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

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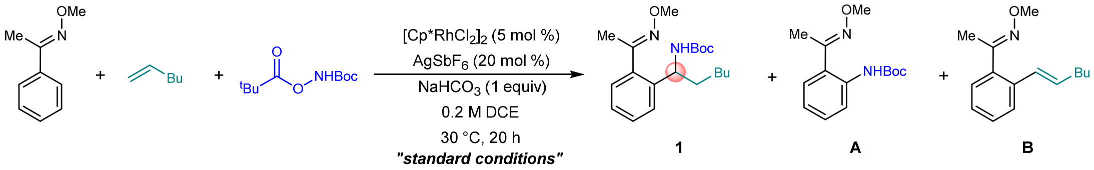
Supplementary Information

Supplementary Tables

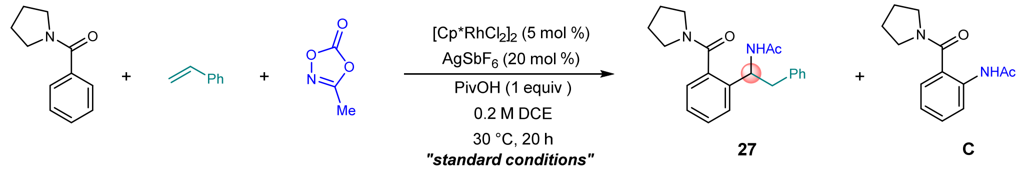
Supplementary Table 1. Optimization of reaction conditions with oxime C-H bond substrate.



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	$[Cp^{*}Co(CO)I_2]$ (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	$[RuCl_2(\textit{p}\text{-cymene})]_2$ (5 mol %) and $AgSbF_6$ (20 mol %) as catalyst system	0%	0%	0%

[a]Conditions: 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. [b]Yields determined by ^{1}H NMR relative to 1,3,5-trimethoxybenzene as an external standard.

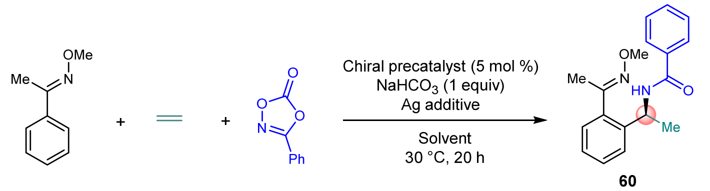
Supplementary Table 2. Optimization of reaction conditions with amide C-H bond substrate.



Entry[a]	Variation from the standard conditions	Yield **27**[b]	Yield **C**[b]
1	None	70%	0%
2	No $[Cp^*RhCl_2]_2$	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	$[Cp^*Rh(MeCN_3)][SbF_6]_2$ (10 mol %) as catalyst system	traces	0%
13	$[Cp^*Co(CO)I_2]$ (10 mol %) and $AgSbF_6$ (20 mol %) as catalyst system	0%	0%
14	$[Cp^*IrCl_2]_2$ (5 mol %) and $AgSbF_6$ (20 mol %) as catalyst system	0%	59%
15	$[RuCl_2(p\text{-cymene})]_2$ (5 mol %) and $AgSbF_6$ (20 mol %) as catalyst system	0%	26%

[a]Conditions: 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. [b]Yields 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.



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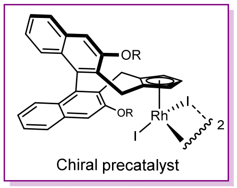


Chiral precatalyst

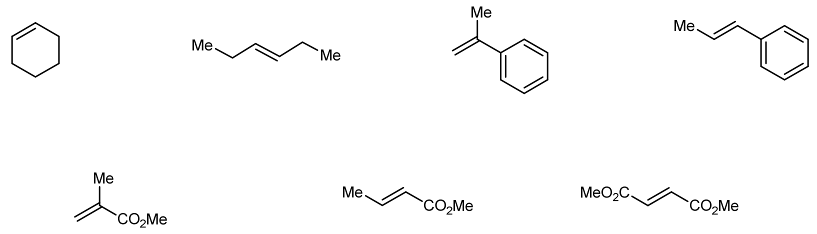
Entry[a]	Chiral precatalyst	Ag additive	Solvent	Yield[b]	er[c]
1	R = Me	$AgSbF_6$ (40 mol %)	DCE (0.2 M)	48%	88:12
2	**R = Me**	**$AgB(C_6F_5)_4$ (40 mol %)**	**DCE (0.2 M)**	**56%**	**91:9**
3	R = *i*Pr	$AgB(C_6F_5)_4$ (40 mol %)	DCE (0.2 M)	60%	90:10
4	R = TBDPS	$AgB(C_6F_5)_4$ (40 mol %)	DCE (0.2 M)	30%	85:15
5	R = Me	$AgB(C_6F_5)_4$ (80 mol %)	DCE (0.2 M)	77%	88:12
6	R = Me	$AgB(C_6F_5)_4$ (40 mol %)	DCE (0.5 M)	50%	88:12
7	R = Me	$AgB(C_6F_5)_4$ (40 mol %)	DCE (0.1 M)	52%	91:9
8	R = Me	$AgB(C_6F_5)_4$ (40 mol %)	Dioxane (0.2 M)	13%	-

[a]Conditions: Reactions were performed on 0.05 mmol of C–H bond substrate with 0.075 mmol of aminating agent and excess ethylene. [b]Yields 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. [c]Enantiomeric ratio determined by chiral HPLC, see Supplementary Information for conditions and HPLC traces.

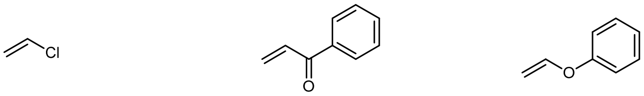
Supplementary Figures

Supplementary Figure 1. List of unreactive alkene coupling partners.

disubstituted alkenes



monosubstituted alkenes



Supplementary Methods

1. General Information

Unless otherwise indicated, all Rh(III)-catalysed reactions were set up in a N_2 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 N_2 atmosphere. Solvents were purified by elution through a column of activated alumina under N_2 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 $KMnO_4$ or anisaldehyde. Flash-column chromatography was performed on SiliaFlash® P60 (230-400 mesh) silica gel, and preparative thin-layer chromatrography, plates from Analtech (1 mm SiO_2, 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: $CDCl_3$ (7.26 ppm for ^1H and 77.16 ppm for ^{13}C), DMSO-d_6 (2.50 ppm for ^1H and 39.52 ppm for ^{13}C), or CD_3OD (3.31 ppm for ^1H and 49.00 ppm for ^{13}C). 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:

$[Cp^*RhCl_2]_2$[1], chiral Rh precatalyst **59**[2,3,4], $AgB(C_6F_5)_4$[5], and $[Cp^*Rh(MeCN)_3][SbF_6]_2$[6] were synthesized according to published literature procedures.

C-H bond Substrates:

(*E*)-1-Phenylethan-1-one *O*-methyl oxime[7], 2-(*m*-tolyl)pyridine[8], 2-(*m*-tolyl)pyrimidine[9], 1-benzyl-4-(*m*-tolyl)-1*H*-1,2,3-triazole[10], 1-(*m*-tolyl)-1*H*-pyrazole[11], phenyl(pyrrolidin-1-yl)methanone[12], (4-chlorophenyl)(pyrrolidin-1-yl)methanone[12], (4-methoxyphenyl)(pyrrolidin-1-yl)methanone[12], furan-3-yl(pyrrolidin-1-yl)methanone[13], 2-methyl-3,4-dihydroisoquinolin-1(2*H*)-one[14], (*E*)-3,4-dihydronaphthalen-1(2*H*)-one *O*-methyl oxime[7], 1-(*o*-tolyl)-1*H*-pyrazole[15], and 1-(pyridin-2-yl)-1*H*-indole[16] 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 procedures[17].

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-dimethylpropanoate[18], benzyloxycarbonylamino 2,2-dimethylpropanoate[19], 9*H*-fluoren-9-ylmethoxycarbonylamino 2,2-dimethylpropanoate[18], and *N*-acetoxy-4-methylbenzenesulfonamide[20] were synthesized according to published literature procedures.

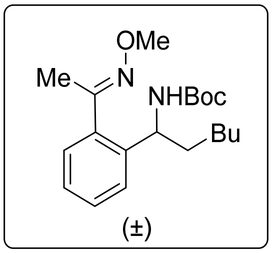
The dioxazolones 3-phenyl-1,4,2-dioxazol-5-one, 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one, 3-(4-(trifluoromethyl)phenyl)-1,4,2-dioxazol-5-one, 3-(2-chlorophenyl)-1,4,2-dioxazol-5-one, 3-(thiophen-2-yl)-1,4,2-dioxazol-5-one, 3-methyl-1,4,2-dioxazol-5-one, 3-heptyl-1,4,2-dioxazol-5-one, and 3-isopropyl-1,4,2-dioxazol-5-one were synthesized according to published literature procedures[21].

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

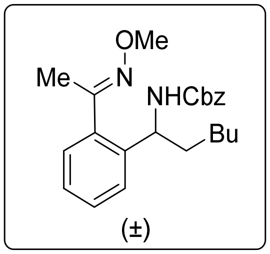
General procedure:

In a N_2-filled glove box, a 2–5 mL microwave vial was charged with $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol, 0.050 equiv), $AgSbF_6$ (21 mg, 0.06 mmol, 0.20 equiv), and, if indicated, an additive (0.30 mmol, 1 equiv). 1,2-Dicholoroethane (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.

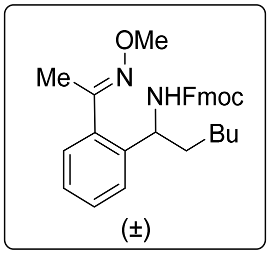
Characterization Data:



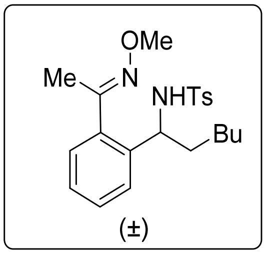
(±) *tert*-Butyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)hexyl)carbamate (1): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), hex-1-ene (50 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (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 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{20}H_{33}N_2O_3^+$: 349.2486. Found 349.2491.



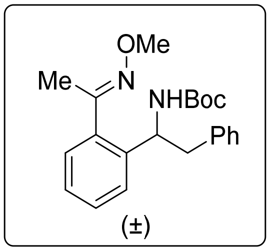
(±) Benzyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)hexyl)carbamate (2): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), 1-hexene (50 mg, 0.60 mmol, 2.0 equiv), and benzyloxycarbonylamino 2,2-dimethylpropanoate (113 mg, 0.450 mmol, 1.50 equiv). $NaHCO_3$ (25 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% MeCN:H_2O 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{23}H_{31}N_2O_3^+$: 383.2329. Found 383.2320.



(±) (9*H*-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 (9*H*-fluoren-9-ylmethoxycarbonylamino) 2,2-dimethylpropanoate (153 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 purified by C18 reverse phase purification (15.5 g column, 10% to 90% MeCN:H_2O containing 0.1% TFA gradient). Fractions containing product were combined and diluted with sat. aq. $NaHCO_3$ (100 mL) and extracted with CH_2Cl_2. The combined organic layers were then dried over Na_2SO_4 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}; ^{1}H NMR (500 MHz, $CDCl_3$) 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{30}H_{35}N_2O_3^+$: 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). $NaHCO_3$ (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 **4** (82.7 mg, 63% yield) as an off-white/grey solid (mp: 75-76 ºC). IR (neat): 3262, 2949, 2865, 1322, 1153, 1040 cm^{-1}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{22}H_{31}N_2O_3S^+$: 403.2050. Found 403.2079.

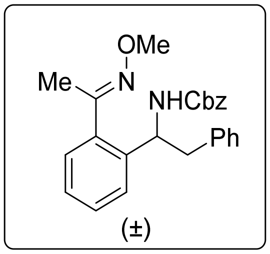


(±) *tert*-Butyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethyl)carbamate (5): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). 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 ºC). IR (neat): 3404 (br), 2974, 2938, 1688, 1503, 1165, 1054, 1043 cm^{-1}; ^{1}H NMR (500 MHz, CD$_3$OD) 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$_3$OD) 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/[M+H]$^+$) calcd. for $C_{22}H_{29}N_2O_3^+$: 369.2173. Found 369.2178.

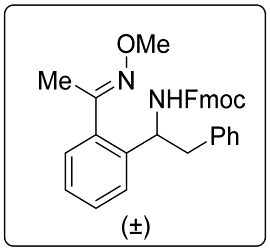
For reaction with 1 mol% Rh-dimer loading, a slightly different procedure has been used:

In a N$_2$-filled glovebox, a 2-5 mL microwave vial was charged with [Cp*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-Dicholoroethane (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

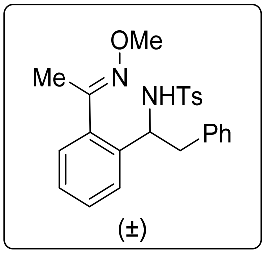
mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction vial was then equipped with a magnetic stir bar, sealed with a microwave cap, and taken outside the glove box. The reaction mixture was then stirred at 30 °C in a preheated oil bath. 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.



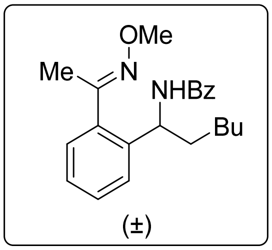
(±) Benzyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethyl)carbamate (6): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and benzyloxycarbonylamino 2,2-dimethylpropanoate (113 mg, 0.450 mmol, 1.50 equiv). $NaHCO_3$ (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 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). ^{13}C 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 $C_{25}H_{27}N_2O_3^+$: 403.2016. Found 403.2003.



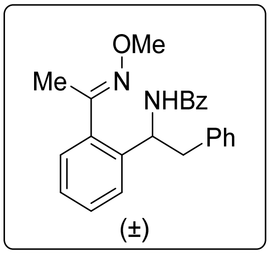
(±) (9*H*-Fluoren-9-yl)methyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethyl)carbamate (7): Derived from (*E*)-1-phenylethan-1-one O-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (9*H*-fluoren-9-ylmethoxycarbonylamino) 2,2-dimethylpropanoate (153 mg, 0.450 mmol, 1.50 equiv). $NaHCO_3$ (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 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, $CDCl_3$) 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{32}H_{31}N_2O_3^+$: 491.2329. Found 491.2335.



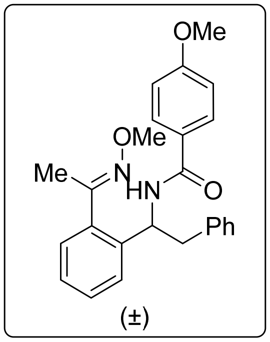
(±) (*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)-4-methylbenzenesulfonamide (8): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and *N*-acetoxy-4-methylbenzenesulfonamide (103 mg, 0.450 mmol, 1.50 equiv). $NaHCO_3$ (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% MeCN:H_2O 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 **8** (74.0 mg, 58% yield) as a colorless waxy solid. IR (neat): 3291, 2938, 1319, 1154, 1040 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{24}H_{27}N_2O_3S^+$: 423.1737. Found 423.1758.



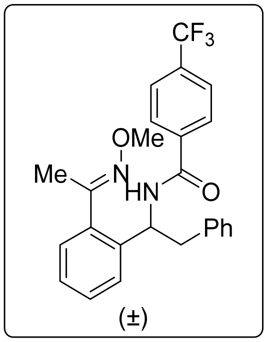
(±) (*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)hexyl)benzamide (9): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), 1-hexene (50 mg, 0.60 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (73 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (25 mg, 0.30 mmol, 1.0 equiv) 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 acetone: hexanes as the eluent to afford the product **9** (58.0 mg, 55% yield) as a white solid (mp: 76-77 ºC). IR (neat): 3293, 3061, 2954, 2928, 2856, 1632, 1538, 1047 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{22}H_{29}N_2O_2^+$: 353.2224. Found 353.2223.



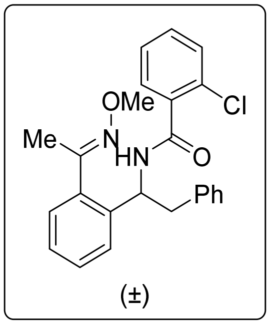
(±) (*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)benzamide (10): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (73 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (25 mg, 0.30 mmol, 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 ºC). 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/$[M+H]^+$) calcd. for $C_{24}H_{25}N_2O_2^+$: 373.1911. Found 373.1918.



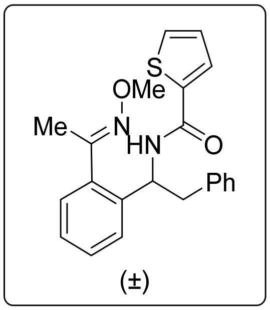
(±) (*E*)-4-Methoxy-*N*-(1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethyl)benzamide (11): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (87 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (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 ºC). IR (neat): 3286 (br), 2937, 1625, 1606, 1508, 1251, 1177, 1040, 1028 cm^{-1}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{25}H_{27}N_2O_3^+$: 403.2016. Found 403.2013.



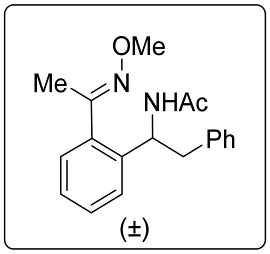
(±) (*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)-4-(trifluoromethyl)benzamide (12): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-[4-(trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (104 mg, 0.450 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 °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 ºC). IR (neat): 3304 (br), 3028, 2938, 1636, 1540, 1323, 1122, 1044 cm^{-1}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{25}H_{24}F_3N_2O_2^+$: 441.1784. Found 441.1773.



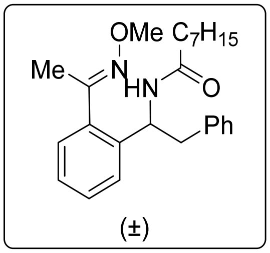
(±) (*E*)-2-Chloro-*N*-(1-(2-(1-(methoxyimino)ethyl)phenyl)-2-phenylethyl)benzamide (13): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-(2-chlorophenyl)-1,4,2-dioxazol-5-one (89 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (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 **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, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{24}H_{24}ClN_2O_2^+$: 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). $NaHCO_3$ (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 **14** (96.6 mg, 85% yield) as a white solid (mp: 125-126 ºC). IR (neat): 3337 (br), 3087, 2969, 2818, 1619, 1531, 1508, 1297, 1034 cm^{-1}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{22}H_{23}N_2O_2S^+$: 379.1475. Found 379.1494.

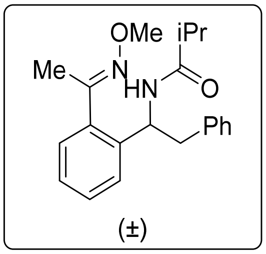


(±) (*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)acetamide (15): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). NaHCO$_3$ (25 mg, 0.30 mmol, 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 ºC). IR (neat): 3288 (br), 3065, 2939, 2818, 1643, 1534, 1298, 1038 cm^{-1}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{19}H_{23}N_2O_2^+$: 311.1754. Found 311.1749.

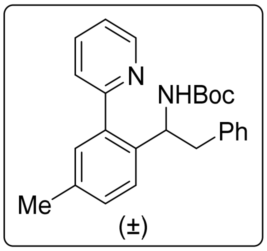


(±) (*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)octanamide (16): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene

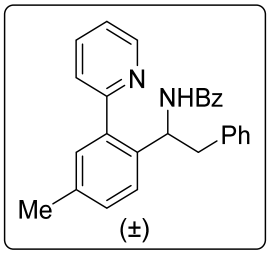
(62 mg, 0.60 mmol, 2.0 equiv), and 3-heptyl-1,4,2-dioxazol-5-one (83 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (25 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of ethyl acetate: hexanes as the eluent to afford the product **16** (104 mg, 88% yield) as a white solid (mp: 69-70 ºC). 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/$[M+H]^+$) calcd. for $C_{25}H_{35}N_2O_2^+$: 395.2693. Found 395.2690.



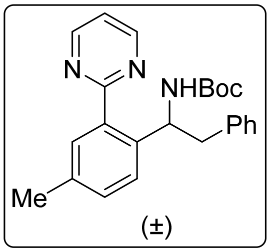
(±) (*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)-2-phenylethyl)isobutyramide (17): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-isopropyl-1,4,2-dioxazol-5-one (58 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (25 mg, 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 ºC). 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/$[M+H]^+$) calcd. for $C_{21}H_{27}N_2O_2^+$: 339.2067. Found 339.2082.



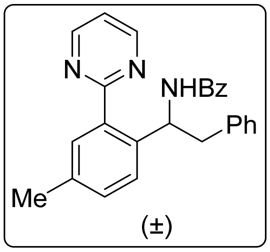
(±) *tert*-Butyl (1-(4-methyl-2-(pyridin-2-yl)phenyl)-2-phenylethyl)carbamate (18): Derived from 2-(*m*-tolyl)pyridine (50.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted 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 ºC). IR (neat): 3400, 3063, 2980, 2919, 1689, 1514, 1169, 1018 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{25}H_{29}N_2O_2^+$: 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 ºC). IR (neat): 3380, 3082, 3061, 3030, 2925, 1638, 1525, 1488, 1302, 1276 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) 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 $C_{27}H_{25}N_2O^+$: 393.1961. Found 393.1946.

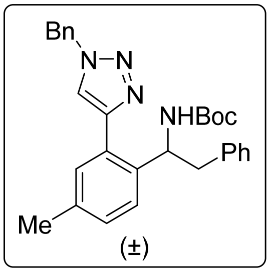


(±) *tert*-Butyl (1-(4-methyl-2-(pyrimidin-2-yl)phenyl)-2-phenylethyl)carbamate (20): Derived from 2-(*m*-tolyl)pyrimidine (51.1 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction was 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: ^{1}H 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 $C_{24}H_{28}N_3O_2^+$: 390.2176. Found 390.2181.

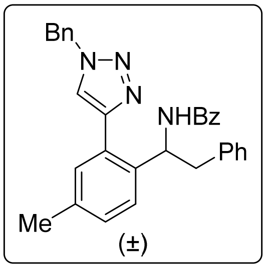


(±) *N*-(1-(4-Methyl-2-(pyrimidin-2-yl)phenyl)-2-phenylethyl)benzamide (21): Derived from 2-(*m*-tolyl)pyrimidine (51.1 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (73 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 30 °C. The product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

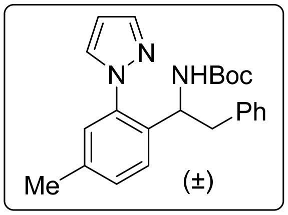
10:90 mixture of ethyl acetate: hexanes as the eluent to afford the product **21** (81.0 mg, 69% yield) as an off-white solid (mp: 129-130 °C). IR (neat): 3288 (br), 3029, 1632, 1425, 822 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (d, *J* = 8.8 Hz, 1H), 8.93 (d, *J* = 4.9 Hz, 2H), 7.85 – 7.83 (m, 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{26}H_{24}N_3O^+$: 394.1914. Found 394.1919.



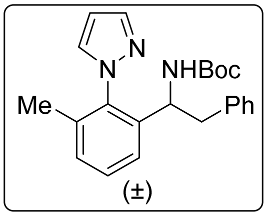
(±) *tert*-Butyl (1-(2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)-4-methylphenyl)-2-phenylethyl)carbamate (22): Derived from 1-benzyl-4-(*m*-tolyl)triazole (74.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 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 ºC). IR (neat): 3398, 3028, 2979, 1690, 1516, 1495, 1168, 1044, 1018, 722, 699 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{29}H_{33}N_4O_2^+$: 469.2598. Found 469.2596.



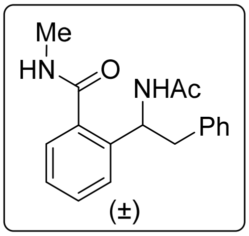
(±) *N*-(1-(2-(1-Benzyl-1*H*-1,2,3-triazol-4-yl)-4-methylphenyl)-2-phenylethyl)benzamide (23): Derived from 1-benzyl-4-(*m*-tolyl)triazole (74.8 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-phenyl-1,4,2-dioxazol-5-one (73 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 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 ºC). IR (neat): 3337 (br), 3060, 3030, 1635, 1532, 1490, 1051 cm^{-1}; ^{1}H NMR (600 MHz, CDCl$_3$) 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). ^{13}C NMR (151 MHz, CDCl$_3$) 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 $C_{31}H_{29}N_4O^+$: 473.2336. Found 473.2318.



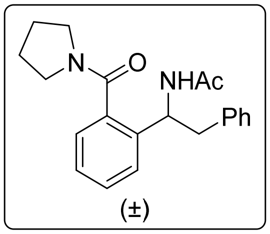
(±) *tert*-butyl (1-(4-Methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-phenylethyl)carbamate (24): Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction 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}; ^{1}H NMR (500 MHz, CDCl$_3$) 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{23}H_{28}N_3O_2^+$: 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 ºC). IR (neat): 3395, 3146, 3004, 2978, 2928, 1696, 1507, 1247, 1168, 775 cm^{-1}; ^{1}H 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). ^{13}C 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 $C_{23}H_{28}N_3O_2^+$: 378.2176. Found 378.2202.



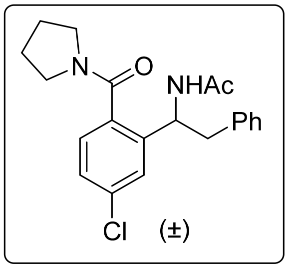
(±) 2-(1-Acetamido-2-phenylethyl)-*N*-methylbenzamide (26): Derived from *N*-methyl benzamide (40.6 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the 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 ºC). IR (neat): 3272 (br), 3066, 1631, 1536, 1304, 698 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{18}H_{21}N_2O_2^+$: 297.1598. Found 297.1587.



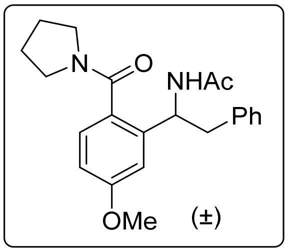
(±) *N*-(2-Phenyl-1-(2-(pyrrolidine-1-carbonyl)phenyl)ethyl)acetamide (27): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was 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 ºC). IR (neat): 3285 (br), 2968, 2887, 1650, 1609, 1598, 1427, 761, 700 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{21}H_{25}N_2O_2^+$: 337.1911. Found 337.1894.

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

In a N_2-filled glovebox, a 2-5 mL microwave vial was charged with $[Cp^*RhCl_2]_2$ (1.85 mg, 0.003 mmol, 0.010 equiv), $AgSbF_6$ (4.1 mg, 0.012 mmol, 0.04 equiv), and PivOH (30 mg, 0.30 mmol, 1.0 equiv). 1,2-Dicholoroethane (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.

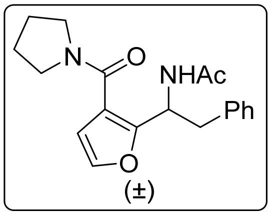


(±) *N*-(1-(5-Chloro-2-(pyrrolidine-1-carbonyl)phenyl)-2-phenylethyl)acetamide (28): Derived from (4-chlorophenyl)-pyrrolidin-1-yl-methanone (62.9 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{21}H_{24}ClN_2O_2^+$: 371.1521. Found 371.1526.

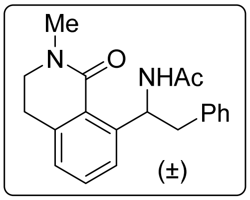


(±) *N*-(1-(5-Methoxy-2-(pyrrolidine-1-carbonyl)phenyl)-2-phenylethyl)acetamide (29): Derived from (4-methoxyphenyl)(pyrrolidin-1-yl)methanone (61.6 mg, 0.300 mmol, 1.00

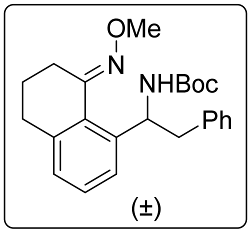
equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) was used as an additive and the reaction was conducted at 30 °C. The product was then purified by silica gel chromatography using a 17:83 mixture of acetone: 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}; ^{1}H NMR (500 MHz, CDCl$_3$) 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). ^{13}C NMR (126 MHz, CDCl$_3$) 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 $C_{22}H_{27}N_2O_3^+$: 367.2016. Found 367.2022.



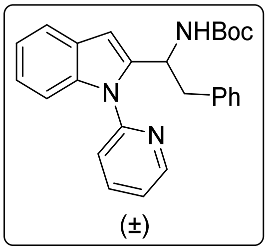
(±) *N*-(2-Phenyl-1-(3-(pyrrolidine-1-carbonyl)furan-2-yl)ethyl)acetamide (30): Derived from 3-furyl(pyrrolidin-1-yl)methanone (49.6 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 equiv) 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}; ^{1}H NMR (600 MHz, CDCl$_3$) 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). ^{13}C NMR (151 MHz, CDCl$_3$) 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 $C_{19}H_{23}N_2O_3^+$: 327.1703. Found 327.1689.



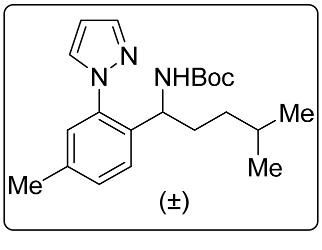
(±) *N*-(1-(2-Methyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-8-yl)-2-phenylethyl)acetamide (31): Derived from 2-methyl-3,4-dihydroisoquinolin-1-one (48.4 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 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}; ^{1}H NMR (500 MHz, $CDCl_3$) 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{20}H_{23}N_2O_2^{+}$: 323.1754. Found 323.1760.



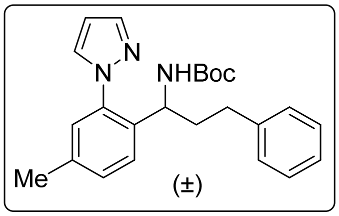
(±) *tert*-butyl (*E*)-(1-(8-(methoxyimino)-5,6,7,8-tetrahydronaphthalen-1-yl)-2-phenylethyl)carbamate (32): Derived from (*E*)-3,4-dihydronaphthalen-1(2*H*)-one-*O*-methyl oxime (52.6 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (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 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: ^{1}H NMR (500 MHz, CD_3OD) 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/[M+H]$^+$) calcd. for $C_{24}H_{31}N_2O_3^+$: 395.2329. Found 395.2335.



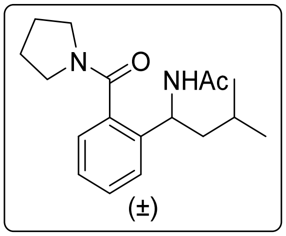
(±) *tert*-Butyl (2-phenyl-1-(1-(pyridin-2-yl)-1*H*-indol-2-yl)ethyl)carbamate (33): Derived from 1-(pyridin-2-yl)-1*H*-indole (58.3 mg, 0.300 mmol, 1.00 equiv), styrene (62 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction 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}; ^{1}H 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 C*Me*$_3$, 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/[M+H]$^+$) calcd. for $C_{26}H_{28}N_3O_2^+$: 414.2176. Found 414.2181.



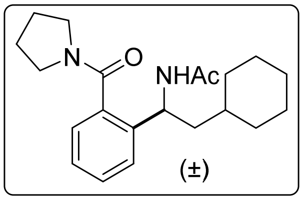
(±) *tert*-Butyl (4-methyl-1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pentyl)carbamate (34): Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), 4-methylpent-1-ene (50 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{21}H_{32}N_3O_2^+$: 358.2489. Found 358.2495.



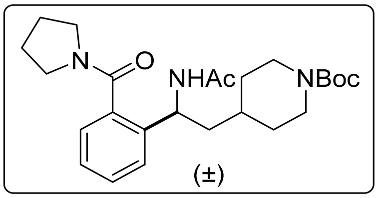
(±) *tert*-Butyl (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-3-phenylpropyl)carbamate (35): Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), allylbenzene (70 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{24}H_{30}N_3O_2^+$: 392.2333. Found 392.2338.



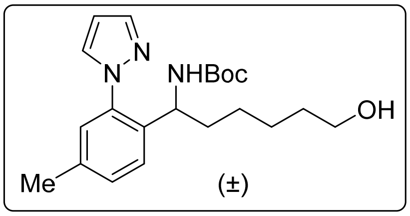
(±) *N*-(3-Methyl-1-(2-(pyrrolidine-1-carbonyl)phenyl)butyl)acetamide (36): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv) and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 1 minute using a reagent cannister of 3-methyl-1-butene 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}; ^{1}H NMR (600 MHz, CDCl$_3$) 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). ^{13}C NMR (151 MHz, CDCl$_3$) 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 $C_{18}H_{27}N_2O_2^+$: 303.2067. Found 303.2056.



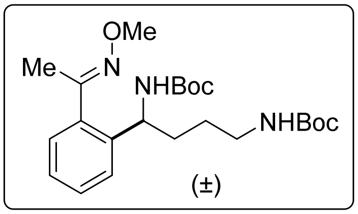
(±) *N*-(2-Cyclohexyl-1-(2-(pyrrolidine-1-carbonyl)phenyl)ethyl)acetamide (37): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), vinyl cyclohexane (66 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 1.0 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}; ^{1}H NMR (500 MHz, CDCl$_3$) 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 $C_{21}H_{31}N_2O_2^+$: 343.2380. Found 343.2386.



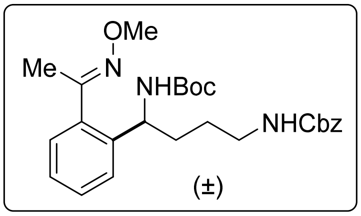
(±)-*tert*-Butyl-4-(2-acetamido-2-(2-(pyrrolidine-1-carbonyl)phenyl)ethyl)piperidine-1-carboxylate (38): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), *tert*-butyl 4-vinylpiperidine-1-carboxylate (127 mg, 0.600 mmol, 2.00 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 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}; ^{1}H 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 $C_{25}H_{38}N_3O_4^+$: 444.2857. Found 444.2862.



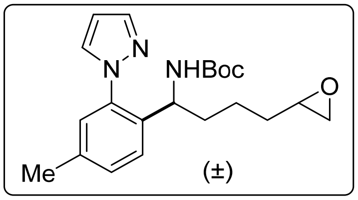
(±) *tert*-Butyl (6-hydroxy-1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)hexyl)carbamate (39): Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), hex-5-en-1-ol (60 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{21}H_{32}N_3O_3^+$: 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 °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 °C). IR (neat): 3388 (br), 2977, 2935, 1679, 1404, 1153, 1040 cm^{-1}; ^{1}H NMR (500 MHz, CD$_3$OD) 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$_3$OD) 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/[M+H]$^+$) calcd. for $C_{23}H_{38}N_3O_5^+$: 436.2806. Found 436.2812.

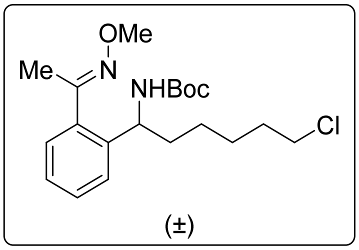


(±) benzyl *tert*-butyl (1-(2-(1-(methoxyimino)ethyl)phenyl)butane-1,4-diyl)(*E*)-dicarbamate (41): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), benzyl *N*-but-3-enylcarbamate (123 mg, 0.600 mmol, 2.00 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (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 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}; ^{1}H NMR (500 MHz, CD_3OD) 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). ^{13}C NMR (126 MHz, CD_3OD) 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 $C_{26}H_{36}N_3O_5^+$: 470.2649. Found 470.2648.

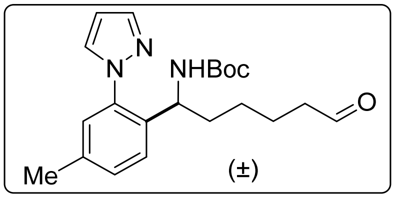


(±) *tert*-Butyl (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-4-(oxiran-2-yl)butyl)carbamate (42): Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), 2-but-3-enyloxirane (58 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 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}. ^{1}H NMR (500 MHz, CD_3OD) 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). ^{13}C NMR

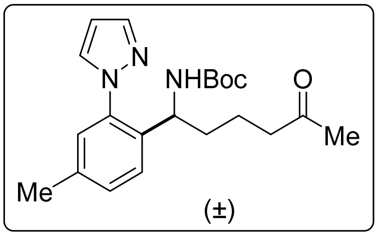
(126 MHz, CD_3OD) δ 157.7, 141.4, 139.7, 139.2, 138.7, 133.6, 131.3, 128.5, 128.2, 107.7, 80.1, 53.3 and 53.2 (1:1 dr), 51.2, 47.84 and 47.77 (1:1 dr), 37.5 and 37.4 (1:1 dr), 33.0 and 32.9 (1:1 dr), 29.0 and 28.9 (1:1 dr), 24.03 and 23.98 (1:1 dr), 20.97 and 20.93 (1:1 dr). HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{30}N_3O_3^+$: 372.2282. Found 372.2287.



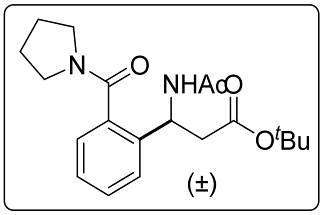
(±) *tert*-Butyl (*E*)-(6-chloro-1-(2-(1-(methoxyimino)ethyl)phenyl)hexyl)carbamate (43): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.00 equiv), 6-chlorohex-1-ene (71 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). $NaHCO_3$ (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. 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, CD_3OD) 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). ^{13}C NMR (151 MHz, CD_3OD) 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 $C_{20}H_{32}ClN_2O_3^+$: 383.2096. Found 383.2122.



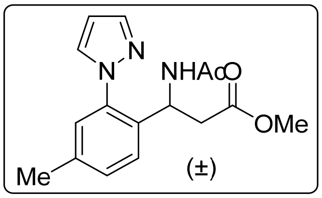
(±) *tert*-Butyl (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-6-oxohexyl)carbamate (44): Derived from 1-(m-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), hex-5-enal (59 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{21}H_{30}N_3O_3^+$: 372.2282. Found 372.2287.



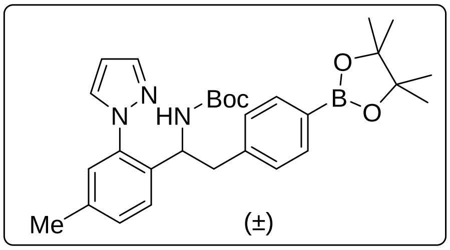
(±) *tert*-Butyl (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-5-oxohexyl)carbamate (45): Derived from 1-(m-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), hex-5-en-2-one (59 mg, 0.60 mmol, 2.0 equiv), and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{21}H_{30}N_3O_3^+$: 372.2282. Found 372.2287.



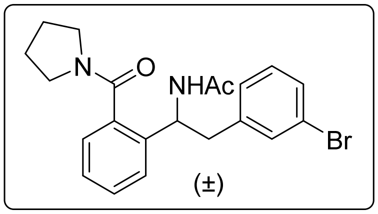
(±) *tert*-Butyl 3-acetamido-3-(2-(pyrrolidine-1-carbonyl)phenyl)propanoate (46): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), *tert*-butyl acrylate (77 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 mmol, 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{20}H_{29}N_2O_4^+$: 361.2122. Found 361.2127.



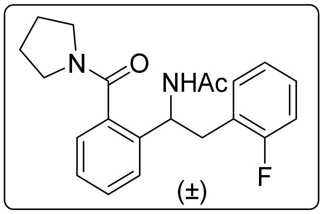
(±) Methyl 3-acetamido-3-(4-methyl-2-(1H-pyrazol-1-yl)phenyl)propanoate (47): Derived from 1-(*m*-tolyl)-1H-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), methyl prop-2-enoate (52 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). The reaction was conducted at 70 °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}; ^{1}H 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 $C_{16}H_{20}N_3O_3^+$: 302.1499. Found 302.1505.



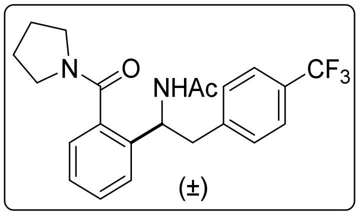
(±) *tert*-Butyl- (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)-2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethyl)carbamate (48): Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.00 equiv), 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (138 mg, 0.600 mmol, 2.0 equiv) 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). ^{13}C 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 $C_{29}H_{39}BN_3O_4^+$: 504.3028. Found 504.3039.



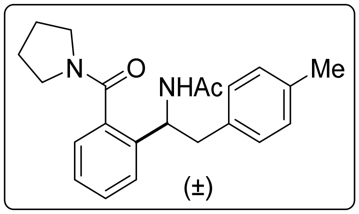
(±) *N*-(2-(3-Bromophenyl)-1-(2-(pyrrolidine-1-carbonyl)phenyl)ethyl)acetamide (49): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), 1-bromo-3-vinyl-benzene (110 mg, 0.600 mmol, 2.00 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{21}H_{24}BrN_2O_2^+$: 415.1016. Found 415.1021.



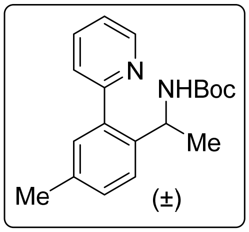
(±) *N*-(2-(2-Fluorophenyl)-1-(2-(pyrrolidine-1-carbonyl)phenyl)ethyl)acetamide (50): Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), 1-fluoro-2-vinyl-benzene (73 mg, 0.60 mmol, 2.0 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{21}H_{24}FN_2O_2^+$: 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}; ^{1}H 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/[M+H]$^+$) calcd. for $C_{22}H_{24}F_3N_2O_2^+$: 405.1784. Found 405.1790.

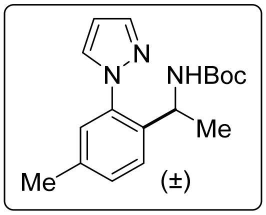


***N*-(1-(2-(pyrrolidine-1-carbonyl) phenyl)-2-(*p*-tolyl)ethyl)acetamide (52):** Derived from phenyl(pyrrolidin-1-yl)methanone (52.6 mg, 0.300 mmol, 1.00 equiv), 1-methyl-4-vinylbenzene (71 mg, 0.600 mmol, 2.00 equiv), and 3-methyl-1,4,2-dioxazol-5-one (45 mg, 0.45 mmol, 1.5 equiv). PivOH (30 mg, 0.30 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}; ^{1}H 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{22}H_{27}N_2O_2^+$: 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}; ^{1}H NMR (600 MHz, CD_3OD) 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). ^{13}C NMR (151 MHz, CD_3OD) 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 $C_{19}H_{25}N_2O_2^+$: 313.1911. Found 313.1916.

For reaction conducted using a Parr reactor, a different procedure was used: In a N_2-filled glovebox, a 2-5 mL microwave vial was charged with $[Cp^*RhCl_2]_2$ (9.27 mg, 0.015 mmol, 0.050 equiv) and $AgSbF_6$ (21 mg, 0.06 mmol, 0.20 equiv). 1,2-Dicholoroethane (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.

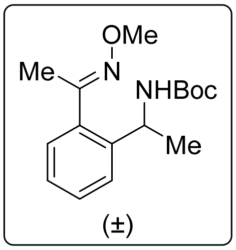


(±) *tert*-Butyl (1-(4-methyl-2-(1*H*-pyrazol-1-yl)phenyl)ethyl)carbamate (54): Derived from 1-(*m*-tolyl)-1*H*-pyrazole (47.5 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 3 minutes using a balloon 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}; ^{1}H NMR (500 MHz, CD_3OD) 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). ^{13}C NMR (126 MHz, CD_3OD) 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 $C_{17}H_{24}N_3O_2^+$: 302.1863. Found 302.1869.

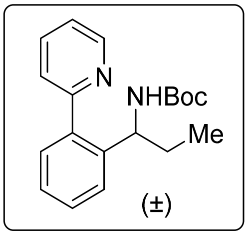
For reaction conducted using a Parr reactor, a different procedure was used: In a N_2-filled glovebox, a 2-5 mL microwave vial was charged with $[Cp^*RhCl_2]_2$ (9.27 mg, 0.015 mmol, 0.050 equiv) and $AgSbF_6$ (21 mg, 0.06 mmol, 0.20 equiv). 1,2-Dicholoroethane (1.5 mL, 0.2 M) was added followed by 1-(*m*-tolyl)-1*H*-pyrazole (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.

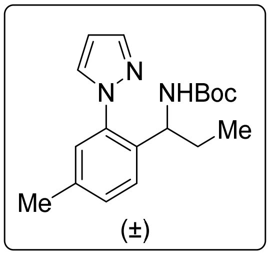
For the larger 5g scale reaction conducted using a Parr reactor, the following procedure was used: In a N_2-filled glovebox, a 50 - 60 mL glass vessel (the inner part of Parr reactor) was charged with $[Cp^*RhCl_2]_2$ (198 mg, 0.320 mmol, 0.010 equiv) and $AgSbF_6$ (440 mg, 1.28 mmol, 0.04 equiv). 1,2-Dicholoroethane (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. $NaHCO_3$ (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 10:90 mixture of ethyl acetate: hexanes with 1% Et_3N 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}; ^{1}H NMR (600 MHz, CD$_3$OD) 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$_3$OD) 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/[M+H]$^+$) calcd. for $C_{16}H_{25}N_2O_3^+$: 293.1860. Found 293.1865.

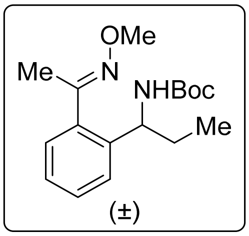


(±) *tert*-Butyl (1-(2-(pyridin-2-yl)phenyl)propyl)carbamate (56): Derived from 2-phenylpyridine (46.6 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 3 minutes using a balloon of propylene with a needle 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}; ^{1}H NMR (500 MHz, CD$_3$OD) 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$_3$OD) 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/[M+H]$^+$) calcd. for $C_{19}H_{25}N_2O_2^+$: 313.1911. Found 313.1916.



(±) *tert*-Butyl (1-(4-methyl-2-(1*H*-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}; ^{1}H 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/[M+H]$^{+}$) calcd. for $C_{18}H_{26}N_3O_2^{+}$: 316.2020. Found 316.2049.



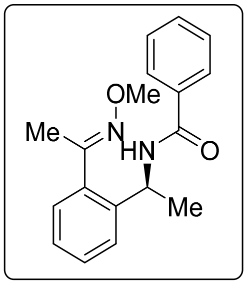
(±) *tert*-Butyl (*E*)-(1-(2-(1-(methoxyimino)ethyl)phenyl)propyl)carbamate (58): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (44.8 mg, 0.300 mmol, 1.0 equiv) and (*tert*-butoxycarbonylamino) 2,2-dimethylpropanoate (98 mg, 0.45 mmol, 1.5 equiv). The reaction mixture was sparged for 3 minutes 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}; ^{1}H 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/[M+H]$^{+}$) calcd. for $C_{17}H_{27}N_2O_3^{+}$: 307.2016. Found 307.2027.

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

General Procedure:

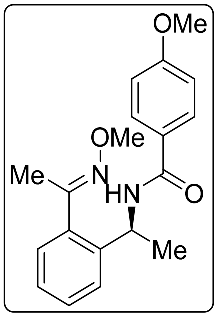
In a N_2-filled glove box, a 2–5 mL microwave vial was charged with precatalyst **59** (3.8 mg, 0.0025 mmol, 0.050 equiv), $AgB(C_6F_5)_4$ (21 mg, 0.020 mmol, 0.40 equiv, 75 w%), and, if indicated, $NaHCO_3$ (4 mg, 0.3 mmol, 1 equiv). 1,2-Dicholoroethane (0.25 mL, 0.2 M) was added followed by the indicated 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 $[Cp^*RhCl_2]_2$ as the precatalyst.



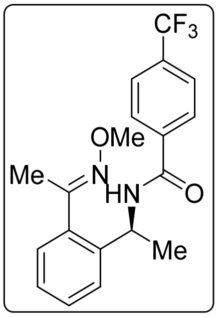
(*S*,*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)ethyl)benzamide (60): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (7.5 mg, 0.050 mmol, 1.0 equiv) and 3-phenyl-1,4,2-dioxazol-5-one (12.2 mg, 0.0750 mmol, 1.50 equiv). $NaHCO_3$ (4 mg, 0.3 mmol, 1 equiv) was used as an additive. The product 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 ºC). $[\alpha]_D^{20}$ -112.76° (*c* = 0.1, $CHCl_3$). 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, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{18}H_{21}N_2O_2^+$: 297.1598. Found 297.1621.

For the 0.2 mmol scale reaction, the following procedure was used: In a N_2-filled glove box, a 2–5 mL microwave vial was charged with precatalyst **59** (15.2 mg, 0.0100 mmol, 0.050 equiv), $AgB(C_6F_5)_4$ (84 mg, 0.080 mmol, 0.40 equiv, 75 w%), and $NaHCO_3$ (16.8 mg, 0.2 mmol, 1 equiv). 1,2-Dicholoroethane (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.

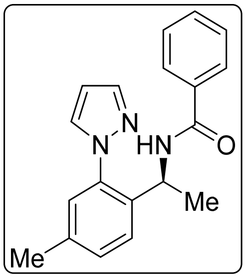


(*S*,*E*)-4-Methoxy-*N*-(1-(2-(1-(methoxyimino)ethyl)phenyl)ethyl)benzamide (61): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (7.5 mg, 0.050 mmol, 1.0 equiv) and 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (14.5 mg, 0.0750 mmol, 1.50 equiv). $NaHCO_3$ (4 mg, 0.3 mmol, 1 equiv) was used as an 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 ºC). $[\alpha]^{20}_{D}$ -37.12° (*c* = 0.1, $CHCl_3$). 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}; ^{1}H

NMR (600 MHz, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{19}H_{23}N_2O_3^+$: 327.1703. Found 327.1710.



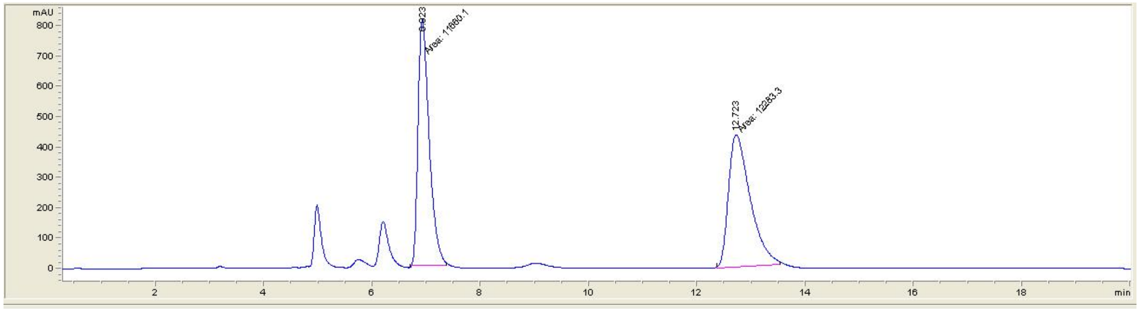
(*S*,*E*)-*N*-(1-(2-(1-(Methoxyimino)ethyl)phenyl)ethyl)-4-(trifluoromethyl)benzamide (62): Derived from (*E*)-1-phenylethan-1-one *O*-methyl oxime (7.5 mg, 0.050 mmol, 1.0 equiv) and 3-[4-(trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (17.3 mg, 0.0750 mmol, 1.50 equiv). $NaHCO_3$ (4 mg, 0.3 mmol, 1 equiv) 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 ºC). $[\alpha]_D^{20}$ -62.72° (*c* = 0.1, $CHCl_3$). 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, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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. ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.92. HRMS (ESI/$[M+H]^+$) calcd. for $C_{19}H_{20}F_3N_2O_2^+$: 365.1471. Found 365.1490.



(*S*)-*N*-(1-(4-Methyl-2-(1*H*-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, $CHCl_3$). 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, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{19}H_{20}N_3O^+$: 306.1601. Found 306.1611.

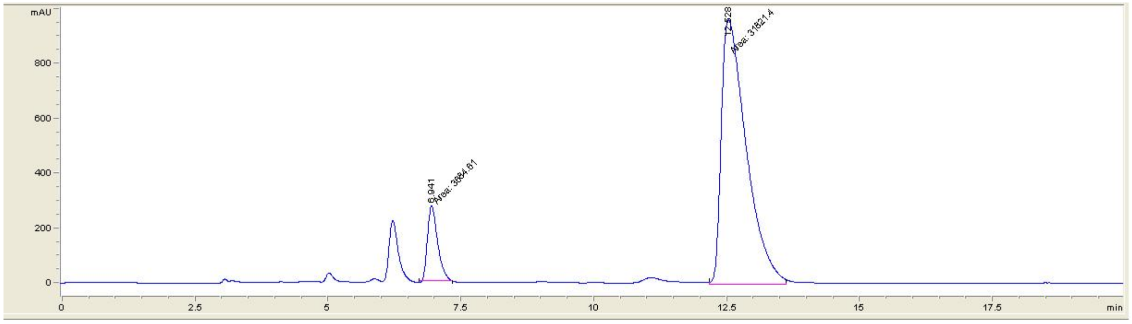
HPLC traces:

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



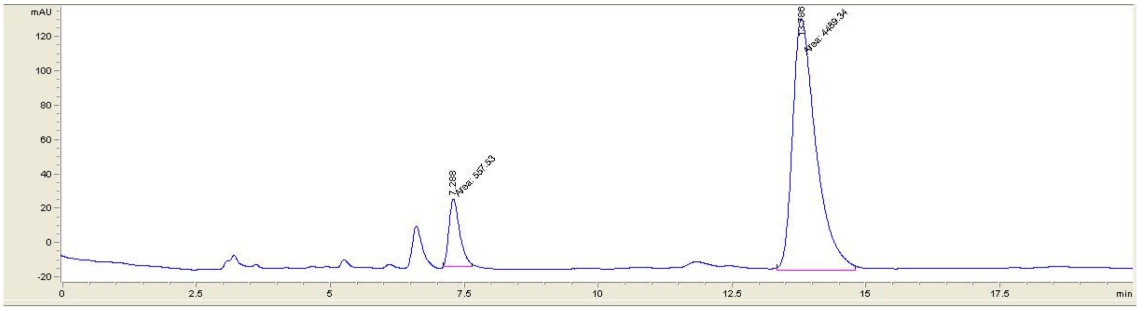
```
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   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):



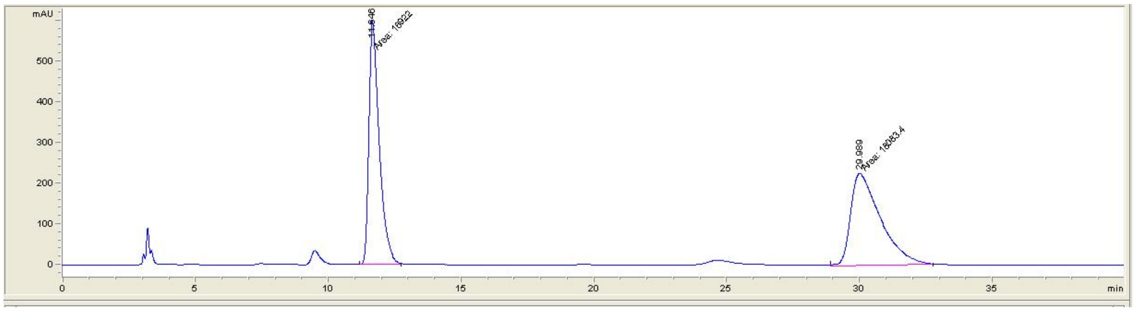
```
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   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):



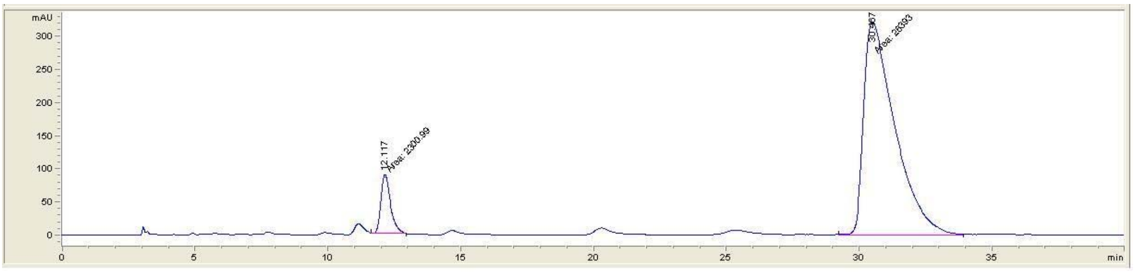
```
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   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):



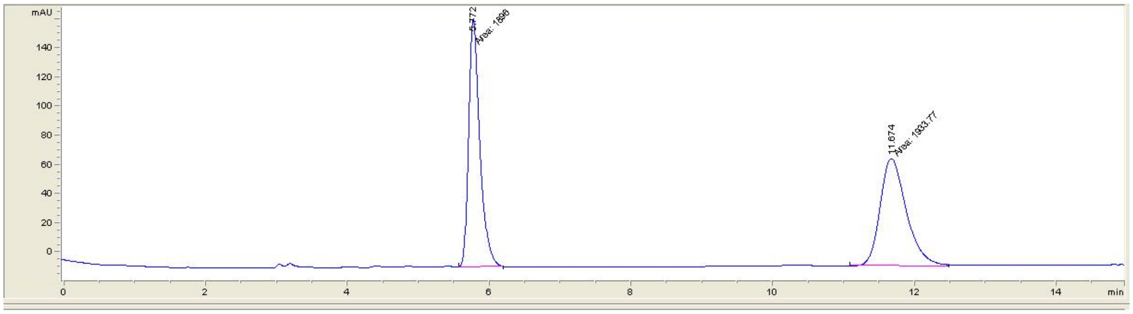
```
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]         [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.646 MM    0.4685 1.69220e4   601.98792  48.3411
   2  29.989 MM    1.3208 1.80834e4   228.19379  51.6589

Totals :                  3.50055e4   830.18170
```

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



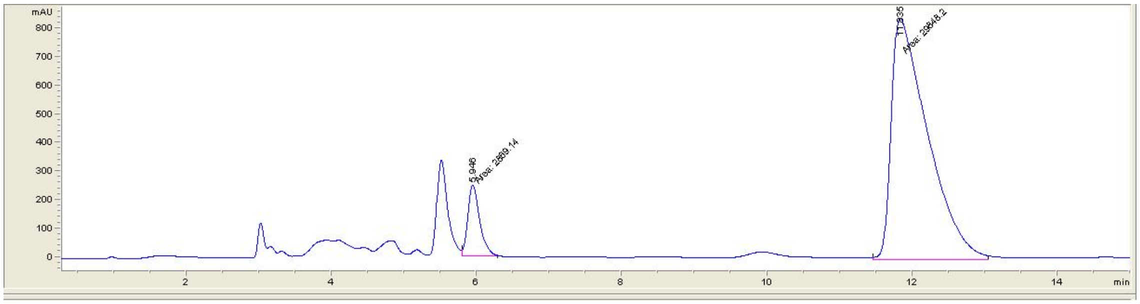
```
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]         [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  12.117 MM    0.4275 2300.98926   89.70274   8.0191
   2  30.467 MM    1.3713 2.63930e4   320.77377  91.9809

Totals :                  2.86940e4   410.47651
```

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



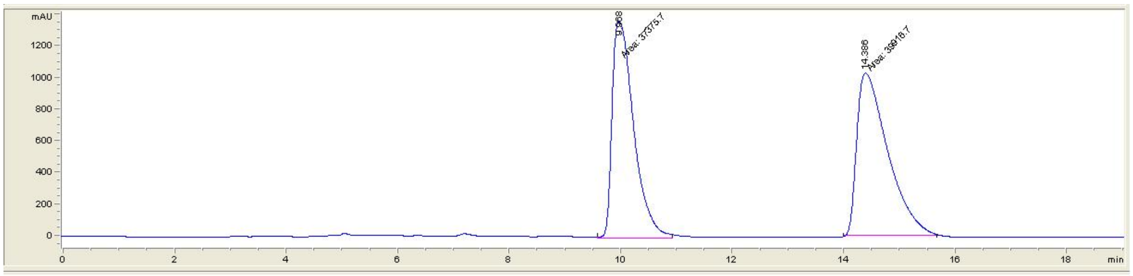
```
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.772 MM    0.1853 1896.00415  170.50522  49.5069
   2  11.674 MM    0.4365 1933.77246   73.83468  50.4931

Totals :                  3829.77661  244.33990
```

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



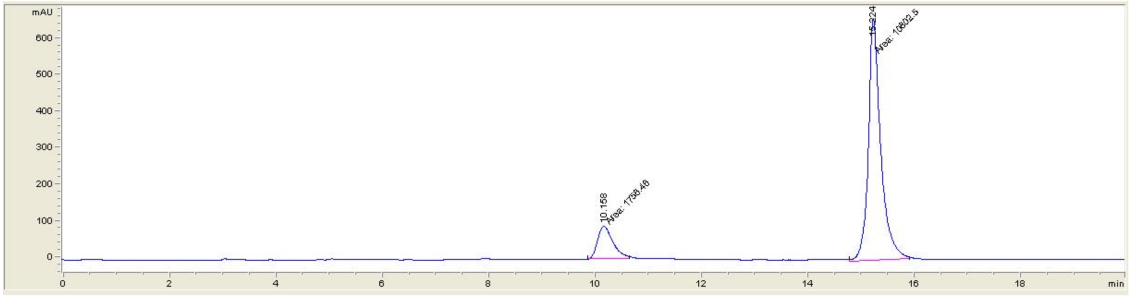
```
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   5.946 MM    0.1921 2869.14063  248.89761   8.7695
   2  11.835 MM    0.5872 2.98482e4   847.19690  91.2305

Totals :                  3.27173e4  1096.09451
```

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 Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   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
```

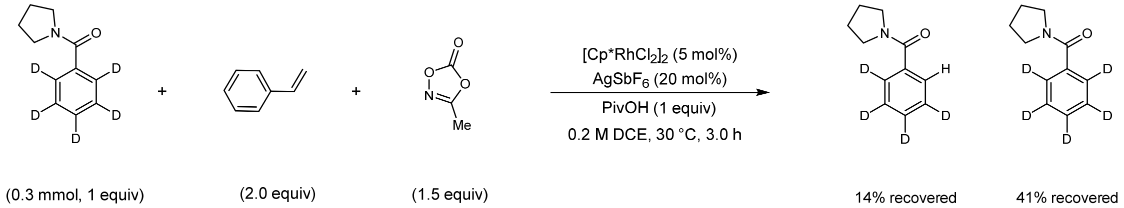
Enantiomerically enriched **63** (86:14 er):

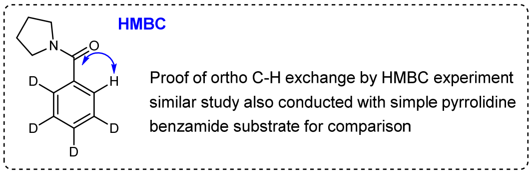


```
Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   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

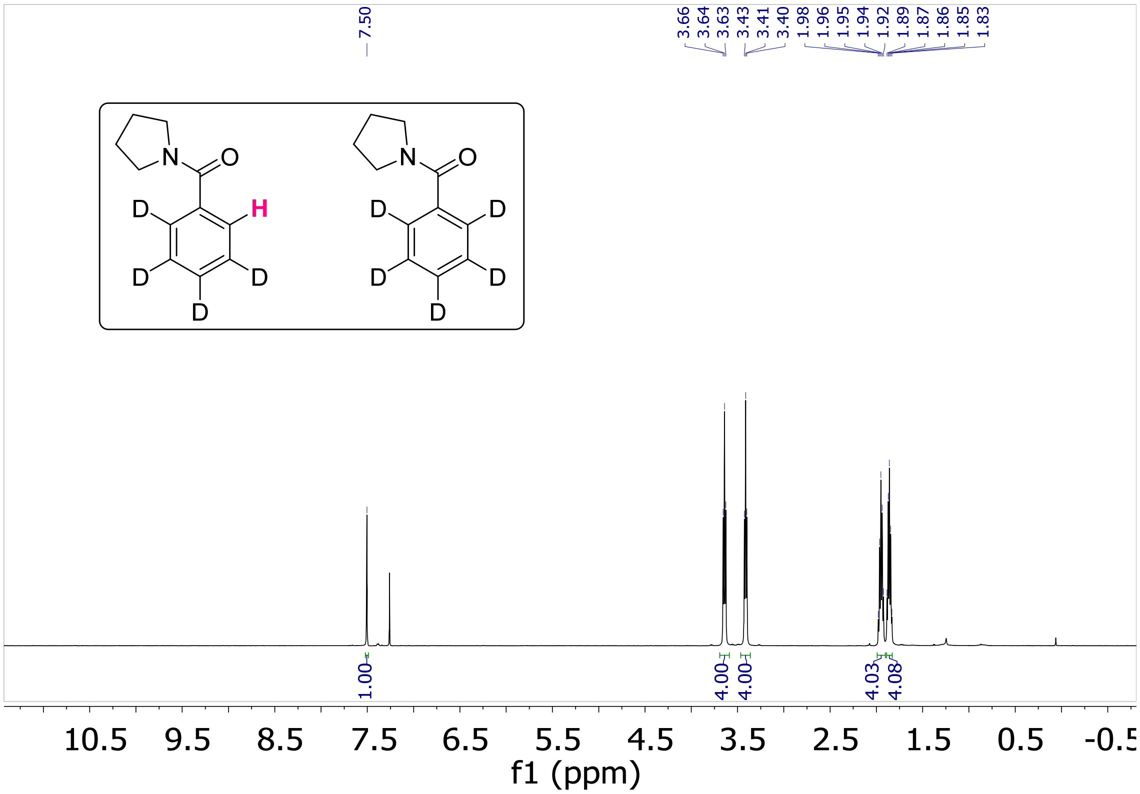
Supplementary Figure 2. Reversibility of C–H bond activation step.

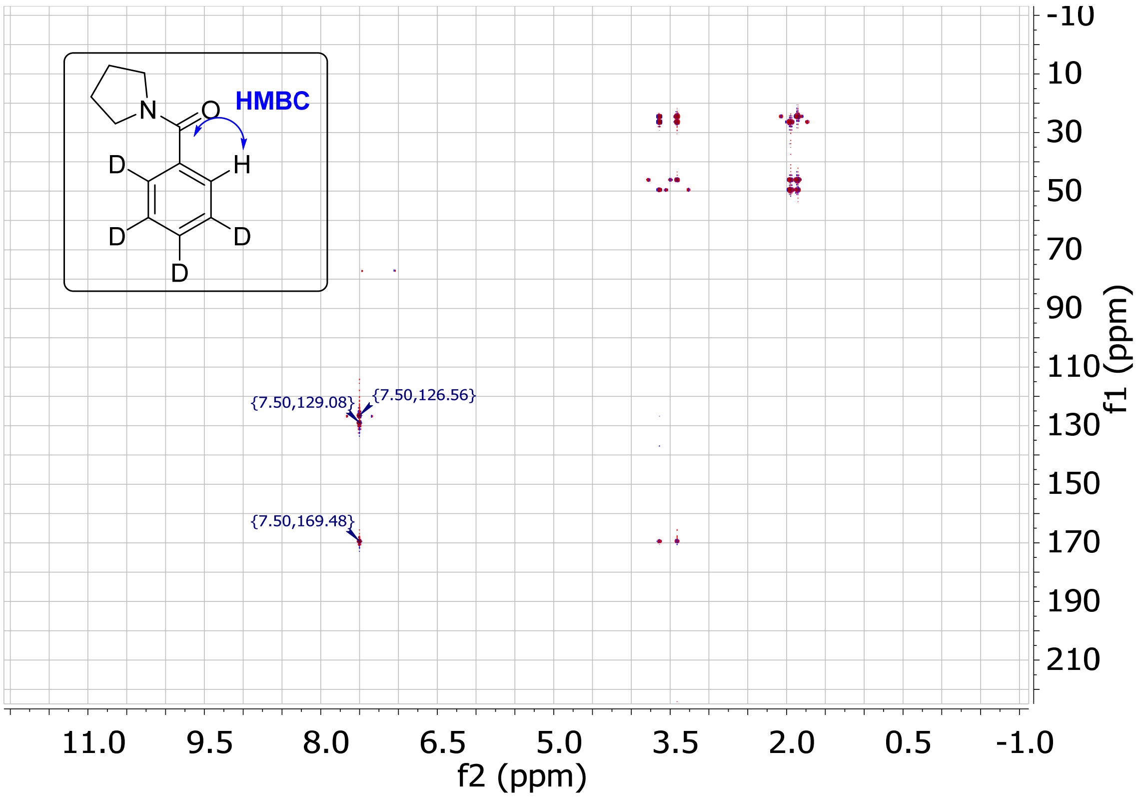




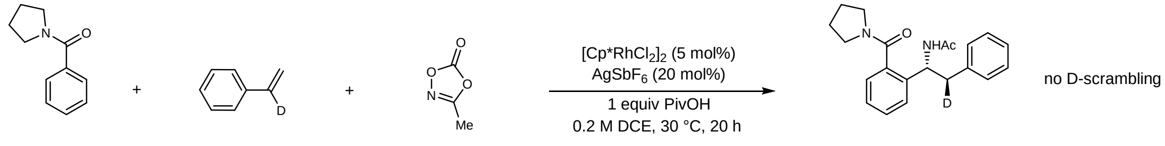
Proof of ortho C-H exchange by HMBC experiment similar study also conducted with simple pyrrolidine benzamide substrate for comparison

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 $[Cp^*RhCl_2]_2$ (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-Dicholoroethane (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 ^{1}H 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 ^{1}H 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.


7.50
3.66
3.64
3.63
3.43
3.41
3.40
1.98
1.96
1.95
1.94
1.92
1.89
1.87
1.86
1.85
1.83
N
O
D
H
D
D
D
N
O
D
D
D
D
D
1.00
4.00
4.00
4.03
4.08
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)


N
O
HMBC
D
H
D
D
D
{7.50,129.08}
{7.50,126.56}
{7.50,169.48}
-10 10 30 50 70 90 110 130 150 170 190 210
f1 (ppm)
11.0 9.5 8.0 6.5 5.0 3.5 2.0 0.5 -1.0
f2 (ppm)

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



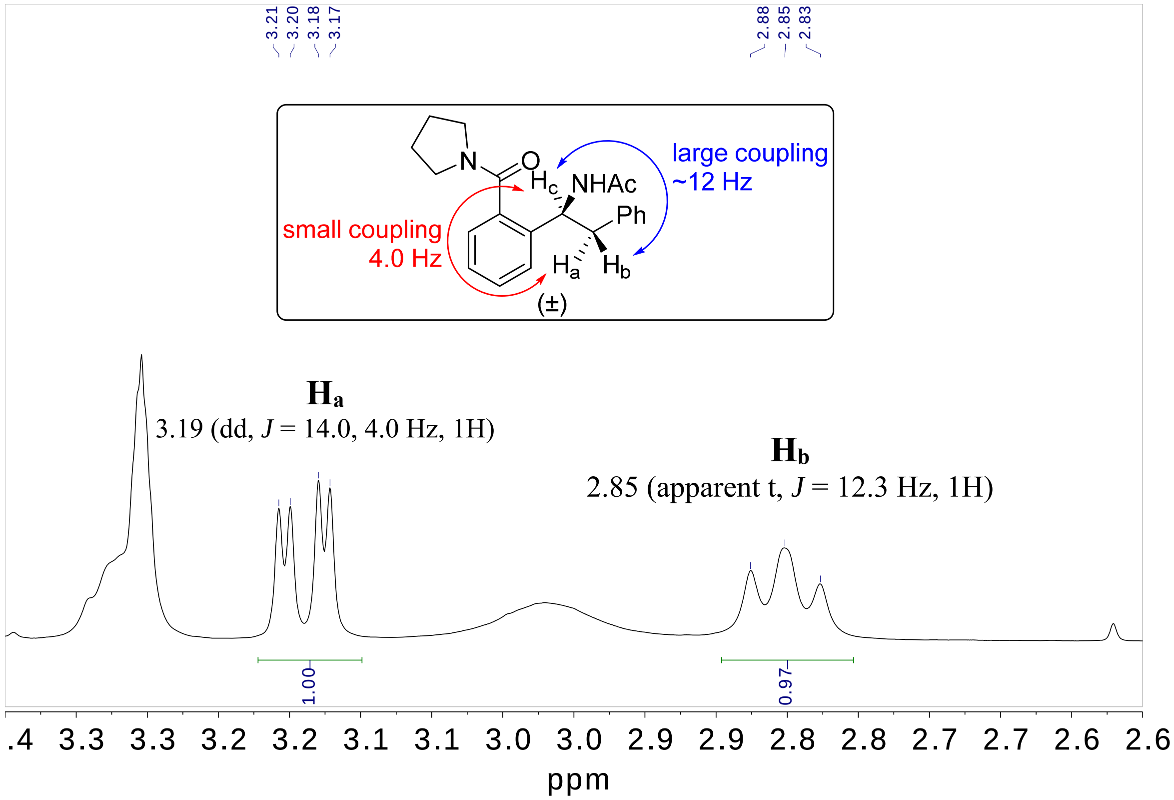
(0.3 mmol, 1 equiv) (2 equiv) (1.5 equiv)

64, 72%

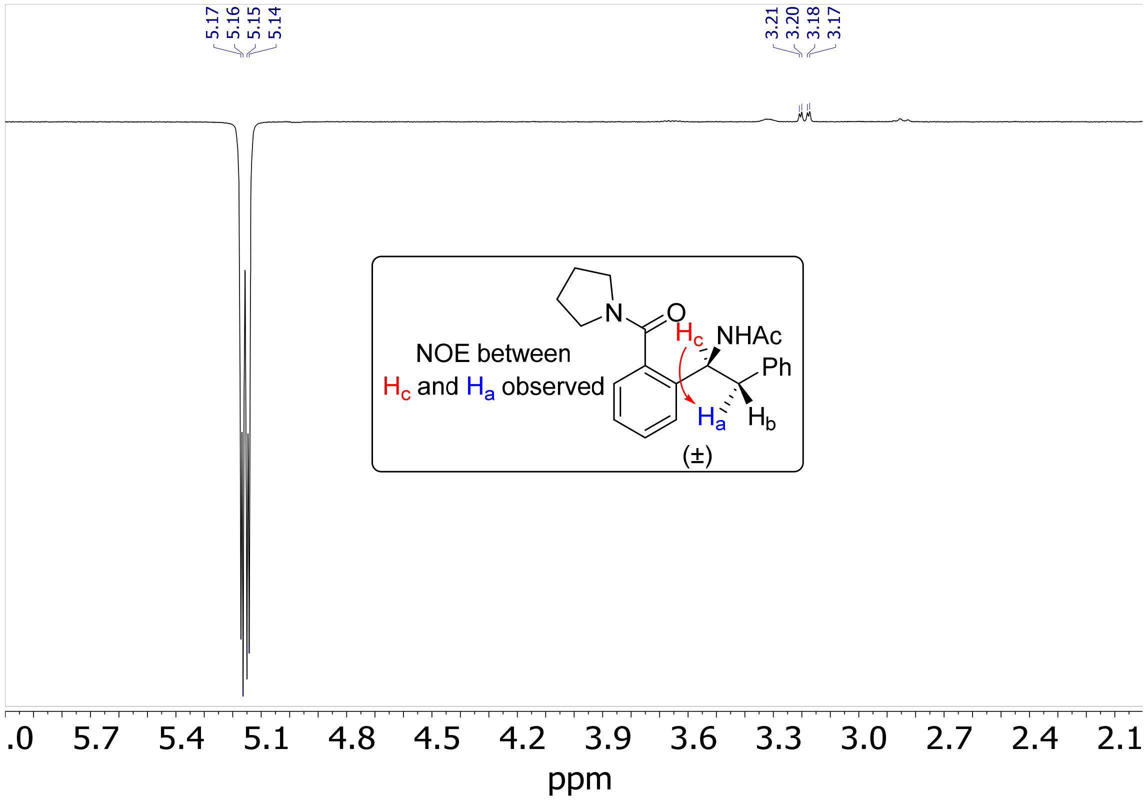
In a N_2-filled glove box, a 2–5 mL microwave vial was charged with $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol, 0.050 equiv), $AgSbF_6$ (21 mg, 0.060 mmol, 0.20 equiv), and PivOH (30 mg, 0.30 mmol, 1 equiv). 1,2-Dicholoroethane (1.5 mL, 0.2 M) was added followed by the phenyl(pyrrolidin-1-yl) methanone (52.6 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}; ^{1}H NMR (500 MHz, $CDCl_3$) 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). ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{21}H_{24}DN_2O_2^+$: 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 ^{1}H and 1D NOE NMR experiments for the proteo 27 and deutero 64 in CD_3OD.

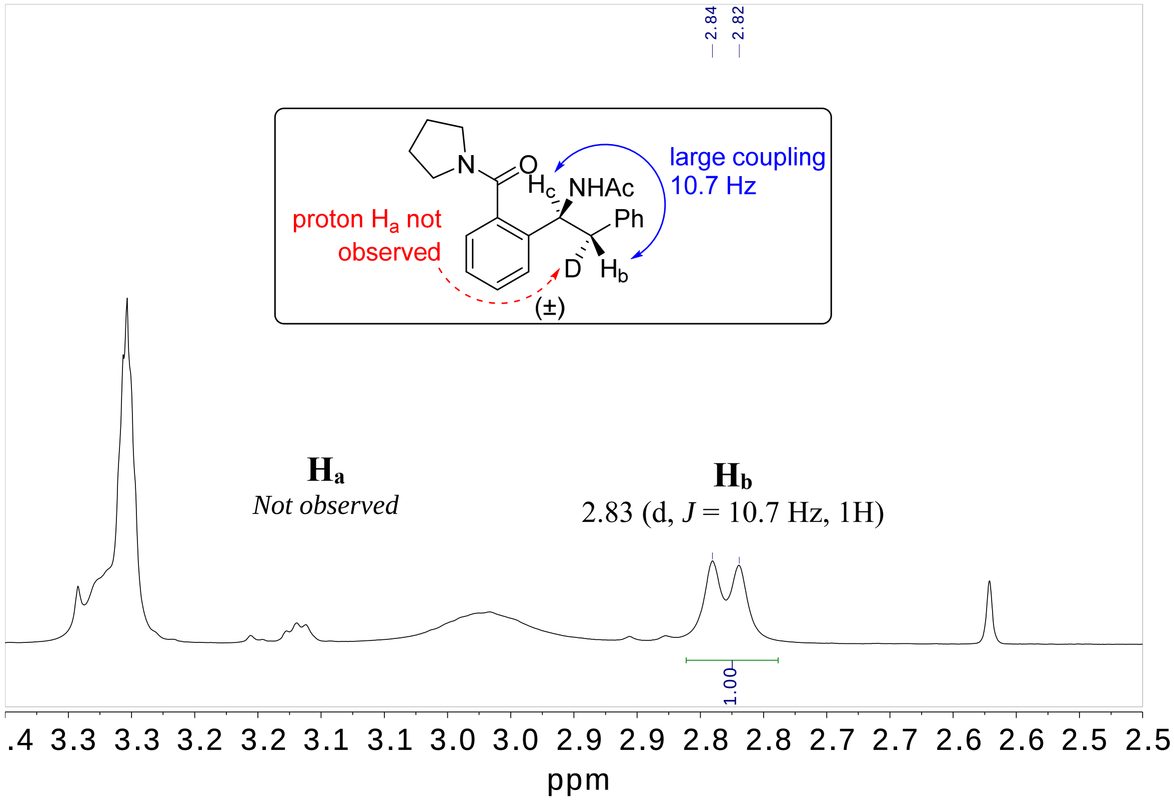
Assignment of the diastereotopic methylene protons $\mathbf{H_a}$ *and* $\mathbf{H_b}$ *in proteo product* ***27***: Protons $\mathbf{H_a}$ and $\mathbf{H_b}$ are found at 3.19 ppm (dd, J = 14.0, 4.0 Hz, 1H) and 2.85 ppm (apparent t, *J* = 12.3 Hz, 1H) in CD_3OD, respectively. Proton $\mathbf{H_a}$ has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



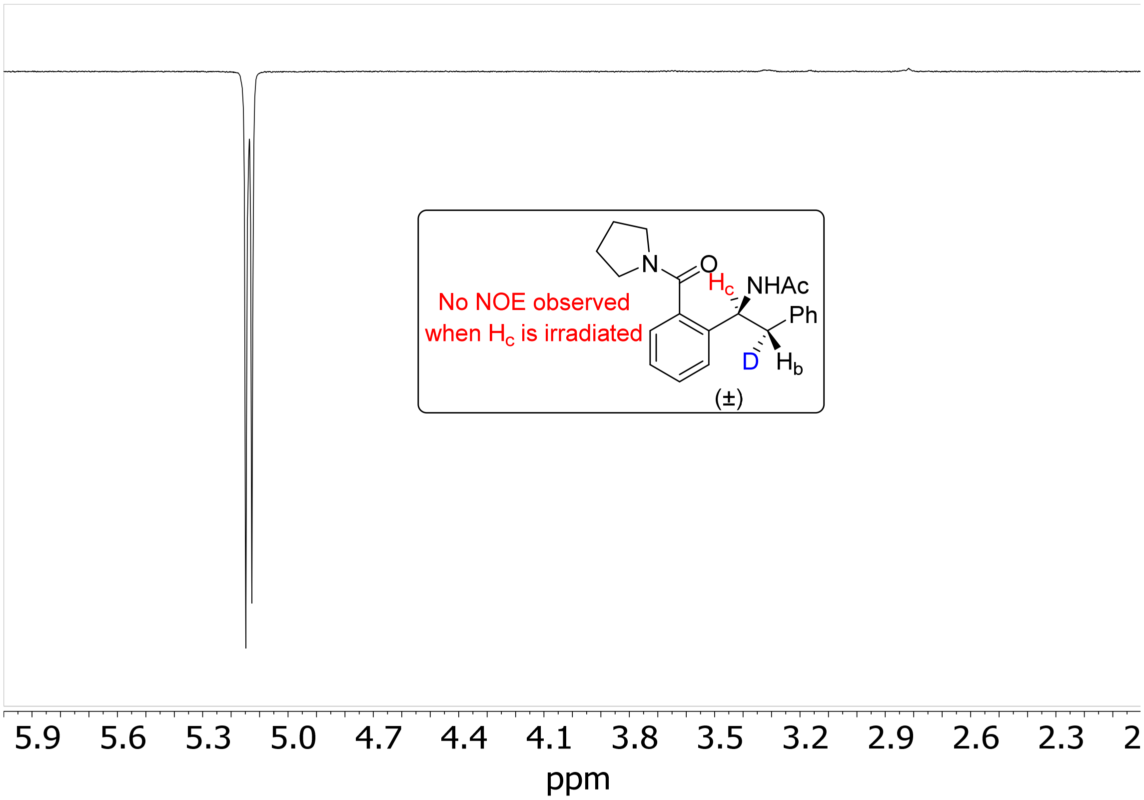
The assignment of $\mathbf{H_a}$ *and* $\mathbf{H_b}$ *is further supported by 1D NOE NMR experiments of proteo product* ***27****:* When proton $\mathbf{H_c}$ (5.16 ppm, dd, *J* = 10.6, 4.1 Hz, 1H) is selected in the 1D NOE experiment, an NOE is observed exclusively to proton $\mathbf{H_a}$ (3.19 ppm).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



*The ^1H spectra for deutero product **64** confirm the stereospecific incorporation of D at the **H_a** site:* Proton **H_a** was not observed in the deutero 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.

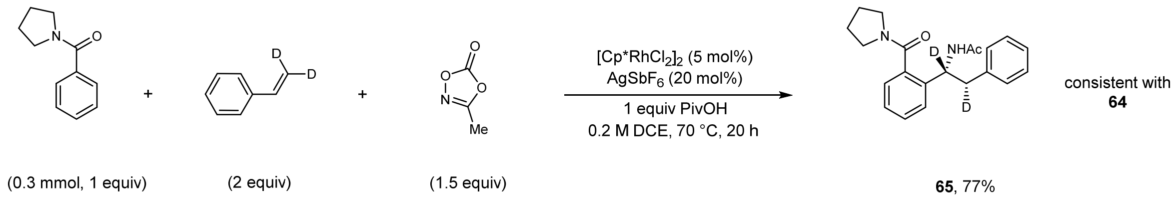


1D NOE NMR experiments for deutero product ***64*** *further confirm the stereospecific incorporation of D at the* $\boldsymbol{H_a}$ *site:* When proton $\mathbf{H_c}$ (5.14 ppm, d, J = 10.6 Hz, 1H) is selected in the 1D NOE experiment, no NOE is observed. Additional 1D NOE NMR data are included in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



In summary, these NMR experiments indicate that the rhodium-hydride undergoes a *syn*-addition, resulting in the deutero 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.

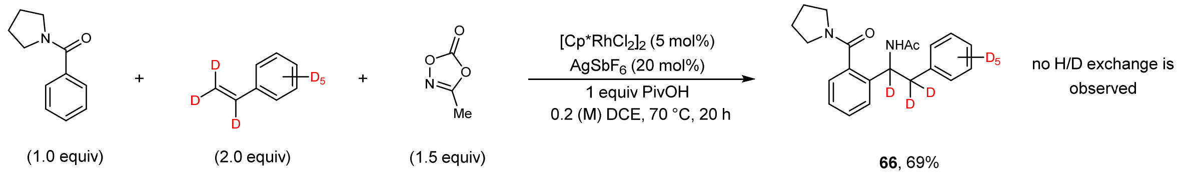


65, 77%

In a N_2-filled glove box, a 2–5 mL microwave vial was charged with $[Cp^*RhCl_2]_2$ (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-Dicholoroethane (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/$[M+H]^+$) calcd. for $C_{21}H_{23}D_2N_2O_2^+$: 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.



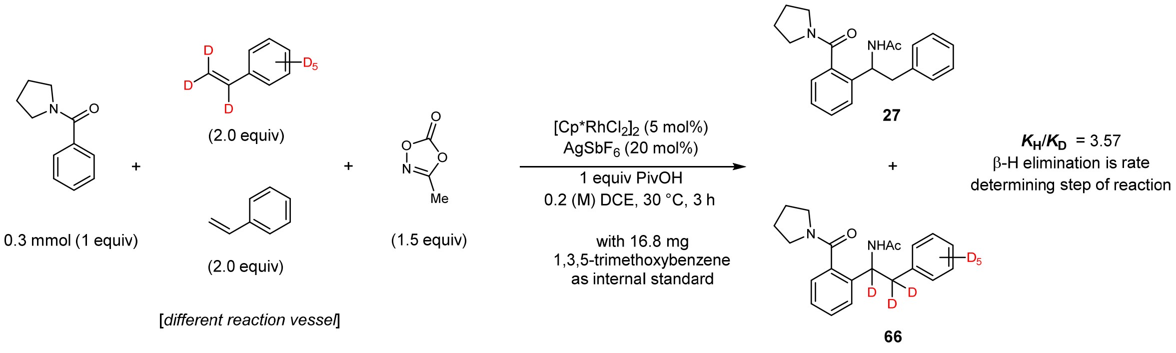
t = 20 h, T = 30 °C, y = 30%
t = 40 h, T = 30 °C, y = 59%
t = 20 h, T = 70 °C, y = 72%

reactions with D8-styrene were found to proceed more slowly than the analogous reaction with simple styrene; yields reported here were determined by ^{1}H NMR with trimethoxybenzene as an external standard

In a N_2-filled glove box, a 2–5 mL microwave vial was charged with $[Cp^*RhCl_2]_2$ (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-Dicholoroethane (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}; ^{1}H NMR (600 MHz, $CDCl_3$) 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). ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{21}H_{17}D_8N_2O_2^+$: 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 ß-D to α-position.

Supplementary Figure 6. Kinetic isotope effect studies and determination.



K_H/K_D = 3.57
β-H elimination is rate
determining step of reaction

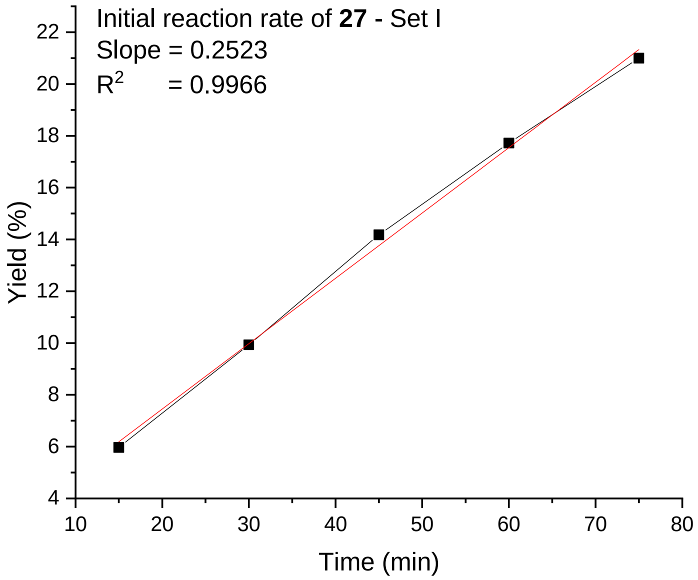
In a N2-filled glove box, a 2–5 mL microwave vial was charged with 16.8 mg of 1,3,5-trimethoxybenzene as the internal standard, $[Cp^*RhCl_2]_2$ (9.3 mg, 0.015 mmol, 0.050 equiv), $AgSbF_6$ (21 mg, 0.060 mmol, 0.20 equiv), and pivalic acid (30 mg, 0.30 mmol, 1 equiv). 1,2-Dicholoroethane (1.5 mL, 0.2 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 N_2. This aliquot workup procedure was carried out for each time interval. Each of these concentrated extracts was analyzed by ^1H NMR using $CDCl_3$ as solvent to obtain NMR yields of the products **27** and **66**.

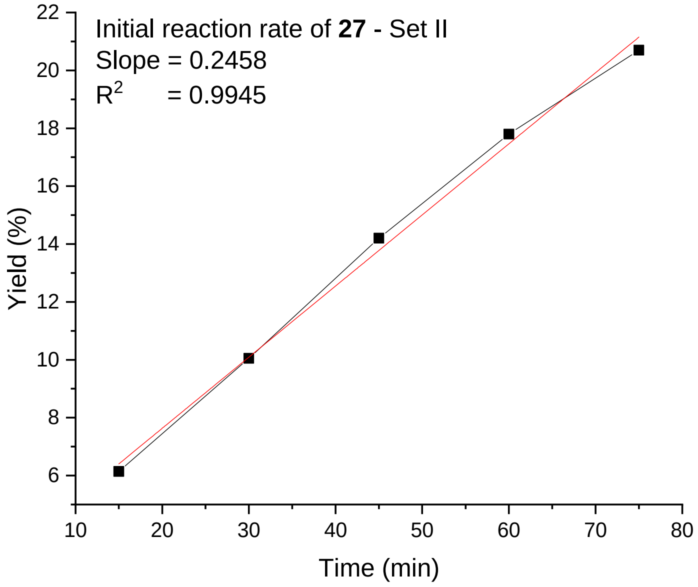
Supplementary Table 4. Initial rate determination for 27.

*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

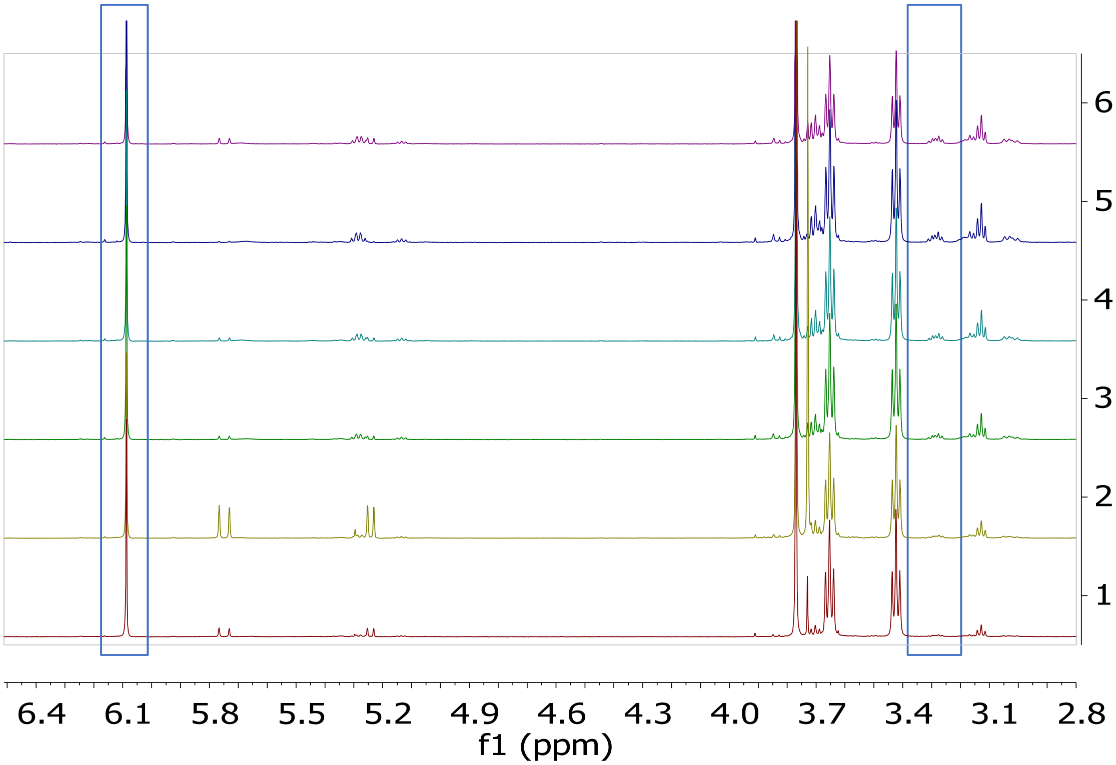
60	17.8
75	20.7

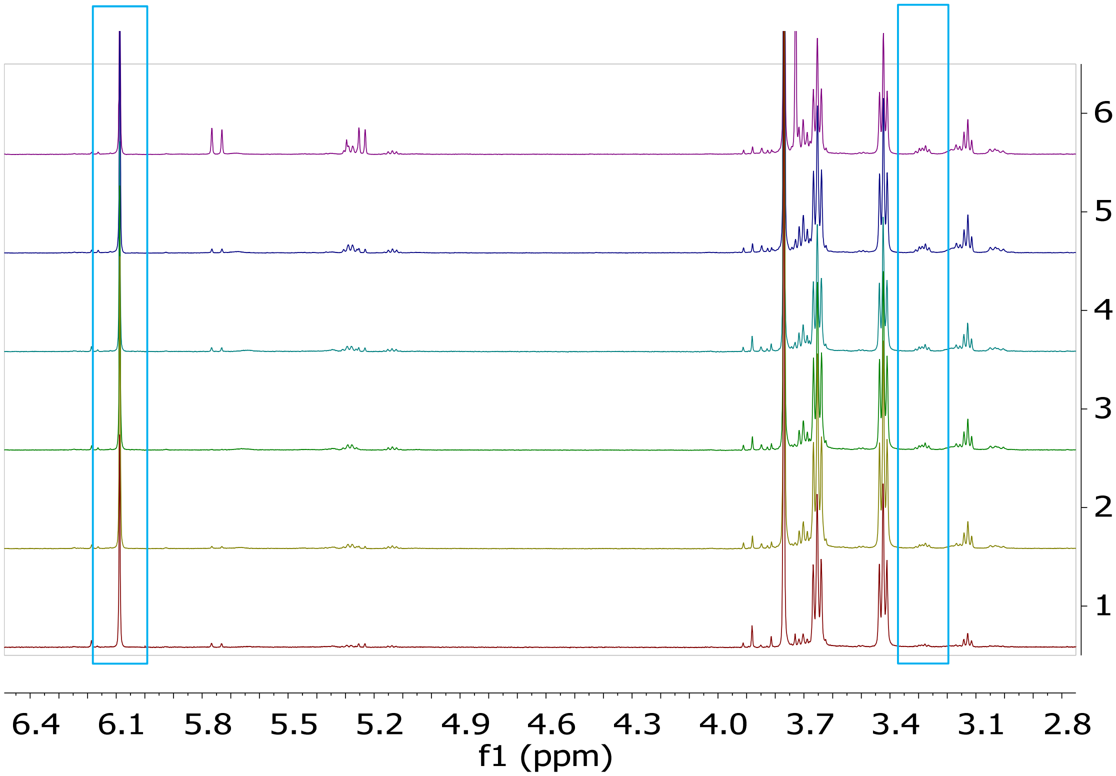
Supplementary Figure 7. Initial reaction rate graphs for 27.





Stacked ^{1}H 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*]

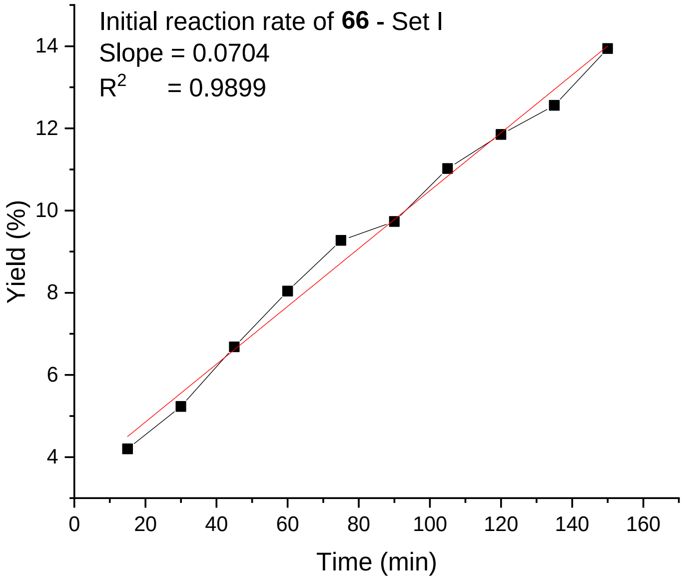


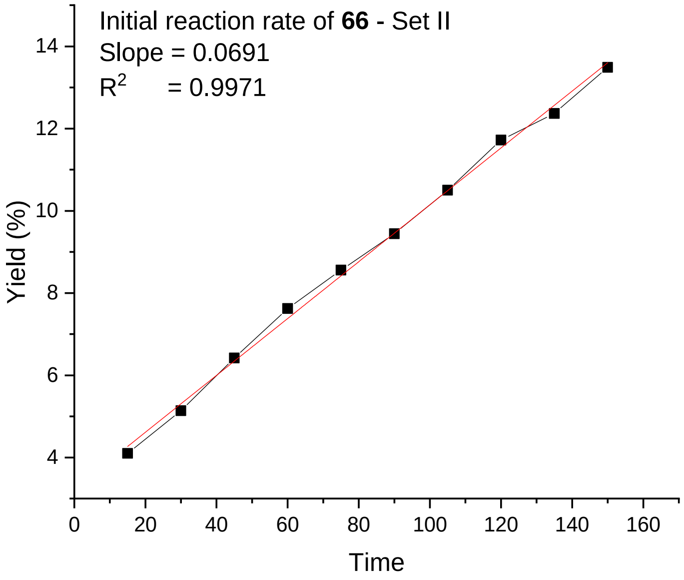


Supplementary Table 5. Initial rate determination for 66.

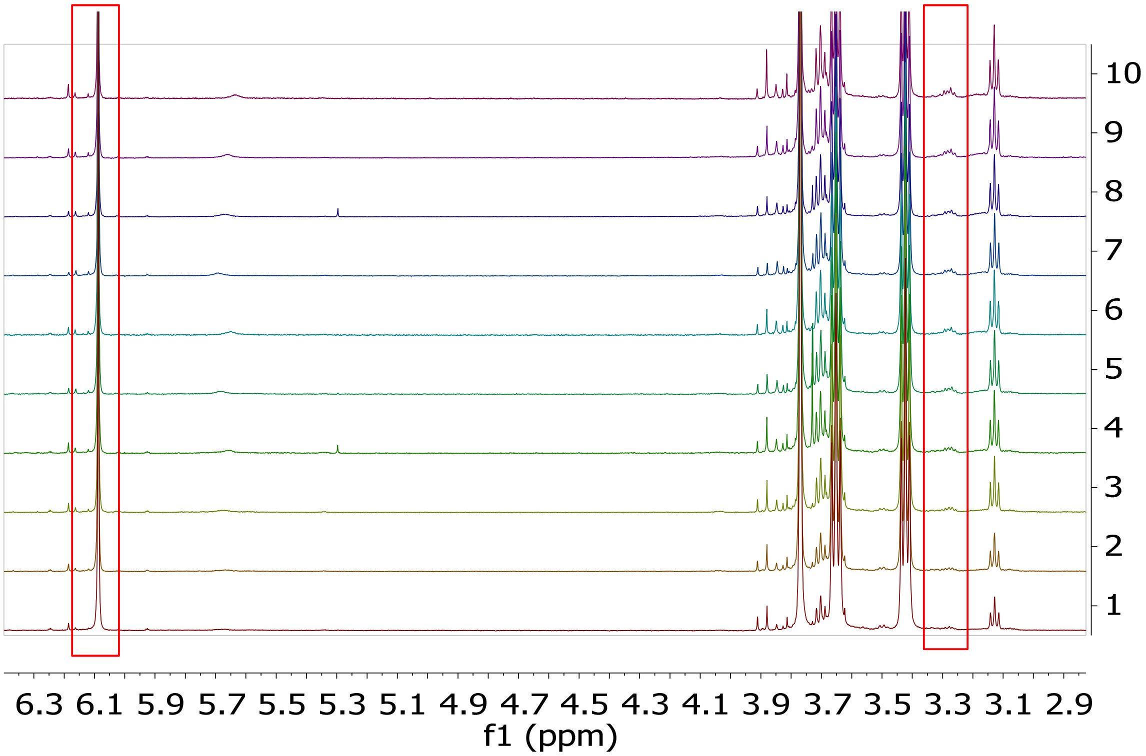
*Initial rates for **66** (First run)*	
Time (min)	Yield of product **66** (%)
15	4.2
30	5.23
45	6.68
60	8.04
75	9.27
90	9.73
105	11.02
120	11.85
135	12.56
150	13.94
*Initial rates for **66** (Second run)*	
Time (min)	Yield of product **66** (%)
15	4.1
30	5.14
45	6.42
60	7.62
75	8.56
90	9.44
105	10.50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

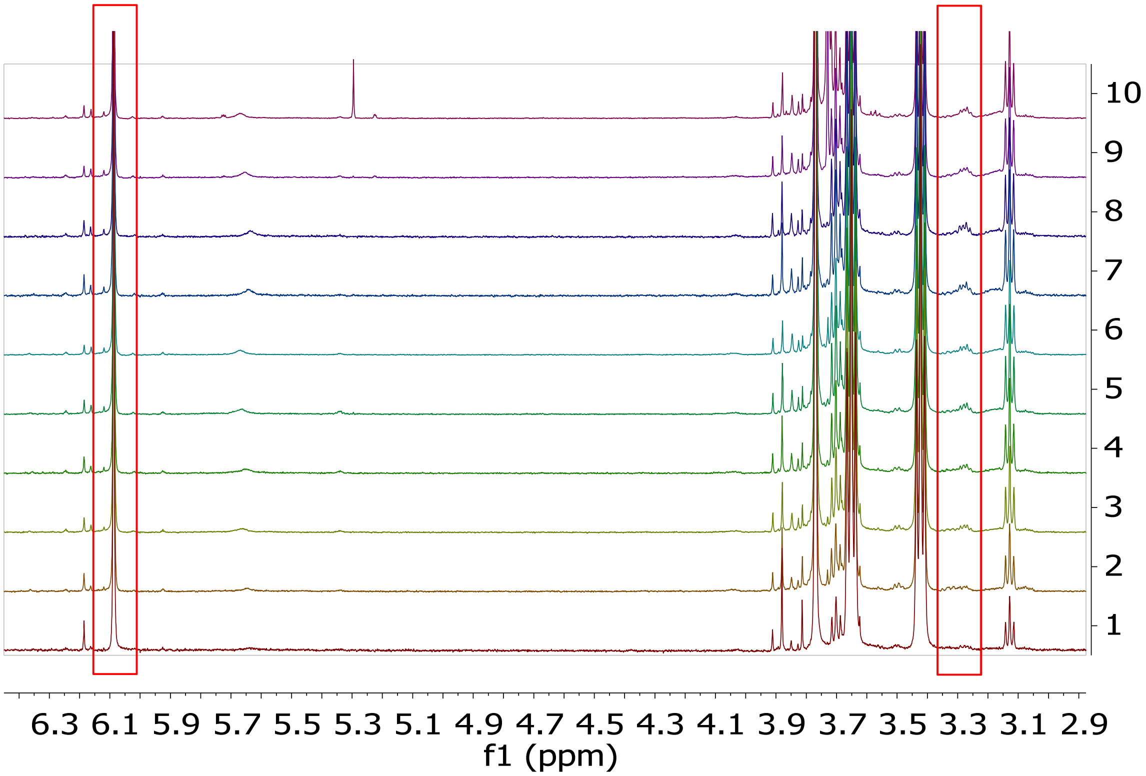
Supplementary Figure 8. Initial reaction rate graphs for 66.





Stacked ^{1}H 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.

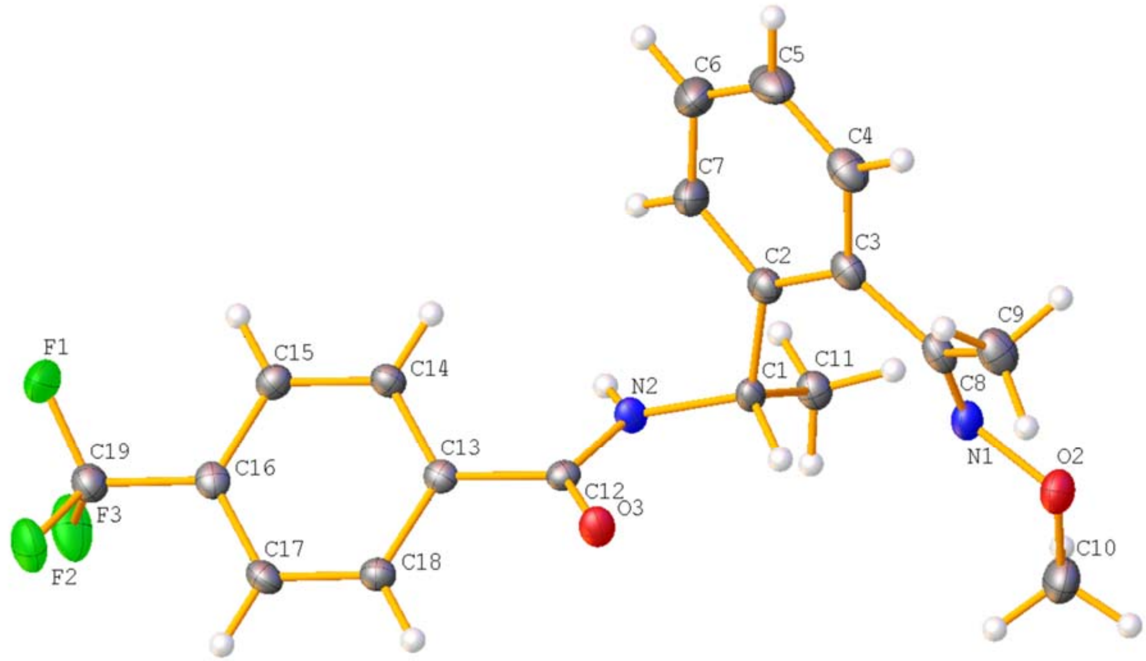
Initial rates for **27**	
Slope first run	0.2523
Slope second run	0.2458
Average slope	0.2491
Standard deviation	0.0046
Initial rates for **66**	
Slope first run	0.0704
Slope second run	0.0691
Average slope	0.0697
Standard deviation	0.0009
KIE	**3.57 ± 0.08 SD**

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/CH_2Cl_2 (~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 Kα (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	C19 H19 F3 N2 O2	
Formula weight	364.36	
Temperature	93(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
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	
Diffractometer	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 > 2sigma(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>2sigma(I)]	R1 = 0.0296, wR2 = 0.0755	
R indices (all data)	R1 = 0.0296, wR2 = 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 (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **62** (007b-19043). U(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 (Å^{2}x 10^3) for **62** (007b-19043). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
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 (x 10^4) and isotropic displacement parameters (Å^{2}x 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:

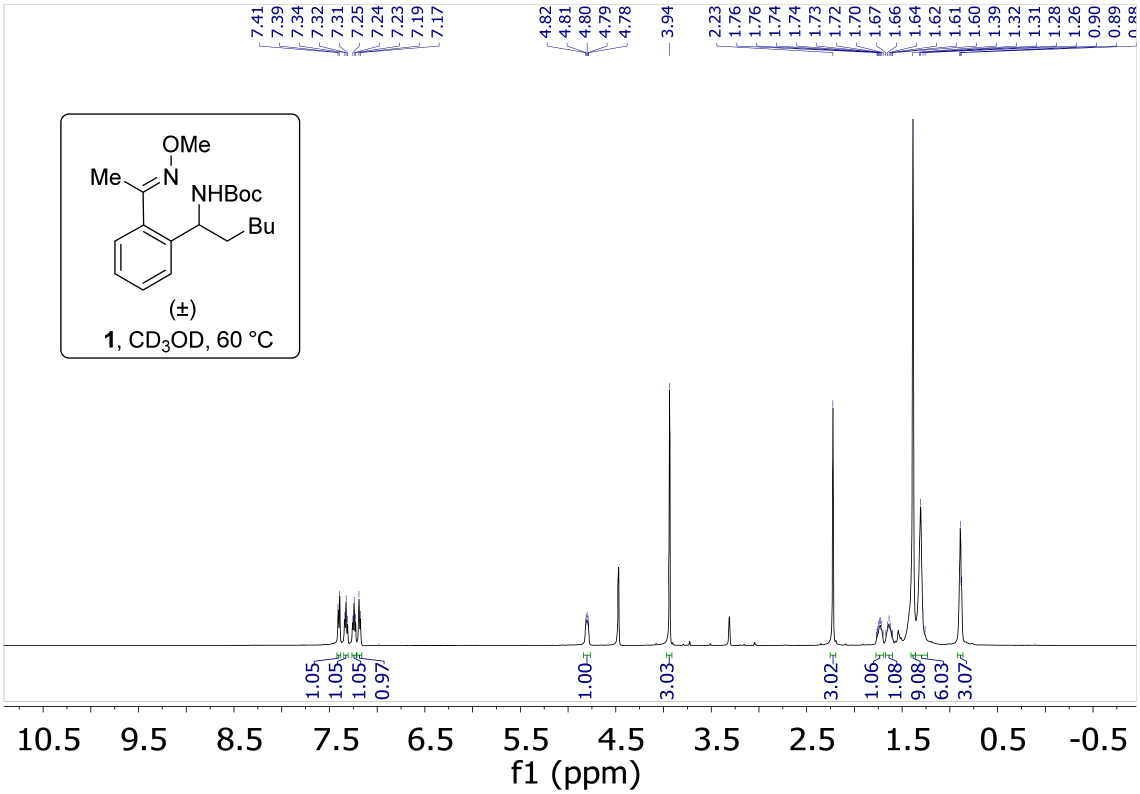
Supplementary Table 13. Hydrogen bonds for **62** (007b-19043) [Å and °].

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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7.23
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4.80
4.79
4.78
3.94
2.23
1.76
1.76
1.74
1.74
1.73
1.72
1.70
1.67
1.66
1.64
1.62
1.61
1.60
1.39
1.32
1.31
1.28
1.26
0.90
0.89
0.8
OMe
Me
N
NHBoc
Bu
(±)
1, CD3OD, 60 °C
1.05
1.05
1.05
0.97
1.00
3.03
3.02
1.06
1.08
9.08
6.03
3.07
10.5
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1.5
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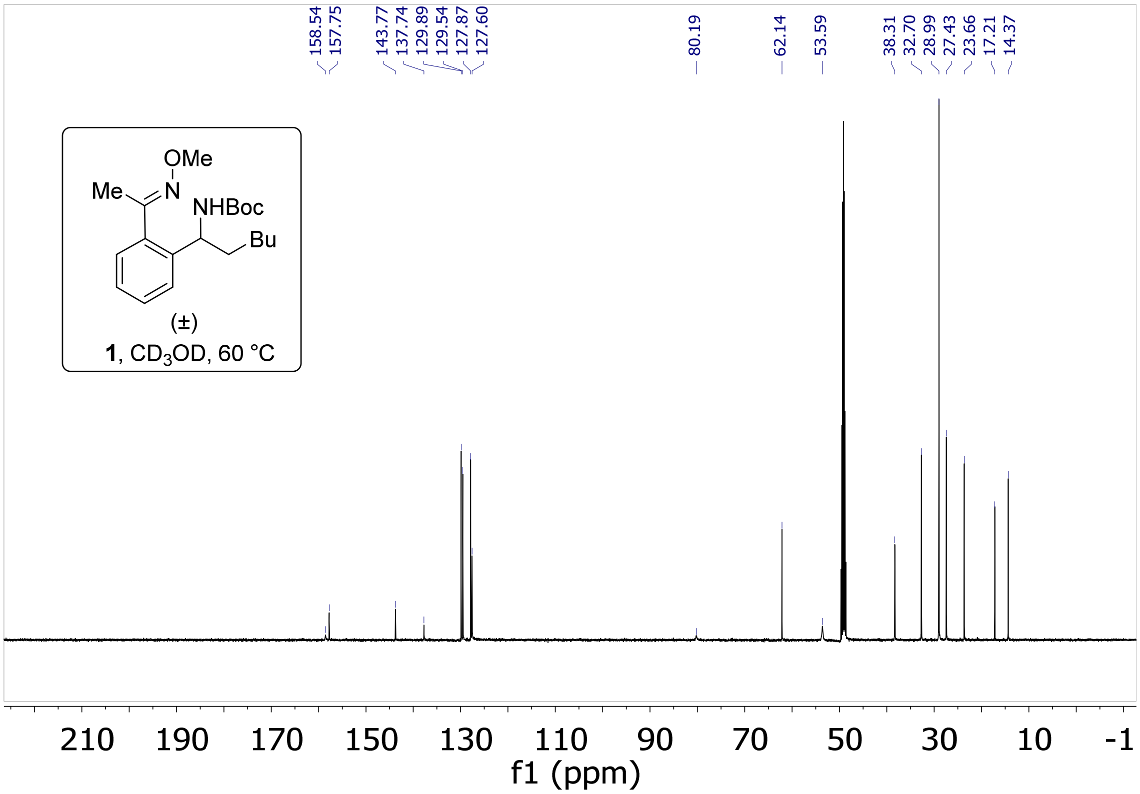
f1 (ppm)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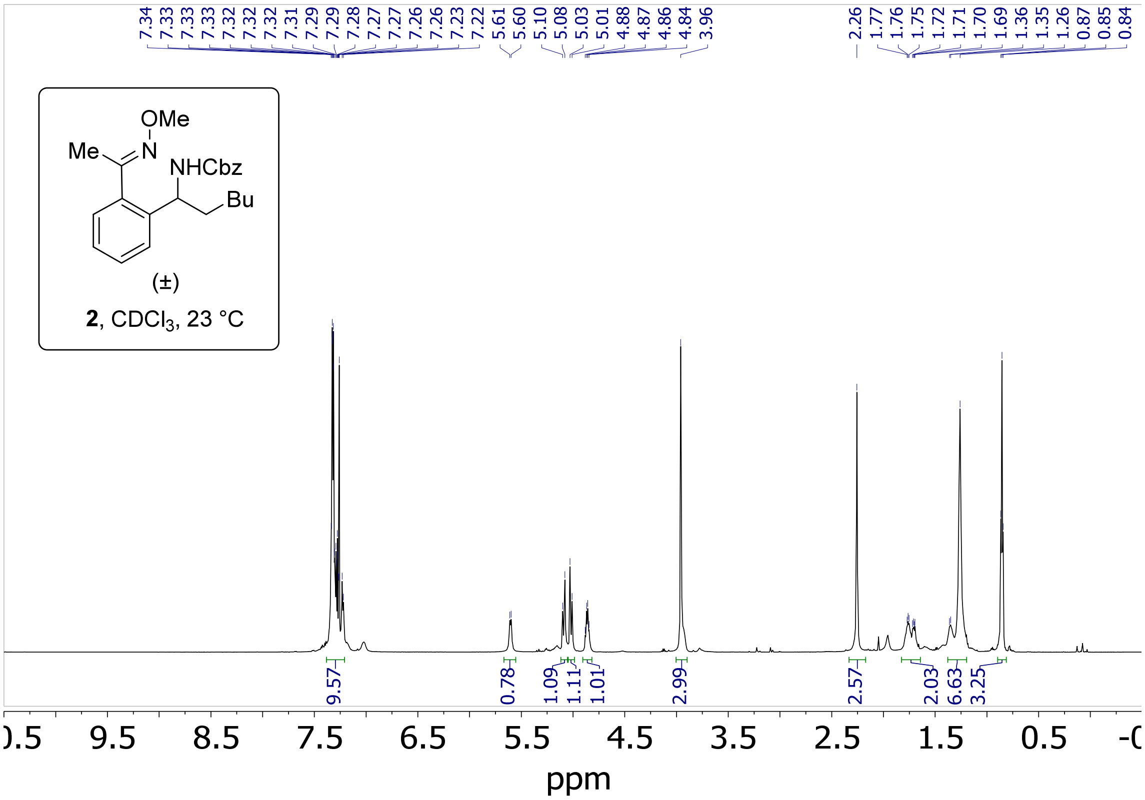
32.70
28.99
27.43
23.66
17.21
14.37
OMe
Me
N
NHBoc
Bu
(±)
1, CD3OD, 60 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)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2.26 1.77 1.76 1.75 1.72 1.71 1.70 1.69 1.36 1.35 1.26 0.87 0.85 0.84
OMe
Me
N
NHCbz
Bu
(±)
2, CDCl3, 23 °C
9.57
0.78
1.09
1.11
1.01
2.99
2.57
2.03
6.63
3.25
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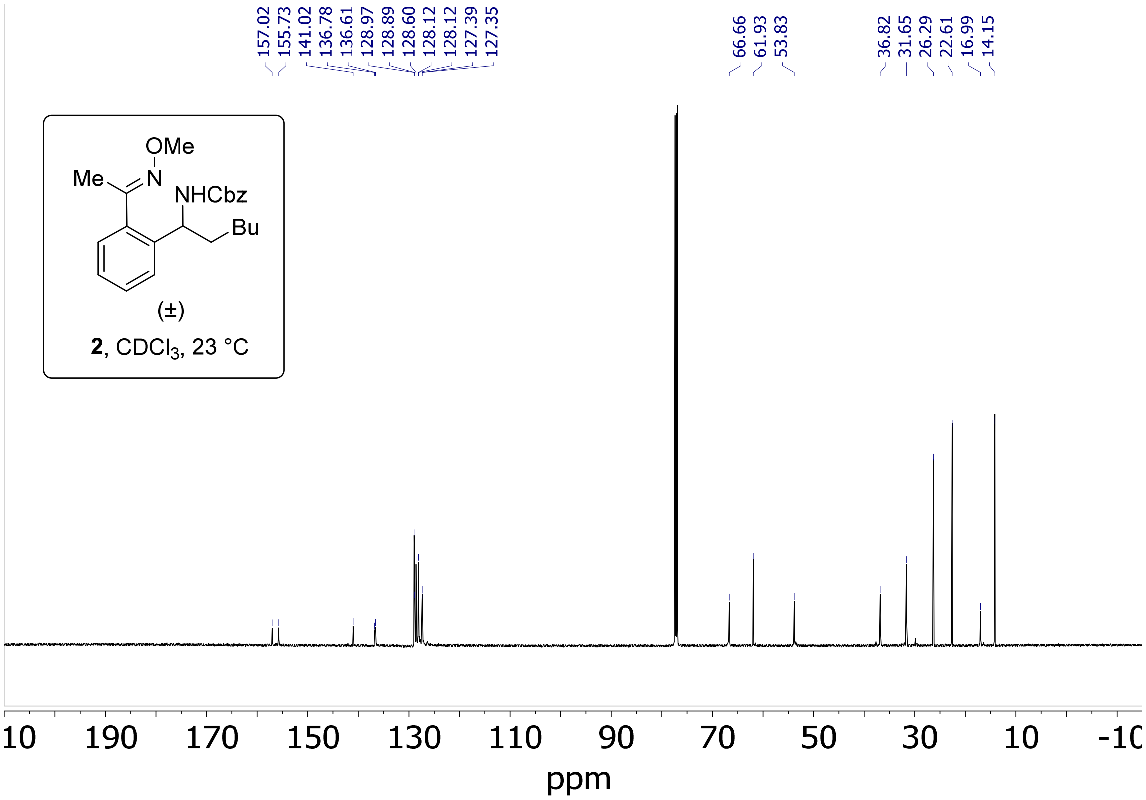
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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66.66 61.93 53.83
36.82 31.65 26.29 22.61 16.99 14.15
OMe
Me
N
NHCbz
Bu
(±)
2, CDCl3, 23 °C
190
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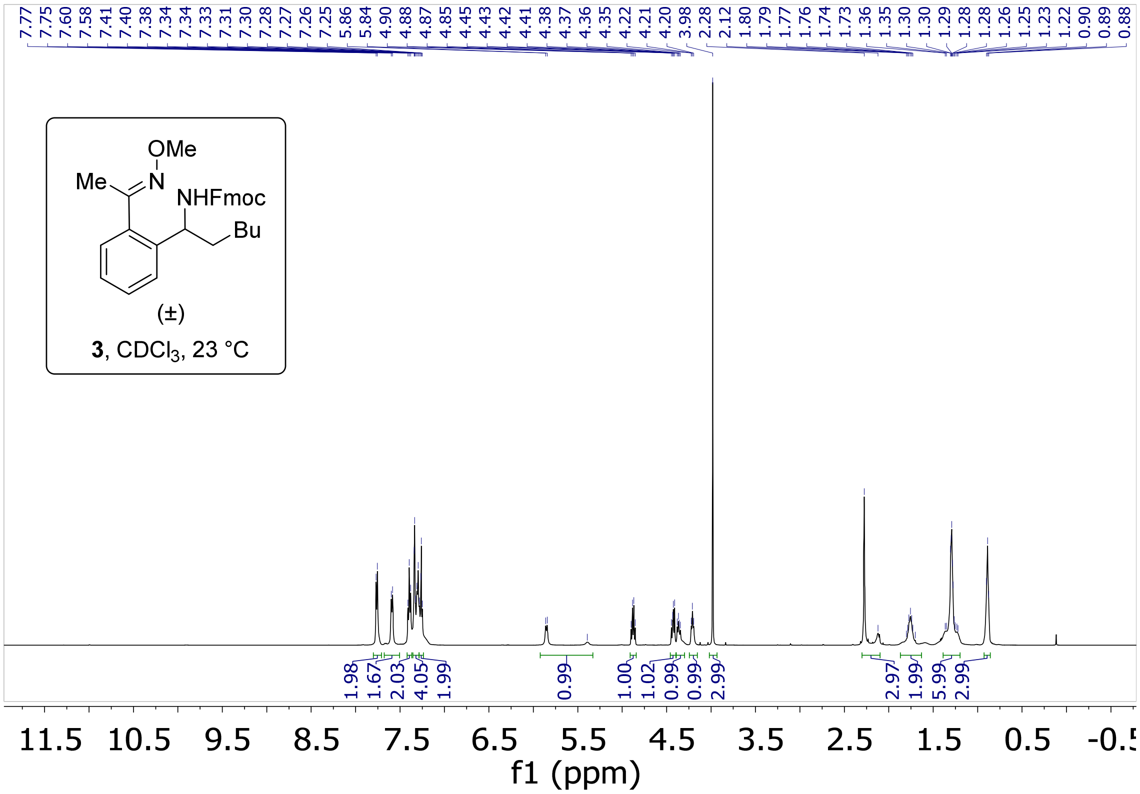
30
10
ppm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7.25
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4.87
4.85
4.45
4.43
4.42
4.41
4.38
4.37
4.36
4.35
4.22
4.21
4.20
3.98
2.28
2.12
1.80
1.79
1.77
1.76
1.74
1.73
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1.30
1.30
1.29
1.28
1.28
1.26
1.25
1.23
1.22
0.90
0.89
0.88
OMe
Me
N
NHFmoc
Bu
(±)
3, CDCl$_3$, 23 °C
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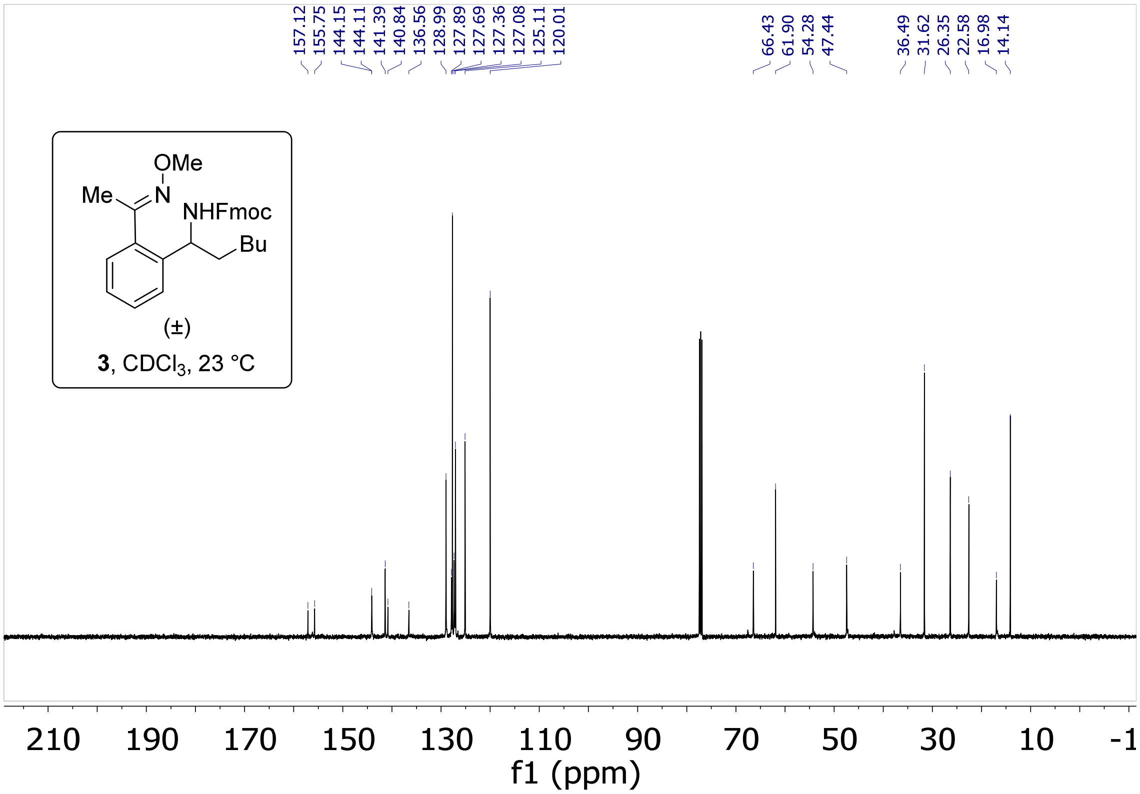
1.67
2.03
4.05
1.99
0.99
1.00
1.02
0.99
0.99
2.99
2.97
1.99
5.99
2.99
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.
f1 (ppm)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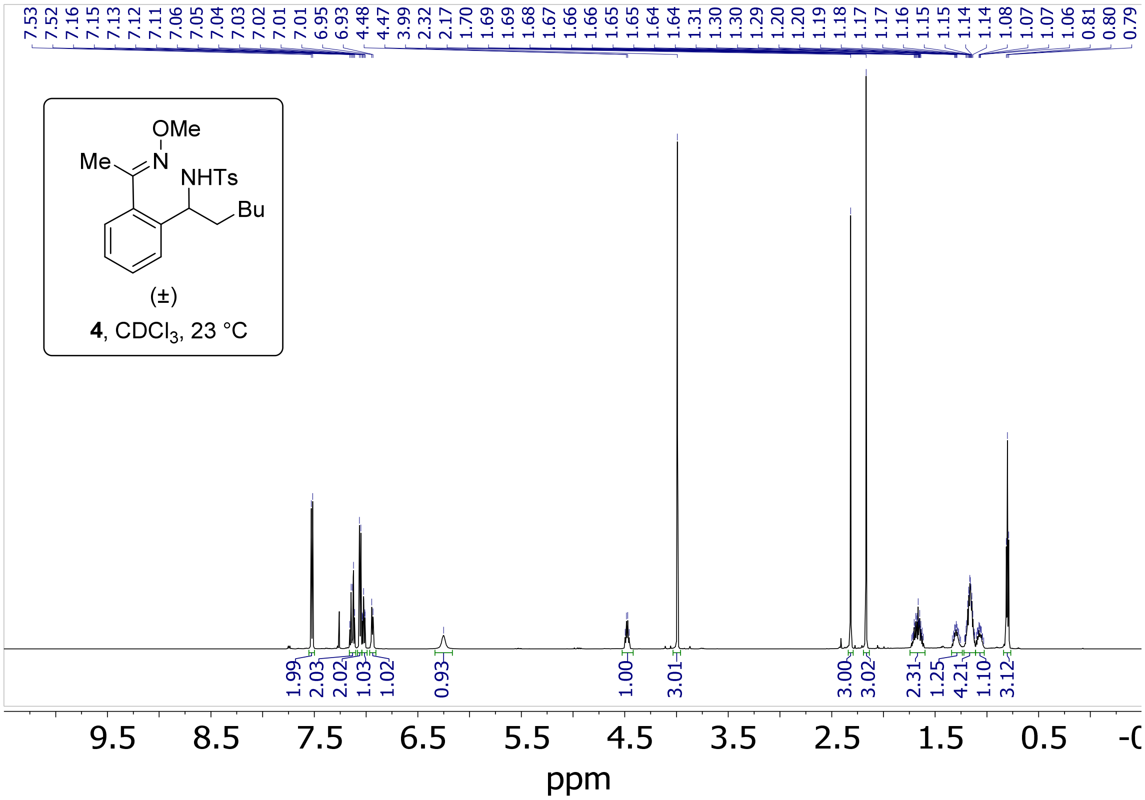
125.11
120.01
66.43
61.90
54.28
47.44
36.49
31.62
26.35
22.58
16.98
14.14
OMe
Me
N
NHFmoc
Bu
(±)
3, CDCl$_3$, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)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7.01
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6.93
4.48
4.47
3.99
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2.17
1.70
1.69
1.69
1.68
1.67
1.66
1.66
1.65
1.65
1.64
1.64
1.31
1.30
1.30
1.29
1.20
1.20
1.19
1.18
1.17
1.17
1.16
1.15
1.15
1.14
1.14
1.08
1.07
1.07
1.06
0.81
0.80
0.79
OMe
Me
N
NHTs
Bu
(±)
4, CDCl3, 23 °C
1.99
2.03
2.02
1.03
1.02
0.93
1.00
3.01
3.00
3.02
2.31
1.25
4.21
1.10
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2.5
1.5
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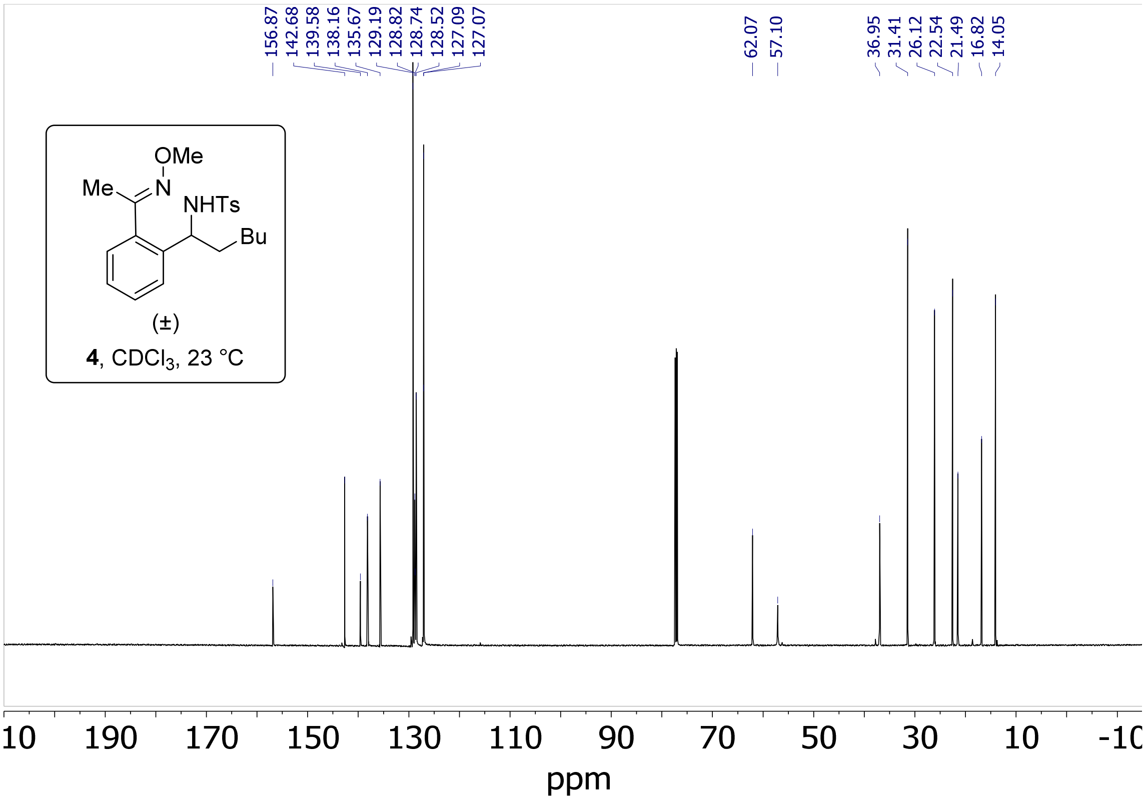
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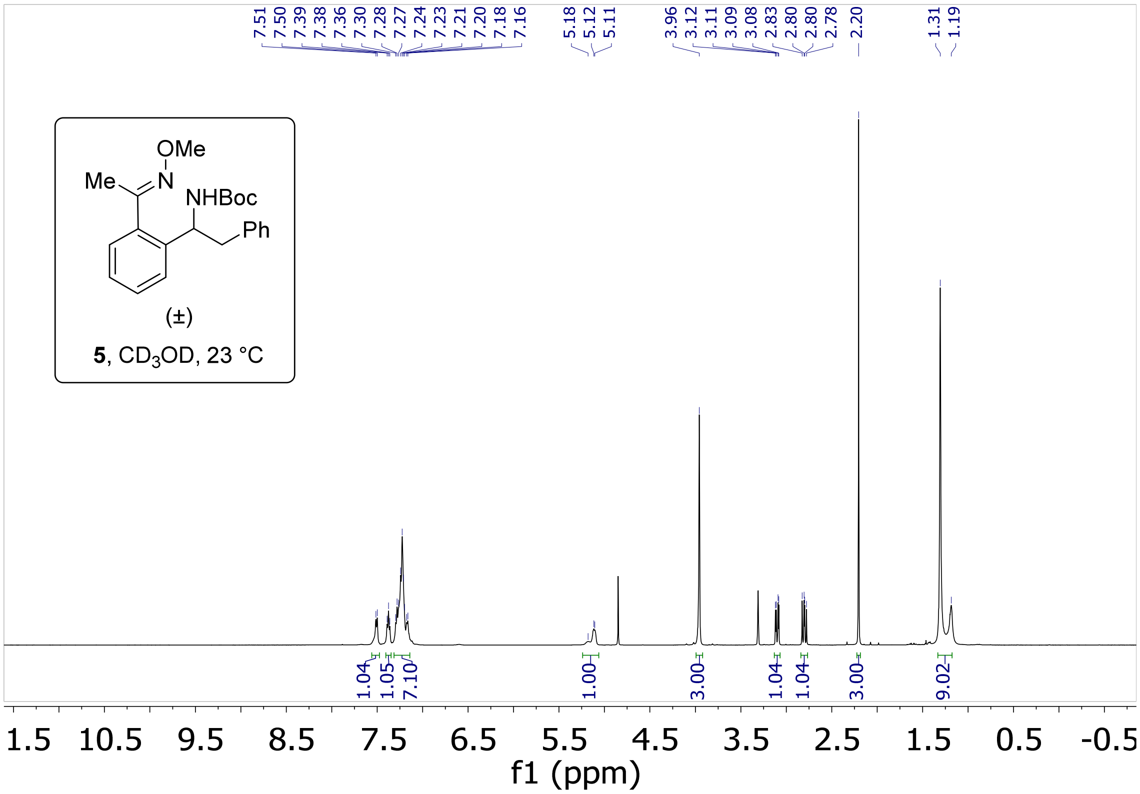
135.67
129.19
128.82
128.74
128.52
127.09
127.07
62.07
57.10
36.95
31.41
26.12
22.54
21.49
16.82
14.05
OMe
Me
N
NHTs
Bu
(±)
4, CDCl3, 23 °C
10
190
170
150
130
110
90
70
50
30
10
ppm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7.39
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7.36
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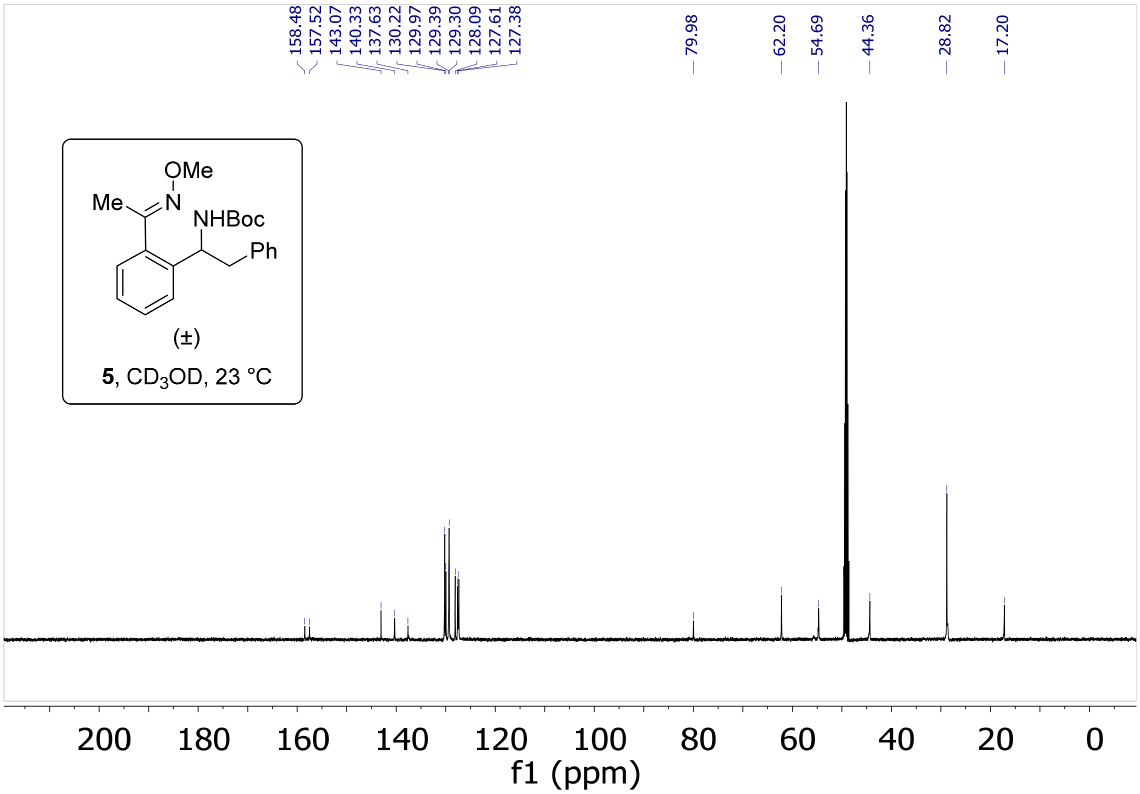
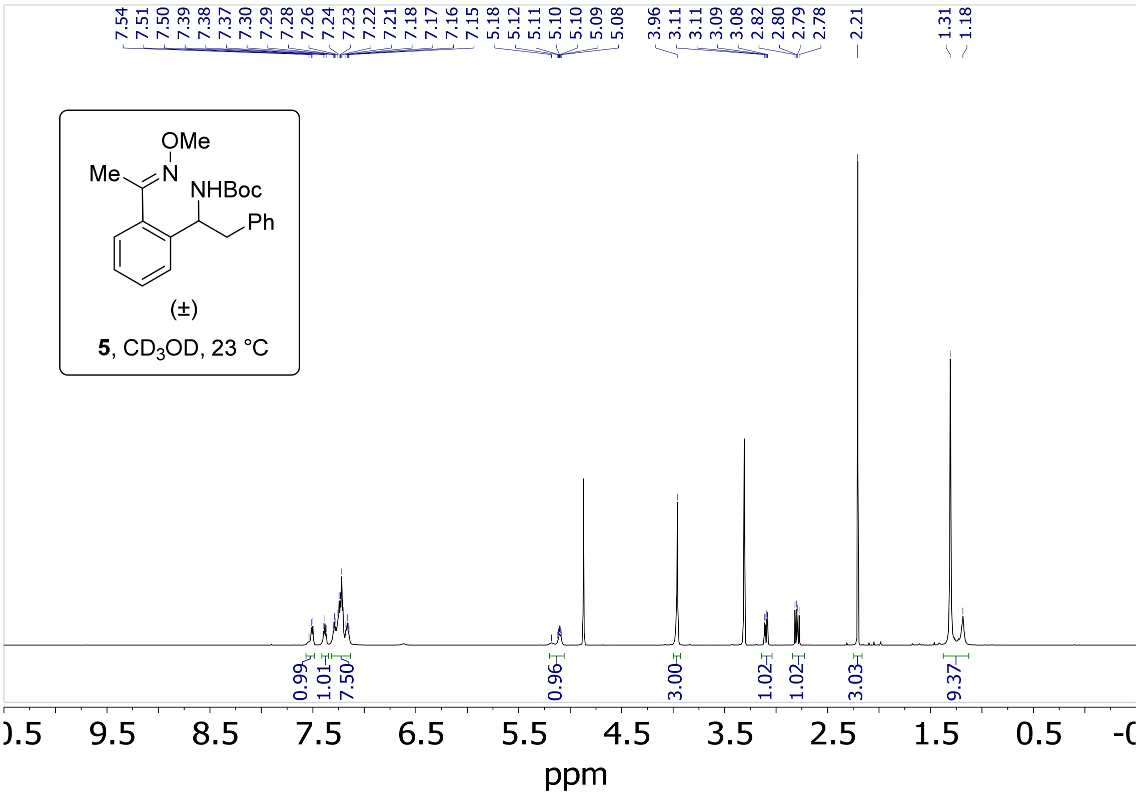
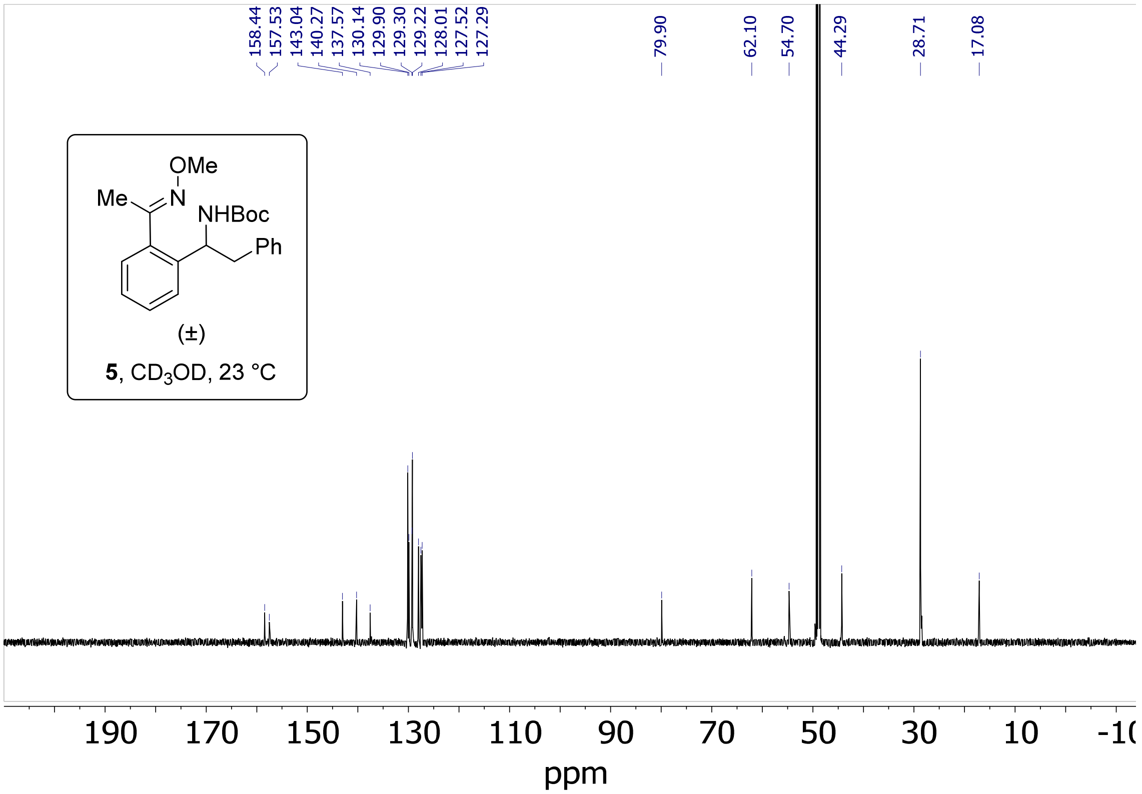
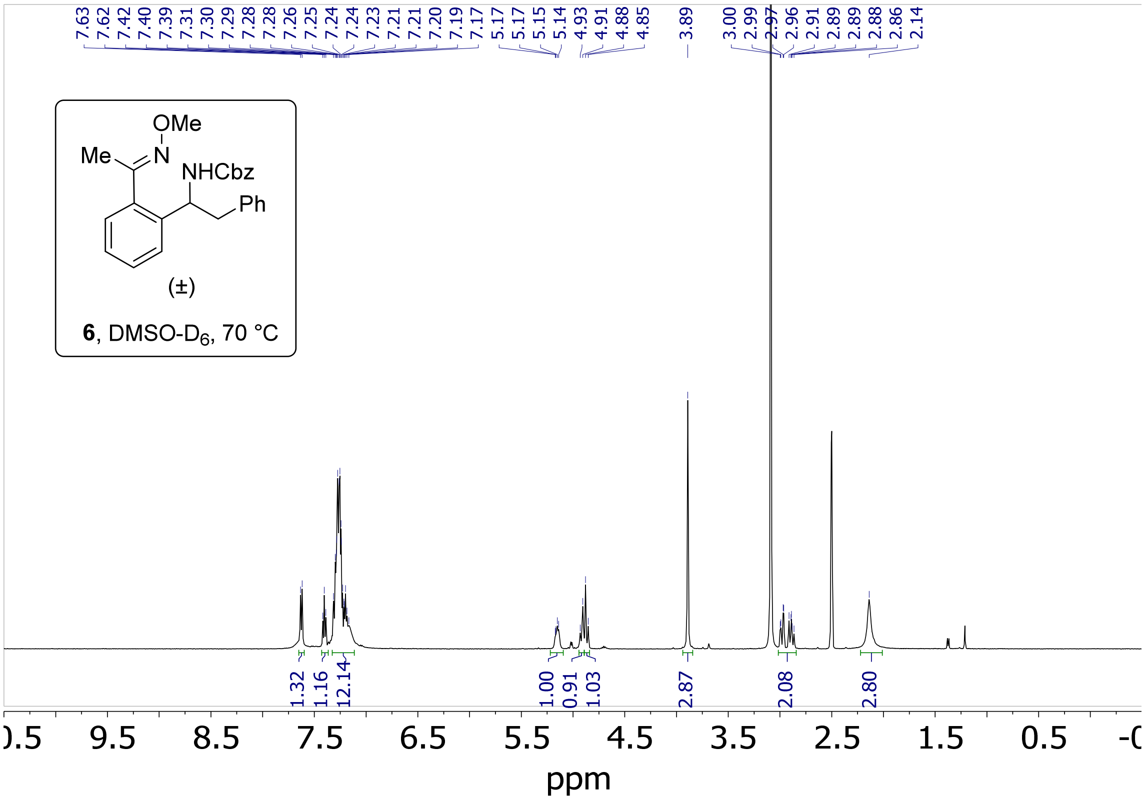
7.27
7.24
7.23
7.21
7.20
7.18
7.16
5.18
5.12
5.11
3.96
3.12
3.11
3.09
3.08
2.83
2.80
2.80
2.78
2.20
1.31
1.19
OMe
Me
N
NHBoc
Ph
(±)
5, CD3OD, 23 °C
1.04
1.05
7.10
1.00
3.00
1.04
1.04
3.00
9.02
1.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


158.48
157.52
143.07
140.33
137.63
130.22
129.97
129.39
129.30
128.09
127.61
127.38
79.98
62.20
54.69
44.36
28.82
17.20
OMe
Me
N
NHBoc
Ph
(±)
5, CD3OD, 23 °C
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

Reaction with 1 mol% Rh-dimer cat. loading



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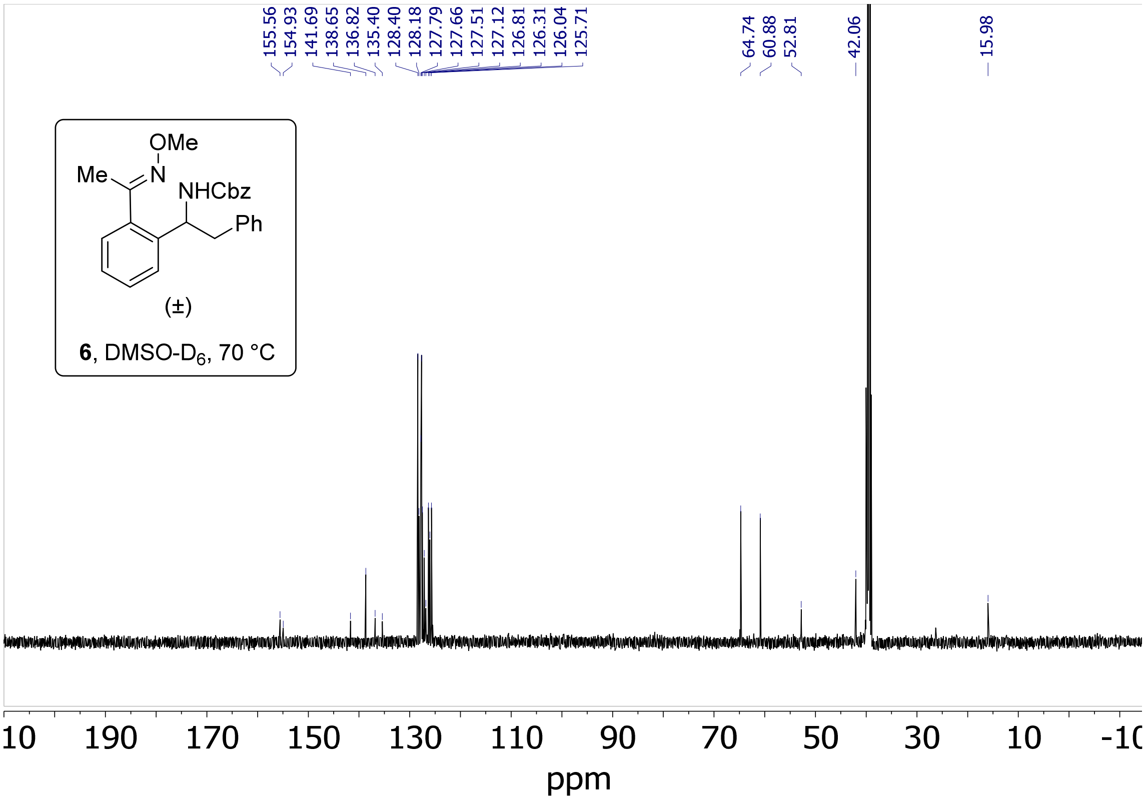
7.28
7.26
7.25
7.24
7.24
7.23
7.21
7.21
7.20
7.19
7.17
5.17
5.17
5.15
5.14
4.93
4.91
4.88
4.85
3.89
3.00
2.99
2.97
2.96
2.91
2.89
2.89
2.88
2.86
2.14
OMe
Me
N
NHCbz
Ph
(±)
6, DMSO-D$_6$, 70 °C
1.32
1.16
12.14
1.00
0.91
1.03
2.87
2.08
2.80
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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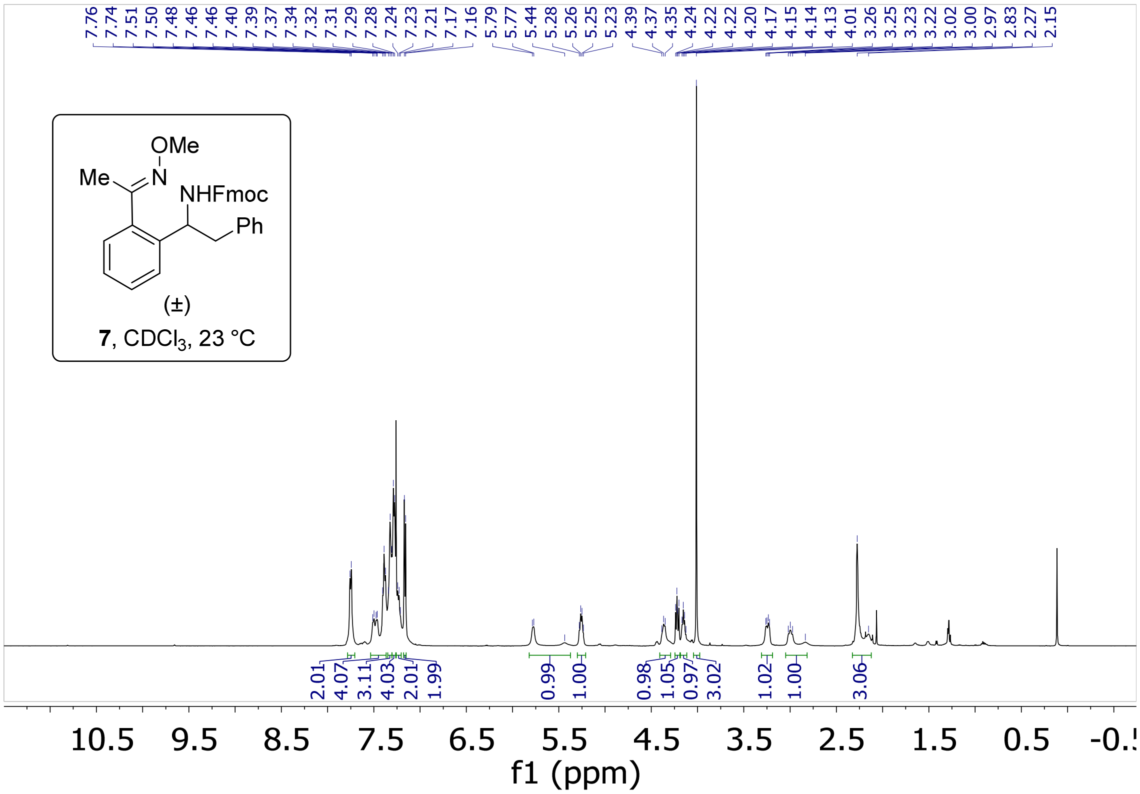
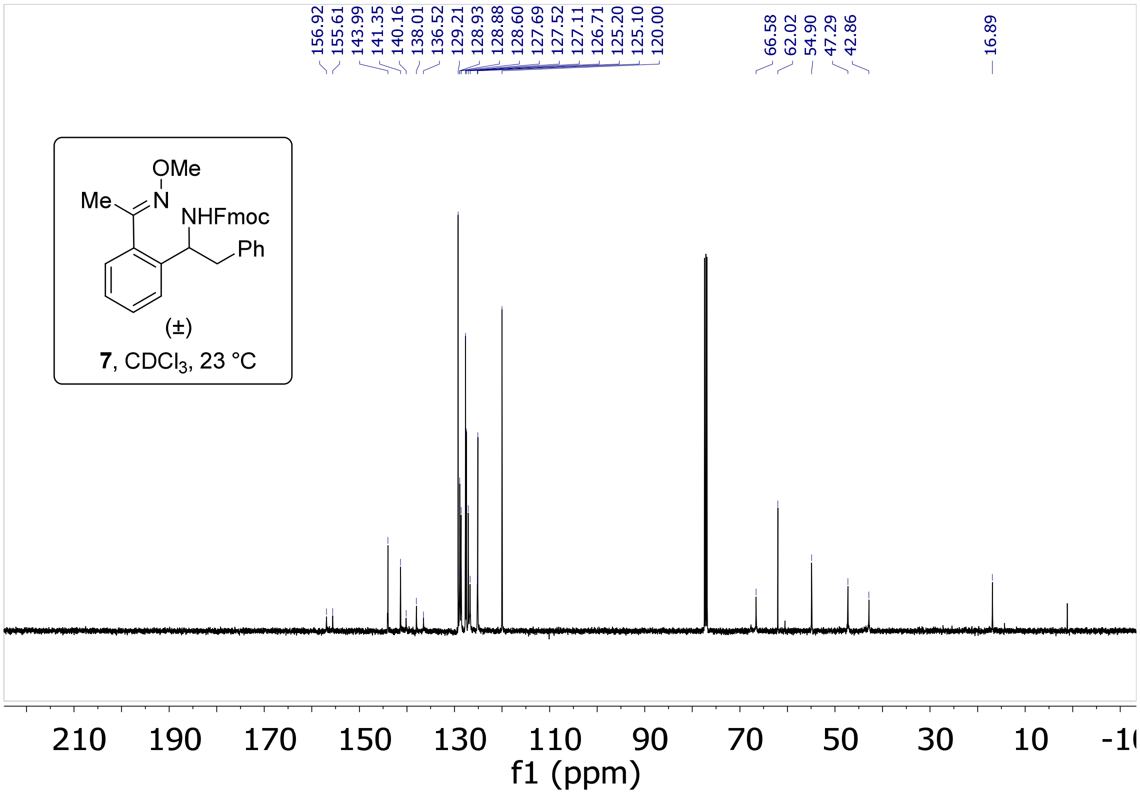
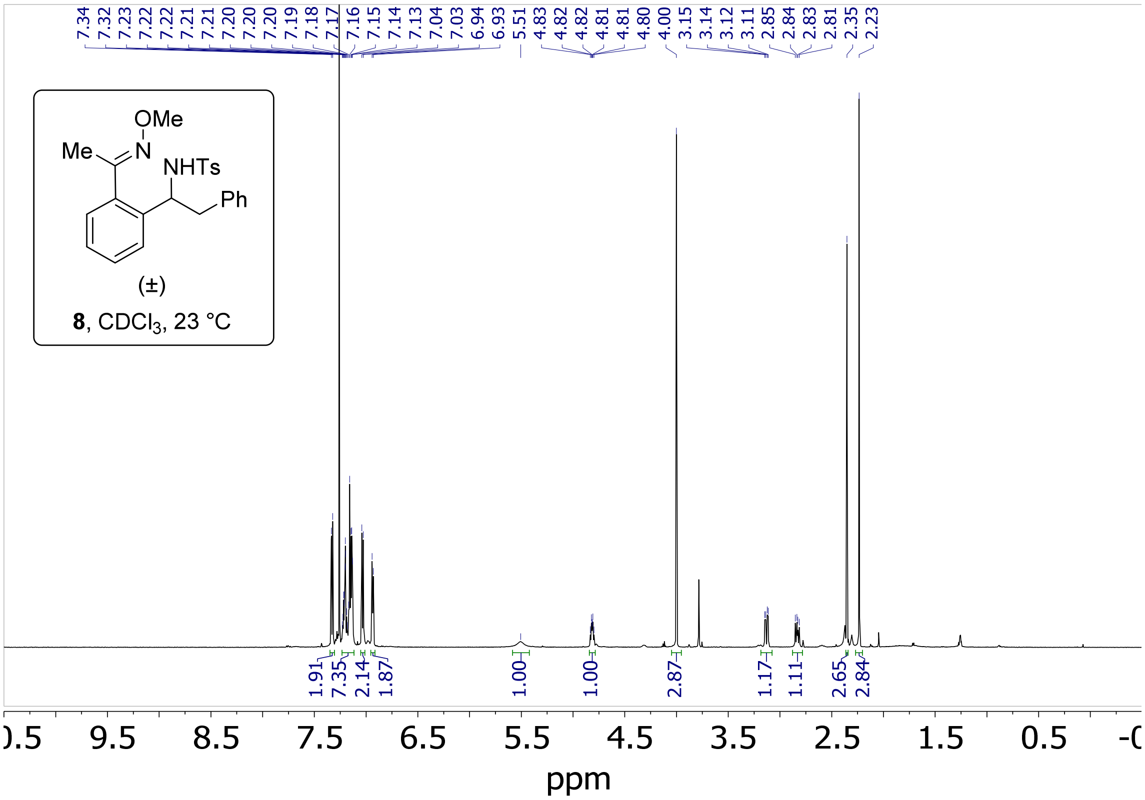
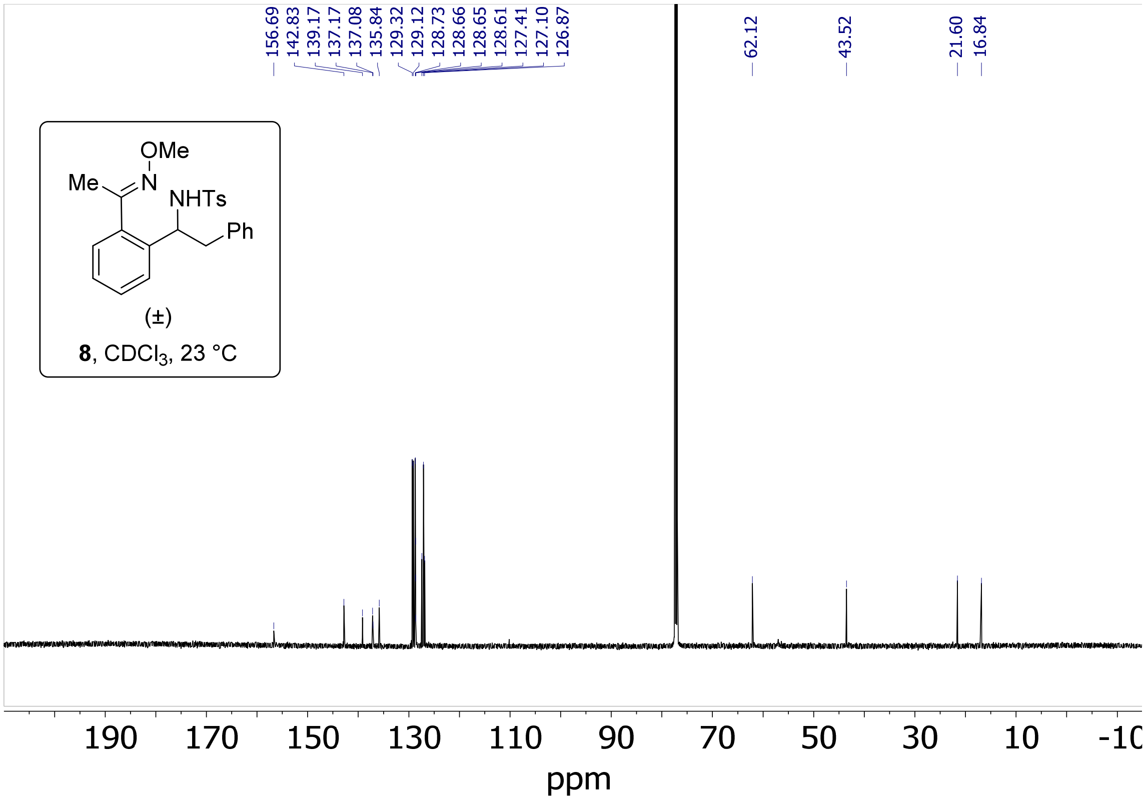
154.93
141.69
138.65
136.82
135.40
128.40
128.18
127.79
127.66
127.51
127.12
126.81
126.31
126.04
125.71
64.74
60.88
52.81
42.06
15.98
OMe
Me
N
NHCbz
Ph
(±)
6, DMSO-D$_6$, 70 °C
190
170
150
130
110
90
70
50
30
10
ppm


7.76 7.74 7.51 7.50 7.48 7.46 7.46 7.40 7.39 7.37 7.34 7.32 7.31 7.29 7.28 7.24 7.23 7.21 7.17 7.16 5.79 5.77 5.44 5.28 5.26 5.25 5.23 4.39 4.37 4.35 4.24 4.22 4.22 4.20 4.17 4.15 4.14 4.13 4.01 3.26 3.25 3.23 3.22 3.02 3.00 2.97 2.83 2.27 2.15
OMe
Me
N
NHFmoc
Ph
(±)
7, CDCl₃, 23 °C
2.01 4.07 3.11 4.03 2.01 1.99 0.99 1.00 0.98 1.05 0.97 3.02 1.02 1.00 3.06
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.
f1 (ppm)


156.92 155.61 143.99 141.35 140.16 138.01 136.52 129.21 128.93 128.88 128.60 127.69 127.52 127.11 126.71 125.20 125.10 120.00 66.58 62.02 54.90 47.29 42.86 16.89
OMe
Me
N
NHFmoc
Ph
(±)
7, CDCl₃, 23 °C
210 190 170 150 130 110 90 70 50 30 10 -1
f1 (ppm)


7.34
7.32
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.20
7.19
7.18
7.17
7.16
7.15
7.14
7.13
7.04
7.03
6.94
6.93
5.51
4.83
4.82
4.82
4.81
4.81
4.80
4.00
3.15
3.14
3.12
3.11
2.85
2.84
2.83
2.81
2.35
2.23
OMe
Me
N
NHTs
Ph
(±)
8, CDCl$_3$, 23 °C
1.91
7.35
2.14
1.87
1.00
1.00
2.87
1.17
1.11
2.65
2.84
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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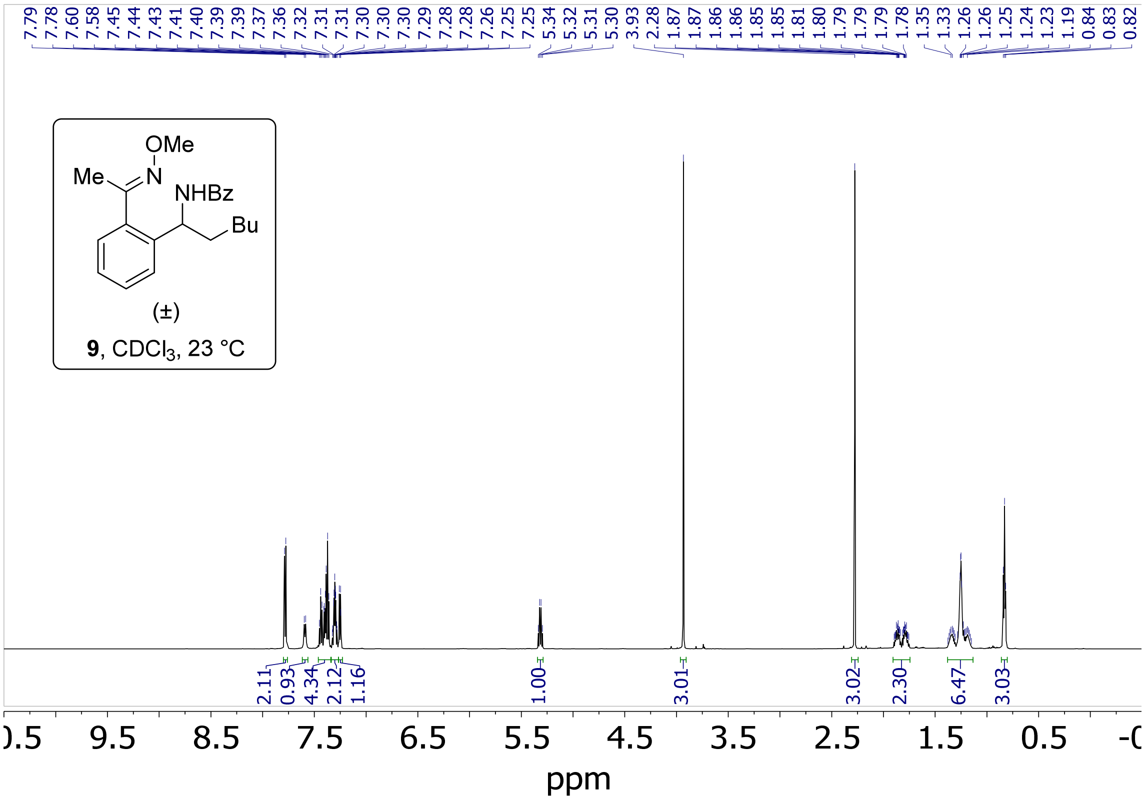
142.83
139.17
137.17
137.08
135.84
129.32
129.12
128.73
128.66
128.65
128.61
127.41
127.10
126.87
62.12
43.52
21.60
16.84
OMe
Me
N
NHTs
Ph
(±)
8, CDCl$_3$, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm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7.60
7.58
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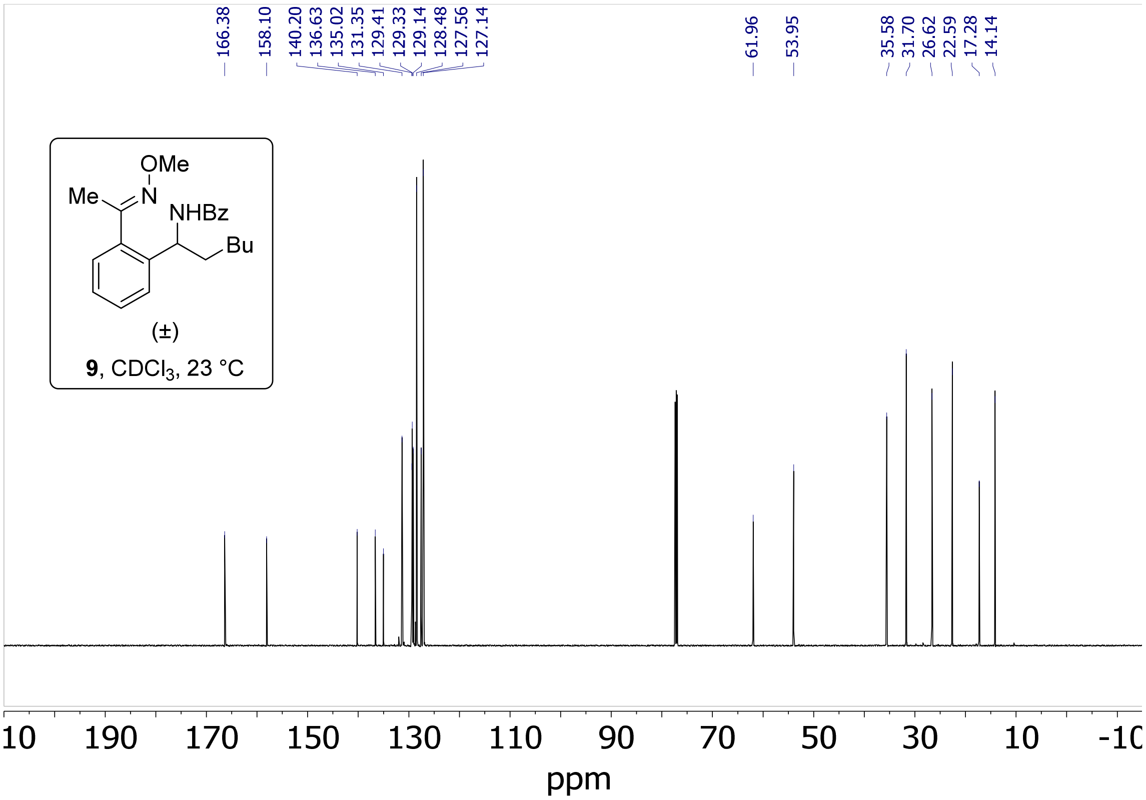
7.43
7.41
7.40
7.39
7.39
7.37
7.36
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.28
7.28
7.26
7.25
7.25
5.34
5.32
5.31
5.30
3.93
2.28
1.87
1.87
1.86
1.86
1.85
1.85
1.81
1.80
1.79
1.79
1.79
1.78
1.35
1.33
1.26
1.26
1.25
1.24
1.23
1.19
0.84
0.83
0.82
OMe
Me
N
NHBz
Bu
(±)
9, CDCl3, 23 °C
2.11
0.93
4.34
2.12
1.16
1.00
3.01
3.02
2.30
6.47
3.03
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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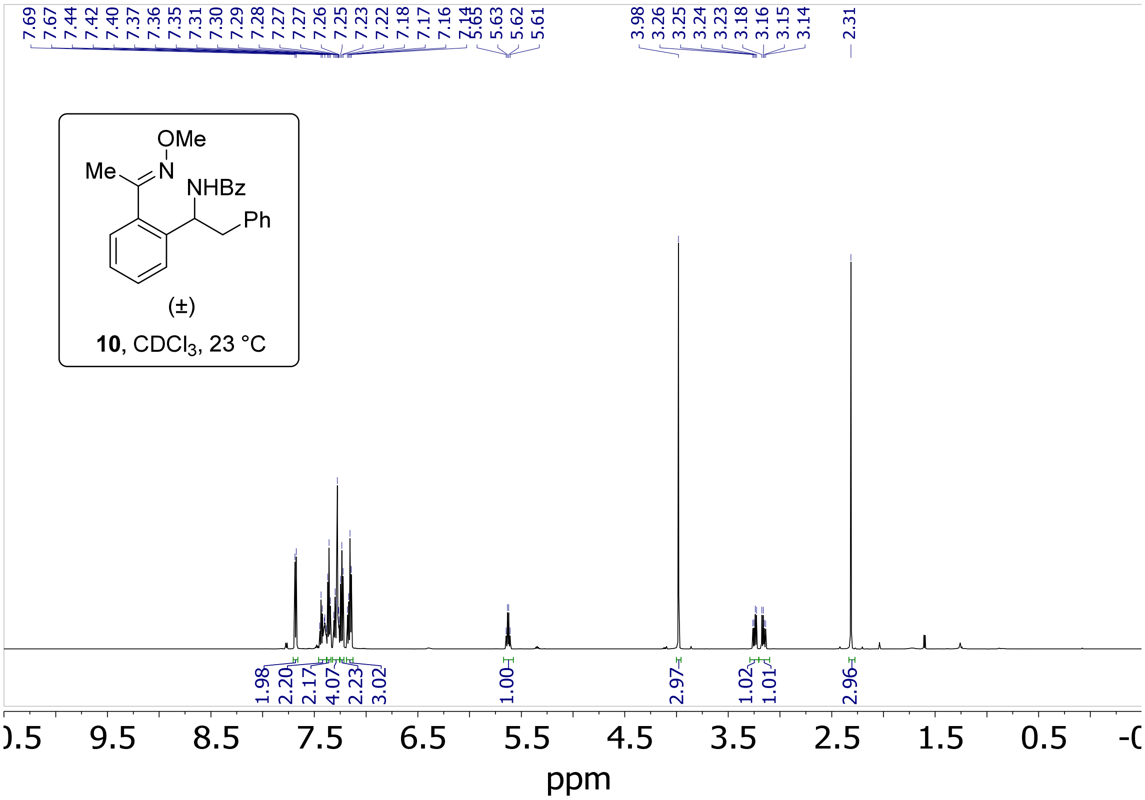
158.10
140.20
136.63
135.02
131.35
129.41
129.33
129.14
128.48
127.56
127.14
61.96
53.95
35.58
31.70
26.62
22.59
17.28
14.14
OMe
Me
N
NHBz
Bu
(±)
9, CDCl3, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm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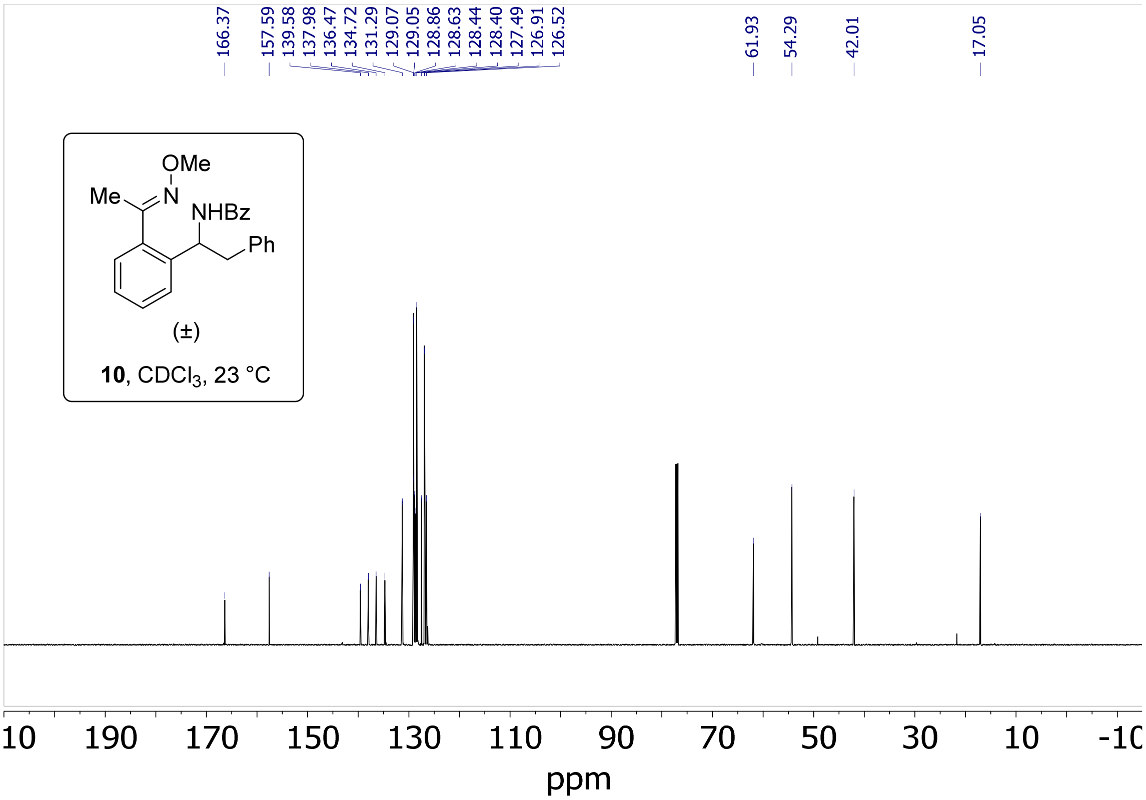
7.44
7.42
7.40
7.37
7.36
7.35
7.31
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.23
7.22
7.18
7.17
7.16
7.14
5.65
5.63
5.62
5.61
3.98
3.26
3.25
3.24
3.23
3.18
3.16
3.15
3.14
2.31
OMe
Me
N
NHBz
Ph
(±)
10, CDCl3, 23 °C
1.98
2.20
2.17
4.07
2.23
3.02
1.00
2.97
1.02
1.01
2.96
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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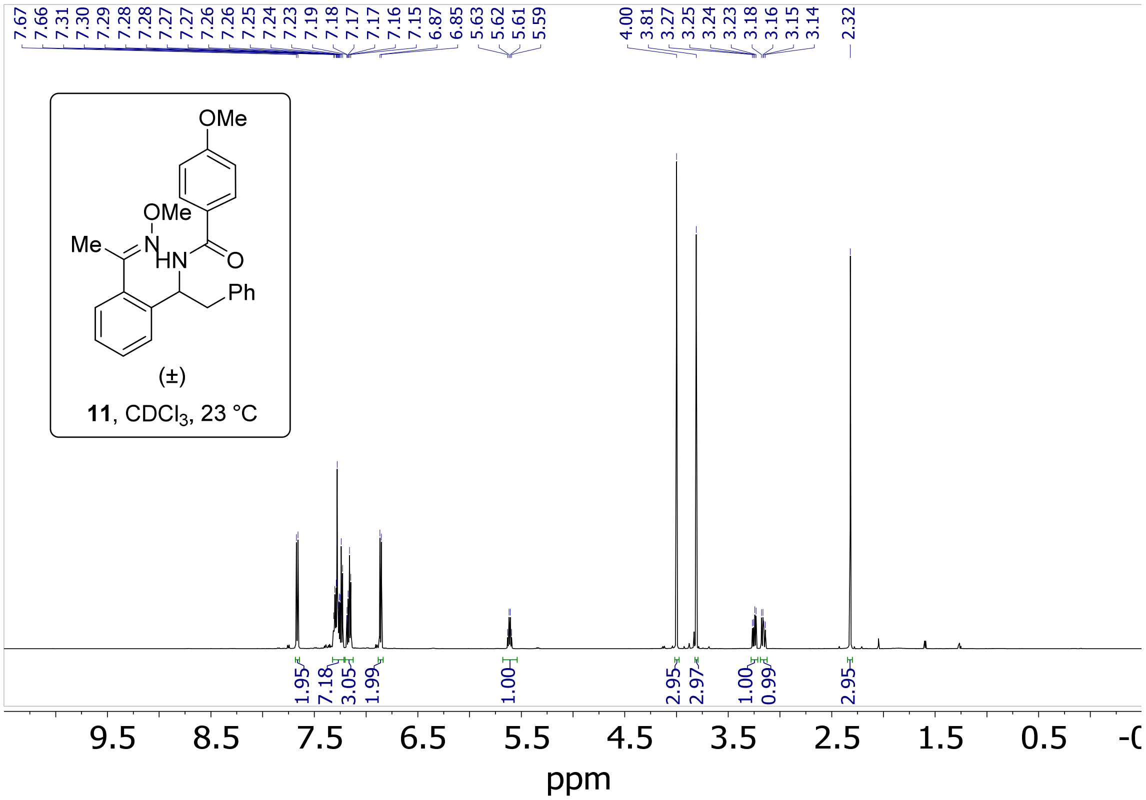
134.72
131.29
129.07
129.05
128.86
128.63
128.44
128.40
127.49
126.91
126.52
61.93
54.29
42.01
17.05
OMe
Me
N
NHBz
Ph
(±)
10, CDCl3, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm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7.66
7.31
7.30
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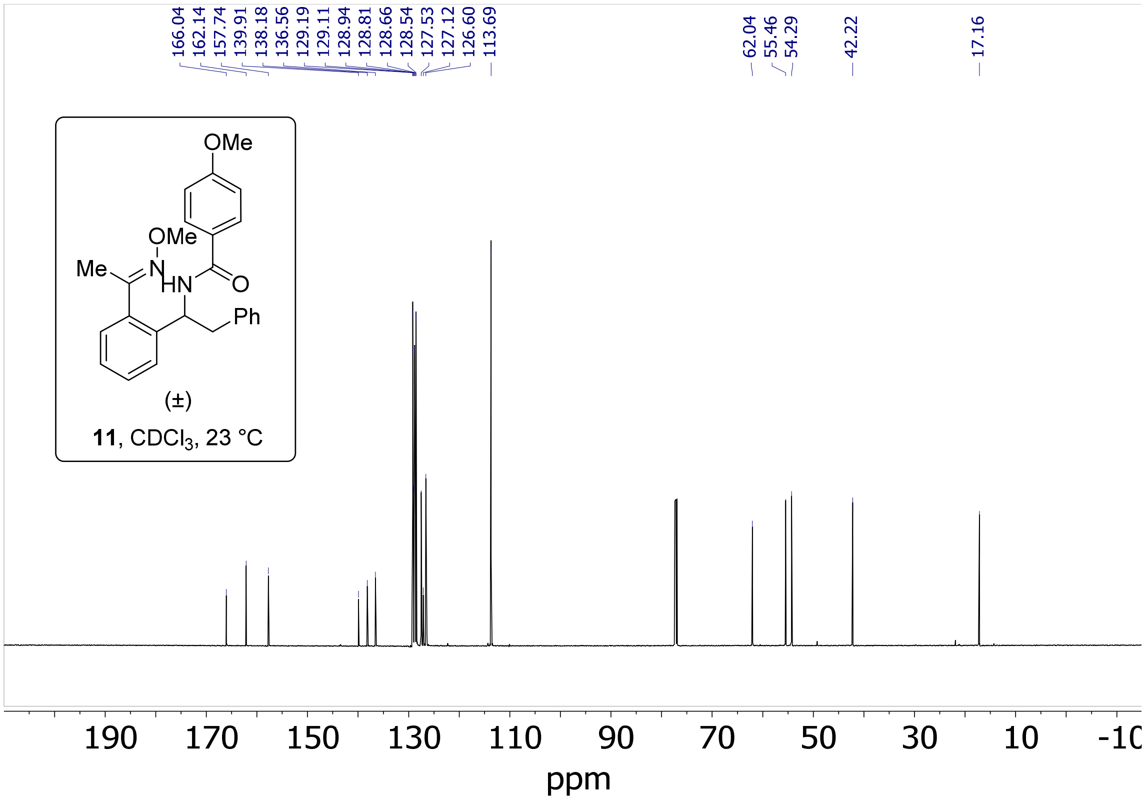
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.23
7.19
7.18
7.17
7.17
7.16
7.15
6.87
6.85
5.63
5.62
5.61
5.59
4.00
3.81
3.27
3.25
3.24
3.23
3.18
3.16
3.15
3.14
2.32
OMe
OMe
N
Me
HN
O
Ph
(±)
11, CDCl3, 23 °C
1.95
7.18
3.05
1.99
1.00
2.95
2.97
1.00
0.99
2.95
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-(
ppm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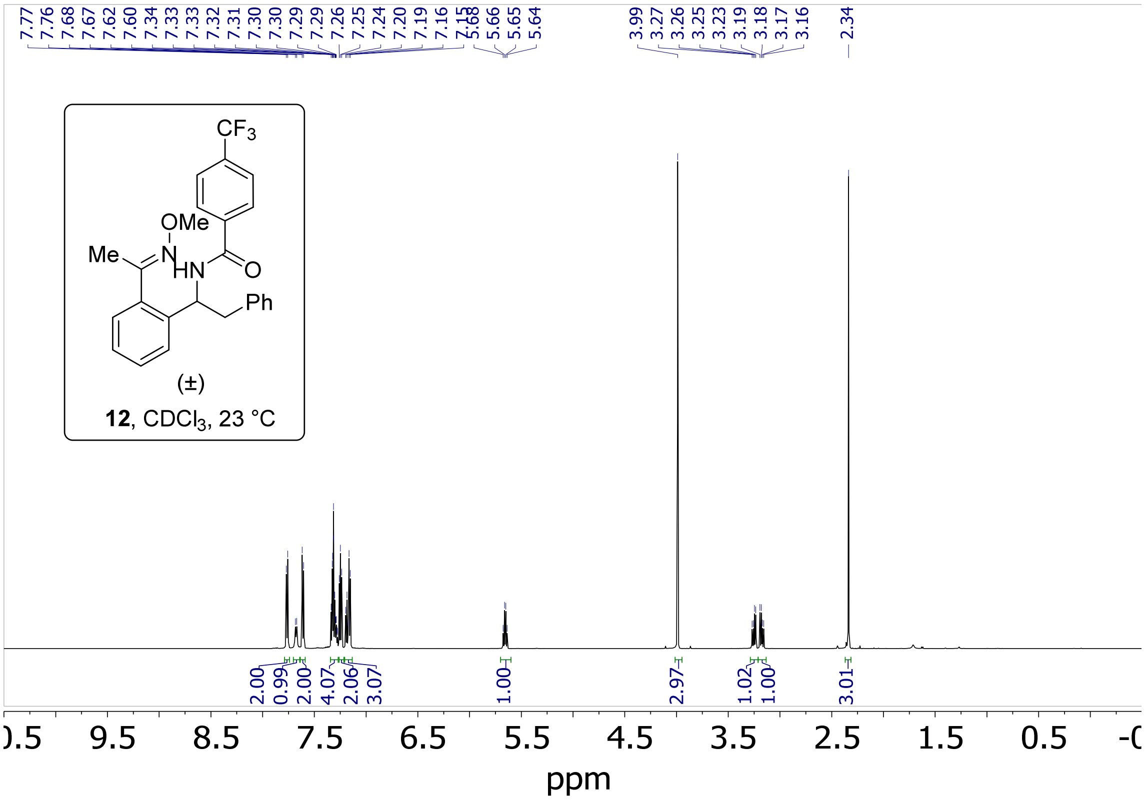
138.18
136.56
129.19
129.11
128.94
128.81
128.66
128.54
127.53
127.12
126.60
113.69
62.04
55.46
54.29
42.22
17.16
OMe
OMe
N
Me
HN
O
Ph
(±)
11, CDCl3, 23 °C
190
170
150
130
110
90
70
50
30
10
-1(
ppm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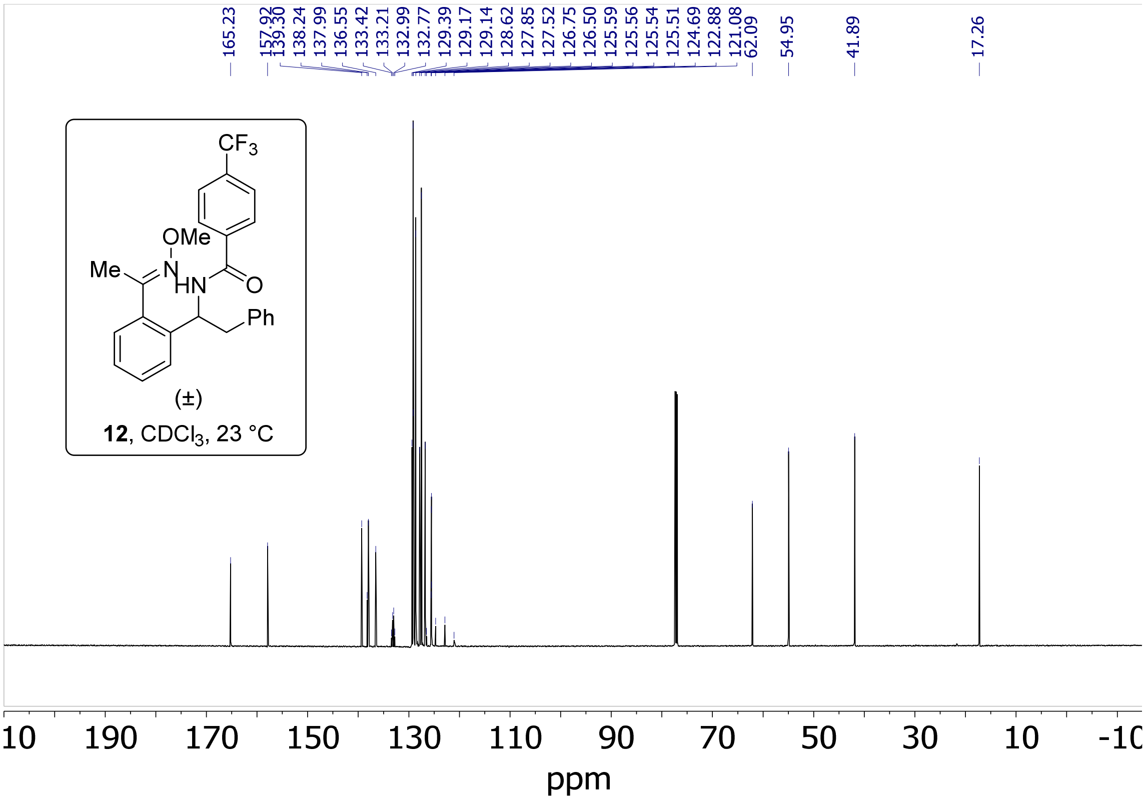
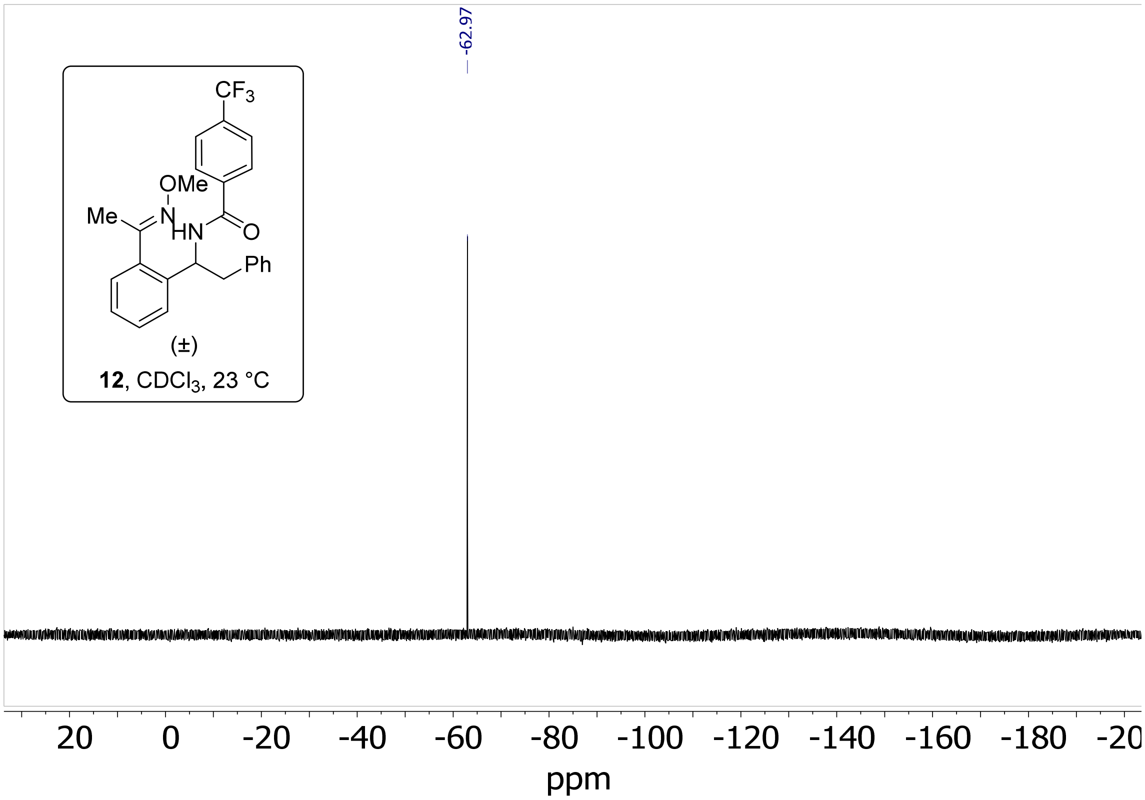
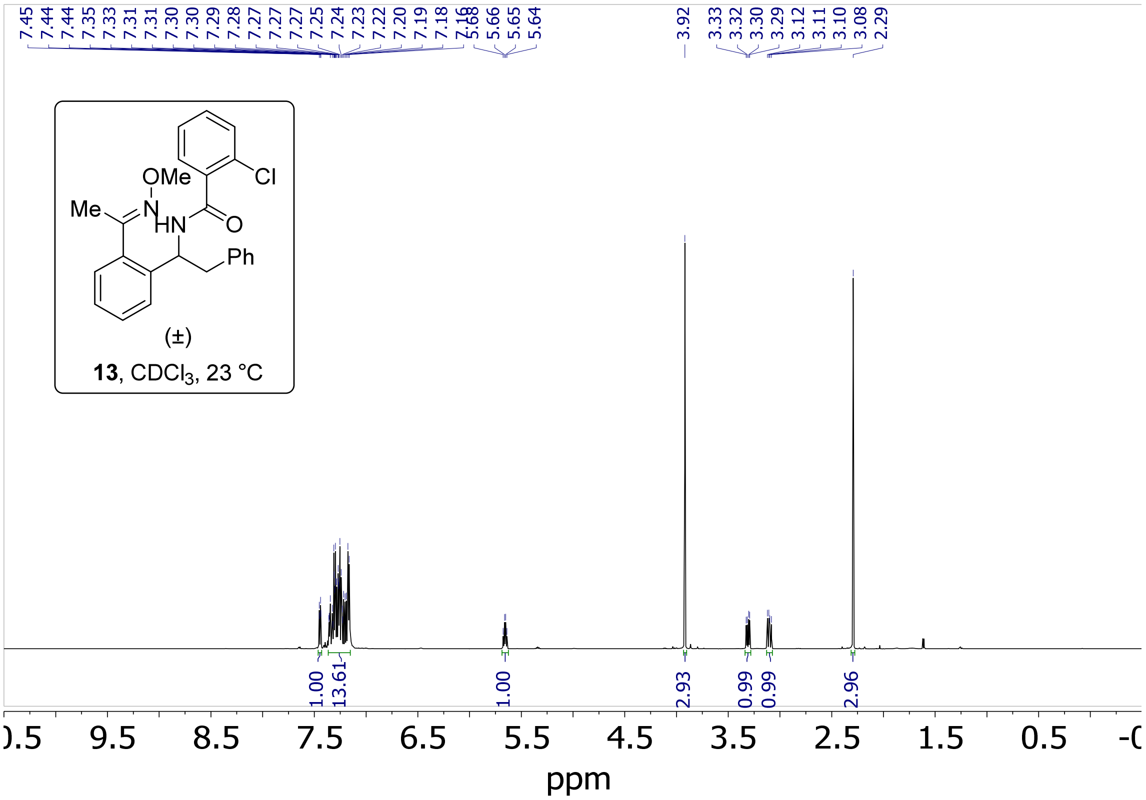
7.60
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.29
7.26
7.25
7.24
7.20
7.19
7.16
7.15
5.68
5.66
5.65
5.64
3.99
3.27
3.26
3.25
3.23
3.19
3.18
3.17
3.16
2.34
CF3
OMe
Me
N
HN
O
Ph
(±)
12, CDCl3, 23 °C
2.00
0.99
2.00
4.07
2.06
3.07
1.00
2.97
1.02
1.00
3.01
.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-(
ppm


165.23
157.92
139.30
138.24
137.99
136.55
133.42
133.21
132.99
132.77
129.39
129.17
129.14
128.62
127.85
127.52
126.75
126.50
125.59
125.56
125.54
125.51
124.69
122.88
121.08
62.09
54.95
41.89
17.26
CF3
OMe
Me
N
HN
O
Ph
(±)
12, CDCl3, 23 °C
10
190
170
150
130
110
90
70
50
30
10
-1(
ppm



-62.97
CF3
OMe
Me
N
HN
O
Ph
(±)
12, CDCl3, 23 °C
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-20
ppm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7.44
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7.31
7.30
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7.29
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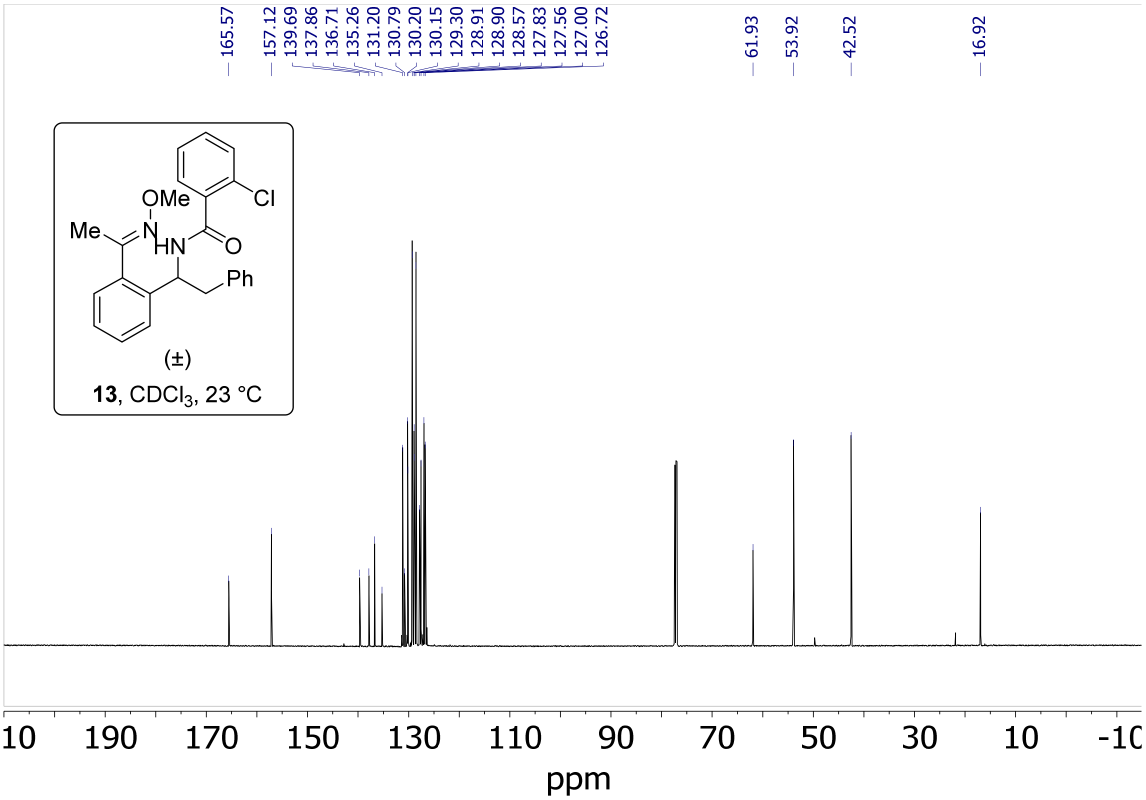
7.27
7.27
7.25
7.24
7.23
7.22
7.20
7.19
7.18
7.16
5.68
5.66
5.65
5.64
3.92
3.33
3.32
3.30
3.29
3.12
3.11
3.10
3.08
2.29
OMe
Cl
Me
N
HN
O
Ph
(±)
13, CDCl3, 23 °C
1.00
13.61
1.00
2.93
0.99
0.99
2.96
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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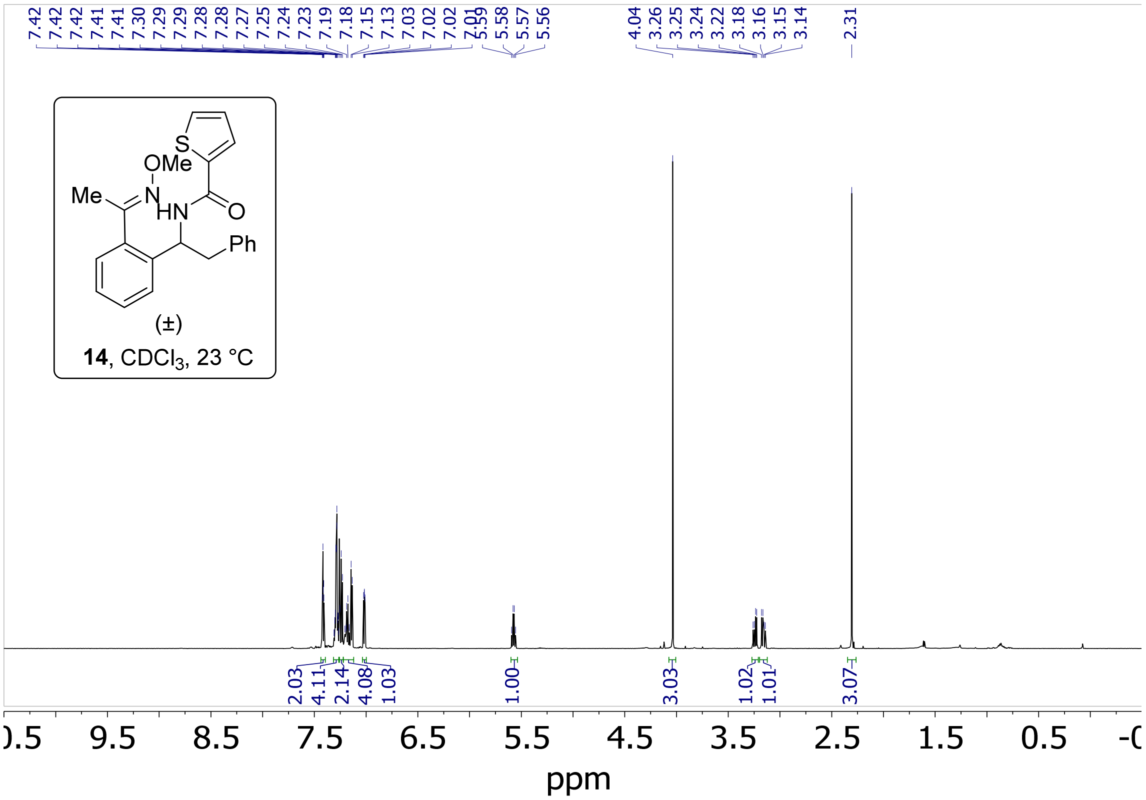
129.30
128.91
128.90
128.57
127.83
127.56
127.00
126.72
61.93
53.92
42.52
16.92
OMe
Cl
Me
N
HN
O
Ph
(±)
13, CDCl3, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm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7.29
7.28
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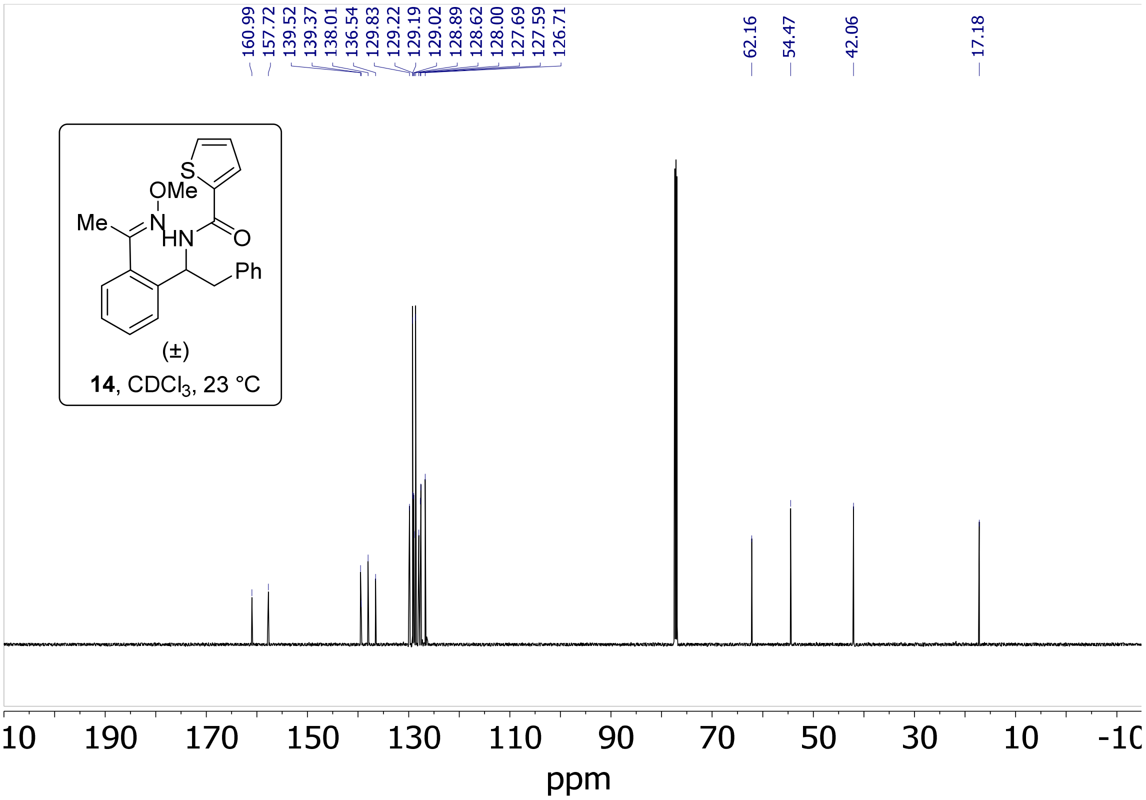
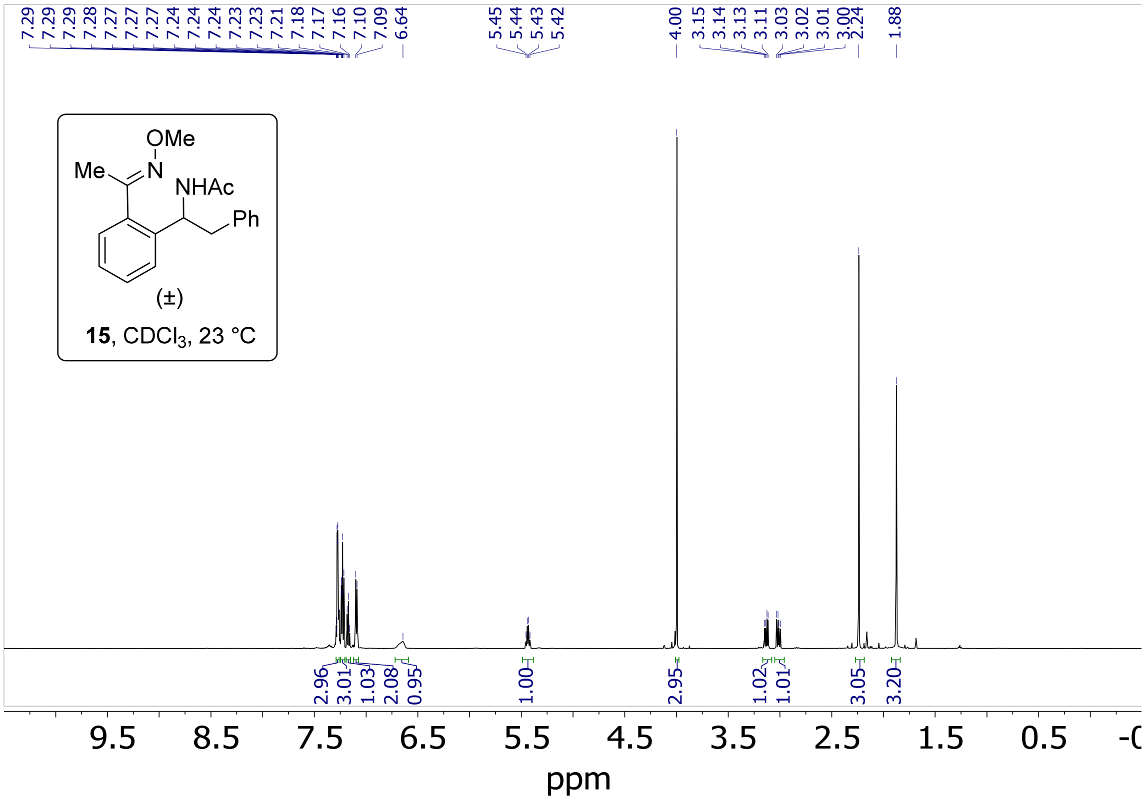
7.27
7.25
7.24
7.23
7.19
7.18
7.15
7.13
7.03
7.02
7.02
7.01
5.59
5.58
5.57
5.56
4.04
3.26
3.25
3.24
3.22
3.18
3.16
3.15
3.14
2.31
S
OMe
N
Me
HN
O
Ph
(±)
14, CDCl3, 23 °C
2.03
4.11
2.14
4.08
1.03
1.00
3.03
1.02
1.01
3.07
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0
ppm


160.99
157.72
139.52
139.37
138.01
136.54
129.83
129.22
129.19
129.02
128.89
128.62
128.00
127.69
127.59
126.71
62.16
54.47
42.06
17.18
S
OMe
N
Me
HN
O
Ph
(±)
14, CDCl3, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-10
ppm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7.29
7.28
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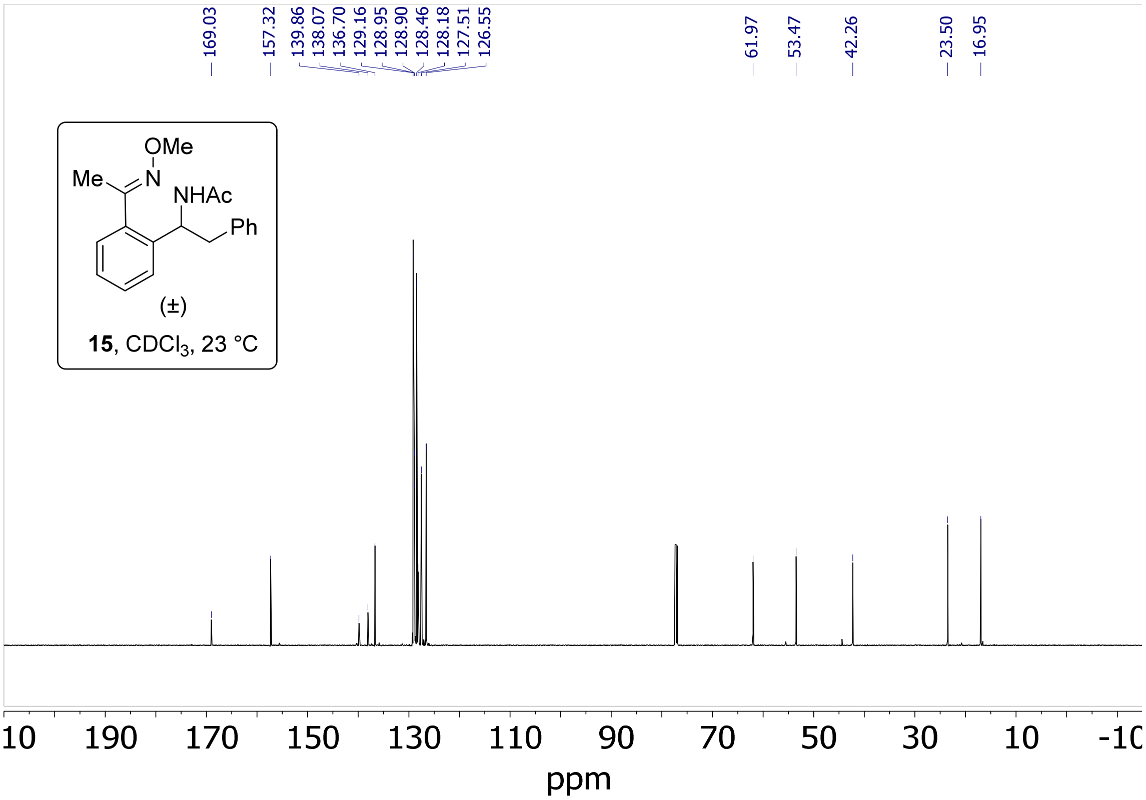
7.27
7.27
7.24
7.24
7.24
7.23
7.23
7.21
7.18
7.17
7.16
7.10
7.09
6.64
5.45
5.44
5.43
5.42
4.00
3.15
3.14
3.13
3.11
3.03
3.02
3.01
3.00
2.24
1.88
OMe
N
Me
NHAc
Ph
(±)
15, CDCl3, 23 °C
2.96
3.01
1.03
2.08
0.95
1.00
2.95
1.02
1.01
3.05
3.20
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-
ppm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128.95
128.90
128.46
128.18
127.51
126.55
61.97
53.47
42.26
23.50
16.95
OMe
N
Me
NHAc
Ph
(±)
15, CDCl3, 23 °C
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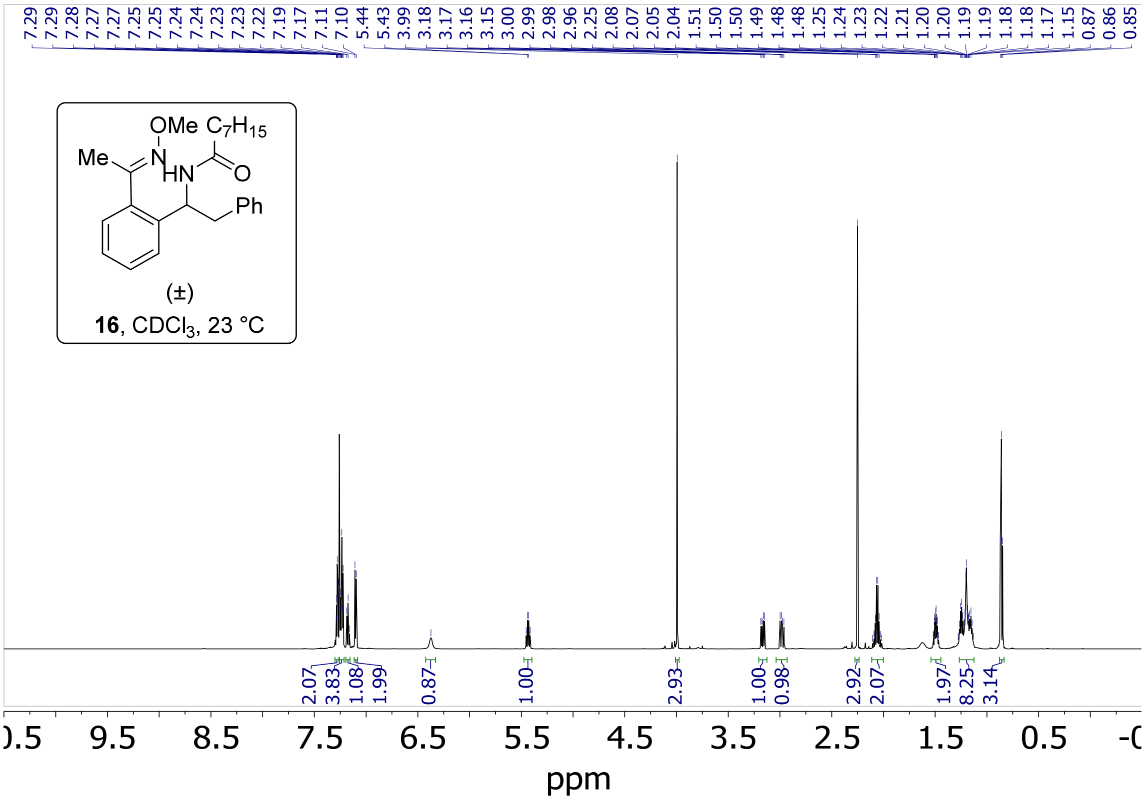
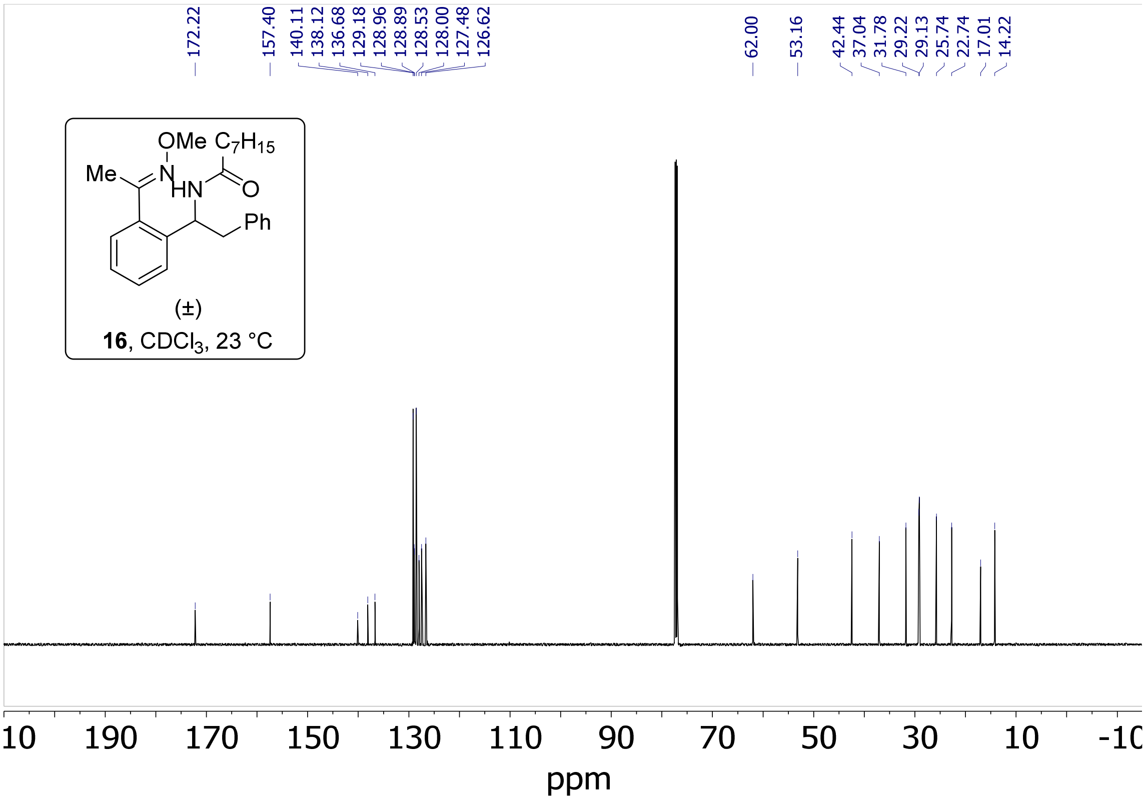
190
170
150
130
110
90
70
50
30
10
-1
ppm


7.29 7.29 7.28 7.27 7.27 7.25 7.25 7.24 7.24 7.23 7.23 7.22 7.19 7.17 7.11 7.10 5.44 5.43 3.99 3.18 3.17 3.16 3.15 3.00 2.99 2.98 2.96 2.25 2.08 2.07 2.05 2.04 1.51 1.50 1.50 1.49 1.48 1.48 1.25 1.24 1.23 1.22 1.21 1.20 1.20 1.19 1.19 1.18 1.18 1.17 1.15 0.87 0.86 0.85
OMe
C7H15
Me
N
HN
O
Ph
(±)
16, CDCl3, 23 °C
2.07
3.83
1.08
1.99
0.87
1.00
2.93
1.00
0.98
2.92
2.07
1.97
8.25
3.14
).5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -(
ppm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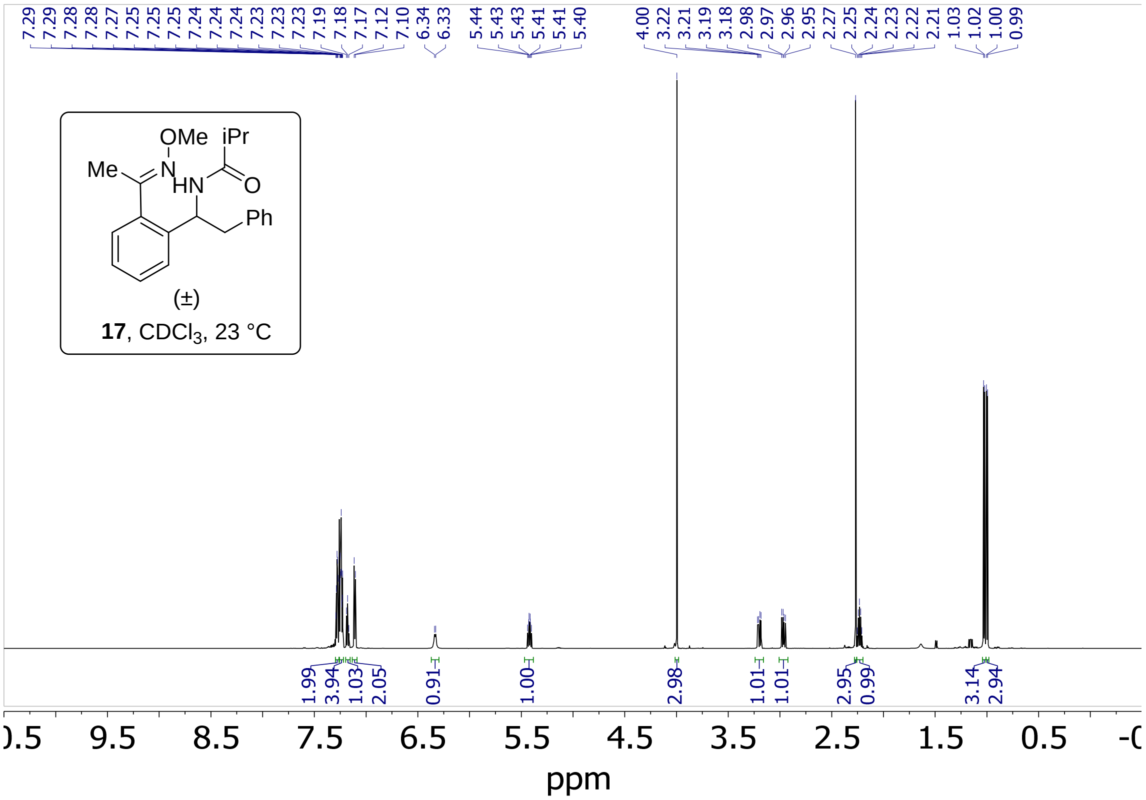
157.40
140.11 138.12 136.68 129.18 128.96 128.89 128.53 128.00 127.48 126.62
62.00
53.16
42.44 37.04 31.78 29.22 29.13 25.74 22.74 17.01 14.22
OMe
C7H15
Me
N
HN
O
Ph
(±)
16, CDCl3, 23 °C
10 190 170 150 130 110 90 70 50 30 10 -1(
ppm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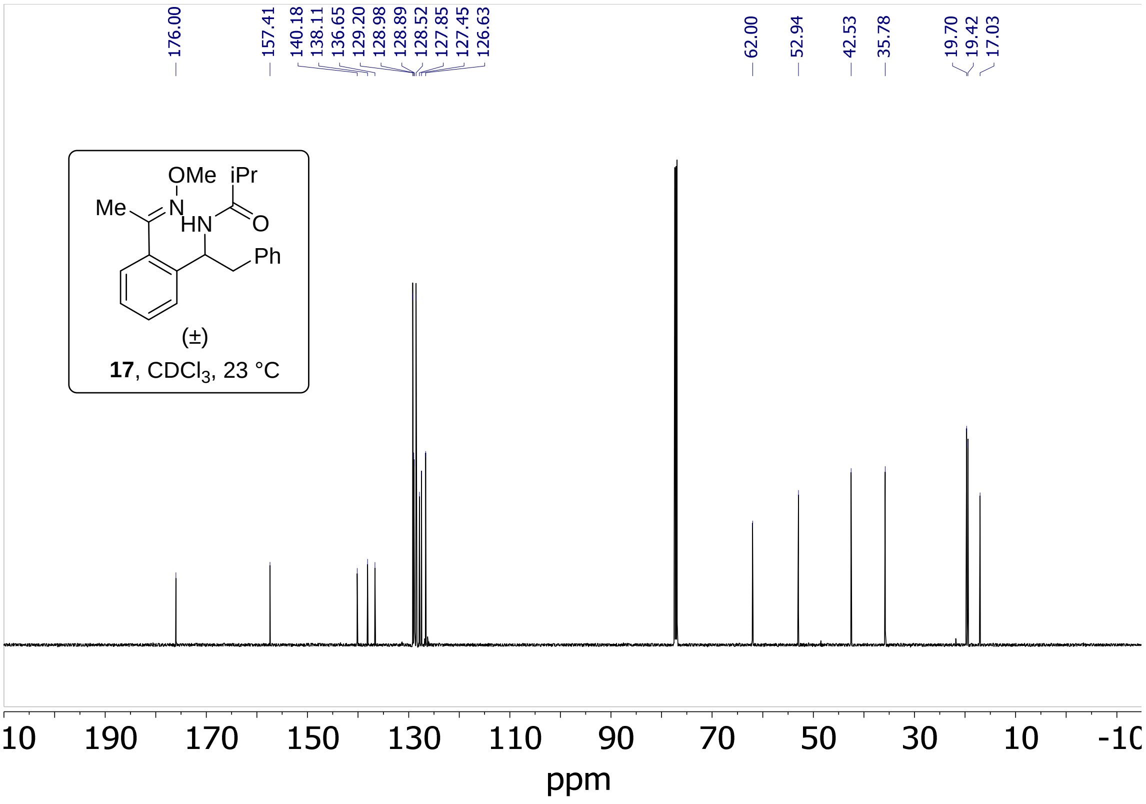
7.25
7.25
7.24
7.24
7.24
7.23
7.23
7.23
7.19
7.18
7.17
7.12
7.10
6.34
6.33
5.44
5.43
5.43
5.41
5.41
5.40
4.00
3.22
3.21
3.19
3.18
2.98
2.97
2.96
2.95
2.27
2.25
2.24
2.23
2.22
2.21
1.03
1.02
1.00
0.99
OMe
iPr
Me
N
HN
O
Ph
(±)
17, CDCl3, 23 °C
1.99
3.94
1.03
2.05
0.91
1.00
2.98
1.01
1.01
2.95
0.99
3.14
2.94
).5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-(
ppm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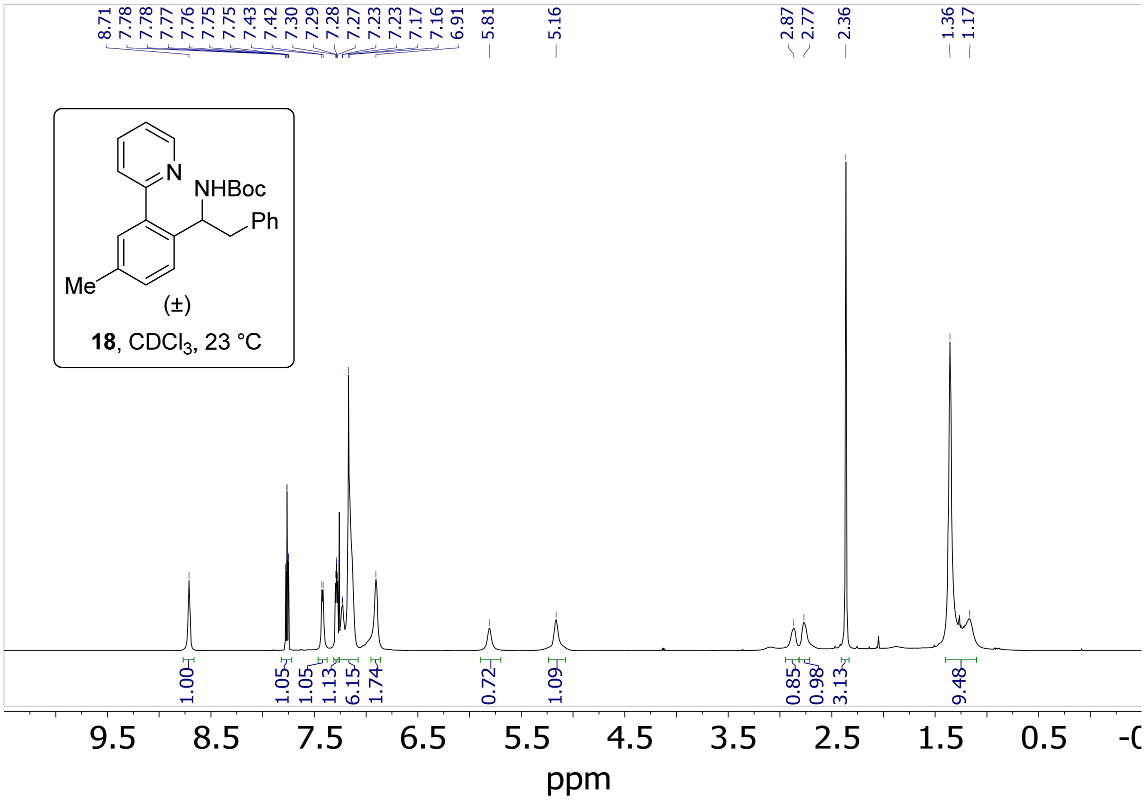
157.41
140.18
138.11
136.65
129.20
128.98
128.89
128.52
127.85
127.45
126.63
62.00
52.94
42.53
35.78
19.70
19.42
17.03
OMe
iPr
Me
N
HN
O
Ph
(±)
17, CDCl3, 23 °C
10
190
170
150
130
110
90
70
50
30
10
-1(
ppm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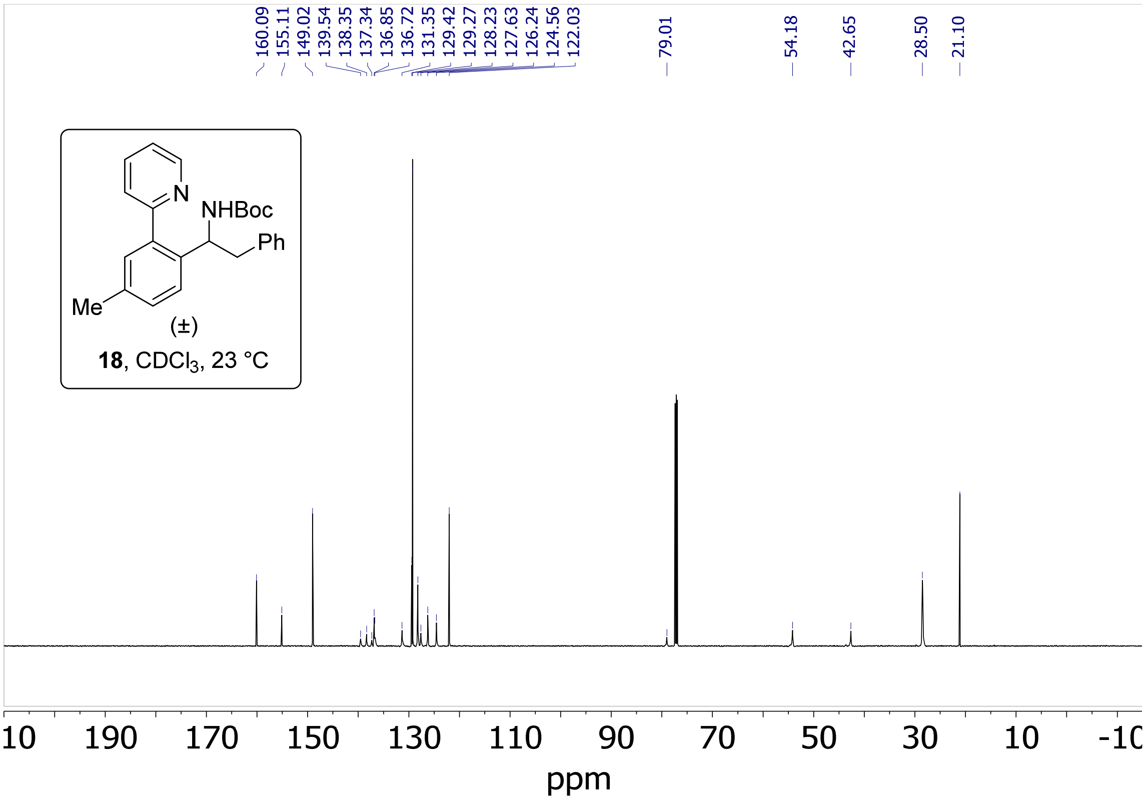
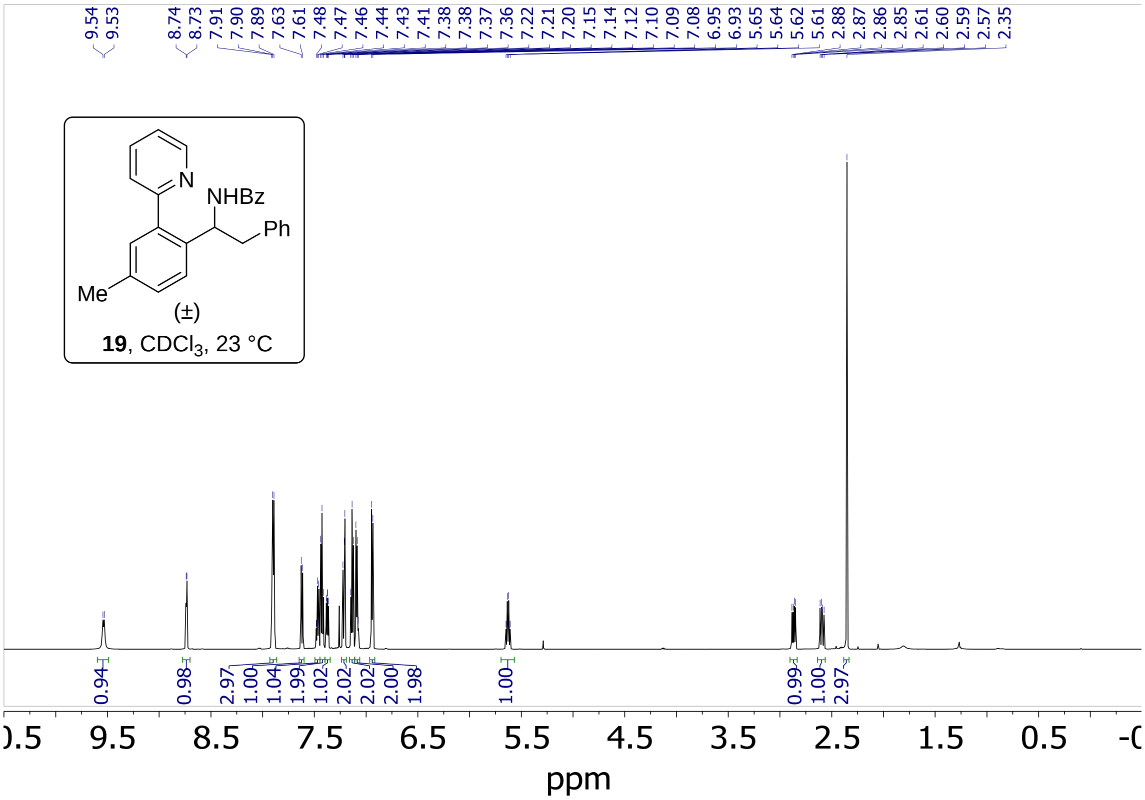
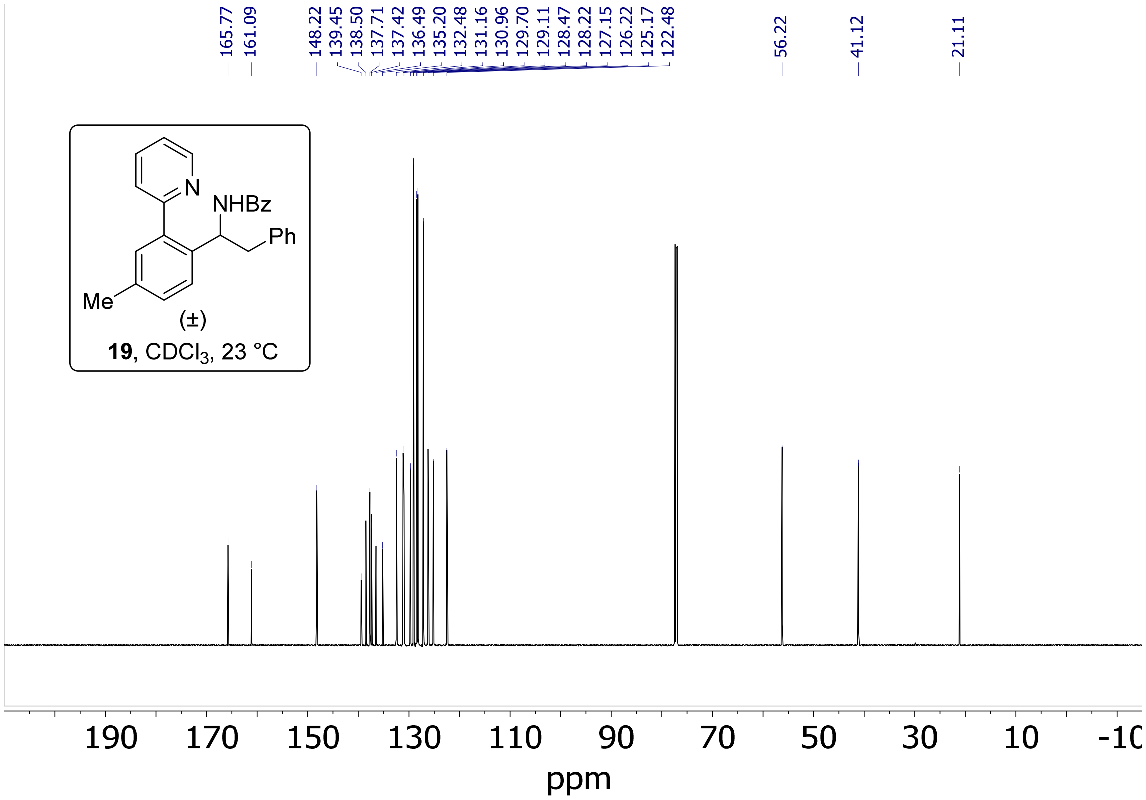
7.78
7.78
7.77
7.76
7.75
7.75
7.43
7.42
7.30
7.29
7.28
7.27
7.23
7.23
7.17
7.16
6.91
5.81
5.16
2.87
2.77
2.36
1.36
1.17
N
NHBoc
Ph
Me
(±)
18, CDCl$_3$, 23 °C
1.00
1.05
1.05
1.13
6.15
1.74
0.72
1.09
0.85
0.98
3.13
9.48
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm


160.09
155.11
149.02
139.54
138.35
137.34
136.85
136.72
131.35
129.42
129.27
128.23
127.63
126.24
124.56
122.03
79.01
54.18
42.65
28.50
21.10
N
NHBoc
Ph
Me
(±)
18, CDCl$_3$, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm


9.54
9.53
8.74
8.73
7.91
7.90
7.89
7.63
7.61
7.48
7.47
7.46
7.44
7.43
7.41
7.38
7.38
7.37
7.36
7.22
7.21
7.20
7.15
7.14
7.12
7.10
7.09
7.08
6.95
6.93
5.65
5.64
5.62
5.61
2.88
2.87
2.86
2.85
2.61
2.60
2.59
2.57
2.35
N
NHBz
Ph
Me
(±)
19, CDCl3, 23 °C
0.94
0.98
2.97
1.00
1.04
1.99
1.02
2.02
2.02
2.00
1.98
1.00
0.99
1.00
2.97
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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137.71
137.42
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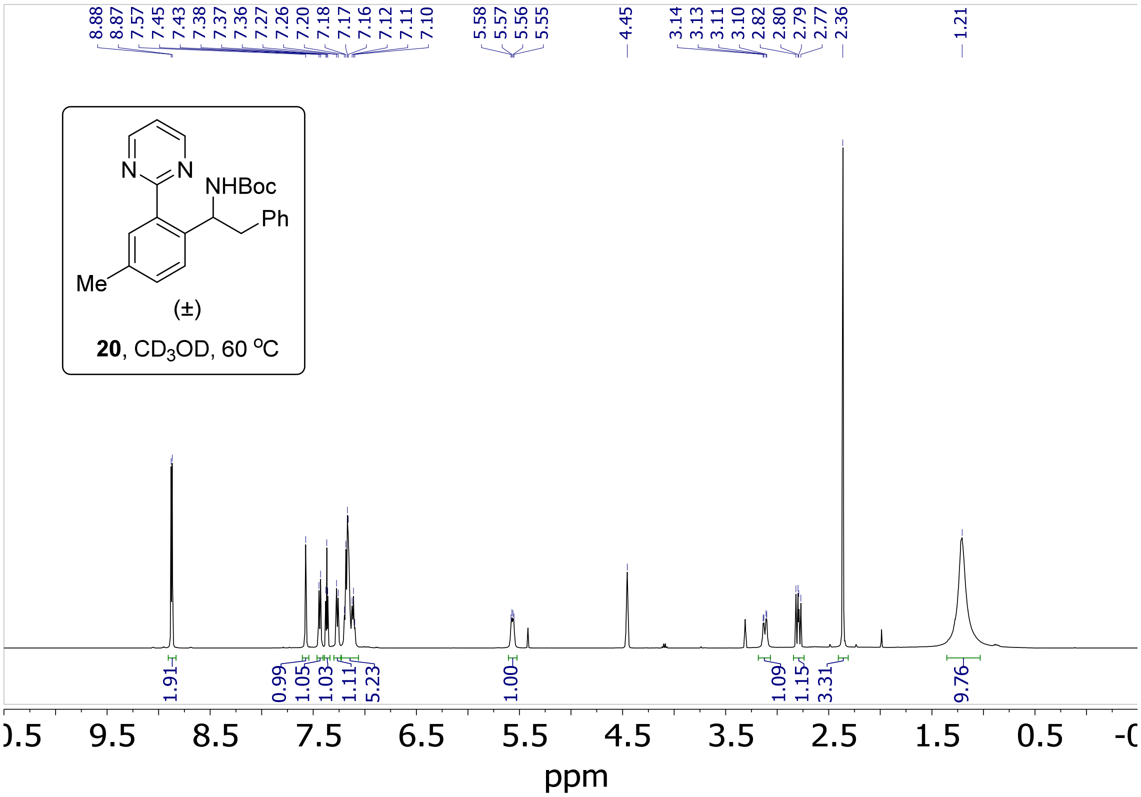
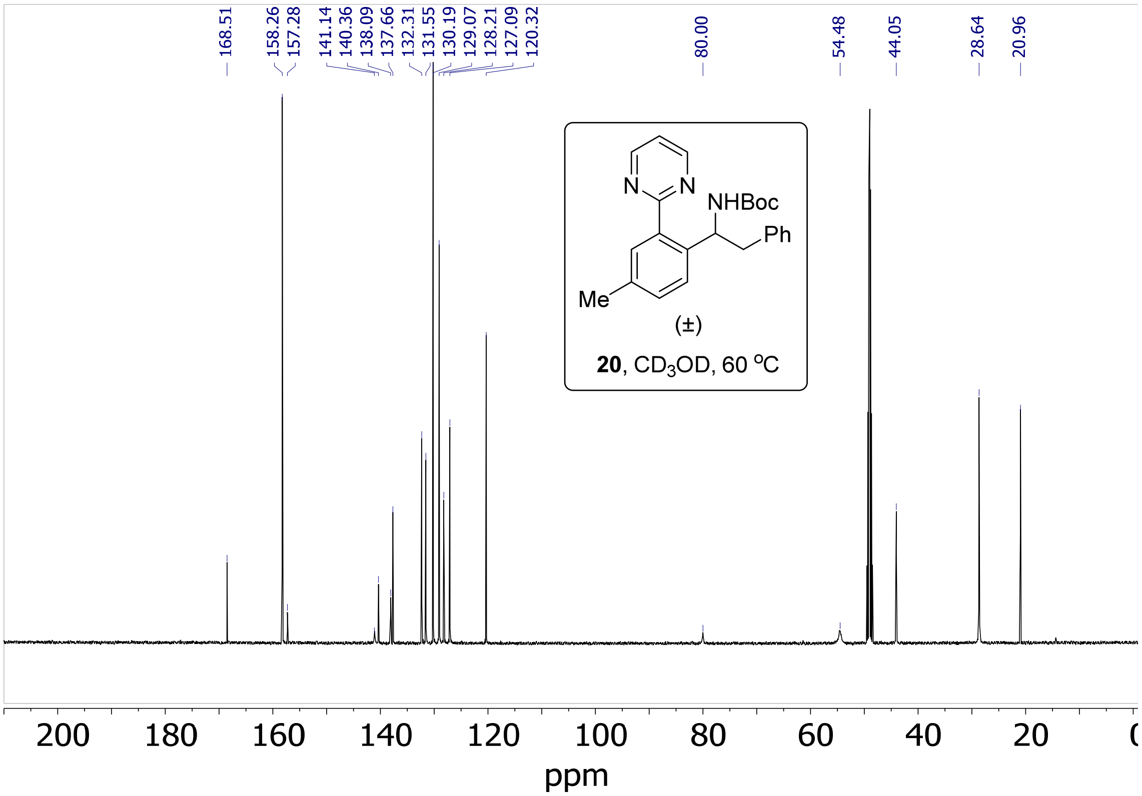
135.20
132.48
131.16
130.96
129.70
129.11
128.47
128.22
127.15
126.22
125.17
122.48
56.22
41.12
21.11
N
NHBz
Ph
Me
(±)
19, CDCl3, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm


8.88
8.87
7.57
7.45
7.43
7.38
7.37
7.36
7.27
7.26
7.20
7.18
7.17
7.16
7.12
7.11
7.10
5.58
5.57
5.56
5.55
4.45
3.14
3.13
3.11
3.10
2.82
2.80
2.79
2.77
2.36
1.21
N
N
NHBoc
Ph
Me
(±)
20, CD_3OD, 60 °C
1.91
0.99
1.05
1.03
1.11
5.23
1.00
1.09
1.15
3.31
9.76
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm


168.51
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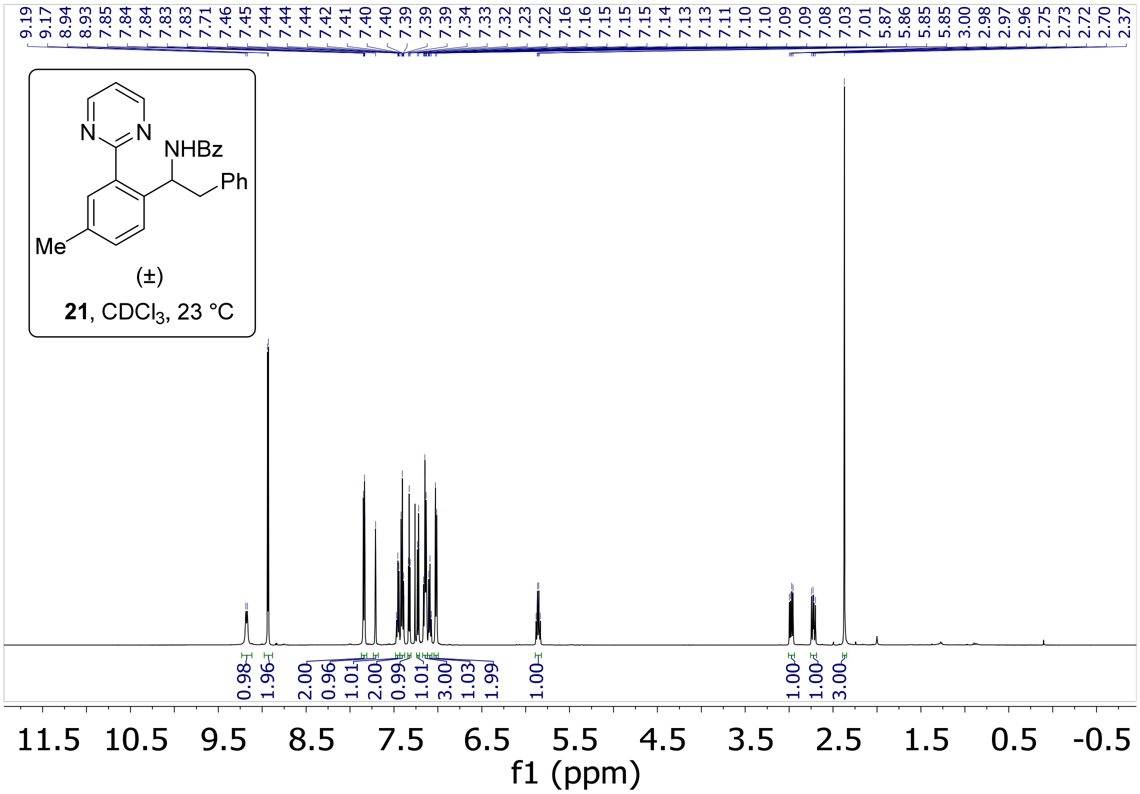
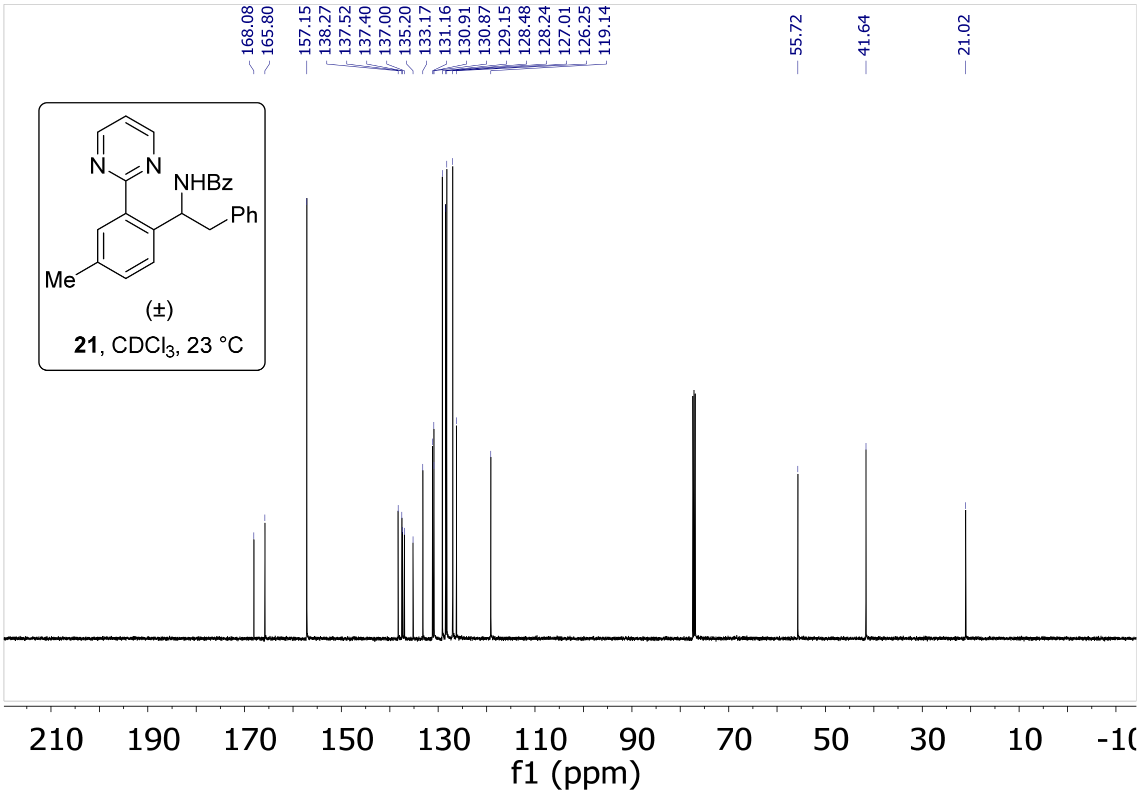
157.28
141.14
140.36
138.09
137.66
132.31
131.55
130.19
129.07
128.21
127.09
120.32
80.00
54.48
44.05
28.64
20.96
N
N
NHBoc
Ph
Me
(±)
20, CD_3OD, 60 °C
200
180
160
140
120
100
80
60
40
20
ppm


9.19
9.17
8.94
8.93
7.85
7.84
7.84
7.83
7.83
7.71
7.46
7.45
7.44
7.44
7.44
7.42
7.41
7.40
7.40
7.39
7.39
7.39
7.34
7.33
7.32
7.23
7.22
7.16
7.16
7.15
7.15
7.15
7.14
7.13
7.13
7.11
7.10
7.10
7.09
7.09
7.08
7.03
7.01
5.87
5.86
5.85
5.85
3.00
2.98
2.97
2.96
2.75
2.73
2.72
2.70
2.37
N
N
NHBz
Ph
Me
(±)
21, CDCl3, 23 °C
0.98
1.96
2.00
0.96
1.01
2.00
0.99
1.01
3.00
1.03
1.99
1.00
1.00
1.00
3.00
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)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138.27
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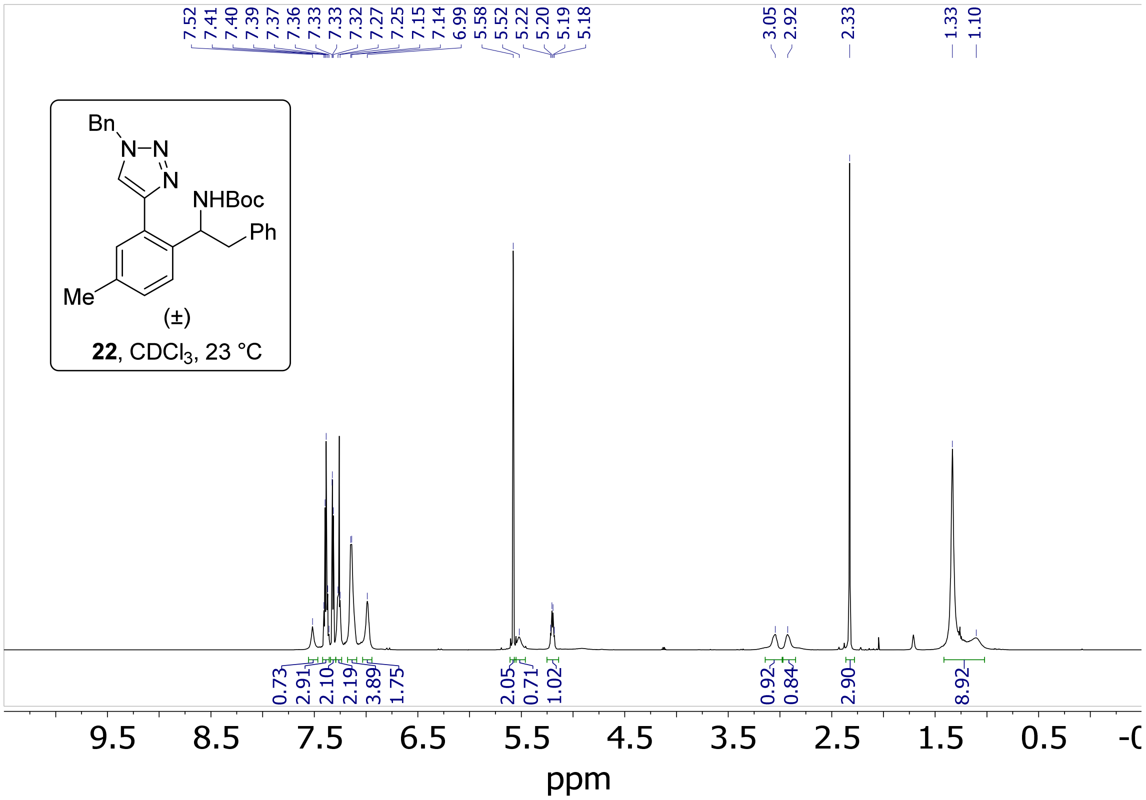
137.40
137.00
135.20
133.17
131.16
130.91
130.87
129.15
128.48
128.24
127.01
126.25
119.14
55.72
41.64
21.02
N
N
NHBz
Ph
Me
(±)
21, CDCl3, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)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7.40
7.39
7.37
7.36
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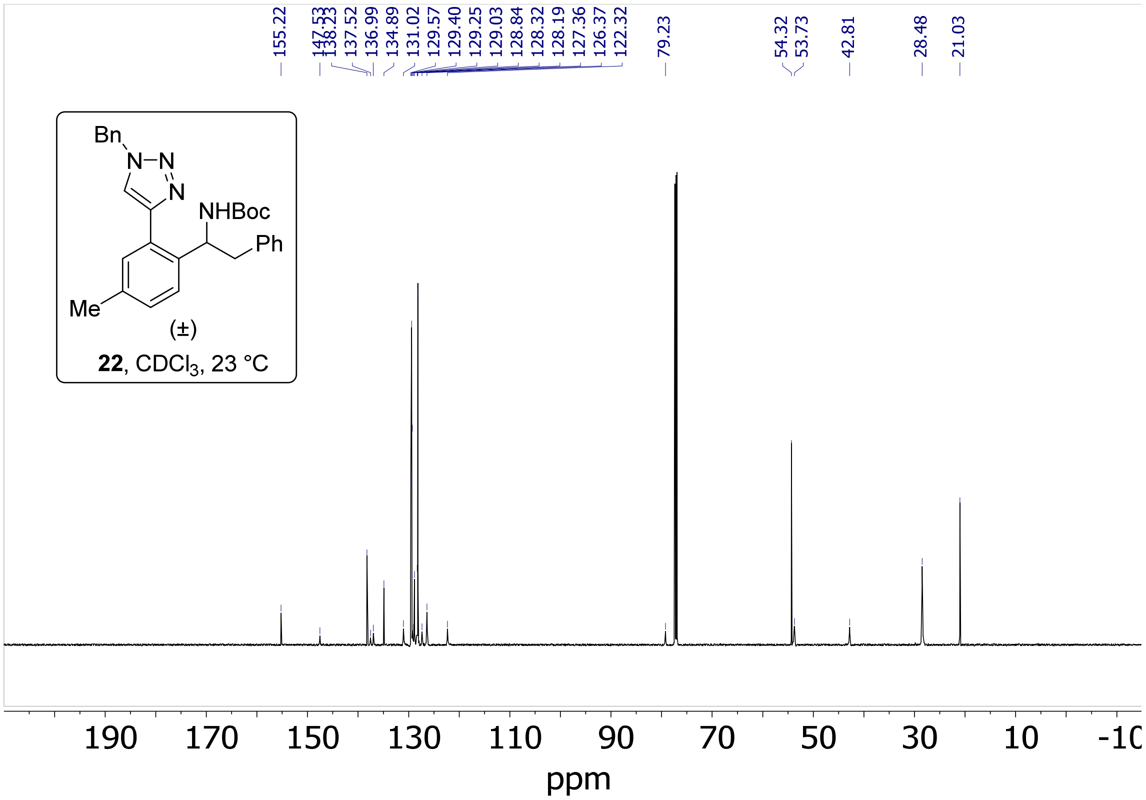
7.33
7.32
7.27
7.25
7.15
7.14
6.99
5.58
5.52
5.22
5.20
5.19
5.18
3.05
2.92
2.33
1.33
1.10
Bn
N
N
N
NHBoc
Ph
Me
(±)
22, CDCl$_3$, 23 °C
0.73
2.91
2.10
2.19
3.89
1.75
2.05
0.71
1.02
0.92
0.84
2.90
8.92
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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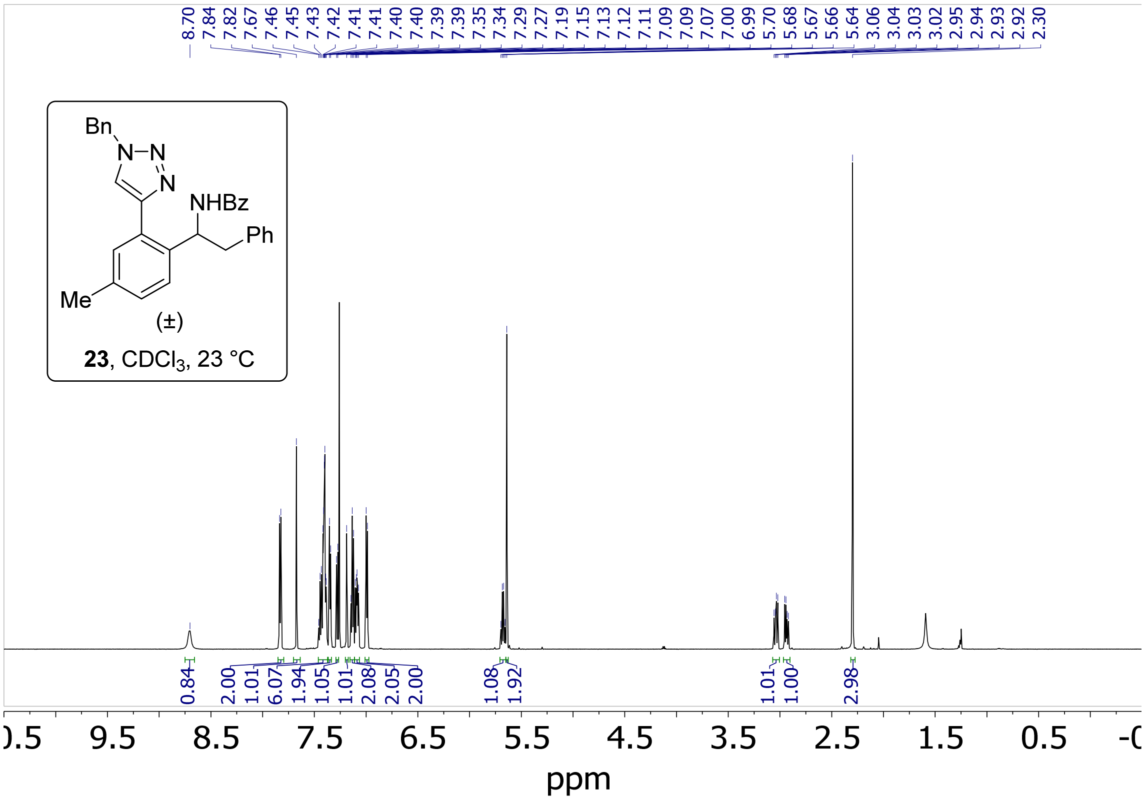
138.23
137.52
136.99
134.89
131.02
129.57
129.40
129.25
129.03
128.84
128.32
128.19
127.36
126.37
122.32
79.23
54.32
53.73
42.81
28.48
21.03
Bn
N
N
N
NHBoc
Ph
Me
(±)
22, CDCl$_3$, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm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7.84
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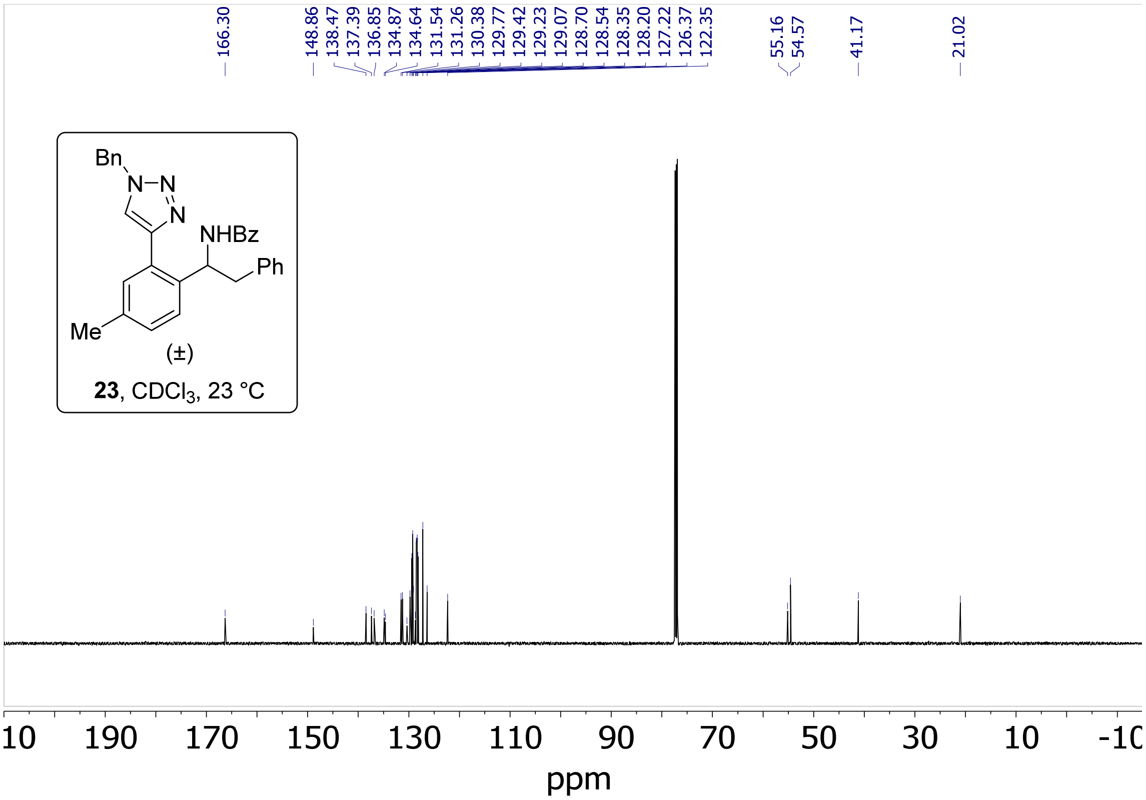
7.67
7.46
7.45
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.35
7.34
7.29
7.27
7.19
7.15
7.13
7.12
7.11
7.09
7.09
7.07
7.00
6.99
5.70
5.68
5.67
5.66
5.64
3.06
3.04
3.03
3.02
2.95
2.94
2.93
2.92
2.30
Bn
N
N
N
NHBz
Ph
Me
(±)
23, CDCl$_3$, 23 °C
0.84
2.00
1.01
6.07
1.94
1.05
1.01
2.08
2.05
2.00
1.08
1.92
1.01
1.00
2.98
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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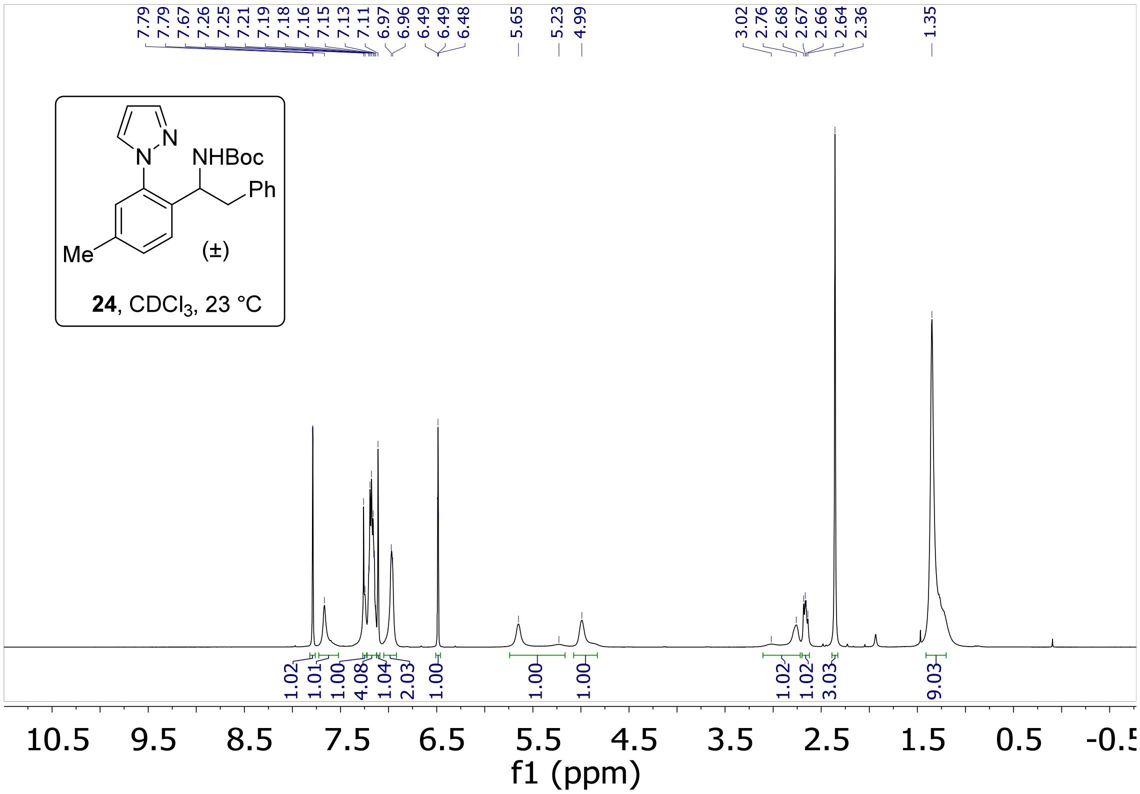
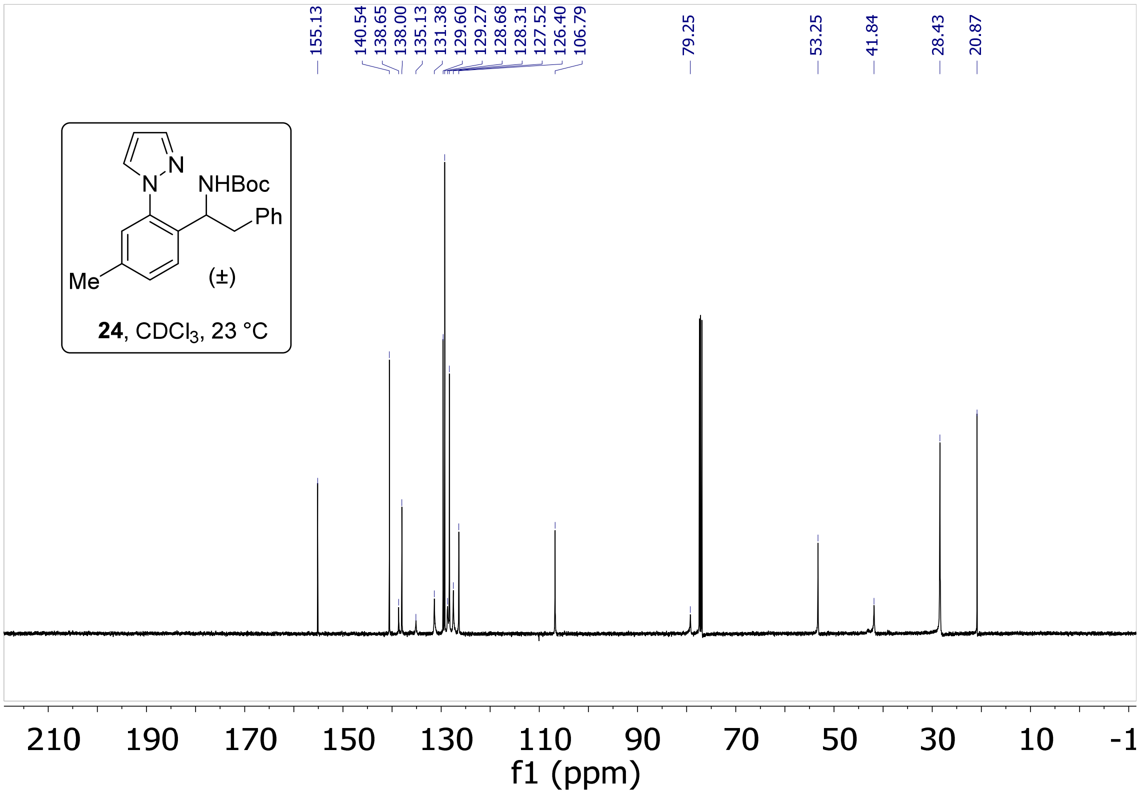
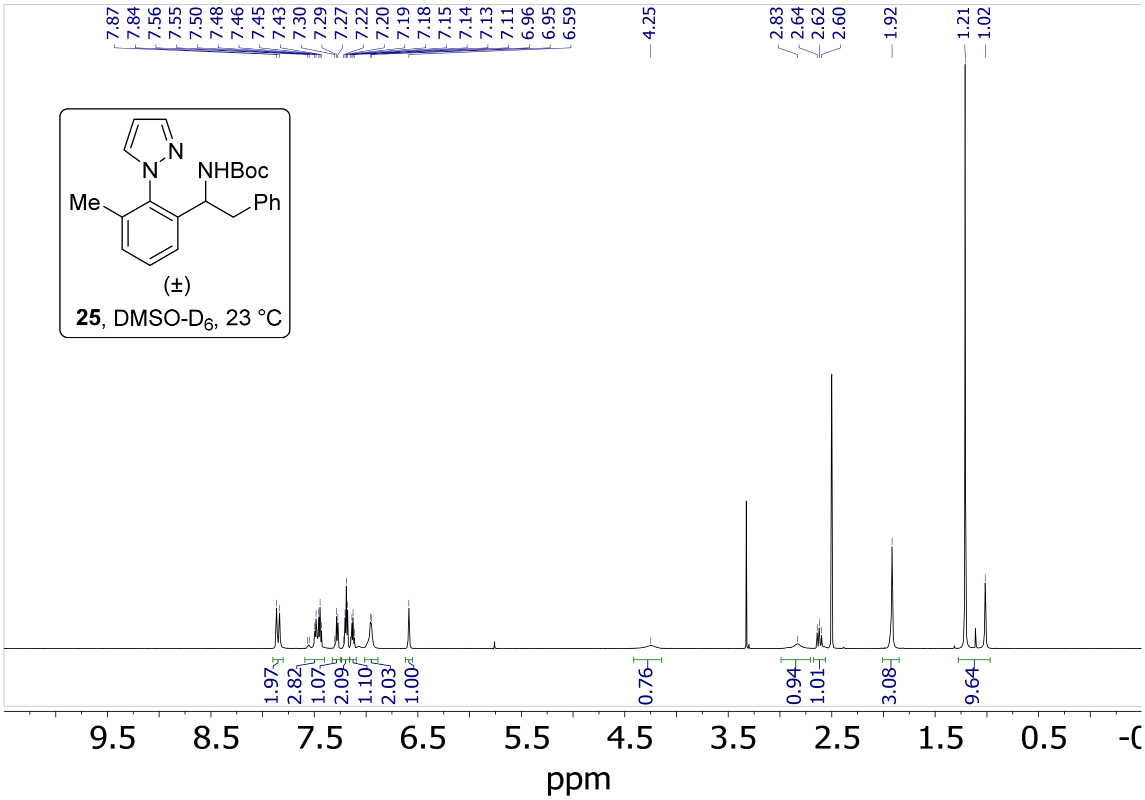
134.87
134.64
131.54
131.26
130.38
129.77
129.42
129.23
129.07
128.70
128.54
128.35
128.20
127.22
126.37
122.35
55.16
54.57
41.17
21.02
Bn
N
N
N
NHBz
Ph
Me
(±)
23, CDCl$_3$, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm


7.79
7.79
7.67
7.26
7.25
7.21
7.19
7.18
7.16
7.15
7.13
7.11
6.97
6.96
6.49
6.49
6.48
5.65
5.23
4.99
3.02
2.76
2.68
2.67
2.66
2.64
2.36
1.35
N
N
NHBoc
Ph
Me
(±)
24, $CDCl_3$, 23 °C
1.02
1.01
1.00
4.08
1.04
2.03
1.00
1.00
1.00
1.02
1.02
3.03
9.03
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


155.13
140.54
138.65
138.00
135.13
131.38
129.60
129.27
128.68
128.31
127.52
126.40
106.79
79.25
53.25
41.84
28.43
20.87
N
N
NHBoc
Ph
Me
(±)
24, $CDCl_3$, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)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7.84
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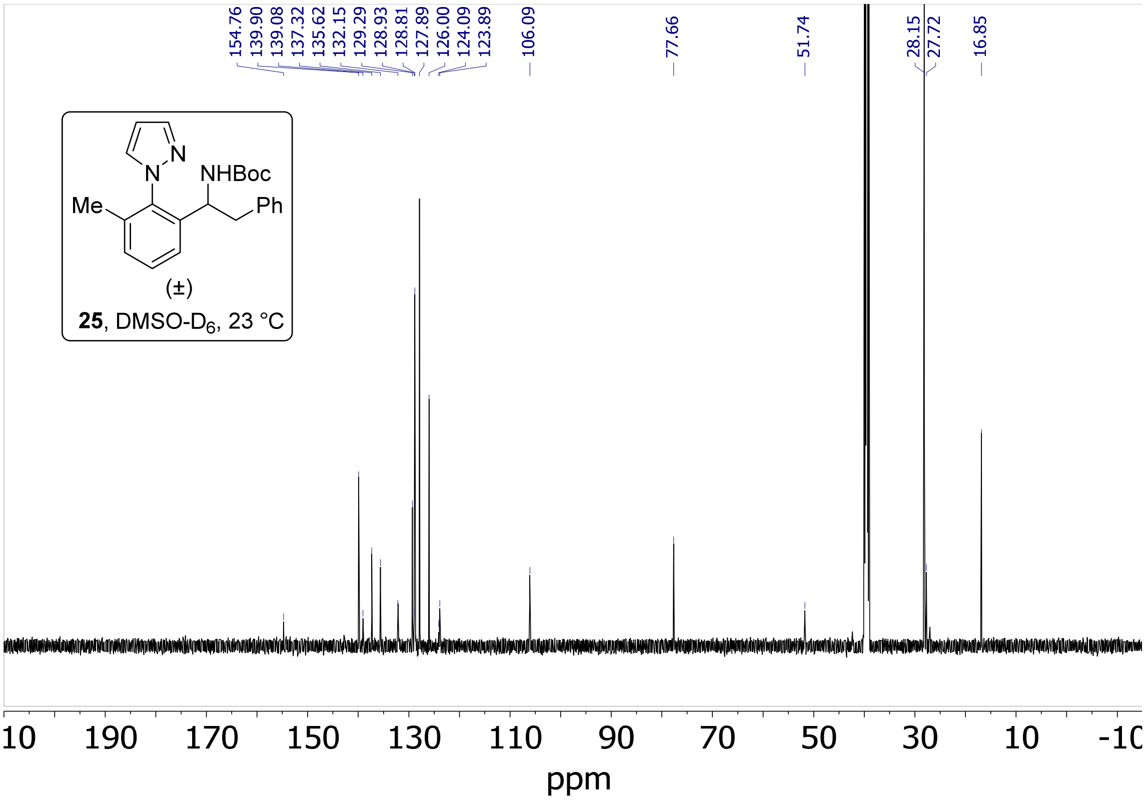
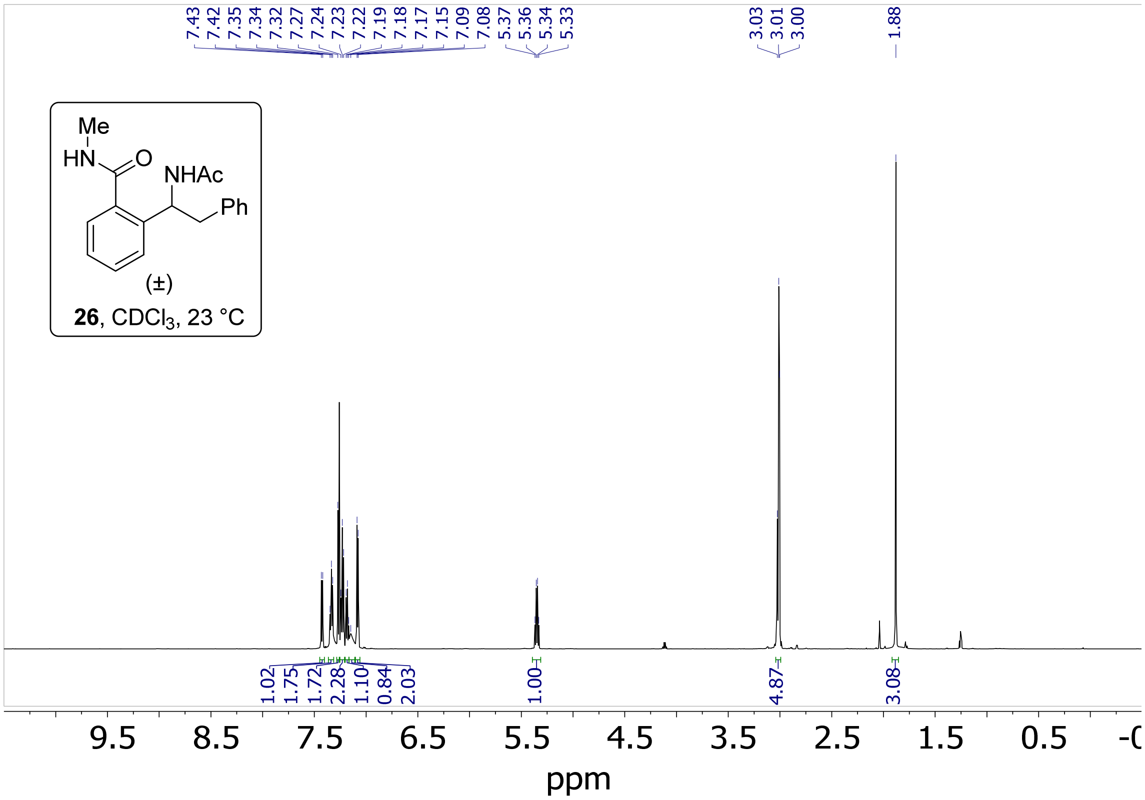
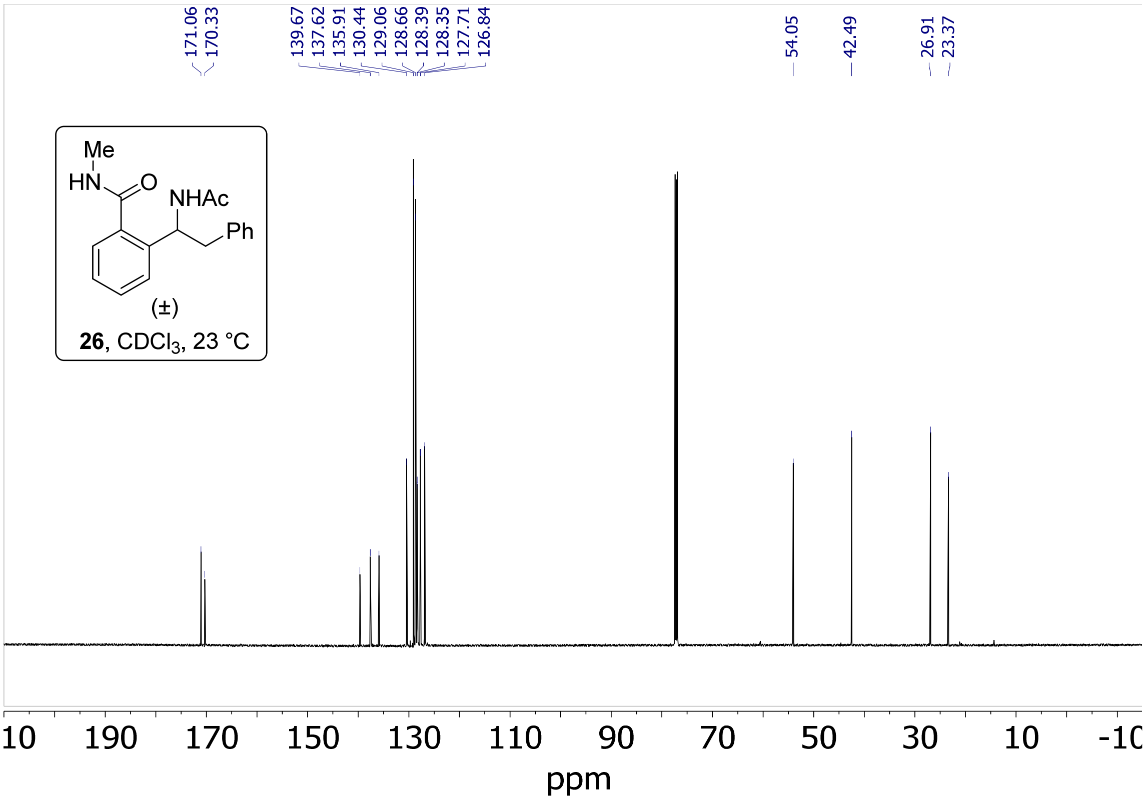
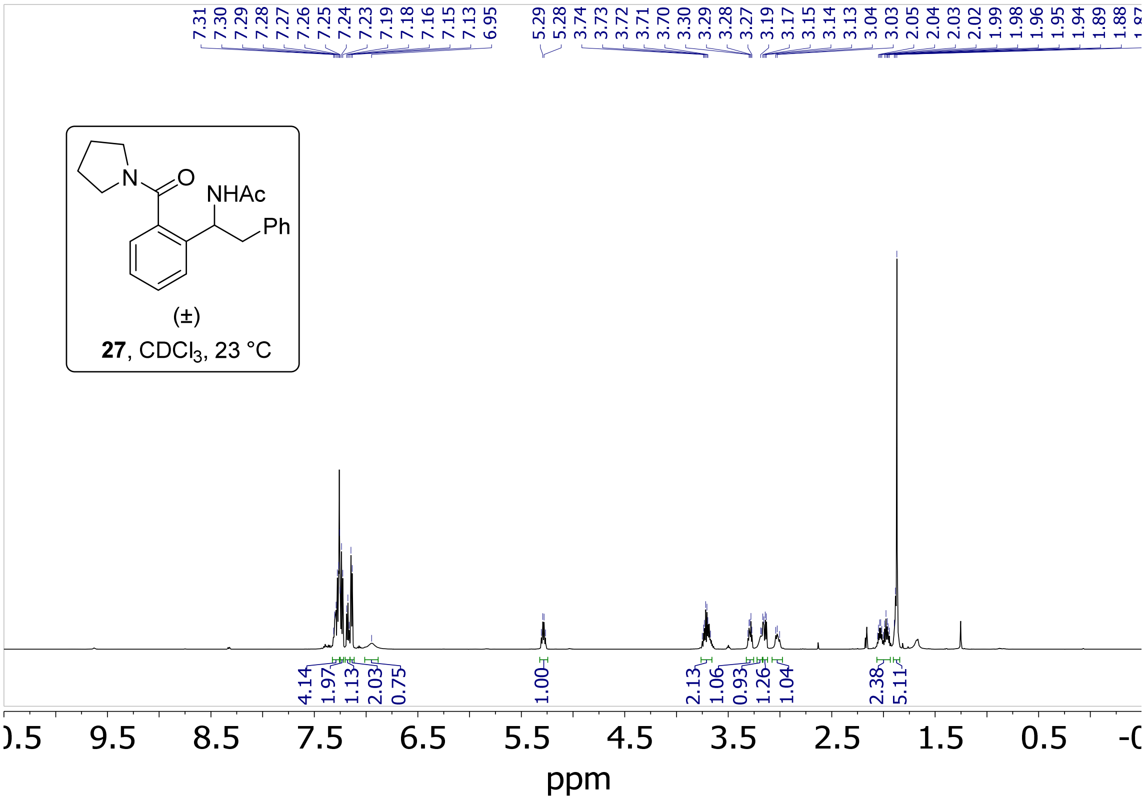
7.55
7.50
7.48
7.46
7.45
7.43
7.30
7.29
7.27
7.22
7.20
7.19
7.18
7.15
7.14
7.13
7.11
6.96
6.95
6.59
4.25
2.83
2.64
2.62
2.60
1.92
1.21
1.02
N
N
NHBoc
Me
Ph
(±)
25, DMSO-D6, 23 °C
1.97
2.82
1.07
2.09
1.10
2.03
1.00
0.76
0.94
1.01
3.08
9.64
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-
ppm


154.76
139.90
139.08
137.32
135.62
132.15
129.29
128.93
128.81
127.89
126.00
124.09
123.89
106.09
77.66
51.74
28.15
27.72
16.85
N
N
NHBoc
Me
Ph
(±)
25, DMSO-D6, 23 °C
10
190
170
150
130
110
90
70
50
30
10
-1
ppm


7.43
7.42
7.35
7.34
7.32
7.27
7.24
7.23
7.22
7.19
7.18
7.17
7.15
7.09
7.08
5.37
5.36
5.34
5.33
3.03
3.01
3.00
1.88
Me
HN
O
NHAc
Ph
(±)
26, CDCl3, 23 °C
1.02
1.75
1.72
2.28
1.10
0.84
2.03
1.00
4.87
3.08
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm


171.06
170.33
139.67
137.62
135.91
130.44
129.06
128.66
128.39
128.35
127.71
126.84
54.05
42.49
26.91
23.37
Me
HN
O
NHAc
Ph
(±)
26, CDCl3, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm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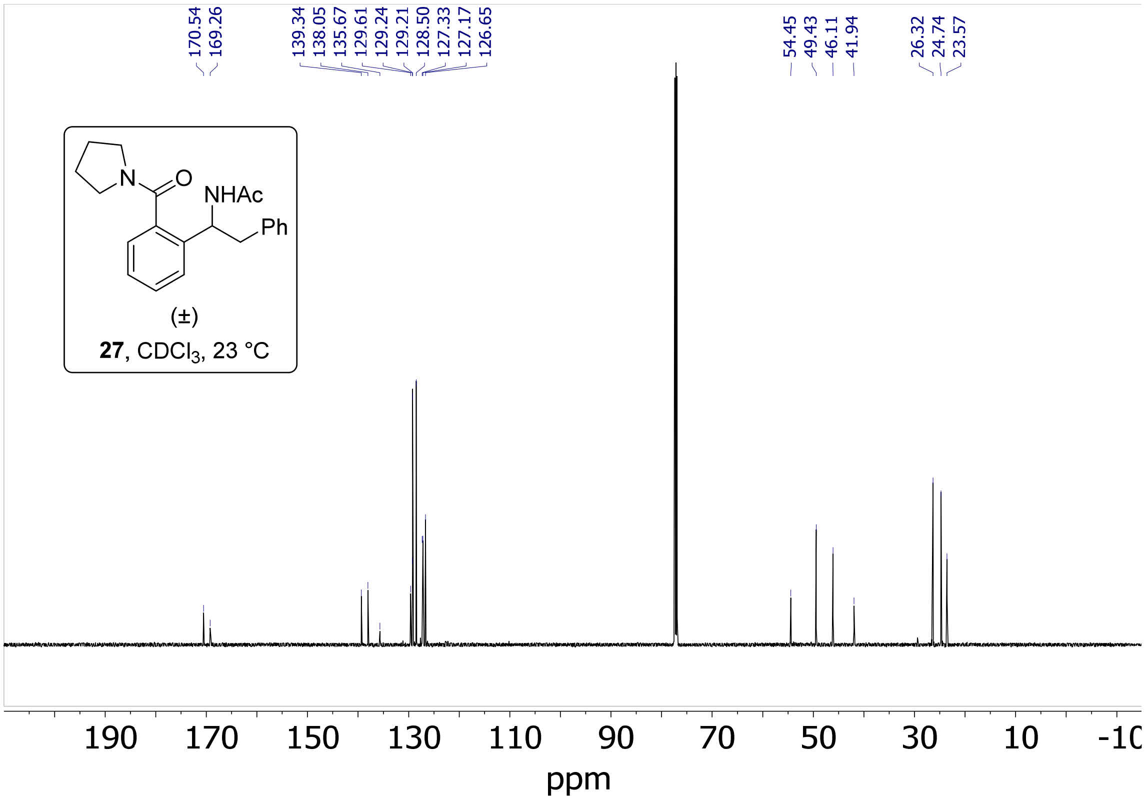
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.19
7.18
7.16
7.15
7.13
6.95
5.29
5.28
3.74
3.73
3.72
3.71
3.70
3.30
3.29
3.28
3.27
3.19
3.17
3.15
3.14
3.13
3.04
3.03
2.05
2.04
2.03
2.02
1.99
1.98
1.96
1.95
1.94
1.89
1.88
N
O
NHAc
Ph
(±)
27, $CDCl_3$, 23 °C
4.14
1.97
1.13
2.03
0.75
1.00
2.13
1.06
0.93
1.26
1.04
2.38
5.11
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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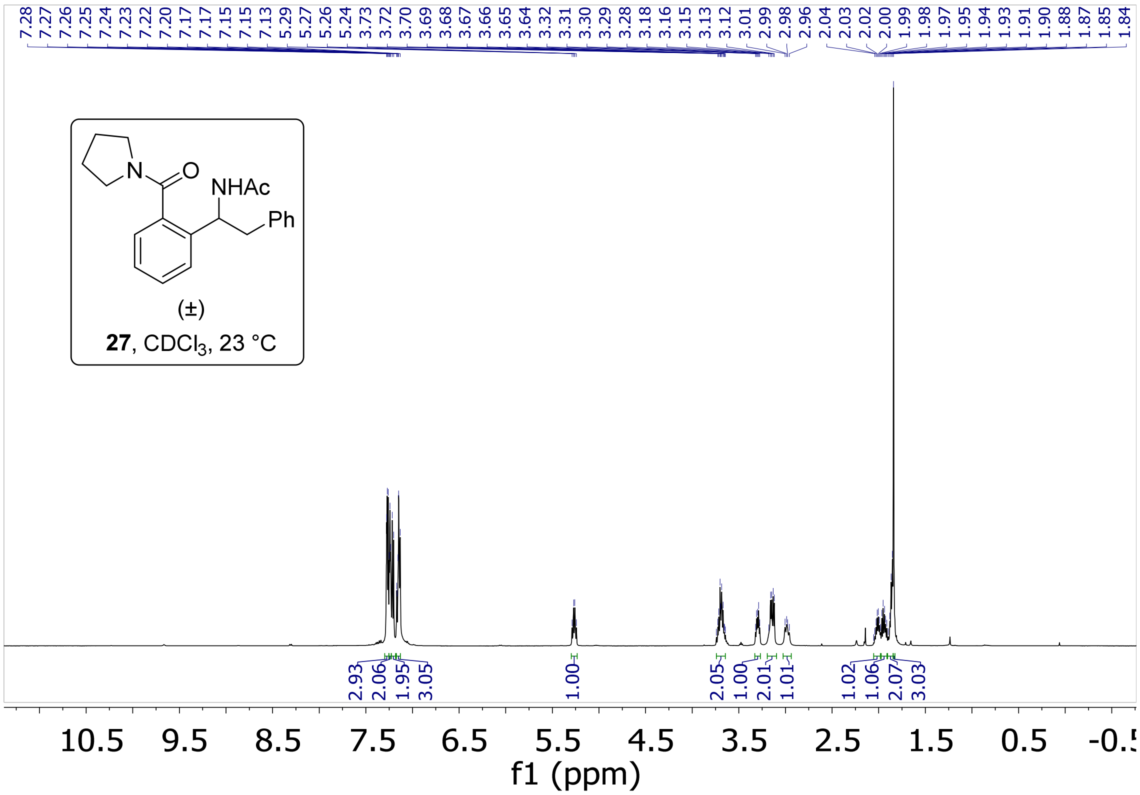
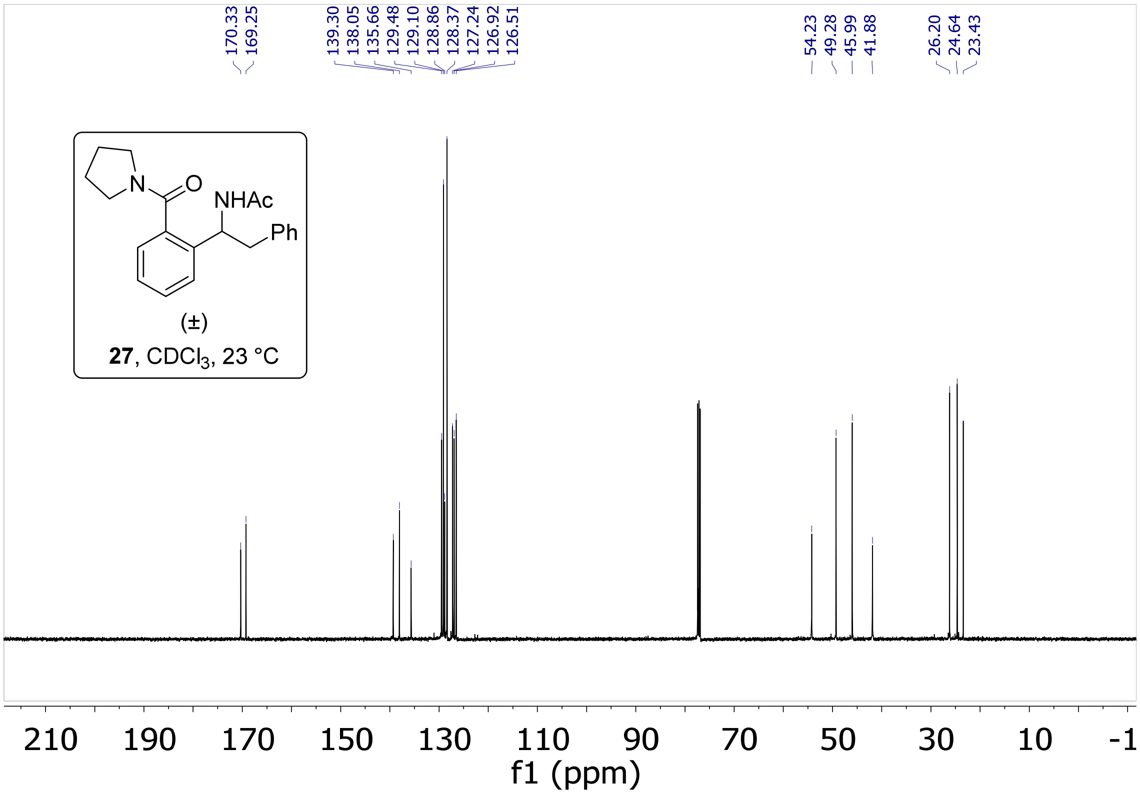
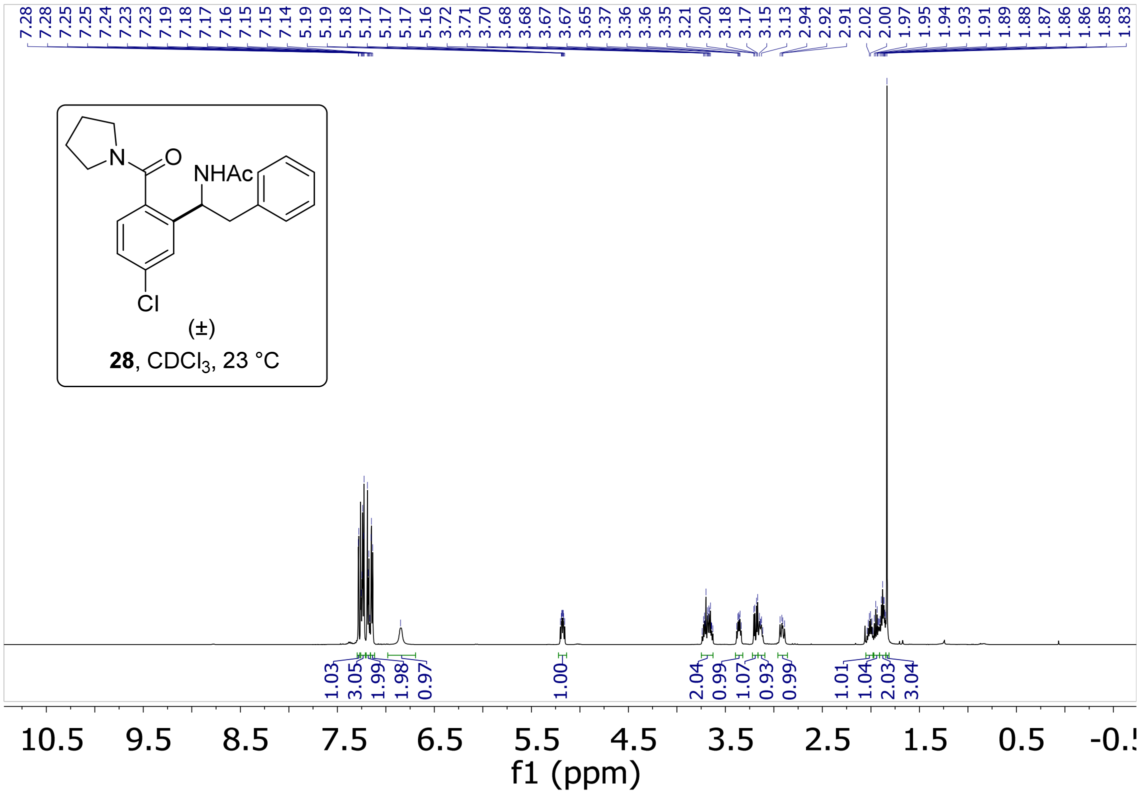
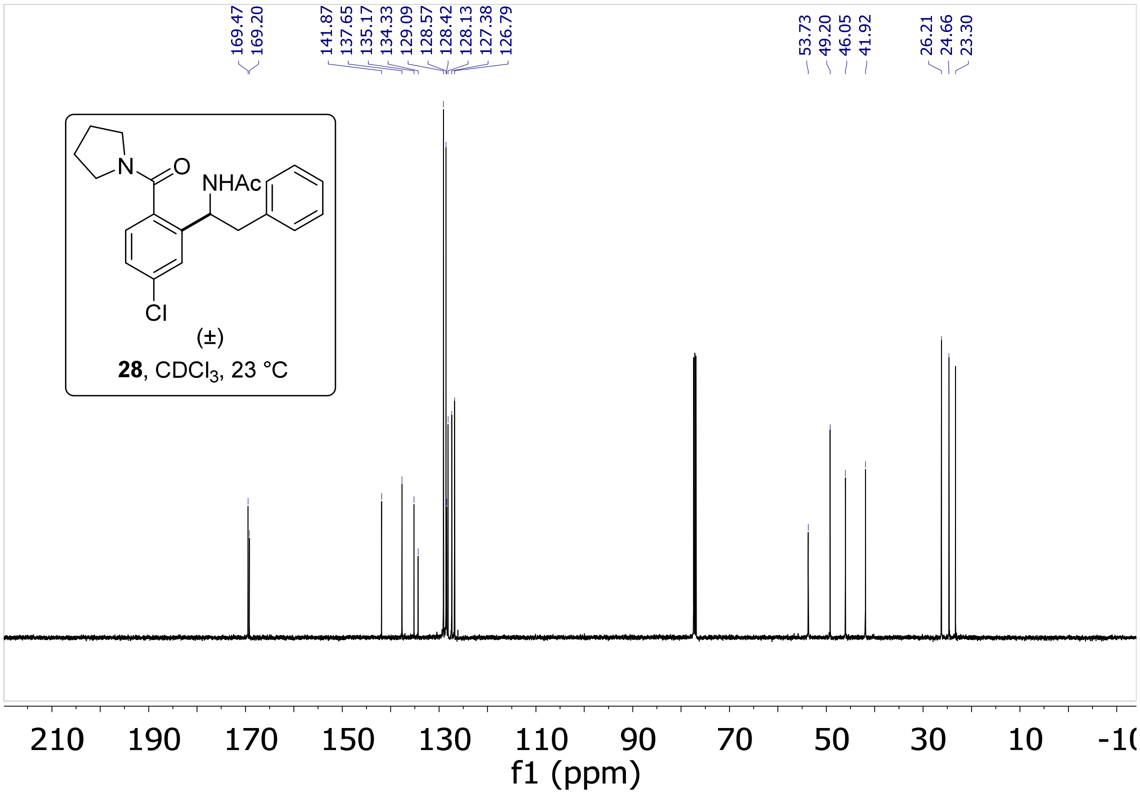
169.26
139.34
138.05
135.67
129.61
129.24
129.21
128.50
127.33
127.17
126.65
54.45
49.43
46.11
41.94
26.32
24.74
23.57
N
O
NHAc
Ph
(±)
27, $CDCl_3$, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm

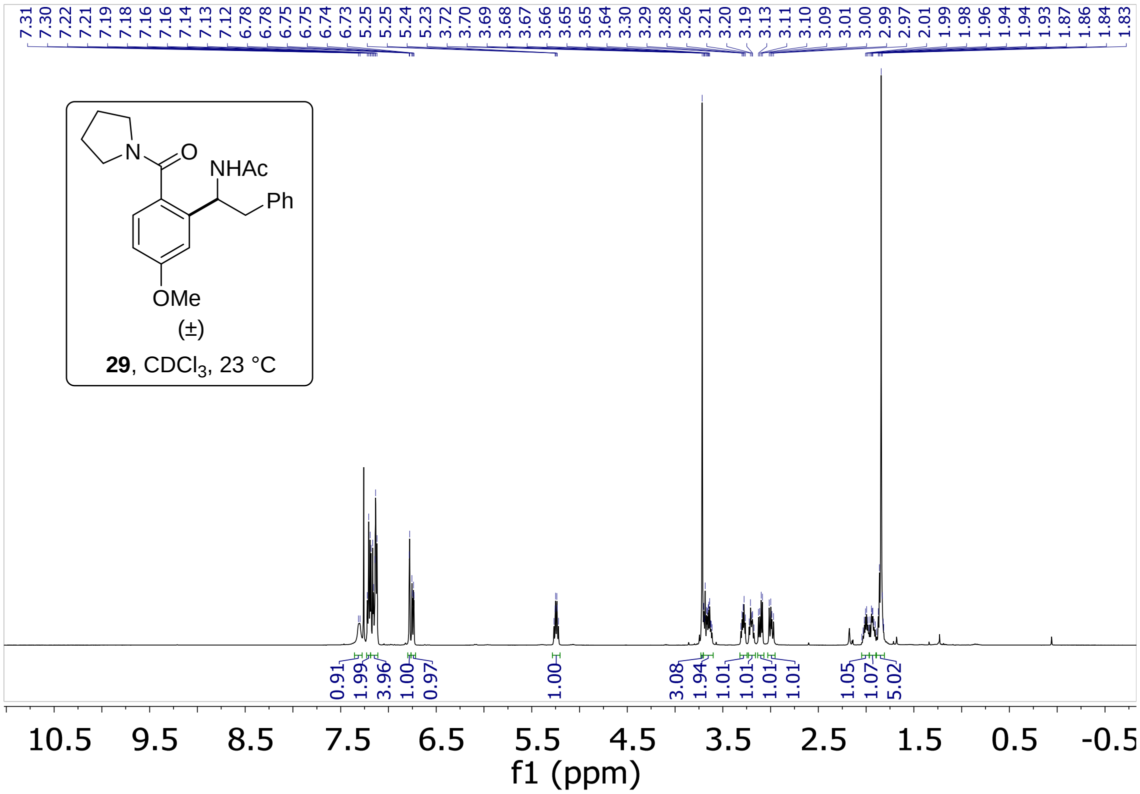
Reaction with 1 mol% Rh-dimer cat loading

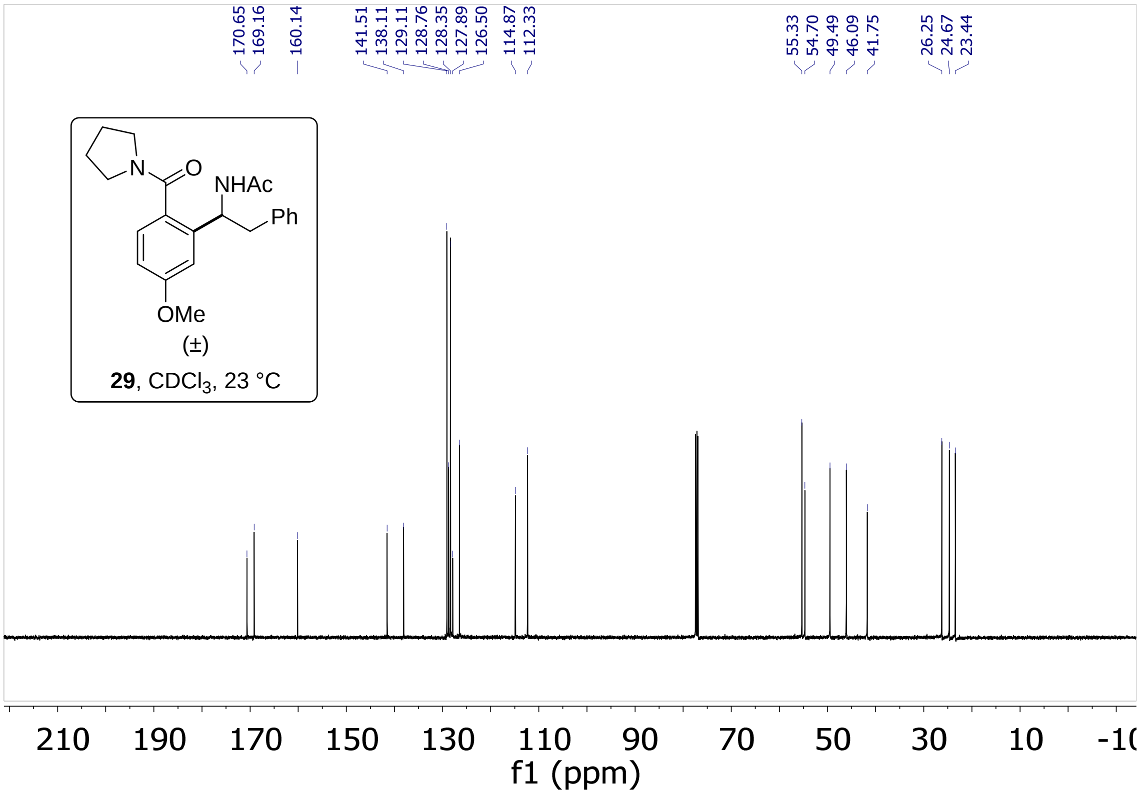


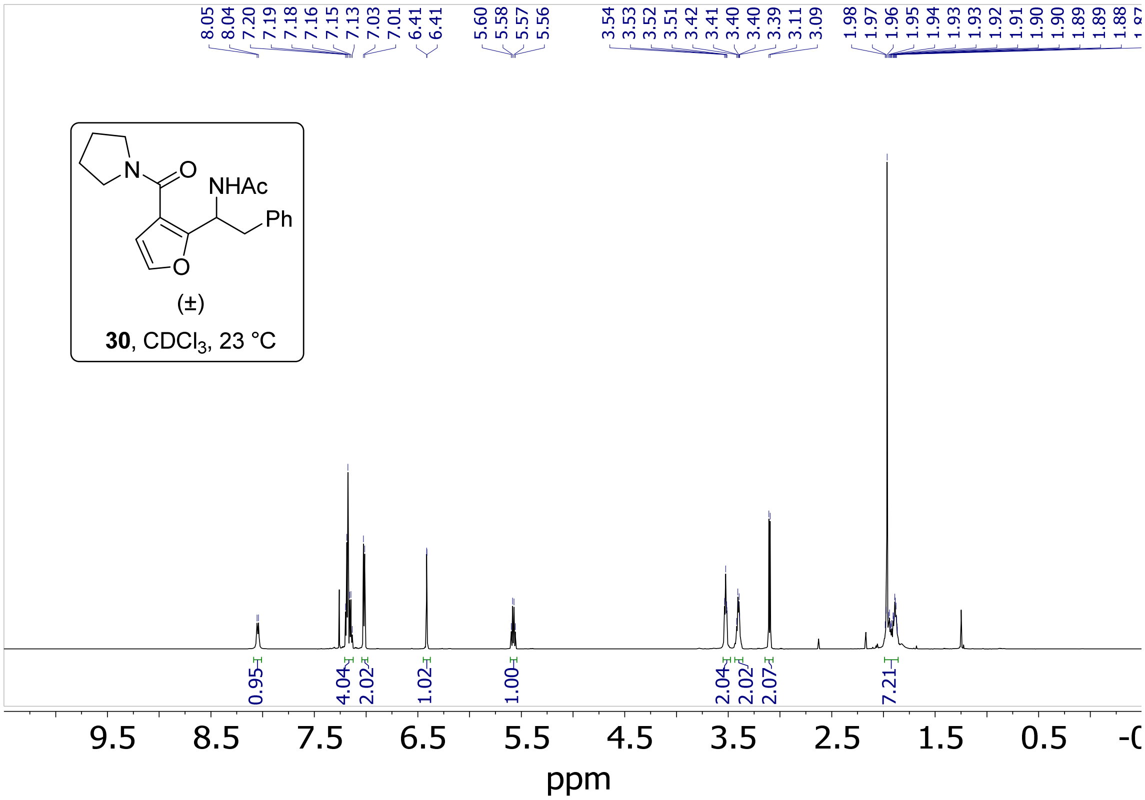


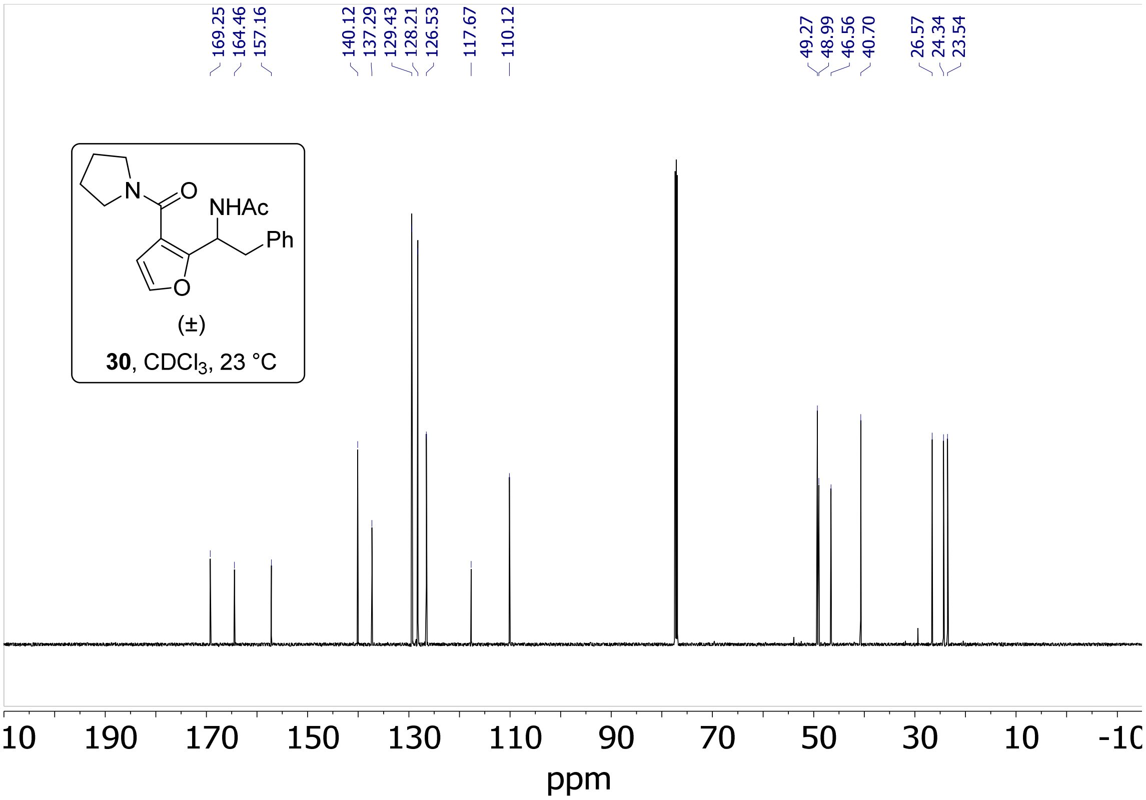

7.28 7.28 7.25 7.25 7.24 7.23 7.23 7.19 7.18 7.17 7.16 7.15 7.15 7.14 5.19 5.19 5.18 5.17 5.17 5.17 5.16 3.72 3.71 3.70 3.68 3.68 3.67 3.67 3.65 3.37 3.36 3.36 3.35 3.21 3.20 3.18 3.17 3.15 3.13 2.94 2.92 2.91 2.02 2.00 1.97 1.95 1.94 1.93 1.91 1.89 1.88 1.87 1.86 1.86 1.85 1.83
N
O
NHAc
Cl
(±)
28, $CDCl_3$, 23 °C
1.03 3.05 1.99 1.98 0.97
1.00
2.04 0.99 1.07 0.93 0.99
1.01 1.04 2.03 3.04
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)


169.47 169.20
141.87 137.65 135.17 134.33 129.09 128.57 128.42 128.13 127.38 126.79
53.73 49.20 46.05 41.92
26.21 24.66 23.30
N
O
NHAc
Cl
(±)
28, $CDCl_3$, 23 °C
210 190 170 150 130 110 90 70 50 30 10 -10
f1 (ppm)


7.31
7.30
7.22
7.21
7.19
7.18
7.16
7.16
7.14
7.13
7.12
6.78
6.78
6.75
6.75
6.74
6.73
5.25
5.25
5.24
5.23
3.72
3.70
3.69
3.68
3.67
3.66
3.65
3.65
3.64
3.30
3.29
3.28
3.26
3.21
3.20
3.19
3.13
3.11
3.10
3.09
3.01
3.00
2.99
2.97
2.01
1.99
1.98
1.96
1.94
1.94
1.93
1.87
1.86
1.84
1.83
N
O
NHAc
Ph
OMe
(±)
29, CDCl3, 23 °C
0.91
1.99
3.96
1.00
0.97
1.00
3.08
1.94
1.01
1.01
1.01
1.01
1.05
1.07
5.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


170.65
169.16
160.14
141.51
138.11
129.11
128.76
128.35
127.89
126.50
114.87
112.33
55.33
54.70
49.49
46.09
41.75
26.25
24.67
23.44
N
O
NHAc
Ph
OMe
(±)
29, CDCl3, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1(
f1 (ppm)


8.05
8.04
7.20
7.19
7.18
7.16
7.15
7.13
7.03
7.01
6.41
6.41
5.60
5.58
5.57
5.56
3.54
3.53
3.52
3.51
3.42
3.41
3.40
3.40
3.39
3.11
3.09
1.98
1.97
1.96
1.95
1.94
1.93
1.93
1.92
1.91
1.90
1.90
1.89
1.88
N
O
NHAc
Ph
O
(±)
30, $CDCl_3$, 23 °C
0.95
4.04
2.02
1.02
1.00
2.04
2.02
2.07
7.21
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm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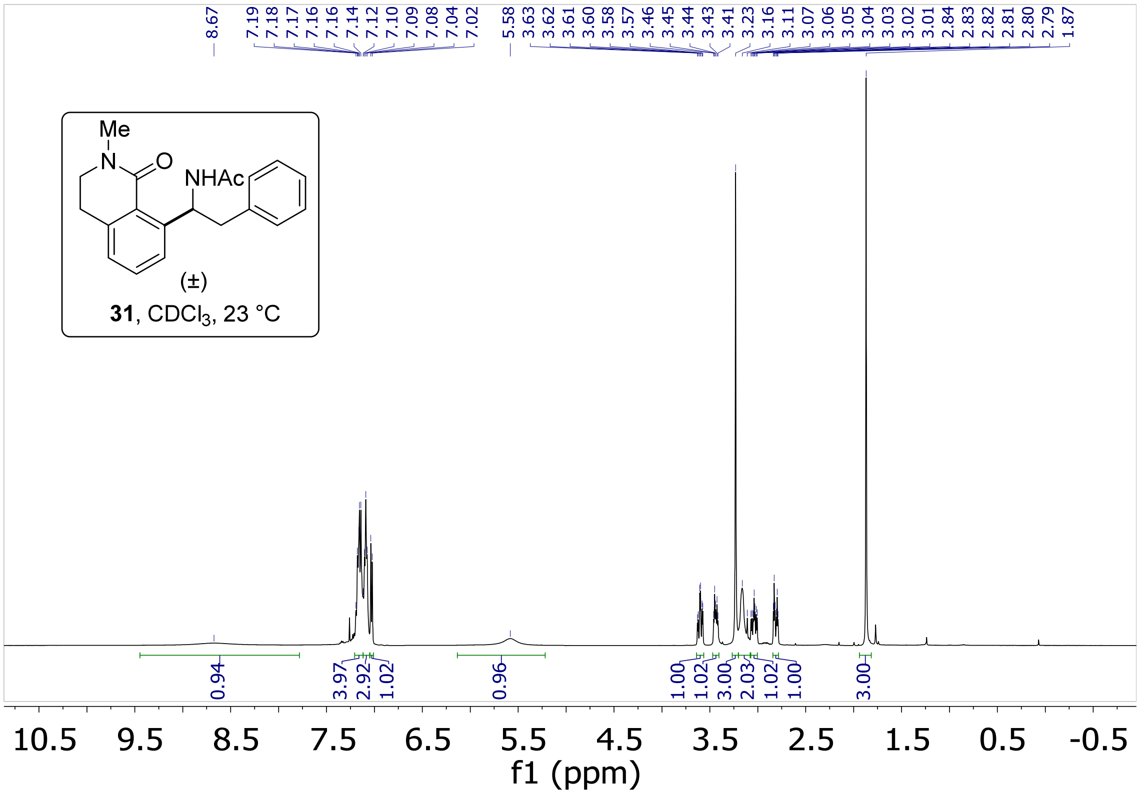
164.46
157.16
140.12
137.29
129.43
128.21
126.53
117.67
110.12
49.27
48.99
46.56
40.70
26.57
24.34
23.54
N
O
NHAc
Ph
O
(±)
30, $CDCl_3$, 23 °C
10
190
170
150
130
110
90
70
50
30
10
ppm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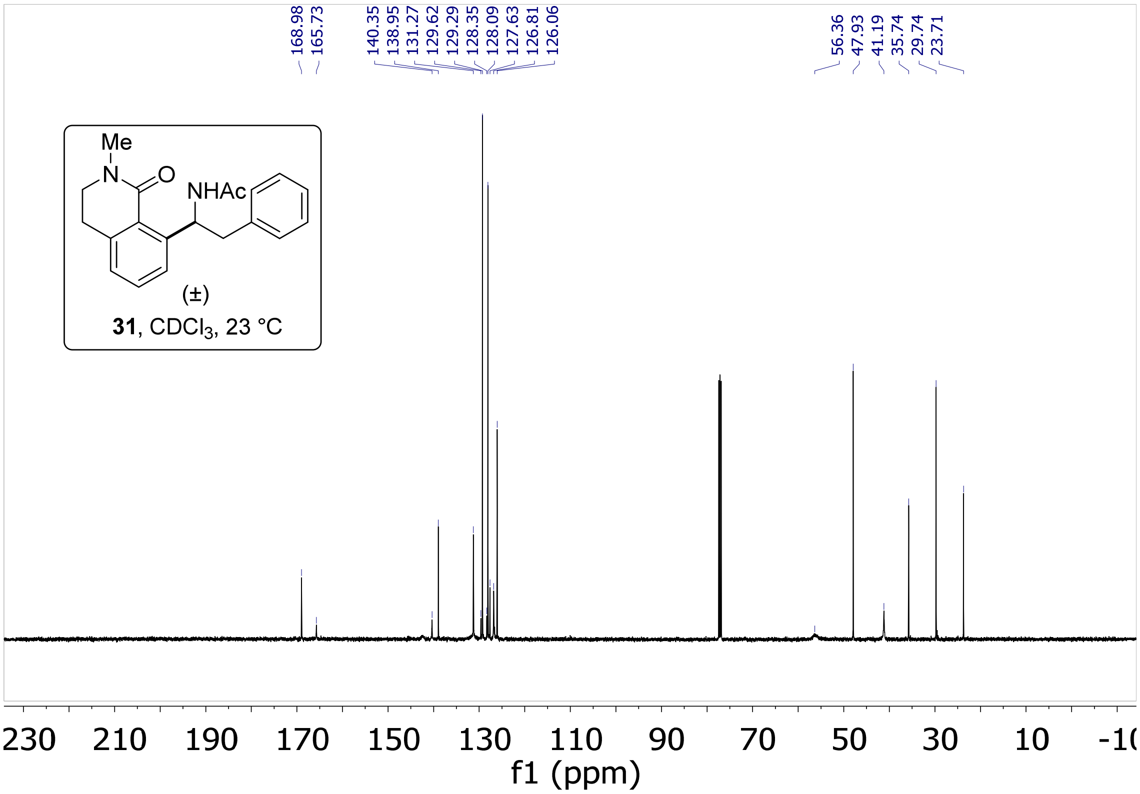
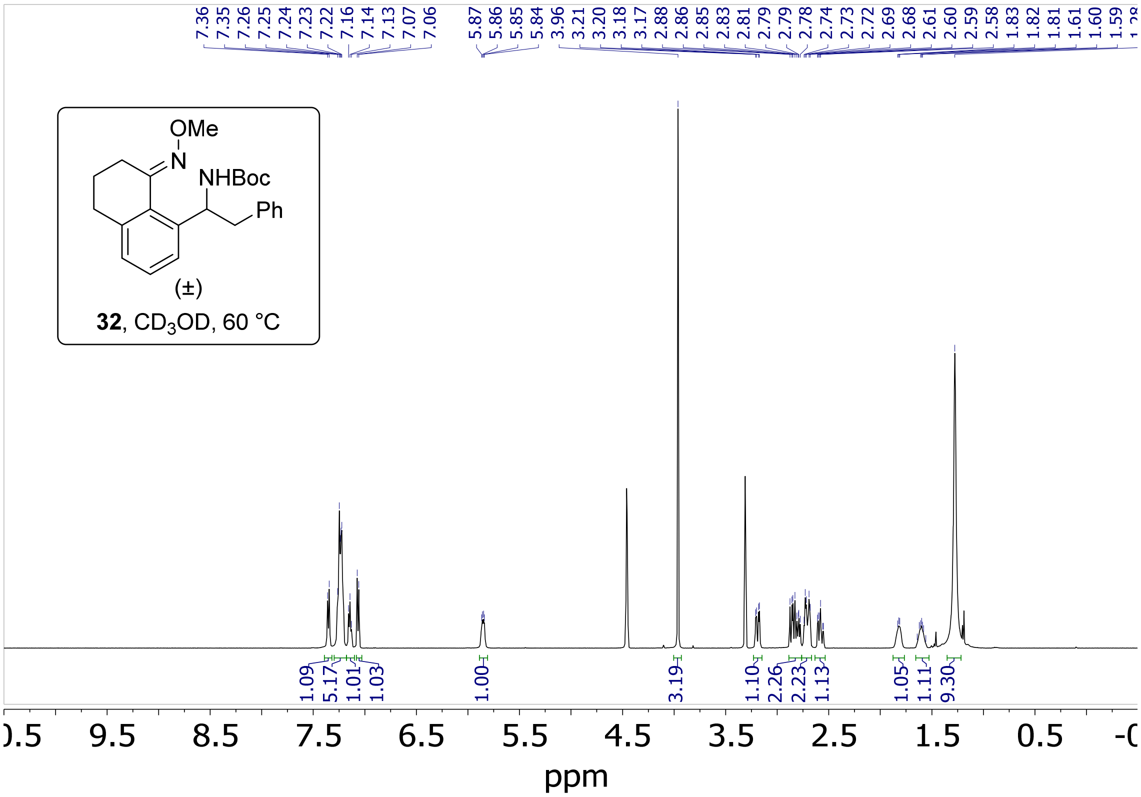
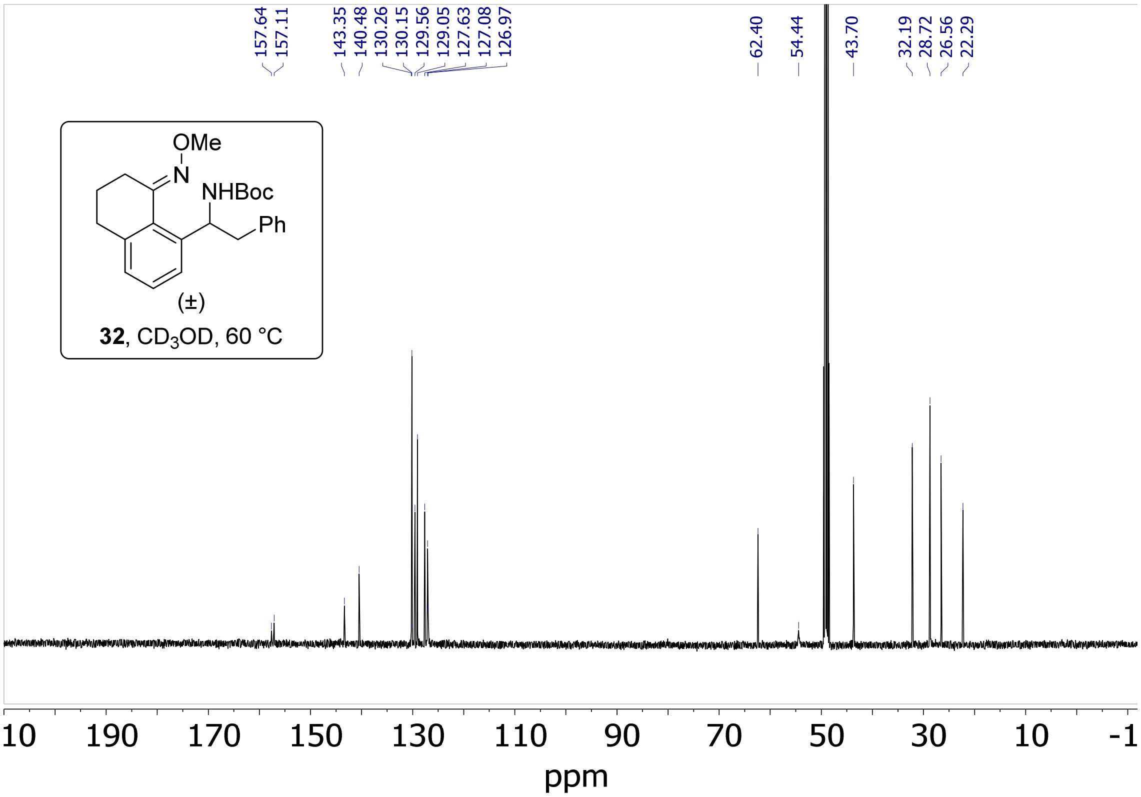
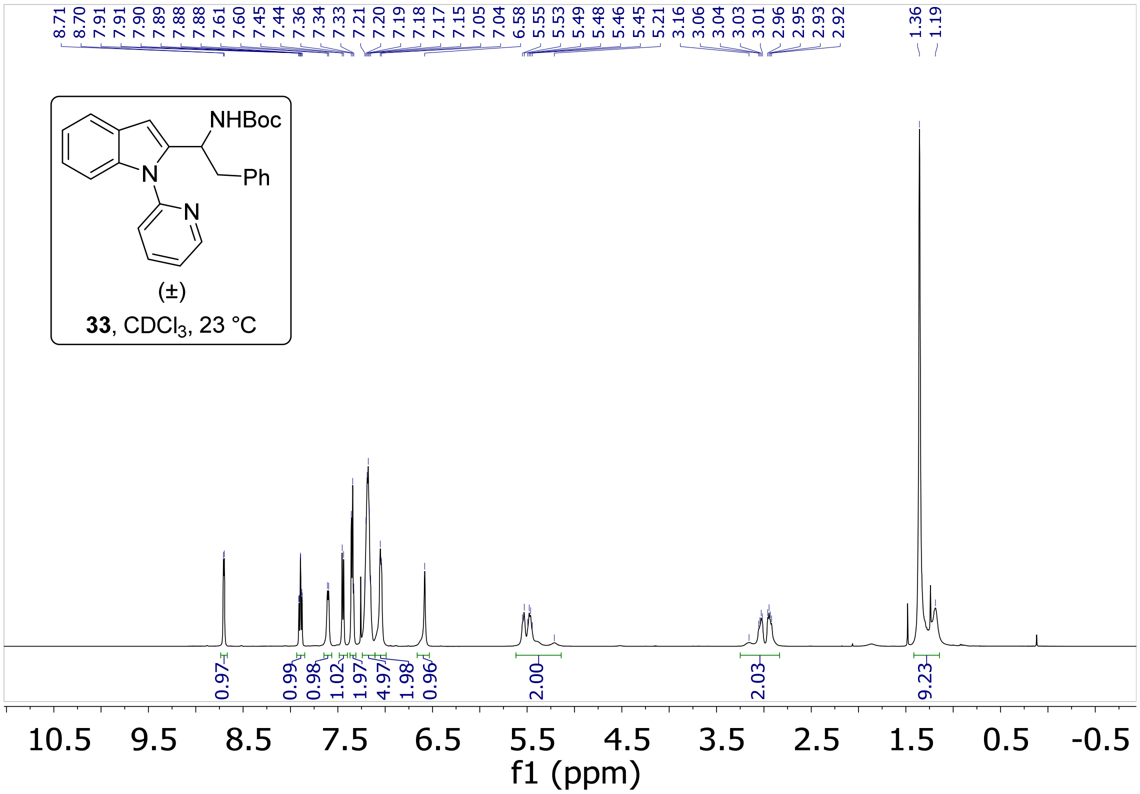
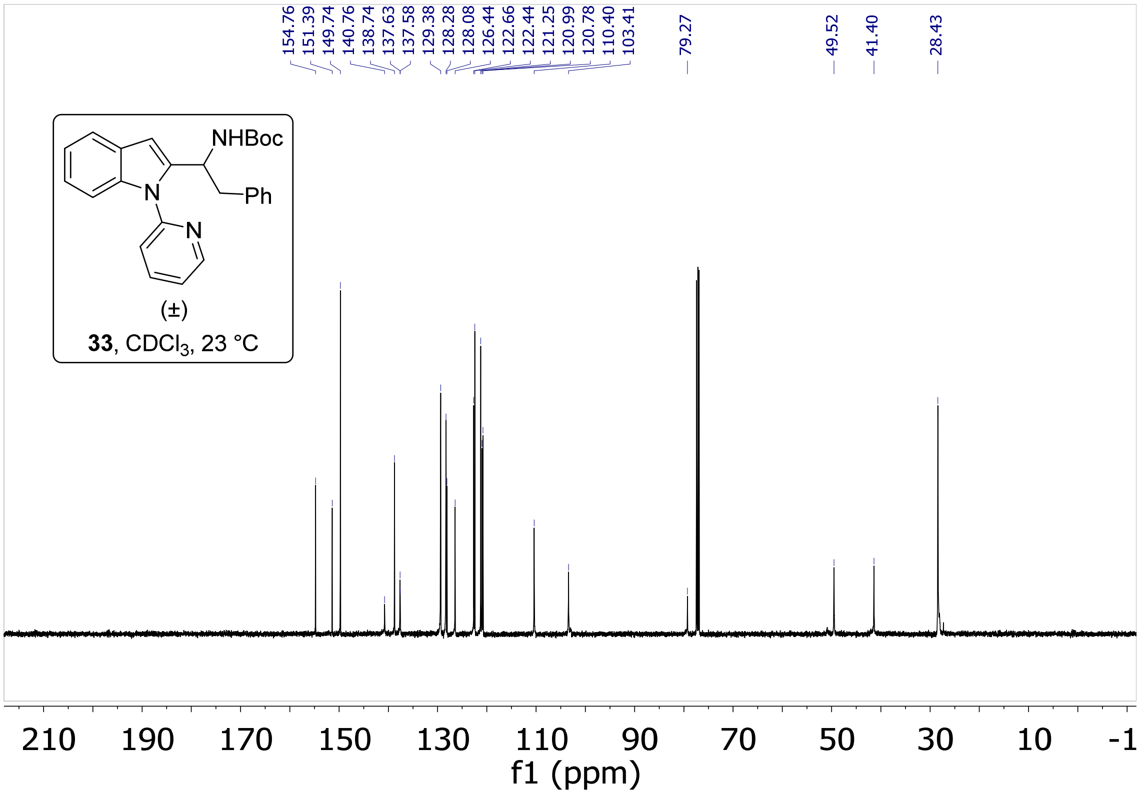
7.19
7.18
7.17
7.16
7.16
7.14
7.12
7.10
7.09
7.08
7.04
7.02
5.58
3.63
3.62
3.61
3.60
3.58
3.57
3.46
3.45
3.44
3.43
3.41
3.23
3.16
3.11
3.07
3.06
3.05
3.04
3.03
3.02
3.01
2.84
2.83
2.82
2.81
2.80
2.79
1.87
Me
N
O
NHAc
(±)
31, CDCl3, 23 °C
0.94
3.97
2.92
1.02
0.96
1.00
1.02
3.00
2.03
1.02
1.00
3.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

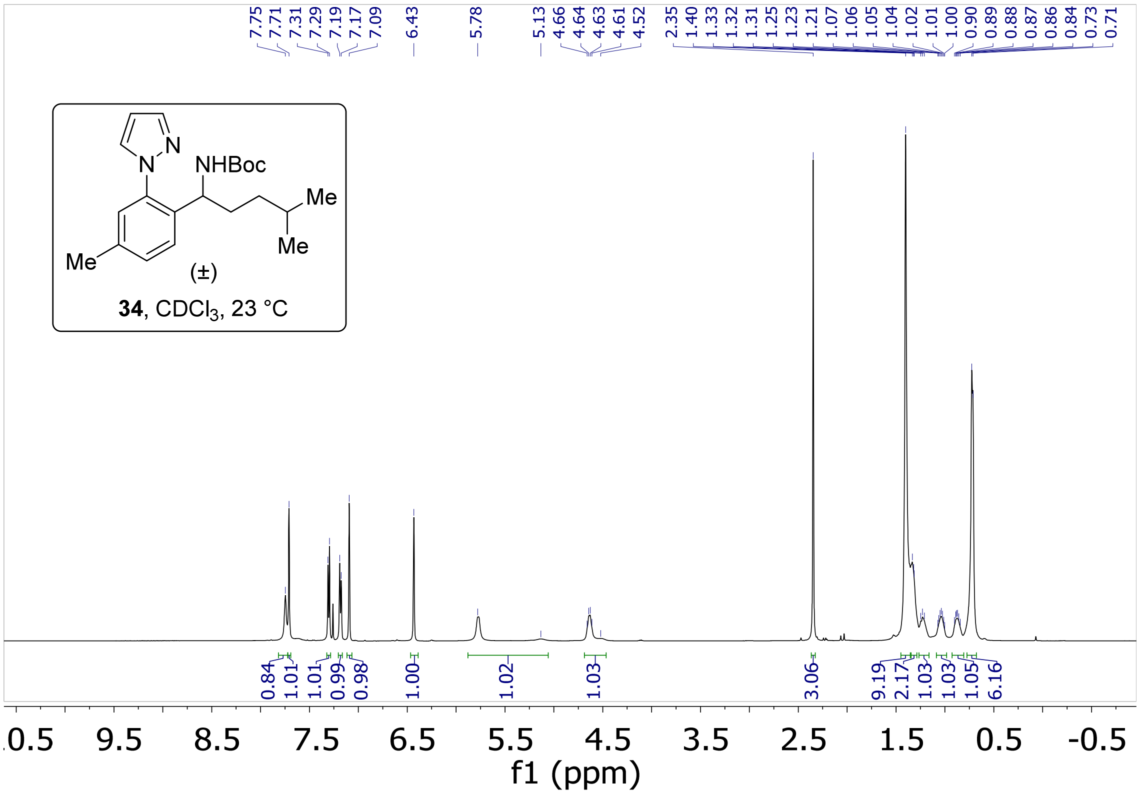

168.98
165.73
140.35
138.95
131.27
129.62
129.29
128.35
128.09
127.63
126.81
126.06
56.36
47.93
41.19
35.74
29.74
23.71
Me
N
O
NHAc
(±)
31, CDCl3, 23 °C
230
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)


7.36
7.35
7.26
7.25
7.24
7.23
7.22
7.16
7.14
7.13
7.07
7.06
5.87
5.86
5.85
5.84
3.96
3.21
3.20
3.18
3.17
2.88
2.86
2.85
2.83
2.81
2.79
2.79
2.78
2.74
2.73
2.72
2.69
2.68
2.61
2.60
2.59
2.58
1.83
1.82
1.81
1.61
1.60
1.59
OMe
N
NHBoc
Ph
(±)
32, CD_3OD, 60 °C
1.09
5.17
1.01
1.03
1.00
3.19
1.10
2.26
2.23
1.13
1.05
1.11
9.30
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm


157.64
157.11
143.35
140.48
130.26
130.15
129.56
129.05
127.63
127.08
126.97
62.40
54.44
43.70
32.19
28.72
26.56
22.29
OMe
N
NHBoc
Ph
(±)
32, CD_3OD, 60 °C
190
170
150
130
110
90
70
50
30
10
ppm


8.71
8.70
7.91
7.91
7.90
7.89
7.88
7.88
7.61
7.60
7.45
7.44
7.36
7.34
7.33
7.21
7.20
7.19
7.18
7.17
7.15
7.05
7.04
6.58
5.55
5.53
5.49
5.48
5.46
5.45
5.21
3.16
3.06
3.04
3.03
3.01
2.96
2.95
2.93
2.92
1.36
1.19
NHBoc
N
Ph
N
(±)
33, $CDCl_3$, 23 °C
0.97
0.99
0.98
1.02
1.97
4.97
1.98
0.96
2.00
2.03
9.23
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


154.76
151.39
149.74
140.76
138.74
137.63
137.58
129.38
128.28
128.08
126.44
122.66
122.44
121.25
120.99
120.78
110.40
103.41
79.27
49.52
41.40
28.43
NHBoc
N
Ph
N
(±)
33, $CDCl_3$, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)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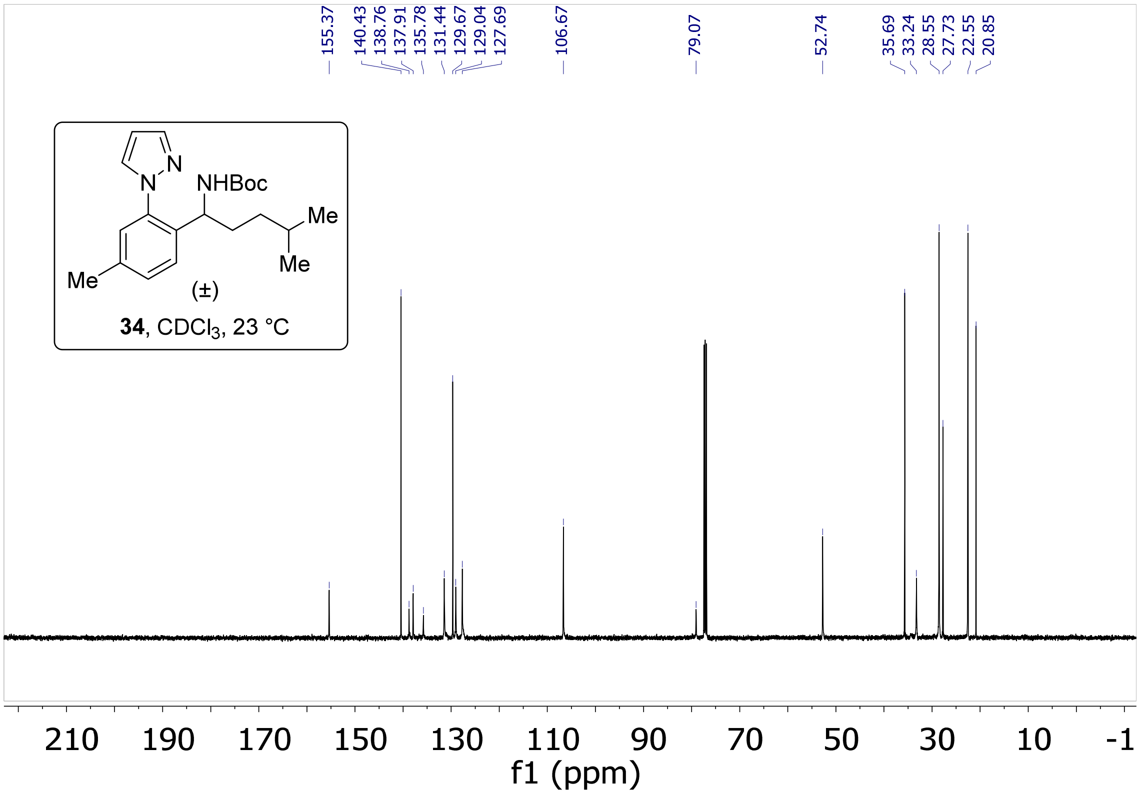
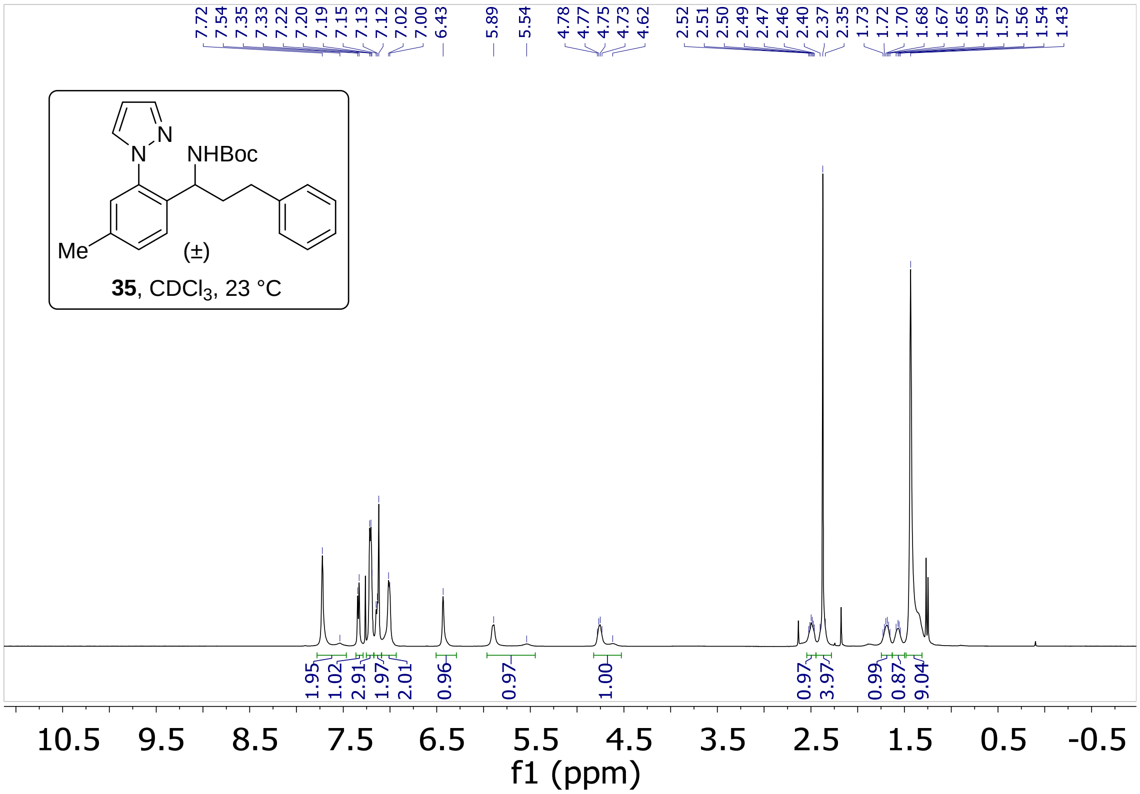
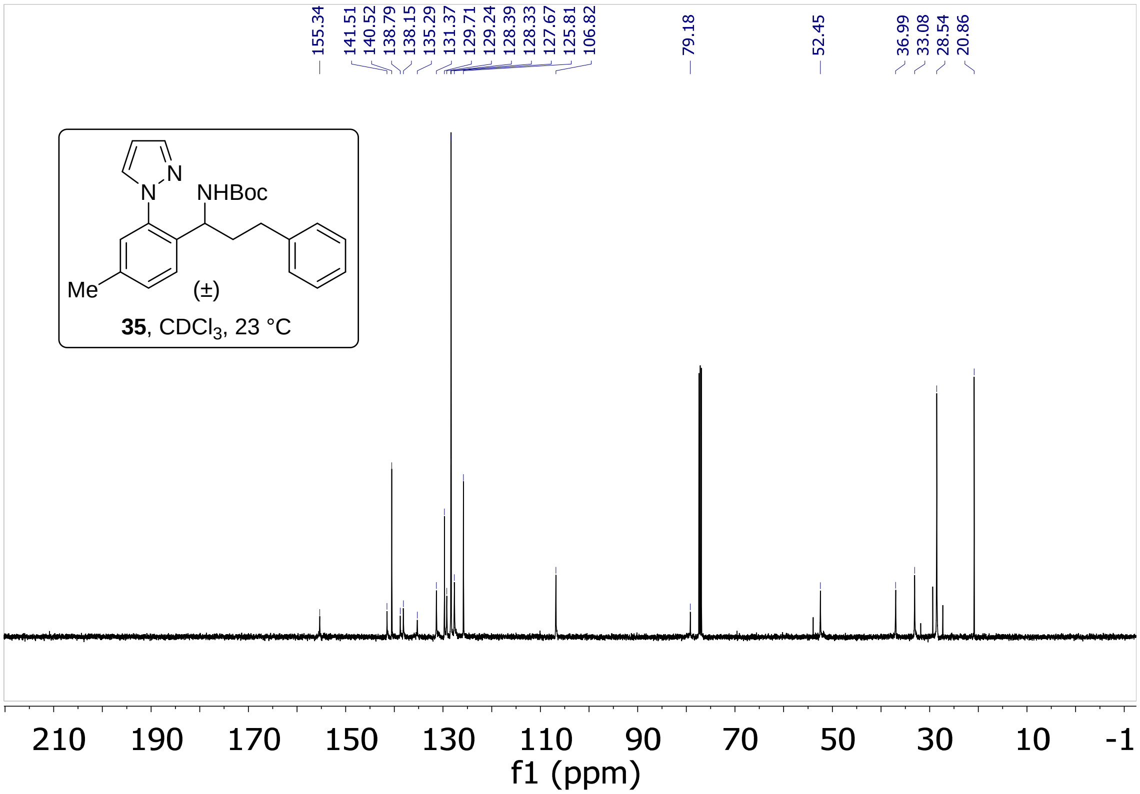
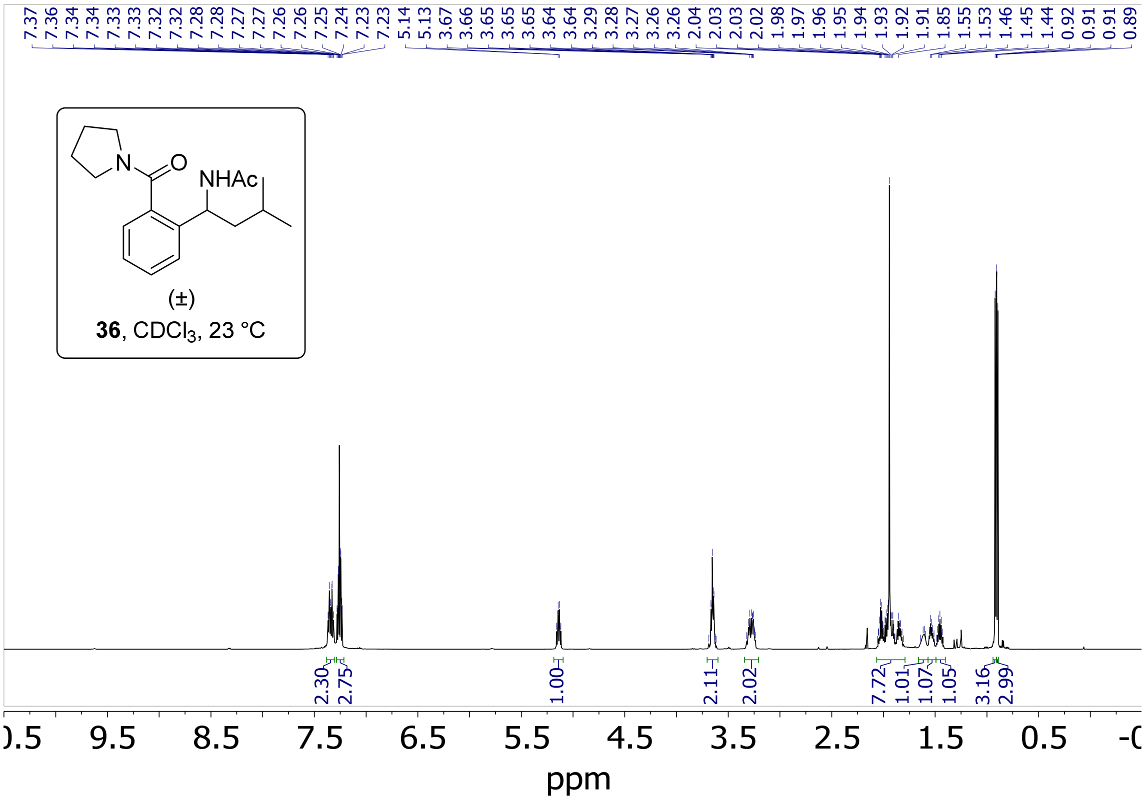
7.71
7.31
7.29
7.19
7.17
7.09
6.43
5.78
5.13
4.66
4.64
4.63
4.61
4.52
2.35
1.40
1.33
1.32
1.31
1.25
1.23
1.21
1.07
1.06
1.05
1.04
1.02
1.01
1.00
0.90
0.89
0.88
0.87
0.86
0.84
0.73
0.71
NHBoc
N
N
Me
Me
Me
(±)
34, CDCl3, 23 °C
0.84
1.01
1.01
0.99
0.98
1.00
1.02
1.03
3.06
9.19
2.17
1.03
1.03
1.05
6.16
0.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


155.37
140.43
138.76
137.91
135.78
131.44
129.67
129.04
127.69
106.67
79.07
52.74
35.69
33.24
28.55
27.73
22.55
20.85
NHBoc
N
N
Me
Me
Me
(±)
34, CDCl3, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)


7.72
7.54
7.35
7.33
7.22
7.20
7.19
7.15
7.13
7.12
7.02
7.00
6.43
5.89
5.54
4.78
4.77
4.75
4.73
4.62
2.52
2.51
2.50
2.49
2.47
2.46
2.40
2.37
2.35
1.73
1.72
1.70
1.68
1.67
1.65
1.59
1.57
1.56
1.54
1.43
NHBoc
N
N
Me
(±)
35, CDCl3, 23 °C
1.95
1.02
2.91
1.97
2.01
0.96
0.97
1.00
0.97
3.97
0.99
0.87
9.04
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


155.34
141.51
140.52
138.79
138.15
135.29
131.37
129.71
129.24
128.39
128.33
127.67
125.81
106.82
79.18
52.45
36.99
33.08
28.54
20.86
NHBoc
N
N
Me
(±)
35, CDCl3, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)


7.37
7.36
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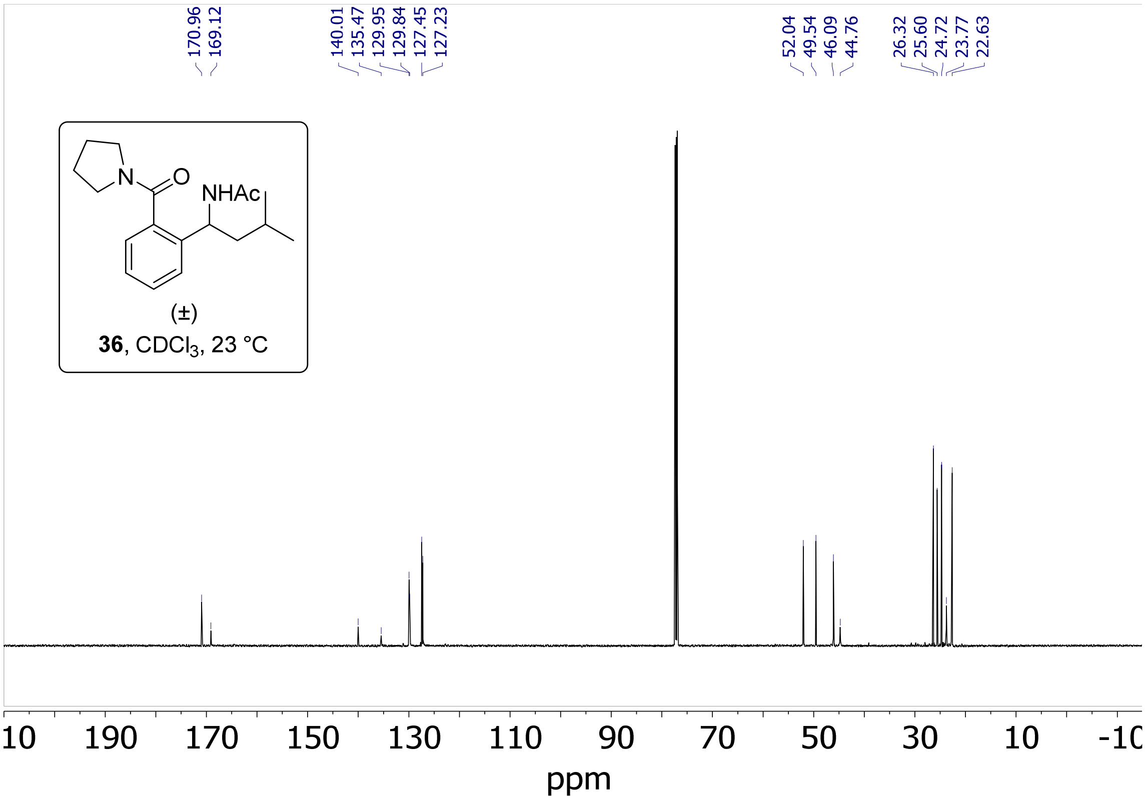
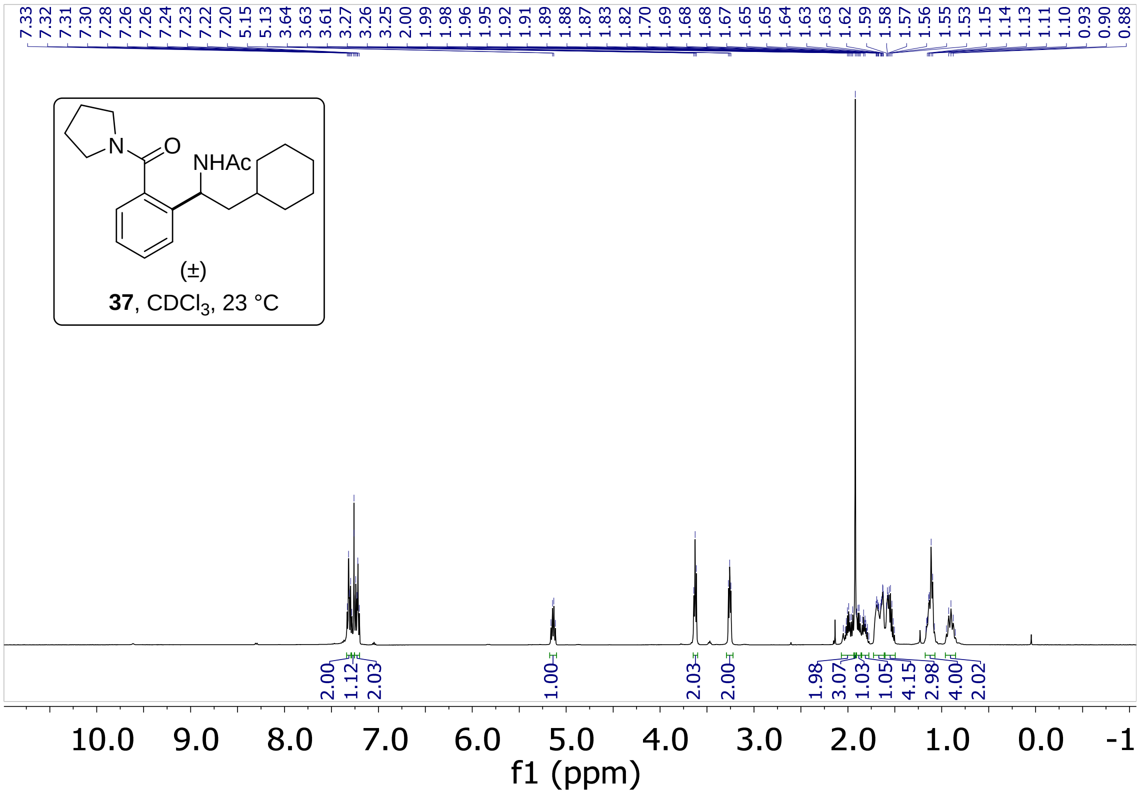
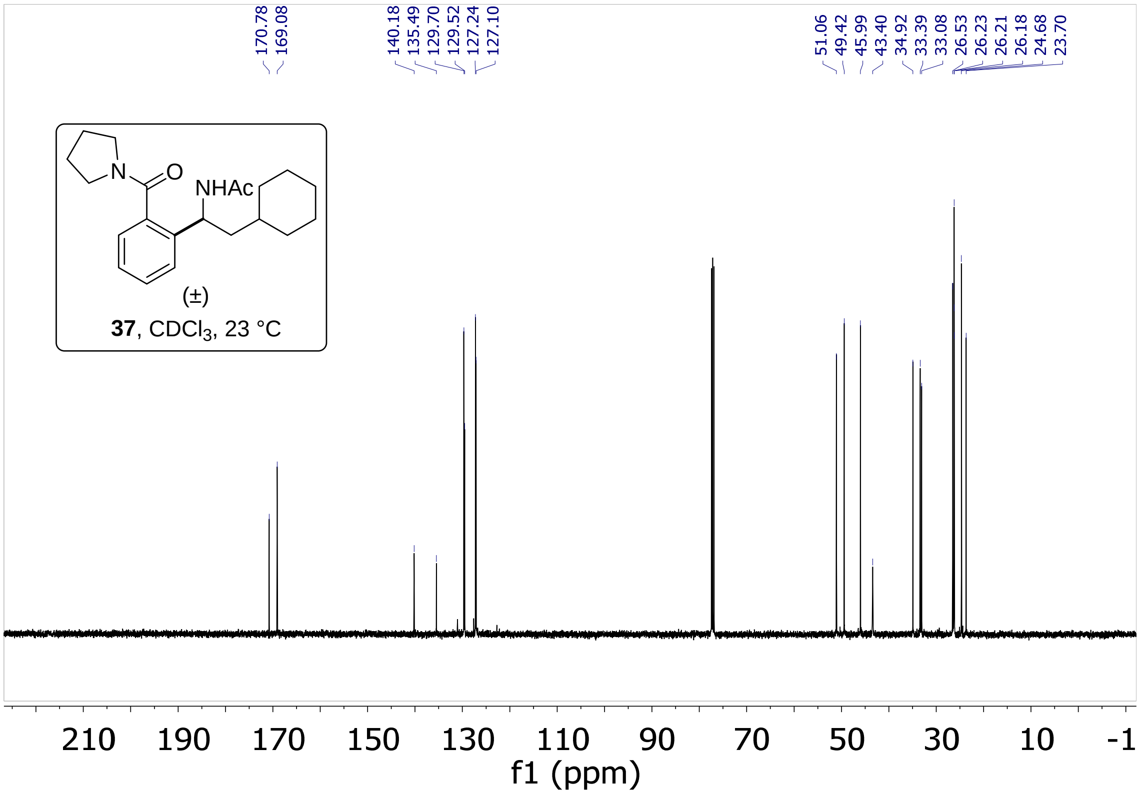
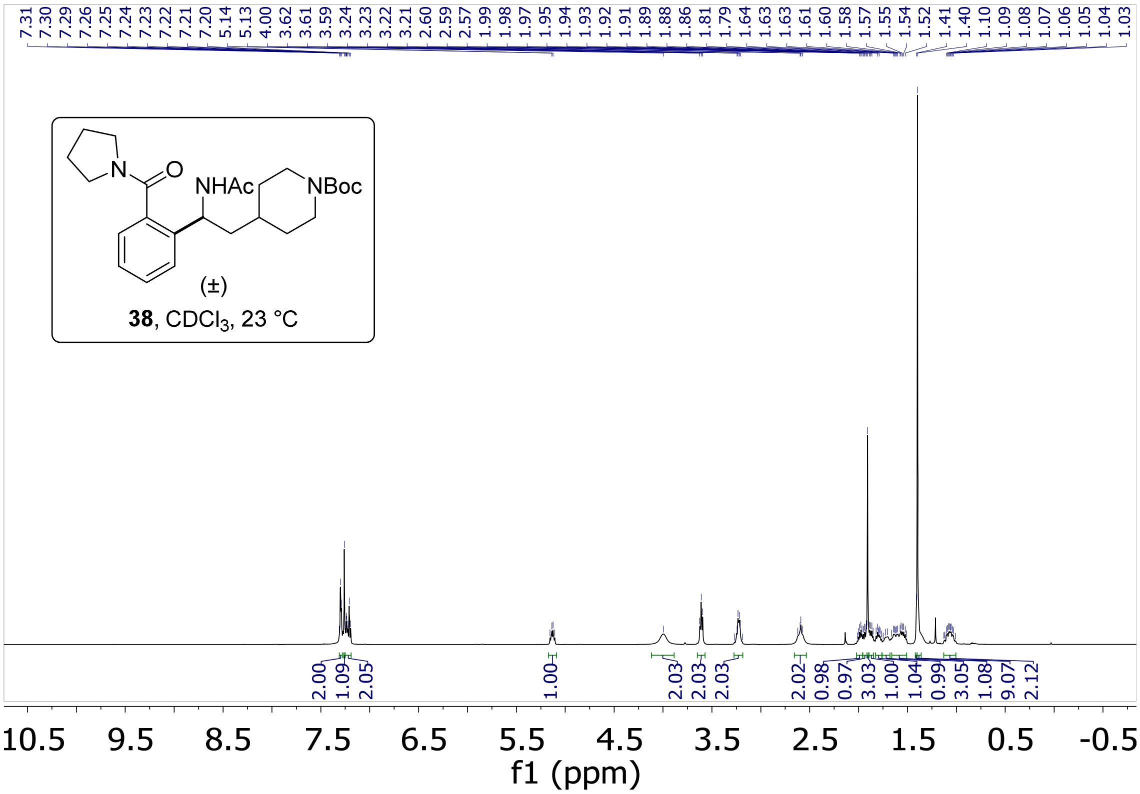
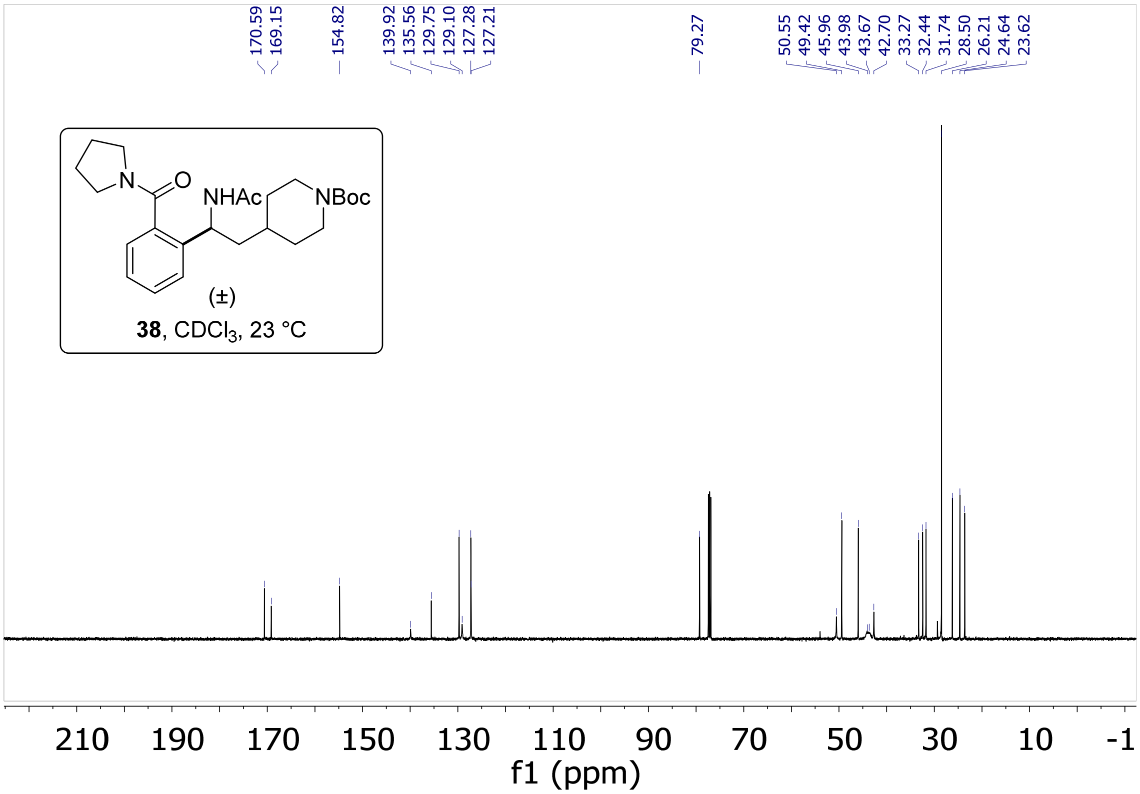
7.33
7.33
7.32
7.32
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.23
7.23
5.14
5.13
3.67
3.66
3.65
3.65
3.64
3.64
3.29
3.28
3.27
3.26
3.26
2.04
2.03
2.03
2.02
1.98
1.97
1.96
1.95
1.94
1.93
1.92
1.91
1.85
1.55
1.53
1.46
1.45
1.44
0.92
0.91
0.91
0.89
N
O
NHAc
(±)
36, $CDCl_3$, 23 °C
2.30
2.75
1.00
2.11
2.02
7.72
1.01
1.07
1.05
3.16
2.99
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm

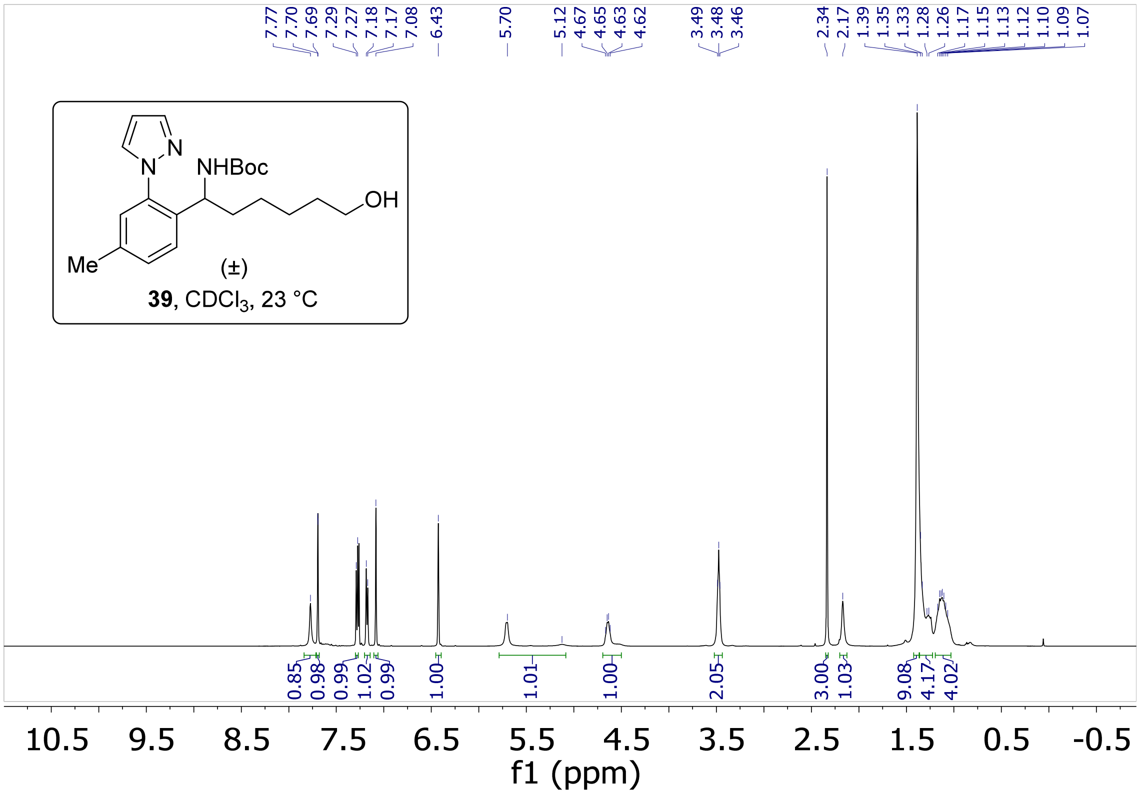

170.96
169.12
140.01
135.47
129.95
129.84
127.45
127.23
52.04
49.54
46.09
44.76
26.32
25.60
24.72
23.77
22.63
N
O
NHAc
(±)
36, $CDCl_3$, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm

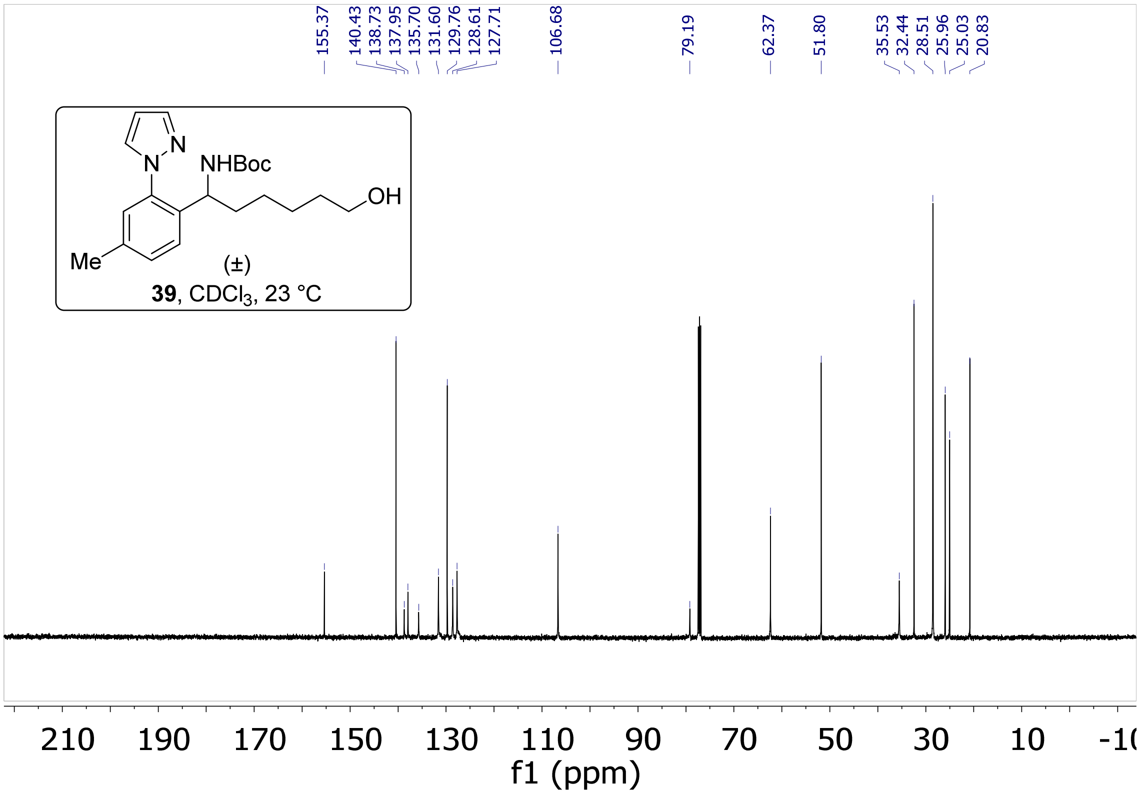

7.33
7.32
7.31
7.30
7.28
7.26
7.26
7.24
7.23
7.22
7.20
5.15
5.13
3.64
3.63
3.61
3.27
3.26
3.25
2.00
1.99
1.98
1.96
1.95
1.92
1.91
1.89
1.88
1.87
1.83
1.82
1.70
1.69
1.68
1.68
1.67
1.65
1.65
1.64
1.63
1.63
1.62
1.59
1.58
1.57
1.56
1.55
1.53
1.15
1.14
1.13
1.11
1.10
0.93
0.90
0.88
N
O
NHAc
(±)
37, CDCl$_3$, 23 °C
2.00
1.12
2.03
1.00
2.03
2.00
1.98
3.07
1.03
1.05
4.15
2.98
4.00
2.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)

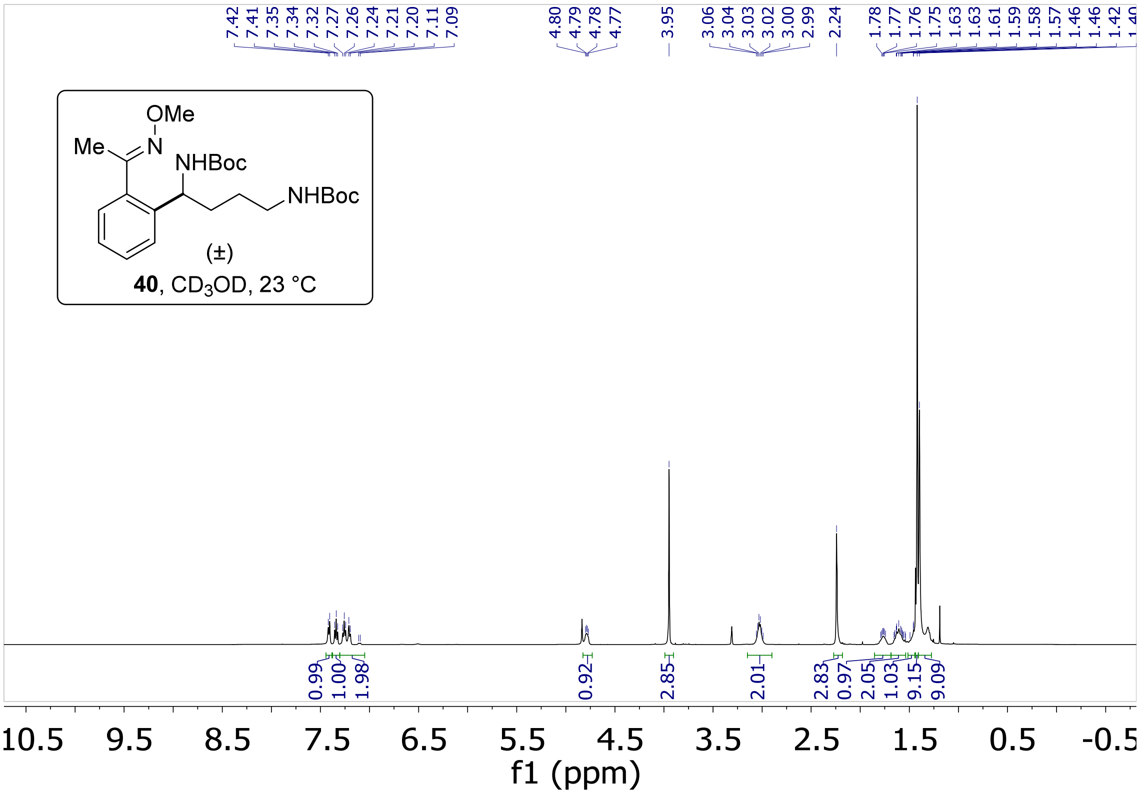

170.78
169.08
140.18
135.49
129.70
129.52
127.24
127.10
51.06
49.42
45.99
43.40
34.92
33.39
33.08
26.53
26.23
26.21
26.18
24.68
23.70
N
O
NHAc
(±)
37, CDCl$_3$, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

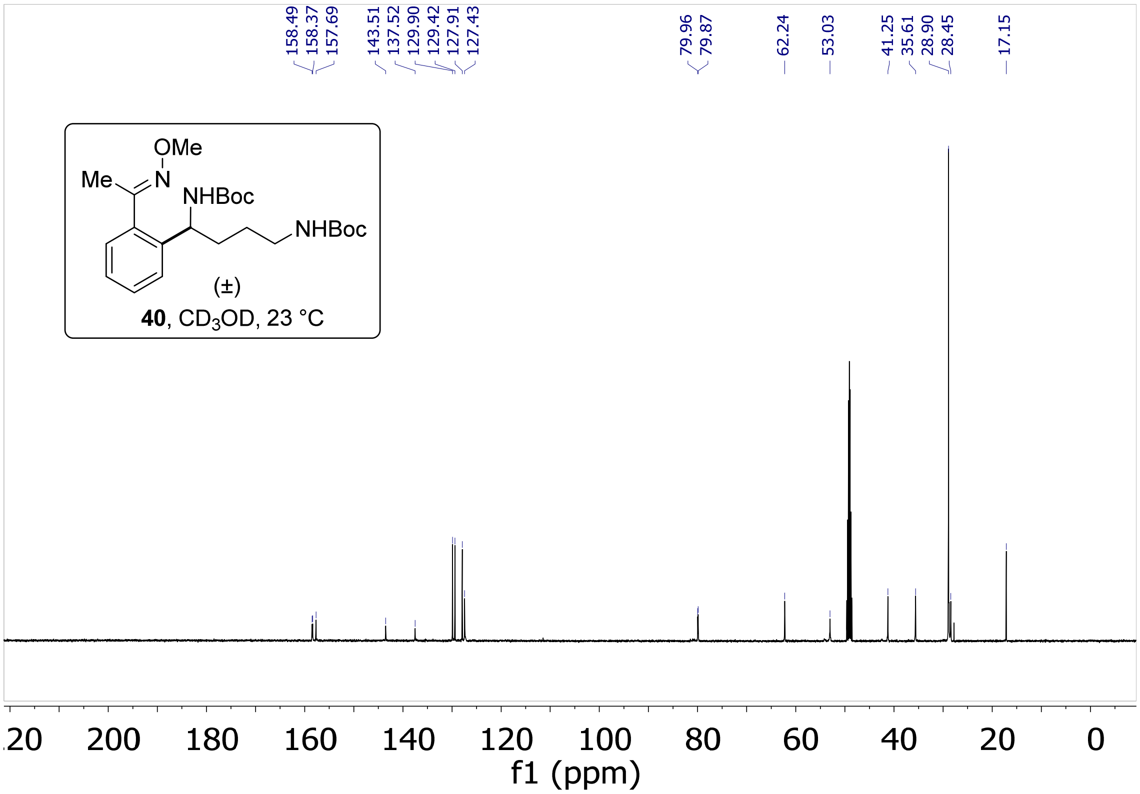

7.31 7.30 7.29 7.26 7.25 7.24 7.23 7.22 7.21 7.20 5.14 5.13 4.00 3.62 3.61 3.59 3.24 3.23 3.22 3.21 2.60 2.59 2.57 1.99 1.98 1.97 1.95 1.94 1.93 1.92 1.91 1.89 1.88 1.86 1.81 1.79 1.64 1.63 1.63 1.61 1.60 1.58 1.57 1.55 1.54 1.52 1.41 1.40 1.10 1.09 1.08 1.07 1.06 1.05 1.04 1.03
NHAc
NBoc
N
O
(±)
38, CDCl$_3$, 23 °C
2.00 1.09 2.05
1.00
2.03 2.03 2.03
2.02 0.98 0.97 3.03 1.00 1.04 0.99 3.05 1.08 9.07 2.12
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

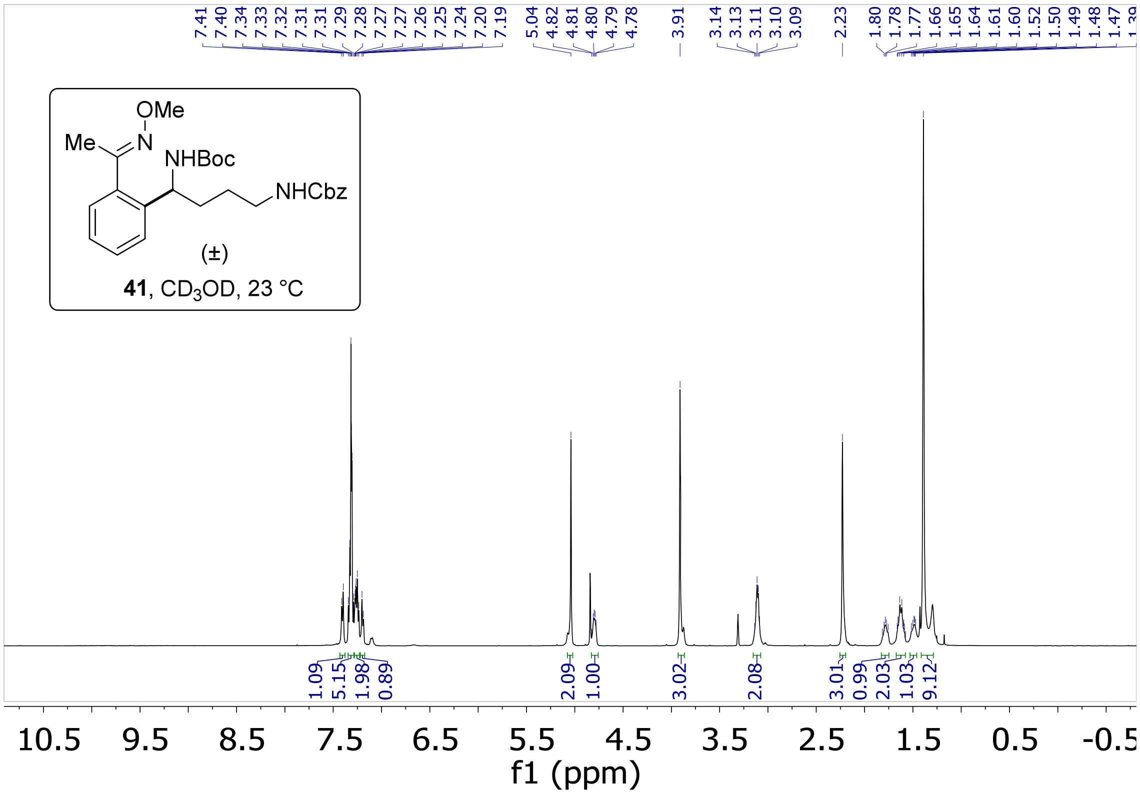

170.59 169.15
154.82
139.92 135.56 129.75 129.10 127.28 127.21
79.27
50.55 49.42 45.96 43.98 43.67 42.70 33.27 32.44 31.74 28.50 26.21 24.64 23.62
NHAc
NBoc
N
O
(±)
38, CDCl$_3$, 23 °C
210 190 170 150 130 110 90 70 50 30 10 -1
f1 (ppm)

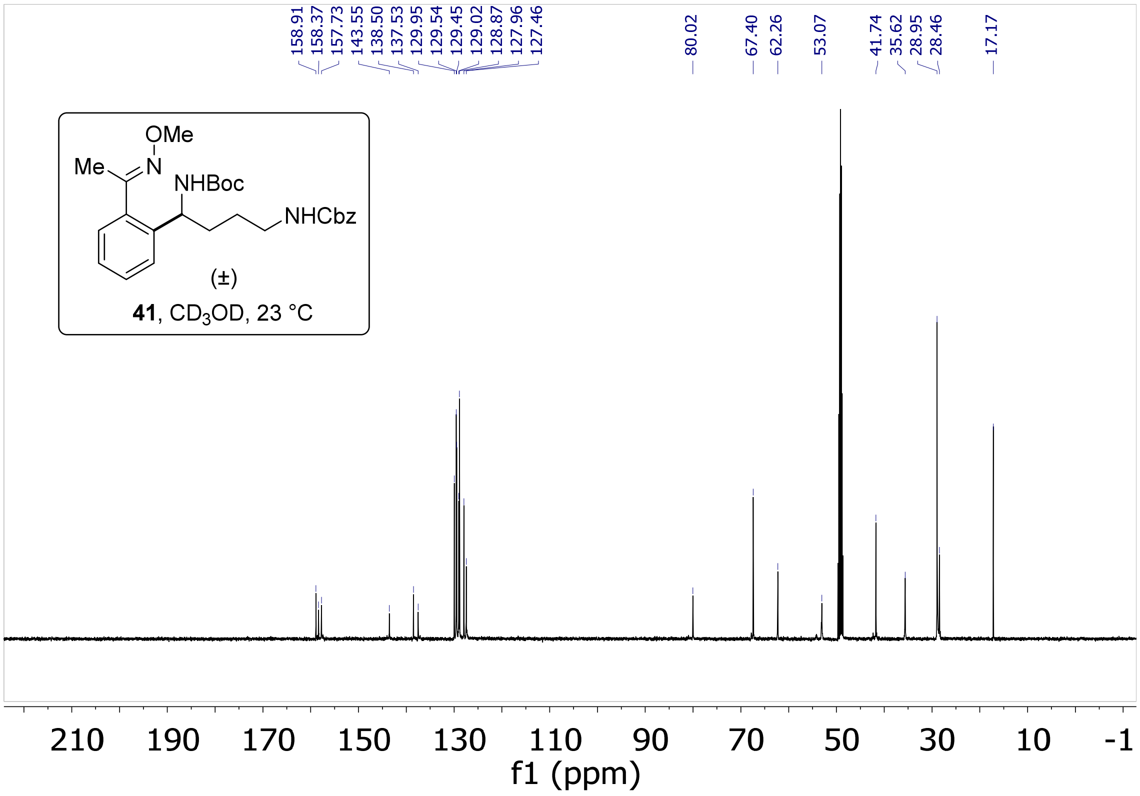

7.77
7.70
7.69
7.29
7.27
7.18
7.17
7.08
6.43
5.70
5.12
4.67
4.65
4.63
4.62
3.49
3.48
3.46
2.34
2.17
1.39
1.35
1.33
1.28
1.26
1.17
1.15
1.13
1.12
1.10
1.09
1.07
NHBoc
N
N
OH
Me
(±)
39, CDCl$_3$, 23 °C
0.85
0.98
0.99
1.02
0.99
1.00
1.01
1.00
2.05
3.00
1.03
9.08
4.17
4.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

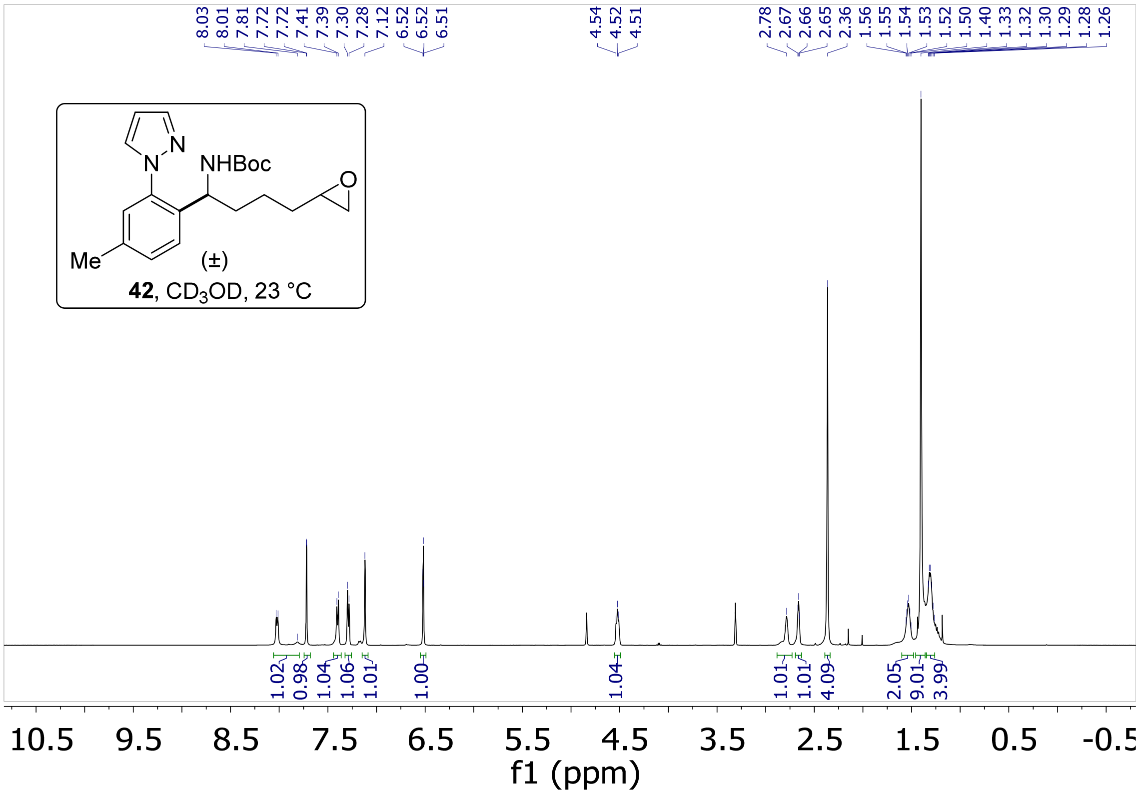

155.37
140.43
138.73
137.95
135.70
131.60
129.76
128.61
127.71
106.68
79.19
62.37
51.80
35.53
32.44
28.51
25.96
25.03
20.83
NHBoc
N
N
OH
Me
(±)
39, CDCl$_3$, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

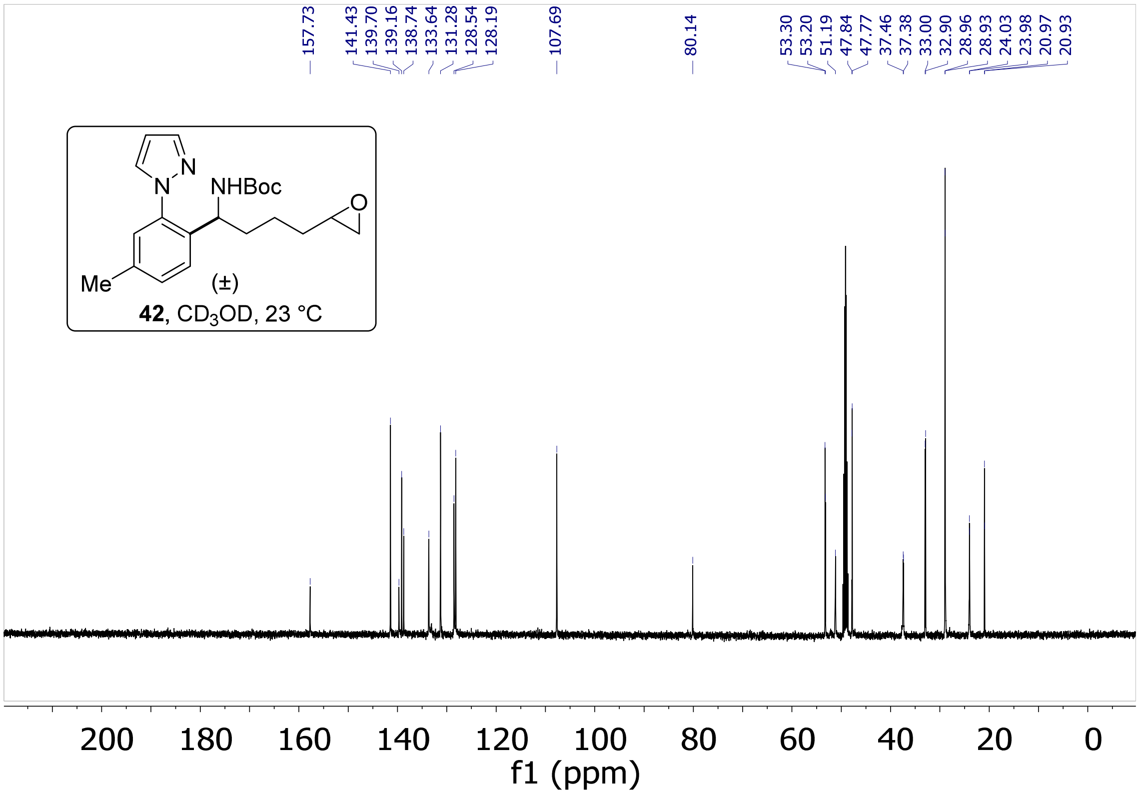

7.42
7.41
7.35
7.34
7.32
7.27
7.26
7.24
7.21
7.20
7.11
7.09
4.80
4.79
4.78
4.77
3.95
3.06
3.04
3.03
3.02
3.00
2.99
2.24
1.78
1.77
1.76
1.75
1.63
1.63
1.61
1.59
1.58
1.57
1.46
1.46
1.42
OMe
Me
N
NHBoc
NHBoc
(±)
40, CD$_3$OD, 23 °C
0.99
1.00
1.98
0.92
2.85
2.01
2.83
0.97
2.05
1.03
9.15
9.09
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

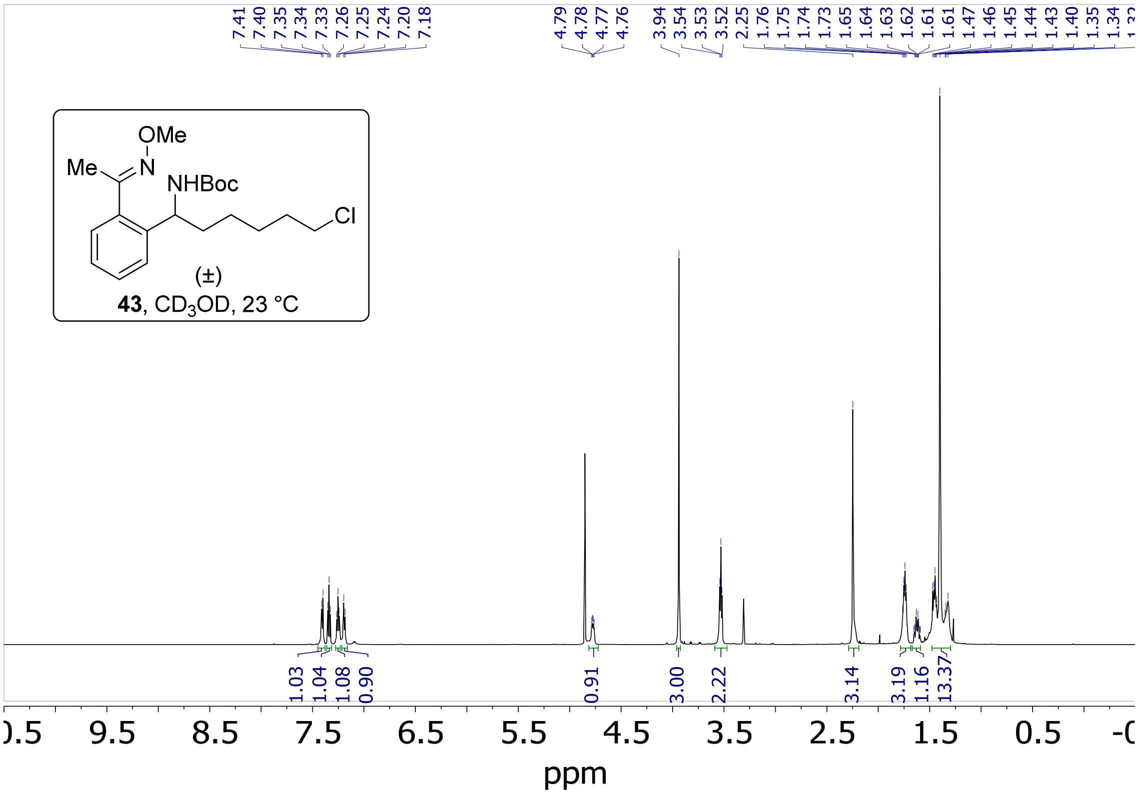

158.49
158.37
157.69
143.51
137.52
129.90
129.42
127.91
127.43
79.96
79.87
62.24
53.03
41.25
35.61
28.90
28.45
17.15
OMe
Me
N
NHBoc
NHBoc
(±)
40, CD$_3$OD, 23 °C
20
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

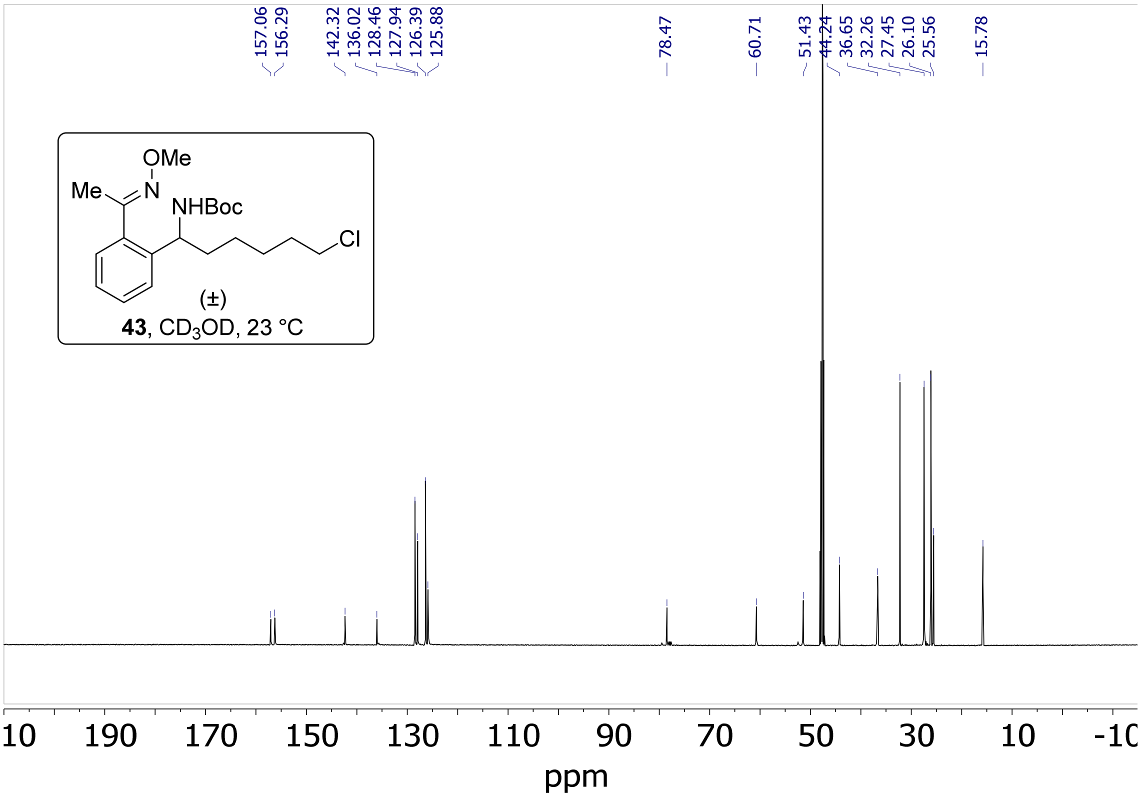

7.41
7.40
7.34
7.33
7.32
7.31
7.31
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.20
7.19
5.04
4.82
4.81
4.80
4.79
4.78
3.91
3.14
3.13
3.11
3.10
3.09
2.23
1.80
1.78
1.77
1.66
1.65
1.64
1.61
1.60
1.52
1.50
1.49
1.48
1.47
OMe
Me
N
NHBoc
NHCbz
(±)
41, CD_3OD, 23 °C
1.09
5.15
1.98
0.89
2.09
1.00
3.02
2.08
3.01
0.99
2.03
1.03
9.12
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

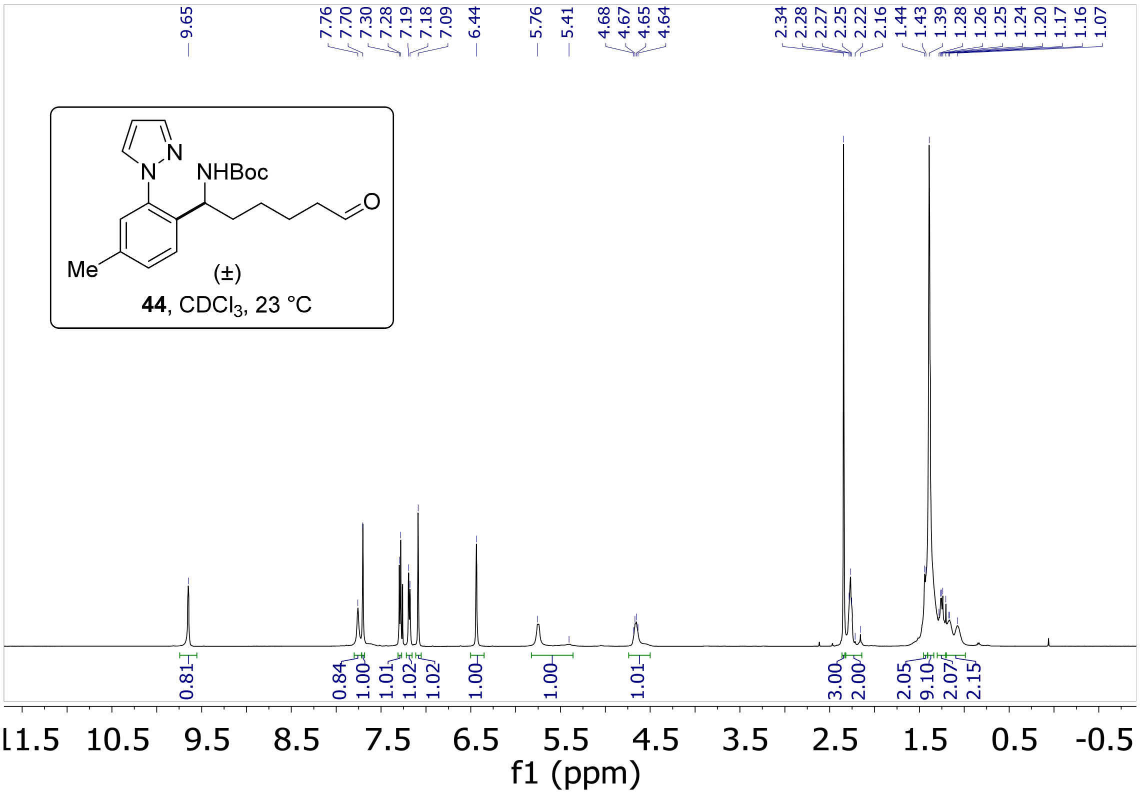

158.91
158.37
157.73
143.55
138.50
137.53
129.95
129.54
129.45
129.02
128.87
127.96
127.46
80.02
67.40
62.26
53.07
41.74
35.62
28.95
28.46
17.17
OMe
Me
N
NHBoc
NHCbz
(±)
41, CD_3OD, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

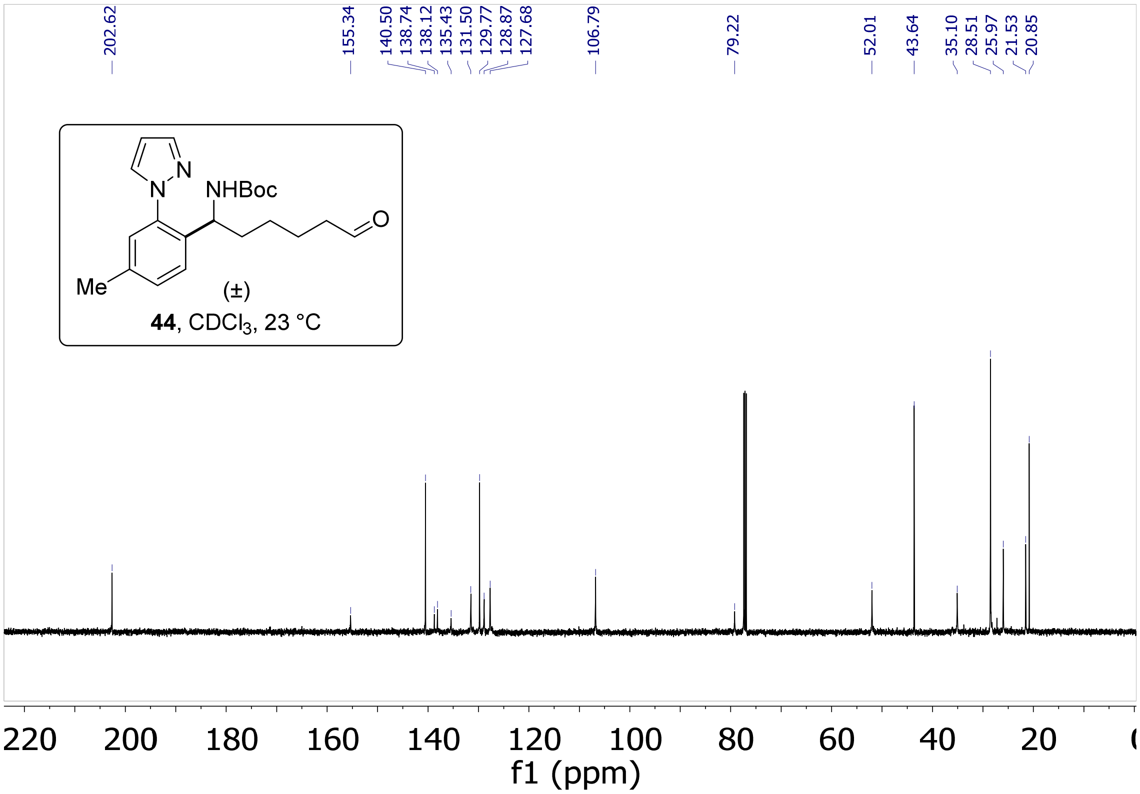

8.03
8.01
7.81
7.72
7.72
7.41
7.39
7.30
7.28
7.12
6.52
6.52
6.51
4.54
4.52
4.51
2.78
2.67
2.66
2.65
2.36
1.56
1.55
1.54
1.53
1.52
1.50
1.40
1.33
1.32
1.30
1.29
1.28
1.26
N
N
NHBoc
O
Me
(±)
42, CD$_3$OD, 23 °C
1.02
0.98
1.04
1.06
1.01
1.00
1.04
1.01
1.01
4.09
2.05
9.01
3.99
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

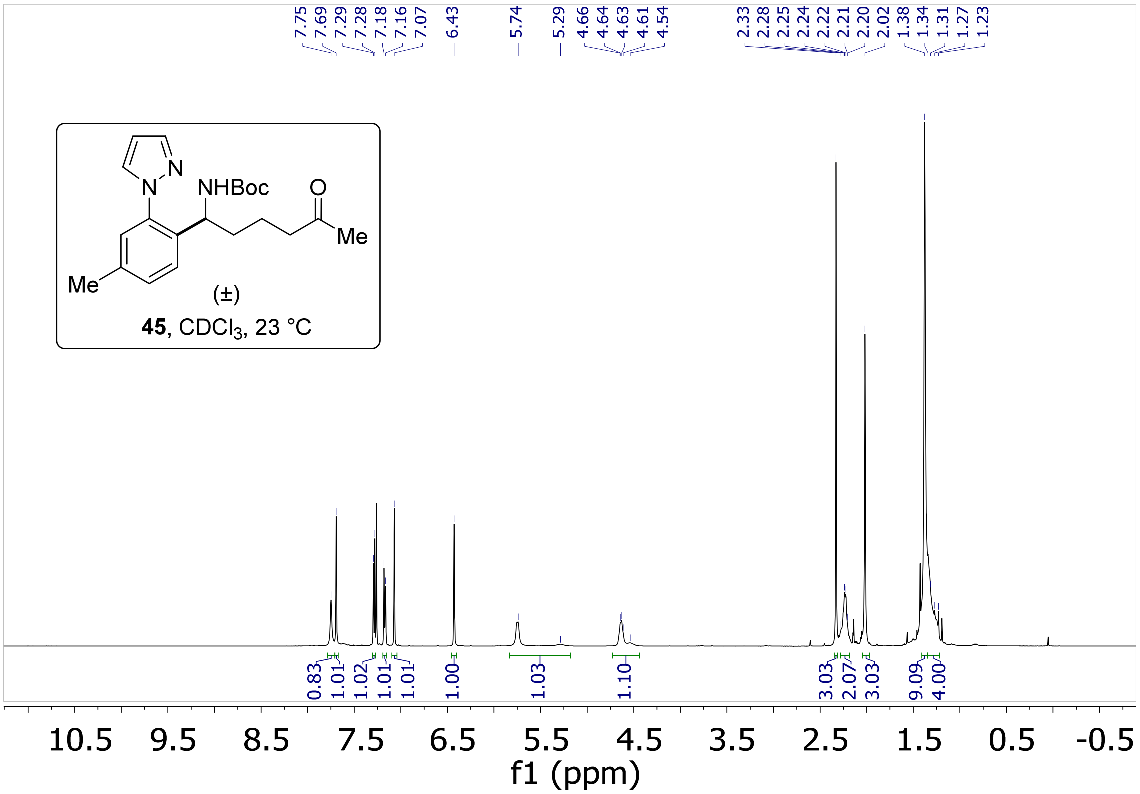

157.73
141.43
139.70
139.16
138.74
133.64
131.28
128.54
128.19
107.69
80.14
53.30
53.20
51.19
47.84
47.77
37.46
37.38
33.00
32.90
28.96
28.93
24.03
23.98
20.97
20.93
N
N
NHBoc
O
Me
(±)
42, CD$_3$OD, 23 °C
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

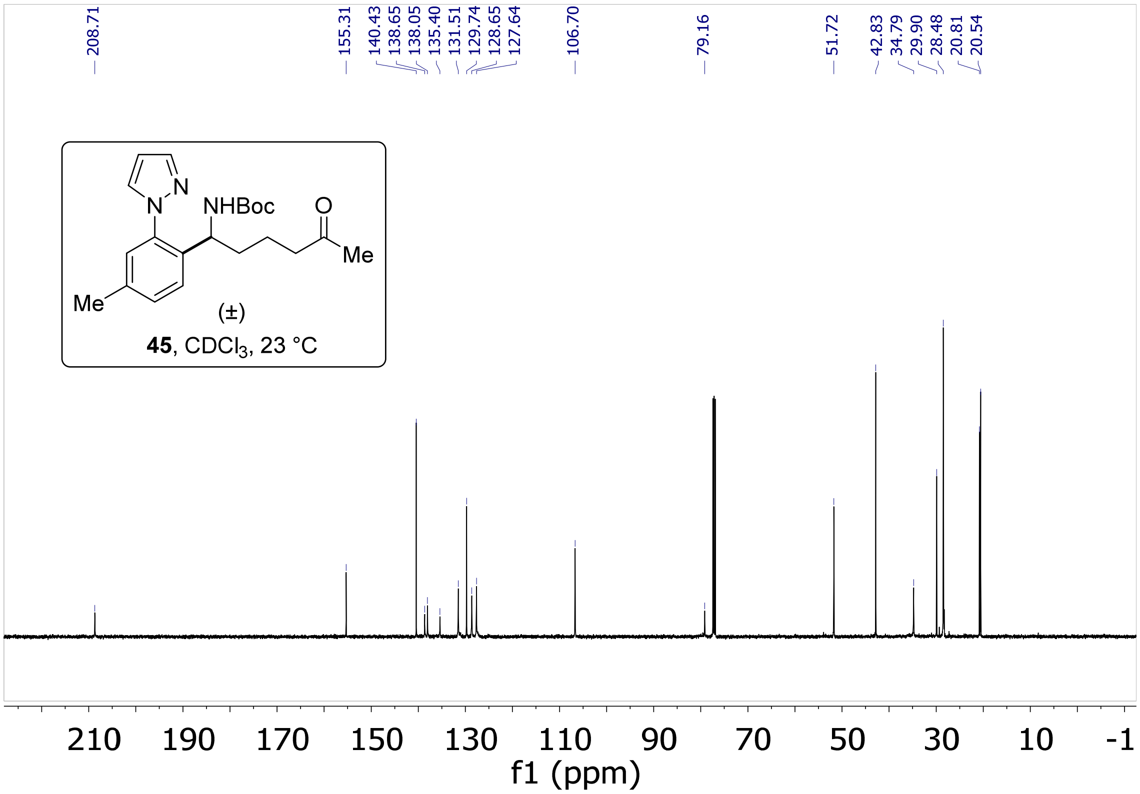

7.41
7.40
7.35
7.34
7.33
7.26
7.25
7.24
7.20
7.18
4.79
4.78
4.77
4.76
3.94
3.54
3.53
3.52
2.25
1.76
1.75
1.74
1.73
1.65
1.64
1.63
1.62
1.61
1.61
1.47
1.46
1.45
1.44
1.43
1.40
1.35
1.34
OMe
Me
N
NHBoc
Cl
(±)
43, CD3OD, 23 °C
1.03
1.04
1.08
0.90
0.91
3.00
2.22
3.14
3.19
1.16
13.37
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm

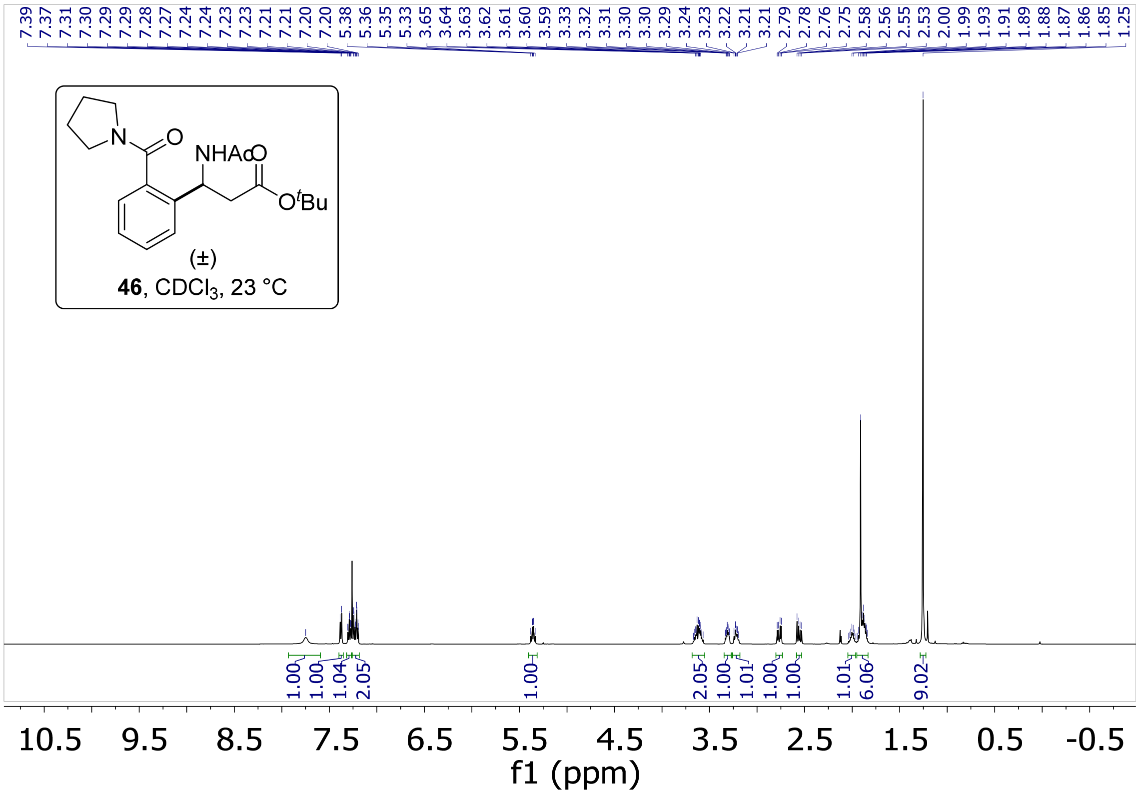

157.06
156.29
142.32
136.02
128.46
127.94
126.39
125.88
78.47
60.71
51.43
44.24
36.65
32.26
27.45
26.10
25.56
15.78
OMe
Me
N
NHBoc
Cl
(±)
43, CD3OD, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm

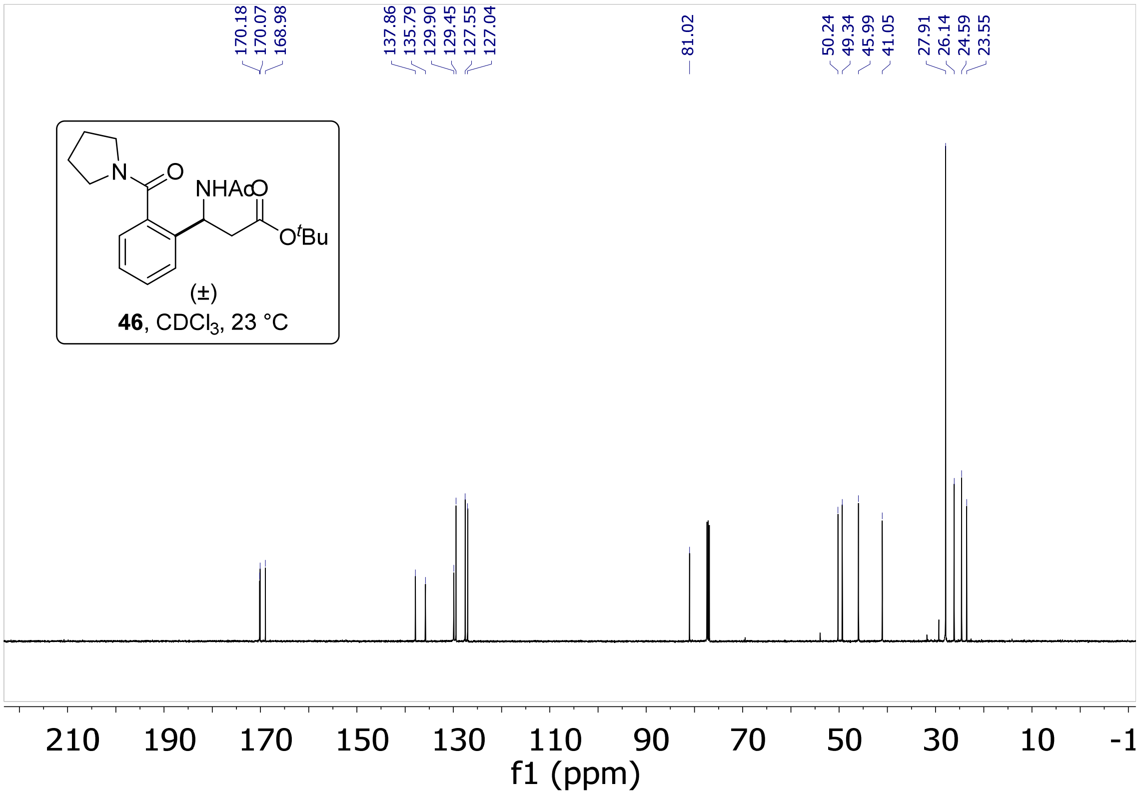

9.65
7.76 7.70 7.30 7.28 7.19 7.18 7.09
6.44
5.76
5.41
4.68 4.67 4.65 4.64
2.34 2.28 2.27 2.25 2.22 2.16 1.44 1.43 1.39 1.28 1.26 1.25 1.24 1.20 1.17 1.16 1.07
NHBoc
N
N
O
Me
(±)
44, CDCl3, 23 °C
0.81
0.84 1.00 1.01 1.02 1.02
1.00
1.00
1.01
3.00 2.00
2.05 9.10 2.07 2.15
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

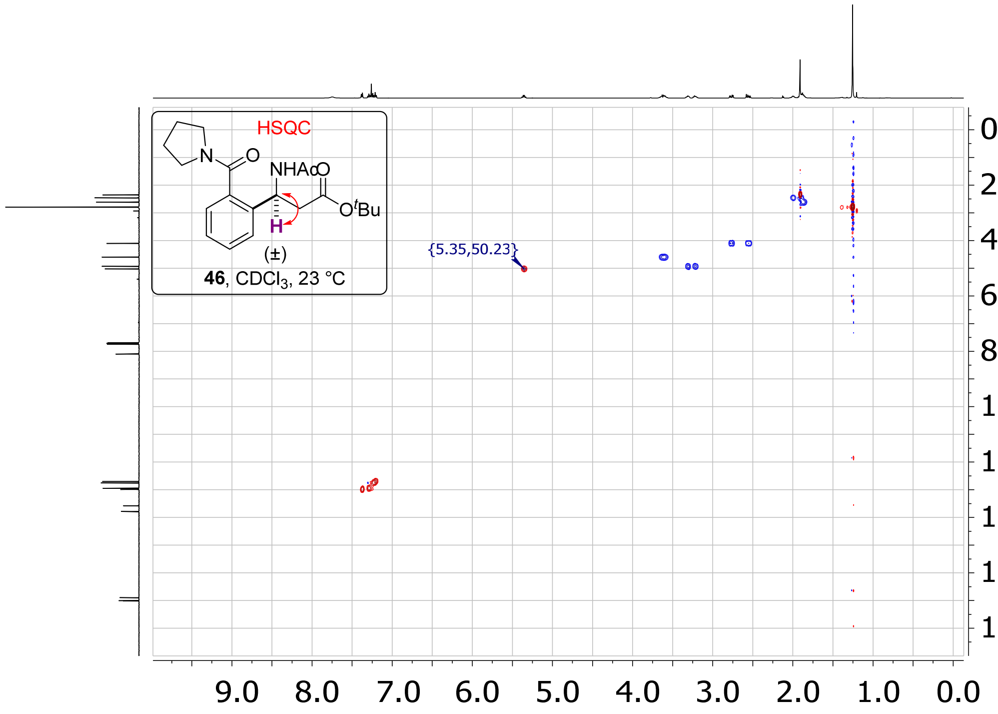

202.62
155.34
140.50 138.74 138.12 135.43 131.50 129.77 128.87 127.68
106.79
79.22
52.01
43.64
35.10 28.51 25.97 21.53 20.85
NHBoc
N
N
O
Me
(±)
44, CDCl3, 23 °C
220 200 180 160 140 120 100 80 60 40 20
f1 (ppm)

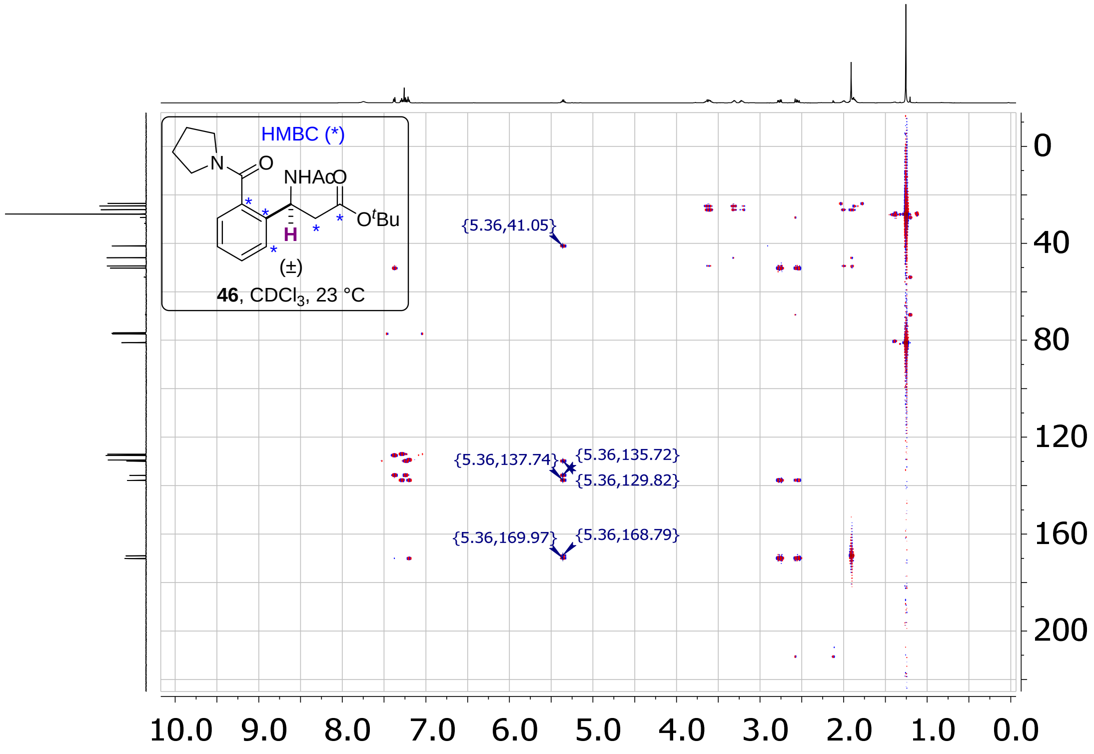

7.75 7.69 7.29 7.28 7.18 7.16 7.07 6.43 5.74 5.29 4.66 4.64 4.63 4.61 4.54 2.33 2.28 2.25 2.24 2.22 2.21 2.20 2.02 1.38 1.34 1.31 1.27 1.23
NHBoc
N
N
O
Me
Me
(±)
45, CDCl3, 23 °C
0.83 1.01 1.02 1.01 1.01 1.00 1.03 1.10 3.03 2.07 3.03 9.09 4.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

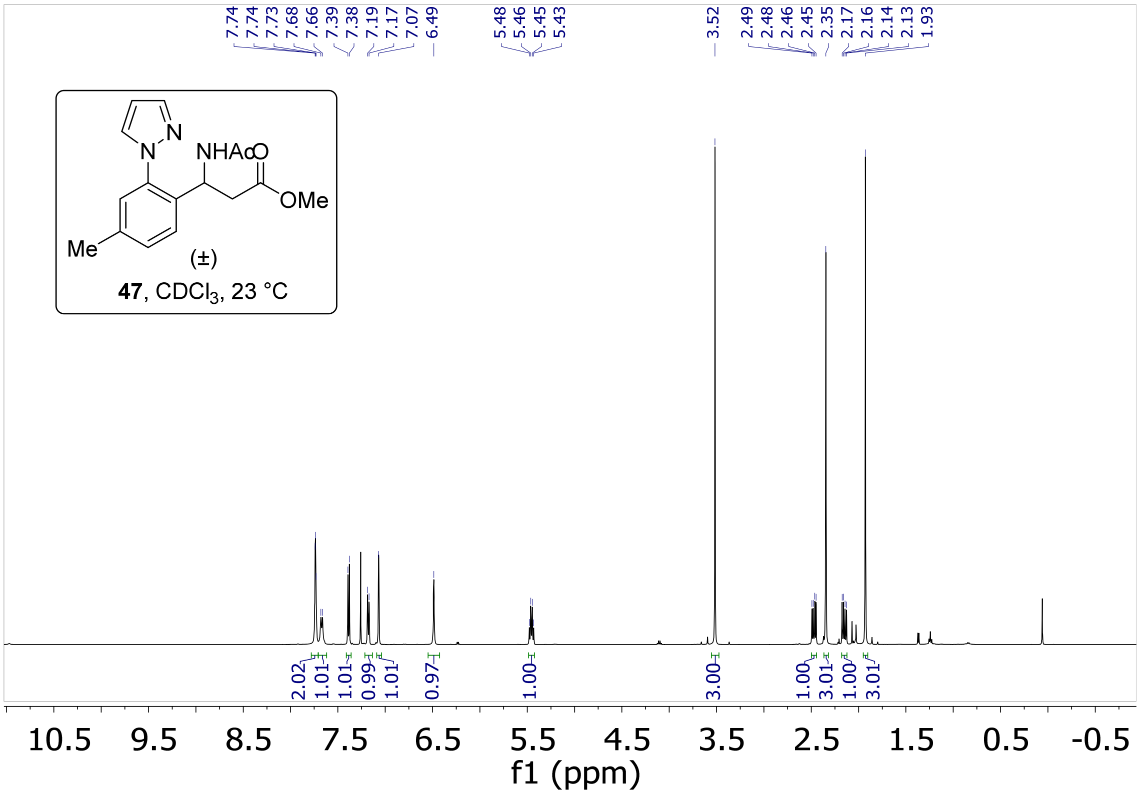

208.71 155.31 140.43 138.65 138.05 135.40 131.51 129.74 128.65 127.64 106.70 79.16 51.72 42.83 34.79 29.90 28.48 20.81 20.54
NHBoc
N
N
O
Me
Me
(±)
45, CDCl3, 23 °C
210 190 170 150 130 110 90 70 50 30 10 -1
f1 (ppm)

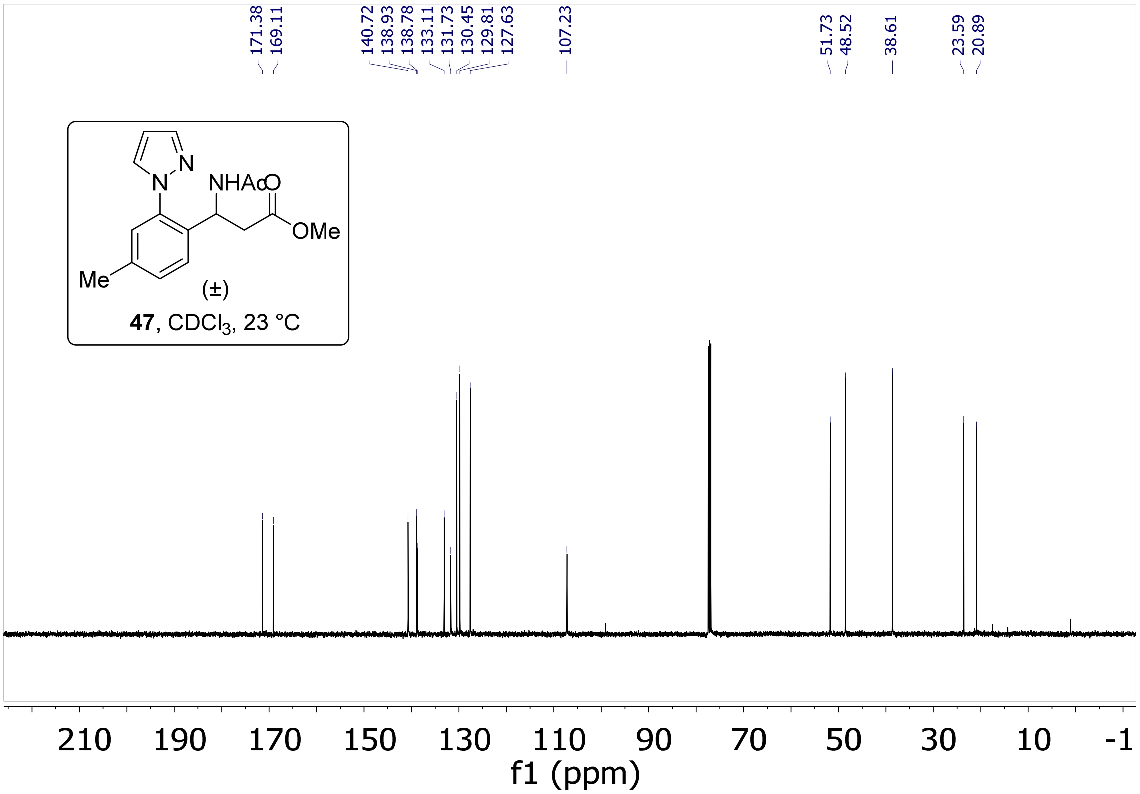

7.39
7.37
7.31
7.30
7.29
7.29
7.28
7.27
7.24
7.24
7.23
7.23
7.21
7.21
7.20
7.20
5.38
5.36
5.35
5.33
3.65
3.64
3.63
3.62
3.61
3.60
3.59
3.33
3.32
3.31
3.30
3.30
3.29
3.24
3.23
3.22
3.21
3.21
2.79
2.78
2.76
2.75
2.58
2.56
2.55
2.53
2.00
1.99
1.93
1.91
1.89
1.88
1.87
1.86
1.85
1.25
NHAc
O
N
O
O
^{t}Bu
(±)
46, CDCl$_3$, 23 °C
1.00
1.00
1.04
2.05
1.00
2.05
1.00
1.01
1.00
1.00
1.01
6.06
9.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

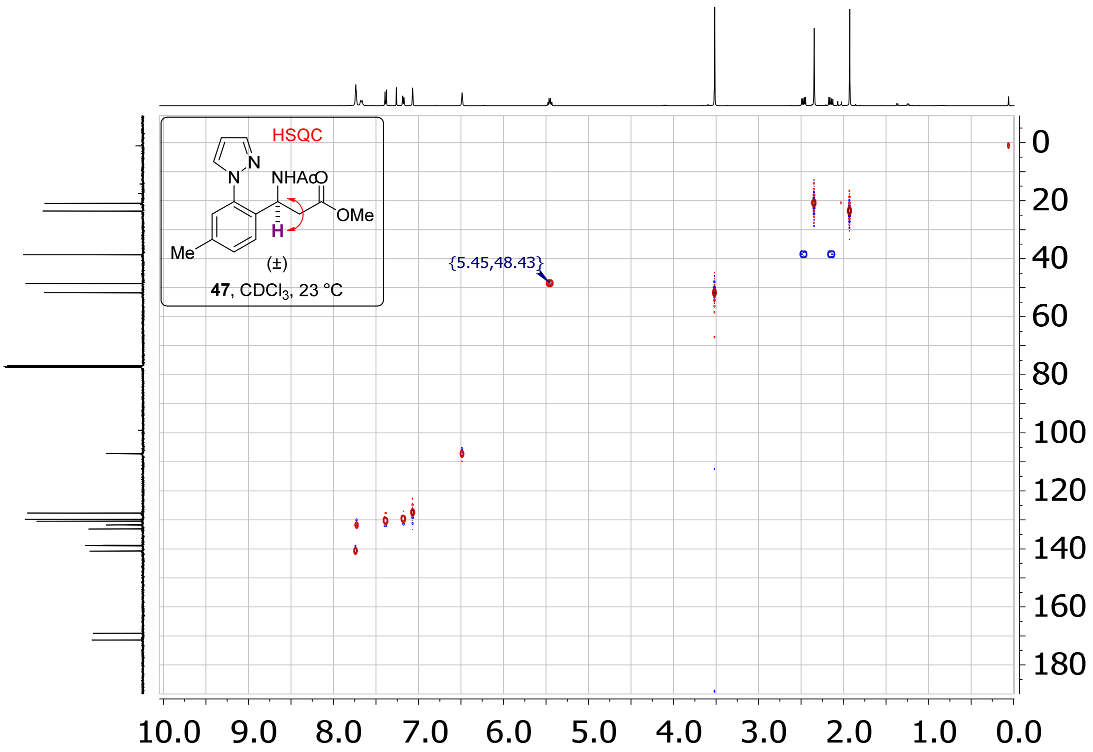

170.18
170.07
168.98
137.86
135.79
129.90
129.45
127.55
127.04
81.02
50.24
49.34
45.99
41.05
27.91
26.14
24.59
23.55
NHAc
O
N
O
O
^{t}Bu
(±)
46, CDCl$_3$, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

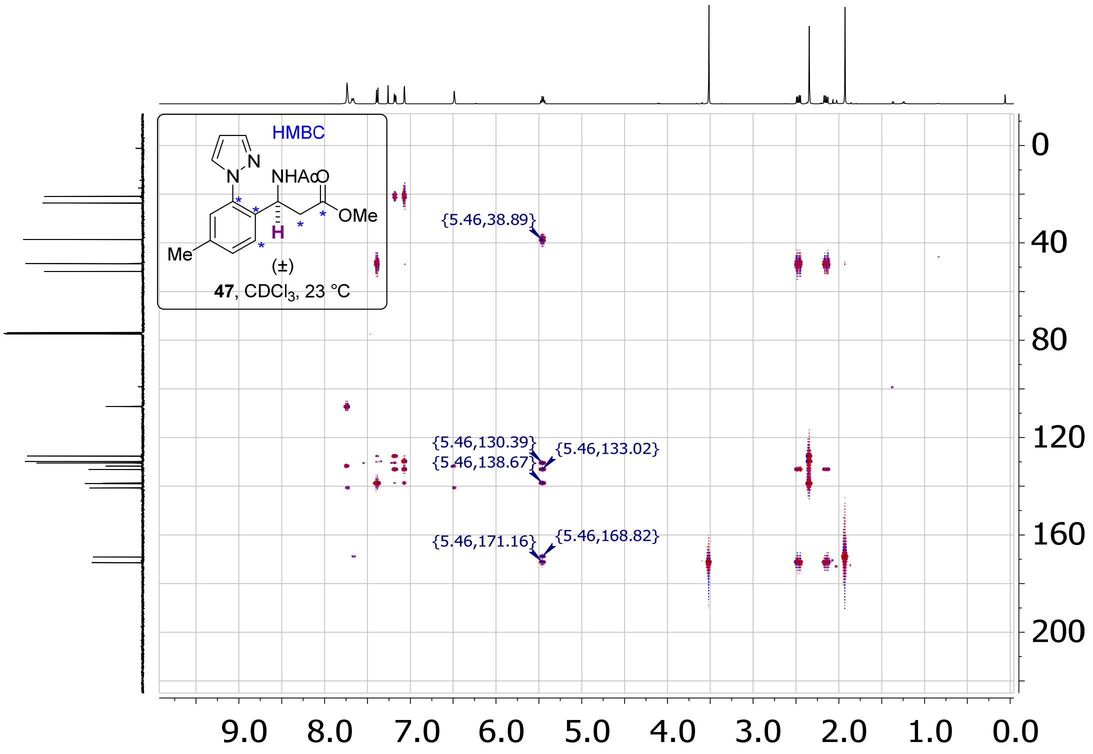

HSQC
N
O
NHAc
O
O^tBu
H
(±)
46, CDCl3, 23 °C
{5.35,50.23}
0
20
40
60
80
100
120
140
160
180
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

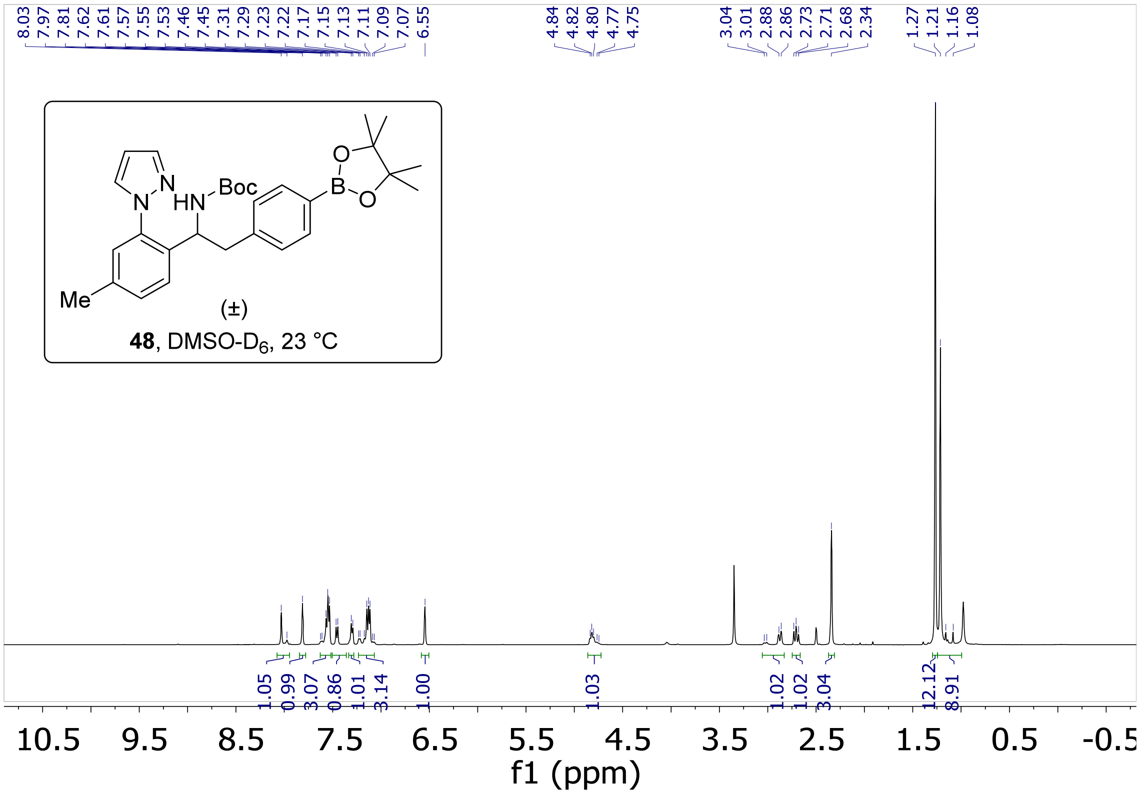

HMBC (*)
N
O
NHAc
O
O^tBu
H
(±)
46, CDCl3, 23 °C
{5.36,41.05}
{5.36,137.74}
{5.36,135.72}
{5.36,129.82}
{5.36,169.97}
{5.36,168.79}
0
40
80
120
160
200
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

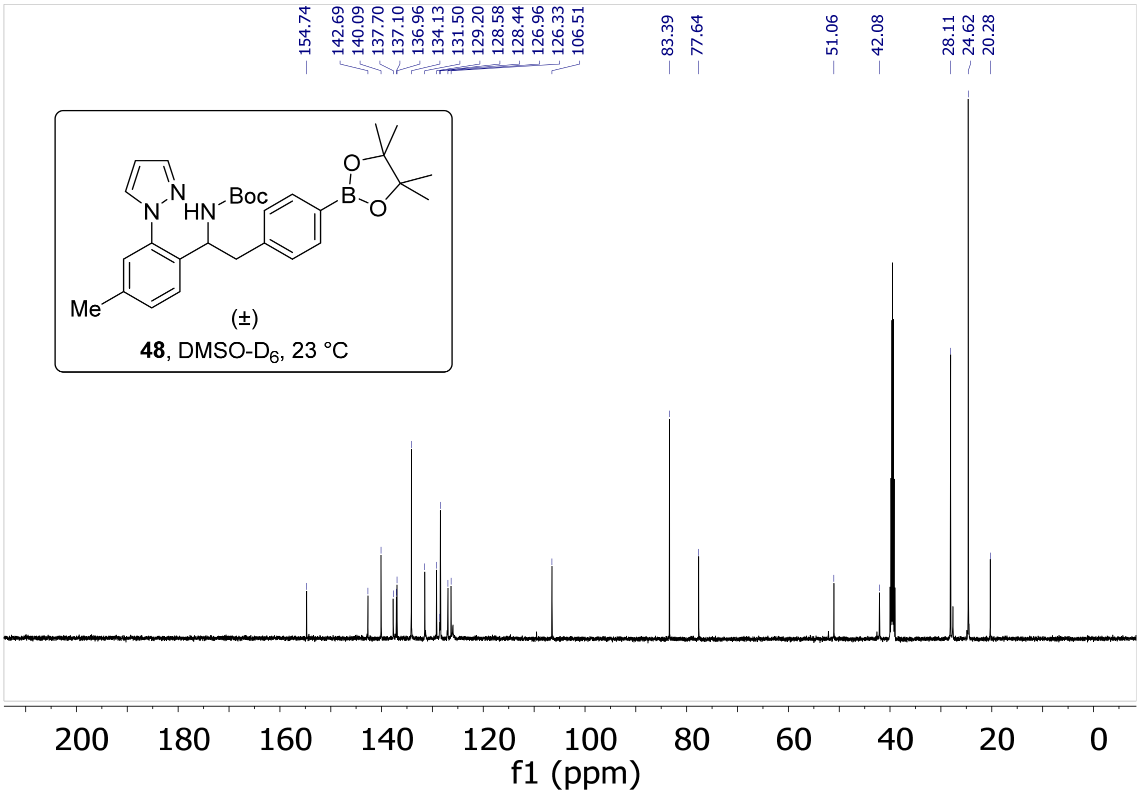

7.74
7.74
7.73
7.68
7.66
7.39
7.38
7.19
7.17
7.07
6.49
5.48
5.46
5.45
5.43
3.52
2.49
2.48
2.46
2.45
2.35
2.17
2.16
2.14
2.13
1.93
NHAc
O
N
N
OMe
Me
(±)
47, CDCl3, 23 °C
2.02
1.01
1.01
0.99
1.01
0.97
1.00
3.00
1.00
3.01
1.00
3.01
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

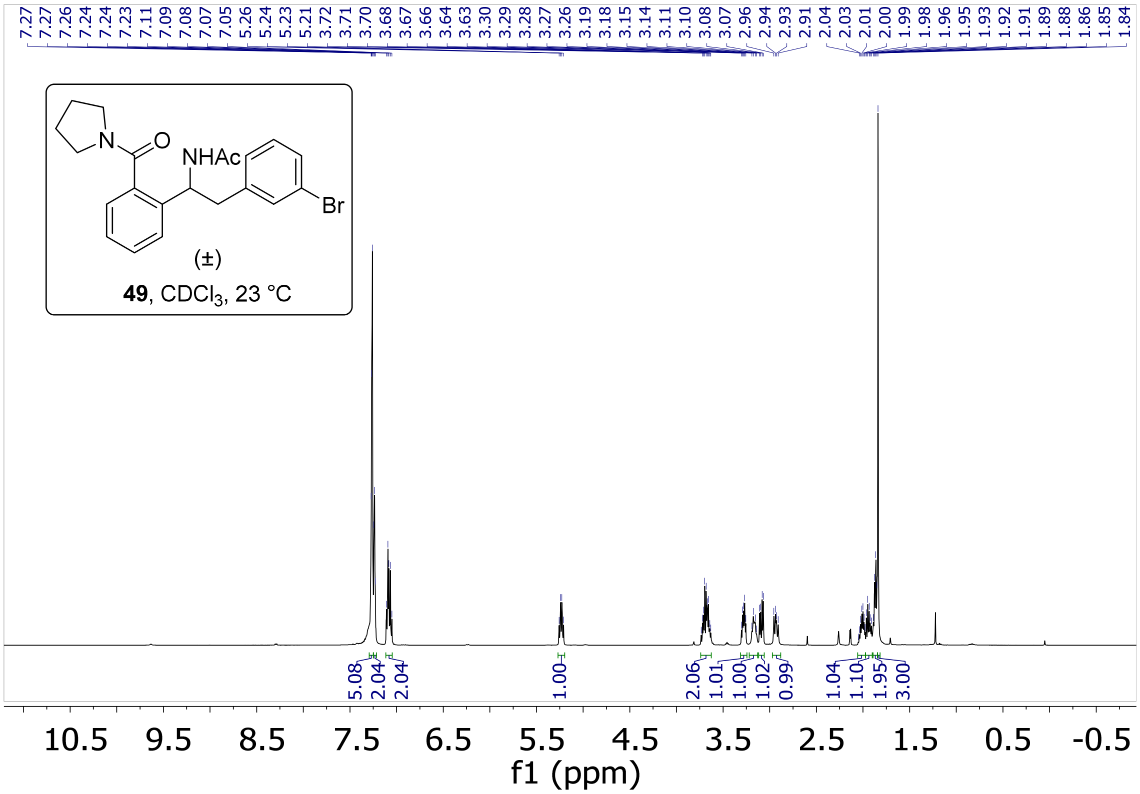

171.38
169.11
140.72
138.93
138.78
133.11
131.73
130.45
129.81
127.63
107.23
51.73
48.52
38.61
23.59
20.89
NHAc
O
N
N
OMe
Me
(±)
47, CDCl3, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

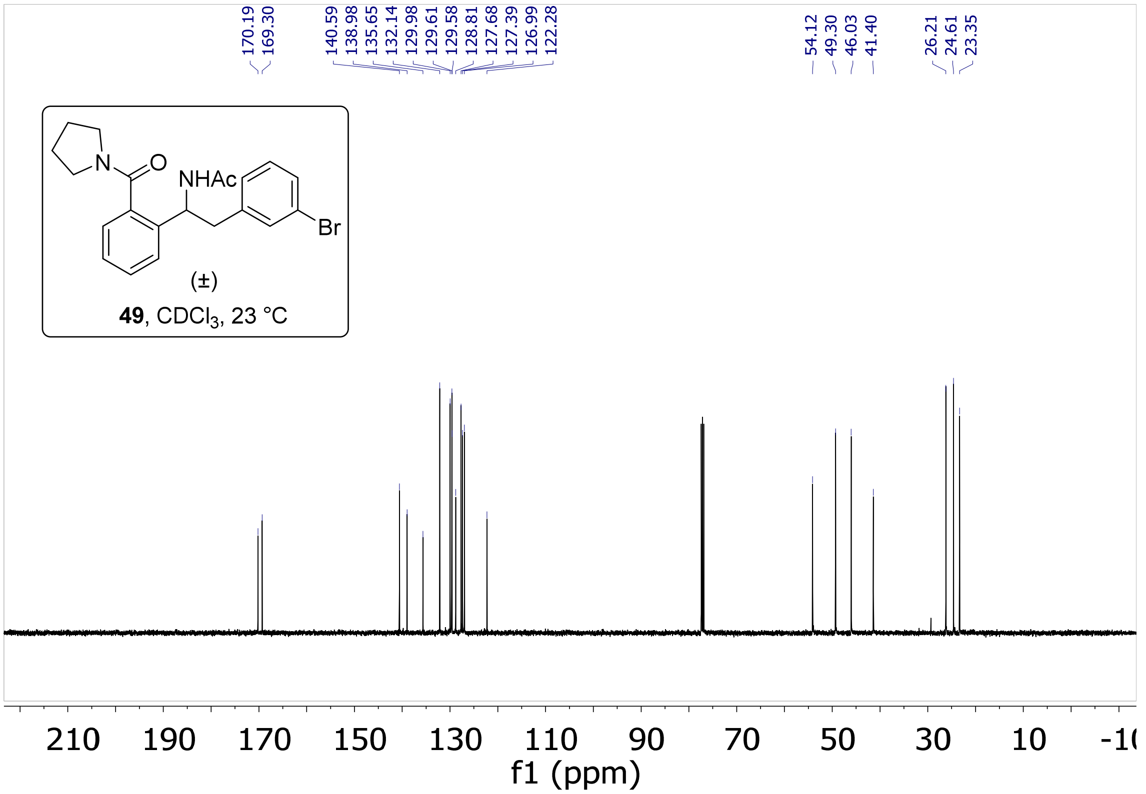

HSQC
N
N
NHAc
O
OMe
H
Me
(±)
47, CDCl$_3$, 23 °C
{5.45,48.43}
0
20
40
60
80
100
120
140
160
180
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

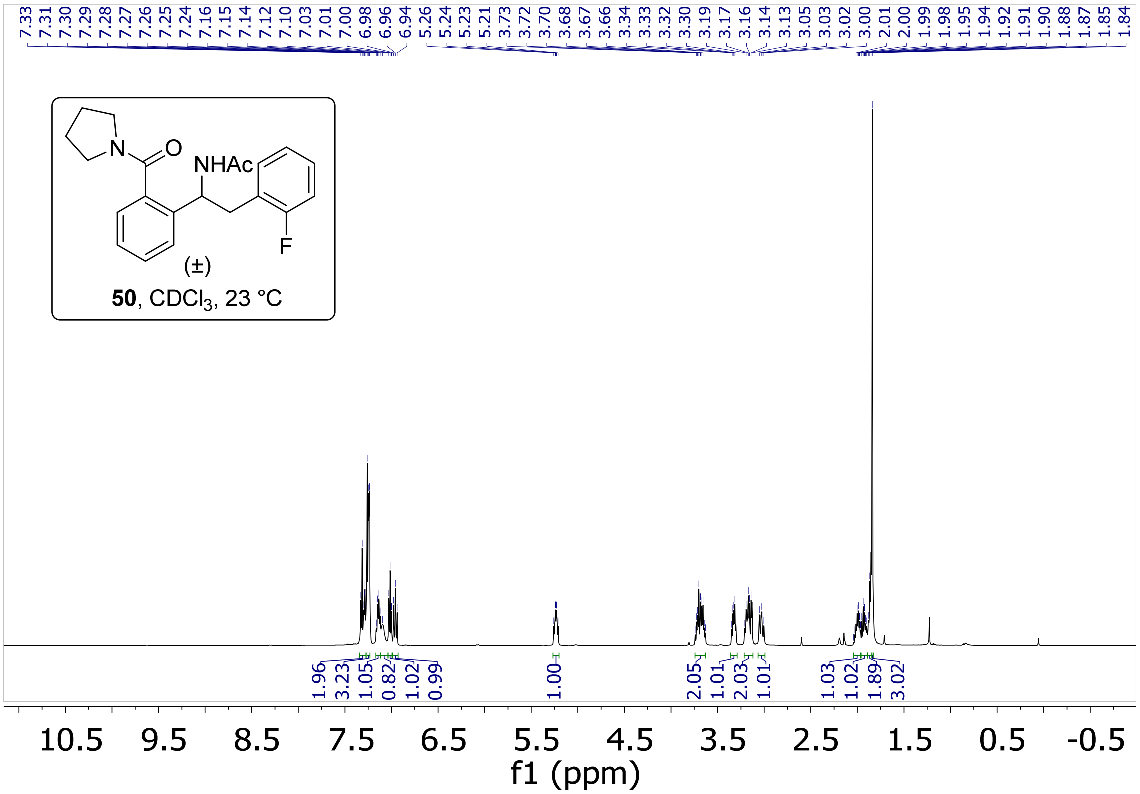

HMBC
N
N
NHAc
O
OMe
*
*
*
*
*
H
Me
(±)
47, CDCl$_3$, 23 °C
{5.46,38.89}
{5.46,130.39}
{5.46,138.67}
{5.46,133.02}
{5.46,171.16}
{5.46,168.82}
0
40
80
120
160
200
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

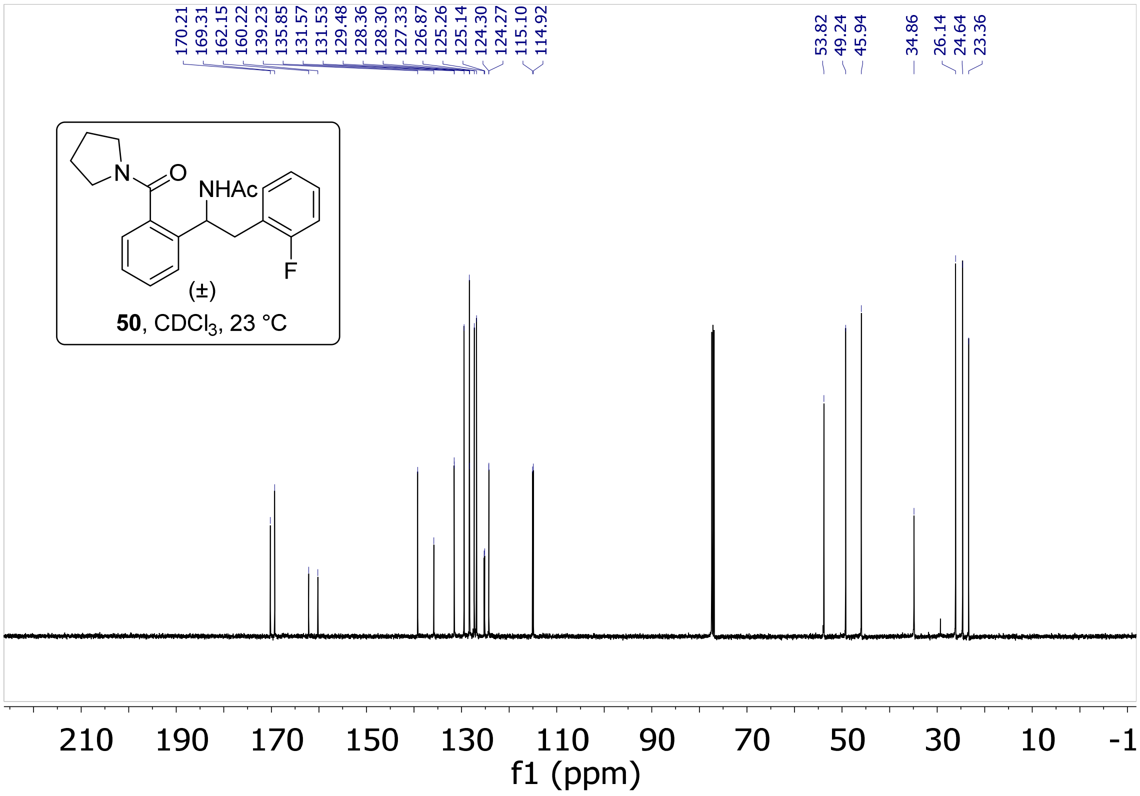

8.03
7.97
7.81
7.62
7.61
7.57
7.55
7.53
7.46
7.45
7.31
7.29
7.23
7.22
7.17
7.15
7.13
7.11
7.09
7.07
6.55
4.84
4.82
4.80
4.77
4.75
3.04
3.01
2.88
2.86
2.73
2.71
2.68
2.34
1.27
1.21
1.16
1.08
N
N
N
HN
Boc
O
B
O
Me
(±)
48, DMSO-D6, 23 °C
1.05
0.99
3.07
0.86
1.01
3.14
1.00
1.03
1.02
1.02
3.04
12.12
8.91
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

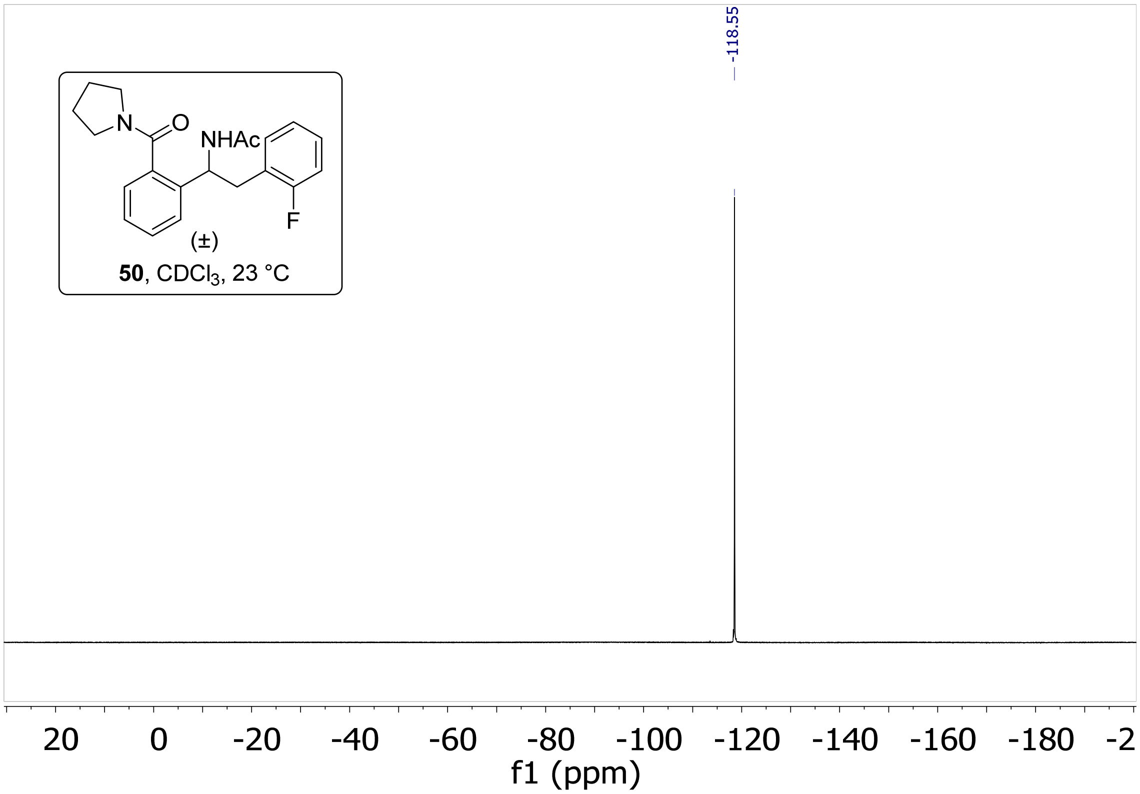

154.74
142.69
140.09
137.70
137.10
136.96
134.13
131.50
129.20
128.58
128.44
126.96
126.33
106.51
83.39
77.64
51.06
42.08
28.11
24.62
20.28
N
N
N
HN
Boc
O
B
O
Me
(±)
48, DMSO-D6, 23 °C
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

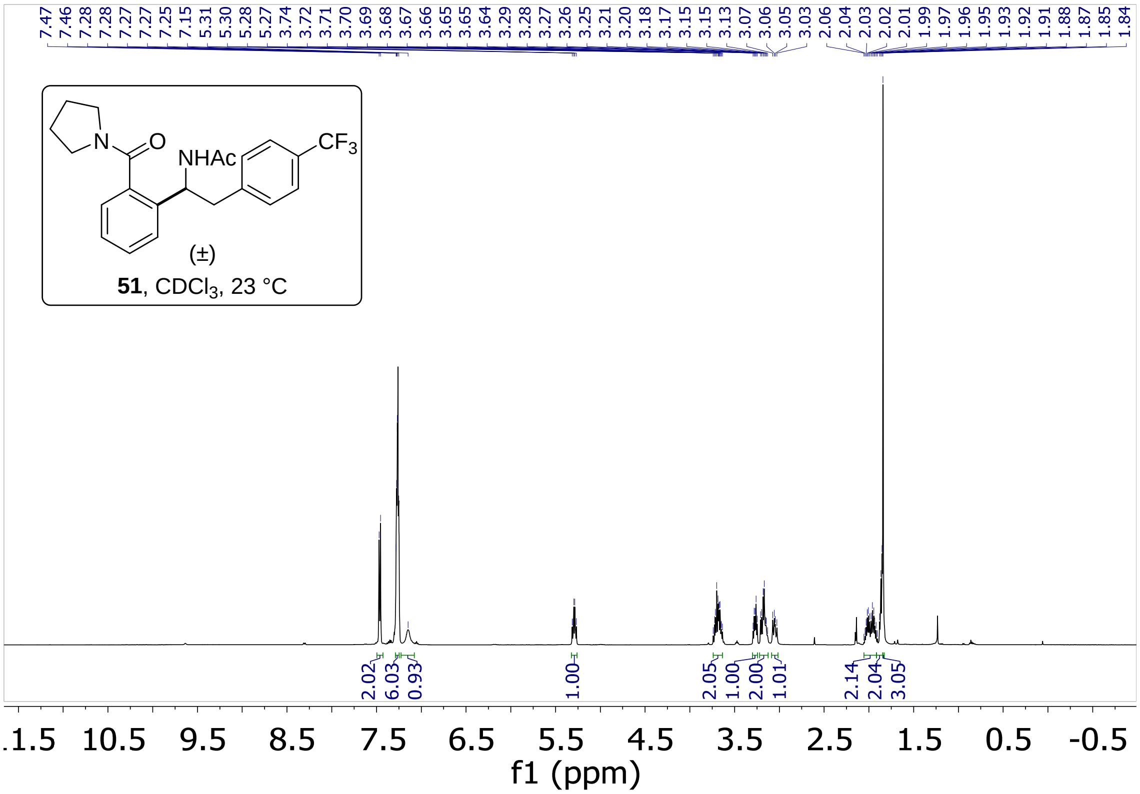

7.27 7.27 7.26 7.24 7.24 7.23 7.11 7.09 7.08 7.07 7.05 5.26 5.24 5.23 5.21 3.72 3.71 3.70 3.68 3.67 3.66 3.64 3.63 3.30 3.29 3.28 3.27 3.26 3.19 3.18 3.15 3.14 3.11 3.10 3.08 3.07 2.96 2.94 2.93 2.91 2.04 2.03 2.01 2.00 1.99 1.98 1.96 1.95 1.93 1.92 1.91 1.89 1.88 1.86 1.85 1.84
NHAc
O
N
Br
(±)
49, CDCl3, 23 °C
5.08 2.04 2.04
1.00
2.06 1.01 1.00 1.02 0.99
1.04 1.10 1.95 3.00
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

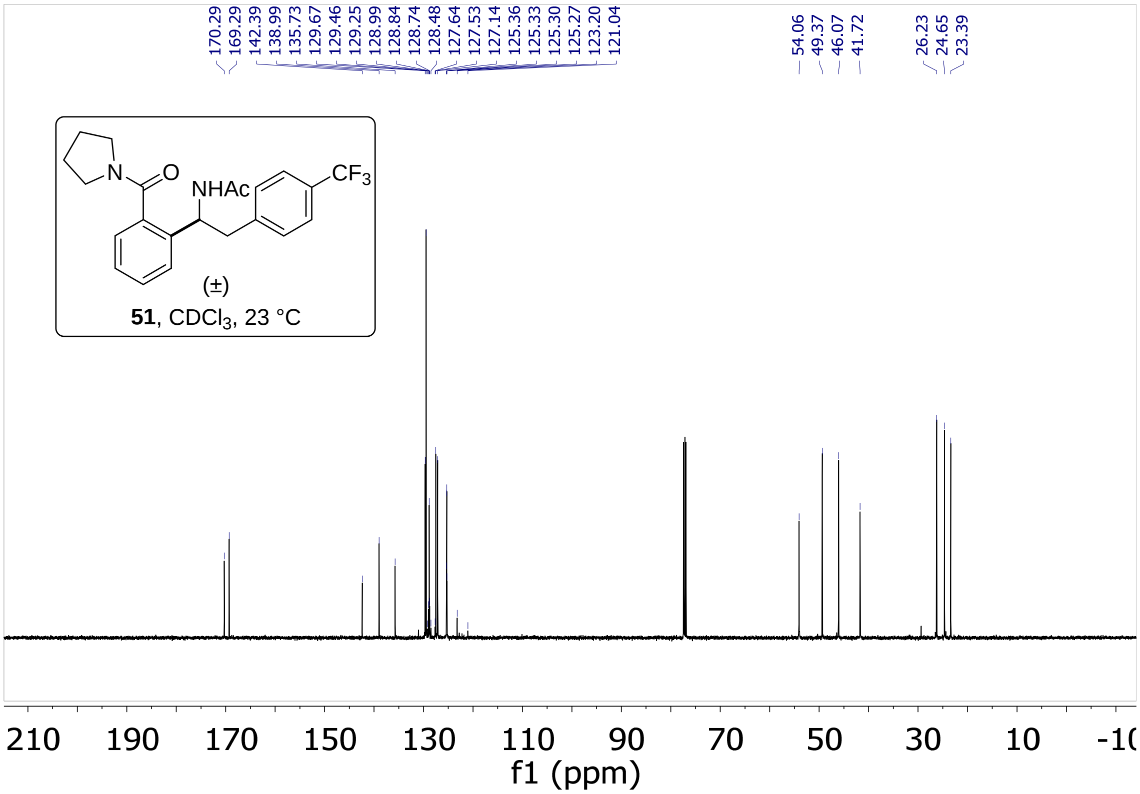

170.19 169.30
140.59 138.98 135.65 132.14 129.98 129.61 129.58 128.81 127.68 127.39 126.99 122.28
54.12 49.30 46.03 41.40
26.21 24.61 23.35
NHAc
O
N
Br
(±)
49, CDCl3, 23 °C
210 190 170 150 130 110 90 70 50 30 10 -1
f1 (ppm)

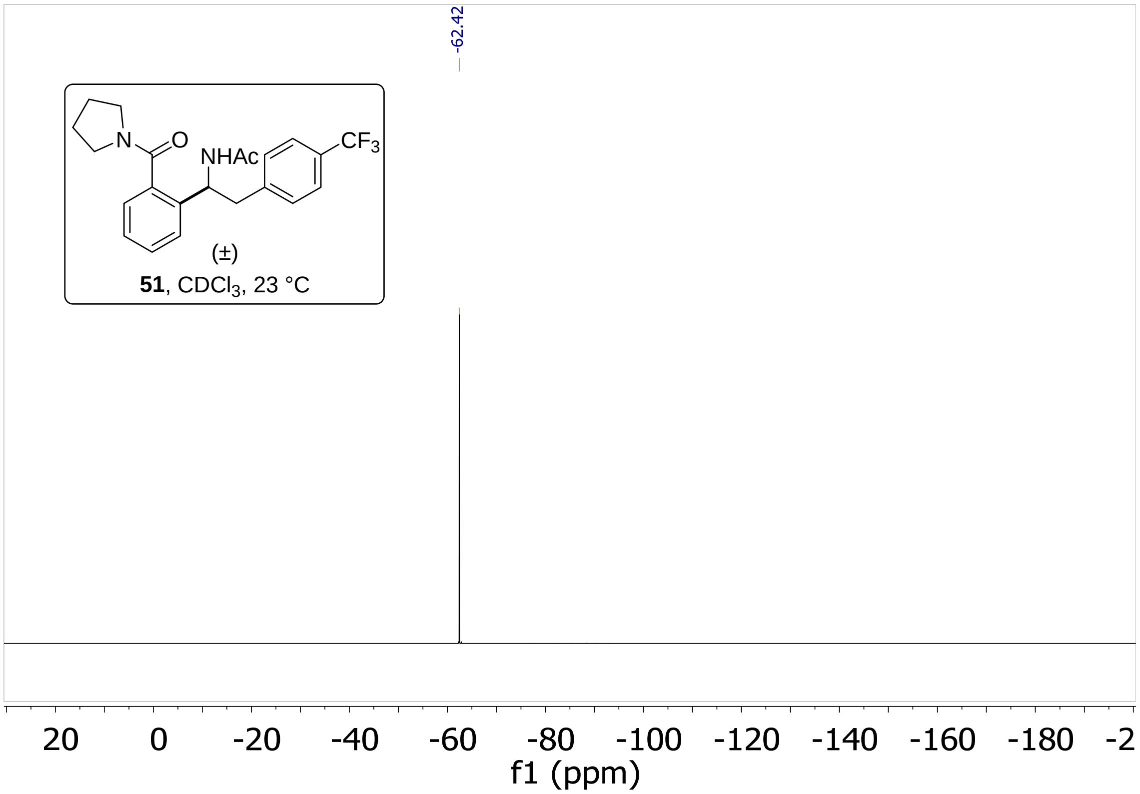

7.33
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.16
7.15
7.14
7.12
7.10
7.03
7.01
7.00
6.98
6.96
6.94
5.26
5.24
5.23
5.21
3.73
3.72
3.70
3.68
3.67
3.66
3.34
3.33
3.32
3.30
3.19
3.17
3.16
3.14
3.13
3.05
3.03
3.02
3.00
2.01
2.00
1.99
1.98
1.95
1.94
1.92
1.91
1.90
1.88
1.87
1.85
1.84
NHAc
N
O
F
(±)
50, $CDCl_3$, 23 °C
1.96
3.23
1.05
0.82
1.02
0.99
1.00
2.05
1.01
2.03
1.01
1.03
1.02
1.89
3.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

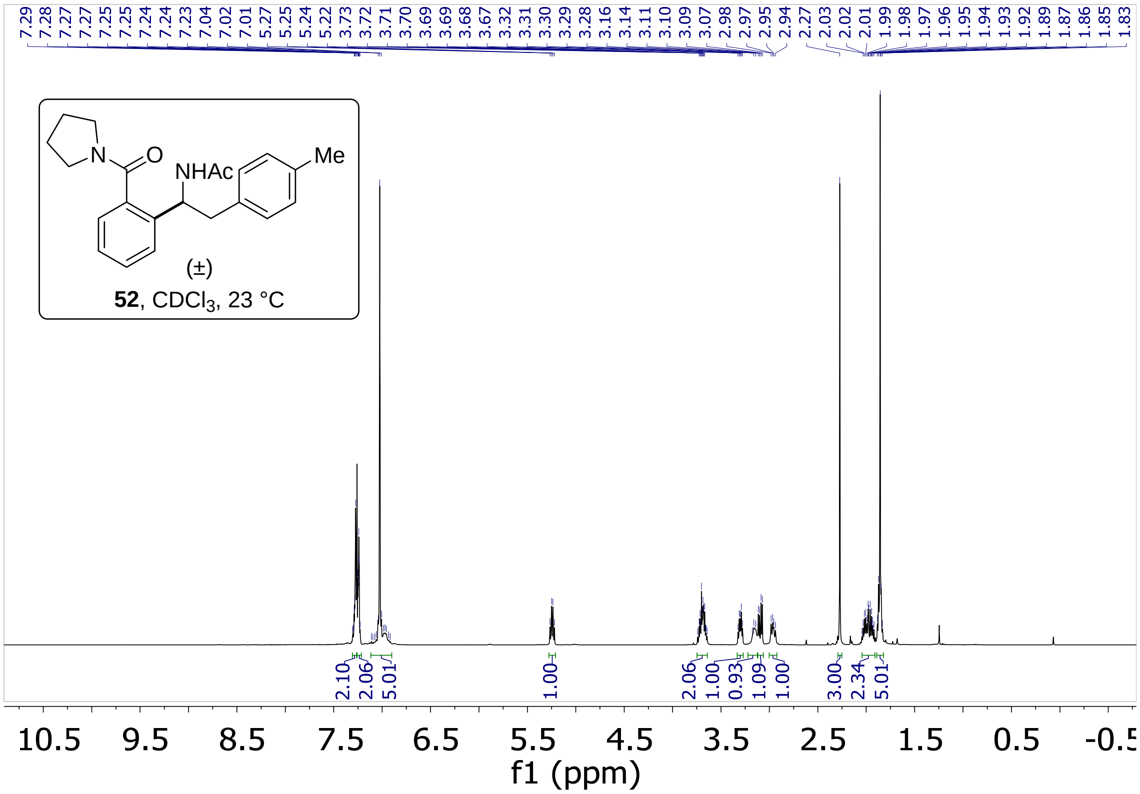

170.21
169.31
162.15
160.22
139.23
135.85
131.57
131.53
129.48
128.36
128.30
127.33
126.87
125.26
125.14
124.30
124.27
115.10
114.92
53.82
49.24
45.94
34.86
26.14
24.64
23.36
NHAc
N
O
F
(±)
50, $CDCl_3$, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

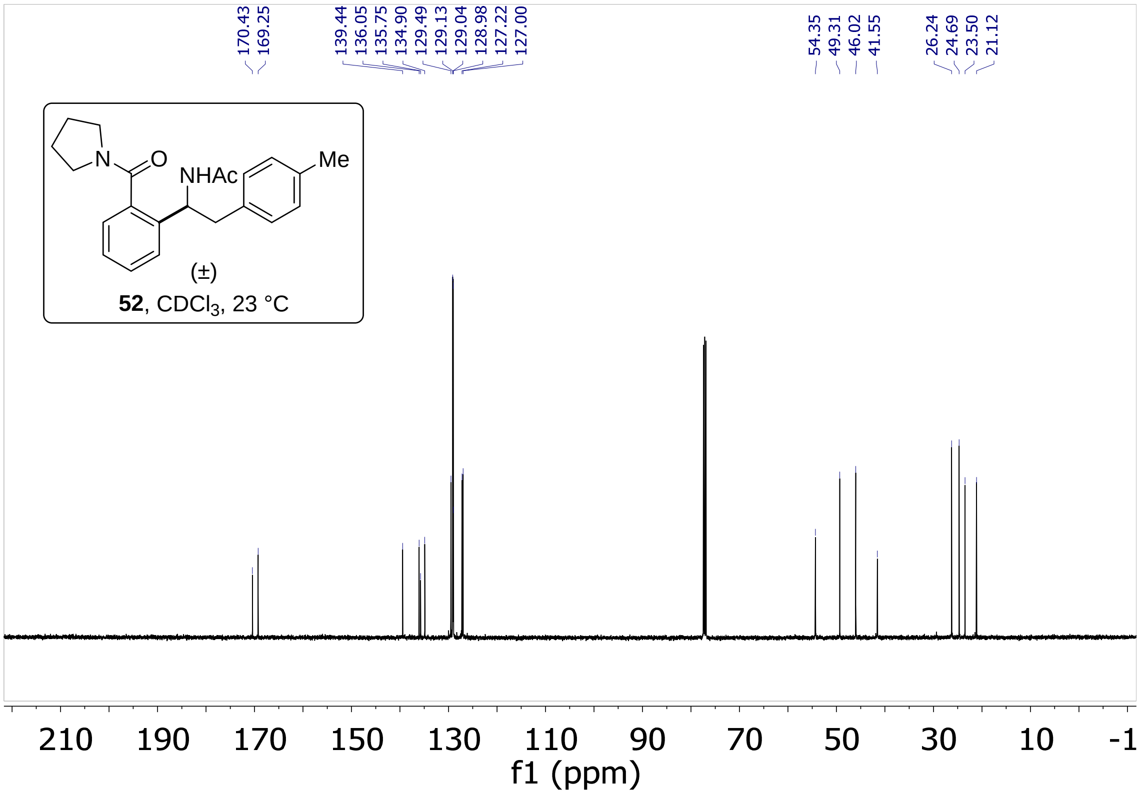

-118.55
NHAc
N
O
F
(±)
50, CDCl$_3$, 23 °C
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-2
f1 (ppm)

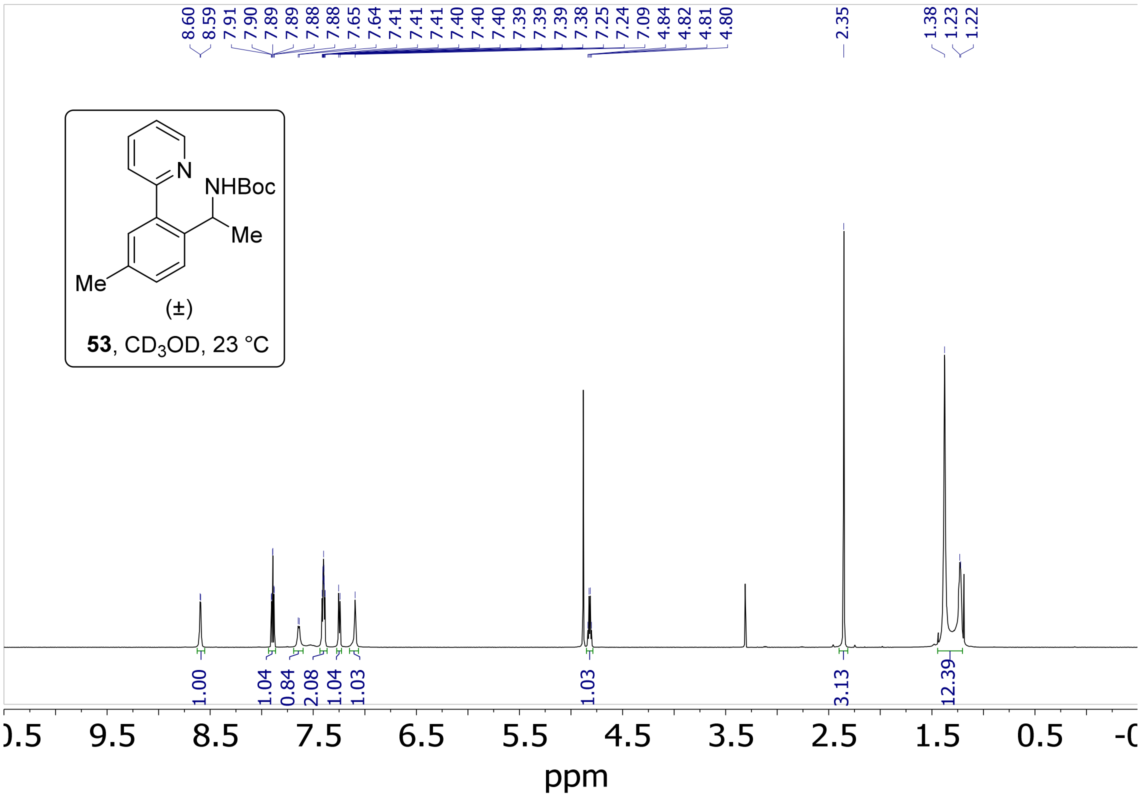

7.47
7.46
7.28
7.28
7.27
7.27
7.25
7.15
5.31
5.30
5.28
5.27
3.74
3.72
3.71
3.70
3.69
3.68
3.67
3.66
3.65
3.65
3.64
3.29
3.28
3.27
3.26
3.25
3.21
3.20
3.18
3.17
3.15
3.15
3.13
3.07
3.06
3.05
3.03
2.06
2.04
2.03
2.02
2.01
1.99
1.97
1.96
1.95
1.93
1.92
1.91
1.88
1.87
1.85
1.84
NHAc
O
N
CF3
(±)
51, CDCl3, 23 °C
2.02
6.03
0.93
1.00
2.05
1.00
2.00
1.01
2.14
2.04
3.05
.1.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

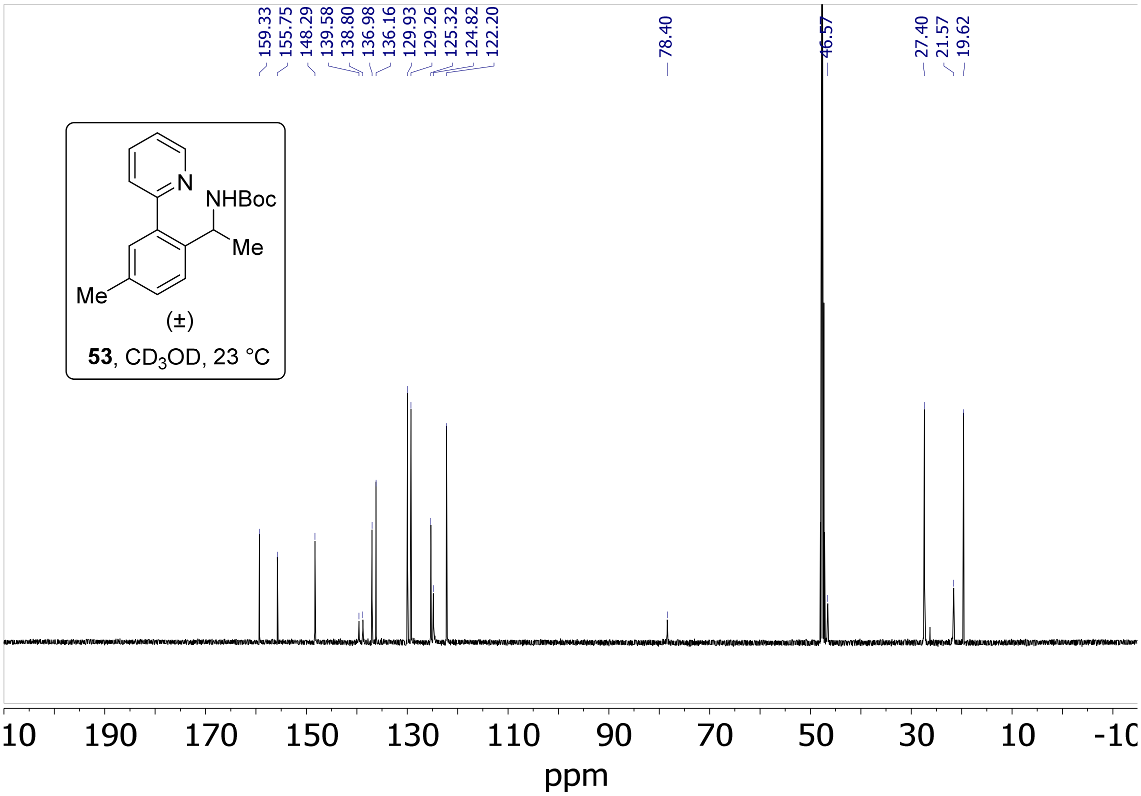

170.29
169.29
142.39
138.99
135.73
129.67
129.46
129.25
128.99
128.84
128.74
128.48
127.64
127.53
127.14
125.36
125.33
125.30
125.27
123.20
121.04
54.06
49.37
46.07
41.72
26.23
24.65
23.39
NHAc
O
N
CF3
(±)
51, CDCl3, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1(
f1 (ppm)


-62.42
NHAc
N
O
CF3
(±)
51, CDCl3, 23 °C
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-2
f1 (ppm)

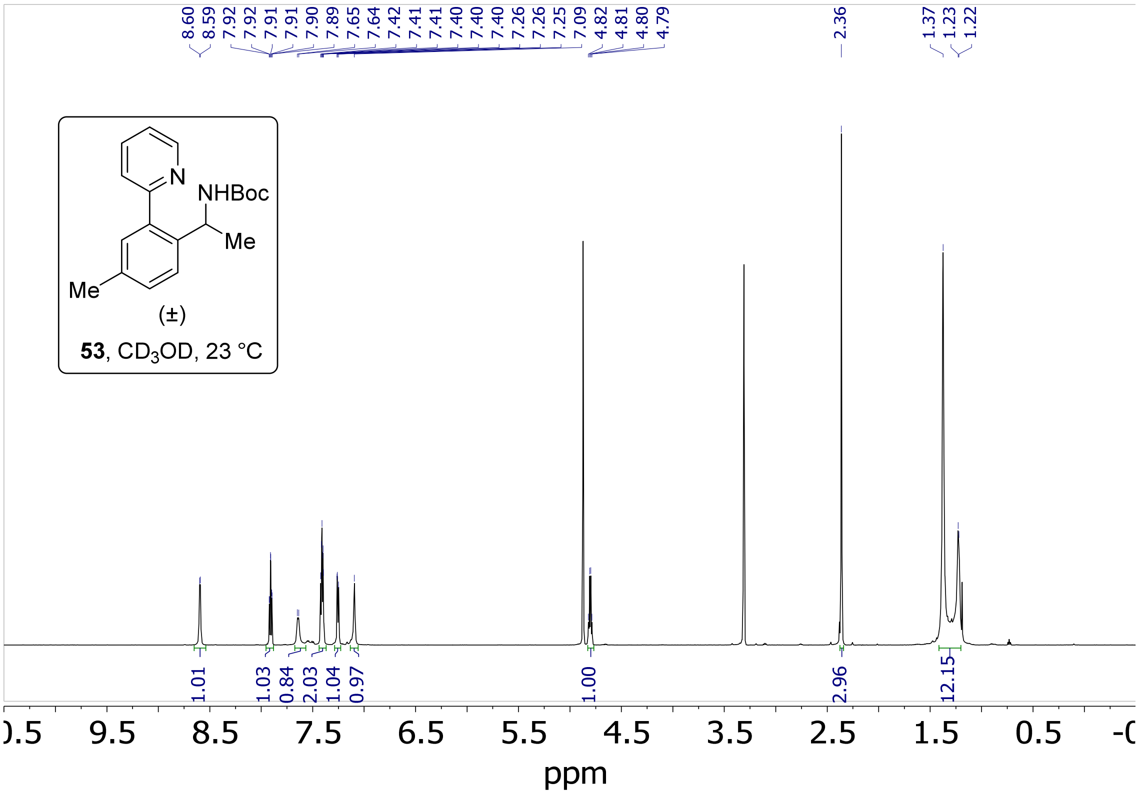

7.29 7.28 7.27 7.27 7.25 7.25 7.24 7.24 7.23 7.04 7.02 7.01 5.27 5.25 5.24 5.22 3.73 3.72 3.71 3.70 3.69 3.69 3.68 3.67 3.32 3.31 3.30 3.29 3.28 3.16 3.14 3.11 3.10 3.09 3.07 2.98 2.97 2.95 2.94 2.27 2.03 2.02 2.01 1.99 1.98 1.97 1.96 1.95 1.94 1.93 1.92 1.89 1.87 1.86 1.85 1.83
NHAc
Me
N
O
(±)
52, CDCl3, 23 °C
2.10 2.06 5.01 1.00 2.06 1.00 0.93 1.09 1.00 3.00 2.34 5.01
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

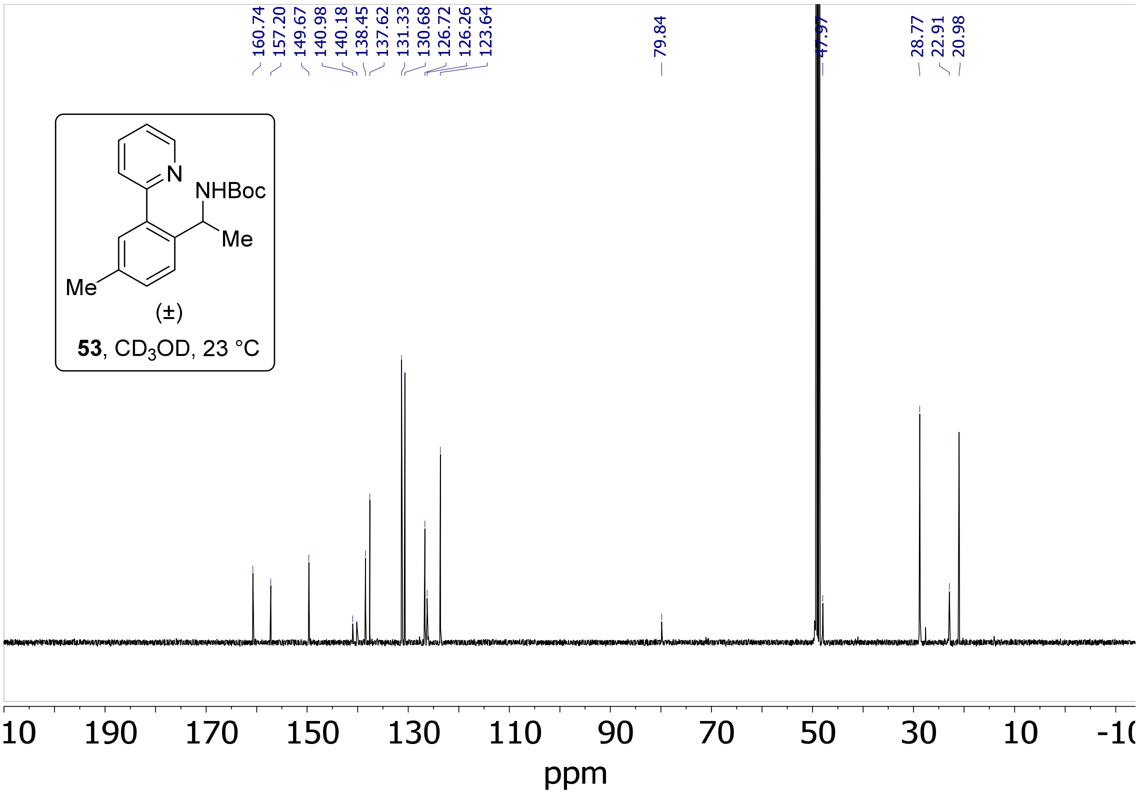

170.43 169.25 139.44 136.05 135.75 134.90 129.49 129.13 129.04 128.98 127.22 127.00 54.35 49.31 46.02 41.55 26.24 24.69 23.50 21.12
NHAc
Me
N
O
(±)
52, CDCl3, 23 °C
210 190 170 150 130 110 90 70 50 30 10 -1
f1 (ppm)

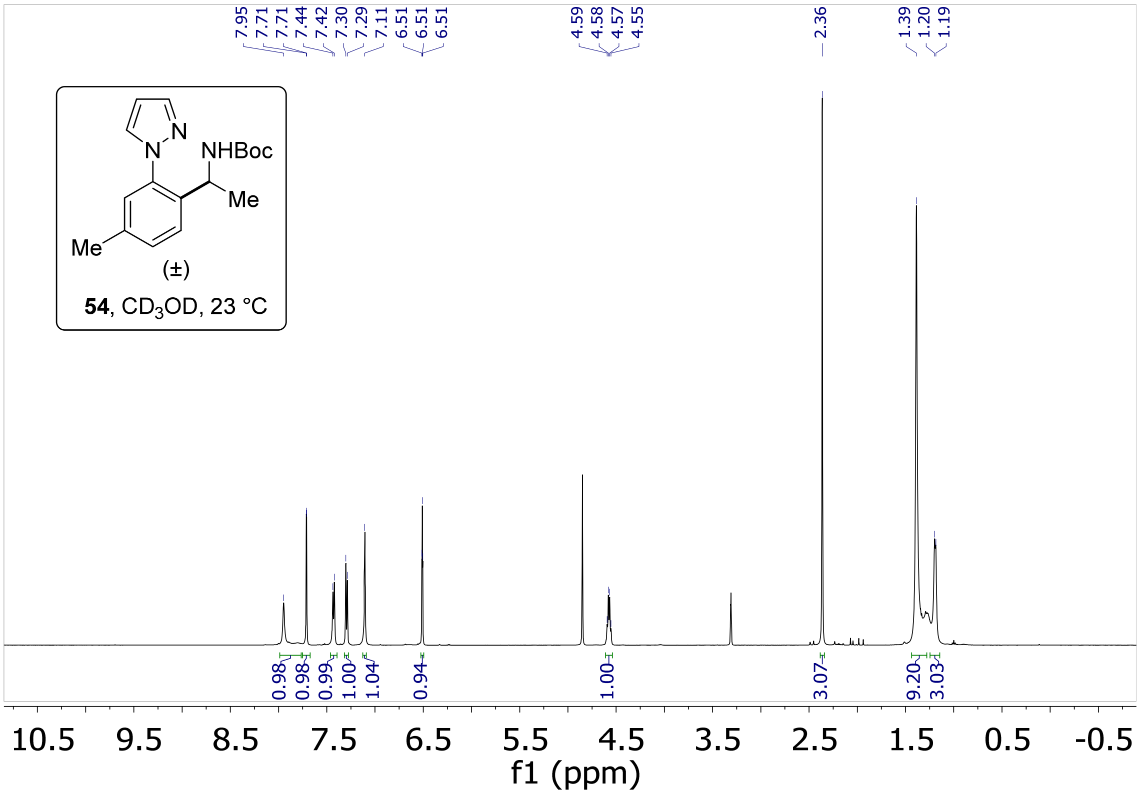

8.60
8.59
7.91
7.90
7.89
7.89
7.88
7.88
7.65
7.64
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.25
7.24
7.09
4.84
4.82
4.81
4.80
2.35
1.38
1.23
1.22
N
NHBoc
Me
Me
(±)
53, CD3OD, 23 °C
1.00
1.04
0.84
2.08
1.04
1.03
1.03
3.13
12.39
).5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-(
ppm

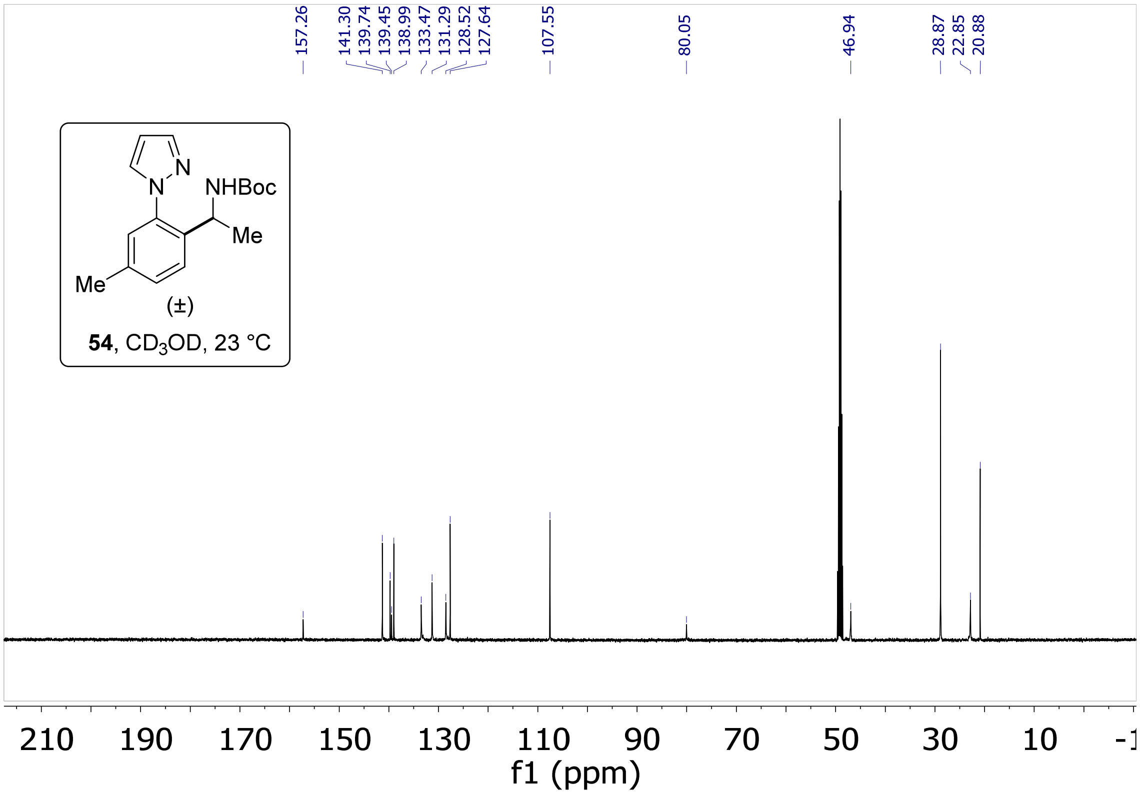

159.33
155.75
148.29
139.58
138.80
136.98
136.16
129.93
129.26
125.32
124.82
122.20
78.40
46.57
27.40
21.57
19.62
N
NHBoc
Me
Me
(±)
53, CD3OD, 23 °C
10
190
170
150
130
110
90
70
50
30
10
-1(
ppm

Reaction at 150 psi pressure in Parr reactor

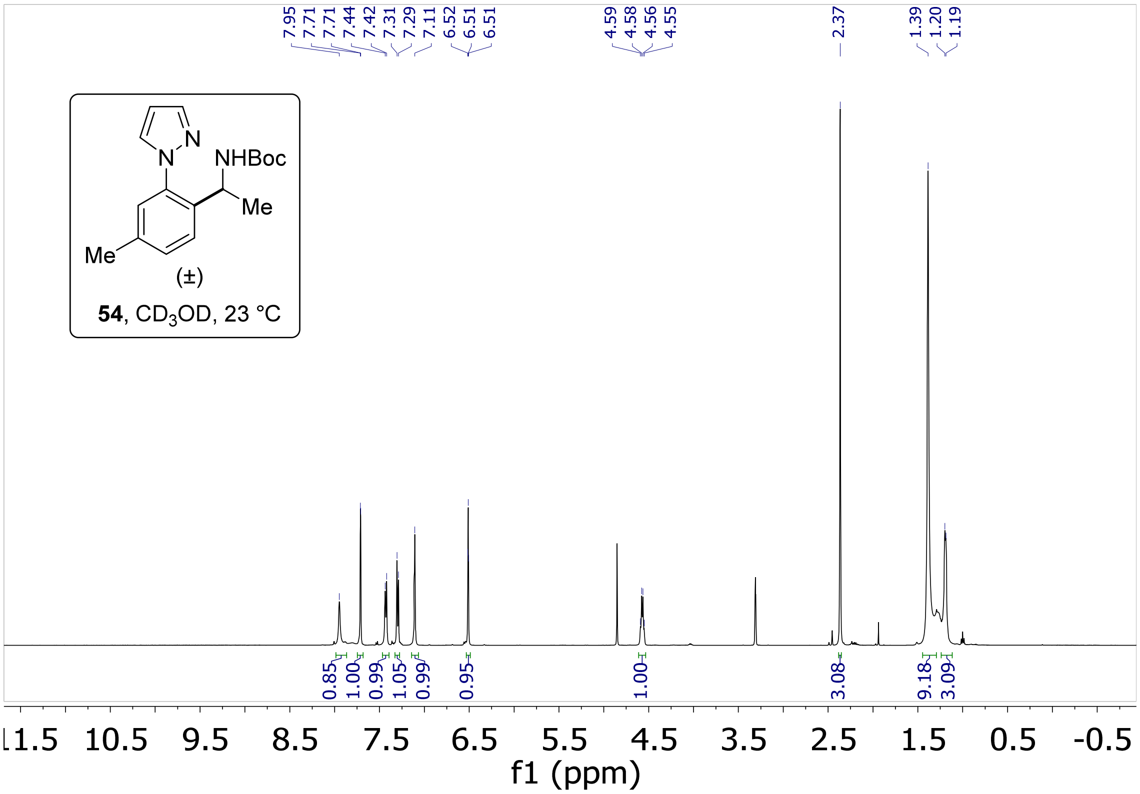


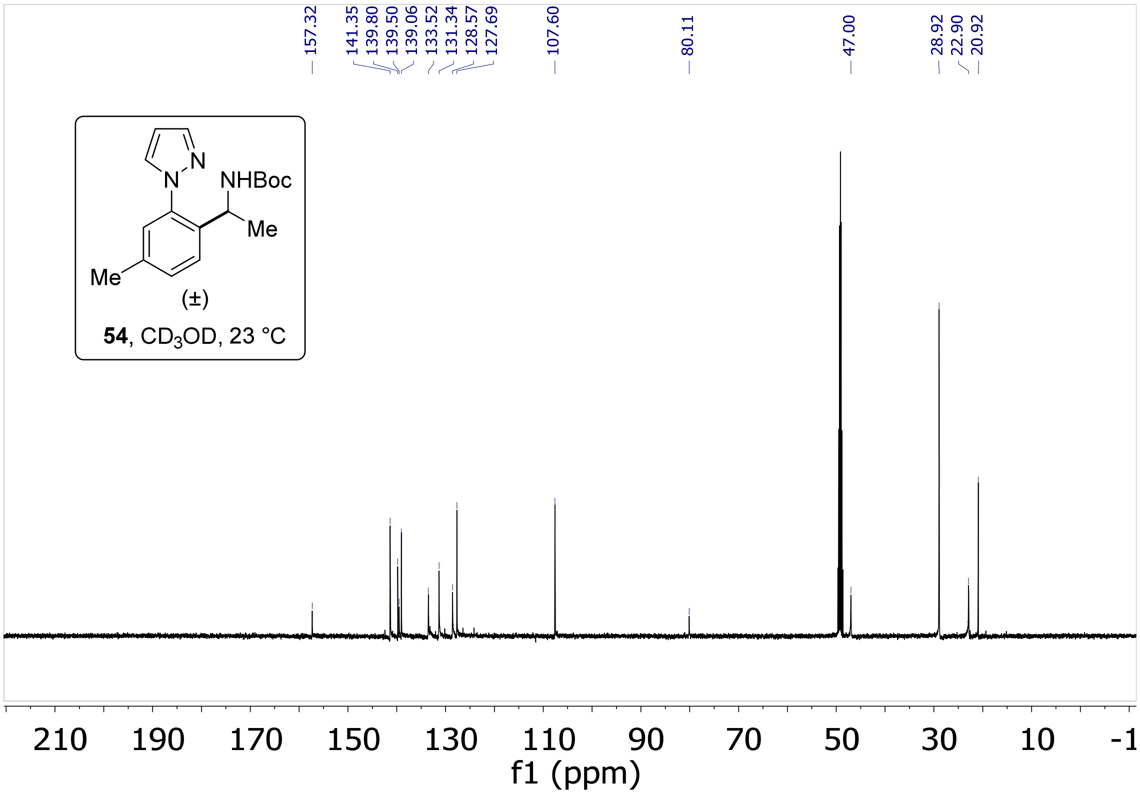



7.95
7.71
7.71
7.44
7.42
7.30
7.29
7.11
6.51
6.51
6.51
4.59
4.58
4.57
4.55
2.36
1.39
1.20
1.19
NHBoc
N
N
Me
Me
(±)
54, CD3OD, 23 °C
0.98
0.98
0.99
1.00
1.04
0.94
1.00
3.07
9.20
3.03
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

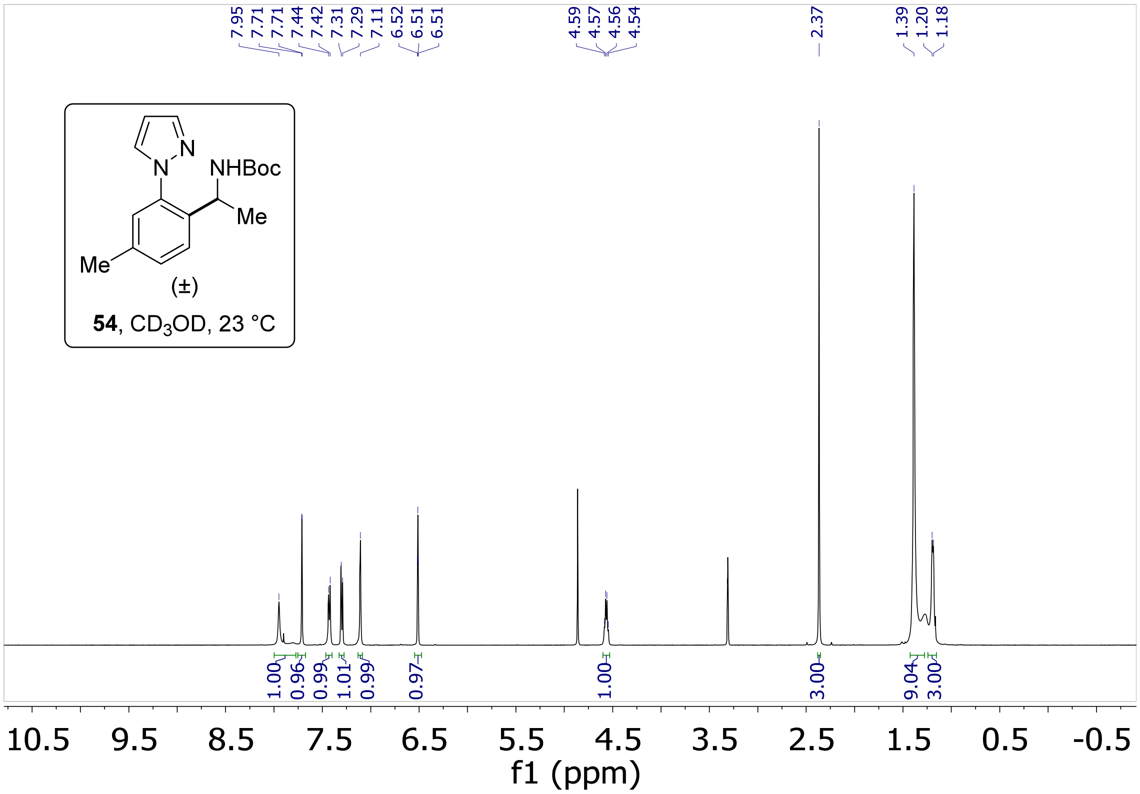

157.26
141.30
139.74
139.45
138.99
133.47
131.29
128.52
127.64
107.55
80.05
46.94
28.87
22.85
20.88
NHBoc
N
N
Me
Me
(±)
54, CD3OD, 23 °C
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)

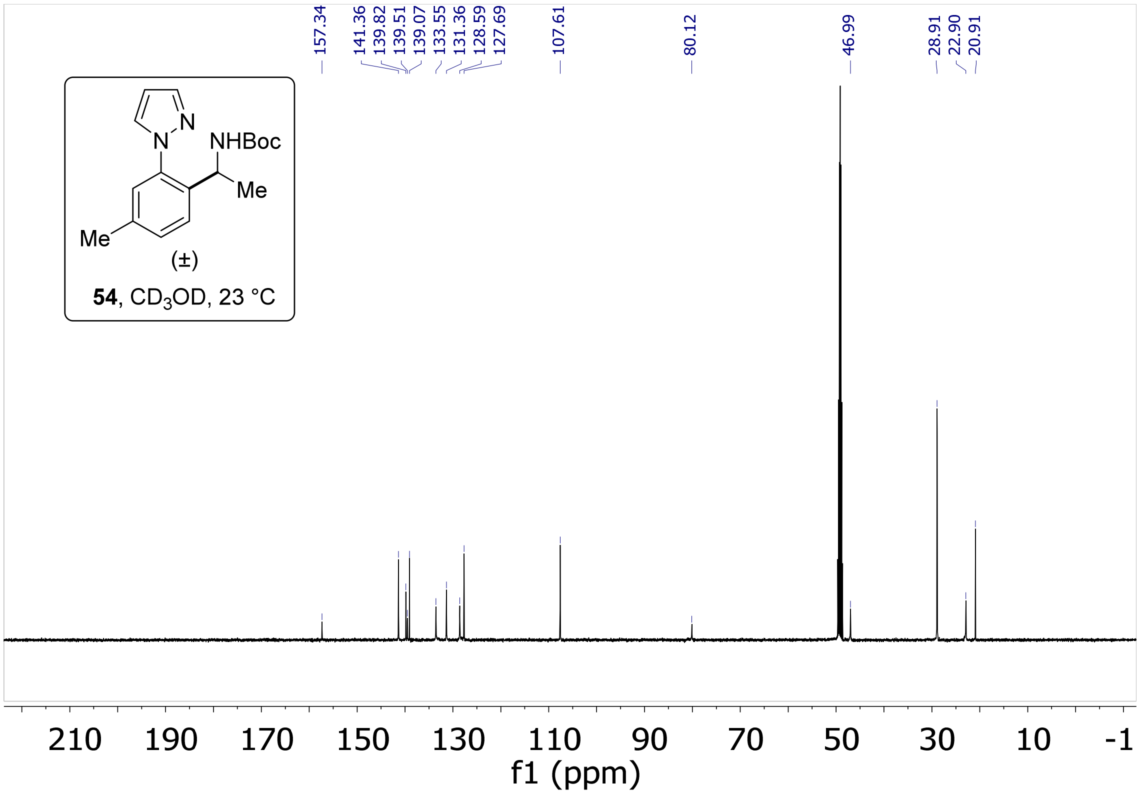
Reaction at 150 psi pressure in Parr reactor

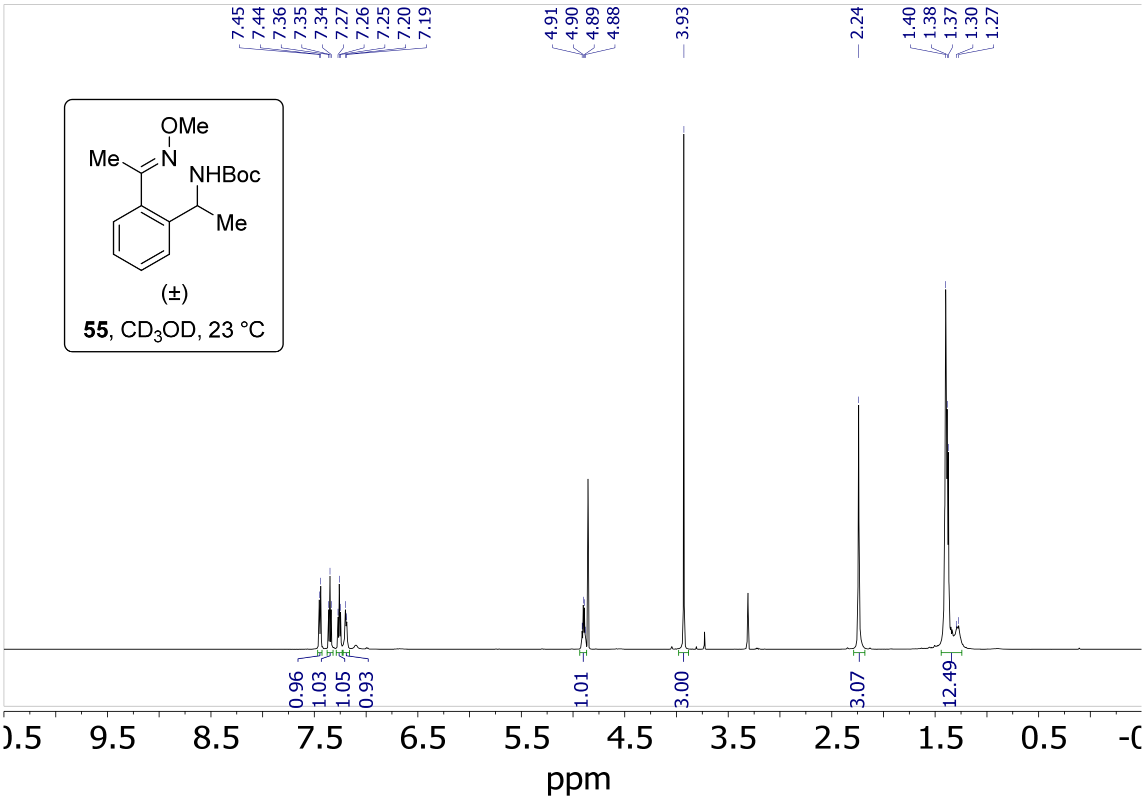


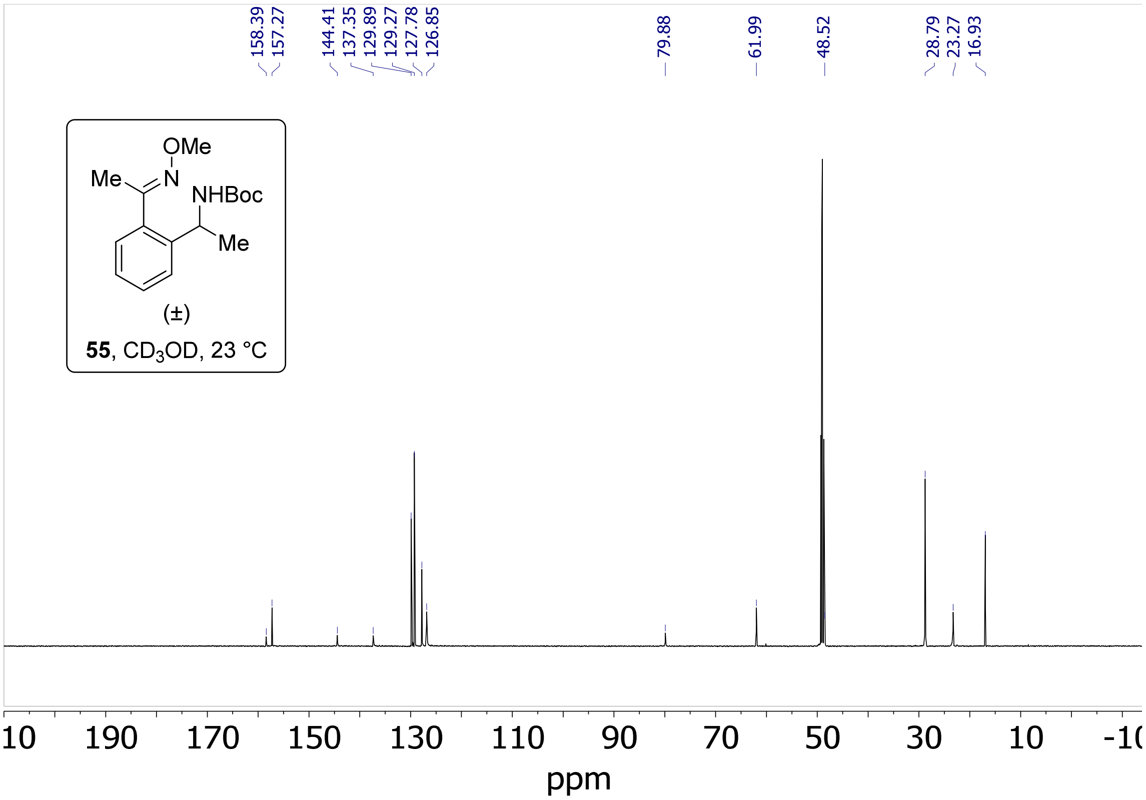


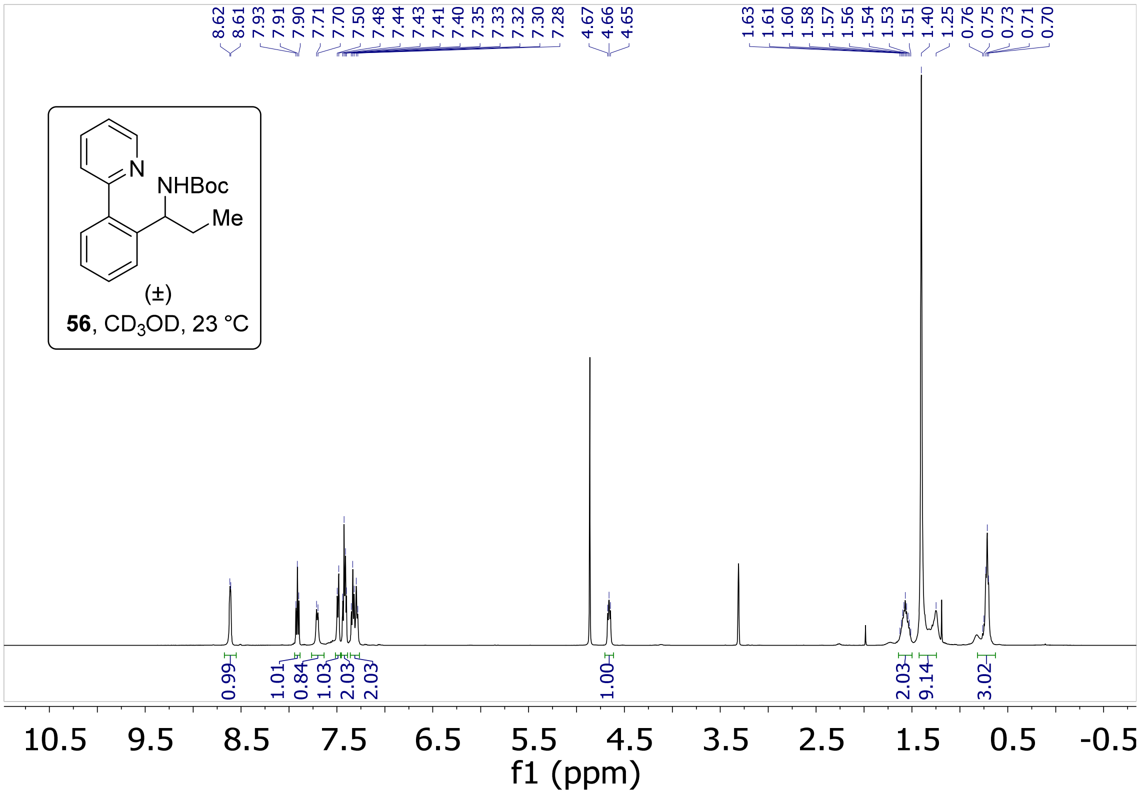
Large scale reaction in Parr reactor

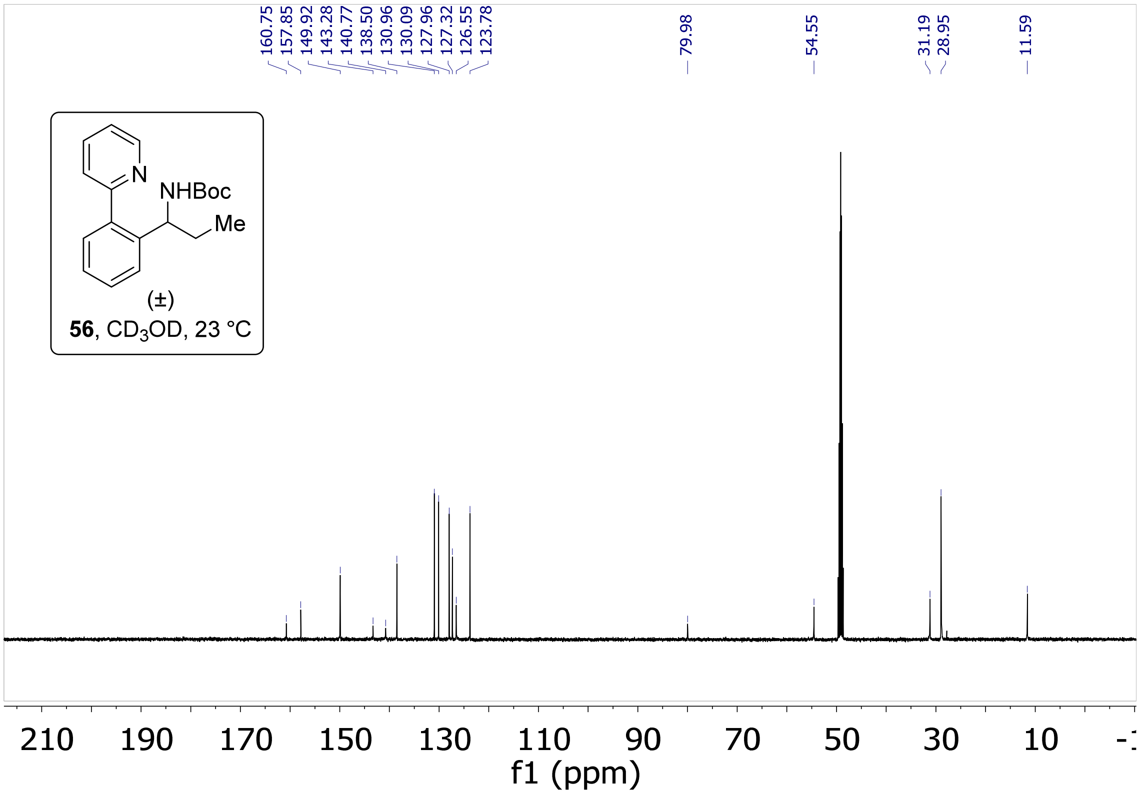


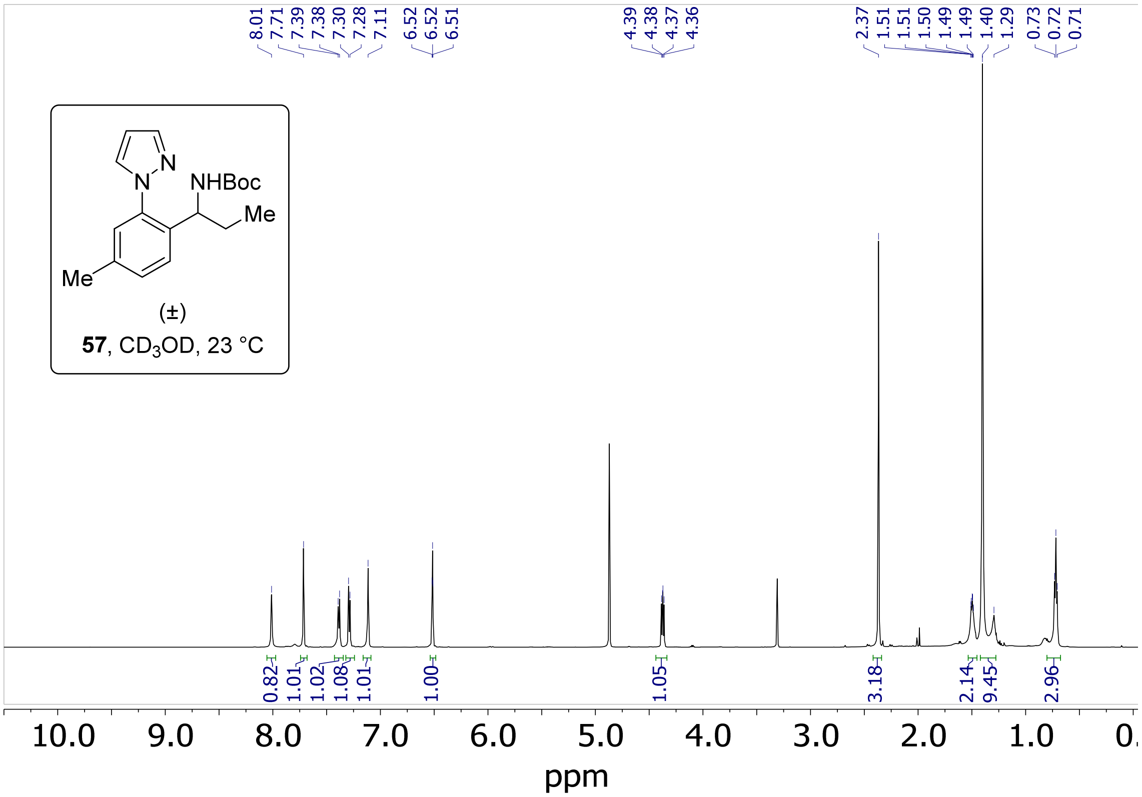


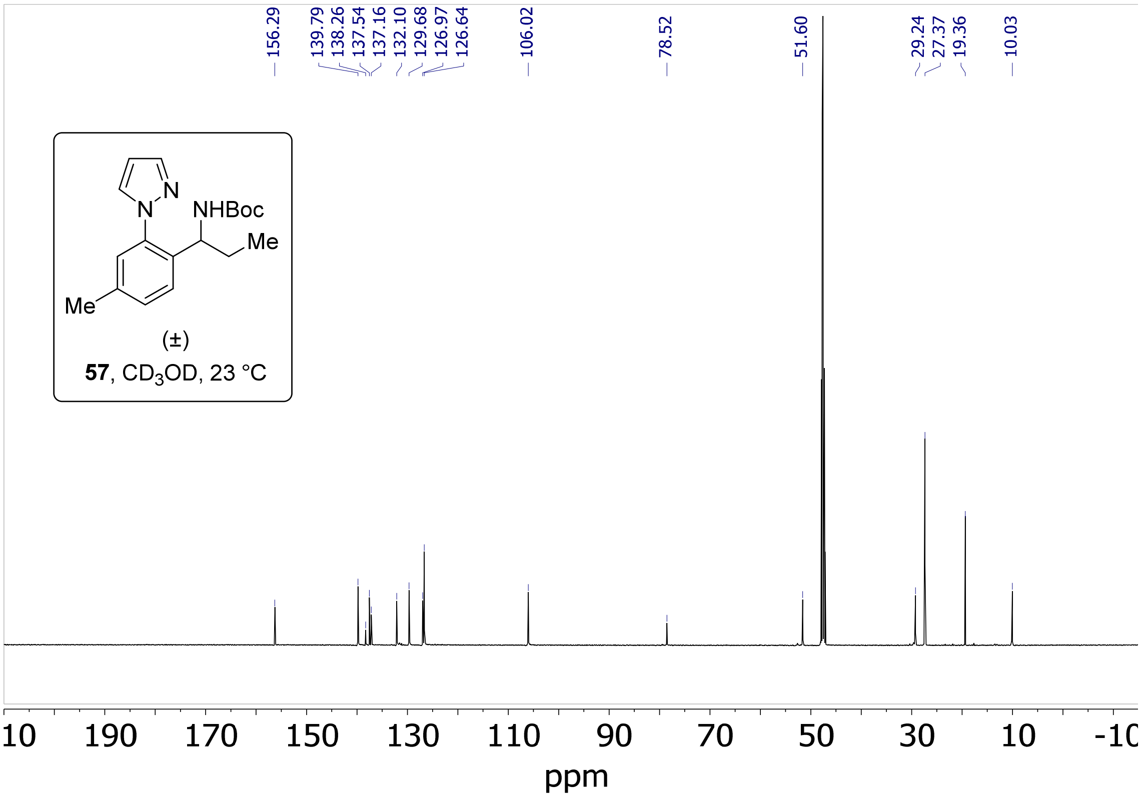

7.45
7.44
7.36
7.35
7.34
7.27
7.26
7.25
7.20
7.19
4.91
4.90
4.89
4.88
3.93
2.24
1.40
1.38
1.37
1.30
1.27
OMe
N
Me
NHBoc
Me
(±)
55, CD$_3$OD, 23 °C
0.96
1.03
1.05
0.93
1.01
3.00
3.07
12.49
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
ppm

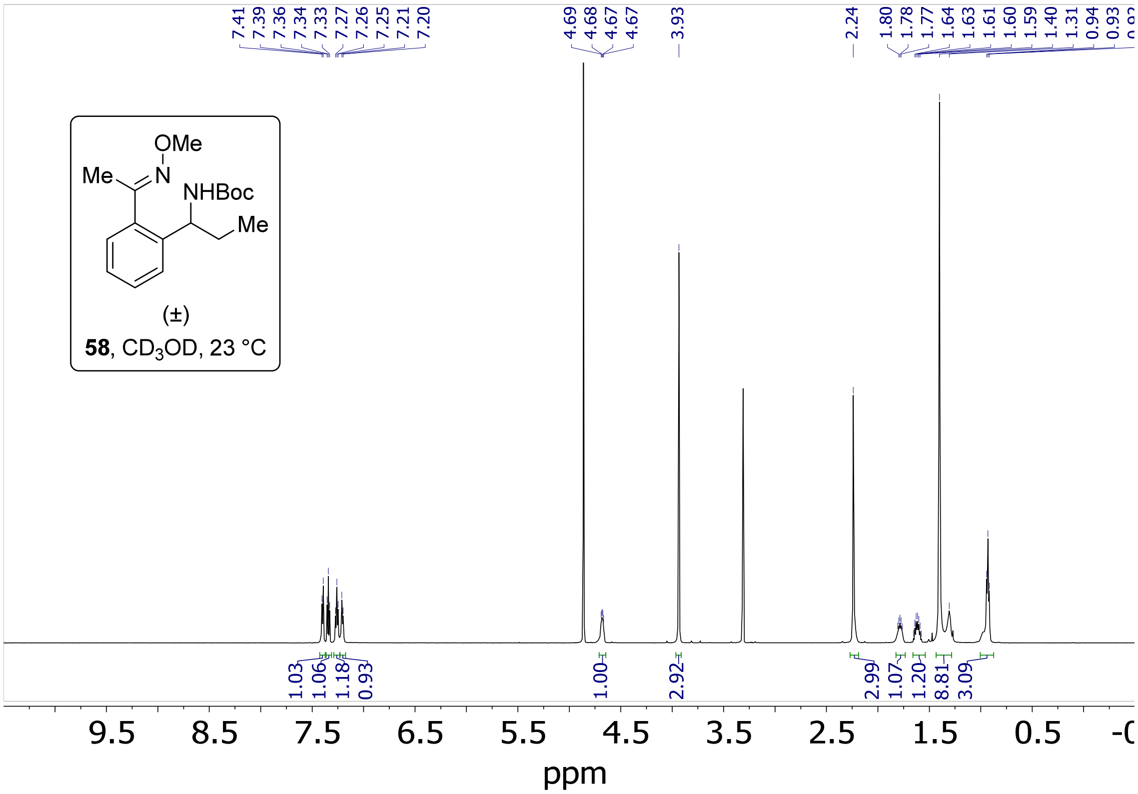

158.39
157.27
144.41
137.35
129.89
129.27
127.78
126.85
79.88
61.99
48.52
28.79
23.27
16.93
OMe
N
Me
NHBoc
Me
(±)
55, CD$_3$OD, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm


8.62
8.61
7.93
7.91
7.90
7.71
7.70
7.50
7.48
7.44
7.43
7.41
7.40
7.35
7.33
7.32
7.30
7.28
4.67
4.66
4.65
1.63
1.61
1.60
1.58
1.57
1.56
1.54
1.53
1.51
1.40
1.25
0.76
0.75
0.73
0.71
0.70
N
NHBoc
Me
(±)
56, CD3OD, 23 °C
0.99
1.01
0.84
1.03
2.03
2.03
1.00
2.03
9.14
3.02
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


160.75
157.85
149.92
143.28
140.77
138.50
130.96
130.09
127.96
127.32
126.55
123.78
79.98
54.55
31.19
28.95
11.59
N
NHBoc
Me
(±)
56, CD3OD, 23 °C
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)


8.01
7.71
7.39
7.38
7.30
7.28
7.11
6.52
6.52
6.51
4.39
4.38
4.37
4.36
2.37
1.51
1.51
1.50
1.49
1.49
1.40
1.29
0.73
0.72
0.71
NHBoc
Me
Me
(±)
57, CD3OD, 23 °C
0.82
1.01
1.02
1.08
1.01
1.00
1.05
3.18
2.14
9.45
2.96
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.
ppm


156.29
139.79
138.26
137.54
137.16
132.10
129.68
126.97
126.64
106.02
78.52
51.60
29.24
27.37
19.36
10.03
NHBoc
Me
Me
(±)
57, CD3OD, 23 °C
10
190
170
150
130
110
90
70
50
30
10
-10
ppm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4.67
4.67
3.93
2.24
1.80
1.78
1.77
1.64
1.63
1.61
1.60
1.59
1.40
1.31
0.94
0.93
OMe
Me
N
NHBoc
Me
(±)
58, CD3OD, 23 °C
1.03
1.06
1.18
0.93
1.00
2.92
2.99
1.07
1.20
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8.5
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3.5
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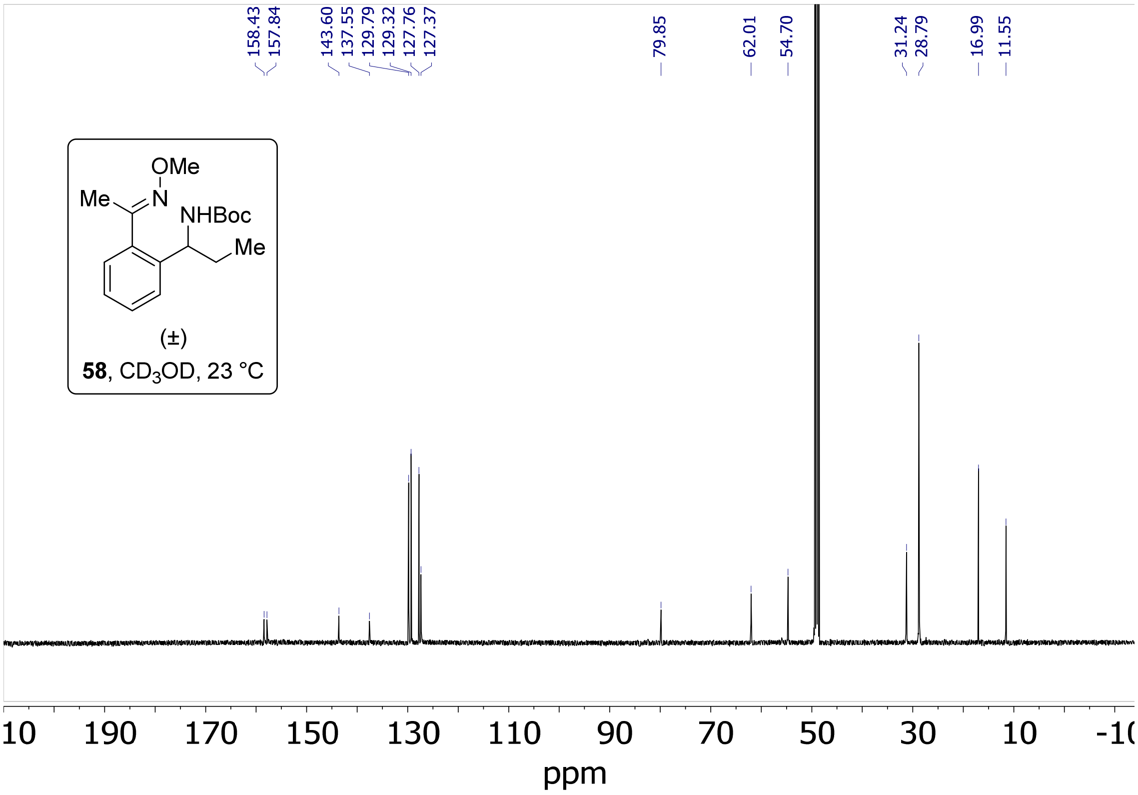
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54.70
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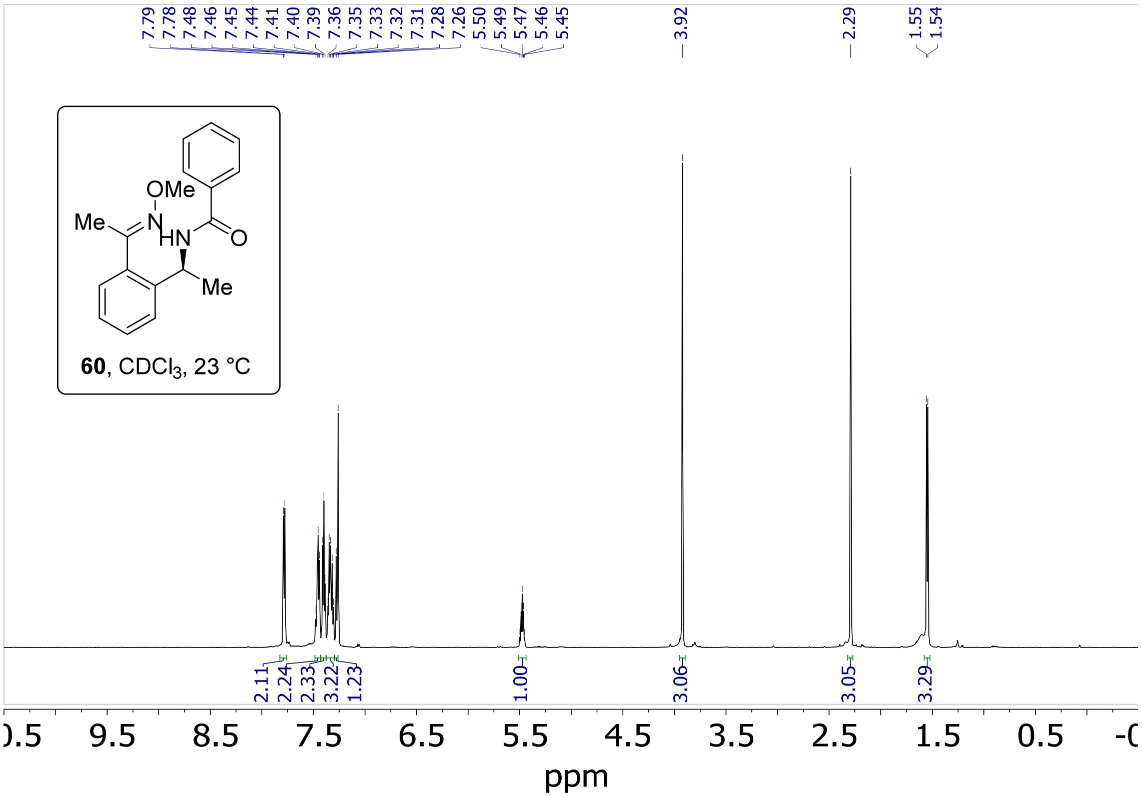
28.79
16.99
11.55
OMe
Me
N
NHBoc
Me
(±)
58, CD3OD, 23 °C
10
190
170
150
130
110
90
70
50
30
10
ppm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7.40
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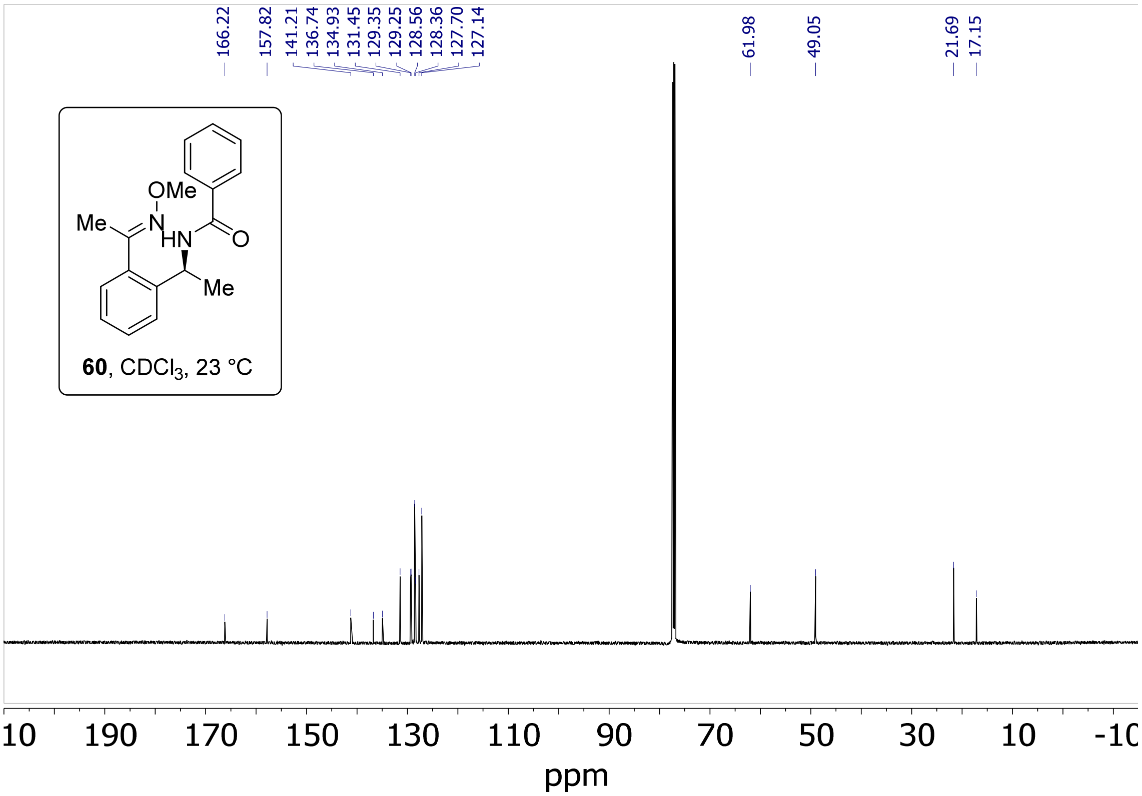
7.33
7.32
7.31
7.28
7.26
5.50
5.49
5.47
5.46
5.45
3.92
2.29
1.55
1.54
OMe
Me
N
HN
O
Me
60, CDCl$_3$, 23 °C
2.11
2.24
2.33
3.22
1.23
1.00
3.06
3.05
3.29
).5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-(
ppm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128.36
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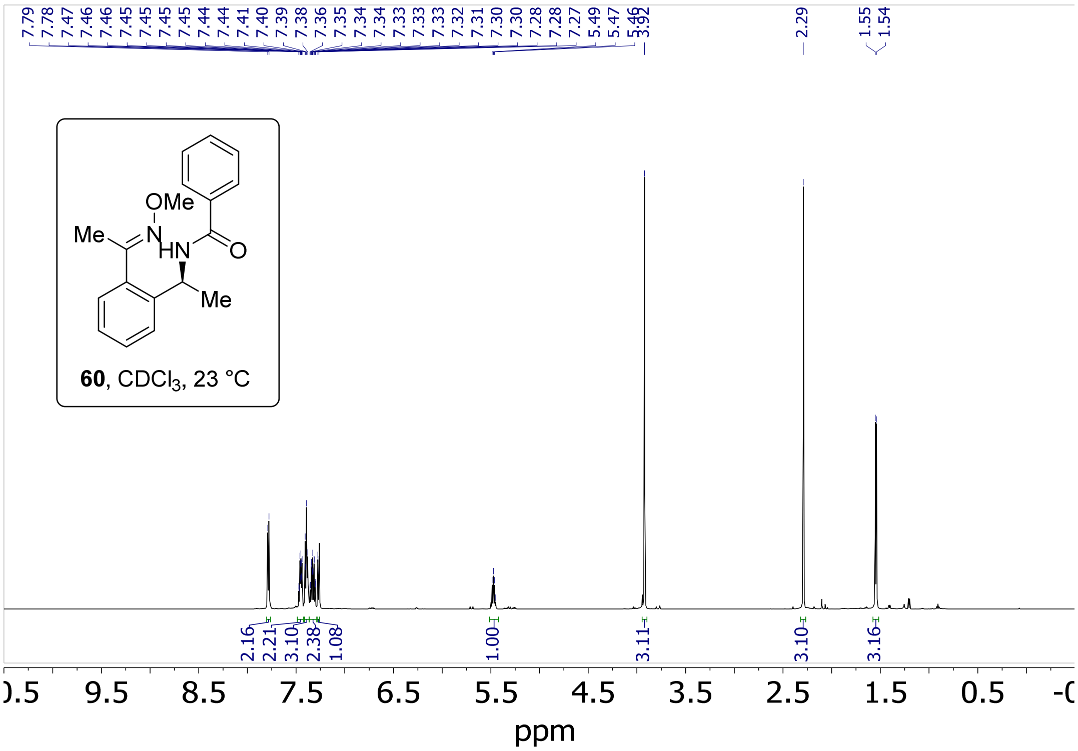
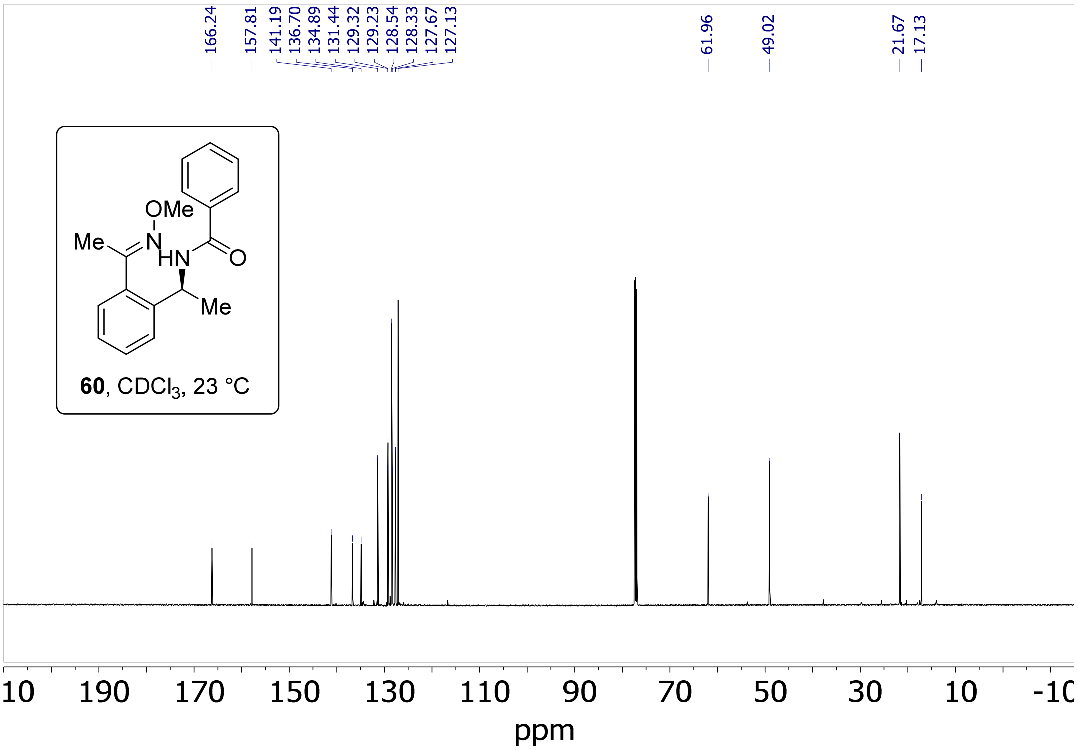
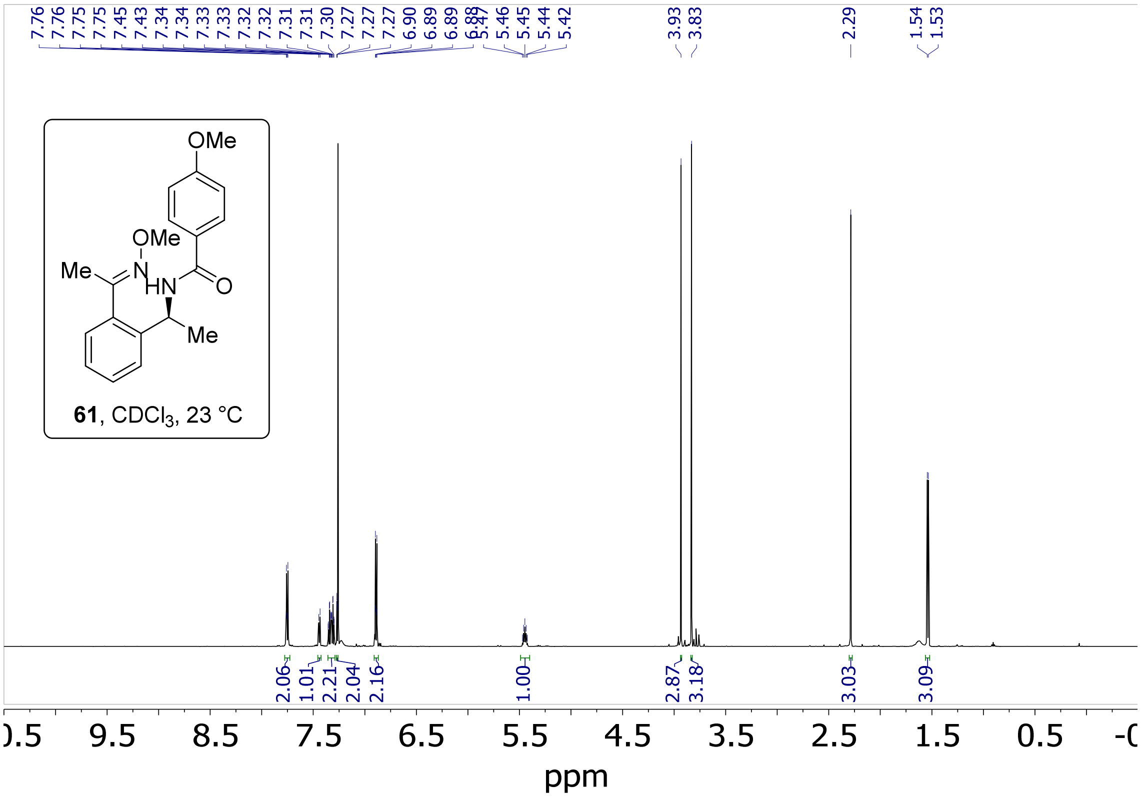
127.14
61.98
49.05
21.69
17.15
OMe
Me
N
HN
O
Me
60, CDCl$_3$, 23 °C
10
190
170
150
130
110
90
70
50
30
10
-1(
ppm

0.2 mmol scale reaction



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7.75
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7.34
7.33
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7.32
7.32
7.31
7.31
7.30
7.27
7.27
7.27
6.90
6.89
6.89
6.88
5.47
5.46
5.45
5.44
5.42
3.93
3.83
2.29
1.54
1.53
OMe
OMe
Me
N
HN
O
Me
61, CDCl3, 23 °C
2.06
1.01
2.21
2.04
2.16
1.00
2.87
3.18
3.03
3.09
9.5
8.5
7.5
6.5
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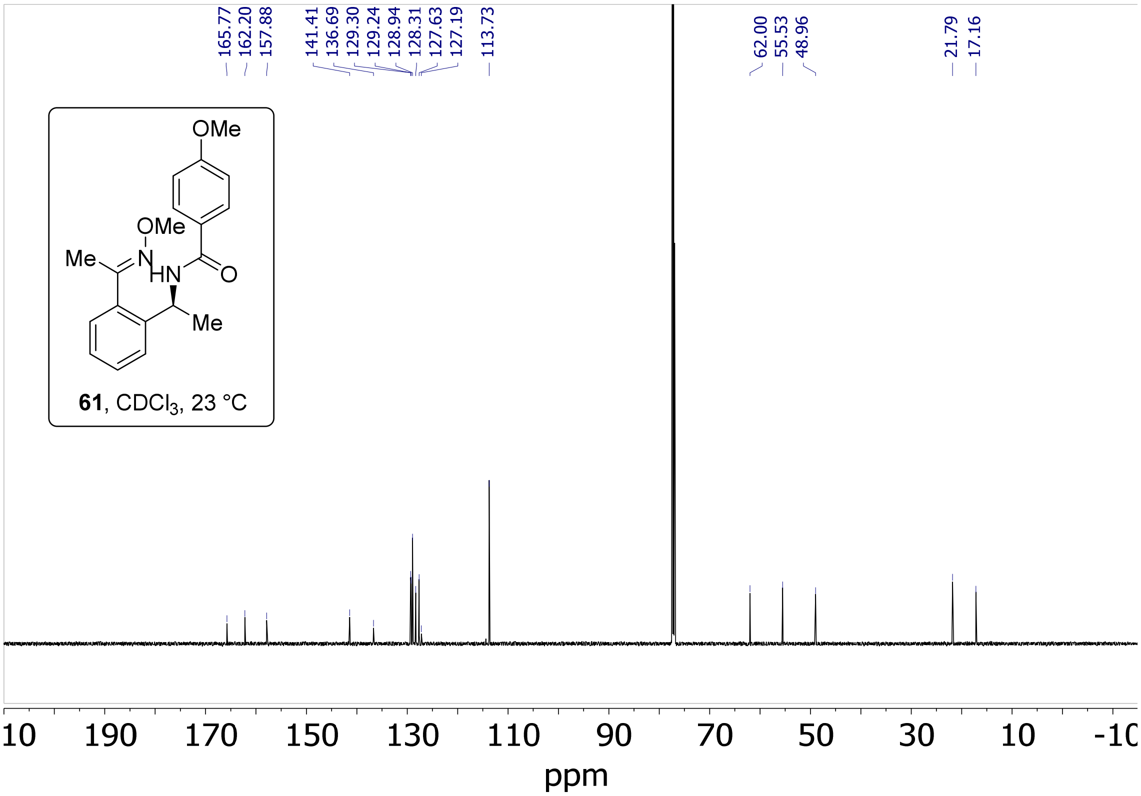
4.5
3.5
2.5
1.5
0.5
ppm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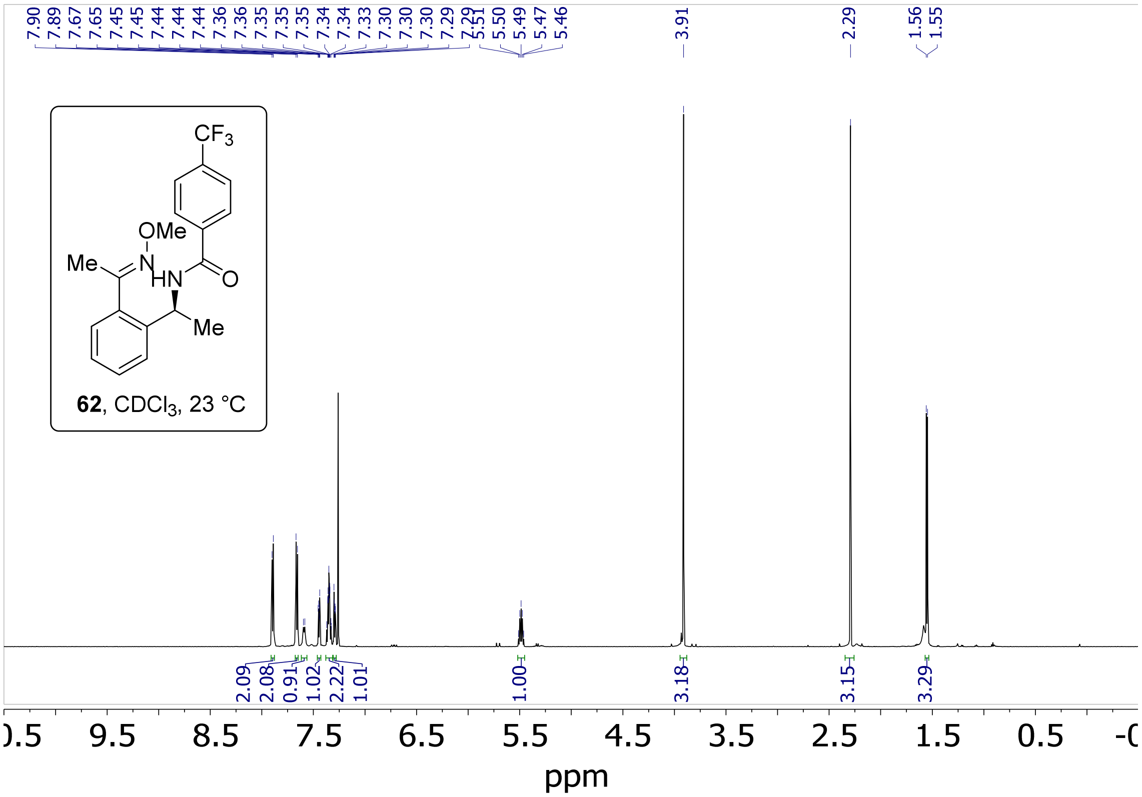
127.19
113.73
62.00
55.53
48.96
21.79
17.16
OMe
OMe
Me
N
HN
O
Me
61, CDCl3, 23 °C
190
170
150
130
110
90
70
50
30
10
ppm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7.45
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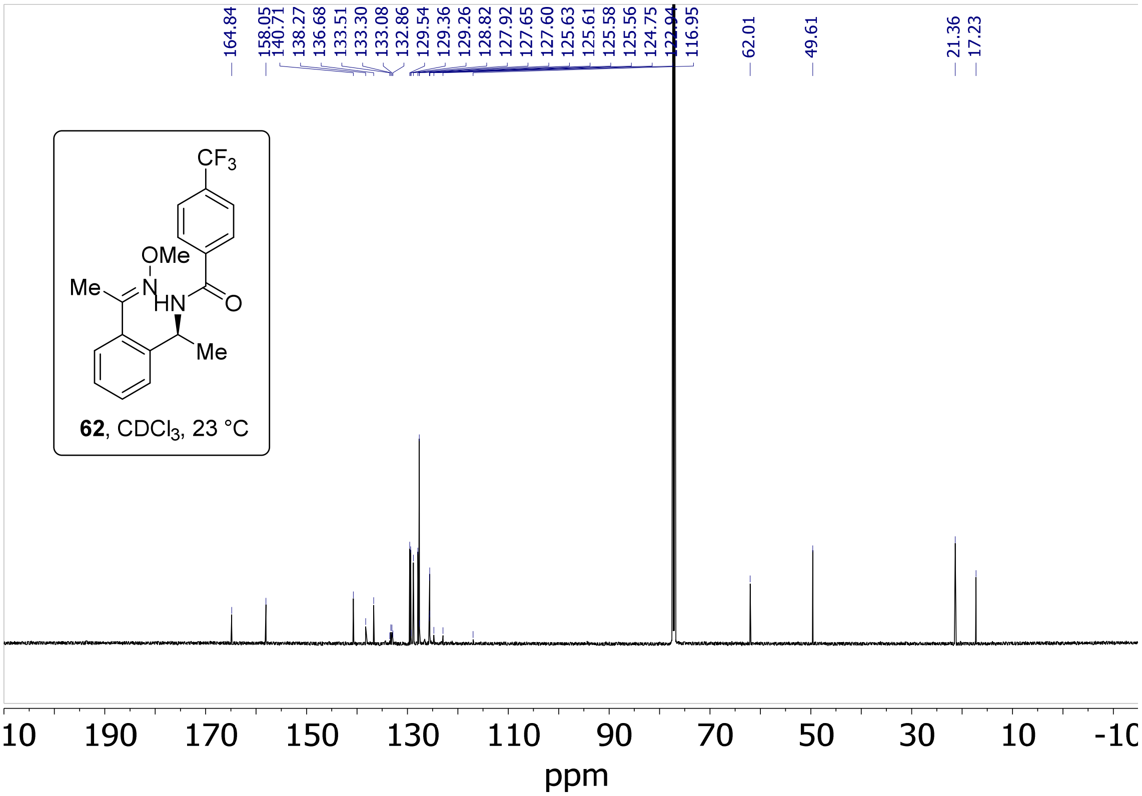
7.35
7.35
7.35
7.34
7.34
7.33
7.30
7.30
7.30
7.29
7.29
5.51
5.50
5.49
5.47
5.46
3.91
2.29
1.56
1.55
CF3
OMe
Me
N
HN
O
Me
62, CDCl3, 23 °C
2.09
2.08
0.91
1.02
2.22
1.01
1.00
3.18
3.15
3.29
).5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-(
ppm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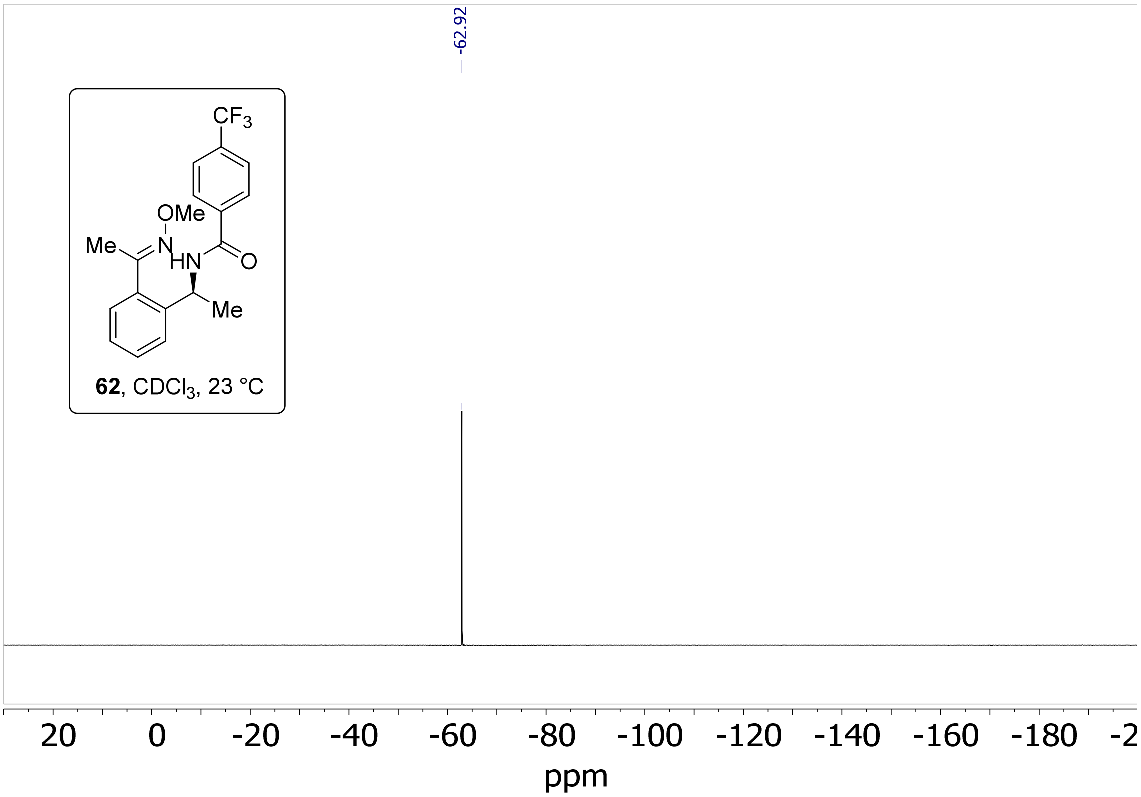
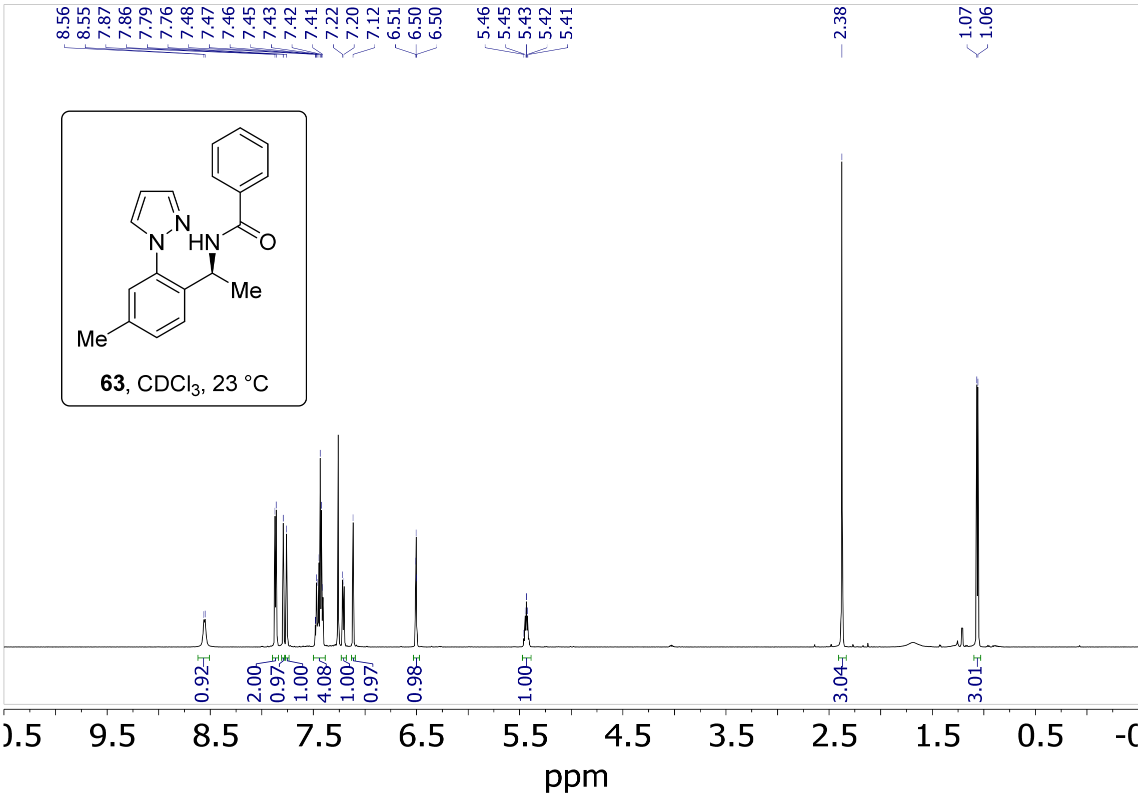
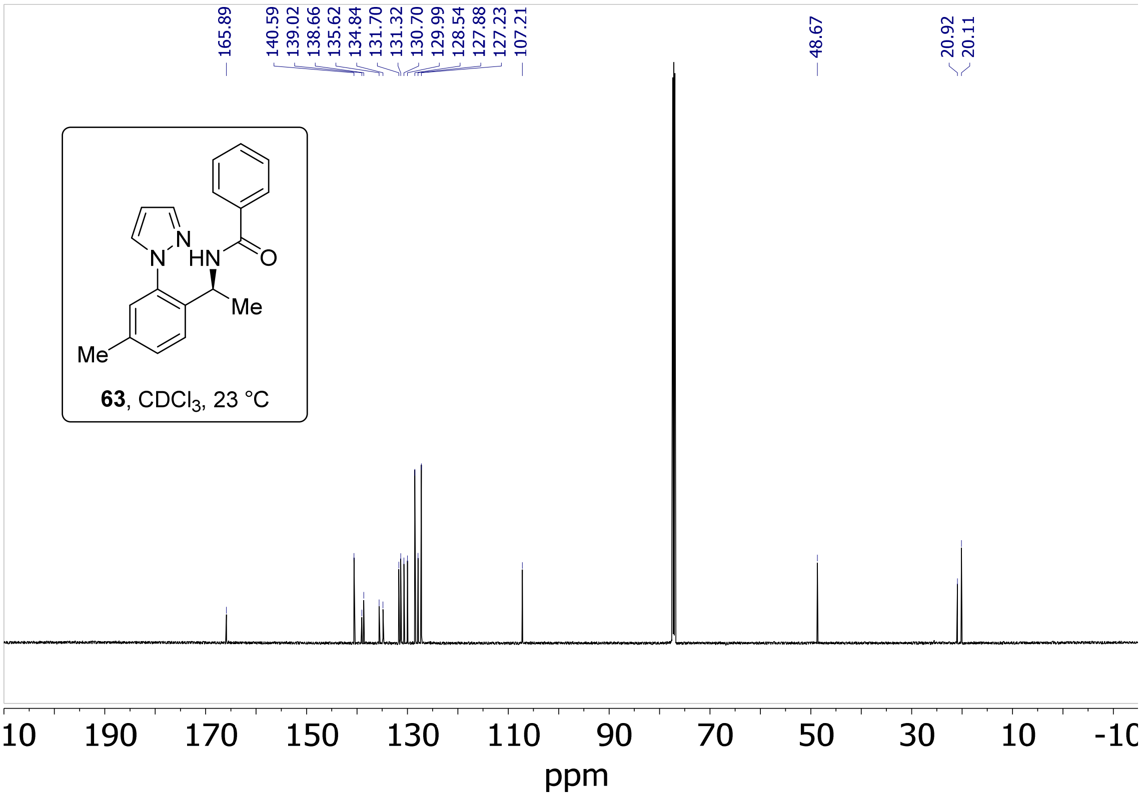
140.71
138.27
136.68
133.51
133.30
133.08
132.86
129.54
129.36
129.26
128.82
127.92
127.65
127.60
125.63
125.61
125.58
125.56
124.75
122.04
116.95
62.01
49.61
21.36
17.23
CF3
OMe
Me
N
HN
O
Me
62, CDCl3, 23 °C
10
190
170
150
130
110
90
70
50
30
10
-1C
ppm


-62.92
CF3
OMe
Me
N
HN
O
Me
62, CDCl3, 23 °C
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-2
ppm


8.56
8.55
7.87
7.86
7.79
7.76
7.48
7.47
7.46
7.45
7.43
7.42
7.41
7.22
7.20
7.12
6.51
6.50
6.50
5.46
5.45
5.43
5.42
5.41
2.38
1.07
1.06
N
N
HN
O
Me
Me
63, CDCl3, 23 °C
0.92
2.00
0.97
1.00
4.08
1.00
0.97
0.98
1.00
3.04
3.01
.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-
ppm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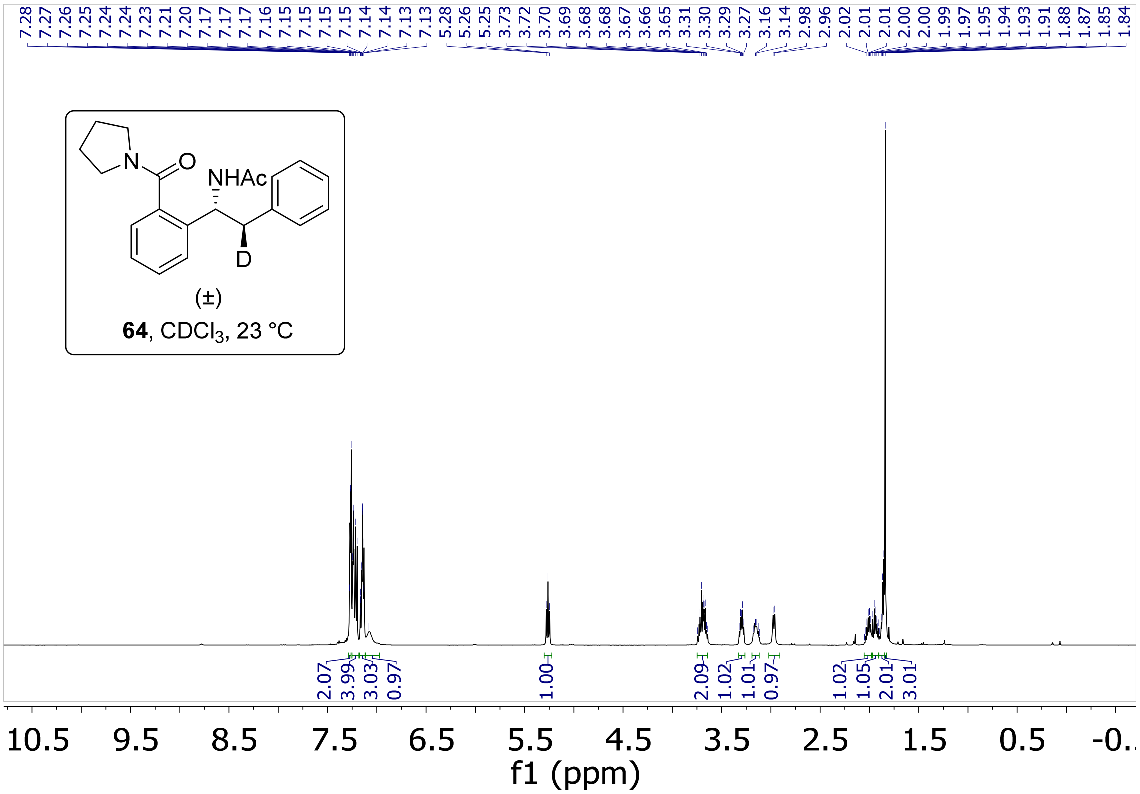
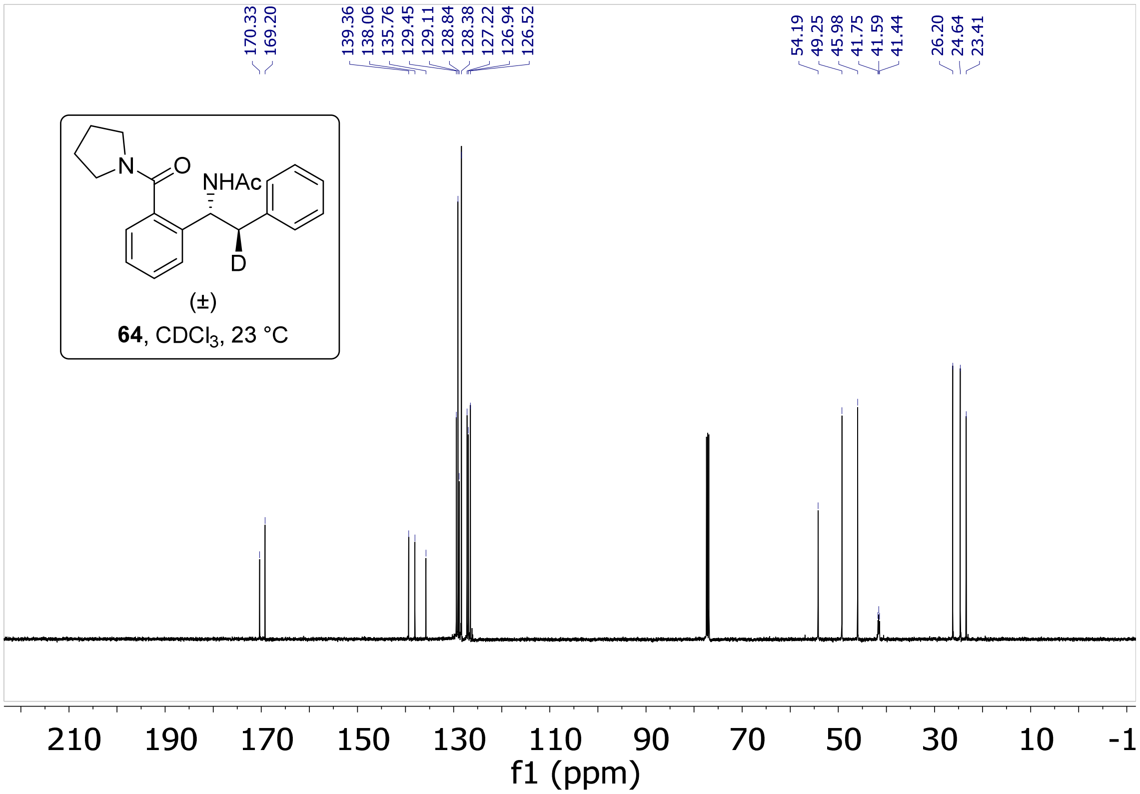
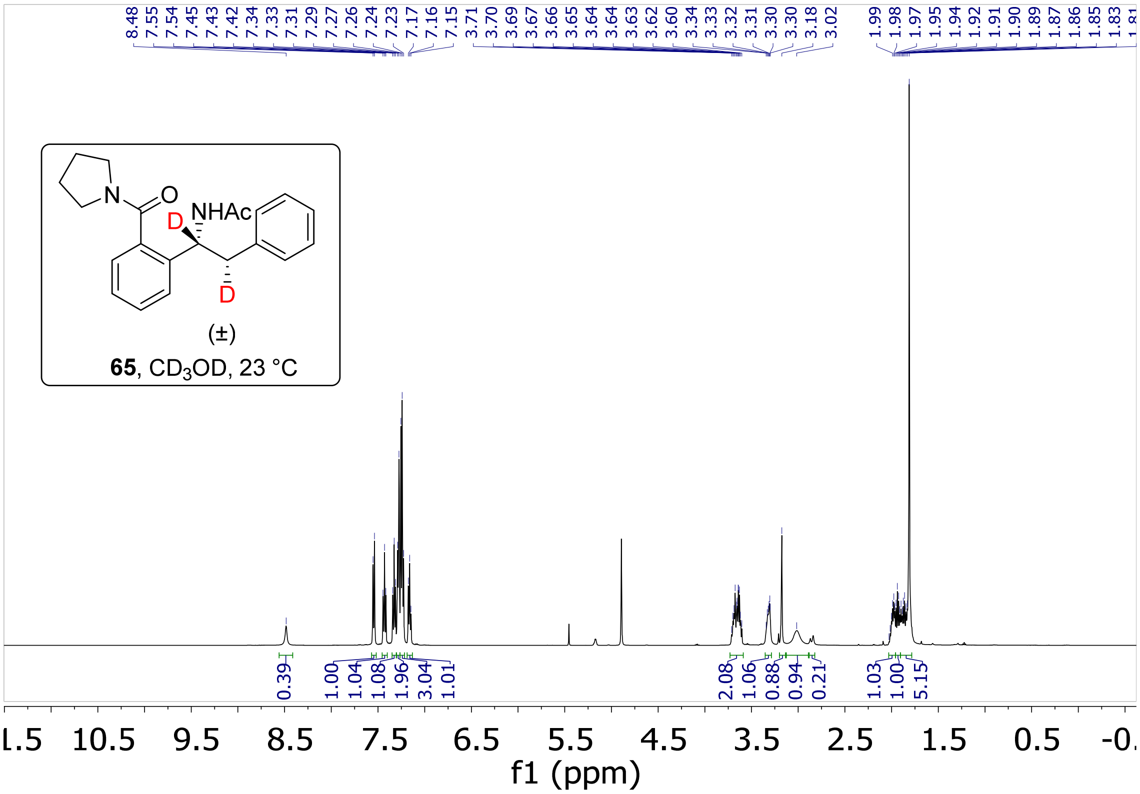
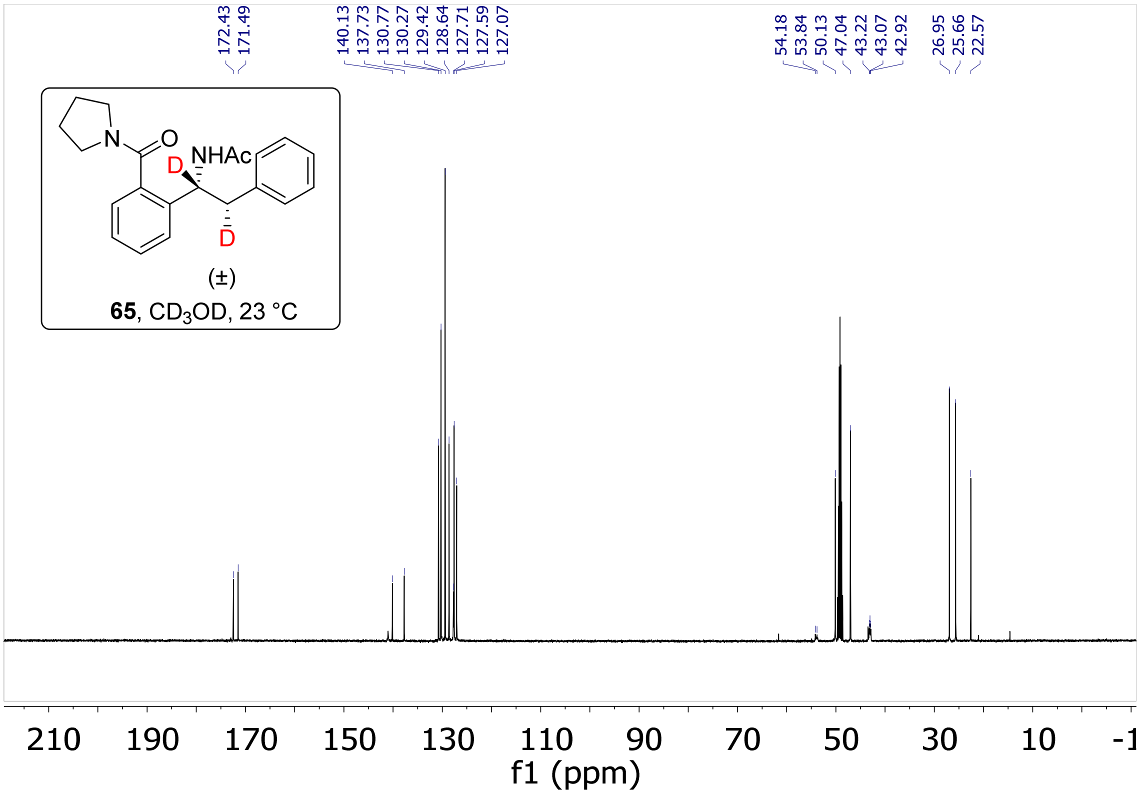
131.32
130.70
129.99
128.54
127.88
127.23
107.21
48.67
20.92
20.11
N
N
HN
O
Me
Me
63, CDCl3, 23 °C
10
190
170
150
130
110
90
70
50
30
10
-1
ppm


7.28 7.27 7.26 7.25 7.24 7.24 7.23 7.21 7.20 7.17 7.17 7.17 7.16 7.15 7.15 7.15 7.14 7.14 7.13 7.13 5.28 5.26 5.25 3.73 3.72 3.70 3.69 3.68 3.68 3.67 3.66 3.65 3.31 3.30 3.29 3.27 3.16 3.14 2.98 2.96 2.02 2.01 2.01 2.00 2.00 1.99 1.97 1.95 1.94 1.93 1.91 1.88 1.87 1.85 1.84
NHAc
O
N
D
(±)
64, CDCl$_3$, 23 °C
2.07 3.99 3.03 0.97
1.00
2.09 1.02 1.01 0.97
1.02 1.05 2.01 3.01
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.
f1 (ppm)


170.33 169.20
139.36 138.06 135.76 129.45 129.11 128.84 128.38 127.22 126.94 126.52
54.19 49.25 45.98 41.75 41.59 41.44
26.20 24.64 23.41
NHAc
O
N
D
(±)
64, CDCl$_3$, 23 °C
210 190 170 150 130 110 90 70 50 30 10 -1
f1 (ppm)


8.48
7.55
7.54
7.45
7.43
7.42
7.34
7.33
7.31
7.29
7.27
7.26
7.24
7.23
7.17
7.16
7.15
3.71
3.70
3.69
3.67
3.66
3.65
3.64
3.64
3.63
3.62
3.60
3.34
3.33
3.32
3.31
3.30
3.30
3.18
3.02
1.99
1.98
1.97
1.95
1.94
1.92
1.91
1.90
1.89
1.87
1.86
1.85
1.83
NHAc
N
O
D
D
(±)
65, CD3OD, 23 °C
0.39
1.00
1.04
1.08
1.96
3.04
1.01
2.08
1.06
0.88
0.94
0.21
1.03
1.00
5.15
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


172.43
171.49
140.13
137.73
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130.27
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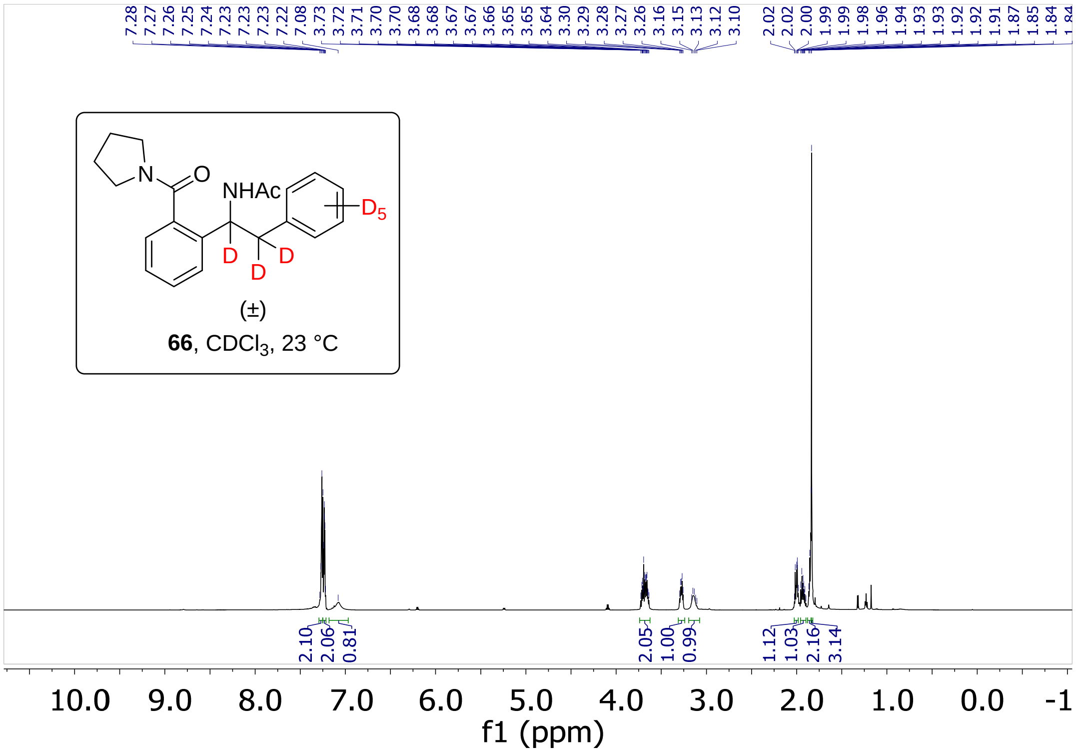
128.64
127.71
127.59
127.07
54.18
53.84
50.13
47.04
43.22
43.07
42.92
26.95
25.66
22.57
NHAc
N
O
D
D
(±)
65, CD3OD, 23 °C
210
190
170
150
130
110
90
70
50
30
10
f1 (ppm)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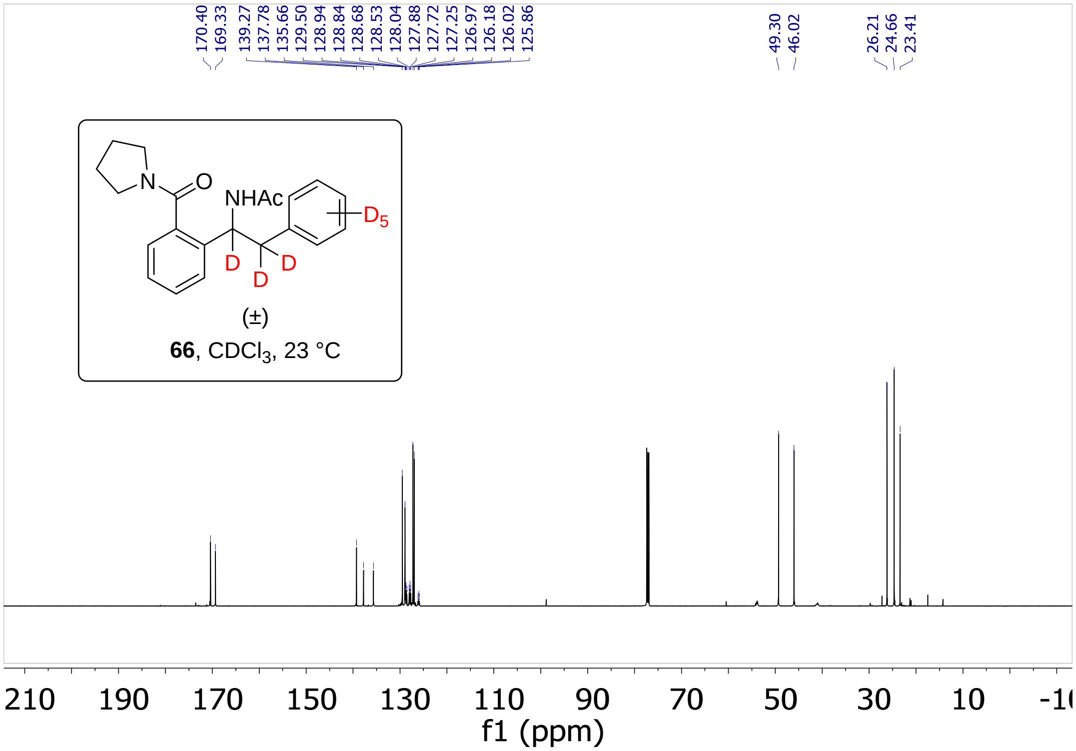
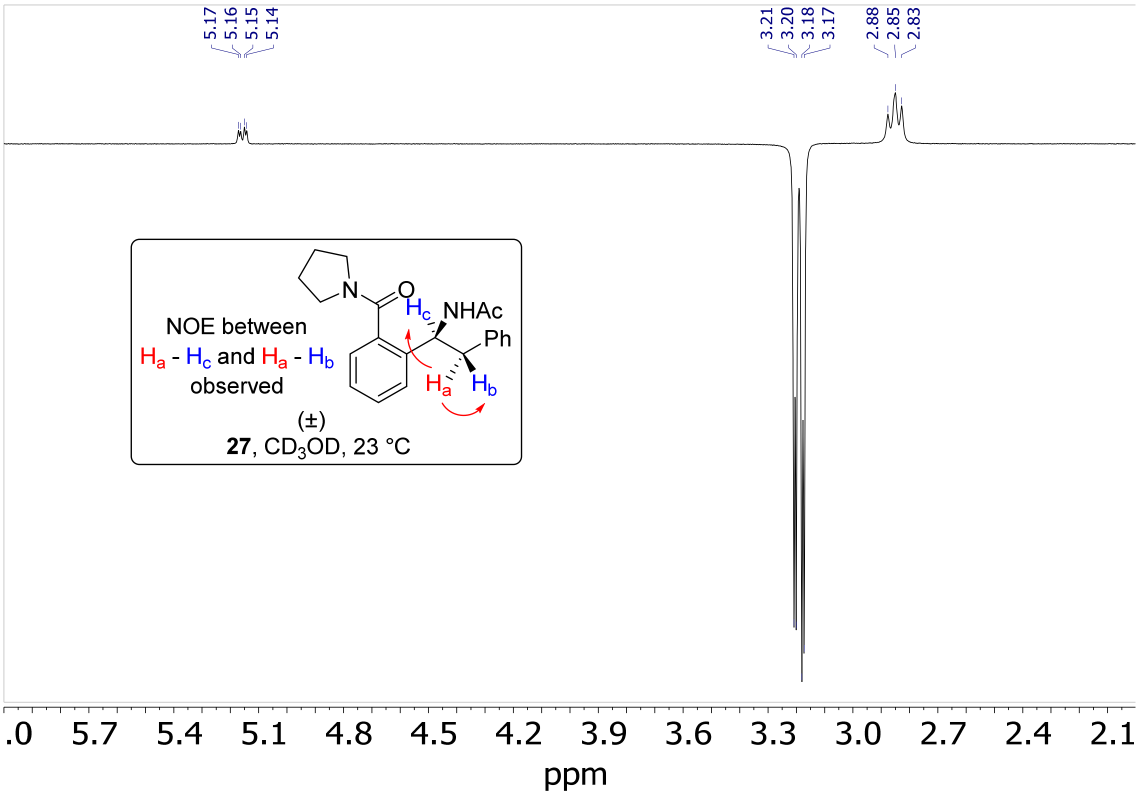
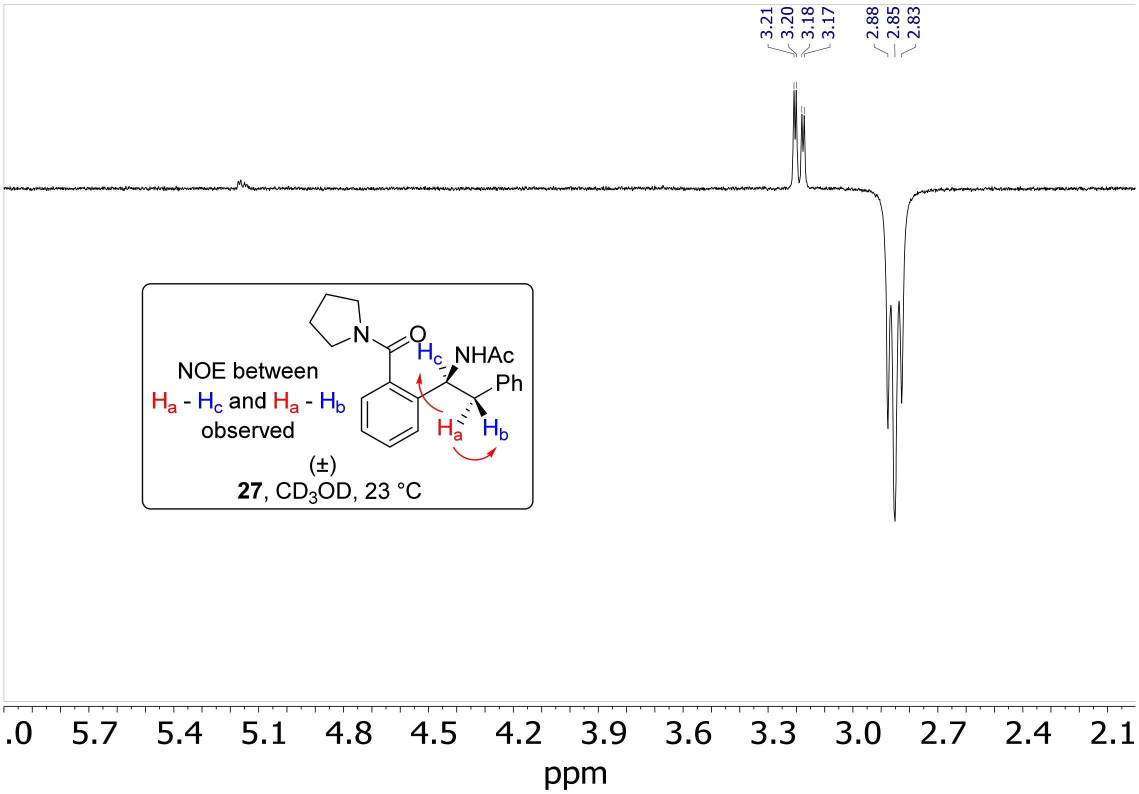
7.25
7.24
7.23
7.23
7.23
7.22
7.08
3.73
3.72
3.71
3.70
3.70
3.68
3.68
3.67
3.67
3.66
3.65
3.65
3.64
3.30
3.29
3.28
3.27
3.26
3.16
3.15
3.13
3.12
3.10
2.02
2.02
2.00
1.99
1.99
1.98
1.96
1.94
1.93
1.93
1.92
1.92
1.91
1.87
1.85
1.84
1.84
N
O
NHAc
D5
D
D
D
(±)
66, CDCl3, 23 °C
2.10
2.06
0.81
2.05
1.00
0.99
1.12
1.03
2.16
3.14
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)

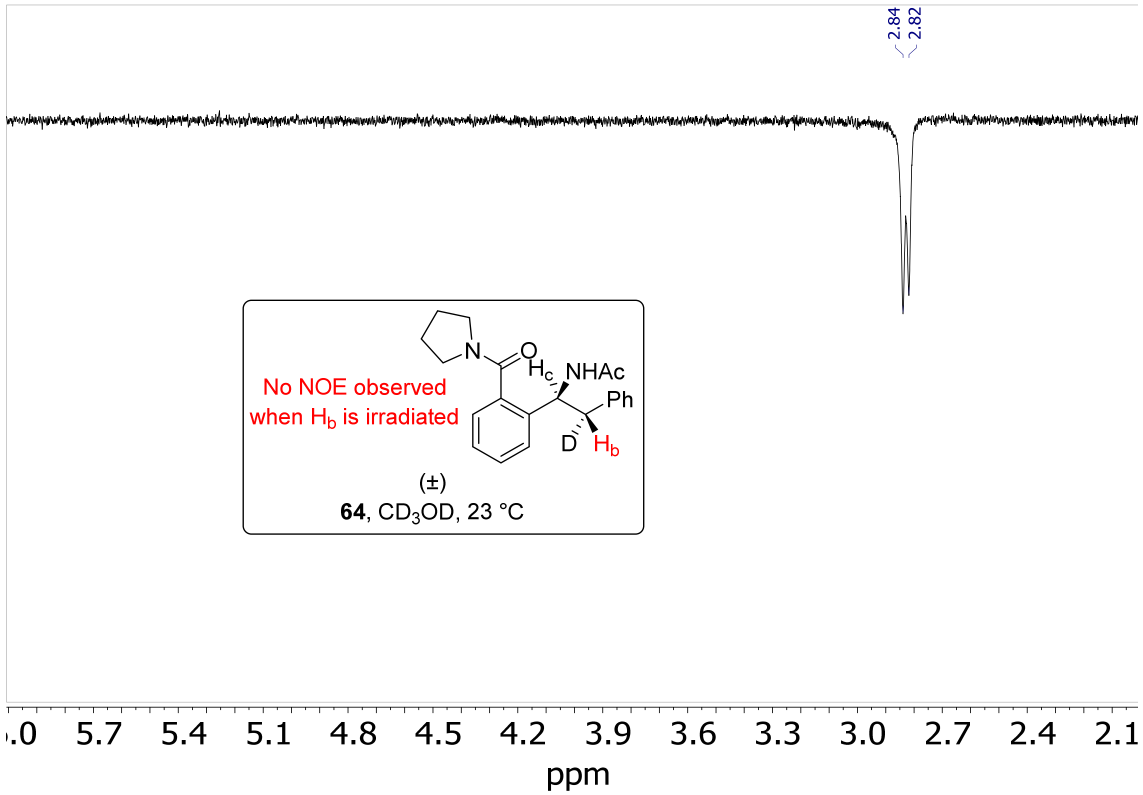

170.40
169.33
139.27
137.78
135.66
129.50
128.94
128.84
128.68
128.53
128.04
127.88
127.72
127.25
126.97
126.18
126.02
125.86
49.30
46.02
26.21
24.66
23.41
N
O
NHAc
D5
D
D
D
(±)
66, CDCl3, 23 °C
210
190
170
150
130
110
90
70
50
30
10
-1
f1 (ppm)

Additional NOE data for compound 27





Additional NOE data for compound 64



No NOE observed when H$_b$ is irradiated

(±)

64, CD_3OD, 23 °C

Supplementary References

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