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α -Branched amines by catalytic 1,1-addition of C-H bonds and aminating agents to terminal alkenes

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Supplementary Tables

Supplementary Table 1. Optimization of reaction conditions with oxime C-H bond substrate.

Reaction scheme showing the optimization of reaction conditions for the amination of an oxime C-H bond substrate. The reaction involves 1-methoxy-2-phenylpropan-2-ylidenehydrazine, 1-butene, and tert-butyl N-hydroxybenzotriazole-5-carboxylate (NHBOC) in the presence of [Cp*RhCl₂]₂ (5 mol %), AgSbF₆ (20 mol %), and NaHCO₃ (1 equiv) in 0.2 M DCE at 30 °C for 20 h. The products are 1-methoxy-2-phenylpropan-2-ylidenehydrazine-1-butylamine (**1**), 1-methoxy-2-phenylpropan-2-ylidenehydrazine-NHBOC (**A**), and 1-methoxy-2-phenylpropan-2-ylidenehydrazine-1-butene (**B**).

Entry ^a	Variation from the standard conditions	Yield 1 ^b	Yield A ^b	Yield B ^b
1	None	71%	10%	trace
2	No [Cp*RhCl ₂] ₂	0%	0%	0%
3	No AgSbF ₆	0%	0%	0%
4	No NaHCO ₃	54%	10%	1%
5	1 equiv PivOH in place of NaHCO ₃	45%	9%	trace
6	Performed at 70 °C	39%	15%	1%
7	Performed at [0.5 M]	69%	11%	trace
8	Performed at [1.0 M]	64%	11%	1%
9	In dioxane	70%	11%	1%
10	AcNHBOC as the aminating agent	62%	4%	1%
11	1 equiv alkene and 1 equiv PivNHBOC aminating agent	55%	2%	trace
12	[Cp*Rh(MeCN) ₃][SbF ₆] ₂ (10 mol %) as catalyst system	10%	32%	1%
13	[Cp*Co(CO) ₂] ₂ (10 mol %) and AgSbF ₆ (20 mol %) as catalyst system	0%	0%	0%
14	[Cp*IrCl ₂] ₂ (5 mol %) and AgSbF ₆ (20 mol %) as catalyst system	0%	0%	0%
15	[RuCl ₂ (<i>p</i> -cymene)] ₂ (5 mol %) and AgSbF ₆ (20 mol %) as catalyst system	0%	0%	0%

^aConditions: Reactions were performed on 0.1 mmol of C–H bond substrate with 0.15 mmol of aminating agent and 0.2 mmol of alkene. ^bYields determined by ¹H NMR relative to 1,3,5-trimethoxybenzene as an external standard.

Supplementary Table 2. Optimization of reaction conditions with amide C-H bond substrate.

Standard conditions: $[\text{Cp}^*\text{RhCl}_2]_2$ (5 mol %), AgSbF_6 (20 mol %), PivOH (1 equiv), 0.2 M DCE, 30 °C, 20 h.

Entry ^a	Variation from the standard conditions	Yield 27 ^b	Yield C ^b
1	None	70%	0%
2	No $[\text{Cp}^*\text{RhCl}_2]_2$	0%	0%
3	No AgSbF_6	0%	0%
4	No PivOH	40%	0%
5	1 equiv NaHCO_3 in place of PivOH	27%	0%
6	1 equiv NaOPiv in place of PivOH	0%	0%
7	Performed at 70 °C	66%	0%
8	Performed at [0.5 M]	55%	0%
9	Performed at [1.0 M]	36%	0%
10	In dioxane	51%	11%
11	PivNHBoc as the aminating agent	12%	0%
12	$[\text{Cp}^*\text{Rh}(\text{MeCN})_3][\text{SbF}_6]_2$ (10 mol %) as catalyst system	traces	0%
13	$[\text{Cp}^*\text{Co}(\text{CO})_2]_2$ (10 mol %) and AgSbF_6 (20 mol %) as catalyst system	0%	0%
14	$[\text{Cp}^*\text{IrCl}_2]_2$ (5 mol %) and AgSbF_6 (20 mol %) as catalyst system	0%	59%
15	$[\text{RuCl}_2(p\text{-cymene})]_2$ (5 mol %) and AgSbF_6 (20 mol %) as catalyst system	0%	26%

^aConditions: Reactions were performed on 0.1 mmol of C–H bond substrate with 0.15 mmol of aminating agent and 0.2 mmol of alkene. ^bYields determined by ^1H NMR relative to 1,3,5-trimethoxybenzene as an external standard. Yields of C–H alkenylated products not determined due to overlap of characteristic peaks in NMR spectra of crude reaction mixture.

Supplementary Table 3. Optimization of asymmetric reaction.

Standard conditions: Chiral precatalyst (5 mol %), NaHCO_3 (1 equiv), Ag additive, Solvent, 30 °C, 20 h.

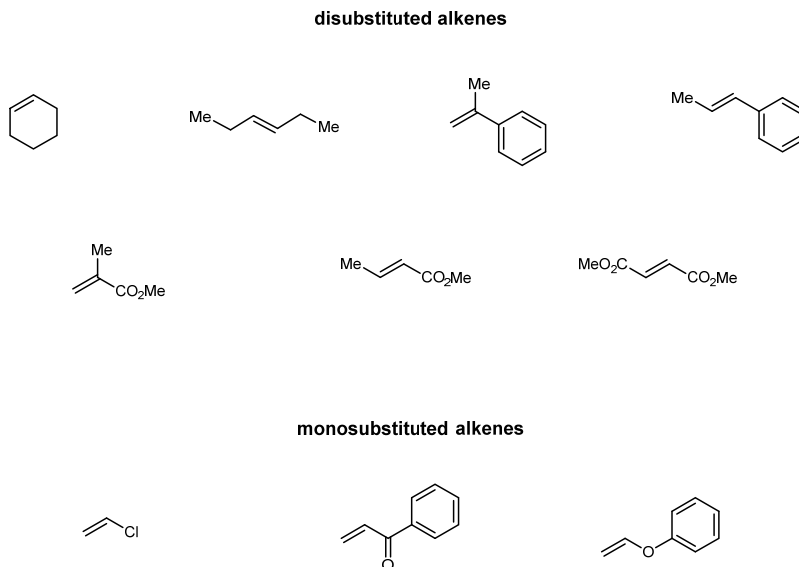
Chiral precatalyst

Entry ^a	Chiral precatalyst	Ag additive	Solvent	Yield ^b	er ^c
1	R = Me	AgSbF_6 (40 mol %)	DCE (0.2 M)	48%	88:12
2	R = Me	$\text{AgB}(\text{C}_6\text{F}_5)_4$ (40 mol %)	DCE (0.2 M)	56%	91:9
3	R = <i>i</i> Pr	$\text{AgB}(\text{C}_6\text{F}_5)_4$ (40 mol %)	DCE (0.2 M)	60%	90:10
4	R = TBDPS	$\text{AgB}(\text{C}_6\text{F}_5)_4$ (40 mol %)	DCE (0.2 M)	30%	85:15
5	R = Me	$\text{AgB}(\text{C}_6\text{F}_5)_4$ (80 mol %)	DCE (0.2 M)	77%	88:12
6	R = Me	$\text{AgB}(\text{C}_6\text{F}_5)_4$ (40 mol %)	DCE (0.5 M)	50%	88:12
7	R = Me	$\text{AgB}(\text{C}_6\text{F}_5)_4$ (40 mol %)	DCE (0.1 M)	52%	91:9
8	R = Me	$\text{AgB}(\text{C}_6\text{F}_5)_4$ (40 mol %)	Dioxane (0.2 M)	13%	-

^aConditions: Reactions were performed on 0.05 mmol of C–H bond substrate with 0.075 mmol of aminating agent and excess ethylene. ^bYields determined by ^1H NMR relative to trimethyl(phenyl)silane as an external standard. C–H alkenylated and C–H amidated products were not observed by NMR analysis of unpurified material. ^cEnantiomeric ratio determined by chiral HPLC, see Supplementary Information for conditions and HPLC traces.

Supplementary Figures

Supplementary Figure 1. List of unreactive alkene coupling partners.



Supplementary Methods

1. General Information

Unless otherwise indicated, all Rh(III)-catalysed reactions were set up in a N₂ filled glovebox, using glassware that was oven-dried (150 °C) and evacuated while hot prior to use. Unless otherwise indicated, all reactions for substrate preparation were carried out on the benchtop under a N₂ atmosphere. Solvents were purified by elution through a column of activated alumina under N₂ before use. Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Products and starting materials were visualized on TLC using UV-light or by staining with KMnO₄ or anisaldehyde. Flash-column chromatography was performed on SiliaFlash® P60 (230-400 mesh) silica gel, and preparative thin-layer chromatography, plates from Analtech (1 mm SiO₂, 20 x 20 cm) were used. For NMR characterization the magnetic field strength of the instrument is indicated for each spectra. Data are reported in the following format: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad signal, m = multiplet, dd = doublet of doublets, etc.), coupling constant *J* in Hz, and integration. NMR chemical shifts are reported in ppm relative to residual solvent peaks: CDCl₃ (7.26 ppm for ¹H and 77.16 ppm for ¹³C), DMSO-*d*₆ (2.50 ppm for ¹H and 39.52 ppm for ¹³C), or CD₃OD (3.31 ppm for ¹H and 49.00 ppm for ¹³C). For IR spectra, only partial data are provided. Melting points are reported uncorrected. High-resolution mass spectra (HRMS) were obtained using electrospray

ionization (ESI) on a time of flight (TOF) mass spectrometer. Enantiomeric ratios were determined using an Agilent 1100 series HPLC equipped with a Chiralpak AD-H column and a multiwavelength detector.

2. Preparation of Starting Materials:

Catalysts/Additives:

[Cp*RhCl₂]₂¹, chiral Rh precatalyst **59**^{2,3,4}, AgB(C₆F₅)₄⁵, and [Cp*Rh(MeCN)₃][SbF₆]₂⁶ were synthesized according to published literature procedures.

C-H bond Substrates:

(*E*)-1-Phenylethan-1-one *O*-methyl oxime⁷, 2-(*m*-tolyl)pyridine⁸, 2-(*m*-tolyl)pyrimidine⁹, 1-benzyl-4-(*m*-tolyl)-1*H*-1,2,3-triazole¹⁰, 1-(*m*-tolyl)-1*H*-pyrazole¹¹, phenyl(pyrrolidin-1-yl)methanone¹², (4-chlorophenyl)(pyrrolidin-1-yl)methanone¹², (4-methoxyphenyl)(pyrrolidin-1-yl)methanone¹², furan-3-yl(pyrrolidin-1-yl)methanone¹³, 2-methyl-3,4-dihydroisoquinolin-1(2*H*)-one¹⁴, (*E*)-3,4-dihydronaphthalen-1(2*H*)-one *O*-methyl oxime⁷, 1-(*o*-tolyl)-1*H*-pyrazole¹⁵, and 1-(pyridin-2-yl)-1*H*-indole¹⁶ were synthesized according to published literature procedures.

2-Phenylpyridine and *N*-methylbenzamide were purchased from commercial sources and used without further purification.

Alkene Substrates:

tert-Butyl but-3-en-1-ylcarbamate and benzyl but-3-en-1-ylcarbamate were synthesized according to published literature procedures¹⁷.

Styrene-*d*₈ was purchased from commercial sources and purified by silica gel flash chromatography with pentane before use.

All other alkene substrates were purchased from commercial sources and used without further purification.

Amine Substrates:

tert-Butoxycarbonylamino 2,2-dimethylpropanoate¹⁸, benzyloxycarbonylamino 2,2-dimethylpropanoate¹⁹, 9*H*-fluoren-9-ylmethoxycarbonylamino 2,2-dimethylpropanoate¹⁸, and *N*-acetoxy-4-methylbenzenesulfonamide²⁰ were synthesized according to published literature procedures.

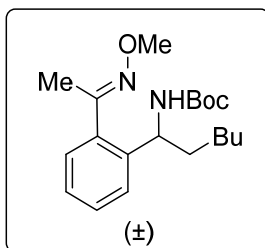
The dioxazolones 3-phenyl-1,4,2-dioxazol-5-one, 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one, 3-(4-(trifluoromethyl)phenyl)-1,4,2-dioxazol-5-one, 3-(2-chlorophenyl)-1,4,2-dioxazol-5-one, 3-(thiophen-2-yl)-1,4,2-dioxazol-5-one, 3-methyl-1,4,2-dioxazol-5-one, 3-heptyl-1,4,2-dioxazol-5-one, and 3-isopropyl-1,4,2-dioxazol-5-one were synthesized according to published literature procedures²¹.

3. Rh(III)-Catalysed α -Branched Amine Synthesis

General procedure:

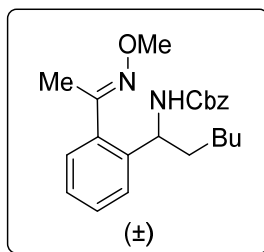
In a N₂-filled glove box, a 2–5 mL microwave vial was charged with [Cp*RhCl₂]₂ (9.3 mg, 0.015 mmol, 0.050 equiv), AgSbF₆ (21 mg, 0.06 mmol, 0.20 equiv), and, if indicated, an additive (0.30 mmol, 1 equiv). 1,2-Dichloroethane (1.5 mL, 0.2 M) was added followed by the indicated C–H bond substrate (0.300 mmol, 1.0 equiv), alkene (0.60 mmol, 2 equiv), and amine substrate (0.45 mmol, 1.50 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was then stirred at 30 or 70 °C in a preheated oil bath. After 20 h, the reaction mixture was then allowed to cool to room temperature. The reaction mixture was filtered through a small celite plug, (1 cm long in a pipette), which was washed with ethyl acetate. The resulting mixture was then concentrated and purified by the corresponding chromatographic method to afford the desired product.

Characterization Data:

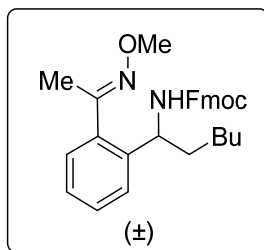


(±) *tert*-Butyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)hexyl)carbamate (**1**): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), hex-1-ene (50 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive, and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 1:99 mixture of ethyl acetate: hexanes as the eluent to afford the product **1** (63.0 mg, 60% yield) as a colorless oil. IR (neat): 3266 (br), 2957, 2931, 2858, 1699,

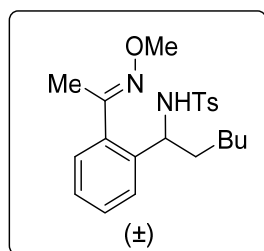
1364, 1167, 1047 cm^{-1} ; ^1H NMR (500 MHz, CD_3OD) δ 7.40 (d, $J = 7.7$ Hz, 1H), 7.32 (t, $J = 7.1$ Hz, 1H), 7.24 (t, $J = 6.9$ Hz, 1H), 7.18 (d, $J = 8.2$ Hz, 1H), 4.82 – 4.78 (m, 1H), 3.94 (s, 3H), 2.23 (s, 3H), 1.77 – 1.70 (m, 1H), 1.67 – 1.60 (m, 1H), 1.39 (s, 9H), 1.32 – 1.26 (m, 6H), 0.90 – 0.88 (m, 3H). ^{13}C NMR (126 MHz, CD_3OD) δ 158.5, 157.8, 143.8, 137.7, 129.9, 129.5, 127.9, 127.6, 80.2, 62.1, 53.6, 38.3, 32.7, 29.0, 27.4, 23.7, 17.2, 14.4. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{20}\text{H}_{33}\text{N}_2\text{O}_3^+$: 349.2486. Found 349.2491.



(±) Benzyl (*E*)-1-(2-(1-(methoxyimino)ethyl)phenyl)hexylcarbamate (2): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), 1-hexene (50 mg, 0.60 mmol, 2.0 equiv), and benzyloxycarbonylamino 2,2-dimethylpropanoate (113 mg, 0.450 mmol, 1.50 equiv). NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent. Residual impurities were removed by C18 reverse phase purification (15.5 g column, 0% to 70% $\text{MeCN}:\text{H}_2\text{O}$ containing 0.1% TFA gradient). Fractions containing product were combined and diluted with sat. aq. NaHCO_3 (50 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were then dried over MgSO_4 and concentrated to afford the product **2** (75.0 mg, 65% yield) as a colorless oil. IR (neat): 3327 (br), 2931, 2856, 1701, 1499, 1237, 1042, 882, 757, 696 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.39 – 7.19 (m, 9H), 5.60 (d, $J = 7.6$ Hz, 1H), 5.09 (d, $J = 12.2$ Hz, 1H), 5.02 (d, $J = 12.2$ Hz, 1H), 4.86 (q, $J = 7.6$ Hz, 1H), 3.96 (s, 3H), 2.26 (s, 3H), 1.84 – 1.63 (m, 2H), 1.41 – 1.12 (m, 6H), 0.85 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 157.0, 155.7, 141.0, 136.8, 136.6, 129.0, 128.9, 128.6, 128.1, 128.1, 127.4, 127.3, 66.7, 61.9, 53.8, 36.8, 31.7, 26.3, 22.6, 17.0, 14.1. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_3^+$: 383.2329. Found 383.2320.

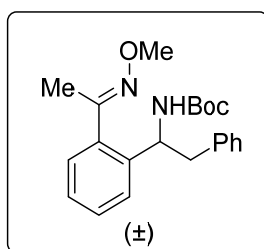


(±) (9H-Fluoren-9-yl)methyl (E)-(1-(2-(1-(methoxyimino)ethyl)phenyl)hexyl)carbamate (3): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), 1-hexene (50 mg, 0.60 mmol, 2.0 equiv), and (9H-fluoren-9-ylmethoxycarbonylamino) 2,2-dimethylpropanoate (153 mg, 0.450 mmol, 1.50 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was purified by C18 reverse phase purification (15.5 g column, 10% to 90% MeCN:H₂O containing 0.1% TFA gradient). Fractions containing product were combined and diluted with sat. aq. NaHCO₃ (100 mL) and extracted with CH₂Cl₂. The combined organic layers were then dried over Na₂SO₄ and concentrated to afford the product **3** (73.0 mg, 52% yield) as an off-white solid (mp: 100-101 °C). IR (neat): 3357 (br), 2951, 2929, 1695, 1525, 1240, 1044, 1025 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.28 – 7.25 (m, 2H) 5.86 – 5.39 (m, 1H), 4.90 – 4.85 (m, 1H), 4.45 – 4.41 (m, 1H), 4.38 – 4.35 (m, 1H), 4.22 – 4.20 (m, 1H), 3.98 (s, 3H), 2.28 (s, 3H), 1.80 – 1.70 (m, 2H), 1.36 – 1.22 (m, 6H), 0.90 – 0.88 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 157.1, 155.7, 144.1, 144.1, 141.4, 140.8, 136.6, 129.0, 127.9, 127.7, 127.4, 127.1, 125.1, 120.0, 66.4, 61.9, 54.3, 47.4, 36.5, 31.6, 26.3, 22.6, 17.0, 14.1. HRMS (ESI/[M+H]⁺) calcd. for C₃₀H₃₅N₂O₃⁺: 471.2642. Found 471.2648.



(±) (E)-N-(1-(2-(1-(Methoxyimino)ethyl)phenyl)hexyl)-4-methylbenzenesulfonamide (4): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), 1-hexene (50 mg, 0.60 mmol, 2.0 equiv), and *N*-acetoxy-4-methylbenzenesulfonamide (103 mg, 0.450 mmol, 1.50 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel

chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **4** (82.7 mg, 63% yield) as an off-white/grey solid (mp: 75-76 °C). IR (neat): 3262, 2949, 2865, 1322, 1153, 1040 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.52 (d, J = 8.2 Hz, 2H), 7.17 – 7.10 (m, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.05 – 7.01 (m, 1H), 6.94 (d, J = 7.7 Hz, 1H), 6.25 (s, 1H), 4.48 (q, J = 7.9 Hz, 1H), 3.99 (s, 3H), 2.32 (s, 3H), 2.17 (s, 3H), 1.76 – 1.59 (m, 2H), 1.36 – 1.25 (m, 1H), 1.23 – 1.11 (m, 4H), 1.11 – 1.03 (m, 1H), 0.80 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 156.8, 142.7, 139.6, 138.2, 135.67, 129.2, 128.8, 128.7, 128.5, 127.1, 127.1, 62.1, 57.1, 36.9, 31.4, 26.1, 22.5, 21.5, 16.8, 14.1. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{22}\text{H}_{31}\text{N}_2\text{O}_3\text{S}^+$: 403.2050. Found 403.2079.



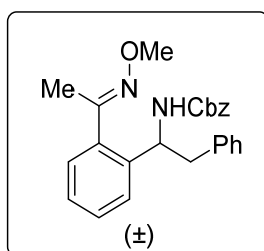
(±) *tert*-Butyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethyl)carbamate (5**):**

Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 5:95 mixture of ethyl acetate: hexanes as the eluent to afford the product **5** (66.0 mg, 60% yield) as an off-white solid (mp: 75-76 °C). IR (neat): 3404 (br), 2974, 2938, 1688, 1503, 1165, 1054, 1043 cm^{-1} ; ^1H NMR (500 MHz, CD_3OD) δ 7.51 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.30 – 7.16 (m, 7H), 5.18 – 5.11 (m, 1H), 3.96 (s, 3H), 3.12 – 3.08 (m, 1H), 2.83 – 2.78 (m, 1H), 2.20 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (126 MHz, CD_3OD) δ 158.5, 157.5, 143.1, 140.3, 137.6, 130.2, 130.0, 129.4, 129.3, 128.1, 127.6, 127.4, 80.0, 62.2, 54.7, 44.4, 28.8, 17.2. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{22}\text{H}_{29}\text{N}_2\text{O}_3^+$: 369.2173. Found 369.2178.

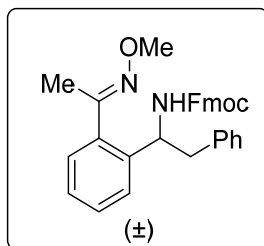
For reaction with 1 mol% Rh-dimer loading, a slightly different procedure has been used:

In a N_2 -filled glovebox, a 2-5 mL microwave vial was charged with $[\text{Cp}^*\text{RhCl}_2]_2$ (1.85 mg, 0.003 mmol, 0.010 equiv), AgSbF_6 (4.1 mg, 0.012 mmol, 0.04 equiv), and NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv). 1,2-Dichloroethane (0.3 mL, 1.0 M) was added followed by (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60

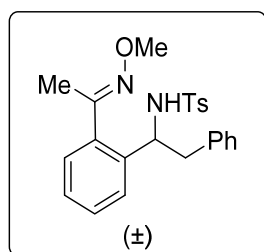
mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was then stirred at 30 °C in a preheated oil bath. After 20 h, the reaction mixture was then allowed to cool to room temperature. The reaction mixture was filtered through a small celite plug (1 cm long in a pipette) eluting with ethyl acetate and concentrated. The product was then purified by silica gel chromatography using a 5:95 mixture of ethyl acetate: hexanes as the eluent to afford the product **5** (70.0 mg, 63% yield) as an off-white solid. The spectroscopic data matches with that of the above conditions.



(±) Benzyl (E)-(1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethyl)carbamate (6): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and benzyloxycarbonylamino 2,2-dimethylpropanoate (113 mg, 0.450 mmol, 1.50 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of acetone: hexanes as the eluent to afford the product **6** (89.0 mg, 74% yield) as a colorless oil. IR (neat): 3267 (br), 3029, 2937, 1712, 1532, 1248, 1026, 1009, 875 cm⁻¹; NMR experiments conducted at 70 °C: ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.14 (m, 12H), 5.16 (dd, *J* = 11.6, 5.0 Hz, 1H), 4.92 (d, *J* = 12.7 Hz, 1H), 4.87 (d, *J* = 12.8 Hz, 1H), 3.89 (s, 3H), 3.01 – 2.95 (m, 1H), 2.89 (dd, *J* = 13.6, 11.0 Hz, 1H), 2.14 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 155.6, 154.9, 141.7, 138.7, 136.8, 135.4, 128.4, 128.2, 127.8, 127.7, 127.5, 127.1, 126.8, 126.3, 126.0, 125.7, 64.7, 60.9, 52.8, 42.1, 16.0. HRMS (ESI/[M+H]⁺) calcd. for C₂₅H₂₇N₂O₃⁺: 403.2016. Found 403.2003.

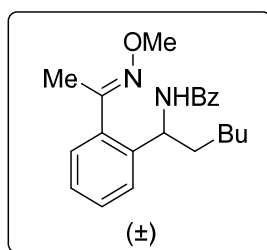


(±) **(9H-Fluoren-9-yl)methyl (E)-1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethylcarbamate (7)**: Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (9*H*-fluoren-9-ylmethoxycarbonylamino) 2,2-dimethylpropanoate (153 mg, 0.450 mmol, 1.50 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a gradient up to 5:95 mixture of ethyl acetate: hexanes as the eluent to afford the product **7** (66.0 mg, 45% yield) as an off-white solid (mp: 75-76 °C). IR (neat): 3372 (br), 2966, 1690, 1527, 1250, 1029, 891 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 7.7 Hz, 2H), 7.51 – 7.37 (m, 4H), 7.34 – 7.31 (m, 3H), 7.31 – 7.28 (m, 4H), 7.24 – 7.21 (m, 2H), 7.16 (d, *J* = 6.8 Hz, 2H), 5.79 (apparent broad s, 1H), 5.28 – 5.23 (m, 1H), 4.39 – 4.35 (m, 1H), 4.24 – 4.20 (m, 1H), 4.17 – 4.13 (m, 1H), 4.01 (s, 3H), 3.26 – 3.22 (m, 1H), 3.02 – 2.83 (m, 1H), 2.27 (broad s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 156.9, 155.6, 144.0, 141.3, 140.2, 138.0, 136.5, 129.2, 128.9, 128.9, 128.6, 127.7, 127.5, 127.1, 126.7, 125.2, 125.1, 120.0, 66.6, 62.0, 54.9, 47.3, 42.9, 16.9. HRMS (ESI/[M+H]⁺) calcd. for C₃₂H₃₁N₂O₃⁺: 491.2329. Found 491.2335.

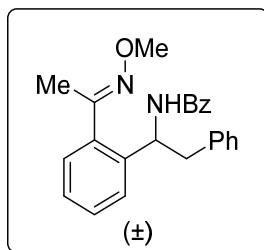


(±) **(E)-N-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)-4-methylbenzenesulfonamide (8)**: Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and *N*-acetoxy-4-methylbenzenesulfonamide (103 mg, 0.450 mmol, 1.50 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent. Residual impurities were removed by C18 reverse phase purification (15.5 g

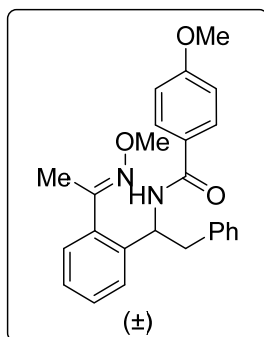
column, 0% to 70% MeCN:H₂O containing 0.1% TFA gradient). Fractions containing product were combined and diluted with sat. aq. NaHCO₃ (50 mL) and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were then dried over MgSO₄ and concentrated to afford the product **8** (74.0 mg, 58% yield) as a colorless waxy solid. IR (neat): 3291, 2938, 1319, 1154, 1040 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.33 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.11 (m, 7H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 7.7 Hz, 2H), 5.51 (s, 1H), 4.90 – 4.74 (m, 1H), 4.00 (s, 3H), 3.13 (dd, *J* = 14.1, 5.7 Hz, 1H), 2.83 (dd, *J* = 14.1, 9.0 Hz, 1H), 2.35 (s, 3H), 2.23 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 156.7, 142.8, 139.2, 137.2, 137.1, 135.8, 129.3, 129.1, 128.7, 128.66, 128.65, 128.6, 127.4, 127.1, 126.9, 62.1, 43.5, 21.6, 16.8. HRMS (ESI/[M+H]⁺) calcd. for C₂₄H₂₇N₂O₃S⁺: 423.1737. Found 423.1758.



(±) (E)-N-(1-(2-(1-(Methoxyimino)ethyl)phenyl)hexyl)benzamide (9): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), 1-hexene (50 mg, 0.60 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (73 mg, 0.45 mmol, 1.5 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of acetone: hexanes as the eluent to afford the product **9** (58.0 mg, 55% yield) as a white solid (mp: 76-77 °C). IR (neat): 3293, 3061, 2954, 2928, 2856, 1632, 1538, 1047 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.78 (d, *J* = 7.3 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 1H), 7.46 – 7.35 (m, 4H), 7.33 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 5.32 (q, *J* = 7.9 Hz, 1H), 3.93 (s, 3H), 2.28 (s, 3H), 1.91 – 1.74 (m, 2H), 1.39 – 1.14 (m, 6H), 0.83 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.4, 158.1, 140.2, 136.6, 135.0, 131.3, 129.4, 129.3, 129.1, 128.5, 127.6, 127.1, 62.0, 53.9, 35.6, 31.7, 26.6, 22.6, 17.3, 14.1. HRMS (ESI/[M+H]⁺) calcd. for C₂₂H₂₉N₂O₂⁺: 353.2224. Found 353.2223.

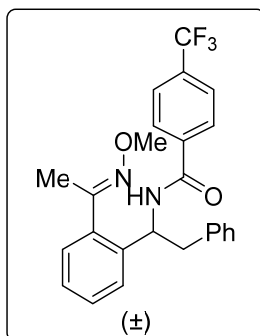


(±) (E)-N-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)benzamide (10): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (73 mg, 0.45 mmol, 1.5 equiv). NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **10** (72.0 mg, 64% yield) as a white solid (mp: 110-112 °C). IR (neat): 3363, 1635, 1523, 1488, 1306, 1282, 1042, 891 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.68 (d, J = 7.8 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.23 (t, J = 7.5 Hz, 2H), 7.20 – 7.12 (m, 3H), 5.63 (q, J = 7.7 Hz, 1H), 3.98 (s, 3H), 3.24 (dd, J = 14.0, 7.0 Hz, 1H), 3.16 (dd, J = 14.0, 8.0 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 166.4, 157.6, 139.6, 138.0, 136.5, 134.7, 131.3, 129.07, 129.05, 128.9, 128.6, 128.4, 128.4, 127.5, 126.9, 126.5, 61.9, 54.3, 42.0, 17.1. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}_2^+$: 373.1911. Found 373.1918.

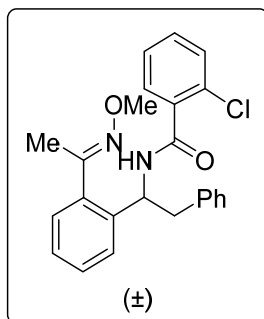


(±) (E)-4-Methoxy-N-(1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethyl)benzamide (11): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (87 mg, 0.45 mmol, 1.5 equiv). NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 25:75 mixture of ethyl acetate: hexanes as the eluent to afford the product **11** (78.2 mg, 65% yield) as a white solid (mp: 119-120 °C). IR (neat): 3286 (br), 2937,

1625, 1606, 1508, 1251, 1177, 1040, 1028 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.67 (d, J = 8.8 Hz, 2H), 7.33 – 7.21 (m, 7H), 7.20 – 7.13 (m, 3H), 6.86 (d, J = 8.8 Hz, 2H), 5.61 (q, J = 7.5 Hz, 1H), 4.00 (s, 3H), 3.81 (s, 3H), 3.25 (dd, J = 14.0, 6.9 Hz, 1H), 3.16 (dd, J = 14.0, 8.0 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 166.0, 162.1, 157.7, 139.9, 138.2, 136.6, 129.2, 129.1, 128.9, 128.8, 128.7, 128.5, 127.5, 127.1, 126.6, 113.7, 62.0, 55.5, 54.3, 42.2, 17.2. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_3^+$: 403.2016. Found 403.2013.

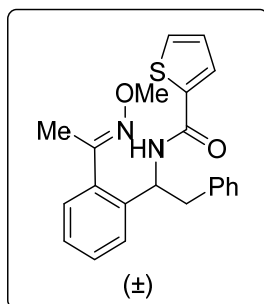


(±) **(*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)-4-(trifluoromethyl)benzamide (**12**):** Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-[4-(trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (104 mg, 0.450 mmol, 1.50 equiv). NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 $^\circ\text{C}$. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **12** (65.0 mg, 49% yield) as a white solid (mp: 56-58 $^\circ\text{C}$). IR (neat): 3304 (br), 3028, 2938, 1636, 1540, 1323, 1122, 1044 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.76 (d, J = 8.2 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 8.2 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.27 – 7.22 (m, 2H), 7.21 – 7.14 (m, 3H), 5.66 (q, J = 8.0 Hz, 1H), 3.99 (s, 3H), 3.25 (dd, J = 14.0, 7.1 Hz, 1H), 3.18 (dd, J = 14.0, 8.2 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 165.2, 157.9, 139.3, 138.2, 138.0, 136.5, 133.1 (q, J = 32.6 Hz), 129.4, 129.2, 129.1, 128.6, 127.9, 127.5, 126.7, 126.5, 125.5 (q, J = 3.6 Hz), 123.8 (q, J = 272.5 Hz), 62.1, 54.9, 41.9, 17.3. ^{19}F NMR (376 MHz, CDCl_3) δ -63.0. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{25}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_2^+$: 441.1784. Found 441.1773.



(±) (E)-2-Chloro-N-(1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethyl)benzamide (13):

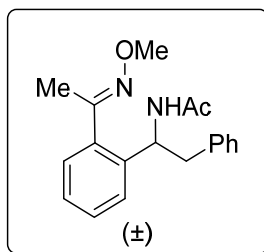
Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-(2-chlorophenyl)-1,4,2-dioxazol-5-one (89 mg, 0.45 mmol, 1.5 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **13** (70.3 mg, 58% yield) as a colorless waxy solid. IR (neat): 3277 (br), 3063, 1640, 1530, 1496, 1313, 1042, 753, 698 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.47 – 7.43 (m, 1H), 7.37 – 7.14 (m, 13H), 5.66 (q, *J* = 7.7 Hz, 1H), 3.92 (s, 3H), 3.31 (dd, *J* = 14.1, 6.3 Hz, 1H), 3.10 (dd, *J* = 14.1, 8.6 Hz, 1H), 2.29 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.6, 157.1, 139.7, 137.9, 136.7, 135.3, 131.2, 130.8, 130.2, 130.1, 129.3, 128.9, 128.9, 128.6, 127.8, 127.6, 127.0, 126.7, 61.9, 53.9, 42.5, 16.9. HRMS (ESI/[M+H]⁺) calcd. for C₂₄H₂₄ClN₂O₂⁺: 407.1521. Found 407.1548.



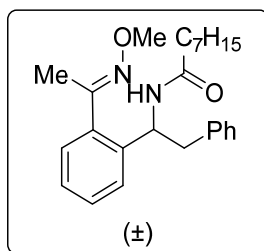
(±) (E)-N-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)thiophene-2-carboxamide (14):

Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-(2-thienyl)-1,4,2-dioxazol-5-one (76 mg, 0.45 mmol, 1.5 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **14** (96.6 mg, 85% yield) as a white solid (mp: 125-126 °C). IR (neat): 3337 (br), 3087,

2969, 2818, 1619, 1531, 1508, 1297, 1034 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.44 – 7.39 (m, 2H), 7.31 – 7.27 (m, 4H), 7.24 (t, $J = 7.4$ Hz, 2H), 7.21 – 7.11 (m, 4H), 7.04 – 7.00 (m, 1H), 5.57 (q, $J = 7.7$ Hz, 1H), 4.04 (s, 3H), 3.24 (dd, $J = 14.0, 7.0$ Hz, 1H), 3.16 (dd, $J = 14.0, 7.9$ Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 161.0, 157.7, 139.5, 139.4, 138.0, 136.5, 129.8, 129.2, 129.2, 129.0, 128.9, 128.6, 128.0, 127.7, 127.6, 126.7, 62.2, 54.5, 42.1, 17.2. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_2\text{S}^+$: 379.1475. Found 379.1494.

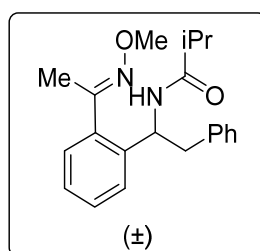


(±) **(E)-N-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)acetamide (15)**: Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **15** (67.4 mg, 72% yield) as a white solid (mp: 74-75 °C). IR (neat): 3288 (br), 3065, 2939, 2818, 1643, 1534, 1298, 1038 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.30 – 7.26 (m, 3H), 7.25 – 7.21 (m, 3H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.09 (d, $J = 7.8$ Hz, 2H), 6.64 (br, 1H), 5.44 (q, $J = 7.7$ Hz, 1H), 4.00 (s, 3H), 3.13 (dd, $J = 14.0, 6.8$ Hz, 1H), 3.01 (dd, $J = 14.0, 8.1$ Hz, 1H), 2.24 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 169.0, 157.3, 139.9, 138.1, 136.7, 129.2, 128.9, 128.9, 128.5, 128.2, 127.5, 126.55, 62.0, 53.5, 42.3, 23.5, 16.9. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2^+$: 311.1754. Found 311.1749.

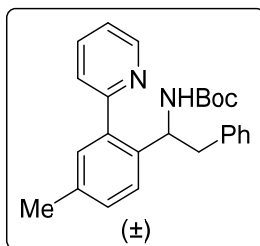


(±) **(E)-N-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)octanamide (16)**: Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene

(62 mg, 0.60 mmol, 2.0 equiv), and 3-heptyl-1,4,2-dioxazol-5-one (83 mg, 0.45 mmol, 1.5 equiv). NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **16** (104 mg, 88% yield) as a white solid (mp: 69-70 °C). IR (neat): 3263, 3064, 2925, 2856, 1637, 1550, 1044 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.30 – 7.27 (m, 2H), 7.26 – 7.21 (m, 4H), 7.17 (t, J = 7.3 Hz, 1H), 7.10 (d, J = 7.3 Hz, 2H), 6.37 (s, 1H), 5.43 (q, J = 8.0 Hz, 1H), 3.99 (s, 3H), 3.17 (dd, J = 14.1, 6.5 Hz, 1H), 2.98 (dd, J = 14.1, 8.5 Hz, 1H), 2.25 (s, 3H), 2.12 – 2.00 (m, 2H), 1.54 – 1.44 (m, 2H), 1.30 – 1.11 (m, 8H), 0.86 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 172.2, 157.4, 140.1, 138.1, 136.7, 129.2, 129.0, 128.9, 128.5, 128.0, 127.5, 126.6, 62.0, 53.2, 42.4, 37.0, 31.8, 29.2, 29.1, 25.7, 22.7, 17.0, 14.2. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{25}\text{H}_{35}\text{N}_2\text{O}_2^+$: 395.2693. Found 395.2690.

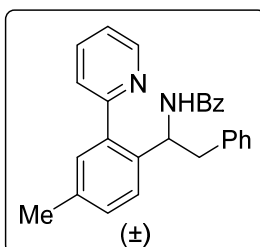


(±) (E)-N-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)isobutyramide (17): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (58 mg, 0.45 mmol, 1.5 equiv). NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **17** (85.0 mg, 84% yield) as a white solid (mp: 106-107 °C). IR (neat): 3279, 2970, 2938, 1640, 1539, 1244, 1037, 882 cm^{-1} ; ^1H NMR (600 MHz, CDCl_3) δ 7.29 – 7.26 (m, 2H), 7.26 – 7.22 (m, 4H), 7.18 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 7.0 Hz, 2H), 6.33 (d, J = 7.1 Hz, 1H), 5.45 – 5.40 (m, 1H), 4.00 (s, 3H), 3.20 (dd, J = 14.1, 6.4 Hz, 1H), 2.97 (dd, J = 14.1, 8.6 Hz, 1H), 2.27 (s, 3H), 2.26 – 2.20 (m, 1H), 1.03 (d, J = 6.9 Hz, 3H), 1.00 (d, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 176.0, 157.4, 140.2, 138.1, 136.7, 129.2, 129.0, 128.9, 128.5, 127.9, 127.5, 126.6, 62.0, 52.9, 42.5, 35.8, 19.7, 19.4, 17.0. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_2^+$: 339.2067. Found 339.2082.



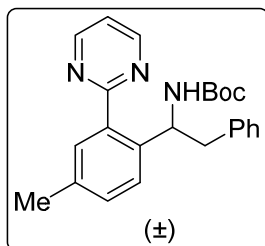
(±) *tert*-Butyl (1-(4-methyl-2-(pyridin-2-yl)phenyl)-2-phenylethyl)carbamate (18):

Derived from 2-(*m*-tolyl)pyridine (50.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 70 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes gradient as the eluent to afford the product **18** (71.0 mg, 70% yield) as a white solid (mp: 101-102 °C). IR (neat): 3400, 3063, 2980, 2919, 1689, 1514, 1169, 1018 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.71 (s, 1H), 7.81 – 7.71 (m, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.10 (m, 6H), 6.91 (m, 2H), 5.81 (s, 1H), 5.16 (m, 1H), 2.87 (m, 1H), 2.77 (m, 1H), 2.36 (s, 3H), 1.36 (broad s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 160.1, 155.1, 149.0, 139.5, 138.3, 137.3, 136.9, 136.7, 131.3, 129.4, 129.3, 128.2, 127.6, 126.2, 124.6, 122.0, 79.0, 54.2, 42.7, 28.5, 21.1. HRMS (ESI/[M+H]⁺) calcd. for C₂₅H₂₉N₂O₂⁺: 389.2224. Found 389.2216.



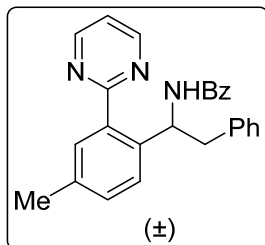
(±) *N*-(1-(4-Methyl-2-(pyridin-2-yl)phenyl)-2-phenylethyl)benzamide (19): Derived from 2-(*m*-tolyl)pyridine (50.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (73 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 25:75 mixture of ethyl acetate: hexanes as the eluent to afford the product **19** (95.0 mg, 81% yield) as a white solid (mp: 156-157 °C). IR (neat): 3380, 3082, 3061, 3030, 2925, 1638, 1525, 1488, 1302, 1276 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 9.54 (d, *J* = 8.0 Hz, 1H), 8.76 – 8.69 (m, 1H), 7.93 – 7.87 (m, 3H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.24 – 7.19 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 2H), 7.11 – 7.06 (m, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 5.63 (q, *J* = 8.2 Hz, 1H), 2.87 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.59 (dd, *J* = 13.6,

8.9 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, CDCl_3) δ 165.8, 161.1, 148.2, 139.5, 138.5, 137.7, 137.4, 136.5, 135.2, 132.5, 131.2, 131.0, 129.7, 129.1, 128.5, 128.2, 127.1, 126.2, 125.2, 122.5, 56.2, 41.1, 21.1. HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{27}\text{H}_{25}\text{N}_2\text{O}^+$: 393.1961. Found 393.1946.



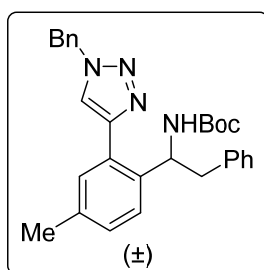
(±) *tert*-Butyl (1-(4-methyl-2-(pyrimidin-2-yl)phenyl)-2-phenylethyl)carbamate (20):

Derived from 2-(*m*-tolyl)pyrimidine (51.1 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 10:90 mixture of ethyl acetate: hexanes as the eluent to afford the product **20** (95.0 mg, 81% yield) as a white solid (mp: 104-105 °C). IR (neat): 3392 (br), 2976, 1682, 1413, 1171, 1019 cm^{-1} ; NMR experiments conducted at 60 °C: ^1H NMR (500 MHz, CD_3OD) δ 8.87 (d, J = 4.9 Hz, 2H), 7.57 (s, 1H), 7.44 (d, J = 7.9 Hz, 1H), 7.37 (t, J = 4.9 Hz, 1H), 7.27 (d, J = 7.8 Hz, 1H), 7.22 – 7.06 (m, 5H), 5.64 – 5.51 (m, 1H), 3.12 (dd, J = 13.7, 3.7 Hz, 1H), 2.79 (dd, J = 13.8, 9.9 Hz, 1H), 2.36 (s, 3H), 1.21 (broad s, 9H). ^{13}C NMR (126 MHz, CD_3OD) δ 168.5, 158.3, 157.3, 141.1, 140.4, 138.1, 137.7, 132.3, 131.6, 130.2, 129.1, 128.2, 127.1, 120.3, 80.0, 54.5, 44.1, 28.6, 21.0. HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{24}\text{H}_{28}\text{N}_3\text{O}_2^+$: 390.2176. Found 390.2181.

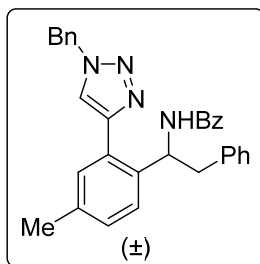


(±) *N*-(1-(4-Methyl-2-(pyrimidin-2-yl)phenyl)-2-phenylethyl)benzamide (21): Derived from 2-(*m*-tolyl)pyrimidine (51.1 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (73 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a

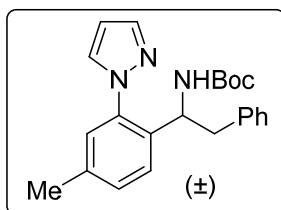
10:90 mixture of ethyl acetate: hexanes as the eluent to afford the product **21** (81.0 mg, 69% yield) as an off-white solid (mp: 129-130 °C). IR (neat): 3288 (br), 3029, 1632, 1425, 822 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.18 (d, *J* = 8.8 Hz, 1H), 8.93 (d, *J* = 4.9 Hz, 2H), 7.85 – 7.83 (m, 2H), 7.71 (s, 1H), 7.47 – 7.44 (m, 1H), 7.42 – 7.39 (m, 2H), 7.33 (t, *J* = 4.9 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.16 – 7.13 (m, 3H), 7.11 – 7.07 (m, 1H), 7.03 – 7.01 (m, 2H), 5.88 – 5.83 (m, 1H), 3.00 – 2.96 (m, 1H), 2.75 – 2.70 (m, 1H), 2.37 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 168.1, 165.8, 157.1, 138.3, 137.5, 137.4, 137.0, 135.2, 133.2, 131.2, 130.9, 130.9, 129.1, 128.5, 128.2, 127.0, 126.3, 119.1, 55.7, 41.6, 21.0. HRMS (ESI/[M+H]⁺) calcd. for C₂₆H₂₄N₃O⁺: 394.1914. Found 394.1919.



(±) **tert-Butyl (1-(2-(1-benzyl-1H-1,2,3-triazol-4-yl)-4-methylphenyl)-2-phenylethyl)carbamate (22)**: Derived from 1-benzyl-4-(*m*-tolyl)triazole (74.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 70 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **22** (89.0 mg, 63% yield) as a white solid (mp: 122-123 °C). IR (neat): 3398, 3028, 2979, 1690, 1516, 1495, 1168, 1044, 1018, 722, 699 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.55 – 7.46 (broad s, 1H), 7.43 – 7.35 (m, 3H), 7.34 – 7.30 (m, 2H), 7.29 – 7.22 (m, 2H), 7.20 – 7.08 (m, 4H), 7.02 – 6.93 (m, 2H), 5.58 (s, 2H), 5.54 – 5.48 (m, 1H), 5.20 (q, *J* = 7.3 Hz, 1H), 3.11 – 2.99 (m, 1H), 2.97 – 2.85 (m, 1H), 2.33 (s, 3H), 1.46 – 1.02 (broad s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 155.2, 147.5, 138.2, 137.5, 137.0, 134.9, 131.0, 129.6, 129.4, 129.3, 129.0, 128.8, 128.3, 128.2, 127.4, 126.4, 122.3, 79.2, 54.3, 53.7, 42.8, 28.5, 21.0. HRMS (ESI/[M+H]⁺) calcd. for C₂₉H₃₃N₄O₂⁺: 469.2598. Found 469.2596.

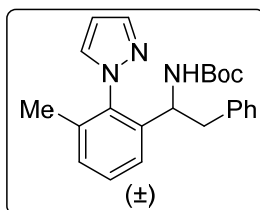


(±) ***N*-(1-(2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-4-methylphenyl)-2-phenylethyl)benzamide (23)**: Derived from 1-benzyl-4-(*m*-tolyl)triazole (74.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (73 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 33:66 mixture of acetone: hexanes as the eluent to afford the product **23** (115 mg, 81% yield) as a white solid (mp: 148-150 °C). IR (neat): 3337 (br), 3060, 3030, 1635, 1532, 1490, 1051 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.74 – 8.66 (broad s, 1H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.67 (s, 1H), 7.47 – 7.37 (m, 6H), 7.35 (d, *J* = 6.7 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.19 (s, 1H), 7.13 (t, *J* = 7.2 Hz, 2H), 7.11 – 7.06 (m, 2H), 6.99 (d, *J* = 7.1 Hz, 2H), 5.68 (q, *J* = 8.0 Hz, 1H), 5.64 (s, 2H), 3.04 (dd, *J* = 13.7, 7.8 Hz, 1H), 2.94 (dd, *J* = 13.7, 7.9 Hz, 1H), 2.30 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.3, 148.9, 138.5, 137.4, 136.9, 134.9, 134.6, 131.5, 131.3, 130.4, 129.8, 129.4, 129.2, 129.1, 128.7, 128.5, 128.3, 128.2, 127.2, 126.4, 122.3, 55.2, 54.6, 41.2, 21.0. HRMS (ESI/[M+H]⁺) calcd. for C₃₁H₂₉N₄O⁺: 473.2336. Found 473.2318.



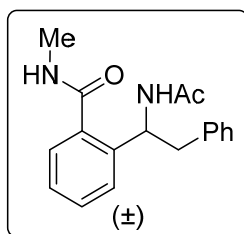
(±) ***tert*-butyl (1-(4-Methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-phenylethyl)carbamate (24)**: Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 70 °C. The product was then purified by silica gel chromatography using a 10:90 mixture of ethyl acetate: hexanes as the eluent to afford the product **24** (77.0 mg, 68% yield) as a white solid (mp: 158-159 °C). IR (neat): 3406 (br), 2973, 1689, 1509, 1245, 1162, 1016 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 1.8 Hz, 1H), 7.67 (broad s, 1H), 7.26 – 7.25 (m, 1H), 7.21 – 7.13 (m, 4H), 7.11 (s, 1H), 6.97 – 6.96 (m, 2H), 6.49 – 6.48 (m, 1H), 5.65 (broad s, 1H), 4.99 (apparent broad s, 1H), 2.76 (apparent broad s,

1H), 2.68 – 2.64 (m, 1H), 2.36 (s, 3H), 1.35 (broad s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 155.1, 140.5, 138.7, 138.0, 135.1, 131.4, 129.6, 129.3, 128.7, 128.3, 127.5, 126.4, 106.8, 79.3, 53.3, 41.8, 28.4, 20.9. HRMS (ESI/[M+H]⁺) calcd. for C₂₃H₂₈N₃O₂⁺: 378.2176. Found 378.2181.



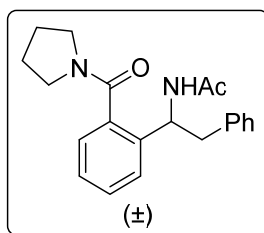
(±) *tert*-butyl (1-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-phenylethyl)carbamate (25):

Derived from 1-(*o*-tolyl)pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 70 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **25** (58.0 mg, 51% yield) as a white solid (mp: 135-136 °C). IR (neat): 3395, 3146, 3004, 2978, 2928, 1696, 1507, 1247, 1168, 775 cm⁻¹; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.85 (m, 2H), 7.58 – 7.40 (m, 3H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.4 Hz, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.00 – 6.91 (m, 2H), 6.59 (s, 1H), 4.35 – 4.16 (apparent broad s, 1H), 2.92 – 2.73 (broad s, 1H), 2.66 – 2.57 (m, 1H), 1.92 (s, 3H), 1.24 – 0.97 (broad s, 9H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 154.8, 139.9, 139.1, 137.3, 135.6, 132.1, 129.3, 128.9, 128.8, 127.9, 126.0, 124.1, 123.9, 106.1, 77.7, 51.7, 28.1, 27.7, 16.9. HRMS (ESI/[M+H]⁺) calcd. for C₂₃H₂₈N₃O₂⁺: 378.2176. Found 378.2202.



(±) 2-(1-Acetamido-2-phenylethyl)-*N*-methylbenzamide (26): Derived from *N*-methyl benzamide (40.6 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 33:66 mixture of acetone: hexanes as the eluent

to afford the product **26** (60.0 mg, 68% yield) as a white solid (mp: 58-60 °C). IR (neat): 3272 (br), 3066, 1631, 1536, 1304, 698 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.27 (m, 2H), 7.23 (t, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.16 – 7.12 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 2H), 5.35 (q, *J* = 7.5 Hz, 1H), 3.04 – 2.99 (m, 2H), 3.01 (s, 3H), 1.88 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.1, 170.3, 139.7, 137.6, 135.9, 130.4, 129.1, 128.7, 128.4, 128.3, 127.7, 126.8, 54.1, 42.5, 26.9, 23.4. HRMS (ESI/[M+H]⁺) calcd. for C₁₈H₂₁N₂O₂⁺: 297.1598. Found 297.1587.

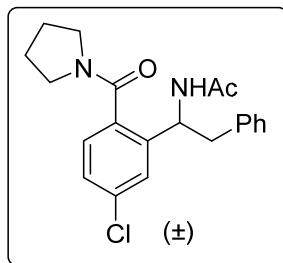


(±) N-(2-Phenyl-1-(2-(pyrrolidine-1-carbonyl)phenyl)ethyl)acetamide (27): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 33:66 mixture of acetone: hexanes as the eluent to afford the product **27** (71.0 mg, 70% yield) as a white solid (mp: 125-126 °C). IR (neat): 3285 (br), 2968, 2887, 1650, 1609, 1598, 1427, 761, 700 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.32 – 7.26 (m, 4H), 7.25 – 7.22 (m, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 2H), 6.99 – 6.91 (broad s, 1H), 5.29 (q, *J* = 8.0 Hz, 1H), 3.77 – 3.63 (m, 2H), 3.33 – 3.25 (m, 1H), 3.21 – 3.17 (m, 1H), 3.15 (dd, *J* = 14.2, 6.5 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.08 – 1.93 (m, 2H), 1.92 – 1.84 (m, 2H), 1.87 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.5, 169.3, 139.3, 138.1, 135.7, 129.6, 129.2, 129.2, 128.5, 127.3, 127.2, 126.7, 54.5, 49.4, 46.1, 41.9, 26.3, 24.7, 23.6. HRMS (ESI/[M+H]⁺) calcd. for C₂₁H₂₅N₂O₂⁺: 337.1911. Found 337.1894.

For reaction with 1 mol% Rh-dimer loading, a slightly different procedure was used:

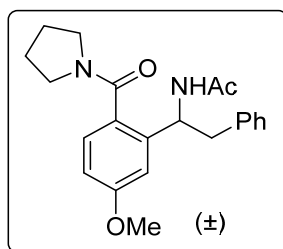
In a N₂-filled glovebox, a 2-5 mL microwave vial was charged with [Cp*RhCl₂]₂ (1.85 mg, 0.003 mmol, 0.010 equiv), AgSbF₆ (4.1 mg, 0.012 mmol, 0.04 equiv), and PivOH (30 mg, 0.30 mmol, 1.0 equiv). 1,2-Dichloroethane (1.5 mL, 0.2 M) was added followed phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove

box. The reaction mixture was then stirred at 70 °C in a preheated oil bath. After 20 h, the reaction mixture was then allowed to cool to room temperature. The reaction mixture was filtered through a small celite plug (1 cm long in a pipette) eluting with ethyl acetate and concentrated. The product was then purified by silica gel chromatography using a 33:66 mixture of acetone: hexanes as the eluent to afford the product **27** (72.0 mg, 71% yield) as a white solid. The spectroscopic data matches with that of the above conditions.



(±) N-(1-(5-Chloro-2-(pyrrolidine-1-carbonyl)phenyl)-2-phenylethyl)acetamide (28):

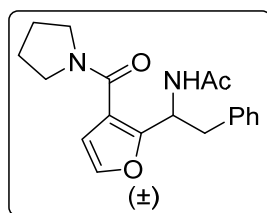
Derived from (4-chlorophenyl)-pyrrolidin-1-yl-methanone (62.9 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 20:80 mixture of acetone: hexanes as the eluent to afford the product **28** (61.1 mg, 55% yield) as a colorless oil. IR (neat): 3300 (br), 2973, 1673, 1606, 1434, 1104, 910 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.28 (d, $J = 2.1$ Hz, 1H), 7.25 – 7.23 (m, 3H), 7.19 – 7.16 (m, 2H), 7.15 – 7.14 (m, 2H), 6.85 (broad s, 1H), 5.20 – 5.16 (m, 1H), 3.74 – 3.63 (m, 2H), 3.38 – 3.34 (m, 1H), 3.21 – 3.17 (m, 1H), 3.15 – 3.11 (m, 1H), 2.94 – 2.89 (m, 1H), 2.04 – 1.98 (m, 1H), 1.97 – 1.91 (m, 1H), 1.91 – 1.85 (m, 2H), 1.83 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.5, 169.2, 141.9, 137.7, 135.2, 134.3, 129.1, 128.6, 128.4, 128.1, 127.4, 126.8, 53.7, 49.2, 46.1, 41.9, 26.2, 24.7, 23.3. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{21}\text{H}_{24}\text{ClN}_2\text{O}_2^+$: 371.1521. Found 371.1526.



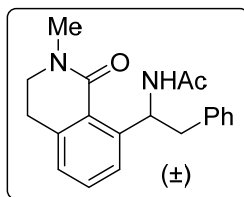
(±) N-(1-(5-Methoxy-2-(pyrrolidine-1-carbonyl)phenyl)-2-phenylethyl)acetamide (29):

Derived from (4-methoxyphenyl)(pyrrolidin-1-yl)methanone (61.6 mg, 0.300 mmol, 1.00

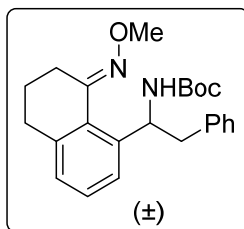
equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of acetone: hexanes as the eluent to afford the product **29** (80.0 mg, 73% yield) as a colorless oil. IR (neat): 3379 (br), 3287, 2975, 1605, 1516, 1452, 1434, 1242, 1164, 1026, 912 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 9.4 Hz, 1H), 7.22 – 7.19 (m, 2H), 7.18 – 7.12 (m, 4H), 6.78 (d, *J* = 2.5 Hz, 1H), 6.75 – 6.73 (m, 1H), 5.27 – 5.22 (m, 1H), 3.72 (s, 3H), 3.70 – 3.61 (m, 2H), 3.31 – 3.26 (m, 1H), 3.22 – 3.17 (m, 1H), 3.13 – 3.09 (m, 1H), 3.01 – 2.97 (m, 1H), 2.04 – 1.97 (m, 1H), 1.96 – 1.90 (m, 1H), 1.89 – 1.82 (m, 2H), 1.84 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 170.7, 169.2, 160.1, 141.5, 138.1, 129.1, 128.8, 128.3, 127.9, 126.5, 114.9, 112.3, 55.3, 54.7, 49.5, 46.1, 41.8, 26.3, 24.7, 23.4. HRMS (ESI/[M+H]⁺) calcd. for C₂₂H₂₇N₂O₃⁺: 367.2016. Found 367.2022.



(±) **N-(2-Phenyl-1-(3-(pyrrolidine-1-carbonyl)furan-2-yl)ethyl)acetamide (30)**: Derived from 3-furyl(pyrrolidin-1-yl)methanone (49.6 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 50:50 mixture of acetone: hexanes as the eluent to afford the product **30** (84.0 mg, 86% yield) as an orange waxy solid. IR (neat): 3276 (br), 2972, 2877, 1655, 1606, 1510, 1436, 730, 699 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.05 (d, *J* = 8.6 Hz, 1H), 7.23 – 7.10 (m, 4H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.41 (d, *J* = 1.9 Hz, 1H), 5.58 (q, *J* = 7.4 Hz, 1H), 3.57 – 3.47 (m, 2H), 3.44 – 3.35 (m, 2H), 3.10 (m, 2H), 2.02 – 1.81 (m, 4H), 1.96 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 169.3, 164.5, 157.2, 140.1, 137.3, 129.4, 128.2, 126.5, 117.7, 110.1, 49.3, 49.0, 46.6, 40.7, 26.6, 24.3, 23.5. HRMS (ESI/[M+H]⁺) calcd. for C₁₉H₂₃N₂O₃⁺: 327.1703. Found 327.1689.

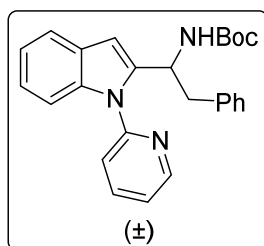


(±) ***N*-(1-(2-Methyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-8-yl)-2-phenylethyl)acetamide (31)**: Derived from 2-methyl-3,4-dihydroisoquinolin-1-one (48.4 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 70:30 mixture of acetone: hexanes as the eluent to afford the product **31** (65.0 mg, 67% yield) as a white solid (mp: 161-162 °C). IR (neat): 3351 (br), 3043, 2948, 1639, 1526, 1340, 1107 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.67 (broad s, 1H), 7.19 – 7.12 (m, 4H), 7.10 – 7.08 (m, 3H), 7.03 (d, *J* = 7.3 Hz, 1H), 5.58 (broad s, 1H), 3.63 – 3.57 (m, 1H), 3.46 – 3.41 (m, 1H), 3.23 (s, 3H), 3.16 (apparent broad s, 2H), 3.07 – 3.01 (m, 1H), 2.84 – 2.79 (m, 1H), 1.87 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 169.0, 165.7, 140.3, 138.9, 131.3, 129.6, 129.3, 128.3, 128.1, 127.6, 126.8, 126.1, 56.4, 47.9, 41.2, 35.7, 29.7, 23.7. HRMS (ESI/[M+H]⁺) calcd. for C₂₀H₂₃N₂O₂⁺: 323.1754. Found 323.1760.

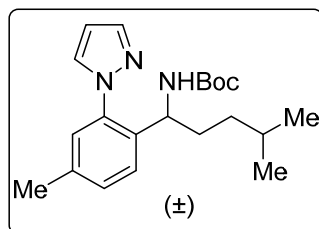


(±) ***tert*-butyl (*E*)-(1-(8-(methoxyimino)-5,6,7,8-tetrahydronaphthalen-1-yl)-2-phenylethyl)carbamate (32)**: Derived from (*E*)-3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyl oxime (52.6 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 1:99 mixture of ethyl acetate: hexanes as the eluent to afford the product **32** (85.0 mg, 72% yield) as a white solid (mp: 122-123 °C). IR (neat): 3397 (br), 2966, 2938, 1686, 1518, 1409, 1172, 1059, 1015 cm⁻¹; NMR experiments conducted at 60 °C: ¹H NMR (500 MHz, CD₃OD) δ 7.35 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.18 (m, 5H), 7.14 (t, *J* = 7.0 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 5.90 – 5.80 (m,

1H), 3.96 (s, 3H), 3.19 (dd, $J = 14.3, 4.5$ Hz, 1H), 2.90 – 2.76 (m, 2H), 2.76 – 2.67 (m, 2H), 2.64 – 2.54 (m, 1H), 1.86 – 1.77 (m, 1H), 1.67 – 1.54 (m, 1H), 1.28 (broad s, 9H). ^{13}C NMR (126 MHz, CD_3OD) δ 157.6, 157.1, 143.3, 140.5, 130.3, 130.1, 129.6, 129.1, 127.6, 127.1, 127.0, 62.4, 54.4, 43.7, 32.2, 28.7, 26.6, 22.3. HRMS (ESI/ $[\text{M}+\text{H}]^+$) calcd. for $\text{C}_{24}\text{H}_{31}\text{N}_2\text{O}_3^+$: 395.2329. Found 395.2335.

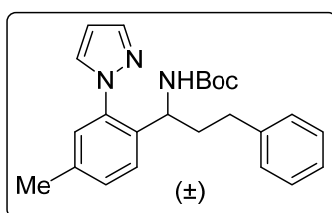


(±) **tert-Butyl (2-phenyl-1-(1-(pyridin-2-yl)-1H-indol-2-yl)ethyl)carbamate (33)**: Derived from 1-(pyridin-2-yl)-1H-indole (58.3 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 15:85 mixture of ethyl acetate: hexanes as the eluent to afford the product **33** (99.0 mg, 80% yield) as a white solid (mp: 147-148 °C). IR (neat): 3391 (br), 3059, 2973, 1689, 1508, 1435, 1252, 1167, 1018 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.70 (d, $J = 4.8$ Hz, 1H), 7.91 – 7.88 (m, 1H), 7.60 (d, $J = 7.1$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.36 – 7.33 (m, 2H), 7.21 – 7.15 (m, 5H), 7.04 (d, $J = 7.2$ Hz, 2H), 6.58 (s, 1H), 5.55 – 5.21 (m, 2H), 3.16 – 2.92 (m, 2H), 1.36 and 1.19 (rotamers of CMe_3 , 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 154.8, 151.4, 149.7, 140.8, 138.7, 137.6, 137.6, 129.4, 128.3, 128.1, 126.4, 122.7, 122.4, 121.3, 121.0, 120.8, 110.4, 103.4, 79.3, 49.5, 41.4, 28.4. HRMS (ESI/ $[\text{M}+\text{H}]^+$) calcd. for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}_2^+$: 414.2176. Found 414.2181.

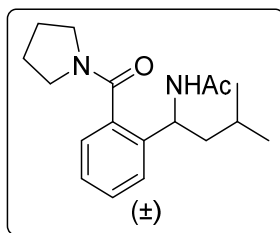


(±) **tert-Butyl (4-methyl-1-(4-methyl-2-(1H-pyrazol-1-yl)phenyl)pentyl)carbamate (34)**: Derived from 1-(*m*-tolyl)-1H-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), 4-methylpent-1-ene (50 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product was then

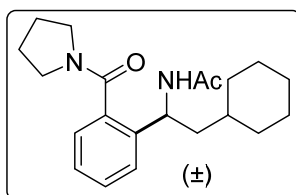
purified by silica gel chromatography using a 2:98 mixture of acetone: hexanes as the eluent to afford the product **34** (75.0 mg, 70% yield) as a colorless oil. IR (neat): 3322 (br), 2955, 2869, 1698, 1365, 1167, 1041 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.75 (broad s, 1H), 7.71 (s, 1H), 7.30 (d, $J = 7.9$ Hz, 1H), 7.18 (d, $J = 7.9$ Hz, 1H), 7.09 (s, 1H), 6.43 (s, 1H), 5.78 (s, 1H), 4.66 – 4.52 (m, 1H), 2.35 (s, 3H), 1.40 (s, 9H), 1.33 – 1.31 (m, 2H), 1.25 – 1.21 (m, 1H), 1.07 – 1.00 (m, 1H), 0.90 – 0.84 (m, 1H), 0.72 (d, $J = 6.7$ Hz, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 155.4, 140.4, 138.8, 137.9, 135.8, 131.4, 129.7, 129.0, 127.7, 106.7, 79.1, 52.7, 35.7, 33.2, 28.5, 27.7, 22.5, 20.9. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{21}\text{H}_{32}\text{N}_3\text{O}_2^+$: 358.2489. Found 358.2495.



(±) *tert*-Butyl (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-3-phenylpropyl)carbamate (35): Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), allylbenzene (70 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 2:98 mixture of acetone: hexanes as the eluent to afford the product **35** (76.0 mg, 65% yield) as a colorless oil. IR (neat): 3302 (br), 2975, 2929, 1697, 1516, 1496, 1365, 1243, 1164, 1043 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.72 (apparent broad s, 2H), 7.34 (d, $J = 7.9$ Hz, 1H), 7.22 – 7.19 (m, 3H), 7.15 – 7.12 (m, 2H), 7.01 (d, $J = 7.4$ Hz, 2H), 6.43 (s, 1H), 5.89 (apparent broad s, 1H), 4.78 – 4.62 (m, 1H), 2.52 – 2.46 (m, 1H), 2.40 – 2.35 (m, 1H), 2.37 (s, 3H), 1.73 – 1.65 (m, 1H), 1.59 – 1.54 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 155.3, 141.5, 140.5, 138.8, 138.1, 135.3, 131.4, 129.7, 129.2, 128.4, 128.3, 127.7, 125.8, 106.8, 79.2, 52.5, 37.0, 33.1, 28.5, 20.9. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{24}\text{H}_{30}\text{N}_3\text{O}_2^+$: 392.2333. Found 392.2338.

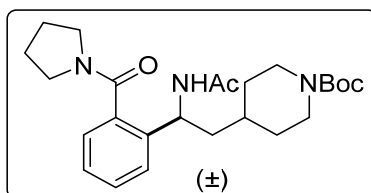


(±) *N*-(3-Methyl-1-(2-(pyrrolidine-1-carbonyl)phenyl)butyl)acetamide (36): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv) and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 1 minute using a reagent cannister of 3-methyl-1-butene with a needle and an exit needle pierced through the vial cap. PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 25:75 mixture of acetone: hexanes as the eluent to afford the product **36** (55.0 mg, 61% yield) as a colorless waxy solid. IR (neat): 3292 (br), 2955, 2872, 1651, 1611, 1430, 728 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.39 – 7.31 (m, 2H), 7.30 – 7.22 (m, 2H), 5.14 (q, *J* = 8.7 Hz, 1H), 3.71 – 3.60 (m, 2H), 3.34 – 3.19 (m, 2H), 2.07 – 1.80 (m, 4H), 1.94 (s, 3H), 1.65 – 1.58 (m, 1H), 1.57 – 1.50 (m, 1H), 1.50 – 1.42 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 171.0, 169.1, 140.0, 135.5, 123.0, 129.8, 127.5, 127.2, 52.0, 49.5, 46.1, 44.8, 26.3, 25.6, 24.7, 23.8, 22.6. HRMS (ESI/[M+H]⁺) calcd. for C₁₈H₂₇N₂O₂⁺: 303.2067. Found 303.2056.



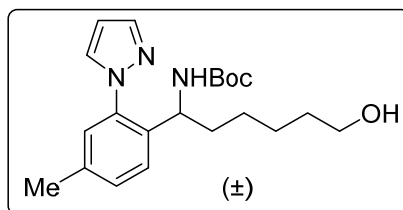
(±) *N*-(2-Cyclohexyl-1-(2-(pyrrolidine-1-carbonyl)phenyl)ethyl)acetamide (37): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), vinyl cyclohexane (66 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 20:80 mixture of acetone: hexanes as the eluent to afford the product **37** (55.0 mg, 54% yield) as a white solid (mp: 97-98 °C). IR (neat): 3297 (br), 2921, 2851, 1608, 1433, 1292, 923 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.30 (m, 2H), 7.28 – 7.26 (m, 1H), 7.24 – 7.20 (m, 2H), 5.16 – 5.11 (m, 1H), 3.63 (t, *J* = 7.0 Hz, 2H), 3.27 – 3.25 (m, 2H), 2.05 – 1.95 (m, 2H), 1.92 (s, 3H),

1.91 – 1.87 (m, 1H), 1.85 – 1.78 (m, 1H), 1.70 – 1.62 (m, 4H), 1.59 – 1.50 (m, 3H), 1.17 – 1.08 (m, 4H), 0.95 – 0.86 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.8, 169.1, 140.2, 135.5, 129.7, 129.5, 127.2, 127.1, 51.1, 49.4, 46.0, 43.4, 34.9, 33.4, 33.1, 26.5, 26.23, 26.21, 26.18, 24.7, 23.7. HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{21}\text{H}_{31}\text{N}_2\text{O}_2^+$: 343.2380. Found 343.2386.



(±)-tert-Butyl 4-(2-acetamido-2-(2-(pyrrolidine-1-carbonyl)phenyl)ethyl)piperidine-1-

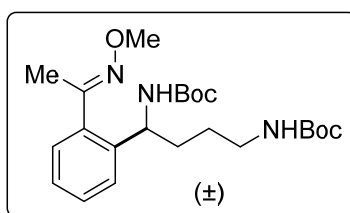
carboxylate (38): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), *tert*-butyl 4-vinylpiperidine-1-carboxylate (127 mg, 0.600 mmol, 2.00 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 20:80 mixture of acetone: hexanes as the eluent to afford the product **38** (74.0 mg, 56% yield) as a white solid (mp: 90-91 °C). IR (neat): 3301 (br), 2975, 2931, 1662, 1609, 1423, 1366, 1165, 1143, 932 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.29 (m, 2H), 7.26 (s, 1H), 7.25 – 7.20 (m, 2H), 5.16 – 5.11 (m, 1H), 4.00 (m, 2H), 3.62 – 3.59 (m, 2H), 3.27 – 3.19 (m, 2H), 2.62 – 2.57 (m, 2H), 2.01 – 1.97 (m, 1H), 1.95 – 1.92 (m, 1H), 1.91 (s, 3H), 1.89 – 1.85 (m, 1H), 1.82 – 1.77 (m, 1H), 1.75 – 1.70 (m, 1H), 1.66 – 1.51 (m, 3H), 1.41 – 1.40 (m, 1H), 1.40 (s, 9H), 1.13 – 1.01 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.6, 169.1, 154.8, 139.9, 135.6, 129.7, 129.1, 127.3, 127.2, 79.3, 50.5, 49.4, 46.0, 44.0, 43.7, 42.70, 33.3, 32.4, 31.7, 28.5, 26.2, 24.6, 23.6. HRMS (ESI/[M+H] $^+$) calcd. for $\text{C}_{25}\text{H}_{38}\text{N}_3\text{O}_4^+$: 444.2857. Found 444.2862.



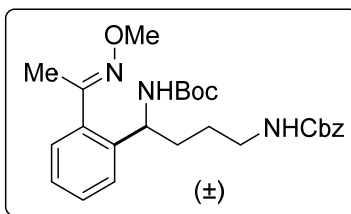
(±) tert-Butyl (6-hydroxy-1-(4-methyl-2-(1H-pyrazol-1-yl)phenyl)hexyl)carbamate (39):

Derived from 1-(*m*-tolyl)-1H-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), hex-5-en-1-ol (60 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product was then purified

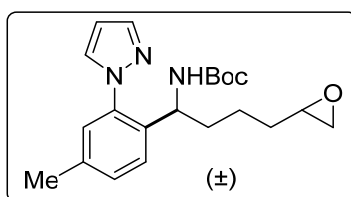
by silica gel chromatography using a 20:80 mixture of acetone: hexanes as the eluent to afford the product **39** (88.0 mg, 79% yield) as a colorless oil. IR (neat): 3315 (br), 2931, 2859, 1691, 1516, 1365, 1165, 1042, 909 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.77 (broad s, 1H), 7.69 (d, $J = 1.9$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.18 (d, $J = 7.9$ Hz, 1H), 7.08 (s, 1H), 6.43 (s, 1H), 5.70 (apparent broad s, 1H), 4.67 – 4.62 (m, 1H), 3.48 (t, $J = 6.6$ Hz, 2H), 2.34 (s, 3H), 2.17 (broad s, 1H), 1.39 (s, 9H), 1.35 – 1.26 (m, 4H), 1.17 – 1.07 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 155.4, 140.4, 138.7, 138.0, 135.7, 131.6, 129.8, 128.6, 127.7, 106.7, 79.2, 62.4, 51.8, 35.5, 32.4, 28.5, 26.0, 25.0, 20.8. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{21}\text{H}_{32}\text{N}_3\text{O}_3^+$: 374.2438. Found 374.2444.



(±) di-*tert*-Butyl (1-(2-(1-(methoxyimino)ethyl)phenyl)butane-1,4-diyl)(*E*)-dicarbamate (40): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), *tert*-butyl *N*-but-3-enylcarbamate (103 mg, 0.600 mmol, 2.00 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 $^\circ\text{C}$. The product was then purified by silica gel chromatography using a 10:90 mixture of acetone: hexanes as the eluent to afford the product **40** (91.0 mg, 70% yield) as a white solid (mp: 99–100 $^\circ\text{C}$). IR (neat): 3388 (br), 2977, 2935, 1679, 1404, 1153, 1040 cm^{-1} ; ^1H NMR (500 MHz, CD_3OD) δ 7.41 (d, $J = 7.8$ Hz, 1H), 7.34 (t, $J = 7.6$ Hz, 1H), 7.27 – 7.09 (m, 2H), 4.80 – 4.77 (m, 1H), 3.95 (s, 3H), 3.06 – 2.99 (m, 2H), 2.24 (s, 3H), 1.79 – 1.74 (m, 1H), 1.66 – 1.54 (m, 2H), 1.49 – 1.46 (m, 1H), 1.42 (s, 9H), 1.40 (broad s, 9H). ^{13}C NMR (126 MHz, CD_3OD) δ 158.5, 158.4, 157.7, 143.5, 137.5, 129.9, 129.4, 127.9, 127.4, 80.0, 79.9, 62.2, 53.0, 41.3, 35.6, 28.9, 28.5, 17.1. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{23}\text{H}_{38}\text{N}_3\text{O}_5^+$: 436.2806. Found 436.2812.

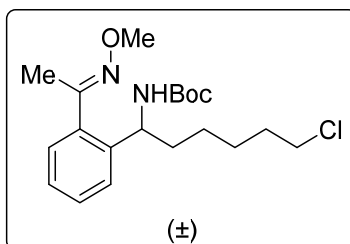


(±) **benzyl *tert*-butyl (1-(2-(1-(methoxyimino)ethyl)phenyl)butane-1,4-diyl)(*E*)-dicarbamate (41):** Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), benzyl *N*-but-3-enylcarbamate (123 mg, 0.600 mmol, 2.00 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 10:90 mixture of acetone: hexanes as the eluent to afford the product **41** (100.0 mg, 71% yield) as a light yellowish oil. IR (neat): 2975, 2935, 2479, 1682, 1391, 1363, 1150, 1040 cm⁻¹; ¹H NMR (500 MHz, CD₃OD) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.29 (m, 5H), 7.28 – 7.24 (m, 2H), 7.19 (d, *J* = 7.7 Hz, 1H), 5.04 (s, 2H), 4.82 – 4.78 (m, 1H), 3.91 (s, 3H), 3.14 – 3.09 (m, 2H), 2.23 (s, 3H), 1.81 – 1.76 (m, 1H), 1.66 – 1.58 (m, 2H), 1.52 – 1.47 (m, 1H), 1.39 (s, 9H). ¹³C NMR (126 MHz, CD₃OD) δ 158.9, 158.4, 157.7, 143.5, 138.5, 137.5, 129.9, 129.5, 129.5, 129.0, 128.9, 128.0, 127.5, 80.0, 67.4, 62.3, 53.1, 41.7, 35.6, 28.9, 28.5, 17.2. HRMS (ESI/[M+H]⁺) calcd. for C₂₆H₃₆N₃O₅⁺: 470.2649. Found 470.2648.



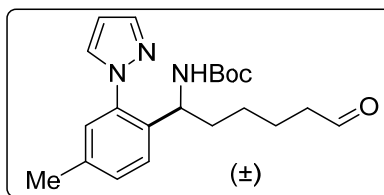
(±) ***tert*-Butyl (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-4-(oxiran-2-yl)butyl)carbamate (42):** Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), 2-but-3-enyloxirane (58 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 3:97 mixture of acetone: hexanes as the eluent to afford the product **42** (77.0 mg, 69% yield) as a colorless oil. IR (neat): 2976, 2931, 1684, 1391, 1364, 1163, 1041 cm⁻¹. ¹H NMR (500 MHz, CD₃OD) δ 8.03 – 7.81 (m, 1H), 7.72 (d, *J* = 1.8 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.12 (s, 1H), 6.52 (t, *J* = 2.2 Hz, 1H), 4.54 – 4.51 (m, 1H), 2.78 (m, 1H), 2.67 – 2.65 (m, 1H), 2.36 (s, 3H), 2.38 – 2.34 (m, 1H), 1.56 – 1.50 (m, 2H), 1.40 (s, 9H), 1.33 – 1.26 (m, 4H). ¹³C NMR

(126 MHz, CD₃OD) δ 157.7, 141.4, 139.7, 139.2, 138.7, 133.6, 131.3, 128.5, 128.2, 107.7, 80.1, 53.3 and 53.2 (1:1 dr), 51.2, 47.84 and 47.77 (1:1 dr), 37.5 and 37.4 (1:1 dr), 33.0 and 32.9 (1:1 dr), 29.0 and 28.9 (1:1 dr), 24.03 and 23.98 (1:1 dr), 20.97 and 20.93 (1:1 dr). HRMS (ESI/[M+H]⁺) calcd. for C₂₁H₃₀N₃O₃⁺: 372.2282. Found 372.2287.



(±) *tert*-Butyl (*E*)-(6-chloro-1-(2-(1-(methoxyimino)ethyl)phenyl)hexyl)carbamate (43):

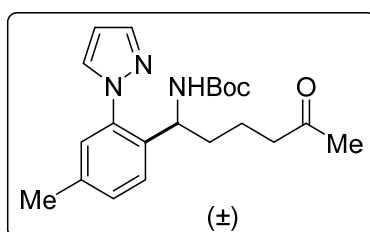
Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), 6-chlorohex-1-ene (71 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes. Additional impurities were removed by prep plate (10:90 mixture of ethyl acetate: hexanes as eluent, ran up 3 times) to afford the product **43** (69.0 mg, 60% yield) as a colorless oil. IR (neat): 3282 (br), 2970, 2934, 1697, 1493, 1365, 1167, 1046, 729 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) δ 7.41 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 4.81 – 4.75 (m, 1H), 3.94 (s, 3H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.25 (s, 3H), 1.80 – 1.70 (m, 3H), 1.66 – 1.58 (m, 1H), 1.52 – 1.30 (m, 4H), 1.40 (s, 9H). ¹³C NMR (151 MHz, CD₃OD) δ 157.1, 156.3, 142.3, 136.0, 128.5, 127.9, 126.4, 125.9, 78.5, 60.7, 51.4, 44.2, 36.7, 32.3, 27.5, 26.1, 25.6, 15.8. HRMS (ESI/[M+H]⁺) calcd. for C₂₀H₃₂ClN₂O₃⁺: 383.2096. Found 383.2122.



(±) *tert*-Butyl (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-6-oxohexyl)carbamate (44):

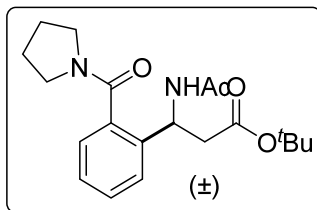
Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), hex-5-enal (59 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product was then purified by

silica gel chromatography using a 17:83 mixture of acetone: hexanes as the eluent to afford the product **44** (57.0 mg, 51% yield) as a colorless oil. IR (neat): 3357 (br), 2931, 1695, 1516, 1164, 1044 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.65 (s, 1H), 7.76 (broad s, 1H), 7.70 (s, 1H), 7.29 (d, $J = 7.9$ Hz, 1H), 7.18 (d, $J = 7.7$ Hz, 1H), 7.09 (s, 1H), 6.44 (s, 1H), 5.76 (apparent broad s, 1H), 4.68 – 4.64 (m, 1H), 2.34 (s, 3H), 2.28 – 2.16 (m, 2H), 1.44 – 1.43 (m, 2H), 1.39 (s, 9H), 1.28 – 1.20 (m, 2H), 1.17 – 1.07 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 202.6, 155.3, 140.5, 138.7, 138.1, 135.4, 131.5, 129.8, 128.9, 127.7, 106.8, 79.2, 52.0, 43.6, 35.1, 28.5, 26.0, 21.5, 20.9. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{21}\text{H}_{30}\text{N}_3\text{O}_3^+$: 372.2282. Found 372.2287.

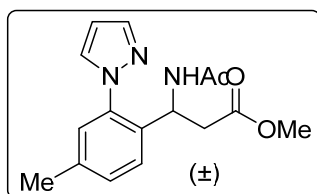


(±) *tert*-Butyl (1-(4-methyl-2-(1H-pyrazol-1-yl)phenyl)-5-oxohexyl)carbamate (45):

Derived from 1-(*m*-tolyl)-1H-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), hex-5-en-2-one (59 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 70 °C. The product was then purified by silica gel chromatography using a 10:90 mixture of acetone: hexanes as the eluent to afford the product **45** (84.0 mg, 75% yield) as a light orange solid (mp: 95-96 °C). IR (neat): 3380 (br), 2977, 2929, 1708, 1687, 1516, 1278, 1164, 1025, 951 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.75 (broad s, 1H), 7.69 (s, 1H), 7.29 (d, $J = 7.9$ Hz, 1H), 7.17 (d, $J = 7.9$ Hz, 1H), 7.07 (s, 1H), 6.43 (s, 1H), 5.74 (apparent broad s, 1H), 4.66 – 4.54 (m, 1H), 2.33 (s, 3H), 2.28 – 2.20 (m, 2H), 2.02 (s, 3H), 1.38 (s, 9H), 1.34 – 1.23 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 208.7, 155.3, 140.4, 138.7, 138.1, 135.4, 131.5, 129.7, 128.7, 127.6, 106.7, 79.2, 51.7, 42.8, 34.8, 29.9, 28.5, 20.8, 20.5. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{21}\text{H}_{30}\text{N}_3\text{O}_3^+$: 372.2282. Found 372.2287.

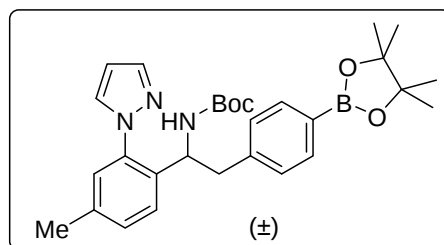


(±) *tert*-Butyl 3-acetamido-3-(2-(pyrrolidine-1-carbonyl)phenyl)propanoate (46): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), *tert*-butyl acrylate (77 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 70 °C. The product was then purified by silica gel chromatography using a 20:80 mixture of acetone: hexanes as the eluent to afford the product **46** (86.0 mg, 79% yield) as a light yellowish oil. IR (neat): 3286 (br), 2976, 2878, 1613, 1431, 1367, 1150 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.75 (s, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.24 – 7.20 (m, 2H), 5.38 – 5.33 (m, 1H), 3.67 – 3.57 (m, 2H), 3.33 – 3.29 (m, 1H), 3.24 – 3.19 (m, 1H), 2.79 – 2.75 (m, 1H), 2.58 – 2.53 (m, 1H), 2.04 – 1.96 (m, 1H), 1.95 – 1.84 (m, 3H), 1.91 (s, 3H) 1.25 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.2, 170.1, 169.0, 137.9, 135.8, 129.9, 129.5, 127.5, 127.0, 81.0, 50.2, 49.3, 46.0, 41.1, 27.9, 26.1, 24.6, 23.5. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{20}\text{H}_{29}\text{N}_2\text{O}_4^+$: 361.2122. Found 361.2127.

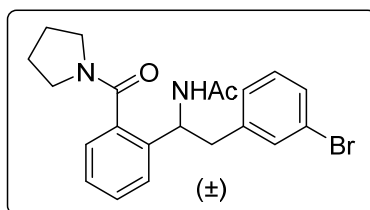


(±) Methyl 3-acetamido-3-(4-methyl-2-(1H-pyrazol-1-yl)phenyl)propanoate (47): Derived from 1-(*m*-tolyl)-1H-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), methyl prop-2-enoate (52 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 70 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of acetone: hexanes as the eluent to afford the product **47** (62.0 mg, 69% yield) as a colorless oil. IR (neat): 3280 (br), 2951, 1737, 1653, 1517, 1436, 1168, 910 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.74 – 7.73 (m, 2H), 7.67 (d, J = 8.9 Hz, 1H), 7.39 (d, J = 7.9 Hz, 1H), 7.18 (d, J = 7.4 Hz, 1H), 7.07 (s, 1H), 6.49 (s, 1H), 5.48 – 5.43 (m, 1H), 3.52 (s, 3H), 2.49 – 2.45 (m, 1H), 2.35 (s, 3H), 2.17 – 2.13 (m, 1H), 1.93 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 171.4, 169.1, 140.7, 138.9, 138.8, 133.1, 131.7, 130.5, 129.8, 127.6,

107.2, 51.7, 48.5, 38.6, 23.6, 20.9. HRMS (ESI/[M+H]⁺) calcd. for C₁₆H₂₀N₃O₃⁺: 302.1499. Found 302.1505.

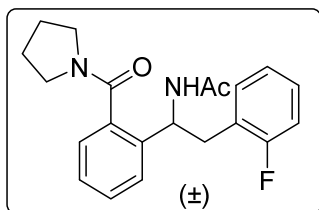


(±) **tert-Butyl- (1-(4-methyl-2-(1H-pyrazol-1-yl)phenyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)carbamate (48)**: Derived from 1-(*m*-tolyl)-1H-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (138 mg, 0.600 mmol, 2.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 70 °C. The product was then purified by silica gel chromatography using a gradient up to 10:90 mixture of ethyl acetate: hexanes followed by another silica gel chromatography with 15:85 acetone: hexane as the eluent to afford the product **48** (70.0 mg, 47% yield) as a colorless oil. IR (neat): 3265 (br), 2976, 2249, 1703, 1358, 1167, 1144, 1024, 858 cm⁻¹; ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.03 – 7.97 (m, 1H), 7.81 (s, 1H), 7.62 – 7.53 (m, 3H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.07 (m, 3H), 6.55 (s, 1H), 4.84 – 4.75 (m, 1H), 3.04 – 2.86 (m, 1H), 2.73 – 2.68 (m, 1H), 2.34 (s, 3H), 1.27 (s, 12H), 1.21 – 1.08 (broad s, 9H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 154.7, 142.7, 140.1, 137.7, 137.1, 137.0, 134.1, 131.5, 129.2, 128.6, 128.4, 127.0, 126.3, 106.5, 83.4, 77.6, 51.1, 42.1, 28.1, 24.6, 20.3. HRMS (ESI/[M+H]⁺) calcd. for C₂₉H₃₉BN₃O₄⁺: 504.3028. Found 504.3039.



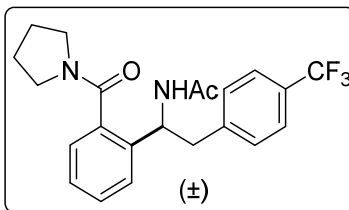
(±) **N-(2-(3-Bromophenyl)-1-(2-(pyrrolidine-1-carbonyl)phenyl)ethyl)acetamide (49)**: Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), 1-bromo-3-vinyl-benzene (110 mg, 0.600 mmol, 2.00 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel

chromatography using a 20:80 mixture of acetone: hexanes as the eluent to afford the product **49** (85.0 mg, 68% yield) as a colorless oil. IR (neat): 3293 (br), 2975, 1608, 1597, 1427, 908 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.27 – 7.26 (m, 5H), 7.24 – 7.23 (m, 2H), 7.11 – 7.05 (m, 2H), 5.26 – 5.21 (m, 1H), 3.74 – 3.63 (m, 2H), 3.30 – 3.26 (m, 1H), 3.19 – 3.14 (m, 1H), 3.11 – 3.07 (m, 1H), 2.96 – 2.91 (m, 1H), 2.05 – 1.98 (m, 1H), 1.96 – 1.91 (m, 1H), 1.89 – 1.85 (m, 2H), 1.84 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.2, 169.3, 140.6, 139.0, 135.7, 132.1, 123.0, 129.6, 129.6, 128.8, 127.7, 127.4, 127.0, 122.3, 54.1, 49.3, 46.0, 41.4, 26.2, 24.6, 23.3. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{21}\text{H}_{24}\text{BrN}_2\text{O}_2^+$: 415.1016. Found 415.1021.



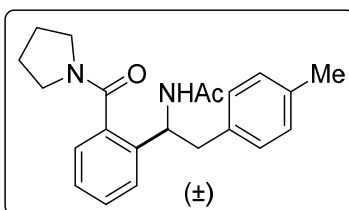
(±) N-(2-(2-Fluorophenyl)-1-(2-(pyrrolidin-1-carbonyl)phenyl)ethyl)acetamide (50):

Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), 1-fluoro-2-vinyl-benzene (73 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 20:80 mixture of acetone: hexanes as the eluent to afford the product **50** (80.0 mg, 75% yield) as a colorless oil. IR (neat): 3291 (br), 2973, 1655, 1611, 1492, 1432, 1229, 908 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.27 (m, 2H), 7.26 – 7.24 (m, 3H), 7.16 – 7.12 (m, 1H), 7.10 (broad s, 1H), 7.01 (t, J = 7.4 Hz, 1H), 6.96 (t, J = 9.2 Hz, 1H), 5.26 – 5.21 (m, 1H), 3.74 – 3.63 (m, 2H), 3.35 – 3.30 (m, 1H), 3.21 – 3.13 (m, 2H), 3.05 – 3.00 (m, 1H), 2.04 – 1.97 (m, 1H), 1.95 – 1.90 (m, 1H), 1.88 – 1.85 (m, 2H), 1.84 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.2, 169.3, 161.2 (d, J = 243.2 Hz), 139.2, 135.9, 131.5 (d, J = 5.0 Hz), 129.5, 128.4, 128.3 (d, J = 7.6 Hz), 127.3, 126.9, 125.2 (d, J = 15.1 Hz), 124.3 (d, J = 3.8 Hz), 115.0 (d, J = 22.7 Hz), 53.8, 49.2, 45.9, 34.9, 26.1, 24.6, 23.4. ^{19}F NMR (470 MHz, CDCl_3) δ -118.55. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{21}\text{H}_{24}\text{FN}_2\text{O}_2^+$: 355.1816. Found 355.1822.



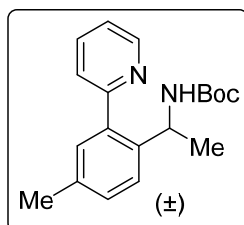
(±)N-(1-(2-(Pyrrolidine-1-carbonyl)phenyl)-2-(4-

(trifluoromethyl)phenyl)ethyl)acetamide (51): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), 1-(trifluoromethyl)-4-vinyl-benzene (103 mg, 0.600 mmol, 2.00 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 20:80 mixture of acetone: hexanes as the eluent to afford the product **51** (72.0 mg, 59% yield) as a colorless oil. IR (neat): 3289 (br), 2975, 2878, 1610, 1432, 1322, 1115, 1066 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.46 (d, J = 8.0 Hz, 2H), 7.28 – 7.25 (m, 6H), 7.15 (broad s, 1H), 5.31 – 5.27 (m, 1H), 3.74 – 3.64 (m, 2H), 3.29 – 3.25 (m, 1H), 3.21 – 3.13 (m, 2H), 3.07 – 3.03 (m, 1H), 2.06 – 1.92 (m, 2H), 1.91 – 1.85 (m, 2H), 1.84 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 170.3, 169.3, 142.4, 139.0, 135.7, 129.7, 129.5, 128.9 (q, J = 31.5 Hz), 128.8, 127.5, 127.1, 125.3 (q, J = 3.8 Hz), 124.3 (q, J = 272.2 Hz), 54.1, 49.4, 46.1, 41.7, 26.2, 24.7, 23.4. ^{19}F NMR (470 MHz, CDCl_3) δ -62.42. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{22}\text{H}_{24}\text{F}_3\text{N}_2\text{O}_2^+$: 405.1784. Found 405.1790.



N-(1-(2-(pyrrolidine-1-carbonyl) phenyl)-2-(p-tolyl)ethyl)acetamide (52): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), 1-methyl-4-vinylbenzene (71 mg, 0.600 mmol, 2.00 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 70 °C. The product was then purified by silica gel chromatography using a 25:75 mixture of acetone: hexanes as the eluent to afford the product **52** (58.0 mg, 55% yield) as a colorless oil. IR (neat): 3288 (br), 2976, 1610, 1599, 1431, 748, 729 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.27 (m, 2H), 7.25 – 7.23 (m, 2H), 7.11 – 6.92 (m, 5H), 5.27 – 5.22 (m, 1H), 3.74 – 3.64 (m, 2H), 3.32 – 3.28 (m, 1H), 3.18 – 3.14 (m, 1H), 3.11 – 3.07 (m,

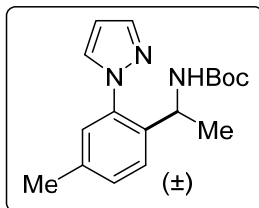
1H), 2.98 – 2.94 (m, 1H), 2.27 (s, 3H), 2.04 – 1.92 (m, 2H), 1.89 – 1.83 (m, 2H), 1.86 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 170.4, 169.3, 139.4, 136.1, 135.8, 134.9, 129.5, 129.1, 129.04, 129.0, 127.2, 127.0, 54.3, 49.3, 46.0, 41.5, 26.2, 24.7, 23.5, 21.1. HRMS (ESI/[M+H]⁺) calcd. for C₂₂H₂₇N₂O₂⁺: 351.2067. Found 351.2049.



(±) *tert*-butyl (1-(4-methyl-2-(pyridin-2-yl)phenyl)ethyl)carbamate (53): Derived from (*m*-tolyl)pyridine (50.8 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 3 minutes using a balloon of ethylene with a needle and an exit needle pierced through the vial cap. The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 15:85 mixture of ethyl acetate: hexanes as the eluent to afford the product **53** (61.3 mg, 65% yield) as a colorless oil. IR (neat): 2975, 2928, 1685, 1391, 1052 cm⁻¹; ¹H NMR (600 MHz, CD₃OD) δ 8.60 (d, *J* = 4.3 Hz, 1H), 7.94 – 7.84 (m, 1H), 7.64 (d, *J* = 6.7 Hz, 1H), 7.45 – 7.35 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 1H), 7.09 (s, 1H), 4.82 (q, *J* = 6.9 Hz, 1H), 2.35 (s, 3H), 1.38 (s, 9H), 1.22 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CD₃OD) δ 159.3, 155.8, 148.3, 139.6, 138.8, 137.0, 136.2, 129.9, 129.3, 125.3, 124.8, 122.2, 78.4, 46.6, 27.4, 21.6, 19.6. HRMS (ESI/[M+H]⁺) calcd. for C₁₉H₂₅N₂O₂⁺: 313.1911. Found 313.1916.

For reaction conducted using a Parr reactor, a different procedure was used: In a N₂-filled glovebox, a 2-5 mL microwave vial was charged with [Cp*RhCl₂]₂ (9.27 mg, 0.015 mmol, 0.050 equiv) and AgSbF₆ (21 mg, 0.06 mmol, 0.20 equiv). 1,2-Dichloroethane (1.5 mL, 0.2 M) was added followed by 2-(*m*-tolyl)pyridine (50.8 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The vial was uncapped just prior to placing into the Parr reactor equipped with a pressure gauge. The reactor was sealed and flushed with ethylene three times before being pressurized to 150 psi of ethylene. After stirring at room temperature for 20 h, the pressure was released, and the microwave vial was taken out from the reactor. The reaction mixture was filtered through a small celite plug (1 cm long in a pipette) eluting with ethyl acetate and

concentrated. The product was then purified by silica gel chromatography using a 10:90 mixture of ethyl acetate: hexanes as the eluent to afford the product **53** (64.0 mg, 68% yield) as a colorless oil. The spectroscopic data matches with that of the above conditions.

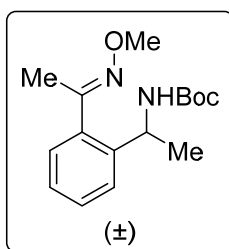


(±) *tert*-Butyl (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)ethyl)carbamate (54**):** Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 3 minutes using a balloon of ethylene with a needle and an exit needle pierced through the vial cap. The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 5:95 mixture of acetone: hexanes as the eluent to afford the product **54** (71.0 mg, 78% yield) as a colorless oil. IR (neat): 2976, 2931, 2466, 1683, 1391, 1364, 1149, 1041 cm⁻¹; ¹H NMR (500 MHz, CD₃OD) δ 7.95 (s, 1H), 7.71 (d, *J* = 1.9 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.11 (s, 1H), 6.51 (t, *J* = 2.2 Hz, 1H), 4.59 – 4.55 (m, 1H), 2.36 (s, 3H), 1.39 (s, 9H), 1.20 – 1.19 (m, 3H). ¹³C NMR (126 MHz, CD₃OD) δ 157.3, 141.3, 139.7, 139.5, 139.0, 133.5, 131.3, 128.5, 127.6, 107.5, 80.1, 46.9, 28.9, 22.9, 20.9. HRMS (ESI/[M+H]⁺) calcd. for C₁₇H₂₄N₃O₂⁺: 302.1863. Found 302.1869.

For reaction conducted using a Parr reactor, a different procedure was used: In a N₂-filled glovebox, a 2-5 mL microwave vial was charged with [Cp*RhCl₂]₂ (9.27 mg, 0.015 mmol, 0.050 equiv) and AgSbF₆ (21 mg, 0.06 mmol, 0.20 equiv). 1,2-Dichloroethane (1.5 mL, 0.2 M) was added followed by 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The vial was uncapped just prior to placing into the Parr reactor equipped with a pressure gauge. The reactor was sealed and flushed with ethylene three times before being pressurized to 150 psi of ethylene. After stirring at room temperature for 20 h, the pressure was released, and the microwave vial was taken out from the reactor. The reaction mixture was filtered through a small celite plug (1 cm long in a pipette) eluting with ethyl acetate and concentrated. The product was then purified by silica gel chromatography using a

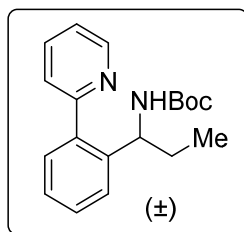
5:95 mixture of acetone: hexanes as the eluent to afford the product **54** (62.4 mg, 69% yield) as a colorless oil. The spectroscopic data matches with that of the above conditions.

For the larger 5g scale reaction conducted using a Parr reactor, the following procedure was used: In a N₂-filled glovebox, a 50 - 60 mL glass vessel (the inner part of Parr reactor) was charged with [Cp*RhCl₂]₂ (198 mg, 0.320 mmol, 0.010 equiv) and AgSbF₆ (440 mg, 1.28 mmol, 0.04 equiv). 1,2-Dichloroethane (32.0 mL, 1.0 M) was added followed by 1-(*m*-tolyl)-1*H*-pyrazole (5.06 g, 32.0 mmol, 1.00 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (10.43 g, 48.0 mmol, 1.5 equiv). The glass vessel was then equipped with an egg-shaped magnetic stir bar and taken outside the glove box. The glass vessel was placed into the Parr reactor equipped with a pressure gauge. The reactor was sealed and flushed three times with ethylene before being pressurized to 150 psi. The ethylene inlet remained attached and a positive flow of ethylene was maintained from the cylinder throughout the reaction. After stirring at room temperature for 20 h, the flow of ethylene was stopped, and the inlet was detached. Then the pressure was released from the reactor, and the glass vessel was taken out. The reaction mixture was filtered through a celite plug (fritted-funnel) eluting with ethyl acetate and concentrated. The product was then purified by silica gel chromatography using a 15:85 mixture of ethyl acetate: hexanes as the eluent to afford the product **54** (6.56 g, 68% yield) as a colorless oil. The spectroscopic data matches with that of the above conditions.

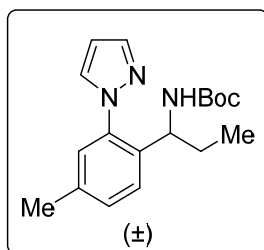


(±) *tert*-Butyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)ethyl)carbamate (55**):** Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 3 minutes using a balloon of ethylene with a needle and an exit needle pierced through the vial cap. NaHCO₃ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 10:90 mixture of ethyl acetate: hexanes with 1% Et₃N as the eluent to afford the product **55** (55.0 mg, 63% yield) as a colorless oil. IR (neat): 3355 (br), 2972, 2934,

2817, 1698, 1365, 1168, 1042, 758 cm^{-1} ; ^1H NMR (600 MHz, CD_3OD) δ 7.45 (d, $J = 7.8$ Hz, 1H), 7.35 (t, $J = 7.6$ Hz, 1H), 7.26 (t, $J = 7.4$ Hz, 1H), 7.19 (d, $J = 7.2$ Hz, 1H), 4.90 (q, $J = 6.7$ Hz, 1H), 3.93 (s, 3H), 2.24 (s, 3H), 1.45 – 1.23 (m, 3H), 1.40 (s, 9H). ^{13}C NMR (151 MHz, CD_3OD) δ 158.4, 157.3, 144.4, 137.3, 129.9, 129.3, 127.8, 126.9, 79.9, 62.0, 48.5, 28.8, 23.3, 16.9. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{16}\text{H}_{25}\text{N}_2\text{O}_3^+$: 293.1860. Found 293.1865.

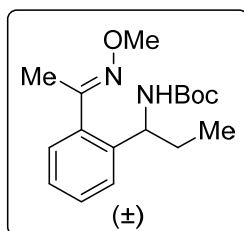


(±) **tert-Butyl (1-(2-(pyridin-2-yl)phenyl)propyl)carbamate (56)**: Derived from 2-phenylpyridine (46.6 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 3 minutes using a balloon of propylene with a needle and an exit needle pierced through the vial cap. The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a gradient up to 10:90 mixture of ethyl acetate: hexanes as the eluent to afford the product **56** (62.9 mg, 67% yield) as a colorless oil. IR (neat): 2971, 2931, 2459, 1682, 1392, 1363, 1157, 989 cm^{-1} ; ^1H NMR (500 MHz, CD_3OD) δ 8.61 (d, $J = 5.0$ Hz, 1H), 7.91 (t, $J = 7.4$ Hz, 1H), 7.71 (d, $J = 7.8$ Hz, 1H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.44 – 7.40 (m, 2H), 7.35 – 7.28 (m, 2H), 4.67 – 4.65 (m, 1H), 1.63 – 1.51 (m, 2H), 1.40 (broad s, 9H), 0.76 – 0.70 (m, 3H). ^{13}C NMR (126 MHz, CD_3OD) δ 160.7, 157.9, 149.9, 143.3, 140.8, 138.5, 131.0, 130.1, 128.0, 127.3, 126.5, 123.8, 80.0, 54.5, 31.2, 28.9, 11.6. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{19}\text{H}_{25}\text{N}_2\text{O}_2^+$: 313.1911. Found 313.1916.



(±) **tert-Butyl (1-(4-methyl-2-(1H-pyrazol-1-yl)phenyl)propyl)carbamate (57)**: Derived from 1-(*m*-tolyl)pyrazole (47.5 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for

3 minutes using a balloon of propylene with a needle and an exit needle pierced through the vial cap. The reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 10:90 mixture of ethyl acetate: toluene. Additional impurities were removed by prep plate (10:90 mixture of ethyl acetate: hexanes as eluent, ran up 3 times) to afford the product **57** (52.0 mg, 55% yield) as a colorless oil. IR (neat): 3303 (br), 3314, 2971, 2930, 2874, 1698, 1516, 1243, 1167, 752, 731 cm^{-1} ; ^1H NMR (600 MHz, CD_3OD) δ 8.01 (s, 1H), 7.71 (s, 1H), 7.39 (d, $J = 7.9$ Hz, 1H), 7.29 (d, $J = 7.9$ Hz, 1H), 7.11 (s, 1H), 6.52 (t, $J = 2.2$ Hz, 1H), 4.44 – 4.30 (m, 1H), 2.37 (s, 3H), 1.53 – 1.46 (m, 2H), 1.45 – 1.27 (broad s, 9H), 0.72 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 156.3, 139.8, 138.3, 137.5, 137.2, 132.1, 129.7, 127.0, 126.6, 106.0, 78.5, 51.6, 29.2, 27.4, 19.4, 10.0. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{18}\text{H}_{26}\text{N}_3\text{O}_2^+$: 316.2020. Found 316.2049.



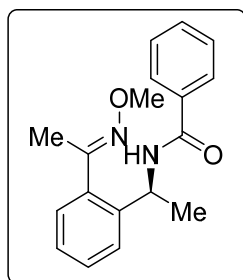
(±) *tert*-Butyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)propyl)carbamate (58): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 3 minutes using a balloon of propylene with a needle and an exit needle pierced through the vial cap. NaHCO_3 (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes with 1% Et_3N . Additional impurities were removed by prep plate (10:90 mixture of ethyl acetate: hexanes as eluent, ran up 3 times) to afford the product **58** (54.0 mg, 59% yield) as a colorless oil. IR (neat): 3336 (br), 2972, 2934, 1698, 1365, 1170, 1047, 883, 759 cm^{-1} ; ^1H NMR (600 MHz, CD_3OD) δ 7.40 (d, $J = 7.8$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.26 (t, $J = 7.3$ Hz, 1H), 7.20 (d, $J = 7.4$ Hz, 1H), 4.70 – 4.66 (m, 1H), 3.93 (s, 3H), 2.24 (s, 3H), 1.82 – 1.74 (m, 1H), 1.67 – 1.56 (m, 1H), 1.46 – 1.27 (broad s, 9H), 1.03 – 0.87 (m, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 158.4, 157.8, 143.6, 137.5, 129.8, 129.3, 127.8, 127.4, 79.9, 62.0, 54.7, 31.2, 28.8, 17.0, 11.5. HRMS (ESI/[$\text{M}+\text{H}$] $^+$) calcd. for $\text{C}_{17}\text{H}_{27}\text{N}_2\text{O}_3^+$: 307.2016. Found 307.2027.

4. Asymmetric α -Branched Amine Synthesis and Chiral HPLC Data

General Procedure:

In a N₂-filled glove box, a 2–5 mL microwave vial was charged with precatalyst **59** (3.8 mg, 0.0025 mmol, 0.050 equiv), AgB(C₆F₅)₄ (21 mg, 0.020 mmol, 0.40 equiv, 75 w%), and, if indicated, NaHCO₃ (4 mg, 0.3 mmol, 1 equiv). 1,2-Dichloroethane (0.25 mL, 0.2 M) was added followed by the indicated C–H bond substrate (0.050 mmol, 1.0 equiv) and aminating reagent (0.075 mmol, 1.50 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was sparged for 30 seconds using a balloon of ethylene with a needle and an exit needle pierced through the vial cap. The reaction mixture was then stirred at 30 °C in a preheated oil bath. After 20 h, the reaction mixture was filtered through a small celite plug, (1 cm long in a pipette), which was washed with ethyl acetate. The resulting mixture was then concentrated and purified by preparative TLC to afford the desired product.

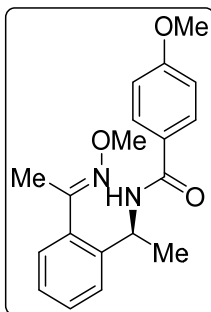
Authentic racemic products were synthesized by the same method using [Cp*RhCl₂]₂ as the precatalyst.



(*S,E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)ethyl)benzamide (60**):** Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (7.5 mg, 0.050 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (12.2 mg, 0.0750 mmol, 1.50 equiv). NaHCO₃ (4 mg, 0.3 mmol, 1 equiv) was used as an additive. The product was purified by silica gel chromatography using a 25:75 mixture of acetone: hexanes as the eluent to afford the product **60** (8.9 mg, 60% yield) as a white solid (mp: 85-87 °C). [α]_D²⁰ -112.76° (*c* = 0.1, CHCl₃). 90:10 er. (Chiralpak AD-H, 90:10 hexanes:ethanol, 1 mL/min, 250 nm, *t*_r (minor) = 6.94 min, *t*_r (major) = 12.53 min). IR (neat): 3297 (br), 2934, 1632, 1533, 1489, 1039, 884 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.37 – 7.29 (m, 3H), 7.29 – 7.26 (m, 1H), 5.47 (p, *J* = 7.0 Hz, 1H), 3.92 (s, 3H), 2.29 (s, 3H), 1.55 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 166.2, 157.8, 141.2, 136.7, 134.9, 131.5, 129.35, 129.25, 128.6, 128.4,

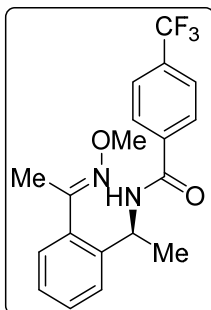
127.7, 127.1, 62.0, 49.1, 21.7, 17.1. HRMS (ESI/[M+H]⁺) calcd. for C₁₈H₂₁N₂O₂⁺: 297.1598. Found 297.1621.

For the 0.2 mmol scale reaction, the following procedure was used: In a N₂-filled glove box, a 2–5 mL microwave vial was charged with precatalyst **59** (15.2 mg, 0.0100 mmol, 0.050 equiv), AgB(C₆F₅)₄ (84 mg, 0.080 mmol, 0.40 equiv, 75 w%), and NaHCO₃ (16.8 mg, 0.2 mmol, 1 equiv). 1,2-Dichloroethane (1.0 mL, 0.2 M) was added followed by (*E*)-1-phenylethan-1-one *O*-methyl oxime (30 mg, 0.20 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (49 mg, 0.30 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was sparged for 60 seconds using a balloon of ethylene with a needle and an exit needle pierced through the vial cap. The reaction mixture was then stirred at 30 °C in a preheated oil bath. After 20 h, the reaction mixture was filtered through a small celite plug, (1 cm long in a pipette), which was washed with ethyl acetate. The resulting mixture was then concentrated and purified by silica gel chromatography using a 25:75 mixture of acetone: hexanes as the eluent to afford the product **60** (36.7 mg, 62% yield) as a white solid. 89:11 er. (Chiralpak AD-H, 90:10 hexanes:ethanol, 1 mL/min, 250 nm, t_r (minor) = 7.29 min, t_r (major) = 13.79 min). The spectroscopic data matches with that of the above conditions.



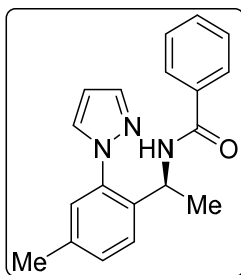
(*S,E*)-4-Methoxy-*N*-(1-(2-(1-(methoxyimino)ethyl)phenyl)ethyl)benzamide (61**):** Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (7.5 mg, 0.050 mmol, 1.0 equiv) and 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (14.5 mg, 0.0750 mmol, 1.50 equiv). NaHCO₃ (4 mg, 0.3 mmol, 1 equiv) was used as an additive. The product was purified by silica gel chromatography using a 25:75 mixture of acetone: hexanes as the eluent to afford the product **61** (9.7 mg, 59% yield) as a white solid (mp: 120-121 °C). [α]_D²⁰ -37.12° (*c* = 0.1, CHCl₃). 92:8 er. (Chiralpak AD-H, 90:10 hexanes:ethanol, 1 mL/min, 250 nm, t_r (minor) = 12.12 min, t_r (major) = 30.45 min). IR (neat): 3254 (br), 2964, 2933, 1623, 1605, 1504, 1254, 1041 cm⁻¹; ¹H

NMR (600 MHz, CDCl₃) δ 7.75 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 7.5 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.28 – 7.25 (m, 2H), 6.93 – 6.86 (m, 2H), 5.45 (p, J = 7.0 Hz, 1H), 3.93 (s, 3H), 3.83 (s, 3H), 2.29 (s, 3H), 1.54 (d, J = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.8, 162.2, 157.9, 141.4, 136.7, 129.3, 129.2, 128.9, 128.3, 127.6, 127.2, 113.7, 62.0, 55.5, 49.0, 21.8, 17.2. HRMS (ESI/[M+H]⁺) calcd. for C₁₉H₂₃N₂O₃⁺: 327.1703. Found 327.1710.



(*S,E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)ethyl)-4-(trifluoromethyl)benzamide (62**):**

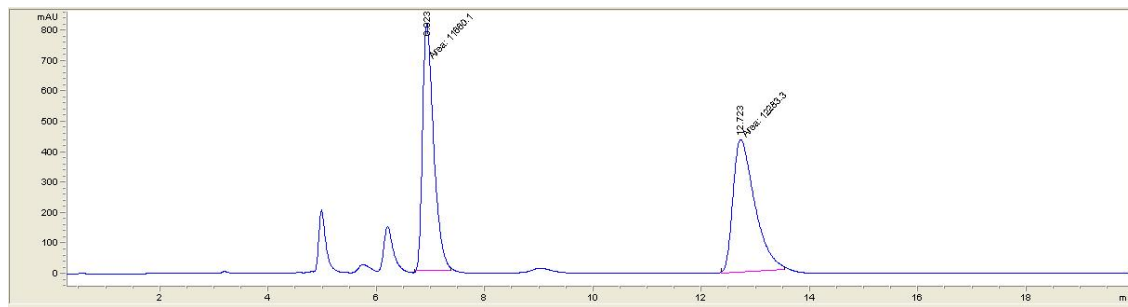
Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (7.5 mg, 0.050 mmol, 1.0 equiv) and 3-[4-(trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (17.3 mg, 0.0750 mmol, 1.50 equiv). NaHCO₃ (4 mg, 0.3 mmol, 1 equiv) was used as an additive. The product was purified by silica gel chromatography using a 25:75 mixture of acetone: hexanes as the eluent to afford the product **62** (10.7 mg, 59% yield) as a white solid (mp: 130-132 °C). [α]_D²⁰ -62.72° (c = 0.1, CHCl₃). 91:9 er. (Chiralpak AD-H, 90:10 hexanes:ethanol, 1 mL/min, 250 nm, t_r (minor) = 5.95 min, t_r (major) = 11.84 min). IR (neat): 3314, 2960, 2932, 1635, 1547, 1330, 1311, 1133, 1065, 1044, 1016 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.89 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.59 (d, J = 7.8 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 5.49 (p, J = 7.1 Hz, 1H), 3.91 (s, 3H), 2.29 (s, 3H), 1.55 (d, J = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 164.8, 158.1, 140.7, 138.3, 136.7, 133.2 (q, J = 32.5 Hz), 129.5, 129.4, 128.8, 127.9, 127.7, 125.6 (q, J = 3.8 Hz), 123.8 (q, J = 272.5 Hz), 62.0, 49.6, 21.4, 17.2. ¹⁹F NMR (471 MHz, CDCl₃) δ -62.92. HRMS (ESI/[M+H]⁺) calcd. for C₁₉H₂₀F₃N₂O₂⁺: 365.1471. Found 365.1490.



(S)-N-(1-(4-Methyl-2-(1H-pyrazol-1-yl)phenyl)ethyl)benzamide (63): Derived from 1-(*m*-tolyl)pyrazole (7.9 mg, 0.050 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (12.2 mg, 0.0750 mmol, 1.50 equiv). The product was purified by silica gel chromatography using a 25:75 mixture of acetone: hexanes as the eluent to afford the product **63** (10.9 mg, 71% yield) as a viscous oil. $[\alpha]_D^{20}$ -125.56° ($c = 0.1$, CHCl₃). 86:14 er. (Chiralpak AD-H, 90:10 hexanes:ethanol, 1 mL/min, 250 nm, t_r (minor) = 10.16 min, t_r (major) = 15.22 min). IR (neat): 3305 (br), 2974, 2932, 1636, 1516, 1488, 1044 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 8.56 (d, $J = 7.5$ Hz, 1H), 7.87 (d, $J = 7.6$ Hz, 2H), 7.79 (s, 1H), 7.76 (s, 1H), 7.50 – 7.40 (m, 4H), 7.21 (d, $J = 7.8$ Hz, 1H), 7.12 (s, 1H), 6.50 (t, $J = 2.1$ Hz, 1H), 5.43 (p, $J = 7.2$ Hz, 1H), 2.38 (s, 3H), 1.06 (d, $J = 7.1$ Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 165.9, 140.6, 139.0, 138.7, 135.6, 134.8, 131.7, 131.3, 130.7, 130.0, 128.5, 127.9, 127.2, 107.2, 48.7, 20.9, 20.1. HRMS (ESI/[M+H]⁺) calcd. for C₁₉H₂₀N₃O⁺: 306.1601. Found 306.1611.

HPLC traces:

Racemic **60** (Chiralpak AD-H, 90:10 hexanes:ethanol, 1 mL/min, 250 nm):

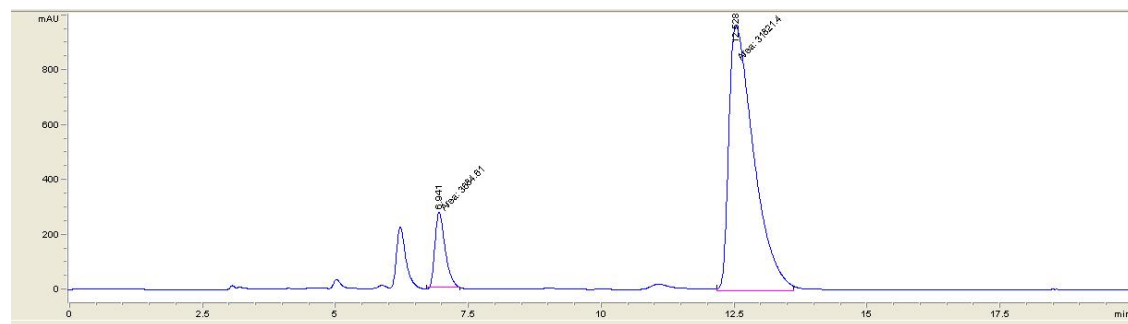


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.923	MM	0.2392	1.16601e4	812.43781	48.6986
2	12.723	MM	0.4677	1.22833e4	437.74887	51.3014

Totals : 2.39435e4 1250.18668

Enantiomerically enriched **60** (90:10 er):

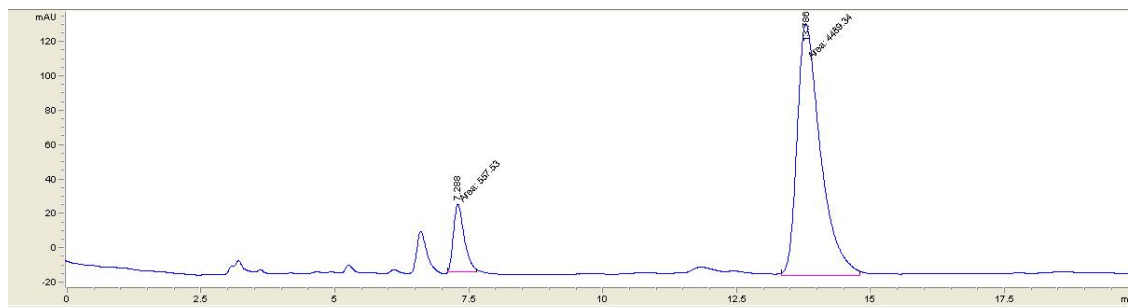


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.941	MM	0.2237	3684.60840	274.56967	10.3774
2	12.528	MM	0.5486	3.18214e4	966.76239	89.6226

Totals : 3.55060e4 1241.33206

Enantiomerically enriched **60**, 0.2 mmol scale (89:11 er):

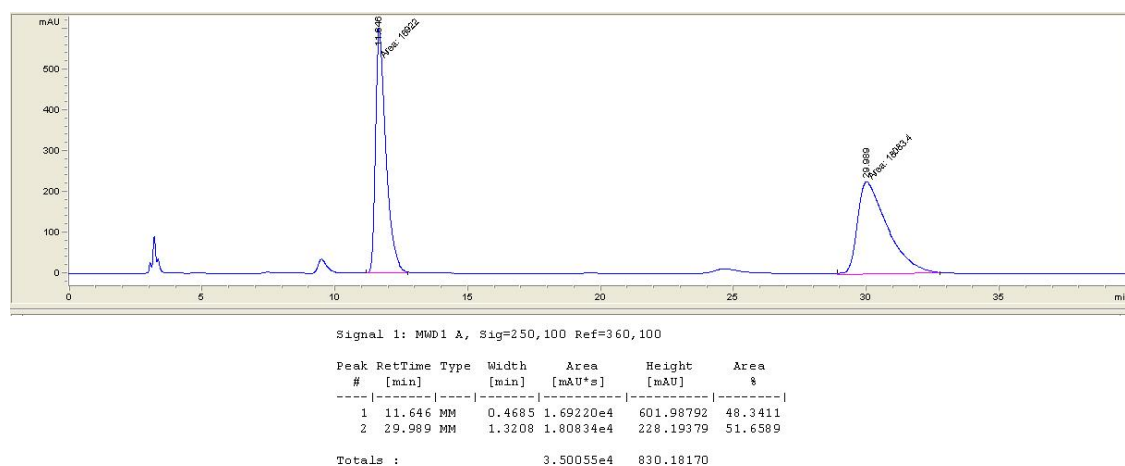


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

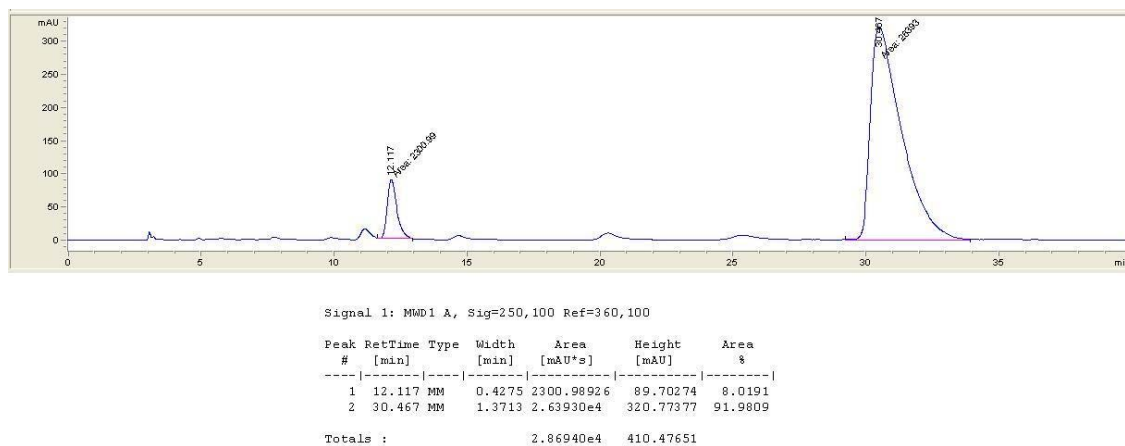
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.288	MM	0.2353	557.53033	39.49524	11.0470
2	13.786	MM	0.5102	4489.34131	146.66486	88.9530

Totals : 5046.87164 186.16010

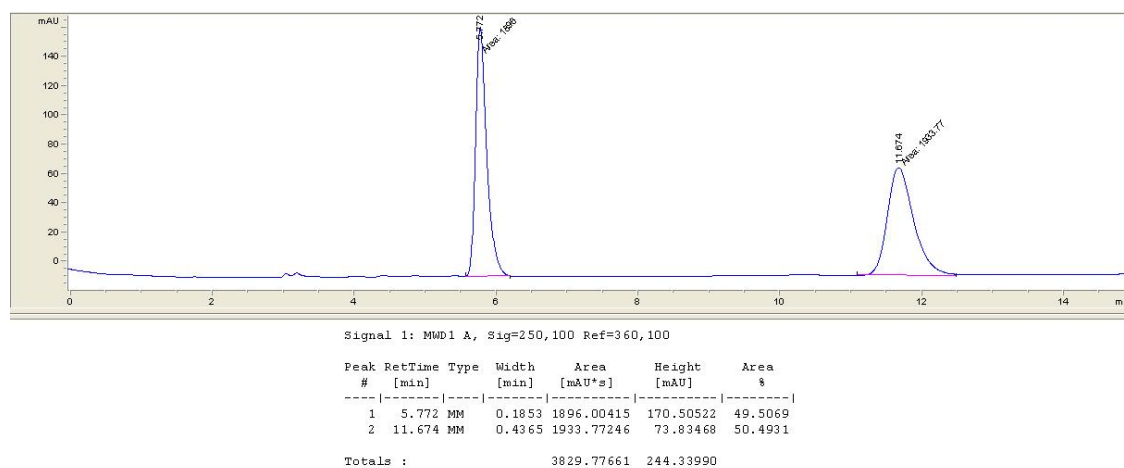
Racemic **61** (Chiralpak AD-H, 90:10 hexanes:ethanol, 1 mL/min, 250 nm):



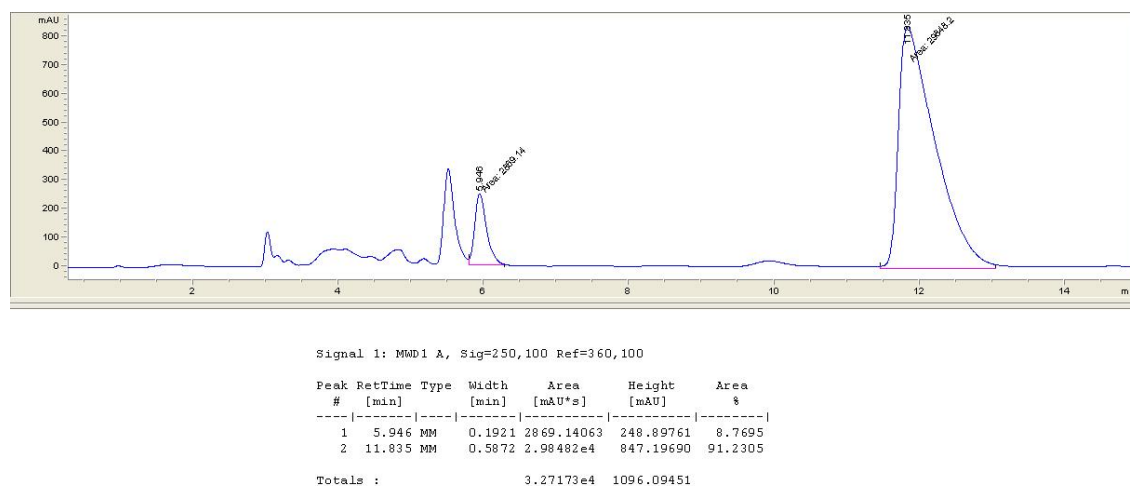
Enantiomerically enriched **61** (92:8 er):



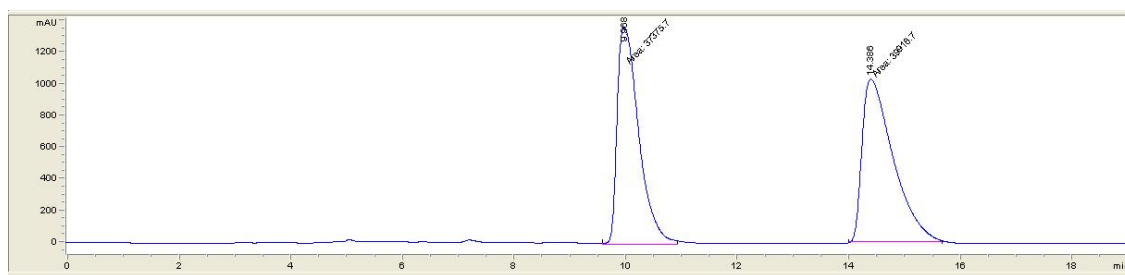
Racemic **62** (Chiralpak AD-H, 90:10 hexanes:ethanol, 1 mL/min, 250 nm):



Enantiomerically enriched **62** (91:9 er):



Racemic **63** (Chiralpak AD-H, 90:10 hexanes:ethanol, 1 mL/min, 250 nm):

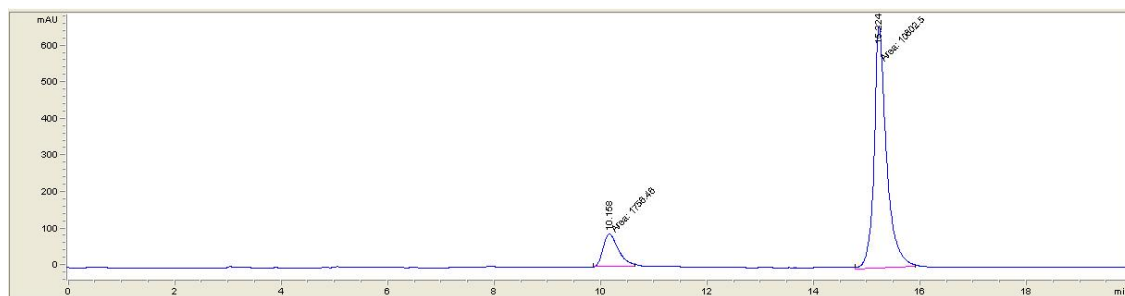


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.968	MM	0.4534	3.73757e4	1373.82690	48.3562
2	14.386	MM	0.6468	3.99167e4	1028.55457	51.6438

Totals : 7.72924e4 2402.38147

Enantiomerically enriched **63** (86:14 er):



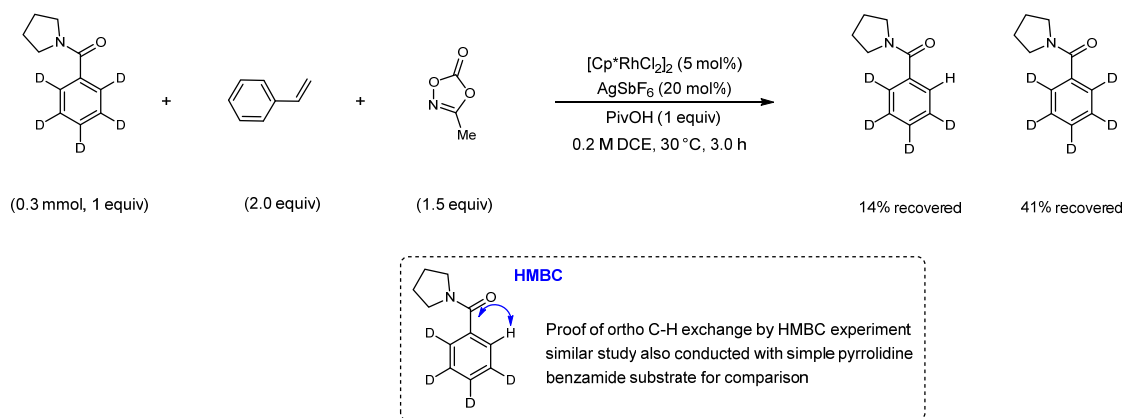
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.158	MM	0.3320	1756.46082	88.18140	13.9857
2	15.224	MM	0.2717	1.08025e4	662.58154	86.0143

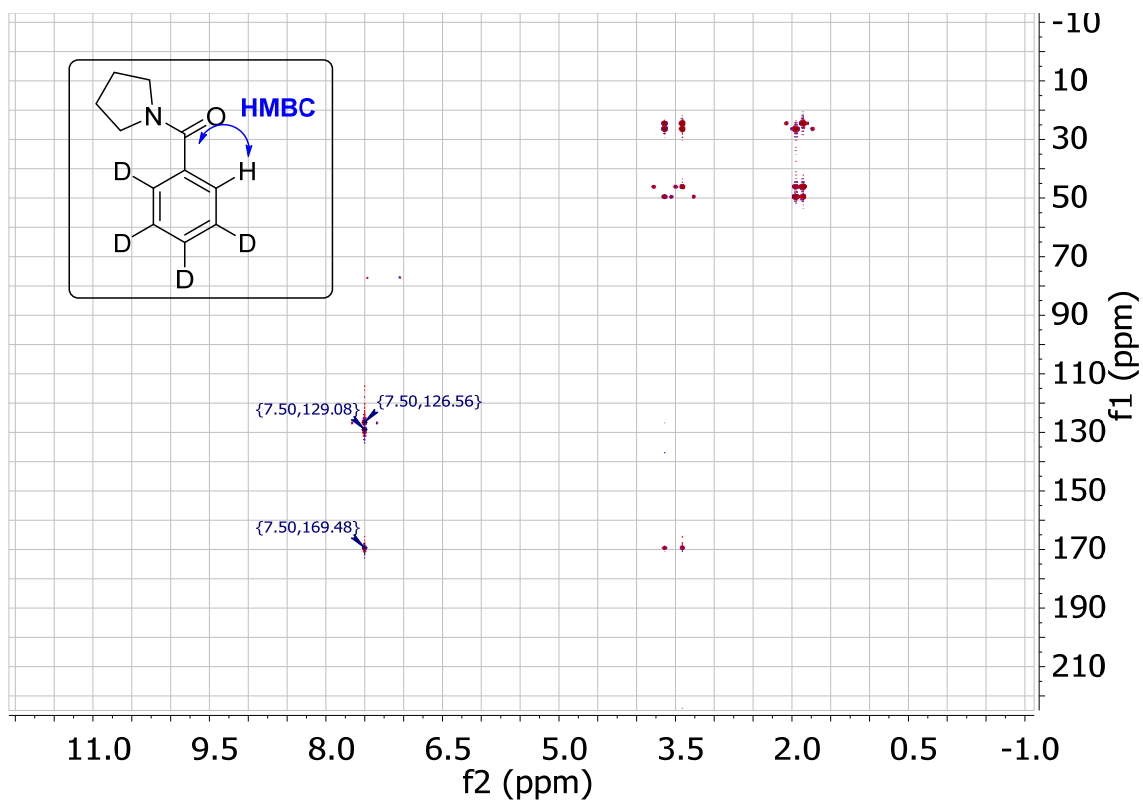
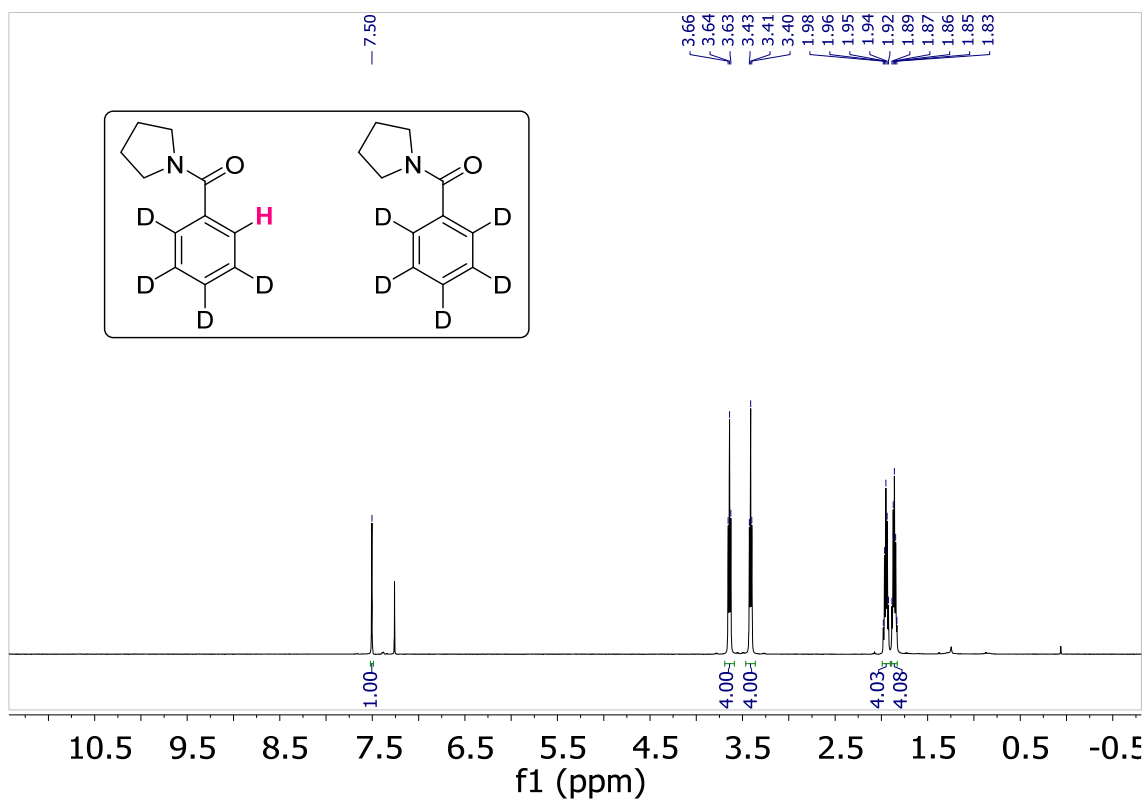
Totals : 1.25590e4 750.76295

5. Mechanistic Experiments

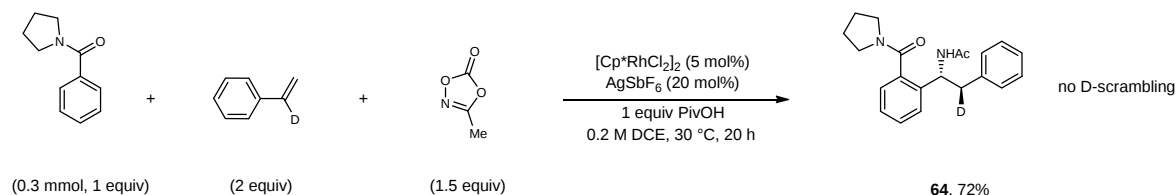
Supplementary Figure 2. Reversibility of C–H bond activation step.



In order to investigate the reversibility of the C–H bond activation step, studies were conducted with (phenyl- d_5)(pyrrolidin-1-yl)methanone. In a N_2 -filled glove box, a 2–5 mL microwave vial was charged with $[\text{Cp}^*\text{RhCl}_2]_2$ (9.3 mg, 0.015 mmol, 0.050 equiv), AgSbF_6 (21 mg, 0.060 mmol, 0.20 equiv), and pivalic acid (30 mg, 0.30 mmol, 1 equiv). 1,2-Dichloroethane (1.5 mL, 0.2 M) was added followed by the (phenyl- d_5)(pyrrolidin-1-yl)methanone substrate (54.1 mg, 0.300 mmol, 1.0 equiv), styrene (62.0 mg, 0.600 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45.0 mg, 0.450 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was then stirred at 30 °C in a preheated oil bath. After 3 h, the reaction mixture was filtered through a small celite plug, (1 cm long in a pipette), and washed with ethyl acetate. The NMR yield (15%) of the α -branched amine product was determined relative to trimethoxybenzene as an external standard. The material was purified by silica gel chromatography. The starting material C–H bond substrate was recovered as a colorless oil (30.0 mg corresponding to 55% recovery). The ^1H NMR spectrum of the recovered starting material was taken in CDCl_3 to ascertain the amount of H/D exchange. Approximately 25% H/D exchange at the ortho positions was observed by ^1H NMR, indicating reversible C–H activation. The site of H/D exchange was further confirmed by HMBC experiments of the recovered C–H bond starting material mixture in CDCl_3 solvent. The spectra are shown below.



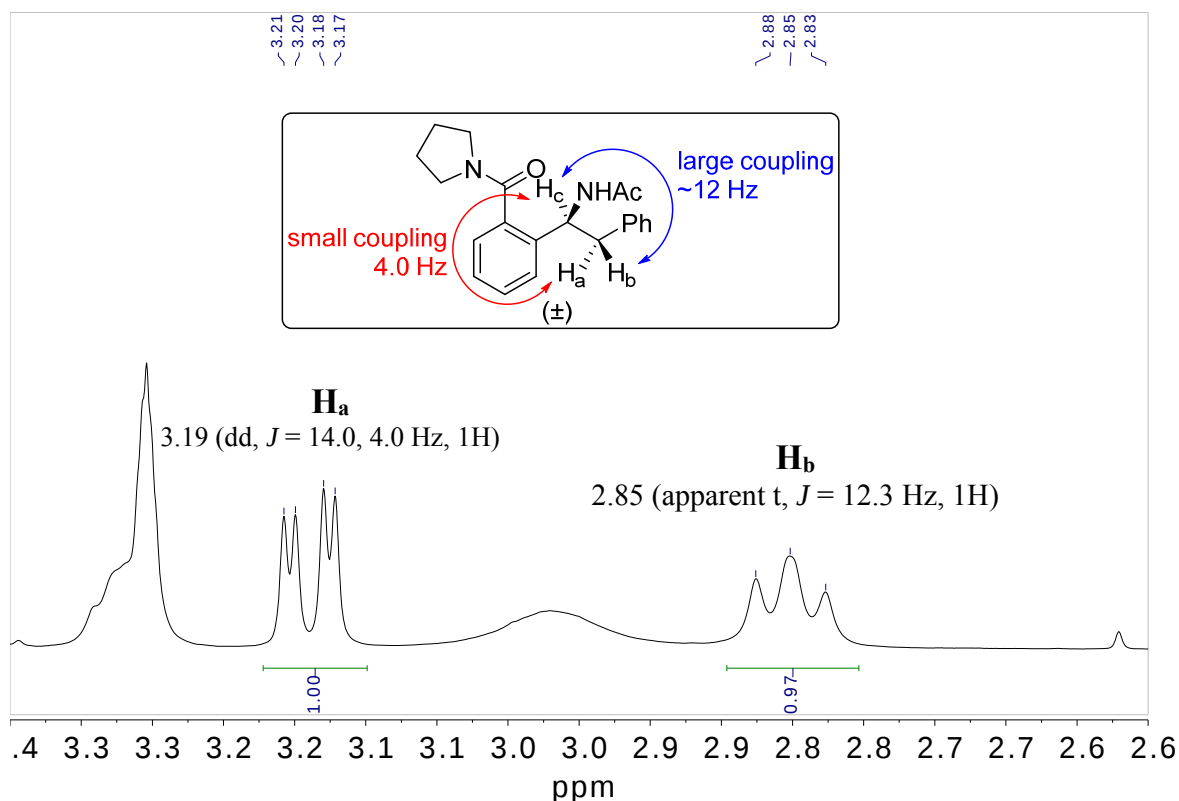
Supplementary Figure 3. Stereospecificity of β -H re-insertion step with α -deuterostyrene.



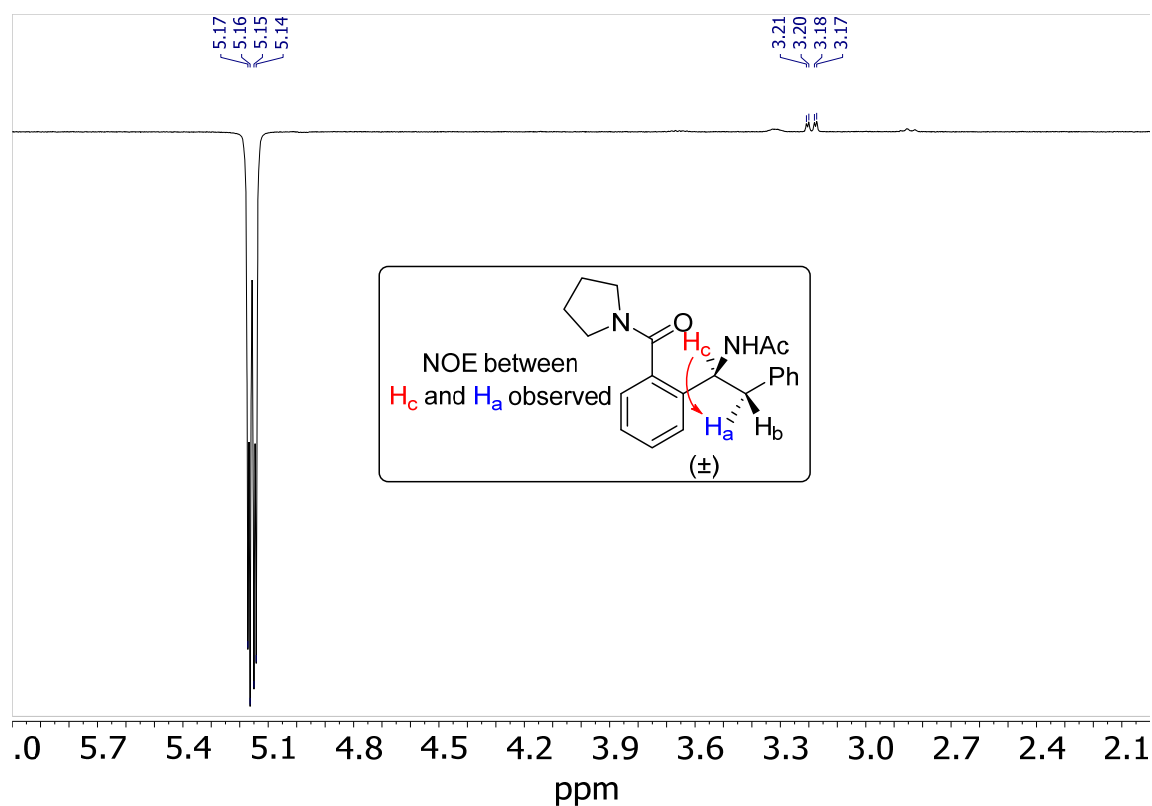
In a N₂-filled glove box, a 2–5 mL microwave vial was charged with [Cp*RhCl₂]₂ (9.3 mg, 0.015 mmol, 0.050 equiv), AgSbF₆ (21 mg, 0.060 mmol, 0.20 equiv), and PivOH (30 mg, 0.30 mmol, 1 equiv). 1,2-Dichloroethane (1.5 mL, 0.2 M) was added followed by the phenyl(pyrrolidin-1-yl) methanone (52.6 mg, 0.300 mmol, 1.0 equiv), α -deuterostyrene (63.1 mg, 0.600 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45.0 mg, 0.450 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was then stirred at 30 °C in a preheated oil bath. After 20 h, the reaction mixture was filtered through a small celite plug (1 cm long in a pipette), and washed with ethyl acetate. The material was concentrated and purified by silica gel chromatography with a 20:80 mixture of acetone: hexane as the eluent to afford the product **64** (73.0 mg, 72% yield) as a colorless oil. IR (neat): 3316 (br), 2922, 1601, 1429, 1288, 767 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.27 (d, J = 3.3 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.17 – 7.13 (m, 3H), 7.08 (broad s, 1H), 5.26 (t, J = 8.5 Hz, 1H), 3.74 – 3.64 (m, 2H), 3.32 – 3.27 (m, 1H), 3.18 – 3.12 (m, 1H), 2.97 (d, J = 9.0 Hz, 1H), 2.05 – 1.99 (m, 1H), 1.97 – 1.91 (m, 1H), 1.90 – 1.85 (m, 2H), 1.84 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 170.3, 169.2, 139.4, 138.1, 135.8, 129.5, 129.1, 128.8, 128.4, 127.2, 126.9, 126.5, 54.2, 49.3, 45.9, 41.7, 41.6, 41.4, 26.2, 24.6, 23.4. HRMS (ESI/[M+H]⁺) calcd. for C₂₁H₂₄DN₂O₂⁺: 338.1973. Found 338.1953. NMR analysis of the isolated product clearly indicated that no H/D scrambling had occurred.

The relative stereochemistry for deuterium incorporation for **64** was determined by comparing the data for the ^1H and 1D NOE NMR experiments for the proteo **27** and deuterio **64** in CD_3OD .

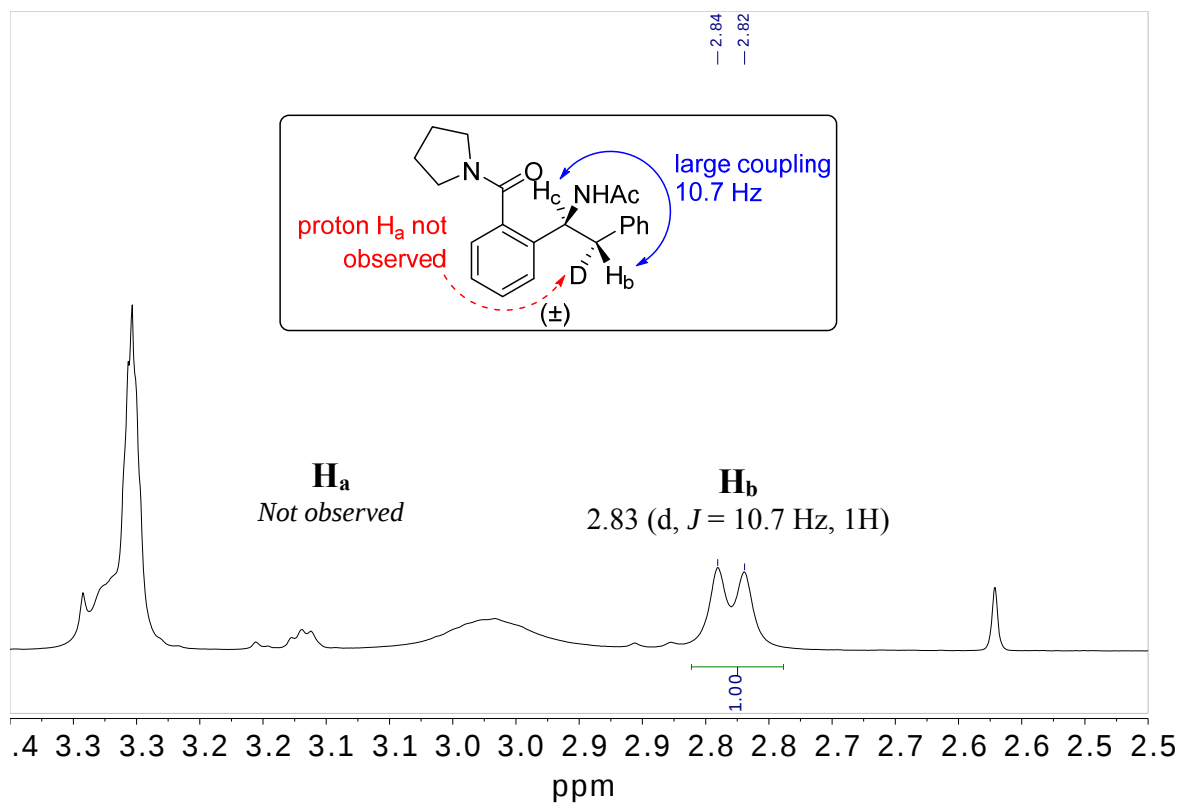
Assignment of the diastereotopic methylene protons **H_a** and **H_b** in proteo product **27**: Protons **H_a** and **H_b** are found at 3.19 ppm (dd, $J = 14.0, 4.0$ Hz, 1H) and 2.85 ppm (apparent t, $J = 12.3$ Hz, 1H) in CD_3OD , respectively. Proton **H_a** has a large geminal coupling to **H_b** (14.0 Hz) and a small vicinal coupling (4.0 Hz) to the proton alpha to the nitrogen (**H_c**); this small coupling of 4.0 Hz indicates a small dihedral angle (approximately 60° based on the Karplus equation). Proton **H_b** has a large geminal coupling to **H_a** (~ 10 -14 Hz) and a large vicinal coupling (~ 10 -14 Hz) to **H_c** indicating a larger dihedral angle (closer to 180° based on the Karplus equation). These data support the assignment of **H_a** having a syn relationship with **H_c**, and **H_b** having an anti-relationship with **H_c**.



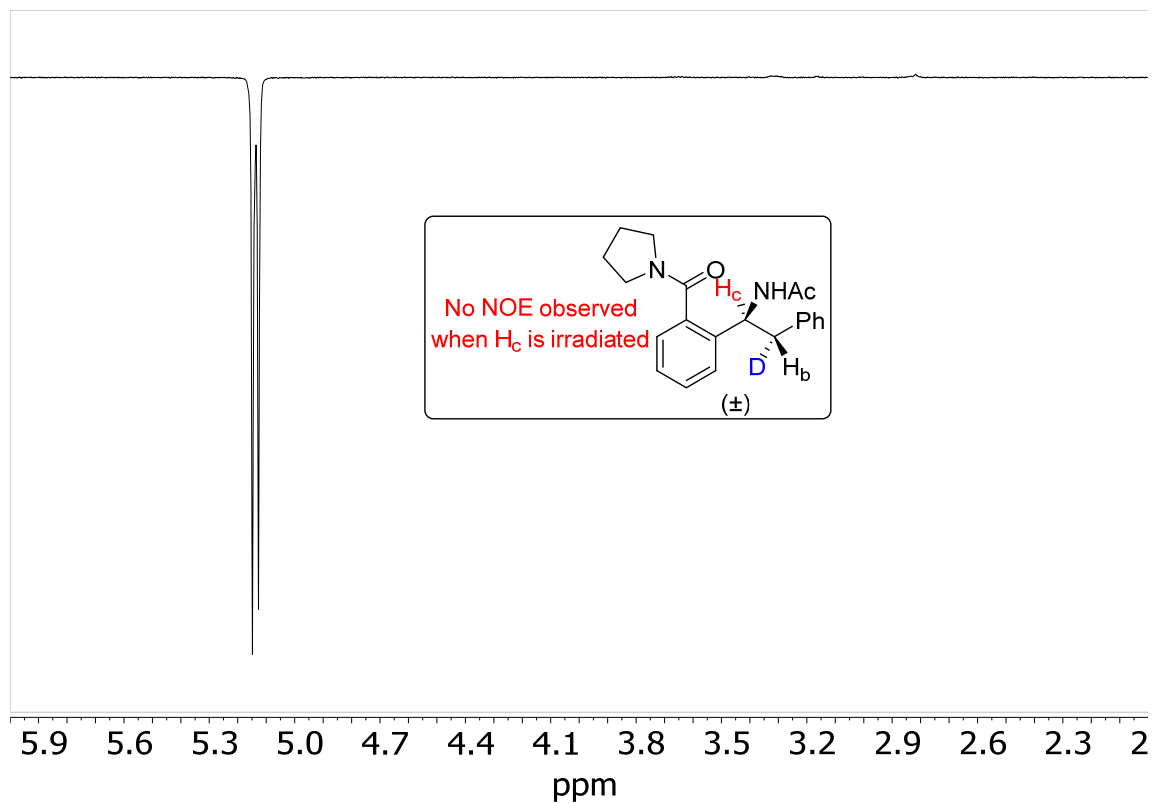
The assignment of **H_a** and **H_b** is further supported by 1D NOE NMR experiments of proteo product **27**: When proton **H_c** (5.16 ppm, dd, *J* = 10.6, 4.1 Hz, 1H) is selected in the 1D NOE experiment, an NOE is observed exclusively to proton **H_a** (3.19 ppm). Additional 1D NOE NMR data showing an NOE between **H_a** and **H_b** are included in the NMR data section.



The ^1H spectra for deuterio product **64** confirm the stereospecific incorporation of D at the H_a site: Proton H_a was not observed in the deuterio product **64** and proton H_b was found at 2.83 ppm (d, $J = 10.7$ Hz, 1H). This indicates that proton H_a was replaced with a deuterium.

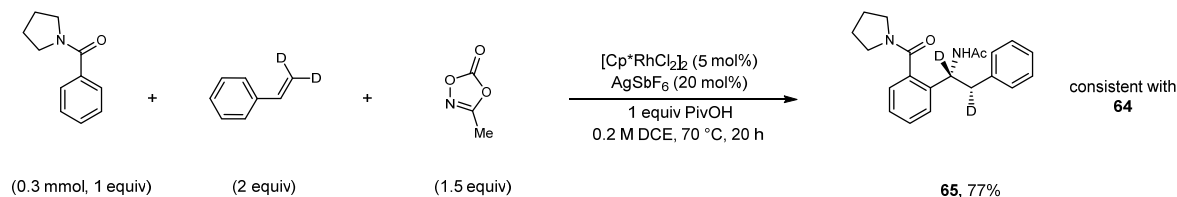


1D NOE NMR experiments for deuterio product **64** further confirm the stereospecific incorporation of D at the **H_a** site: When proton **H_c** (5.14 ppm, d, *J* = 10.6 Hz, 1H) is selected in the 1D NOE experiment, no NOE is observed. Additional 1D NOE NMR data are included in the NMR data section.



In summary, these NMR experiments indicate that the rhodium-hydride undergoes a *syn*-addition, resulting in the deuterio product **64** having an *anti*-relationship between the -NHAc and D groups.

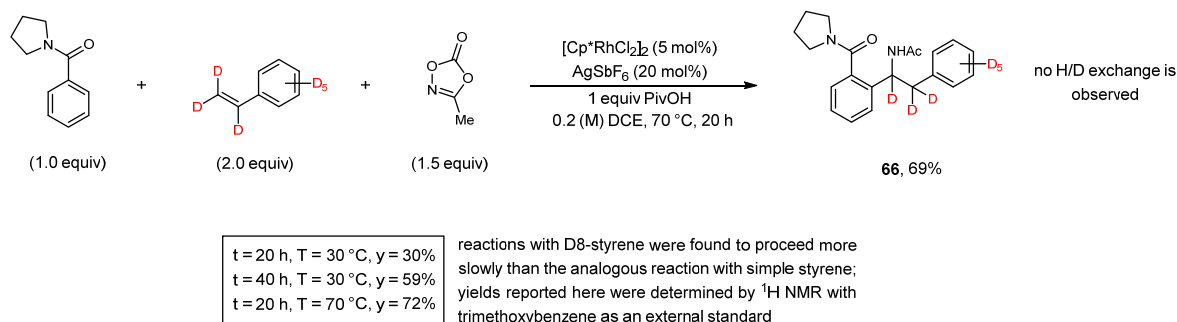
Supplementary Figure 4. Stereospecificity of β -H re-insertion step confirmed with β,β -di-deuterostyrene.



In a N_2 -filled glove box, a 2–5 mL microwave vial was charged with $[\text{Cp}^*\text{RhCl}_2]_2$ (9.3 mg, 0.015 mmol, 0.050 equiv), AgSbF_6 (21 mg, 0.060 mmol, 0.20 equiv), and PivOH (30 mg, 0.30 mmol, 1 equiv). 1,2-Dichloroethane (1.5 mL, 0.2 M) was added followed by the phenyl(pyrrolidin-1-yl) methanone (52.6 mg, 0.300 mmol, 1.0 equiv), β,β -di-deuterostyrene (63.7 mg, 0.600 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45.0 mg, 0.450 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was then stirred at 70 °C in a preheated oil bath. After 20 h, the reaction mixture was filtered through a small celite plug (1 cm long in a pipette) and washed with ethyl acetate. The material was concentrated and purified by silica gel chromatography with a 20:80 mixture of acetone: hexane as the eluent to afford the product **65** (78.0 mg, 77% yield) as a colorless oil. IR (neat): 3314 (br), 2920, 1600, 1429, 1287, 767 cm^{-1} ; ^1H NMR (500 MHz, CD_3OD) δ 7.55 (d, $J = 7.8$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 7.7$ Hz, 1H), 7.28 (d, $J = 7.4$ Hz, 2H), 7.24 (t, $J = 7.5$ Hz, 3H), 7.16 (t, $J = 7.1$ Hz, 1H), 3.71 – 3.60 (m, 2H), 3.34 – 3.30 (m, 1H), 3.18 (s, 1H) [**corresponds to H_a in spectra for **27****], 3.02 (broad s, 1H), 2.03 – 1.97 (m, 1H), 1.95 – 1.91 (m, 1H), 1.90 – 1.83 (m, 2H), 1.81 (s, 3H). ^{13}C NMR (126 MHz, CD_3OD) δ 172.4, 171.5, 140.1, 137.7, 130.8, 130.3, 129.4, 128.6, 127.7, 127.6, 127.1, 54.2, 53.8, 50.1, 47.0, 43.2, 43.1, 42.9, 26.9, 25.7, 22.6. HRMS (ESI/ $[\text{M}+\text{H}]^+$) calcd. for $\text{C}_{21}\text{H}_{23}\text{D}_2\text{N}_2\text{O}_2^+$: 339.2036. Found 339.2036.

NMR analysis of the isolated product established that the rhodium-hydride undergoes a *syn*-addition consistent with the stereochemical outcome observed for **64**.

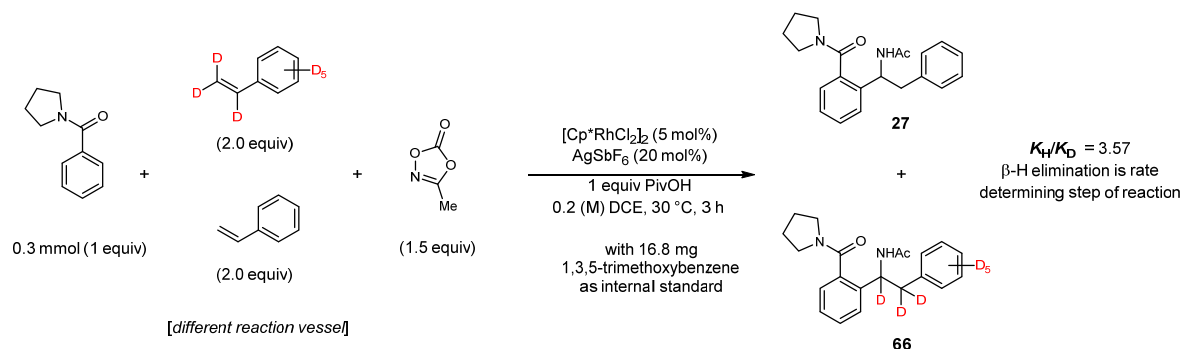
Supplementary Figure 5. Investigation of migration of β -H to α -position.



In a N₂-filled glove box, a 2–5 mL microwave vial was charged with [Cp*RhCl₂]₂ (9.3 mg, 0.015 mmol, 0.050 equiv), AgSbF₆ (21 mg, 0.060 mmol, 0.20 equiv), and pivalic acid (30 mg, 0.30 mmol, 1 equiv). 1,2-Dichloroethane (1.5 mL, 0.2 M) was added followed by the phenyl(pyrrolidin-1-yl) methanone (52.6 mg, 0.300 mmol, 1.0 equiv), D8-styrene (67 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was then stirred at 70 °C in a preheated oil bath. After 20 h, the reaction flask was cooled to rt and the mixture was filtered through a small celite plug (1 cm long in a pipette) and washed with ethyl acetate. The material was concentrated and purified by silica gel chromatography with 20:80 mixture of acetone: hexane as the eluent to afford the product **66** (71.2 mg, 69% yield) as a colorless oil. IR (neat): 3298 (br), 2973, 1608, 1599, 1450, 1430, 909 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 7.28 – 7.25 (m, 2H), 7.25 – 7.22 (m, 2H), 7.08 (broad s, 1H), 3.73 – 3.64 (m, 2H), 3.30 – 3.26 (m, 1H), 3.16 – 3.10 (m, 1H), 2.02 – 1.98 (m, 1H), 1.96 – 1.90 (m, 1H), 1.87 – 1.84 (m, 2H), 1.84 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 170.4, 169.3, 139.3, 137.8, 135.7, 129.5, 128.9, 128.8, 128.7, 128.5, 128.0, 127.9, 127.7, 127.3, 126.9, 126.2, 126.0, 125.9, 49.3, 46.0, 26.2, 24.7, 23.4. HRMS (ESI/[M+H]⁺) calcd. for C₂₁H₁₇D₈N₂O₂⁺: 345.2413. Found 345.2407.

Reactions with D8-styrene proceeded more slowly than analogous reactions with simple styrene with a longer reaction time or a higher reaction temperature necessary to achieve high conversion to α -branched amine product **66**. No H/D exchange had occurred in the migration of β -D to α -position.

Supplementary Figure 6. Kinetic isotope effect studies and determination.



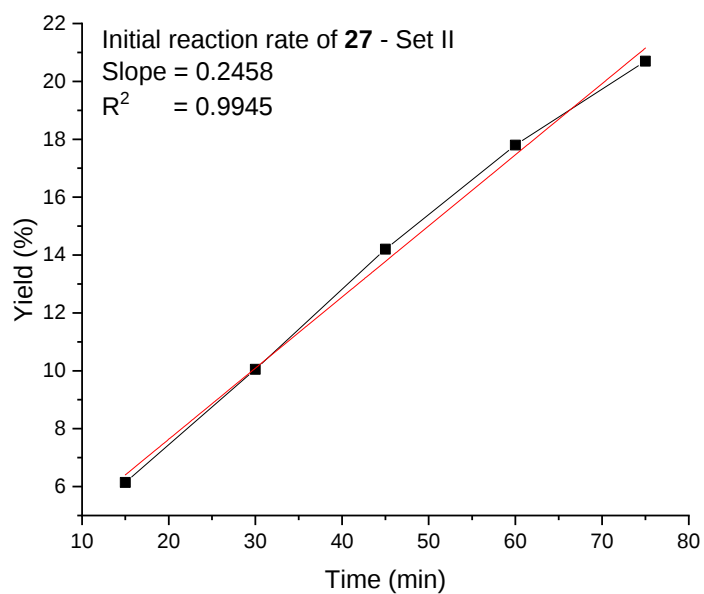
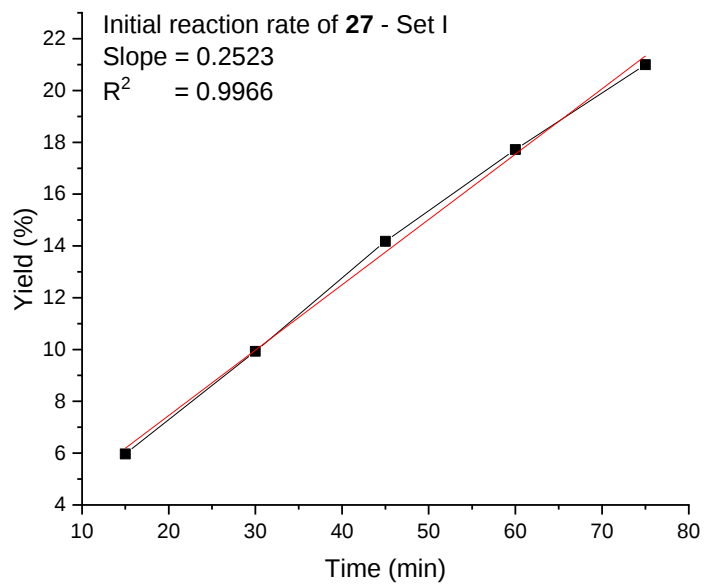
In a N₂-filled glove box, a 2–5 mL microwave vial was charged with 16.8 mg of 1,3,5-trimethoxybenzene as the internal standard, [Cp^{*}RhCl₂]₂ (9.3 mg, 0.015 mmol, 0.050 equiv), AgSbF₆ (21 mg, 0.060 mmol, 0.20 equiv), and pivalic acid (30 mg, 0.30 mmol, 1 equiv). 1,2-Dichloroethane (1.5 mL, 0.2 M) was added followed by the phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.0 equiv), styrene (62.5 mg, 0.600 mmol, 2.0 equiv) or D₈-styrene (67.3 mg, 0.600 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45.0 mg, 0.450 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was then stirred at 30 °C in a preheated oil bath. At the designated time, 0.1 mL aliquot was taken out and worked up with 1 mL of water and extracted two times with 1 mL of dichloromethane. The combined organic extract was concentrated under a positive flow of N₂. This aliquot workup procedure was carried out for each time interval. Each of these concentrated extracts was analyzed by ¹H NMR using CDCl₃ as solvent to obtain NMR yields of the products **27** and **66**.

Supplementary Table 4. Initial rate determination for **27**.

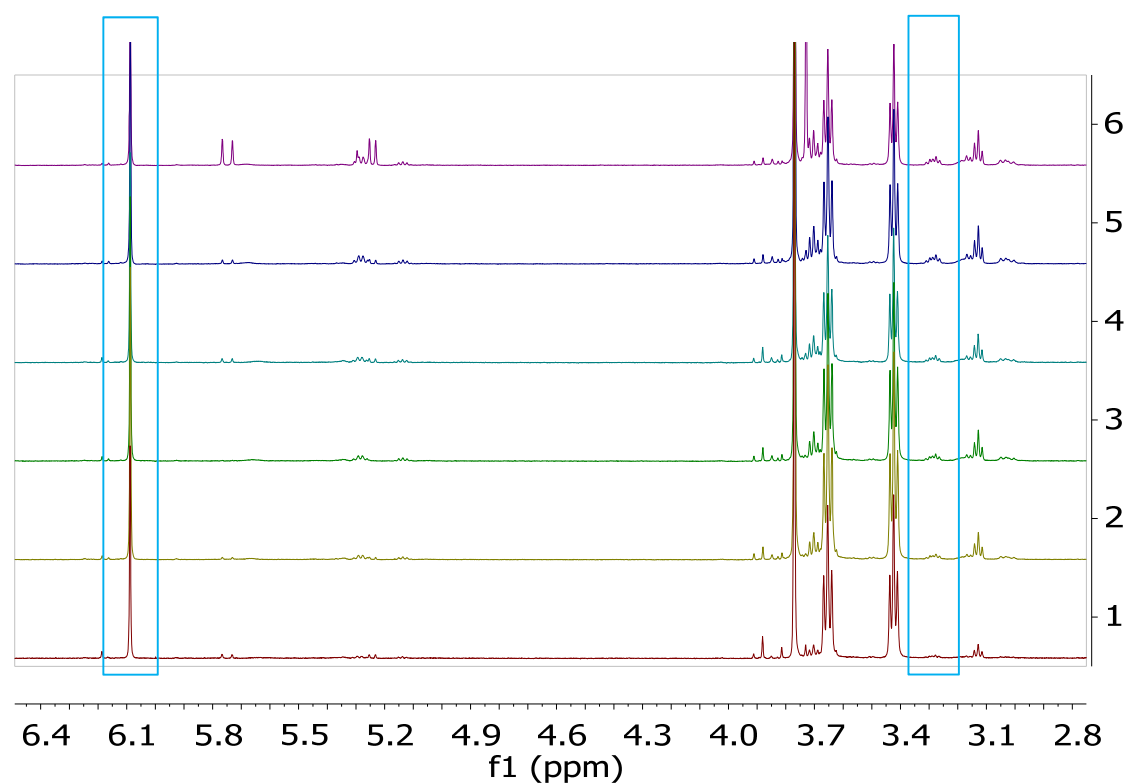
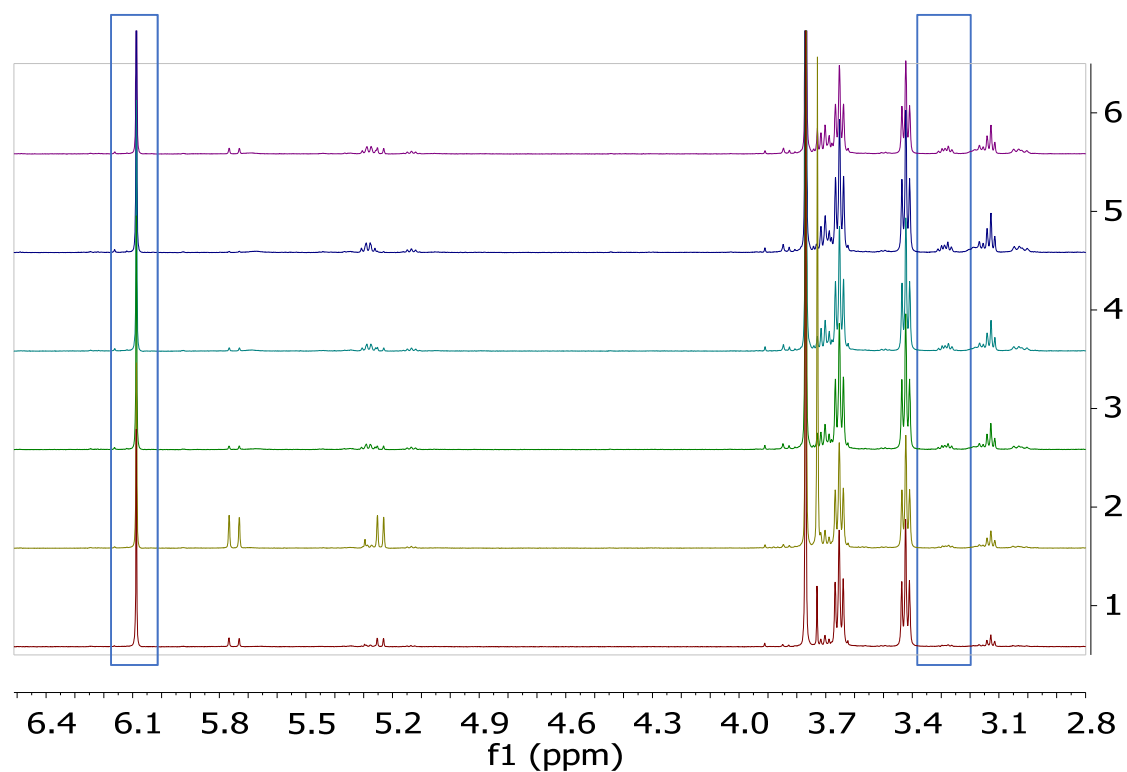
Initial rates for 27 (First run)	
Time (min)	Yield of product 27 (%)
15	5.97
30	9.93
45	14.18
60	17.72
75	21.00
Initial rates for 27 (Second run)	
Time (min)	Yield of product 27 (%)
15	6.14
30	10.05
45	14.2

60	17.8
75	20.7

Supplementary Figure 7. Initial reaction rate graphs for 27.



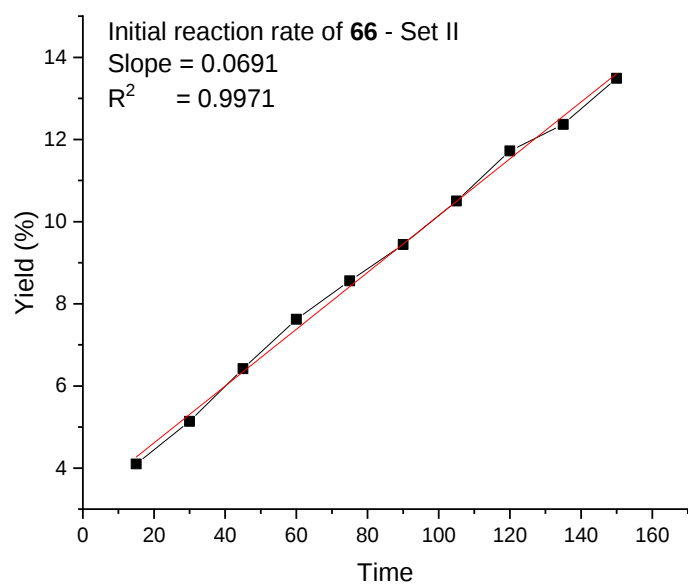
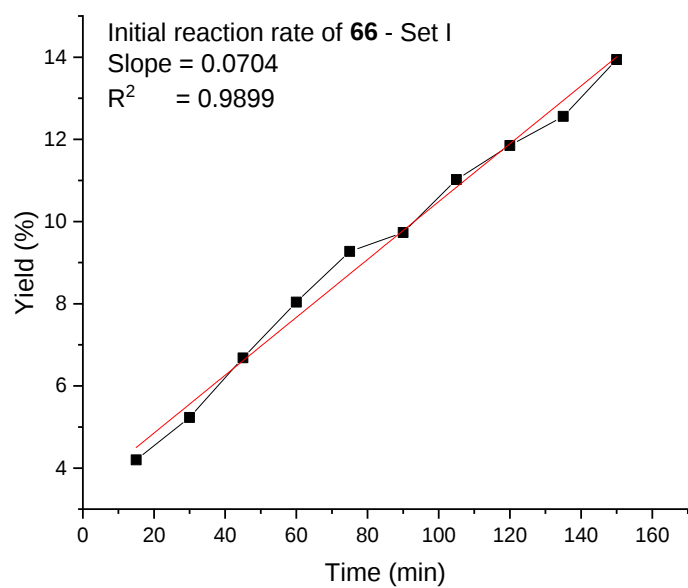
Stacked ^1H NMR spectra for determining yields of **27** at different time points [integration of standard at 6.1 ppm and product multiplet at 3.31 – 3.26 ppm]



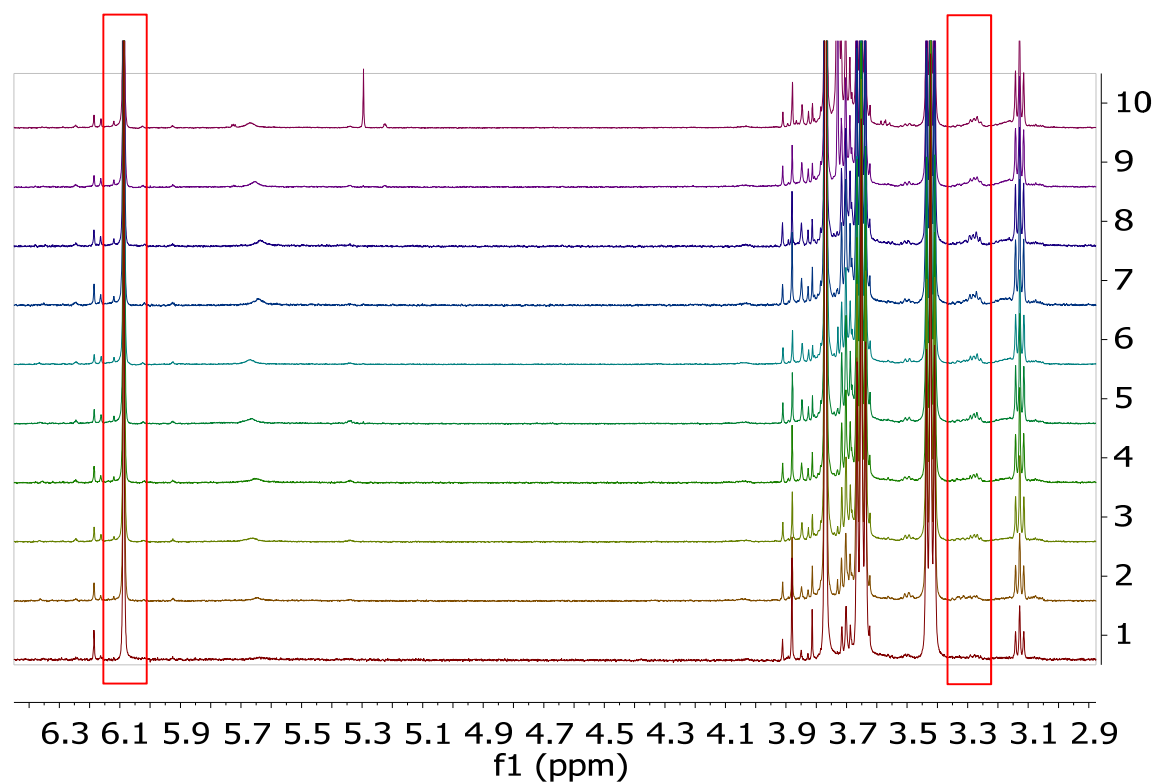
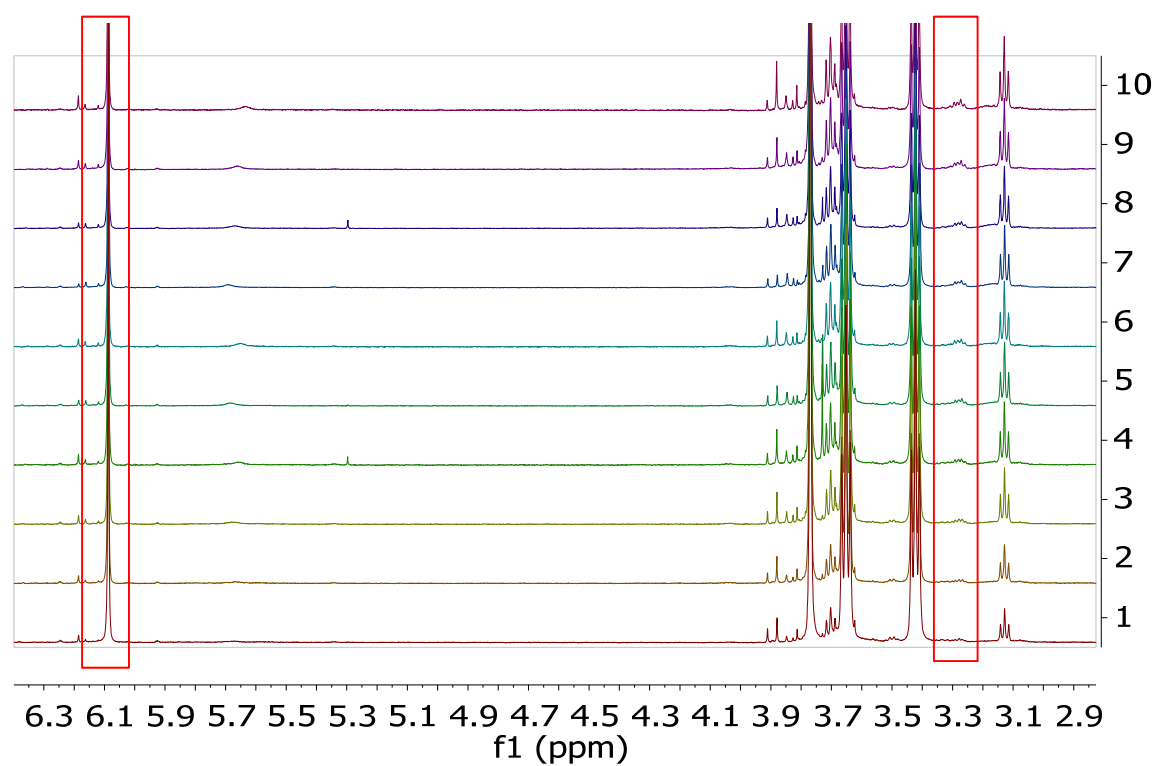
Supplementary Table 5. Initial rate determination for 66.

<i>Initial rates for 66 (First run)</i>	
Time (min)	Yield of product 66 (%)
15	4.2
30	5.23
45	6.68
60	8.04
75	9.27
90	9.73
105	11.02
120	11.85
135	12.56
150	13.94
<i>Initial rates for 66 (Second run)</i>	
Time (min)	Yield of product 66 (%)
15	4.1
30	5.14
45	6.42
60	7.62
75	8.56
90	9.44
105	10.50
120	11.72
135	12.37
150	13.49

Supplementary Figure 8. Initial reaction rate graphs for 66.



Stacked ^1H NMR spectra for determining yields of **66** at different time points [integration of standard at 6.1 ppm and product multiplet at 3.31 – 3.26 ppm]



Supplementary Table 6. Determination of the kinetic isotope effect.

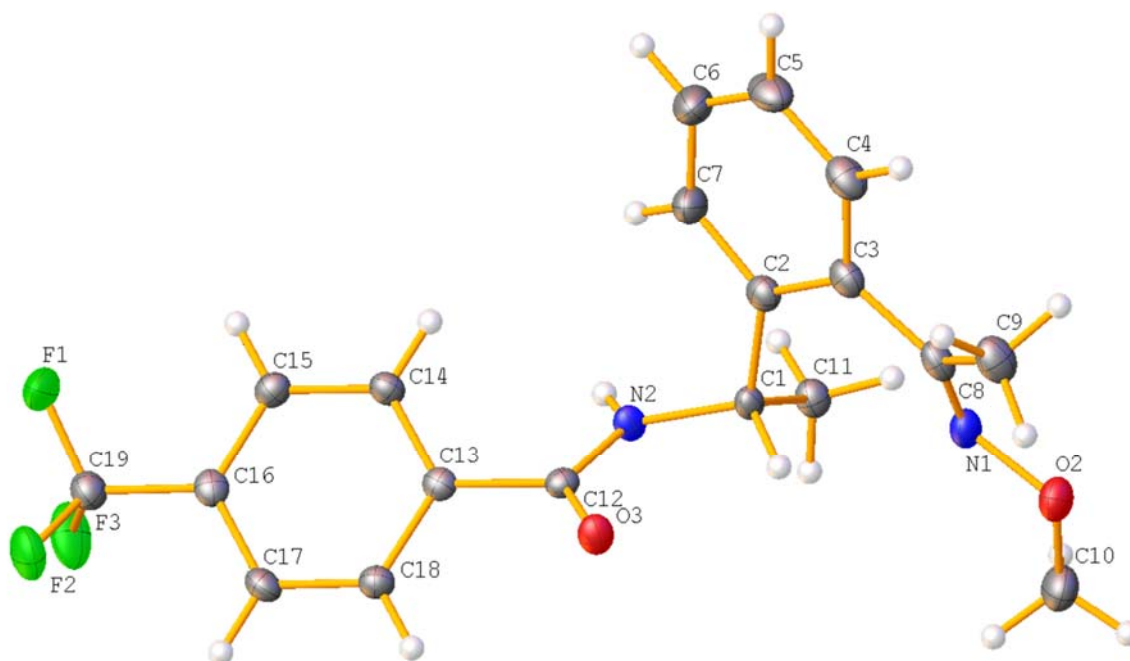
<i>Initial rates for 27</i>	
Slope first run	0.2523
Slope second run	0.2458
Average slope	0.2491
Standard deviation	0.0046
<i>Initial rates for 66</i>	
Slope first run	0.0704
Slope second run	0.0691
Average slope	0.0697
Standard deviation	0.0009
KIE	3.57 ± 0.08 SD

6. X-Ray Crystallographic Data

The single major enantiomer of **62** was obtained by purification by chiral HPLC (AD-H column). X-ray quality crystals of **62** were obtained by slow evaporation of a solution of **62** (1 mg) in hexane/CH₂Cl₂ (~10:1, about 0.25 mL) in an NMR tube overnight.

X-ray experimental details

Low-temperature diffraction data (ω -scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu K α (λ = 1.54178 Å) for the structure of **62** (007b-19043). The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). The only exception is H2, which was found in the difference map and freely refined. The full numbering scheme of compound **62** (007b-19043) can be found in the full details of the X-ray structure determination (CIF), which is included as Supporting Information. CCDC number 1903974 (007b-19043) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.



Supplementary Figure 9. The complete numbering scheme of **62** (007b-19043) with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Supplementary Table 7. Crystal data and structure refinement for **62** (007b-19043).

Identification code	007b-19043	
Empirical formula	C ₁₉ H ₁₉ F ₃ N ₂ O ₂	
Formula weight	364.36	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	a = 5.13960(10) Å	α = 90°.
	b = 16.6370(3) Å	β = 90°.
	c = 20.0930(3) Å	γ = 90°.
Volume	1718.10(5) Å ³	
Z	4	
Density (calculated)	1.409 Mg/m ³	
Absorption coefficient	0.970 mm ⁻¹	
F(000)	760	
Crystal size	0.200 x 0.080 x 0.030 mm ³	
Crystal color and habit	Colorless Plate	
Diffractionmeter	Rigaku Saturn 944+ CCD	
Theta range for data collection	3.449 to 66.586°.	
Index ranges	-6 ≤ h ≤ 6, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	
Reflections collected	59645	
Independent reflections	3023 [R(int) = 0.0435]	
Observed reflections (I > 2σ(I))	3021	
Completeness to theta = 66.586°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.79935	
Solution method	SHELXT-2014/5 (Sheldrick, 2014)	
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)	
Data / restraints / parameters	3023 / 0 / 243	
Goodness-of-fit on F ²	1.152	
Final R indices [I > 2σ(I)]	R ₁ = 0.0296, wR ₂ = 0.0755	
R indices (all data)	R ₁ = 0.0296, wR ₂ = 0.0756	
Absolute structure parameter	-0.02(3)	
Extinction coefficient	0.0292(12)	
Largest diff. peak and hole	0.213 and -0.203 e.Å ⁻³	

Supplementary Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **62** (007b-19043). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	-1435(3)	10530(1)	5236(1)	44(1)
F(2)	2073(3)	10291(1)	5772(1)	34(1)
F(3)	-1391(3)	9643(1)	6011(1)	40(1)
O(2)	5328(3)	4742(1)	1815(1)	26(1)
O(3)	5091(3)	7338(1)	3485(1)	22(1)
N(1)	3695(3)	5416(1)	1895(1)	22(1)
N(2)	806(3)	7093(1)	3303(1)	17(1)
C(1)	1181(4)	6515(1)	2759(1)	16(1)
C(2)	1085(4)	6946(1)	2082(1)	20(1)
C(3)	2602(4)	6719(1)	1526(1)	21(1)
C(4)	2456(4)	7192(1)	949(1)	27(1)
C(5)	813(5)	7848(1)	902(1)	32(1)
C(6)	-773(5)	8042(1)	1435(1)	33(1)
C(7)	-613(4)	7594(1)	2016(1)	27(1)
C(8)	4300(4)	5994(1)	1499(1)	21(1)
C(9)	6508(4)	5949(1)	1009(1)	28(1)
C(10)	4938(5)	4236(1)	2380(1)	31(1)
C(11)	-897(4)	5867(1)	2818(1)	21(1)
C(12)	2778(4)	7478(1)	3602(1)	16(1)
C(13)	1986(3)	8110(1)	4096(1)	16(1)
C(14)	-158(4)	8604(1)	3985(1)	18(1)
C(15)	-792(4)	9206(1)	4435(1)	19(1)
C(16)	700(4)	9304(1)	5004(1)	18(1)
C(17)	2834(4)	8810(1)	5125(1)	19(1)
C(18)	3493(4)	8222(1)	4667(1)	18(1)
C(19)	-17(4)	9939(1)	5501(1)	23(1)

Supplementary Table 9. Bond lengths [Å] and angles [°] for **62** (007b-19043) .

F(1)-C(19)	1.334(2)
F(2)-C(19)	1.340(2)
F(3)-C(19)	1.339(2)
O(2)-N(1)	1.410(2)
O(2)-C(10)	1.428(2)
O(3)-C(12)	1.234(2)
N(1)-C(8)	1.286(3)
N(2)-C(12)	1.341(2)
N(2)-C(1)	1.469(2)
N(2)-H(2)	0.82(3)
C(1)-C(11)	1.522(3)
C(1)-C(2)	1.538(2)
C(1)-H(1)	1.0000
C(2)-C(7)	1.394(3)
C(2)-C(3)	1.413(3)
C(3)-C(4)	1.404(3)
C(3)-C(8)	1.489(3)
C(4)-C(5)	1.382(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.383(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.388(3)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-C(9)	1.505(3)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.504(2)
C(13)-C(14)	1.392(3)

C(13)-C(18)	1.396(2)
C(14)-C(15)	1.388(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.387(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.391(3)
C(16)-C(19)	1.499(3)
C(17)-C(18)	1.385(3)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
N(1)-O(2)-C(10)	107.18(14)
C(8)-N(1)-O(2)	112.38(15)
C(12)-N(2)-C(1)	123.11(15)
C(12)-N(2)-H(2)	120.3(17)
C(1)-N(2)-H(2)	116.6(17)
N(2)-C(1)-C(11)	108.23(14)
N(2)-C(1)-C(2)	110.42(14)
C(11)-C(1)-C(2)	112.13(15)
N(2)-C(1)-H(1)	108.7
C(11)-C(1)-H(1)	108.7
C(2)-C(1)-H(1)	108.7
C(7)-C(2)-C(3)	118.45(17)
C(7)-C(2)-C(1)	117.72(17)
C(3)-C(2)-C(1)	123.83(17)
C(4)-C(3)-C(2)	118.30(18)
C(4)-C(3)-C(8)	117.06(17)
C(2)-C(3)-C(8)	124.61(17)
C(5)-C(4)-C(3)	122.04(19)
C(5)-C(4)-H(4)	119.0
C(3)-C(4)-H(4)	119.0
C(4)-C(5)-C(6)	119.47(19)
C(4)-C(5)-H(5)	120.3
C(6)-C(5)-H(5)	120.3
C(5)-C(6)-C(7)	119.4(2)
C(5)-C(6)-H(6)	120.3
C(7)-C(6)-H(6)	120.3
C(6)-C(7)-C(2)	122.22(19)

C(6)-C(7)-H(7)	118.9
C(2)-C(7)-H(7)	118.9
N(1)-C(8)-C(3)	116.20(16)
N(1)-C(8)-C(9)	123.34(18)
C(3)-C(8)-C(9)	120.41(17)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
O(2)-C(10)-H(10A)	109.5
O(2)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
O(2)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(1)-C(11)-H(11A)	109.5
C(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
O(3)-C(12)-N(2)	123.62(16)
O(3)-C(12)-C(13)	121.21(16)
N(2)-C(12)-C(13)	115.16(16)
C(14)-C(13)-C(18)	119.52(16)
C(14)-C(13)-C(12)	121.39(16)
C(18)-C(13)-C(12)	119.05(16)
C(15)-C(14)-C(13)	120.50(17)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(16)-C(15)-C(14)	119.41(17)
C(16)-C(15)-H(15)	120.3
C(14)-C(15)-H(15)	120.3
C(15)-C(16)-C(17)	120.69(17)
C(15)-C(16)-C(19)	119.69(17)
C(17)-C(16)-C(19)	119.62(17)

C(18)-C(17)-C(16)	119.65(17)
C(18)-C(17)-H(17)	120.2
C(16)-C(17)-H(17)	120.2
C(17)-C(18)-C(13)	120.22(17)
C(17)-C(18)-H(18)	119.9
C(13)-C(18)-H(18)	119.9
F(1)-C(19)-F(3)	106.73(18)
F(1)-C(19)-F(2)	106.14(16)
F(3)-C(19)-F(2)	105.77(15)
F(1)-C(19)-C(16)	112.88(16)
F(3)-C(19)-C(16)	112.33(15)
F(2)-C(19)-C(16)	112.48(17)

Symmetry transformations used to generate equivalent atoms:

Supplementary Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **62** (007b-19043). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	62(1)	35(1)	34(1)	-13(1)	-12(1)	27(1)
F(2)	35(1)	31(1)	36(1)	-14(1)	-2(1)	-5(1)
F(3)	52(1)	40(1)	30(1)	-11(1)	22(1)	-10(1)
O(2)	28(1)	23(1)	26(1)	-6(1)	4(1)	4(1)
O(3)	15(1)	24(1)	25(1)	-5(1)	1(1)	1(1)
N(1)	21(1)	21(1)	22(1)	-6(1)	0(1)	3(1)
N(2)	12(1)	21(1)	18(1)	-4(1)	2(1)	1(1)
C(1)	14(1)	18(1)	17(1)	-4(1)	0(1)	2(1)
C(2)	20(1)	19(1)	19(1)	-1(1)	-2(1)	-3(1)
C(3)	22(1)	23(1)	19(1)	-3(1)	-2(1)	-4(1)
C(4)	32(1)	31(1)	19(1)	-1(1)	2(1)	-6(1)
C(5)	45(1)	26(1)	23(1)	6(1)	-7(1)	-4(1)
C(6)	47(1)	25(1)	28(1)	-1(1)	-7(1)	9(1)
C(7)	34(1)	25(1)	22(1)	-4(1)	-2(1)	8(1)
C(8)	19(1)	26(1)	17(1)	-6(1)	1(1)	-3(1)
C(9)	24(1)	35(1)	24(1)	-6(1)	4(1)	-2(1)
C(10)	39(1)	22(1)	31(1)	-3(1)	-1(1)	1(1)
C(11)	20(1)	23(1)	21(1)	-3(1)	1(1)	-1(1)
C(12)	16(1)	16(1)	15(1)	3(1)	1(1)	1(1)
C(13)	15(1)	16(1)	16(1)	2(1)	2(1)	-3(1)
C(14)	16(1)	21(1)	17(1)	-1(1)	-2(1)	0(1)
C(15)	16(1)	18(1)	21(1)	1(1)	1(1)	0(1)
C(16)	21(1)	18(1)	16(1)	2(1)	4(1)	-3(1)
C(17)	21(1)	22(1)	14(1)	0(1)	-2(1)	-2(1)
C(18)	17(1)	19(1)	18(1)	1(1)	-1(1)	0(1)
C(19)	27(1)	23(1)	19(1)	-1(1)	0(1)	0(1)

Supplementary Table 11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **62** (007b-19043).

	x	y	z	U(eq)
H(1)	2929	6259	2811	20
H(4)	3519	7058	578	32
H(5)	773	8162	508	38
H(6)	-1961	8478	1403	40
H(7)	-1697	7734	2381	33
H(9A)	7862	5591	1182	42
H(9B)	7236	6488	941	42
H(9C)	5864	5740	584	42
H(10A)	5841	3724	2311	46
H(10B)	3073	4136	2439	46
H(10C)	5633	4500	2778	46
H(11A)	-631	5564	3231	32
H(11B)	-776	5502	2437	32
H(11C)	-2621	6119	2826	32
H(14)	-1194	8528	3599	22
H(15)	-2235	9549	4353	22
H(17)	3833	8876	5518	23
H(18)	4975	7893	4741	22
H(2)	-700(50)	7184(14)	3415(12)	24(6)

Supplementary Table 12. Torsion angles [°] for **62** (007b-19043).

C(10)-O(2)-N(1)-C(8)	165.25(16)
C(12)-N(2)-C(1)-C(11)	146.38(16)
C(12)-N(2)-C(1)-C(2)	-90.5(2)
N(2)-C(1)-C(2)-C(7)	-34.9(2)
C(11)-C(1)-C(2)-C(7)	85.9(2)
N(2)-C(1)-C(2)-C(3)	145.43(18)
C(11)-C(1)-C(2)-C(3)	-93.8(2)
C(7)-C(2)-C(3)-C(4)	4.3(3)
C(1)-C(2)-C(3)-C(4)	-176.08(18)
C(7)-C(2)-C(3)-C(8)	-173.69(18)
C(1)-C(2)-C(3)-C(8)	6.0(3)
C(2)-C(3)-C(4)-C(5)	-2.4(3)
C(8)-C(3)-C(4)-C(5)	175.68(18)
C(3)-C(4)-C(5)-C(6)	-1.0(3)
C(4)-C(5)-C(6)-C(7)	2.5(3)
C(5)-C(6)-C(7)-C(2)	-0.6(3)
C(3)-C(2)-C(7)-C(6)	-2.9(3)
C(1)-C(2)-C(7)-C(6)	177.44(19)
O(2)-N(1)-C(8)-C(3)	177.29(14)
O(2)-N(1)-C(8)-C(9)	-0.1(3)
C(4)-C(3)-C(8)-N(1)	-153.69(18)
C(2)-C(3)-C(8)-N(1)	24.3(3)
C(4)-C(3)-C(8)-C(9)	23.8(3)
C(2)-C(3)-C(8)-C(9)	-158.26(18)
C(1)-N(2)-C(12)-O(3)	-5.8(3)
C(1)-N(2)-C(12)-C(13)	173.72(15)
O(3)-C(12)-C(13)-C(14)	141.70(18)
N(2)-C(12)-C(13)-C(14)	-37.8(2)
O(3)-C(12)-C(13)-C(18)	-36.0(2)
N(2)-C(12)-C(13)-C(18)	144.50(17)
C(18)-C(13)-C(14)-C(15)	0.4(3)
C(12)-C(13)-C(14)-C(15)	-177.27(16)
C(13)-C(14)-C(15)-C(16)	-1.3(3)
C(14)-C(15)-C(16)-C(17)	0.7(3)
C(14)-C(15)-C(16)-C(19)	-178.37(17)
C(15)-C(16)-C(17)-C(18)	0.7(3)

C(19)-C(16)-C(17)-C(18)	179.83(17)
C(16)-C(17)-C(18)-C(13)	-1.7(3)
C(14)-C(13)-C(18)-C(17)	1.1(3)
C(12)-C(13)-C(18)-C(17)	178.80(16)
C(15)-C(16)-C(19)-F(1)	-22.9(3)
C(17)-C(16)-C(19)-F(1)	158.00(18)
C(15)-C(16)-C(19)-F(3)	97.8(2)
C(17)-C(16)-C(19)-F(3)	-81.3(2)
C(15)-C(16)-C(19)-F(2)	-142.96(17)
C(17)-C(16)-C(19)-F(2)	37.9(2)

Symmetry transformations used to generate equivalent atoms:

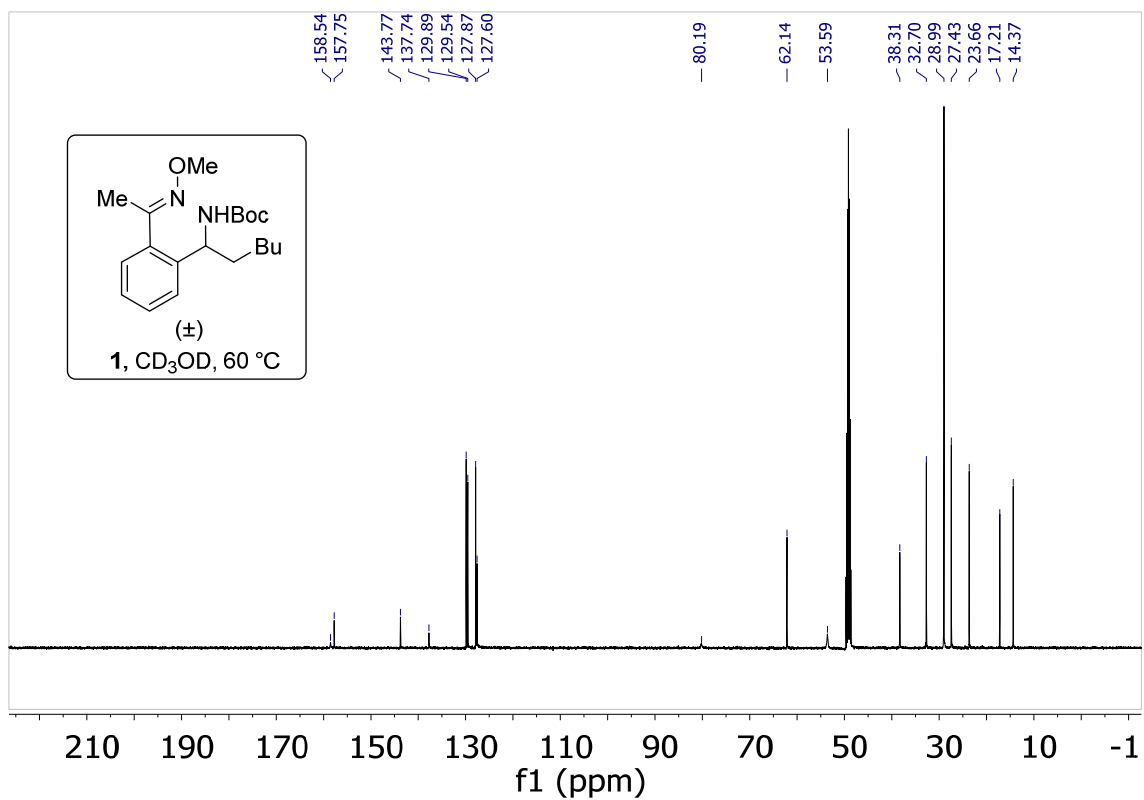
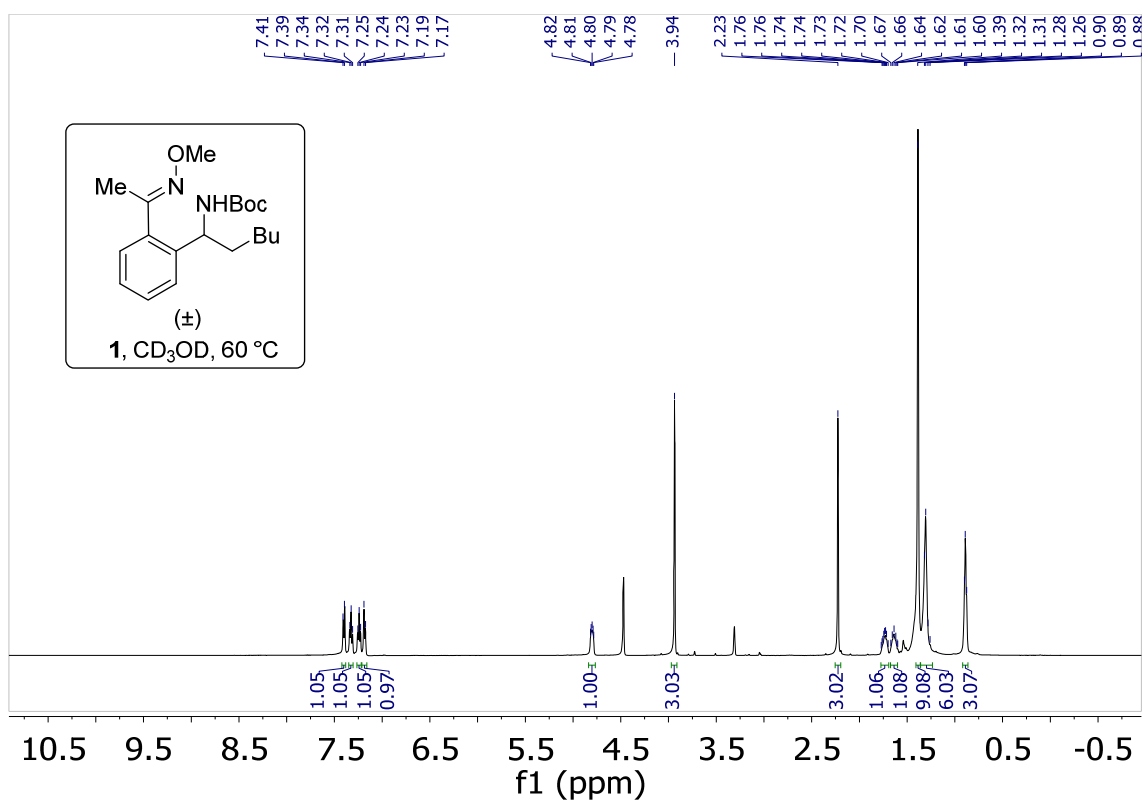
Supplementary Table 13. Hydrogen bonds for **62** (007b-19043) [$\text{\AA}$ and $^\circ$].

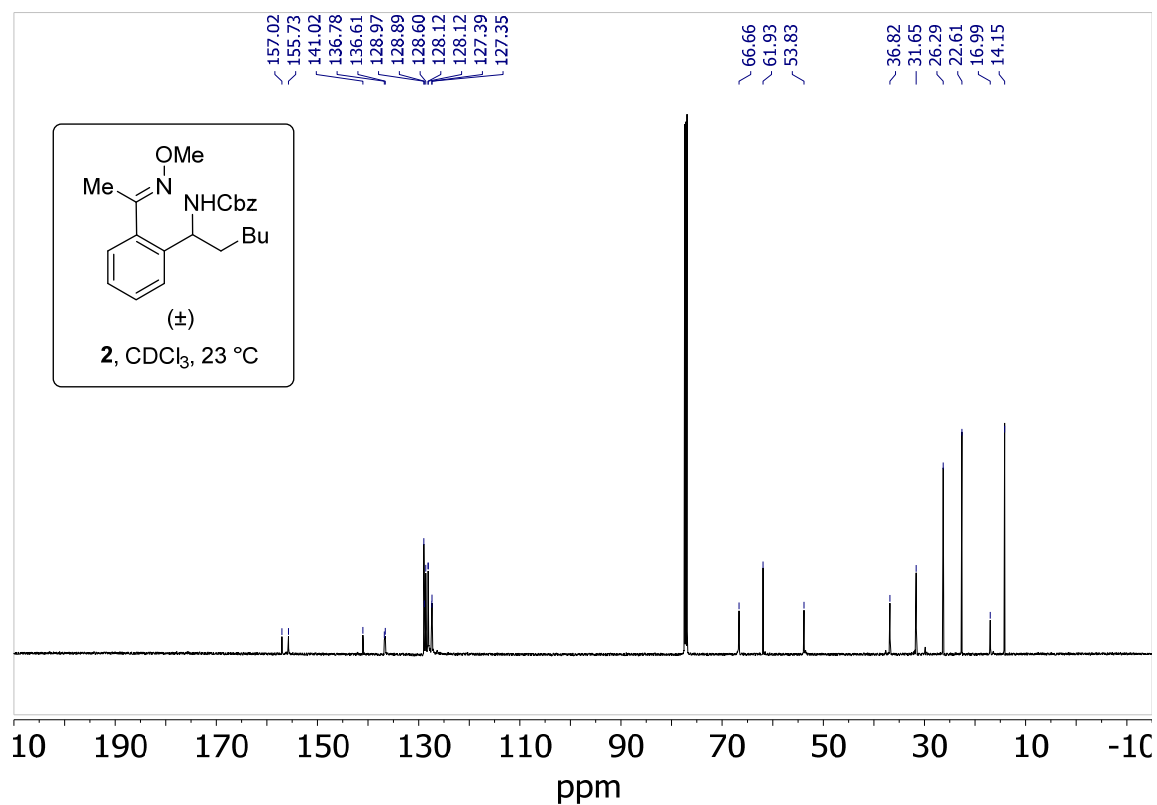
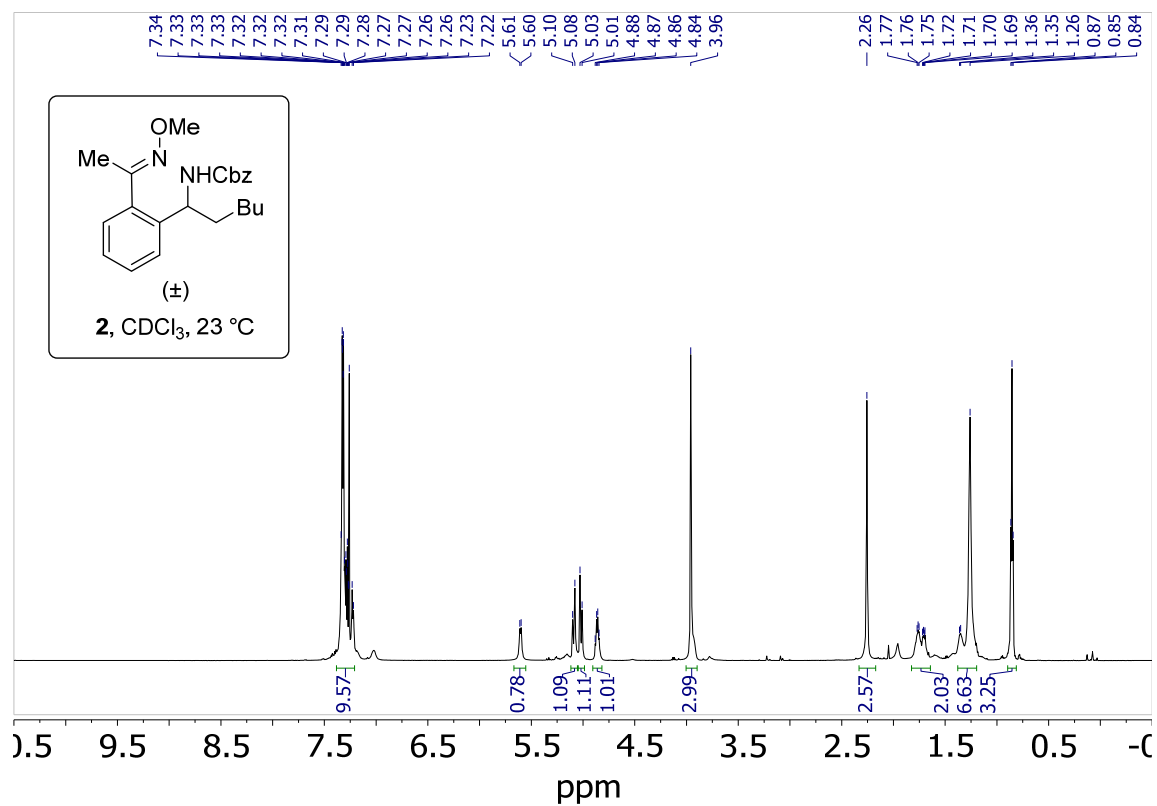
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2)...O(3)#1	0.82(3)	2.18(3)	2.988(2)	167(2)

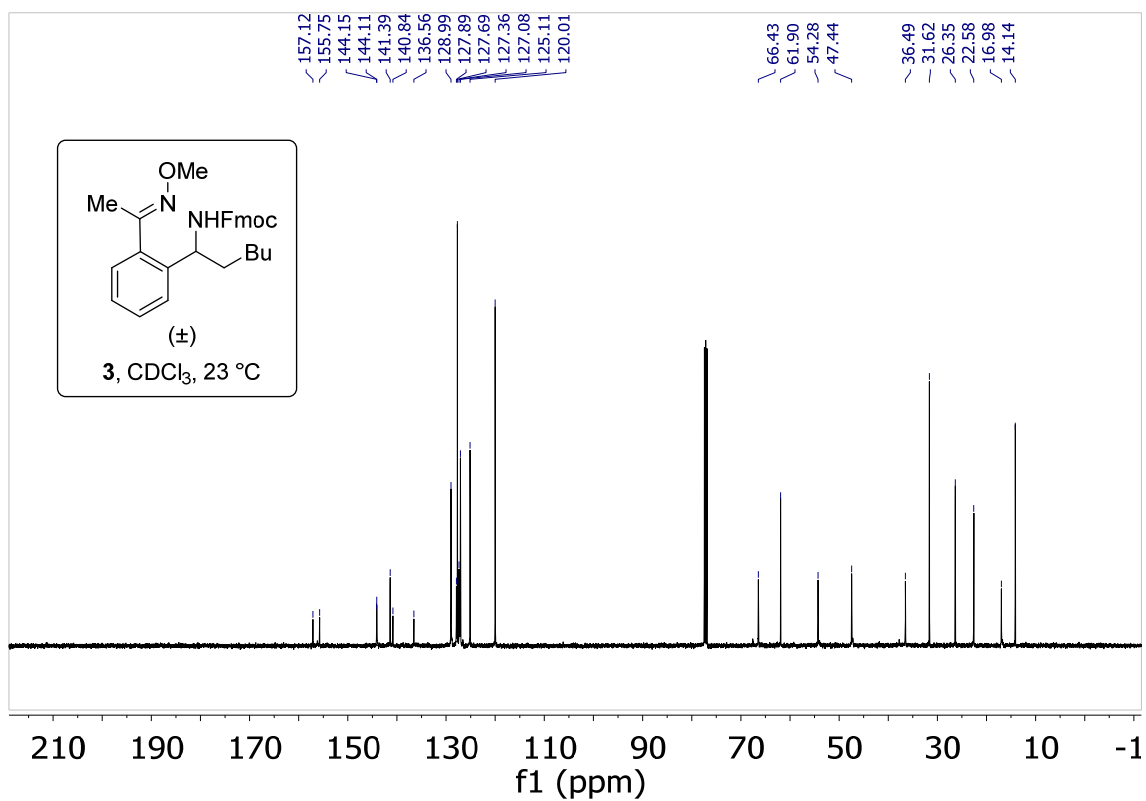
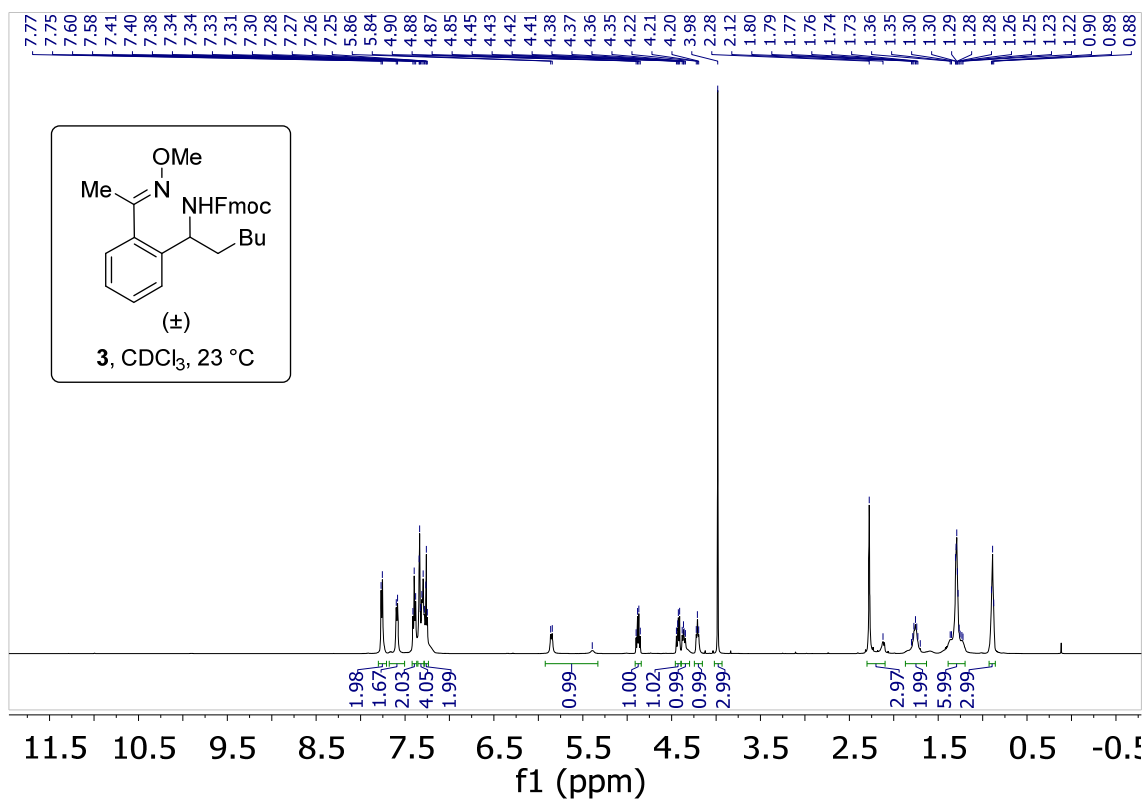
Symmetry transformations used to generate equivalent atoms:

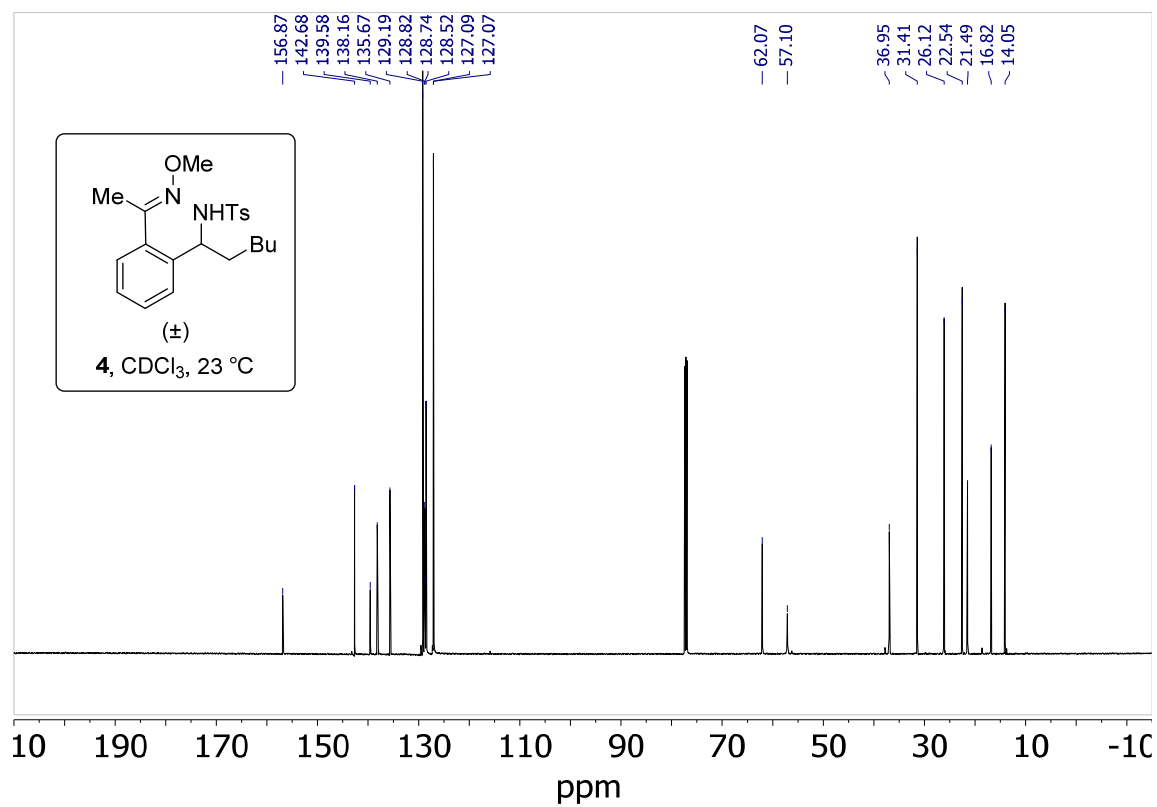
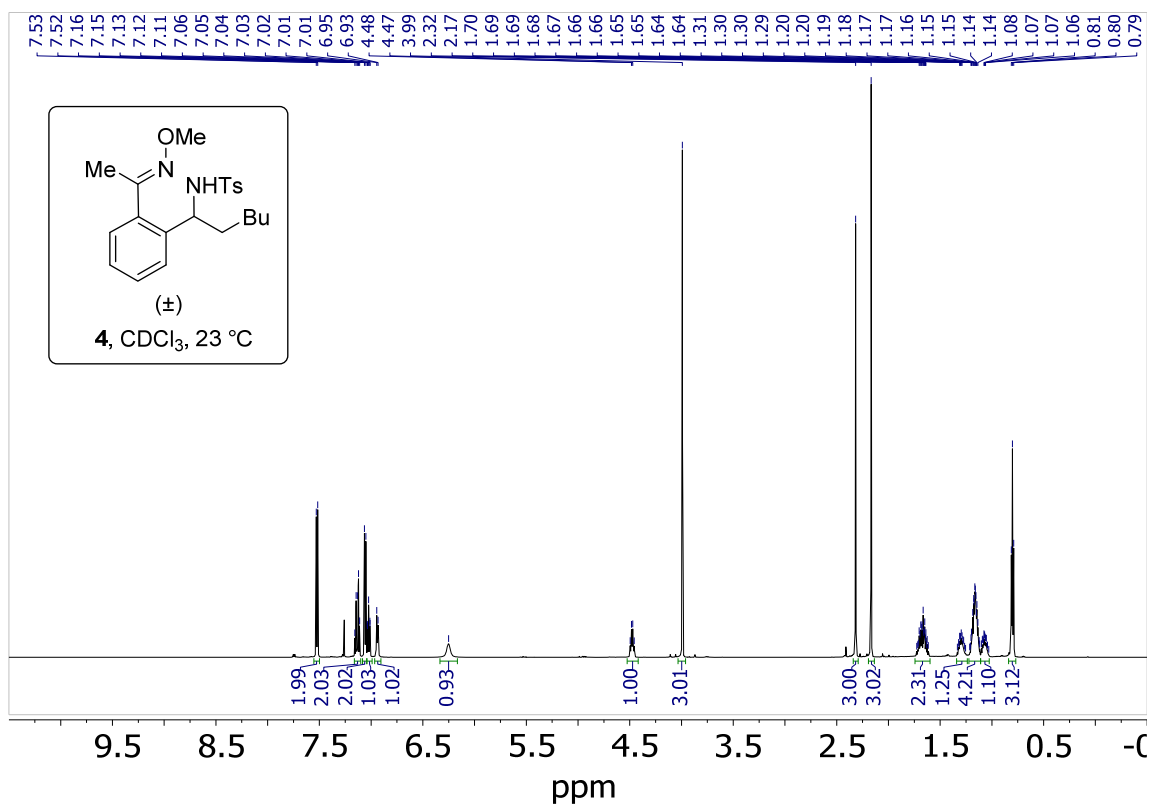
#1 x-1,y,z

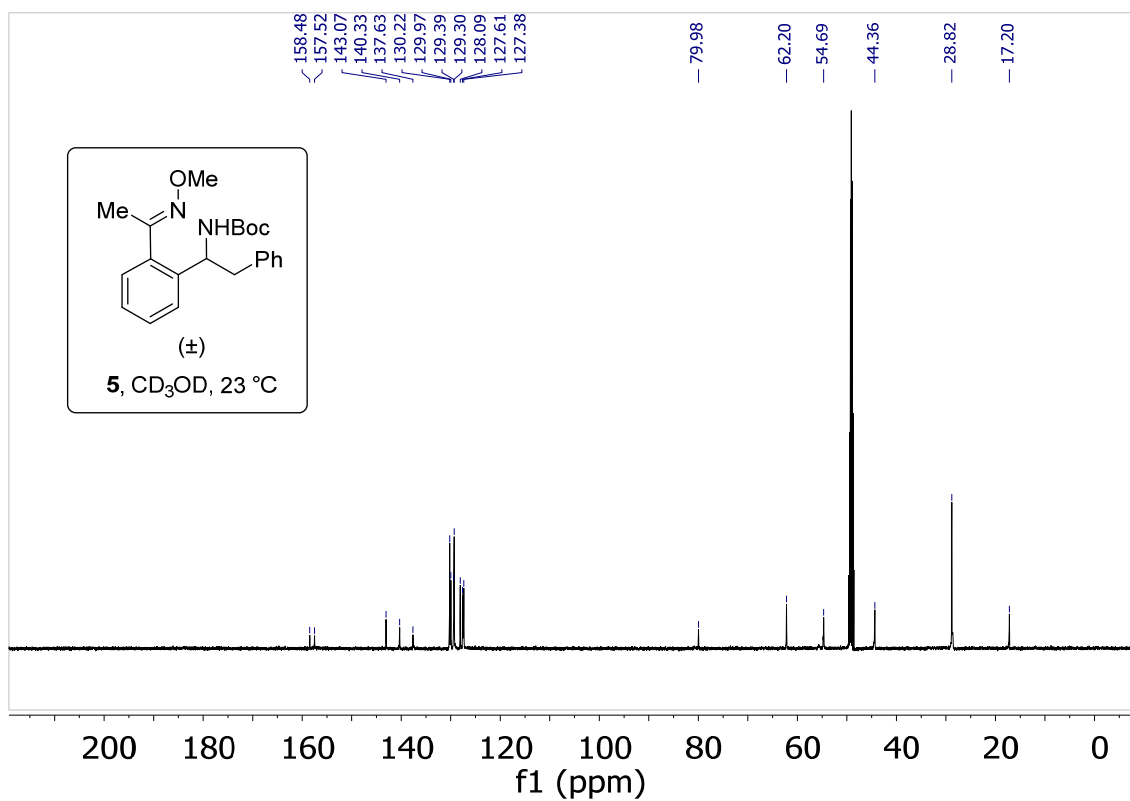
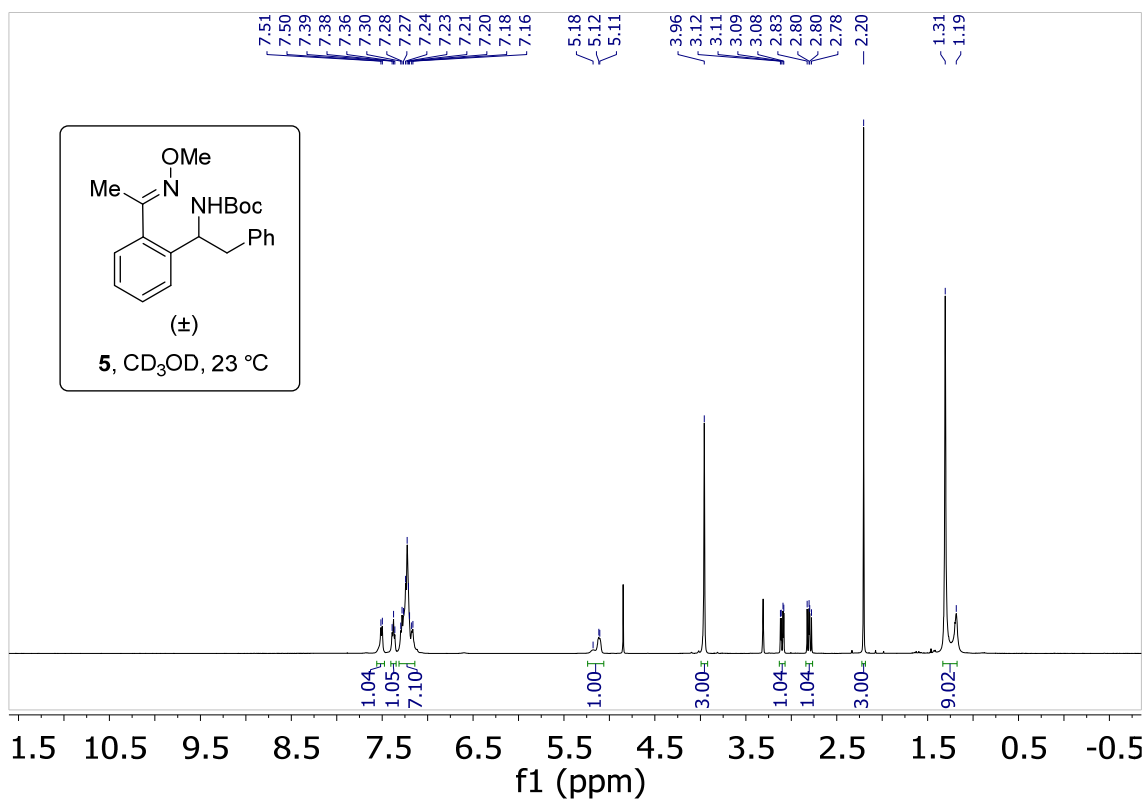
7. NMR Data



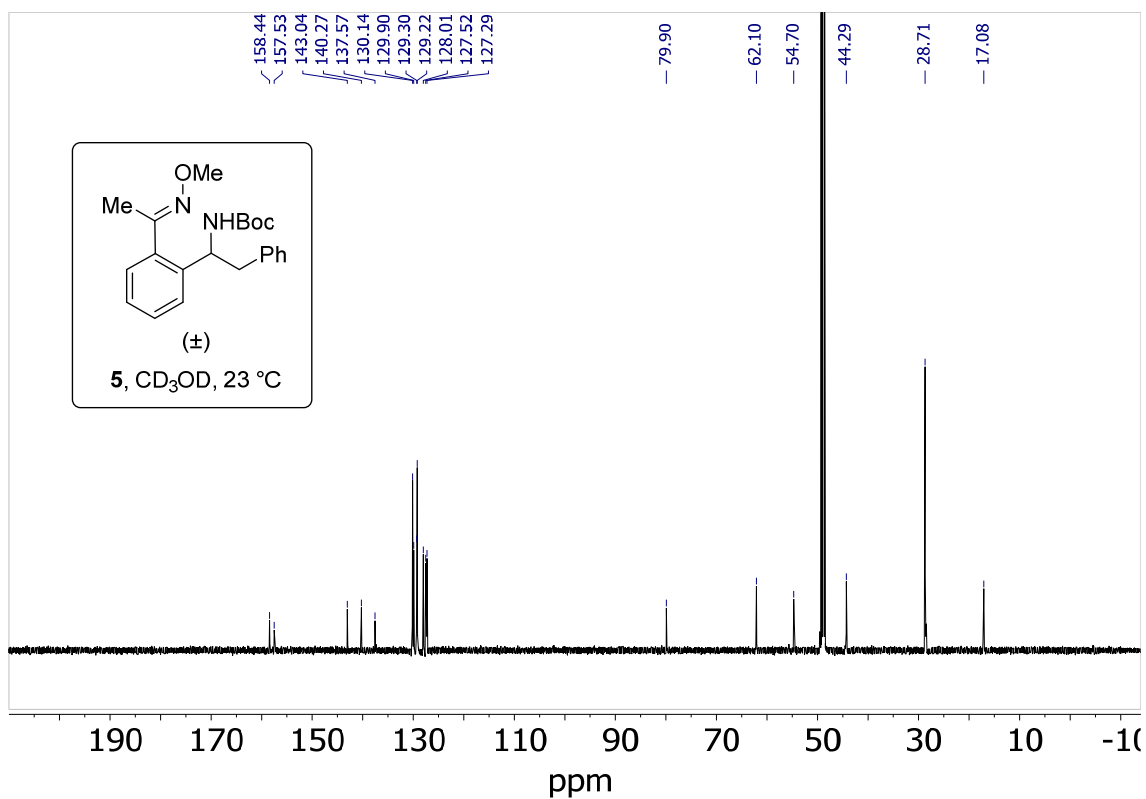
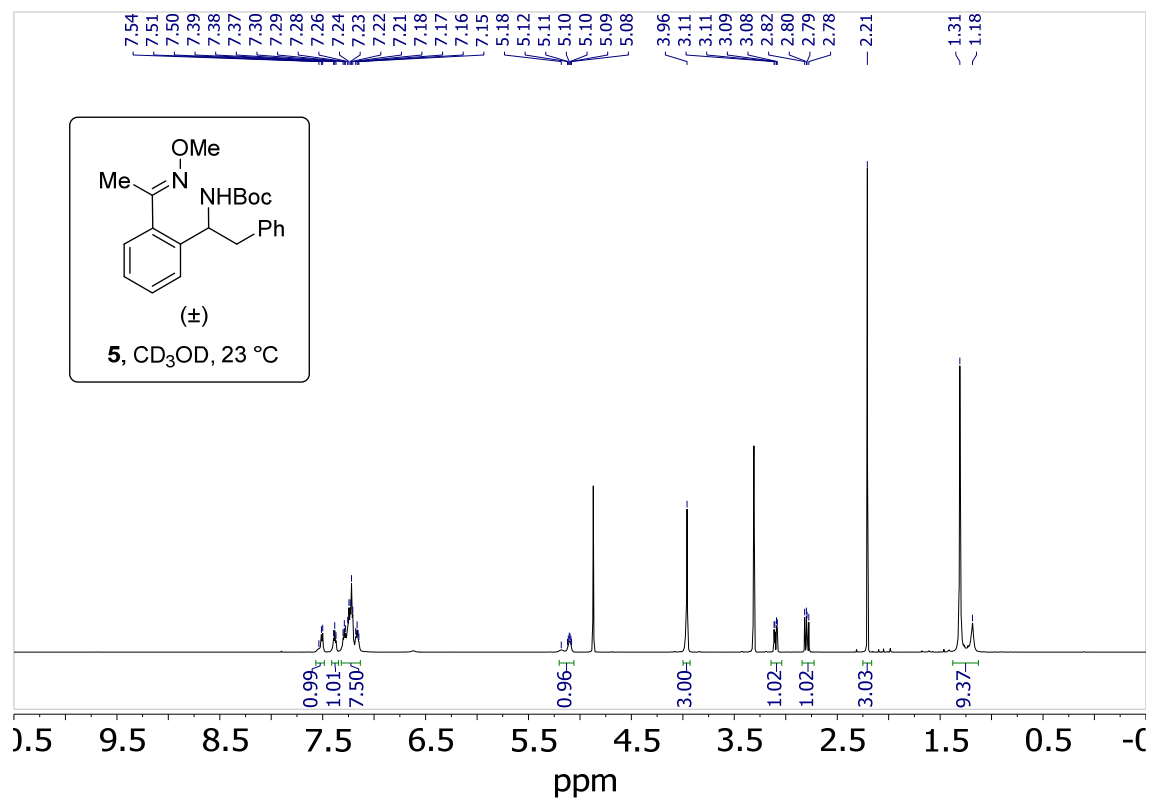


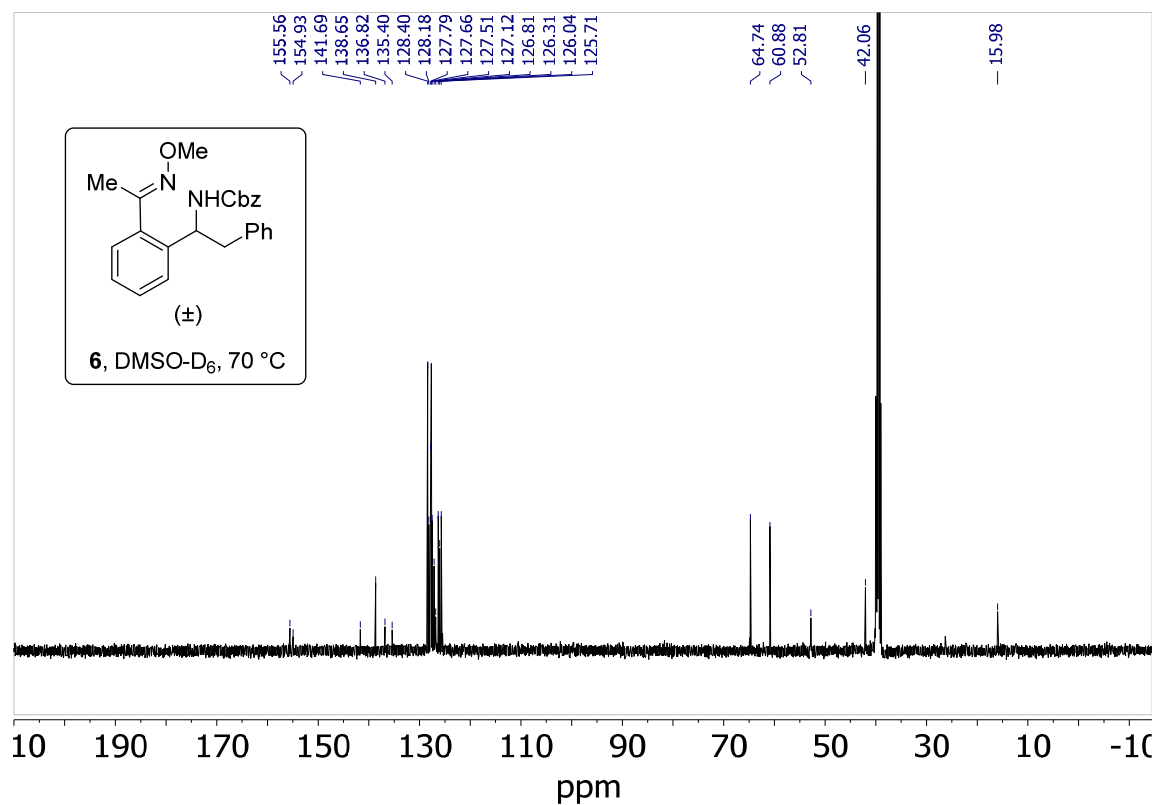
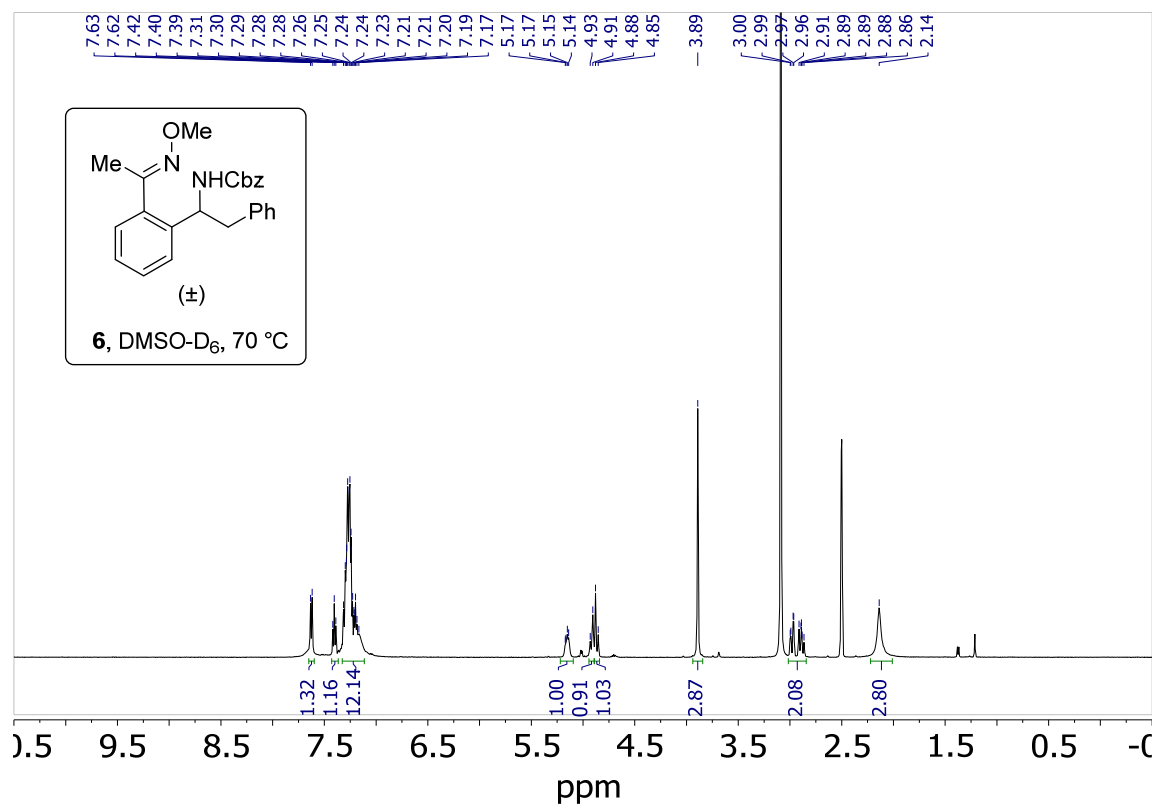


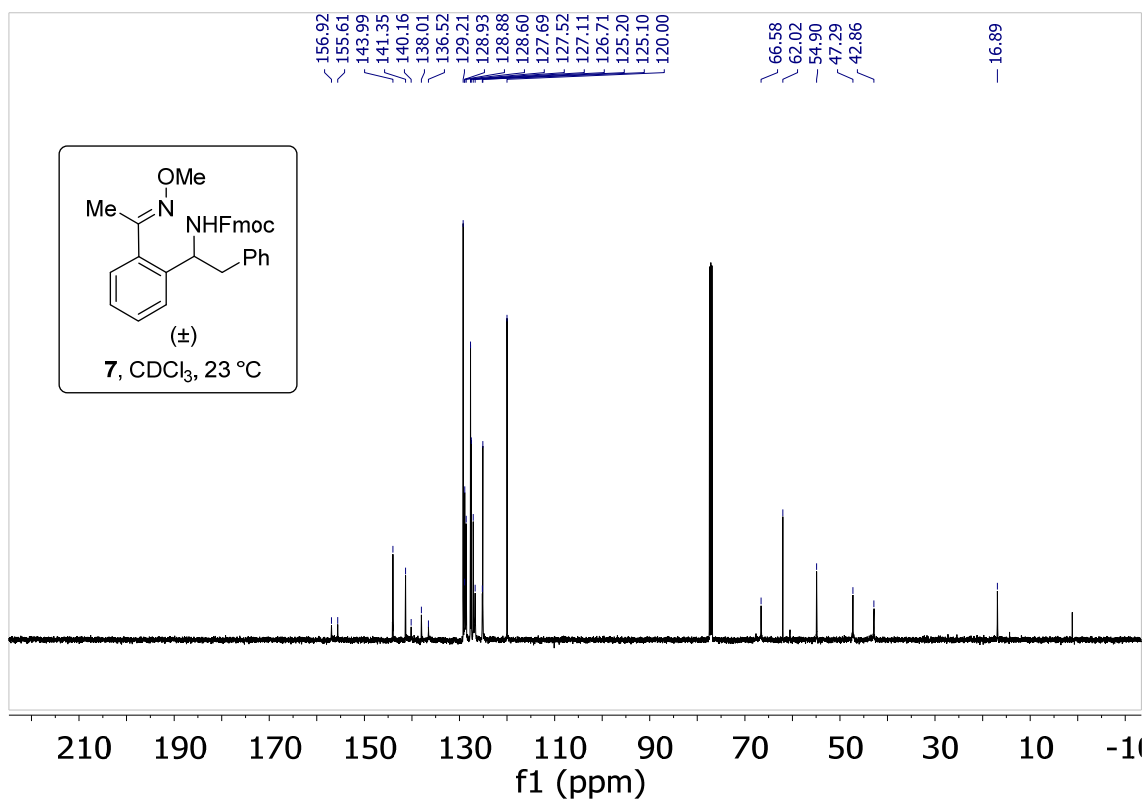
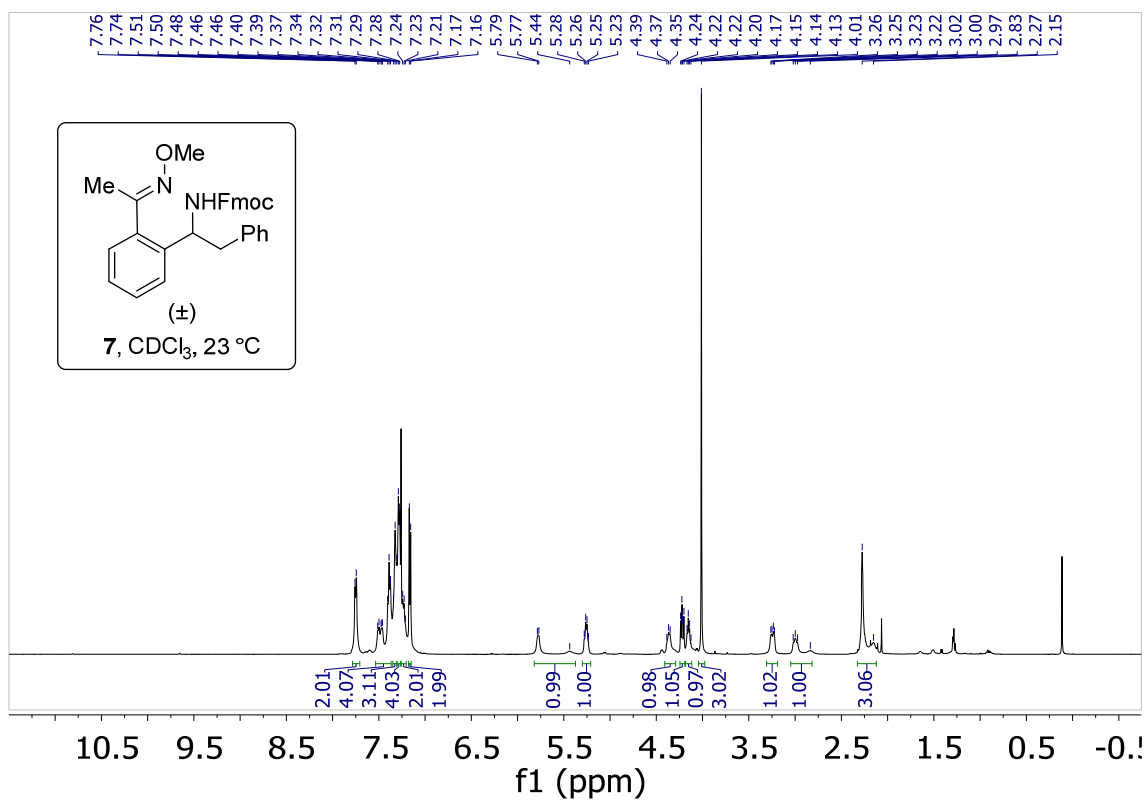


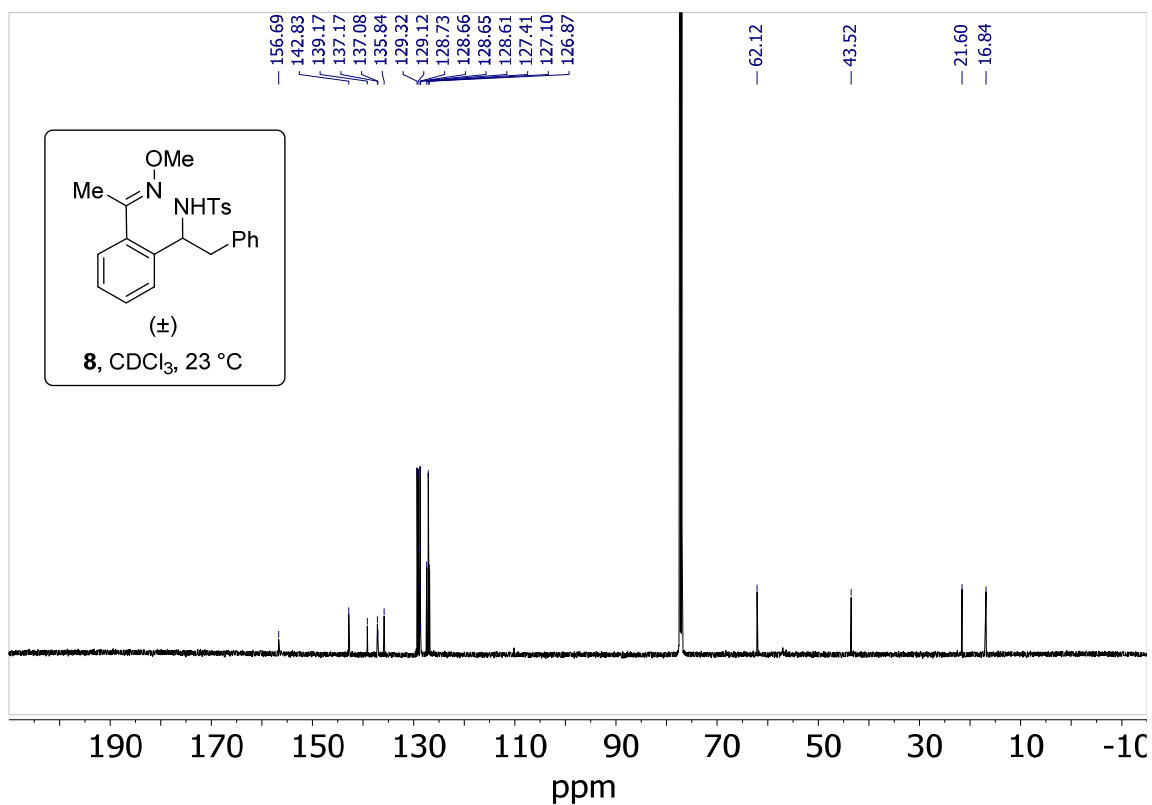
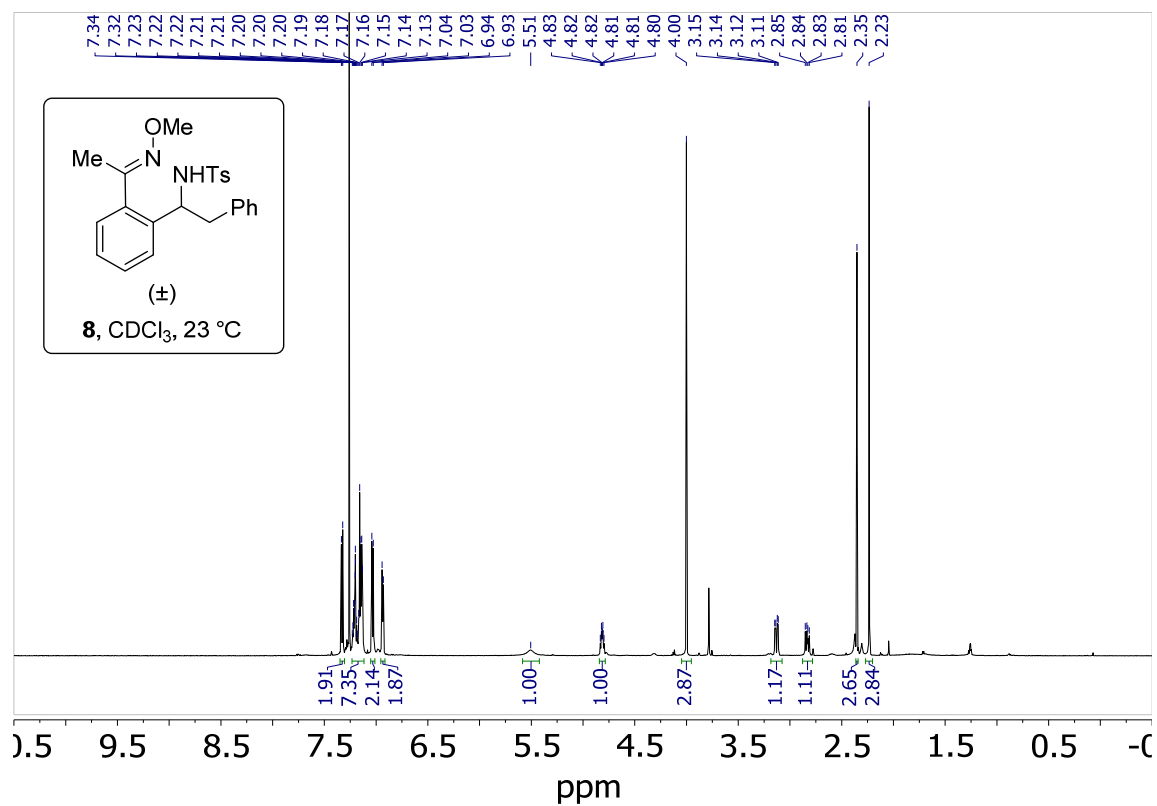


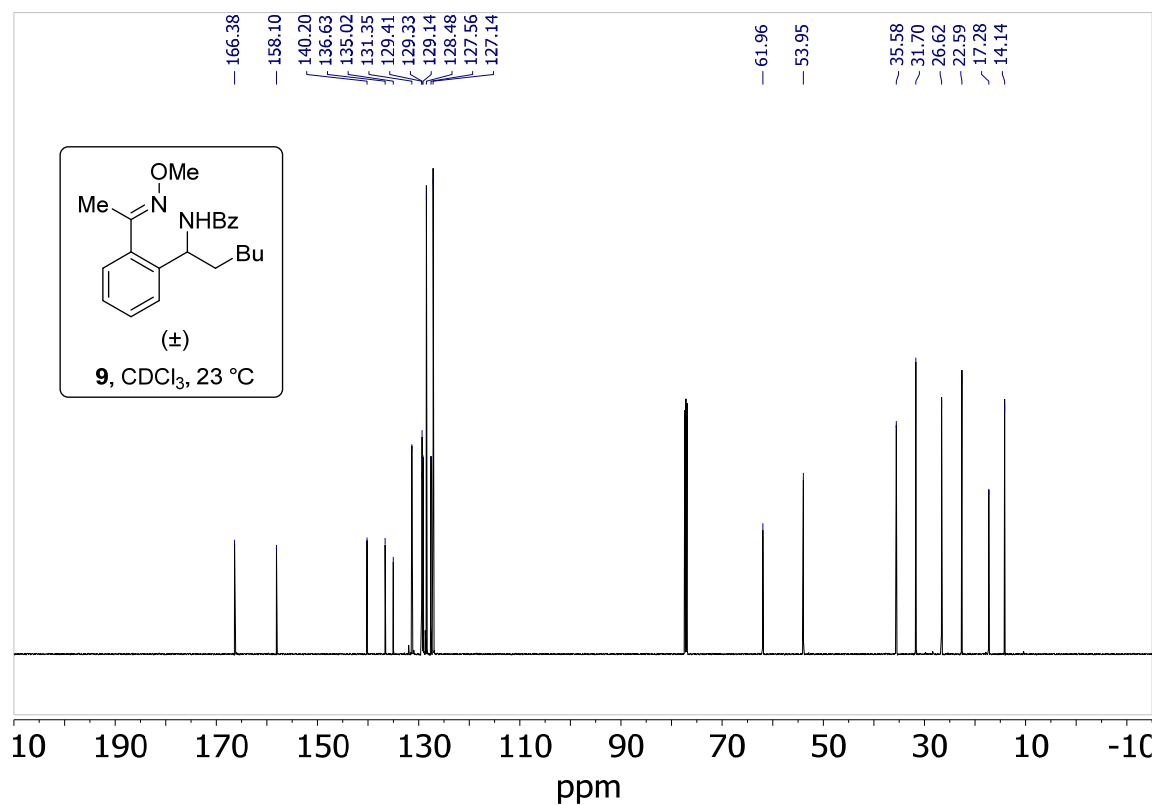
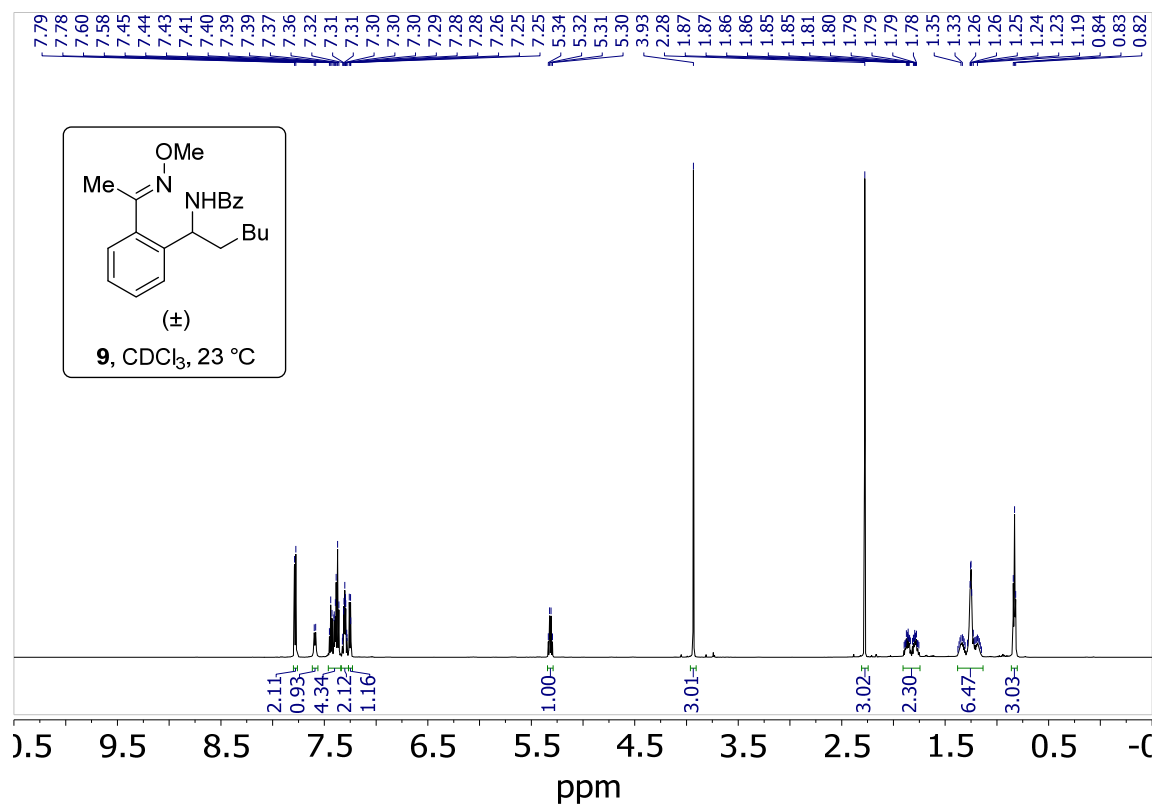
Reaction with 1 mol% Rh-dimer cat. loading

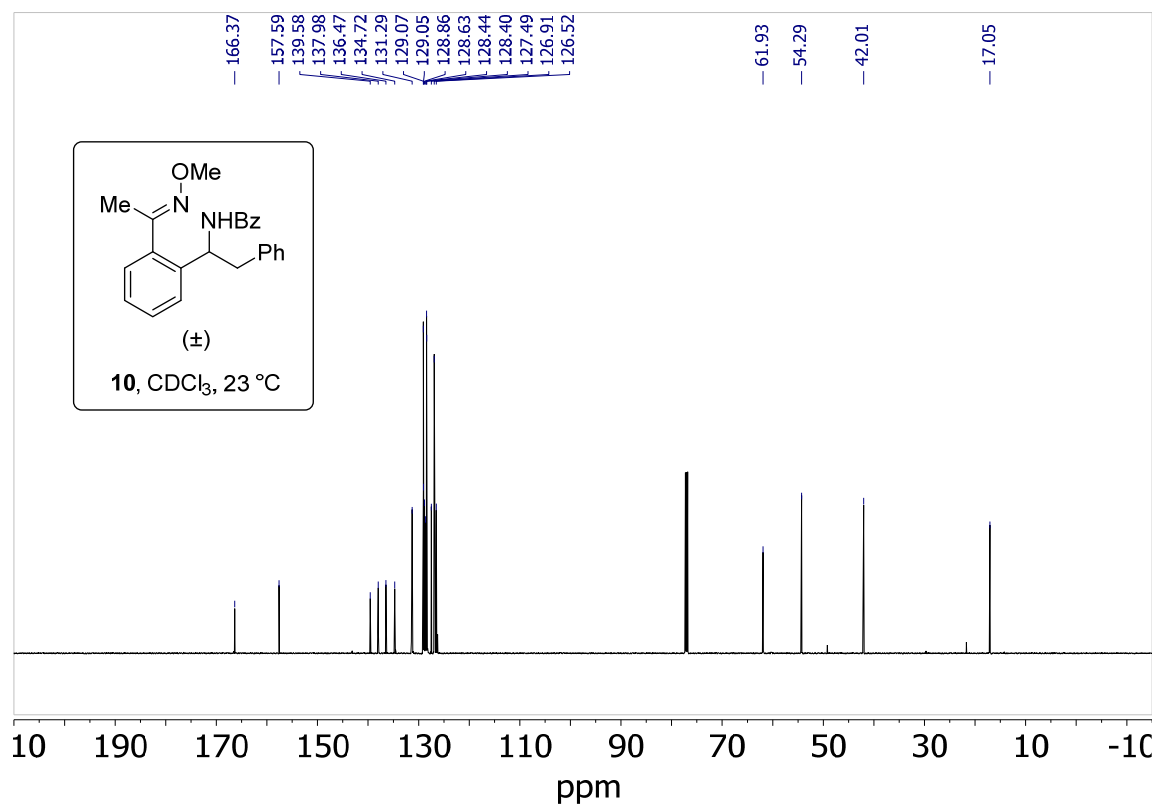
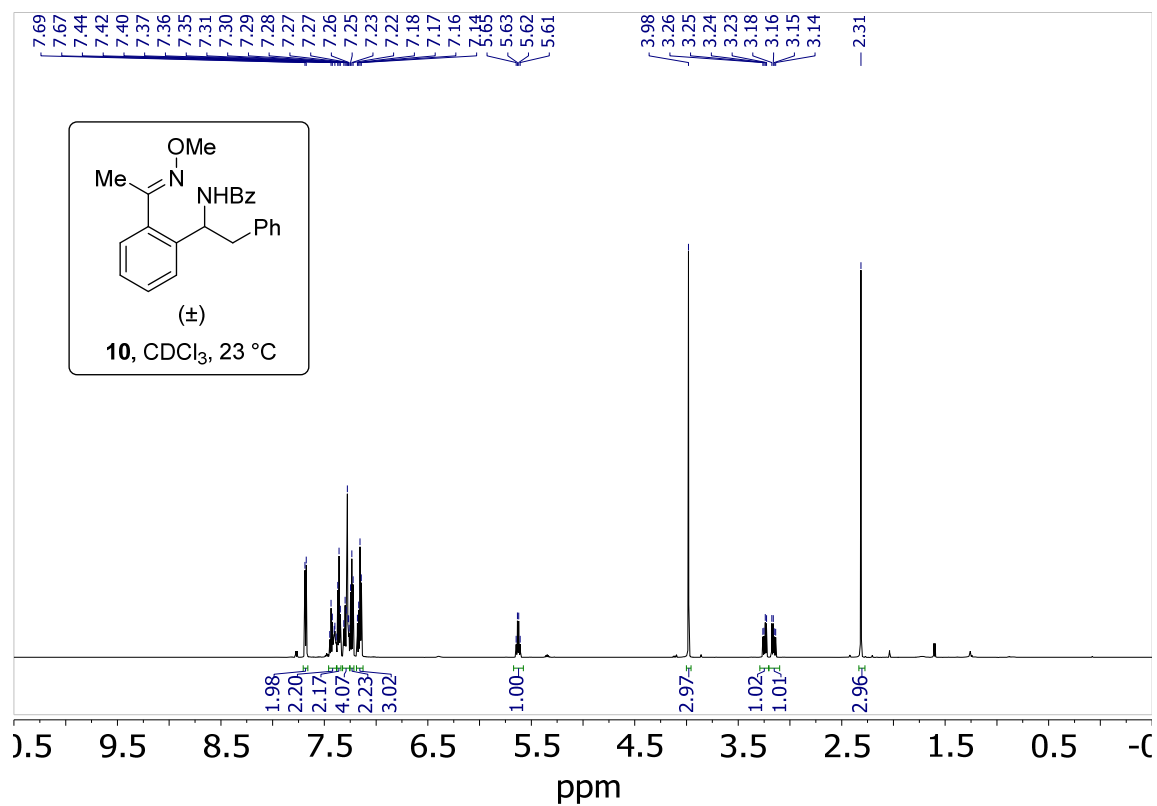


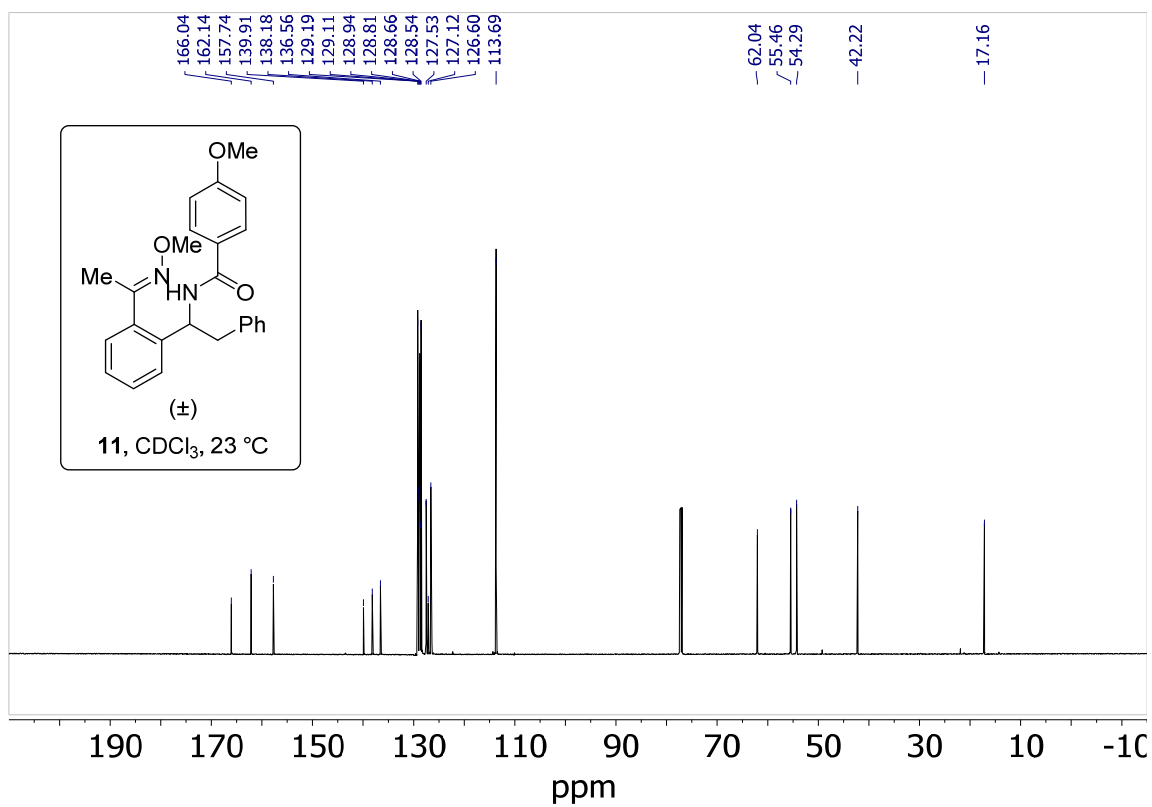
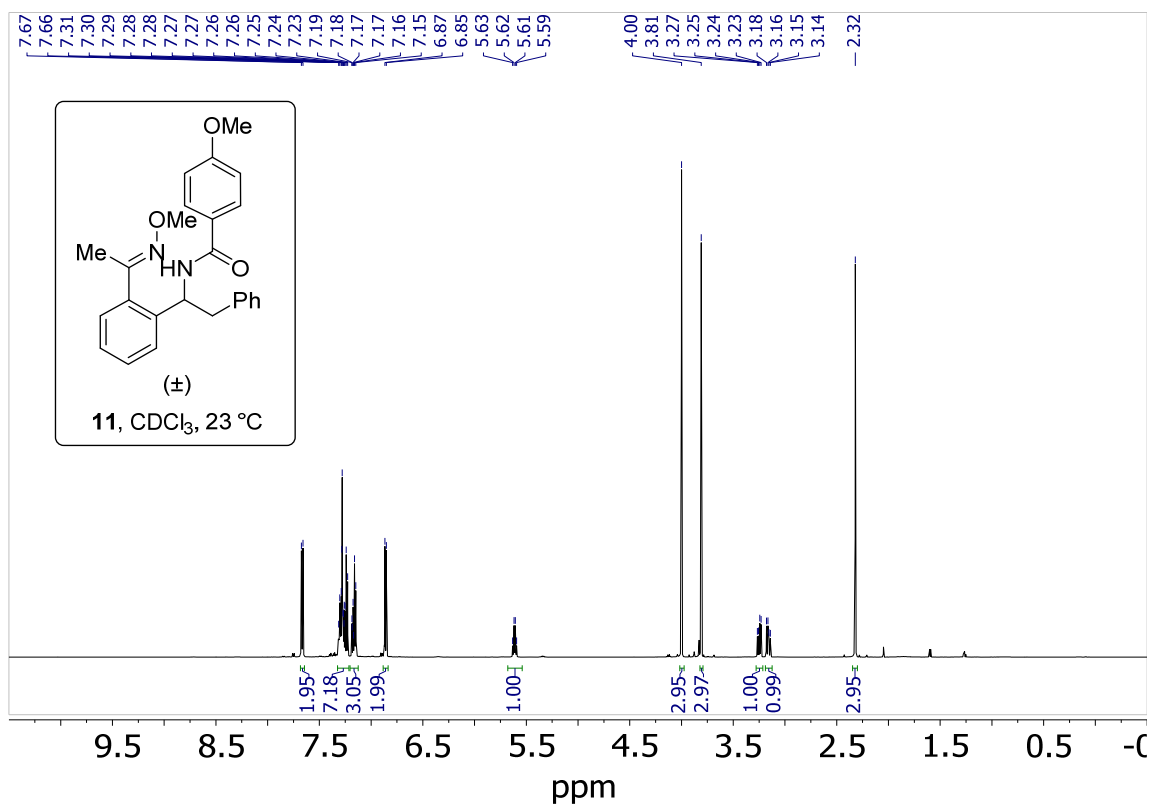


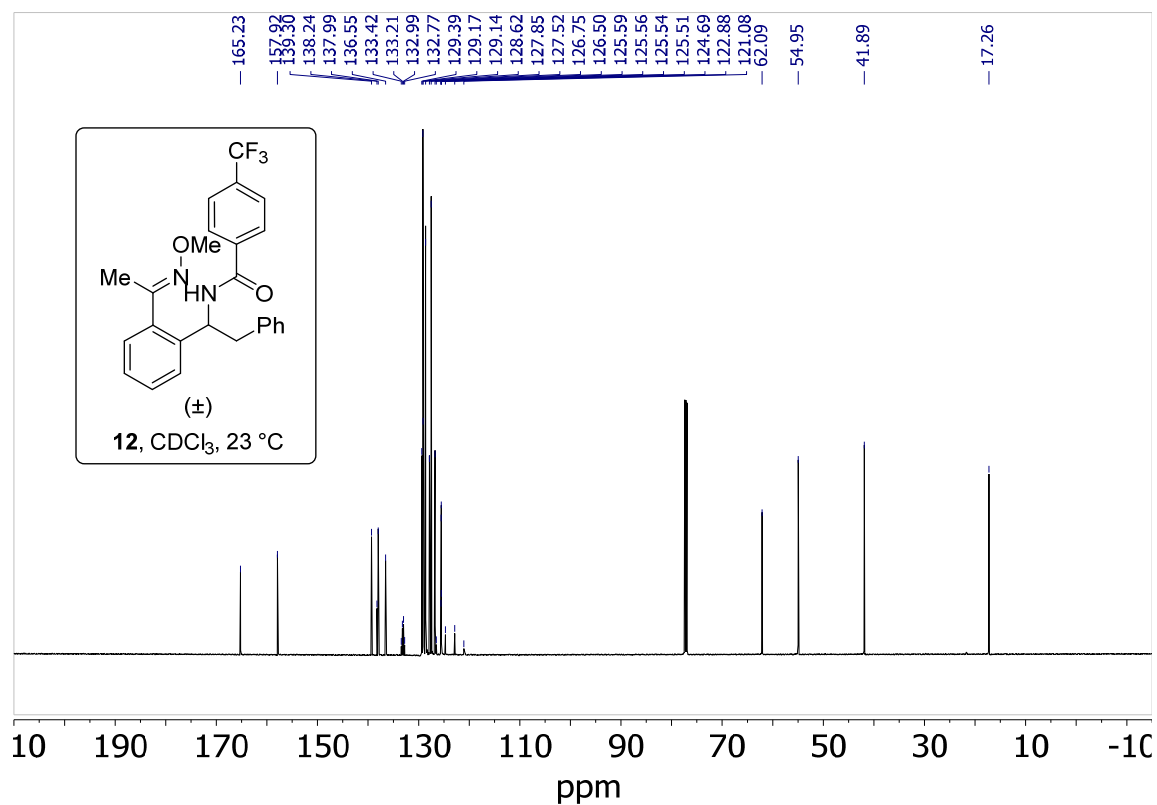
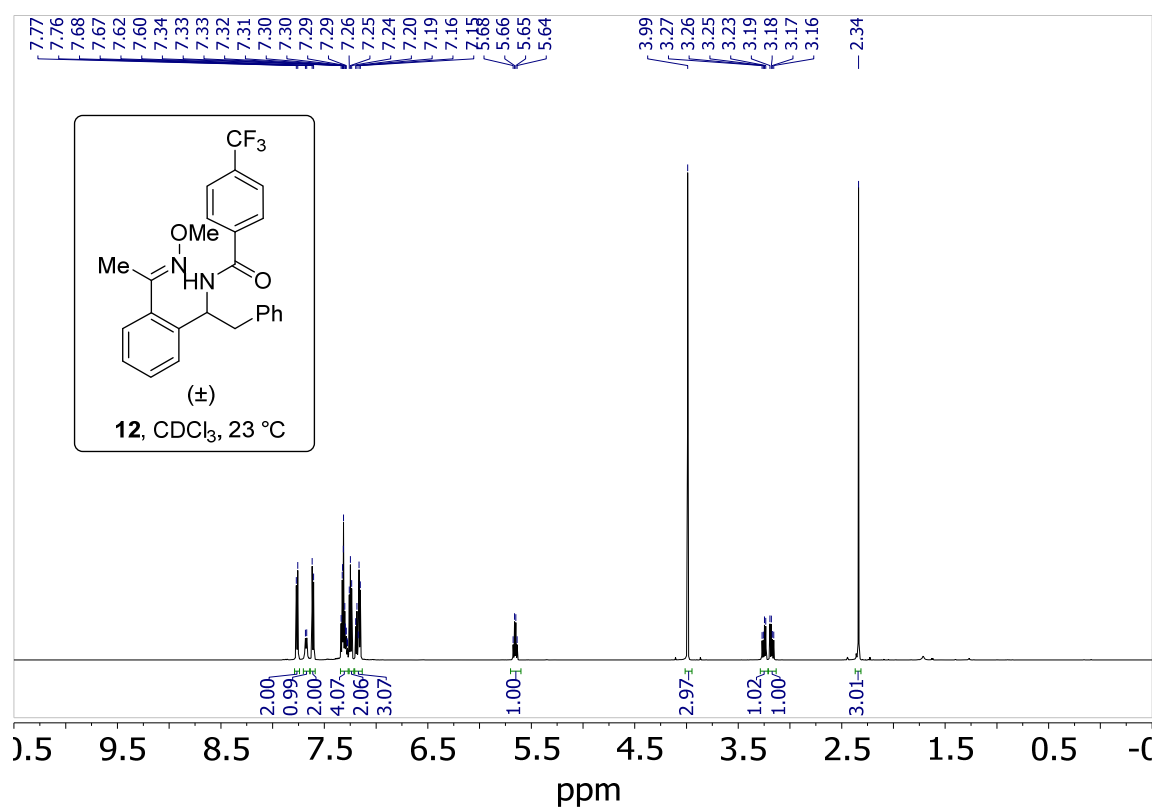


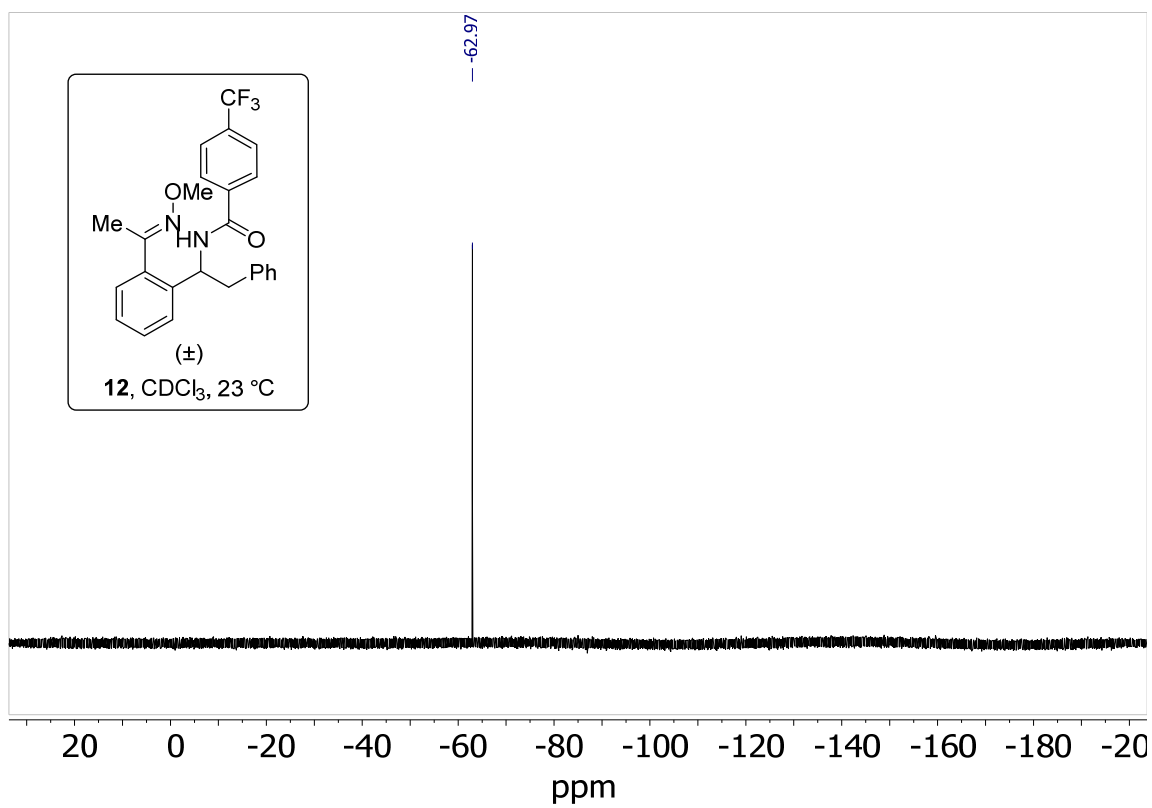


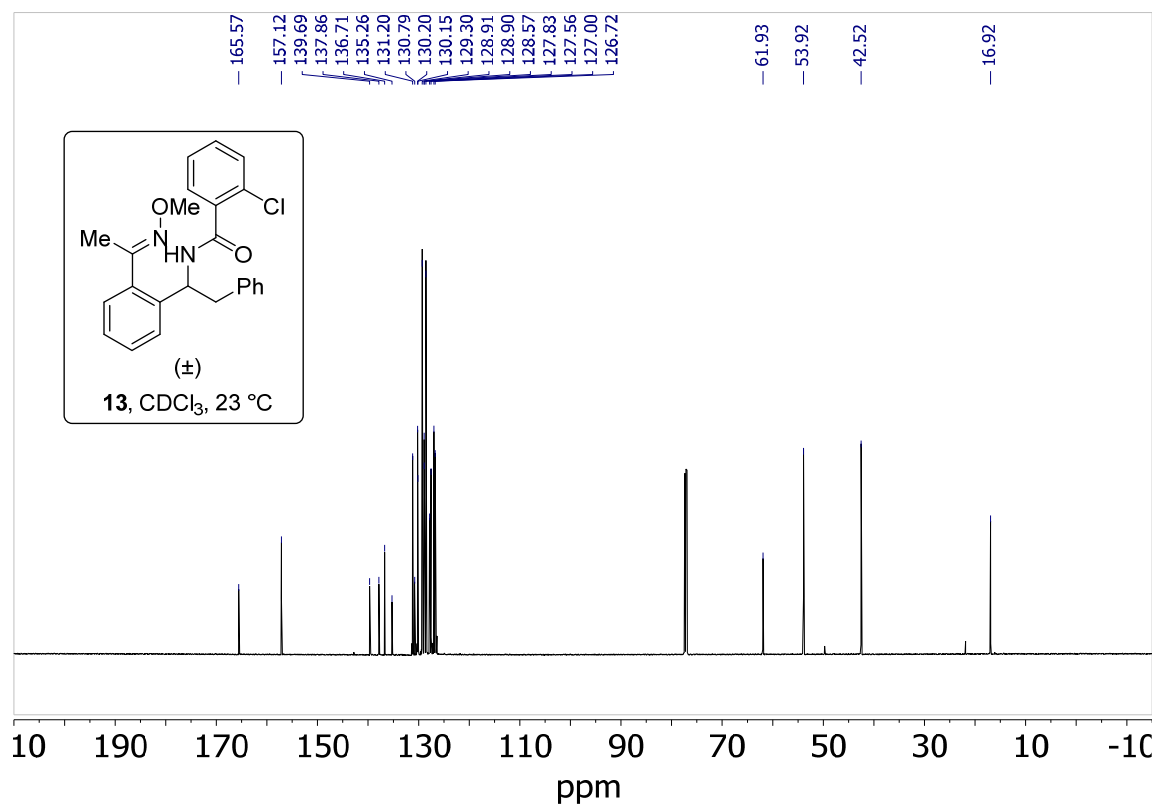
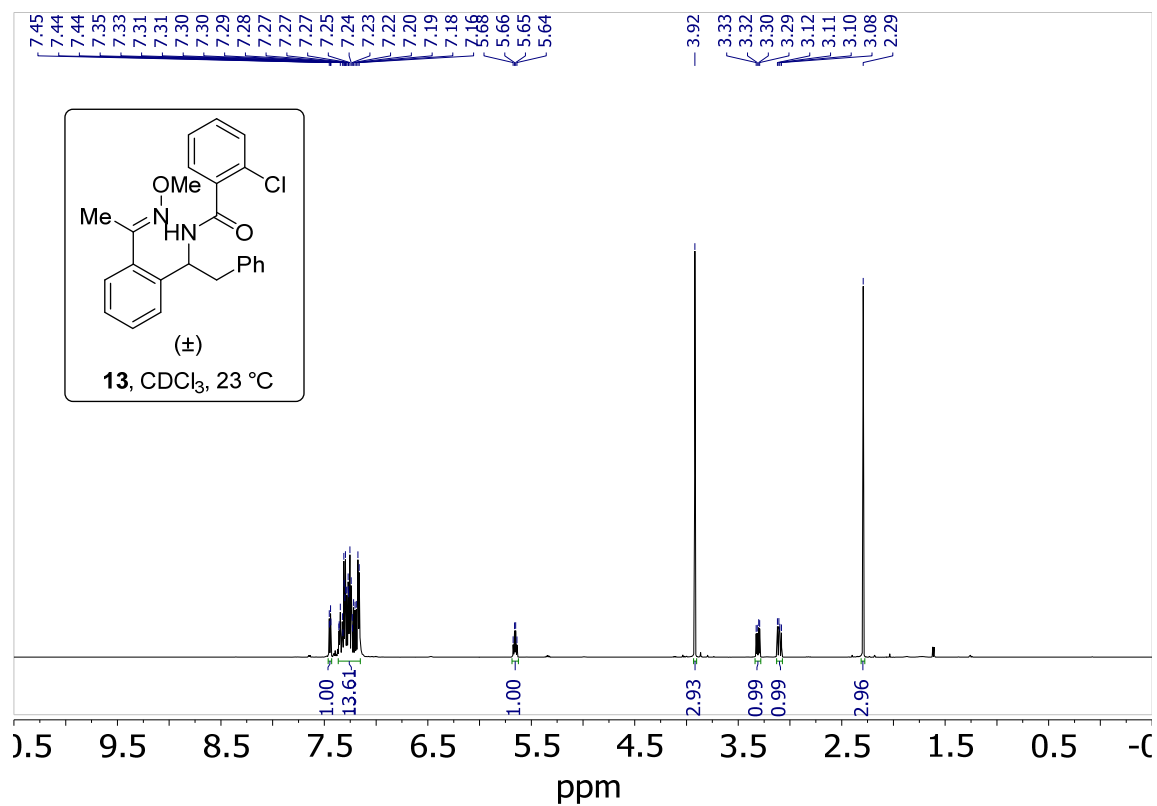


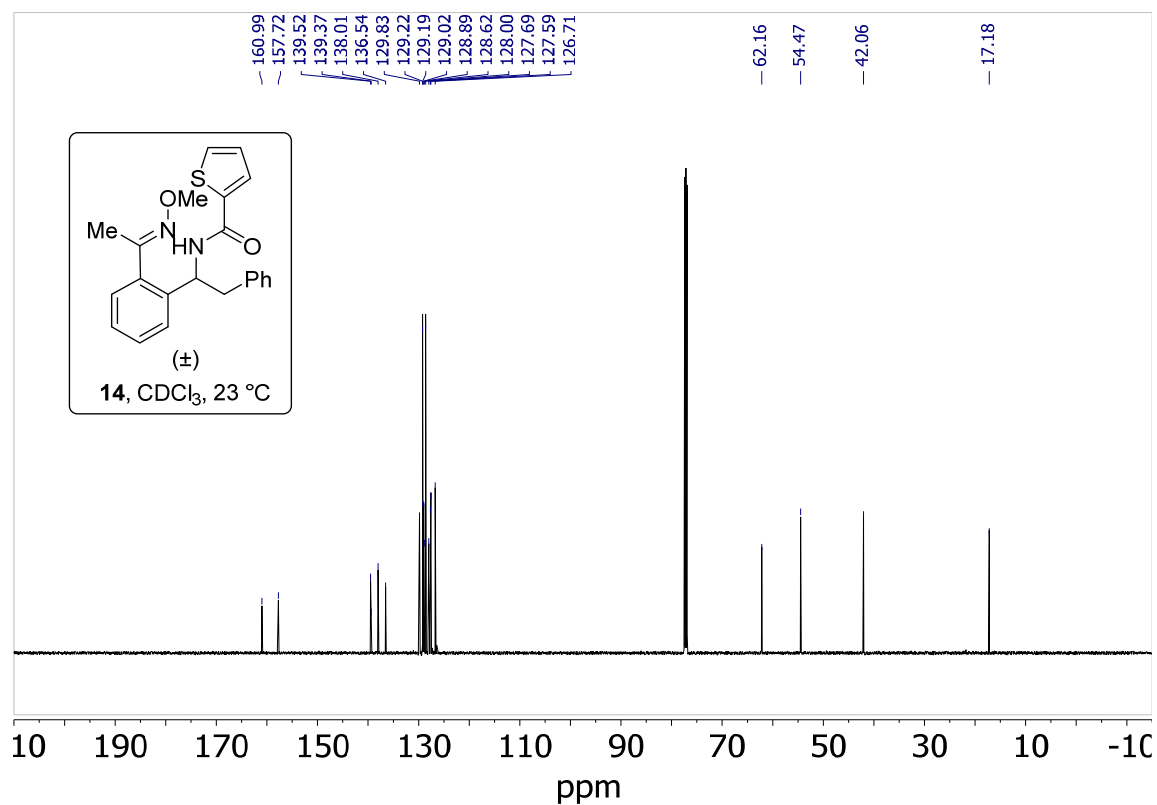
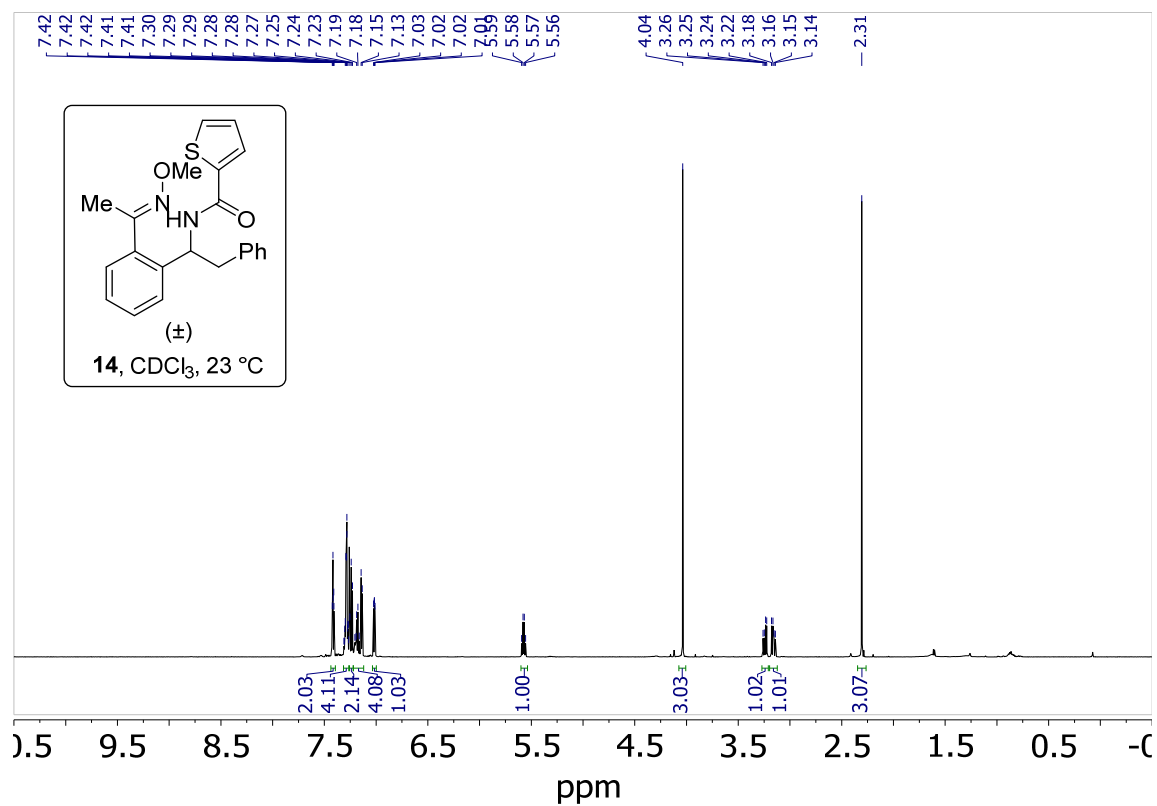


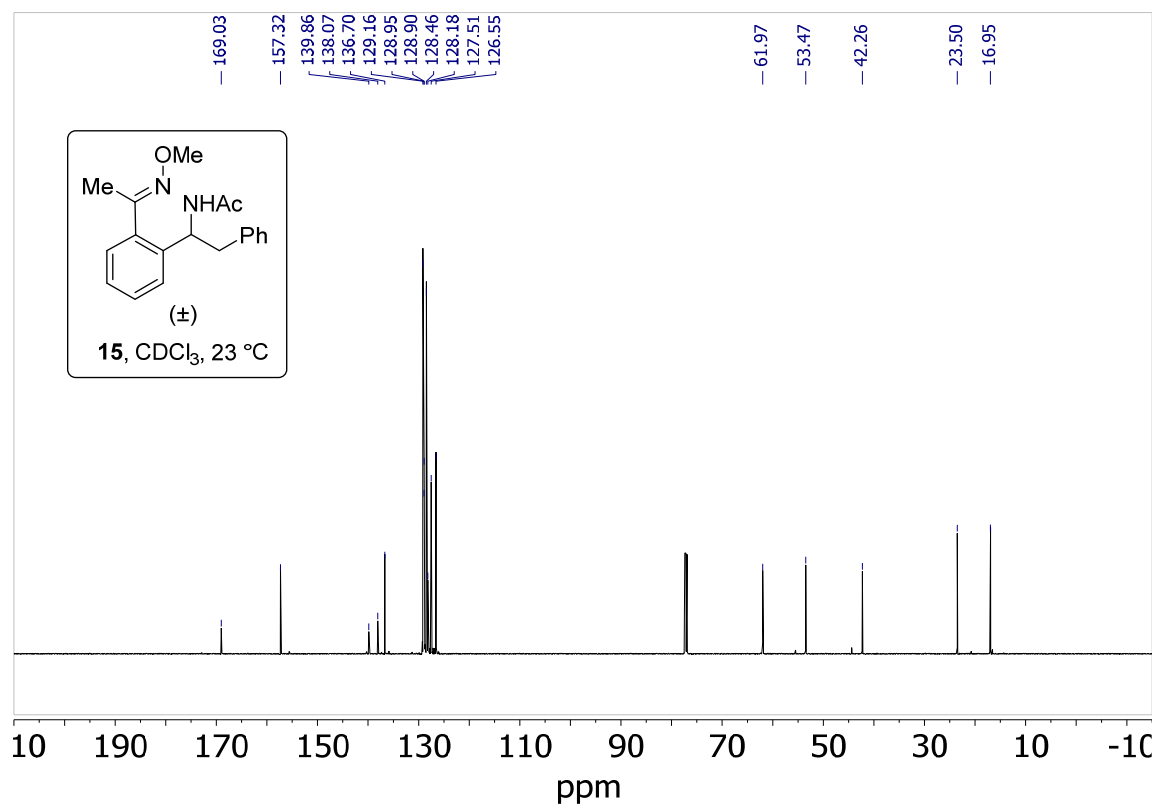
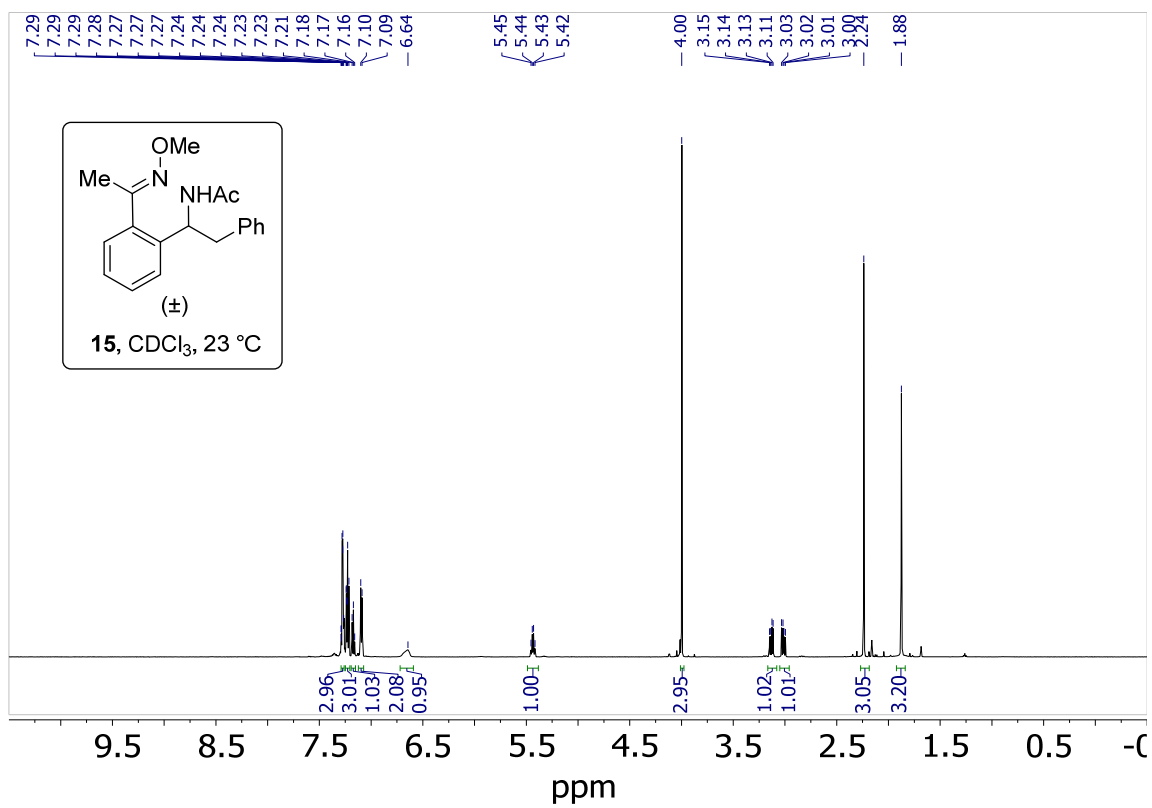


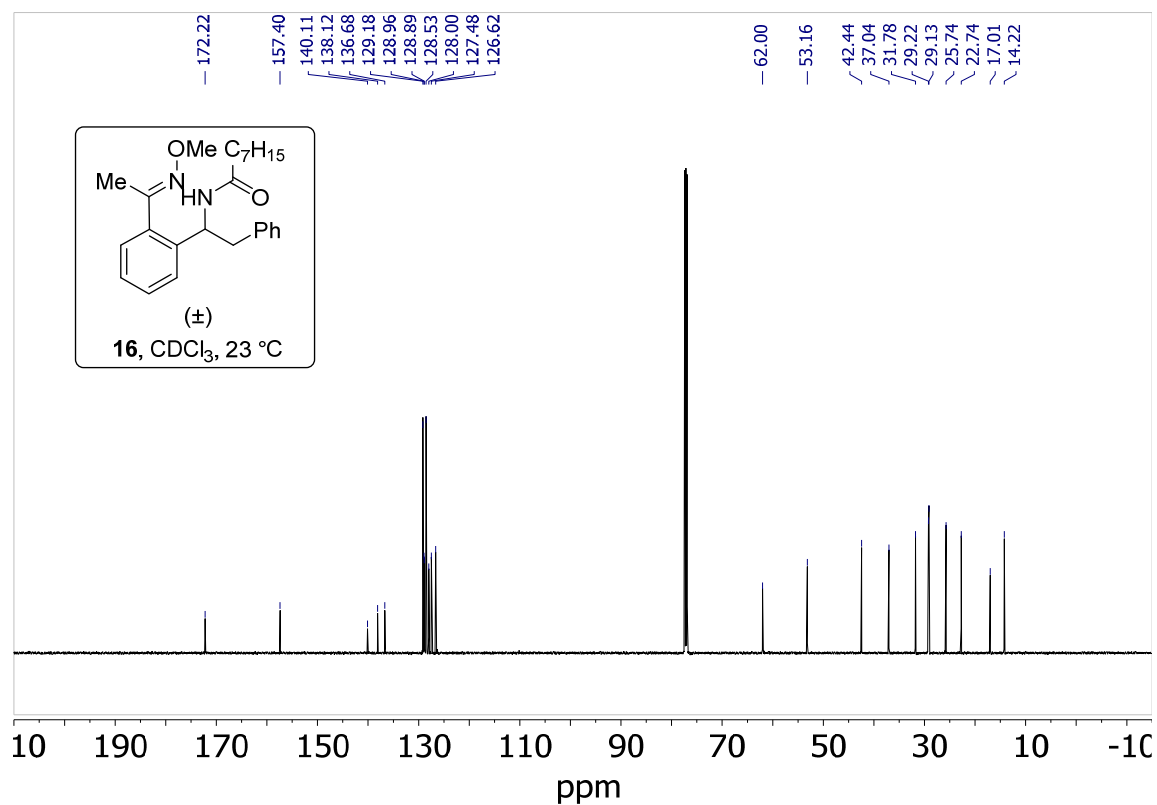
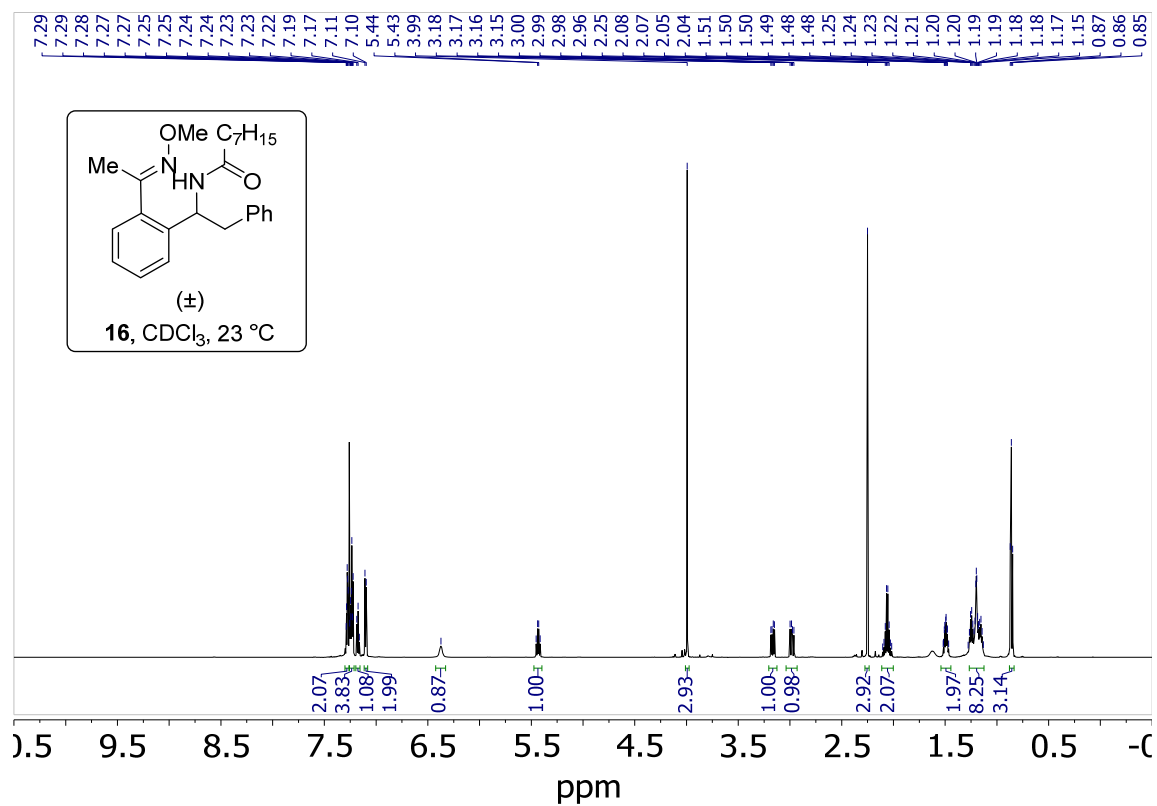


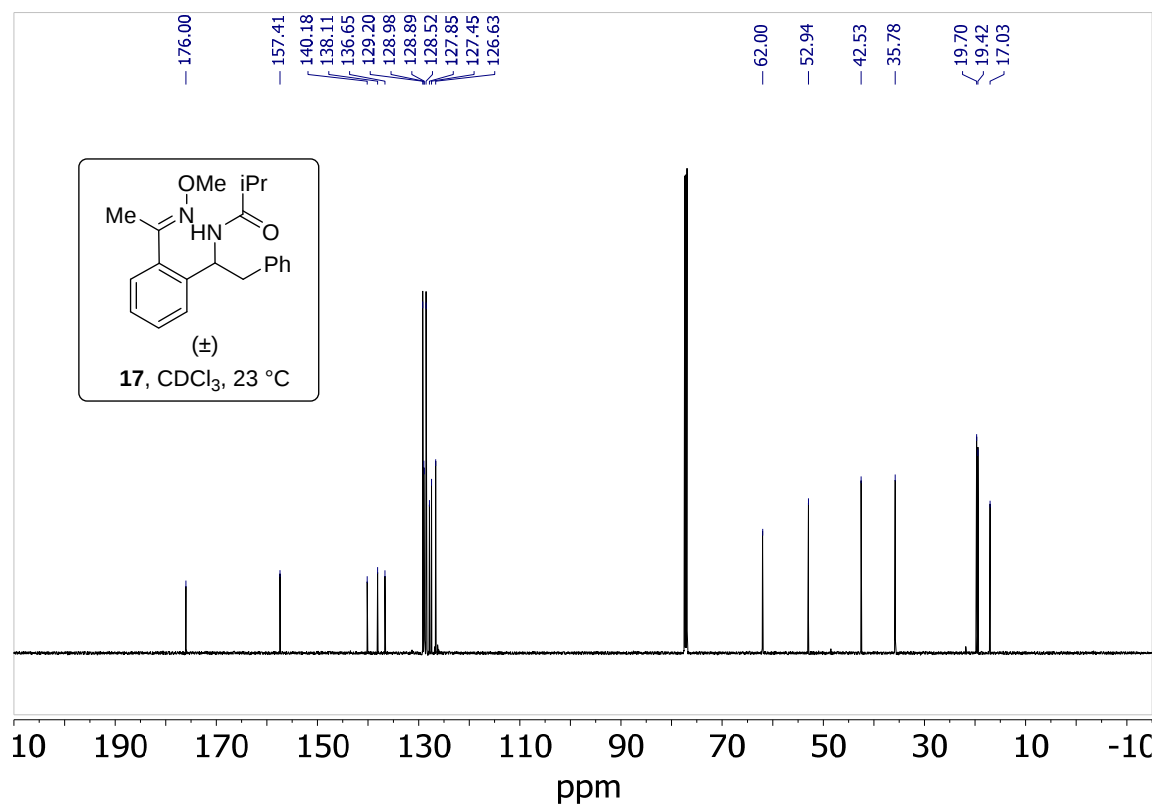
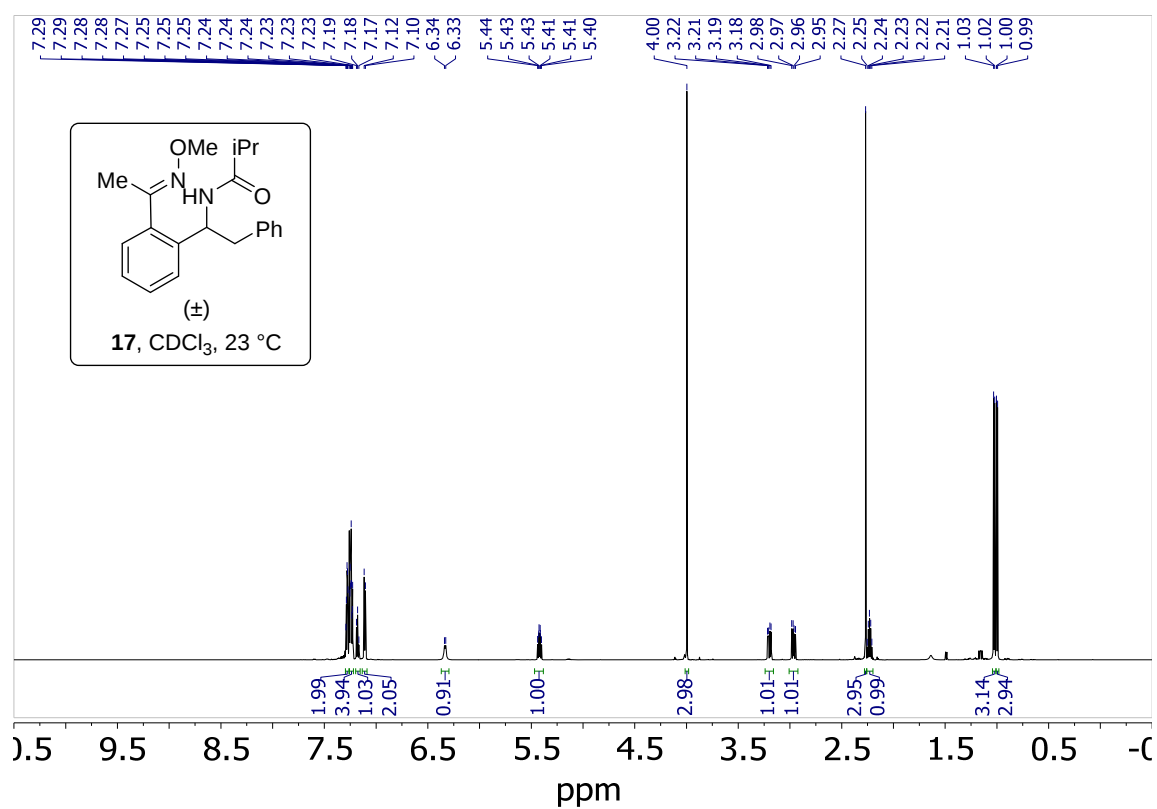


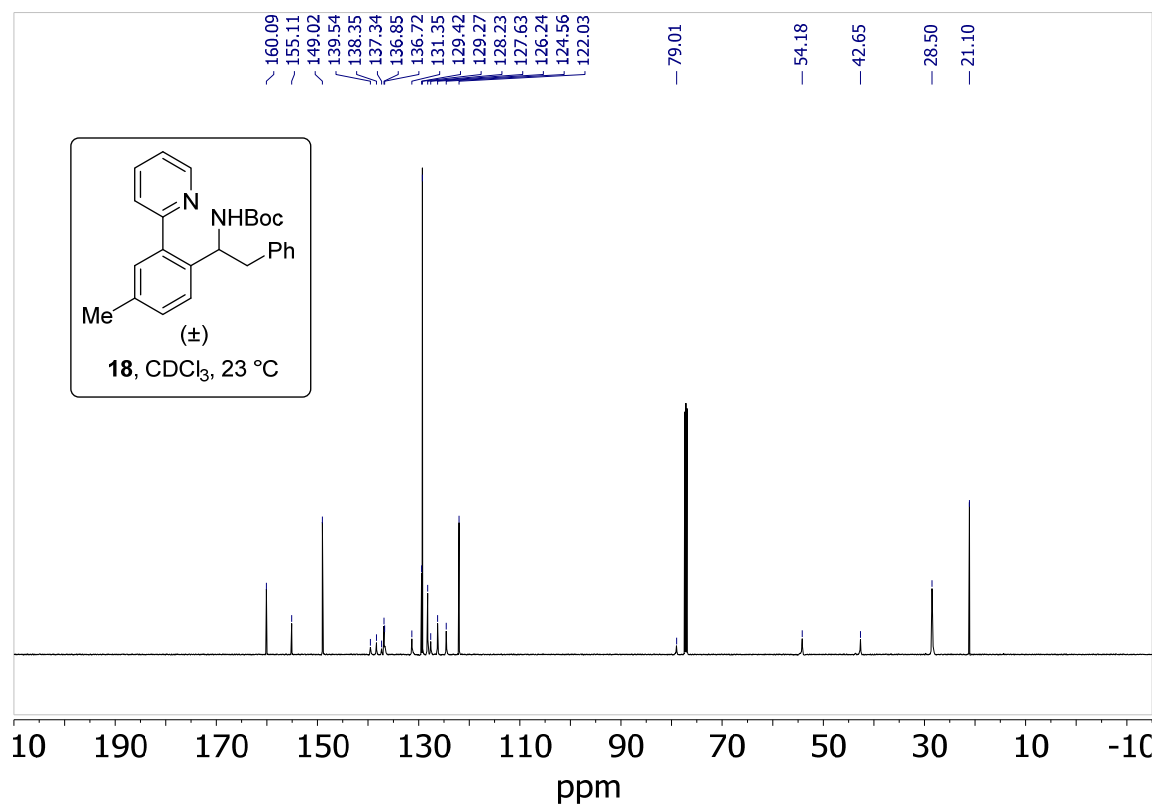
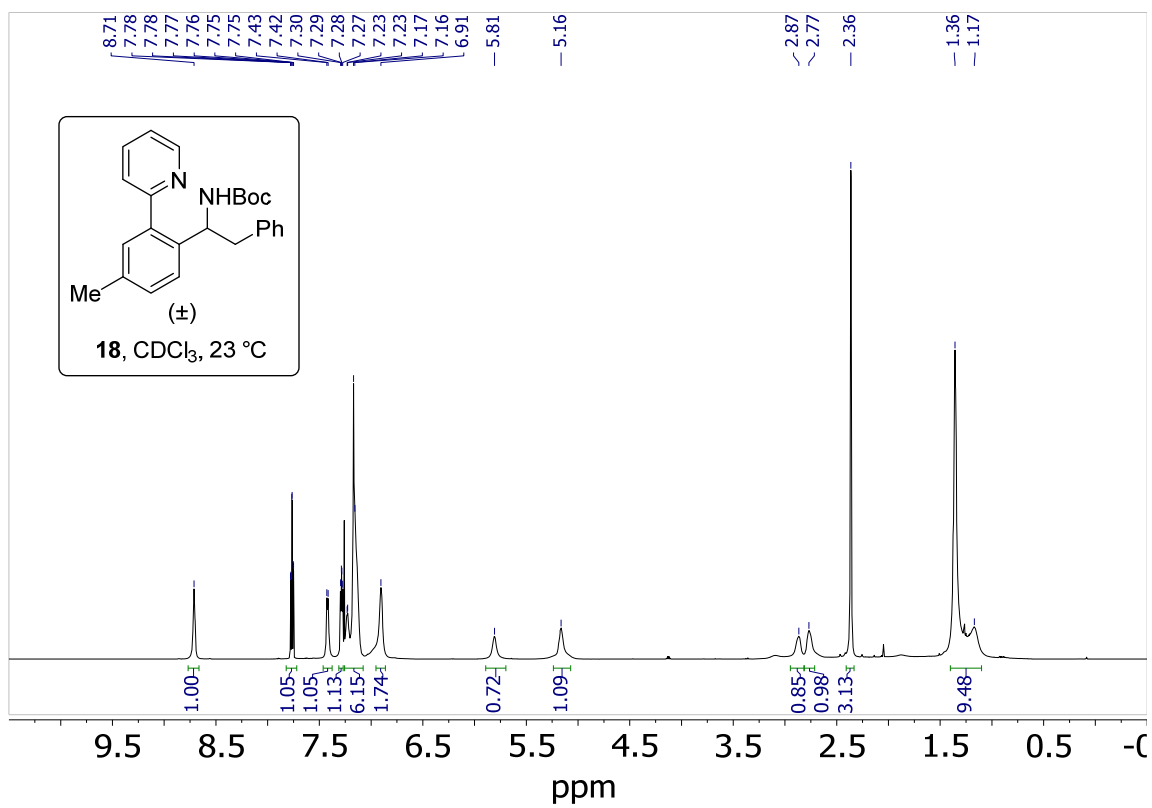


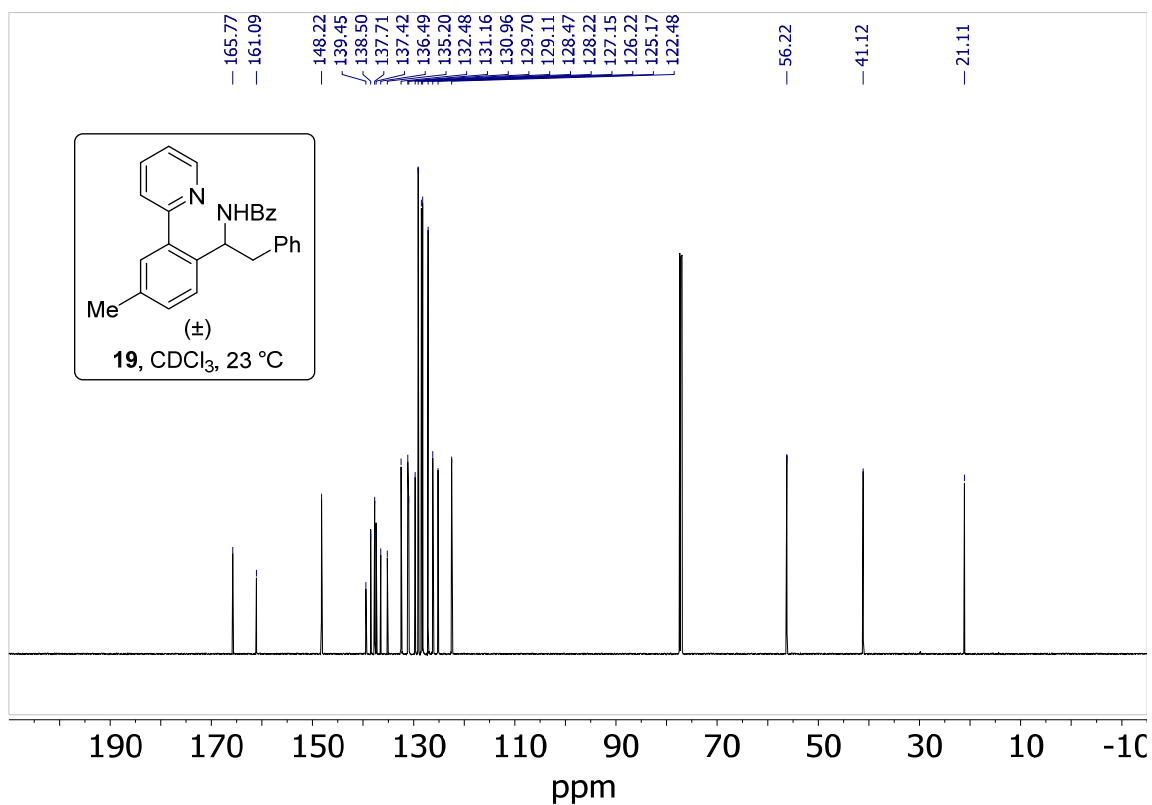
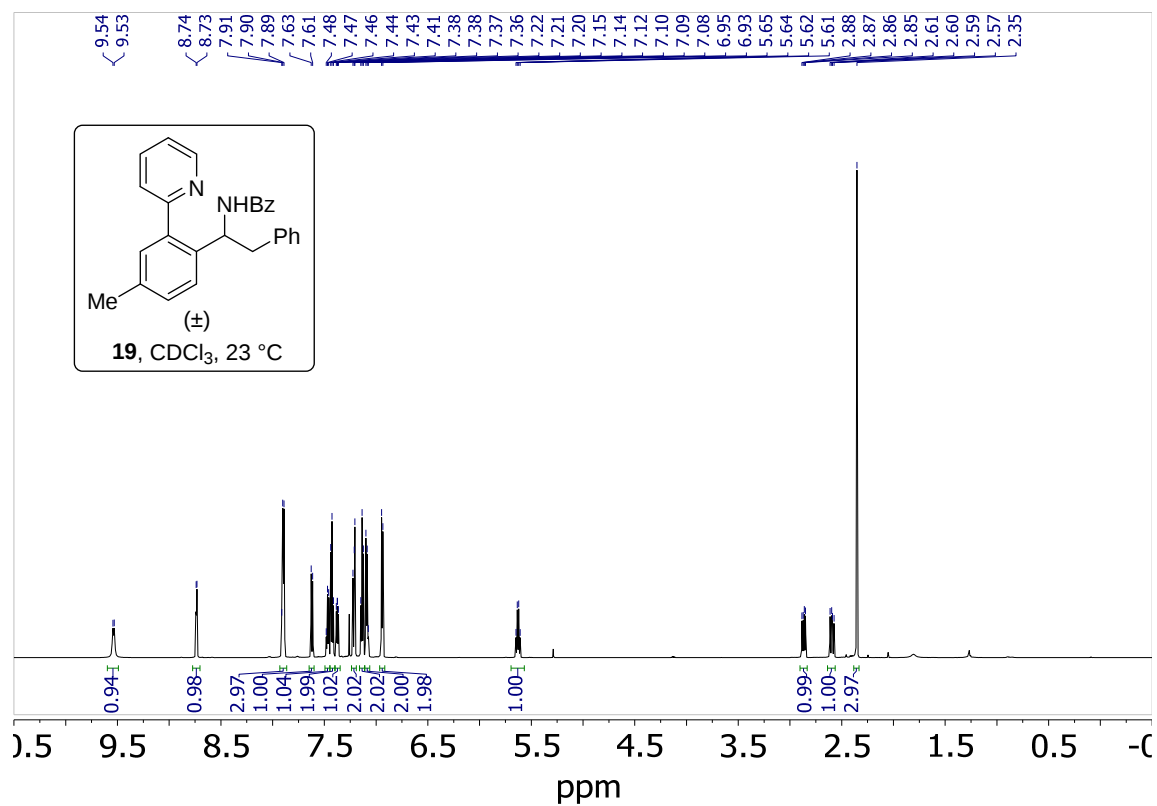


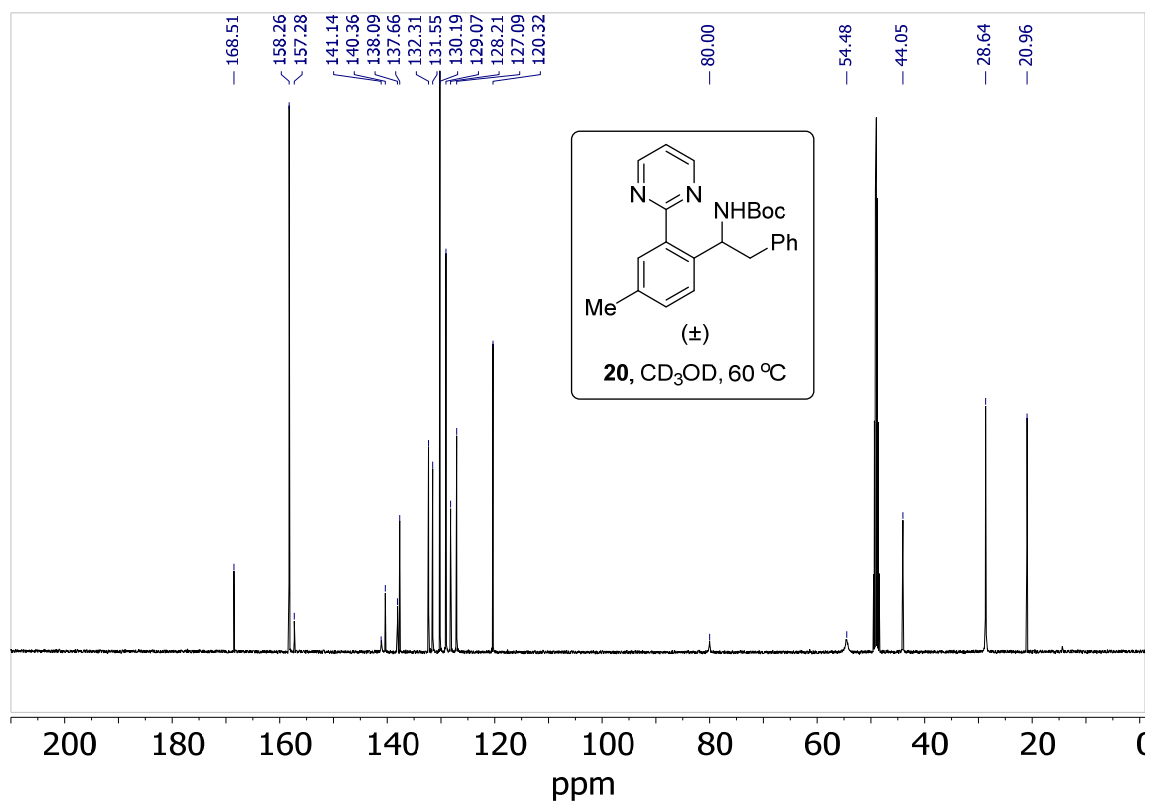
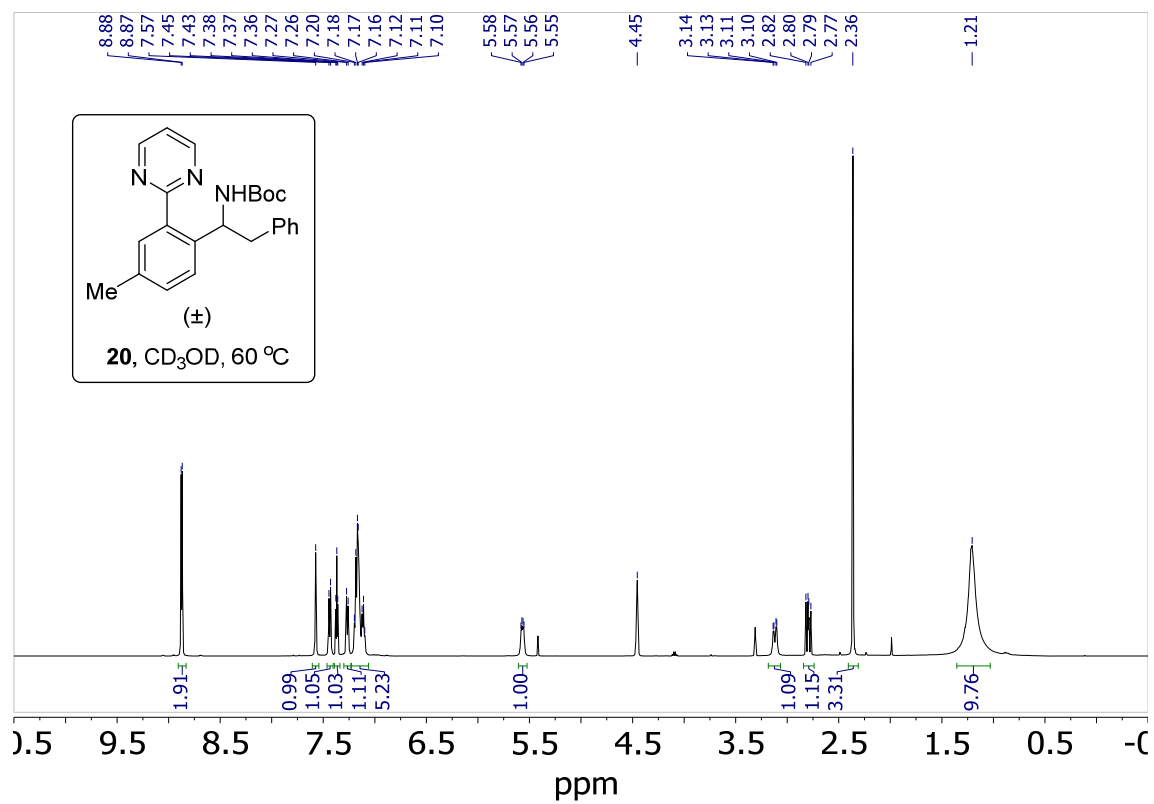


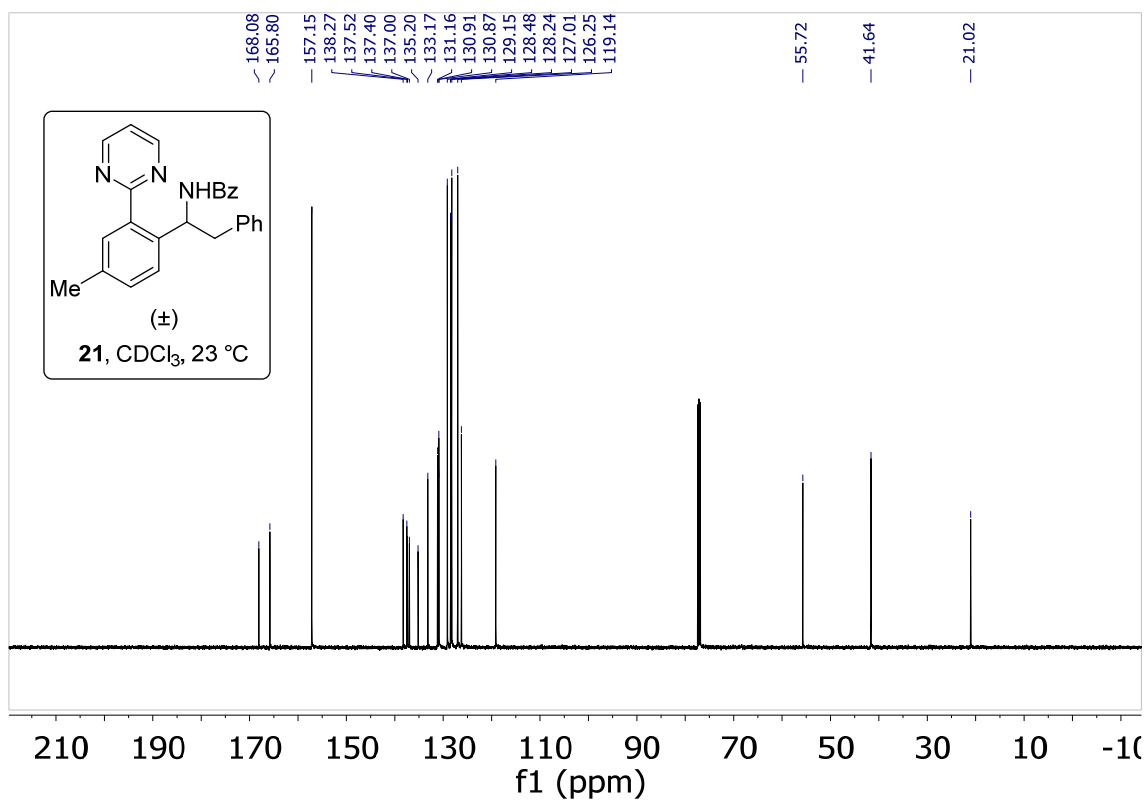
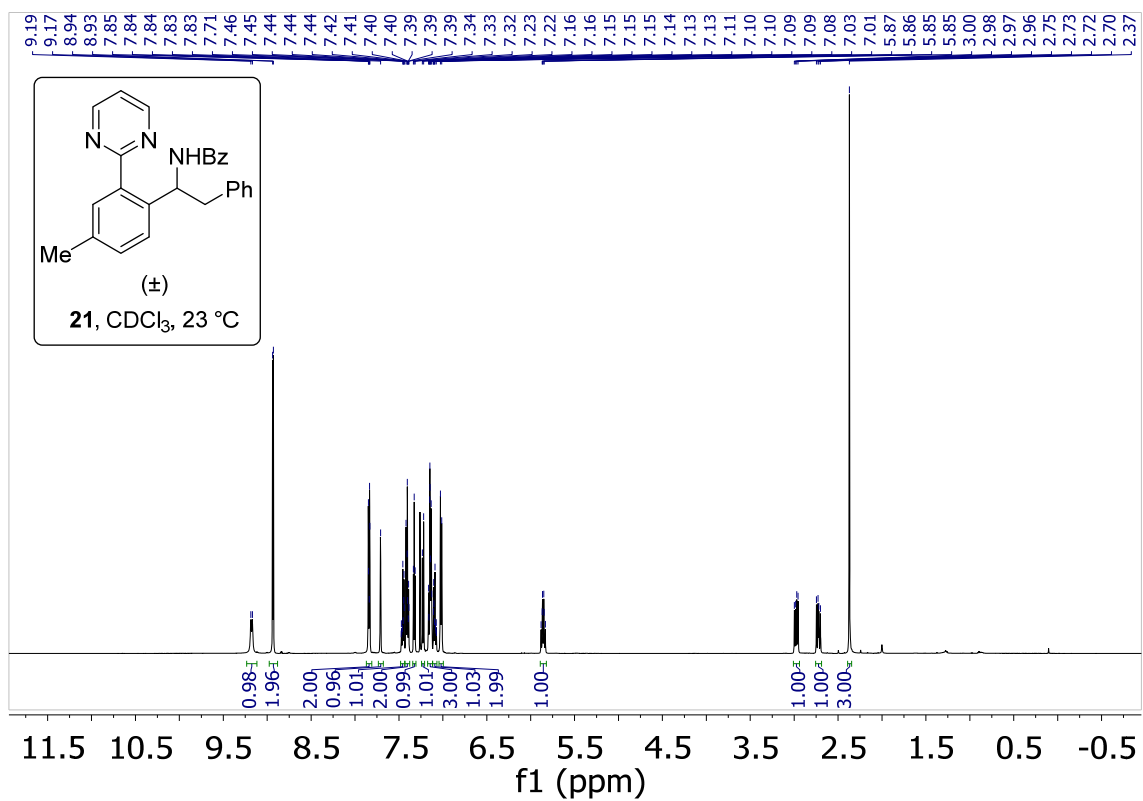


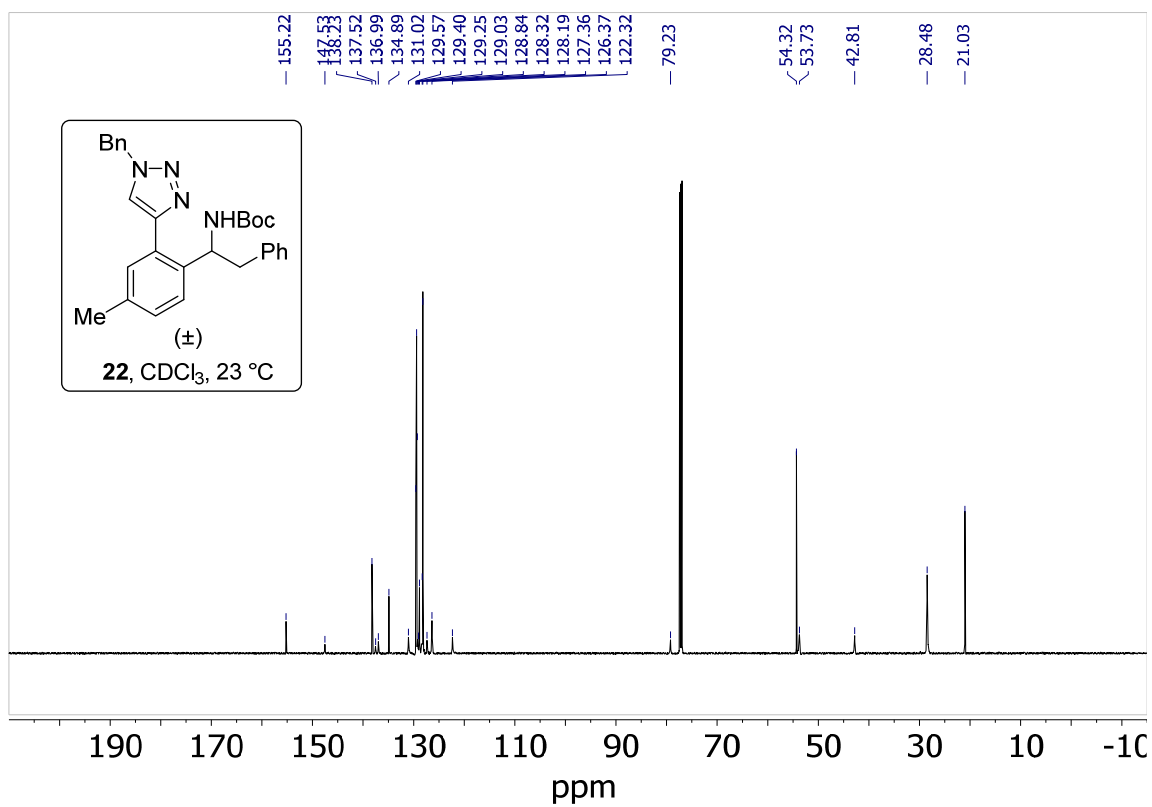
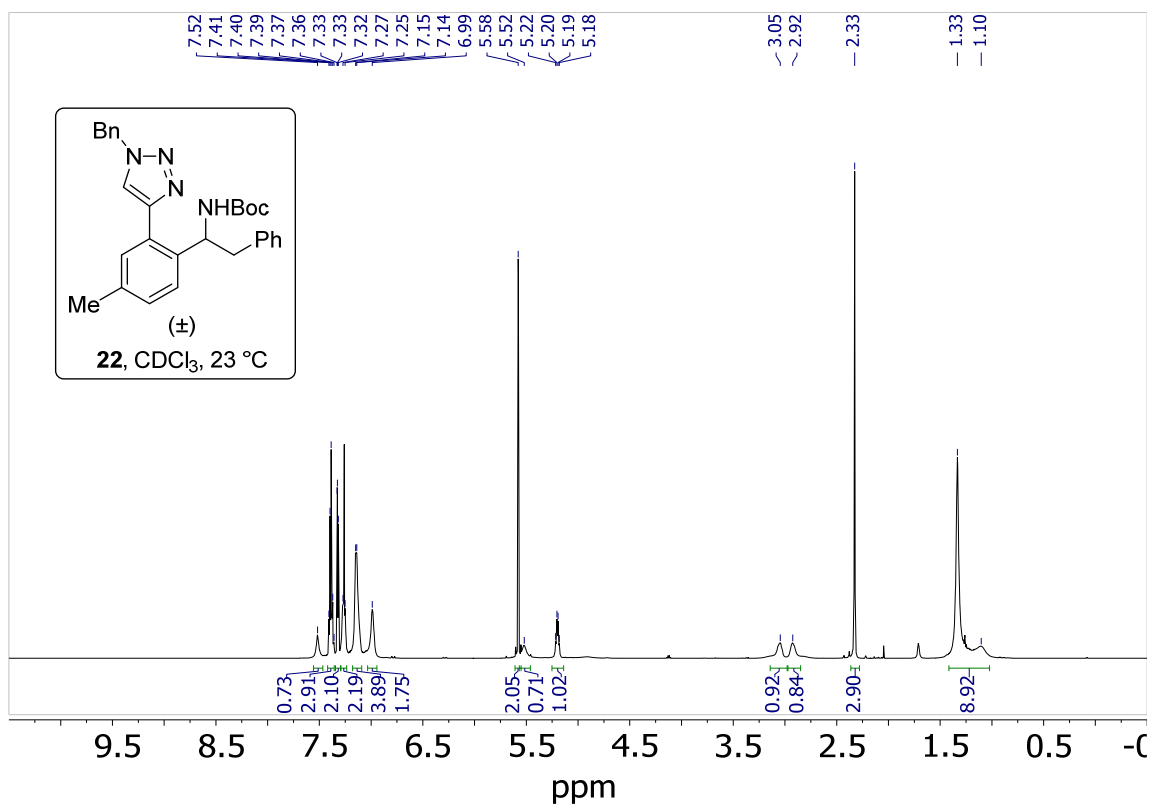


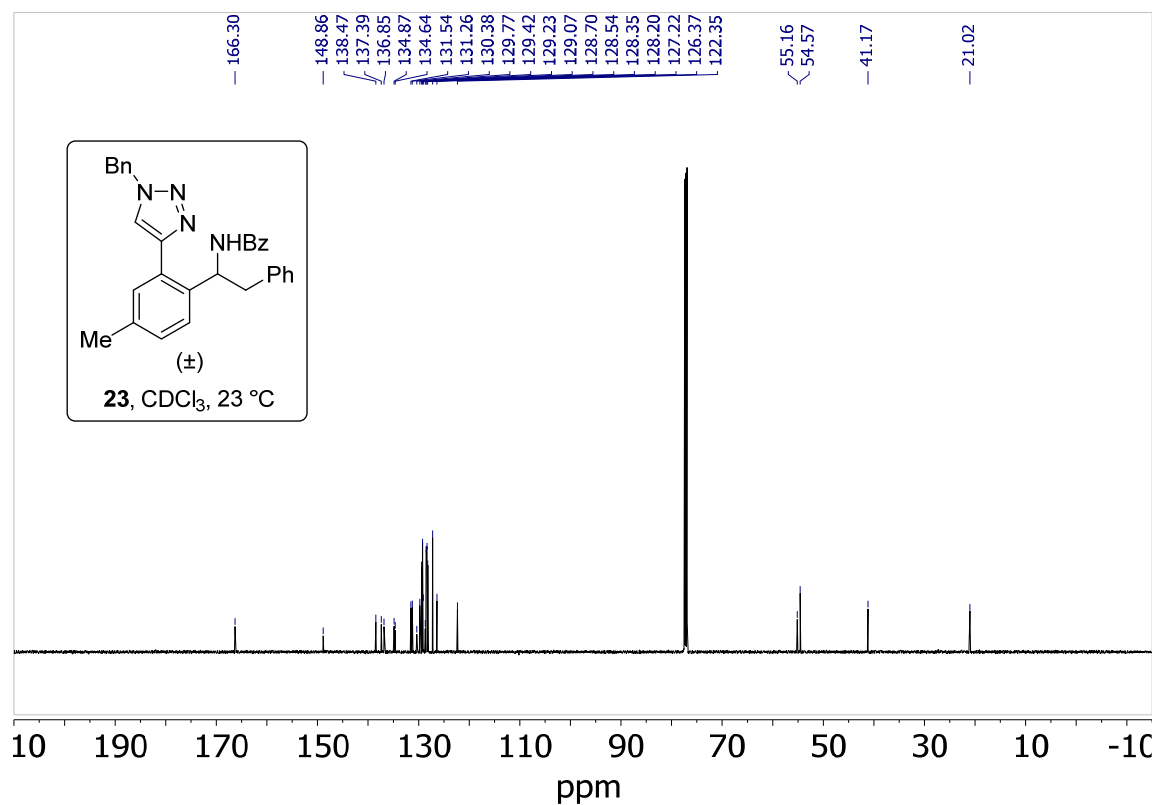
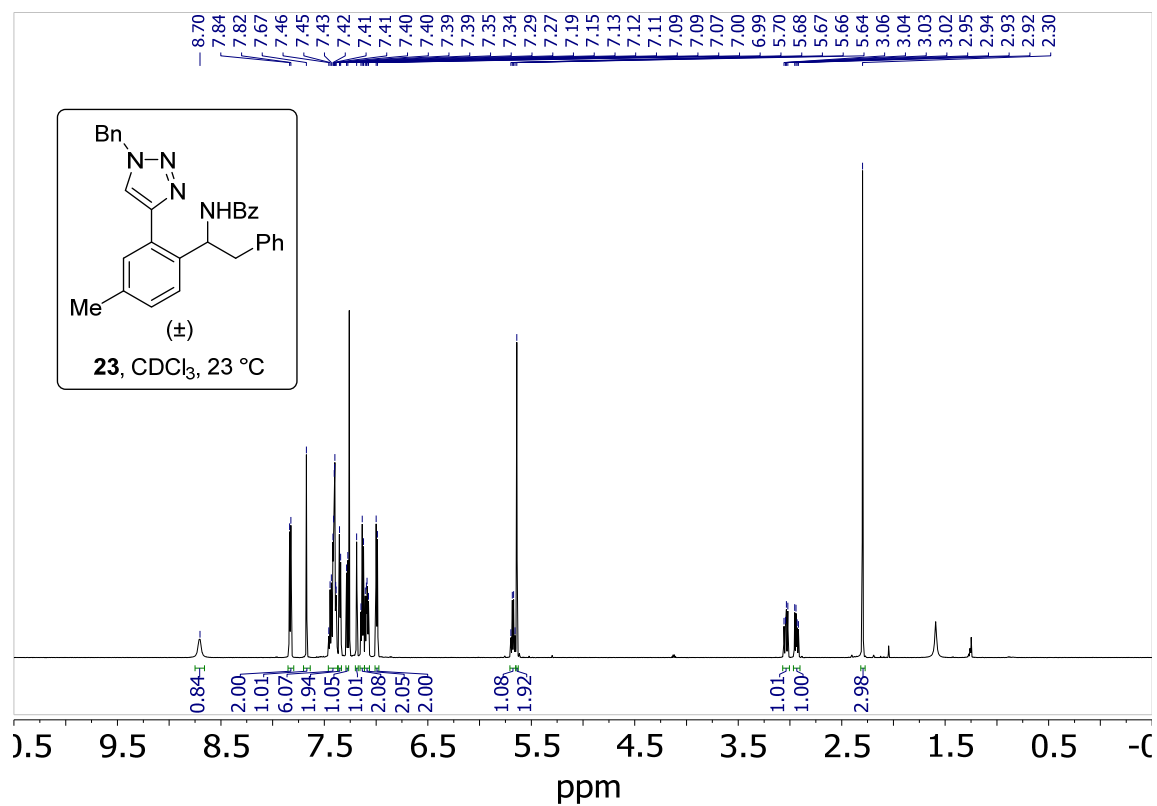


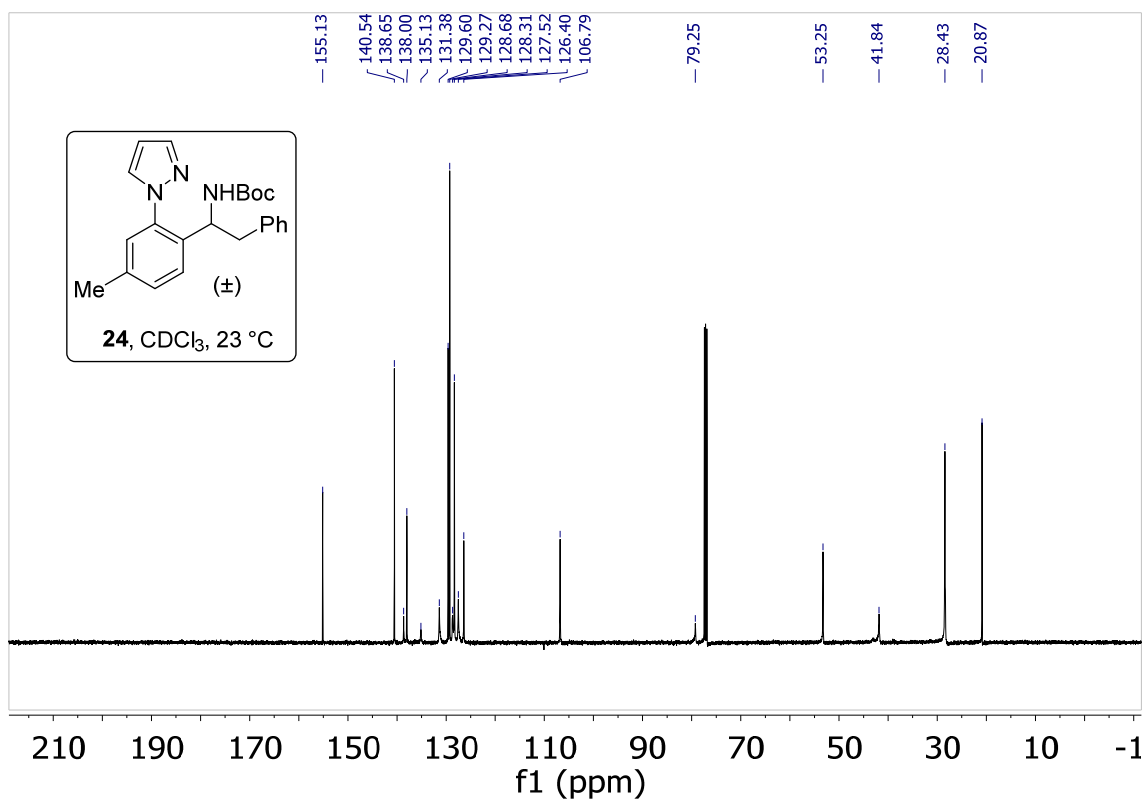
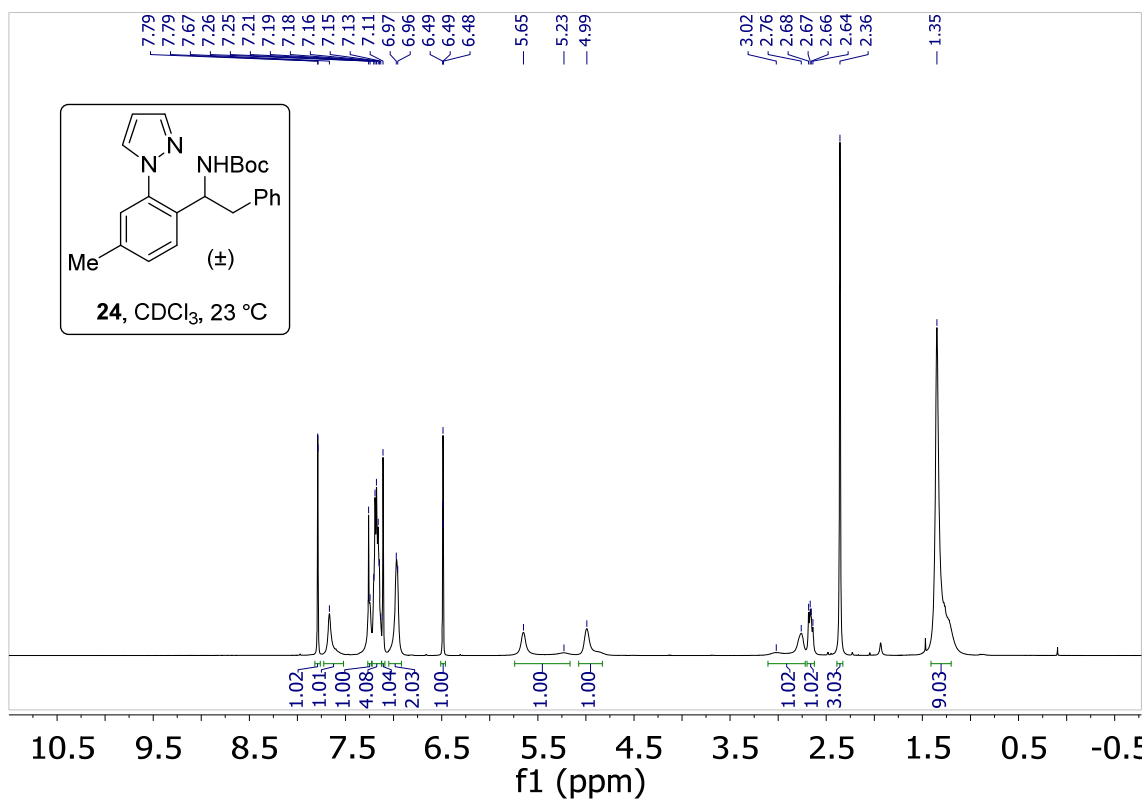


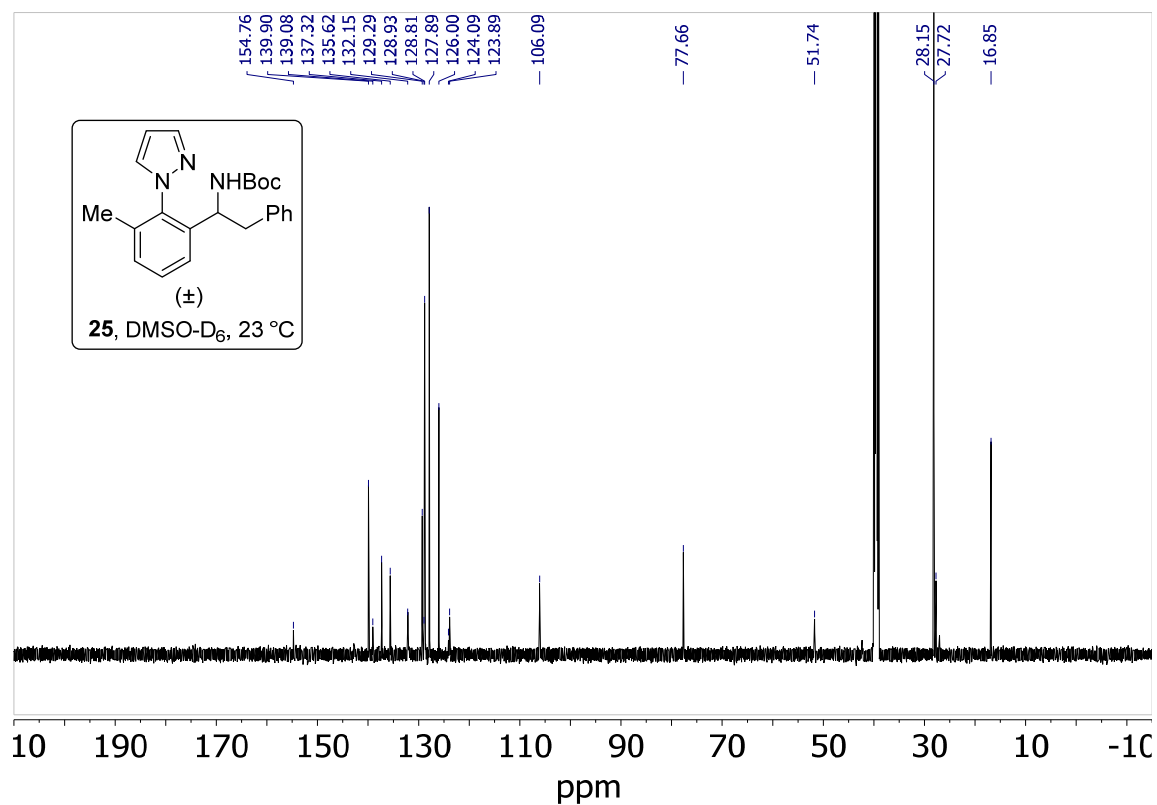
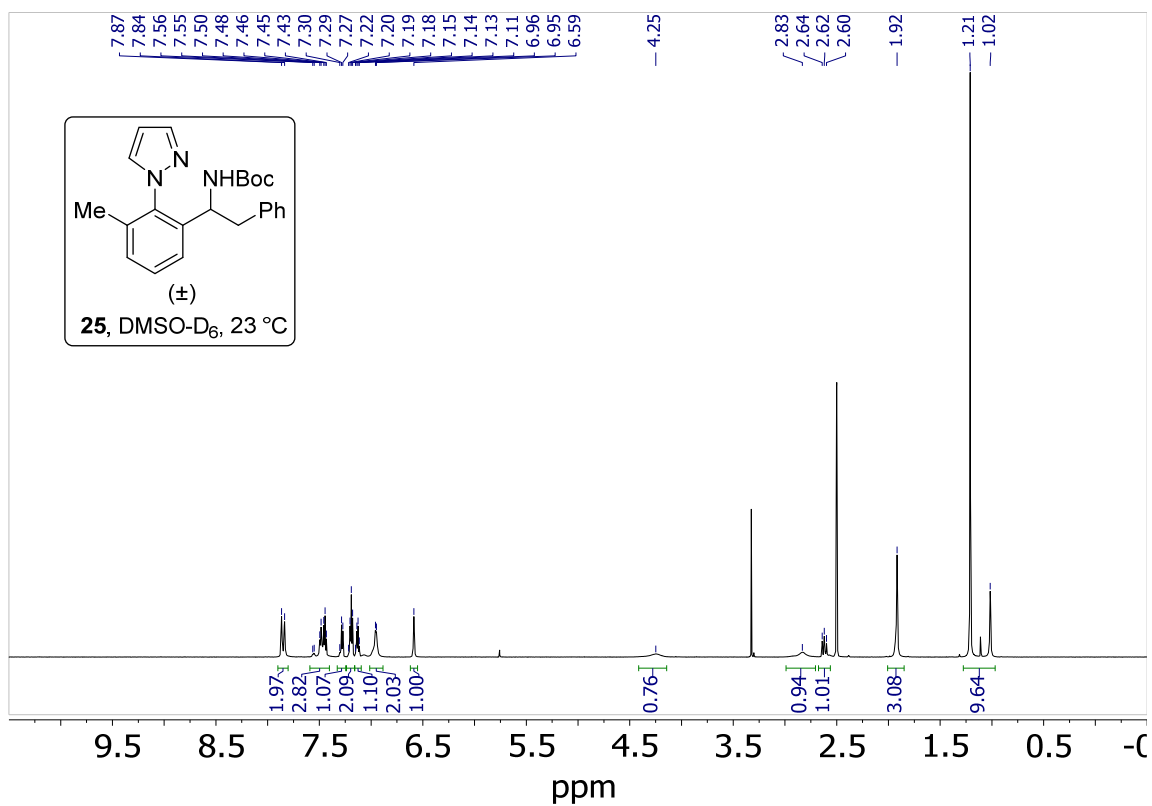


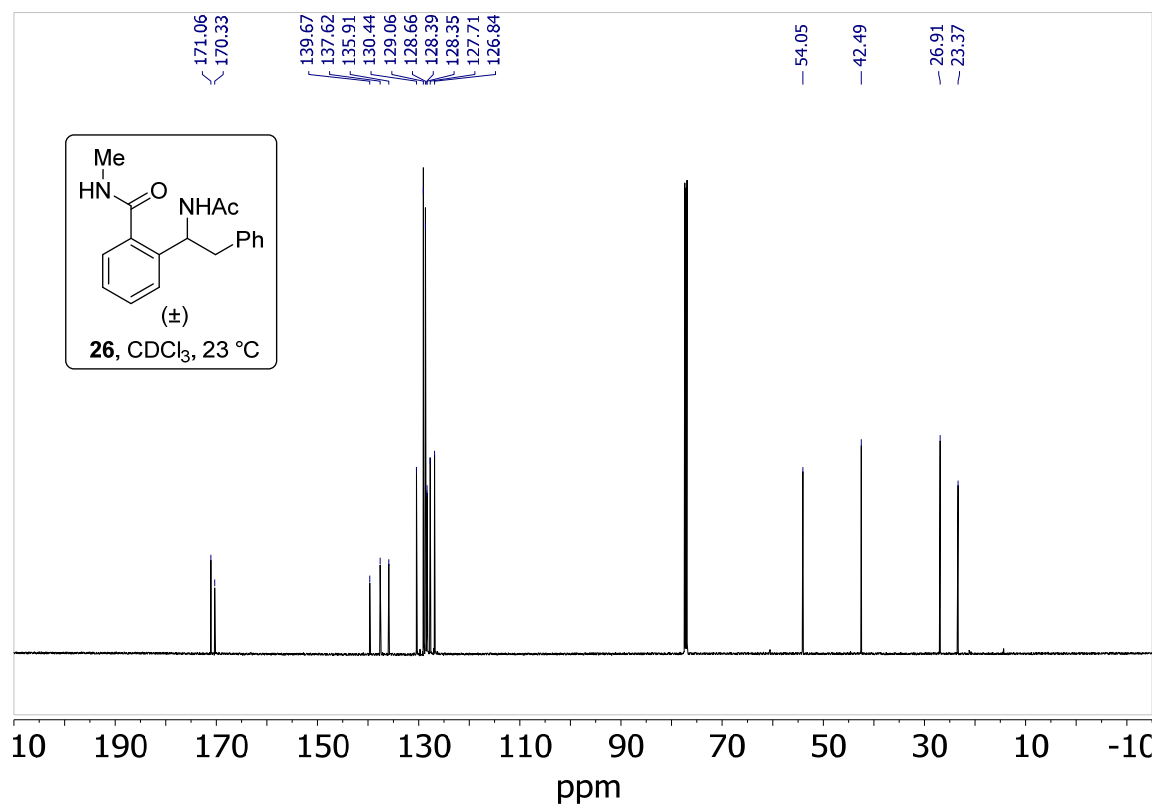
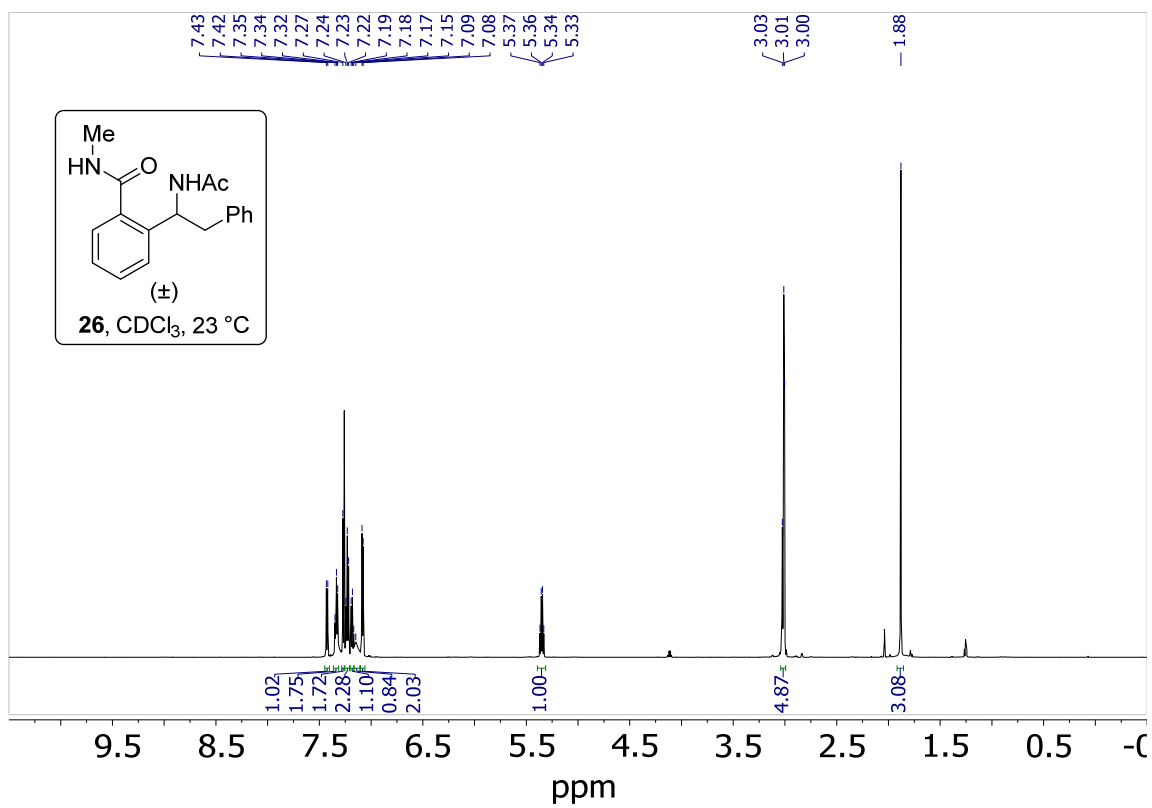


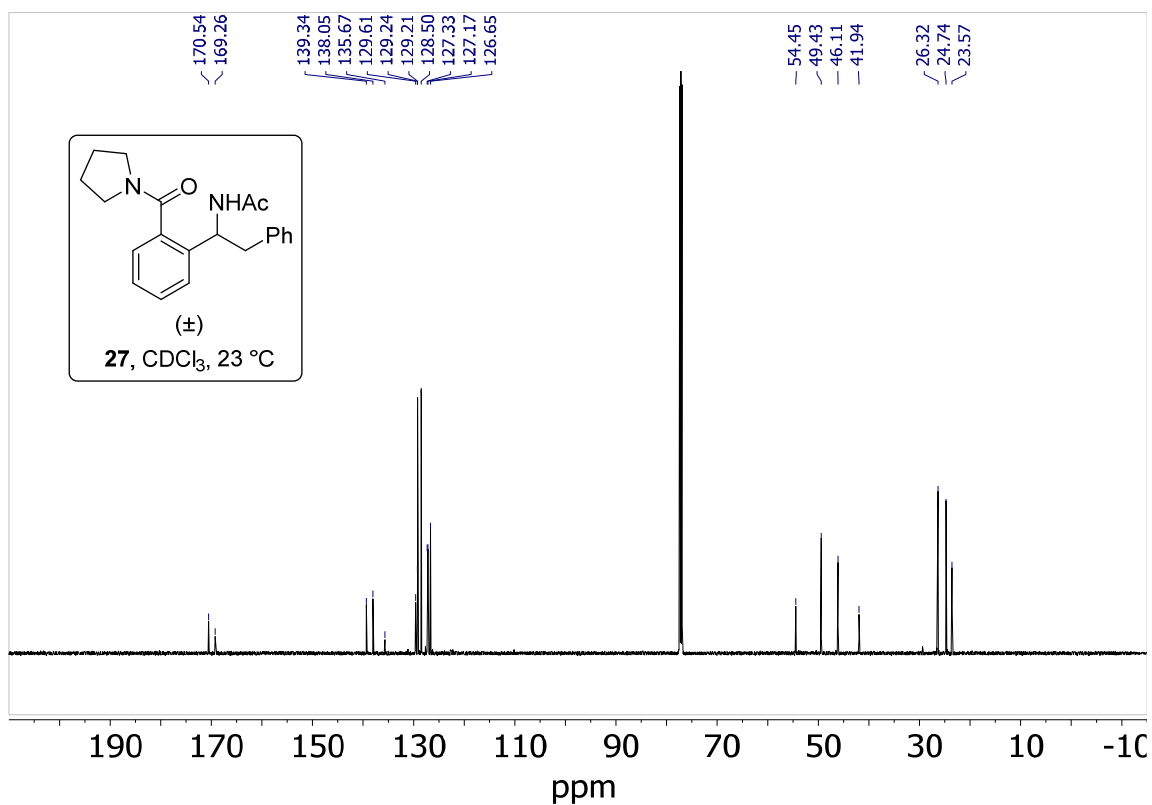
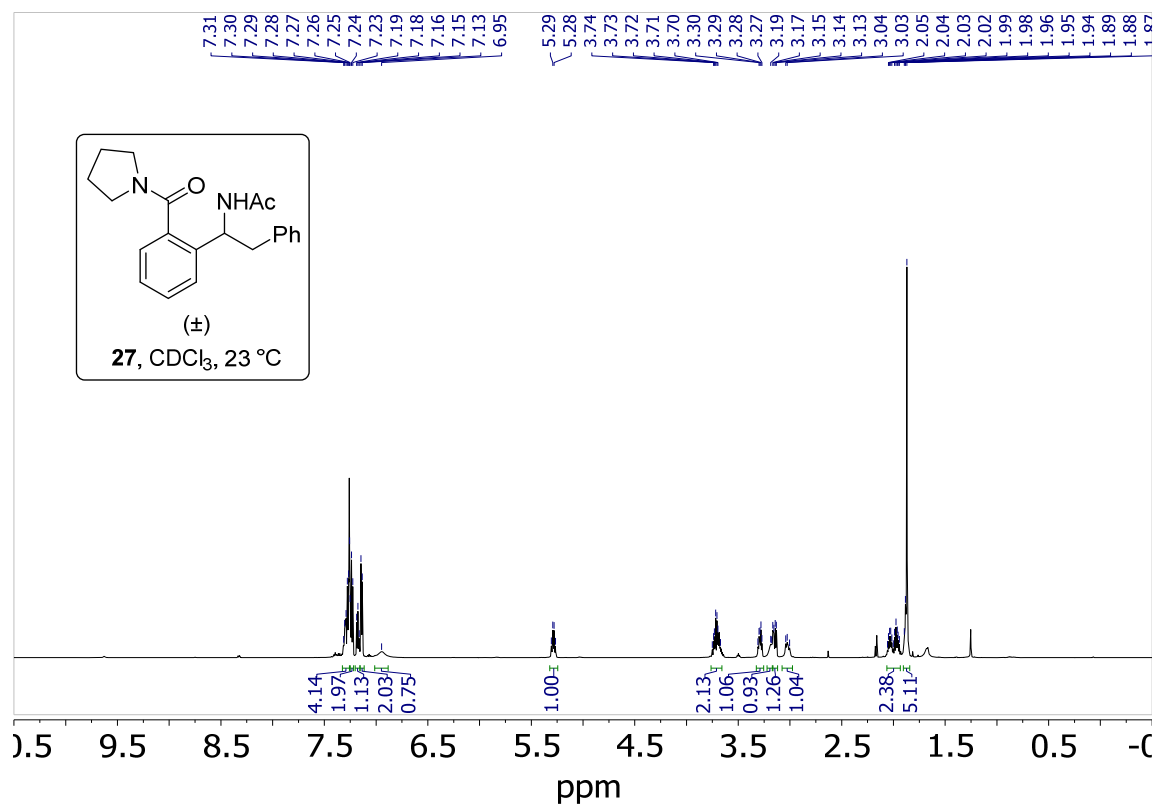




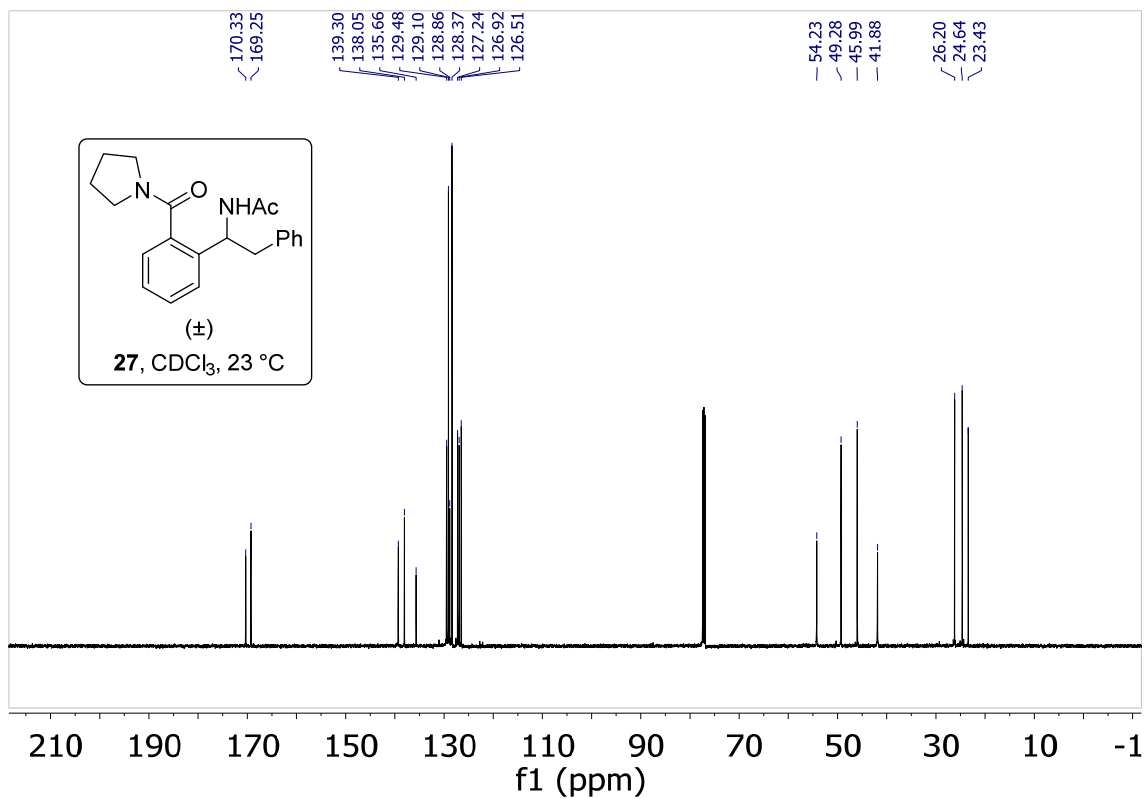
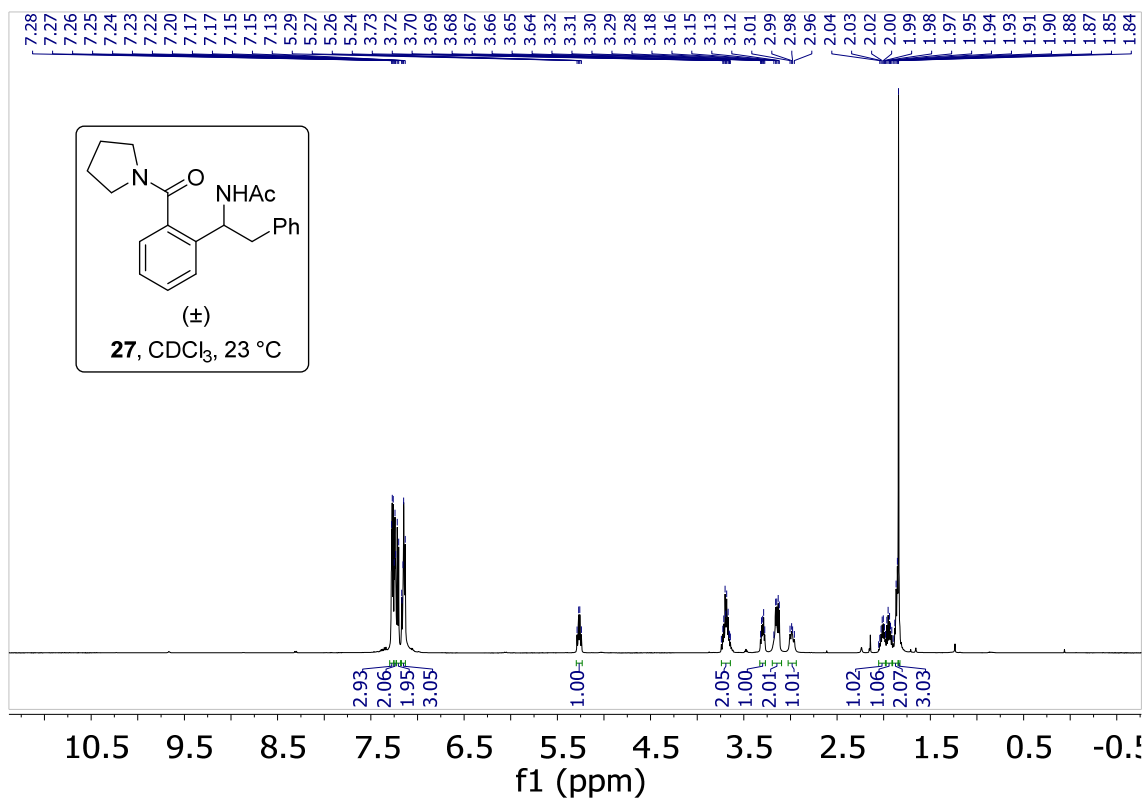


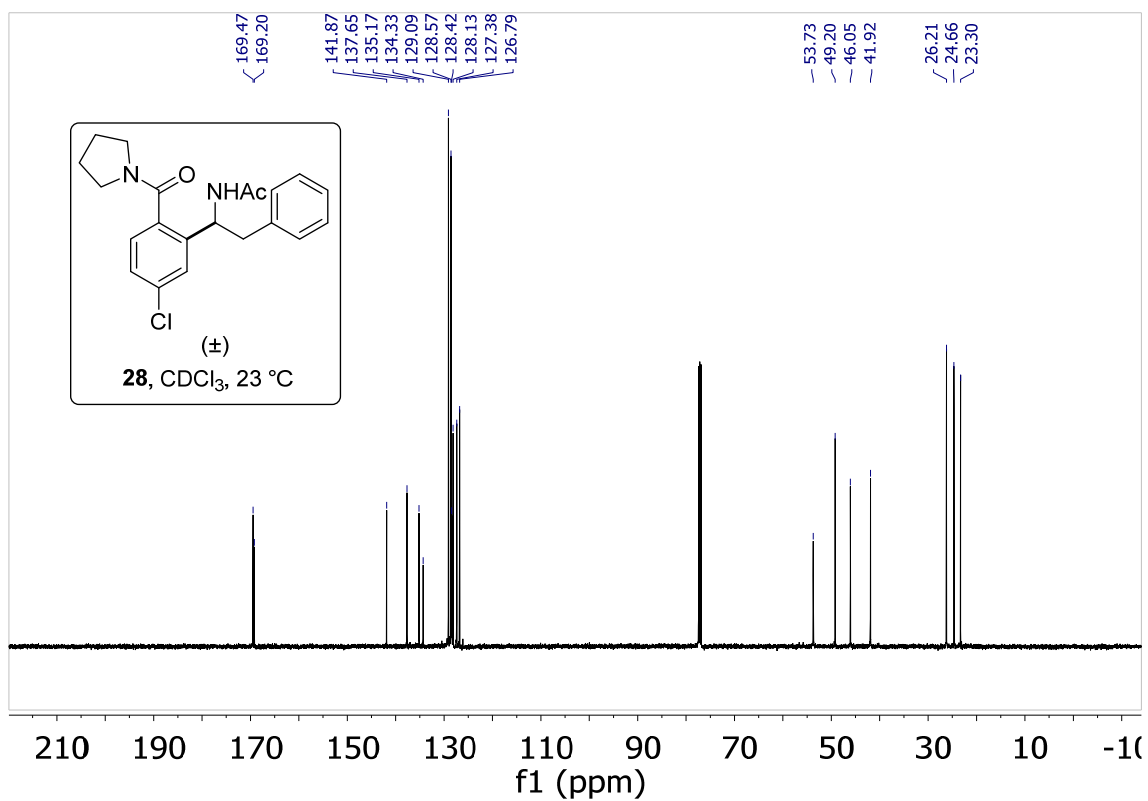
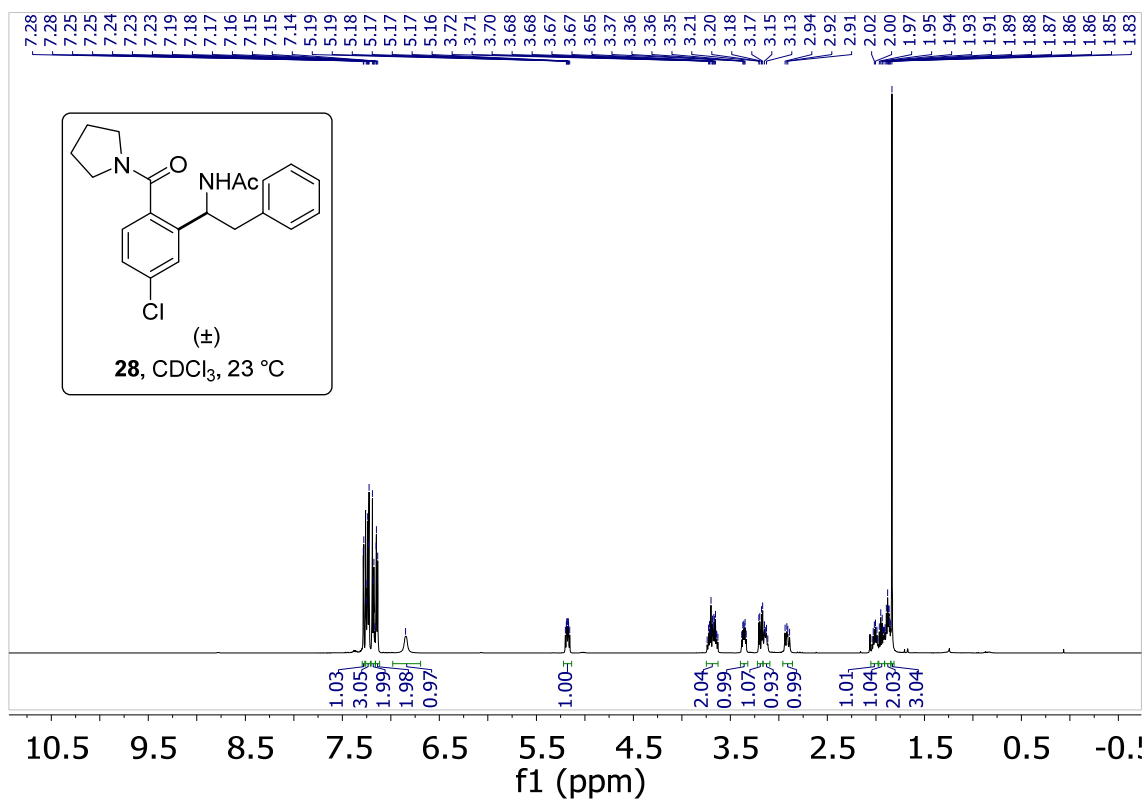


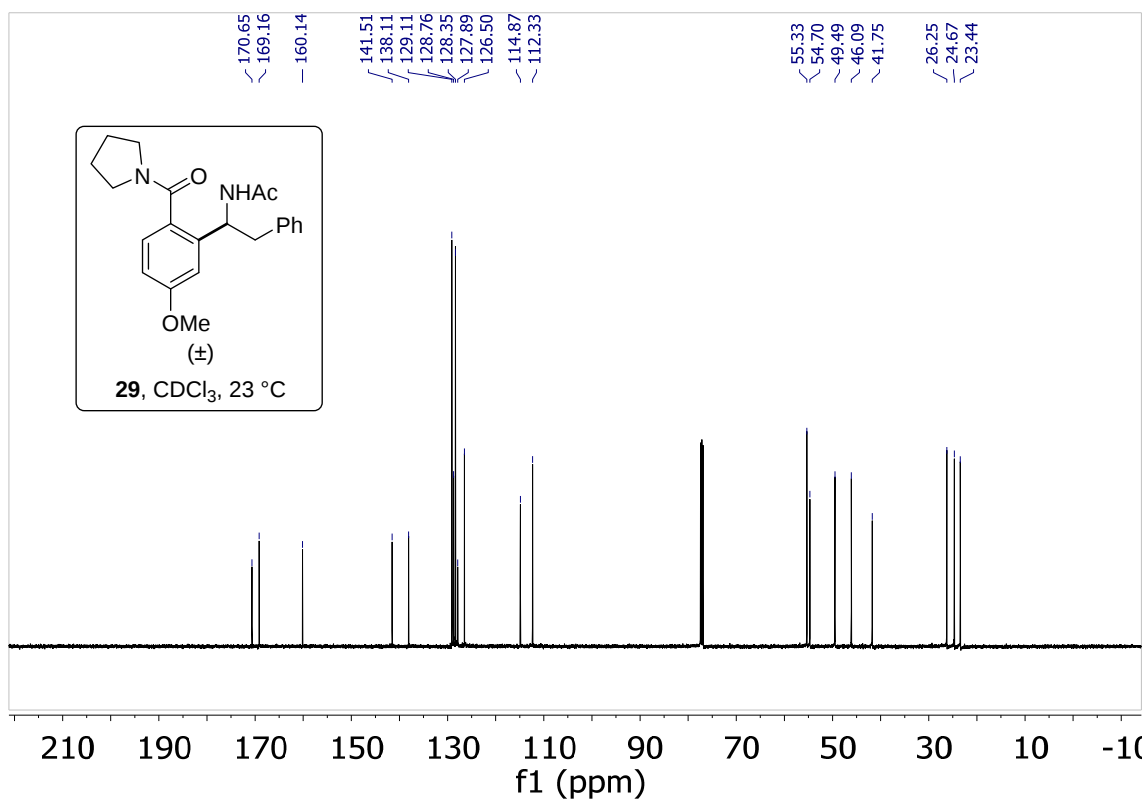
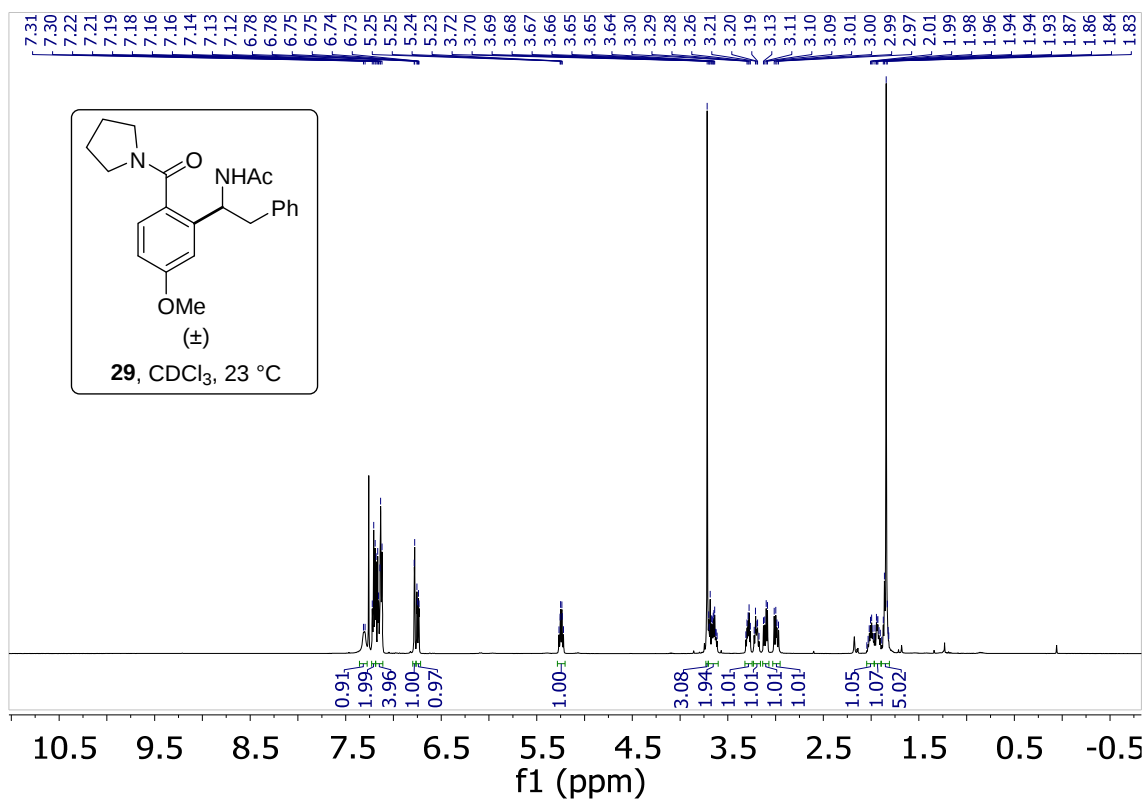


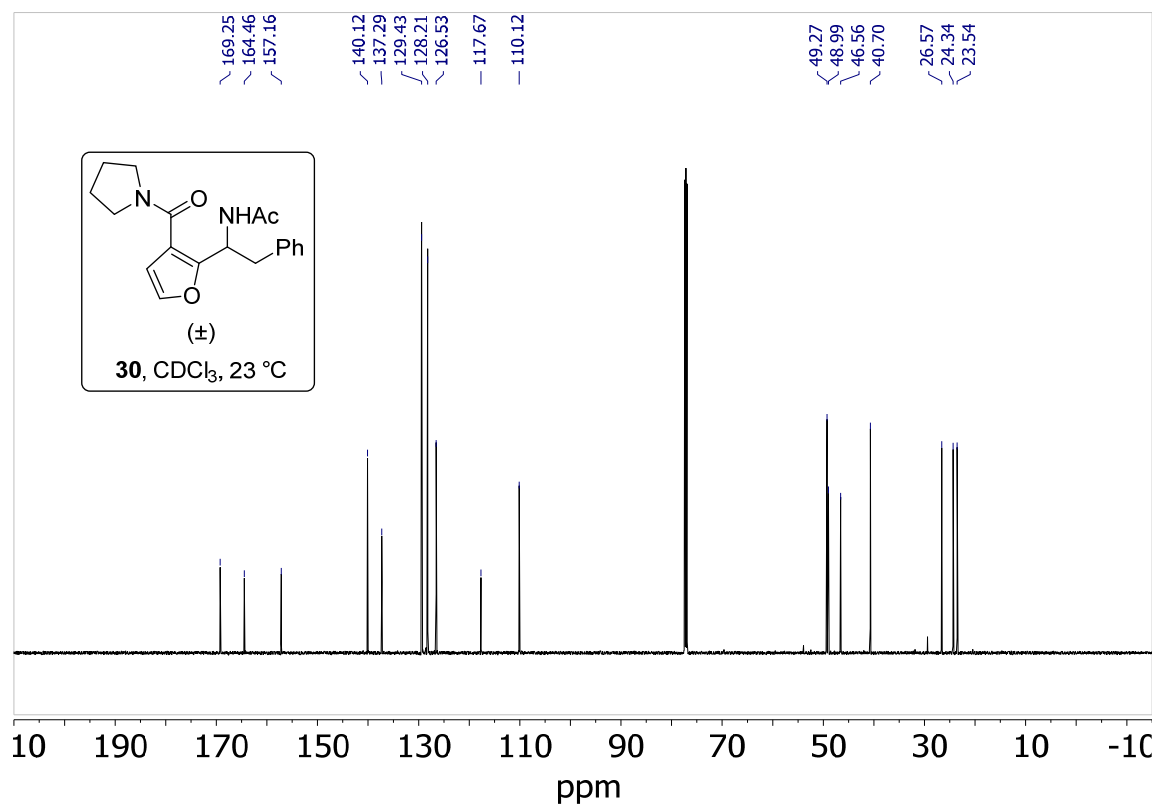
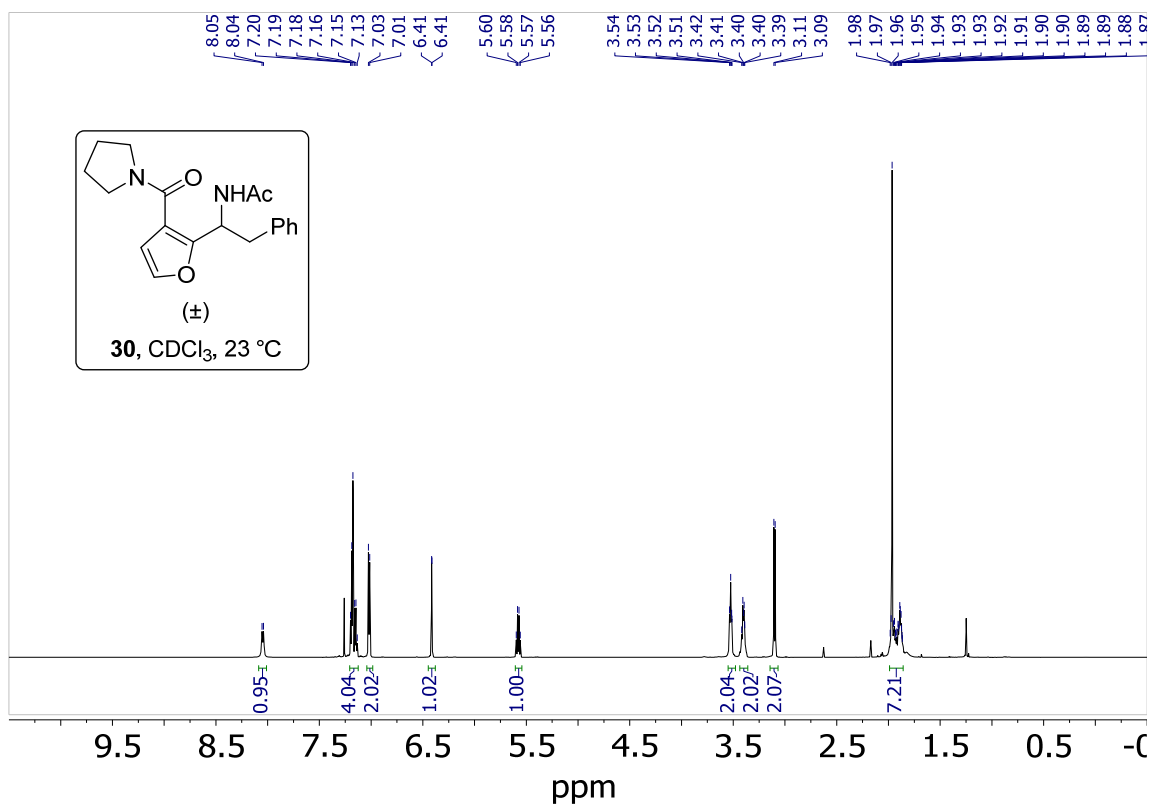


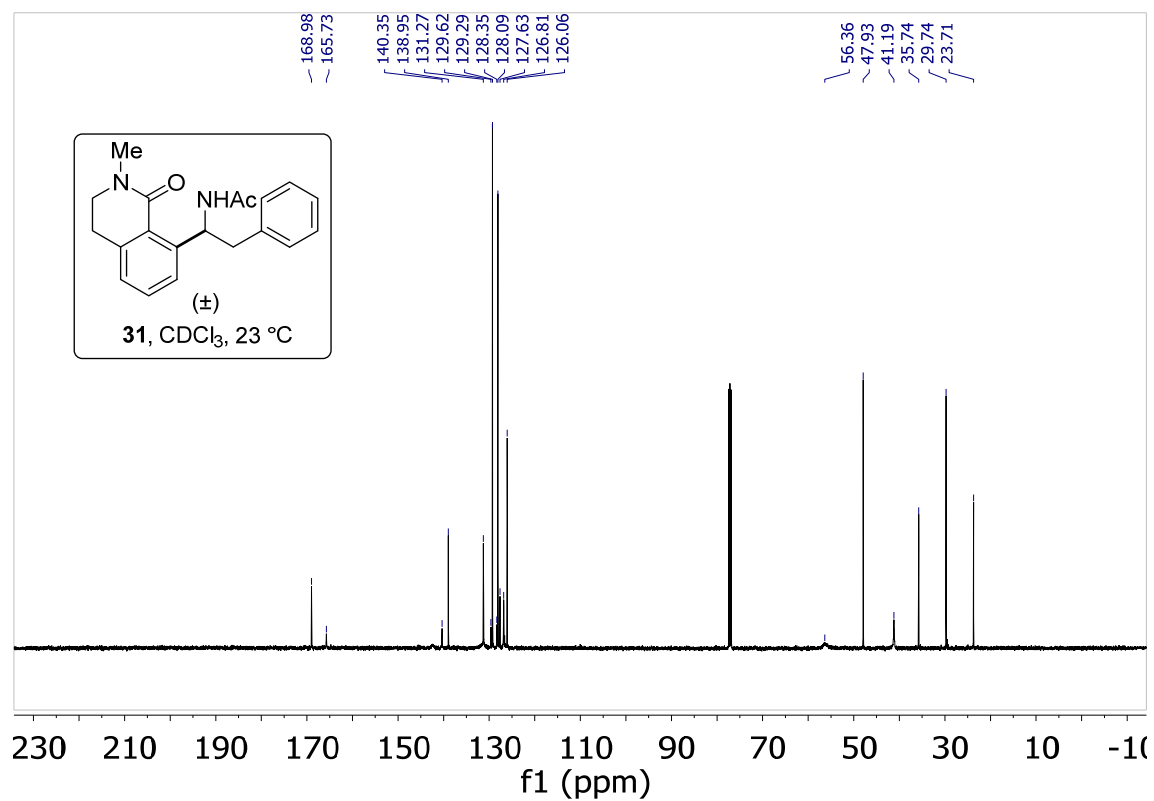
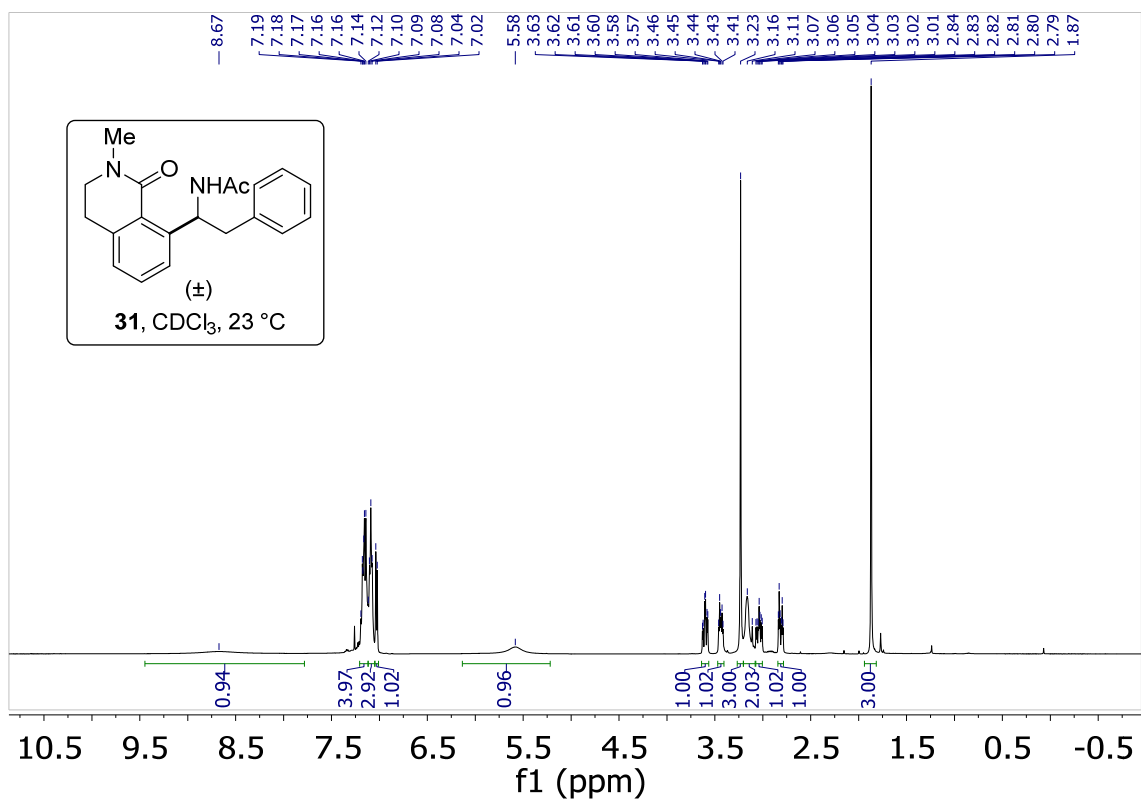
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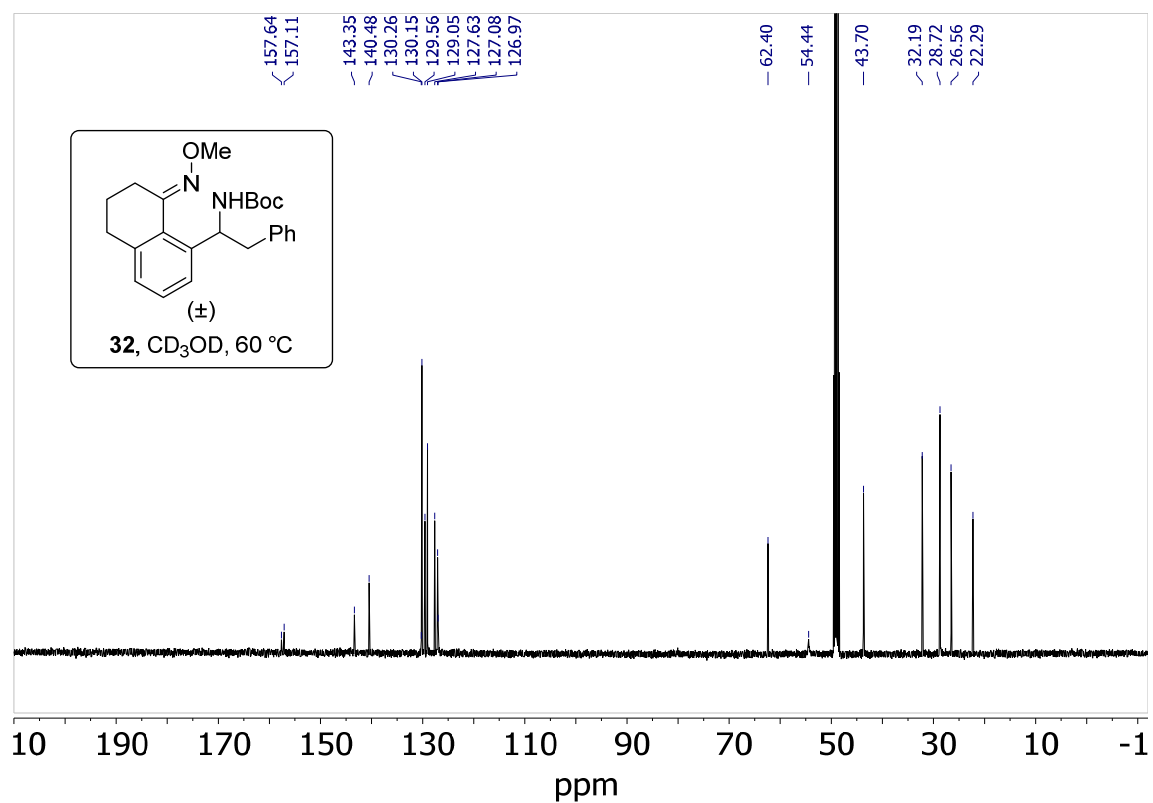
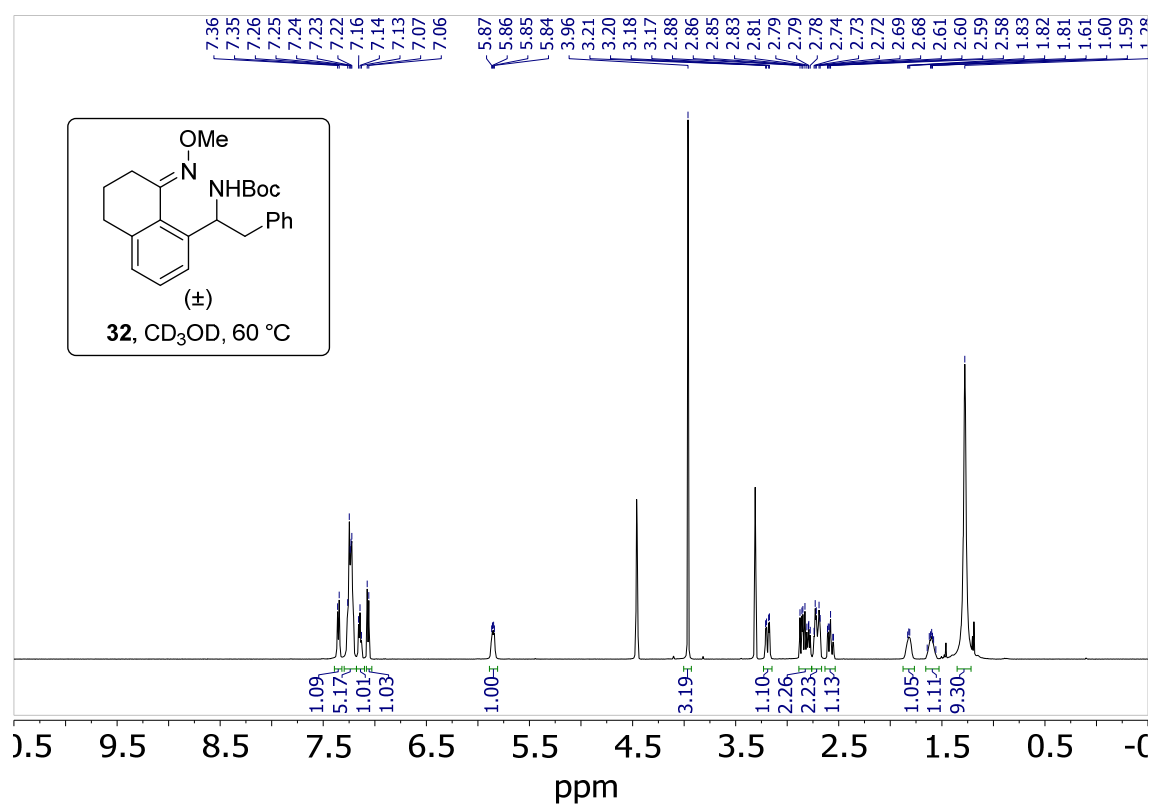


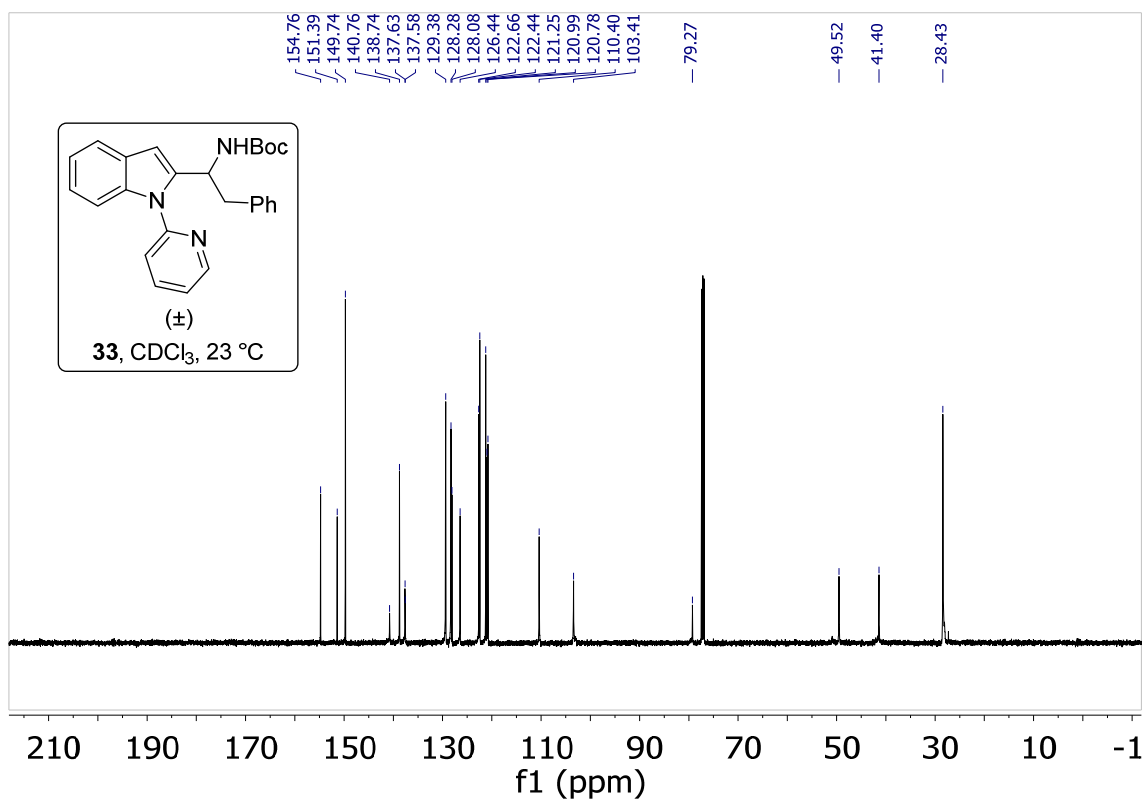
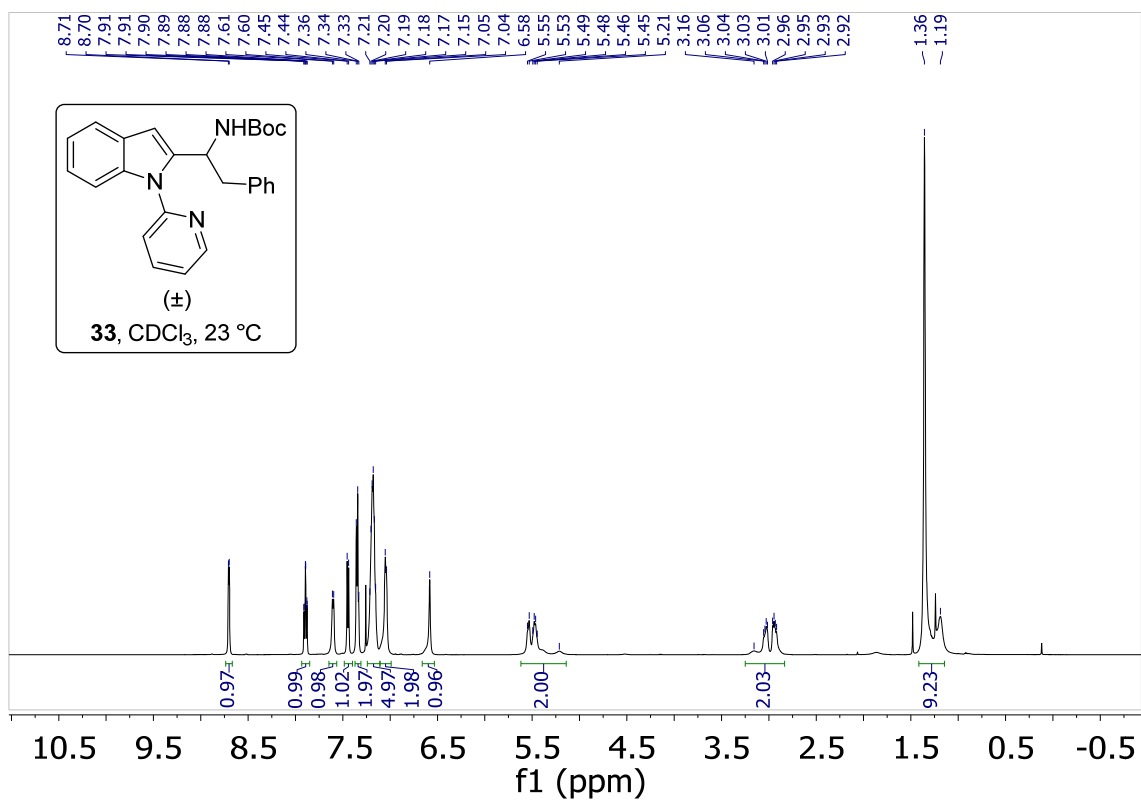


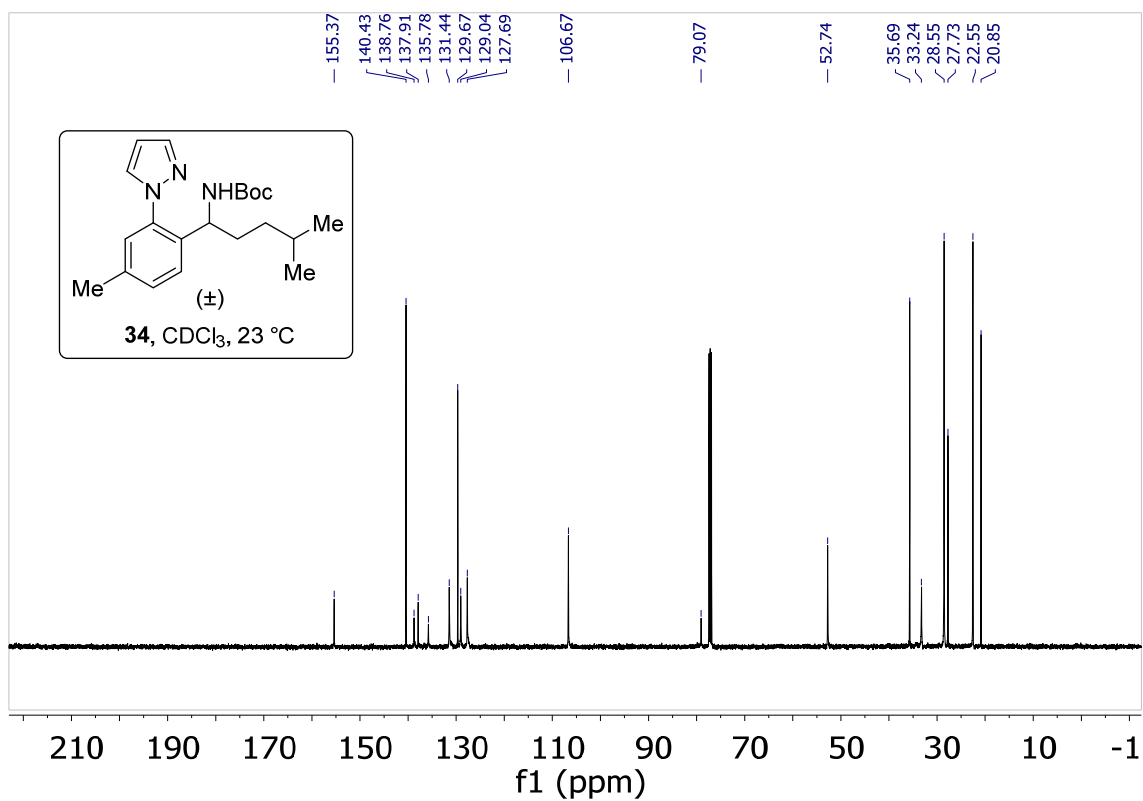
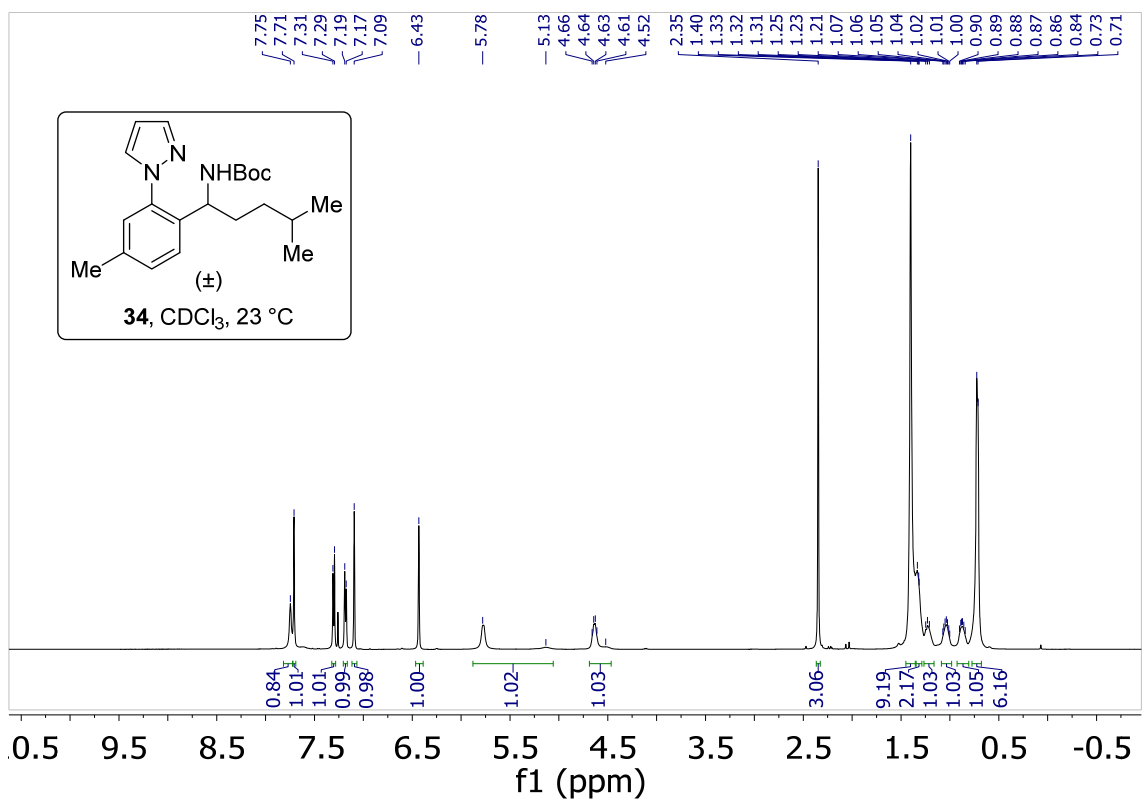


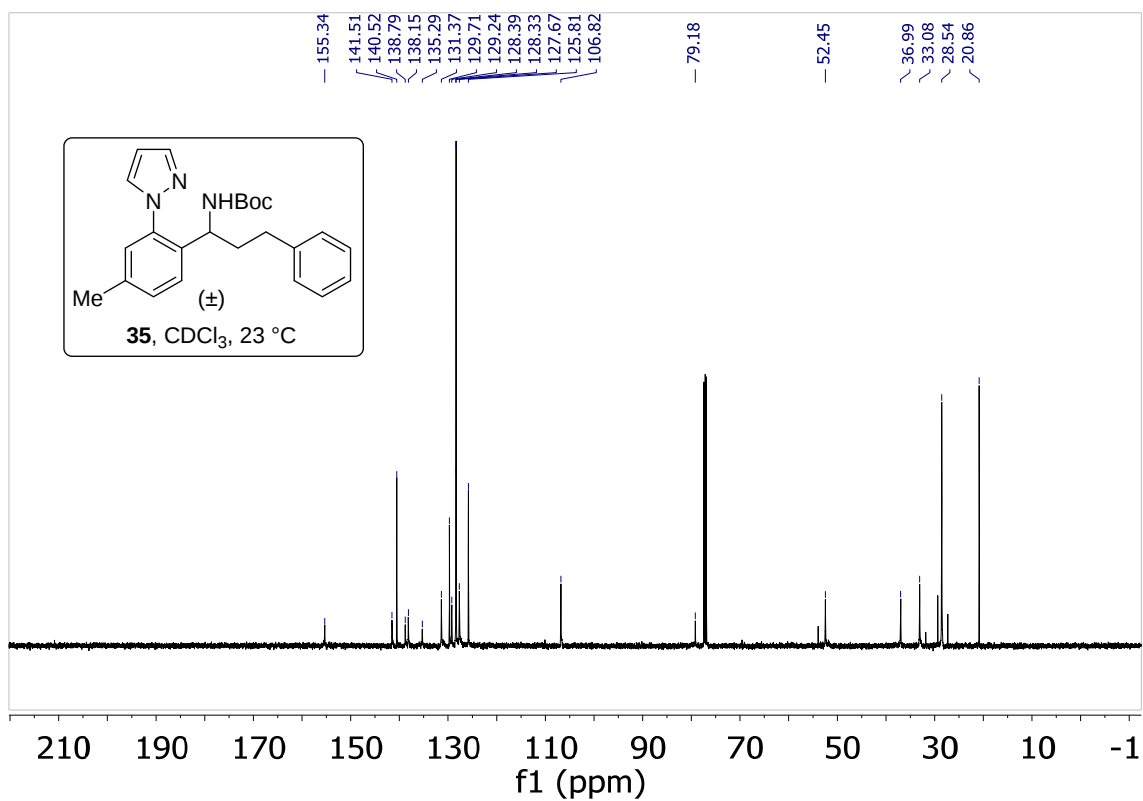
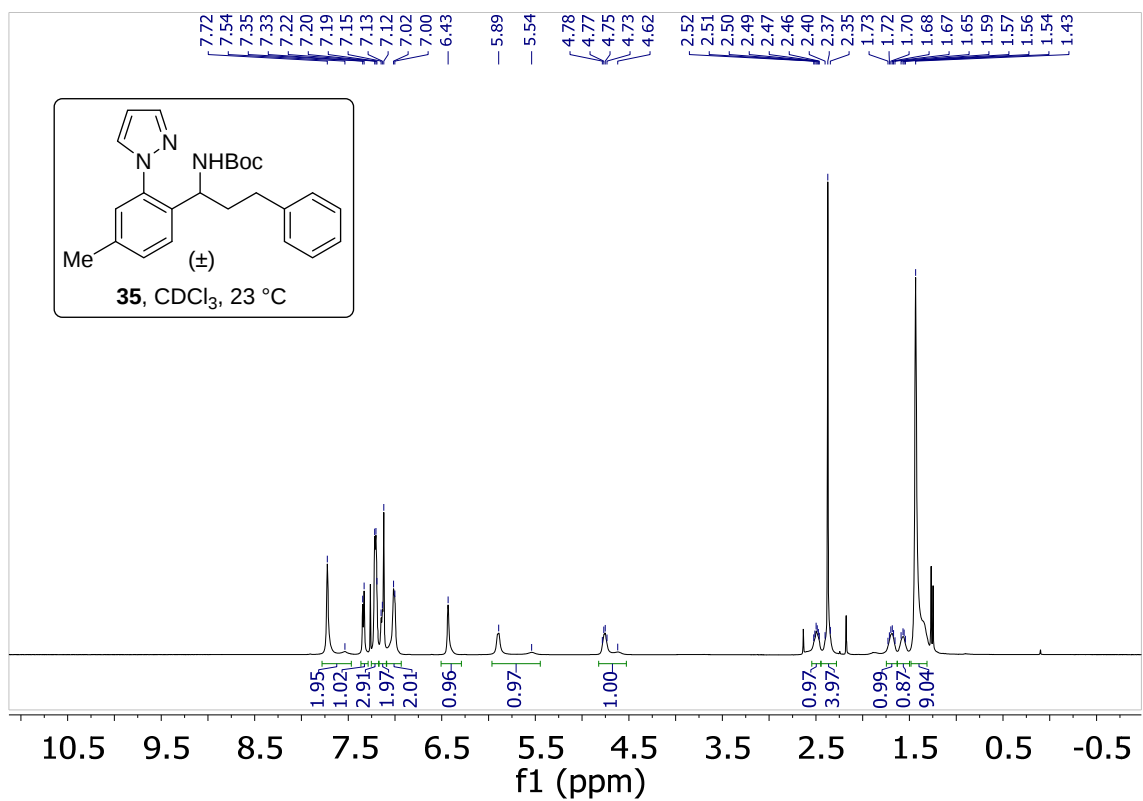


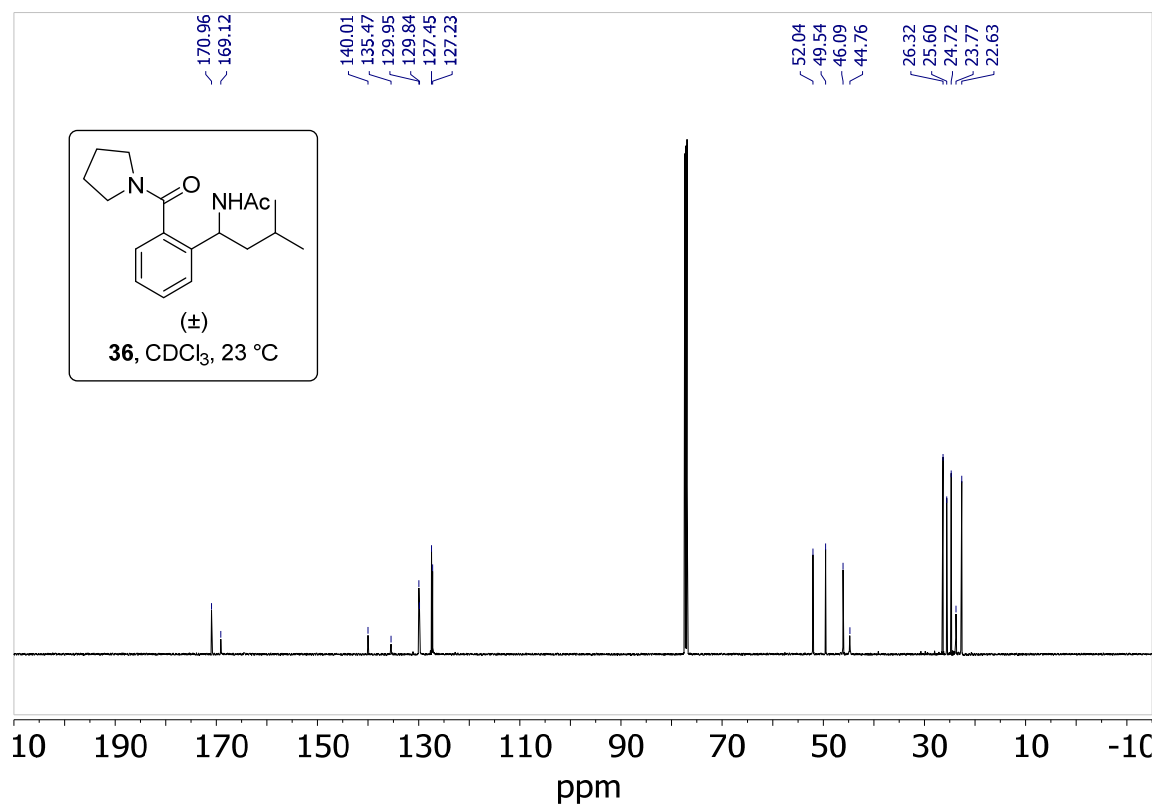
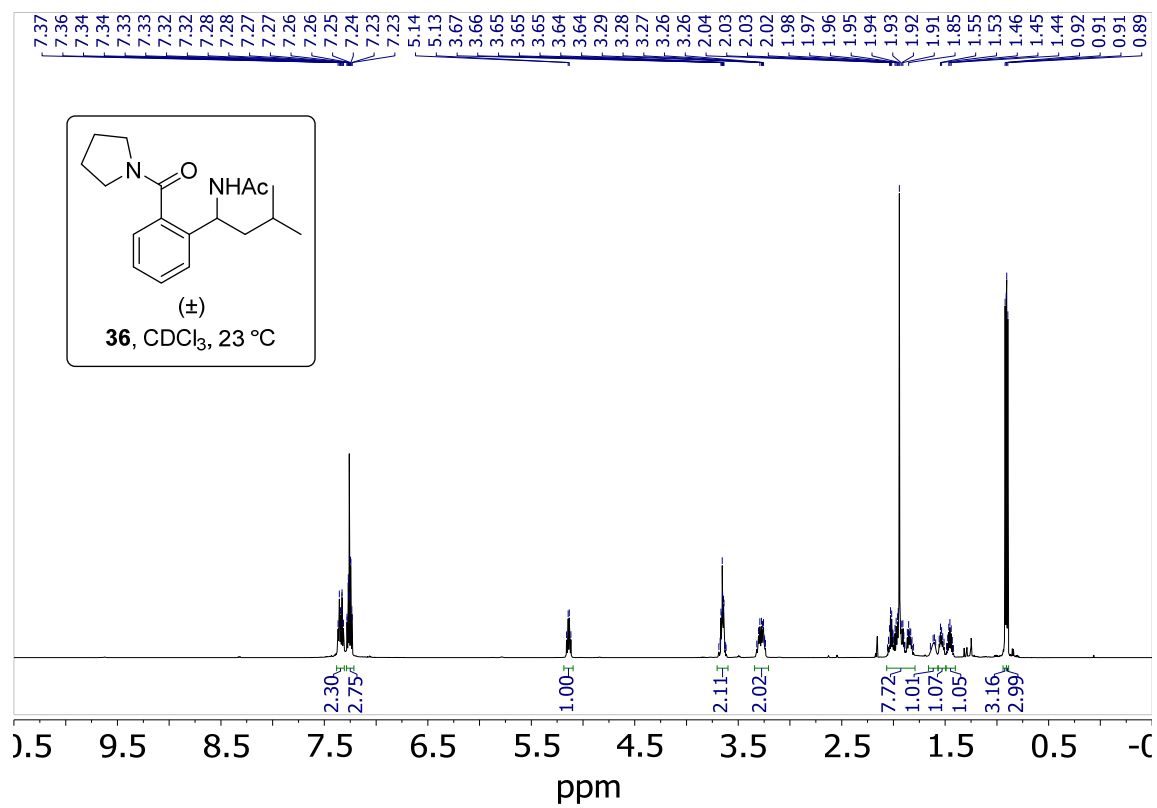


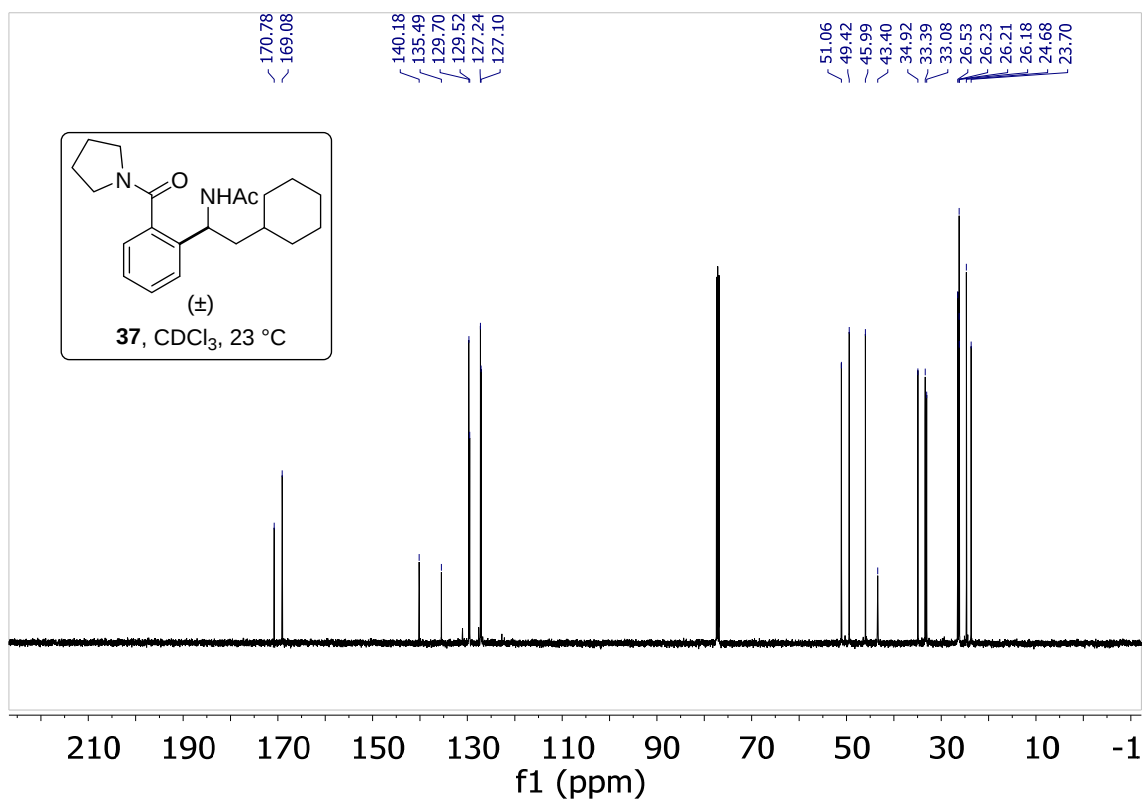
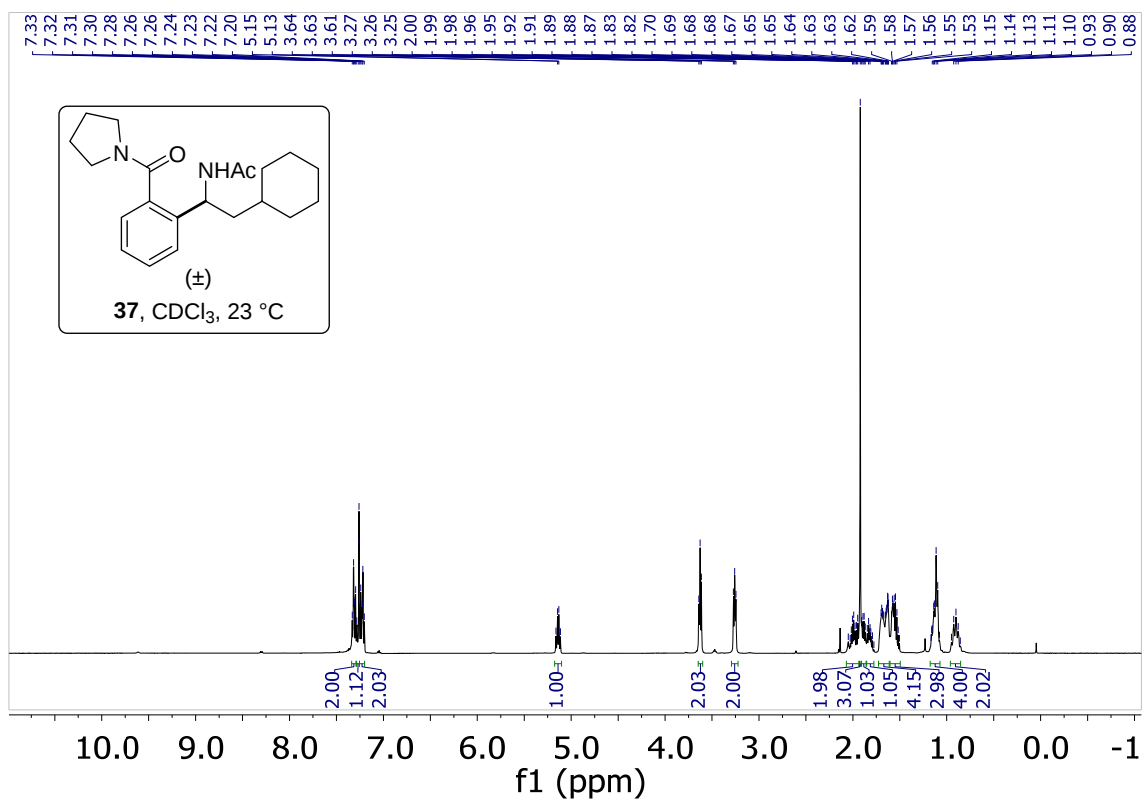


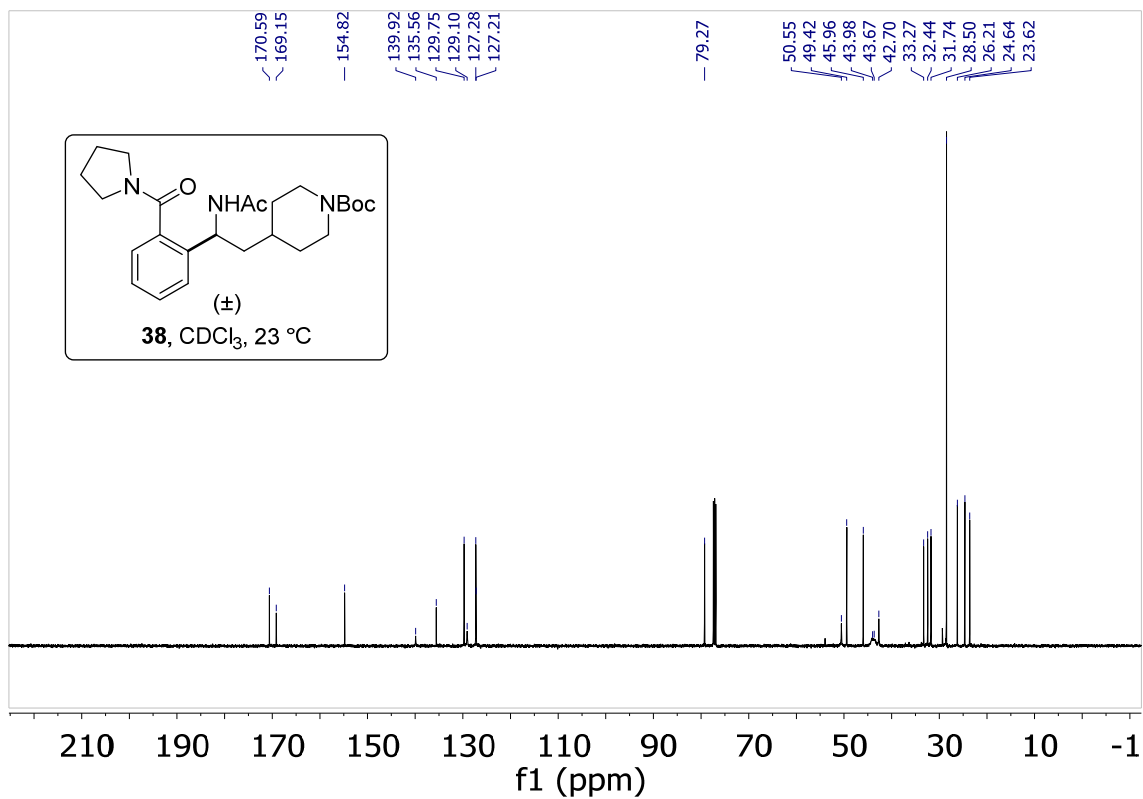
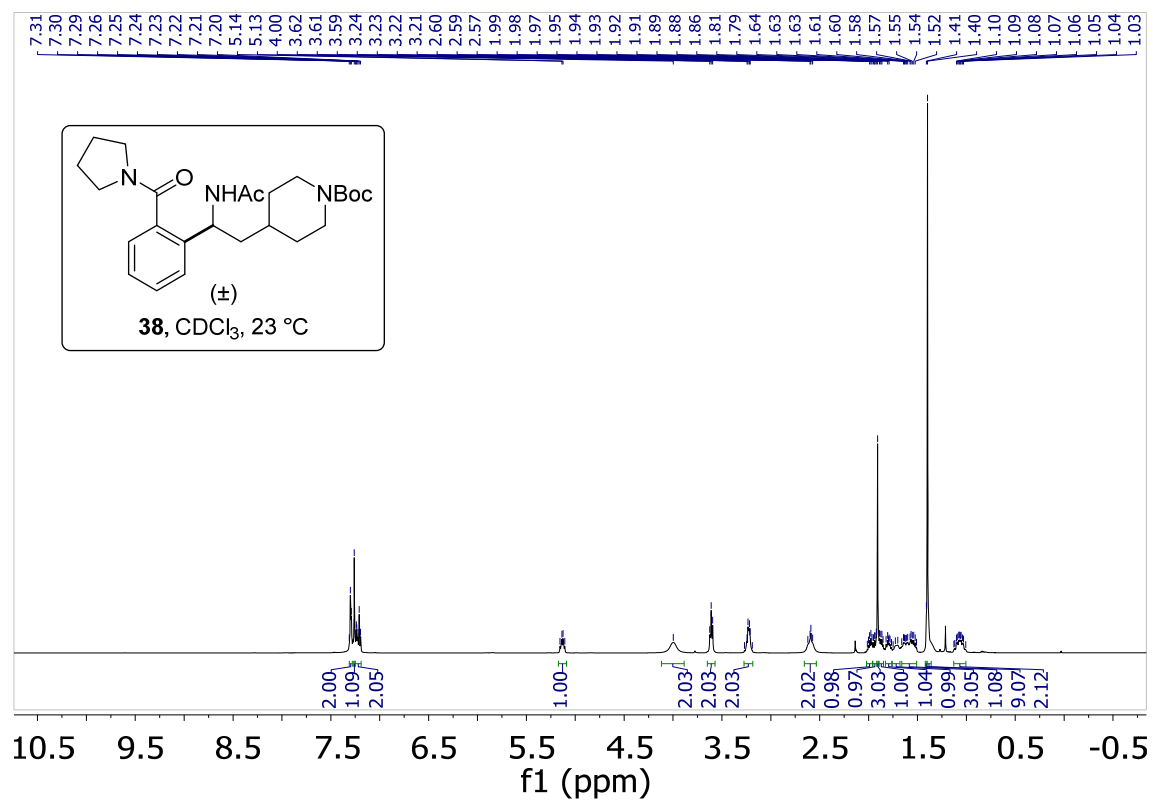


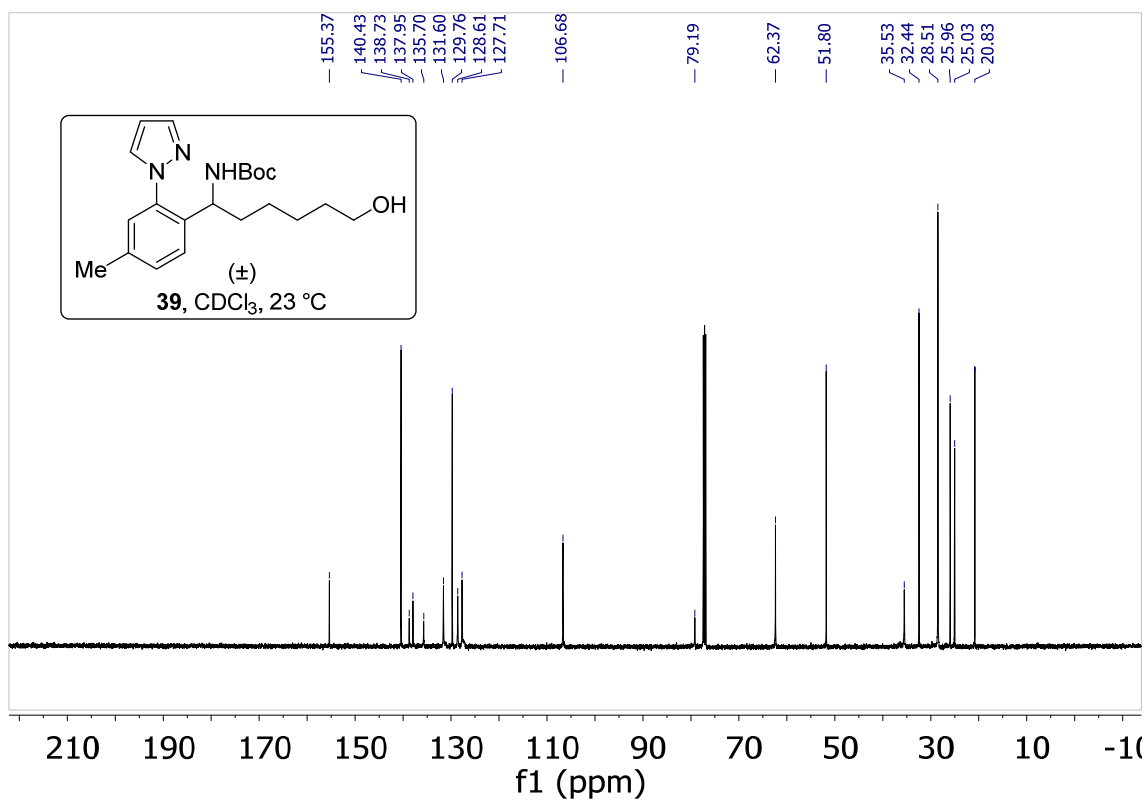
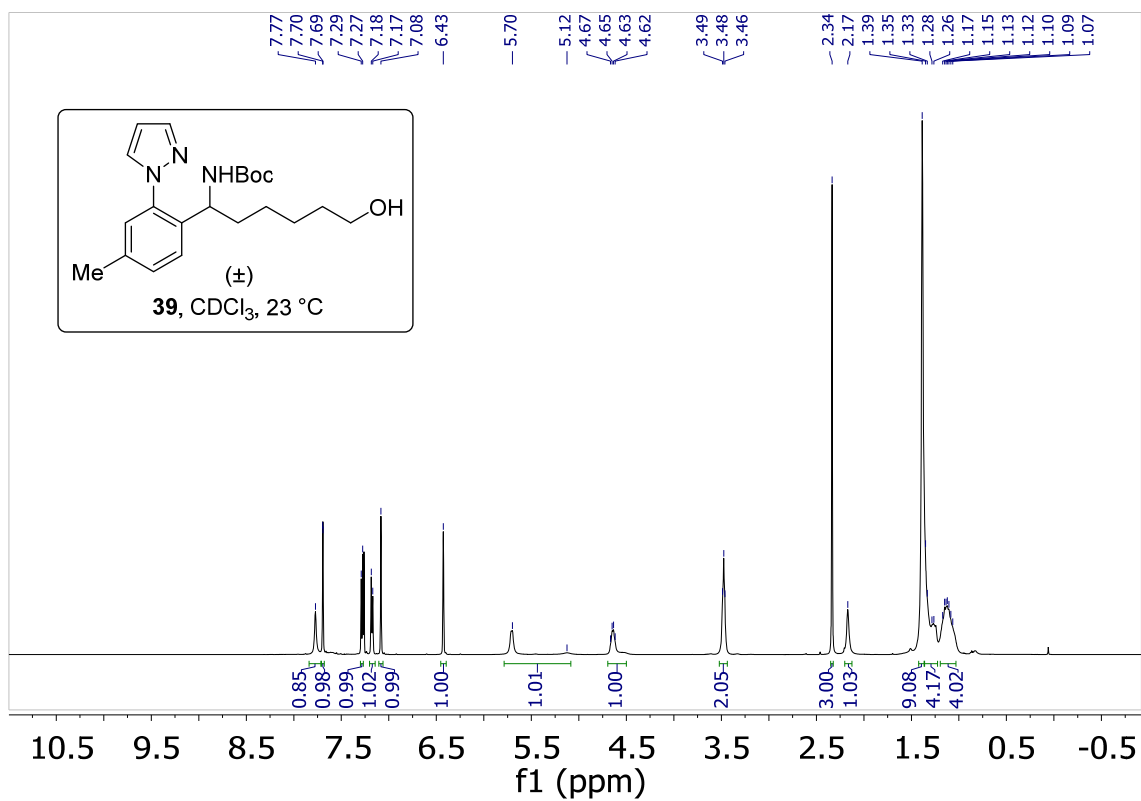


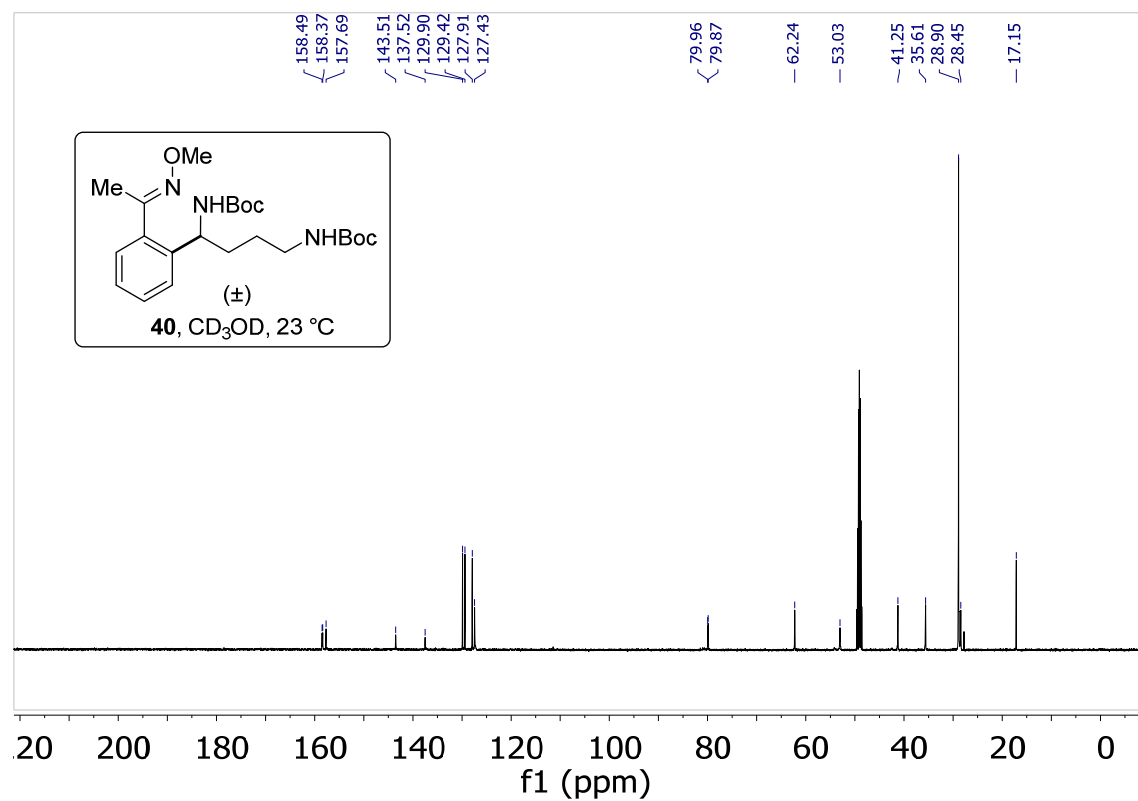
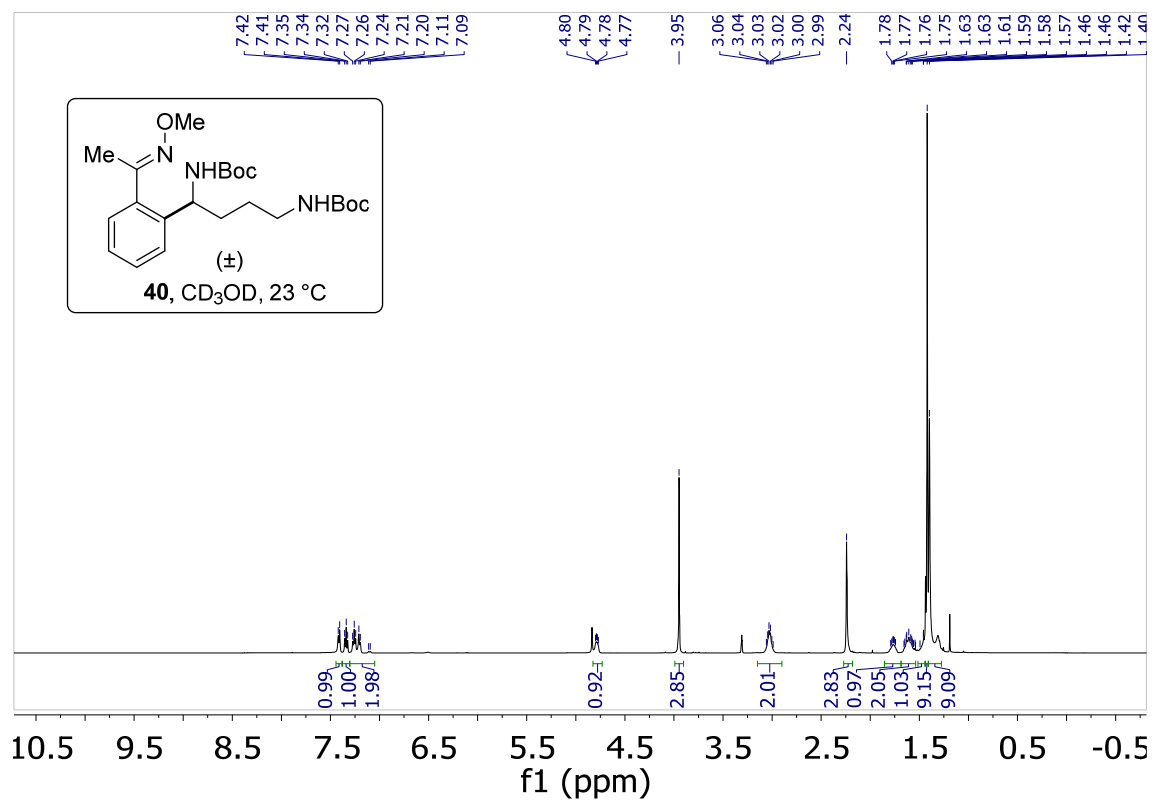


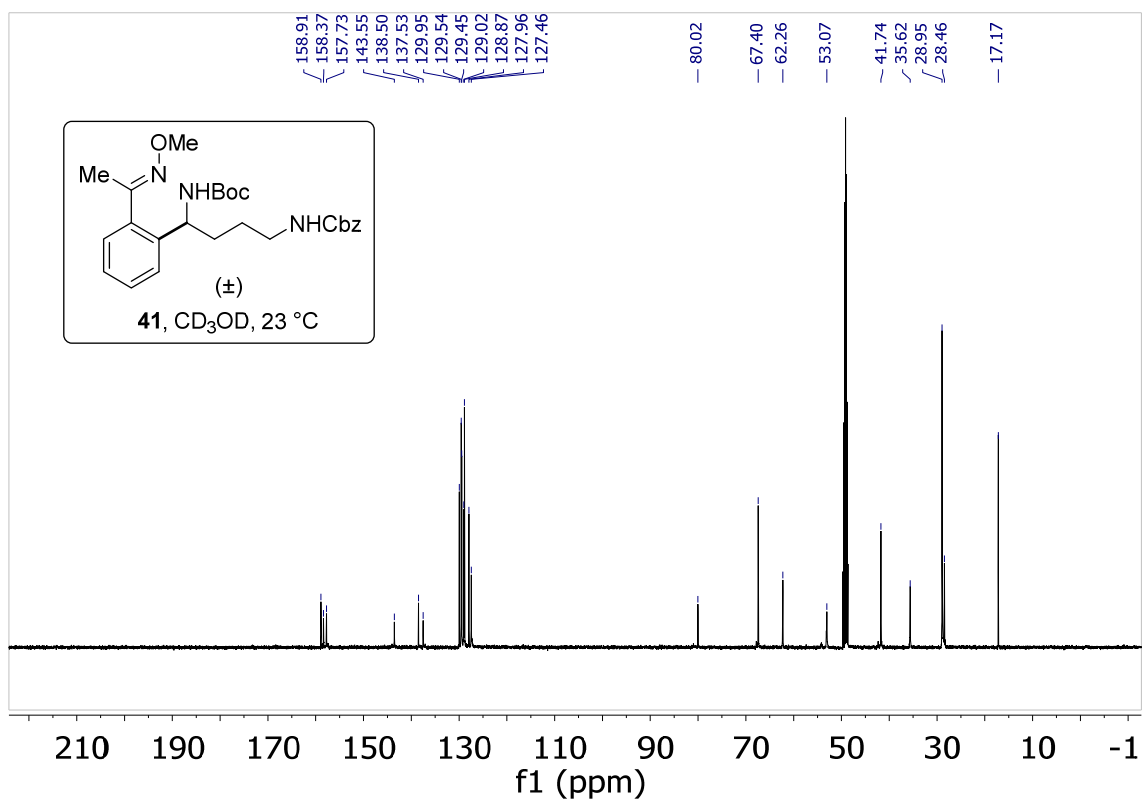
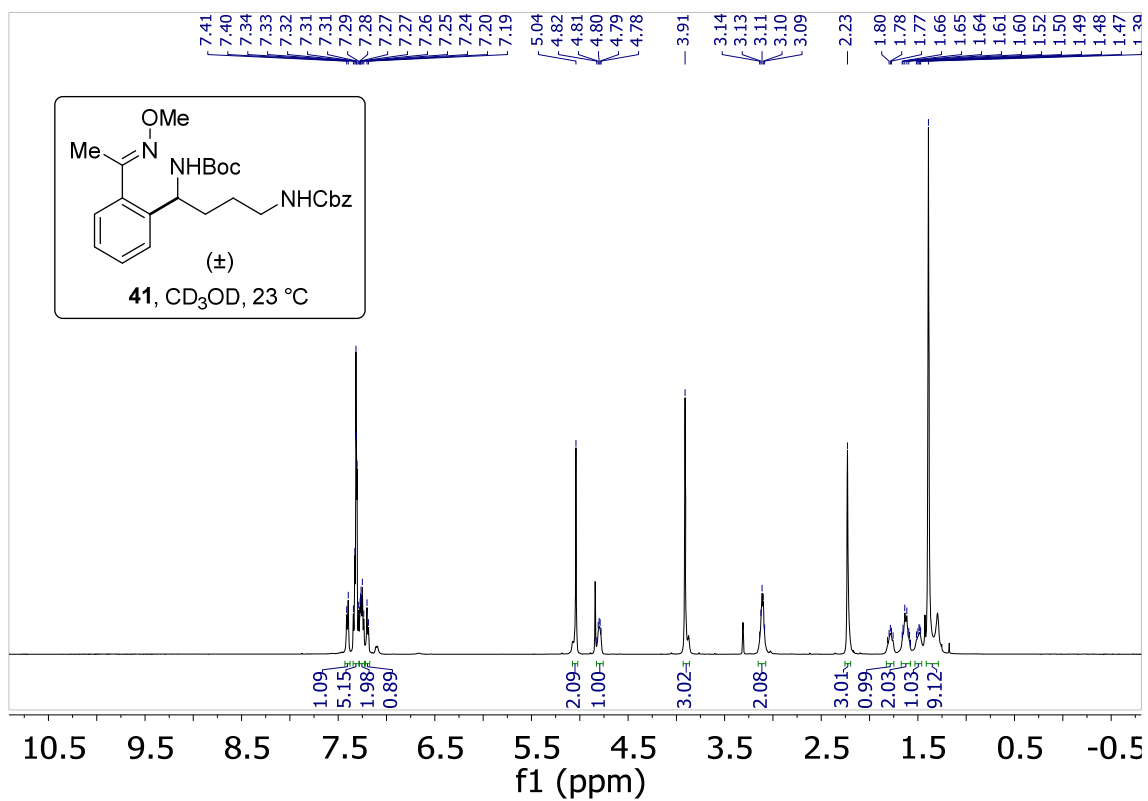


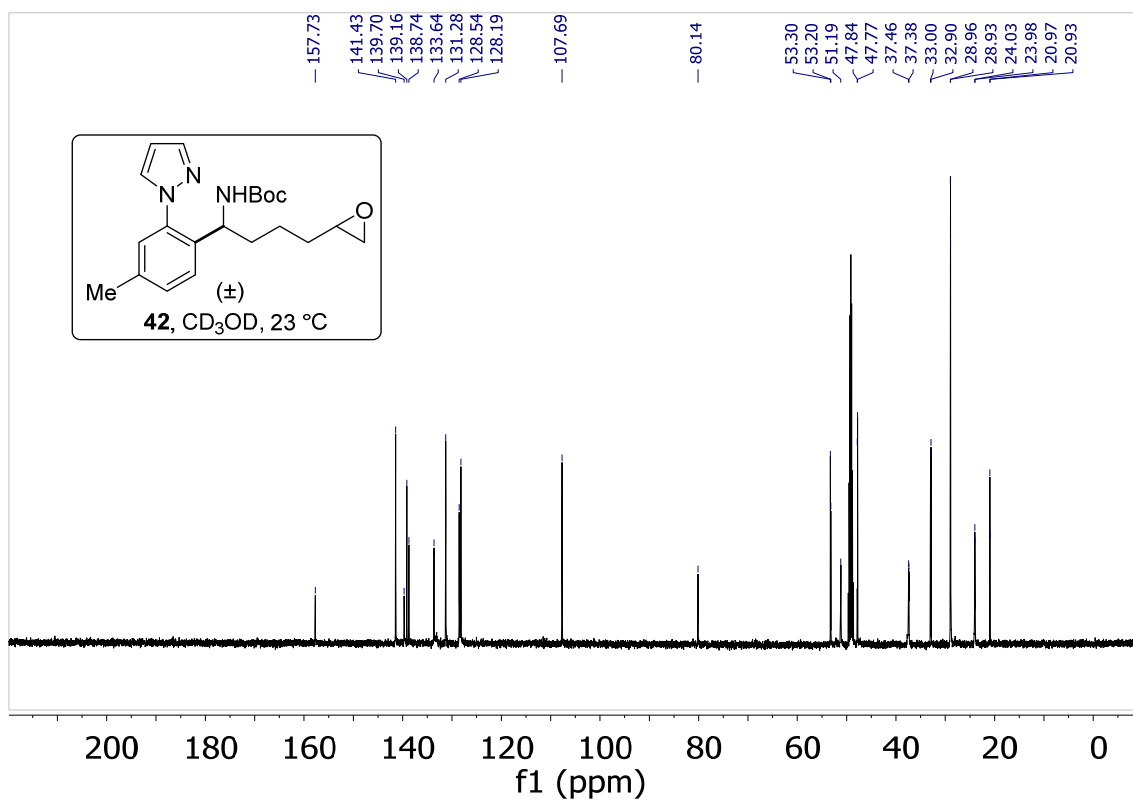
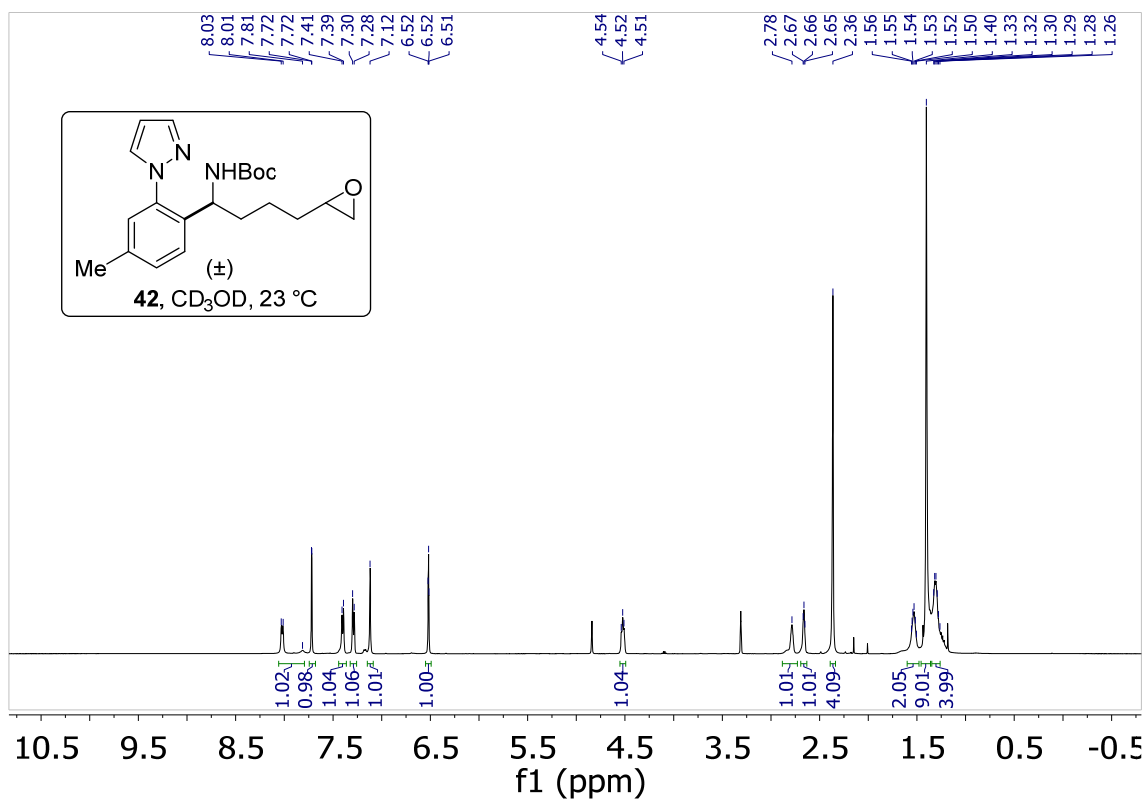


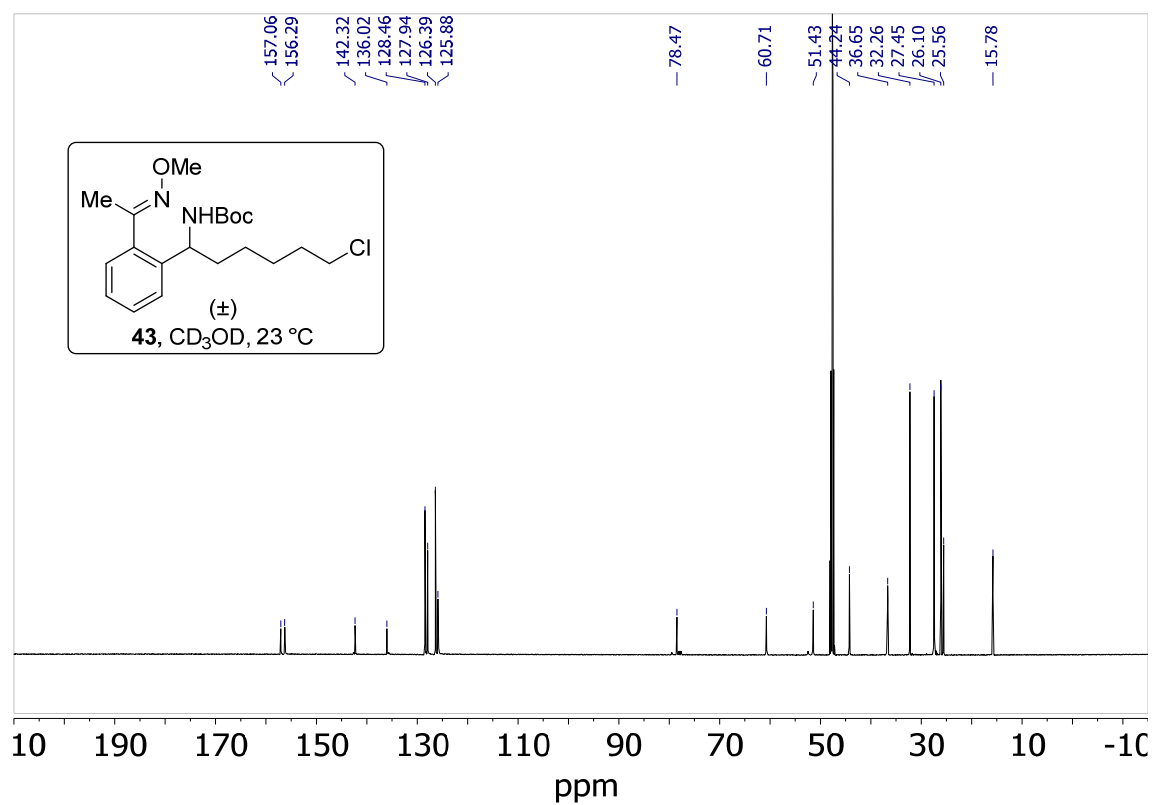
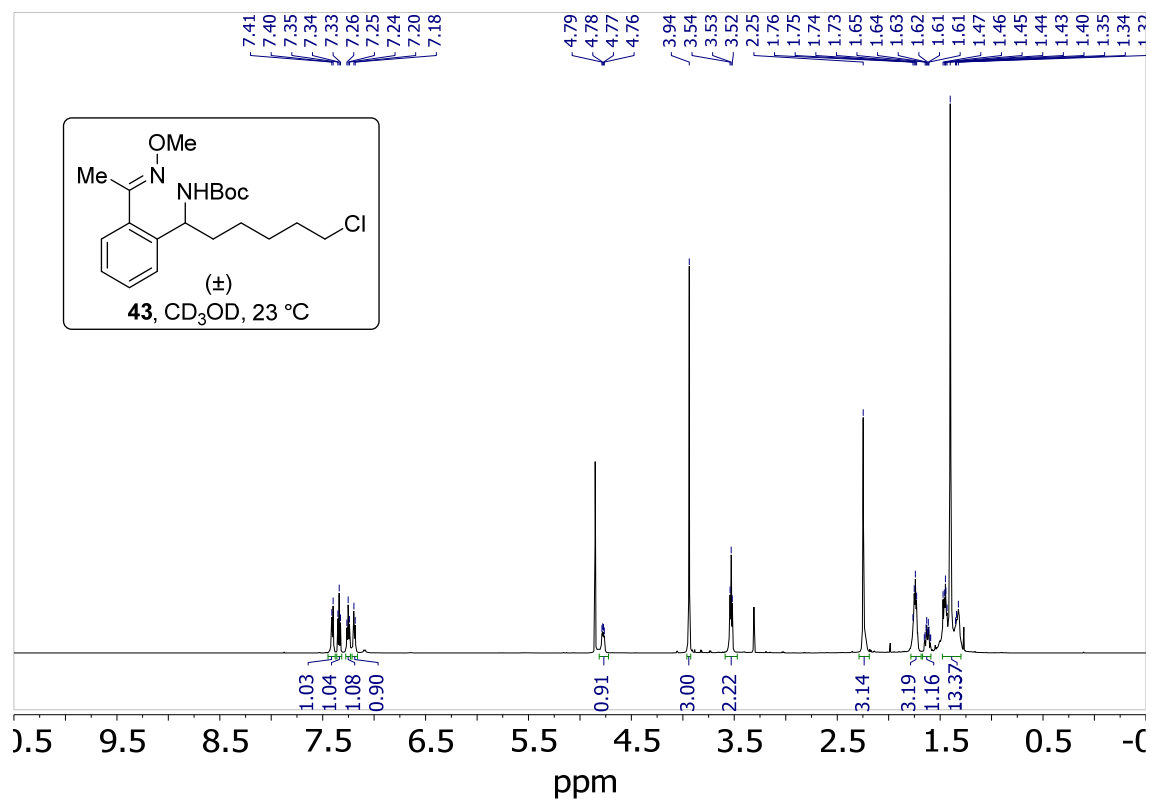


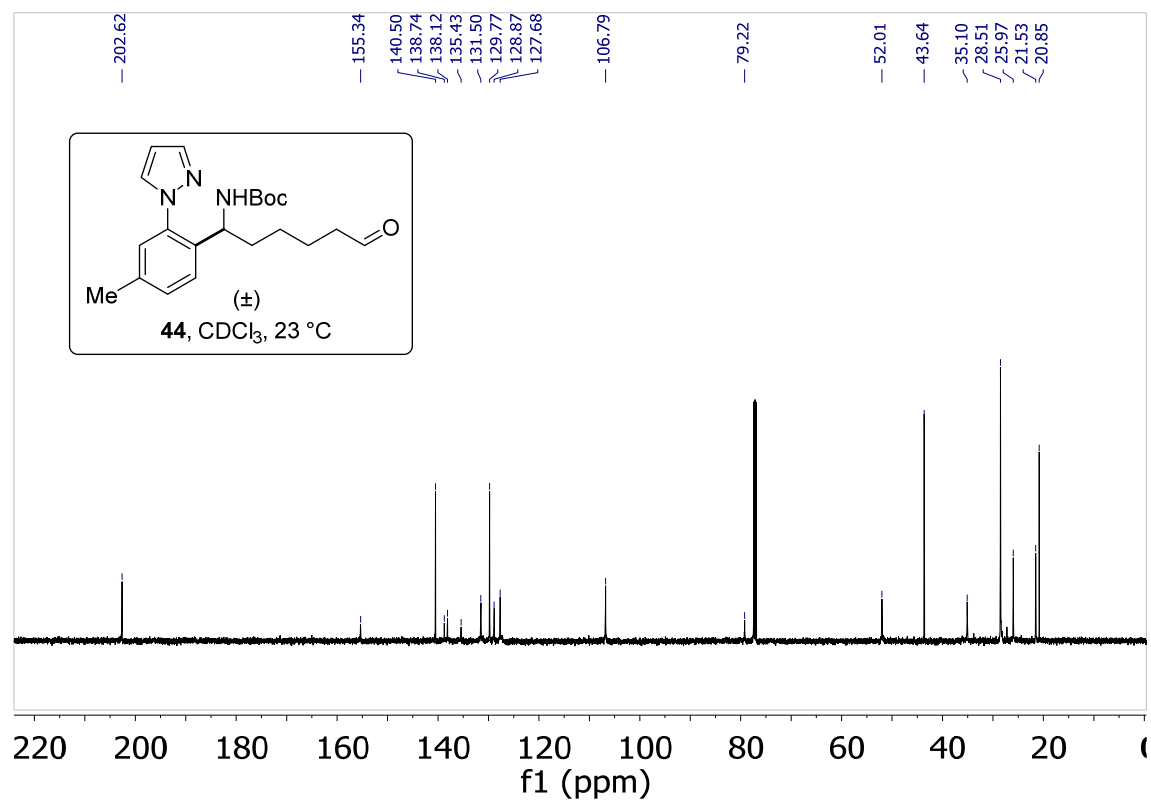
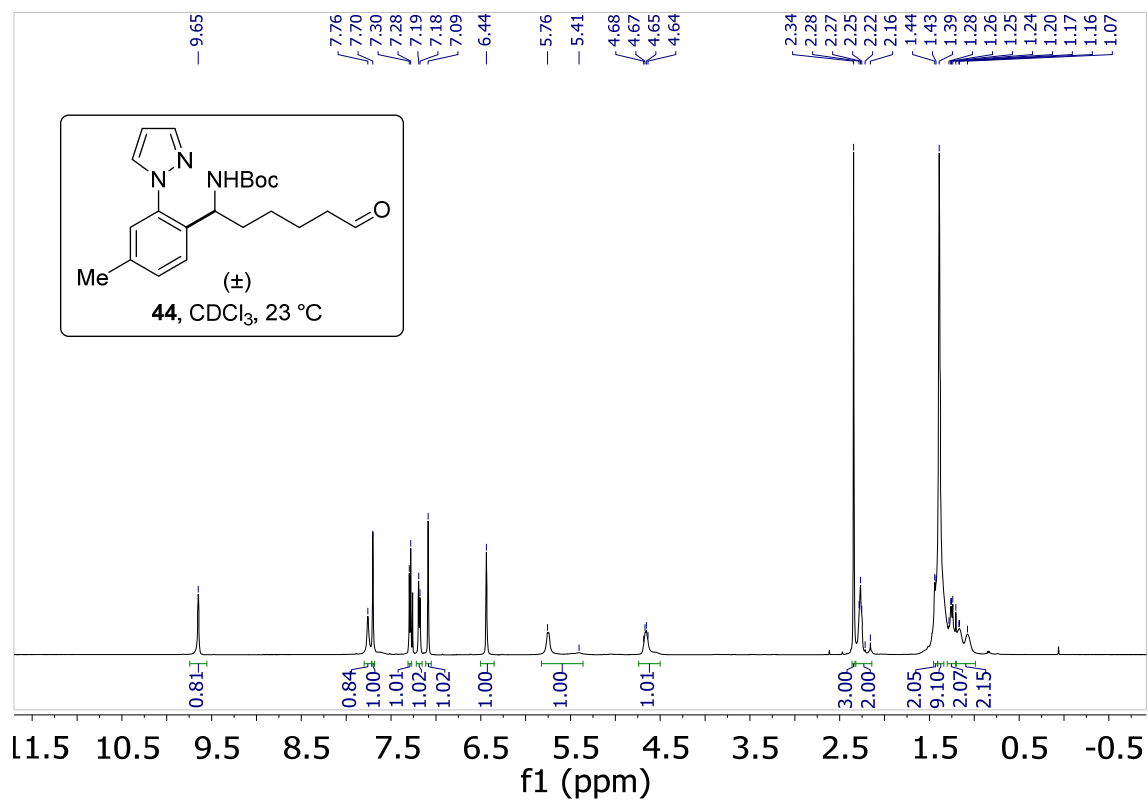


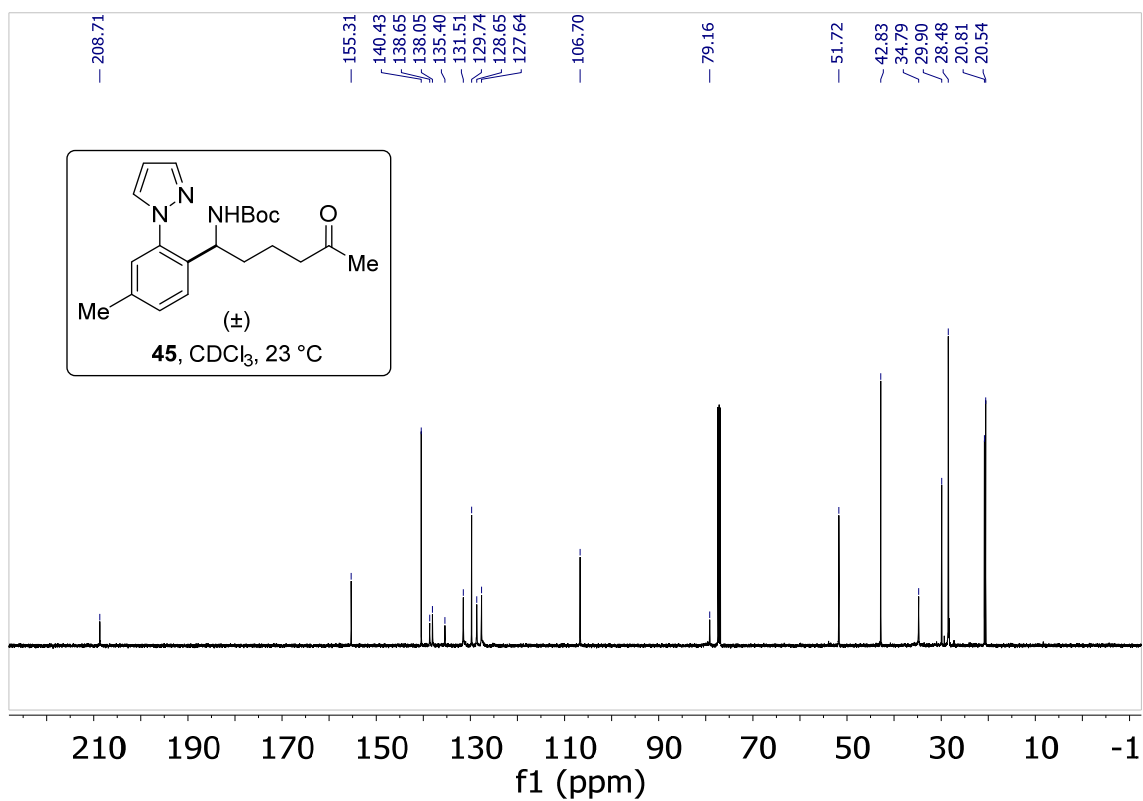
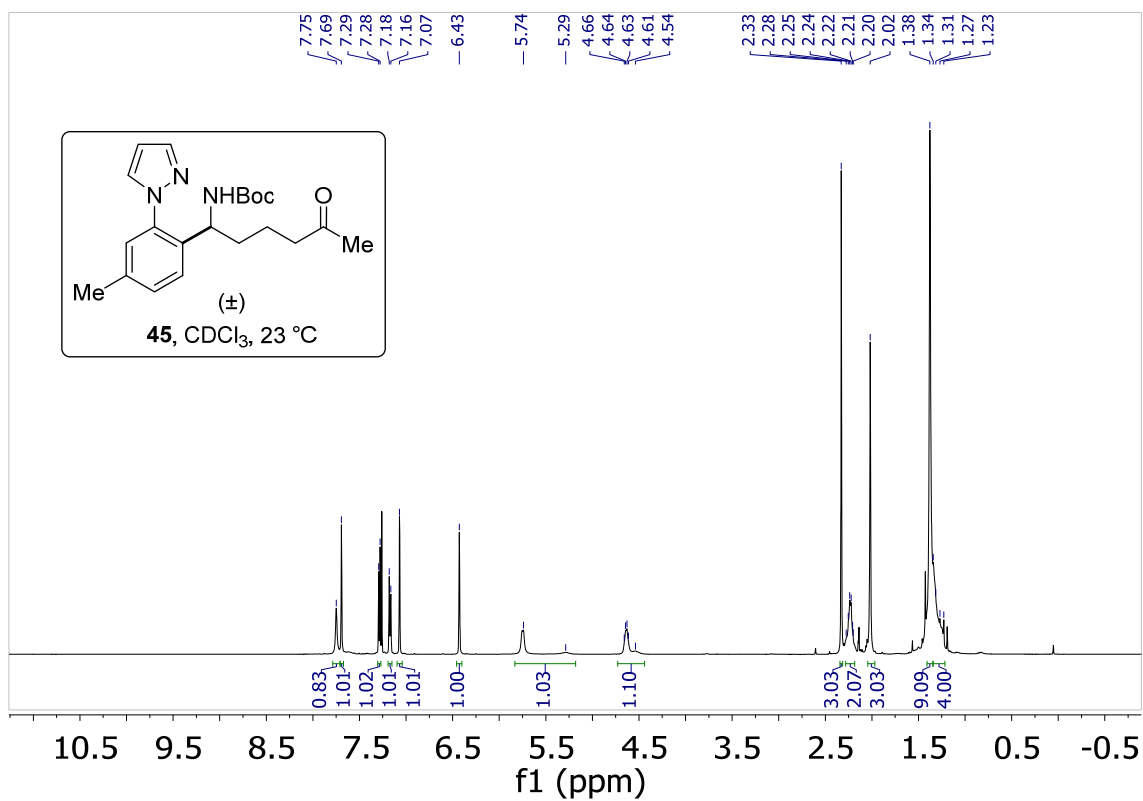


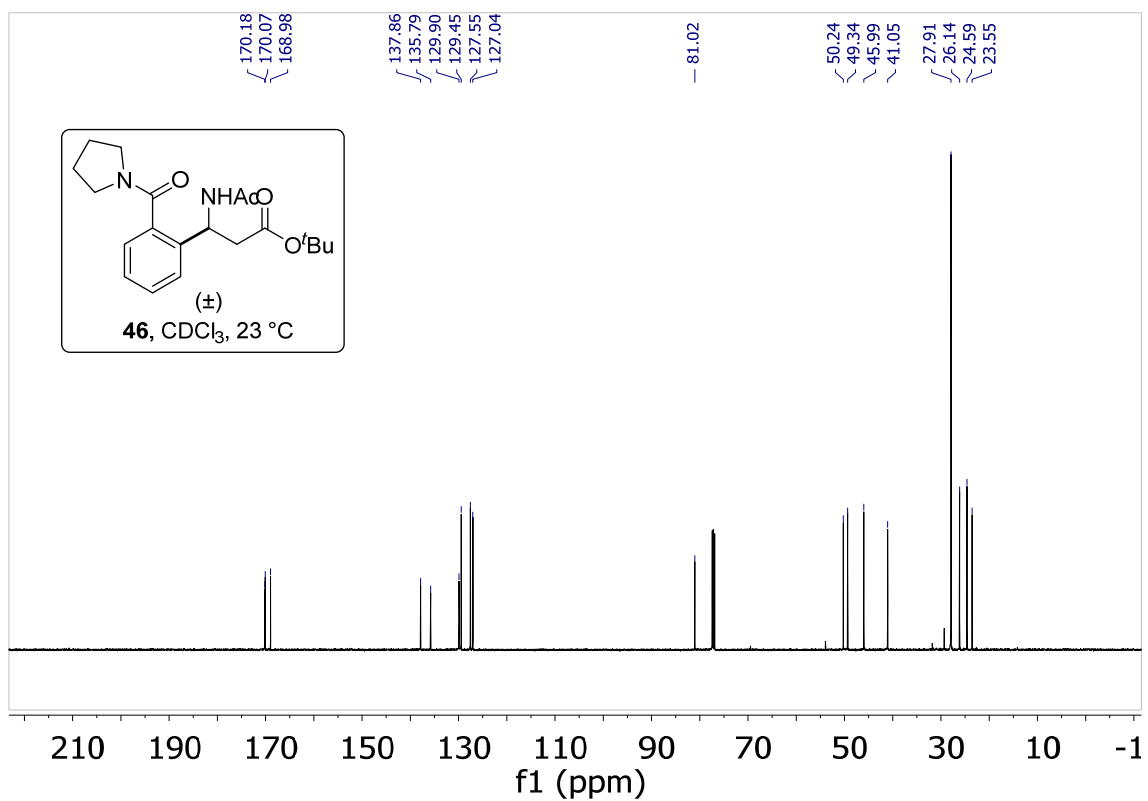
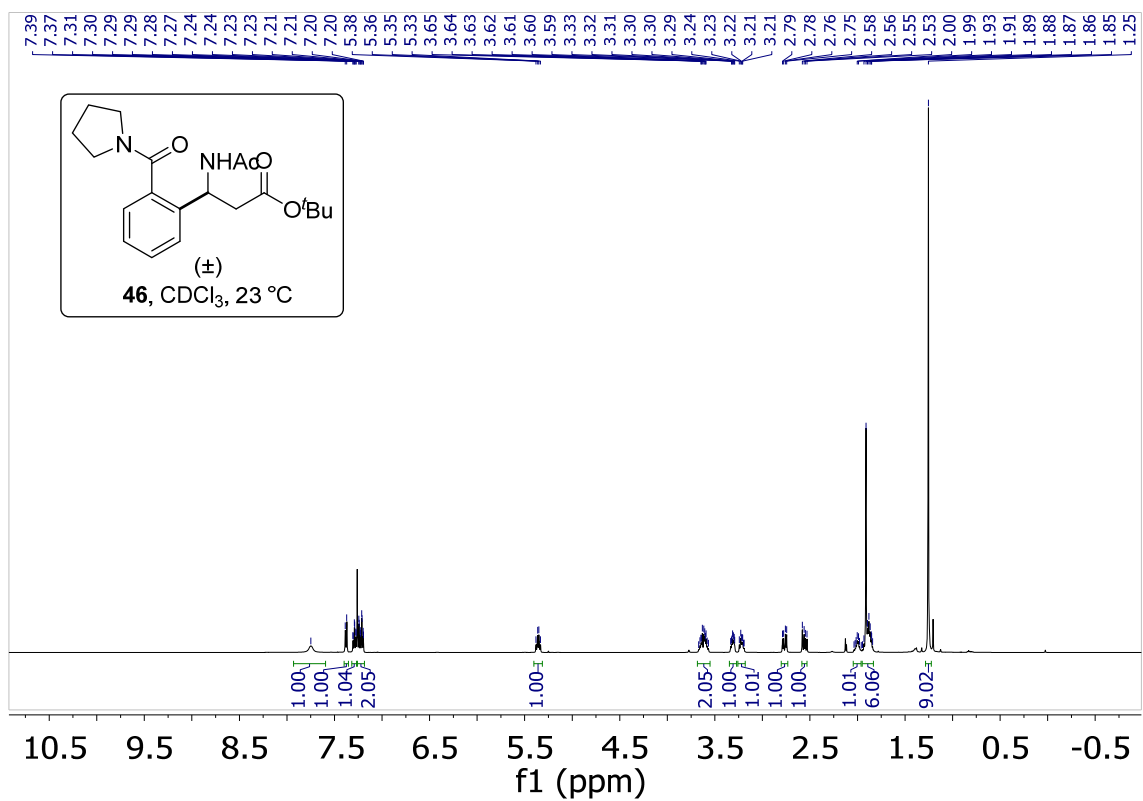


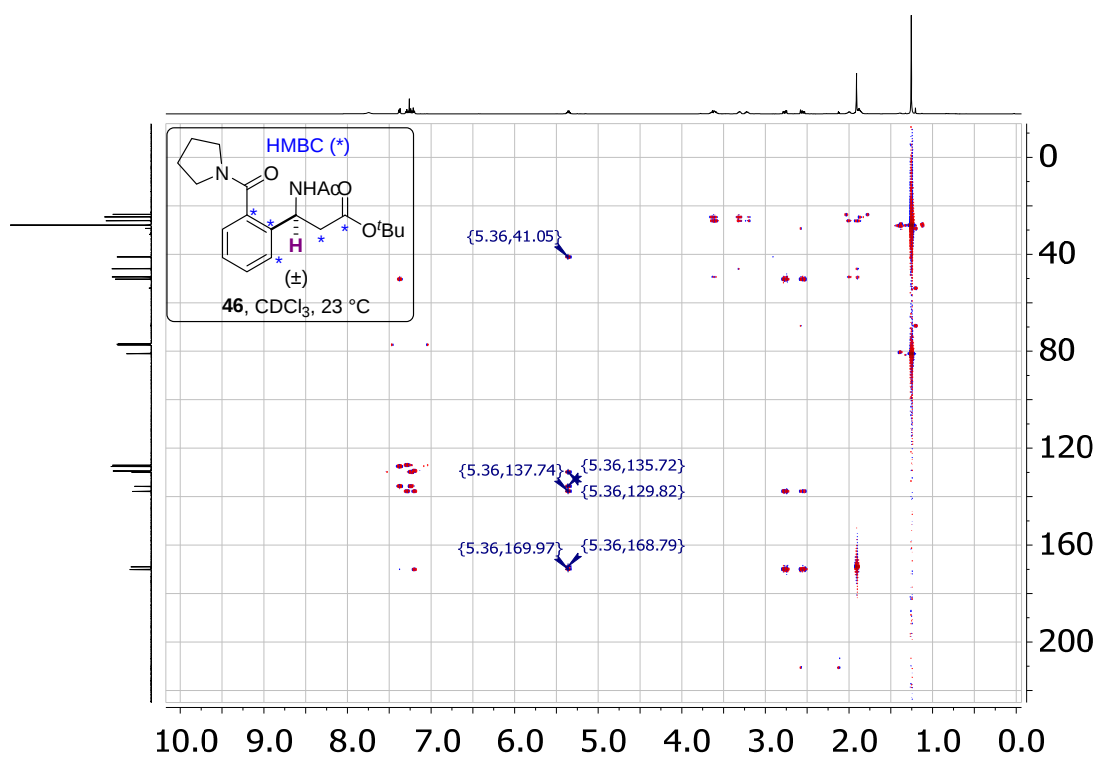
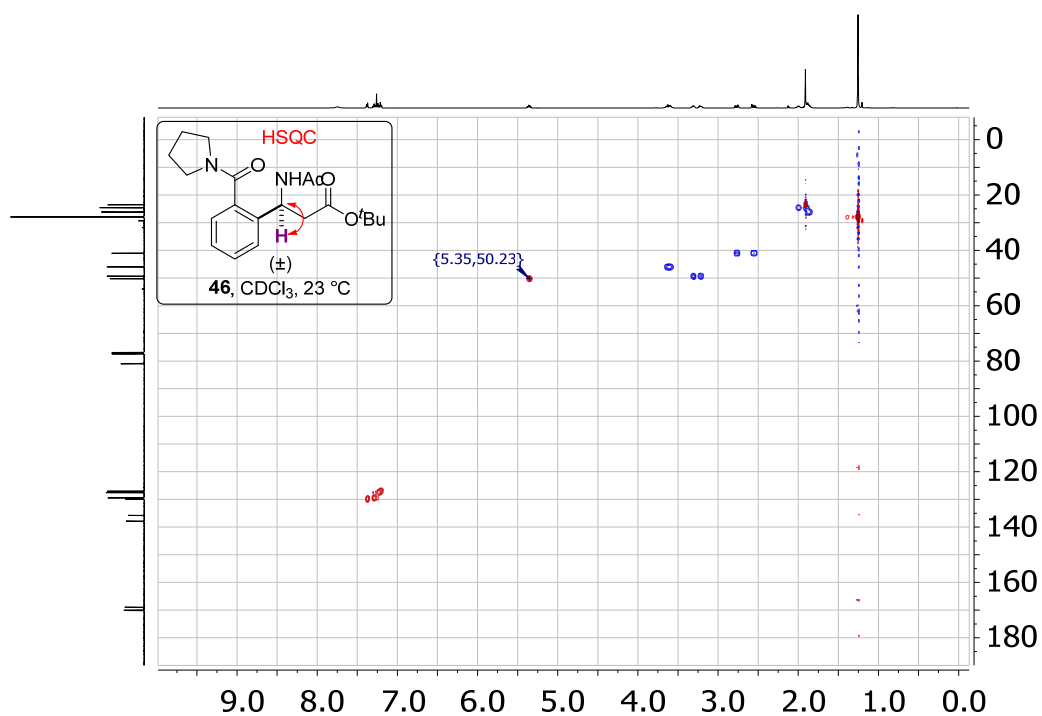


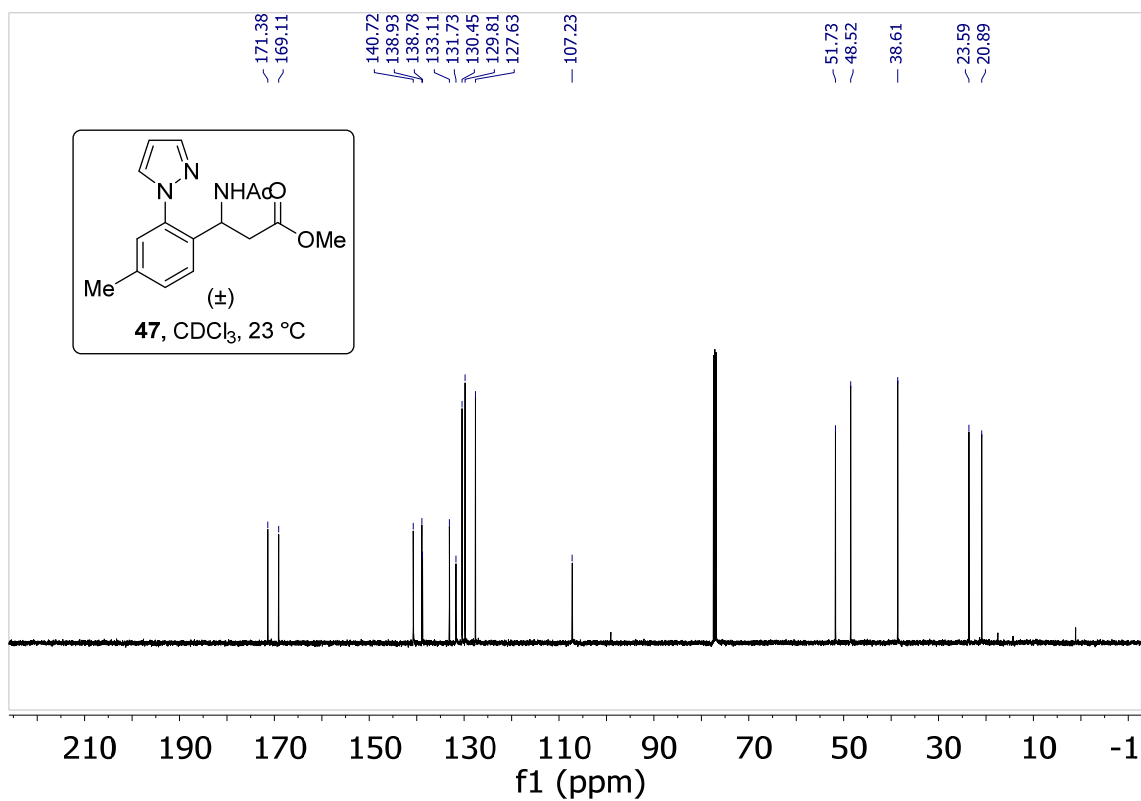
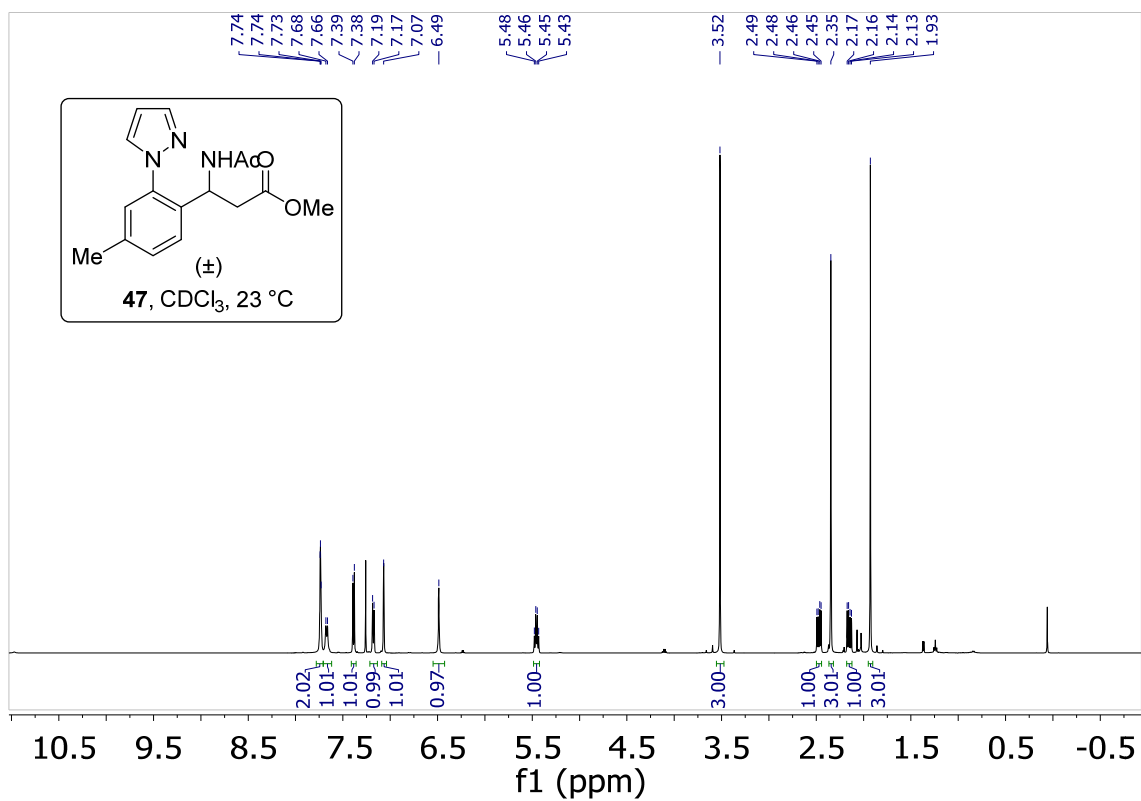


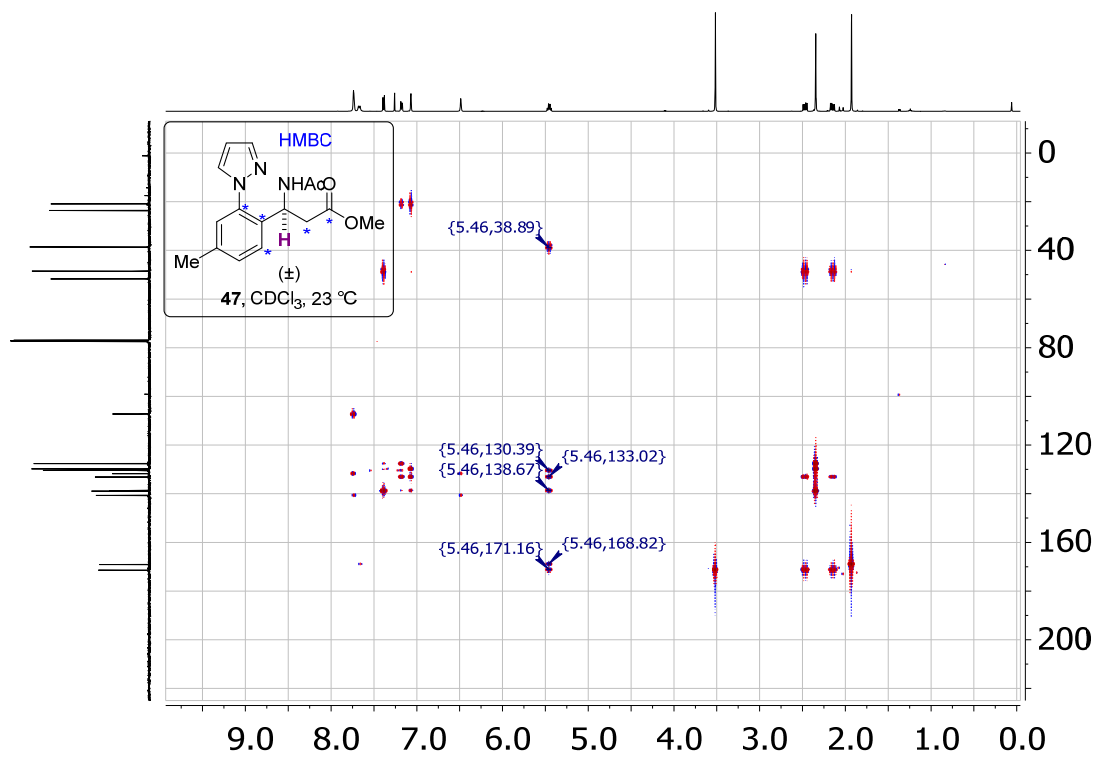
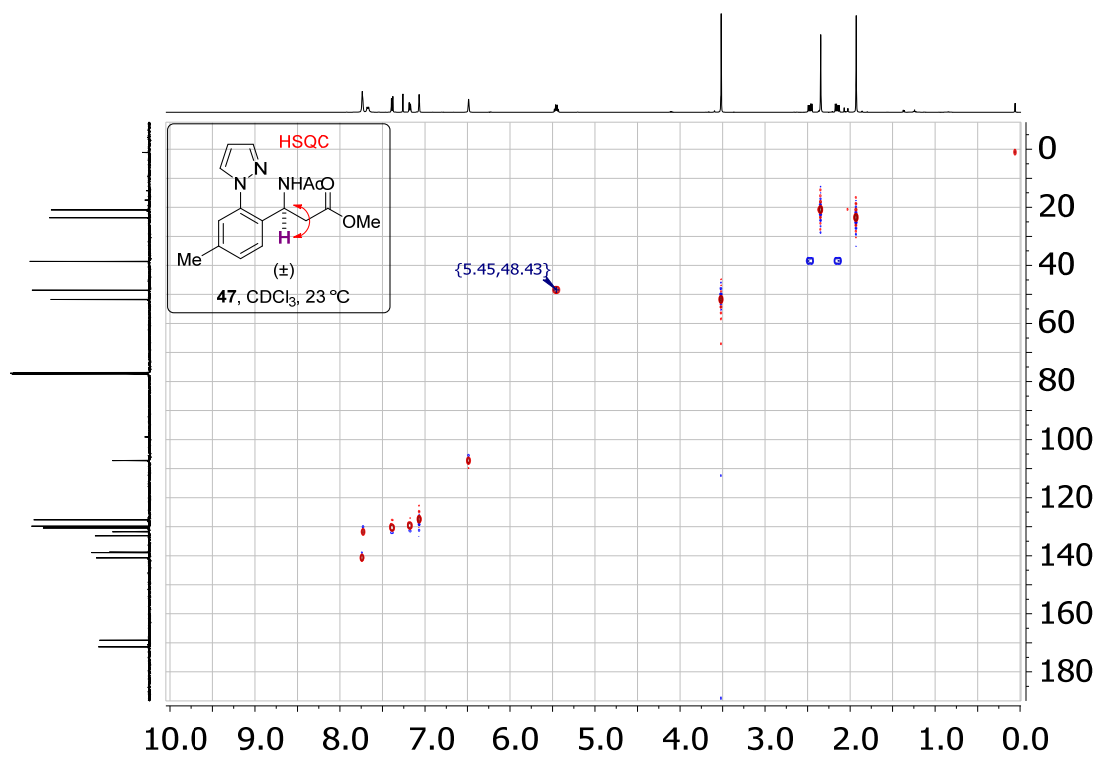


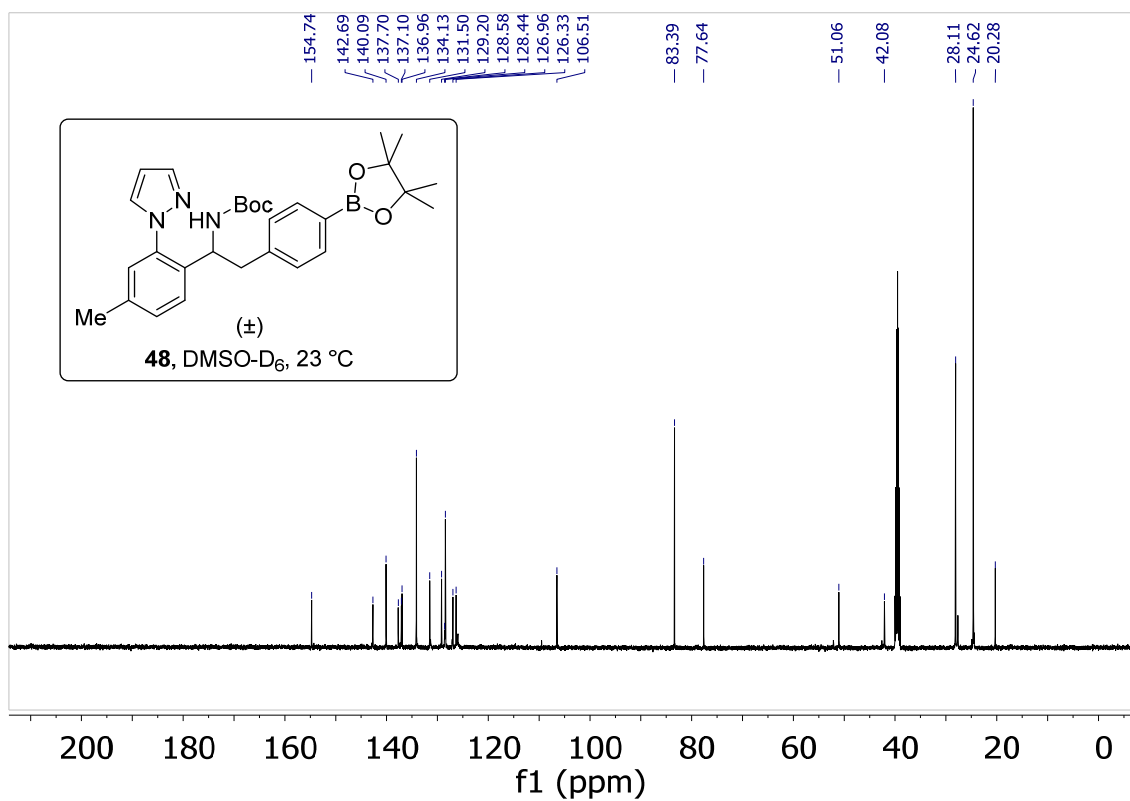
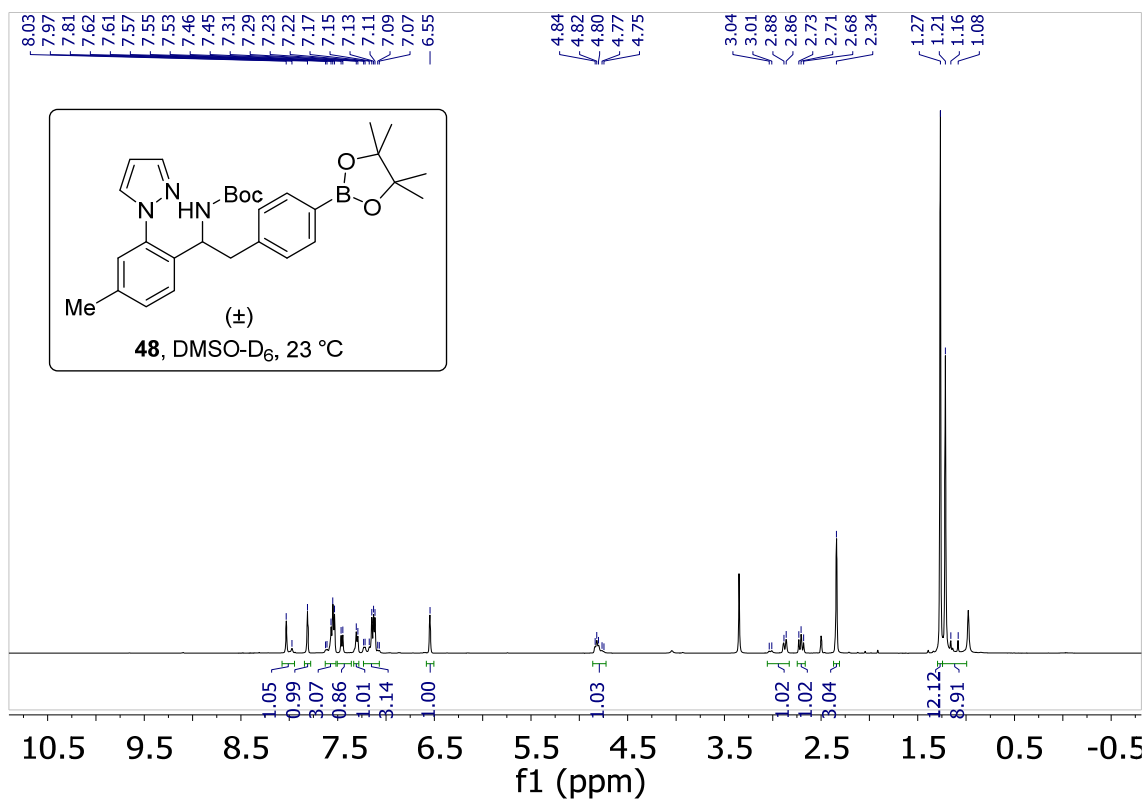


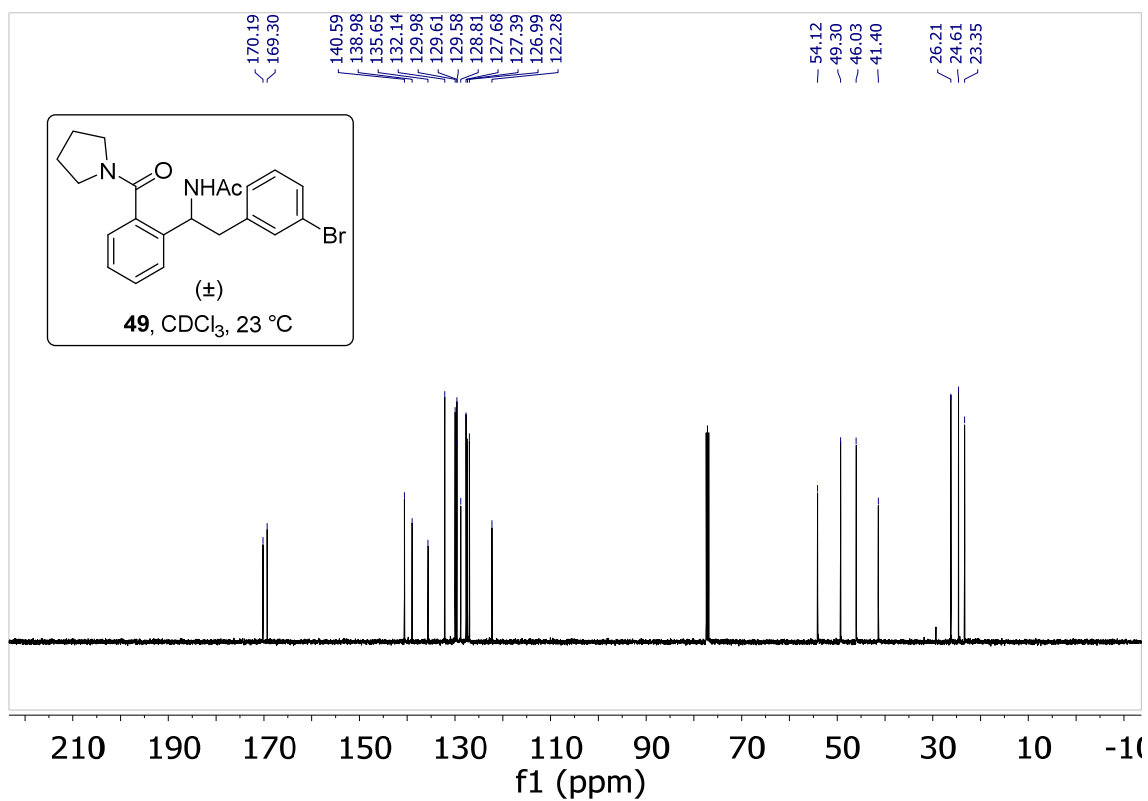
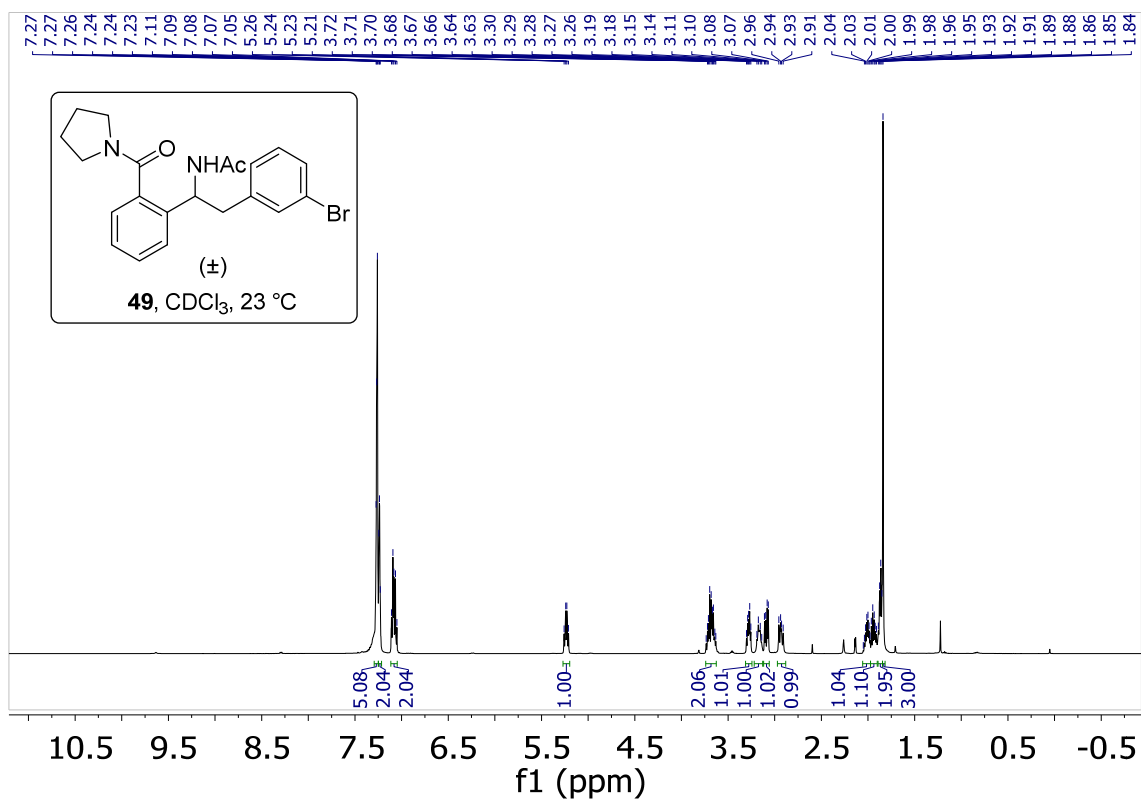


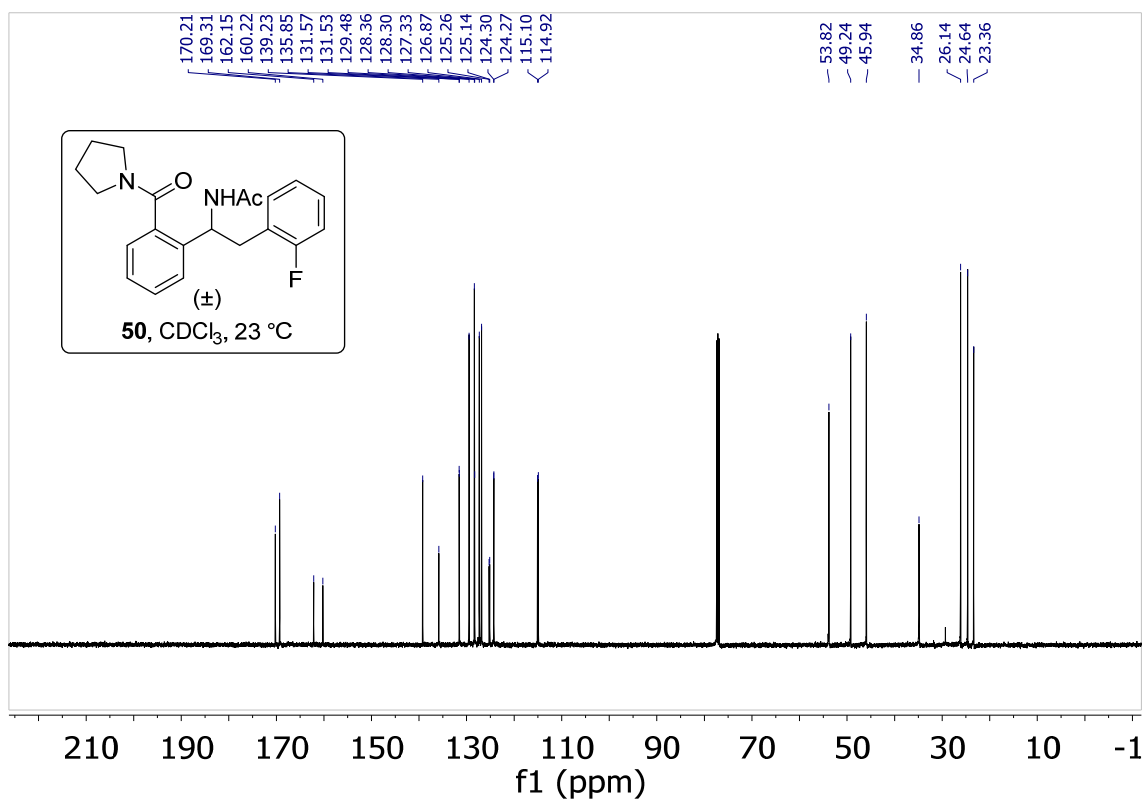
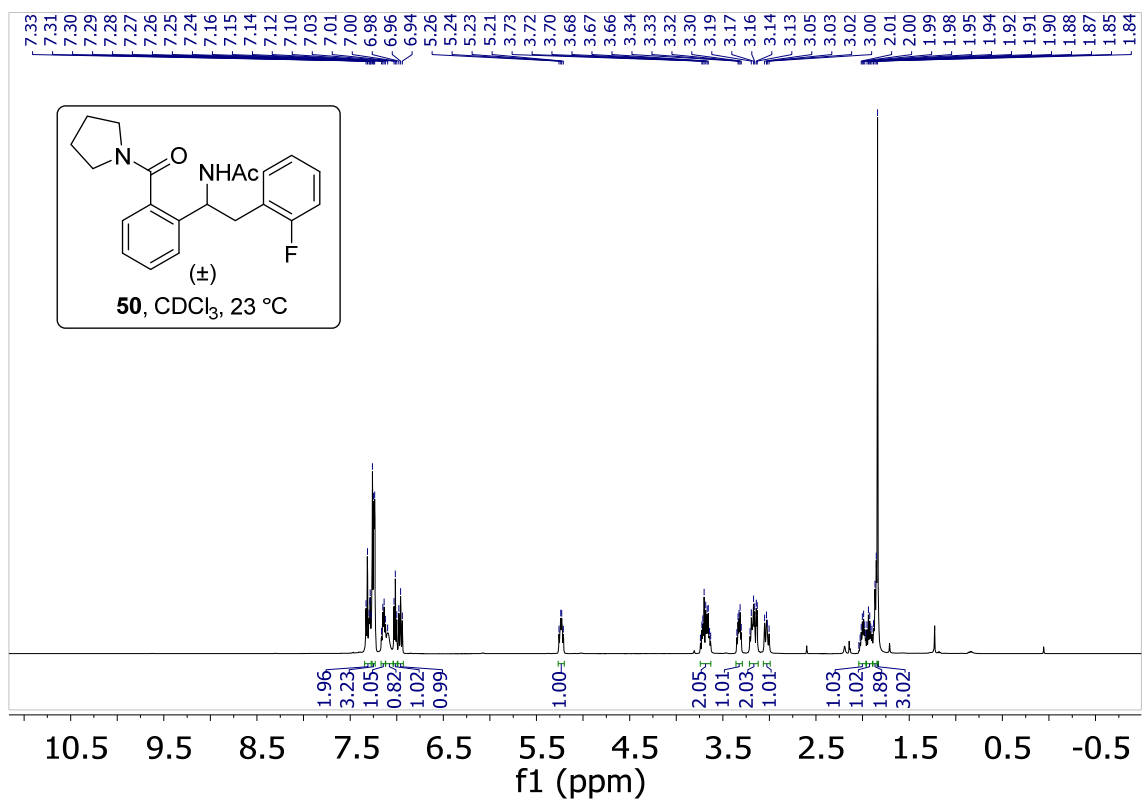


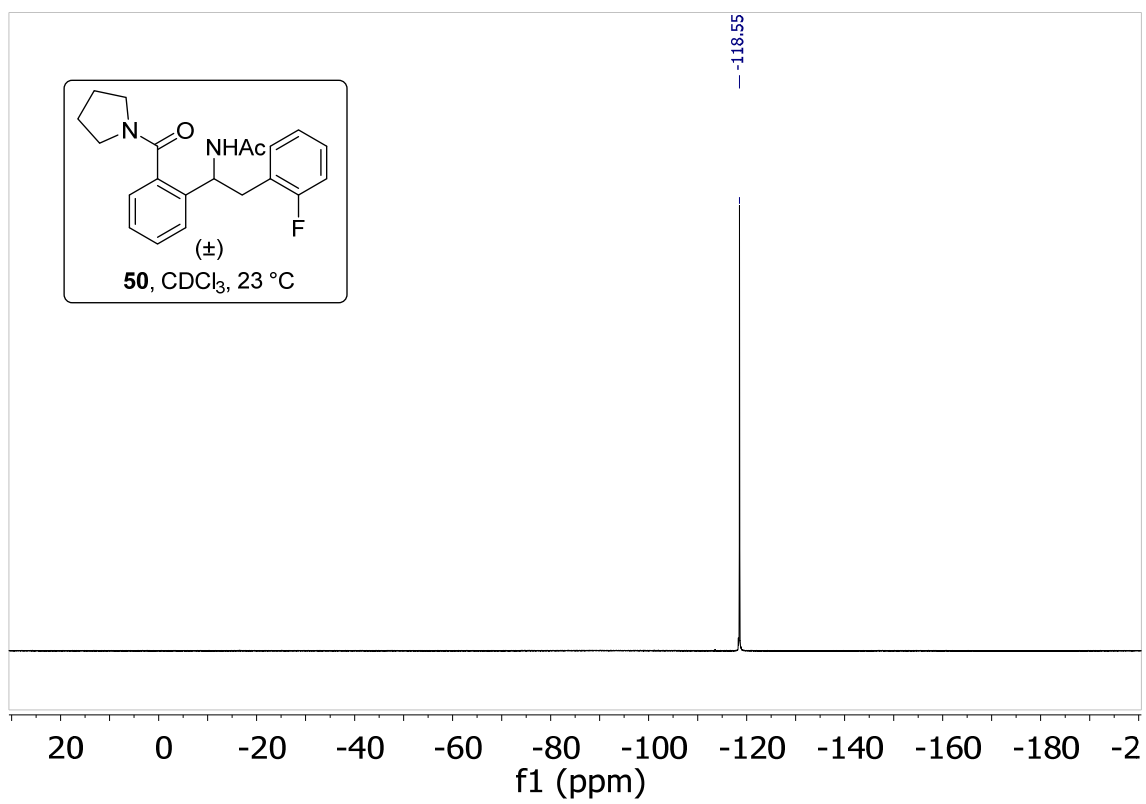


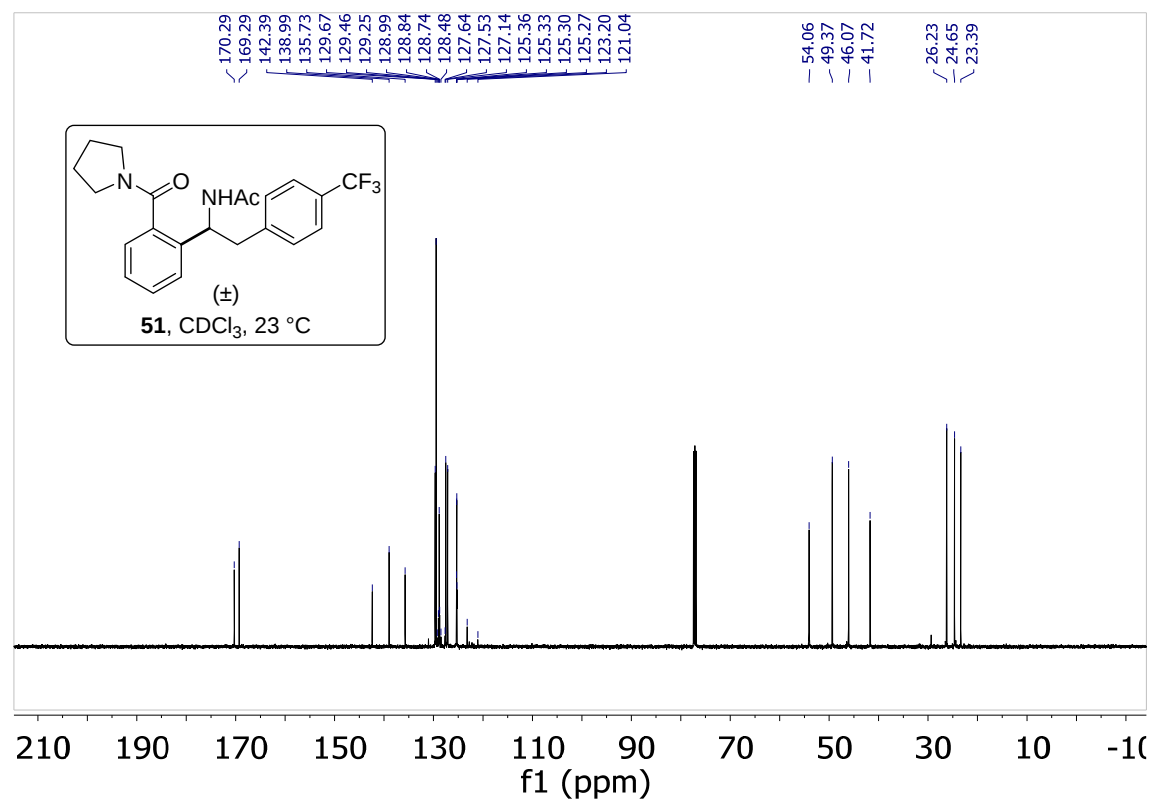
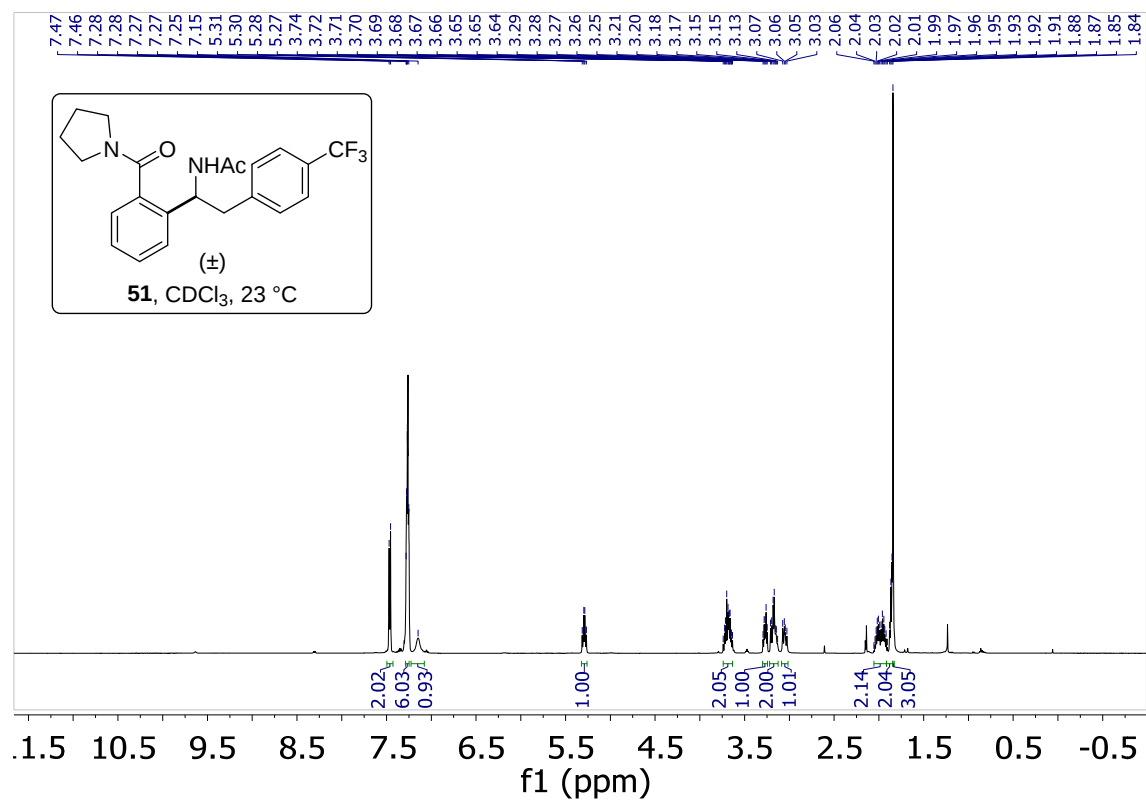


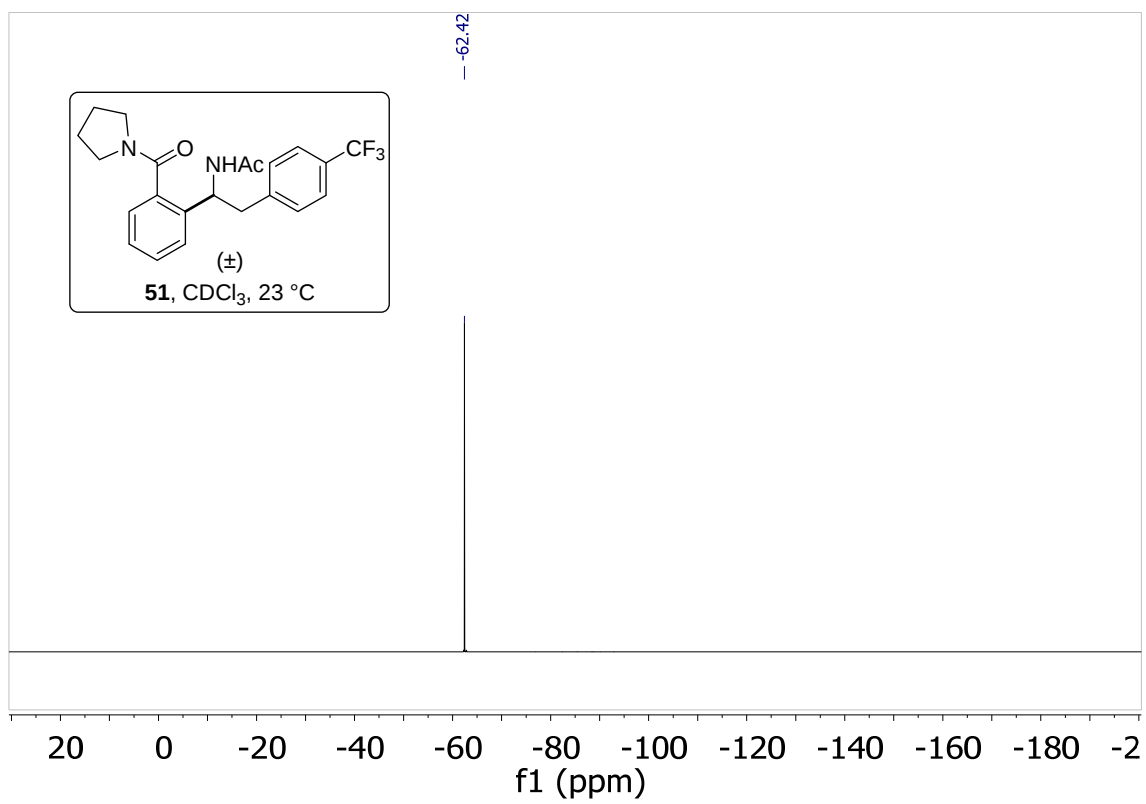


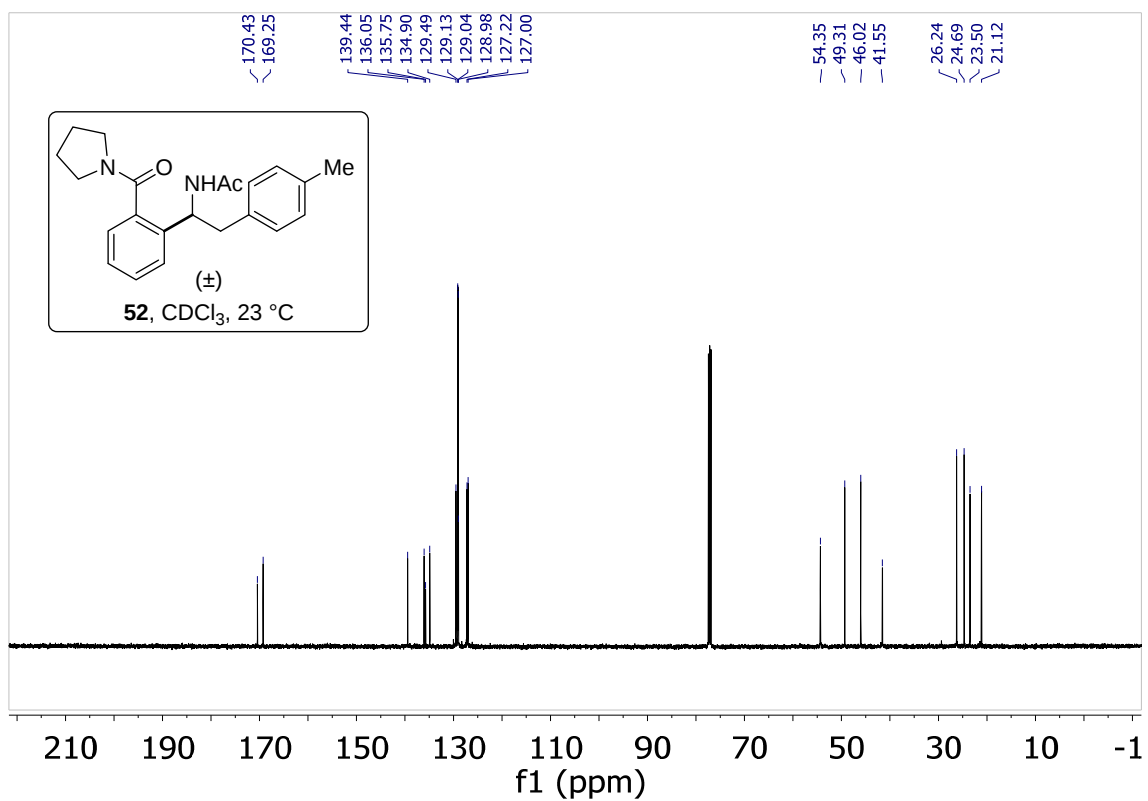
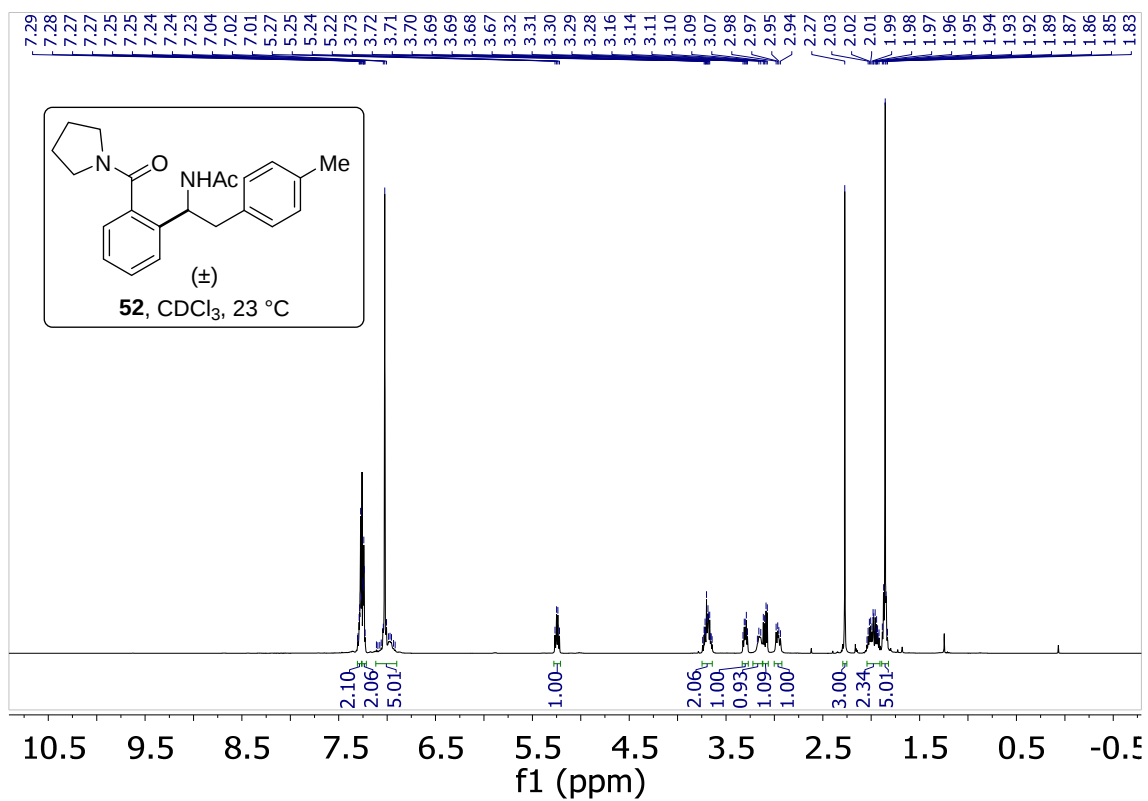


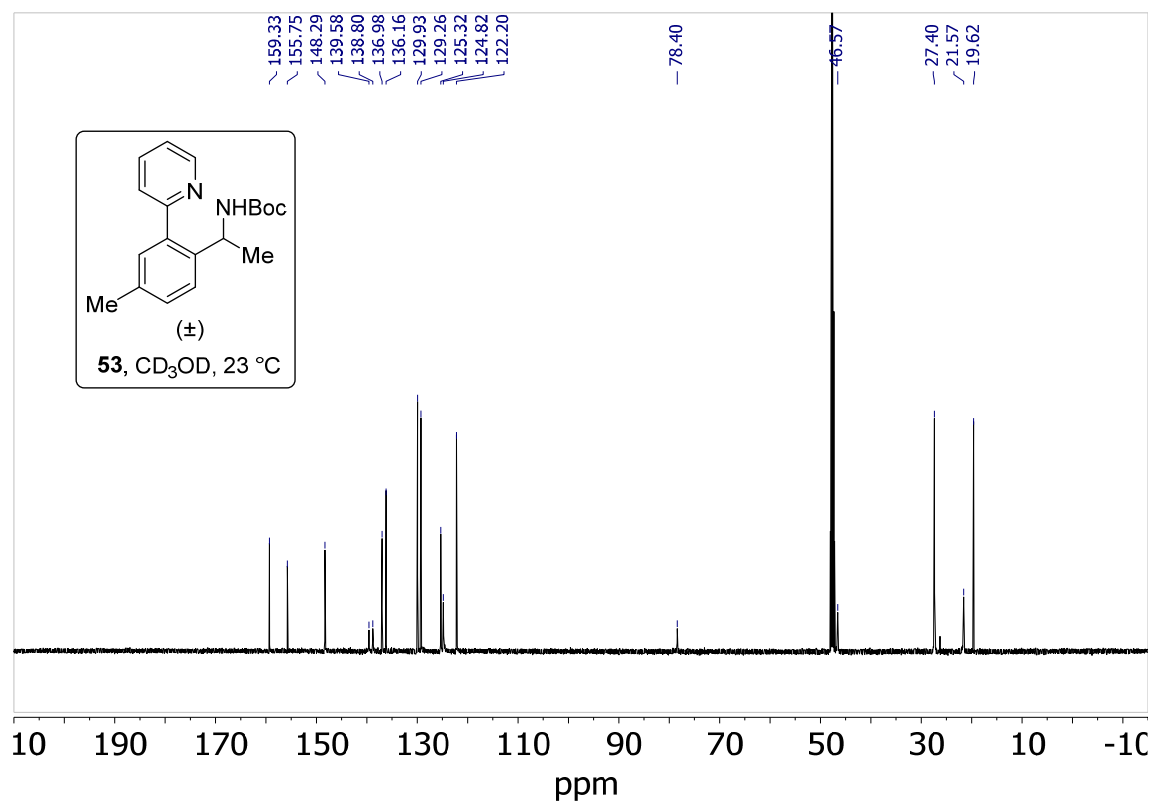
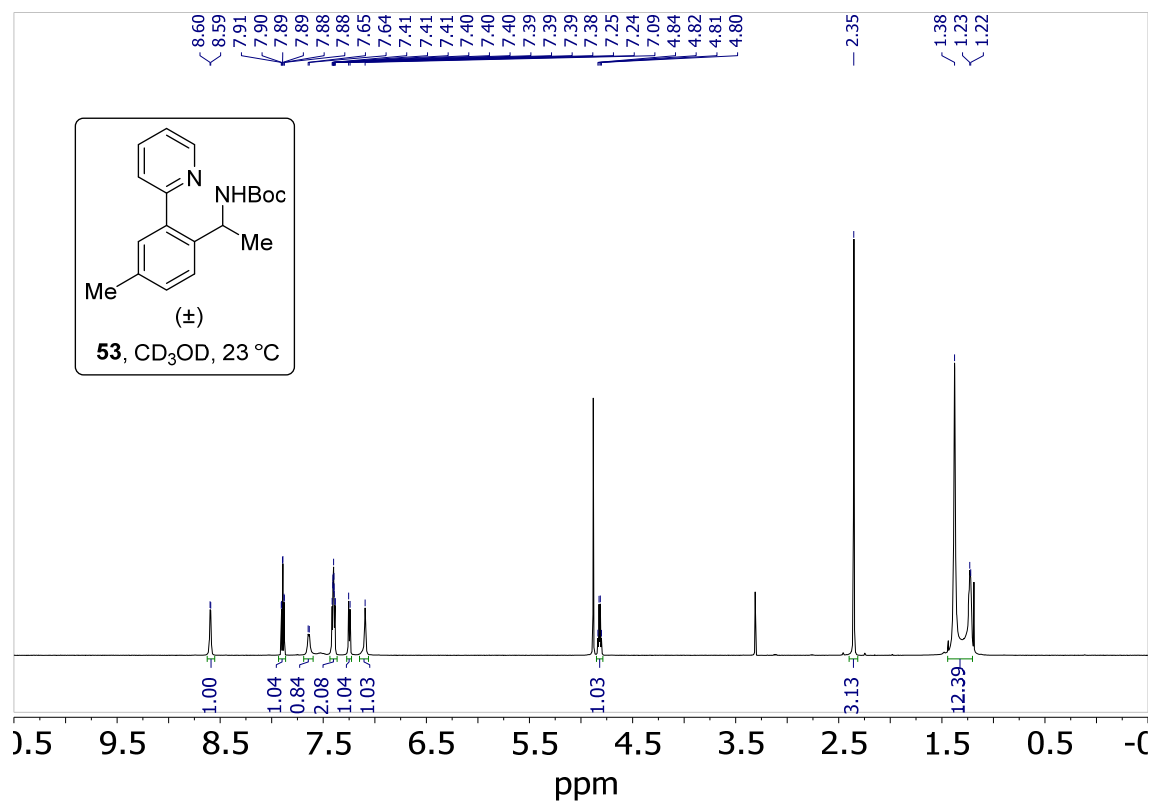




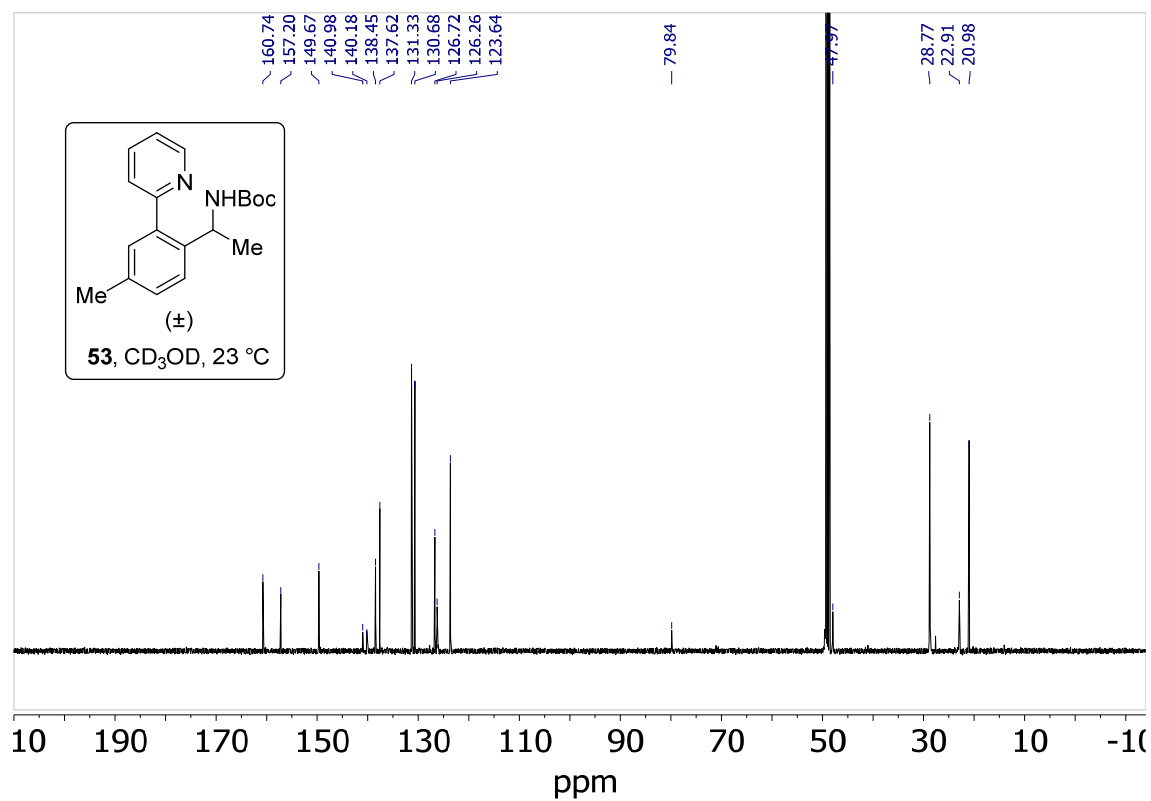
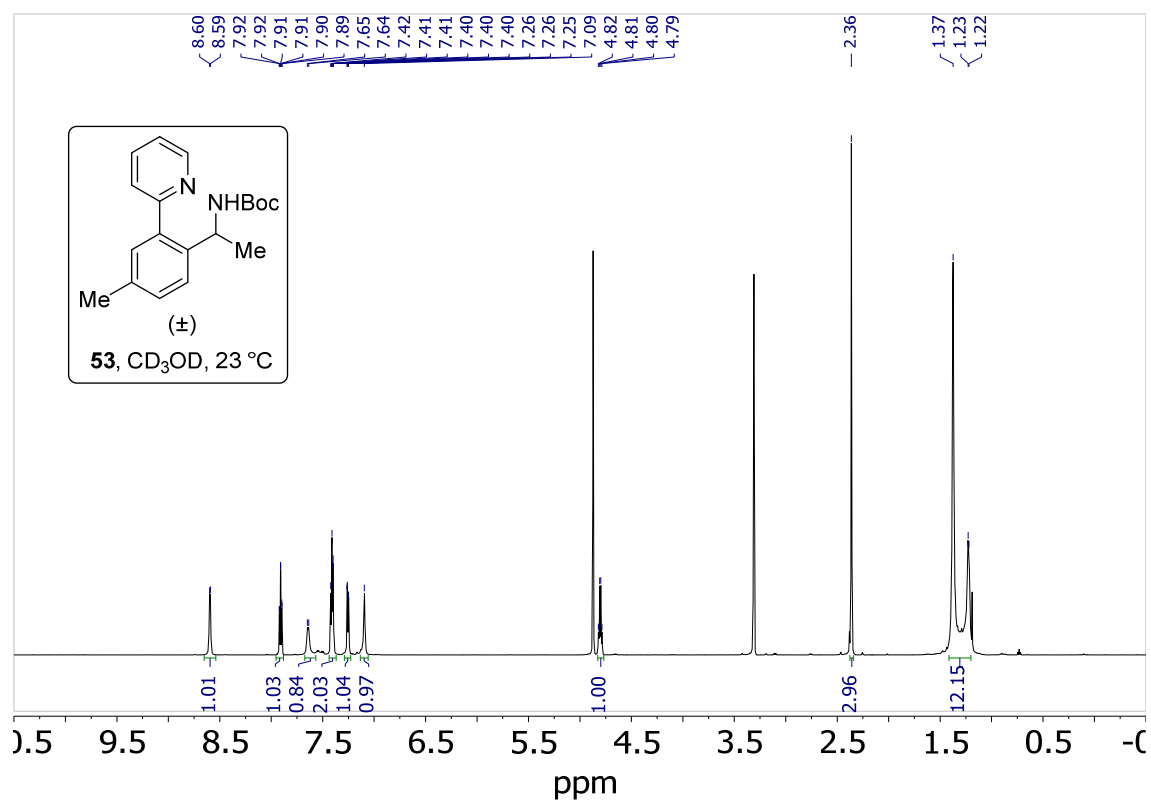


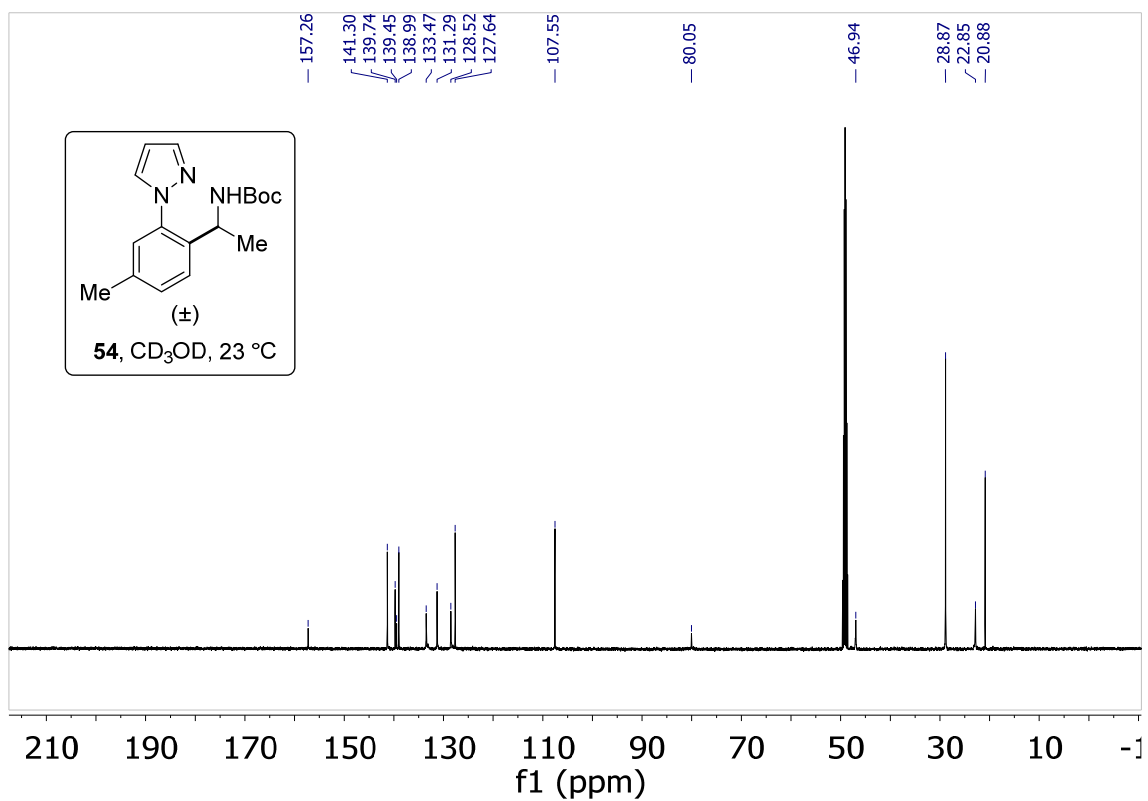
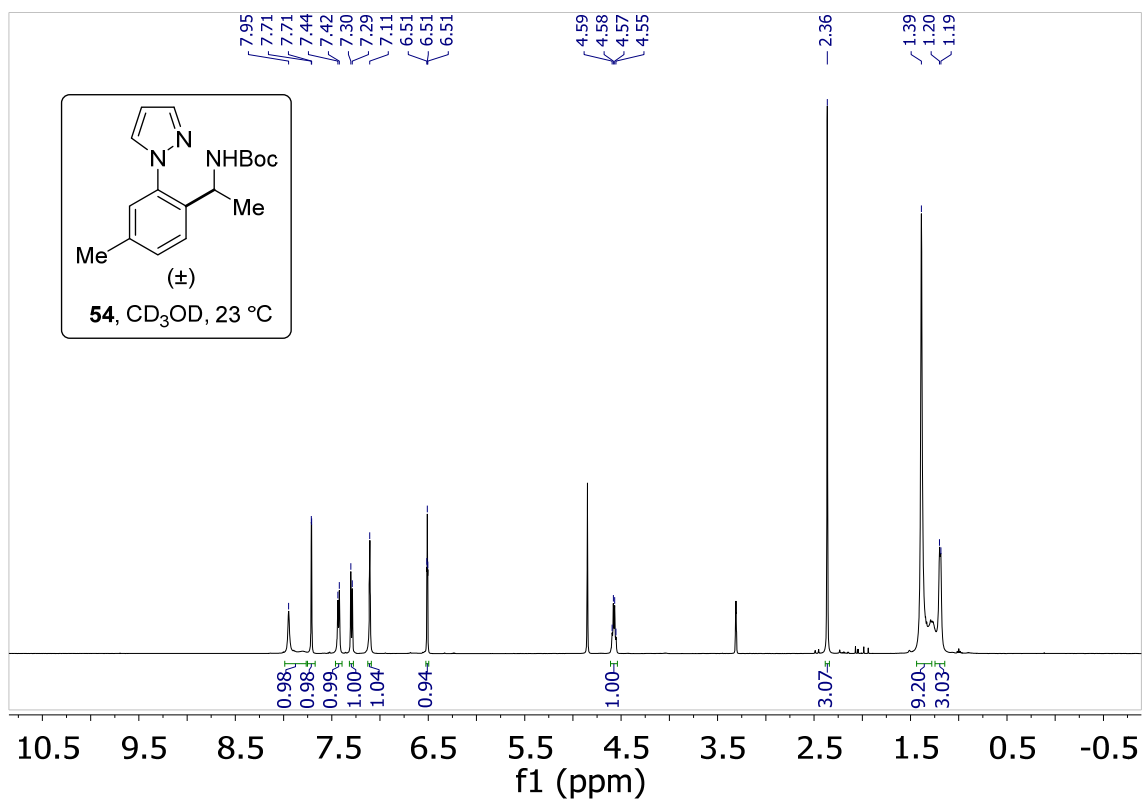




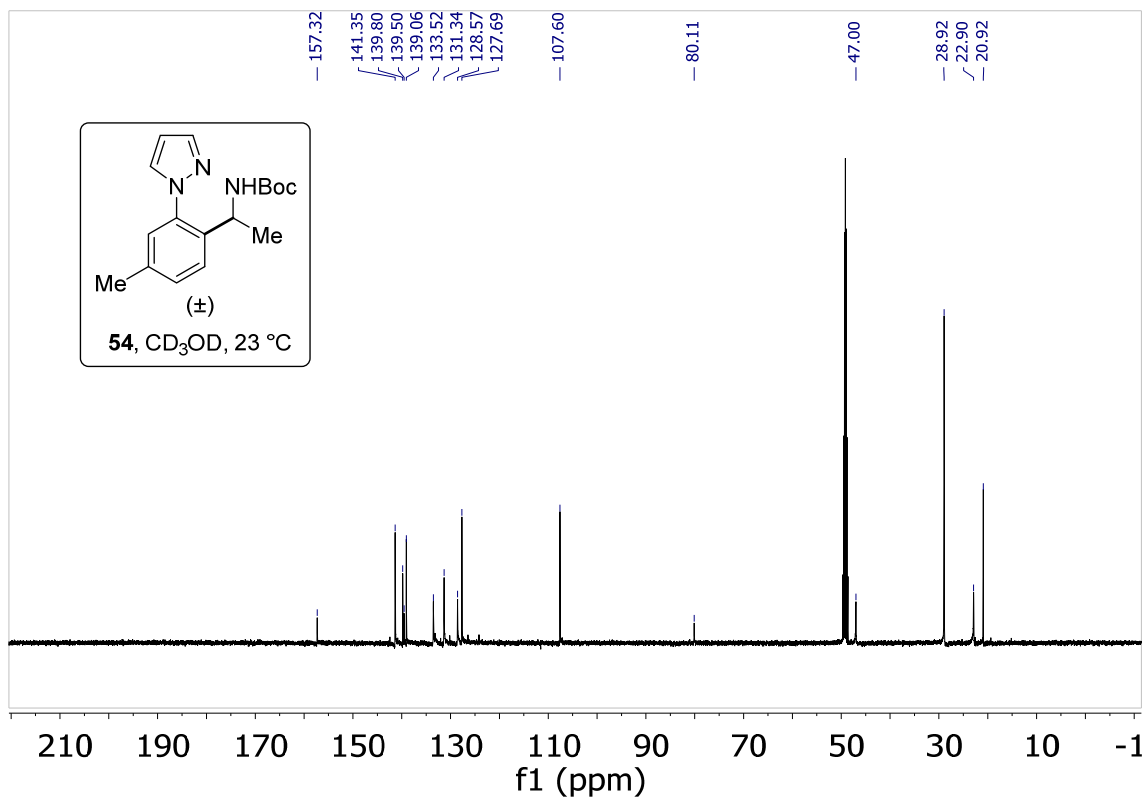
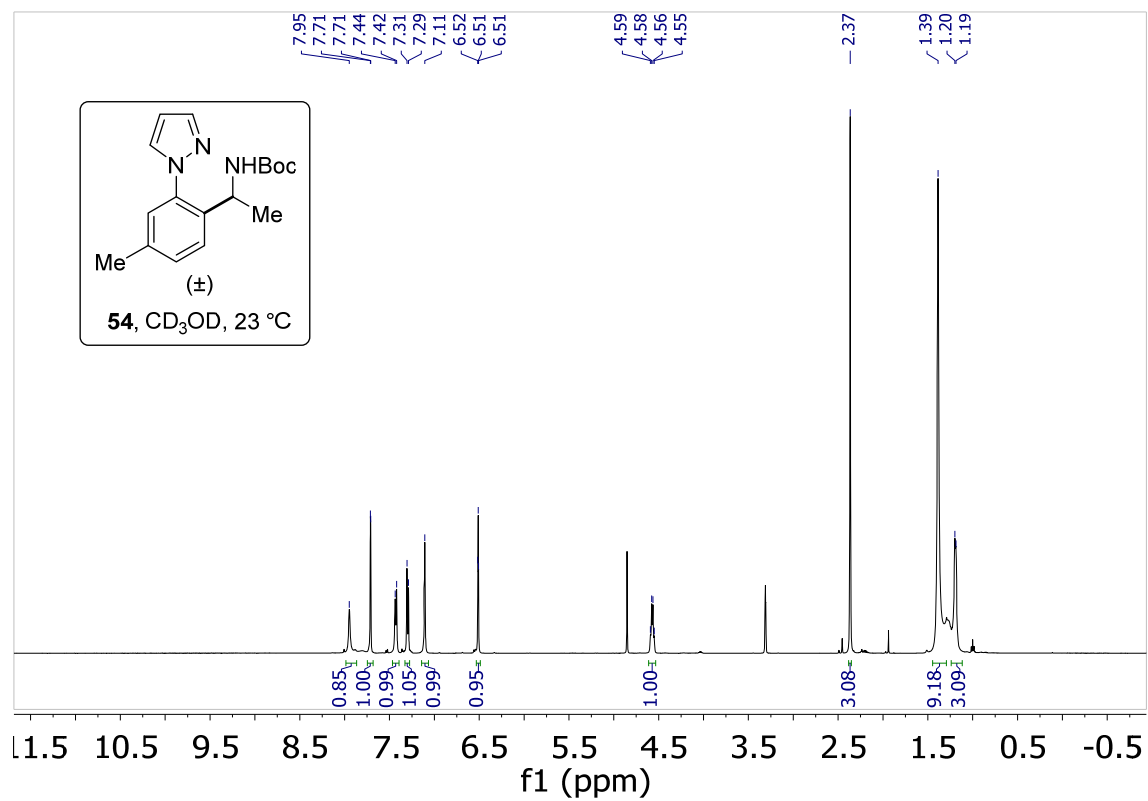


Reaction at 150 psi pressure in Parr reactor

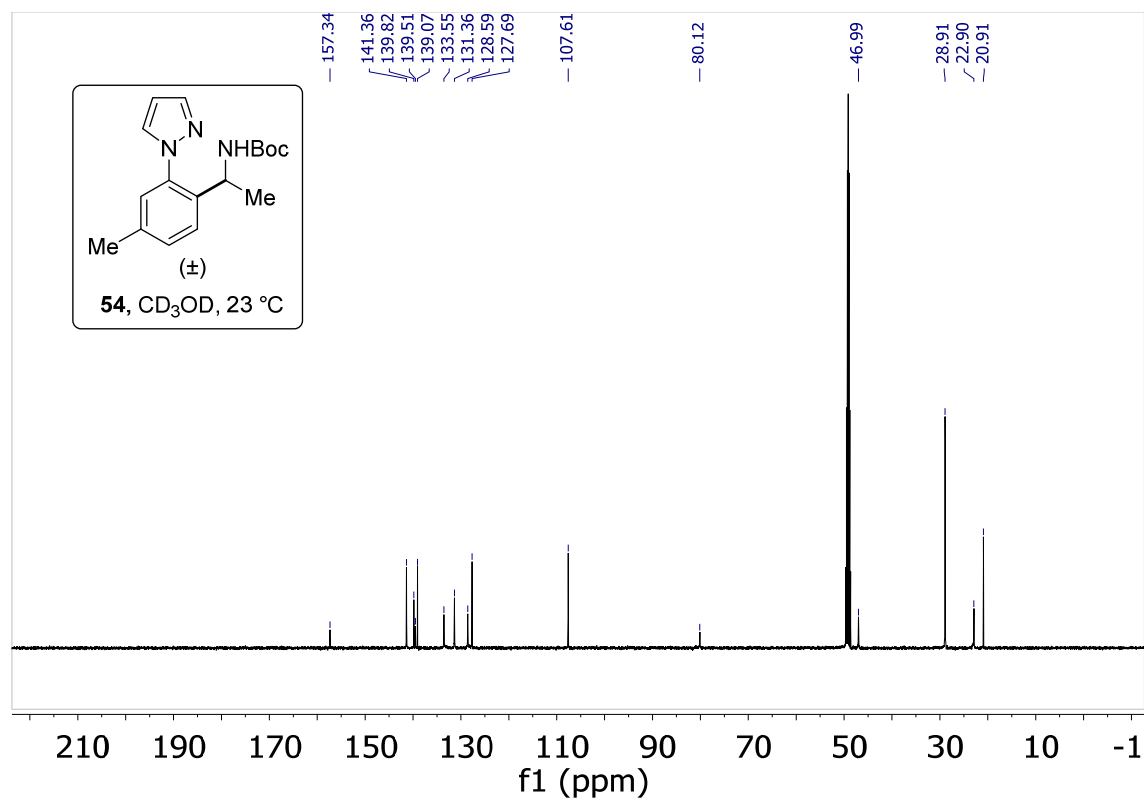
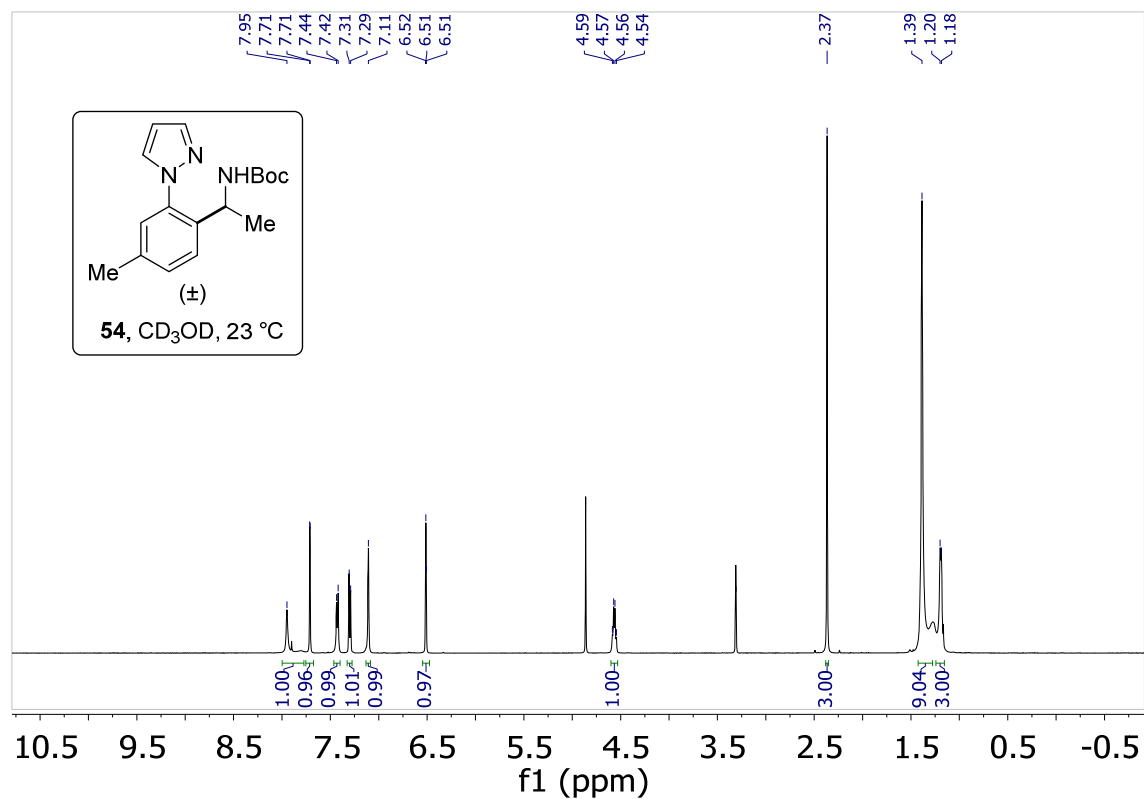


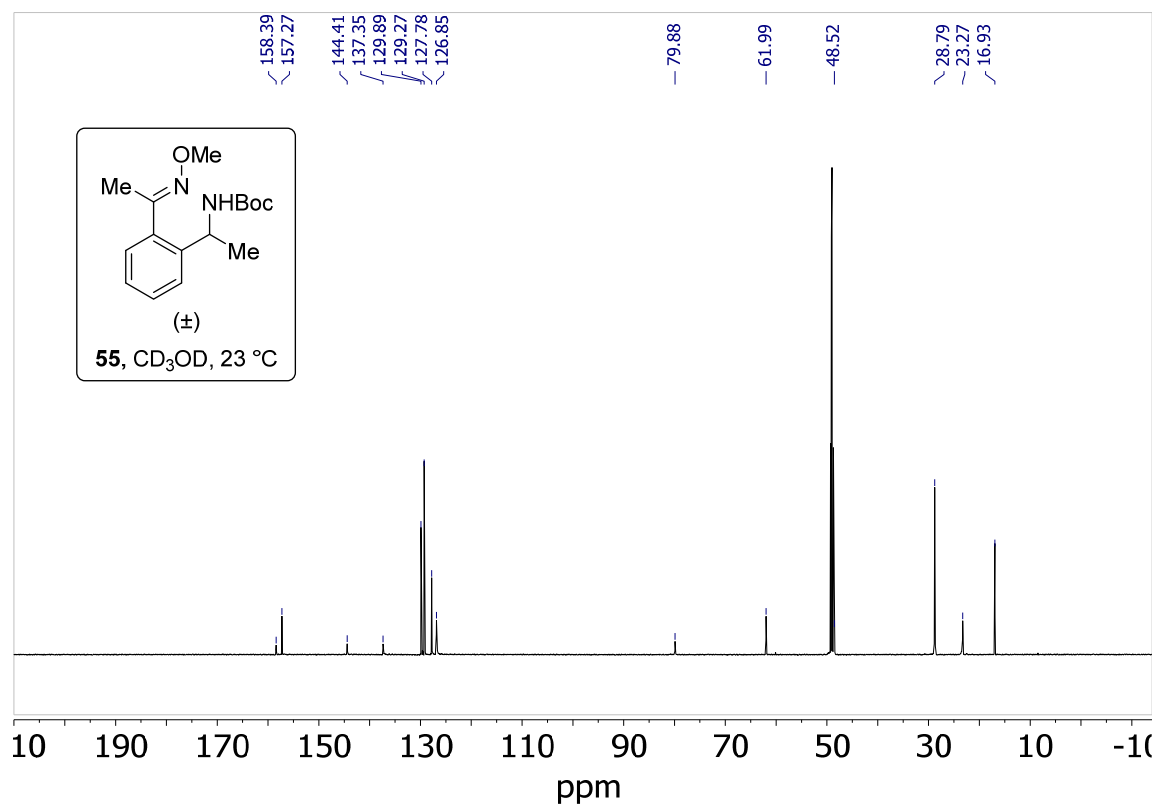
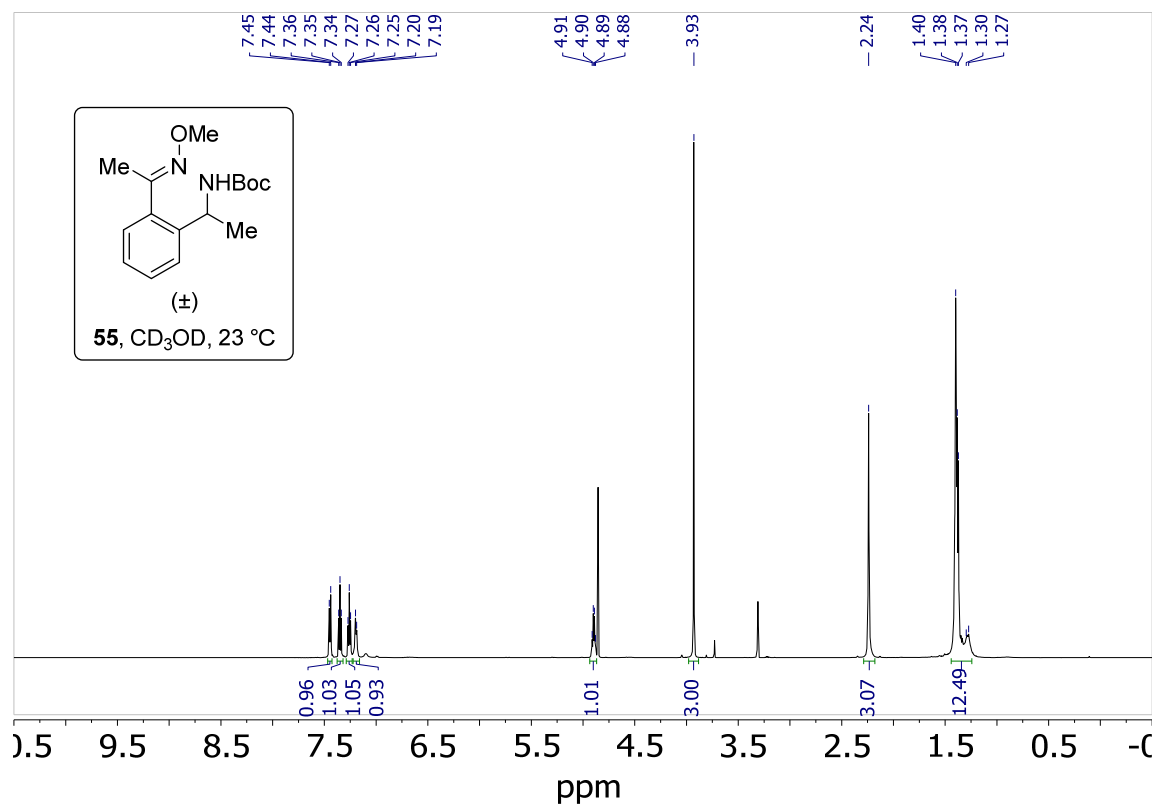


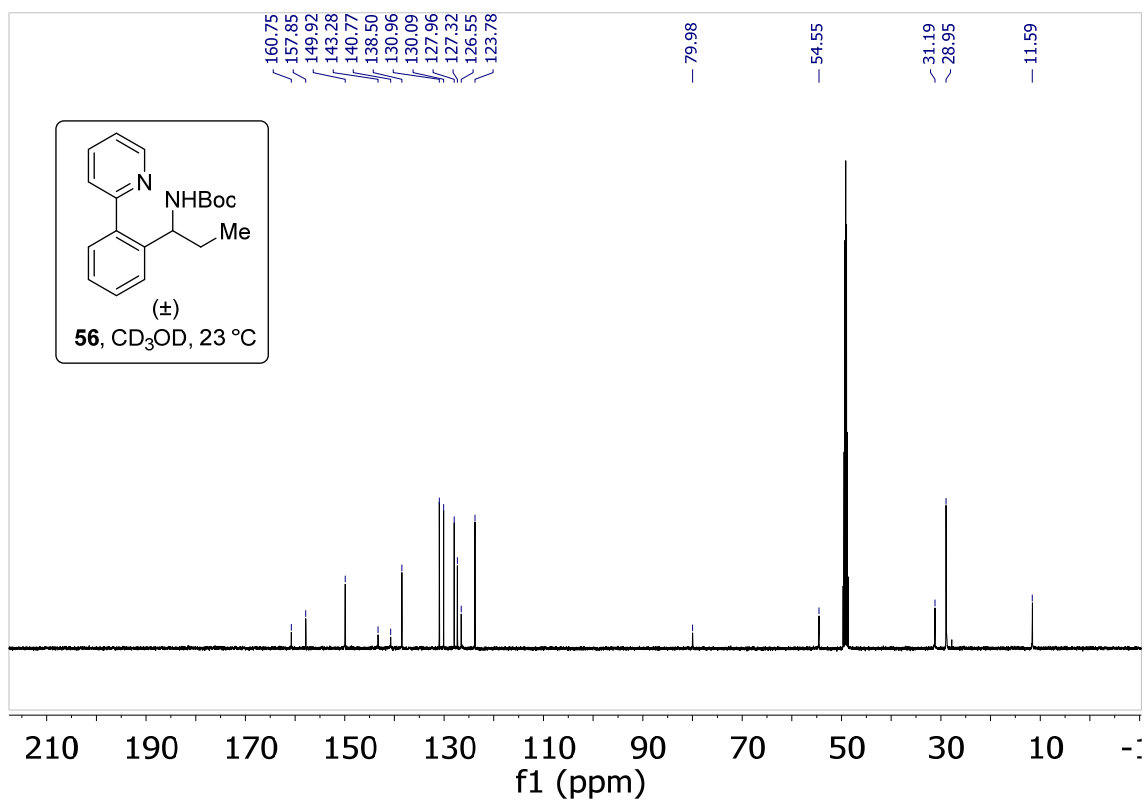
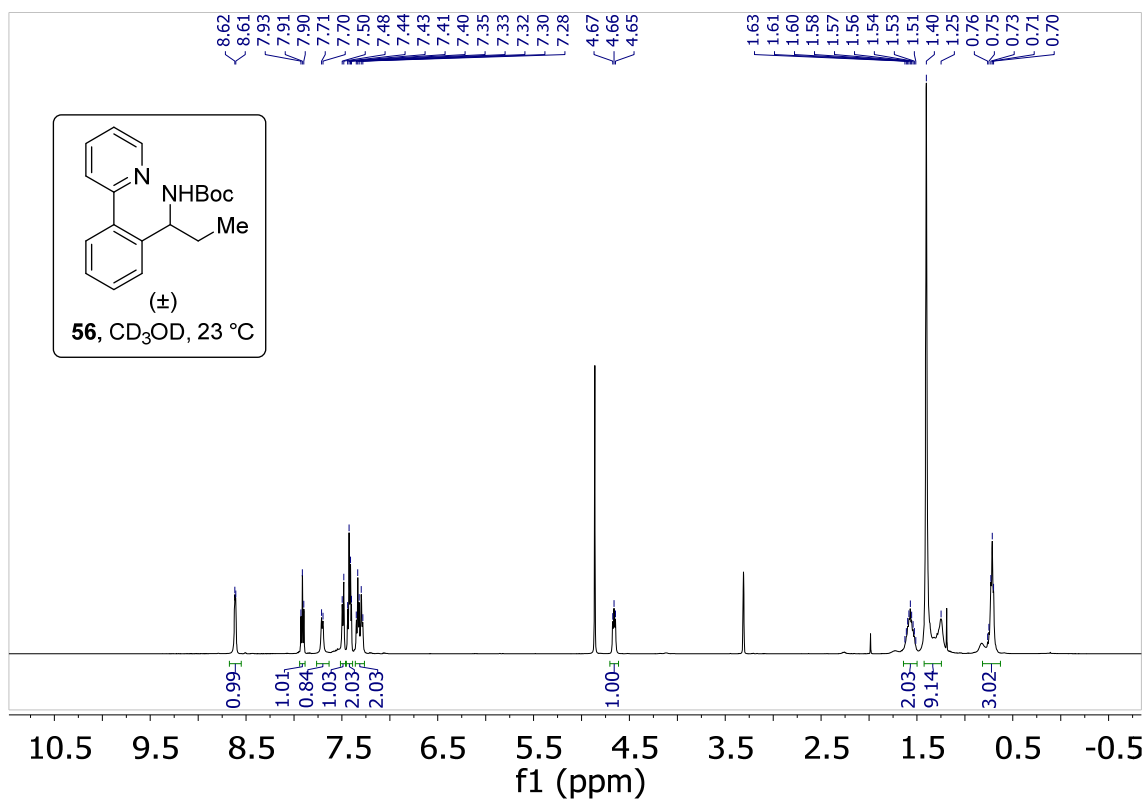
Reaction at 150 psi pressure in Parr reactor

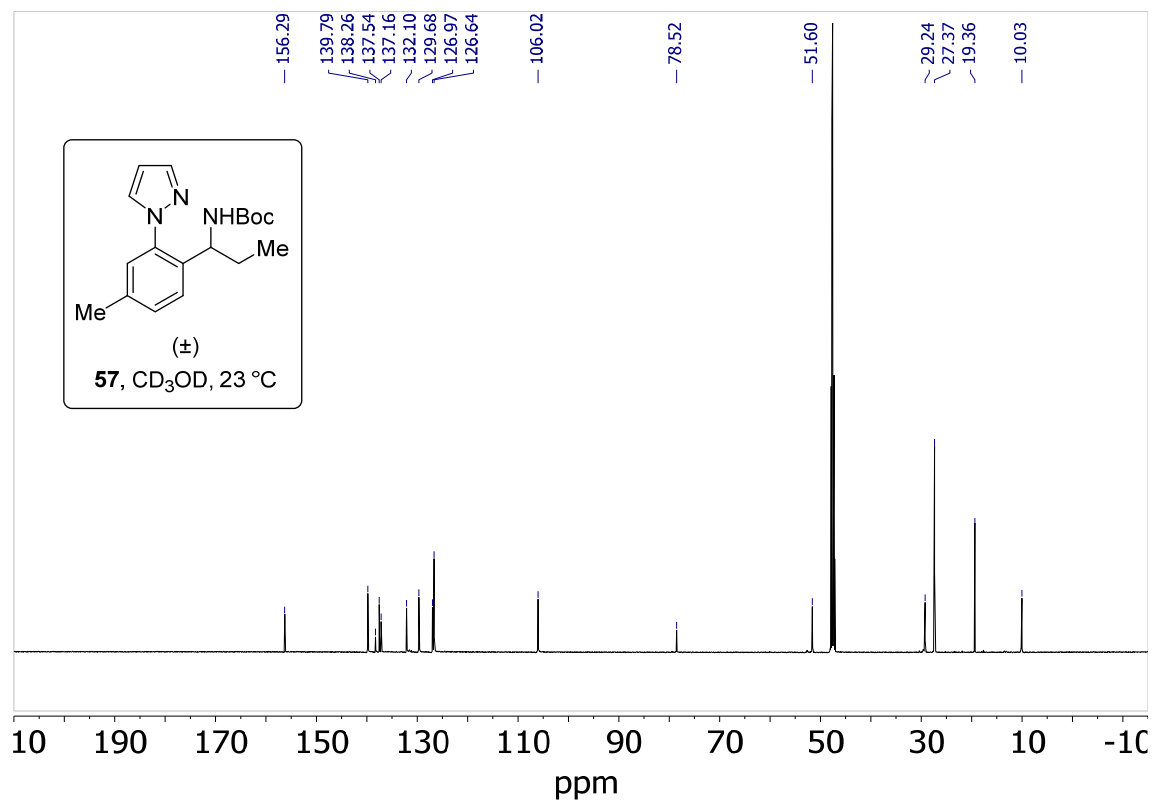
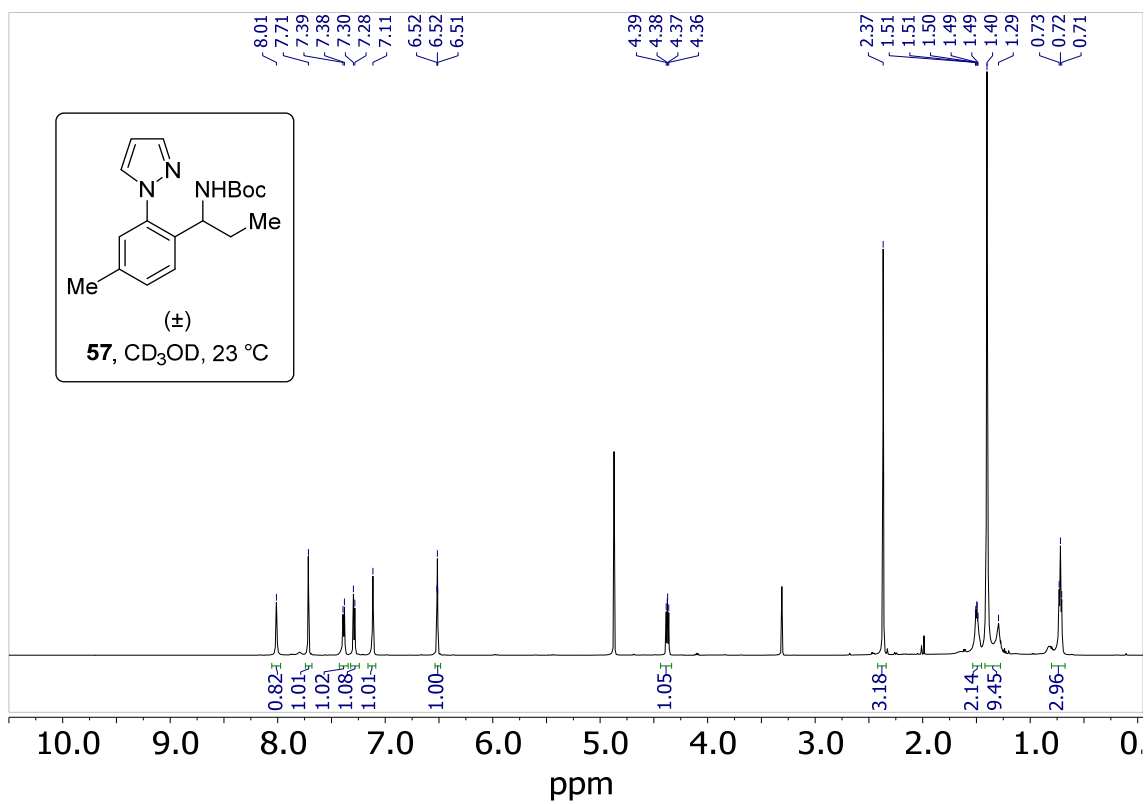


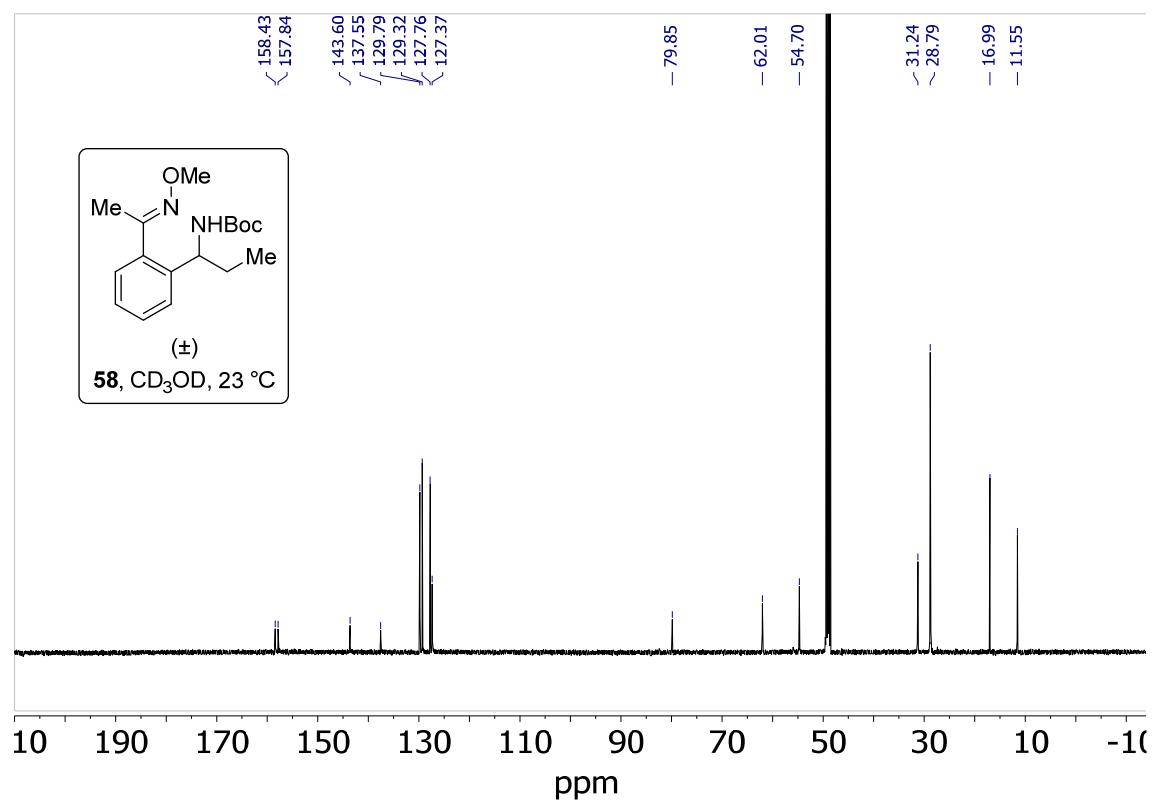
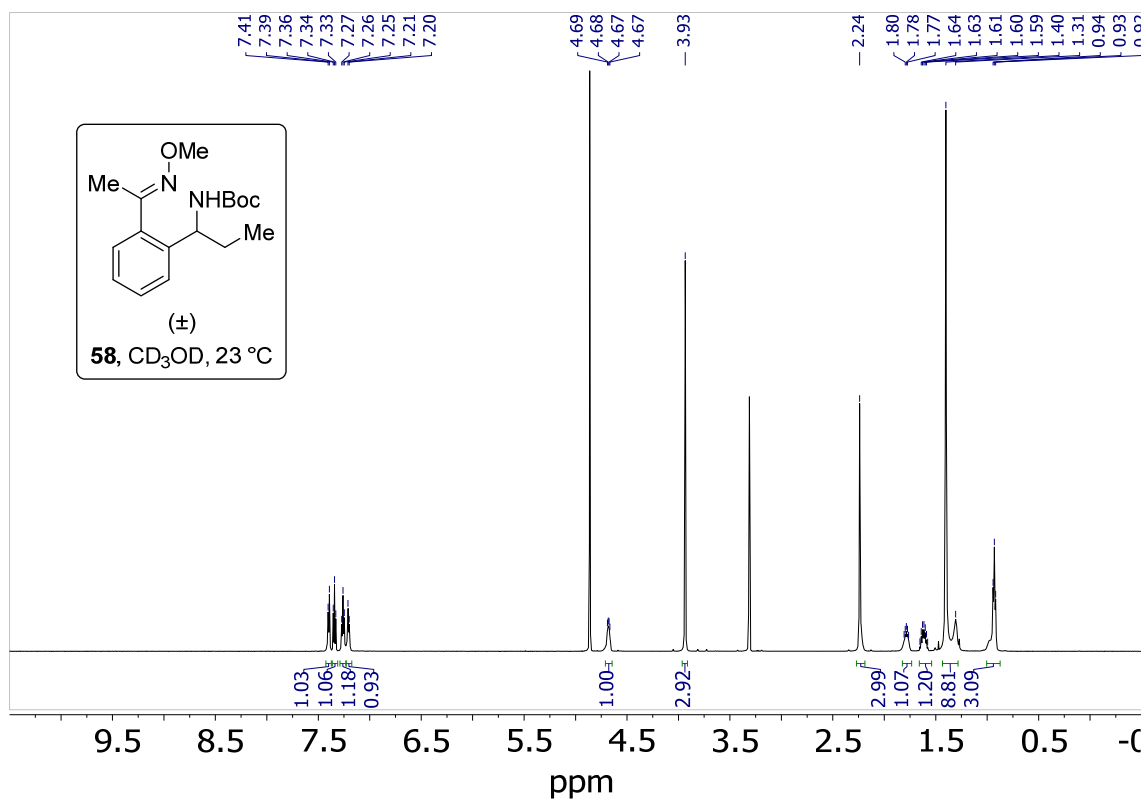
Large scale reaction in Parr reactor

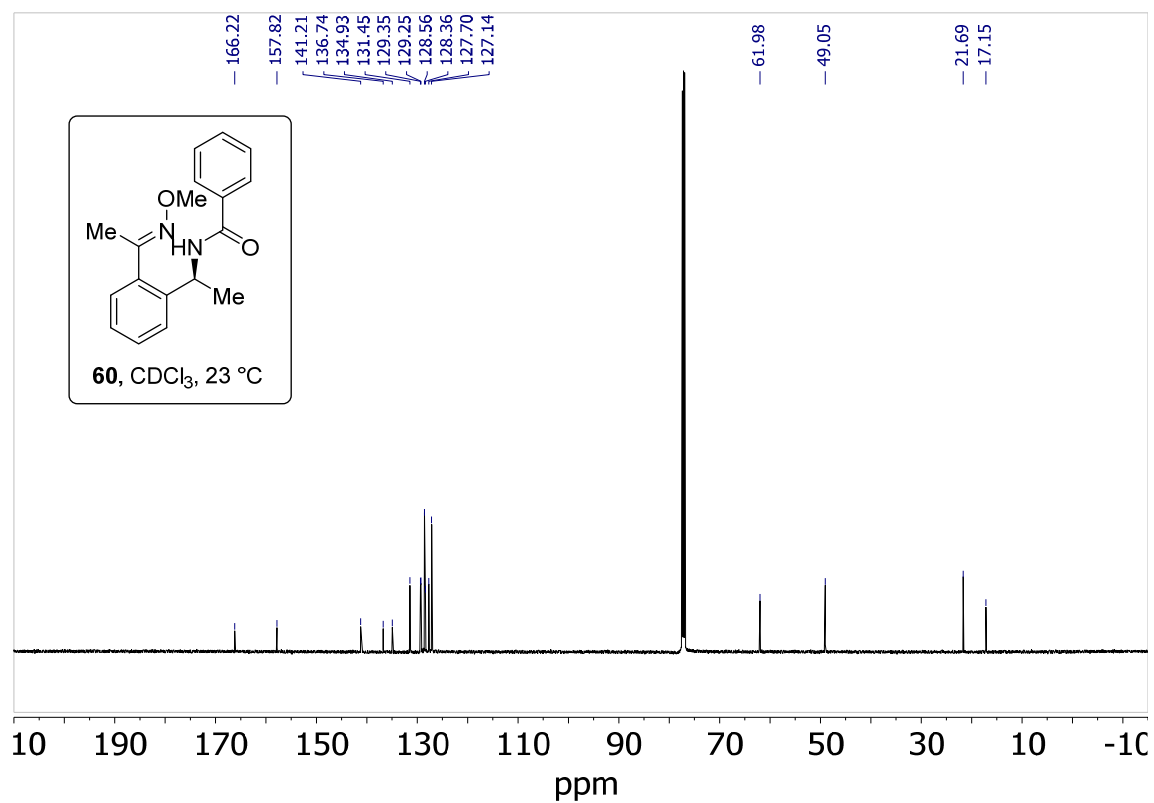
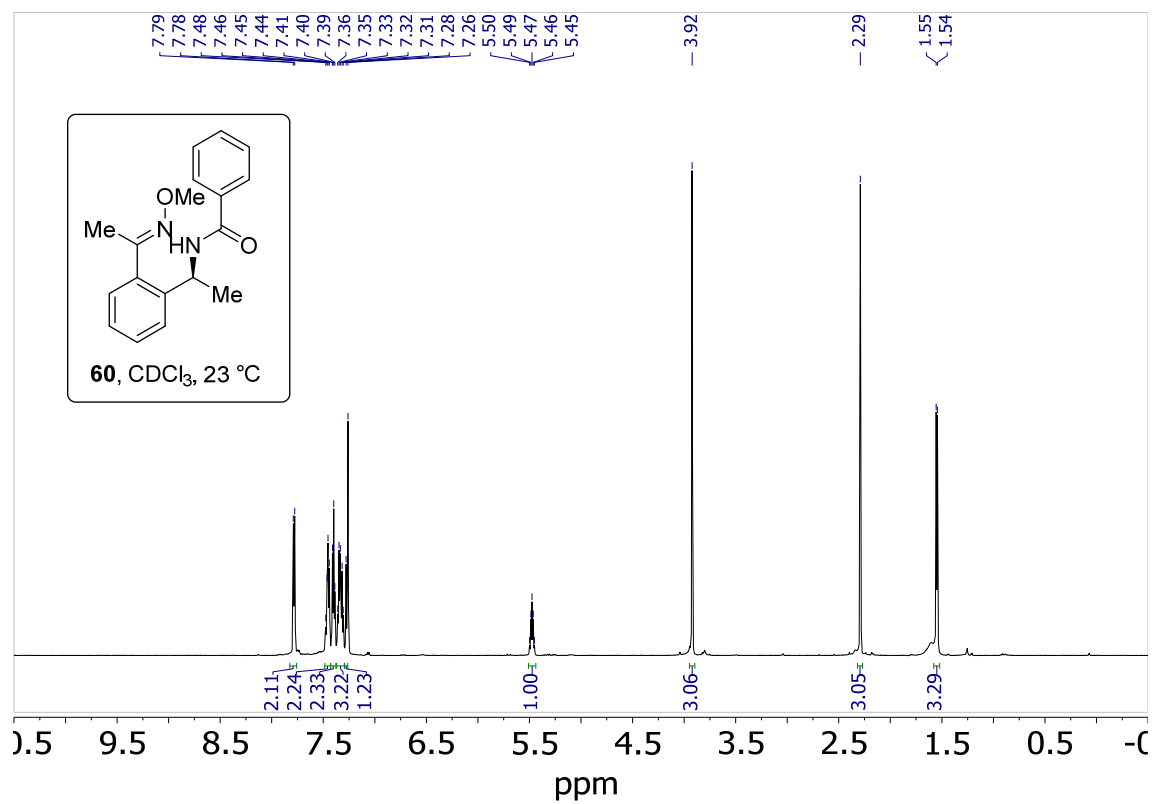




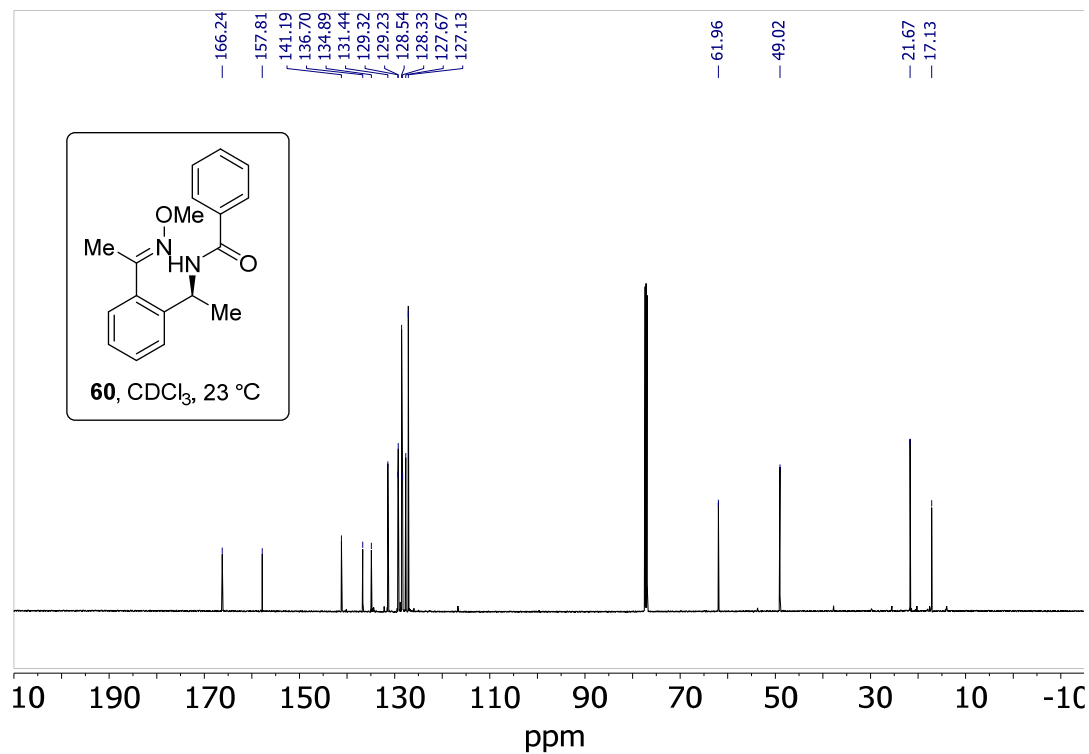
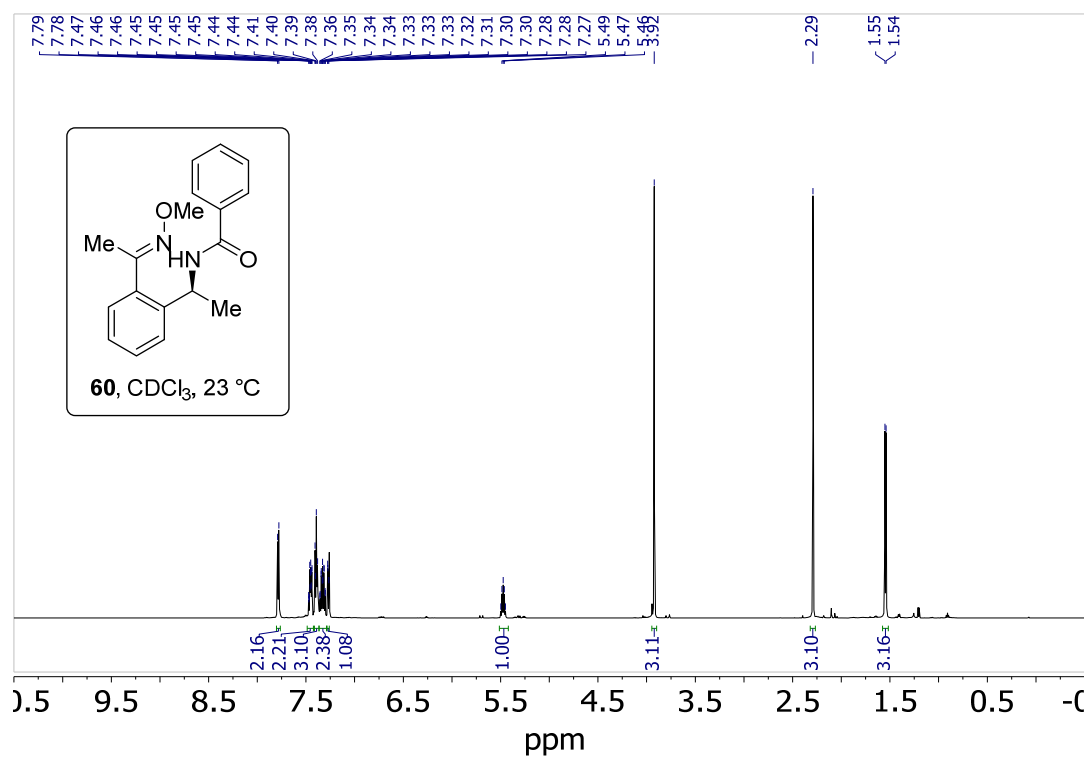


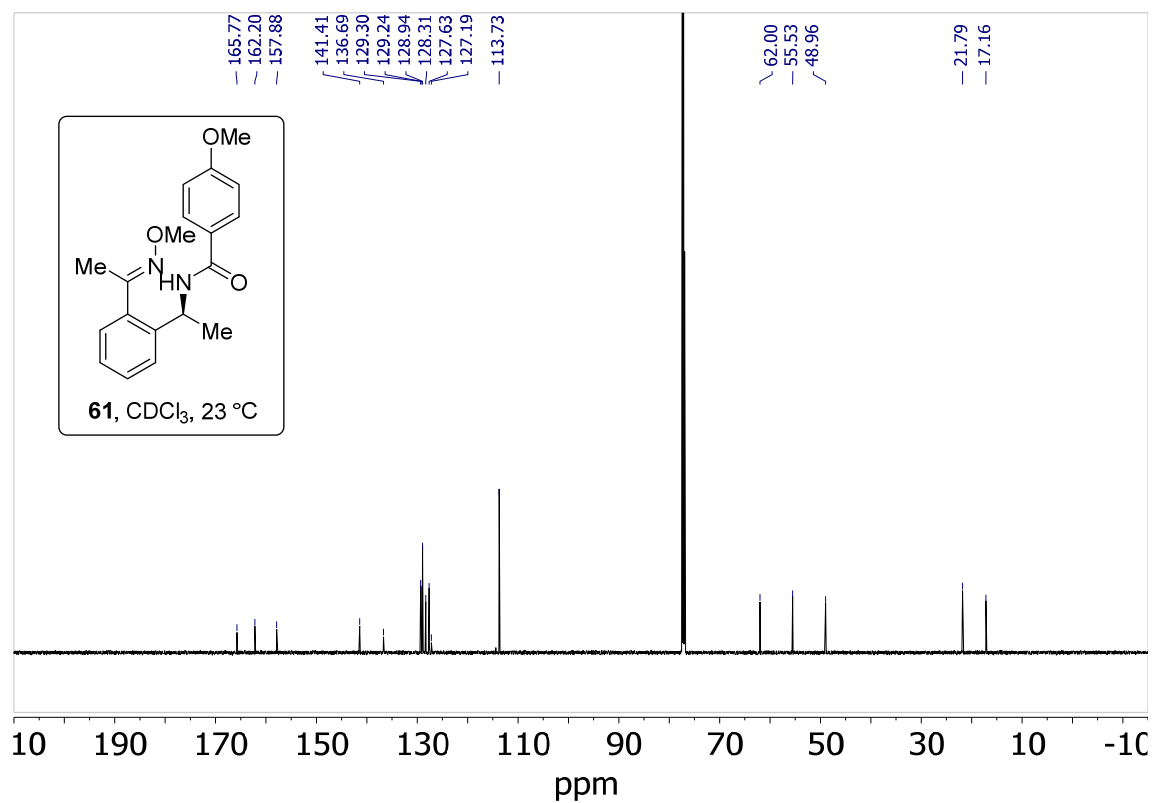
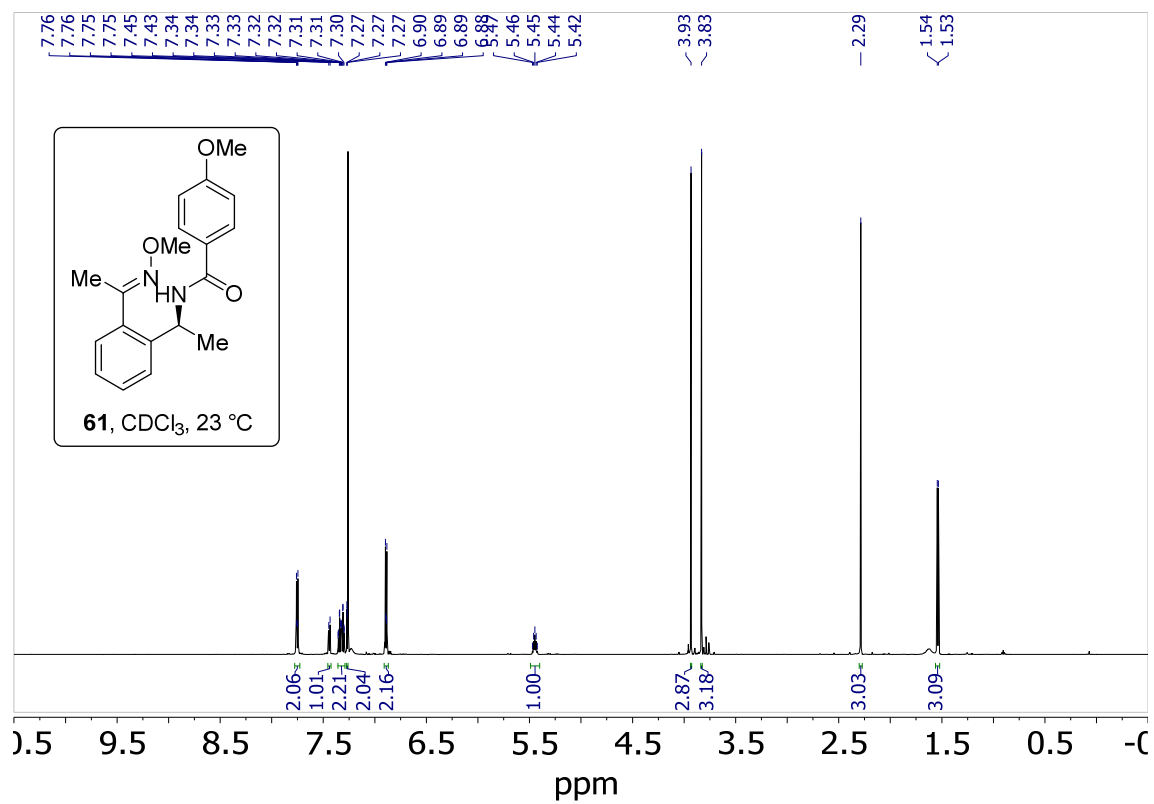


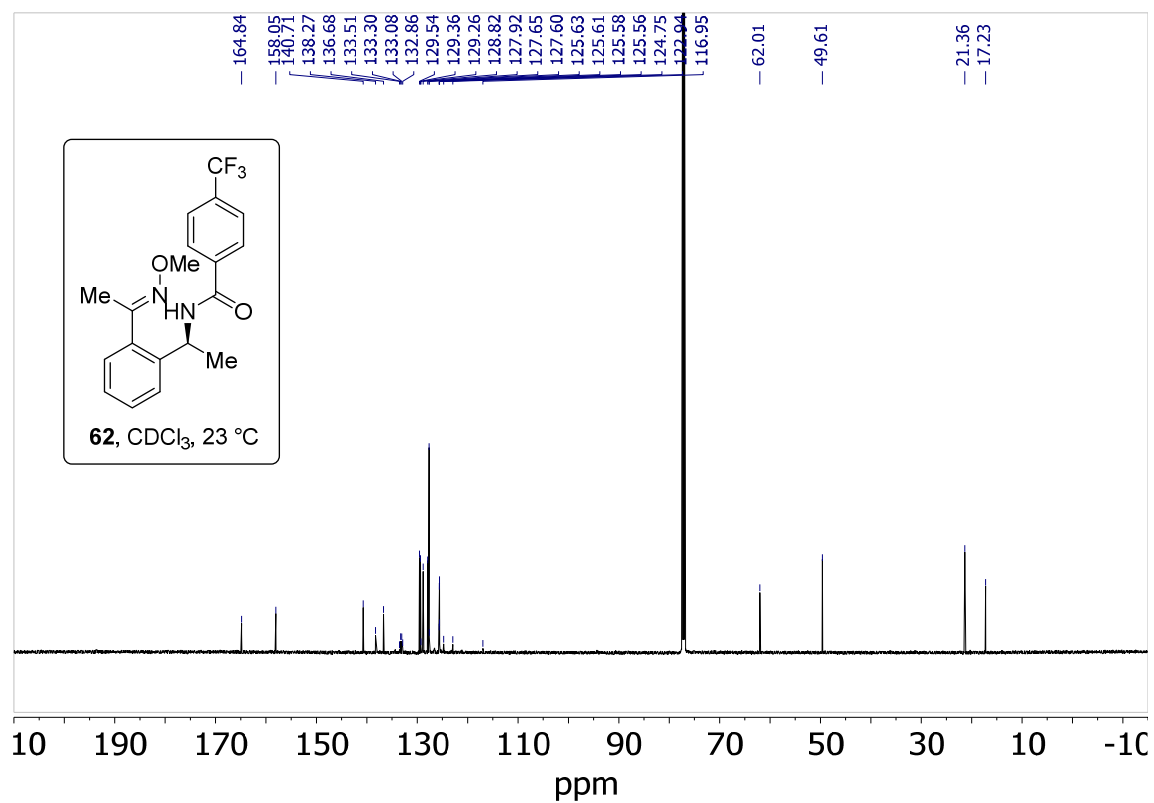
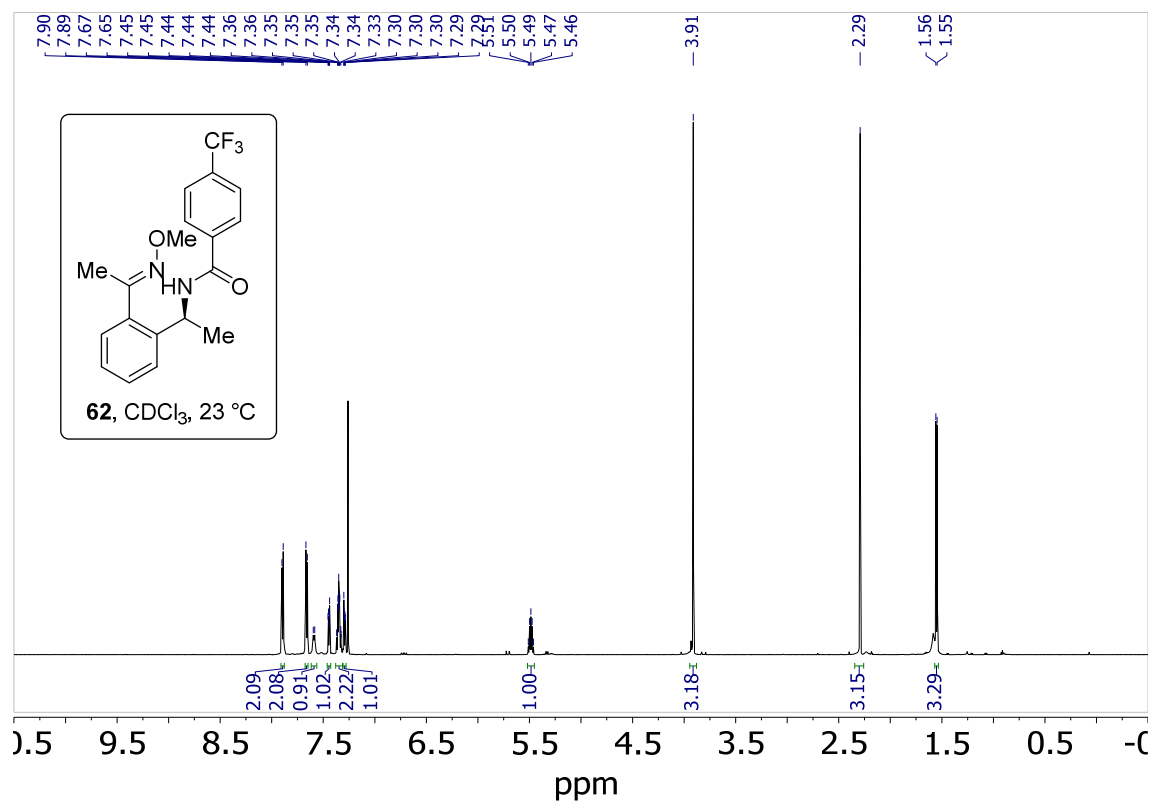


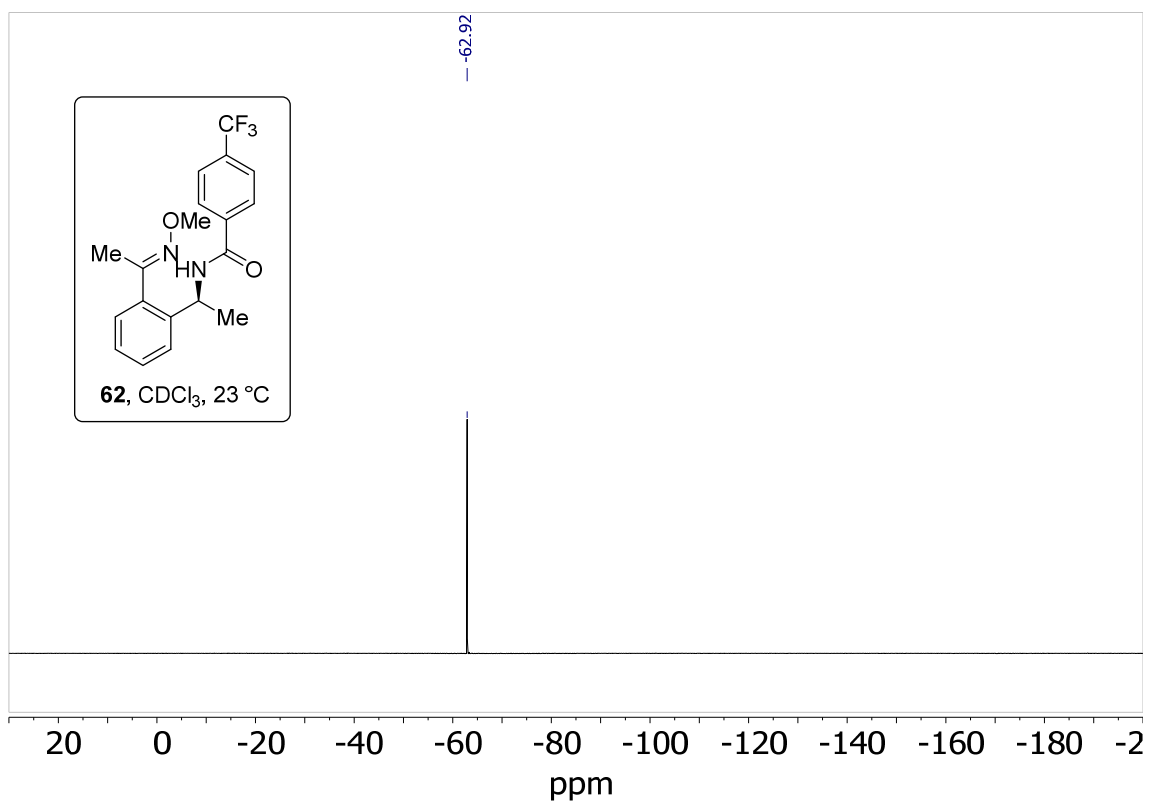


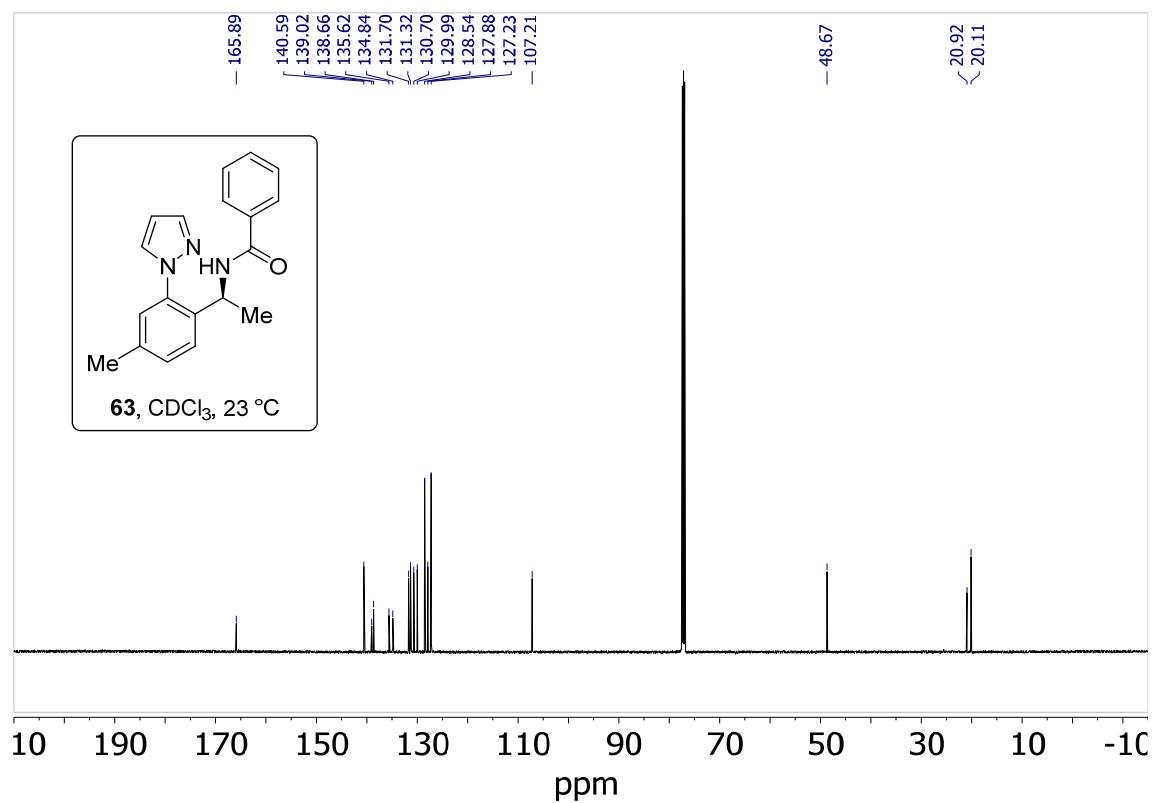
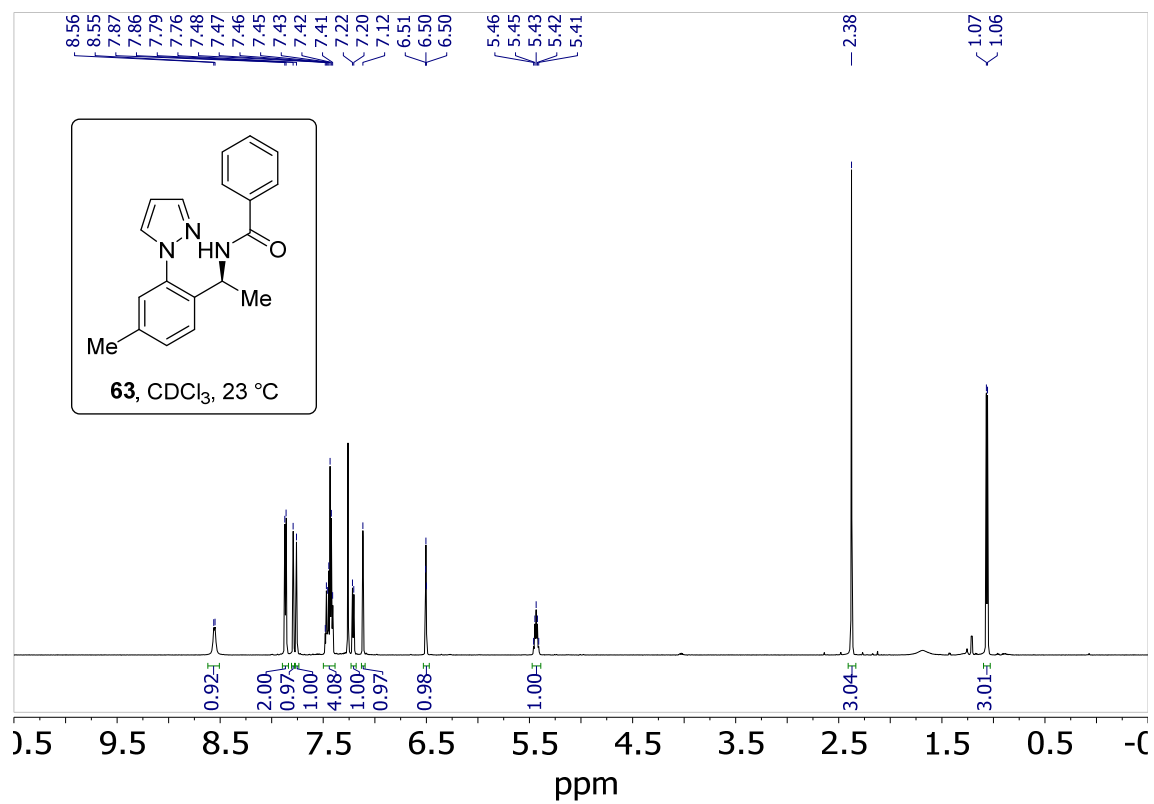
0.2 mmol scale reaction

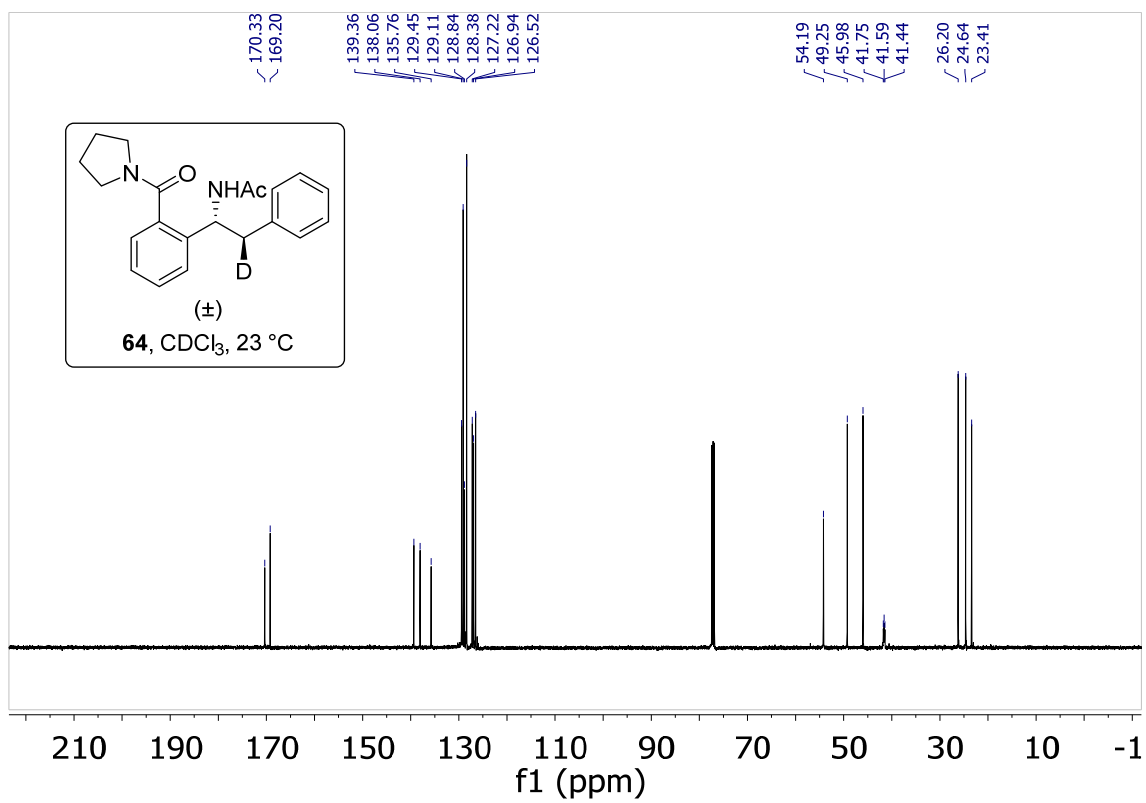
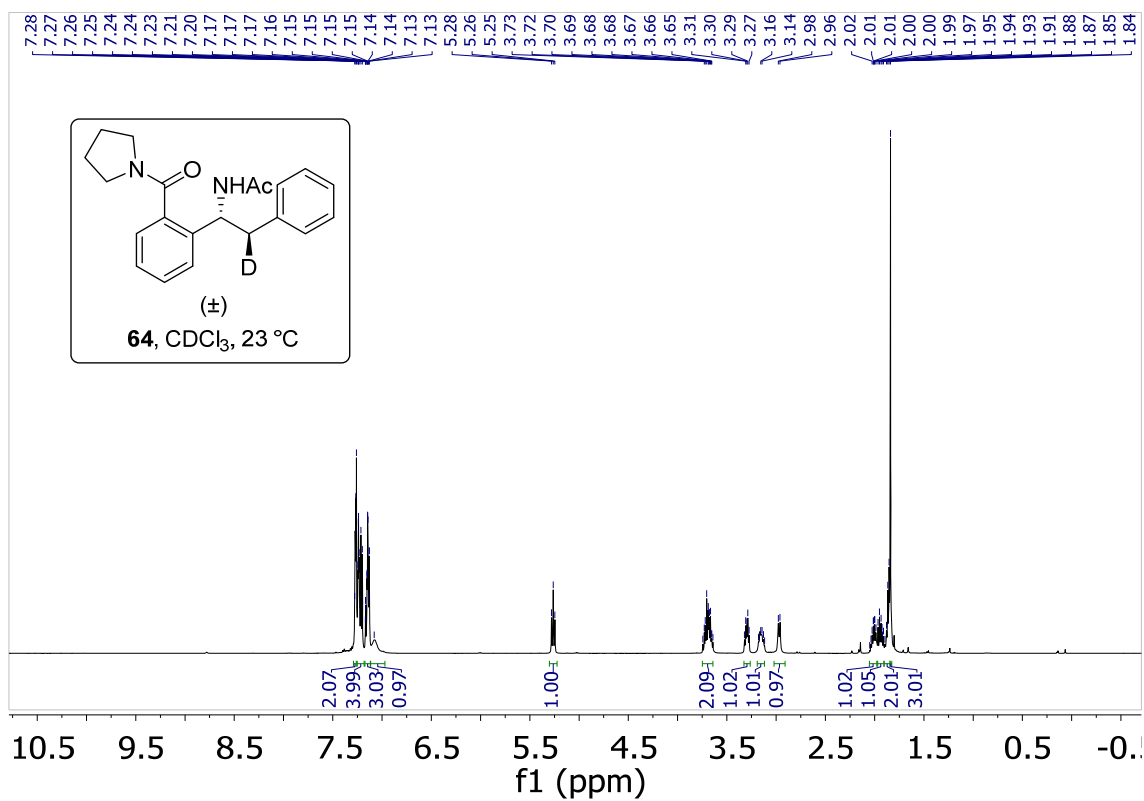


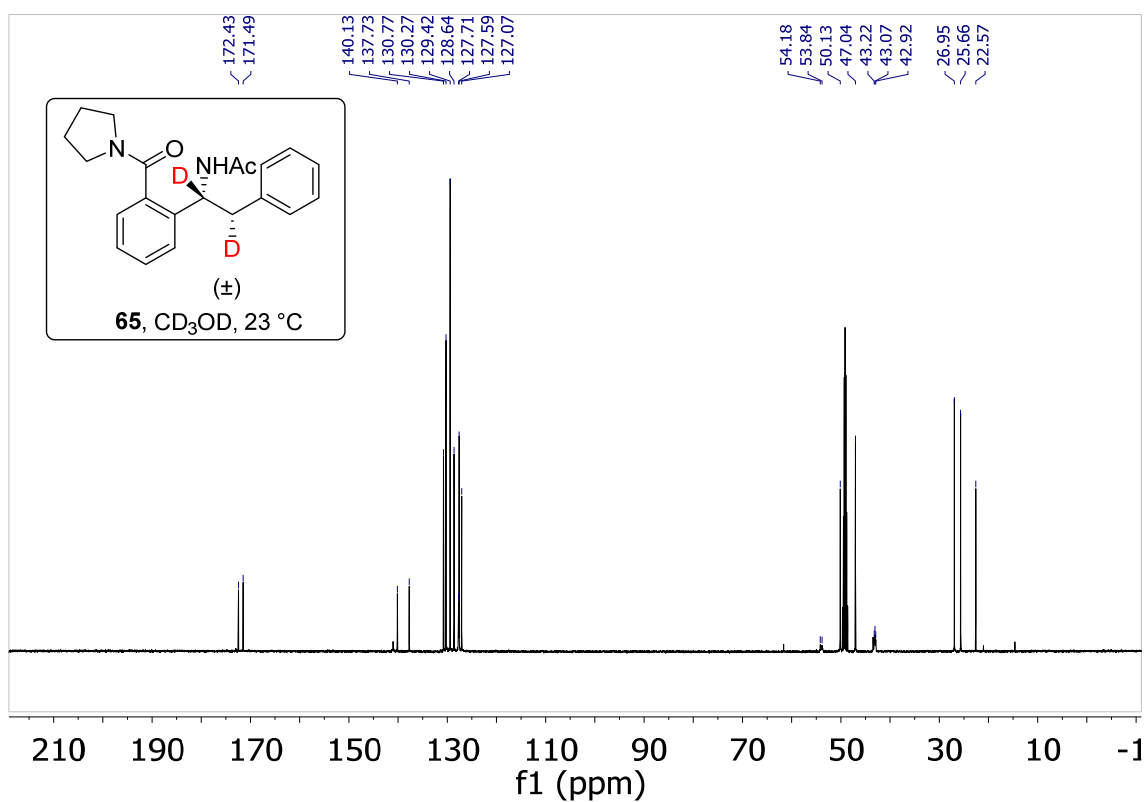
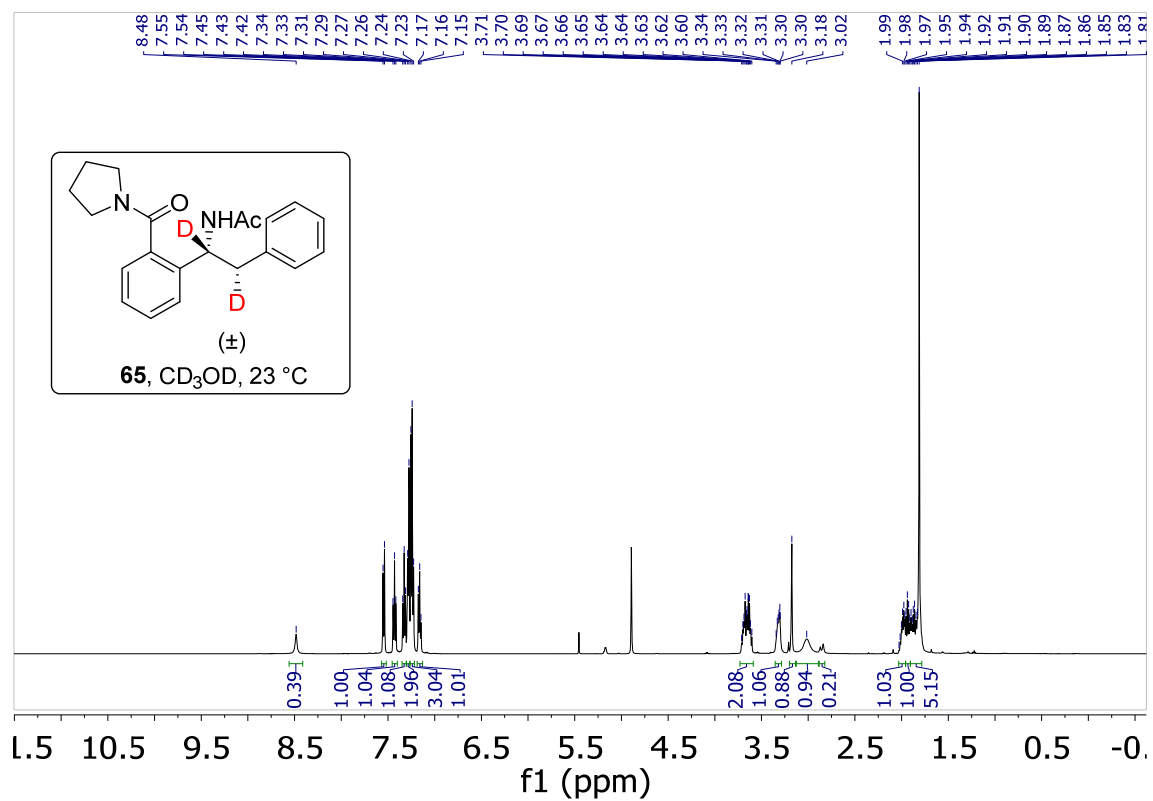


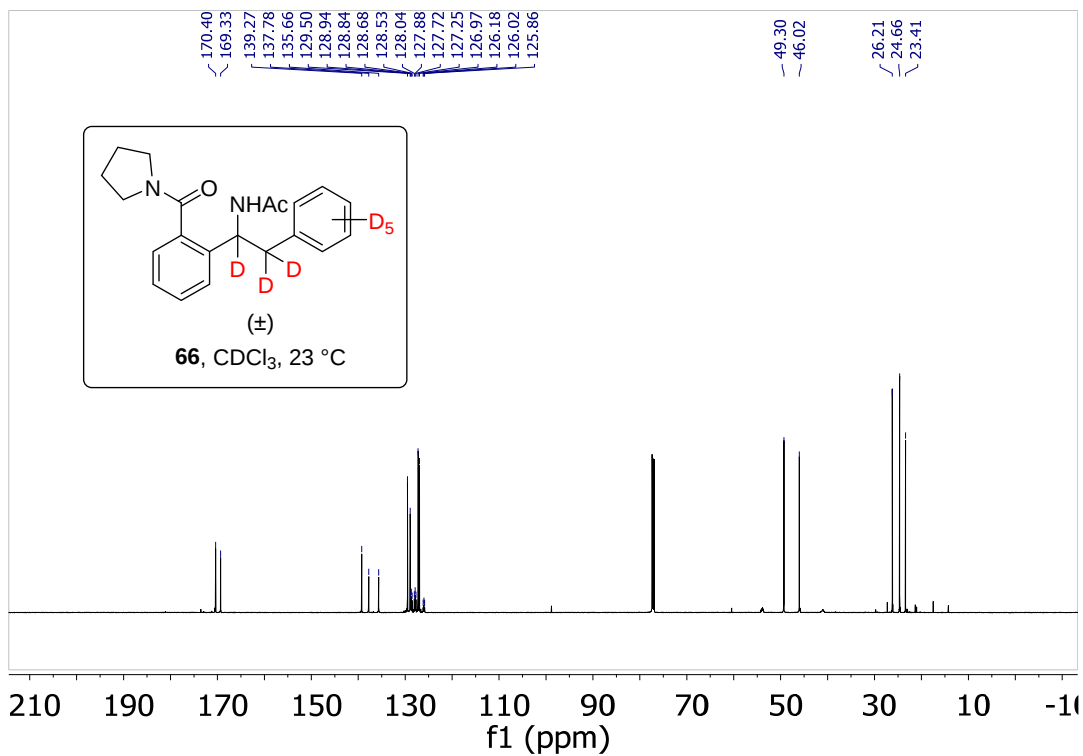
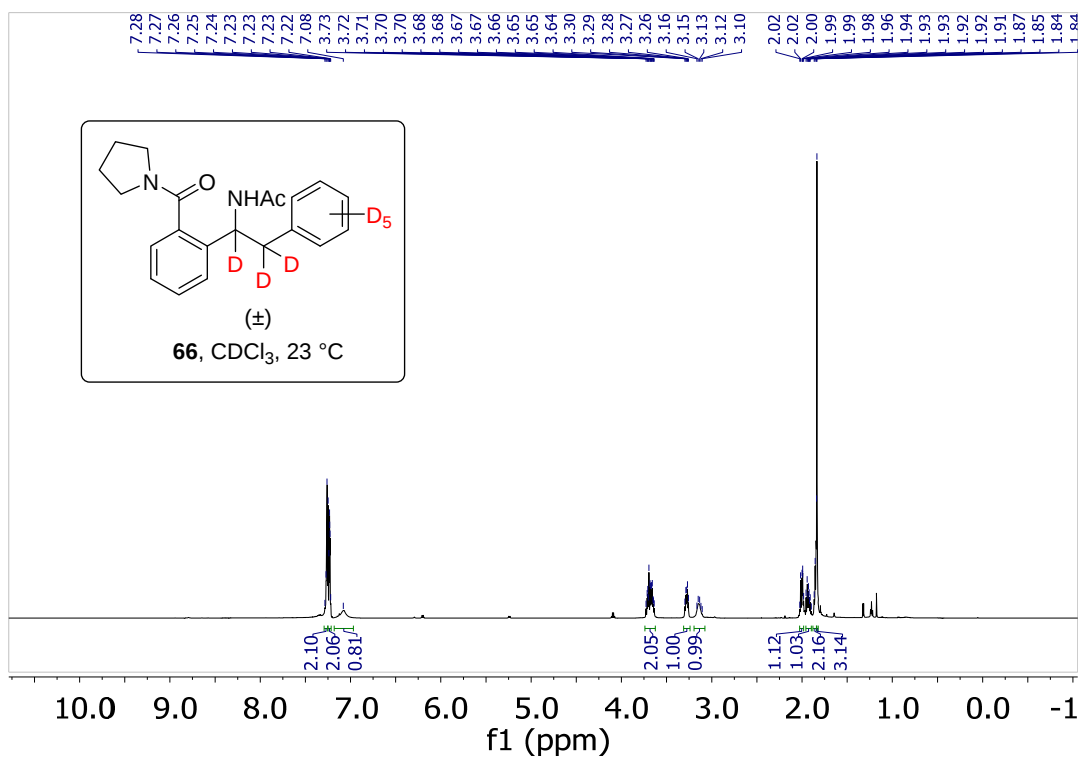




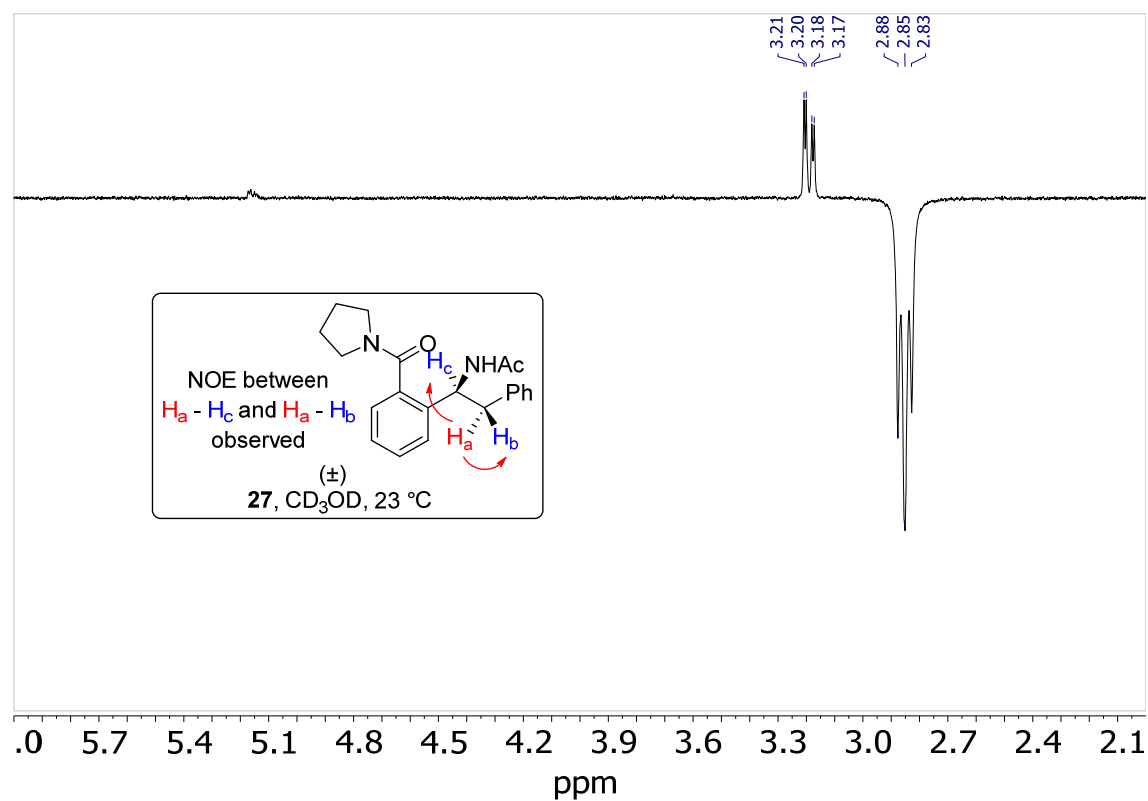
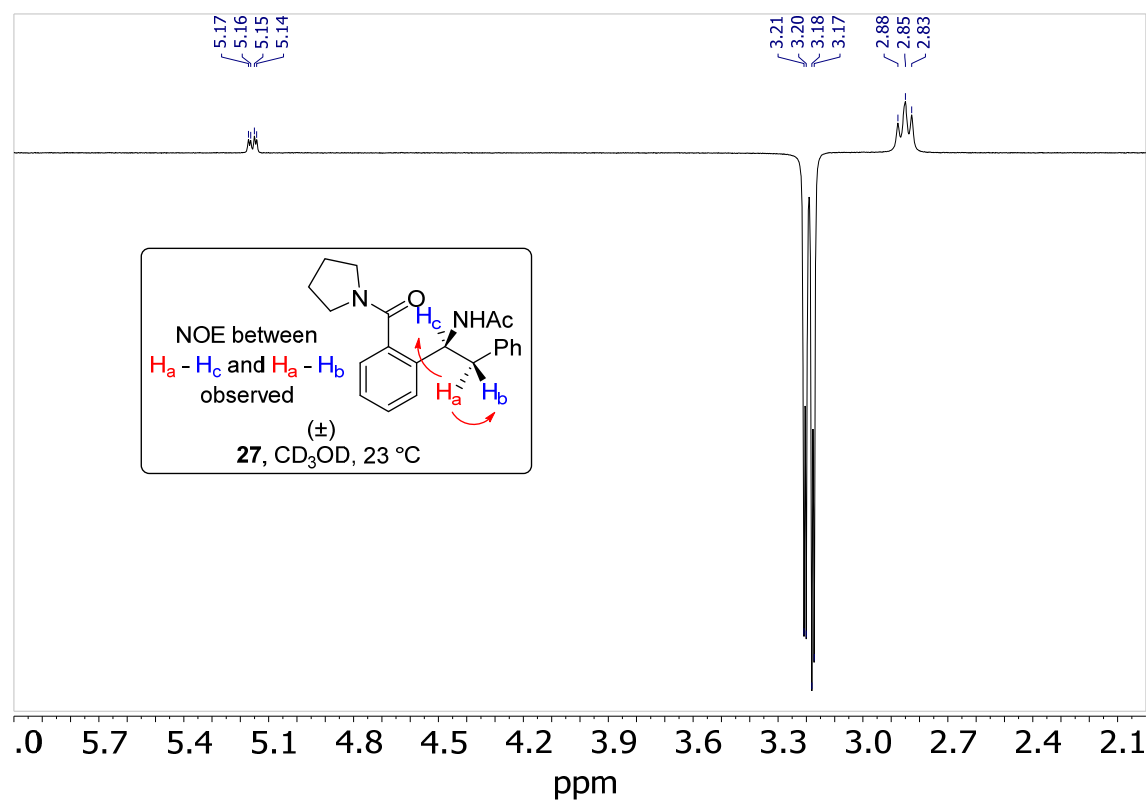




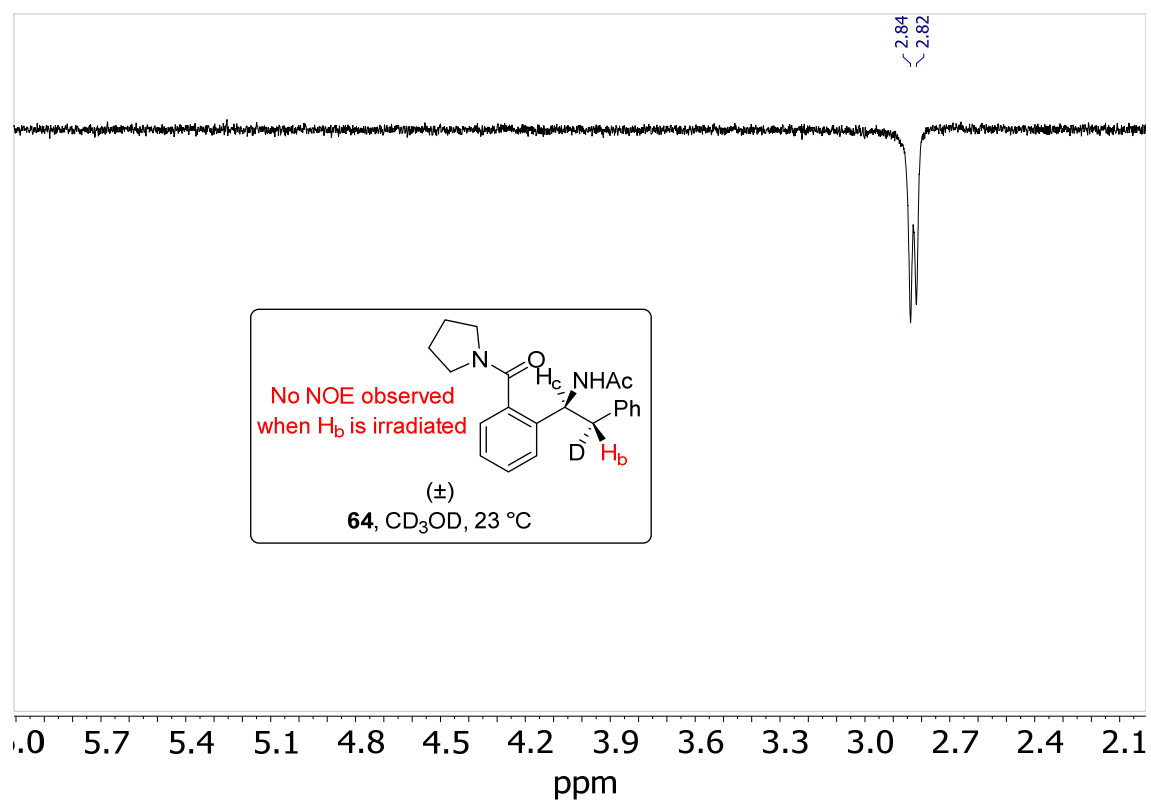




Additional NOE data for compound 27



Additional NOE data for compound 64



Supplementary References

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