## Supporting Information

# Rh(III)-Catalyzed Three-Component *syn*-Carboamination of Alkenes Using Arylboronic Acids and Dioxazolones

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# Contents

## 1. General information

All reactions were carried out using oven-dried glassware with magnetic stirring unless otherwise noted. Anhydrous solvents and reagents were purchased from commercial sources and used without further purification. Flash chromatography was conducted either manually on SiliCycle® SilicaFlash® P60 (230-400 mesh) silica gel, SiliCycle® prep TLC (TLG-R10011B-341, thickness 1000um) or automatically *via* a Teledyne Isco Lumen CombiFlash with RediSep Rf Disposable Flash columns. Thin layer chromatography (TLC) was performed on Silicycle 250μm silica gel 60 Å plates. Visualization was accomplished with UV light (254 nm) and $KMnO_4$. $^1H$, $^{19}F$ NMR, and $^{13}C$ NMR spectra were collected at ambient temperature on Bruker 400 MHz or Bruker Avance III 500 MHz spectrometers unless otherwise noted. Chemical shifts ($\delta$) are reported in parts per million (ppm), coupling constants ($J$) are reported in Hz, and multiplicity is described using the following abbreviations: singlet (s), broad (b), multiplet (m), doublet (d), triplet (t), quartet (q), or combinations thereof. $^1H$ NMR spectra were referenced to 7.26 ppm ($CHCl_3$) or 0.0 ppm (TMS). $^{13}C$ NMR spectra were referenced to 77.16 ppm ($CDCl_3$) and all peaks given are singlet unless otherwise noted. Diastereomeric and regioisomeric ratios were measured by integration of $^1H$ NMR spectra of product mixtures prior to purification. High resolution mass spectra (HRMS) were obtained from Columbia University Mass Spectrometry Facility on a JOEL JMSHX110HF mass spectrometer using the ASAP ionization model. Infrared spectra were collected on a Perkin Elmer Spectrum Two FT-IR Spectrometer.

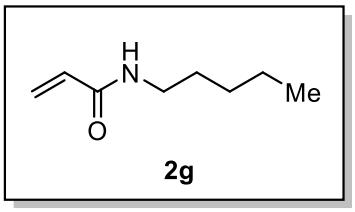
## 2. Preparation of Starting Materials

All boronic acids (**1a**-**1r**), alkenes **2b**, **2c**, **2d**, **2e**, and **2i** were purchased from commercial sources and used without purification. Alkene **2f**,[1] **2j**,[2] **2k**,[3] **2l**[4], **2m**[5] and dioxazolone **3c**,[6] **3d**,[7] **3e**,[8] **3f**,[7] **3g**,[6] and **3h**[7] were synthesized following literatures. Alkenes **2g**, **2h**, and dioxazolone **3b** were synthesized following the procedures below.

**General procedure A: the synthesis of acrylamides (2g-2h)**

To a solution of primary amine (or corresponding HCl salt, 1 equiv) and triethylamine (1.1 equiv) in dichloromethane (0.5 M) was added acryloyl chloride (1.1 equiv) in dichloromethane at 0 °C. The mixture was stirred at 0 °C for 15 minutes and warmed to room temperature. The reaction was stirred at room temperature for 3 hours. The volatiles was removed by a rotary evaporator then ethyl acetate was added and filtered through celite. The filtrate was washed with 1M HCl, saturated $NaHCO_3$ solution, and brine.

The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/ethyl acetate) to afford the corresponding acrylamides.




**2g**

**Yield**: Prepared according to general procedure **A** from 1-aminopentane (10 mmol). 78%, 1.11g, colorless oil.

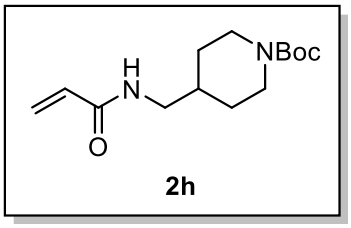
$\mathbf{R_f}$ = 0.39 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 6.23 (d, $J$ = 17.1 Hz, 1H), 6.11 (dd, $J$ = 17.0, 10.2 Hz, 1H), 6.05 (s, 1H), 5.58 (dt, $J$ = 10.0 Hz, 1H), 3.28 (q, $J$ = 7.3, 6.7 Hz, 2H), 1.50 (q, $J$ = 7.2 Hz, 2H), 1.36 – 1.21 (m, 4H), 0.87 (t, $J$ = 6.8, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.75, 131.22, 125.99, 39.70, 29.33, 29.18, 22.43, 14.04.

**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3276, 3079, 2957, 2929, 2861, 1656, 1623, 1548, 1407, 1245, 985, 954, 727.

**HRMS** (ASAP) m/z $[C_8H_{16}NO]^+$ ($[M+H]^+$) calculated 142.1232, found 142.1236.




**2h**

**Yield**: Prepared according to general procedure **A** from 1-Boc-4-(aminomethyl)piperidine (10 mmol). 65%, 1.74g, colorless oil.

$\mathbf{R_f}$ = 0.18 (EA/Hex 2:3).

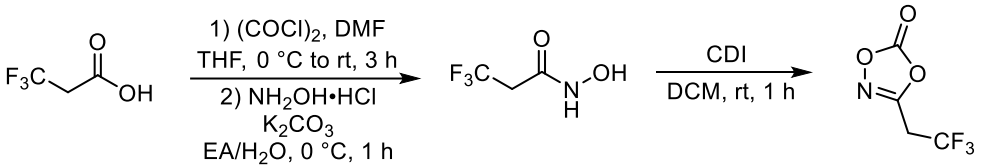
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 6.26 (dd, $J$ = 17.0, 1.6 Hz, 1H), 6.10 (dd, $J$ = 17.0, 10.2 Hz, 1H), 6.06 (s, 1H), 5.61 (dd, $J$ = 10.2, 1.6 Hz, 1H), 4.16 – 3.97 (m, 2H), 3.30 – 3.12 (m, 2H), 2.65 (t, $J$ = 12.7 Hz, 2H), 1.73 – 1.61 (m, 3H), 1.42 (s, 9H), 1.19 – 1.04 (m, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 165.82, 154.95, 130.86, 126.74, 79.57, 45.10, 43.76, 36.57, 29.92, 28.59.

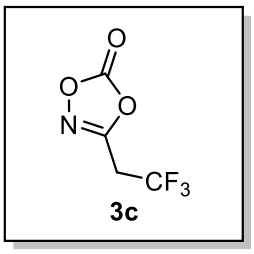
**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3302, 3080, 2976, 2926, 2854, 2244, 1658, 1546, 1424, 1365, 1226, 1167, 1143, 906, 727, 647.

**HRMS** (ESI) m/z $[C_{14}H_{24}N_2NaO_3]^+$ ($[M+Na]^+$) calculated 291.1685, found 291.1699.

**Preparation of 3c**




Oxalyl chloride (9.8 mmol, 0.98 equiv) and catalytic amount (5 – 10 drops) of DMF were added dropwise to a solution of 3,3,3-trifluoropropanoic acid (10 mmol, 1.0 equiv) in THF (0.3 M) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 hours. After the full conversion of acid, the crude material was taken without concentration. In a separate flask, hydroxylamine hydrochloride (11 mmol, 1.1 equiv) was dissolved in 0.1 M of ethyl acetate/$H_2O$ 2:1 biphasic mixture. $K_2CO_3$ (20 mmol, 2 equiv) was added to the solution and cooled to 0 °C. The crude THF solution of acid chloride was added dropwise to the mixture and stirred for 1 hour at 0 °C. After completion of the reaction, the reaction mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was used without further purification. To a solution of 3,3,3-trifluoro-*N*-hydroxypropanamide (3.22 mmol, 1.0 equiv) in DCM (0.2 M), CDI (3.53 mmol, 1.2 equiv) was added as one portion. After stirring for 1 hour at room temperature, the reaction was quenched with 1 M HCl and extracted with DCM three times. The combined organic layer was washed with brine and dried over sodium sulfate. The solvent was removed under reduced pressure to afford 3-(2,2,2-trifluoroethyl)-1,4,2-dioxazol-5-one (**3c**). No further purification was required.



**3c**

**Yield**: 44% (over 2 steps), 2.05 mmol, 346 mg, colorless oil.

**$^{1}$H NMR** (400 MHz, $CDCl_3$) $\delta$ 3.56 (q, $J$ = 9.1 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 158.61 (q, $J$ = 3.9 Hz), 153.03, 122.37 (q, $J$ = 278.2 Hz), 31.48 (q, $J$ = 34.9 Hz).

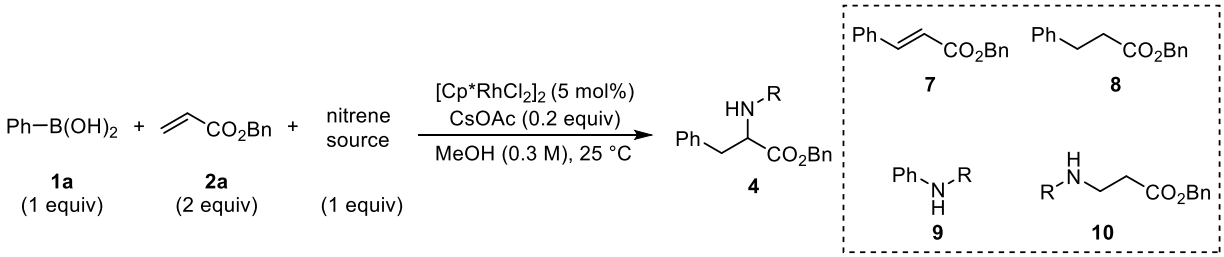
**$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ -63.40 (t, $J$ = 9.1 Hz).

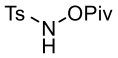
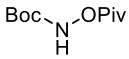
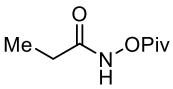
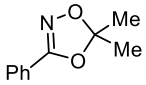
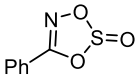
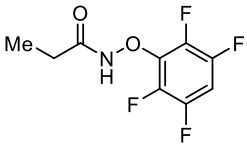
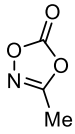
## 3. General procedure for the carboamination of alkenes

$[Cp^*RhCl_2]_2$ (0.0050 mmol, 5 mol%), sodium bicarbonate (0.03 mmol, 0.3 equiv), and boronic acid (0.25 mmol, 2.5 equiv) were measured in a 0.5-dram vial with a magnetic stir bar. In a separate vial, dioxazolone (0.1 mmol, 1 equiv) and alkene (0.3 mmol, 3 equiv) were dissolved in 0.10 mL of MeOH and transferred to the first vial. It was rinsed with an additional 0.07 mL of MeOH and transferred again to the first vial. The reaction mixture was then stirred at 25 $^{o}$C for 16 hours. After the completion of the reaction, the solvent was removed by a rotary evaporator. Ethyl acetate was added to the residue and filtered through a short pad of celite and washed with ethyl acetate three times. The filtrate was concentrated by rotary evaporator and a crude $^{1}$H NMR spectrum was collected with 1,3,5-trimethoxybenzene as the internal standard. Purification was performed by flash chromatography or preparational TLC using ethyl acetate and hexane or DCM and MeOH as the eluent.

## 4. Detailed optimization table

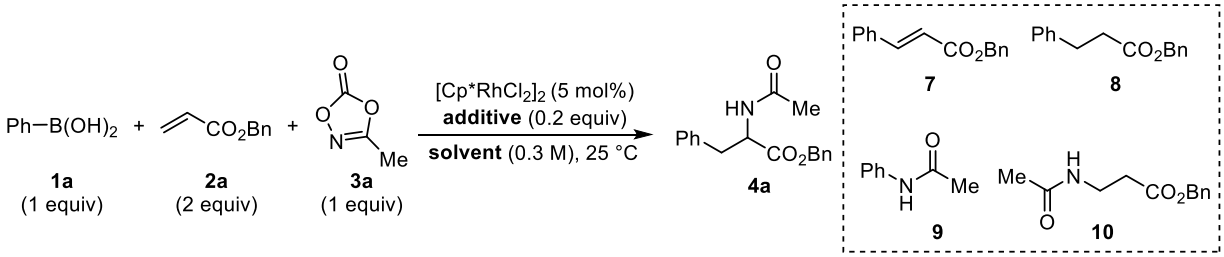
**Table S1.** Nitrene precursor screening.[a]




| entry | nitrene source (0.2 equiv) | **4** (%) | **7** (%) | **8** (%) | **9** (%) | **10** (%) |
|---|---|---|---|---|---|---|
| 1 |  | - | - | - | - | - |
| 2 |  | - | - | - | - | - |
| 3 |  | - | - | - | >95 | - |
| 4 |  | - | - | - | >95 | - |
| 5 |  | - | - | - | - | - |
| 6 |  | - | - | - | - | - |
| 7 |  | - | 80 | 6 | - | - |
| 8 |  | 8 | 24 | < 5 | 10 | < 5 |

[a]Reaction were conducted on 0.1 mmol scale according to the general procedure. Yield was determined by $^1$H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. The yield of side products was calculated based on 0.1 mmol.

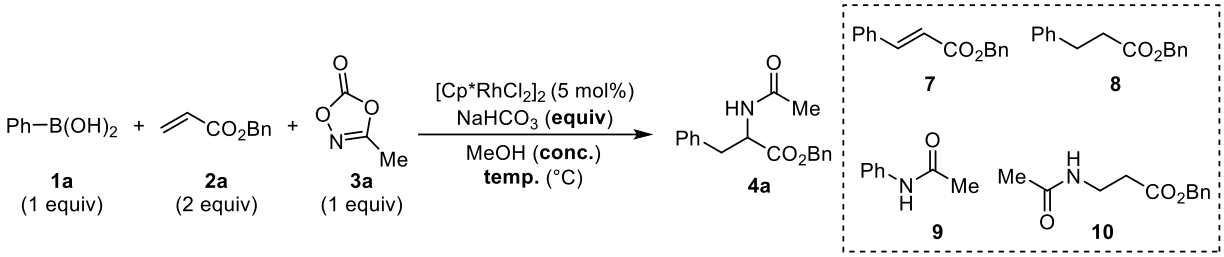
**Table S2.** Solvent and additive screening.[a]




| entry | solvent (0.3 M) | additive (0.2 equiv) | **4a** (%) | **7** (%) | **8** (%) | **9** (%) | **10** (%) |
|---|---|---|---|---|---|---|---|
| 1 | MeOH | CsOAc | 8 | 24 | <5 | 10 | <5 |
| 2 | MeOH | CsOPiv | <5 | 13 | <5 | <5 | <5 |
| 3 | MeOH | $Cs_2CO_3$ | 48 | 28 | <5 | 9 | 6 |
| 4 | THF | $Cs_2CO_3$ | 29 | 20 | <5 | <5 | 6 |
| 5 | TFE | $Cs_2CO_3$ | 16 | 20 | <5 | 46 | 9 |
| 6 | DCE | $Cs_2CO_3$ | 17 | 46 | <5 | 21 | 11 |
| 7 | EtOH | $Cs_2CO_3$ | 28 | 30 | <5 | 24 | <5 |
| 8 | HFIP | $Cs_2CO_3$ | <5 | 10 | <5 | 35 | 6 |
| 9 | MeCN | $Cs_2CO_3$ | < 5 | 24 | < 5 | 10 | 8 |
| 10 | Acetone | $Cs_2CO_3$ | 15 | 22 | < 5 | 7 | < 5 |
| 11 | *i*-PrOH | $Cs_2CO_3$ | 16 | 14 | < 5 | 11 | < 5 |
| 12 | *t*-BuOH | $Cs_2CO_3$ | 6 | 10 | < 5 | 8 | < 5 |
| 13 | MeOH | $Li_2CO_3$ | 44 | 30 | 6 | 9 | <5 |
| 14 | MeOH | $Na_2CO_3$ | 45 | 29 | 6 | 8 | 5 |
| 15 | MeOH | $K_2CO_3$ | 42 | 30 | 7 | 8 | 5 |
| 16 | MeOH | $NaHCO_3$ | 44 | 28 | 8 | 8 | <5 |
| 17 | MeOH | NaF | 48 | 33 | <5 | 7 | 8 |
| 18 | MeOH | NaOAc | <5 | 20 | <5 | 6 | <5 |

[a]Reaction were conducted on 0.1 mmol scale according to the general procedure. Yield was determined by $^1$H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. The yield of side products was calculated based on 0.1 mmol.

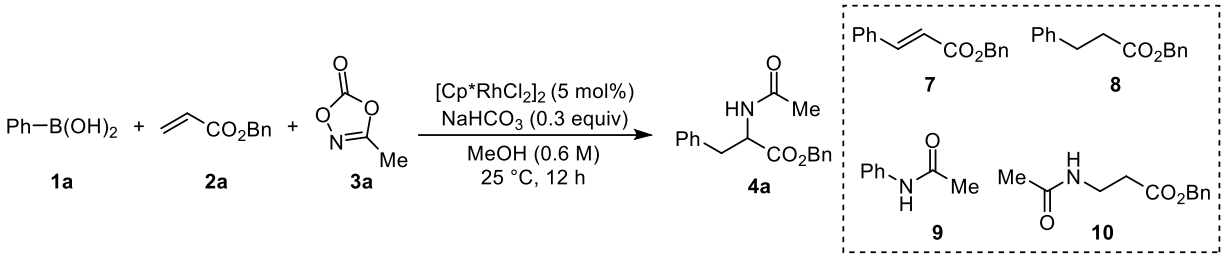
**Table S3.** Concentration, additive, and temperature screening[a]




| entry | concentration (M) | additive (equiv) | temperature (°C) | **4a** (%) | **7** (%) | **8** (%) | **9** (%) | **10** (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.1 | $NaHCO_3$ (0.2) | 25 | 32 | 32 | 7 | 8 | 9 |
| 2 | 0.3 | $NaHCO_3$ (0.2) | 25 | 45 | 24 | 5 | 8 | 6 |
| 3 | 0.6 | $NaHCO_3$ (0.2) | 25 | 59 | 22 | <5 | 8 | 6 |
| 4 | 0.6 | $NaHCO_3$ (0.1) | 25 | 56 | 20 | <5 | 8 | 6 |
| 5 | 0.6 | $NaHCO_3$ (0.3) | 25 | 59 | 20 | <5 | 9 | 6 |
| 6 | 0.6 | $NaHCO_3$ (0.6) | 25 | 60 | 20 | <5 | 8 | 6 |
| 7 | 0.6 | $NaHCO_3$ (1.0) | 25 | 59 | 20 | <5 | 8 | 6 |
| 8 | 0.6 | $NaHCO_3$ (0.3) | 40 | 56 | 34 | <5 | 11 | 13 |
| 9 | 0.6 | $NaHCO_3$ (0.3) | 60 | 42 | 40 | < 5 | 13 | 20 |

[a]Reaction were conducted on 0.1 mmol scale according to the general procedure. Yield was determined by $^1H$ NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. The yield of side products was calculated based on 0.1 mmol.

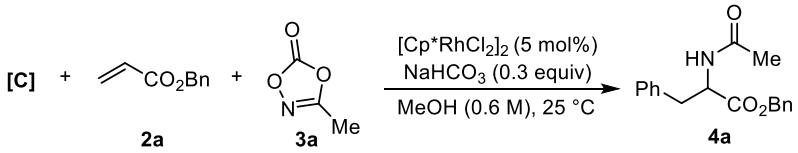
**Table S4.** Effect of ratio of each component.[a]

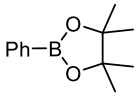



| entry | **1a** (equiv) / **2a** (equiv) / **3a** (equiv) | **4a** (%) | **7** (%) | **8** (%) | **9** (%) | **10** (%) |
|---|---|---|---|---|---|---|
| 1 | 1 / 1 / 1 | 55 | 20 | <5 | 16 | 5 |
| 2 | 1 / 1 / 2 | 54 | 10 | <5 | 35 | <5 |
| 3 | 1 / 1 / 3 | 44 | 6 | <5 | 51 | <5 |
| 4 | 1 / 2 / 1 | 59 | 22 | <5 | 8 | 6 |
| 5 | 1 / 3 / 1 | 57 | 22 | <5 | 5 | 5 |
| 6 | 2 / 1 / 1 | 64 | 20 | 5 | 22 | 8 |
| 7 | 3 / 1 / 1 | 58 | 16 | <5 | 24 | 7 |
| 8 | 2 / 2 / 1 | 71 | 36 | <5 | 8 | 13 |
| 9 | 3 / 2 / 1 | 73 | 32 | < 5 | 9 | 14 |
| 10 | 4 / 2 / 1 | 75 | 34 | 6 | 9 | 15 |
| 11 | 2 / 3 / 1 | 76 | 30 | <5 | 6 | 15 |
| 12 | 2 / 4 / 1 | 76 | 32 | <5 | <5 | 15 |
| 13 | 3 / 3 / 1 | 77 | 34 | <5 | <5 | 15 |
| 14 | 2.5 / 3 / 1 | 77 | 35 | < 5 | <5 | 15 |

[a]Reaction were conducted on 0.1 mmol scale according to the general procedure. Yield was determined by $^1$H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. The yield of side products was calculated based on 0.1 mmol.

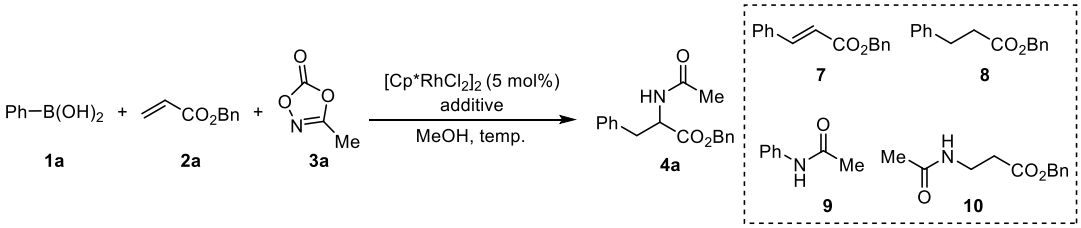
**Table S5.** Carbon source screening.[a]



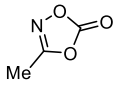
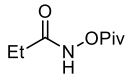
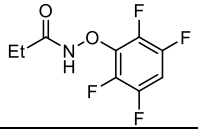

| entry | **carbon source** (2.5 equiv) | yield (%) |
|---|---|---|
| 1 | Ph–B(OH)$_2$ | 77 |
| 2 |  | 39 |
| 3 | Ph–BF$_3$K | trace |

[a]Reaction were conducted on 0.1 mmol scale according to the general procedure. Yield was determined by $^1$H NMR spectroscopy of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

**Table S6.** Summary of the detailed optimization table.




- Different nitrene sources give different side products.

| nitrene source | **4a** (%) | **7** (%) | **8** (%) | **9** (%) | **10** (%) |
|---|---|---|---|---|---|
|  | 8 | 24 | < 5 | 10 | <5 |
|  | - | - | - | >95 | - |
|  | - | 80 | 6 | - | - |

**1a** (1 equiv), **2a** (2 equiv), **3a** (1 equiv), CsOAc (0.2 equiv), MeOH (0.3 M)

- Acetates inhibit product formation, **7** becomes major product.

| additive | **4a** (%) | **7** (%) | **8** (%) | **9** (%) | **10** (%) |
|---|---|---|---|---|---|
| $NaHCO_3$ | 44 | 28 | 8 | 8 | 5 |
| NaOAc | <5 | 20 | <5 | 6 | <5 |

**1a** (1 equiv), **2a** (2 equiv), **3a** (1 equiv), additive (0.2 equiv), MeOH (0.3 M)

- Acidic solvent leads to more direct C-N coupling product (**9**).

| solvent | **4a** (%) | **7** (%) | **8** (%) | **9** (%) | **10** (%) |
|---|---|---|---|---|---|
| MeOH | 48 | 28 | <5 | 9 | 6 |
| TFE | 16 | 20 | <5 | 46 | 9 |

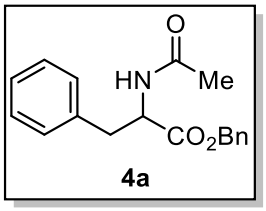
**1a** (1 equiv), **2a** (2 equiv), **3a** (1 equiv), $Cs_2CO_3$ (0.3 equiv), MeOH (0.3 M)

- Higher temperature give low chemoselectivity

| temperature | **4a** (%) | **7** (%) | **8** (%) | **9** (%) | **10** (%) |
|---|---|---|---|---|---|
| 25 °C | 59 | 20 | <5 | 9 | 6 |
| 60 °C | 42 | 40 | <5 | 13 | 20 |

**1a** (1 equiv), **2a** (2 equiv), **3a** (1 equiv), $NaHCO_3$ (0.3 equiv), MeOH (0.6 M)

## 5. Product characterization




**4a**

**Yield**: 68%, 20 mg, white solid.

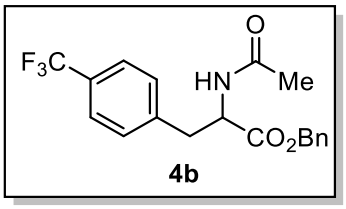
**$R_f$** = 0.26 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41 – 7.29 (m, 3H), 7.31 – 7.26 (m, 2H), 7.26 – 7.17 (m, 3H), 7.04 – 6.95 (m, 2H), 5.93 (d, *J* = 7.9 Hz, 1H), 5.17 (d, *J* = 12.1 Hz, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 4.92 (dt, *J* = 7.9, 5.7 Hz, 1H), 3.18 – 3.03 (m, 2H), 1.98 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.62, 169.68, 135.82, 135.17, 129.43, 128.76, 128.72, 128.69, 128.67, 127.20, 67.40, 53.26, 37.94, 23.27.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3277, 3063, 3031, 2932, 1738, 1652, 1540, 1372, 1209, 1173, 734, 696.

**HRMS** (ASAP) m/z $[C_{18}H_{20}NO_3]^+$ ($[M+H]^+$) calculated 298.1443, found 298.1437.




**4b**

**Yield**: 62%, 23 mg, white solid.

**$R_f$** = 0.38 (EA/Hex 2:3).

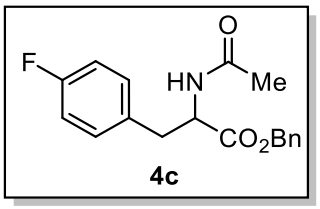
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.44 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.34 (m, 3H), 7.31 – 7.24 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 5.98 (d, *J* = 7.3 Hz, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.09 (d, *J* = 12.0 Hz, 1H), 4.97 – 4.90 (m, 1H), 3.23 – 3.11 (m, 2H), 1.99 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.28, 169.74, 140.03 (d, *J* = 1.6 Hz), 134.89, 129.80, 129.45 (q, *J* = 32.7 Hz), 128.92, 128.84, 125.51 (q, *J* = 3.7 Hz), 124.17 (q, *J* = 270.9 Hz), 67.66, 53.10, 37.80, 23.28.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ -62.51.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3276, 3066, 3036, 2939, 1740, 1654, 1541, 1324, 1164, 1122, 1067, 904, 729, 699.

**HRMS** (ASAP) m/z $[C_{19}H_{19}F_3NO_3]^+$ ($[M+H]^+$) calculated 366.1317, found 366.1310.




**4c**

**Yield**: 60%, 20 mg, white solid

**$R_f$** = 0.25 (EA/Hex 2:3).

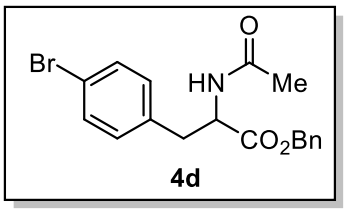
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.34 (m, 3H), 7.33 – 7.19 (m, 2H), 6.96 – 6.84 (m, 4H), 5.97 (d, *J* = 7.7 Hz, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.10 (d, *J* = 12.1 Hz, 1H), 4.89 (dt, *J* = 7.8, 5.7 Hz, 1H), 3.15 – 3.00 (m, 2H), 1.98 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.49, 169.69, 162.08 (d, *J* = 245.4 Hz), 135.05, 131.51 (d, *J* = 3.3 Hz), 130.91 (d, *J* = 8.0 Hz), 128.85, 128.81, 115.48 (d, *J* = 21.3 Hz), 67.50, 53.30, 37.17, 23.28. (Two aromatic peaks overlapped).

**$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ -115.54 – -115.76 (m).

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3278, 3066, 2935, 1738, 1653, 1541, 1508, 1373, 1220, 1176, 905, 828, 729, 698.

**HRMS** (ASAP) m/z $[C_{18}H_{19}FNO_3]^+$ ($[M+H]^+$) calculated 316.1349, found 316.1348.




**4d**

**Yield**: 65%, 25 mg, white solid.

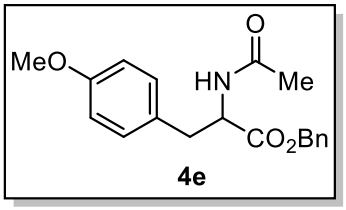
**$R_f$** = 0.31 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.42 – 7.34 (m, 3H), 7.33 – 7.25 (m, 4H), 6.87 – 6.79 (m, 2H), 5.96 (d, *J* = 7.7 Hz, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.09 (d, *J* = 12.1 Hz, 1H), 4.89 (dt, *J* = 7.8, 5.7 Hz, 1H), 3.13 – 2.99 (m, 2H), 1.98 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.38, 169.70, 134.99, 134.84, 131.73, 131.14, 128.87, 128.85, 128.83, 121.21, 67.54, 53.11, 37.40, 23.26.

**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3277, 3063, 3034, 2930, 1739, 1652, 1539, 1488, 1209, 1128, 1071, 813, 749.

**HRMS** (ASAP) m/z $[C_{18}H_{19}BrNO_3]^+$ ($[M+H]^+$) calculated 376.0548, found 376.0555.




**4e**

**Yield**: 60%, 20 mg, white solid.

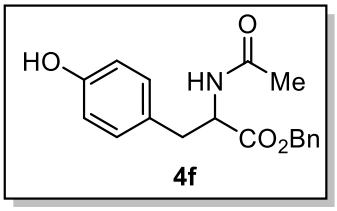
**$R_f$** = 0.33 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41 – 7.33 (m, 3H), 7.33 – 7.27 (m, 2H), 6.94 – 6.86 (m, 2H), 6.78 – 6.70 (m, 2H), 5.91 (d, $J$ = 7.9 Hz, 1H), 5.17 (d, $J$ = 12.1 Hz, 1H), 5.11 (d, $J$ = 12.1 Hz, 1H), 4.88 (dt, $J$ = 7.9, 5.7 Hz, 1H), 3.76 (s, 3H), 3.14 – 3.00 (m, 2H), 1.97 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.70, 169.69, 158.76, 135.17, 130.40, 128.72, 128.66, 127.68, 114.05, 67.33, 55.29, 53.38, 37.05, 23.26. (Two aromatic peaks overlapped)

**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3278, 3063, 3034, 2953, 2934, 2836, 1739, 1653, 1511, 1373, 1246, 1177, 1033, 698.

**HRMS** (ASAP) m/z $[C_{19}H_{22}NO_4]^+$ ($[M+H]^+$) calculated 328.1549, found 328.1549.




**4f**

**Yield**: 70%, 22 mg, white solid.

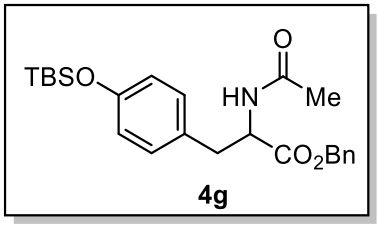
**$R_f$** = 0.17 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41 – 7.23 (m, 5H), 7.02 (s, 1H), 6.87 – 6.79 (m, 2H), 6.77 – 6.62 (m, 2H), 6.10 (d, $J$ = 8.1 Hz, 1H), 5.18 (d, $J$ = 12.1 Hz, 1H), 5.12 (d, $J$ = 12.1 Hz, 1H), 4.90 (dt, $J$ = 8.0, 5.9 Hz, 1H), 3.06 (dd, $J$ = 14.1, 5.8 Hz, 1H), 2.97 (dd, $J$ = 14.1, 6.0 Hz, 1H), 1.97 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.84, 170.51, 155.65, 135.10, 130.43, 128.78, 128.73, 128.71, 126.90, 115.70, 67.52, 53.54, 37.22, 23.16.

**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3298, 3062, 3033, 2930, 1737, 1652, 1514, 1451, 1374, 1213, 905, 730, 699.

**HRMS** (ASAP) m/z $[C_{18}H_{20}NO_4]^+$ ($[M+H]^+$) calculated 314.1392, found 314.1390.



**4g**

**Yield**: 66%, 28 mg, colorless oil.

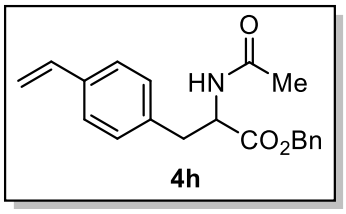
**$R_f$** = 0.38 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41 – 7.29 (m, 5H), 6.89 – 6.79 (m, 2H), 6.73 – 6.63 (m, 2H), 5.89 (d, $J$ = 7.9 Hz, 1H), 5.16 (d, $J$ = 12.1 Hz, 1H), 5.11 (d, $J$ = 12.2 Hz, 1H), 4.88 (dt, $J$ = 7.9, 5.7 Hz, 1H), 3.11 – 2.96 (m, 2H), 1.97 (s, 3H), 0.97 (s, 9H), 0.18 (s, 6H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.71, 169.65, 154.88, 135.24, 130.41, 128.77, 128.72, 128.67, 128.36, 120.21, 67.36, 53.35, 37.16, 25.79, 23.28, 18.30, -4.29.

**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3282, 3063, 3033, 2954, 2930, 2888, 2857, 1740, 1655, 1508, 1254, 906, 838, 728, 697.

**HRMS** (ASAP) m/z $[C_{24}H_{34}NO_4Si]^+$ ($[M+H]^+$) calculated 428.2257, found 428.2254.



**4h**

**Yield**: 55%, 18 mg, white solid.

**$R_f$** = 0.31 (EA/Hex 2:3).

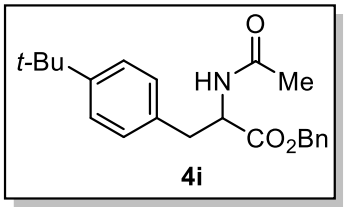
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.39 – 7.33 (m, 3H), 7.34 – 7.22 (m, 4H), 6.99 – 6.91 (m, 2H), 6.67 (dd, $J$ = 17.6, 10.9 Hz, 1H), 5.94 (d, $J$ = 7.9 Hz, 1H), 5.70 (dd, $J$ = 17.6, 1.0 Hz, 1H), 5.23 (dd, $J$ = 10.9, 0.9 Hz,

1H), 5.17 (d, *J* = 12.1 Hz, 1H), 5.11 (d, *J* = 12.1 Hz, 1H), 4.92 (dt, *J* = 7.8, 5.8 Hz, 1H), 3.17 – 3.03 (m, 2H), 1.98 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.59, 169.72, 136.58, 136.51, 135.40, 135.12, 129.61, 128.77, 128.74, 128.70, 126.50, 113.90, 67.43, 53.25, 37.69, 23.27.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3278, 3063, 2930, 2252, 1739, 1654, 1539, 1511, 1373, 1209, 1178, 904, 727, 699, 649.

**HRMS** (ASAP) m/z $[C_{20}H_{22}NO_3]^+$ ($[M+H]^+$) calculated 324.1600, found 324.1605.



**4i**

**Yield**: 55%, 19 mg, white solid.

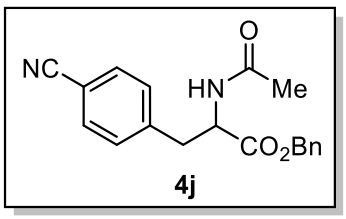
**$R_f$** = 0.37 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.38 – 7.33 (m, 3H), 7.32 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H), 6.97 – 6.91 (m, 2H), 5.93 (d, *J* = 7.7 Hz, 1H), 5.18 – 5.09 (m, 2H), 4.92 (dt, *J* = 7.9, 5.7 Hz, 1H), 3.08 (d, *J* = 5.7 Hz, 2H), 1.98 (s, 3H), 1.29 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.76, 169.74, 150.05, 135.21, 132.63, 129.10, 128.74, 128.70, 128.66, 125.60, 67.39, 53.26, 37.39, 34.55, 31.45, 23.29.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3280, 3062, 3033, 2960, 2868, 1740, 1654, 1537, 1515, 1368, 1190, 906, 730, 697.

**HRMS** (ASAP) m/z $[C_{22}H_{28}NO_3]^+$ ($[M+H]^+$) calculated 354.2069, found 354.2072.



**4j**

**Yield**: 51%, 16 mg, yellow oil.

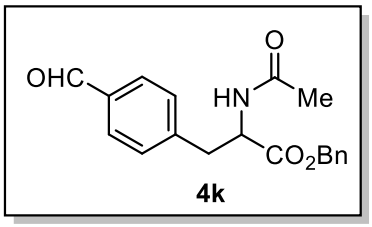
**$R_f$** = 0.23 (EA/Hex 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.48 – 7.38 (m, 2H), 7.42 – 7.31 (m, 3H), 7.31 – 7.28 (m, 2H), 7.08 – 7.02 (m, 2H), 6.03 (d, *J* = 7.5 Hz, 1H), 5.22 (d, *J* = 12.0 Hz, 1H), 5.08 (d, *J* = 11.9 Hz, 1H), 4.92 (dt, *J* = 7.5, 5.8 Hz, 1H), 3.16 (qd, *J* = 13.8, 5.9 Hz, 2H), 1.99 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.07, 169.75, 141.57, 134.82, 132.27, 130.22, 129.01, 128.99, 128.86, 118.76, 111.11, 67.70, 53.00, 38.13, 23.24.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3283, 3064, 3035, 2936, 2228, 1736, 1656, 1534, 1505, 1374, 1268, 1211, 1175, 905, 731, 698.

**HRMS** (ASAP) m/z $[C_{19}H_{19}N_2O_3]^+$ ($[M+H]^+$) calculated 323.1396, found 323.1390.



**4k**

**Yield**: 64%, 21 mg, white solid.

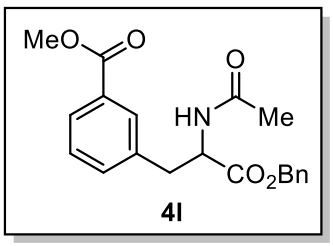
**$R_f$** = 0.20 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 9.94 (s, 1H), 7.73 – 7.66 (m, 2H), 7.41 – 7.31 (m, 3H), 7.32 – 7.27 (m, 2H), 7.17 – 7.10 (m, 2H), 6.05 (d, *J* = 7.7 Hz, 1H), 5.20 (d, *J* = 12.1 Hz, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 4.96 (dt, *J* = 7.7, 5.9 Hz, 1H), 3.19 (qd, *J* = 13.8, 5.9 Hz, 2H), 1.99 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 191.90, 171.23, 169.76, 143.15, 135.40, 134.90, 130.15, 129.97, 128.90, 128.89, 128.83, 67.63, 53.06, 38.20, 23.24.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3284, 3062, 3034, 2932, 2831, 2738, 2251, 1738, 1695, 1656, 1606, 1534, 1374, 1306, 1211, 1170, 905, 730, 698.

**HRMS** (ASAP) m/z $[C_{19}H_{20}NO_4]^+$ ($[M+H]^+$) calculated 326.1392, found 326.1387.



**4l**

**Yield**: 65%, 23 mg, yellow oil.

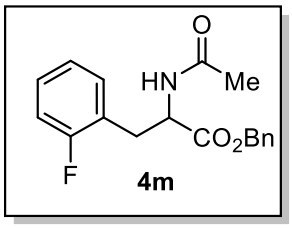
**$R_f$** = 0.19 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.90 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.79 (t, *J* = 1.8 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.36 – 7.24 (m, 3H), 7.19 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.04 (d, *J* = 7.8 Hz, 1H), 5.28 – 5.09 (m, 2H), 4.94 (dt, *J* = 7.7, 5.9 Hz, 1H), 3.89 (s, 3H), 3.20 (dd, *J* = 13.8, 6.0 Hz, 1H), 3.13 (dd, *J* = 13.9, 5.7 Hz, 1H), 1.99 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.42, 169.79, 166.94, 136.35, 134.99, 133.92, 130.58, 130.49, 128.77, 128.73, 128.68, 128.46, 67.57, 53.28, 52.25, 37.79, 23.22. (Two aromatic peaks overlapped)

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3282, 3064, 3034, 2951, 1719, 1655, 1537, 1436, 1283, 1202, 1109, 908, 747, 733, 697.

**HRMS** (ASAP) m/z $[C_{20}H_{22}NO_5]^+$ ($[M+H]^+$) calculated 356.1498, found 356.1502.



**4m**

**Yield**: 74%, 23 mg, yellow oil.

**$R_f$** = 0.45 (EA/Hex 2:3).

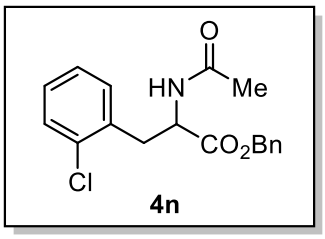
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.01 – 7.33 (m, 3H), 7.33 – 7.28 (m, 2H), 7.24 – 7.17 (m, 1H), 7.08 – 6.95 (m, 3H), 6.04 (d, *J* = 8.0 Hz, 1H), 5.17 (d, *J* = 12.2, 1H), 5.12 (d, *J* = 12,2 Hz, 1H), 4.91 (dt, *J* = 8.0, 6.0 Hz, 1H), 3.22 (ddd, *J* = 13.9, 6.0, 1.2 Hz, 1H), 3.12 (ddd, *J* = 13.9, 6.1, 1.1 Hz, 1H), 1.96 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.52, 169.79, 161.48 (d, *J* = 245.2 Hz), 135.17, 131.80 (d, *J* = 5.1 Hz), 129.12 (d, *J* = 8.3 Hz), 128.73, 128.64, 128.60, 124.32 (d, *J* = 3.9 Hz), 123.02 (d, *J* = 16.0 Hz), 115.49 (d, *J* = 22.5 Hz), 67.56, 52.67, 31.52 (d, *J* = 1.8 Hz), 23.17.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ -117.50 (m).

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3277, 3064, 3036, 2936, 1739, 1654, 1539, 1493, 1454, 1373, 1271, 1209, 1230, 1176, 1132, 755, 697.

**HRMS** (ASAP) m/z $[C_{18}H_{19}FNO_3]^+$ ($[M+H]^+$) calculated 316.1349, found 316.1350.




**Yield**: 37%, 12 mg, colorless liquid.

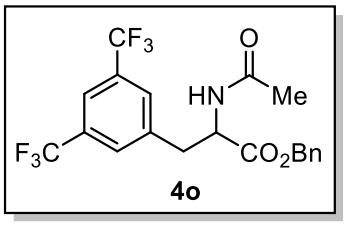
**$R_f$** = 0.26 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.24 (m, 6H), 7.21 – 7.05 (m, 3H), 6.01 (d, *J* = 8.2 Hz, 1H), 5.17 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 12.2 Hz, 1H), 4.96 (ddd, *J* = 8.2, 7.1, 6.3 Hz, 1H), 3.32 (dd, *J* = 13.9, 6.3 Hz, 1H), 3.18 (dd, *J* = 13.9, 7.1 Hz, 1H), 1.95 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.65, 169.76, 135.18, 134.62, 134.17, 131.46, 129.78, 128.73, 128.69, 128.61, 128.50, 127.08, 67.52, 52.70, 35.55, 23.23.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3275, 3064, 2939, 1742, 1653, 1543, 1444, 1373, 1269, 1177, 1134, 1052, 751, 697.

**HRMS** (ASAP) m/z $[C_{18}H_{19}ClNO_3]^+$ ($[M+H]^+$) calculated 332.1053, found 332.1052.




**Yield**: 52%, 23 mg, white solid.

**$R_f$** = 0.46 (EA/Hex 2:3).

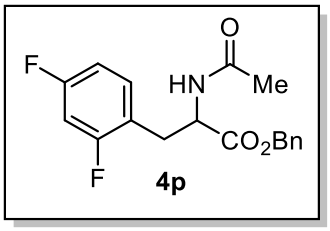
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.74 (s, 1H), 7.54 – 7.49 (m, 2H), 7.42 – 7.33 (m, 3H), 7.33 – 7.25 (m, 2H), 6.07 (d, *J* = 7.2 Hz, 1H), 5.14 (s, 2H), 4.93 (ddd, *J* = 7.2, 6.4, 5.3 Hz, 1H), 3.32 (dd, *J* = 13.9, 6.3 Hz, 1H), 3.21 (dd, *J* = 13.9, 5.3 Hz, 1H), 2.00 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 170.93, 169.87, 138.76, 134.58, 131.84 (q, *J* = 33.3 Hz), 129.72 (d, *J* = 3.9 Hz), 129.03, 128.94, 128.63, 123.31 (q, *J* = 272.7 Hz), 121.24 (p, *J* = 3.9 Hz), 67.95, 53.19, 37.62, 23.13.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ -62.87 (s).

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3271, 3068, 2957, 1741, 1654, 1545, 1378, 1276, 1171, 1129, 900, 700, 682.

**HRMS** (ASAP) m/z $[C_{20}H_{18}F_6NO_3]^+$ ($[M+H]^+$) calculated 434.1191, found 434.1189.




**4p**

**Yield**: 65%, 22 mg, colorless oil.

$\mathbf{R_f}$ = 0.28 (EA/Hex 2:3).

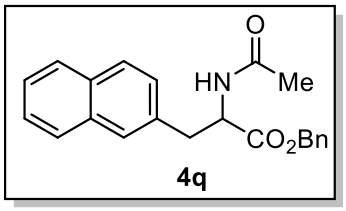
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.42 – 7.28 (m, 5H), 6.97 (td, *J* = 8.6, 6.3 Hz, 1H), 6.78 – 6.67 (m, 2H), 6.03 (d, *J* = 7.9 Hz, 1H), 5.14 (s, 2H), 4.89 (dt, *J* = 7.9, 6.0 Hz, 1H), 3.19 (ddd, *J* = 14.1, 6.1, 1.2 Hz, 1H), 3.07 (dd, *J* = 14.1, 5.9 Hz, 1H), 1.97 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.41, 169.77, 162.26 (dd, *J* = 248.4, 12.1 Hz), 161.42 (dd, *J* = 247.8, 11.9 Hz), 135.05, 132.37 (dd, *J* = 9.6, 6.2 Hz), 128.77, 128.75, 128.70, 118.91 (dd, *J* = 16.3, 3.8 Hz), 111.46 (dd, *J* = 21.2, 3.7 Hz), 103.93 (dd, *J* = 25.7, 26.0 Hz), 67.66, 52.61, 31.10, 23.18.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ -111.23 (p, *J* = 7.7 Hz), -113.16 (q, *J* = 8.7 Hz).

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3278, 3066, 3029, 2939, 1740, 1654, 1540, 1504, 1374, 1273, 1174, 1136, 1094, 965, 850, 747, 697.

**HRMS** (ASAP) m/z $[C_{18}H_{18}F_2NO_3]^+$ ($[M+H]^+$) calculated 334.1255, found 334.1255.




**4q**

**Yield**: 52%, 18 mg, white solid.

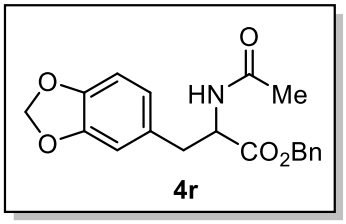
$\mathbf{R_f}$ = 0.26 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.08 (d, *J* = 8.6 Hz, 1H), 7.89 – 7.80 (m, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.41 (m, 2H), 7.34 – 7.23 (m, 4H), 7.20 – 7.09 (m, 3H), 5.99 (d, *J* = 7.8 Hz, 1H), 5.10 – 4.97 (m, 3H), 3.65 – 3.49 (m, 2H), 1.91 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.88, 169.84, 135.03, 134.01, 132.46, 132.37, 128.93, 128.67, 128.58, 128.49, 128.06, 127.63, 126.42, 125.90, 125.41, 123.72, 67.36, 53.47, 35.22, 23.23.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3277, 3062, 2953, 2251, 1739, 1652, 1539, 1511, 1372, 1176, 905, 778, 728, 698.

**HRMS** (ASAP) m/z $[C_{22}H_{22}NO_3]^+$ ($[M+H]^+$) calculated 348.1600, found 348.1603.




**4r**

**Yield**: 65%, 22 mg, white solid.

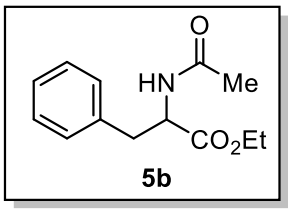
**$R_f$** = 0.37 (EA/Hex 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.34 (m, 3H), 7.34 – 7.29 (m, 2H), 6.64 (d, *J* = 7.9 Hz, 1H), 6.49 (d, *J* = 1.7 Hz, 1H), 6.42 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.95 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 2H), 5.18 (d, *J* = 12.1 Hz, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 4.87 (dt, *J* = 7.8, 5.7 Hz, 1H), 3.07 – 2.98 (m, 2H), 1.99 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.59, 169.70, 147.87, 146.81, 135.14, 129.40, 128.79, 128.74, 128.71, 122.53, 109.71, 108.41, 101.09, 67.43, 53.42, 37.68, 23.31.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3281, 3065, 3034, 2927, 2893, 1738, 1654, 1537, 1501, 1489, 1443, 1371, 1246, 1191, 1037, 904, 729, 699.

**HRMS** (ASAP) m/z $[C_{19}H_{20}NO_5]^+$ ($[M+H]^+$) calculated 342.1341, found 342.1337.




**5b**

**Yield**: 68%, 16 mg, white solid.

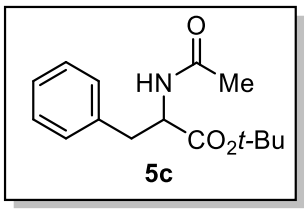
**$R_f$** = 0.30 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.33 – 7.19 (m, 3H), 7.14 – 7.07 (m, 2H), 5.93 (d, *J* = 7.8 Hz, 1H), 4.86 (dt, *J* = 7.9, 5.8 Hz, 1H), 4.17 (qd, *J* = 7.2, 1.2 Hz, 2H), 3.19 – 3.05 (m, 2H), 1.98 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.79, 169.72, 136.02, 129.42, 128.62, 127.18, 61.62, 53.26, 38.02, 23.25, 14.21.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3283, 3063, 3030, 2982, 2932, 1737, 1656, 1542, 1374, 1212, 1028, 701.

**HRMS** (ASAP) m/z $[C_{13}H_{18}NO_3]^+$ ($[M+H]^+$) calculated 236.1287, found 236.1284.



**5c**

**Yield**: 63%, 17 mg, yellowish oil.

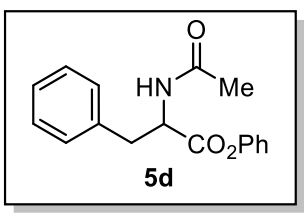
**$R_f$** = 0.31 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.35 – 7.18 (m, 3H), 7.18 – 7.05 (m, 2H), 5.97 (d, *J* = 7.7 Hz, 1H), 4.76 (dt, *J* = 7.8, 6.0 Hz, 1H), 3.09 (d, *J* = 6.0 Hz, 2H), 1.98 (s, 3H), 1.41 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 170.94, 169.64, 136.32, 129.62, 128.49, 127.08, 82.53, 53.65, 38.18, 28.07, 23.34.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3285, 3064, 3030, 2978, 2931, 1732, 1655, 1544, 1498, 1369, 1257, 1226, 1154, 755, 738, 699.

**HRMS** (ESI) m/z $[C_{15}H_{21}NO_3Na]^+$ ($[M+H]^+$) calculated 286.1419, found 286.1433.



**5d**

**Yield**: 65%, 18 mg, white solid.

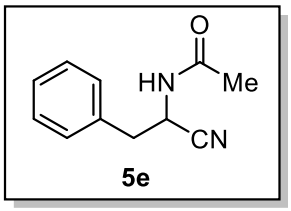
**$R_f$** = 0.28 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41 – 7.19 (m, 8H), 7.03 – 6.95 (m, 2H), 6.04 (d, $J$ = 7.8 Hz, 1H), 5.12 (dt, $J$ = 7.7, 6.0 Hz, 1H), 3.34 – 3.20 (m, 2H), 2.01 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 170.50, 169.89, 150.38, 135.72, 129.63, 129.57, 128.86, 127.49, 126.33, 121.37, 53.44, 38.08, 23.23.

**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3267, 3033, 2936, 1760, 1653, 1537, 1491, 1372, 1190, 1162, 1121, 908, 734, 699, 494.

**HRMS** (ESI) m/z $[C_{17}H_{18}NO_3]^+$ ($[M+H]^+$) calculated 284.1287, found 284.1281.



**5e**

**Yield**: 70%, 13 mg, white solid.

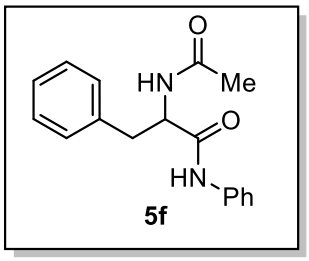
**$R_f$** = 0.27 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.41 – 7.28 (m, 3H), 7.31 – 7.24 (m, 2H), 6.17 (d, $J$ = 8.6 Hz, 1H), 5.14 (ddd, $J$ = 8.7, 7.4, 5.8 Hz, 1H), 3.08 (m, 2H), 1.98 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 169.56, 134.03, 129.57, 129.14, 128.09, 118.30, 41.66, 38.88, 22.89.

**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3270, 3032, 2932, 2856, 2244, 1954, 1658, 1531, 1497, 1372, 1289, 749, 700.

**HRMS** (ASAP) m/z $[C_{11}H_{13}N_2O]^+$ ($[M+H]^+$) calculated 189.1028, found 189.1029.



**5f**

**Yield**: 71%, 20 mg, white solid.

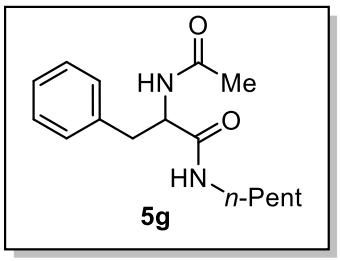
**$R_f$** = 0.42 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, DMSO-$d_6$) $\delta$ 10.07 (s, 1H), 8.27 (d, $J$ = 8.2 Hz, 1H), 7.57 (d, $J$ = 7.9 Hz, 2H), 7.34 – 7.24 (m, 6H), 7.21 – 7.16 (m, 1H), 7.05 (t, $J$ = 7.3 Hz, 1H), 4.66 (td, $J$ = 8.9, 5.3 Hz, 1H), 3.02 (dd, $J$ = 13.7, 5.3 Hz, 1H), 2.84 (dd, $J$ = 13.7, 9.4 Hz, 1H), 1.79 (s, 3H).

**$^{13}$C NMR** (101 MHz, DMSO-$d_6$) $\delta$ 170.34, 169.26, 138.81, 137.72, 129.14, 128.68, 128.06, 126.33, 123.37, 119.34, 54.86, 37.76, 22.39.

**IR** (DMSO-$d_6$, cm$^{-1}$) $v$ 3446, 2249, 2123, 1767, 1665, 1548, 1222, 1052, 1024, 1006, 820, 757, 621.

**HRMS** (ASAP) m/z $[C_{17}H_{19}N_2O_2]^+$ ($[M+H]^+$) calculated 283.1447, found 283.1446.



**5g**

**Yield**: 59%, 16 mg, yellow solid.

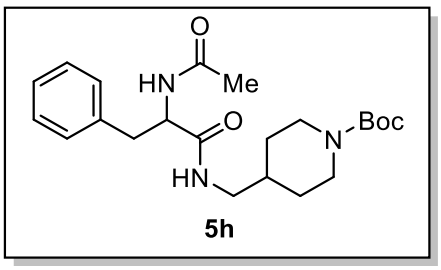
**$R_f$** = 0.29 (EA/Hex 1:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.30 – 7.24 (m, 2H), 7.27 – 7.16 (m, 3H), 6.70 (d, $J$ = 8.1 Hz, 1H), 6.15 (t, $J$ = 5.7 Hz, 1H), 4.64 (td, $J$ = 8.3, 6.4 Hz, 1H), 3.24 – 3.11 (m, 1H), 3.10 – 2.94 (m, 3H), 1.96 (s, 3H), 1.40 – 1.18 (m, 4H), 1.23 – 1.06 (m, 2H), 0.85 (t, $J$ = 7.3 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 170.96, 170.11, 137.01, 129.39, 128.67, 127.00, 54.93, 39.59, 39.03, 29.01, 28.99, 23.25, 22.38, 14.02.

**IR** ($CDCl_3$, cm$^{-1}$) $v$ 3277, 3085, 3030, 2956, 2929, 2859, 1638, 1552, 1497, 1372, 743, 698.

**HRMS** (ASAP) m/z $[C_{16}H_{25}N_2O_2]^+$ ($[M+H]^+$) calculated 277.1916, found 277.1913.



**5h**

**Yield**: 74%, 30 mg, yellow oil.

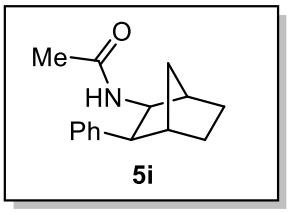
**$R_f$** = 0.22 (EA 100%).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.31 – 7.12 (m, 5H), 6.63 (d, $J$ = 8.1 Hz, 1H), 6.43 (t, $J$ = 5.6 Hz, 1H), 4.68 (td, $J$ = 8.5, 6.3 Hz, 1H), 4.00 (s, 2H), 3.22 – 3.08 (m, 1H), 3.03 (dd, $J$ = 13.4, 6.3 Hz, 1H), 2.96 (dd, $J$ = 13.4, 8.7 Hz, 1H), 2.86 (s, 1H), 2.66 – 2.45 (m, 2H), 1.96 (s, 3H), 1.43 (s, 9H), 1.41 – 1.21 (m, 3H), 1.01 – 0.84 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.19, 170.17, 154.86, 136.81, 129.37, 128.72, 127.06, 79.52, 54.95, 44.91, 43.75, 38.98, 36.21, 29.64, 28.56, 23.26.

**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3281, 2972, 2923, 2849, 1686, 1640, 1547, 1421, 1365, 1277, 1226, 1168, 1141, 734, 698.

**HRMS** (ESI) m/z $[C_{22}H_{33}N_3NaO_4]^+$ ($[M+Na]^+$) calculated 426.2369, found 426.2367.




**5i**

**Yield**: 61%, 14 mg, white solid.

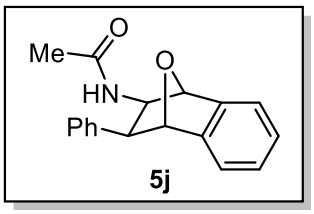
**$R_f$** = 0.42 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.45 – 7.35 (m, 2H), 7.32 – 7.22 (m, 3H), 4.79 (d, $J$ = 8.7 Hz, 1H), 4.29 (t, $J$ = 8.6 Hz, 1H), 3.19 (d, $J$ = 8.6 Hz, 1H), 2.70 (s, 1H), 2.41 – 2.35 (m, 1H), 1.84 – 1.64 (m, 3H), 1.62 (s, 3H), 1.57 – 1.38 (m, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 169.17, 140.13, 128.54, 128.40, 126.47, 56.52, 52.12, 42.61, 40.28, 35.54, 30.09, 26.39, 23.24.

**IR** ($CDCl_3$, $cm^{-1}$) $\nu$ 3293, 3061, 2955, 2872, 1646, 1549, 1496, 1451, 1373, 1290, 1154, 905, 726, 700, 494.

**HRMS** (ASAP) m/z $[C_{15}H_{20}NO]^+$ ($[M+H]^+$) calculated 230.1545, found 230.1547.




**Yield**: 89%, 25 mg, white solid.

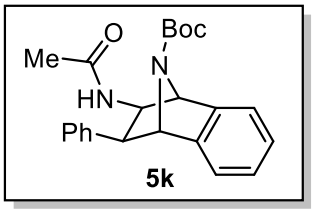
**$R_f$** = 0.42 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.47 – 7.26 (m, 7H), 7.30 – 7.20 (m, 2H), 5.56 (s, 1H), 5.31 – 5.23 (m, 2H), 4.49 (t, *J* = 8.5 Hz, 1H), 3.34 (d, *J* = 7.9 Hz, 1H), 1.58 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 169.86, 146.12, 143.36, 138.74, 128.93, 128.84, 127.64, 127.30, 127.27, 120.84, 119.13, 84.45, 84.30, 54.24, 50.12, 22.98.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3428, 3308, 3040, 3006, 1656, 1495, 1371, 904, 727, 703, 648.

**HRMS** (ASAP) m/z $[C_{18}H_{18}NO_2]^+$ ($[M+H]^+$) calculated 280.1338, found 280.1337.




**Yield**: 55%, 21 mg, white solid.

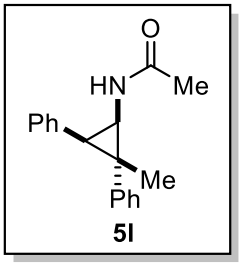
**$R_f$** = 0.26 (EA/Hex 2:3).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.35 (m, 1H), 7.35 – 7.28 (m, 2H), 7.28 – 7.20 (m, 4H), 7.19 – 7.13 (m, 2H), 5.26 (s, 1H), 5.18 (d, *J* = 9.4 Hz, 1H), 4.91 (s, 1H), 4.46 – 4.29 (m, 1H), 3.20 (d, *J* = 8.1 Hz, 1H), 1.51 (s, 3H), 1.34 (s, 9H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 169.62, 156.59, 146.57, 143.71, 138.95, 128.83, 128.68, 127.54, 127.29, 127.16, 121.79, 120.04, 99.74, 81.11, 67.68, 66.46, 53.64, 50.12, 28.44, 22.96. (Measured at 60 °C.)

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3315, 3028, 2979, 2927, 1698, 1667, 1367, 1336, 1278, 1255, 1158, 909, 729.

**HRMS** (ESI) m/z $[C_{23}H_{26}N_2NaO_3]^+$ ($[M+Na]^+$) calculated 401.1841, found 401.1851.




**5l**

**Yield**: 43%, 11 mg, colorless oil.

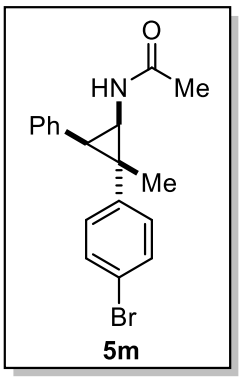
**$R_f$** = 0.37 (EA/Hex 2:3).

(major diastereomer) **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.64 – 7.58 (m, 2H), 7.48 – 7.42 (m, 2H), 7.42 – 7.32 (m, 5H), 7.32 – 7.25 (m, 1H), 5.37 – 5.32 (m, 1H), 3.50 (dd, *J* = 8.6, 5.0 Hz, 1H), 2.69 (dd, *J* = 8.6, 1.2 Hz, 1H), 2.02 (s, 3H), 1.27 (s, 3H).

(major diastereomer) **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.48, 146.83, 134.92, 130.58, 129.25, 128.74, 128.57, 127.14, 126.65, 37.19, 30.92, 30.24, 23.36, 18.07.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3303, 3056, 3024, 2927, 1651, 1601, 1495, 1444, 1370, 1268, 907, 763, 732, 700.

**HRMS** (ASAP) m/z $[C_{18}H_{20}NO]^+$ ($[M+H]^+$) calculated 266.1545, found 266.1544.




**5m**

**Yield**: 38%, 13 mg, white solid.

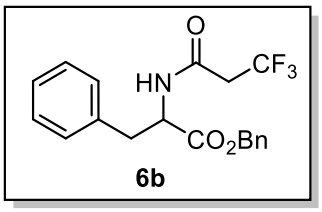
**$R_f$** = 0.32 (EA/Hex 2:3).

(major diastereomer) **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.54 – 7.42 (m, 6H), 7.39 – 7.30 (m, 3H), 5.34 (s, 1H), 3.41 (dd, *J* = 8.7, 4.7 Hz, 1H), 2.65 (dd, *J* = 8.7, 1.1 Hz, 1H), 2.01 (s, 3H), 1.23 (s, 3H).

(major diastereomer) **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 171.57, 145.93, 134.53, 131.83, 130.53, 130.46, 129.37, 127.32, 120.50, 37.15, 30.69, 30.17, 23.32, 17.94.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3302, 3054, 3026, 2931, 2979, 1653, 1492, 1444, 1369, 1090, 1009, 825, 734, 702, 532.

**HRMS** (ASAP) m/z $[C_{18}H_{19}BrNO]^+$ ($[M+H]^+$) calculated 344.0650, found 344.0644.




**6b**

**Yield**: 73%, 27 mg, white solid.

$\mathbf{R}_f$ = 0.30 (EA/Hex 1:4).

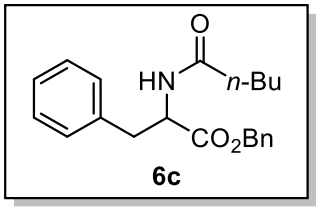
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.42 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 7.24 – 7.17 (m, 3H), 7.01 – 6.92 (m, 2H), 6.19 (d, *J* = 7.6 Hz, 1H), 5.20 (d, *J* = 12.1 Hz, 1H), 5.14 (d, *J* = 12.1 Hz, 1H), 4.94 (dt, *J* = 7.7, 5.6 Hz, 1H), 3.24 – 3.09 (m, 2H), 3.04 (q, *J* = 10.5 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 170.94, 162.13 (q, *J* = 3.6 Hz), 135.23, 134.94, 129.44, 128.85, 128.84, 128.77, 127.42, 123.97 (q, *J* = 276.9 Hz), 67.74, 53.59, 41.69 (q, *J* = 29.7 Hz), 37.68. (Two aromatic peaks overlapped)

**$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ -62.86 (t, *J* = 10.5 Hz)

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3313, 3066, 3032, 2957, 1740, 1664, 1542, 1388, 1261, 1240, 1213, 1191, 1136, 905, 733, 699.

**HRMS** (ASAP) m/z $[C_{19}H_{19}F_3NO_3]^+$ ($[M+H]^+$) calculated 366.1317, found 366.1319.




**6c**

**Yield**: 53%, 18 mg, white solid.

$\mathbf{R}_f$ = 0.23 (EA/Hex 1:4).

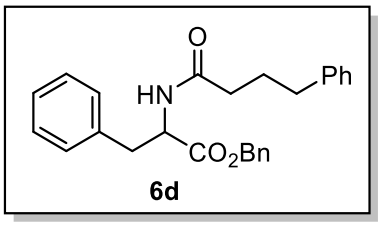
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.42 – 7.30 (m, 3H), 7.33 – 7.27 (m, 2H), 7.24 – 7.19 (m, 3H), 7.03 – 6.96 (m, 2H), 5.87 (d, *J* = 7.8 Hz, 1H), 5.17 (d, *J* = 12.2 Hz, 1H), 5.11 (d, *J* = 12.1 Hz, 1H), 4.95 (dt, *J* = 7.9, 5.8

Hz, 1H), 3.19 – 3.04 (m, 2H), 2.20 – 2.12 (m, 2H), 1.62 – 1.50 (m, 2H), 1.35 – 1.24 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 172.76, 171.72, 135.89, 135.20, 129.45, 128.75, 128.72, 128.68, 128.65, 127.17, 67.39, 53.04, 38.01, 36.40, 27.73, 22.42, 13.88.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3288, 3063, 3031, 2956, 2930, 2869, 1740, 1648, 1537, 1497, 1454, 1210, 1174, 742, 697.

**HRMS** (ASAP) m/z $[C_{21}H_{26}NO_3]^+$ ($[M+H]^+$) calculated 340.1913, found 340.1908.



**6d**

**Yield**: 54%, 22 mg, white solid.

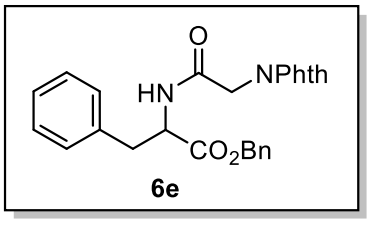
**$R_f$** = 0.25 (EA/Hex 1:4).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.42 – 7.08 (m, 13H), 7.04 – 6.95 (m, 2H), 5.86 (d, *J* = 7.9 Hz, 1H), 5.17 (d, *J* = 12.1 Hz, 1H), 5.11 (d, *J* = 12.1 Hz, 1H), 4.94 (dt, *J* = 7.9, 5.9 Hz, 1H), 3.19 – 3.03 (m, 2H), 2.59 (t, *J* = 7.5 Hz, 2H), 2.16 (dd, *J* = 7.9, 6.6 Hz, 2H), 1.92 (p, *J* = 7.6 Hz, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 172.37, 171.67, 141.50, 135.84, 135.17, 129.41, 128.74, 128.71, 128.67, 128.59, 128.49, 127.19, 126.06, 67.40, 53.07, 37.97, 35.70, 35.14, 27.01. (Two aromatic peaks overlapped)

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3290, 3062, 3028, 2930, 2859, 1738, 1648, 1534, 1496, 1453, 1175, 907, 734, 696.

**HRMS** (ASAP) m/z $[C_{26}H_{28}NO_3]^+$ ($[M+H]^+$) calculated 402.2069, found 402.2067.



**6e**

**Yield**: 56%, 25 mg, white solid.

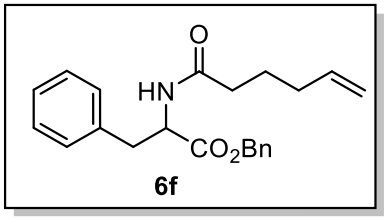
**$R_f$** = 0.44 (EA/Hex 2:3).

**$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.95 – 7.85 (m, 2H), 7.79 – 7.73 (m, 2H), 7.41 – 7.32 (m, 3H), 7.31 – 7.27 (m, 2H), 7.19 – 7.13 (m, 3H), 7.03 – 6.90 (m, 2H), 6.24 (d, *J* = 7.6 Hz, 1H), 5.18 (d, *J* = 12.1 Hz, 1H), 5.12 (d, *J* = 12.0 Hz, 1H), 4.91 (dt, *J* = 7.8, 5.5 Hz, 1H), 4.38 (d, *J* = 16.1 Hz, 1H), 4.30 (d, *J* = 16.1 Hz, 1H), 3.18 – 3.07 (m, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) $\delta$ 171.00, 167.76, 165.66, 135.39, 134.99, 134.38, 132.13, 129.58, 128.84, 128.80, 128.79, 128.68, 127.24, 123.80, 67.62, 53.53, 40.80, 37.69.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3346, 3066, 3033, 2947, 1774, 1716, 1419, 1393, 1192, 954, 904, 730, 716, 701.

**HRMS** (ASAP) m/z $[C_{26}H_{23}N_2O_5]^+$ ($[M+H]^+$) calculated 443.1607, found 4431608.



**6f**

**Yield**: 61%, 21 mg, colorless oil.

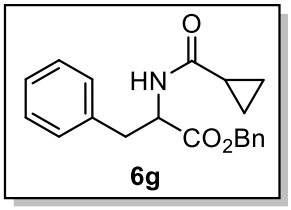
**$R_f$** = 0.22 (EA/Hex 1:4).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.42 – 7.33 (m, 3H), 7.33 – 7.28 (m, 2H), 7.24 – 7.19 (m, 3H), 7.03 – 6.96 (m, 2H), 5.86 (d, *J* = 7.9 Hz, 1H), 5.75 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.18 (d, *J* = 12.1 Hz, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 5.02 – 4.92 (m, 3H), 3.20 – 3.05 (m, 2H), 2.19 – 2.15 (m, 2H), 2.07 - 2.02 (m, 2H), 1.76 – 1.66 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 172.45, 171.68, 137.90, 135.86, 135.19, 129.44, 128.76, 128.73, 128.69, 128.67, 127.20, 115.48, 67.41, 53.06, 38.00, 35.76, 33.11, 24.64.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3293, 3064, 3031, 2931, 1742, 1648, 1539, 1498, 1454, 1175, 744, 698.

**HRMS** (ASAP) m/z $[C_{22}H_{26}NO_3]^+$ ($[M+H]^+$) calculated 352.1913, found 352.1911.




**6g**

**Yield**: 53%, 17 mg, white solid.

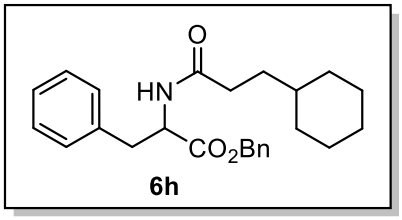
**$R_f$** = 0.27 (EA/Hex 1:4).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.40 – 7.34 (m, 3H), 7.32 – 7.28 (m, 2H), 7.25 – 7.19 (m, 3H), 7.07 – 6.98 (m, 2H), 6.10 (d, *J* = 7.8 Hz, 1H), 5.18 (d, *J* = 12.2 Hz, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 4.95 (dt, *J* = 7.9, 5.8 Hz, 1H), 3.18 – 3.07 (m, 2H), 1.36 (tt, *J* = 7.9, 4.6 Hz, 1H), 1.02 – 0.91 (m, 2H), 0.79 – 0.68 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 173.24, 171.74, 135.92, 135.21, 129.51, 128.74, 128.71, 128.66, 128.64, 127.15, 67.35, 53.34, 38.10, 14.75, 7.52, 7.45.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3302, 3063, 3029, 3006, 2941, 2838, 1739, 1650, 1599, 1498, 1455, 1203, 1150, 1066, 732, 699.

**HRMS** (ASAP) m/z $[C_{20}H_{22}NO_3]^+$ ($[M+H]^+$) calculated 324.1600, found 324.1601.




**6h**

**Yield**: 57%, 22 mg, colorless oil.

**$R_f$** = 0.33 (EA/Hex 1:4).

**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.44 – 7.31 (m, 3H), 7.34 – 7.28 (m, 2H), 7.28 – 7.18 (m, 3H), 7.04 – 6.95 (m, 2H), 5.86 (d, *J* = 7.8 Hz, 1H), 5.18 (d, *J* = 12.1 Hz, 1H), 5.12 (d, *J* = 12.1 Hz, 1H), 4.95 (dt, *J* = 7.9, 5.8 Hz, 1H), 3.19 – 3.05 (m, 2H), 2.24 – 2.12 (m, 2H), 1.74 – 1.59 (m, 5H), 1.54 – 1.42 (m, 2H), 1.28 – 1.05 (m, 4H), 0.94 – 0.79 (m, 2H).

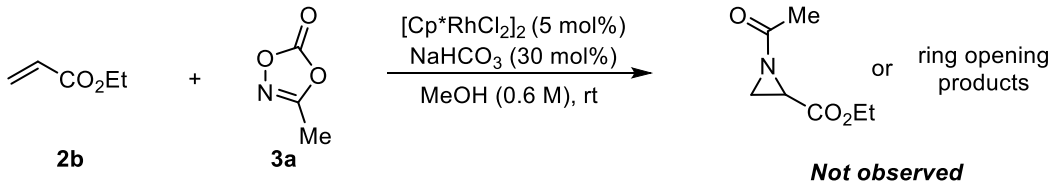
**$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 173.03, 171.73, 135.89, 135.21, 129.46, 128.76, 128.73, 128.68, 128.64, 127.18, 67.39, 53.05, 38.00, 37.34, 34.16, 33.17, 33.11, 33.03, 26.65, 26.33.

**IR** ($CDCl_3$, $cm^{-1}$) *v* 3298, 3070, 3029, 2921, 2850, 1740, 1648, 1536, 1498, 1451, 1174, 905, 730, 698.

**HRMS** (ASAP) m/z $[C_{25}H_{32}NO_3]^+$ ($[M+H]^+$) calculated 394.2387, found 394.2384.

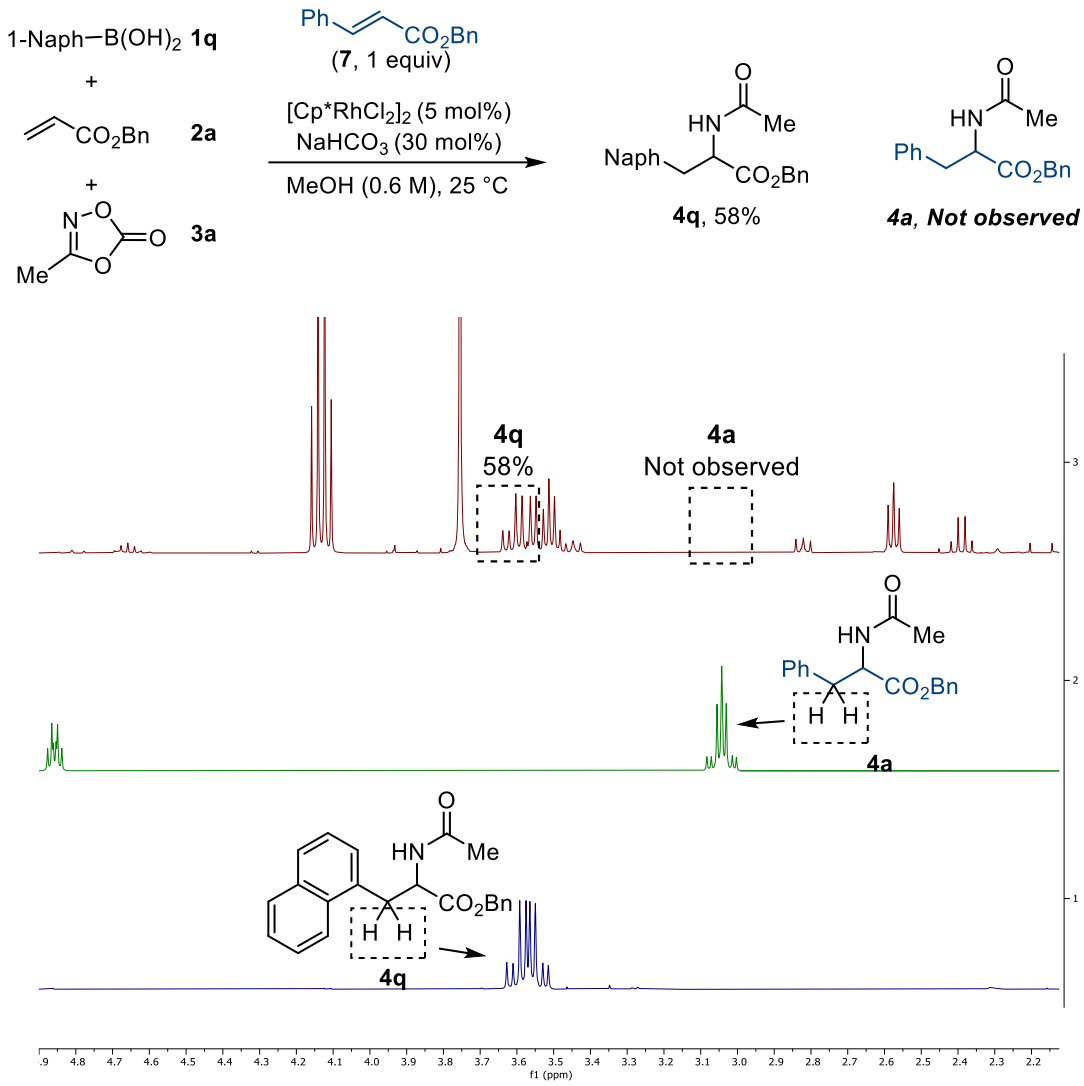
## 6. Mechanistic studies

### Possible aziridine intermediate




$[Cp^*RhCl_2]_2$ (0.0050 mmol, 5 mol%) and sodium bicarbonate (0.03 mmol, 30 mol%) were measured in a 0.5-dram vial with a magnetic stir bar. In a separate vial, dioxazolone **3a** (0.1 mmol, 1 equiv) and ethyl acrylate **2b** (0.3 mmol, 3 equiv) were dissolved in 0.10 mL of MeOH and transferred to the first vial. It was rinsed with an additional 0.07 mL of MeOH and transferred again to the first vial. The reaction mixture was then stirred at room temperature for 16 hours. After the completion of the reaction, the solvent was removed by rotary evaporator. Ethyl acetate was added to the residue and filtered through a short pad of celite and washed with ethyl acetate three times. The filtrate was concentrated by rotary evaporator and a crude $^1H$ NMR spectrum was collected with 1,3,5-trimethoxybenzene as the internal standard. As a result, neither aziridine nor ring-opening products by methanol were observed. This result suggests Rh(III)-catalyzed aziridination and subsequent ring-opening by phenylboronic acid is unlikely for the mechanism of the carboamination.

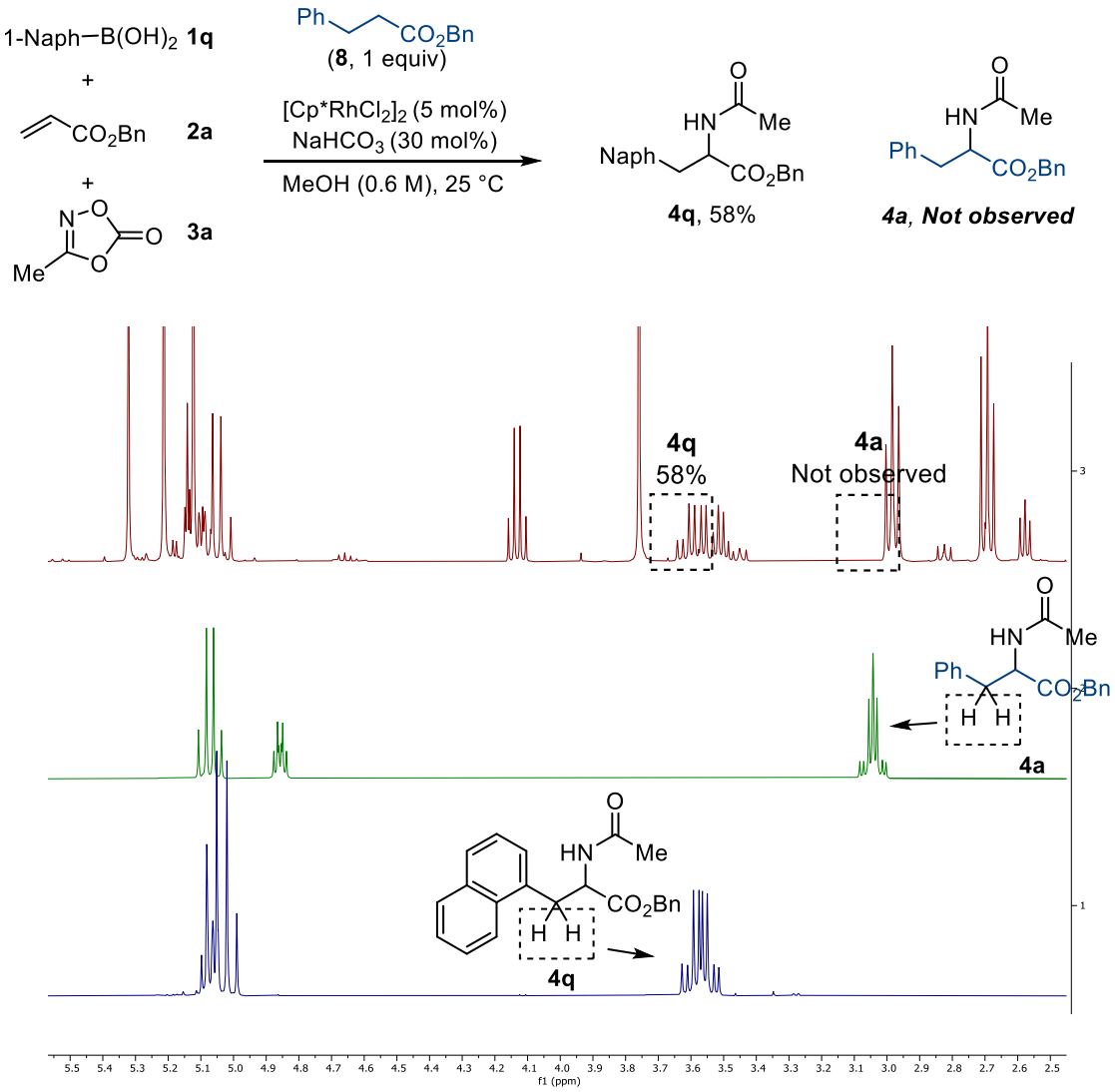
**Reversibility of $\beta$-hydride elimination**




Benzyl cinnamate **7** was prepared according to literature procedures.[9] $[Cp^*RhCl_2]_2$ (0.0050 mmol, 5 mol%) and sodium bicarbonate (0.03 mmol, 30 mol%), and naphthalene-1-boronic acid **1q** (0.25 mmol, 2.5 equiv) were measured in a 0.5-dram vial with a magnetic stir bar. In a separate vial, benzyl cinnamate **7** (0.1 mmol, 1 equiv) was dissolved 0.10 mL of MeOH and transferred to the first vial. It was rinsed with an additional 0.07 mL of MeOH and transferred again to the first vial. Sequentially benzyl acrylate **2a** (0.3 mmol, 3 equiv) and dioxazolone **3a** (0.1 mmol, 1 equiv) were added to the reaction mixture using a micropipette. The reaction mixture was then stirred at room temperature for 16 hours. After the completion of the reaction, the solvent was removed by a rotary evaporator. Ethyl acetate was added to the residue and filtered through a short pad of celite and washed with ethyl acetate three times. The filtrate was concentrated by rotary

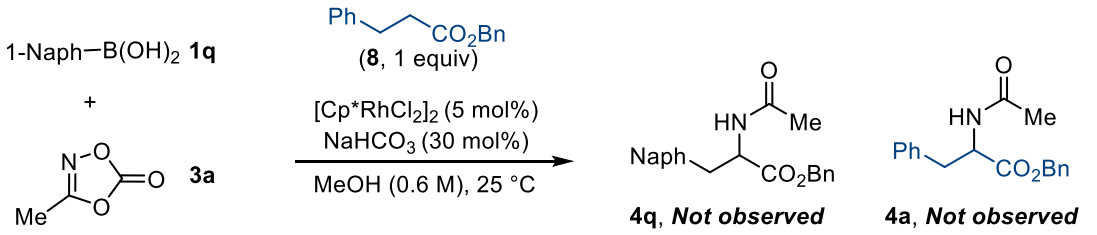
evaporator and a crude $^1$H NMR spectrum was collected with 1,3,5-trimethoxybenzene as the internal standard).

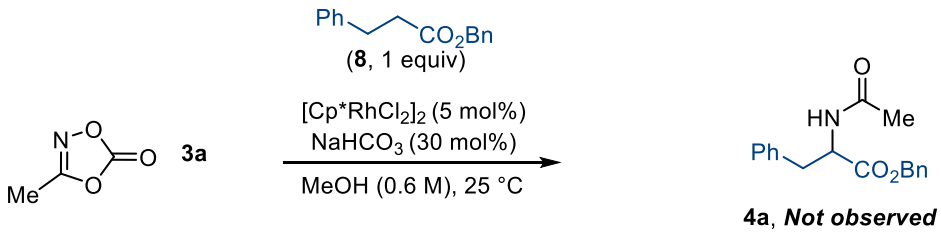
**Reversibility of proto-demetalation step**




Benzyl 3-phenylpropanoate **8** was prepared according to literature procedures.[10] $[Cp^*RhCl_2]_2$ (0.0050 mmol, 5 mol%) and sodium bicarbonate (0.03 mmol, 30 mol%), and naphthalene-1-boronic acid **1q** (0.25 mmol, 2.5 equiv) were measured in a 0.5-dram vial with a magnetic stir bar. In a separate vial, Benzyl 3-phenylpropanoate **8** (0.1 mmol, 1 equiv) were dissolved 0.10 mL of MeOH and transferred to the first vial. It was rinsed with an additional 0.7 mL of MeOH and transferred again to the first vial. Sequentially benzyl acrylate **2a** (0.3 mmol, 3 equiv) and dioxazolone **3a** (0.1 mmol, 1 equiv) were added to the reaction mixture

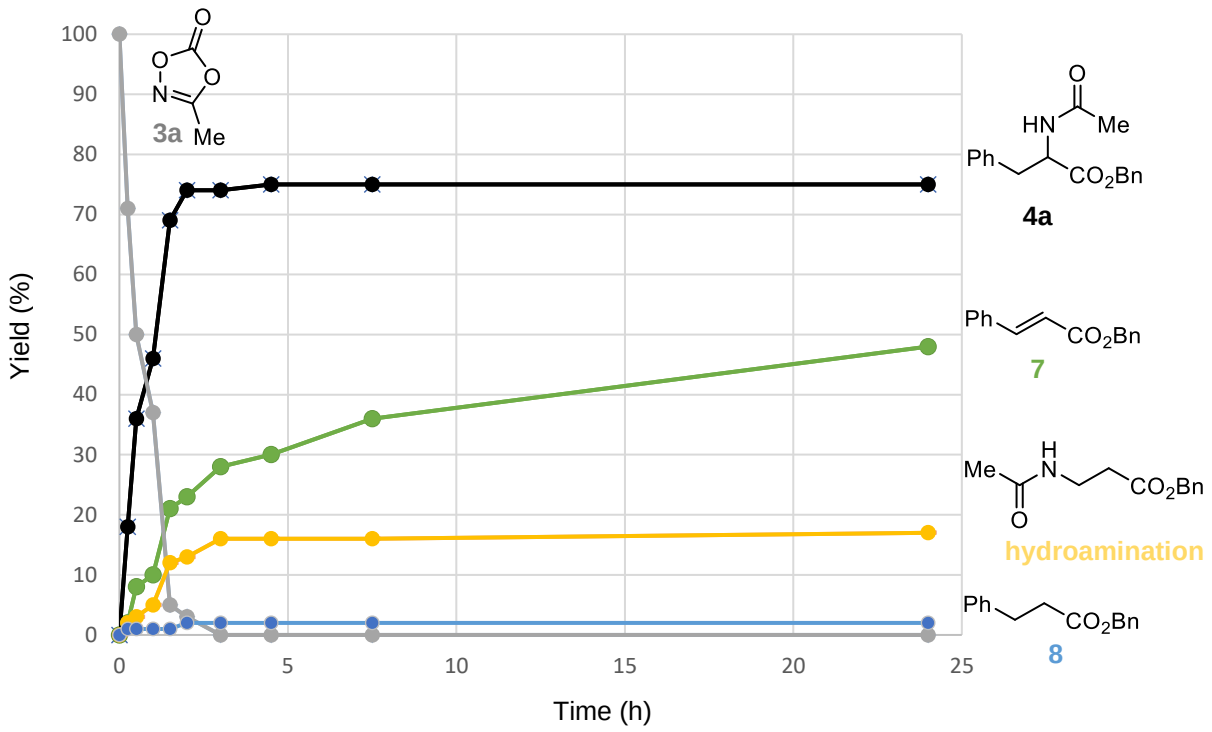
using a micropipette. The reaction mixture was then stirred at room temperature for 16 hours. After the completion of the reaction, the solvent was removed by a rotary evaporator. Ethyl acetate was added to the residue and filtered through a short pad of celite and washed with ethyl acetate three times. The filtrate was concentrated by rotary evaporator and a crude $^{1}H$ NMR spectrum was collected with 1,3,5-trimethoxybenzene as the internal standard. While both reactions give the desired product (**4q**) from 1-naphthyl boronic acid (**2q**) in good yield, carboamination products (**4a**) from these side products (**7** or **8**) are not observed. This experiment suggests **7** and **8** are off-cycle side products that do not re-enter the catalytic cycle.




The same experiments were conducted without benzyl acrylate (**2a**) and without both naphthalene-1-boronic acid (**1q**) and benzyl acrylate (**2a**). As a result, carboamination products are not observed after the reaction, which again supports benzyl 3-phenylpropanoate (**8**) as an off-cycle side product.

**Reaction progress monitoring**



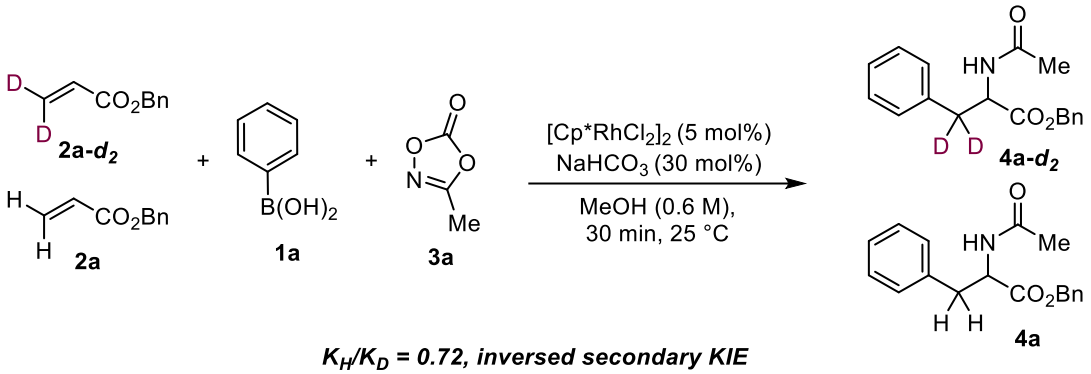

$[Cp^*RhCl_2]_2$ (0.0050 mmol, 5 mol%) and sodium bicarbonate (0.03 mmol, 30 mol%), and phenylboronic acid **1a** (0.25 mmol, 2.5 equiv) were measured in a 0.5-dram vial with a magnetic stir bar. In a separate vial, benzyl acrylate **2a** (0.3 mmol, 3 equiv) and dioxazolone **3a** (0.1 mmol, 1 equiv) were dissolved in 0.10 mL of MeOH. It was rinsed with an additional 0.07 mL of MeOH and transferred again to the first vial. 10 separate reactions were set up and each time the solvent was removed by rotary evaporator and ethyl acetate was added to the residue and filtered through a short pad of celite and washed with ethyl acetate three times. The filtrate was concentrated by rotary evaporator and a crude $^1$H NMR spectrum was collected with 1,3,5-trimethoxybenzene as the internal standard.

**Synthesis of benzyl acrylate-3,3-*d*$_2$ (2a-*d*$_2$)**

Benzyl acrylate-3,3-*d*$_2$ (**2a-*d*$_2$**) was synthesized following literature[11] using (benzyloxycarbonylmethyl)triphenylphosphonium bromide and paraformaldehyde-*d*$_2$. To a solution of (benzyloxycarbonylmethyl)triphenylphosphonium bromide (10 mmol, 1 equiv) in a 2:1 mixture of $Et_2O/H_2O$ (40 mL/20 mL), $K_2CO_3$ was added portionwise over 15 minutes. After stirring 24 hours at 35 °C, the layers were separated, and the water layer was extracted with $Et_2O$ (10 mL) three times. The combined

organic layer was dried with $MgSO_4$ and filtered. To this solution, paraformaldehyde-$d_2$ (10.5 mmol, 1.05 equiv) was added and refluxed for 24 hours. After careful removal of the solvent, the crude material was purified by column chromatography using pentane and $Et_2O$. Yield: 48%, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) $\delta$ 7.44 – 7.30 (m, 5H), 6.18 (bs, 1H), 5.22 (s, 2H).

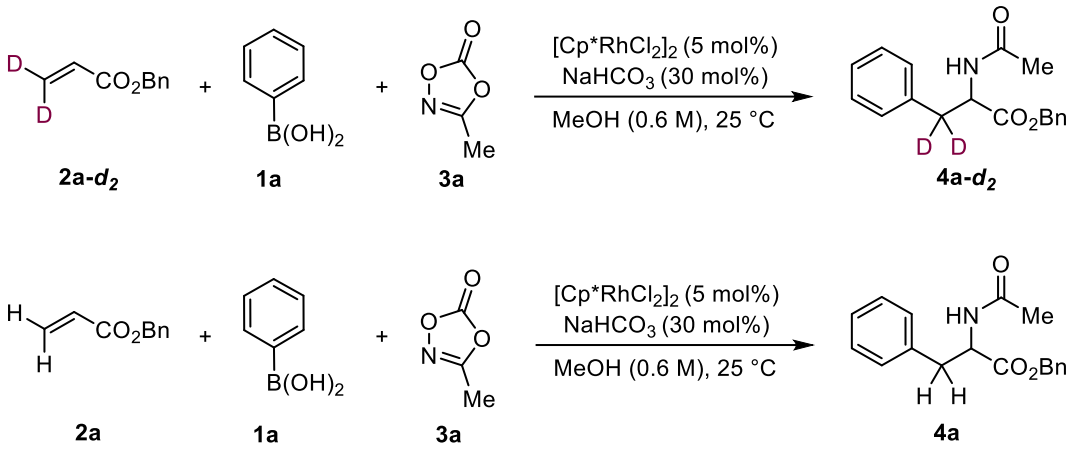
**Intermolecular competition KIE**




***$K_H/K_D$ = 0.72, inversed secondary KIE***

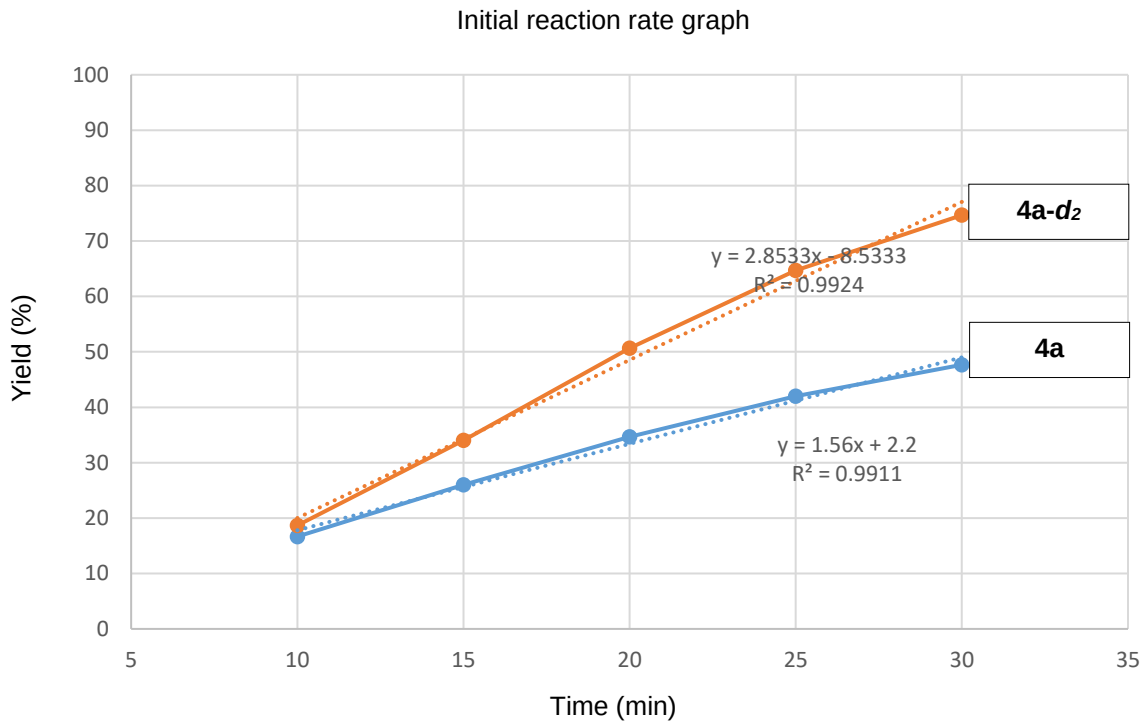
$[Cp^*RhCl_2]_2$ (0.010 mmol, 5 mol%), sodium bicarbonate (0.06 mmol, 30 mol%), and phenylboronic acid **1a** (0.50 mmol, 2.5 equiv) were measured in a 1-dram vial with a magnetic stir bar. In a separate vial, **2a** (0.15 mmol, 1.5 equiv) and **2a-*d*$_2$** (0.15 mmol, 1.5 equiv) were dissolved in 0.20 mL of MeOH containing 1,3,5-trimethoxybenzene as standard and transferred to the first vial. It was rinsed with an additional 0.13 mL of MeOH and transferred again to the first vial. After the addition of dioxazolone **3a** (0.20 mmol, 1 equiv), the reaction mixture was stirred at room temperature for 30 min. 20 uL aliquot was taken and diluted with 0.5 mL of MeCN-$d_3$ then analyzed by $^1$H NMR. The KIE value was calculated based on the area of the 4.92 ppm (contribution from both molecules, **4a** and **4a-*d*$_2$**) and at 3.12 ppm (contribution solely from **4a**). The experiment was repeated three times and an average KIE value of 0.72 indicates $sp^2 \rightarrow sp^3$ hybridization change during the turnover limiting step, which suggests alkene migratory insertion as the turnover limiting step of the reaction.

**Intermolecular parallel KIE**



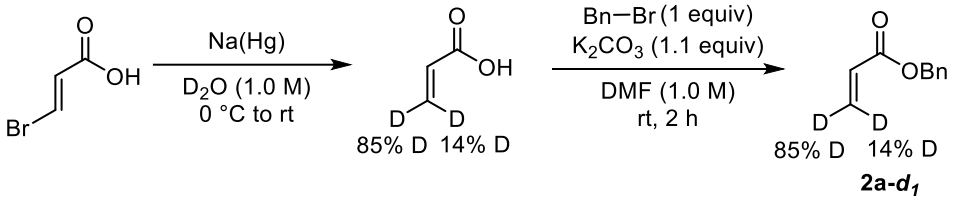

***$K_H/K_D$ = 0.55, inversed secondary KIE***

KIE was measured from two separated reactions, one with benzyl acrylate (**2a**) containing two C-H bonds and benzyl acrylate-3,3-*d*$_2$ (**2a-*d*$_2$**) containing two C-D bonds. $[Cp^*RhCl_2]_2$ (0.010 mmol, 5 mol%), sodium bicarbonate (0.06 mmol, 30 mol%), and phenylboronic acid **1a** (0.50 mmol, 2.5 equiv) were measured in a 1-dram vial with a magnetic stir bar. In a separate vial, **2a** (or **2a-*d*$_2$**) (0.60 mmol, 3 equiv) were dissolved in 0.20 mL of MeOH containing 1,3,5-trimethoxybenzene as standard and transferred to the first vial. It was rinsed with an additional 0.13 mL of MeOH and transferred again to the first vial. Dioxazolone **3a** (0.20 mmol, 1 equiv) was added to the reaction mixture using a micropipette and the reaction mixture was stirred at room temperature. To monitor the reaction progress, 20 uL aliquot was taken every 5 min and diluted with 0.5 mL of MeCN-*d*$_3$. KIE value was calculated by comparing the initial reaction rate (slope) of each reaction (repeated 3 times each) by using $^1$H NMR. Observed inversed secondary KIE ($K_H/K_D$) value of 0.55 suggests $sp^2 \rightarrow sp^3$ hybridization change occurs during the turnover limiting step.



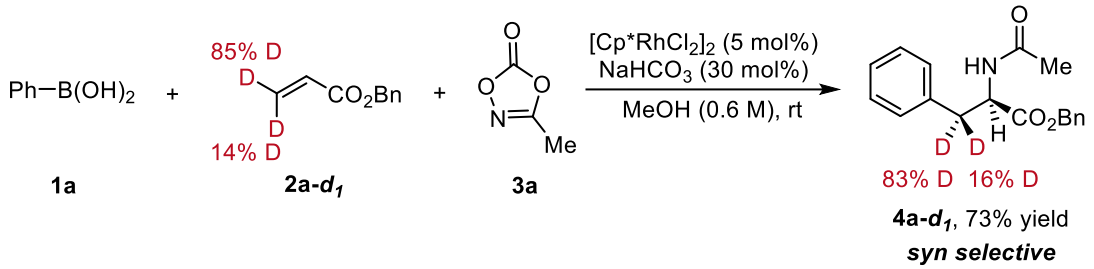

**Syn addition of alkenes**

**Synthesis of benzyl acrylate-3-*d*$_1$ (2a-*d*$_1$)**

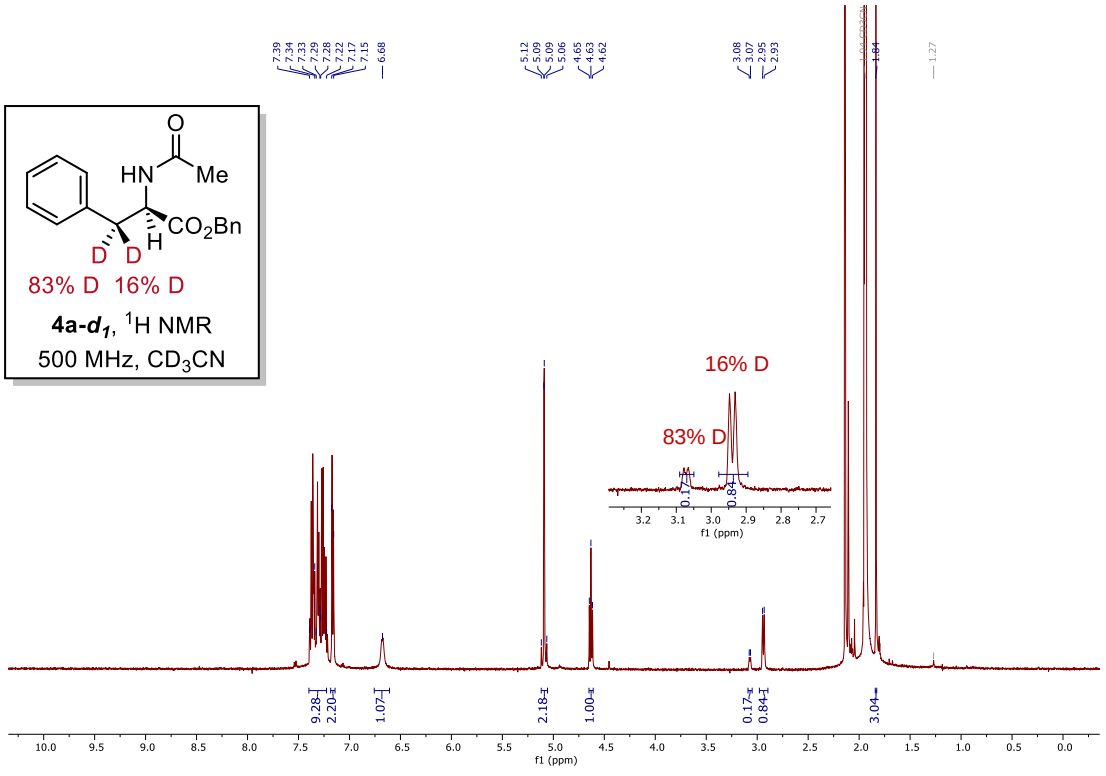


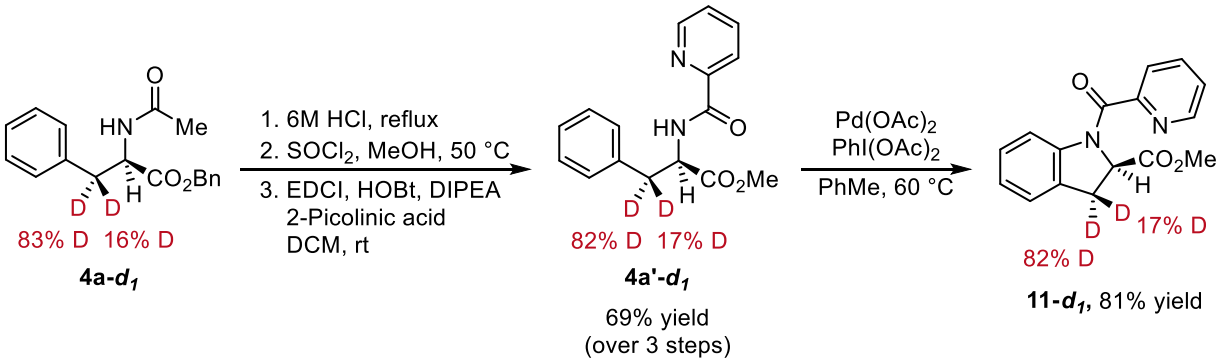

(*E*)-3-bromoacrylic acid was synthesized following literature.[12] To a solution of (*E*)-3-bromoacrylic acid (1.0 g, 6.62 mmol) in $D_2O$ (1.0 M), 5.0 g of 20% sodium amalgam was added as one portion at 0 °C. After stirring 5 min at 0 °C for 5 min, the reaction mixture was warmed to room temperature and stirred additional 30 min. The reaction mixture was decanted and washed with water. The reaction mixture was acidified to pH ≈ 1 with 6 M HCl, then extracted with diethyl ether 3 times. The combined organic layer was washed with brine and dried over $MgSO_4$ and solvent was removed by a rotary evaporator. (*E*)-acrylic-3-*d* acid was used without further purification (around 20% of over reduction product was observed). To a mixture of $K_2CO_3$ (1.1 equiv) and benzyl bromide (1 equiv) in DMF (1.0 M), (*E*)-acrylic-3-*d* acid was added dropwise at room temperature. After stirring for two hours at room temperature, the reaction mixture was diluted

with diethyl ether and washed with water and brine. The organic layer was dried with $MgSO_4$ and concentrated. The crude material was purified by column chromatography using pentane and diethyl ether as eluent. **2a-*d*$_1$**. Yield: 20% (over two steps). Colorless oil. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 7.44 – 7.30 (m, 5H), 6.44 (d, $J$ = 17.3 Hz, 0.86H), 6.17 (dt, $J$ = 17.2, 1.5 Hz, 1H), 5.84 (d, $J$ = 10.5 Hz, 0.15H).

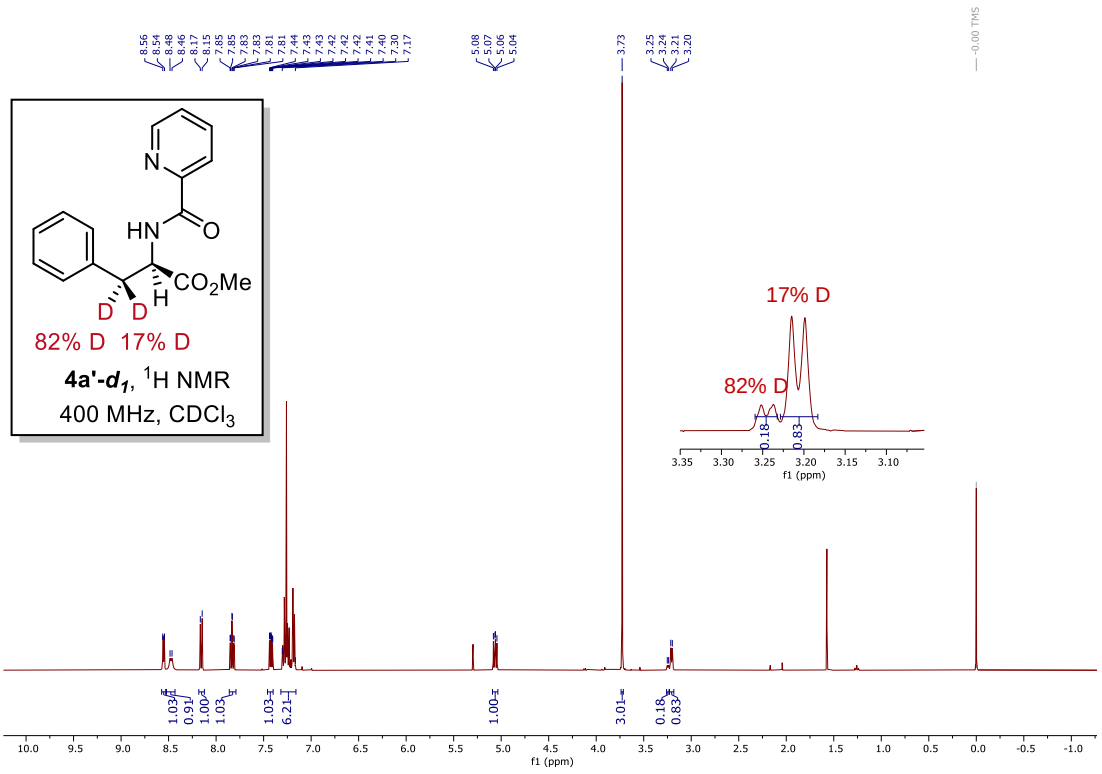



To a solution of $[Cp^*RhCl_2]_2$ (0.05 mmol, 5 mol%), sodium bicarbonate (0.30 mmol, 30 mol%), and phenylboronic acid **1a** (2.5 mmol, 2.5 equiv) in MeOH (1.7 mL, 0.6 M), **2a-*d*$_1$** (3.0 mmol, 3.0 equiv) and **3a** (1.0 mmol, 1 equiv) were added at room temperature and stirred overnight. The volatiles were removed by rotary evaporator and ethyl acetate was added and filtered through short pad of celite. After removing solvent using rotary evaporator, the crude material was purified by column chromatography using ethyl acetate and hexane as eluent to obtain **4a-*d*$_1$**. Yield: 73%, white solid. **$^1$H NMR** (500 MHz, $CD_3CN$) $\delta$ 7.40 – 7.22 (m, 8H), 7.18 – 7.14 (m, 2H), 6.67 (s, 1H), 5.12 – 5.06 (m, 2H), 4.63 (t, $J$ = 7.8 Hz, 1H), 3.07 (d, $J$ = 6.1 Hz, 0.17H), 2.94 (d, $J$ = 8.0 Hz, 0.84H), 1.84 (s, 3H).

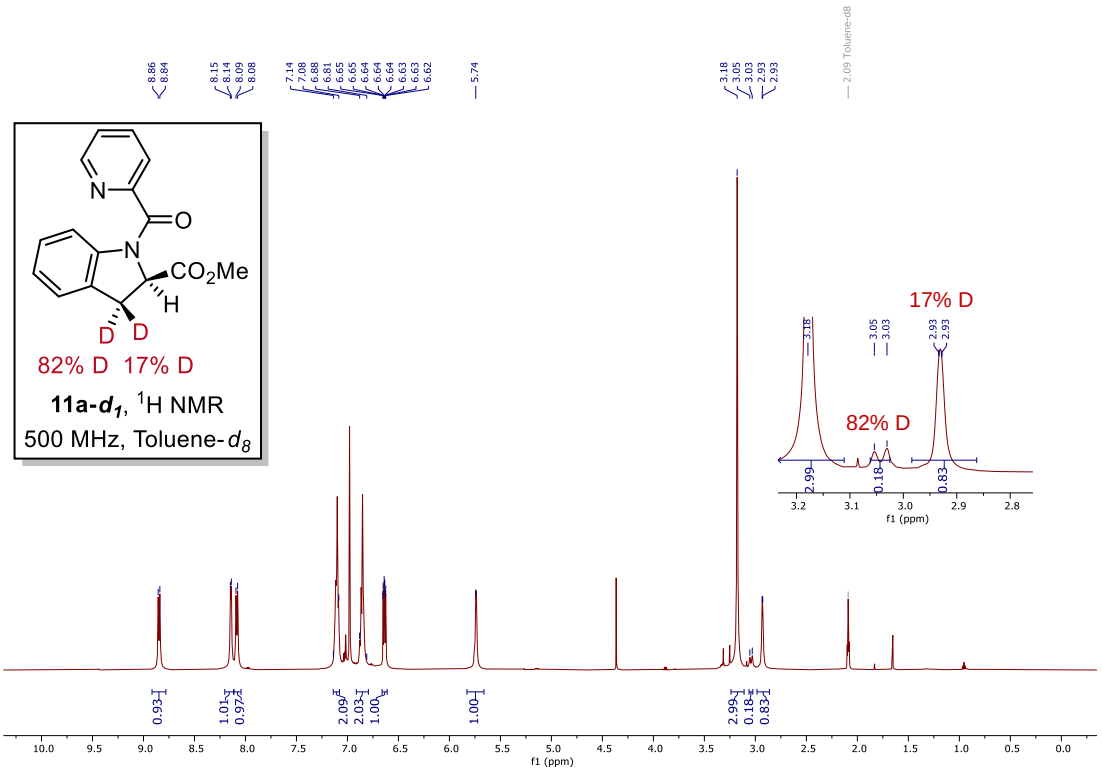




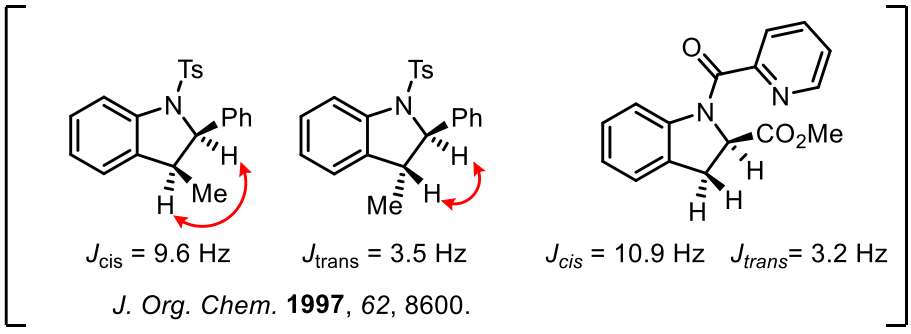

6 M HCl (0.1 M) was added to **4a-*d*$_1$** (1.38 mmol) and refluxed for 4 hours. After removing volatiles, diethyl ether was added, and the white solid was collected by filteration. The resulting solid was washed with diethyl ether and dried under high vacuum. The deprotected product was dissolved in MeOH (0.25 M) and $SOCl_2$ (1.5 equiv) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and heated at 50 °C for 3 hours. The volatiles were removed by a rotary evaporator and diethyl ether was added. After stirring for 10 min at 0 °C, the white solid was filtered and washed with diethyl ether to give crude deuterated phenylalanine methyl ester hydrochloride. The crude material (1 equiv) and 2-picolinic acid (1.1 equiv) were dissolved in DCM (0.2 M) and HOBt hydrate (1.1 equiv) and DIPEA (3.0 equiv) were added at room temperature. The reaction mixture was cooled to 0 °C and EDCI (1.1 equiv) was added. After stirring for 5 min, the reaction mixture was warmed to room temperature and stirred overnight. Water was added and extracted with DCM three times. The combined organic layer was washed with water and brine and dried with $Na_2SO_4$. After removing the solvent, the crude material was purified by column chromatography using ethyl acetate and hexane as eluent to obtain **4a'-*d*$_1$**. Yield: 69% (over three steps). White solid. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ 8.55 (ddd, $J$ = 4.8, 1.8, 0.9 Hz, 1H), 8.47 (d, $J$ = 8.4 Hz, 1H), 8.16 (dt, $J$ = 7.8, 1.1 Hz, 1H), 7.83 (td, $J$ = 7.7, 1.7 Hz, 1H), 7.42 (ddd, $J$ = 7.6, 4.8, 1.3 Hz, 1H), 7.33 – 7.14 (m, 5H), 5.06 (dd, $J$ = 8.4, 6.3 Hz, 1H), 3.73 (s, 3H), 3.24 (d, $J$ = 5.8 Hz, 0.18H), 3.21 (d, $J$ = 6.5 Hz, 0.83H).

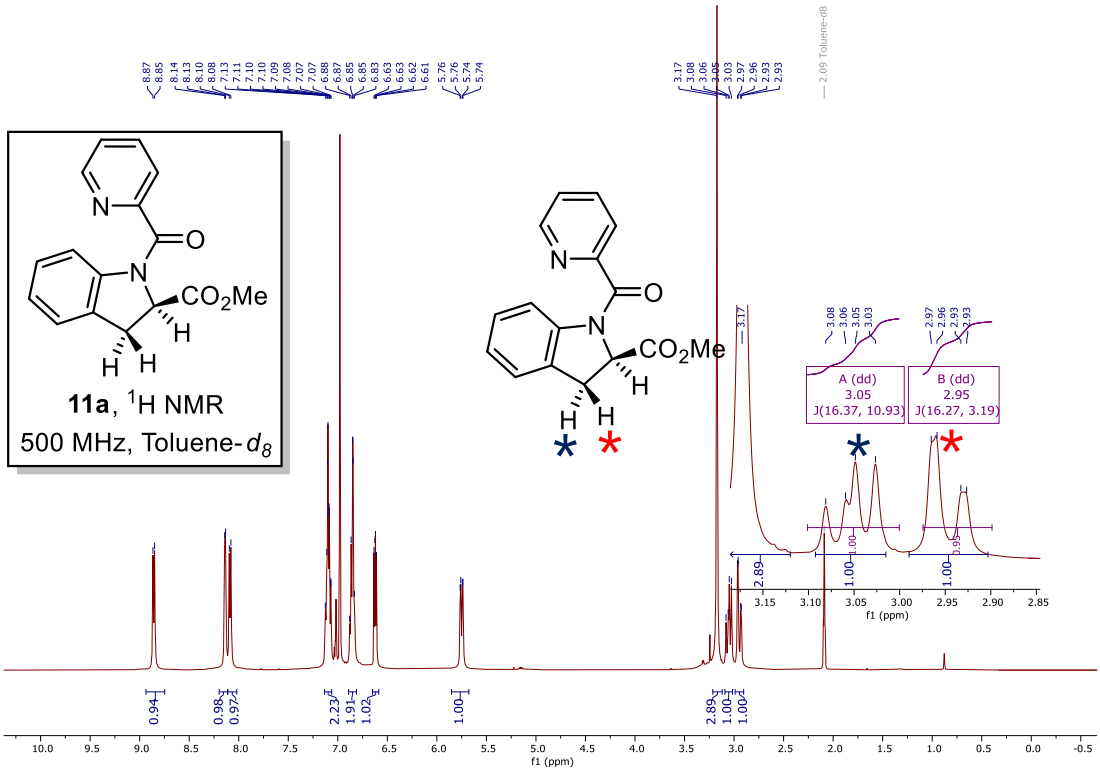



**9a-*d*$_1$** was prepared following the literature.[13] In a 20 mL vial, $Pd(OAc)_2$ (2 mol%, 0.018 mmol) and $PhI(OAc)_2$ (2 equiv. 1.78 mmol) were measured in the glovebox. In a separate flask, **4a'-*d*$_1$** (1 equiv, 0.89 mmol) was dissolved in toluene (0.125 M) and transferred to the first vial. After purging with Ar for 10 min, the vial was sealed and heated at 60 °C for 24 hours. The reaction mixture was concentrated and purified by column chromatography using ethyl acetate and hexane as eluent. **11a-*d*$_1$**. Yield: 81%, white solid. **$^1$H NMR** (500 MHz, toluene-$d_8$) $\delta$ 8.85 (d, $J$ = 8.2 Hz, 1H), 8.14 (d, $J$ = 4.8 Hz, 1H), 8.09 (d, $J$ = 7.9 Hz, 1H), 7.15 – 7.16 (m, 2H), 6.89 – 6.81 (m, 2H), 7.04 – 6.96 (m, 2H), 6.64 (ddd, $J$ = 7.6, 4.7, 1.2 Hz, 1H), 5.77 – 5.71 (m, 1H), 3.18 (s, 3H), 3.04 (d, $J$ = 11.8 Hz, 0.18H), 2.93 (s, 0.83H).



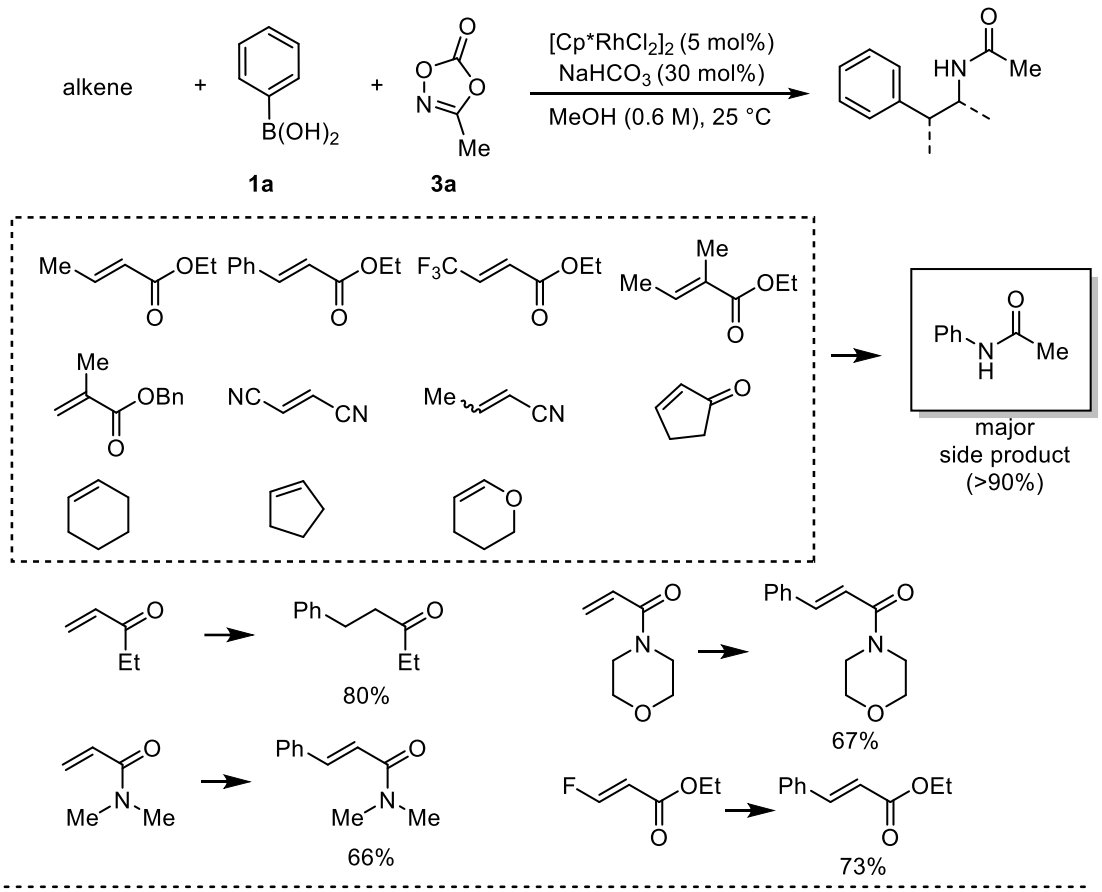

**11a** was synthesized from phenylalanine using same procedure described above. **11a**. White solid. **$^1$H NMR** (500 MHz, toluene-$d_8$) $\delta$ 8.86 (d, $J$ = 8.2 Hz, 1H), 8.14 (d, $J$ = 4.5 Hz, 1H), 8.09 (d, $J$ = 7.9 Hz, 1H), 7.09 (td, $J$ = 9.6, 7.8, 6.0 Hz, 2H), 6.89 – 6.81 (m, 2H), 6.62 (dd, $J$ = 7.7, 4.8 Hz, 1H), 5.75 (dd, $J$ = 10.9, 3.2 Hz, 1H), 3.17 (s, 3H), 3.05 (dd, $J$ = 16.4, **10.9** Hz, 1H), 2.95 (dd, $J$ = 16.3, **3.2** Hz, 1H). The relative stereochemistry was assigned based on the literature.[14] Benzylic proton with 10.9 Hz coupling constant was assigned as cis proton and proton with 3.2 Hz was assigned as trans proton which confirms the syn-carboamination of the reaction.



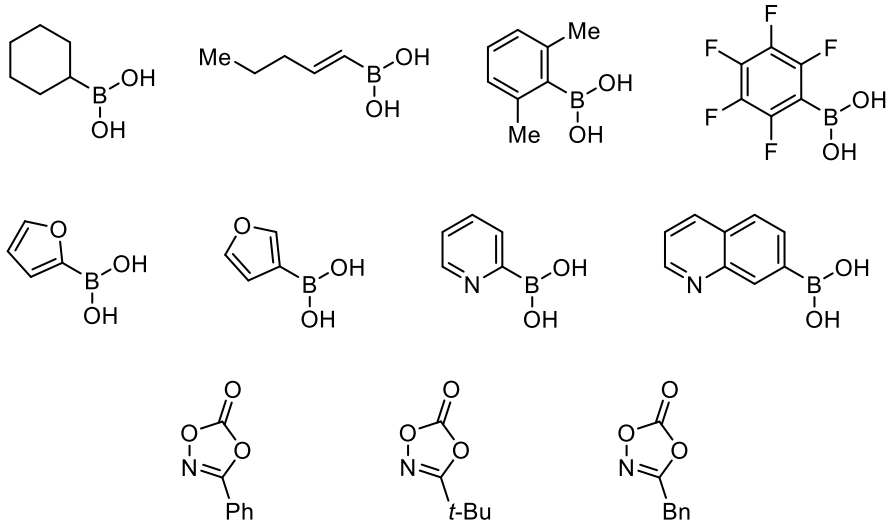

11a, 1H NMR
500 MHz, Toluene-d8
CO2Me
A (dd)
3.05
J(16.37, 10.93)
B (dd)
2.95
J(16.27, 3.19)
f1 (ppm)

## 7. Limitation

<Unsuccessful alkene coupling partners>




<Unsuccessful boronic acids and dioxazolones>



## 8. Reference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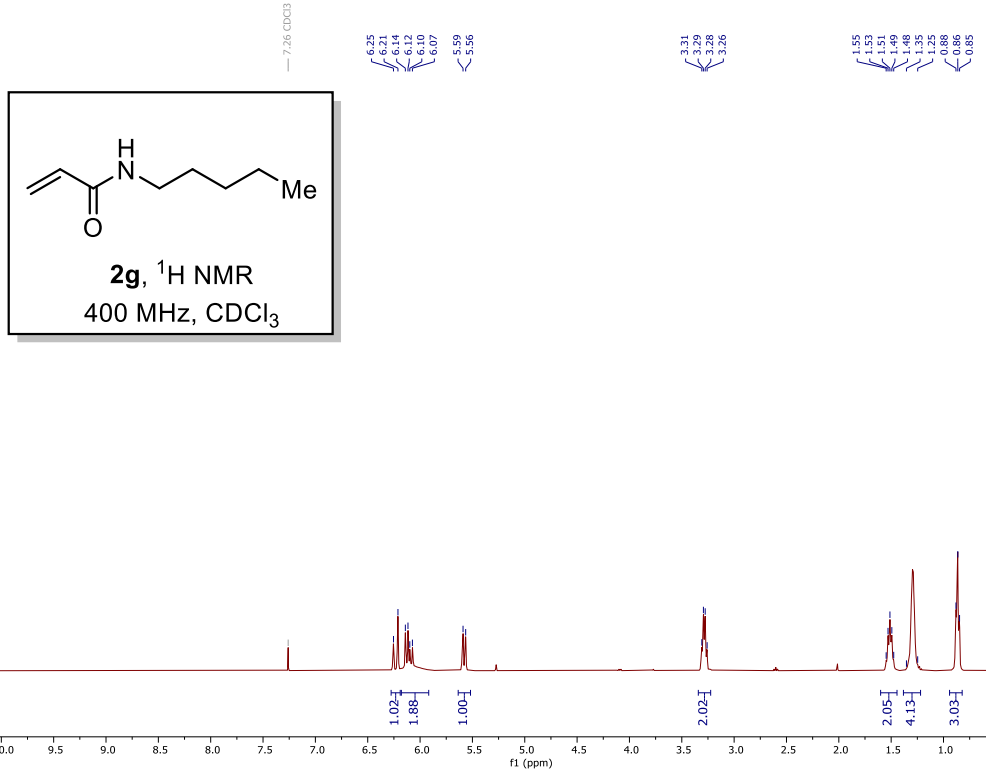
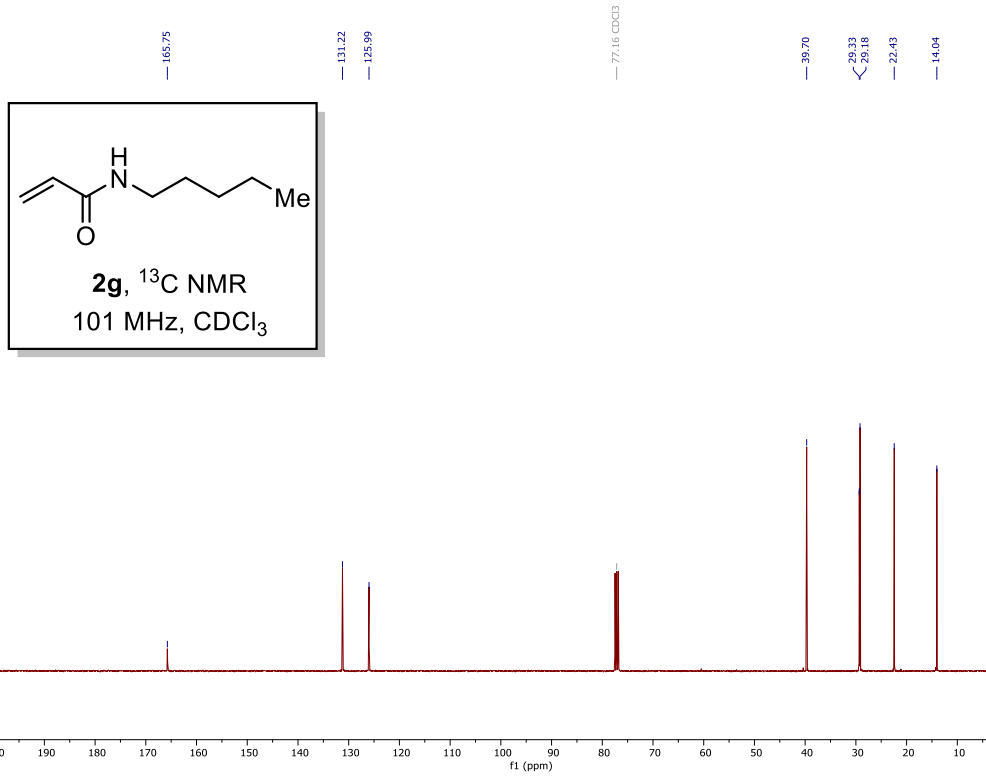
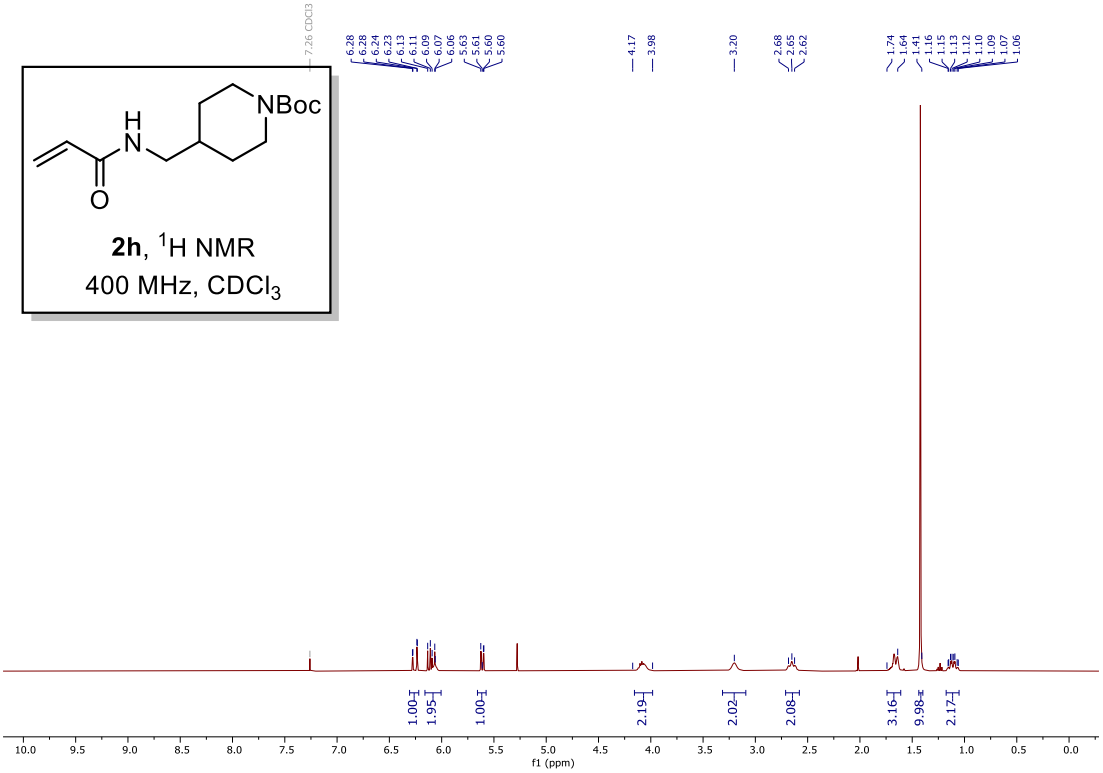
## 9. NMR Spectra




NBoc
H
N
O
2h, 1H NMR
400 MHz, CDCl3
7.26 CDCl3
6.28
6.28
6.24
6.23
6.13
6.11
6.09
6.07
6.06
5.63
5.61
5.60
5.60
4.17
3.98
3.20
2.68
2.65
2.62
1.74
1.64
1.41
1.16
1.15
1.13
1.12
1.10
1.09
1.07
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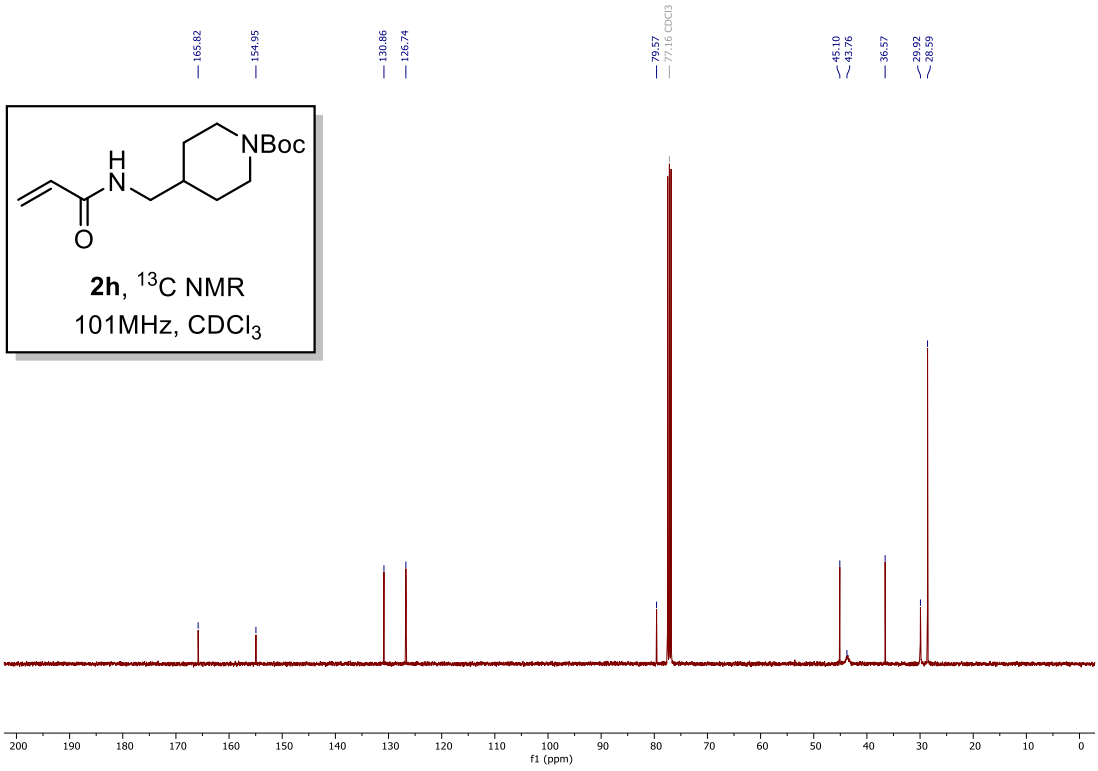
2.08
3.16
9.98
2.17
f1 (ppm)


NBoc
H
N
O
2h, 13C NMR
101MHz, CDCl3
165.82
154.95
130.86
126.74
79.57
77.16 CDCl3
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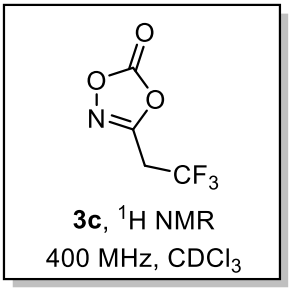
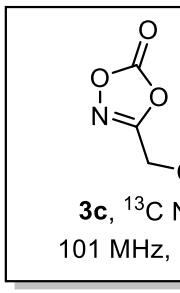
43.76
36.57
29.92
28.59
f1 (ppm)

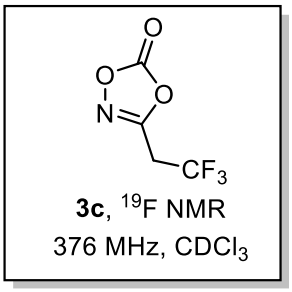


**3c**, $^{1}$H NMR
400 MHz, $CDCl_3$



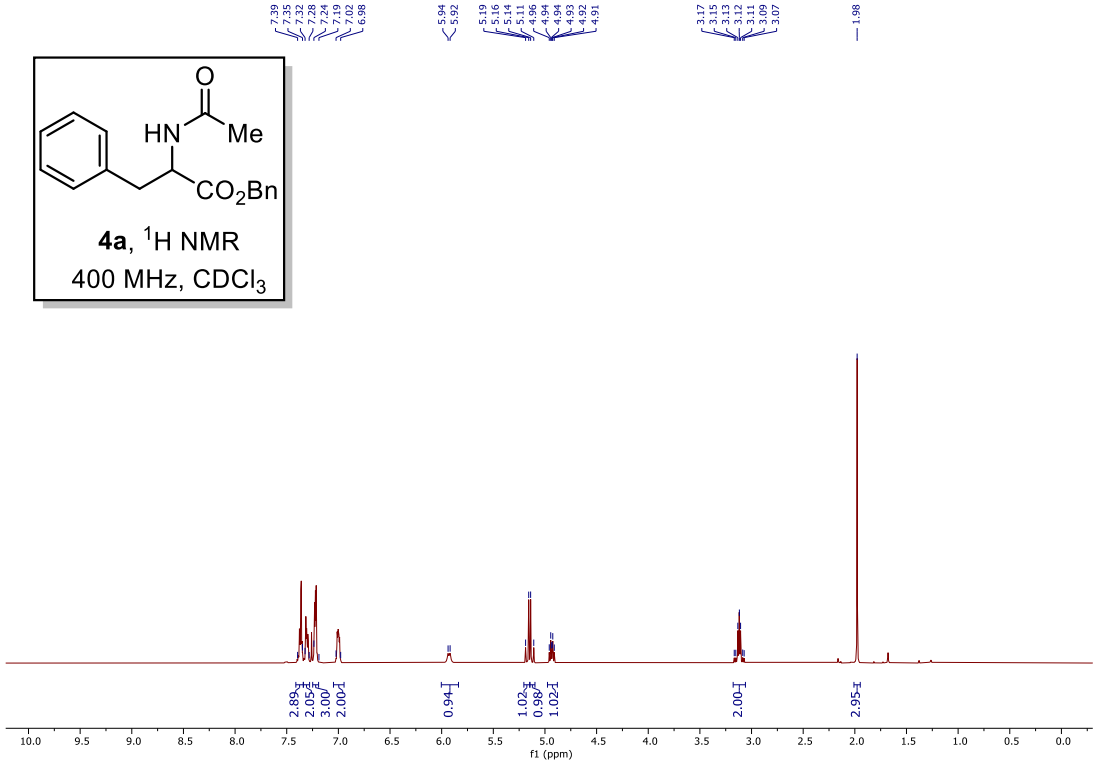



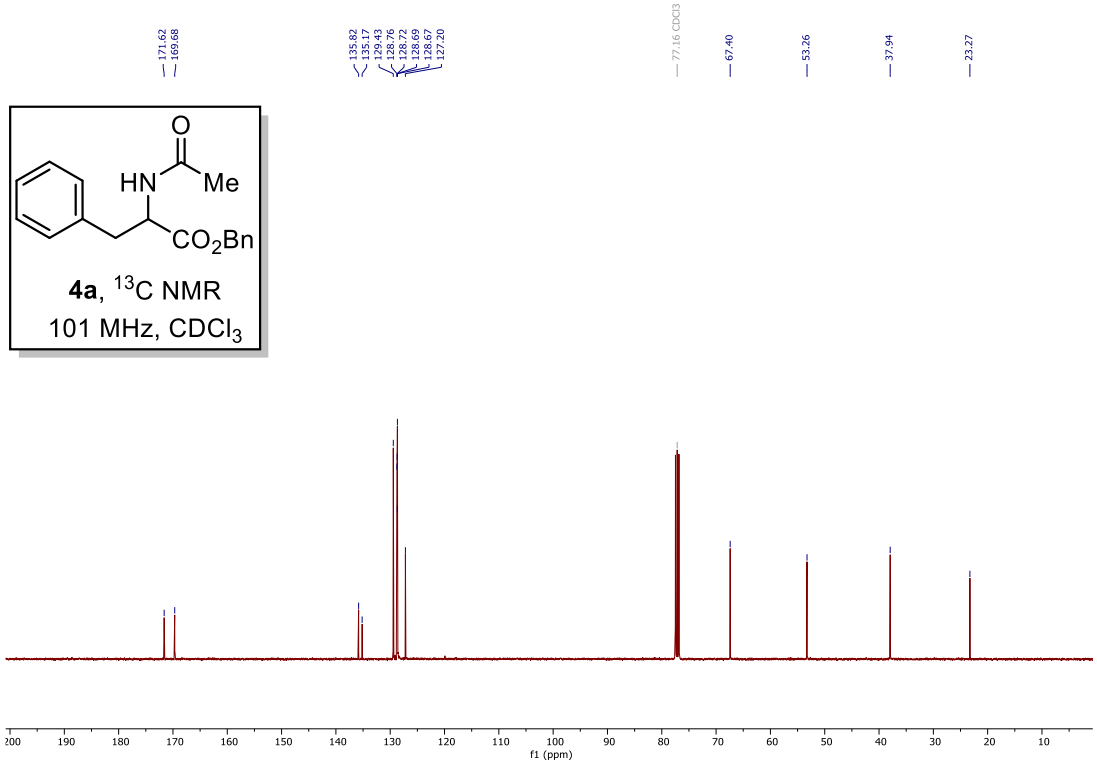
**3c**, $^{13}$C NMR
101 MHz, $CDCl_3$

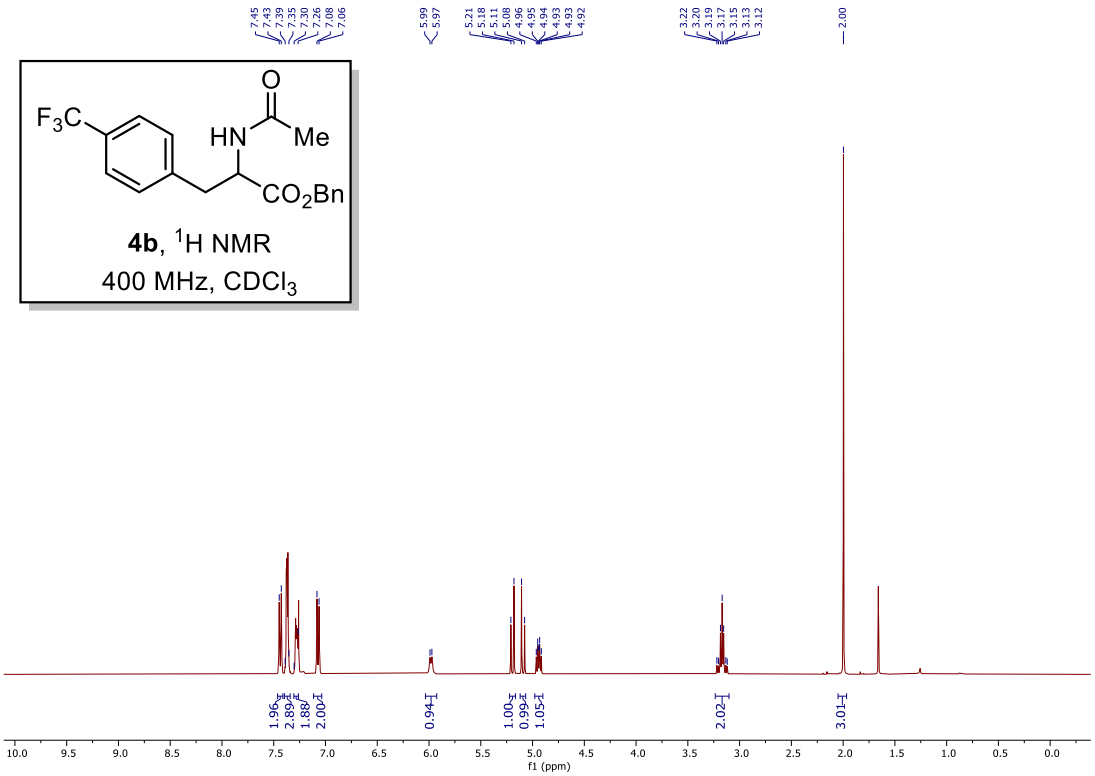



**3c**, $^{19}$F NMR

376 MHz, $CDCl_3$


7.39
7.35
7.32
7.28
7.24
7.19
7.02
6.98
5.94
5.92
5.19
5.16
5.14
5.11
4.96
4.94
4.94
4.93
4.92
4.91
3.17
3.15
3.13
3.12
3.11
3.09
3.07
1.98
O
HN
Me
CO2Bn
4a, 1H NMR
400 MHz, CDCl3
2.89
2.05
3.00
2.00
0.94
1.02
0.98
1.02
2.00
2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


171.62
169.68
135.82
135.17
129.43
128.76
128.72
128.69
128.67
127.20
77.16 CDCl3
67.40
53.26
37.94
23.27
O
HN
Me
CO2Bn
4a, 13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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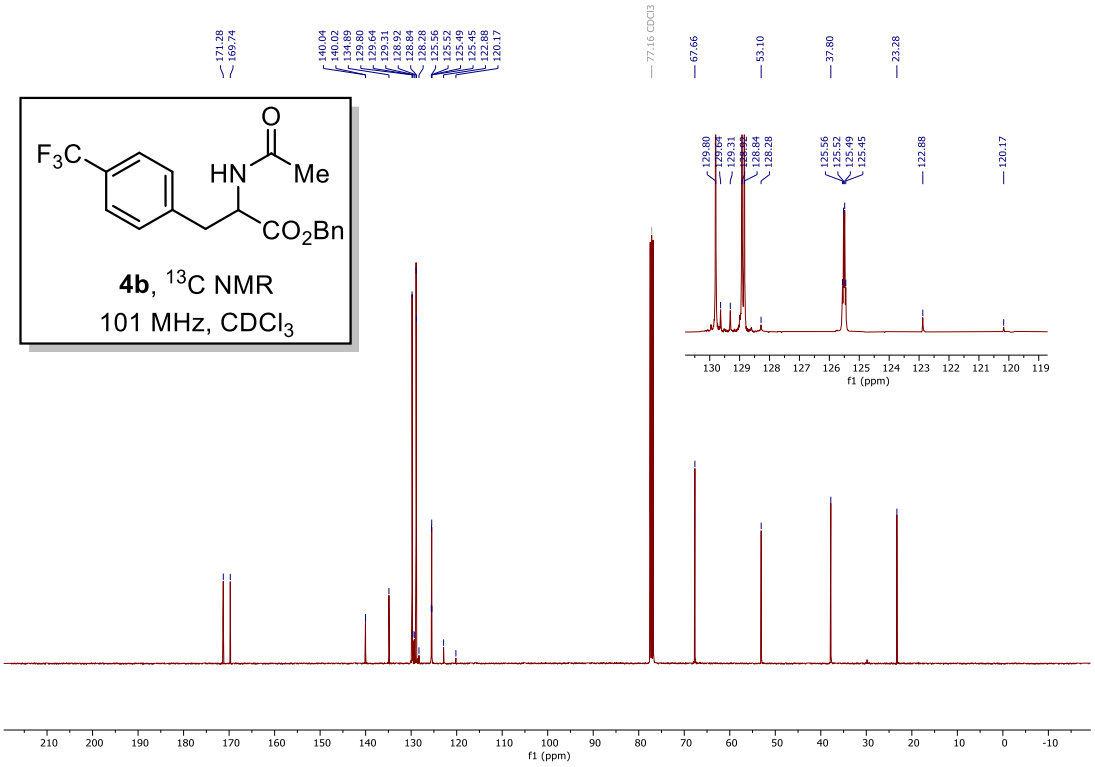
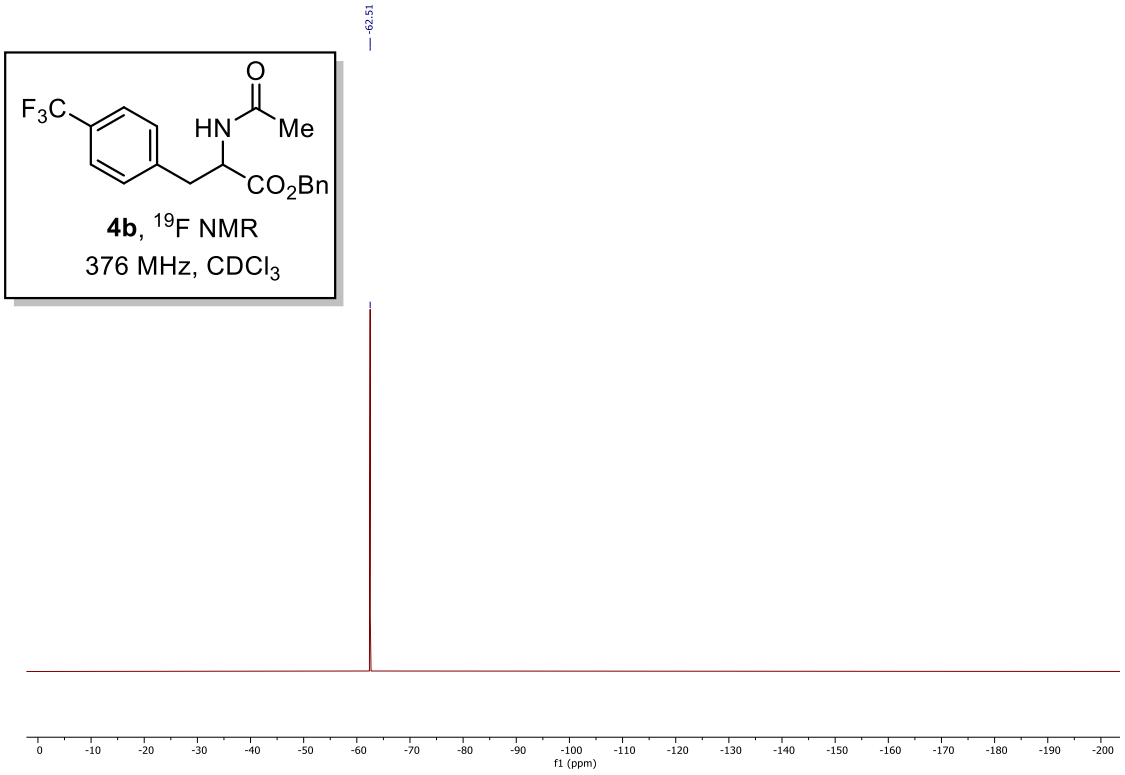
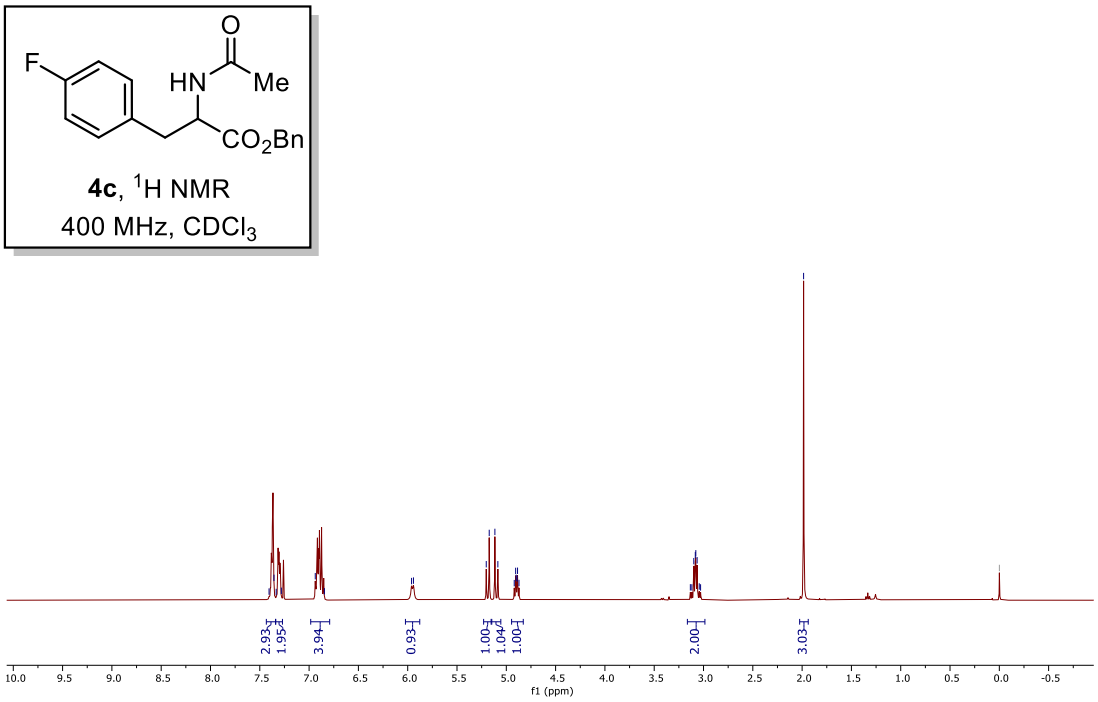
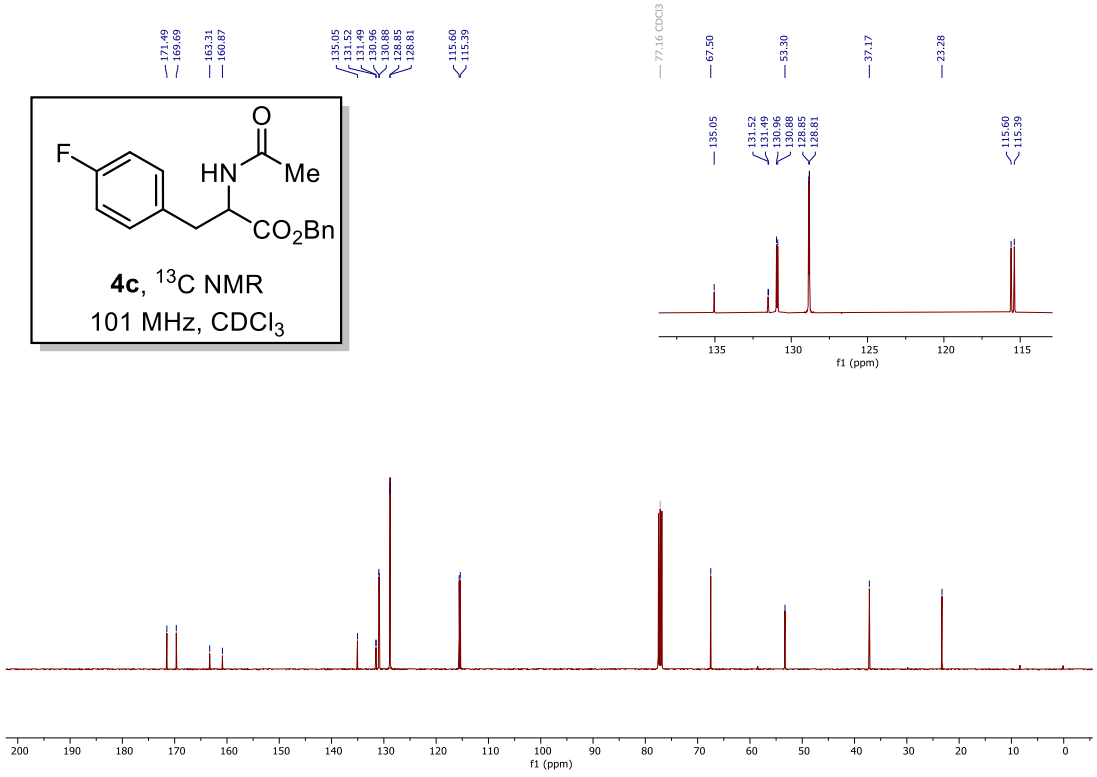
O
Me
CO2Bn
4b, 1H NMR
400 MHz, CDCl3
f1 (ppm)


F3C
HN
O
Me
CO2Bn
4b, 13C NMR
101 MHz, CDCl3
f1 (ppm)


-62.51
O
F3C
HN
Me
CO2Bn
4b, 19F NMR
376 MHz, CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


F
HN
O
Me
CO2Bn
4c, 1H NMR
400 MHz, CDCl3
f1 (ppm)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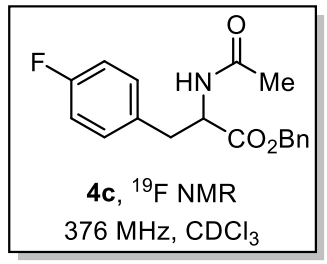
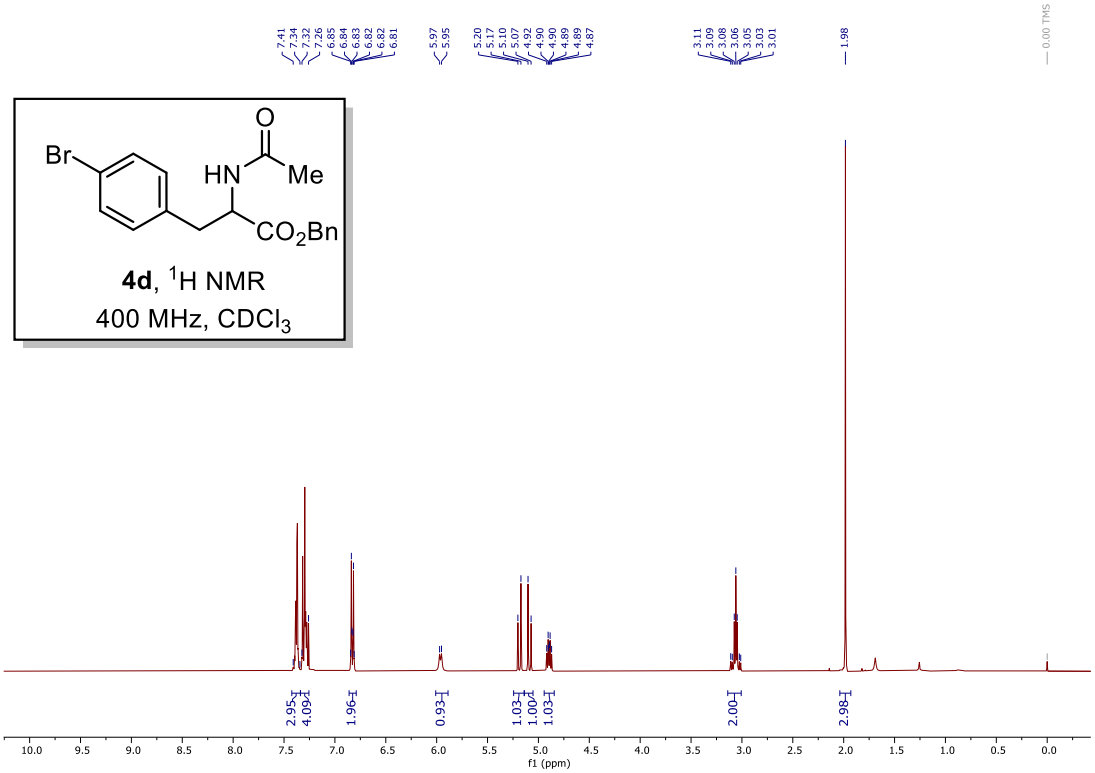
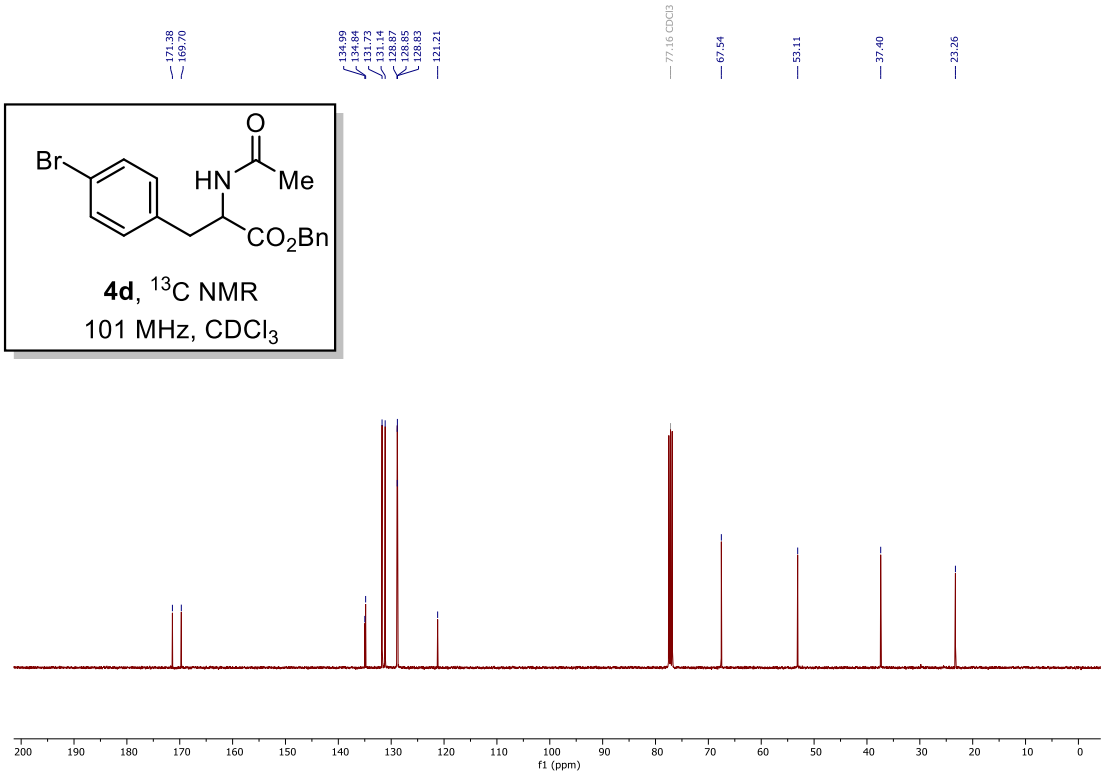
HN
O
Me
CO2Bn
4c, 13C NMR
101 MHz, CDCl3
f1 (ppm)




**4c**, $^{19}$F NMR
376 MHz, $CDCl_3$


7.41
7.34
7.32
7.26
6.85
6.84
6.83
6.82
6.82
6.81
5.97
5.95
5.20
5.17
5.10
5.07
4.92
4.90
4.90
4.89
4.89
4.87
3.11
3.09
3.08
3.06
3.05
3.03
3.01
1.98
0.00 TMS
Br
HN
O
Me
CO2Bn
4d, 1H NMR
400 MHz, CDCl3
2.95
4.09
1.96
0.93
1.03
1.00
1.03
2.00
2.98
f1 (ppm)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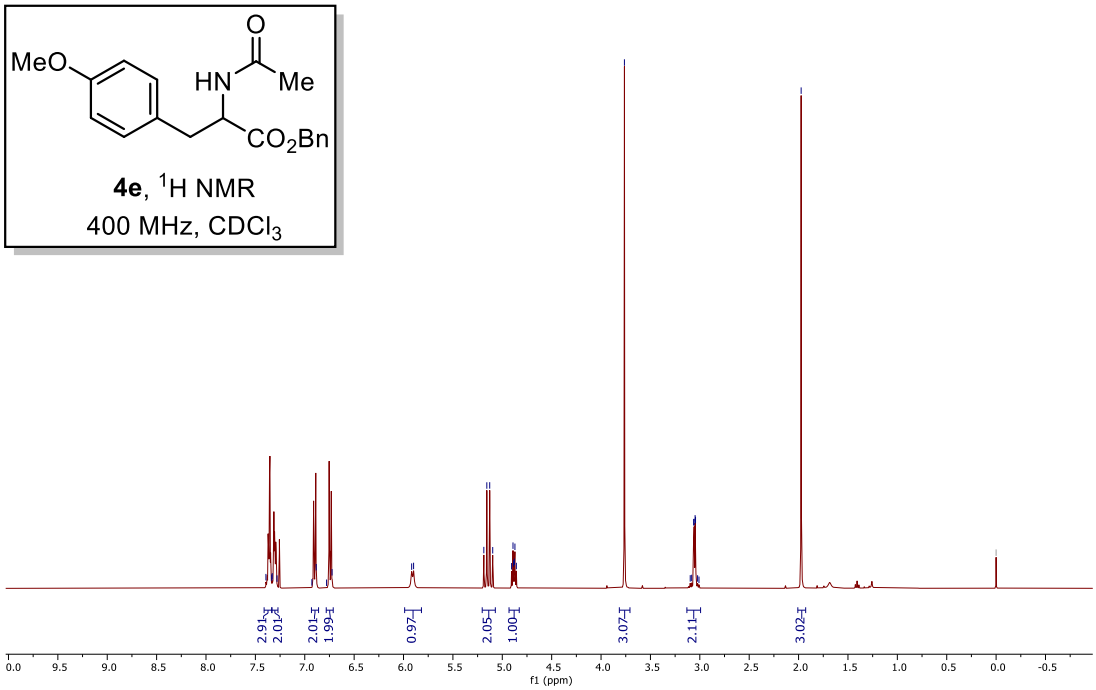
131.14
128.87
128.85
128.83
121.21
77.16 CDCl3
67.54
53.11
37.40
23.26
Br
HN
O
Me
CO2Bn
4d, 13C NMR
101 MHz, CDCl3
f1 (ppm)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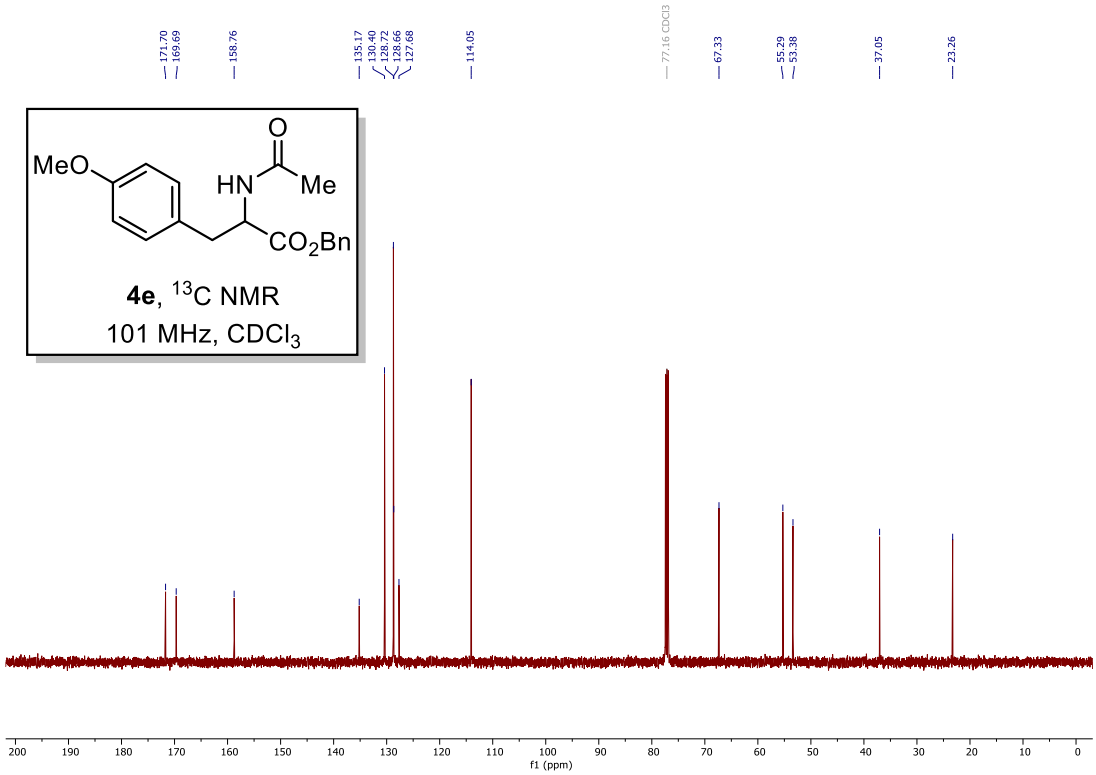
HN
O
Me
CO2Bn
4e, 1H NMR
400 MHz, CDCl3
f1 (ppm)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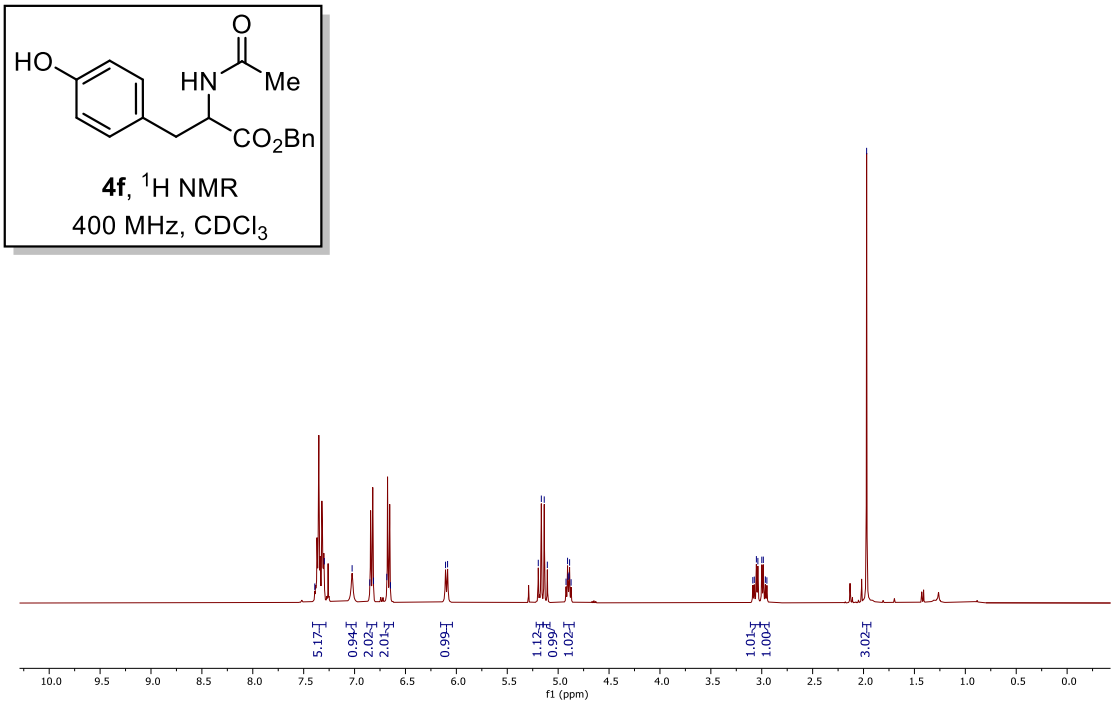
HN
O
Me
CO2Bn
4e, 13C NMR
101 MHz, CDCl3
f1 (ppm)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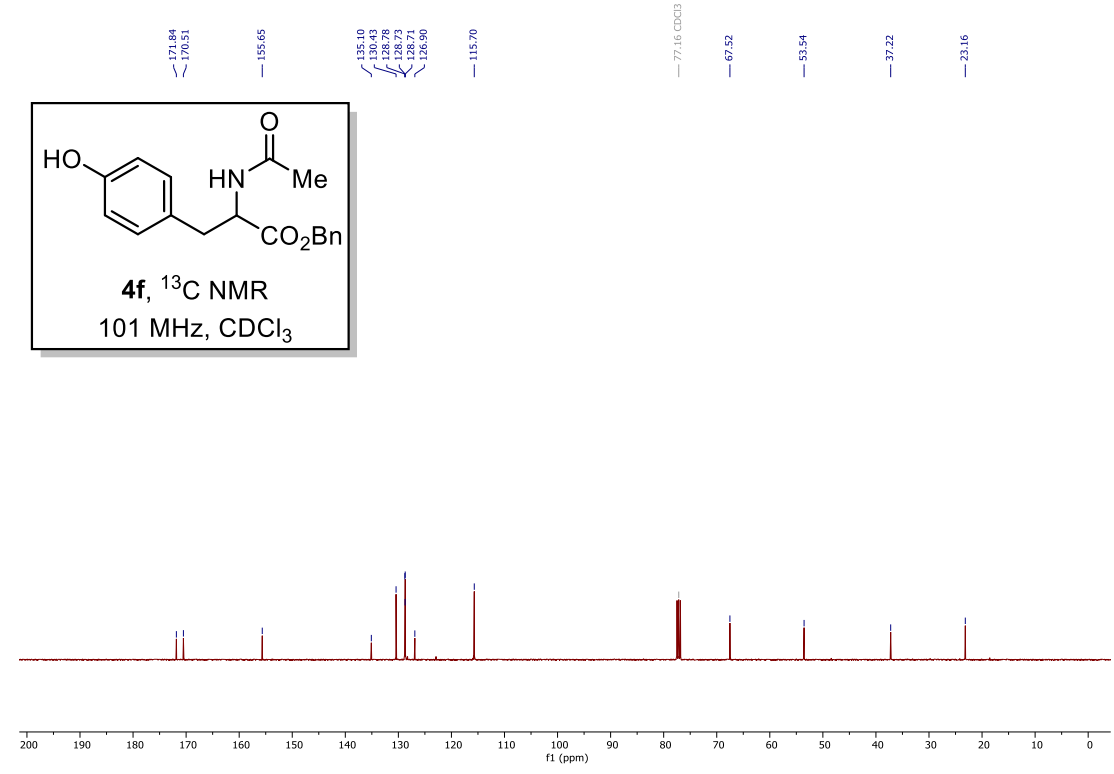
HN
O
Me
CO2Bn
4f, 1H NMR
400 MHz, CDCl3
f1 (ppm)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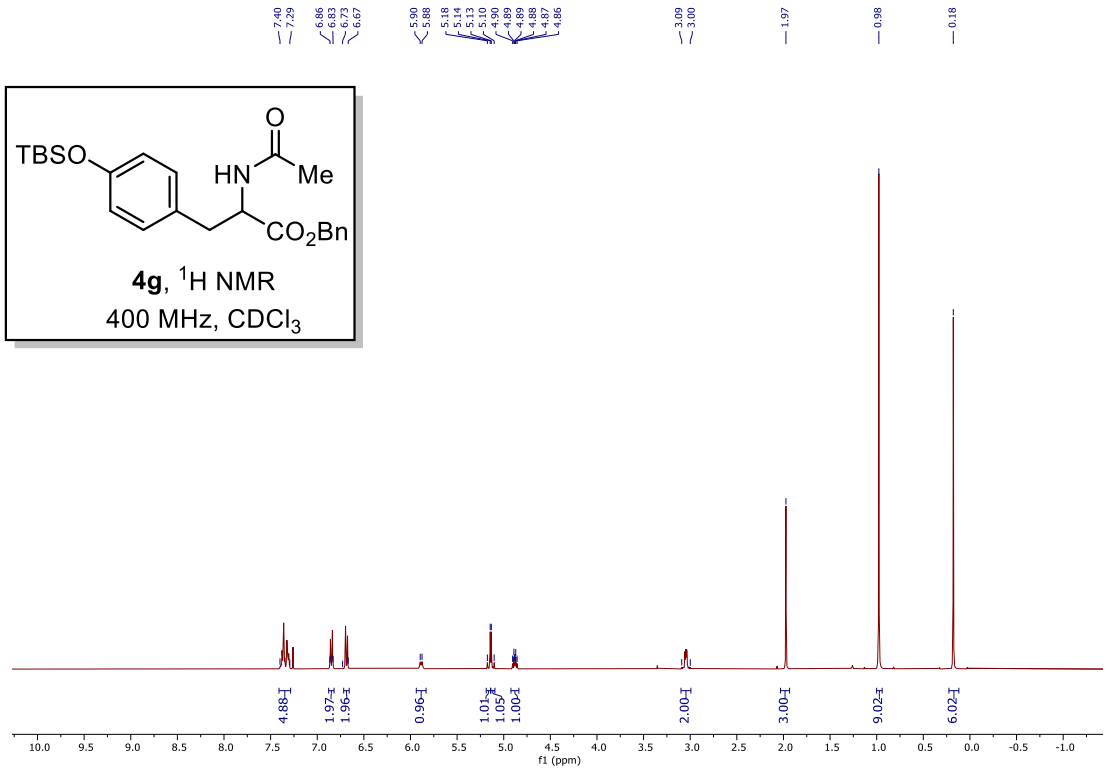
HN
O
Me
CO2Bn
4f, 13C NMR
101 MHz, CDCl3
f1 (ppm)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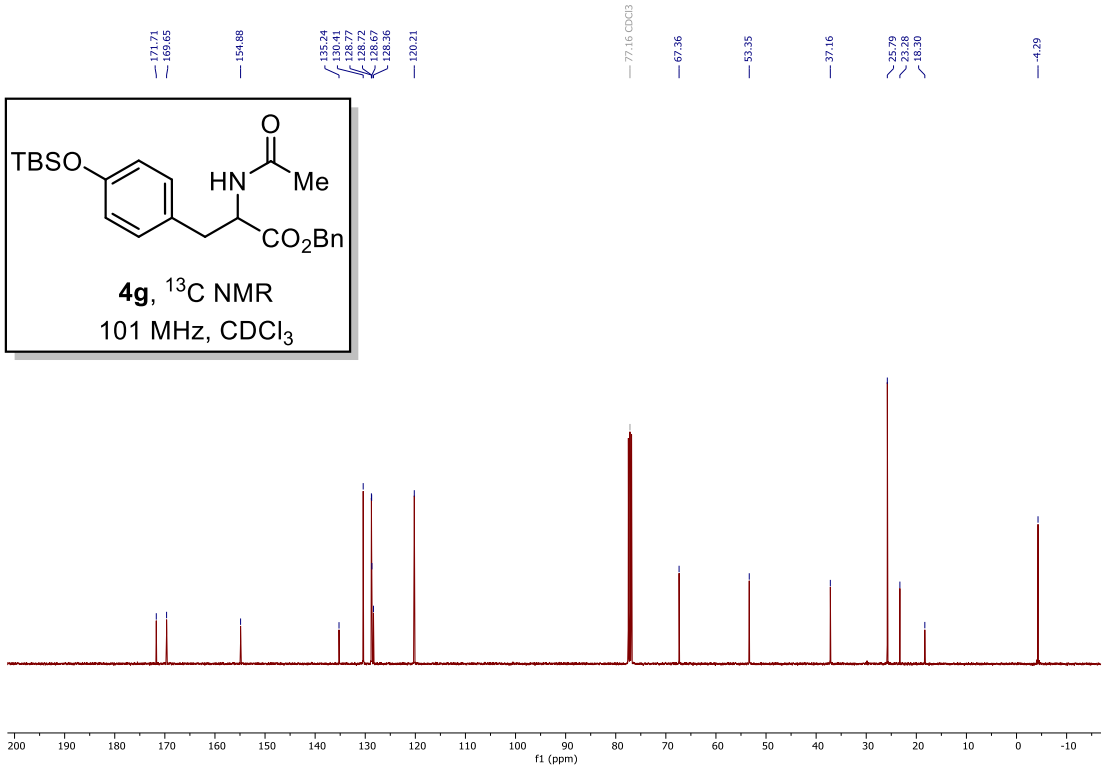
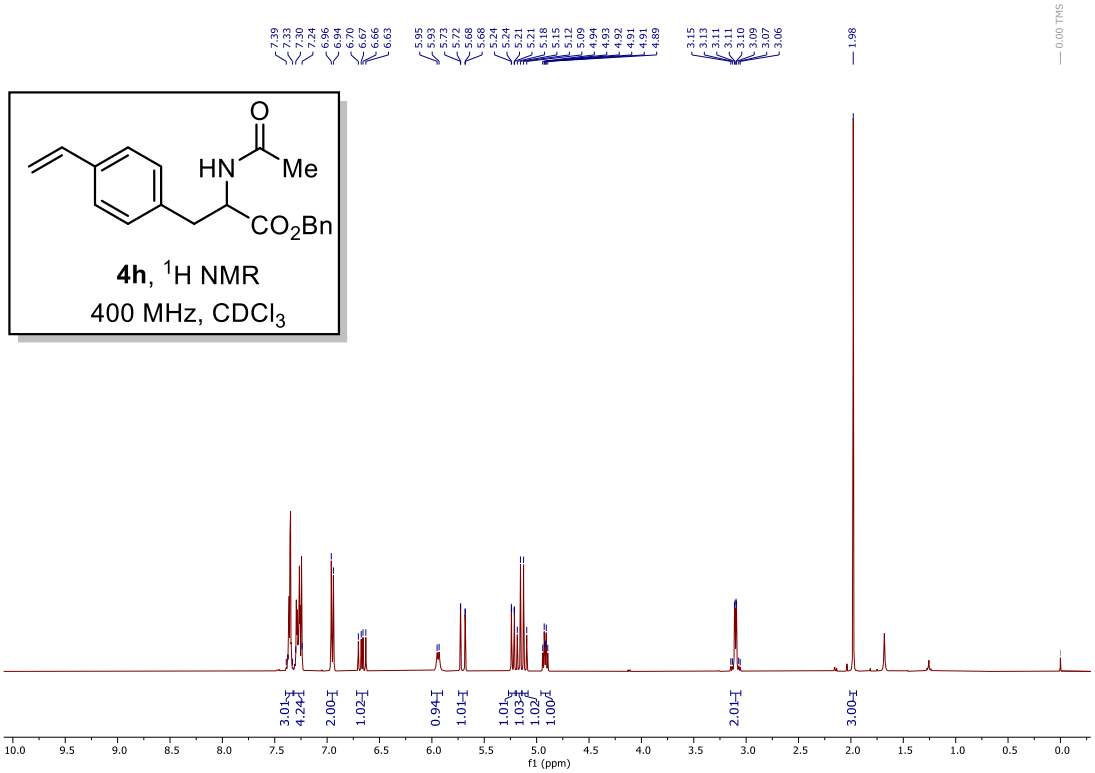
HN
O
Me
CO2Bn
4g, 1H NMR
400 MHz, CDCl3
f1 (ppm)


TBSO
HN
O
Me
CO2Bn
4g, 13C NMR
101 MHz, CDCl3
f1 (ppm)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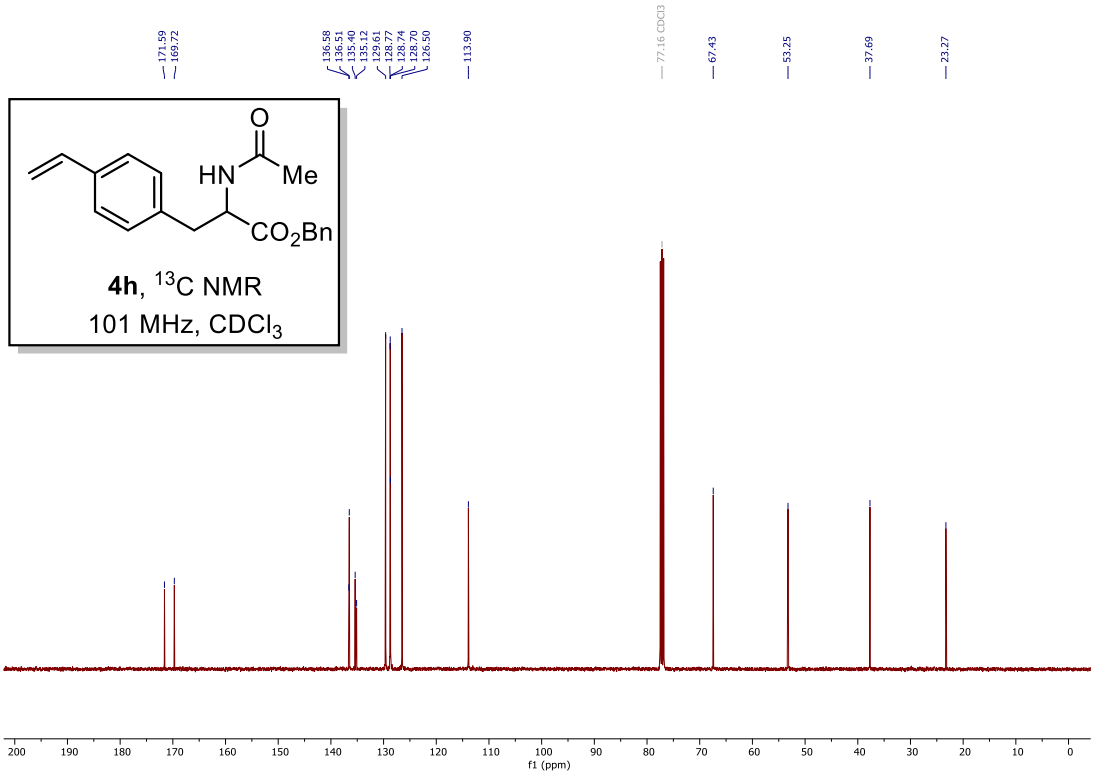
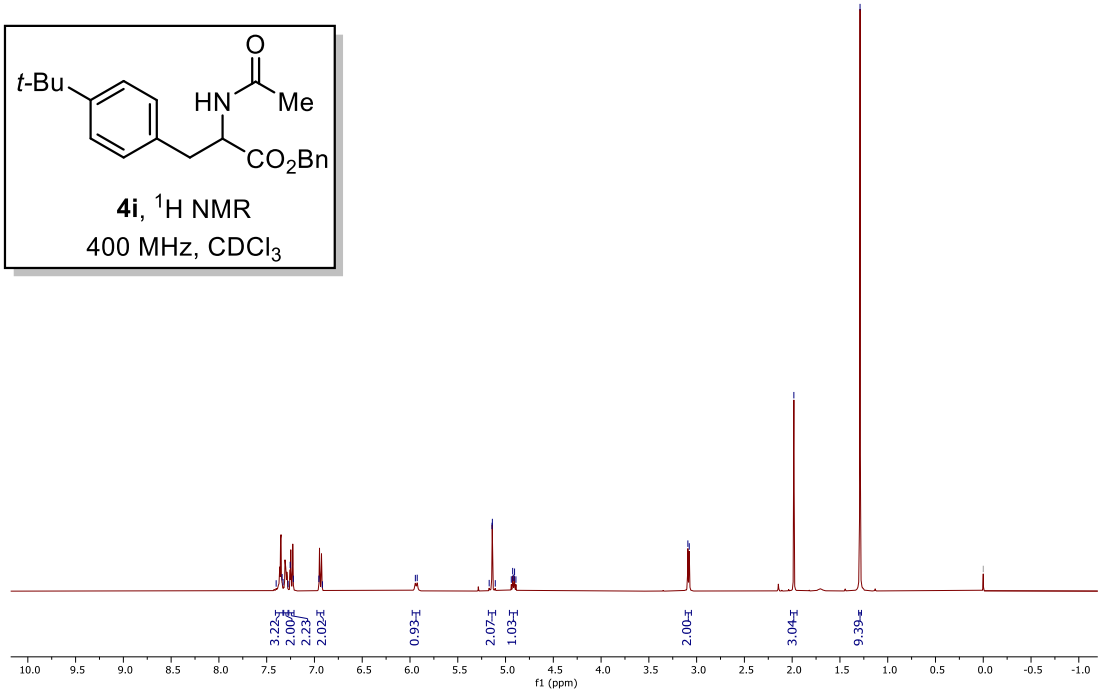
Me
O
CO2Bn
4h, 1H NMR
400 MHz, CDCl3
f1 (ppm)


HN
Me
O
CO2Bn
4h, 13C NMR
101 MHz, CDCl3
f1 (ppm)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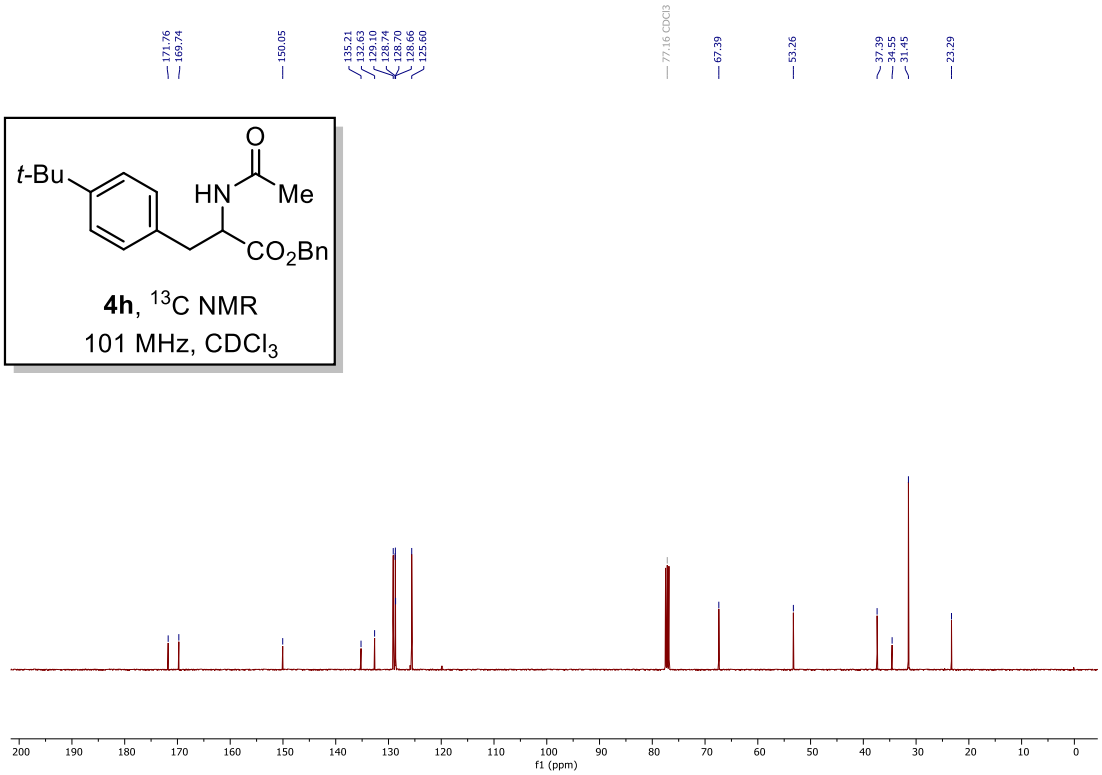
7.34
7.33
7.28
7.25
7.22
6.95
6.92
5.94
5.92
5.17
5.14
5.14
5.11
4.94
4.93
4.92
4.91
4.91
4.89
3.09
3.08
1.98
1.29
0.00 TMS
t-Bu
HN
O
Me
CO2Bn
4i, 1H NMR
400 MHz, CDCl3
3.22
2.00
2.23
2.02
0.93
2.07
1.03
2.00
3.04
9.39
f1 (ppm)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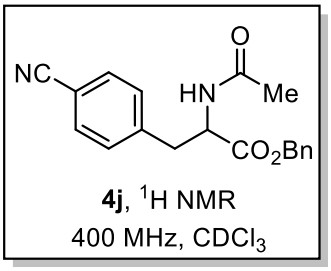
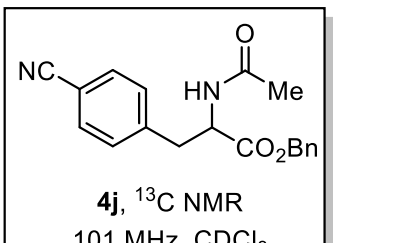
169.74
150.05
135.21
132.63
129.10
128.74
128.70
126.66
125.60
77.16 CDCl3
67.39
53.26
37.39
34.55
31.45
23.29
t-Bu
HN
O
Me
CO2Bn
4h, 13C NMR
101 MHz, CDCl3
f1 (ppm)

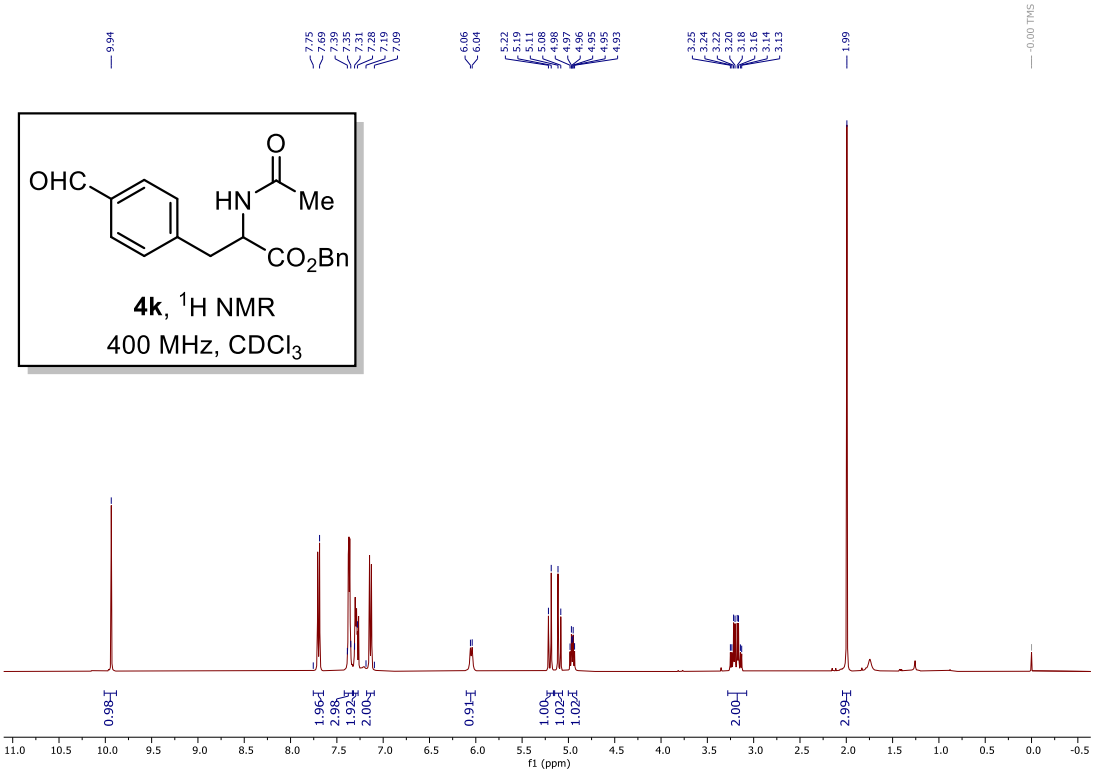


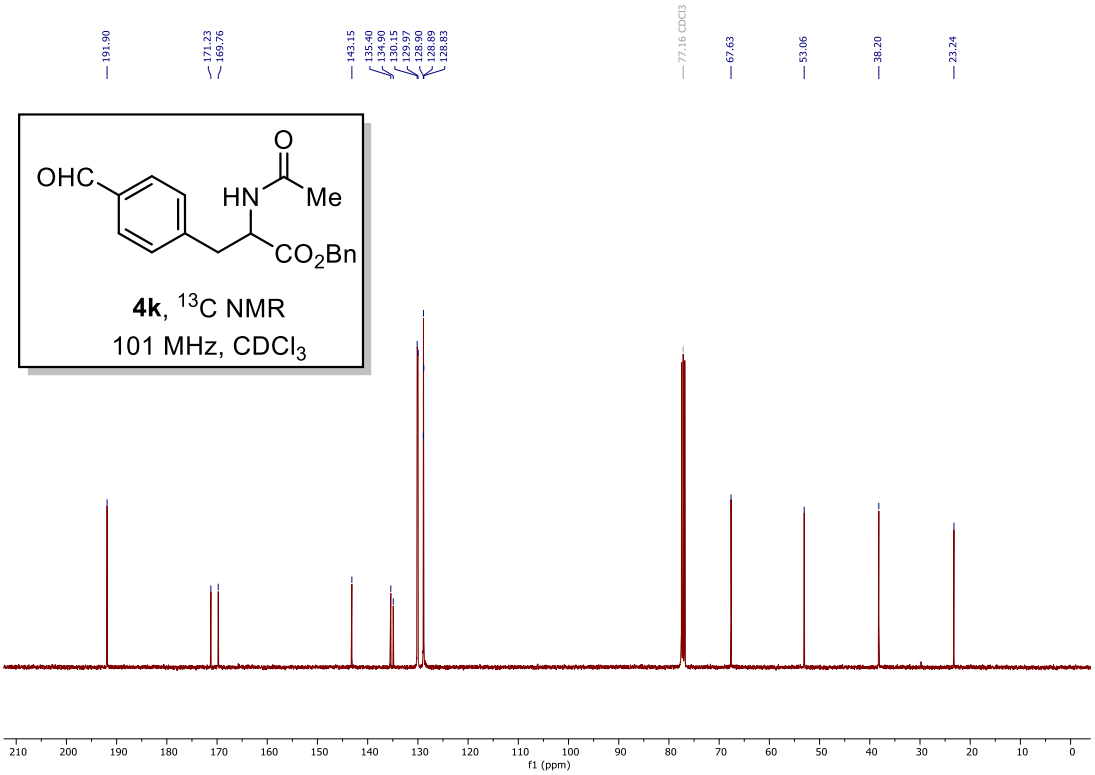

**4j**, $^{1}$H NMR
400 MHz, $CDCl_3$




**4j**, $^{13}$C NMR
101 MHz, $CDCl_3$


9.94
7.75
7.69
7.39
7.35
7.31
7.28
7.19
7.09
6.06
6.04
5.22
5.19
5.11
5.08
4.98
4.97
4.96
4.95
4.95
4.93
3.25
3.24
3.22
3.20
3.18
3.16
3.14
3.13
1.99
-0.00 TMS
OHC
HN
O
Me
CO2Bn
4k, 1H NMR
400 MHz, CDCl3
0.98
1.96
2.98
1.92
2.00
0.91
1.00
1.02
1.02
2.00
2.99
f1 (ppm)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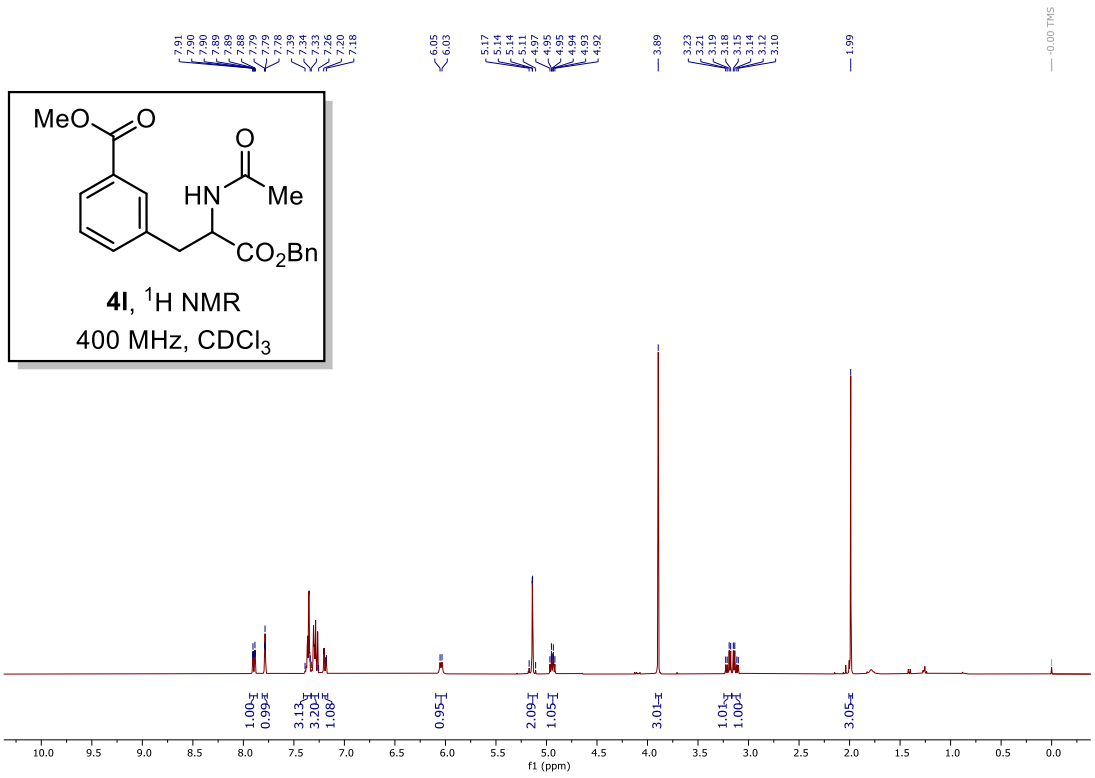
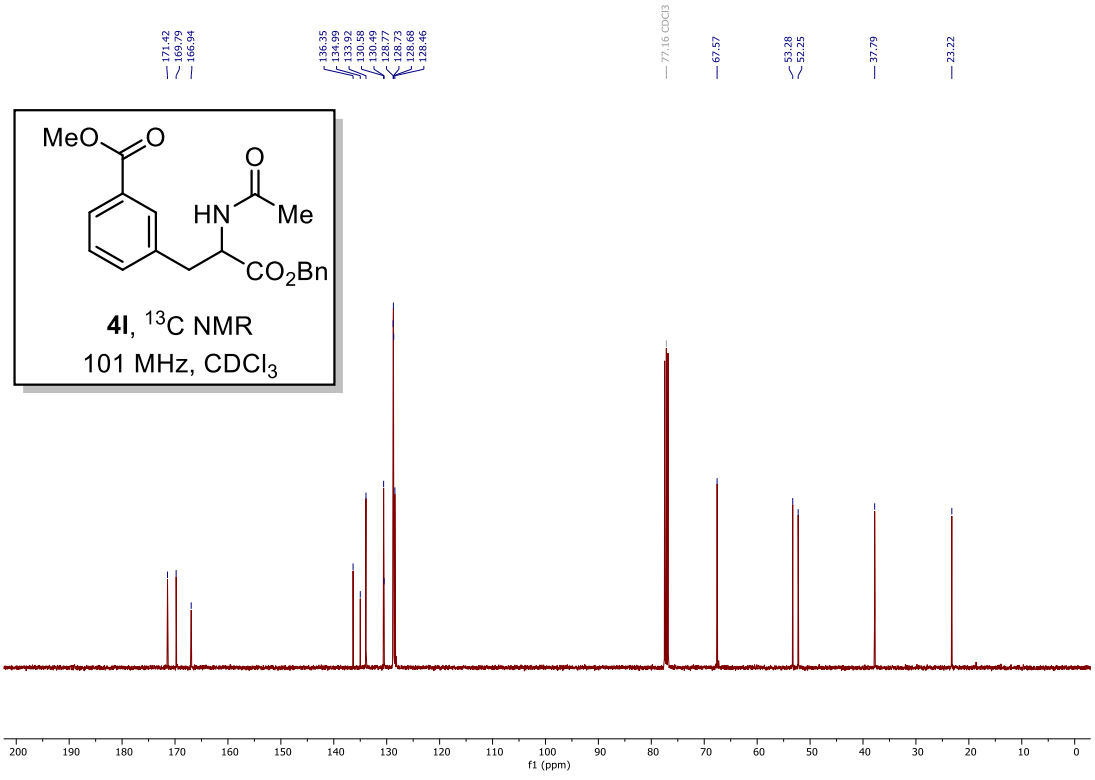
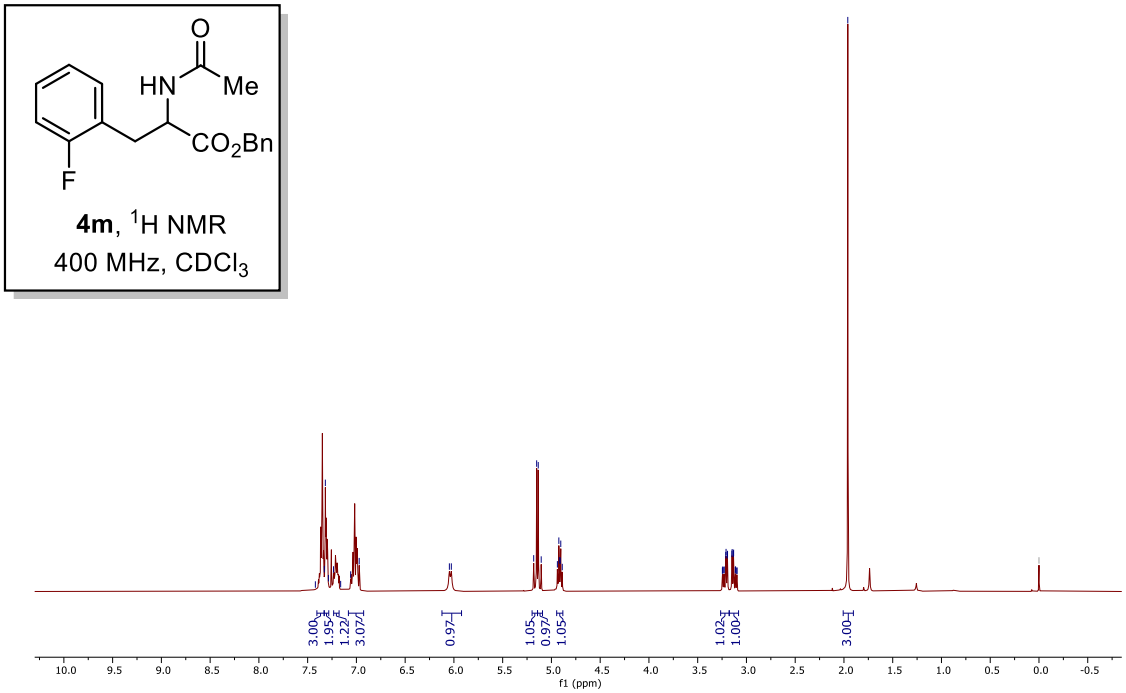
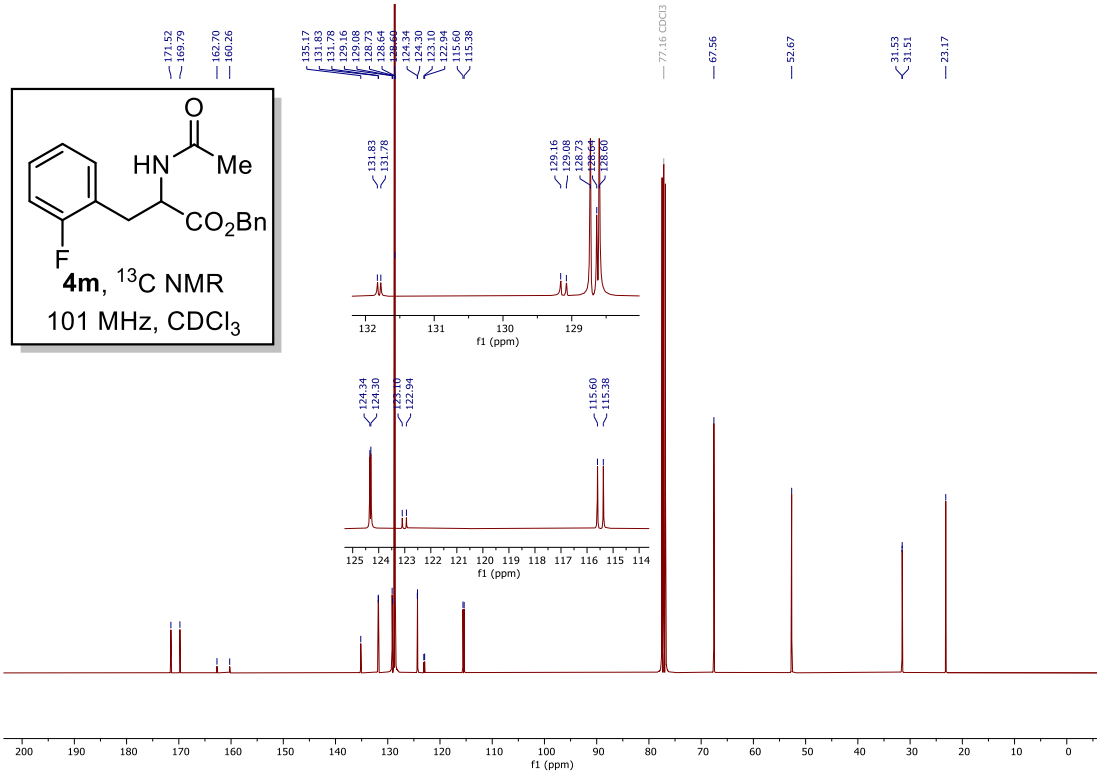
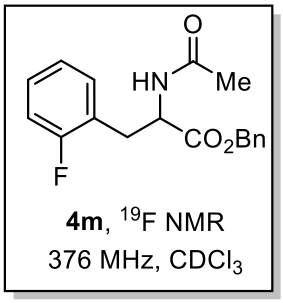
171.23
169.76
143.15
135.40
134.90
130.15
129.97
128.90
128.90
128.83
77.16 CDCl3
67.63
53.06
38.20
23.24
OHC
HN
O
Me
CO2Bn
4k, 13C NMR
101 MHz, CDCl3
f1 (ppm)


MeO
O
HN
O
Me
CO2Bn
4l, 1H NMR
400 MHz, CDCl3
f1 (ppm)

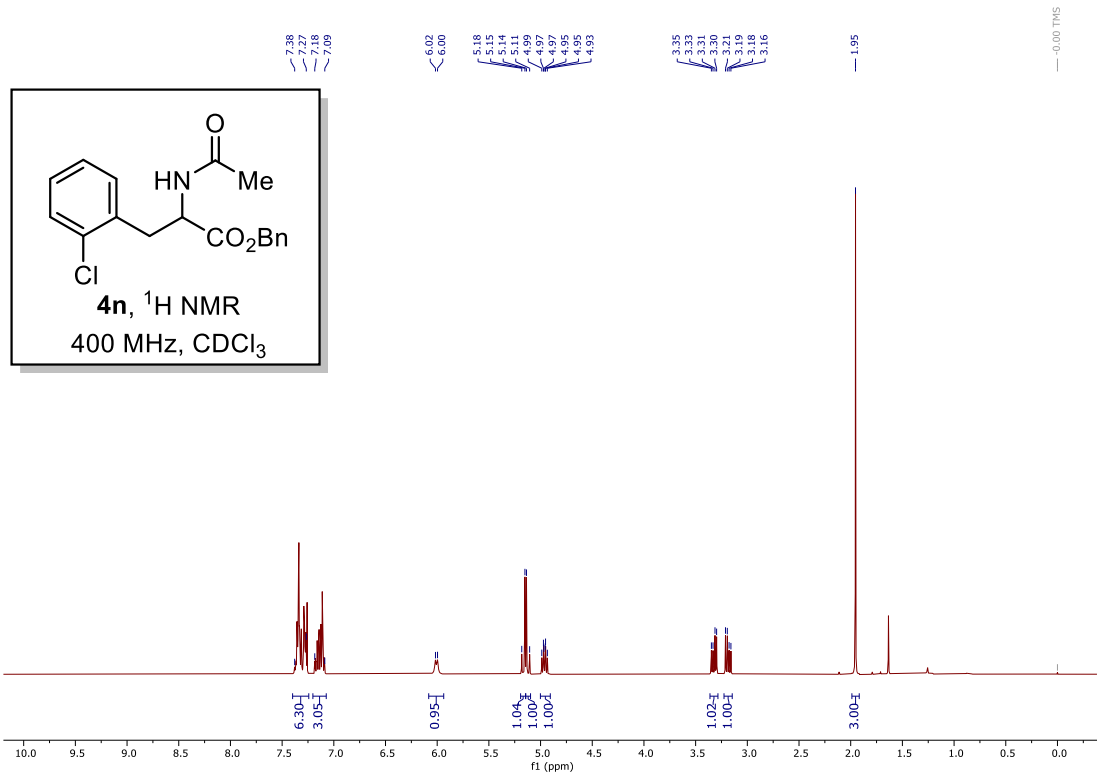

MeO
O
HN
O
Me
CO2Bn
4l, 13C NMR
101 MHz, CDCl3
f1 (ppm)


HN
Me
O
CO2Bn
F
4m, 1H NMR
400 MHz, CDCl3
f1 (ppm)


HN
Me
O
CO2Bn
F
4m, 13C NMR
101 MHz, CDCl3
f1 (ppm)




**4m**, $^{19}$F NMR
376 MHz, $CDCl_3$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7.27
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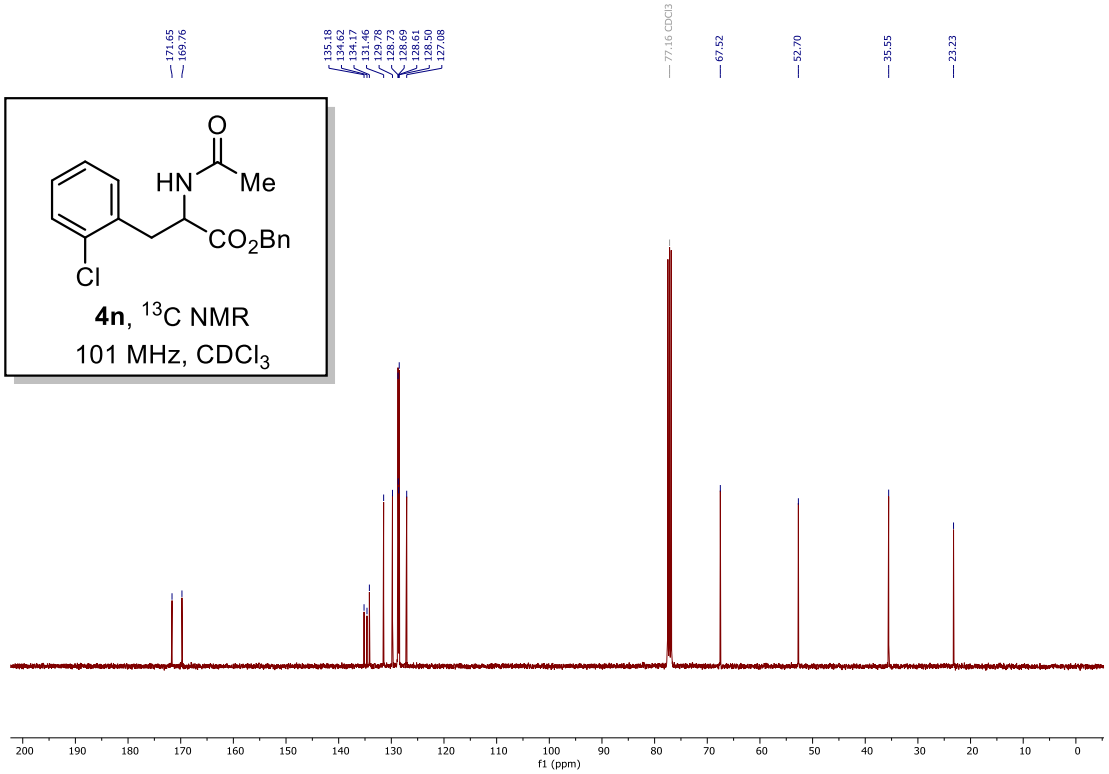
7.09
6.02
6.00
5.18
5.15
5.14
5.11
4.99
4.97
4.97
4.95
4.95
4.93
3.35
3.33
3.31
3.30
3.21
3.19
3.18
3.16
1.95
0.00 TMS
O
HN
Me
CO2Bn
Cl
4n, 1H NMR
400 MHz, CDCl3
6.30
3.05
0.95
1.04
1.00
1.00
1.02
1.00
3.00
f1 (ppm)


171.65
169.76
135.18
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128.73
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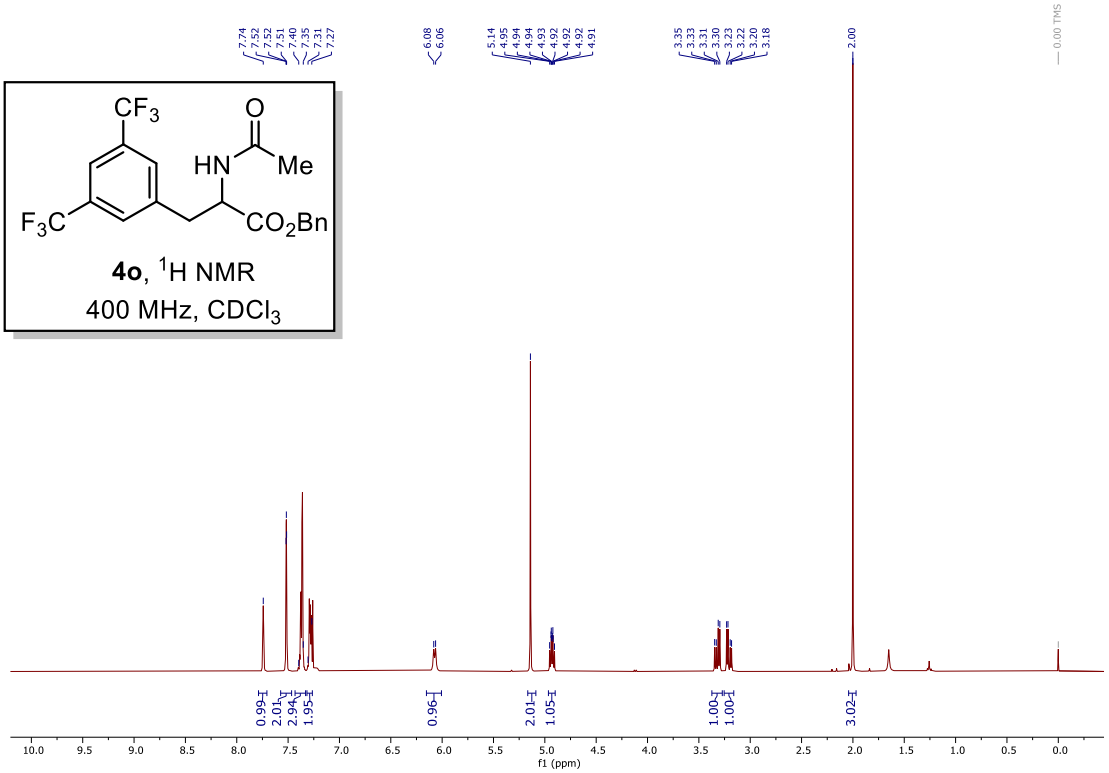
128.61
128.50
127.08
77.16 CDCl3
67.52
52.70
35.55
23.23
O
HN
Me
CO2Bn
Cl
4n, 13C NMR
101 MHz, CDCl3
f1 (ppm)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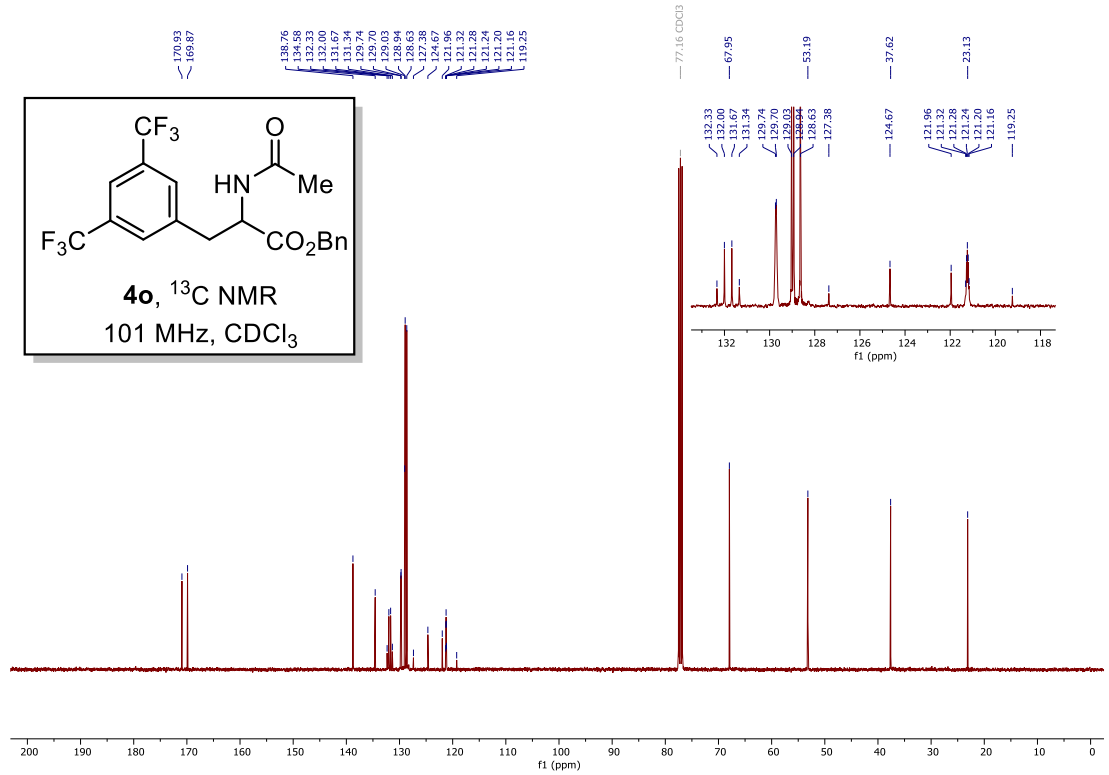
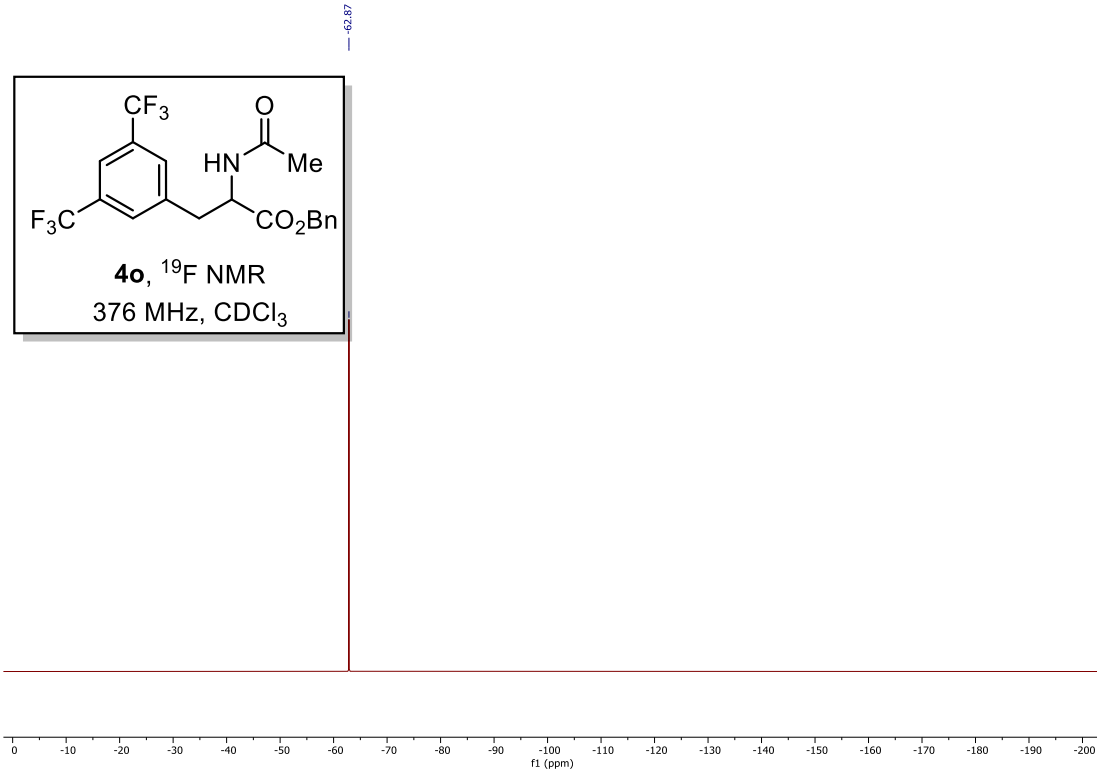
O
HN
Me
F3C
CO2Bn
4o, 1H NMR
400 MHz, CDCl3
f1 (ppm)


CF3
O
HN
Me
F3C
CO2Bn
4o, 13C NMR
101 MHz, CDCl3
f1 (ppm)


-62.87
CF3
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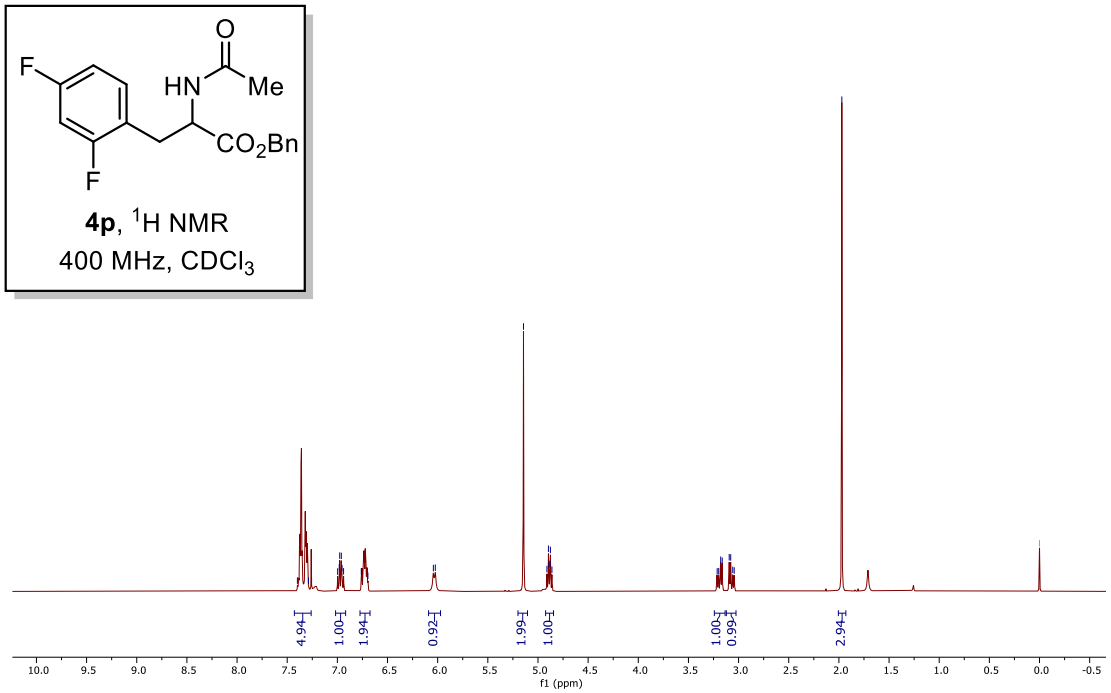
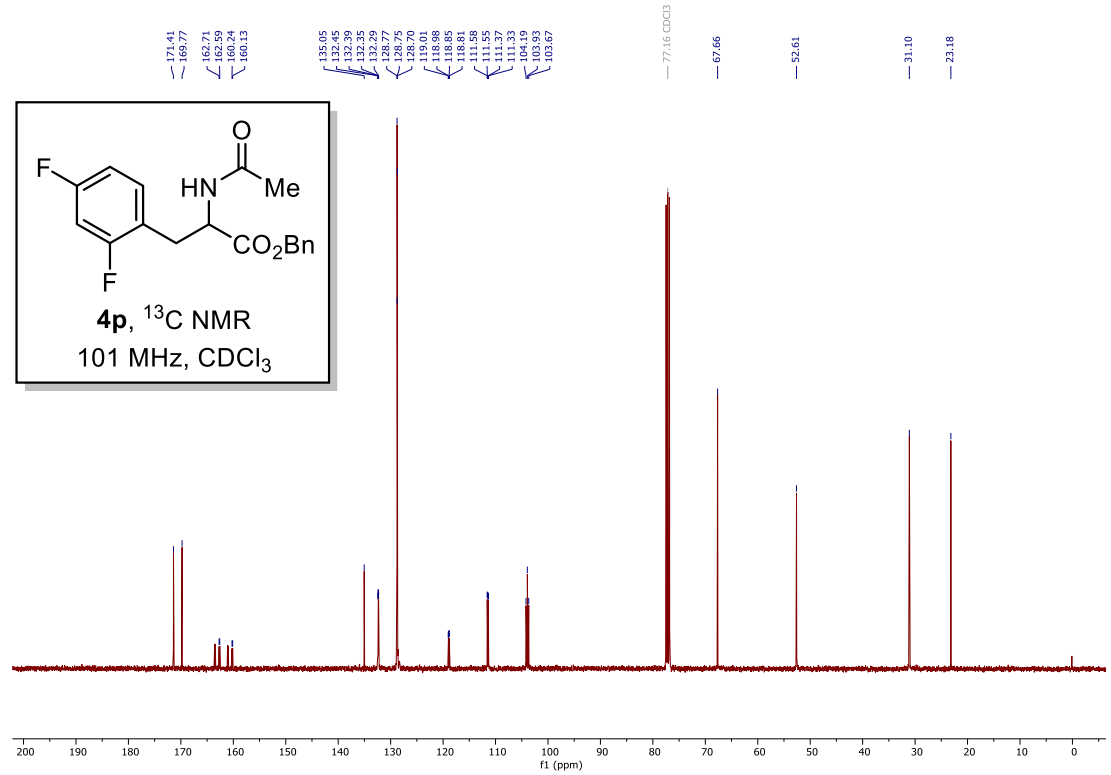
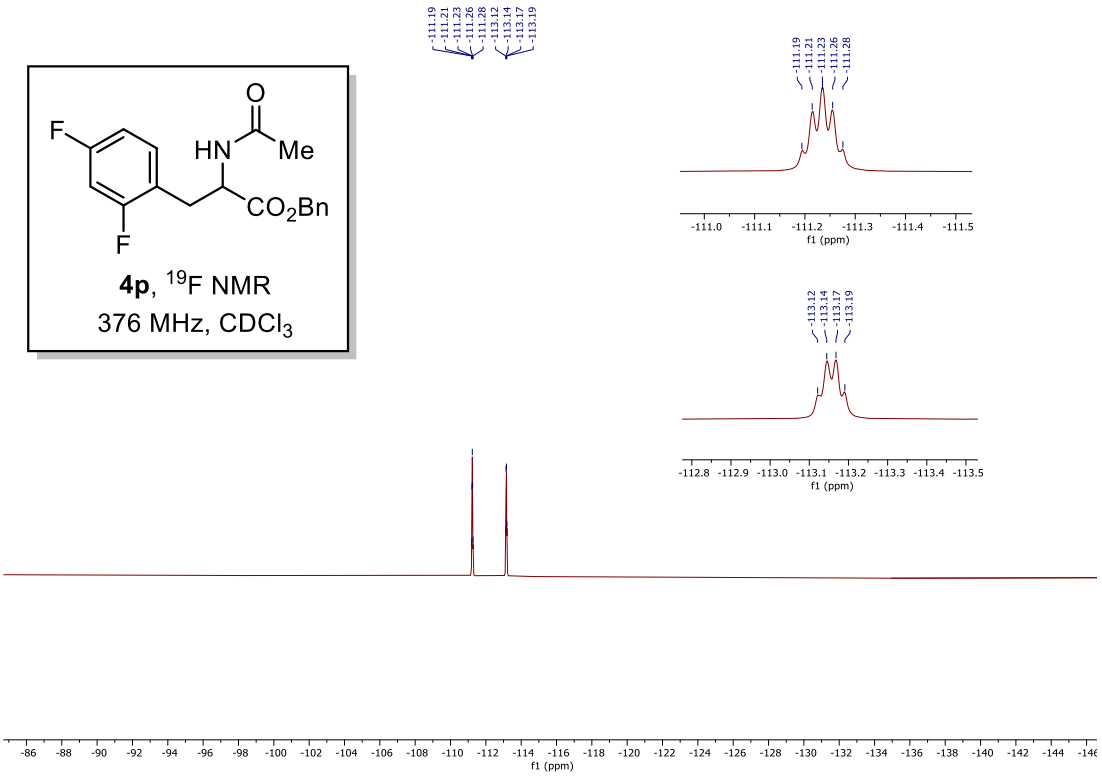
HN
Me
F3C
CO2Bn
4o, 19F NMR
376 MHz, CDCl3
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)


F
O
HN
Me
CO2Bn
F
4p, 1H NMR
400 MHz, CDCl3
f1 (ppm)


F
O
HN
Me
CO2Bn
F
4p, 13C NMR
101 MHz, CDCl3
f1 (ppm)


F
O
HN
Me
CO2Bn
F
4p, 19F NMR
376 MHz, CDCl3
-111.19
-111.21
-111.23
-111.26
-111.28
-113.12
-113.14
-113.17
-113.19
-111.0
-111.1
-111.2
-111.3
-111.4
-111.5
f1 (ppm)
-112.8
-112.9
-113.0
-113.1
-113.2
-113.3
-113.4
-113.5
f1 (ppm)
-86
-88
-90
-92
-94
-96
-98
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-104
-106
-108
-110
-112
-114
-116
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-130
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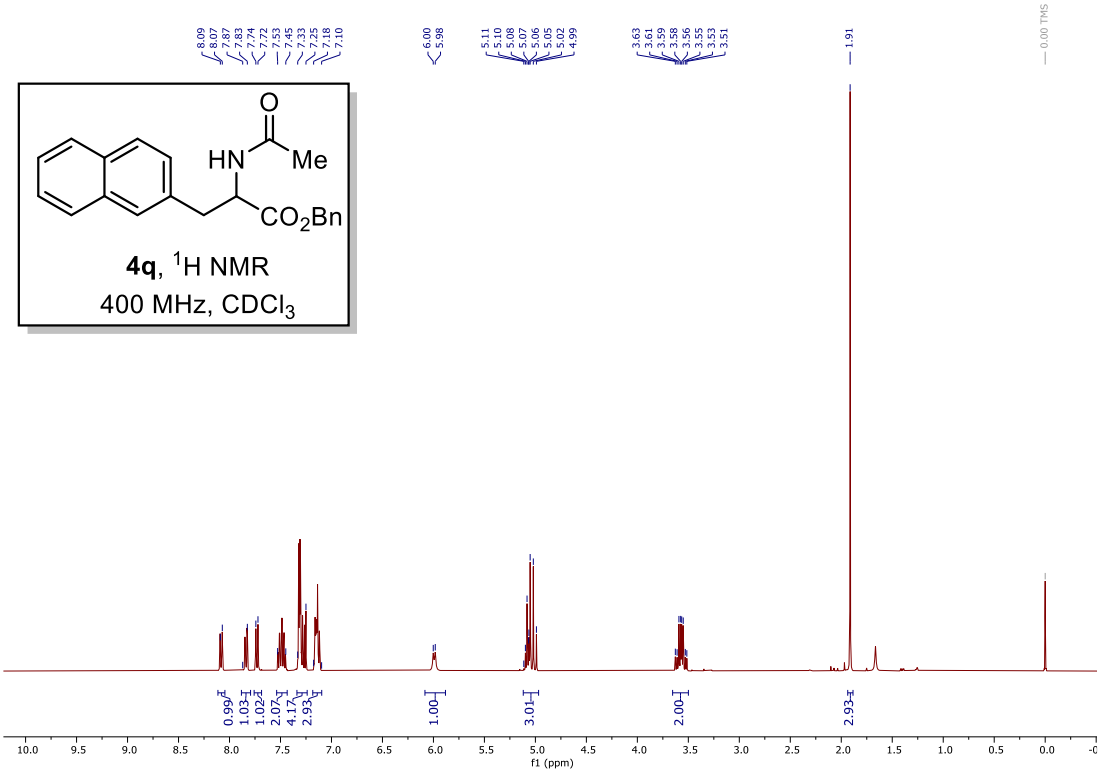
-134
-136
-138
-140
-142
-144
f1 (ppm)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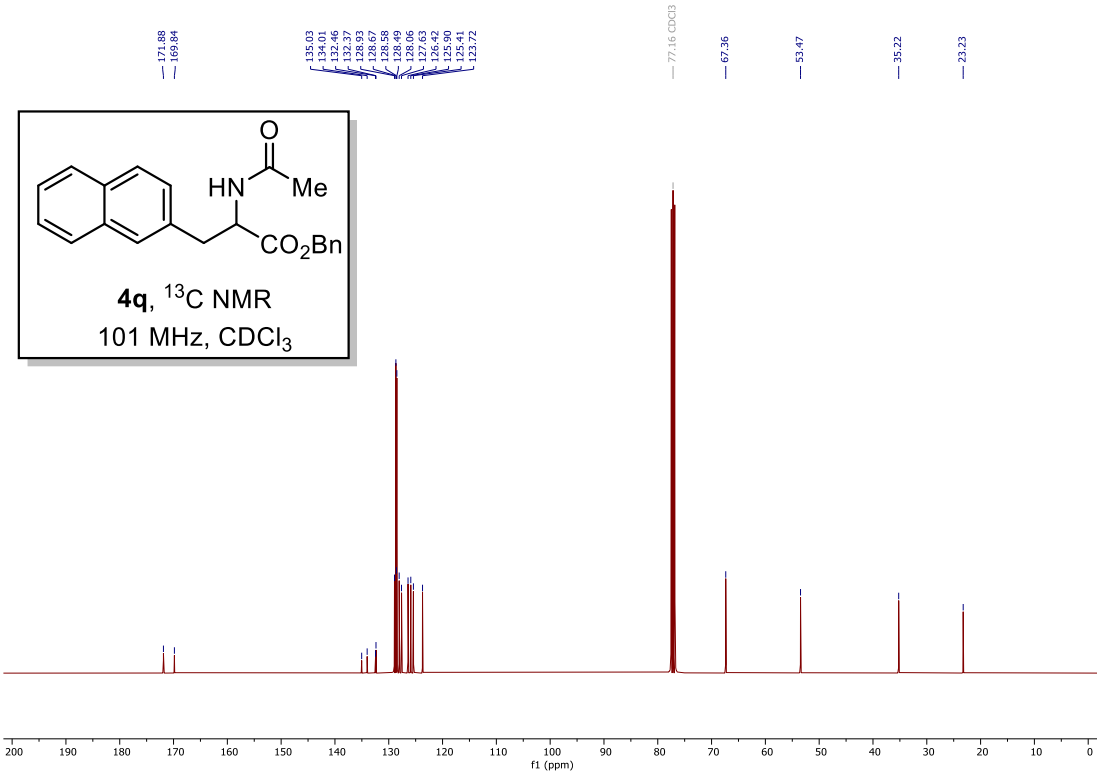
O
Me
CO2Bn
4q, 1H NMR
400 MHz, CDCl3
f1 (ppm)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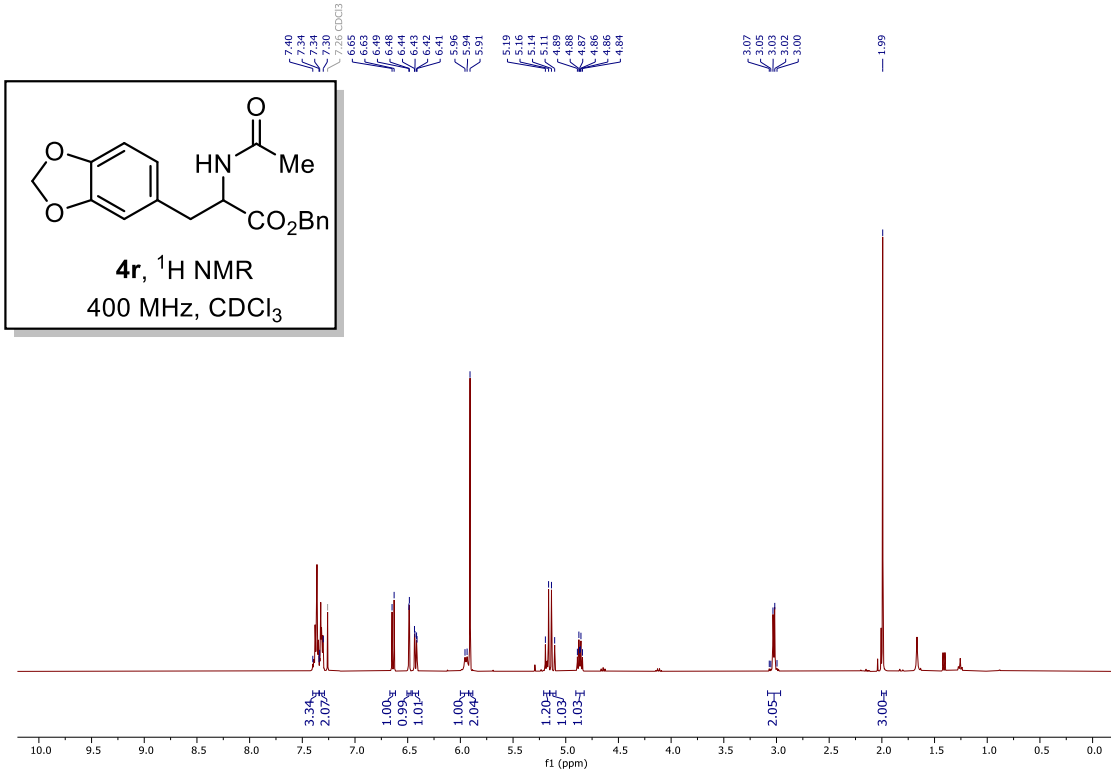
O
Me
CO2Bn
4q, 13C NMR
101 MHz, CDCl3
f1 (ppm)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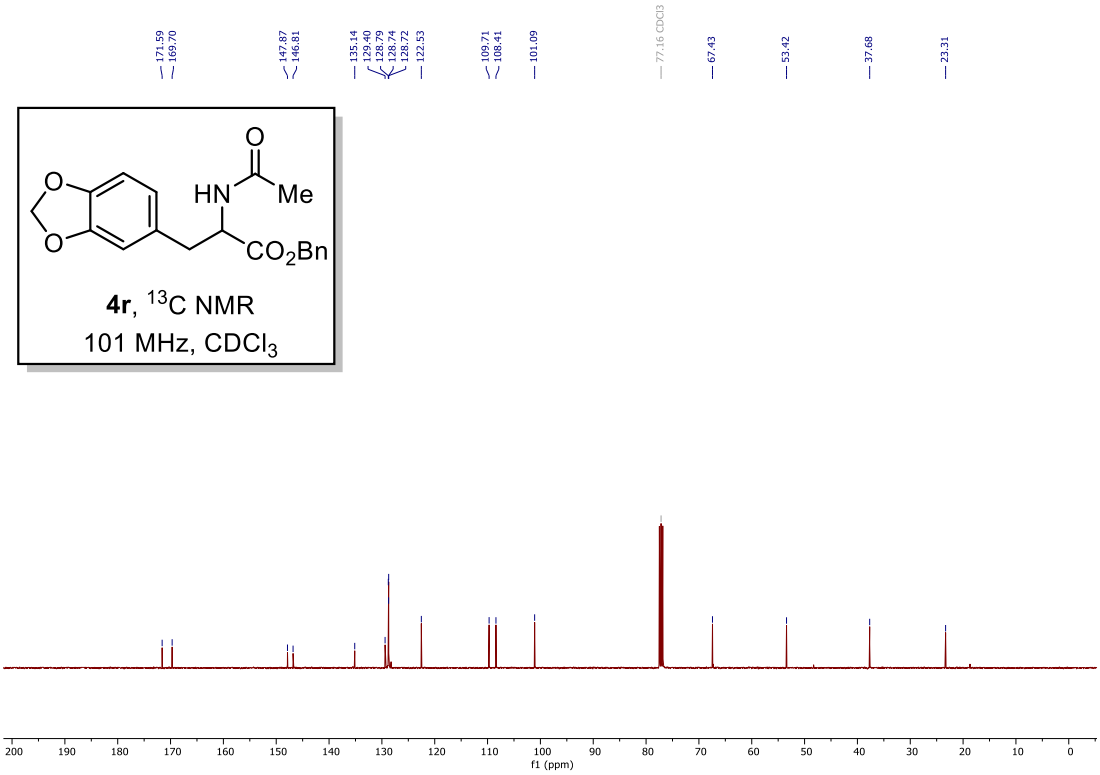
O
O
O
CO2Bn
4r, 1H NMR
400 MHz, CDCl3
f1 (ppm)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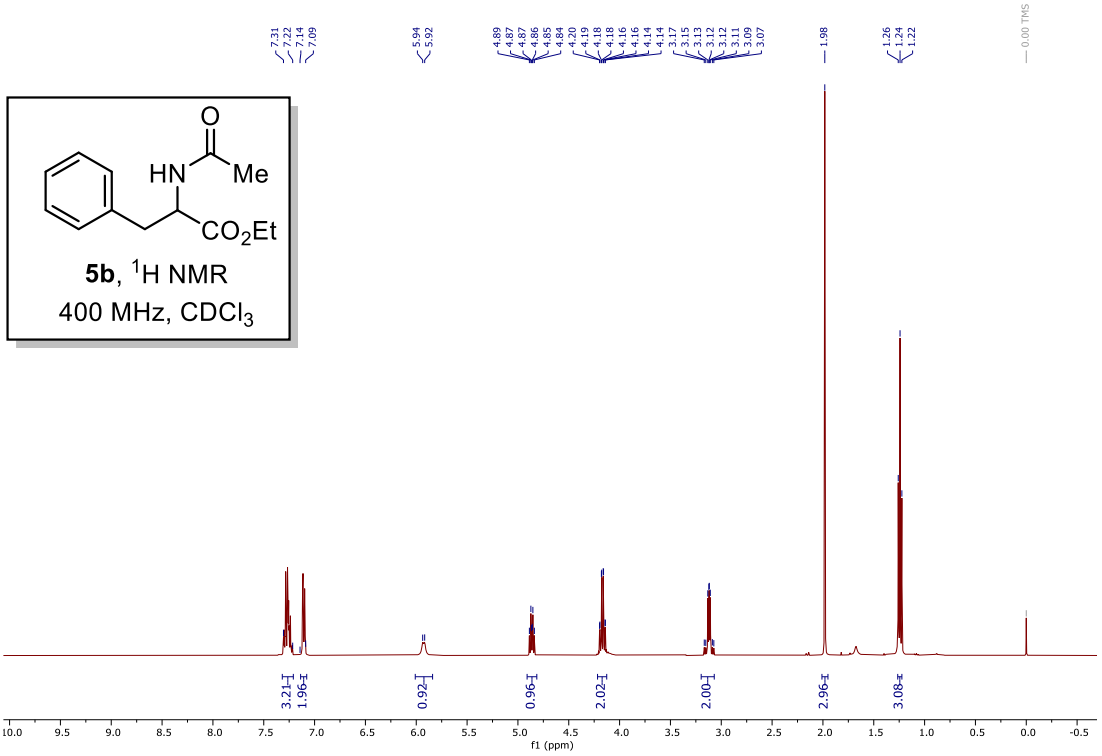
Me
O
O
O
CO2Bn
4r, 13C NMR
101 MHz, CDCl3
f1 (ppm)


O
HN
Me
CO2Et
5b, 1H NMR
400 MHz, CDCl3
7.31
7.22
7.14
7.09
5.94
5.92
4.89
4.87
4.87
4.86
4.85
4.84
4.20
4.19
4.18
4.18
4.16
4.16
4.14
4.14
3.17
3.15
3.13
3.12
3.12
3.11
3.09
3.07
1.98
1.26
1.24
1.22
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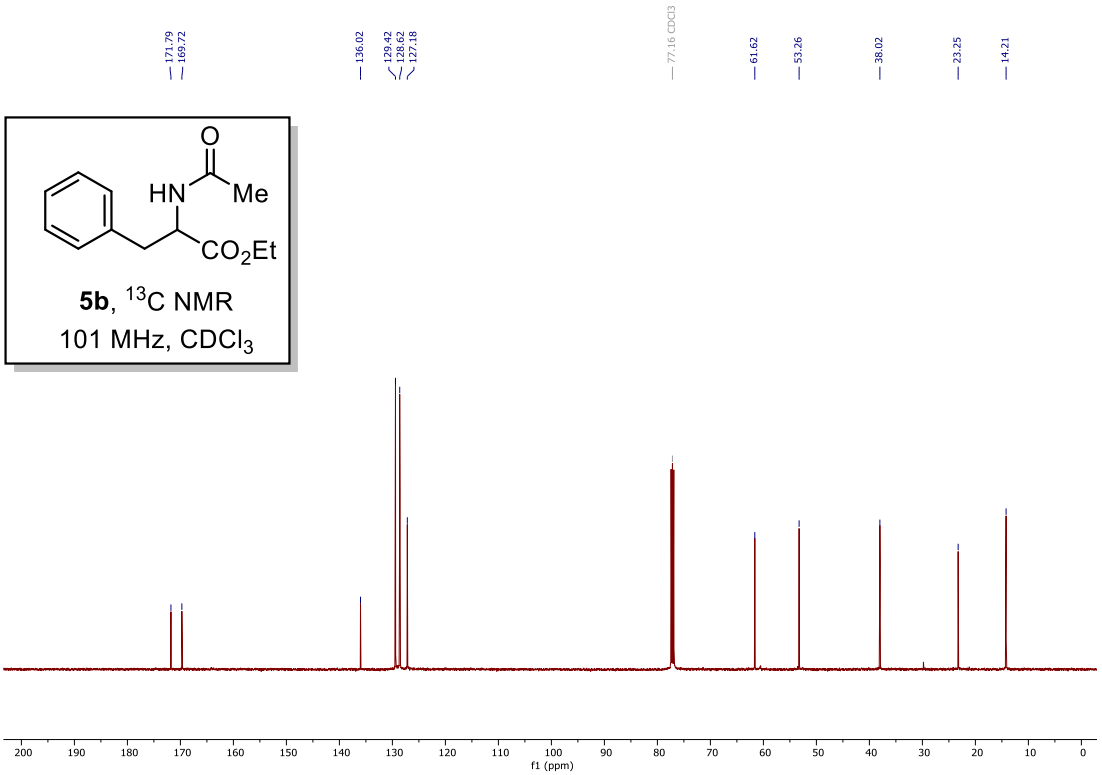
0.92
0.96
2.02
2.00
2.96
3.08
f1 (ppm)


O
HN
Me
CO2Et
5b, 13C NMR
101 MHz, CDCl3
171.79
169.72
136.02
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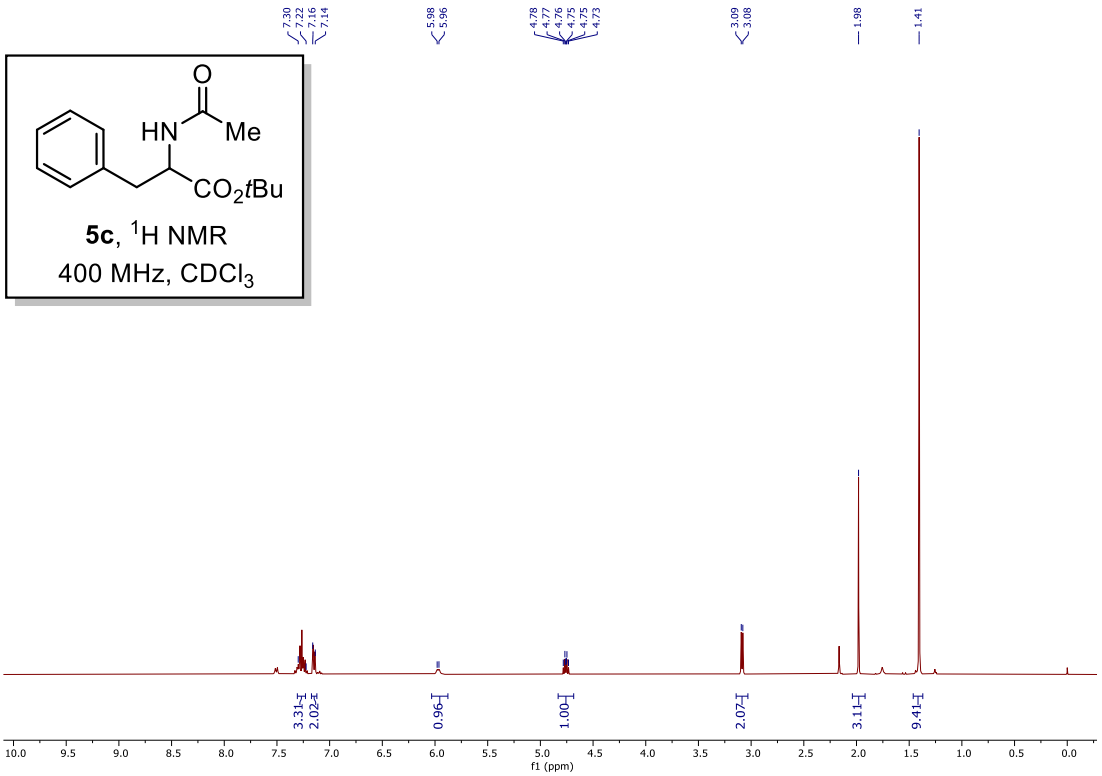
128.62
127.18
77.16 CDCl3
61.62
53.26
38.02
23.25
14.21
f1 (ppm)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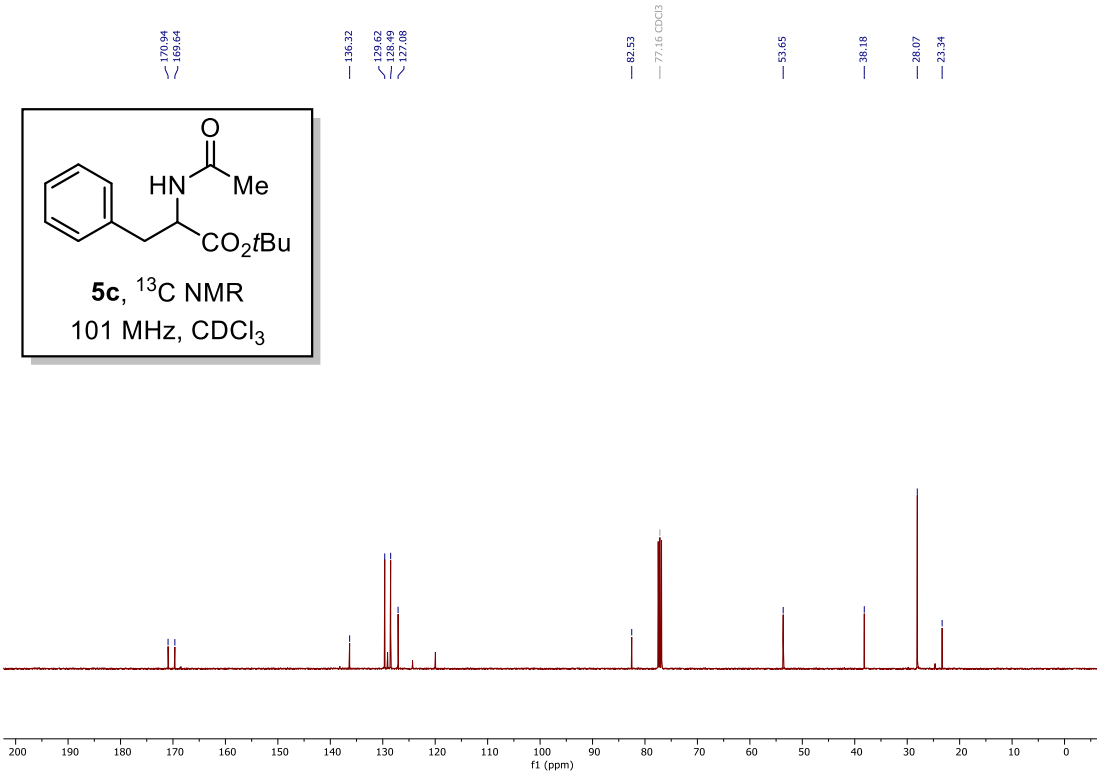
5.96
4.78
4.77
4.76
4.75
4.75
4.73
3.09
3.08
1.98
1.41
O
HN
Me
CO2tBu
5c, 1H NMR
400 MHz, CDCl3
3.31
2.02
0.96
1.00
2.07
3.11
9.41
f1 (ppm)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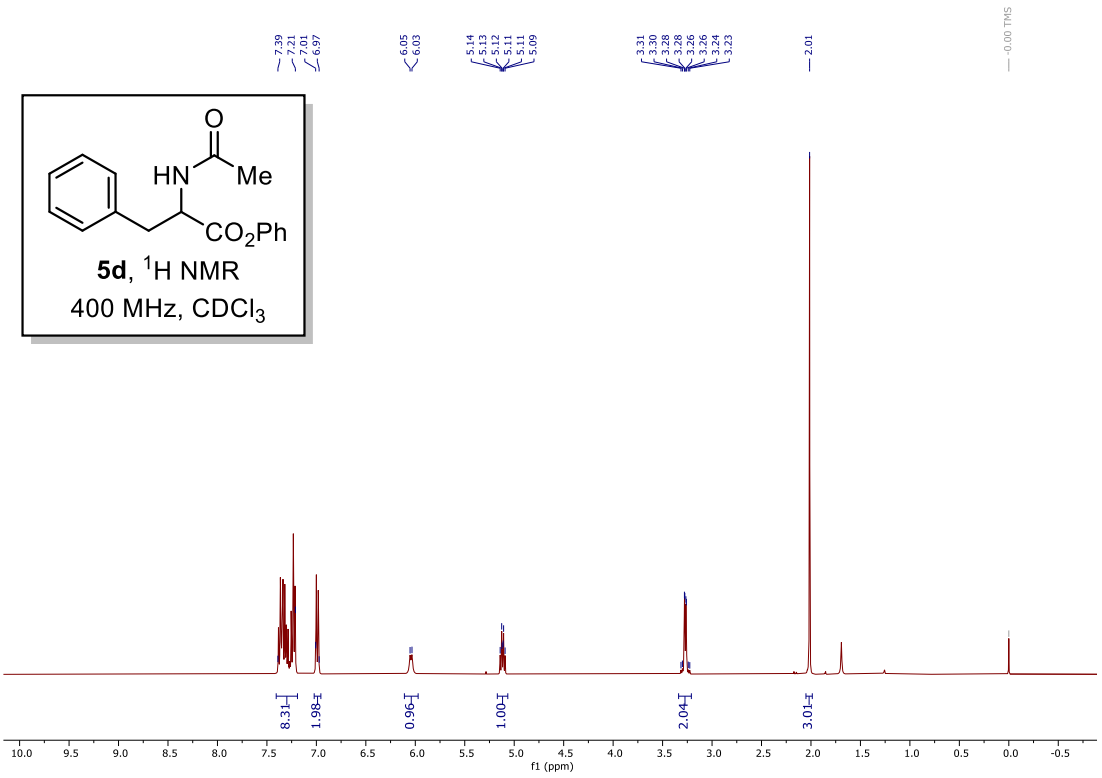
129.62
128.49
127.08
82.53
77.16 CDCl3
53.65
38.18
28.07
23.34
O
HN
Me
CO2tBu
5c, 13C NMR
101 MHz, CDCl3
f1 (ppm)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6.03
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5.13
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5.11
5.11
5.09
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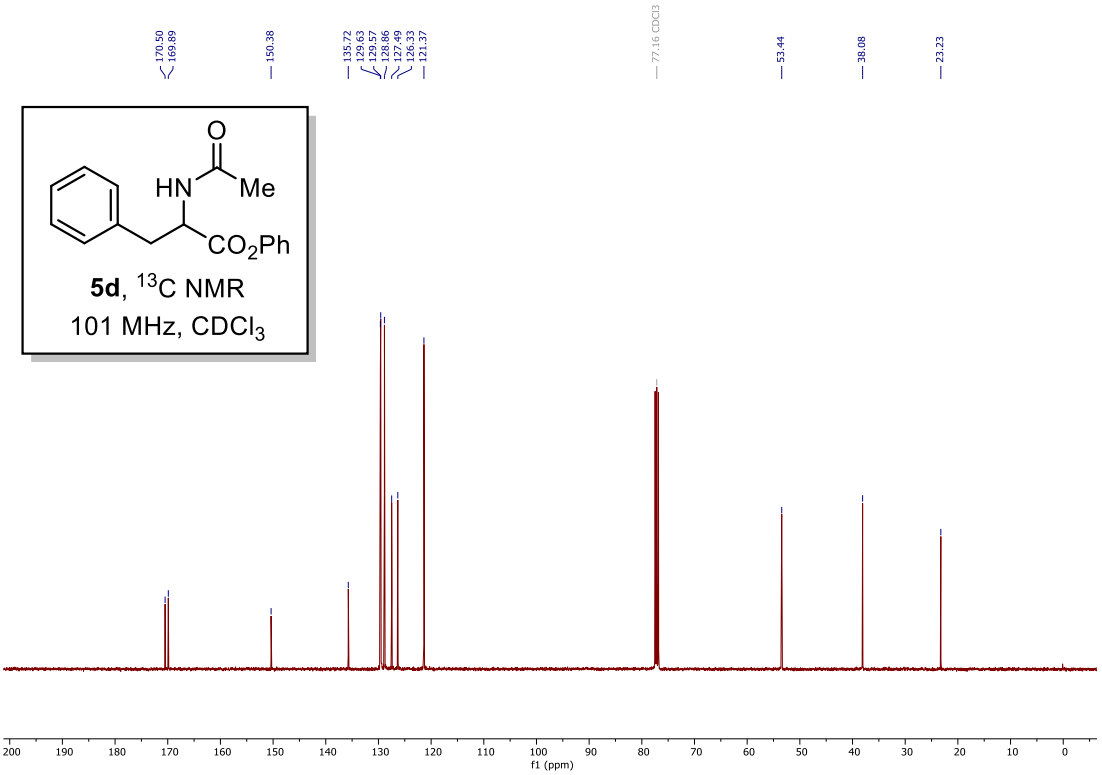
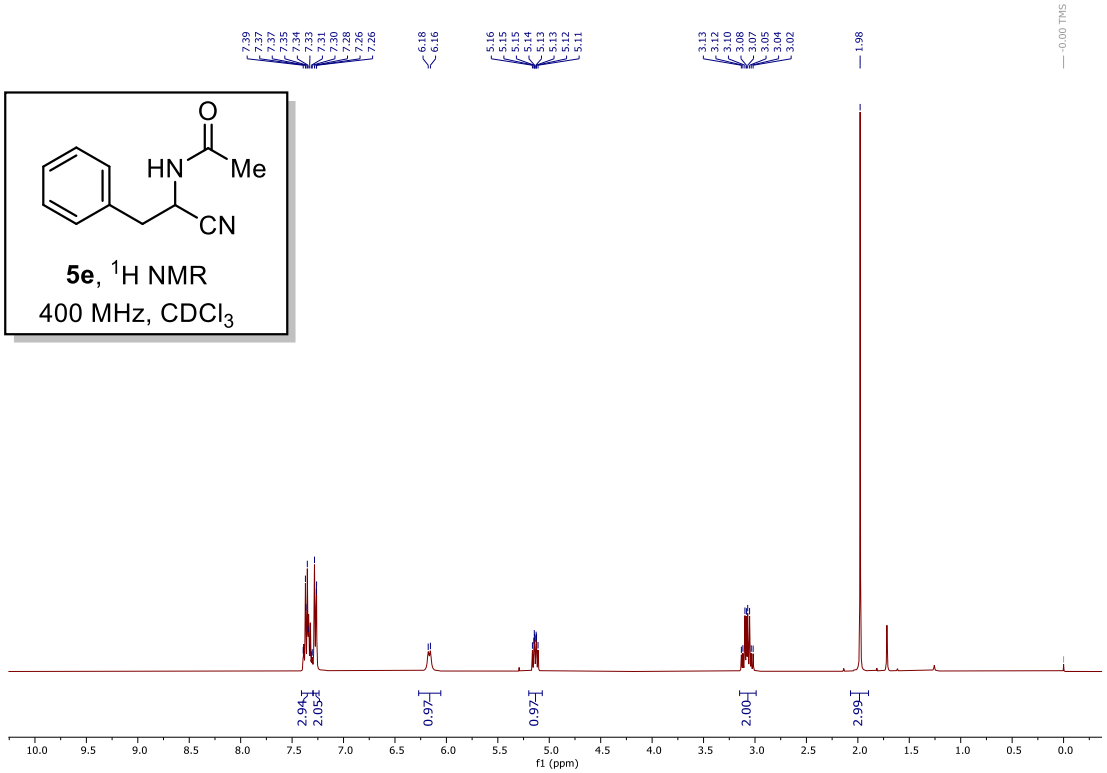
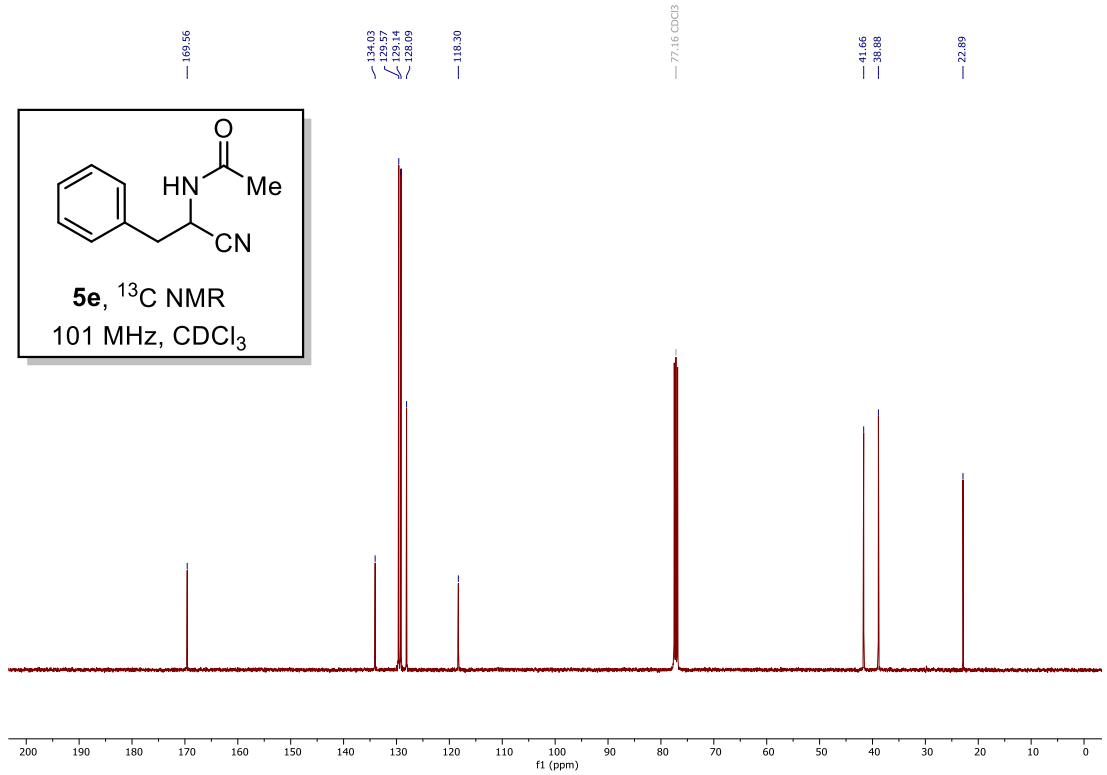
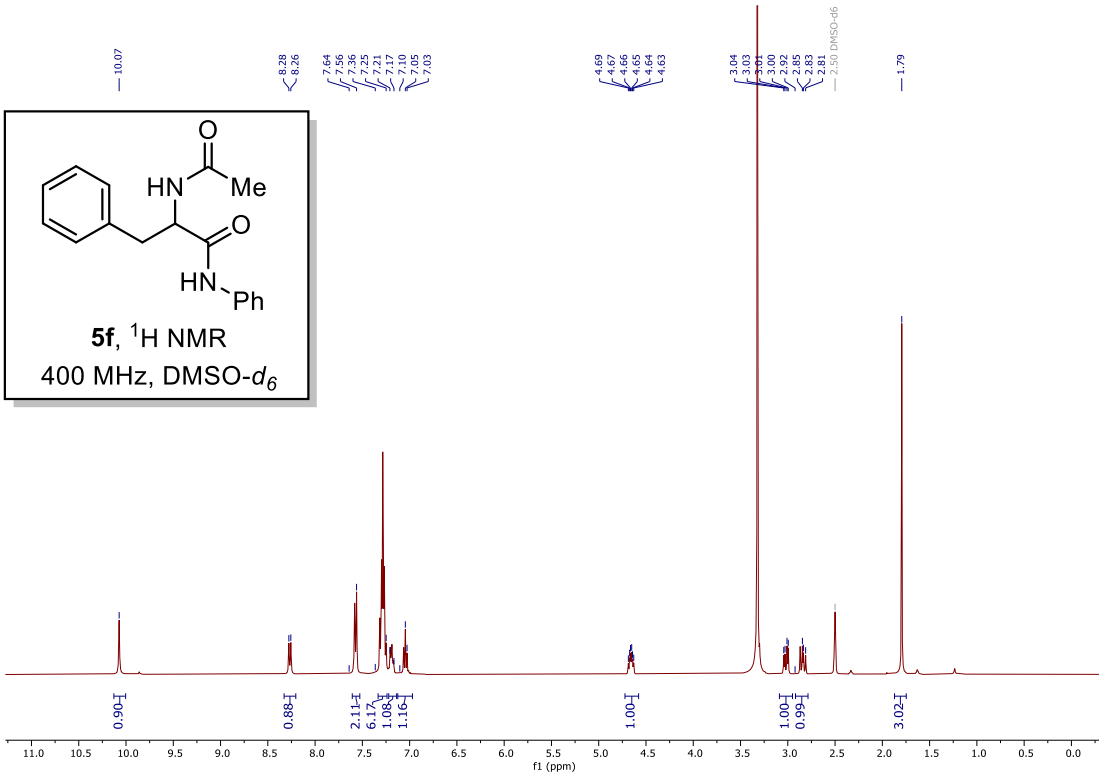
3.30
3.28
3.28
3.26
3.26
3.24
3.23
2.01
0.00 TMS
HN
O
Me
CO2Ph
5d, 1H NMR
400 MHz, CDCl3
8.31
1.98
0.96
1.00
2.04
3.01
f1 (ppm)

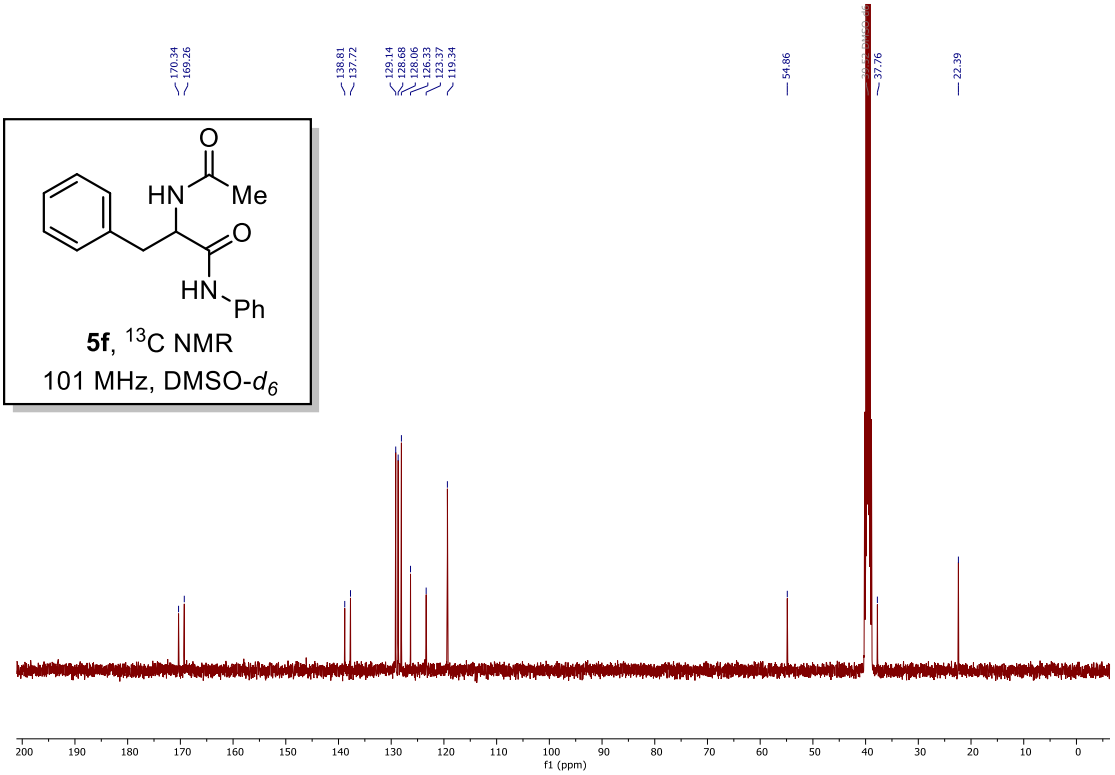

170.50
169.89
150.38
135.72
129.63
129.57
128.86
127.49
126.33
121.37
77.16 CDCl3
53.44
38.08
23.23
HN
O
Me
CO2Ph
5d, 13C NMR
101 MHz, CDCl3
f1 (ppm)


HN
O
Me
CN
5e, 1H NMR
400 MHz, CDCl3
f1 (ppm)

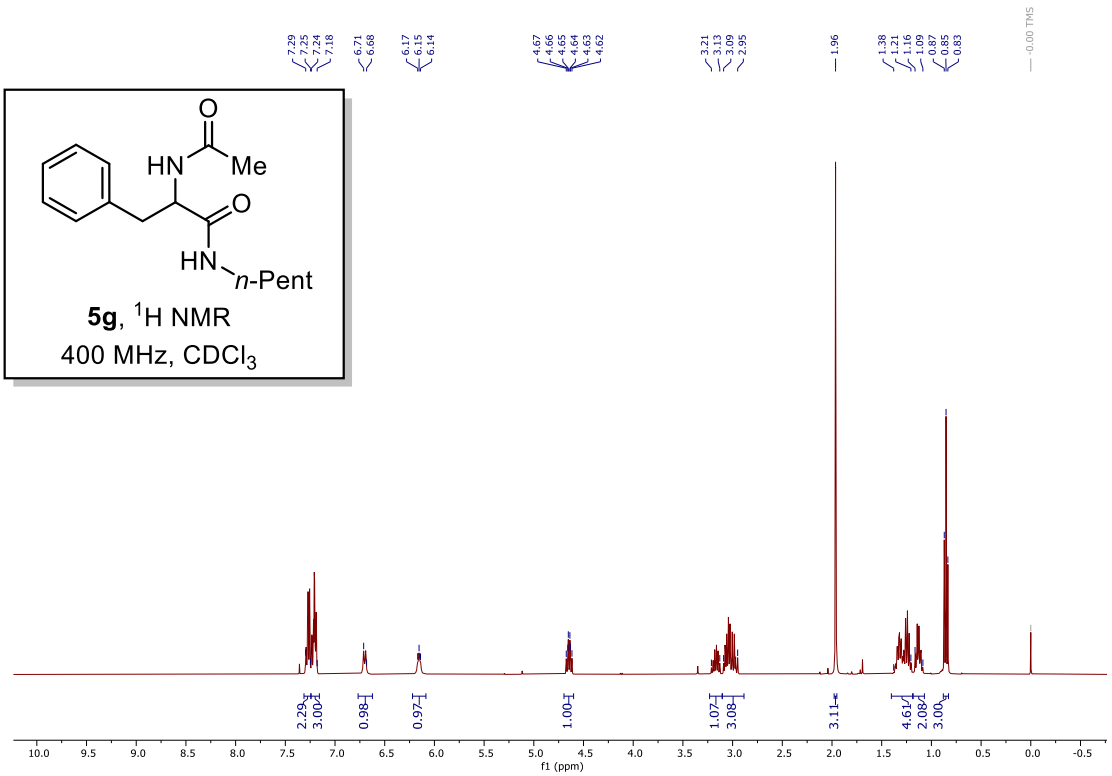

HN
O
Me
CN
5e, 13C NMR
101 MHz, CDCl3
f1 (ppm)

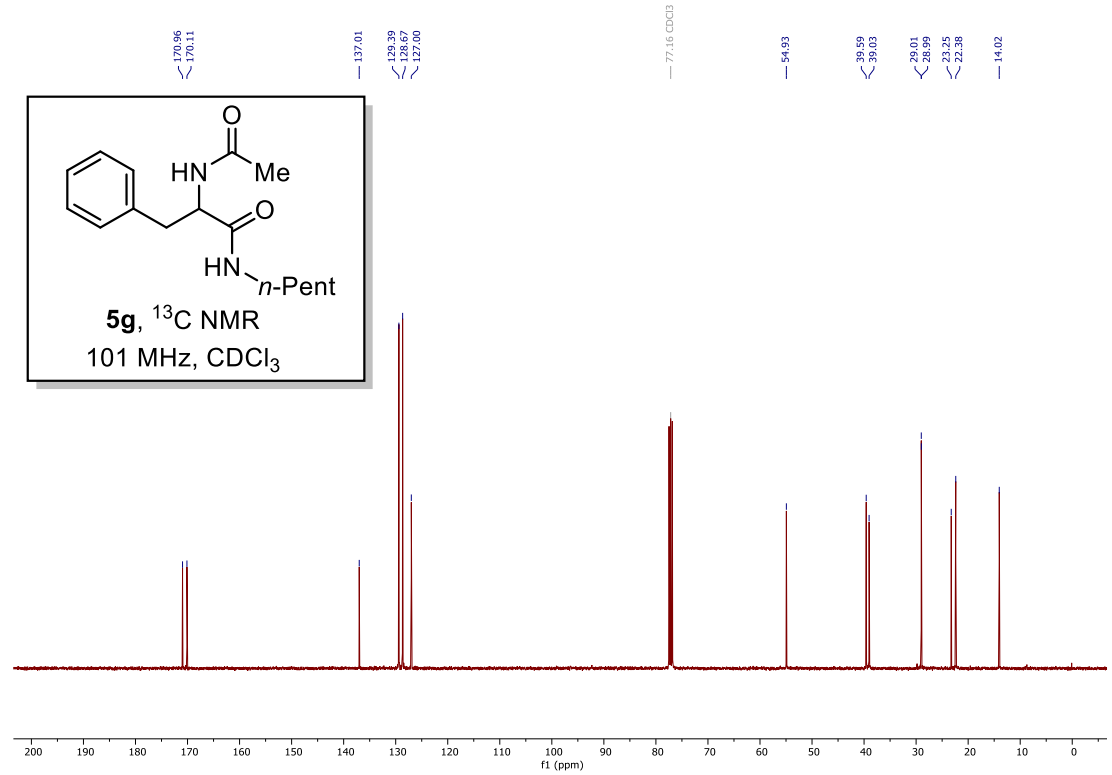


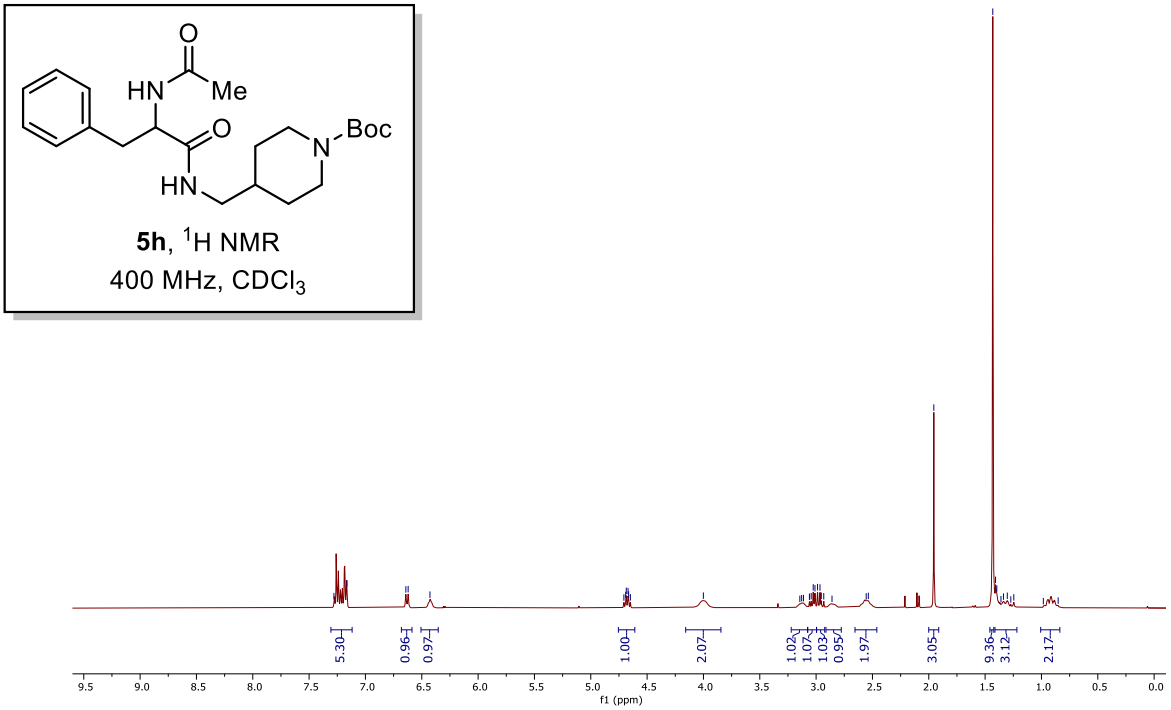

**5f**, $^{1}$H NMR
400 MHz, DMSO-$d_6$

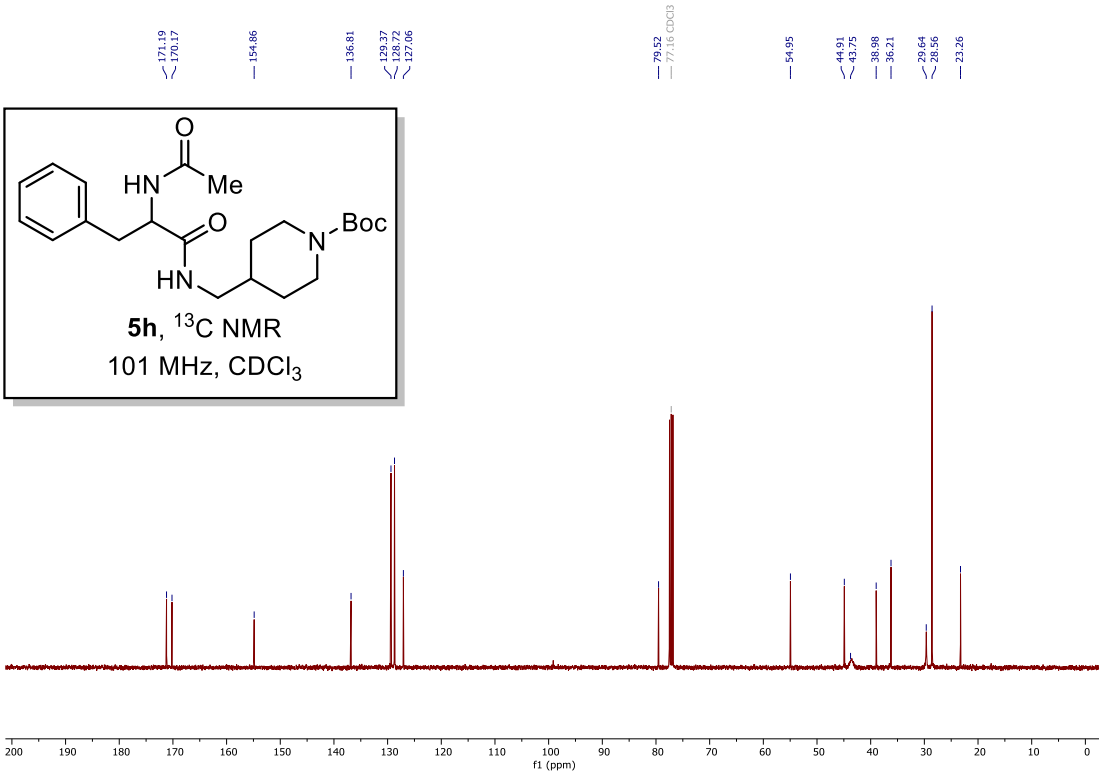


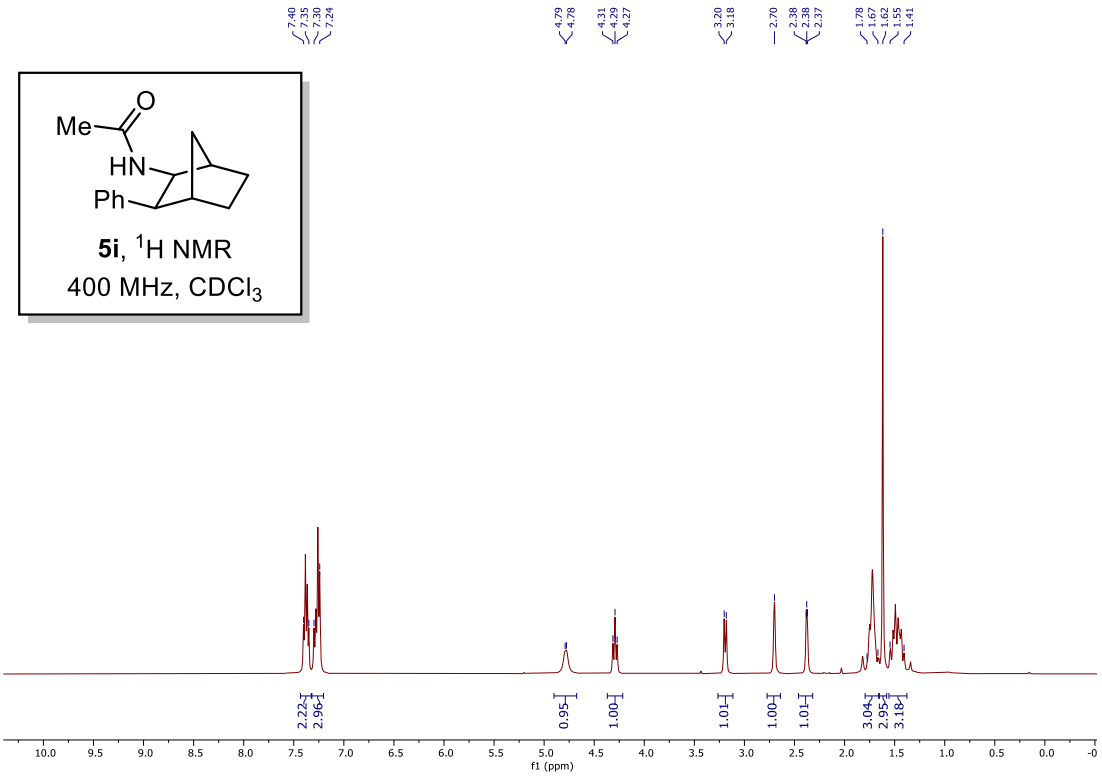

**5f**, $^{13}$C NMR
101 MHz, DMSO-$d_6$

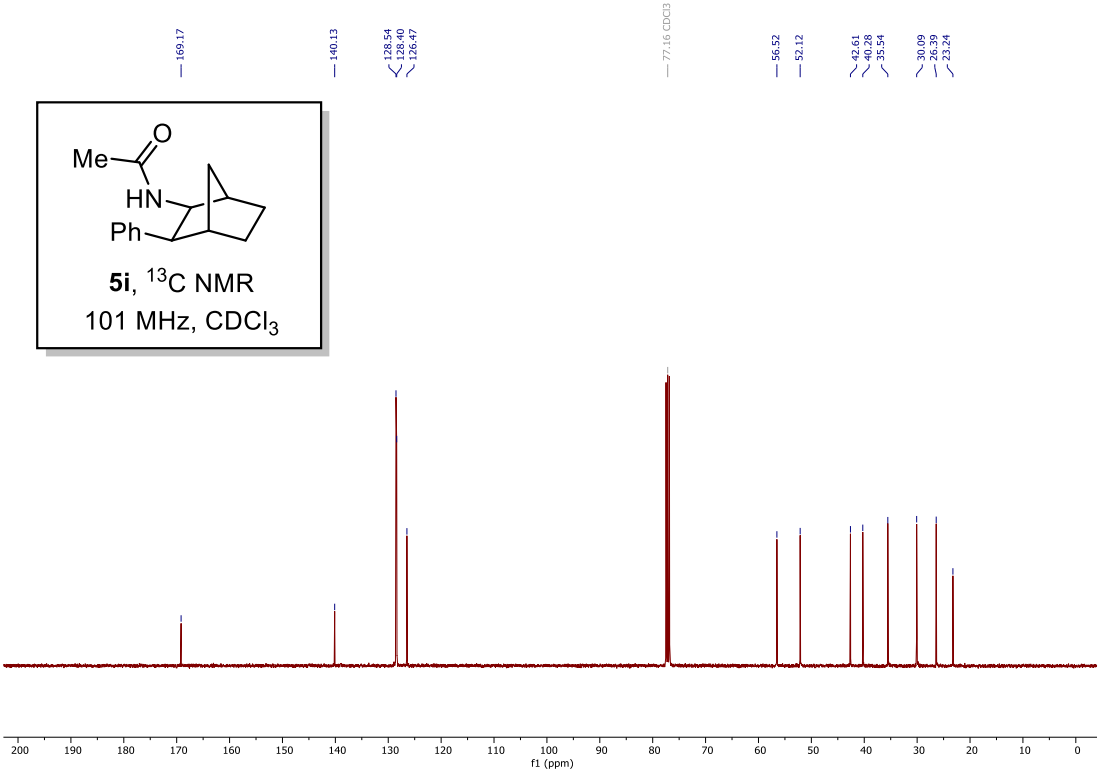

HN
Me
O
O
HN
n-Pent
5g, 1H NMR
400 MHz, CDCl3
f1 (ppm)

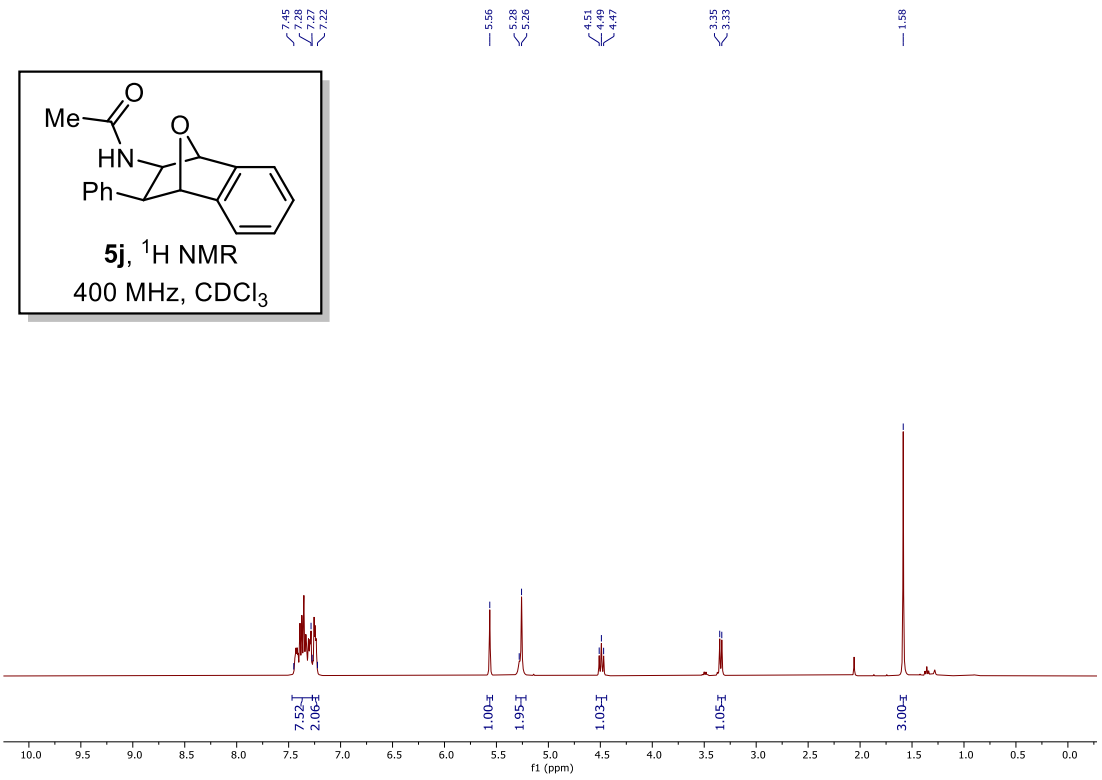

HN
Me
O
O
HN
n-Pent
5g, 13C NMR
101 MHz, CDCl3
f1 (ppm)

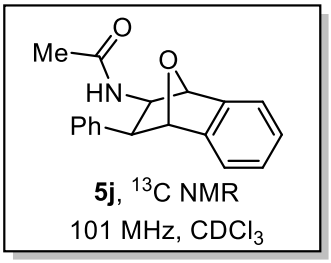

HN
Me
O
O
HN
N
Boc
5h, 1H NMR
400 MHz, CDCl3
f1 (ppm)


HN
Me
O
O
HN
N
Boc
5h, 13C NMR
101 MHz, CDCl3
f1 (ppm)


Me
O
HN
Ph
5i, 1H NMR
400 MHz, CDCl3
7.40
7.35
7.30
7.24
4.79
4.78
4.31
4.29
4.27
3.20
3.18
2.70
2.38
2.38
2.37
1.78
1.67
1.62
1.55
1.41
2.22
2.96
0.95
1.00
1.01
1.00
1.01
3.04
2.95
3.18
f1 (ppm)

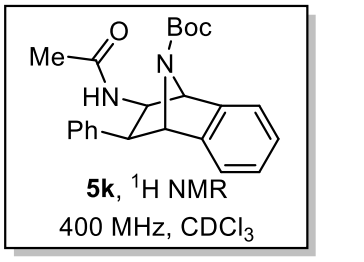

169.17
140.13
128.54
128.40
126.47
77.16 CDCl3
56.52
52.12
42.61
40.88
35.54
30.09
26.39
23.24
Me
O
HN
Ph
5i, 13C NMR
101 MHz, CDCl3
f1 (ppm)


7.45
7.28
7.27
7.22
5.56
5.28
5.26
4.51
4.49
4.47
3.35
3.33
1.58
Me
O
HN
O
Ph
5j, 1H NMR
400 MHz, CDCl3
7.52
2.06
1.00
1.95
1.03
1.05
3.00
f1 (ppm)

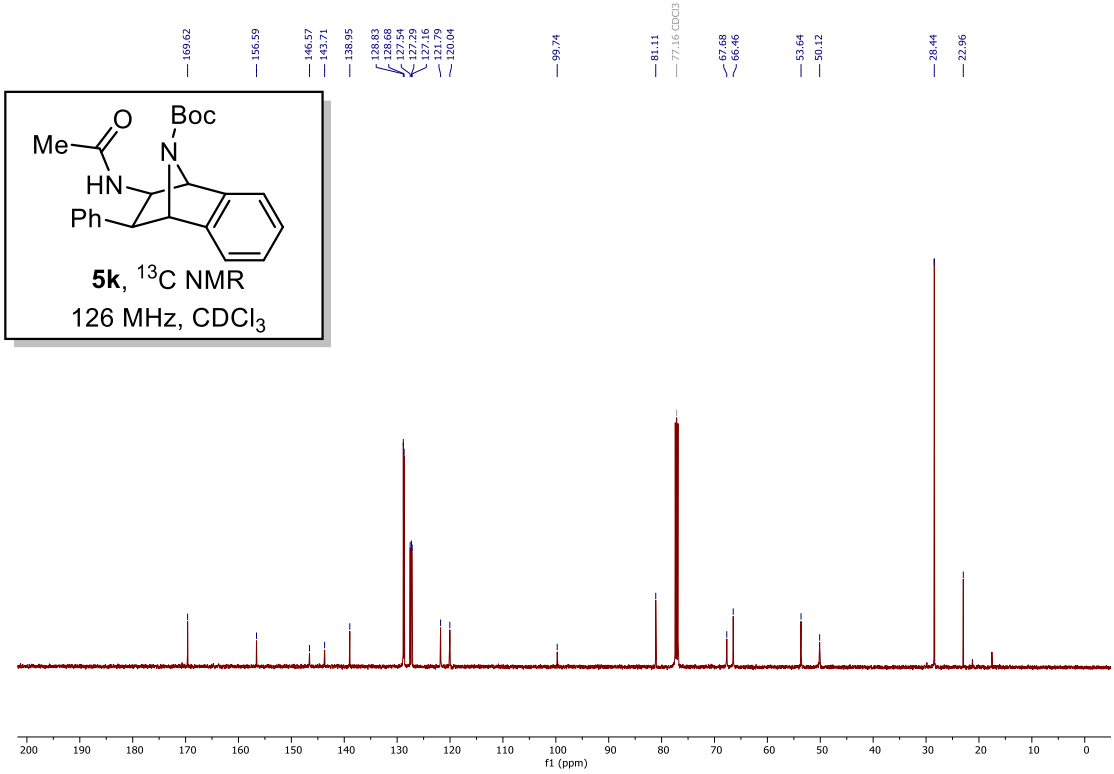



**5j**, $^{13}$C NMR
101 MHz, $CDCl_3$




**5k**, $^{1}$H NMR
400 MHz, $CDCl_3$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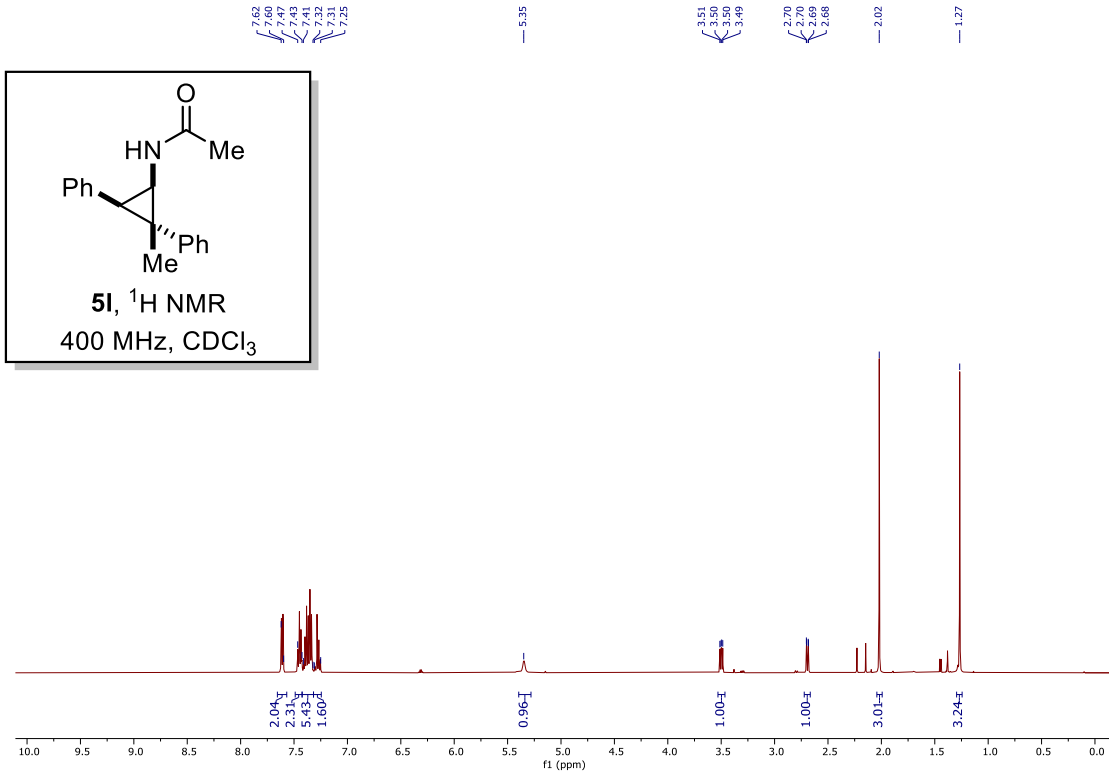
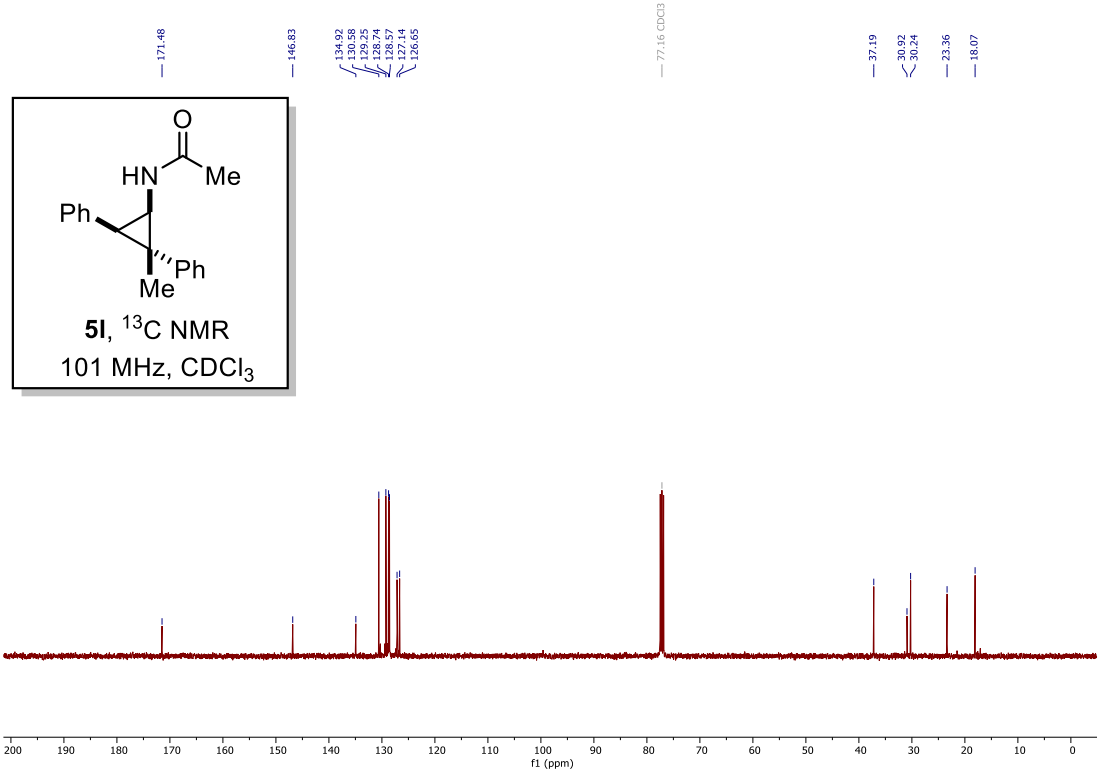
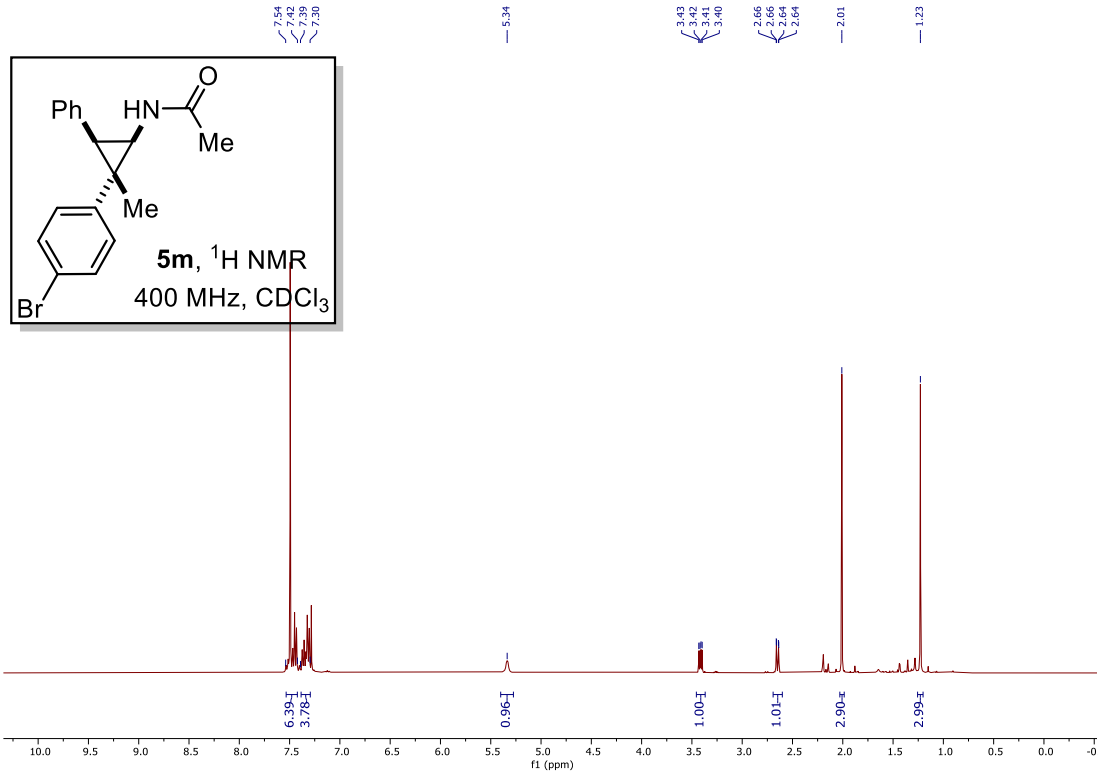
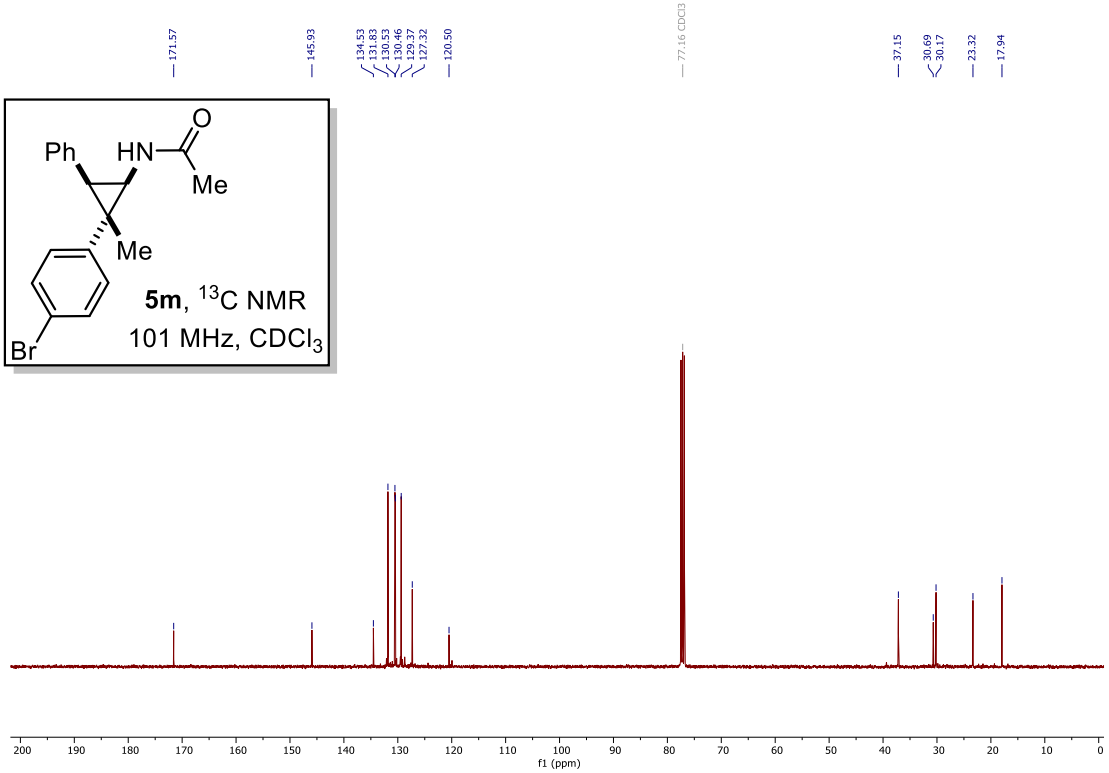
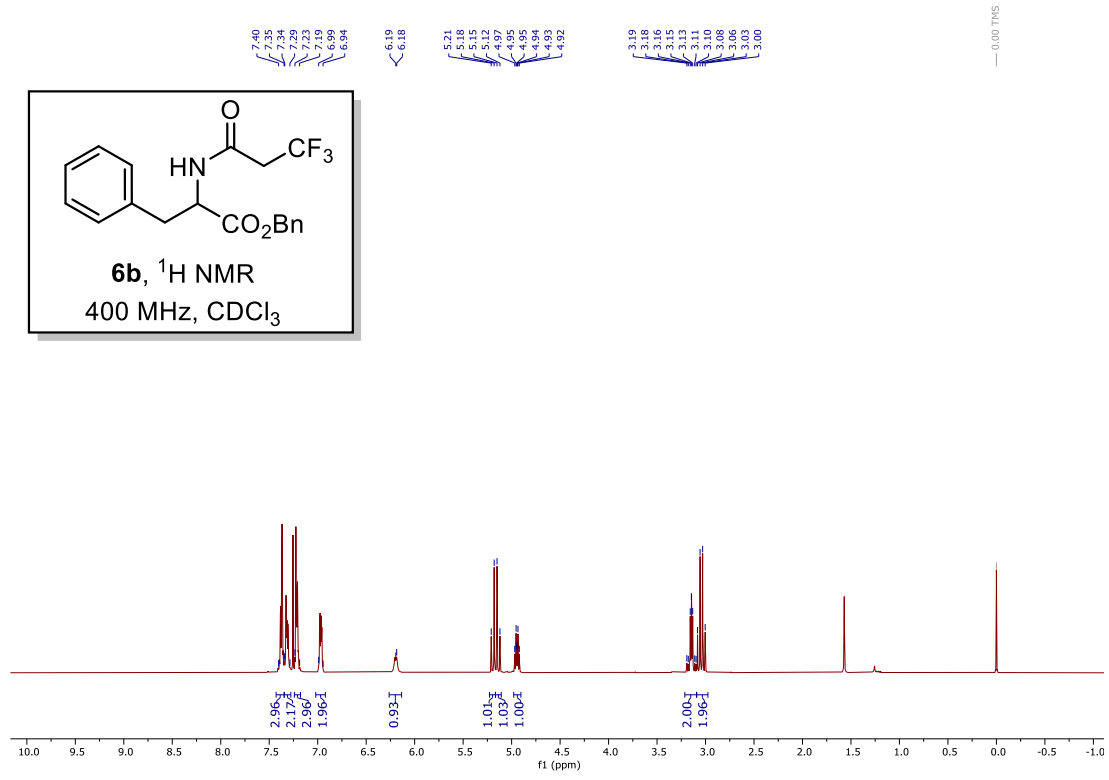
156.59
146.57
143.71
138.95
128.83
128.68
127.54
127.29
127.16
121.79
120.04
99.74
81.11
77.16 CDCl3
67.68
66.46
53.64
50.12
28.44
22.96
Me
O
Boc
N
HN
Ph
5k, 13C NMR
126 MHz, CDCl3
f1 (ppm)


7.62
7.60
7.47
7.43
7.41
7.32
7.31
7.25
5.35
3.51
3.50
3.50
3.49
2.70
2.70
2.69
2.68
2.02
1.27
O
HN
Me
Ph
Ph
Me
5l, 1H NMR
400 MHz, CDCl3
2.04
2.31
5.43
1.60
0.96
1.00
1.00
3.01
3.24
f1 (ppm)


171.48
146.83
134.92
130.58
129.35
128.74
128.57
127.14
126.65
77.16 CDCl3
37.19
30.92
30.24
23.36
18.07
O
HN
Me
Ph
Ph
Me
5l, 13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.54
7.42
7.39
7.30
5.34
3.43
3.42
3.41
3.40
2.66
2.66
2.64
2.64
2.01
1.23
O
HN
Me
Ph
Me
Br
5m, 1H NMR
400 MHz, CDCl3
6.39
3.78
0.96
1.00
1.01
2.90
2.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


171.57
145.93
134.53
131.83
130.53
130.46
129.37
127.32
120.50
77.16 CDCl3
37.15
30.69
30.17
23.32
17.94
Ph
HN
O
Me
Me
Br
5m, 13C NMR
101 MHz, CDCl3
f1 (ppm)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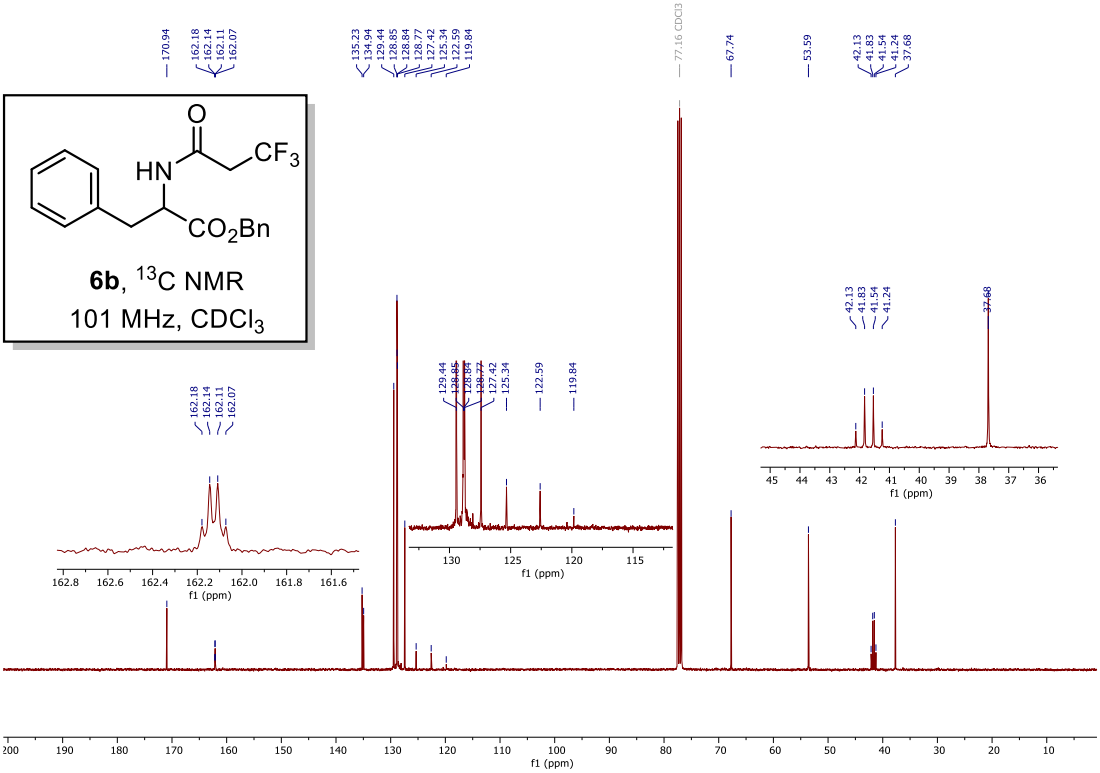
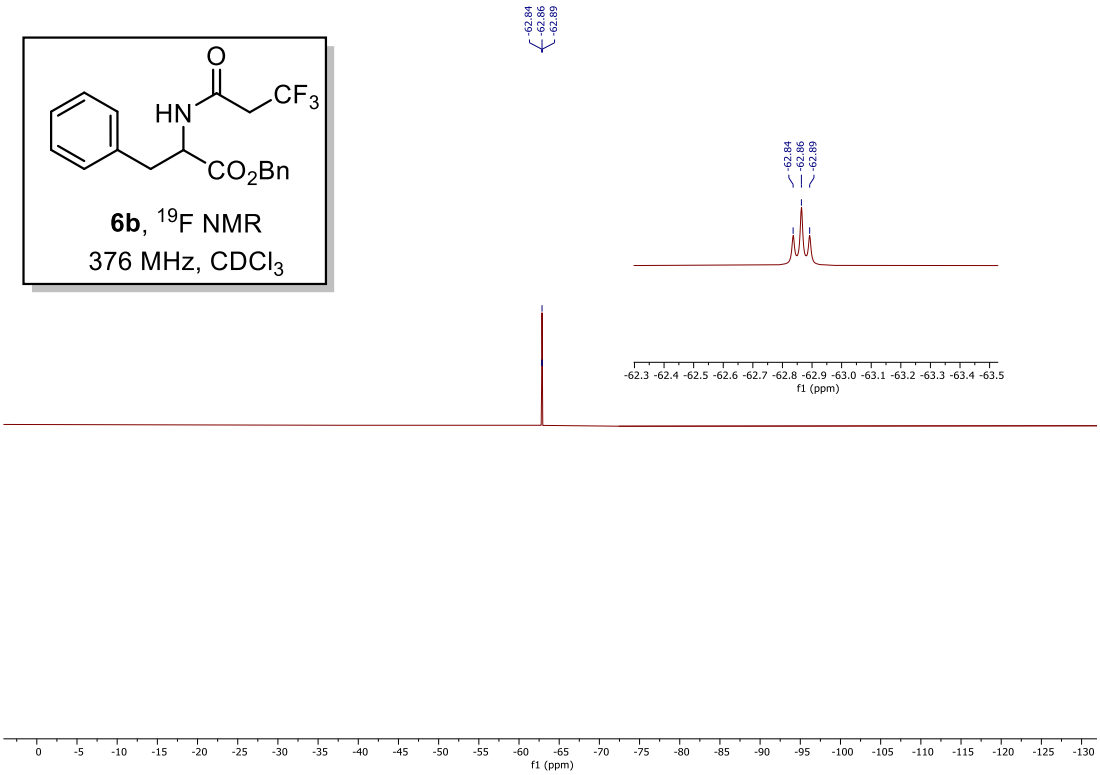
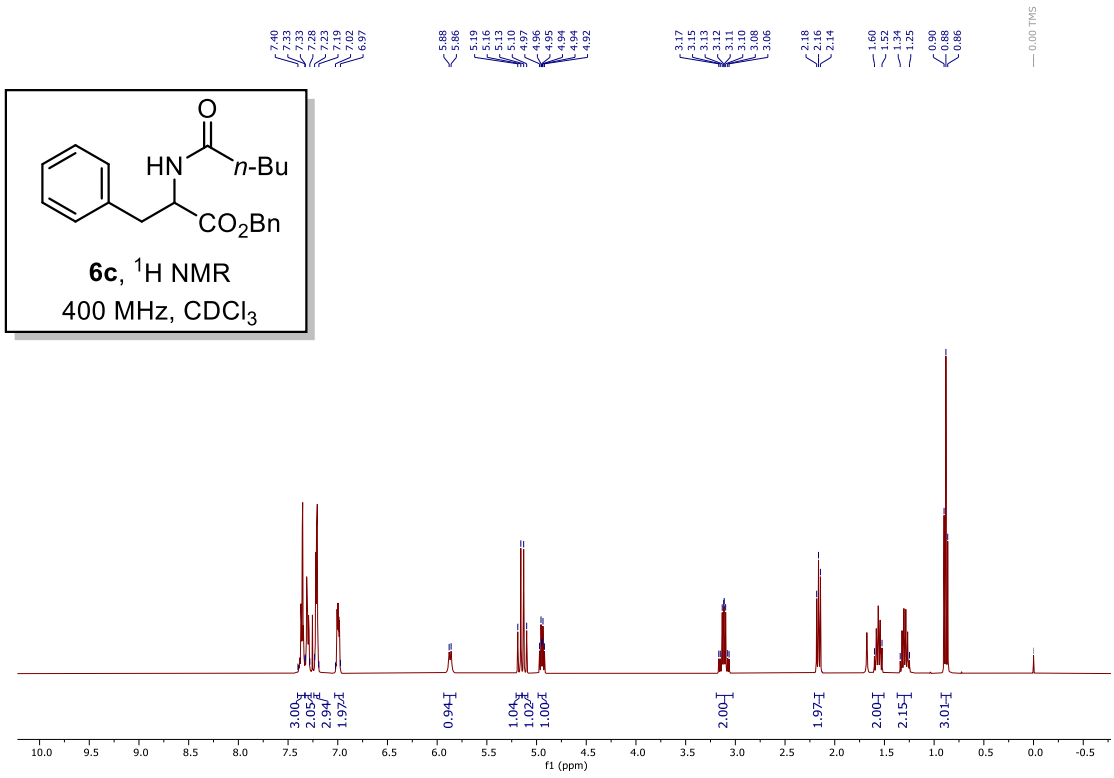
7.35
7.34
7.29
7.23
7.19
6.99
6.94
6.19
6.18
5.21
5.18
5.15
5.12
4.97
4.95
4.95
4.94
4.93
4.92
3.19
3.18
3.16
3.15
3.13
3.11
3.10
3.08
3.06
3.03
3.00
0.00 TMS
HN
O
CF3
CO2Bn
6b, 1H NMR
400 MHz, CDCl3
2.96
2.17
2.96
1.96
0.93
1.01
1.03
1.00
2.00
1.96
f1 (ppm)


O
HN
CF3
CO2Bn
6b, 13C NMR
101 MHz, CDCl3
170.94
162.18
162.14
162.11
162.07
135.23
134.94
129.44
126.85
128.84
128.77
127.42
125.34
122.59
119.84
77.16 CDCl3
67.74
53.59
42.13
41.83
41.54
41.24
37.68
f1 (ppm)


O
HN
CF3
CO2Bn
6b, 19F NMR
376 MHz, CDCl3
-62.84
-62.86
-62.89
f1 (ppm)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7.33
7.33
7.28
7.23
7.19
7.02
6.97
5.88
5.86
5.19
5.16
5.13
5.10
4.97
4.96
4.95
4.94
4.94
4.94
4.92
3.17
3.15
3.13
3.12
3.11
3.10
3.08
3.06
2.18
2.16
2.14
1.60
1.52
1.34
1.25
0.90
0.88
0.86
0.00 TMS
O
HN
n-Bu
CO2Bn
6c, 1H NMR
400 MHz, CDCl3
3.00
2.05
2.94
1.97
0.94
1.04
1.02
1.00
2.00
1.97
2.00
2.15
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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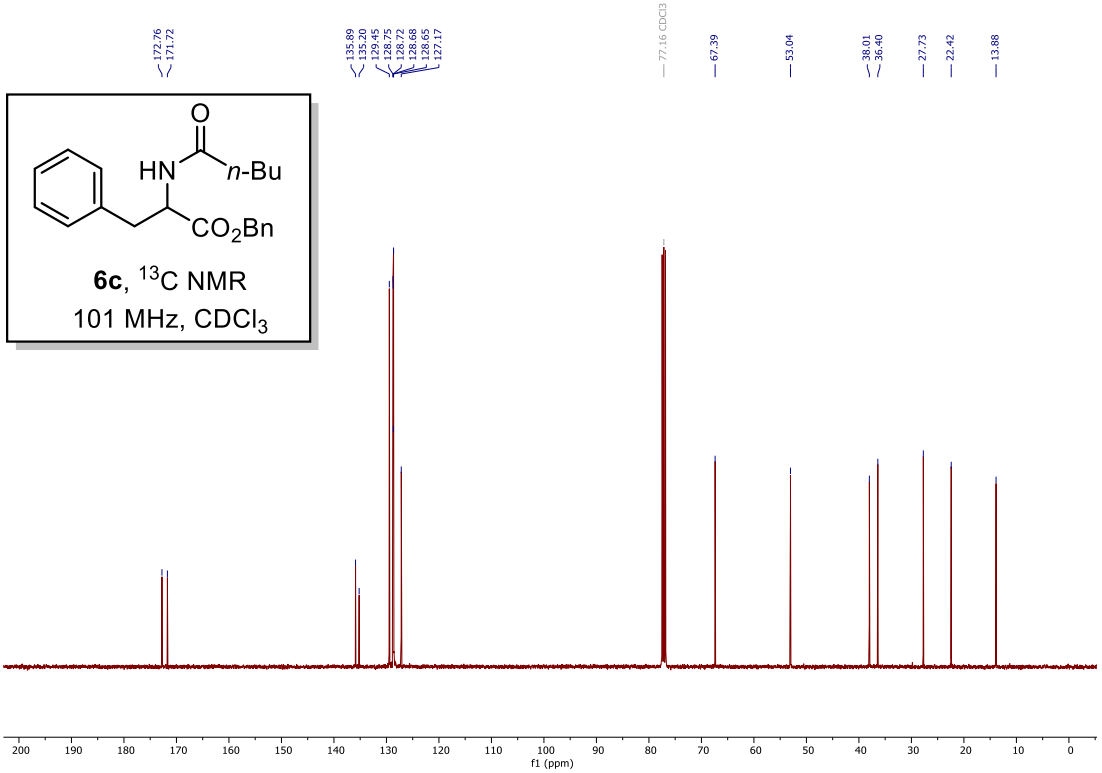
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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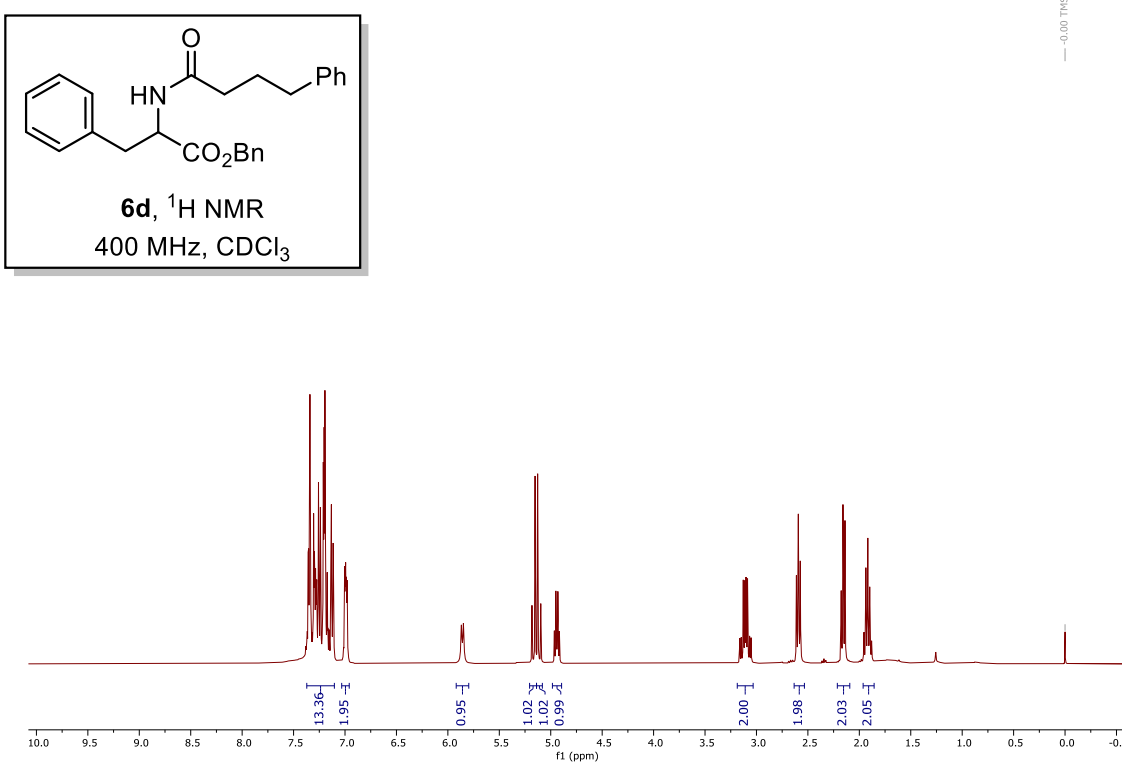
128.75
128.72
128.68
128.65
127.17
77.16 CDCl3
67.39
53.04
38.01
36.40
27.73
22.42
13.88
O
HN
n-Bu
CO2Bn
6c, 13C NMR
101 MHz, CDCl3
f1 (ppm)


0.00 TMS
O
HN
Ph
CO2Bn
6d, 1H NMR
400 MHz, CDCl3
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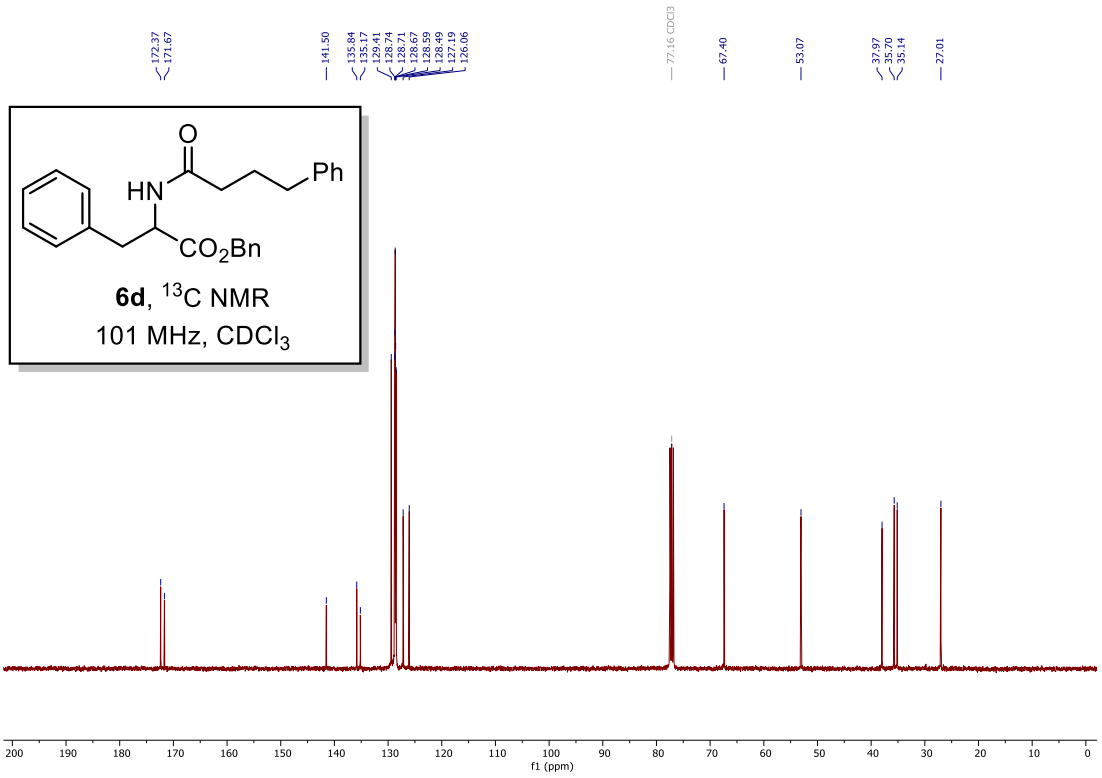
1.95
0.95
1.02
1.02
0.99
2.00
1.98
2.03
2.05
f1 (ppm)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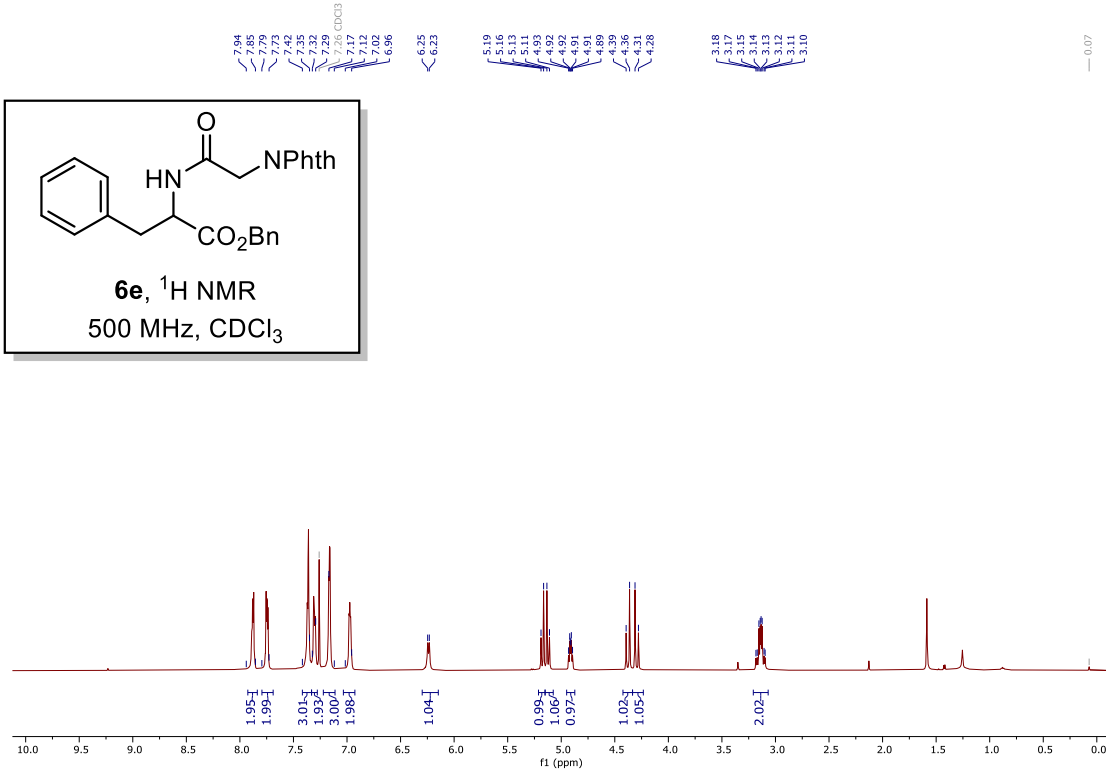
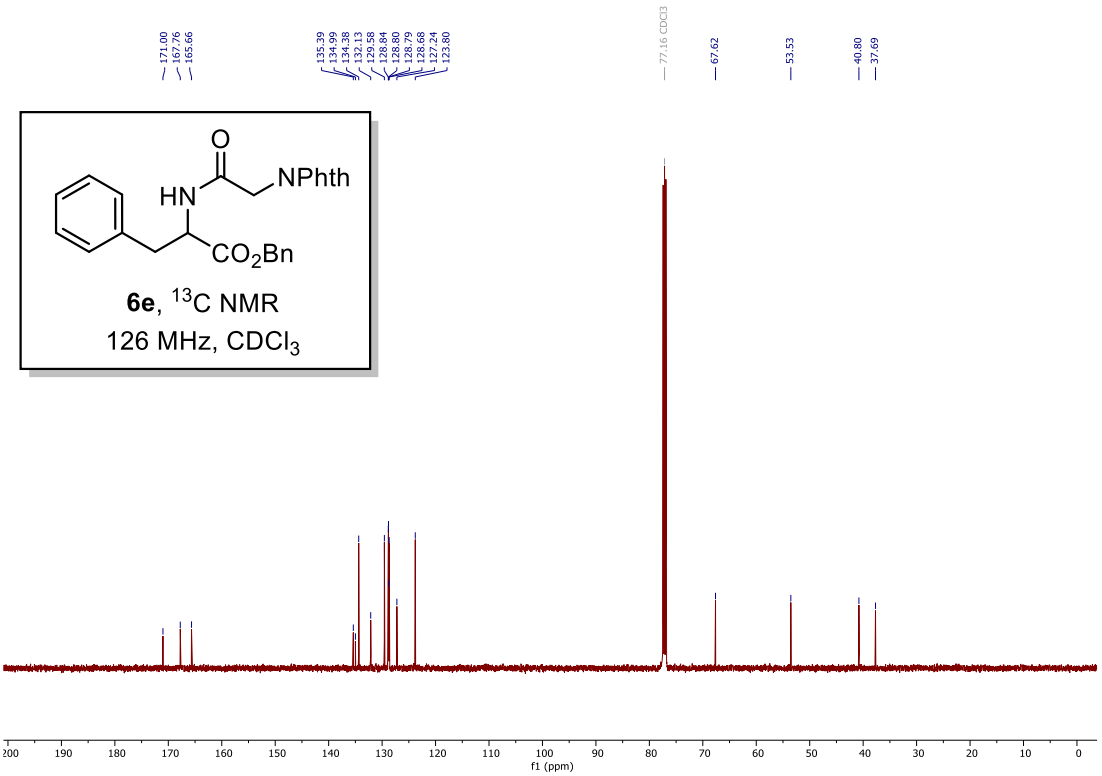
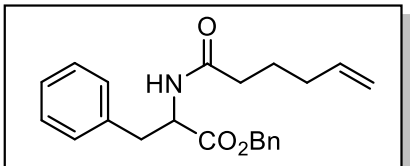
141.50
135.84
135.17
129.41
128.74
128.71
128.67
128.59
128.49
127.19
126.06
77.16 CDCl3
67.40
53.07
37.97
35.70
35.14
27.01
O
HN
Ph
CO2Bn
6d, 13C NMR
101 MHz, CDCl3
f1 (ppm)

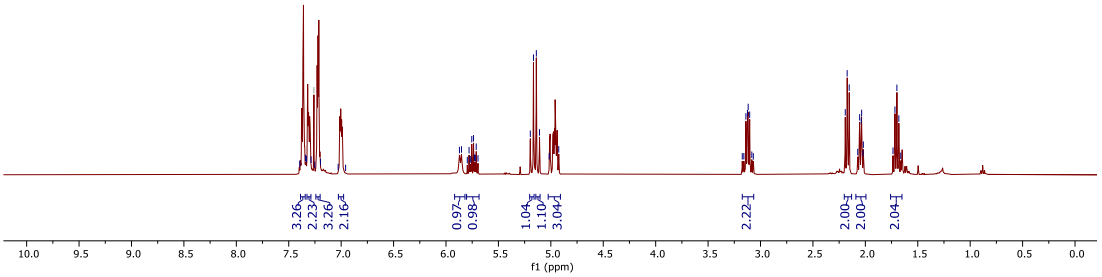

7.94
7.85
7.79
7.73
7.42
7.35
7.32
7.29
7.26 CDCl3
7.17
7.12
7.02
6.96
6.25
6.23
5.19
5.16
5.13
5.11
4.93
4.92
4.92
4.91
4.91
4.89
4.39
4.36
4.31
4.28
3.18
3.17
3.15
3.14
3.13
3.12
3.11
3.10
0.07
O
HN
NPhth
CO2Bn
6e, 1H NMR
500 MHz, CDCl3
1.95
1.99
3.01
1.93
3.00
1.98
1.04
0.99
1.06
0.97
1.02
1.05
2.02
f1 (ppm)

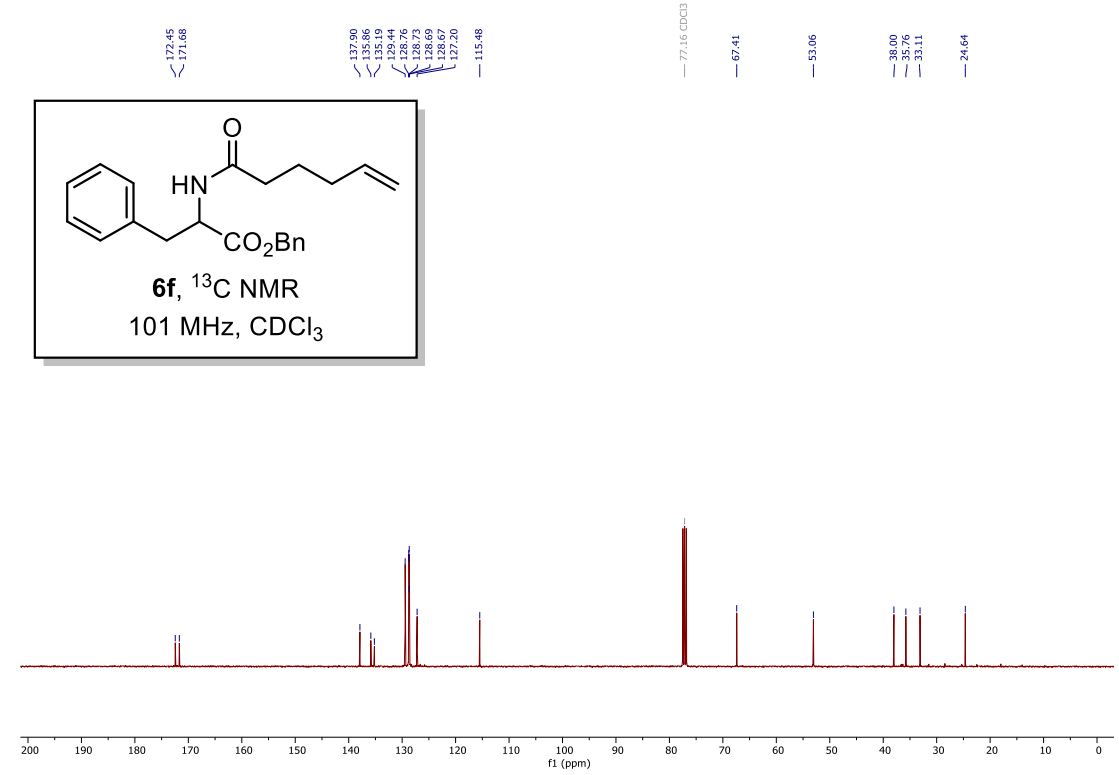


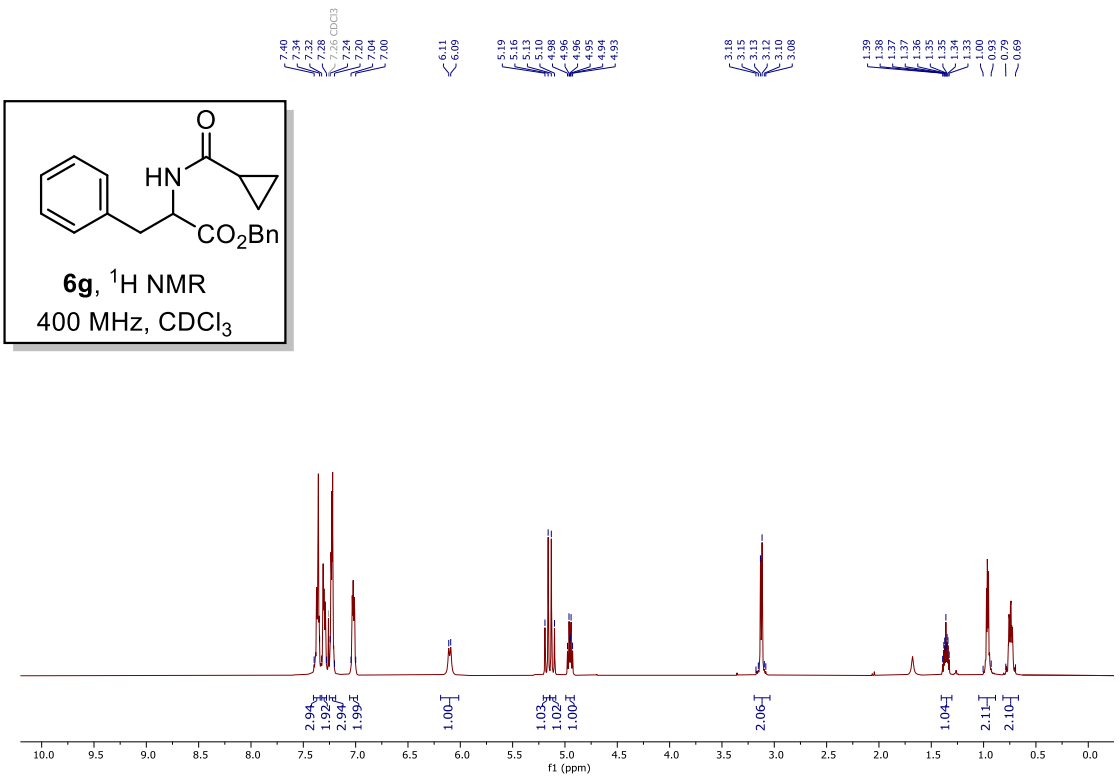

**6e**, $^{13}$C NMR
126 MHz, $CDCl_3$

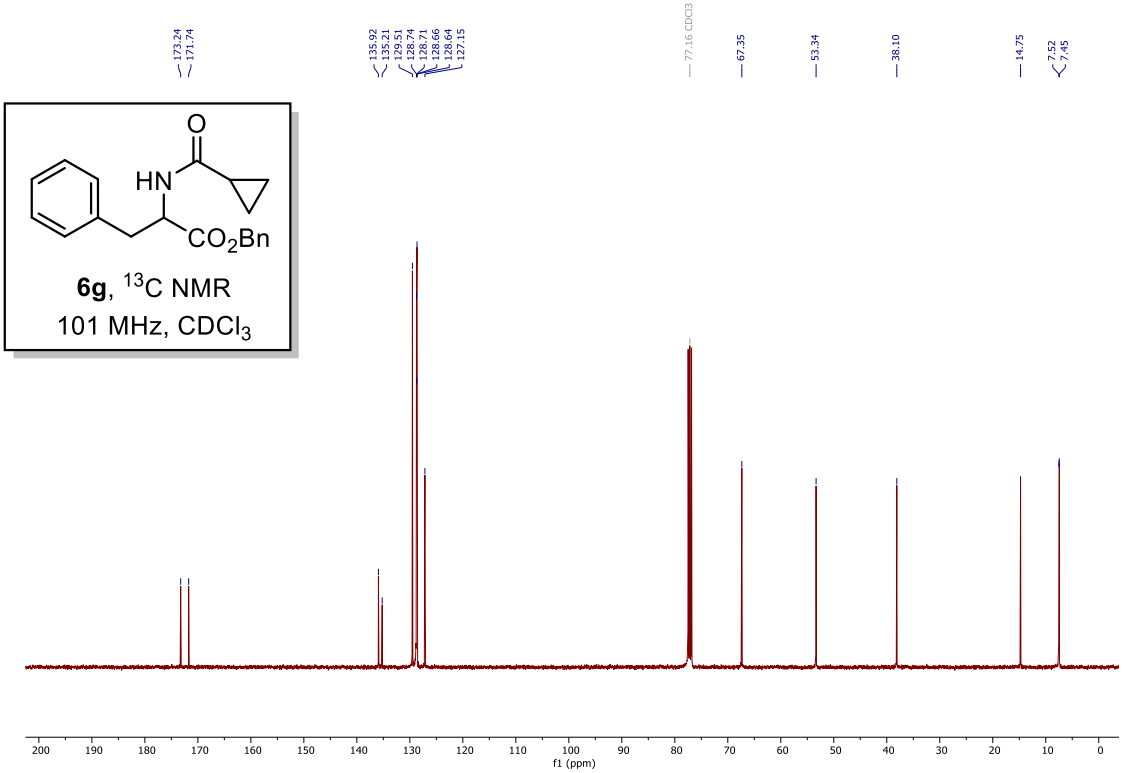



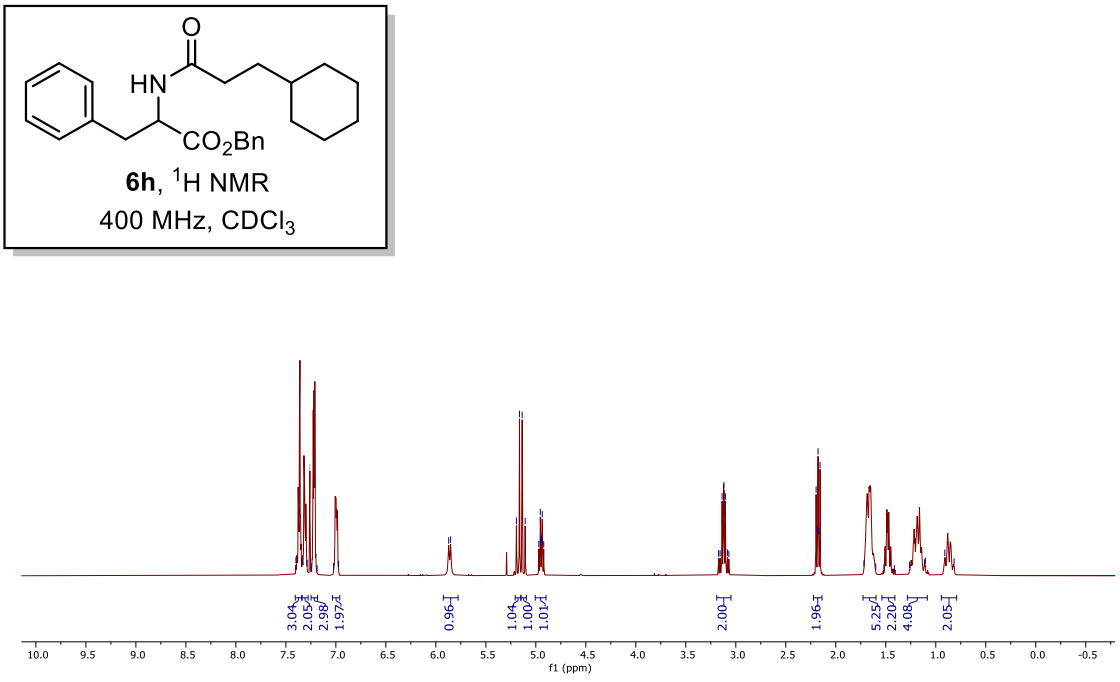

**6f**, $^{1}$H NMR
400 MHz, $CDCl_3$

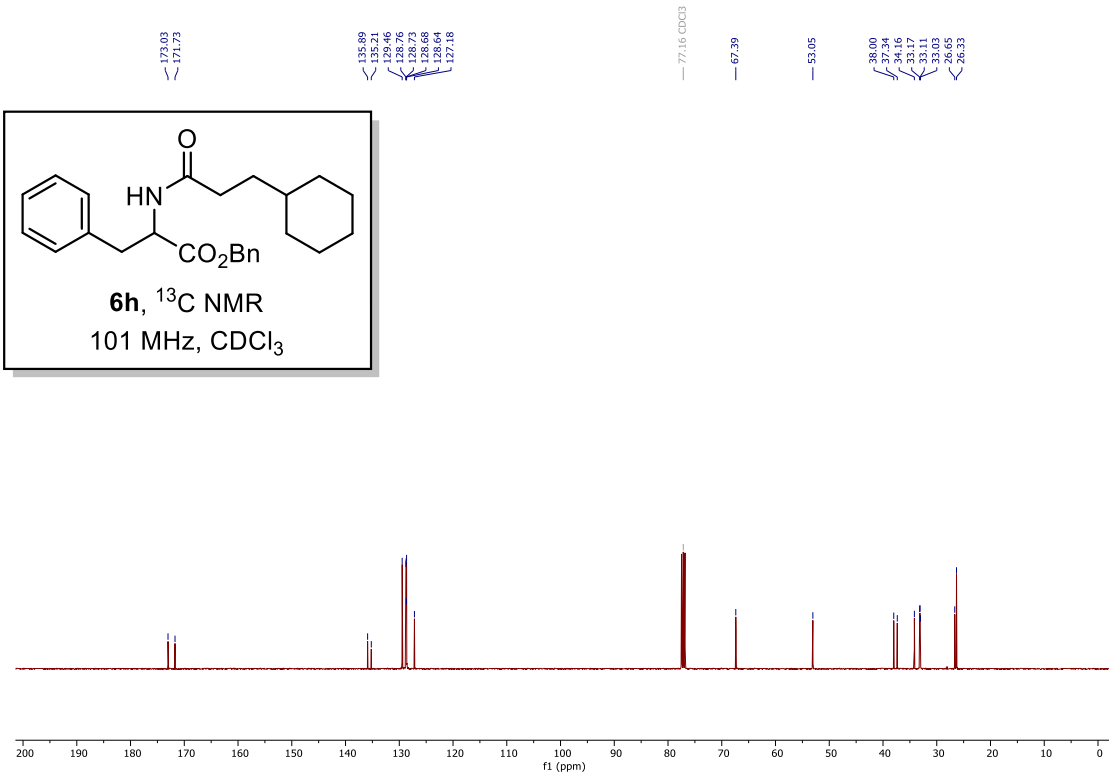



172.45
171.68
137.90
135.86
135.19
129.44
128.76
128.73
128.69
128.67
127.20
115.48
77.16 CDCl3
67.41
53.06
38.00
35.76
33.11
24.64
O
HN
CO2Bn
6f, 13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.40
7.34
7.32
7.28
7.26 CDCl3
7.24
7.20
7.04
7.00
6.11
6.09
5.19
5.16
5.13
5.10
4.98
4.96
4.96
4.95
4.94
4.93
3.18
3.15
3.13
3.12
3.10
3.08
1.39
1.38
1.37
1.37
1.36
1.35
1.35
1.34
1.33
1.00
0.93
0.79
0.69
O
HN
CO2Bn
6g, 1H NMR
400 MHz, CDCl3
2.94
1.92
2.94
1.99
1.00
1.03
1.02
1.00
2.06
1.04
2.11
2.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


O
HN
CO2Bn
6g, 13C NMR
101 MHz, CDCl3
f1 (ppm)


O
HN
CO2Bn
6h, 1H NMR
400 MHz, CDCl3
f1 (ppm)


173.03
171.73
135.89
135.21
129.46
128.76
128.73
128.68
128.64
127.18
77.16 CDCl3
67.39
53.05
38.00
37.34
34.16
33.17
33.11
33.03
26.65
26.33
O
HN
CO2Bn
6h, 13C NMR
101 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)