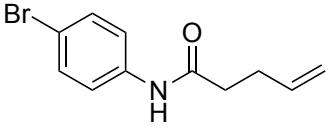
1b

***N*-(4-Fluorophenyl)pent-4-enamide (1b):** Following General Procedure B, 4-pentenoic acid (1.22 mL, 12.0 mmol), 4-fluoroaniline (1.33 g, 12.0 mmol), DMAP (146 mg, 1.22 mmol), and EDC (2.53 g, 13.2 mmol) in DCM (20 mL) were used, affording the product as a white solid (1.83 g, 79% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.45 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.19 (s, 1H), 7.00 (t, *J* = 8.5 Hz, 2H), 5.88 (td, *J* = 10.5, 5.1 Hz, 1H), 5.13 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 2.46 (dq, *J* = 12.3, 6.7 Hz, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 170.0, 158.9 (d, $J_{C–F}$ = 243.6 Hz), 136.3, 133.3, 121.2 (dd, $J_{C–F}$ = 7.8, 3.5 Hz), 115.6, 115.1 (d, $J_{C–F}$ = 22.6 Hz), 36.2, 28.9 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = –118.2 ppm. Spectroscopic data for **1b** match those previously reported in the literature.[3]



1c

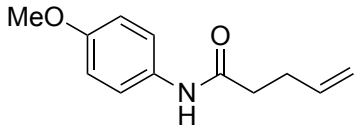
***N*-(4-Chlorophenyl)pent-4-enamide (1c):** Following General Procedure B, 4-pentenoic acid (1.22 mL, 12.0 mmol), 4-chloroaniline (1.53 g, 12.0 mmol), DMAP (146 mg, 1.22 mmol), and EDC (2.53 g, 13.2 mmol) in DCM (20 mL) were used, affording the product as a white solid (2.21 g, 88% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 8.3 Hz, 2H), 7.30–7.22 (m, 2H), 7.20 (s, 1H), 5.95–5.76 (m, 1H), 5.18–4.98 (m, 2H), 2.47 (m, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 170.6, 136.8, 136.5, 129.3, 129.1, 121.1, 116.2, 36.9, 29.4 ppm. Spectroscopic data for **1c** match those previously reported in the literature.[3]



1d

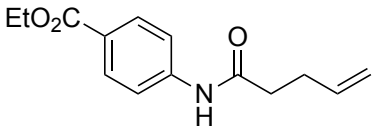
***N*-(4-Bromophenyl)pent-4-enamide (1d):** Following General Procedure B, 4-pentenoic acid (1.22 mL, 12.0 mmol), 4-bromoaniline (2.064 g, 12.0 mmol), DMAP (146 mg, 1.22 mmol), and EDC (2.53 g, 13.2 mmol) in DCM (20 mL) were used, affording the product as a white solid (1.93 g, 62% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.58–7.31 (m, 4H), 6.05–5.74 (m, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 5.08 (d, *J* = 10.3 Hz, 1H), 2.48 (tt, *J* = 14.6, 10.5, 8.4 Hz, 4H) ppm. **^{13}C NMR**

(151 MHz, $CDCl_3$) δ = 170.8, 137.0, 136.8, 132.0, 121.5, 116.9, 116.1, 36.8, 29.4 ppm. Spectroscopic data for **1d** match those previously reported in the literature.[4]



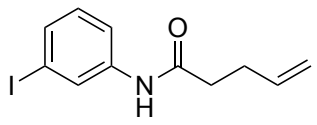
1e

***N*-(4-Methoxyphenyl)pent-4-enamide (1e):** Following General Procedure A, 4-pentenoic acid (0.5 mL, 4.89 mmol), *p*-anisidine (615 mg, 5.38 mmol), DMAP (61 mg, 0.48 mmol), and DCC (1.03g, 7.34 mmol) in DCM (15 mL) were used, affording the product as a brown solid (832 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.50–7.31 (m, 2H), 7.24 (bs, 1H), 6.90–6.77 (m, 2H), 5.88 (ddt, *J* = 16.8, 10.2, 6.3 Hz, 1H), 5.09 (dd, *J* = 17.1, 10.2 Hz, 2H), 3.75 (s, 3H), 2.54–2.38 (m, 4H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.4, 156.4, 136.9, 130.9, 121.8, 115.8, 114.1, 55.5, 36.6, 29.5 ppm. Spectroscopic data for **1e** match those previously reported in the literature.[3]



1f

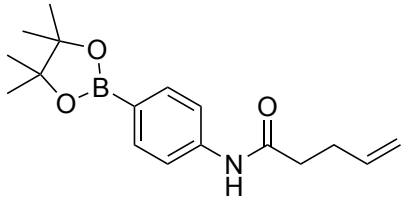
Ethyl 4-(pent-4-enamido)benzoate (1f): Following General Procedure A, 4-pentenoic acid (0.5 mL, 4.89 mmol), *p*-anisidine (826 mg, 5.38 mmol), DMAP (61 mg, 0.48 mmol), and DCC (1.03 g, 7.34 mmol) in DCM (15 mL) were used, affording the product as a white solid (966 mg, 80% yield). **^{1}H NMR** (500 MHz, CDCl3) δ = 8.08–7.90 (m, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.53 (s, 1H), 5.96–5.77 (m, 1H), 5.22–4.97 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.49 (dt, *J* = 3.5, 0.9 Hz, 4H), 1.38 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 170.7, 166.1, 141.9, 136.6, 130.8, 125.9, 118.7, 116.1, 60.8, 36.9, 29.2, 14.3 ppm. Spectroscopic data for **1f** match those previously reported in the literature.[5]



1g

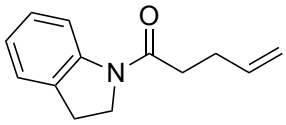
***N*-(3-Iodophenyl)pent-4-enamide (1g):** Following General Procedure B, 4-pentenoic acid (1.22 mL, 12.0 mmol), 3-iodoaniline (2.62 g, 12.0 mmol), DMAP (146 mg, 1.22 mmol), and EDC (2.53 g, 13.2 mmol) in DCM (20 mL) were used, affording the product as a white solid (2.11 g, 58%

yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.92 (s, 1H), 7.45 (dd, *J* = 14.8, 8.0 Hz, 2H), 7.02 (dd, *J* = 8.9, 7.2 Hz, 1H), 5.87 (ddt, *J* = 16.9, 10.6, 5.9 Hz, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 10.2 Hz, 1H), 2.47 (m, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 170.6, 139.0, 136.8, 133.4, 130.6, 128.6, 119.0, 116.2, 94.2, 36.8, 29.4 ppm. Spectroscopic data for **1g** match those previously reported in the literature.[6]



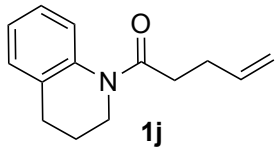
1h

***N*-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-4-enamide (1h):** Following General Procedure B, 4-pentenoic acid (2.00 mL, 20.0 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (4.38 g, 20.0 mmol), DMAP (244 mg, 2.00 mmol), and EDC (4.17 g, 22.0 mmol) in DCM (40 mL) were used, affording the product as a white solid (4.49 g, 75% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 5.88 (ddt, *J* = 16.8, 10.6, 6.0 Hz, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 10.3 Hz, 1H), 2.47 (m, 4H), 1.33 (s, 12H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 170.5, 140.6, 136.9, 135.9, 118.6, 116.1, 83.8, 37.1, 29.4, 25.0 ppm. *(The carbon attached to boron was not observed due to quadrupolar relaxation).* **HRMS** calcd. for ($C_{17}H_{25}NO_3B$) $[M+H]^+$: 302.1922, found 302.1920.



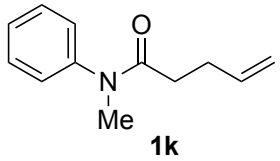
1i

1-(Indolin-1-yl)pent-4-en-1-one (1i): Following General Procedure B, 4-pentenoic acid (2.00 mL, 20.0 mmol), indoline (2.25 mL, 20.0 mmol), DMAP (244 mg, 2.0 mmol) and EDC-HCl (4.17 g, 22.0 mmol) in DCM (40 mL) were used, affording the product as a white solid (2.04 g, 51% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.1 Hz, 1H), 7.19 (q, *J* = 7.0, 6.2 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 5.93 (ddt, *J* = 16.1, 11.0, 5.7 Hz, 1H), 5.15–5.07 (m, 1H), 5.03 (d, *J* = 10.1 Hz, 1H), 4.06 (t, *J* = 8.5 Hz, 2H), 3.20 (t, *J* = 8.5 Hz, 2H), 2.51 (q, *J* = 5.9, 5.1 Hz, 4H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 170.6, 143.1, 137.5, 131.1, 127.7, 124.6, 123.6, 117.1, 115.4, 48.0, 35.3, 28.7, 28.1 ppm. **HRMS** calcd. for ($C_{13}H_{16}NO$) $[M+H]^+$: 202.1226, found 202.1224.



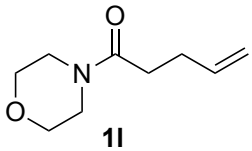
1j

1-(3,4-Dihydroquinolin-1(2*H*)-yl)pent-4-en-1-one (1j): Following General Procedure D, pent-4-enoic acid (0.60 mL, 6.00 mmol), 1,2,3,4-tetrahydroquinoline (615 mg, 4.61 mmol), HATU (2.281 g, 6.00 mmol), pyridine (0.75 mL, 9.24 mmol) in DCM (12 mL) were used, affording the product as a colorless oil (723 mg, 73% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.20–7.08 (m, 4H), 5.79 (d, *J* = 7.3 Hz, 1H), 4.99 (d, *J* = 17.3 Hz, 1H), 4.96–4.89 (m, 1H), 3.79 (t, *J* = 6.6 Hz, 2H), 2.71 (t, *J* = 6.7 Hz, 2H), 2.60 (dd, *J* = 8.5, 6.6 Hz, 2H), 2.45–2.36 (m, 2H), 1.95 (p, *J* = 6.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 172.3, 137.5, 128.6, 128.6, 128.6, 126.2, 125.4, 124.8, 115.3, 43.0, 33.9, 29.9, 26.9, 24.3 ppm. **HRMS** calcd. for ($C_{14}H_{18}NO$) $[M+H]^+$: 216.1383, found 203.1384.



1k

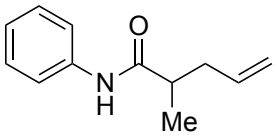
***N*-Methyl-*N*-phenylpent-4-enamide (1k):** Following the General Procedure C, 4-pentenoic acid (1.0 mL, 9.78 mmol), *N*-methylaniline (1.62 mL, 15.11 mmol), Et_3N (5.71 mL, 40.9 mmol) and methyl carbonochloridate (0.87 mL, 9.78 mmol) in THF (30 mL) were used, affording the product as a yellow oil (1.40 g, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.43–7.38 (m, 2H), 7.36–7.30 (m, 1H), 7.22–7.10 (m, 2H), 5.76–5.68 (m, 1H), 4.99–4.82 (m, 2H), 3.26 (s, 3H), 2.32 (q, *J* = 7.2 Hz, 2H), 2.15 (t, *J* = 7.6 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 172.3, 144.1, 137.5, 129.7, 127.7, 127.3, 114.9, 37.3, 33.4, 29.4 ppm. Spectroscopic data for **1k** match those previously reported in the literature.[7]



1l

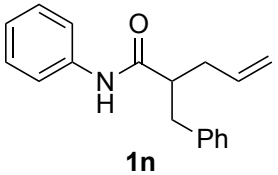
1-Morpholinopent-4-en-1-one (1l): Following General Procedure D, pent-4-enoic acid (0.70 mL, 6.86 mmol), morpholine (0.54 mL, 6.24 mmol), HATU (2.61 g, 6.86 mmol), and pyridine (0.50 mL, 6.24 mmol) in DCM (12 mL) were used, affording the product as a colorless oil (550 mg, 52% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 5.91–5.77 (m, 1H), 5.05 (dd, *J* = 17.0, 1.7 Hz, 1H), 4.99 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.70–3.56 (m, 6H), 3.48–3.42 (m, 2H), 2.42–2.36 (m, 4H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ = 171.1, 137.4, 115.5, 67.1, 66.8, 46.1, 42.0, 32.4, 29.3 ppm. Spectroscopic data for **1l** match those previously reported in the literature.[8]



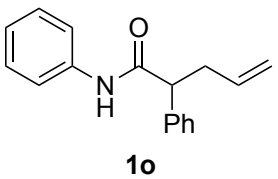
1m

2-Methyl-*N*-phenylpent-4-enamide (1m): Following the General Procedure D, 2-methylpent-4-enoic acid (0.80 mL, 6.86 mmol), aniline (0.57 mL, 6.24 mmol), HATU (2.61 g, 6.86 mmol) and pyridine (0.50 mL, 6.24 mmol) in DCM (12 mL) were used, affording the product as a beige solid (980 mg, 83% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.56–7.46 (m, 2H), 7.38 (s, 1H), 7.36–7.27 (m, 2H), 7.14–7.00 (m, 1H), 5.89–5.74 (m, 1H), 5.11 (d, *J* = 17.1 Hz, 1H), 5.06 (d, *J* = 8.4 Hz, 1H), 2.55–2.36 (m, 2H), 2.28–2.16 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 174.3, 138.0, 135.8, 129.1, 124.4, 120.1, 117.4, 42.3, 38.5, 17.6 ppm. Spectroscopic data for **1m** match those previously reported in the literature.[9]



1n

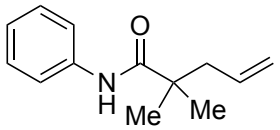
2-Benzyl-*N*-phenylpent-4-enamide (1n): Following General Procedure B, 2-benzylpent-4-enoic acid (500 mg, 2.63 mmol), aniline (240 µL, 2.63 mmol), DMAP (32 mg, 0.26 mmol), and EDC-HCl (554 mg, 2.63 mmol) in DCM (20 mL) were used, affording the product as a white solid (390 mg, 56% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37–7.18 (m, 9H), 7.15–7.05 (m, 1H), 6.85 (s, 1H), 5.87 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.17 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.11 (ddt, *J* = 10.1, 1.9, 1.0 Hz, 1H), 3.03 (dd, *J* = 13.5, 9.0 Hz, 1H), 2.88 (dd, *J* = 13.5, 5.1 Hz, 1H), 2.56 (m, 2H), 2.45–2.28 (m, 1H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 172.6, 139.7, 137.5, 135.5, 129.0, 128.7, 126.6, 124.4, 120.3, 117.6, 51.1, 38.9, 36.9 ppm. **HRMS** calcd. for ($C_{18}H_{20}NO$) $[M+H]^+$: 266.1539, found 266.1538.



1o

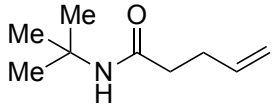
2-Phenyl-*N*-phenylpent-4-enamide (1o): Following General Procedure B, 2-phenyl-pent-4-enoic acid[10] (370 mg, 2.10 mmol), aniline (287 µL, 3.15 mmol), HATU (1.198 g, 3.150 mmol)

and pyridine (0.50 mL, 6.24 mmol) in DCM (15 mL) were used, affording the product as a white solid (210 mg, 40% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37–7.18 (m, 9H), 7.15–7.05 (m, 1H), 6.85 (s, 1H), 5.87 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.17 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.11 (ddt, *J* = 10.1, 1.9, 1.0 Hz, 1H), 3.57 (t, *J* = 7.5 Hz, 1H), 3.01 (dt, *J* = 14.3, 7.1 Hz, 1H), 2.60 (dt, *J* = 14.6, 7.4 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 172.6, 139.7, 137.5, 135.5, 129.0, 128.7, 126.6, 124.4, 120.3, 117.6, 51.1, 38.9, 36.9 ppm. **HRMS** calcd. for ($C_{17}H_{18}NO$) $[M+H]^+$: 252.1383, found 252.1383.



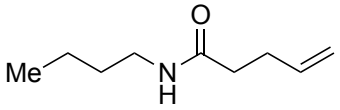
1p

2,2-Dimethyl-*N*-phenylpent-4-enamide (1p): Following General Procedure D, 2,2-dimethylpent-4-enoic acid (0.5 g, 3.9 mmol), aniline (0.42 mL, 4.68 mmol), Et_3N (1.36 mL, 9.4 mmol), and HATU (1.76 g, 4.68 mmol) in DMF (20 mL) were used, affording the product as a white solid (657 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.53–7.48 (m, 2H), 7.36–7.29 (m, 3H), 7.13–7.07 (m, 1H), 5.93–5.76 (m, 1H), 5.21–5.09 (m, 2H), 2.38 (d, *J* = 7.4 Hz, 2H), 1.30 (s, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 175.6, 138.0, 134.4, 129.1, 124.4, 120.2, 118.6, 45.4, 43.0, 25.4 ppm. **HRMS** calcd. for ($C_{13}H_{18}NO$) $[M+H]^+$: 206.1539, found 206.1540.



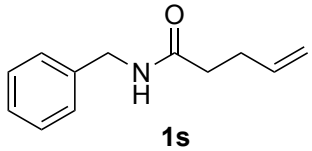
1q

***N*-(*tert*-Butyl)pent-4-enamide (1q):** Following General Procedure D, 4-pentenoic acid (0.5 mL, 4.89 mmol), *t*-butylamine (0.61 mL, 5.85 mmol), Et_3N (1.7 mL, 11.75 mmol) and HATU (2.2 g, 5.85 mmol) in DMF (25 mL) were used, affording the product as a pale yellow oil (521 mg, 68% yield). **^{1}H NMR** (500 MHz, CDCl3) δ = 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.51 (s, 1H), 5.10–4.83 (m, 2H), 2.35 (q, *J* = 7.4 Hz, 2H), 2.17 (t, *J* = 7.5 Hz, 2H), 1.33 (s, 9H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 171.6, 137.2, 115.4, 51.2, 36.7, 29.7, 28.8 ppm. **HRMS** calcd. for ($C_9H_{17}NNaO$) $[M+Na]^+$: 178.1202, found 178.1195.



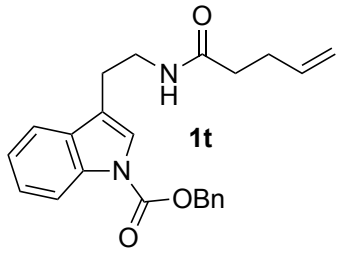
1r

***N*-Butylpent-4-enamide (1r):** Following General Procedure D, 4-pentenoic acid (0.5 mL, 4.89 mmol), *n*-butylamine (0.58 mL, 5.85 mmol), Et_3N (1.7 mL, 11.75 mmol), and HATU (2.2 g, 5.85 mmol) in DMF (25 mL) were used, affording the product as pale-yellow oil (623 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.81 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.57 (bs, 1H), 5.19–4.89 (m, 2H), 3.24 (td, *J* = 7.2, 5.6 Hz, 2H), 2.43–2.35 (m, 2H), 2.29–2.12 (m, 2H), 1.46 (m, *J* = 7.4 Hz, 2H), 1.33 (dq, *J* = 14.3, 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 172.2, 137.1, 115.5, 39.2, 35.9, 31.7, 29.7, 20.0, 13.7 ppm. Spectroscopic data for **1r** match those previously reported in the literature.[11]



1s

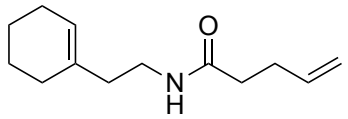
***N*-Benzylpent-4-enamide (1s):** Following General Procedure B, 4-pentenoic acid (2.00 mL, 20.0 mmol), benzylamine (2.143 g, 20.0 mmol), DMAP (244 mg, 2.0 mmol), and EDC-HCl (4.17 g, 22.0 mmol) in DCM (40 mL) were used, affording the product as a white solid (3.36 g, 89% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.38–7.31 (m, 2H), 7.31–7.26 (m, 3H), 5.83 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.74 (s, 1H), 5.07 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.01 (dq, *J* = 10.3, 1.4 Hz, 1H), 4.44 (d, *J* = 5.6 Hz, 2H), 2.43 (dd, *J* = 6.0, 1.1 Hz, 2H), 2.37–2.23 (m, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 172.1, 138.4, 137.1, 128.8, 127.9, 127.6, 115.8, 43.7, 36.0, 29.7 ppm. **HRMS** calcd. for ($C_{12}H_{16}NO$) $[M+H]^+$: 190.1226, found 190.1226.



1t

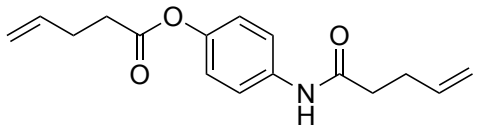
Benzyl 3-(2-(pent-4-enamido)ethyl)-1*H*-indole-1-carboxylate (1t): The indole nitrogen was protected according to known procedure.[12] Benzyl 1*H*-imidazole-1-carboxylate (222 mg, 1.1 mmol) and *N*-(2-(1H-indol-3-yl)ethyl)pent-4-enamide (242 mg, 1.00 mmol)[13] were dissolved in

MeCN (3 mL), and DBU (30 μL, 0.200 mmol) was added. The resulting mixture was stirred at room temperature for 1 h. The reaction was quenched with 1M HCl (10 mL), and the mixture was stirred for 10 min before being extracted with EtOAc (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated. The crude material was then purified by flash silica column chromatography using EtOAc:hexane (1:3) as eluent to afford the product as a white solid (310 mg, 83% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 20.1 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.53–7.30 (m, 8H), 5.77 (ddt, *J* = 16.9, 10.3, 6.5 Hz, 1H), 5.45 (s, 3H), 5.13–4.86 (m, 2H), 3.59 (q, *J* = 6.6 Hz, 2H), 2.90 (t, *J* = 6.8 Hz, 2H), 2.43–2.30 (m, 2H), 2.22 (dd, *J* = 8.2, 6.7 Hz, 2H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 172.6, 137.4, 135.5, 129.2, 128.9, 125.3, 123.4, 123.1, 119.4, 119.1, 116.0, 115.7, 69.1, 39.3, 36.2, 29.9, 25.5 ppm. **HRMS** calcd. For ($C_{23}H_{25}N_2O_3$) $[M+H]^+$: 377.1860, found 377.1862.



1u

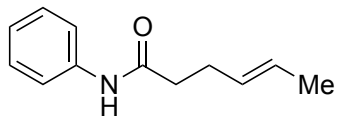
***N*-(2-(Cyclohex-1-en-1-yl)ethyl)pent-4-enamide (1u):** Following General Procedure D, 4-pentenoic acid (0.5 mL, 4.89 mmol), 2-(cyclohex-1-en-1-yl)ethan-1-amine (0.82 mL, 5.85 mmol), Et_3N (1.7 mL, 11.75 mmol), and HATU (2.2 g, 5.85 mmol) in DMF (25 mL) were used, affording the product as pale-yellow semisolid (670 mg, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 5.95–5.68 (m, 1H), 5.45 (s, 2H), 5.10–4.96 (m, 2H), 3.32 (q, *J* = 6.2 Hz, 2H), 2.37 (q, *J* = 7.2 Hz, 2H), 2.25 (t, *J* = 7.4 Hz, 2H), 2.11 (t, *J* = 6.7 Hz, 2H), 1.99 (s, 2H), 1.91 (s, 2H), 1.62 (m, 2H), 1.55 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 172.1, 137.1, 134.6, 123.5, 115.5, 37.6, 37.0, 35.9, 29.6, 27.8, 25.2, 22.8, 22.3 ppm. **HRMS** calcd. for ($C_{13}H_{21}NO$) $[M+H]^+$: 208.1696, found 208.1692.



1v

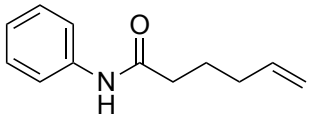
4-(Pent-4-enamido)phenyl pent-4-enoate (1v): Following General Procedure A, 4-pentenoic acid (0.5 mL, 4.89 mmol), 4-aminophenol (545 mg, 5.38 mmol), DMAP (61 mg, 0.48 mmol) and DCC (1.03g, 7.34 mmol) in DCM (15 mL), affording the product as a pale-brown solid (400 mg, 59% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.55–7.36 (m, 2H), 7.23 (bs, 1H), 7.10–6.96 (m, 2H),

5.89 (m, 2H), 5.20–4.95 (m, 4H), 2.65 (t, J = 7.4 Hz, 2H), 2.55–2.39 (m, 6H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 171.7, 170.4, 146.8, 136.8, 136.2, 135.5, 121.9, 120.8, 115.9, 36.7, 33.6, 29.4, 28.8 ppm. **HRMS** calcd. for ($C_{16}H_{20}NO_3$) $[M+H]^+$: 272.1292, found 272.1284.



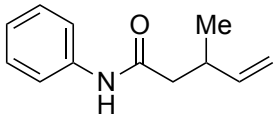
1xa

(*E*)-*N*-Phenylhex-4-enamide (1xa): Following General Procedure A, (*E*)-hex-4-enoic acid (1.14 g, 10.0 mmol), aniline (0.91 mL, 11.1 mmol), DMAP (120 mg, 1.0 mmol), and DCC (2.05 g, 13.35 mmol) in DCM (30 mL) were used, affording the product as a white solid (1.2 g, 63% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.56–7.46 (m, 2H), 7.38–7.25 (m, 2H), 7.21 (s, 1H), 7.10 (t, J = 7.4 Hz, 1H), 5.89 (ddt, J = 16.8, 10.9, 6.0 Hz, 1H), 5.35–4.94 (m, 2H), 2.63–2.37 (m, 4H), 1.66 (d, J = 6.0 Hz 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 170.4, 137.8, 136.9, 129. 0, 124.3, 119.8, 116.0, 36.9, 29.4 ppm. Spectroscopic data for **1xa** match those previously reported in the literature.[2]



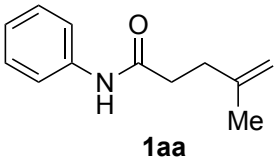
1xb

***N*-Phenylhex-5-enamide (1xb)** Following General Procedure A, 5-pentenoic acid (1.0 g, 8.76 mmol), aniline (0.8 mL, 9.63 mmol), DMAP (106 mg, 0.88 mmol) and DCC (1.80g, 13.14 mmol) in DCM (30 mL) were used, affording the product as a white solid (1.28 g, 77% yield). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.55–7.50 (m, 2H), 7.36–7.28 (m, 2H), 7.16–7.13 (s, 1H), 7.14–7.08 (m, 1H), 5.91–5.69 (m, 1H), 5.18–4.87 (m, 2H), 2.36 (t, J = 7.5 Hz, 2H), 2.16 (q, J = 7.1 Hz, 2H), 1.84 (p, J = 7.4 Hz, 2H) ppm. **^{13}C NMR** (101 MHz, CDCl3) δ = 171.0, 137.8, 129.0, 124.2, 119.7, 115.5, 36.9, 33.0, 24.5 ppm. Spectroscopic data for **1xb** match those previously reported in the literature.[14]



1z

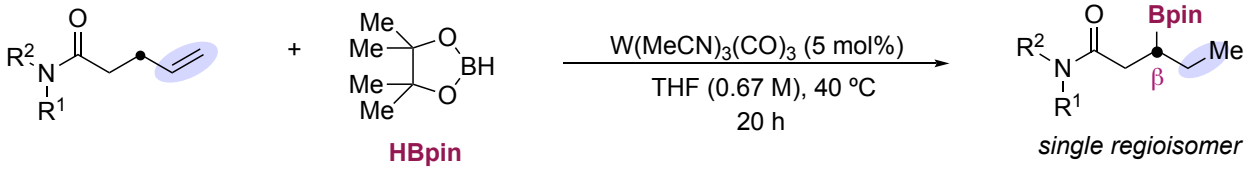
3-Methyl-*N*-phenylpent-4-enamide (1z): Following General Procedure A, 3-methylpent-4-enoic acid (1.0 mL, 8.76 mmol), aniline (0.8 mL, 9.63 mmol), DMAP (106 mg, 0.88 mmol), and DCC (1.80g, 13.14 mmol) in 30 mL of DCM were used, affording the product as a white solid (1.16 g, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.57–7.44 (m, 2H), 7.31 (m, 3H), 7.10 (t, *J* = 7.4 Hz, 1H), 5.84 (ddd, J = 17.3, 10.3, 7.0 Hz, 1H), 5.13–5.12 (m, 2H), 2.80 (q, *J* = 7.0 Hz, 1H), 2.49–2.24 (m, 2H), 1.12 (d, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 167.0, 142.6, 137.8, 129.0, 124.3, 119.9, 113.9, 44.8, 34.8, 19.7 ppm. Spectroscopic data for **1y** match those previously reported in the literature.[9]



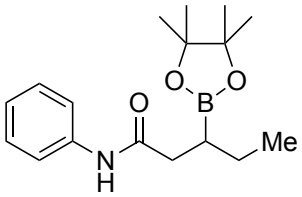
1aa

3-Methyl-*N*-phenylpent-3-enamide (1aa): Following General Procedure D, 4-methylpent-4-enoic acid (250 mg, 2.19 mmol), aniline (0.2 mL, 2.19 mmol), DMAP (106 mg, 0.88 mmol), and HATU (1.083g, 1.85 mmol) in 3 mL of DCM were used, affording the product as a white solid (155 mg, 37% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 2H), 7.32 (t, *J* = 7.9 Hz, 2H), 7.22 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.80 (d, *J* = 23.0 Hz, 2H), 2.52 (m, 2H), 2.45 (m, 2H), 1.79 (s, 3H) ppm**. ^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.60, 147.69, 144.53, 129.16, 124.41, 119.92, 111.05, 35.96, 33.27, 22.67 ppm. Spectroscopic data for **1aa** match those previously reported in the literature.[2]

Catalytic Reactions

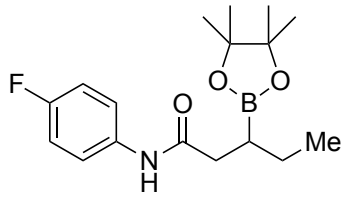


General Procedure E: An oven-dried 8-mL screw-cap test tube containing a Teflon®-coated magnetic stir bar was charged with the alkenyl amide (0.20 mmol). The test tube was introduced into an argon-filled glovebox, where it was further charged with $W(MeCN)_3(CO)_3$ (3.8 mg, 5 mol%) in THF (0.3 mL). Subsequently, HBpin (116 µL, 4 equiv) was added, and the tube was removed from the glovebox and stirred (approximately 800 rpm) at 40 °C for 20 h. After this period of time, the reaction mixture was diluted with EtOAc and transferred to a round-bottom flask. After concentration on a rotavap, the crude material was purified by flash silica column chromatography with a mixture of hexane/EtOAc as eluent.



2a

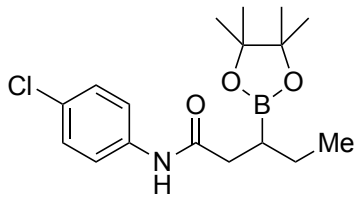
***N*-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (2a):** Following General Procedure E, *N*-(phenyl)pent-4-enamide (**1a**) (35.0 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%), and HBpin (116 µL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (62 mg, 91% yield) by using DCM/MeCN (95/5) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.61 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.06 (t, *J* = 7.4 Hz, 1H), 2.51 (dd, *J* = 14.7, 9.4 Hz, 1H), 2.42 (dd, *J* = 14.7, 5.3 Hz, 1H), 1.52 (ddq, *J* = 39.5, 13.7, 7.0 Hz, 2H), 1.38 (dq, *J* = 9.9, 5.5, 3.9 Hz, 1H), 1.26 (d, *J* = 4.2 Hz, 12H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 171.7, 138.4, 129.0, 123.9, 119.6, 83.5, 39.1, 24.9, 24.9, 24.8, 23.9, 13.4 ppm. **HRMS** calcd. for ($C_{18}H_{27}BNO_3$) $[M+H]^+$: 304.2079, found 304.2078.



2b

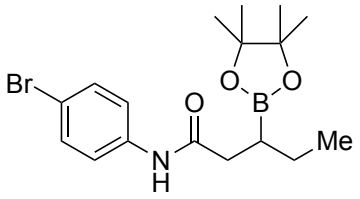
***N*-(4-Fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (2b):** Following General Procedure E, *N*-(4-fluorophenyl)pent-4-enamide (**1b**) (38.6 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (116 µL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (56 mg, 87% yield) by using DCM/MeCN (95/5) as eluent. Single crystals suitable for X-ray diffraction were grown by slow evaporation from a concentrated EtOAc solution. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.61 (s, 1H), 7.45 (dd, *J* = 8.7, 4.8 Hz, 2H), 6.98 (t, *J* =

8.5 Hz, 2H), 2.49 (dd, J = 14.7, 9.5 Hz, 1H), 2.41 (dd, J = 14.7, 5.3 Hz, 1H), 1.54 (dq, J = 14.7, 7.3 Hz, 1H), 1.46 (dq, J = 14.2, 7.2 Hz, 1H), 1.37 (p, J = 6.4, 6.0 Hz, 1H), 1.25 (d, J = 4.8 Hz, 12H) 0.96 (t, J = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 171.1, 158.6 (d, $J_{C–F}$ = 242.7 Hz), 133.8 (d, $J_{C–F}$ = 2.8 Hz), 120.7 (d, $J_{C–F}$ = 7.7 Hz), 115.0 (d, $J_{C–F}$ = 22.5 Hz), 83.0, 38.4, 24.4, 24.3, 23.4, 21.8, 12.8 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = –118.9 ppm. **X-ray** (CCDC 2012996).[16] **HRMS** calcd. for ($C_{18}H_{26}BFNO_3$) $[M+H]^+$: 322.1984, found 322.1984.



2c

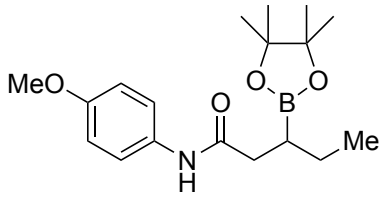
***N*-(4-Chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (2c):** Following General Procedure E, *N*-(4-chlorophenyl)pent-4-enamide (**1c**) (42.0 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (116 μL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (60 mg, 85% yield) by using DCM/MeCN (95/5) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.62 (s, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.25 (s, 2H), 2.52–2.36 (m, 2H), 1.62–1.42 (m, 2H), 1.41–1.33 (m, 1H), 1.25 (d, J = 5.3 Hz, 12H), 0.96 (t, J = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 171.8, 136.9, 129.0, 128.8, 120.8, 83.6, 39.1, 25.0, 24.9, 24.0, 13.3 ppm (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{18}H_{26}BClNO_3$) $[M+H]^+$: 338.1689, found 338.1689.



2d

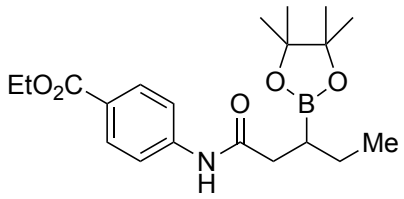
***N*-(4-Bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (2d):** Following General Procedure E, *N*-(4-bromophenyl)pent-4-enamide (**1d**) (50.8 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (116 μL, 4 equiv) were used at 40 ºC affording the title compound as a white solid (62 mg, 81% yield) by using DCM/MeCN (95/5) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.67 (s, 1H), 7.45–7.34 (m, 4H), 2.49 (dd, J = 14.8, 9.5 Hz, 1H), 2.41 (dd, J = 14.8, 5.2 Hz, 1H), 1.60–1.50 (m, 1H), 1.46 (m, J = 14.2, 7.2 Hz, 1H), 1.40–1.33 (m, 1H), 1.25 (d, J = 5.2 Hz, 12H), 0.95 (t, J = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ =

171.8, 137.4, 132.0, 121.1, 116.3, 83.6, 39.1, 24.9, 24.9, 23.9, 22.3, 13.3 ppm. **HRMS** calcd. for ($C_{18}H_{26}BBrNO_3$) $[M+H]^+$: 382.1184, found 382.1183.



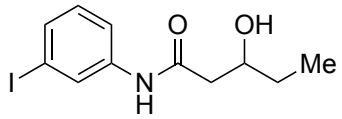
2e

***N*-(4-Methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2e):** Following General Procedure E, *N*-(4-methoxyphenyl)pent-4-enamide (**1e**) (41.0 mg, 0.20 mmol) and HBpin (116 µL, 4 equiv) were used at 40 ºC, affording the title compound as a brown solid (55 mg, 85% yield) by using hexane/EtOAc (70/30) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.51 (bs, 1H), 7.43–7.36 (m, 2H), 6.89–6.77 (m, 2H), 3.77 (s, 3H), 2.53–2.35 (m, 2H), 1.60–1.42 (m, 2H), 1.42–1.35 (m, 1H), 1.25 (s, 12H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 171.4, 156.0, 131.4, 121.3, 114.0, 83.3, 55.4, 38.8, 24.8, 24.7, 23.9, 13.2 ppm. (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{18}H_{29}BNO_4$) $[M+H]^+$: 333.2220, found 333.2224.



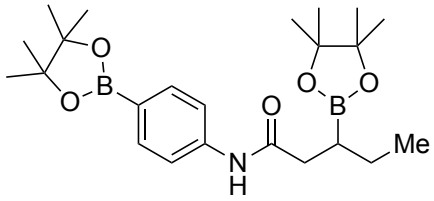
2f

Ethyl 4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamido)benzoate (2f): Following General Procedure E, ethyl 4-(pent-4-enamido)benzoate (**1f**) (50.0 mg, 0.20 mmol) and HBpin (116 µL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (51 mg, 65% yield) by using hexane/EtOAc (75/25) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.08–7.94 (m, 2H), 7.83 (bs, 1H), 7.66–7.52 (m, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.58–2.41 (m, 2H), 1.62–1.43 (m, 2H), 1.42-1.34 (m, 4H), 1.25 (d, *J* = 3.3 Hz, 12H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 171.9, 166.2, 142.4, 130.7, 125.5, 118.4, 83.5, 60.8, 39.1, 24.8, 24.7, 23.8, 14.3, 13.2 ppm. (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{20}H_{31}BNO_5$) $[M+H]^+$: 375.2326, found 375.2324.



2g

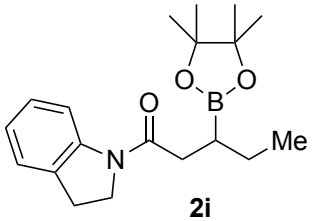
3-Hydroxy-*N*-(3-iodophenyl)pentanamide (2g): Following General Procedure E, *N*-(3-Iodophenyl)pent-4-enamide (**1g**) (60.2 mg, 0.20 mmol) and HBpin (116 µL, 4 equiv) were used at 40 ºC. Prior to isolation, the Bpin group was oxidized to the alcohol upon treatment with H_2O_2 (30 %) (41 µL, 0.400 mmol) in 3 M NaOH (1 mL) and THF (1 mL), affording the title compound as a white powder (48 mg, 75% yield) by using hexane/EtOAc (70/30) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.00 (s, 1H), 7.94 (t, *J* = 2.0 Hz, 1H), 7.51 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 4.05 (qd, *J* = 7.2, 5.9, 2.5 Hz, 1H), 2.58 (dd, *J* = 15.5, 2.6 Hz, 1H), 2.49 (dd, *J* = 15.5, 8.9 Hz, 1H), 2.22–1.69 (s, 1H), 1.69–1.50 (m, *J* = 6.8 Hz, 2H), 1.02 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 170.5, 138.9, 133.4, 130.6, 128.7, 119.2, 94.2, 70.3, 43.6, 30.1, 9.9 ppm. **HRMS** calcd. for ($C_{11}H_{15}INO_2$) $[M+H]^+$: 320.0142, found 320.0141.



2h

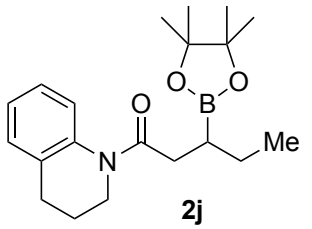
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)hexanamide (2h): Following a modified General Procedure E, *N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pent-4-enamide (**1h**) (60.2 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (145 µL, 5 equiv) were used at 40 ºC for 48 h, affording the title compound as a white solid (58 mg, 65% yield) by using acetone/hexanes (10/90) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 8.2 Hz, 2H), 7.63 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 2H), 2.50 (dd, *J* = 14.7, 9.5 Hz, 1H), 2.43 (dd, *J* = 14.7, 5.3 Hz, 1H), 1.55 (dq, *J* = 14.8, 7.3 Hz, 1H), 1.47 (dp, *J* = 14.1, 7.2 Hz, 1H), 1.43–1.36 (m, 1H), 1.33 (s, 12H), 1.24 (d, *J* = 4.9 Hz, 12H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 171.8, 141.0, 135.9, 118.3, 83.8, 83.6, 39.3, 25.0, 24.8, 24.7, 24.0, 13.3 ppm. (*The carbons attached to boron were not*

observed due to quadrupolar relaxation). **HRMS** calcd. for ($C_{24}H_{38}B_2NO_5$) $[M+H]^+$: 430.2931, found 430.2939.



2i

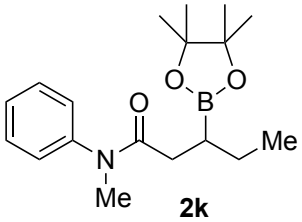
1-(Indolin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (2i): Following General Procedure E, (indolin-1-yl)pent-4-en-1-one (**1i**) (40.2 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (116 μL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (51 mg, 75% yield) by using DCM/MeCN (95/5) as eluent. The same reaction was performed on gram scale (**1i**) (1.05 g, 5 mmol), affording the title compound (1.400 g, 85% yield). Single crystals suitable for X-ray diffraction were grown by slow evaporation from acetone. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 8.6 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.02–6.93 (m, 1H), 4.04 (dtd, *J* = 18.4, 10.1, 8.3 Hz, 2H), 3.17 (t, *J* = 8.5 Hz, 2H), 2.52 (h, *J* = 9.7, 8.9 Hz, 2H), 1.60–1.50 (m, 1H), 1.44 (dp, *J* = 14.4, 7.3 Hz, 1H), 1.37–1.29 (m, 1H), 1.25 (d, *J* = 15.7 Hz, 12H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 171.7, 143.3, 131.0, 127.5, 124.5, 123.3, 117.0, 82.9, 47.8, 38.0, 28.1, 24.9, 24.8, 23.7, 13.7 ppm (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **X-ray** (CCDC 2033217).[16] **HRMS** calcd. for ($C_{19}H_{29}NBO_3$) $[M+H]^+$: 330.2235, found 330.2235.



2j

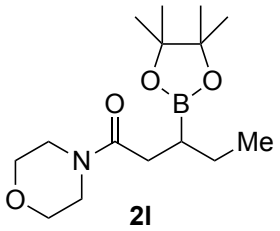
1-(3,4-Dihydroquinolin-1(2*H*)-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one (2j): Following General Procedure E, 1-(dihydroquinolin-1-yl)pent-4-en-1-one (**1i**) (42.2 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (116 μL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (52 mg, 73% yield) by using DCM/MeCN (95/5) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.21–7.00 (m, 4H), 3.82 (dt, *J* = 13.5, 6.7 Hz, 1H), 3.73 (d, *J* = 6.5 Hz, 1H), 2.69 (t, *J* = 6.8 Hz, 2H), 2.61 (qd, *J* = 16.0, 7.6 Hz, 2H), 2.04–1.88 (m, *J* = 6.6 Hz, 2H), 1.45 (dq, *J* = 14.9, 7.5 Hz, 1H), 1.26 (d, *J* = 7.3 Hz, 14H), 0.86 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 173.58, 138.91, 128.51, 128.50, 126.08, 125.08, 124.79, 82.77,

37.12, 26.97, 24.98, 24.94, 24.18, 23.71, 13.63. **HRMS** calcd. for ($C_{20}H_{31}NBO_3$) $[M+H]^+$: 344.2392, found 344.2388.



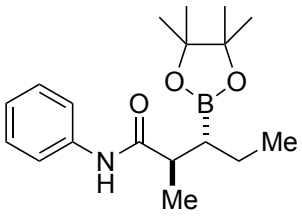
2k

***N*-Methyl-*N*-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2k):** Following General Procedure E, *N*-methyl-*N*-phenylpent-4-enamide (**1k**) (37.9 mg, 0.20 mmol) and HBpin (116 µL, 4 equiv) were used at 40 ºC, affording the title compound as a yellow oil (45.1 mg, 71% yield) by using hexane/EtOAc (90/10) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.38 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 2H), 3.23 (s, 3H), 2.20–2.13 (m, 2H), 1.43–1.32 (m, 1H), 1.25 (d, *J* = 5.5 Hz, 12H), 1.23–1.09 (m, 2H), 0.80 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 173.6, 144.2, 129.5, 127.5, 127.2, 82.6, 37.3, 36.1, 24.8, 24.8, 23.5, 13.4 ppm. (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{18}H_{28}NO_3B$) $[M+H]^+$: 317.2271, found 317.2266.



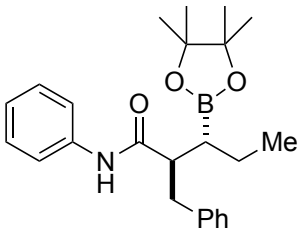
2l

1-Morpholino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one (2l): Following General Procedure E, 1-morpholinopent-4-en-1-one (**1r**) (33.8 mg, 0.20 mmol) and HBpin (116 µL, 4 equiv) were used at 40 ºC, affording the title compound as a colorless oil (35.6 mg, 60% yield) by using hexane/EtOAc (10/90) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 3.69–3.61 (m, 4H), 3.61–3.35 (m, 4H), 2.58–2.30 (m, 2H), 1.57–1.45 (m, 1H), 1.42–1.30 (m, 1H), 1.29–1.17 (m, 13H), 0.93 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 172.5, 82.7, 67.1, 66.7, 45.9, 42.3, 35.0, 25.0, 24.9, 23.8, 13.7 ppm (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{15}H_{28}BNO_4$) $[M+OH]^-$: 313.2175, found 313.2177.



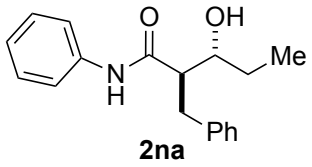
2m

2-Methyl-*N*-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2m): Following General Procedure E, 2-methyl-*N*-phenylpent-4-enamide (**1m**) (37.8 mg, 0.20 mmol) and HBpin (116 μL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (58.8 mg, 93% yield; >20:1 d.r.) by using DCM/MeCN (97.5/2.5) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.88 (bs, 1H), 7.57–7.50 (m, 2H), 7.33–7.27 (m, 2H), 7.18–7.00 (m, 1H), 2.58 (m, 1H), 1.59–1.48 (m, 2H), 1.32–1.18 (m, 16H), 0.95 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 175.2, 138.7, 129.1, 123.8, 119.5, 83.7, 44.1, 25.1, 25.0, 21.9, 17.5, 13.6 ppm (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{18}H_{28}BNO_3$) $[M+H]^+$: 317.2277, found 317.2272.



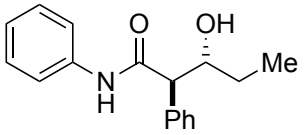
2n

2-Benzyl-*N*-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanamide (2n): Following General Procedure E, 2-benzyl-*N*-phenylpent-4-enamide (**1n**) (53.1 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (116 μL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (66 mg, 81% yield; >20:1 d.r.) by using DCM/MeCN (95/5) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.38–7.18 (m, 10H), 7.06 (t, *J* = 7.3 Hz, 1H), 3.01 (d, *J* = 7.5 Hz, 2H), 2.67 (q, *J* = 7.4 Hz, 1H), 1.65 (p, *J* = 7.3 Hz, 2H), 1.30 (d, *J* = 10.6 Hz, 13H), 1.02 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 173.6, 140.3, 138.1, 129.1, 128.8, 128.6, 126.4, 123.8, 119.7, 83.5, 52.8, 38.4, 25.0, 25.0, 22.2, 13.5 ppm (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{25}H_{35}BNO_3$) $[M+H]^+$: 394.2548, found 394.2550.



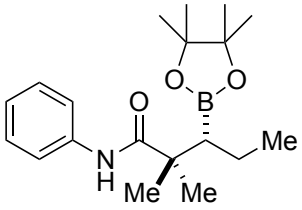
2na

2-Benzyl-3-hydroxy-N-phenylpentanamide (2na): Following General Procedure E, 2-benzyl-*N*-phenylpent-4-enamide (**1n**) (53.1 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (116 μL, 4 equiv) were used at 40 ºC. Prior to isolation, the Bpin group was oxidized to the alcohol upon treatment with H_2O_2 (30 %) (41 μL, 0.400 mmol) in 3 M NaOH (1 mL) and THF (1 mL), affording the title compound as a white powder (39 mg, 69% yield; >20:1 d.r.) by using hexane/EtOAc (70/30) as eluent. Single crystals suitable for X-ray diffraction were grown by slow evaporation from a concentrated acetone solution. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.32 (s, 1H), 7.28–7.12 (m, 9H), 7.03 (t, *J* = 7.2 Hz, 1H), 3.72–3.46 (m, 1H), 3.12 (dd, *J* = 13.4, 8.9 Hz, 1H), 2.97 (dd, *J* = 13.5, 6.7 Hz, 1H), 2.46 (td, *J* = 7.6, 3.5 Hz, 1H), 1.55 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). (*The OH proton could not accurately be identified, likely due to strong H–bonding with the carbonyl oxygen*). **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 173.14, 139.26, 137.28, 129.10, 129.07, 128.87, 126.79, 124.77, 120.56, 73.63, 54.92, 37.09, 29.00, 10.59. **X-ray** (CCDC 2045265).[16] **HRMS** calcd. for ($C_{18}H_{21}NO_2$) $[M+H]^+$: 284.1645, found 284.1645.



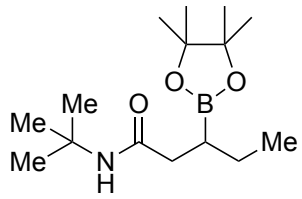
2o

(*Trans*)-3-hydroxy-*N*,2-diphenylpentanamide (2o): Following General Procedure E, 2-phenyl-*N*-phenylpent-4-enamide (**1o**) (60.2 mg, 0.20 mmol) and HBpin (116 μL, 4 equiv) were used at 40 ºC. Prior to isolation, the Bpin group was oxidized to the alcohol upon treatment with H_2O_2 (30 %) (41 μL, 0.400 mmol) in 3 M NaOH (1 mL) and THF (1 mL), affording the title compound as a white powder (41 mg, 76% yield; >20:1 d.r.) by using hexane/EtOAc (70/30) as eluent. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.44–7.27 (m, 8H), 7.22 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 4.20 (tt, *J* = 8.0, 3.6 Hz, 1H), 3.89 (d, *J* = 3.6 Hz, 1H), 3.54 (d, *J* = 8.3 Hz, 1H), 1.42–1.32 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 172.20, 137.42, 137.09, 129.43, 129.14, 128.71, 128.14, 124.86, 120.27, 74.69, 59.73, 27.20, 9.87 ppm. **HRMS** calcd. For ($C_{17}H_{20}NO_2$) $[M+H]^+$: 252.1383, found 252.1383.



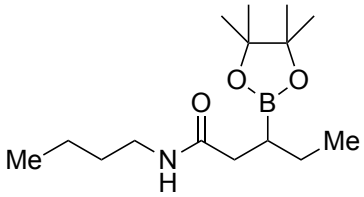
2p

2,2-Dimethyl-*N*-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2p): Following General Procedure E, 2,2-dimethyl-*N*-phenylpent-4-enamide (**1p**) (40.6 mg, 0.20 mmol) and HBpin (116 μL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (38 mg, 57% yield) by using hexane/EtOAc (80/20) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.37 (bs, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 1.53–1.41 (m, 2H), 1.32 (d, *J* = 1.9 Hz, 12H), 1.29 (bs, 3H), 1.30–1.17 (m, 3H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 176.2, 138.8, 128.8, 123.6, 119.5, 83.8, 44.9, 26.5, 25.7, 25.0, 24.9, 20.5, 14.5 ppm. (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{19}H_{30}BNO_3Na$) $[M+Na]^+$: 353.2247, found 353.2248.



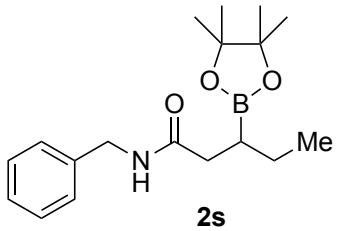
2q

***N*-(*tert*-Butyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2q):** Following General Procedure E, *N*-(*tert*-butyl)pent-4-enamide (**1q**) (31.0 mg, 0.20 mmol) and HBpin (116 μL, 4 equiv) were used at 40 ºC, affording the title compound as a white powder (51 mg, 91% yield) by using hexane/EtOAc (90/10) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.47 (s, 1H), 2.15–2.12 (m, 2H), 1.50–1.37 (m, 2H), 1.36–1.32 (m, 1H), 1.30 (s, 9H), 1.23 (d, *J* = 2.7 Hz, 12H), 0.90 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 172.6, 83.0, 50.9, 38.7, 28.8, 24.8, 24.7, 23.7, 13.3 ppm. (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{15}H_{30}NO_3B$) $[M+H]^+$: 283.2428, found 283.2427.



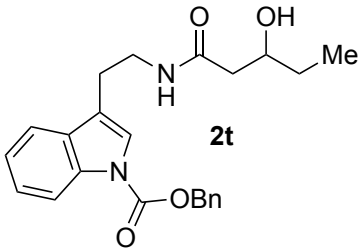
2r

***N*-Butyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2r):** Following General Procedure E, *N*-butylpent-4-enamide (**1r**) (31.0 mg, 0.20 mmol) and HBpin (116 µL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (29 mg, 51% yield) by using hexane/EtOAc (90/10) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.59 (s, 1H), 3.31–3.18 (m, 2H), 2.40–2.17 (m, 2H), 1.54–1.39 (m, 4H), 1.39–1.30 (m, 2H), 1.30–1.28 (m, 1H), 1.25 (d, *J* = 2.4 Hz, 12H), 0.97–0.89 (m, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 173.1, 83.1, 39.2, 38.0, 31.8, 24.8, 24.8, 23.8, 20.1, 13.7, 13.3 ppm. (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{15}H_{31}BNO_3$) $[M+H]^+$: 283.2428, found 283.2434.



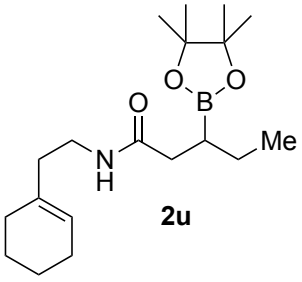
2s

***N*-Benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2s):** Following General Procedure E, *N*-benzylbut-3-enamide (**1s**) (35 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (116 µL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (52 mg, 82% yield) by using EtOAc/hexanes (85/15) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.49–7.22 (m, 5H), 6.01 (s, 1H), 4.51–4.37 (m, 2H), 2.47–2.25 (m, 2H), 1.50 (ddq, *J* = 41.4, 13.7, 7.1 Hz, 2H), 1.38–1.32 (m, 1H), 1.31–1.15 (m, 12H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 173.2, 138.64, 128.7, 128.0, 127.5, 83.3, 43.7, 37.9, 24.8, 24.8, 24.0, 13.4 ppm (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{18}H_{29}NBO_3$) $[M+H]^+$: 318.2235, found 318.2234.



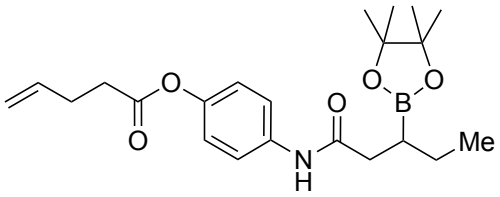
2t

Benzyl 3-(2-(3-hydroxypentanamido)ethyl)-1*H*-indole-1-carboxylate (2t): Following General Procedure E, benzyl 3-(2-(pent-4-enamido)ethyl)-1*H*-indole-1-carboxylate (**1t**) (78 mg, 0.20 mmol) and HBpin (116 μL, 4 equiv) were used at 40 ºC. Prior to isolation, the Bpin group was oxidized to the alcohol upon treatment with H_2O_2 (30 %) (41 μL, 0.400 mmol) in 3 M NaOH (1 mL) and THF (1 mL), affording the title compound as a white powder (65 mg, 80% yield) by using hexane/EtOAc (70/30) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.18 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 4H), 7.45–7.37 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 5.84 (s, 1H), 5.45 (s, 2H), 3.87 (qd, *J* = 5.8, 2.8 Hz, 1H), 3.60 (hept, *J* = 6.8 Hz, 2H), 3.39 (d, *J* = 3.4 Hz, 1H), 2.92 (t, *J* = 6.8 Hz, 2H), 2.30 (dd, *J* = 15.3, 2.6 Hz, 1H), 2.20 (dd, *J* = 15.3, 9.2 Hz, 1H), 1.54–1.38 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 172.6, 134.9, 129.0, 128.9, 128.7, 125.1, 123.2, 119.1, 118.7, 115.6, 70.1, 42.2, 39.0, 29.9, 25.2, 9.9 ppm. **HRMS** calcd. For ($C_{23}H_{27}N_2O_4$) $[M+H]^+$: 395.1965, found 395.1920.



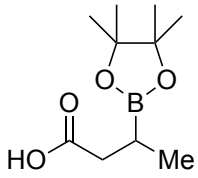
2u

***N*-(2-(Cyclohex-1-en-1-yl)ethyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamide (2u):** Following General Procedure E, *N*-(2-(cyclohex-1-en-1-yl)ethyl)pent-4-enamide (**1u**) (41.4 mg, 0.20 mmol) and HBpin (116 μL, 4 equiv) were used at 40 ºC, affording the title compound as a colorless oil (34 mg, 50% yield) by using hexane/EtOAc (90/10) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 5.51 (bs, 1H), 5.45 (bs, 1H), 3.30 (m, 2H), 2.35–2.16 (m, 2H), 2.10 (t, *J* = 6.8 Hz, 2H), 2.02–1.95 (m, 2H), 1.93–1.88 (m, *J* = 5.7 Hz, 2H), 1.65–1.59 (m, 1H), 1.58–1.50 (m, 2H), 1.50–1.35 (m, 2H), 1.24 (d, *J* = 3.3 Hz, 12H), 0.91 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 173.0, 134.7, 123.3, 83.1, 37.9, 37.7, 37.1, 27.9, 25.2, 24.8, 24.8, 23.7, 22.8, 22.3, 13.3 ppm. (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{19}H_{33}BNO_3$) $[M+H]^+$: 333.2595, found 333.2604.



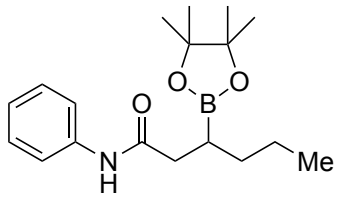
2v

4-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pentanamido)phenyl pent-4-enoate (2v): Following General Procedure E, 4-(pent-4-enamido)phenyl pent-4-enoate (**1v**) (54.6 mg, 0.20 mmol) and HBpin (116 µL, 4 equiv) were used at 40 ºC, affording the title compound as a white solid (42 mg, 52% yield) by using hexane/EtOAc (75/25) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.64 (bs, 1H), 7.57–7.39 (m, 2H), 7.08–6.85 (m, 2H), 5.98–5.81 (m, 1H), 5.21–5.01 (m, 2H), 2.64 (td, *J* = 7.3, 0.9 Hz, 2H), 2.55–2.41 (m, 4H), 1.68-1.35 (m, 2H), 1.41–1.31 (m, 1H), 1.25 (d, *J* = 3.1 Hz, 12H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 171.7, 171.5, 146.5, 136.3, 135.9, 121.8, 120.3, 115.9, 83.4, 38.9, 33.6, 28.8, 24.8, 24.7, 23.8, 13.2 ppm (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{22}H_{33}BNO_5$) $[M+H]^+$: 401.2483, found 401.2483.



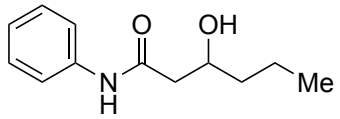
2w

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butanoic acid (2w): Following General Procedure E, vinyl acetic acid (17 µL, 0.20 mmol), $W(CO)_3(MeCN)_3$ (4 mg, 5 mol%) and HBpin (116 µL, 4 equiv) were used at 40 °C, affording the title compound as a white solid (32 mg, 75% yield) by filtering the crude reaction through celite followed by evaporation of the solvent and overnight vacuum at ~0.1 mtorr. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 2.43 (qd, *J* = 16.8, 7.1 Hz, 2H), 1.40–1.31 (m, 1H), 1.25–1.18 (m, 12H), 1.00 (d, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 178.2, 83.4, 37.4, 24.8, 15.1 ppm. (*The carbon attached to boron was not observed due to quadrupolar relaxation*). The desired product **2w** is a known compound and our data matched the published spectra.[15]



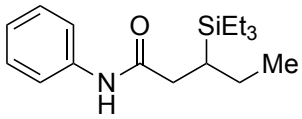
2x

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-phenylhexanamide (2x): Following a modified General Procedure E, *N*-phenylhex-5-enamide (**1xb**) (37.9 mg, 0.200 mmol), B_2Pin_2 (76 mg, 1.5 equiv), CsF (30.4 mg, 1 equiv), PCy_3 (8.0 mg, 0.15 equiv), and CuF_2 (5.7 mg, 0.25 equiv) were used at 100 ºC in 2-Me-THF (1.0 mL) and 2-propanol (31 µL, 2 equiv), affording the title compound as a white solid (26 mg, 41% yield) by using hexane/EtOAc (80/20) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.55–7.43 (m, 3H), 7.34–7.27 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 2.54–2.38 (m, 2H), 1.53–1.43 (m, 2H), 1.38 (q, *J* = 6.6, 4.9 Hz, 3H), 1.26 (d, *J* = 4.4 Hz, 12H), 0.91 (t, *J* = 7.1 Hz, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ = 171.1, 137.8, 128.5, 123.4, 118.9, 82.9, 38.8, 32.6, 24.4, 24.3, 21.5, 13.8 ppm. Spectroscopic data for **2x** match those previously reported in the literature.[12]



2xa

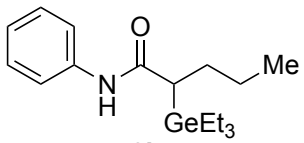
3-Hydroxy-*N*-phenylhexanamide (2xa): Following General Procedure E, (*E*)-*N*-phenylhex-4-enamide (**1xa**) (39.0 mg, 0.20 mmol) and HBpin (116 µL, 4 equiv) were used at 40 ºC. Prior to isolation, the Bpin group was oxidized to the alcohol upon treatment with H_2O_2 (30 %) (41 µL, 0.400 mmol) in 3 M NaOH (1 mL) and THF (1 mL), affording the title compound as a white powder (21 mg, 50% yield) by using hexane/EtOAc (70/30) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.77 (s, 1H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.33 (t, *J* = 7.9 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 4.12 (td, *J* = 7.7, 3.2 Hz, 1H), 2.62–2.37 (m, 2H), 2.03 (s, 1H), 1.63–1.41 (m, 4H), 0.96 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 170.4, 137.6, 129.0, 124.4, 120.0, 68.5, 43.9, 39.1, 18.7, 13.9 ppm. Spectroscopic data for **2xa** match those previously reported in the literature.[12]



3a

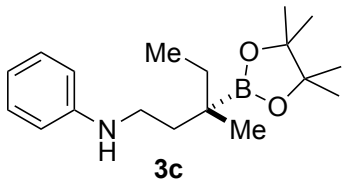
3-Triethylsilyl-*N*-phenylpent-4-enamide (3a): Following a modified General Procedure E, *N*-phenylpent-4-enamide (**1a**) (35.0 mg, 0.20 mmol), B_2Pin_2 (76 mg, 1.5 equiv), CsF (30.4 mg, 1

equiv), and CuF_2 (11.2 mg, 0.5 equiv) were used at 100 ºC in 2-Me-THF (1.0 mL), affording the title compound as a white powder (52 mg, 89% yield) by using hexane/EtOAc (80/20) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.52 (d, *J* = 7.8 Hz, 2H), 7.34–7.24 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 2.44 (dd, *J* = 15.0, 3.8 Hz, 1H), 2.28–2.14 (m, 1H), 1.64–1.54 (m, 1H), 1.47–1.37 (m, 2H), 0.97 (t, *J* = 7.9 Hz, 12H), 0.59 (q, *J* = 7.9 Hz, 6H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 172.0, 138.1, 128.9, 124.1, 119.7, 38.4, 23.5, 21.6, 14.0, 7.7, 2.7 ppm. **HRMS** calcd. for ($C_{17}H_{29}NO_2Si$) $[M-H]^-$: 290.1946, found 290.1942.



3b

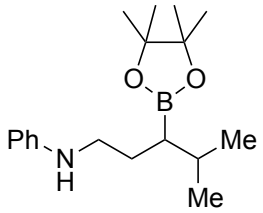
***N*-Phenyl-2-(triethylgermyl)pentanamide (3b):** Following a modified General Procedure E, *N*-(phenyl)pent-4-enamide (**1a**) (35.0 mg, 0.20 mmol) and $HGeEt_3$ (65 µL, 2 equiv) were used at 40 ºC in THF (0.3 mL), affording the title compound as a white powder (18 mg, 27% yield) by using hexane/EtOAc (90/10) as eluent. Single crystals suitable for X-ray diffraction were grown by slow evaporation from an acetone solution. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 8.0 Hz, 2H), 7.36–7.30 (m, 2H), 7.09 (s, 1H), 6.89 (s, 1H), 2.14–1.93 (m, 3H), 1.57–1.49 (m, 1H), 1.44 (dddd, *J* = 12.7, 10.0, 5.7, 2.1 Hz, 1H), 1.09 (t, *J* = 7.9 Hz, 9H), 1.00–0.87 (m, 9H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 169.3, 138.5, 129.1, 123.8, 119.7, 38.1, 30.1, 23.7, 14.1, 9.1, 3.9 ppm. **X-ray** (CCDC 2035216).[16] **HRMS** calcd. for ($C_{17}H_{29}NO_2Ge$) $[M+H]^+$: 338.1534, found 338.1530.



3c

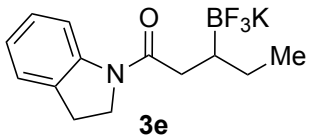
***N*-(3-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)aniline (3c):** Following a modified General Procedure E, 3-methyl-*N*-phenylpent-4-enamide (**1y**) (39.0 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (6 mg, 7.5 mol%) and HBpin (230 µL, 8 equiv) were used at 100 ºC, affording the title compound as a brown oil (24 mg, 40% yield) by using hexane/EtOAc (80/20) as eluent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.22–7.12 (m, 2H), 6.69 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 2H), 3.10 (ddd, *J* = 8.7, 6.4, 2.1 Hz, 2H), 1.77 (ddd, *J* = 13.2, 8.9, 6.9 Hz, 2H), 1.54–1.41 (m, 2H), 1.31 (dd, *J* = 13.6, 7.5 Hz, 1H), 1.24 (d, *J* = 3.4 Hz, 12H), 0.96 (s, 3H), 0.87 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 129.2, 117.3, 113.1, 41.5, 38.1, 31.8, 24.9, 24.8, 24.6, 21.0,

9.8 ppm (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{18}H_{31}BNO_2$) $[M+H]^+$: 303.2484, found 303.2474.



3d

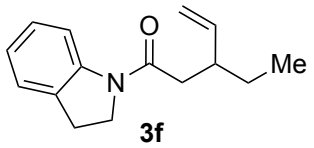
***N*-(4-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)aniline (3d):** Following a modified General Procedure E, 4-methyl-*N*-phenylpent-4-enamide (**1aa**) (39.0 mg, 0.20 mmol), $W(CO)_3(MeCN)_3$ (6 mg, 7.5 mol%) and HBpin (230 μL, 8 equiv) were used at 100 ºC, affording the title compound as a white solid (27 mg, 46% yield) by using hexane/EtOAc (80/20) as eluent. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.20–7.12 (m, 2H), 6.73–6.64 (m, 1H), 6.62–6.57 (m, 2H), 4.17–3.46 (s, 1H), 3.16–2.95 (m, 2H), 1.82–1.58 (m, 3H), 1.26 (d, *J* = 5.3 Hz, 12H), 0.95 (d, *J* = 3.1 Hz, 3H), 0.94 (d, *J* = 3.1 Hz, 3H), 0.82 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.76, 129.30, 117.05, 112.84, 83.23, 44.43, 29.92, 28.99, 25.12, 25.10, 22.29, 21.77. **HRMS** calcd. For ($C_{18}H_{31}BNO_2$) $[M+H]^+$: 303.2484, found 303.2495.



3e

(Indolin-1-yl)-3-(trifluoro-l4-boraneyl)pentan-1-one, potassium salt (3e): The title compound was prepared following a modified literature procedure.[11] To a solution of 1-(indolin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one (**2i**) (150 mg, 0.46 mmol) in MeCN (2 mL) under nitrogen, was added saturated aq. KHF_2 (142 mg, 1.82 mmol, 0.4 mL). The resulting solution was stirred at ambient temperature for 2 h, before being concentrated and azeotroped with MeOH with a rotavap. The crude product was placed under high vacuum overnight, extracted with hot MeCN (3 × 10 mL), filtered, and concentrated with a rotavap. The resulting residue was taken up in Et_2O (2 mL) and sonicated for 30 min, before being filtered to afford the title compound as a white solid (123 mg, 87% yield). **^{1}H NMR** (600 MHz, d_6-DMSO) δ = 8.08 (d, *J* = 8.1 Hz, 1H), 7.18 (d, *J* = 7.4 Hz, 1H), 7.15–7.00 (m, 1H), 6.98–6.86 (m, 1H), 4.24–3.94 (m, 2H), 3.25–2.96 (m,

2H), 2.43–2.28 (m, 1H), 2.10–1.75 (m, 1H), 1.39–1.01 (m, 2H), 0.80 (t, J = 7.5 Hz, 3H), 0.63–0.49 (m, 1H) ppm. **^{13}C NMR** (151 MHz, d_6-DMSO) δ = 174.6, 143.7, 131.6, 126.7, 124.5, 122.3, 115.9, 47.7, 38.0, 27.5, 23.9, 13.8 ppm. (*The carbon attached to boron was not observed due to quadrupolar relaxation*). **HRMS** calcd. for ($C_{13}H_{16}BF_3KNO$) $[M-K]^-$: 269.1313, found 269.1308



3f

3-Ethyl-1-(indolin-1-yl)pent-4-en-1-one (3f): The title compound was prepared following a modified literature procedure.[12] To a solution of 1-(indolin-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one (**3f**) (50.0 mg, 0.15 mmol) in THF (1.5 mL), was added vinylmagnesium bromide (0.87 mL, 0.7 M, 0.61 mmol) dropwise, and the reaction was stirred at ambient temperature for 30 min. The reaction mixture was then cooled to –78 ºC, before a solution of iodine (155 mg, 0.61 mmol) in MeOH (2.0 mL) was added dropwise. The mixture was stirred at –78 ºC for a further 30 min, before a solution of NaOMe (64.8 mg, 1.2 mmol) in MeOH (2.5 mL) was added dropwise. The solution was warmed to ambient temperature and stirred for another 1.5 h, before being diluted with pentane (10 mL) and washed with saturated aq. $Na_2S_2O_3$ (5 mL) and brine (5 mL). The organic extracts were combined, dried over Na_2SO_4, and concentrated in *vacuo*. Purification of the crude residue by flash silica column chromatography with hexane/EtOAc (90/10) as eluent afforded the title compound as an orange oil (33.5 mg, 96%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 8.25 (d, J = 8.1 Hz, 1H), 7.21–7.10 (m, 2H), 7.07–6.93 (m, 1H), 5.81–5.63 (m, 1H), 5.15–4.95 (m, 2H), 4.16–3.95 (m, 2H), 3.26–3.07 (m, 2H), 2.78–2.33 (m, 3H), 1.71–1.32 (m, 2H), 0.95–0.85 (m, 3H) ppm. **^{13}C NMR** (151 MHz, $CDCl_3$) δ = 170.4, 143.2, 141.4, 131.2, 127.6, 124.6, 123.6, 117.3, 115.2, 48.3, 41.6, 41.2, 28.1, 27.5, 11.7 ppm. **HRMS** calcd. for ($C_{15}H_{19}NO$) $[M+H]^+$: 230.1545, found 230.1541.

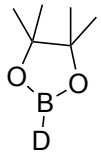
DETERMINATION OF DEUTERIUM INCORPORATION

Deuterium Labeling Procedure: DBpin was synthesized according to a known procedure by Morken, which yielded 81% D-incorporation in Morken's prior study.[17] In a 6-mL vial equipped with magnetic stir bar, a 1 M solution of borane-*d*$_3$•THF complex (1 mL, 1.00 mmol) was added under argon at 0 °C, then freshly sublimed pinacol (118 mg, 1.00 mmol) was added. The reaction mixture was stirred, and when gas evolution slowed, the reaction was allowed to warm up to room

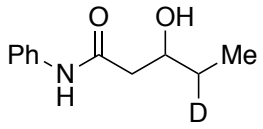
temperature overnight. The solution of deuterated pinacol borane was immediately used directly without further purification.

The sublimed pinacol was directly moved into the glovebox and dissolved in THF. 4Å molecular sieves were added to the solution and allowed to sit overnight. The solution was then filtered to remove the sieves and the THF evaporated. The dried pinacol was then directly used for the preparation of DBpin. ^{11}B NMR was used to determine the purity of the DBpin. The sample was prepared by adding 0.2 mL the DBpin THF solution and diluted out an additional 0.2 mL of d8-THF. The sample was then analyzed in a quartz NMR tube with the purity determined to be 84% by ^{11}B NMR (Note: the 84% purity includes HBpin impurities as they have the same chemical shift).

Inside an argon-filled glovebox, a 6-mL vial containing freshly prepared DBpin (1 mL, 1 M solution, 5 equiv) was charged with $W(MeCN)_3(CO)_3$ (7.8 mg, 0.02 mmol) and the alkene of interest (0.2 mmol) with care taken to ensure that the solids on the wall were washed into the bottom of the tube. The vial was removed from the glovebox and placed in a preheated oil bath (40 °C) and allowed to heat for 20 h. The vial was then cooled to 0 °C, and oxidation to the alcohol was performed by adding NaOH (1 mL, 1M) and H_2O_2 (82 μL, 0.8 mmol). The reaction was allowed to warm up to room temperature and stir for 3 h. The crude reaction mixture was diluted with acetone and filtered through a plug of celite and evaporated to dryness. The crude material was purified by flash silica column chromatography using 20% acetone:hexanes, and the purified product was analyzed by ^{1}H NMR to determine the site(s) and extent of deuterium incorporation. All compounds were analyzed by quantitative ^{1}H NMR using standard protocols outlined by Bruker, and the integral values below are reported as their relative quantities. d_6-DMSO was used as the solvent of choice, as the water and grease chemical shifts in these solvents did not overlap with the peaks of interest in the compound being analyzed. ^{13}C NMR spectral data for the corresponding non-deuterated products are given above.

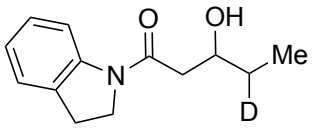


(DBpin) ^{11}B NMR (160 MHz, THF) δ 29.89 – 25.97 (m, 0.84), 22.18 (s, 0.16, impurity).



2a-*d*

(2a-*d*) ^{1}H NMR (600 MHz, d_6-DMSO) δ = 9.84 (s, 0.95H), 7.68–7.52 (m, 1.94H), 7.28 (t, *J* = 7.9 Hz, 1.92H), 7.02 (t, *J* = 7.4 Hz, 1.04H), 4.69 (dd, *J* = 5.2, 3.0 Hz, 0.99H), 3.85 (t, *J* = 5.9 Hz, 1.00H), 2.38 (d, *J* = 6.5 Hz, 1.92H), 1.53–1.30 (m, 1.34H), 0.89 (dd, *J* = 9.0, 7.4 Hz, 3.02H).



2i-*d*

(2i-*d*) ^{1}H NMR (600 MHz, d_6-DMSO) δ = 8.09 (d, *J* = 8.1 Hz, 0.90H), 7.21 (d, *J* = 7.4 Hz, 1.02H), 7.13 (t, *J* = 7.8 Hz, 0.95H), 7.01–6.94 (m, 0.95H), 4.63 (dd, *J* = 5.1, 3.1 Hz, 1.04H), 4.20–4.03 (m, 2.00H), 3.89 (td, *J* = 7.4, 3.6 Hz, 1.04H), 3.11 (t, *J* = 8.6 Hz, 1.85H), 2.54–2.42 (m, 4.09H), 1.55–1.34 (m, 1.33H), 0.94–0.85 (m, 3.23H).

DETERMINATION OF ENANTIOMERIC EXCESS

(*rac*)-1m was separated on preparative scale using SFC.

Method. The samples were analyzed on a Waters UPC2 SFC with a Daicel IG column (3 μm, 4.6×250 mm) under isocratic conditions (4 mL/min, 5% MeOH / CO_2, 1600 psi backpressure) at 30 °C. The enantiomers were detected by UV light (260 nm).

Figure S1. Chromatogram for preptartive separation of **(*rac*)-1m** by SFC.

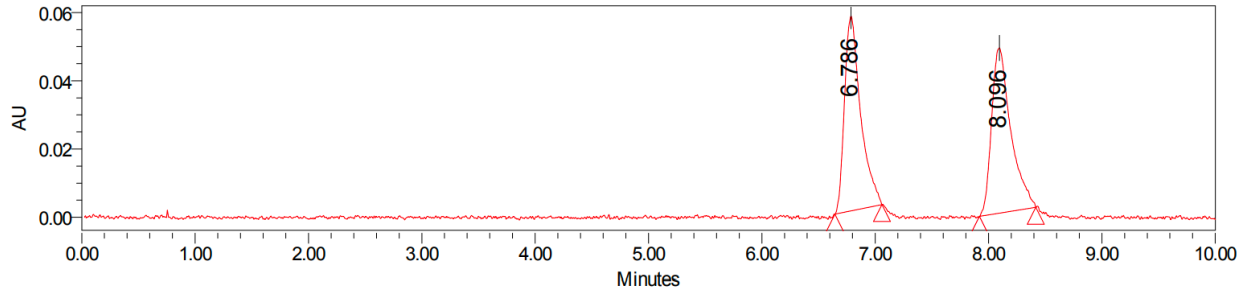
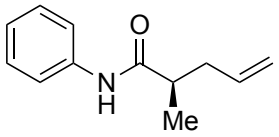
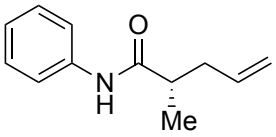


Table S11. Integrations from preprative SFC separation of **(*rac*)-1m**

Peak	Retention time	Area
Ent2 (1.777)	6.786	565455
Ent1 (2.003)	8.096	571661



(*Ent2*)-1m



(*Ent1*)-1m

Figure S2. Chromatogram of *ee* measurement for peak from ***(Ent2)*-1m**

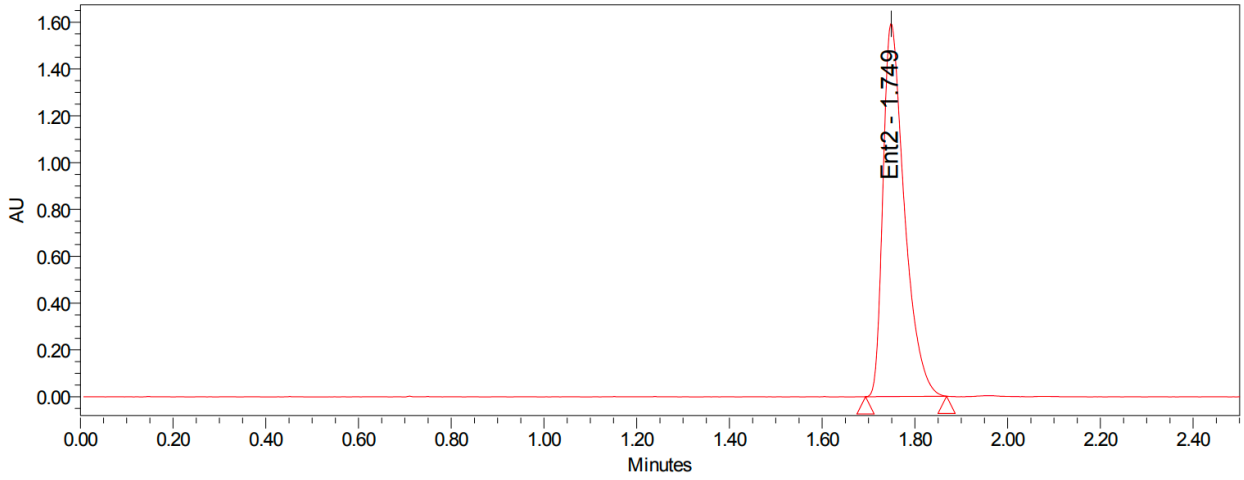


Figure S3. Chromatogram of *ee* measurement for peak from ***(Ent1)*-1m**

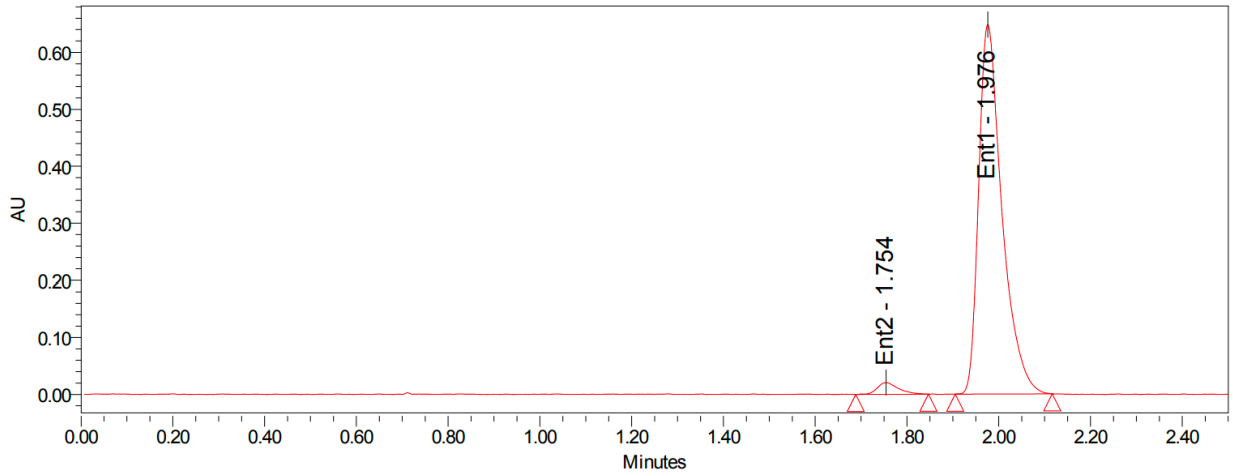
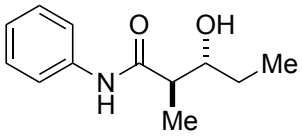


Table S12. Determination of *ee* for **(*rac*)-1m** sample

Sample	Area% *Ent2*	Area% *Ent1*	*ee*	Area *Ent2*	Area *Ent1*
Ent2 (Figure S2)	100	-	100	5116190	-
Ent1 (Figure S3)	2.81	97.19	94.37	66154	2284637



(*rac*)-2m

Figure S4. Chromatogram of *ee* measurement for ***(rac)*-2m**

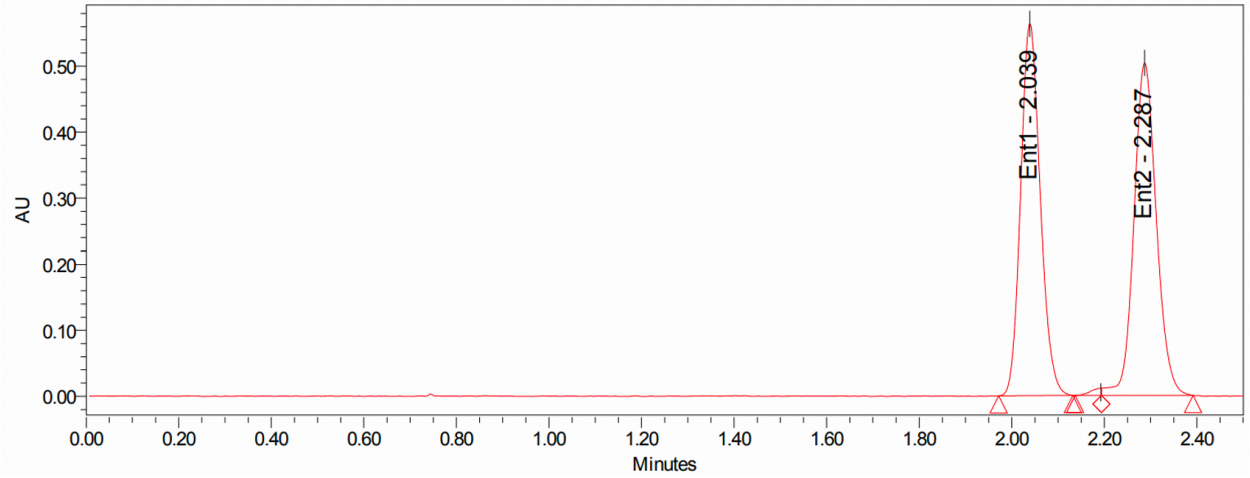


Table S13. Determination of *ee* for **(*rac*)-2m** sample

Sample	Area% *Ent1*	Area% *Ent2*	*ee*	Area *Ent1*	Area *Ent2*
(rac)-2m	49.44	50.56	-1.13	1659281	1697180

Figure S5. Chromatogram of *ee* measurement for ***(Ent2)*-2m**

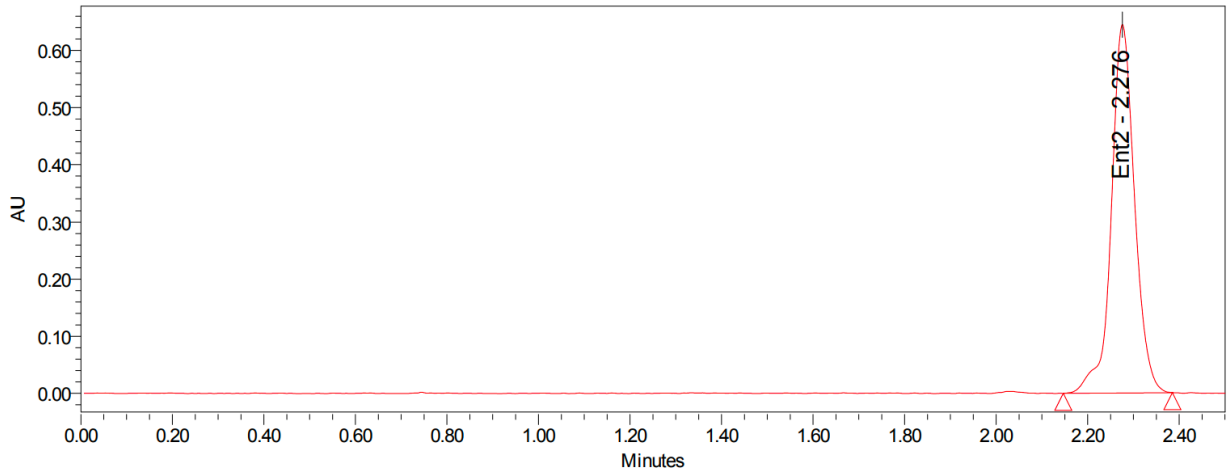


Table S14. Determination of *ee* for **(*rac*)-2m** sample

Sample	Area% *Ent1*	Area% *Ent2*	*ee*	Area *Ent1*	Area *Ent2*
(Ent)-2m	-	100	100	-	2279170

IN SITU MONITORING OF REACTIONS BY ^{1}H NMR

General Procedure F: A J. Young NMR tube containing the alkenyl amide (0.10 mmol) was introduced in an argon-filled glovebox, where it was further charged with $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%) and *d8*-THF (0.5 mL). For reaction (1) no HBpin was added, for reaction (2) HBpin (58 µL, 4 equiv) was added, and the tube was removed from the glovebox and shaken vigorously until completely homogeneous. The sample was then placed in the NMR and heated to 40 °C. After the temperature was reached, ^{1}H spectra were collected every 15 min for 3 h. The time from all reagents added to collection of the first time point was 30 minutes.

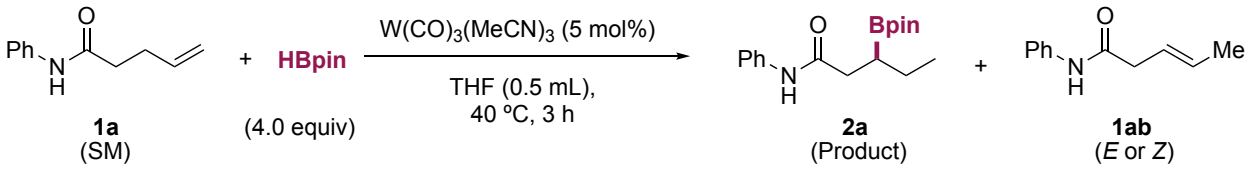
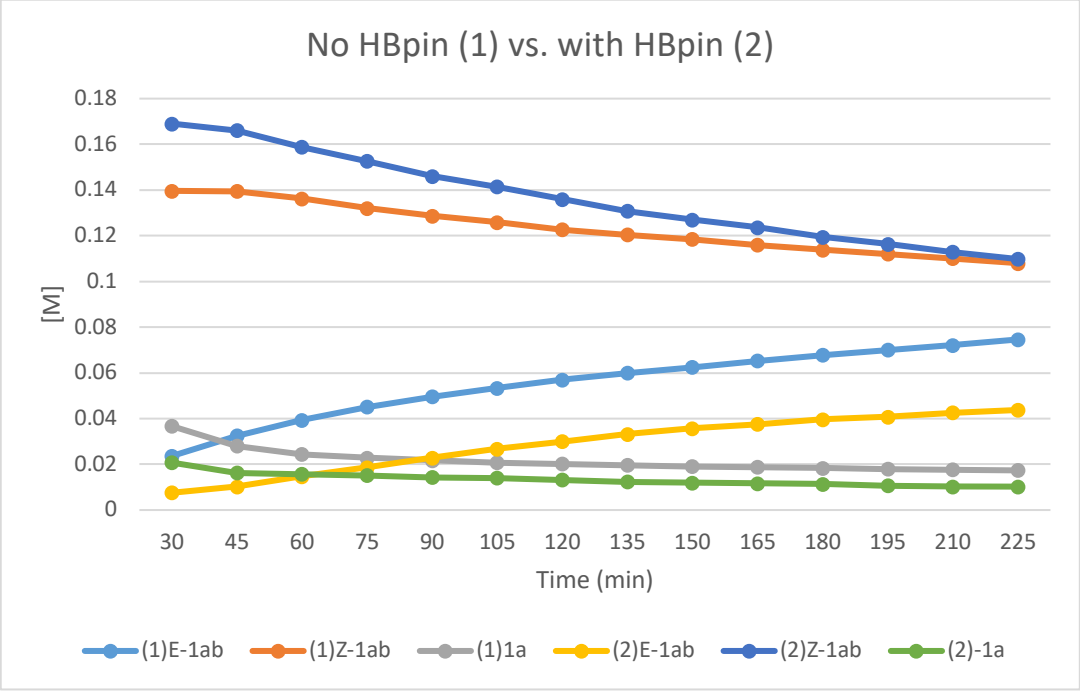


Figure S6. Time point analysis from the catalytic reactions run using General Procedure F without HBpin (1) and with HBpin (2).



X-RAY CRYSTALLOGRAPHY

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker APEX II ultra CCD diffractometer equipped with Mo K_α radiation (λ = 0.71073). Crystals of the subject compound were used as received (grown from Acetone/Ether). A 0.175 x 0.150 x 0.120 mm colorless block was mounted on a Cryoloop with Paratone oil.

Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 45 mm using exposure time 5.0s (depending on the detector 2θ position) with a scan width of 0.80°. Data collection was 100.00% complete to 25.242° in A total of 13436 reflections were collected covering the indices, -8<=h<=8, -14<=k<=14, -14<=l<=14. 3277 reflections were found to be symmetry independent, with a R_{int} of 0.0491. Indexing and unit cell refinement indicated a **Primitive**, **Triclinic** lattice. The space group was found to be ***P* -1**. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Crystallographic data are summarized in Table S15.

Notes: Excellent data and model refinement.

Note: “racemic” space group

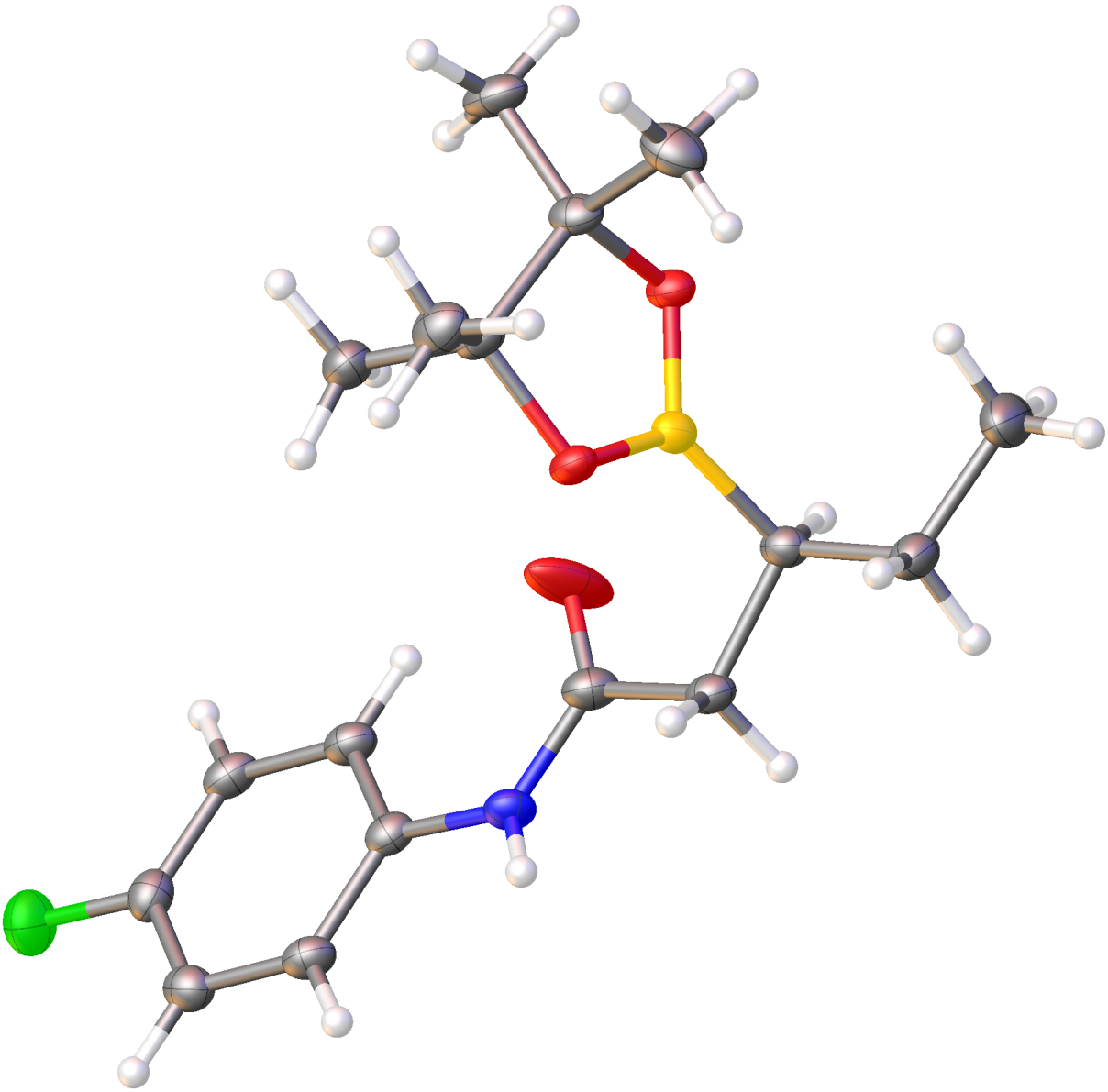


Table S15. Crystal data and structure refinement for **2b**.

Report date	2020-06-29	
Empirical formula	C17 H25 B F N O3	
Molecular formula	C17 H25 B F N O3	
Formula weight	321.19	
Temperature	100.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.650(4) Å	α= 71.589(13)°.
	b = 11.516(6) Å	β= 79.394(14)°.
	c = 12.213(6) Å	γ = 79.986(14)°.
Volume	865.5(8) $Å^3$	
Z	2	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	344	
Crystal size	0.22 x 0.18 x 0.035 mm^3	
Crystal color, habit	colorless plate	
Theta range for data collection	1.774 to 25.675°.	
Index ranges	-8<=h<=8, -14<=k<=14, -14<=l<=14	
Reflections collected	13436	
Independent reflections	3277 [R(int) = 0.0491]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5624 and 0.4744	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3277 / 1 / 216	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.0886	
R indices (all data)	R1 = 0.0643, wR2 = 0.0995	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.211 and -0.206 $e.Å^{-3}$	

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	12756(2)	654(1)	9880(1)	32(1)
O(1)	6846(2)	4804(1)	6644(1)	56(1)
O(2)	5170(2)	7651(1)	7101(1)	21(1)
O(3)	2473(2)	6982(1)	6653(1)	20(1)
N(1)	10178(2)	4971(1)	6632(1)	21(1)
C(1)	3652(3)	8739(2)	3812(2)	41(1)
C(2)	5768(3)	8351(2)	4223(2)	27(1)
C(3)	5896(2)	7112(2)	5176(1)	21(1)
C(4)	8125(2)	6664(2)	5416(1)	21(1)
C(5)	8302(2)	5399(2)	6286(2)	25(1)
C(6)	10768(2)	3844(1)	7450(1)	20(1)
C(7)	12689(2)	3694(2)	7814(1)	23(1)
C(8)	13367(3)	2624(2)	8621(1)	24(1)
C(9)	12122(3)	1698(2)	9055(1)	23(1)
C(10)	10260(2)	1797(2)	8687(1)	23(1)
C(11)	9563(2)	2876(2)	7884(1)	23(1)
C(12)	3580(2)	7548(2)	8119(1)	21(1)
C(13)	1612(2)	7508(2)	7619(1)	22(1)
C(14)	4209(3)	6361(2)	9031(1)	27(1)
C(15)	3513(3)	8645(2)	8553(2)	29(1)
C(16)	92(3)	6686(2)	8462(2)	30(1)
C(17)	502(3)	8771(2)	7084(2)	35(1)
B(1)	4495(3)	7219(2)	6330(2)	19(1)

Table S17. Bond lengths [Å] and angles [°] for **2b**.

F(1)-C(9)	1.3612(19)	C(13)-C(16)	1.520(2)
O(1)-C(5)	1.218(2)	C(13)-C(17)	1.514(2)
O(2)-C(12)	1.4645(19)	C(14)-H(14A)	0.9800
O(2)-B(1)	1.367(2)	C(14)-H(14B)	0.9800
O(3)-C(13)	1.473(2)	C(14)-H(14C)	0.9800
O(3)-B(1)	1.379(2)	C(15)-H(15A)	0.9800
N(1)-H(1)	0.868(13)	C(15)-H(15B)	0.9800
N(1)-C(5)	1.351(2)	C(15)-H(15C)	0.9800
N(1)-C(6)	1.409(2)	C(16)-H(16A)	0.9800
C(1)-H(1A)	0.9800	C(16)-H(16B)	0.9800
C(1)-H(1B)	0.9800	C(16)-H(16C)	0.9800
C(1)-H(1C)	0.9800	C(17)-H(17A)	0.9800
C(1)-C(2)	1.526(2)	C(17)-H(17B)	0.9800
C(2)-H(2A)	0.9900	C(17)-H(17C)	0.9800
C(2)-H(2B)	0.9900		
C(2)-C(3)	1.531(2)	B(1)-O(2)-C(12)	107.95(12)
C(3)-H(3)	1.0000	B(1)-O(3)-C(13)	107.10(12)
C(3)-C(4)	1.532(2)	C(5)-N(1)-H(1)	115.5(12)
C(3)-B(1)	1.566(2)	C(5)-N(1)-C(6)	127.83(14)
C(4)-H(4A)	0.9900	C(6)-N(1)-H(1)	115.2(12)
C(4)-H(4B)	0.9900	H(1A)-C(1)-H(1B)	109.5
C(4)-C(5)	1.508(2)	H(1A)-C(1)-H(1C)	109.5
C(6)-C(7)	1.394(2)	H(1B)-C(1)-H(1C)	109.5
C(6)-C(11)	1.396(2)	C(2)-C(1)-H(1A)	109.5
C(7)-H(7)	0.9500	C(2)-C(1)-H(1B)	109.5
C(7)-C(8)	1.377(2)	C(2)-C(1)-H(1C)	109.5
C(8)-H(8)	0.9500	C(1)-C(2)-H(2A)	109.0
C(8)-C(9)	1.376(2)	C(1)-C(2)-H(2B)	109.0
C(9)-C(10)	1.368(2)	C(1)-C(2)-C(3)	112.80(14)
C(10)-H(10)	0.9500	H(2A)-C(2)-H(2B)	107.8
C(10)-C(11)	1.385(2)	C(3)-C(2)-H(2A)	109.0
C(11)-H(11)	0.9500	C(3)-C(2)-H(2B)	109.0
C(12)-C(13)	1.556(2)	C(2)-C(3)-H(3)	108.6
C(12)-C(14)	1.514(2)	C(2)-C(3)-C(4)	110.71(13)
C(12)-C(15)	1.508(2)	C(2)-C(3)-B(1)	110.80(14)

C(4)-C(3)-H(3)	108.6	O(3)-C(13)-C(16)	108.90(13)
C(4)-C(3)-B(1)	109.52(13)	O(3)-C(13)-C(17)	106.55(14)
B(1)-C(3)-H(3)	108.6	C(16)-C(13)-C(12)	114.85(14)
C(3)-C(4)-H(4A)	109.4	C(17)-C(13)-C(12)	113.54(14)
C(3)-C(4)-H(4B)	109.4	C(17)-C(13)-C(16)	110.04(15)
H(4A)-C(4)-H(4B)	108.0	C(12)-C(14)-H(14A)	109.5
C(5)-C(4)-C(3)	111.33(13)	C(12)-C(14)-H(14B)	109.5
C(5)-C(4)-H(4A)	109.4	C(12)-C(14)-H(14C)	109.5
C(5)-C(4)-H(4B)	109.4	H(14A)-C(14)-H(14B)	109.5
O(1)-C(5)-N(1)	122.57(17)	H(14A)-C(14)-H(14C)	109.5
O(1)-C(5)-C(4)	121.80(15)	H(14B)-C(14)-H(14C)	109.5
N(1)-C(5)-C(4)	115.63(14)	C(12)-C(15)-H(15A)	109.5
C(7)-C(6)-N(1)	117.28(14)	C(12)-C(15)-H(15B)	109.5
C(7)-C(6)-C(11)	119.08(15)	C(12)-C(15)-H(15C)	109.5
C(11)-C(6)-N(1)	123.62(15)	H(15A)-C(15)-H(15B)	109.5
C(6)-C(7)-H(7)	119.6	H(15A)-C(15)-H(15C)	109.5
C(8)-C(7)-C(6)	120.77(15)	H(15B)-C(15)-H(15C)	109.5
C(8)-C(7)-H(7)	119.6	C(13)-C(16)-H(16A)	109.5
C(7)-C(8)-H(8)	120.6	C(13)-C(16)-H(16B)	109.5
C(9)-C(8)-C(7)	118.79(16)	C(13)-C(16)-H(16C)	109.5
C(9)-C(8)-H(8)	120.6	H(16A)-C(16)-H(16B)	109.5
F(1)-C(9)-C(8)	119.06(15)	H(16A)-C(16)-H(16C)	109.5
F(1)-C(9)-C(10)	118.96(14)	H(16B)-C(16)-H(16C)	109.5
C(10)-C(9)-C(8)	121.98(16)	C(13)-C(17)-H(17A)	109.5
C(9)-C(10)-H(10)	120.3	C(13)-C(17)-H(17B)	109.5
C(9)-C(10)-C(11)	119.38(15)	C(13)-C(17)-H(17C)	109.5
C(11)-C(10)-H(10)	120.3	H(17A)-C(17)-H(17B)	109.5
C(6)-C(11)-H(11)	120.0	H(17A)-C(17)-H(17C)	109.5
C(10)-C(11)-C(6)	119.94(16)	H(17B)-C(17)-H(17C)	109.5
C(10)-C(11)-H(11)	120.0	O(2)-B(1)-O(3)	112.60(14)
O(2)-C(12)-C(13)	102.40(13)	O(2)-B(1)-C(3)	121.30(14)
O(2)-C(12)-C(14)	106.98(13)	O(3)-B(1)-C(3)	125.97(15)
O(2)-C(12)-C(15)	108.11(13)		
C(14)-C(12)-C(13)	113.08(13)		
C(15)-C(12)-C(13)	114.84(14)		
C(15)-C(12)-C(14)	110.68(14)		
O(3)-C(13)-C(12)	102.25(12)		

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker APEX II Ultra diffractometer equipped with Cu K_α radiation (λ = 1.54178). Crystals of the subject compound were used as received (grown from Acetone). A 0.180 x 0.150 x 0.085 mm red crystal was mounted on a Cryoloop with Paratone oil.

Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm using exposure times 4, 6, 20.0s (depending on the detector 2θ position) with a scan width of 1.40°. Data collection was 99.9% complete to 58.031° in θ. A total of 45664 reflections were collected covering the indices, -11<=h<=11, -15<=k<=15, -27<=l<=27. 5246 reflections were found to be symmetry independent, with a R_{int} of 0.0627. Indexing and unit cell refinement indicated a **Primitive**, **Monoclinic** lattice. The space group was found to be ***P*2$_1$/c**. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Crystallographic data are summarized in Table S18.

Notes: Twinned dataset, confident in connectivity.

Final refinement using HKL 5 file format.

Two molecules in asymmetric unit.

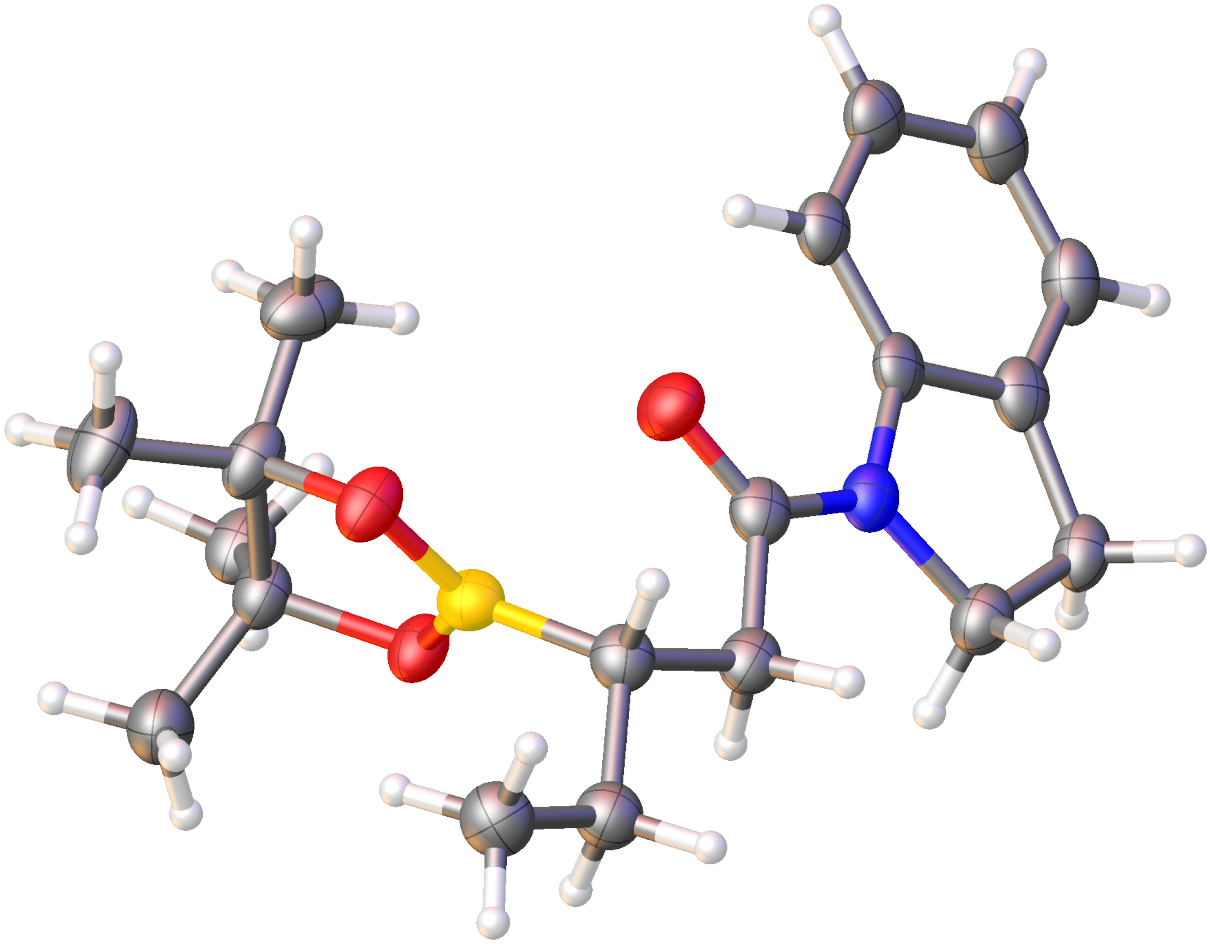


Table S18. Crystal data and structure refinement for **2i**.

Report date	2020-09-21	
Identification code	engle265	
Empirical formula	C19 H28 B N O3	
Molecular formula	C19 H28 B N O3	
Formula weight	329.23	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.5238(3) Å	α= 90°.
	b = 14.0554(3) Å	β= 96.2420(10)°.
	c = 25.2685(6) Å	γ = 90°.
Volume	3715.46(16) $Å^3$	
Z	8	
Density (calculated)	1.177 Mg/m^3	
Absorption coefficient	0.614 mm^{-1}	
F(000)	1424	
Crystal size	0.18 x 0.15 x 0.085 mm^3	
Crystal color, habit	colorless plate	
Theta range for data collection	3.519 to 58.031°.	
Index ranges	-11<=h<=11, 0<=k<=15, 0<=l<=27	
Reflections collected	45664	
Independent reflections	5245 [R(int) = 0.0627]	
Completeness to theta = 58.031°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.751 and 0.504	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5245 / 0 / 444	
Goodness-of-fit on F^2	1.126	
Final R indices [I>2sigma(I)]	R1 = 0.0505, wR2 = 0.1257	
R indices (all data)	R1 = 0.0591, wR2 = 0.1308	
Largest diff. peak and hole	0.304 and -0.202 e.$Å^{-3}$	

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2i**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	10057(2)	3596(2)	7053(1)	41(1)
O(1')	4619(2)	1993(2)	6783(1)	41(1)
O(2')	3739(2)	411(1)	6001(1)	36(1)
O(2)	7808(2)	3903(1)	6120(1)	38(1)
O(3)	9133(2)	5188(1)	6260(1)	35(1)
O(3')	2312(2)	1632(1)	5828(1)	36(1)
N(1')	6729(2)	1725(2)	7009(1)	32(1)
N(1)	12134(2)	3943(2)	7315(1)	33(1)
C(1')	5739(4)	2644(3)	4919(1)	50(1)
C(1)	9394(3)	3476(2)	4993(1)	46(1)
C(2')	4818(3)	1924(2)	5126(1)	46(1)
C(2)	10490(3)	3783(2)	5405(1)	40(1)
C(3)	10203(3)	3638(2)	5982(1)	35(1)
C(3')	4661(3)	2019(2)	5715(1)	37(1)
C(4)	11406(3)	3851(2)	6362(1)	35(1)
C(4')	5913(3)	1824(2)	6069(1)	37(1)
C(5')	5692(3)	1857(2)	6644(1)	33(1)
C(5)	11138(3)	3782(2)	6936(1)	34(1)
C(6)	13459(3)	4159(2)	7197(1)	38(1)
C(6')	8056(3)	1581(2)	6868(1)	36(1)
C(7')	8878(3)	1425(2)	7402(1)	34(1)
C(7)	14233(3)	4288(2)	7743(1)	38(1)
C(8')	7965(3)	1555(2)	7814(1)	30(1)
C(8)	13282(3)	4101(2)	8136(1)	35(1)
C(9')	8186(3)	1510(2)	8360(1)	34(1)
C(9)	13470(3)	4102(2)	8687(1)	42(1)
C(10')	7170(3)	1645(2)	8666(1)	37(1)
C(10)	12444(3)	3904(2)	8969(1)	44(1)
C(11')	5952(3)	1821(2)	8417(1)	34(1)
C(11)	11244(3)	3714(2)	8702(1)	39(1)
C(12)	11043(3)	3715(2)	8149(1)	34(1)
C(12')	5706(3)	1862(2)	7868(1)	32(1)

C(13)	12083(3)	3910(2)	7872(1)	31(1)
C(13')	6728(3)	1732(2)	7569(1)	29(1)
C(14')	2474(3)	-23(2)	5999(1)	34(1)
C(14)	7052(3)	4633(2)	6357(1)	38(1)
C(15)	7839(3)	5559(2)	6280(1)	35(1)
C(15')	1590(3)	859(2)	6049(1)	33(1)
C(16')	2527(3)	-713(2)	6458(1)	42(1)
C(16)	7018(4)	4365(2)	6939(1)	49(1)
C(17)	5710(3)	4632(3)	6069(2)	54(1)
C(17')	2212(4)	-538(2)	5469(1)	48(1)
C(18)	7871(3)	6257(2)	6738(1)	42(1)
C(18')	1461(3)	1125(2)	6625(1)	42(1)
C(19')	293(3)	802(2)	5725(1)	42(1)
C(19)	7473(3)	6050(3)	5754(1)	48(1)
B(1)	9043(4)	4240(2)	6134(1)	34(1)
B(1')	3561(4)	1359(3)	5869(1)	35(1)

Table S20. Bond lengths [Å] and angles [°] for **2i**.

O(1)-C(5)	1.235(4)	C(7')-H(7'A)	0.9900
O(1')-C(5')	1.233(4)	C(7')-H(7'B)	0.9900
O(2')-C(14')	1.464(4)	C(7')-C(8')	1.503(4)
O(2')-B(1')	1.381(4)	C(7)-H(7A)	0.9900
O(2)-C(14)	1.464(4)	C(7)-H(7B)	0.9900
O(2)-B(1)	1.380(4)	C(7)-C(8)	1.506(5)
O(3)-C(15)	1.464(4)	C(8')-C(9')	1.376(4)
O(3)-B(1)	1.371(4)	C(8')-C(13')	1.401(4)
O(3')-C(15')	1.470(3)	C(8)-C(9)	1.387(5)
O(3')-B(1')	1.362(4)	C(8)-C(13)	1.388(4)
N(1')-C(5')	1.362(4)	C(9')-H(9')	0.9500
N(1')-C(6')	1.492(4)	C(9')-C(10')	1.398(4)
N(1')-C(13')	1.416(4)	C(9)-H(9)	0.9500
N(1)-C(5)	1.361(4)	C(9)-C(10)	1.385(5)
N(1)-C(6)	1.488(4)	C(10')-H(10')	0.9500
N(1)-C(13)	1.416(4)	C(10')-C(11')	1.386(4)
C(1')-H(1'A)	0.9800	C(10)-H(10)	0.9500
C(1')-H(1'B)	0.9800	C(10)-C(11)	1.391(5)
C(1')-H(1'C)	0.9800	C(11')-H(11')	0.9500
C(1')-C(2')	1.531(5)	C(11')-C(12')	1.385(4)
C(1)-H(1A)	0.9800	C(11)-H(11)	0.9500
C(1)-H(1B)	0.9800	C(11)-C(12)	1.389(4)
C(1)-H(1C)	0.9800	C(12)-H(12)	0.9500
C(1)-C(2)	1.528(5)	C(12)-C(13)	1.389(4)
C(2')-H(2'A)	0.9900	C(12')-H(12')	0.9500
C(2')-H(2'B)	0.9900	C(12')-C(13')	1.392(4)
C(2')-C(3')	1.521(4)	C(14')-C(15')	1.564(4)
C(2)-H(2A)	0.9900	C(14')-C(16')	1.509(4)
C(2)-H(2B)	0.9900	C(14')-C(17')	1.519(4)
C(2)-C(3)	1.536(4)	C(14)-C(15)	1.567(4)
C(3)-H(3)	1.0000	C(14)-C(16)	1.523(5)
C(3)-C(4)	1.532(4)	C(14)-C(17)	1.517(5)
C(3)-B(1)	1.566(5)	C(15)-C(18)	1.515(4)
C(3')-H(3')	1.0000	C(15)-C(19)	1.510(5)
C(3')-C(4')	1.535(4)	C(15')-C(18')	1.522(4)
C(3')-B(1')	1.565(5)	C(15')-C(19')	1.517(4)
C(4)-H(4A)	0.9900	C(16')-H(16D)	0.9800
C(4)-H(4B)	0.9900	C(16')-H(16E)	0.9800
C(4)-C(5)	1.510(4)	C(16')-H(16F)	0.9800
C(4')-H(4'A)	0.9900	C(16)-H(16A)	0.9800
C(4')-H(4'B)	0.9900	C(16)-H(16B)	0.9800
C(4')-C(5')	1.498(4)	C(16)-H(16C)	0.9800
C(6)-H(6A)	0.9900	C(17)-H(17A)	0.9800
C(6)-H(6B)	0.9900	C(17)-H(17B)	0.9800
C(6)-C(7)	1.535(4)	C(17)-H(17C)	0.9800
C(6')-H(6'A)	0.9900	C(17')-H(17D)	0.9800
C(6')-H(6'B)	0.9900	C(17')-H(17E)	0.9800
C(6')-C(7')	1.537(4)	C(17')-H(17F)	0.9800

C(18)-H(18A)	0.9800	C(4)-C(3)-H(3)	107.6
C(18)-H(18B)	0.9800	C(4)-C(3)-B(1)	110.8(2)
C(18)-H(18C)	0.9800	B(1)-C(3)-H(3)	107.6
C(18')-H(18D)	0.9800	C(2')-C(3')-H(3')	107.5
C(18')-H(18E)	0.9800	C(2')-C(3')-C(4')	112.1(3)
C(18')-H(18F)	0.9800	C(2')-C(3')-B(1')	110.7(3)
C(19')-H(19D)	0.9800	C(4')-C(3')-H(3')	107.5
C(19')-H(19E)	0.9800	C(4')-C(3')-B(1')	111.1(3)
C(19')-H(19F)	0.9800	B(1')-C(3')-H(3')	107.5
C(19)-H(19A)	0.9800	C(3)-C(4)-H(4A)	109.4
C(19)-H(19B)	0.9800	C(3)-C(4)-H(4B)	109.4
C(19)-H(19C)	0.9800	H(4A)-C(4)-H(4B)	108.0
		C(5)-C(4)-C(3)	111.1(3)
B(1')-O(2')-C(14')	107.6(2)	C(5)-C(4)-H(4A)	109.4
B(1)-O(2)-C(14)	107.6(2)	C(5)-C(4)-H(4B)	109.4
B(1)-O(3)-C(15)	108.3(2)	C(3')-C(4')-H(4'A)	109.6
B(1')-O(3')-C(15')	107.3(2)	C(3')-C(4')-H(4'B)	109.6
C(5')-N(1')-C(6')	124.0(2)	H(4'A)-C(4')-H(4'B)	108.1
C(5')-N(1')-C(13')	126.0(3)	C(5')-C(4')-C(3')	110.3(3)
C(13')-N(1')-C(6')	110.0(2)	C(5')-C(4')-H(4'A)	109.6
C(5)-N(1)-C(6)	124.0(3)	C(5')-C(4')-H(4'B)	109.6
C(5)-N(1)-C(13)	125.9(3)	O(1')-C(5')-N(1')	121.4(3)
C(13)-N(1)-C(6)	110.1(2)	O(1')-C(5')-C(4')	121.6(3)
H(1'A)-C(1')-H(1'B)	109.5	N(1')-C(5')-C(4')	117.0(3)
H(1'A)-C(1')-H(1'C)	109.5	O(1)-C(5)-N(1)	121.7(3)
H(1'B)-C(1')-H(1'C)	109.5	O(1)-C(5)-C(4)	121.1(3)
C(2')-C(1')-H(1'A)	109.5	N(1)-C(5)-C(4)	117.2(3)
C(2')-C(1')-H(1'B)	109.5	N(1)-C(6)-H(6A)	110.7
C(2')-C(1')-H(1'C)	109.5	N(1)-C(6)-H(6B)	110.7
H(1A)-C(1)-H(1B)	109.5	N(1)-C(6)-C(7)	105.1(3)
H(1A)-C(1)-H(1C)	109.5	H(6A)-C(6)-H(6B)	108.8
H(1B)-C(1)-H(1C)	109.5	C(7)-C(6)-H(6A)	110.7
C(2)-C(1)-H(1A)	109.5	C(7)-C(6)-H(6B)	110.7
C(2)-C(1)-H(1B)	109.5	N(1')-C(6')-H(6'A)	110.7
C(2)-C(1)-H(1C)	109.5	N(1')-C(6')-H(6'B)	110.7
C(1')-C(2')-H(2'A)	108.6	N(1')-C(6')-C(7')	105.2(2)
C(1')-C(2')-H(2'B)	108.6	H(6'A)-C(6')-H(6'B)	108.8
H(2'A)-C(2')-H(2'B)	107.6	C(7')-C(6')-H(6'A)	110.7
C(3')-C(2')-C(1')	114.6(3)	C(7')-C(6')-H(6'B)	110.7
C(3')-C(2')-H(2'A)	108.6	C(6')-C(7')-H(7'A)	110.9
C(3')-C(2')-H(2'B)	108.6	C(6')-C(7')-H(7'B)	110.9
C(1)-C(2)-H(2A)	108.9	H(7'A)-C(7')-H(7'B)	108.9
C(1)-C(2)-H(2B)	108.9	C(8')-C(7')-C(6')	104.4(2)
C(1)-C(2)-C(3)	113.4(3)	C(8')-C(7')-H(7'A)	110.9
H(2A)-C(2)-H(2B)	107.7	C(8')-C(7')-H(7'B)	110.9
C(3)-C(2)-H(2A)	108.9	C(6)-C(7)-H(7A)	110.9
C(3)-C(2)-H(2B)	108.9	C(6)-C(7)-H(7B)	110.9
C(2)-C(3)-H(3)	107.6	H(7A)-C(7)-H(7B)	108.9
C(2)-C(3)-B(1)	113.5(3)	C(8)-C(7)-C(6)	104.2(3)
C(4)-C(3)-C(2)	109.5(3)	C(8)-C(7)-H(7A)	110.9

C(8)-C(7)-H(7B)	110.9	O(3)-C(15)-C(18)	108.3(2)
C(9')-C(8')-C(7')	129.7(3)	O(3)-C(15)-C(19)	106.4(2)
C(9')-C(8')-C(13')	119.9(3)	C(18)-C(15)-C(14)	114.3(3)
C(13')-C(8')-C(7')	110.4(3)	C(19)-C(15)-C(14)	113.7(3)
C(9)-C(8)-C(7)	129.0(3)	C(19)-C(15)-C(18)	111.0(3)
C(9)-C(8)-C(13)	120.3(3)	O(3')-C(15')-C(14')	102.6(2)
C(13)-C(8)-C(7)	110.7(3)	O(3')-C(15')-C(18')	106.6(2)
C(8')-C(9')-H(9')	120.3	O(3')-C(15')-C(19')	107.8(2)
C(8')-C(9')-C(10')	119.4(3)	C(18')-C(15')-C(14')	112.9(3)
C(10')-C(9')-H(9')	120.3	C(19')-C(15')-C(14')	115.0(2)
C(8)-C(9)-H(9)	120.6	C(19')-C(15')-C(18')	111.2(3)
C(10)-C(9)-C(8)	118.9(3)	C(14')-C(16')-H(16D)	109.5
C(10)-C(9)-H(9)	120.6	C(14')-C(16')-H(16E)	109.5
C(9')-C(10')-H(10')	120.0	C(14')-C(16')-H(16F)	109.5
C(11')-C(10')-C(9')	119.9(3)	H(16D)-C(16')-H(16E)	109.5
C(11')-C(10')-H(10')	120.0	H(16D)-C(16')-H(16F)	109.5
C(9)-C(10)-H(10)	119.8	H(16E)-C(16')-H(16F)	109.5
C(9)-C(10)-C(11)	120.4(3)	C(14)-C(16)-H(16A)	109.5
C(11)-C(10)-H(10)	119.8	C(14)-C(16)-H(16B)	109.5
C(10')-C(11')-H(11')	119.2	C(14)-C(16)-H(16C)	109.5
C(12')-C(11')-C(10')	121.6(3)	H(16A)-C(16)-H(16B)	109.5
C(12')-C(11')-H(11')	119.2	H(16A)-C(16)-H(16C)	109.5
C(10)-C(11)-H(11)	119.4	H(16B)-C(16)-H(16C)	109.5
C(12)-C(11)-C(10)	121.3(3)	C(14)-C(17)-H(17A)	109.5
C(12)-C(11)-H(11)	119.4	C(14)-C(17)-H(17B)	109.5
C(11)-C(12)-H(12)	121.2	C(14)-C(17)-H(17C)	109.5
C(13)-C(12)-C(11)	117.6(3)	H(17A)-C(17)-H(17B)	109.5
C(13)-C(12)-H(12)	121.2	H(17A)-C(17)-H(17C)	109.5
C(11')-C(12')-H(12')	121.1	H(17B)-C(17)-H(17C)	109.5
C(11')-C(12')-C(13')	117.9(3)	C(14')-C(17')-H(17D)	109.5
C(13')-C(12')-H(12')	121.1	C(14')-C(17')-H(17E)	109.5
C(8)-C(13)-N(1)	109.8(3)	C(14')-C(17')-H(17F)	109.5
C(8)-C(13)-C(12)	121.5(3)	H(17D)-C(17')-H(17E)	109.5
C(12)-C(13)-N(1)	128.7(3)	H(17D)-C(17')-H(17F)	109.5
C(8')-C(13')-N(1')	109.8(3)	H(17E)-C(17')-H(17F)	109.5
C(12')-C(13')-N(1')	129.0(3)	C(15)-C(18)-H(18A)	109.5
C(12')-C(13')-C(8')	121.3(3)	C(15)-C(18)-H(18B)	109.5
O(2')-C(14')-C(15')	102.6(2)	C(15)-C(18)-H(18C)	109.5
O(2')-C(14')-C(16')	107.9(2)	H(18A)-C(18)-H(18B)	109.5
O(2')-C(14')-C(17')	106.3(2)	H(18A)-C(18)-H(18C)	109.5
C(16')-C(14')-C(15')	114.8(3)	H(18B)-C(18)-H(18C)	109.5
C(16')-C(14')-C(17')	111.1(3)	C(15')-C(18')-H(18D)	109.5
C(17')-C(14')-C(15')	113.4(3)	C(15')-C(18')-H(18E)	109.5
O(2)-C(14)-C(15)	102.3(2)	C(15')-C(18')-H(18F)	109.5
O(2)-C(14)-C(16)	107.0(3)	H(18D)-C(18')-H(18E)	109.5
O(2)-C(14)-C(17)	108.8(2)	H(18D)-C(18')-H(18F)	109.5
C(16)-C(14)-C(15)	113.2(3)	H(18E)-C(18')-H(18F)	109.5
C(17)-C(14)-C(15)	114.7(3)	C(15')-C(19')-H(19D)	109.5
C(17)-C(14)-C(16)	110.2(3)	C(15')-C(19')-H(19E)	109.5
O(3)-C(15)-C(14)	102.4(2)	C(15')-C(19')-H(19F)	109.5

H(19D)-C(19')-H(19E)	109.5
H(19D)-C(19')-H(19F)	109.5
H(19E)-C(19')-H(19F)	109.5
C(15)-C(19)-H(19A)	109.5
C(15)-C(19)-H(19B)	109.5
C(15)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
O(2)-B(1)-C(3)	124.5(3)
O(3)-B(1)-O(2)	112.3(3)
O(3)-B(1)-C(3)	123.1(3)
O(2')-B(1')-C(3')	123.2(3)
O(3')-B(1')-O(2')	113.2(3)
O(3')-B(1')-C(3')	123.2(3)

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker SMART APEX II diffractometer equipped with Cu K_α radiation (λ = 1.54179). Crystals of the subject compound were used as received (grown from Acetone solution). A 0.220 x 0.125 x 0.090 mm colorless crystal was mounted on a Cryoloop with Paratone oil.

Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 40 mm using exposure time 5.0, 10.0 and 30s (depending on the detector 2θ position) with a scan width of 1.25°. Data collection was 100.0% complete to 67.679° in θ. A total of 31889 reflections were collected. 2939 reflections were found to be symmetry independent, with a R_{int} of 0.0456. Indexing and unit cell refinement indicated a **Primitive**, **Orthorhombic** lattice. The space group was found to be $\boldsymbol{P2_12_12_1}$. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Crystallographic data are summarized in Table S21.

Notes: Excellent data and refinement.
Racemic TWIN, final refinement using HKL 4 file format

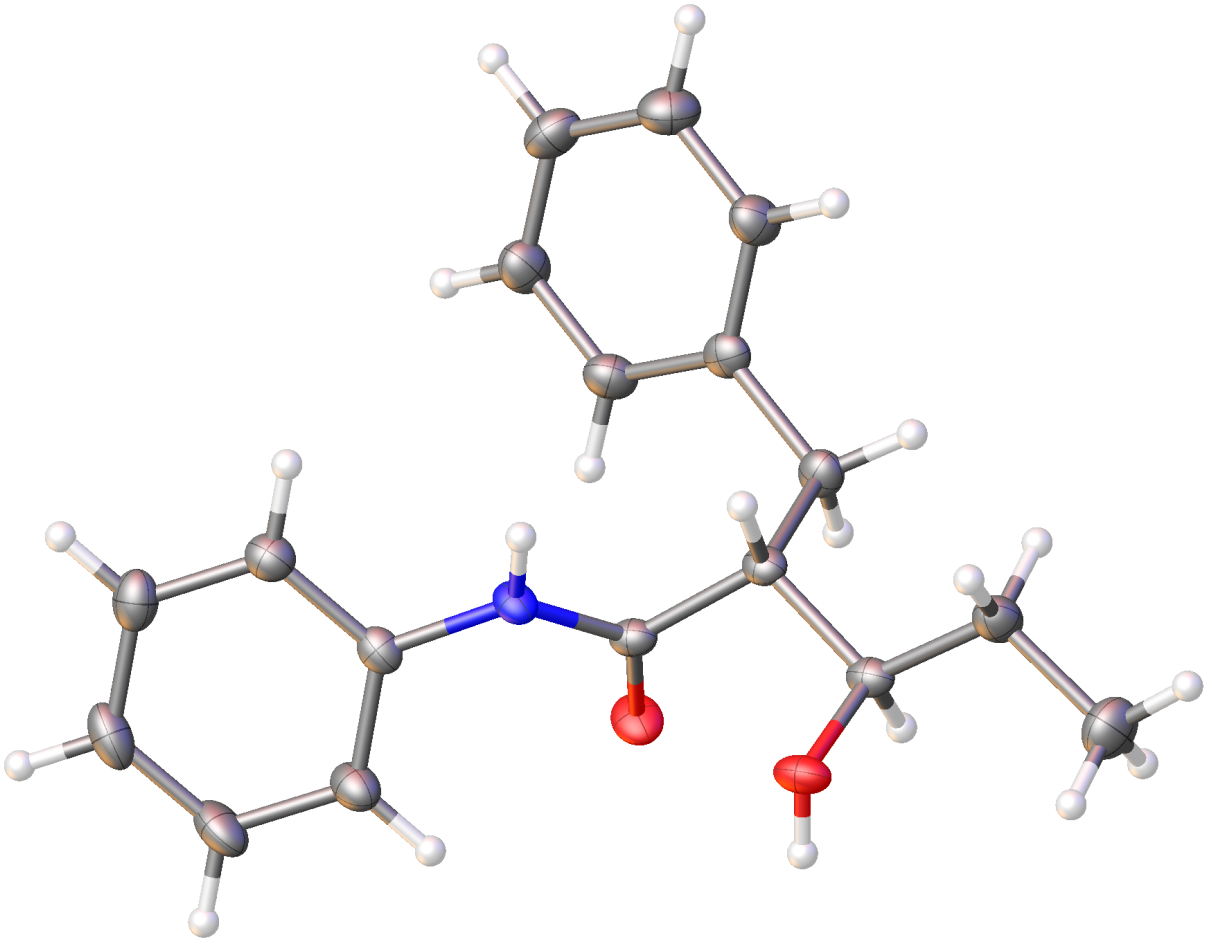


Table S21. Crystal data and structure refinement for **2m**.

Report date	2020-11-18	
Identification code	engle291	
Empirical formula	C18 H21 N O2	
Molecular formula	C18 H21 N O2	
Formula weight	283.36	
Temperature	100.0 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 4.9552(3) Å	α= 90°.
	b = 15.4018(10) Å	β= 90°.
	c = 20.3511(13) Å	γ = 90°.
Volume	1553.18(17) $Å^3$	
Z	4	
Density (calculated)	1.212 Mg/m^3	
Absorption coefficient	0.621 mm^{-1}	
F(000)	608	
Crystal size	0.22 x 0.125 x 0.09 mm^3	
Crystal color, habit	colorless plank	
Theta range for data collection	3.599 to 70.087°.	
Reflections collected	31889	
Independent reflections	2939 [R(int) = 0.0456]	
Completeness to theta = 67.679°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.753 and 0.637	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2939 / 0 / 196	
Goodness-of-fit on F^2	1.106	
Final R indices [I>2sigma(I)]	R1 = 0.0335, wR2 = 0.0762	
R indices (all data)	R1 = 0.0370, wR2 = 0.0774	
Absolute structure parameter	0.3(3)	
Largest diff. peak and hole	0.146 and -0.148 $e.Å^{-3}$	

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)for **2m**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5445(3)	2781(1)	5211(1)	23(1)
O(2)	8197(3)	4589(1)	4857(1)	24(1)
N(1)	3776(3)	4761(1)	4586(1)	18(1)
C(1)	6400(5)	1996(2)	6535(1)	34(1)
C(2)	4968(5)	2848(1)	6387(1)	25(1)
C(3)	6070(4)	3299(1)	5777(1)	19(1)
C(4)	4906(4)	4212(1)	5671(1)	17(1)
C(5)	5783(4)	4530(1)	4997(1)	18(1)
C(6)	5952(4)	4854(1)	6196(1)	22(1)
C(7)	4769(4)	5755(1)	6151(1)	20(1)
C(8)	2727(5)	6012(1)	6582(1)	26(1)
C(9)	1604(5)	6833(2)	6545(1)	31(1)
C(10)	2487(5)	7417(1)	6074(1)	29(1)
C(11)	4518(5)	7173(1)	5646(1)	28(1)
C(12)	5651(5)	6351(1)	5684(1)	25(1)
C(13)	4124(4)	5125(1)	3950(1)	19(1)
C(14)	6114(4)	4829(2)	3526(1)	25(1)
C(15)	6339(5)	5196(2)	2906(1)	31(1)
C(16)	4621(5)	5852(2)	2708(1)	30(1)
C(17)	2610(5)	6137(2)	3129(1)	28(1)
C(18)	2357(4)	5771(1)	3751(1)	23(1)

Table S23. Bond lengths [Å] and angles [°] for **2m**.

O(1)-H(1)	0.8400	C(14)-C(15)	1.388(3)
O(1)-C(3)	1.435(2)	C(15)-H(15)	0.9500
O(2)-C(5)	1.233(2)	C(15)-C(16)	1.381(4)
N(1)-H(1A)	0.87(3)	C(16)-H(16)	0.9500
N(1)-C(5)	1.347(3)	C(16)-C(17)	1.386(4)
N(1)-C(13)	1.421(2)	C(17)-H(17)	0.9500
C(1)-H(1B)	0.9800	C(17)-C(18)	1.391(3)
C(1)-H(1C)	0.9800	C(18)-H(18)	0.9500
C(1)-H(1D)	0.9800		
C(1)-C(2)	1.523(3)	C(3)-O(1)-H(1)	109.5
C(2)-H(2A)	0.9900	C(5)-N(1)-H(1A)	117.3(16)
C(2)-H(2B)	0.9900	C(5)-N(1)-C(13)	125.44(17)
C(2)-C(3)	1.524(3)	C(13)-N(1)-H(1A)	116.7(16)
C(3)-H(3)	1.0000	H(1B)-C(1)-H(1C)	109.5
C(3)-C(4)	1.535(3)	H(1B)-C(1)-H(1D)	109.5
C(4)-H(4)	1.0000	H(1C)-C(1)-H(1D)	109.5
C(4)-C(5)	1.520(3)	C(2)-C(1)-H(1B)	109.5
C(4)-C(6)	1.545(3)	C(2)-C(1)-H(1C)	109.5
C(6)-H(6A)	0.9900	C(2)-C(1)-H(1D)	109.5
C(6)-H(6B)	0.9900	C(1)-C(2)-H(2A)	109.0
C(6)-C(7)	1.509(3)	C(1)-C(2)-H(2B)	109.0
C(7)-C(8)	1.396(3)	C(1)-C(2)-C(3)	112.78(19)
C(7)-C(12)	1.392(3)	H(2A)-C(2)-H(2B)	107.8
C(8)-H(8)	0.9500	C(3)-C(2)-H(2A)	109.0
C(8)-C(9)	1.384(3)	C(3)-C(2)-H(2B)	109.0
C(9)-H(9)	0.9500	O(1)-C(3)-C(2)	108.83(17)
C(9)-C(10)	1.385(3)	O(1)-C(3)-H(3)	108.7
C(10)-H(10)	0.9500	O(1)-C(3)-C(4)	108.40(16)
C(10)-C(11)	1.383(3)	C(2)-C(3)-H(3)	108.7
C(11)-H(11)	0.9500	C(2)-C(3)-C(4)	113.41(17)
C(11)-C(12)	1.387(3)	C(4)-C(3)-H(3)	108.7
C(12)-H(12)	0.9500	C(3)-C(4)-H(4)	109.5
C(13)-C(14)	1.387(3)	C(3)-C(4)-C(6)	111.29(16)
C(13)-C(18)	1.386(3)	C(5)-C(4)-C(3)	108.32(16)
C(14)-H(14)	0.9500	C(5)-C(4)-H(4)	109.5

C(5)-C(4)-C(6)	108.77(16)	C(16)-C(15)-H(15)	119.5
C(6)-C(4)-H(4)	109.5	C(15)-C(16)-H(16)	120.2
O(2)-C(5)-N(1)	123.63(19)	C(15)-C(16)-C(17)	119.6(2)
O(2)-C(5)-C(4)	120.61(17)	C(17)-C(16)-H(16)	120.2
N(1)-C(5)-C(4)	115.73(17)	C(16)-C(17)-H(17)	120.0
C(4)-C(6)-H(6A)	108.6	C(16)-C(17)-C(18)	120.0(2)
C(4)-C(6)-H(6B)	108.6	C(18)-C(17)-H(17)	120.0
H(6A)-C(6)-H(6B)	107.6	C(13)-C(18)-C(17)	120.0(2)
C(7)-C(6)-C(4)	114.61(17)	C(13)-C(18)-H(18)	120.0
C(7)-C(6)-H(6A)	108.6	C(17)-C(18)-H(18)	120.0
C(7)-C(6)-H(6B)	108.6		
C(8)-C(7)-C(6)	120.25(19)		
C(12)-C(7)-C(6)	121.70(19)		
C(12)-C(7)-C(8)	118.1(2)		
C(7)-C(8)-H(8)	119.5		
C(9)-C(8)-C(7)	121.1(2)		
C(9)-C(8)-H(8)	119.5		
C(8)-C(9)-H(9)	119.9		
C(8)-C(9)-C(10)	120.3(2)		
C(10)-C(9)-H(9)	119.9		
C(9)-C(10)-H(10)	120.4		
C(11)-C(10)-C(9)	119.3(2)		
C(11)-C(10)-H(10)	120.4		
C(10)-C(11)-H(11)	119.7		
C(10)-C(11)-C(12)	120.5(2)		
C(12)-C(11)-H(11)	119.7		
C(7)-C(12)-H(12)	119.6		
C(11)-C(12)-C(7)	120.8(2)		
C(11)-C(12)-H(12)	119.6		
C(14)-C(13)-N(1)	121.54(19)		
C(18)-C(13)-N(1)	118.21(18)		
C(18)-C(13)-C(14)	120.21(18)		
C(13)-C(14)-H(14)	120.4		
C(13)-C(14)-C(15)	119.3(2)		
C(15)-C(14)-H(14)	120.4		
C(14)-C(15)-H(15)	119.5		
C(16)-C(15)-C(14)	120.9(2)		

Table S24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2m**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	16(1)	28(1)	24(1)	-11(1)	1(1)	0(1)
O(2)	10(1)	38(1)	26(1)	2(1)	2(1)	-2(1)
N(1)	11(1)	26(1)	17(1)	-1(1)	1(1)	-2(1)
C(1)	36(1)	26(1)	40(1)	6(1)	-2(1)	-1(1)
C(2)	30(1)	22(1)	23(1)	-2(1)	2(1)	0(1)
C(3)	14(1)	22(1)	20(1)	-5(1)	-1(1)	0(1)
C(4)	11(1)	22(1)	19(1)	-2(1)	-1(1)	0(1)
C(5)	13(1)	20(1)	20(1)	-5(1)	0(1)	0(1)
C(6)	24(1)	22(1)	20(1)	-3(1)	-4(1)	-1(1)
C(7)	20(1)	22(1)	20(1)	-5(1)	-5(1)	-2(1)
C(8)	28(1)	23(1)	25(1)	1(1)	4(1)	-4(1)
C(9)	26(1)	31(1)	36(1)	-5(1)	6(1)	1(1)
C(10)	28(1)	22(1)	37(1)	-3(1)	-4(1)	3(1)
C(11)	34(1)	23(1)	27(1)	1(1)	2(1)	-3(1)
C(12)	25(1)	25(1)	24(1)	-5(1)	2(1)	-2(1)
C(13)	16(1)	23(1)	17(1)	-2(1)	-1(1)	-6(1)
C(14)	19(1)	36(1)	21(1)	-1(1)	1(1)	0(1)
C(15)	25(1)	50(2)	19(1)	-1(1)	4(1)	-4(1)
C(16)	31(1)	41(1)	18(1)	6(1)	-3(1)	-12(1)
C(17)	29(1)	28(1)	27(1)	4(1)	-8(1)	-5(1)
C(18)	20(1)	26(1)	24(1)	-2(1)	0(1)	-2(1)

Table S25. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2m**.

	x	y	z	U(eq)
H(1)	6884	2622	5029	34
H(1A)	2140(50)	4753(16)	4742(12)	22
H(1B)	6234	1607	6156	51
H(1C)	5574	1723	6921	51
H(1D)	8312	2109	6623	51
H(2A)	5165	3241	6769	30
H(2B)	3019	2734	6325	30
H(3)	8076	3345	5818	22
H(4)	2891	4186	5690	21
H(6A)	5548	4615	6636	26
H(6B)	7939	4898	6155	26
H(8)	2099	5616	6906	31
H(9)	221	6997	6843	37
H(10)	1706	7979	6045	34
H(11)	5143	7572	5324	34
H(12)	7046	6193	5387	30
H(14)	7311	4380	3659	30
H(15)	7694	4993	2613	38
H(16)	4815	6105	2285	36
H(17)	1406	6582	2993	33
H(18)	973	5964	4039	28

Table S26. Hydrogen bonds for **2m** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(1)#1	0.84	1.93	2.7615(12)	168.4
N(1)-H(1A)...O(2)#2	0.87(3)	1.98(3)	2.831(2)	164(2)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,-z+1 #2 x-1,y,z

Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker D8 Venture Ultra diffractometer equipped with Mo K_α radiation (λ = 0.71073). Crystals of the subject compound were used as received (grown from Acetone/Et_2O). A 0.400 x 0.030 x 0.030 mm colorless crystal was mounted on a Cryoloop with Paratone oil.

Data were collected in a nitrogen gas stream at 100(2) K using ϕ and ϖ scans. Crystal-to-detector distance was 50 mm using exposure time 4.0s (depending on the detector 2θ position) with a scan width of 0.80°. Data collection was 99.7% complete to 25.242° in θ. A total of 52216 reflections were collected covering the indices, -14<=h<=14, -11<=k<=10, -38<=l<=38. 3186 reflections were found to be symmetry independent, with a R_{int} of 0.0926. Indexing and unit cell refinement indicated a **Primitive**, **Orthorhombic** lattice. The space group was found to be ***P*bca**. The data were integrated using the Bruker SAINT Software program and scaled using the SADABS software program. Solution by direct methods (SHELXT) produced a complete phasing model consistent with the proposed structure.

All nonhydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All carbon bonded hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

Crystallographic data are summarized in Table S27.

Notes: Minor disorder group modeled.

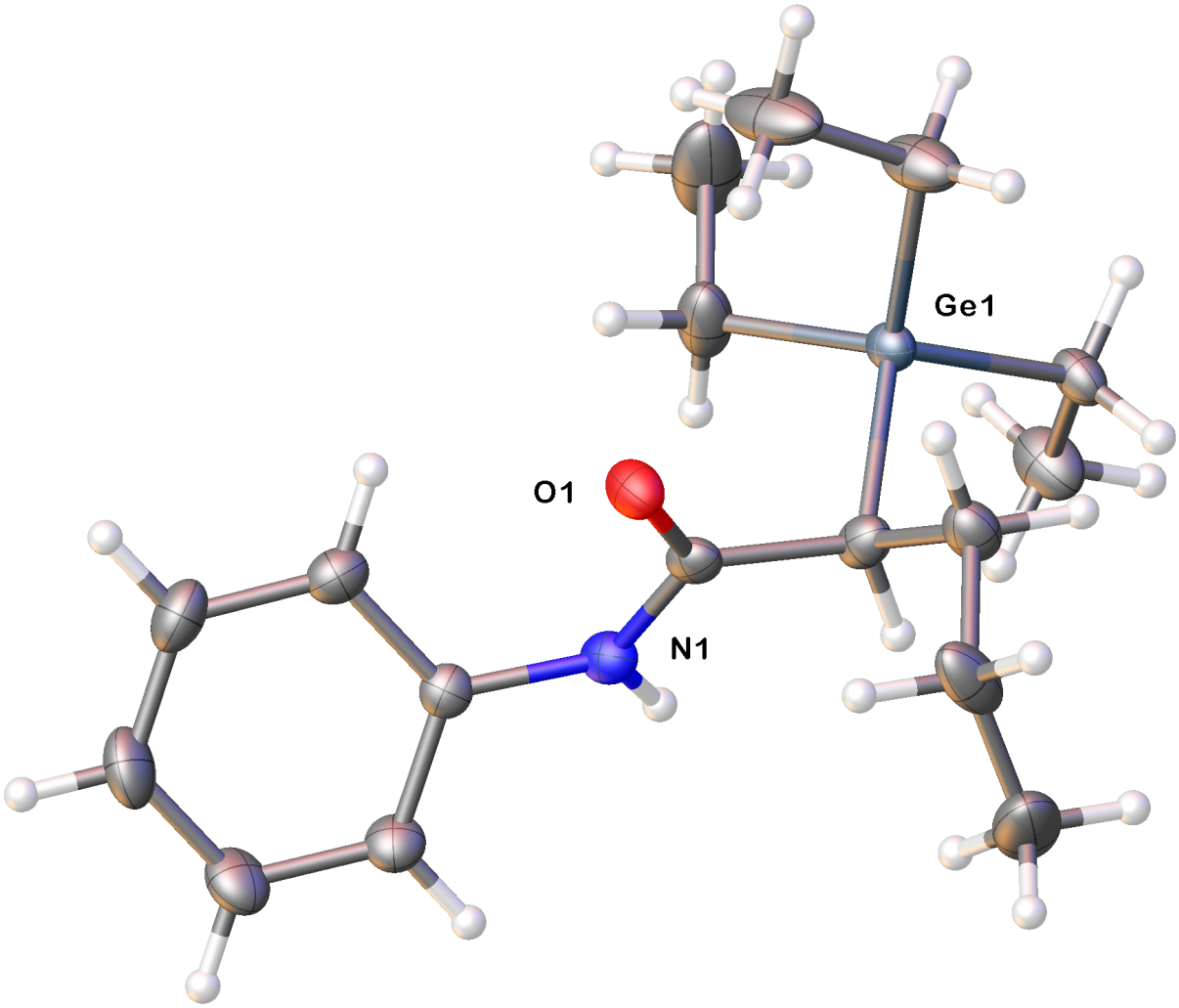

Ge1
O1
N1

Table S27. Crystal data and structure refinement for **3b**.

Report date	2020-10-02	
Identification code	engle277	
Empirical formula	C17 H29 Ge N O	
Molecular formula	C17 H29 Ge N O	
Formula weight	336.00	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 11.7114(4) Å	α= 90°.
	b = 9.2986(3) Å	β= 90°.
	c = 32.1084(10) Å	γ = 90°.
Volume	3496.6(2) $Å^3$	
Z	8	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	1.749 mm^{-1}	
F(000)	1424	
Crystal size	0.4 x 0.03 x 0.03 mm^3	
Crystal color, habit	colorless needle	
Theta range for data collection	3.384 to 25.344°.	
Index ranges	-14<=h<=14, -11<=k<=10, -38<=l<=38	
Reflections collected	52216	
Independent reflections	3186 [R(int) = 0.0926]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5568 and 0.4601	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3186 / 18 / 208	
Goodness-of-fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0667	
R indices (all data)	R1 = 0.0449, wR2 = 0.0727	
Largest diff. peak and hole	0.361 and -0.366 $e.Å^{-3}$	

Table S28. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ge(1)	5202(1)	5277(1)	6002(1)	20(1)
O(1)	3158(2)	2681(2)	6200(1)	26(1)
N(1)	2403(2)	4757(2)	6456(1)	22(1)
C(1)	3035(2)	4002(3)	6177(1)	21(1)
C(2)	3595(2)	4872(3)	5842(1)	24(1)
C(6)	6209(3)	3711(3)	5830(1)	39(1)
C(7)	6033(3)	2308(3)	6072(1)	54(1)
C(8)	5647(2)	7035(3)	5711(1)	25(1)
C(9)	5319(3)	8402(3)	5940(1)	38(1)
C(10)	5266(3)	5536(4)	6604(1)	38(1)
C(11)	6476(3)	5777(5)	6771(1)	61(1)
C(12)	1818(2)	4180(3)	6803(1)	20(1)
C(13)	2280(2)	3090(3)	7045(1)	26(1)
C(14)	1656(3)	2541(3)	7378(1)	33(1)
C(15)	594(3)	3078(3)	7472(1)	36(1)
C(16)	149(3)	4188(3)	7237(1)	33(1)
C(17)	756(2)	4737(3)	6904(1)	26(1)
C(3)	3593(4)	4076(5)	5415(1)	29(1)
C(4)	2392(3)	3755(5)	5242(1)	38(1)
C(5)	1689(4)	5075(6)	5155(2)	58(2)
C(3')	3237(15)	4480(30)	5416(5)	29(1)
C(4')	1938(14)	4530(20)	5352(5)	27(4)
C(5')	1654(16)	4230(20)	4901(5)	39(5)

Table S29. Bond lengths [Å] and angles [°] for **3b**.

Ge(1)-C(2)	1.988(3)	C(14)-H(14)	0.9500
Ge(1)-C(6)	1.953(3)	C(14)-C(15)	1.373(4)
Ge(1)-C(8)	1.954(3)	C(15)-H(15)	0.9500
Ge(1)-C(10)	1.949(3)	C(15)-C(16)	1.381(4)
O(1)-C(1)	1.239(3)	C(16)-H(16)	0.9500
N(1)-H(1)	0.8800	C(16)-C(17)	1.383(4)
N(1)-C(1)	1.356(3)	C(17)-H(17)	0.9500
N(1)-C(12)	1.415(3)	C(3)-H(3A)	0.9900
C(1)-C(2)	1.498(4)	C(3)-H(3B)	0.9900
C(2)-H(2A)	1.0000	C(3)-C(4)	1.542(5)
C(2)-H(2B)	1.0000	C(4)-H(4A)	0.9900
C(2)-C(3)	1.555(4)	C(4)-H(4B)	0.9900
C(2)-C(3')	1.476(15)	C(4)-C(5)	1.505(6)
C(6)-H(6A)	0.9900	C(5)-H(5A)	0.9800
C(6)-H(6B)	0.9900	C(5)-H(5B)	0.9800
C(6)-C(7)	1.532(4)	C(5)-H(5C)	0.9800
C(7)-H(7A)	0.9800	C(3')-H(3'A)	0.9900
C(7)-H(7B)	0.9800	C(3')-H(3'B)	0.9900
C(7)-H(7C)	0.9800	C(3')-C(4')	1.536(11)
C(8)-H(8A)	0.9900	C(4')-H(4'A)	0.9900
C(8)-H(8B)	0.9900	C(4')-H(4'B)	0.9900
C(8)-C(9)	1.518(4)	C(4')-C(5')	1.510(10)
C(9)-H(9A)	0.9800	C(5')-H(5'A)	0.9800
C(9)-H(9B)	0.9800	C(5')-H(5'B)	0.9800
C(9)-H(9C)	0.9800	C(5')-H(5'C)	0.9800
C(10)-H(10A)	0.9900		
C(10)-H(10B)	0.9900	C(6)-Ge(1)-C(2)	110.93(13)
C(10)-C(11)	1.532(4)	C(6)-Ge(1)-C(8)	109.15(12)
C(11)-H(11A)	0.9800	C(8)-Ge(1)-C(2)	106.68(11)
C(11)-H(11B)	0.9800	C(10)-Ge(1)-C(2)	108.44(12)
C(11)-H(11C)	0.9800	C(10)-Ge(1)-C(6)	110.45(15)
C(12)-C(13)	1.388(4)	C(10)-Ge(1)-C(8)	111.13(13)
C(12)-C(17)	1.386(4)	C(1)-N(1)-H(1)	117.0
C(13)-H(13)	0.9500	C(1)-N(1)-C(12)	125.9(2)
C(13)-C(14)	1.390(4)	C(12)-N(1)-H(1)	117.0

O(1)-C(1)-N(1)	122.5(2)	H(9B)-C(9)-H(9C)	109.5
O(1)-C(1)-C(2)	121.8(2)	Ge(1)-C(10)-H(10A)	108.8
N(1)-C(1)-C(2)	115.7(2)	Ge(1)-C(10)-H(10B)	108.8
Ge(1)-C(2)-H(2A)	109.0	H(10A)-C(10)-H(10B)	107.7
Ge(1)-C(2)-H(2B)	102.1	C(11)-C(10)-Ge(1)	113.7(2)
C(1)-C(2)-Ge(1)	109.31(18)	C(11)-C(10)-H(10A)	108.8
C(1)-C(2)-H(2A)	109.0	C(11)-C(10)-H(10B)	108.8
C(1)-C(2)-H(2B)	102.1	C(10)-C(11)-H(11A)	109.5
C(1)-C(2)-C(3)	112.0(3)	C(10)-C(11)-H(11B)	109.5
C(3)-C(2)-Ge(1)	108.6(2)	C(10)-C(11)-H(11C)	109.5
C(3)-C(2)-H(2A)	109.0	H(11A)-C(11)-H(11B)	109.5
C(3')-C(2)-Ge(1)	123.8(8)	H(11A)-C(11)-H(11C)	109.5
C(3')-C(2)-C(1)	114.0(10)	H(11B)-C(11)-H(11C)	109.5
C(3')-C(2)-H(2B)	102.1	C(13)-C(12)-N(1)	122.1(2)
Ge(1)-C(6)-H(6A)	108.7	C(17)-C(12)-N(1)	118.5(2)
Ge(1)-C(6)-H(6B)	108.7	C(17)-C(12)-C(13)	119.5(2)
H(6A)-C(6)-H(6B)	107.6	C(12)-C(13)-H(13)	120.2
C(7)-C(6)-Ge(1)	114.2(2)	C(12)-C(13)-C(14)	119.6(3)
C(7)-C(6)-H(6A)	108.7	C(14)-C(13)-H(13)	120.2
C(7)-C(6)-H(6B)	108.7	C(13)-C(14)-H(14)	119.6
C(6)-C(7)-H(7A)	109.5	C(15)-C(14)-C(13)	120.7(3)
C(6)-C(7)-H(7B)	109.5	C(15)-C(14)-H(14)	119.6
C(6)-C(7)-H(7C)	109.5	C(14)-C(15)-H(15)	120.2
H(7A)-C(7)-H(7B)	109.5	C(14)-C(15)-C(16)	119.6(3)
H(7A)-C(7)-H(7C)	109.5	C(16)-C(15)-H(15)	120.2
H(7B)-C(7)-H(7C)	109.5	C(15)-C(16)-H(16)	119.9
Ge(1)-C(8)-H(8A)	108.8	C(15)-C(16)-C(17)	120.3(3)
Ge(1)-C(8)-H(8B)	108.8	C(17)-C(16)-H(16)	119.9
H(8A)-C(8)-H(8B)	107.7	C(12)-C(17)-H(17)	119.9
C(9)-C(8)-Ge(1)	113.66(19)	C(16)-C(17)-C(12)	120.3(3)
C(9)-C(8)-H(8A)	108.8	C(16)-C(17)-H(17)	119.9
C(9)-C(8)-H(8B)	108.8	C(2)-C(3)-H(3A)	108.7
C(8)-C(9)-H(9A)	109.5	C(2)-C(3)-H(3B)	108.7
C(8)-C(9)-H(9B)	109.5	H(3A)-C(3)-H(3B)	107.6
C(8)-C(9)-H(9C)	109.5	C(4)-C(3)-C(2)	114.2(3)
H(9A)-C(9)-H(9B)	109.5	C(4)-C(3)-H(3A)	108.7
H(9A)-C(9)-H(9C)	109.5	C(4)-C(3)-H(3B)	108.7

C(3)-C(4)-H(4A)	108.7
C(3)-C(4)-H(4B)	108.7
H(4A)-C(4)-H(4B)	107.6
C(5)-C(4)-C(3)	114.1(4)
C(5)-C(4)-H(4A)	108.7
C(5)-C(4)-H(4B)	108.7
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(2)-C(3')-H(3'A)	108.9
C(2)-C(3')-H(3'B)	108.9
C(2)-C(3')-C(4')	113.4(13)
H(3'A)-C(3')-H(3'B)	107.7
C(4')-C(3')-H(3'A)	108.9
C(4')-C(3')-H(3'B)	108.9
C(3')-C(4')-H(4'A)	109.7
C(3')-C(4')-H(4'B)	109.7
H(4'A)-C(4')-H(4'B)	108.2
C(5')-C(4')-C(3')	109.9(13)
C(5')-C(4')-H(4'A)	109.7
C(5')-C(4')-H(4'B)	109.7
C(4')-C(5')-H(5'A)	109.5
C(4')-C(5')-H(5'B)	109.5
C(4')-C(5')-H(5'C)	109.5
H(5'A)-C(5')-H(5'B)	109.5
H(5'A)-C(5')-H(5'C)	109.5
H(5'B)-C(5')-H(5'C)	109.5

Table S30. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ge(1)	18(1)	17(1)	25(1)	3(1)	2(1)	-2(1)
O(1)	27(1)	17(1)	35(1)	2(1)	7(1)	-1(1)
N(1)	22(1)	15(1)	30(1)	1(1)	0(1)	-2(1)
C(1)	15(1)	21(1)	27(1)	1(1)	-2(1)	-3(1)
C(2)	22(1)	22(1)	29(1)	7(1)	-3(1)	-4(1)
C(6)	27(2)	21(2)	67(2)	5(2)	9(2)	3(1)
C(7)	30(2)	24(2)	109(3)	18(2)	10(2)	7(1)
C(8)	23(1)	22(1)	31(2)	1(1)	9(1)	-2(1)
C(9)	39(2)	24(2)	51(2)	-1(1)	13(2)	-3(1)
C(10)	32(2)	54(2)	28(2)	8(2)	-4(1)	-18(2)
C(11)	46(2)	98(3)	38(2)	15(2)	-17(2)	-36(2)
C(12)	23(1)	16(1)	21(1)	-2(1)	-1(1)	-2(1)
C(13)	28(2)	24(2)	28(2)	-1(1)	-5(1)	1(1)
C(14)	46(2)	28(2)	25(2)	6(1)	-5(1)	-1(1)
C(15)	49(2)	34(2)	24(2)	-2(1)	13(1)	-4(2)
C(16)	37(2)	28(2)	35(2)	-5(1)	11(1)	5(1)
C(17)	30(2)	20(1)	29(2)	-2(1)	2(1)	4(1)
C(3)	23(2)	35(3)	28(2)	-1(2)	1(2)	-6(2)
C(4)	28(2)	63(3)	25(2)	-13(2)	4(2)	-9(2)
C(5)	30(2)	98(5)	44(3)	26(3)	-8(2)	-3(2)
C(3')	23(2)	35(3)	28(2)	-1(2)	1(2)	-6(2)
C(4')	23(4)	30(11)	27(8)	-13(8)	-2(5)	-7(6)
C(5')	39(9)	50(12)	26(8)	-15(8)	-1(5)	-10(9)

Table S31. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for **3b**.

	x	y	z	U(eq)
H(1)	2352	5692	6416	26
H(2A)	3177	5804	5811	29
H(2B)	3226	5833	5878	29
H(6A)	6085	3519	5530	46
H(6B)	7011	4024	5865	46
H(7A)	5254	1955	6026	81
H(7B)	6148	2486	6370	81
H(7C)	6582	1587	5976	81
H(8A)	6484	7027	5669	30
H(8B)	5282	7043	5432	30
H(9A)	5730	8447	6205	57
H(9B)	4495	8402	5993	57
H(9C)	5520	9239	5770	57
H(10A)	4786	6371	6680	45
H(10B)	4938	4674	6740	45
H(11A)	6964	4968	6690	91
H(11B)	6452	5848	7075	91
H(11C)	6786	6670	6655	91
H(13)	3018	2721	6985	32
H(14)	1967	1785	7541	40
H(15)	169	2689	7697	43
H(16)	-578	4576	7304	40
H(17)	444	5500	6743	32
H(3A)	4013	4668	5210	35
H(3B)	4011	3157	5447	35
H(4A)	2470	3196	4982	46
H(4B)	1977	3147	5446	46
H(5A)	1536	5584	5416	86
H(5B)	965	4792	5026	86
H(5C)	2109	5710	4965	86
H(3'A)	3508	3489	5355	35
H(3'B)	3606	5135	5215	35
H(4'A)	1562	3813	5533	32
H(4'B)	1648	5497	5430	32
H(5'A)	1810	5089	4734	58
H(5'B)	845	3976	4877	58
H(5'C)	2124	3431	4801	58

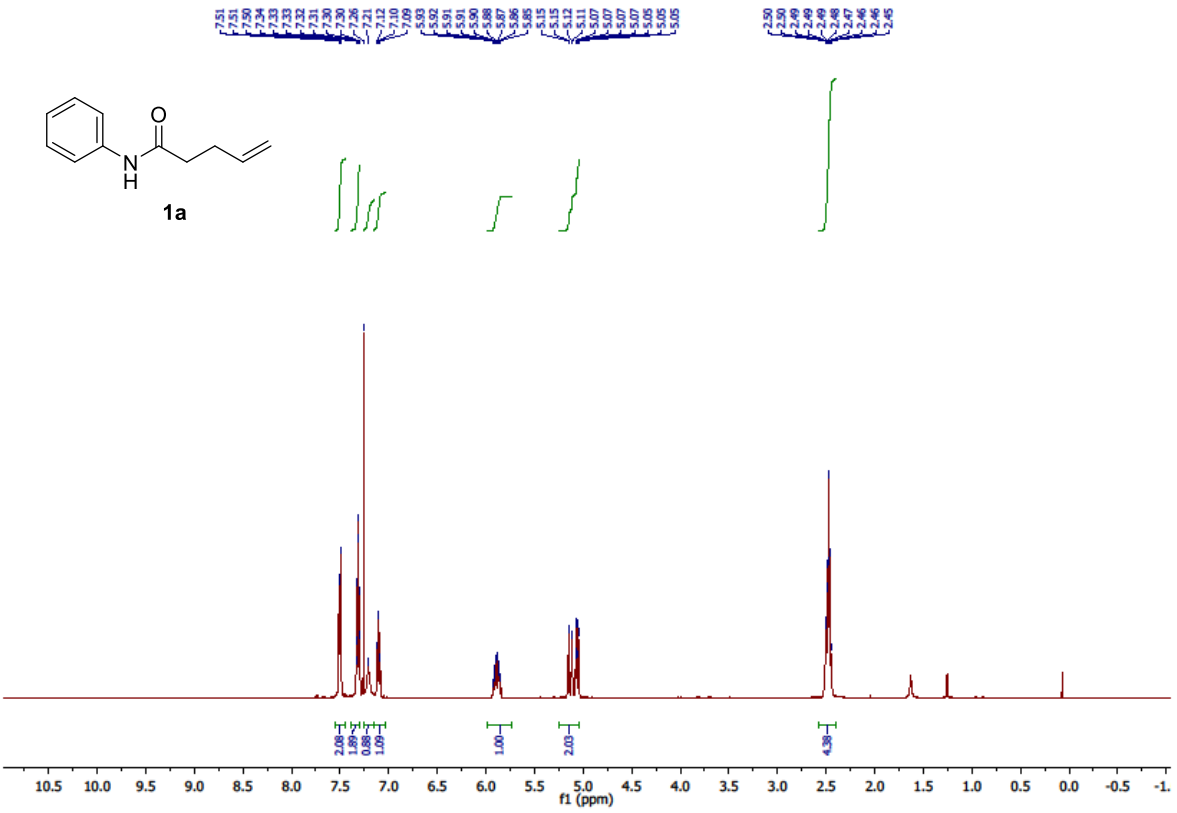
Table S32. Hydrogen bonds for **3b** [Å and °].

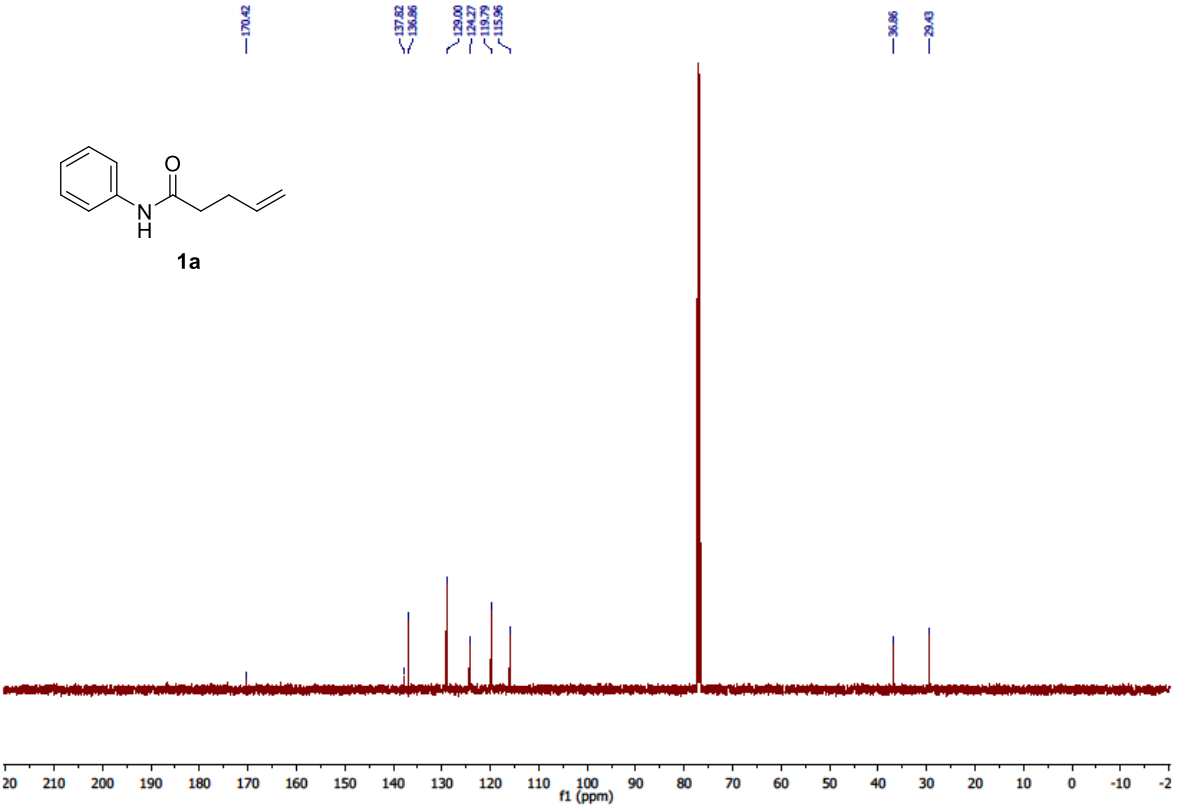
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...O(1)#1	0.88	2.06	2.914(3)	162.2

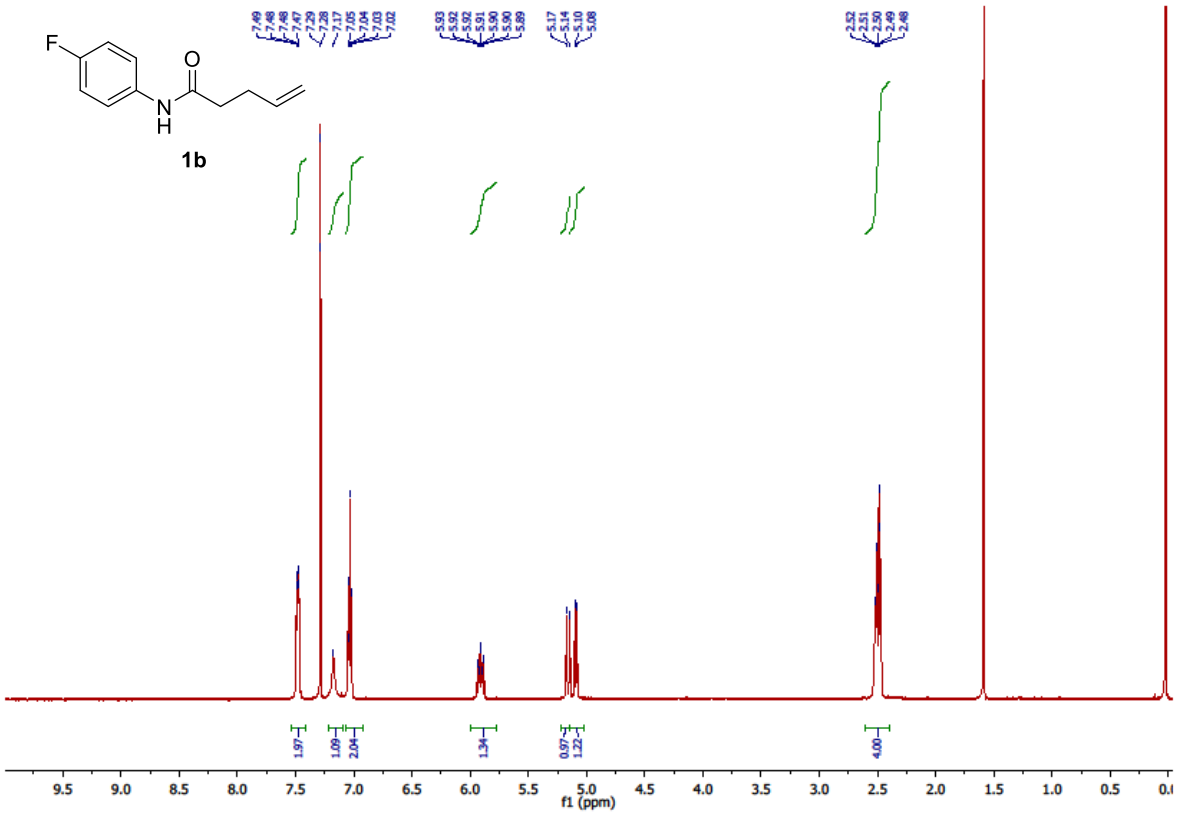
Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,y+1/2,z

NMR SPECTRA



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O
N
H
1b
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7.48
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7.29
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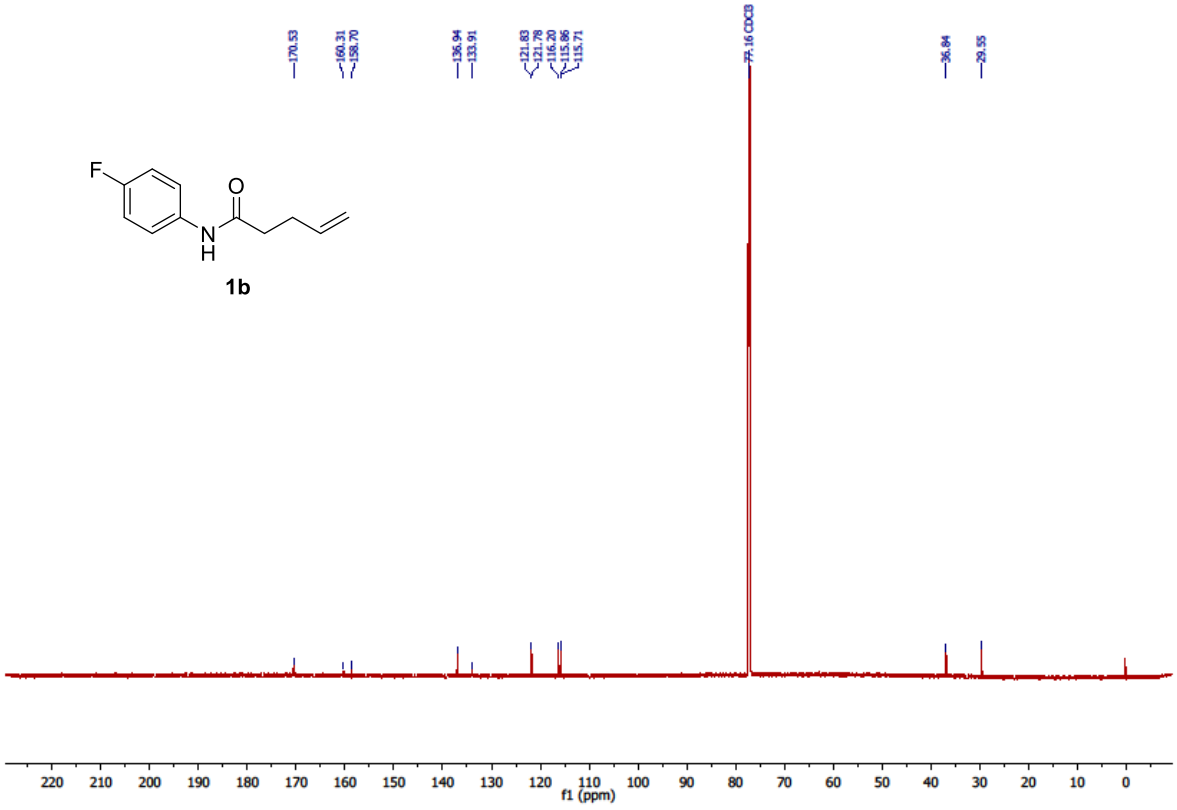
7.05
7.04
7.03
7.02
5.93
5.92
5.92
5.91
5.90
5.90
5.89
5.17
5.14
5.10
5.08
2.52
2.51
2.50
2.49
2.48
1.97
1.09
2.04
1.34
0.97
1.22
4.00
f1 (ppm)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O
N
H
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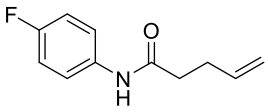
115.71
77.16 CDCl3
36.84
29.55
f1 (ppm)


F
O
N
H

1b

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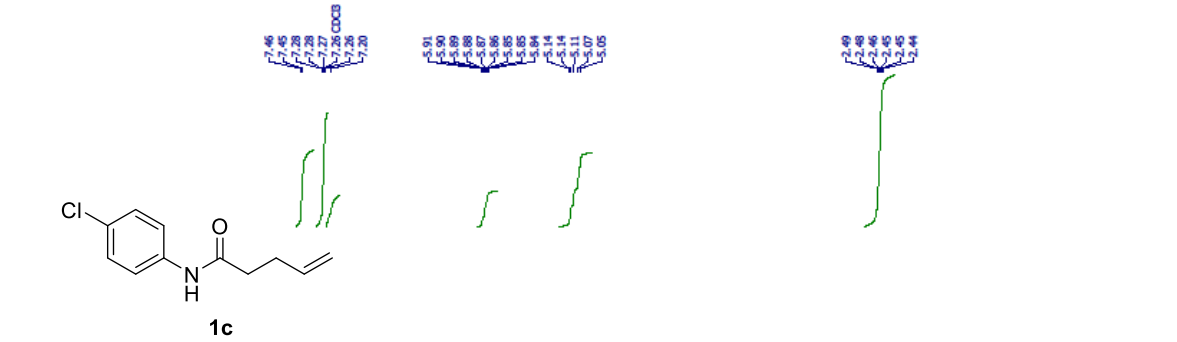
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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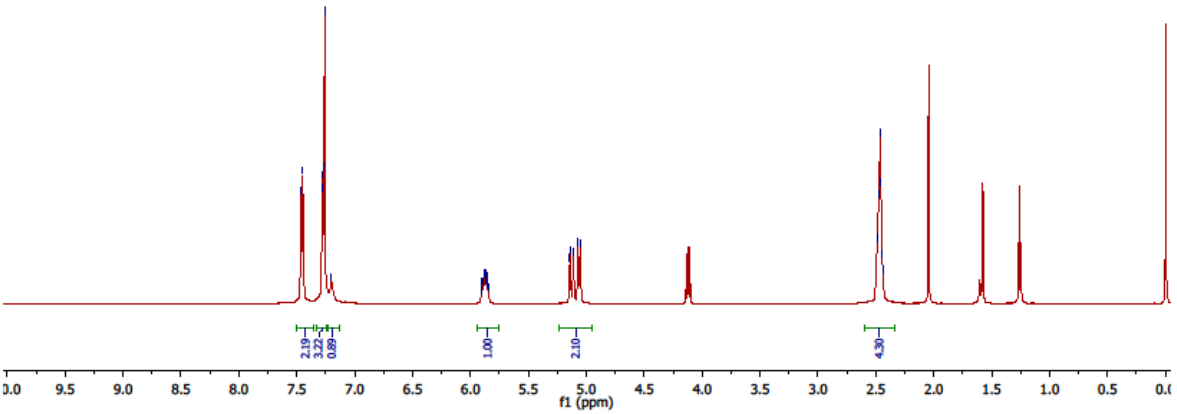
N
H
1c


f1 (ppm)


Cl
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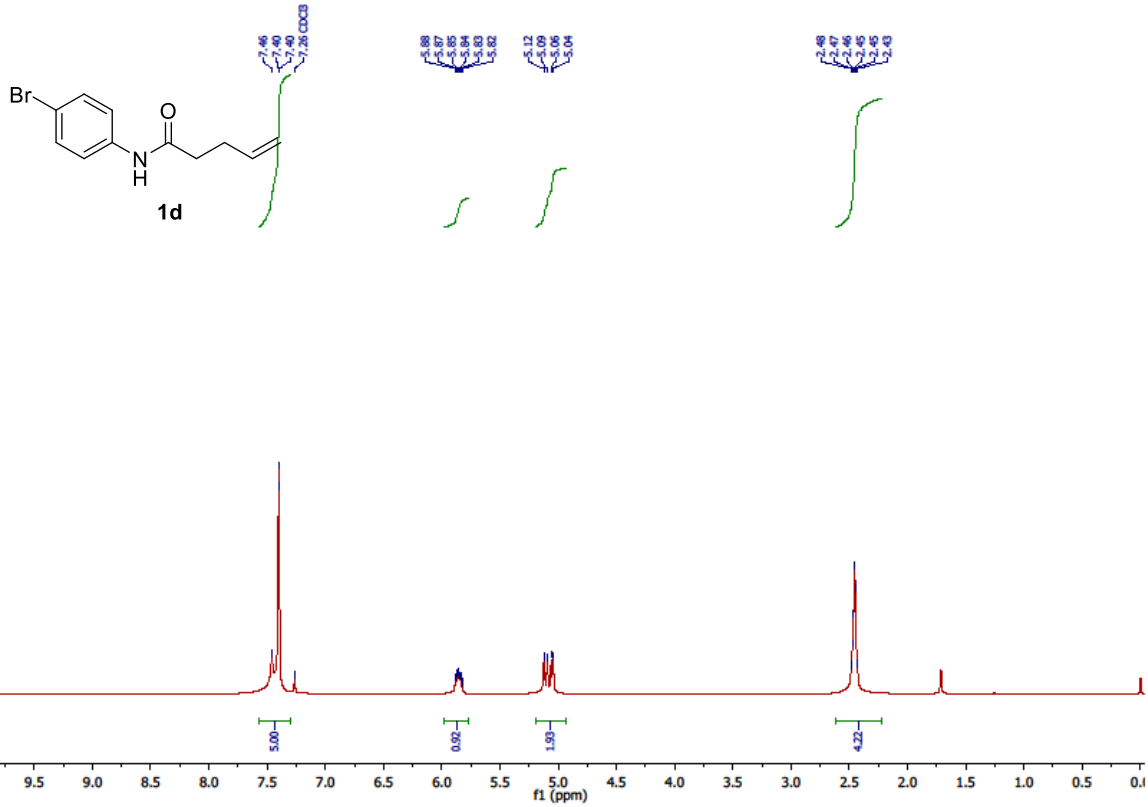
N
H
1c

f1 (ppm)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N
H
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5.68
5.67
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5.62
5.12
5.09
5.06
5.04
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2.45
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1.93
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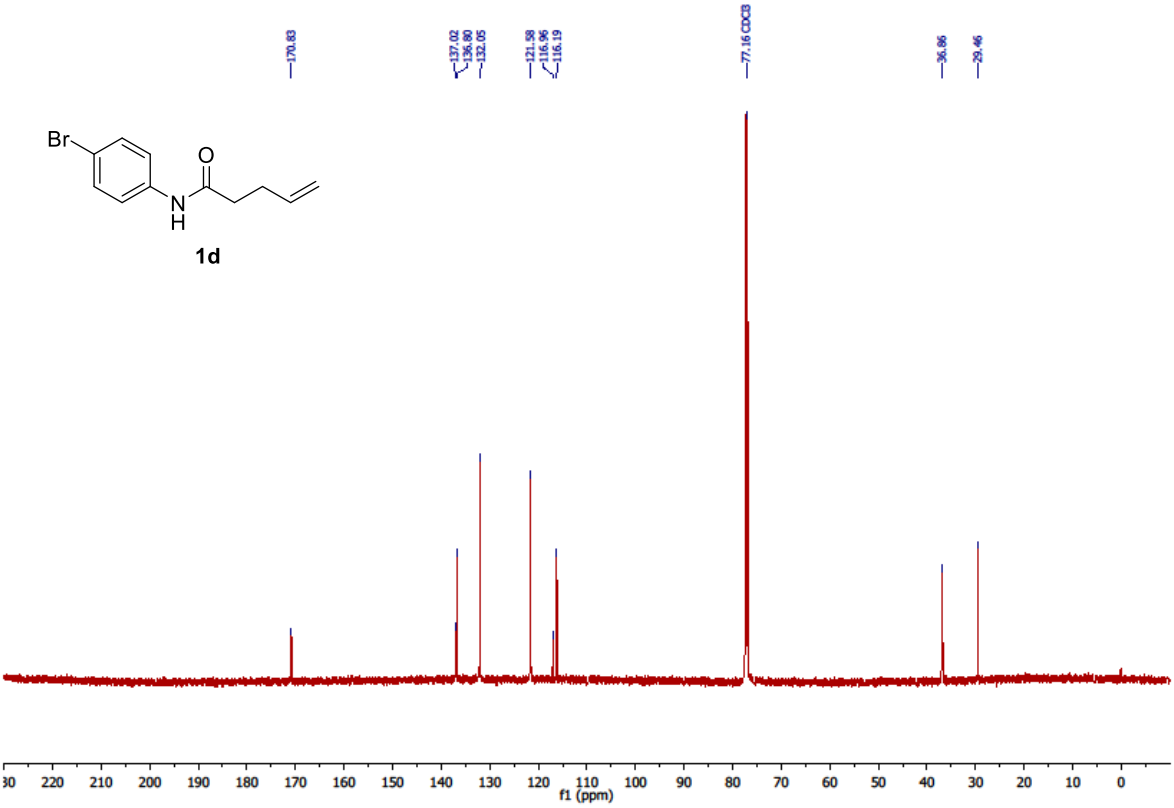
f1 (ppm)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N
H
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132.05
121.58
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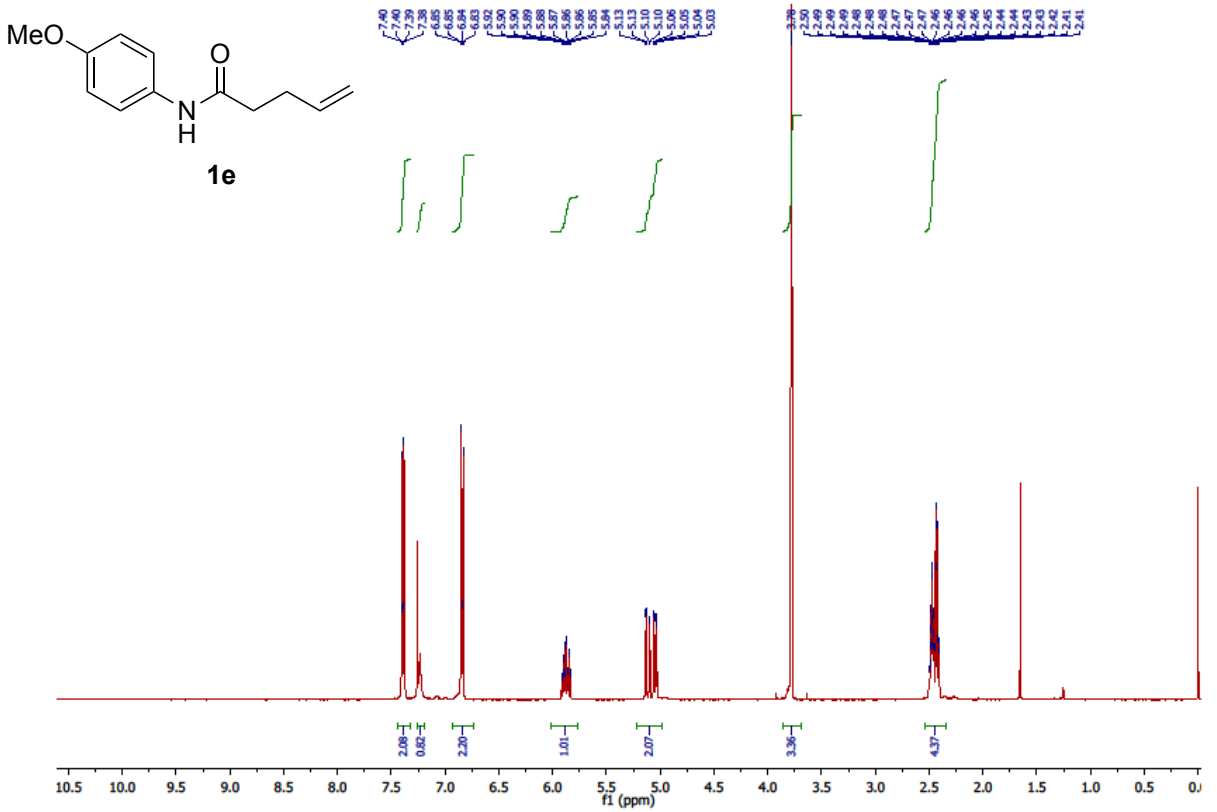
116.19
77.16 CDCl3
36.86
29.46
f1 (ppm)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O
N
H
1e
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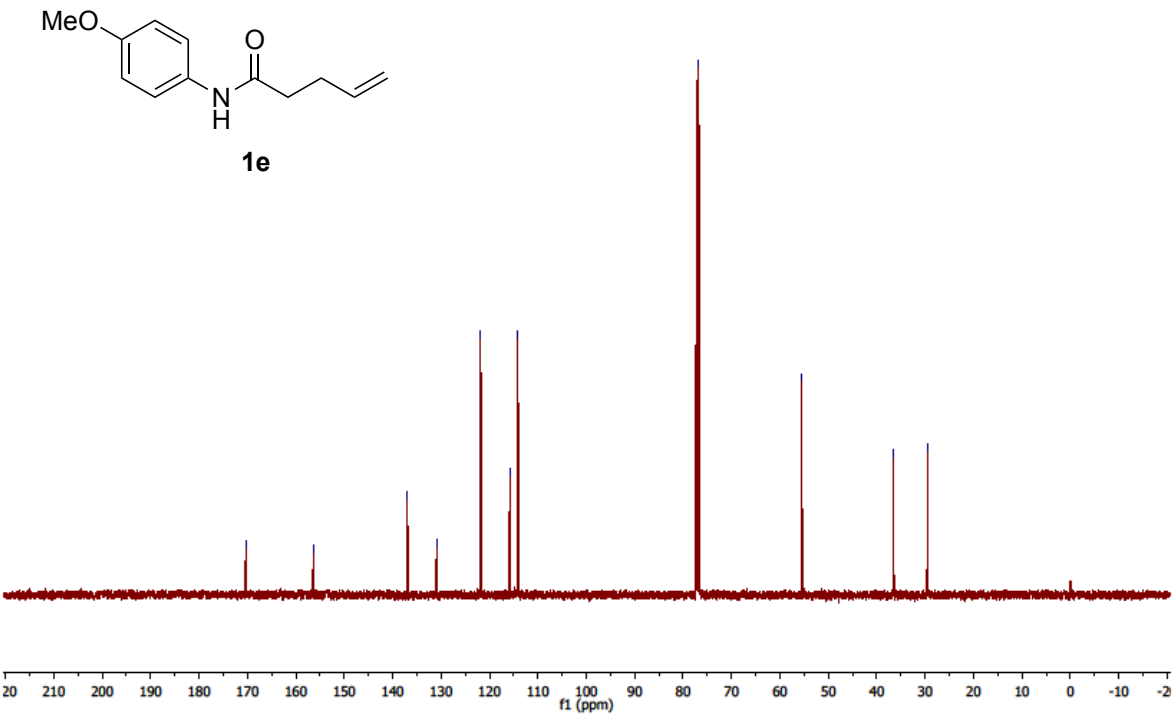
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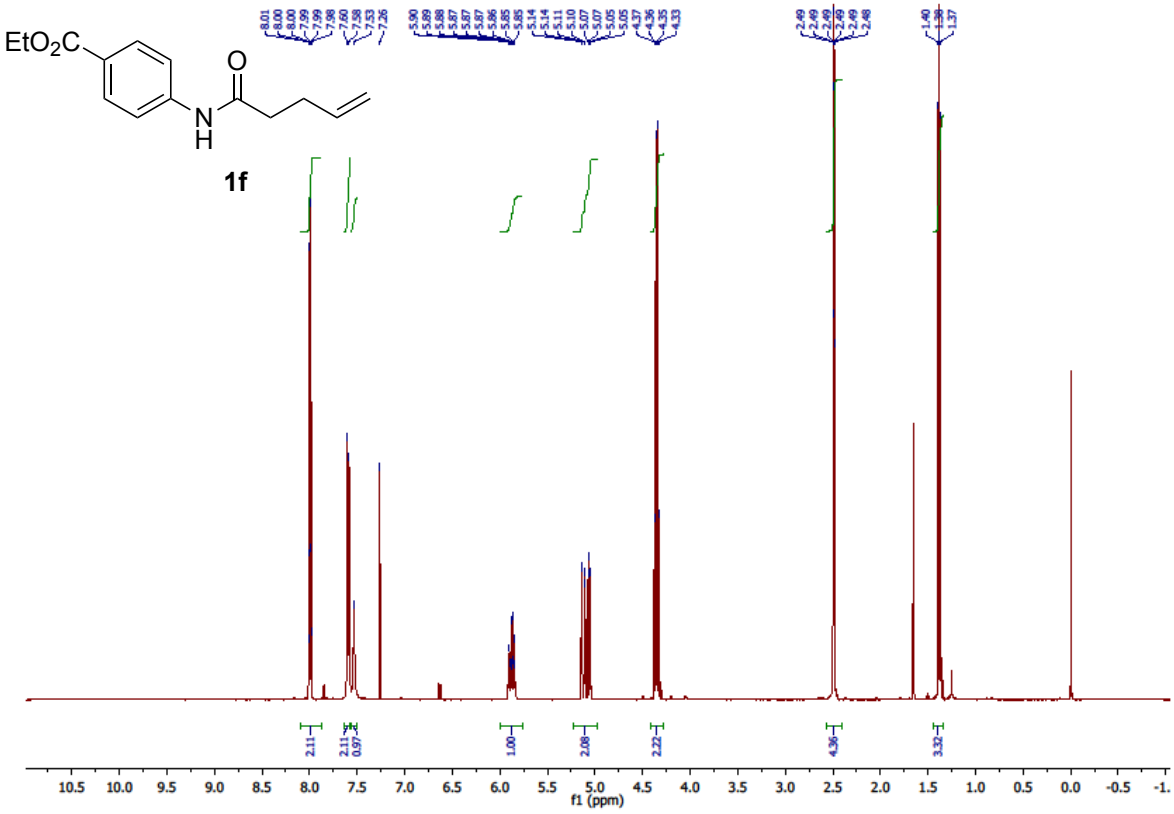
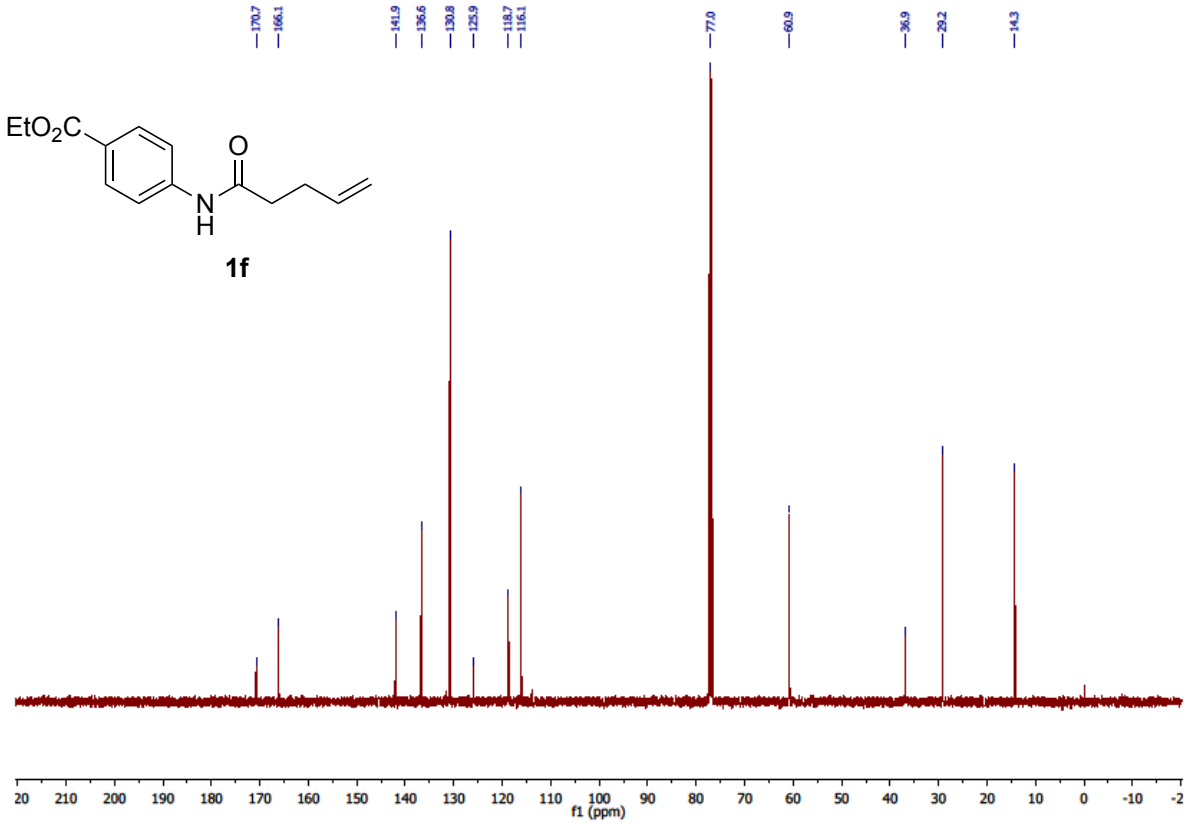
O
N
H
1e
f1 (ppm)


EtO2C
O
N
H
1f
f1 (ppm)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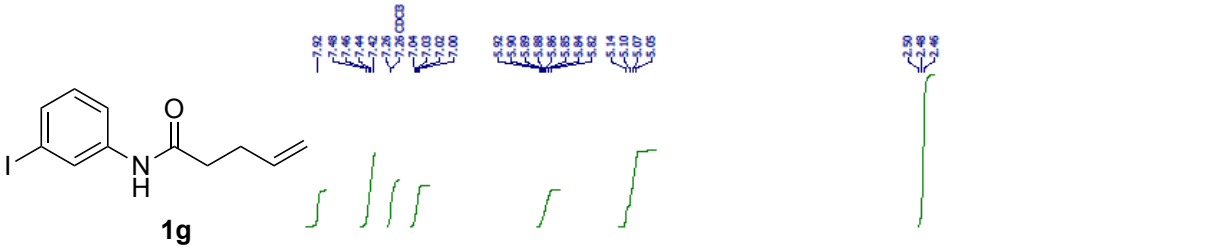
O
N
H
1f
f1 (ppm)



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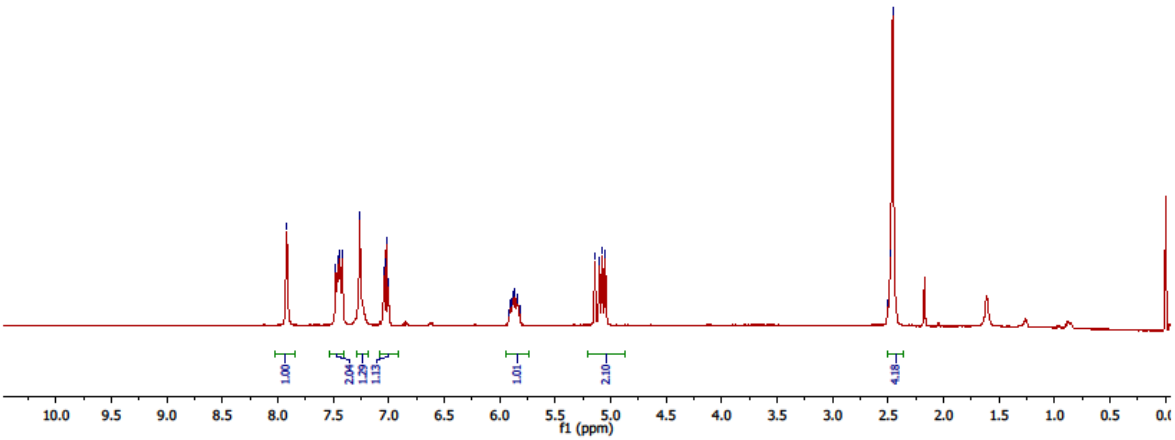

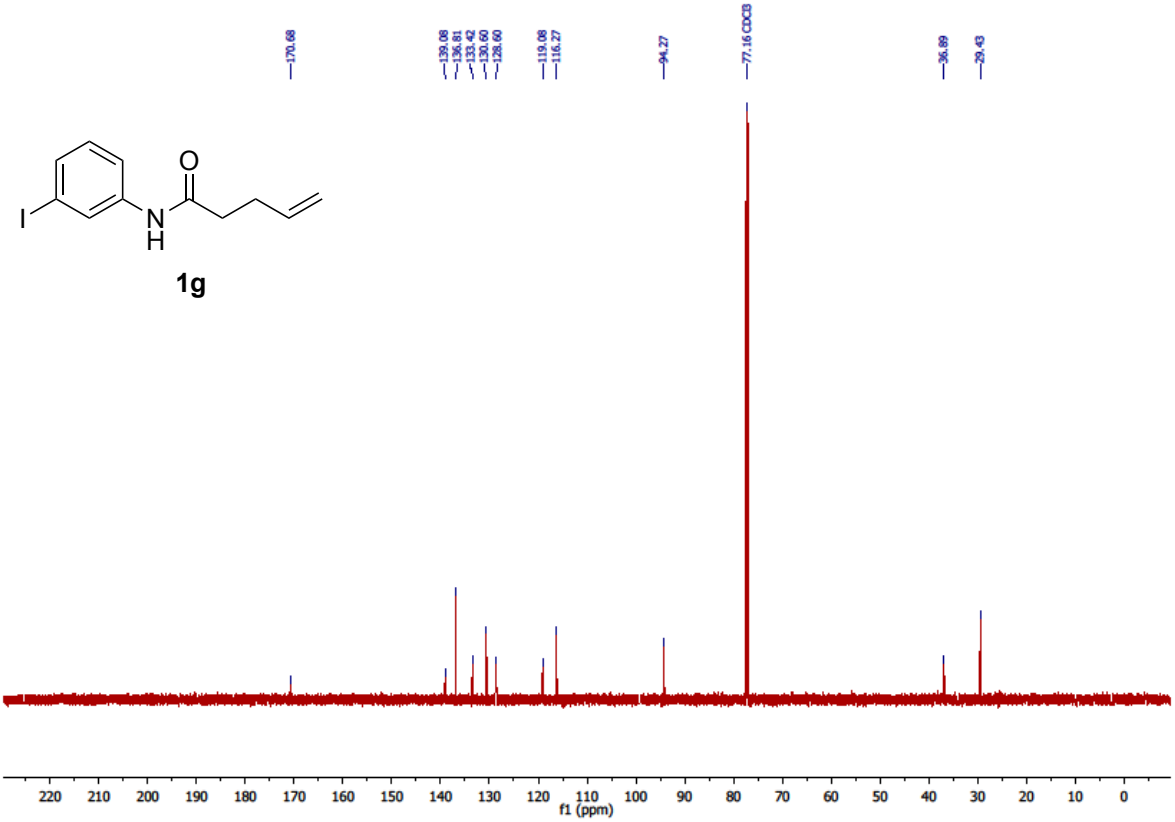

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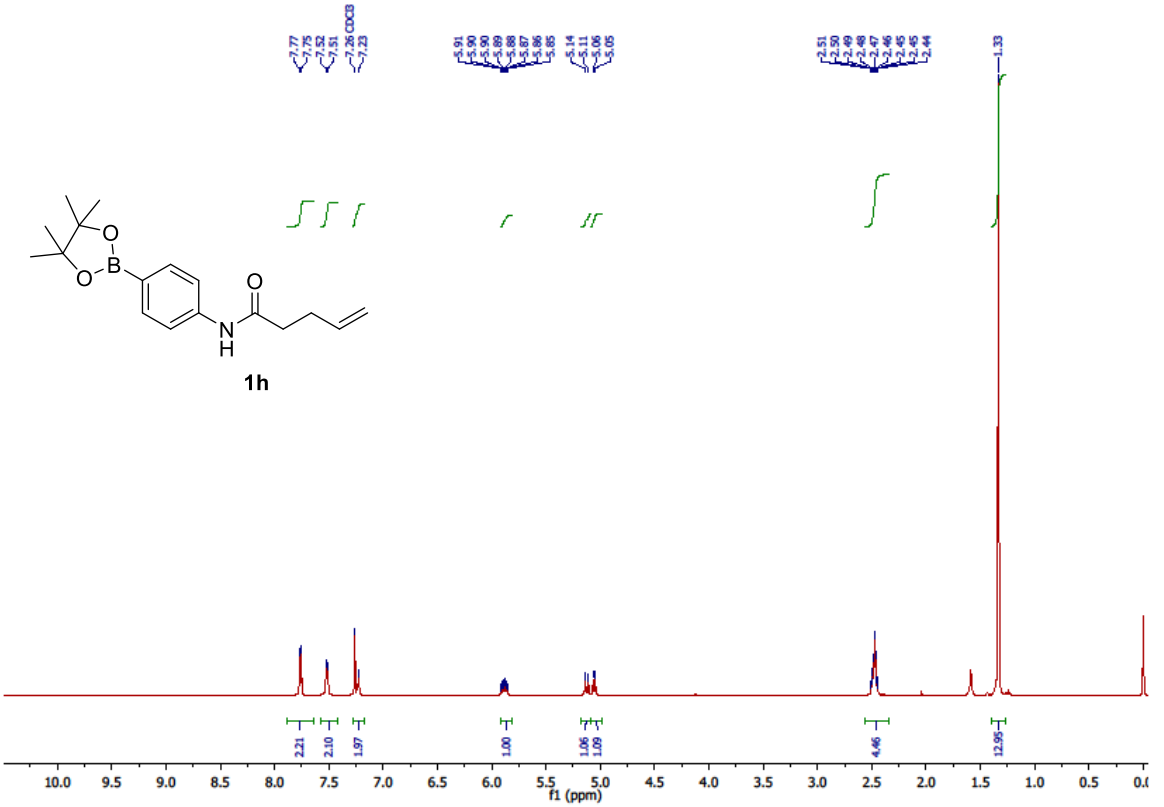
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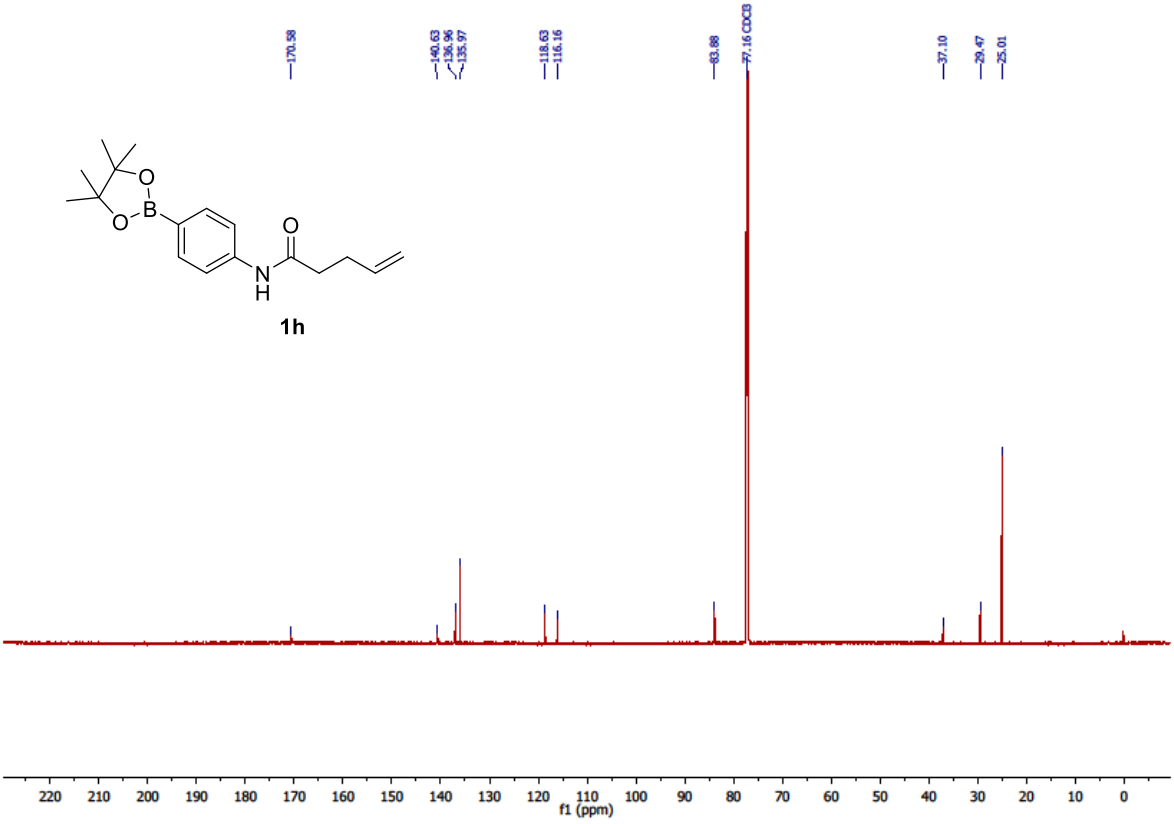
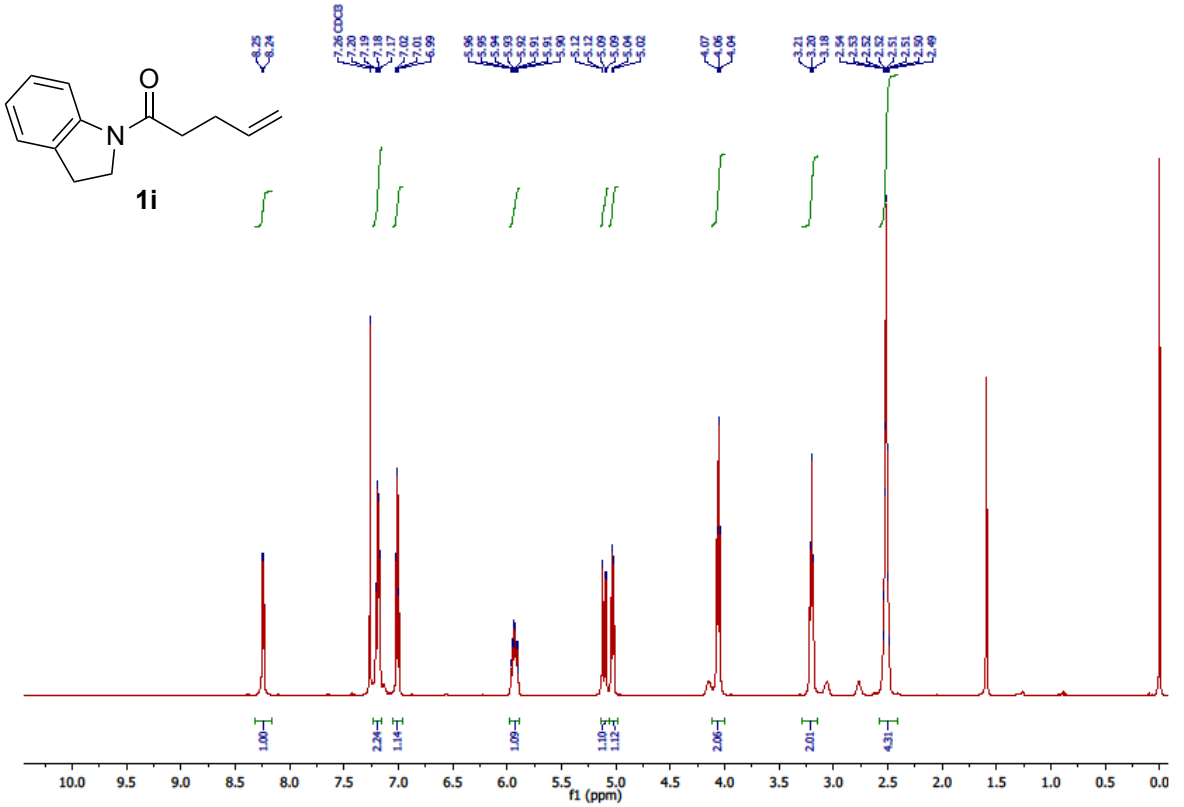
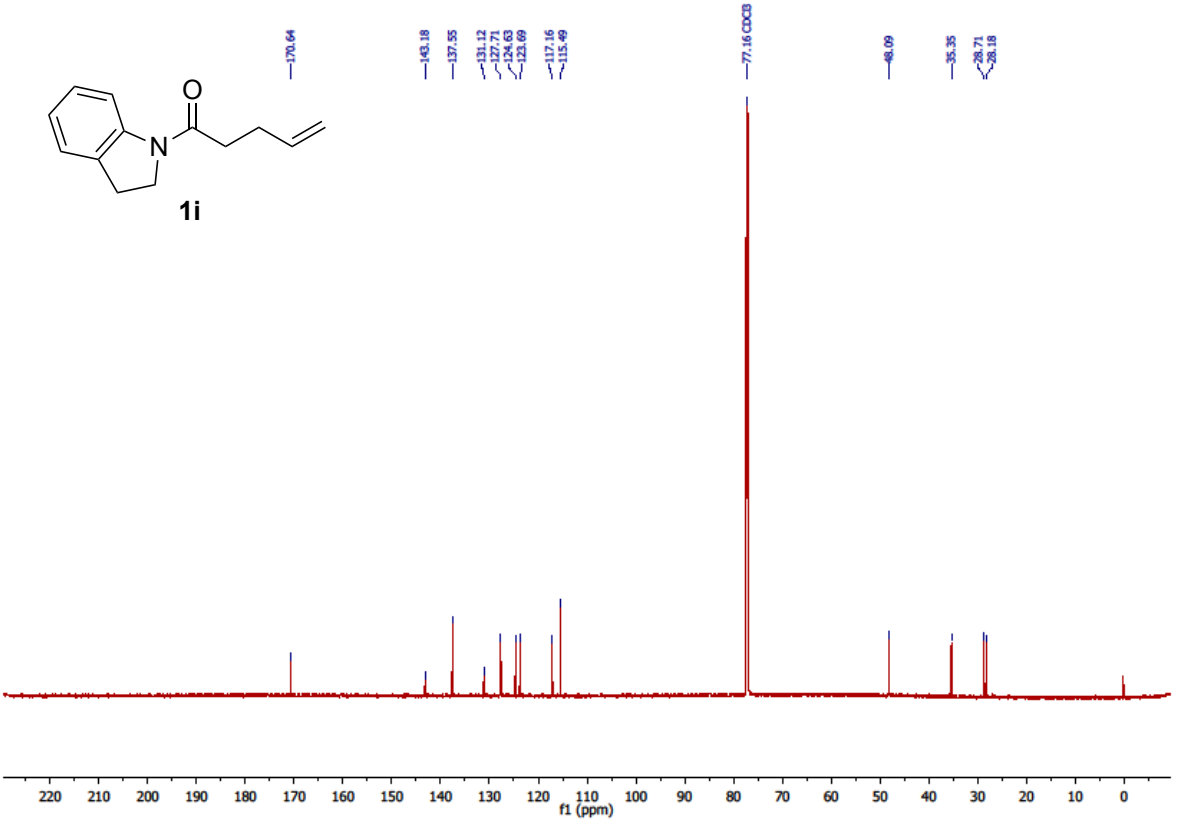
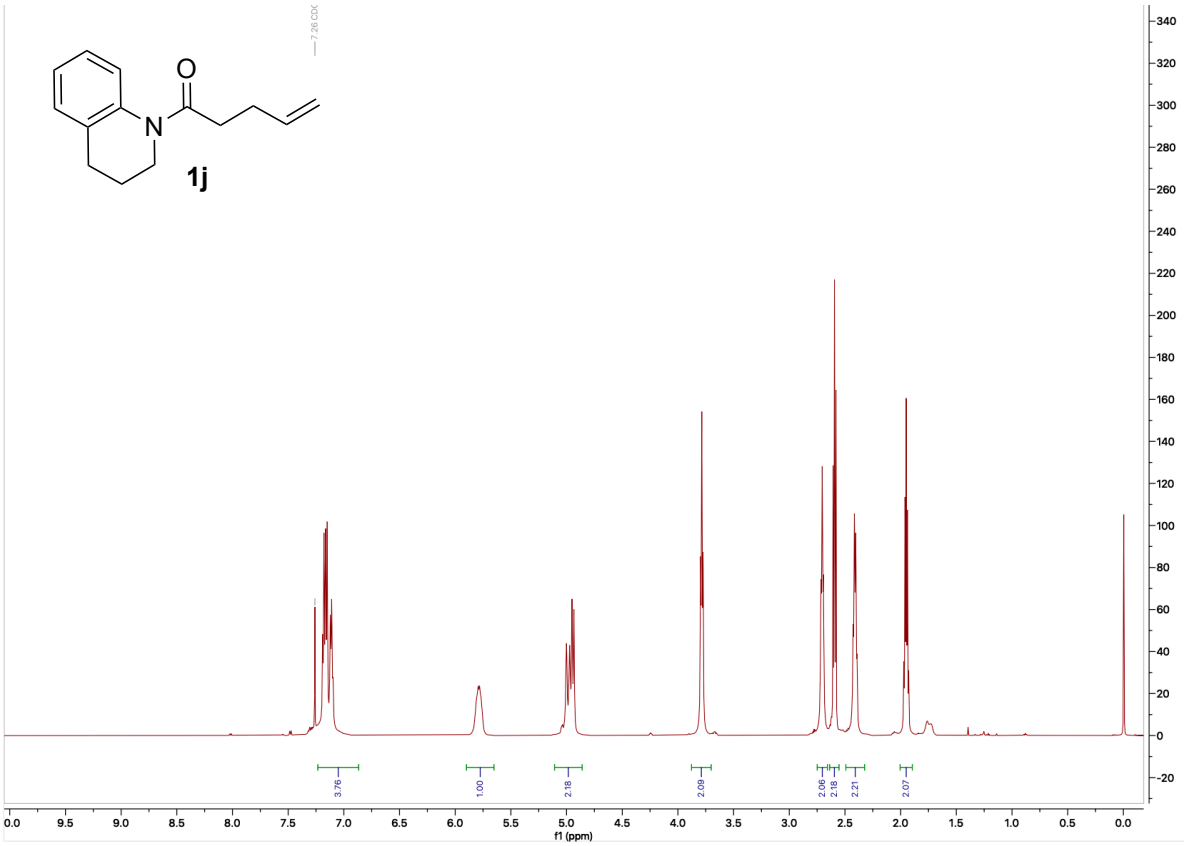
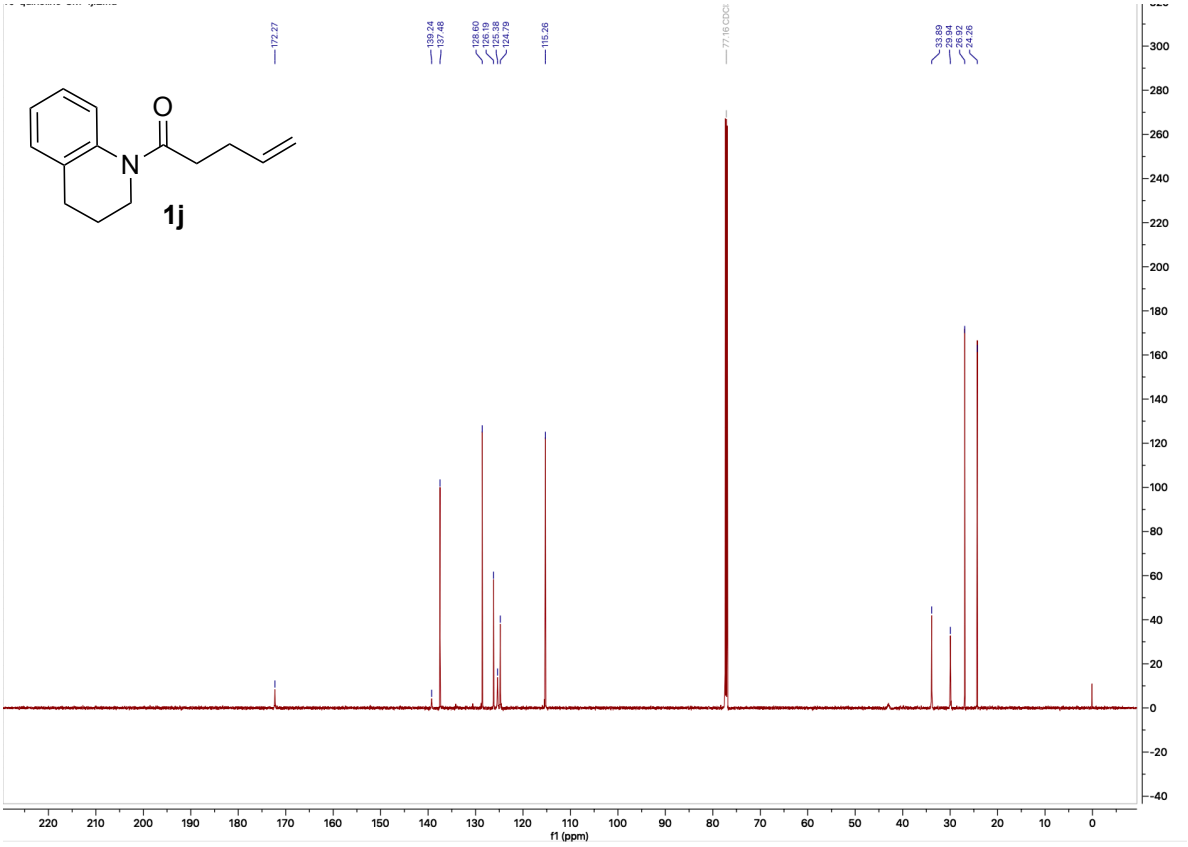
5.91
5.90
5.90
5.89
5.88
5.87
5.86
5.85
5.14
5.11
5.06
5.05
2.51
2.50
2.49
2.48
2.47
2.46
2.45
2.45
2.44
1.33
O
B
O
N
H
O
1h
2.21
2.10
1.97
1.00
1.06
1.09
4.46
12.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

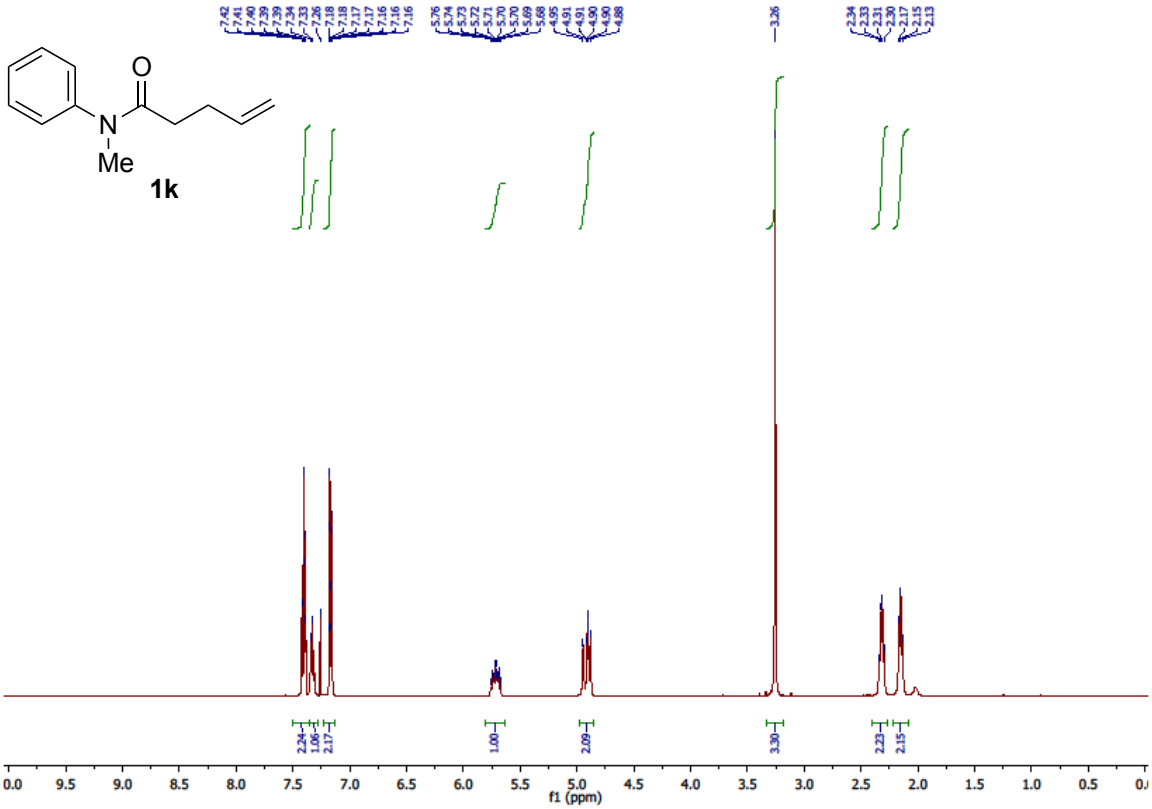

170.58
140.63
136.96
135.97
118.63
116.16
83.88
77.16 CDCl3
37.10
29.47
25.01
O
B
O
N
H
O
1h
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1i
f1 (ppm)


1i
f1 (ppm)


1j
f1 (ppm)


1j
f1 (ppm)


O
N
Me
1k
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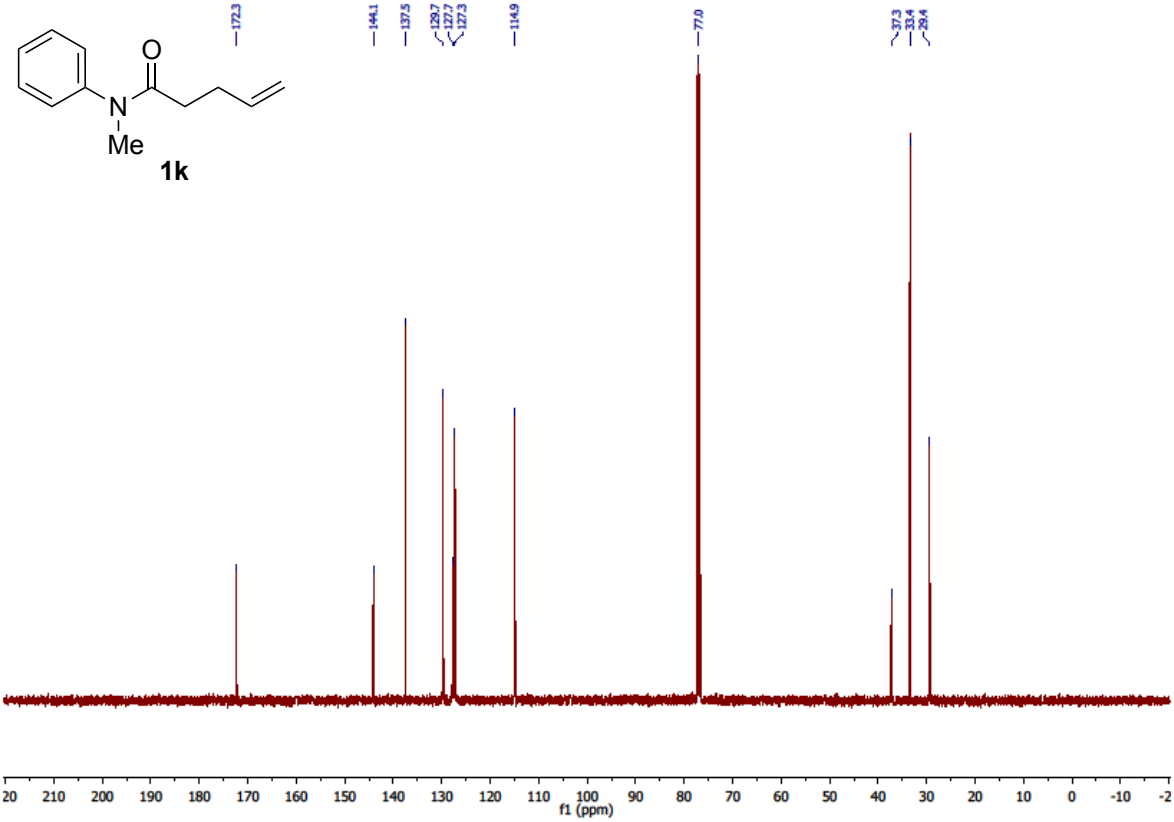
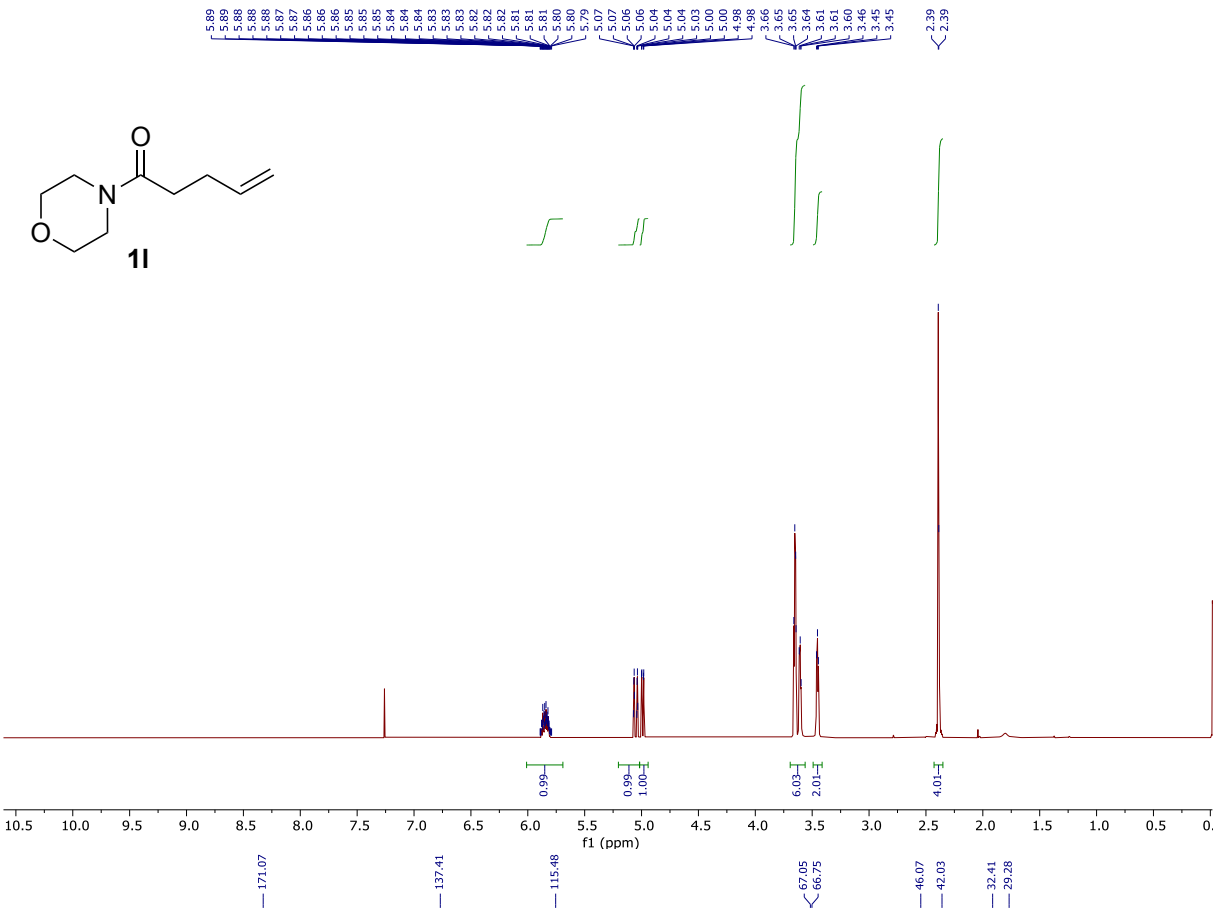
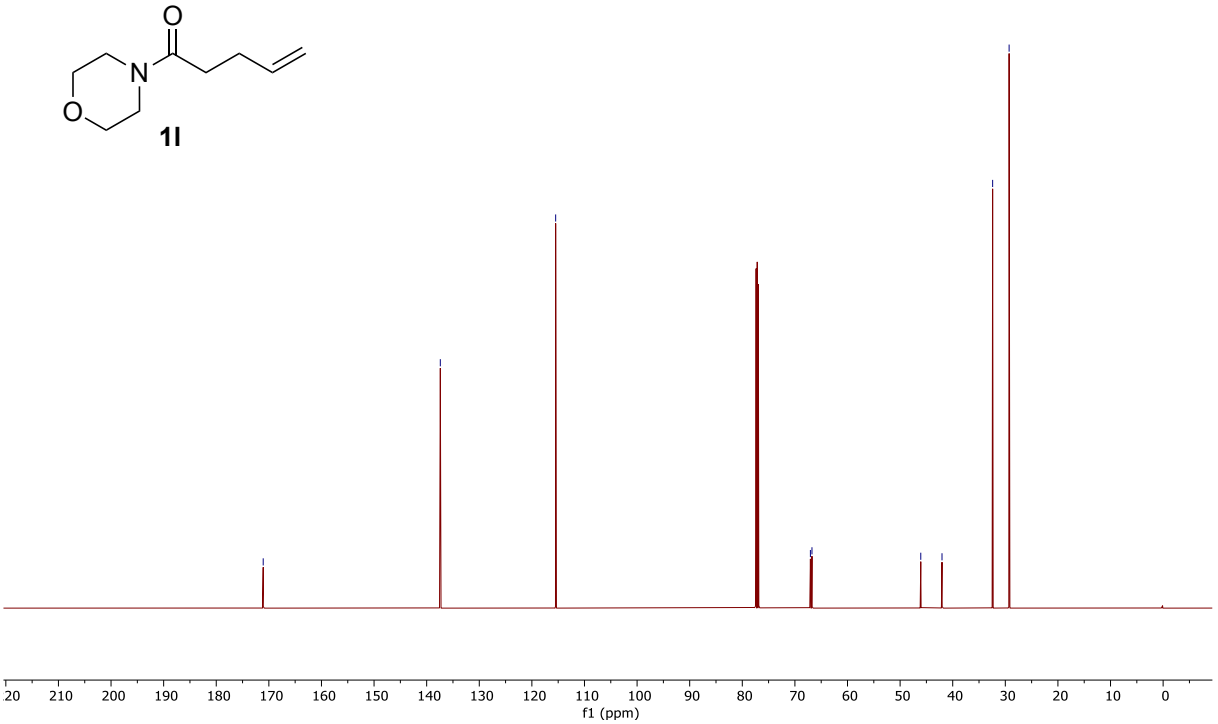
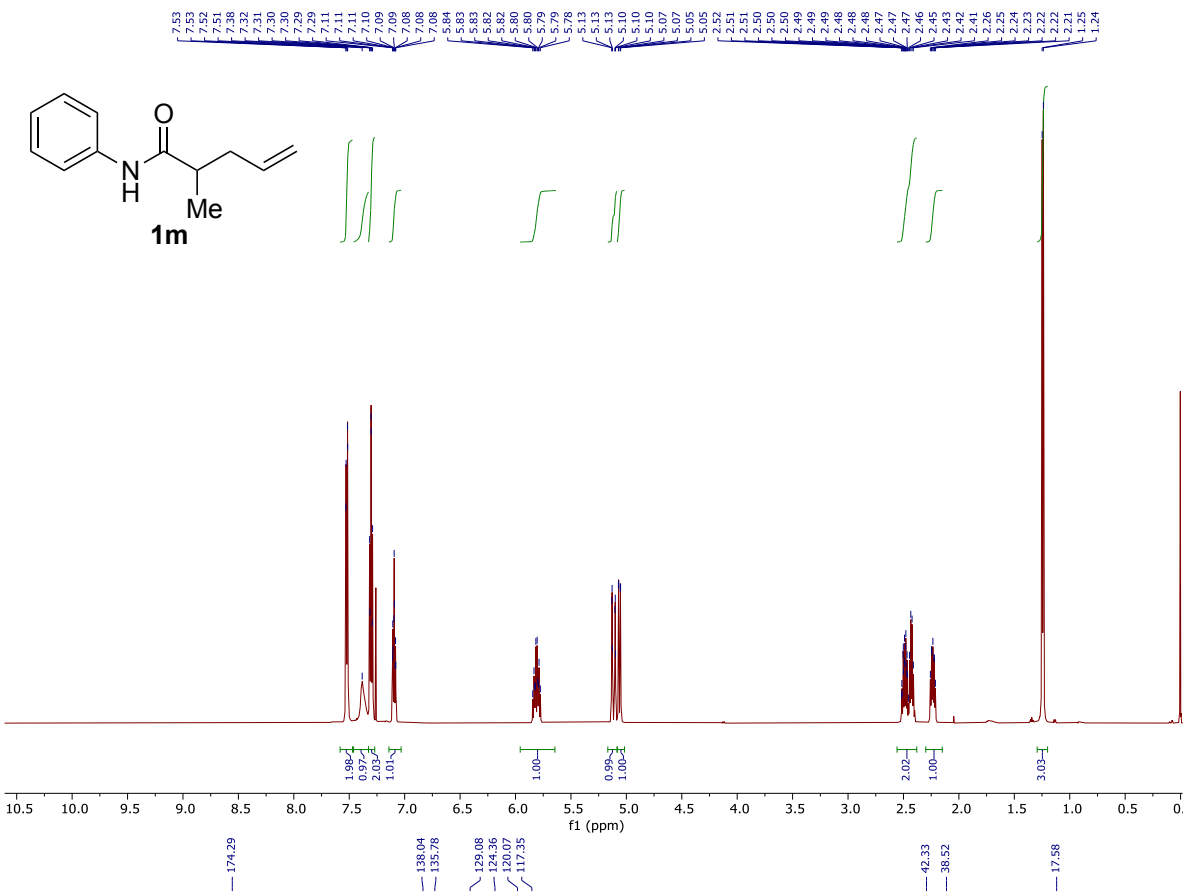
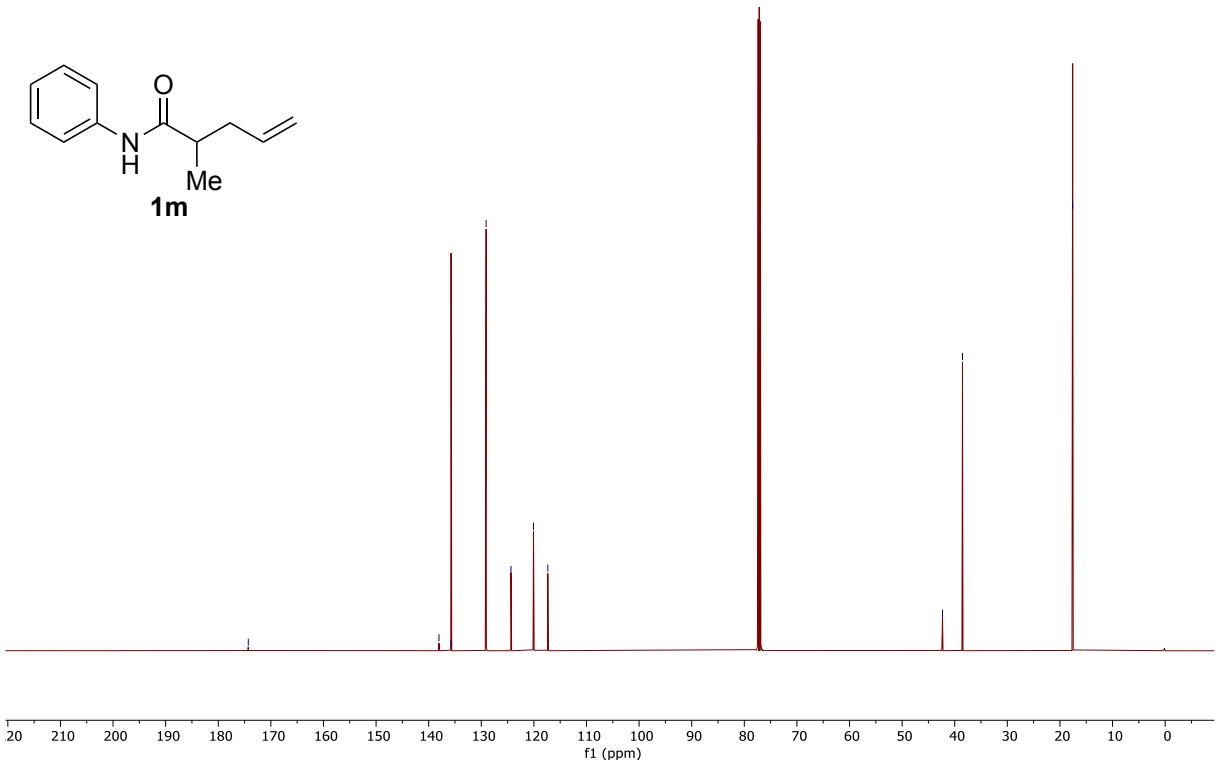
7.41
7.40
7.39
7.39
7.34
7.33
7.26
7.18
7.18
7.17
7.17
7.16
7.16
7.16
5.76
5.74
5.73
5.72
5.71
5.70
5.70
5.69
5.68
4.95
4.91
4.91
4.90
4.89
4.88
3.26
2.34
2.33
2.31
2.30
2.17
2.15
2.13
2.24
1.06
2.17
1.00
2.09
3.30
2.23
2.15
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

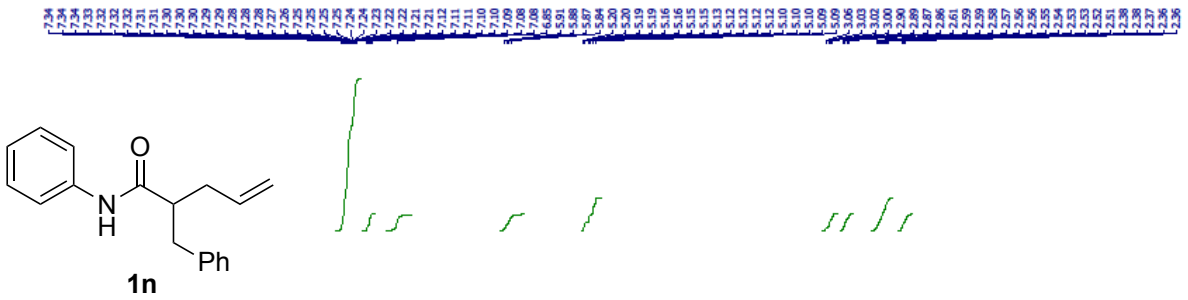

O
N
Me
1k
172.3
144.1
137.5
129.7
127.7
127.3
114.9
77.0
37.3
33.4
28.4
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


1l
f1 (ppm)


1l
f1 (ppm)

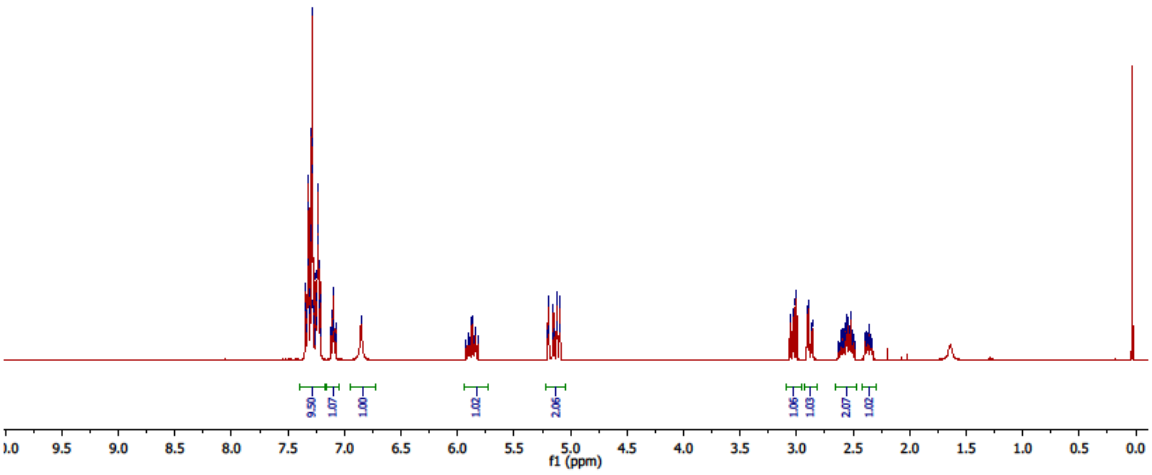

O
N
H
Me
1m
f1 (ppm)

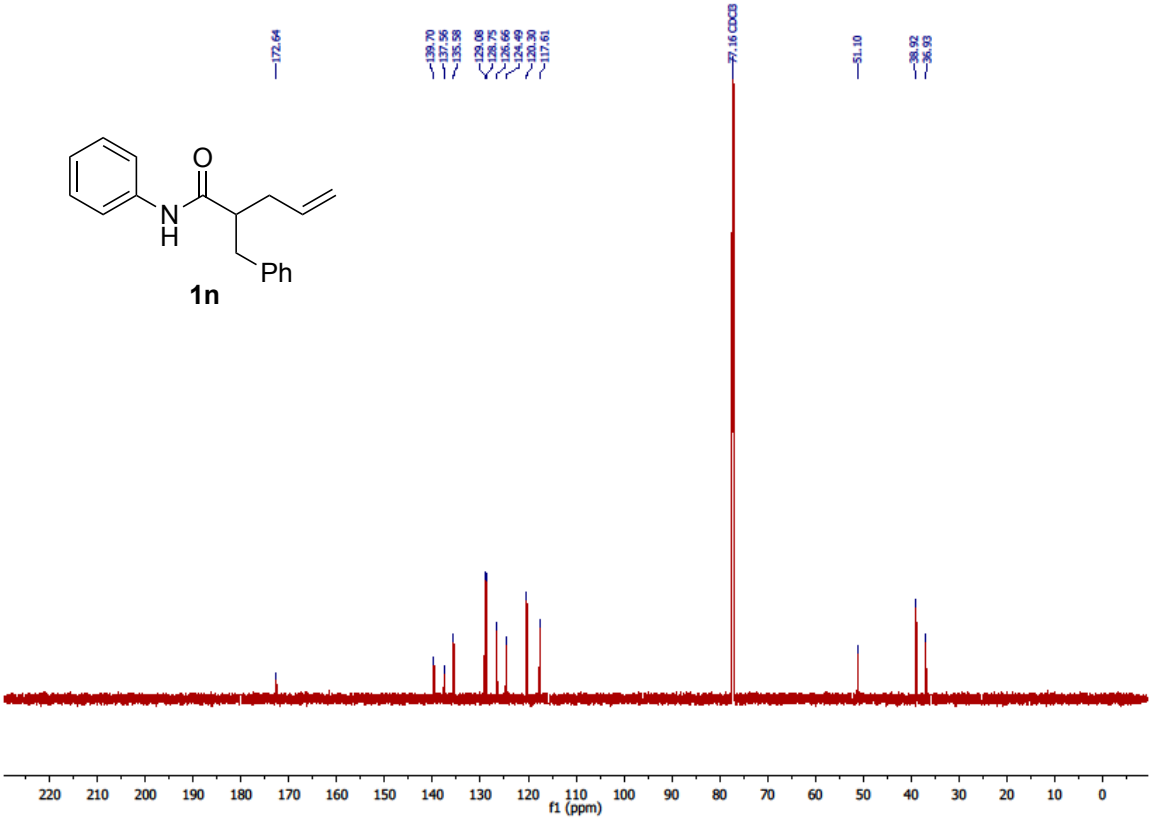

O
N
H
Me
1m
f1 (ppm)



O
N
H
Ph

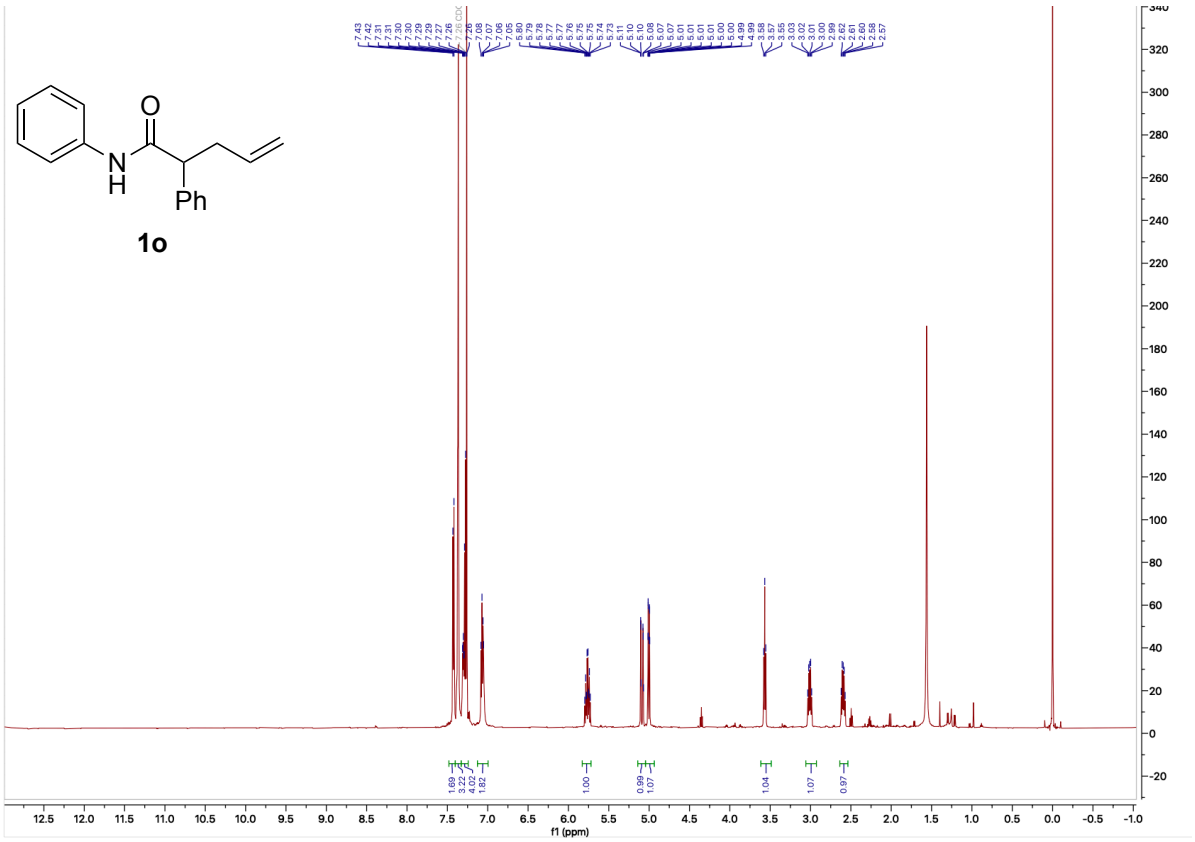
1n

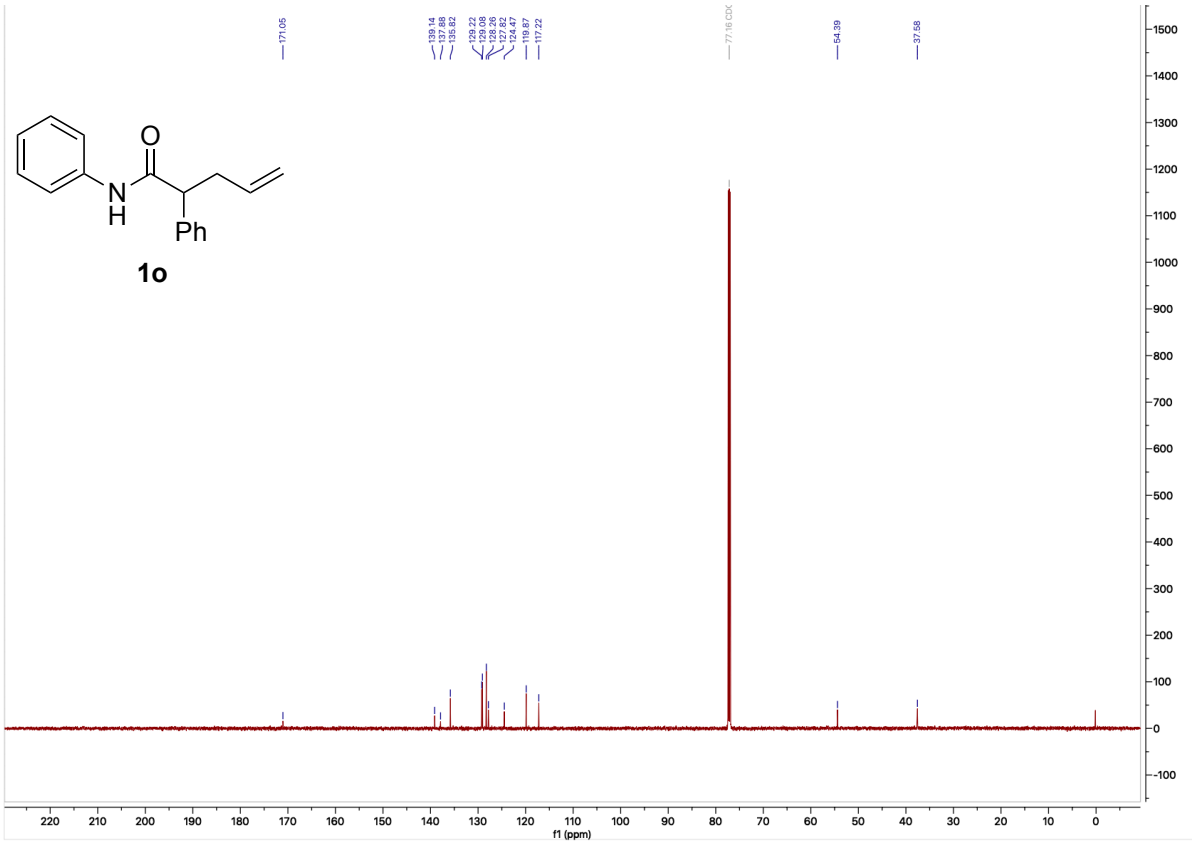

9.50
1.07
1.00
1.02
2.06
1.06
1.03
2.07
1.02
f1 (ppm)

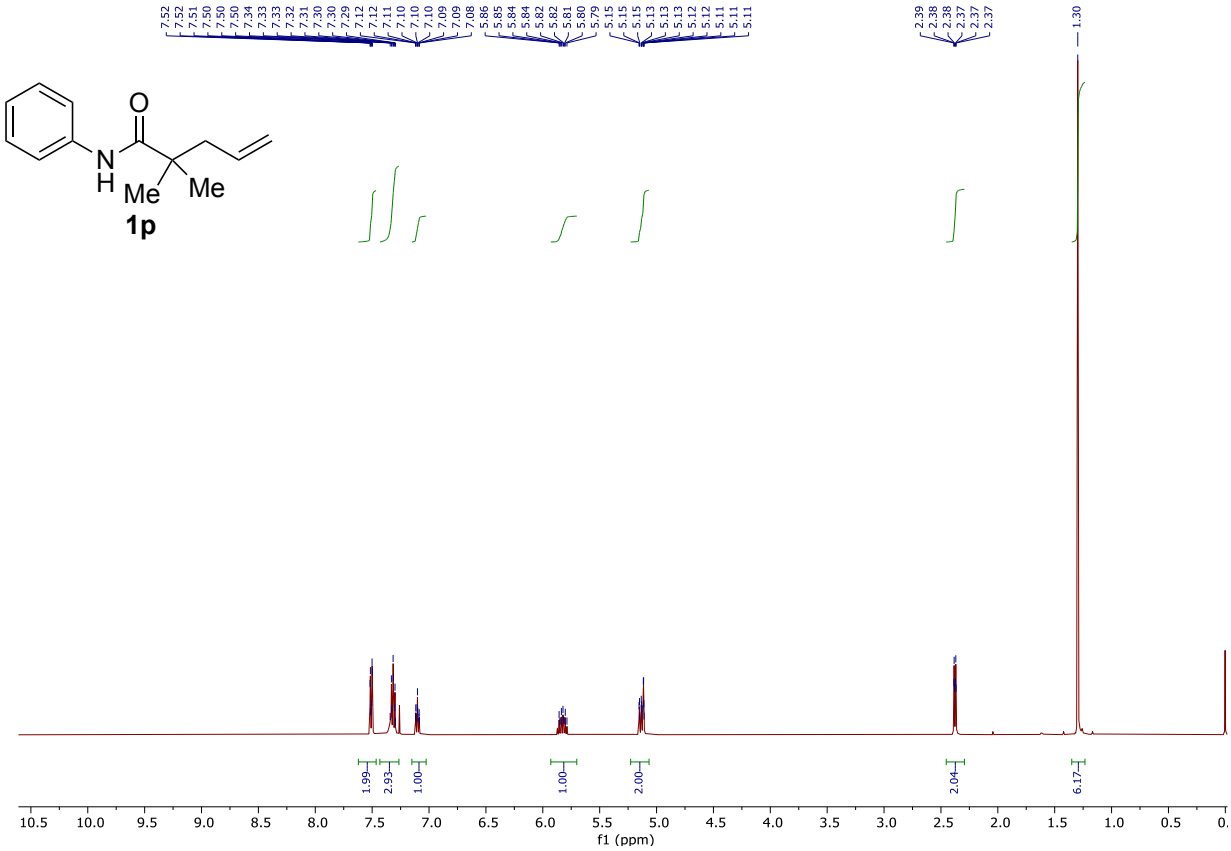

172.64
139.70
137.56
135.58
129.08
128.75
126.66
124.49
120.30
117.61
77.16 CDCl3
51.10
38.92
36.93
f1 (ppm)

O
N
H
Ph

1n


O
N
H
Ph
1o
f1 (ppm)


O
N
H
Ph
1o
f1 (ppm)


7.52
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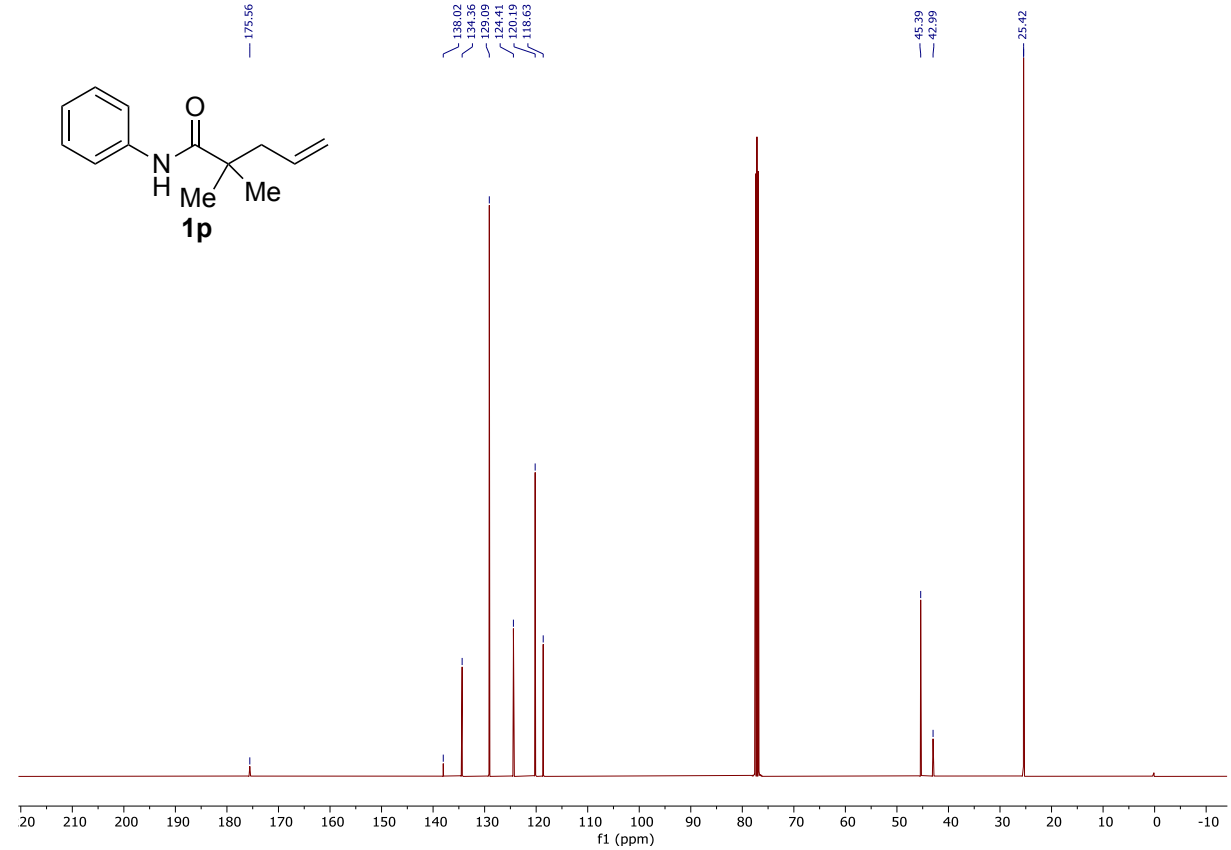
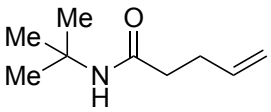
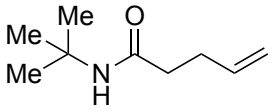
7.51
7.50
7.50
7.50
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.12
7.11
7.10
7.10
7.10
7.09
7.09
7.08
5.86
5.85
5.85
5.84
5.82
5.82
5.81
5.80
5.79
5.15
5.15
5.15
5.13
5.13
5.12
5.12
5.11
5.11
5.11
2.39
2.38
2.38
2.37
2.37
2.37
1.30
O
N
H
Me
Me
1p
1.99
2.93
1.00
1.00
2.00
2.04
6.17
10.5
10.0
9.5
9.0
8.5
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
f1 (ppm)


175.56
138.02
134.36
129.09
124.41
120.13
118.63
45.39
42.99
25.42
O
N
H
Me
Me
1p
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
Me
O
Me
N
H

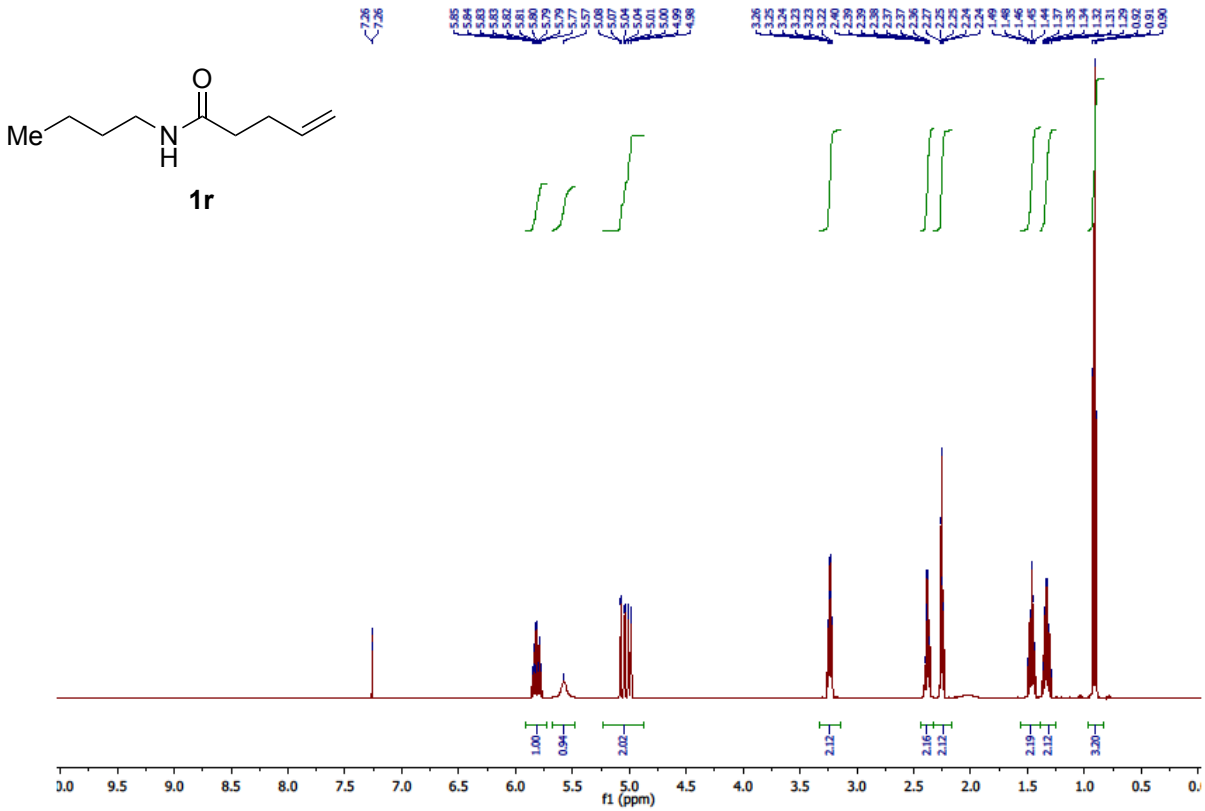
1q

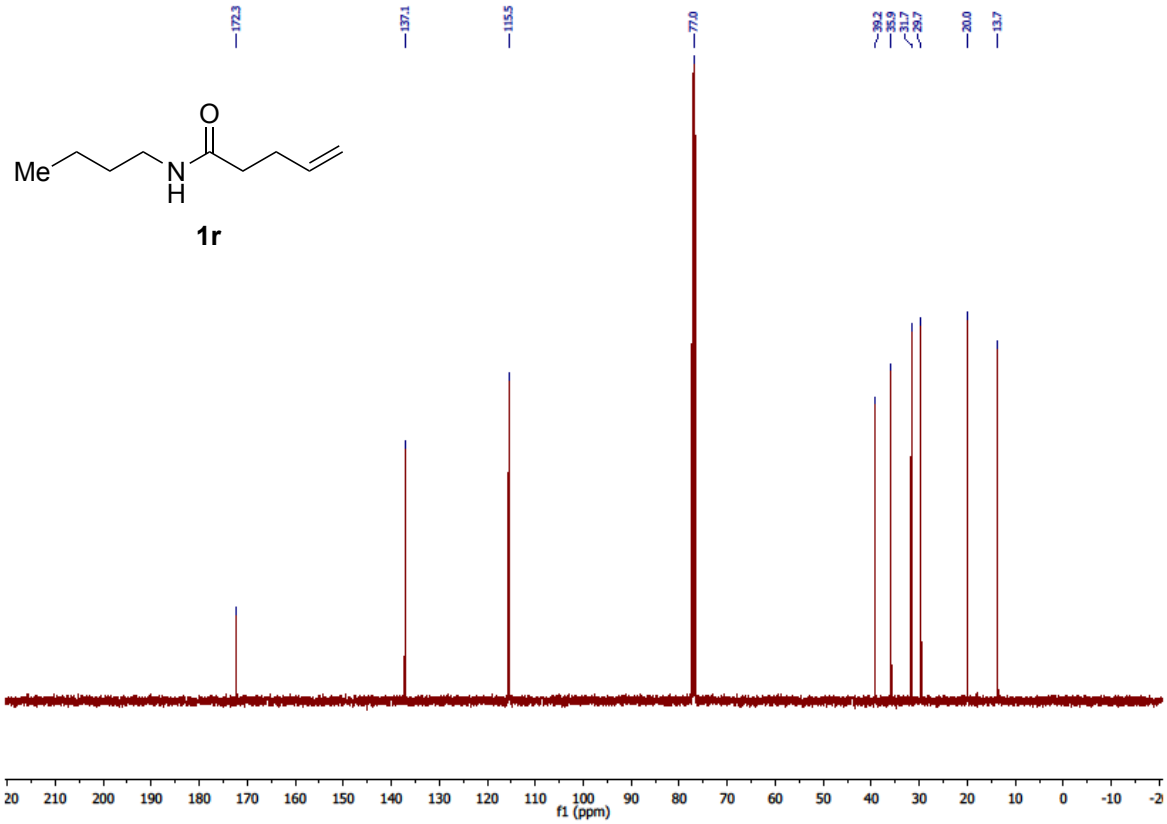
5.85
5.84
5.83
5.82
5.81
5.80
5.79
5.78
5.77
5.07
5.07
5.04
5.03
5.00
5.00
4.98
4.98
2.37
2.36
2.35
2.33
2.19
2.17
2.16
1.33
1.00
0.83
2.08
2.15
2.17
9.30
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

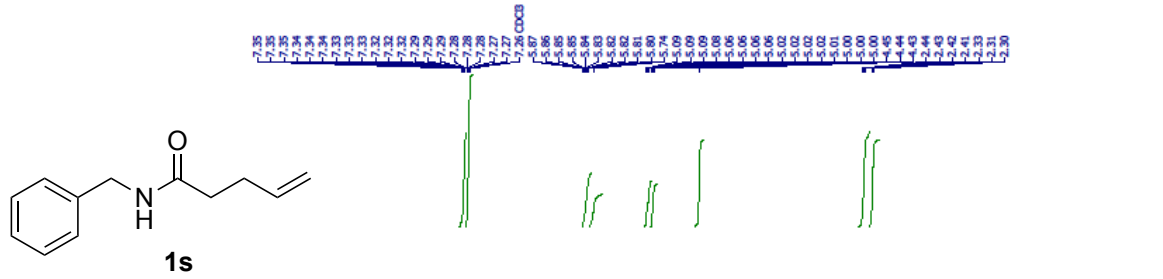

Me
Me
O
Me
N
H

1q

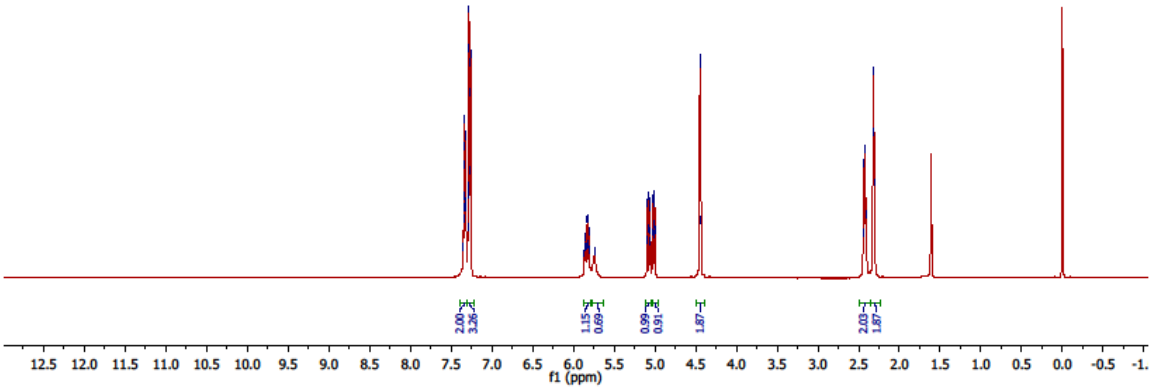
171.6
137.2
115.4
77.0
51.2
36.7
29.7
28.8
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

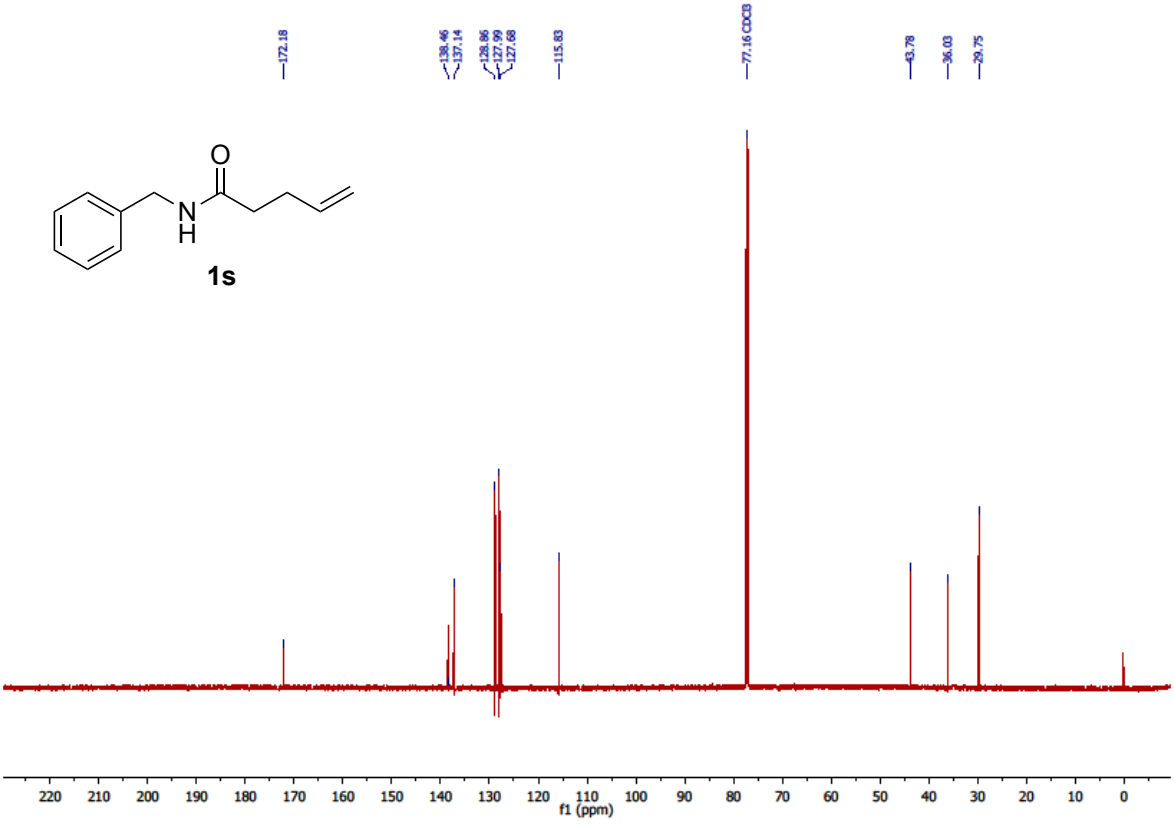

Me
N
H
O
1r
f1 (ppm)


Me
N
H
O
1r
f1 (ppm)

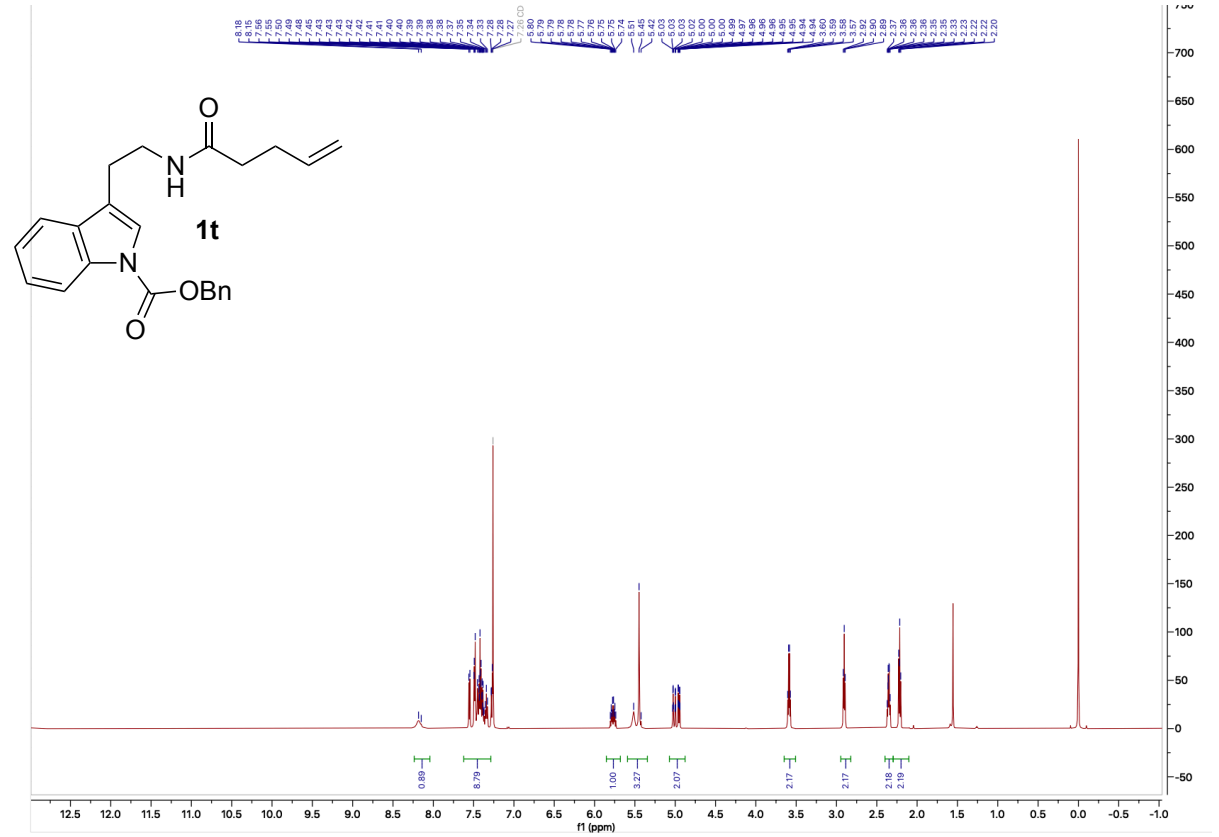


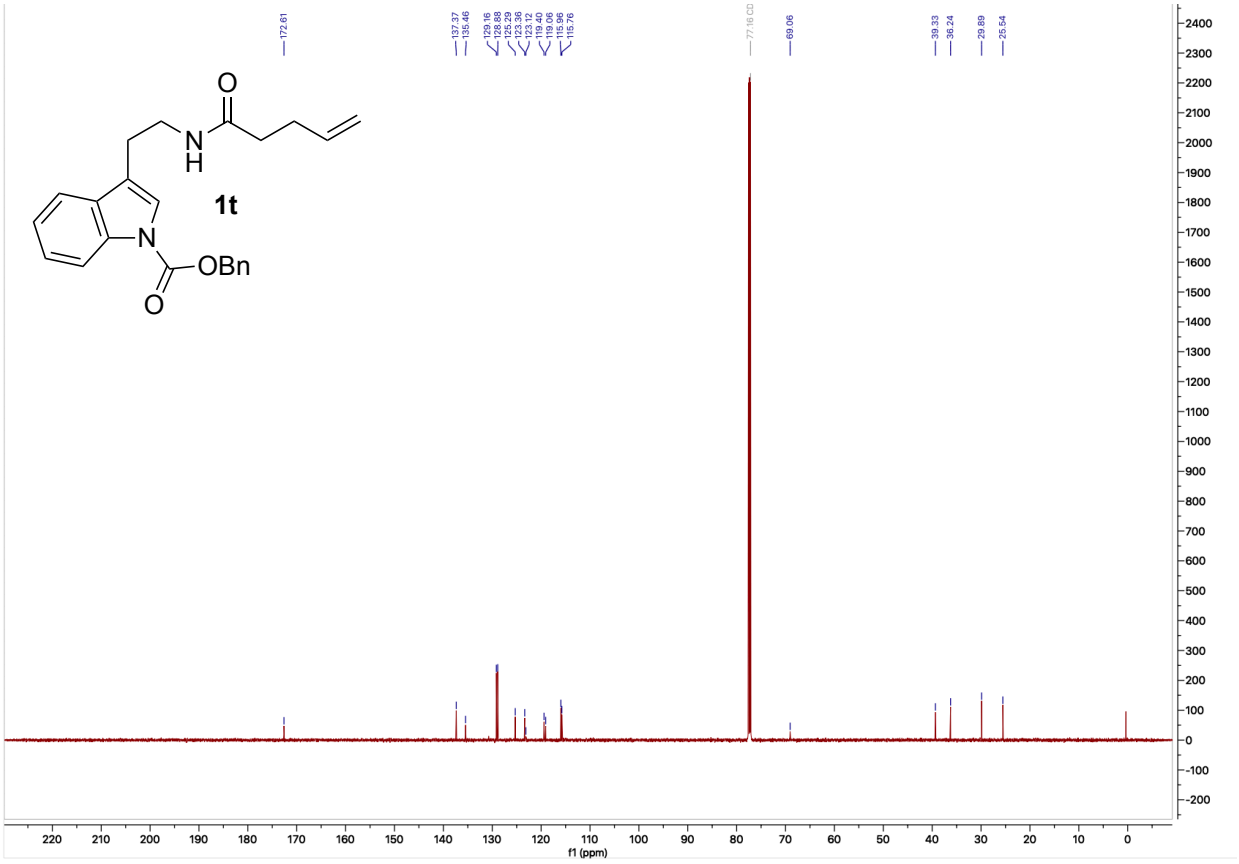
1s

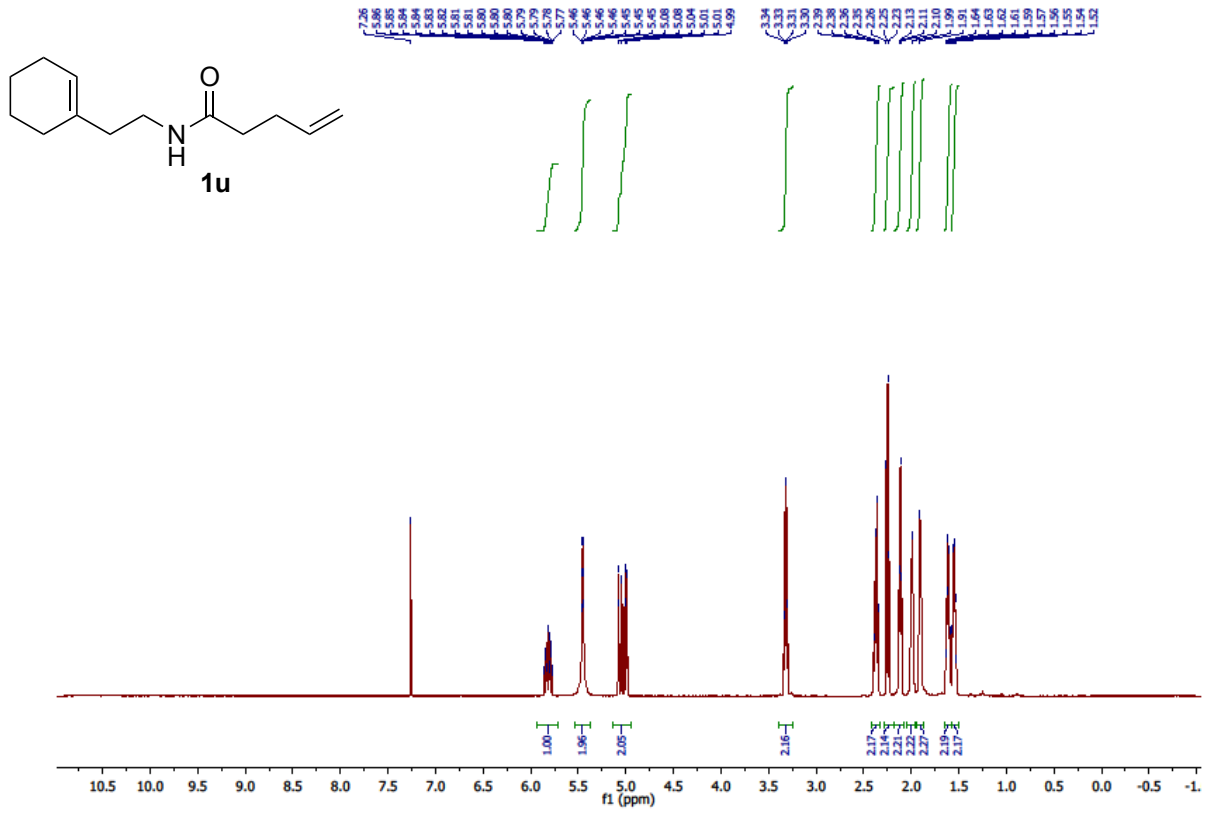


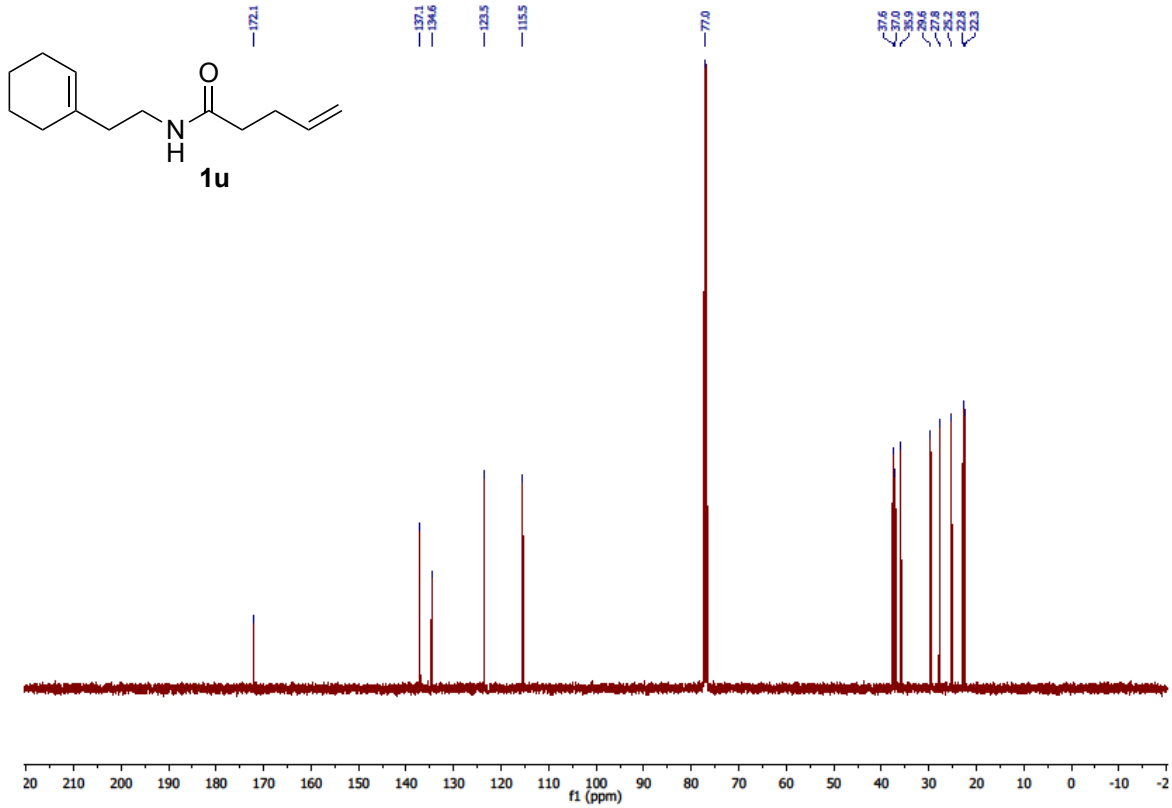


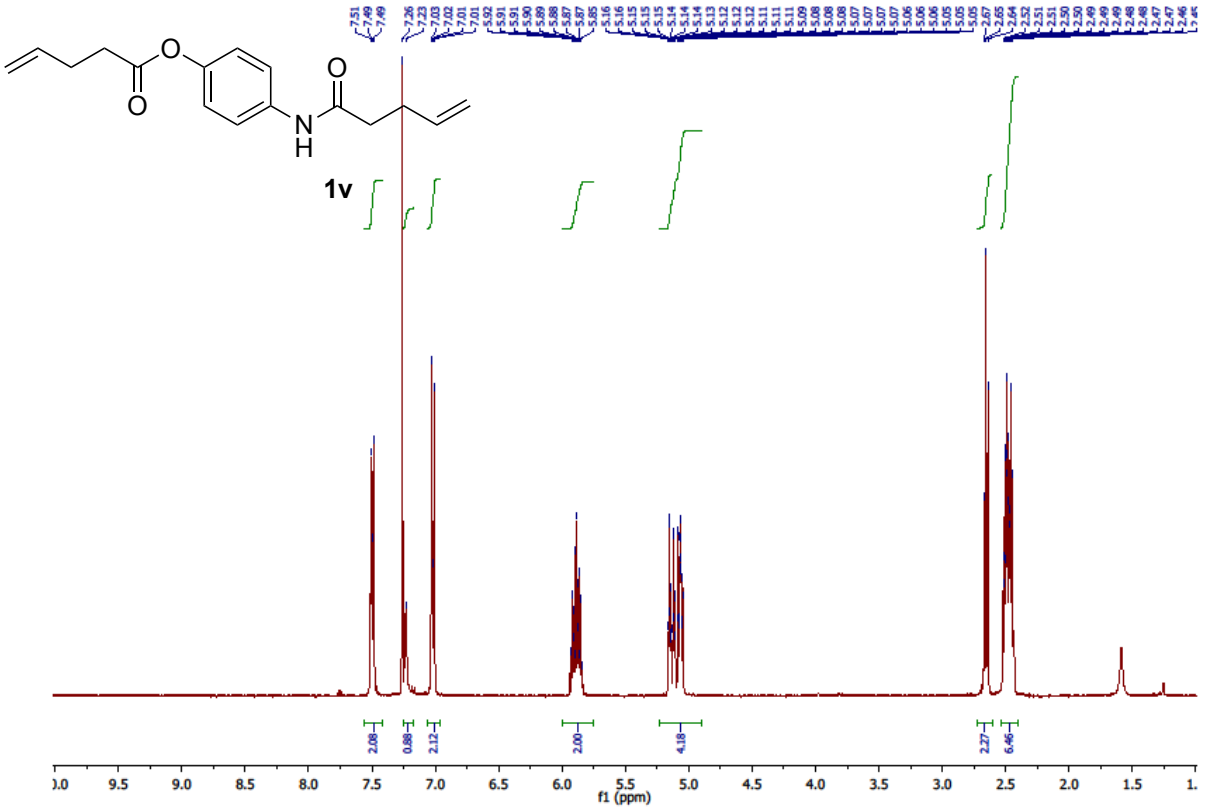
1s

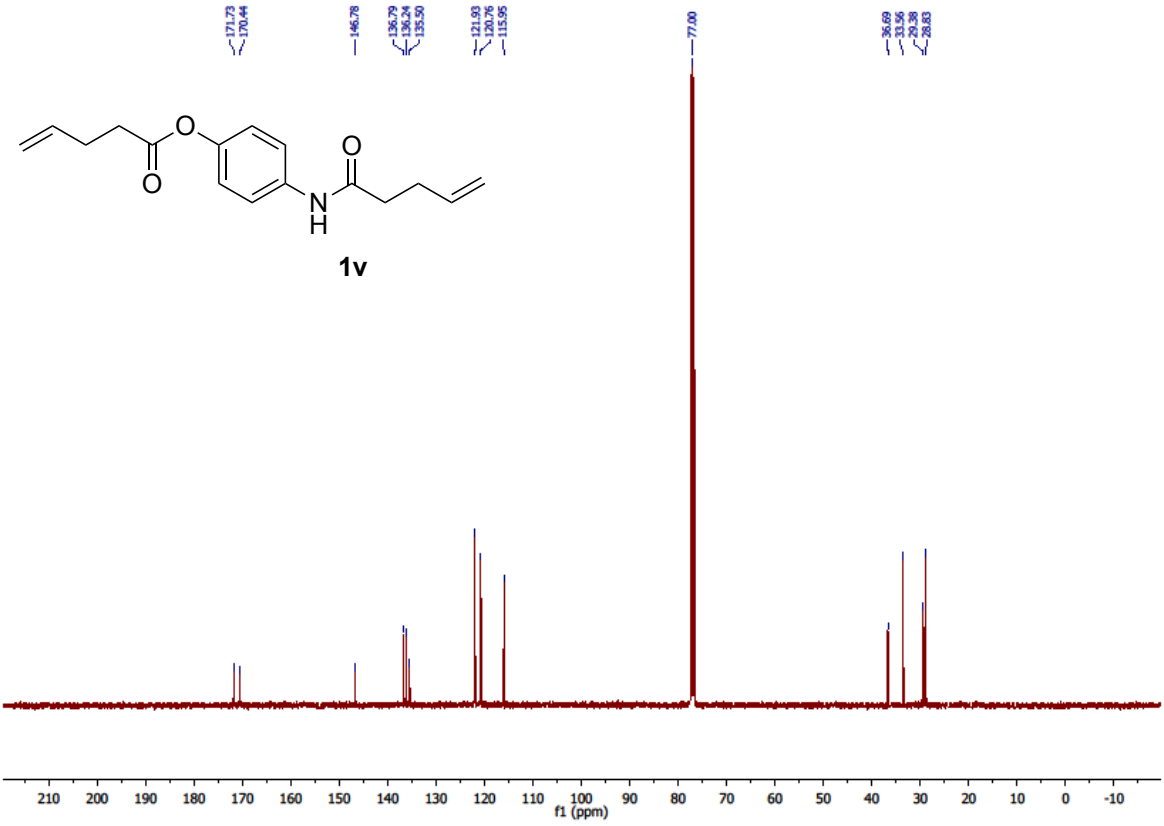

1t
OBn
f1 (ppm)

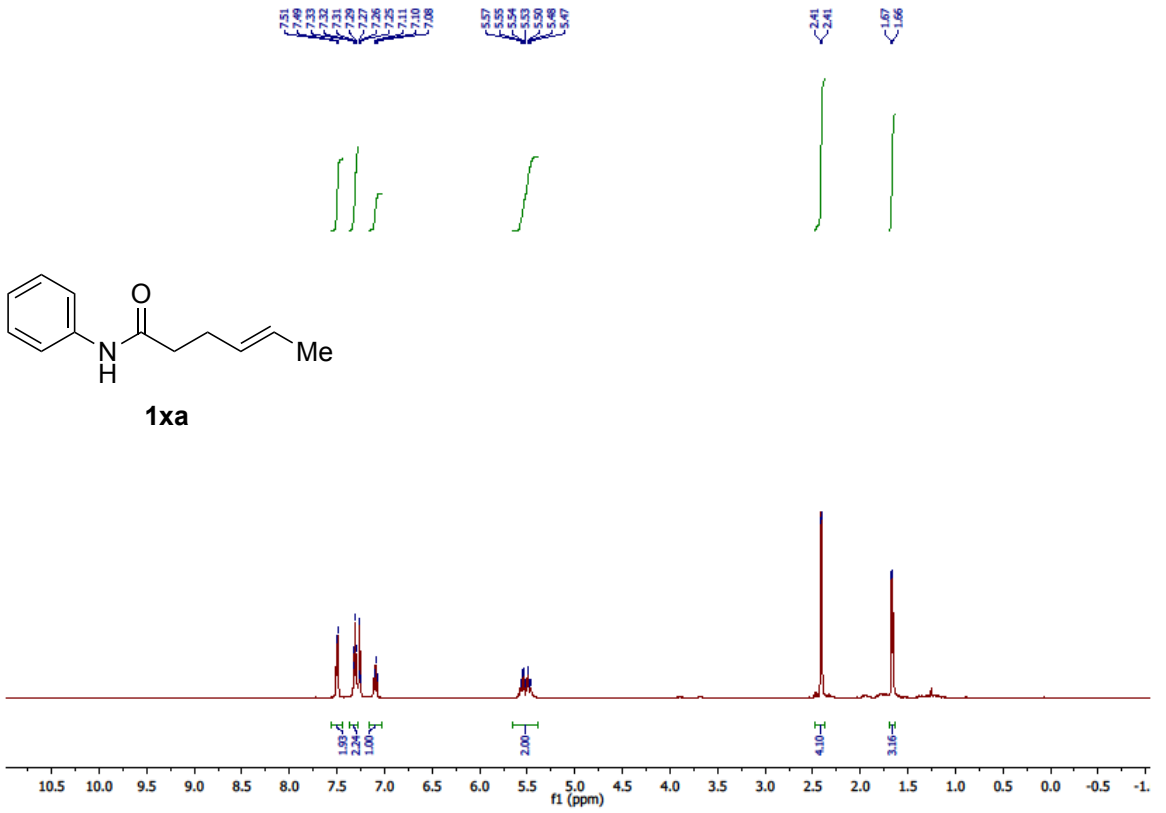

1t
OBn
f1 (ppm)


O
N
H
1u
f1 (ppm)

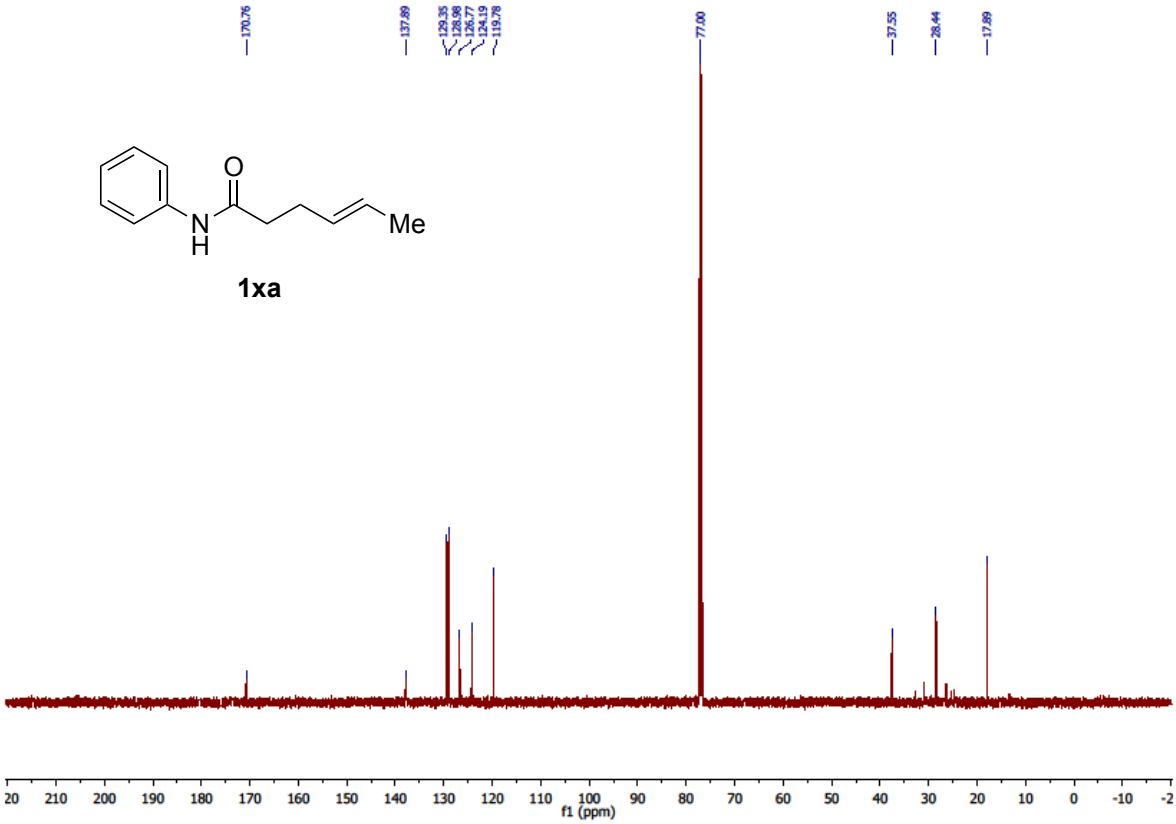

O
N
H
1u
f1 (ppm)


1v
f1 (ppm)

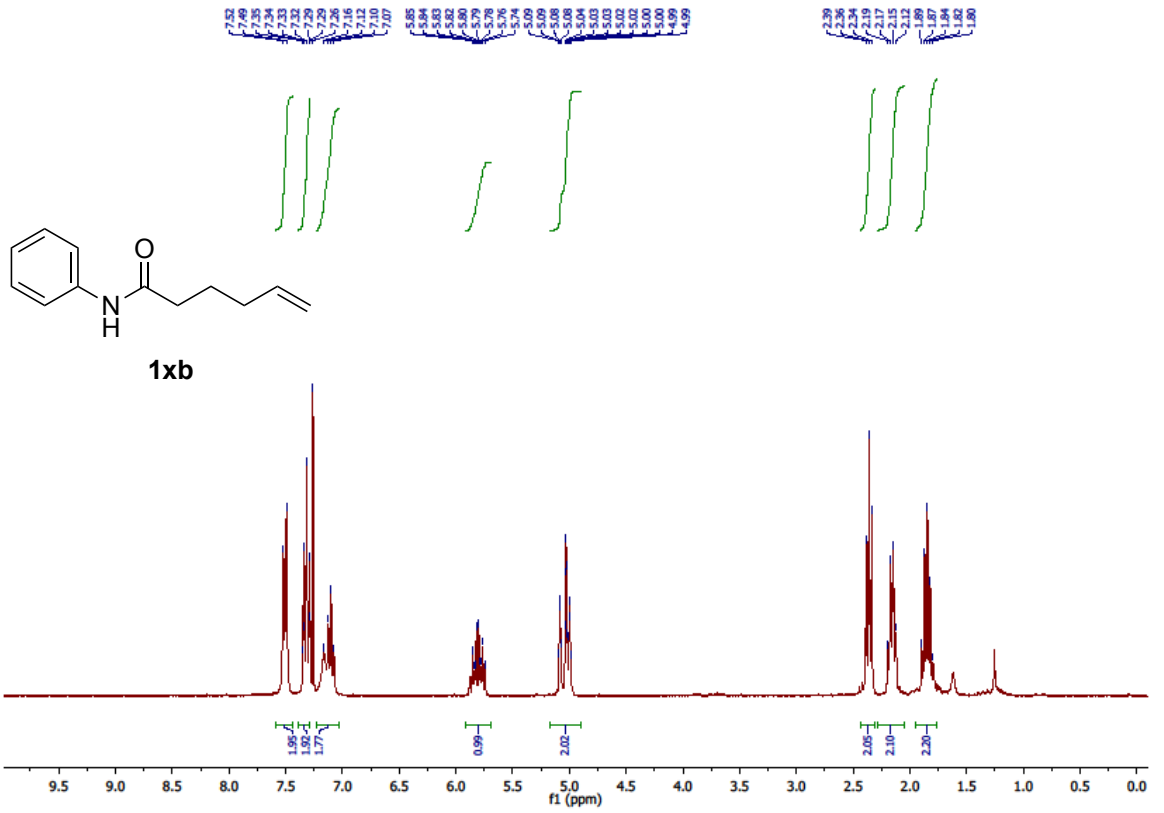

1v
f1 (ppm)

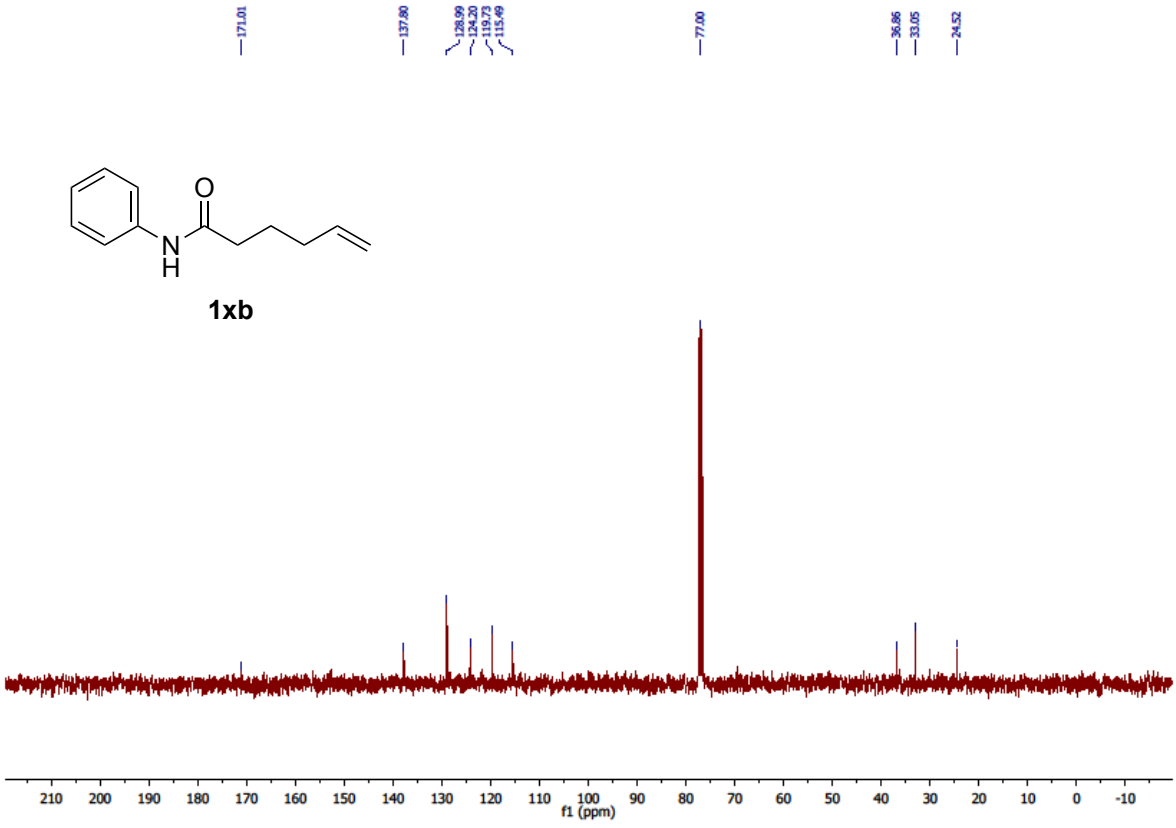


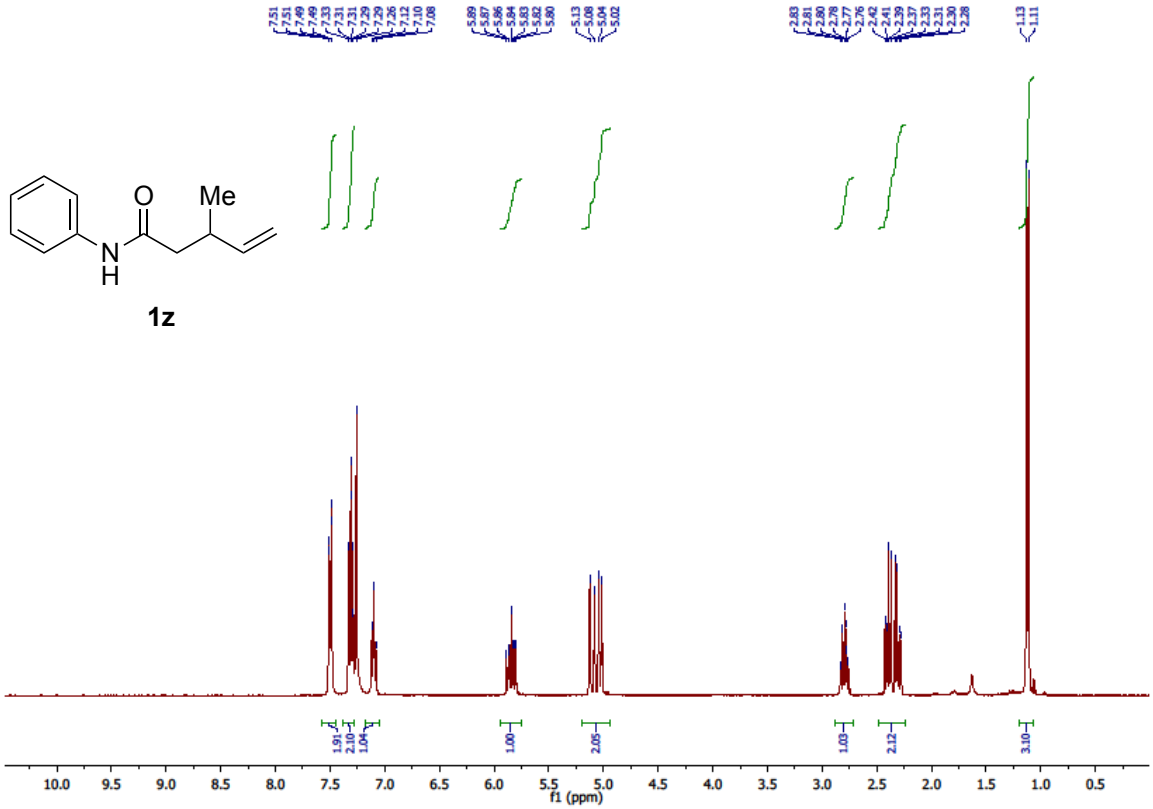
1xa

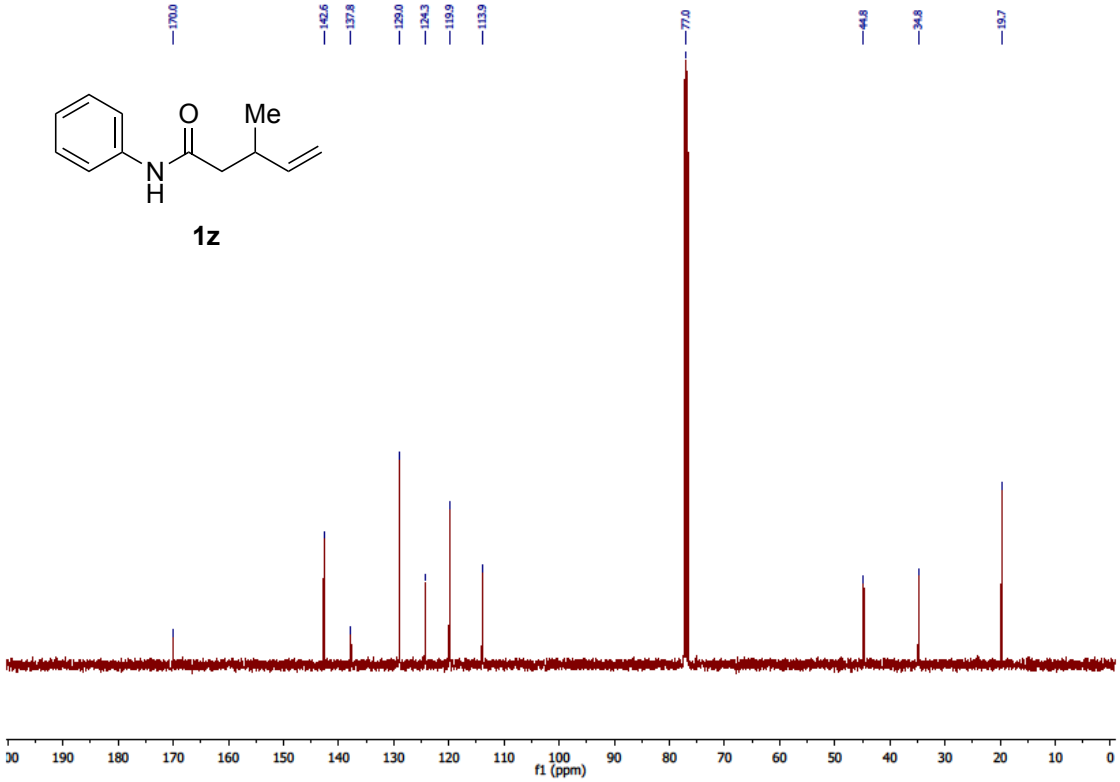


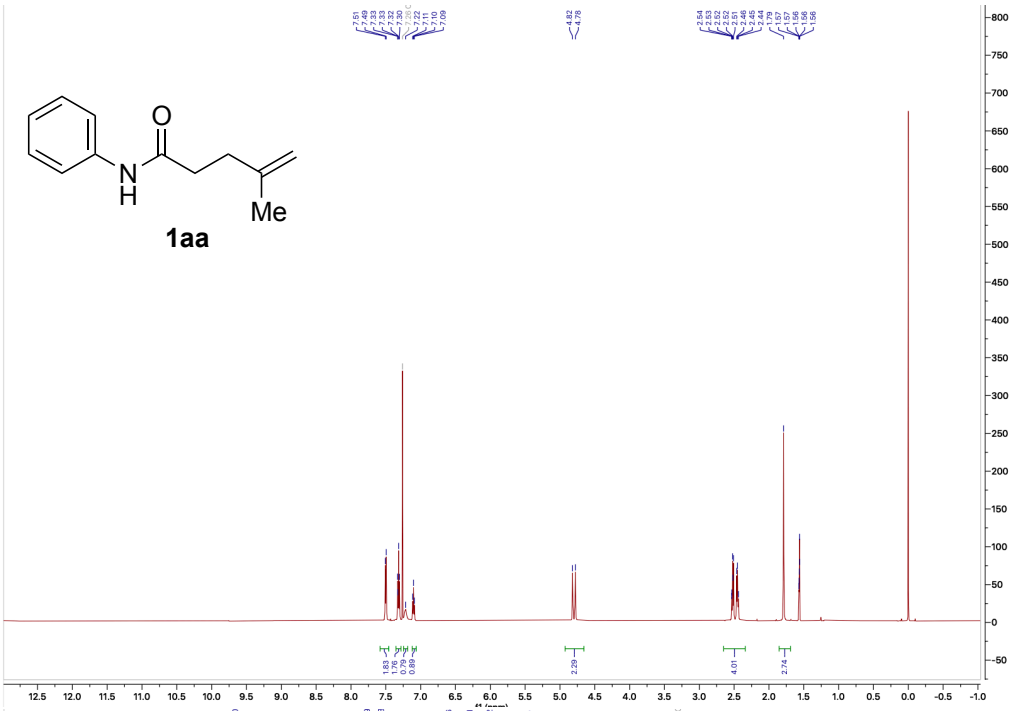
1xa

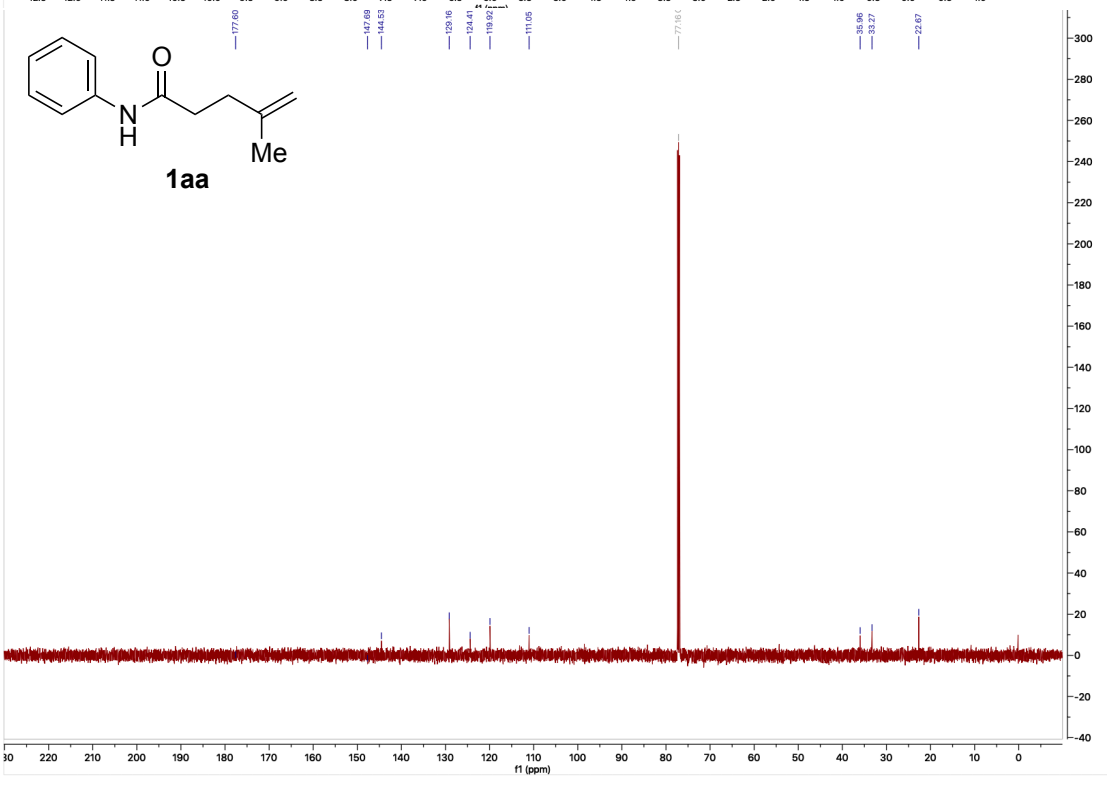

1xb
f1 (ppm)

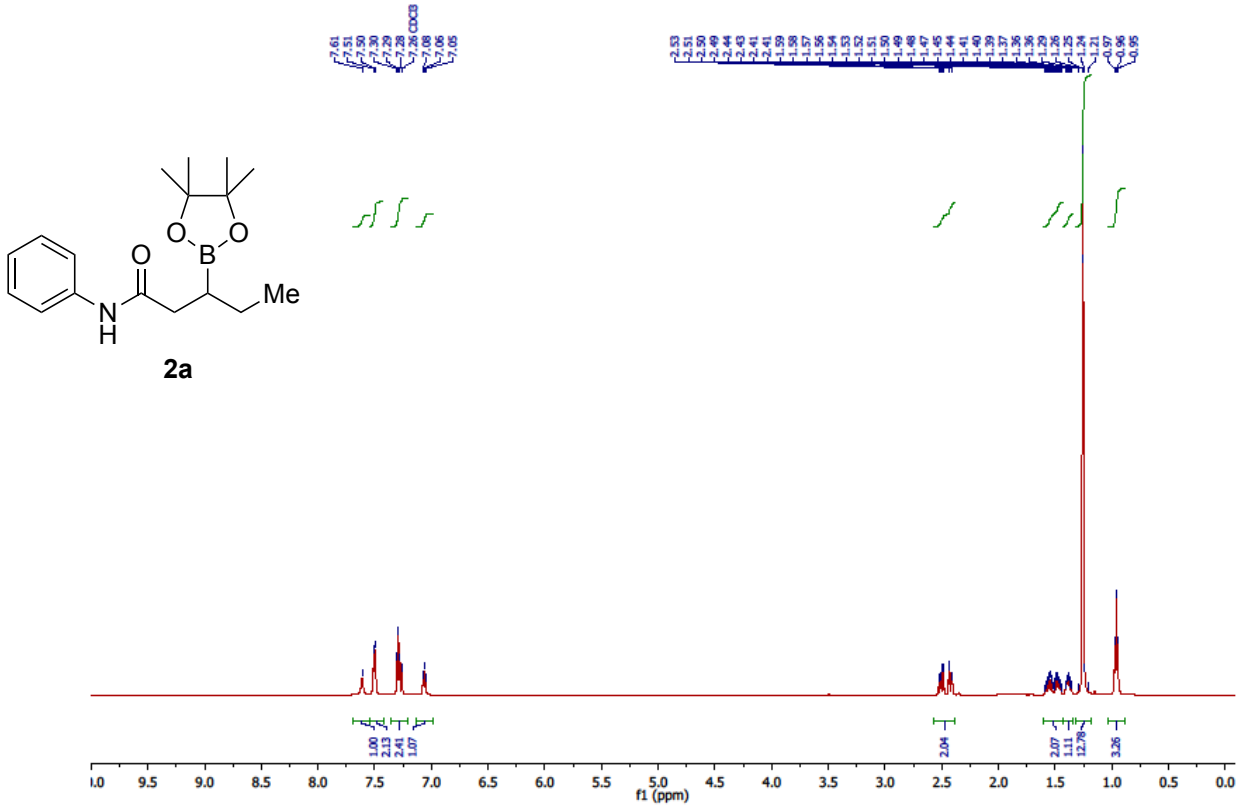

1xb
f1 (ppm)

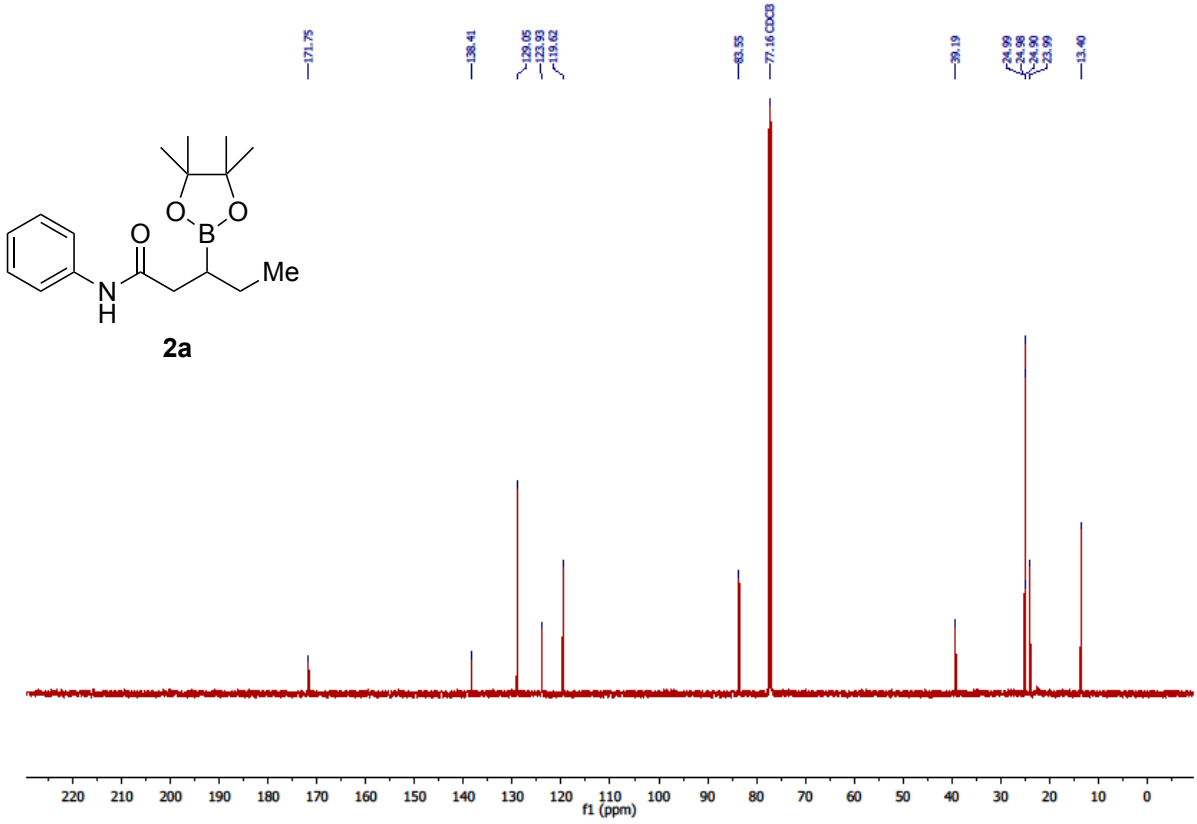

O
Me
N
H
1z
f1 (ppm)

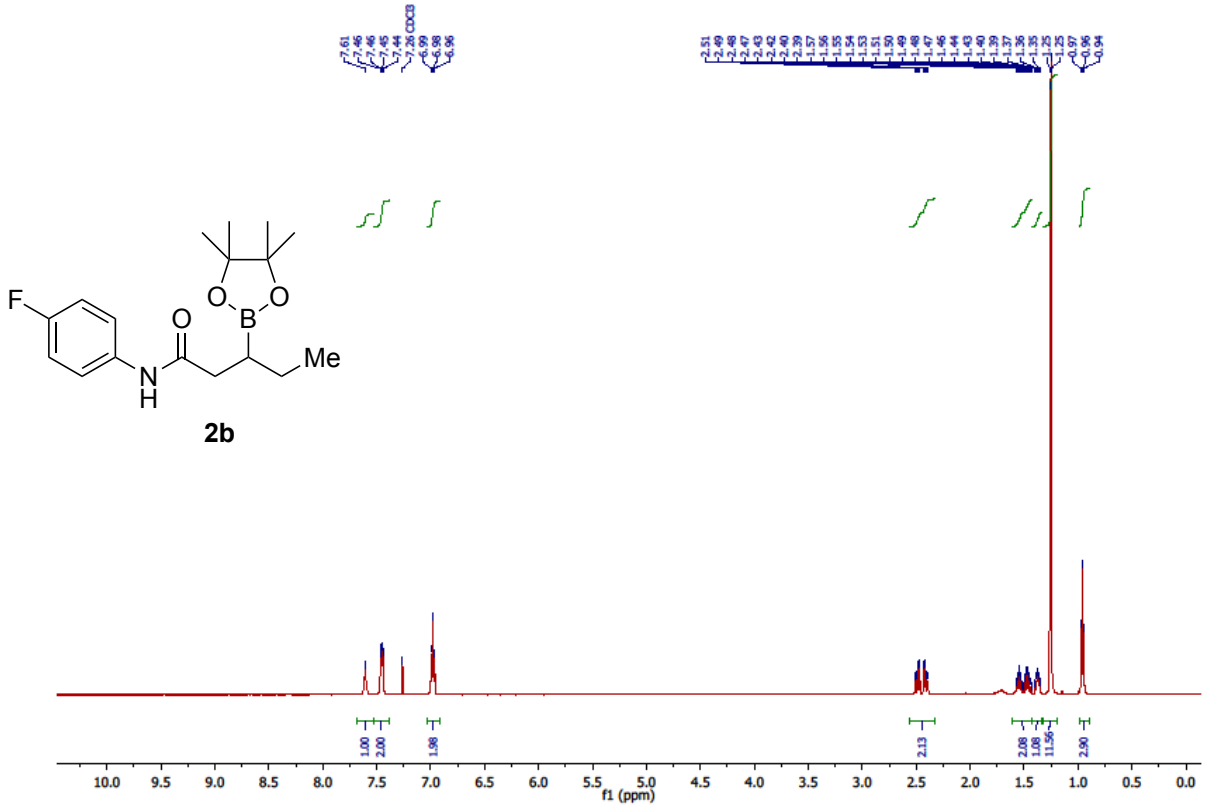

O
Me
N
H
1z
f1 (ppm)


O
N
H
Me
1aa

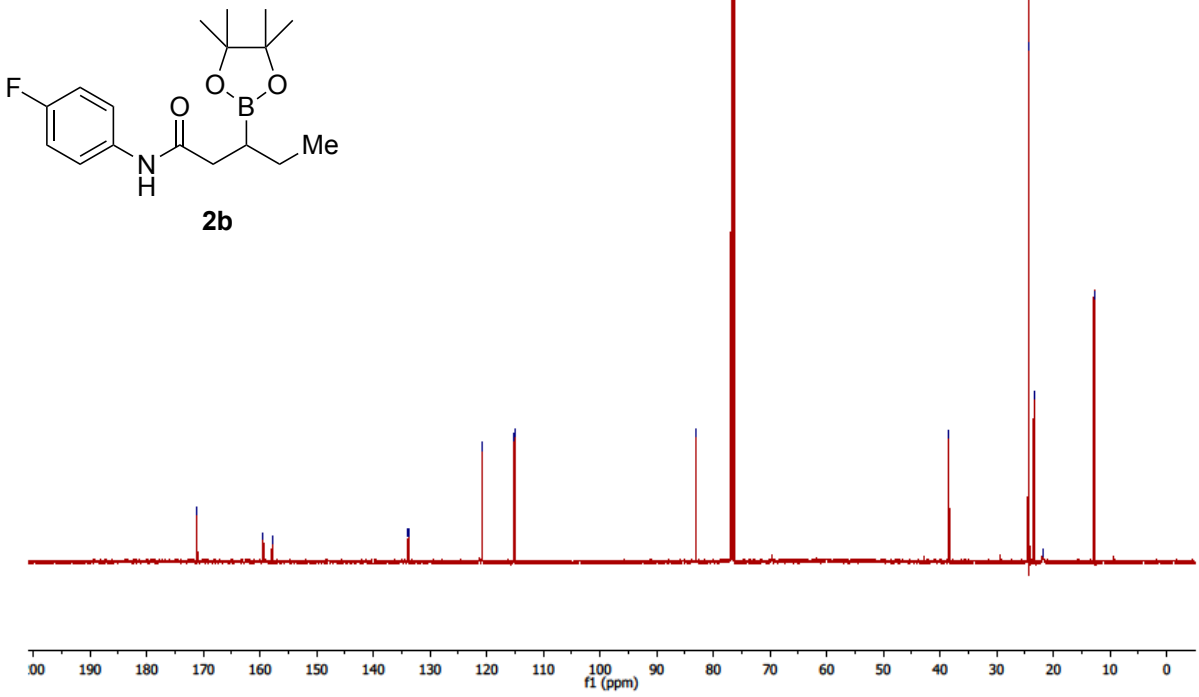

O
N
H
Me
1aa
f1 (ppm)


O
O
B
O
N
H
O
Me
2a
f1 (ppm)

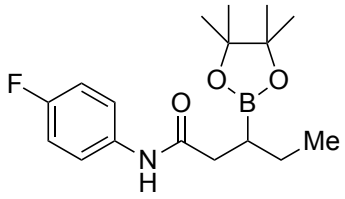

O
O
B
O
N
H
O
Me
2a
f1 (ppm)



2b

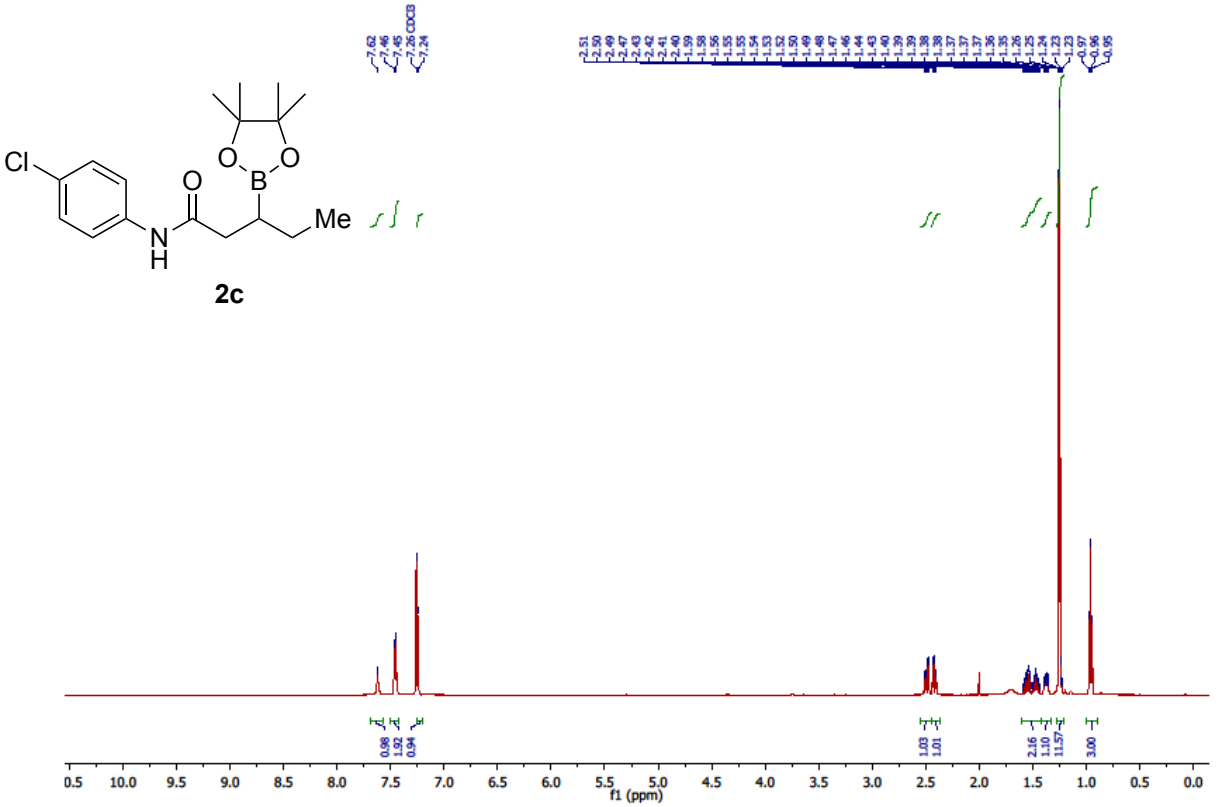


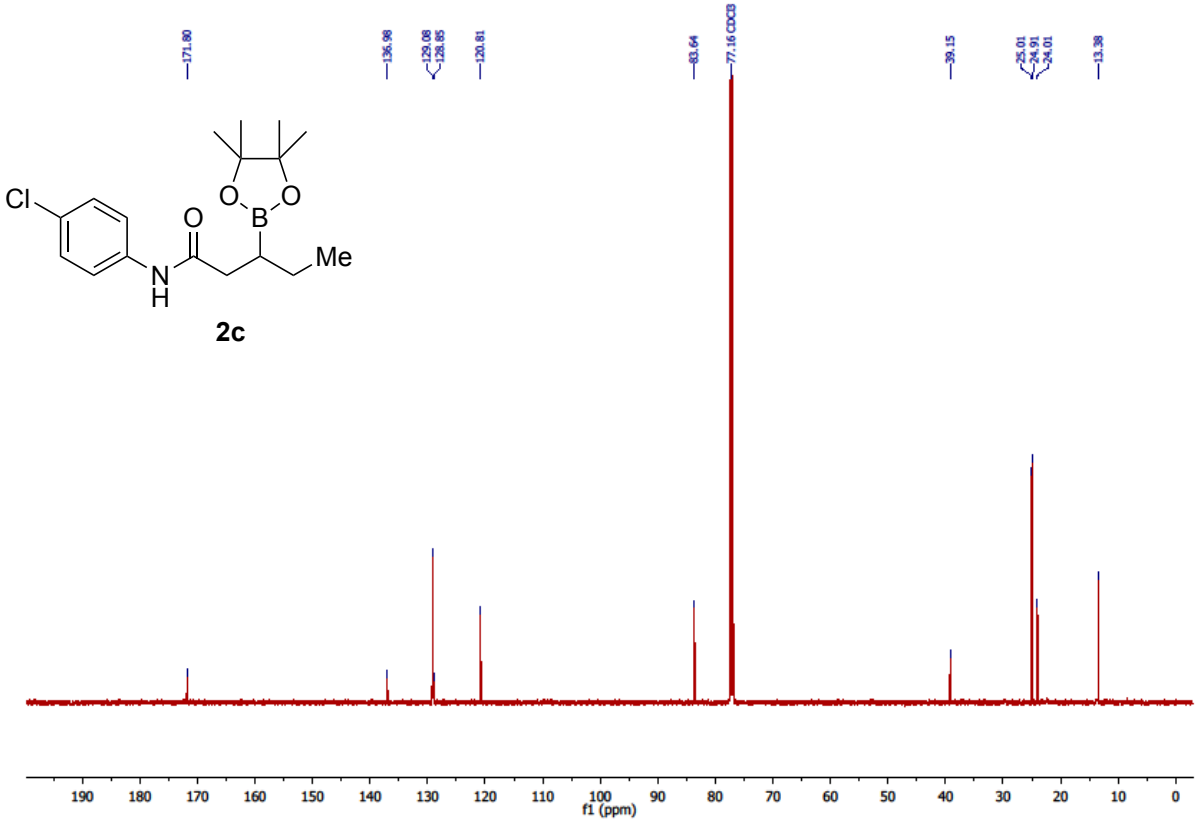
2b

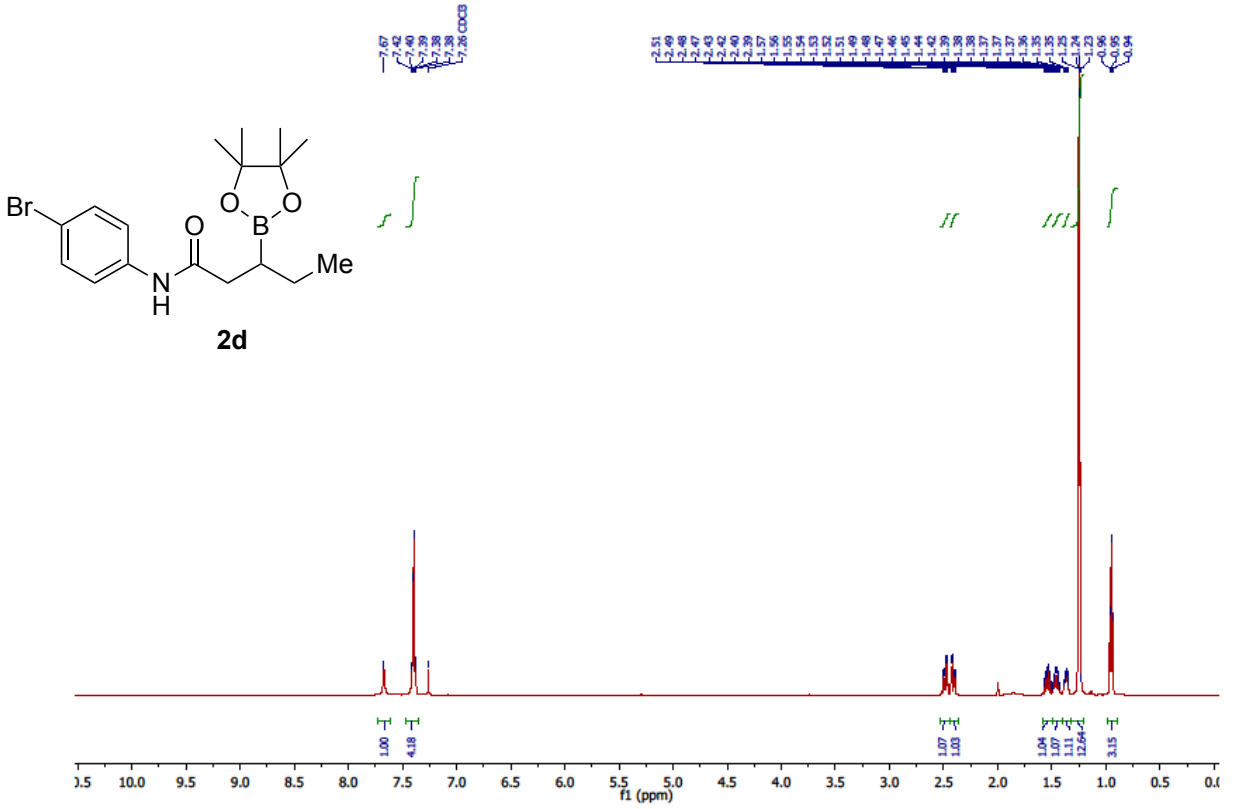

F
O
O
B
O
Me
N
H

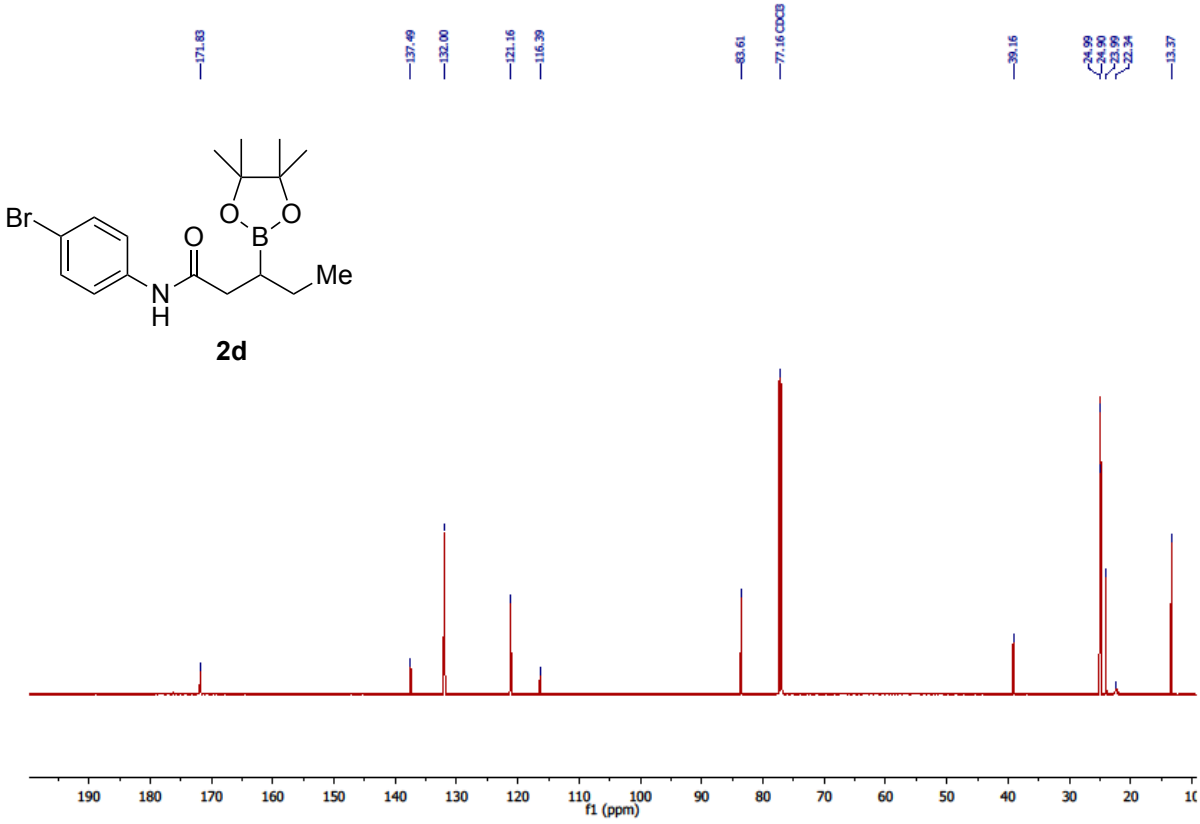
2b

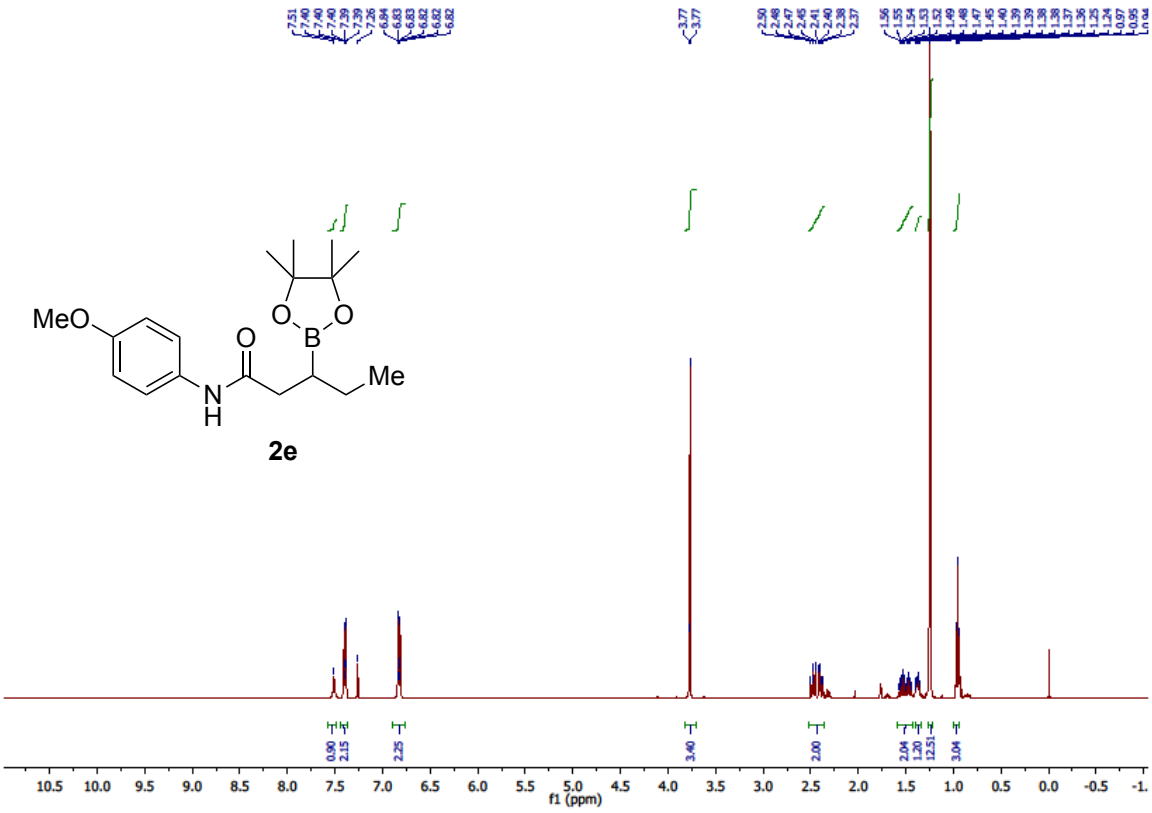
-118.94
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

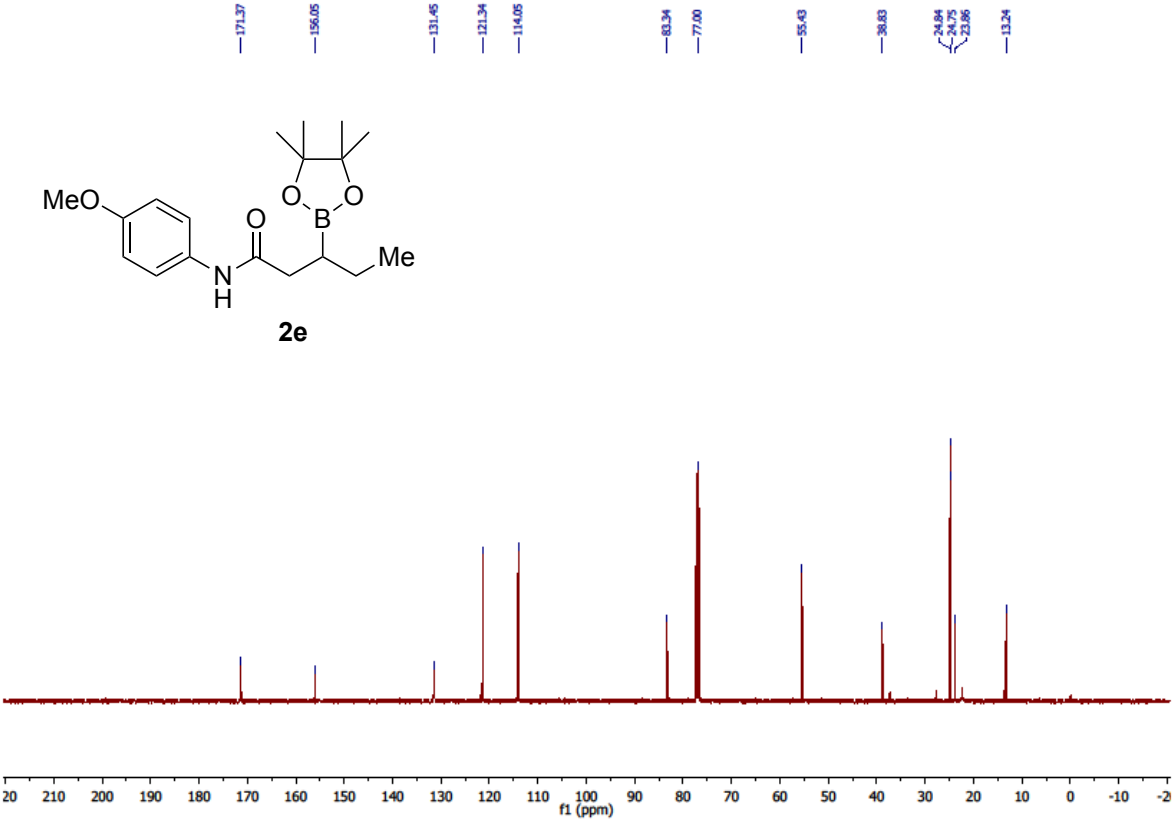

Cl
O
B
O
O
N
H
Me
2c
f1 (ppm)

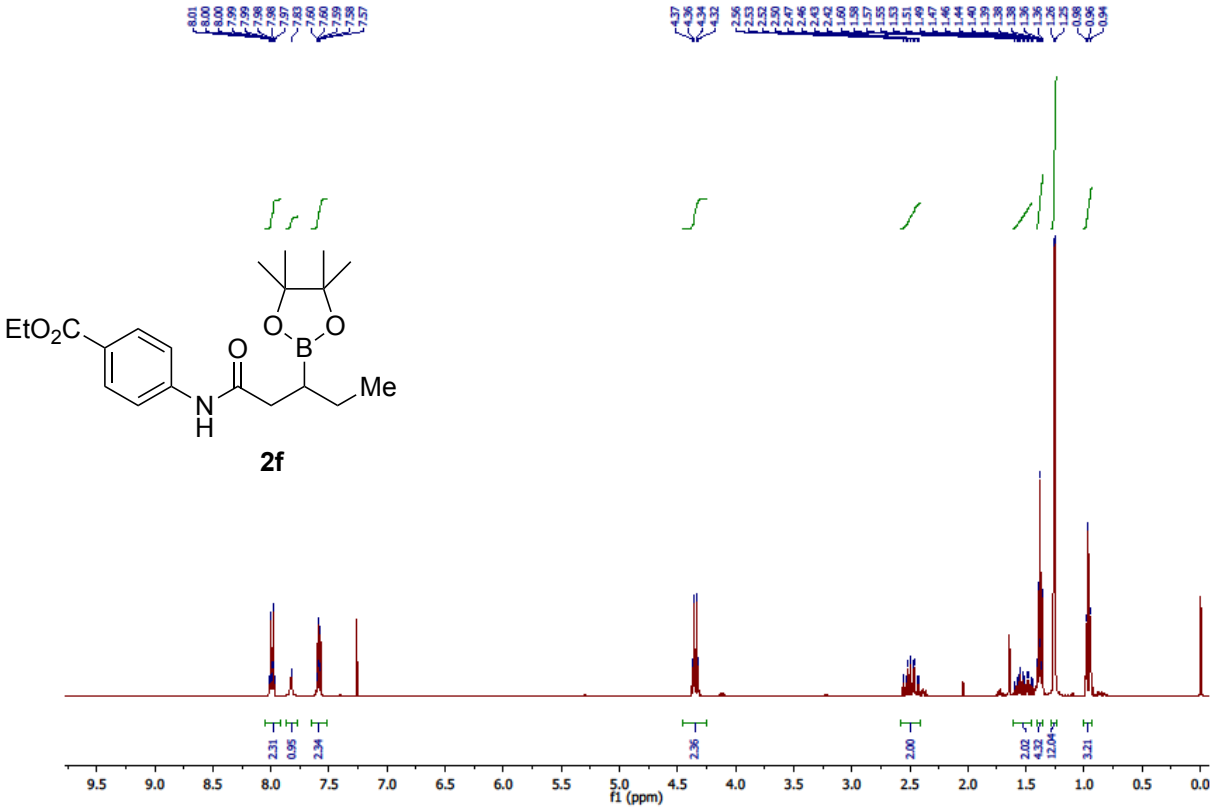

Cl
O
B
O
O
N
H
Me
2c
f1 (ppm)

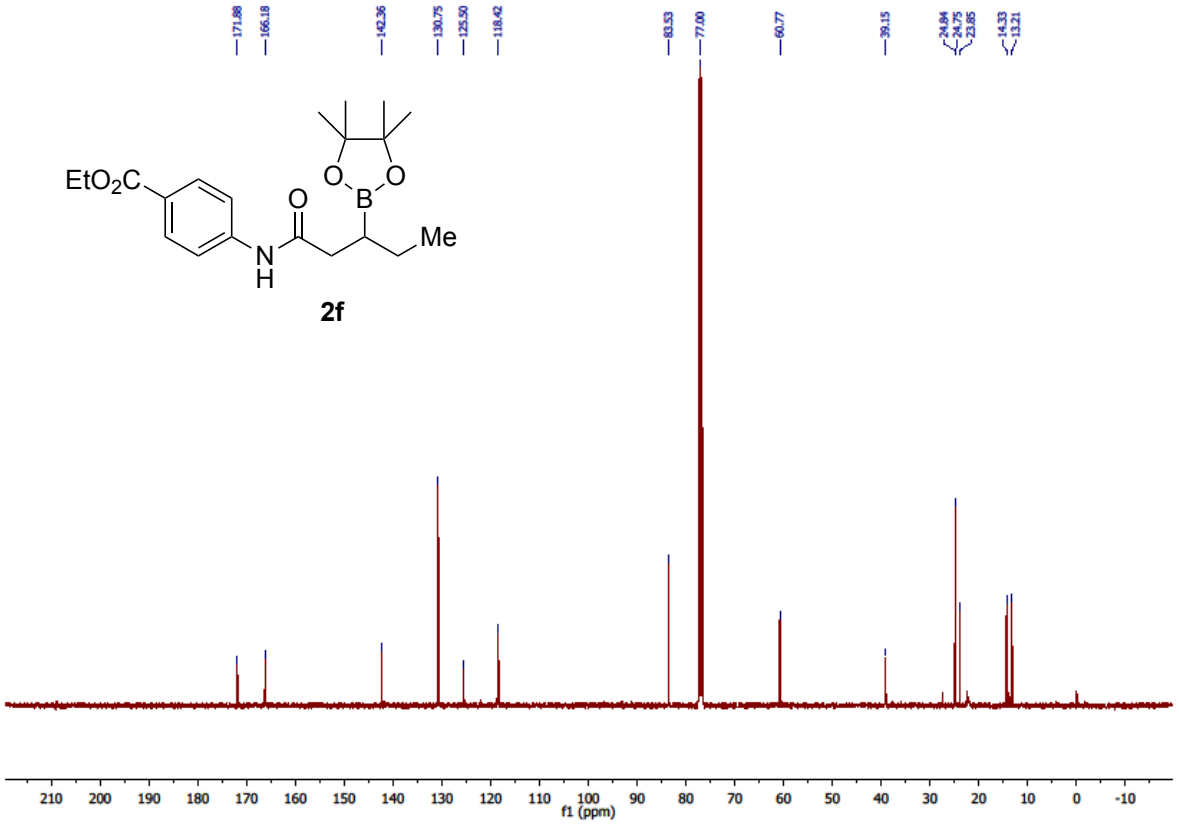

Br
O
O
B
O
N
H
Me
2d
f1 (ppm)

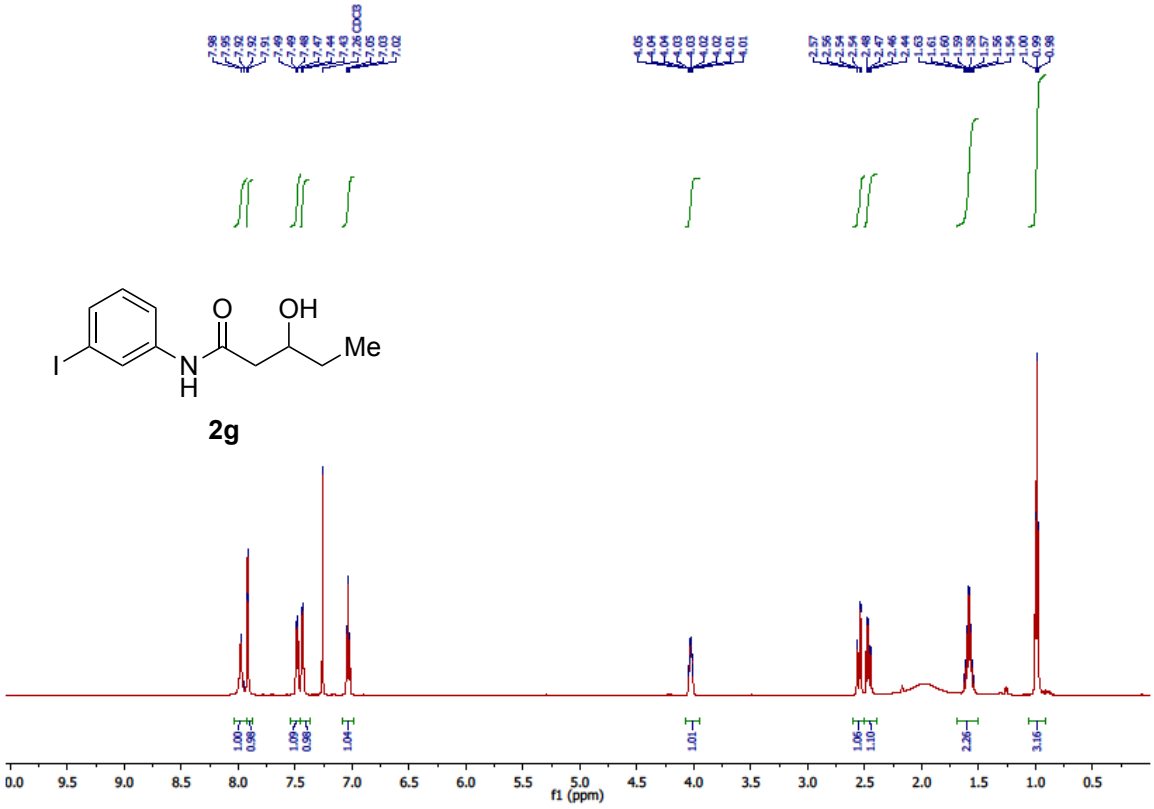

Br
O
O
B
O
N
H
Me
2d
f1 (ppm)


MeO
O
B
O
O
N
H
Me
2e
f1 (ppm)

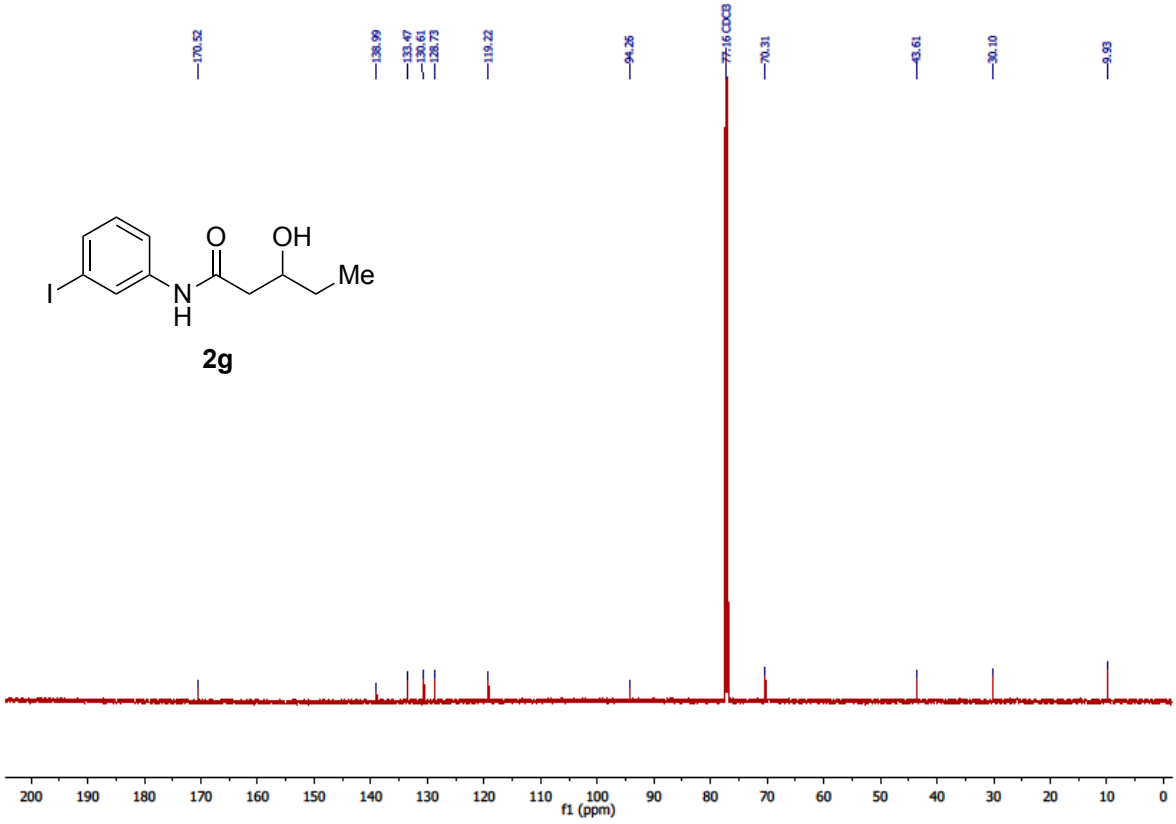

MeO
O
B
O
O
N
H
Me
2e
f1 (ppm)


EtO2C
O
B
O
O
N
H
Me
2f
f1 (ppm)

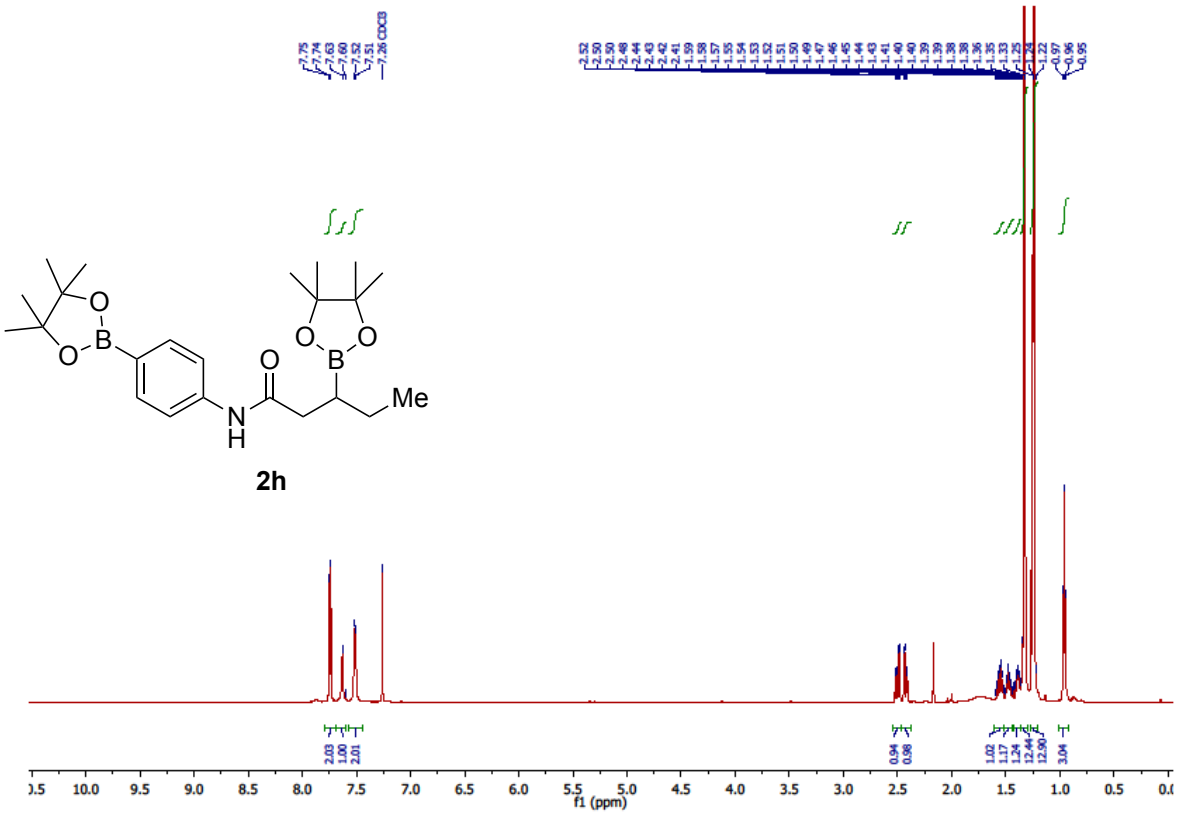

EtO2C
O
B
O
O
N
H
Me
2f
f1 (ppm)

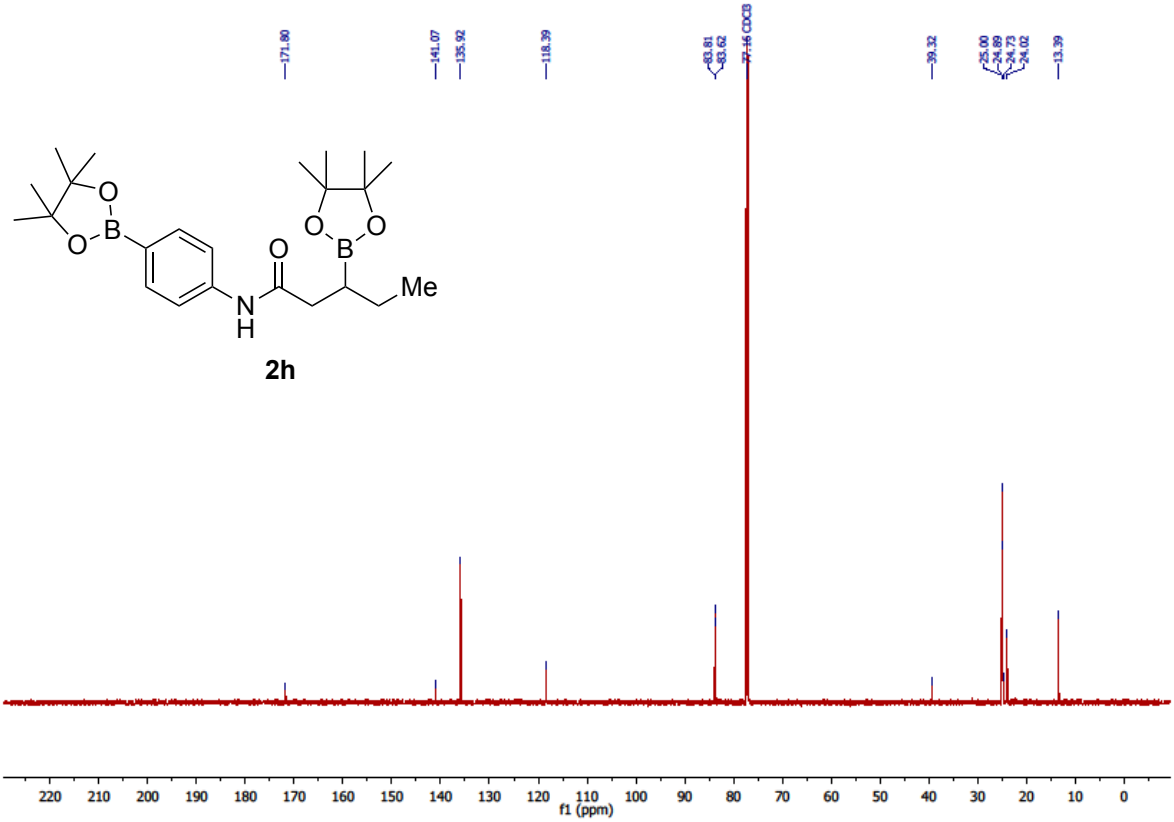


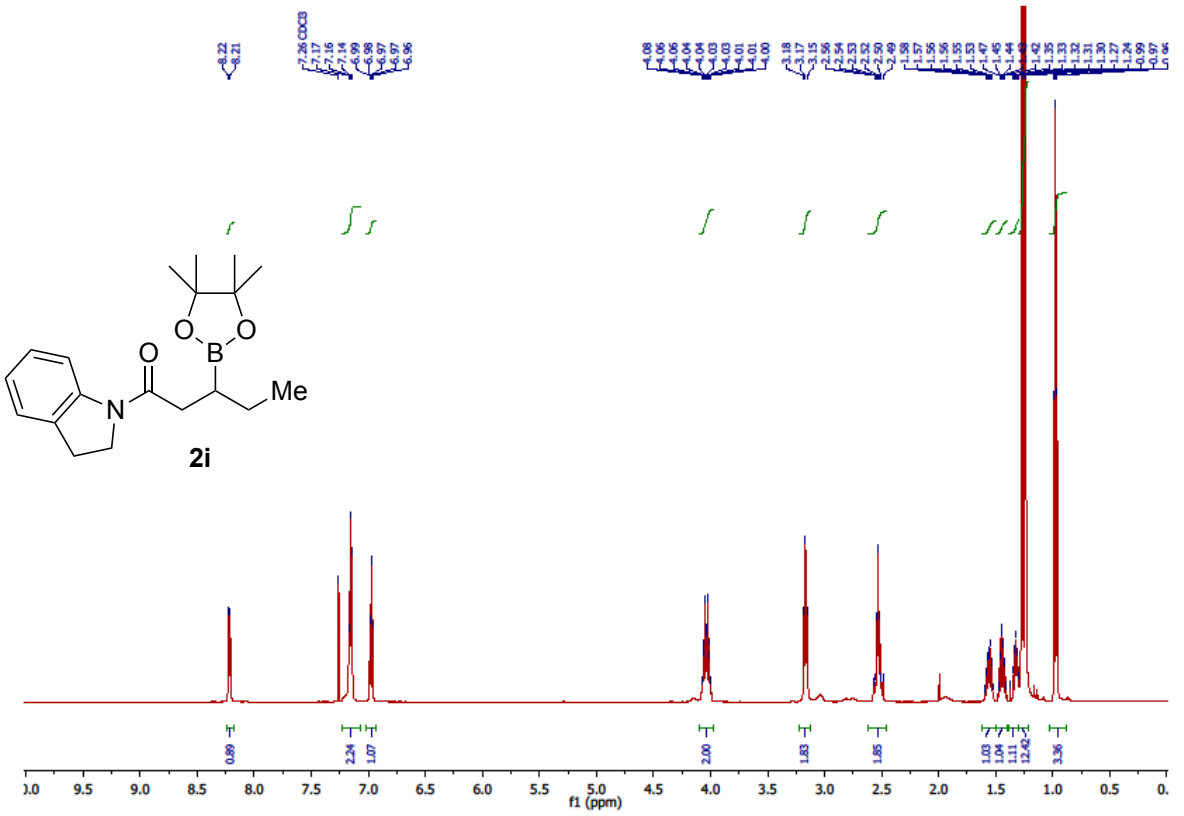
2g

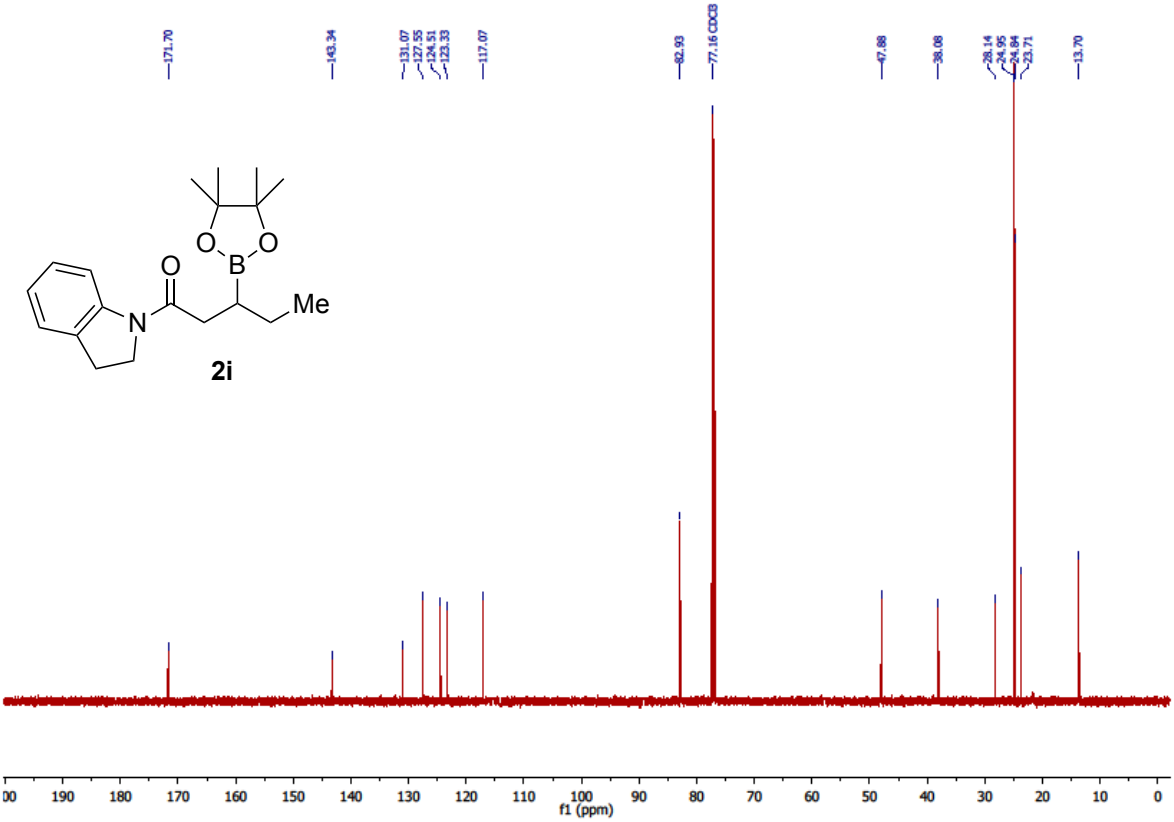


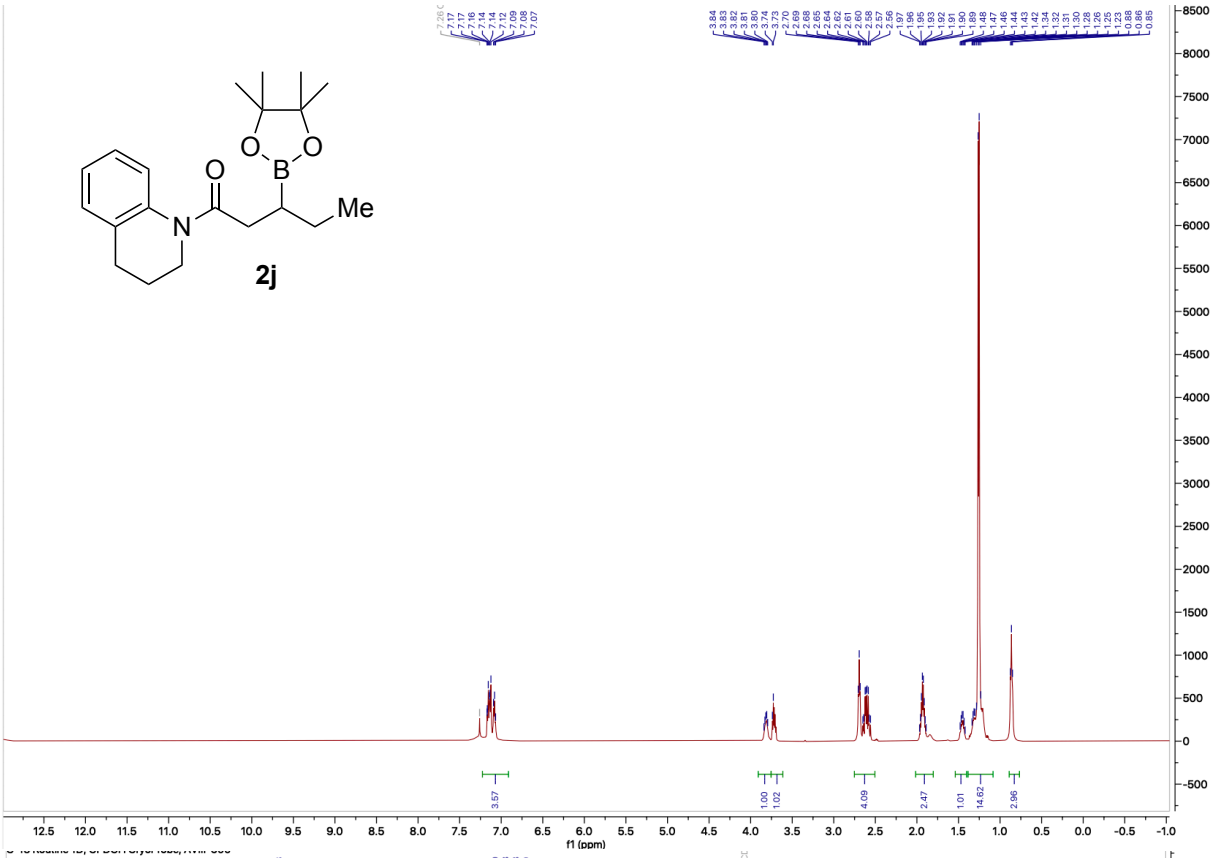
2g

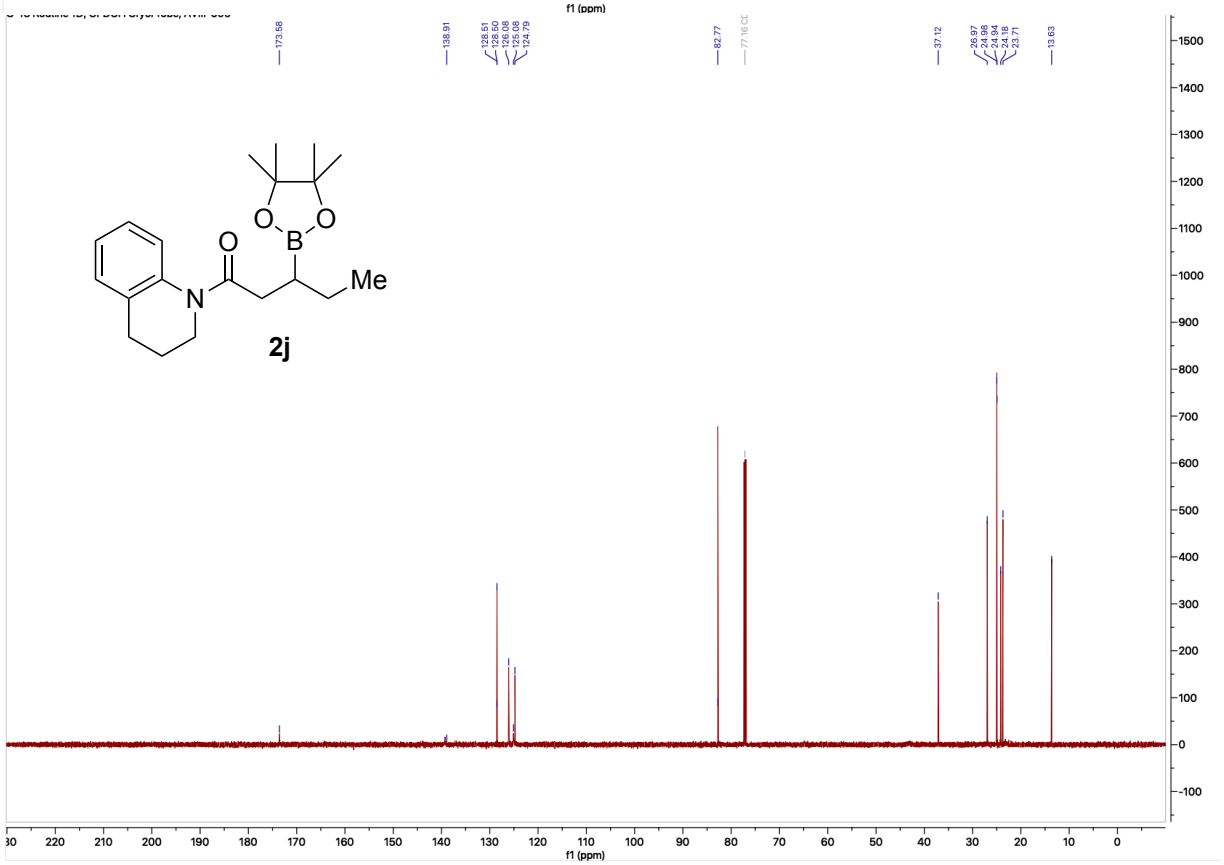

Me
2h
f1 (ppm)

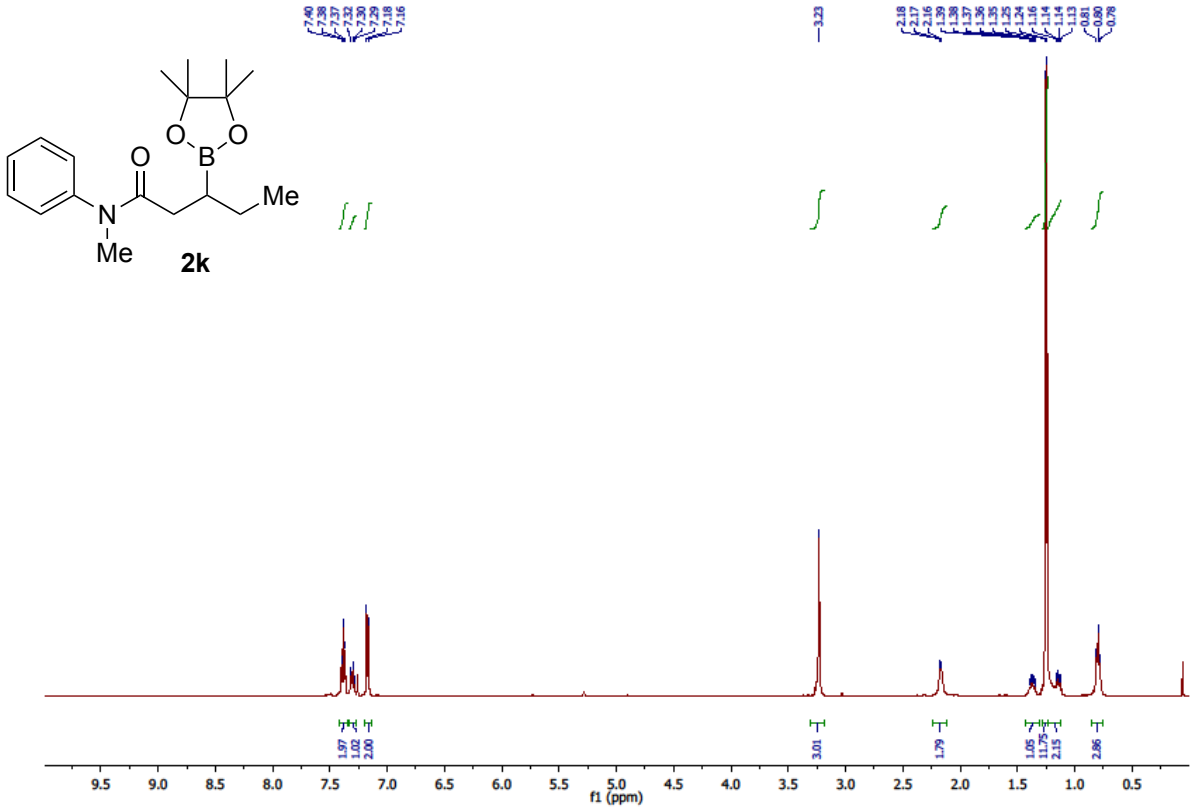

Me
2h
f1 (ppm)

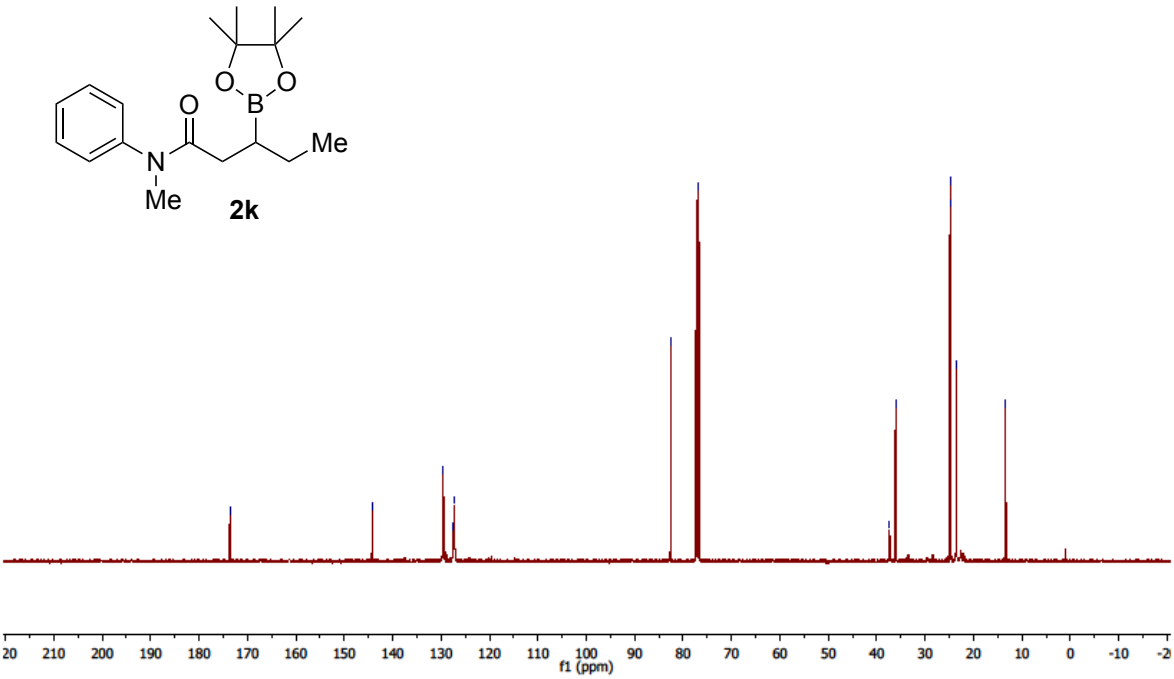

O
B
O
O
N
Me
2i
f1 (ppm)

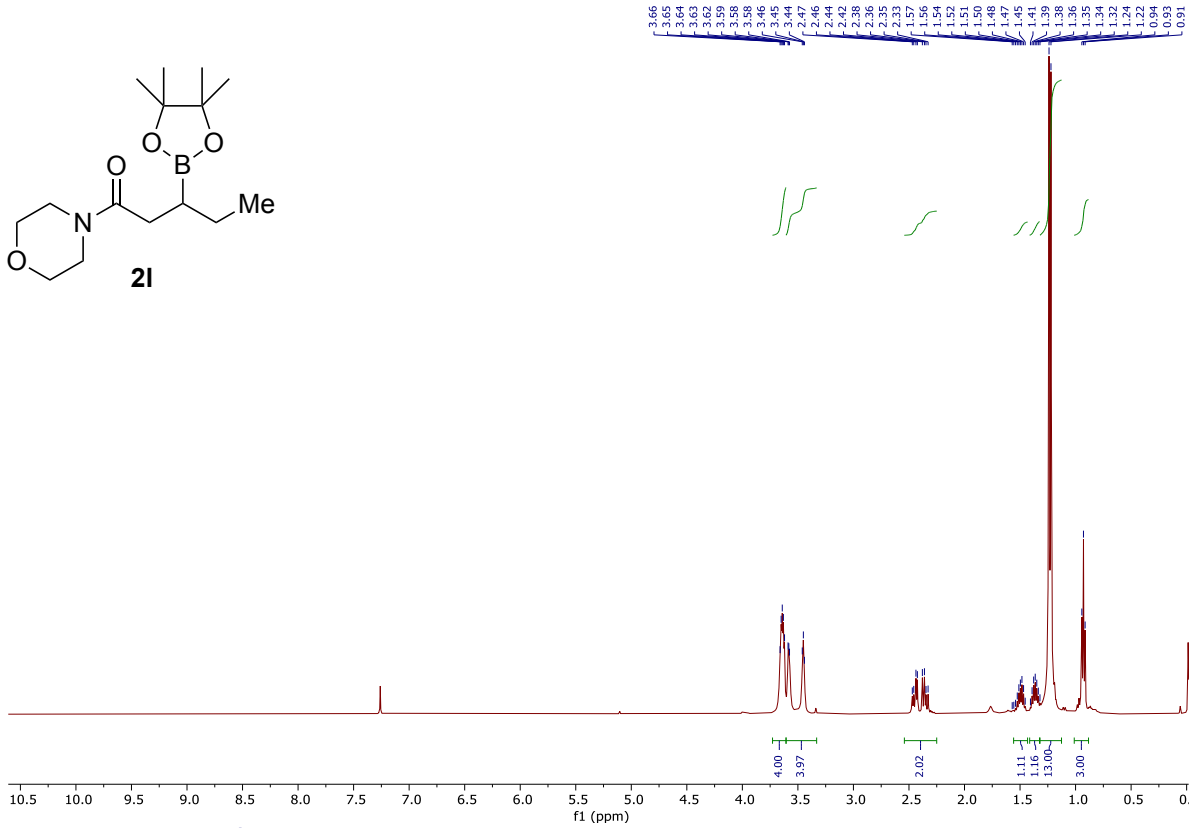

O
B
O
O
N
Me
2i
f1 (ppm)

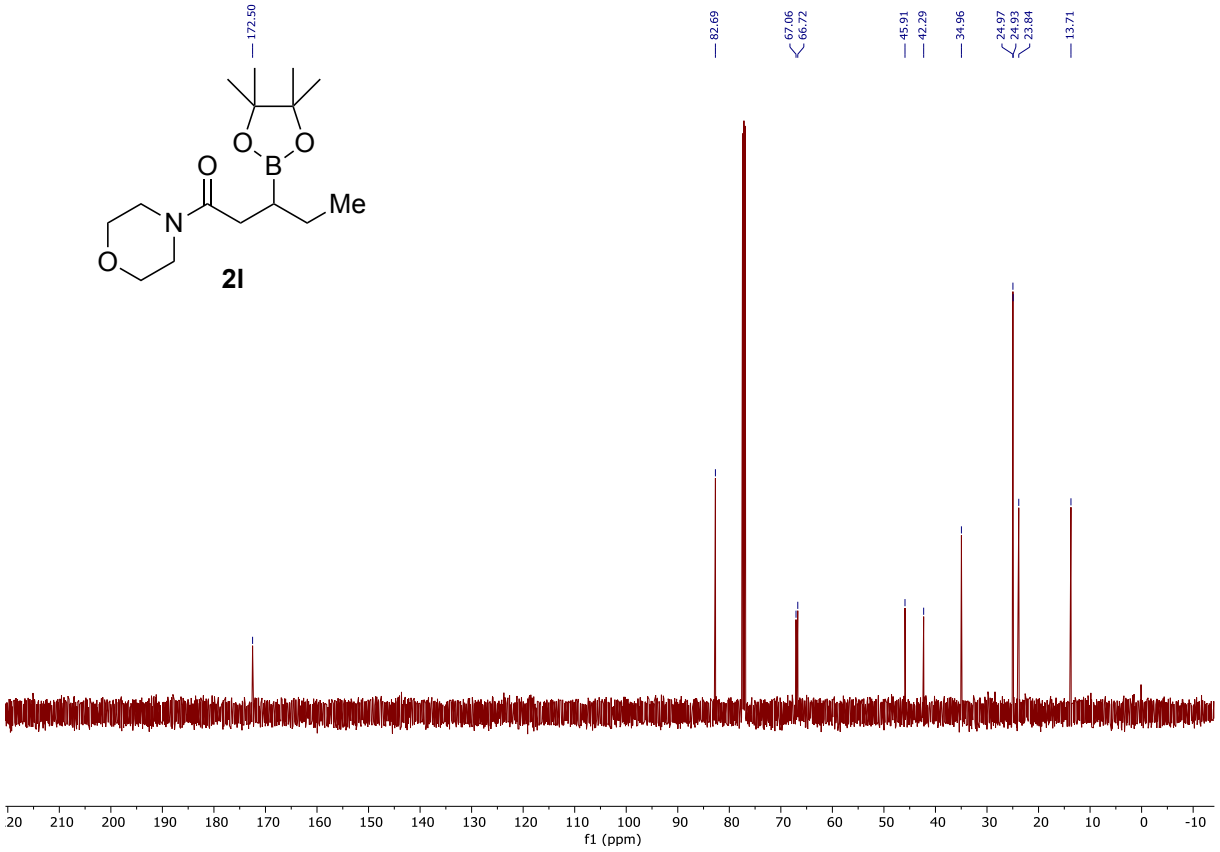

O
O
B
O
N
Me
2j
f1 (ppm)

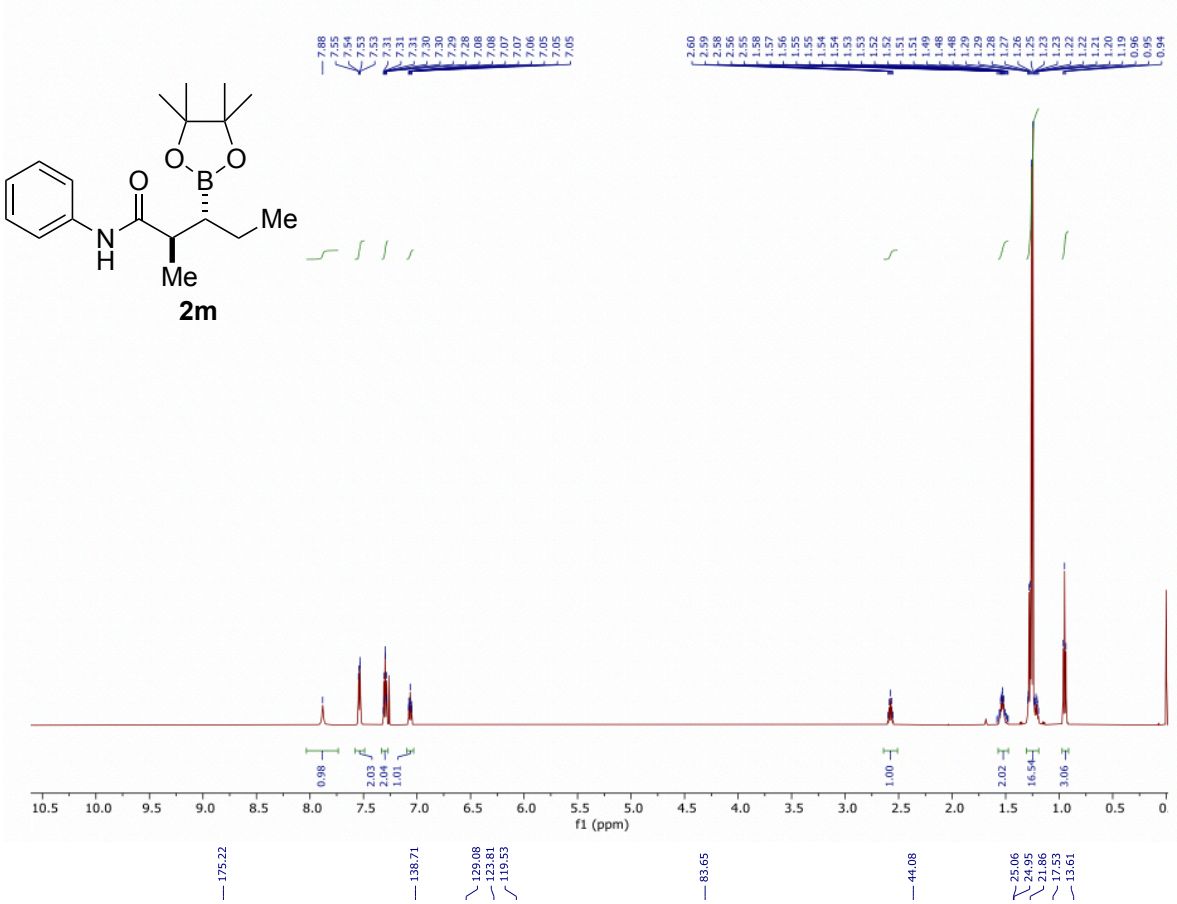

O
O
B
O
N
Me
2j
f1 (ppm)

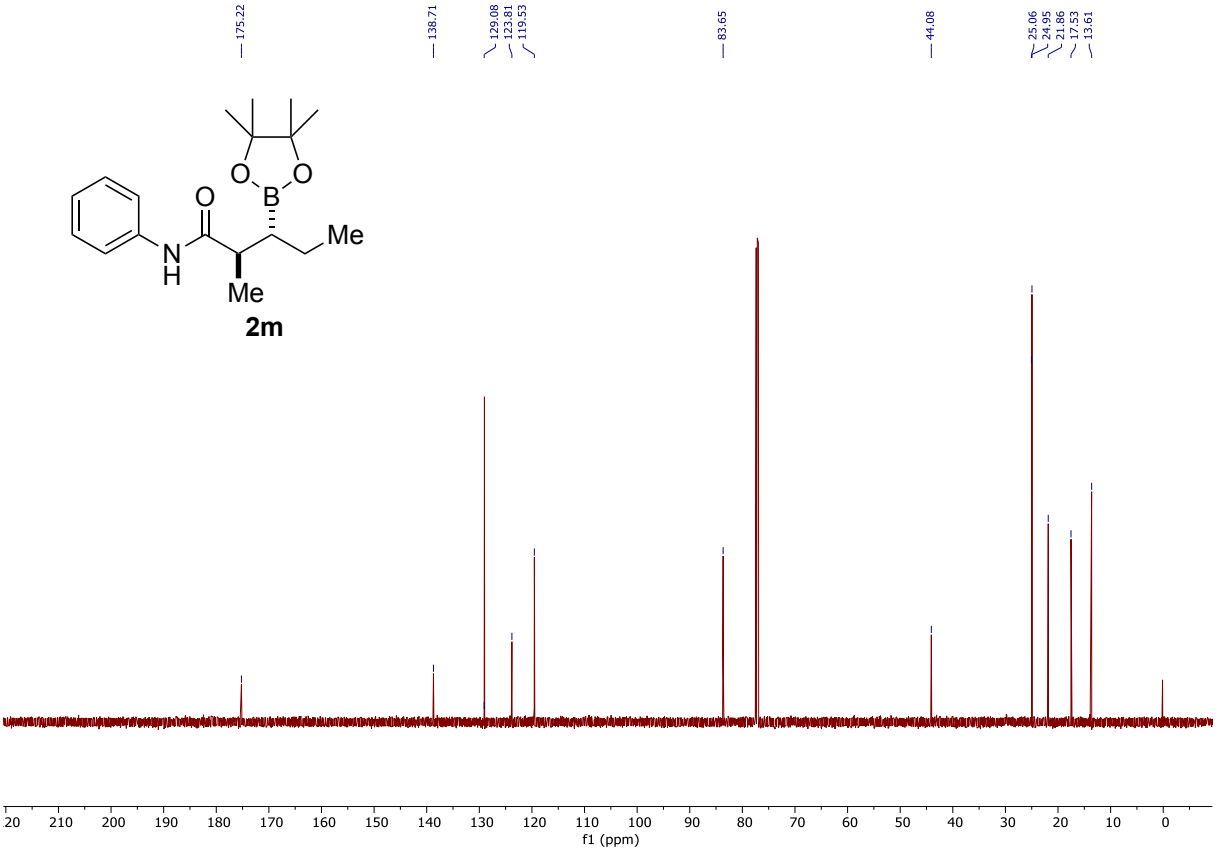

O
B
O
N
Me
Me
Me
2k
f1 (ppm)

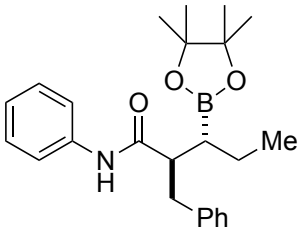

O
B
O
N
Me
Me
Me
2k
f1 (ppm)


2l
f1 (ppm)

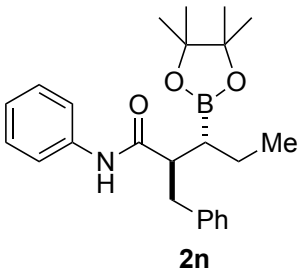

2l
f1 (ppm)


O
O
B
N
H
Me
Me
2m
f1 (ppm)

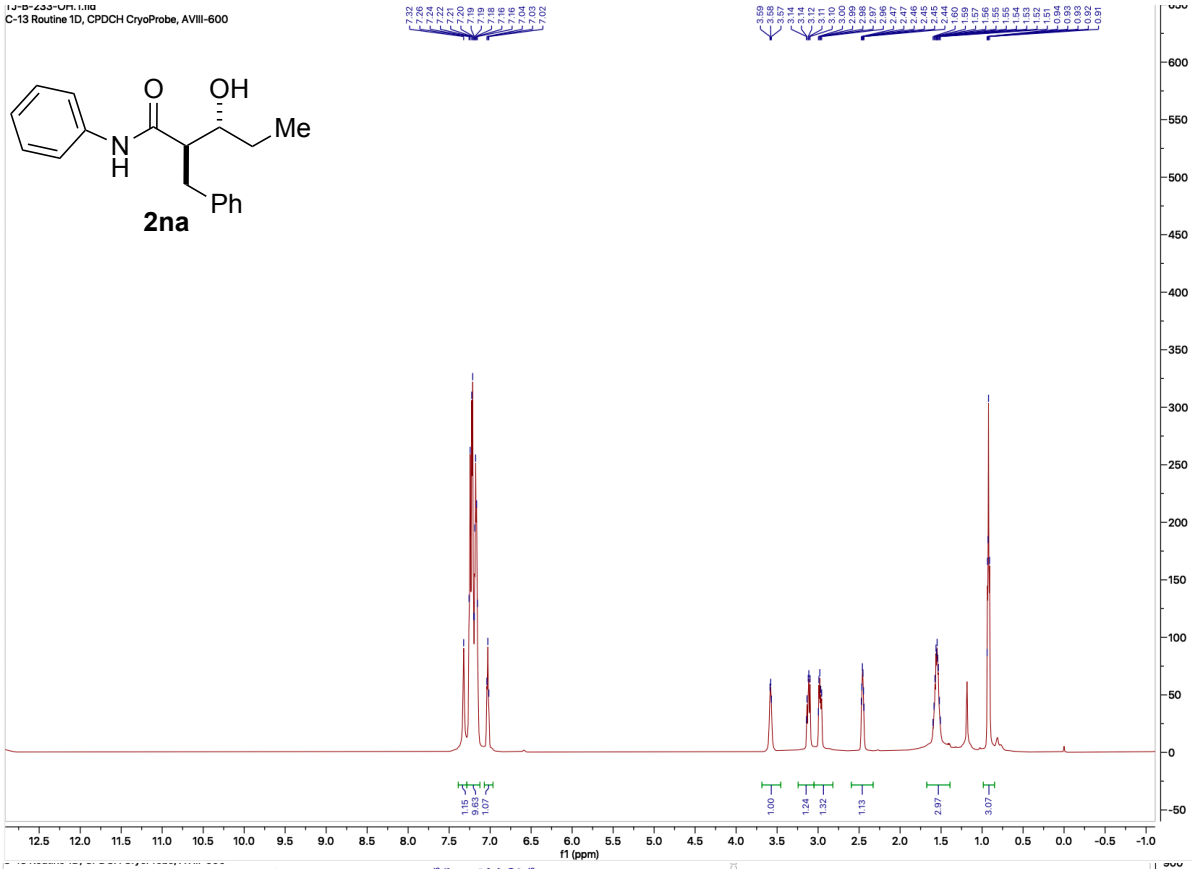

O
O
B
N
H
Me
Me
2m
f1 (ppm)

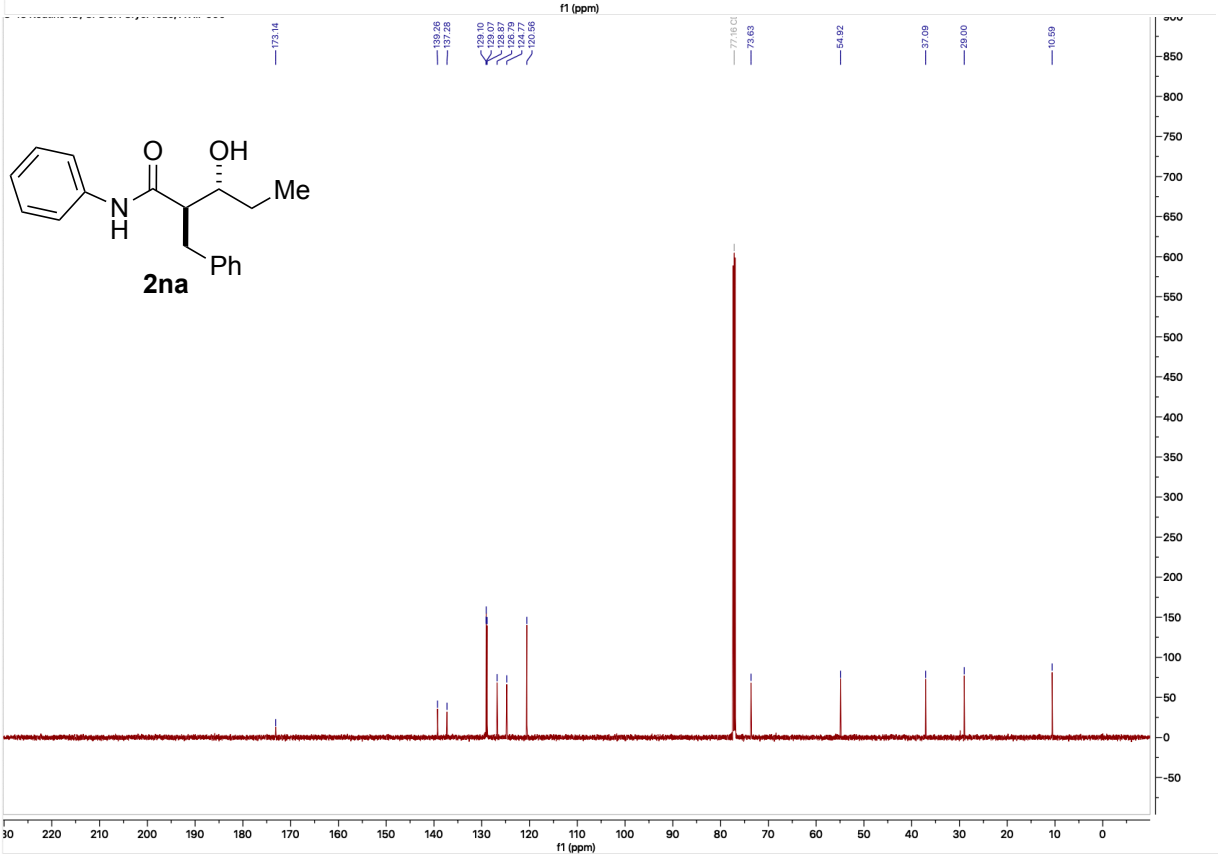


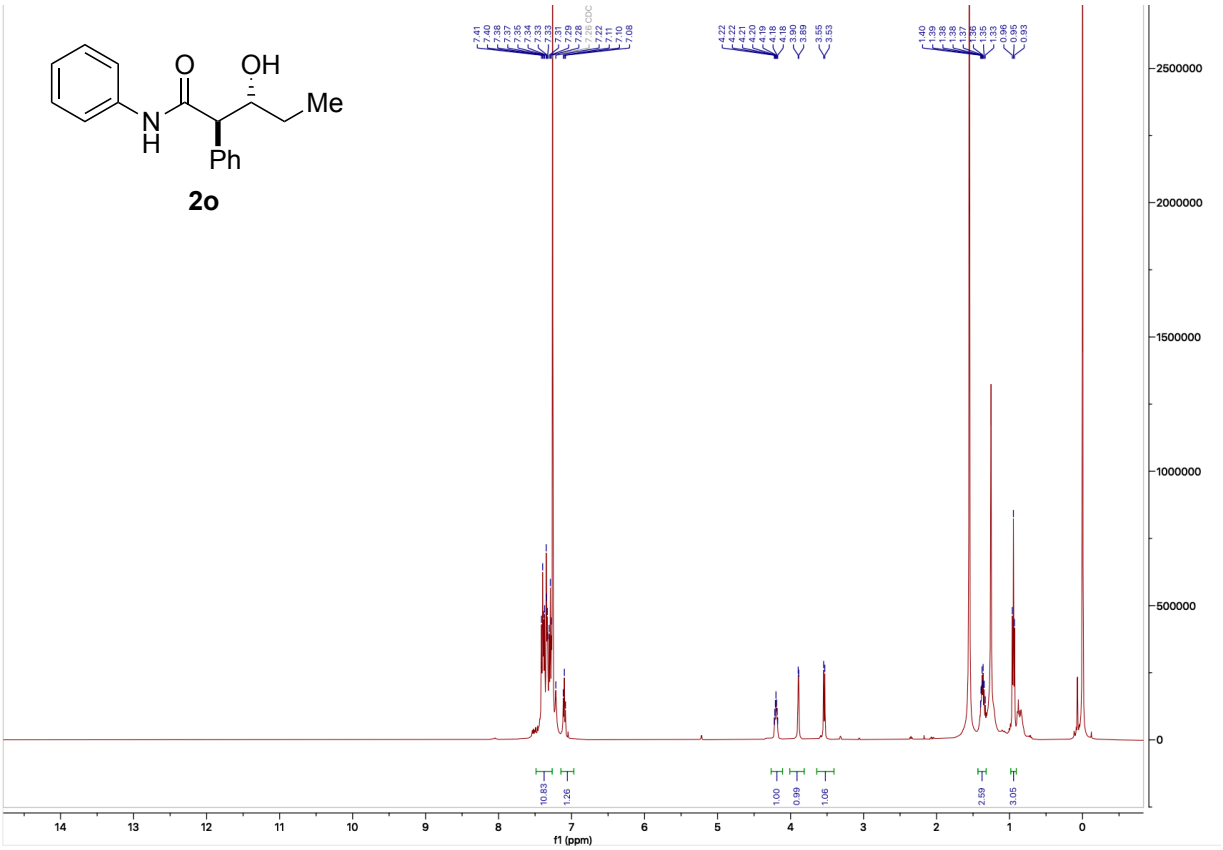
2n

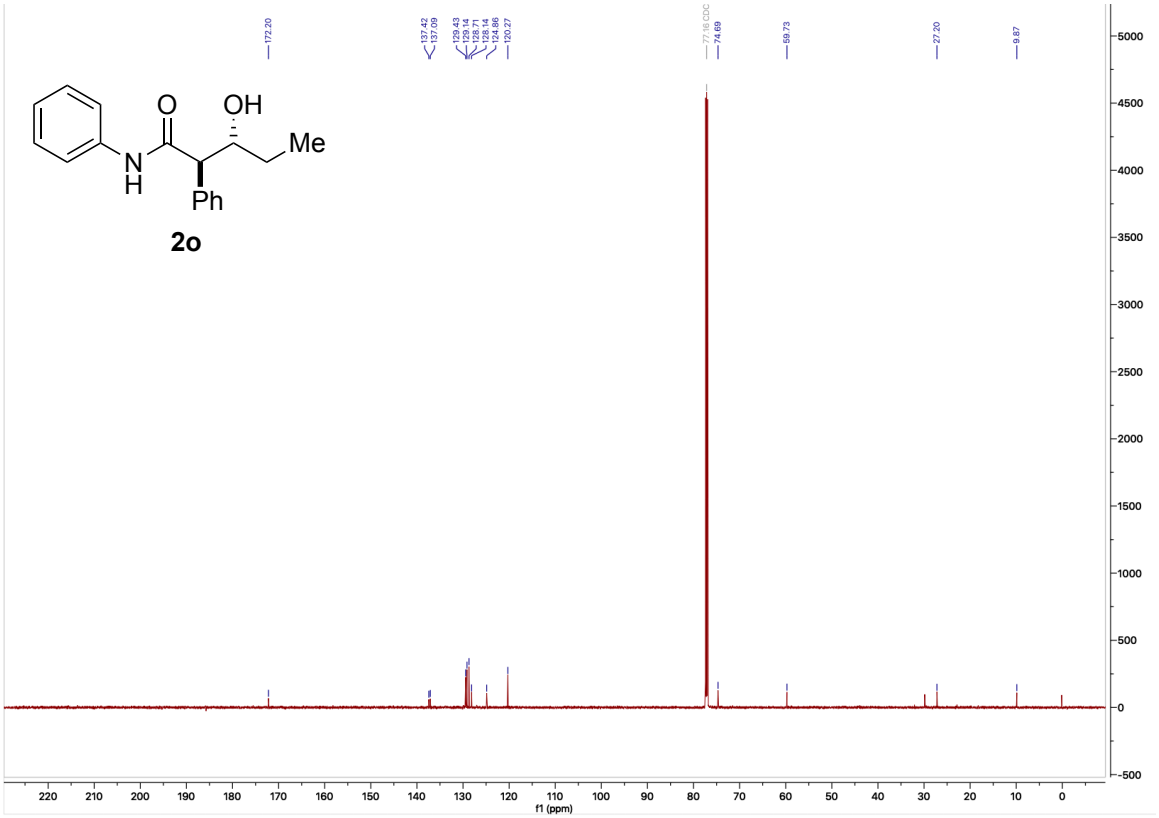


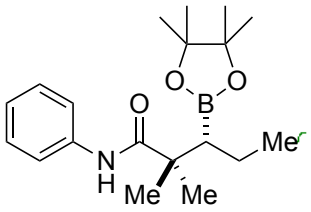
2n


C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
O
OH
N
H
Me
Ph
2na
f1 (ppm)

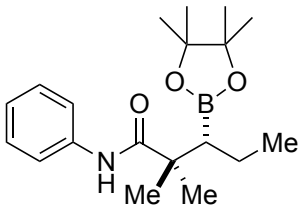

O
OH
N
H
Me
Ph
2na
f1 (ppm)


O
OH
N
H
Me
Ph
2o
f1 (ppm)

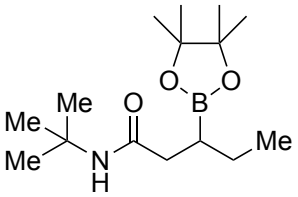

O
OH
N
H
Me
Ph
2o
f1 (ppm)



2p

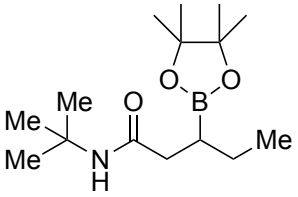


2p


Me
Me
O
B
O
Me
Me
N
H
Me

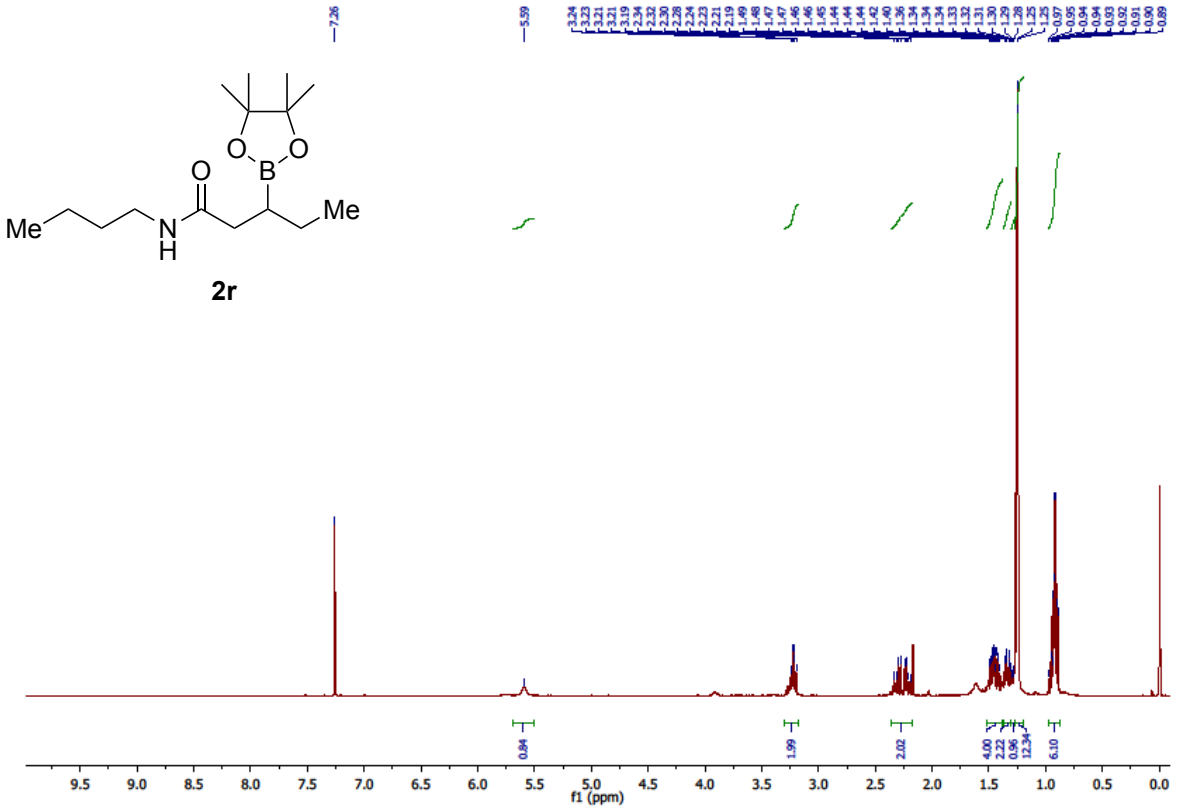
2q

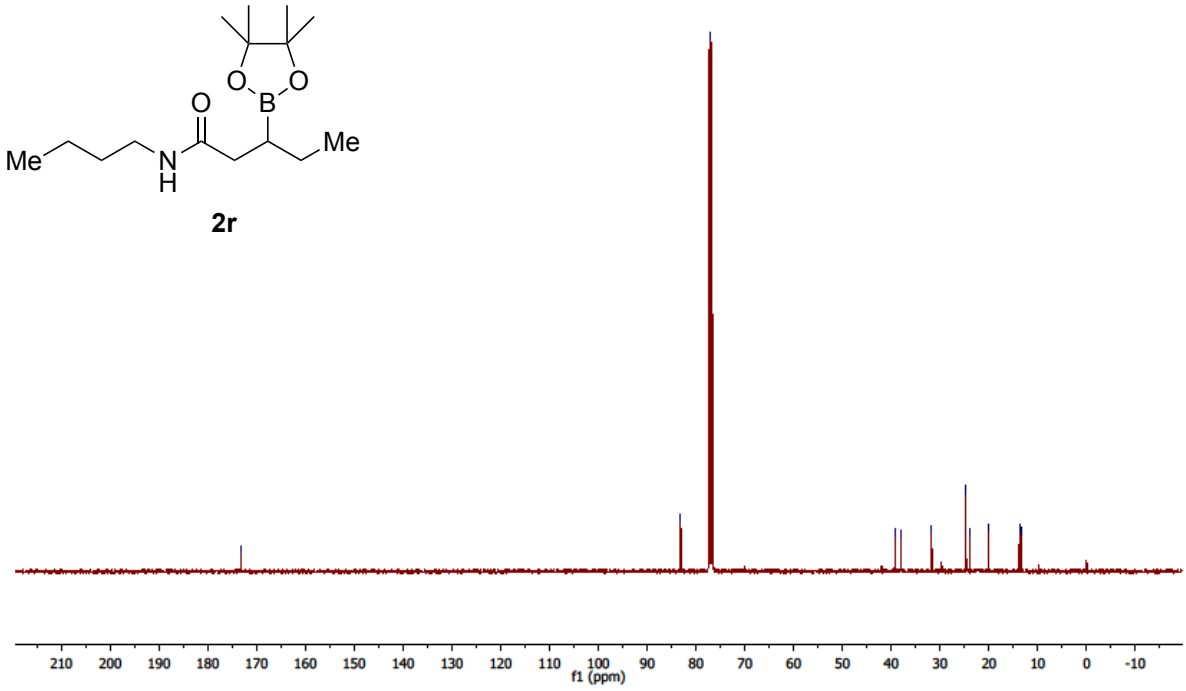
7.26
5.47
1.48
1.46
1.46
1.44
1.42
1.41
1.41
1.39
1.39
1.37
1.36
1.36
1.35
1.34
1.30
1.23
1.22
0.92
0.90
0.88
0.89
2.02
2.00
0.99
8.96
12.12
3.23
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

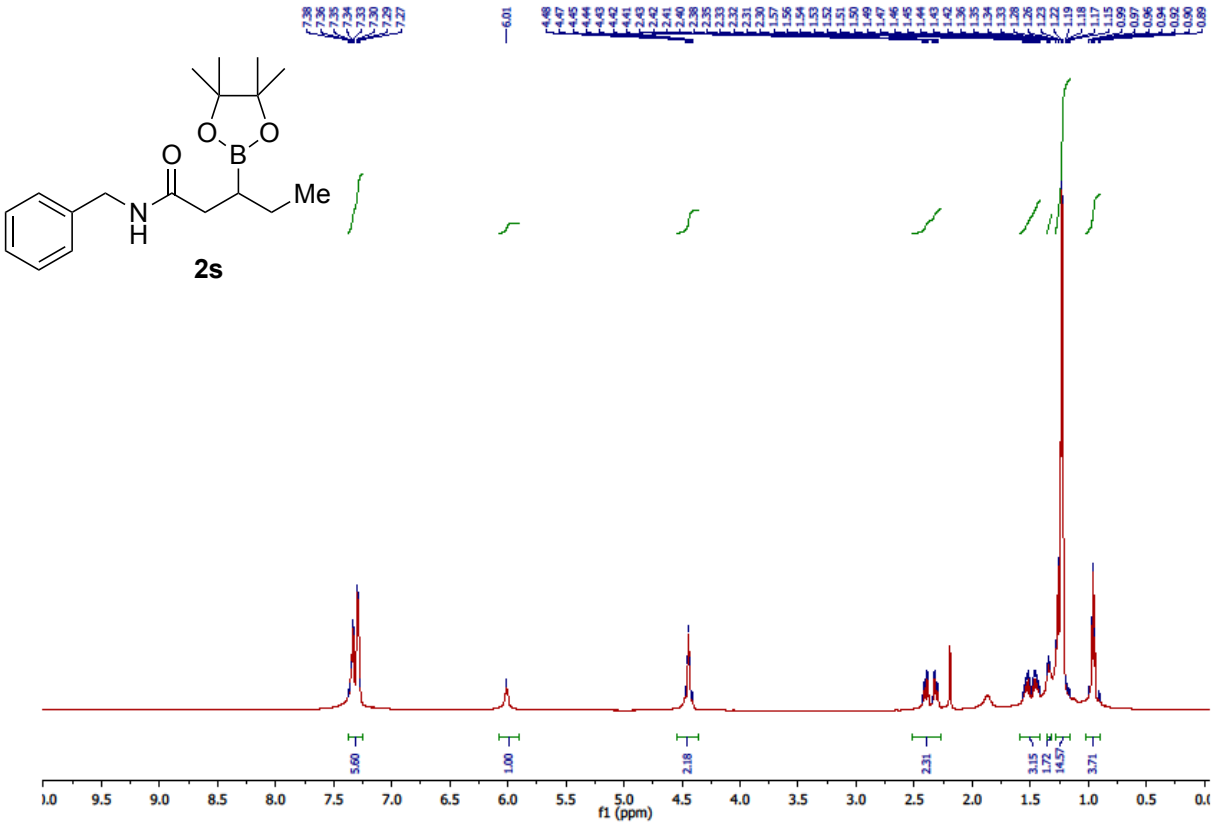

Me
Me
O
B
O
Me
Me
N
H
Me

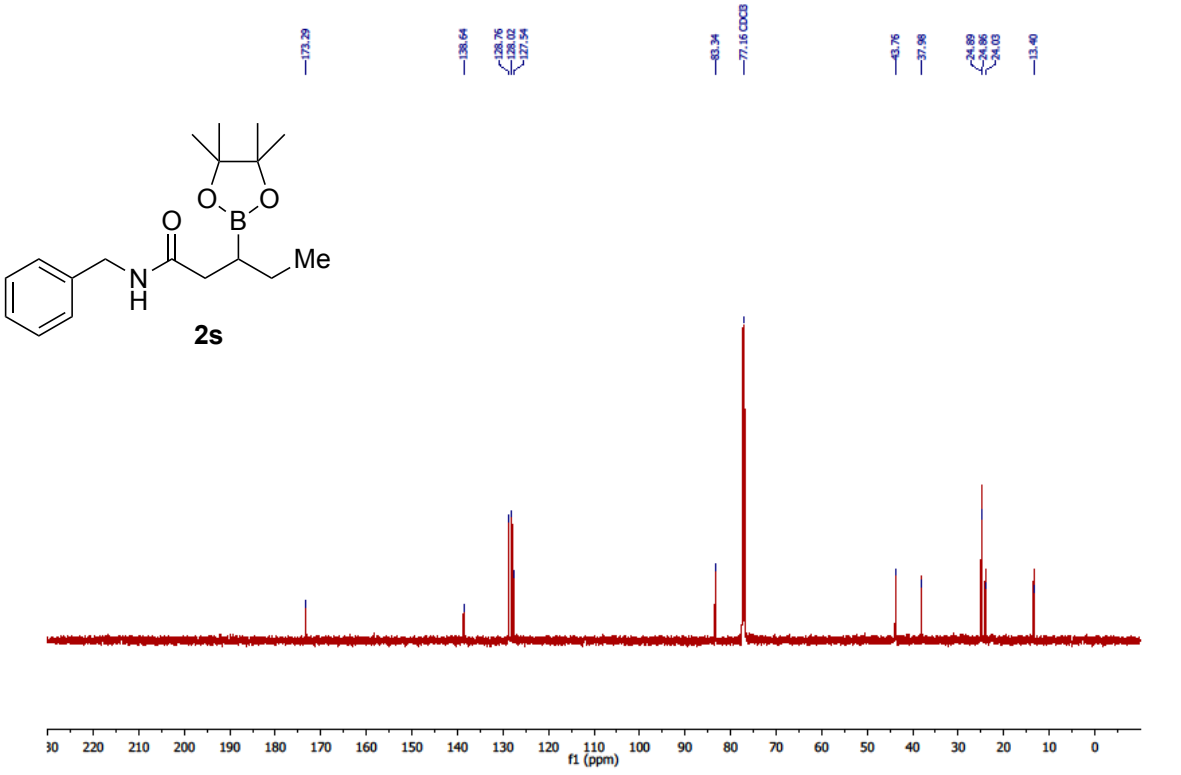
2q

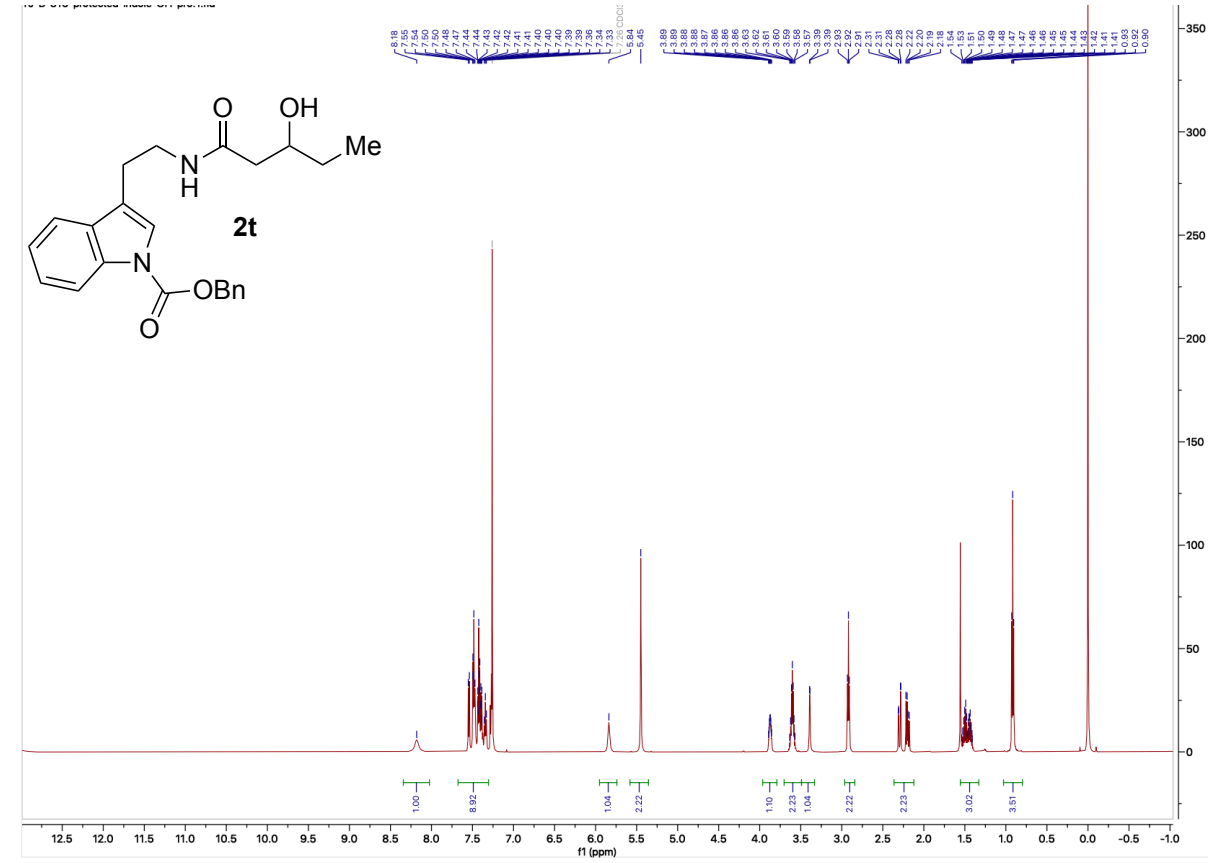
172.63
82.97
77.00
50.93
38.66
28.81
24.80
24.75
23.71
13.31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

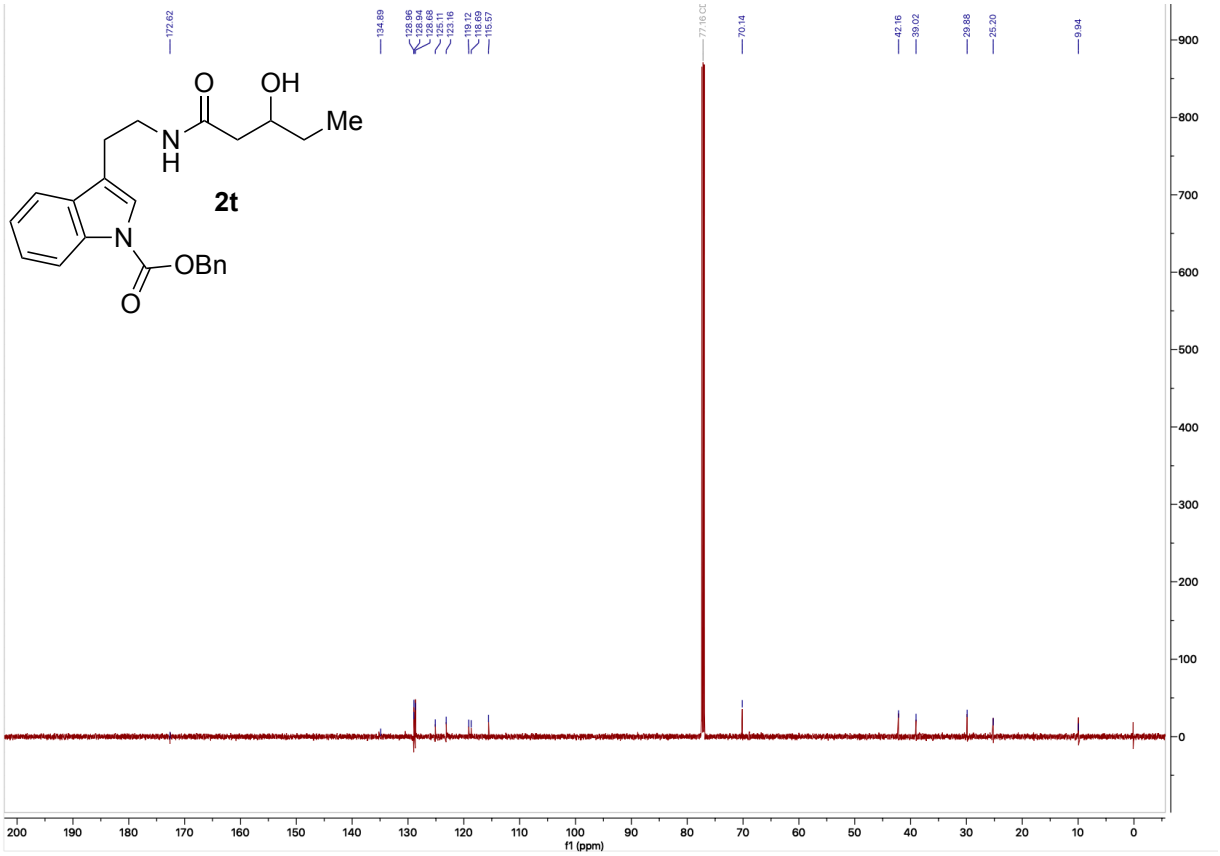

Me
N
H
O
O
B
O
Me
2r
f1 (ppm)

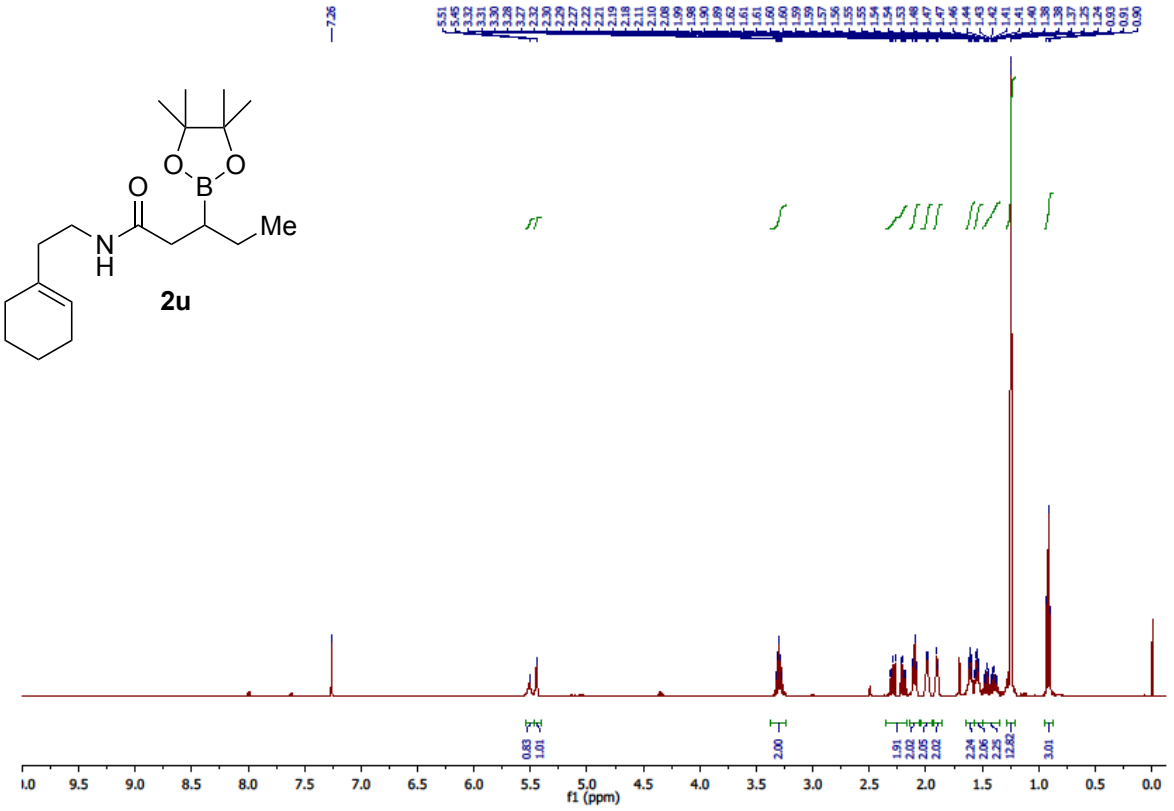

Me
N
H
O
O
B
O
Me
2r
f1 (ppm)

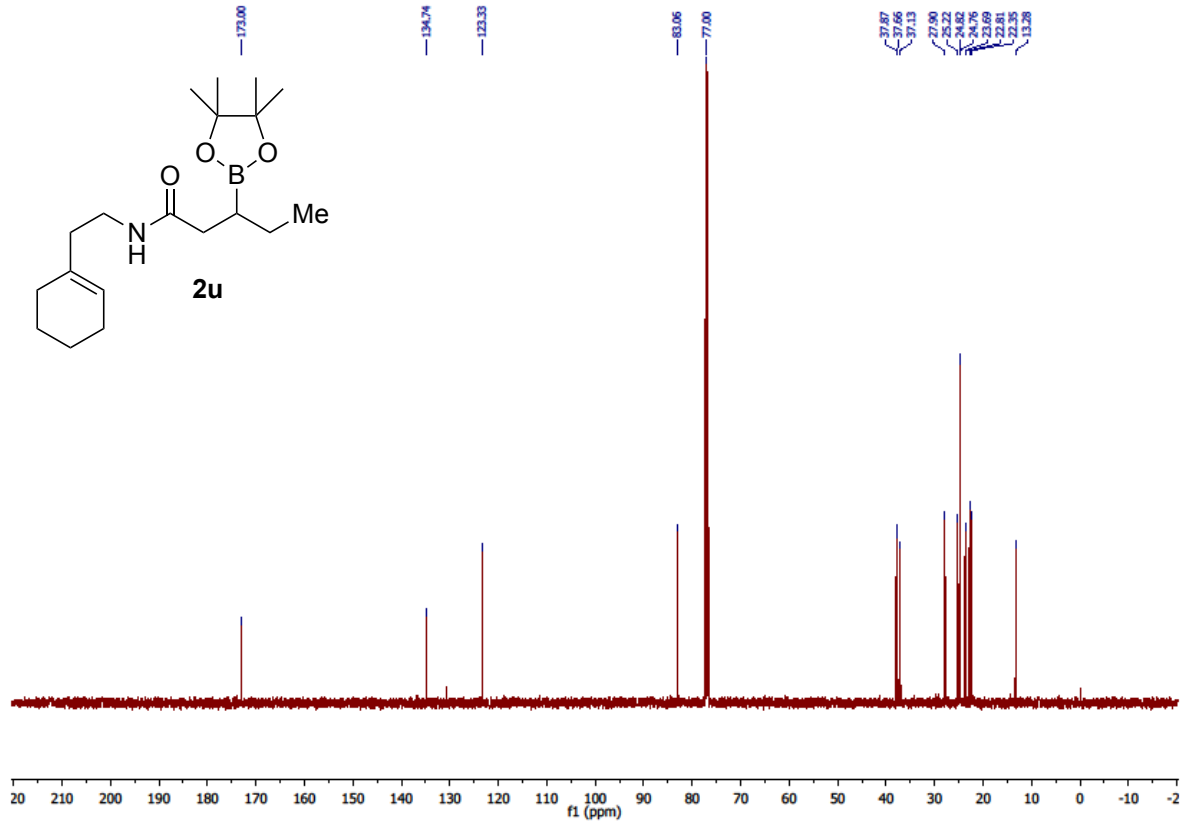

O
B
O
O
N
H
Me
2s
f1 (ppm)

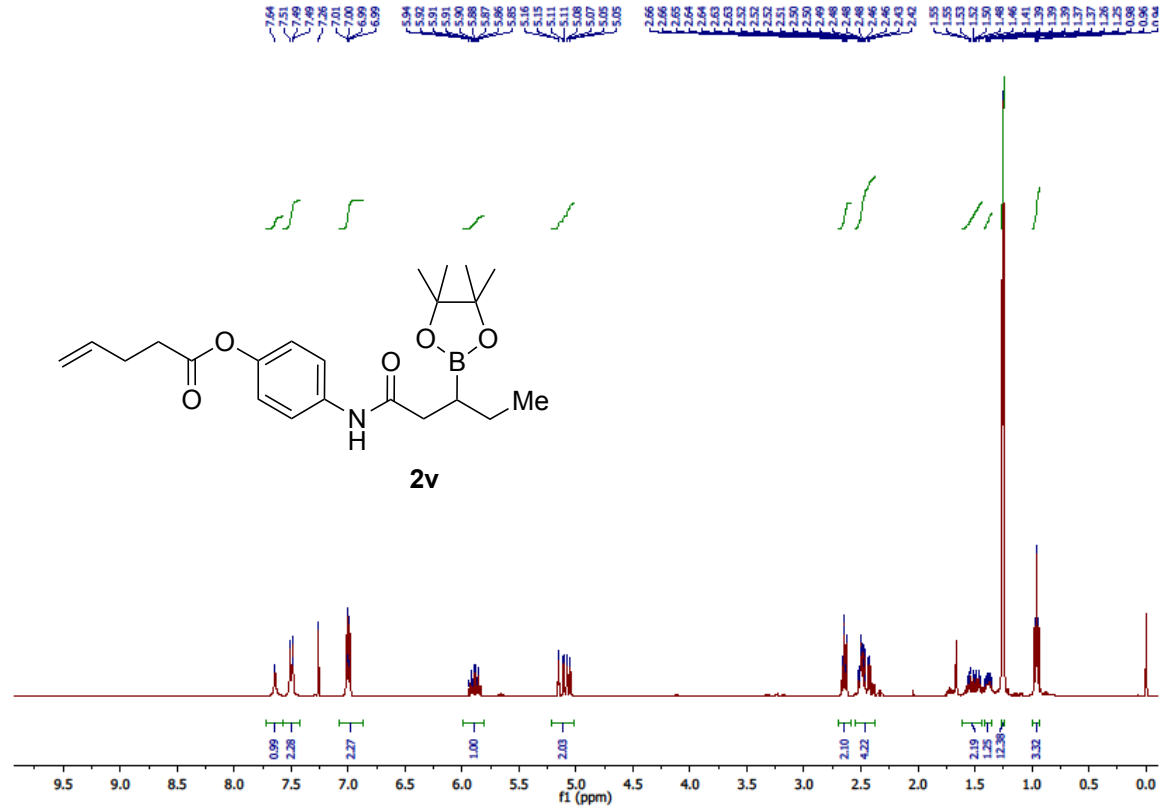

O
B
O
O
N
H
Me
2s
f1 (ppm)

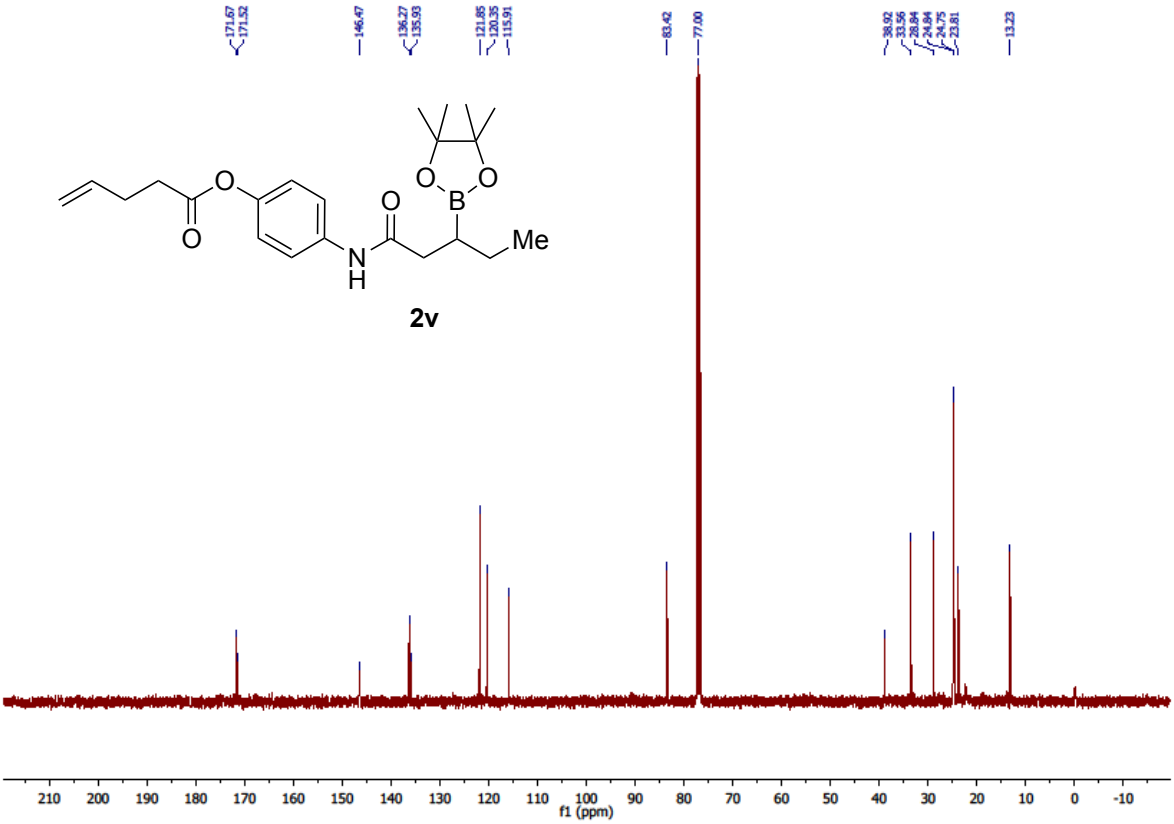

O
OH
Me
N
H
2t
N
OBn
O
f1 (ppm)

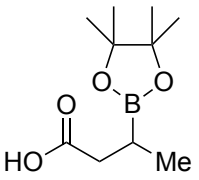

O
OH
Me
N
H
2t
N
OBn
O
f1 (ppm)


2u
f1 (ppm)


2u
f1 (ppm)

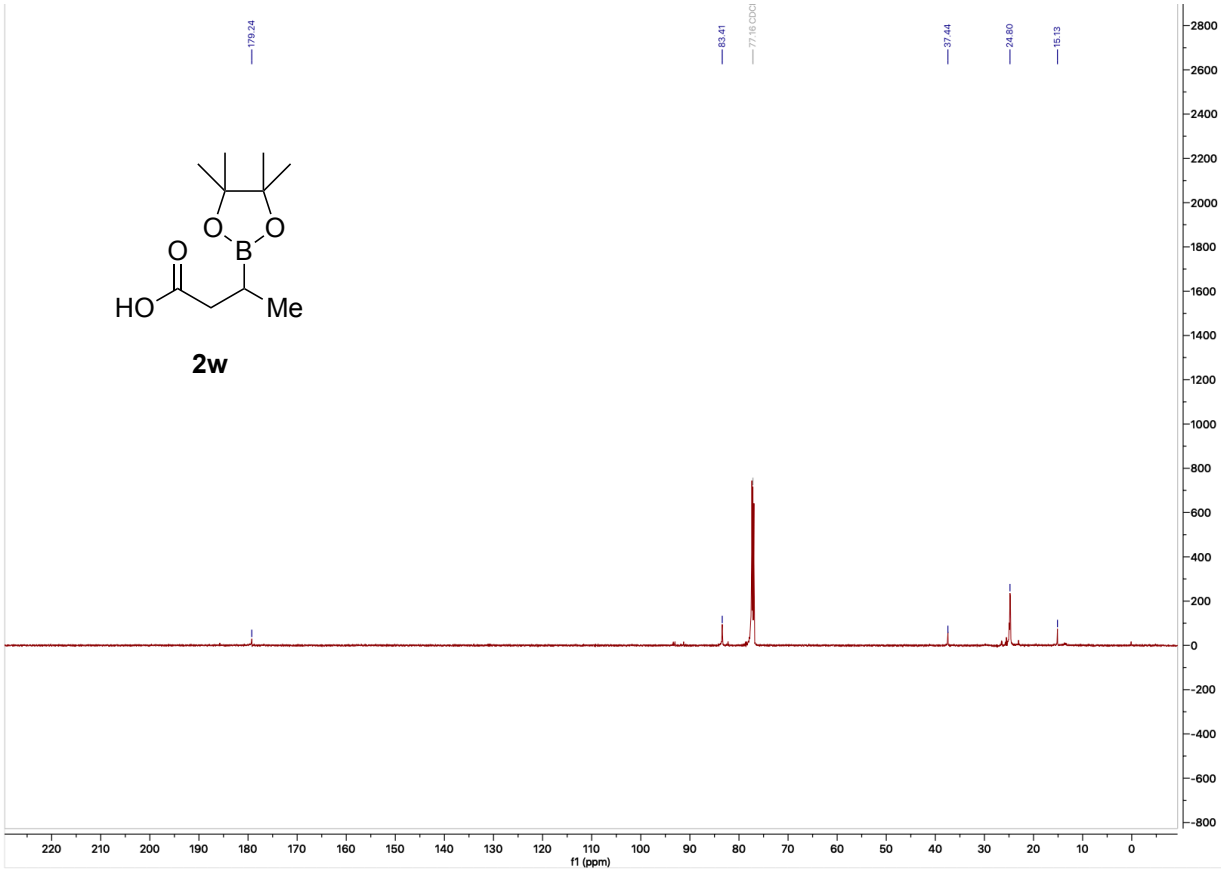

O
O
O
O
B
O
N
H
Me
2v
f1 (ppm)


O
O
O
O
B
O
N
H
Me
2v
f1 (ppm)


O
O
B
O
HO
Me

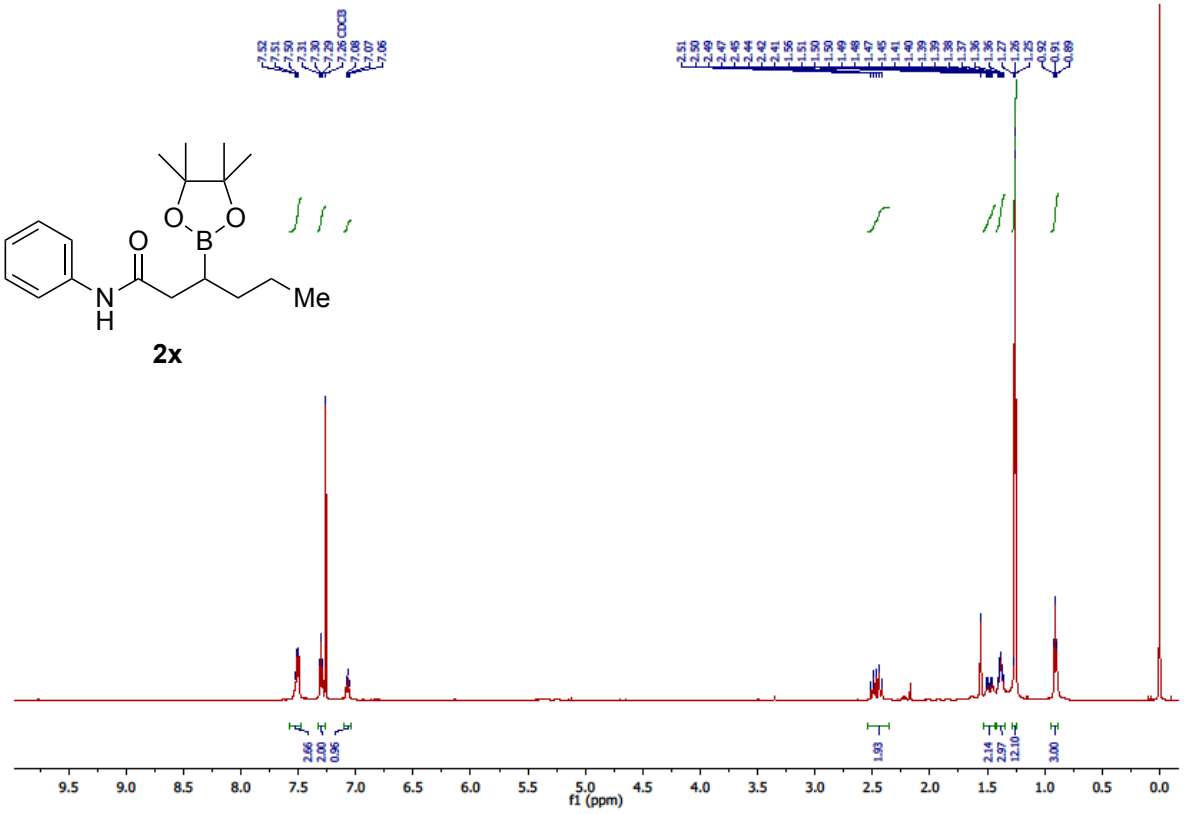
2w

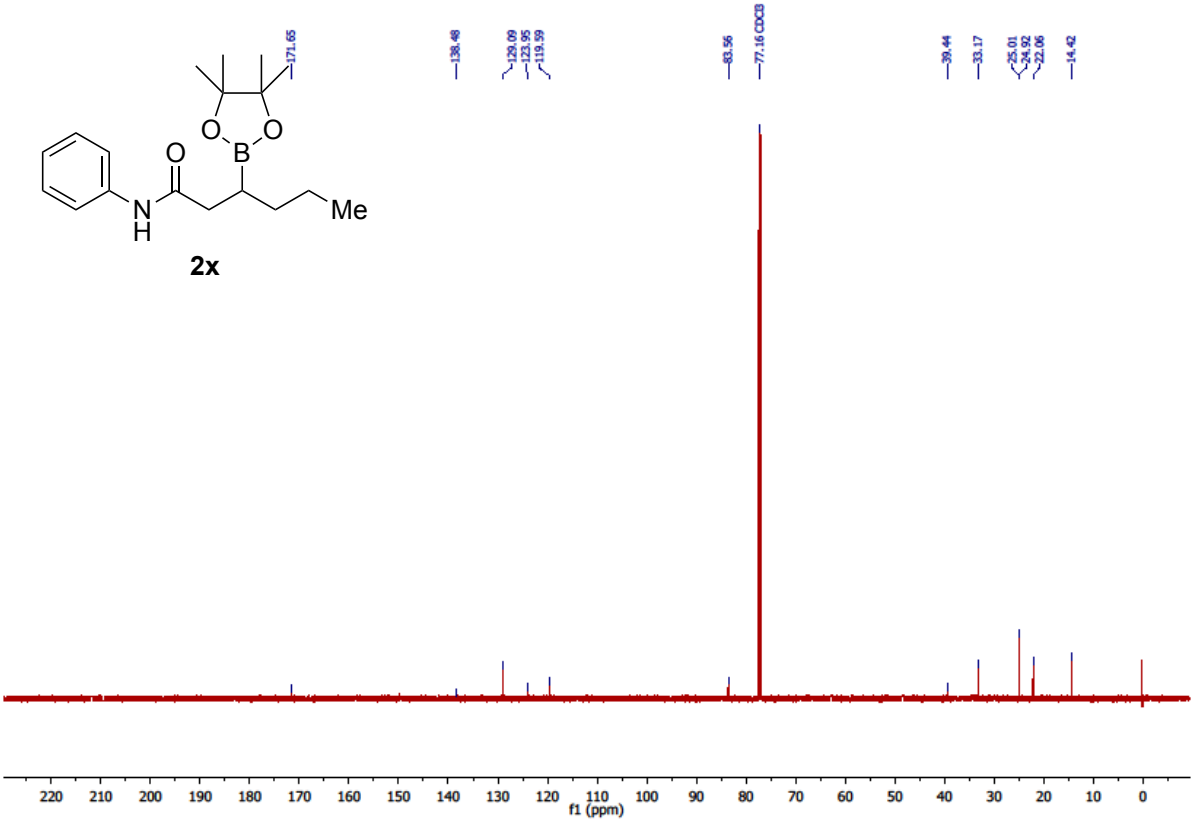
7.26 CDCl3
2.48
2.46
2.45
2.44
2.42
2.41
2.39
2.38
1.37
1.37
1.36
1.35
1.34
1.34
1.33
1.33
1.32
1.24
1.23
1.22
1.22
1.21
1.20
1.01
1.00
1.84
1.46
23.06
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)

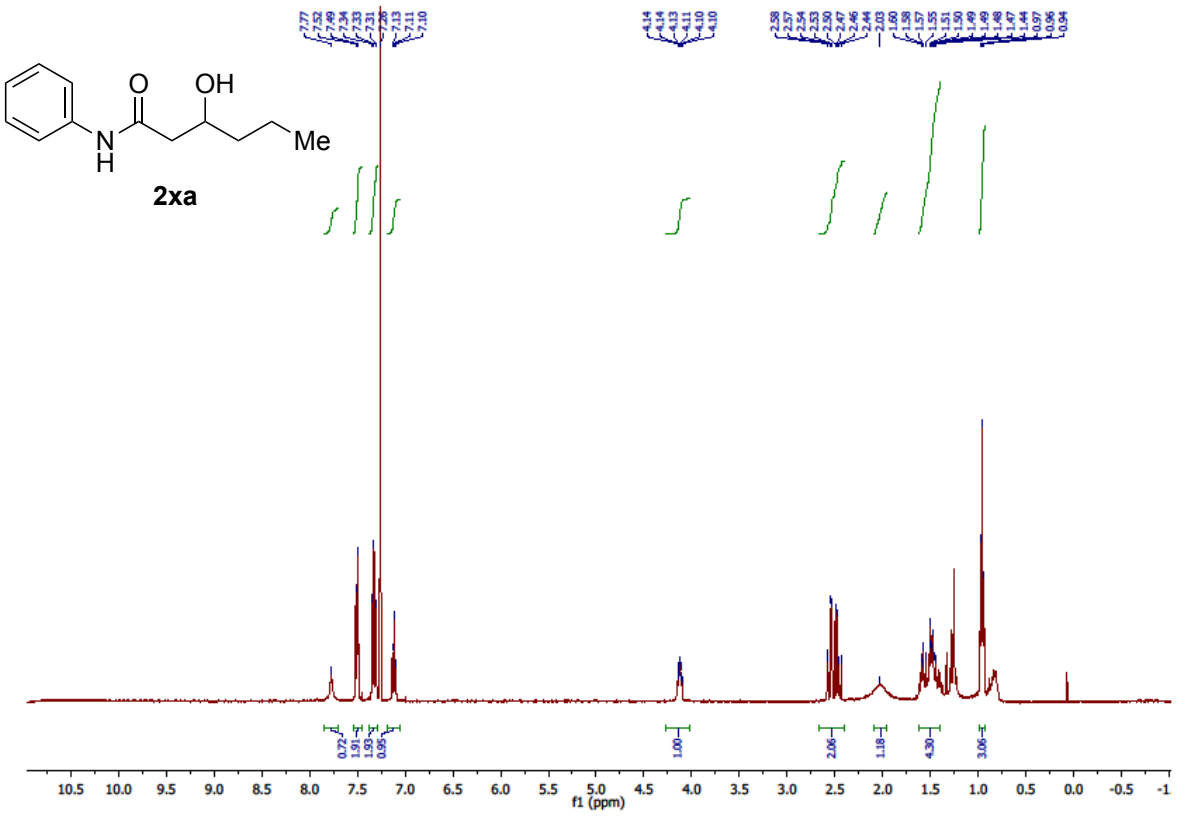

179.24
83.41
77.16 CDCl
37.44
24.80
15.13
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600
-800
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

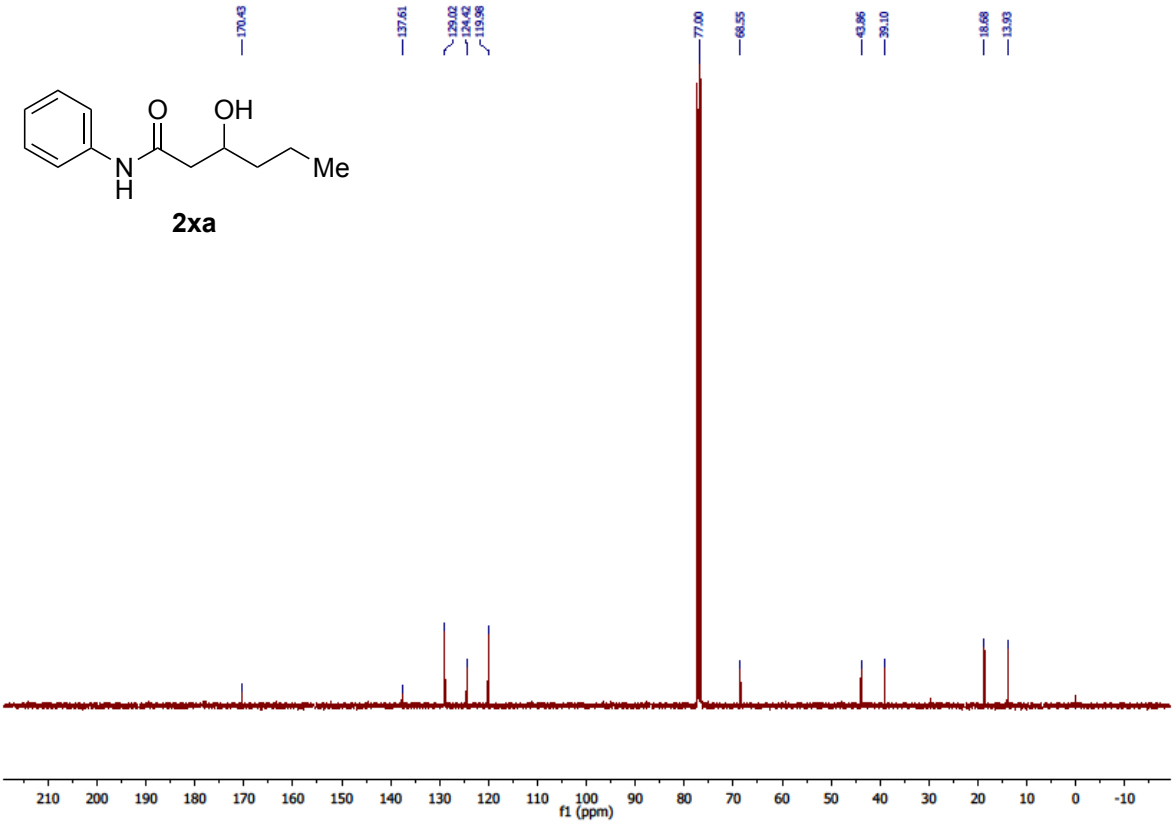
O
O
B
O
HO
Me

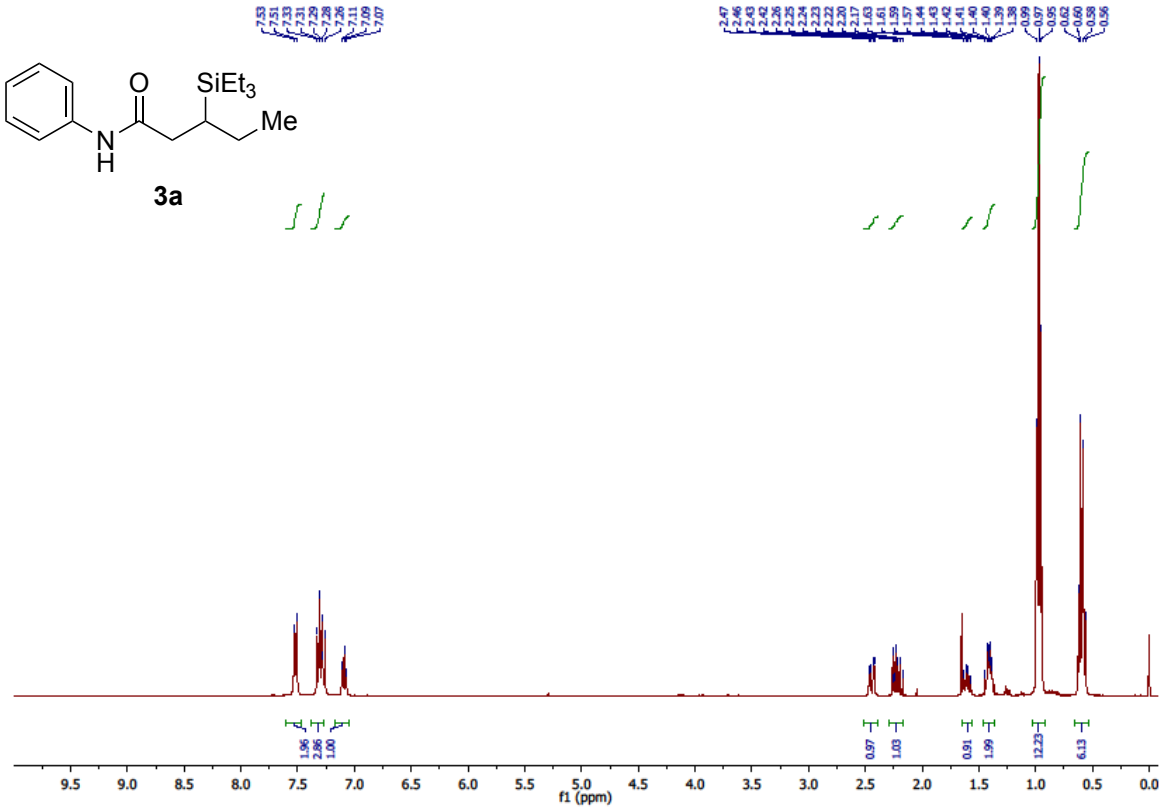
2w

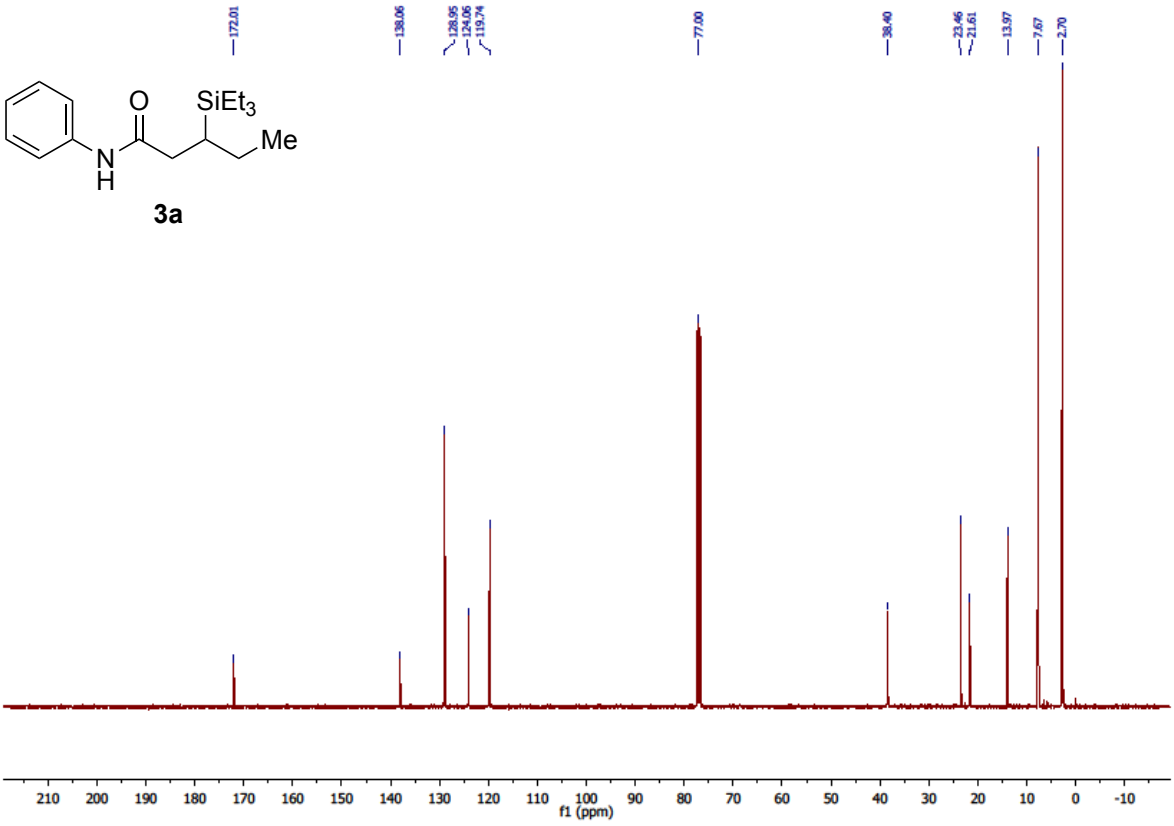

Me
2x
f1 (ppm)

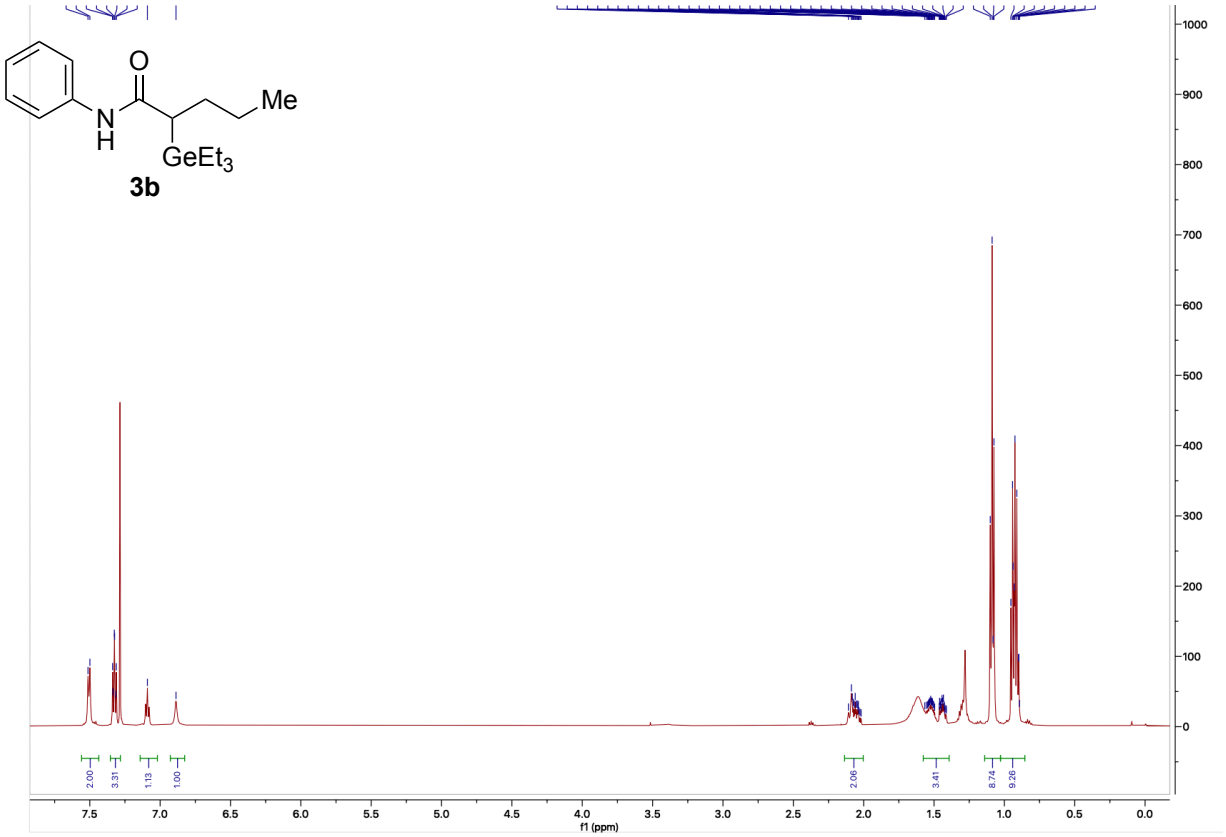

Me
2x
f1 (ppm)

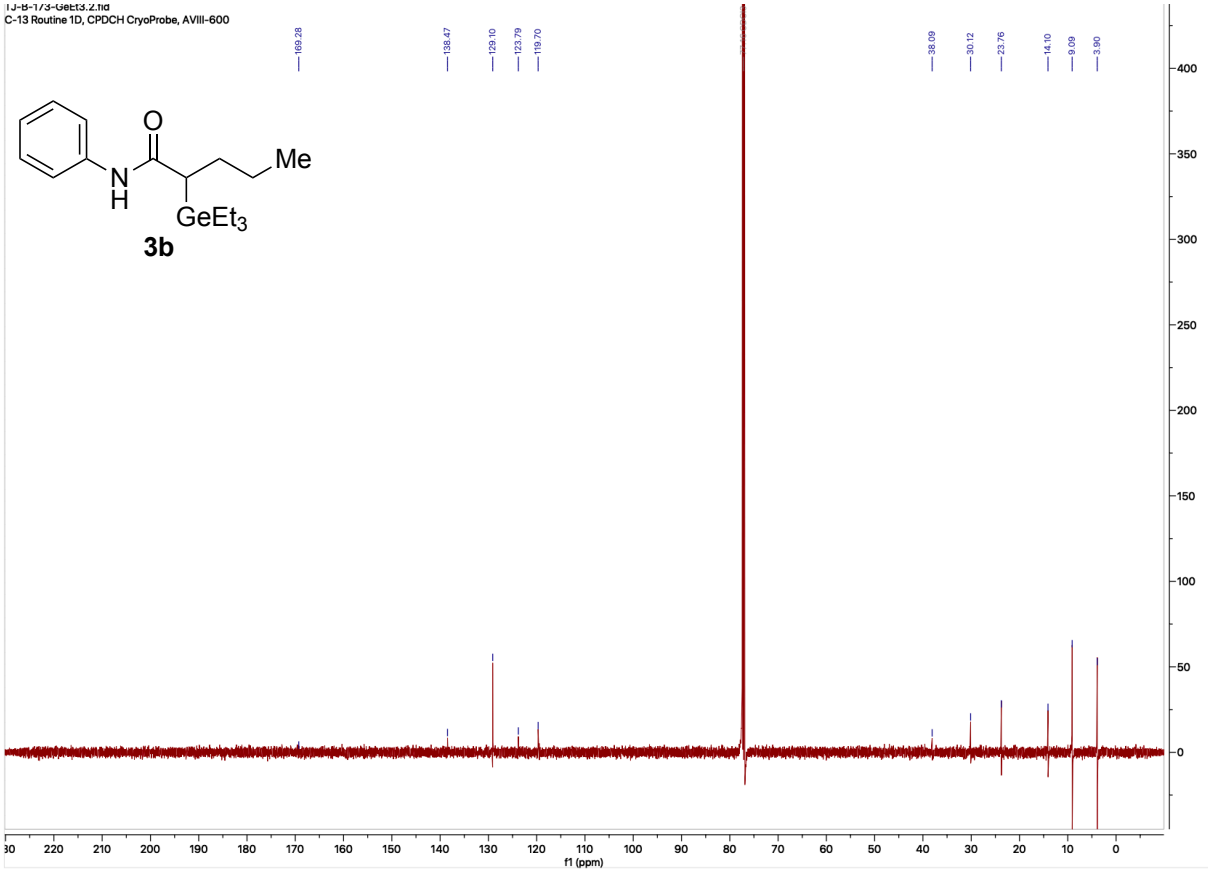

O
OH
N
H
Me
2xa
f1 (ppm)

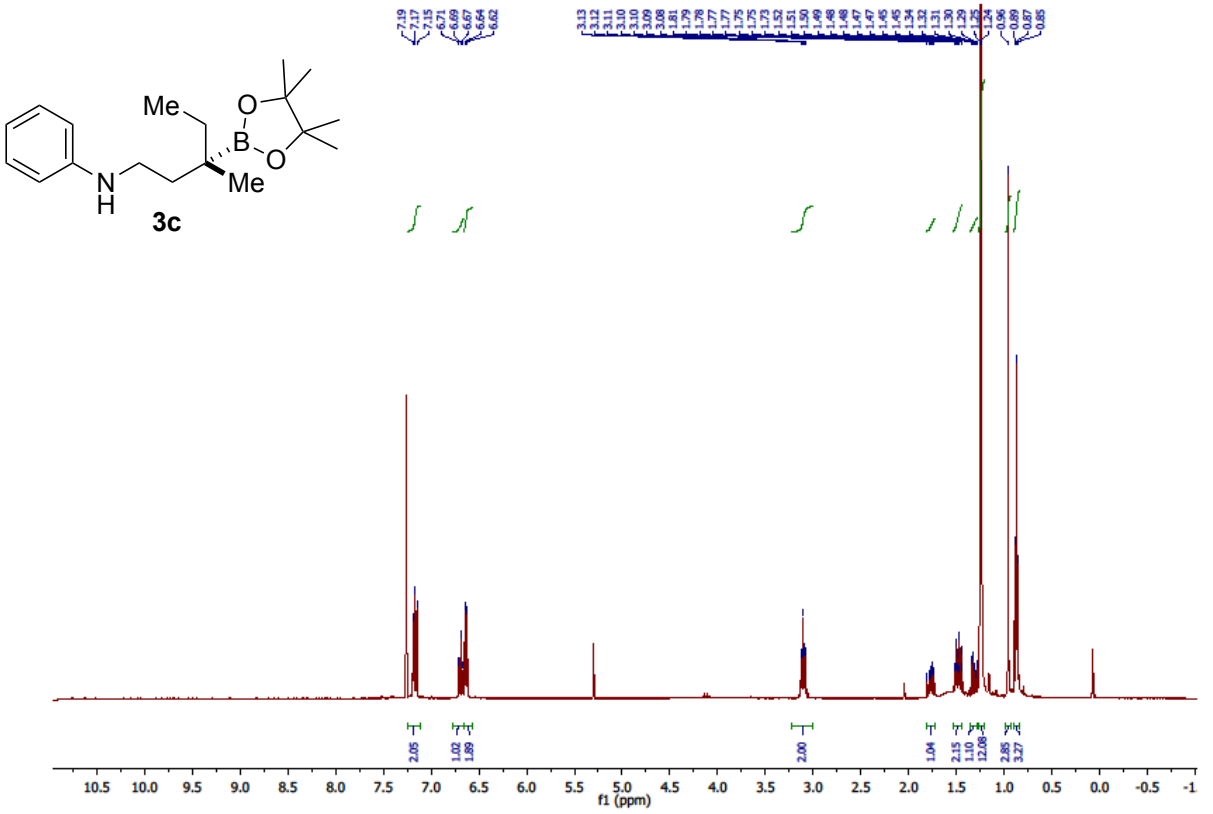

O
OH
N
H
Me
2xa
f1 (ppm)

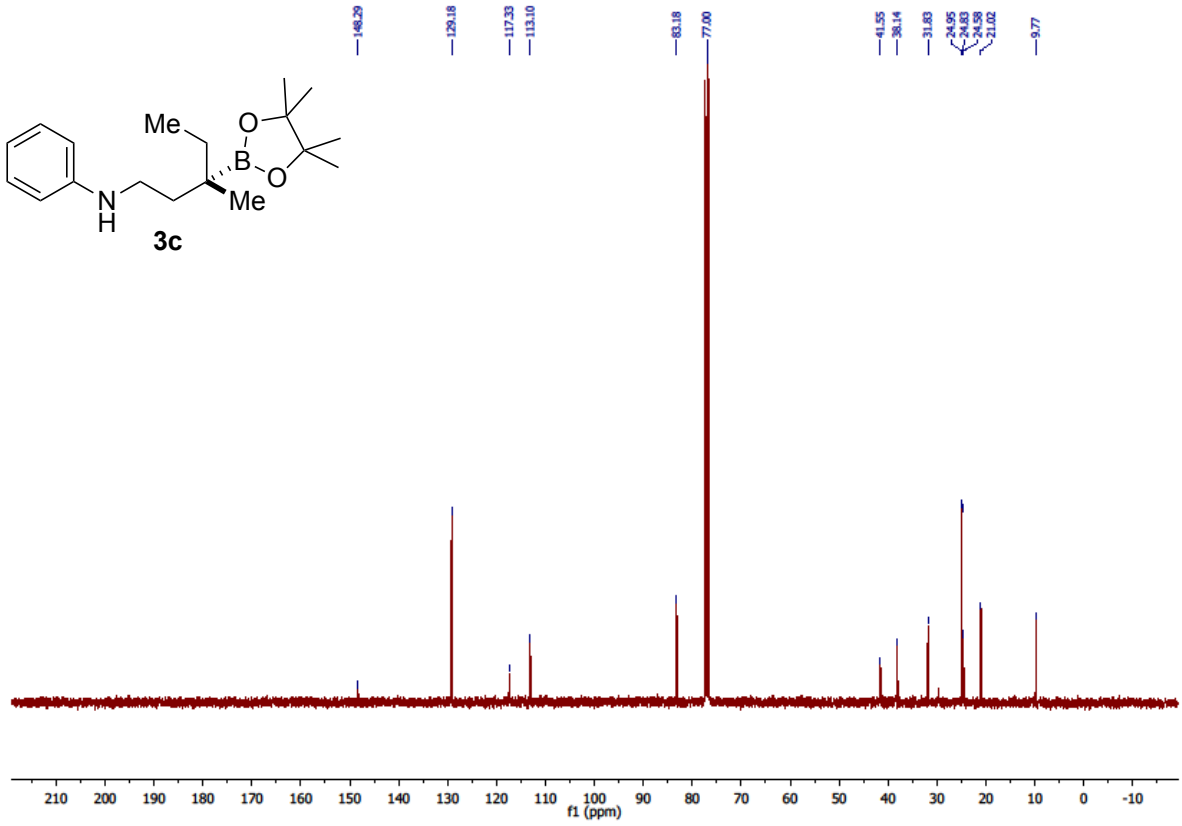

O
SiEt3
Me
N
H
3a
f1 (ppm)

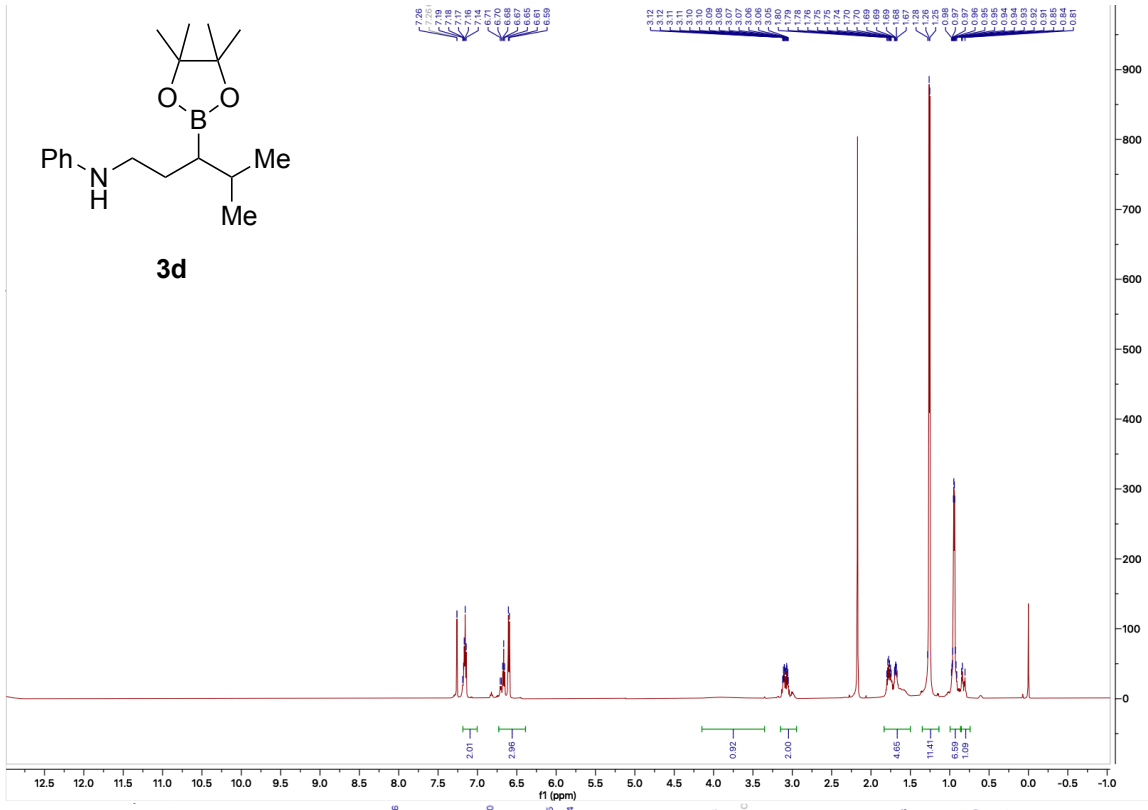

O
SiEt3
Me
N
H
3a
f1 (ppm)

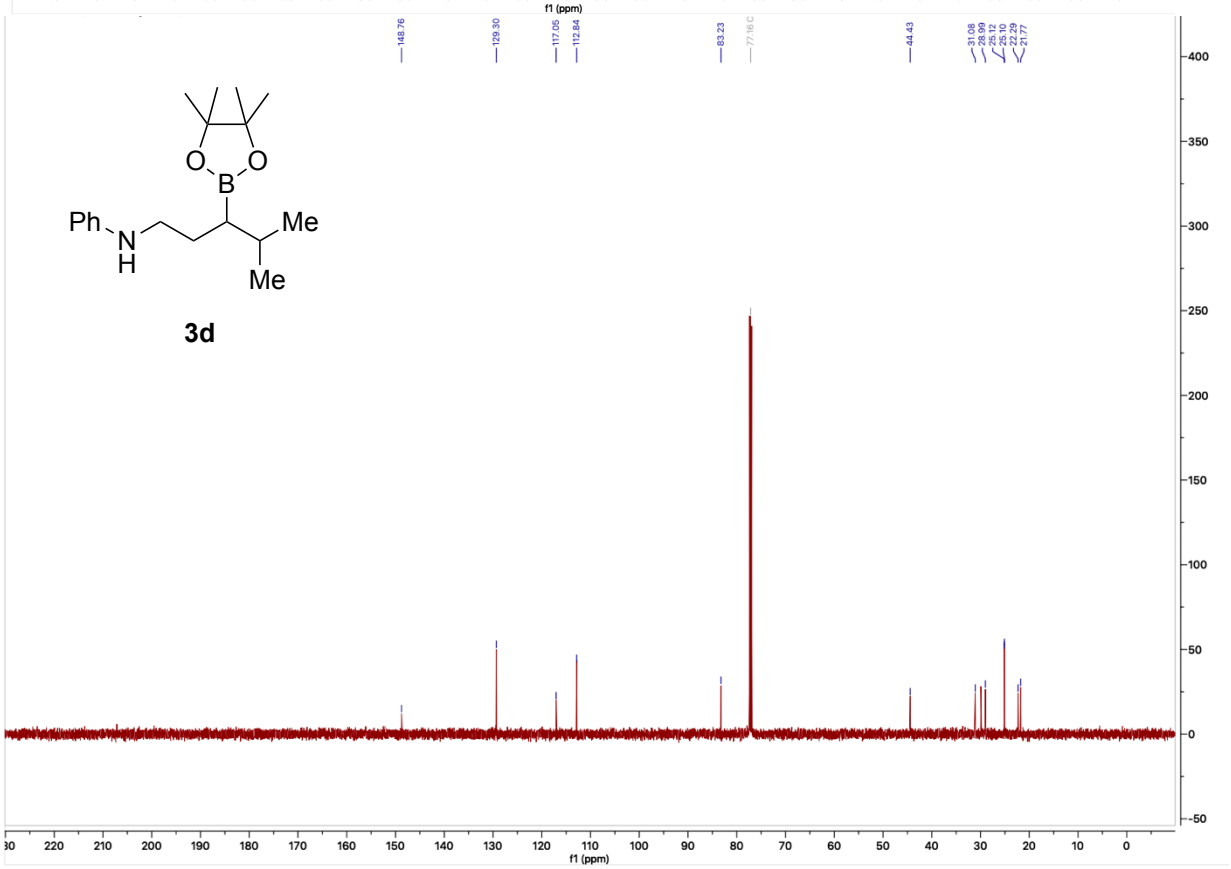

O
N
H
Me
GeEt3
3b
2.00
3.31
1.13
1.00
2.06
3.41
8.74
9.26
f1 (ppm)

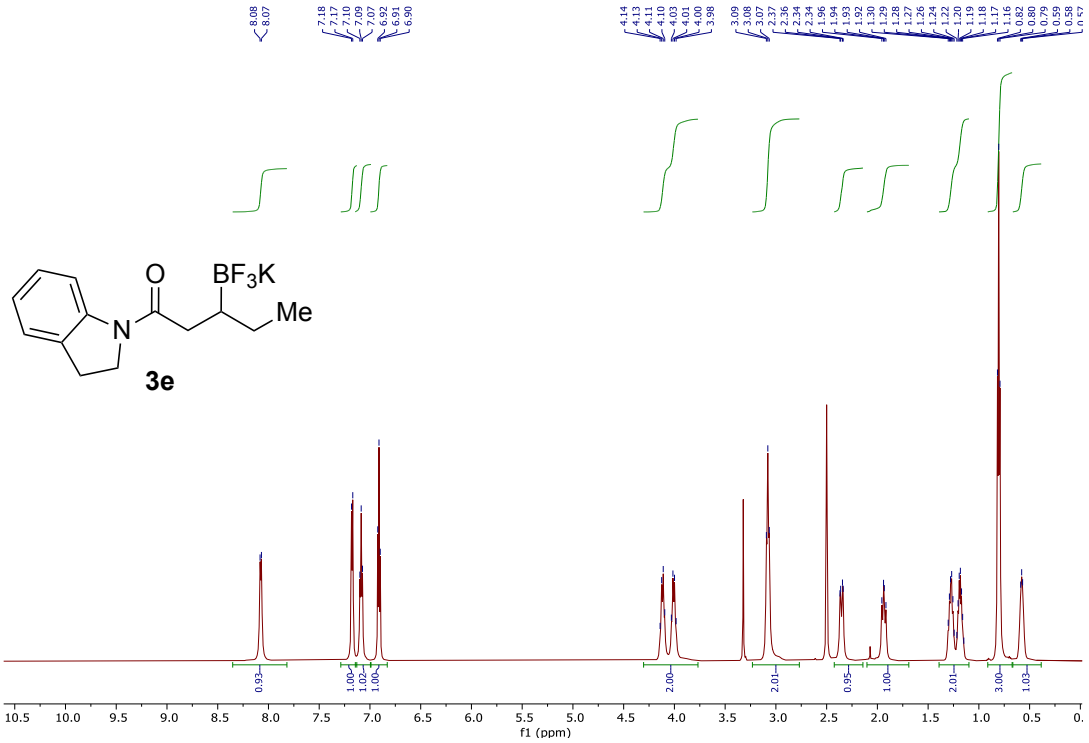

C-13 Routine 1D, CPDCH CryoProbe, AVIII-600
169.28
138.47
129.10
123.79
119.70
38.09
30.12
23.76
14.10
9.09
3.90
O
N
H
Me
GeEt3
3b
f1 (ppm)

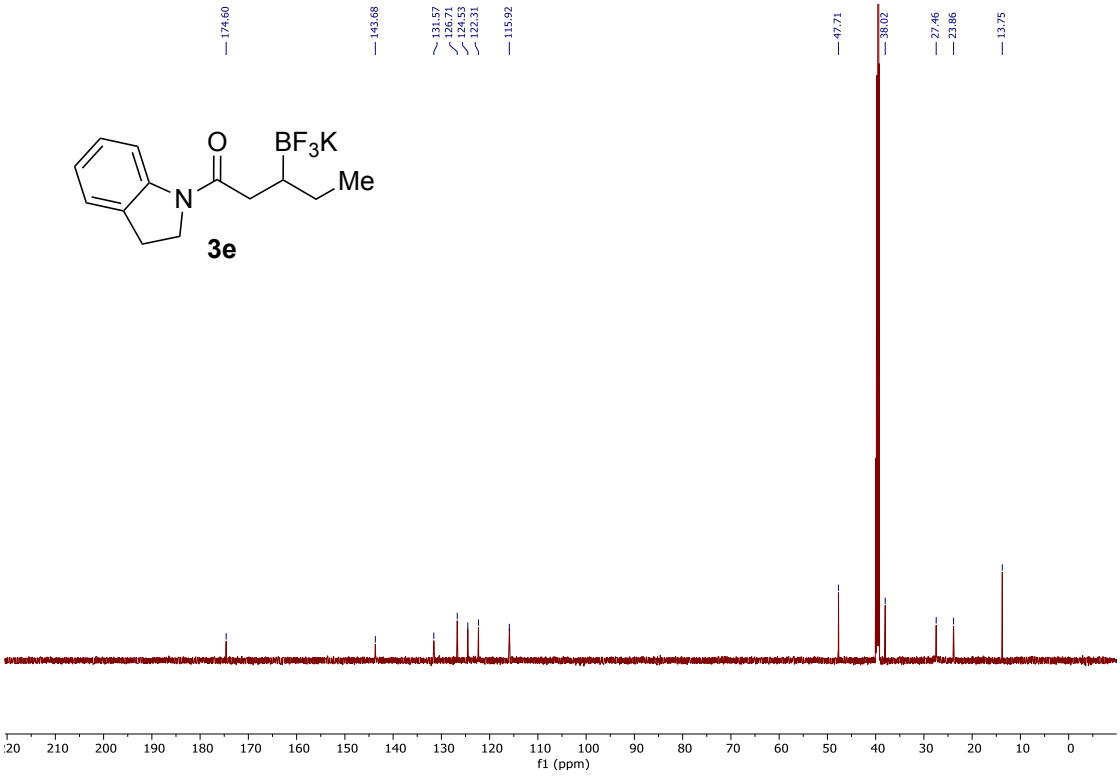

Me
O
B
O
N
H
Me
3c
f1 (ppm)

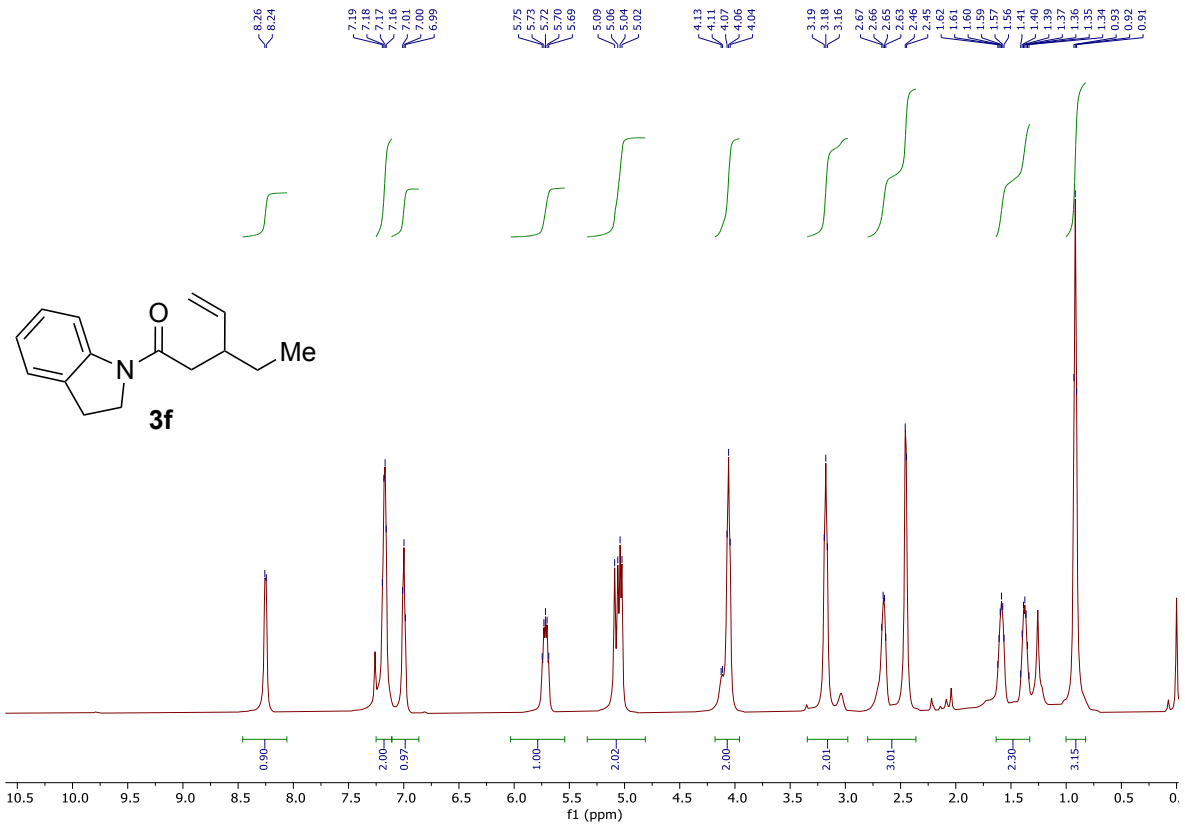

Me
O
B
O
N
H
Me
3c
f1 (ppm)

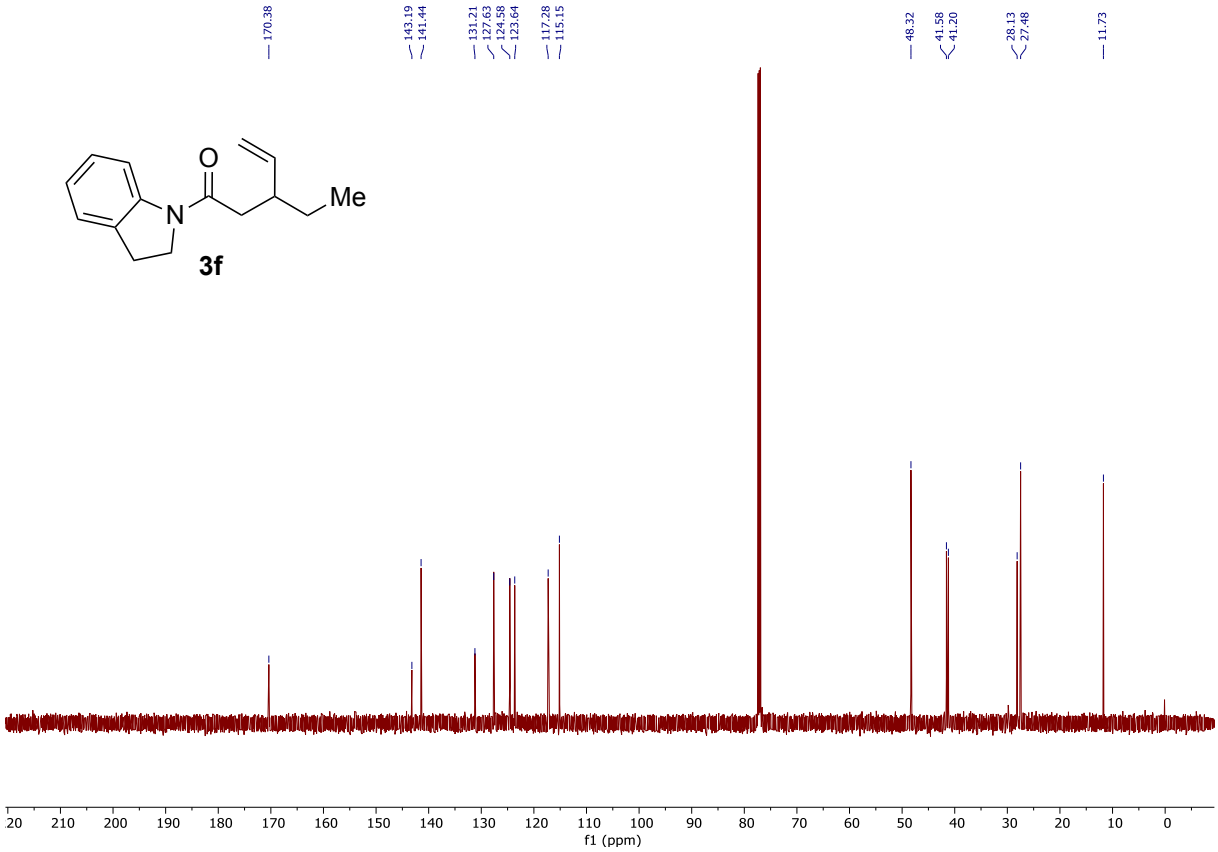

Ph
N
H
O
O
B
Me
Me
3d
f1 (ppm)

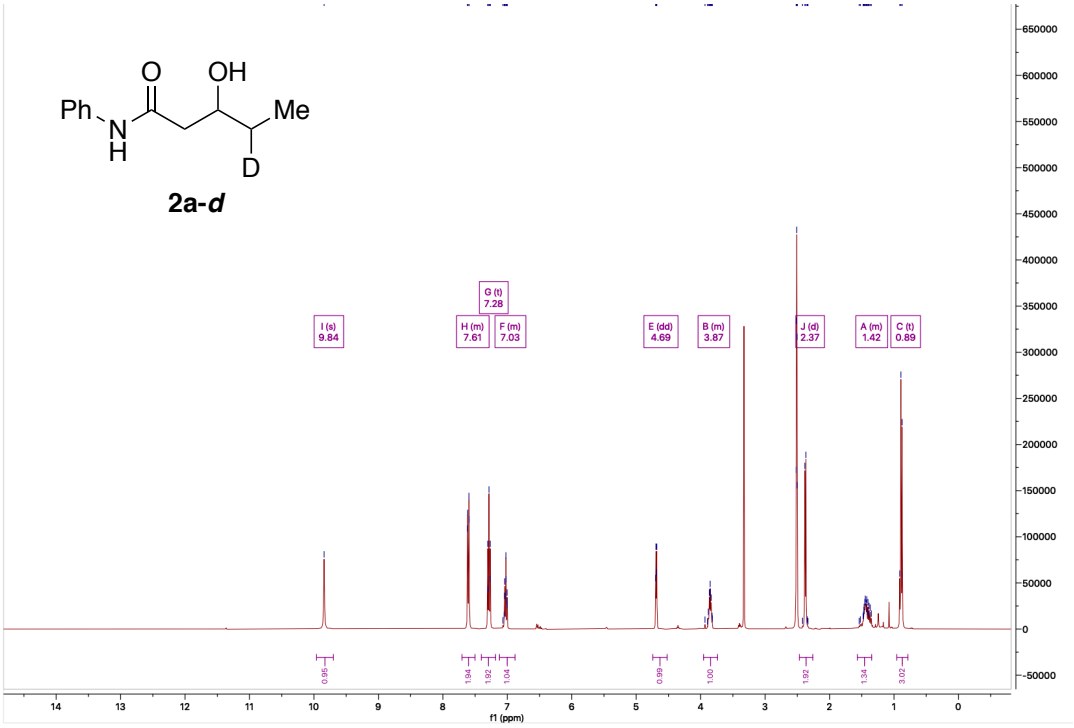

Ph
N
H
O
O
B
Me
Me
3d
f1 (ppm)


8.08
8.07
7.18
7.17
7.10
7.09
7.07
6.92
6.91
6.90
4.14
4.13
4.11
4.10
4.03
4.01
4.00
3.98
3.09
3.08
3.07
2.37
2.36
2.34
1.96
1.94
1.93
1.92
1.30
1.29
1.28
1.27
1.26
1.24
1.22
1.20
1.19
1.18
1.17
1.15
0.82
0.80
0.79
0.59
0.58
O
BF3K
N
Me
3e
0.93
1.00
1.02
1.00
2.00
2.01
0.95
1.00
2.01
3.00
1.03
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
f1 (ppm)

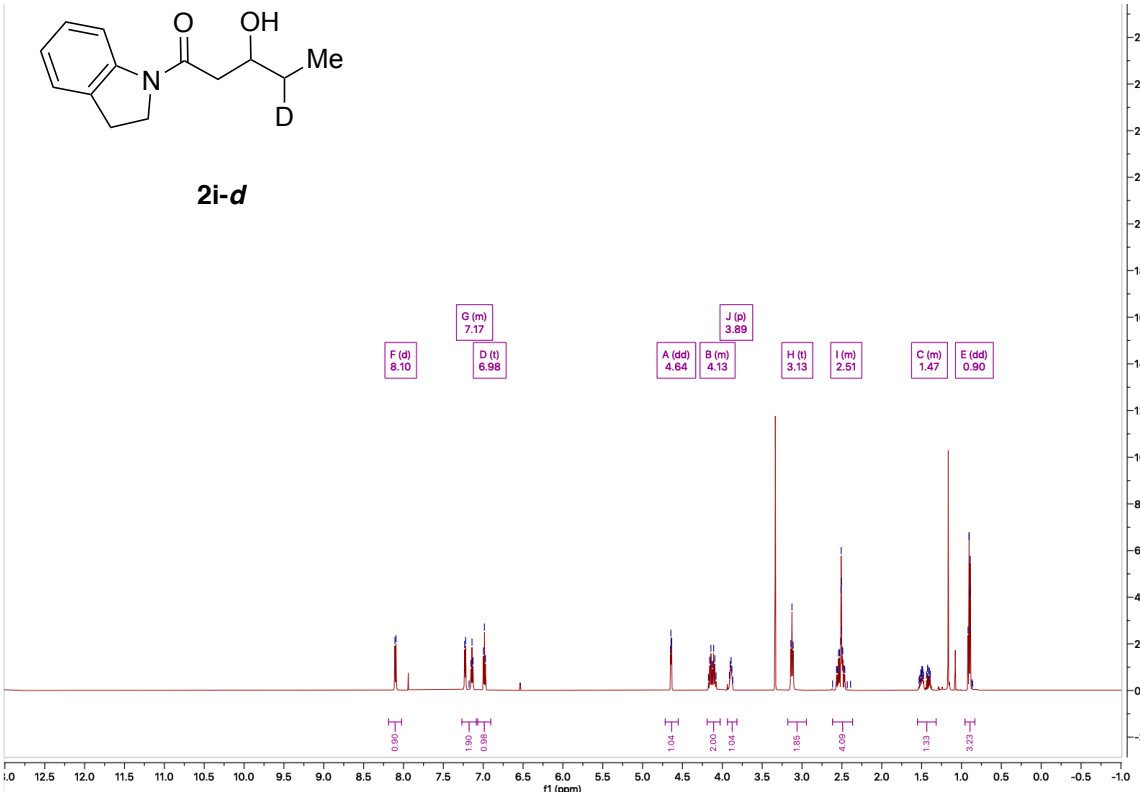

174.60
143.68
131.57
126.71
124.53
122.31
115.92
47.71
38.02
27.46
23.86
13.75
O
BF3K
N
Me
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.26
8.24
7.19
7.18
7.17
7.16
7.01
7.00
6.99
5.75
5.73
5.72
5.70
5.69
5.09
5.06
5.04
5.02
4.13
4.11
4.07
4.06
4.04
3.19
3.18
3.16
2.67
2.66
2.65
2.63
2.46
2.45
1.62
1.61
1.60
1.59
1.57
1.56
1.41
1.40
1.39
1.37
1.36
1.35
1.34
0.93
0.92
0.91
O
N
Me
3f
0.90
2.00
0.97
1.00
2.02
2.00
2.01
3.01
2.30
3.15
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
f1 (ppm)

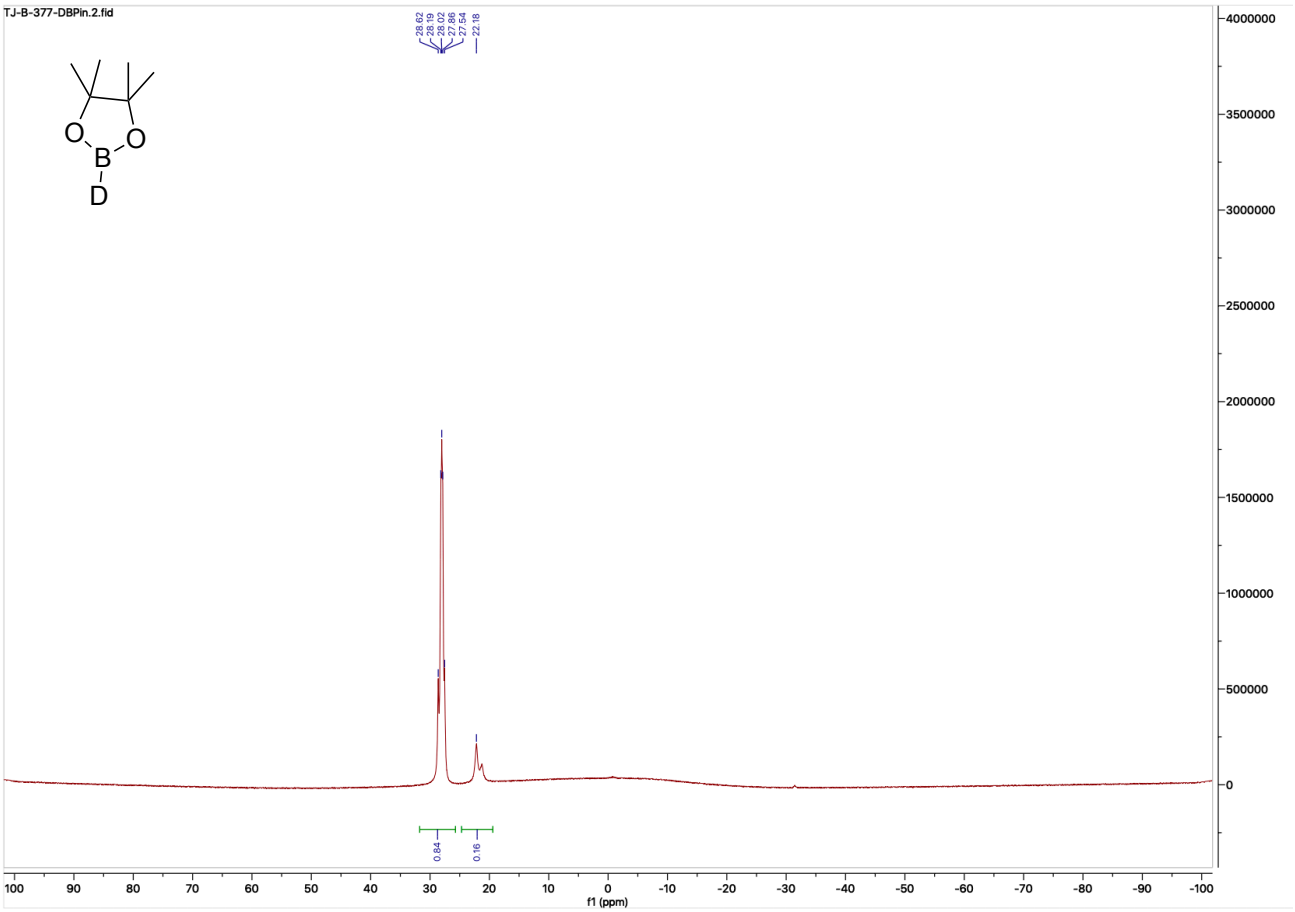

170.38
143.19
141.44
131.21
127.63
124.58
123.64
117.28
115.15
48.32
41.58
41.20
28.13
27.48
11.73
O
N
Me
3f
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
OH
Ph
N
H
Me
D
I (s) 9.84
G (t) 7.28
H (m) 7.61
F (m) 7.03
E (dd) 4.69
B (m) 3.87
J (d) 2.37
A (m) 1.42
C (t) 0.89
f1 (ppm)

2a-*d*


O
OH
N
Me
D
F (d) 8.10
G (m) 7.17
D (t) 6.98
A (dd) 4.64
B (m) 4.13
J (p) 3.89
H (t) 3.13
I (m) 2.51
C (m) 1.47
E (dd) 0.90
f1 (ppm)

2i-*d*



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