Enantioselective C–H Amination Catalyzed by Nickel Iminyl Complexes Supported by Anionic Bisoxazoline (BOX) Ligands

Supporting Information

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General Considerations

All manipulations of metal complexes were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in an MBraun inert atmosphere drybox under a dinitrogen atmosphere (O_2 < 0.1 ppm, H_2O < 0.1 ppm). All glassware was oven dried overnight and cooled in an evacuated antechamber prior to use in the drybox. Benzene, diethyl ether, THF, and hexanes were dried over 4 Å molecular sieves (Strem) prior to use in the box. Chloroform-*d* was purchased from Cambridge Isotope Labs and used as received. Benzene-d_6, toluene-d_8, DMSO-d_6, methanol-d_4 and tetrahydrofuran-d_8 were purchased from Cambridge Isotope Labs, degassed, and stored over 4 Å molecular sieves prior to use. Dichloromethane, ethyl acetate and hexanes were purchased from Aldrich and used as received outside the box. Compounds sodium azide, trifluoracetic acid, trimethylsilyl azide, boron trifluoride diethyl ether adduct, triethyl amine, sodium hydroxide, hydrochloric acid (12 M), methylmagnesium bromide solution (3.0 M in diethyl ether), *n*-butyllithium solution (2.5 M in hexanes), 3,3,3-triphenylpropionic acid, (S)-4-Benzyl-2-oxazolidinone, oxalyl chloride, tosyl azide, perfluorobenzene, potassium hydride, 1-adamantyl azide, potassium, graphite, diethyl malonimidate dihydrochloride, (S)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride and 4-ethoxy-4-oxobutylzinc bromide solution (0.5 M) were purchased from Aldrich. Potassium hydride was washed thoroughly with hexanes and stored as a grey powder inside the glovebox. Compounds (^{AdF}L)Ni(py), $NiI_2(py)_2$ and (4-azido-4-methyl-pentyl-1,1-d_2)-4-fluorobenzene (**9$_{D2}$**) were prepared according to published procedures.[1] Celite® 545 (J. T. Baker) was dried in a Schlenk flask for 24 h under dynamic vacuum while heating to at least 150 °C prior to use in a drybox. Silica gel 32-63 μ (AIC, Framingham, MA) was used as received.

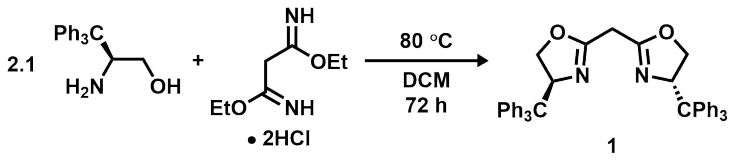
Characterization and Physical Measurement

^{1}H, ^{13}C and ^{19}F NMR were recorded on Varian Unity/Inova 500 MHz- spectrometers. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to $SiMe_4$ using the chemical shift of residual solvent peaks as reference. The ^{19}F NMR chemical shifts are reported relative to an external standard of boron trifluoride diethyl etherate.

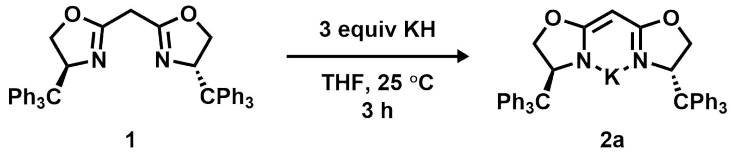
Elemental analysis was carried out using PerkinElmer 2400 CHNS/O Series II System.

EPR spectra were obtained on a Bruker EleXsys E-500 CW-EPR spectrometer. Spectra were measured as frozen toluene glasses at a microwave power of 0.6325–2 mW at 77 K. Spectral fitting incorporating spin state, hyperfine splitting and rhombicity were performed using EasySpin.[2]

Ligand Syntheses

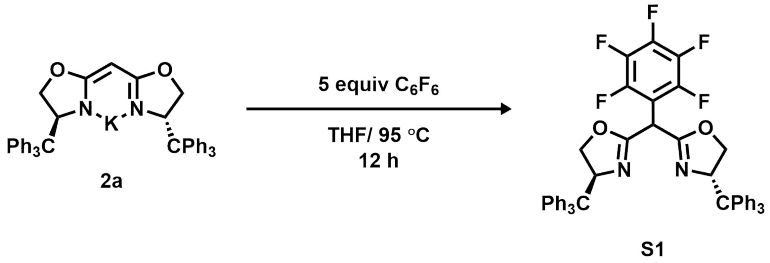


Bis((S)-4-trityl-4,5-dihydrooxazol-2-yl)methane (1a): To a 1 L storage flask in a N_2 filled drybox, (S)-2-amino-3,3,3-triphenylpropan-1-ol[3] (20.0 g, 65.9 mmol, 2.1 equiv) and diethyl malonimidate dihydrochloride (7.26 g, 31.4 mmol, 1.0 equiv) was added, followed by 300 mL of DCM. The flask was sealed under partial vacuum, and the suspension was heated to 80 °C for 72 h. After completion, the reaction is cooled to room temperature before 150 mL of water was added. The aqueous layer was extracted with DCM (3×100 mL). The organic phases were combined and dried with $MgSO_4$. All volatiles were evaporated to give crude product as a yellow oil, which is then purified by silica chromatography to yield pure **1a** (10.4 g, 52%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ/ppm: 7.63–6.90 (m, 30H), 5.85 (dd, J = 10.1, 6.5 Hz, 2H), 4.45 (t, J = 9.7 Hz, 2H), 4.12 (dd, J = 9.0, 6.5 Hz, 2H), 2.87 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.51, 129.52 (br.), 127.91 (br.), 126.40, 71.83, 70.69, 61.59, 28.31. Anal. Calc. for $C_{45}H_{38}N_2O_2$: C 84.61, H 6.00, N 4.39; Found C 84.26, H 6.07, N 4.27.

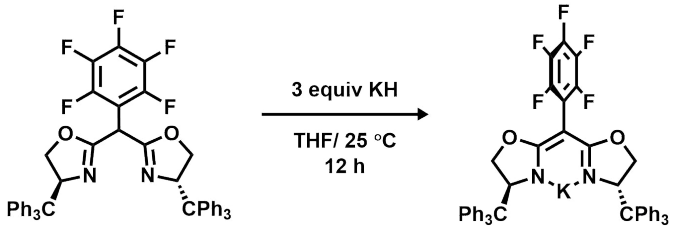


(^{Tr}L)K (2a): To a 20 mL scintillation vial, KH (93.9 mg, 2.35 mmol, 3.0 equiv) was added followed by 5 mL of THF. To the stirring suspension, a solution of **1a** (0.500 g, 0.78 mmol, 1.0 equiv) in 10 mL of THF was added dropwise. The suspension was left stirring for 3 h at room temperature before filtered to removed unreacted KH. The volatiles were removed to give an off-

white solid. The solid was triturated with 5 mL of hexanes, lyophilized with 5 mL of benzene and washed with an additional 5 mL of benzene to yield **2a** (0.397 g, 75%) as a white solid. ^{1}H NMR (500 MHz, THF-d_8) δ 9.16–8.89 (m, 30H), 7.34 (dd, J = 9.1, 6.6 Hz, 2H), 6.01 (t, J = 8.5 Hz, 2H), 5.31 (t, J = 7.2 Hz, 2H), 4.94 (s, 1H). ^{13}C NMR (126 MHz, THF-d_8) δ/ppm: 171.84, 132.12 (br.), 129.16 (br.), 127.43, 78.26, 63.99, 53.18, 25.86. Anal. Calc. for $C_{45}H_{37}KN_2O_2$: C 79.85, H 5.51, N 4.14; Found C 80.22, H 5.77, N 4.02.

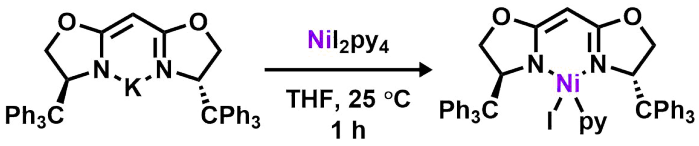


(4S,4'S)-2,2'-((perfluorophenyl)methylene)bis(4-trityl-4,5-dihydrooxazole) (S1): To a 250 mL storage flask in a N_2 filled drybox, a solution of **2a** (0.26 g, 0.38 mmol, 1 equiv) in 100 ml of THF was added, followed by dropwise addition of C_6F_6 (0.22 mL, 1.92 mmol, 5 equiv). The flask was sealed and heated to 95 °C for 12 h. After cooling to room temperature, the solution was poured into ice-water mixture and extracted with EtOAc (3×100 mL). The organic phases were combined, washed with brine and dried with $MgSO_4$. The volatiles were removed in vacuo to give dark red crude product, which is purified using column chromatography to yield **S1** (0.24 g, 78%) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ/ppm: 9.06 (s, 1H), 7.96–6.34 (m, 30H), 5.14 (dd, J = 8.5, 4.9 Hz, 2H), 4.07–3.61 (m, 4H). ^{13}C NMR (126 MHz, C_6D_6) δ/ppm: 165.02, 145.35 (t, J = 242.49 Hz), 139.48 (d, J = 260.25 Hz), 137.24 (d, J = 254.98 Hz), 129.23 (br.), 128.02 (br.), 126.16 (br.), 110.08 (t, J = 19.5 Hz), 69.97, 66.25, 61.53, 58.70. ^{19}F NMR (471 MHz, C_6D_6): −139.17 (dd, J = 24.9, 7.1 Hz), −159.17 (t, J = 21.6 Hz), −165.56 (td, J = 24.9, 7.1 Hz). Anal. Calc. for $C_{51}H_{37}F_5N_2O_2$: C 76.11, H 4.63, N 3.48; Found C 76.32, H 4.65, N 3.57.

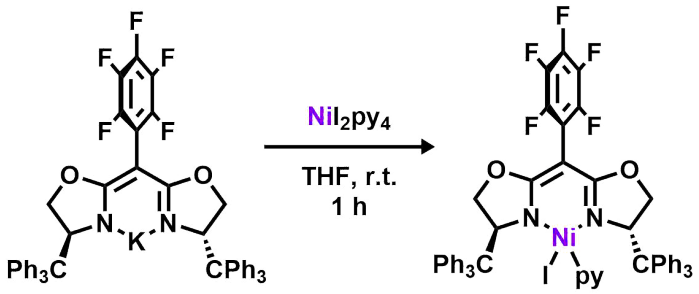


To a 20 mL scintillation vial, KH (35.8 mg, 2.35 mmol, 3.0 equiv) was added followed by 5 mL of THF. To the stirring suspension, a solution of above proteo-ligand (0.24 g, 0.30 mmol, 1.0 equiv) in 10 mL of THF was added dropwise. The suspension was left stirring for 3 h at room temperature before filtered to removed unreacted KH. The volatiles were removed to give a yellow solid. The solid was triturated with 5 mL of hexanes, lyophilized with 5 mL of benzene and washed with an additional 5 mL of benzene to yield **2d** (0.16 g, 63%) as a yellow solid. ^{1}H NMR (500 MHz, THF-d_8) δ 7.94–6.08 (m, 30H), 5.18 (dd, J = 9.4, 6.3 Hz, 2H), 4.28–4.04 (m, 2H), 3.67 (dd, J = 7.9, 6.4 Hz, 2H). ^{19}F NMR (471 MHz, THF-d_8) δ −140.24 (d, J = 21.5 Hz, 2F), −168.20 (t, J = 21.2 Hz, 1F), −170.17–−171.21 (m, 2F). Satisfactory ^{13}C NMR cannot be obtained for this compound due to its low solubility in common NMR solvents such as THF-d_8 and C_6D_6. Anal. Calc. for $C_{51}H_{36}F_5KN_2O_2$: C 72.67, H 4.30, N 3.32; Found C 72.70, H 4.42, N 3.46.

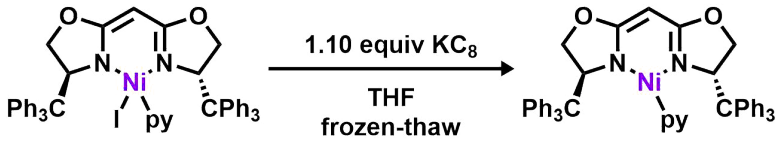
Transition Metal Complexes Syntheses



(^{Tr}L)Ni(py)I (3): A suspension of $Ni(py)_4I_2$ (177 mg, 0.28 mmol, 1 equiv) in 2 mL of THF was frozen. A solution of **2a** (200 mg, 0.30 mmol, 1.05 equiv) in 8 mL of THF was added to the frozen suspension. The mixture was warmed to room temperature and stirred for 1 h, during which time the solution turned from light yellow to maroon. The volatiles were then removed *in vacuo* and the resulting red solid was dissolved in benzene, frozen, and lyophilized. The resulting solid was washed with 20 mL of hexanes, dissolved in 20 mL of benzene, filtered through a Celite plug (20 cm^3), and lyophilized again to afford **(^{Tr}L)Ni(py)I (3)** as a dark maroon microcrystalline powder (167 mg, 66%). Needle-shaped crystals suitable for X-ray diffraction were grown from layering hexanes on a concentrated benzene solution of **3** at 25 °C overnight. ^{1}H NMR (600 MHz, C_6D_6) δ 181.91, 155.46, 133.70, 46.78, 26.52, 16.31, 15.11, 11.16, 9.90, 9.21, 8.45, 7.98, 0.30, −1.13, −13.93, −63.95. Anal. Calc. for $C_{50}H_{41}IN_3NiO_2$: C 66.54, H 4.69, N 4.66; Found C 66.52, H 4.76, N 4.62.

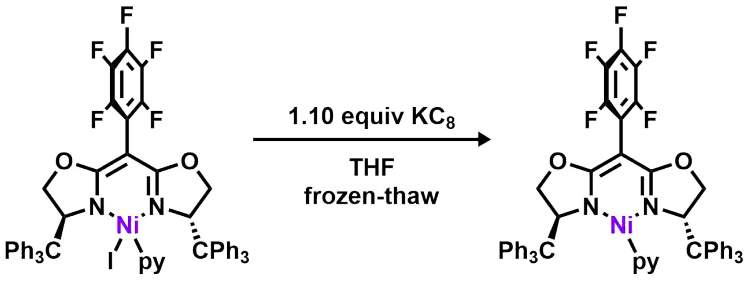


(^{TrF}L)Ni(py)I (3$_F$): A suspension of $Ni(py)_4I_2$ (142 mg, 0.23 mmol, 1 equiv) in 2 mL of THF was frozen. A solution of **2d** (200 mg, 0.24 mmol, 1.05 equiv) in 8 mL of THF was added to the frozen suspension. The mixture was warmed to room temperature and stirred for 1 h, during which time the solution turned from light yellow to maroon. The volatiles were then removed *in vacuo* and the resulting red solid was dissolved in benzene, frozen, and lyophilized. The resulting solid was washed with 20 mL of hexanes, dissolved in 20 mL of benzene, filtered through a Celite plug (20 cm^3), and lyophilized again to afford **(^{TrF}L)Ni(py)I (3$_F$)** as a dark maroon microcrystalline powder (176 mg, 73%). Needle-shaped crystals suitable for X-ray diffraction were grown from layering hexanes on a concentrated benzene solution of **3$_F$** at 25 °C overnight. ^{1}H NMR (500 MHz, C_6D_6) δ 168.42, 146.39, 47.00, 28.48, 15.84, 15.56, 11.53, 10.14, 9.13, 8.55, 8.06, 0.01, −1.70, −13.35. ^{19}F NMR (471 MHz, C_6D_6) δ −114.75 (d, J = 22.0 Hz), −117.88 (d, J = 20.2 Hz), −156.03 (t, J = 20.8 Hz), −163.09 (t, J = 18.5 Hz), −164.84 (t, J = 18.9 Hz). Anal. Calc. for $C_{56}H_{41}F_5IN_3NiO_2$: C 62.95, H 3.87, N 3.93; Found C 62.67, H 3.96, N 3.65.

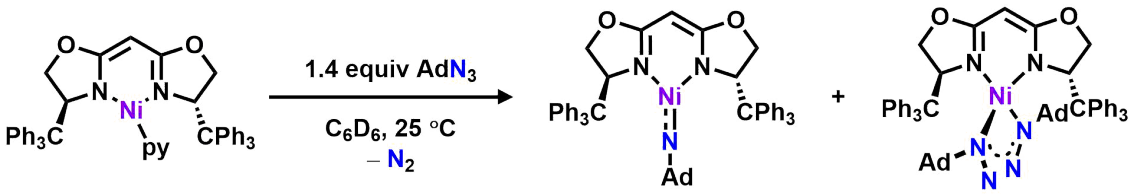


(^{Tr}L)Ni(py) (4): A solution of **3** (150 mg, 0.18 mmol, 1.00 equiv) in 5 mL of THF was frozen. Potassium graphite (27.1 mg, 0.20 mmol, 1.10 equiv) was added in one portion as soon as the solution started stirring, causing an instantaneous color change from maroon to dark yellow. The solution was stirred for 3 min before filtering through a Celite plug (20 cm^3). The volatiles were then removed *in vacuo*. The resulting dark yellow solid residue was dissolved in benzene, frozen, and lyophilized. The resulting solid was washed with 2 mL of hexanes, dissolved in 20 ml of

benzene, filtered through a Celite plug (20 cm^3), and lyophilized again to afford **(^{Tr}L)Ni(py) (4)** as a dark yellow microcrystalline powder (102 mg, 80%). Needle-shaped X-ray quality crystals were grown by layering hexanes on a concentrated THF solution at 25 °C overnight. ^{1}H NMR (500 MHz, C_6D_6): δ ppm 19.22 (br.), −1.71 (br.). EPR (toluene, 77 K): g_1 = 2.12, g_2 = 2.06, g_3 = 1.98. Anal. Calc. for $C_{50}H_{42}N_3NiO_2$: C 77.43, H 5.46, N 5.42; Found C 77.15, H 5.38, N 5.47.



(^{TrF}L)Ni(py) (4$_F$): A solution of **3$_F$** (100 mg, 0.11 mmol, 1.00 equiv) in 5 mL of THF was frozen. Potassium graphite (15.8 mg, 0.12 mmol, 1.10 equiv) was added in one portion as soon as the solution started stirring, causing an instantaneous color change from maroon to dark yellow. The solution was stirred for 3 min before filtering through a Celite plug (20 cm^3). The volatiles were then removed in vacuo. The resulting dark yellow solid residue was dissolved in benzene, frozen, and lyophilized. The resulting solid was washed with 2 mL of hexanes, dissolved in 20 ml of benzene, filtered through a Celite plug (20 cm^3), and lyophilized again to afford **(^{TrF}L)Ni(py) (4$_F$)** as a dark yellow microcrystalline powder (68.6 mg, 78%). Needle-shaped X-ray quality crystals were grown by storing a concentrated hexanes solution at −35 °C overnight. ^{1}H NMR (500 MHz, THF): δ ppm 16.51, −1.31. ^{19}F NMR (470 MHz, THF): δ ppm −137.65, −161.60, −169.28. EPR (toluene, 77 K): S = ½, g_1 = 2.43, g_2 = 2.13, g_3 = 2.07. Anal. Calc. for $C_{56}H_{41}F_5N_3NiO_2$: C 71.43, H 4.39, N 4.46; Found C 71.08, H 4.54, N 4.17.

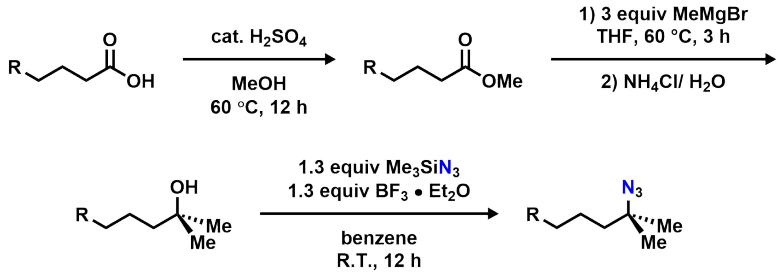


(^{Tr}L)Ni(NAd) (6): A solution of (^{Tr}L)Ni(py) (**4**) (100 mg, 0.140 mmol, 1.00 equiv) in 5 mL of benzene was frozen in a 20 mL scintillation vial and removed from the freezer. As the solution is thawing and stirring, another solution of AdN_3 (35.6 mg, 0.201 mmol, 1.40 equiv) in 3 mL of benzene was added dropwise slowly over 30 min, during which the solution changed from dark yellow to dark orange. The solution was then lyophilized, and the solid residue was extracted with 5 mL of diethyl ether. All volatiles were removed in vacuo and the resulting green was recrystallized from a concentrated THF solution vapor diffusing into hexanes at −35 °C over 3 days to give **(^{Tr}L)Ni(NAd) (6)** (8.5 mg, 7%) as dark green plate-shaped crystals suitable for X-ray diffraction. ^{1}H NMR (500 MHz, C_6D_6): this compound is ^{1}H NMR silent. EPR (toluene, 77 K): S = ½, g_1 = 2.19, g_2 = 2.06, g_3 = 1.93, $A(^{14}N)$ = 20.9 G. Anal. Calc. for $C_{55}H_{52}N_3NiO_2$: C 78.11, H 6.20, N 4.97; Found C 77.96, H 5.93, N 4.89.

(^{Tr}L)Ni(κ^2-N$_4$Ad$_2$) (5): The orange solid residue after diethyl ether extraction above was recrystallized from layering hexanes on a concentrated benzene solution overnight to give **(^{Tr}L)Ni(κ^2-N$_4$Ad$_2$) (5)** (35.2 mg, 24%) as dark orange long needle-shaped crystals suitable for X-ray diffraction. ^{1}H NMR (500 MHz, C_6D_6): this compound is ^{1}H NMR silent. EPR (toluene, 77 K): S = ½, g_1 = 2.33, g_2 = 2.17, g_3 = 2.01. Anal. Calc. for $C_{65}H_{67}N_6NiO_2$: C 76.32, H 6.60, N 8.22; Found C 75.99, H 6.59, N 8.60.

Organoazide Syntheses

General procedures for preparation of organoazides.[1]



Procedure A:

Step 1: Catalytic amount of concentrated H_2SO_4 was added to a solution of the corresponding carboxylic acid (1 equiv) in 200 mL methanol. The reaction mixture was stirred at 60 °C for 12 hours. Upon completion, 10 ml of water was added to the reaction mixture before it was concentrated and diluted in EtOAc. The aqueous phase was extracted three times with 150 ml of EtOAc, and the combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated. The product was carried onto the next step without further purification.

Step 2: In an air-free storage flask, corresponding ester was added followed by 200 ml of air-free, dry THF under N_2 atmosphere. The solution was cooled to – 78 °C using a dry ice/acetone bath. To the cooled mixture, MeMgBr (3 equiv, 3 M solution in Et_2O) was added dropwise. The flask was then sealed and heated to 60 °C for 3 hours. The reaction was then poured into an ice/water mixture and extracted three time with 150 ml of EtOAc. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated. The product was carried onto the next step without further purification.

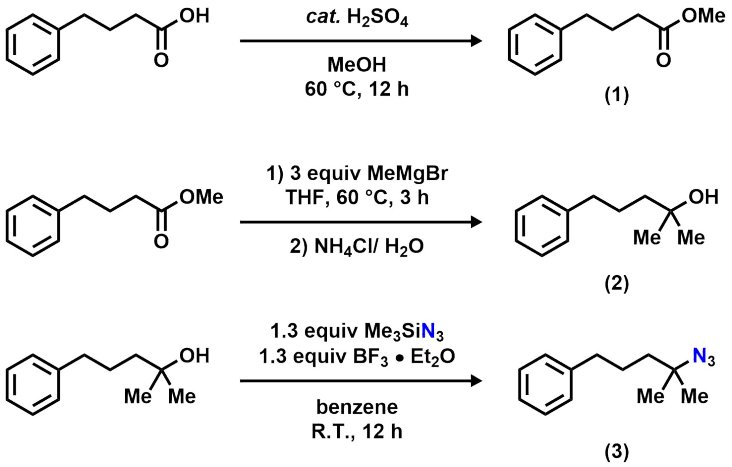
Step 3: In a Schlenk flask under N_2 atmosphere, the corresponding alcohol was added followed by 200 ml of air-free, dry benzene. The solution was cooled to 0 °C using an ice bath before $TMSN_3$

(1.3 equiv) was added followed by $BF_3 \cdot Et_2O$ (1.3 equiv) added as one portion. The reaction was then stirred for 12 hours, poured into water and extracted three times with 150 ml of EtOAc. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated. The product was purified using silica chromatography to yield the final organoazide.

Drying: The resulting organoazide was brought into a N_2-filled glovebox, dissolved in either hexanes or Et_2O and let sit over 4 Å molecular sieves overnight. The solution was then filtered through a short silica plug and concentrated to provide dry, degassed organoazide for catalysis.

Characterization of Organoazides

(4-Azido-4-methylpentyl)benzene (9)[1]

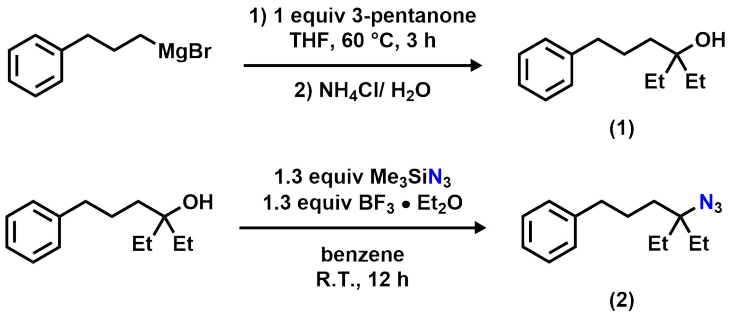


1. Methyl 4-phenylbutanoate (S2): Synthesized following previously reported procedure.

2. 2-Methyl-5-phenylpentan-2-ol (S3): Synthesized following previously reported procedure.

3. (4-azido-4-methylpentyl)benzene (9): Synthesized following previously reported procedure.

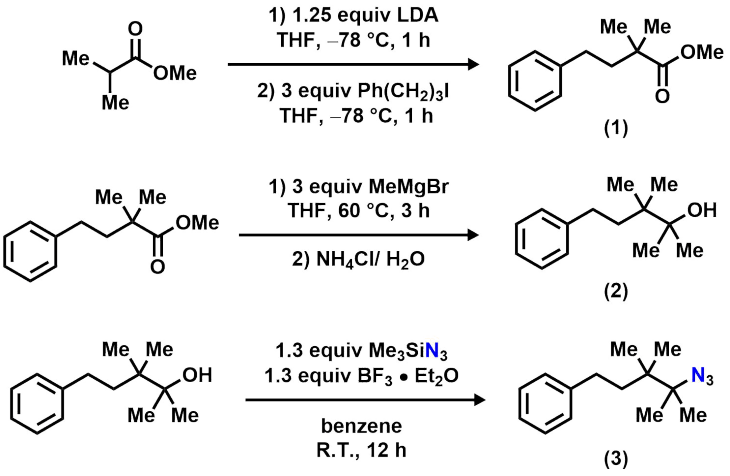
(4-Azido-4-ethylhexyl)benzene (S4)



1. 3-Ethyl-6-phenylhexan-3-ol (S4): Synthesized following previously reported procedure.[4]

2. (4-Azido-4-ethylhexyl)benzene (S5): Synthesized following Procedure A, step 3. The reaction was run on 4.00 mmol scale to give 0.56 g (61% yield) of **S5** as a colorless oil. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.43–7.36 (m, 2H), 7.35–7.26 (m, 3H), 2.75 (t, *J* = 7.5 Hz, 2H), 1.84–1.72 (m, 2H), 1.71–1.57 (m, 6H), 0.99 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 142.67, 128.84, 128.78, 126.28, 67.56, 36.58, 35.50, 29.01, 25.92, 8.25. HRMS (ESI^+) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2074 $[M+NH_4]^+$.

(4-Azido-4-ethylhexyl)benzene (S4)



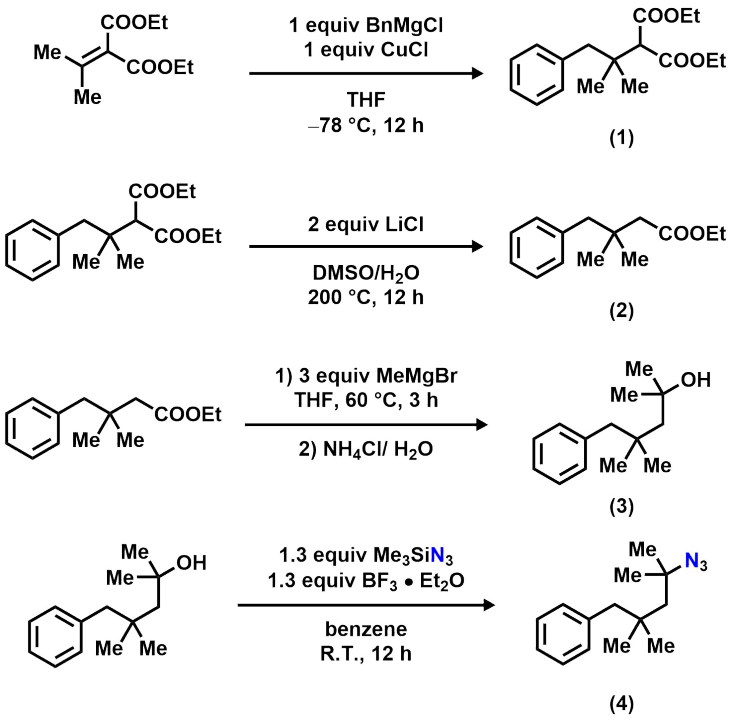
1. Methyl 2,2-dimethyl-4-phenylbutanoate (S6): Synthesized following previously reported procedure.[5]

2. 2,3,3-Trimethyl-5-phenylpentan-2-ol (S7): Synthesized following Procedure A, step 2. The reaction was run on 10.0 mmol scale to give 1.82 g (88% yield) of **S7** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.42–7.37 (m, 2H), 7.36–7.32 (m, 2H), 7.31–7.27 (m, 1H), 2.79–2.68 (m, 2H), 1.80–1.72 (m, 3H), 1.31 (s, 6H), 1.13 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 144.27, 128.86, 128.76, 125.99, 75.71, 40.43, 40.16, 31.90, 25.77, 21.78. HRMS (ESI^+) m/z Calc. 206.1665 $[C_{14}H_{22}O-e]^+$, Found. 206.1666 $[M-e]^+$.

3. (4-Azido-3,3,4-trimethylpentyl)benzene (S8): Synthesized following Procedure A, step 3. Separated as a 72:28 mixture of **S8** and (3-azido-3,4,4-trimethylpentyl)benzene (**S9**). The reaction was run on 3.33 mmol scale to give 0.49 g (53% yield) of **S8**/**S9** as a colorless oil. **S8**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.37–7.30 (m, 2H), 7.30–7.16 (m, 3H), 2.70–2.52 (m, 2H), 1.73–1.58 (m, 2H), 1.34 (s, 6H), 1.05 (s, 6H). **S9**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.38–7.29 (m, 2H), 7.29–7.19 (m, 3H), 2.83–2.70 (m, 2H), 2.04–1.89 (m, 1H), 1.87–1.72 (m, 1H), 1.42 (s, 3H), 1.03 (s, 9H). ^{13}C

NMR (126 MHz, CD_2Cl_2) δ 143.41, 142.44, 128.39, 128.34, 128.30, 125.82, 125.60, 69.29, 67.91, 40.17, 39.67, 39.45, 37.81, 31.16, 31.13, 25.44, 21.50, 21.34, 16.95. HRMS (ESI^+) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2076 $[M+NH_4]^+$.

(4-Azido-2,2,4-trimethylpentyl)benzene (S10)



1. Diethyl 2-(2-methyl-1-phenylpropan-2-yl)malonate (S9): Synthesized following Procedure A, step 2. The reaction was run on 10.0 mmol scale to give 2.49 g (85% yield) of **S9** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.30–7.25 (m, 2H), 7.24–7.20 (m, 1H), 7.20–7.15 (m, 2H), 4.18 (q, J = 7.2 Hz, 4H), 3.24 (s, 1H), 2.82 (s, 2H), 1.26 (t, J = 7.2 Hz, 6H), 1.08 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 169.03, 138.77, 131.59, 128.54, 126.95, 61.64, 60.08, 46.68, 37.69, 25.59, 14.66. HRMS (ESI$^+$) m/z Calc. 293.1747 $[C_{17}H_{24}O_4+H]^+$, Found. 293.1748 $[M+H]^+$.

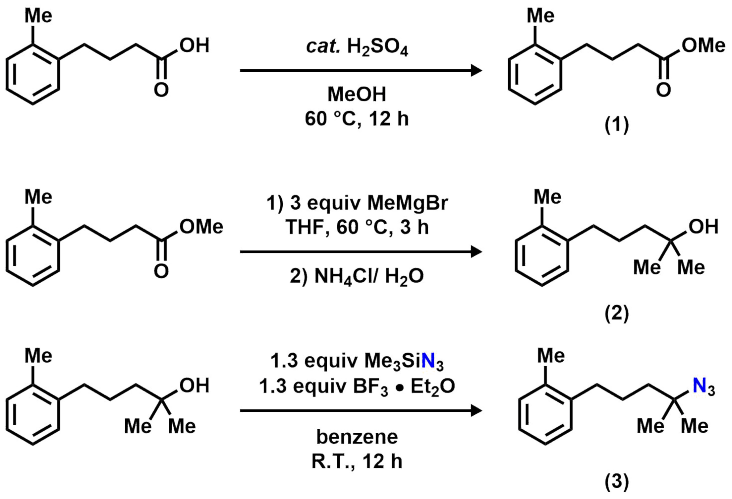
2. Ethyl 3,3-dimethyl-4-phenylbutanoate (S10): Synthesized following Procedure A, step 2. The reaction was run on 8.00 mmol scale to give 0.97 g (55% yield) of **S10** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.29 (t, J = 6.9 Hz, 2H), 7.26–7.17 (m, 3H), 4.14 (q, J = 7.1 Hz, 2H), 2.68 (s, 2H), 2.18 (s, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.02 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.78,

138.42, 130.44, 127.45, 125.73, 59.60, 47.53, 45.13, 33.89, 26.68, 13.87. HRMS (ESI^+) m/z Calc. 221.1536 $[C_{14}H_{20}O_2+H]^+$, Found. 221.1537 $[M+H]^+$.

3. 2,4,4-Trimethyl-5-phenylpentan-2-ol (S11): Synthesized following Procedure A, step 2. The reaction was run on 4.00 mmol scale to give 0.76 g (92% yield) of **S11** as a colorless oil. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.26 (d, J = 7.5 Hz, 2H), 7.22–7.13 (m, 3H), 2.63 (s, 2H), 1.55 (s, 2H), 1.36 (s, 1H), 1.30 (s, 6H), 1.02 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 139.08, 130.62, 127.22, 125.43, 71.87, 53.72, 50.50, 34.72, 31.76, 27.52. HRMS (ESI^+) m/z Calc. 206.1665 $[C_{14}H_{22}O-e]^+$, Found. 206.1664 $[M-e]^+$.

4. (4-Azido-2,2,4-trimethylpentyl)benzene (S12): Synthesized following Procedure A, step 3. The reaction was run on 3.00 mmol scale to give 0.36 g (52% yield) of **S12** as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.41–7.36 (m, 2H), 7.35–7.31 (m, 1H), 7.29–7.24 (m, 2H), 2.74 (s, 2H), 1.68 (s, 2H), 1.47 (s, 6H), 1.15 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.72, 130.85, 127.66, 125.96, 61.83, 51.57, 50.60, 35.13, 28.69, 27.64. HRMS (ESI^+) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2074 $[M+NH_4]^+$.

1-(4-Azido-4-methylpentyl)-2-methylbenzene (S13)

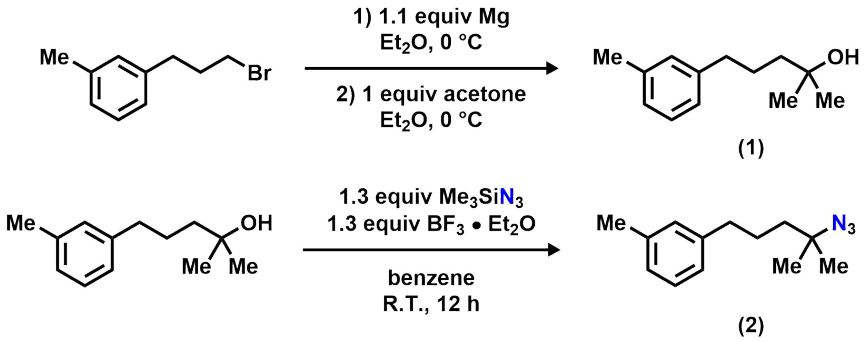


1. Methyl 4-(o-tolyl)butanoate (S13): Synthesized following Procedure A, step 1. Spectral features are consistent with reported data.[6]

2. 2-Methyl-5-(o-tolyl)pentan-2-ol (S14): Synthesized following Procedure A, step 2. The reaction was run on 5.00 mmol scale to give 0.80 g (83% yield) of **S14** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.39–6.74 (m, 4H), 2.86–2.55 (m, 2H), 2.36 (s, 3H), 1.80–1.44 (m, 5H), 1.23 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 141.29, 136.30, 130.46, 129.18, 126.23, 126.18, 70.96, 44.23, 34.07, 29.49, 25.56, 19.50. HRMS (ESI$^+$) m/z Calc. 206.1665 $[C_{14}H_{22}O-e]^+$, Found. 206.1665 $[M-e]^+$.

3. (4-Azido-2,2,4-trimethylpentyl)benzene (S15): Synthesized following Procedure A, step 3. The reaction was run on 4.00 mmol scale to give 0.39 g (45% yield) of **5** as a colorless oil. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.27–7.11 (m, 4H), 2.74–2.62 (m, 2H), 2.39 (s, 3H), 1.77–1.68 (m, 2H), 1.68–1.61 (m, 2H), 1.33 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.85, 136.30, 130.52, 129.12, 126.32, 126.30, 61.96, 41.70, 33.76, 26.16, 25.42, 19.49. HRMS (ESI$^+$) m/z Calc. 235.1917 $[C_{13}H_{19}N_3+NH_4]^+$, Found. 235.1919 $[M+NH_4]^+$.

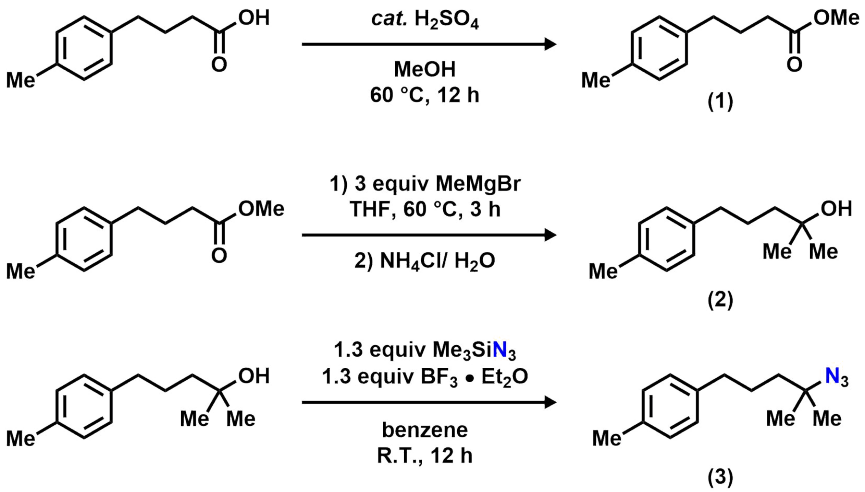
1-(4-Azido-4-methylpentyl)-3-methylbenzene (S15)



1. 2-Methyl-5-(m-tolyl)pentan-2-ol (S16): Synthesized following previously reported procedure.[7]

2. 1-(4-Azido-4-methylpentyl)-3-methylbenzene (S17): Synthesized following Procedure A, step 3. The reaction was run on 4.00 mmol scale to give 0.49 g (56% yield) of **S17** as a colorless oil. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.29 (t, J = 7.5 Hz, 1H), 7.17–7.08 (m, 3H), 2.70 (t, J = 7.7 Hz, 2H), 2.45 (s, 3H), 1.85–1.76 (m, 2H), 1.68–1.61 (m, 2H), 1.36 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 142.60, 138.31, 129.64, 128.67, 127.00, 125.86, 61.96, 41.53, 36.45, 26.71, 26.21, 21.66. HRMS (ESI$^+$) m/z Calc. 235.1917 $[C_{13}H_{19}N_3+NH_4]^+$, Found. 235.1918 $[M+NH_4]^+$.

1-(4-Azido-4-methylpentyl)-4-methylbenzene (S18)

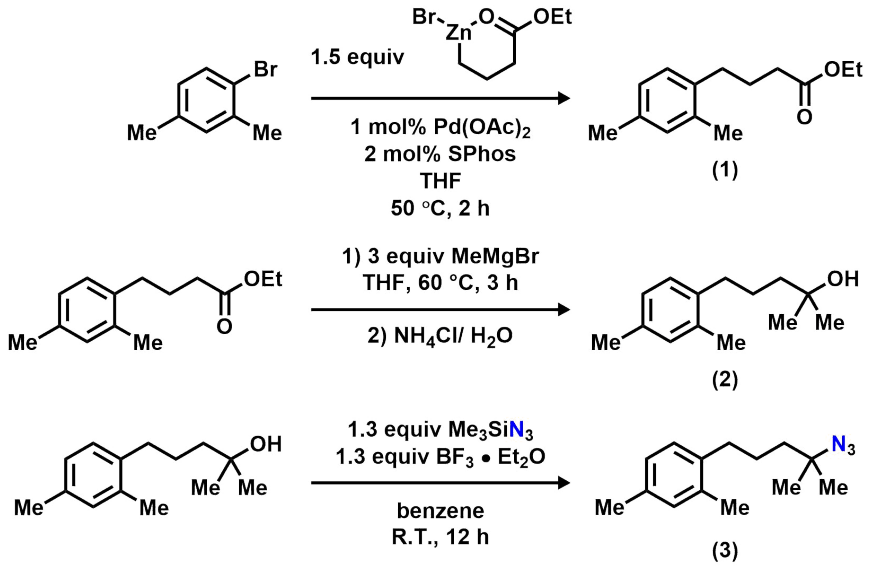


1. Methyl 4-(p-tolyl)butanoate (S18): Synthesized following previously reported procedure.[8]

2. 2-Methyl-5-(p-tolyl)pentan-2-ol (S19): Synthesized following previously reported procedure.[8]

3. 1-(4-Azido-4-methylpentyl)-4-methylbenzene (S20): Synthesized following previously reported procedure.[8]

1-(4-Azido-4-methylpentyl)-2,4-dimethylbenzene (S23)



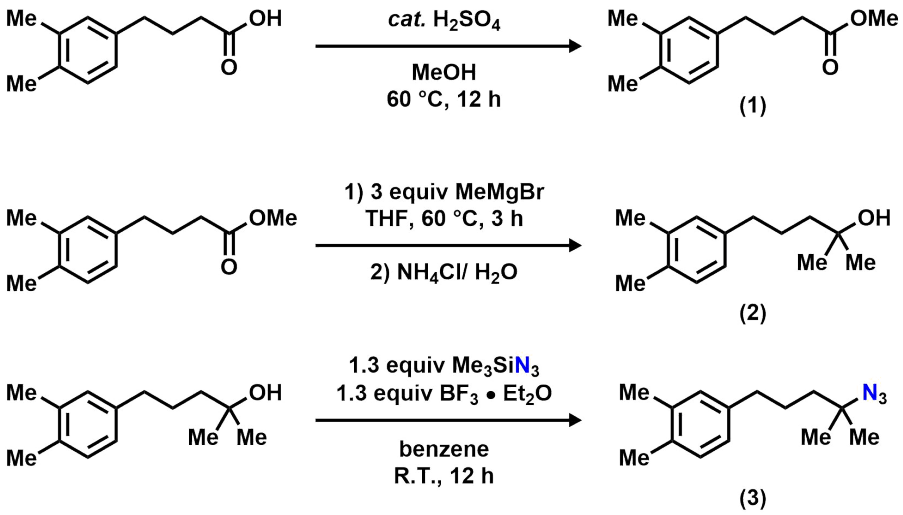
1. Ethyl 4-(2,4-dimethylphenyl)butanoate (S21): Synthesized following previously reported procedure. The reaction was run on 10.0 mmol scale to give 1.45 g (66% yield) of **S21** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ/ppm: 7.02 (d, J = 7.6 Hz, 1H), 6.98 (s, 1H), 6.95 (d, J = 7.6 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.66–2.55 (m, 2H), 2.35 (t, J = 7.4 Hz, 2H), 2.29 (s, 6H), 1.87 (dt, J = 15.2, 7.5 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ/ppm: 173.64, 137.17, 136.16, 135.84, 131.30, 129.24, 126.86, 60.54, 34.29, 32.50, 26.02, 21.01, 19.30, 14.49. HRMS (ESI$^+$) m/z Calc. 221.1536 $[C_{14}H_{20}O_2+H]^+$, Found. 221.1537 $[M+H]^+$.

2. 5-(2,4-Dimethylphenyl)-2-methylpentan-2-ol (S22): Synthesized following previously reported procedure. The reaction was run on 6.00 mmol scale to give 1.16 g (94% yield) of **S22** as a colorless oil. 1H NMR (600 MHz, CD_2Cl_2) δ 7.06 (d, J = 7.6 Hz, 1H), 7.00 (s, 1H), 6.96 (d, J = 7.6 Hz, 1H), 2.66–2.53 (m, 2H), 2.31 (s, 6H), 1.69–1.60 (m, 2H), 1.59–1.50 (m, 2H), 1.44 (s, 1H), 1.22 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ/ppm: 138.13, 136.04, 135.55, 131.23, 129.10, 126.83,

70.97, 44.23, 33.65, 29.48, 25.69, 21.04, 19.43. HRMS (ESI^+) m/z Calc. 206.1665 $[C_{14}H_{22}O-e]^+$, Found. 206.1667 $[M-e]^+$.

3. 1-(4-Azido-4-methylpentyl)-2,4-dimethylbenzene (S23): Synthesized following Procedure A, step 3. The reaction was run on 4.00 mmol scale to give 0.38 g (41% yield) of **S23** as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ/ppm: 7.10 (d, J = 7.6 Hz, 1H), 7.05 (s, 1H), 7.02 (d, J = 7.6 Hz, 1H), 2.69–2.62 (m, 2H), 2.37 (s, 3H), 2.36 (s, 3H), 1.75–1.68 (m, 2H), 1.68–1.62 (m, 2H), 1.34 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ/ppm: 137.73, 136.06, 135.73, 131.37, 129.12, 126.97, 62.00, 41.76, 33.43, 26.20, 25.60, 21.11, 19.47. HRMS (ESI^+) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2073 $[M+NH_4]^+$.

4-(4-zido-4-methylpentyl)-1,2-dimethylbenzene (S26)

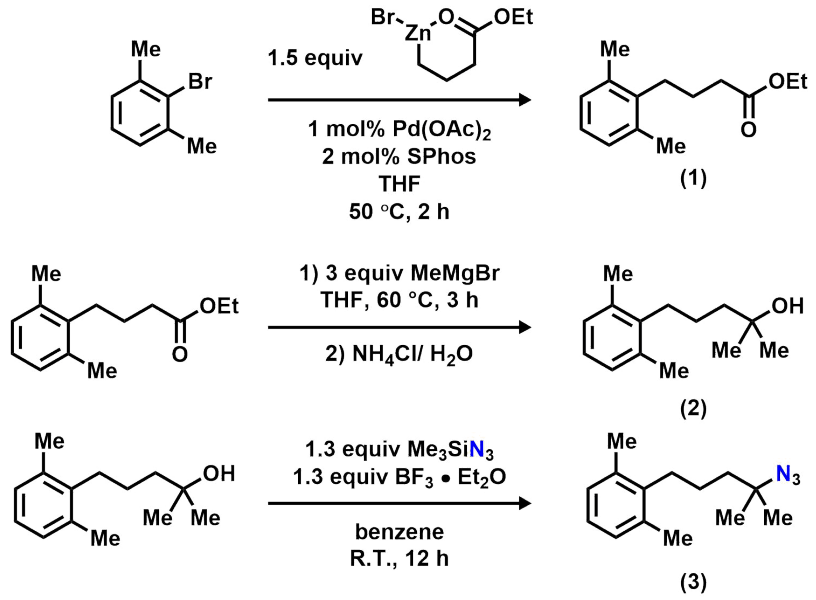


1. Methyl 4-(3,4-dimethylphenyl)butanoate (S24): Synthesized following Procedure A, step 1. The reaction was run on 2.60 mmol scale to give 0.48 g (90% yield) of **S24** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (d, J = 7.6 Hz, 1H), 6.99 (s, 1H), 6.95 (d, J = 7.6 Hz, 1H), 3.69 (s, 3H), 2.66–2.56 (m, 2H), 2.36 (t, J = 7.5 Hz, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 1.97 (p, J = 7.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.00, 138.81, 136.43, 134.03, 129.85, 129.64, 125.85, 51.46, 34.69, 33.45, 26.67, 19.75, 19.31. HRMS (ESI^+) m/z Calc. 207.1380 $[C_{13}H_{18}O_2+H]^+$, Found. 207.1380 $[M+H]^+$.

2. 5-(3,4-Dimethylphenyl)-2-methylpentan-2-ol (S25): Synthesized following Procedure A, step 2. The reaction was run on 2.00 mmol scale to give 0.33 g (79% yield) of **S25** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (d, J = 7.6 Hz, 1H), 7.00 (s, 1H), 6.96 (d, J = 7.6 Hz, 1H), 2.59 (t, J = 7.7 Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 1.75–1.66 (m, 2H), 1.58–1.51 (m, 2H), 1.46 (s, 1H), 1.23 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.94, 136.36, 133.79, 129.83, 129.61, 125.77, 70.96, 43.65, 35.97, 29.25, 26.55, 19.81, 19.36. HRMS (ESI^+) m/z Calc. 206.1665 $[C_{14}H_{22}O-e]^+$, Found. 206.1667 $[M-e]^+$.

3. 4-(4-Azido-4-methylpentyl)-1,2-dimethylbenzene (S26): Synthesized following Procedure A, step 3. The reaction was run on 1.00 mmol scale to give 0.12 g (52% yield) of **S26** as a colorless oil. 1H NMR (500 MHz, CD_2Cl_2) δ 7.14 (d, *J* = 7.6 Hz, 1H), 7.07 (s, 1H), 7.02 (dd, *J* = 7.6, 1.4 Hz, 1H), 2.66 (t, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 2.33 (s, 3H), 1.84–1.72 (m, 2H), 1.66–1.58 (m, 2H), 1.35 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.01, 136.80, 134.28, 130.13, 129.95, 126.15, 61.99, 41.54, 36.05, 26.79, 26.19, 19.98, 19.52. HRMS (ESI^+) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2073 $[M+NH_4]^+$.

2-(4-Azido-4-methylpentyl)-1,3-dimethylbenzene (S29)



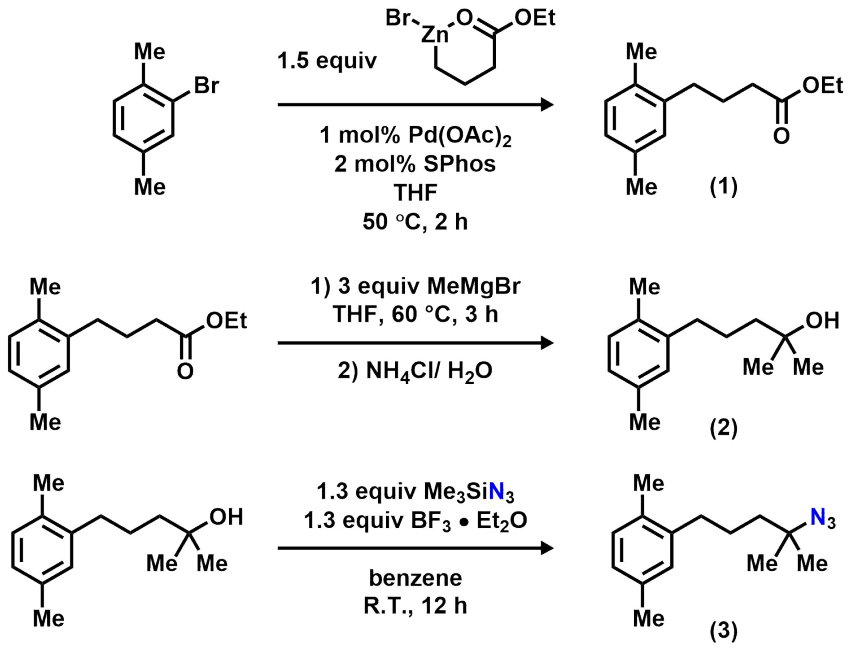
1. Ethyl 4-(2,6-dimethylphenyl)butanoate (S27): Synthesized following previously reported procedure.[9]

2. 5-(2,6-Dimethylphenyl)-2-methylpentan-2-ol (S28): Synthesized following Procedure A, step 2. The reaction was run on 6.00 mmol scale to give 1.02 g (82% yield) of **S28** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.11–7.00 (m, 3H), 2.75–2.64 (m, 2H), 2.40 (s, 6H), 1.73 (s, 1H), 1.70–1.63 (m, 2H), 1.63–1.53 (m, 2H), 1.27 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ/ppm: 142.01, 138.33, 130.46, 127.88, 72.98, 46.77, 32.58, 31.48, 26.57, 22.08. HRMS (ESI^+) m/z Calc. 206.1665 $[C_{14}H_{22}O-e]^+$, Found. 206.1669 $[M-e]^+$.

3. 2-(4-Azido-4-methylpentyl)-1,3-dimethylbenzene (S29): Synthesized following Procedure A, step 3. The reaction was run on 4.00 mmol scale to give 0.45 g (49% yield) of **S29** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.19–7.10 (m, 3H), 2.84–2.72 (m, 2H), 2.48 (s, 6H), 1.84–1.76 (m, 2H), 1.74–1.66 (m, 2H), 1.41 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 139.59, 136.32, 128.62,

126.12, 61.97, 42.22, 30.37, 26.23, 24.49, 20.12. HRMS (ESI^+) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2074 $[M+NH_4]^+$.

2-(4-Azido-4-methylpentyl)-1,4-dimethylbenzene (S32)



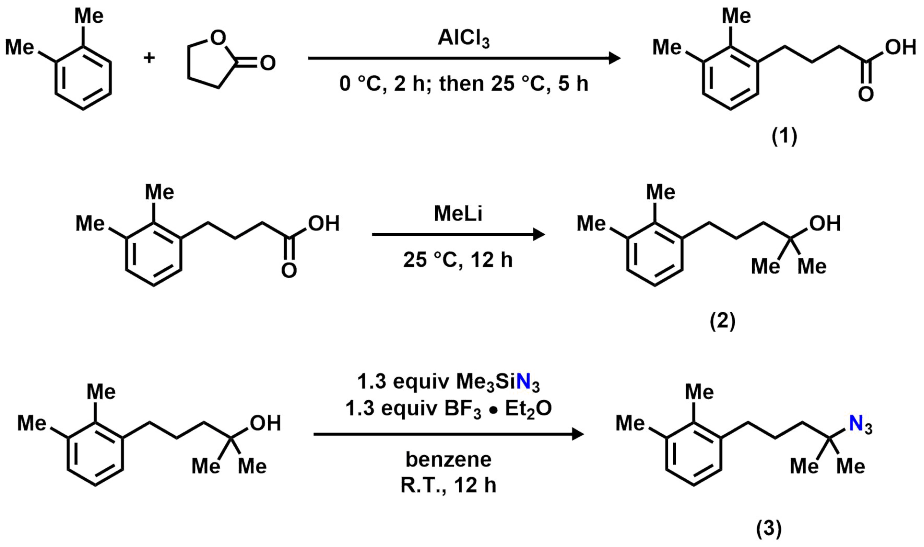
1. Ethyl 4-(2,5-dimethylphenyl)butanoate (S30): Synthesized following previously reported procedure.[9]

2. 5-(2,5-Dimethylphenyl)-2-methylpentan-2-ol (S31): Synthesized following Procedure A, step 2. The reaction was run on 6.00 mmol scale to give 1.10 g (89% yield) of **S31** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (d, J = 7.7 Hz, 1H), 7.07 (s, 1H), 7.01 (d, J = 7.7 Hz, 1H), 2.71–2.63 (m, 2H), 2.40 (s, 3H), 2.37 (s, 3H), 2.03 (s, 1H), 1.80–1.70 (m, 2H), 1.69–1.60 (m, 2H), 1.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.43, 135.07, 132.49, 130.00, 129.55, 126.48, 70.75, 43.82, 33.66, 29.13, 25.17, 20.94, 18.81. HRMS (ESI$^+$) m/z Calc. 206.1665 [$C_{14}H_{22}O-e]^+$, Found. 206.1666 [$M-e]^+$.

3. 2-(4-Azido-4-methylpentyl)-1,4-dimethylbenzene (S32): Synthesized following Procedure A, step 3. The reaction was run on 4.00 mmol scale to give 0.41 g (44% yield) of **S32** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.03 (d, J = 7.6 Hz, 1H), 6.97 (s, 1H), 6.92 (d, J = 7.6 Hz, 1H),

2.61–2.55 (m, 2H), 2.30 (s, 3H), 2.27 (s, 3H), 1.71–1.55 (m, 4H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 140.63, 135.64, 133.03, 130.36, 129.88, 126.90, 62.00, 41.72, 33.75, 26.14, 25.51, 21.08, 18.95. HRMS (ESI^+) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2074 $[M+NH_4]^+$.

1-(4-Azido-4-methylpentyl)-2,3-dimethylbenzene (S35)

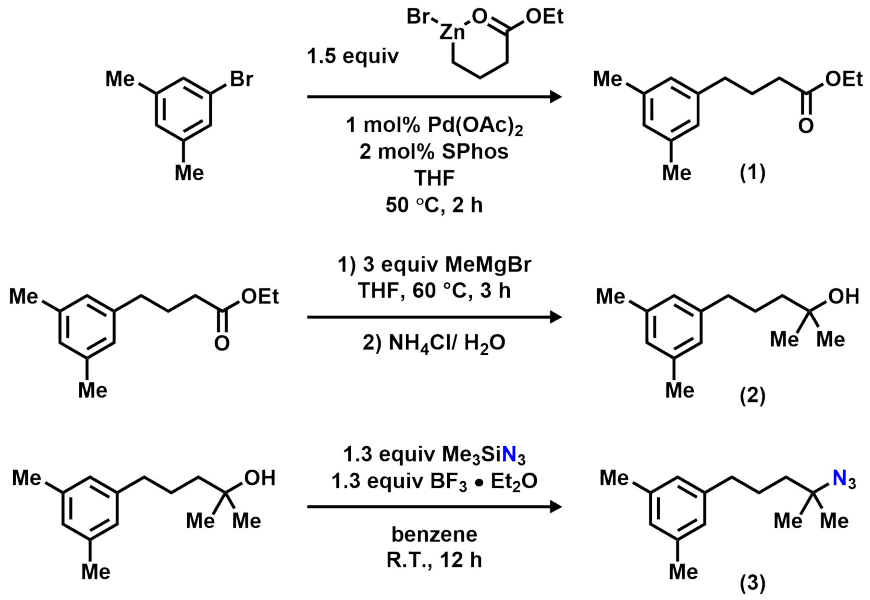


1. 4-(2,3-Dimethylphenyl)butanoic acid (S33): Synthesized following previously reported procedure.[10]

2. 5-(2,3-Dimethylphenyl)-2-methylpentan-2-ol (S34): Synthesized following previously reported procedure.[11]

3. 1-(4-azido-4-methylpentyl)-2,3-dimethylbenzene (S35): Synthesized following Procedure A, step 3. The reaction was run on 4.00 mmol scale to give 0.49 g (53% yield) of **S35** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.24–6.93 (m, 3H), 2.72 (t, J = 7.6 Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H), 1.82–1.61 (m, 4H), 1.35 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 140.69, 137.28, 134.82, 128.11, 127.31, 125.73, 61.99, 41.79, 34.62, 26.20, 25.88, 20.92, 15.22. HRMS (ESI$^+$) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2074 $[M+NH_4]^+$.

1-(4-Azido-4-methylpentyl)-3,5-dimethylbenzene (S38)

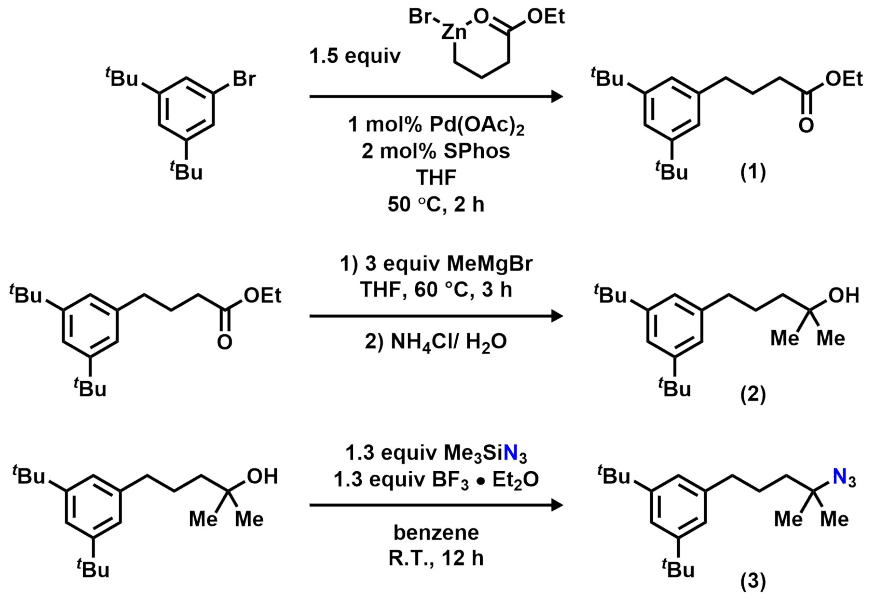


1. Ethyl 4-(3,5-dimethylphenyl)butanoate (S36): Synthesized following previously reported procedure.[9] The reaction was run on 10.0 mmol scale to give 1.67 g (76% yield) of **S36** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 6.86 (s, 1H), 6.84 (s, 2H), 4.14 (q, J = 7.1 Hz, 2H), 2.74–2.48 (m, 2H), 2.45–2.19 (m, 8H), 2.06–1.78 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 173.65, 141.95, 138.19, 127.91, 126.76, 60.54, 35.43, 34.10, 27.18, 21.46, 14.56. HRMS (ESI$^+$) m/z Calc. 221.1536 [$C_{14}H_{20}O_2$+H]$^+$, Found. 221.1537 [M+H]$^+$.

2. 5-(3,5-dimethylphenyl)-2-methylpentan-2-ol (S37): Synthesized following Procedure A, step 2. The reaction was run on 6.00 mmol scale to give 1.01 g (82% yield) of **S37** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 6.86 (s, 3H), 2.58 (t, J = 7.8 Hz, 2H), 2.33 (s, 6H), 1.77–1.63 (m, 2H), 1.59–1.47 (m, 2H), 1.22 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 142.98, 138.06, 127.68, 126.70, 70.97, 44.09, 36.72, 29.52, 26.91, 21.50. HRMS (ESI$^+$) m/z Calc. 206.1665 [$C_{14}H_{22}O$−e]$^+$, Found. 206.1666 [M−e]$^+$.

3. 2-(4-Azido-4-methylpentyl)-3,5-dimethylbenzene (S38): Synthesized following Procedure A, step 3. The reaction was run on 4.00 mmol scale to give 0.49 g (53% yield) of **S38** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ/ppm: 6.89 (s, 1H), 6.87 (s, 2H), 2.60 (t, J = 7.7 Hz, 2H), 2.35 (s, 5H), 1.78 – 1.68 (m, 3H), 1.63 – 1.54 (m, 2H), 1.31 (s, 4H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ/ppm: 13C NMR (151 MHz, cd2cl2) δ 142.50, 138.13, 127.73, 126.57, 62.00, 41.51, 36.31, 26.67, 26.15, 21.44. HRMS (ESI^+) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2074 $[M+NH_4]^+$.

1-(4-Azido-4-methylpentyl)-3,5-di-tert-butylbenzene (S41)

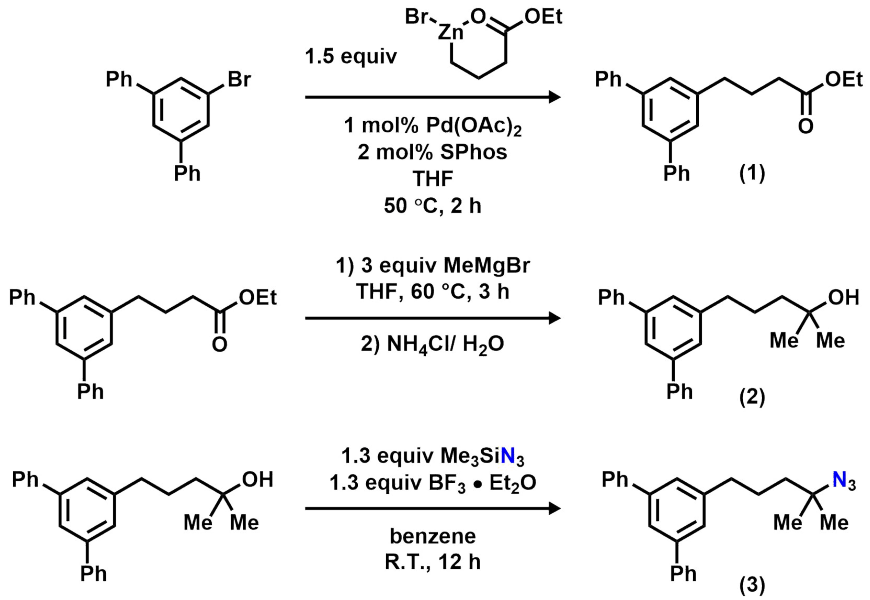


1. Ethyl 4-(3,5-bis-tert-butylphenyl)butanoate (S39): Synthesized following previously reported procedure.[9] The reaction was run on 10.0 mmol scale to give 1.43 g (47% yield) of **S39** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.26 (t, *J* = 1.7 Hz, 1H), 7.03 (d, *J* = 1.7 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.81–2.58 (m, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.07–1.76 (m, 2H), 1.32 (s, 18H), 1.24 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (151 MHz, CD_2Cl_2) δ 173.72, 151.14, 141.23, 123.08, 120.31, 60.54, 36.09, 35.08, 34.23, 31.70, 27.46, 14.54. HRMS (ESI$^+$) m/z Calc. 305.2475 $[C_{20}H_{32}O_2+H]^+$, Found. 305.2477 $[M+H]^+$.

2. 5-(3,5-bis-tert-butylphenyl)-2-methylpentan-2-ol (S40): Synthesized following Procedure A, step 2. The reaction was run on 4.00 mmol scale to give 0.90 g (77% yield) of **S40** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.26 (t, *J* = 1.8 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 2H), 2.66–2.56 (m, 2H), 1.74–1.64 (m, 2H), 1.58–1.50 (m, 2H), 1.33 (s, 18H), 1.20 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 151.04, 142.21, 122.97, 120.08, 71.01, 44.28, 37.41, 35.08, 31.73, 29.54, 27.19. HRMS (ESI$^+$) m/z Calc. 290.2604 $[C_{20}H_{34}O-e]^+$, Found. 290.2600 $[M-e]^+$.

3. 2-(4-Azido-4-methylpentyl)-3,5-bis-tert-butylbenzene (S41): Synthesized following Procedure A, step 3. The reaction was run on 2.00 mmol scale to give 0.28 g (45% yield) of **S41** as a colorless oil. 1H NMR (600 MHz, CD_2Cl_2) δ 7.37 (t, J = 1.8 Hz, 1H), 7.15 (d, J = 1.8 Hz, 2H), 2.71 (t, J = 7.8 Hz, 2H), 1.86–1.76 (m, 2H), 1.71–1.64 (m, 2H), 1.44 (s, 18H), 1.36 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 151.21, 141.85, 123.07, 120.31, 62.07, 41.78, 37.16, 35.22, 31.90, 27.05, 26.32. HRMS (ESI^+) m/z Calc. 333.3013 $[C_{20}H_{33}N_3+NH_4]^+$, Found. 333.3014 $[M+NH_4]^+$.

5'-(4-Azido-4-methylpentyl)-1,1':3',1''-terphenyl (S44)



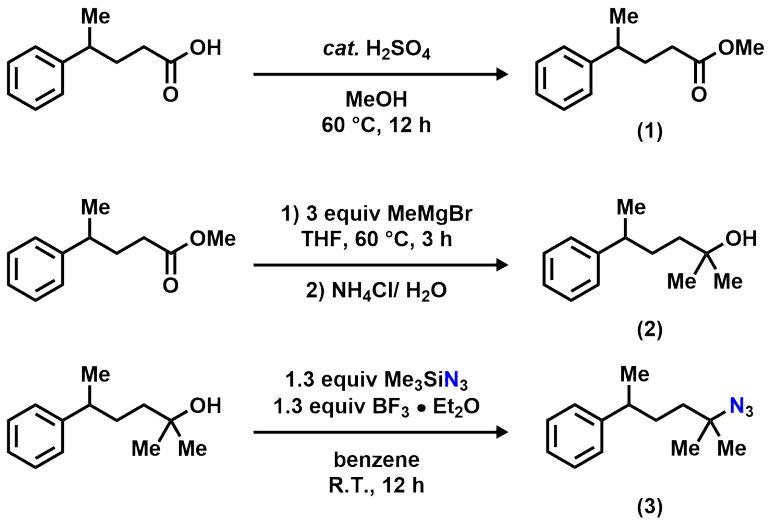
1. Ethyl 4-([1,1':3',1''-terphenyl]-5'-yl)butanoate (S42): Synthesized following previously reported procedure.[9] The reaction was run on 10.0 mmol scale to give 2.85 g (83% yield) of **S42** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.71–7.65 (m, 5H), 7.51–7.41 (m, 6H), 7.41–7.34 (m, 2H), 4.11 (q, J = 7.1 Hz, 2H), 2.80 (t, J = 7.6 Hz, 2H), 2.38 (t, J = 7.6 Hz, 2H), 2.04 (p, J = 7.5 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 173.59, 143.21, 142.19, 141.59, 129.19, 127.80, 127.59, 126.82, 124.13, 60.60, 35.65, 34.05, 27.10, 14.49. HRMS (ESI^+) m/z Calc. 345.1849 $[C_{24}H_{24}O_2+H]^+$, Found. 345.1851 $[M+H]^+$.

2. 5-([1,1':3',1''-Terphenyl]-5'-yl)-2-methylpentan-2-ol (S43): Synthesized following Procedure A, step 2. The reaction was run on 6.00 mmol scale to give 1.75 g (88% yield) of **S43** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.79–7.70 (m, 5H), 7.57–7.49 (m, 6H), 7.48–7.38 (m, 2H), 2.83 (t, J = 7.8 Hz, 2H), 1.95–1.80 (m, 2H), 1.72–1.58 (m, 2H), 1.51 (s, 1H), 1.27 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 144.24, 142.12, 141.69, 129.20, 127.78, 127.62, 126.75,

123.94, 70.95, 44.01, 36.95, 29.54, 26.88. HRMS (ESI^+) m/z Calc. 330.1978 $[C_{24}H_{26}O-e]^+$, Found. 330.1981 $[M-e]^+$.

3. 5'-(4-Azido-4-methylpentyl)-1,1':3',1''-terphenyl (S44): Synthesized following Procedure A, step 3. The reaction was run on 4.00 mmol scale to give 0.78 g (55% yield) of **S44** as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.74–7.68 (m, 5H), 7.53–7.48 (m, 4H), 7.47 (d, *J* = 1.7 Hz, 2H), 7.44–7.39 (m, 2H), 2.80 (t, *J* = 7.7 Hz, 2H), 1.87–1.79 (m, 2H), 1.67–1.61 (m, 2H), 1.30 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 143.80, 142.17, 141.63, 129.19, 127.79, 127.60, 126.69, 124.04, 61.98, 41.48, 36.58, 26.69, 26.16. HRMS (ESI^+) m/z Calc. 373.2387 $[C_{24}H_{25}N_3+NH_4]^+$, Found. 373.2390 $[M+NH_4]^+$.

(5-Azido-5-methylhexan-2-yl)benzene (S47)

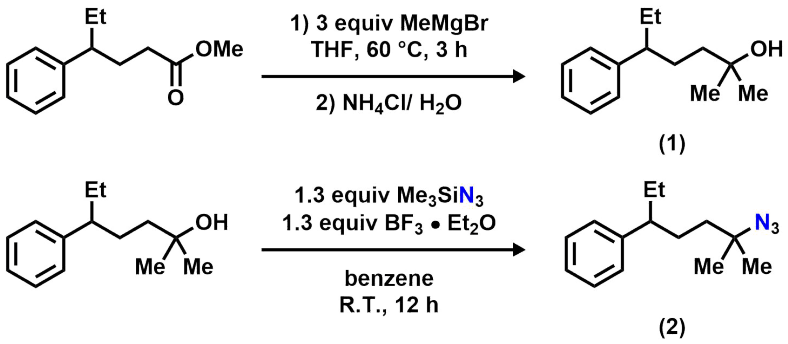


1. Methyl 4-phenylpentanoate (S45): Synthesized following previously reported procedure.[1]

2. 2-Methyl-5-phenylhexan-2-ol (S46): Synthesized following previously reported procedure.[1]

3. (5-Azido-5-methylhexan-2-yl)benzene (S47): Synthesized following previously reported procedure.[1]

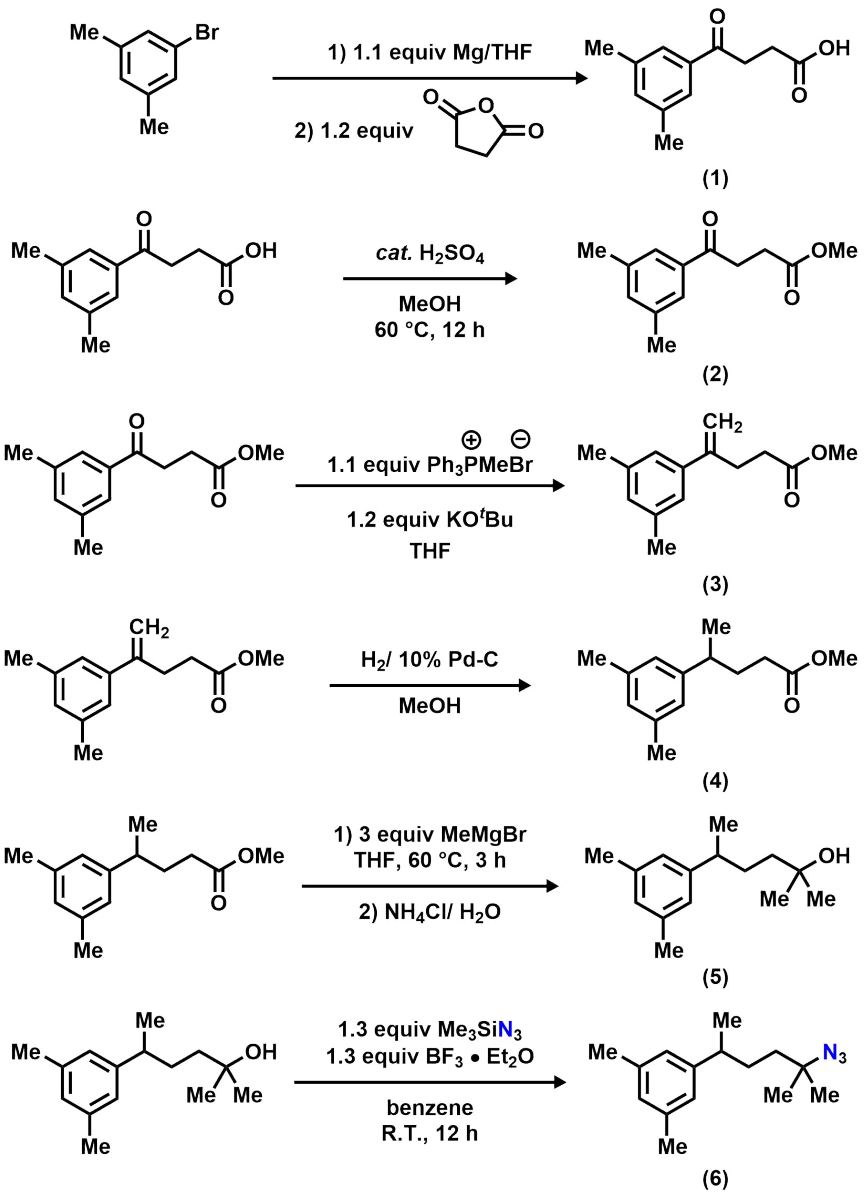
(6-Azido-6-methylheptan-3-yl)benzene (S49)



1. 2-Methyl-5-phenylheptan-2-ol (S48): Synthesized following Procedure A, step 2. The reaction was run on 2.40 mmol scale to give 0.40 g (80% yield) of **S48** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.37–7.32 (m, 2H), 7.26–7.18 (m, 3H), 2.43 (tt, *J* = 9.6, 5.2 Hz, 1H), 1.84–1.73 (m, 2H), 1.72–1.58 (m, 3H), 1.43 (td, *J* = 13.0, 4.5 Hz, 1H), 1.26 (td, *J* = 13.0, 4.5 Hz, 1H), 1.17 (s, 3H), 1.17 (s, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 146.28, 128.64, 128.19, 126.27, 70.92, 48.76, 42.34, 31.43, 30.33, 29.54, 29.34, 12.46. HRMS (ESI$^+$) m/z Calc. 206.1665 $[C_{14}H_{22}O-e]^+$, Found. 206.1667 $[M-e]^+$.

2. (6-Azido-6-methylheptan-3-yl)benzene (S49): Synthesized following Procedure A, step 3. The reaction was run on 1.50 mmol scale to give 0.17 g (49% yield) of **S49** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.41–7.34 (m, 2H), 7.30–7.26 (m, 1H), 7.26–7.21 (m, 2H), 2.51–2.43 (m, 1H), 1.88–1.62 (m, 4H), 1.51 (ddd, *J* = 13.7, 12.5, 4.5 Hz, 1H), 1.35 (ddd, *J* = 13.7, 12.5, 4.5 Hz, 1H), 1.28 (s, 3H), 1.27 (s, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 145.84, 128.77, 126.46, 61.98, 48.57, 39.92, 31.28, 30.41, 26.33, 26.06, 12.44. HRMS (ESI$^+$) m/z Calc. 249.2074 $[C_{14}H_{21}N_3+NH_4]^+$, Found. 249.2075 $[M+NH_4]^+$.

1-(5-azido-5-methylhexan-2-yl)-3,5-dimethylbenzene (S55)



1. 4-(3,5-Dimethylphenyl)-4-oxobutanoic acid (S50): Synthesized following previously reported procedure.[12] The reaction was run on 20.0 mmol scale to give 2.60 g (63% yield) of **S50** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.60 (s, 2H), 7.25 (s, 1H), 3.30 (t, J = 6.5 Hz, 2H), 2.78 (t, J = 6.5 Hz, 2H), 2.38 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ/ppm: 198.52, 179.40, 138.78,

136.90, 135.24, 126.12, 33.63, 28.45, 21.35. HRMS (ESI^+) m/z Calc. 207.1016 $[C_{12}H_{14}O_3+H]^+$, Found. 207.1017 $[M+H]^+$.

2. Methyl 4-(3,5-dimethylphenyl)-4-oxobutanoate (S51): Synthesized following previously reported procedure.[1] The reaction was run on 12.0 mmol scale to give 2.41 g (91% yield) of **S65** as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.20 (s, 1H), 3.70 (s, 3H), 3.29 (t, *J* = 6.7 Hz, 2H), 2.75 (t, *J* = 6.7 Hz, 2H), 2.36 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 198.59, 173.61, 138.35, 136.73, 134.98, 125.95, 51.94, 33.62, 28.21, 21.34. HRMS (ESI^+) m/z Calc. 221.1172 $[C_{13}H_{16}O_3+H]^+$, Found. 221.1174 $[M+H]^+$.

3. Methyl 4-(3,5-dimethylphenyl)pent-4-enoate (S52): Synthesized following previously reported procedure.[13] The reaction was run on 10.0 mmol scale to give 1.35 g (62% yield) of **S52** as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.06 (s, 2H), 6.96 (s, 1H), 5.32–5.29 (m, 1H), 5.09–5.05 (m, 1H), 3.66 (s, 3H), 2.90–2.79 (m, 2H), 2.56–2.46 (m, 2H), 2.34 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 174.98, 149.08, 142.27, 139.54, 130.92, 125.64, 113.71, 53.05, 34.72, 32.21, 22.82. HRMS (ESI^+) m/z Calc. 219.1380 $[C_{14}H_{18}O_2+H]^+$, Found. 219.1381 $[M+H]^+$.

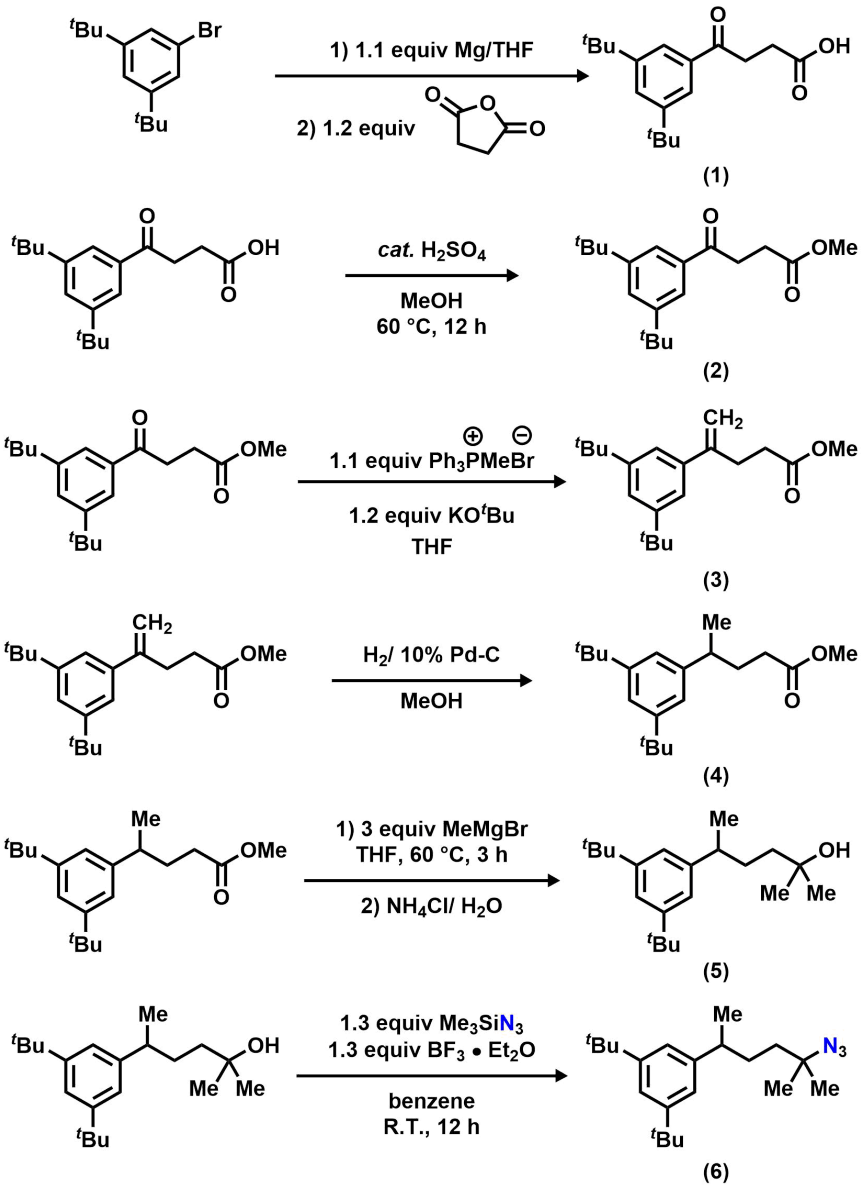
4. Methyl 4-(3,5-dimethylphenyl)pentanoate (S53): Synthesized following previously reported procedure.[14] The reaction was run on 5.00 mmol scale to give 0.95 g (86% yield) of **S53** as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 6.85 (s, 1H), 6.80 (s, 2H), 3.61 (s, 3H), 2.69–2.58 (m, 1H), 2.30 (s, 6H), 2.26–2.12 (m, 2H), 1.95–1.81 (m, 2H), 1.24 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 174.58, 147.10, 138.54, 128.42, 125.53, 51.94, 40.01, 33.90, 33.02, 22.79, 21.81. HRMS (ESI^+) m/z Calc. 221.1536 $[C_{14}H_{20}O_2+H]^+$, Found. 221.1535 $[M+H]^+$.

5. 5-(3,5-Dimethylphenyl)-2-methylhexan-2-ol (S54): Synthesized following Procedure A, step 2. The reaction was run on 4.00mmol scale to give 0.68 g (77% yield) of **S54** as a colorless oil. ^1H

NMR (600 MHz, CD_2Cl_2) δ 6.82 (s, 1H), 6.80 (s, 2H), 2.61–2.50 (m, 1H), 2.29 (s, 6H), 1.66–1.54 (m, 2H), 1.47–1.39 (m, 1H), 1.31–1.24 (m, 2H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.14 (s, 6H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 149.38, 139.37, 129.09, 126.48, 72.25, 43.80, 42.04, 34.53, 30.77, 30.70, 24.10, 22.81. HRMS (ESI^+) m/z Calc. 220.1822 $[C_{15}H_{24}O-e]^+$, Found. 220.1822 $[M-e]^+$.

6. 1-(5-Azido-5-methylhexan-2-yl)-3,5-dimethylbenzene (S55): Synthesized following Procedure A, step 3. The reaction was run on 2.00 mmol scale to give 0.24 g (49% yield) of **S55** as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 6.85 (s, 1H), 6.81 (s, 2H), 2.57 (h, *J* = 6.9 Hz, 1H), 2.31 (s, 6H), 1.71–1.58 (m, 2H), 1.48 (ddd, *J* = 13.7, 11.9, 5.1 Hz, 1H), 1.33 (ddd, *J* = 13.7, 11.9, 5.1 Hz, 1H), 1.26–1.21 (m, 9H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 147.62, 138.15, 127.89, 125.10, 62.01, 40.51, 39.95, 32.94, 26.18, 26.06, 22.88, 21.48. HRMS (ESI^+) m/z Calc. 263.2230 $[C_{15}H_{23}N_3+NH_4]^+$, Found. 263.2230 $[M+NH_4]^+$.

1-(5-Azido-5-methylhexan-2-yl)-3,5-di-tert-butylbenzene (S61)



1. 4-(3,5-Di-tert-butylphenyl)-4-oxobutanoic acid (S56): Synthesized following previously reported procedure.[12] The reaction was run on 20.0 mmol scale to give 2.44 g (42% yield) of **S56** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.85 (d, J = 1.8 Hz, 2H), 7.71 (t, J = 1.8 Hz, 1H), 3.36 (t, J = 6.5 Hz, 2H), 2.81 (t, J = 6.5 Hz, 2H), 1.38 (s, 18H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ

198.82, 179.53, 151.77, 136.56, 128.03, 122.57, 35.31, 33.73, 31.52, 28.58. HRMS (ESI^+) m/z Calc. 291.1955 $[C_{18}H_{26}O_3+H]^+$, Found. 291.1955 $[M+H]^+$.

2. Methyl 4-(3,5-di-tert-butylphenyl)-4-oxobutanoate (S57): Synthesized following previously reported procedure.[6] The reaction was run on 8.00 mmol scale to give 2.19 g (90% yield) of **S57** as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.83 (d, J = 1.9 Hz, 2H), 7.68 (t, J = 1.9 Hz, 1H), 3.67 (s, 3H), 3.32 (t, J = 6.6 Hz, 2H), 2.72 (t, J = 6.6 Hz, 2H), 1.36 (s, 18H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 199.25, 174.05, 152.04, 137.06, 128.19, 122.84, 52.31, 35.62, 34.23, 31.84, 28.79. HRMS (ESI^+) m/z Calc. 305.2111 $[C_{19}H_{28}O_3+H]^+$, Found. 305.2113 $[M+H]^+$.

3. Methyl 4-(3,5-di-tert-butylphenyl)pent-4-enoate (S58): Synthesized following previously reported procedure.[13] The reaction was run on 7.00 mmol scale to give 1.08 g (51% yield) of **S58** as a colorless oil. ^1H NMR (500 MHz, CD_2Cl_2) δ 7.38 (t, J = 1.8 Hz, 1H), 7.25 (d, J = 1.8 Hz, 2H), 5.30–5.25 (m, 2H), 5.07 (d, J = 1.3 Hz, 1H), 3.64 (s, 3H), 2.85 (t, J = 7.7 Hz, 2H), 2.58–2.38 (m, 2H), 1.35 (s, 18H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 174.06, 151.44, 148.93, 140.78, 122.50, 121.08, 112.61, 52.10, 35.51, 33.71, 31.98, 31.36. HRMS (ESI^+) m/z Calc. 303.2319 $[C_{20}H_{30}O_2+H]^+$, Found. 303.2321 $[M+H]^+$.

4. Methyl 4-(3,5-di-tert-butylphenyl)pentanoate (S59): Synthesized following previously reported procedure.[14] The reaction was run on 3.00 mmol scale to give 0.71 g (78% yield) of **S59** as a colorless oil. ^1H NMR (600 MHz, CD_2Cl_2) δ 7.35 (t, J = 1.7 Hz, 1H), 7.10 (d, J = 1.7 Hz, 2H), 3.66 (s, 3H), 2.88–2.70 (m, 1H), 2.39–2.17 (m, 2H), 2.06–1.89 (m, 2H), 1.41 (s, 18H), 1.35 (d, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 174.65, 151.50, 146.39, 121.96, 120.94, 51.99, 40.68, 35.57, 34.23, 33.15, 32.18, 22.84. HRMS (ESI^+) m/z Calc. 305.2475 $[C_{20}H_{32}O_2+H]^+$, Found. 305.2476 $[M+H]^+$.

5. 5-(3,5-di-tert-butylphenyl)-2-methylhexan-2-ol (S60): Synthesized following Procedure A, step 2. The reaction was run on 2.00 mmol scale to give 0.54 g (88% yield) of **S60** as a colorless oil. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.34 (t, *J* = 1.8 Hz, 1H), 7.12 (d, *J* = 1.8 Hz, 2H), 2.80–2.62 (m, 1H), 1.81–1.65 (m, 2H), 1.61–1.48 (m, 2H), 1.41 (s, 18H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.23 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 151.36, 147.67, 121.91, 120.59, 71.40, 42.97, 41.70, 35.56, 33.73, 32.20, 30.00, 29.76, 23.39. HRMS (ESI^+) m/z Calc. 304.2761 $[C_{21}H_{36}O-e]^+$, Found. 304.2759 $[M-e]^+$.

6. 1-(5-Azido-5-methylhexan-2-yl)-3,5-di-tert-butylbenzene (S61): Synthesized following Procedure A, step 3. The reaction was run on 1.50 mmol scale to give 0.26 g (52% yield) of **S61** as a colorless oil. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.36 (t, *J* = 1.8 Hz, 1H), 7.13 (d, *J* = 1.8 Hz, 2H), 2.77–2.69 (m, 1H), 1.84–1.68 (m, 2H), 1.65–1.54 (m, 1H), 1.42 (s, 19H), 1.35 (d, *J* = 6.9 Hz, 3H), 1.31 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 151.14, 146.88, 121.57, 120.43, 62.06, 41.19, 40.07, 35.27, 33.12, 31.88, 26.36, 26.19, 23.21. HRMS (ESI^+) m/z Calc. 347.3169 $[C_{21}H_{35}N_3+NH_4]^+$, Found. 347.3170 $[M+NH_4]^+$.

Procedure for Catalytic C–H Amination

Pyrrolidine preparation:

In a shell vial, organoazide substrate (0.10 mmol, 1 equiv) was dissolved in 0.3 ml of C_6D_6 and transferred to an NMR tube. In a separated shell vial, catalyst (^{TrF}BOX)Ni(py) (**4$_F$**) (5 mol% unless otherwise specified) was dissolved in 0.3 ml of C_6D_6 and also transferred to the NMR tube. The NMR tube was capped, taped and taken out of the glovebox to reacted at specified temperature. The reaction progress was monitored by ^{1}H NMR spectroscopy and the fate of the catalyst was determined by ^{19}F NMR spectroscopy. After either complete consumption of the organoazide or decomposition of the catalyst, the mixture was poured into a vial containing 3 ml of diethyl ether. The mixture was extracted three times with 0.1 M HCl aqueous solution (3×10 ml). To the combined aqueous layer, 1.0 M NaOH aqueous solution was added dropwise until a pH = 14 was reached. The cloudy solution was then extracted three times with DCM (3×10 ml). The combined organic phase was dried with $MgSO_4$, filtered and concentrated to yield the corresponding substituted pyrrolidine. Racemic substituted pyrrolidines were prepared in a similar fashion using previously published dipyrrinato monovalent nickel catalyst (^{AdF}L)Ni(py).

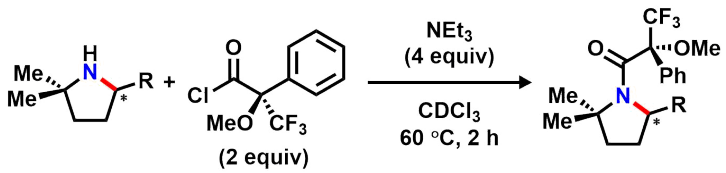
Enantiomeric excess (ee) measurement:[15-17]

Procedure A: In separate shell vials, the following stock solutions were prepared:

A: 1 ml of a 0.02 M stock solution of the pyrrolidine in $CDCl_3$.

B: 1 ml of a 0.04 M stock solution of (S)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (Mosher's acid chloride) in $CDCl_3$.

C: 1 ml of a 0.08 M stock solution of triethylamine (NEt_3) in $CDCl_3$.



To an NMR tube was added 0.3 ml of each stock solution A, B and C. The NMR tube was capped, taped, and heated to 60 °C. The reaction was monitored by ^{1}H NMR spectroscopy until all pyrrolidine was consumed (ca. 2 h), and the final ^{1}H and ^{19}F NMR spectra were used for *ee* calculation. The same procedure was repeated with racemic sample.

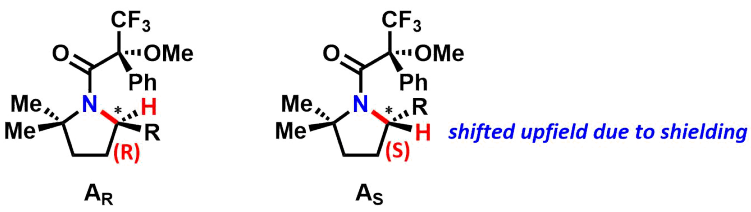
Procedure B:

Due to the extra steric shielding of 2,2,5,5-tetra-substituted pyrrolidines (**27**, **29**, **31**, **33**), a the *ee* of these compounds were determined by chiral gas chromatography (GC). Such analysis is hindered for 2,2,5-tri-substituted pyrrolidines due to trailing.

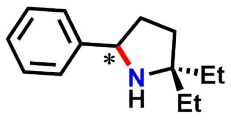
Pyrrolidine **10** does not condense with Mosher's acid chloride under standard condition, possibly due to the additional steric hindrance. Therefore, the *ee* of **10** was determined by chiral GC after condensed with acidic anhydride using similar conditions.

Absolute configuration determination:

The absolute configuration of the chiral centers was determined by Mosher's method.[16-17] Similar 2,2,5-trisubstituted pyrrolidines have the Mosher amide in predominant configuration $A_{R/S}$, leaving the proton *cis* to phenyl group (A_S) shifted upfield due to shielding of the π-system.[18-19]

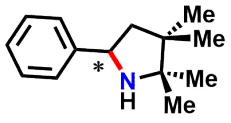


Characterization of Substituted Pyrrolidine



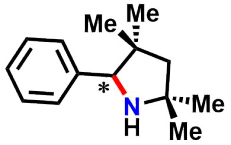
(11)

Yield: 10.0 mg, 49%. Procedure A, *ee* = 5% ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.32–7.27 (m, 2H), 7.21 (tt, *J* = 6.9, 1.3 Hz, 1H), 4.28–4.22 (m, 1H), 2.19–2.08 (m, 1H), 1.78–1.61 (m, 3H), 1.61–1.41 (m, 5H), 0.94 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 146.36, 128.45, 126.94, 126.86, 64.39, 62.11, 36.35, 35.84, 32.66, 31.98, 9.07, 9.03. HRMS (ESI$^+$) m/z Calc. 204.1747 $[C_{14}H_{21}N+H]^+$, Found. 204.1747 $[M+H]^+$.



(12)

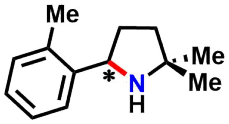
Yield: 5.9 mg, 29%. Procedure B, *ee* = 0 %. (50 mol% catalyst loading) ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.43–7.38 (m, 2H), 7.31–7.26 (m, 2H), 7.19–7.14 (m, 1H), 4.37 (t, *J* = 8.5 Hz, 1H), 2.11 (dd, *J* = 12.8, 8.6 Hz, 1H), 1.77 (s, 1H), 1.72 (dd, *J* = 12.8, 8.6 Hz, 1H), 1.11 (s, 3H), 1.10 (s, 3H), 1.02 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.23, 127.76, 126.10, 125.75, 62.46, 57.50, 49.36, 43.24, 26.42, 24.27, 23.90. HRMS (ESI$^+$) m/z Calc. 204.1747 $[C_{14}H_{21}N+H]^+$, Found. 204.1748 $[M+H]^+$.



(13)

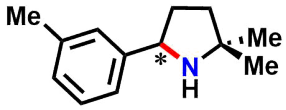
Yield: 7.5 mg, 37%. Procedure A, *ee* = 6% ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.41–7.35 (m, 2H), 7.34–7.27 (m, 2H), 7.27–7.21 (m, 1H), 4.08 (s, 1H), 1.75–1.56 (m, 3H), 1.31 (s, 3H), 1.26 (s, 3H), 1.05 (s, 3H), 0.67 (s, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 141.46, 128.03, 127.90, 127.03, 70.85,

55.44, 55.18, 43.07, 32.34, 31.44, 27.83, 24.56. HRMS (ESI^+) m/z Calc. 204.1747 $[C_{14}H_{21}N+H]^+$, Found. 204.1749 $[M+H]^+$.



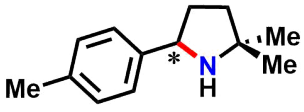
(14)

Yield: 14.0 mg, 74%. Procedure A, *ee* = 2% ^1H NMR (600 MHz, CD_2Cl_2) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.19–7.13 (m, 1H), 7.12–7.03 (m, 2H), 4.53 (t, *J* = 7.7 Hz, 1H), 2.34 (s, 3H), 2.32–2.18 (m, 1H), 1.79–1.53 (m, 3H), 1.43 (s, 1H), 1.28 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 144.50, 135.64, 130.27, 126.39, 126.20, 125.69, 58.93, 58.19, 40.04, 34.04, 30.86, 29.58, 19.50. HRMS (ESI^+) m/z Calc. 190.1590 $[C_{13}H_{19}N+H]^+$, Found. 190.1590 $[M+H]^+$.



(15)

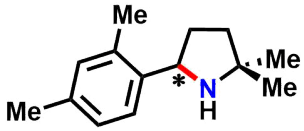
Yield: 14.9 mg, 79%. Procedure A, *ee* = 38% ^1H NMR (600 MHz, CD_2Cl_2) δ 7.21–7.12 (m, 3H), 7.10–6.99 (m, 1H), 4.34–4.20 (m, 1H), 2.34 (s, 3H), 2.29–2.15 (m, 1H), 1.82–1.56 (m, 4H), 1.27 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 148.04, 140.14, 130.37, 129.61, 129.58, 125.93, 64.18, 61.30, 42.32, 37.63, 32.84, 31.64, 23.56. HRMS (ESI^+) m/z Calc. 190.1590 $[C_{13}H_{19}N+H]^+$, Found. 190.1591 $[M+H]^+$.



(16)

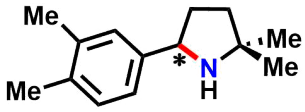
Yield: 16.4 mg, 87%. Procedure A, *ee* = 27% 1H NMR (600 MHz, CD_2Cl_2) δ 7.26 (d, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 4.26 (t, *J* = 7.0 Hz, 1H), 2.32 (s, 3H), 2.26–2.11 (m, 1H), 1.84–1.60 (m, 3H), 1.51 (s, 1H), 1.25 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 145.43, 138.68,

131.39, 129.02, 64.20, 61.44, 42.61, 38.01, 33.16, 31.95, 23.36. HRMS (ESI^+) m/z Calc. 190.1590 $[C_{13}H_{19}N+H]^+$, Found. 190.1592 $[M+H]^+$.



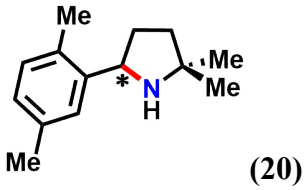
(17)

Yield: 10.8 mg, 53%. Procedure A, *ee* = 30% ^1H NMR (600 MHz, CD_2Cl_2) δ 7.45 (d, *J* = 7.9 Hz, 1H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.93 (s, 1H), 4.48 (t, *J* = 7.7 Hz, 1H), 2.30 (s, 3H), 2.27 (s, 3H), 2.26–2.18 (m, 1H), 1.77–1.44 (m, 4H), 1.27 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 140.55, 135.20, 134.81, 130.42, 126.16, 124.94, 58.24, 57.40, 39.44, 33.46, 30.17, 28.91, 20.29, 18.73. HRMS (ESI^+) m/z Calc. 204.1747 $[C_{14}H_{21}N+H]^+$, Found. 204.1749 $[M+H]^+$.



(18)

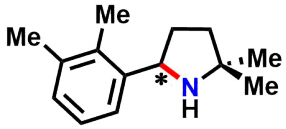
Yield: 15.2 mg, 75%. Procedure A, *ee* = 21% ^1H NMR (500 MHz, CD_2Cl_2) δ 7.14 (s, 1H), 7.11–7.03 (m, 2H), 4.30–4.16 (m, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 2.22–2.12 (m, 1H), 1.78–1.65 (m, 3H), 1.55 (s, 1H), 1.26 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 143.45, 136.66, 135.09, 129.66, 128.14, 124.22, 62.02, 59.23, 40.39, 35.70, 30.88, 29.69, 19.92, 19.46. HRMS (ESI^+) m/z Calc. 204.1747 $[C_{14}H_{21}N+H]^+$, Found. 204.1749 $[M+H]^+$.



(20)

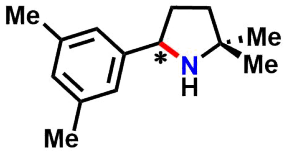
Yield: 12.6 mg, 62%. Procedure A, *ee* = 23% ^1H NMR (500 MHz, CD_2Cl_2) δ 7.42 (s, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.96–6.83 (m, 1H), 4.50 (t, *J* = 7.7 Hz, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.29–

2.22 (m, 1H), 1.80–1.48 (m, 4H), 1.30 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 143.89, 135.59, 132.48, 130.21, 127.06, 126.32, 58.97, 58.18, 40.03, 34.01, 30.78, 29.51, 21.31, 19.04. HRMS (ESI$^+$) m/z Calc. 204.1747 $[C_{14}H_{21}N+H]^+$, Found. 204.1748 $[M+H]^+$.



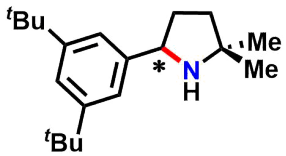
(21)

Yield: 13.9 mg, 68%. Procedure A, *ee* = 1% ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 4.58 (t, *J* = 7.7 Hz, 1H), 2.31–2.26 (m, 4H), 2.25 (s, 3H), 1.77–1.59 (m, 3H), 1.55 (s, 1H), 1.29 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 144.01, 136.87, 134.30, 128.18, 125.63, 123.49, 59.01, 58.59, 40.03, 34.14, 30.83, 29.61, 20.79, 14.94. HRMS (ESI$^+$) m/z Calc. 204.1747 $[C_{14}H_{21}N+H]^+$, Found. 204.1749 $[M+H]^+$.



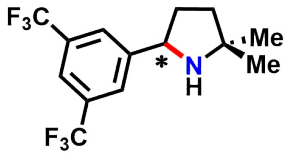
(22)

Yield: 16.5 mg, 81%. Procedure A, *ee* = 53% ^{1}H NMR (600 MHz, CD_2Cl_2) δ 6.98 (s, 2H), 6.86 (s, 1H), 4.29–4.19 (m, 1H), 2.30 (s, 6H), 2.24–2.12 (m, 1H), 1.79–1.64 (m, 3H), 1.56 (s, 1H), 1.26 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 145.97, 138.00, 128.45, 124.68, 62.22, 59.26, 40.38, 35.64, 30.88, 29.68, 21.45. HRMS (ESI$^+$) m/z Calc. 204.1747 $[C_{14}H_{21}N+H]^+$, Found. 204.1748 $[M+H]^+$.



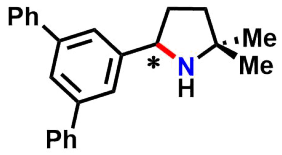
(23)

Yield: 22.1 mg, 77%. Procedure A, *ee* = 73% ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.29 (t, *J* = 1.8 Hz, 1H), 7.22 (d, *J* = 1.8 Hz, 2H), 4.32–4.27 (m, 1H), 2.27–2.19 (m, 1H), 1.83–1.64 (m, 4H), 1.33 (s, 18H), 1.28 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 150.52, 144.70, 120.69, 120.59, 62.50, 58.96, 40.07, 35.29, 34.71, 31.24, 30.40, 29.30. HRMS (ESI^+) m/z Calc. 288.2686 $[C_{20}H_{33}N+H]^+$, Found. 288.2688 $[M+H]^+$.



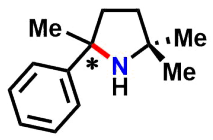
(24)

Yield: 24.8 mg, 80%. Procedure A, *ee* = 67% Spectral features match previously published result.[1]



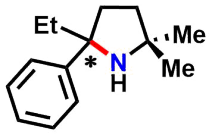
(25)

Yield: 13.5 mg, 41%. Procedure A, *ee* = 24% ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.71–7.66 (m, 5H), 7.66–7.62 (m, 2H), 7.51–7.43 (m, 4H), 7.41–7.34 (m, 2H), 4.50 (t, J = 7.8 Hz, 1H), 2.43 – 2.25 (m, 1H), 1.99–1.64 (m, 2H), 1.30 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.28, 141.97, 141.72, 129.15, 127.73, 127.61, 124.95, 124.71, 62.22, 59.66, 40.27, 35.62, 30.77, 29.57. HRMS (ESI^+) m/z Calc. 328.2060 $[C_{24}H_{25}N+H]^+$, Found. 328.2061 $[M+H]^+$.



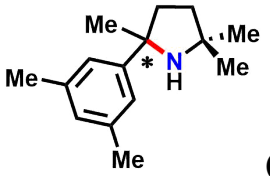
(27)

Yield: 9.4 mg, 50%. (20 mol% catalyst loading) Procedure B, *ee* = 53% Spectral features match previously published result.



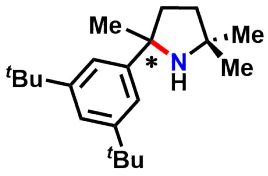
(29)

Yield: 15.8 mg, 78%. (20 mol% catalyst loading) Procedure B, *ee* = 76% ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.56–7.43 (m, 2H), 7.36–7.23 (m, 2H), 7.22–7.11 (m, 1H), 2.28–2.16 (m, 1H), 2.14–2.04 (m, 1H), 1.82–1.73 (m, 1H), 1.73–1.45 (m, 4H), 1.27 (s, 3H), 1.03 (s, 3H), 0.66 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 150.13, 127.85, 126.91, 125.85, 69.30, 59.67, 40.03, 39.25, 38.11, 31.21, 30.57, 9.38. HRMS (ESI$^+$) m/z Calc. 204.1747 $[C_{14}H_{21}N+H]^+$, Found. 204.1748 $[M+H]^+$.



(31)

Yield: 11.7 mg, 54%. (20 mol% catalyst loading) Procedure B, *ee* = 79% ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.15 (s, 2H), 6.82 (s, 1H), 2.30 (s, 6H), 2.23–2.09 (m, 1H), 2.10–1.97 (m, 1H), 1.76–1.67 (m, 1H), 1.67–1.55 (m, 1H), 1.38 (s, 3H), 1.27 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 154.22, 139.70, 129.74, 126.07, 67.94, 62.04, 43.03, 42.42, 35.51, 33.74, 32.86, 23.83. HRMS (ESI$^+$) m/z Calc. 218.1903 $[C_{15}H_{23}N+H]^+$, Found. 218.1904 $[M+H]^+$.

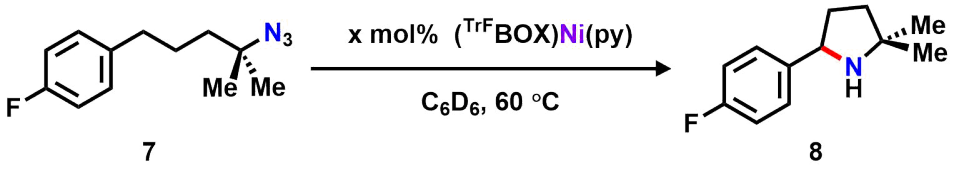


(33)

Yield: 18.6 mg, 62%. (20 mol% catalyst loading) Procedure B, *ee* = 64% ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.43 (d, J = 1.8 Hz, 2H), 7.25 (t, J = 1.8 Hz, 1H), 2.23–2.13 (m, 1H), 2.13–2.03 (m, 1H), 1.78–1.66 (m, 1H), 1.66–1.54 (m, 1H), 1.43 (s, 4H), 1.33 (s, 18H), 1.29 (s, 3H), 1.10 (s, 3H). ^{13}C

NMR (126 MHz, CD_2Cl_2) δ 151.00, 150.31, 120.38, 119.91, 66.35, 59.88, 41.34, 40.26, 35.24, 33.19, 31.75, 31.56, 30.74. HRMS (ESI^+) m/z Calc. 302.2842 $[C_{21}H_{35}N+H]^+$, Found. 302.2843 $[M+H]^+$.

Experimental Details for Mechanistic Studies



7 8

Stock solution A: substrate **7** (50.0 mg, 0.226 mmol) and internal standard trifluorotoluene (9.0 μL, 0.073 mmol) were dissolved in 5.0 mL of C_6D_6.

Stock solution B: catalyst (^{TrF}BOX)Ni(py) (20.0 mg, 0.021 mmol) was dissolved in 2.0 mL of C_6D_6.

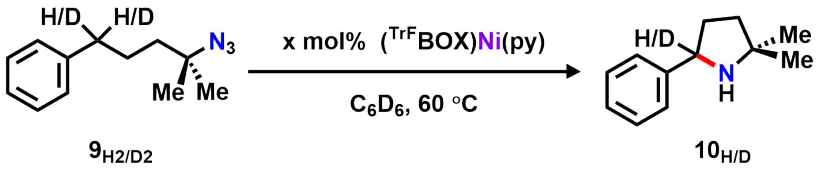
1. *Reaction order on substrate concentration*: To a J-Young tube, 0.10 mL of stock solution B was added using a 1 mL microsyringe. The solution was frozen in a cold well cooled using liquid nitrogen before the appropriate amount of C_6D_6 was carefully layered followed by 0.10, 0.20, 0.30, and 0.40 mL of stock solution A to bring the total volume to 0.50 mL. The sample was thawed, quickly shaken and immediately inserted into an NMR spectrometer preset to take 120 spectra with 50-second time interval at 60 °C. The rate for the first 10% conversion was plotted against the initial substrate concentrations. The measurement was repeated three times, and the standard deviations were used as error bars.

Stock solution C: substrate **7** (80.0 mg, 0.362 mmol) and internal standard trifluorotoluene (14.0 μL, 0.114 mmol) were dissolved in 2.0 mL of C_6D_6.

Stock solution D: catalyst (^{TrF}BOX)Ni(py) (40.0 mg, 0.042 mmol) was dissolved in 4.0 mL of C_6D_6.

2. *Reaction order on catalyst concentration*: To a J-Young tube, 0.10 mL of stock solution C was added using a 1 mL microsyringe. The solution was frozen in a cold well cooled using liquid

nitrogen before the appropriate amount of C_6D_6 was carefully layered followed by 50.0, 75.0, 100.0, 125.0, and 150.0 µL of stock solution D to bring the total volume to 0.50 mL. The sample was thawed, quickly shaken and immediately inserted into an NMR spectrometer preset to take 120 spectra with 50-second time interval at 60 °C. The rate for the first 10% conversion was plotted against the initial catalyst concentrations. The measurement was repeated three times, and the standard deviations were used as error bars.



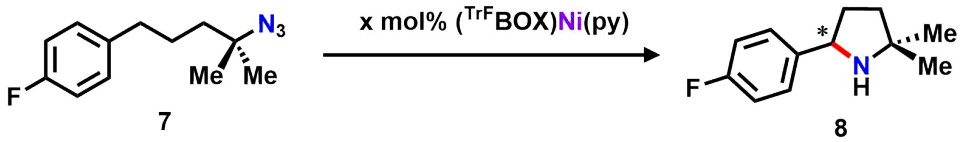
$\mathbf{9_{H2/D2}}$ $\mathbf{10_{H/D}}$

Stock solution E: substrate $\mathbf{9_{H2}}$ (37.0 mg, 0.182 mmol) and internal standard trifluorotoluene (7 µL, 0.057 mmol) were dissolved in 1.0 mL of C_6D_6.

Stock solution F: substrate $\mathbf{9_{D2}}$ (37.0 mg, 0.182 mmol) and internal standard trifluorotoluene (7 µL, 0.057 mmol) were dissolved in 1.0 mL of C_6D_6.

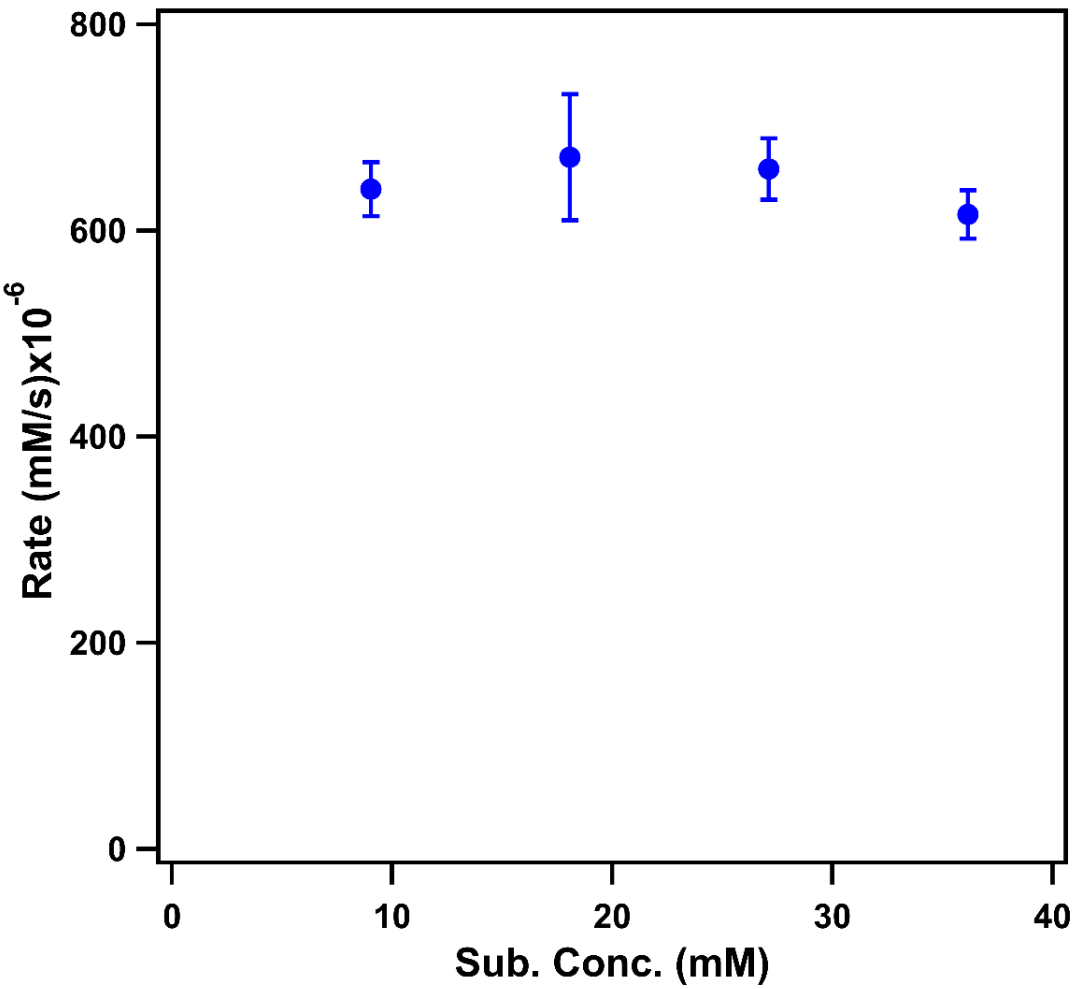
3. *Intermolecular KIE*: To a J-Young tube, 0.10 mL of stock solution E or F was added using a 1 mL microsyringe. The solution was frozen in a cold well cooled using liquid nitrogen before 0.10 mL of C_6D_6 was carefully layered followed by 0.30 mL of stock solution D to bring the total volume to 0.50 mL. The sample was thawed, quickly shaken and immediately inserted into an NMR spectrometer preset to take 120 spectra with 45- (for E) or 250-second time interval at 60 °C. The first 10% conversion was plotted against time, and the ratio between slopes of the resulting curves for E and F was calculated as the KIE. The measurement was repeated three times, and the standard deviations were used as error bars.

Table S1. Optimization of Amination Conditions



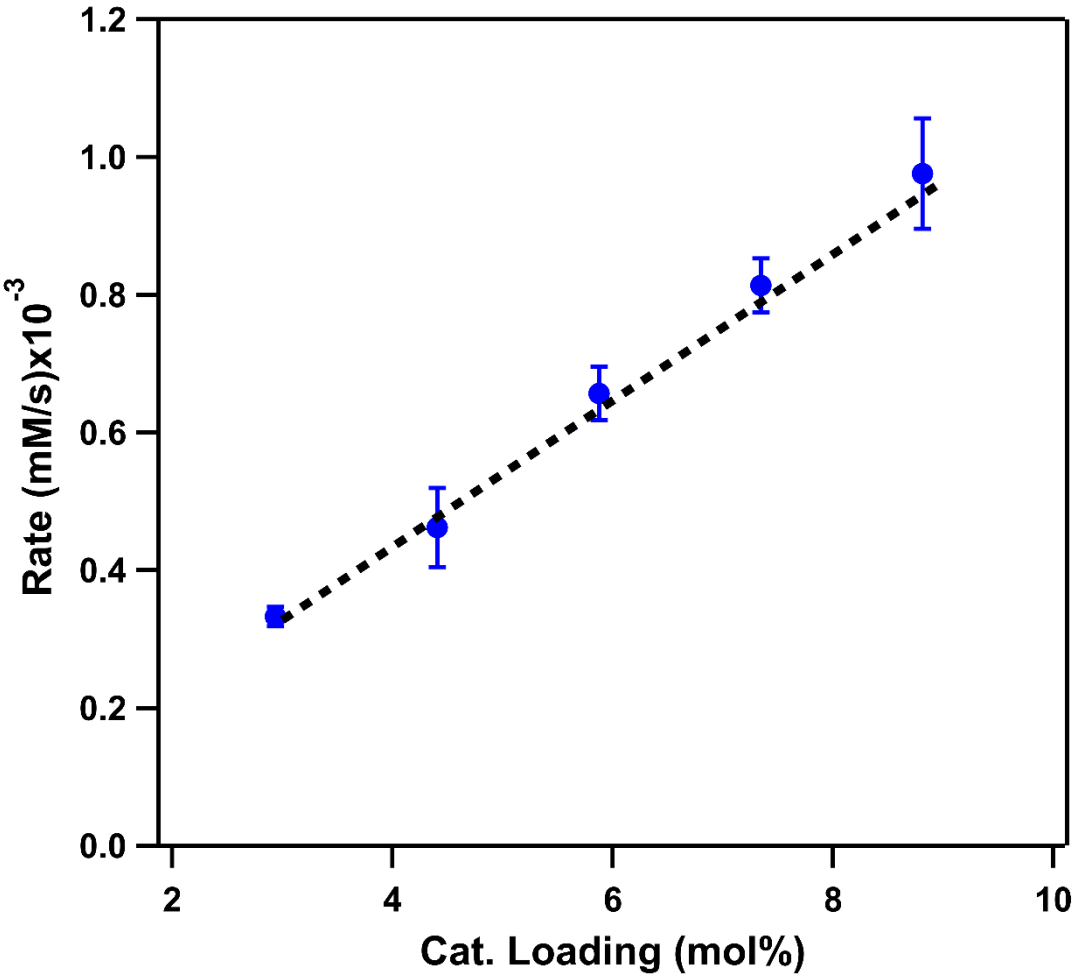
	Cat. Loading (mol%)[a]	Solvent	Time (h)	Temp. (°C)	Yield (%)[b]	*ee* (%)[c]
1	10	C_6D_6	12	60	85	28
2	5	C_6D_6	24	60	85	28
3	5	C_6D_6	12	80	73	22
4	5	C_6D_6	72	40	42	35
5	1	C_6D_6	168	60	36	28
6	5	d_8-toluene	24	60	78	28
7	5	d_8-THF	15	60	88	28

[a]Hexanes and ether are not suitable due to low solubility; DCM reacts with catalyst to generate $LNi^{II}Cl$; [b]Isolation yield; [c]Determined by Mosher analysis.



	Substrate Concentration (mM)	Initial Rate (× 10^{-4} mM/s)
1	9.0	6.4 ± 0.3
2	18	6.7 ± 0.6
3	27	6.6 ± 0.3
4	36	6.2 ± 0.4

Figure S1. Plot of initial rate vs. substrate concentrations. Initial rate for the first 10% conversion of **7** into **8** as a function of initial substrate **7** concentration while holding catalyst concentration constant at 2.1 mM. Every measurement is done in triplicate, and error bars represent standard deviations. ($k = 18.2 \pm 0.7 \times 10^{-3}$ min^{-1})



	Catalyst Concentration (mM)	Catalyst Loadings (mol%)	Initial Rate (× 10^{-4} mM/s)
1	1.1	2.9	3.3 ± 0.2
2	1.6	4.4	4.6 ± 0.5
3	2.1	5.9	6.6 ± 0.6
4	2.7	7.3	8.1 ± 0.3
5	3.2	8.8	9.8 ± 0.6

Figure S2. Plot of initial rate vs. catalyst loadings. Initial rate for the first 10% conversion of **7** into **8** as a function of catalyst loadings while holding initial substrate **7** concentration constant at 36.1 mM. Every measurement is done in triplicate, and error bars represent standard deviations. (k = 18.6 ± 0.6 × 10^{-3} min^{-1})

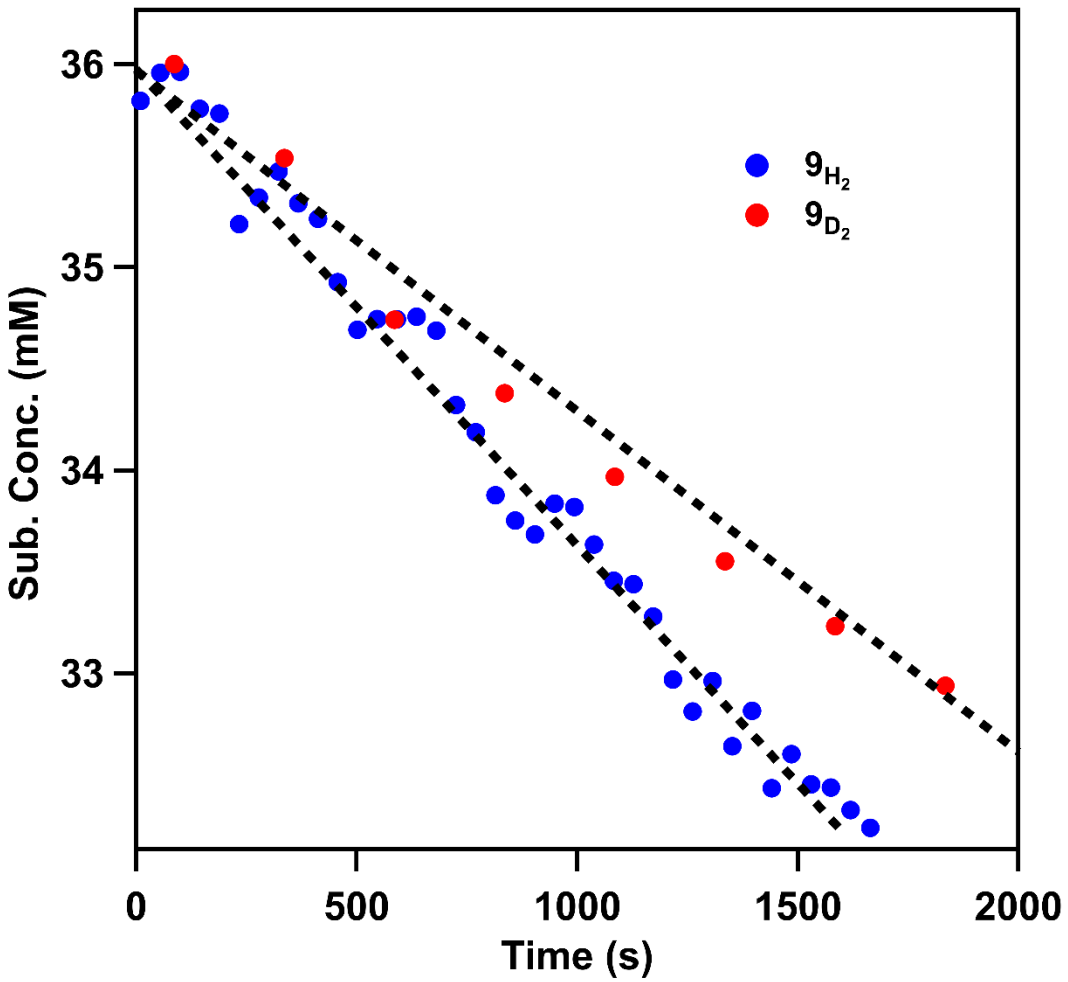


Figure S3. Intermolecular kinetic isotope effect reaction profile. Plotting the first 10% conversion of $\mathbf{9}_{H2}$ (blue) and $\mathbf{9}_{D2}$ (red) into $\mathbf{10}_{H2}$ and $\mathbf{10}_{D2}$ over time, respectively. Intermolecular KIE is derived by taking the ratio of the slopes of the linear fits. Every measurement is done in triplicates. (Intermolecular KIE = 1.35 ± 0.03, [$\mathbf{4}_F$] = 6.4 mM)

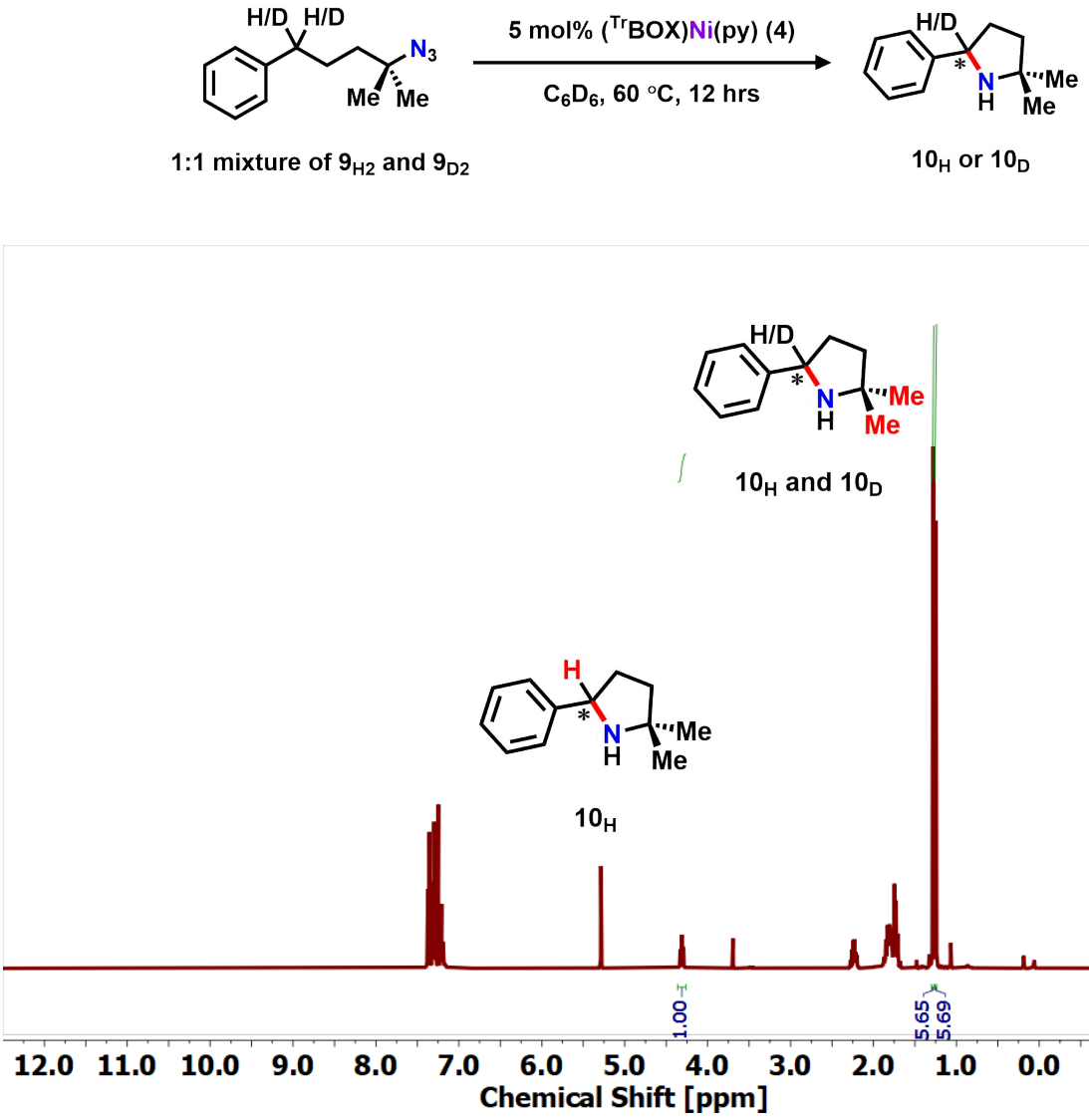


Figure S4. Competition KIE measurement. Reaction is carried out by subjecting a 1:1 mixture of $\mathbf{9}_{H2}$ and $\mathbf{9}_{D2}$ to standard catalytic conditions (5 mol% **4**, 60 °C, 12 h), and the product is isolated by aqueous acid-base extraction. The experiment is done in triplicate, and competition KIE is measured to be 1.13(6) based on integration of the product ^{1}H NMR spectra.

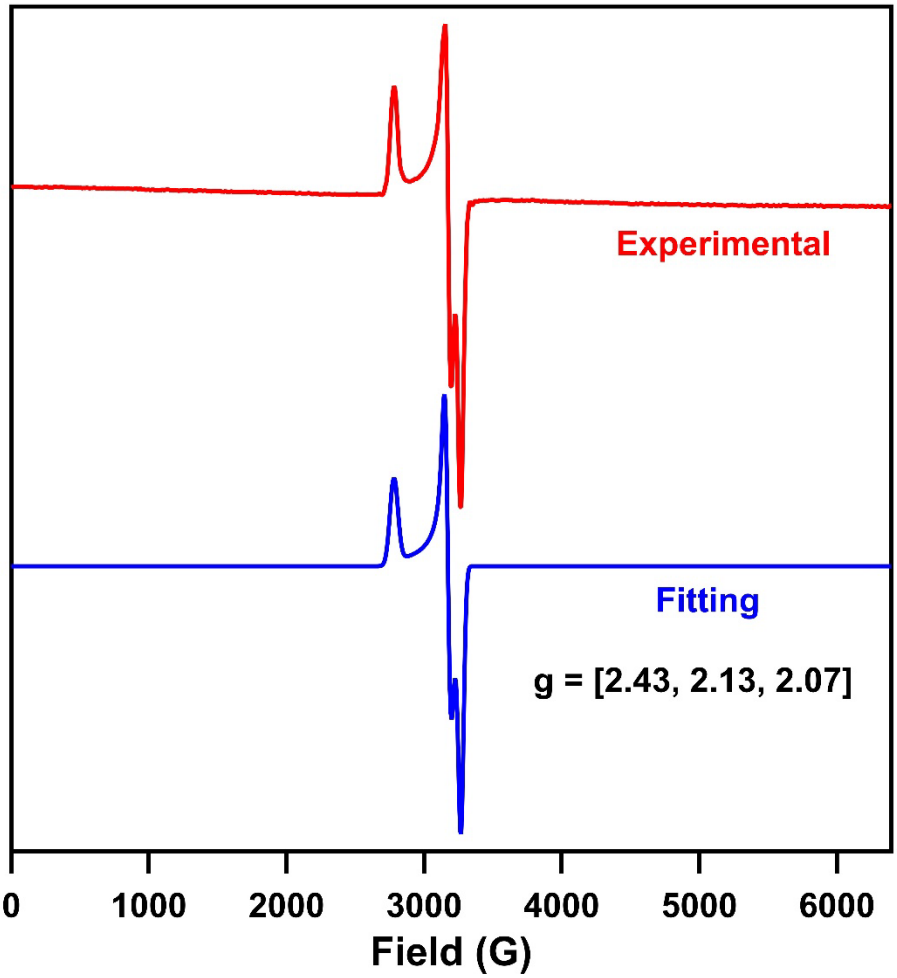


Figure S5. Frozen solution EPR spectrum of (^{TrH}BOX)Ni(py) (4) collected at 77 K in toluene (Red). Blue line represents a fit of the data using the program EasySpin. Fitting parameters: $S = ½$, $g_1 = 2.43$, $g_2 = 2.13$, $g_3 = 2.07$.

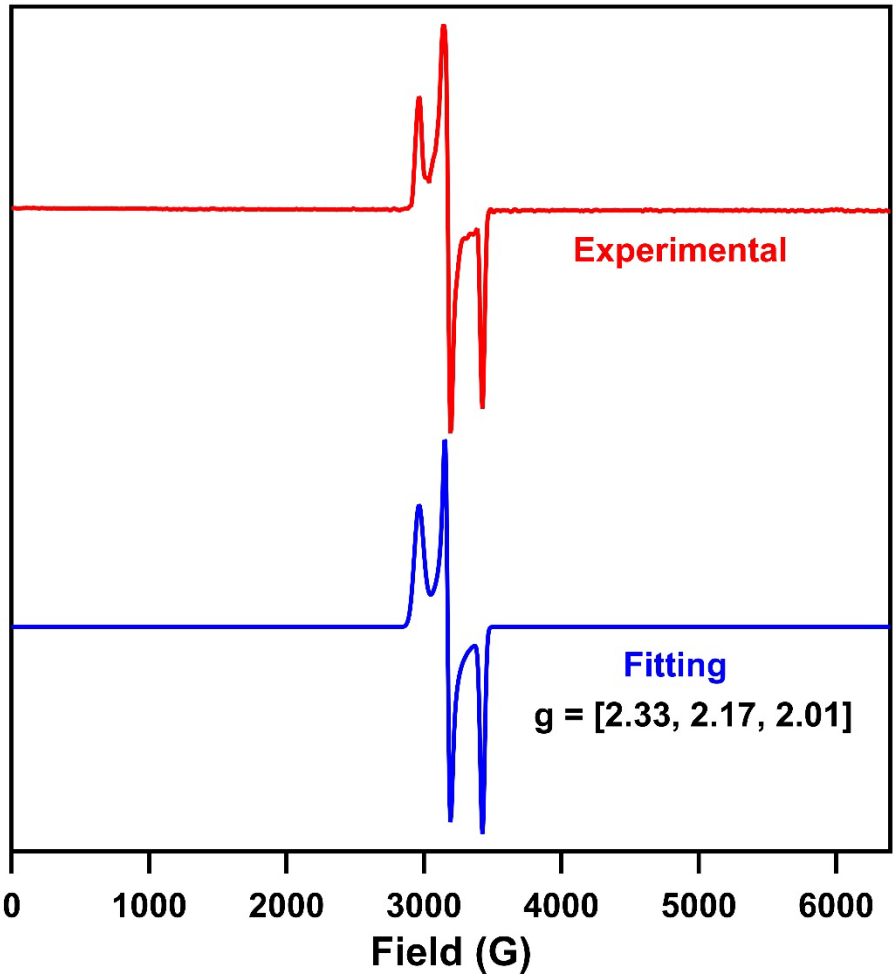


Figure S6. Frozen solution EPR spectrum of (^{TrH}BOX)Ni(κ^2-N$_4$Ad$_2$) (5) collected at 77 K in toluene (Red). Blue line represents a fit of the data using the program EasySpin. Fitting parameters: S = ½, g_1 = 2.33, g_2 = 2.17, g_3 = 2.01.

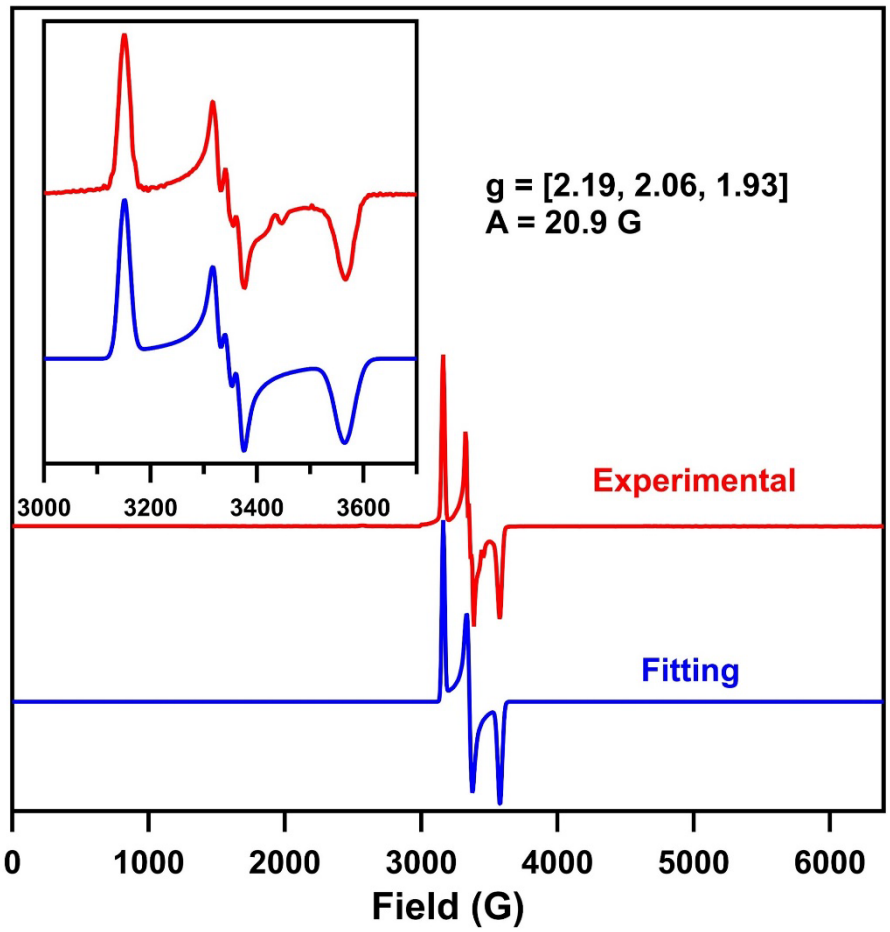


Figure S7. Frozen solution EPR spectrum of (^{TrH}BOX)Ni(NAd) (6) collected at 77 K in toluene (Red). Blue line represents a fit of the data using the program EasySpin. Fitting parameters: $S = ½$, $g_1 = 2.19$, $g_2 = 2.06$, $g_3 = 1.93$; $A(^{14}N) = 20.9$ G.

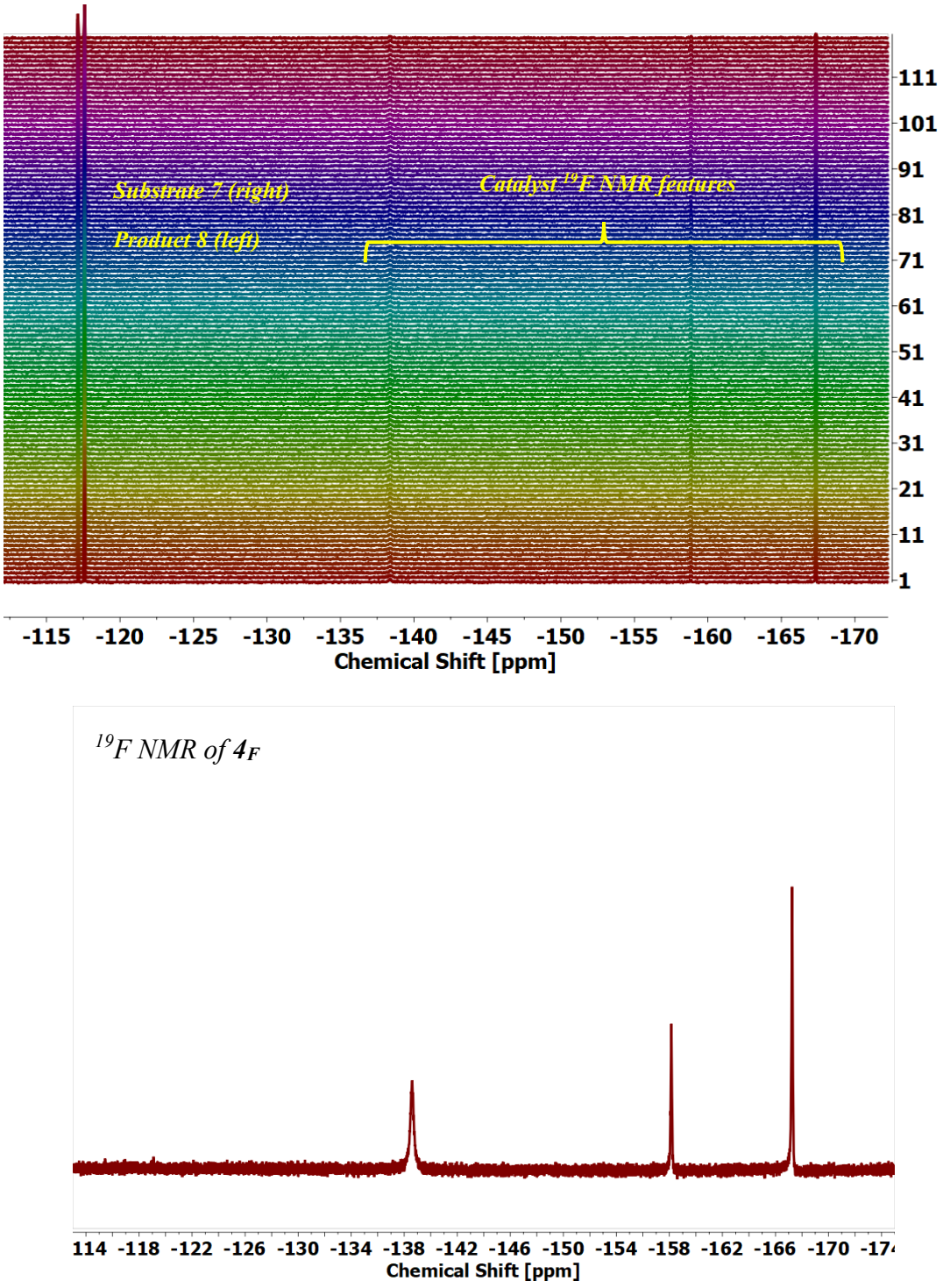


Figure S8. ^{19}F NMR spectra of reaction mixture during catalytic conversion of 7 to 8 up to 30% conversion. Spectra suggests that the resting state of Ni catalyst during the transformation has similar spectroscopic features to that of pre-catalyst (^{TrH}BOX)Ni(py) ($\mathbf{4_F}$).

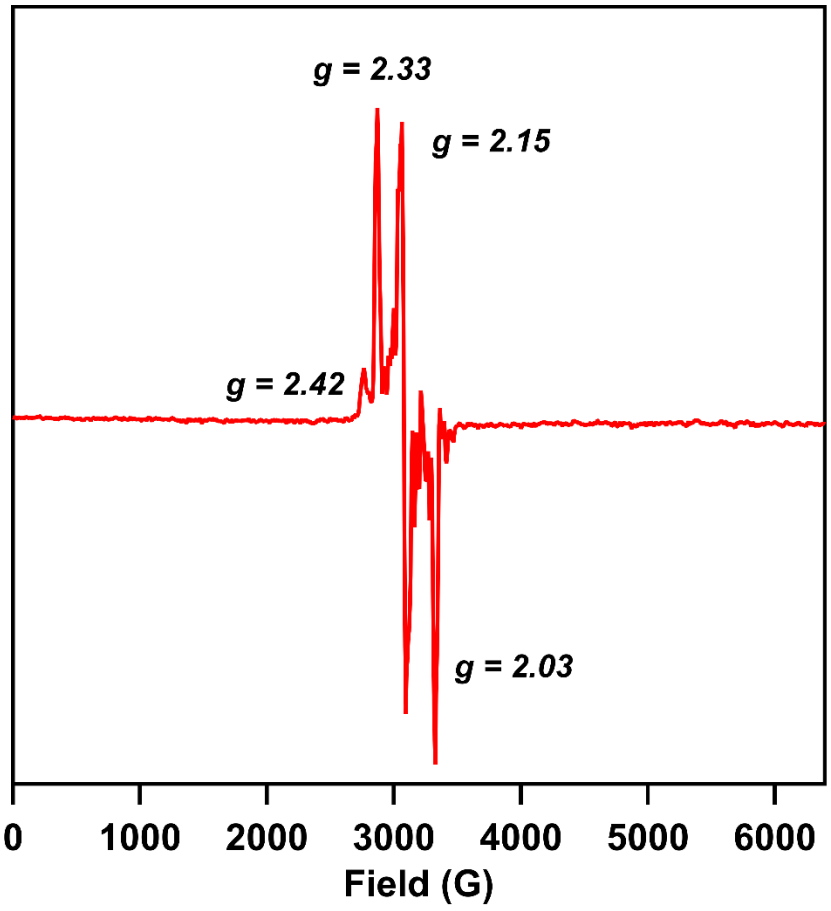
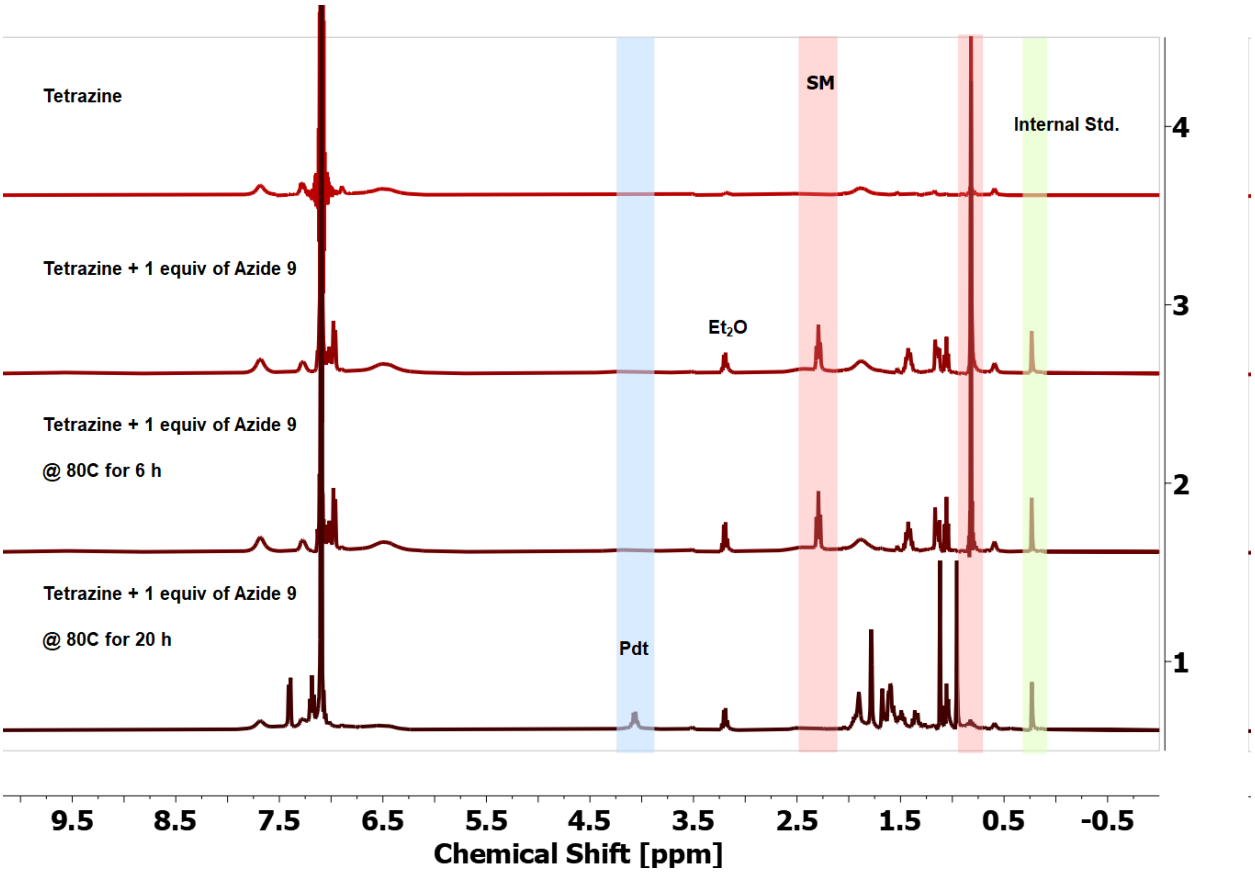
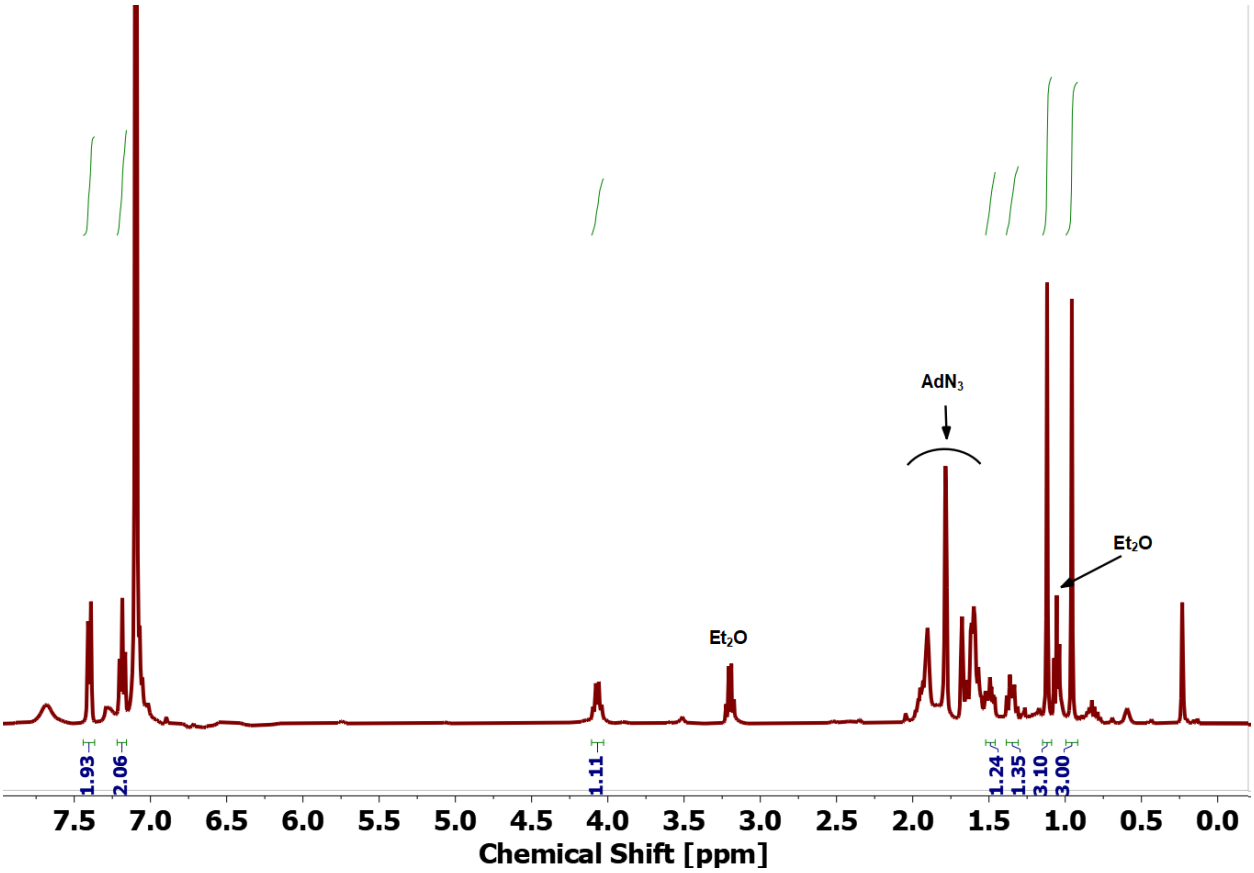


Figure S9. Frozen solution EPR spectrum of reaction mixture during catalytic conversion of 7 to 8 at 80% conversion collected at 77 K in toluene (Red). Spectrum suggests a mixture of tetrazido Ni-complex ($S = ½$, $g_1 = 2.33$, $g_2 = 2.17$, $g_3 = 2.01$) and at least one species with features similar to that of (^{TrF}BOX)Ni(py) (**4$_F$**, $S = ½$, $g_1 = 2.43$, $g_2 = 2.13$, $g_3 = 2.07$). No features at $g = 1.93$ (Ni-iminyl) is observed.

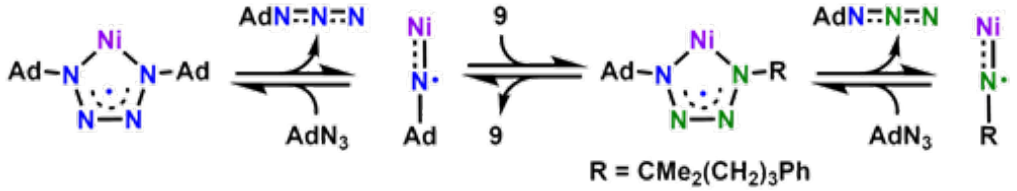
Figure S10. ^{1}H and ^{19}F NMR spectra for reaction of Ad-tetrazido complex 5_F and substrate 9 testing for reversible tetrazine formation

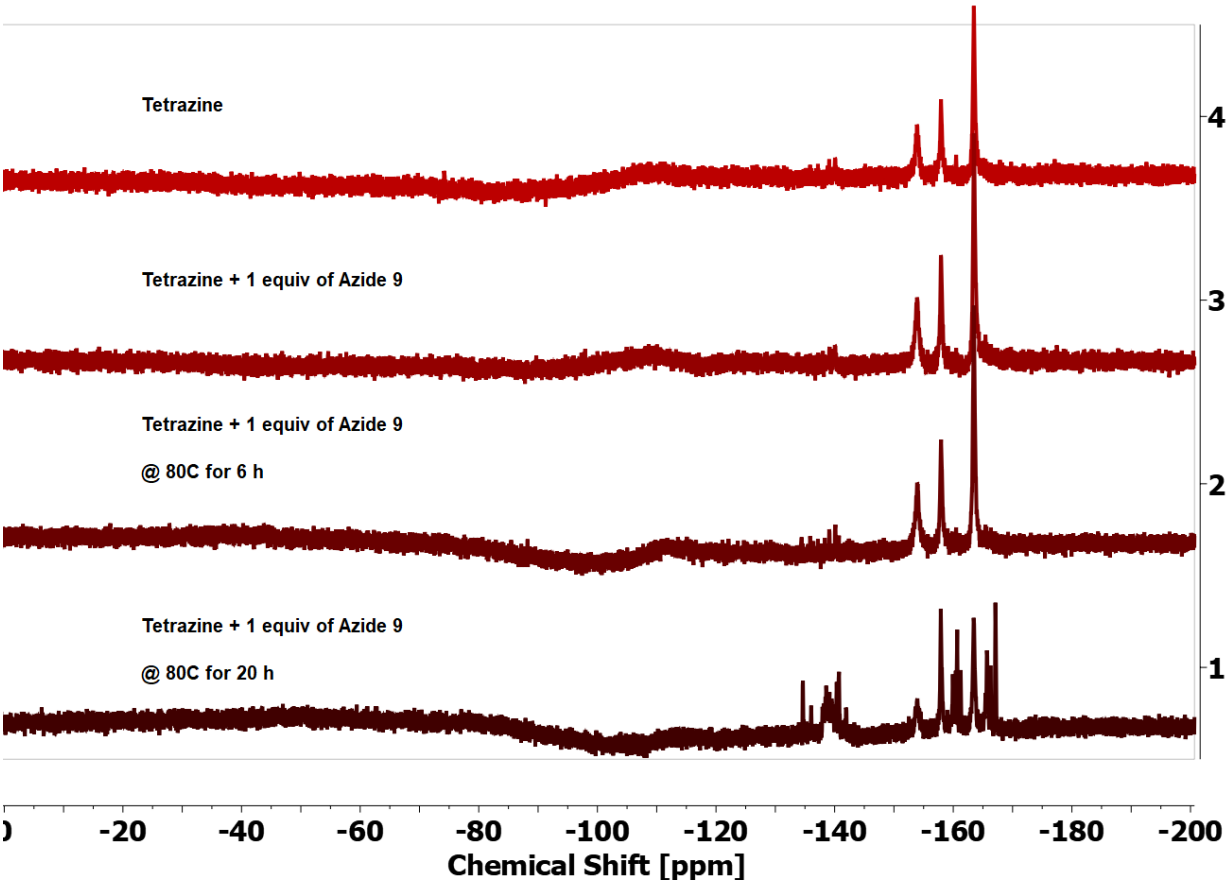


^{1}H NMR stack for an equimolar C_6D_6 solution of tetrazido complex $\mathbf{5_F}$ and azide substrate **9** showing a long induction period (no product observed during the first 6 h of the reaction) and full disappearance of substrate **9** along with generation of product **10** after 20 h. (small amount of Et_2O left over from workup of $\mathbf{5_F}$)



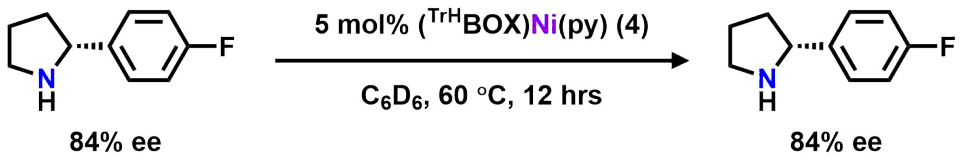
^{1}H NMR of final reaction mixture showing the generation of product **10** as well as AdN_3 liberated from tetrazido complex $\mathbf{5_F}$ via azide shuffling.





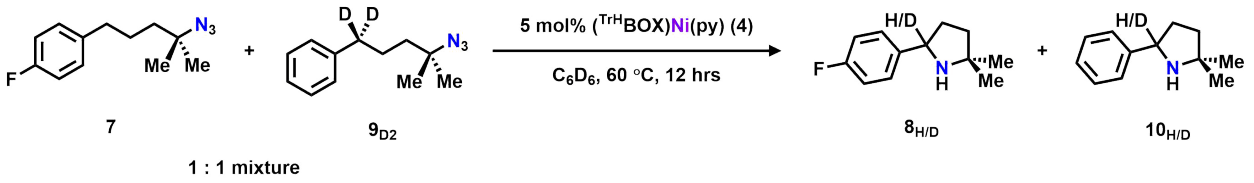
^{19}F NMR stack for an equimolar C_6D_6 solution of tetrazido complex $\mathbf{5_F}$ and azide substrate **9** showing partial decomposition of $\mathbf{5_F}$ into a mixture of indiscernible complexes at the end of the transformation.

Pyrrolidine enantio-enrichment test for C–N bond formation reversibility



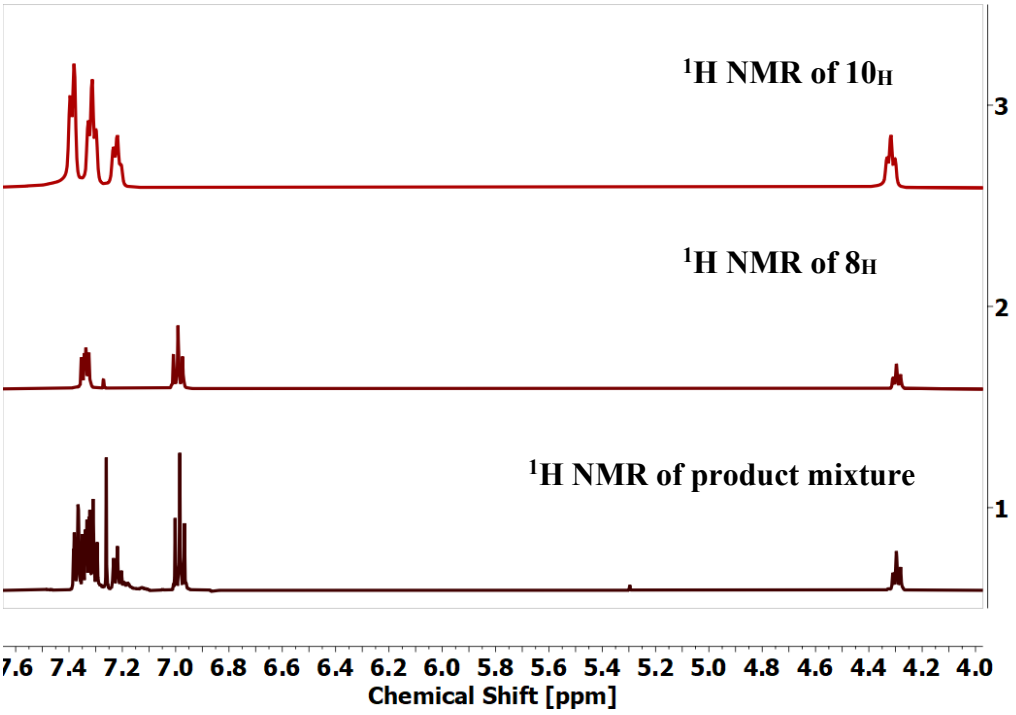
To test for the reversibility of C–N bond forming step, enantio-enriched (R)-2-(4-fluorophenyl) pyrrolidine (84% *ee* determined by Mosher analysis using ^{19}F NMR spectroscopy) prepared according to literature procedures was subjected to catalytic conditions (5 mol% 60 °C, 12 h). ^{1}H and ^{19}F NMR spectra taken during the reaction suggest no additional organic species formation. The pyrrolidine recovered via aqueous acid-base workup is similarly analyzed using Mosher analysis, showing the same level of enantio-enrichment (84 % *ee*). The overall result suggests that the C–N bond formation step is irreversible.

Figure S11. Crossover catalytic reaction using 7 and 9_{D2}

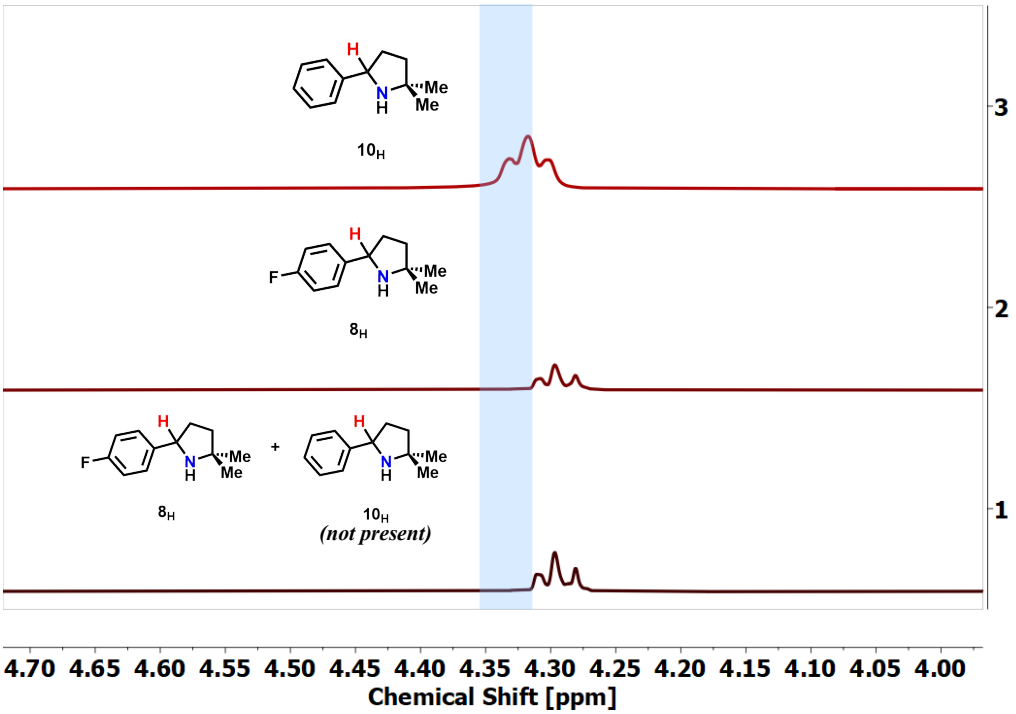


To test the possibility for intermolecular H-atom transfer, a 1:1 mixture of 1-(4-azido-4-methylpentyl)-4-fluorobenzene (**7**) and (4-azido-4-methylpentyl-1,1-d2)benzene (**9_{D2}**) is subjected to catalytic condition (5 mol% **4**, 60 °C, 12 h). Integration from ^{1}H NMR spectrum of the isolated product mixture suggests the presence of only **8_H** and **10_D** with no H/D crossover product (8_D and 10_H).

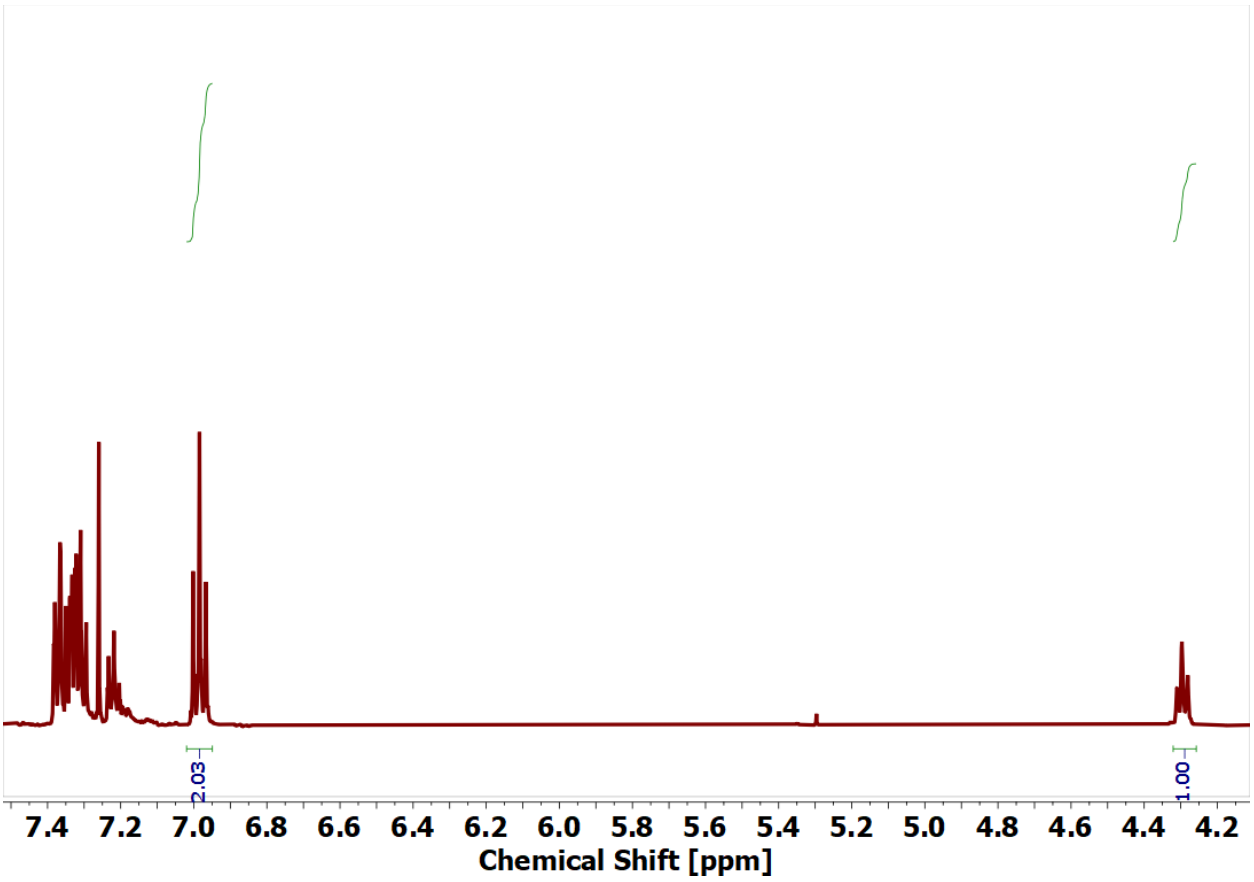
Furthermore, intermolecular HAT will result in the formation of a Ni(II) amide species without the capability of pyrrolidine formation, ultimately lead to corresponding amine product after quenching the reaction. Since in every catalytic run the work up procedure only involves an aqueous acid-base extraction, and no amine formation was observed in the product NMR spectra, the result overall suggest no intermolecular H-atom transfer takes place under the catalytic conditions.



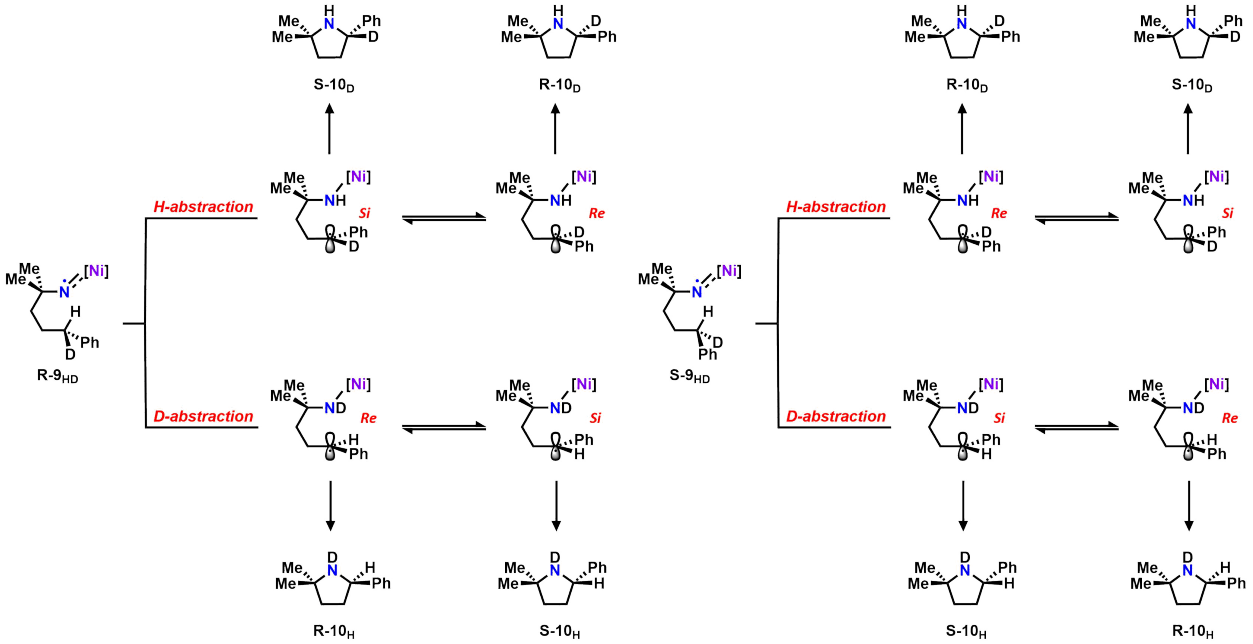
^{1}H NMR stack of **10$_H$**, **8$_H$** and product mixture from the crossover experiment



^{1}H NMR region corresponding to the *a*-H next to nitrogen atom in **10$_H$**, **8$_H$** and product mixture showing the absence of **10$_H$**



Integration value for peaks corresponding to **8**$_H$ showing no significant amount of **8**$_D$ formation



Azide	**S-10$_H$**	**R-10$_H$**	**S-10$_D$**	**R-10$_D$**	**(R-10$_D$+S-10$_D$)/ (R-10$_H$+S-10$_H$)**	**S-10$_H$/R-10$_H$**	**S-10$_D$/R-10$_D$**
S-9$_{HD}$	3.5%	1.7%	60.4%	34.4%	18.3:1	2.08	1.76
R-9$_{HD}$	23.2%	11.6%	49.9%	15.3%	1.88:1	2.00	3.25

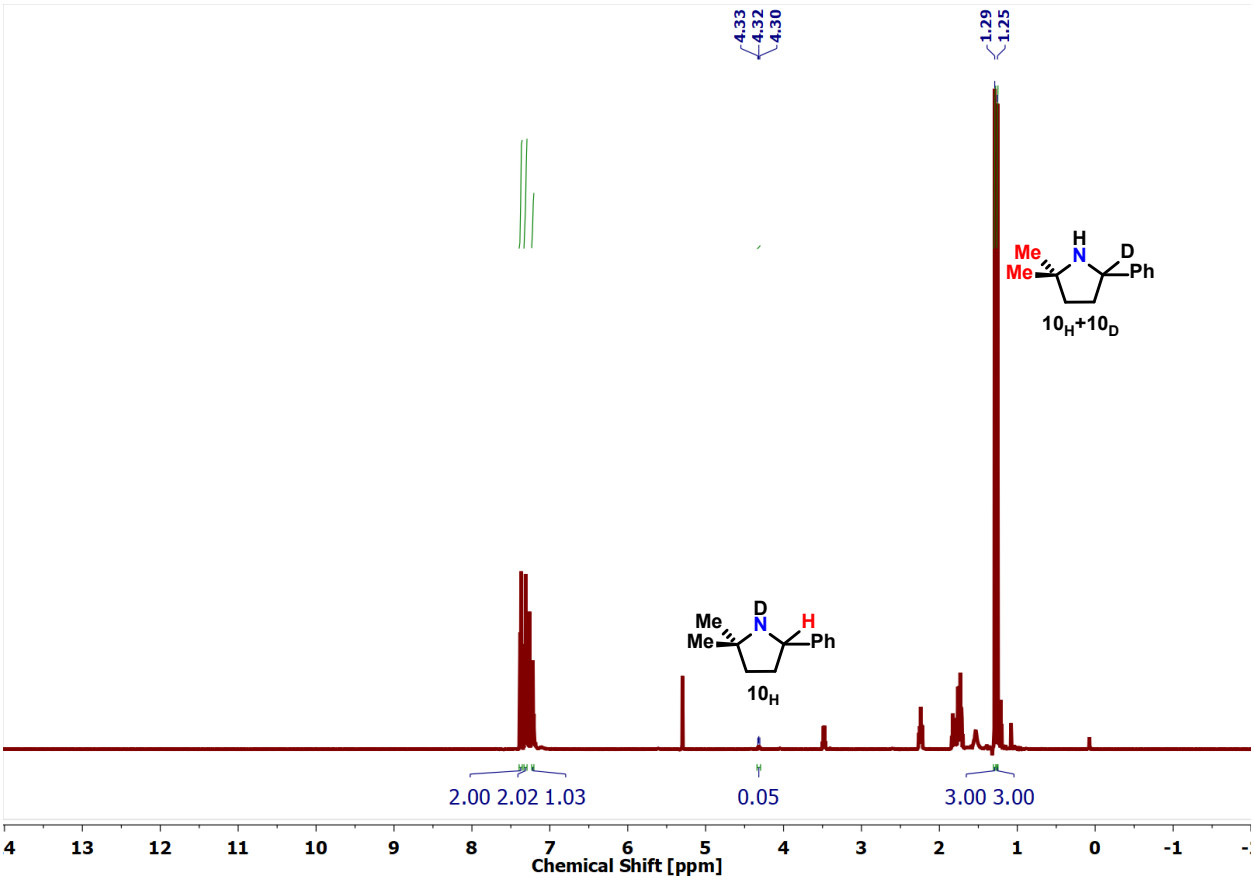
To test the possibility of a time-dependent product distribution in the intramolecular KIE experiment, we subjected **R-9$_{HD}$** to catalytic condition in two separate trials and quenched the reaction at 30% and 50% conversion as observed by ^{1}H NMR spectroscopy. No significant differences were noted in the product distribution at various conversions.

Conv.	**S-10$_H$**	**R-10$_H$**	**S-10$_D$**	**R-10$_D$**
30%	24.0%	12.2%	49.3%	14.5%
50%	25.0%	11.8%	48.7%	14.4%
full	23.2%	11.6%	49.9%	15.3%

Figure S12. Product distribution using enantiopure mono D-labeled substrates S-10$_{HD}$ and R-10$_{HD}$. The two pairs of enantiomers (**S-10$_H$** and **R-10$_H$**; **S-10$_D$** and **R-10$_D$**) are resolved using Mosher analysis and the ratios are obtained using ^{1}H NMR spectroscopy. All reactions were carried out using standard catalytic conditions at room temperature.

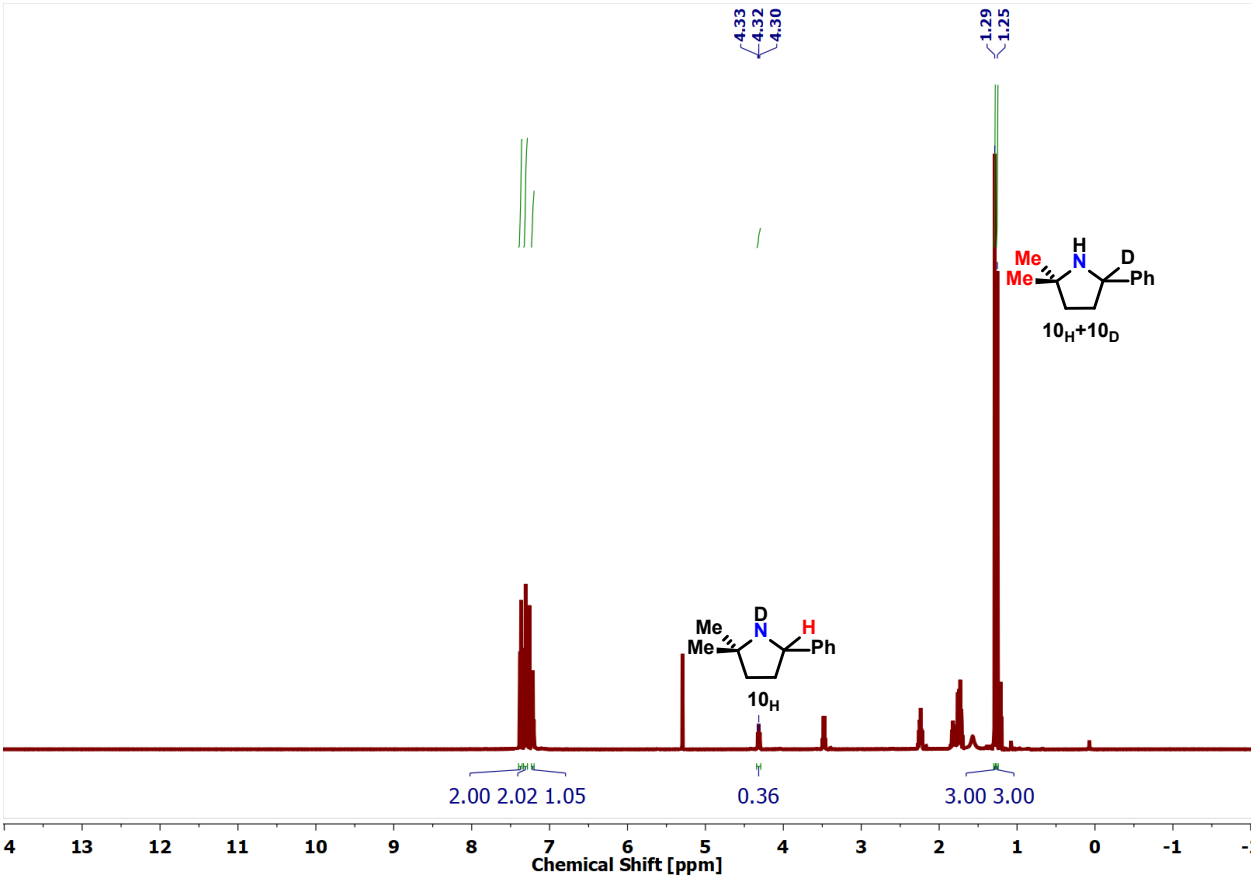
Analysis of intramolecular isotope labelling experiment

Product mixture from S-9$_{HD}$



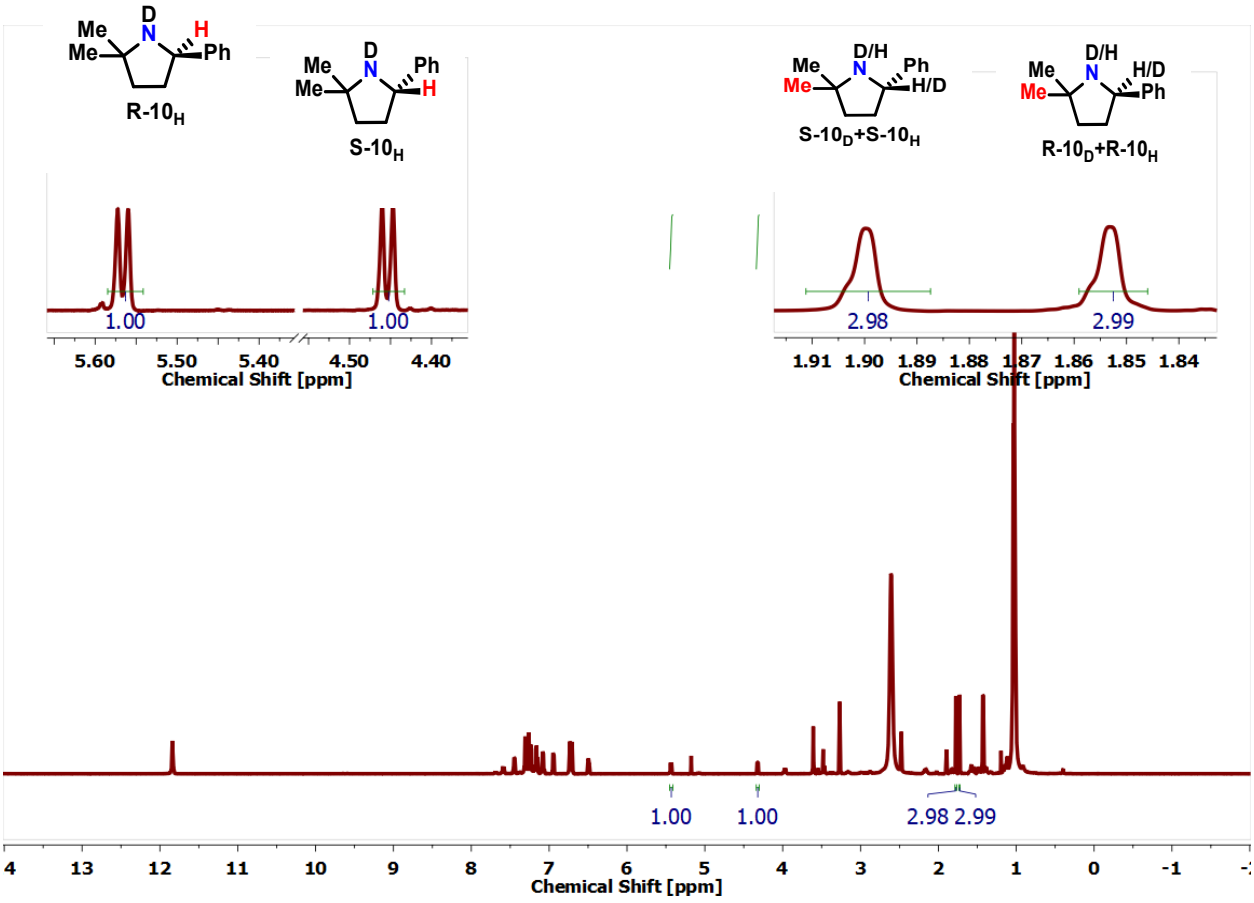
Chemical Shift/ppm	Absolute Integration	$10_D/10_H$
4.32 (t)	180.12	17.97
1.29 (s)	10252.41	
1.25 (s)	10252.15	

Product mixture from R-9$_{HD}$

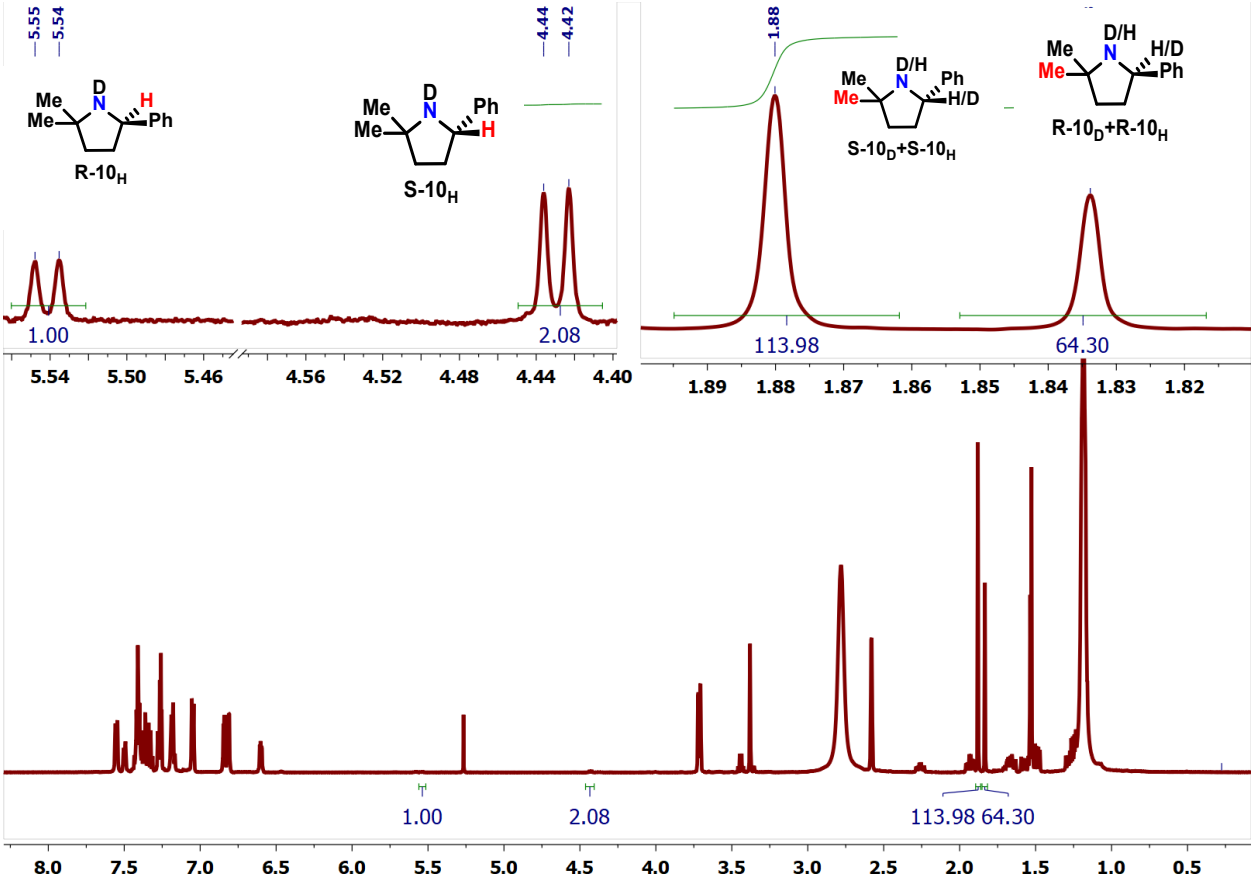


Chemical Shift/ppm	Absolute Integration	$3_D/3_H$
4.32 (t)	1139.93	1.80
1.29 (s)	9576.34	
1.25 (s)	9554.17	

Mosher analysis of product mixture from racemic-9[1]



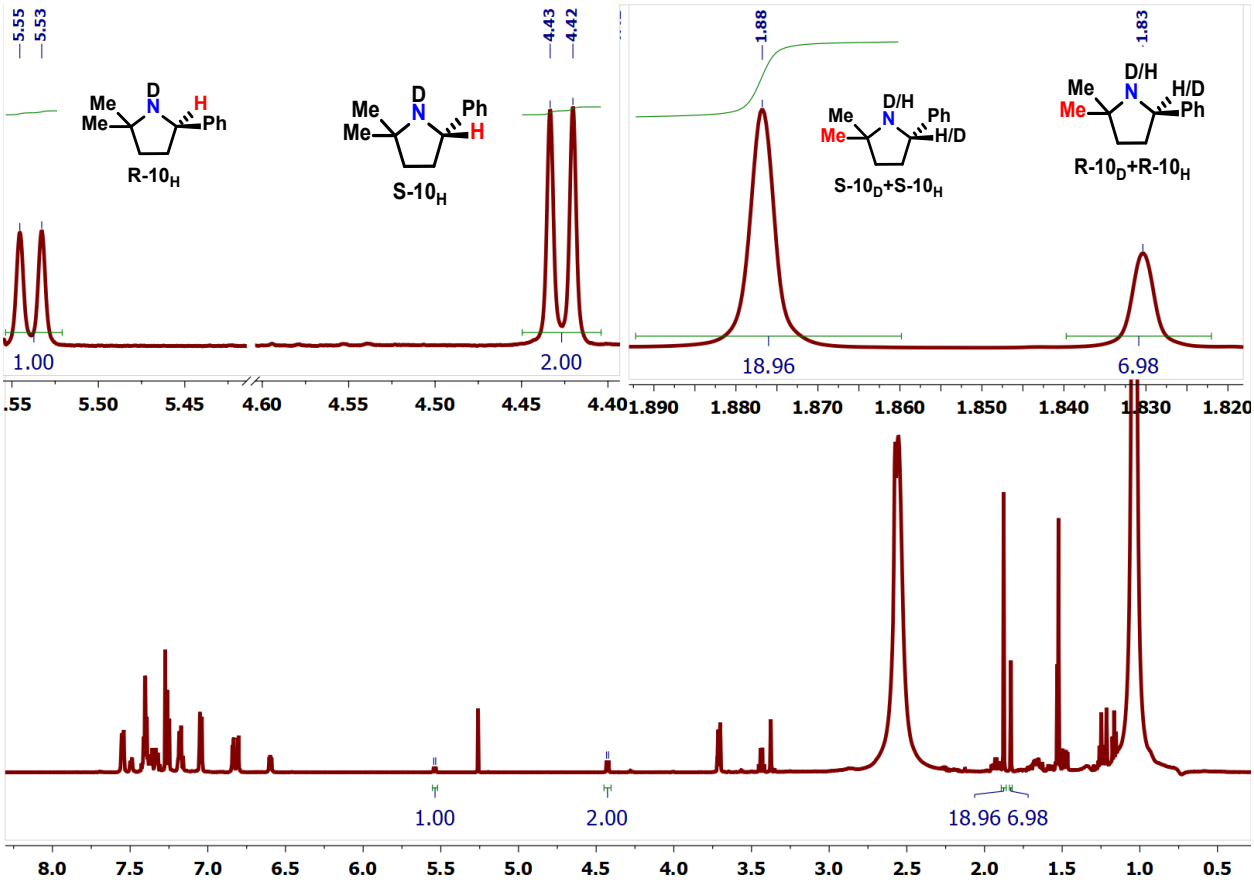
Mosher analysis of product mixture from S-9$_{HD}$[1]



Full conversion:

Chemical Shift/ppm		Absolute Integration	
5.55 (d)		12.56	
4.43 (d)		26.12	
1.88 (s)		1431.13	
1.83 (s)		807.32	
R-10$_H$	**S-10$_H$**	**R-10$_D$**	**S-10$_D$**
1.7%	3.5%	34.4%	60.4%

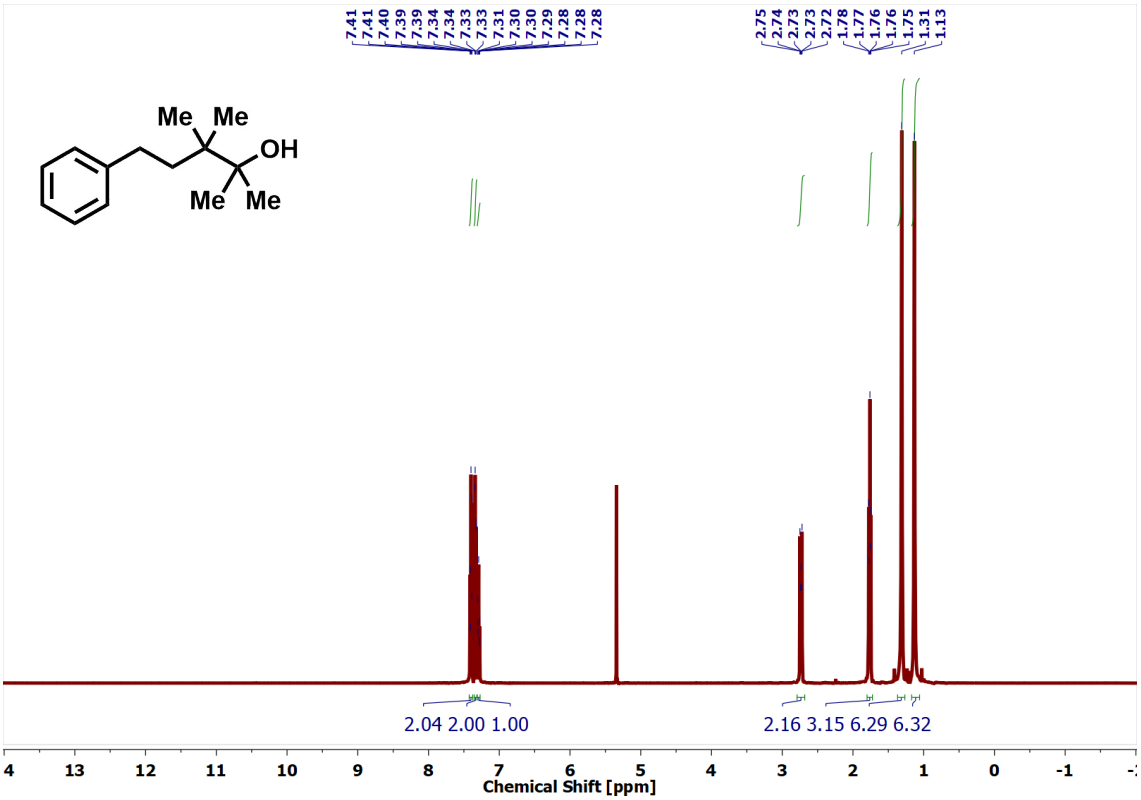
Mosher analysis of product mixture from R-9$_{HD}$[1]

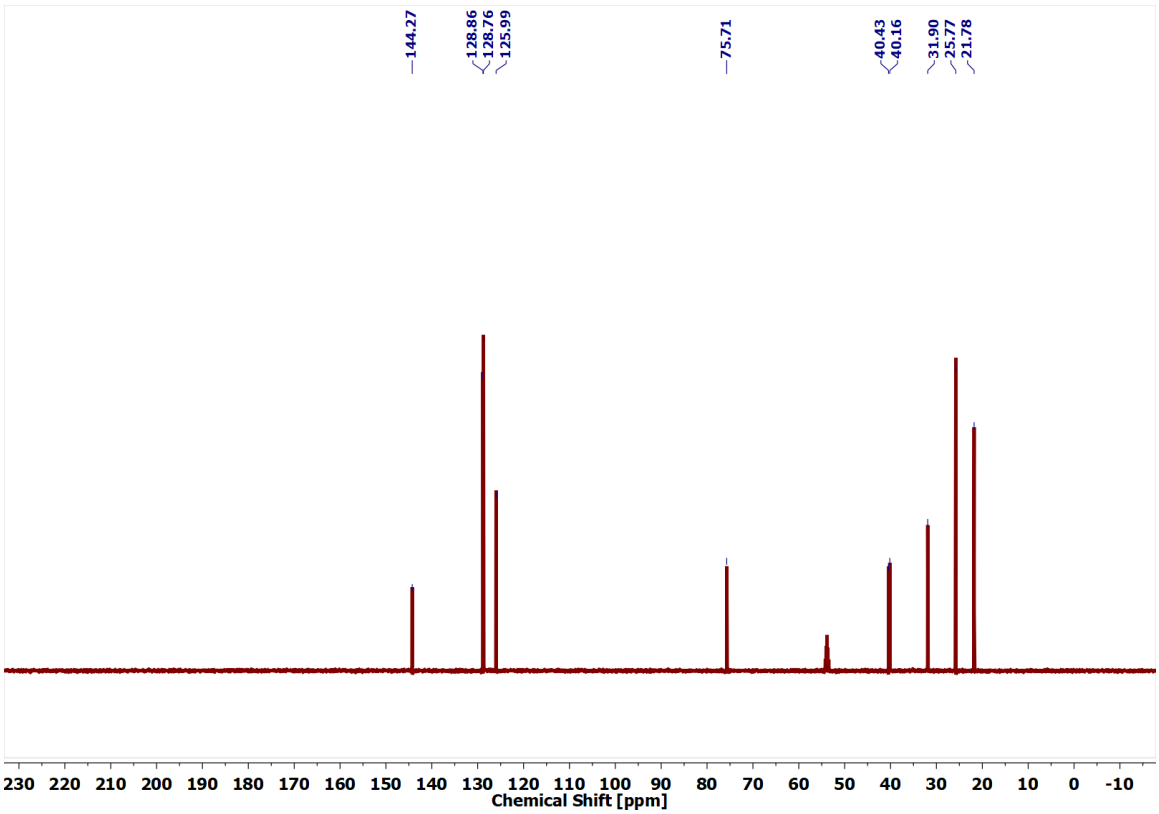


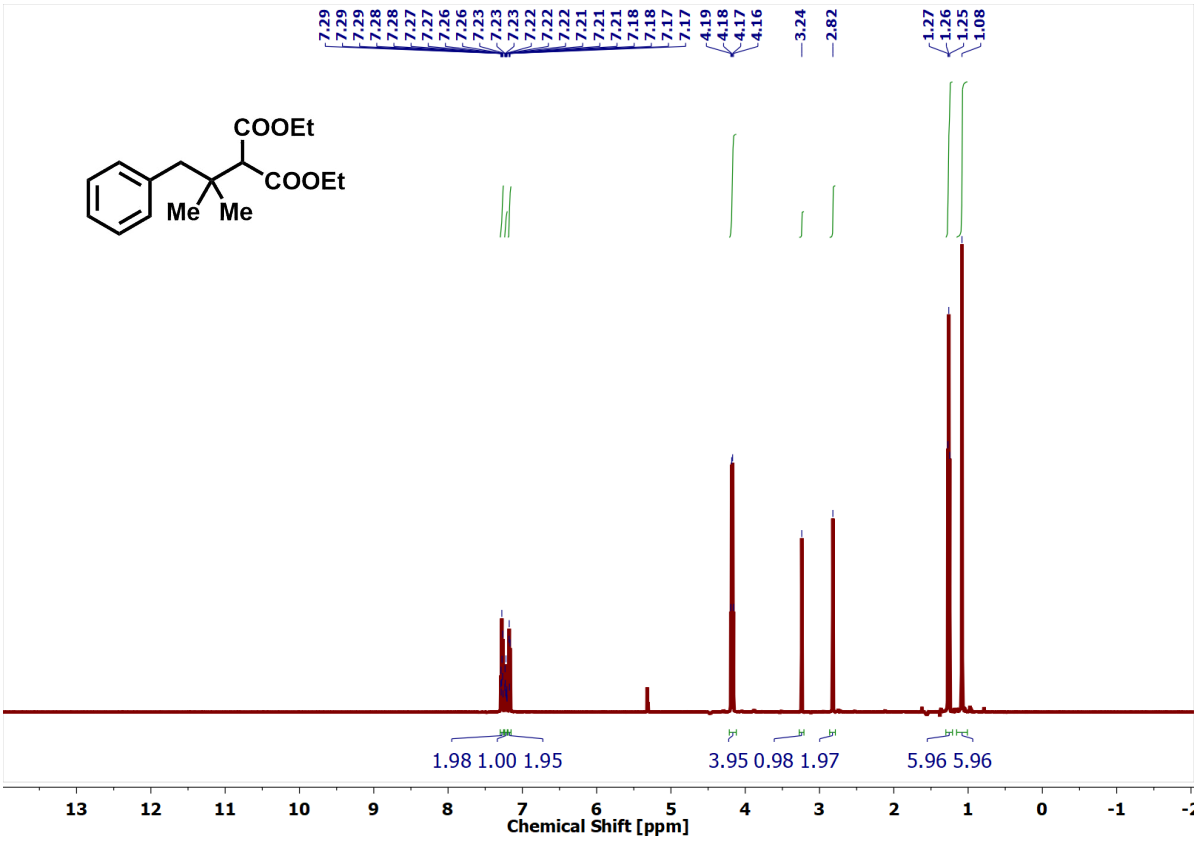
Full conversion:

Chemical Shift/ppm		Absolute Integration	
5.59-5.54		74.27	
4.48-4.43		148.72	
1.91-1.89		1406.47	
1.86-1.84		517.90	
R-10$_H$	**S-10$_H$**	**R-10$_D$**	**S-10$_D$**
11.6%	23.2%	15.3%	49.9%

NMR spectra of intermediates in organoazide synthesis



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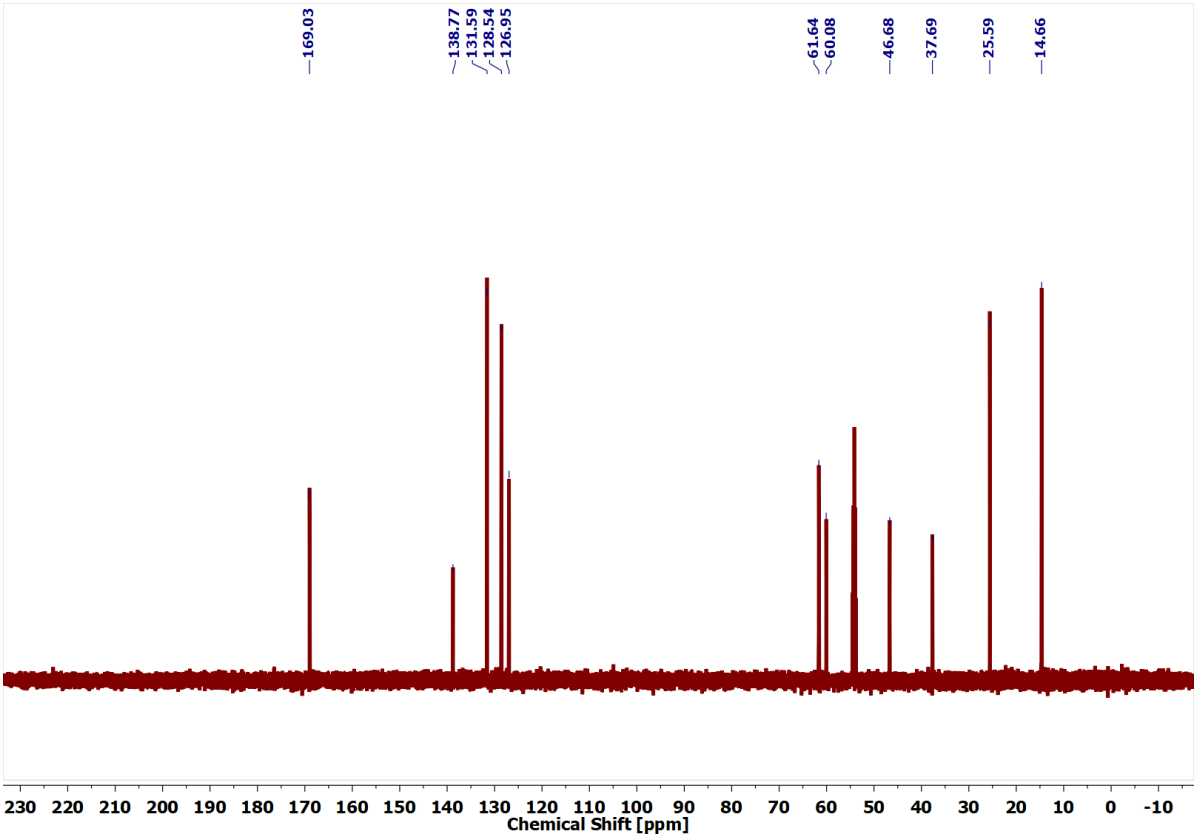
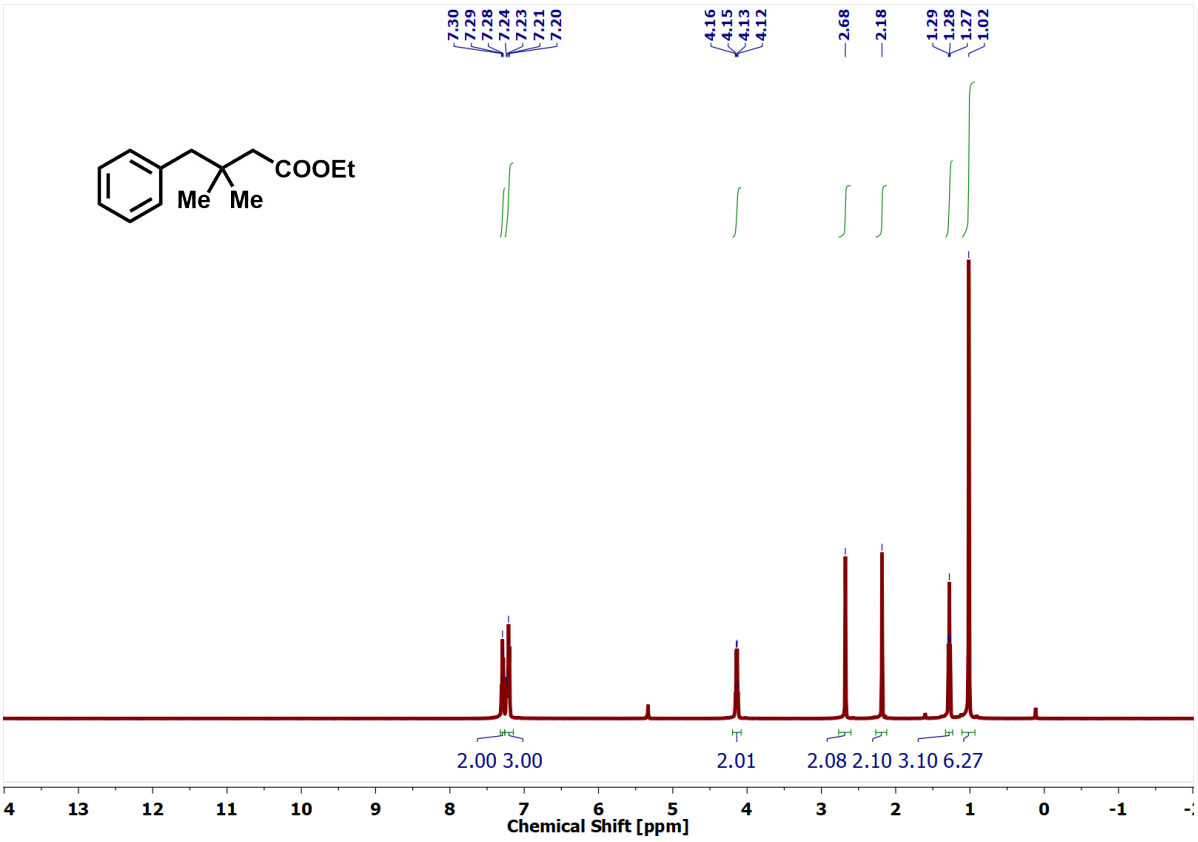
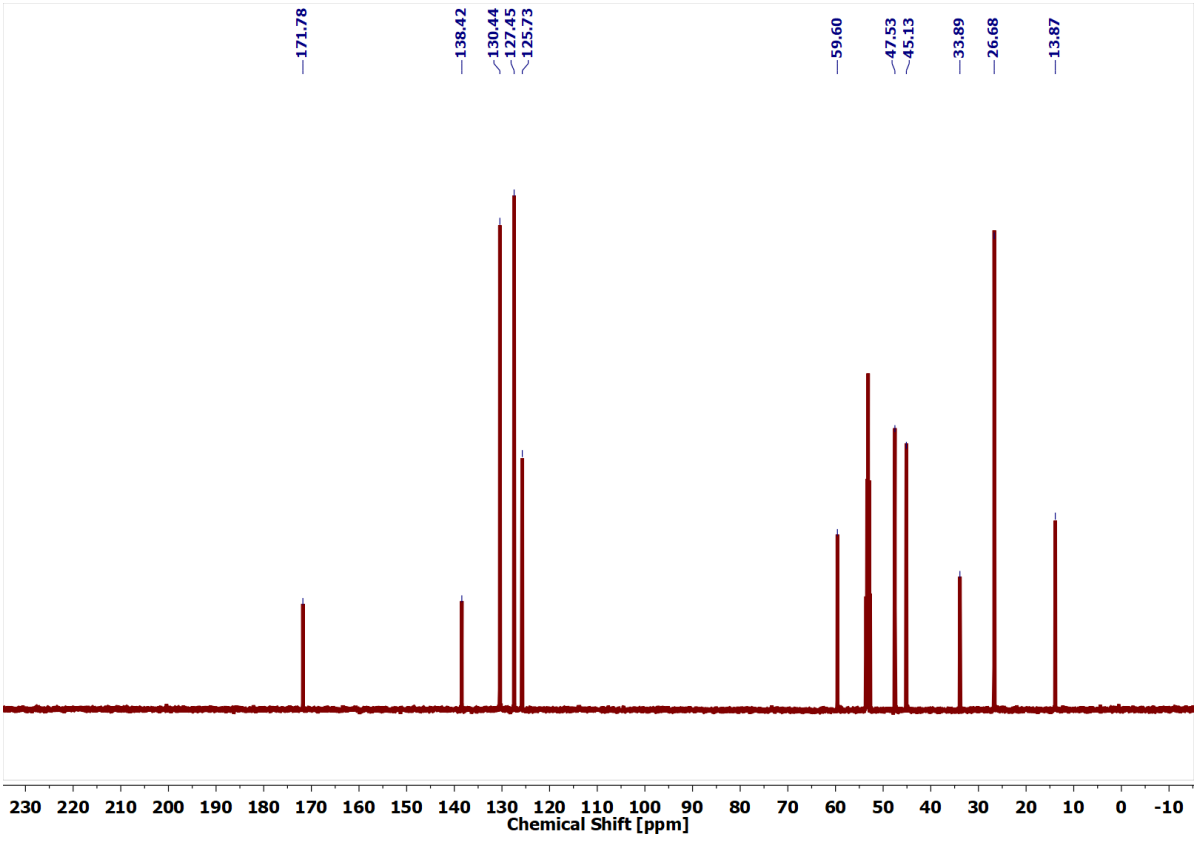
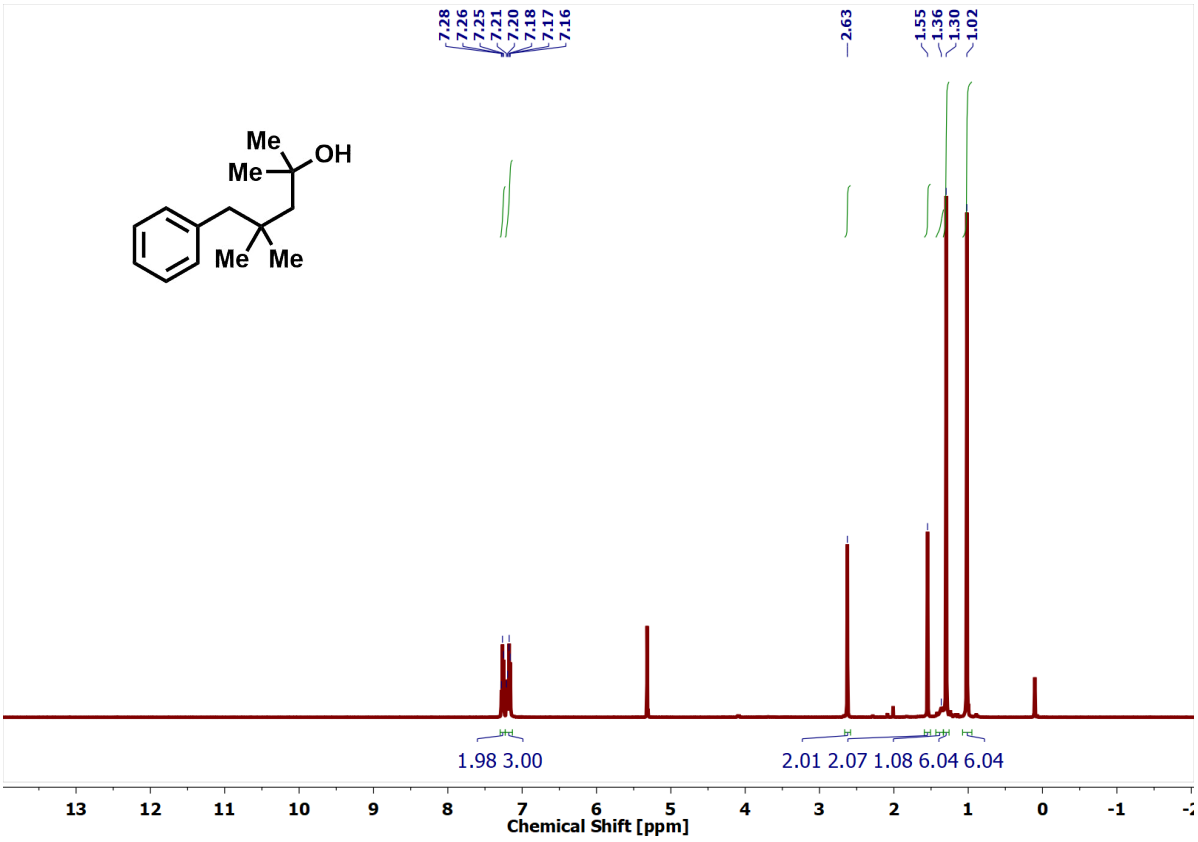
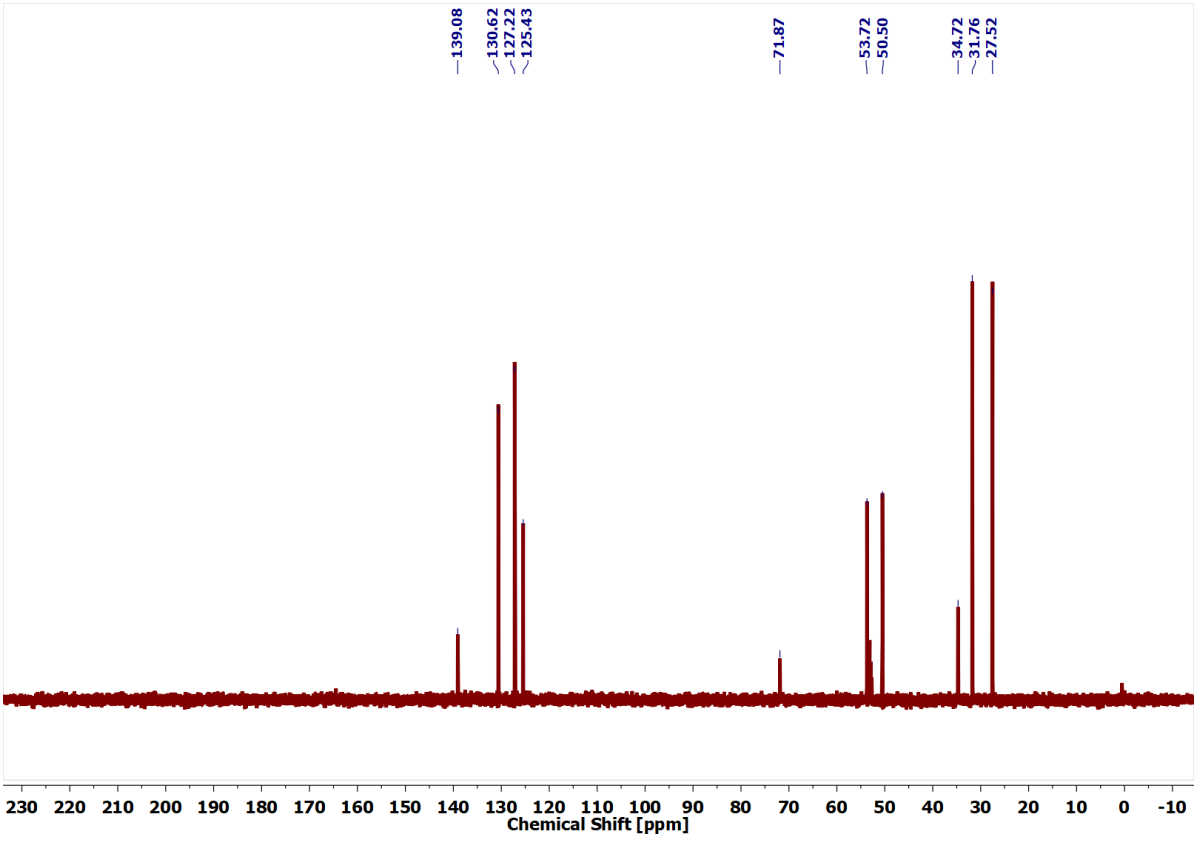
3.95 0.98 1.97
5.96 5.96
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

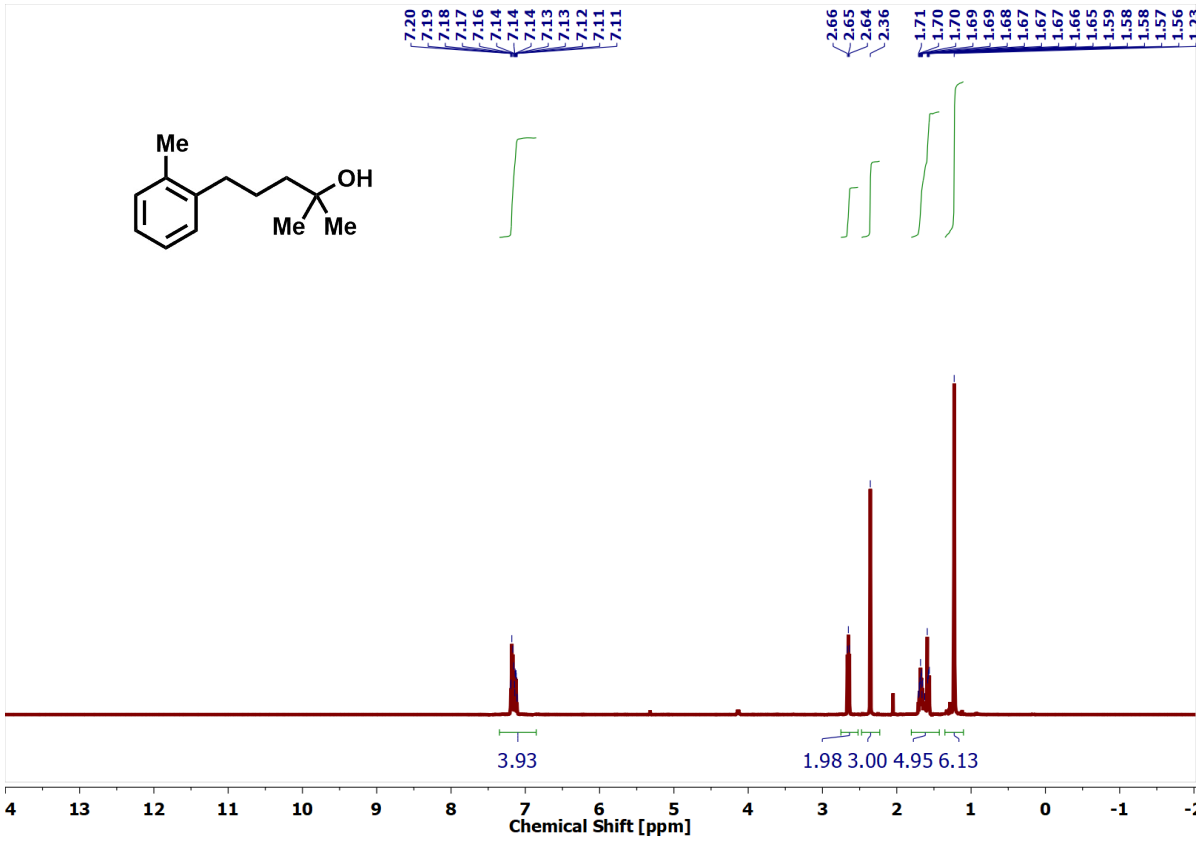

169.03
138.77
131.59
128.54
126.95
61.64
60.08
46.68
37.69
25.59
14.66
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

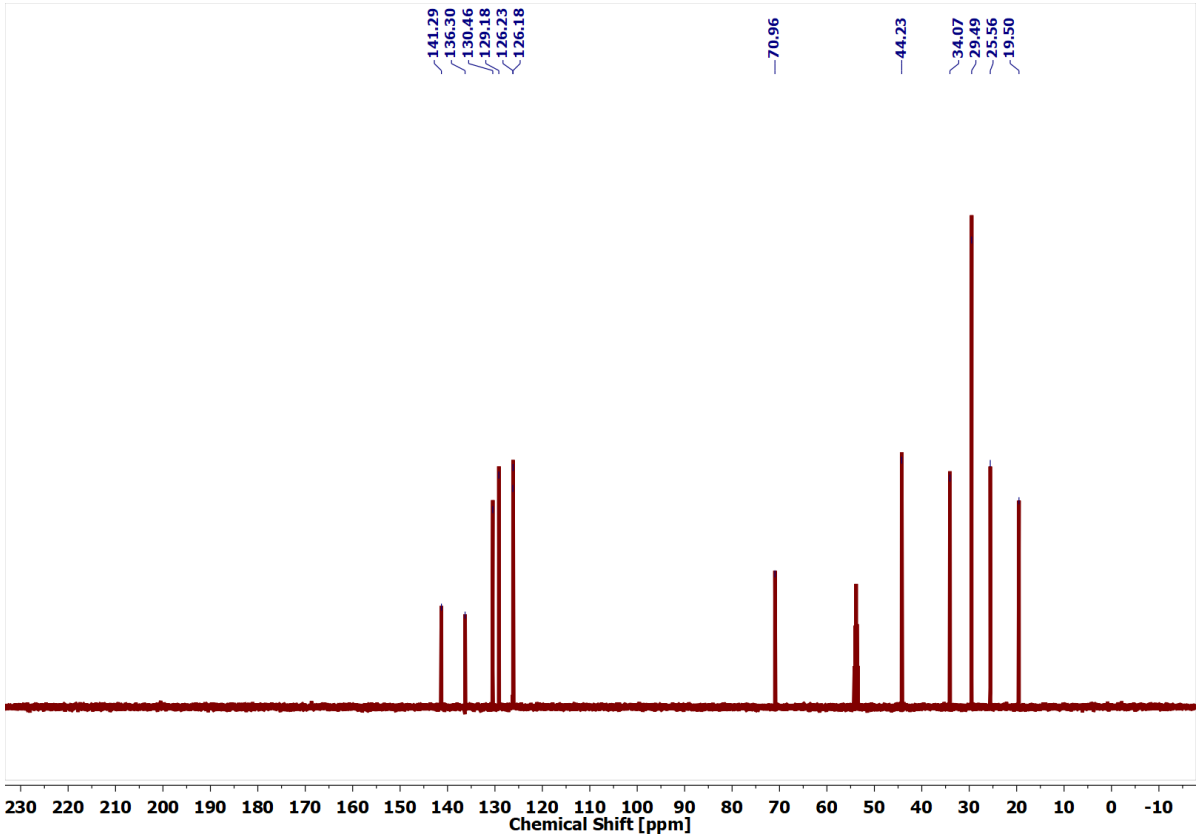

7.30
7.29
7.28
7.24
7.23
7.21
7.20
4.16
4.15
4.13
4.12
2.68
2.18
1.29
1.28
1.27
1.02
COOEt
Me Me
2.00 3.00
2.01
2.08 2.10 3.10 6.27
Chemical Shift [ppm]

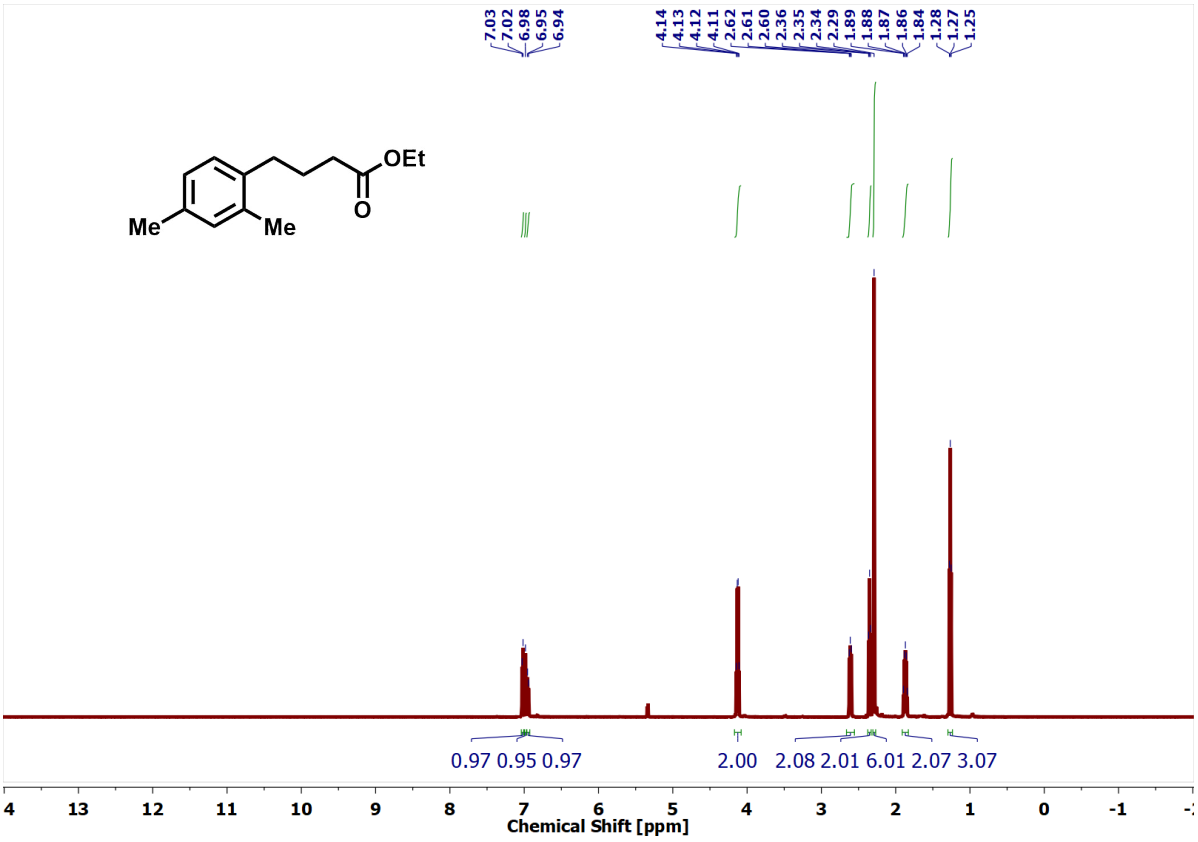

171.78
138.42
130.44
127.45
125.73
59.60
47.53
45.13
33.89
26.68
13.87
Chemical Shift [ppm]

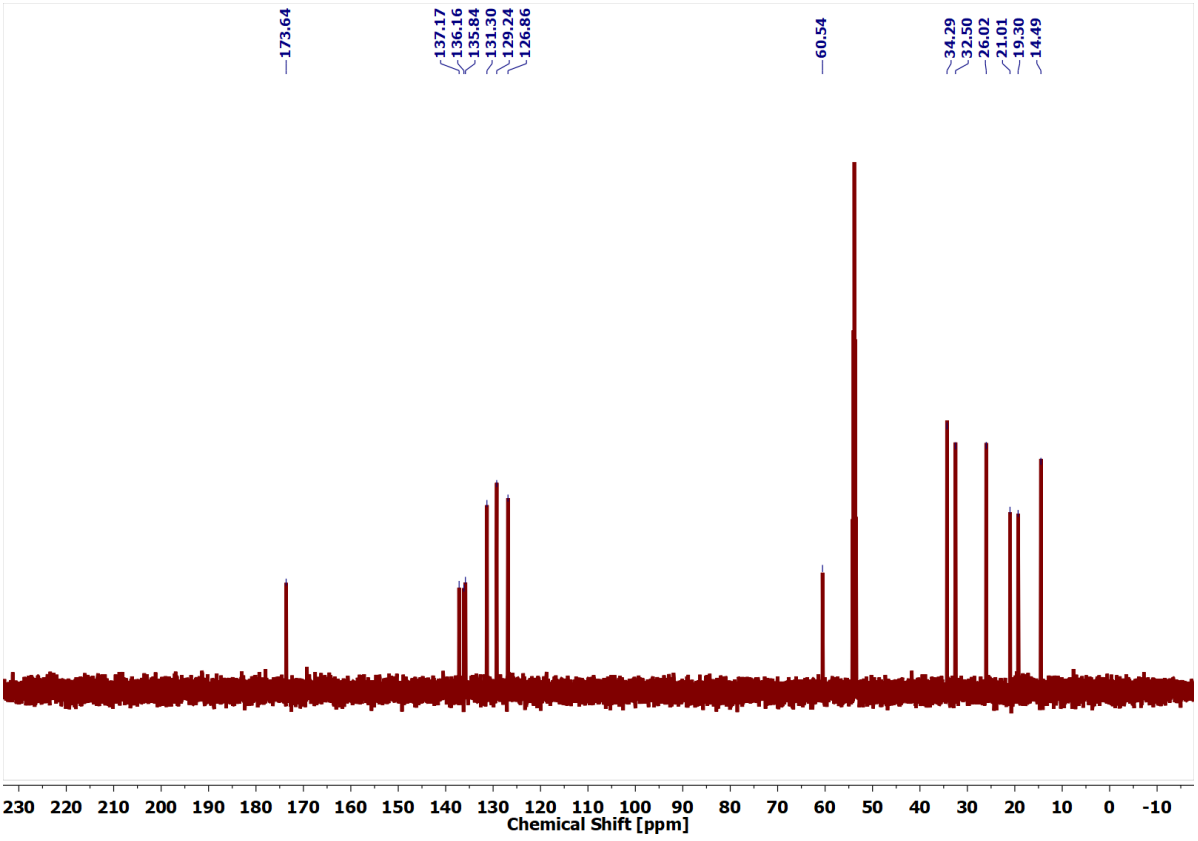

7.28
7.26
7.25
7.21
7.20
7.18
7.17
7.16
2.63
1.55
1.36
1.30
1.02
Me
Me
OH
Me
Me
1.98 3.00
2.01 2.07 1.08 6.04 6.04
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

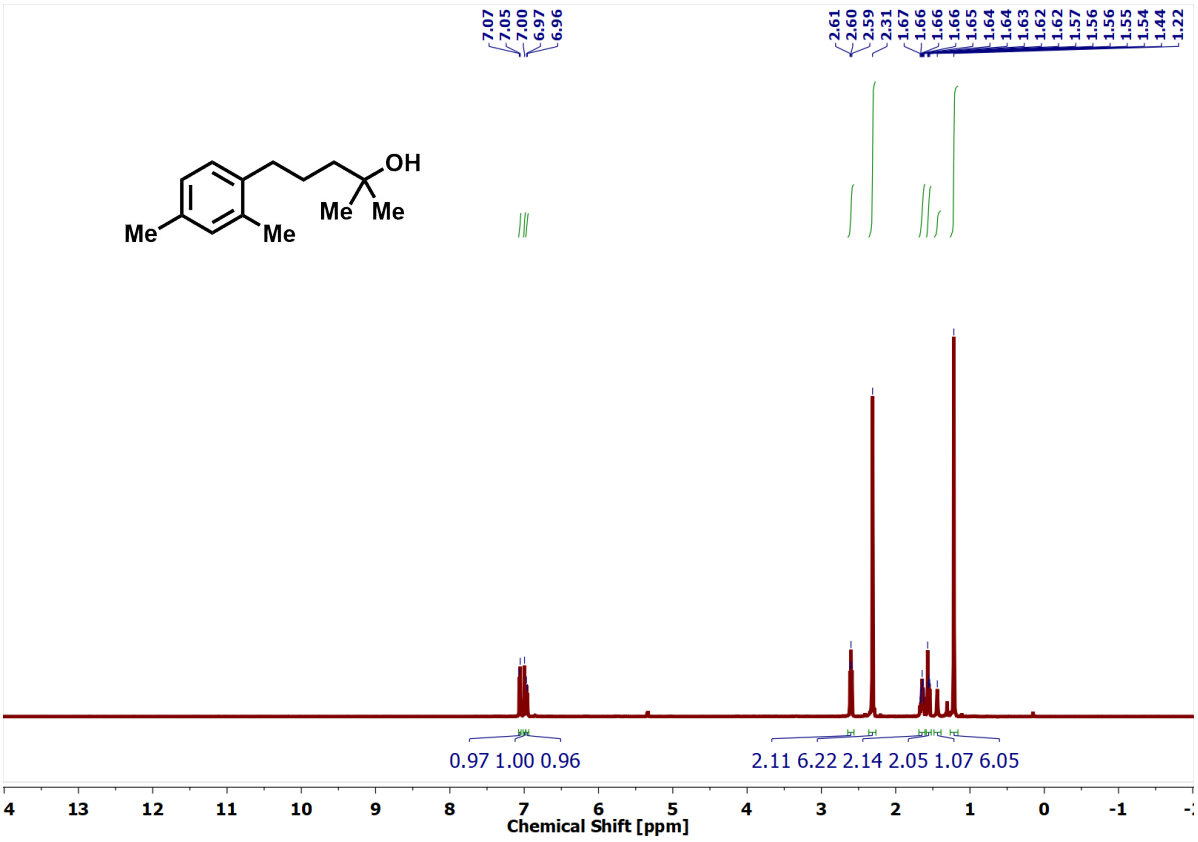

139.08
130.62
127.22
125.43
71.87
53.72
50.50
34.72
31.76
27.52
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

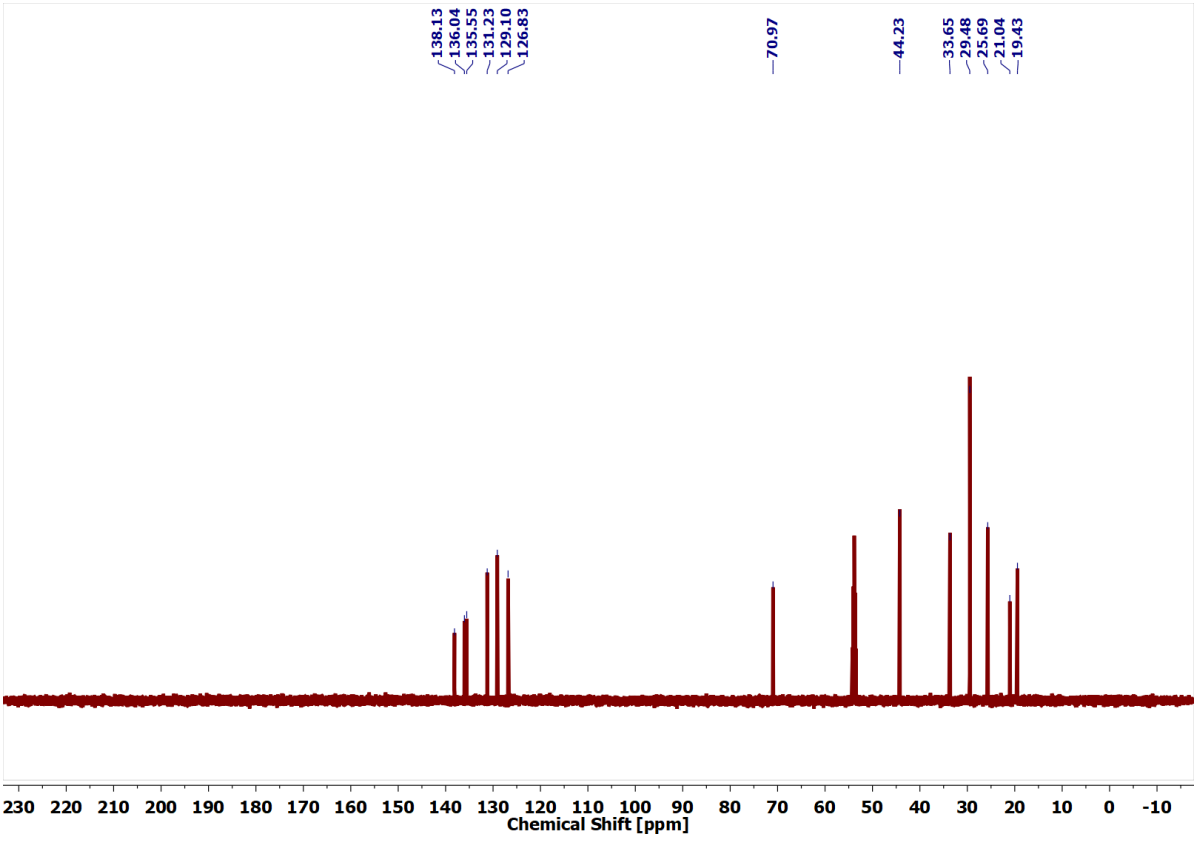

Me
OH
Me
Me
7.20
7.19
7.18
7.17
7.16
7.14
7.14
7.14
7.13
7.13
7.12
7.11
7.11
2.66
2.65
2.64
2.36
1.71
1.70
1.70
1.69
1.69
1.68
1.67
1.67
1.67
1.66
1.65
1.59
1.58
1.58
1.57
1.56
3.93
1.98 3.00 4.95 6.13
Chemical Shift [ppm]

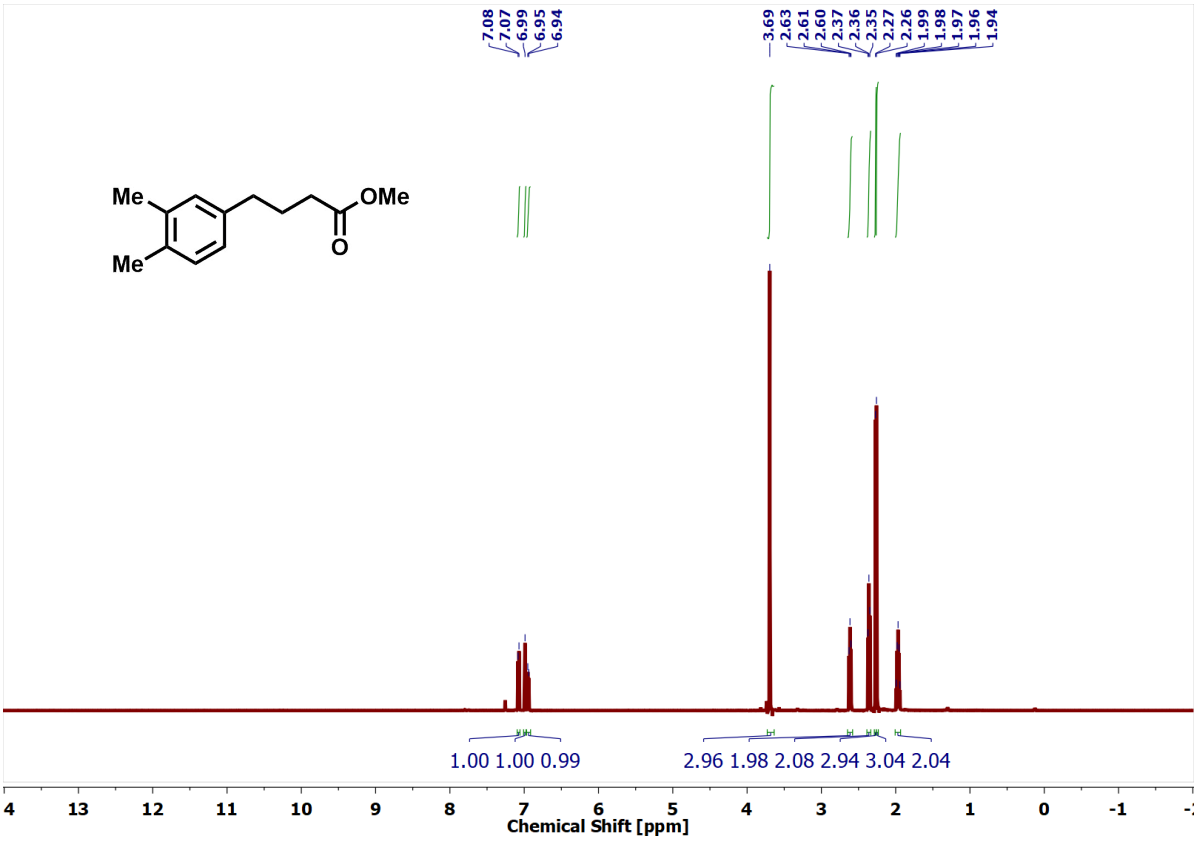

141.29
136.30
130.46
129.18
126.23
126.18
70.96
44.23
34.07
29.49
25.56
19.50
Chemical Shift [ppm]

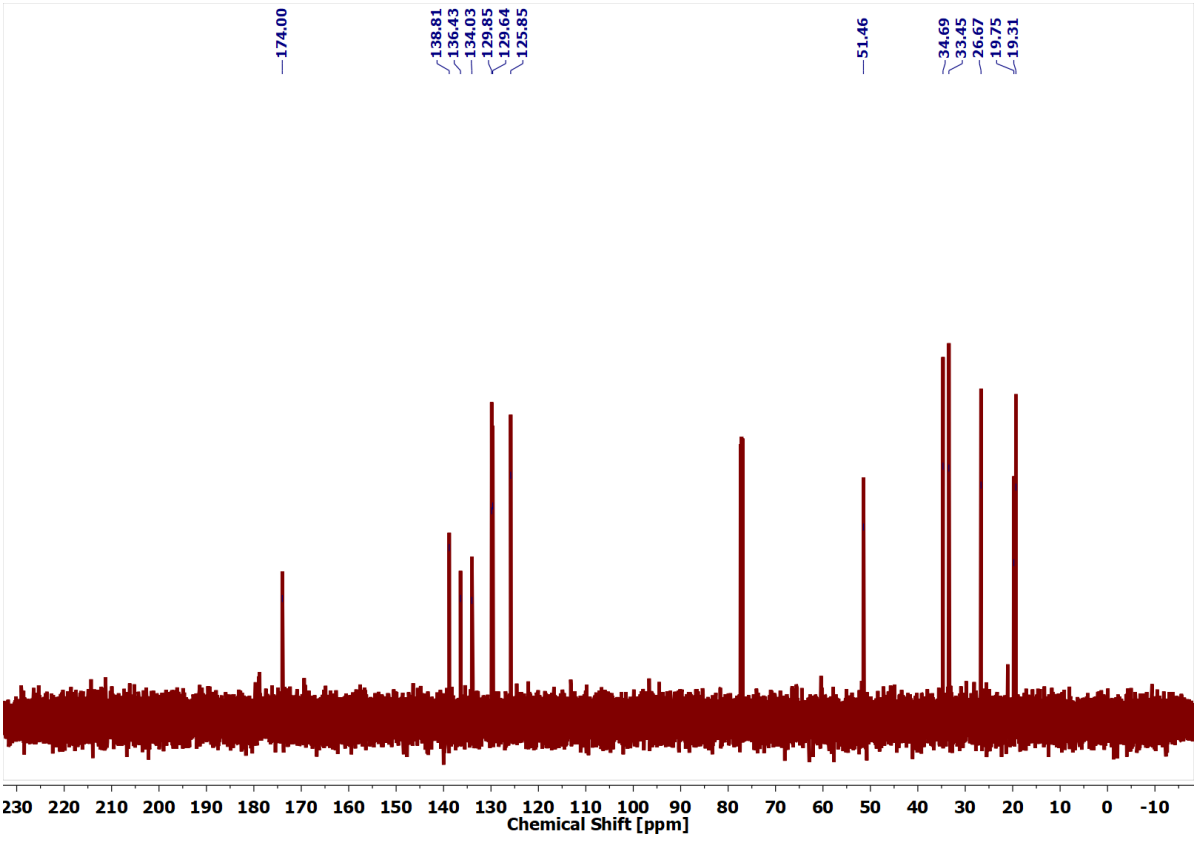

7.03
7.02
6.98
6.95
6.94
4.14
4.13
4.12
4.11
2.62
2.61
2.60
2.36
2.35
2.34
2.29
1.89
1.88
1.87
1.86
1.84
1.28
1.27
1.25
OEt
O
Me
Me
0.97 0.95 0.97
2.00
2.08 2.01 6.01 2.07 3.07
Chemical Shift [ppm]

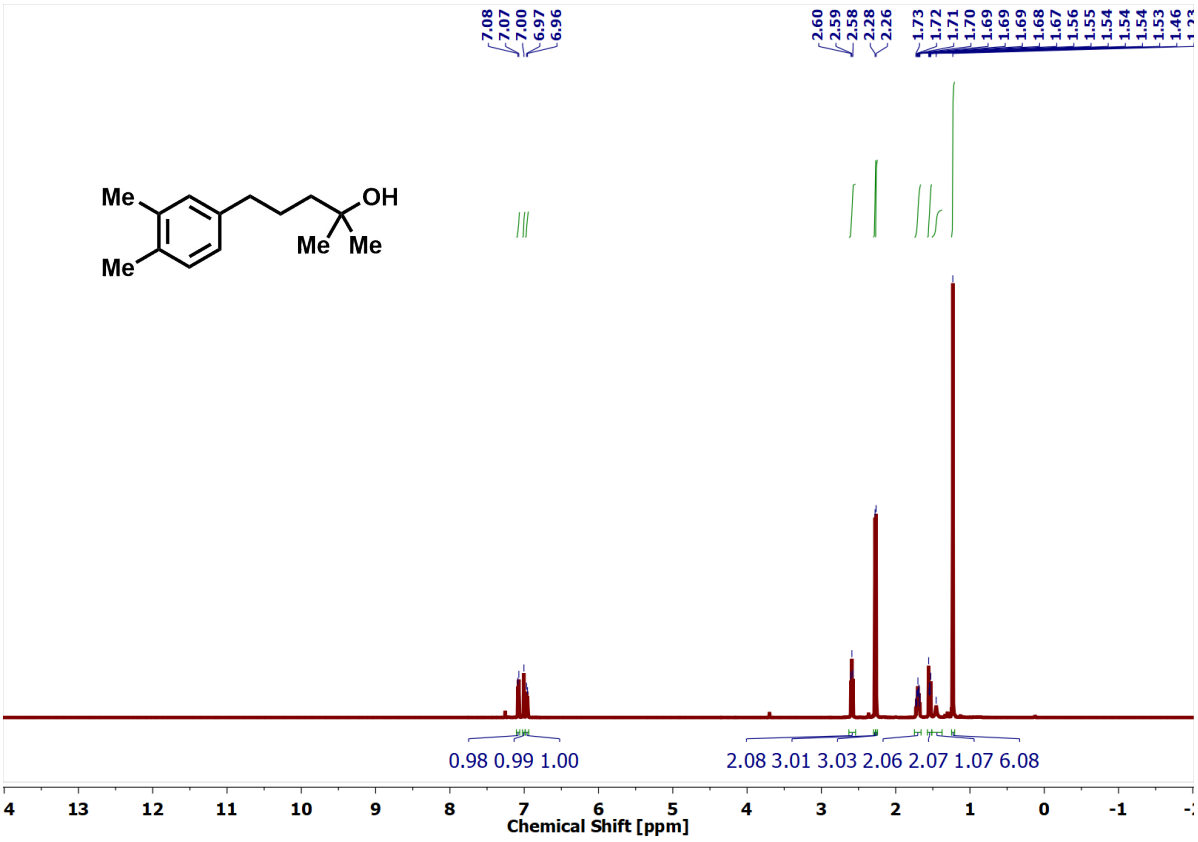

173.64
137.17
136.16
135.84
131.30
129.24
126.86
60.54
34.29
32.50
26.02
21.01
19.30
14.49
Chemical Shift [ppm]

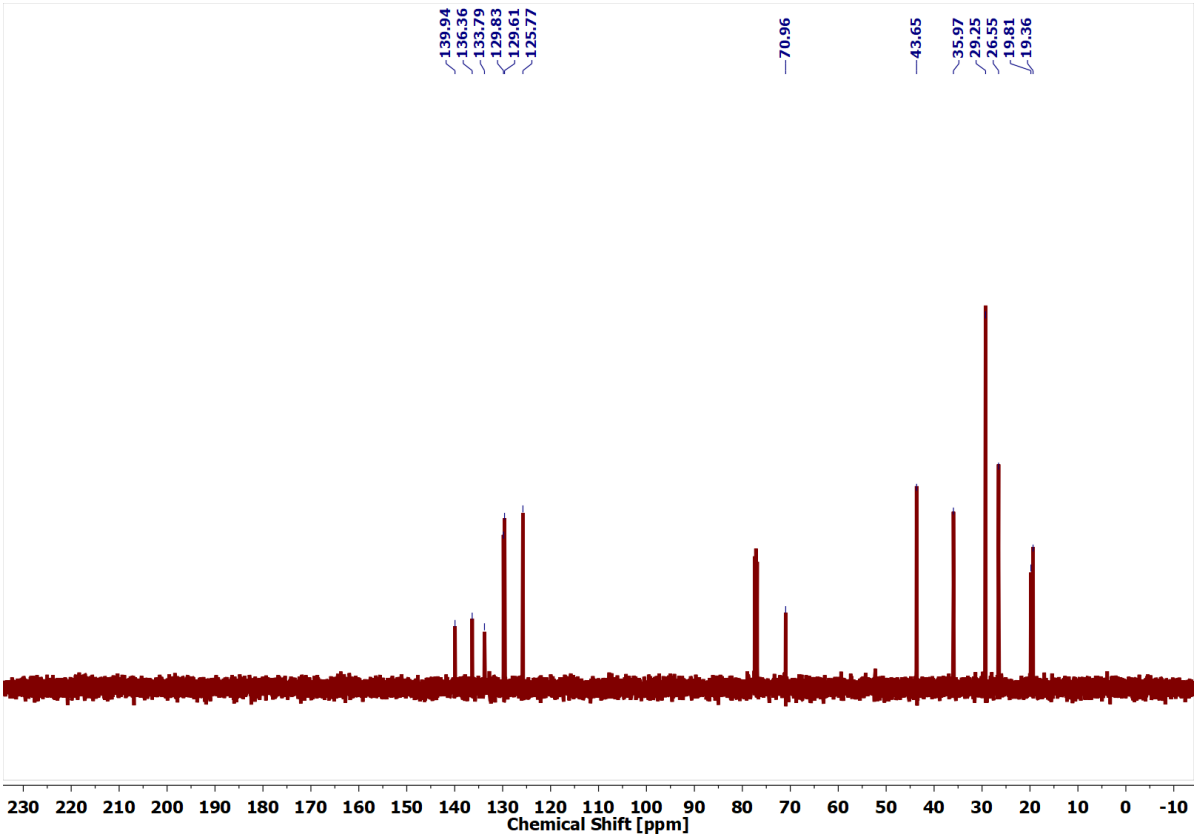

7.07
7.05
7.00
6.97
6.96
2.61
2.60
2.59
2.31
1.67
1.66
1.66
1.66
1.65
1.64
1.64
1.63
1.62
1.62
1.57
1.56
1.56
1.55
1.54
1.44
1.22
OH
Me
Me
Me
Me
0.97 1.00 0.96
2.11 6.22 2.14 2.05 1.07 6.05
Chemical Shift [ppm]

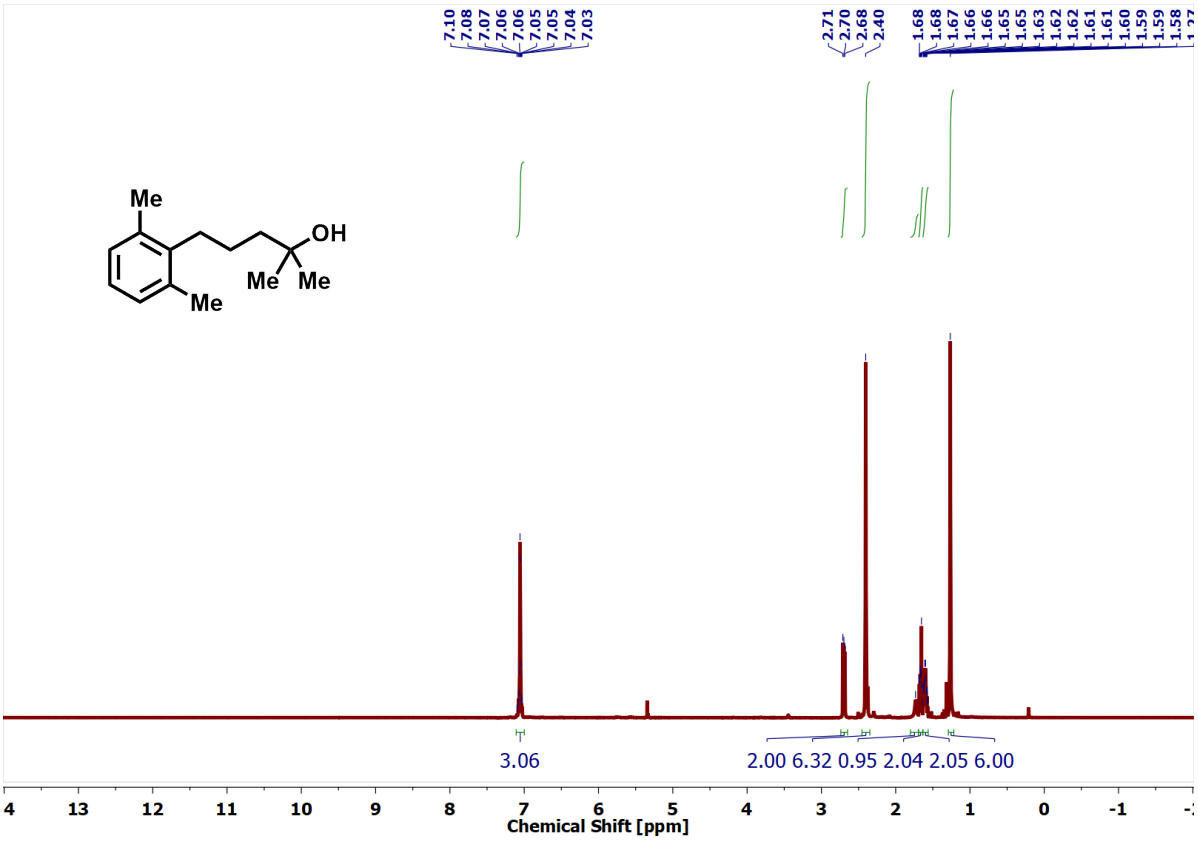

138.13
136.04
135.55
131.23
129.10
126.83
70.97
44.23
33.65
29.48
25.69
21.04
19.43
Chemical Shift [ppm]

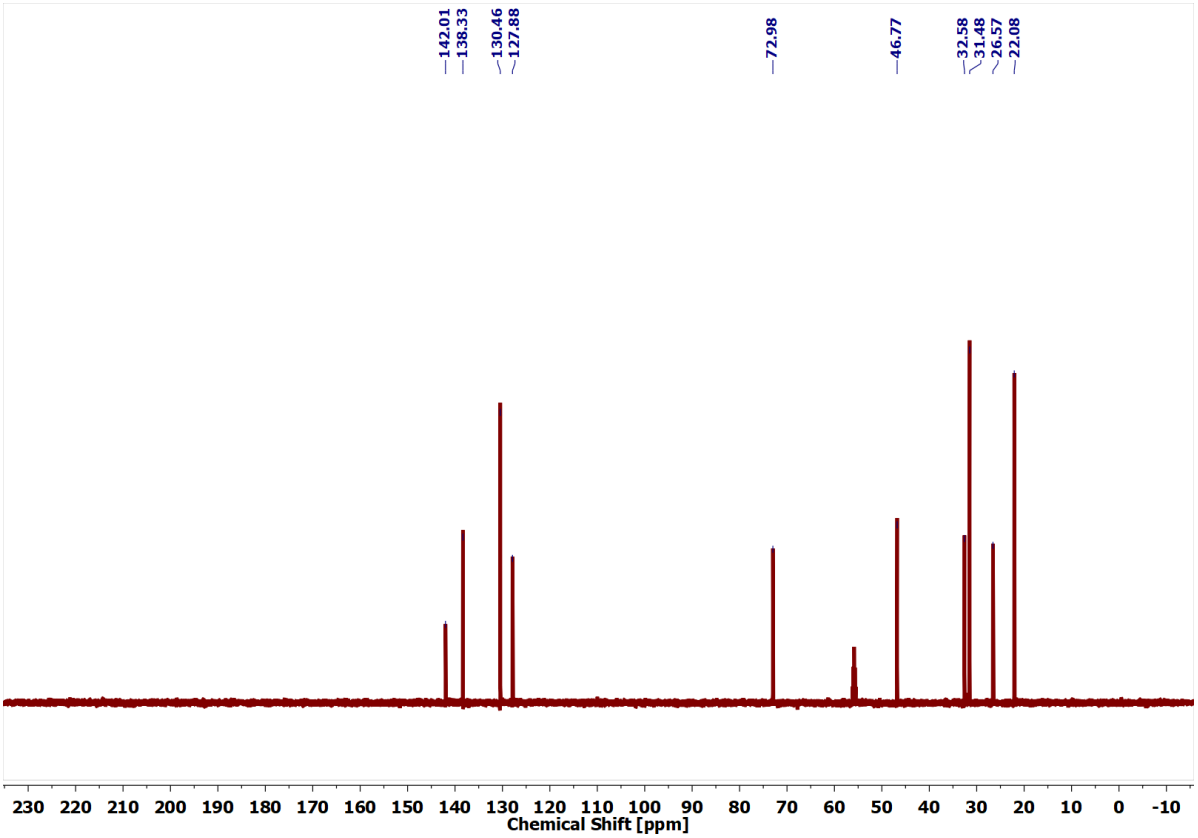

7.08
7.07
6.99
6.95
6.94
3.69
2.63
2.61
2.60
2.37
2.36
2.35
2.27
2.26
1.99
1.98
1.97
1.96
1.94
Me
Me
OMe
O
1.00 1.00 0.99
2.96 1.98 2.08 2.94 3.04 2.04
Chemical Shift [ppm]

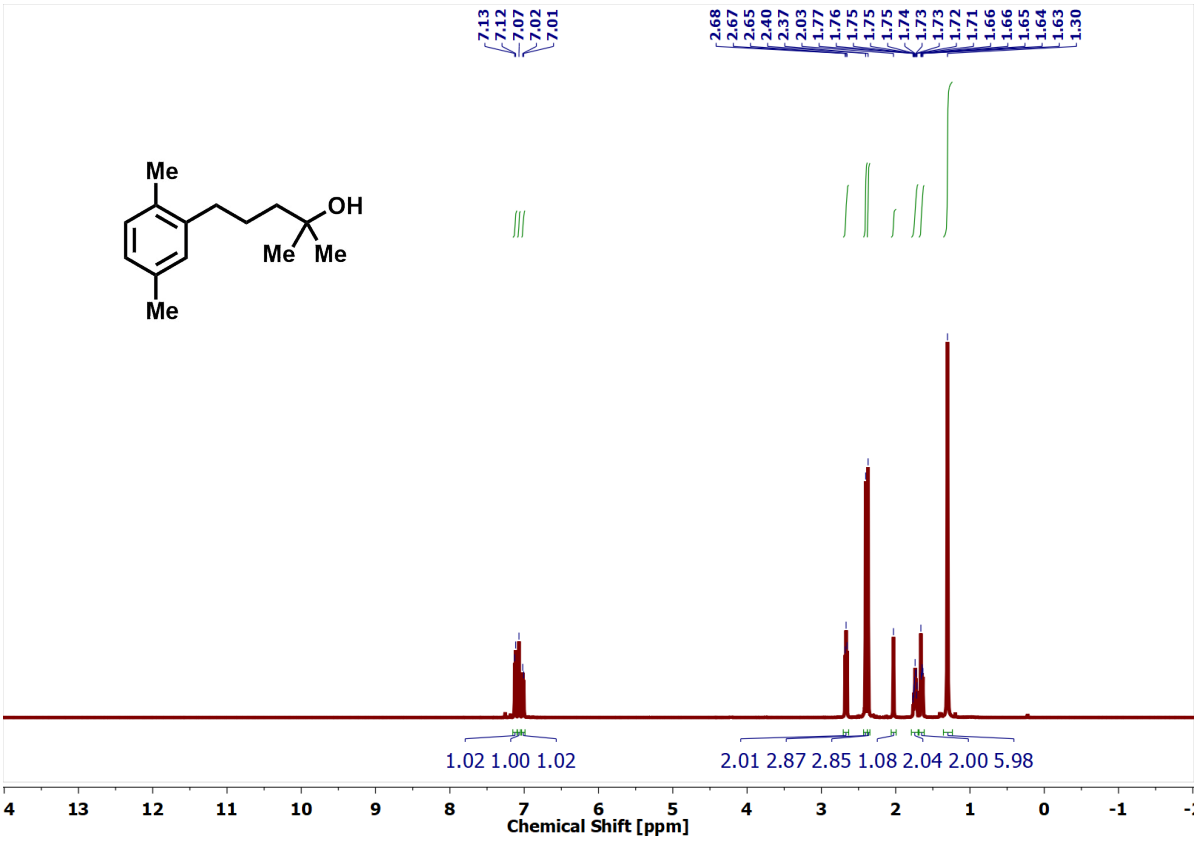

174.00
138.81
136.43
134.03
129.85
129.64
125.85
51.46
34.69
33.45
26.67
19.75
19.31
Chemical Shift [ppm]

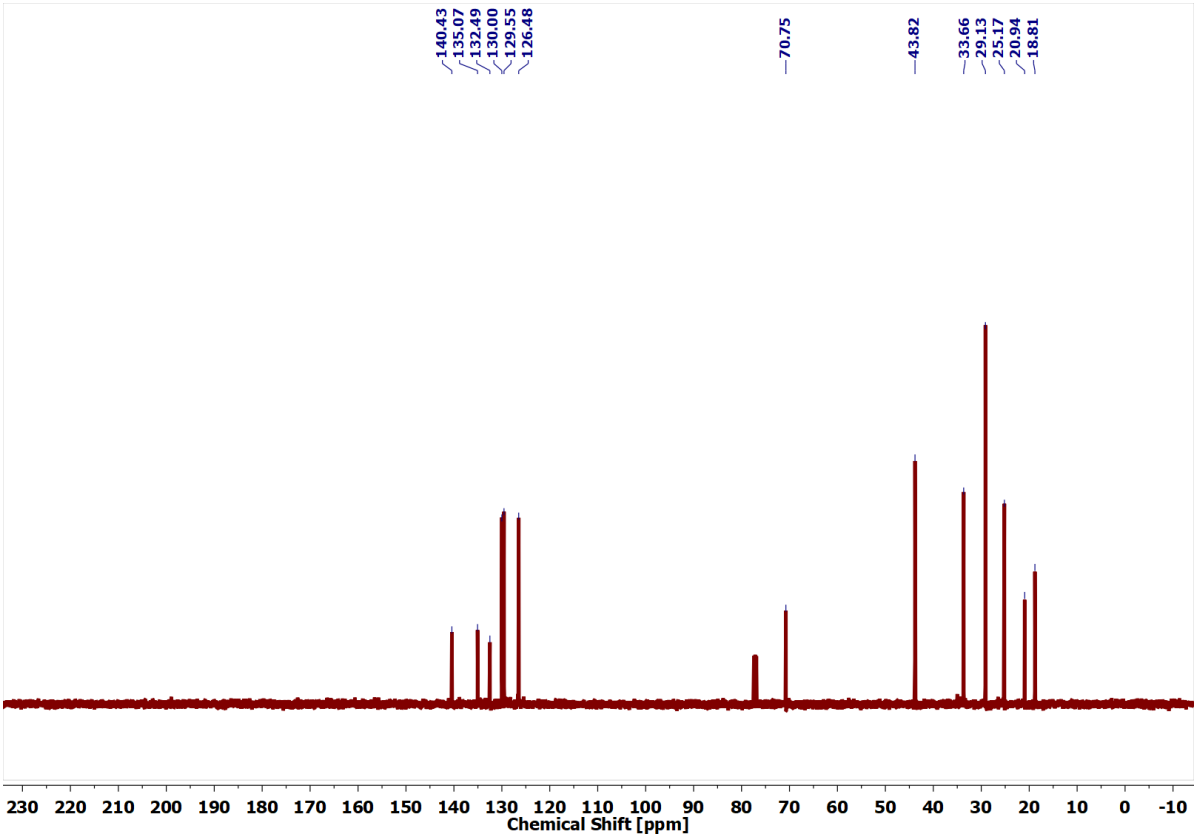

7.08
7.07
7.00
6.97
6.96
2.60
2.59
2.58
2.28
2.26
1.73
1.72
1.71
1.70
1.69
1.69
1.69
1.68
1.67
1.56
1.55
1.54
1.54
1.54
1.53
1.46
Me
Me
OH
Me
Me
0.98 0.99 1.00
2.08 3.01 3.03 2.06 2.07 1.07 6.08
Chemical Shift [ppm]

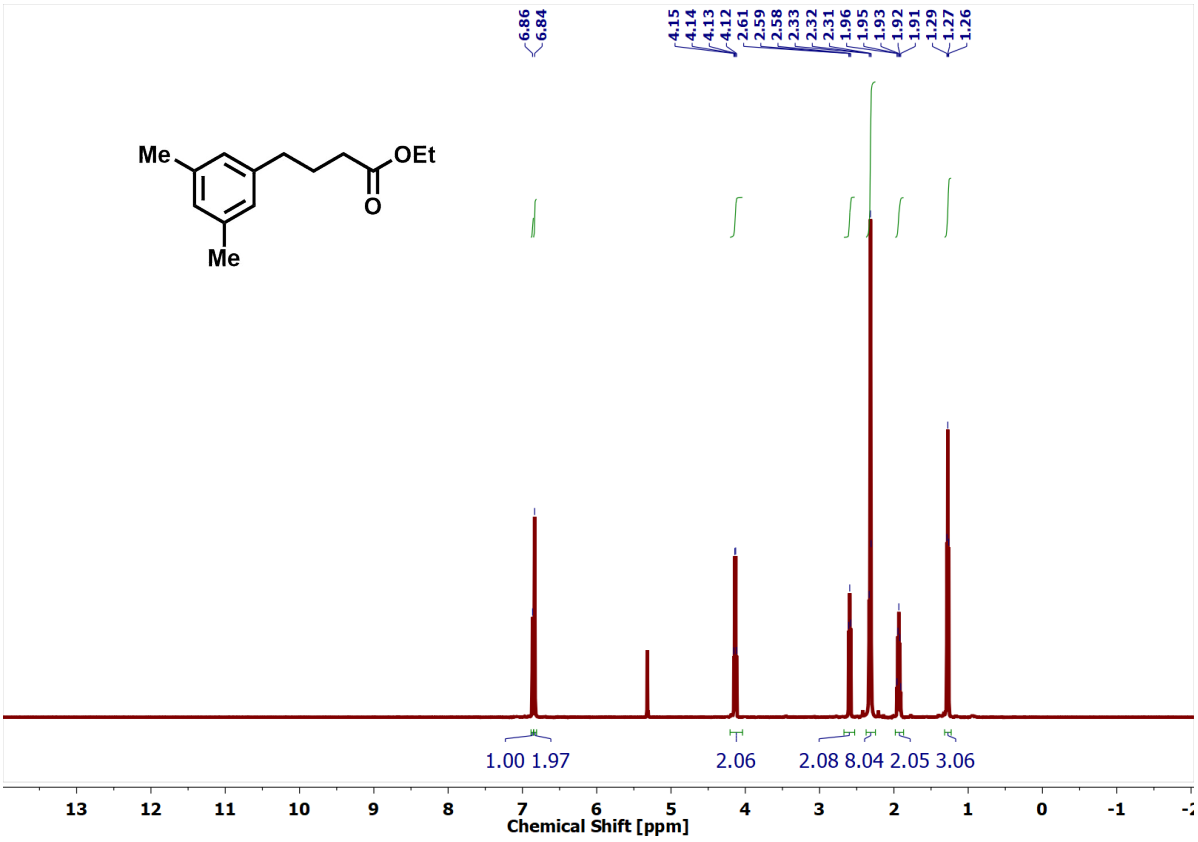

139.94
136.36
133.79
129.83
129.61
125.77
70.96
43.65
35.97
29.25
26.55
19.81
19.36
Chemical Shift [ppm]

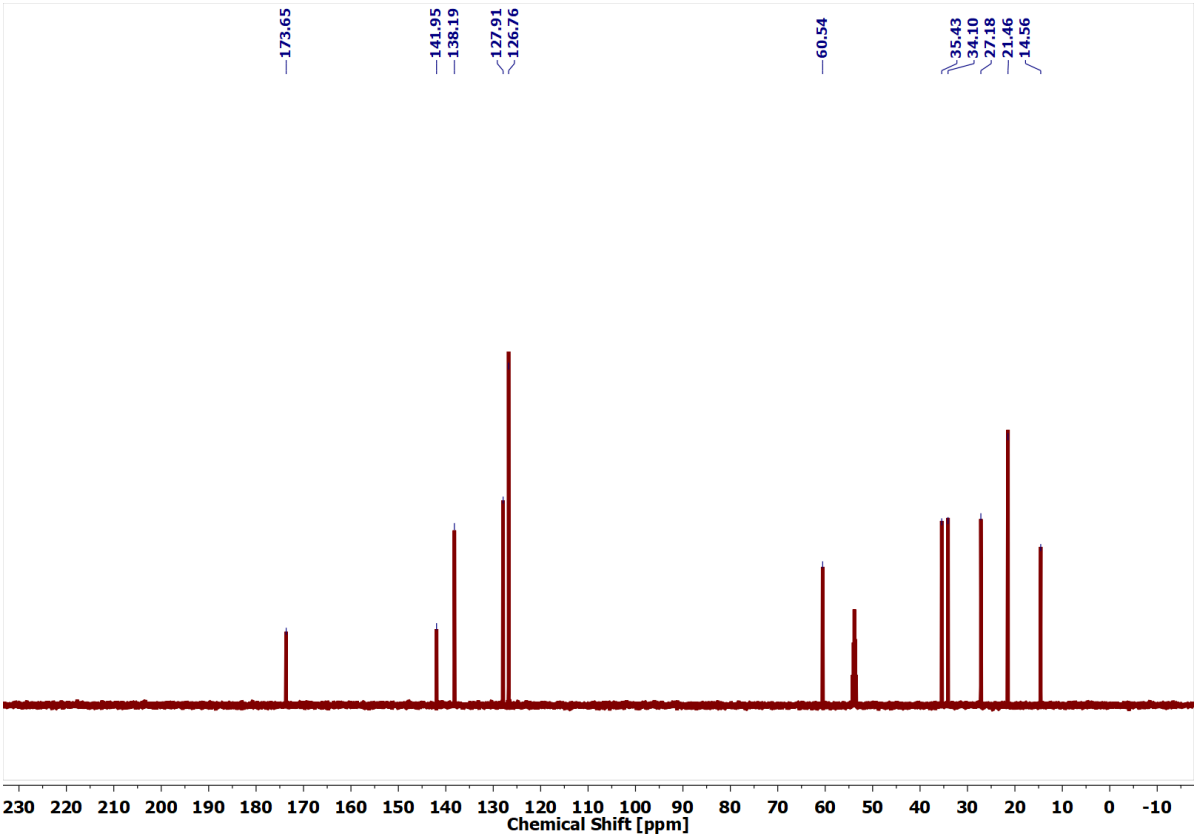

Me
OH
Me
Me
Me
7.10
7.08
7.07
7.06
7.06
7.05
7.05
7.04
7.03
2.71
2.70
2.68
2.40
1.68
1.68
1.67
1.66
1.66
1.65
1.65
1.63
1.62
1.62
1.61
1.61
1.60
1.59
1.59
1.58
3.06
2.00 6.32 0.95 2.04 2.05 6.00
Chemical Shift [ppm]

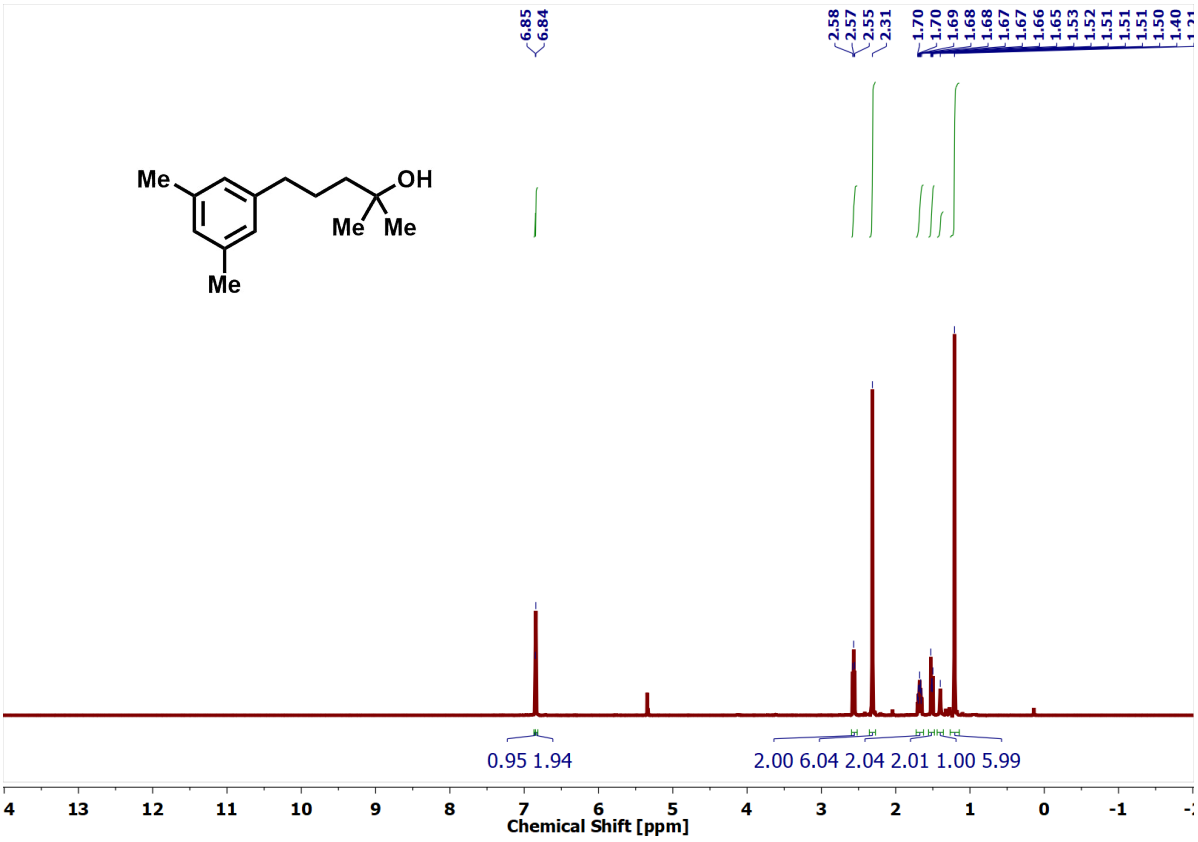

142.01
138.33
130.46
127.88
72.98
46.77
32.58
31.48
26.57
22.08
Chemical Shift [ppm]

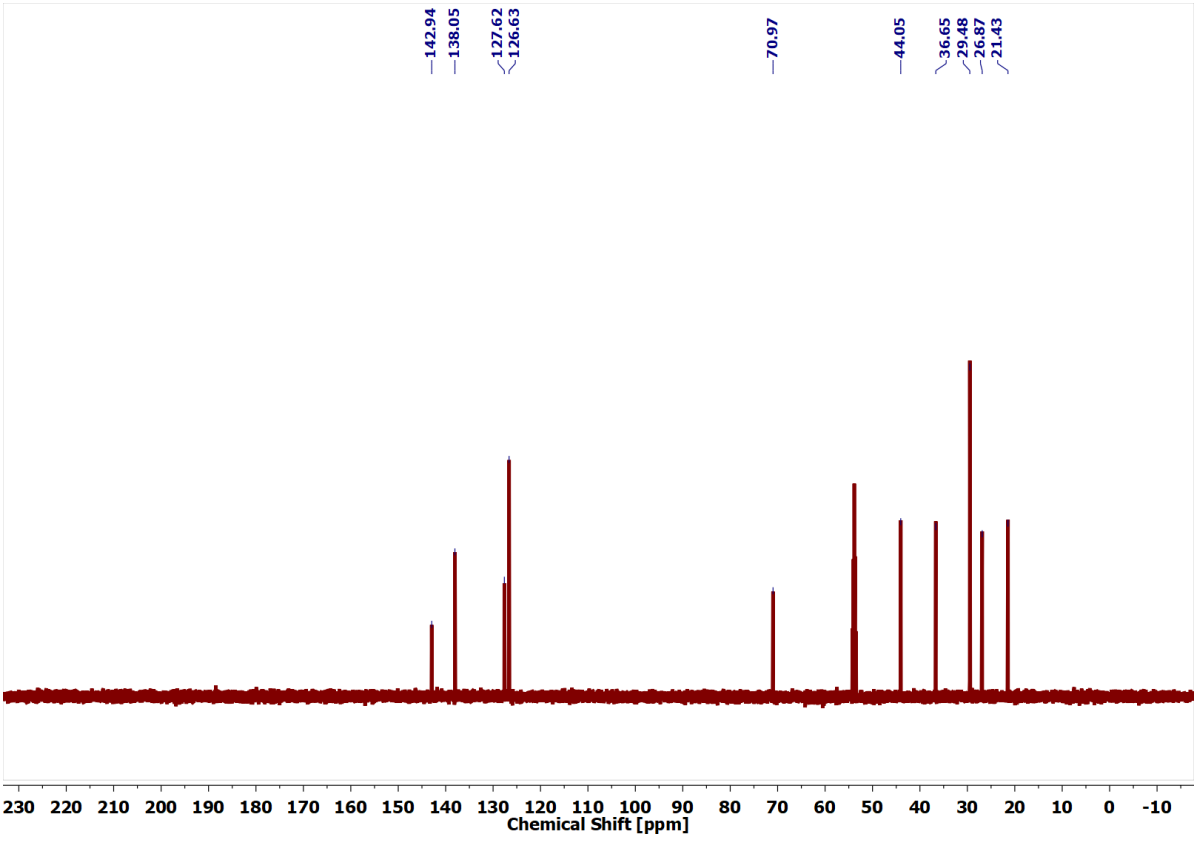

7.13
7.12
7.07
7.02
7.01
2.68
2.67
2.65
2.40
2.37
2.03
1.77
1.76
1.75
1.75
1.75
1.74
1.73
1.73
1.72
1.71
1.66
1.66
1.65
1.64
1.63
1.30
Me
OH
Me
Me
Me
1.02 1.00 1.02
2.01 2.87 2.85 1.08 2.04 2.00 5.98
Chemical Shift [ppm]

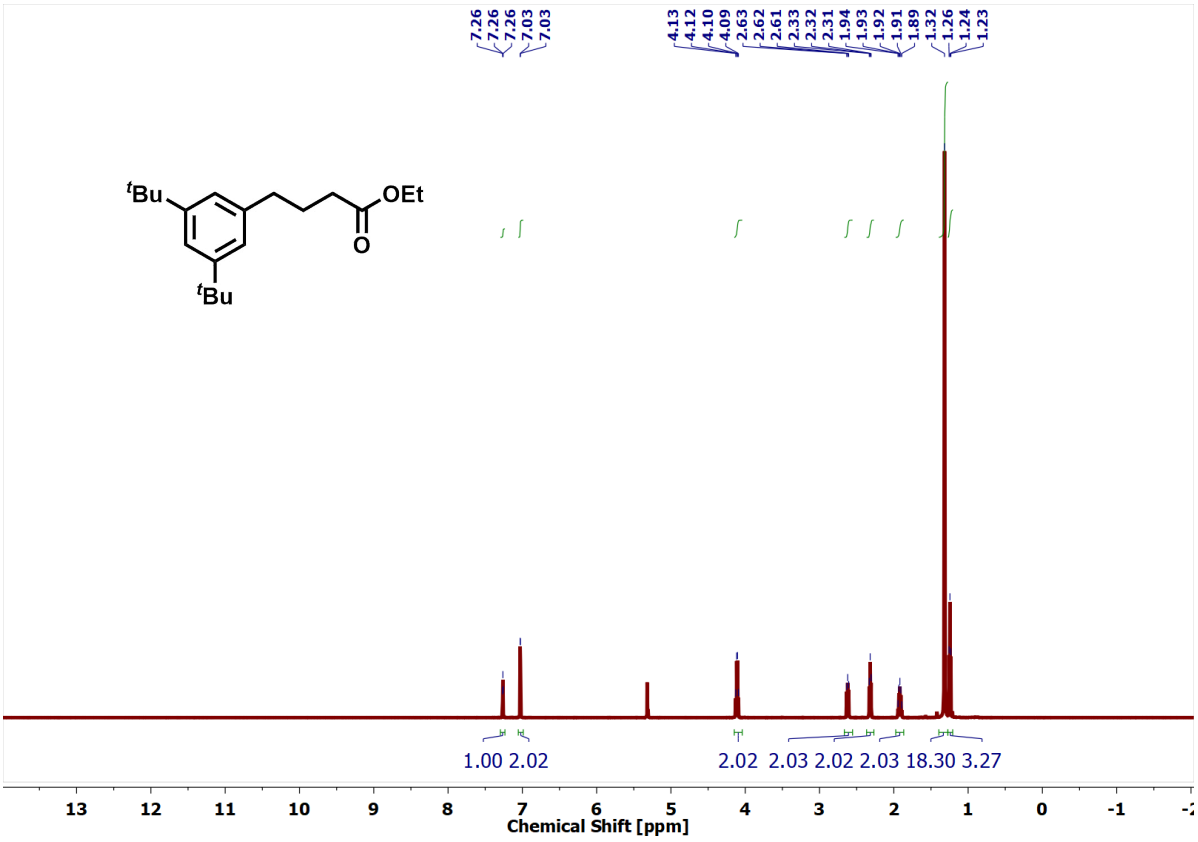

140.43
135.07
132.49
130.00
129.55
126.48
70.75
43.82
33.66
29.13
25.17
20.94
18.81
Chemical Shift [ppm]

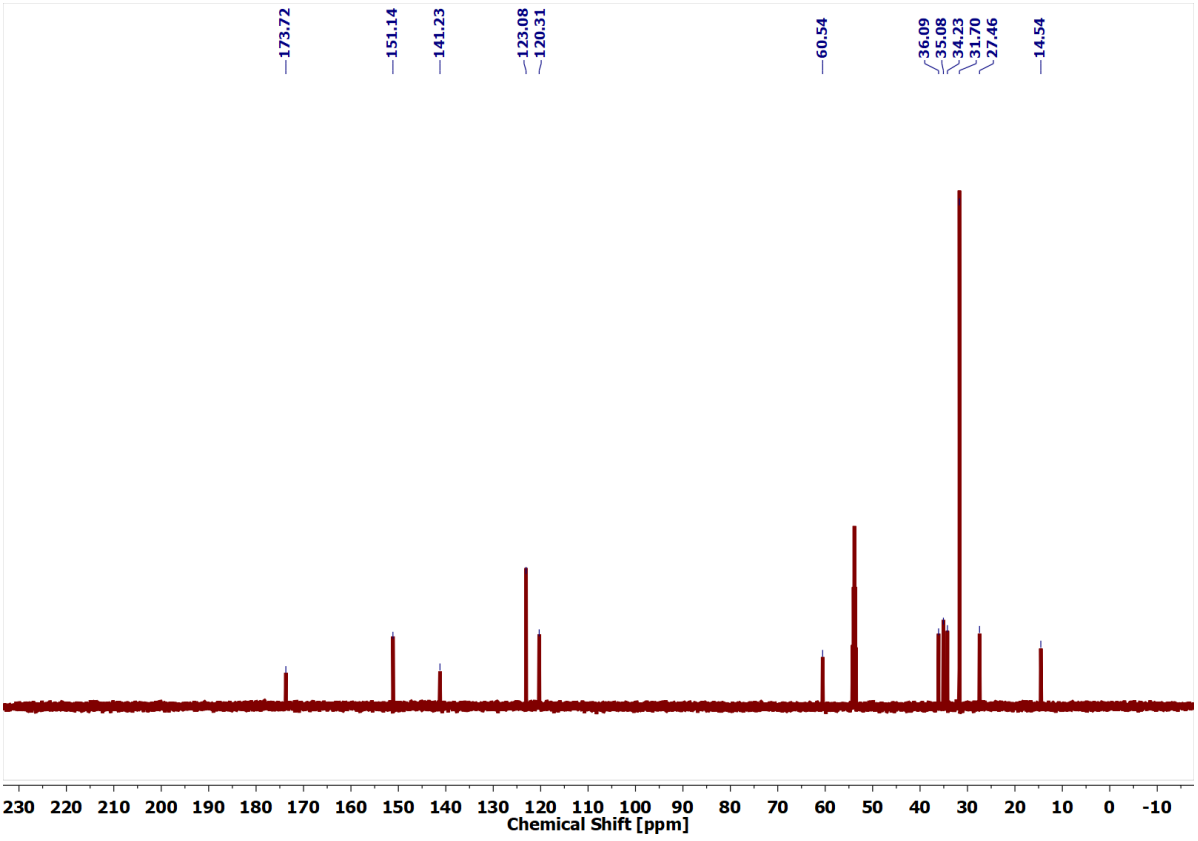

6.86
6.84
4.15
4.14
4.13
4.12
2.61
2.59
2.58
2.33
2.32
2.31
1.96
1.95
1.93
1.92
1.91
1.29
1.27
1.26
Me
OEt
O
Me
1.00 1.97
2.06
2.08 8.04 2.05 3.06
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

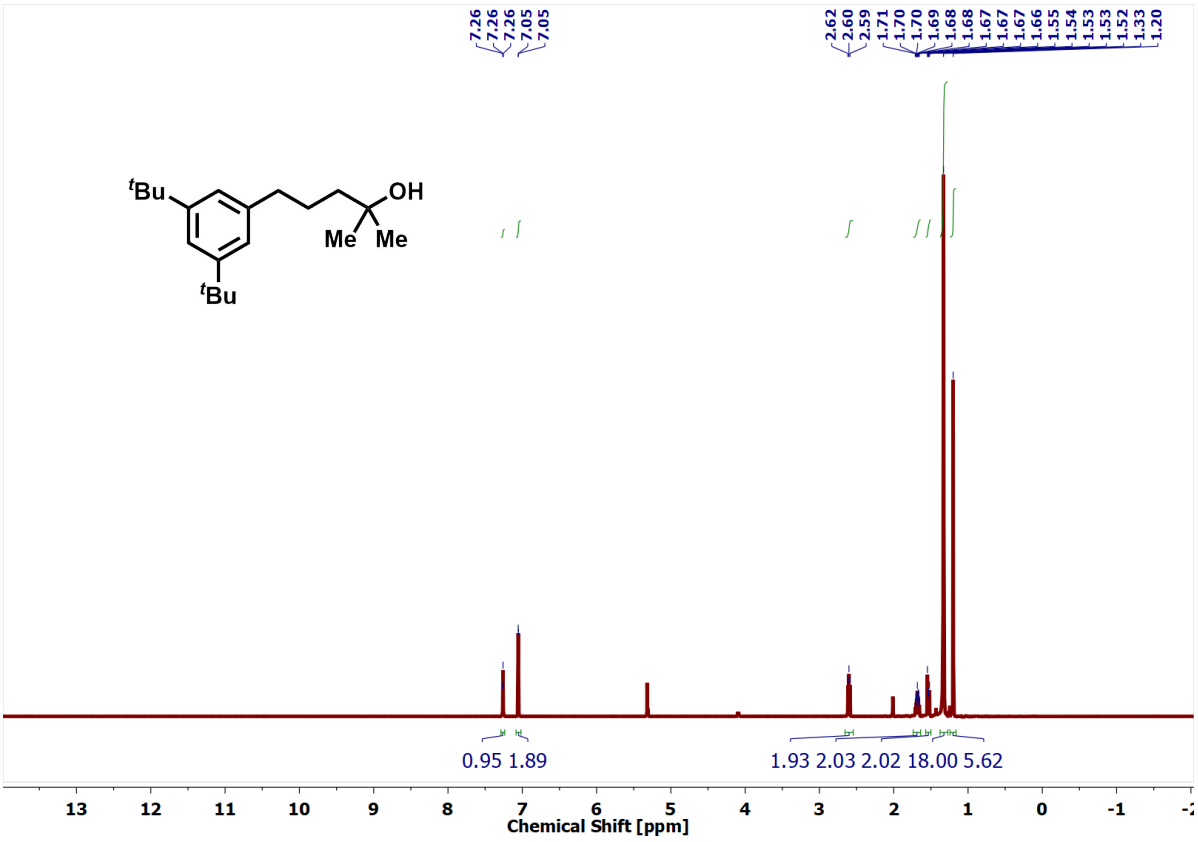

173.65
141.95
138.19
127.91
126.76
60.54
35.43
34.10
27.18
21.46
14.56
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

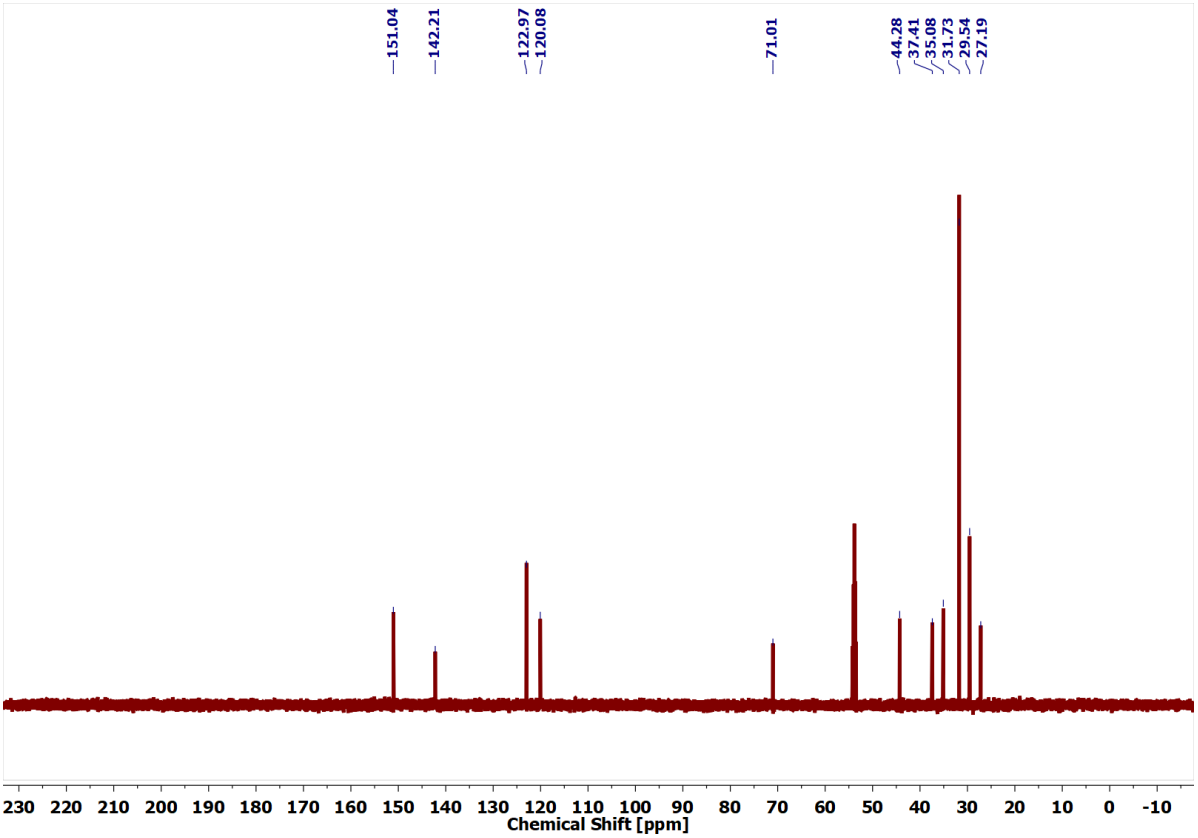

Me
OH
Me
Me
Me
6.85
6.84
2.58
2.57
2.55
2.31
1.70
1.69
1.68
1.67
1.66
1.65
1.53
1.52
1.51
1.50
0.95 1.94
2.00 6.04 2.04 2.01 1.00 5.99
Chemical Shift [ppm]

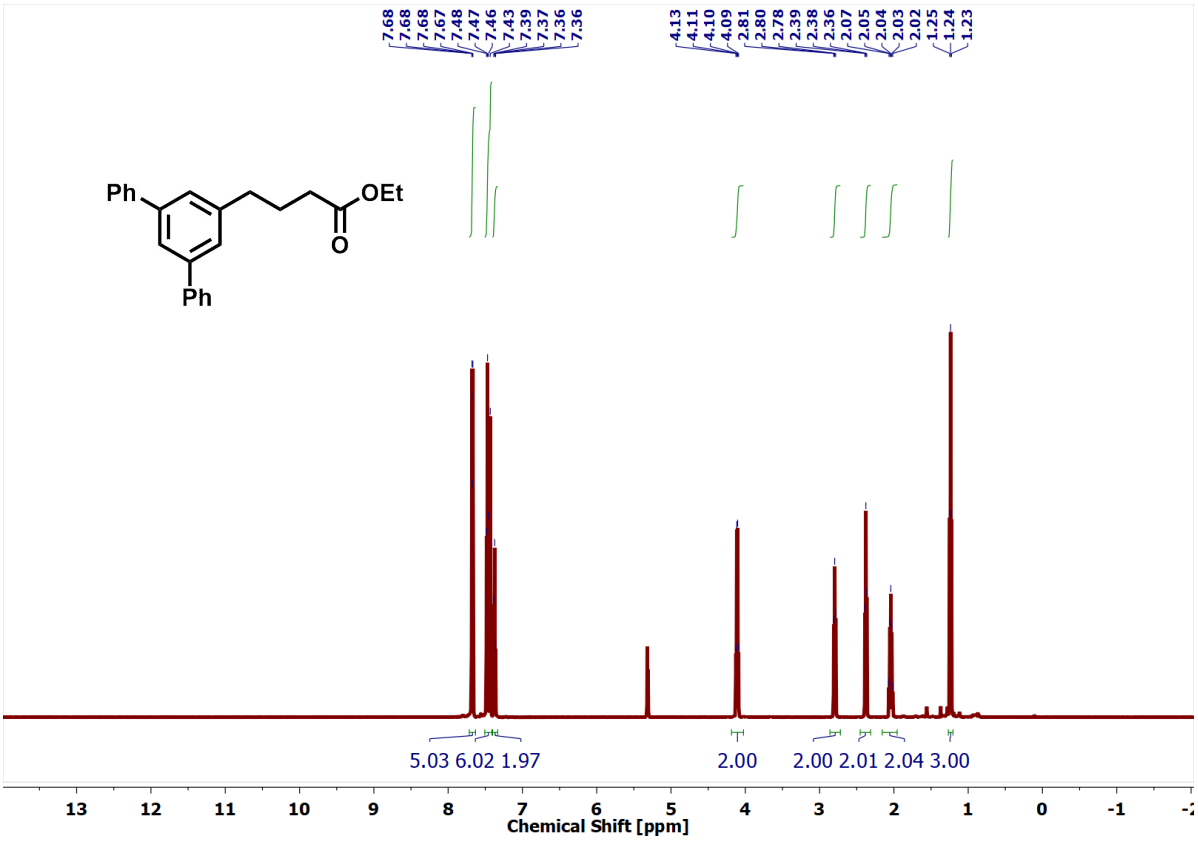

142.94
138.05
127.62
126.63
70.97
44.05
36.65
29.48
26.87
21.43
Chemical Shift [ppm]


7.26
7.26
7.26
7.03
7.03
4.13
4.12
4.10
4.09
2.63
2.62
2.61
2.33
2.32
2.31
1.94
1.93
1.92
1.91
1.89
1.32
1.26
1.24
1.23
tBu
OEt
O
tBu
1.00 2.02
2.02 2.03 2.02 2.03 18.30 3.27
Chemical Shift [ppm]


173.72
151.14
141.23
123.08
120.31
60.54
36.09
35.08
34.23
31.70
27.46
14.54
Chemical Shift [ppm]


7.26
7.26
7.26
7.05
7.05
2.62
2.60
2.59
1.71
1.70
1.70
1.69
1.68
1.68
1.67
1.67
1.67
1.66
1.55
1.54
1.53
1.53
1.52
1.33
1.20
tBu
OH
Me
Me
tBu
0.95 1.89
1.93 2.03 2.02 18.00 5.62
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]


151.04
142.21
122.97
120.08
71.01
44.28
37.41
35.08
31.73
29.54
27.19
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]


7.68
7.68
7.68
7.67
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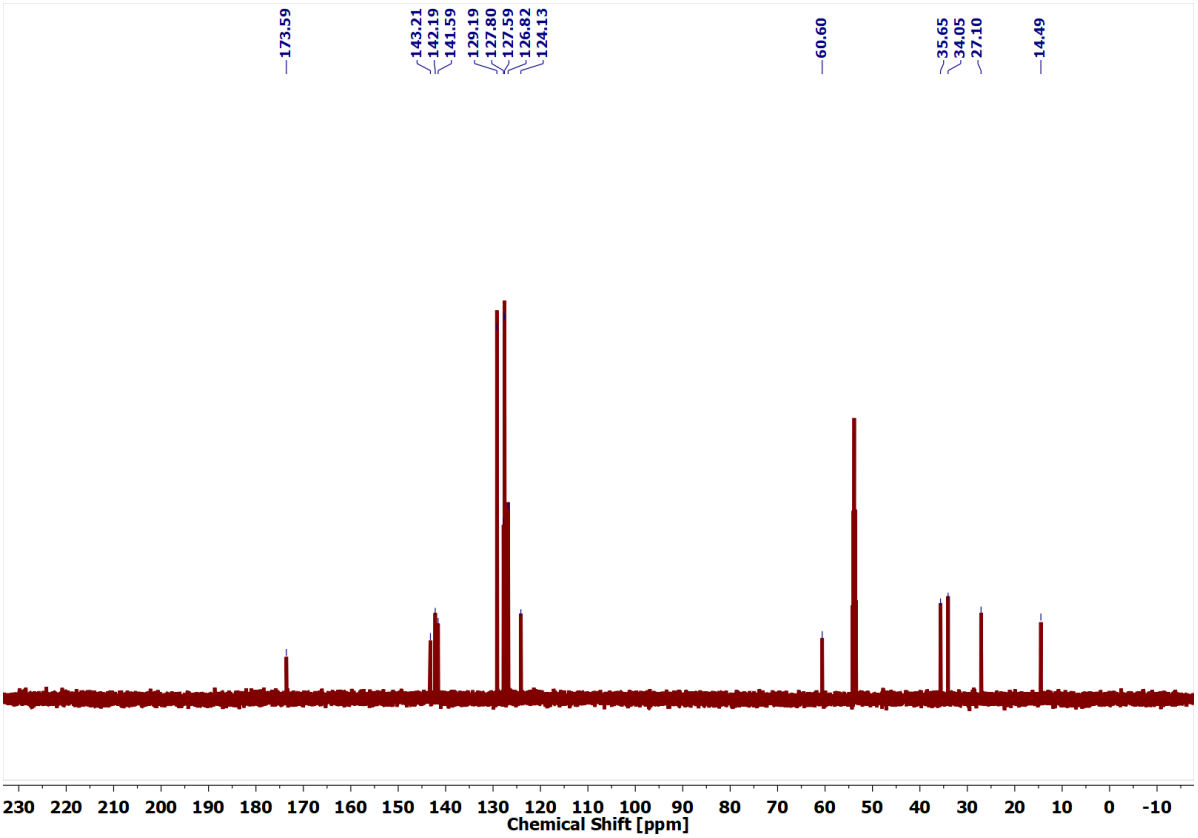
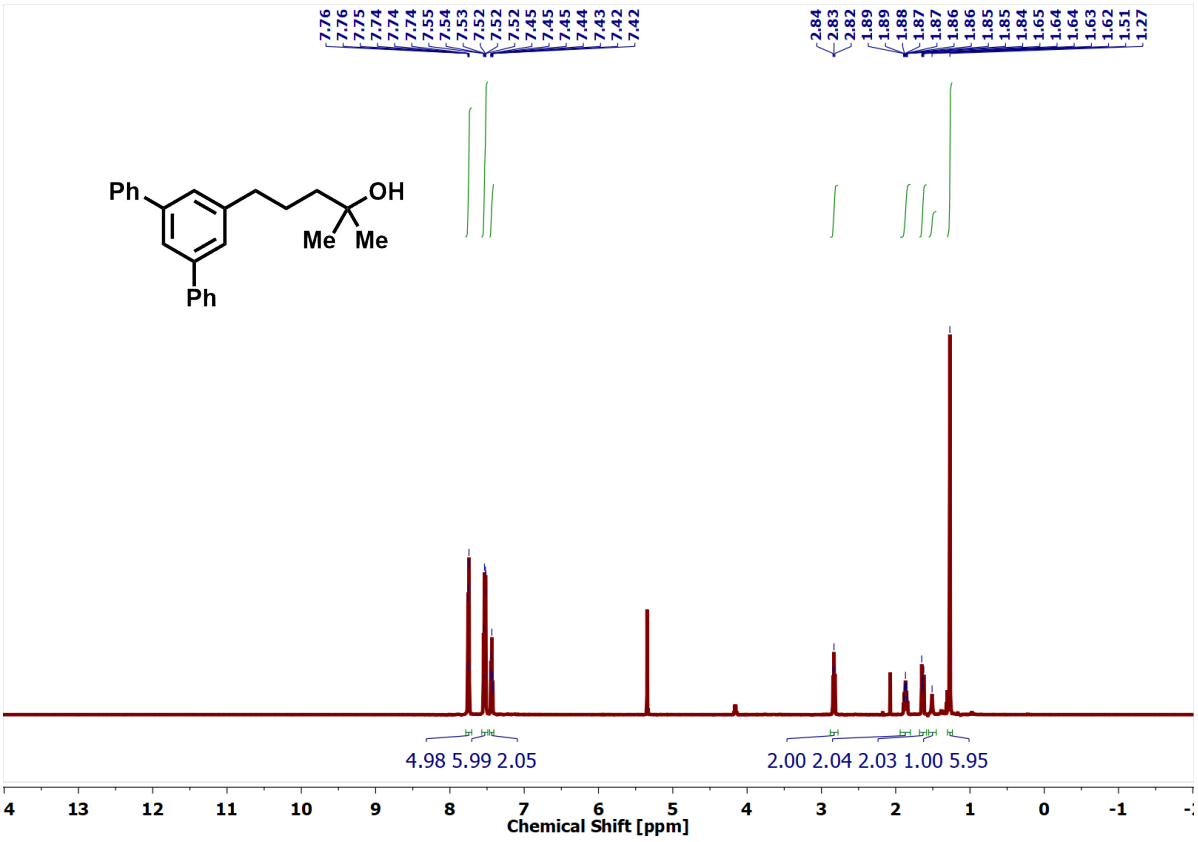
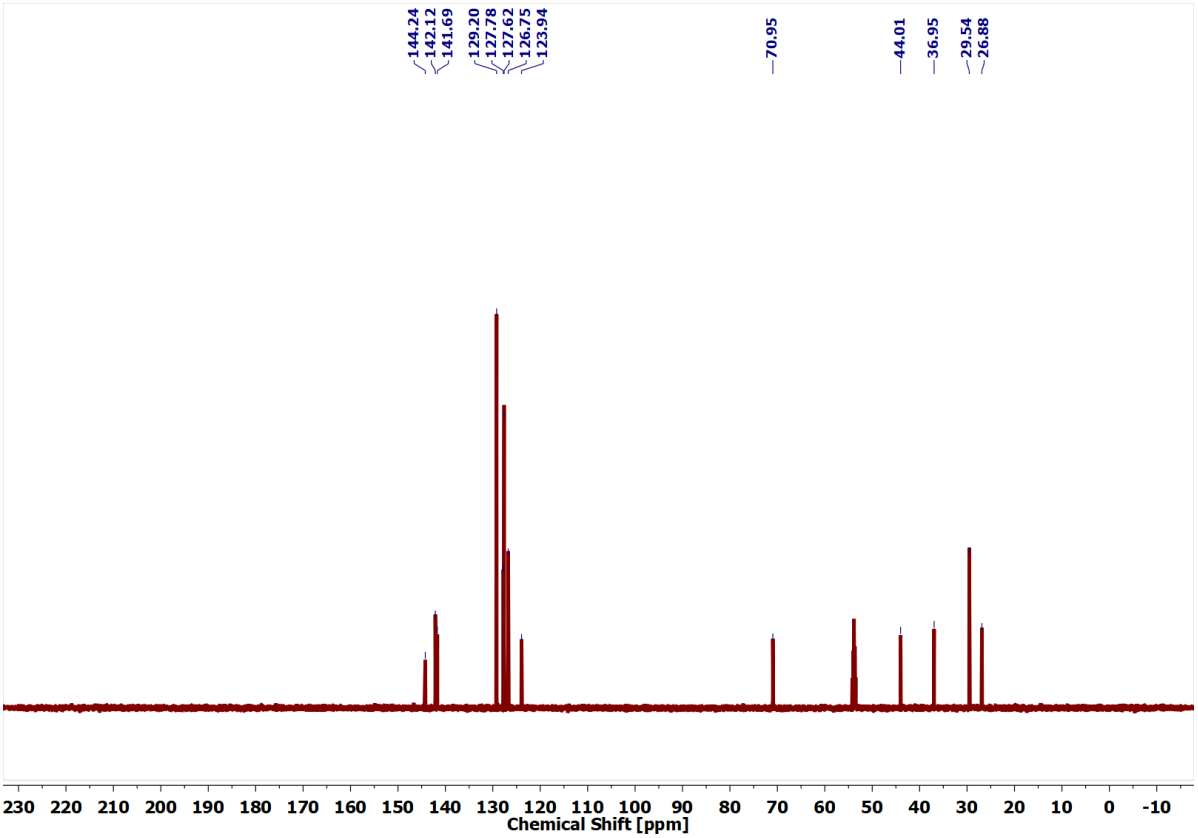
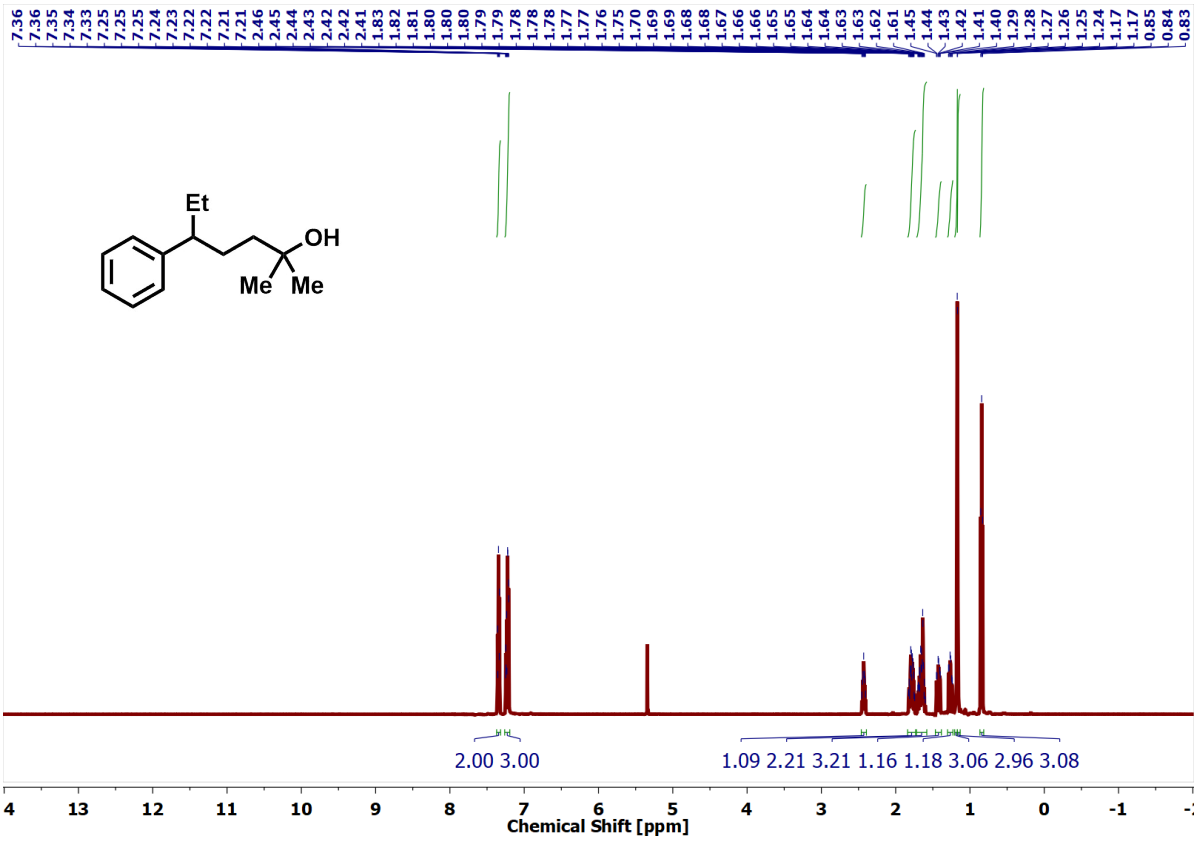
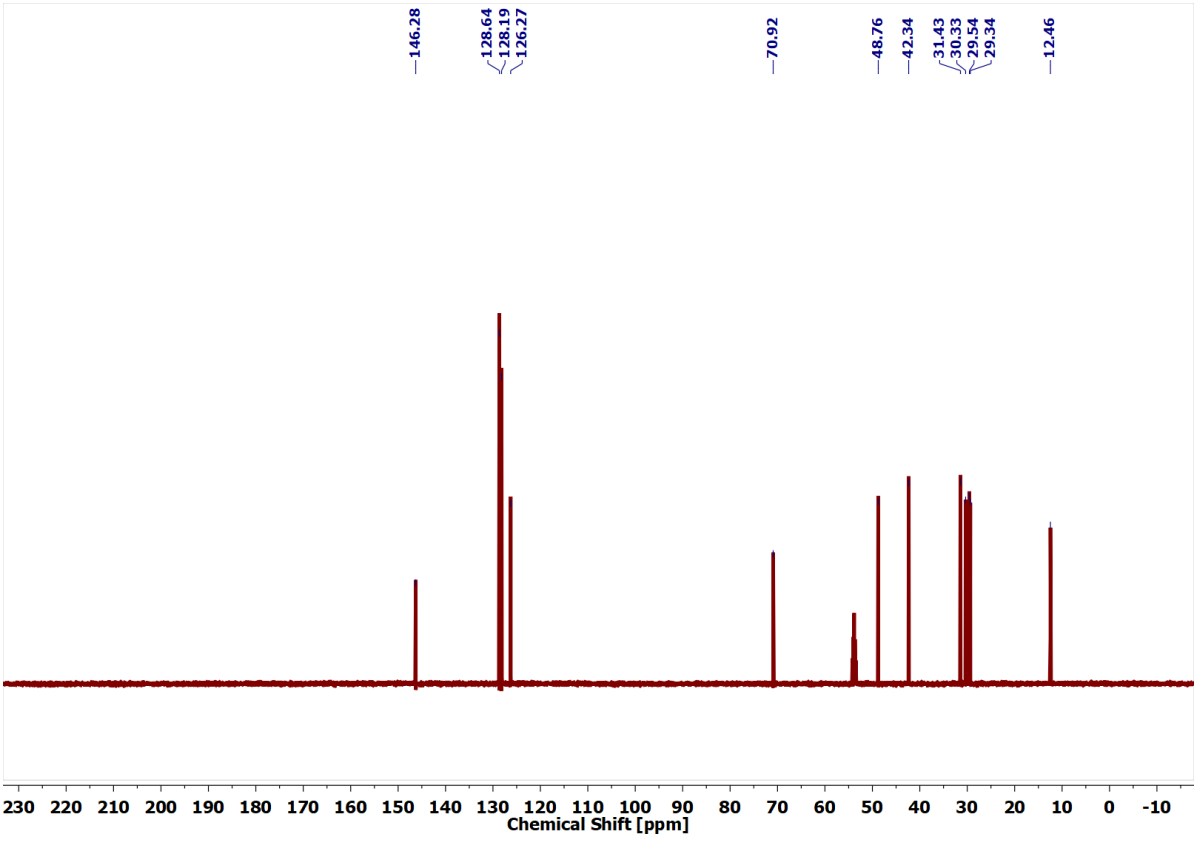
7.47
7.46
7.43
7.39
7.37
7.36
7.36
4.13
4.11
4.10
4.09
2.81
2.80
2.78
2.39
2.38
2.36
2.07
2.05
2.04
2.03
2.02
1.25
1.24
1.23
Ph
OEt
O
Ph
5.03 6.02 1.97
2.00
2.00 2.01 2.04 3.00
Chemical Shift [ppm]

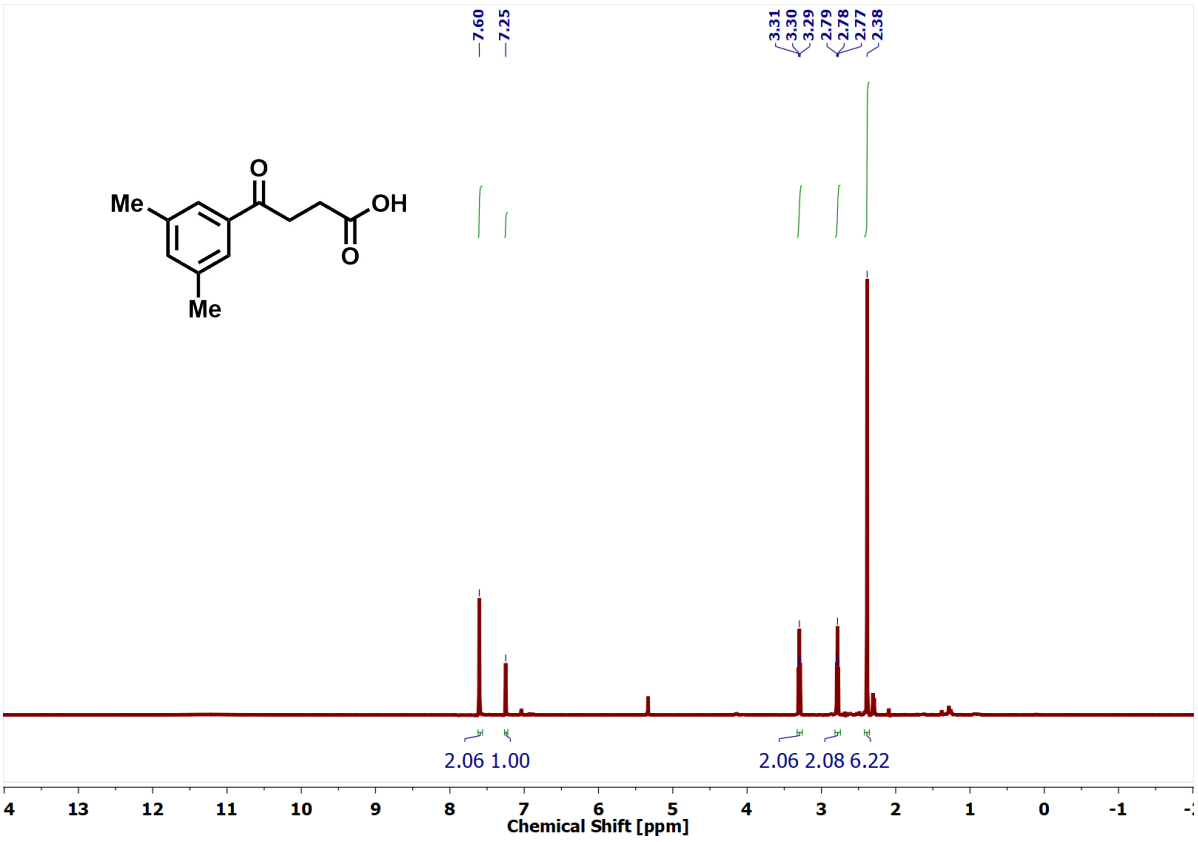

173.59
143.21
142.19
141.59
129.19
127.80
127.59
126.82
124.13
60.60
35.65
34.05
27.10
14.49
Chemical Shift [ppm]

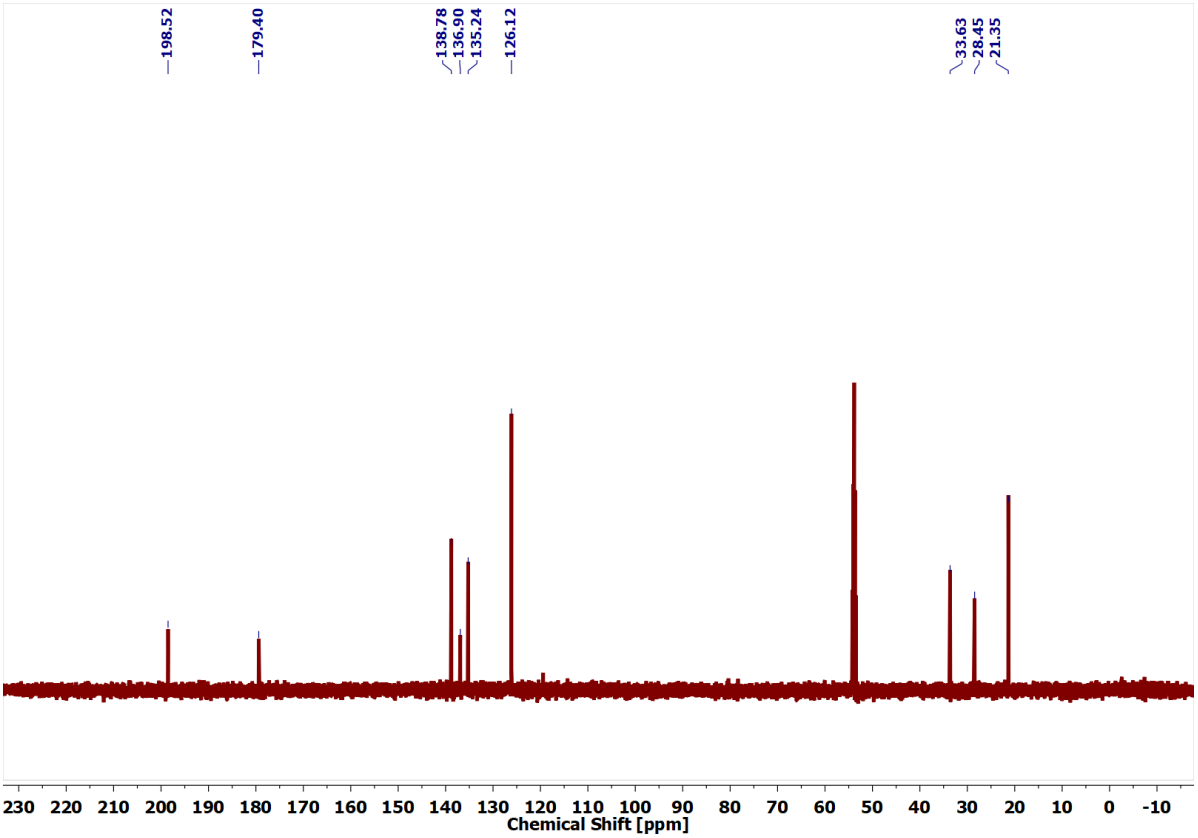

7.76
7.76
7.75
7.74
7.74
7.74
7.55
7.54
7.53
7.52
7.52
7.52
7.45
7.45
7.45
7.44
7.43
7.42
7.42
2.84
2.83
2.82
1.89
1.89
1.88
1.87
1.87
1.86
1.86
1.85
1.85
1.84
1.65
1.64
1.64
1.63
1.62
1.51
1.27
Ph
OH
Me
Me
Ph
4.98 5.99 2.05
2.00 2.04 2.03 1.00 5.95
Chemical Shift [ppm]

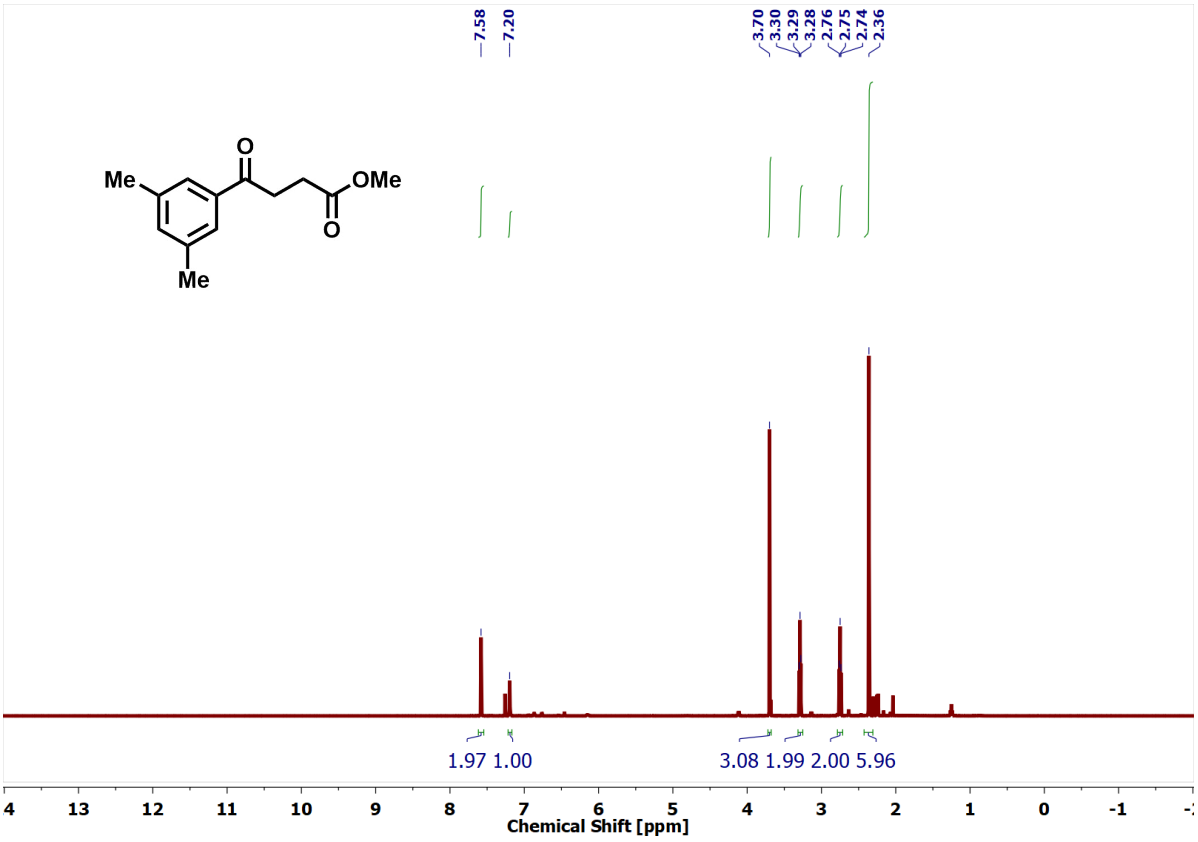

144.24
142.12
141.69
129.20
127.78
127.62
126.75
123.94
70.95
44.01
36.95
29.54
26.88
Chemical Shift [ppm]

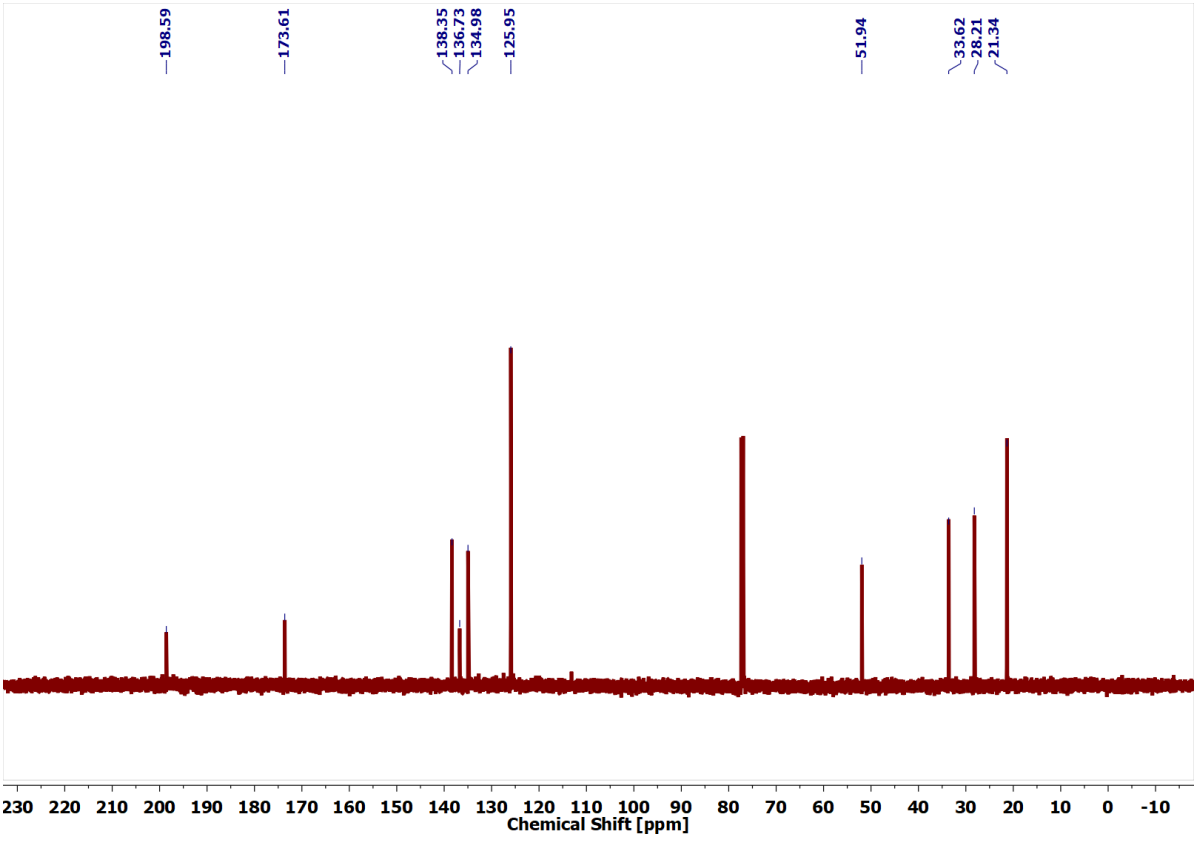

Et
OH
Me Me
2.00 3.00
1.09 2.21 3.21 1.16 1.18 3.06 2.96 3.08
Chemical Shift [ppm]

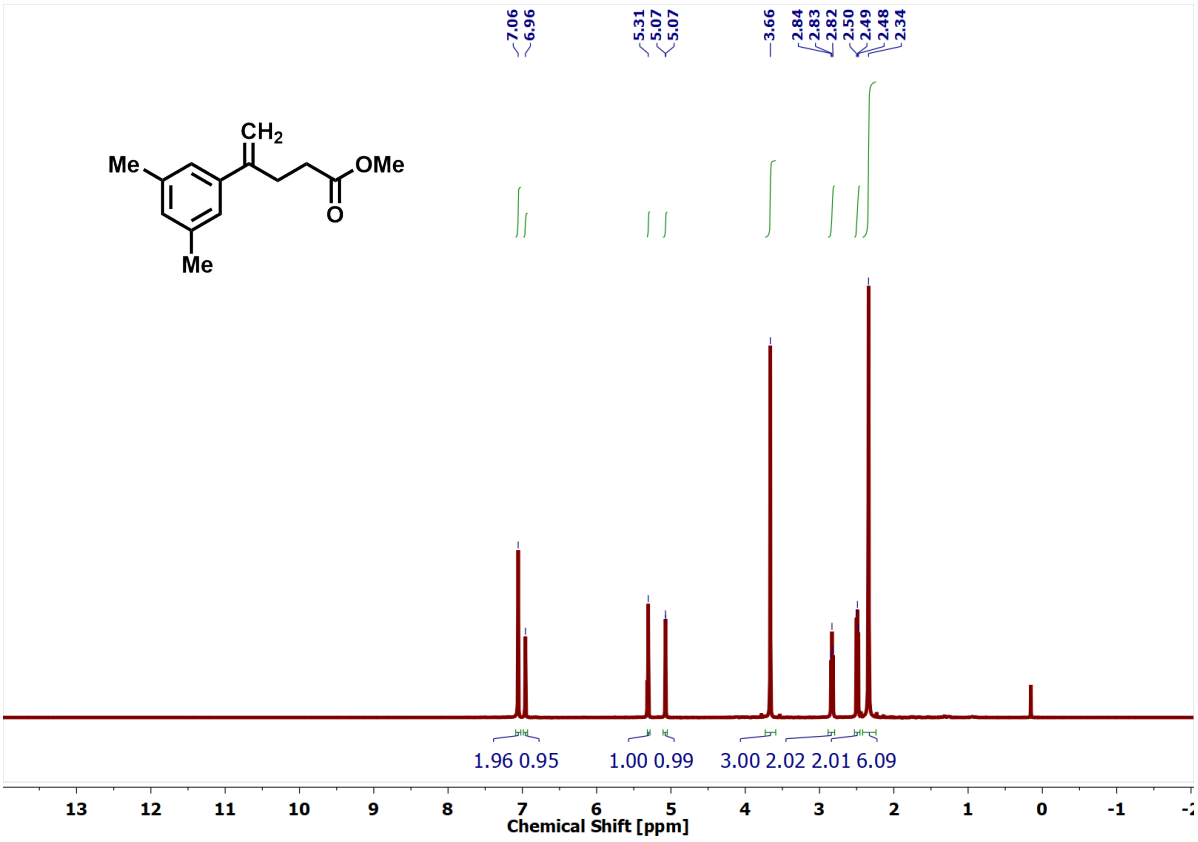

146.28
128.64
128.19
126.27
70.92
48.76
42.34
31.43
30.33
29.54
29.34
12.46
Chemical Shift [ppm]

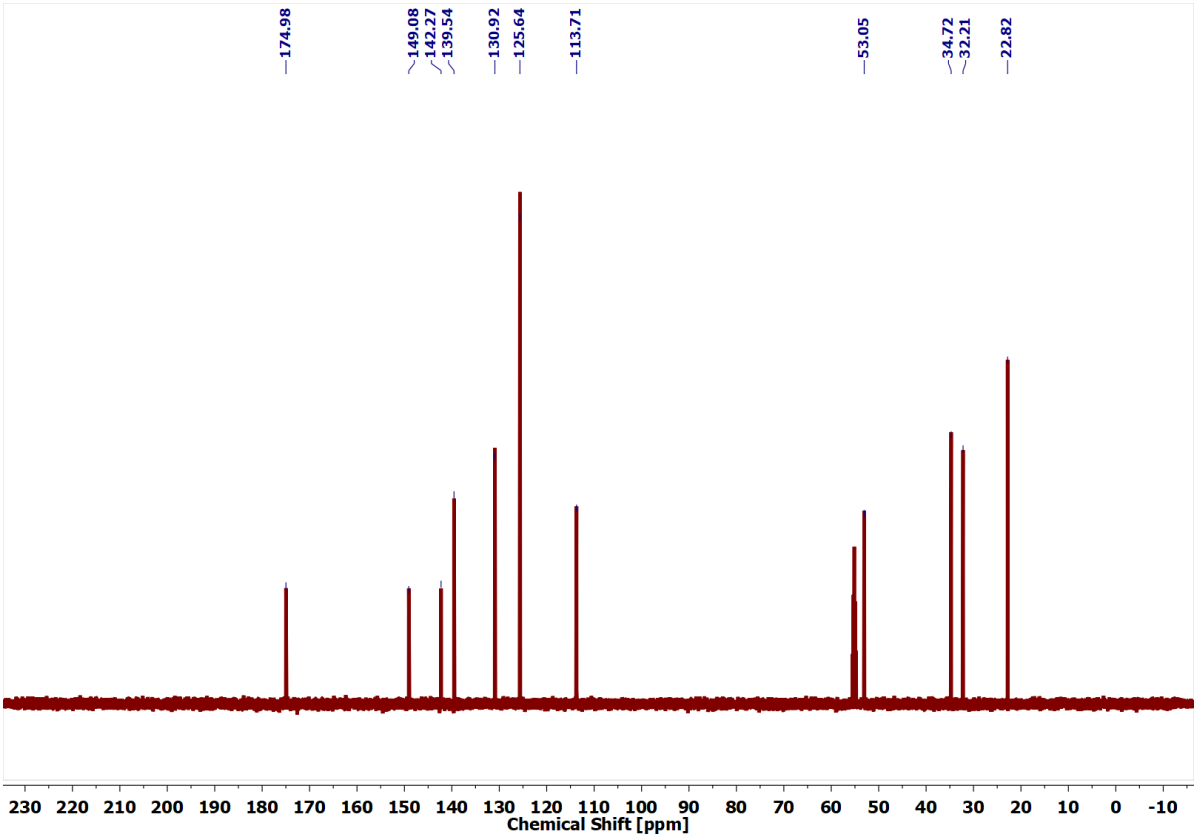

7.60
7.25
3.31
3.30
3.29
2.79
2.78
2.77
2.38
Me
O
OH
O
Me
2.06 1.00
2.06 2.08 6.22
Chemical Shift [ppm]

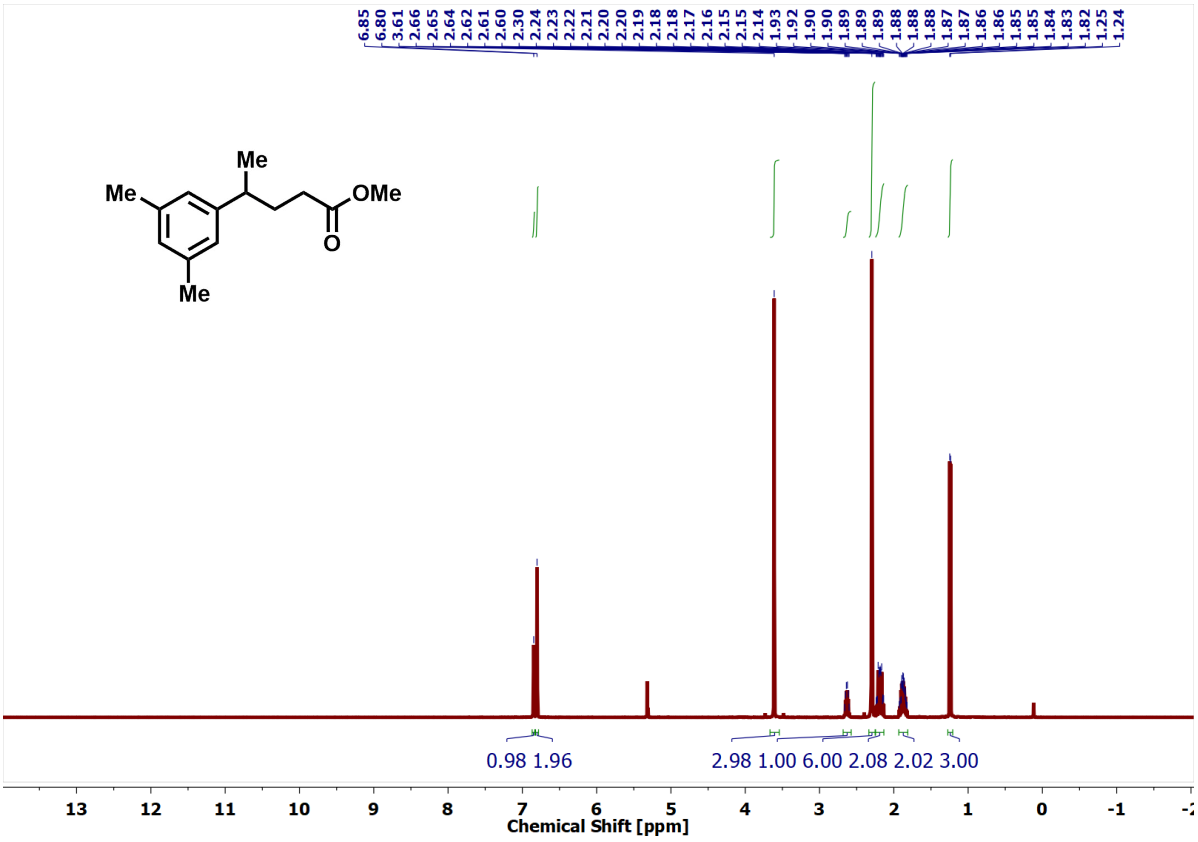

198.52
179.40
138.78
136.90
135.24
126.12
33.63
28.45
21.35
Chemical Shift [ppm]

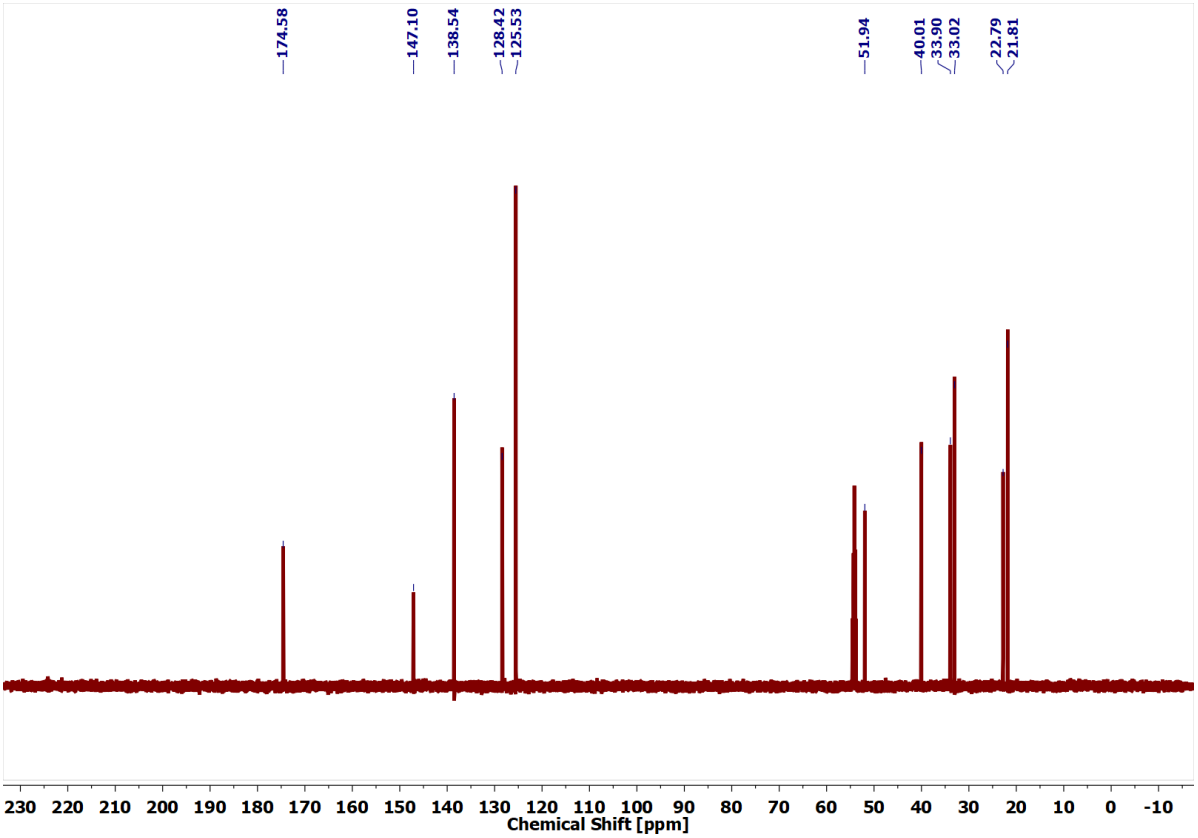

7.58
7.20
3.70
3.30
3.29
3.28
2.76
2.75
2.74
2.36
Me
O
OMe
O
Me
1.97 1.00
3.08 1.99 2.00 5.96
Chemical Shift [ppm]

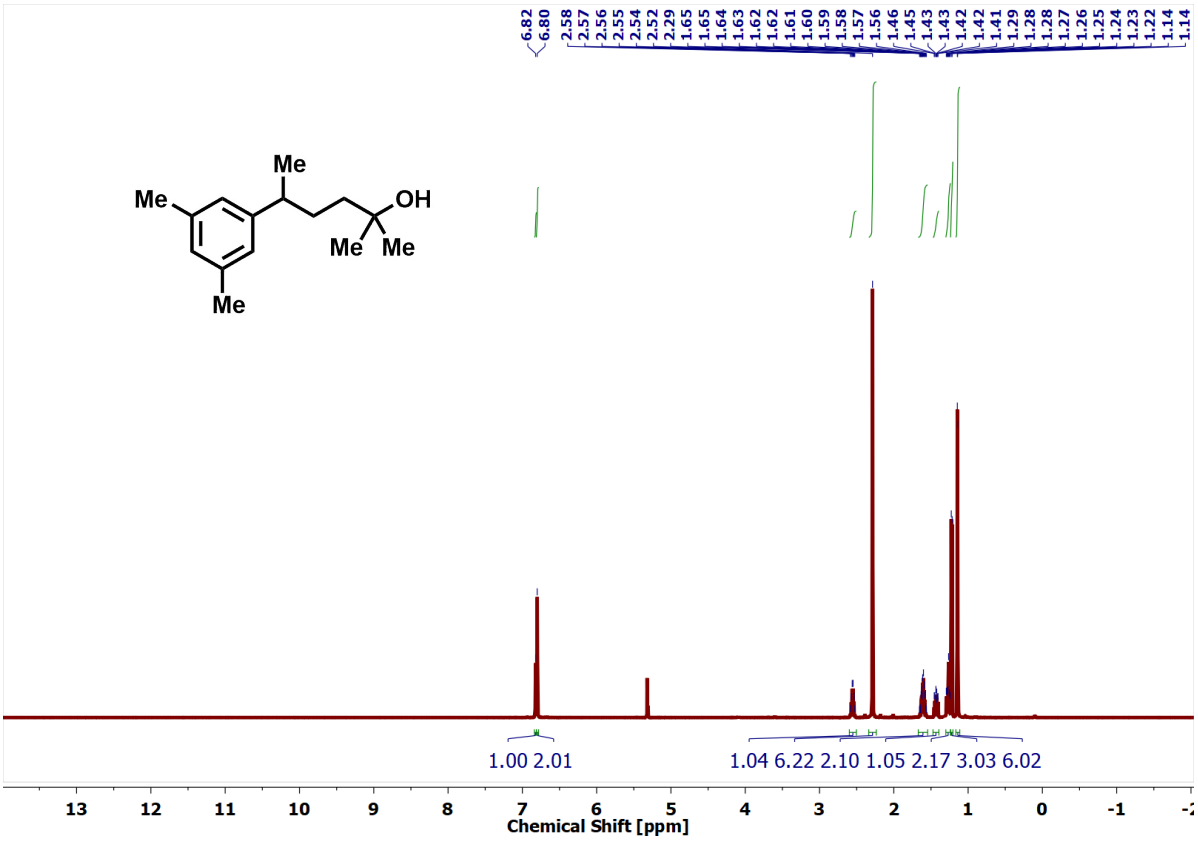

198.59
173.61
138.35
136.73
134.98
125.95
51.94
33.62
28.21
21.34
Chemical Shift [ppm]

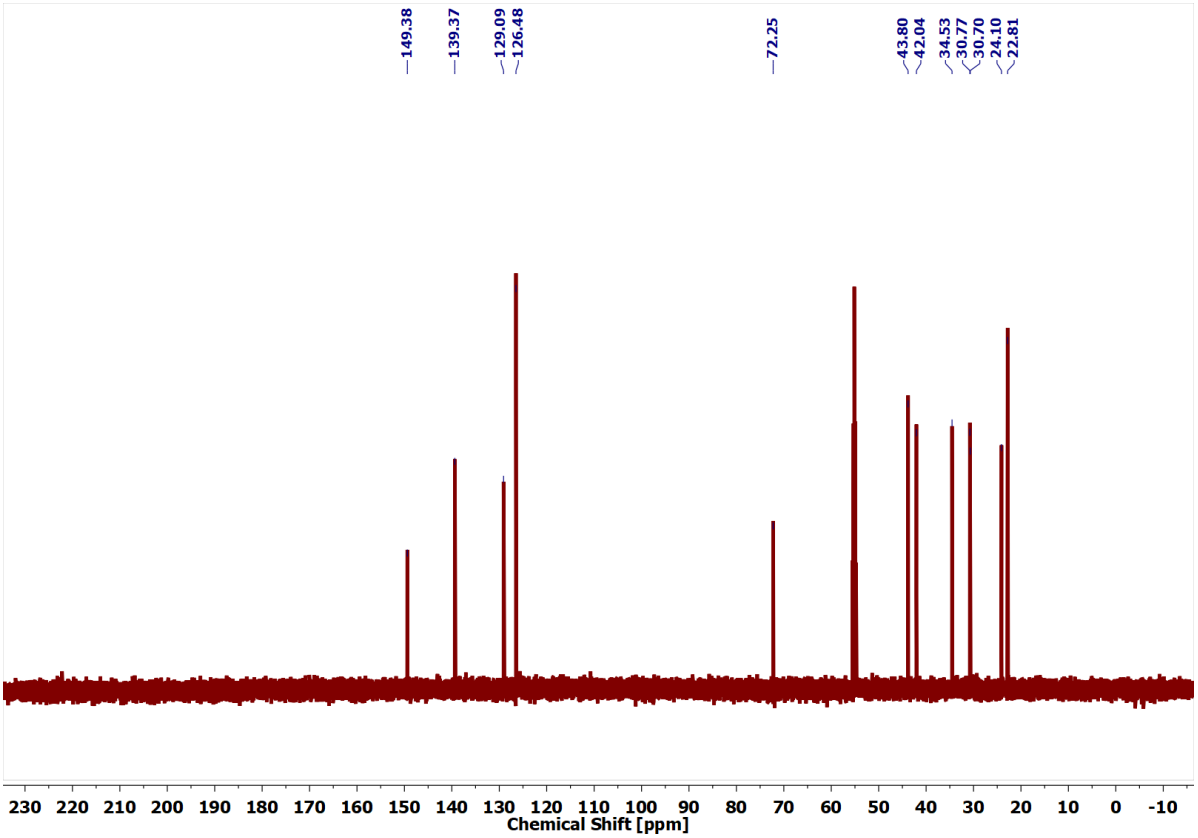

7.06
6.96
5.31
5.07
5.07
3.66
2.84
2.83
2.82
2.50
2.49
2.48
2.34
CH2
Me
OMe
O
Me
1.96 0.95
1.00 0.99
3.00 2.02 2.01 6.09
Chemical Shift [ppm]

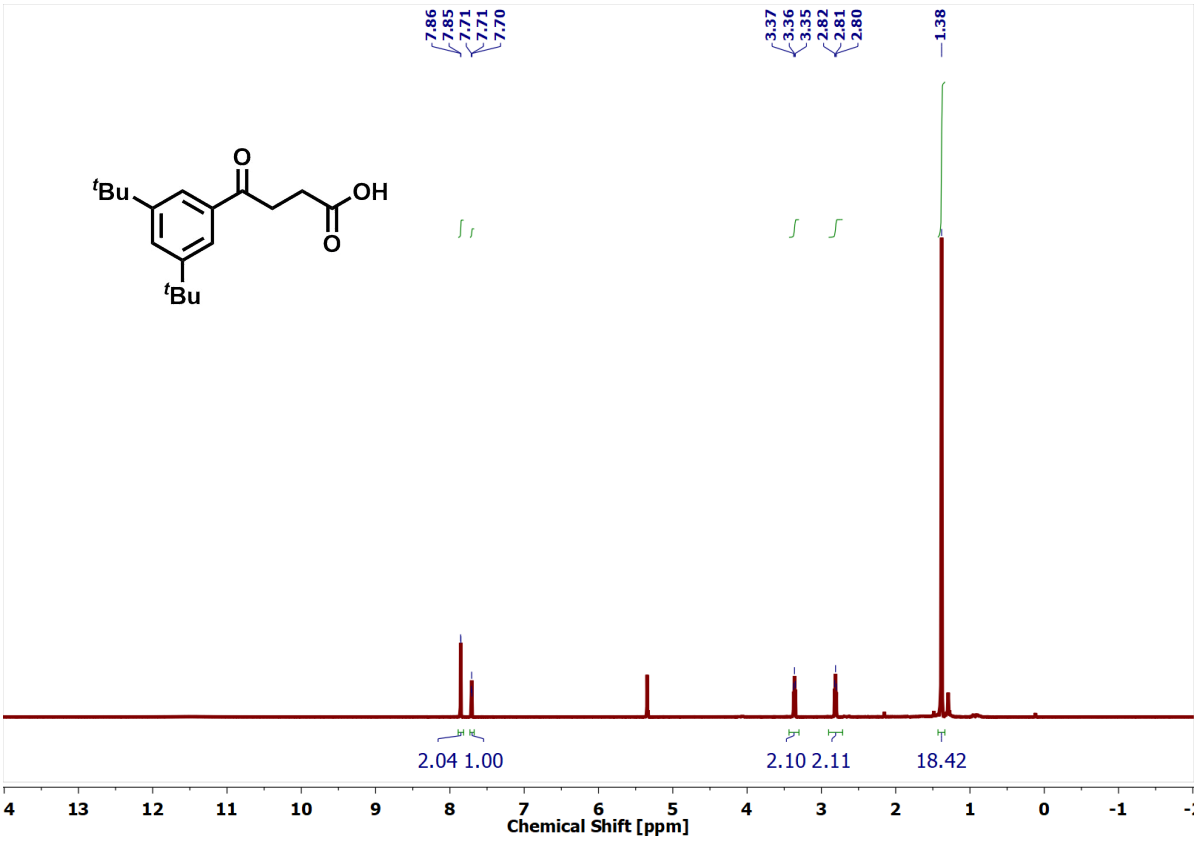

174.98
149.08
142.27
139.54
130.92
125.64
113.71
53.05
34.72
32.21
22.82
Chemical Shift [ppm]

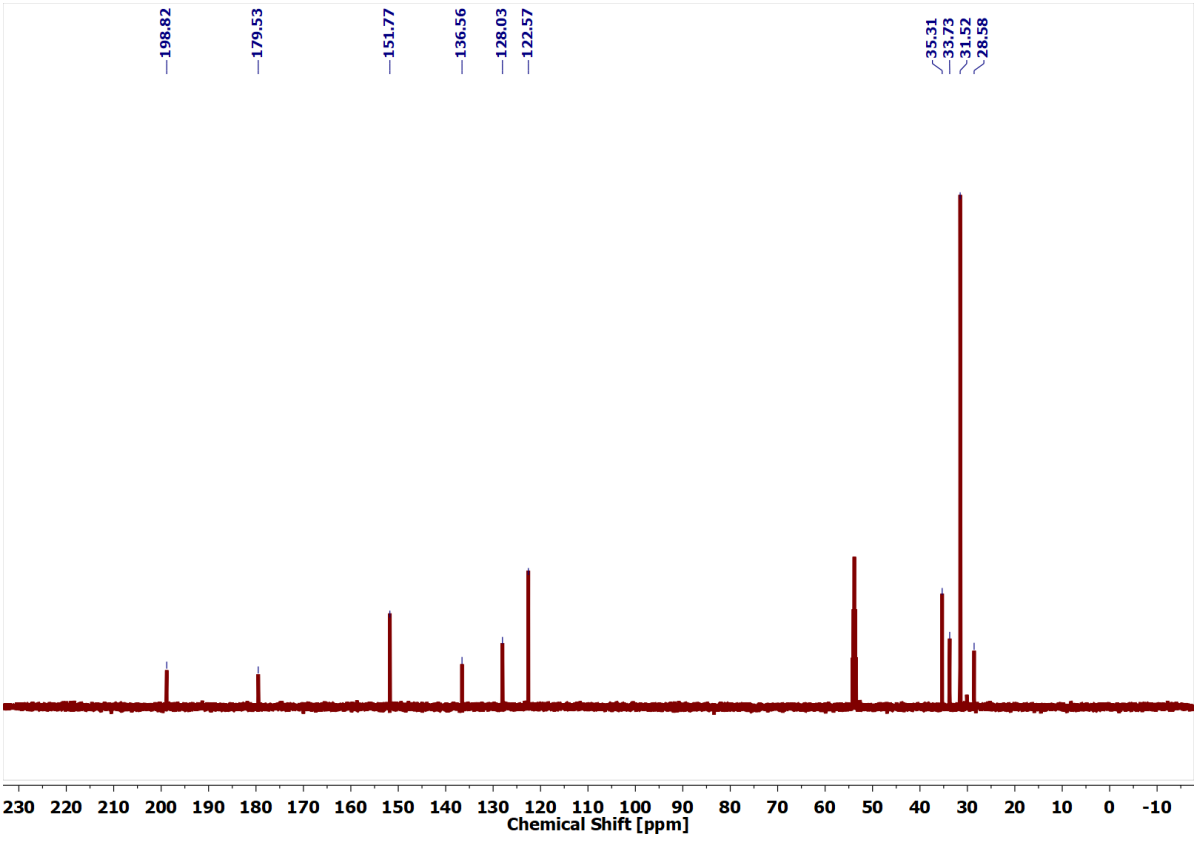

6.85 6.80 3.61 2.66 2.65 2.64 2.62 2.61 2.60 2.30 2.24 2.23 2.22 2.21 2.20 2.20 2.19 2.18 2.18 2.17 2.16 2.15 2.15 2.14 1.93 1.92 1.90 1.90 1.89 1.89 1.89 1.88 1.88 1.88 1.87 1.87 1.86 1.86 1.85 1.85 1.84 1.83 1.82 1.25 1.24
Me
Me
OMe
O
Me
0.98 1.96
2.98 1.00 6.00 2.08 2.02 3.00
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

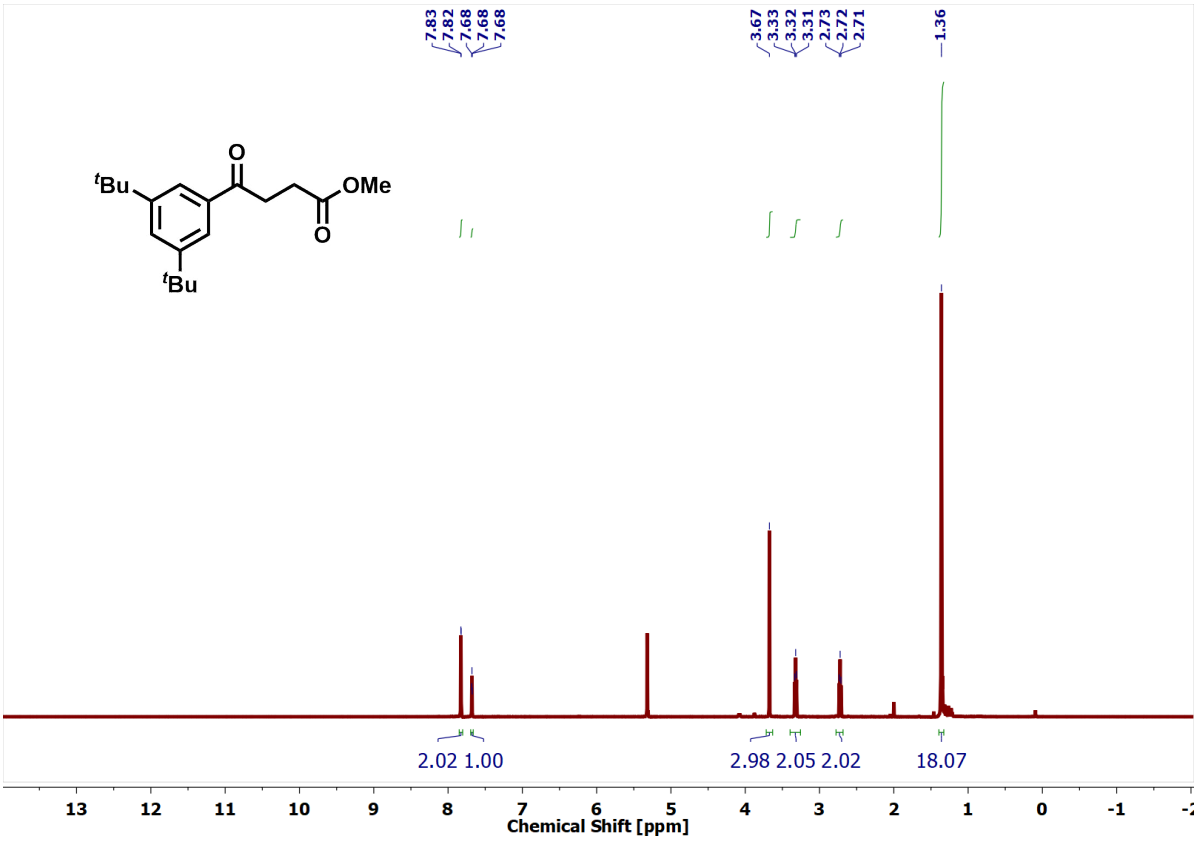

174.58
147.10
138.54
128.42
125.53
51.94
40.01
33.90
33.02
22.79
21.81
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

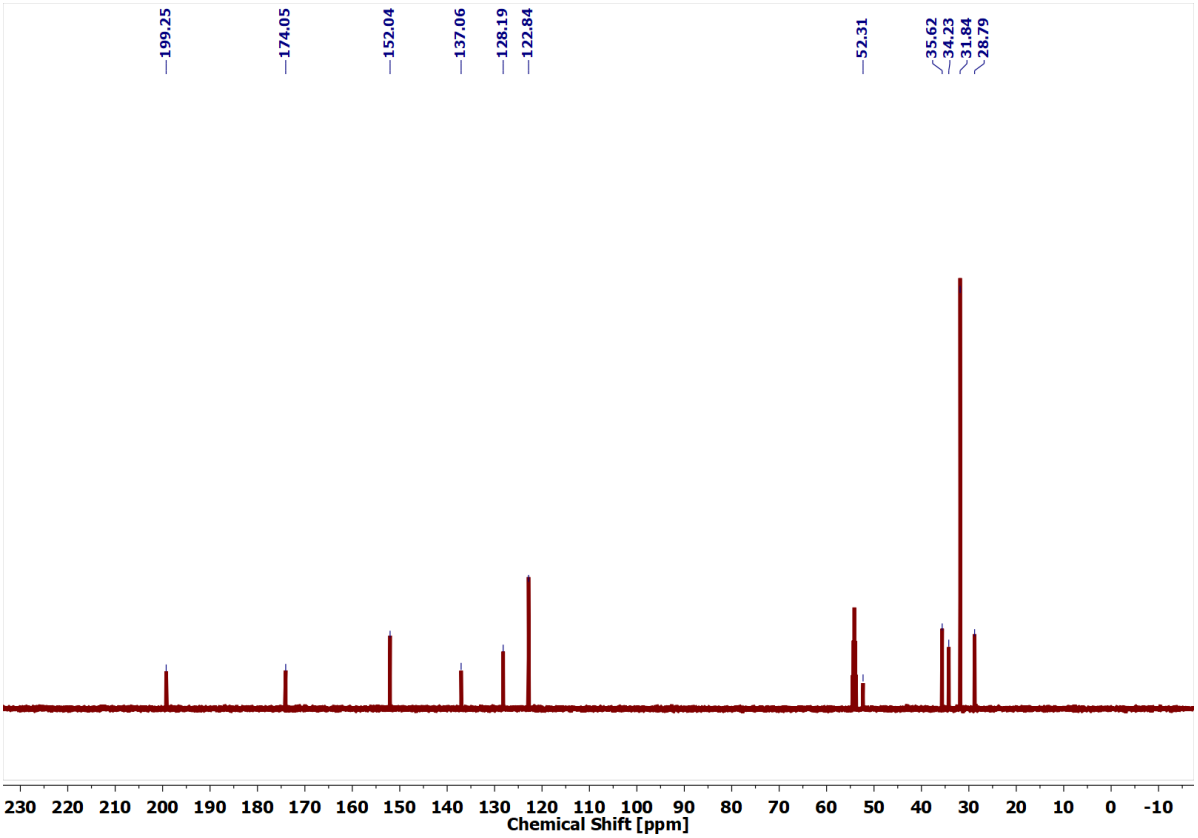

Me
Me
OH
Me
Me
Me
6.82
6.80
2.58
2.57
2.56
2.55
2.54
2.52
2.29
1.65
1.64
1.63
1.62
1.62
1.61
1.60
1.59
1.58
1.57
1.56
1.46
1.45
1.43
1.43
1.42
1.42
1.41
1.29
1.28
1.27
1.26
1.25
1.24
1.23
1.22
1.14
1.14
1.00 2.01
1.04 6.22 2.10 1.05 2.17 3.03 6.02
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

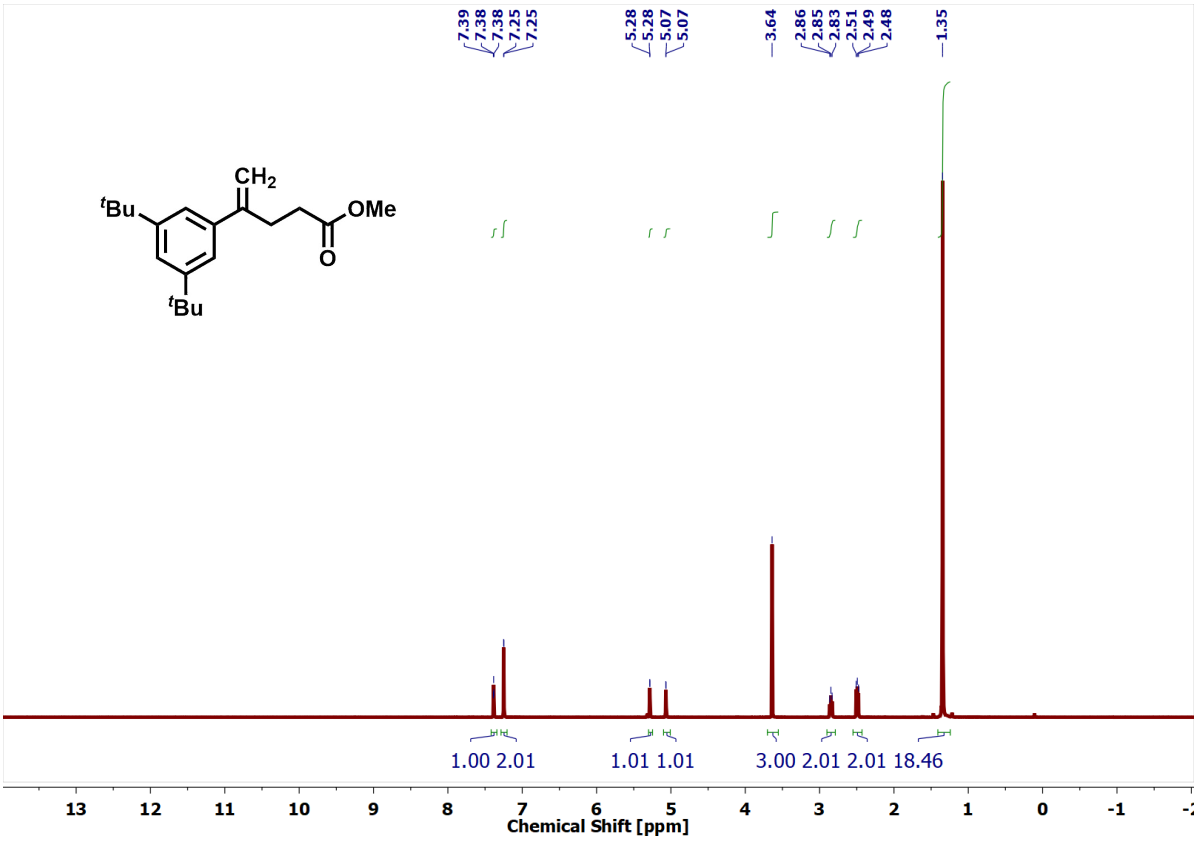

149.38
139.37
129.09
126.48
72.25
43.80
42.04
34.53
30.77
30.70
24.10
22.81
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

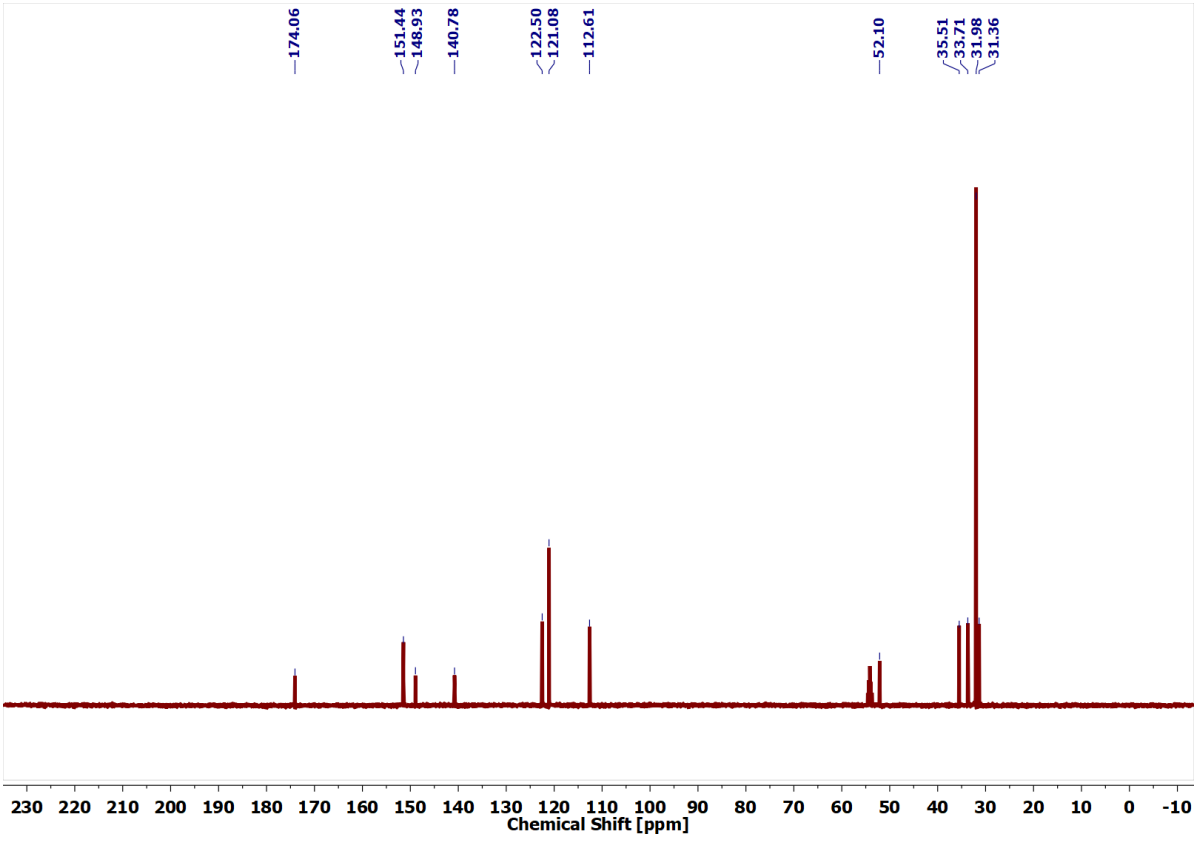

7.86
7.85
7.71
7.71
7.70
3.37
3.36
3.35
2.82
2.81
2.80
1.38
tBu
O
OH
O
tBu
2.04 1.00
2.10 2.11
18.42
Chemical Shift [ppm]


198.82
179.53
151.77
136.56
128.03
122.57
35.31
33.73
31.52
28.58
Chemical Shift [ppm]


7.83
7.82
7.68
7.68
7.68
3.67
3.33
3.32
3.31
2.73
2.72
2.71
1.36
tBu
O
OMe
O
tBu
2.02 1.00
2.98 2.05 2.02
18.07
Chemical Shift [ppm]


199.25
174.05
152.04
137.06
128.19
122.84
52.31
35.62
34.23
31.84
28.79
Chemical Shift [ppm]


7.39
7.38
7.38
7.25
7.25
5.28
5.28
5.07
5.07
3.64
2.86
2.85
2.83
2.51
2.49
2.48
1.35
CH2
tBu
OMe
O
tBu
1.00 2.01
1.01 1.01
3.00 2.01 2.01 18.46
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]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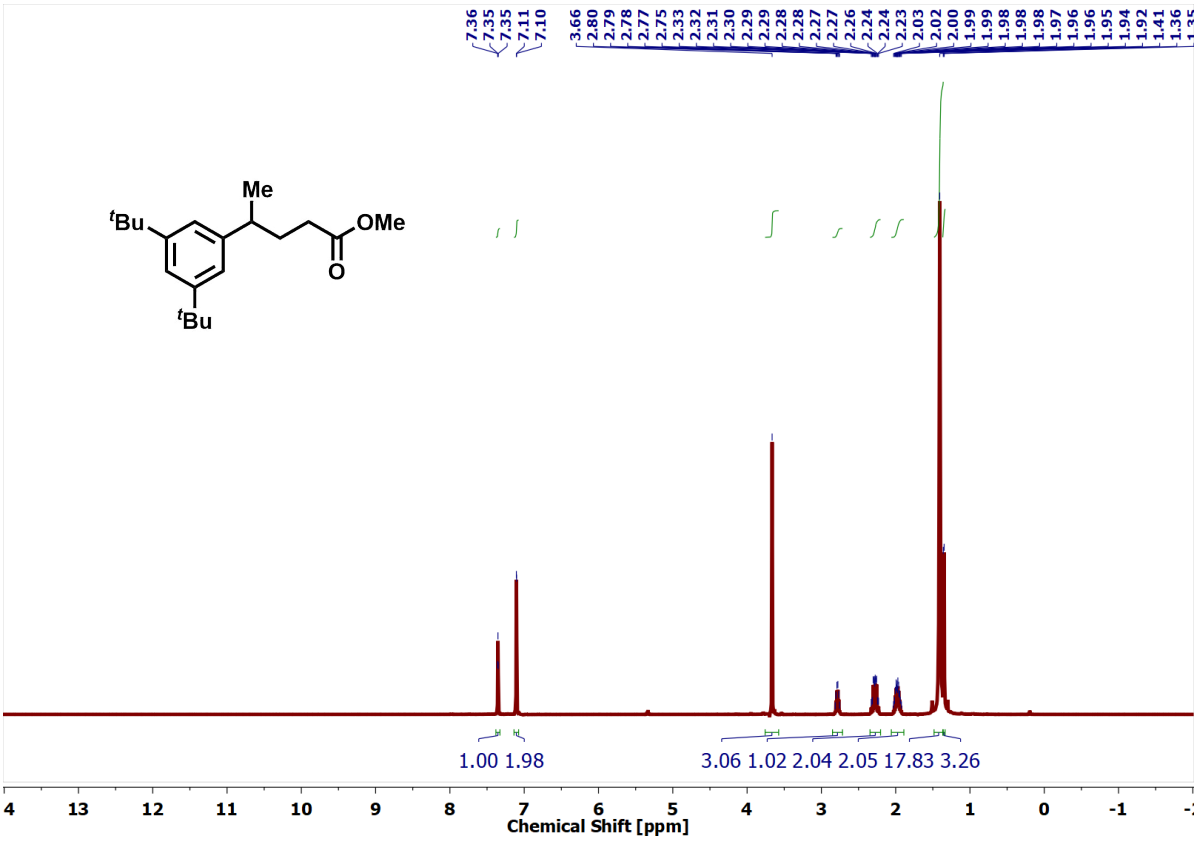
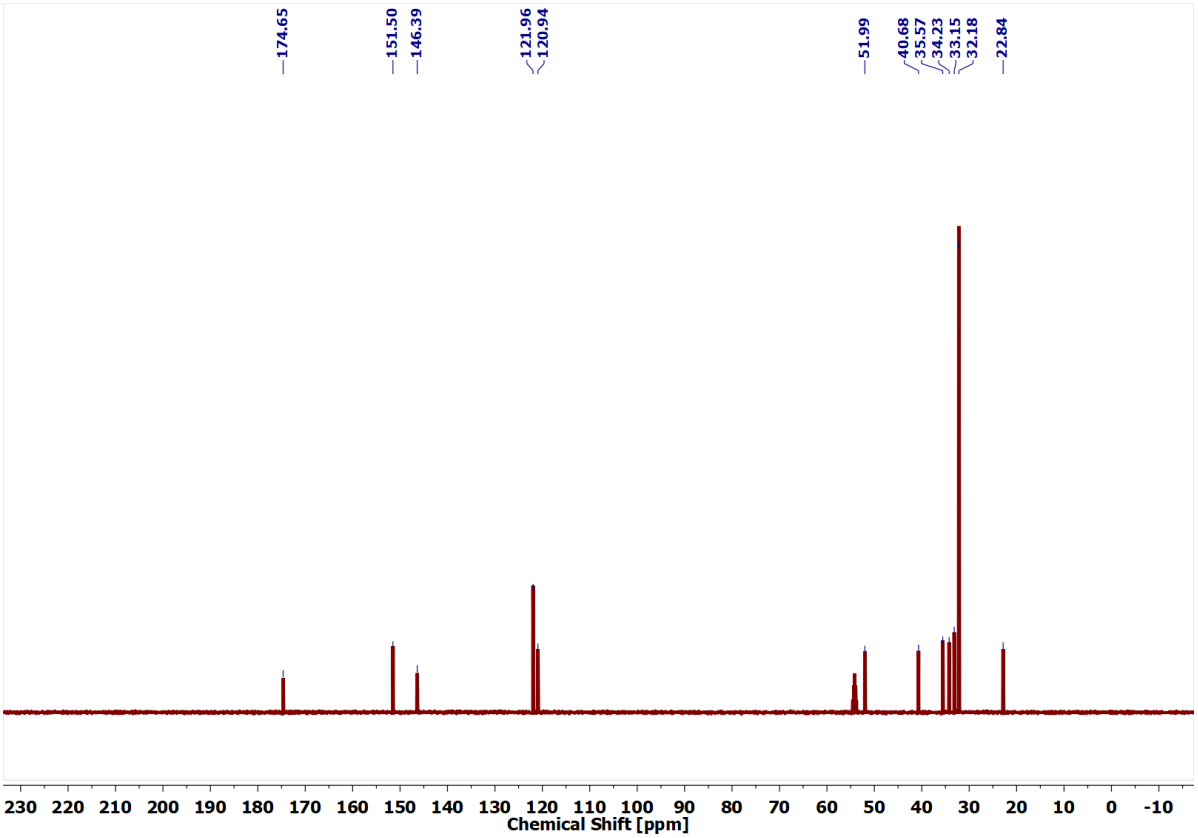
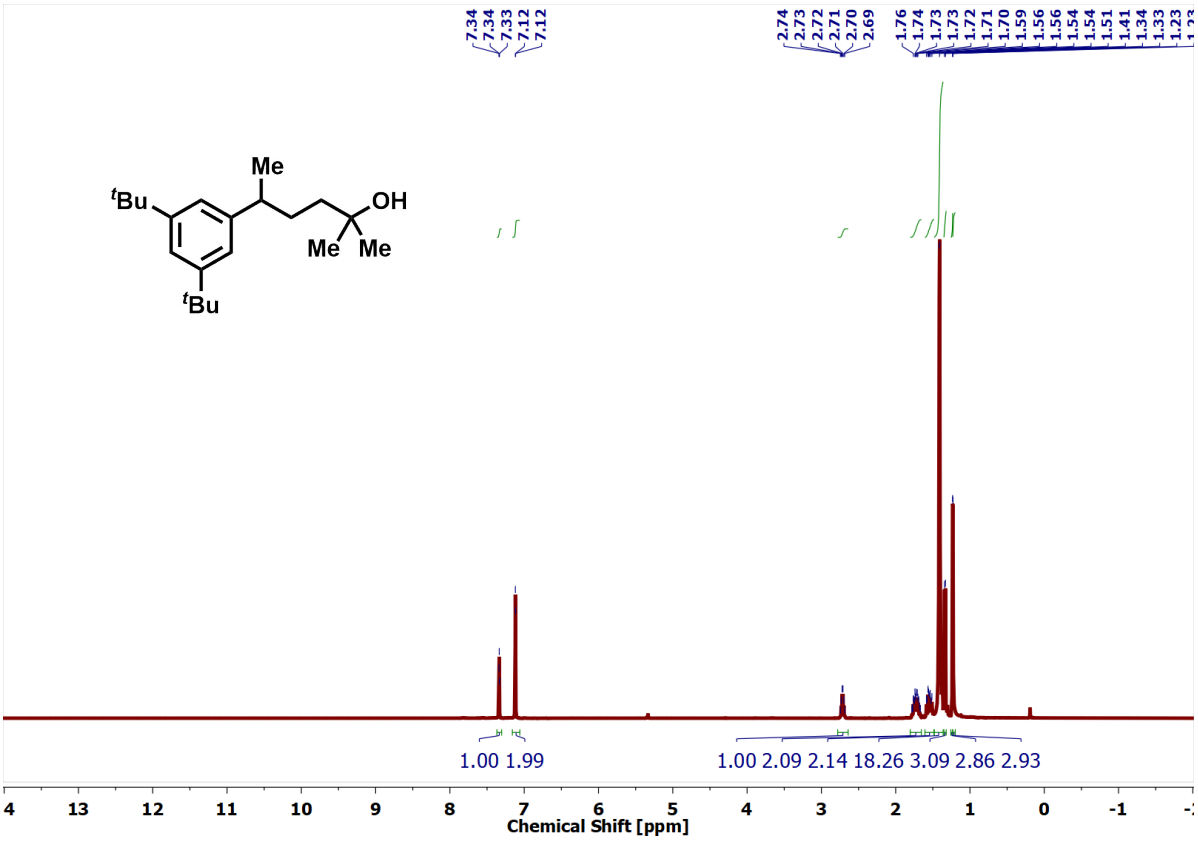
151.44
148.93
140.78
122.50
121.08
112.61
52.10
35.51
33.71
31.98
31.36
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]


Me
tBu
OMe
O
tBu
1.00 1.98
3.06 1.02 2.04 2.05 17.83 3.26
Chemical Shift [ppm]


174.65
151.50
146.39
121.96
120.94
51.99
40.68
35.57
34.23
33.15
32.18
22.84
Chemical Shift [ppm]


7.34
7.34
7.33
7.12
7.12
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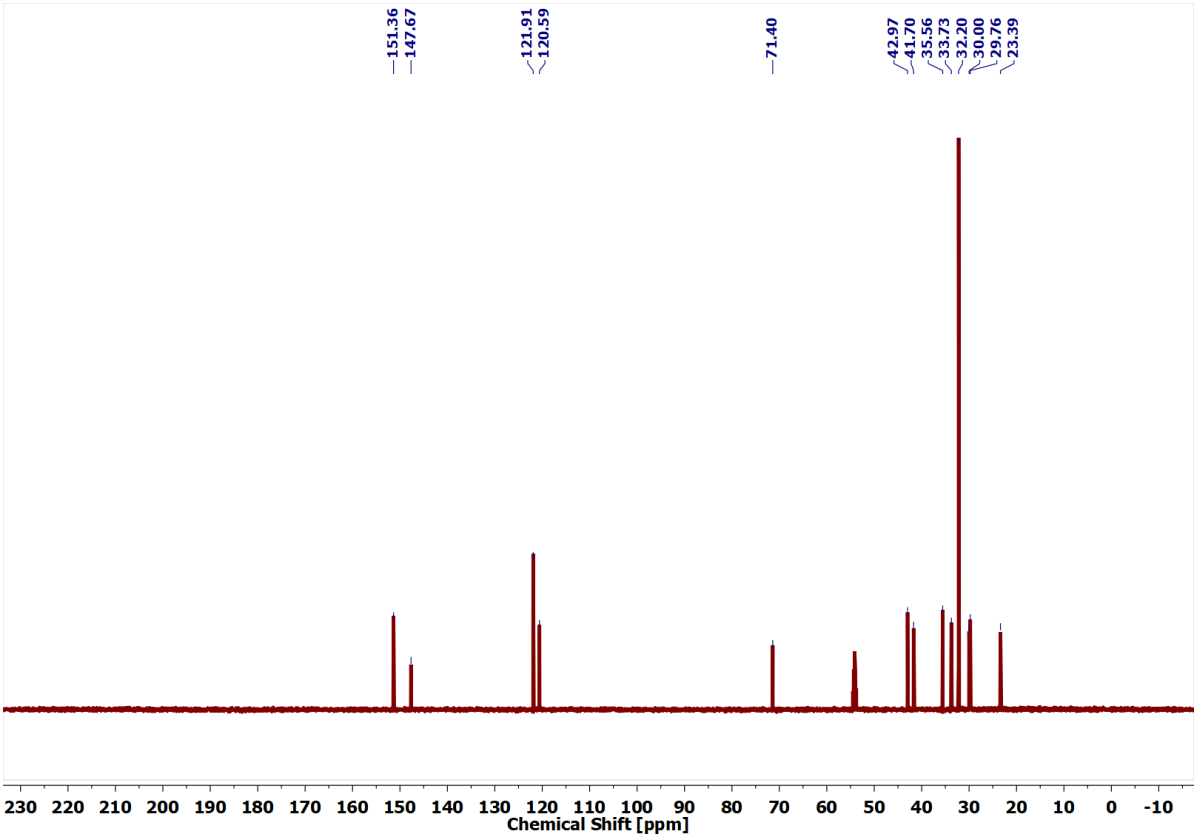
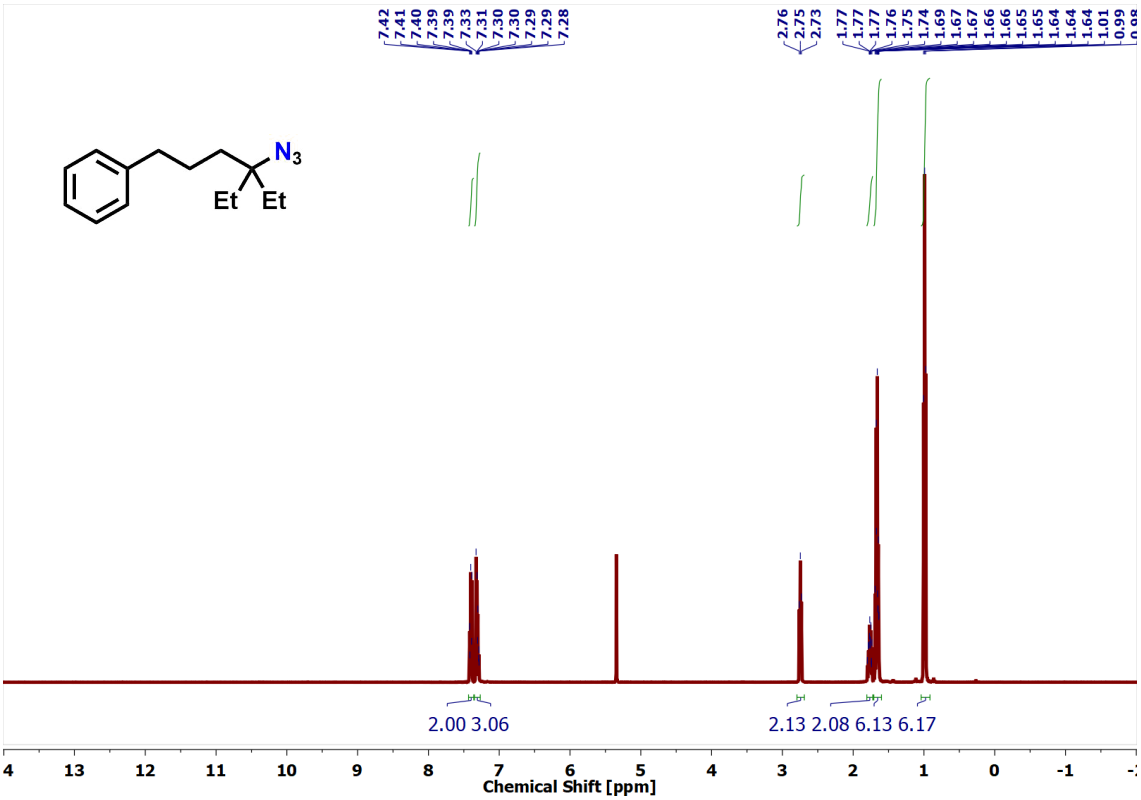
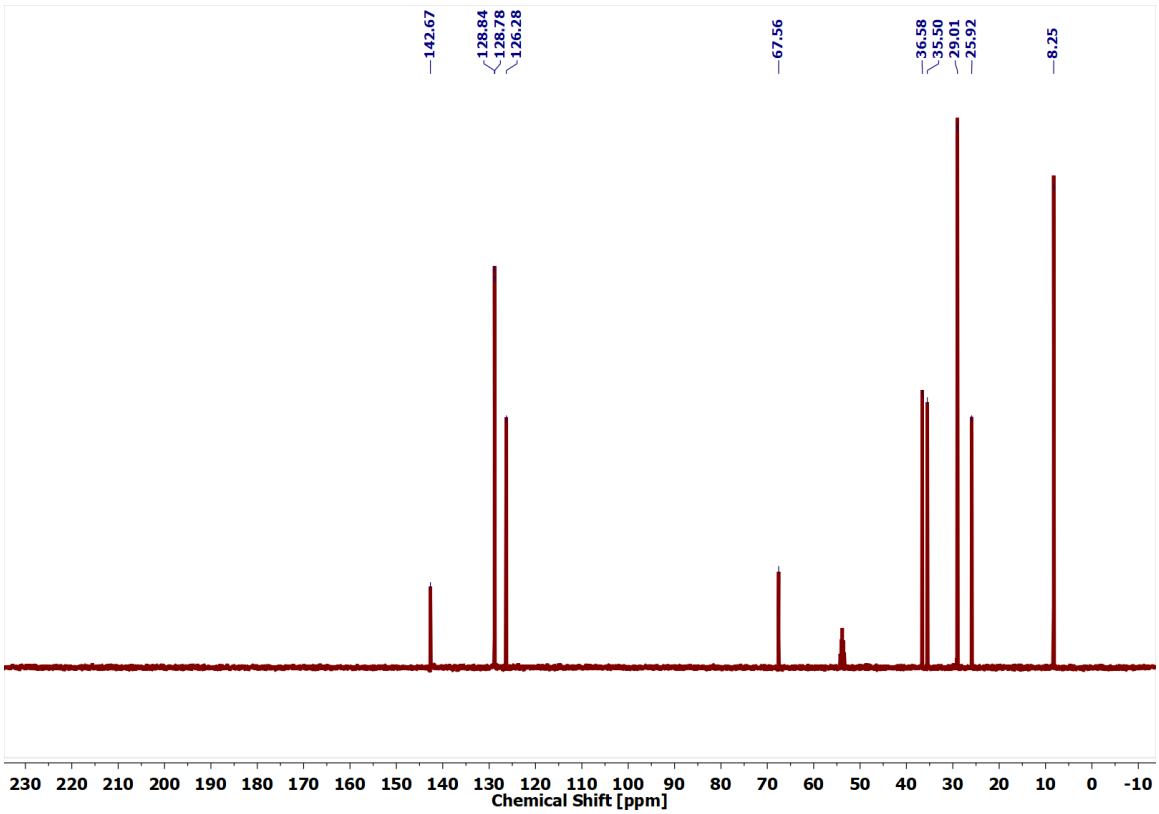
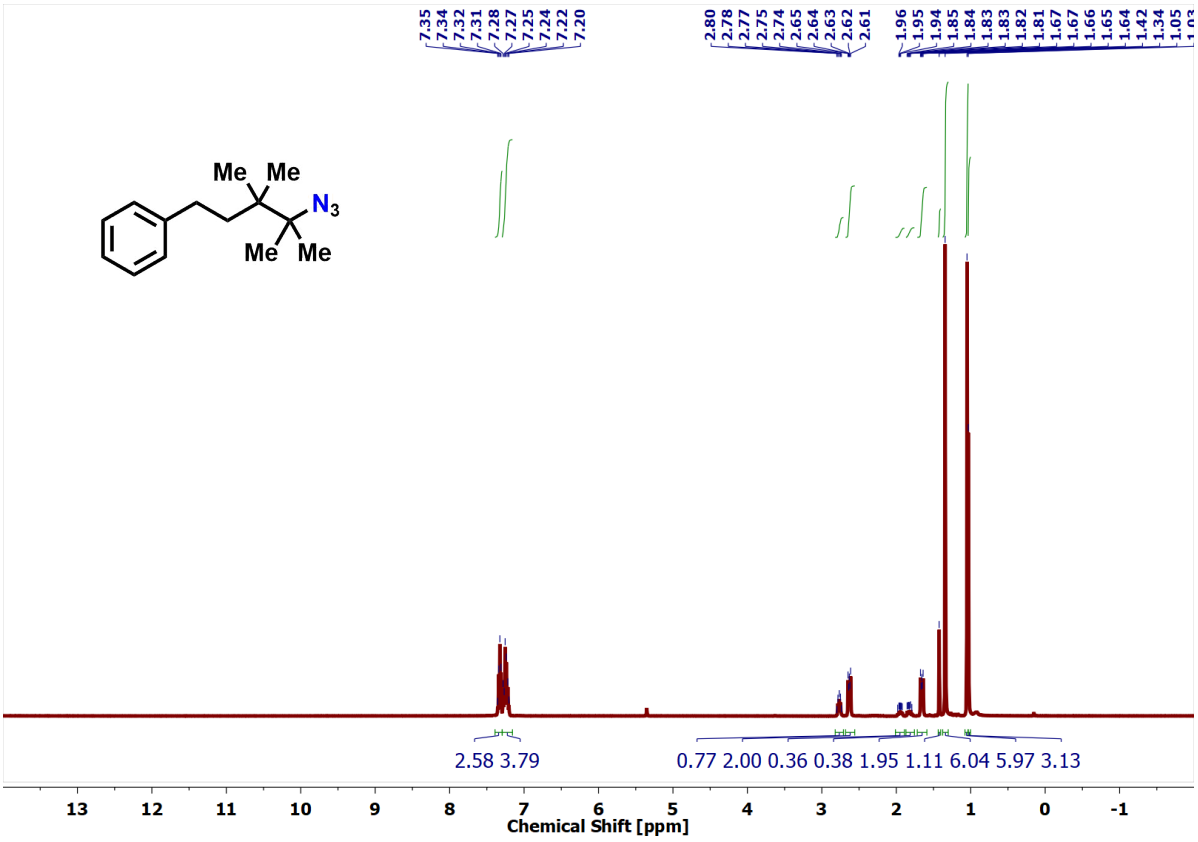
2.73
2.72
2.71
2.70
2.69
1.76
1.74
1.73
1.73
1.72
1.71
1.70
1.59
1.56
1.56
1.54
1.54
1.51
1.41
1.34
1.33
1.23
Me
tBu
OH
Me
Me
tBu
1.00 1.99
1.00 2.09 2.14 18.26 3.09 2.86 2.93
Chemical Shift [ppm]

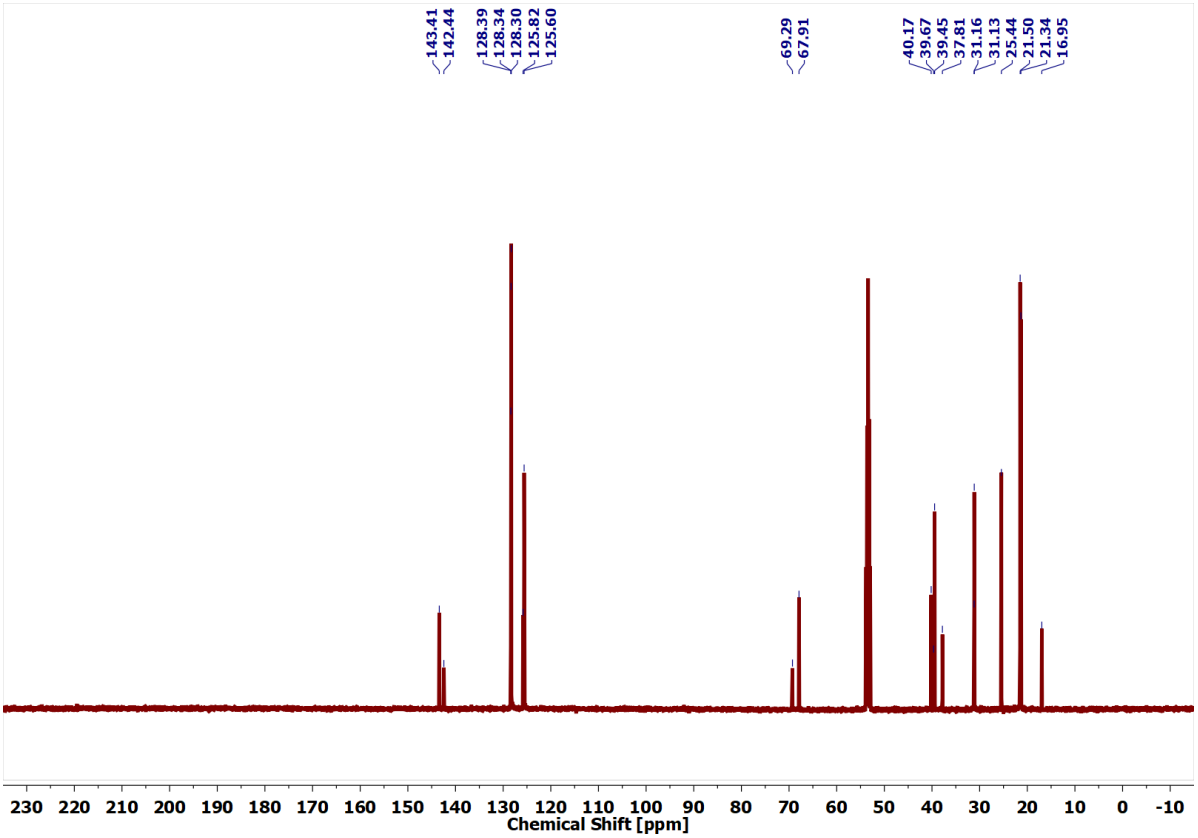

151.36
147.67
121.91
120.59
71.40
42.97
41.70
35.56
33.73
32.20
30.00
29.76
23.39
Chemical Shift [ppm]

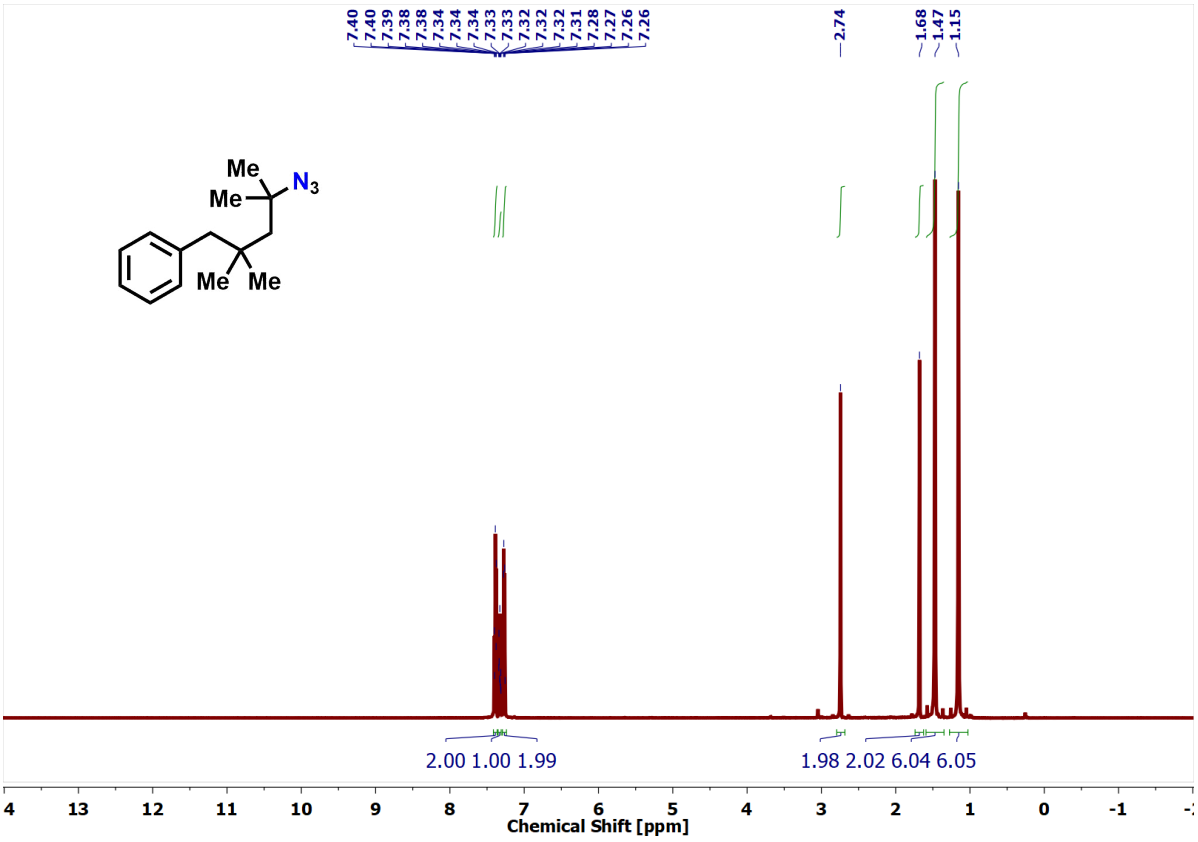
NMR spectra of organoazides

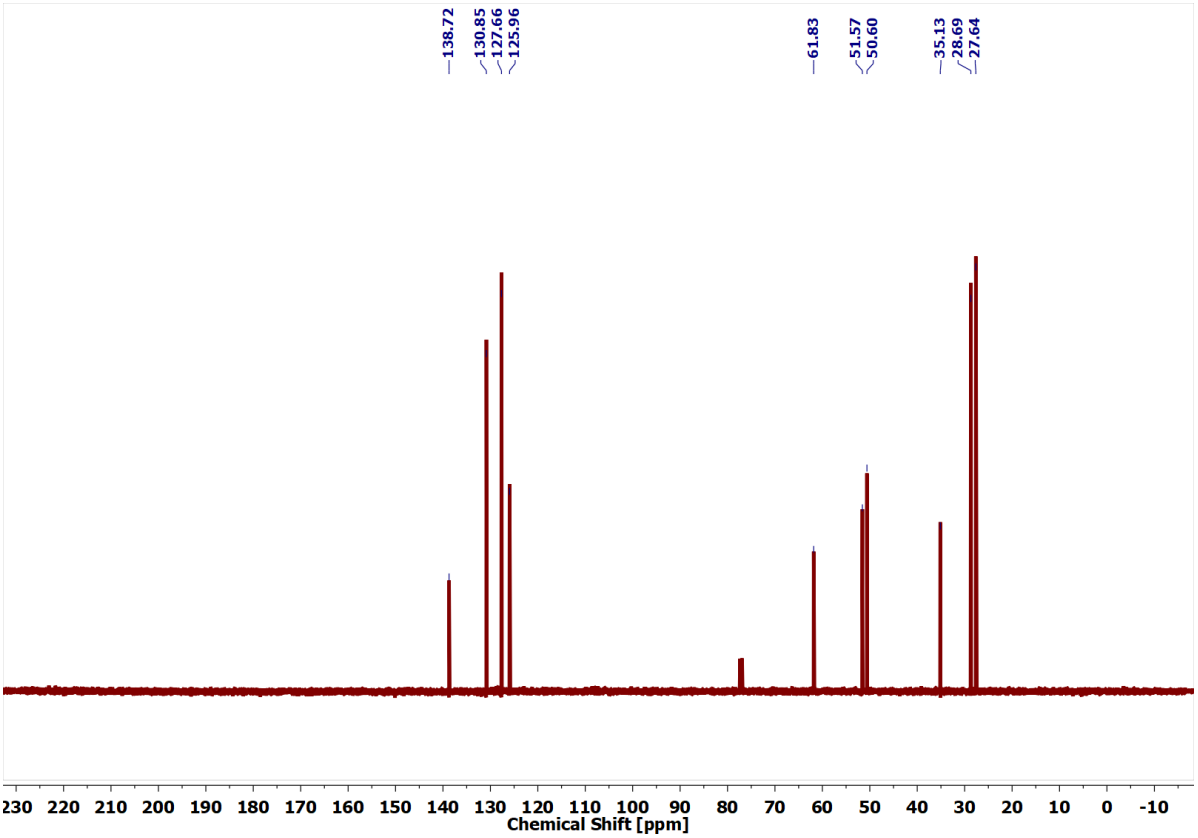


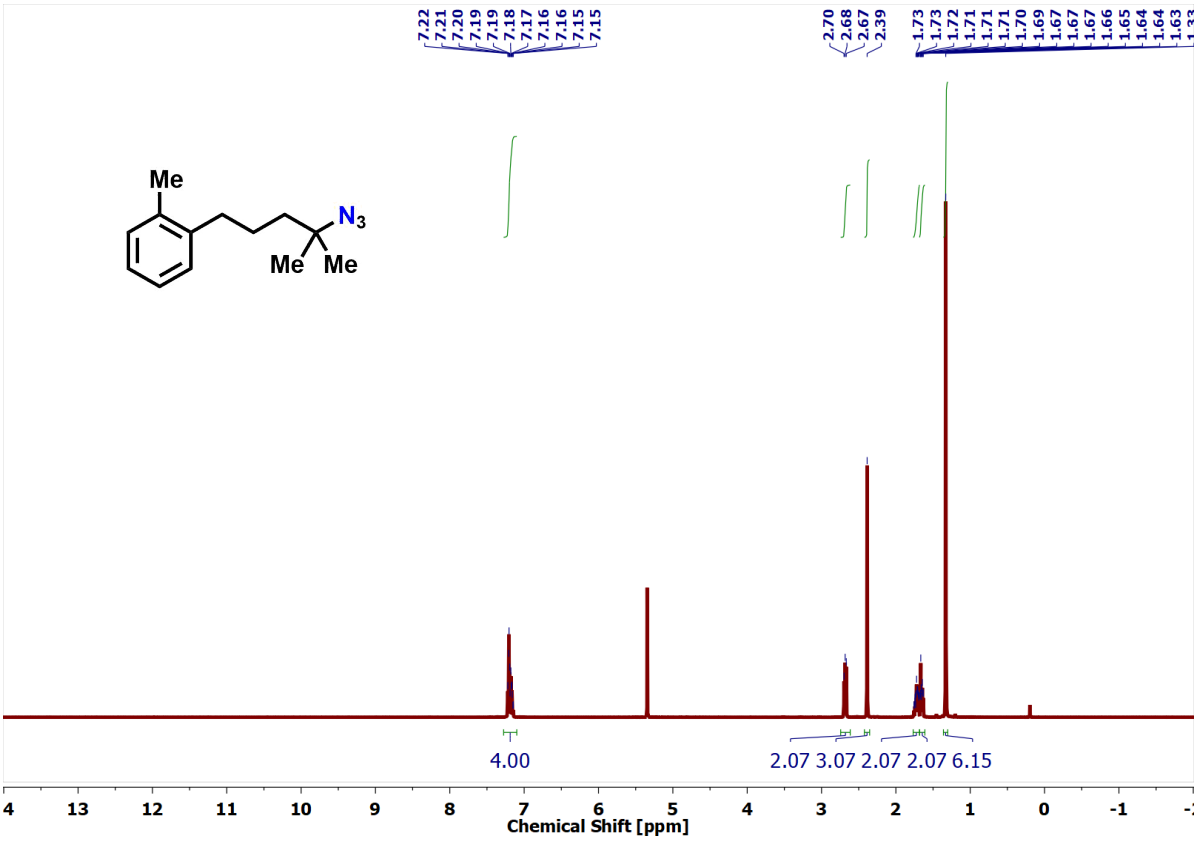


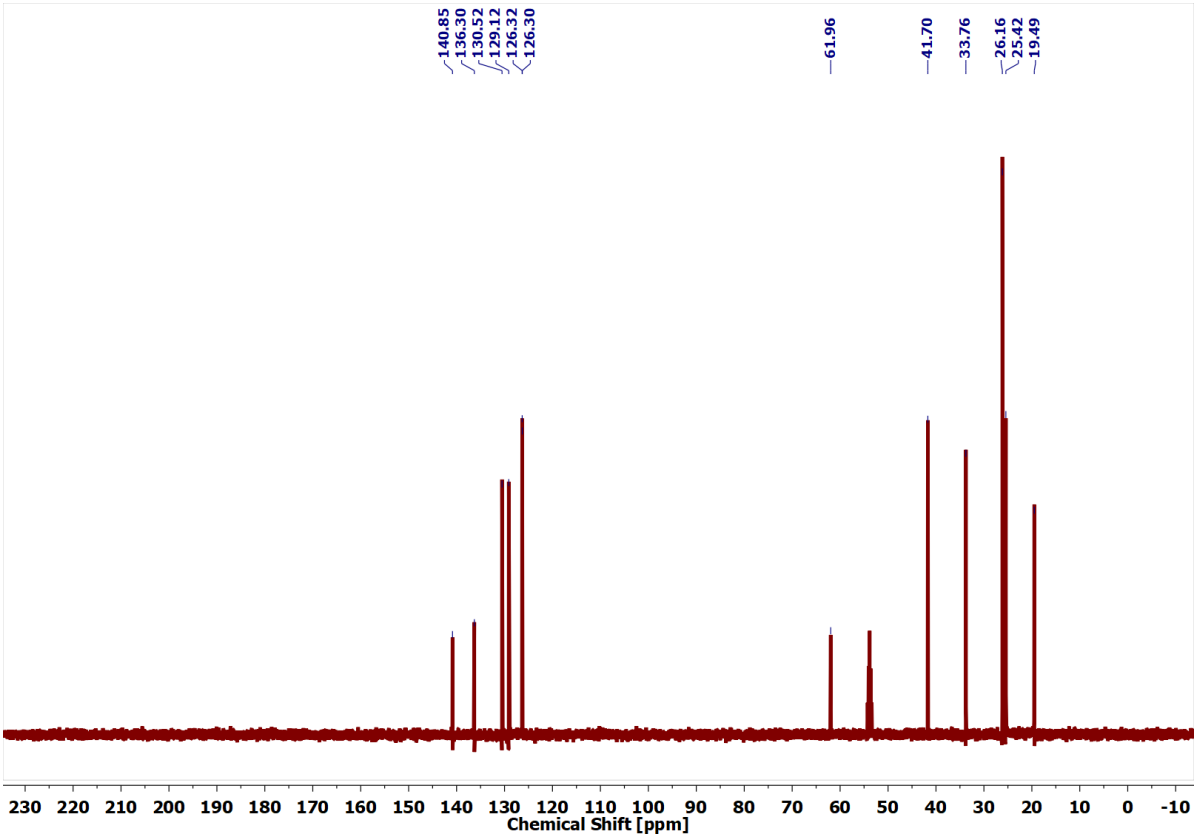

7.35
7.34
7.32
7.31
7.28
7.27
7.25
7.24
7.22
7.20
2.80
2.78
2.77
2.75
2.74
2.65
2.64
2.63
2.62
2.61
1.96
1.95
1.94
1.85
1.84
1.83
1.83
1.82
1.81
1.67
1.67
1.66
1.65
1.64
1.42
1.34
1.05
Me Me
N3
Me Me
2.58 3.79
0.77 2.00 0.36 0.38 1.95 1.11 6.04 5.97 3.13
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

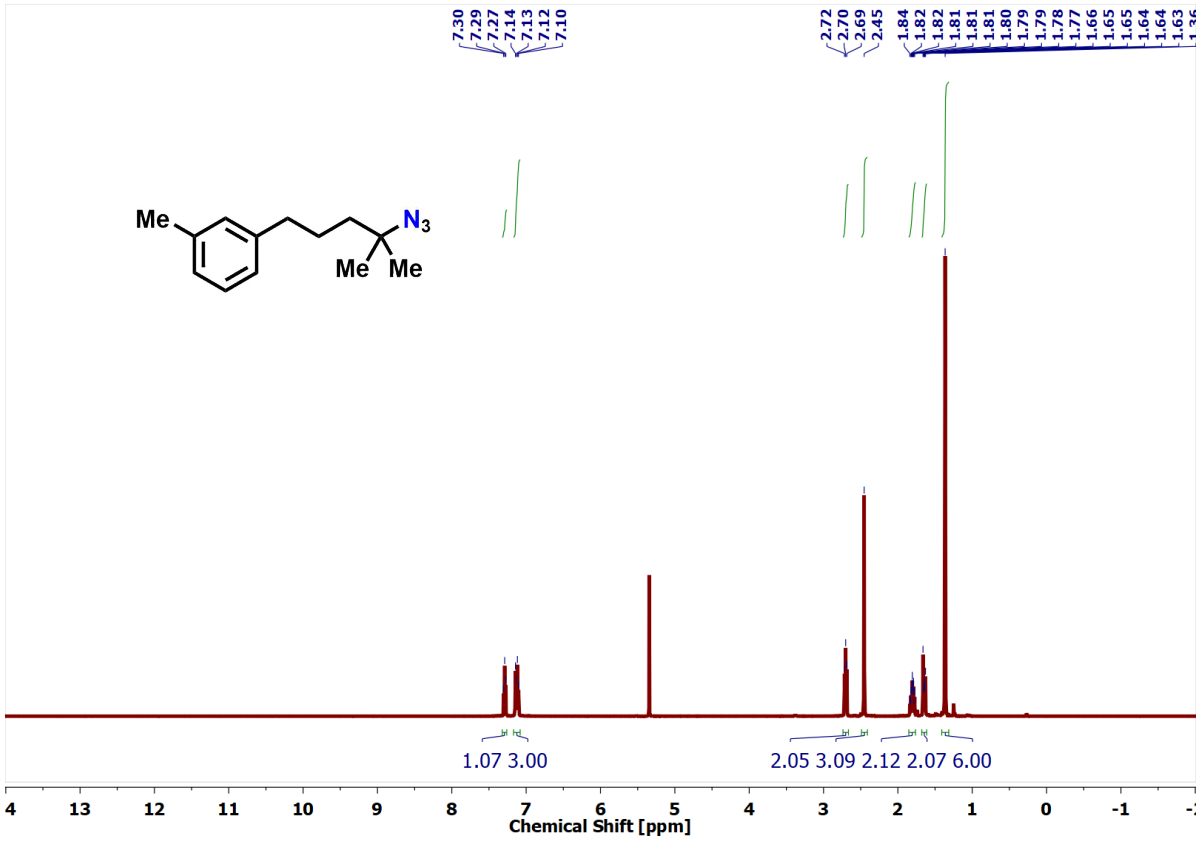

143.41
142.44
128.39
128.34
128.30
125.82
125.60
69.29
67.91
40.17
39.67
39.45
37.81
31.16
31.13
25.44
21.50
21.34
16.95
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

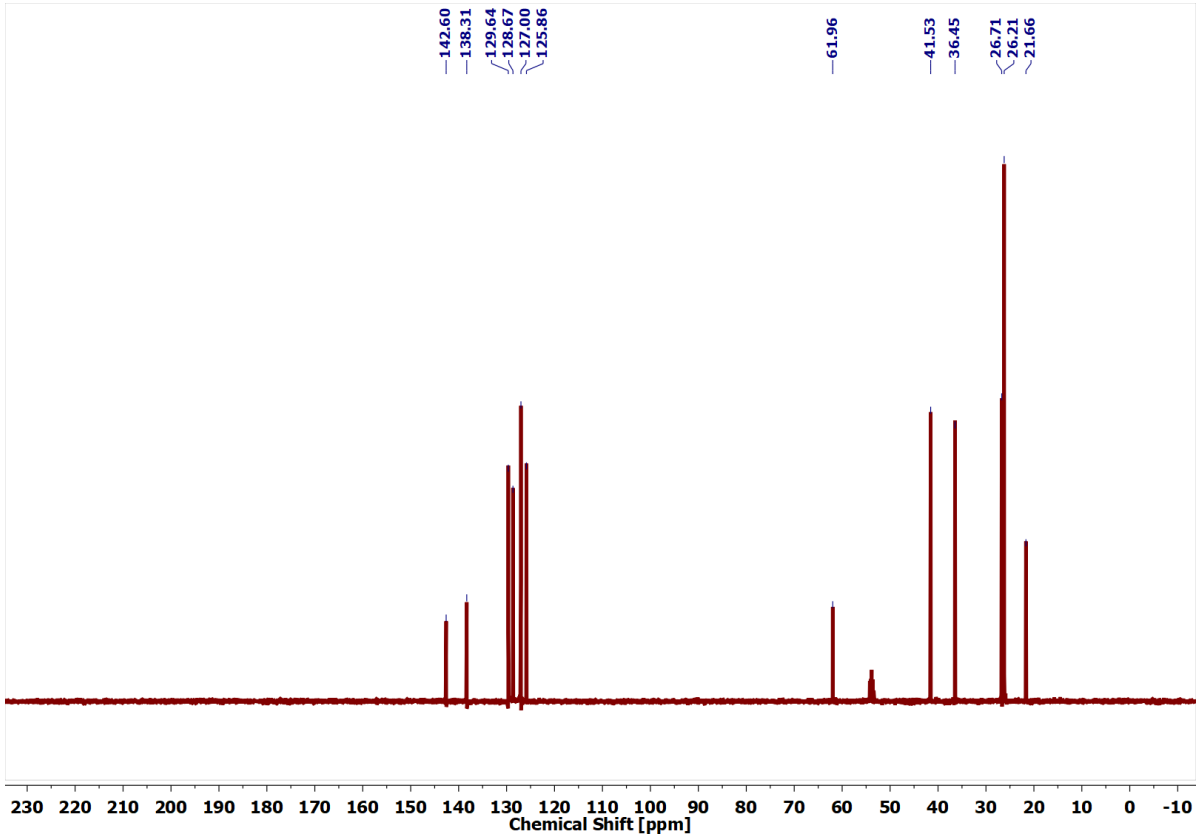

7.40
7.40
7.39
7.38
7.38
7.34
7.34
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.28
7.27
7.26
7.26
2.74
1.68
1.47
1.15
Me
Me
N3
Me
Me
2.00 1.00 1.99
1.98 2.02 6.04 6.05
Chemical Shift [ppm]

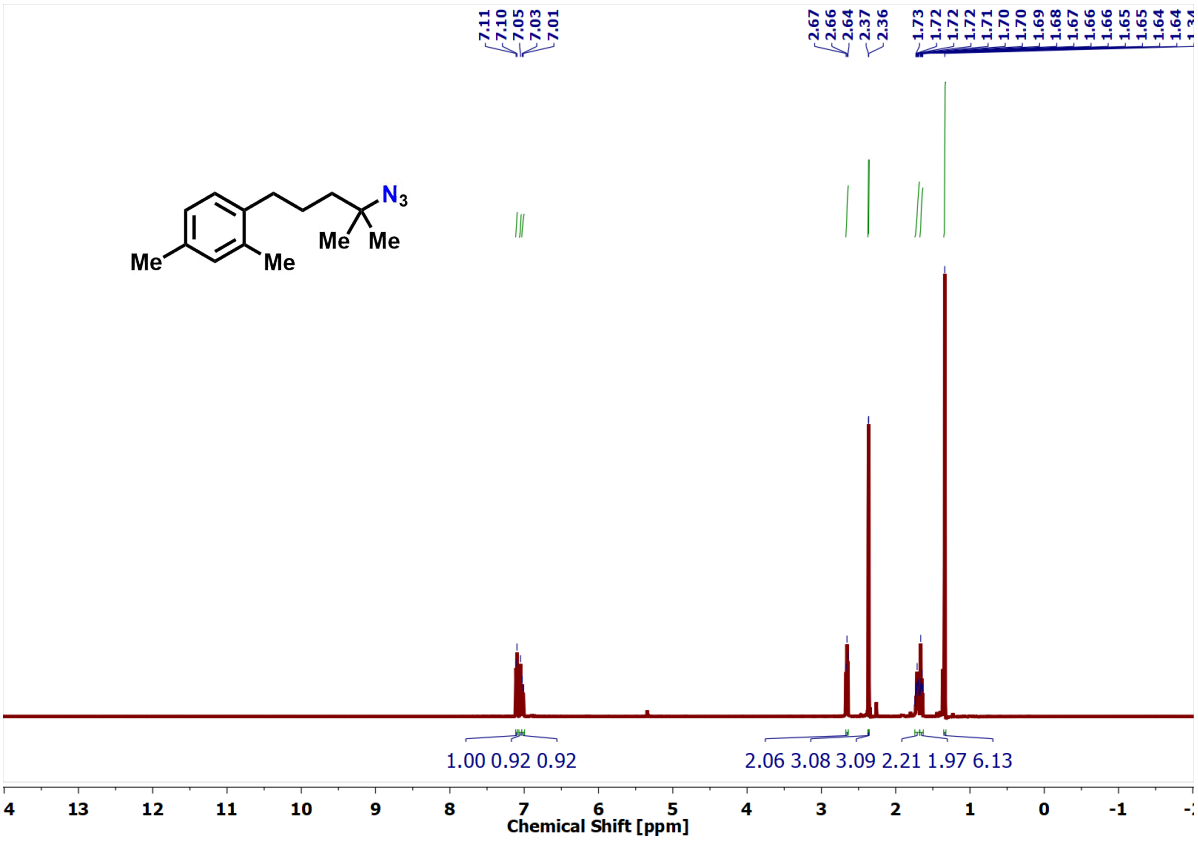

138.72
130.85
127.66
125.96
61.83
51.57
50.60
35.13
28.69
27.64
Chemical Shift [ppm]

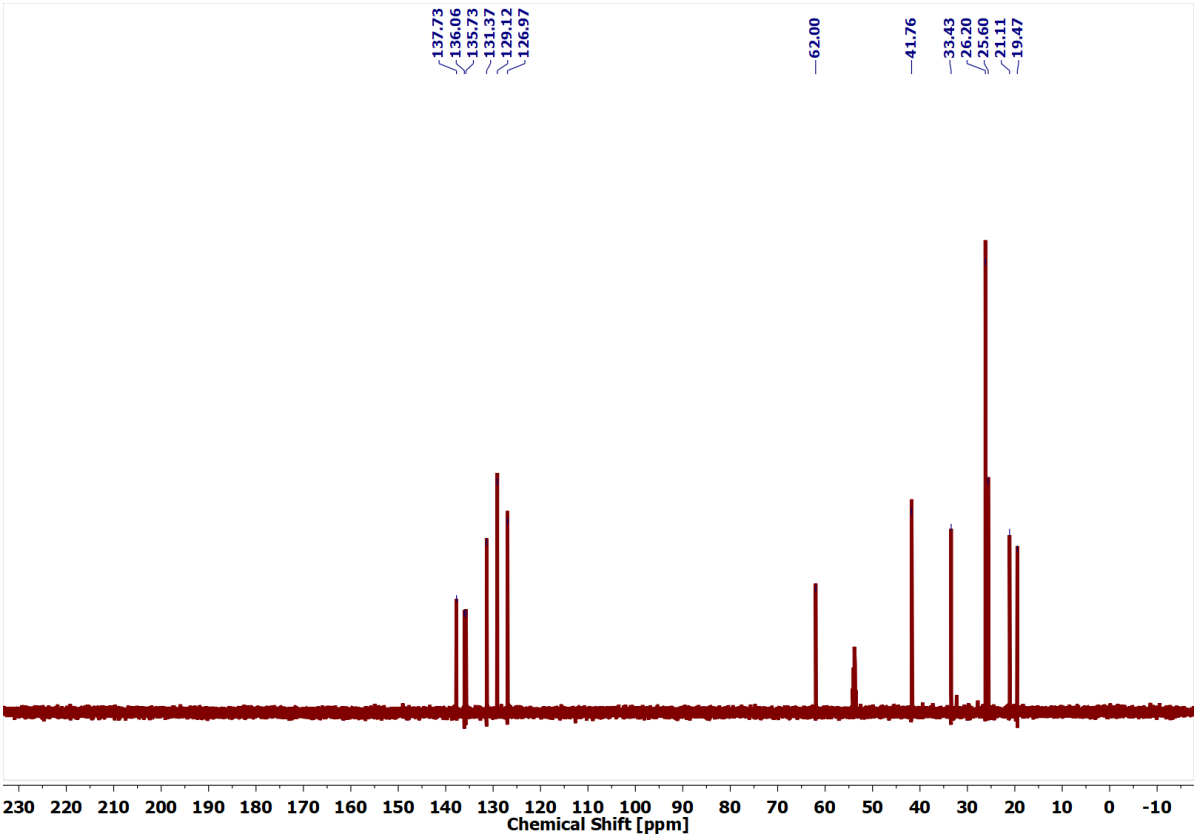

7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.16
7.16
7.15
7.15
2.70
2.68
2.67
2.39
1.73
1.73
1.72
1.71
1.71
1.71
1.70
1.69
1.67
1.67
1.67
1.66
1.65
1.64
1.64
1.63
Me
N3
Me
Me
4.00
2.07 3.07 2.07 2.07 6.15
Chemical Shift [ppm]

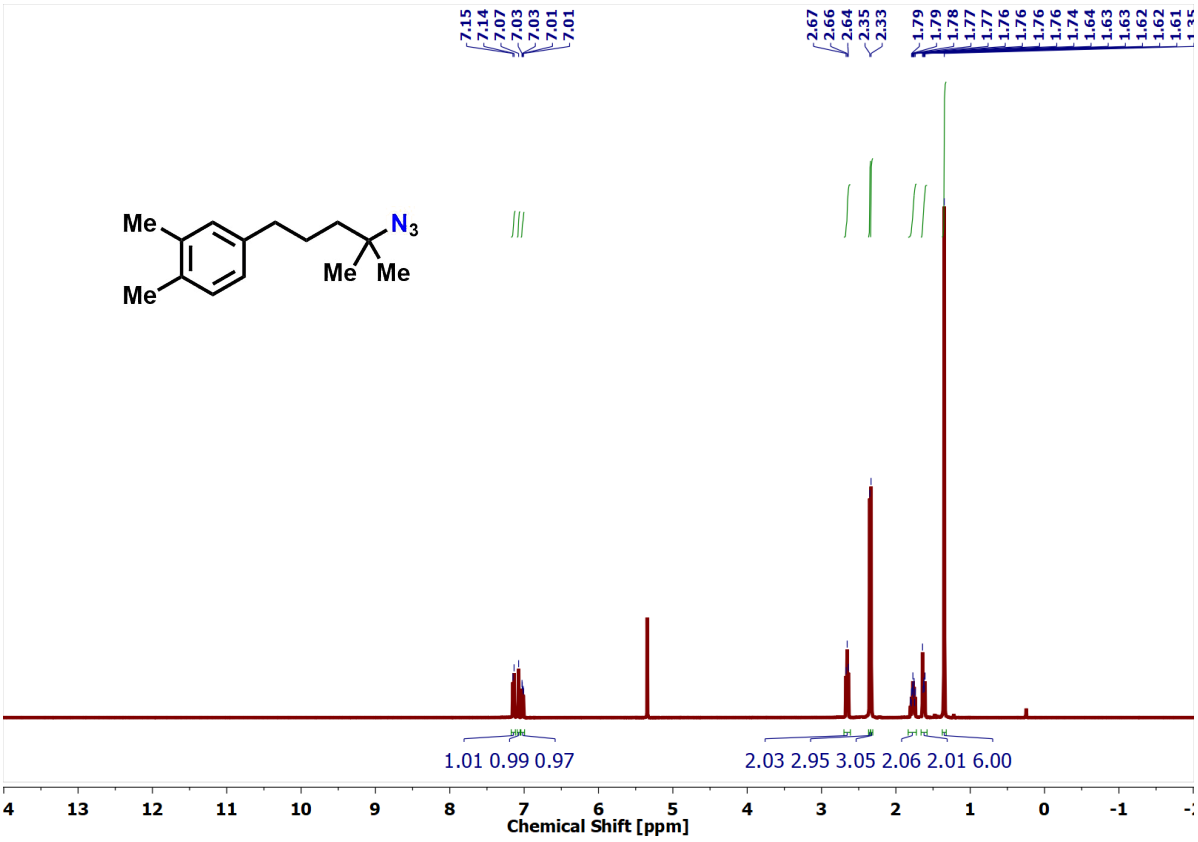

140.85
136.30
130.52
129.12
126.32
126.30
61.96
41.70
33.76
26.16
25.42
19.49
Chemical Shift [ppm]

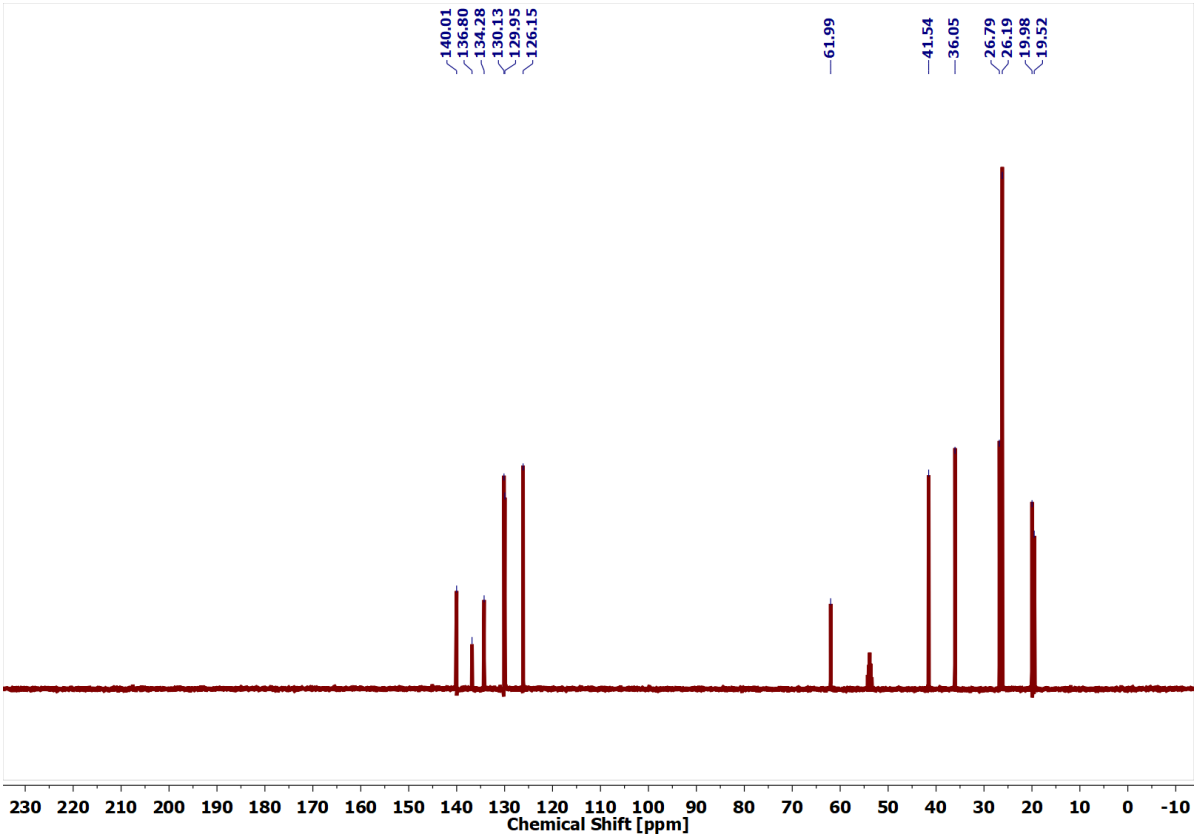

7.30
7.29
7.27
7.14
7.13
7.12
7.10
2.72
2.70
2.69
2.45
1.84
1.82
1.82
1.81
1.81
1.81
1.80
1.79
1.79
1.78
1.77
1.66
1.65
1.65
1.64
1.64
1.63
Me
N3
Me
Me
1.07 3.00
2.05 3.09 2.12 2.07 6.00
Chemical Shift [ppm]

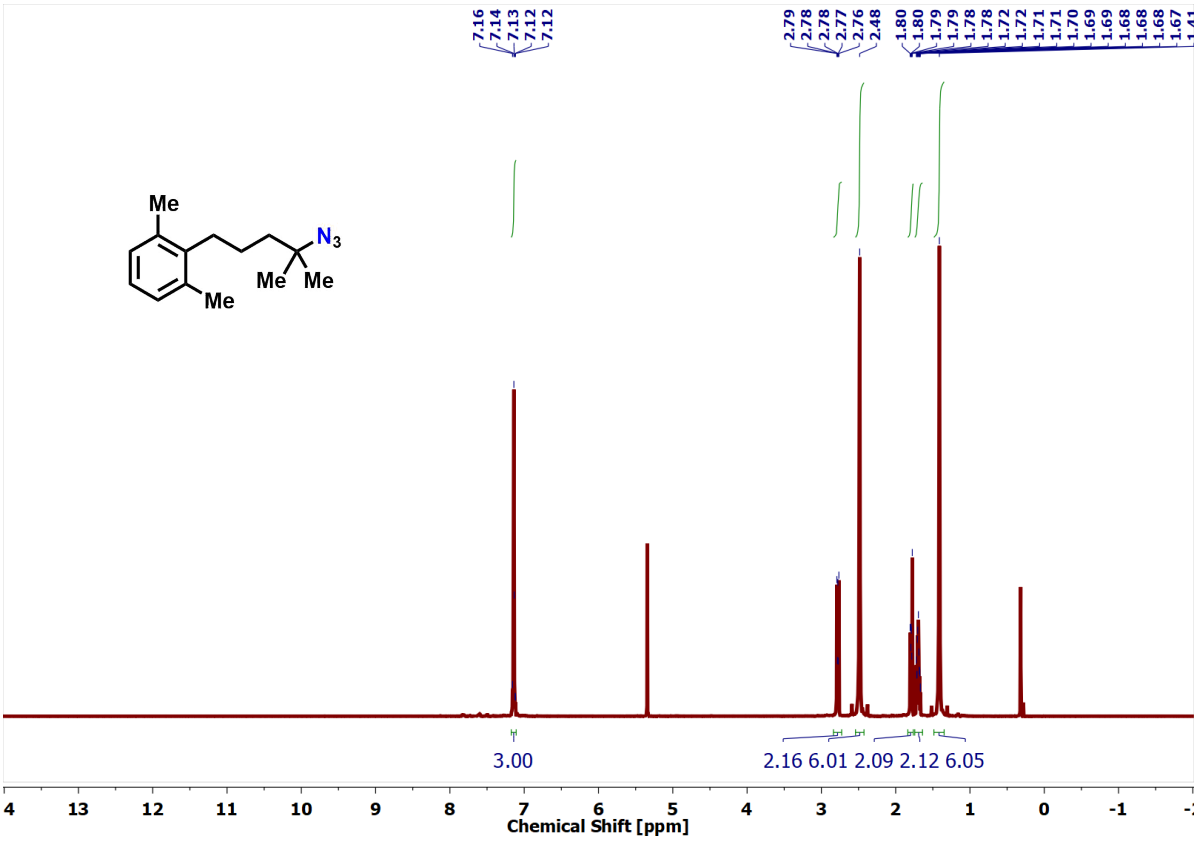

142.60
138.31
129.64
128.67
127.00
125.86
61.96
41.53
36.45
26.71
26.21
21.66
Chemical Shift [ppm]

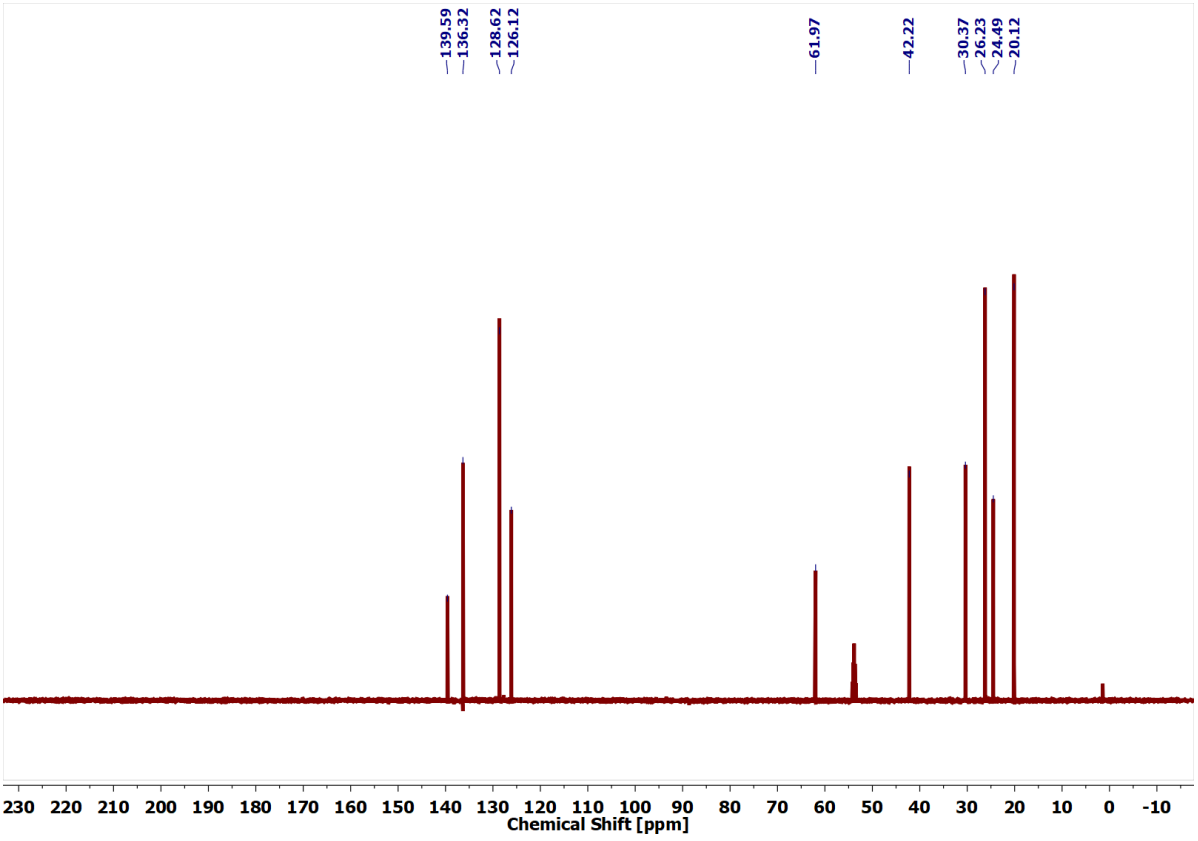

7.11
7.10
7.05
7.03
7.01
2.67
2.66
2.64
2.37
2.36
1.73
1.72
1.72
1.72
1.71
1.70
1.70
1.69
1.68
1.67
1.66
1.66
1.65
1.65
1.64
1.64
N3
Me
Me
Me
Me
1.00 0.92 0.92
2.06 3.08 3.09 2.21 1.97 6.13
Chemical Shift [ppm]

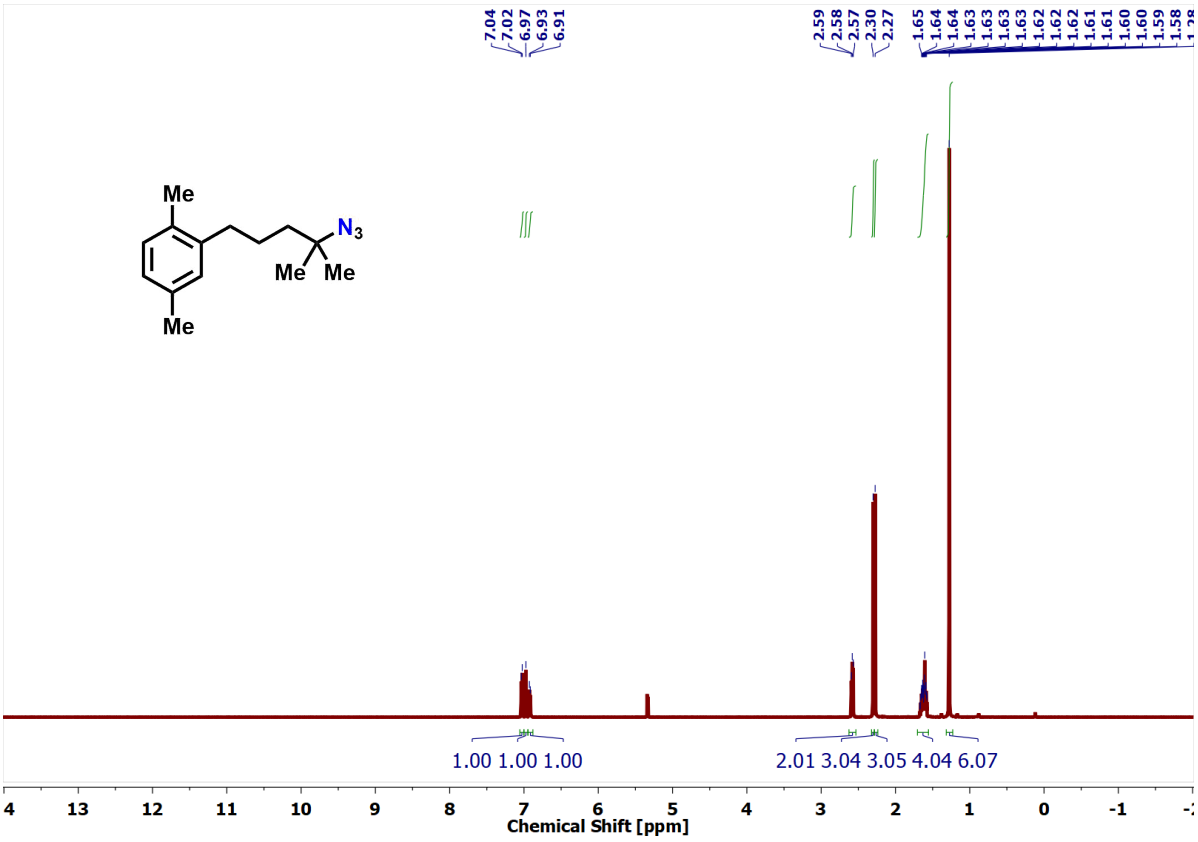

137.73
136.06
135.73
131.37
129.12
126.97
62.00
41.76
33.43
26.20
25.60
21.11
19.47
Chemical Shift [ppm]

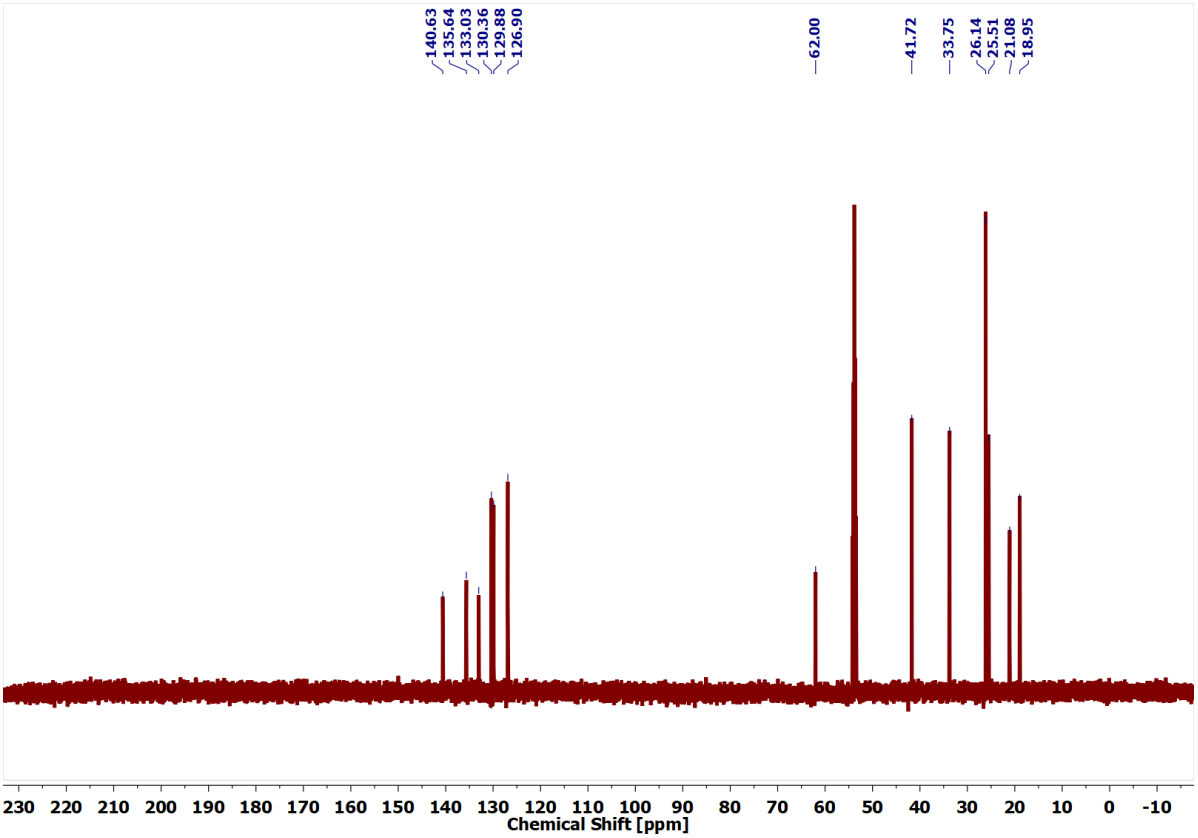

7.15
7.14
7.07
7.03
7.03
7.01
7.01
2.67
2.66
2.64
2.35
2.33
1.79
1.79
1.78
1.77
1.77
1.76
1.76
1.76
1.76
1.74
1.64
1.63
1.63
1.62
1.62
1.61
Me
Me
N3
Me
Me
1.01 0.99 0.97
2.03 2.95 3.05 2.06 2.01 6.00
Chemical Shift [ppm]

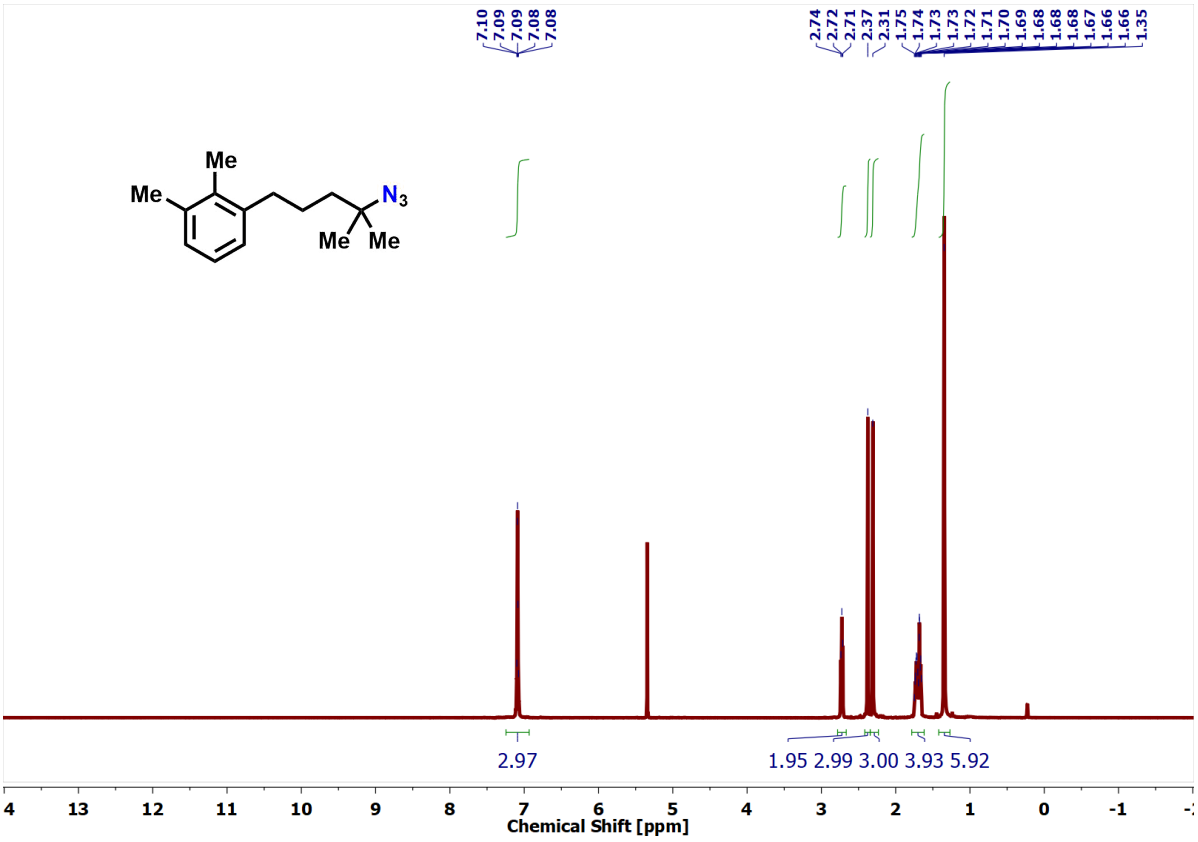

140.01
136.80
134.28
130.13
129.95
126.15
61.99
41.54
36.05
26.79
26.19
19.98
19.52
Chemical Shift [ppm]

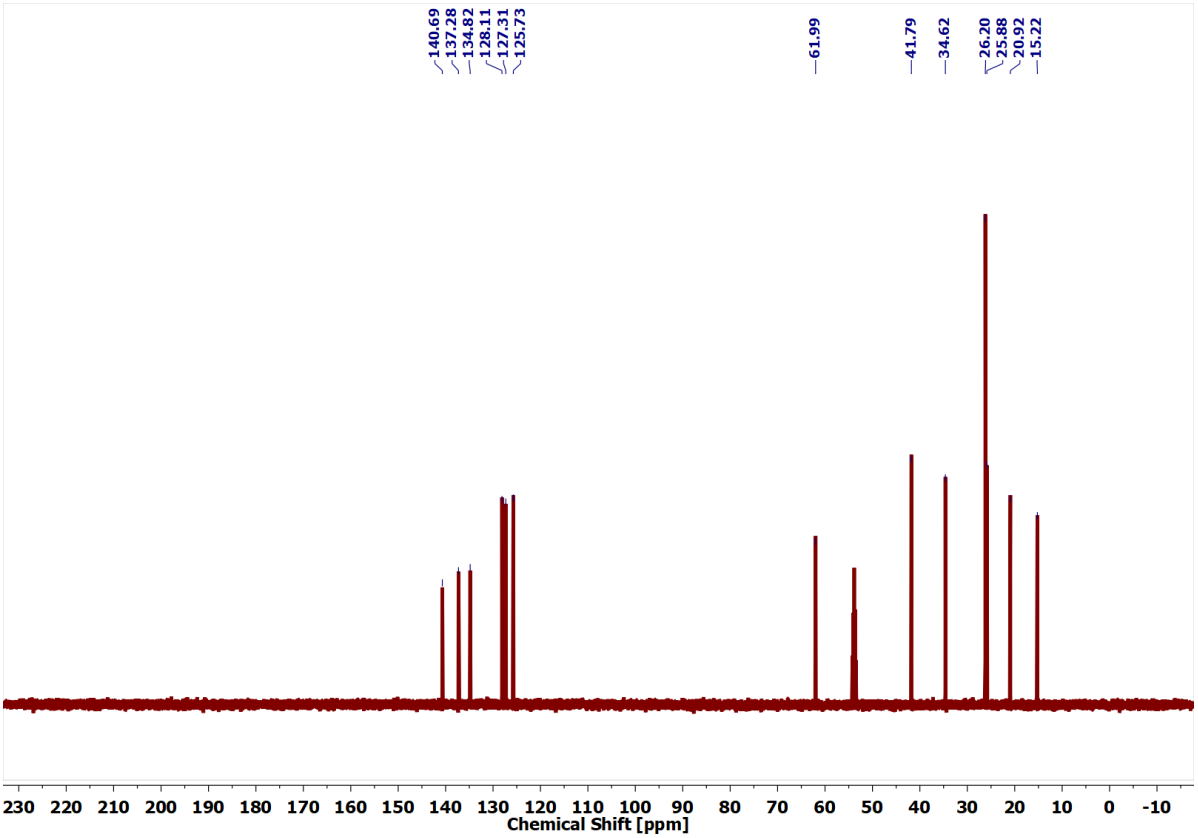

Me
N3
Me
Me
Me
7.16
7.14
7.13
7.12
7.12
2.79
2.78
2.78
2.77
2.76
2.48
1.80
1.80
1.79
1.79
1.78
1.78
1.72
1.72
1.71
1.71
1.70
1.69
1.69
1.68
1.68
1.67
3.00
2.16 6.01 2.09 2.12 6.05
Chemical Shift [ppm]


139.59
136.32
128.62
126.12
61.97
42.22
30.37
26.23
24.49
20.12
Chemical Shift [ppm]


7.04
7.02
6.97
6.93
6.91
2.59
2.58
2.57
2.30
2.27
1.65
1.64
1.64
1.63
1.63
1.63
1.63
1.62
1.62
1.62
1.61
1.61
1.60
1.60
1.59
1.58
Me
N3
Me
Me
Me
1.00 1.00 1.00
2.01 3.04 3.05 4.04 6.07
Chemical Shift [ppm]


140.63
135.64
133.03
130.36
129.88
126.90
62.00
41.72
33.75
26.14
25.51
21.08
18.95
Chemical Shift [ppm]


7.10
7.09
7.09
7.08
7.08
2.74
2.72
2.71
2.37
2.31
1.75
1.74
1.73
1.73
1.72
1.71
1.70
1.69
1.68
1.68
1.68
1.67
1.66
1.66
1.35
Me
Me
N3
Me
Me
2.97
1.95 2.99 3.00 3.93 5.92
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift [ppm]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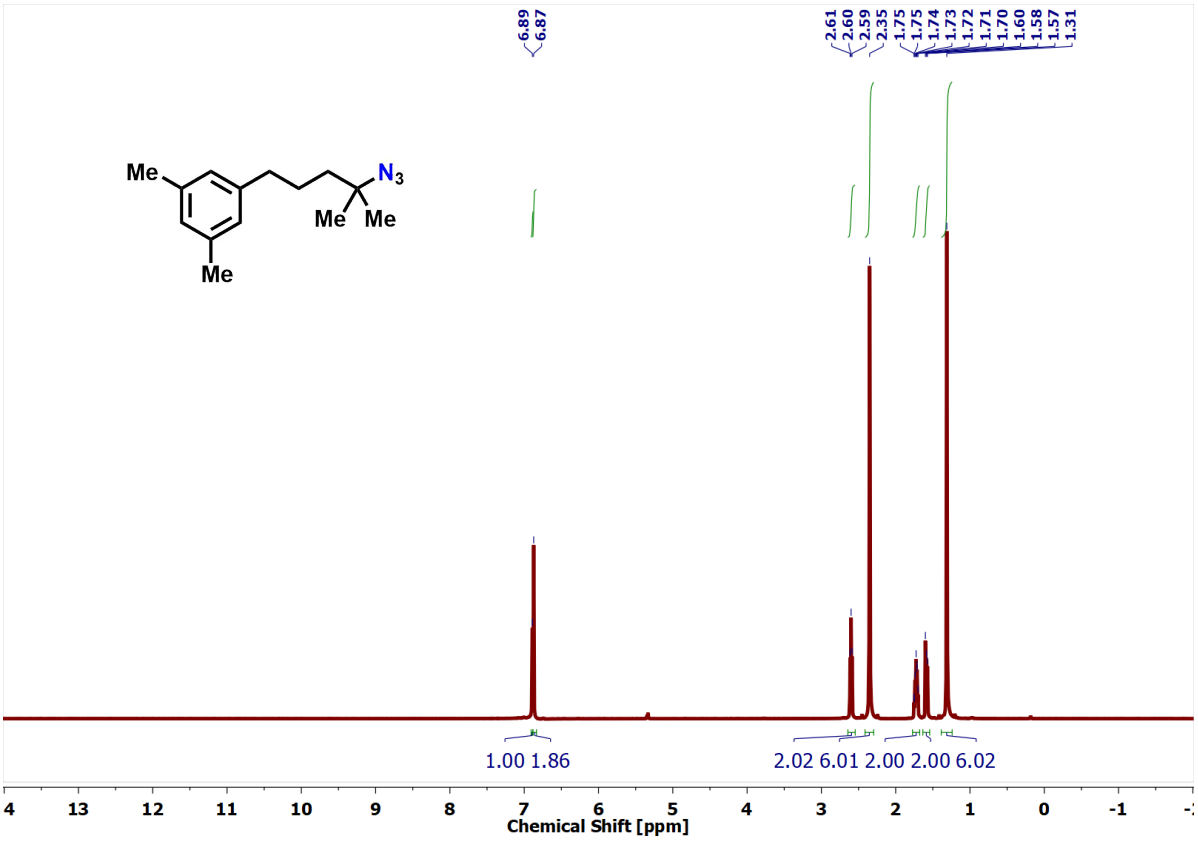
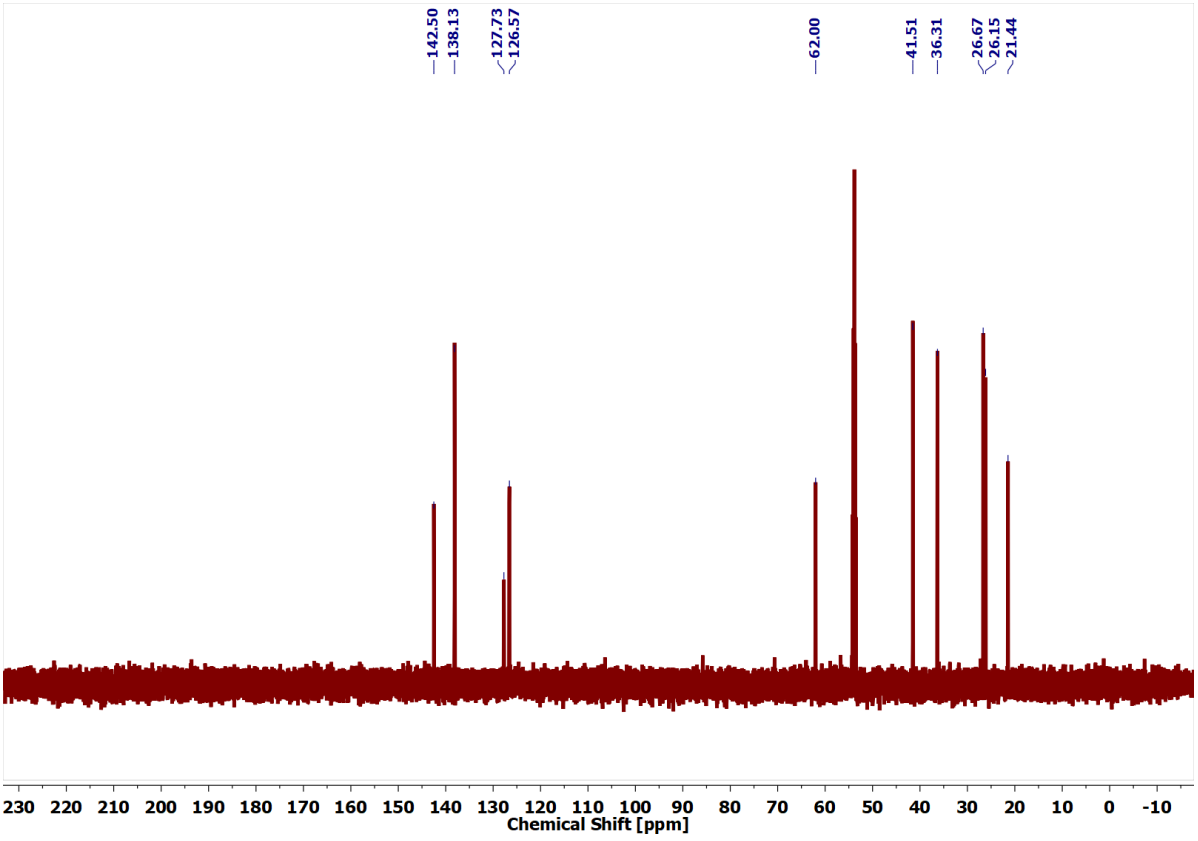
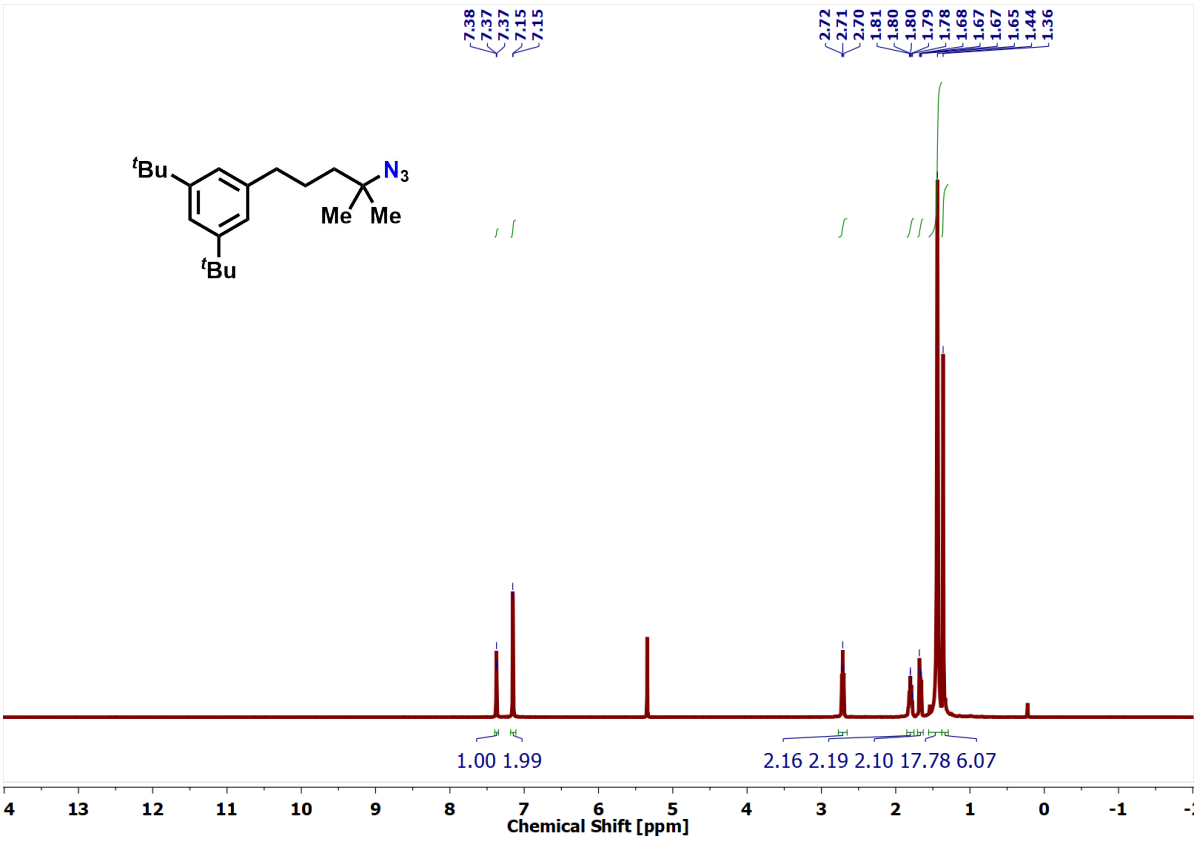
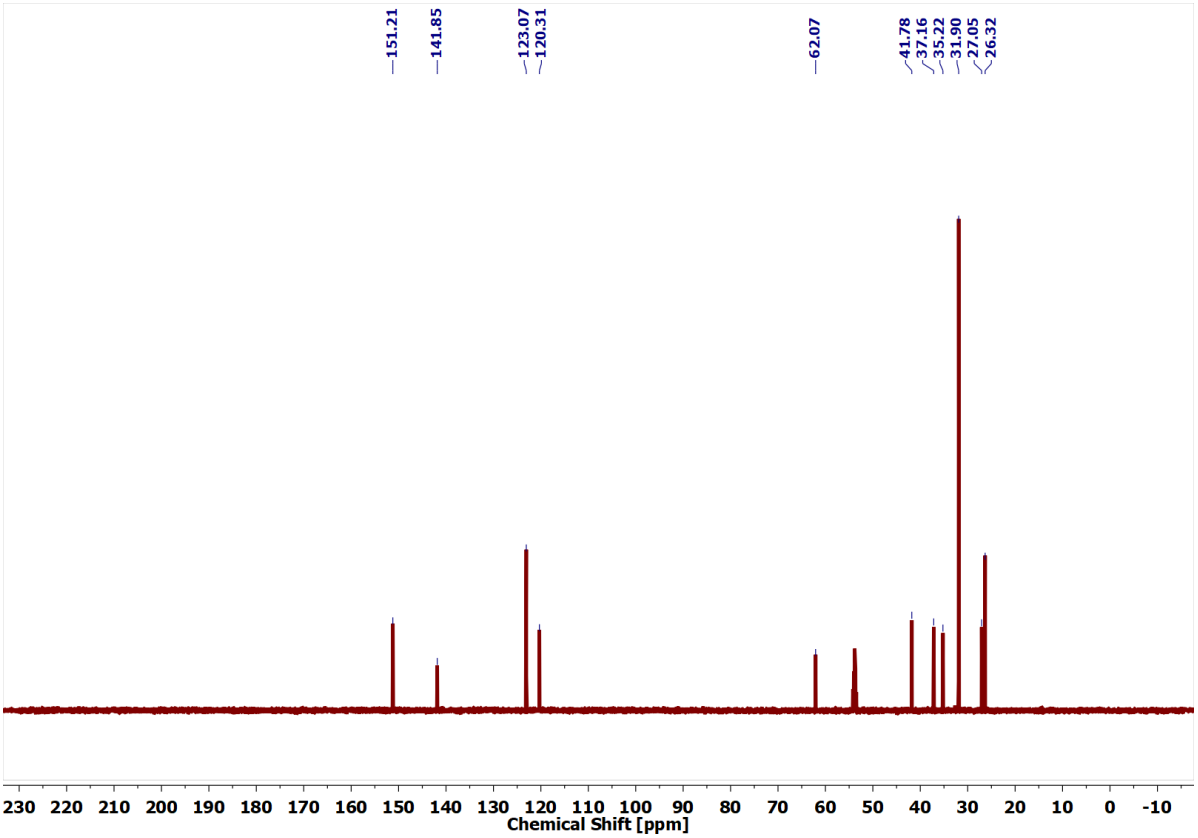
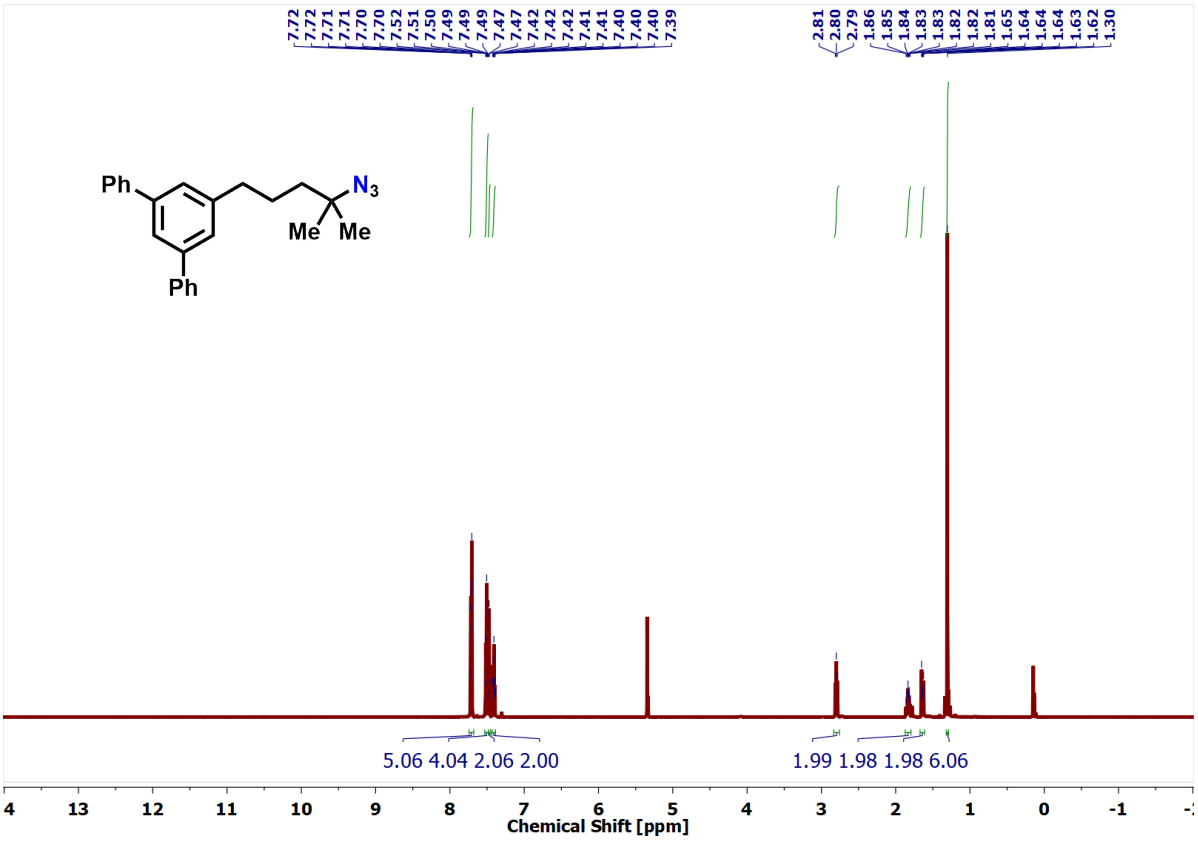
137.28
134.82
128.11
127.31
125.73
61.99
41.79
34.62
26.20
25.88
20.92
15.22
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift [ppm]

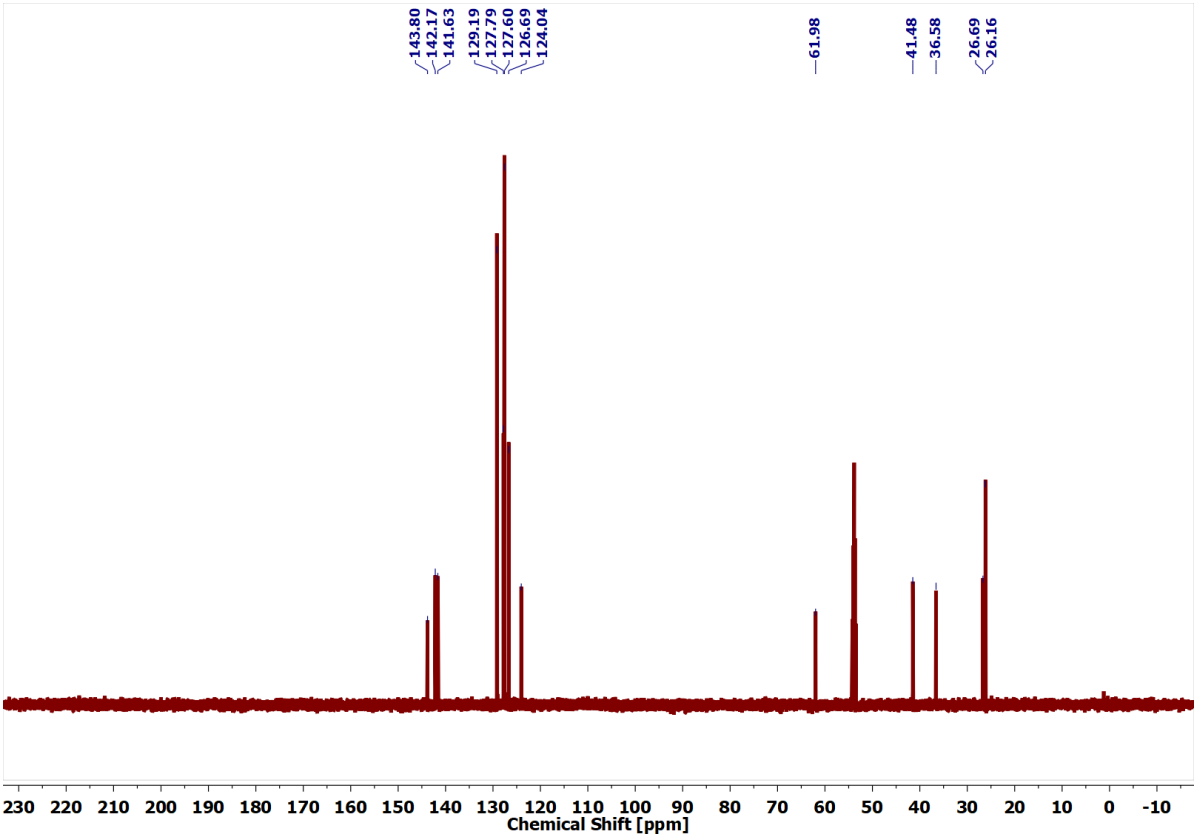

6.89
6.87
2.61
2.60
2.59
2.35
1.75
1.75
1.74
1.73
1.72
1.71
1.70
1.60
1.58
1.57
1.31
Me
N3
Me
Me
Me
1.00 1.86
2.02 6.01 2.00 2.00 6.02
Chemical Shift [ppm]

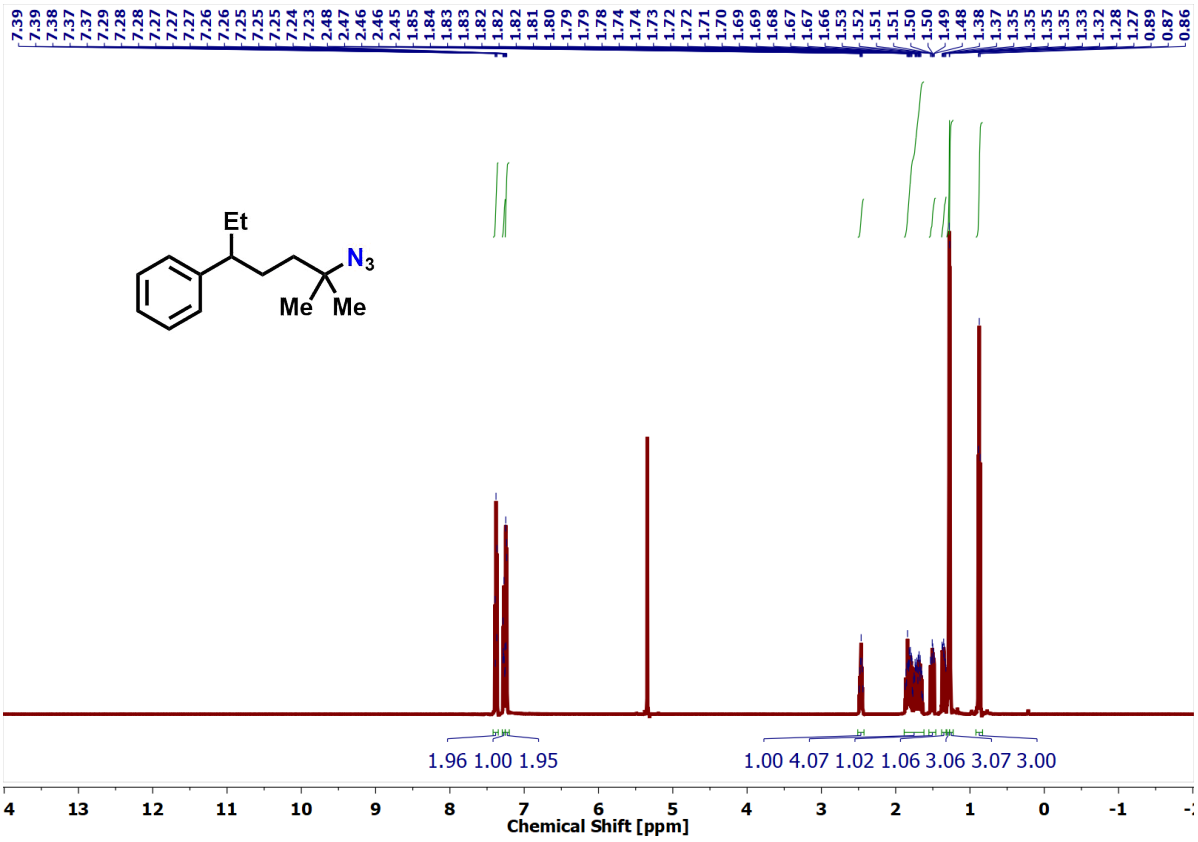

142.50
138.13
127.73
126.57
62.00
41.51
36.31
26.67
26.15
21.44
Chemical Shift [ppm]

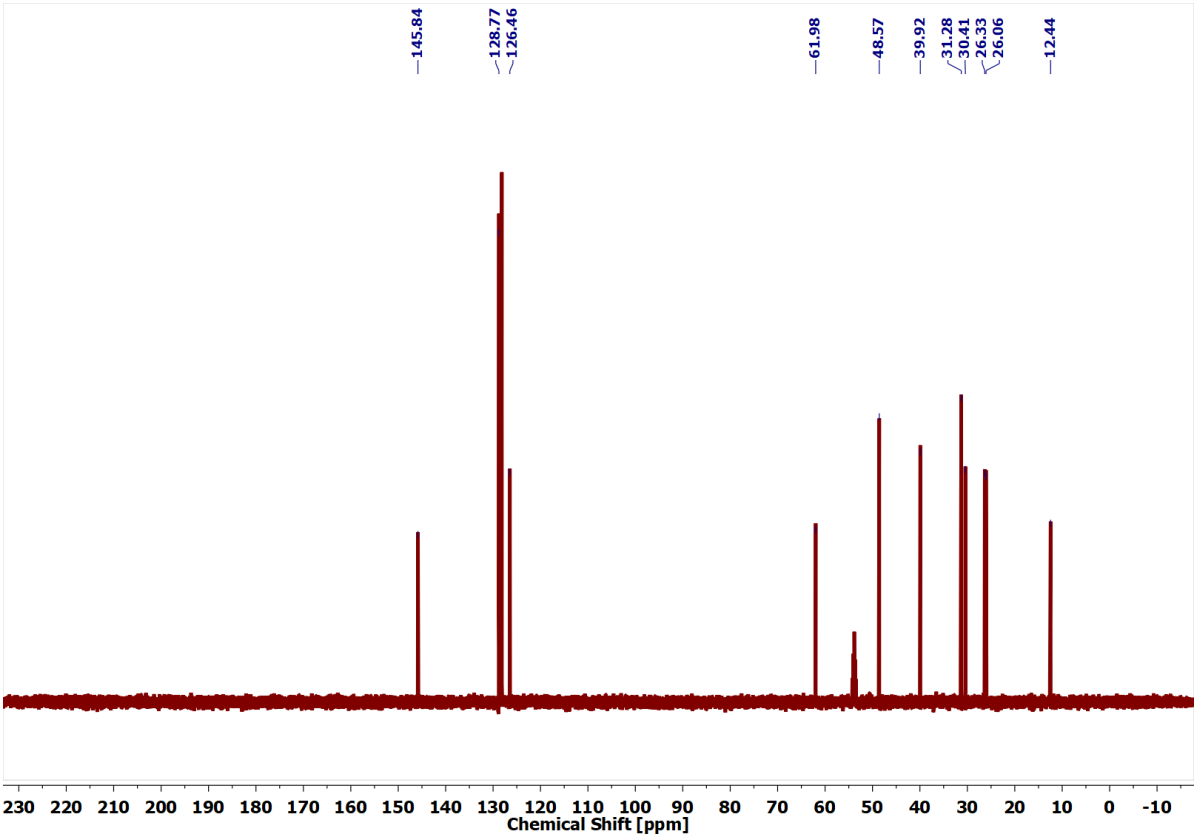

7.38
7.37
7.37
7.15
7.15
2.72
2.71
2.70
1.81
1.80
1.80
1.79
1.78
1.68
1.67
1.67
1.65
1.44
1.36
tBu
N3
Me
Me
tBu
1.00 1.99
2.16 2.19 2.10 17.78 6.07
Chemical Shift [ppm]

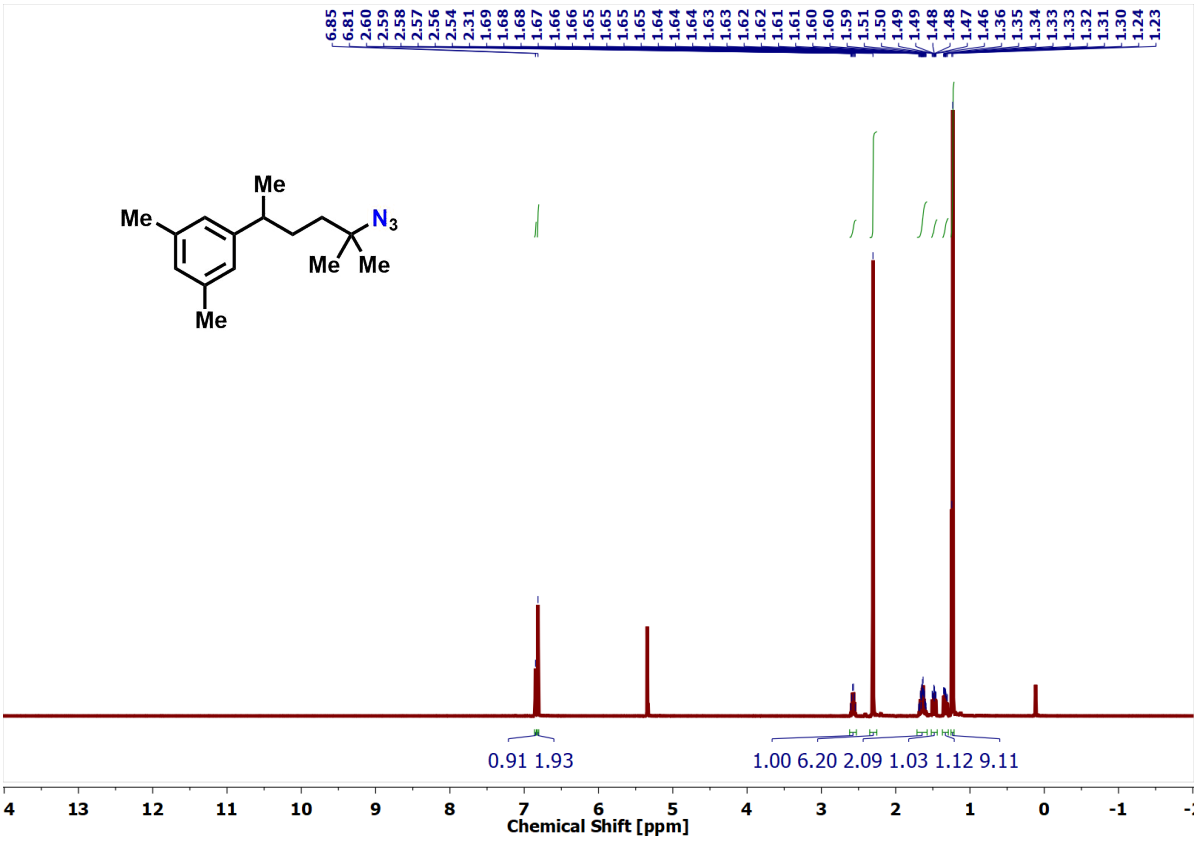

151.21
141.85
123.07
120.31
62.07
41.78
37.16
35.22
31.90
27.05
26.32
Chemical Shift [ppm]

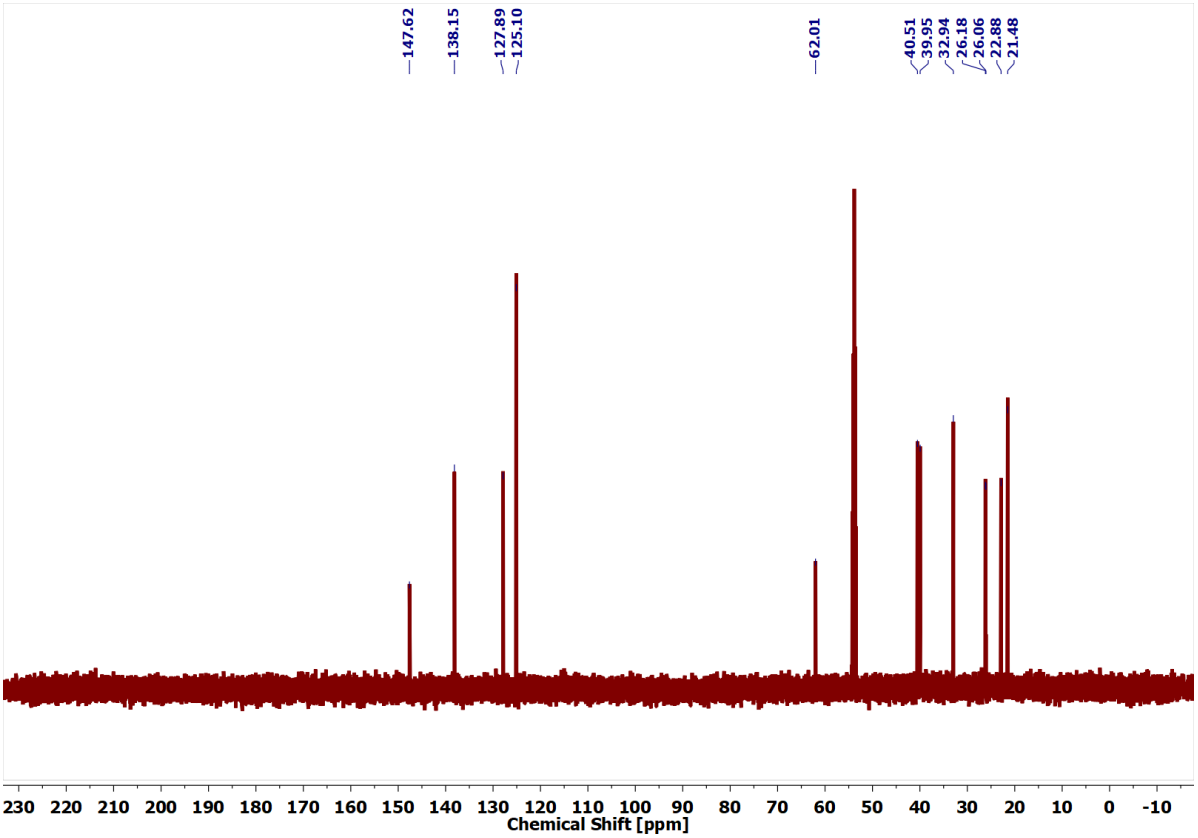

7.72
7.72
7.71
7.71
7.70
7.70
7.52
7.51
7.50
7.49
7.49
7.49
7.47
7.47
7.42
7.42
7.42
7.41
7.41
7.40
7.40
7.40
7.39
2.81
2.80
2.79
1.86
1.85
1.84
1.83
1.83
1.82
1.82
1.81
1.65
1.64
1.64
1.64
1.63
1.62
1.30
Ph
N3
Me
Me
Ph
5.06 4.04 2.06 2.00
1.99 1.98 1.98 6.06
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

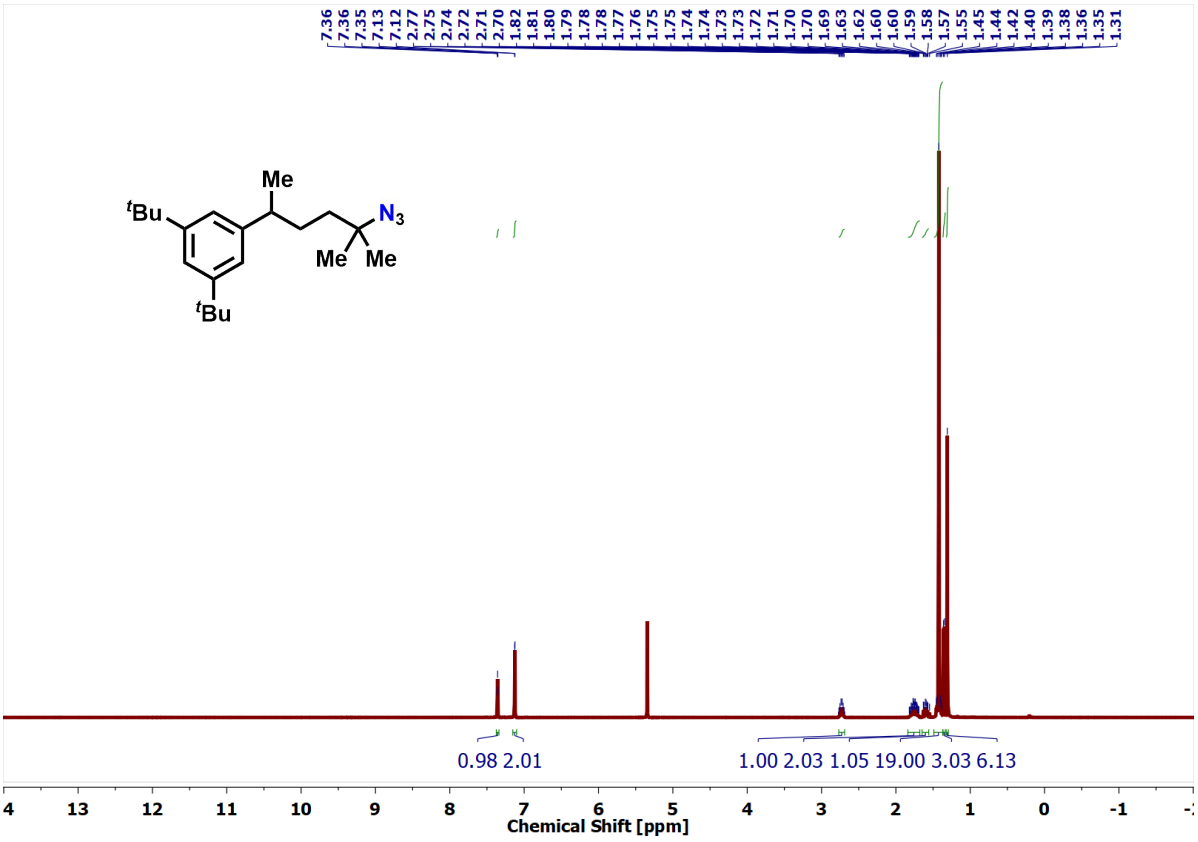

143.80
142.17
141.63
129.19
127.79
127.60
126.69
124.04
61.98
41.48
36.58
26.69
26.16
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

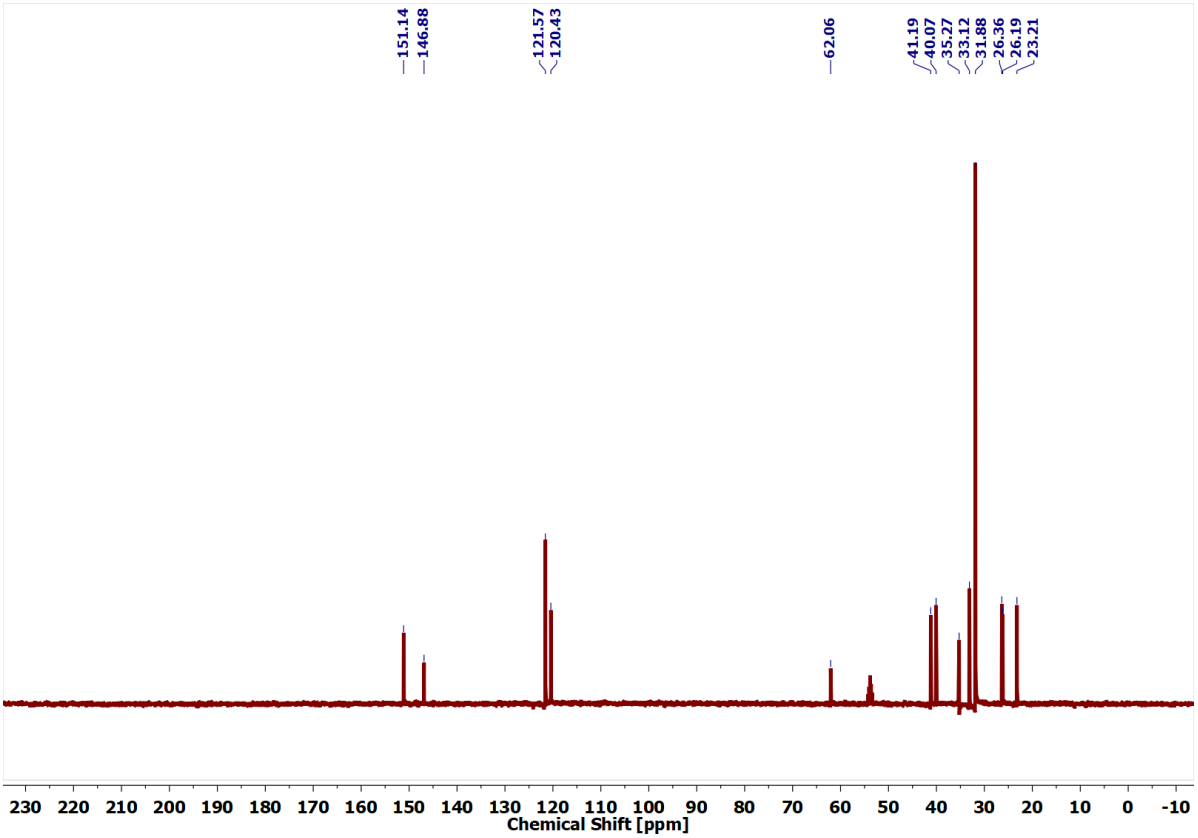

Et
N3
Me Me
1.96 1.00 1.95
1.00 4.07 1.02 1.06 3.06 3.07 3.00
Chemical Shift [ppm]


145.84
128.77
126.46
61.98
48.57
39.92
31.28
30.41
26.33
26.06
12.44
Chemical Shift [ppm]

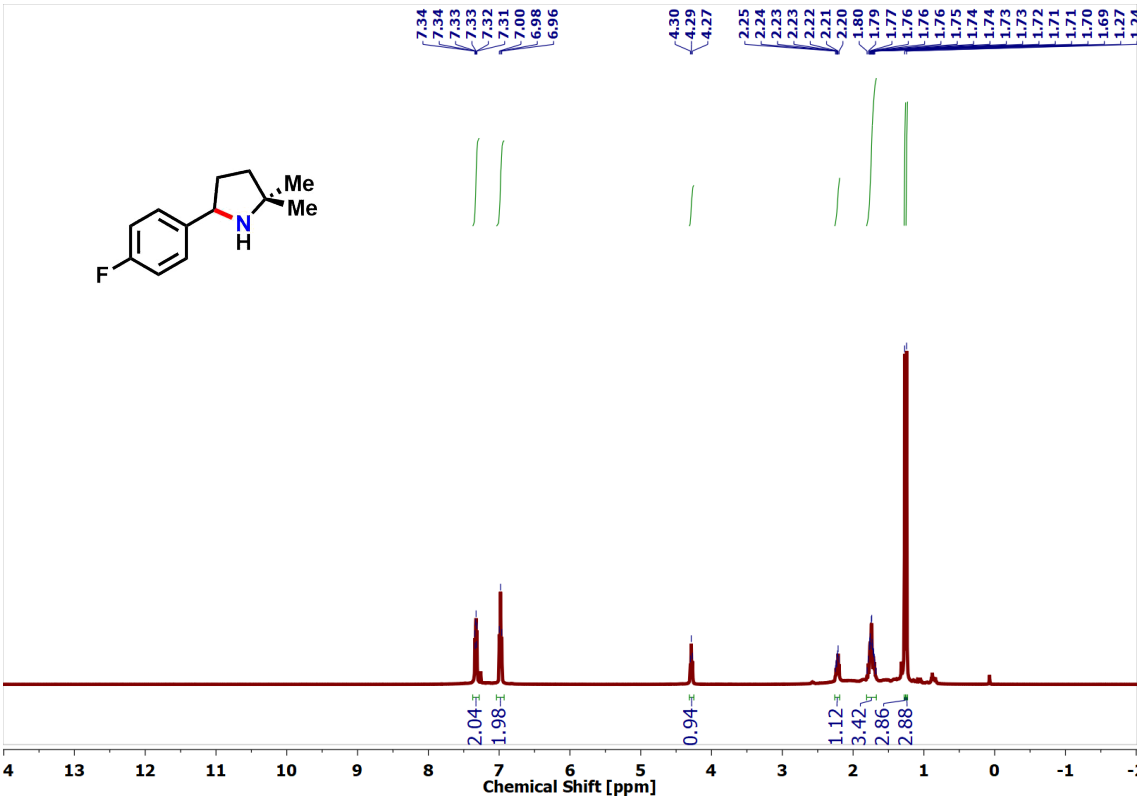

6.85 6.81 2.60 2.59 2.58 2.57 2.56 2.54 2.31 1.69 1.68 1.68 1.67 1.66 1.66 1.65 1.65 1.65 1.65 1.64 1.64 1.64 1.63 1.63 1.62 1.62 1.61 1.61 1.60 1.60 1.59 1.51 1.50 1.49 1.49 1.48 1.48 1.47 1.46 1.36 1.35 1.34 1.33 1.33 1.32 1.31 1.30 1.24 1.23
Me
Me
N3
Me
Me
Me
0.91 1.93
1.00 6.20 2.09 1.03 1.12 9.11
Chemical Shift [ppm]

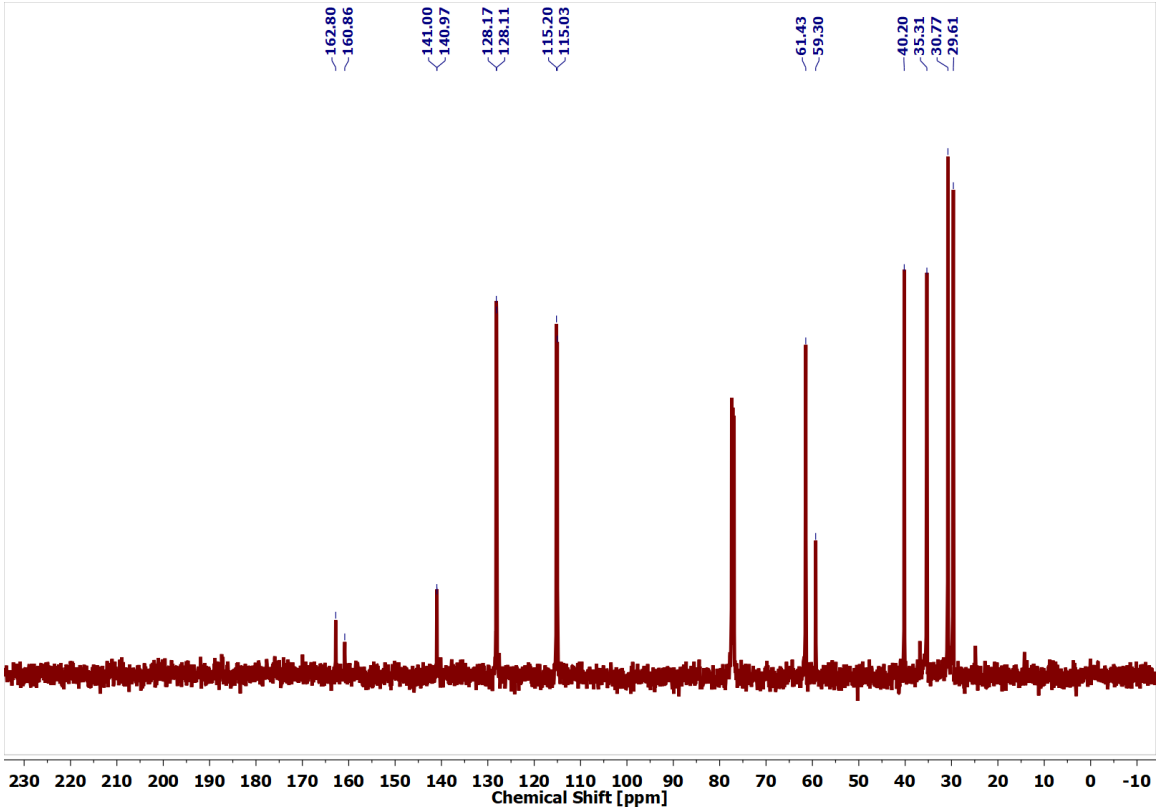

147.62
138.15
127.89
125.10
62.01
40.51
39.95
32.94
26.18
26.06
22.88
21.48
Chemical Shift [ppm]

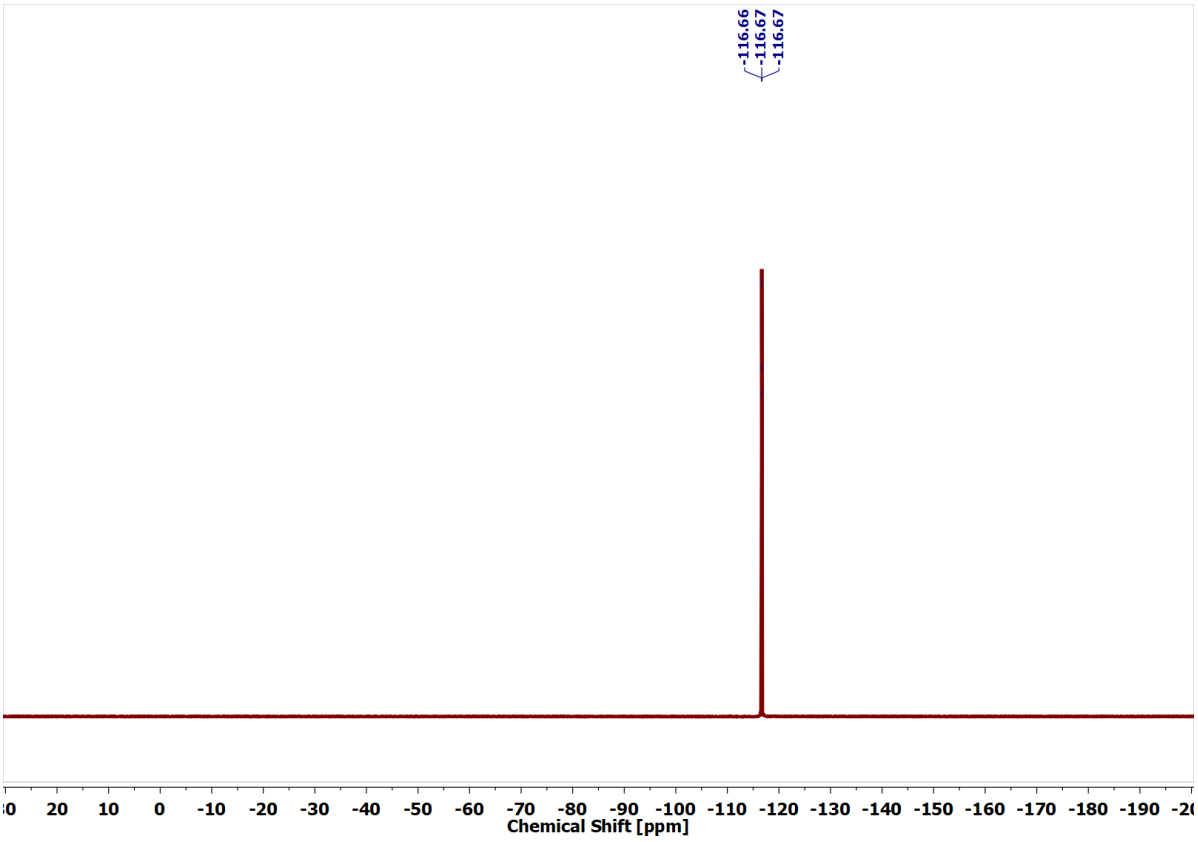

7.36 7.36 7.35 7.13 7.12 2.77 2.75 2.74 2.72 2.71 2.70 1.82 1.81 1.80 1.79 1.78 1.78 1.77 1.76 1.75 1.75 1.74 1.74 1.73 1.73 1.72 1.71 1.70 1.70 1.69 1.63 1.62 1.60 1.60 1.59 1.58 1.57 1.55 1.45 1.44 1.42 1.40 1.39 1.38 1.36 1.35 1.31
tBu
Me
N3
Me Me
tBu
0.98 2.01
1.00 2.03 1.05 19.00 3.03 6.13
Chemical Shift [ppm]

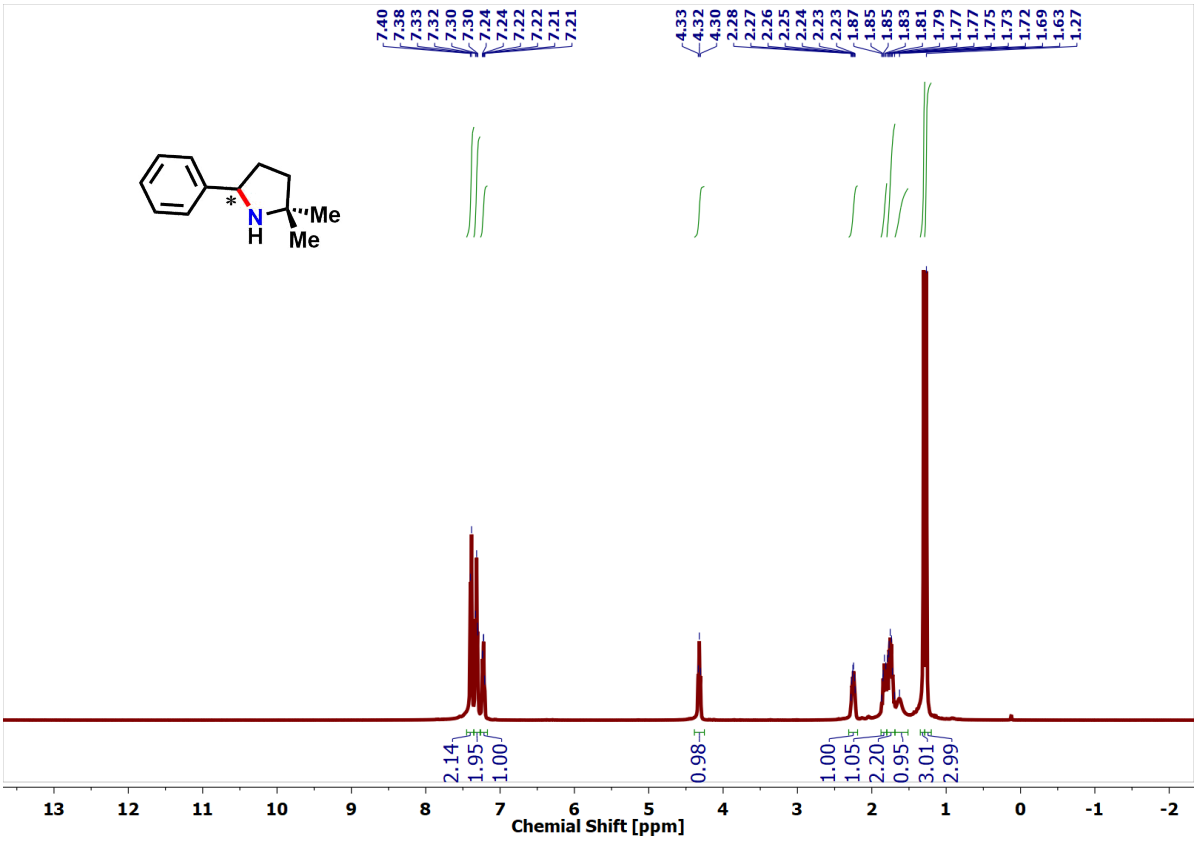

151.14
146.88
121.57
120.43
62.06
41.19
40.07
35.27
33.12
31.88
26.36
26.19
23.21
Chemical Shift [ppm]

NMR spectra of pyrrolidines






-116.66
-116.67
-116.67
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
Chemical Shift [ppm]


7.40
7.38
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7.32
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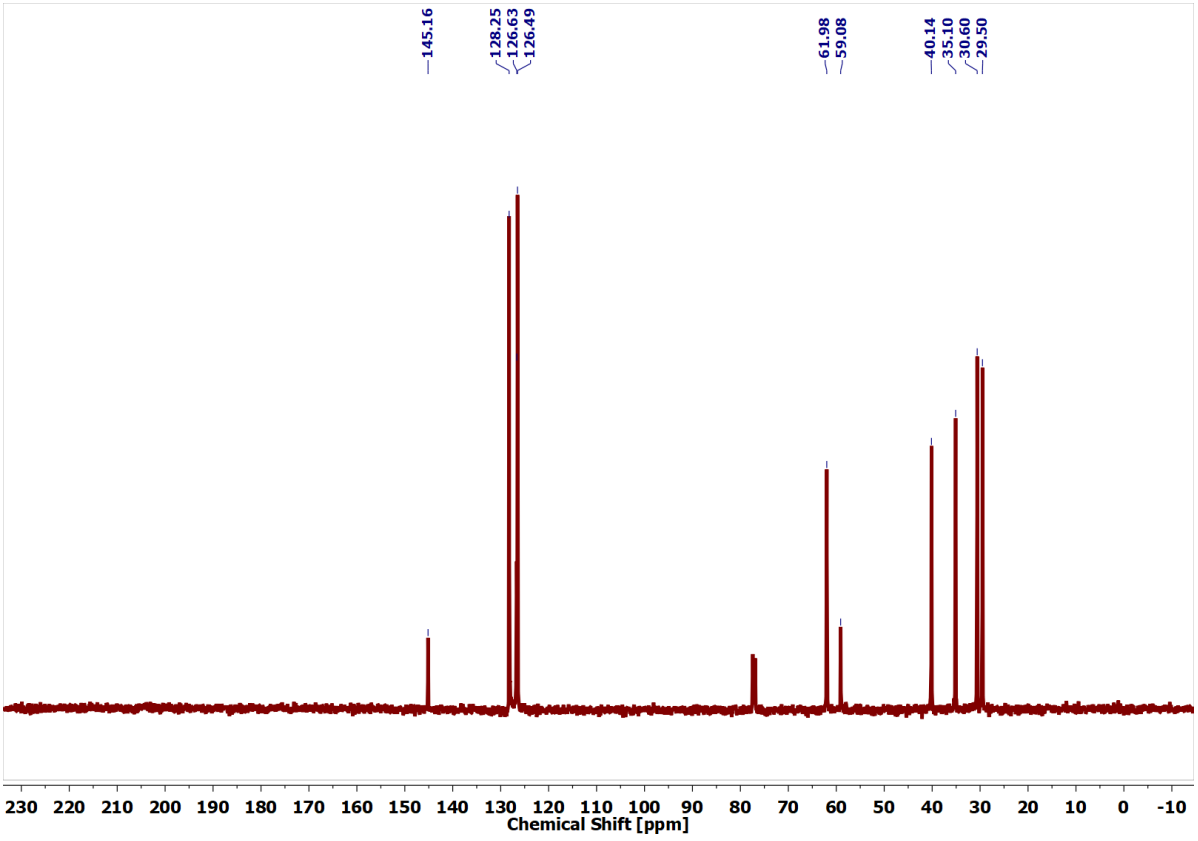
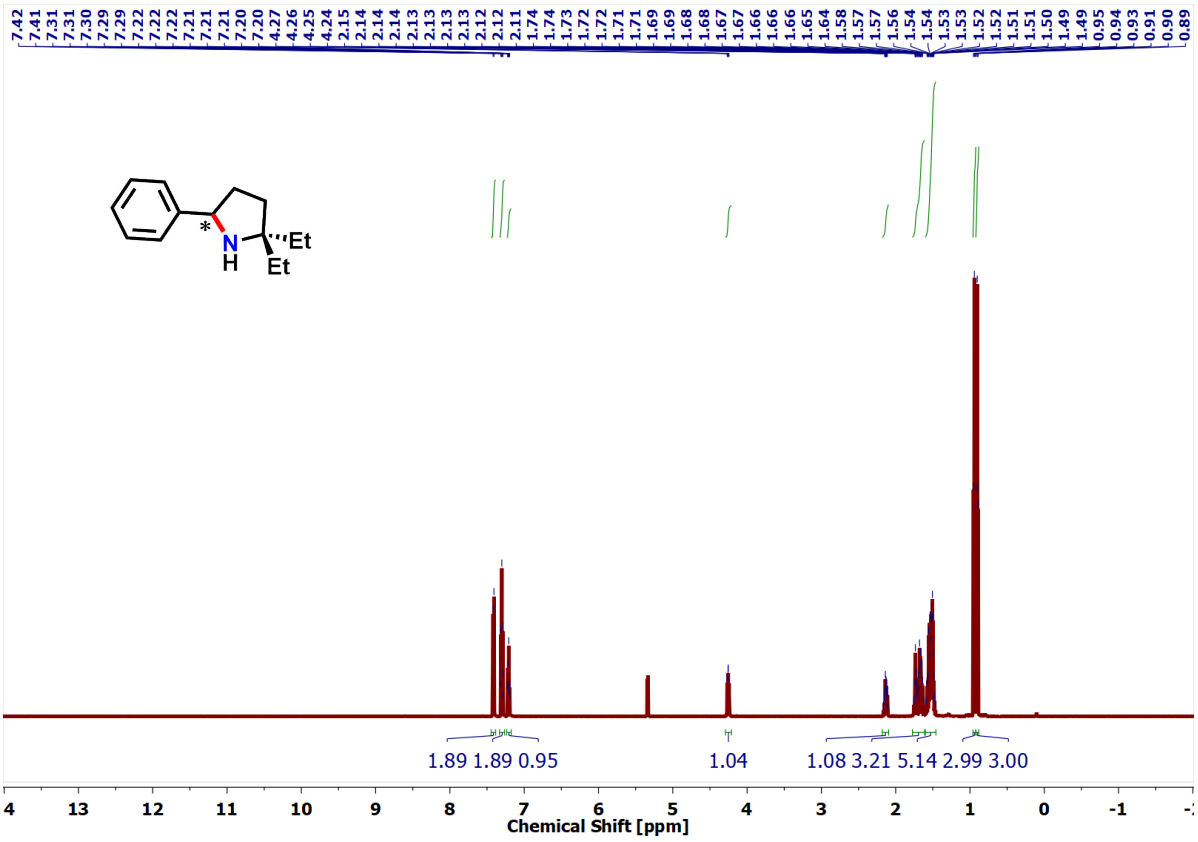
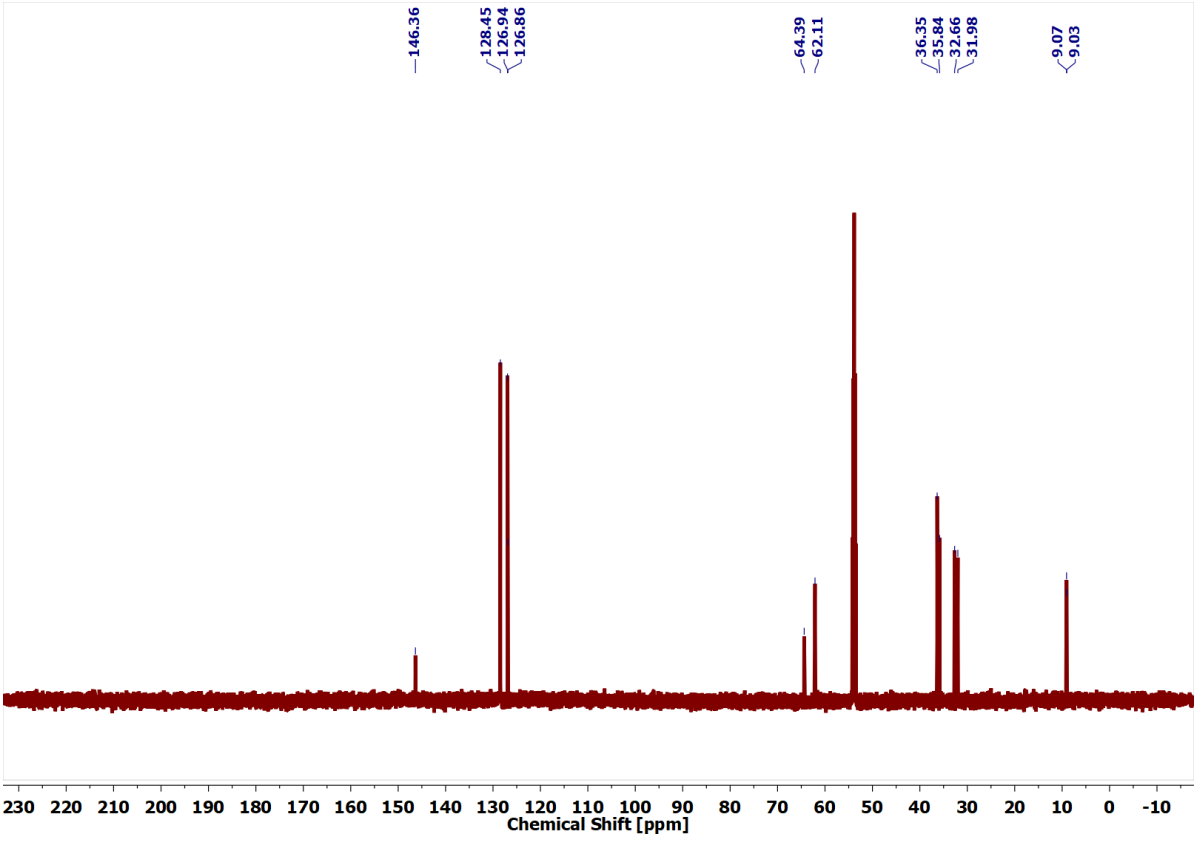
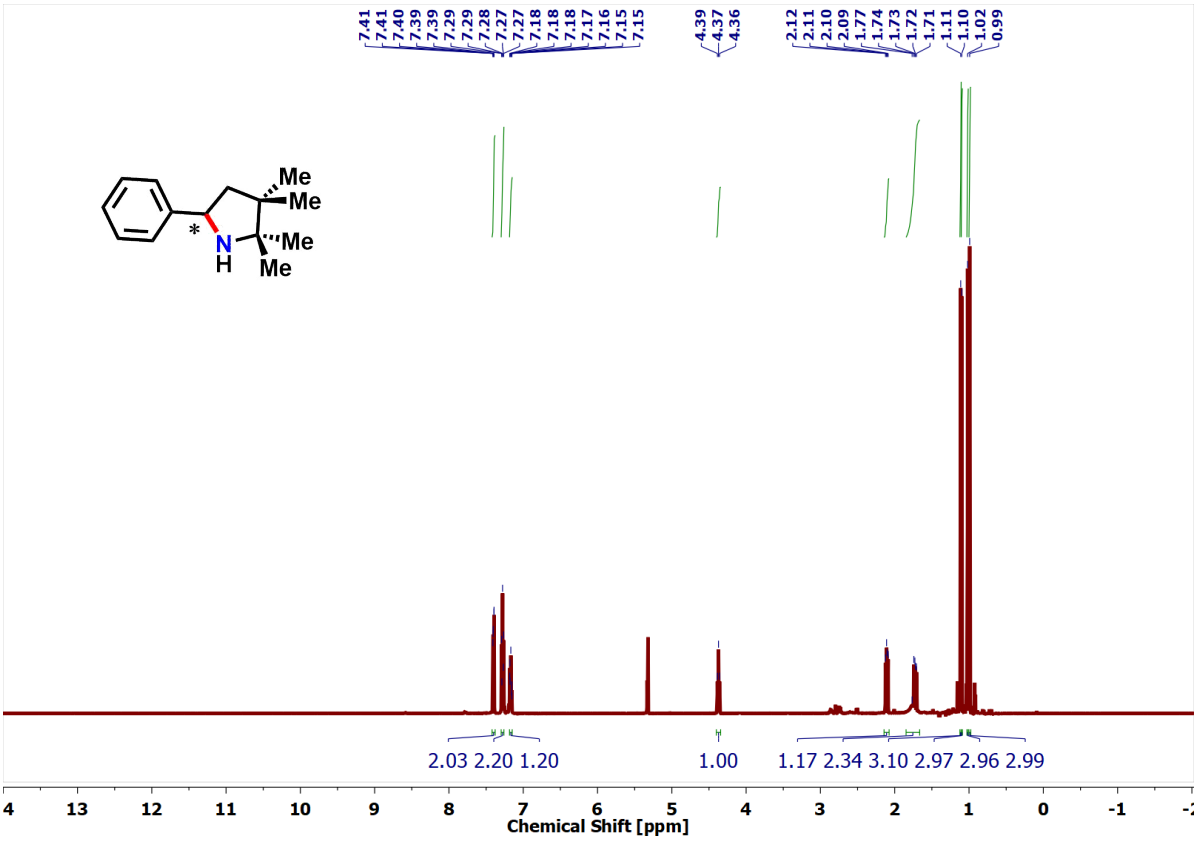
7.30
7.24
7.24
7.22
7.22
7.21
7.21
4.33
4.32
4.30
2.28
2.27
2.26
2.25
2.24
2.23
2.23
1.87
1.85
1.85
1.83
1.81
1.79
1.77
1.77
1.75
1.73
1.72
1.69
1.63
1.27
Me
Me
N
H
2.14
1.95
1.00
0.98
1.00
1.05
2.20
0.95
3.01
2.99
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
Chemial Shift [ppm]


145.16
128.25
126.63
126.49
61.98
59.08
40.14
35.10
30.60
29.50
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]


7.42 7.41 7.31 7.31 7.30 7.29 7.29 7.22 7.22 7.22 7.21 7.21 7.21 7.20 7.20 4.27 4.26 4.25 4.24 2.15 2.14 2.14 2.14 2.13 2.13 2.13 2.13 2.12 2.12 2.11 1.74 1.74 1.73 1.72 1.72 1.71 1.71 1.69 1.69 1.68 1.68 1.67 1.67 1.66 1.66 1.66 1.65 1.64 1.58 1.57 1.57 1.56 1.54 1.54 1.53 1.53 1.52 1.52 1.51 1.51 1.50 1.49 1.49 0.95 0.94 0.93 0.91 0.90 0.89
*
N
H
Et
Et
1.89 1.89 0.95
1.04
1.08 3.21 5.14 2.99 3.00
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]


146.36
128.45
126.94
126.86
64.39
62.11
36.35
35.84
32.66
31.98
9.07
9.03
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]


7.41
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7.39
7.39
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7.28
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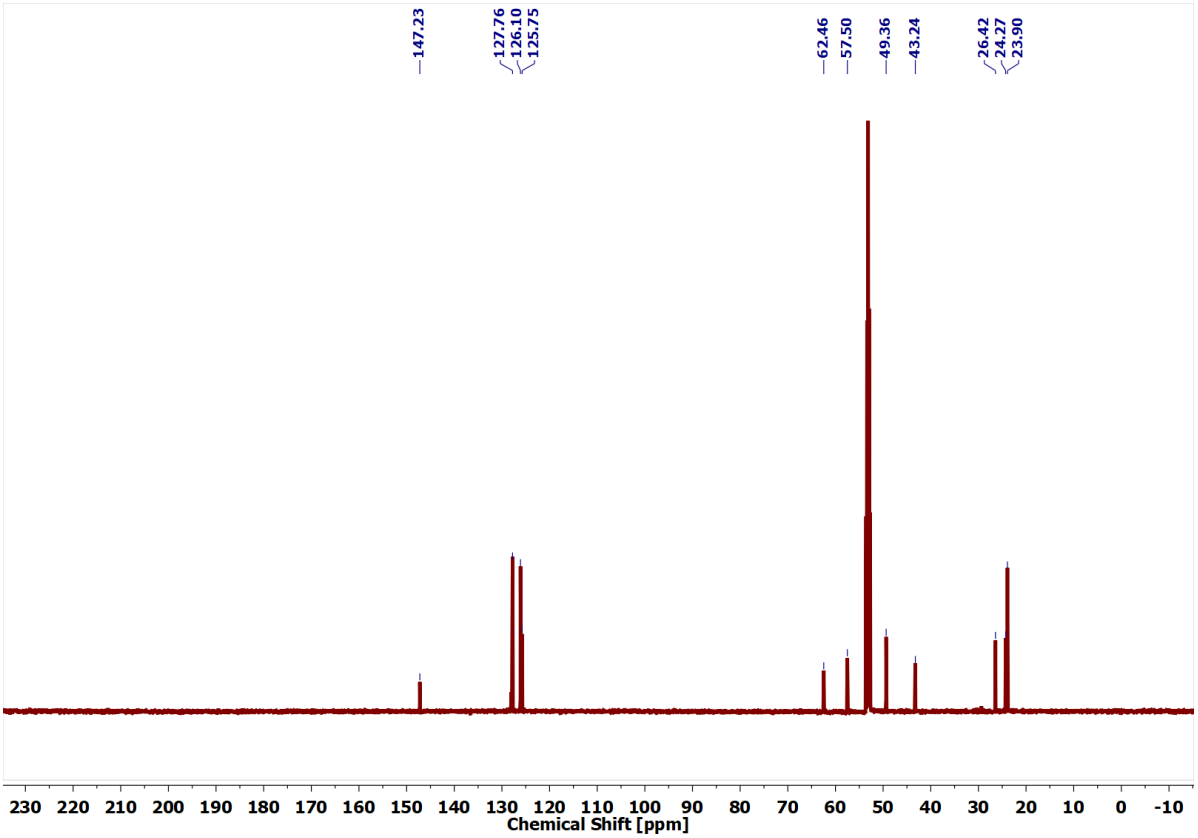
7.27
7.18
7.18
7.18
7.17
7.16
7.15
7.15
4.39
4.37
4.36
2.12
2.11
2.10
2.09
1.77
1.74
1.73
1.72
1.71
1.11
1.10
1.02
0.99
Me
Me
Me
Me
N
H
2.03 2.20 1.20
1.00
1.17 2.34 3.10 2.97 2.96 2.99
Chemical Shift [ppm]


147.23
127.76
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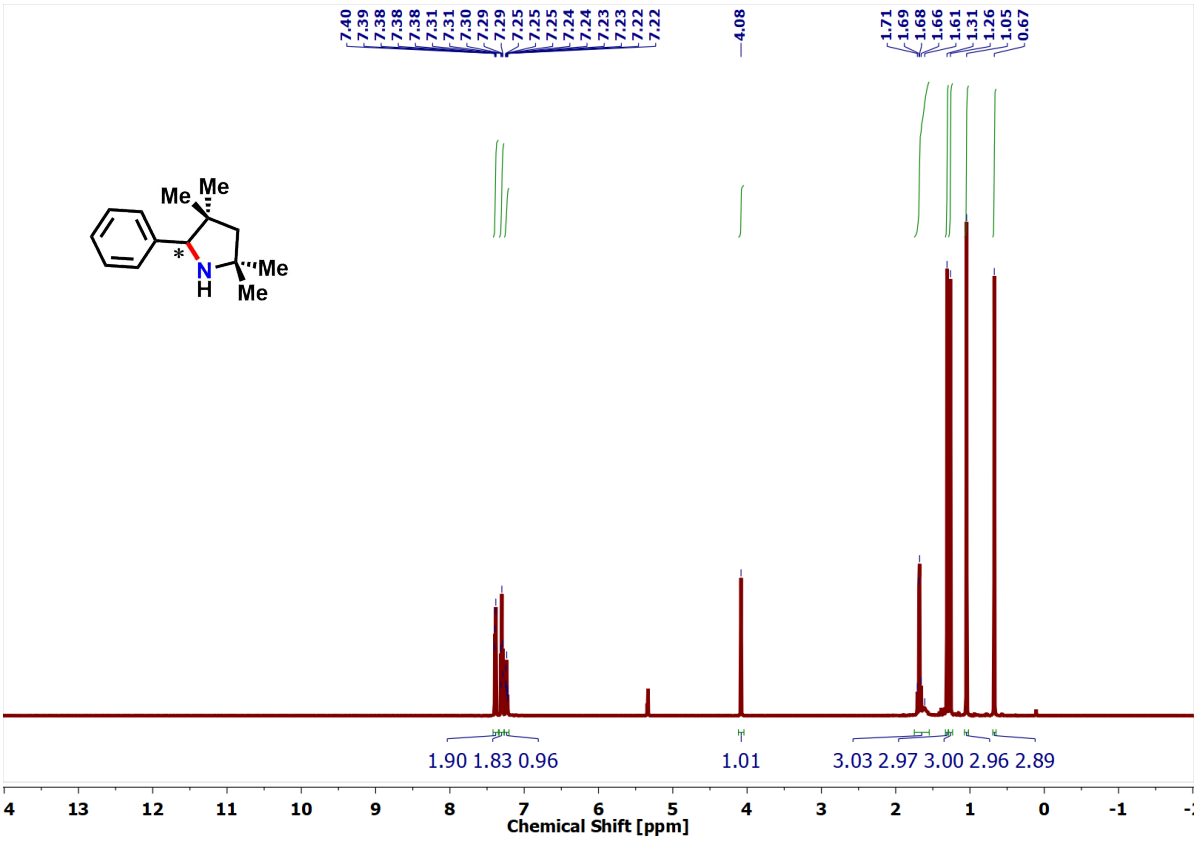
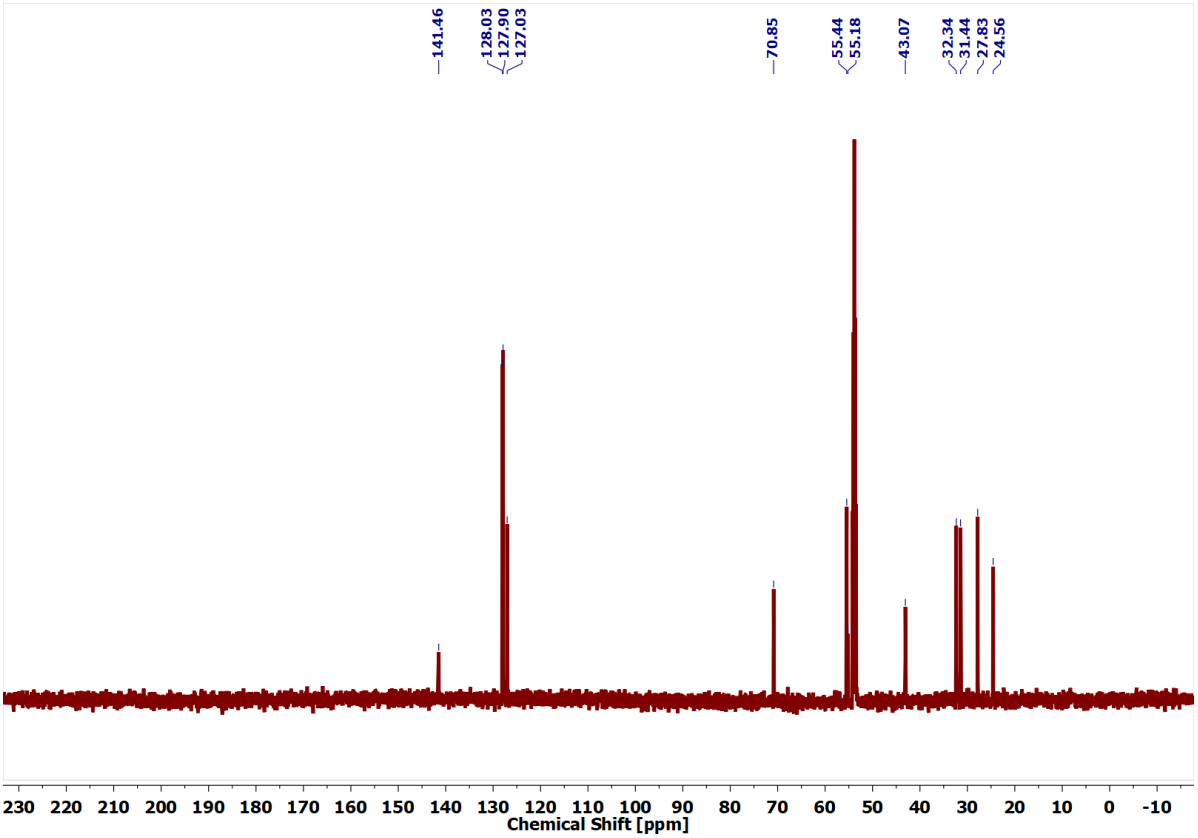
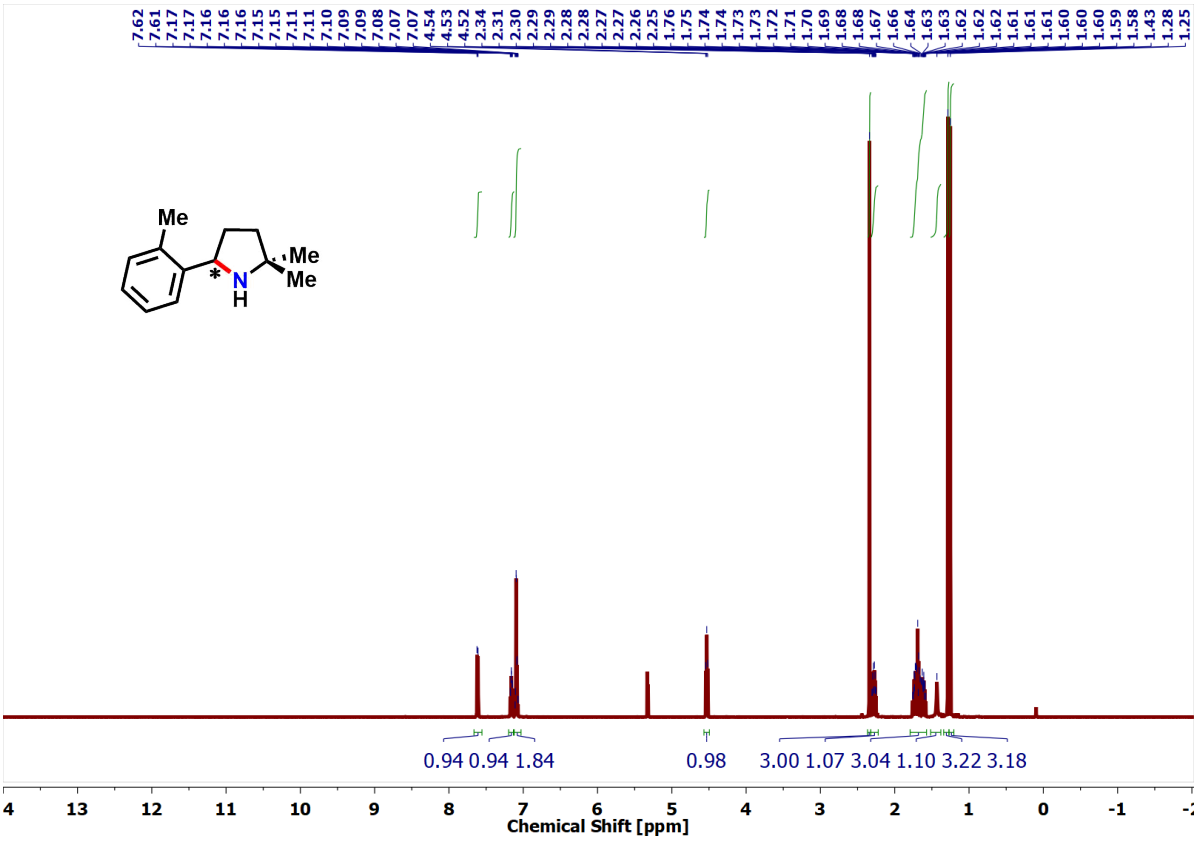
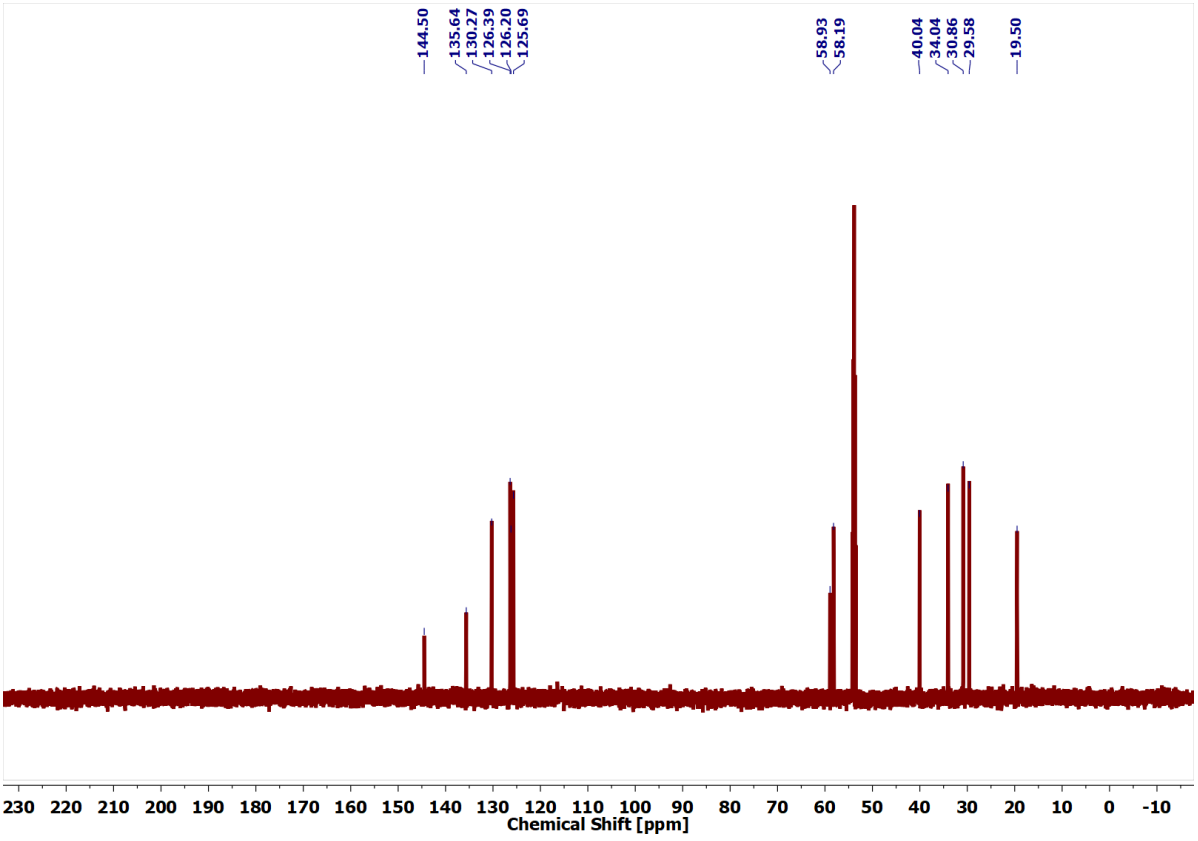
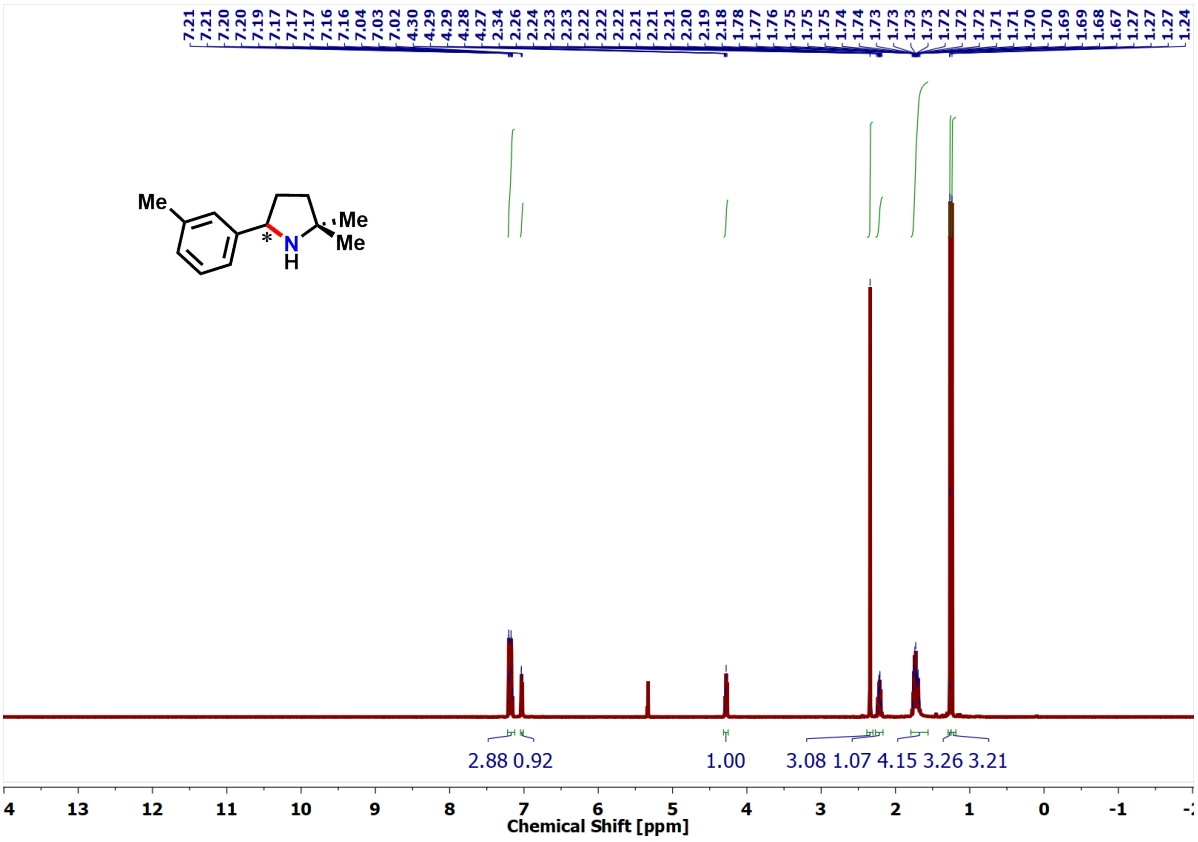
125.75
62.46
57.50
49.36
43.24
26.42
24.27
23.90
Chemical Shift [ppm]

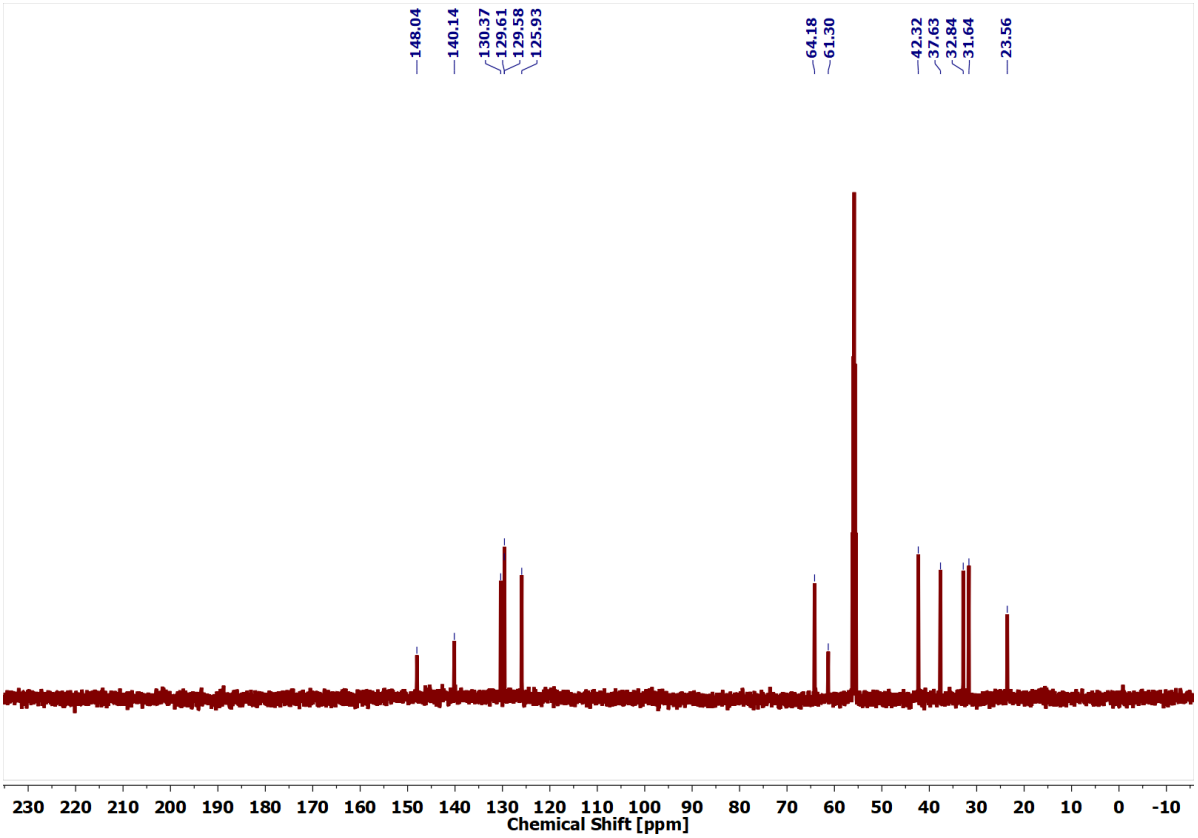

7.40
7.39
7.38
7.38
7.38
7.31
7.31
7.30
7.29
7.29
7.25
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
4.08
1.71
1.69
1.68
1.66
1.61
1.31
1.26
1.05
0.67
Me
Me
Me
Me
N
H
1.90 1.83 0.96
1.01
3.03 2.97 3.00 2.96 2.89
Chemical Shift [ppm]

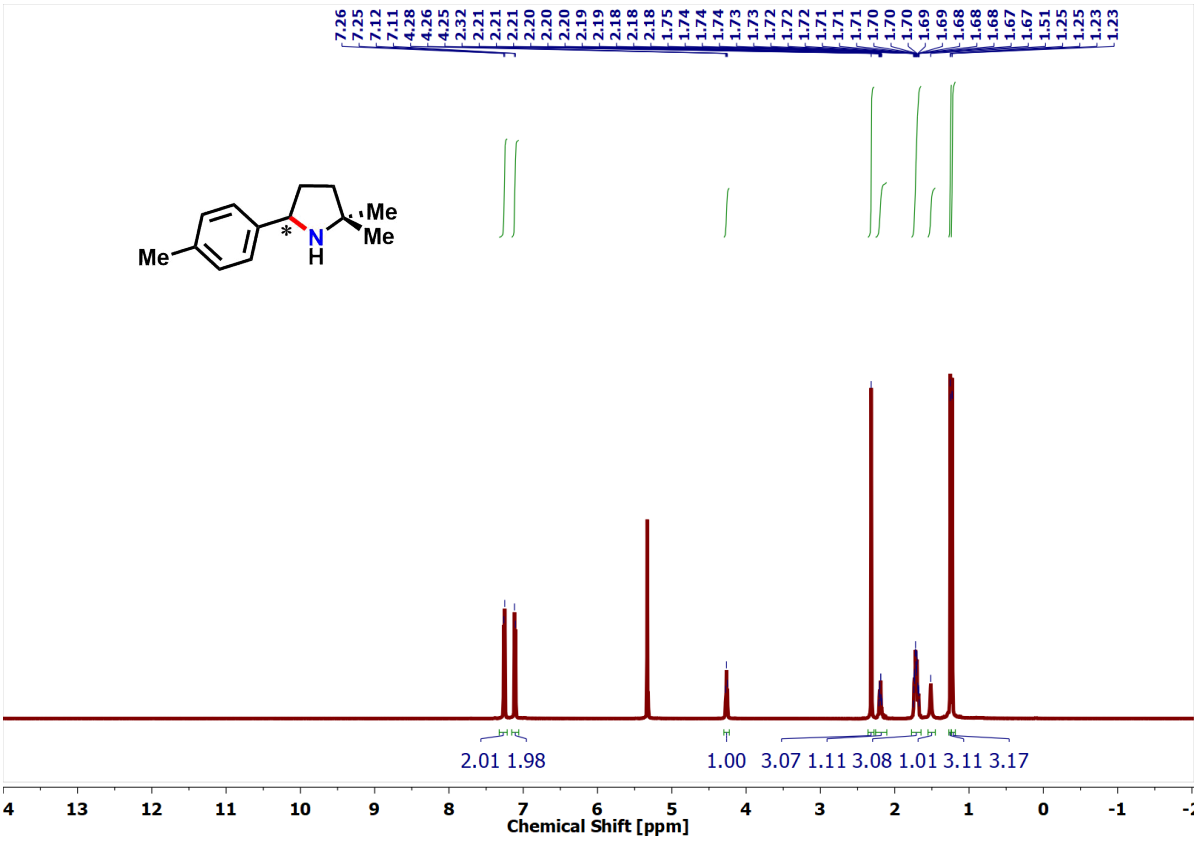

141.46
128.03
127.90
127.03
70.85
55.44
55.18
43.07
32.34
31.44
27.83
24.56
Chemical Shift [ppm]

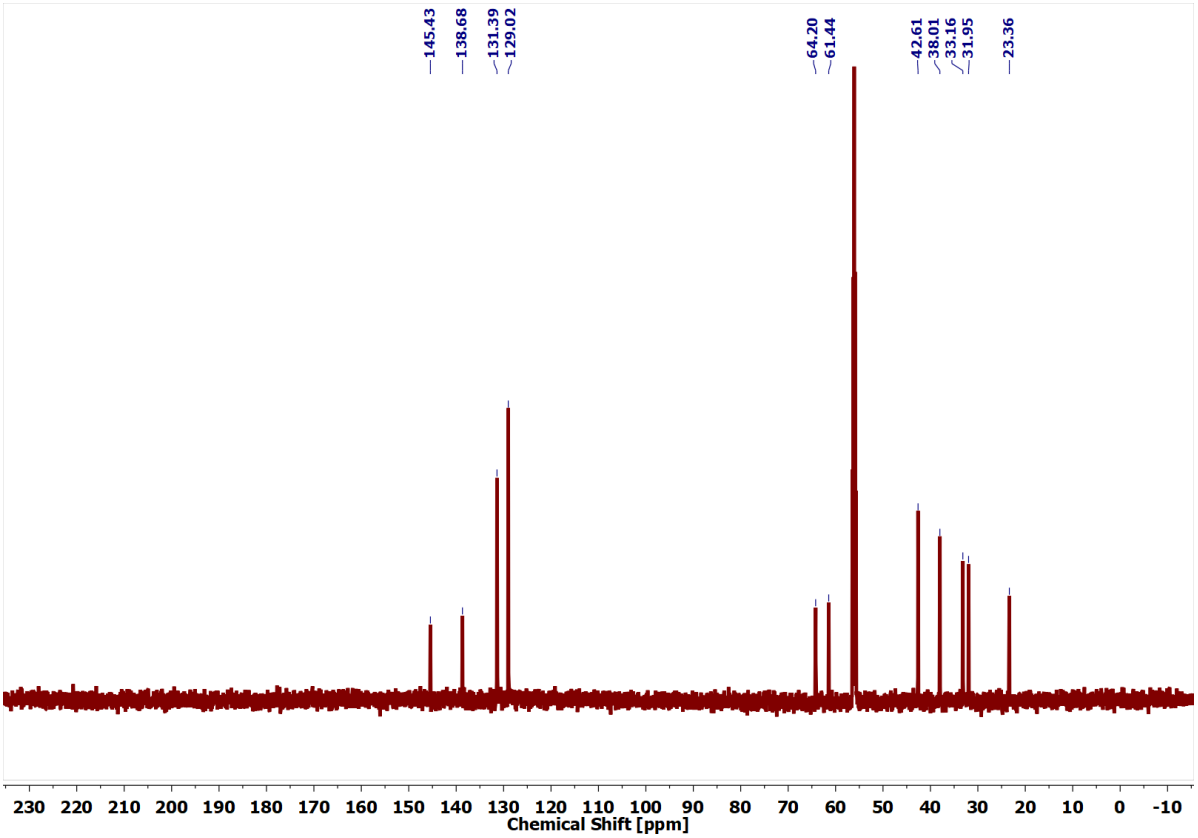

Me
Me
Me
N
H
0.94 0.94 1.84
0.98
3.00 1.07 3.04 1.10 3.22 3.18
Chemical Shift [ppm]

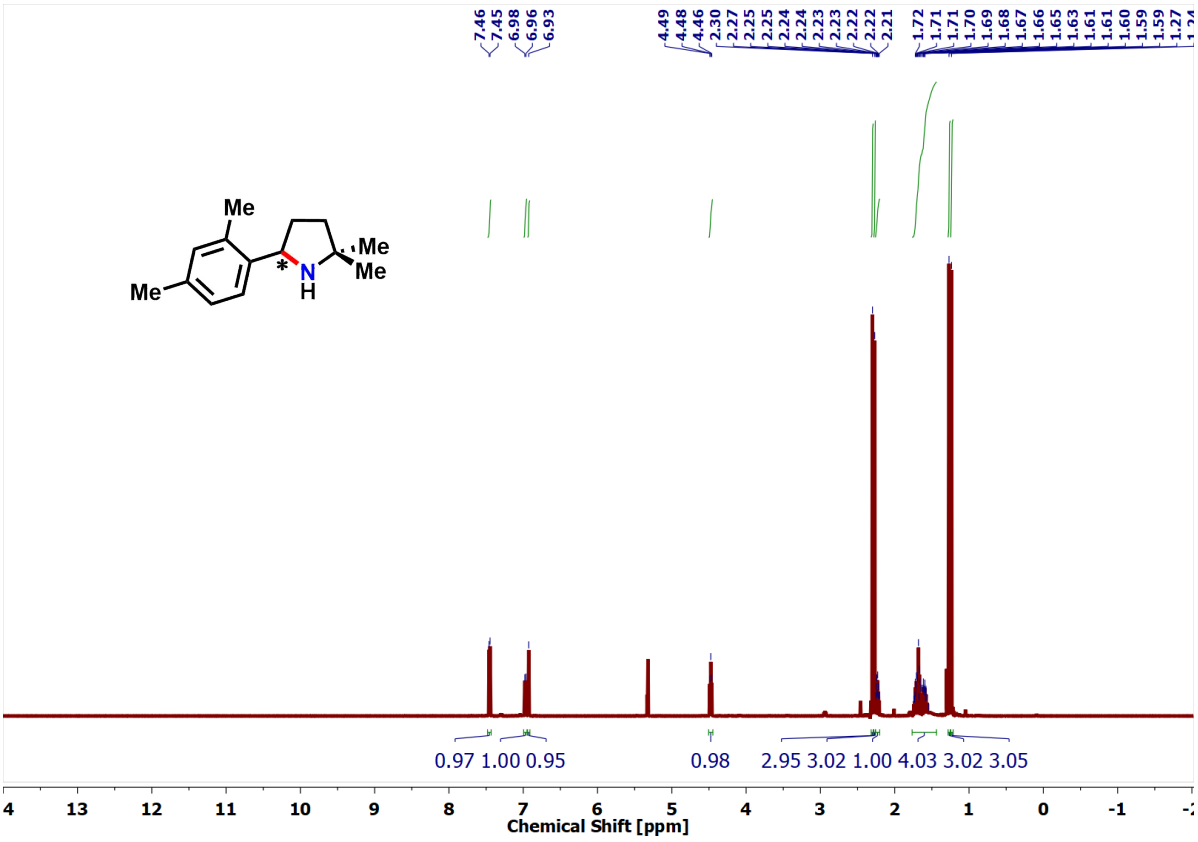

144.50
135.64
130.27
126.39
126.20
125.69
58.93
58.19
40.04
34.04
30.86
29.58
19.50
Chemical Shift [ppm]

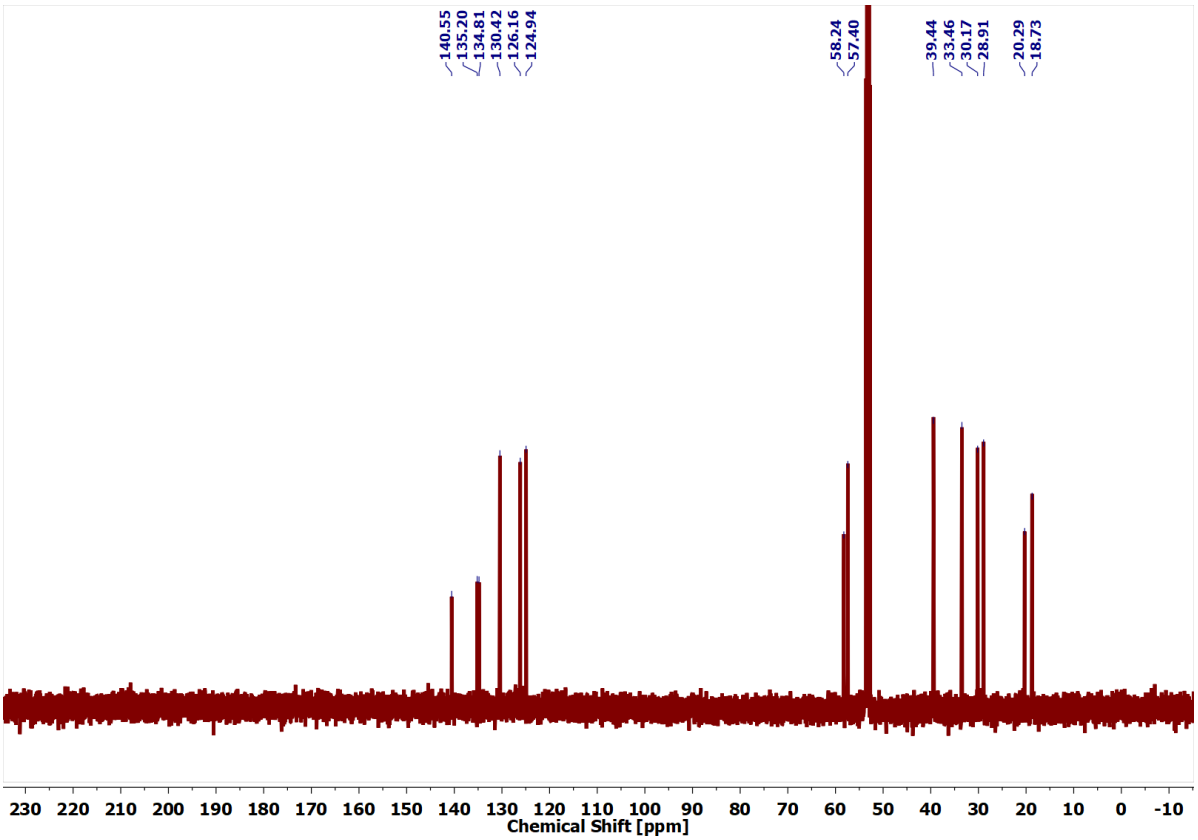

7.21 7.21 7.20 7.20 7.19 7.17 7.17 7.17 7.16 7.16 7.04 7.03 7.02 4.30 4.29 4.29 4.28 4.27 2.34 2.26 2.24 2.23 2.23 2.22 2.22 2.22 2.21 2.21 2.21 2.20 2.19 2.18 1.78 1.77 1.76 1.75 1.75 1.74 1.74 1.73 1.73 1.73 1.72 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.69 1.68 1.67 1.27 1.27 1.27 1.24
Me
Me
Me
N
H
2.88 0.92
1.00
3.08 1.07 4.15 3.26 3.21
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

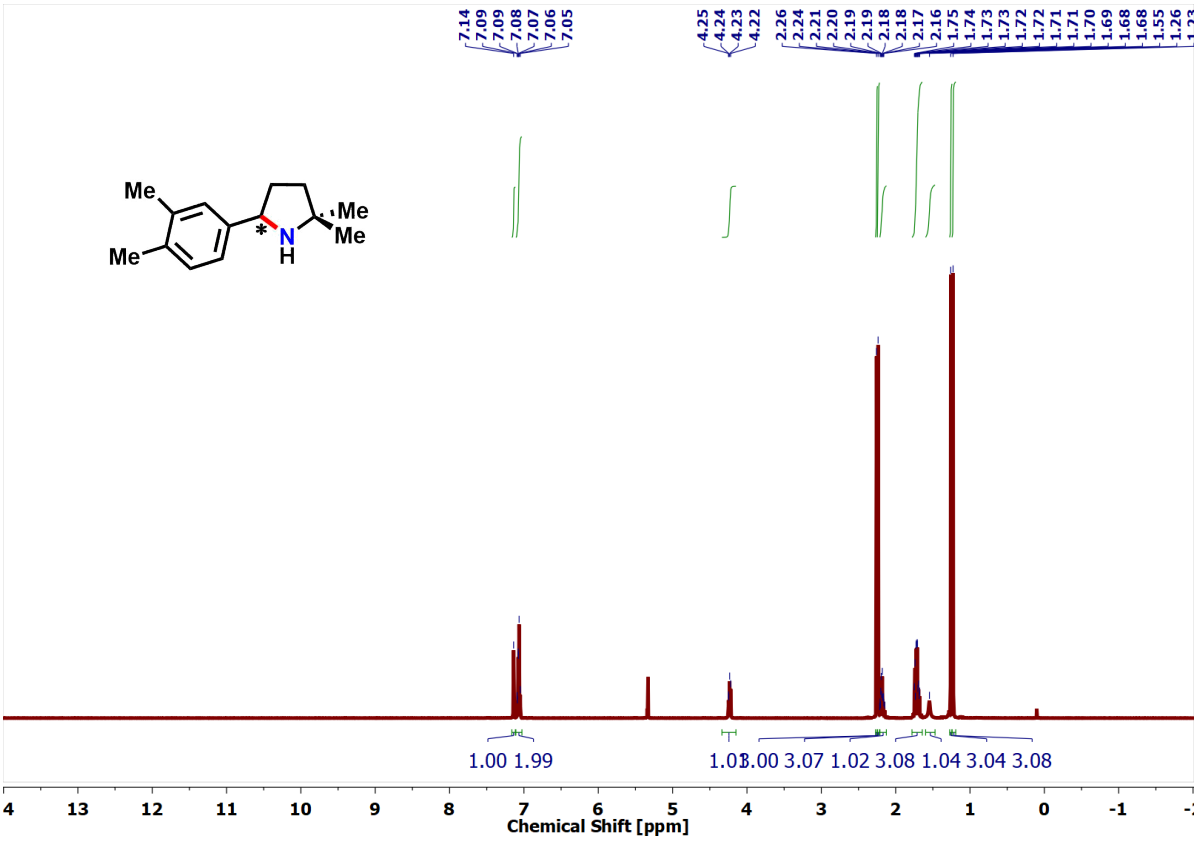

148.04
140.14
130.37
129.61
129.58
125.93
64.18
61.30
42.32
37.63
32.84
31.64
23.56
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

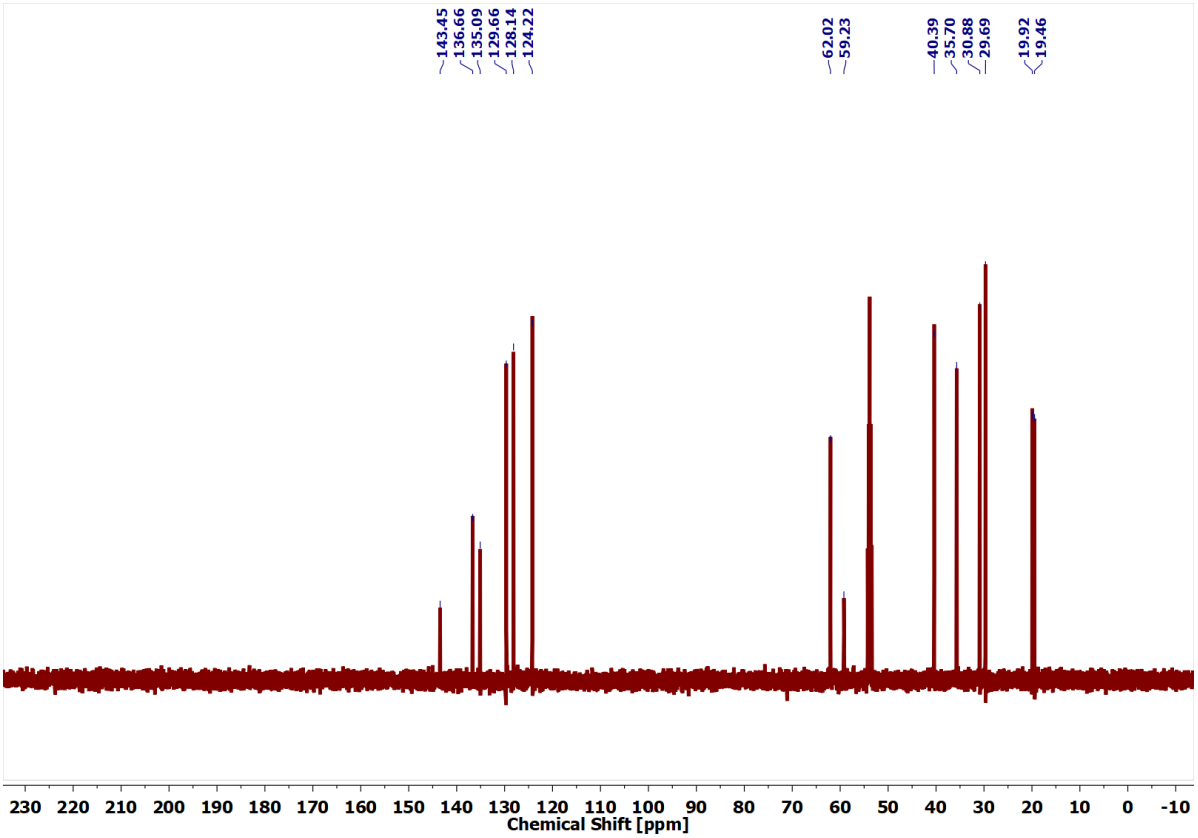

7.26 7.25 7.12 7.11 4.28 4.26 4.25 2.32 2.21 2.21 2.20 2.20 2.19 2.18 2.18 2.18 1.75 1.74 1.74 1.73 1.73 1.72 1.72 1.72 1.71 1.71 1.71 1.70 1.70 1.70 1.69 1.69 1.68 1.68 1.68 1.67 1.67 1.51 1.25 1.25 1.23 1.23
Me
Me
Me
N
H
2.01 1.98
1.00
3.07 1.11 3.08 1.01 3.11 3.17
Chemical Shift [ppm]

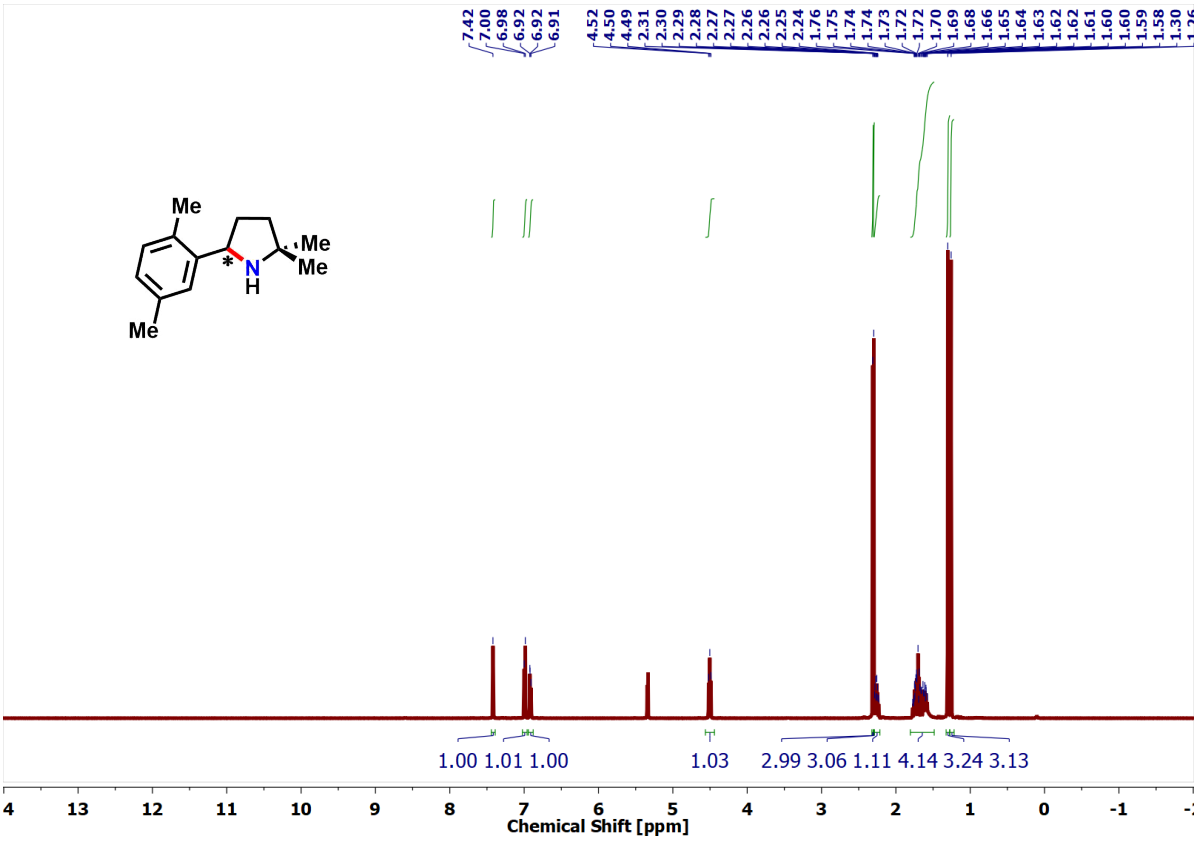

145.43
138.68
131.39
129.02
64.20
61.44
42.61
38.01
33.16
31.95
23.36
Chemical Shift [ppm]

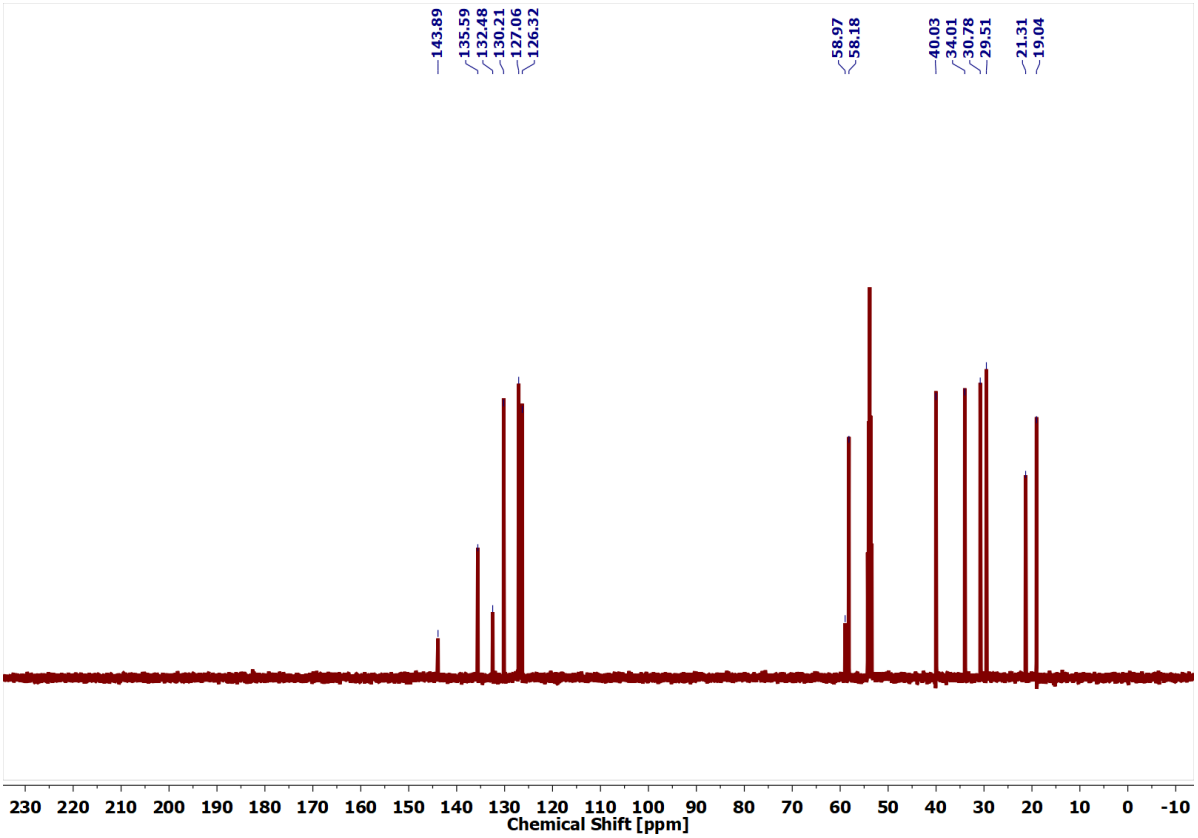

7.46
7.45
6.98
6.96
6.93
4.49
4.48
4.46
2.30
2.27
2.25
2.25
2.24
2.24
2.23
2.23
2.22
2.22
2.21
1.72
1.71
1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.63
1.61
1.61
1.60
1.59
1.59
1.27
Me
Me
Me
N
H
0.97 1.00 0.95
0.98
2.95 3.02 1.00 4.03 3.02 3.05
Chemical Shift [ppm]

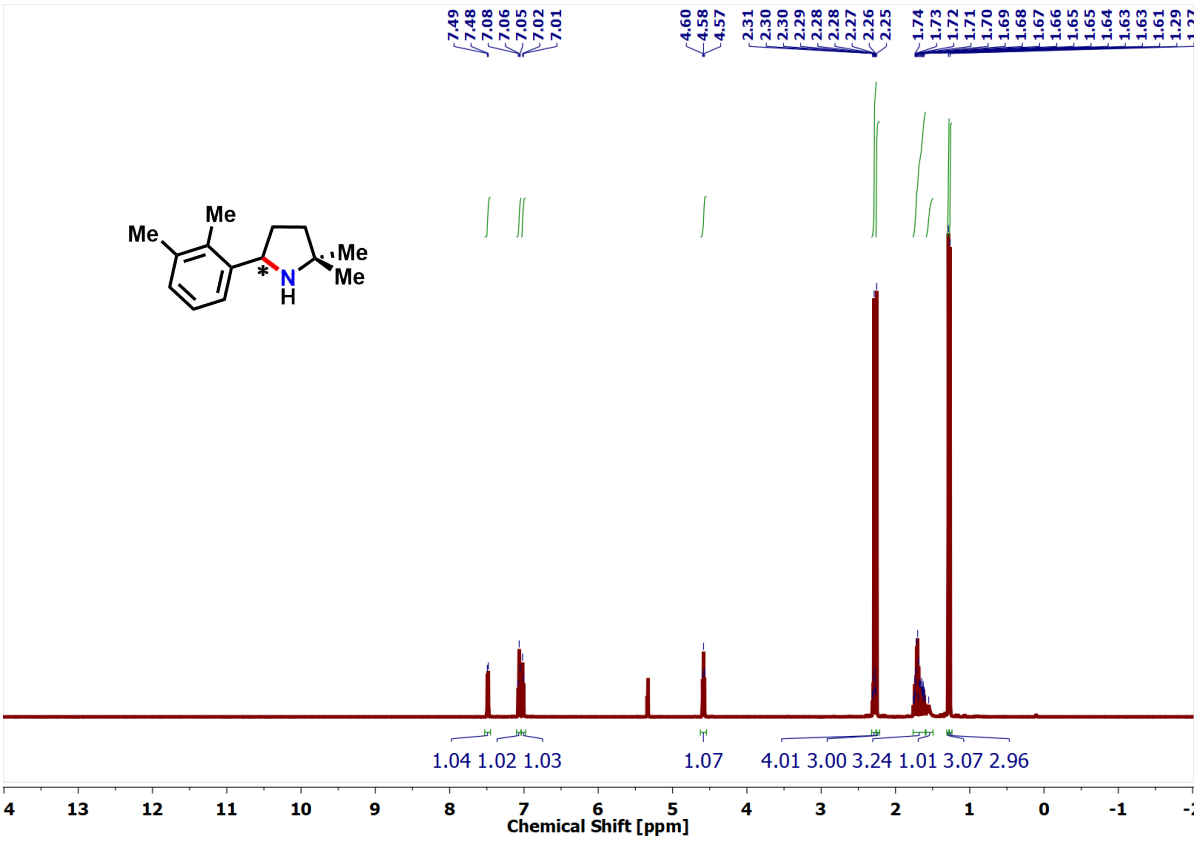

140.55
135.20
134.81
130.42
126.16
124.94
58.24
57.40
39.44
33.46
30.17
28.91
20.29
18.73
Chemical Shift [ppm]

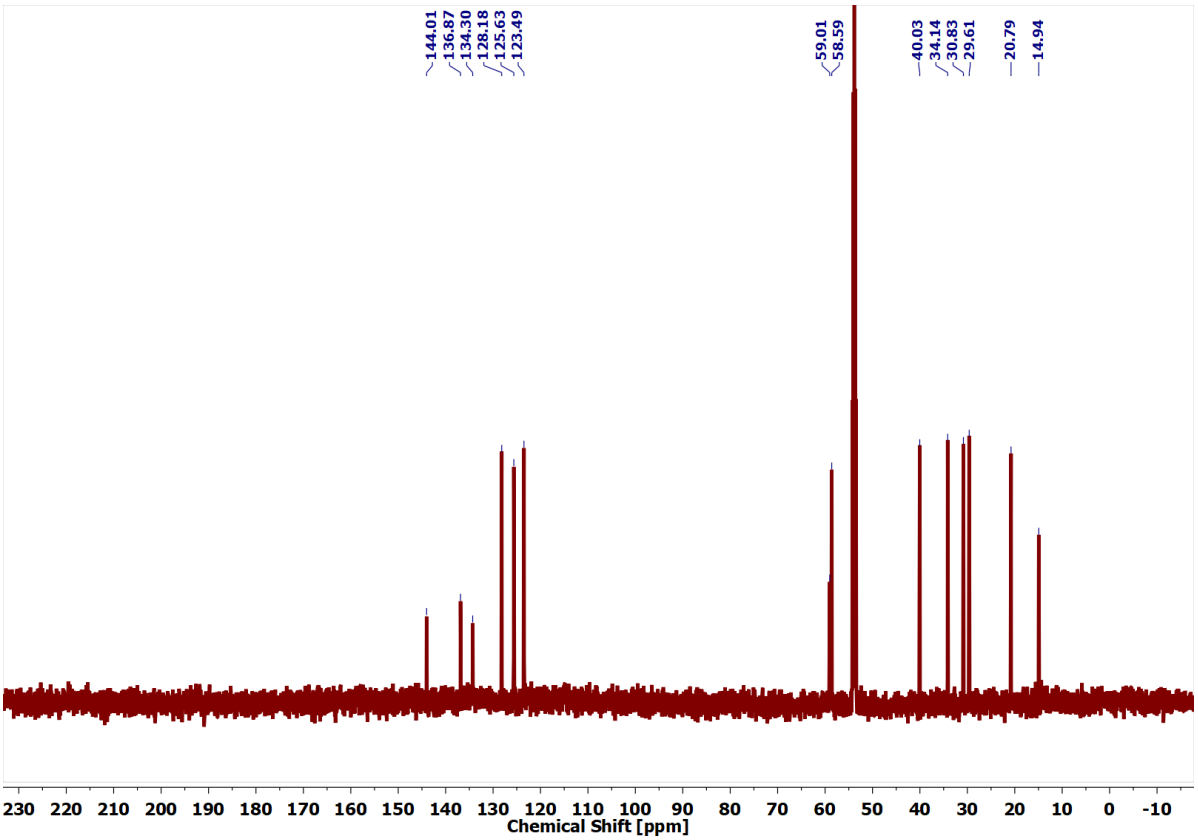

Me
Me
Me
Me
N
H
7.14 7.09 7.09 7.08 7.07 7.06 7.05
4.25 4.24 4.23 4.22
2.26 2.24 2.21 2.20 2.19 2.19 2.18 2.18 2.17 2.16 1.75 1.74 1.73 1.73 1.72 1.72 1.71 1.71 1.70 1.69 1.68 1.68 1.55 1.26
1.00 1.99
1.01 3.00 3.07 1.02 3.08 1.04 3.04 3.08
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

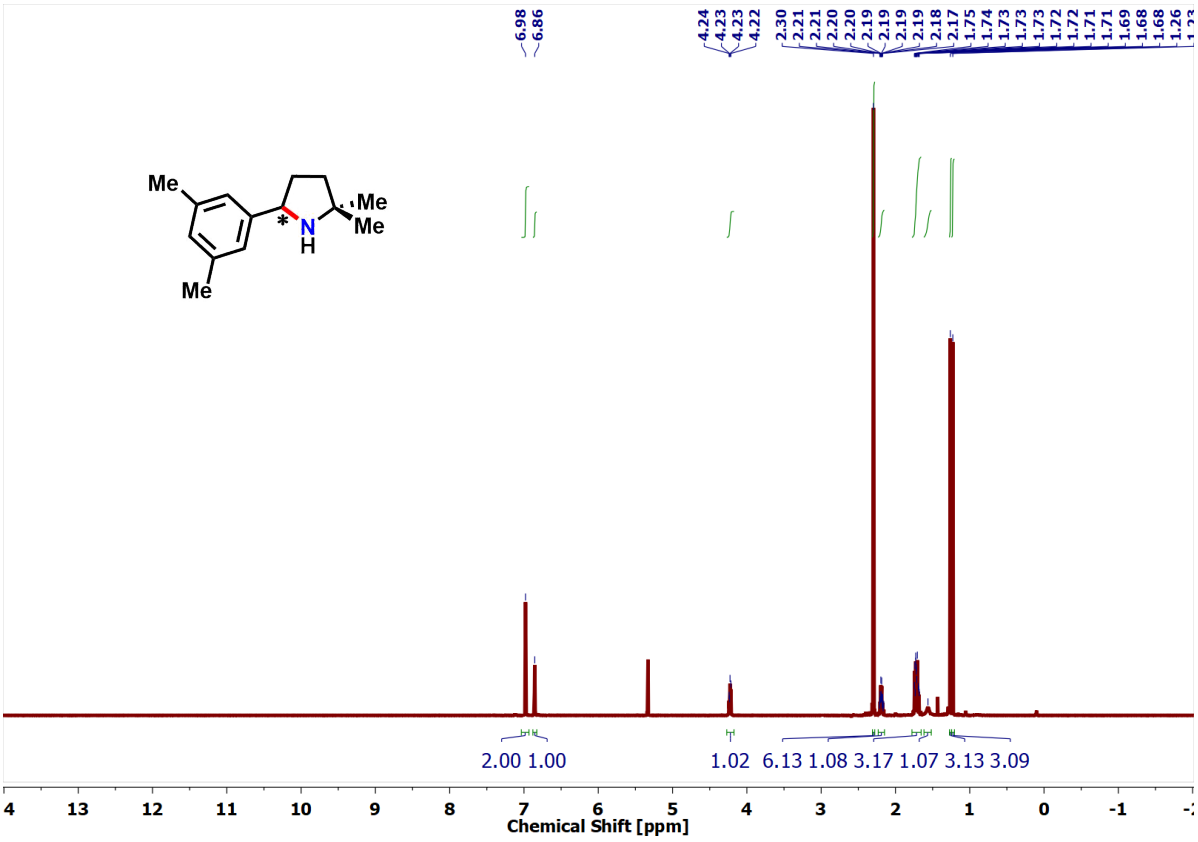

143.45
136.66
135.09
129.66
128.14
124.22
62.02
59.23
40.39
35.70
30.88
29.69
19.92
19.46
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

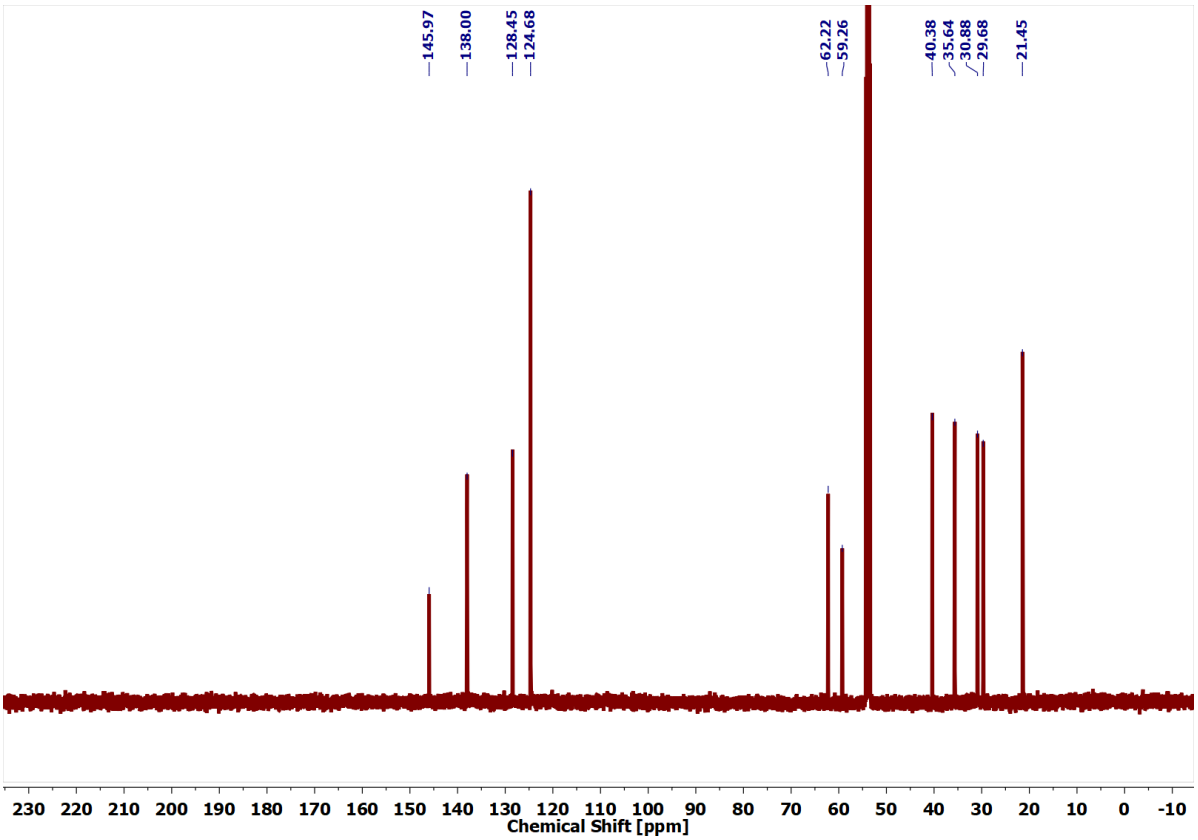

Me
Me
Me
Me
N
H
7.42
7.00
6.98
6.92
6.92
6.91
4.52
4.50
4.49
2.31
2.30
2.29
2.28
2.27
2.27
2.26
2.26
2.25
2.24
1.76
1.75
1.74
1.74
1.73
1.72
1.72
1.70
1.69
1.68
1.66
1.65
1.64
1.63
1.62
1.62
1.61
1.60
1.60
1.59
1.58
1.30
1.00 1.01 1.00
1.03
2.99 3.06 1.11 4.14 3.24 3.13
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

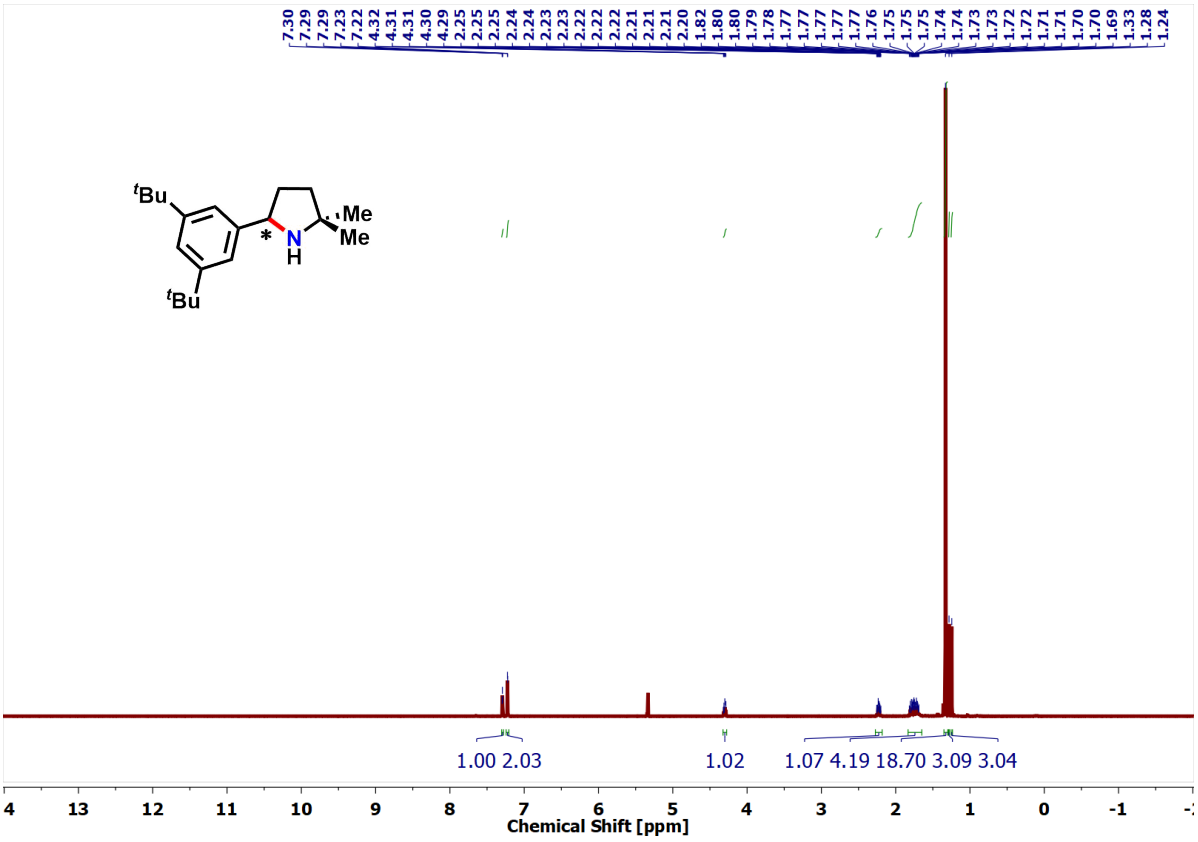

143.89
135.59
132.48
130.21
127.06
126.32
58.97
58.18
40.03
34.01
30.78
29.51
21.31
19.04
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

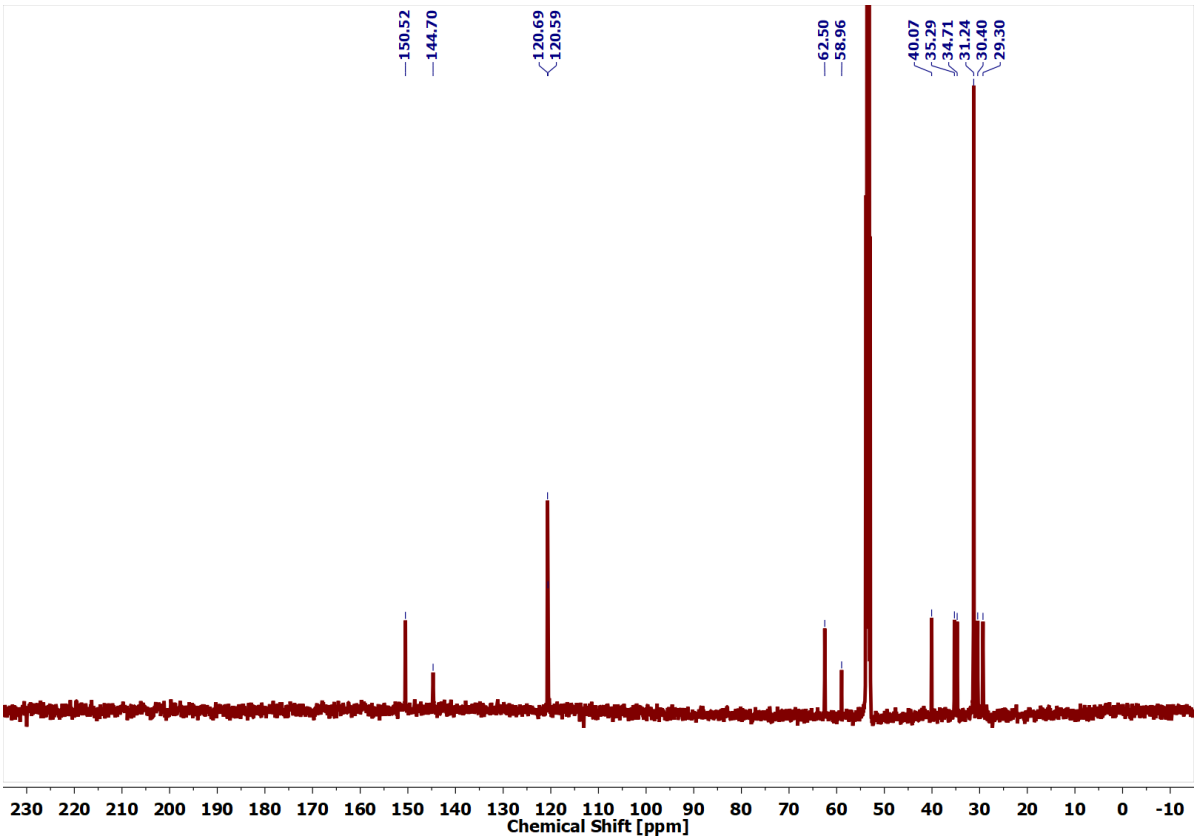

7.49
7.48
7.08
7.06
7.05
7.02
7.01
4.60
4.58
4.57
2.31
2.30
2.30
2.29
2.28
2.28
2.27
2.26
2.25
1.74
1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.66
1.65
1.65
1.64
1.63
1.63
1.61
1.29
Me
Me
Me
Me
*
N
H
1.04 1.02 1.03
1.07
4.01 3.00 3.24 1.01 3.07 2.96
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

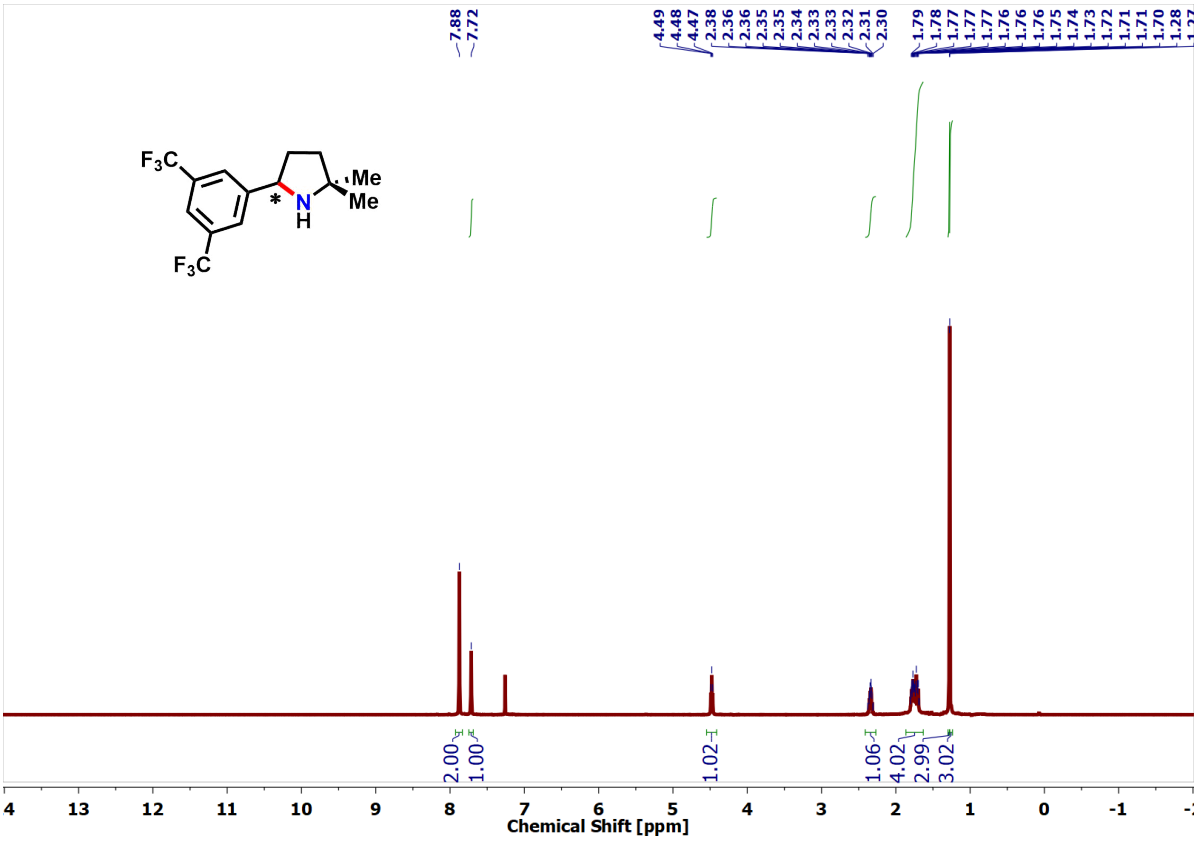

144.01
136.87
134.30
128.18
125.63
123.49
59.01
58.59
40.03
34.14
30.83
29.61
20.79
14.94
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

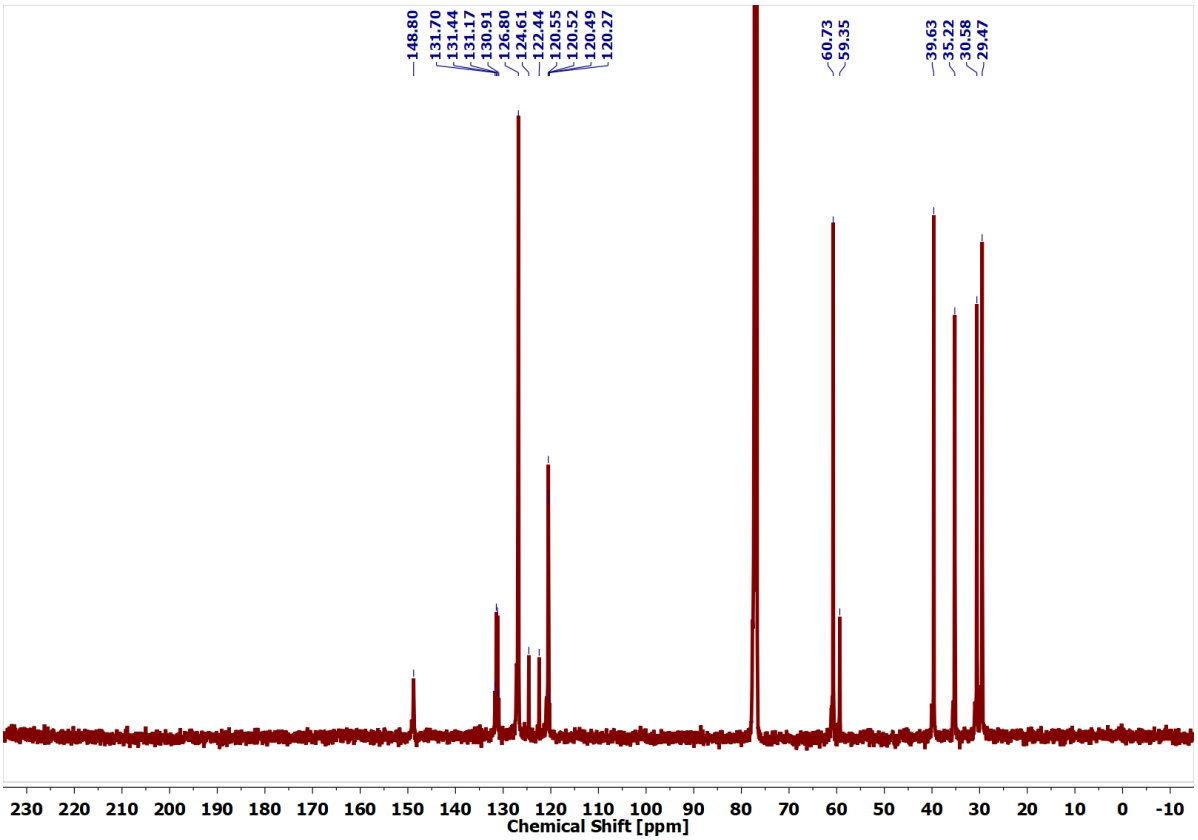

Me
Me
Me
Me
N
H
6.98
6.86
4.24
4.23
4.23
4.22
2.30
2.21
2.21
2.20
2.20
2.19
2.19
2.19
2.19
2.18
2.17
1.75
1.74
1.73
1.73
1.73
1.72
1.72
1.71
1.71
1.69
1.68
1.68
1.26
2.00 1.00
1.02 6.13 1.08 3.17 1.07 3.13 3.09
Chemical Shift [ppm]

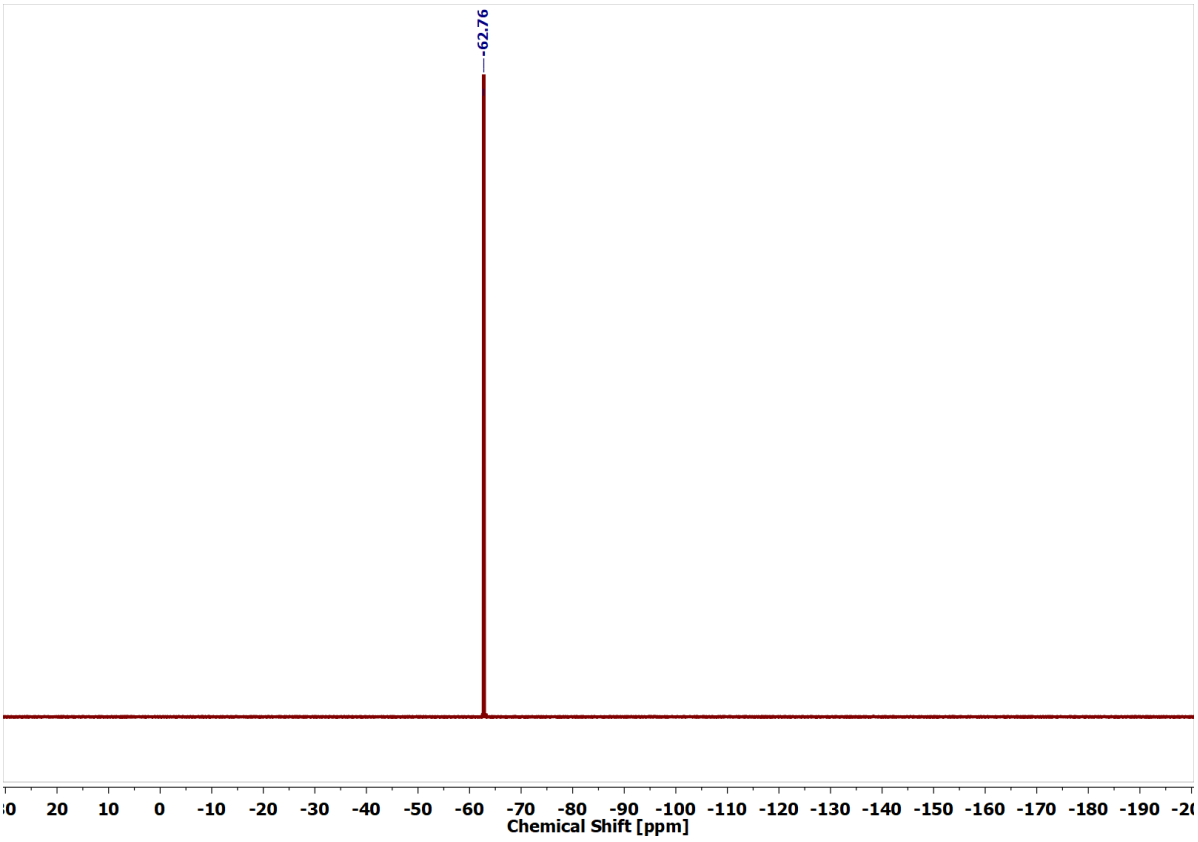

145.97
138.00
128.45
124.68
62.22
59.26
40.38
35.64
30.88
29.68
21.45
Chemical Shift [ppm]

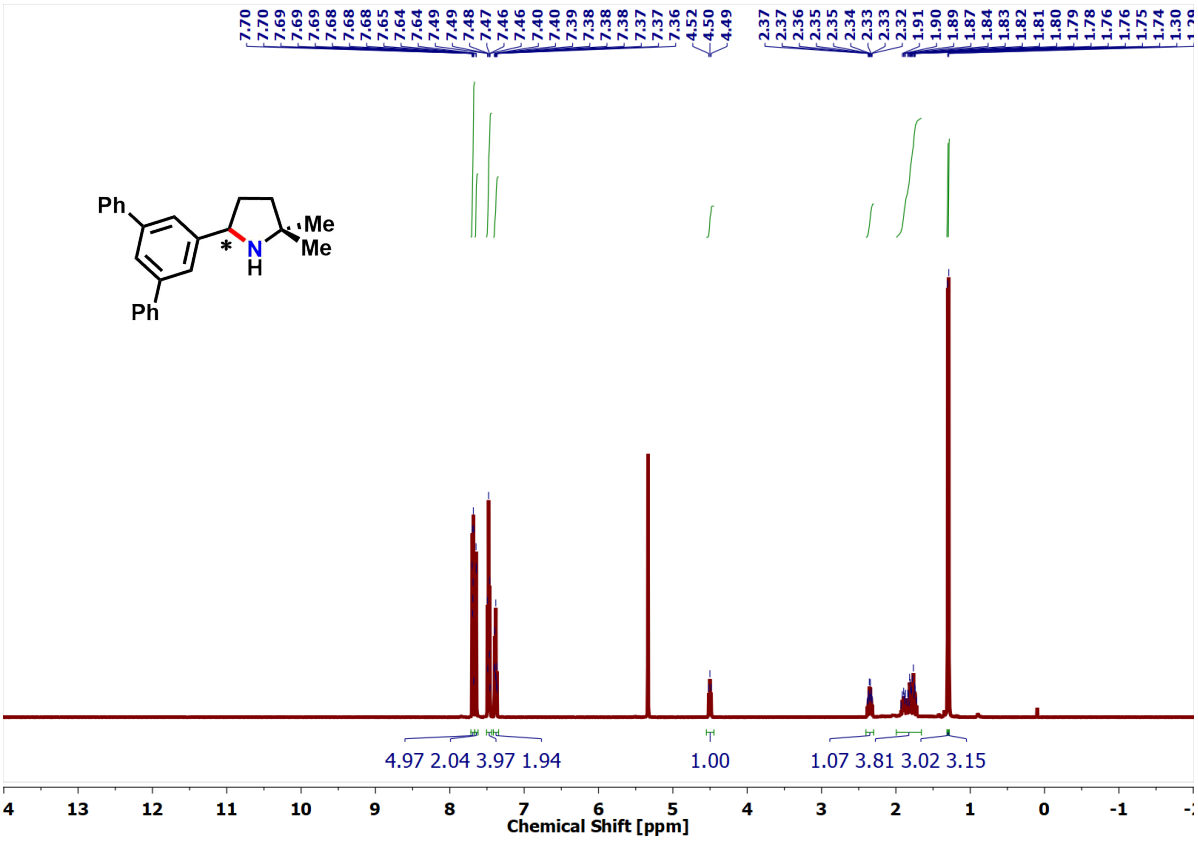

7.30 7.29 7.29 7.23 7.22 4.32 4.31 4.31 4.30 4.29 2.25 2.25 2.24 2.24 2.23 2.23 2.22 2.22 2.22 2.21 2.21 2.21 2.20 1.82 1.80 1.80 1.79 1.78 1.77 1.77 1.77 1.77 1.76 1.75 1.75 1.75 1.74 1.74 1.73 1.73 1.72 1.72 1.71 1.71 1.70 1.70 1.69 1.33 1.28 1.24
tBu
tBu
Me
Me
N
H
*
1.00 2.03
1.02
1.07 4.19 18.70 3.09 3.04
4 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
Chemical Shift [ppm]

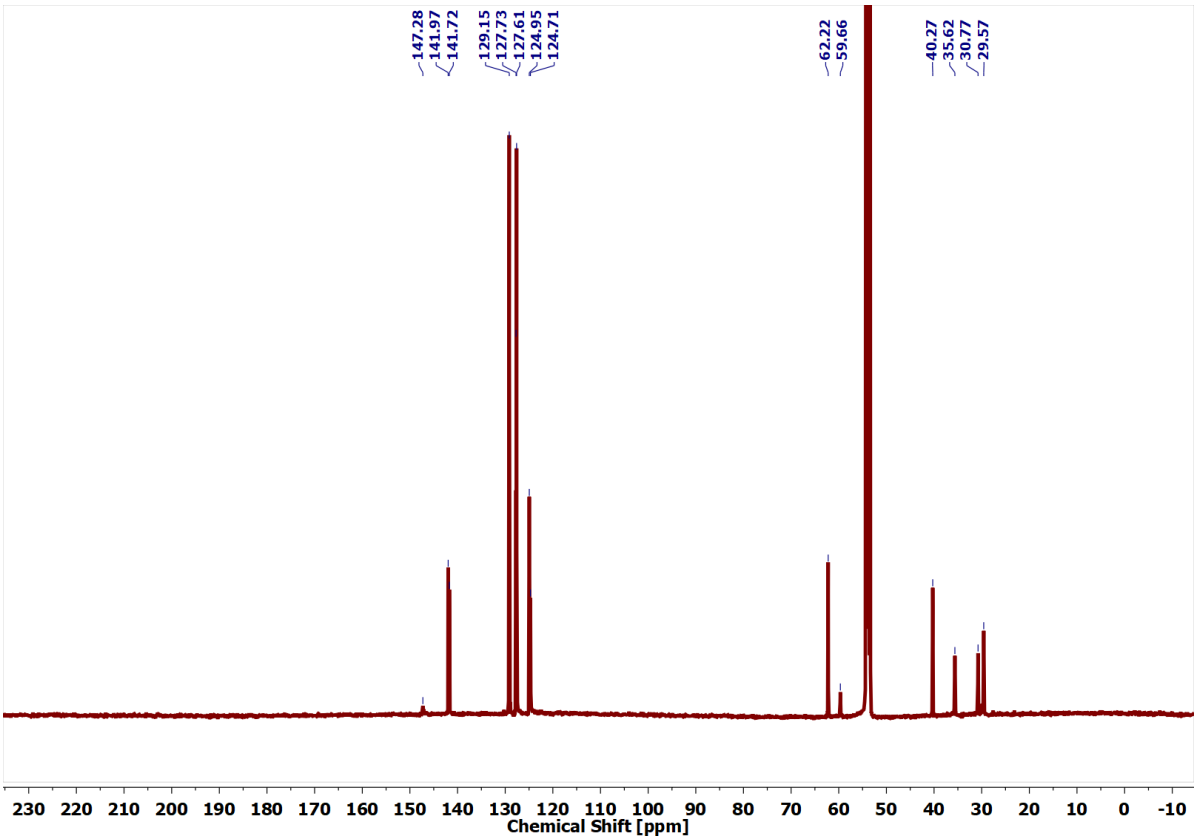

150.52
144.70
120.69
120.59
62.50
58.96
40.07
35.29
34.71
31.24
30.40
29.30
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift [ppm]

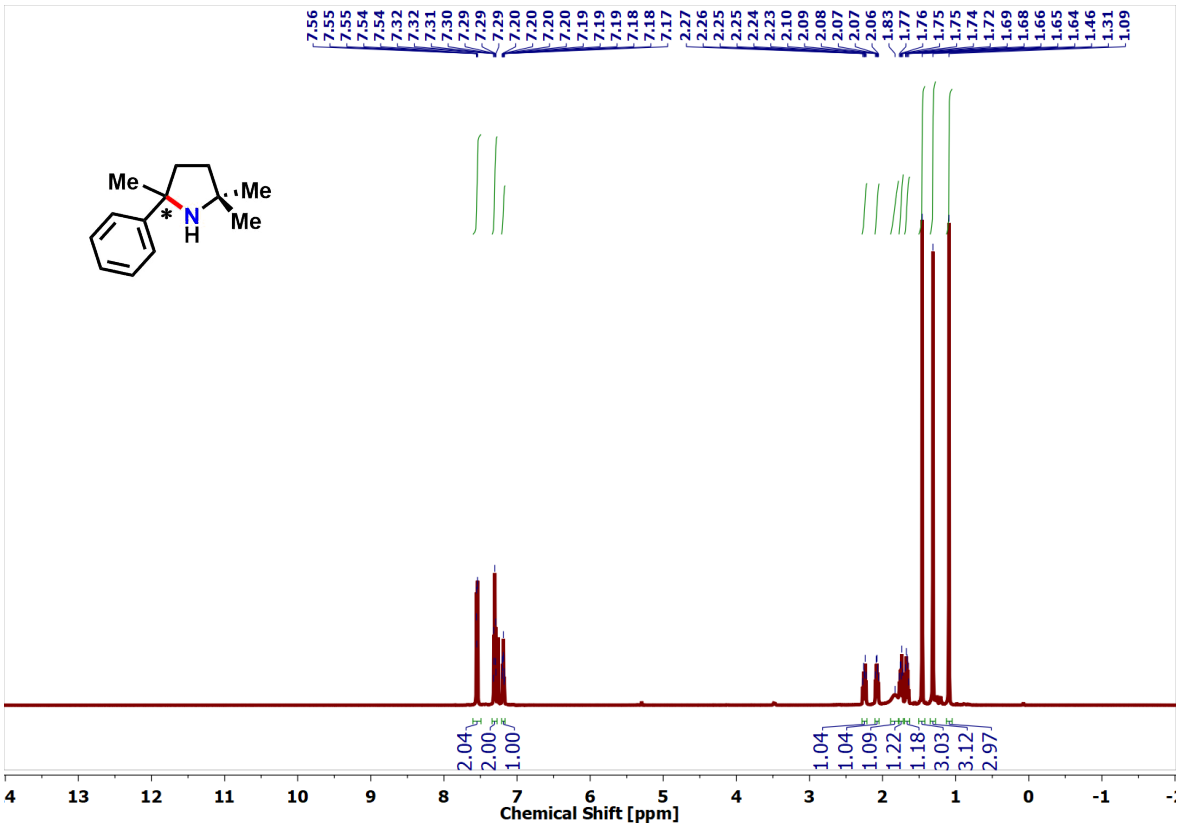

7.88
7.72
4.49
4.48
4.47
2.38
2.36
2.36
2.35
2.35
2.34
2.33
2.33
2.32
2.31
2.30
1.79
1.78
1.77
1.77
1.77
1.76
1.76
1.76
1.75
1.74
1.73
1.72
1.71
1.71
1.70
1.28
F3C
Me
Me
N
H
F3C
2.00
1.00
1.02
1.06
4.02
2.99
3.02
Chemical Shift [ppm]

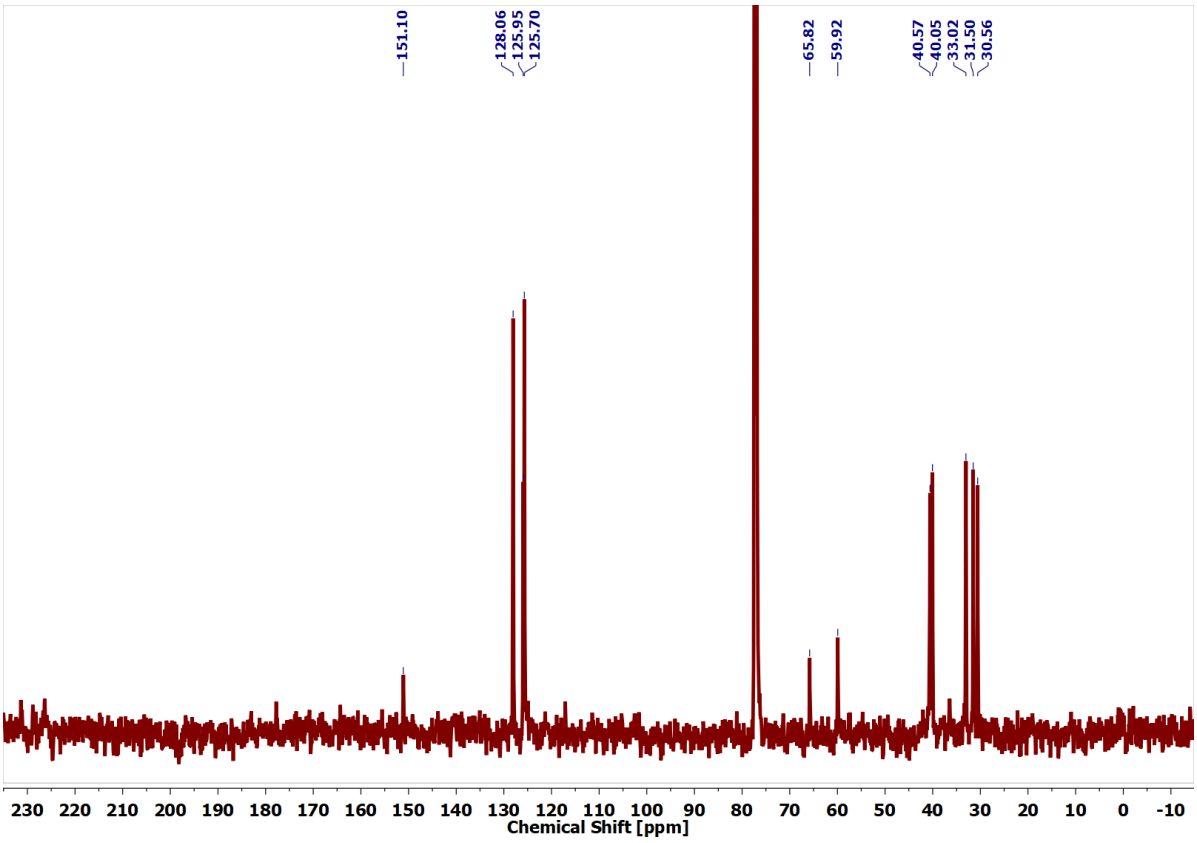

148.80
131.70
131.44
131.17
130.91
126.80
124.61
122.44
120.55
120.52
120.49
120.27
60.73
59.35
39.63
35.22
30.58
29.47
Chemical Shift [ppm]

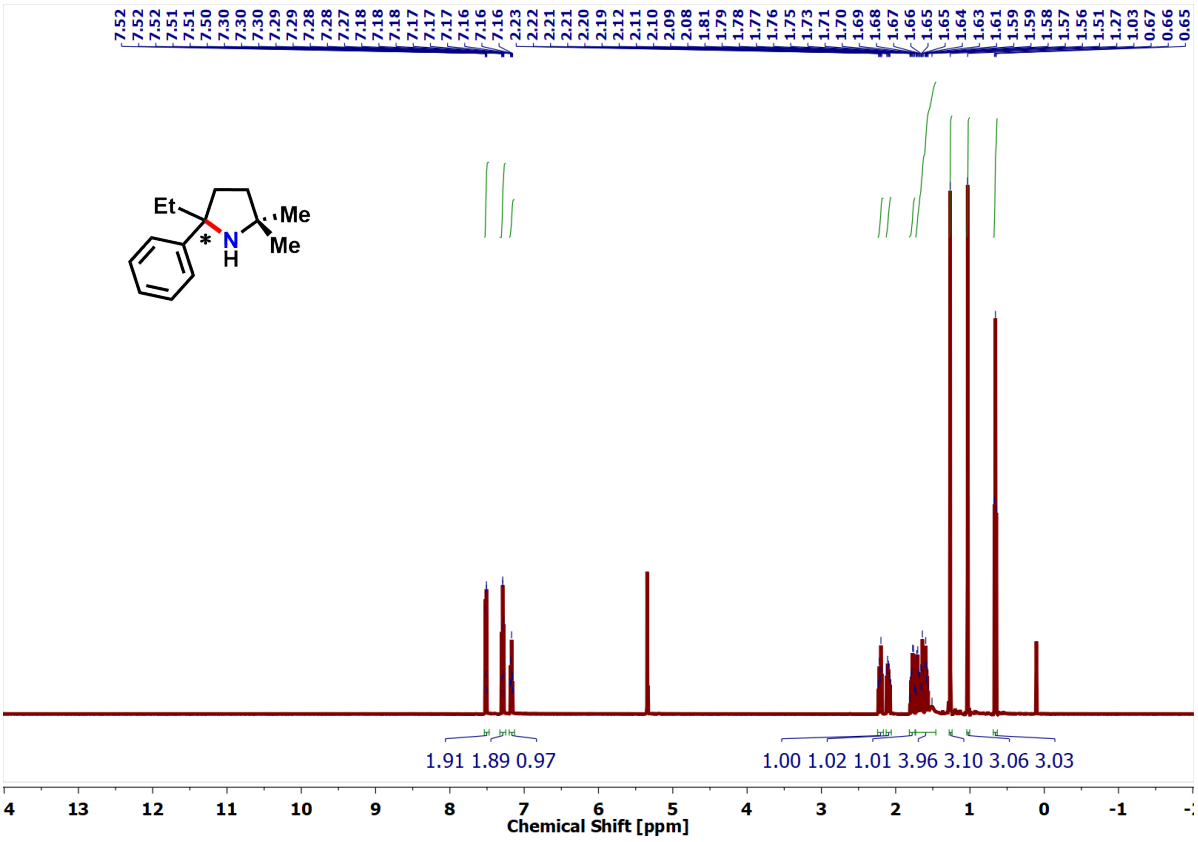

-62.76
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
Chemical Shift [ppm]

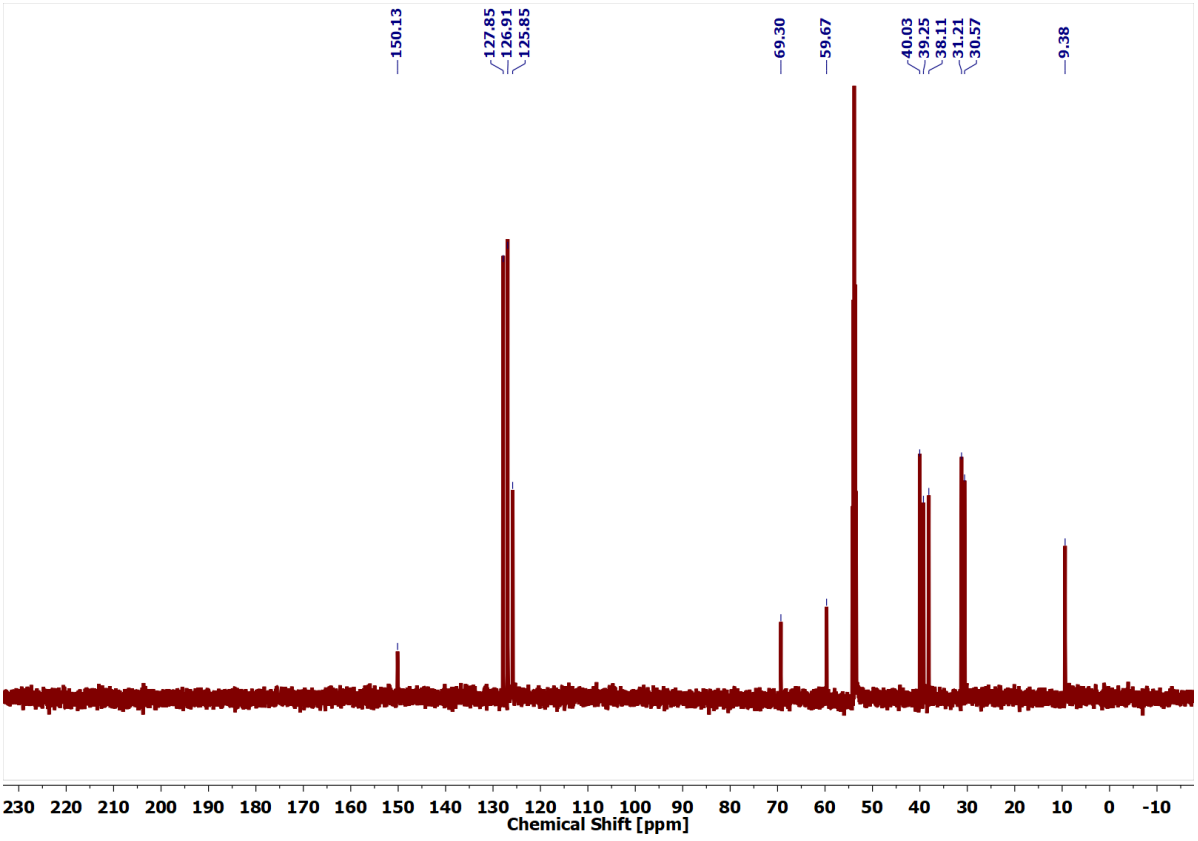

Ph
Me
Me
N
H
Ph
4.97 2.04 3.97 1.94
1.00
1.07 3.81 3.02 3.15
Chemical Shift [ppm]

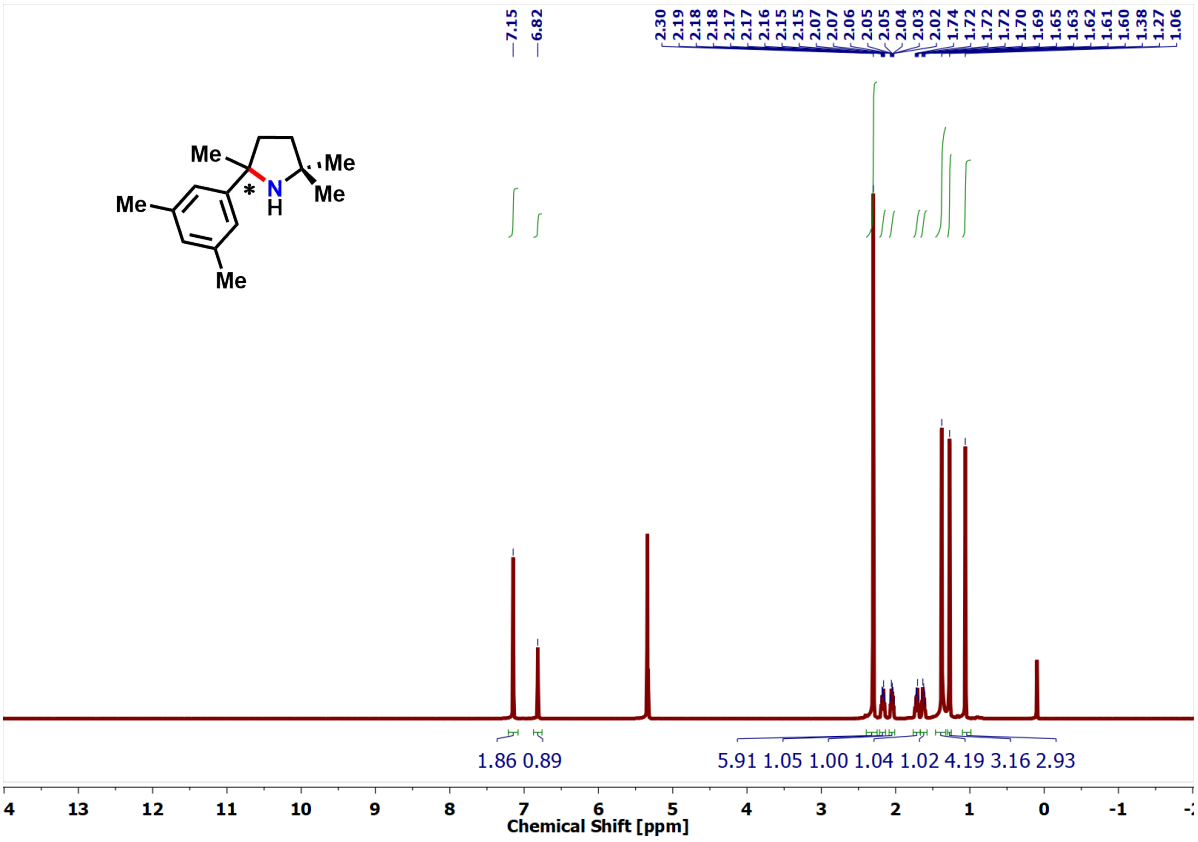

147.28
141.97
141.72
129.15
127.73
127.61
124.95
124.71
62.22
59.66
40.27
35.62
30.77
29.57
Chemical Shift [ppm]

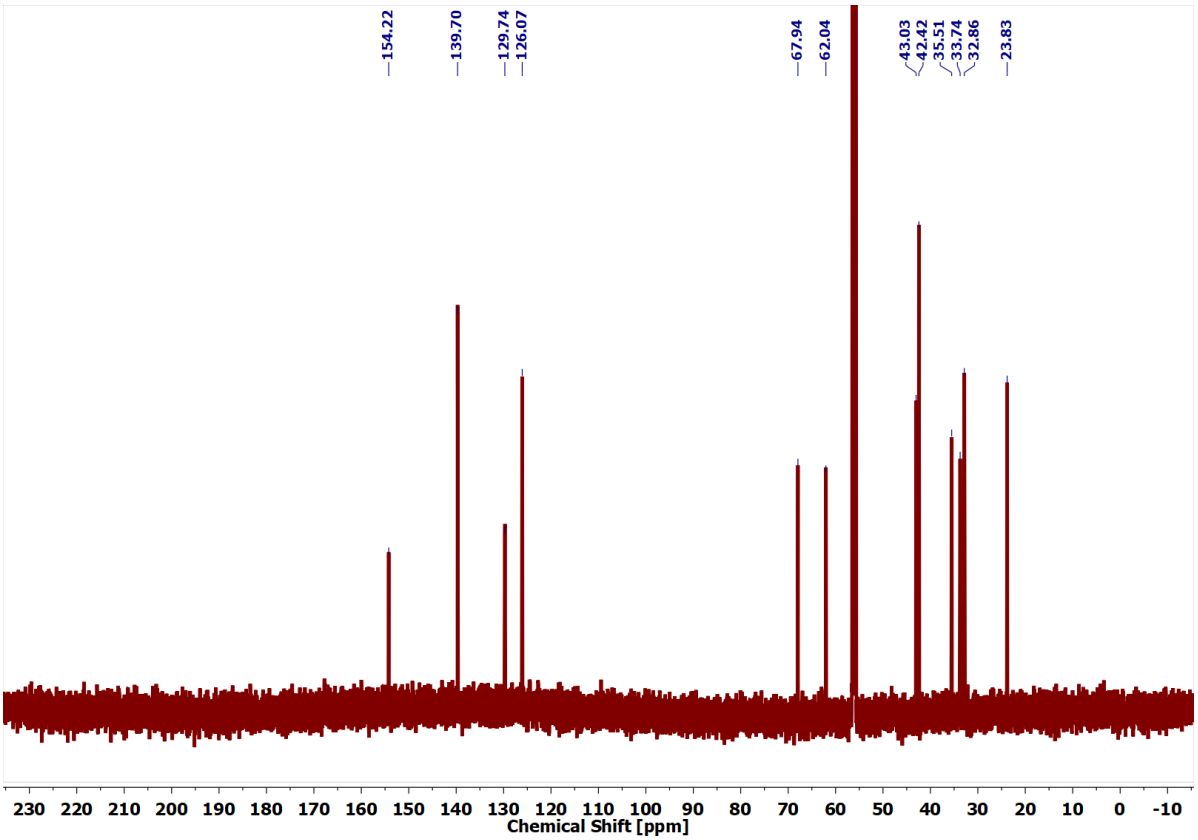

Me
Me
Me
N
H
Chemical Shift [ppm]

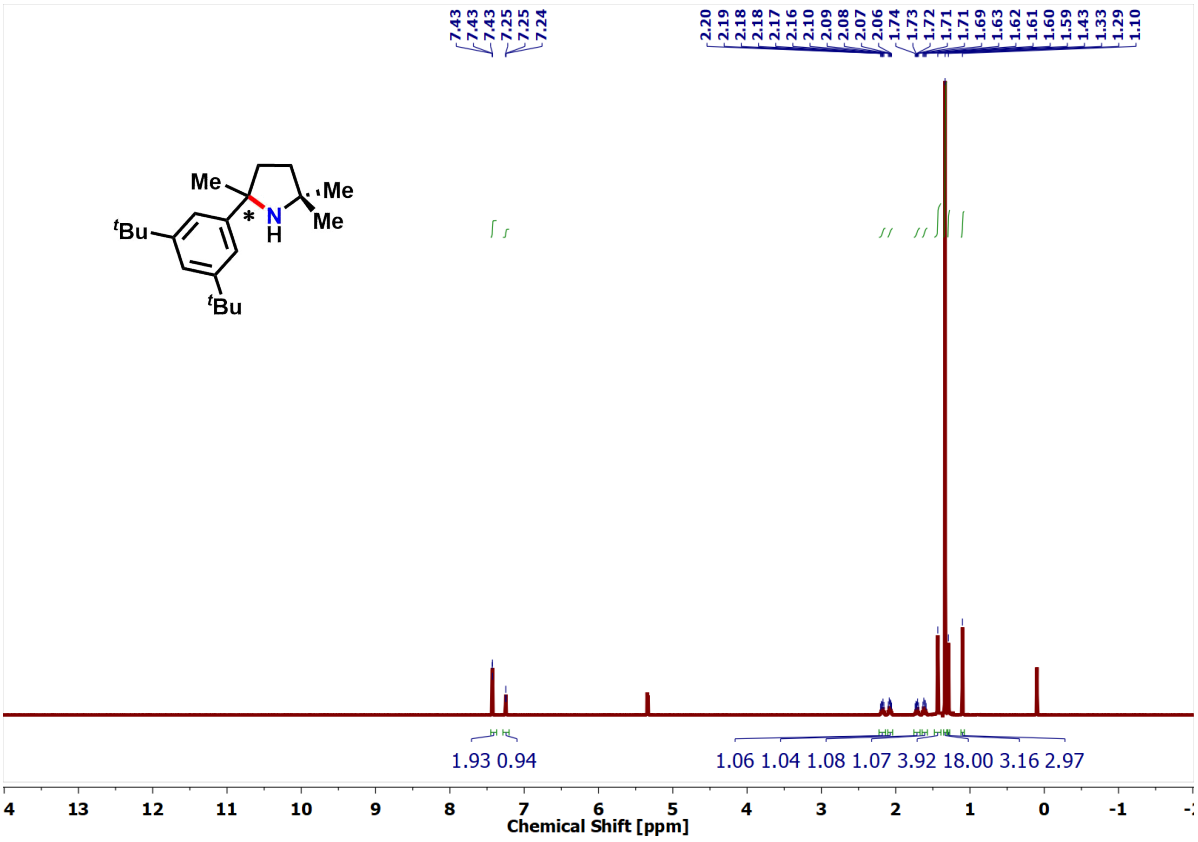

Chemical Shift [ppm]

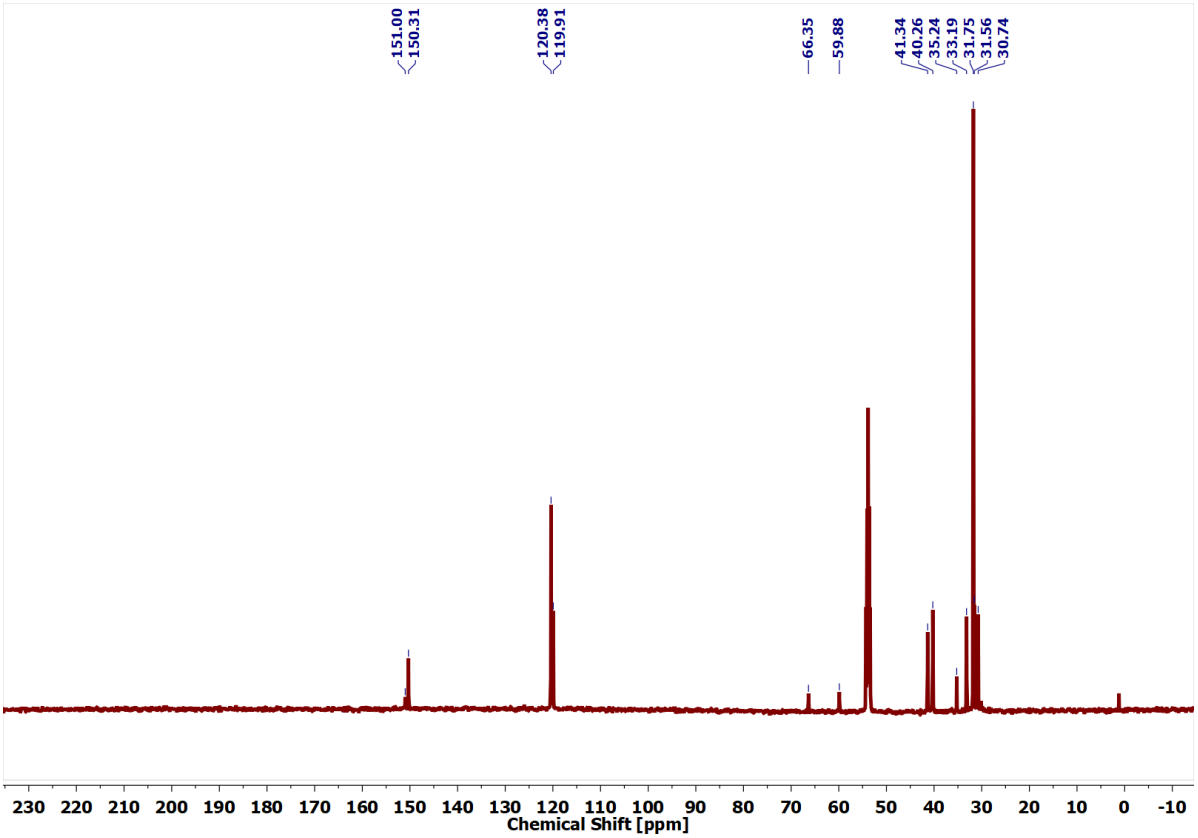

Et
Me
Me
N
H
1.91 1.89 0.97
1.00 1.02 1.01 3.96 3.10 3.06 3.03
Chemical Shift [ppm]


150.13
127.85
126.91
125.85
69.30
59.67
40.03
39.25
38.11
31.21
30.57
9.38
Chemical Shift [ppm]

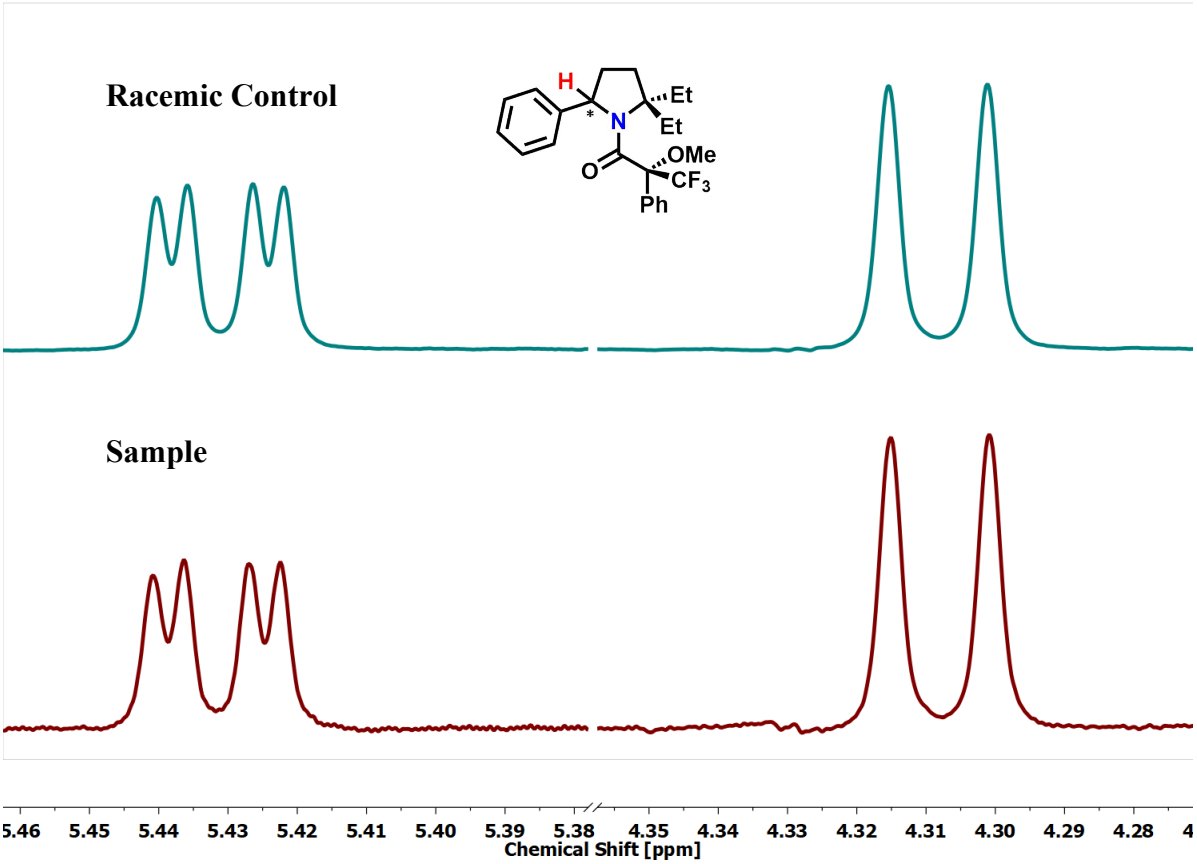

7.15
6.82
2.30
2.19
2.18
2.18
2.17
2.17
2.16
2.15
2.15
2.07
2.07
2.06
2.05
2.05
2.04
2.03
2.02
1.74
1.72
1.72
1.72
1.70
1.69
1.65
1.63
1.62
1.61
1.60
1.38
1.27
1.06
Me
Me
Me
Me
Me
*
N
H
1.86 0.89
5.91 1.05 1.00 1.04 1.02 4.19 3.16 2.93
Chemical Shift [ppm]


154.22
139.70
129.74
126.07
67.94
62.04
43.03
42.42
35.51
33.74
32.86
23.83
Chemical Shift [ppm]


7.43
7.43
7.43
7.25
7.25
7.24
2.20
2.19
2.18
2.18
2.17
2.16
2.10
2.09
2.08
2.07
2.06
1.74
1.73
1.72
1.71
1.71
1.69
1.63
1.62
1.61
1.60
1.59
1.43
1.33
1.29
1.10
Me
Me
Me
*
N
H
tBu
tBu
1.93 0.94
1.06 1.04 1.08 1.07 3.92 18.00 3.16 2.97
Chemical Shift [ppm]

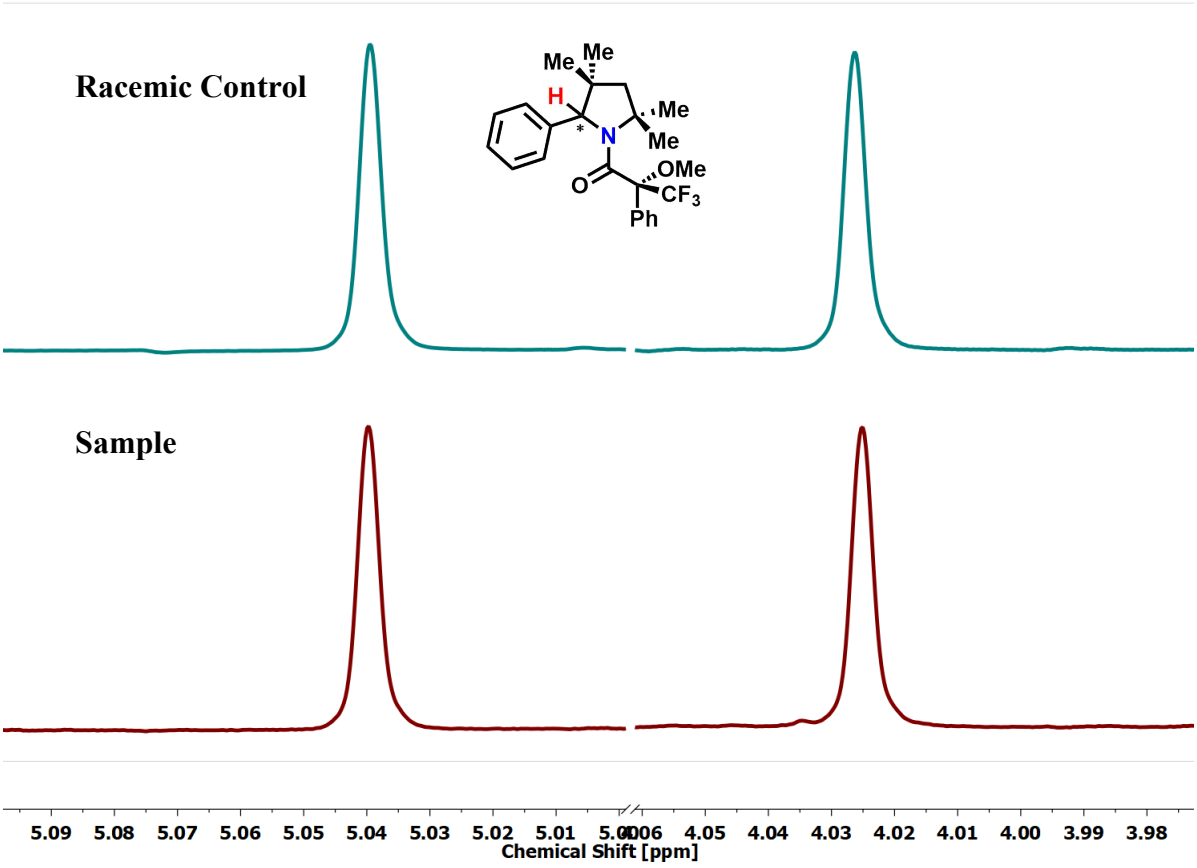

151.00
150.31
120.38
119.91
66.35
59.88
41.34
40.26
35.24
33.19
31.75
31.56
30.74
Chemical Shift [ppm]

NMR spectra for ee determination



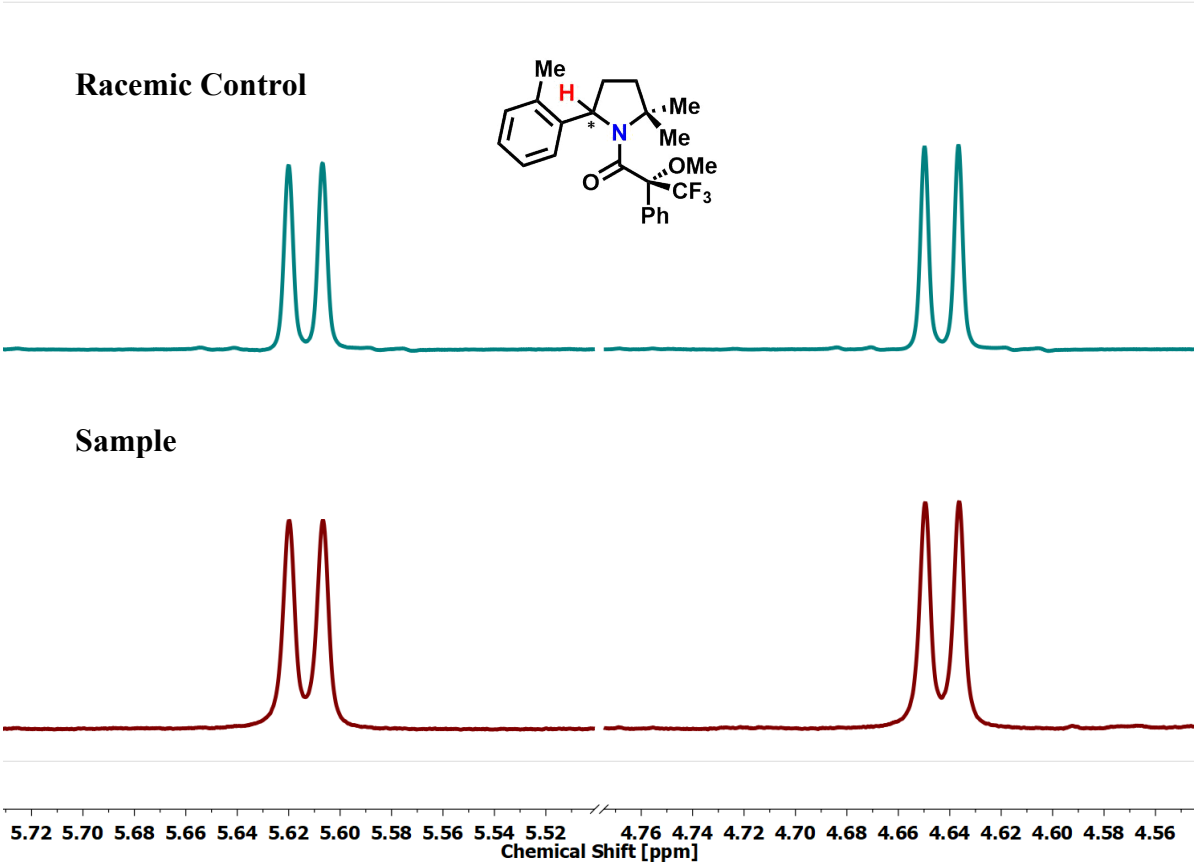
Integration Table

	5.46–5.40	**4.33–4.28**	**ee%**
Racemic Control	176.73	176.97	0
Sample	43.68	48.13	5%



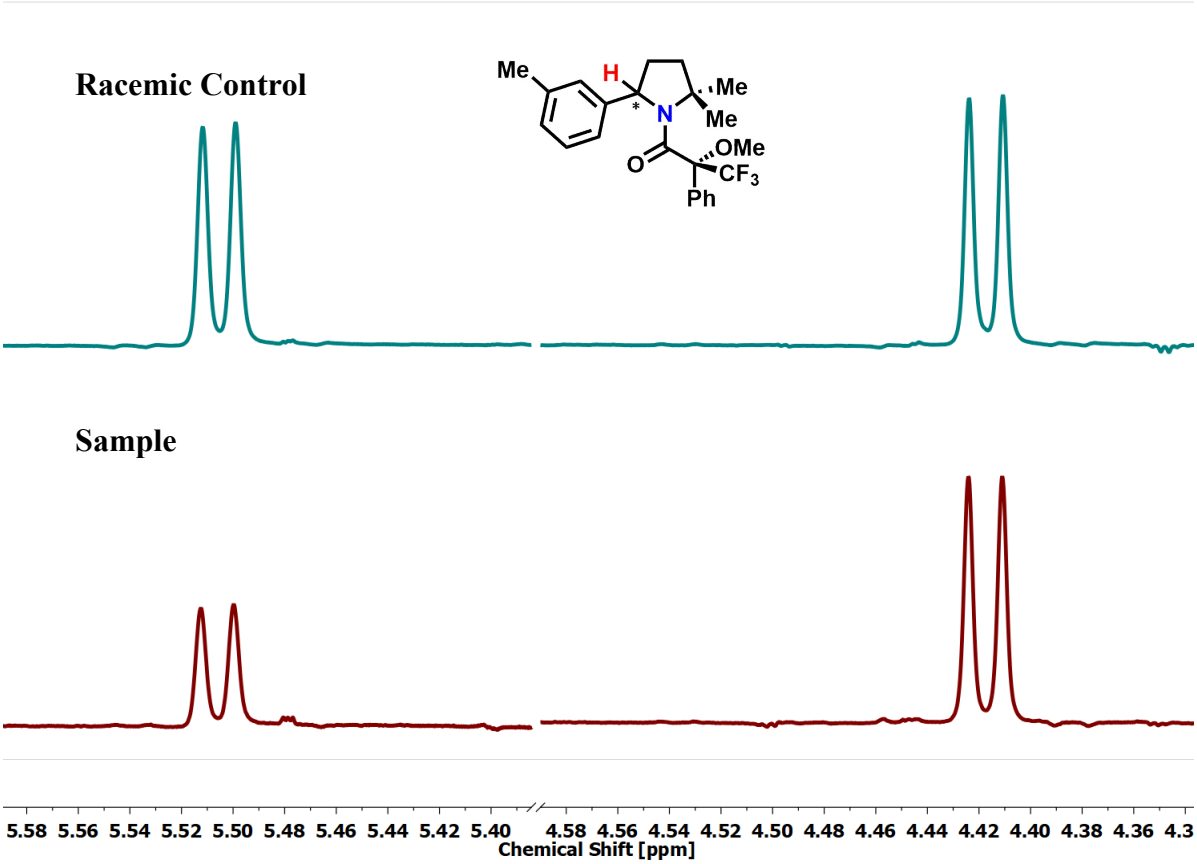
Integration Table

	5.07–5.01	**4.06–4.00**	**ee%**
Racemic Control	250.50	251.10	0
Sample	103.92	118.35	6%



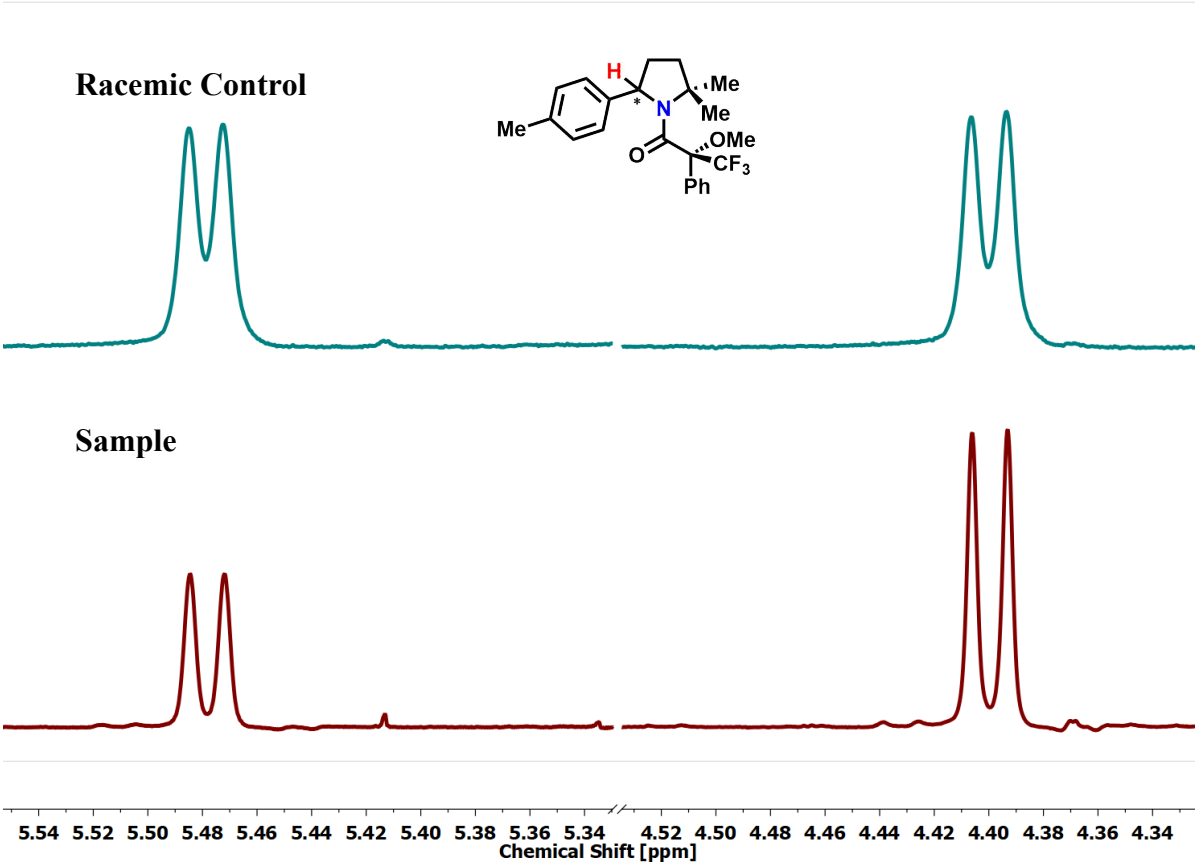
Integration Table

	5.07–5.01	**4.06–4.00**	**ee%**
Racemic Control	274.61	276.01	0
Sample	137.57	142.69	2%



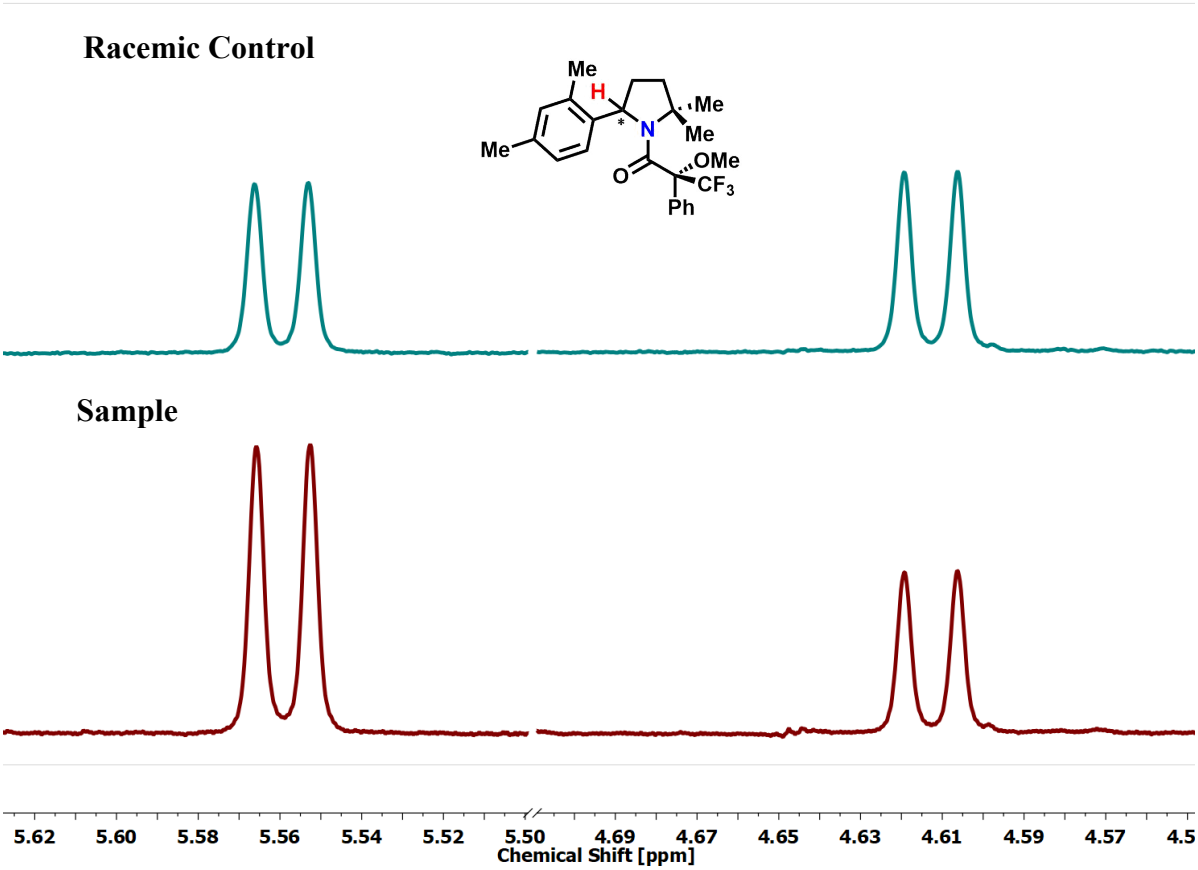
Integration Table

	5.55–5.45	**4.46–4.36**	**ee%**
Racemic Control	354.72	358.16	0
Sample	267.85	594.12	38%



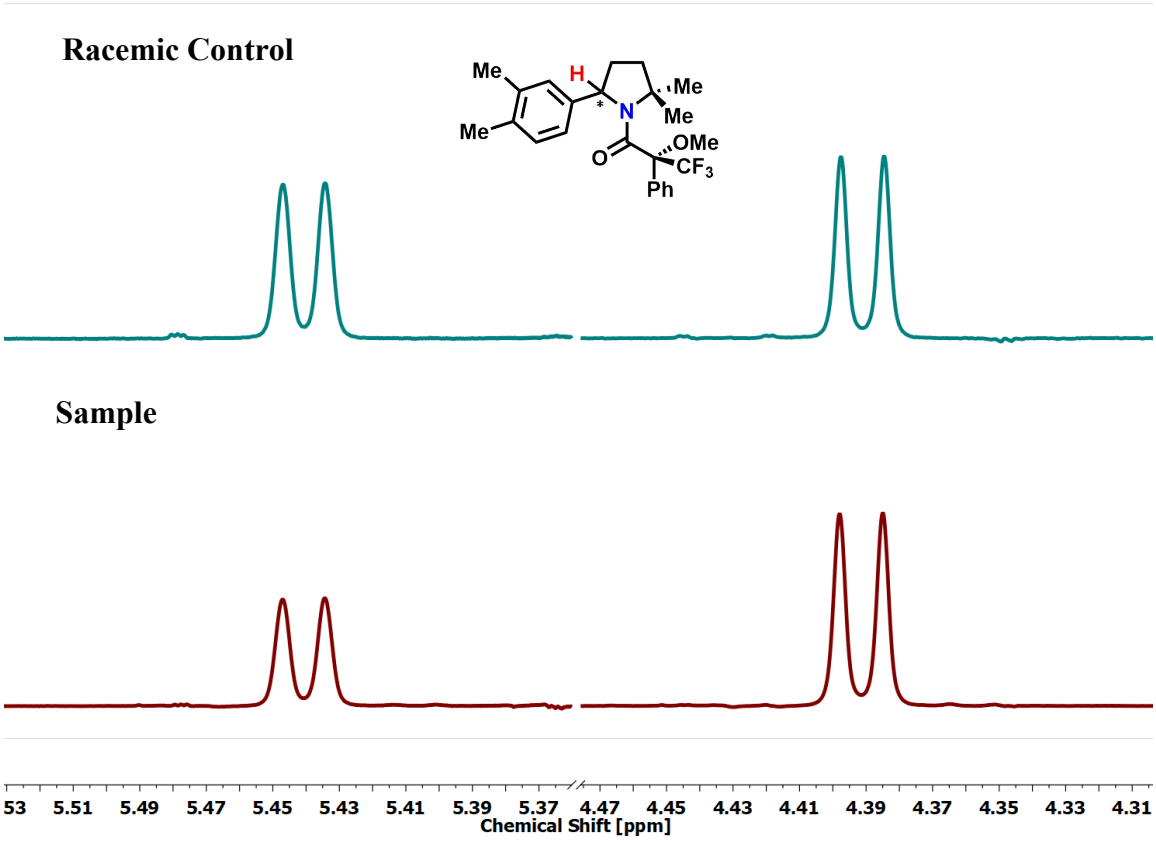
Integration Table

	5.53–5.43	**4.45–4.35**	**ee%**
Racemic Control	236.60	238.40	0
Sample	129.75	225.34	27%



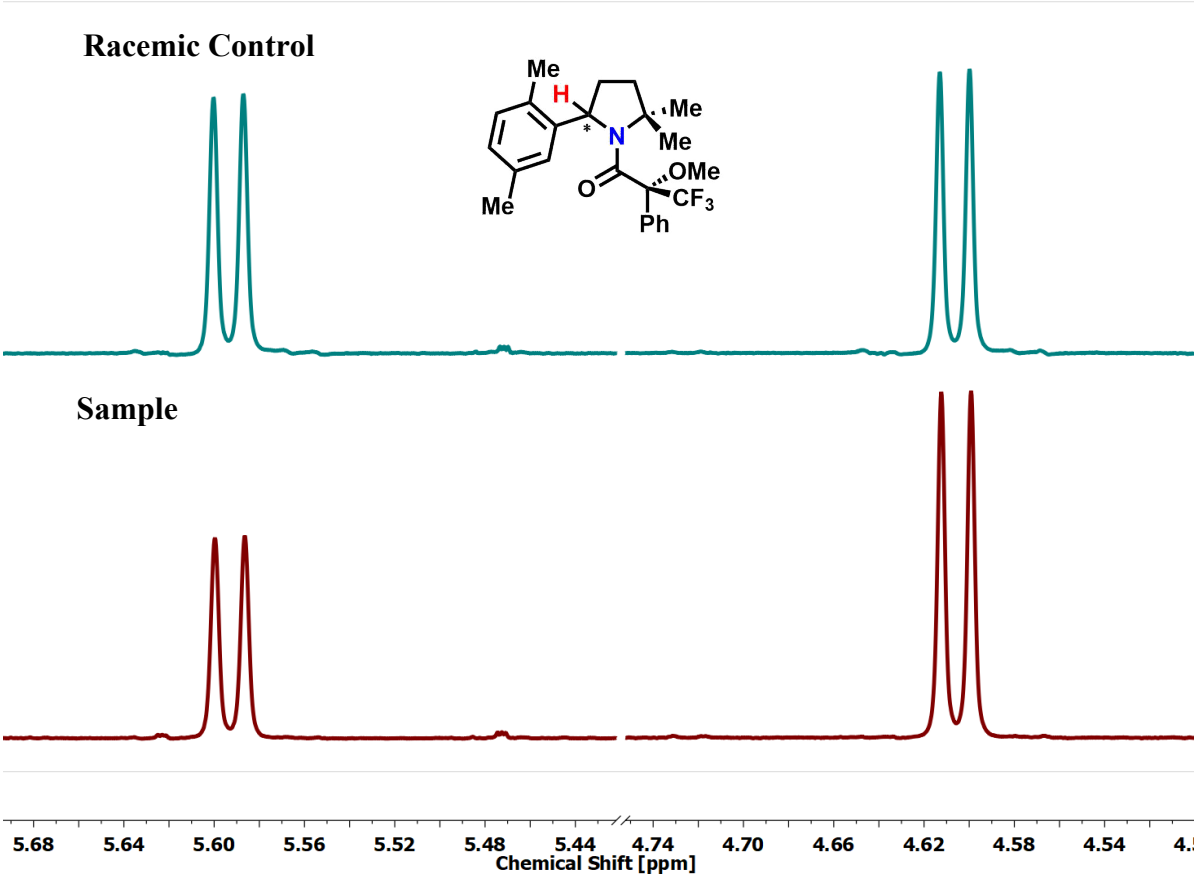
Integration Table

	5.61–5.51	**4.66–4.56**	**ee%**
Racemic Control	56.85	57.60	1%
Sample	80.47	43.52	30%



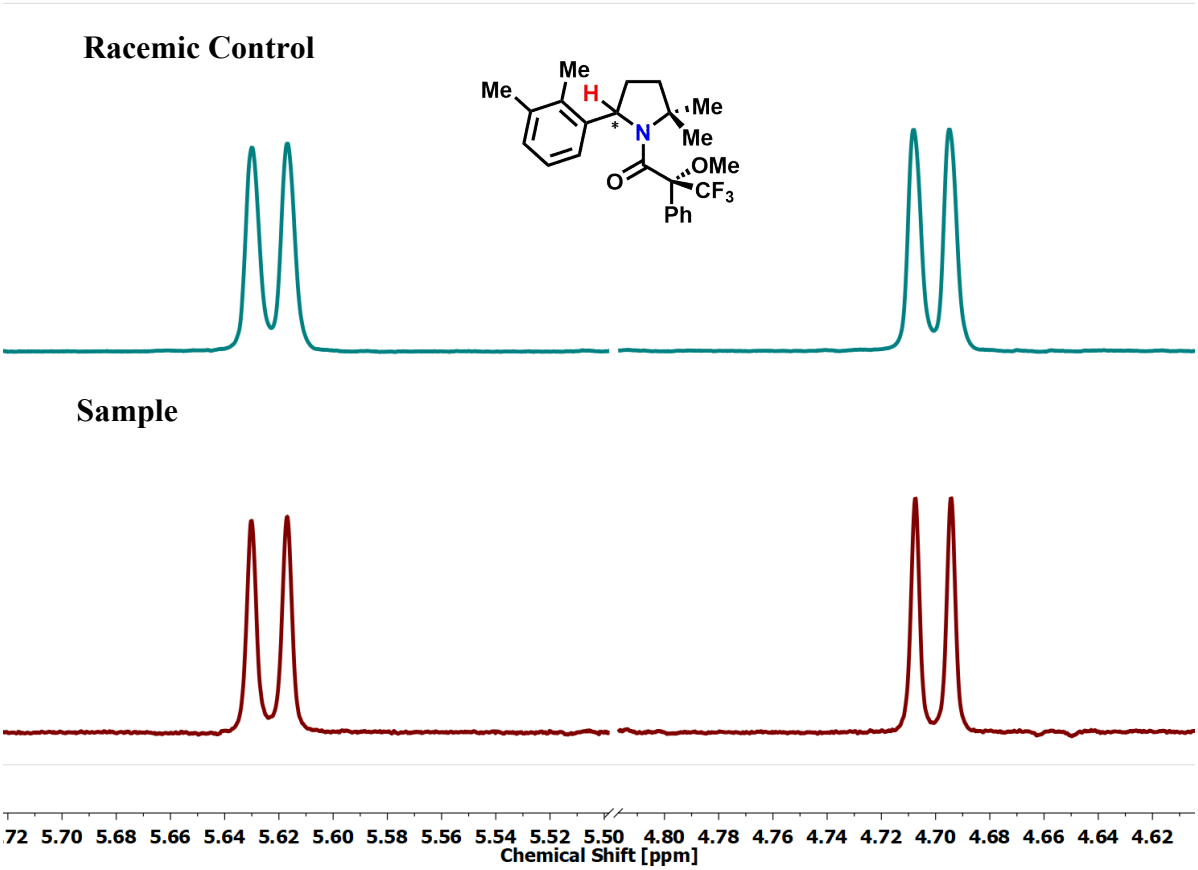
Integration Table

	5.50–5.40	**4.44–4.34**	**ee%**
Racemic Control	106.83	107.18	0
Sample	253.95	390.81	21%



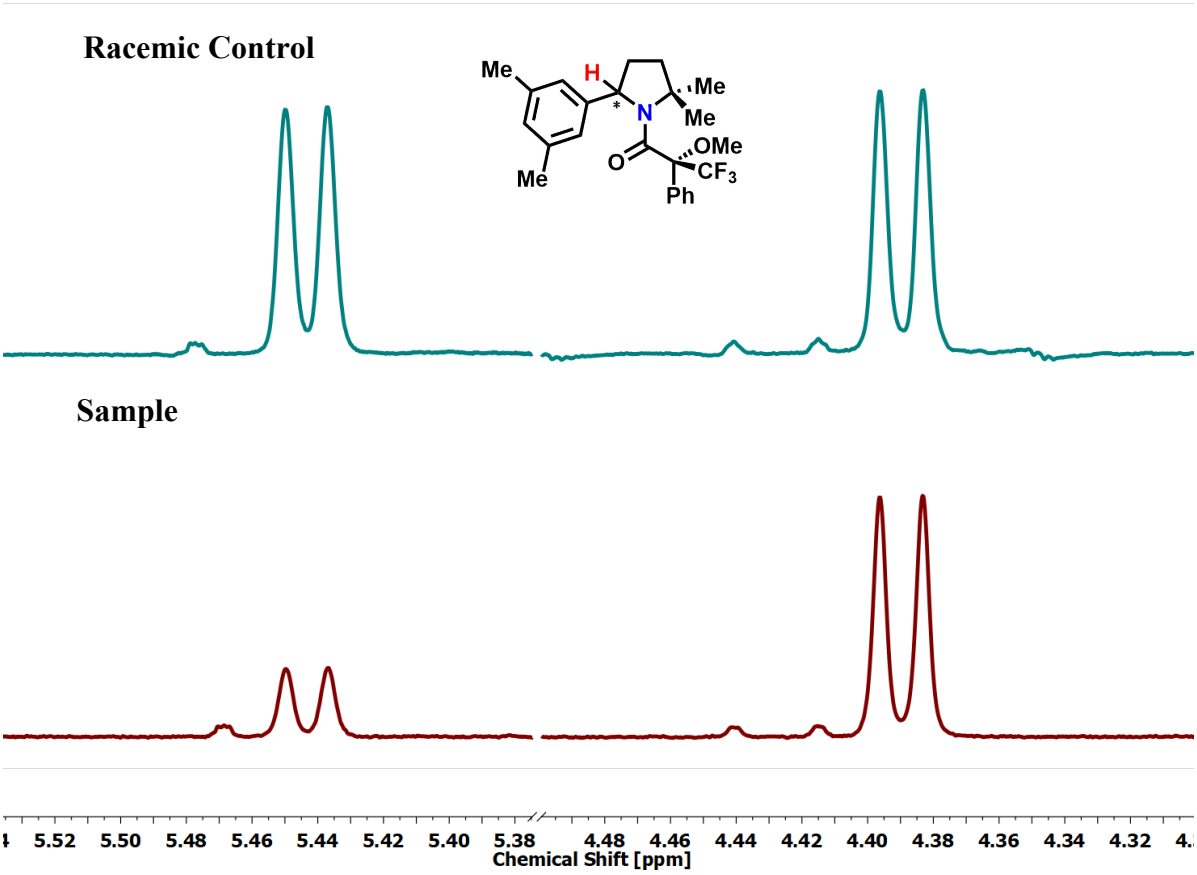
Integration Table

	5.65–5.55	**4.65–4.55**	**ee%**
Racemic Control	166.70	167.93	0
Sample	131.29	209.53	23%



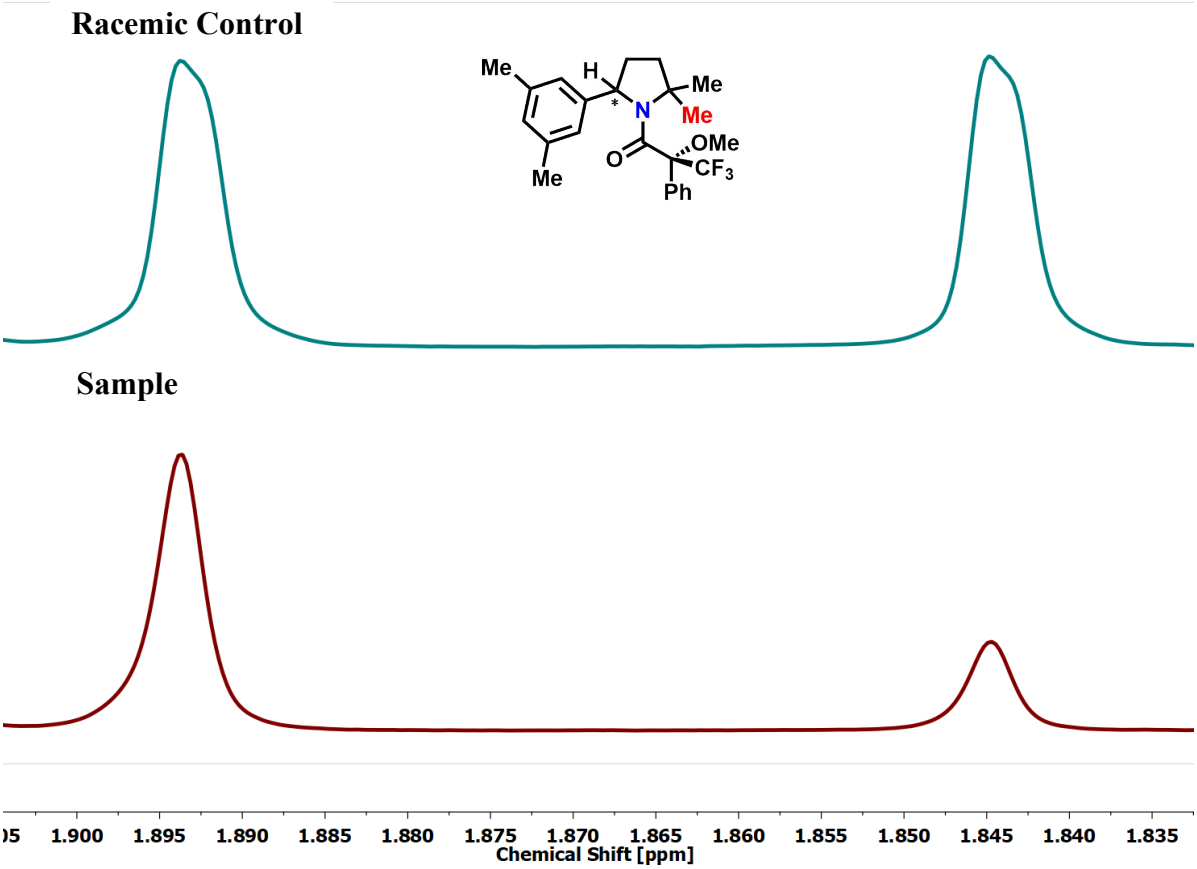
Integration Table

	5.67–5.57	**4.75–4.65**	**ee%**
Racemic Control	235.96	235.46	0
Sample	48.41	49.09	1%



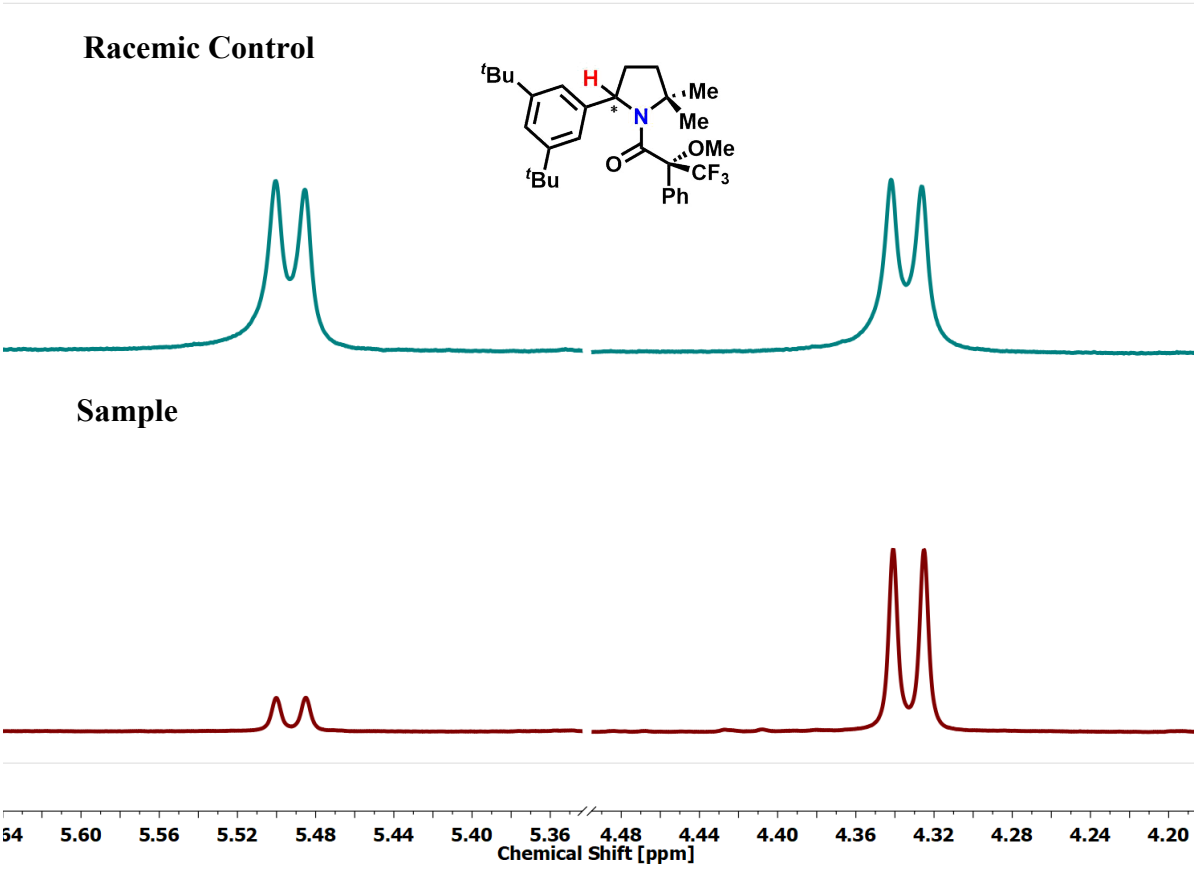
Integration Table

	5.49–5.39	**4.44–4.34**	**ee%**
Racemic Control	118.51	120.79	1%
Sample	30.81	100.54	53%



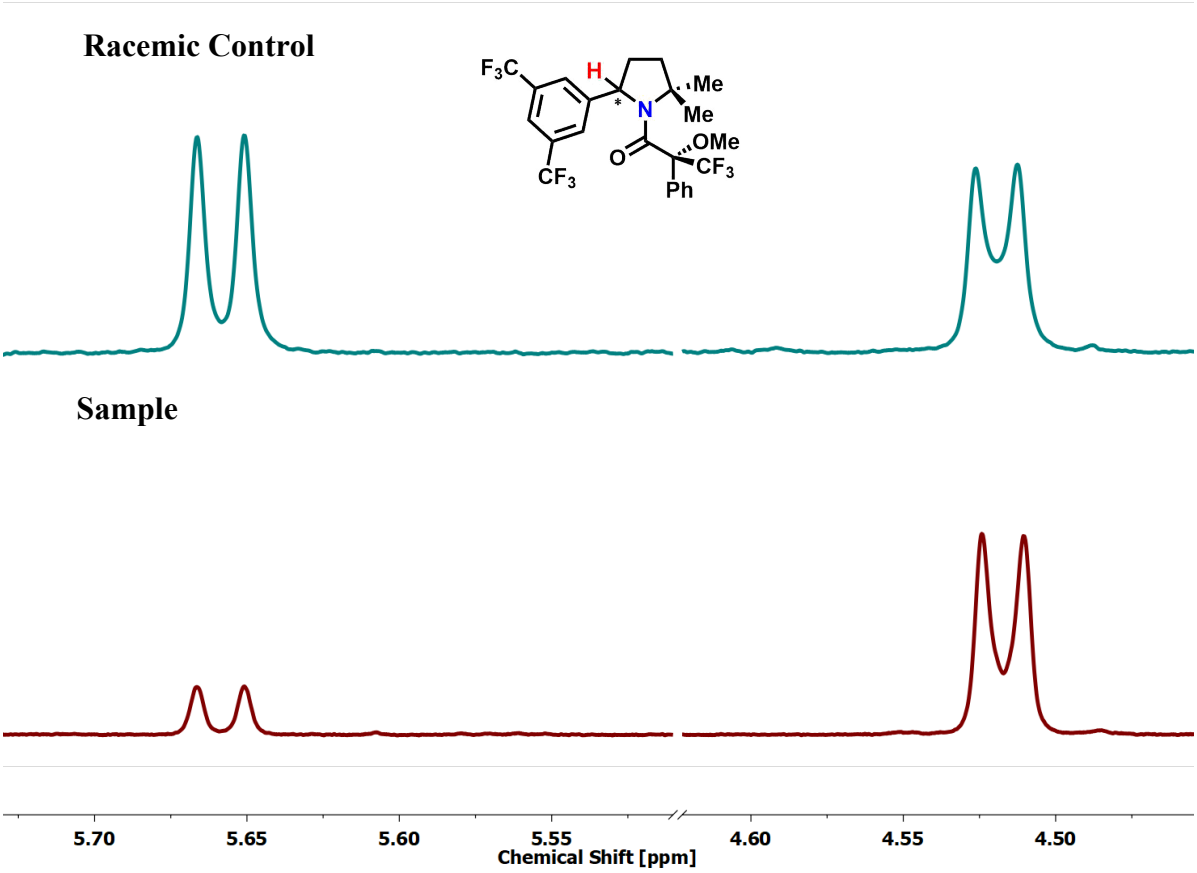
Integration Table

	1.90–1.88	**1.85–1.83**	**ee%**
Racemic Control	376.05	366.07	1%
Sample	282.21	89.86	52%



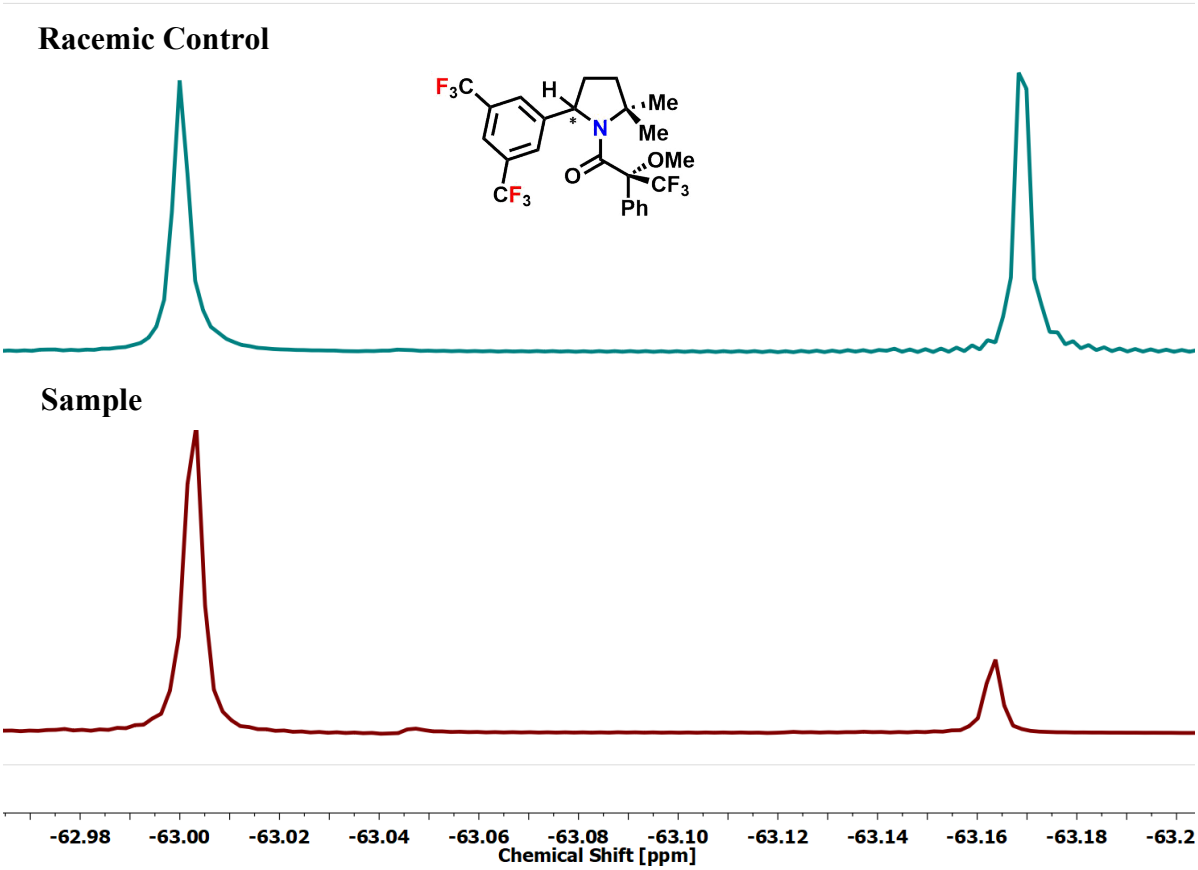
Integration Table

	5.55–5.45	**4.38–4.28**	**ee%**
Racemic Control	197.73	198.44	0
Sample	69.51	450.47	73%



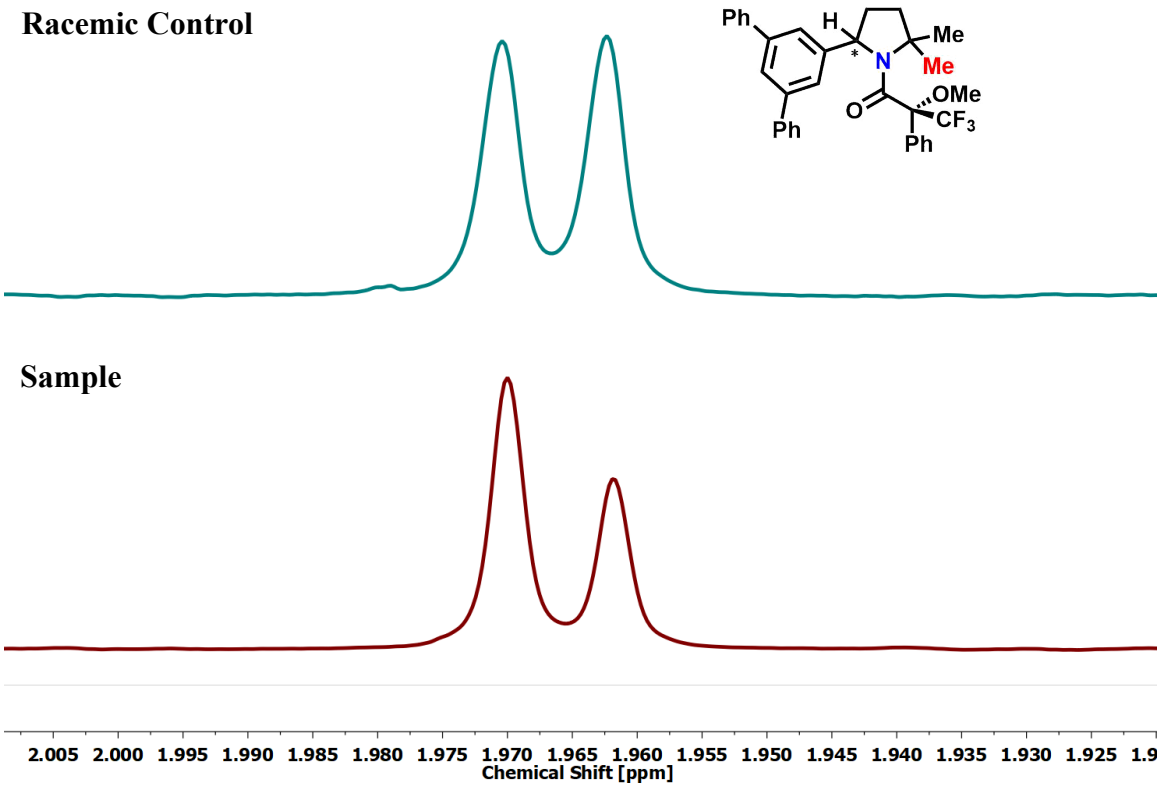
Integration Table

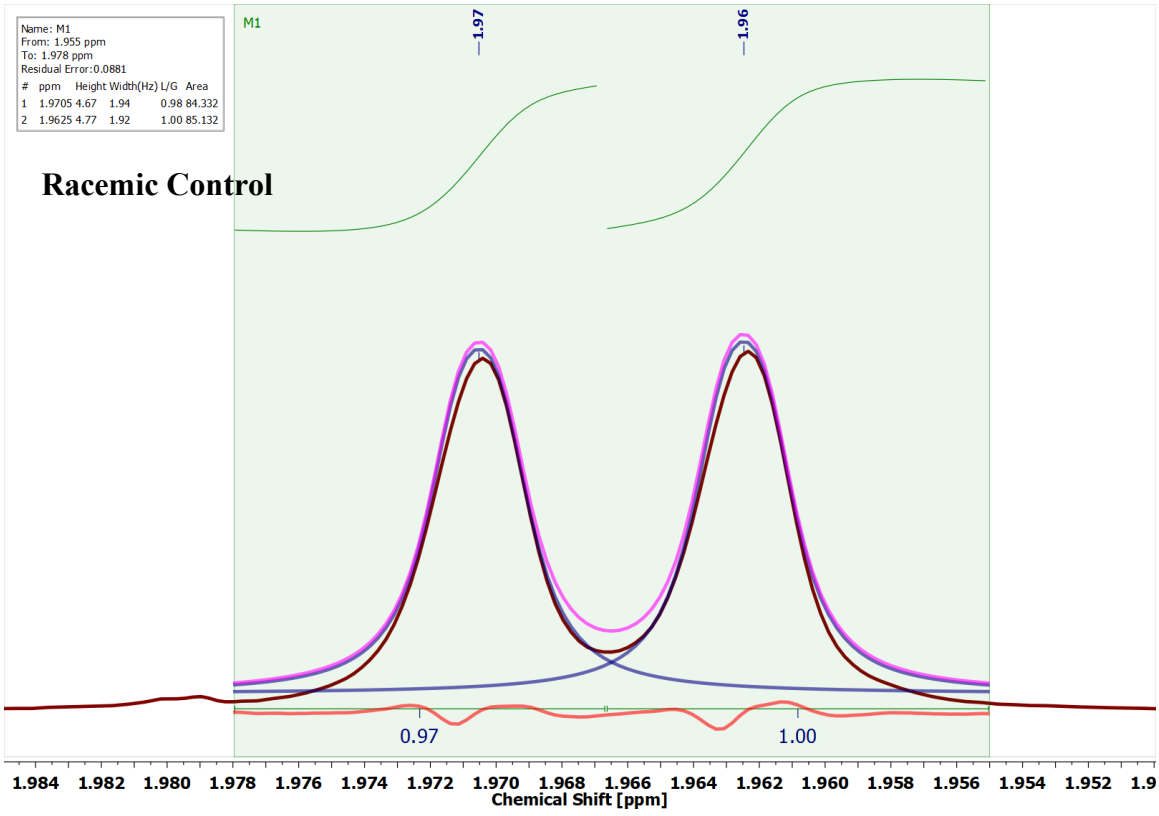
	5.70–5.60	**4.57–4.47**	**ee%**
Racemic Control	61.36	62.08	1%
Sample	97.35	496.89	67%

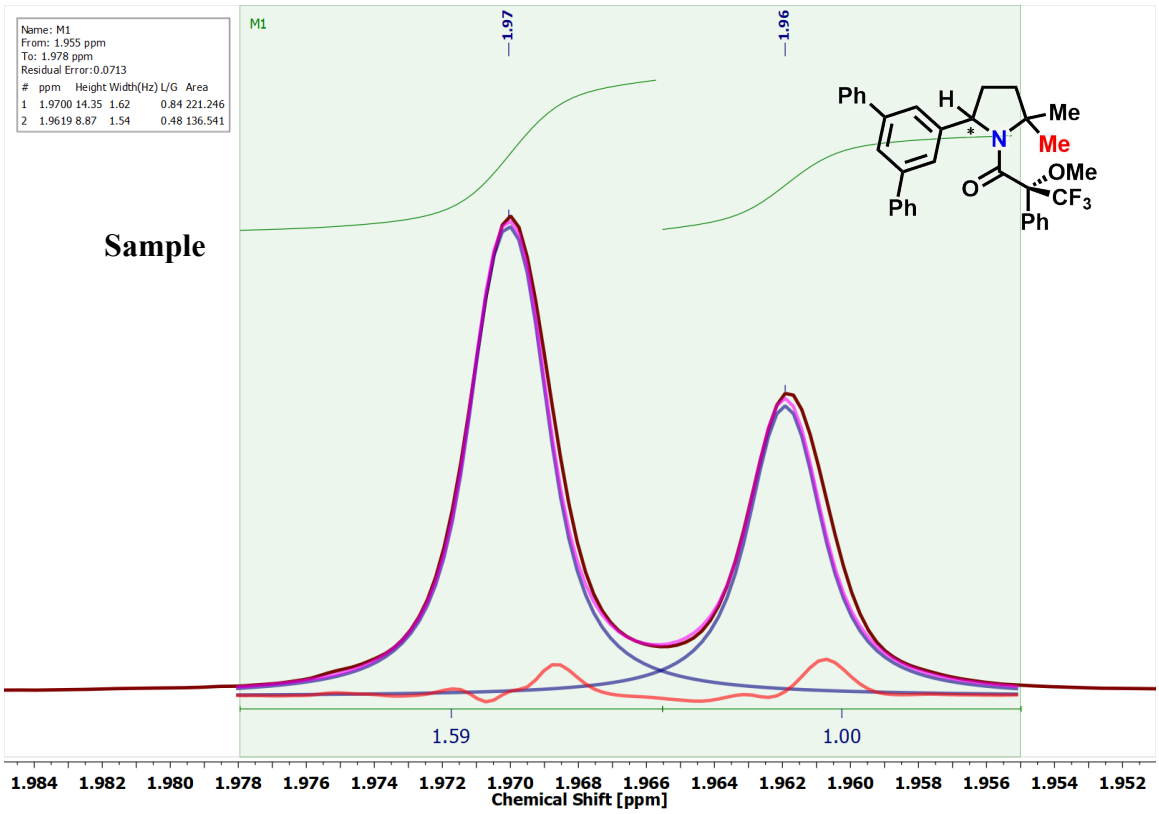


Integration Table

	−62.97 – −63.04	**−63.13 – −63.20**	**ee%**
Racemic Control	7628.98	7290.50	2%
Sample	25389.70	4859.21	68%


Racemic Control
Sample
Ph
H
Me
N
Me
OMe
CF3
O
Ph
Ph
2.005 2.000 1.995 1.990 1.985 1.980 1.975 1.970 1.965 1.960 1.955 1.950 1.945 1.940 1.935 1.930 1.925 1.9
Chemical Shift [ppm]


Name: M1
From: 1.955 ppm
To: 1.978 ppm
Residual Error:0.0881
ppm Height Width(Hz) L/G Area
1 1.9705 4.67 1.94 0.98 84.332
2 1.9625 4.77 1.92 1.00 85.132
M1
1.97
1.96
Racemic Control
0.97
1.00
1.984 1.982 1.980 1.978 1.976 1.974 1.972 1.970 1.968 1.966 1.964 1.962 1.960 1.958 1.956 1.954 1.952 1.9
Chemical Shift [ppm]

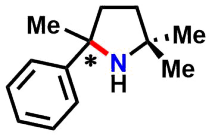


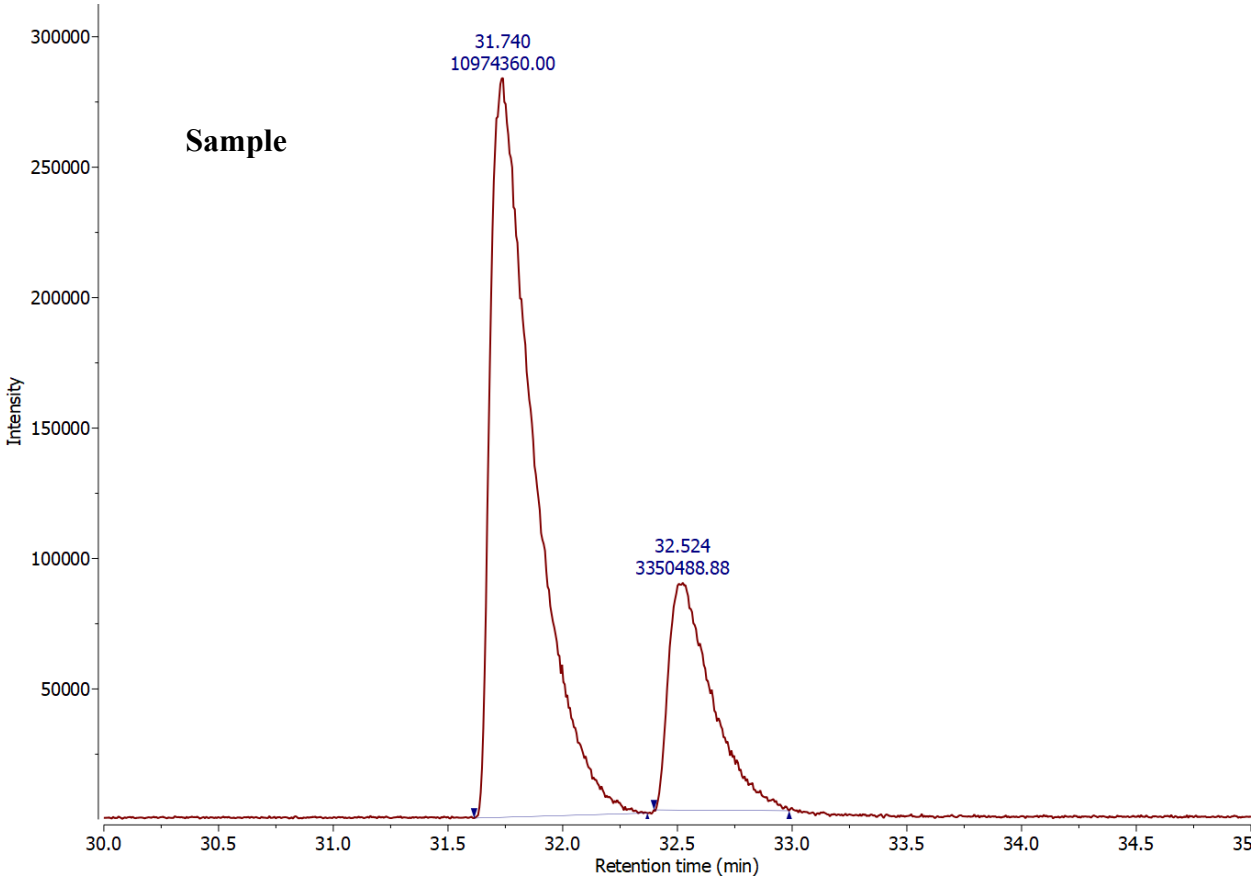
Integration Table

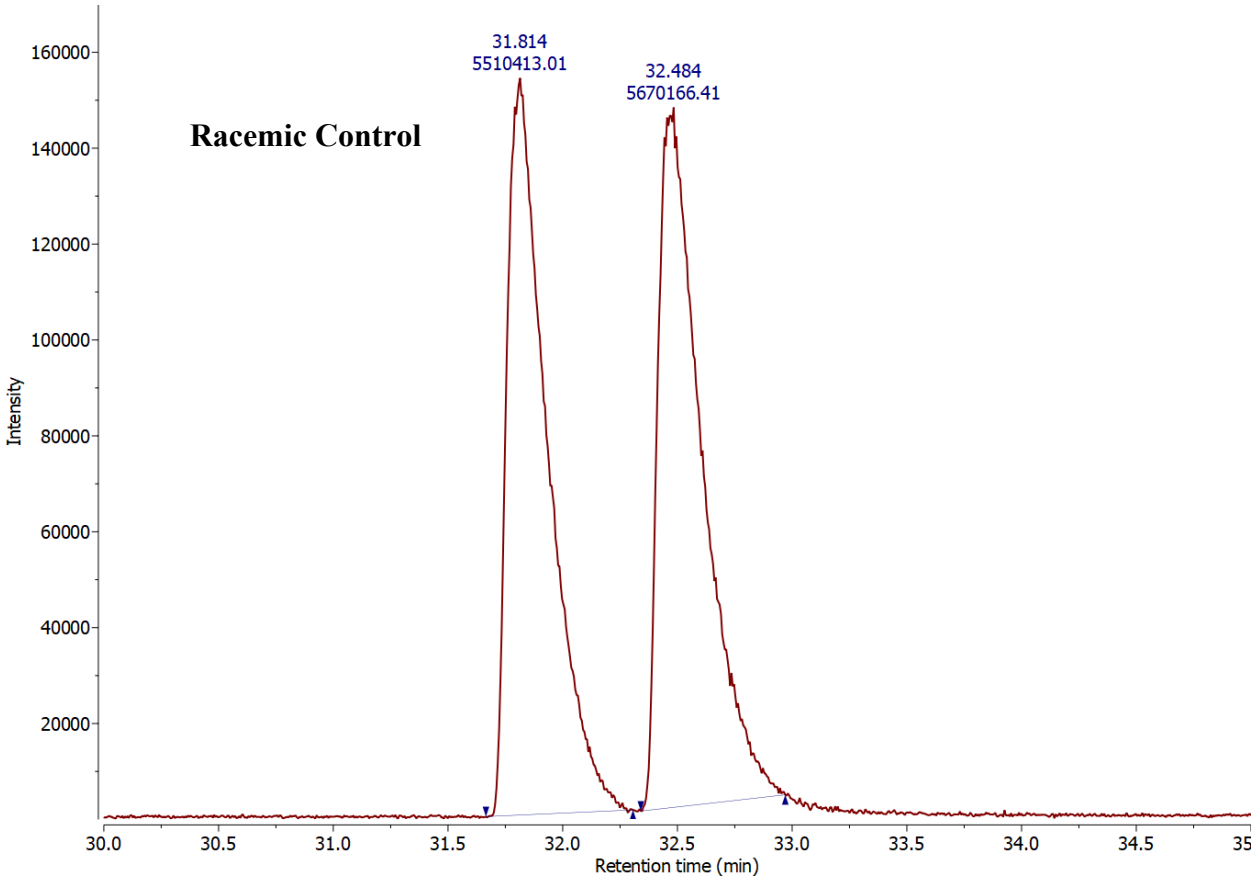
	δ = 1.97 ppm, (s)	δ = 1.96 ppm, (s)	ee%
Racemic Control	84.322	85.132	0%
Sample	221.246	136.541	24%

Chiral GC spectra for ee determination

2,2,5-trimethyl-5-phenylpyrrolidine



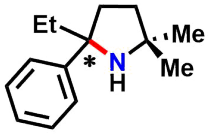


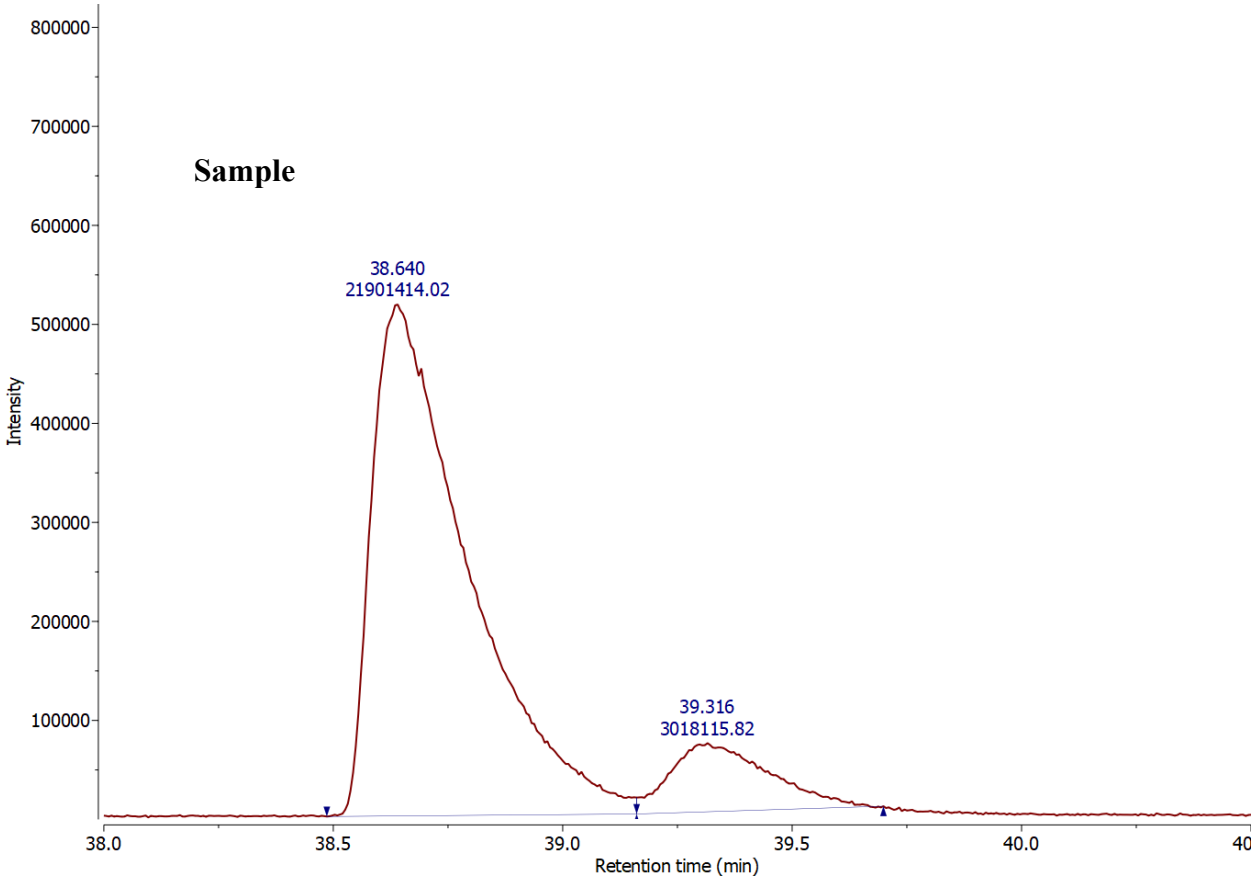


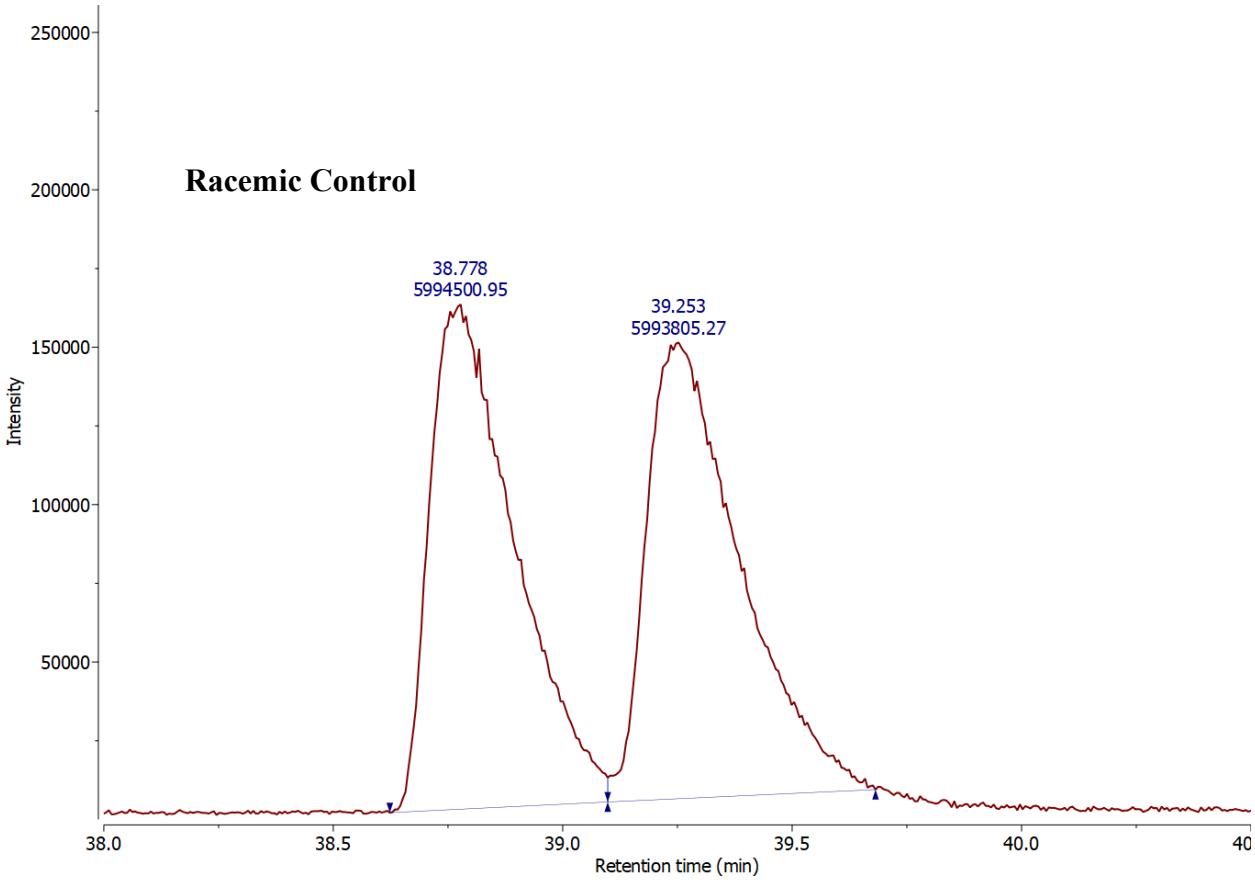
Integration Table

	31.6–32.4 min	**32.4–32.9 min**	**ee%**
Racemic Control	5510413.01	5670166.41	−1%
Sample	10974360.00	3350488.88	53%

2,2-dimethyl-5-ethyl-5-phenylpyrrolidine



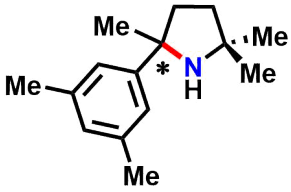


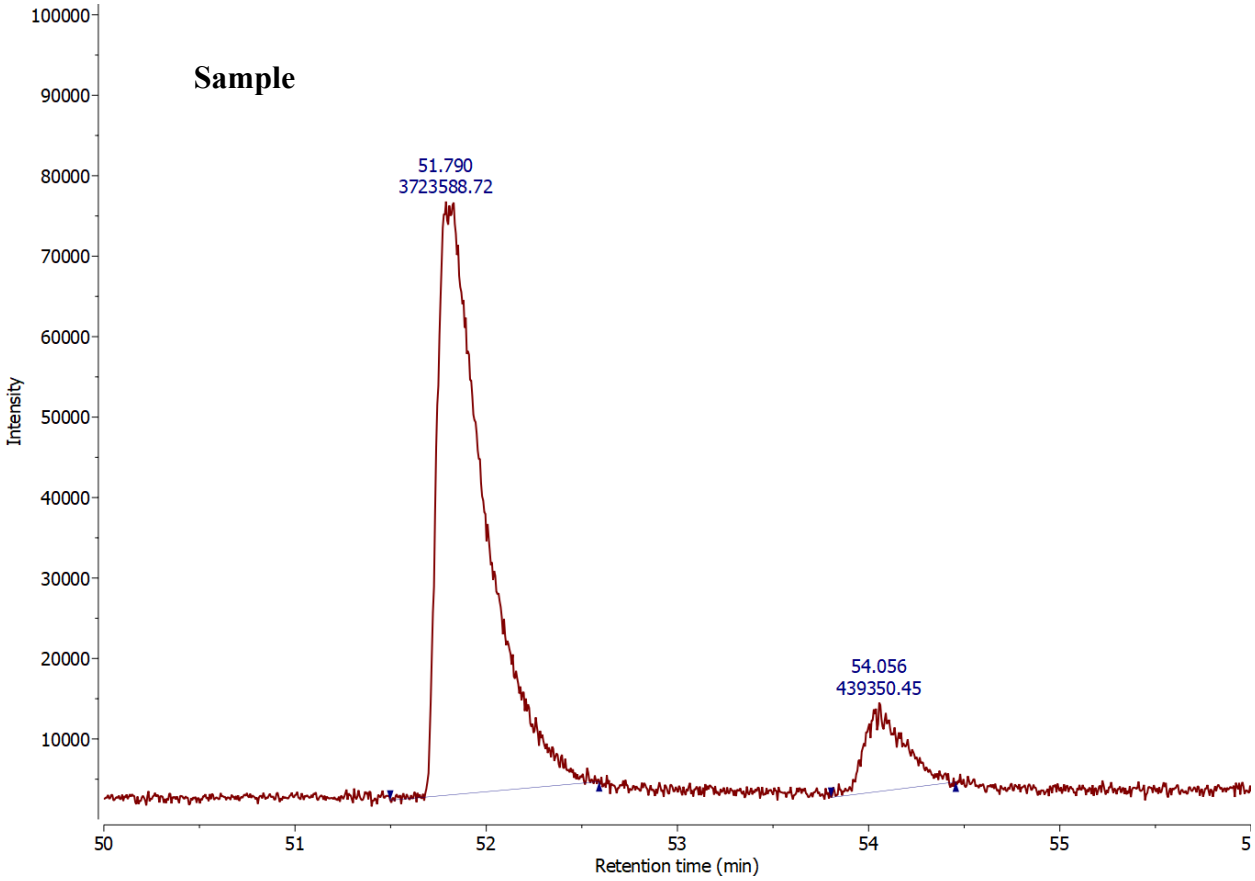


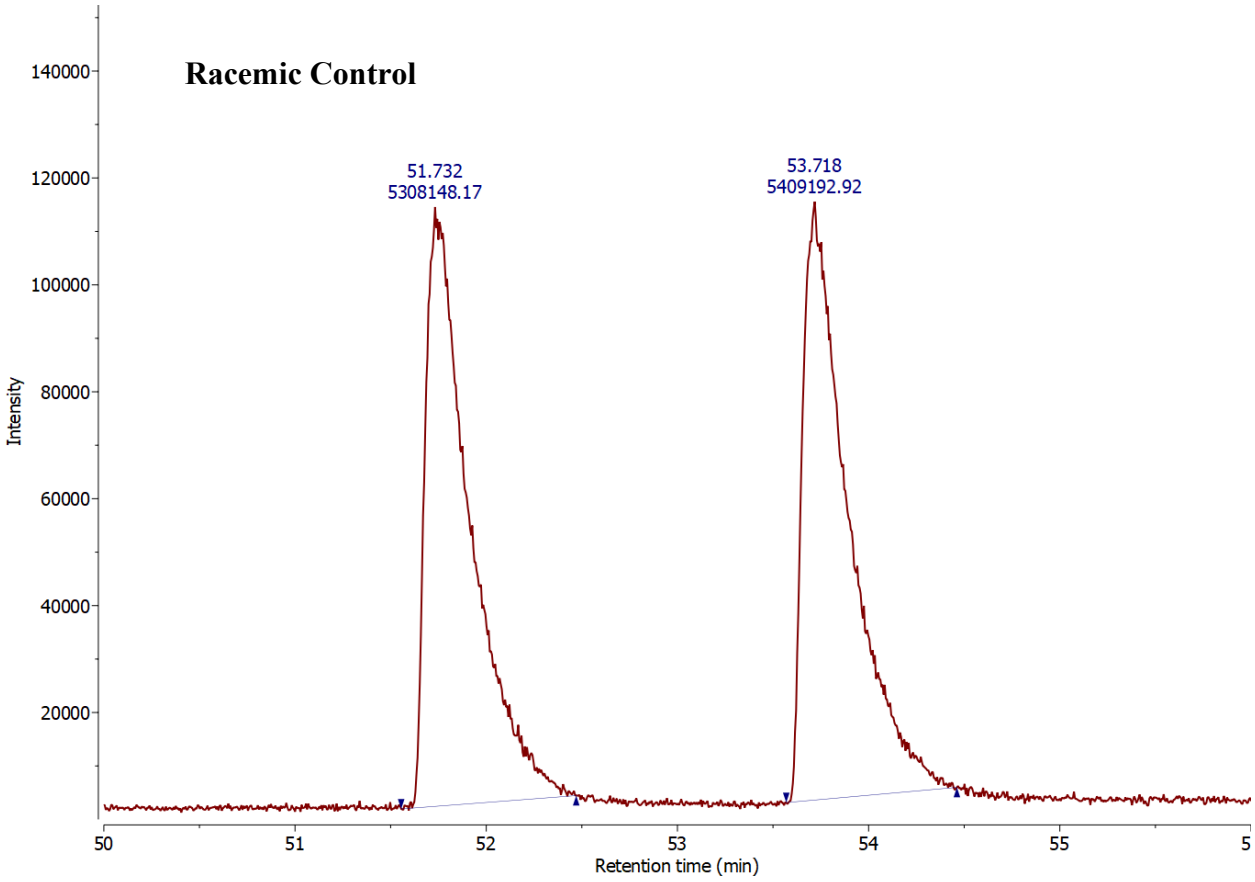
Integration Table

	38.5–39.2 min	**39.2–39.7 min**	**ee%**
Racemic Control	5994500.95	5993805.27	0%
Sample	21901414.02	3018115.82	76%

2-(3,5-dimethylphenyl)-2,5,5-trimethylpyrrolidine



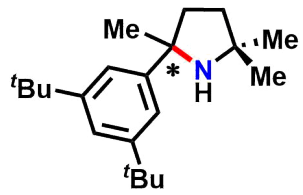


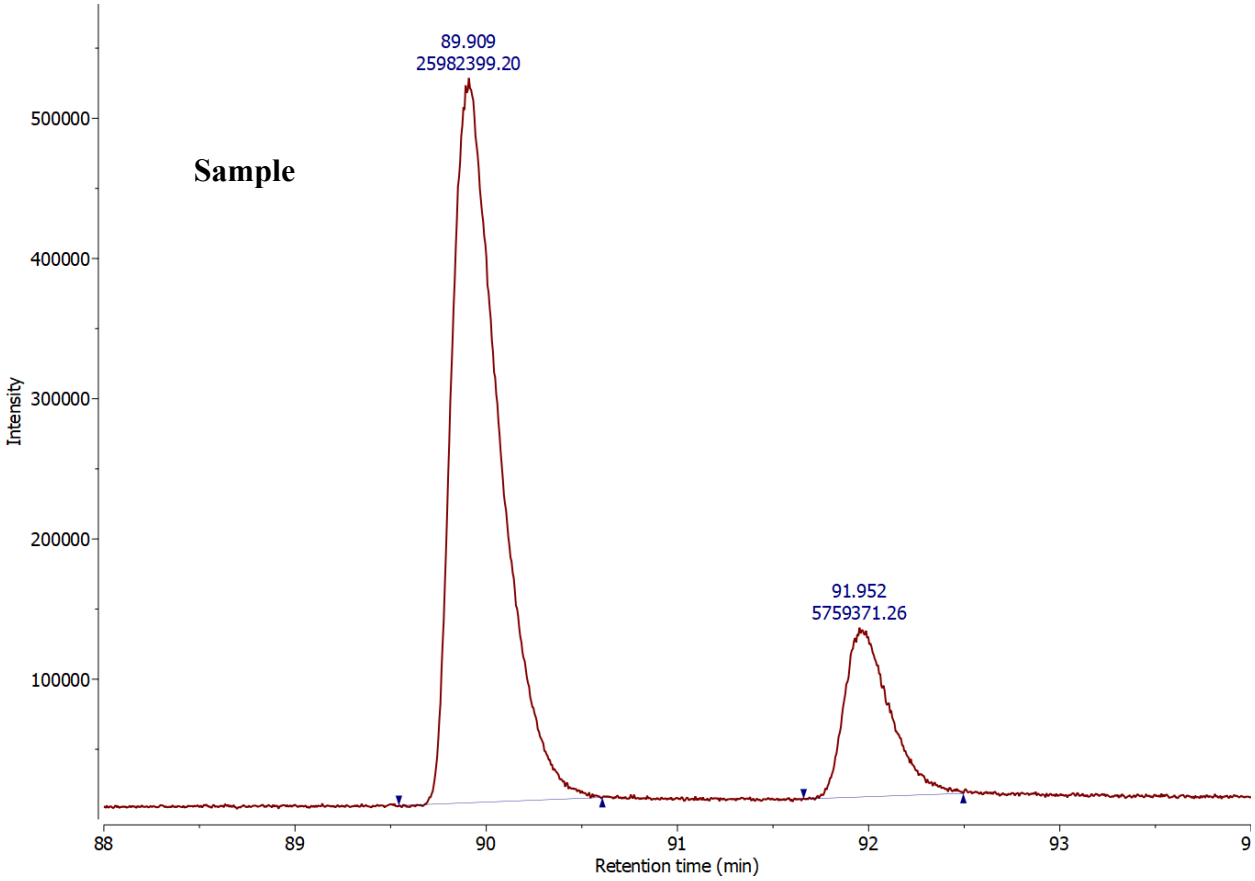


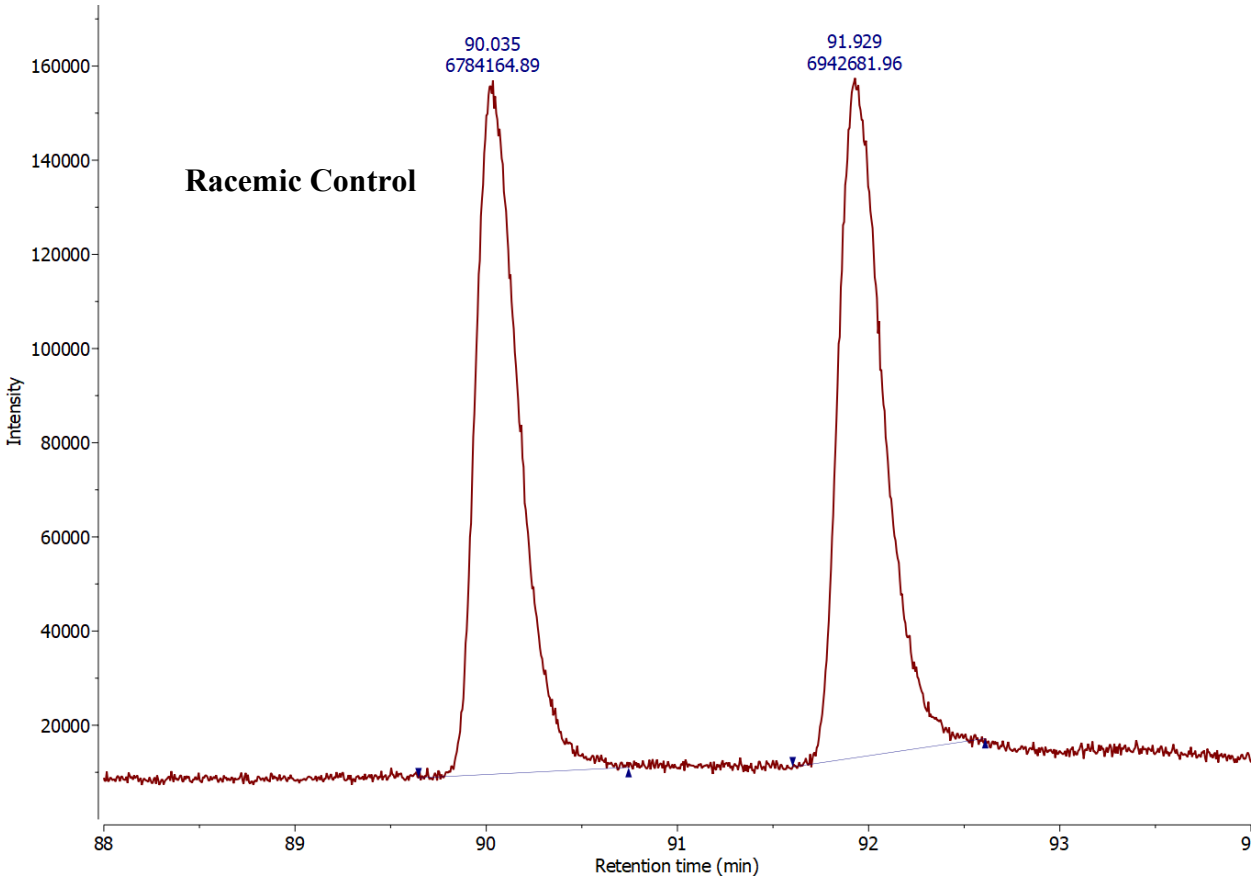
Integration Table

	51.5–52.6 min	53.8–54.4 min	ee%
Racemic Control	5308148.17	5409192.92	−1%
Sample	3723588.72	439350.45	79%

2-(3,5-di-tert-butylphenyl)-2,5,5-trimethylpyrrolidine



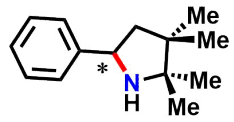




Integration Table

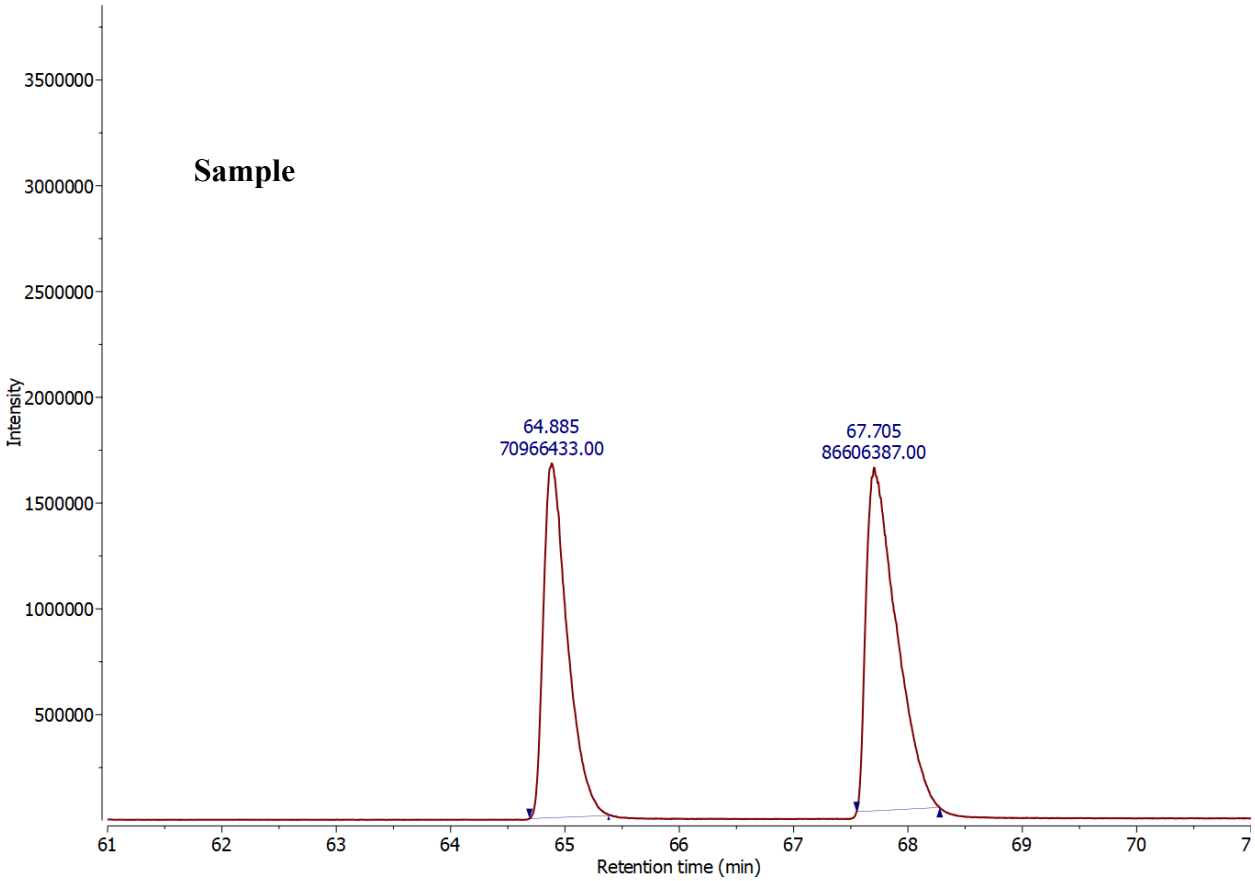
	89.5–90.6 min	91.6–92.5 min	ee%
Racemic Control	6784164.89	6942681.96	−1%
Sample	25982399.20	5759371.26	64%

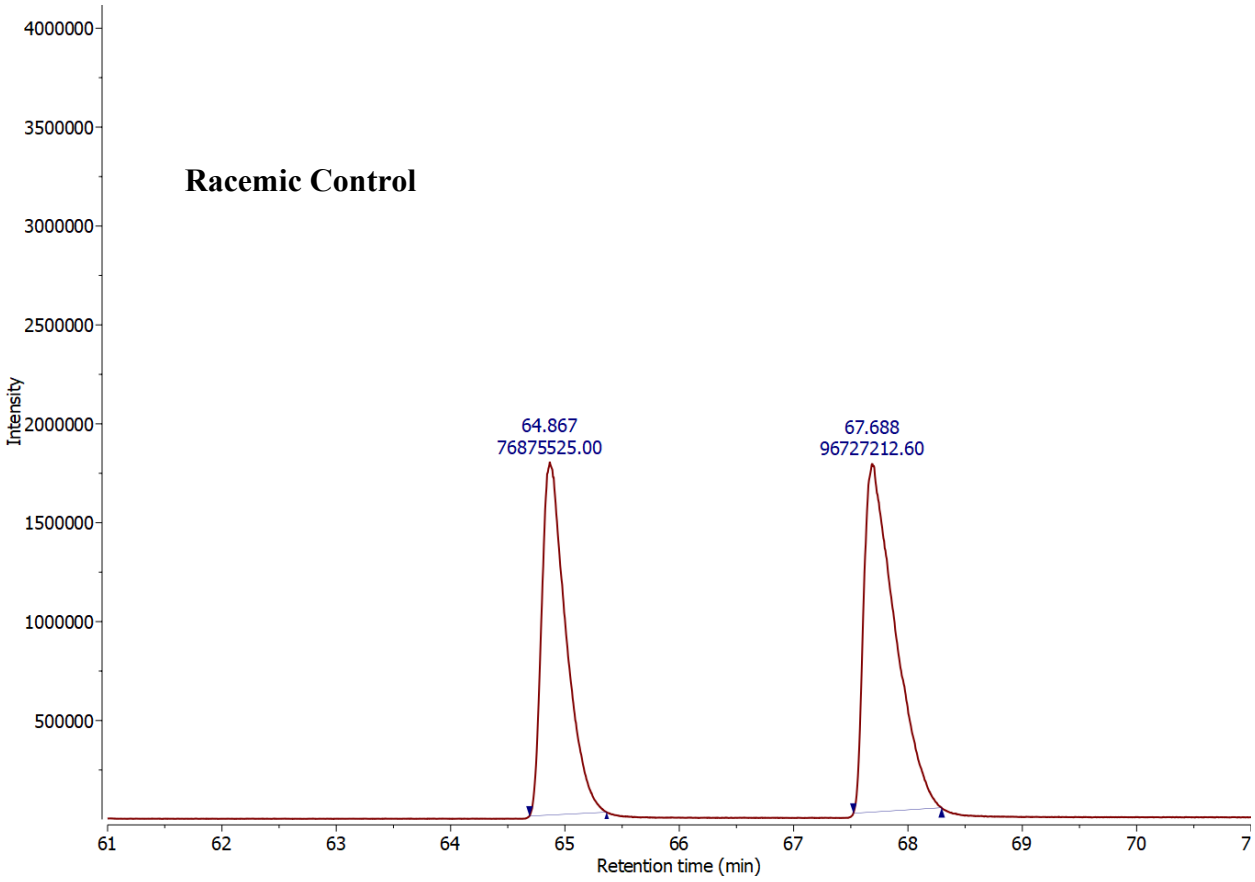
2,2,3,3-tetramethyl-5-phenylpyrrolidine



Acylation with acetyl chloride first

Acylation Procedure: To an NMR tube was added 6 mg of 2,2,3,3-tetramethyl-5-phenylpyrrolidine solution in 0.6 ml of $CDCl_3$, followed by 2.3 µl of acetyl chloride (1.1 equiv) and 4.5 µl of triethylamine (1.1 equiv). The NMR tube was capped, and the solution was shaken to be fully mixed and left at room temperature (23 °C). The reaction is fully complete in 2 h as indicated by ^{1}H NMR spectroscopy.





Integration Table

	64.7–65.4 min	**67.5–68.3 min**	**ee%**
Racemic Control	76875525.00	96727212.60	11%
Sample	70966433.00	86606387.00	10%

The non-zero ee% of the racemic control is likely due to baseline and line broadening. The difference in ee% obtained from both racemic control and sample of interest is 1%; therefore, the mixture is determined to be fully racemic (0% *ee*).

X-ray diffraction techniques

Structures of **3**-**6** were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device. Radiation was from a graphite fine focus sealed tube Mo Kα (0.71073 Å) source or a I/mS microfocus tube Cu Kα (1.54178 Å) source. Crystals were mounted on a cryoloop or glass fiber pin using Paratone N oil. Structures were collected at 100 K. Data were collected as a series of φ and/or ω scans.

Data were integrated using SAINT and scaled with multi-scan absorption correction using SADABS.[20-21] The structures were solved by intrinsic phasing, direct methods or Patterson maps using SHELXS-2014 and refined against F_2 on all data by full matrix least squares with SHELXL-2014.[20-21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were constrained to be 1.2 times the parameter of the atoms they were linked to (1.5 times for methyl groups). Further details on particular structures are noted below.

(^{TrH}BOX)NiI(py) (3): The structure was solved in the monoclinic space group $P2_1$ with two molecules per unit cell and one molecule in the asymmetric unit. (CCDC 1971707)

(^{TrH}BOX)Ni(py) (4): The structure was solved in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell and one molecule in the asymmetric unit. The asymmetric unit also contained half of a molecule of pyridine and disordered THF, in which the crystal was grown. The molecule has one rotational disordered pyridine molecule bound to Ni. (CCDC 1971708)

(^{TrH}BOX)Ni(κ^2-N$_4$Ad$_2$) (5): The structure was solved in the monoclinic space group $P2_1$ with two molecules per unit cell and one molecule in the asymmetric unit. The asymmetric unit also contained one molecule of hexane, in which the crystal was grown (CCDC 1971709)

(^{TrH}BOX)Ni(NAd) (6): The structure was solved in the orthorhombic space group $P2_12_12_1$ with eight molecules per unit cell and two molecules in the asymmetric unit. Cracking of the crystal even under

cryogenic stream was observed. Due to the low crystal quality, several atoms were refined using thermal ellipsoid restrains and constraints, and disordered solvents in the asymmetric unit is refined using solvent mask.[20-21] (CCDC 1971710)

Table S2. X-ray diffraction experimental details

	(^{TrH}BOX)NiI(py) (3)	(^{TrH}BOX)Ni(py) (4)
Moiety Formula	$C_{50}H_{42}IN_3NiO_2$	$C_{50}H_{42}N_3NiO_2 \cdot 0.5\ C_2H_4O \cdot 0.5\ C_5H_5N$
FW	902.46	851.18
Crystal System	Monoclinic	Orthorhombic
Space Group (Z)	$P2_1$	$P2_12_12_1$
a (Å)	8.8548(7)	10.06432(11)
b (Å)	27.5888(19)	13.6461(2)
c (Å)	9.0559(7)	35.0160(4)
α (°)	90	90
β (°)	115.112(5)	90
γ (°)	90	90
Volume (Å^3)	2003.2(3)	4809.05(10)
Calc. ρ (mg/m^3)	1.496	1.176
μ (cm^{-1})	7.100	0.920
Crystal size (mm)	0.14×0.04×0.04	0.20×0.05×0.05
Reflections	7092	8478
Completeness (to 2θ)	0.977	0.954
GOF on F^2	0.973	1.048
R_1, wR_2[c] [I > 2σ(I)]	0.0477, 0.1010	0.0635, 0.1794

	$(^{TrH}BOX)Ni(\kappa^2\text{-}N_4Ad_2)$ (5)	$(^{TrH}BOX)Ni(NAd)$ (6)
Moiety Formula	$C_{65}H_{67}N_6NiO_2 \cdot C_6H_{14}$	$C_{55}H_{52}N_3NiO_2$
FW	1109.11	845.69
Crystal System	Monoclinic	Orthorhombic
Space Group (Z)	$P2_1$	$P2_12_12_1$
a (Å)	15.9739(11)	9.6441(8)
b (Å)	10.4011(8)	28.862(2)
c (Å)	18.7687(15)	42.241(2)
α (°)	90	90
β (°)	111.217(4)	90
γ (°)	90	90
Volume ($Å^3$)	2907.0(4)	11757.7(14)
Calc. ρ (mg/m^3)	1.267	0.956
μ (mm^{-1})	0.884	0.365
Crystal size (mm)	0.20×0.18×0.04	0.14×0.04×0.03
Reflections	10307	21009
Completeness (to 2θ)	0.992	0.995
GOF on F^2	1.024	0.961
R_1, wR_2^c [$I > 2\sigma(I)$]	0.0472, 0.1254	0.0820, 0.2031

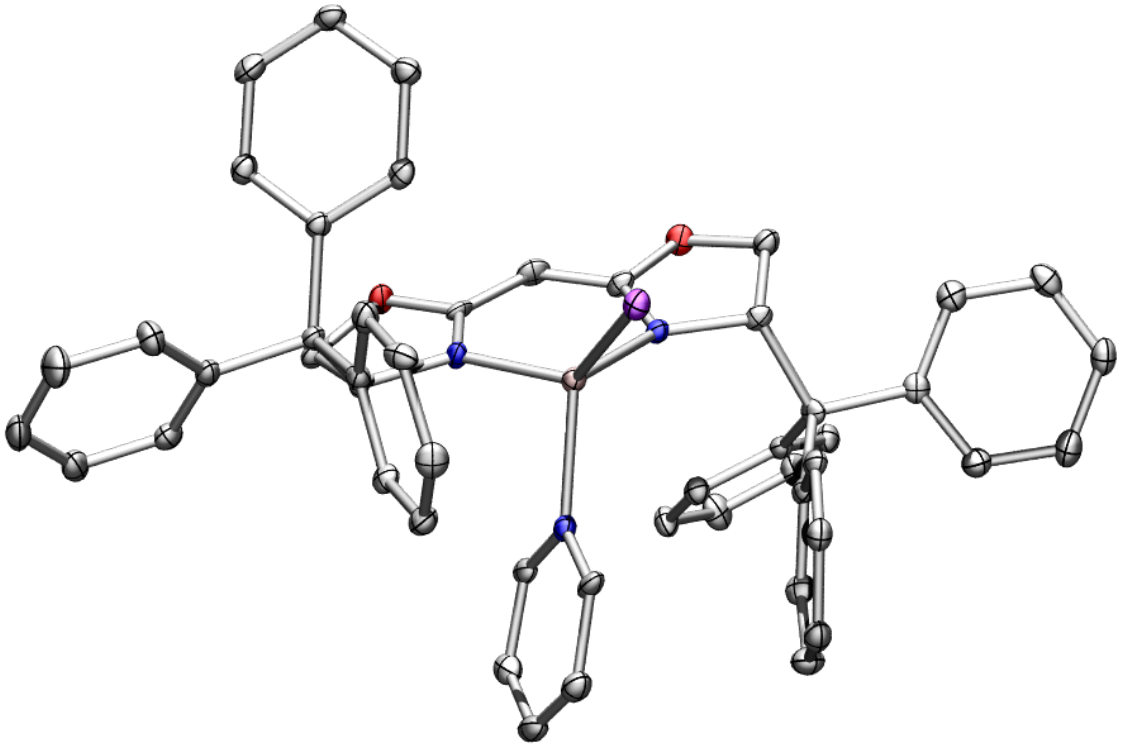


Figure S13. Solid-state molecular structure for (^{TrH}BOX)NiI(py) (3) with thermal ellipsoids at 50% probability level. Hydrogen atoms omitted for clarity. nickel = pink, oxygen = red, nitrogen = blue, carbon = gray, iodine = purple.

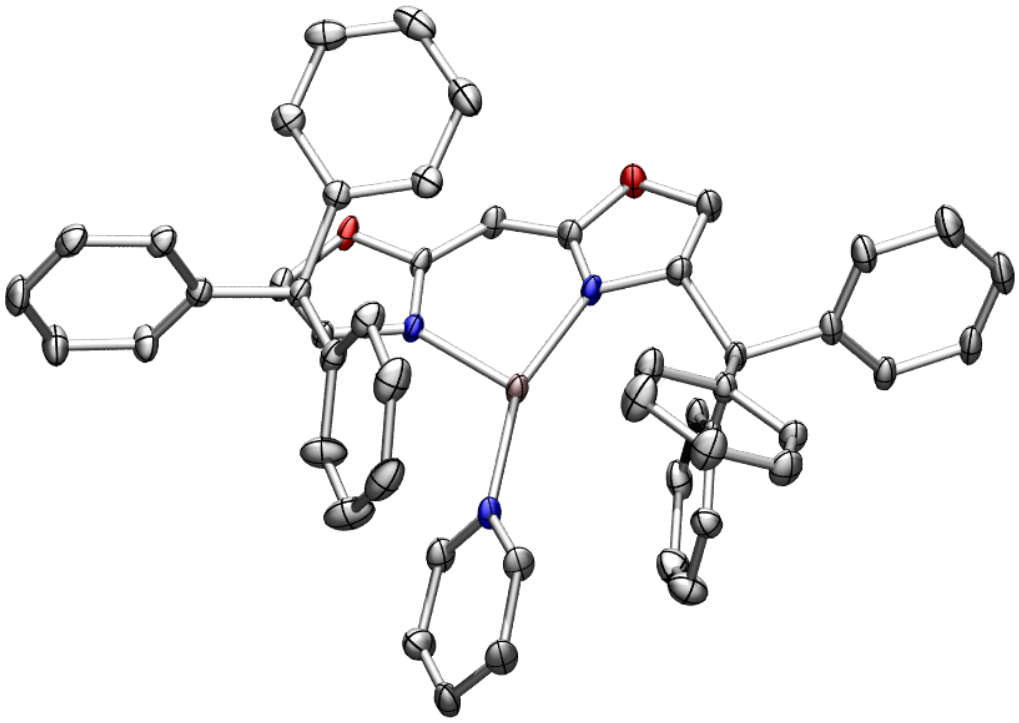


Figure S14. Solid-state molecular structure for (^{TrH}BOX)Ni(py) (4) with thermal ellipsoids at 50% probability level. Hydrogen atoms omitted for clarity. nickel = pink, oxygen = red, nitrogen = blue, carbon = gray.

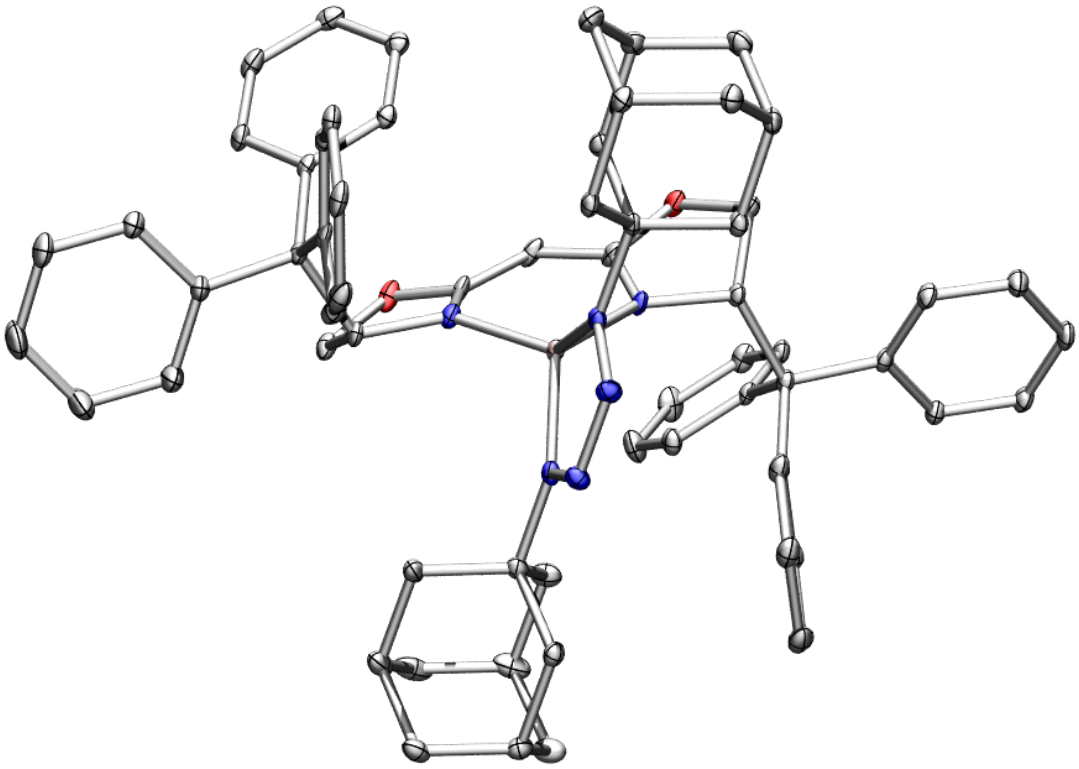


Figure S15. Solid-state molecular structure for (^{TrH}BOX)Ni(κ^2-N_4Ad_2) (5) with thermal ellipsoids at 50% probability level. Hydrogen atoms omitted for clarity. nickel = pink, oxygen = red, nitrogen = blue, carbon = gray.

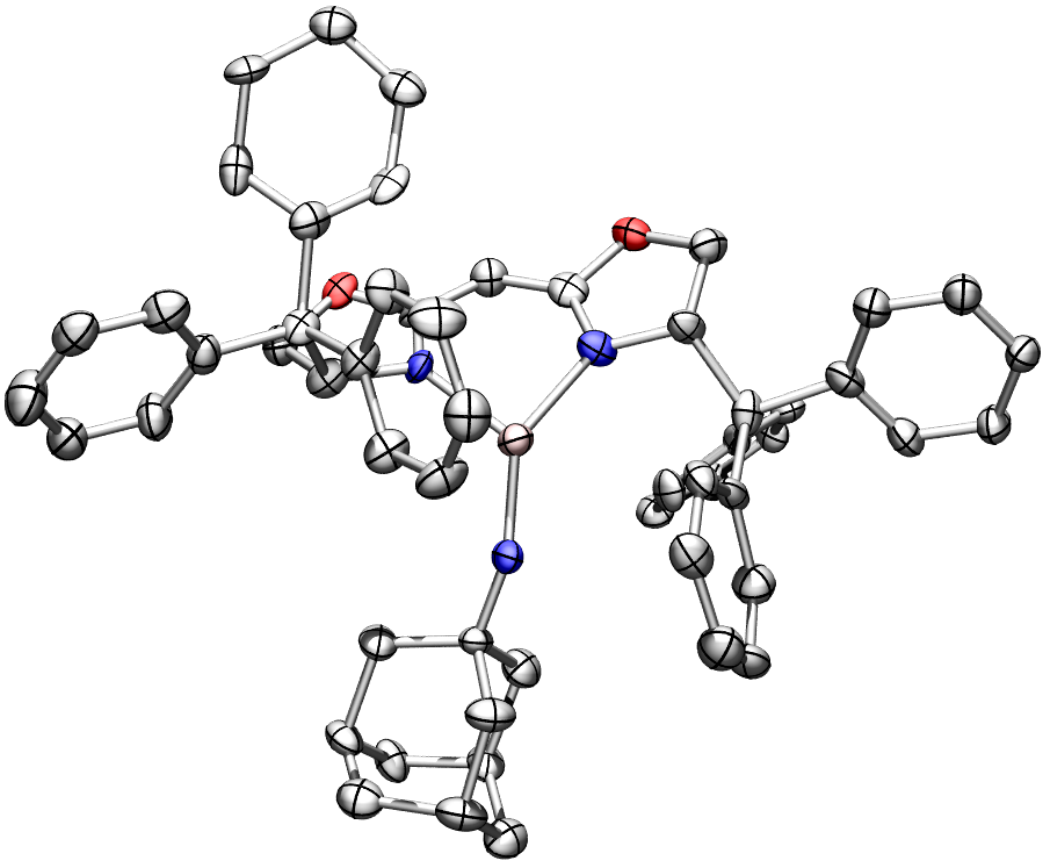


Figure S16. Solid-state molecular structure for (^{TrH}BOX)Ni(NAd) (6) with thermal ellipsoids at 50% probability level. Hydrogen atoms omitted for clarity. nickel = pink, oxygen = red, nitrogen = blue, carbon = gray.

Computational Methods

1. Structure optimization and MO analysis of (^{TrH}BOX)Ni(NAd) (**6**) and (^{AdF}L)Ni(NAd).

Computations were carried out using the Orca program package.[22] The B3LYP[23-26] functional was used with the def2-TZVP (Ni, N), def2-SVP (C, H, O, F) basis sets and the W06 density fitting function of Ahlrich and co-workers'.[27-28] Frequency calculations were performed at the same level of theory in order to confirm the optimized structures were minima on the potential energy surfaces.

2. Potential energy surface for transformation from **9** to **10** catalyzed by (^{TrH}BOX)Ni(py) (**4**).

All calculations employed the Gaussian16 suite of programs.[29] Structures were divided into two layers for computational analysis. The CPh_3 groups were placed in a lower level partition and modeled using molecular mechanics (MM) while the remainder of the molecule remained in a higher level partition and was modeled using quantum mechanics (QM).[30] All QM calculations were conducted at the B3LYP/6-31+G(d) level of theory; the 5D 7F (spherical harmonic) option was applied. For the MM simulation the UFF forcefield was used.[31] All calculated transition states possess one imaginary frequency while all minimization calcs exhibited zero. All calculations assumed 298.15 K and 1 atm.

Optimized geometry coordinates for (^{TrH}BOX)Ni(NAd) (6)

28	2.367041000	16.789019000	30.649695000
8	4.786342000	13.979407000	29.069624000
8	3.637713000	17.993894000	26.929275000
7	2.608326000	17.708714000	28.914701000
7	2.358017000	17.016739000	32.362662000
7	3.094821000	15.097972000	30.036053000
6	2.153245000	20.260195000	29.140219000
6	5.439750000	16.944926000	34.612262000
6	4.028424000	15.097833000	29.089664000
6	1.394138000	20.215356000	30.498560000
6	4.273895000	16.081648000	28.131510000
6	1.456022000	21.425467000	28.373391000
6	0.540180000	13.488381000	30.719087000
6	4.642543000	16.826394000	33.299788000
6	-0.603585000	13.290027000	29.924893000
6	0.242697000	19.431408000	30.684597000
6	1.975282000	18.911637000	28.333937000
6	1.904325000	12.814208000	30.397769000
6	3.119135000	13.792298000	30.717202000
6	1.968996000	11.575926000	31.343309000
6	2.585375000	18.954773000	26.909870000

6	2.009927000	12.383519000	28.914994000
6	2.631171000	16.018946000	34.601549000
6	5.247050000	18.358687000	35.198650000
6	3.494844000	17.242048000	28.043056000
6	2.946919000	18.479910000	34.181848000
6	1.760623000	21.079166000	31.548697000
6	0.128865000	23.605268000	27.117981000
6	-0.502637000	19.497031000	31.867560000
6	-0.176868000	22.291079000	26.765717000
6	5.742546000	20.091758000	30.545356000
6	1.737268000	22.761100000	28.723478000
6	0.476416000	21.218834000	27.387786000
6	4.371649000	19.889980000	30.366987000
6	3.668089000	20.513927000	29.320109000
6	-1.982300000	14.556883000	31.469760000
6	3.752173000	18.594055000	35.490684000
6	0.954472000	10.600309000	31.252805000
6	0.378104000	14.220724000	31.907699000
6	3.437839000	16.133480000	35.909457000
6	4.412236000	21.303737000	28.423949000
6	5.787276000	21.500543000	28.592354000
6	2.499292000	11.122075000	28.532130000
6	3.254969000	17.543804000	36.503687000

6	4.488684000	13.241899000	30.257734000
6	1.951988000	9.281769000	33.025566000
6	0.943061000	9.472805000	32.073399000
6	2.960306000	10.237819000	33.139942000
6	1.092465000	23.832992000	28.107105000
6	1.686119000	13.292394000	27.888710000
6	-0.119188000	20.355449000	32.898107000
6	1.017998000	21.151942000	32.728704000
6	2.966776000	11.370041000	32.311093000
6	-0.859082000	14.754619000	32.276703000
6	2.648372000	10.775143000	27.184865000
6	3.125852000	17.059636000	33.552872000
6	-1.847067000	13.814995000	30.294001000
6	6.457173000	20.909282000	29.665301000
6	4.931740000	15.890291000	35.614922000
6	2.310746000	11.684769000	26.182269000
6	1.830059000	12.946810000	26.543160000
1	3.274440000	19.238970000	33.455929000
1	1.875485000	18.657644000	34.362450000
1	4.997873000	17.561034000	32.559055000
1	4.783002000	15.827846000	32.851647000
1	2.734416000	15.003840000	34.180152000
1	1.557492000	16.185617000	34.787878000

1	3.071585000	15.377722000	36.625719000
1	6.509305000	16.770908000	34.399691000
1	3.607239000	19.607150000	35.906049000
1	5.840090000	18.474603000	36.122471000
1	5.618629000	19.115975000	34.486426000
1	3.817894000	17.632004000	37.448975000
1	2.192493000	17.720405000	36.746545000
1	5.514584000	15.936473000	36.550855000
1	5.077357000	14.877706000	35.197087000
1	5.028291000	15.898318000	27.370717000
1	0.897290000	18.721010000	28.257283000
1	3.006254000	19.925994000	26.623940000
1	1.851553000	18.654407000	26.142458000
1	3.119011000	13.964561000	31.799039000
1	5.274387000	13.450640000	31.006982000
1	4.501211000	12.174757000	30.005327000
1	-0.104903000	18.756696000	29.901550000
1	-1.386746000	18.864699000	31.978845000
1	-0.698762000	20.402818000	33.823741000
1	1.338871000	21.831700000	33.523382000
1	2.648532000	21.704397000	31.450576000
1	2.482808000	22.974576000	29.490202000
1	1.349381000	24.852818000	28.407999000

1	-0.378823000	24.441524000	26.631089000
1	-0.930294000	22.085056000	26.000315000
1	0.191311000	20.212258000	27.081568000
1	3.834144000	19.241635000	31.058965000
1	3.915137000	21.804176000	27.591556000
1	6.331776000	22.128943000	27.882189000
1	7.525499000	21.086549000	29.817572000
1	6.255539000	19.605922000	31.379810000
1	1.223198000	14.378812000	32.574059000
1	-0.940791000	15.326996000	33.204085000
1	-2.951095000	14.971682000	31.761699000
1	-2.714410000	13.632471000	29.653125000
1	-0.534446000	12.710501000	29.003839000
1	1.308388000	14.281679000	28.147809000
1	1.563617000	13.673279000	25.771526000
1	2.424539000	11.411863000	25.129133000
1	3.035239000	9.786882000	26.921432000
1	2.764316000	10.386462000	29.292622000
1	0.157059000	10.725918000	30.517627000
1	0.139043000	8.738239000	31.968431000
1	1.949329000	8.397094000	33.667981000
1	3.756366000	10.109340000	33.879174000
1	3.776329000	12.086592000	32.451839000

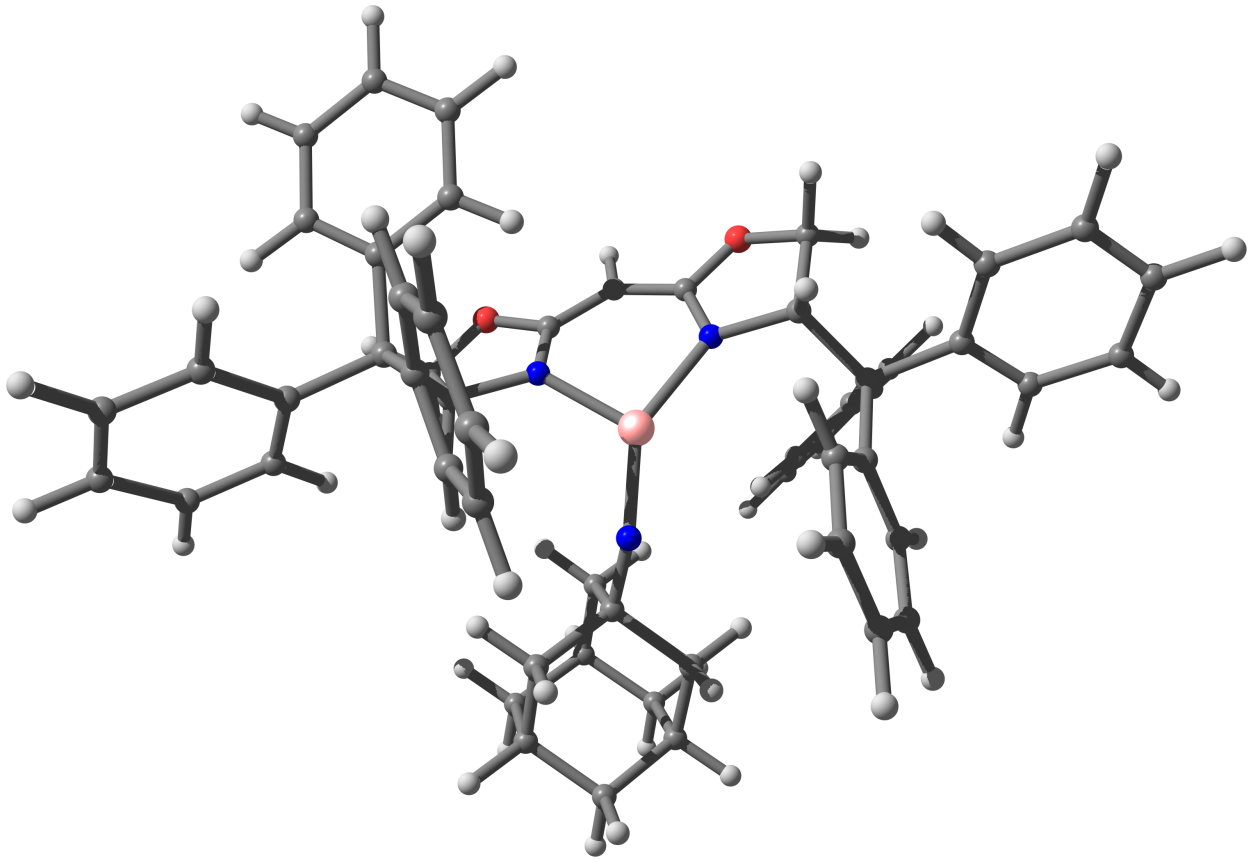


Figure S17 DFT optimized structure for (^{TrH}BOX)Ni(NAd) (6) Color scheme: nickel = pink, oxygen = red, nitrogen = blue, carbon = gray, hydrogen = white.

Optimized geometry coordinates for (^{AdF}L)Ni(NAd)

28	-0.682410000	-0.094835000	-0.447639000
9	4.682797000	0.817745000	-2.014996000
9	7.277081000	0.799062000	-1.245513000
9	7.966030000	-0.160130000	1.204270000
9	3.448016000	-1.064468000	2.149647000
7	0.590816000	-1.508861000	-0.921963000
7	-2.047687000	-0.173002000	0.630112000
6	-0.918140000	-3.445257000	-1.581765000
6	-0.707864000	-4.737135000	-2.420741000
1	-0.177539000	-4.488892000	-3.356799000
1	-0.066447000	-5.443257000	-1.869160000
6	-1.849527000	-2.501785000	-2.389675000
1	-1.348148000	-2.203604000	-3.326386000
1	-2.040771000	-1.577499000	-1.820665000
6	-1.649184000	-3.848755000	-0.263194000
1	-0.998295000	-4.518474000	0.324356000
1	-1.817296000	-2.948268000	0.348155000
6	-2.993806000	-4.537666000	-0.573730000
1	-3.485321000	-4.813114000	0.376285000
6	-2.746839000	-5.807247000	-1.411022000
1	-2.121693000	-6.519862000	-0.844138000

1	-3.702732000	-6.320228000	-1.617707000
6	-2.052896000	-5.421245000	-2.732363000
1	-1.862117000	-6.329860000	-3.329588000
6	-2.955107000	-4.457448000	-3.525754000
1	-3.913810000	-4.948348000	-3.770751000
1	-2.479799000	-4.190202000	-4.486269000
6	-3.197900000	-3.187612000	-2.689367000
1	-3.837254000	-2.487324000	-3.254457000
6	-3.890812000	-3.564326000	-1.363747000
1	-4.085870000	-2.658482000	-0.764397000
1	-4.870312000	-4.029938000	-1.571803000
6	0.419713000	-2.803892000	-1.257827000
6	1.675255000	-3.484203000	-1.214399000
1	1.851429000	-4.527830000	-1.461795000
6	2.625777000	-2.561041000	-0.824859000
1	3.693702000	-2.731654000	-0.700331000
6	1.945559000	-1.318971000	-0.652873000
6	2.530841000	-0.080643000	-0.332547000
6	3.980141000	-0.113485000	0.046935000
6	4.989581000	0.350663000	-0.806834000
6	6.334541000	0.341811000	-0.424748000
6	6.691409000	-0.152997000	0.831965000
6	4.367088000	-0.611102000	1.297645000

6	5.705173000	-0.633247000	1.697797000
9	6.042327000	-1.104968000	2.894148000
7	0.576585000	1.412106000	-0.691330000
6	-0.869189000	3.476627000	-1.146098000
6	-0.496997000	4.580337000	-2.183195000
1	-0.018461000	4.115641000	-3.062015000
1	0.242772000	5.269880000	-1.746022000
6	-1.930816000	2.555251000	-1.791615000
1	-1.491411000	2.046929000	-2.667058000
1	-2.235647000	1.772727000	-1.080156000
6	-1.511980000	4.193353000	0.081727000
1	-0.770995000	4.864486000	0.548902000
1	-1.781008000	3.443482000	0.837626000
6	-2.761210000	4.993117000	-0.342829000
1	-3.197345000	5.477927000	0.548337000
6	-2.359406000	6.066104000	-1.373049000
1	-1.637389000	6.770310000	-0.921931000
1	-3.240648000	6.661098000	-1.670728000
6	-1.742604000	5.381103000	-2.608407000
1	-1.441561000	6.146750000	-3.343931000
6	-2.777707000	4.433361000	-3.240863000
1	-3.665909000	5.001458000	-3.569298000
1	-2.354185000	3.954231000	-4.141131000

6	-3.177925000	3.360413000	-2.211564000
1	-3.913448000	2.669862000	-2.658495000
6	-3.792833000	4.036197000	-0.969467000
1	-4.094347000	3.270107000	-0.234494000
1	-4.707651000	4.588038000	-1.248224000
6	0.396280000	2.747778000	-0.727687000
6	1.607950000	3.413017000	-0.356090000
1	1.760173000	4.489073000	-0.295087000
6	2.550355000	2.438487000	-0.112687000
1	3.585663000	2.591095000	0.184576000
6	1.913290000	1.181122000	-0.343202000
6	-4.259149000	-0.622904000	3.704295000
1	-5.268675000	-1.049372000	3.838191000
6	-4.260353000	0.860423000	4.123712000
1	-4.573218000	0.959537000	5.178039000
1	-4.990100000	1.426640000	3.519898000
6	-2.847395000	1.444173000	3.933998000
1	-2.842569000	2.510581000	4.219478000
6	-1.841599000	0.671612000	4.805699000
1	-0.831417000	1.102348000	4.689522000
1	-2.111815000	0.771209000	5.871529000
6	-1.839850000	-0.811736000	4.388360000
1	-1.119827000	-1.370845000	5.009417000

6	-1.422703000	-0.929446000	2.908531000
1	-0.410252000	-0.522032000	2.753162000
1	-1.396551000	-1.988313000	2.601434000
6	-2.422063000	-0.160788000	1.997380000
6	-3.852543000	-0.737731000	2.220010000
1	-4.561479000	-0.191336000	1.576265000
1	-3.872605000	-1.792424000	1.896199000
6	-3.253235000	-1.397650000	4.577468000
1	-3.550633000	-1.334126000	5.639410000
1	-3.261217000	-2.467913000	4.306395000
6	-2.434561000	1.333511000	2.454192000
1	-1.430212000	1.759083000	2.300006000
1	-3.137374000	1.891412000	1.815982000

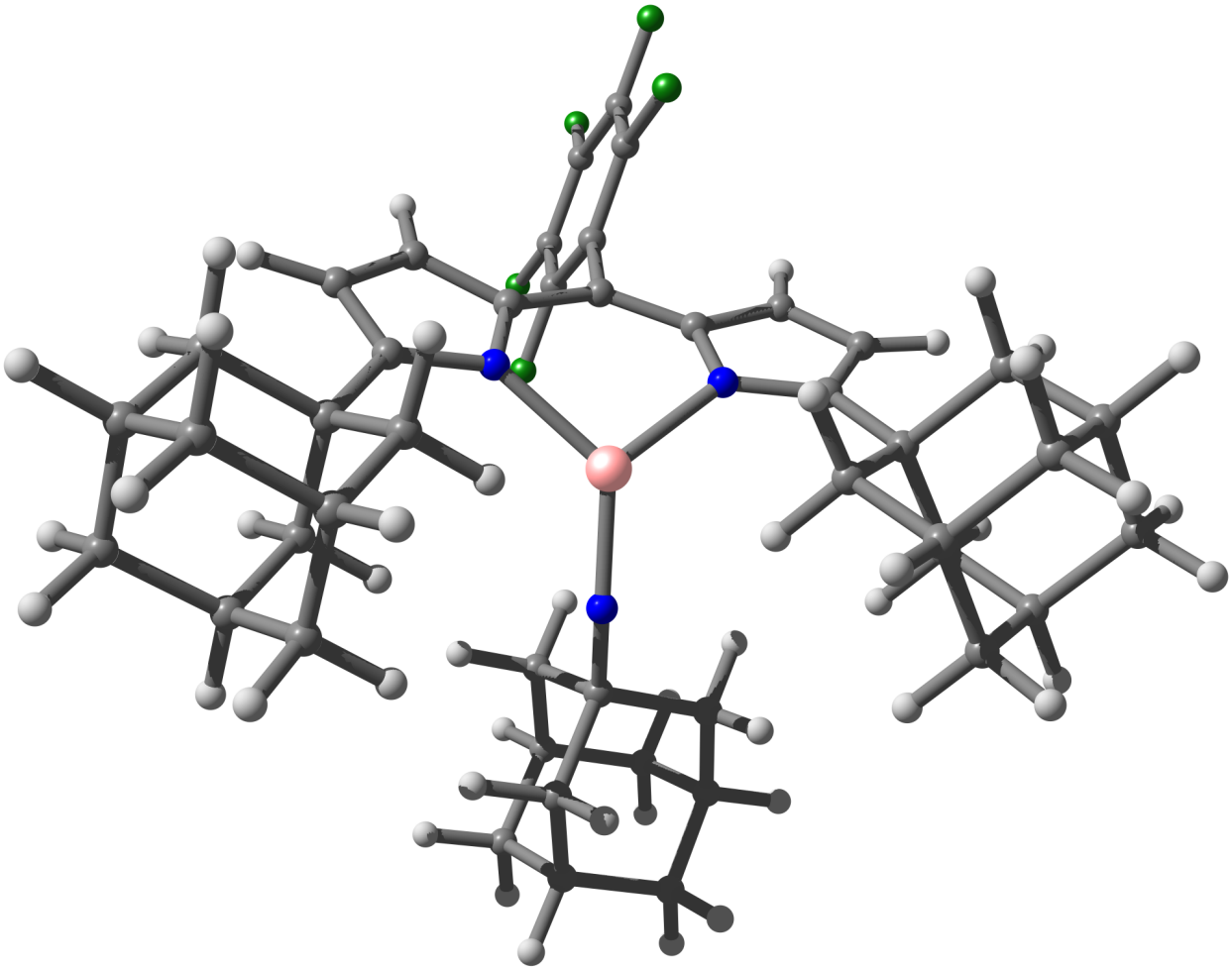


Figure S18. DFT optimized structure for (^{AdF}L)Ni(NAd) Color scheme: nickel = pink, nitrogen = blue, carbon = gray, fluorine = green, hydrogen = white.

Optimized geometry coordinates for imide (^{TrH}BOX)Ni(NR)

doublet

28	-0.213037000	-0.200247000	0.249093000
8	2.319685000	-0.697209000	-2.831896000
8	-2.365748000	-0.871062000	-3.149285000
7	-1.544602000	-0.739063000	-1.043786000
7	0.181645000	0.800376000	1.513581000
7	1.195814000	-0.712825000	-0.877588000
6	-3.816764000	-0.050394000	-0.099801000
6	1.117055000	-0.589063000	-2.200751000
6	-3.298708000	0.173054000	1.348050000
6	-0.043275000	-0.473537000	-2.962471000
1	0.018286000	-0.416103000	-4.039758000
6	-5.293948000	-0.495047000	0.081367000
6	1.700617000	-2.871404000	1.139607000
6	0.937189000	-4.061147000	1.255964000
1	0.996848000	-4.848069000	0.518781000
6	-2.814416000	-0.898872000	2.139615000
1	-2.715029000	-1.899733000	1.754628000
6	-2.962615000	-1.129379000	-0.857876000
1	-2.975140000	-2.079198000	-0.324378000
6	2.669222000	-2.615478000	-0.048876000
6	2.567544000	-1.108380000	-0.505450000
1	2.896824000	-0.447594000	0.296717000
6	4.073507000	-2.969407000	0.506647000
6	-3.411696000	-1.421980000	-2.329946000
1	-3.444324000	-2.502147000	-2.515883000
1	-4.358215000	-0.988891000	-2.656343000

6	2.333068000	-3.503140000	-1.285107000
6	-1.283757000	-0.677977000	-2.345238000
6	-3.483694000	1.421297000	1.995408000
1	-3.901868000	2.269120000	1.471312000
6	-7.985452000	-1.200565000	0.534912000
1	-9.019008000	-1.475630000	0.702882000
6	-2.482120000	-0.710507000	3.484259000
1	-2.118139000	-1.541271000	4.072737000
6	-7.083695000	-2.157185000	0.064486000
1	-7.421298000	-3.168273000	-0.124172000
6	-2.426499000	3.204343000	-1.664566000
1	-1.533030000	3.811044000	-1.591486000
6	-6.248150000	0.428051000	0.574291000
1	-5.972168000	1.452293000	0.779396000
6	-5.746034000	-1.816217000	-0.156180000
1	-5.092719000	-2.600859000	-0.501067000
6	-2.557158000	2.057680000	-0.878341000
1	-1.747636000	1.797459000	-0.212702000
6	-3.718880000	1.253135000	-0.942790000
6	0.061414000	-3.357220000	3.397468000
1	-0.570158000	-3.539551000	4.257105000
6	4.314476000	-4.288522000	0.959987000
1	3.539461000	-5.040789000	0.896550000
6	1.684837000	-1.986962000	2.242704000
1	2.337355000	-1.131546000	2.278095000
6	-4.721237000	1.624580000	-1.871119000
1	-5.607142000	1.021353000	-2.013192000
6	-4.584495000	2.773493000	-2.655252000

1	-5.363797000	3.044449000	-3.355850000
6	3.346311000	-4.125617000	-2.055767000
1	4.391947000	-4.023372000	-1.801276000
6	3.339740000	-0.741901000	-1.808990000
1	3.780634000	0.259021000	-1.729009000
1	4.110535000	-1.439595000	-2.140010000
6	6.584650000	-3.723977000	1.570084000
1	7.545820000	-4.012491000	1.975518000
6	5.555379000	-4.658755000	1.482786000
1	5.718550000	-5.674400000	1.819480000
6	6.375011000	-2.416980000	1.133886000
1	7.176237000	-1.692364000	1.203242000
6	-7.579996000	0.051981000	0.783481000
1	-8.289715000	0.782768000	1.150190000
6	0.999282000	-3.623477000	-1.746257000
1	0.186577000	-3.144832000	-1.216357000
6	-2.650017000	0.534236000	4.083534000
1	-2.398365000	0.672497000	5.127013000
6	-3.160634000	1.595735000	3.342480000
1	-3.308101000	2.559427000	3.812719000
6	5.136184000	-2.037333000	0.608754000
1	5.038138000	-1.012152000	0.290482000
6	0.856426000	-2.214866000	3.344161000
1	0.847228000	-1.512549000	4.167817000
6	3.030207000	-4.867848000	-3.197046000
1	3.818777000	-5.338427000	-3.770054000
6	0.871355000	2.019009000	1.849463000
6	0.110835000	-4.284588000	2.360095000

1	-0.475201000	-5.192573000	2.421284000
6	-3.441610000	3.564975000	-2.548685000
1	-3.337830000	4.452184000	-3.159808000
6	1.704947000	-4.990928000	-3.610632000
1	1.464768000	-5.562658000	-4.497664000
6	0.691250000	-4.364731000	-2.888725000
1	-0.336848000	-4.447963000	-3.216973000
6	2.099383000	1.699585000	2.737176000
1	1.802443000	1.055909000	3.571941000
1	2.878809000	1.185318000	2.162961000
1	2.535542000	2.616980000	3.149094000
6	-0.115730000	2.894865000	2.658606000
1	0.362137000	3.830794000	2.967951000
1	-1.000914000	3.134747000	2.060209000
1	-0.433723000	2.364316000	3.561172000
6	1.301002000	2.737339000	0.532924000
1	1.932564000	2.039376000	-0.032836000
1	0.399597000	2.888930000	-0.073793000
6	2.035411000	4.078657000	0.675649000
1	1.419422000	4.798153000	1.229755000
1	2.962575000	3.954772000	1.250374000
6	2.381147000	4.688136000	-0.701515000
1	3.011412000	3.981164000	-1.258103000
1	1.455414000	4.801952000	-1.281692000
6	3.084628000	6.025081000	-0.598216000
6	2.352621000	7.221530000	-0.548186000
6	4.483585000	6.100686000	-0.515779000
6	2.995679000	8.455401000	-0.415271000

1	1.266915000	7.185940000	-0.619982000
6	5.132978000	7.331283000	-0.382631000
1	5.071093000	5.185245000	-0.562054000
6	4.390073000	8.514621000	-0.330818000
1	2.408249000	9.369938000	-0.383058000
1	6.218326000	7.366059000	-0.324768000
1	4.892814000	9.473281000	-0.231128000

quartet

28	0.135787000	-0.188300000	-0.014953000
8	2.204723000	1.540627000	-3.127275000
8	-0.440659000	-2.312213000	-3.477711000
7	-0.258234000	-1.560449000	-1.346967000
7	-0.333298000	1.079048000	1.146670000
7	1.476769000	0.755602000	-1.134408000
6	-1.719365000	-3.251276000	-0.087140000
6	1.416687000	0.653849000	-2.452113000
6	-1.095733000	-2.768210000	1.248251000
6	0.690696000	-0.267756000	-3.218662000
1	0.745431000	-0.209132000	-4.296891000
6	-1.978679000	-4.766001000	0.136052000
6	3.469704000	0.508309000	1.245111000
6	4.129122000	-0.668243000	1.684689000
1	4.838385000	-1.187579000	1.056820000
6	0.240405000	-3.106017000	1.573329000
1	0.867901000	-3.652046000	0.885876000
6	-0.724278000	-2.973246000	-1.265989000
1	0.179339000	-3.585693000	-1.160805000

6	3.788340000	1.156502000	-0.129721000
6	2.489683000	1.772404000	-0.779752000
1	2.017161000	2.483119000	-0.102492000
6	4.851721000	2.234380000	0.206865000
6	-1.264541000	-3.204153000	-2.701451000
1	-1.107184000	-4.209119000	-3.094982000
1	-2.307774000	-2.915336000	-2.871291000
6	4.345823000	0.121926000	-1.151846000
6	0.005549000	-1.329894000	-2.636864000
6	-1.877935000	-2.163016000	2.263237000
1	-2.931156000	-1.966675000	2.123164000
6	-2.515605000	-7.474649000	0.700741000
1	-2.720451000	-8.516756000	0.910884000
6	0.781392000	-2.791742000	2.821235000
1	1.800403000	-3.071864000	3.051058000
6	-1.610963000	-7.138270000	-0.308557000
1	-1.116688000	-7.920477000	-0.870472000
6	-4.270993000	-0.405546000	-0.696971000
1	-4.301314000	0.673891000	-0.631469000
6	-2.875560000	-5.165601000	1.157046000
1	-3.397826000	-4.426866000	1.750033000
6	-1.335863000	-5.796787000	-0.590996000
1	-0.614591000	-5.602276000	-1.365537000
6	-3.100356000	-1.096222000	-0.371605000
1	-2.238761000	-0.527616000	-0.059869000
6	-3.045630000	-2.507687000	-0.417558000
6	3.101761000	-0.500748000	3.867564000
1	2.953690000	-0.890710000	4.866205000

6	6.128201000	1.822493000	0.659395000
1	6.372956000	0.770997000	0.730099000
6	2.688272000	1.201605000	2.200678000
1	2.265705000	2.169106000	1.987286000
6	-4.198970000	-3.190433000	-0.879681000
1	-4.204163000	-4.261899000	-1.020272000
6	-5.364732000	-2.493234000	-1.208599000
1	-6.237367000	-3.032974000	-1.553311000
6	5.387645000	0.450770000	-2.052779000
1	5.854570000	1.425802000	-2.040800000
6	2.711449000	2.476778000	-2.156789000
1	2.110914000	3.392358000	-2.226548000
1	3.740420000	2.713308000	-2.433268000
6	6.832892000	4.118637000	0.935533000
1	7.592130000	4.839875000	1.209088000
6	7.107314000	2.754744000	1.009594000
1	8.080551000	2.417173000	1.341821000
6	5.575710000	4.552619000	0.518839000
1	5.359944000	5.612526000	0.475879000
6	-3.127448000	-6.518319000	1.412224000
1	-3.824948000	-6.793518000	2.193208000
6	3.731158000	-1.146253000	-1.299649000
1	2.898162000	-1.433452000	-0.670423000
6	0.003438000	-2.152941000	3.783468000
1	0.423408000	-1.918634000	4.752939000
6	-1.327576000	-1.851255000	3.508921000
1	-1.943758000	-1.393987000	4.272211000
6	4.589838000	3.626265000	0.166291000

1	3.629497000	4.022576000	-0.122150000
6	2.484840000	0.686457000	3.483435000
1	1.870639000	1.226561000	4.192160000
6	5.827199000	-0.467030000	-3.010735000
1	6.629070000	-0.199009000	-3.686564000
6	-1.260396000	2.079389000	1.584648000
6	3.932041000	-1.170748000	2.972900000
1	4.439270000	-2.075164000	3.283279000
6	-5.403617000	-1.103779000	-1.109297000
1	-6.307971000	-0.566784000	-1.364789000
6	5.225217000	-1.720337000	-3.111576000
1	5.564726000	-2.426048000	-3.858623000
6	4.173897000	-2.056801000	-2.261169000
1	3.693289000	-3.022439000	-2.351687000
6	-0.501890000	3.172010000	2.378786000
1	-0.007616000	2.735016000	3.252642000
1	0.262342000	3.645060000	1.751855000
1	-1.189271000	3.952029000	2.727355000
6	-2.299045000	1.418444000	2.524789000
1	-2.975664000	2.173568000	2.939221000
1	-2.901206000	0.669327000	2.001056000
1	-1.784009000	0.935621000	3.360693000
6	-1.934069000	2.697060000	0.315824000
1	-1.162717000	3.265698000	-0.222399000
1	-2.211618000	1.871572000	-0.348895000
6	-3.162987000	3.588902000	0.540221000
1	-3.964710000	3.013365000	1.019679000
1	-2.928811000	4.421366000	1.217381000

6	-3.701993000	4.160586000	-0.789972000
1	-2.928985000	4.790254000	-1.250725000
1	-3.880705000	3.328536000	-1.484629000
6	-4.977511000	4.957844000	-0.617421000
6	-6.229506000	4.324418000	-0.658973000
6	-4.941573000	6.339975000	-0.378113000
6	-7.409788000	5.046794000	-0.463521000
1	-6.279387000	3.254095000	-0.852520000
6	-6.118523000	7.068428000	-0.181891000
1	-3.981315000	6.852187000	-0.351056000
6	-7.358200000	6.423365000	-0.223005000
1	-8.368985000	4.536144000	-0.504645000
1	-6.067174000	8.139692000	-0.002284000
1	-8.274988000	6.988334000	-0.074600000

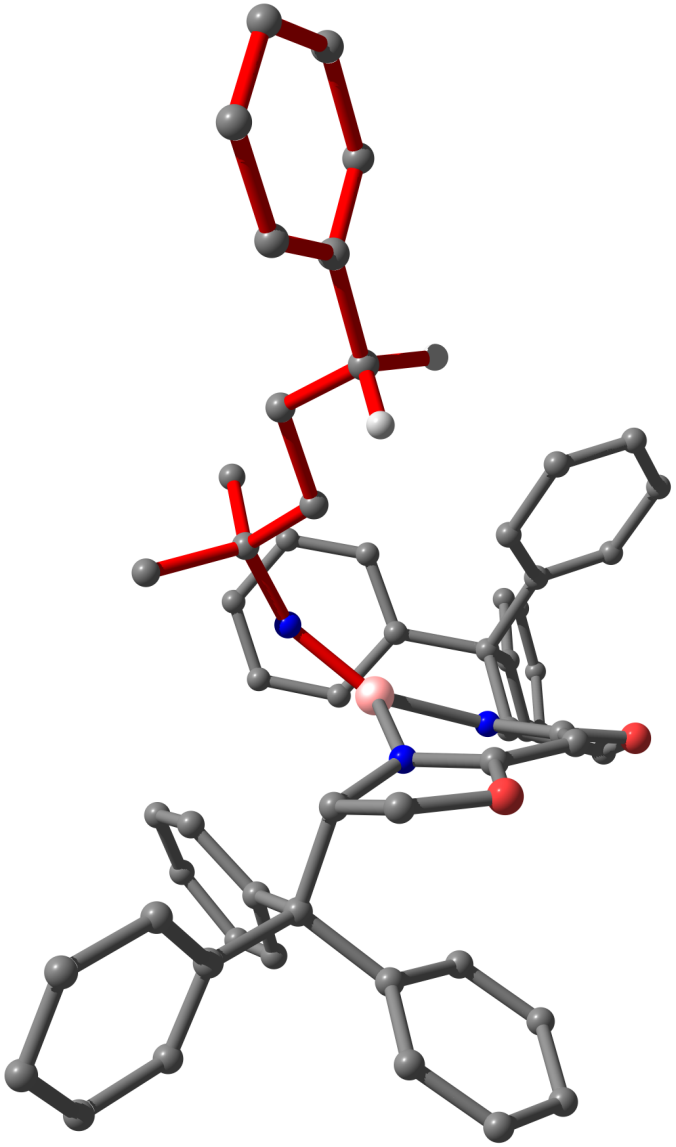


Figure S19. DFT optimized structure for imide (^{AdF}L)Ni(NR) Color scheme: nickel = pink, nitrogen = blue, carbon = gray, fluorine = green, hydrogen = white. The fragment corresponding to the substrate **9** is labeled in red.

Optimized geometry coordinates for amide (^{TrH}BOX)Ni(NHR)

doublet

28	-0.335076000	-0.240486000	0.336737000
8	2.432327000	-0.264157000	-2.700857000
8	-2.208545000	-0.047048000	-3.294518000
7	-1.583599000	-0.443965000	-1.151125000
7	0.009313000	0.616100000	1.914496000
7	1.241184000	-0.506792000	-0.795109000
6	-3.897186000	0.155986000	-0.244828000
6	1.219378000	-0.191482000	-2.081438000
6	-3.462857000	-0.000626000	1.238172000
6	0.098405000	0.111772000	-2.862096000
1	0.231944000	0.352862000	-3.907462000
6	-5.397459000	-0.241260000	-0.248116000
6	1.643971000	-2.841477000	1.054841000
6	0.792094000	-3.975002000	1.070135000
1	0.777010000	-4.684854000	0.256670000
6	-3.208210000	-1.281215000	1.789396000
1	-3.241865000	-2.176691000	1.190449000
6	-3.032115000	-0.763587000	-1.179963000
1	-3.139981000	-1.810887000	-0.894851000
6	2.609753000	-2.537255000	-0.124346000
6	2.587893000	-0.994089000	-0.441644000
1	2.927411000	-0.426311000	0.426442000
6	3.994925000	-3.021649000	0.376203000
6	-3.365037000	-0.661983000	-2.707848000
1	-3.471919000	-1.660241000	-3.148835000
1	-4.238875000	-0.069468000	-2.984655000

6	2.208941000	-3.282569000	-1.433415000
6	-1.193976000	-0.119252000	-2.384810000
6	-3.522461000	1.091134000	2.141373000
1	-3.798826000	2.082042000	1.810161000
6	-8.138144000	-0.880853000	-0.108279000
1	-9.190881000	-1.129138000	-0.061359000
6	-2.956190000	-1.444352000	3.154070000
1	-2.768266000	-2.432093000	3.553091000
6	-7.262648000	-1.713181000	-0.809155000
1	-7.640130000	-2.603095000	-1.296402000
6	-2.279310000	3.592275000	-0.986506000
1	-1.351948000	4.105000000	-0.765448000
6	-6.326968000	0.556618000	0.461912000
1	-6.006357000	1.456421000	0.968696000
6	-5.900595000	-1.405490000	-0.877500000
1	-5.269732000	-2.093723000	-1.415710000
6	-2.495944000	2.301946000	-0.498917000
1	-1.719329000	1.839369000	0.090495000
6	-3.703589000	1.612901000	-0.755898000
6	0.016002000	-3.431668000	3.296322000
1	-0.610647000	-3.652539000	4.150504000
6	4.165691000	-4.392484000	0.684112000
1	3.350467000	-5.090798000	0.546262000
6	1.718979000	-2.076898000	2.243143000
1	2.435506000	-1.278813000	2.348285000
6	-4.662532000	2.258904000	-1.573888000
1	-5.579048000	1.765178000	-1.865156000
6	-4.439842000	3.550406000	-2.060028000

1	-5.186613000	4.029854000	-2.679747000
6	3.175961000	-3.886870000	-2.274737000
1	4.227879000	-3.873222000	-2.026144000
6	3.419763000	-0.541468000	-1.684410000
1	3.957829000	0.390601000	-1.475792000
1	4.124325000	-1.266322000	-2.096075000
6	6.461874000	-4.015644000	1.339957000
1	7.406701000	-4.395829000	1.706317000
6	5.385769000	-4.881288000	1.156020000
1	5.495909000	-5.934653000	1.379169000
6	6.318986000	-2.658863000	1.054371000
1	7.155049000	-1.987491000	1.202972000
6	-7.684238000	0.218374000	0.509241000
1	-8.373957000	0.852884000	1.051337000
6	0.867291000	-3.273548000	-1.888030000
1	0.089236000	-2.800128000	-1.304481000
6	-2.981416000	-0.346404000	4.009929000
1	-2.793400000	-0.478426000	5.067496000
6	-3.275417000	0.917558000	3.505422000
1	-3.326095000	1.766187000	4.175287000
6	5.101330000	-2.160741000	0.581282000
1	5.051467000	-1.101373000	0.388682000
6	0.898131000	-2.355446000	3.338623000
1	0.960854000	-1.744460000	4.229914000
6	2.806322000	-4.493067000	-3.478599000
1	3.560092000	-4.952556000	-4.104961000
6	0.673986000	1.875055000	2.286255000
6	-0.028784000	-4.246896000	2.168011000

1	-0.684009000	-5.108304000	2.152286000
6	-3.252912000	4.218444000	-1.762183000
1	-3.082851000	5.217329000	-2.142555000
6	1.473279000	-4.493042000	-3.885282000
1	1.191850000	-4.959109000	-4.820678000
6	0.505795000	-3.878790000	-3.093224000
1	-0.527607000	-3.865305000	-3.415129000
6	1.736277000	1.586063000	3.374169000
1	1.290421000	1.014403000	4.197715000
1	2.565974000	0.998531000	2.966641000
1	2.148300000	2.510302000	3.797883000
6	-0.367266000	2.859619000	2.867409000
1	0.091280000	3.806682000	3.175927000
1	-1.152322000	3.079403000	2.136072000
1	-0.840633000	2.426785000	3.757782000
6	1.334558000	2.454962000	1.014946000
1	2.001356000	1.687606000	0.604768000
1	0.551995000	2.608965000	0.261314000
6	2.128095000	3.762528000	1.169687000
1	1.484165000	4.547246000	1.601009000
1	2.945627000	3.626480000	1.893940000
6	2.682127000	4.237233000	-0.142806000
1	2.328277000	3.738541000	-1.044397000
1	-0.516856000	0.278904000	2.722233000
6	3.596493000	5.307265000	-0.309439000
6	4.110110000	6.063358000	0.786754000
6	4.041422000	5.674504000	-1.615849000
6	5.006167000	7.106573000	0.582029000

1	3.794135000	5.821453000	1.797472000
6	4.936389000	6.717489000	-1.808950000
1	3.663881000	5.117422000	-2.470753000
6	5.428924000	7.444318000	-0.712371000
1	5.381005000	7.666274000	1.435952000
1	5.256539000	6.972889000	-2.816350000
1	6.129340000	8.260972000	-0.865142000

quartet

28	-0.335147000	-0.240515000	0.336818000
8	2.432450000	-0.263811000	-2.700615000
8	-2.208417000	-0.046936000	-3.294472000
7	-1.583522000	-0.443936000	-1.151078000
7	0.009027000	0.616066000	1.914603000
7	1.241266000	-0.506658000	-0.794928000
6	-3.897165000	0.155840000	-0.244821000
6	1.219470000	-0.191247000	-2.081227000
6	-3.462911000	-0.000898000	1.238199000
6	0.098519000	0.112009000	-2.861926000
1	0.232116000	0.353187000	-3.907264000
6	-5.397445000	-0.241405000	-0.248236000
6	1.643976000	-2.841583000	1.054637000
6	0.792174000	-3.975166000	1.069669000
1	0.777274000	-4.684927000	0.256121000
6	-3.208411000	-1.281544000	1.789366000
1	-3.242150000	-2.176987000	1.190375000
6	-3.032017000	-0.763642000	-1.179982000
1	-3.139842000	-1.810963000	-0.894932000

6	2.609901000	-2.537150000	-0.124377000
6	2.587973000	-0.993941000	-0.441472000
1	2.927416000	-0.426268000	0.426713000
6	3.995054000	-3.021497000	0.376280000
6	-3.364879000	-0.662004000	-2.707879000
1	-3.471637000	-1.660256000	-3.148908000
1	-4.238764000	-0.069569000	-2.984705000
6	2.209309000	-3.282344000	-1.433582000
6	-1.193873000	-0.119132000	-2.384738000
6	-3.522434000	1.090809000	2.141476000
1	-3.798707000	2.081768000	1.810333000
6	-8.138148000	-0.881003000	-0.108633000
1	-9.190889000	-1.129288000	-0.061804000
6	-2.956420000	-1.444787000	3.154033000
1	-2.768591000	-2.432570000	3.552996000
6	-7.262595000	-1.713313000	-0.809460000
1	-7.640038000	-2.603214000	-1.296758000
6	-2.279233000	3.592177000	-0.986149000
1	-1.351897000	4.104893000	-0.764945000
6	-6.327016000	0.556453000	0.461735000
1	-6.006452000	1.456247000	0.968568000
6	-5.900537000	-1.405620000	-0.877688000
1	-5.269640000	-2.093841000	-1.415875000
6	-2.495921000	2.301824000	-0.498652000
1	-1.719388000	1.839226000	0.090838000
6	-3.703532000	1.612789000	-0.755793000
6	0.015666000	-3.432113000	3.295780000
1	-0.611115000	-3.653111000	4.149832000

6	4.165870000	-4.392344000	0.684109000
1	3.350693000	-5.090693000	0.546155000
6	1.718747000	-2.077135000	2.243037000
1	2.435219000	-1.279031000	2.348383000
6	-4.662379000	2.258819000	-1.573873000
1	-5.578857000	1.765100000	-1.865272000
6	-4.439638000	3.550345000	-2.059933000
1	-5.186337000	4.029816000	-2.679721000
6	3.176474000	-3.886500000	-2.274845000
1	4.228360000	-3.872811000	-2.026124000
6	3.419869000	-0.541114000	-1.684141000
1	3.957821000	0.390994000	-1.475407000
1	4.124530000	-1.265855000	-2.095832000
6	6.461987000	-4.015431000	1.340138000
1	7.406809000	-4.395591000	1.706539000
6	5.385938000	-4.881117000	1.156075000
1	5.496115000	-5.934490000	1.379168000
6	6.319056000	-2.658641000	1.054612000
1	7.155081000	-1.987240000	1.203296000
6	-7.684290000	0.218210000	0.508947000
1	-8.374052000	0.852711000	1.050999000
6	0.867718000	-3.273354000	-1.888368000
1	0.089558000	-2.800046000	-1.304865000
6	-2.981536000	-0.346887000	4.009955000
1	-2.793537000	-0.478986000	5.067516000
6	-3.275409000	0.917133000	3.505514000
1	-3.325998000	1.765732000	4.175424000
6	5.101409000	-2.160551000	0.581467000

1	5.051522000	-1.101179000	0.388898000
6	0.897731000	-2.355850000	3.338349000
1	0.960272000	-1.744961000	4.229719000
6	2.807022000	-4.492597000	-3.478815000
1	3.560898000	-4.951976000	-4.105129000
6	0.673834000	1.874959000	2.286352000
6	-0.028879000	-4.247225000	2.167374000
1	-0.684050000	-5.108670000	2.151447000
6	-3.252744000	4.218377000	-1.761916000
1	-3.082644000	5.217282000	-2.142219000
6	1.474030000	-4.492610000	-3.885665000
1	1.192746000	-4.958602000	-4.821143000
6	0.506409000	-3.878497000	-3.093668000
1	-0.526954000	-3.865044000	-3.415701000
6	1.736368000	1.585865000	3.373996000
1	1.290759000	1.014008000	4.197534000
1	2.566059000	0.998514000	2.966194000
1	2.148373000	2.510078000	3.797792000
6	-0.367326000	2.859441000	2.867816000
1	0.091251000	3.806477000	3.176373000
1	-1.152500000	3.079279000	2.136624000
1	-0.840549000	2.426484000	3.758213000
6	1.334170000	2.455042000	1.014984000
1	2.000850000	1.687718000	0.604550000
1	0.551506000	2.609239000	0.261498000
6	2.127781000	3.762553000	1.169821000
1	1.483912000	4.547179000	1.601428000
1	2.945447000	3.626371000	1.893882000

6	2.681495000	4.237553000	-0.142706000
1	2.327118000	3.739299000	-1.044330000
1	-0.517175000	0.278965000	2.722349000
6	3.595975000	5.307493000	-0.309318000
6	4.110351000	6.062974000	0.786957000
6	4.040279000	5.675258000	-1.615788000
6	5.006493000	7.106114000	0.582242000
1	3.794879000	5.820654000	1.797724000
6	4.935332000	6.718164000	-1.808878000
1	3.662171000	5.118641000	-2.470747000
6	5.428603000	7.444388000	-0.712232000
1	5.381899000	7.665350000	1.436219000
1	5.254999000	6.973969000	-2.816330000
1	6.129098000	8.260973000	-0.865007000

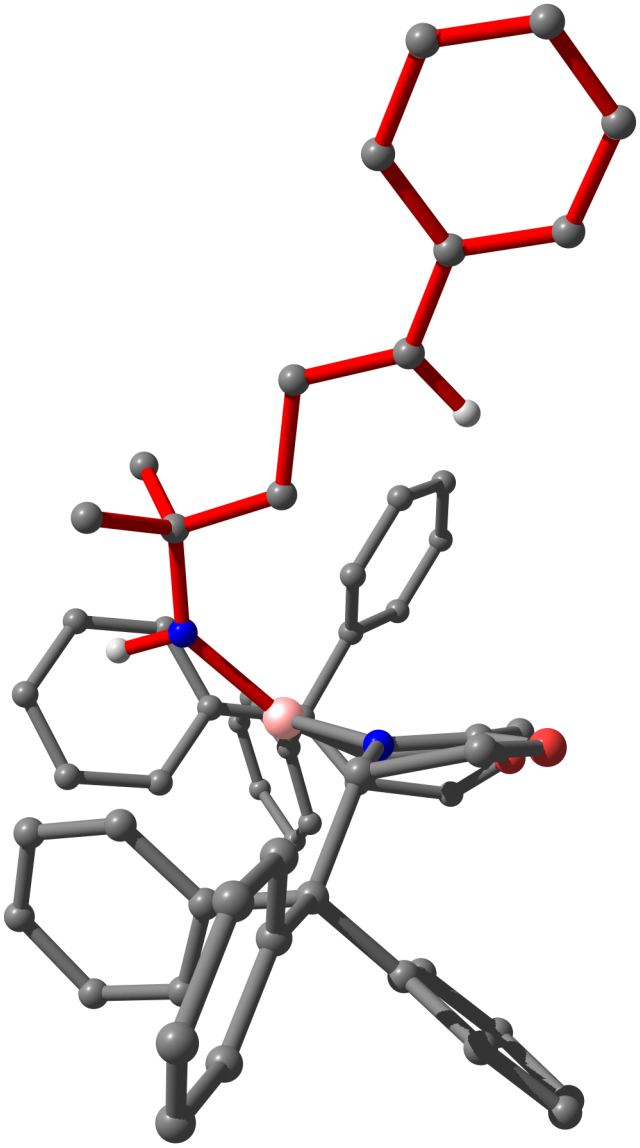


Figure S20. DFT optimized structure for amide (^{AdF}L)Ni(NHR) Color scheme: nickel = pink, nitrogen = blue, carbon = gray, fluorine = green, hydrogen = white. The fragment corresponding to the substrate **9** is labeled in red.

Optimized geometry coordinates for product adduct (^{TrH}BOX)Ni(pyrrolidine)

S-pyrrolidine adduct

28	-0.126937000	0.428193000	-0.762032000
8	2.288094000	-2.250093000	-2.715893000
8	-1.887155000	-3.291282000	-0.962126000
7	-1.208852000	-1.200446000	-0.393844000
7	0.040058000	2.399774000	-1.525829000
7	1.434077000	-0.706198000	-1.296534000
6	-3.544549000	-0.711311000	0.547408000
6	1.179458000	-1.751541000	-2.063163000
6	-3.220072000	0.798047000	0.704860000
6	-0.029145000	-2.450517000	-2.166094000
1	-0.072195000	-3.346748000	-2.769847000
6	-4.515575000	-1.020449000	1.717960000
6	2.533940000	-0.634127000	1.398094000
6	2.305258000	-1.408313000	2.565268000
1	2.749644000	-2.386296000	2.687537000
6	-2.380736000	1.240196000	1.756047000
1	-1.897959000	0.542734000	2.422541000
6	-2.223897000	-1.564233000	0.624764000
1	-1.754326000	-1.444605000	1.603536000
6	3.433158000	-1.143307000	0.231175000
6	2.892075000	-0.586927000	-1.154263000
1	3.138045000	0.476323000	-1.242408000
6	4.867318000	-0.624377000	0.535675000
6	-2.415899000	-3.092038000	0.356018000
1	-1.809017000	-3.681429000	1.056445000
1	-3.437834000	-3.476976000	0.375342000

6	3.427394000	-2.698344000	0.170824000
6	-1.018252000	-2.246788000	-1.185000000
6	-3.910178000	1.791534000	-0.035212000
1	-4.643809000	1.532753000	-0.784574000
6	-6.359001000	-1.437035000	3.807128000
1	-7.064802000	-1.602994000	4.611118000
6	-2.199490000	2.601587000	2.012508000
1	-1.561315000	2.918158000	2.827220000
6	-5.139577000	-2.118154000	3.806870000
1	-4.906408000	-2.804713000	4.610680000
6	-4.194174000	-0.855331000	-3.263639000
1	-3.748569000	-0.455729000	-4.165553000
6	-5.761645000	-0.350653000	1.773775000
1	-6.048040000	0.342913000	0.994507000
6	-4.218234000	-1.913833000	2.775395000
1	-3.290477000	-2.459500000	2.832340000
6	-3.646969000	-0.540859000	-2.018458000
1	-2.781484000	0.100300000	-1.984140000
6	-4.213311000	-1.031790000	-0.820982000
6	0.941810000	0.341333000	3.529219000
1	0.323957000	0.712252000	4.336721000
6	5.468821000	-0.935682000	1.779617000
1	4.954570000	-1.542998000	2.508484000
6	1.984335000	0.664601000	1.371776000
1	2.159712000	1.315152000	0.538169000
6	-5.326519000	-1.901079000	-0.934557000
1	-5.769171000	-2.369012000	-0.066625000
6	-5.870826000	-2.213069000	-2.183788000

1	-6.724056000	-2.875780000	-2.250331000
6	4.605584000	-3.441934000	-0.086012000
1	5.557860000	-2.954195000	-0.240920000
6	3.370279000	-1.336721000	-2.430174000
1	3.459958000	-0.635256000	-3.271127000
1	4.292285000	-1.917196000	-2.361603000
6	7.480636000	0.262629000	1.178303000
1	8.477354000	0.604797000	1.425183000
6	6.753912000	-0.490116000	2.096881000
1	7.189721000	-0.737128000	3.056412000
6	6.929312000	0.558538000	-0.065989000
1	7.503814000	1.126411000	-0.786662000
6	-6.660202000	-0.579900000	2.821967000
1	-7.609025000	-0.058639000	2.835403000
6	2.215227000	-3.418526000	0.294779000
1	1.283430000	-2.901572000	0.479272000
6	-2.865270000	3.554645000	1.246183000
1	-2.736239000	4.607896000	1.458635000
6	-3.715023000	3.150410000	0.220903000
1	-4.249371000	3.891582000	-0.359320000
6	5.644214000	0.116070000	-0.392831000
1	5.295551000	0.349292000	-1.385676000
6	1.190427000	1.141118000	2.417306000
1	0.771380000	2.136165000	2.366344000
6	4.570094000	-4.835911000	-0.181010000
1	5.480990000	-5.386634000	-0.377435000
6	-0.386151000	2.491282000	-3.006915000
6	1.505457000	-0.929777000	3.606564000

1	1.331730000	-1.544060000	4.480623000
6	-5.309158000	-1.686934000	-3.346265000
1	-5.731244000	-1.933199000	-4.311963000
6	3.363868000	-5.519677000	-0.037146000
1	3.340056000	-6.598944000	-0.114614000
6	2.187205000	-4.811052000	0.197165000
1	1.248840000	-5.340430000	0.301442000
6	-1.832262000	3.007226000	-3.064745000
1	-2.508834000	2.362413000	-2.495016000
1	-1.913342000	4.027119000	-2.665583000
1	-2.189991000	3.023949000	-4.100139000
6	-0.261273000	1.143533000	-3.724652000
1	-0.475098000	1.285852000	-4.792591000
1	0.752152000	0.743881000	-3.629702000
1	-0.945398000	0.386221000	-3.335483000
6	0.592774000	3.515933000	-3.647819000
1	1.414814000	2.983276000	-4.142169000
1	0.093278000	4.122133000	-4.411610000
6	1.131500000	4.337555000	-2.482978000
1	2.091201000	4.822813000	-2.691913000
1	0.425256000	5.124167000	-2.187648000
6	1.250838000	3.294727000	-1.354075000
1	2.130990000	2.670719000	-1.542047000
1	-0.708983000	2.842996000	-0.990982000
6	1.390747000	3.941917000	0.010069000
6	2.626871000	3.937356000	0.672713000
6	0.329091000	4.645425000	0.596741000
6	2.785493000	4.575313000	1.905831000

1	3.471080000	3.414346000	0.227798000
6	0.477250000	5.277633000	1.832673000
1	-0.623504000	4.721225000	0.077358000
6	1.707057000	5.238445000	2.496338000
1	3.749685000	4.545792000	2.406700000
1	-0.365547000	5.803572000	2.273753000
1	1.824325000	5.726009000	3.460444000

R-pyrrolidine adduct

28	0.145977000	0.732240000	0.569625000
8	-2.187125000	-1.411935000	3.146100000
8	2.098265000	-2.624716000	1.980759000
7	1.334805000	-0.878960000	0.745342000
7	0.287277000	2.862170000	0.472069000
7	-1.362815000	-0.309333000	1.346632000
6	3.609780000	-0.684661000	-0.430162000
6	-1.081049000	-1.020139000	2.425905000
6	3.197109000	0.680370000	-1.041327000
6	0.169432000	-1.522405000	2.815629000
1	0.227493000	-2.165751000	3.683064000
6	4.513805000	-1.340697000	-1.509986000
6	-2.355042000	-1.032231000	-1.331450000
6	-1.806936000	-2.027428000	-2.180749000
1	-1.969683000	-3.079671000	-2.000401000
6	2.249908000	0.735633000	-2.092121000
1	1.748078000	-0.152156000	-2.443104000
6	2.332081000	-1.550215000	-0.121865000
1	1.821349000	-1.806462000	-1.053674000

6	-3.203583000	-1.373213000	-0.072971000
6	-2.813873000	-0.390206000	1.106404000
1	-3.159325000	0.615390000	0.868569000
6	-4.678306000	-1.188475000	-0.520361000
6	2.611596000	-2.874542000	0.665247000
1	2.038425000	-3.704788000	0.231462000
1	3.654389000	-3.186731000	0.758130000
6	-2.969232000	-2.834137000	0.413917000
6	1.181331000	-1.605639000	1.841451000
6	3.893105000	1.875924000	-0.730823000
1	4.690814000	1.891960000	-0.002107000
6	6.229046000	-2.385015000	-3.487544000
1	6.885235000	-2.791721000	-4.246562000
6	1.968382000	1.936488000	-2.749653000
1	1.237803000	1.957905000	-3.547429000
6	5.075995000	-3.084229000	-3.124485000
1	4.844580000	-4.026545000	-3.604442000
6	4.489328000	0.427339000	3.169361000
1	4.055213000	1.049712000	3.941278000
6	5.694185000	-0.673932000	-1.919987000
1	5.982604000	0.264086000	-1.465656000
6	4.219485000	-2.571778000	-2.145564000
1	3.344574000	-3.154927000	-1.909673000
6	3.836150000	0.280484000	1.944238000
1	2.896457000	0.789352000	1.802537000
6	4.382884000	-0.512222000	0.909873000
6	-0.901225000	-0.342801000	-3.661734000
1	-0.333156000	-0.077192000	-4.543806000

6	-5.156141000	-1.935938000	-1.623327000
1	-4.511337000	-2.641190000	-2.130122000
6	-2.233761000	0.309324000	-1.753347000
1	-2.737392000	1.095668000	-1.222900000
6	5.590526000	-1.200950000	1.185799000
1	6.031300000	-1.881679000	0.471868000
6	6.239878000	-1.050530000	2.414509000
1	7.164074000	-1.580877000	2.604897000
6	-4.037544000	-3.658238000	0.847618000
1	-5.060308000	-3.308337000	0.838714000
6	-3.326730000	-0.784364000	2.521559000
1	-3.582115000	0.114147000	3.100468000
1	-4.164837000	-1.482237000	2.575656000
6	-7.338385000	-0.910433000	-1.445192000
1	-8.354950000	-0.801675000	-1.800437000
6	-6.468499000	-1.794539000	-2.079565000
1	-6.811439000	-2.374624000	-2.926566000
6	-6.900485000	-0.173448000	-0.346562000
1	-7.580925000	0.505677000	0.151086000
6	6.528860000	-1.217027000	-2.903337000
1	7.427498000	-0.687173000	-3.192966000
6	-1.658304000	-3.352809000	0.535555000
1	-0.804387000	-2.763718000	0.234018000
6	2.643870000	3.103589000	-2.400179000
1	2.426479000	4.030747000	-2.914298000
6	3.610790000	3.071003000	-1.398159000
1	4.152376000	3.972684000	-1.143089000
6	-5.589841000	-0.311007000	0.119175000

1	-5.321615000	0.271600000	0.985139000
6	-1.496924000	0.651205000	-2.889542000
1	-1.402757000	1.688749000	-3.181537000
6	-3.801299000	-4.945894000	1.337351000
1	-4.631188000	-5.560294000	1.662035000
6	0.671591000	3.639224000	1.748771000
6	-1.067308000	-1.681427000	-3.314900000
1	-0.639490000	-2.456177000	-3.938023000
6	5.694180000	-0.232322000	3.402258000
1	6.198173000	-0.120772000	4.353539000
6	-2.499744000	-5.436958000	1.424236000
1	-2.320516000	-6.433099000	1.807581000
6	-1.428915000	-4.639190000	1.027177000
1	-0.416741000	-5.015429000	1.102535000
6	2.186079000	3.919474000	1.751734000
1	2.776901000	3.003425000	1.693948000
1	2.479566000	4.568356000	0.917752000
1	2.468383000	4.426619000	2.680873000
6	0.288247000	2.856008000	3.006898000
1	0.515706000	3.451835000	3.900140000
1	-0.777763000	2.612483000	3.024697000
1	0.839812000	1.911684000	3.070605000
6	-0.079811000	4.985377000	1.605298000
1	-1.080989000	4.922583000	2.045941000
1	0.451569000	5.794773000	2.117004000
6	-0.180443000	5.199043000	0.091789000
1	-0.933407000	5.939508000	-0.193186000
1	0.782685000	5.524455000	-0.322176000

6	-0.525428000	3.778398000	-0.418767000
1	-0.172425000	3.625666000	-1.443407000
1	1.166906000	2.754974000	-0.032422000
6	-2.031269000	3.575299000	-0.426954000
6	-2.723931000	3.888095000	-1.608893000
6	-2.777917000	3.199138000	0.696489000
6	-4.117136000	3.822359000	-1.671069000
1	-2.162957000	4.174940000	-2.496677000
6	-4.174714000	3.145027000	0.642637000
1	-2.272665000	2.916392000	1.612544000
6	-4.850745000	3.452408000	-0.539721000
1	-4.627295000	4.053726000	-2.602645000
1	-4.733456000	2.848552000	1.527023000
1	-5.935296000	3.395903000	-0.581930000

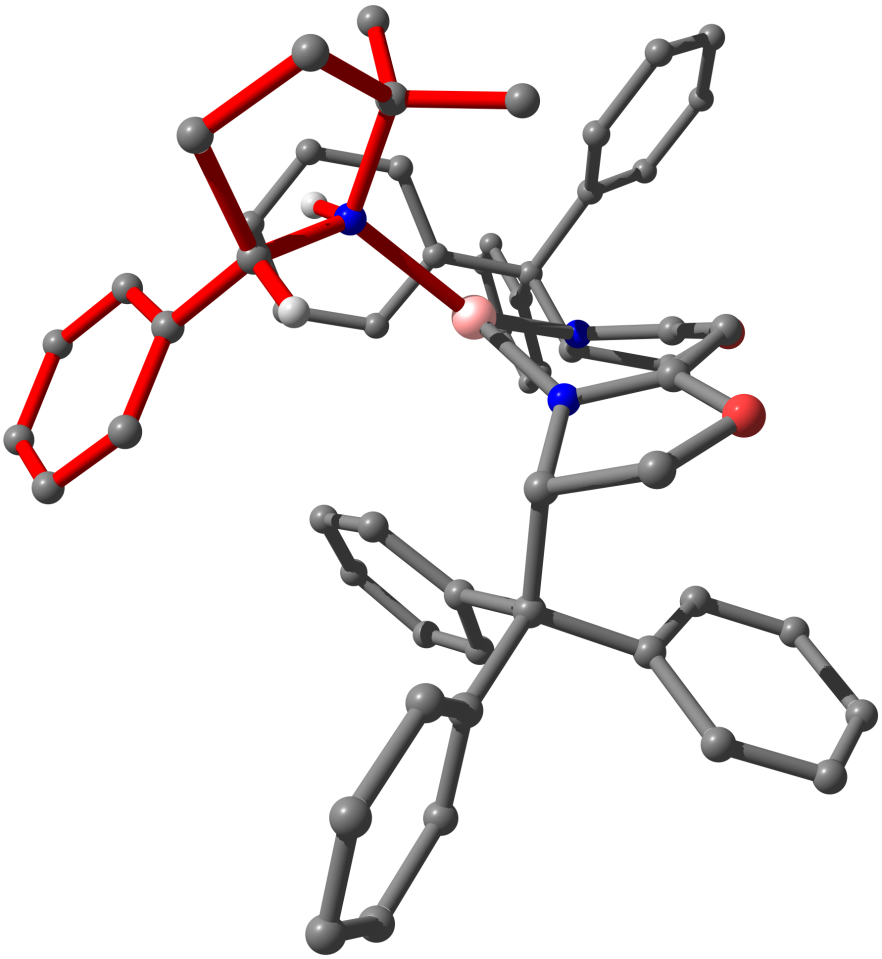


Figure S21. DFT optimized structure for product adduct (^{AdF}L)Ni(*S*-pyrrolidine) Color scheme: nickel = pink, nitrogen = blue, carbon = gray, fluorine = green, hydrogen = white. The fragment corresponding to the substrate **9** is labeled in red.

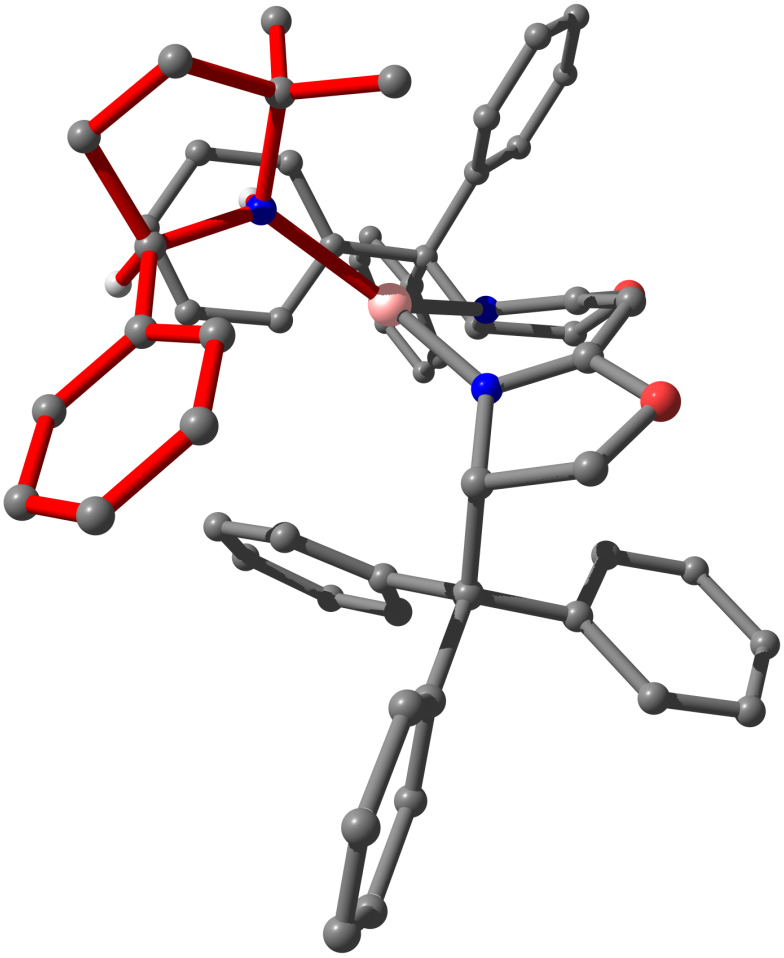


Figure S22. DFT optimized structure for product adduct (^{AdF}L)Ni(*R*-pyrrolidine) Color scheme: nickel = pink, nitrogen = blue, carbon = gray, fluorine = green, hydrogen = white. The fragment corresponding to the substrate **9** is labeled in red.

Optimized geometry coordinates for (^{TrH}BOX)Ni(NR) HAA transition state

Pro-S

28	-0.232467000	0.084656000	-0.912954000
8	2.035890000	-2.824477000	-2.353971000
8	-2.106826000	-3.487018000	-0.208373000
7	-1.340083000	-1.360593000	-0.235565000
7	-0.108006000	1.665080000	-1.693612000
7	1.183020000	-1.144748000	-1.118373000
6	-3.597188000	-0.457577000	0.548704000
6	0.943961000	-2.314269000	-1.711293000
6	-3.141134000	0.996799000	0.253666000
6	-0.232717000	-3.052807000	-1.611391000
1	-0.301032000	-4.045761000	-2.032185000
6	-4.536886000	-0.333676000	1.777737000
6	2.883446000	-0.317177000	1.432886000
6	1.925346000	0.709363000	1.278575000
1	1.478265000	0.928785000	0.329681000
6	-2.201428000	1.639137000	1.096454000
1	-1.739660000	1.121769000	1.923337000
6	-2.351357000	-1.366777000	0.845466000
1	-1.848722000	-1.032577000	1.755550000
6	3.306958000	-1.271230000	0.285528000
6	2.637703000	-0.908649000	-1.104754000
1	2.807352000	0.139868000	-1.349478000
6	4.849843000	-1.109935000	0.179100000
6	-2.658808000	-2.895436000	0.984251000
1	-2.124682000	-3.320726000	1.842207000
1	-3.708365000	-3.186450000	1.051725000

6	2.861479000	-2.719122000	0.656418000
6	-1.206882000	-2.591825000	-0.707802000
6	-3.784234000	1.793992000	-0.726711000
1	-4.581914000	1.401884000	-1.340812000
6	-6.314594000	0.020911000	3.934553000
1	-6.995116000	0.152959000	4.766164000
6	-1.876719000	2.987356000	0.919625000
1	-1.166227000	3.464618000	1.580327000
6	-5.171999000	-0.765988000	4.095044000
1	-4.972948000	-1.237254000	5.049130000
6	-4.414453000	-1.631033000	-3.046706000
1	-3.971272000	-1.558607000	-4.031506000
6	-5.707640000	0.454974000	1.672948000
1	-5.961992000	0.940176000	0.740413000
6	-4.284361000	-0.945525000	3.029908000
1	-3.418422000	-1.560420000	3.213356000
6	-3.787675000	-1.026884000	-1.955139000
1	-2.864314000	-0.495138000	-2.124282000
6	-4.348023000	-1.090523000	-0.658829000
6	2.055514000	1.259162000	3.633110000
1	1.736662000	1.863017000	4.472753000
6	5.744965000	-1.973954000	0.859181000
1	5.387506000	-2.787123000	1.473935000
6	3.413533000	-0.523739000	2.730049000
1	4.122860000	-1.316640000	2.917409000
6	-5.544625000	-1.832994000	-0.500719000
1	-5.994469000	-1.980998000	0.470795000
6	-6.167257000	-2.435770000	-1.597351000

1	-7.082110000	-2.996989000	-1.457005000
6	3.485593000	-3.855993000	0.087078000
1	4.336294000	-3.755045000	-0.570618000
6	3.058777000	-1.792671000	-2.306194000
1	2.995617000	-1.217209000	-3.237383000
1	4.032011000	-2.281109000	-2.263657000
6	7.652306000	-0.701871000	0.088604000
1	8.723165000	-0.551293000	0.045689000
6	7.127072000	-1.781787000	0.793877000
1	7.791527000	-2.463402000	1.309165000
6	6.794658000	0.204105000	-0.530427000
1	7.201374000	1.065056000	-1.045426000
6	-6.574484000	0.612190000	2.760360000
1	-7.465153000	1.217535000	2.649797000
6	1.707514000	-2.943019000	1.451275000
1	1.129761000	-2.119907000	1.849300000
6	-2.492504000	3.732724000	-0.082236000
1	-2.251625000	4.779668000	-0.207145000
6	-3.448921000	3.138575000	-0.899539000
1	-3.949263000	3.726571000	-1.658006000
6	5.411172000	0.018012000	-0.469991000
1	4.794018000	0.781678000	-0.916406000
6	3.010036000	0.261685000	3.811947000
1	3.428483000	0.084723000	4.794250000
6	3.022938000	-5.146435000	0.356790000
1	3.524442000	-6.001244000	-0.078314000
6	-0.114517000	2.029256000	-3.116848000
6	1.508609000	1.474939000	2.371198000

1	0.768814000	2.250226000	2.235422000
6	-5.606045000	-2.331102000	-2.869027000
1	-6.089151000	-2.802154000	-3.715234000
6	1.909710000	-5.336714000	1.172581000
1	1.549883000	-6.337337000	1.374072000
6	1.248354000	-4.236010000	1.712160000
1	0.366207000	-4.382530000	2.321959000
6	-1.452909000	1.596935000	-3.750884000
1	-1.547086000	0.506658000	-3.744672000
1	-2.304119000	2.026208000	-3.215883000
1	-1.497376000	1.932988000	-4.794661000
6	1.028002000	1.321334000	-3.884827000
1	1.047489000	1.644717000	-4.934188000
1	2.007872000	1.535975000	-3.446775000
1	0.877292000	0.237399000	-3.860825000
6	0.021646000	3.571054000	-3.220902000
1	-0.088700000	3.884896000	-4.267173000
1	-0.813057000	4.015090000	-2.662290000
6	1.362727000	4.093059000	-2.661262000
1	2.151467000	3.922979000	-3.404895000
1	1.297994000	5.180318000	-2.530281000
6	1.768423000	3.419047000	-1.342745000
1	0.780313000	2.502764000	-1.244929000
1	2.650398000	2.779454000	-1.442191000
6	1.813928000	4.204806000	-0.096504000
6	2.825365000	3.967872000	0.859399000
6	0.858619000	5.200578000	0.198536000
6	2.867433000	4.671998000	2.062349000

1	3.584231000	3.216096000	0.649991000
6	0.896967000	5.903497000	1.402080000
1	0.075780000	5.418910000	-0.522363000
6	1.897805000	5.640507000	2.344803000
1	3.656960000	4.464264000	2.780665000
1	0.141727000	6.658478000	1.607185000
1	1.924797000	6.187364000	3.283677000

Pro-R

28	-0.345928000	0.368582000	-0.763745000
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8	-2.430439000	-3.158600000	-0.739889000
7	-1.531788000	-1.118871000	-0.357198000
7	-0.211291000	2.073128000	-1.209382000
7	1.002529000	-0.871225000	-1.239953000
6	-3.764330000	-0.262852000	0.546211000
6	0.688376000	-1.902905000	-2.022599000
6	-3.238061000	1.197637000	0.540475000
6	-0.531793000	-2.575083000	-2.048291000
1	-0.656323000	-3.469914000	-2.640918000
6	-4.733584000	-0.326487000	1.756337000
6	2.736868000	-0.619294000	1.412432000
6	1.883401000	0.507767000	1.419973000
1	1.487501000	0.927924000	0.515942000
6	-2.291814000	1.623960000	1.504581000
1	-1.875297000	0.939945000	2.227917000
6	-2.566134000	-1.267427000	0.693142000
1	-2.071733000	-1.129572000	1.656951000

6	3.092398000	-1.409496000	0.124423000
6	2.475682000	-0.756167000	-1.182017000
1	2.735252000	0.301302000	-1.235636000
6	4.647465000	-1.402626000	0.049449000
6	-2.948670000	-2.776231000	0.548135000
1	-2.435466000	-3.378606000	1.307096000
1	-4.011849000	-3.021616000	0.572584000
6	2.510877000	-2.850108000	0.244716000
6	-1.474096000	-2.240049000	-1.062298000
6	-3.819389000	2.195097000	-0.282211000
1	-4.618494000	1.964278000	-0.971687000
6	-6.564912000	-0.304603000	3.896858000
1	-7.266907000	-0.301903000	4.721028000
6	-1.896436000	2.962181000	1.585592000
1	-1.174834000	3.270277000	2.330096000
6	-5.456507000	-1.153532000	3.936267000
1	-5.304961000	-1.801341000	4.790170000
6	-4.536613000	-0.691656000	-3.220930000
1	-4.066333000	-0.451174000	-4.165658000
6	-5.870543000	0.516691000	1.772198000
1	-6.077829000	1.175712000	0.940092000
6	-4.542627000	-1.168984000	2.878489000
1	-3.705759000	-1.842871000	2.965206000
6	-3.911502000	-0.341306000	-2.022638000
1	-2.960212000	0.164322000	-2.068056000
6	-4.507489000	-0.623889000	-0.773069000
6	1.976479000	0.632926000	3.835589000
1	1.679306000	1.109344000	4.760730000

6	5.426087000	-2.423615000	0.652849000
1	4.964410000	-3.257389000	1.162473000
6	3.200788000	-1.090339000	2.665554000
1	3.820041000	-1.971463000	2.733095000
6	-5.737430000	-1.327771000	-0.781256000
1	-6.217446000	-1.638650000	0.135781000
6	-6.358226000	-1.677201000	-1.983793000
1	-7.299910000	-2.210763000	-1.969679000
6	3.046765000	-3.926759000	-0.503059000
1	3.913639000	-3.789960000	-1.133615000
6	2.842528000	-1.447066000	-2.519079000
1	2.837689000	-0.714344000	-3.335342000
1	3.773772000	-2.011824000	-2.561081000
6	7.480580000	-1.303862000	0.042631000
1	8.562346000	-1.269939000	0.032130000
6	6.822257000	-2.379264000	0.633055000
1	7.394234000	-3.176356000	1.090542000
6	6.743450000	-0.261078000	-0.513049000
1	7.255636000	0.587930000	-0.947378000
6	-6.765667000	0.504446000	2.847634000
1	-7.630747000	1.155162000	2.829352000
6	1.334524000	-3.101737000	0.996114000
1	0.826691000	-2.309118000	1.528434000
6	-2.446814000	3.910577000	0.727493000
1	-2.138728000	4.945990000	0.793596000
6	-3.413514000	3.528879000	-0.198293000
1	-3.863117000	4.271605000	-0.844607000
6	5.346254000	-0.299693000	-0.498921000

1	4.829687000	0.549313000	-0.912332000
6	2.832819000	-0.464070000	3.858093000
1	3.196136000	-0.845463000	4.803606000
6	2.473273000	-5.199741000	-0.449398000
1	2.906762000	-6.011736000	-1.018754000
6	-0.200398000	2.722334000	-2.525967000
6	1.494970000	1.109043000	2.619535000
1	0.820339000	1.952597000	2.604950000
6	-5.762133000	-1.354504000	-3.201837000
1	-6.244662000	-1.628733000	-4.130987000
6	1.337527000	-5.425431000	0.325858000
1	0.891528000	-6.410903000	0.360414000
6	0.766319000	-4.376526000	1.042628000
1	-0.129207000	-4.546880000	1.625860000
6	-1.491629000	2.366168000	-3.292227000
1	-1.532001000	1.293084000	-3.504049000
1	-2.381737000	2.646546000	-2.722197000
1	-1.515885000	2.900245000	-4.250687000
6	1.004623000	2.226615000	-3.362267000
1	1.952091000	2.373803000	-2.835343000
1	0.898172000	1.156423000	-3.565835000
1	1.058752000	2.759347000	-4.321129000
6	-0.144548000	4.264697000	-2.338567000
1	-0.173846000	4.750521000	-3.322688000
1	-1.051132000	4.576679000	-1.803061000
6	1.098702000	4.729315000	-1.565044000
1	1.993769000	4.573708000	-2.177100000
1	1.036991000	5.815745000	-1.395848000

6	1.231321000	4.007990000	-0.227755000
1	0.575822000	2.859797000	-0.528435000
1	0.519517000	4.386284000	0.513794000
6	2.566569000	3.787178000	0.361778000
6	2.761371000	3.947383000	1.751511000
6	3.688212000	3.400042000	-0.405112000
6	3.999399000	3.711381000	2.348858000
1	1.920601000	4.261198000	2.366775000
6	4.930683000	3.178469000	0.188423000
1	3.588841000	3.269117000	-1.479178000
6	5.094225000	3.321212000	1.570551000
1	4.111531000	3.838287000	3.422897000
1	5.777021000	2.889330000	-0.430543000
1	6.061557000	3.137723000	2.030718000

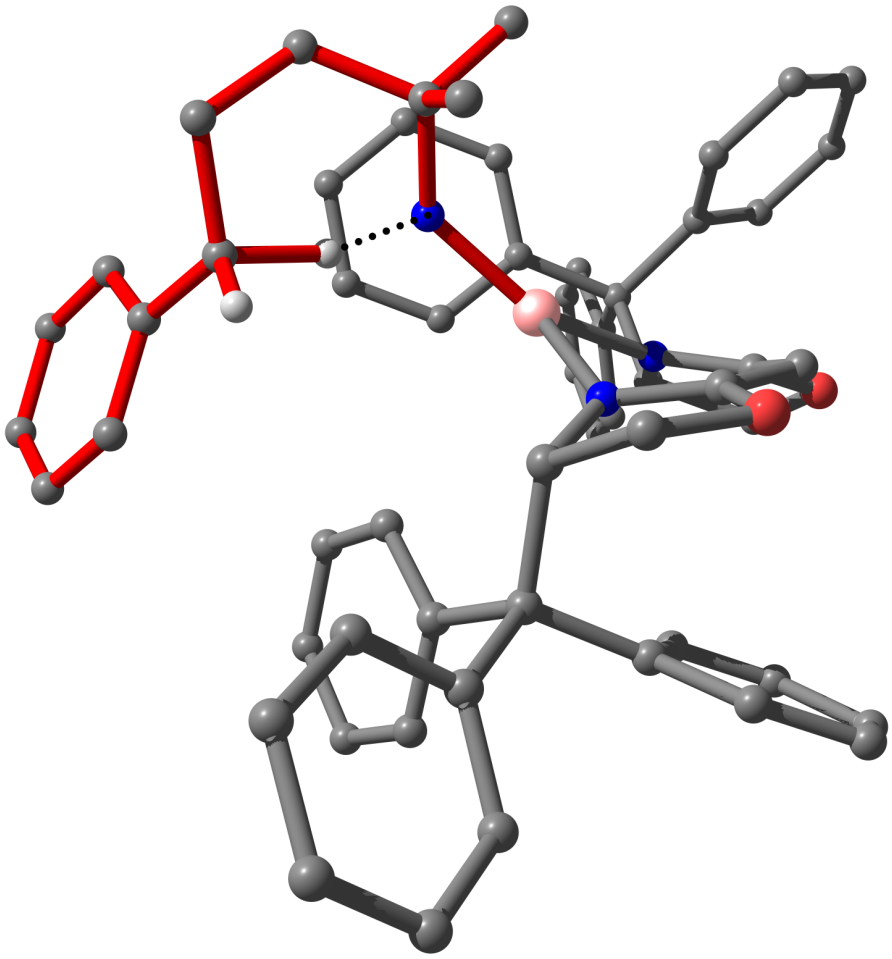

Figure S23. DFT optimized structure for (^{AdF}L)Ni(NR) HAA transition state, *pro*-S hydrogen

Color scheme: nickel = pink, nitrogen = blue, carbon = gray, fluorine = green, hydrogen = white.

The fragment corresponding to the substrate **9** is labeled in red.

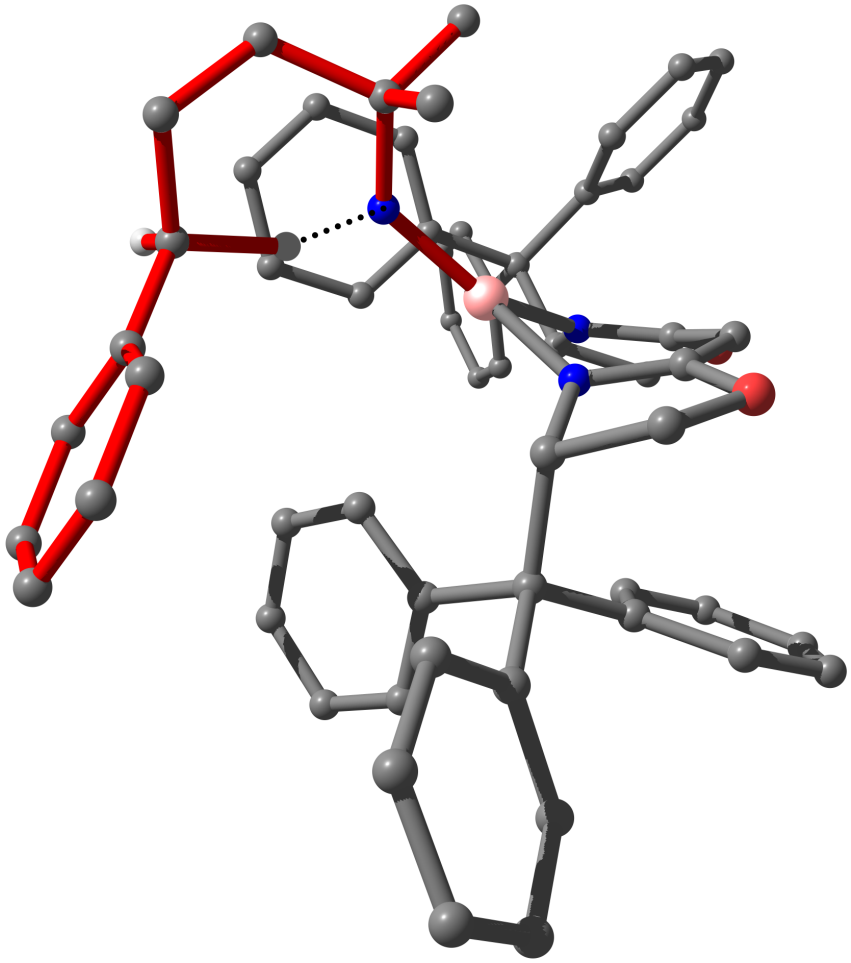

Figure S24. DFT optimized structure for (^{AdF}L)Ni(NR) HAA transition state, *pro*-R hydrogen

Color scheme: nickel = pink, nitrogen = blue, carbon = gray, fluorine = green, hydrogen = white.

The fragment corresponding to the substrate **9** is labeled in red.

Optimized geometry coordinates for (^{TrH}BOX)Ni(NR) HAA transition state

Re

28	-0.261237000	0.296144000	-0.621131000
8	1.804315000	-2.673238000	-2.532510000
8	-2.397684000	-3.237809000	-0.520328000
7	-1.518625000	-1.170557000	-0.208250000
7	-0.094694000	2.075015000	-1.311845000
7	1.110250000	-0.999362000	-1.187009000
6	-3.847119000	-0.338546000	0.500687000
6	0.769393000	-2.093859000	-1.845145000
6	-3.389868000	1.144004000	0.449809000
6	-0.469711000	-2.740914000	-1.795960000
1	-0.598324000	-3.690946000	-2.295680000
6	-4.895538000	-0.376004000	1.644736000
6	2.358157000	-0.774848000	1.359317000
6	2.208230000	-1.526059000	2.553875000
1	2.751732000	-2.447099000	2.711907000
6	-2.584191000	1.672694000	1.487200000
1	-2.225841000	1.050333000	2.292750000
6	-2.615929000	-1.277681000	0.788774000
1	-2.185397000	-1.046949000	1.765431000
6	3.256447000	-1.259025000	0.181925000
6	2.576439000	-0.872705000	-1.200006000
1	2.795794000	0.176554000	-1.421498000
6	4.628666000	-0.544522000	0.336898000
6	-2.936891000	-2.803876000	0.737554000
1	-2.402069000	-3.333965000	1.536399000
1	-3.989482000	-3.091359000	0.772488000

6	3.445754000	-2.802248000	0.239110000
6	-1.426910000	-2.329252000	-0.856756000
6	-3.923805000	2.063858000	-0.488555000
1	-4.632077000	1.756499000	-1.243791000
6	-6.861102000	-0.295532000	3.661238000
1	-7.614301000	-0.270350000	4.438503000
6	-2.271179000	3.033814000	1.538967000
1	-1.651003000	3.415677000	2.339553000
6	-5.716093000	-1.076485000	3.834270000
1	-5.587396000	-1.649174000	4.743859000
6	-4.335937000	-1.033042000	-3.275279000
1	-3.812255000	-0.827866000	-4.200075000
6	-6.070740000	0.404571000	1.526407000
1	-6.251570000	0.993092000	0.636661000
6	-4.734533000	-1.118308000	2.839701000
1	-3.868243000	-1.730018000	3.032303000
6	-3.815958000	-0.573633000	-2.063539000
1	-2.891450000	-0.019635000	-2.077871000
6	-4.481560000	-0.811653000	-0.840144000
6	0.675862000	0.111640000	3.455650000
1	0.015636000	0.443958000	4.246233000
6	5.249920000	-0.472534000	1.607788000
1	4.779420000	-0.892387000	2.483966000
6	1.709784000	0.476577000	1.298552000
1	1.838981000	1.119323000	0.443901000
6	-5.669194000	-1.584017000	-0.884262000
1	-6.194182000	-1.866339000	0.017255000
6	-6.185994000	-2.040850000	-2.100148000

1	-7.096658000	-2.625821000	-2.113709000
6	4.714893000	-3.415815000	0.091666000
1	5.613450000	-2.835109000	-0.058408000
6	2.928234000	-1.763217000	-2.428329000
1	2.958260000	-1.158040000	-3.342862000
1	3.838225000	-2.363759000	-2.378414000
6	7.179262000	0.642129000	0.667957000
1	8.150567000	1.102063000	0.795533000
6	6.500784000	0.127509000	1.769814000
1	6.950220000	0.181974000	2.752939000
6	6.612551000	0.548844000	-0.601103000
1	7.149811000	0.931266000	-1.459433000
6	-7.032668000	0.422855000	2.542928000
1	-7.924992000	1.024080000	2.422871000
6	2.323246000	-3.651877000	0.384432000
1	1.332693000	-3.238555000	0.514649000
6	-2.774210000	3.906813000	0.577319000
1	-2.532733000	4.960709000	0.622685000
6	-3.602343000	3.422701000	-0.432633000
1	-4.015432000	4.105870000	-1.163382000
6	5.357735000	-0.042153000	-0.771462000
1	4.989739000	-0.118904000	-1.782466000
6	0.854615000	0.896764000	2.320197000
1	0.328193000	1.834618000	2.232144000
6	4.846894000	-4.807137000	0.107720000
1	5.824340000	-5.257644000	-0.007624000
6	-0.002127000	2.367435000	-2.765224000
6	1.366002000	-1.091076000	3.580034000

1	1.251723000	-1.688245000	4.475486000
6	-5.523677000	-1.761312000	-3.294411000
1	-5.924564000	-2.120169000	-4.233553000
6	3.724003000	-5.618381000	0.261276000
1	3.830666000	-6.695363000	0.271522000
6	2.463504000	-5.040976000	0.398460000
1	1.591149000	-5.670378000	0.518317000
6	-1.215901000	1.797810000	-3.528292000
1	-2.159175000	2.155398000	-3.096386000
1	-1.211016000	0.703896000	-3.502961000
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6	1.279561000	1.740912000	-3.335055000
1	1.407658000	2.020511000	-4.388018000
1	2.167472000	2.062896000	-2.783209000
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6	0.010234000	3.904002000	-2.934874000
1	0.159329000	4.183151000	-3.986092000
1	-0.975966000	4.295568000	-2.640412000
6	1.090226000	4.517751000	-2.040651000
1	2.083646000	4.313949000	-2.451974000
1	0.984743000	5.615503000	-2.037960000
6	0.971015000	4.007053000	-0.634903000
1	0.064249000	4.317902000	-0.117614000
1	-0.939739000	2.553930000	-0.993492000
6	2.106251000	3.819815000	0.239537000
6	1.945783000	3.978236000	1.639604000
6	3.401855000	3.479780000	-0.226468000
6	3.003669000	3.782861000	2.522862000

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1	3.577436000	3.347317000	-1.289805000
6	4.271013000	3.434392000	2.039157000
1	2.842853000	3.906301000	3.591070000
1	5.443812000	3.044847000	0.270452000
1	5.099703000	3.279142000	2.724784000

Si

28	0.022526000	0.157233000	-0.986965000
8	3.122264000	-1.872521000	-2.741448000
8	-1.060454000	-3.697947000	-1.909977000
7	-0.822026000	-1.635260000	-0.990258000
7	-0.377074000	1.930334000	-1.489265000
7	1.836706000	-0.539122000	-1.430849000
6	-3.082225000	-1.383847000	0.250253000
6	1.886462000	-1.605641000	-2.223711000
6	-2.716378000	-0.765466000	1.632205000
6	0.871327000	-2.514979000	-2.537808000
1	1.094387000	-3.327337000	-3.215780000
6	-4.337254000	-2.284188000	0.417436000
6	3.138143000	0.472693000	1.346353000
6	3.003167000	-0.017322000	2.671788000
1	3.249243000	-1.039434000	2.922011000
6	-1.418874000	-0.264739000	1.881390000
1	-0.662129000	-0.264867000	1.115249000
6	-1.891848000	-2.311193000	-0.209800000
1	-1.420710000	-2.744533000	0.688651000

6	3.784576000	-0.406324000	0.240095000
6	3.228000000	-0.069799000	-1.201536000
1	3.260606000	0.998507000	-1.394375000
6	5.297152000	-0.089557000	0.375202000
6	-2.245979000	-3.532597000	-1.116310000
1	-2.383443000	-4.452177000	-0.541776000
1	-3.104837000	-3.416149000	-1.787063000
6	3.499160000	-1.918856000	0.465683000
6	-0.322140000	-2.550552000	-1.814167000
6	-3.675724000	-0.633404000	2.670561000
1	-4.709814000	-0.912182000	2.522880000
6	-6.570705000	-3.977445000	0.793427000
1	-7.425944000	-4.624883000	0.937234000
6	-1.069350000	0.230977000	3.138887000
1	-0.067140000	0.585249000	3.316217000
6	-5.388992000	-4.217423000	1.491949000
1	-5.327485000	-5.051217000	2.179236000
6	-4.328843000	1.969338000	-1.235377000
1	-4.753627000	2.898717000	-0.882415000
6	-5.551784000	-2.058317000	-0.276468000
1	-5.673296000	-1.235798000	-0.965238000
6	-4.284697000	-3.382296000	1.309165000
1	-3.383079000	-3.588093000	1.872152000
6	-3.905962000	1.000829000	-0.321318000
1	-4.041873000	1.220867000	0.726883000
6	-3.366526000	-0.236336000	-0.759380000
6	2.341648000	2.161729000	3.481696000
1	2.030304000	2.805742000	4.293918000

6	6.025130000	-0.604884000	1.474841000
1	5.551034000	-1.261433000	2.191779000
6	2.925440000	1.860392000	1.151683000
1	3.122500000	2.343513000	0.209942000
6	-3.295409000	-0.450630000	-2.157662000
1	-2.934870000	-1.373851000	-2.573033000
6	-3.727078000	0.520869000	-3.062425000
1	-3.669451000	0.330692000	-4.126516000
6	4.448482000	-2.911997000	0.127121000
1	5.424200000	-2.646192000	-0.255609000
6	3.977854000	-0.778229000	-2.374574000
1	4.061789000	-0.105767000	-3.238185000
1	4.963955000	-1.194813000	-2.162095000
6	8.021523000	0.564803000	0.772802000
1	9.065576000	0.809113000	0.920078000
6	7.373506000	-0.291465000	1.660448000
1	7.914646000	-0.709416000	2.499540000
6	7.318178000	1.120790000	-0.294197000
1	7.817237000	1.803283000	-0.970106000
6	-6.651682000	-2.899883000	-0.087512000
1	-7.571853000	-2.713341000	-0.626209000
6	2.213639000	-2.353810000	0.872164000
1	1.429203000	-1.638142000	1.078736000
6	-2.012898000	0.290630000	4.161072000
1	-1.737976000	0.686009000	5.130334000
6	-3.320813000	-0.120724000	3.920140000
1	-4.064418000	-0.039594000	4.702484000
6	5.968220000	0.812795000	-0.486248000

1	5.464454000	1.301297000	-1.305641000
6	2.518201000	2.685361000	2.204450000
1	2.365259000	3.743386000	2.034420000
6	4.144365000	-4.270346000	0.255056000
1	4.886512000	-5.015488000	-0.000611000
6	0.010502000	2.585079000	-2.759899000
6	2.597192000	0.814307000	3.717572000
1	2.491997000	0.413226000	4.717392000
6	-4.236156000	1.732141000	-2.603207000
1	-4.569360000	2.482928000	-3.307986000
6	2.882326000	-4.669781000	0.693345000
1	2.648261000	-5.722442000	0.784575000
6	1.915632000	-3.712245000	0.994568000
1	0.927692000	-4.021592000	1.310838000
6	-0.621751000	1.878129000	-3.979882000
1	-1.704229000	2.036141000	-4.010758000
1	-0.424247000	0.801592000	-3.951293000
1	-0.207924000	2.281240000	-4.913456000
6	1.539034000	2.542396000	-2.912777000
1	1.853676000	3.143322000	-3.774651000
1	2.043347000	2.929394000	-2.022022000
1	1.870067000	1.513256000	-3.074168000
6	-0.493109000	4.044670000	-2.714090000
1	-0.182726000	4.592827000	-3.614294000
1	-1.592791000	4.030713000	-2.716178000
6	0.005365000	4.758478000	-1.440505000
1	1.075204000	4.974775000	-1.542529000
1	-0.498606000	5.731020000	-1.351959000

6	-0.217244000	3.926339000	-0.208401000
1	0.657586000	3.505007000	0.267573000
1	-1.380593000	2.082001000	-1.360718000
6	-1.398329000	3.998560000	0.604779000
6	-1.402932000	3.409499000	1.897499000
6	-2.588086000	4.655993000	0.189829000
6	-2.520570000	3.476105000	2.721795000
1	-0.498394000	2.918584000	2.247473000
6	-3.704602000	4.718201000	1.019729000
1	-2.631314000	5.126166000	-0.788532000
6	-3.684812000	4.125786000	2.288791000
1	-2.486505000	3.036476000	3.714921000
1	-4.599628000	5.230698000	0.674819000
1	-4.557761000	4.176885000	2.933773000

κ^1-azide-N-internal linkage isomer

28	0.144786000	-0.270844000	0.560581000
8	1.948391000	2.268447000	-2.077722000
8	-1.381915000	-0.843035000	-3.180955000
7	-0.617038000	-1.065501000	-1.058566000
7	1.495212000	0.763317000	-0.448474000
6	-2.553612000	-2.576909000	-0.378473000
6	1.115472000	1.282398000	-1.604660000
6	-2.095621000	-2.531864000	1.105561000
6	0.044842000	0.880876000	-2.414714000
1	-0.111636000	1.373903000	-3.364337000
6	-3.173140000	-3.987645000	-0.557705000
6	3.640896000	-1.092201000	0.454331000

6	3.899962000	-2.384604000	-0.071771000
1	4.341898000	-2.521919000	-1.047639000
6	-0.928188000	-3.218946000	1.520983000
1	-0.302274000	-3.748442000	0.819981000
6	-1.324843000	-2.335393000	-1.328328000
1	-0.598535000	-3.143397000	-1.214228000
6	3.976431000	0.204965000	-0.335335000
6	2.834351000	1.275540000	-0.118203000
1	2.819316000	1.597159000	0.927193000
6	5.340564000	0.676843000	0.234420000
6	-1.662788000	-2.212806000	-2.853932000
1	-0.991046000	-2.842533000	-3.450147000
1	-2.690063000	-2.430450000	-3.153737000
6	4.091555000	-0.058831000	-1.867396000
6	-0.626011000	-0.326336000	-2.159750000
6	-2.912037000	-1.970017000	2.119630000
1	-3.863440000	-1.512146000	1.889800000
6	-4.382152000	-6.525426000	-0.744347000
1	-4.844056000	-7.501521000	-0.821711000
6	-0.564436000	-3.276296000	2.868779000
1	0.333380000	-3.803225000	3.164109000
6	-3.266155000	-6.225169000	-1.528679000
1	-2.868776000	-6.969670000	-2.206662000
6	-4.255132000	0.888101000	-0.622342000
1	-4.058329000	1.898924000	-0.292385000
6	-4.301894000	-4.348036000	0.217031000
1	-4.746611000	-3.640496000	0.903527000
6	-2.659381000	-4.968754000	-1.439654000

1	-1.798332000	-4.795985000	-2.064046000
6	-3.361803000	-0.135421000	-0.301823000
1	-2.486028000	0.108767000	0.276904000
6	-3.598496000	-1.469808000	-0.700864000
6	3.162306000	-3.432800000	1.977035000
1	2.971496000	-4.326268000	2.557315000
6	6.456803000	-0.188646000	0.138352000
1	6.364974000	-1.152819000	-0.343058000
6	3.219925000	-1.018445000	1.803177000
1	3.106289000	-0.068617000	2.303191000
6	-4.753643000	-1.722310000	-1.481355000
1	-4.964837000	-2.706379000	-1.875494000
6	-5.644514000	-0.693167000	-1.800799000
1	-6.523090000	-0.905527000	-2.396275000
6	5.110697000	0.533485000	-2.653961000
1	5.859094000	1.178612000	-2.215480000
6	2.908494000	2.534661000	-1.034840000
1	2.580628000	3.428716000	-0.487601000
1	3.867559000	2.750775000	-1.509665000
6	7.873953000	1.422096000	1.252603000
1	8.842697000	1.707714000	1.641739000
6	7.705662000	0.181453000	0.641952000
1	8.545576000	-0.495686000	0.554959000
6	6.794065000	2.296661000	1.357684000
1	6.928351000	3.261838000	1.829127000
6	-4.884079000	-5.615536000	0.101824000
1	-5.750422000	-5.861721000	0.702671000
6	3.108754000	-0.821960000	-2.544006000

1	2.291527000	-1.276340000	-1.999640000
6	-1.366999000	-2.680713000	3.838553000
1	-1.086007000	-2.733990000	4.882348000
6	-2.540075000	-2.030978000	3.464498000
1	-3.175383000	-1.588564000	4.220920000
6	5.540143000	1.934926000	0.856220000
1	4.749193000	2.659275000	0.963149000
6	2.976049000	-2.176866000	2.547904000
1	2.660918000	-2.103518000	3.579295000
6	5.163468000	0.331490000	-4.035922000
1	5.951747000	0.790652000	-4.618511000
6	-0.794880000	1.958283000	2.614670000
6	3.634782000	-3.536229000	0.672367000
1	3.822313000	-4.512111000	0.243252000
6	-5.398121000	0.609321000	-1.368432000
1	-6.088244000	1.404395000	-1.619591000
6	4.195786000	-0.445635000	-4.670139000
1	4.237653000	-0.595919000	-5.741142000
6	3.166717000	-1.017547000	-3.925281000
1	2.407389000	-1.610612000	-4.418591000
6	-0.002484000	2.815806000	3.612988000
1	0.057267000	2.353339000	4.604691000
1	1.015397000	2.998481000	3.250820000
1	-0.497839000	3.783970000	3.737785000
6	-2.164498000	1.575207000	3.195419000
1	-2.721730000	2.472647000	3.482600000
1	-2.766039000	1.016500000	2.473070000
1	-2.047649000	0.960677000	4.095919000

6	-0.887491000	2.660870000	1.244603000
1	0.111326000	3.032187000	0.982981000
1	-1.128046000	1.917245000	0.478369000
6	-1.905787000	3.806590000	1.153452000
1	-2.917014000	3.431666000	1.352262000
1	-1.706871000	4.578530000	1.909682000
6	-1.891810000	4.459133000	-0.246764000
1	-0.904779000	4.907317000	-0.423962000
1	-2.015062000	3.675307000	-1.004718000
6	-2.971510000	5.507452000	-0.415169000
6	-4.198993000	5.186341000	-1.014587000
6	-2.783848000	6.818151000	0.050955000
6	-5.212237000	6.141559000	-1.138318000
1	-4.359284000	4.180760000	-1.398494000
6	-3.792609000	7.777708000	-0.070121000
1	-1.833693000	7.092414000	0.506543000
6	-5.013133000	7.441396000	-0.664212000
1	-6.153552000	5.871491000	-1.610938000
1	-3.623513000	8.788571000	0.293308000
1	-5.797960000	8.187031000	-0.763095000
7	-0.021740000	0.645226000	2.348429000
7	0.403303000	0.116640000	3.395233000
7	0.802077000	-0.379219000	4.344537000

κ^1-azide-N-terminal linkage isomer

28	-1.044440000	-0.278563000	0.370922000
8	-3.223280000	1.737464000	3.216667000
8	-3.089101000	-2.932249000	2.710867000

7	-1.899740000	-1.826294000	1.134433000
7	-1.990411000	1.067726000	1.437448000
6	-0.762495000	-3.743926000	-0.103084000
6	-2.677872000	0.699657000	2.510905000
6	-0.380133000	-2.773891000	-1.254146000
6	-2.947460000	-0.591207000	2.981246000
1	-3.499670000	-0.703887000	3.903986000
6	-0.997977000	-5.108327000	-0.805632000
6	-2.367431000	2.535245000	-1.311124000
6	-3.105694000	2.026353000	-2.410239000
1	-4.169612000	1.852324000	-2.346899000
6	-1.374395000	-2.232550000	-2.105258000
1	-2.421961000	-2.443295000	-1.959117000
6	-2.039271000	-3.218668000	0.643640000
1	-2.909952000	-3.231329000	-0.022940000
6	-3.050045000	2.922993000	0.028815000
6	-2.140081000	2.531366000	1.258323000
1	-1.142261000	2.958194000	1.151456000
6	-3.255053000	4.454785000	-0.099355000
6	-2.450304000	-3.970836000	1.941182000
1	-3.189065000	-4.760188000	1.793474000
1	-1.628063000	-4.366407000	2.547396000
6	-4.411457000	2.195185000	0.238910000
6	-2.611868000	-1.731955000	2.253137000
6	0.973057000	-2.536665000	-1.605358000
1	1.784981000	-2.992077000	-1.056519000
6	-1.283126000	-7.557101000	-2.172608000
1	-1.397765000	-8.499482000	-2.693077000

6	-1.032232000	-1.429662000	-3.195907000
1	-1.808933000	-1.026108000	-3.831677000
6	-2.385483000	-6.978580000	-1.540173000
1	-3.348056000	-7.472434000	-1.578544000
6	1.972654000	-2.752643000	2.452352000
1	2.431984000	-1.845167000	2.822886000
6	0.081281000	-5.733951000	-1.476629000
1	1.066435000	-5.288499000	-1.470334000
6	-2.252724000	-5.761675000	-0.864551000
1	-3.143042000	-5.357067000	-0.415442000
6	0.973740000	-2.680505000	1.479091000
1	0.686374000	-1.704812000	1.119615000
6	0.373587000	-3.850009000	0.955592000
6	-1.146795000	2.079732000	-3.828100000
1	-0.676710000	1.892393000	-4.784761000
6	-4.172065000	4.946048000	-1.059184000
1	-4.751362000	4.261462000	-1.665027000
6	-1.021464000	2.902196000	-1.556978000
1	-0.430138000	3.412558000	-0.812428000
6	0.777483000	-5.092333000	1.505029000
1	0.307475000	-6.019759000	1.209846000
6	1.775933000	-5.156857000	2.481003000
1	2.074866000	-6.115720000	2.884538000
6	-5.522655000	2.850413000	0.823280000
1	-5.473805000	3.891189000	1.111805000
6	-2.700990000	2.952167000	2.654697000
1	-1.891175000	3.307722000	3.304765000
1	-3.505320000	3.690394000	2.664026000

6	-3.630705000	7.231806000	-0.486894000
1	-3.778437000	8.294367000	-0.630410000
6	-4.363467000	6.317468000	-1.240830000
1	-5.079457000	6.670995000	-1.971502000
6	-2.697414000	6.776105000	0.442718000
1	-2.116558000	7.488273000	1.014736000
6	-0.087696000	-6.952964000	-2.142970000
1	0.758116000	-7.412061000	-2.638986000
6	-4.534419000	0.806759000	-0.017432000
1	-3.699890000	0.241553000	-0.412734000
6	0.305119000	-1.169493000	-3.485297000
1	0.566175000	-0.550587000	-4.333807000
6	1.306426000	-1.732738000	-2.698497000
1	2.345743000	-1.556216000	-2.942707000
6	-2.499662000	5.404993000	0.630763000
1	-1.741920000	5.112928000	1.340226000
6	-0.415165000	2.651439000	-2.791004000
1	0.621699000	2.919840000	-2.947809000
6	-6.713091000	2.163054000	1.075626000
1	-7.553510000	2.683603000	1.516424000
6	3.810355000	0.887781000	-0.086564000
6	-2.494416000	1.782916000	-3.642572000
1	-3.074357000	1.379512000	-4.462656000
6	2.378066000	-3.989860000	2.948419000
1	3.150375000	-4.043688000	3.704741000
6	-6.816763000	0.804840000	0.779540000
1	-7.738300000	0.274751000	0.982379000
6	-5.725962000	0.126029000	0.240290000

1	-5.798513000	-0.933350000	0.030258000
6	4.036686000	-0.622262000	-0.258867000
1	3.159404000	-1.186867000	0.074558000
1	4.231152000	-0.872393000	-1.307525000
1	4.888521000	-0.958933000	0.341207000
6	3.536816000	1.237043000	1.384521000
1	4.384695000	0.949354000	2.014760000
1	3.365912000	2.312787000	1.505768000
1	2.655210000	0.703609000	1.759469000
6	4.960459000	1.723868000	-0.685564000
1	5.006567000	1.502713000	-1.760645000
1	4.680482000	2.783065000	-0.604240000
6	6.346551000	1.512630000	-0.061772000
1	6.325649000	1.737050000	1.012617000
1	6.655530000	0.463408000	-0.154379000
6	7.418513000	2.401655000	-0.729535000
1	7.445154000	2.180984000	-1.805247000
1	7.118869000	3.454151000	-0.634466000
6	8.798705000	2.209407000	-0.135953000
6	9.224434000	2.975111000	0.960354000
6	9.673414000	1.237893000	-0.646286000
6	10.483120000	2.774485000	1.534137000
1	8.565277000	3.741205000	1.365130000
6	10.933421000	1.032392000	-0.077090000
1	9.366718000	0.640161000	-1.502965000
6	11.342561000	1.800302000	1.017292000
1	10.794091000	3.382342000	2.380378000
1	11.596785000	0.277149000	-0.491681000

1	12.323456000	1.645107000	1.459257000
7	2.615486000	1.301429000	-0.931207000
7	1.527634000	0.837084000	-0.588172000
7	0.442202000	0.488690000	-0.403317000

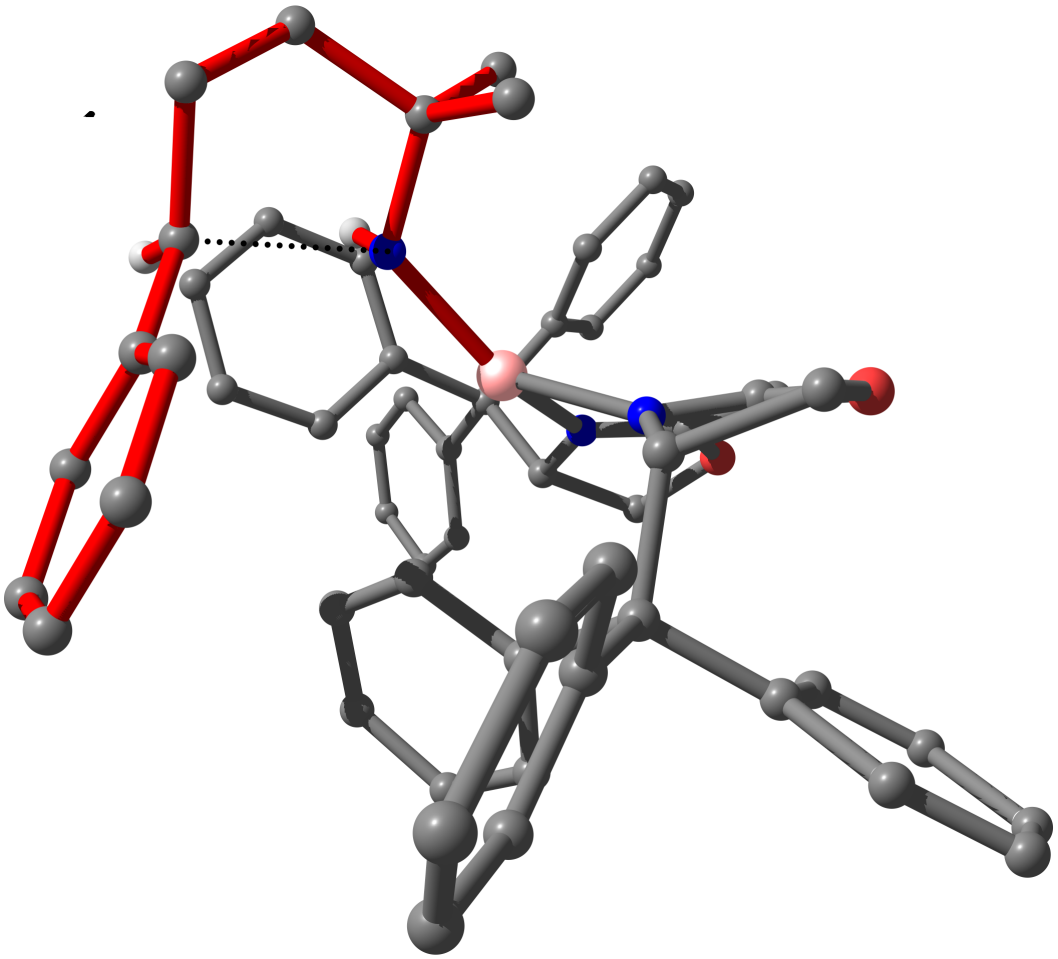


Figure S25. DFT optimized structure for (^{AdF}L)Ni(NHR) RR transition state, *Re* Color scheme: nickel = pink, nitrogen = blue, carbon = gray, fluorine = green, hydrogen = white. The fragment corresponding to the substrate **9** is labeled in red.

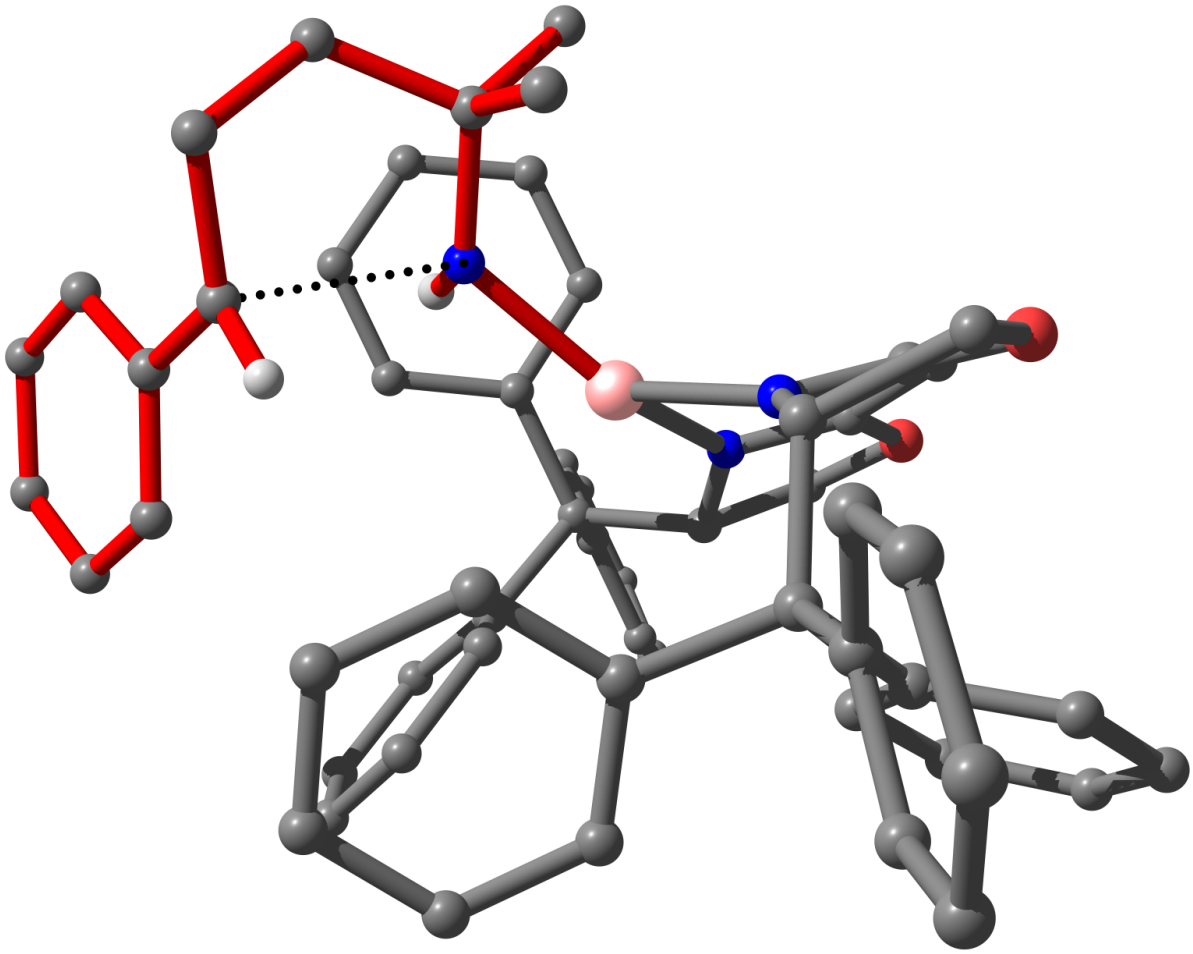


Figure S26. DFT optimized structure for (^{AdF}L)Ni(NHR) RR transition state, *Si* Color scheme: nickel = pink, nitrogen = blue, carbon = gray, fluorine = green, hydrogen = white. The fragment corresponding to the substrate **9** is labeled in red.

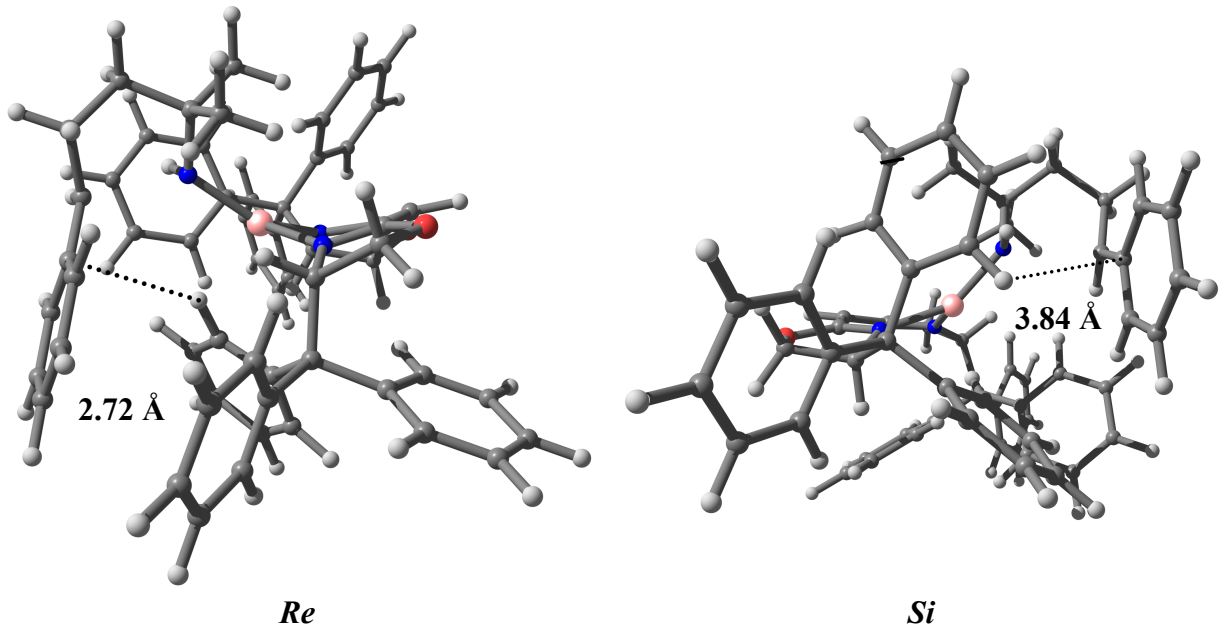


Figure S27. Transition state structures comparison for radical recombination step (RR)

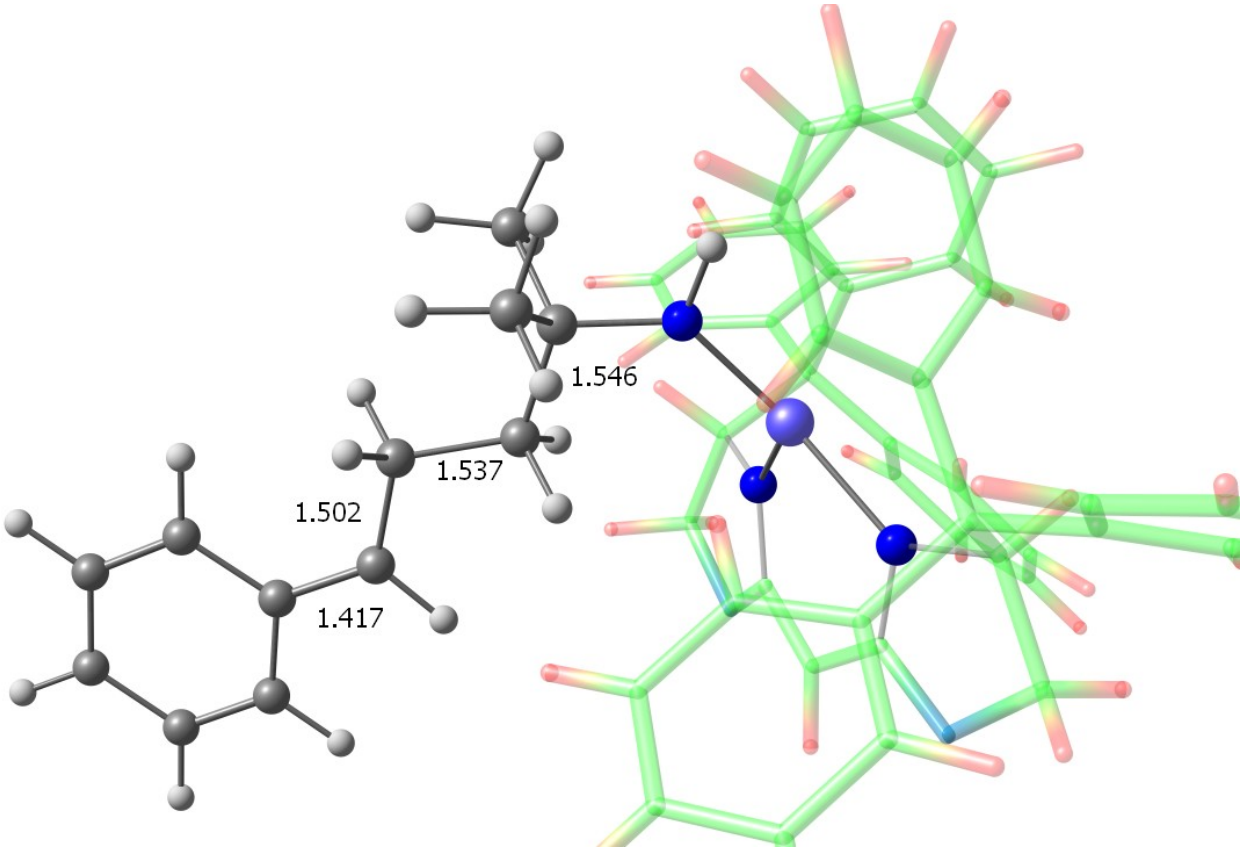
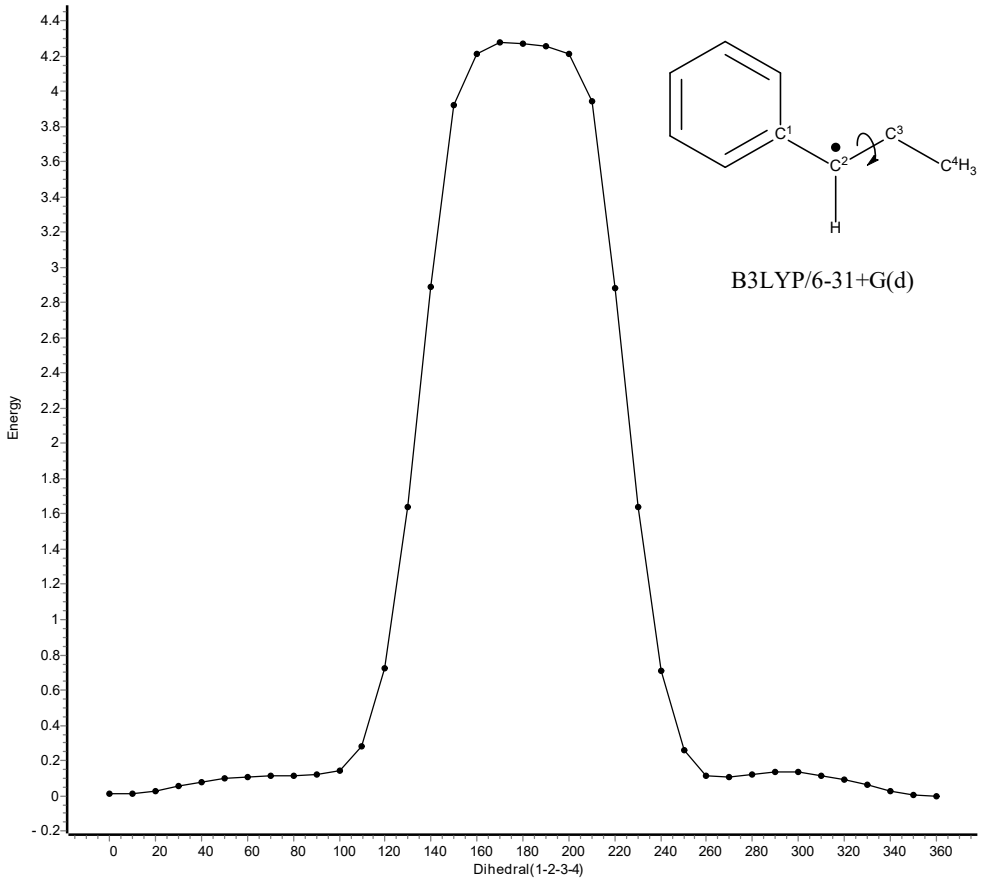


Figure S28. Bond metrics of amide intermediate C and discussion regarding rotational barrier of carboradical



Additionally, we carried out a rotational relaxed surface scan around C^2–C^3 bond of radical Ph–(•)C^2H–C^3H_2–C^4H_3 at the same theory level [B3LYP/6-31+G(d)]. Although the barrier is predicted as 4.3 kcal/mol, additional chiral steric strain imposed by the bulky ligand pocket likely will further energetically differentiate *Re* and *Si* faces of the radical and raise the rotational barrier to a level similar to that of the radical recombination step.

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