SUPPORTING INFORMATION

Tungsten-Catalyzed Stereodivergent Isomerization of Terminal Olefins

Tanner C. Jankins, Camille Z. Rubel, Hang Chi Ho, Raul Martin-Montero, Keary M. Engle*

Department of Chemistry, Scripps Research, 10550 North Torrey Pines Road, La Jolla, California, 92037, United States

**Corresponding author:* keary@scripps.edu

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1. 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 considering 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 fume hood.

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). 1,3-Dimethylimidazolium-2-carboxylate was purchased from MiliporeSigma (technical grade, >80% purity). $CDCl_3$ was ordered from Cambridge Isotopes Laboratories and used without further purification. THF was purchased from MilliporeSigma in 100-mL Sure/Seal bottles and used as received. Grubbs Catalyst, 2nd Generation and dithiolate catalyst M2102 ([1865771-19-2], $C_{43}H_{52}Cl_2N_2ORuS_2$, 848.99 g/mol) were supplied by Materia Inc.

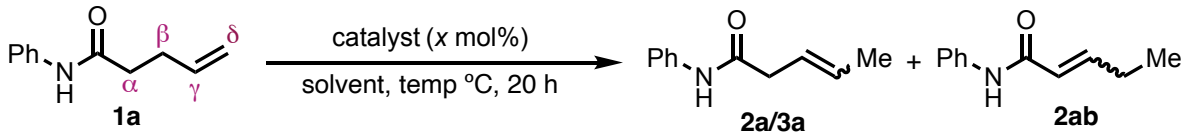
Analytical methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX instrument equipped with a 5-mm DCH cryoprobe (600 MHz and 151 MHz, respectively) or on Bruker 300 MHz, Bruker 400 MHz, or Bruker 500 MHz instruments at 20 °C. ^1H NMR spectra were reported relative to residual solvent signals 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. ^{19}F NMR were obtained with ^1H decoupling unless otherwise indicated. Coupling constants, *J*, are reported in Hertz. The IR spectra of new compounds were recorded on a Thermo scientific Nicolet 380 FT-IR and significant

peaks were reported in cm^{-1}. Flash chromatography was performed with EM Science silica gel 60 (230–400 mesh). Thin layer chromatography (TLC) was used to monitor reaction progress and analyze fractions from column chromatography. Preparative thin layer chromatography (PTLC) was used for isolation of some compounds. For this purpose, TLC Silica gel 60 F254 aluminum sheets, and PLC silica gel 60 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 time of flight (TOF) mass spectrometer with electrospray ionization (positive mode). GC-MS was performed on an Agilent 5977C GC/MSD.

2. Reaction Information

Reaction optimization

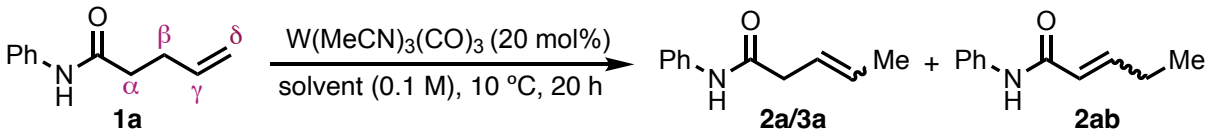
Scheme S1. Screening for reaction optimization.



Screening 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 vial was sealed, removed from the glovebox, and heated in a preheated oil bath for the specified amount of time.

Analysis of crude reactions: After being allowed to cool to room temperature and vented (see above), the crude reaction mixture was analyzed by ^{1}H NMR (or LCMS, GCMS). The regioisomeric ratio (r.r.) was calculated by the relative integration of regioisomers by ^{1}H NMR. Stereoisomeric (*E/Z*) ratio was also determined by ^{1}H NMR by comparison of the allylic CH_2 peaks, which typically have distinct chemical shifts. In cases where alkene isomers could not be distinguished by ^{1}H NMR, LCMS and GCMS were typically able to separate isomers for accurate integration.

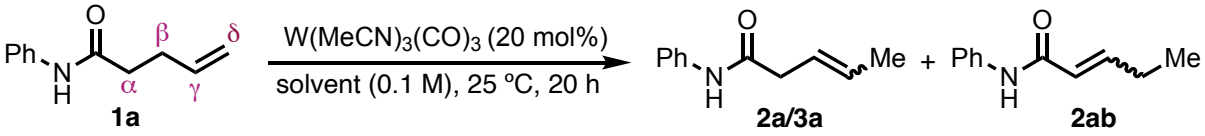
Table S1. Screening of solvents at 10 ºC



Entry	Solvent	Conversion **2/3a** (%)	Conversion **2ab** (%)	*E*/*Z* ratio
1	DCM	62	0	1.2:1
2	1,2-DCE	56	0	1:3
3	$CDCl_3$	7	0	6:1
4	THF	5	0	1:7
5	2-Me-THF	20	0	1:2
6	Et_2O	0	0	–
7	DME	9	0	1:3
8	MTBE	0	0	–

Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR.

Table S2. Screening of solvents at 25 ºC

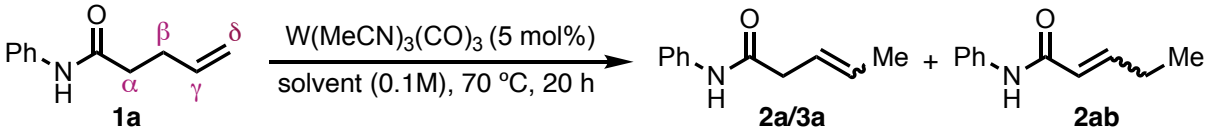


Entry	Solvent	Yield **2/3a** (%)	Yield **2ab** (%)	*E*/*Z* ratio
1	$CDCl_3$	99	0	4:1
2	MeCN	0	0	–
3	MeOH	0	0	–
4	Benzene	92	0	2:1
5	THF	88	0	1:5
6	DCM	96	0	4:1
7	1,2-DCE	99	0	4:1
8	Toluene	98	0	2:1

9	DMF	0	0	–
10	DCM	99	0	3:1
11	1,2-DCE	99	0	3:1
12	THF	90	0	1:5
13	1,4-Dioxane	94	0	3:1
14	Cyclohexane	0	0	–
15	CPME	31	0	1:3
16	2-Me-THF	91	0	1:1

Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR.

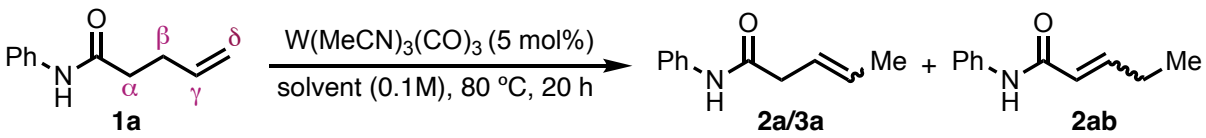
Table S3. Screening of solvents at 70 ºC



Entry	Solvent	Yield **2/3a** (%)	Yield **2ab** (%)	*E*/*Z* ratio
1	DCM	85	5	3:1
2	1,2-DCE	76	2	3:1
3	$CDCl_3$	98	0	3:1
4	THF	90	0	1:2
5	2-Me-THF	96	0	3:1
6	Et_2O	80	10	2:1
7	DME	90	0	3:1
8	MTBE	91	2	3:1

Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR.

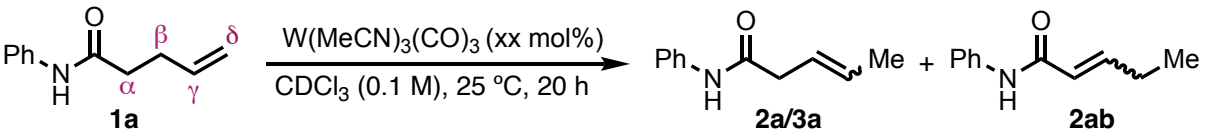
Table S4. Screening of solvents at 80 ºC



Entry	Solvent	Yield **2/3a** (%)	Yield **2ab** (%)	*E/Z* ratio
1	DCM	71	2	3:1
2	1,2-DCE	71	2	3:1
3	$CDCl_3$	96	3	3:1
4	THF	88	11	1:2
5	1,4-Dioxane	94	3	3:1

Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR.

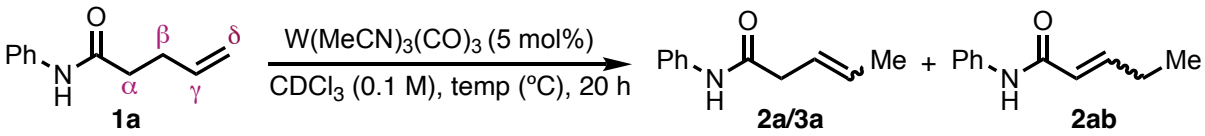
Table S5. Screening of catalyst loading



Entry	*x* mol %	Yield **2/3a** (%)	Yield **2ab** (%)	*E/Z* ratio
1	20	99	0	4:1
2	10	52	0	5:1
3	5	15	0	5:1

Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR.

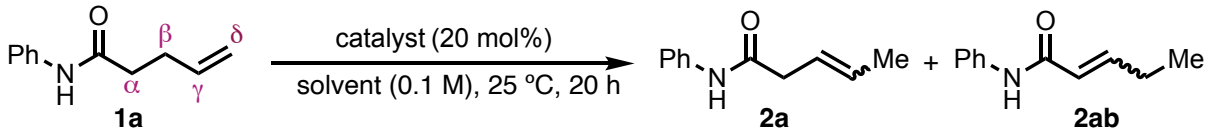
Table S6. Screening of temperature



Entry	Temp (° C)	Yield **2/3a** (%)	Yield **2ab** (%)	*E/Z* ratio
1	25	15	0	5:1
2	80	96	3	3:1
3[a]	10	7	0	6:1
4	70	98	0	3:1

Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR. [a] 20 mol% catalyst used.

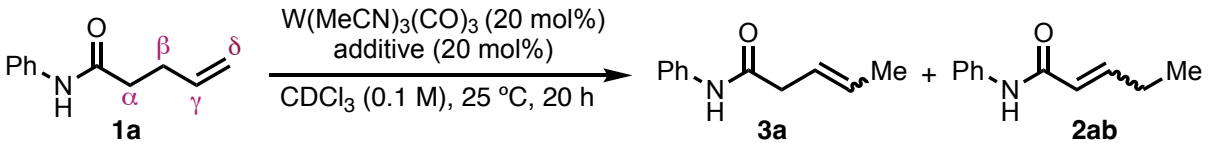
Table S7. Screening of precatalyst.



Entry	Solvent	Metal catalyst	Yield **2a** (%)	*E/Z* ratio **2a**
1	$CDCl_3$	$Mo(\eta^3\text{-}C_7H_8)(CO)_3$	0	–
2	$CDCl_3$	$W(MeCN)_2(CO)_4$	99	3:1
3	$CDCl_3$	$Mo(PrCN)_3(CO)_3$	94	3:1
4	THF	$W(MeCN)_2(CO)_4$	0	–
6	THF	$Mo(PrCN)_3(CO)_3$	0	–
7	THF	$Ni(COD)_2$	7	3:1
8	THF	$[Rh(COD)(MeCN)_2]BF_4$	25	6:1

Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR.

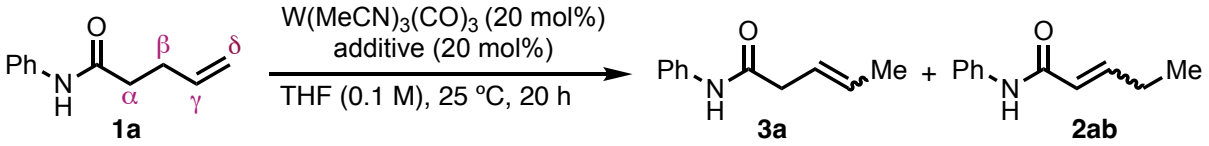
Table S8. Screening of coordinating additive in $CDCl_3$.



Entry	Ligand	Yield **3a** (%)	Yield **2ab** (%)	*E/Z* ratio **3a**
1	PPh_3	12	0	4:1
2	PCy_3	38	0	4:1
3	JohnPhos	13	0	1:1
4	Pyridine	0	0	–
5	2,6-Lutidine	33	0	5:1

Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR.

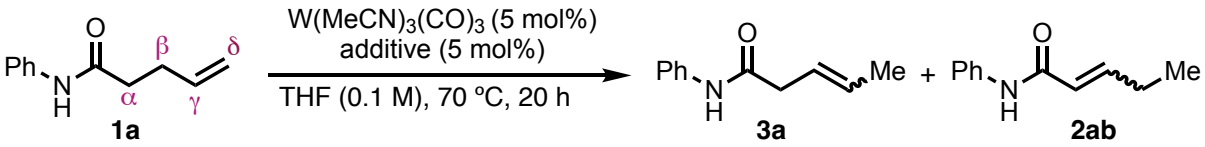
Table S9. Screening of coordinating additive in THF at 25 °C.



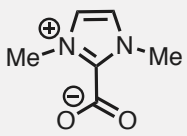
Entry	Ligand	Yield **3a** (%)	Yield **2ab** (%)	*E/Z* ratio **3a**
1	PPh_3	92	2	1:1
2	PCy_3	22	76	1:1
3	JohnPhos	91	0	1:3
4	2,6-Lutidine	92	0	1:2

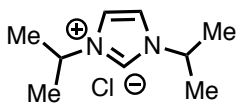
Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR.

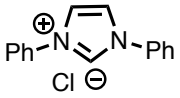
Table S10. Screening of coordinating additive in THF at 70 ºC.

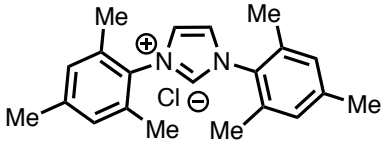


Entry	Ligand	Yield **3a** (%)	Yield **2ab** (%)	*E*/*Z* ratio **3a**
1	PPh_3	42	56	3:1
2	PCy_3	28	71	3:1
3	JohnPhos	52	46	3:1
4	Pyridine	0	0	–
5	2,6-Lutidine	94	0	2:1
6	**NHC-1**•CO_2	86	0	1:18
7[a]	**NHC-3**•HCl[a]	85	0	1:16
8[a]	**NHC-4**•HCl[a]	40	64	–
9[a]	**NHC-5**•HCl[a]	91	0	1:1


NHC-1•CO_2


NHC-3•HCl


NHC-4•HCl

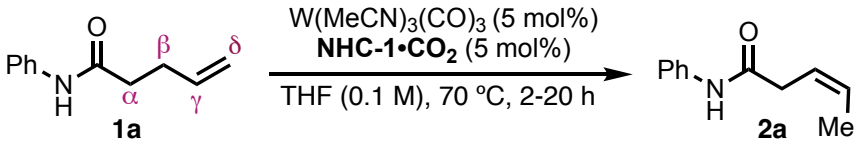

NHC-5•HCl

Reactions were performed on 0.100 mmol scale of **1a**. Conversions and *E*/*Z* ratios were determined by ^{1}H NMR. [a] 5 mol% of KO*t*-Bu also added.

Comparison of reaction at 2h and 20h

All the reaction optimization was performed at 20h, but Scheme 2 in the manuscript is reported at 2h. To enable direct comparison between the two, and demonstrate whether the reaction selectivity may change if the reaction is run for an extended time, the following data was collected:

Table S11. Comparison of reaction yield and selectivity at 2 and 20h.



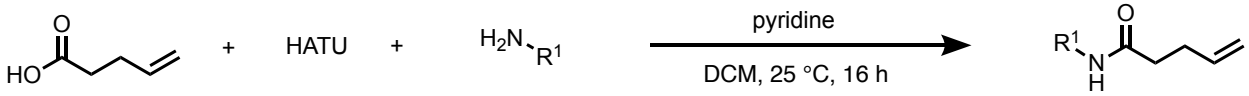
Entry	Time	Yield **2a** (%)	*E*/*Z* ratio 2**a**
1	2 h	75%	>20:1
2	20 h	69%	>20:1

Reactions were performed on 0.100 mmol scale of **1a**. Yields and *E*/*Z* ratios were determined by ^{1}H NMR using CH_2Br_2 as internal standard.

Characterization of new compounds

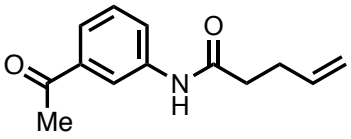
Synthesis of Starting Materials

Scheme S2. Synthesis of starting materials



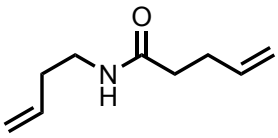
General Procedure A: HATU (1.3 equiv) was added to a solution of the corresponding acid (1.3 equiv), primary amine (1.0 equiv), and pyridine (3 equiv) in DCM (0.5 M). The reaction was left to stir overnight. Then, it was quenched with 1 M NaOH, and the resulting mixture was extracted with DCM. Finally, the organic phase was dried over $MgSO_4$, and the solvent was evaporated with a rotavap. Flash column chromatography on silica gel was performed with a mixture of hexane/EtOAc as eluent.

Starting materials **1a-g**, **1i-m**, **1o-t** were synthesized during a previous study, and their full characterization has previously been reported.[1]



***N*-(3-Acetylphenyl)pent-4-enamide (1g):** The title compound was prepared according to General Procedure A using 4-pentenoic acid (0.96

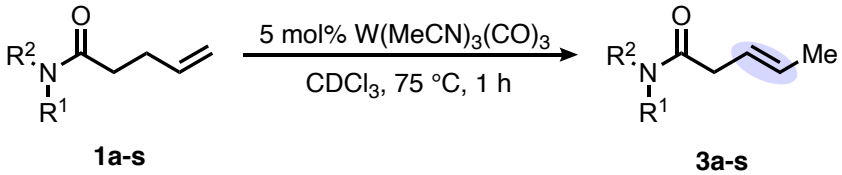
mL, 9.6 mmol), 3-aminoacetophenone (1.00 g, 7.4 mmol), HATU (3.567 g, 9.6 mmol), and pyridine (1.8 mL) in DCM (15 mL), affording the product as a white solid (1.255 g, 78% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.73–7.63 (m, 1H), 7.49–7.41 (m(br), 2H), 6.02–5.76 (m, 1H), 5.14 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.07 (dd, *J* = 10.1, 1.7 Hz, 1H), 2.61 (s, 3H), 2.51 (m, 2H), 2.50 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.50, 171.36, 138.78, 137.66, 136.85, 129.43, 124.75, 124.22, 119.32, 116.01, 36.80, 29.46, 26.87. **HRMS** calcd. for ($C_{13}H_{16}NO_2$) $[M+H]^+$: 218.1176, found 218.1178. **IR** (cm^{-1}) 1666.47, 1591.58, 1543.80, 1484.51, 1431.69, 1357.24, 1271.40, 792.68, 687.74.



***N*-(3-Acetylphenyl)pent-4-enamide (1k):** The title compound was prepared according to General Procedure A using 4-pentenoic acid (0.96 mL, 9.6 mmol), but-3-en-1-amine (1.00 g, 7.4 mmol), HATU (3.567 g, 9.6 mmol), and pyridine (1.8 mL) in DCM (15 mL), affording the product as a colorless oil (1.255 g, 78% yield). The analytical data matches the previous report.[2] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.86–5.70 (m, 2H), 5.55 (s (br), 1H), 5.18–4.94 (m, 4H), 3.32 (q, *J* = 6.5 Hz, 2H), 2.38 (q, *J* = 7.2 Hz, 2H), 2.27–2.23 (m, 4H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ = 172.4, 137.2, 135.4, 117.4, 115.7, 38.4, 36.0, 33.9, 29.8. **HRMS** calcd. for ($C_9H_{16}NO$) $[M+H]^+$: 154.1226, found 154.1227.

Catalytic Reactions

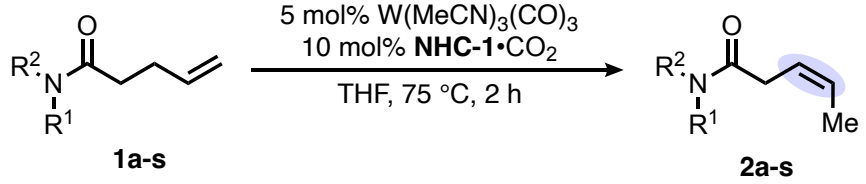
Scheme S3. *E*-selective reaction conditions.



1a-s **3a-s**

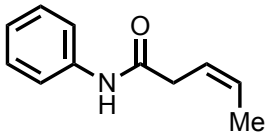
General Procedure B: An oven-dried 8-mL screw-cap reaction vial containing a Teflon®-coated magnetic stir bar was charged with the alkenyl amide **1** (0.10 mmol). The vial was introduced into an argon-filled glovebox, where it was further charged with $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%) in $CDCl_3$ (1.0 mL). The tube was removed from the glovebox and stirred (approximately 800 rpm) at 75 °C for 1 h. After this time, the reaction mixture was directly assayed by ^1H NMR, or the crude material was purified by flash column chromatography on silica gel with a mixture of hexane/EtOAc as eluent. All products were isolated as a mixture of *E* and *Z* isomers. (In some cases, unreacted starting material **1** was also recovered together with the product(s). Reported yields were adjusted for remaining starting material, which was determined by 1H NMR.)

Scheme S4. *Z*-selective reaction conditions.

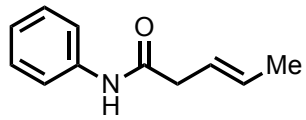


General Procedure C: An oven-dried 8-mL screw-cap reaction vial containing a Teflon®-coated magnetic stir bar was introduced into an argon-filled glovebox, where it was charged with $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%) and **NHC-1•** CO_2 (1.4 mg, 10 mol%) in THF (1.0 mL). The solution was stirred at room temperature for 5 min, at which point alkenyl amide **1** (0.10 mmol) was added. The tube was removed from the glovebox, and the reaction mixture was stirred (approximately 800 rpm) at 75 °C for 2 h. After this time, the reaction mixture was filtered through Celite, and the bed of Celite was rinsed with acetone. The filtrate was concentrated and assayed by ^1H NMR, or the crude material was directly purified by flash column chromatography on silica gel with a mixture of hexane/EtOAc as eluent. All products were isolated as a mixture of *E* and *Z* isomers. (In some cases,

unreacted starting material 1 was also recovered together with the product(s). Reported yields were adjusted for remaining starting material, which was determined by 1H NMR.)



(*Z*)-*N*-phenylpent-3-enamide (2a): The title compound was prepared according to General Procedure C using **1a** (17.5 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 18% of the starting material that could not be separated (18 mg, 82% corrected yield; >20:1 *Z/E*). The analytical data matches that of a previous report.[3] Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz 2H), 7.42 (s (br), 1H), 7.31 (ddd, *J* = 10.1, 5.9, 2.5 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 5.94–5.82 (m, 1H), 5.69 (dtq, *J* = 11.2, 7.6, 1.8 Hz, 1H), 3.20 (d, *J* = 7.6 Hz, 2H), 1.73 (d, *J* = 5.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.1, 137.9, 130.5, 129.1, 124.5, 122.5, 119.9, 36.1, 13.2.



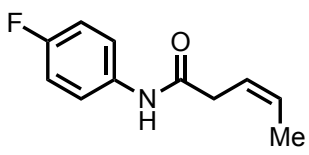
(*E*)-*N*-phenylpent-3-enamide (3a)

The title compound was prepared according to General Procedure B, using **1a** (17.5 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 2% starting material that could not be separated (18 mg, 98% yield; 3.4:1 *E/Z*). The analytical data matches the previous report.[3]

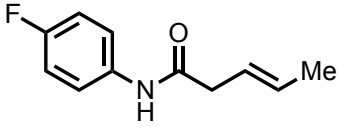
Isolation by preparative SFC: The title compound was prepared according to General Procedure B, except the reaction was performed on 0.200 mmol scale using **1a** (36.0 mg, 0.200 mmol), $W(MeCN)_3(CO)_3$ (3.8 mg, 5 mol%), and $CDCl_3$ (2.0 mL). Preparative SFC was performed on a Waters Prep SFC 150 AP using a Phenomenex i-CEL-5 column (5 µm, 21.2 x 250 mm). The purification was run under isocratic conditions (15% IPA / CO2, 100 mL/min, 1600 psi backpressure)

at 35 °C. Fractionation was triggered by UV light (238 nm). These methods led to isolation of the title compound in high isomeric purity (crude: 36 mg, 99% yield 3.4:1 *E/Z*; isolated: 23.1 mg, 64% yield, >20:1 *E*/*Z*). See **Figure S15** for SFC trace showing separation of isomers.

Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.43 (s (br), 1H), 7.31 (td, *J* = 8.2, 7.3, 1.7 Hz, 2H), 7.10 (tt, *J* = 7.3, 1.3 Hz, 1H), 5.79–5.56 (m, 2H), 3.10 (d, *J* = 7.1 Hz, 2H), 1.77 (dd, *J* = 6.3, 1.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.7, 137.9, 132.0, 129.1, 124.5, 123.6, 119.9, 41.7, 18.2.

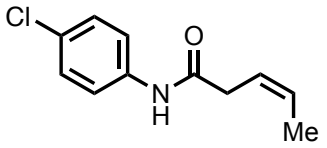


(*Z*)-*N*-(4-fluorophenyl)pent-3-enamide (2b): The title compound was prepared according to General Procedure C, **1b** (19.4 mg, 0.100 mmol) using **NHC-1•**CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 32% of the starting material that could not be separated (19 mg, 68% corrected yield; >20:1 *Z/E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49–7.35 (m(br), 3H), 7.00 (dd, *J* = 9.1, 8.3 Hz, 2H), 5.93–5.81 (m, 1H), 5.68 (dtd, *J* = 10.8, 7.6, 1.8 Hz, 1H), 3.19 (d, *J* = 7.5 Hz, 2H), 1.72 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.1, 160.4, 158.8, 130.6, 122.4, 121.8 (d, $J_{C–F}$ = 7.8 Hz), 115.8 (d, $J_{C–F}$ = 22.6 Hz), 35.9, 13.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –118.1. **HRMS** calcd. for ($C_{11}H_{13}NOF$) $[M+H]^+$: 194.0976, found 194.0990. **IR** (cm^{-1}) 1659.47, 1545.16, 1507.90, 1212.73, 833.10.

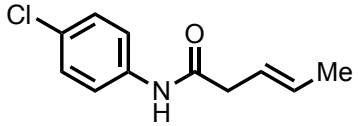


(*E*)-*N*-(4-fluorophenyl)pent-3-enamide (3b): The title compound was prepared according to General Procedure B using **1b** (19.4 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 3% starting material that could not be separated (19

mg, 98% corrected yield; 3.1:1 *E/Z*). The analytical data matches the previous report.[4] Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.54 (s(br), 1H), 7.49 – 7.42 (m, 1H), 6.99 (t, *J* = 8.3 Hz, 1H), 5.72 (dt, *J* = 12.9, 6.7 Hz, 1H), 5.61 (dt, *J* = 14.3, 6.9 Hz, 1H), 3.08 (d, *J* = 7.0 Hz, 2H), 1.76 (d, *J* = 6.1 Hz, 3H).**^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.8, 160.3, 158.7, 132.0, 123.4, 121.9 (d, J_{C-F} = 7.8 Hz), 115.7 (d, J_{C-F} = 22.4 Hz), 41.5, 18.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ –118.1. **HRMS** calcd. for ($C_{11}H_{13}NOF$) $[M+H]^+$: 194.0976, found 194.0975.

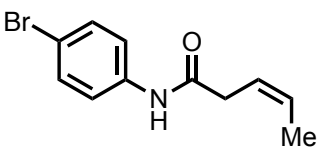


(*Z*)-*N*-(4-chlorophenyl)pent-3-enamide (2c): The title compound was prepared according to General Procedure C using **1c** (21.0 mg, 0.100 mmol), **NHC-1•**CO_2 (2.1 mg, 15 mol%), $W(MeCN)_3(CO)_3$ (2.1 mg, 10 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 21% starting material **1c** that could not be separated (19.6 mg, 74% corrected yield; >20:1 *Z/E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.58 (s(br), 1H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 5.95–5.81 (m, 1H), 5.74 – 5.61 (m, 1H), 3.20 (d, *J* = 7.5 Hz, 2H), 1.73 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.2, 136.9, 130.6, 129.1, 122.2, 121.2, 116.1, 36.0, 13.1. **HRMS** calcd. for ($C_{11}H_{13}NOCl$) $[M+H]^+$: 210.0680, found 210.0694. **IR** (cm^{-1}) 1654.40, 1594.51, 1520.91, 1490.68, 1395.74, 1089.02, 821.54, 670.34

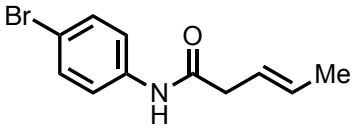


(*E*)-*N*-(4-chlorophenyl)pent-3-enamide (3c): The title compound was prepared according to General Procedure B using **1c** (21.0 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid (21 mg, 99% yield; 3.0:1 *E/Z*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.46 (m(br), 3H), 7.31–7.19 (m, 2H), 5.81–5.46 (m, 2H), 3.09 (d, *J* = 7.1 Hz, 2H), 1.77 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.7, 136.5, 132.3, 129.1, 123.3, 122.25,

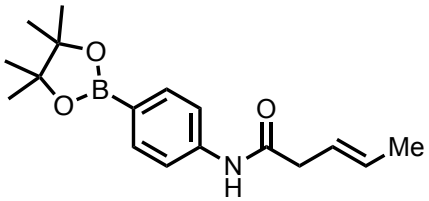
121.2, 41.6, 18.2. **HRMS** calcd. for ($C_{11}H_{13}NOCl$) $[M+H]^+$: 210.0680, found 210.0675. **IR** (cm^{-1}) 1659.07, 1593.70, 1519.31, 1489.55, 1395.50, 1246.51, 1088.81, 965.80, 818.59.



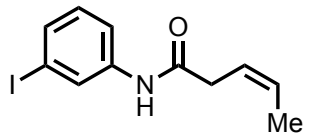
(*Z*)-*N*-(4-bromophenyl)pent-3-enamide (2d): The title compound was prepared according to General Procedure C using **1d** (25.3 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), **NHC-1•**CO_2 (1.4 mg, 10 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 21% starting material that could not be separated (25 mg, 79% corrected yield; >20:1 *Z/E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (m(br), 5H), 5.94 – 5.85 (m, 1H), 5.67 (dtd, *J* = 10.8, 7.5, 1.8 Hz, 1H), 3.18 (d, *J* = 7.5 Hz, 2H), 1.71 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.2, 136.9, 132.1, 130.64, 122.2, 121.5, 117.1, 36.0, 13.2. **HRMS** calcd. for ($C_{11}H_1NOBr$) $[M+H]^+$: 254.0175, found 254.0170. **IR** (cm^{-1}) 1653.98, 1591.87, 1525.36, 1487.23, n1393.02, 1281.03, 1244.96, 1072.80, 1009.79, 819.01, 669.77.



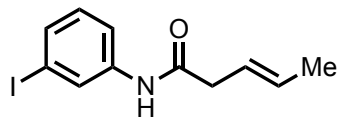
(*E*)-*N*-(4-bromophenyl)pent-3-enamide (3d): The title compound was prepared according to Procedure B using **1d** (25.3 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid (25 mg, 99% yield; 3.0:1 *E/Z*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55–7.38 (m(br), 5H), 5.78–5.47 (m, 2H), 3.08 (d, *J* = 7.1 Hz, 2H), 1.77 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.7, 136.9, 132.0, 132.2, 123.3, 121.5, 117.0, 41.7, 18.2. **HRMS** calcd. for ($C_{11}H_{13}NOBr$) $[M+H]^+$: 254.0175, found 254.0175. **IR** (cm^{-1}) 1659.47, 1589.62, 1519.92, 1487.64, 1391.42, 965.94, 816.47.



(*E*)-*N*-(4-pinacolborane)pent-3-enamide (2e): The title compound was prepared according to General Procedure B using **1e** (30.1 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid (30 mg, 99% yield; 3.0:1 *E/Z*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.51 (m (br), 3H), 5.79–5.46 (m, 2H), 3.09 (d, *J* = 7.1 Hz, 2H), 1.74 (dd, *J* = 34.9, 6.6 Hz, 3H), 1.33 (s, 12H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.7, 140.6, 135.8, 132.1, 123.4, 122.4, 118.6, 83.8, 41.8, 24.9, 18.2. **HRMS** calcd. for ($C_{17}H_{25}NO_3B$) $[M+H]^+$: 302.1922, found 302.1920. **IR** (cm^{-1}) 1594.66, 1398.23, 1359.08, 1144.19, 1089.03.

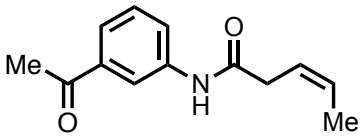


(*Z*)-*N*-(3-iodophenyl)pent-3-enamide (2f): The title compound was prepared according to General Procedure C using **1f** (30.1 mg, 0.100 mmol), **NHC-1•**CO_2 (0.7 mg, 5 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 59% starting material that could not be separated (30 mg, 41% corrected yield; >20:1 *Z/E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.68–7.32 (m, 3H), 7.02 (t, *J* = 8.0 Hz, 1H), 5.88–5.82 (m, 1H), 5.69–5.61 (m, 1H), 3.19 (d, *J* = 7.5 Hz, 2H), 1.71 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.38, 138.94, 136.79, 133.50, 130.68, 128.63, 122.10, 119.19, 94.23, 35.97, 13.20. **HRMS** calcd. for ($C_{11}H_{13}NOI$) $[M+H]^+$: 302.0036, found 302.0025. **IR** (cm^{-1}) 1664.34, 1582.22, 1529.70, 1472.83, 1414.23, 1397.75, 775.59, 679.88.

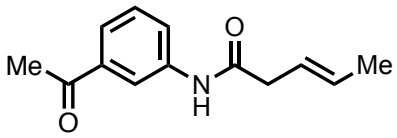


(*E*)-*N*-(3-iodophenyl)pent-3-enamide (3f): The title compound was prepared according to General Procedure B using **1f** (30.1 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel

afforded the product as a white solid (30 mg, 99% yield; 3.0:1 *E/Z*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.59–7.30 (m, 3H), 7.02 (t, *J* = 8.0 Hz, 1H), 5.78–5.55 (m, 2H), 3.08 (d, *J* = 7.1 Hz, 1H), 1.77 (d, *J* = 6.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.7, 139.0, 133.4, 132.3, 130.5, 128.5, 119.1, 94.1, 41.6, 18.2. **HRMS** calcd. for ($C_{11}H_{13}NOI$) $[M+H]^+$: 302.0036, found 302.0029. **IR** (cm^{-1}) 1660.02, 1582.82, 1531.39, 1473.05, 1414.44, 775.47

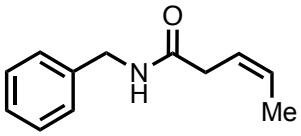


(*Z*)-*N*-(3-acetylphenyl)pent-3-enamide (2g): The title compound was prepared according to General Procedure B using **1g** (21.7 mg, 0.100 mmol), **NHC-1•**CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 18% starting material that could not be separated (22 mg, 82% corrected yield; >20:1 *Z/E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.94 (m, *J* = 8.1 Hz, 1H), 7.78 (s(br), 1H), 7.68 (s, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 5.94–5.82 (m, 1H), 5.71 (dtd, *J* = 10.8, 7.5, 1.8 Hz, 1H), 3.24 (d, *J* = 8.0 Hz, 2H), 2.61 (s, 3H), 1.74 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.1, 169.6, 138.5, 137.8, 130.5, 129.5, 124.6, 124.3, 122.2, 119.2, 36.0, 26.8, 13.2. **HRMS** calcd. for ($C_{11}H_{16}NO_2$) $[M+H]^+$: 218.1176, found 218.1186. **IR** (cm^{-1}) 1670.61, 1592.33, 1547.53, 1485.04, 1433.33, 1357.36, 1273.35, 687.40.

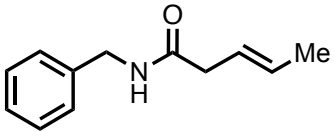


(*E*)-*N*-(3-acetylphenyl)pent-3-enamide (3g): The title compound was prepared according to General Procedure B using **1g** (21.7 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 3% starting material that could not be separated (22 mg, 97% corrected yield; 2.9:1 *E/Z*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.76–7.62 (m(br), 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 5.80–5.51 (m, 2H), 3.13 (d, *J* = 7.1 Hz, 2H), 2.59 (s, 3H), 1.78 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.1, 170.0,

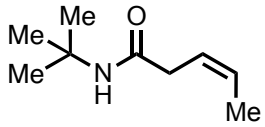
138.4, 137.8, 132.3, 129.4, 124.6, 124.3, 123.2, 119.3, 41.7, 18.3, 13.2. **HRMS** calcd. for ($C_{11}H_{16}NO_2$) $[M+H]^+$: 218.1176, found 218.1169. **IR** (cm^{-1}) 1668.17, 1591.25, 1544.34, 1484.84, 1432.03, 1356.78, 1271.79, 966.78, 792.61, 687.36.



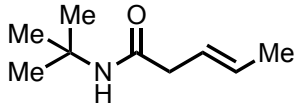
***(Z)*-*N*-benylpent-3-enamide (2h):** The title compound was prepared according to General Procedure C using **1h** (18.9 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 14% starting material that could not be separated (19 mg, 86% corrected yield; >20:1 *Z/E*). The analytical data matches the previous report.[5] Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42–7.14 (m, 5H), 6.03 (s (br), 1H), 5.81–5.68 (m, 1H), 5.67–5.54 (m, 1H), 4.46 (d, *J* = 5.7 Hz, 2H), 3.09 (s, 2H), 1.67 (dd, *J* = 6.8, 1.8 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 138.3, 129.7, 128.8, 127.8, 127.6, 122.7, 43.7, 35.0, 13.0. **HRMS** calcd. for ($C_{12}H_{16}NO$) $[M+H]^+$: 190.1226, found 190.1228.



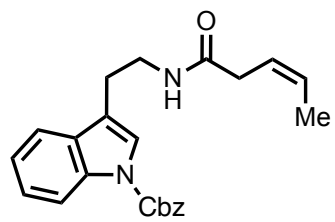
***(E)*-*N*-benylpent-3-enamide (3h):** The title compound was prepared according to General Procedure B using **1h** (18.9 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid (17 mg, 89% yield; 3.4:1 *E/Z*). The analytical data matches the previous report.[5] Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49–7.19 (m, 5H), 5.95 (s (br), 1H), 5.71–5.51 (m, 2H), 4.47 (d, *J* = 5.8 Hz, 2H), 3.01 (d, *J* = 7.1 Hz, 2H), 1.74 (dd, *J* = 6.3, 1.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.8, 138.3, 129.7, 128.8, 127.8, 127.6, 122.7, 43.7, 34.9, 13.0. **HRMS** calcd. for ($C_{12}H_{16}NO$) $[M+H]^+$: 190.1226, found 190.1223.



(*Z*)-*N*-(*tert*-butyl)pent-3-enamide (2i): The title compound was prepared according to General Procedure C using **1i** (15.5 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL), except the reaction was run at room temperature for 2 hours. Filtration through silica gel afforded the product as a yellow oil containing 43% starting material that could not be separated (16 mg, 57% corrected yield, 15:1 *Z*:*E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.76–5.67 (m, 1H), 5.60–5.44 (m, 1H), 5.40 (s (br), 1H), 2.92 (d, J = 7.5 Hz, 2H), 1.63 (d, J = 6.8 Hz, 3H), 1.32 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.19, 129.02, 123.47, 51.16, 36.09, 28.85, 13.00. **HRMS** calcd. for ($C_9H_{18}NO$) $[M+H]^+$: 156.1383, found 156.1382. **IR (cm^{-1})** 1645.51, 1548.01, 1452.84, 1361.97, 1224.63.

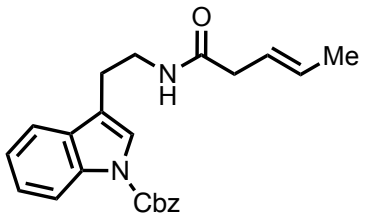


(*E*)-*N*-(*tert*-butyl)pent-3-enamide (3i): The title compound was prepared according to General Procedure B using **1i** (15.5 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a yellow oil (14 mg, 90% yield, 2.6:1 *E*:*Z*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.62–5.55 (m, 1H), 5.50 (dddd, J = 15.3, 7.0, 5.5, 1.5 Hz, 1H), 5.45–5.32 (s (br), 1H), 2.92 (d, J = 7.5 Hz, 2H), 1.66 – 1.61 (m, 3H), 1.34 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.81, 130.55, 124.41, 51.19, 41.69, 28.87, 18.14. **HRMS** calcd. for ($C_9H_{18}NO$) $[M+H]^+$: 156.1383, found 156.1382. **IR (cm^{-1})** 1646.43, 1549.37, 1452.84, 1361.97, 1224.80, 966.88.

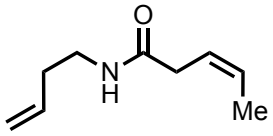


benzyl (*Z*)-3-(2-(pent-3-enamido)ethyl)-1*H*-indole-1-carboxylate (2j): The title compound was prepared according to General Procedure C using **1j** (34.6 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 13% starting material that could not

be separated (35 mg, 87% corrected yield; 10:1 *Z/E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.18 (s (br), 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.44–7.36 (m, 4H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 5.79 (td, *J* = 6.9, 3.1 Hz, 1H), 5.64 (dq, *J* = 13.5, 7.0 Hz, 1H), 5.51–5.39 (m, 3H), 3.55 (q, *J* = 6.6 Hz, 2H), 2.97 (d, *J* = 7.6 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 1.53 (dd, *J* = 6.7, 1.8 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.9, 151.8, 137.1, 135.2, 131.3, 130.4, 129.5, 128.9, 128.6, 125.0, 123.1, 122.8, 122.6, 119.1, 118.8, 115.5, 68.8, 39.2, 35.0, 25.1, 12.9. **HRMS** calcd. for ($C_{22}H_{25}N_2O_3$) $[M+H_3O]^+$: 377.1860, found 377.1846. **IR** (cm^{-1}) 1731.27, 1643.49, 1454.21, 1397.84, 1354.84, 1246.14, 1089.88, 747.37.

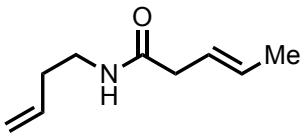


benzyl (*E*)-3-(2-(pent-3-enamido)ethyl)-1*H*-indole-1-carboxylate (3j): The title compound was prepared according to General Procedure B using **1j** (34.6 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid (34 mg, 99% yield; 3.1:1 *E/Z*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.18 (s(br), 1H), 7.55 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.51–7.47 (m, 2H), 7.44 (s(br), 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.40–7.36 (m, 1H), 7.36–7.32 (m, 1H), 7.28–7.25 (m, 1H), 5.82–5.69 (m, 1H), 5.67–5.39 (m, 4H), 3.56 (td, *J* = 6.8, 5.8 Hz, 2H), 2.92–2.82 (m, 4H), 1.61 (dq, *J* = 6.4, 1.2 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.5, 150.8, 135.2, 131.3, 130.5, 129.6, 128.9, 128.6, 125.0, 123.7, 123.1, 122.8, 122.7, 119.2, 118.8, 115.5, 68.8, 40.6, 39.2, 25.1, 18.0. **HRMS** calcd. for ($C_{22}H_{25}N_2O_3$) $[M+H_3O]^+$: 377.1860, found 377.1847. **IR** (cm^{-1}) 1730.87, 1644.32, 1453.99, 1397.64, 1355.05, 1245.59, 1089.38, 747.30, 697.65.

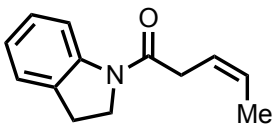


(*Z*)-*N*-(but-3-en-1-yl)pent-3-enamide (2k): The title compound was prepared according to General Procedure C using **1k** (14.5 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), **NHC-1**•CO_2 (1.4 mg, 10 mol%), and THF (1.0 mL) at room

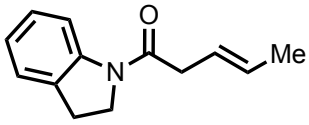
temperature. Crude ^{1}H NMR of the product mixture was collected (33% conversion; 2.6:1 *Z/E*). Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.66–5.44 (m, 3H), 5.04–4.95 (m, 2H), 3.32 (q, *J* = 6.4 Hz, 2H), 3.00 (d, *J* = 5.7 Hz, 2H), 2.24 (m, 2H), 1.64 (d, *J* = 6.8 Hz, 3H).



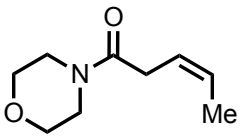
(*E*)-*N*-(but-3-en-1-yl)pent-3-enamide (3k): The title compound was prepared according to General Procedure B using **1k** (14.5 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a colorless oil (13 mg, 91% yield; 2.8:1 *E/Z*). Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.88–5.40 (m, 4H), 5.17–4.95 (m, 2H), 3.30 (q, *J* = 6.6 Hz, 2H), 2.90 (d, *J* = 7.1 Hz, 2H), 2.24 (q, *J* = 6.9 Hz, 2H), 1.71 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$ δ 171.4, 135.4, 131.2, 123.9, 117.3, 40.6, 38.4, 33.8, 18.1. **HRMS** calcd. for ($C_9H_{16}NO$) $[M+H]^+$: 154.1226, found 154.1222. **IR** (cm^{-1}) 3284.32, 1644.48, 1552.84, 1437.72, 976.44, 914.86, 605.67.



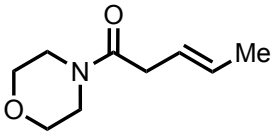
(*Z*)-1-(indolin-1-yl)pent-3-en-1-one (2l): The title compound was prepared according to General Procedure C using **1l** (20.1 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 16% remaining starting material that could not be separated (20 mg, 84% corrected yield; >20:1 *Z/E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.8 Hz, 1H), 7.18 (q, *J* = 7.3, 6.8 Hz, 2H), 7.01 (td, *J* = 7.4, 1.2 Hz, 1H), 5.78–5.64 (m, 2H), 4.08 (t, *J* = 8.6 Hz, 2H), 3.30–3.10 (m, 4H), 1.70 (d, *J* = 5.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.7, 143.2, 131.1, 127.7, 127.4, 124.6, 123.7, 122.4, 117.2, 48.0, 34.9, 28.2, 13.3. **HRMS** calcd. for ($C_{13}H_{14}NO$) $[M+H]^+$: 202.1226, found 202.1227. **IR** (cm^{-1}) 1657.82, 1481.54, 1416.52, 762.87.



(*E*)-1-(indolin-1-yl)pent-3-en-1-one (3l): The title compound was prepared according to General Procedure B using **1l** (20.1 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 3% remaining starting material that could not be separated (20 mg, 97% corrected yield; 4.2:1 *E/Z*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.1 Hz, 1H), 7.18 (q, *J* = 7.5 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 5.66 (m, 2H), 4.07 (q, *J* = 9.3, 8.6 Hz, 2H), 3.26–3.10 (m, 4H), 1.73 (d, *J* = 5.7 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.9, 143.2, 131.1, 129.3, 127.7, 124.6, 123.7, 123.4, 117.2, 48.0, 40.3, 28.2, 18.2. **HRMS** calcd. for ($C_{13}H_{14}NO$) $[M+H]^+$: 202.1226, found 202.1225. **IR** (cm^{-1}) 1658.21, 1480.31, 757.04

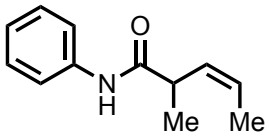


(*Z*) -*N*-morpholino pent-3-enamide (2m): The title compound was prepared according to General Procedure C using **1m** (16.7 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a colorless oil containing 18% remaining starting material that could not be separated (17 mg, 82% corrected yield; 8.0:1 *Z/E*). The analytical data matches the previous report.[6] Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.93–5.46 (m, 2H), 3.68–3.62 (m, 6H), 3.44 (t, *J* = 5.4 Hz, 2H), 3.11 (d, *J* = 6.7 Hz, 2H), 1.64 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 127.1, 122.7, 67.0, 66.7, 46.2, 42.1, 32.4, 13.2. **HRMS** calcd. for ($C_9H_{16}NO_2$) $[M+H]^+$: 170.1176, found 170.1168.

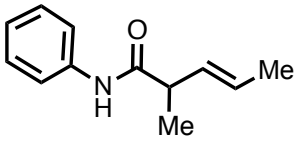


(*E*) -*N*-morpholino pent-3-enamide (3m): The title compound was prepared according to General Procedure C using **1m** (16.7 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a colorless oil (15 mg, 87% yield; 2.9:1 *E/Z*). The analytical data matches the previous

report.[6] Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.62–5.50 (m, 2H), 3.75–3.53 (m, 6H), 3.54–3.42 (m, 2H), 3.12–3.02 (m, 2H), 1.73–1.69 (m, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 128.8, 123.53, 66.6, 46.2, 41.9, 37.4, 32.3, 17.9. **HRMS** calcd. for ($C_9H_{16}NO_2$) $[M+H]^+$: 170.1176, found 170.1185.

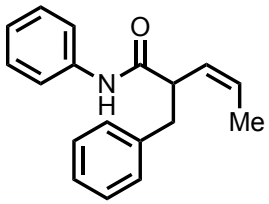


(*Z*)-2-methyl-*N*-phenylpent-3-enamide (2n): The title compound was prepared according to General Procedure C using **1n** (18.9 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Separation by PTLC (3:1 hexane:EtOAc) afforded the pure *Z*-isomer as a white solid (14 mg, 73% yield; >20:1 *Z/E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.39 (s (br), 1H), 7.31 (dd, *J* = 8.6, 7.5 Hz, 2H), 7.09 (tt, *J* = 7.3, 1.1 Hz, 1H), 5.79 (dtd, *J* = 10.7, 7.2, 6.1 Hz, 1H), 5.55 (dddd, *J* = 11.1, 9.4, 3.6, 1.8 Hz, 1H), 3.45 (dtd, *J* = 9.3, 7.4, 6.3 Hz, 1H), 1.75 (dd, *J* = 6.9, 1.8 Hz, 3H), 1.34 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.3, 138.0, 130.5, 129.1, 128.3, 124.3, 119.8, 40.1, 17.6, 13.3. **HRMS** calcd. for ($C_{12}H_{16}NO$) $[M+H]^+$: 190.1226, found 190.1228. **IR** (cm^{-1}) 1660.66, 1600.64, 1544.27, 1499.69, 1441.87, 757.29.

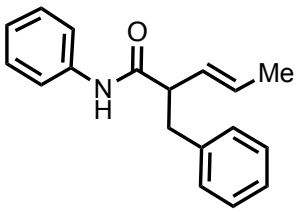


(*E*)-2-methyl-*N*-phenylpent-3-enamide (3n): The title compound was prepared according to General Procedure B using **1n** (18.9 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 3% remaining starting material that could not be separated (19 mg, 97% corrected yield; 5.1:1 *E/Z*). The analytical data matches the previous report.[7] Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.36 (s (br), 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 5.90–5.67 (m, 1H), 5.63–5.52 (m, 1H), 3.09 (p, *J* = 7.2 Hz, 1H), 1.76 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.33 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.4, 138.1, 131.0, 129.1,

129.0, 124.3, 119.7, 45.6, 18.2, 17.2. **HRMS** calcd. for ($C_{12}H_{16}NO$) $[M+H]^+$: 190.1226, found 190.1239.

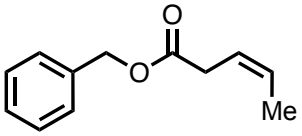


(*Z*)-2-benzyl-*N*-phenylpent-3-enamide (2o): The title compound was prepared according to General Procedure C using **1o** (26.5 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 24% starting material that could not be separated (27 mg, 76% yield; >20:1 *Z/E*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.35–7.11 (m, 8H), 7.07 (dt, *J* = 15.1, 7.4 Hz, 1H), 5.91–5.72 (m, 1H), 5.69–5.49 (m, 1H), 3.57 (td, *J* = 8.9, 6.4 Hz, 1H), 3.31 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.90–2.77 (m, 1H), 1.54 (dd, *J* = 6.9, 1.8 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.3, 139.4, 135.6, 129.3, 129.0, 128.5, 126.4, 124.5, 120.3, 120.1, 117.5, 48.0, 38.9, 13.2. **HRMS** calcd. for ($C_{18}H_{20}NO$) $[M+H]^+$: 266.1539, found 266.1538. **IR** (cm^{-1}) 1656.68, 1600.43, 1541.07, 1497.67, 1441.95, 750.68, 695.11.

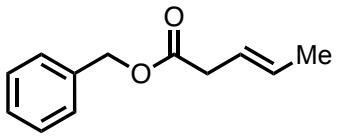


(*E*)-2-benzyl-*N*-phenylpent-3-enamide (3o): The title compound was prepared according to General Procedure B using **1o** (26.5 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid containing 4% starting material that could not be separated (27 mg, 96% corrected yield; 4.0:1 *E/Z*). Major isomer: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.35–7.12 (m, 8H), 7.08 (q, *J* = 7.5 Hz, 1H), 5.69–5.52 (m, 2H), 3.24 (dd, *J* = 13.5, 7.2 Hz, 1H), 3.17 (q, *J* = 7.0 Hz, 1H), 2.86 (dd, *J* = 13.5, 6.7 Hz, 1H), 1.70 (d, *J* = 4.3 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.5, 139.5, 137.8, 129.9, 129.3, 129.1, 129.0, 128.5, 126.4, 124.4,

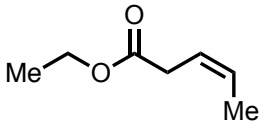
120.0, 53.9, 38.5, 18.1. **HRMS** calculated for ($C_{18}H_{20}NO$) $[M+H]^+$: 266.1539, found 266.1546. **IR** (cm^{-1}) 1654.52, 1600.44, 1541.94, 1496.70, 1441.73, 752.09, 695.45.



benzyl (*Z*)-pent-3-enoate (2p): The title compound was prepared according to General Procedure C for 24 hours using freshly prepared and columned **1p** (19.0 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (4.0 mg, 10 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a colorless oil containing 30% remaining starting material that could not be separated (19 mg, 70% yield; 19:1 *Z*/*E*). The analytical data matches the previous report.[8] Major isomer: **^{1}H NMR**: (500 MHz, $CDCl_3$) δ 7.43–7.28 (m, 5H), 5.72–5.64 (m, 1H), 5.61 (dtq, *J* = 10.8, 7.2, 1.6 Hz, 1H), 5.14 (s, 2H), 3.16 (dt, *J* = 6.8, 1.3 Hz, 2H), 1.69–1.60 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.9, 136.1, 128.7, 128.3, 128.3, 127.8, 121.7, 66.5, 32.8, 13.1.

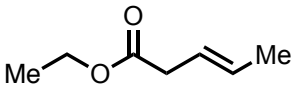


benzyl (*E*)-pent-3-enoate (3p): The title compound was prepared according to General Procedure B using **1p** (19.0 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a colorless oil (19 mg, 100% yield; 2.8:1 *E/Z*). The analytical data matches the previous report.[8] Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40–7.29 (m, 5H), 5.63–5.54 (m, 2H), 5.13 (s, 2H), 3.10–3.06 (m, 2H), 1.76–1.67 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.1, 136.1, 129.7, 128.7, 128.3, 128.3, 122.7, 66.5, 38.2, 18.0.

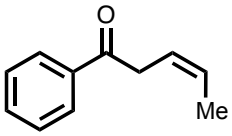


ethyl (*Z*)-pent-3-enoate (2q): The title compound was prepared according to General Procedure C for 24 hours using freshly prepared and columned **1q** (12.8 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (2.0 mg, 5 mol%), and

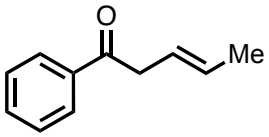
THF (1.0 mL). Filtration through silica gel afforded the product as a colorless oil containing 24% starting material that could not be separated (13 mg, 76% corrected yield; 20:1 *Z*/*E*). The analytical data matches the previous report.[9] Major isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.74–5.53 (m, 2H), 4.15 (q, *J* = 7.14 Hz, 2H), 3.11 (ddd, *J* = 7.0, 1.6, 1.0 Hz, 2H), 1.69 – 1.65 (m, 3H), 1.26 (t, *J* = 7.14 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.1, 127.4, 121.9, 60.61, 32.7, 30.3, 14.2.



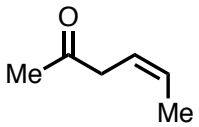
ethyl (*E*)-pent-3-enoate (3q): The title compound was prepared according to General Procedure B using **1q** (12.8 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a colorless oil containing 13% starting material that could not be separated (13 mg, 87% yield; 3.1:1 *E*:*Z*). The analytical data matches the previous report.[9] Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.74–5.47 (m, 2H), 4.23–4.08 (m, 2H), 3.03 (dd, *J* = 5.4, 1.3 Hz, 2H), 1.72 (dt, *J* = 4.7, 1.2 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.2, 129.5, 122.9, 60.5, 33.7, 29.0, 14.4.



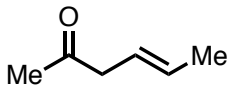
(*Z*)-1-phenylpent-3-en-1-one (2r): The title compound was prepared according to General Procedure C for 24 hours using freshly purified **1r** (16.0 mg, 0.100 mmol), **NHC-1•**CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (4.0 mg, 10 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a colorless oil containing 17% remaining starting material that could not be separated (15 mg, 77% corrected yield; 10:1 *Z*/*E*). The analytical data matches the previous report.[10] Major isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 5.73 (m, *J* = 5.5, 2.7 Hz, 2H), 3.75 (d, *J* = 4.6 Hz, 2H), 1.70 (d, *J* = 4.8 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 198.3, 136.9, 133.2, 128.7, 128.4, 127.7, 122.4, 37.3, 13.3.



(*E*)-1-phenylpent-3-en-1-one (3r): The title compound was prepared according to General Procedure B using **1r** (16.0 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a colorless oil (15 mg, 95% yield; 2.6:1 *E*:*Z*). The analytical data matches the previous report.[10] Major isomer: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 7.3, 1.8 Hz, 2H), 7.60–7.52 (m, 1H), 7.50–7.39 (m, 2H), 5.77–5.55 (m, 2H), 3.68 (d, *J* = 5.9 Hz, 2H), 1.75–1.68 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 198.8, 136.8, 133.2, 129.68, 128.7, 128.4, 123.5, 42.6, 18.2.



(*Z*)-hex-4-en-2-one (2s): The title compound was prepared according to General Procedure C for 24 hours using freshly columned **1s** (9.8 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (4.0 mg, 10 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a colorless oil containing 25% starting material that could not be separated and 63% THF that could not be removed due to substrate volatility (16 mg, 75% corrected yield, >20:1 *Z*/*E*). The analytical data matches the previous report.[10] Major isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.73 – 5.59 (m, 1H), 5.56 (dtdd, *J* = 9.0, 7.3, 3.5, 1.9 Hz, 1H), 3.17 (d, *J* = 6.4 Hz, 2H), 2.16 (s, 3H) 1.62 (d, *J* = 5.8 Hz, 3H).**^{13}C NMR (**126 MHz, $CDCl_3$) δ 207.0, 127.9, 121.8, 42.24, 29.5, 13.0.



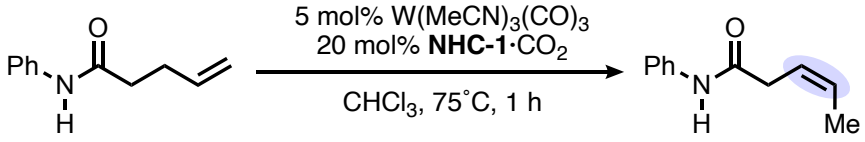
(*E*)-hex-4-en-2-one (3s): The title compound was prepared according to General Procedure B using **1s** (9.8 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a colorless oil containing 3% starting material that could not be separated (9 mg, 92% corrected yield; 2.8:1 *E*:*Z*). The analytical data matches the previous report.[10] Major isomer:**^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.64–5.50 (m, 2H),

3.11 (dd, J = 5.5, 1.3 Hz, 2H), 2.14 (s, 3H), 1.71 (dt, J = 4.8, 1.2 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 207.6, 130.0, 123.1, 47.8, 29.5, 18.2.

Gram-scale Experiments

Z-selective isomerization

Scheme S5. Reaction conditions for Z-selective reaction on gram-scale.

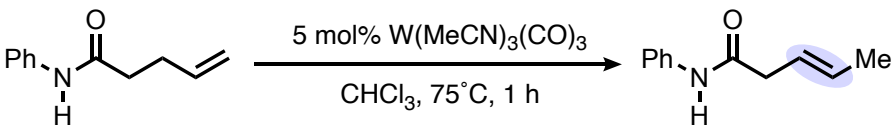


1a **2a**

(Z)-*N*-phenylpent-3-enamide (2a): In a nitrogen-filled glovebox, a 100 mL flask equipped with a Teflon-coated stir bar was charged with $W(MeCN)_3(CO)_3$ (112 mg, 0.29 mmol, 0.05 equiv.), **NHC-1**•CO_2 (160 mg, 1.14 mmol, 0.2 equiv.) and THF (inhibitor-free, 57 mL). The mixture was stirred for 2 minutes before **1a** (1.0 g, 5.71 mmol, 1.0 equiv.) was added. The flask was sealed and brought out of the glovebox, where it was allowed to react at 75˚C for 1 h. After cooling, the reaction mixture was filtered through a short pad of silica, washed with EtOAc and concentrated *in vacuo*. The crude mixture was purified by column chromatography (eluent: hexanes/EtOAc = 7:1 → 3:1) to give **2a** as a yellow solid containing 12% starting material that could not be separated (1.0 g, 88% corrected yield; Z/E >20:1). ^{1}H and ^{13}C NMR spectra are consistent with the data reported above.

E-selective isomerization

Scheme S6. E-selective reaction on gram-scale.



1a **3a**

(*E*)-*N*-phenylpent-3-enamide (3a): In a nitrogen-filled glovebox, a 100 mL flask equipped with a Teflon-coated stir bar was sequentially charged with **1a** (1.0 g, 5.71 mmol, 1.0 equiv.), $W(MeCN)_3(CO)_3$ (112 mg, 0.29 mmol, 0.05 equiv.) and $CHCl_3$ (40 mL). The flask was sealed and brought out of the glovebox, where it was allowed to react at 75˚C for 1 h. After cooling, the reaction mixture was filtered through a short pad of silica, washed with hexanes and EtOAc (1:1 v/v) and concentrated *in vacuo*. The crude mixture was purified by column chromatography (eluent: hexanes/EtOAc = 10:1 → 7:1) to give **3a** as a yellow solid (990 mg, 99% yield; 3.0:1 *E*/*Z*). ^{1}H and ^{13}C NMR spectra are consistent with the data reported above.

Determination of E/Z ratio

E/*Z* ratios were determined by ^{1}H NMR of the isolated reaction mixture unless otherwise noted. The accuracy of this measurement was independently verified by comparing the crude *E/Z* ratios to the isolated ratios for a handful of substrates. An example comparison of selectivities between crude and isolated selectivity for substrate **1a** is shown below.

Table S12. Reaction selectivities determined before and after purification with silica gel chromatography.

Entry	Substrate	Product	Crude *E/Z* ratio	Isolated *E/Z* ratio
1	**1m**	**3m**	2.9:1	2.9:1
2	**1i**	**3i**	2.6:1	2.7:1
3	**1p**	**2p**	1:19	1:18

Determination of isolated percent yield

The isolated products include both isomers of internal alkene, and, in some cases, residual starting material that could not be separated by silica gel chromatography. The reported masses of isolated

products are not corrected for remaining starting material. The percent yields account for both isomers of internal alkene product but are corrected for remaining starting material. The corrected yields are calculated by determining the percent starting material relative to percent product by ^{1}H NMR of the purified material (conversion). To ensure that this calculation is correct and verify that no hidden impurities are present, QNMR of isolated **2a** and **3a** was performed, and the results were compared to the conversion calculation (Table S5). These results validate the implementation of conversion to correct the yields of the isolated products.

Table S13. Comparison of methods to quantify isolated yields to account for remaining starting material.

Entry	Substrate	Product	QNMR yield relative to CH_2Br_2 internal standard [a]	Adjusted yield based on remaining starting material by ^{1}H NMR
1	**1a**	**2a**	89%	88%
2	**1a**	**3a**	95%	97%

Z-Selective reaction troubleshooting

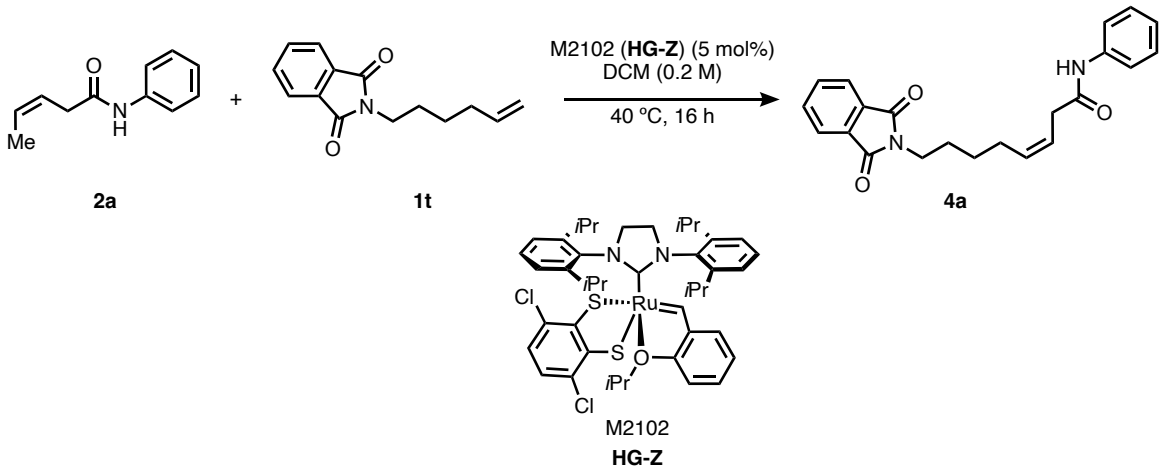
The yield and selectivity of the *Z*-selective reaction can be sensitive to the quality of the ligand and precatalyst. The reaction was optimized using commercial $W(CO)_3(MeCN)_3$ and **NHC-1•CO_2**, which were used without further purification. However, when stored at room temperature, **NHC-1•CO_2** decomposes over time, which alters the metal:ligand ratio in the reaction and negatively affects the reaction selectivity and yield. The purity of the ligand can be checked by ^{1}H NMR in D_2O.[11] Further, the active catalyst decomposes if the ratio of ligand to metal is too high. This may occur if the ligand is of too high purity and is evinced by solids crashing out on the walls of the reaction vessel and yields that are low but selectivities that are high. If impure or too pure ligand is causing the reaction yield or selectivity to drop, there are three advisable modes of action:

1. Purchase new ligand
2. Test the reaction at 5%, 10%, 15%, and 20% ligand loading while maintaining a 5% tungsten loading to find the best ratio for the ligand purity being used.
3. Purify the ligand by dissolving ~200 mg in 100 mL acetonitrile and stirring/sonicating for 1h. Filter out remaining solids and concentrate the filtrate to isolate purified ligand. Utilize dry solvent and an inert atmosphere for this entire process. Then follow step 2 above.

Some batches of $W(CO)_3(MeCN)_3$ may also be of poor quality. This can be difficult to recognize spectroscopically but is often indicated visually when the complex is a gray or brown color rather than yellow. Decomposed tungsten can result in diminished yields and selectivities, especially in the isomerization of ketones and esters. In these instances, it is advisable to prepare a fresh batch of complex according to literature procedure.[12]

Product diversification

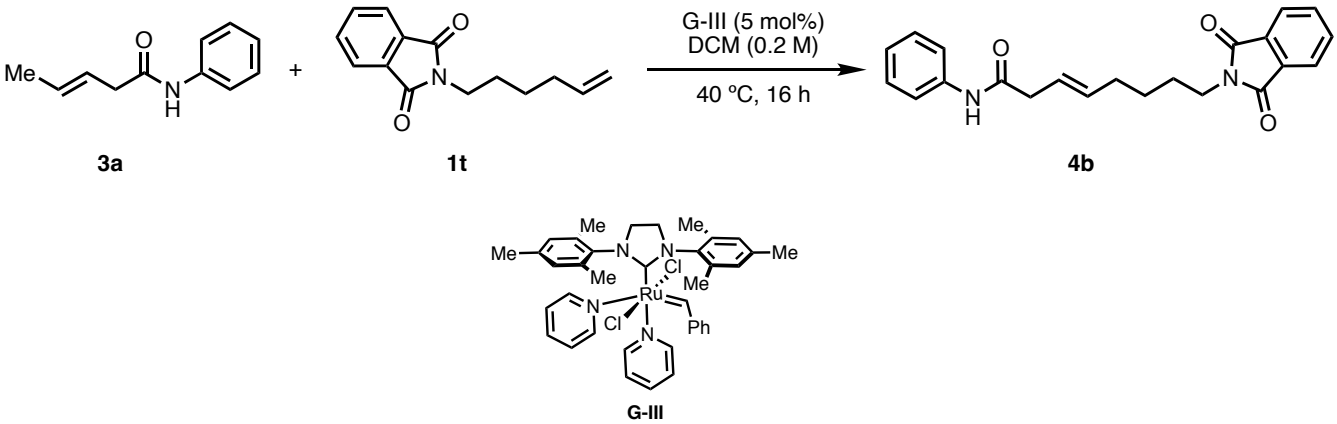
Scheme S7. *Z*-retentive cross-metathesis reaction.



(*Z*)-8-(1,3-dioxoisoindolin-2-yl)-*N*-phenyloct-3-enamide (4a): To a 4-mL reaction vial containing a Teflon®-coated stir bar was added (*Z*)-**2a** (>20:1 *Z/E*) (8.8 mg, 0.050 mmol, 1.0 equiv). The vial was capped, evacuated under high vacuum, and back-filled with N_2. DCM (0.25 mL, 0.2M) was added via

syringe. The vial was pumped into an argon-filled glovebox, and 2-(hex-5-en-1-yl)isoindoline-1,3-dione (57 mg, 0.25 mmol, 5.0 equiv) and dithiolate catalyst **M2102** ([CAS 1865771-19-2], (2.1 mg, 5.0 mol%) were added sequentially. The vial was capped, removed from the glovebox, and stirred at 40 ºC overnight. The solvent was evaporated using a rotavap. The crude material was purified by PTLC (4:1 hexane:EtOAc) to yield an off-white solid (5.4 mg, 30% yield, *Z:E* > 20:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.59 (s(br), 1H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.80–5.63 (m, 2H), 3.71 (t, *J* = 7.1 Hz, 2H), 3.20 (d, *J* = 6.4 Hz, 2H), 2.19 (q, *J* = 7.2 Hz, 2H), 1.73 (p, *J* = 7.3 Hz, 2H), 1.47 (p, *J* = 7.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.1, 168.5, 137.9, 134.7, 134.0, 132.1, 128.9, 124.2, 123.2, 122.2, 119.8, 37.5, 36.4, 27.9, 26.7, 26.2. **HRMS** calculated for $[C_{22}H_{23}N_2O_{12}]^+$ 363.1703, found 363.1704. **IR** (cm^{-1}) 1705.50, 1600.13, 1440.31, 1396.79, 719.69.

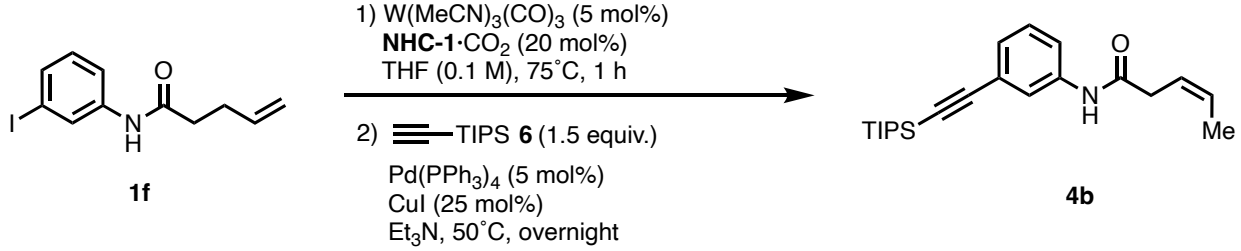
Scheme S8. Cross-metathesis reaction with **2a**.



(*E*)-8-(1,3-dioxoisoindolin-2-yl)-*N*-phenyloct-3-enamide (5a): To a 4-mL reaction vial containing a Teflon®-coated stir bar was added (*E*)-**3a** (3.4:1 *E/Z)* (8.8 mg, 0.050 mmol, 1.0 equiv) and freshly prepared Grubbs catalyst, 3rd-generation[13] (G-III) DCM (0.25 mL, 0.2M) was added followed by 2-(hex-5-en-1-yl)isoindoline-1,3-dione (57 mg, 0.25 mmol, 5.0 equiv). The vial was capped and

removed from the glovebox and stirred at 40 ºC overnight. Once the reaction was complete, the solvent was evaporated using a rotary evaporator. PTLC was used for product purification (4:1 hexane:EtOAc) to yield a white solid (9.8 mg, 54% yield, *Z*:*E* 28:72). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 2.9 Hz, 2H), 7.55–7.45 (m, 2H), 7.40 (s(br), 1H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 5.80–5.57 (m, 2H), 3.70 (dd, *J* = 8.2, 6.3 Hz, 2H), 3.10 (d, *J* = 6.5 Hz, 2H), 2.17 (q, *J* = 7.3 Hz, 2H), 1.77–1.68 (m, 2H), 1.48 (p, *J* = 7.5 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.3, 168.5, 137.8, 136.5, 133.9, 132.1, 128.9, 124.3, 123.2, 123.0, 119.8, 41.6, 37.7, 32.0, 28.0, 26.2. **HRMS** calculated for $[C_{22}H_{23}N_2O_{12}]^+$ 363.1703, found 363.1702. **IR** (cm^{-1}) 1705.34, 1599.62, 1541.77, 1439.88, 1396.37, 755.81, 718.74, 693.71.

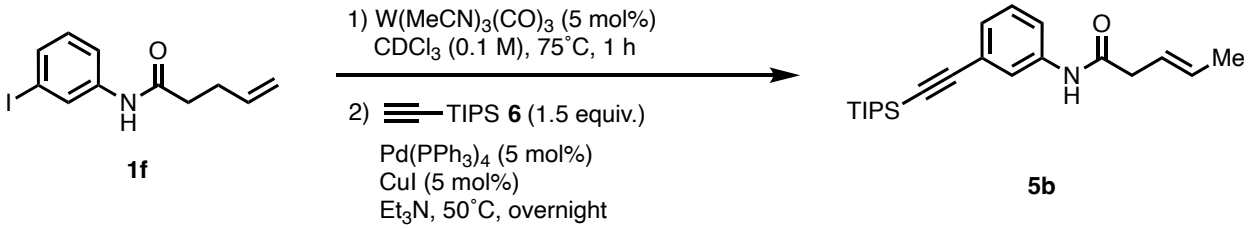
Scheme S9. One-pot *Z*-selective isomerization and Sonogashira cross-coupling.



(*Z*)-*N*-(3-((triisopropylsilyl)ethynyl)phenyl)pent-3-enamide (4b): In a nitrogen-filled glovebox, a 4 mL vial equipped with a Teflon-coated stir bar was charged with $W(MeCN)_3(CO)_3$ (2 mg, 0.005 mmol, 0.05 equiv.), **NHC-1•**CO_2 (2.8 mg, 0.02 mmol, 0.2 equiv.) and THF (1 mL). The reaction was stirred for 2 minutes before **1f** (30.1 mg, 0.1 mmol, 1.0 equiv.) was added. The vial was capped and brought out of the glovebox, where it was allowed to react at 75˚C for 1 h. After the reaction was complete, the mixture was concentrated *in vacuo*. The same vial was then charged with CuI (4.8 mg, 0.025 mmol, 0.25 equiv.) and brought into a glovebox, where $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 0.05 equiv.) was added. The vial was capped and brought out of the glovebox, where Et_3N (0.5 mL, degassed) was added via syringe. The vial was sonicated for 1 minute because the solubility of CuI in

Et_3N was poor. Ethynyltriisopropylsilane (**6**) (34 μL, 0.15 mmol, 1.5 equiv.) was added via microlitre syringe, and the reaction was heated at 50˚C overnight. After this time, the reaction was diluted with ethyl acetate (1 mL) and filtered through a pad of silica. The crude product was concentrated *in vacuo* and purified by column chromatography (eluent: hexane/EtOAc = 7:1) to afford an off-white solid (29.9 mg, 58% yield, >20:1 *Z*/*E*). Major isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59–7.53 (m, 2H), 7.46 (s(br), 1H), 7.24–7.21 (m, 2H), 5.90–5.86 (m, 1H), 5.68–5.66 (m, 1H), 3.19 (d, *J* = 7.6 Hz, 2H), 1.72 (d, *J* = 7.1 Hz, 3H), 1.12 (s, 21H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.2, 137.8, 136.9, 130.6, 129.0, 128.3, 123.0, 122.3, 120.1, 106.6, 91.1, 36.0, 18.8, 13.2, 11.4. **HRMS** calcd. for ($C_{22}H_{34}NOSi$) $[M+H]^+$: 356.2410, found 356.2414. **IR** (cm^{-1}) 2942.26, 2864.38, 1664.80, 1605.84, 1584.42, 1550.79, 1479.43, 1425.20, 883.15, 787.71, 676.27.

Scheme S10. One-pot *E*-selective isomerization and Sonogashira cross-coupling.



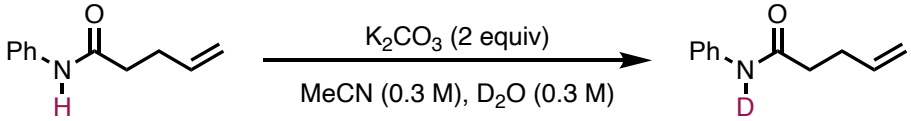
(*E*)-*N*-(3-((triisopropylsilyl)ethynyl)phenyl)pent-3-enamide (5b): In a nitrogen-filled glovebox, a 4 mL vial equipped with a Teflon-coated stir bar was charged with $W(MeCN)_3(CO)_3$ (2 mg, 0.005 mmol, 0.05 equiv), **1f** (30.1 mg, 0.1 mmol, 1.0 equiv.) and $CDCl_3$ (1 mL). The vial was capped and brought out of the glovebox, where it was allowed to react at 75˚C for 1 h. After the reaction was complete, ethyl acetate (1 mL) was added to quench the reaction, and the mixture was concentrated *in vacuo*. The same vial was charged with CuI (0.9 mg, 0.005 mmol, 0.05 equiv.) and brought into a glovebox, where $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol, 0.05 equiv.) was added. The vial was capped and brought out of the glovebox, where Et_3N (0.5 mL, degassed) was added via syringe. Then, the vial

was sonicated for 1 minute. Ethynyltriisopropylsilane (**6**) (34 µL, 0.15 mmol, 1.5 equiv.) was added via microsyringe, and the reaction was heated at 50˚C overnight. After this time, the reaction was diluted with ethyl acetate (1 mL) and filtered through a pad of silica. The crude product was concentrated *in vacuo* and purified by column chromatography (eluent: hexane/EtOAc = 7:1 → 6:1) to afford an orange solid (30.5 mg, 86% yield, E/Z = 2.9:1).

Major isomer: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57–7.53 (m, 2H), 7.37 (s (br), 1H), 7.24–7.21 (m, 2H), 5.81–5.53 (m, 2H), 3.09 (d, *J* = 7.0 Hz, 2H), 1.78 (d, *J* = 6.4 Hz, 3H), 1.12 (s, 21H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.7, 137.8, 135.3, 132.2, 129.0, 128.2, 123.4, 123.0, 120.1, 106.6, 91.0, 41.7, 18.8, 18.3, 11.4. **HRMS** calcd. for ($C_{22}H_{34}NOSi$) $[M+H]^+$: 356.2410, found 356.2420. **IR** (cm^{-1}) 2940.90, 2864.65, 2360.40, 1742.52, 1662.91, 1605.91, 1584.10, 1551.60, 1479.78, 1426.28, 1365.91, 1214.90, 882.91, 787.72, 749.70, 675.24.

Synthesis and reactivity of D-labeled substrates

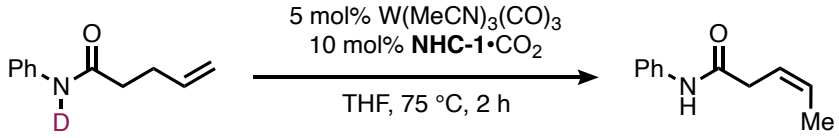
Scheme S11. Preparation of **1a-*d*$_1$**.



1a **1a-*d*$_1$**

***N*-phenylpent-4-enamide-*d*$_1$ (1a-*d*$_1$):** To a flame dried 25 mL flask, **1a** (200 mg, 1.14 mmol) and K_2CO_3 (315 mg, 2.28 mmol) were dissolved in dry MeCN (4 mL) and D_2O (4 mL) then stirred at 23 °C for 16 h. The reaction was diluted with 10 mL of diethyl ether and the organic layer was collected and dried over $MgSO_4$ then concentrated *in vacuo.* The resulting solid was then used directly in the catalytic reactions. The degree of D-incorporation was determined by ^{1}H NMR.

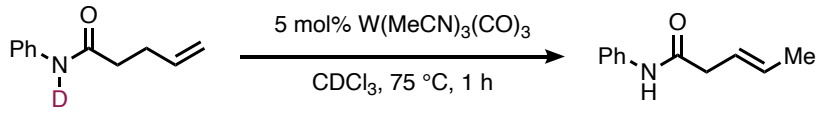
Scheme S12. *Z*-selective isomerization of **1a-*d*$_1$**.



1a-*d*$_1$ (>75% D) **2a** (0% D)

The isomerization reaction was run according to General Procedure C using **1a-*d*$_1$** (17.5 mg, 0.100 mmol), **NHC-1**•CO_2 (1.4 mg, 10 mol%), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and THF (1.0 mL). Filtration through silica gel afforded the product as a white solid. There was no deuterium detected in the product, and the analytical data was identical to **2a**.

Scheme S13. *E*-selective isomerization of **1a-*d*$_1$**.

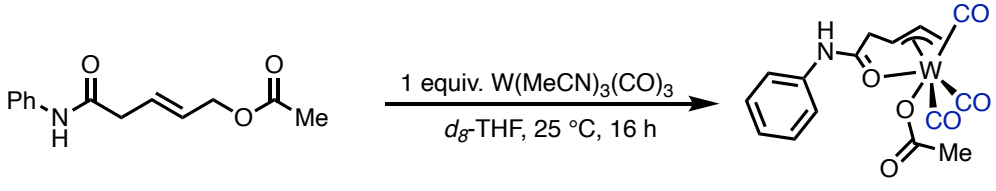


1a-*d*$_1$ (>75% D) **3a** (0% D)

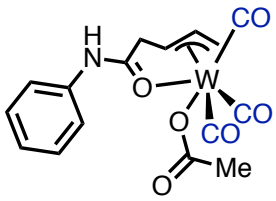
The isomerization reaction was run according to General Procedure B, using **1a-*d*$_1$** (17.5 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CHCl_3$ (1.0 mL). Filtration through silica gel afforded the product as a white solid. There was no deuterium detected in the product and analytical data was identical to **3a**.

Synthesis and reactivity of tungsten complexes

Scheme S14. Synthesis of **W-1**.



7 **W-1**



W-1: A J. Young NMR tube containing allylic acetate[13] (12 mg, 0.05 mmol) was introduced in an argon-filled glovebox, where it was further charged with $W(MeCN)_3(CO)_3$ (20 mg, 0.05 mmol) and *d8*-THF (0.75 mL). The tube was removed from the glovebox and shaken vigorously. The ligand and tungsten are completely insoluble at room temperature without stirring, so the tube was attached to a vortexer until the mixture was completely homogeneous (about 2 h). There are several isomers in solution, and only the major isomer is reported below. Single crystals suitable for X-ray diffraction were obtained by concentration of the solution under vacuum followed by addition of pentanes and leaving at room temperature overnight: **^{1}H NMR** (600 MHz, THF) δ 10.39 (s, 1H), 7.49–7.43 (m, 2H), 7.39–7.28 (m, 2H), 7.20–7.14 (m, 1H), 4.04 (d, J = 19.0 Hz, 1H), 3.14 (dd, J = 7.2, 2.6 Hz, 1H), 2.40 (s, 3H), 2.29 (dt, J = 9.1, 7.5 Hz, 1H), 2.08–2.04 (m, 1H), 1.36 (dd, J = 9.3, 2.6 Hz, 1H). **^{13}C NMR** (151 MHz, THF) δ 207.7, 201.7, 197.2, 180.1, 171.6, 137.5, 129.5, 124.3, 121.3, 57.1, 46.7, 39.4, 23.9, 2.3. **X-ray** (CCDC 2224919).

Figure S1: ^{1}H NMR of mixture of isomers, including **W-1**. 600 MHz, $CDCl_3$, 25 °C

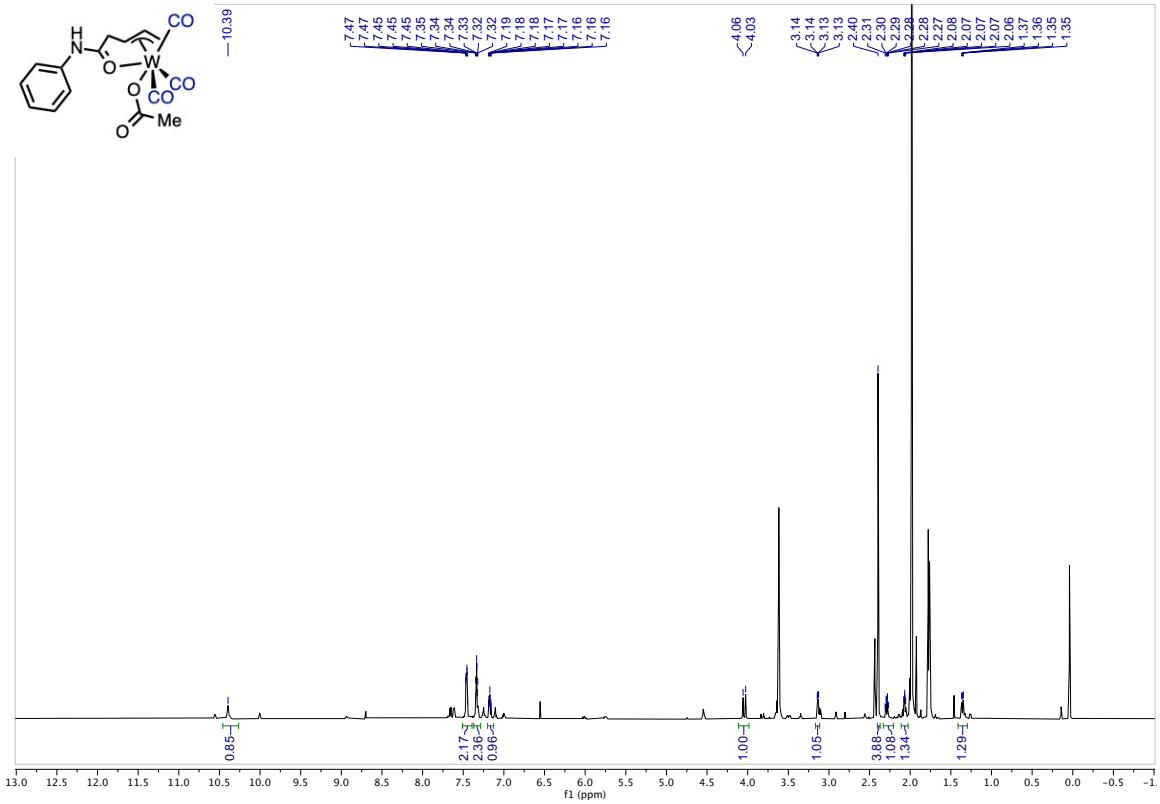
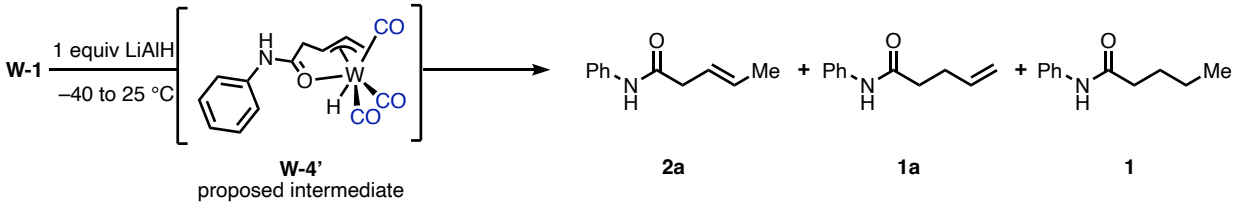
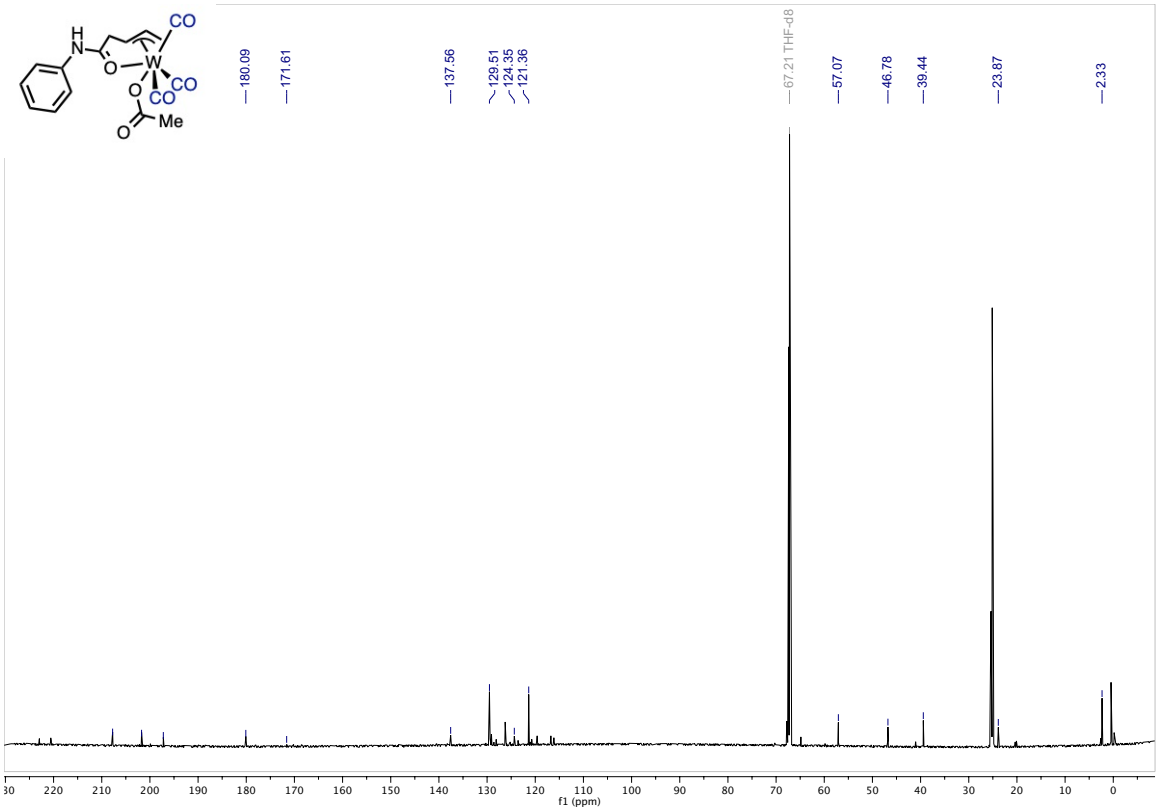


Figure S2: ^{13}C NMR of mixture of isomers, including **W-1**. 151 MHz, $CDCl_3$, 25 °C

Scheme S15. Reduction of **W-1** with $LiAlH_4$.



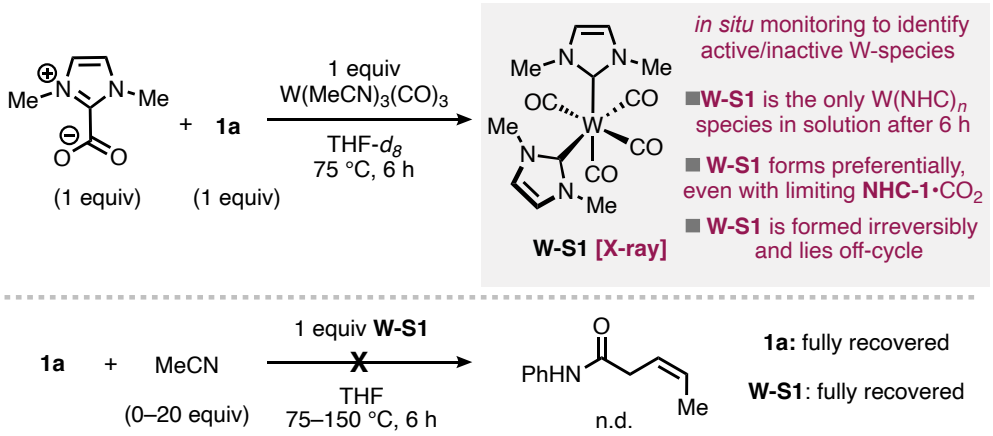
A 4-mL reaction vial containing allylic acetate[13] (12 mg, 0.05 mmol) was introduced in an argon-filled glovebox, where it was further charged with $W(MeCN)_3(CO)_3$ (20 mg, 0.05 mmol) and THF (0.75 mL). The reaction was stirred at room temperature for 2 h, then cooled to –40 °C in the glovebox freezer. Pre-cooled $LiAlH_4$ was added at –40 °C then gradually allowed to warm to room temperature while stirring. This was accompanied by a gradual change in color from yellow/light orange to a deep orange/red color. The reaction was quenched after 2 h with 10% NaOH and extracted with ether. The

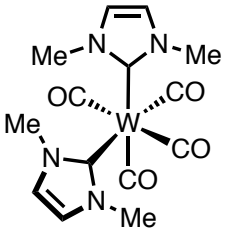


organic layer was filtered through silica gel and the eluant was evaporated to dryness and the crude

material (5 mg) analyzed by ^{1}H NMR and GCMS. The ratio of **1a**:**2a** was 1:3, with a 1:1.3 *E/Z* ratio as determined by ^{1}H NMR. Reduced product **1** was detected as the only other organic byproduct.

Figure S3. Isolation and reactivity of **W-S1**.

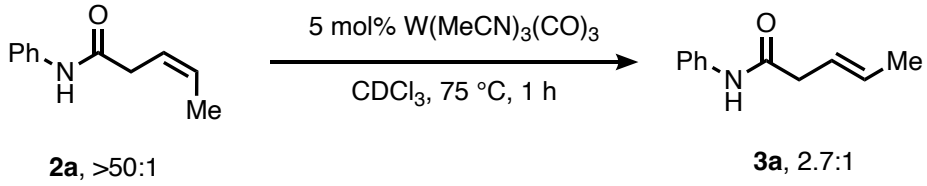




cis-[W(CO)$_4$(N-methylimidazole)$_2$] (**W-S1**): $W(CO)_6$ (1.76 g, 5.0 mmol) and **NHC-1**•CO2 (2.10 g, 15 mmol) were heated to 180 °C together in decalin (20 mL) for 2 h. Carbon monoxide was allowed to escape through the reflux condenser. The solution became yellow, and on cooling yellow microcrystals were filtered off, washed with OEt_2, (4 x 5 mL) and pentane (4 x 10 mL), and dried in vacuo to afford **W-S1** (2.6 g, 95%). Single crystals suitable for X-ray diffraction were obtained directly from this crop. **^{1}H NMR** (600 MHz, THF) δ 7.05 (s, 4H), 3.55 (s, 12H). **^{13}C NMR** (151 MHz, THF) δ 211.6, 206.4, 190.3, 122.6, 40.0. **X-ray** (CCDC 2144251).

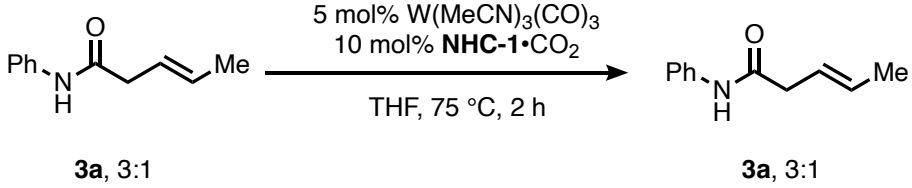
Resubjecting products to reaction conditions

Scheme S16. Reaction of **2a** using *E*-selective conditions.



The reaction was run according to General Procedure B, using **2a** (17.5 mg, 0.100 mmol), $W(MeCN)_3(CO)_3$ (1.9 mg, 5 mol%), and $CDCl_3$ (1.0 mL). Crude ^1H NMR was taken of the product to assess selectivity and conversion (97% conversion, 2.7:1 *E*/*Z*). The analytical data matches the previous report.[3]

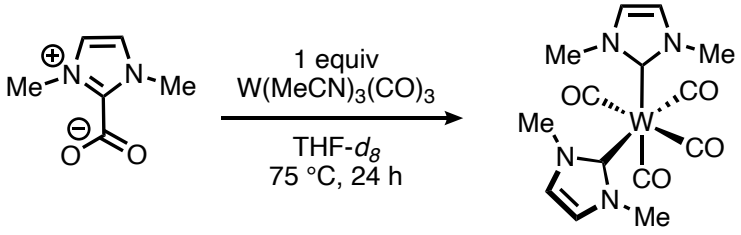
Scheme S17. Reaction of **3a** using *Z*-selective conditions.



The reaction was run according to General Procedure C, using **3a** (10.8 mg, 0.62 mmol), $W(MeCN)_3(CO)_3$ (1.2 mg, 5 mol%), **NHC-1**•CO_2 (0.9 mg, 10 mol%), and THF (0.62 mL). Crude ^1H NMR was taken of the product to assess selectivity and conversion (100% conversion, 3.3:1 *E*/*Z*). The analytical data matches the previous report.[3]

<u>Monitoring of reactions by NMR</u>

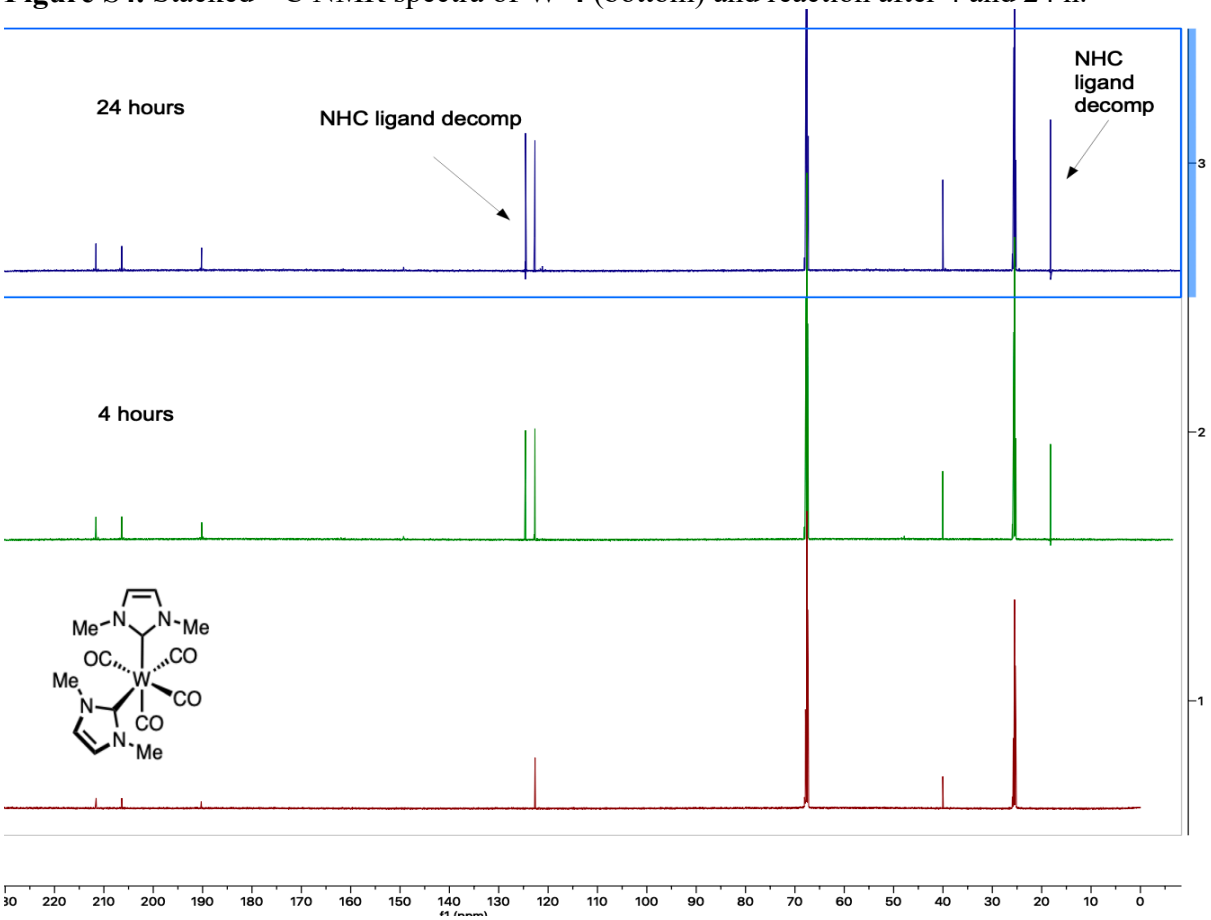
Scheme S18. Setup of reaction for NMR monitoring



A J. Young NMR tube containing **NHC-1**•CO2 (3.6 mg, 0.025 mmol) was introduced in an argon-filled glovebox, where it was further charged with $W(MeCN)_3(CO)_3$ (10 mg, 0.025 mmol) and *d8*-THF (0.5 mL). The tube was removed from the glovebox and shaken vigorously. The ligand and

tungsten are completely insoluble at room temperature without stirring so were heated to 75 °C. ^{13}C spectra were collected at 1 h, 4 h and 24 h. Below are the stacked spectra.

Figure S4. Stacked ^{13}C NMR spectra of **W-4** (bottom) and reaction after 4 and 24 h.



3. 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 radiation (α = 0.71073 Å). Crystals of the subject compound were used as received. A 0.130 x 0.120 x 0.100 mm yellow block crystal was mounted on a Cryoloop with Paratone N oil.

Data were collected in a nitrogen gas stream at 100(2) K using α scans. Crystal-to-detector distance was 45 mm using an exposure time of 0.5 seconds with a scan width of 0.8°. Data collection was 100.0% complete to 25.242° in α. A total of 8406 reflections were collected. 1671 reflections were found to be symmetry independent, with an R_{int} of 0.0583. Indexing and unit cell refinement indicated a **C-Centered**

Monoclinic lattice. The space group was found to be ***C2/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 non-hydrogen 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.

Notes: Excellent data and refinement. There is one-half molecule per asymmetric unit.

Figure S5. X-ray structure of **W-S1**.

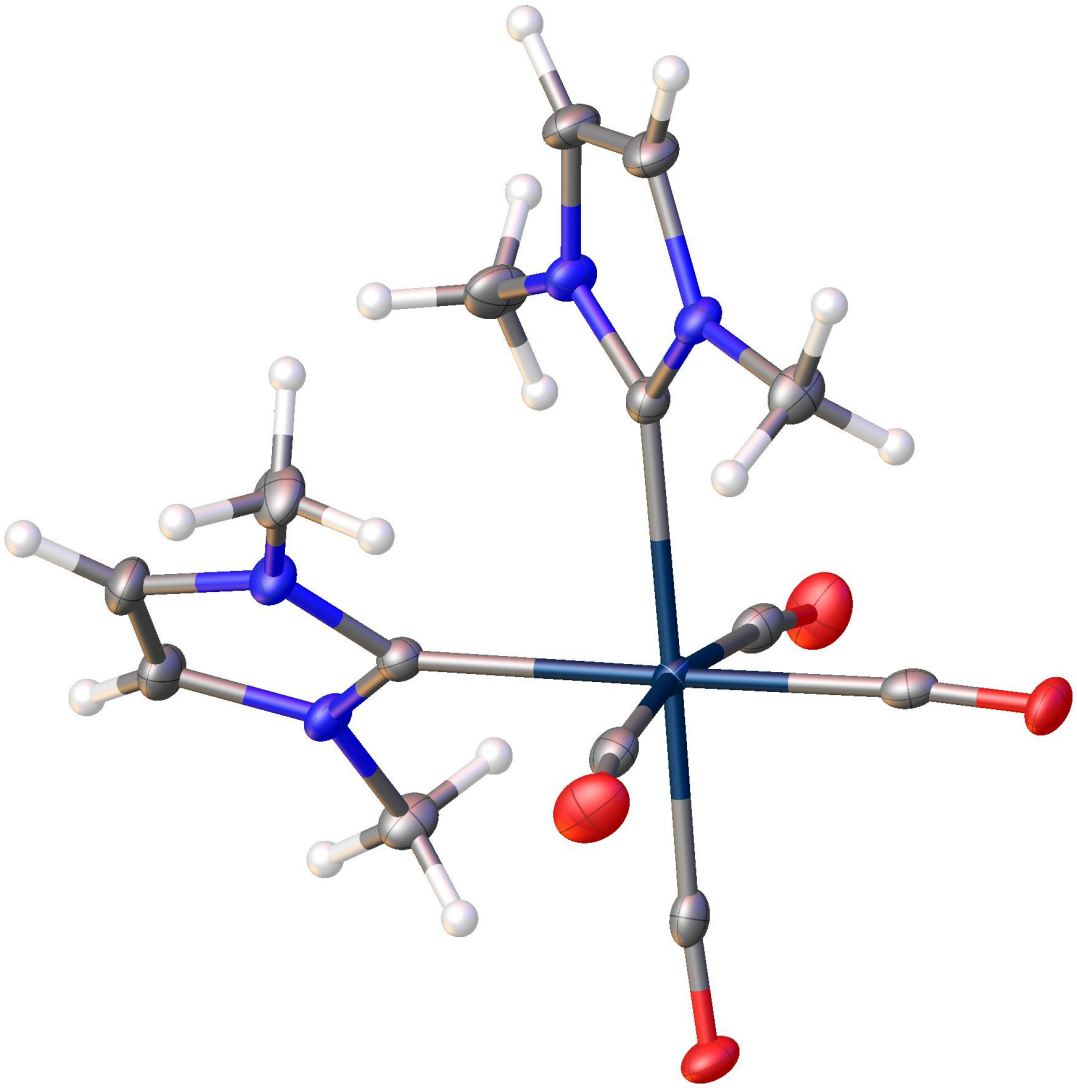


Table S14. Crystal data and structure refinement for **W-S1** (CCDC 2144251).

Report date	2019-09-06	
Empirical formula	C14 H16 N4 O4 W	
Formula weight	488.16	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 8.6484(7) Å	□= 90°.
	b = 14.2399(12) Å	□= 97.4980(10)°.
	c = 13.3208(15) Å	□ = 90°.

Volume	1626.5(3) $Å^3$
Z	4
Density (calculated)	1.994 Mg/m^3
Absorption coefficient	7.127 mm^{-1}
F(000)	936
Crystal size	0.13 x 0.12 x 0.1 mm^3
Theta range for data collection	2.773 to 26.372°.
Index ranges	-10<=h<=10, -17<=k<=17, -16<=l<=16
Reflections collected	8406
Independent reflections	1671 [R(int) = 0.0583]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4910 and 0.3858
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1671 / 0 / 107
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0183, wR2 = 0.0450
R indices (all data)	R1 = 0.0187, wR2 = 0.0452
Extinction coefficient	n/a
Largest diff. peak and hole	0.516 and -0.436 $e.Å^{-3}$

Table S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **W-S1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	5000	6525(1)	2500	12(1)
O(2)	3993(3)	4879(1)	980(2)	22(1)
O(4)	1614(3)	6263(2)	3127(2)	31(1)
N(3)	6516(4)	8510(1)	3454(2)	19(1)
N(4)	5420(3)	7786(2)	4576(2)	16(1)
C(1)	4348(3)	5514(2)	1512(2)	16(1)
C(2)	2833(4)	6414(2)	2910(3)	18(1)
C(3)	5747(3)	7699(2)	3608(2)	15(1)
C(4)	5952(4)	8633(2)	5004(3)	23(1)
C(5)	6644(4)	9085(2)	4300(2)	23(1)
C(6)	4680(4)	7078(2)	5140(2)	21(1)
C(7)	7178(4)	8783(2)	2546(2)	26(1)

Table S16. Bond lengths [Å] and angles [°] for **W-S1**.

W(1)-C(1)	1.982(3)
W(1)-C(1)#1	1.982(3)
W(1)-C(2)#1	2.026(4)
W(1)-C(2)	2.026(4)
W(1)-C(3)	2.267(3)
W(1)-C(3)#1	2.267(3)
O(2)-C(1)	1.165(4)
O(4)-C(2)	1.149(4)
N(3)-C(3)	1.362(4)
N(3)-C(5)	1.385(4)
N(3)-C(7)	1.457(4)
N(4)-C(3)	1.361(4)
N(4)-C(4)	1.387(4)
N(4)-C(6)	1.455(4)
C(4)-H(4)	0.9500
C(4)-C(5)	1.341(5)
C(5)-H(5)	0.9500
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(1)-W(1)-C(1)#1	86.81(16)
C(1)#1-W(1)-C(2)	87.54(12)
C(1)-W(1)-C(2)	85.95(12)
C(1)#1-W(1)-C(2)#1	85.95(12)
C(1)-W(1)-C(2)#1	87.54(12)
C(1)-W(1)-C(3)	179.05(9)
C(1)-W(1)-C(3)#1	94.09(12)
C(1)#1-W(1)-C(3)	94.09(12)

C(1)#1-W(1)-C(3)#1	179.05(9)
C(2)#1-W(1)-C(2)	171.04(15)
C(2)#1-W(1)-C(3)	92.19(11)
C(2)#1-W(1)-C(3)#1	94.42(11)
C(2)-W(1)-C(3)	94.42(11)
C(2)-W(1)-C(3)#1	92.19(11)
C(3)-W(1)-C(3)#1	85.02(14)
C(3)-N(3)-C(5)	111.6(3)
C(3)-N(3)-C(7)	127.1(3)
C(5)-N(3)-C(7)	121.3(2)
C(3)-N(4)-C(4)	111.7(3)
C(3)-N(4)-C(6)	125.9(2)
C(4)-N(4)-C(6)	122.3(3)
O(2)-C(1)-W(1)	175.7(2)
O(4)-C(2)-W(1)	173.6(2)
N(3)-C(3)-W(1)	129.1(2)
N(4)-C(3)-W(1)	127.4(2)
N(4)-C(3)-N(3)	103.4(2)
N(4)-C(4)-H(4)	126.8
C(5)-C(4)-N(4)	106.5(3)
C(5)-C(4)-H(4)	126.8
N(3)-C(5)-H(5)	126.6
C(4)-C(5)-N(3)	106.9(3)
C(4)-C(5)-H(5)	126.6
N(4)-C(6)-H(6A)	109.5
N(4)-C(6)-H(6B)	109.5
N(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
N(3)-C(7)-H(7A)	109.5
N(3)-C(7)-H(7B)	109.5
N(3)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7B)	109.5

H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

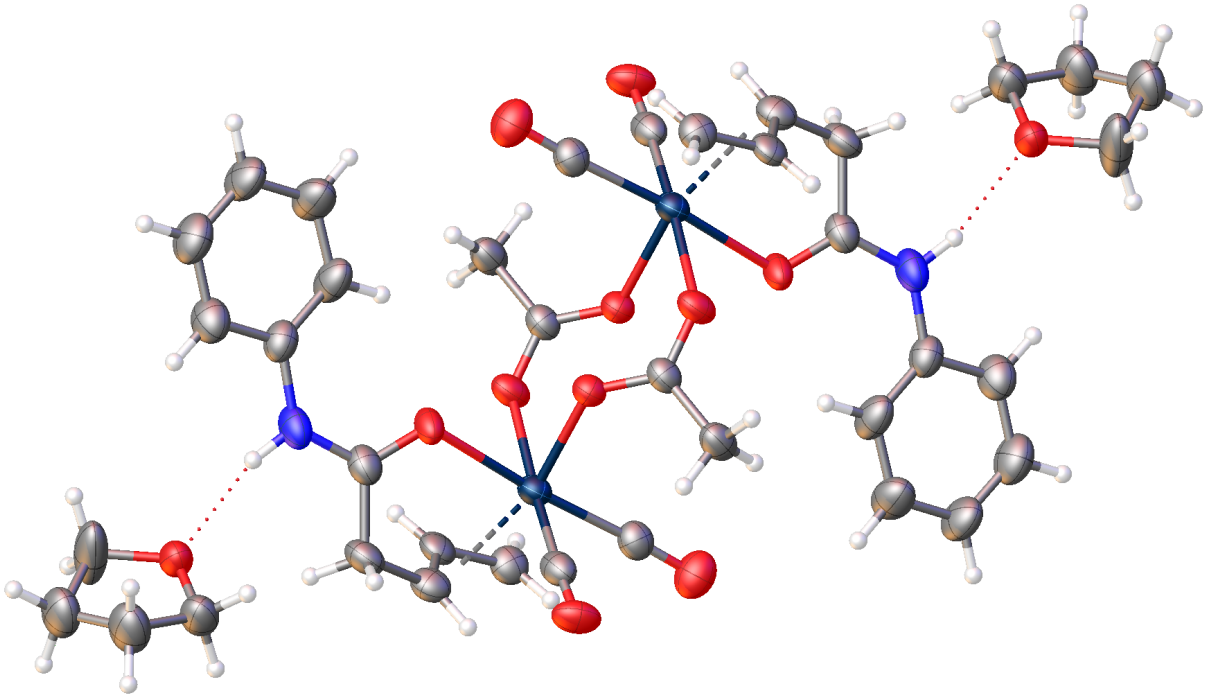
Table S17. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **W-S1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W(1)	14(1)	9(1)	13(1)	0	4(1)	0
O(2)	32(1)	13(1)	20(1)	-4(1)	4(1)	-2(1)
O(4)	22(1)	30(1)	45(2)	-3(1)	14(1)	-3(1)
N(3)	24(2)	14(1)	17(2)	2(1)	3(1)	-4(1)
N(4)	21(1)	11(1)	17(1)	-1(1)	5(1)	2(1)
C(1)	17(1)	16(1)	17(1)	6(1)	6(1)	4(1)
C(2)	23(2)	14(1)	19(2)	-1(1)	5(1)	2(1)
C(3)	17(1)	14(1)	15(1)	1(1)	2(1)	1(1)
C(4)	33(2)	16(1)	20(2)	-5(1)	0(1)	1(1)
C(5)	32(2)	14(1)	24(2)	-3(1)	0(1)	-4(1)
C(6)	29(2)	19(1)	18(1)	2(1)	10(1)	0(1)
C(7)	32(2)	20(1)	25(2)	3(1)	5(1)	-11(1)

Table S18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **W-S1**.

	x	y	z	U(eq)
H(4)	5847	8851	5666	28
H(5)	7129	9684	4368	28
H(6A)	3589	7002	4843	32
H(6B)	4721	7277	5847	32
H(6C)	5230	6479	5110	32
H(7A)	7302	8225	2134	38
H(7B)	8198	9077	2740	38
H(7C)	6480	9230	2155	38

Figure S6. X-ray structure of **W-2**



Experimental Summary

The single crystal X-ray diffraction studies were carried out on a Bruker APEX II Ultra diffractometer equipped with Mo K$_{\square}$ radiation ($\square$ = 0.71073). Crystals of the subject compound were used as received (grown from THF). A 0.040 x 0.020 x 0.015 mm yellow crystal was mounted on a Cryoloop with Paratone oil.

Data were collected in a nitrogen gas stream at 100(2) K using $\square$ and $\square$ scans. Crystal-to-detector distance was 50 mm using exposure time 30.0 s (depending on the detector 2$\square$ position) with a scan width of 0.60°. Data collection was 100.0% complete to 25.242° in $\square$. A total of 44892 reflections were collected. 3992 reflections were found to be symmetry independent, with a R_{int} of 0.0834. 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 S9.

Notes: Good data and refinement.

Nonmerohedral twin, HKL4 file format gives best refinement

Disorder on the THF

Table S19. Crystal data and structure refinement for **W-2** (CCDC 2224919).

Report date	2022-02-08	
Empirical formula	C38 H46 N2 O12 W2	
Molecular formula	2(W), 4(C O), 2(C11 H12 N O), 2(C2 H3 O2), 2(C4 H8 O)	
Formula weight	1090.47	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.9455(7) Å	□= 66.560(2)°.
	b = 10.6935(7) Å	□= 71.070(2)°.
	c = 12.0535(8) Å	□ = 71.049(2)°.
Volume	974.88(12) $Å^3$	
Z	1	
Density (calculated)	1.857 Mg/m^3	
Absorption coefficient	5.959 mm^{-1}	
F(000)	532	
Crystal size	0.04 x 0.02 x 0.015 mm^3	
Crystal color, habit	yellow plank	
Theta range for data collection	2.131 to 26.406°.	
Reflections collected	44892	
Independent reflections	3992 [R(int) = 0.0834]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.490 and 0.352	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3992 / 85 / 291	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0921	
R indices (all data)	R1 = 0.0545, wR2 = 0.0962	
Largest diff. peak and hole	1.988 and -1.639 $e.Å^{-3}$	

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **W-2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	7934(1)	7153(1)	439(1)	34(1)
O(1)	7898(7)	8566(6)	-2365(5)	54(1)
O(2)	4307(6)	7831(5)	377(5)	50(1)
O(3)	7836(7)	5962(5)	2422(4)	41(1)
O(4)	8385(6)	5064(4)	523(4)	35(1)
O(5)	9493(6)	3555(5)	-509(5)	40(1)
N(1)	7117(8)	5947(6)	4409(5)	46(2)
C(1)	8687(9)	9279(7)	-328(7)	40(2)
C(2)	8152(9)	8802(6)	977(7)	39(2)
C(3)	6511(9)	8722(7)	1471(7)	41(2)
C(4)	5943(10)	7975(7)	2825(7)	46(2)
C(5)	7051(9)	6554(7)	3208(6)	41(2)
C(6)	8050(10)	4605(8)	4994(6)	43(2)
C(7)	9321(10)	3832(9)	4348(7)	53(2)
C(8)	10146(10)	2552(10)	4991(8)	61(2)
C(9)	9695(11)	2034(10)	6254(7)	58(2)
C(10)	8466(12)	2807(10)	6891(8)	62(2)
C(11)	7626(11)	4097(9)	6270(7)	53(2)
C(12)	7977(9)	8015(7)	-1327(7)	39(2)
C(13)	5656(10)	7556(7)	444(6)	40(2)
C(14)	8415(8)	4551(7)	-274(6)	35(1)
C(15)	7096(9)	5137(8)	-974(7)	44(2)
O(1S)	5214(15)	7264(13)	6130(11)	57(3)
C(1S)	4980(20)	8410(20)	6480(20)	72(6)
C(2S)	3410(20)	8470(40)	7400(30)	117(10)
C(3S)	2451(19)	7840(20)	7078(19)	63(5)
C(4S)	3750(20)	6780(20)	6620(20)	111(9)
O(1T)	4758(15)	7852(17)	5709(13)	47(4)
C(1T)	4740(20)	7930(40)	6830(20)	90(11)

C(2T)	3010(30)	8370(30)	7430(20)	66(6)
C(3T)	2060(20)	8000(40)	6870(20)	70(7)
C(4T)	3121(19)	8130(20)	5625(16)	56(5)

Table S21. Bond lengths [Å] and angles [°] for **W-2**.

O(1)-C(12)	1.167(9)
O(2)-C(13)	1.168(9)
O(3)-C(5)	1.245(8)
O(4)-C(14)	1.271(8)
O(5)-C(14)	1.242(8)
N(1)-H(1)	0.8800
N(1)-C(5)	1.343(9)
N(1)-C(6)	1.433(10)
C(1)-H(1A)	0.9500
C(1)-H(1B)	0.9500
C(1)-C(2)	1.412(10)
C(2)-H(2)	0.9500
C(2)-C(3)	1.411(11)
C(3)-H(3)	0.9500
C(3)-C(4)	1.499(10)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(4)-C(5)	1.505(10)
C(6)-C(7)	1.382(11)
C(6)-C(11)	1.376(10)
C(7)-H(7)	0.9500
C(7)-C(8)	1.374(12)
C(8)-H(8)	0.9500
C(8)-C(9)	1.366(11)
C(9)-H(9)	0.9500
C(9)-C(10)	1.360(13)
C(10)-H(10)	0.9500
C(10)-C(11)	1.378(12)
C(11)-H(11)	0.9500
C(14)-C(15)	1.497(10)
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800

C(15)-H(15C)	0.9800
O(1S)-C(1S)	1.384(15)
O(1S)-C(4S)	1.425(15)
C(1S)-H(1SA)	0.9900
C(1S)-H(1SB)	0.9900
C(1S)-C(2S)	1.486(12)
C(2S)-H(2SA)	0.9900
C(2S)-H(2SB)	0.9900
C(2S)-C(3S)	1.460(12)
C(3S)-H(3SA)	0.9900
C(3S)-H(3SB)	0.9900
C(3S)-C(4S)	1.473(13)
C(4S)-H(4SA)	0.9900
C(4S)-H(4SB)	0.9900
O(1T)-C(1T)	1.384(15)
O(1T)-C(4T)	1.424(15)
C(1T)-H(1TA)	0.9900
C(1T)-H(1TB)	0.9900
C(1T)-C(2T)	1.483(12)
C(2T)-H(2TA)	0.9900
C(2T)-H(2TB)	0.9900
C(2T)-C(3T)	1.459(12)
C(3T)-H(3TA)	0.9900
C(3T)-H(3TB)	0.9900
C(3T)-C(4T)	1.471(13)
C(4T)-H(4TA)	0.9900
C(4T)-H(4TB)	0.9900

C(5)-N(1)-H(1)	115.8
C(5)-N(1)-C(6)	128.4(6)

C(6)-N(1)-H(1)	115.8
H(1A)-C(1)-H(1B)	120.0
C(2)-C(1)-H(1A)	120.0
C(2)-C(1)-H(1B)	120.0
C(1)-C(2)-H(2)	121.2
C(1)-C(2)-C(3)	117.6(7)
C(3)-C(2)-H(2)	121.2
C(2)-C(3)-H(3)	119.9
C(2)-C(3)-C(4)	120.1(7)
C(4)-C(3)-H(3)	119.9
C(3)-C(4)-H(4A)	109.7
C(3)-C(4)-H(4B)	109.7
C(3)-C(4)-C(5)	110.0(6)
H(4A)-C(4)-H(4B)	108.2
C(5)-C(4)-H(4A)	109.7
C(5)-C(4)-H(4B)	109.7
O(3)-C(5)-N(1)	122.1(7)
O(3)-C(5)-C(4)	119.6(6)
N(1)-C(5)-C(4)	118.3(6)
C(7)-C(6)-N(1)	123.5(6)
C(11)-C(6)-N(1)	116.4(7)
C(11)-C(6)-C(7)	120.1(7)
C(6)-C(7)-H(7)	120.3
C(8)-C(7)-C(6)	119.4(7)
C(8)-C(7)-H(7)	120.3
C(7)-C(8)-H(8)	119.8
C(9)-C(8)-C(7)	120.5(8)
C(9)-C(8)-H(8)	119.8
C(8)-C(9)-H(9)	119.9
C(10)-C(9)-C(8)	120.1(8)
C(10)-C(9)-H(9)	119.9
C(9)-C(10)-H(10)	119.7
C(9)-C(10)-C(11)	120.5(8)
C(11)-C(10)-H(10)	119.7

C(6)-C(11)-H(11)	120.3
C(10)-C(11)-C(6)	119.4(8)
C(10)-C(11)-H(11)	120.3
O(4)-C(14)-C(15)	120.1(6)
O(5)-C(14)-O(4)	123.3(6)
O(5)-C(14)-C(15)	116.5(6)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(1S)-O(1S)-C(4S)	108.2(9)
O(1S)-C(1S)-H(1SA)	110.6
O(1S)-C(1S)-H(1SB)	110.6
O(1S)-C(1S)-C(2S)	105.8(11)
H(1SA)-C(1S)-H(1SB)	108.7
C(2S)-C(1S)-H(1SA)	110.6
C(2S)-C(1S)-H(1SB)	110.6
C(1S)-C(2S)-H(2SA)	110.6
C(1S)-C(2S)-H(2SB)	110.6
H(2SA)-C(2S)-H(2SB)	108.7
C(3S)-C(2S)-C(1S)	105.6(10)
C(3S)-C(2S)-H(2SA)	110.6
C(3S)-C(2S)-H(2SB)	110.6
C(2S)-C(3S)-H(3SA)	111.8
C(2S)-C(3S)-H(3SB)	111.8
C(2S)-C(3S)-C(4S)	100.1(13)
H(3SA)-C(3S)-H(3SB)	109.5
C(4S)-C(3S)-H(3SA)	111.8
C(4S)-C(3S)-H(3SB)	111.8
O(1S)-C(4S)-C(3S)	108.6(10)
O(1S)-C(4S)-H(4SA)	110.0
O(1S)-C(4S)-H(4SB)	110.0

C(3S)-C(4S)-H(4SA)	110.0
C(3S)-C(4S)-H(4SB)	110.0
H(4SA)-C(4S)-H(4SB)	108.4
C(1T)-O(1T)-C(4T)	108.0(9)
O(1T)-C(1T)-H(1TA)	110.4
O(1T)-C(1T)-H(1TB)	110.4
O(1T)-C(1T)-C(2T)	106.7(11)
H(1TA)-C(1T)-H(1TB)	108.6
C(2T)-C(1T)-H(1TA)	110.4
C(2T)-C(1T)-H(1TB)	110.4
C(1T)-C(2T)-H(2TA)	110.4
C(1T)-C(2T)-H(2TB)	110.4
H(2TA)-C(2T)-H(2TB)	108.6
C(3T)-C(2T)-C(1T)	106.4(11)
C(3T)-C(2T)-H(2TA)	110.4
C(3T)-C(2T)-H(2TB)	110.4
C(2T)-C(3T)-H(3TA)	111.7
C(2T)-C(3T)-H(3TB)	111.7
C(2T)-C(3T)-C(4T)	100.5(13)
H(3TA)-C(3T)-H(3TB)	109.4
C(4T)-C(3T)-H(3TA)	111.7
C(4T)-C(3T)-H(3TB)	111.7
O(1T)-C(4T)-C(3T)	108.8(11)
O(1T)-C(4T)-H(4TA)	109.9
O(1T)-C(4T)-H(4TB)	109.9
C(3T)-C(4T)-H(4TA)	109.9
C(3T)-C(4T)-H(4TB)	109.9
H(4TA)-C(4T)-H(4TB)	10

Table S22. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **W-2**. 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}

W(1)	36(1)	28(1)	35(1)	-12(1)	-7(1)	-2(1)
O(1)	56(4)	63(4)	42(3)	-8(3)	-10(3)	-24(3)
O(2)	32(3)	42(3)	70(4)	-20(3)	-13(3)	2(2)
O(3)	62(3)	31(2)	25(2)	-11(2)	-7(2)	-7(2)
O(4)	38(3)	30(2)	36(2)	-13(2)	-9(2)	-4(2)
O(5)	37(3)	35(2)	53(3)	-24(2)	-11(2)	-1(2)
N(1)	61(4)	44(3)	31(3)	-16(3)	1(3)	-16(3)
C(1)	43(4)	37(4)	43(4)	-13(3)	-7(3)	-15(3)
C(2)	50(4)	26(3)	44(4)	-18(3)	-11(3)	-3(3)
C(3)	44(4)	29(3)	46(4)	-12(3)	-7(3)	-8(3)
C(4)	48(4)	36(4)	48(4)	-21(3)	-4(3)	-1(3)
C(5)	50(4)	38(4)	36(4)	-16(3)	-3(3)	-15(3)
C(6)	53(5)	46(4)	31(4)	-8(3)	-9(3)	-18(3)
C(7)	46(5)	71(5)	30(4)	-9(4)	-7(3)	-10(4)
C(8)	43(5)	78(6)	47(5)	-20(4)	-8(4)	3(4)
C(9)	60(5)	67(5)	32(4)	-5(4)	-9(4)	-8(4)
C(10)	76(6)	71(6)	36(4)	-8(4)	-11(4)	-23(5)
C(11)	65(6)	52(5)	38(4)	-12(3)	-3(4)	-18(4)
C(12)	40(4)	41(4)	40(4)	-16(3)	-6(3)	-13(3)
C(13)	49(5)	31(3)	31(4)	-9(3)	-2(3)	-6(3)
C(14)	36(4)	33(3)	37(4)	-15(3)	-3(3)	-9(3)
C(15)	37(4)	48(4)	54(5)	-28(4)	-12(3)	-3(3)
O(1S)	59(6)	60(7)	56(7)	-27(6)	5(5)	-26(5)
C(1S)	49(7)	76(9)	109(14)	-58(10)	2(7)	-19(6)
C(2S)	65(9)	200(20)	151(16)	-138(17)	28(9)	-56(10)
C(3S)	56(6)	78(10)	63(10)	-31(9)	3(6)	-29(6)
C(4S)	71(7)	108(11)	170(20)	-94(14)	38(9)	-51(7)
O(1T)	47(6)	53(9)	40(6)	-23(6)	-15(4)	6(5)
C(1T)	58(8)	170(30)	59(10)	-71(16)	-11(6)	-5(9)
C(2T)	62(10)	88(16)	47(8)	-35(10)	-3(6)	-7(9)
C(3T)	55(7)	95(18)	59(9)	-42(10)	-5(6)	-4(9)
C(4T)	45(6)	69(13)	53(8)	-33(8)	-14(5)	5(6)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **W-2**.

	x	y	z	U(eq)
H(1)	6508	6437	4900	55
H(1A)	7950	9531	-839	48
H(1B)	9783	9346	-694	48
H(2)	8871	8544	1503	47
H(3)	5765	9142	945	49
H(4A)	4824	7871	2988	55
H(4B)	5932	8530	3318	55
H(7)	9622	4182	3468	63
H(8)	11035	2025	4553	73
H(9)	10242	1131	6689	70
H(10)	8185	2454	7772	75
H(11)	6761	4630	6718	64
H(15A)	6162	5697	-549	66
H(15B)	6768	4368	-1013	66
H(15C)	7494	5729	-1817	66
H(1SA)	4952	9276	5755	87
H(1SB)	5872	8294	6859	87
H(2SA)	3568	7944	8254	140
H(2SB)	2853	9455	7347	140
H(3SA)	1880	8530	6423	76
H(3SB)	1655	7414	7812	76
H(4SA)	3894	5883	7313	134
H(4SB)	3460	6619	5972	134
H(1TA)	5350	8614	6703	108
H(1TB)	5234	7002	7365	108
H(2TA)	2810	7879	8335	79
H(2TB)	2714	9390	7276	79
H(3TA)	991	8661	6831	84
H(3TB)	1904	7035	7321	84

H(4TA)	3003	7463	5300	67
H(4TB)	2814	9091	5050	67

3. NMR Spectra

Figure S7: ^{1}H NMR of **1g**. 500 MHz, $CDCl_3$, 25 °C

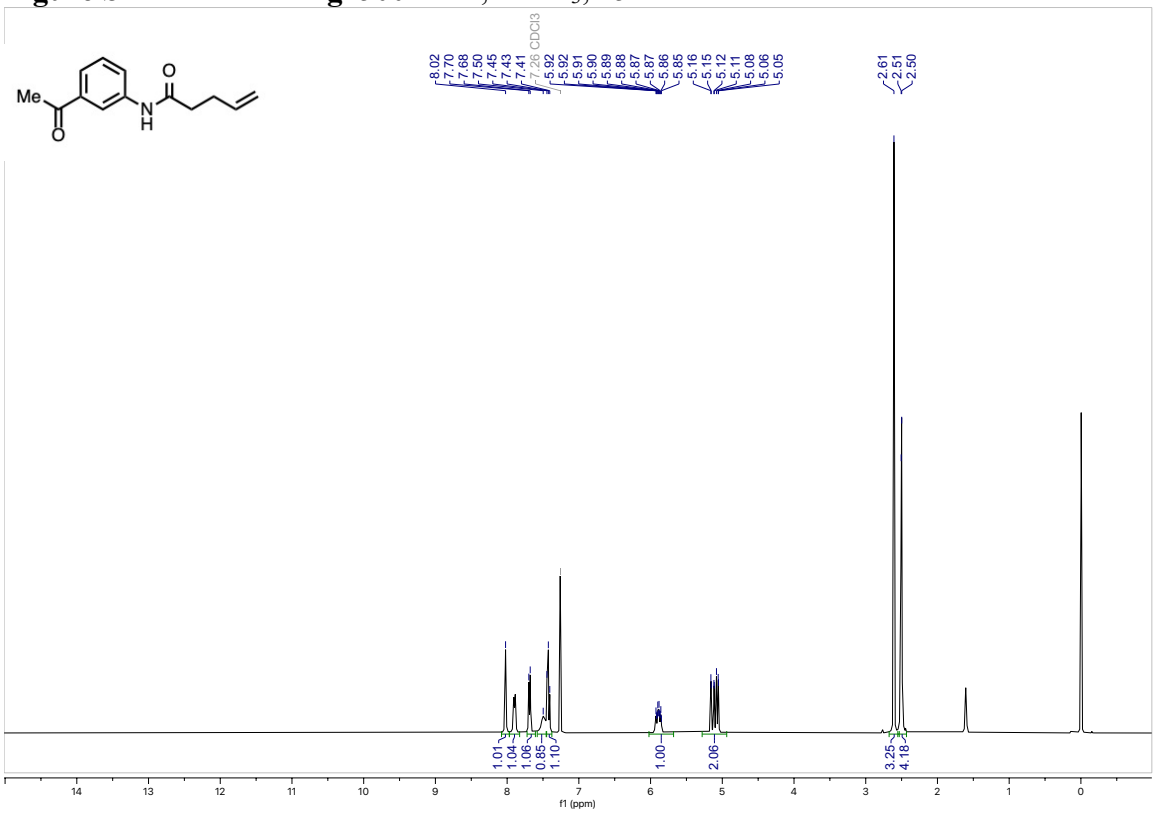


Figure S8: ^{13}C NMR of **1g**. 126 MHz, $CDCl_3$, 25 °C

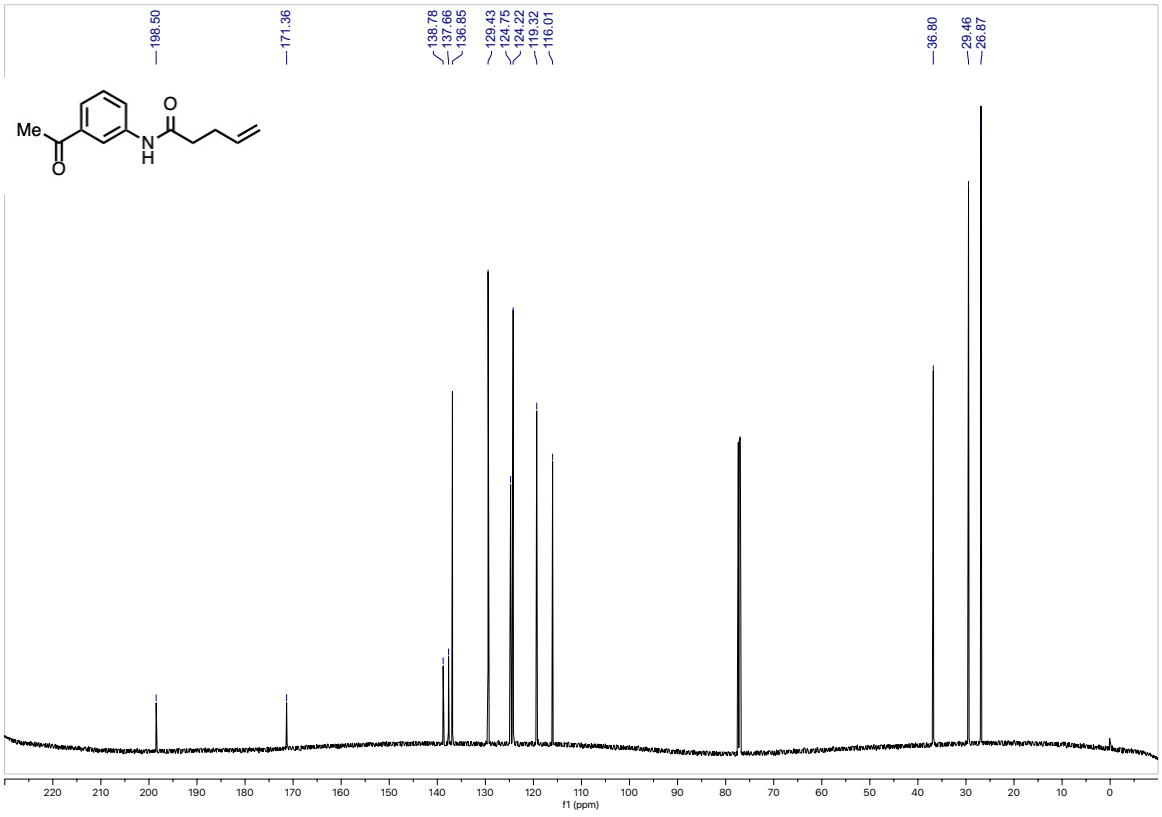


Figure S9: ^{1}H NMR of **1k**. 400 MHz, $CDCl_3$, 25 °C

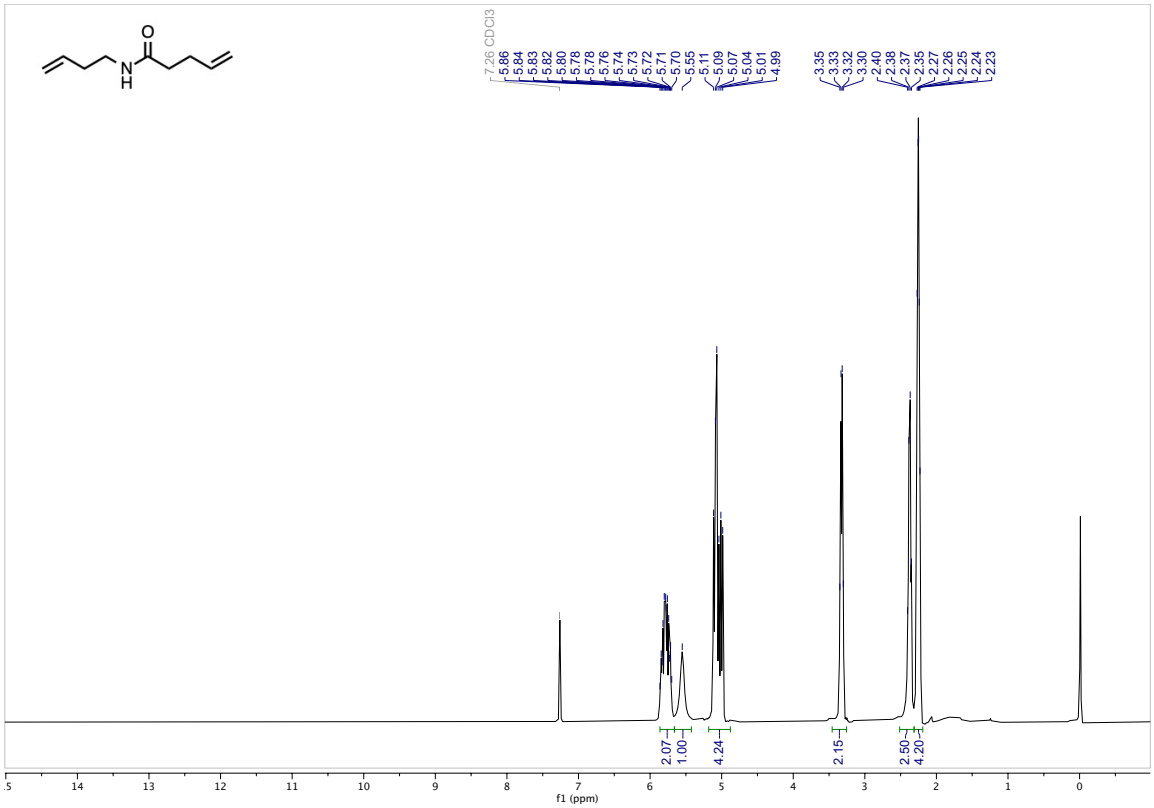


Figure S10: ^{13}C NMR of **1k**. 126 MHz, $CDCl_3$, 25 °C

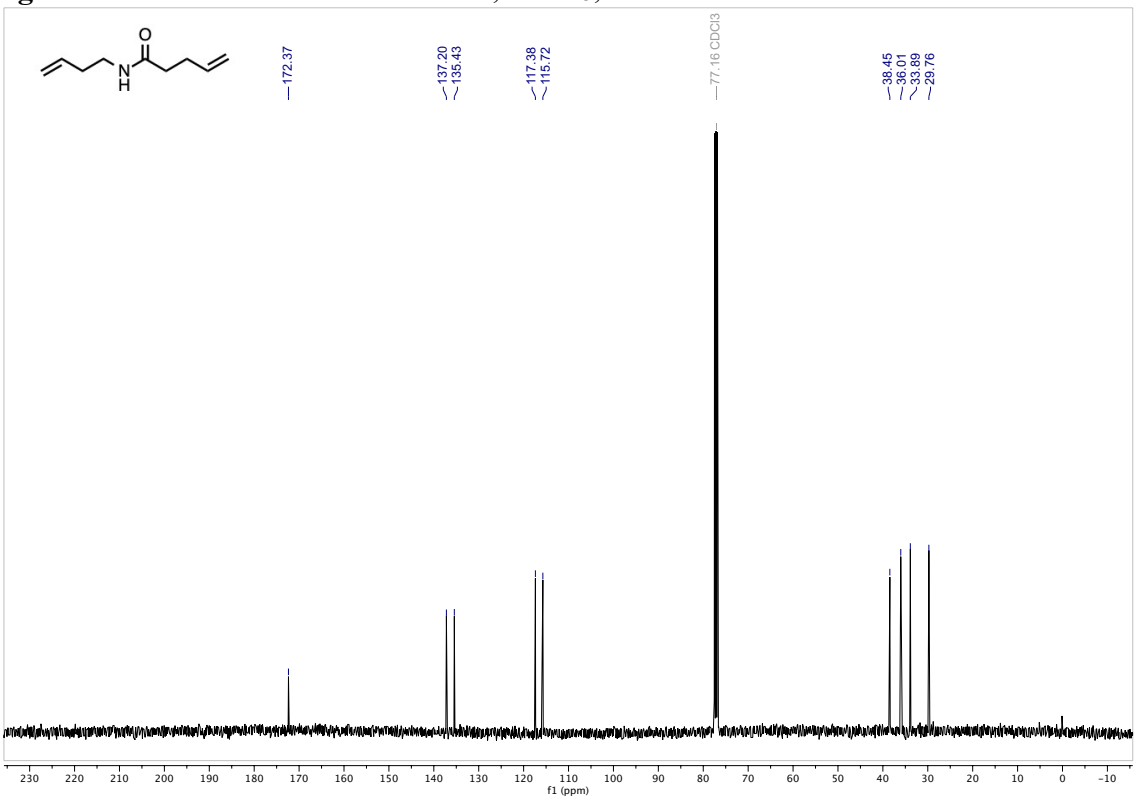


Figure S11: ^{1}H NMR of **2a**. 600 MHz, $CDCl_3$, 25 °C

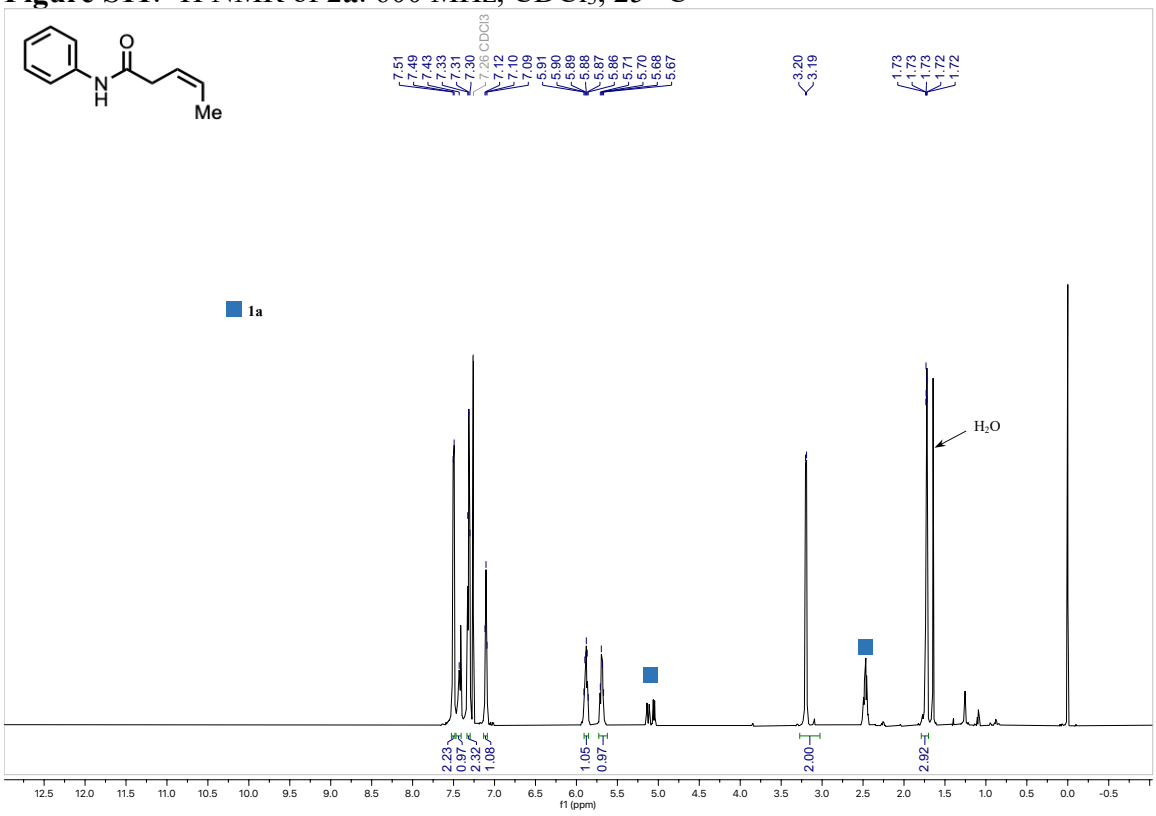


Figure S12: ^{13}C NMR of **2a**. 151 MHz, $CDCl_3$, 25 °C

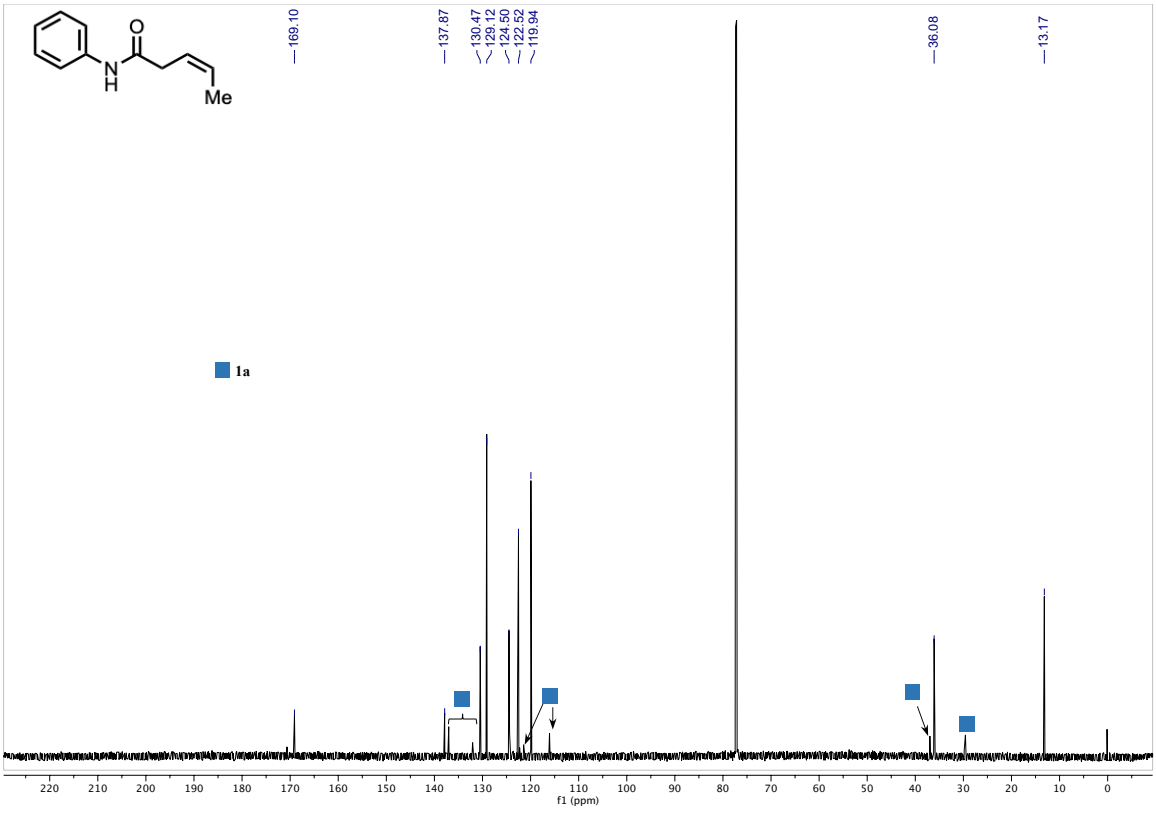


Figure S13: ^{1}H NMR of **3a**. 600 MHz, $CDCl_3$, 25 °C

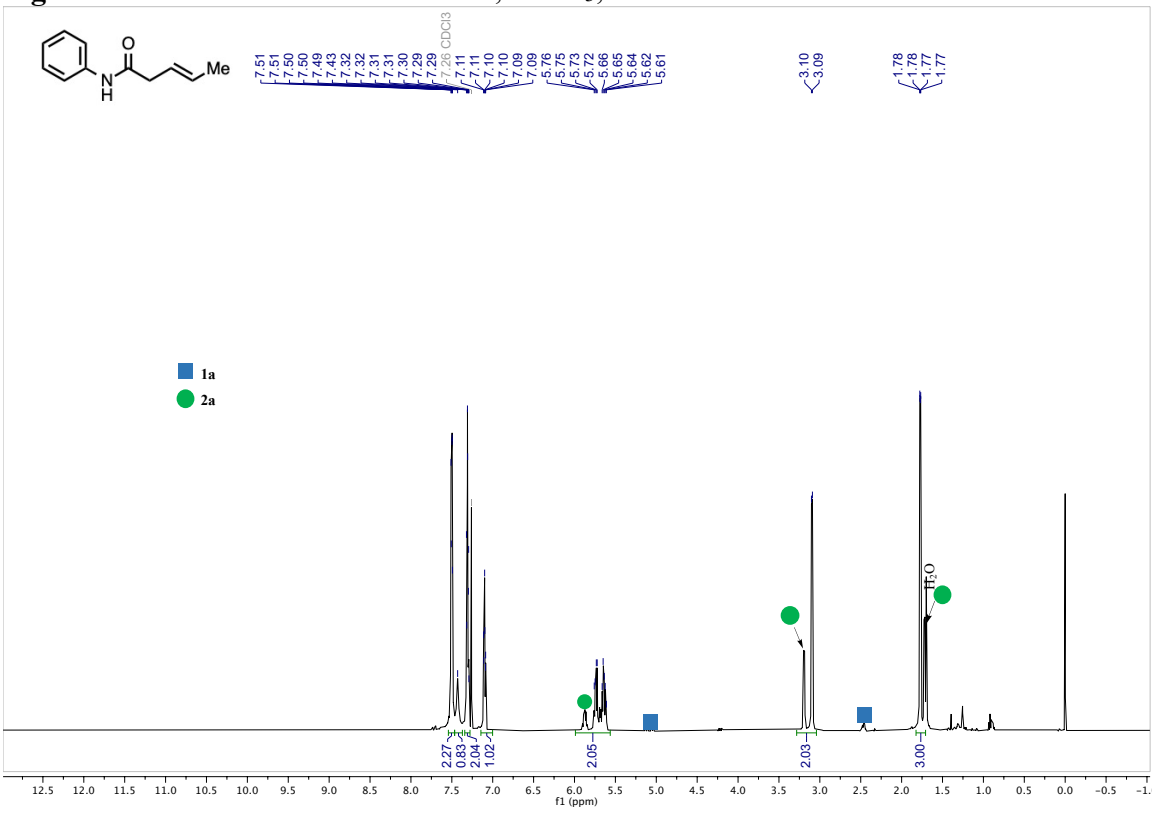


Figure S14: ^{13}C NMR of **3a**. 151 MHz, $CDCl_3$, 25 °C

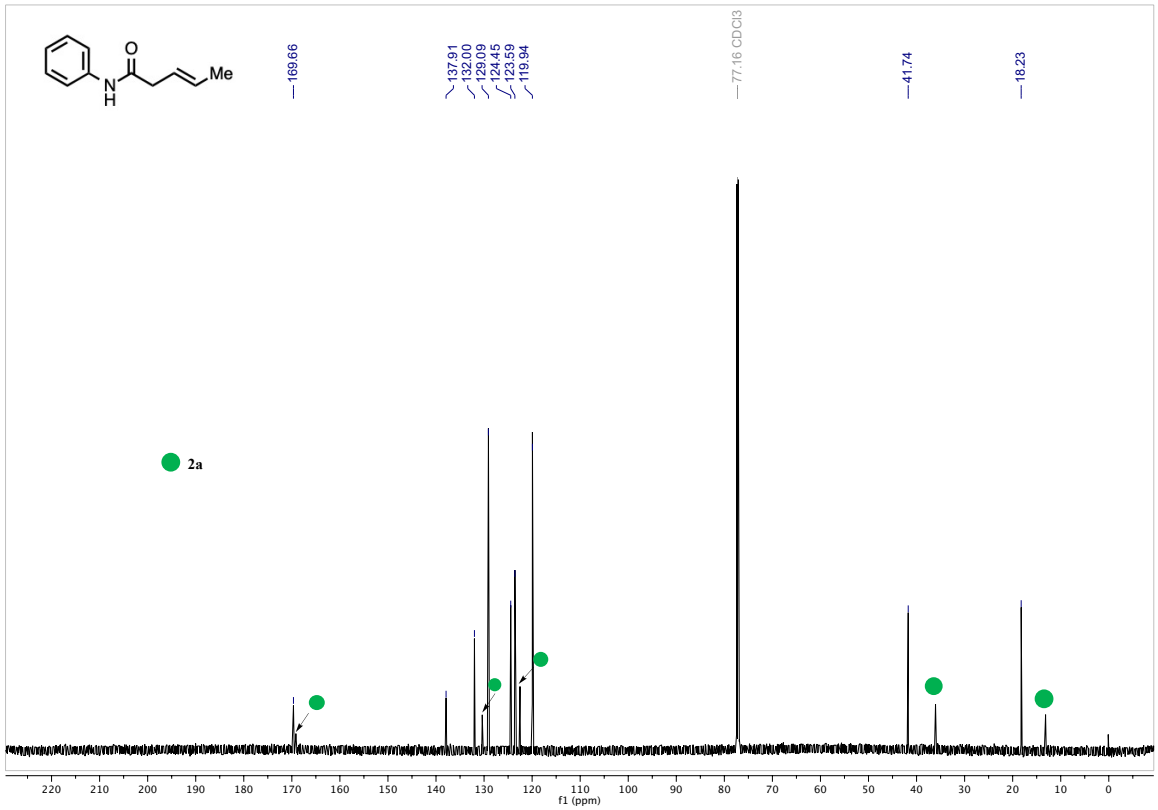


Figure S15: SFC Trace of separation of **3a** from **2a**.

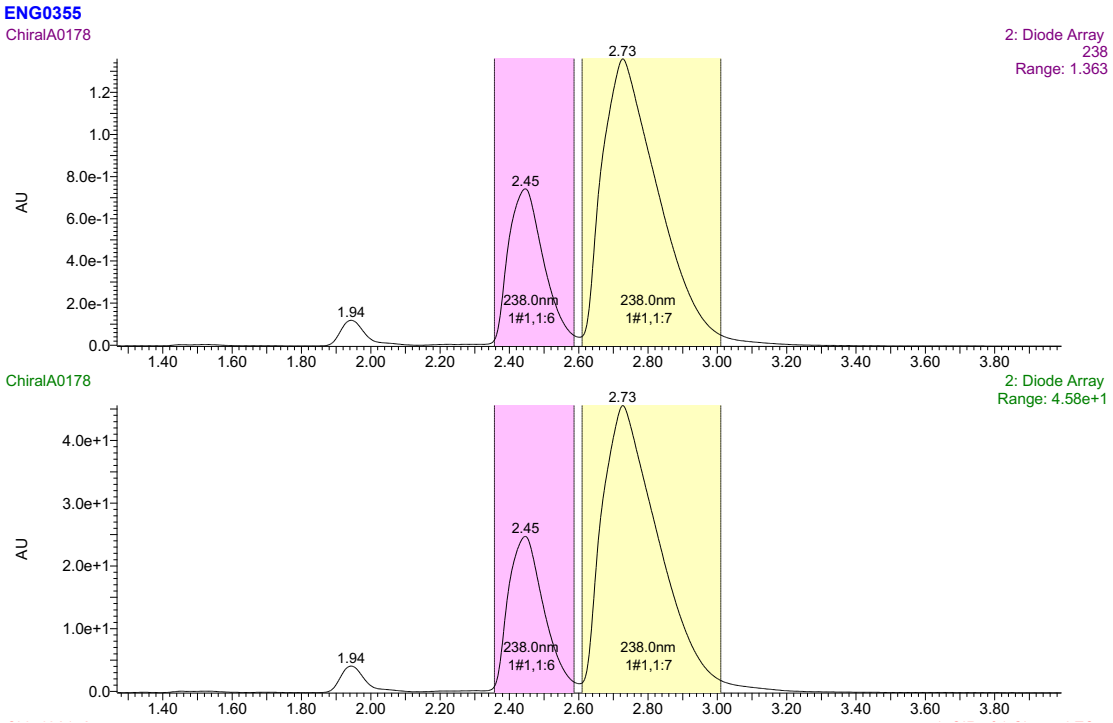


Figure S16: ^{1}H NMR of **3a** separated from **2a** by SFC. 400 MHz, $CDCl_3$, 25 °C

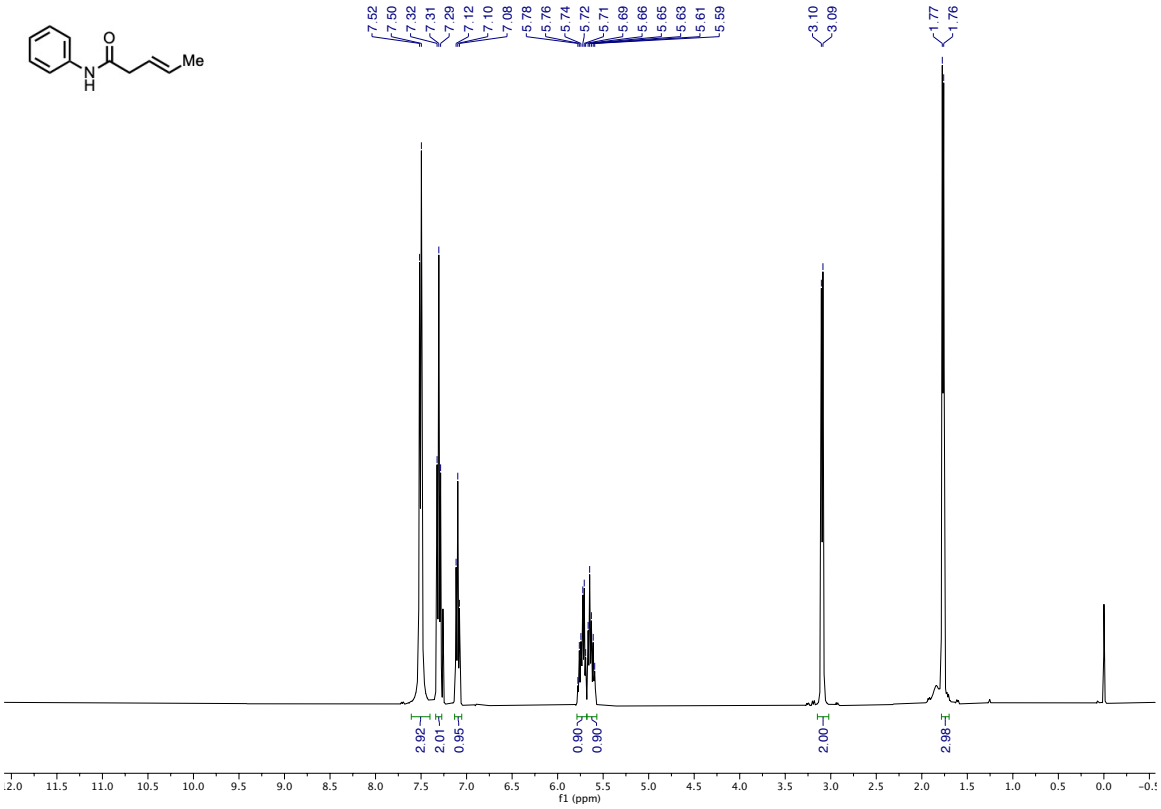


Figure S17: ^{1}H NMR of **2a** separated from **3a** by SFC. 400 MHz, $CDCl_3$, 25 °C

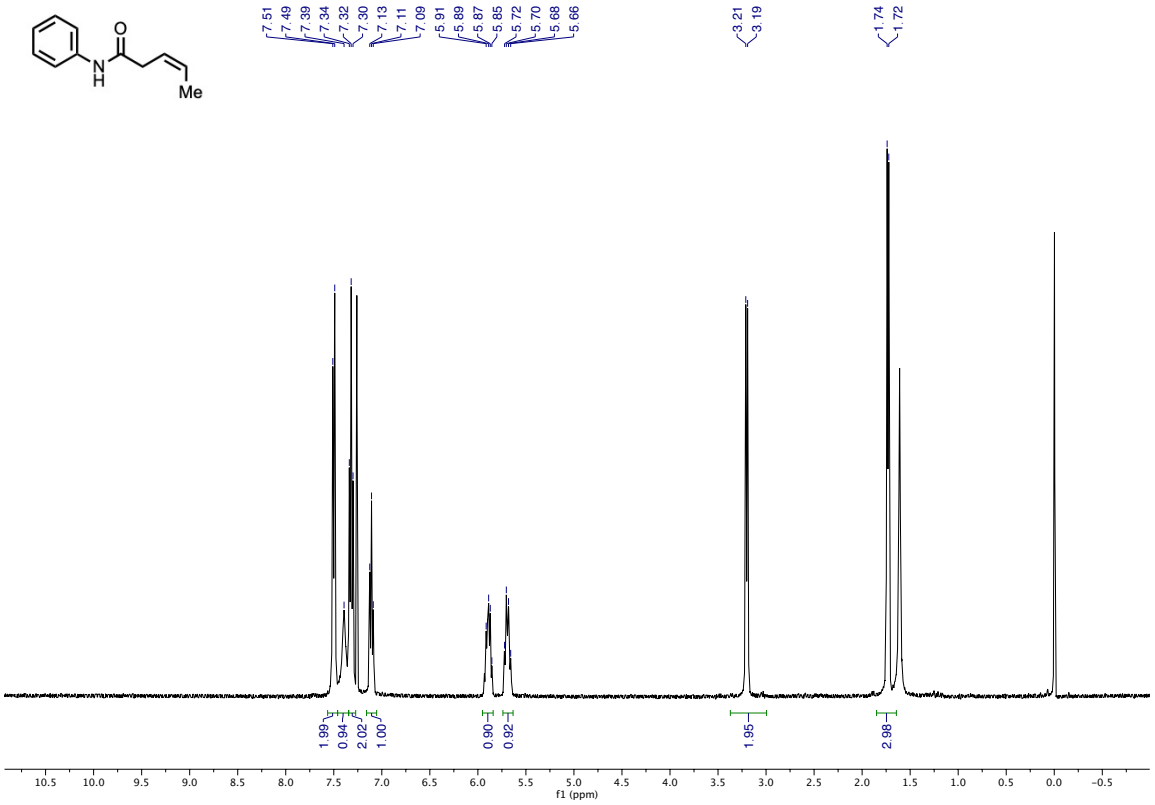


Figure S18: ^{1}H NMR of **2b**. 600 MHz, $CDCl_3$, 25 °C

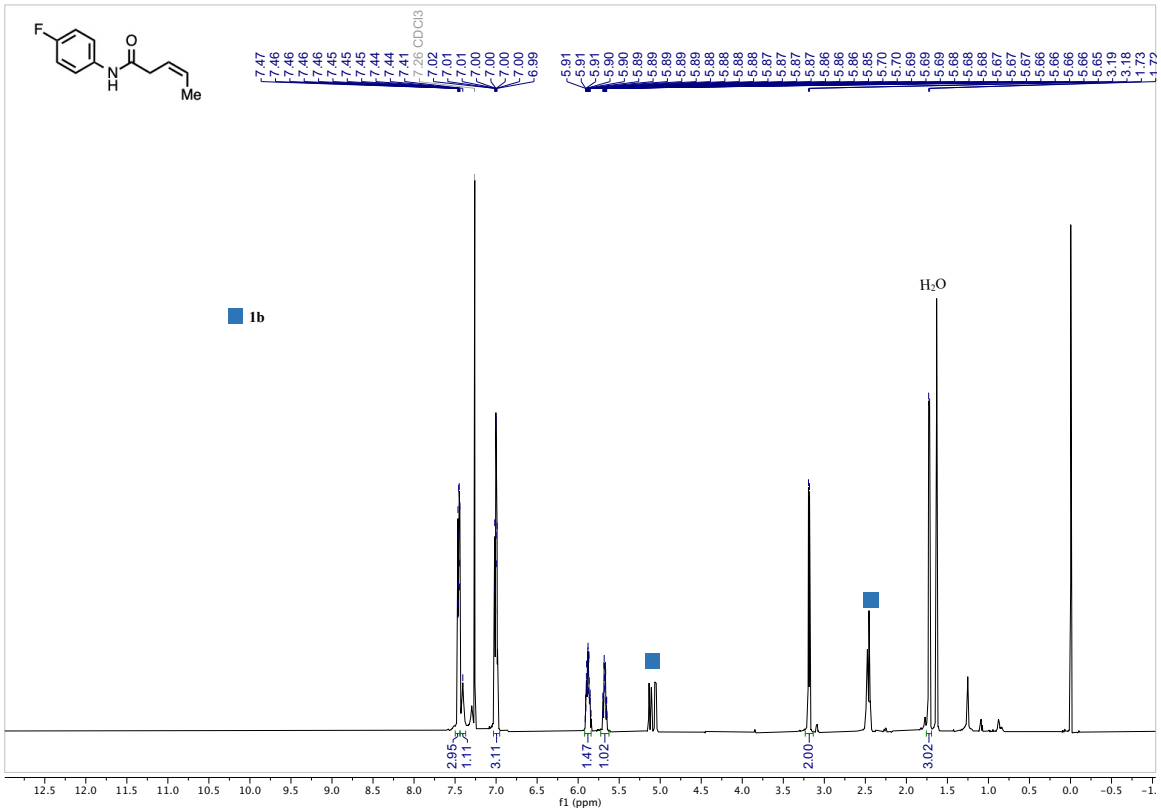


Figure S19: ^{13}C NMR of **2b**. 151 MHz, $CDCl_3$, 25 °C

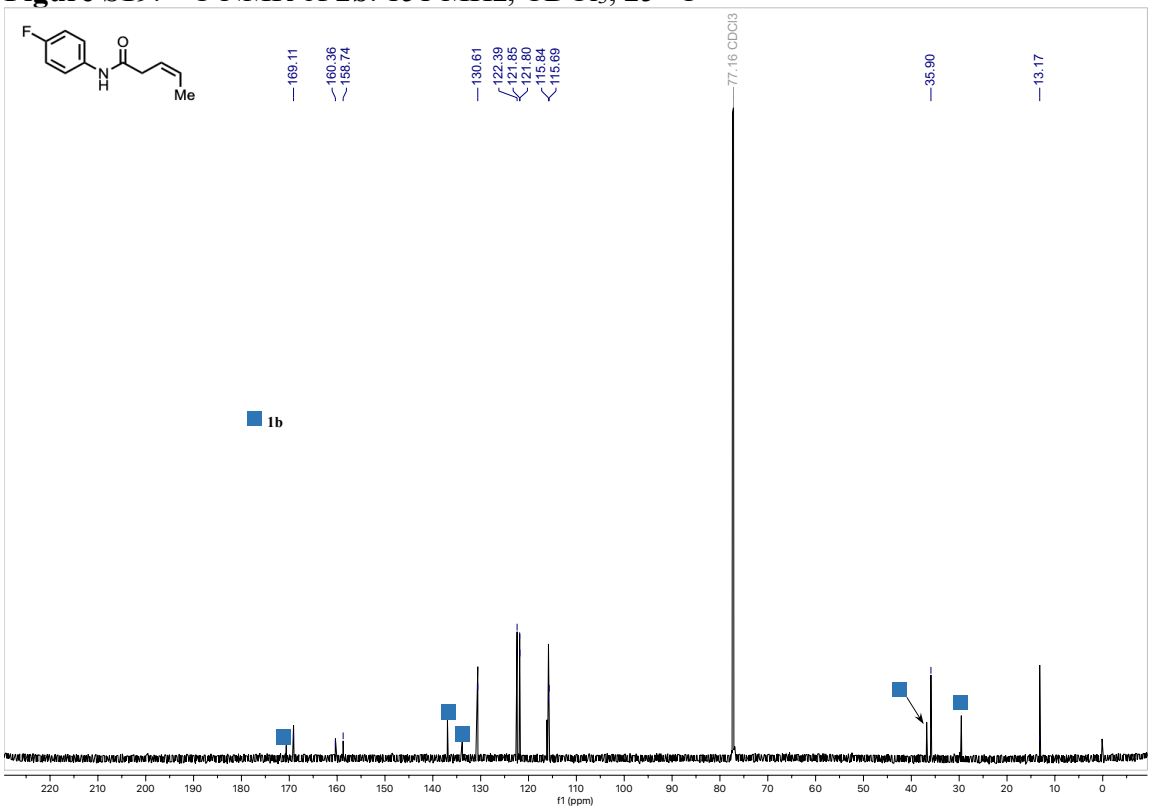


Figure S20: ^{19}F NMR of **2b**. 376 MHz, $CDCl_3$, 25 °C

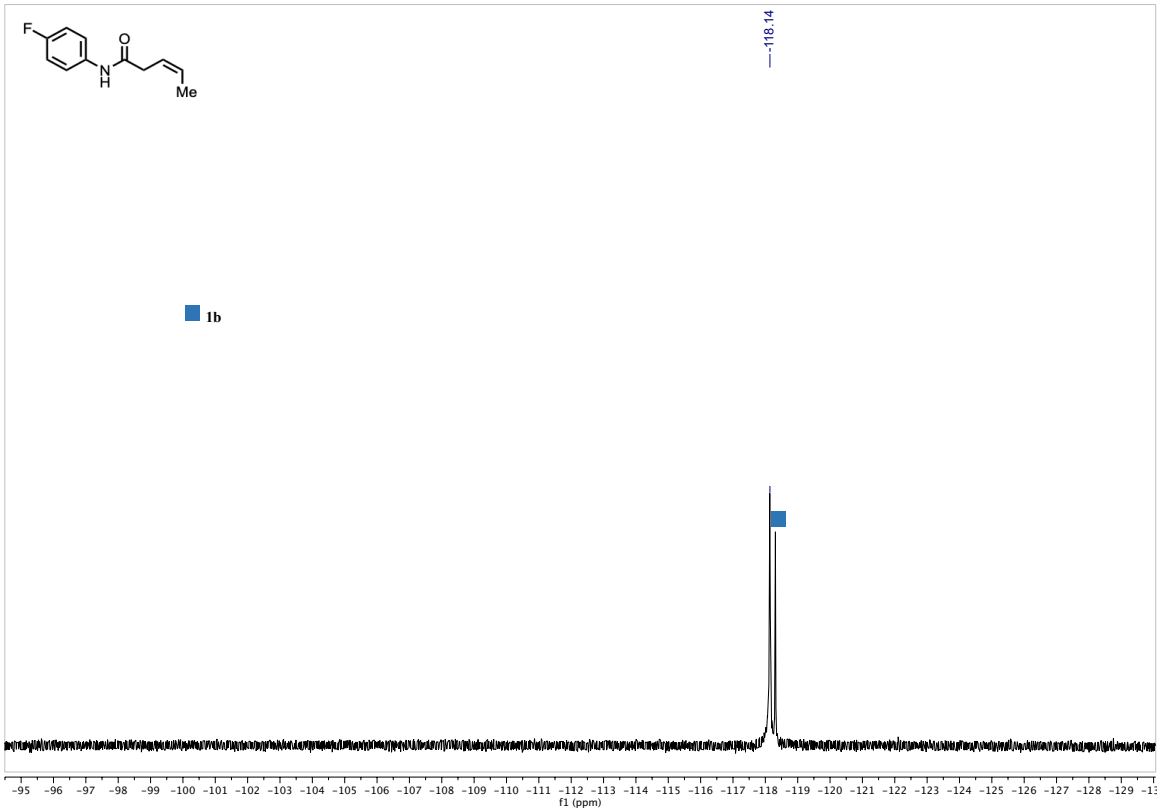


Figure S21: ^{1}H NMR of **3b**. 600 MHz, $CDCl_3$, 25 °C

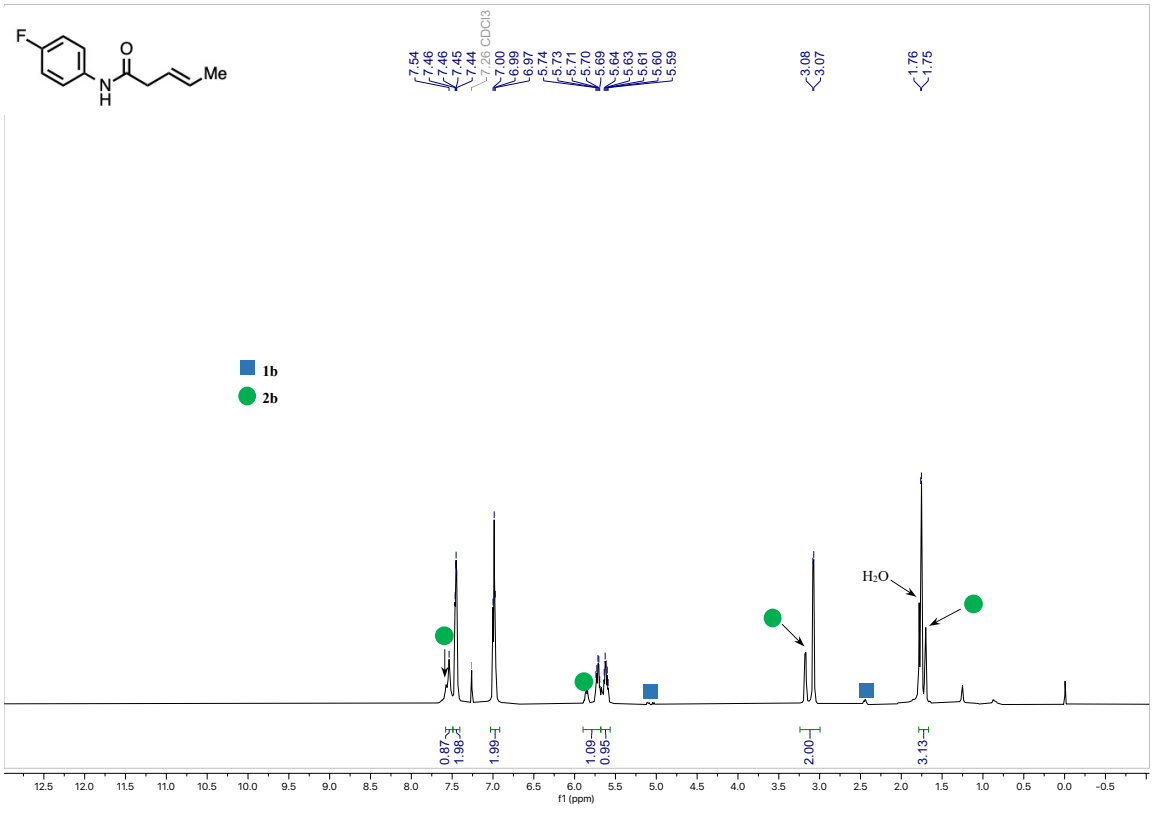


Figure S22: ^{13}C NMR of **3b**. 151 MHz, $CDCl_3$, 25 °C

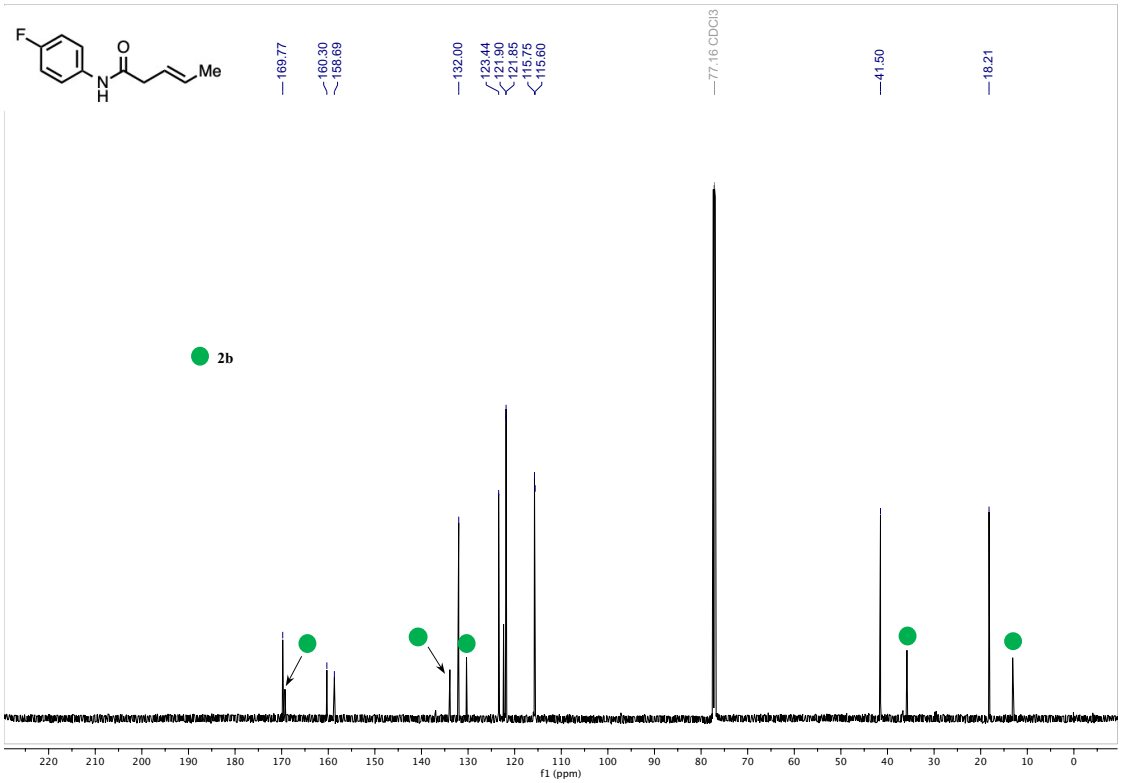


Figure S23: ^{19}F NMR of **3b**. 376 MHz, $CDCl_3$, 25 °C

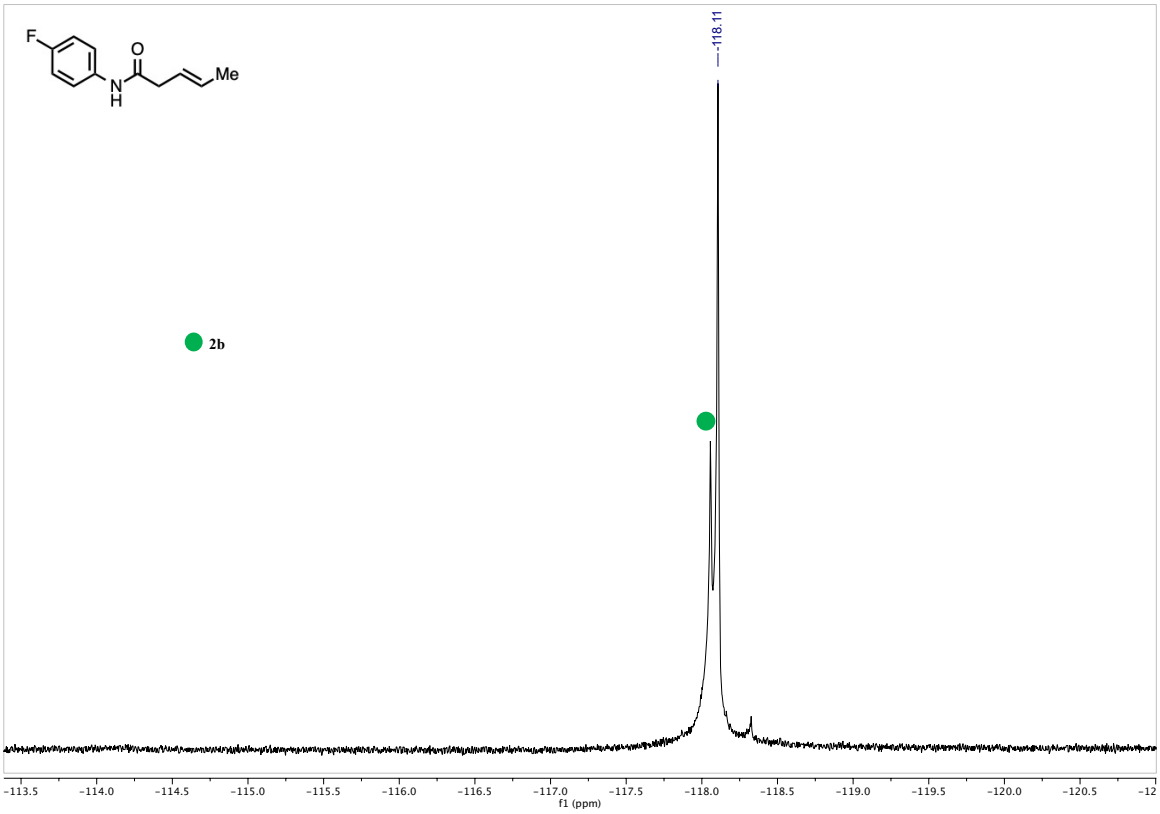


Figure S24: ^{1}H NMR of **2c**. 600 MHz, $CDCl_3$, 25 °C

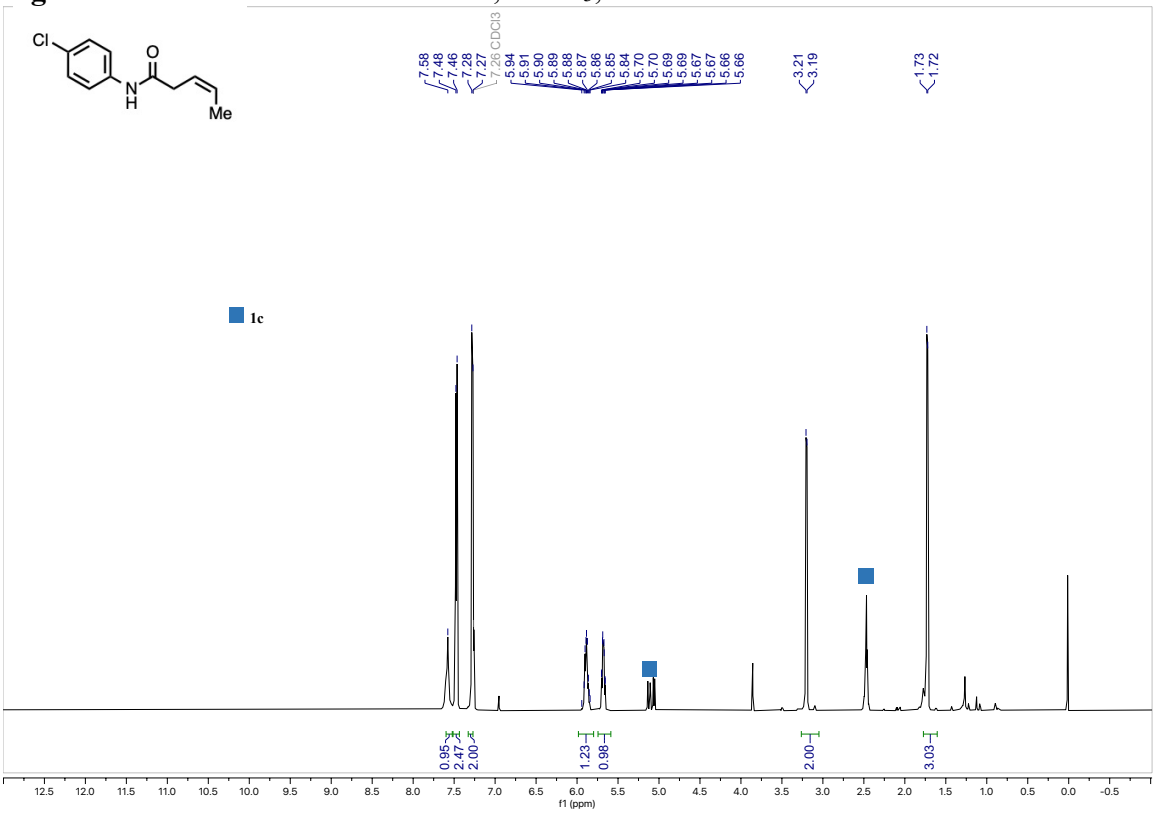


Figure S25: ^{13}C NMR of **2c**. 151 MHz, $CDCl_3$, 25 °C

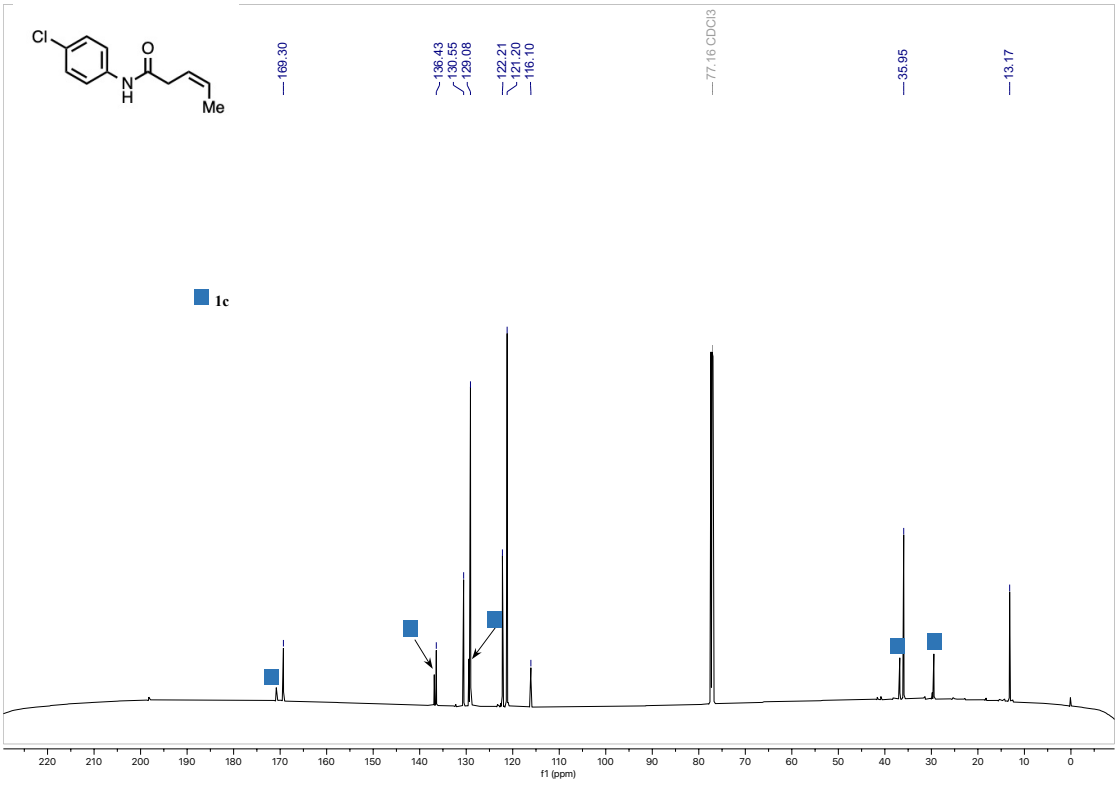


Figure S26: ^{1}H NMR of **3c**. 600 MHz, $CDCl_3$, 25 °C

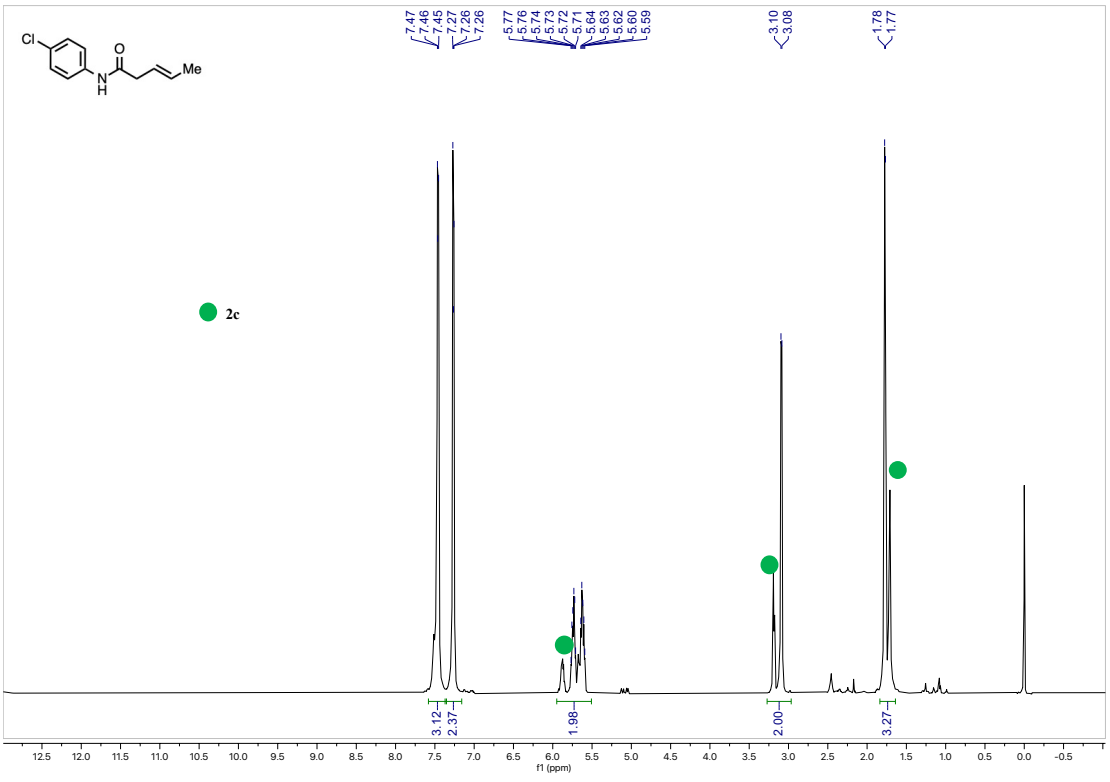


Figure S27: ^{13}C NMR of **3c**. 151 MHz, $CDCl_3$, 25 °C

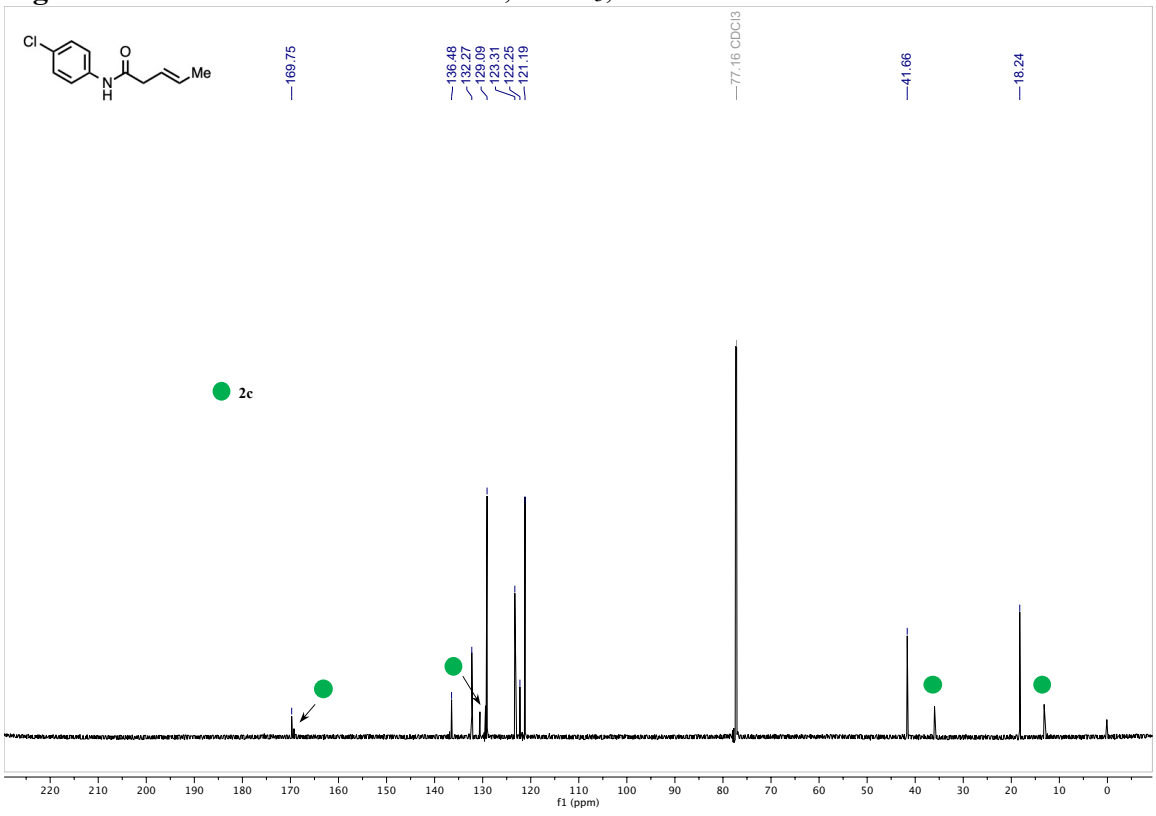


Figure S28: ^{1}H NMR of **2d**. 600 MHz, $CDCl_3$, 25 °C

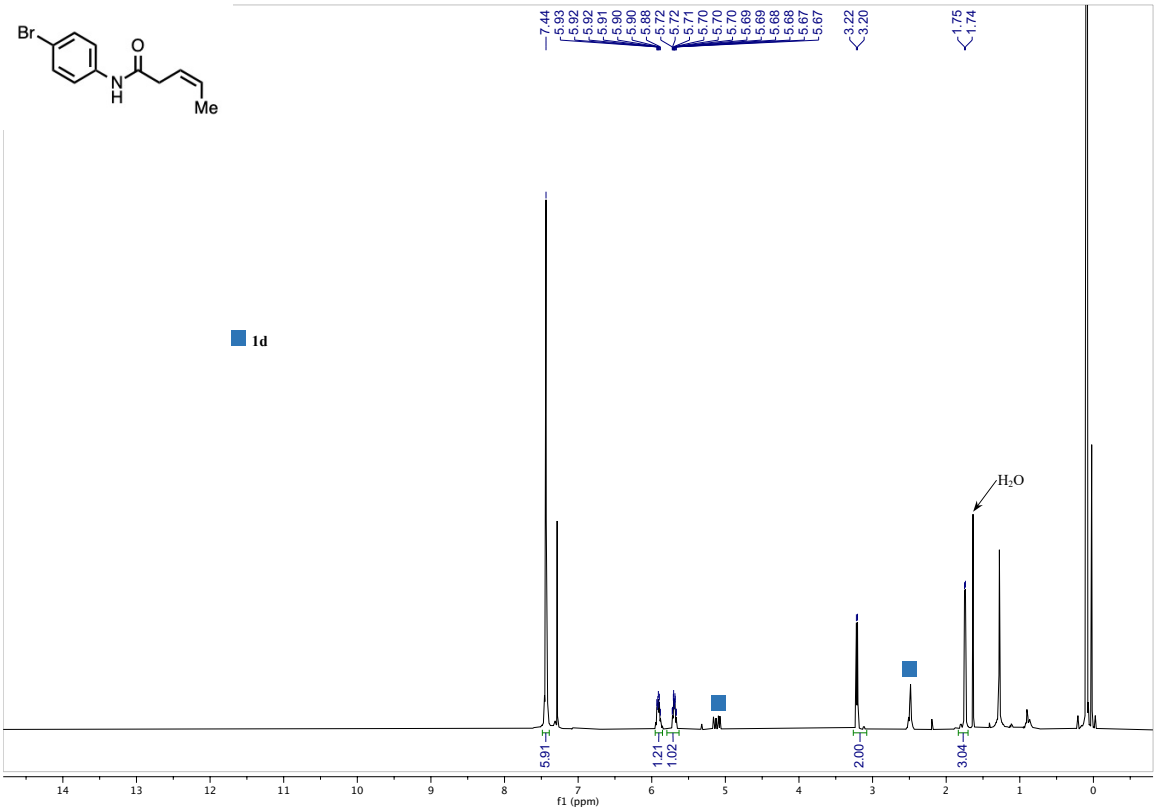


Figure S29: ^{13}C NMR of **2d**. 151 MHz, $CDCl_3$, 25 °C

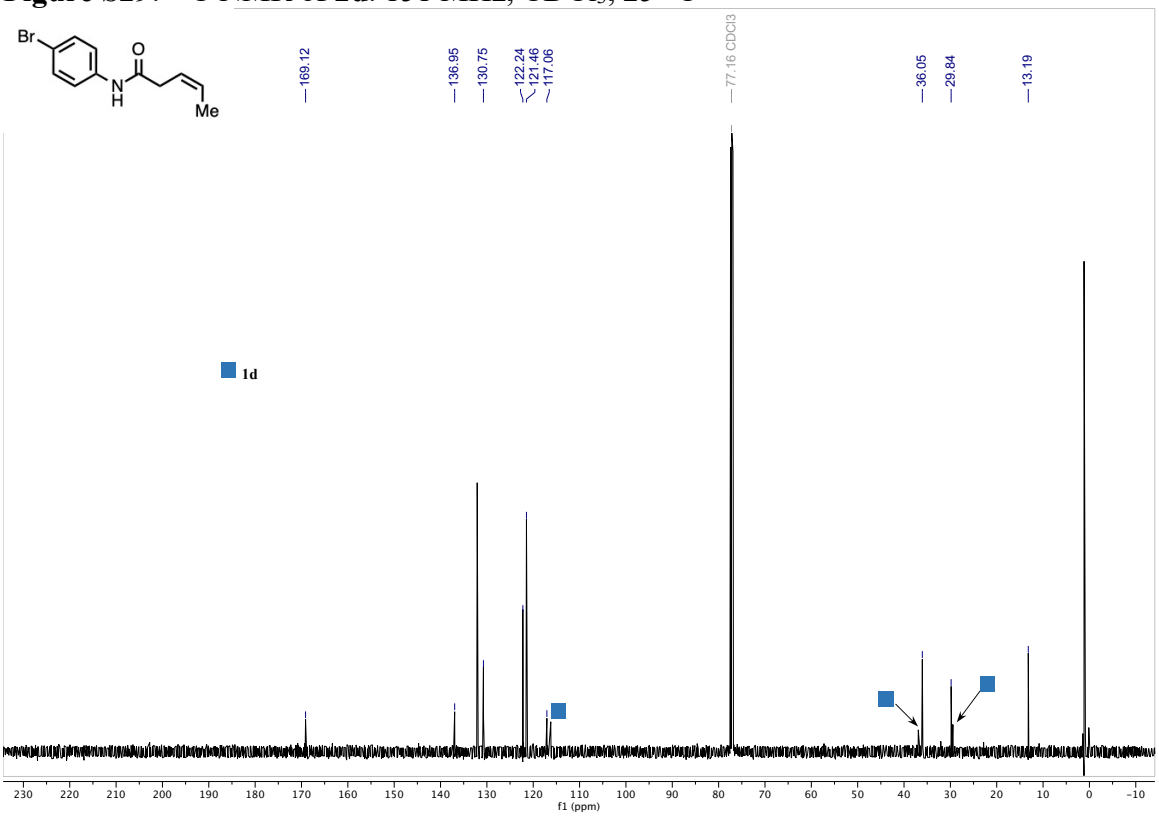


Figure S30: ^{1}H NMR of **3d**. 600 MHz, $CDCl_3$, 25 °C

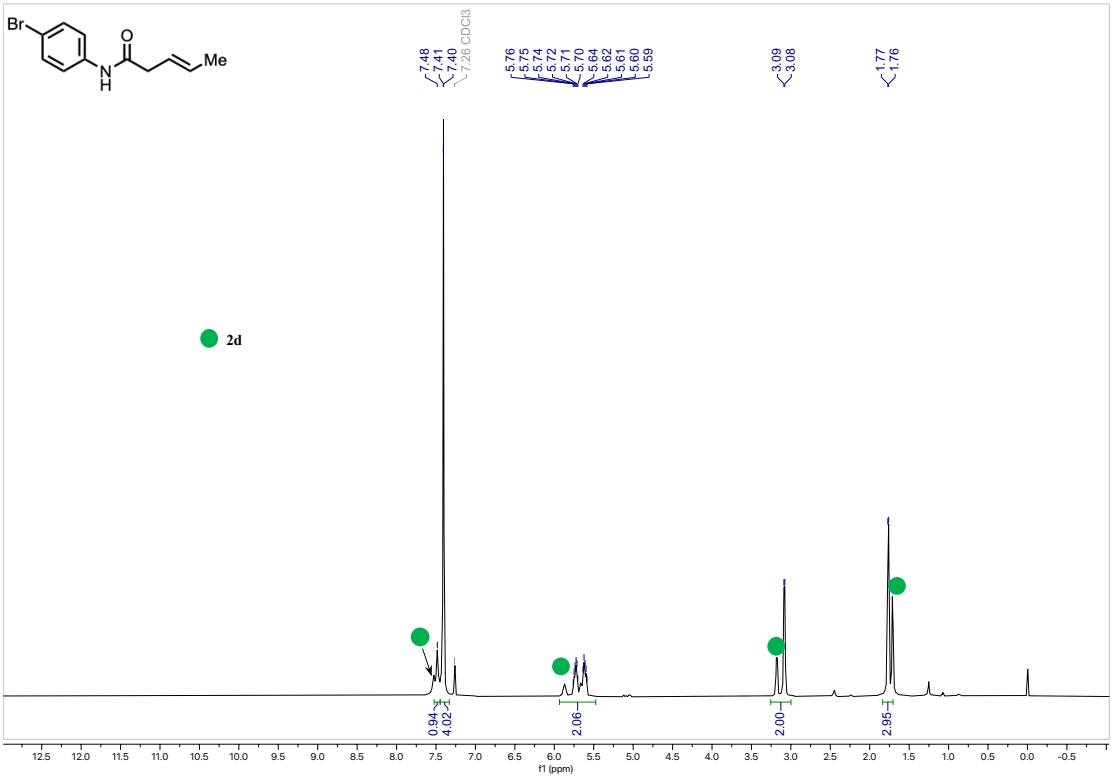


Figure S31: ^{13}C NMR of **3d**. 151 MHz, $CDCl_3$, 25 °C

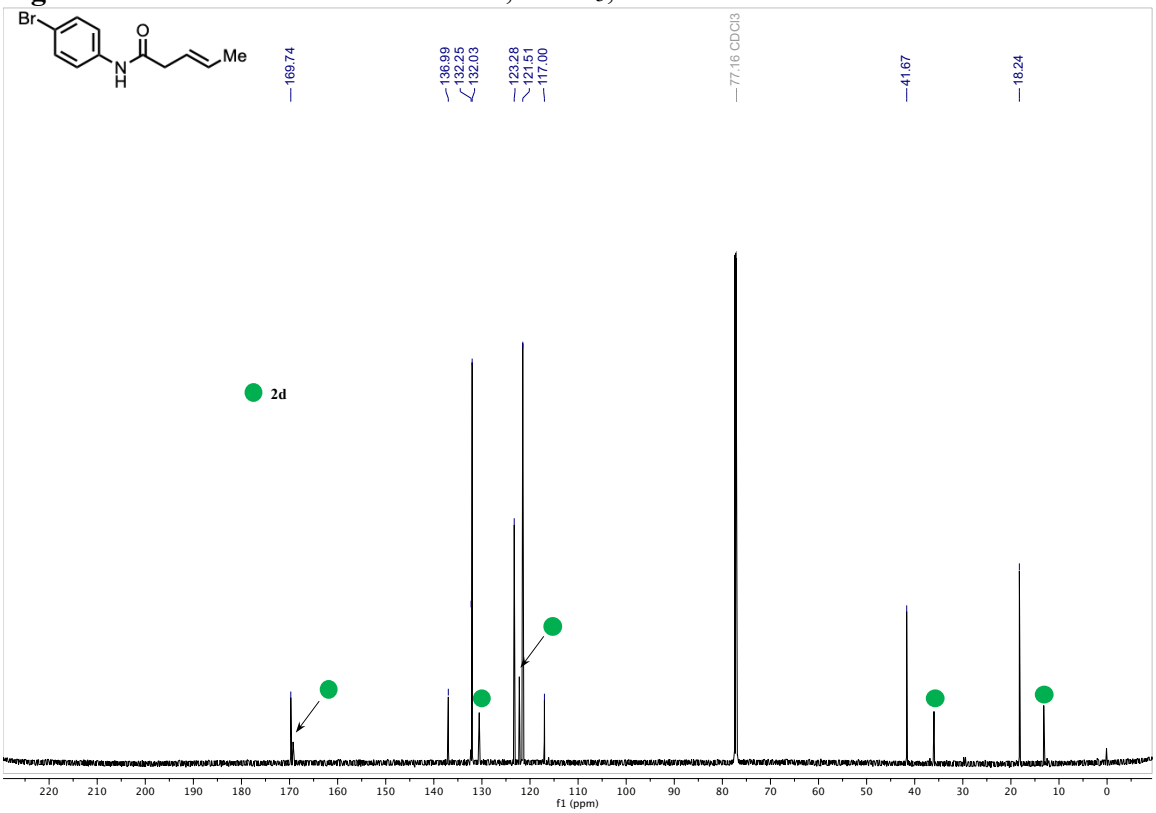


Figure S32: ^{1}H NMR of **3e**. 600 MHz, $CDCl_3$, 25 °C

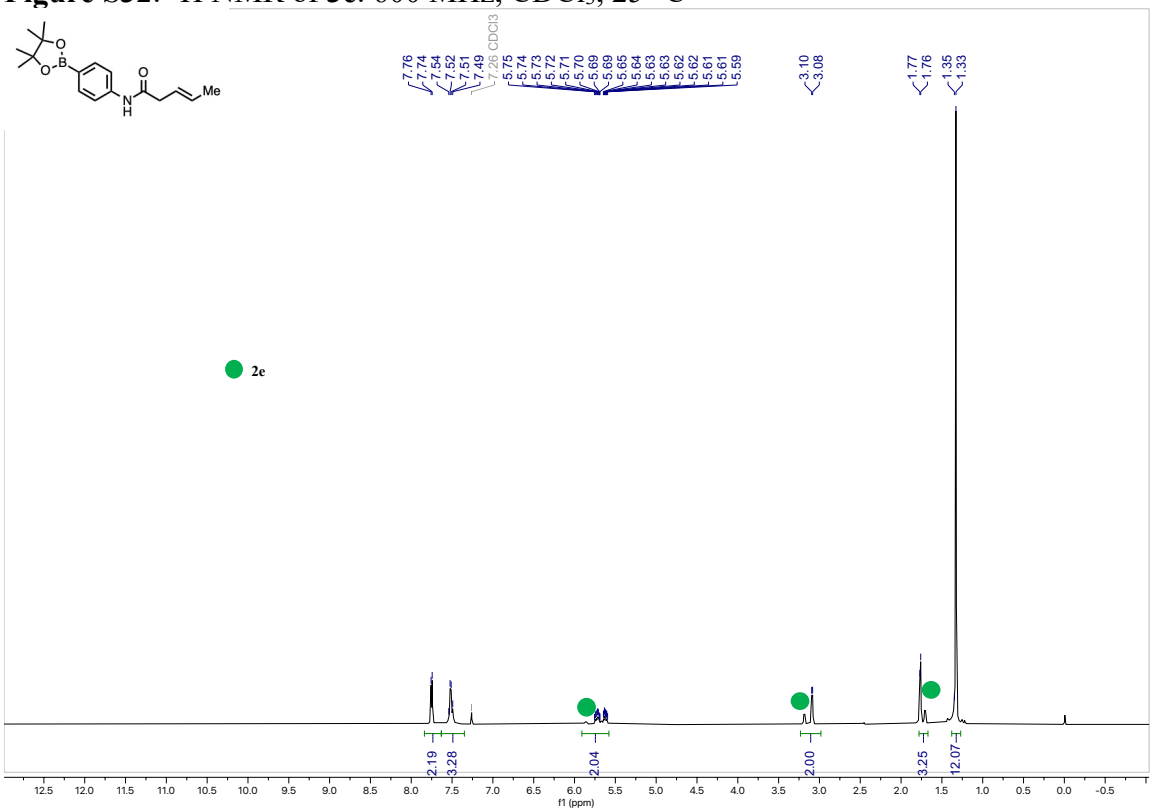


Figure S33: ^{13}C NMR of **3e**. 151 MHz, $CDCl_3$, 25 °C

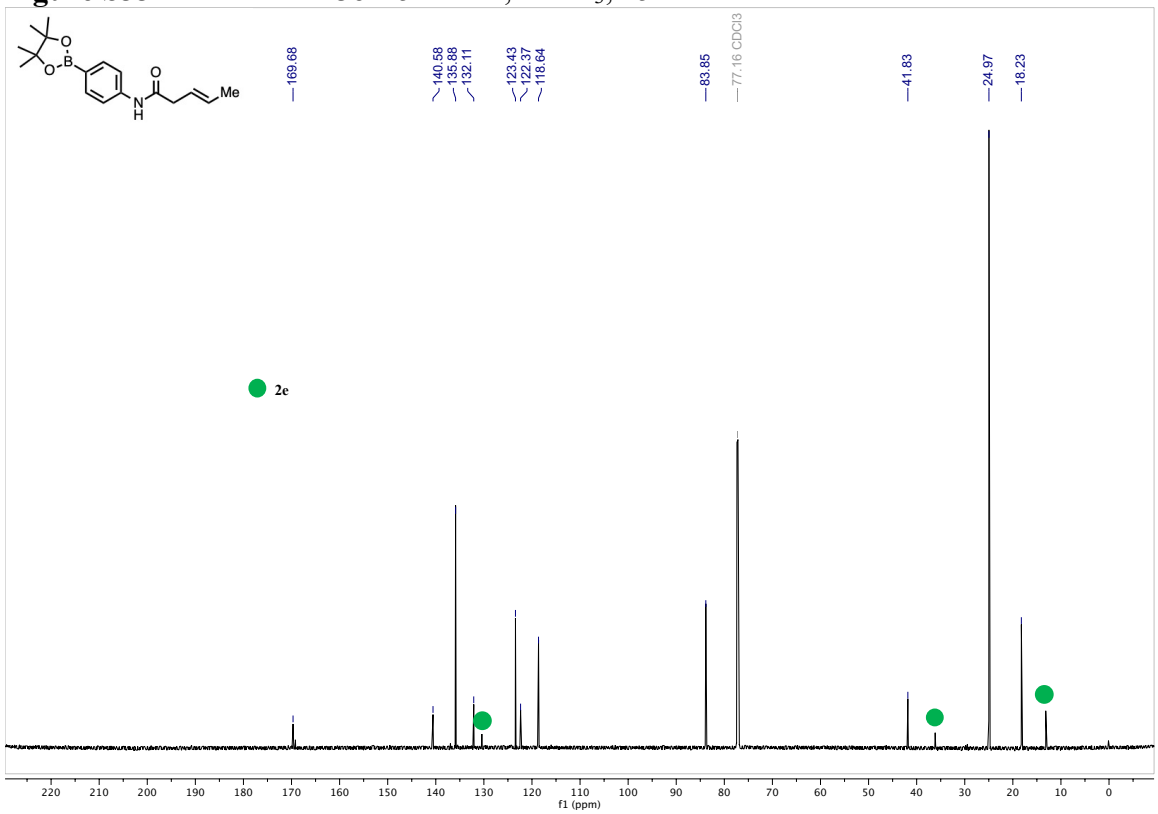


Figure S34: ^{1}H NMR of **2f**. 600 MHz, $CDCl_3$, 25 °C

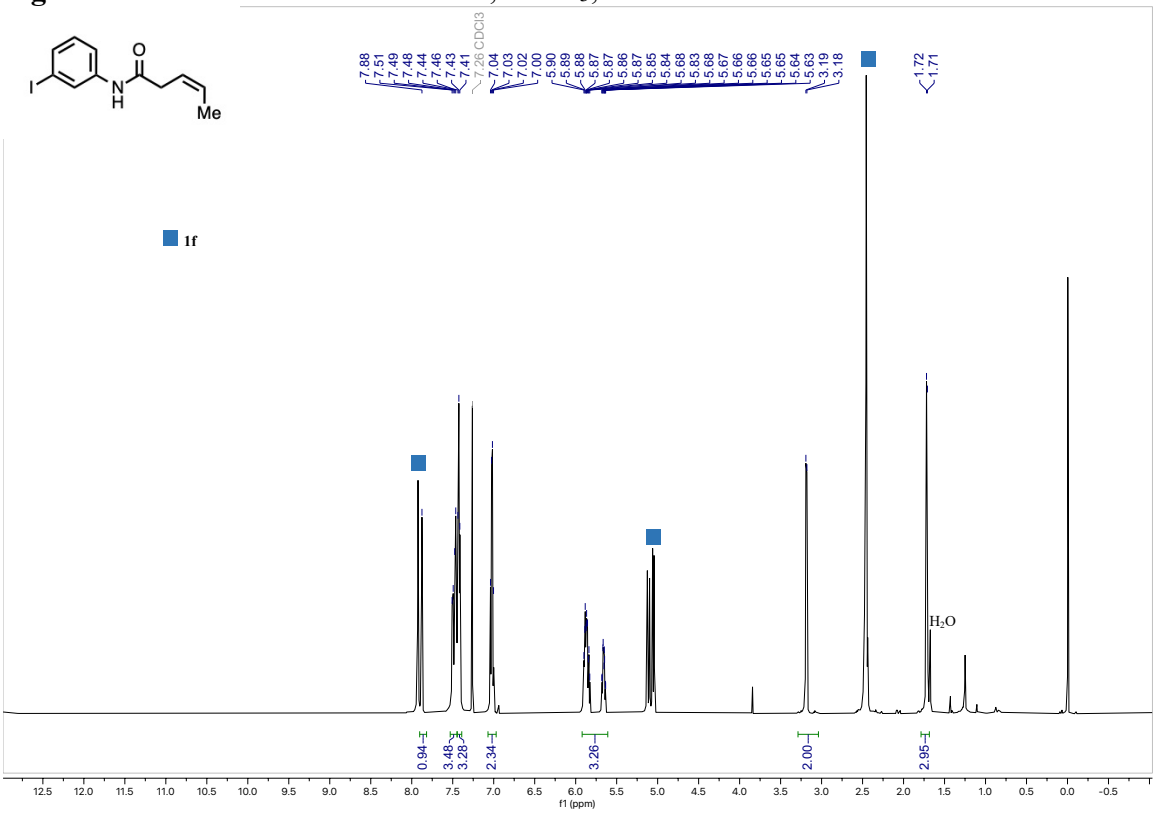


Figure S35: ^{13}C NMR of **2f**. 151 MHz, $CDCl_3$, 25 °C

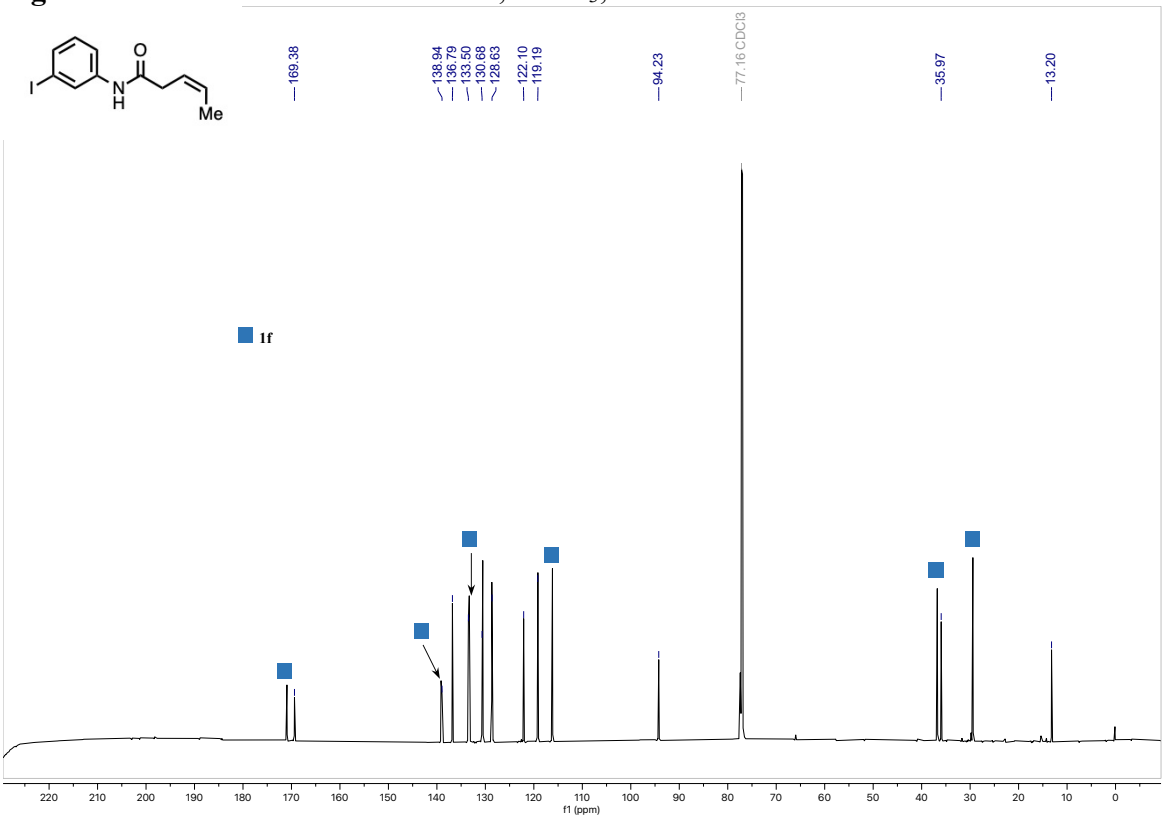


Figure S36: ^{1}H NMR of **3f**. 600 MHz, $CDCl_3$, 25 °C

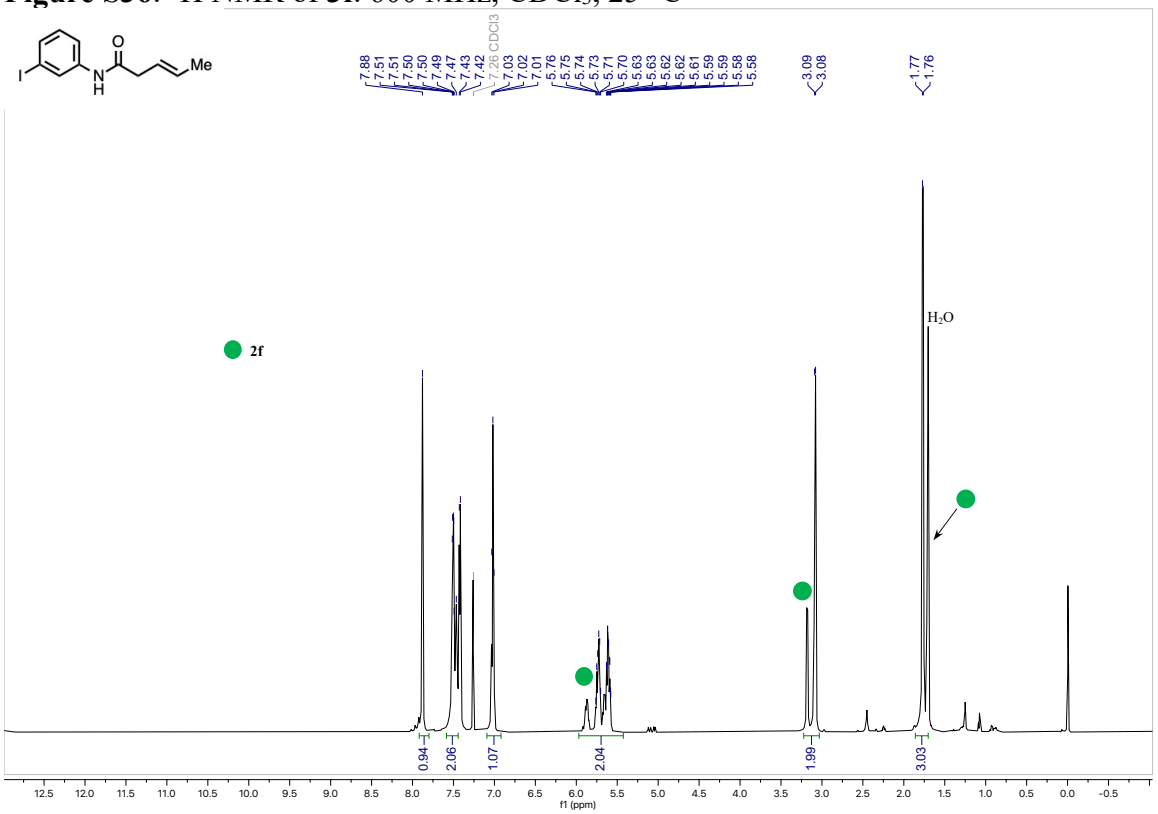


Figure S37: ^{13}C NMR of **3f**. 151 MHz, $CDCl_3$, 25 °C

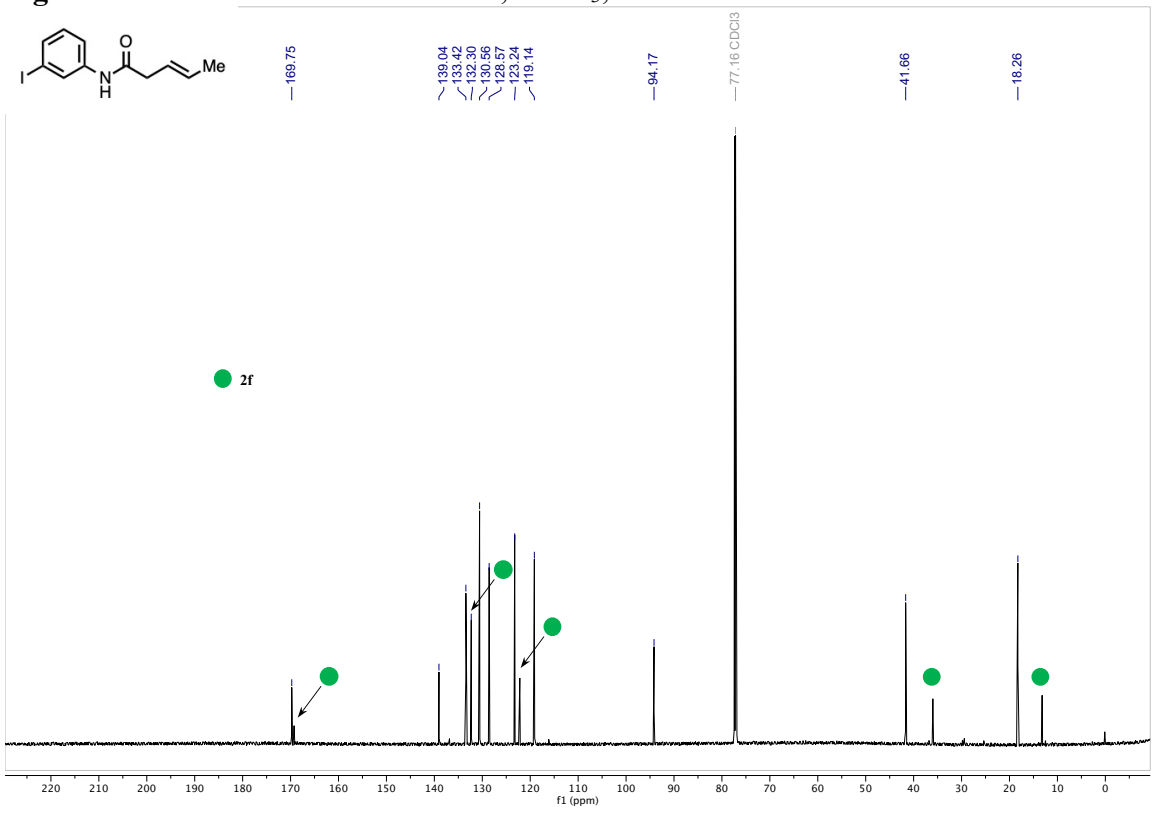


Figure S38: ^{1}H NMR of **2g**. 600 MHz, $CDCl_3$, 25 °C

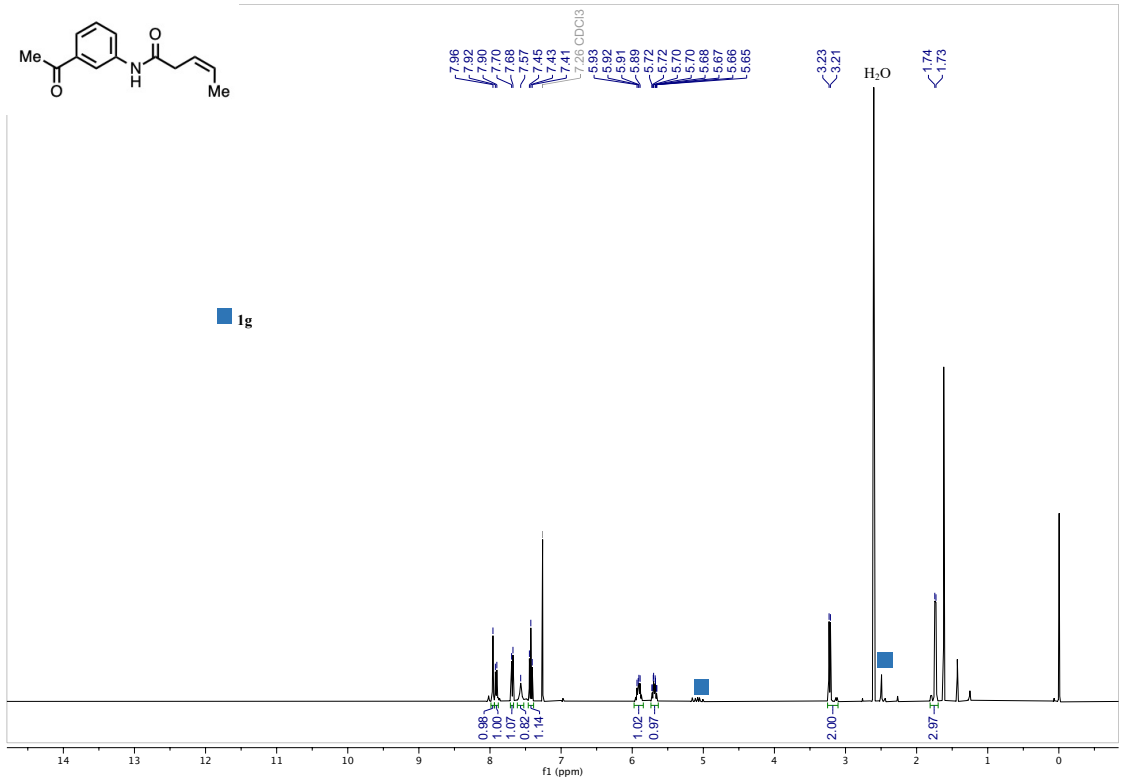


Figure S39: ^{13}C NMR of **2g**. 151 MHz, $CDCl_3$, 25 °C

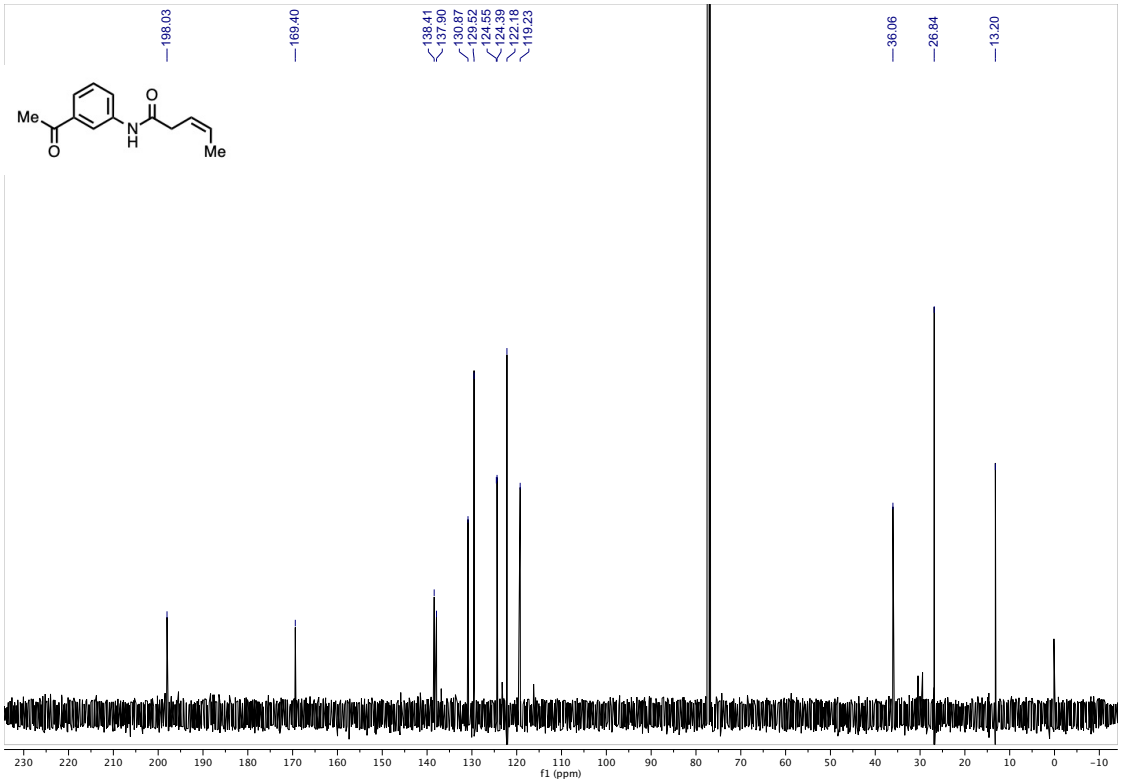


Figure S40: ^{1}H NMR of **3g**. 600 MHz, $CDCl_3$, 25 °C

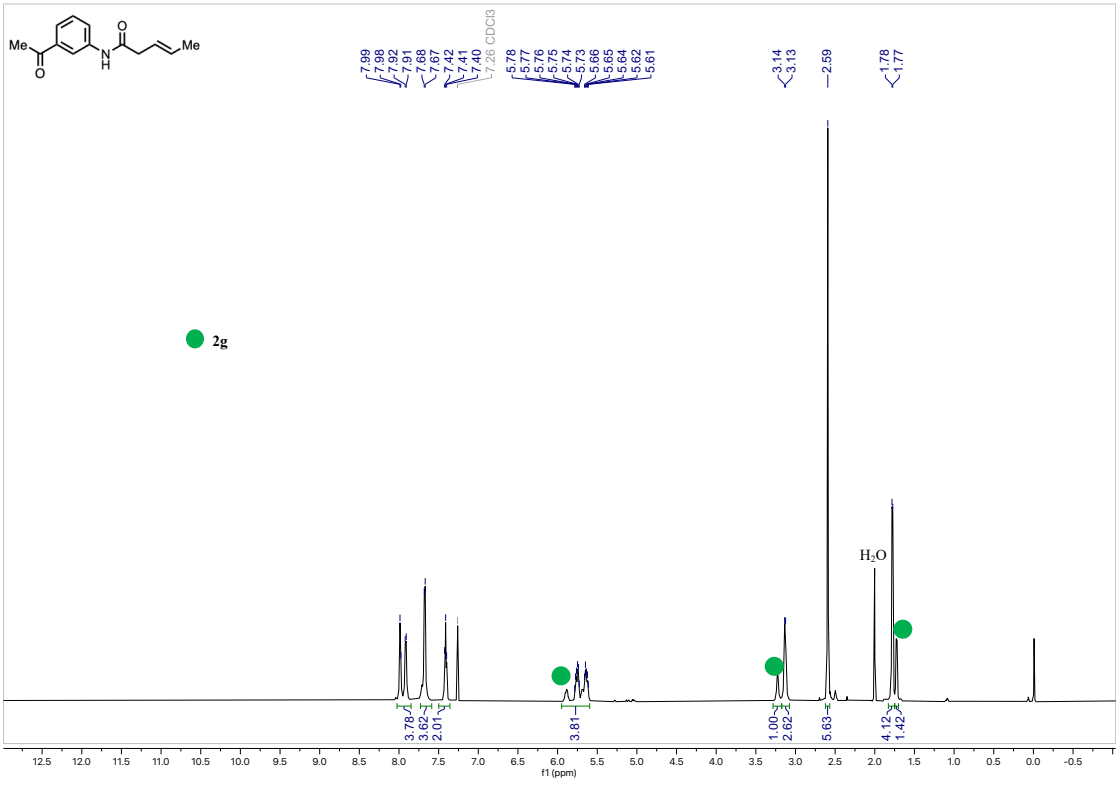


Figure S41: ^{13}C NMR of **3g**. 151 MHz, $CDCl_3$, 25 °C

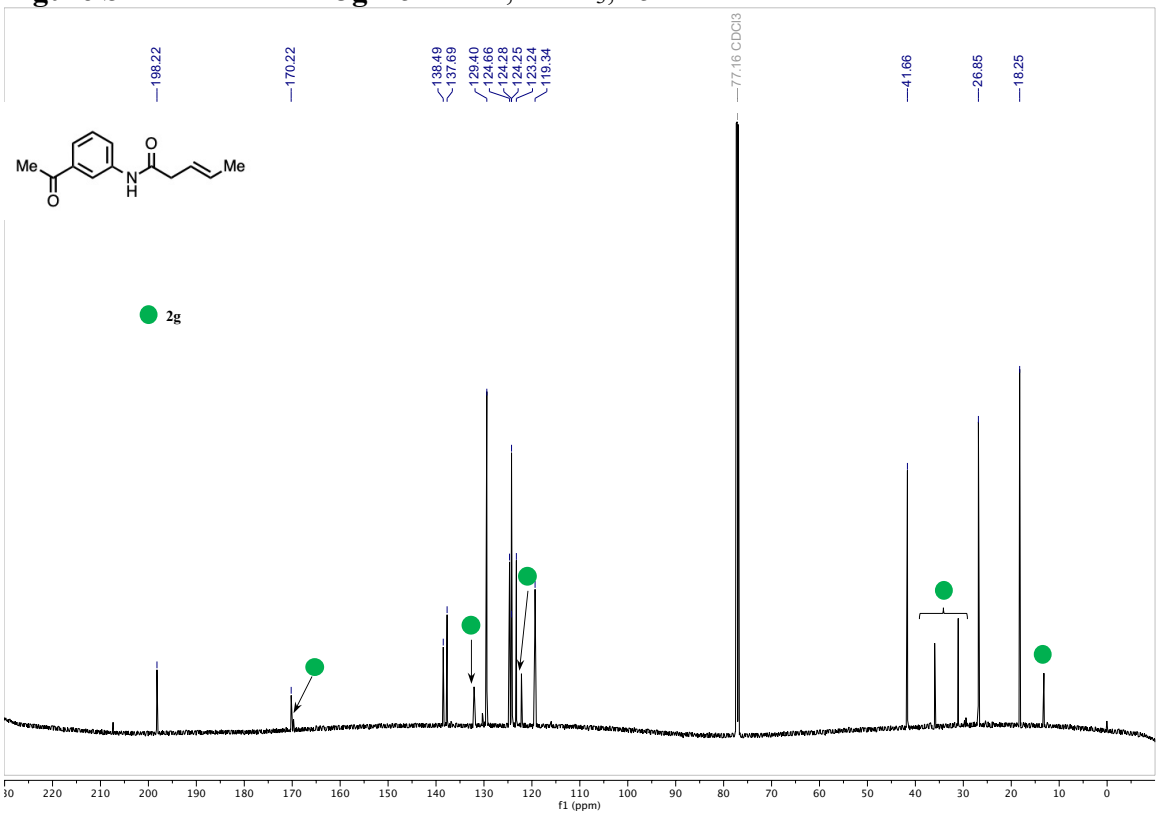


Figure S42: ^{1}H NMR of **2h**. 600 MHz, $CDCl_3$, 25 °C

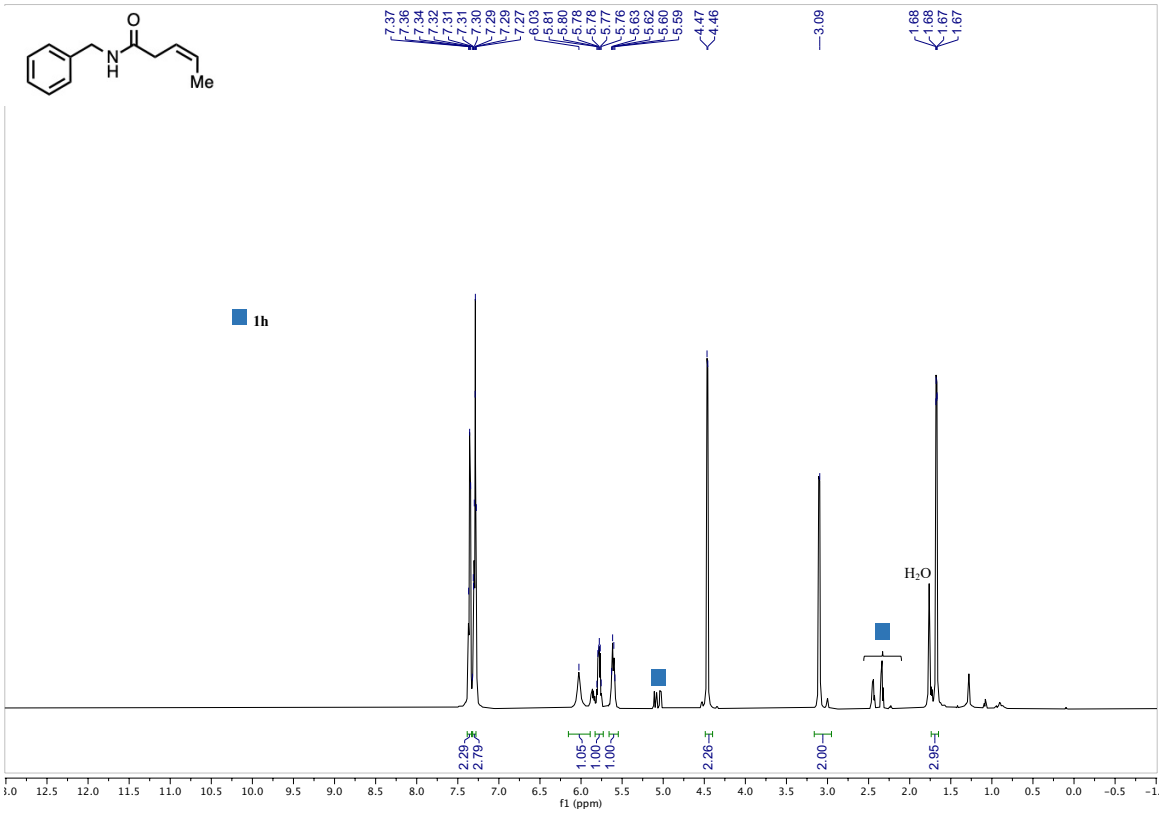


Figure S43: ^{13}C NMR of **2h**. 151 MHz, $CDCl_3$, 25 °C

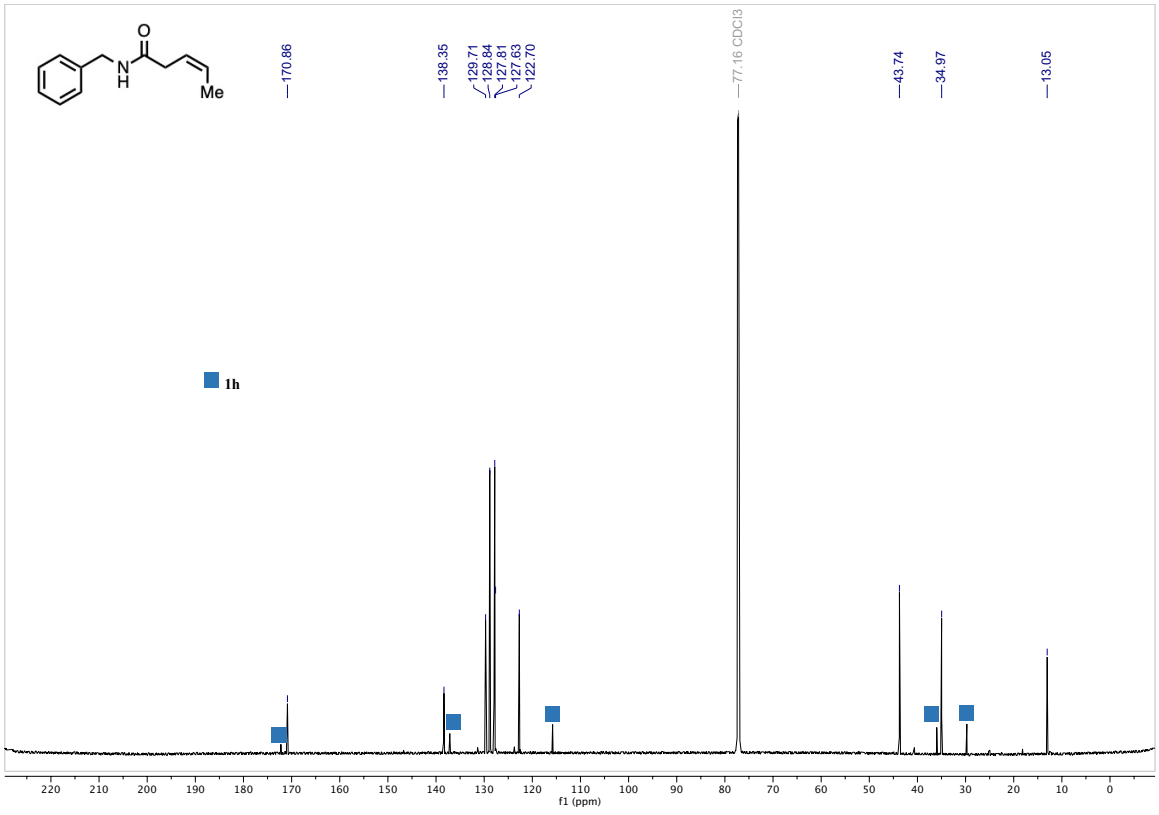


Figure S44: ^{1}H NMR of **3h**. 600 MHz, $CDCl_3$, 25 °C

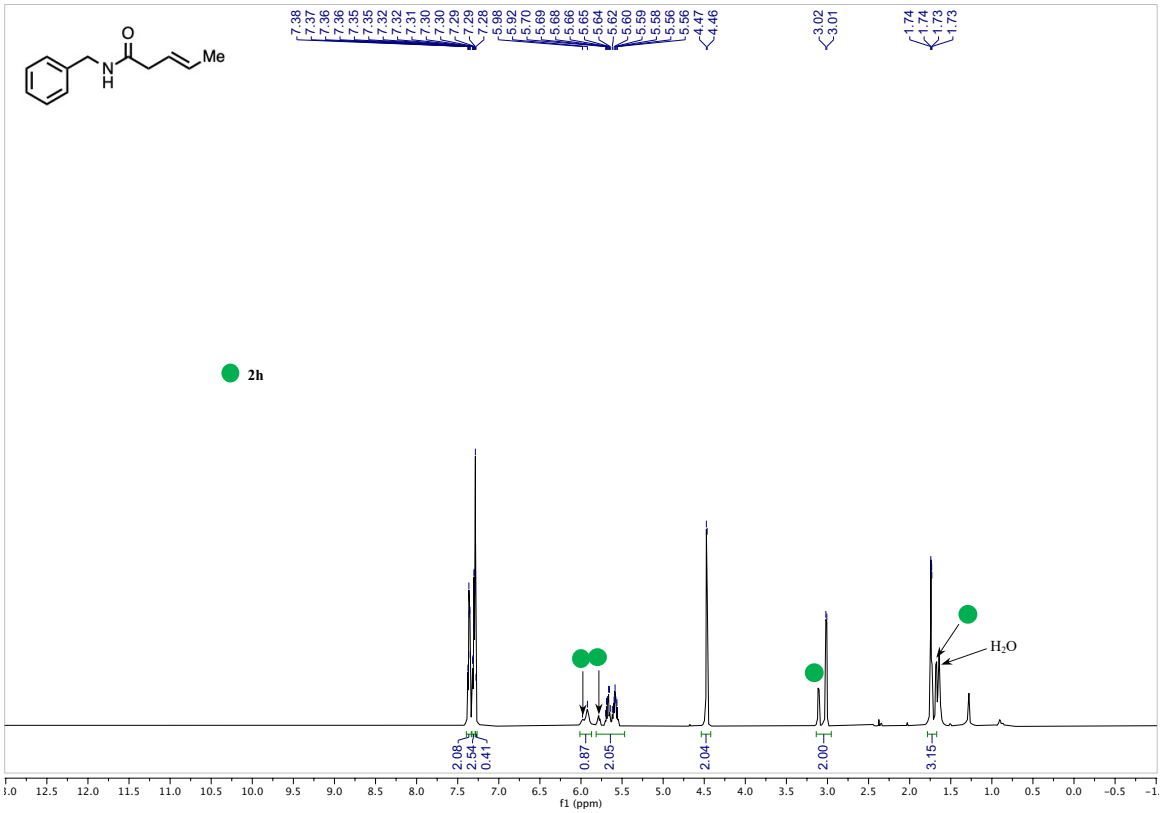


Figure S45: ^{13}C NMR of **3h**. 151 MHz, $CDCl_3$, 25 °C

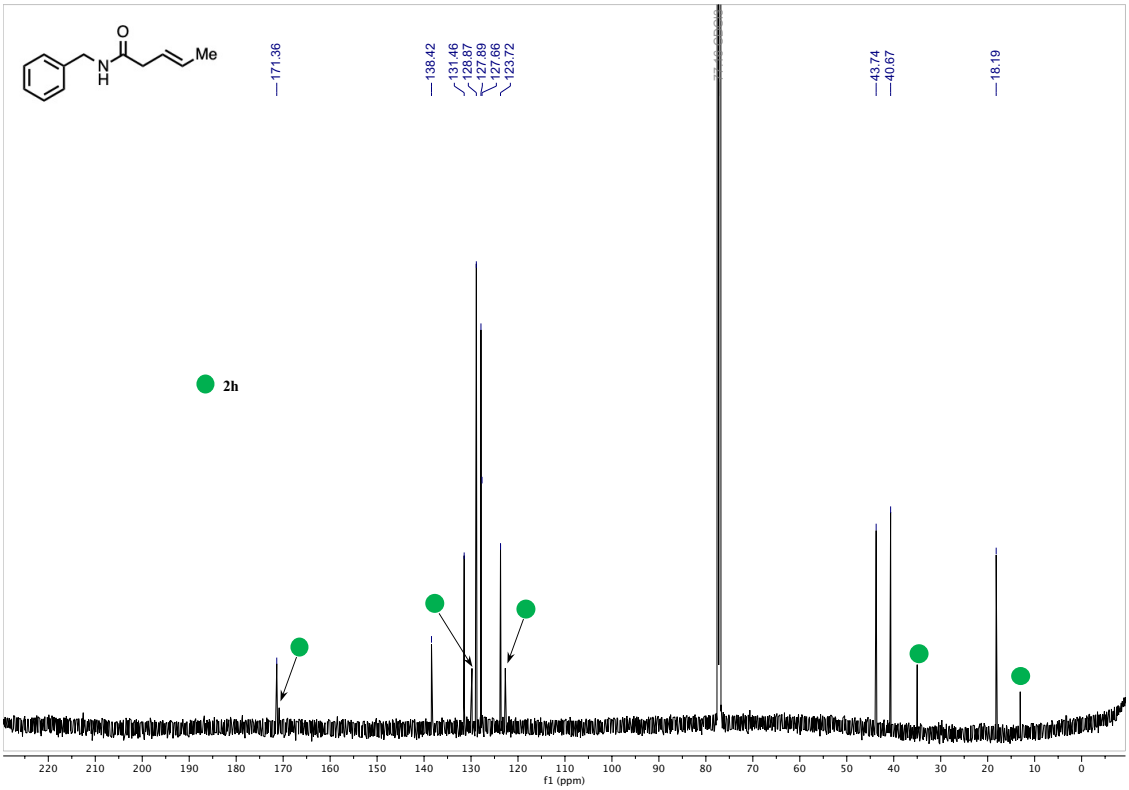


Figure S46: ^{1}H NMR of **2i**. 600 MHz, $CDCl_3$, 25 °C

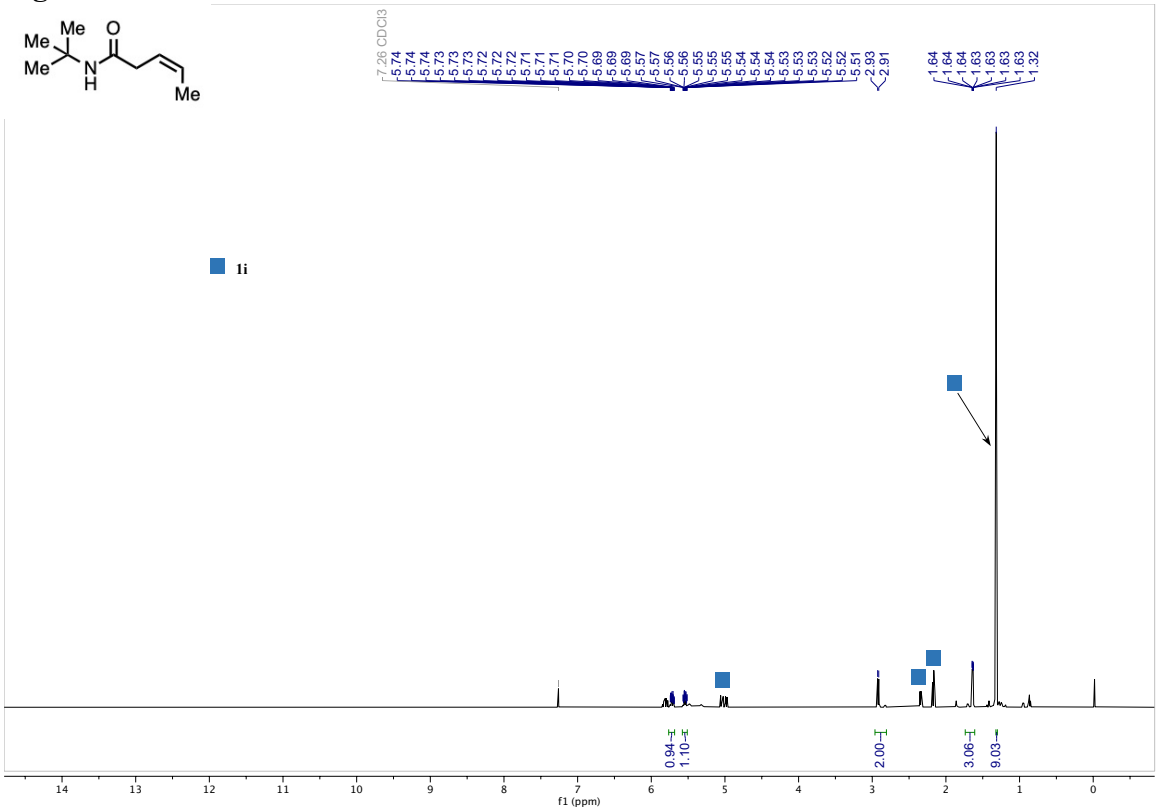


Figure S47: ^{13}C NMR of **2i**. 126 MHz, $CDCl_3$, 25 °C

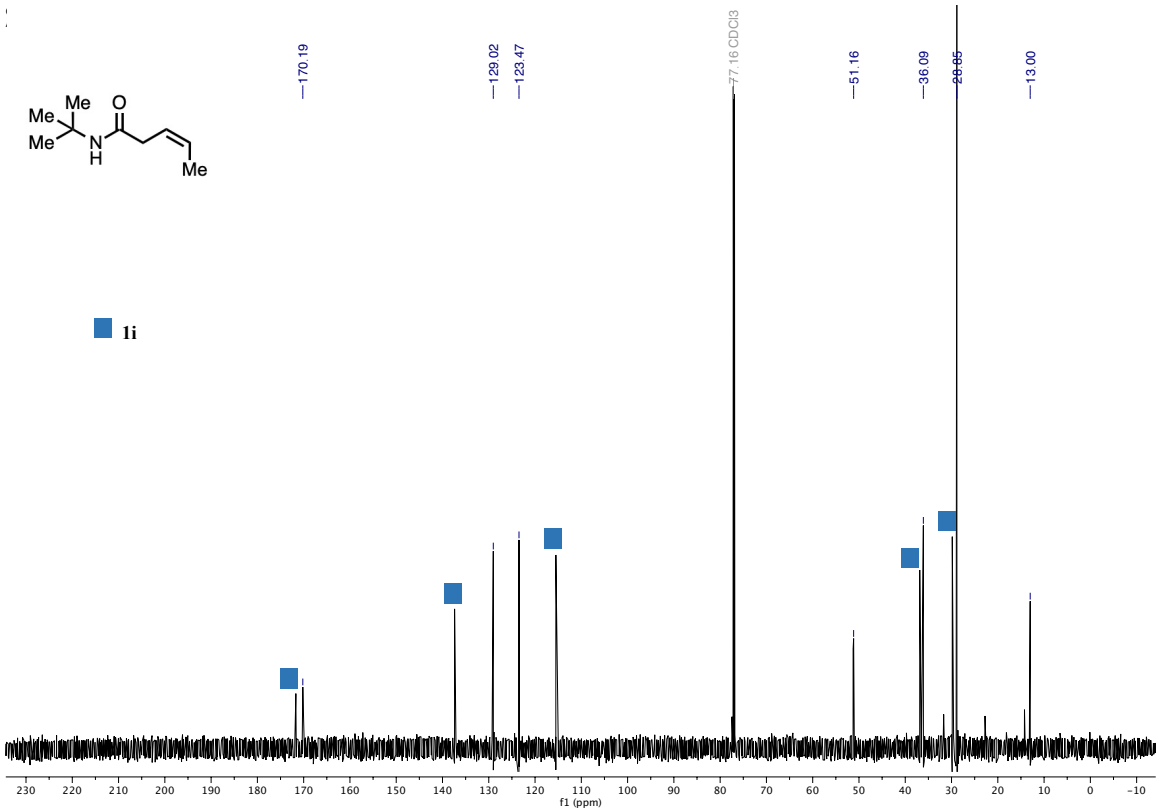


Figure S48: ^{1}H NMR of **3i**. 600 MHz, $CDCl_3$, 25 °C

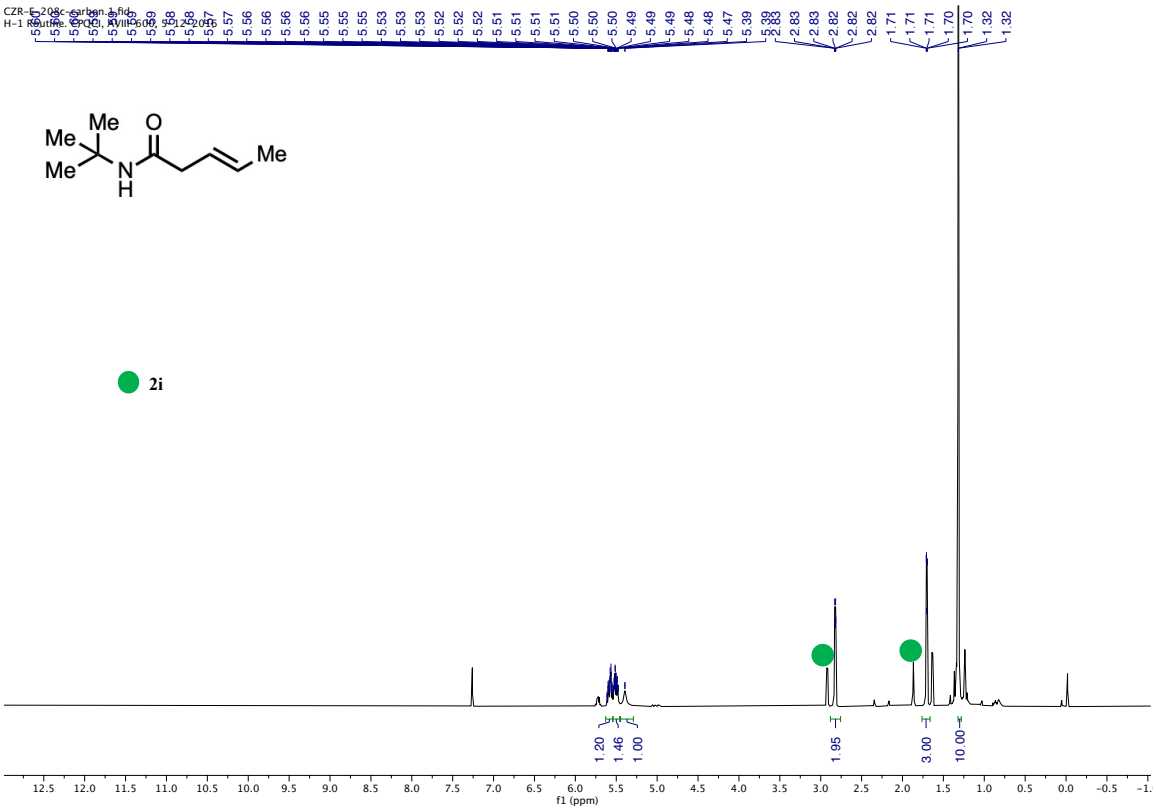


Figure S49: ^{13}C NMR of **3i**. 151 MHz, $CDCl_3$, 25 °C

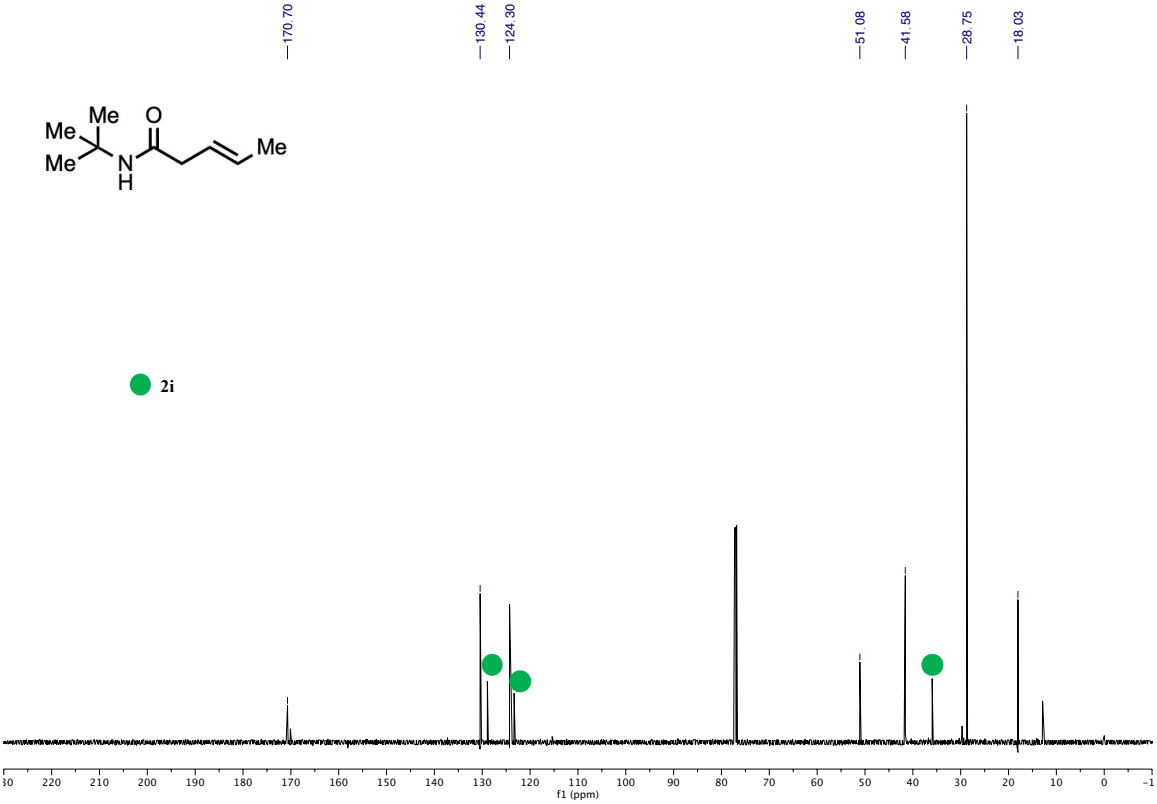


Figure S50: ^{1}H NMR of **2j**. 600 MHz, $CDCl_3$, 25 °C

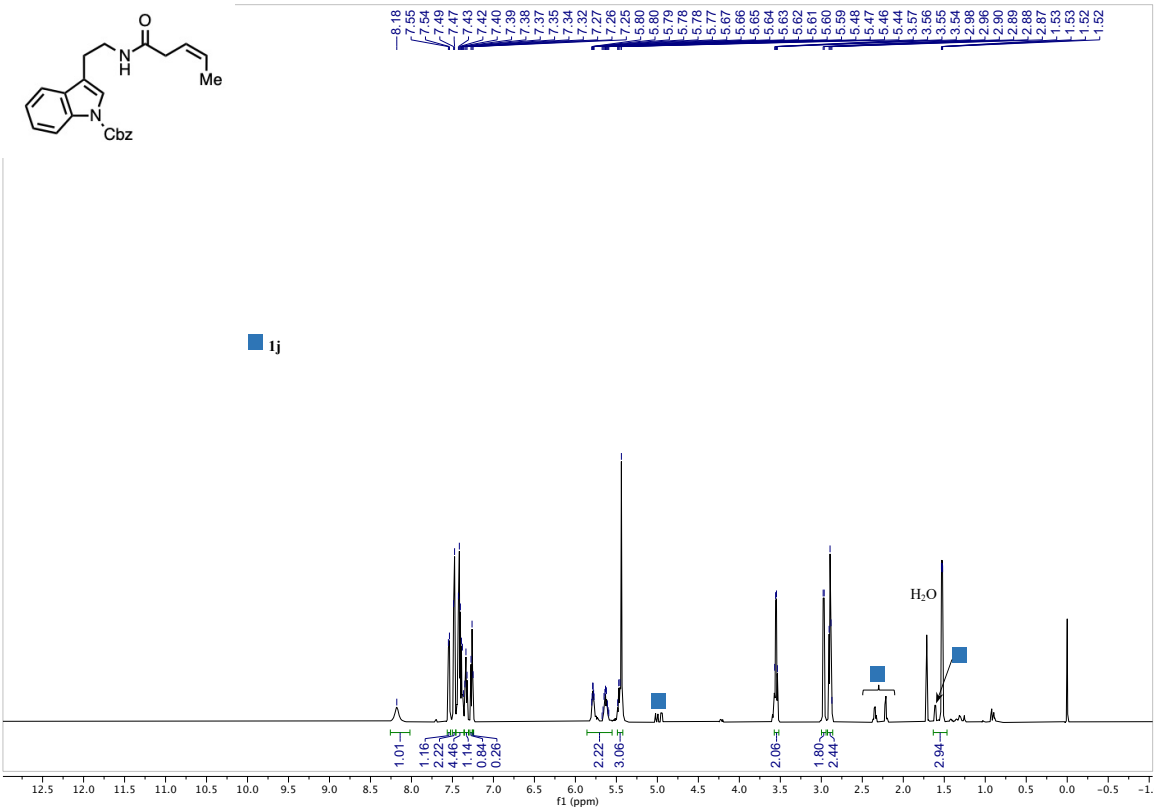


Figure S51: ^{13}C NMR of **2j**. 151 MHz, $CDCl_3$, 25 °C

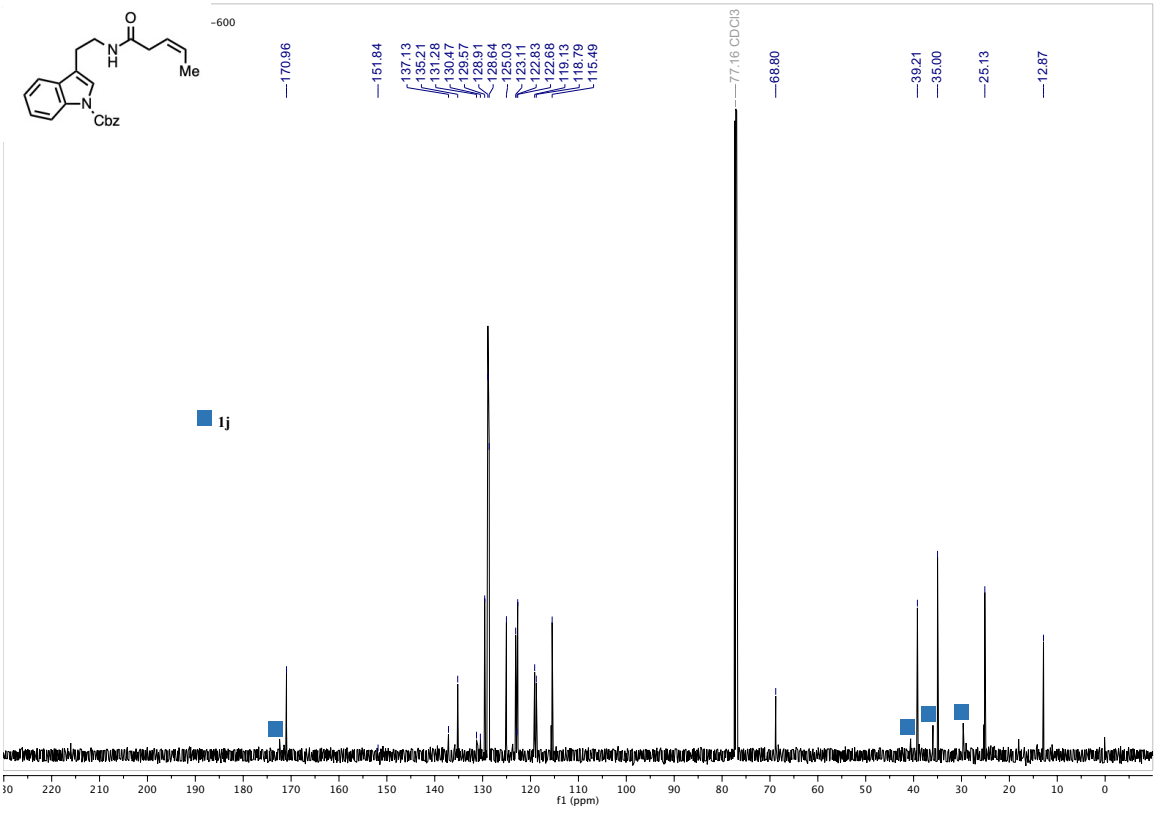


Figure S52: ^{1}H NMR of **3j**. 600 MHz, $CDCl_3$, 25 °C

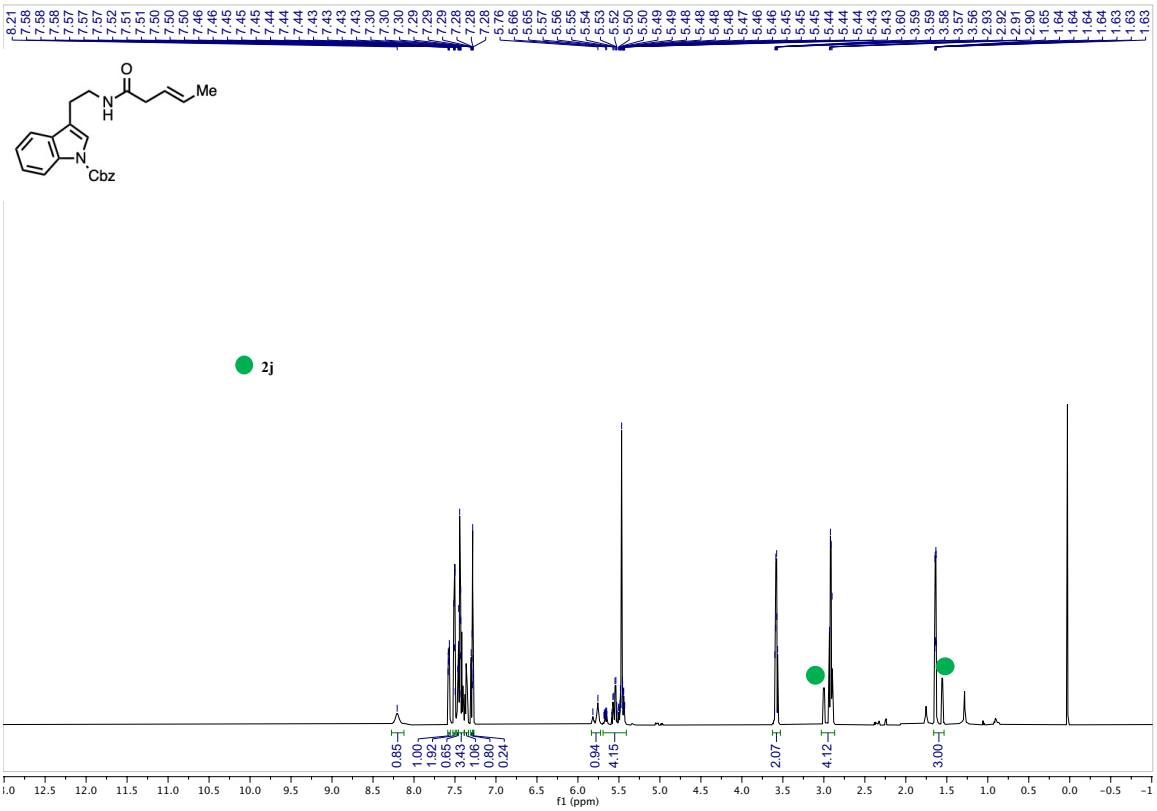


Figure S53: ^{13}C NMR of **3j**. 151 MHz, $CDCl_3$, 25 °C

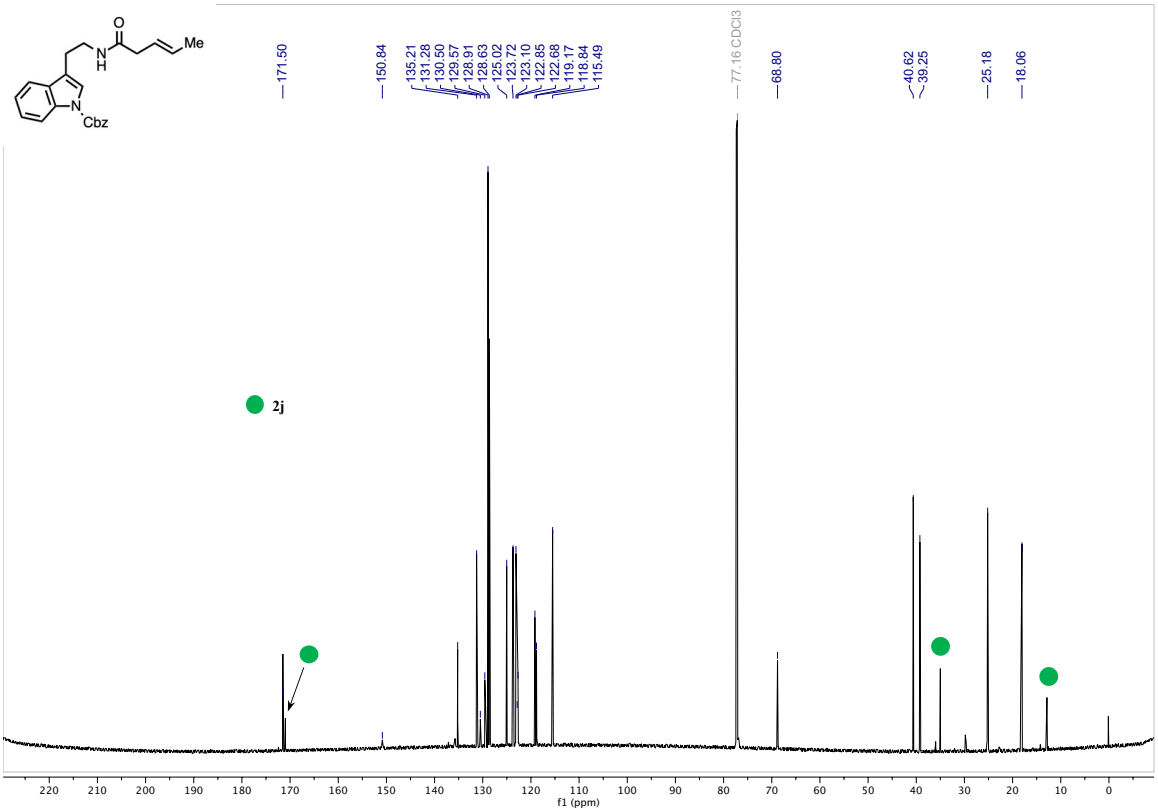


Figure S54: Crude ^{1}H NMR of **2k**. 400 MHz, $CDCl_3$, 25 °C

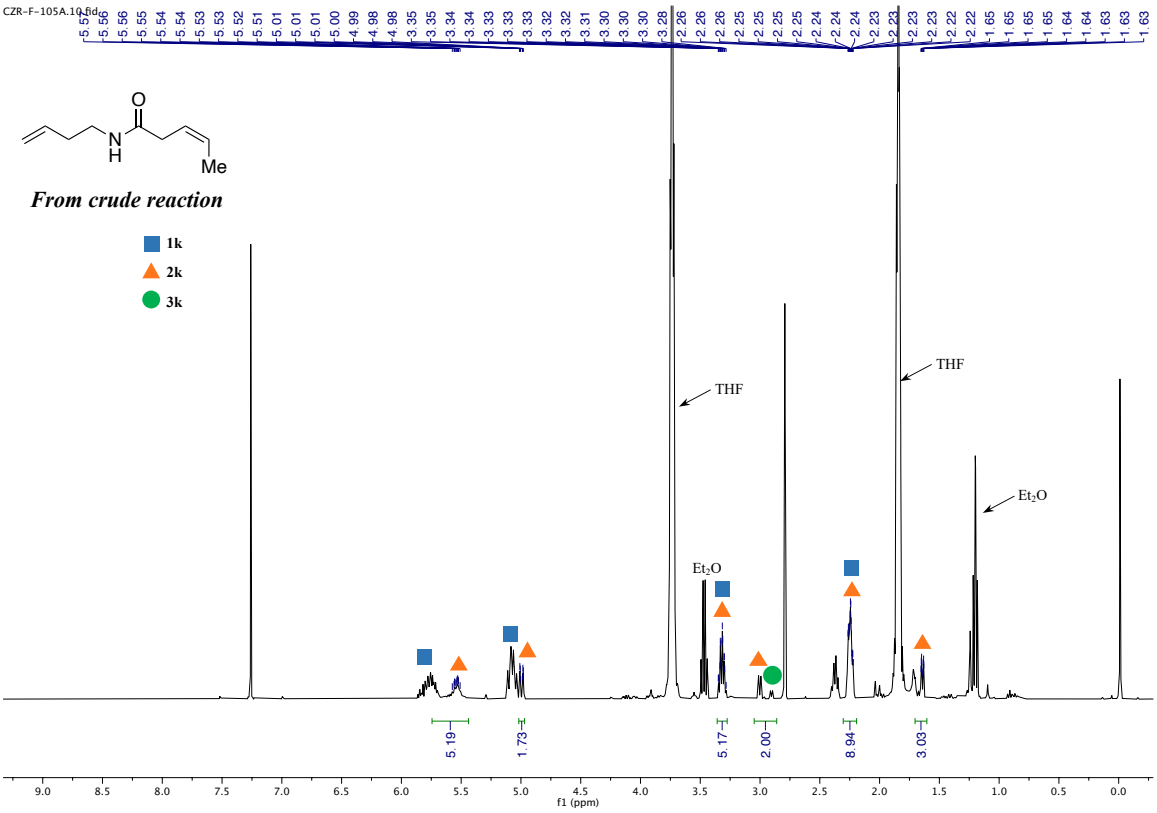


Figure 55: ^{1}H NMR of **3k**. 400 MHz, $CDCl_3$, 25 °C

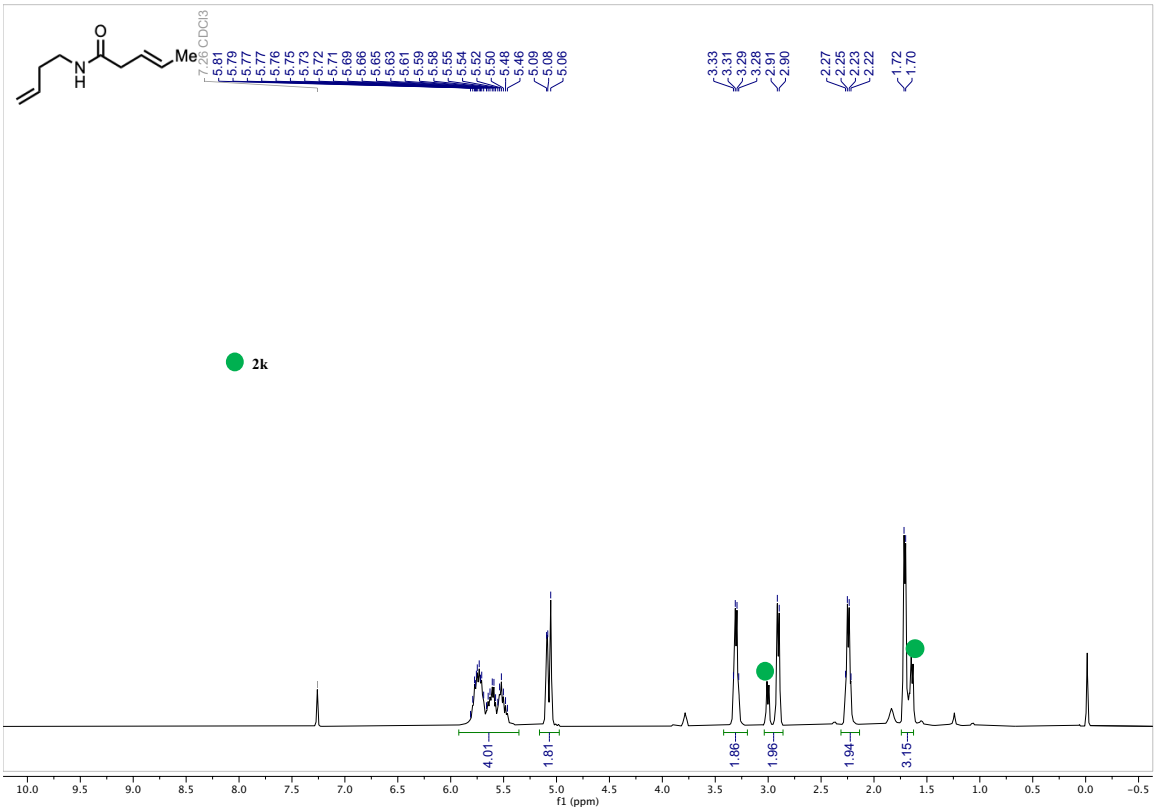


Figure S56: ^{13}C NMR of **3k**. 100 MHz, $CDCl_3$, 25 °C

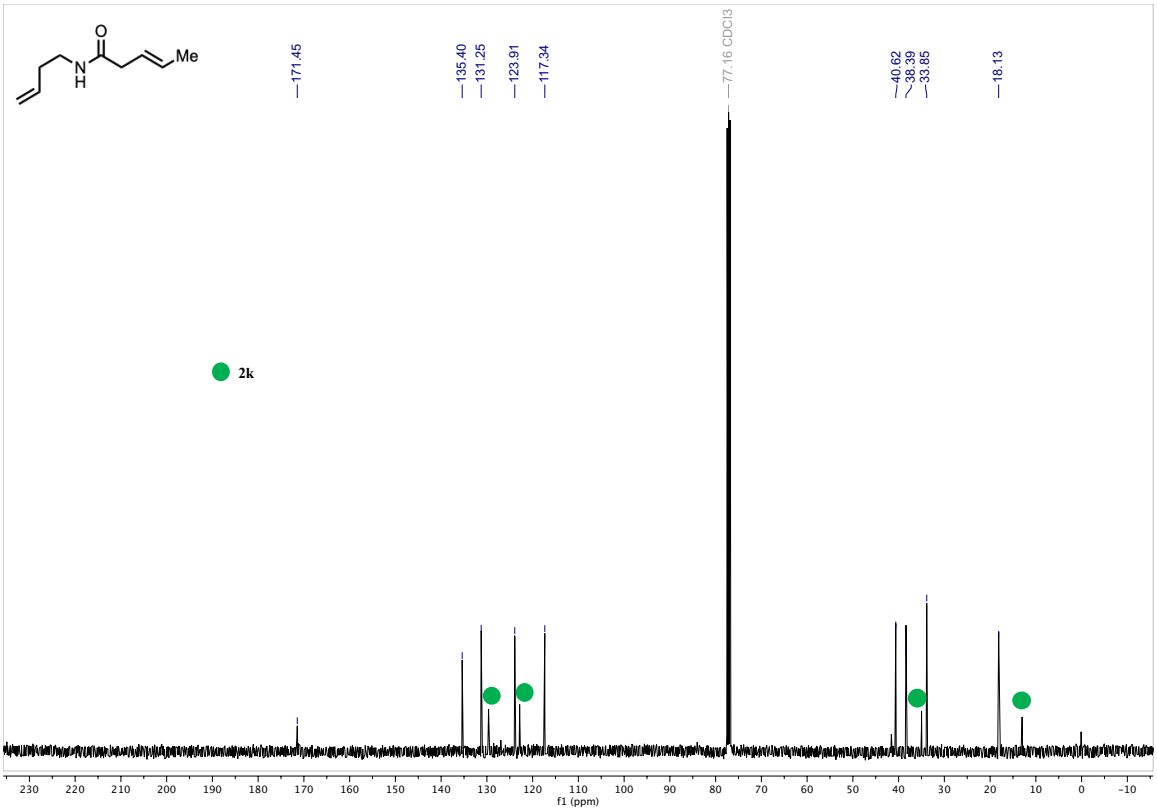


Figure S57: ^{1}H NMR of **2l**. 600 MHz, $CDCl_3$, 25 °C

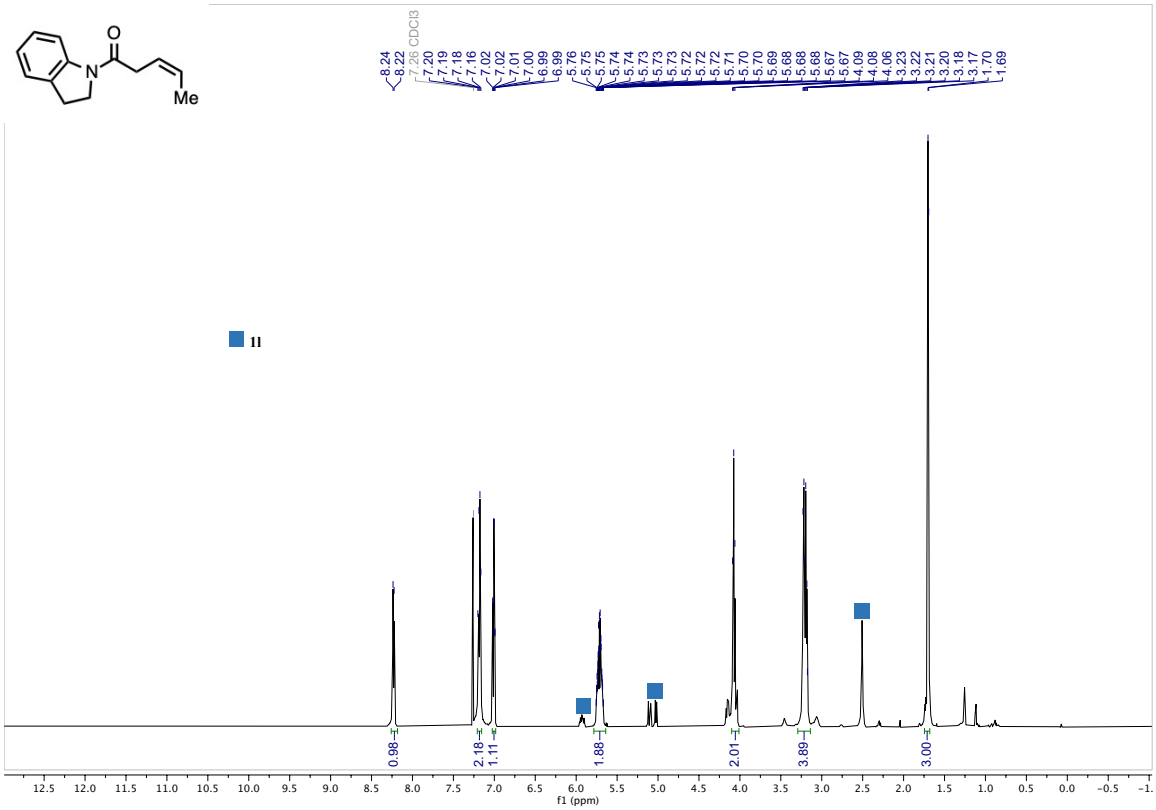


Figure S58: ^{13}C NMR of **2l**. 151 MHz, $CDCl_3$, 25 °C

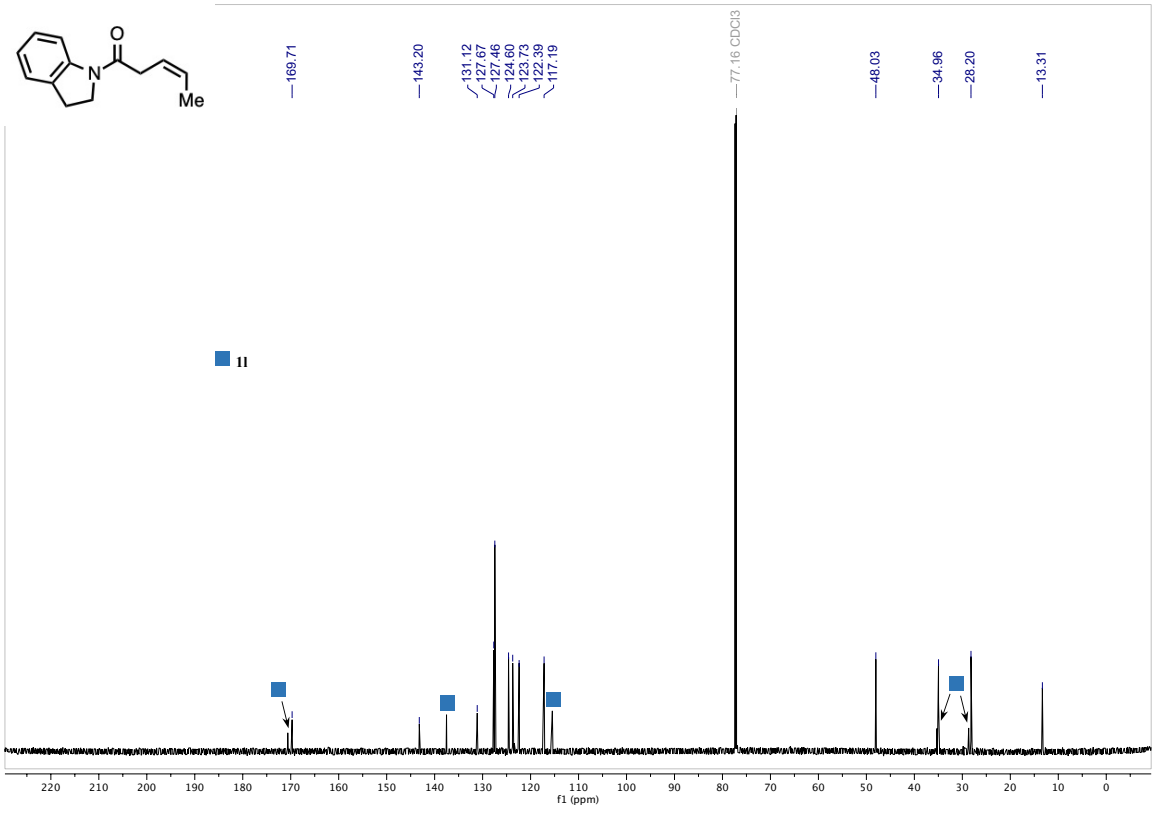


Figure S59: ^{1}H NMR of **3l**. 600 MHz, $CDCl_3$, 25 °C

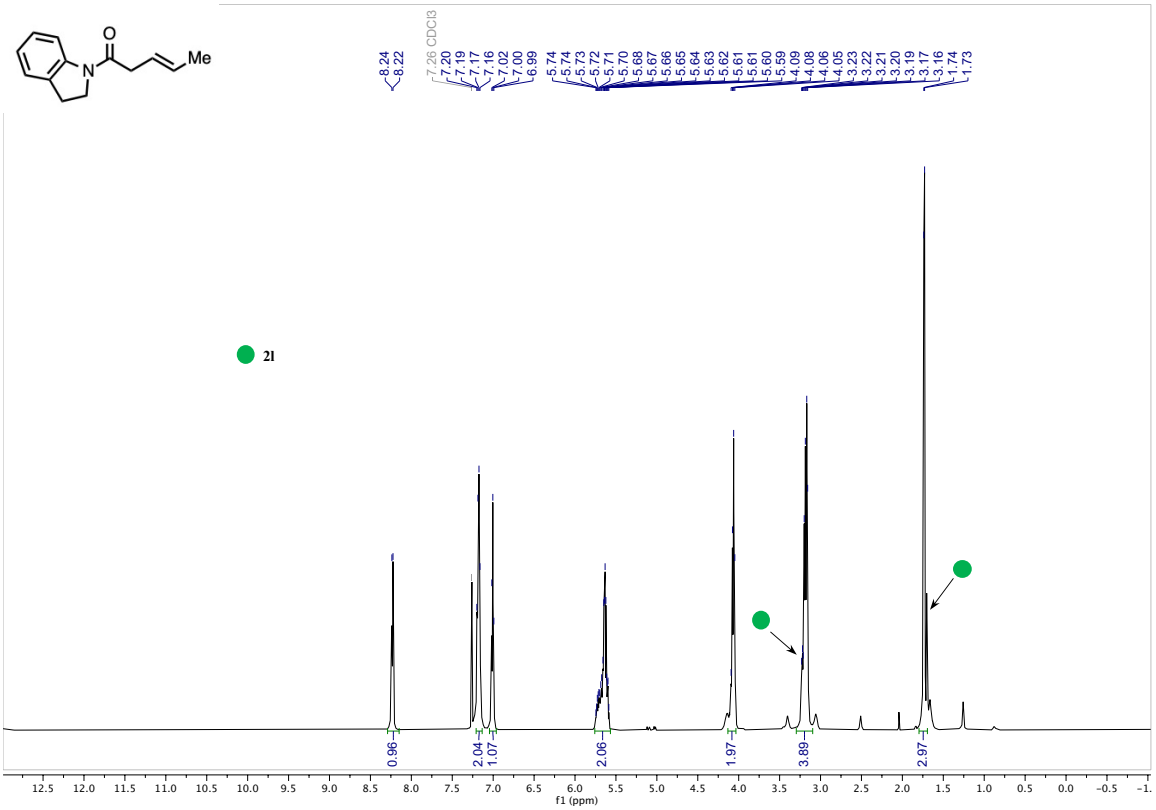


Figure S60: ^{13}C NMR of **3l**. 151 MHz, $CDCl_3$, 25 °C

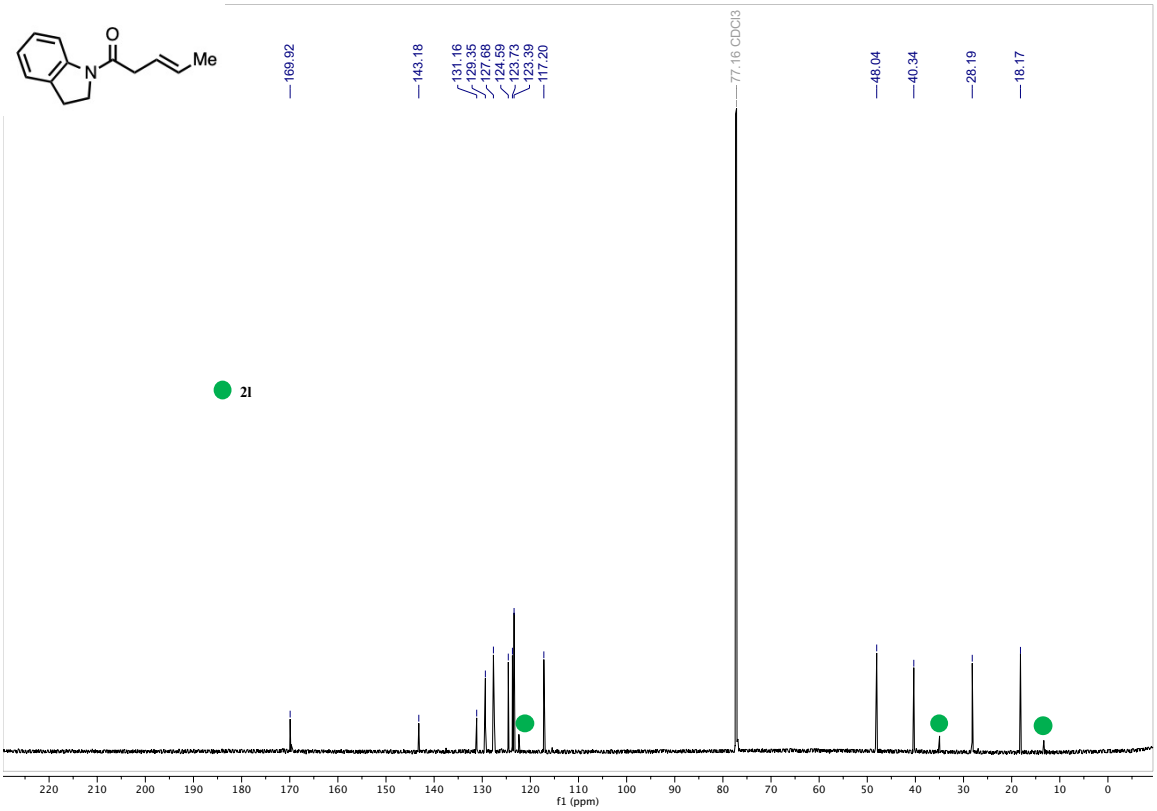


Figure S61: ^{1}H NMR of **2m**. 400 MHz, $CDCl_3$, 25 °C

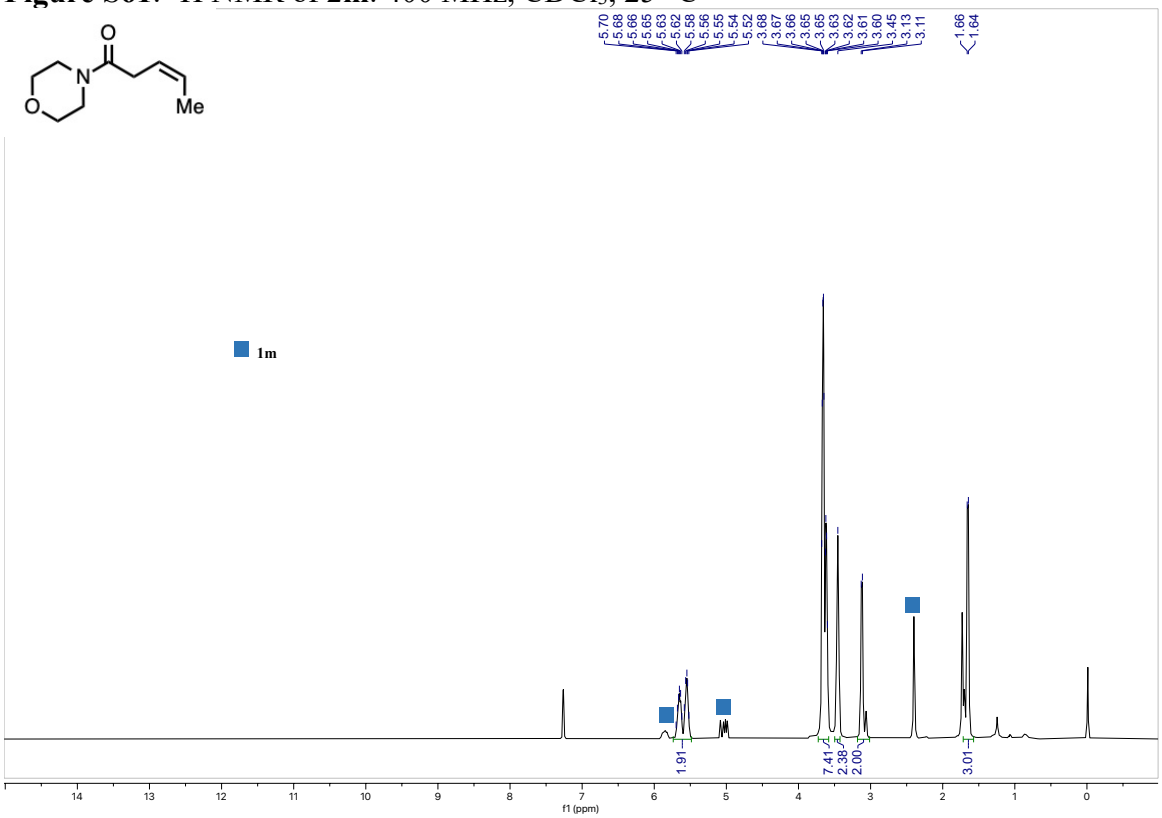


Figure S62: ^{13}C NMR of **2m**. 100 MHz, $CDCl_3$, 25 °C

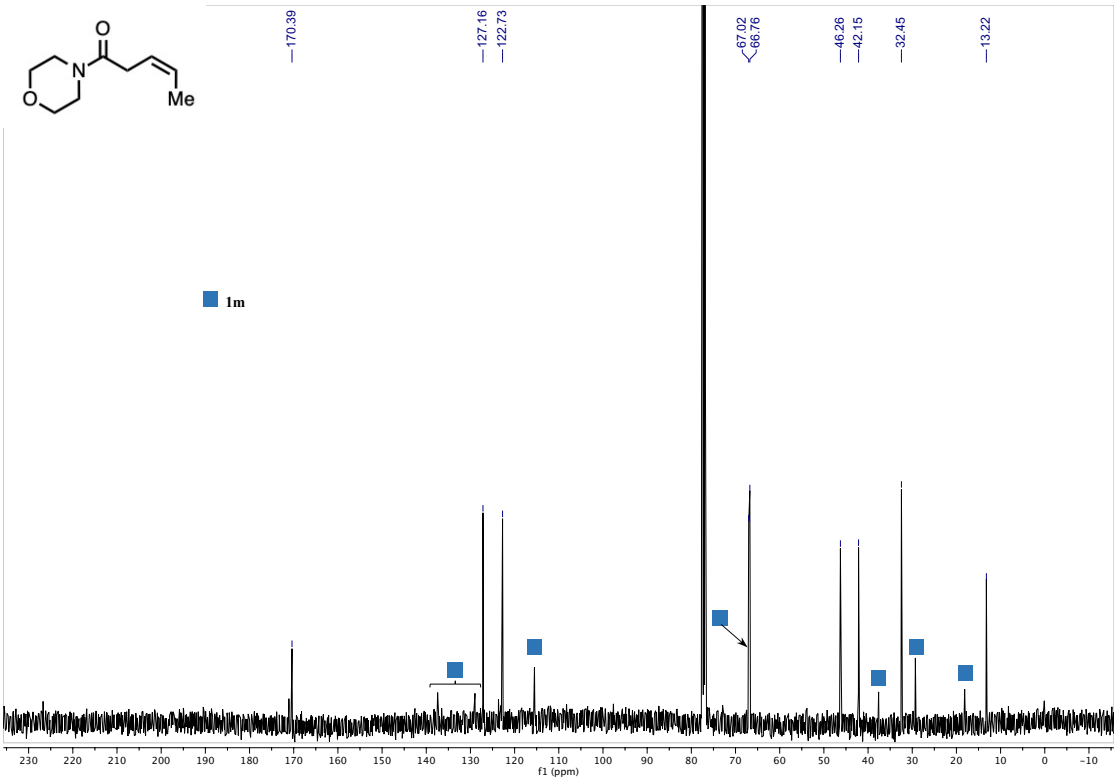


Figure S63: ^{1}H NMR of **3m**. 600 MHz, $CDCl_3$, 25 °C

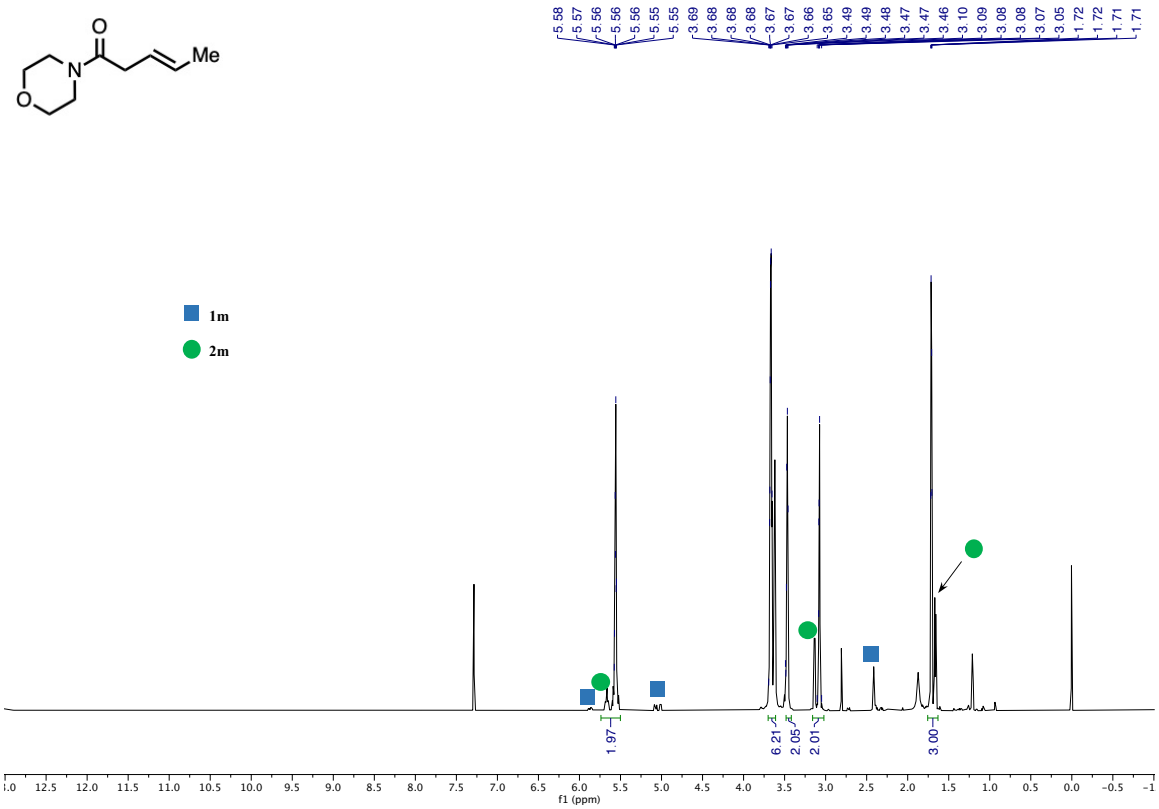


Figure S64: ^{13}C NMR of **3m**. 151 MHz, $CDCl_3$, 25 °C

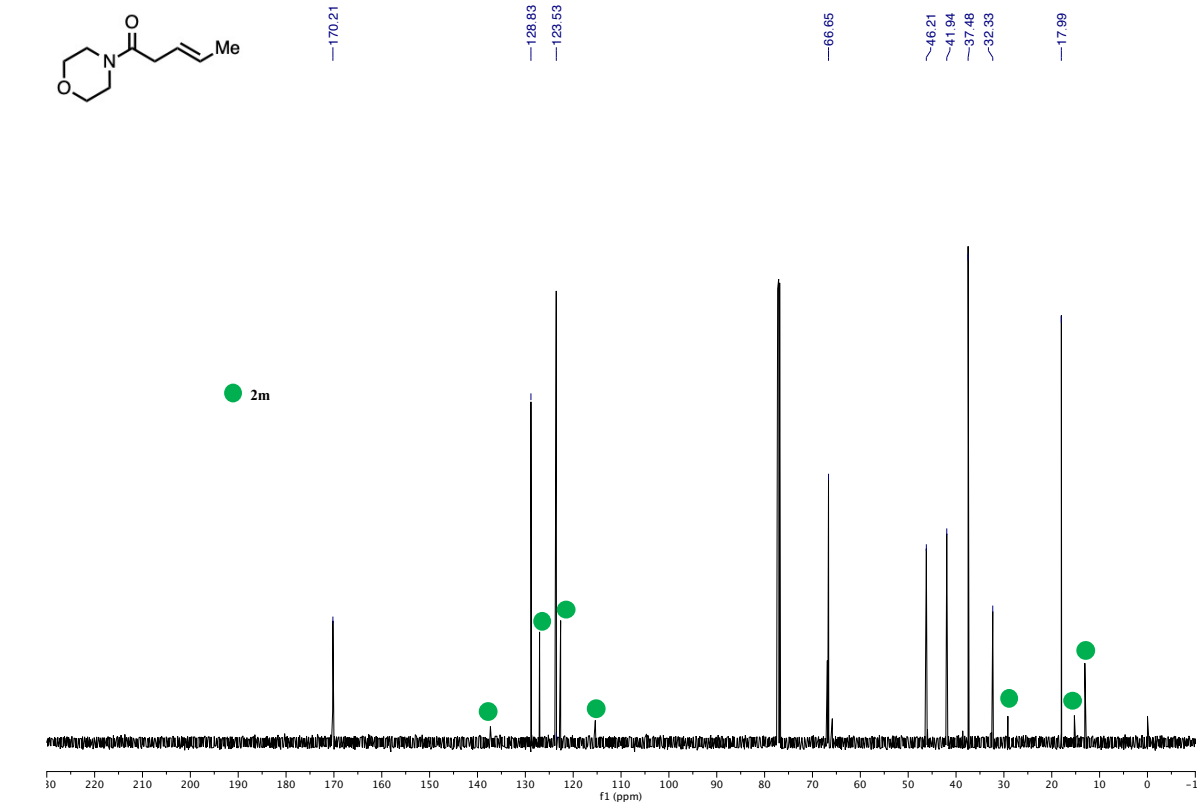


Figure S65: ^{1}H NMR of **2n**. 600 MHz, $CDCl_3$, 25 °C

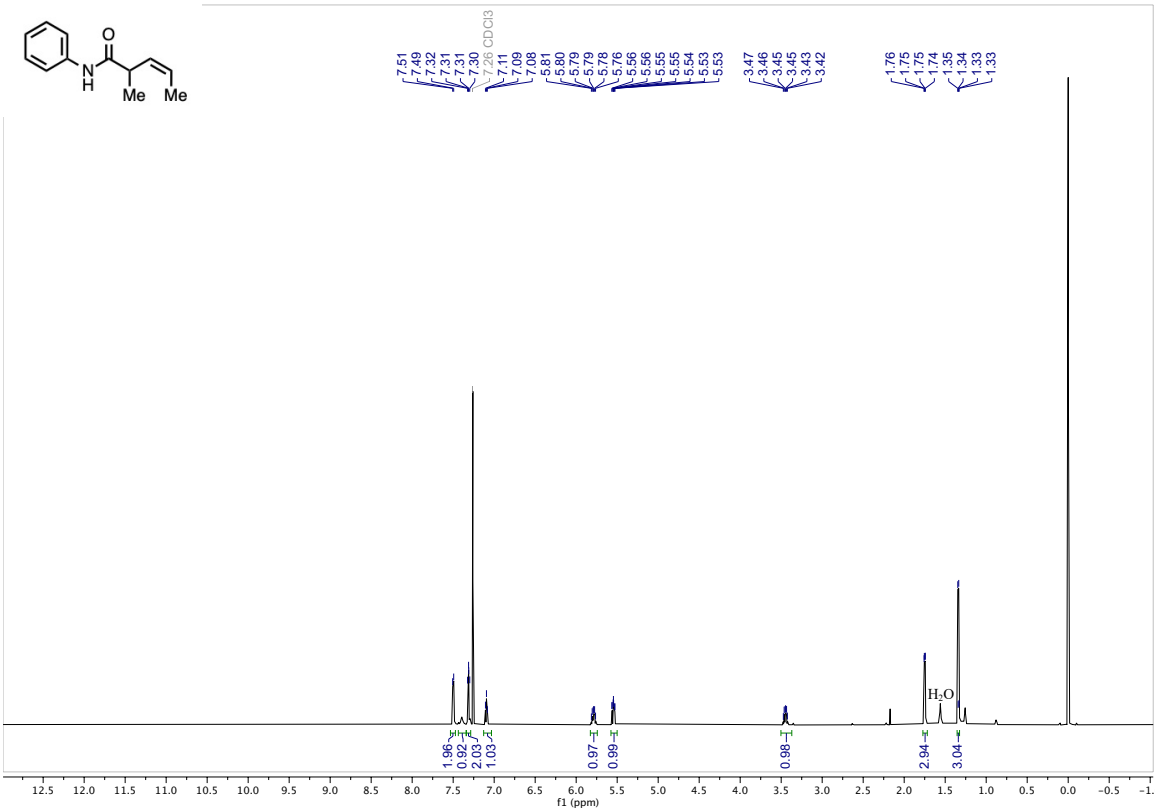


Figure S66: ^{13}C NMR of **2n**. 151 MHz, $CDCl_3$, 25 °C

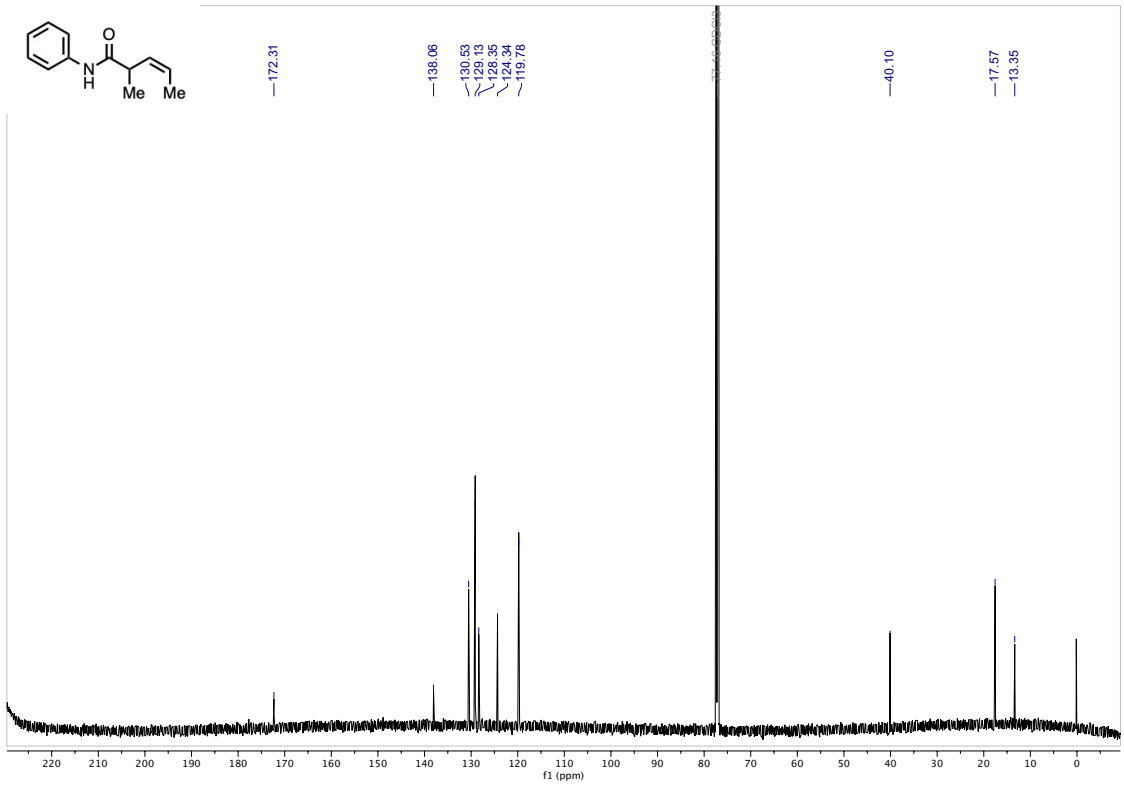


Figure S67: ^{1}H NMR of **3n**. 600 MHz, $CDCl_3$, 25 °C

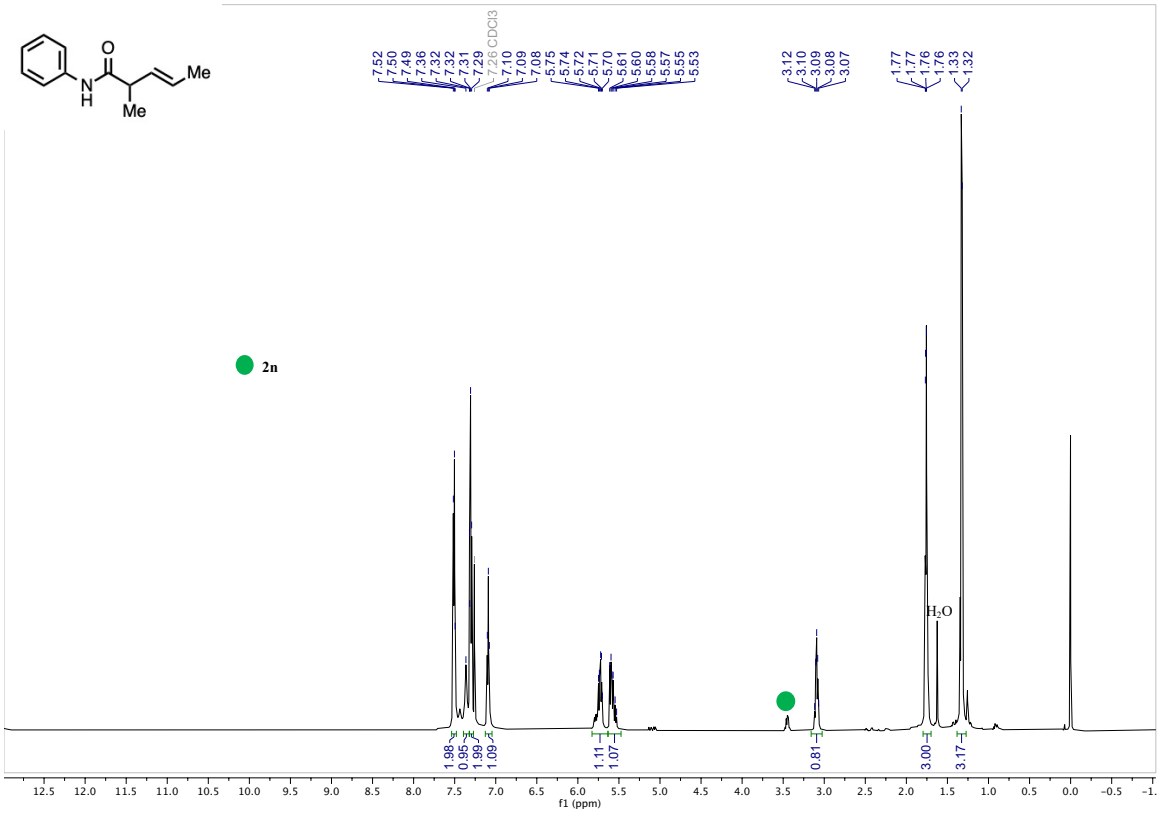


Figure S68: ^{13}C NMR of **3n**. 151 MHz, $CDCl_3$, 25 °C

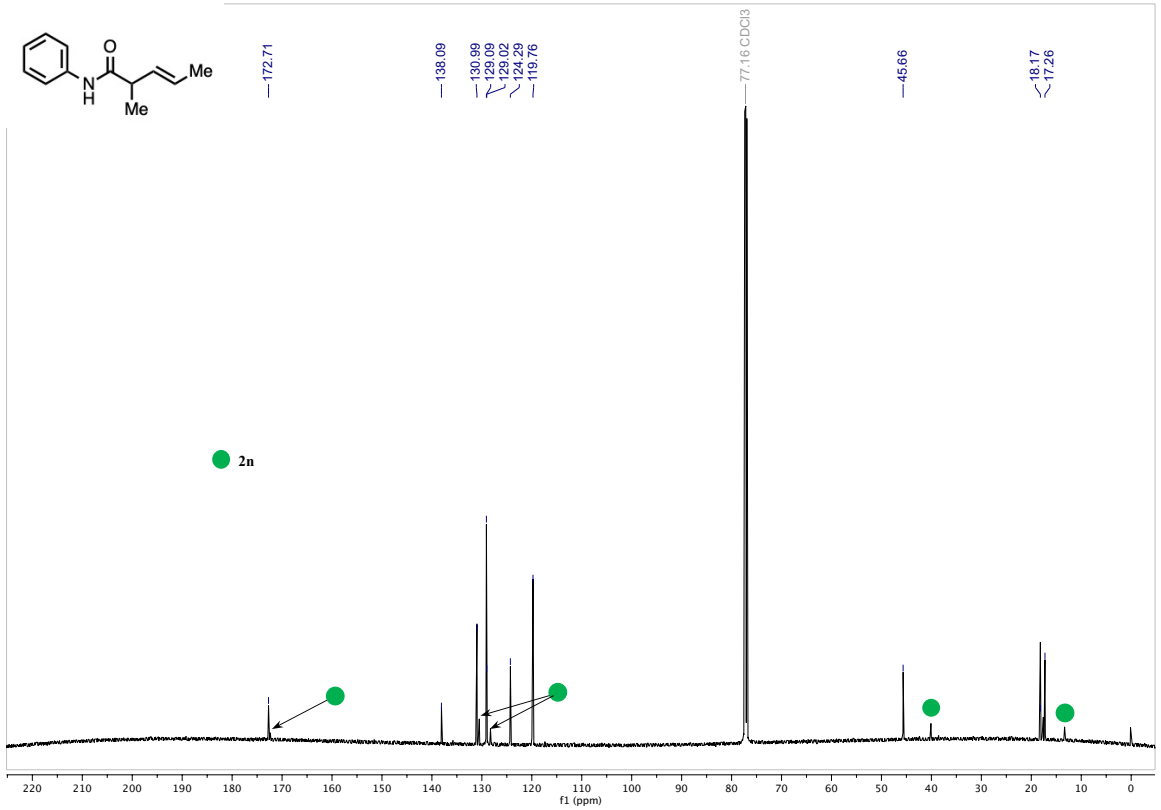


Figure S69: ^{1}H NMR of **2o**. 600 MHz, $CDCl_3$, 25 °C

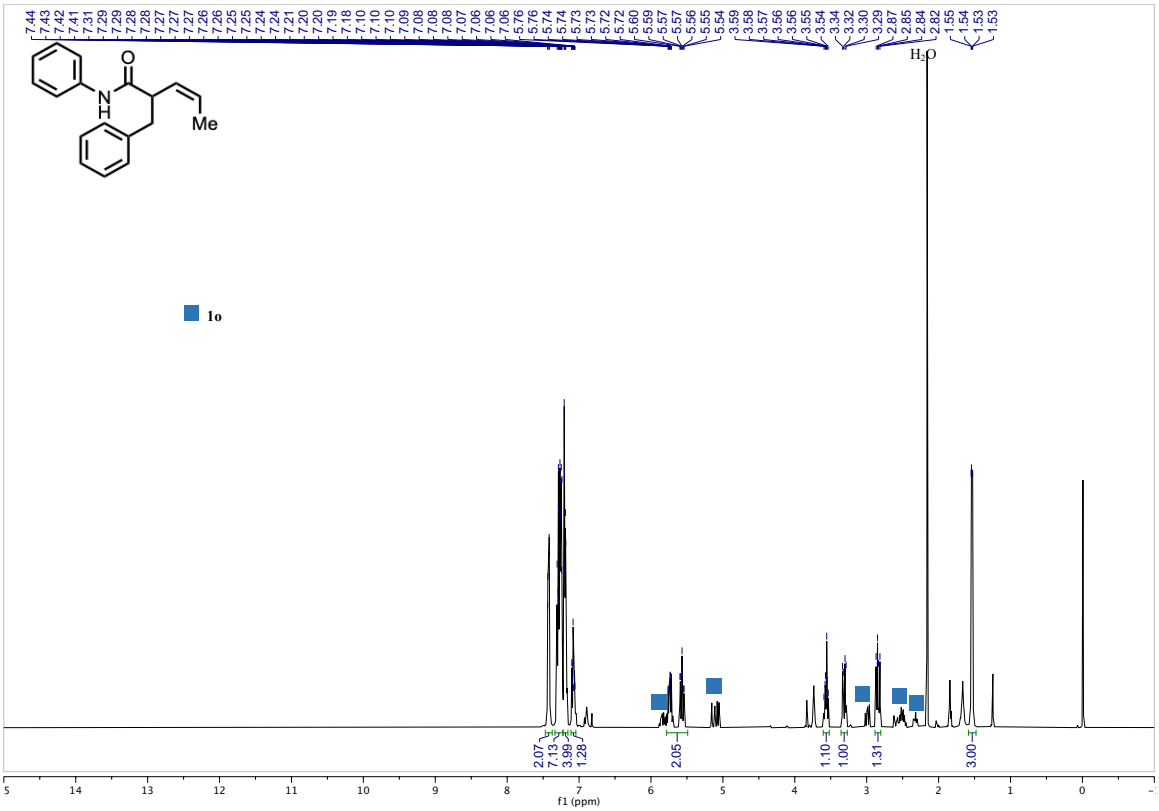


Figure S70: ^{13}C NMR of **2o**. 151 MHz, $CDCl_3$, 25 °C

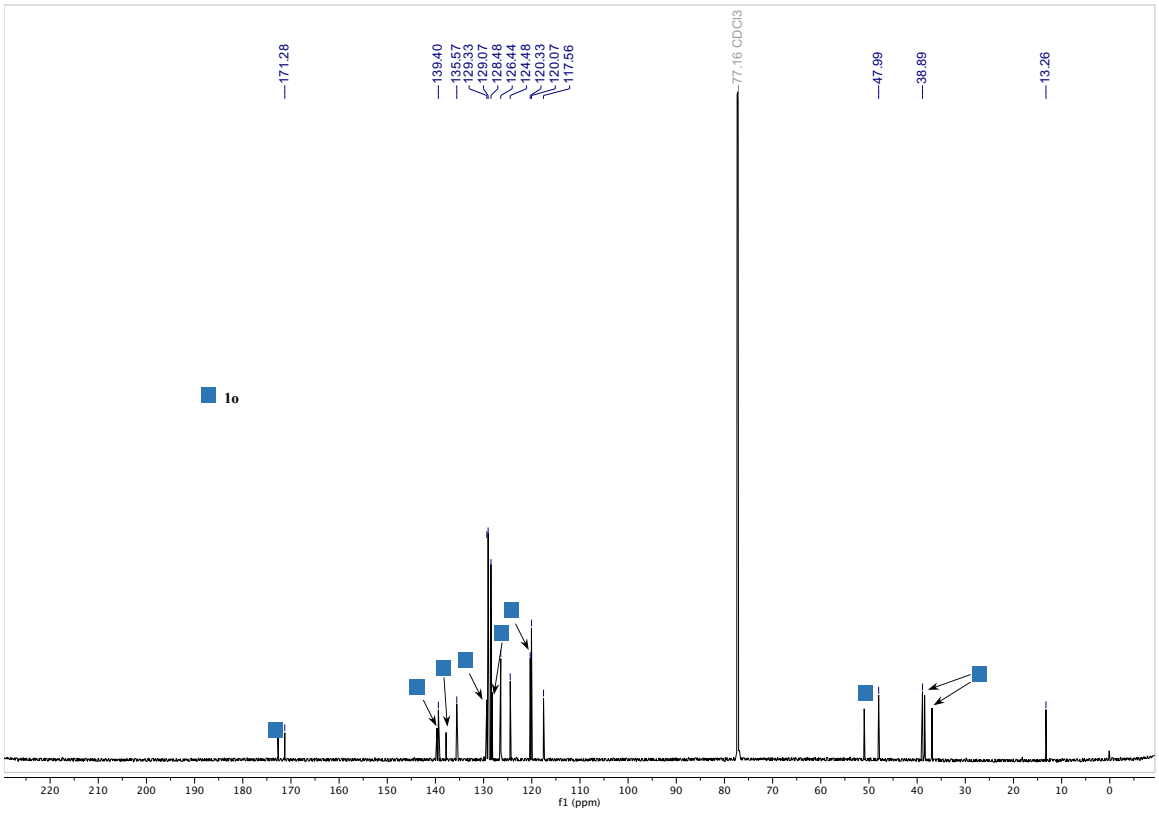


Figure S71: ^{1}H NMR of **3o**. 600 MHz, $CDCl_3$, 25 °C

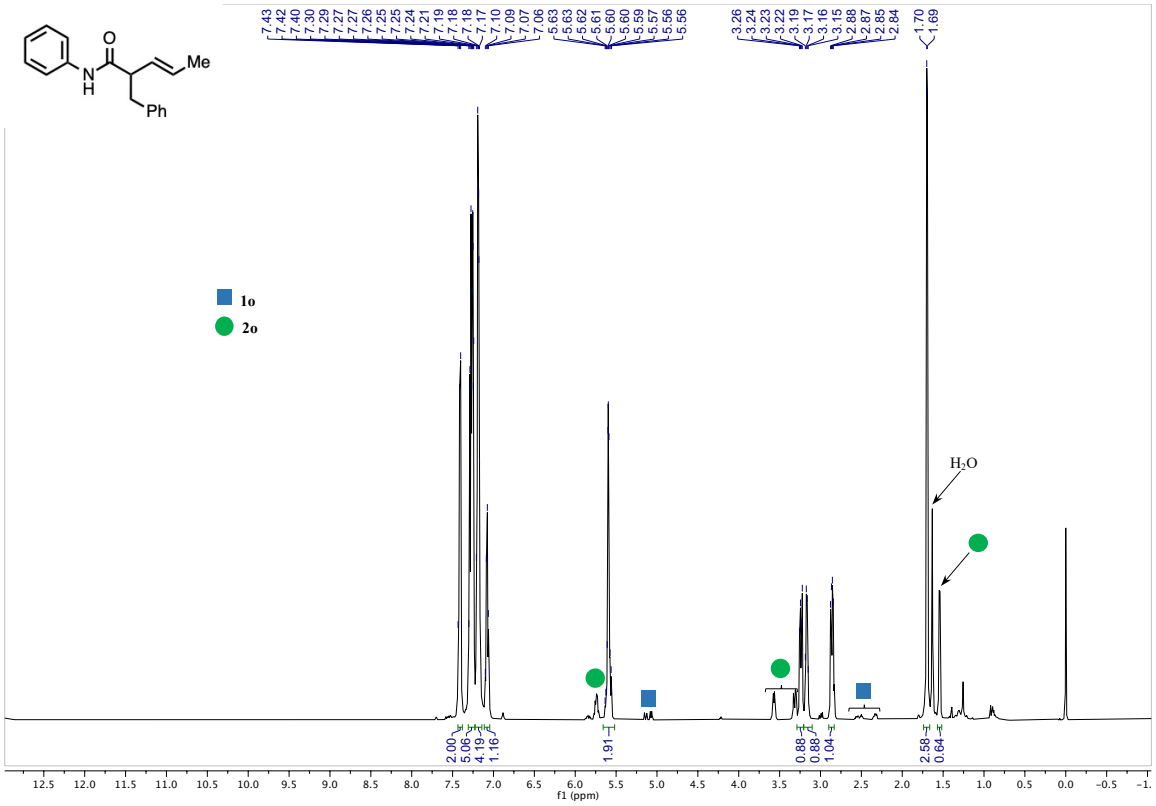


Figure S72: ^{13}C NMR of **3o**. 151 MHz, $CDCl_3$, 25 °C

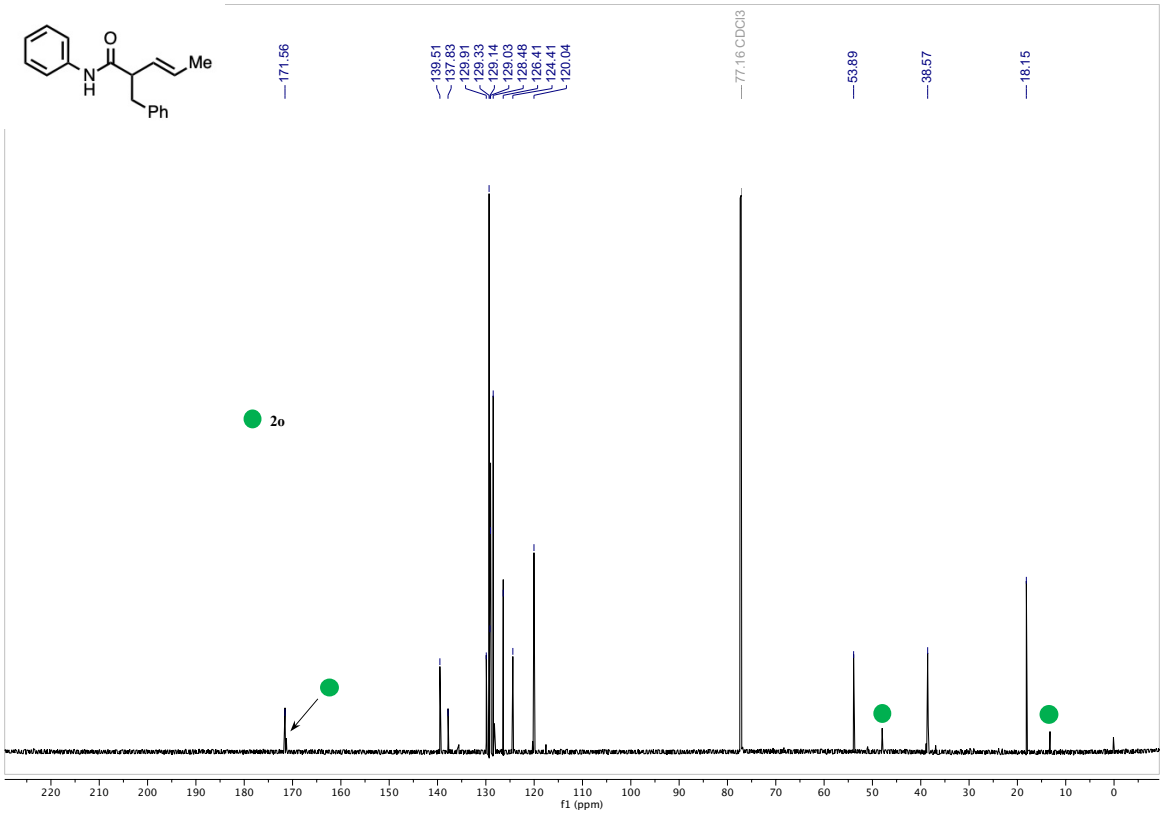


Figure S73: ^{1}H NMR of **2p**. 500 MHz, $CDCl_3$, 25 °C

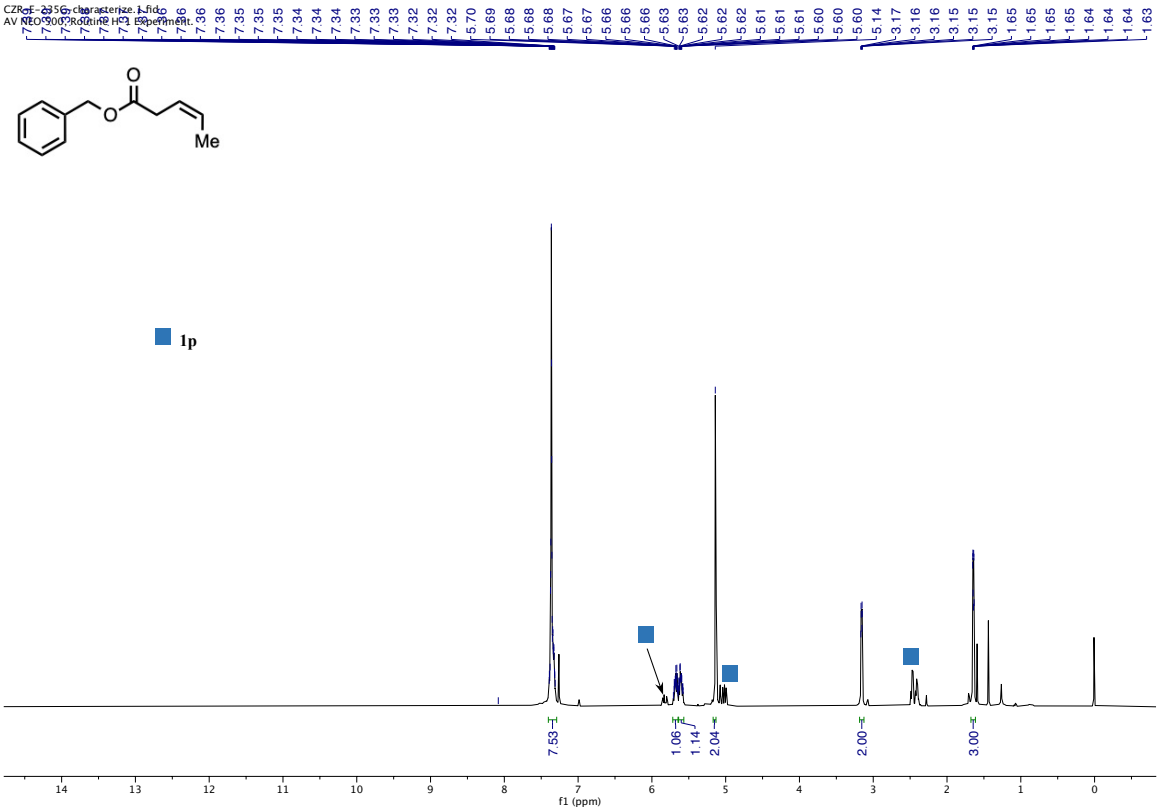


Figure S74: ^{13}C NMR of **2p**. 126 MHz, $CDCl_3$, 25 °C

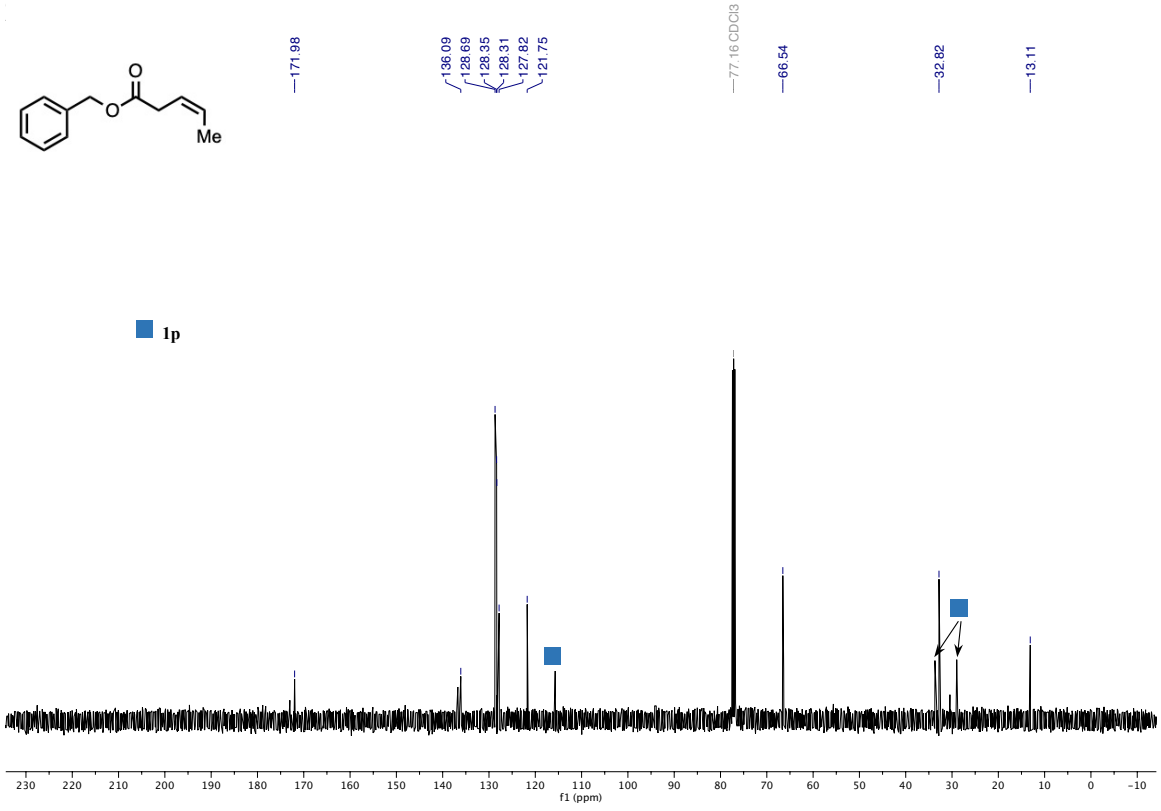


Figure S75: ^{1}H NMR of **3p**. 400 MHz, $CDCl_3$, 25 °C

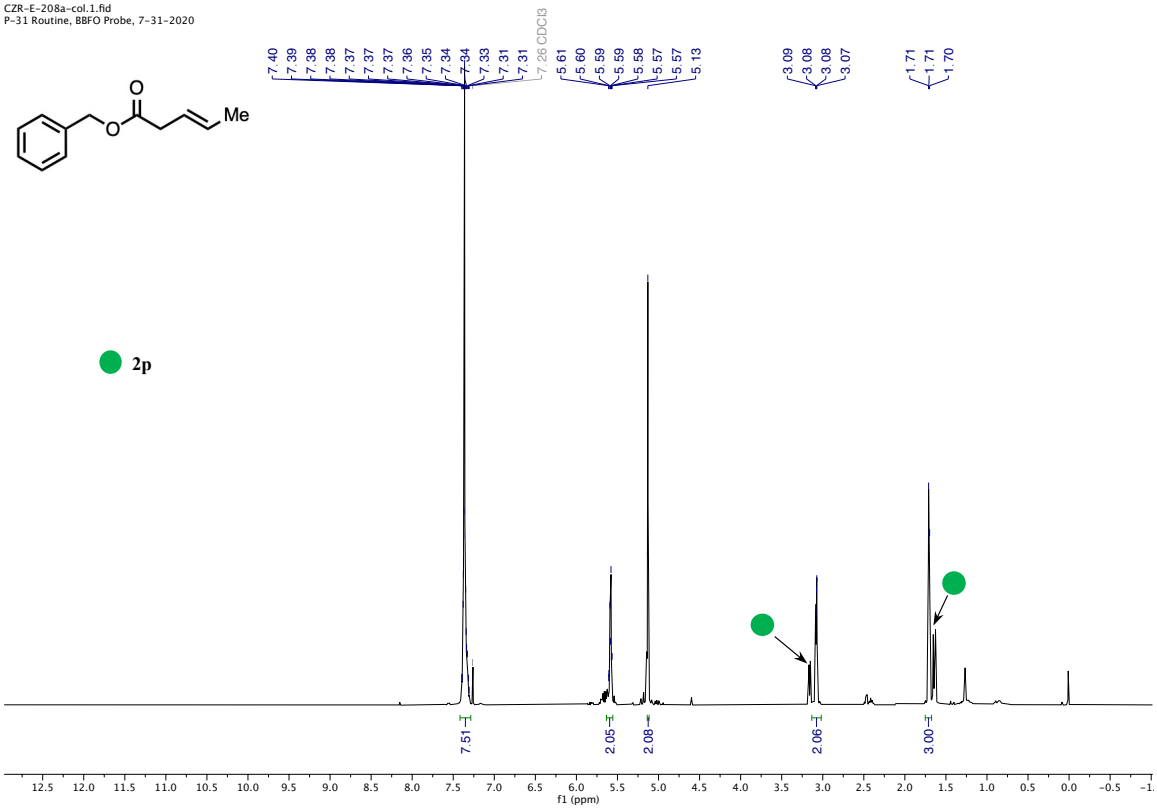


Figure S76: ^{13}C NMR of **3p**. 151 MHz, $CDCl_3$, 25 °C

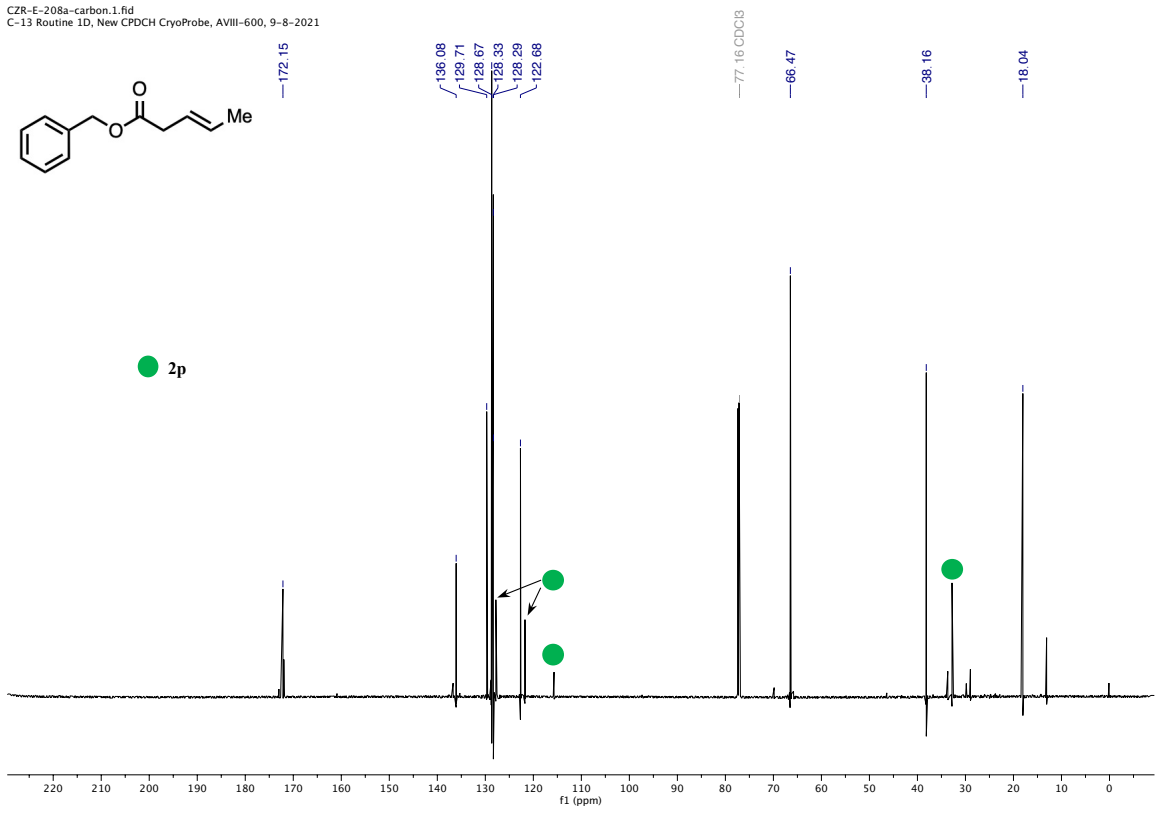


Figure S77: ^{1}H NMR of **2q**. 500 MHz, $CDCl_3$, 25 °C

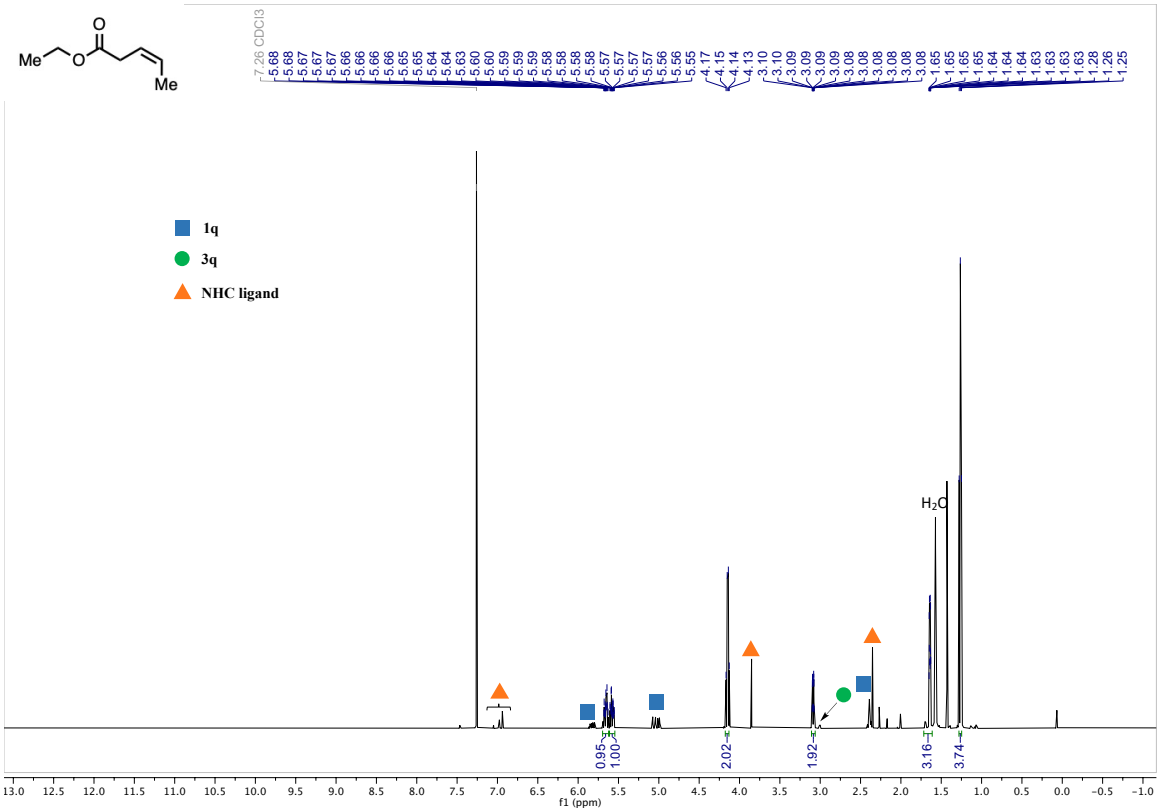


Figure S78: ^{13}C NMR of **2q**. 126 MHz, $CDCl_3$, 25 °C

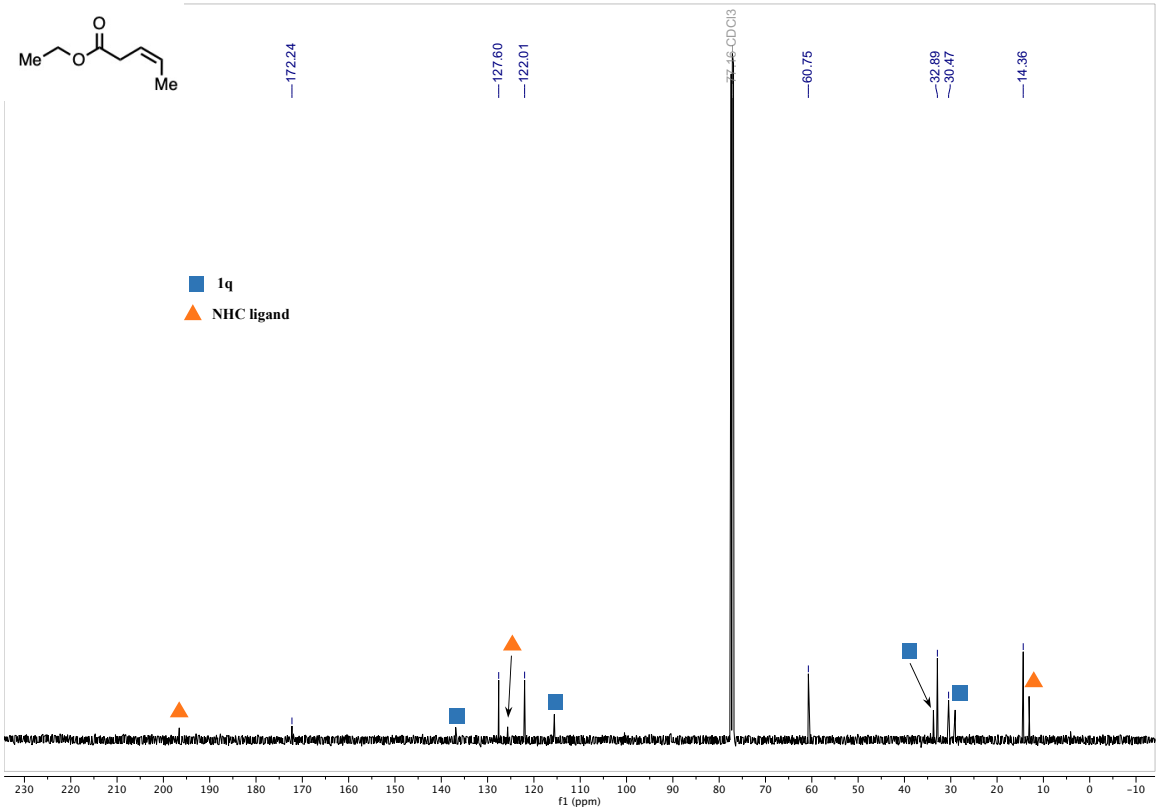


Figure S79: ^{1}H NMR of **3q**. 400 MHz, $CDCl_3$, 25 °C

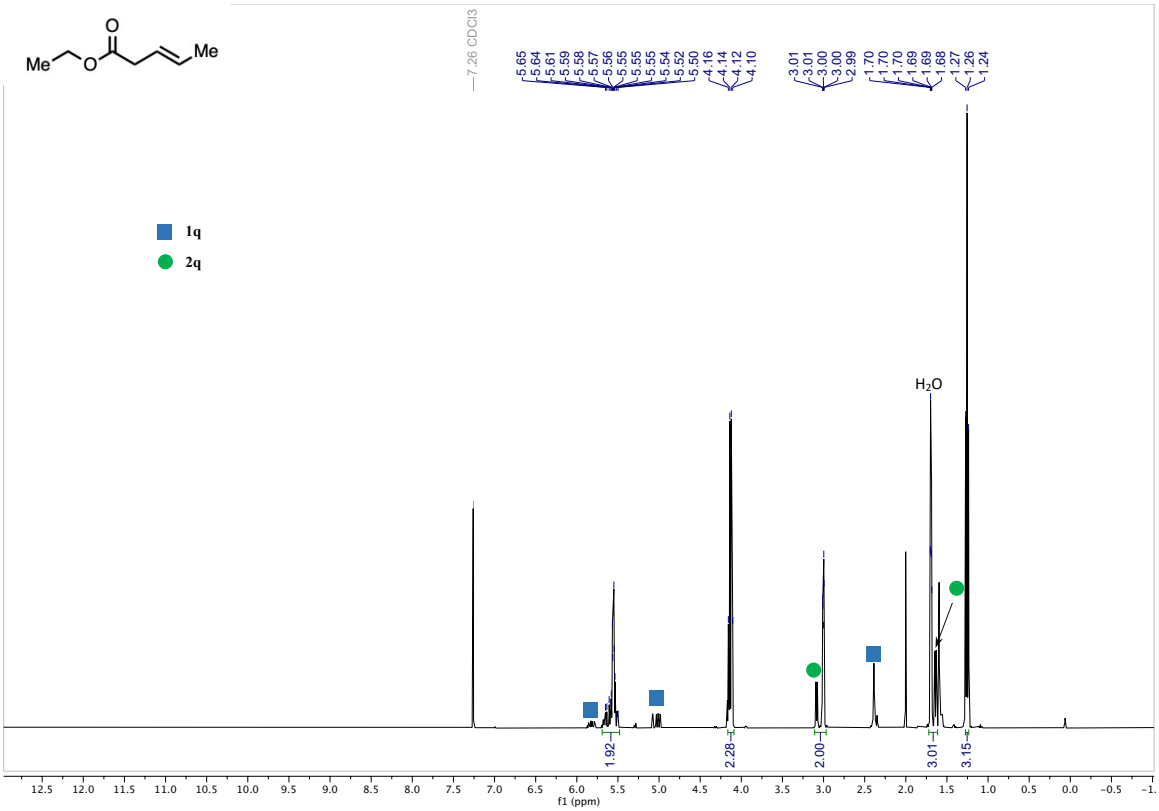


Figure S80: ^{13}C NMR of **3q**. 126 MHz, $CDCl_3$, 25 °C

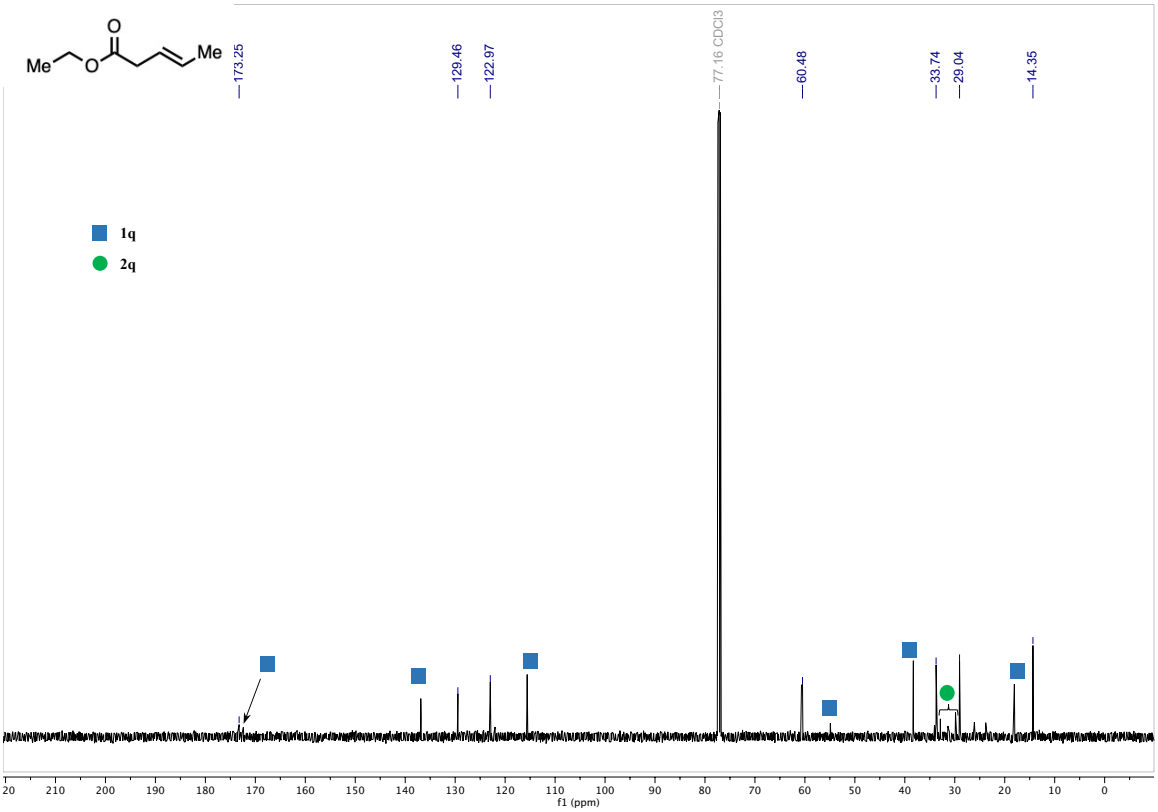


Figure S81: ^{1}H NMR of **2r**. 500 MHz, $CDCl_3$, 25 °C

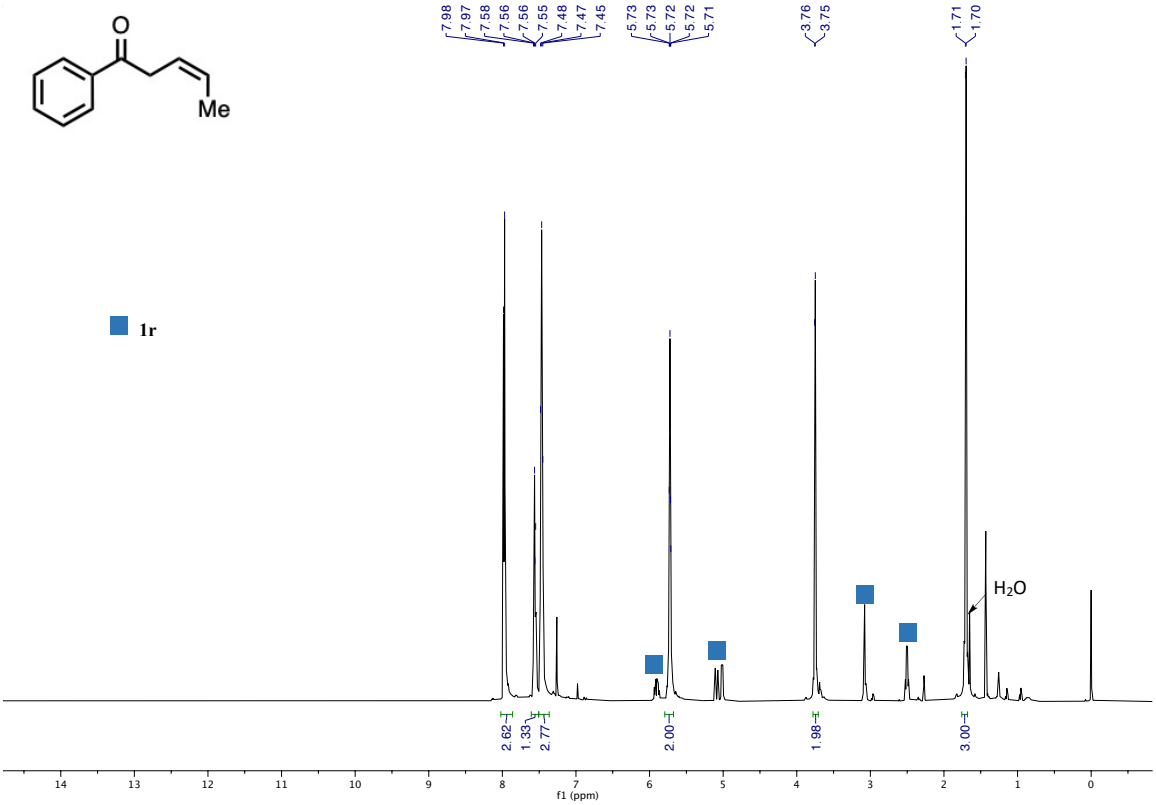


Figure S82: ^{13}C NMR of **2r**. 126 MHz, $CDCl_3$, 25 °C

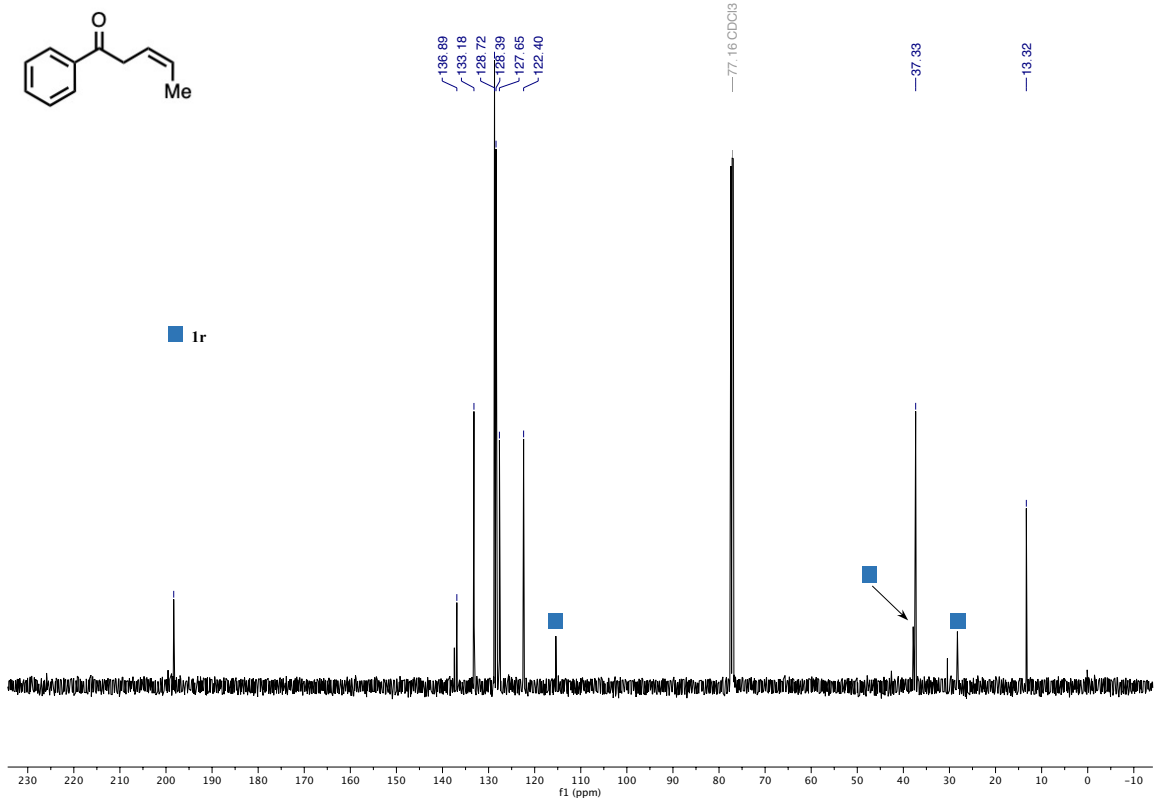


Figure S83: ^{1}H NMR of **3r**. 400 MHz, $CDCl_3$, 25 °C

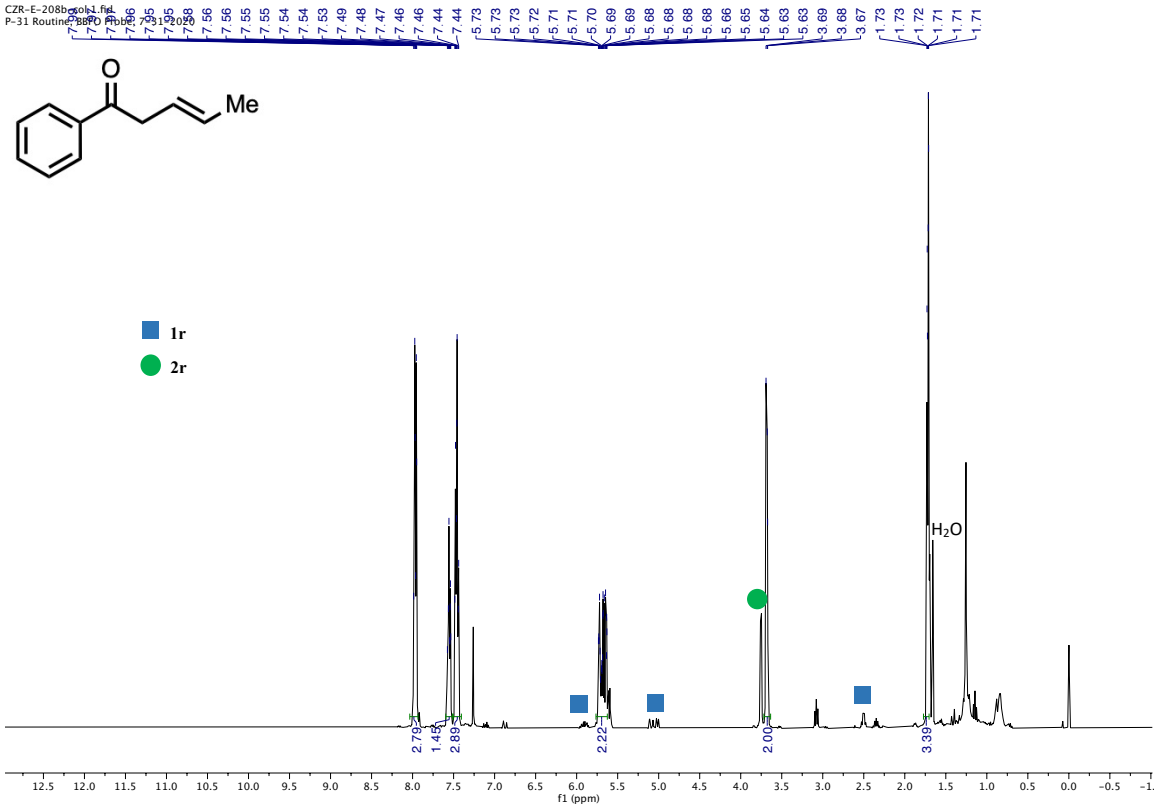


Figure S84: ^{13}C NMR of **3r**. 151 MHz, $CDCl_3$, 25 °C

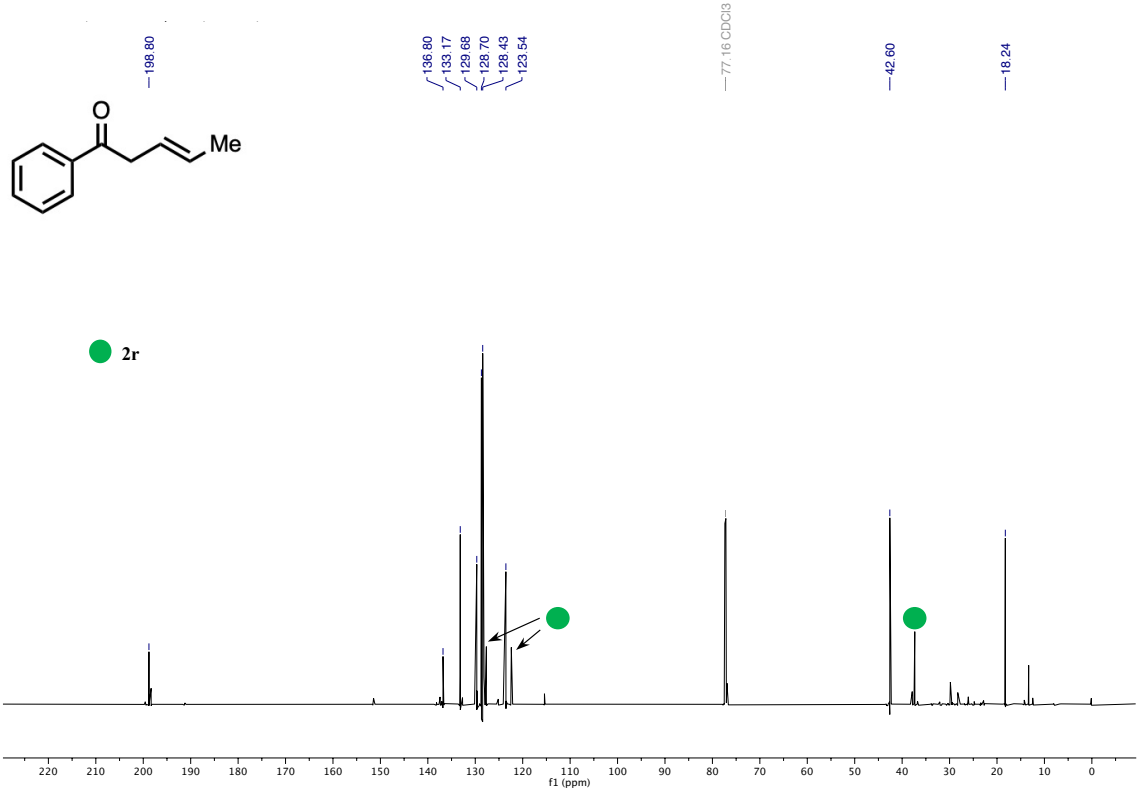


Figure S85: ^{1}H NMR of **2s**. 500 MHz, $CDCl_3$, 25 °C

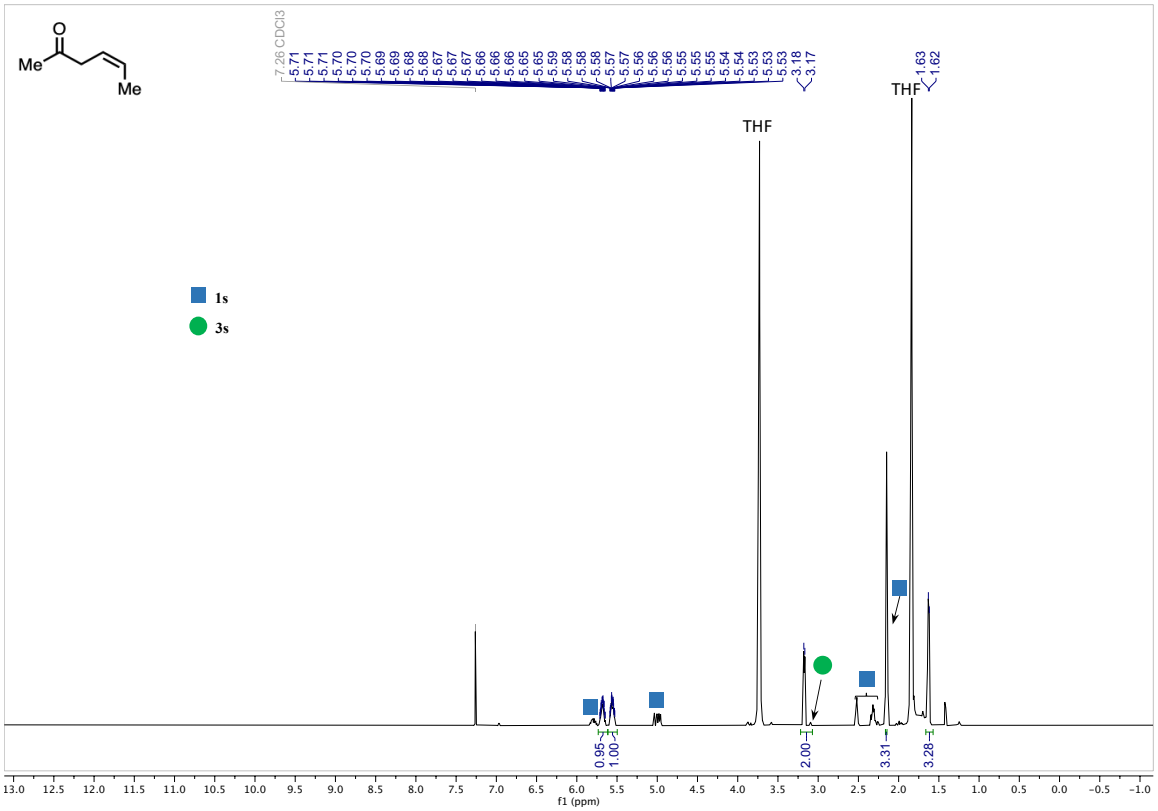


Figure S86: ^{13}C NMR of **2s**. 126 MHz, $CDCl_3$, 25 °C

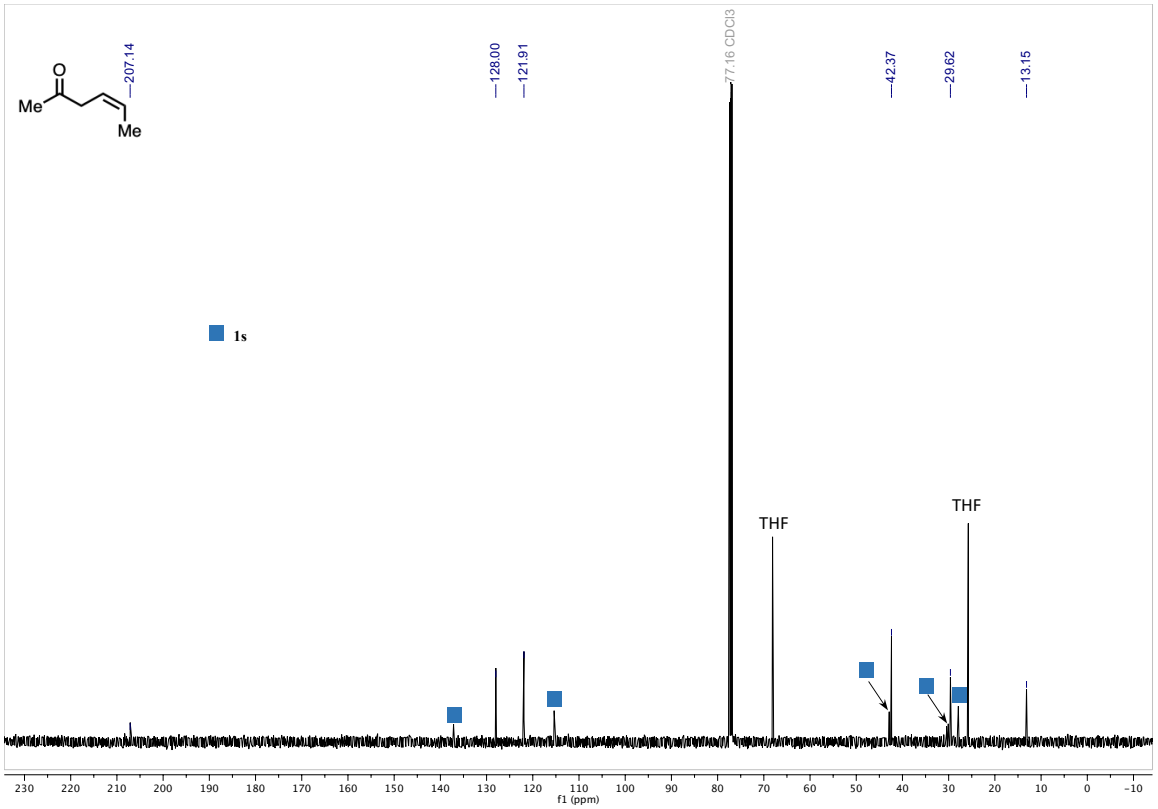


Figure S87: ^{1}H NMR of **3s**. 500 MHz, $CDCl_3$, 25 °C

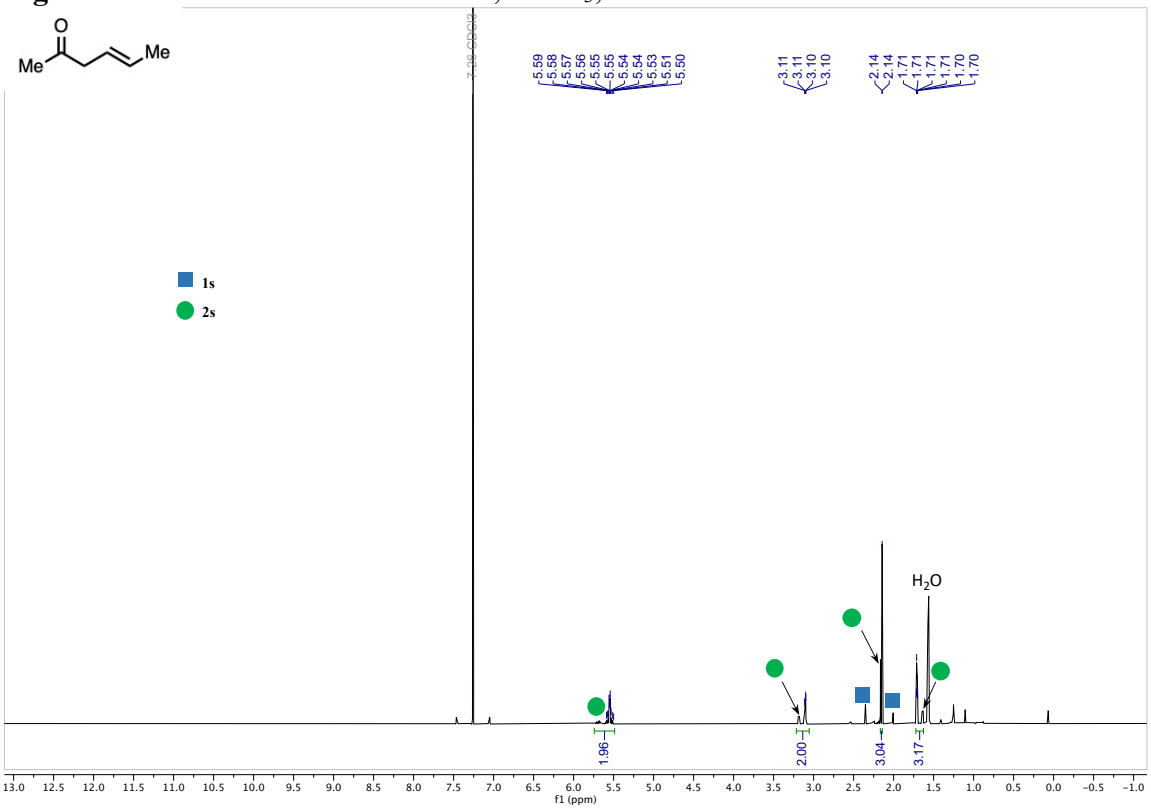


Figure S88: ^{13}C NMR of **3s**. 126 MHz, $CDCl_3$, 25 °C

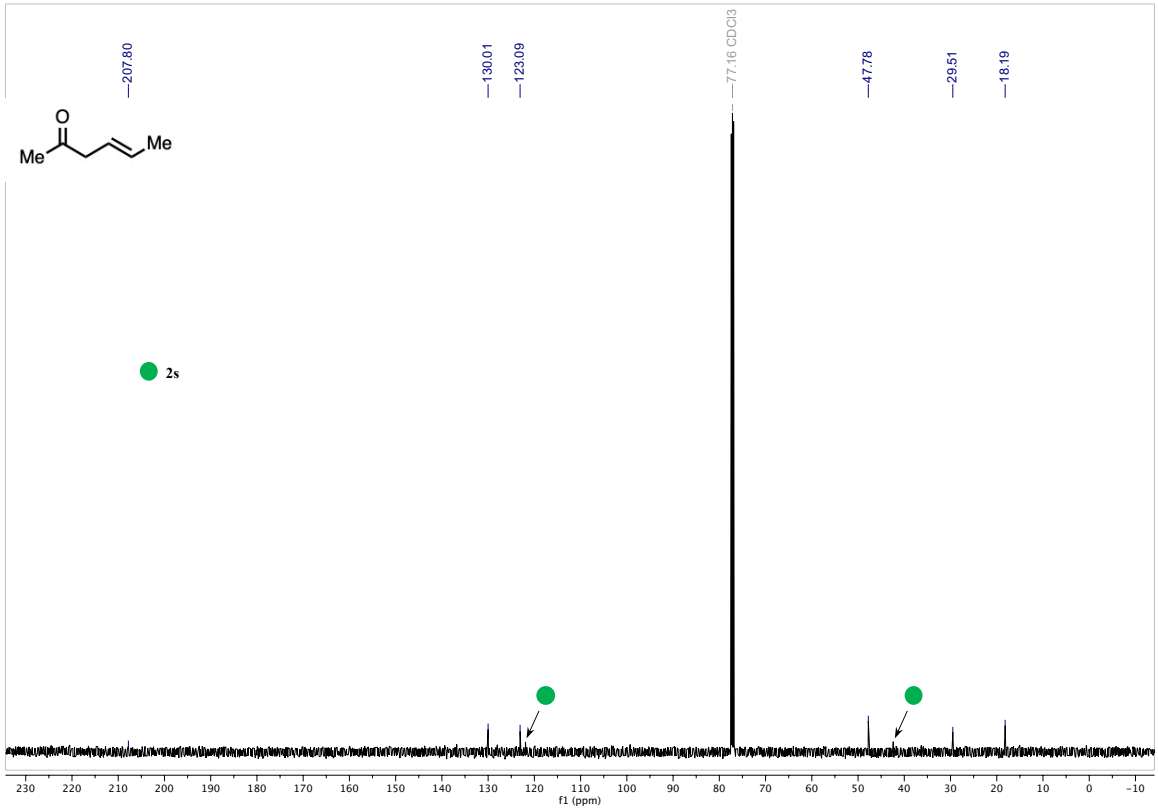


Figure S89: ^{1}H NMR of **4a**. 500 MHz, $CDCl_3$, 25 °C

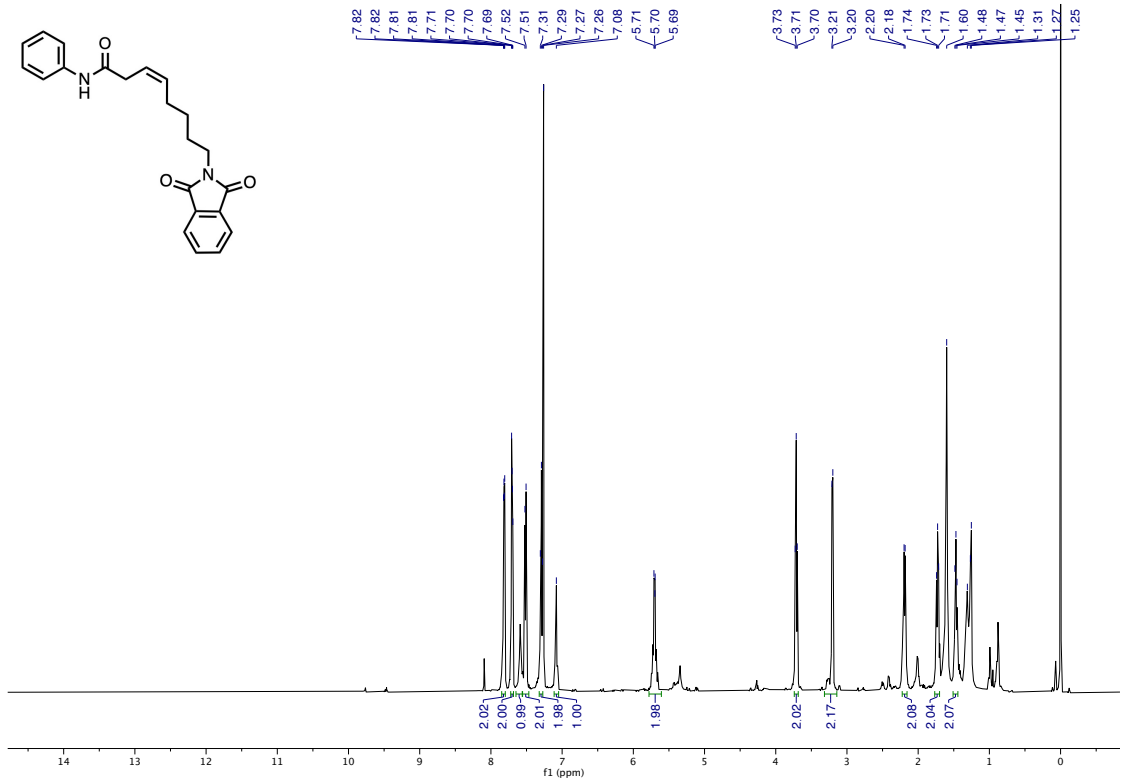


Figure S90: ^{13}C NMR of **4a**. 151 MHz, $CDCl_3$, 25 °C

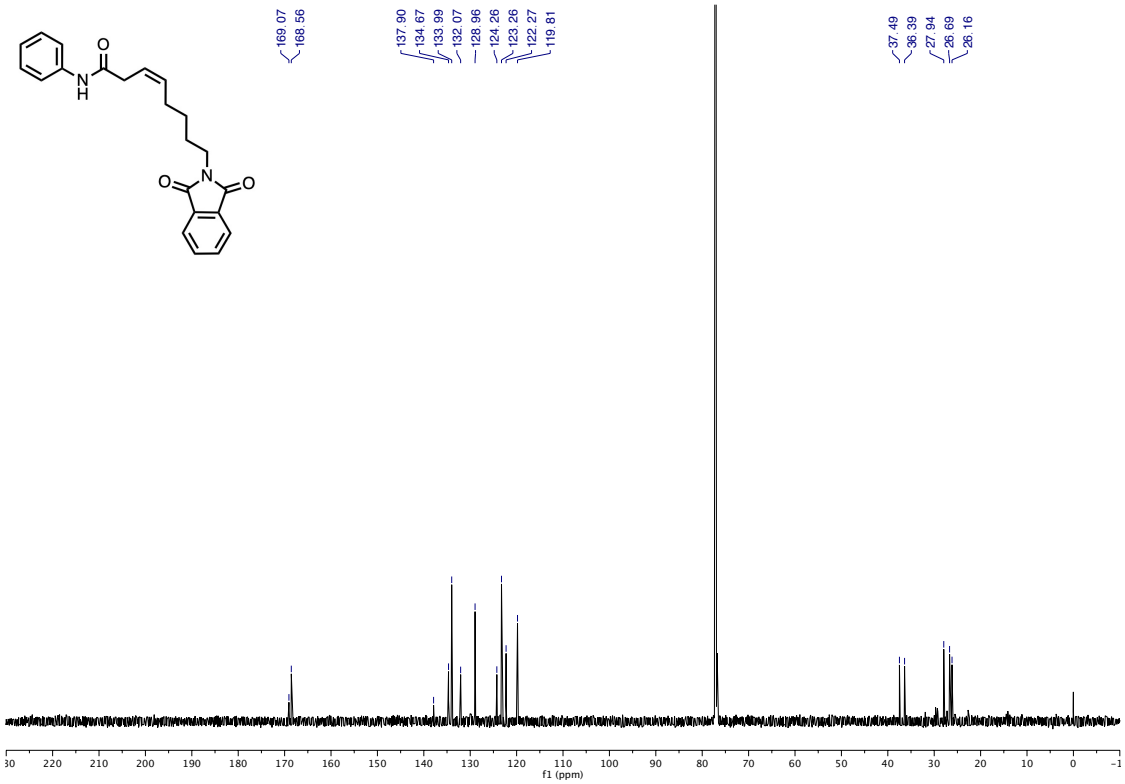


Figure S91: ^{1}H NMR of **5a**. 500 MHz, $CDCl_3$, 25 °C

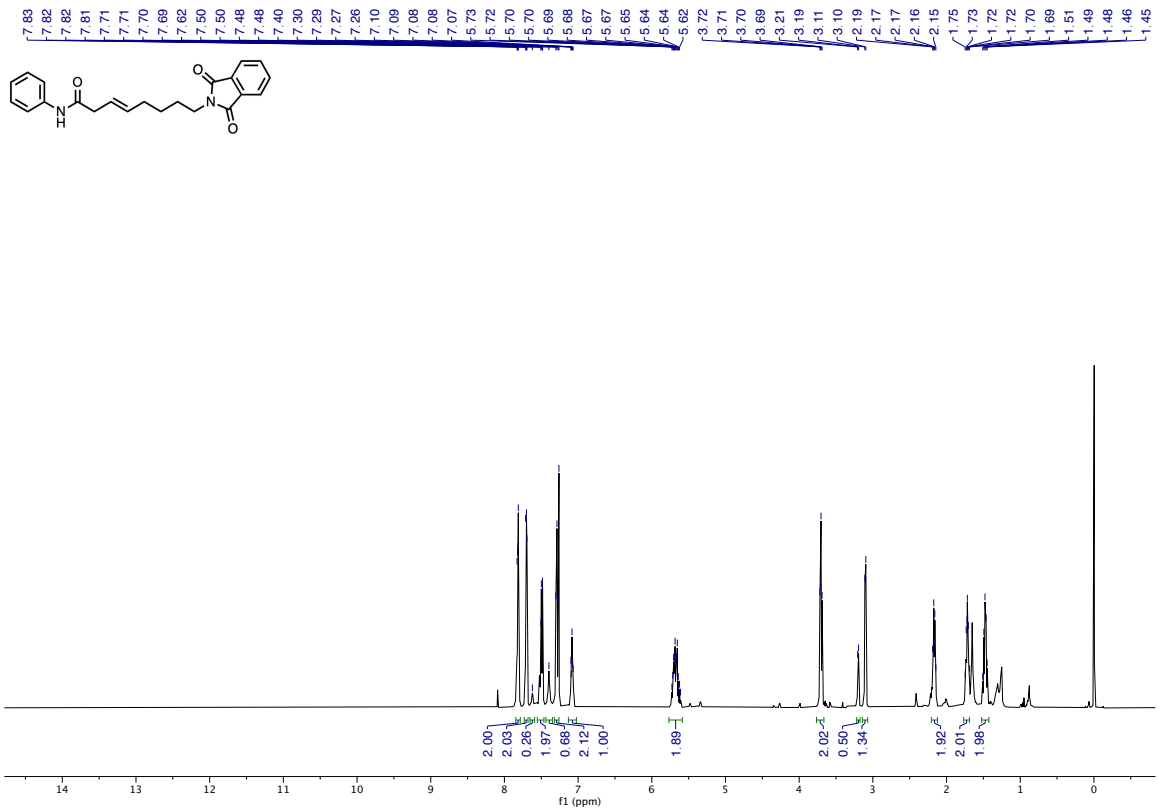


Figure S92: ^{13}C NMR of **5a**. 151 MHz, $CDCl_3$, 25 °C

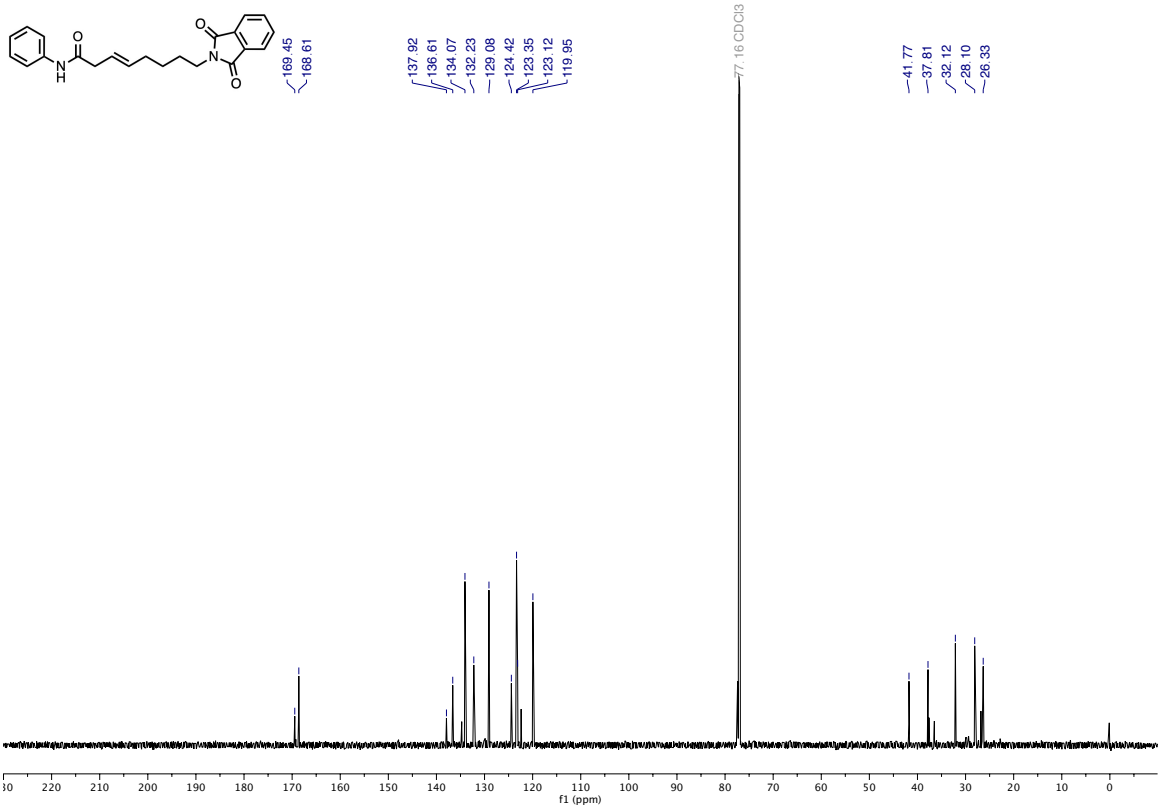


Figure S92: ^{1}H NMR of **4b**. 500 MHz, $CDCl_3$, 25 °C

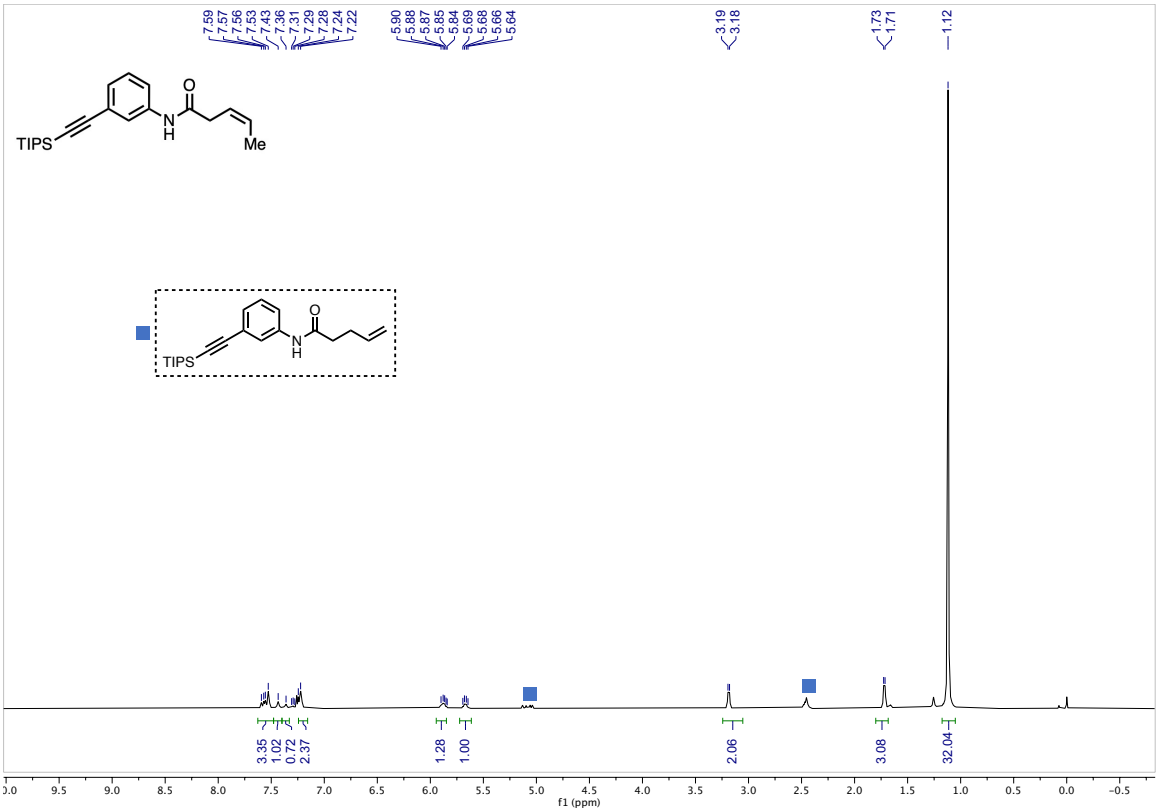


Figure S94: ^{13}C NMR of **4b**. 126 MHz, $CDCl_3$, 25 °C

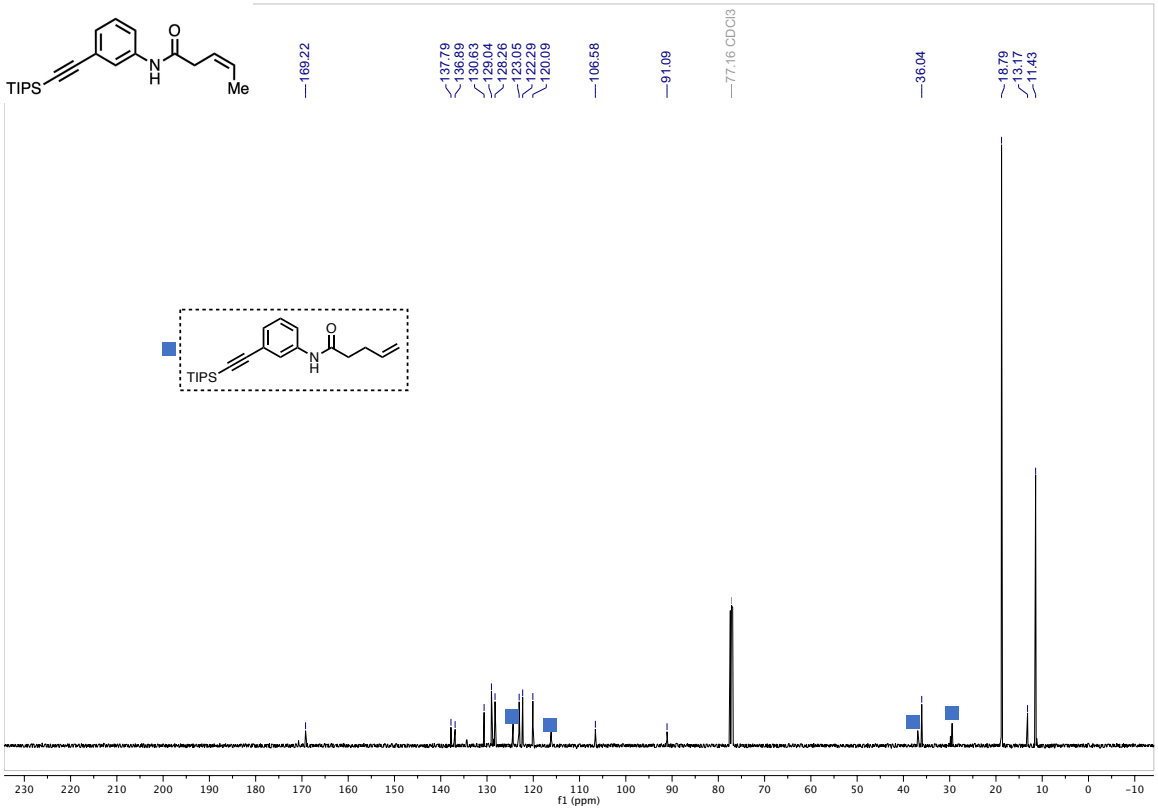


Figure S95: ^{1}H NMR of **5b**. 500 MHz, $CDCl_3$, 25 °C

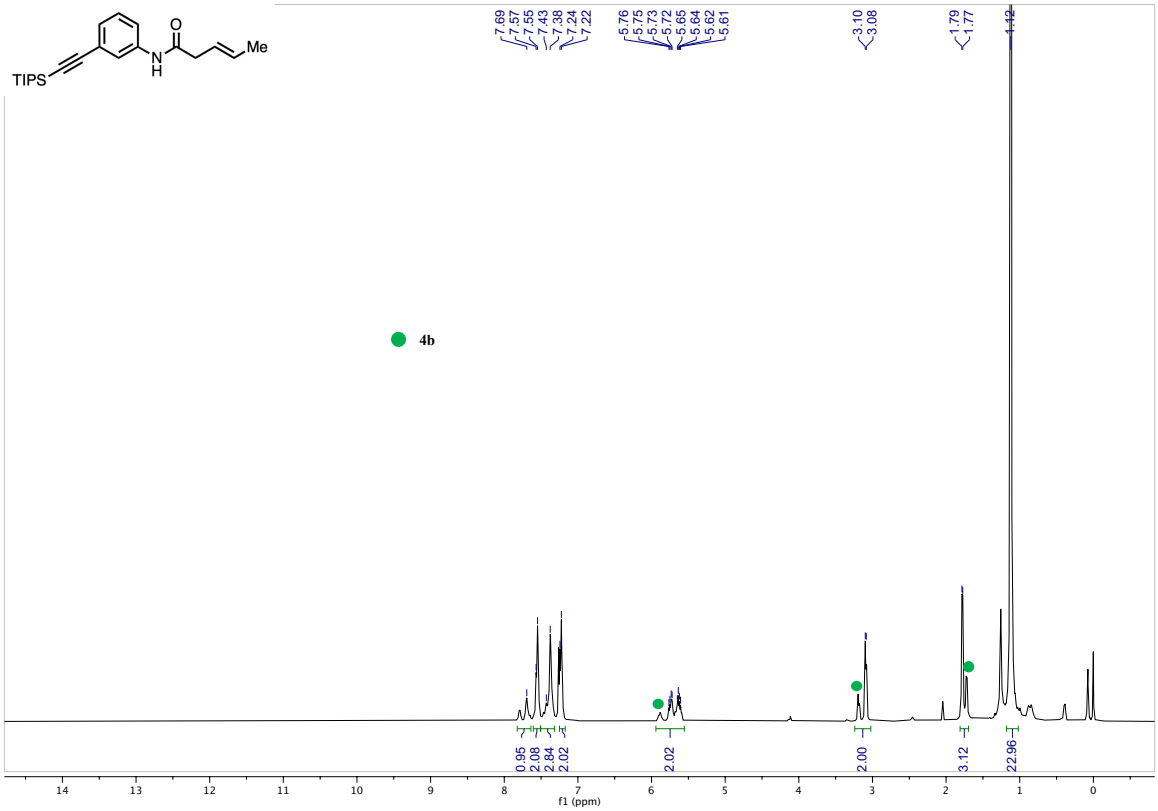


Figure S96: ^{13}C NMR of **5b**. 126 MHz, $CDCl_3$, 25 °C

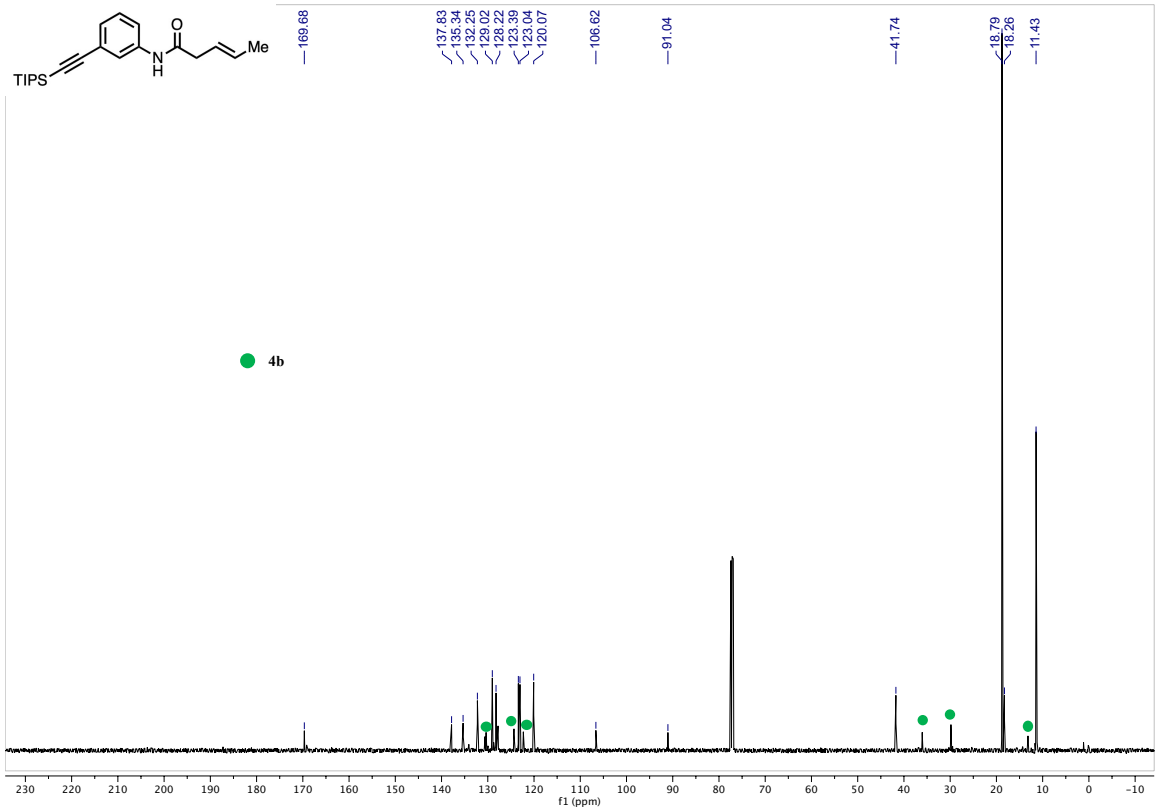


Figure S97: ^{1}H NMR of **1a-*d*$_1$**. $CDCl_3$, 25 °C

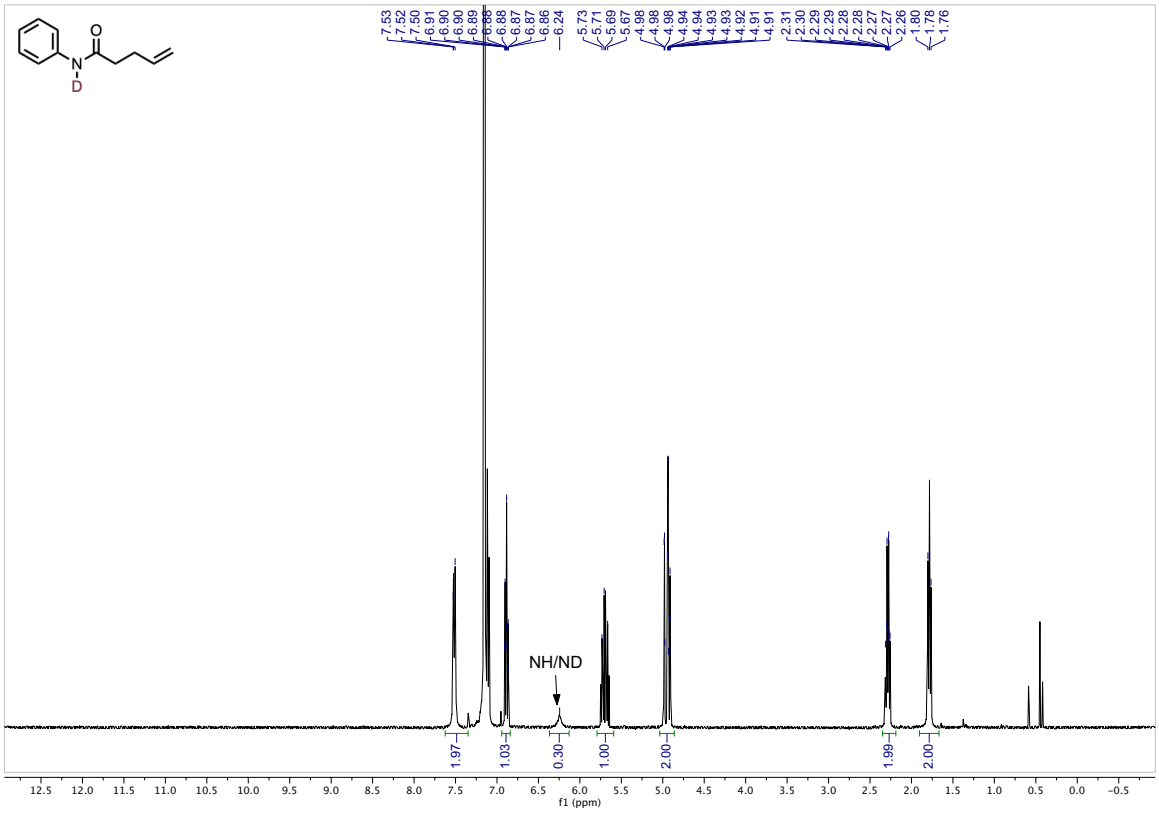


Figure S98: ^{1}H NMR of **W-S1**. 600 MHz, $CDCl_3$, 25 °C

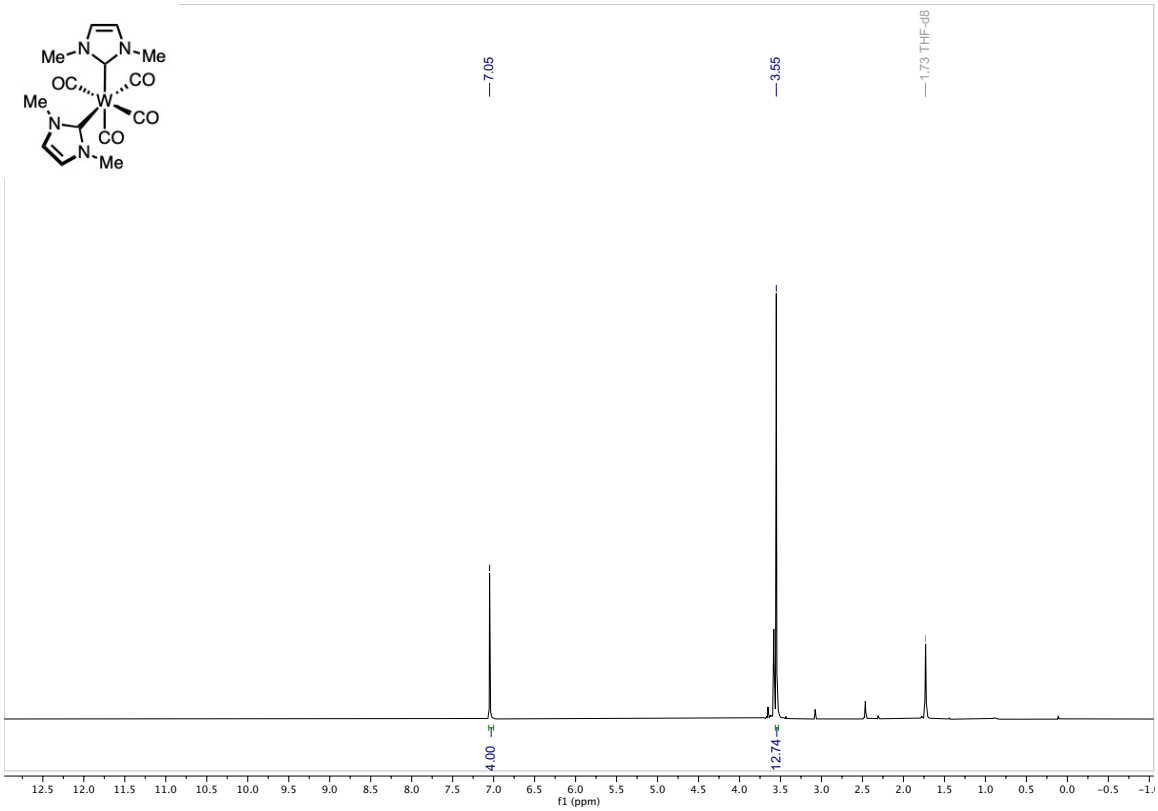
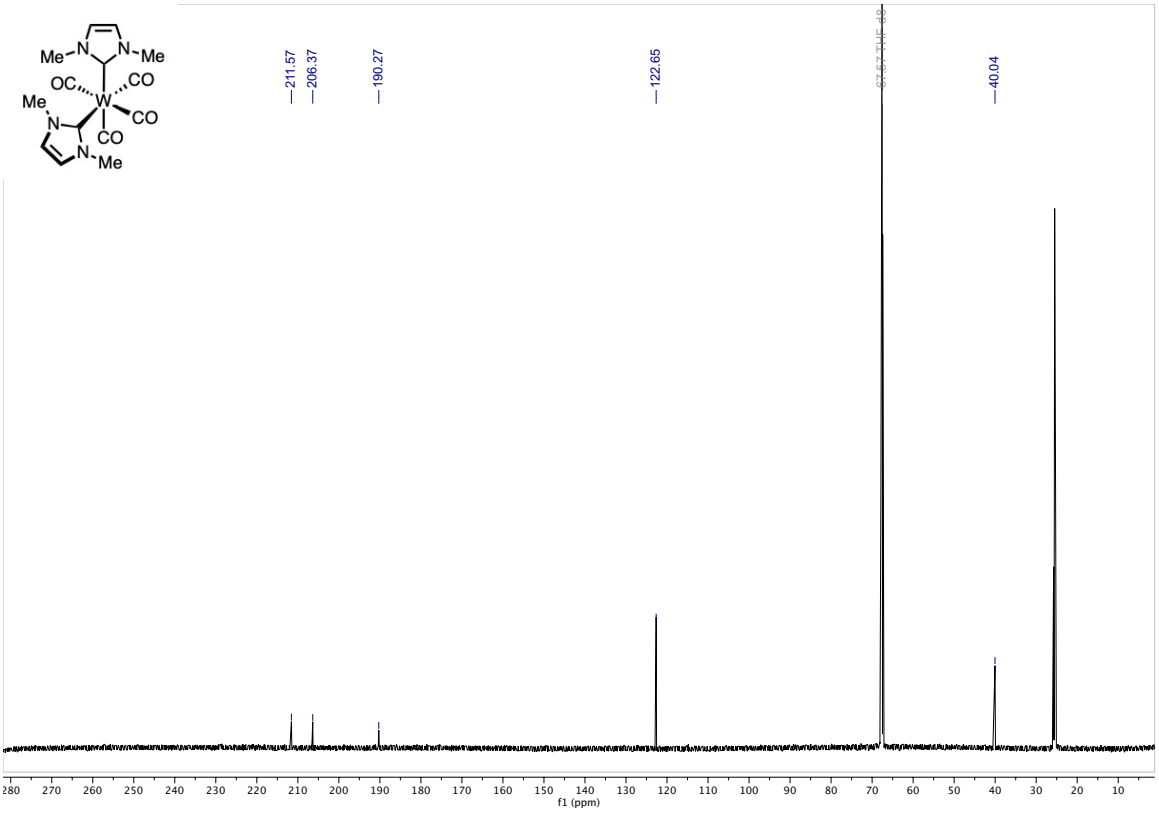


Figure S99: ^{13}C NMR of **W-S1**. 151 MHz, $CDCl_3$, 25 °C



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