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Supplementary Materials for

Aromatic nitrogen scanning by *ipso*-selective nitrene internalization

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The PDF file includes:

General Considerations

Unless noted otherwise, all reactions were performed in oven-dried or flame-dried glassware under an atmosphere of dry N_2. CH_3CN, THF, Et_2O, CH_2Cl_2, toluene, and Et_3N were dried by passing these previously degassed solvents through a PPT Solvent Purification System, and all other solvents were dried over molecular sieves (4 Å) and degassed prior to use or purchased anhydrous and sealed under N_2 (e.g. VWR Dri-solv or equivalent). Reaction temperatures were reported as the temperatures of the bath surrounding the flasks or vials. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Unless otherwise noted, all reagents were used as received. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254) and visualized by UV irradiation or staining as indicated. Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 μm). High resolution mass spectra were recorded on either an Agilent 6224 TOF High Resolution Accurate MS with electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) All mass spectra were processed with Agilent MassHunter.

NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K. ^{1}H-NMR spectra were referenced to residual, nondeuterated chloroform (δ 7.26) in $CDCl_3$, residual DMSO-d_5 (δ 2.50) in DMSO-d_6, and residual MeCN-d_2 (δ 1.94) in MeCN-d_3. ^{13}C-NMR spectra were referenced to $CDCl_3$ (δ 77.16), DMSO-d_6 (δ 39.5), or the nitrile carbon of MeCN-d_3 (δ 118.3), respectively.^{19}F NMR spectra are run with C-F/C-H decoupling (δ –161.64 in $CDCl_3$). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m =multiplet, b = broad), coupling constant J (Hz) and integration.

N-bromocaprolactam (NBC) was prepared using the method published by Toste.(*39*) 2-tert-butylpyridine was prepared using a previously published procedure.(*44*)

SAFETY NOTE: Azides are potentially shock sensitive explosives, especially when concentrated. Appropriate precautions should be taken when working with azides. The procedures below also bear the potential to produce hydrazoic acid, a potent toxin and explosion hazard. The following reactions should be conducted exclusively in a well-ventilated fume hood, with reaction scales minimized as appropriate, and conducted behind a blast shield.

Supplemental experiments

Demonstration of oxidant dependent cyclization

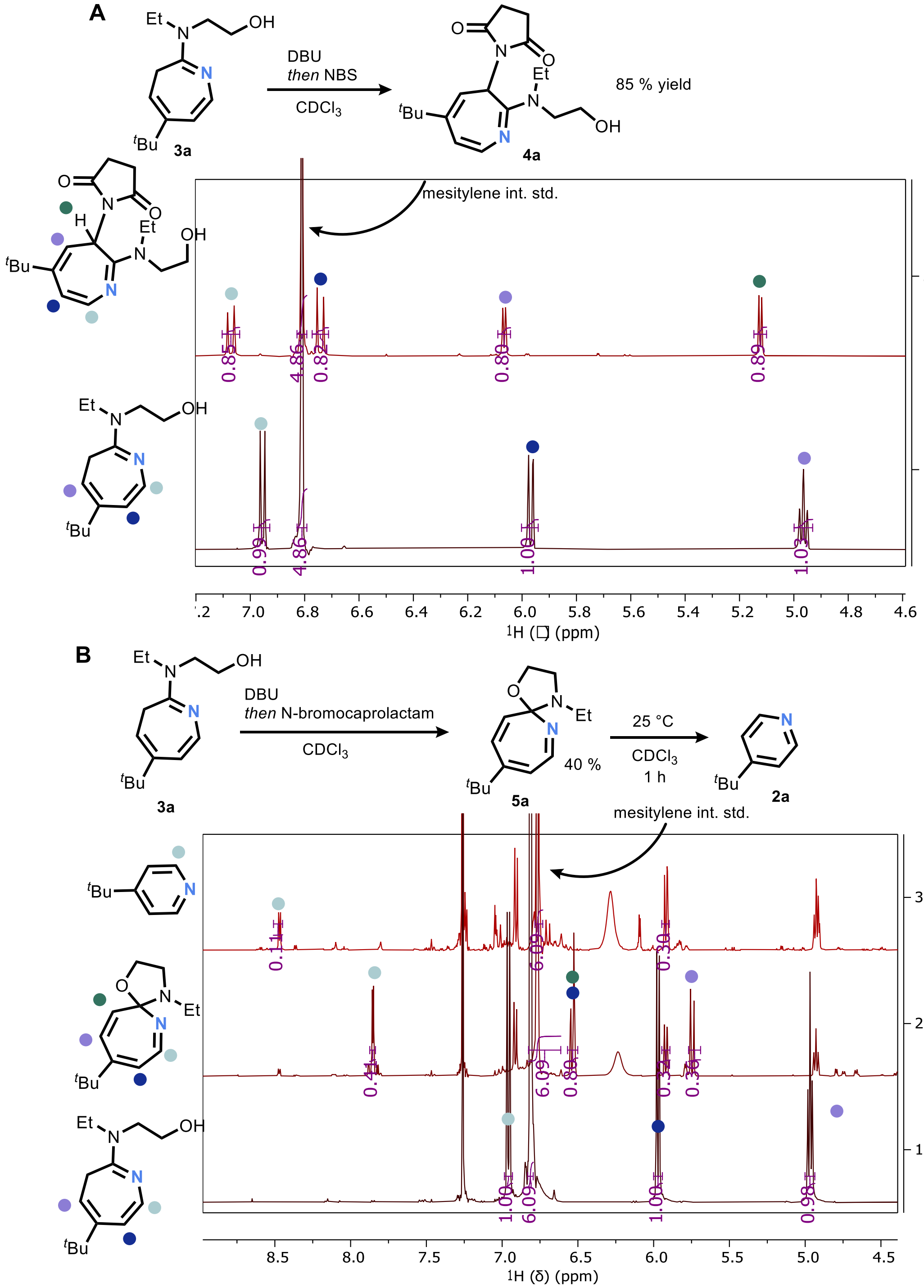


Figure S1: Demonstration of oxidant-dependent reactivity of (**3a**). **(A)** Upon exposure to DBU followed by NBS at room temperature in $CDCl_3$, **3a** cleanly generated **4a** in 86 % yield (see below for full characterization). **(B)** Upon exposure to 1.0 eq. N-bromocaprolactam under the same conditions, spirocyclic ketal **5a** formed with no evidence for formation of analogous caprolactam incorporation product to **4a**. 4-tert-butylpyridine (**2a**) was then formed upon heating at 40 °C for 1 hour with complete loss of **5a.**

NMR-based structural assignment of spirocyclic ketal 5a.

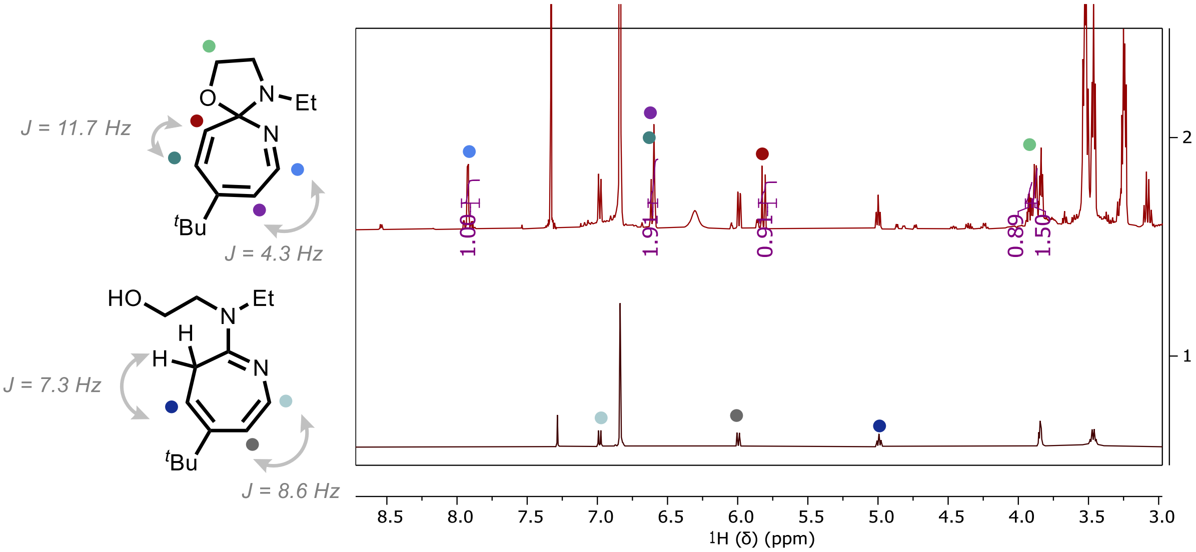
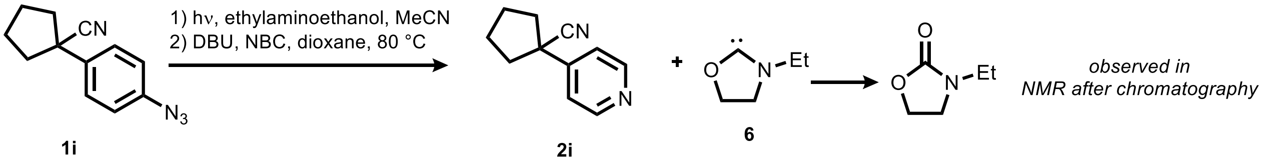


Figure S2. J coupling between the protons attached to C6 and C7 were dramatically reduced from 8.6 Hz in the starting material to 4.3 Hz suggesting a rearrangement of the double bond structure such that they no longer interact via a cis-olefin relationship. In accordance with the change in the double bond arrangement we observed much larger J couplings of 11.7 Hz between the protons of C6 and C7. Evidence for diastereotopicity in the methylene peaks of the ethylaminoethanol moiety (green) suggest the formation of a quaternary center, consistent with spirocyclization.

Identification of N-ethyloxazolidinone byproduct



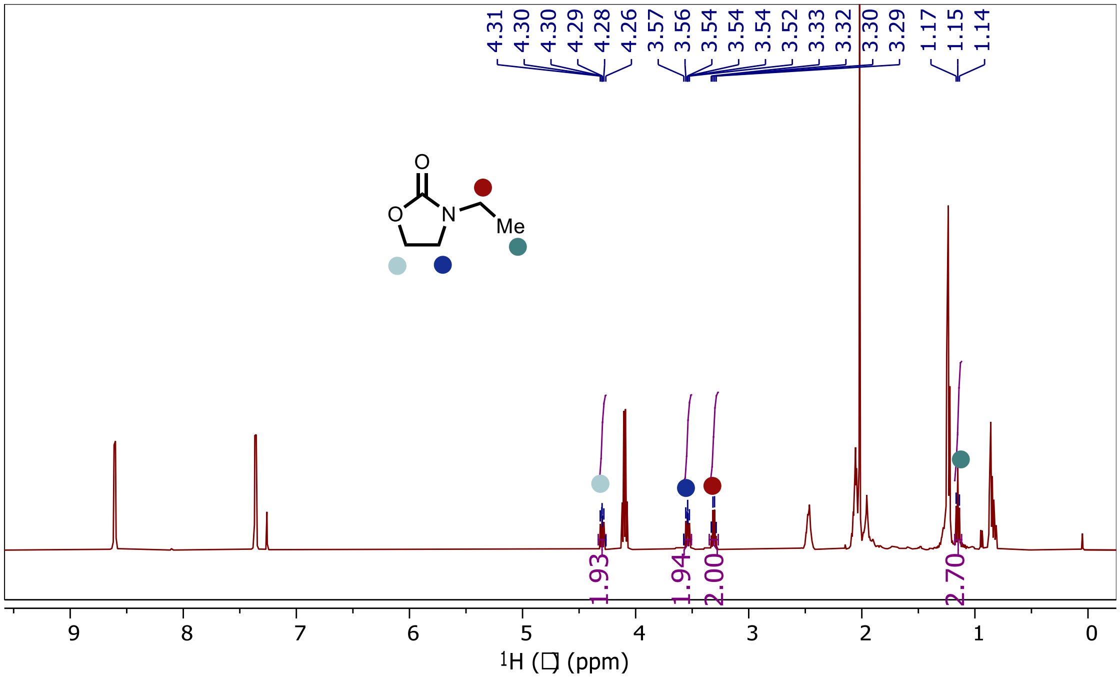


Figure S3: NMR spectrum of collected column fractions of 1-(pyridin-4-yl)cyclopentane-1-carbonitrile (**2i**) with contamination by N-ethyloxazolidinone resulting from oxidation of the extruded carbene **6.** Spectrum of N-ethyloxazolidinone matches that previously reported.(*45*)

Convergence of azepine isomers 3ra and 3rb to common product 2r

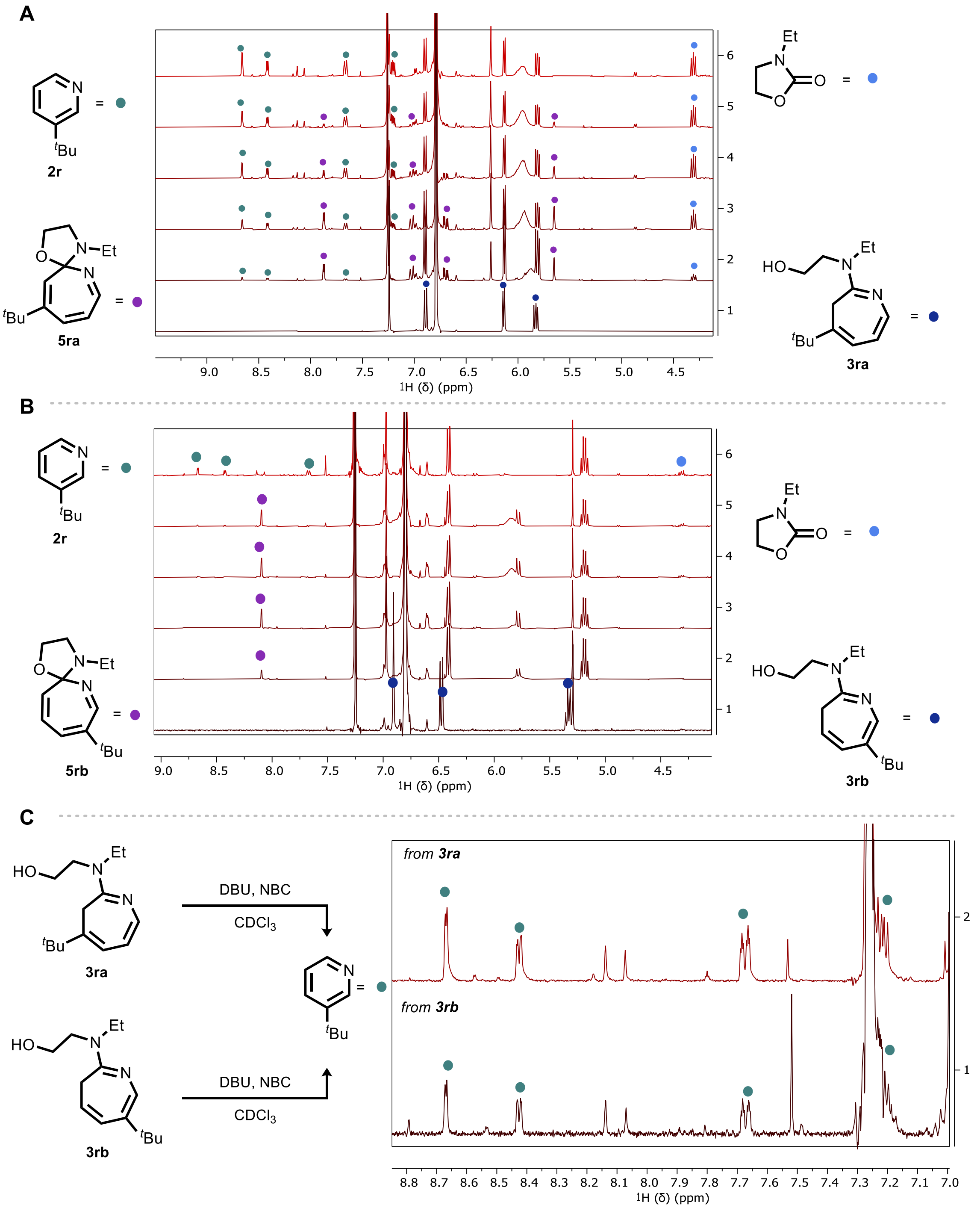


Figure S4: NMR scale experiments addressing separated **3ra** (A) and **3rb** (B) with NBC in the presence of DBU. Spectra show the growth and decay of the putative spirocyclic intermediates **5ra** and **5rb** ultimately giving way to product **2r** after overnight heating at 40 °C (top spectra in **A** and **B**). (C) Stacked spectra after heating both experiments from (A) and (B) at 40 °C overnight demonstrating convergence to common product **2r**.

Demonstration of importance of pendant donor in oxidation behavior.

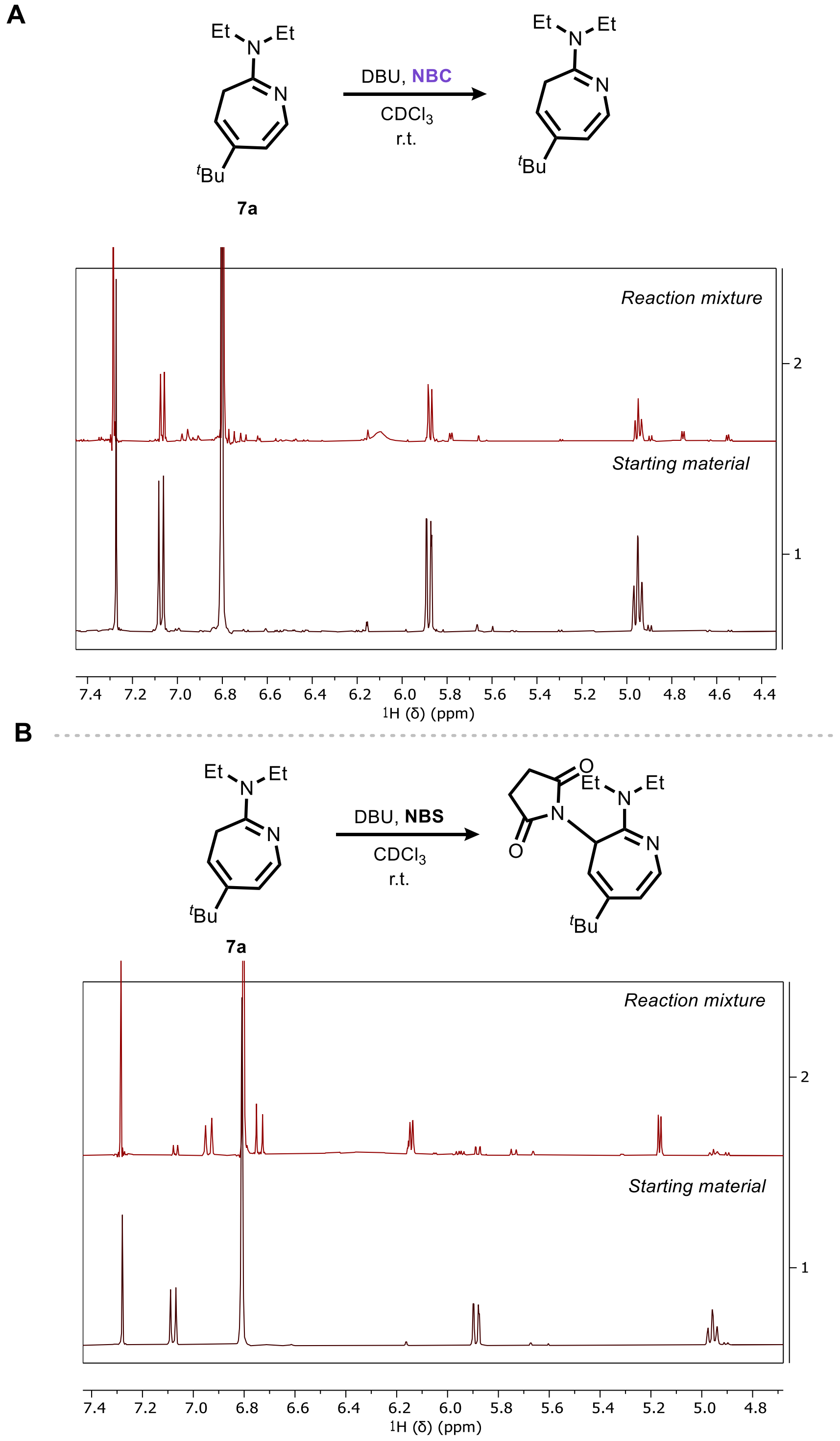
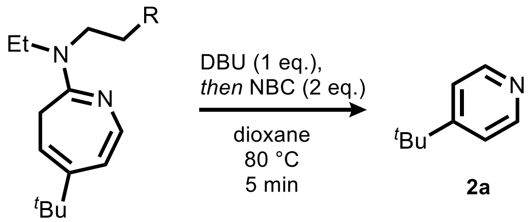


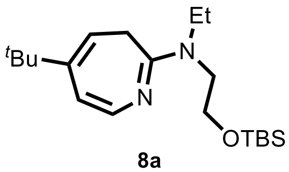
Figure S5: Effect of oxidant on azepine core in absence of pendant hydroxide donor. (A) the addition of DBU followed by N-bromocaprolactam results in no discernible new product formation. In contrast, treatment of **7a** with DBU followed by N-bromosuccinimide (B) results in efficient formation of a succinimide incorporation product analogous to **4a**.

Effect of silylation of pendant donor on pyridine formation

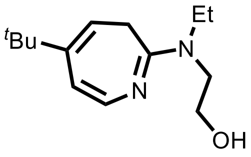
Reaction Conditions



Starting Material:



8a



3a

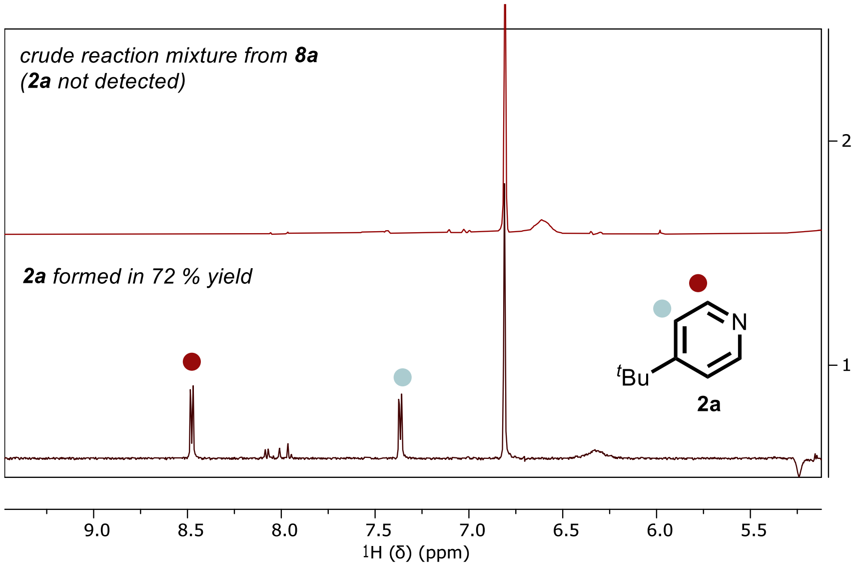


Figure S6: The addition of DBU followed by N-bromocaprolactam at 80 °C in dioxane resulted in the formation of **2a** in 72 % yield when starting from **3a**, but only resulted in nonspecific decomposition when starting from O-silylated azepine **8a**.

Demonstration of Cadogan Cyclization

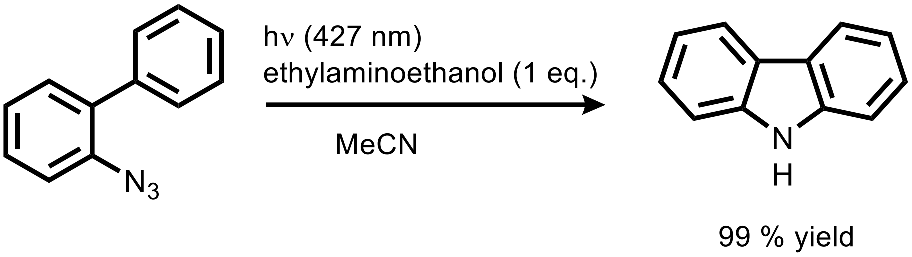
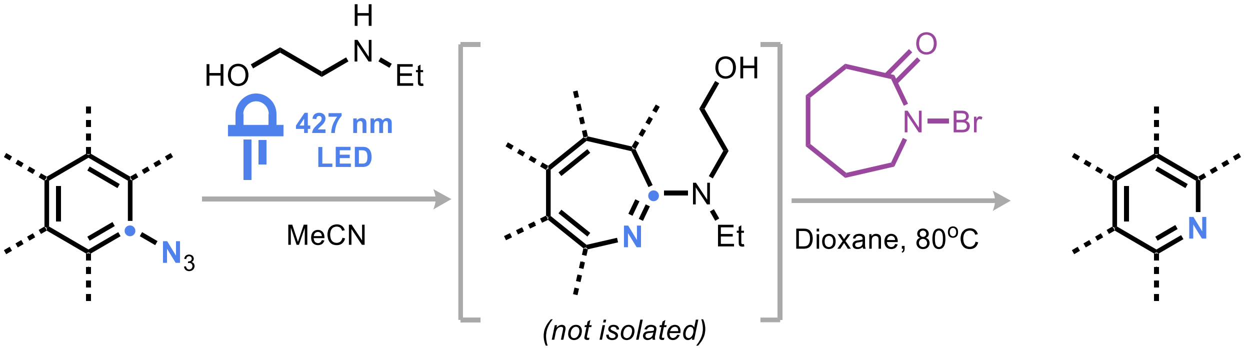


Figure S7: Cadogan type cyclization occurred in quantitative yield upon irradiation of 2-phenylazidobenzene in MeCN at 427 nm in the presence of ethylaminoethanol. Yield was determined by proton NMR against a mesitylene internal standard. Spectrum of 9H-carbazole matches that previously reported.(*46*)

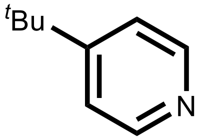
Synthetic Procedures

Synthesis of Pyridines



General Procedure: A 2 dram vial was charged with 0.3 mmol of aryl azide, 0.3 mmol ethylaminoethanol, 3 mL MeCN, and a stir bar. The vial was sealed under a septum cap under air and subjected to photolysis using a 427 nm LED lamp while cooling to room temperature with a fan. After TLC indicated consumption of starting material, the solvent was removed under a stream of nitrogen. The atmosphere was then replaced with dry N_2 and then 3 mL dry, degassed dioxane was added. Then, 1.0 eq. (0.3 mmol) DBU was added, and the reaction was warmed to 80 °C. Separately, a solution of 115 mg (0.6 mmol, 2 eq.) N-bromocaprolactam was prepared in 1 mL dioxane (Note: degassing of this latter solution was found experimentally not to significantly impact yields) and added dropwise to the reaction at 80 °C over the course of 2 minutes. The reaction was then concentrated under a stream of nitrogen and the residue purified by column chromatography on silica gel.

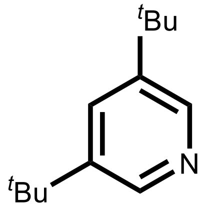
4-(tert-butyl) pyridine:



Synthesized according to the general procedure from 1-azido-4-(tert-butyl)benzene. The title compound was obtained in 57% yield (22.9 mg) as a pale-yellow oil after purification by silica gel chromatography.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.54 – 8.48 (m, 2H), 7.31 – 7.26 (m, 2H), 1.32 (s, 9H). Spectra match those previously reported.(*47*)

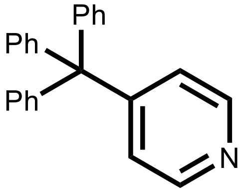
3,5-di-*tert*-butylpyridine



Synthesized from 1-azido-3,5-di-tert-butylbenzene with slight modification from the general procedure. After replacement of solvent with dioxane under N$_2$, 3.0 eq. (0.9 mmol) DBU was added, then, at room temperature, a solution of 1.0 eq. (0.3 mmol) N-bromocaprolactam in 1 mL dioxane added dropwise. The reaction was then warmed to 40 °C and stirred under nitrogen overnight. The reaction was then concentrated and subjected to silica gel chromatography to yield the title compound as a white crystalline powder in 46 % yield (26 mg).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.47 (d, *J* = 2.2 Hz, 2H), 7.64 (t, *J* = 2.3 Hz, 1H), 1.34 (s, 18H). Spectra match those previously reported.(*48*)

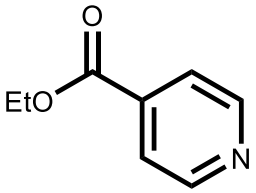
4-tritylpyridine:



Synthesized according to the general procedure with the modification that the photolysis was performed in toluene instead of acetonitrile from 1-azido-4-(trityl)benzene (108 mg, 0.3 mmol). The title compound was obtained in 53 % yield (37 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, C6D6) δ 8.48 – 8.42 (m, 2H), 7.21 – 7.17 (m, 6H), 7.06 – 6.94 (m, 11H). Spectra match those previously reported. (*49*)

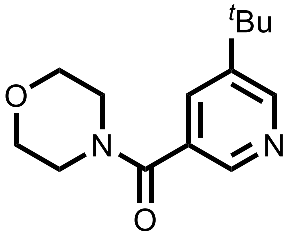
Ethyl isonicotinate



Synthesized following the general procedure from ethyl 4-azidobenzoate (57 mg, 0.3 mmol). The title compound was obtained as a yellow oil in 40 % yield (18 mg) after purification by silica gel chromatography.

^{1}H NMR: (400 MHz, CDCl$_3$) δ 8.78 (d, J = 5.1 Hz, 2H), 7.89 – 7.83 (m, 2H), 4.42 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H). Spectra match those previously reported.(*50*)

(5-(tert-butyl)pyridin-3-yl)(morpholino)methanone



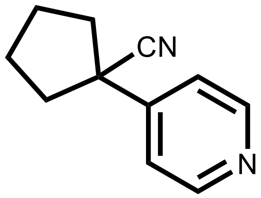
Synthesized following the general procedure from (3-azido-5-(tert-butyl)phenyl)(morpholino)methanone (60 mg, 0.2 mmol). The title compound was obtained as a pale-yellow oil in 25 % yield (12.5 mg) after purification by silica gel chromatography.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, *J* = 2.3 Hz, 1H), 8.46 (d, *J* = 1.9 Hz, 1H), 7.74 (t, *J* = 2.2 Hz, 1H), 3.88 – 3.75 (m, 4H), 3.65 (d, *J* = 11.5 Hz, 2H), 3.46 (s, 2H), 1.36 (s, 9H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.47, 149.07, 146.44, 144.99, 132.28, 130.48, 66.95, 48.42, 42.76, 33.93, 31.02. Rotomeric broadening leads to inequivalence of the α methylenes of the morpholine, which show weak, inequivalent resonances at 48.42 ppm and 42.76 ppm.

HRMS (ESI-TOF) calcd 245.1598 for $C_{14}H_{21}N_2O_2^+$ [M+H]$^+$, found 245.1599.

1-(pyridin-4-yl)cyclopentane-1-carbonitrile



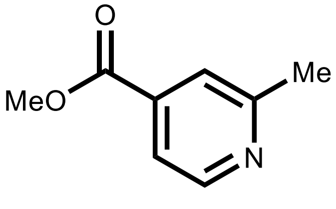
Synthesized according to the general procedure from 1-(4-azidophenyl)cyclopentane-1-carbonitrile (100 mg, 0.47 mmol). The title compound was obtained in 40% yield (32.5 mg) as an off-white solid after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.47 (m, 2H), 7.51 – 7.30 (m, 2H), 2.60 – 2.38 (m, 2H), 2.22 – 1.88 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.6, 149.0, 123.2, 121.1, 47.6, 40.6, 24.7.

HRMS (ESI-TOF) calcd 173.1073 for $C_{11}H_{13}N_2^+$ [M+H]$^+$, found 173.1073.

Methyl-2-methylisonicotinate



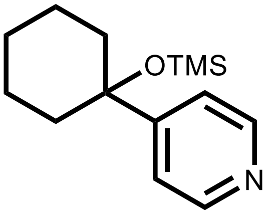
Synthesized according to the general procedure from methyl 4-azido-3-methylbenzoate (57 mg, 0.3 mmol). The title compound was isolated in 25 % yield (11.5 mg) as a pale-yellow oil after purification by silica gel chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 5.3, 1.7 Hz, 1H), 7.69 (s, 1H), 7.61 (d, *J* = 4.9 Hz, 1H), 3.94 – 3.90 (s, 3H), 2.61 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.01, 159.71, 150.04, 137.75, 122.64, 120.06, 52.76, 24.58.

HRMS (ESI-TOF) calcd 152.0706 for $C_8H_{10}NO_2^+$ [M+H]$^+$, found 152.0706.
Spectra match those previously reported.(*51*)

4-(1-((trimethylsilyl)oxy)cyclohexyl)pyridine



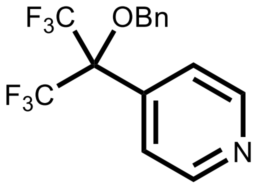
Synthesized according to the general procedure from 86.8 mg (0.3 mmol) of ((1-(4-azidophenyl)cyclohexyl)oxy)trimethylsilane. The title compound was isolated in 39 % yield (28.8 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.8 Hz, 2H), 7.38 – 7.32 (m, 2H), 1.94 – 1.86 (m, 2H), 1.84 – 1.61 (m, 5H), 1.56 (dq, *J* = 12.7, 3.9 Hz, 2H), 1.32 – 1.16 (m, 1H), -0.06 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.15, 149.75, 120.92, 75.37, 38.79, 25.64, 22.27, 2.35.

HRMS: (ESI-TOF) calcd 250.1622 for $C_{14}H_{24}NOSi$ $[M+H]^+$, Found: 250.1634

4-(2-(benzyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)pyridine



Synthesized according to the general procedure from 1-azido-4-(2-benzyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)benzene (112 mg, 0.3 mmol). The title compound was obtained in 30 % yield (30 mg) as a pale-yellow oil after purification by silica gel chromatography.

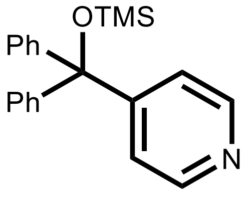
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 – 8.74 (m, 2H), 7.54 (d, *J* = 5.3 Hz, 2H), 7.47 – 7.33 (m, 5H), 4.67 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.73, 137.56, 135.72, 128.90, 128.63, 127.36, 122.70, 122.15 (d, *J* = 290.9 Hz), 83.03 – 81.64 (central doublet observed, *J* = 28.7 Hz), 68.86.

^{19}F NMR: (376 MHz, $CDCl_3$) δ -70.49.

HRMS (ESI-TOF) calcd 336.0818 for $C_{15}H_{12}F_6NO^+$ $[M+H]^+$, found 336.0820

4-(diphenyl((trimethylsilyl)oxy)methyl)pyridine



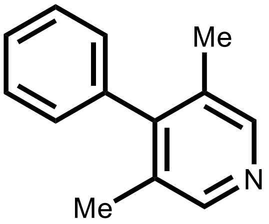
Synthesized from 113 mg ((4-azidophenyl)diphenylmethoxy) trimethylsilane (0.3 mmol) following the general procedure. Product was obtained as a pale-yellow oil in 47 % yield (47.1 mg) after purification via column chromatography on silica gel.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.49 (m, 2H), 7.46 – 7.40 (m, 2H), 7.39 – 7.34 (m, 4H), 7.34 – 7.27 (m, 6H), -0.14 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.03, 149.30, 145.31, 128.82, 128.09, 127.77, 122.61, 83.94, 1.77.

HRMS (ESI-TOF) calcd for $C_{21}H_{24}NOSi^+$ $[M+H]^+$ 334.1622, found 334.1635

3,5-dimethyl-4-phenylpyridine



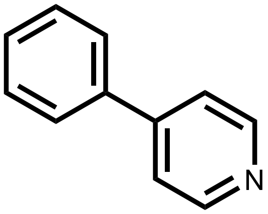
Synthesized from 4-azido-2,6-dimethyl-1,1'-biphenyl (67 mg, 0.3 mmol) according to the general procedure. Product was obtained in 41 % yield (22.8 mg) as a pale-yellow powder after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 2H), 7.50 – 7.42 (m, 2H), 7.42 – 7.34 (m, 1H), 7.15 – 7.08 (m, 2H), 2.03 (d, *J* = 0.8 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.47, 148.54, 138.26, 130.96, 128.85, 128.15, 127.65, 17.43.

HRMS (ESI-TOF) calcd 184.1121 for $C_{13}H_{14}N^+$ [M+H]$^+$, found 184.1123
Spectra match those previously reported.(*52*)

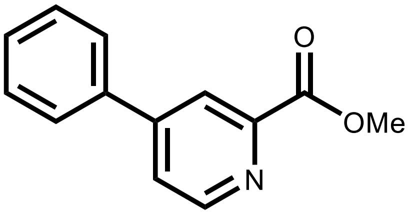
4-phenylpyridine



Synthesized according to a modified procedure from 4-azido-1,1'-biphenyl (59 mg, 0.3 mmol). After concentration of the crude photolysate, DBU (81 μL, 0.9 mmol, 3 eq.) and dioxane (3 mL) were added under nitrogen. Then, at room temperature, NBC (69 mg, 0.36 mmol, 1.2 eq.) was added dropwise in 1 mL dioxane. The reaction was then stirred at room temperature for 1 hour and then raised to 40 °C overnight. The next day, the reaction was concentrated and the residue purified by column chromatography to yield the title compound as a colorless solid in 27 % yield (13 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.63 (m, 2H), 7.68 – 7.60 (m, 2H), 7.55 – 7.38 (m, 5H). Spectra match those previously reported.(*53*)

Methyl 4-phenylpicolinate



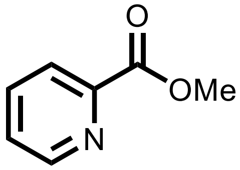
Synthesized according to a slight modification the general procedure from methyl 4-azido-[1,1'-biphenyl]-3-carboxylate (76 mg, 0.3 mmol). N-bromocaprolactam was added using a syringe pump over the course of 30 minutes instead of dropwise over the course of five minutes as in the general procedure. The title compound was isolated as a pale-yellow oil in 60 % yield (38.5 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 5.0, 0.8 Hz, 1H), 8.39 (dd, *J* = 1.9, 0.8 Hz, 1H), 7.70 (dt, *J* = 6.7, 1.4 Hz, 3H), 7.56 – 7.41 (m, 3H), 4.04 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.99, 150.44, 149.90, 148.58, 137.26, 129.77, 129.43, 127.22, 124.82, 123.26, 53.15.

HRMS (ESI-TOF): calcd 214.0863 for $C_{13}H_{12}NO_2^+$ [M+H]$^+$, found 214.0865
Spectra match those previously reported. (*54*)

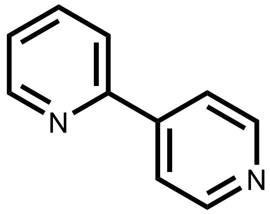
methyl picolinate



Synthesized from methyl 2-azidobenzoate (53 mg, 0.3 mmol) according to the general procedure. Yield was assessed to be 20 % *via* ^{1}H NMR against a mesitylene internal standard.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (ddt, *J* = 4.5, 1.7, 0.9 Hz, 1H), 8.15 – 8.10 (m, 1H), 7.84 (tt, *J* = 7.7, 1.6 Hz, 1H), 7.48 (ddt, *J* = 7.5, 4.7, 1.3 Hz, 1H), 4.00 (d, *J* = 1.7 Hz, 3H). Spectra match those previously reported.(*55*)

2,4'-bipyridine



Synthesized according to a slight modification to the general procedure from 2-(4-azidophenyl)pyridine (58.9 mg, 0.3 mmol). 1.4 equivalents (80 mg) of N-bromocaprolactam was used instead of two equivalents as in the general procedure. The title compound was isolated as a red-orange oil in 29 % yield (13.7 mg) after purification by column chromatography.

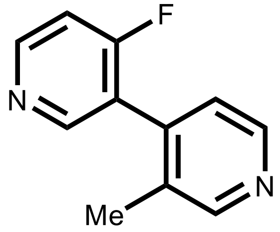
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (dt, *J* = 4.8, 1.4 Hz, 1H), 8.73 – 8.71 (m, 2H), 7.92 – 7.85 (m, 2H), 7.85 – 7.76 (m, 2H), 7.33 (ddd, *J* = 6.2, 4.7, 2.3 Hz, 1H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.79, 150.57, 150.26, 146.52, 137.20, 123.92, 121.20, 121.01.

HRMS (ESI-TOF): calcd 157.0760 for $C_{10}H_9N_2^+$ $[M+H]^+$, found 157.0762.

Spectra match those previously reported.(*56*)

4-fluoro-3'-methyl-3,4'-bipyridine



Synthesized according to the general procedure from 3-(4-azido-2-methylphenyl)-4-fluoropyridine (68.5 mg, 0.3 mmol). The title compound was isolated in 30 % yield (17 mg) as a yellow solid after purification by silica gel chromatography.

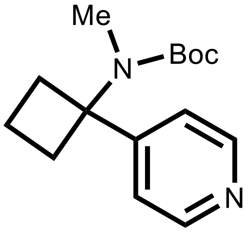
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.52 (d, *J* = 5.0 Hz, 1H), 8.21 (d, *J* = 2.4 Hz, 1H), 7.77 (ddd, *J* = 9.9, 5.9, 1.8 Hz, 1H), 7.14 (d, *J* = 4.9 Hz, 1H), 7.05 (dd, *J* = 8.4, 3.0 Hz, 1H), 2.28 (s, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.43 (d, *J* = 241.0 Hz), 151.77, 147.89, 147.36 (d, *J* = 14.9 Hz), 144.55, 141.36 (d, *J* = 8.1 Hz), 132.79 (d, *J* = 4.8 Hz), 130.93, 124.06, 109.61 (d, *J* = 37.6 Hz), 17.26.

^{19}F NMR (471 MHz, $CDCl_3$) δ -68.28.

HRMS (ESI-TOF) calcd 189.0823 for $C_{11}H_{10}FN_2^+$ $[M+H]^+$, found 189.0827.

tert-butyl methyl(1-(pyridin-4-yl)cyclobutyl)carbamate:



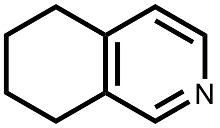
Synthesized according to general procedure A from tert-butyl (1-(4-azidophenyl)cyclobutyl)(methyl)carbamate (96 mg, 0.317 mmol). The title compound was obtained in 55% yield (46 mg) as a pale yellow solid after purification by silica gel chromatography.

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.68 – 8.46 (m, 2H), 7.55 – 7.34 (m, 2H), 2.77 (s, 3H), 2.58 (qd, *J* = 9.8, 2.7 Hz, 2H), 2.44 (ddq, *J* = 10.6, 8.4, 2.5 Hz, 2H), 1.86 – 1.61 (m, 2H), 1.29 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, DMSO-*d*$_6$) δ 154.0, 153.6, 149.7, 120.5, 78.9, 62.0, 33.8, 30.9, 28.0, 13.8.

HRMS (ESI-TOF) calcd 263.1754 for $C_{15}H_{23}N_2O_2^+$ [M+H]$^+$, found 263.1754.

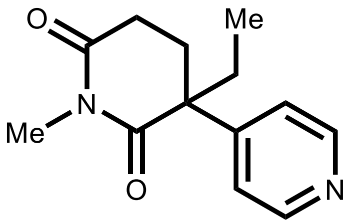
5,6,7,8-tetrahydroisoquinoline



Synthesized according to a modification to the general procedure from 6-azido-1,2,3,4-tetrahydronaphthalene (52 mg, 0.3 mmol). The photolysis proceeded as in the general procedure. The addition of N-bromocaprolactam was performed in two steps, in a departure from the general procedure. First, 1 equivalent of N-bromocaprolactam in 1 mL dioxane was added to 3 mL of a dioxane solution of the crude photolysate and DBU (45 µL) at 50 °C using a syringe pump over the course of one hour. Thereafter NMR analysis showed the persistence of azepine. One more equivalent of DBU (45 µL) was then added to the photolysate solution followed by 1 equivalent more of N-bromocaprolactam at 50 °C over the course of 40 minutes using a syringe pump. The reaction was then concentrated and the residue purified by silica gel chromatography. The title compound was obtained as a colorless oil in 25 % yield (10 mg).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28 (s, 1H), 8.25 (d, *J* = 5.0 Hz, 1H), 6.96 (d, *J* = 5.1 Hz, 1H), 2.82 – 2.69 (m, 4H), 1.81 (p, *J* = 3.3 Hz, 4H). Spectra match those previously reported.(*57*)

3-ethyl-1-methyl-3-(pyridin-4-yl)piperidine-2,6-dione:



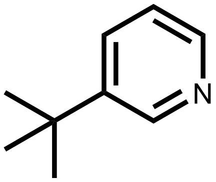
Synthesized according to the general procedure from 3-(4-azidophenyl)-3-ethyl-1-methylpiperidine-2,6-dione (66 mg, 0.24 mmol). The title compound was obtained in 38% yield (21.5 mg) as a colorless liquid after purification by silica gel chromatography.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.64 – 8.52 (m, 2H), 7.18 – 7.00 (m, 2H), 3.20 (s, 3H), 2.70 (ddd, *J* = 17.2, 4.4, 2.7 Hz, 1H), 2.50 – 2.15 (m, 3H), 2.07 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.89 (dq, *J* = 14.6, 7.4 Hz, 1H), 0.85 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 174.3, 171.8, 150.7, 149.0, 121.6, 51.5, 33.5, 29.7, 27.3, 25.5, 9.1.

HRMS (ESI-TOF) calcd 233.1284 for $C_{13}H_{17}N_2O_2^+$ [M+H]$^+$, found 233.1284.

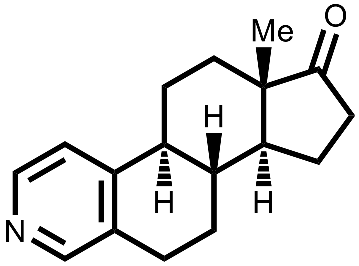
3-(tert-butyl)-pyridine



Synthesized according to the general procedure from 1-azido-3-(tert-butyl)benzene (52.5 mg, 0.3 mmol). The title compound was obtained as a yellow oil in 32 % yield (12.9 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 – 8.65 (m, 1H), 8.43 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.69 (ddd, *J* = 8.1, 2.6, 1.6 Hz, 1H), 7.23 (ddd, *J* = 8.0, 4.8, 0.8 Hz, 1H), 1.35 (s, 9H). Spectra match those previously reported.(*58*)

(4bS,6aS,9aS,9bR)-6a-methyl-4b,5,6,6a,8,9,9a,9b,10,11-decahydro-7H-indeno[5,4-f] isoquinolin-7-one



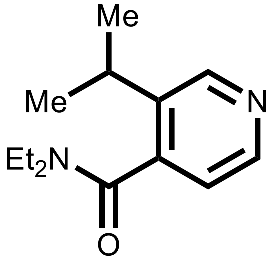
Synthesized according to a variation to the general procedure from (8R,9S,13S,14S)-3-azido-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (40 mg, 0.14 mmol). After photolysis and dissolution in dioxane following the general procedure, the crude material was treated with DBU (22 µL, 0.14 mmol, 1 eq.) and was then heated to 50 °C. Then, N-bromocaprolactam (28 mg, 0.14 mmol, 1 eq.) was added in 1 mL dioxane. The reaction was then concentrated under a stream of nitrogen and the residue passed through a plug of silica eluting with ethyl acetate. Further purification via preparative TLC on silica yielded the title compound in 20 % yield (6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.31 (m, 2H), 7.16 (d, *J* = 5.2 Hz, 1H), 3.00 – 2.80 (m, 2H), 2.59 – 2.48 (m, 1H), 2.43 – 2.37 (m, 1H), 2.29 (td, *J* = 10.7, 4.4 Hz, 1H), 2.22 – 2.04 (m, 3H), 2.02 – 1.95 (m, 1H), 1.72 – 1.38 (m, 6H), 0.92 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 220.42, 150.49, 148.46, 147.25, 132.07, 120.25, 50.59, 48.07, 44.16, 37.68, 35.90, 31.59, 26.33, 26.10, 25.06, 21.67, 13.97.

HRMS: (ESI-TOF) calc'd 256.1696 for $C_{17}H_{22}NO^+$ $[M+H]^+$, found 256.1696.

N,N-diethyl-3-isopropylisonicotinamide



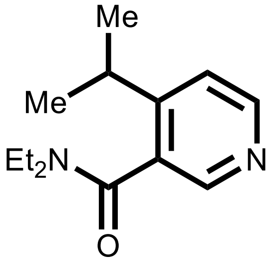
Synthesized according to the general procedure from 4-azido-*N,N*-diethyl-2-isopropylbenzamide (56.2 mg, 0.21 mmol). The title compound was isolated as a pale-yellow oil in 41 % yield (19 mg) after purification by silica gel chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.3 Hz, 1H), 8.36 (s, 1H), 7.25 (d, *J* = 5.3 Hz, 1H), 3.75 (s, 1H), 3.41 (s, 1H), 3.17 – 3.06 (m, 2H), 2.96 (hept, *J* = 7.1 Hz, 1H), 1.32 – 1.18 (m, 9H), 1.07 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 168.31, 154.37, 150.16, 146.35, 132.36, 121.06, 43.15, 39.02, 30.53, 23.77, 22.62, 14.13, 12.87. Inequivalency of the isopropyl carbons was observed as a result of hindered rotation.

HRMS: calcd 221.1648 for $C_{13}H_{21}N_2O^+$ $[M+H]^+$, found 221.1648.

N,N-diethyl-4-isopropylnicotinamide



Synthesized according to the general procedure from 5-azido-*N,N*-diethyl-2-isopropylbenzamide (78.1 mg, 0.3 mmol). The title compound was isolated as a yellow oil in 22 % yield after purification by silica gel chromatography.

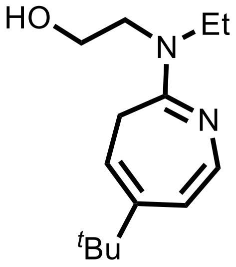
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.46 (d, *J* = 4.9 Hz, 1H), 7.03 (dd, *J* = 4.9, 0.7 Hz, 1H), 3.86 – 3.69 (m, 1H), 3.45 – 3.35 (m, 1H), 3.10 (p, *J* = 7.3 Hz, 2H), 2.93 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 6H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.39, 148.90, 147.45, 143.48, 139.43, 119.77, 42.91, 38.80, 29.53, 24.36, 23.00, 14.04, 12.84. Inequivalency of the isopropyl carbons was observed as a result of hindered rotation.

HRMS: calcd 221.1648 for $C_{13}H_{21}N_2O^+$ $[M+H]^+$, found 221.1648.

Synthesis of compounds for control experiments

2-((5-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol



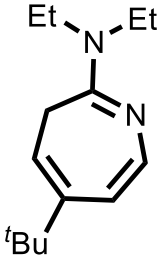
Under air, a 20 mL septum-capped vial was charged with 1-azido-4-(tert-butyl)benzene (175 mg, 1 mmol) and 10 mL acetonitrile. A stirbar was then added and the reaction sealed with a septum cap. Then, ethylaminoethanol (93 µL, 89 mg, 1 mmol), was introduced through the septum cap via microsyringe. The resulting solution was then subjected to photolysis using a 427 nm Kessil lamp using a fan to cool the reaction to room temperature. Photolysis proceeded overnight at which point TLC analysis indicated the complete consumption of the starting material. The reaction was then concentrated under reduced pressure. The title compound was thus isolated without further purification as a red-brown oil in 90 % yield (212 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.5 Hz, 1H), 5.95 (dd, *J* = 8.6, 1.3 Hz, 1H), 4.95 (td, *J* = 7.3, 1.5 Hz, 1H), 3.80 (t, *J* = 4.6 Hz, 2H), 3.47 (m, 4H), 3.43 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 9H). The O-H proton was not observed. The methylene peak of the azepine skeleton (3.47 ppm in this system) is fluxional thus appears with significant broadening. In analogous systems its fluxionality may preclude its observation altogether.(*23*)

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.94, 150.29, 138.97, 112.22, 107.16, 63.91, 53.74, 45.02, 34.62, 30.55, 30.29, 14.02.

HRMS: (ESI-TOF) calcd 237.1961 for $C_{14}H_{25}N_2O^+$ [M+H]$^+$, found 237.1962

5-(tert-butyl)-N,N-diethyl-3H-azepin-2-amine



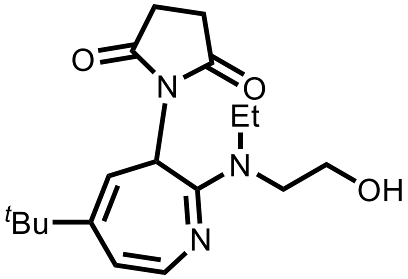
A 20 mL septum-capped vial was charged with 1-azido-4-(tert-butyl)benzene (175 mg, 1 mmol) and 10 mL dry acetonitrile. A stirbar was then added and the reaction sealed with a septum cap. Then, diethylamine (103 µL, 73 mg, 1 mmol) was added through the septum cap via microsyringe. The resulting solution was then subjected to photolysis using a 427 nm Kessil lamp using a fan to cool the reaction to room temperature. Photolysis proceeded overnight at which point TLC analysis indicated the completion of the reaction. The reaction was then concentrated under reduced pressure. The title compound was thus isolated without further purification as a red-brown oil in quantitative yield (221 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.4 Hz, 1H), 5.88 (dd, *J* = 8.4, 1.4 Hz, 1H), 4.94 (td, *J* = 7.2, 1.4 Hz, 1H), 3.36 (bs, 4H), 1.16 – 1.11 (m, 6H), 1.10 (s, 9H). The methylene peak of the azepine skeleton is fluxional thus appears with significant broadening. In this system its fluxionality precludes its observation.(*23*)

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.99, 148.12, 140.58, 110.38, 106.03, 43.20, 34.53, 30.79, 30.38, 13.78.

HRMS: (ESI-TOF) calcd 221.2012 for $C_{14}H_{25}N_2^+$ [M+H]$^+$, found 221.2012.

1-(5-(tert-butyl)-2-(ethyl(2-hydroxyethyl)amino)-3H-azepin-3-yl)pyrrolidine-2,5-dione



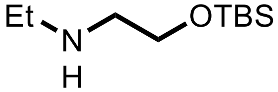
Under air, a 20 mL scintillation vial was charged with 2-((5-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol (118 mg, 0.5 mmol) and 5 mL dichloromethane. Then, DBU (75 µL, 0.5 mmol) was added, followed by N-bromosuccinimide as a solid (89 mg, 0.5 mmol). The reaction was then allowed to stir for ten minutes, at which point it was concentrated under reduced pressure. The crude residue was confirmed to have no starting material remaining by NMR spectroscopy. The resulting residue was partitioned between dichloromethane and water and the dichloromethane portion was washed three times with water, twice with 2 M NaOH solution, washed once more with water, and then washed with brine before being dried over $MgSO_4$. The resulting solution was then concentrated under reduced pressure to yield the title compound as a gray solid in 82 % yield (136 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.06 (dt, *J* = 12.1, 1.0 Hz, 1H), 6.72 (dd, *J* = 12.2, 0.6 Hz, 1H), 6.19 (s, 1H), 6.05 (dt, *J* = 5.3, 0.9 Hz, 1H), 5.12 (dd, *J* = 5.2, 0.8 Hz, 1H), 3.78 – 3.62 (m, 3H), 3.32 (dq, *J* = 14.2, 7.0 Hz, 1H), 3.24 – 3.05 (m, 2H), 2.83 – 2.67 (m, 4H), 1.13 (t, *J* = 7.1 Hz, 3H), 1.10 (s, 9H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 177.05, 158.76, 146.81, 140.30, 126.93, 126.09, 63.73, 63.36, 52.40, 46.73, 34.75, 29.59, 28.38, 14.37.

HRMS: (ESI-TOF) calcd 334.2125 for $C_{18}H_{28}N_2O^+$ $[M+H]^+$, found 334.2128

2-((tert-butyldimethylsilyl)oxy)-N-ethylethan-1-amine



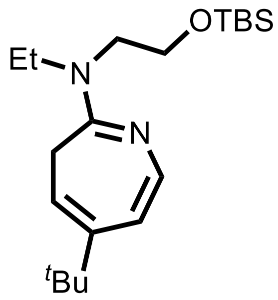
A 20 mL vial was charged with 2-(ethylamino)ethan-1-ol (445.7 mg, 5 mmol), tert-butylchlorodimethylsilane (753.6 mg, 5 mmol), triethylamine (506.0 mg, 5 mmol), 7.5 mL dicholoromethane, and a stir bar. The mixture was stirred at room temperature overnight under N_2. The mixture was concentrated and dissolved in diethyl ether. The precipitates were removed by filtration. The precipitation and filtration sequence were repeated 3 additional times to yield the title compound as a pale-yellow liquid in 83% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.72 (t, *J* = 5.4 Hz, 2H), 2.71 (t, *J* = 5.4 Hz, 2H), 2.66 (q, *J* = 7.1 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 62.54, 51.78, 44.07, 26.09, 18.48, 15.50, -5.17.

HRMS: (ESI-TOF) calcd 204.1778 for $C_{10}H_{26}NOSi^+$ $[M+H]^+$, found 204.1776

5-(tert-butyl)-N-(2-((tert-butyldimethylsilyl)oxy)ethyl)-N-ethyl-3H-azepin-2-amine



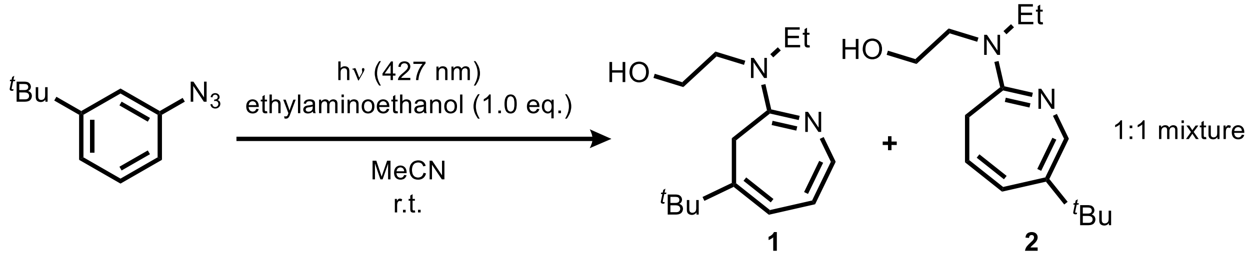
A 2 dram vial was charged with 1-azido-4-(tert-butyl)benzene (53 mg, 0.3 mmol), 2-((tert-butyldimethylsilyl)oxy)-N-ethylethan-1-amine (61 mg, 0.3 mmol), 3 mL MeCN, and a stir bar. The vial was sealed under a septum cap under air and subjected to photolysis using a 427 nm LED lamp while cooling to room temperature with a fan. After TLC indicated consumption of starting material, the solvent was removed under reduced pressure. The title compound was isolated in 74% yield (77.9 mg) as a yellow oil after purification of this residue by silica gel chromatography (0-40% ethyl acetate in hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.4 Hz, 1H), 5.88 (dd, *J* = 8.4, 1.4 Hz, 1H), 5.00 – 4.91 (m, 1H), 3.70 (t, *J* = 5.8 Hz, 2H), 3.53 – 3.35 (m, 4H), 1.18 – 1.07 (m, 12H), 0.87 (s, 9H), 0.02 (s, 6H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.78, 148.38, 140.38, 110.45, 105.99, 61.63, 50.73, 44.81, 34.41, 30.61, 30.19, 25.92, 18.26, -5.34.The carbon of the terminal methyl group of the ethyl moiety of the ethylaminoethanol was not observed (*59*) and the methylene to which it is immediately bound is substantially broadened (observed at 44.81 ppm). This carbon also appears broad in some analogous systems (for example, see spectra for 2-((4-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol). Such broadening precludes its observation here.

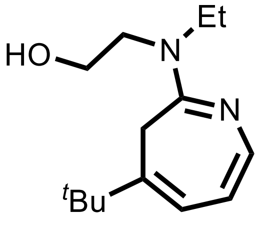
HRMS (ESI-TOF) calcd 351.2826 for $C_{20}H_{39}N_2OSi^+$ $[M+H]^+$, found 351.2825

2-((4-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol and 2-((6-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol



A 20 mL septum-capped vial was charged with 3-tert-butyl-1-azidobenzene (170 mg, 0.97 mmol), 10 mL dry acetonitrile, and a magnetic stir bar. Then, ethylaminoethanol (90 µL, 0.97 mmol) was added via microsyringe. The resulting solution was then subjected to photolysis using a 427 nm Kessil lamp using a fan to cool the reaction to room temperature. Photolysis proceeded overnight at which point TLC analysis indicated the completion of the reaction. The solvent was then removed under reduced pressure. Isomers **1** and **2** were thus isolated in a 1:1 ratio in 78 % yield. The isomers were able to be separated on a silica column using a 0-10 % gradient of methanol in dichloromethane.

2-((4-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol



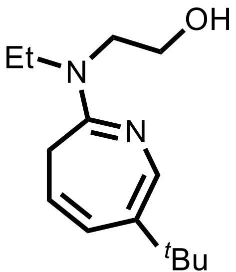
1

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (d, *J* = 8.2 Hz, 1H), 6.14 (d, *J* = 6.0 Hz, 1H), 5.83 (dd, *J* = 8.2, 6.0 Hz, 1H), 3.81 (t, *J* = 4.7 Hz, 2H), 3.70 – 3.41 (m, 4H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.13 (s, 9H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.85, 138.11, 137.11, 120.35, 113.39, 63.37, 54.90, 45.46, 36.26, 31.23, 29.40, 16.03.

HRMS: (ESI-TOF) calcd 237.1961 for $C_{14}H_{25}N_2O^+$ $[M+H]^+$, found 237.1963

2-((6-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol



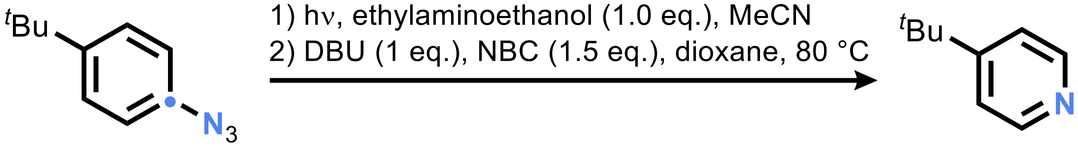
2

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.42 (d, *J* = 9.1 Hz, 1H), 5.26 – 5.18 (m, 1H), 3.81 (dq, *J* = 4.6, 2.5 Hz, 2H), 3.49 – 3.40 (m, 5H), 2.67 (bs, 1H), 1.21 (t, *J* = 7.0 Hz. 3H), 1.15 (s, 9H).

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 148.76, 134.28, 132.27, 129.16, 114.30, 63.34, 53.58, 45.02, 34.52, 30.86, 30.60, 13.83.

HRMS: (ESI-TOF) calcd 237.1961 for $C_{14}H_{25}N_2O^+$ $[M+H]^+$, found 237.1960.

Optimization of Pyridine Synthesis

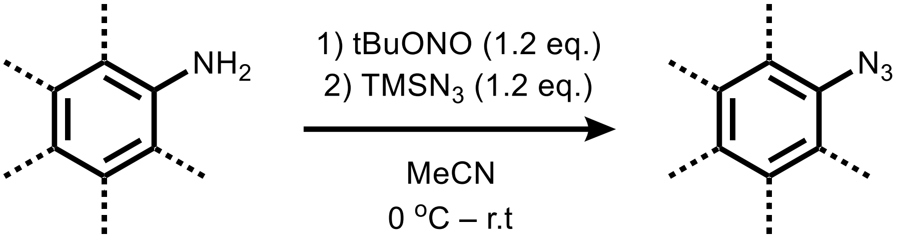


Deviation from above	**Yield from azide (NMR)**
None	58 %
THF as solvent	20 %
MeCN as solvent	18 %
DABCO as base	< 5 %
K_2CO_3 as base	n.d.
Tetramethylguanidine as base	20 %
Diphenylguanidine as base	5 %
60 °C addition temperature	52 %
100 °C addition temperature	23 %
1 eq. N-bromocaprolactam	38 %
2 eq. N-bromocaprolactam	**63 %**

Standard procedure for screening:
1 mmol of 4-azido-tert-butylbenzene and 1 mmol ethylaminoethanol in 10 mL dry MeCN was photolysed at 427 nm using an LED lamp while cooling to room temperature with a fan until TLC analysis indicated the complete consumption of starting material. The reaction was then concentrated under a stream of nitrogen and subsequently kept under nitrogen. The crude photolysate was then taken up in dry dioxane and transferred to a 10 mL volumetric flask. Then, 1 mL portions (each containing 10 % of the crude photolysate) were distributed among separate oven-dried 2-dram reaction vials equipped with septum caps. In the cases of solvent screening, the crude photolysate was first dissolved in DCM instead of dioxane and was apportioned into reaction vials the same way. Then, the DCM was removed under a stream of nitrogen and replaced with the alternate solvent. Subsequently, the solutions of photolysate were heated to 80 °C and the base was added (in cases where a solid base was used, the base was loaded into the 2-dram reaction vial prior to introduction of the substrate). Separately, a solution of 0.15 mmol NBC was prepared in 0.5 mL dioxane (or alternate solvent in the case of solvent screening). This was then introduced to the reaction under nitrogen dropwise via syringe. After addition, the reaction was allowed to cool to room temperature and thereafter analyzed by ^{1}H NMR against a mesitylene internal standard.

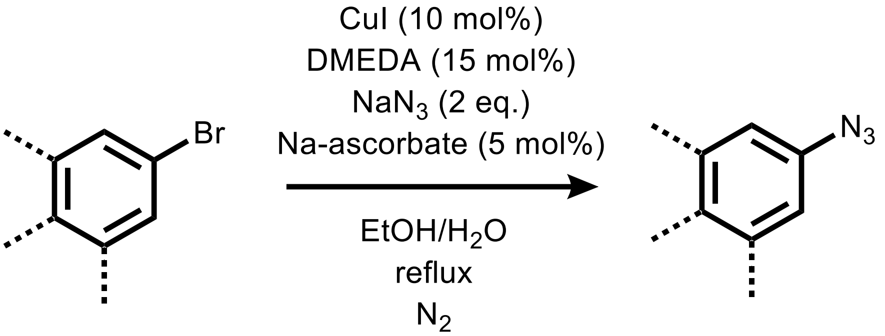
Synthesis of aryl azides

Aryl azide synthesis procedure A:



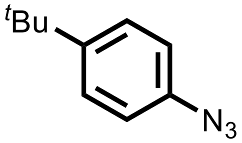
Under air, a 100 mL round bottomed flask was charged with 5 mmol aniline, 50 mL dry acetonitrile, and a stir bar and was cooled to 0 °C. Then, tBuONO (6 mmol, 1.2 eq.) was added, followed by $TMSN_3$ (6 mmol, 1.2 eq.). The reaction was allowed to warm to room temperature overnight. The next day, the reaction was checked for absence of starting material by TLC, the solvent was removed *in vacuo*, and the product eluted through a short plug of silica using hexanes. Pure material was obtained after removal of hexanes *in vacuo*.

Aryl azide synthesis procedure B:



Adapted from a previously reported method.(*60*) Under air, in a 20 mL septum capped vial, 2 mmol aryl bromide, 32 µL dimethylethylenediamine (0.3 mmol, 15 mol%), 38 mg CuI (0.2 mmol, 10 mol%), 260 mg NaN_3 (4 mmol, 2 eq.), and 20 mg sodium ascorbate (0.1 mmol, 5 mol%) were added, followed by 5 mL of a 3:7 mixture of H_2O/EtOH. The vial was sealed, purged with N_2 for 5 min, and then heated to reflux until the starting material had been consumed as indicated by TLC. The reaction was then cooled to room temperature and diluted with ethyl acetate. Then, the organics were washed with water, followed by brine, dried over $MgSO_4$, and concentrated under reduced pressure to give crude material which was then purified on a silica column.

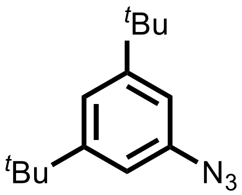
1-azido-4-(tert-butyl)benzene:



Synthesized according to general procedure A from 6 mmol (895 mg) 1-amino-4-(tert-butyl)benzene. The title compound was obtained as a yellow liquid in 99 % yield (1.05 g) after eluting through a silica plug with hexanes.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 – 7.34 (dt, 2H), 7.00 – 6.93 (dt, 2H), 1.31 (s, 9H). Spectrum matches that previously reported.(*61*)

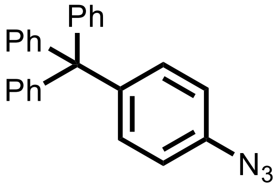
1-azido-3,5-di-tert-butylbenzene:



Synthesized according to general procedure B from 1-bromo-3,5-di-tert-butylbenzene (538 mg, 2 mmol). The title compound was obtained as yellow oil in 90 % yield (415 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20 (t, *J* = 1.7 Hz, 1H), 6.86 (d, *J* = 1.7 Hz, 2H), 1.31 (s, 18H). Spectrum matches that previously reported.(*62*)

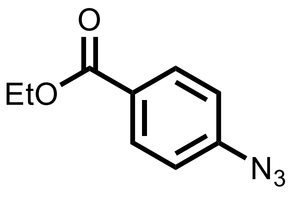
((4-azidophenyl)methanetriyl)tribenzene:



Synthesized according to general procedure A from 4-tritylaniline (335 mg, 1 mmol). The title compound was obtained as a light yellow solid in 49 % yield (177 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, C$_6$D$_6$) δ 7.31 – 7.26 (m, 6H), 7.12 – 7.04 (m, 8H), 7.04–6.97 (m, 3H), 6.57 – 6.52 (m, 2H). Spectra match those previously reported.(*63*)

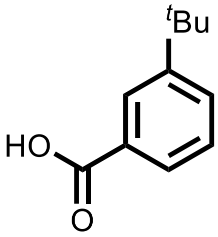
ethyl 4-azidobenzoate:



Synthesized according to general procedure A from ethyl-4-aminobenzoate (1.652 g, 10 mmol). The compound was obtained as a yellow-orange oil in 96 % yield (1.829 g) after purification *via* column chromatography on silica gel.

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.07 – 7.99 (m, 2H), 7.09 – 7.01 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). Spectra match those previously reported.(*23*)

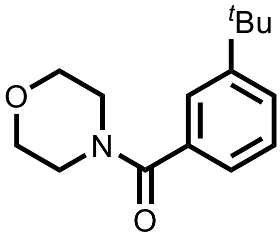
3-(tert-butyl)benzoic acid:



An oven dried 100 mL Schlenk flask was purged and backfilled with dry nitrogen gas three times, and then charged with 3-tert-butylbromobenzene (2.13 g, 10 mmol, 1 eq), and 50 mL dry, degassed tetrahydrofuran. The solution was then cooled to – 78 °C and 2.5 M n-butyllithium in hexane (4.4 mL, 11 mmol, 1.1 eq.) was added slowly under nitrogen. The resulting solution was then quenched with dry carbon dioxide gas supplied through a balloon as the reaction was warmed to room temperature. The resulting solution was quenched with 1 M ammonium chloride solution, and extracted with dichloromethane. The combined organics were then washed with brine, dried over $MgSO_4$, and concentrated. The product was obtained as a white powder in 10 % yield (179 mg) after purification by silica gel chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 1.36 (s, 9H). Spectra match those previously reported.(*64*)

(3-(tert-butyl)phenyl)(morpholino)methanone:



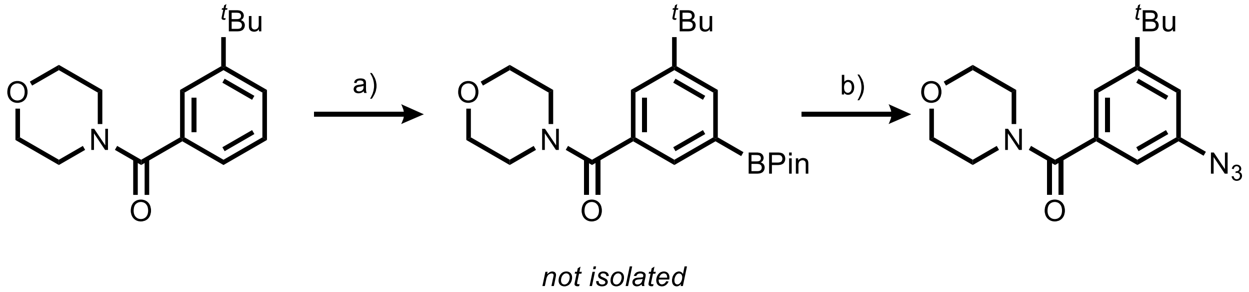
A 20 mL scintillation vial was charged with 3-(tert-butyl)benzoic acid (178 mg, 1.0 mmol, 1 eq), 10 mL dry dimethylformamide, and a magnetic stirbar and cooled to 0 °C. Then, while stirring, HATU (418 mg, 1.1 mmol, 1.1 eq) and morpholine (95 µL, 1.1 mmol, 1.1 eq.) were added. Finally, diisopropylethylamine (522 µL, 3 mmol, 3 eq.) was added, and the reaction was sealed and allowed to stir overnight. The next morning, TLC analysis demonstrated full consumption of starting material. The reaction was diluted with 30 mL ethyl acetate, washed twice with water, washed three times with brine, dried over $MgSO_4$, and concentrated under reduced pressure to yield the title compound as a beige oil in 94 % yield (231 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.42 (d, *J* = 1.8 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.19 (dq, *J* = 7.4, 1.2 Hz, 1H), 3.85 – 3.69 (m, 4H), 3.63 (s, 2H), 3.45 (s, 2H), 1.32 (s, 9H).

^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ 171.11, 151.86, 135.10, 128.31, 127.08, 124.24 (d, *J* = 6.3 Hz), 67.06, 48.34, 42.69, 34.95, 31.38. Rotomeric broadening leads to inequivalence of the α methylenes of the morpholine, which show weak, inequivalent resonances at 48.34 ppm and 42.69 ppm

HRMS (ESI-TOF) calcd 248.1645 for $C_{15}H_{22}NO_2^+$ [M+H]$^+$, found 248.1654

(3-azido-5-(tert-butyl)phenyl)(morpholino)methanone:



a) An oven-dried 20 mL septum-capped vial was charged with dipinacolato diboron (127 mg, 0.5 mmol, 1 eq), 4,4'-di-tert-butyl-2,2'-bipyridine (4 mg, 0.015 mmol, 3 mol%), and a stirbar. The vial was then purged and backfilled with nitrogen three times. Then, 5 mL dry THF was added under N_2 followed by a THF solution of $[Ir(OMe)(cod)]_2$ (5 mg, 0.0075 mmol, 1.5 mol%). This was allowed to stir for ten minutes under nitrogen over the course of which the solution adopted a deep red tint. Then, a THF solution of (3-(tert-butyl)phenyl)(morpholino)methanone (123 mg, 0.5 mmol, 1 eq) was added and the temperature was raised to 70 °C. The reaction was allowed to stir overnight. The next day, TLC analysis indicated the incomplete consumption of starting material, so the reaction mixture was resubjected to catalysis with an additional 5 mg $[Ir(OMe)(cod)]_2$, 4 mg 4,4'-di-tert-butyl-2,2'-bipyridine, and 127 mg dipinacolato diboron (as above). The reaction was then allowed to proceed at 55 °C overnight, over the course of which the reaction reached completion. The reaction was then concentrated under reduced pressure. The product was partially purified by elution through a short silica plug with ethyl acetate and was used without further purification.

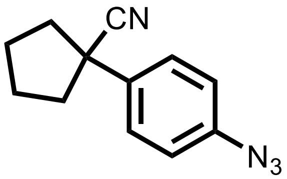
b) A 20 mL septum capped scintillation vial was charged with $Cu(OAc)_2$ (90.5 mg, 0.5 mmol, 1 eq.), 5 mL methanol, and a magnetic stirbar. Then, sodium azide (65 mg, 1 mmol, 2 eq.) was added. Finally, a methanolic solution (~ 1mL) of the crude material from (a) was added slowly. The reaction was then sealed and an O_2 balloon was introduced through the septum cap. The reaction was then heated overnight at 55 °C. The next day, the reaction was quenched with an aqueous solution of EDTA*2Na, extracted with ethyl acetate, washed with water, then brine, and concentrated under reduced pressure. The product was then obtained as a pale yellow oil in 42% overall yield (60.1 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 1.6 Hz, 1H), 7.06 (t, *J* = 1.9 Hz, 1H), 6.89 (dd, *J* = 2.2, 1.4 Hz, 1H), 3.77 (s, 4H), 3.69 – 3.59 (m, 2H), 3.43 (s, 2H), 1.31 (s, 9H).

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.91, 154.16, 140.44, 136.81, 120.84, 117.78, 114.86, 67.00, 48.34, 42.73, 35.20, 31.24. Rotomeric broadening leads to inequivalence of the α methylenes of the morpholine, which show weak, inequivalent resonances at 48.34 ppm and 42.73 ppm.

HRMS (ESI-TOF): calcd 289.1659 for $C_{15}H_{21}N_4O_2^+$ $[M+H]^+$, found 289.1666.

1-(4-azidophenyl)cyclopentane-1-carbonitrile:



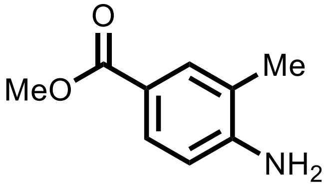
Synthesized according to general procedure A from 1-(4-aminophenyl)cyclopentane-1-carbonitrile (300 mg, 1.61 mmol). The title compound was obtained in 79% yield (270 mg) as a pale-yellow liquid after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 2H), 7.07 – 6.96 (m, 2H), 2.65 – 2.36 (m, 2H), 2.17 – 1.80 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.8, 136.6, 127.7, 124.3, 119.5, 47.4, 40.6, 24.3.

HRMS (ESI-TOF) calcd 213.1135 for $C_{12}H_{13}N_4^+$ [M+H]$^+$, found 213.1135.

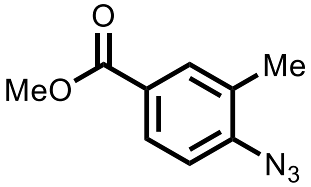
methyl 4-amino-3-methylbenzoate:



A 100 mL round-bottomed flask was charged with 756 mg (5 mmol) 4-amino-3-methylbenzoic acid and 20 mL methanol. Then, 0.5 mL 12.1 M HCl was added. The reaction was then affixed with a reflux condenser and reacted at reflux overnight. The next day, the reaction was quenched with saturated aqueous $NaHCO_3$ solution, extracted with ethyl acetate 3x, and concentrated to give the title compound in quantitative yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.2 Hz, 1H), 7.74 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.20 (s, 2H), 3.86 (d, *J* = 1.4 Hz, 3H), 2.19 (s, 3H). Spectra match those previously reported.(*65*)

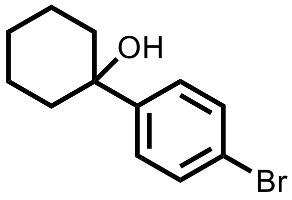
methyl 4-azido-3-methylbenzoate:



Synthesized according to general procedure A from methyl 4-amino-3-methylbenzoate (370 mg, 2.2 mmol). The compound was obtained as a pale-yellow powder in 84 % yield (359 mg) after purification through a silica plug.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 5.3, 1.7 Hz, 1H), 7.69 (s, 1H), 7.61 (d, *J* = 4.9 Hz, 1H), 3.94 – 3.90 (m, 3H), 2.61 (d, *J* = 1.9 Hz, 3H). Spectra match those previously reported.(*23*)

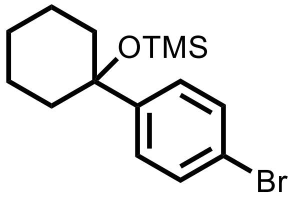
1-(4-bromophenyl)cyclohexan-1-ol:



In an oven dried 100 mL Schlenk flask under nitrogen, 1,4-dibromobenzene (2.4 g, 10 mmol) was dissolved in 40 mL dry THF and stirred at –78 °C. Then, 4.4 mL n-butyllithium solution (2.5 M in hexanes, 11 mmol, 1.1 eq.) was added dropwise, resulting in the formation of a milky white suspension. This was allowed to stir for 30 minutes at –78 °C. Then, cyclohexanone (1.2 mL, 12 mmol, 1.2 eq.) was slowly added, resulting in the clarification of the solution and the adoption of a pale yellow color. This was allowed to stir for 30 minutes at –78 °C and was then warmed to room temperature to stir for 30 minutes more. Then, the reaction was quenched with 40 mL saturated aqueous ammonium chloride solution. The organics were extracted twice with ethyl acetate which was then dried over $MgSO_4$ and concentrated under reduced pressure to give a pale-yellow oil from which the product crystallized after standing at –20 °C. The product was then decanted and rinsed with cold hexanes to yield colorless crystals (1.5 g, 59 % yield).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 1.87 – 1.68 (m, 8H), 1.68 – 1.62 (m, 2H), 1.36 – 1.23 (m, 1H). Spectra match those previously reported.(*66*)

((1-(4-bromophenyl)cyclohexyl)oxy)trimethylsilane:



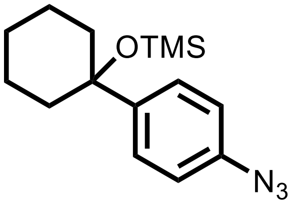
A 20 mL scintillation vial was charged with 1-(4-bromophenyl)cyclohexan-1-ol (255 mg, 1.0 mmol, 1.0 eq.), imidazole (204 mg, 3.0 mmol, 3.0 eq.), and 10 mL dry dichloromethane. The solution was then cooled to 0 °C. Then, trimethylsilyl chloride (320 µL, 2.5 mmol, 2.5 eq.) was added dropwise, resulting in the formation of a white precipitate. The reaction was allowed to slowly warm from 0 °C to room temperature overnight. The next day, TLC analysis indicated the completion of the reaction. The reaction was quenched with deionized water, the layers were separated, and the aqueous layer washed with 5 mL DCM. The combined organic layers were passed through a plug of $MgSO_4$ and concentrated under reduced pressure to yield the title compound as a colorless oil in 91% yield (296 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.38 – 7.30 (m, 2H), 1.97 – 1.89 (m, 2H), 1.84 – 1.60 (m, 5H), 1.53 (dq, *J* = 7.3, 3.6 Hz, 2H), 1.23 (q, *J* = 11.5 Hz, 1H), -0.10 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.24, 131.13, 127.79, 120.76, 75.44, 39.27, 25.81, 22.54, 2.33.

HRMS: calcd 254.0273 for $C_{12}H_{14}Br^+$ [M-OTMS]$^+$, found 254.0277.

((1-(4-azidophenyl)cyclohexyl)oxy)trimethylsilane:



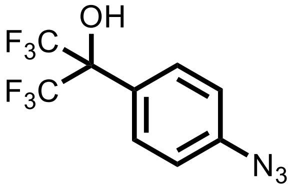
Synthesized according to general procedure B from ((1-(4-bromophenyl)cyclohexyl)oxy)trimethylsilane (287.8 mg, 0.88 mmol). The title compound was obtained as a pale yellow oil in 84% yield (213.9 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 2H), 7.04 – 6.94 (m, 2H), 1.98 – 1.90 (m, 2H), 1.74 (td, *J* = 12.0, 6.2 Hz, 4H), 1.69 – 1.60 (m, 1H), 1.54 (td, *J* = 8.1, 4.1 Hz, 2H), 1.24 (tdd, *J* = 13.1, 10.0, 4.5 Hz, 1H), -0.11 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.98, 138.51, 127.45, 118.63, 75.34, 39.34, 25.85, 22.60, 2.30.

HRMS: calcd 200.1182 for $C_{12}H_{14}N_3^+$ [M-OTMS]$^+$, found 200.1182

2-(4-azidophenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol



Synthesized according to general procedure A from 2-(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (1.30 g, 5 mmol). The title compound was obtained as a yellow-orange solid in quantitative yield (1.43 g) after eluting through a plug of silica gel using 20 % ethyl acetate in hexanes.

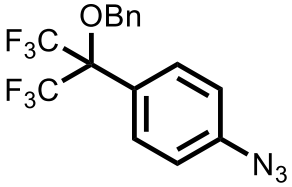
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.15 – 7.07 (m, 2H), 3.41 (s, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.45, 128.35 (t, *J* = 1.7 Hz), 125.74, 122.68 (q, *J* = 287.6 Hz), 119.35, 77.73 – 76.40 (central doublet observed, *J* = 30.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -75.77.

HRMS: calcd 284.0264 for $C_9H_4F_6N_3O^-$ [M-H]$^-$, found 284.0261.

1-azido-4-(2-benzyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)benzene



A 20 mL septum-capped scintillation vial was charged with 285 mg (1 mmol) 2-(4-azidophenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol, 10 mL dimethylformamide, and a stir bar. The reaction was then cooled to 0 °C while stirring. Then, sodium hydride (60% w/w dispersion) (80 mg, 2 mmol, 2 eq.) was added portionwise, followed by 2 eq. benzyl bromide. The reaction was then sealed with a septum cap and a nitrogen line was introduced via a needle through the septum. The reaction was then allowed to slowly warm to room temperature overnight under an atmosphere of nitrogen. The next morning, TLC analysis indicated consumption of the starting material. The reaction was quenched with deionized water and then extracted with ethyl acetate. The organics were washed with brine, dried over $MgSO_4$ and then purified by silica gel chromatography to yield the title compound as an off-white powder in 58 % yield (217 mg).

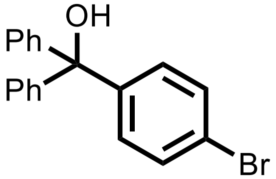
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.32 (m, 5H), 7.16 – 7.09 (m, 2H), 4.64 (s, 2H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.56, 136.23, 129.93, 128.81, 128.38, 127.29, 124.60, 122.55 (q, *J* = 291.0 Hz), 119.53, 83.28 – 82.48 (central doublet observed, *J* = 28.4), 68.19.

^{19}F NMR (470 MHz, $CDCl_3$) δ -70.80.

HRMS: (ESI-TOF) calcd 348.0818 for $C_{16}H_{12}F_6NO^+$ $[M-N_2+H]^+$ found 348.0815. Found mass is in accordance with previously reported fragmentation of analogous compounds. (*67*)

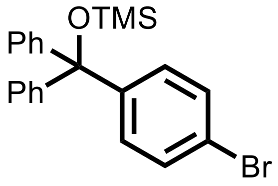
(4-bromophenyl)diphenylmethanol:



In an oven dried 50 mL Schlenk flask under nitrogen, 1,4-dibromobenzene (1.18 g, 5 mmol, 1.0 eq.) was dissolved in 20 mL dry THF and stirred at – 78 °C. Then, n-butyllithium solution (2.2 mL, 2.5 M in hexanes, 5.5 mmol, 1.1 eq) was added dropwise, resulting in the formation of a milky white suspension. This was allowed to stir for 30 minutes at which time benzophenone (1.1 g, 6 mmol, 1.2 eq.) in 5 mL dry THF was added dropwise. This resulted in the clarification of the solution and its adoption of a green tint. The reaction was allowed to react for 30 minutes at – 78 °C and was then raised to room temperature for 30 minutes more. Then, the reaction was quenched with 20 mL saturated aqueous ammonium chloride solution. The organics were extracted with two washes with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude residue was obtained as a colorless oil in 68 % yield (1.16 g) after purification *via* column chromatography on silica gel (0-20 % ethyl acetate in hexanes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.36 – 7.28 (m, 6H), 7.30 – 7.21 (m, 4H), 7.21 – 7.15 (m, 2H), 2.76 (s, 1H). Spectra match those previously reported (*68*)

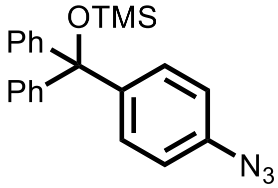
((4-bromophenyl)diphenylmethoxy)trimethylsilane:



To 20 mL scintillation vial containing a magnetically stirred solution of (4-bromophenyl)diphenylmethanol (340 mg, 1.0 mmol, 1.0 eq.), imidazole (204 mg, 3.0 mmol, 3.0 eq.), and 10 mL dry dichloromethane was added trimethylsilyl chloride (320 µL, 2.5 mmol, 2.5 eq) dropwise. The reaction was then allowed to stir at 0 °C for 30 minutes and was then brought to room temperature. The reaction was allowed to stir at room temperature overnight. Then, the reaction was filtered through a plug of silica and eluted with dichloromethane. The filtrate was then concentrated to give the title compound as a colorless oil in 93 % yield (384.1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 6H), 7.31 – 7.27 (m, 4H), 7.26 – 7.22 (m, 2H), 6.97 – 6.91 (m, 2H), -0.15 (s, 9H). Spectra match those previously reported.(*69*)

((4-azidophenyl)diphenylmethoxy)trimethylsilane:



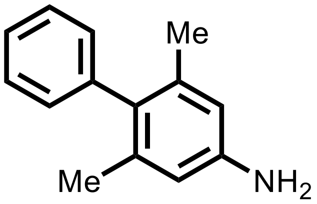
Synthesized according to general procedure B from 382.6 mg (0.93 mmol) ((4-bromophenyl)diphenylmethoxy)trimethylsilane. The title compound was isolated as a yellow oil in 76 % yield (265 mg) after purification by silica gel chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 6H), 7.32 – 7.20 (m, 6H), 6.97 – 6.92 (m, 2H), -0.15 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.88, 144.43, 138.67, 129.89, 128.47, 127.88, 127.19, 118.37, 84.27, 1.86.

HRMS: calcd 284.1182 for $C_{19}H_{14}N_3^+$ [M-OTMS]$^+$ found 284.1183.

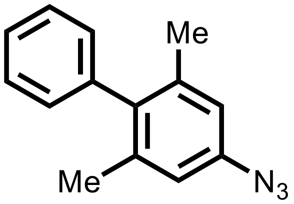
2,6-dimethyl-[1,1'-biphenyl]-4-amine



A 20 mL septum-capped vial was charged with 4-bromo-3,5-dimethylaniline (600 mg, 3 mmol, 1 eq.), phenylboronic acid (549 mg, 4.5 mmol, 1.5 eq), potassium phosphate (1.3 g, 6 mmol, 2 eq.), palladium (II) acetate (3.3 mg, 0.015 mmol, 0.5 mol%), SPhos (12.3 mg, 0.03 mmol, 1 mol%) and a magnetic stir bar. The atmosphere was then purged and backfilled with dry dinitrogen three times. Dry toluene (10 mL) was then added, and the reaction was stirred and heated to 90 °C overnight. The next day, TLC analysis indicated full conversion of the starting material, at which point the reaction was filtered through a short plug of silica gel, eluted with ethyl acetate, and concentrated under reduced pressure. The resulting residue was then purified by column chromatography (0-50 % ethyl acetate in hexanes) on silica gel to yield the title compound as an off-white crystalline powder in 92 % yield (543 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.34 – 7.28 (m, 1H), 7.17 – 7.10 (m, 2H), 6.48 (s, 2H), 3.60 (s, 2H), 1.96 (s, 6H). Spectra match those previously reported.(*70*)

4-azido-2,6-dimethyl-1,1'-biphenyl



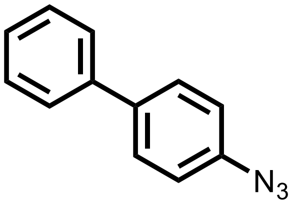
Synthesized according to general procedure A from 2,6-dimethyl[1,1'-biphenyl]-4-amine (197 mg, 1 mmol). The title compound was obtained as a yellow oil in 96 % yield (214 mg) after purification by silica gel chromatography

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (td, *J* = 7.2, 1.4 Hz, 2H), 7.38 – 7.31 (m, 1H), 7.14 – 7.08 (m, 2H), 6.78 (s, 2H), 2.02 (s, 6H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.37, 138.99, 138.45, 138.16, 129.33, 128.66, 127.00, 117.84, 21.07.

HRMS (ESI-TOF) calcd 228.1383 for $C_{15}H_{18}NO^+$ $[M-N_2+(MeOH)+H]^+$ found 228.1377. Found mass is in accordance with previously reported fragmentation of analogous compounds. (*67*)

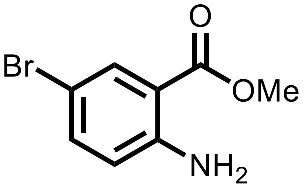
4-azido-1,1'-biphenyl



Synthesized according to general procedure A from 846 mg (5 mmol) 4-amino-1,1'-biphenyl. The title compound was obtained as a cream powder in 88 % yield (859 mg) after purification by eluting through a silica plug with hexanes.

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 4H), 7.49 – 7.40 (tt, 2H), 7.39 – 7.31 (tt, 1H), 7.14 – 7.07 (dt, 2H). Spectra match those previously reported. (*71*)

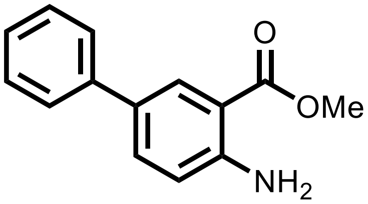
Methyl 2-amino-5-bromobenzoate



A 50 mL round bottomed flask was charged with 1.08 g (5 mmol) 2-amino-5-bromobenzoic acid and a magnetic stir bar. This was then dissolved in 20 mL of methanol and stirred. Then, 10 mL of sulfuric acid was added slowly over the course of 5 minutes. A reflux condenser was then affixed to the reaction vessel and the reaction was heated to 80 °C overnight. The next day, the reaction was poured onto ice and neutralized with sodium bicarbonate. The organics were then extracted with ethyl acetate, washed with water, washed with brine, and then dried over anhydrous $MgSO_4$. The organics were then concentrated under reduced pressure to yield the title compound as a beige powder in 87 % yield (996 mg).

^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.4 Hz, 1H), 7.32 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 1H), 5.79 (bs, 2H), 3.87 (s, 3H). Spectra match those previously reported.(*72*)

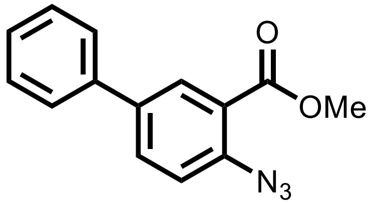
Methyl 4-amino-[1,1'-biphenyl]-3-carboxylate



A 20 mL septum capped vial was charged with 460 mg (2 mmol, 1.0 eq.) methyl 2-amino-5-bromobenzoate, 366 mg (3 mmol, 1.5 eq.) phenylboronic acid, 2.2 mg (0.01 mmol, 0.5 mol%) $Pd(OAc)_2$, 8.2 mg (0.02 mmol, 1 mol%) SPhos, and 1.3 g (6 mmol, 3 eq.) K_3PO_4. Then the vial was purged and backfilled three times with dry nitrogen gas. Then, under nitrogen, 10 mL dry toluene was introduced *via* syringe. The reaction was then heated to 100 °C and stirred overnight under an atmosphere of nitrogen. The next morning, the reaction was filtered through a plug of silica gel and eluted with ethyl acetate. The resulting solution was concentrated under reduced pressure and the crude material thereafter purified by silica gel chromatography. The title compound was obtained as a yellow powder in 82 % yield (371 mg).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.3 Hz, 1H), 7.59 – 7.50 (m, 3H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 5.78 (s, 2H), 3.90 (s, 3H). Spectra match those reported previously.(*73*)

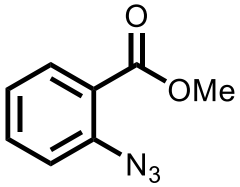
Methyl 4-azido-[1,1’-biphenyl]-3-carboxylate



Synthesized from 227 mg (1 mmol) of methyl 4-amino-[1,1’-biphenyl]-3-carboxylate according to a previously published procedure.(*23*) The title compound was obtained as a pale yellow powder in 64 % yield (163 mg) after purification by silica gel chromatography.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.3 Hz, 1H), 7.78 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.48 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.45 – 7.36 (m, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H). Spectra match those reported previously.(*74*)

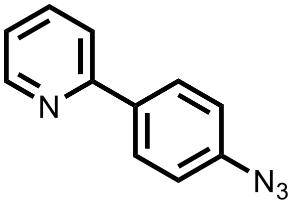
methyl 2-azidobenzoate



Synthesized according to general procedure A from methyl 2-aminobenzoate (302 mg, 2 mmol). The title compound is obtained as yellow oil in 98 % yield (347 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.53 (ddd, *J* = 8.1, 7.4, 1.6 Hz, 1H), 7.24 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.18 (td, *J* = 7.6, 1.1 Hz, 1H), 3.91 (s, 3H). Spectra match those reported previously.(*75*)

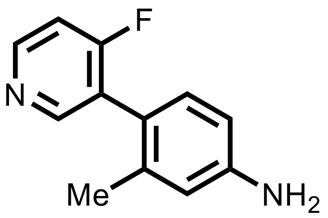
2-(4-azidophenyl)pyridine



Synthesized from 170 mg (1 mmol) of 4-(pyridine-2-yl)aniline according to a previously published procedure.(*23*) The title compound was obtained as a brown powder in 88 % yield (174 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (dt, *J* = 5.2, 1.2 Hz, 1H), 8.04 – 7.97 (m, 2H), 7.74 (td, *J* = 7.6, 1.8 Hz, 1H), 7.69 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.22 (ddd, *J* = 7.5, 4.8, 1.3 Hz, 1H), 7.16 – 7.09 (m, 2H). Spectra match those reported previously.(*23*)

4-(4-fluoropyridin-3-yl)-3-methylaniline



A 20 mL septum capped vial was charged with (4-fluoropyridin-3-yl)boronic acid (634 mg, 4.5 mmol, 1.5 eq.), 4-bromo-3-methyl aniline (558 mg, 3 mmol, 1.0 eq.), $Pd(OAc)_2$ (6.7 mg, 0.03 mmol, 1 mol%), XPhos (29 mg, 0.06 mmol, 2 mol%), K_3PO_4 (1.3 g, 6 mmol, 2 eq.), and a magnetic stirbar. The vial was then sealed and purged and backfilled with nitrogen three times. Then, 10 mL toluene was introduced via syringe under nitrogen and the reaction was raised to 110 °C. The reaction was stirred for four days at this temperature at which point it was filtered through silica, eluted with ethyl acetate, and subsequently purified by silica gel chromatography. The title compound was isolated as a red oil in 22 % yield (136 mg).

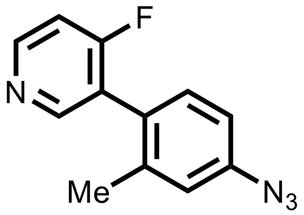
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.5 Hz, 1H), 7.75 – 7.66 (m, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.94 (ddd, *J* = 8.3, 3.0, 0.7 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 6.59 (dd, *J* = 8.0, 2.6 Hz, 1H), 3.74 (bs, 2H), 2.19 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.49 (d, *J* = 238.0 Hz), 147.77 (d, *J* = 14.3 Hz), 146.60, 142.03 (d, *J* = 7.8 Hz), 136.84, 135.56 (d, *J* = 4.6 Hz), 131.09, 127.35, 117.04, 112.93, 108.77 (d, *J* = 37.4 Hz), 20.57.

^{19}F NMR (376 MHz, $CDCl_3$) δ -71.57.

HRMS (ESI-TOF) calcd 203.0979 for $C_{12}H_{12}FN_2$ $[M+H]^+$, found 203.0977.

3-(4-azido-2-methylphenyl)-4-fluoropyridine



Synthesized according to general procedure A from 4-(4-fluoropyridin-3-yl)-3-methylaniline (136 mg, 0.69 mmol). The title compound was obtained as a red oil in 88 % yield (135 mg) after purification by silica gel chromatography.

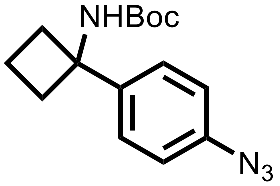
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dt, *J* = 2.6, 0.9 Hz, 1H), 7.72 (ddd, *J* = 8.4, 7.7, 2.5 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 6.99 (ddd, *J* = 8.4, 3.0, 0.7 Hz, 1H), 6.97 – 6.92 (m, 2H), 2.25 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.91 (d, *J* = 239.3 Hz), 147.70 (d, *J* = 14.6 Hz), 141.87 (d, *J* = 7.8 Hz), 140.16, 137.75, 134.60 (d, *J* = 4.7 Hz), 133.82, 131.41, 121.09, 116.97, 109.14 (d, *J* = 37.4 Hz), 20.59.

^{19}F NMR (376 MHz, $CDCl_3$) δ -70.09.

HRMS (ESI-TOF) calcd 229.0889 for $C_{12}H_{10}FN_4$ $[M+H]^+$, found 229.0884.

tert-butyl (1-(4-azidophenyl)cyclobutyl)carbamate



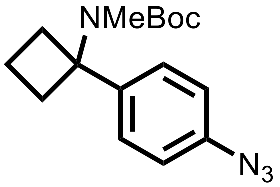
Synthesized according to general procedure A from methyl _tert_-butyl (1-(4-aminophenyl)cyclobutyl)carbamate (400 mg, 1.52 mmol). The title compound was obtained in 82% yield (360 mg) as a pale-yellow solid after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, _J_ = 8.3 Hz, 2H), 7.05 – 6.92 (m, 2H), 5.12 (s, 1H), 2.50 (q, _J_ = 6.1 Hz, 4H), 2.09 (dp, _J_ = 11.3, 7.7 Hz, 1H), 1.84 (dp, _J_ = 11.3, 7.7 Hz, 1H), 1.35 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.6, 143.2, 138.3, 127.1, 118.9, 79.6, 58.8, 34.5, 28.5, 15.3.

HRMS (ESI-TOF) calcd 311.1478 for $C_{15}H_{20}N_4NaO_2^+$ $[M+Na]^+$, found 311.1479.

tert-butyl (1-(4-azidophenyl)cyclobutyl)(methyl)carbamate:



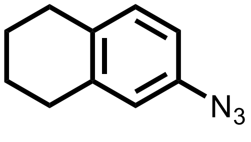
To a magnetically stirred solution of _tert_-butyl (1-(4-azidophenyl)cyclobutyl)carbamate (110 mg, 0.38 mmol) in 5 mL THF at 0 °C was added NaH (14 mg, 0.76 mmol). After 10 min, methyl iodide (47 µL, 0.76 mmol) was added and the reaction was warmed to 23 °C. After 1 h, the reaction mixture was quenched by the aq. NH_4Cl solution (3 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The title compound was obtained in 83% yield (96 mg) as a colorless liquid after purification by silica gel chromatography.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, _J_ = 7.6 Hz, 2H), 7.09 – 6.88 (m, 2H), 2.74 (br. s, 3H), 2.64 – 2.43 (m, 4H), 1.77 (qt, _J_ = 9.2, 2.3 Hz, 1H), 1.72 – 1.58 (m, 1H), 1.39 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.1, 141.3, 138.6, 127.5, 118.8, 79.7, 62.9, 34.8, 30.7, 28.6, 14.4.

HRMS (ESI-TOF) calcd 303.1816 for $C_{16}H_{23}N_4O_2^+$ $[M+H]^+$, found 303.1821.

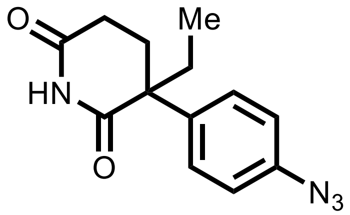
6-azido-1,2,3,4-tetrahydronaphthalene



Synthesized according to general procedure A from 6-amino-1,2,3,4-tetrahydronaphthalene (147 mg, 1 mmol). The title compound was obtained in 99% yield (172 mg) after eluting through a short plug of silica with hexanes.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, _J_ = 8.0 Hz, 1H), 6.79 – 6.70 (m, 2H), 2.78 – 2.68 (m, 4H), 1.85 – 1.72 (m, 4H). Spectra match those previously reported.(_76_)

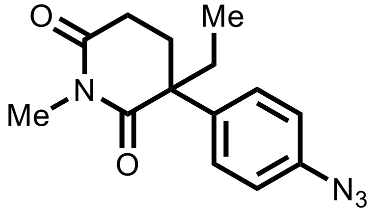
3-(4-azidophenyl)-3-ethylpiperidine-2,6-dione:



Synthesized according to general procedure A from 3-(4-aminophenyl)-3-ethylpiperidine-2,6-dione (aminoglutethimide) (232 mg, 1 mmol). The title compound was obtained as a pale-yellow liquid in 93 % yield (240 mg) after purification by silica gel chromatography.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (s, 1H), 7.31 – 7.23 (m, 2H), 7.07 – 6.99 (m, 2H), 2.67 – 2.57 (m, 1H), 2.46 – 2.32 (m, 2H), 2.30 – 2.16 (m, 1H), 2.10 – 1.99 (m, 1H), 1.96 – 1.85 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H). Spectra match those previously reported.(*77*)

3-(4-azidophenyl)-3-ethyl-1-methylpiperidine-2,6-dione:



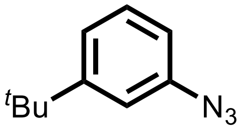
To a magnetically stirred solution of 3-(4-azidophenyl)-3-ethylpiperidine-2,6-dione (160 mg, 0.62 mmol) in 5 mL acetonitrile was added K$_2$CO$_3$ (256 mg, 1.8 mmol), methyl iodide (120 µL, 1.8 mmol) and heated to 70 °C. After 8 h, the reaction mixture was allowed to cool to 23 °C and quenched by the addition of cold water (3 mL). The aqueous layer was extracted with EtOAc (3 × 5 mL), and the combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The title compound was obtained in 89% yield (150 mg) as a colorless liquid after purification by silica gel chromatography.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (dt, *J* = 8.8, 1.5 Hz, 2H), 7.00 (dt, *J* = 8.7, 1.5 Hz, 2H), 3.19 (s, 3H), 2.75 – 2.61 (m, 1H), 2.50 – 2.35 (m, 1H), 2.29 (dddd, *J* = 14.2, 5.3, 2.8, 1.0 Hz, 1H), 2.23 – 2.11 (m, 1H), 2.10 – 1.97 (m, 1H), 1.94 – 1.82 (m, 1H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 175.4, 172.2, 139.4, 136.2, 127.8, 119.6, 51.2, 33.9, 29.8, 27.1, 26.0, 9.1.

HRMS (APCI) calcd 273.1346 for $C_{14}H_{17}N_4O_2^+$ [M+H]$^+$, found 273.1345.

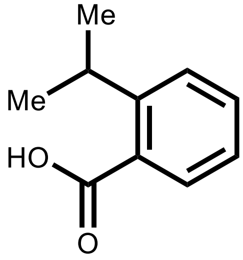
1-azido-3-(tert-butyl)benzene:



Synthesized according to general procedure A from 1-amino-3-(tert-butyl)benzene (373 mg, 2.5 mmol). The title compound was obtained as a yellow oil in 91 % yield (399 mg). after eluting through a plug of silica gel with hexanes.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (t, *J* = 7.9 Hz, 1H), 7.18 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.03 (t, *J* = 2.1 Hz, 1H), 6.88 (ddd, *J* = 7.9, 2.3, 1.0 Hz, 1H), 1.32 (s, 9H). Spectra match those previously reported.(*78*)

2-isopropylbenzoic acid



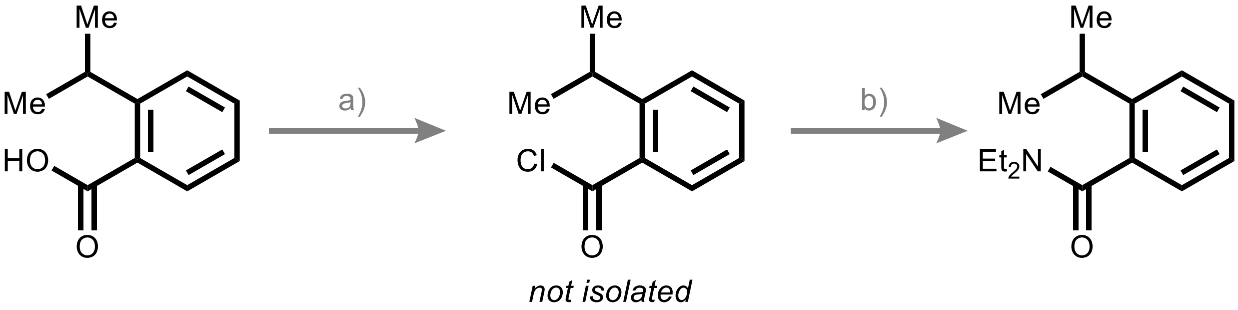
Under nitrogen, a flame-dried 200 mL Schlenk flask was charged with 2 g (10 mmol, 1 eq.) of 2-isopropyl-bromobenzene and 50 mL dry THF. The resulting solution was then cooled to – 78 °C. After stirring at – 78 °C for 15 minutes, 4.4 mL of a 2.5 M n-butyllithium solution (11 mmol, 1.1 eq) was added dropwise. This was then allowed to stir for 1 hour at – 78 °C, at which point CO_2 was bubbled through the solution as it warmed to room temperature. A white precipitate formed during the introduction of CO_2. The resulting mixture was then quenched with saturated aqueous ammonium chloride and transferred to a separatory funnel. The organics were extracted twice with ethyl acetate and once with dichloromethane. The combined organics were then concentrated under reduced pressure to yield the title compound as a yellow oil in 84 % yield (1.38 g). Upon standing, the isolated oil gradually solidified into an off-white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.46 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.27 (ddd, *J* = 7.8, 7.1, 1.5 Hz, 1H), 3.94 (hept, *J* = 6.9 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.69, 151.11, 132.90, 131.00, 128.48, 126.61, 125.69, 29.51, 24.18.

HRMS: (ESI-TOF) calcd 163.0765 for $C_{10}H_{11}O_2^-$ [M-H]$^-$, found 163.0777.

***N,N*-diethyl-2-isopropylbenzamide**



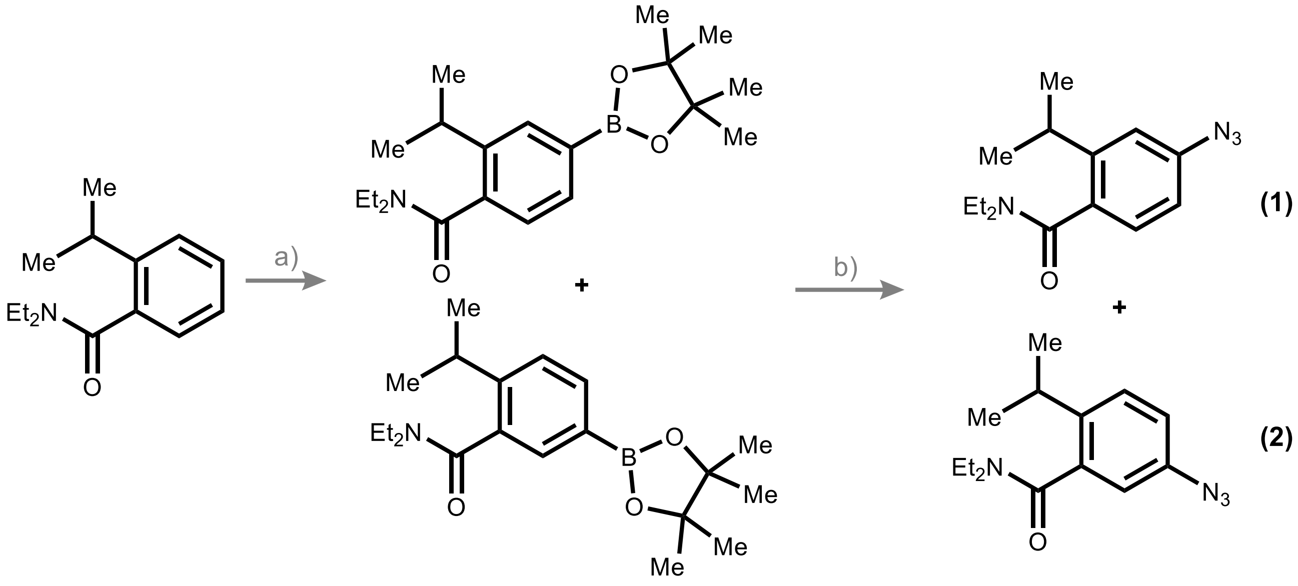
- **a)** A 50 mL round bottomed flask was charged with 2-isopropylbenzoic acid (328 mg, 2 mmol, 1 eq.) and 20 mL dichloromethane. Then, oxalyl chloride (343 µL, 4 mmol, 2 eq.) was added, followed by two drops of dimethyl formamide. The reaction was then stirred for 4 hours, at which point it was concentrated *in vacuo*. The resulting acyl chloride was then used without further purification.
- **b)** The crude residue from **a)** was redissolved in dichloromethane and cooled to 0 °C in an ice bath. Then diethylamine (414 µL, 4 mmol, 2 eq.) was added, followed by triethylamine (836 µL, 6 mmol, 3 eq.). The reaction was then allowed to warm to room temperature overnight. The next day, the reaction was washed with deionized water, then 1 M HCl, then saturated aqueous $NaHCO_3$. The organics were then washed with brine, dried over $MgSO_4$, and then concentrated *in vacuo* to yield the title compound without further purification as an orange oil in 99 % yield (434 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.18 (ddd, *J* = 8.3, 5.1, 3.3 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 1H), 3.78 (dq, *J* = 14.2, 7.2 Hz, 1H), 3.39 (dq, *J* = 13.9, 7.0 Hz, 1H), 3.19 – 3.08 (q, 7.1 Hz, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.30 – 1.20 (m, 9H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.01, 144.98, 136.31, 128.97, 125.88 (two overlapping signals), 125.48, 42.94, 38.62, 30.69, 24.79, 23.37, 14.02, 12.90.

HRMS (ESI-TOF) calcd 220.1701 for $C_{14}H_{22}NO^+$ $[M+H]^+$, found 220.1702

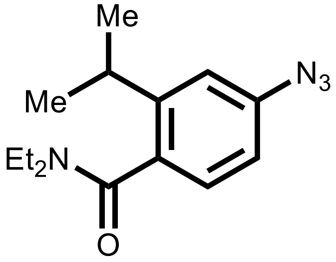
4-azido-*N,N*-diethyl-2-isopropylbenzamide (1) and 5-azido-*N,N*-diethyl-2-isopropylbenzamide (2)



not isolated

- **a)** An oven-dried 20 mL septum-capped vial was charged with dipinacolato diboron (254 mg, 1 mmol, 0.5 eq.), 4,4′-di-tert-butyl-2,2′-bipyridine (10.7 mg, 0.04 mmol, 2 mol%), and a stirbar. The vial was then purged and backfilled with nitrogen three times. Then, 5 mL dry THF was added under N_2 followed by a THF solution of $[Ir(OMe)(cod)]_2$ (13.2 mg, 0.02 mmol, 1 mol%). This was allowed to stir for 10 minutes under nitrogen over the course of which the solution adopted a deep red tint. Then, a THF solution of N,N-diethyl-2-isopropylbenzamide (440 mg, 2 mmol) was added under nitrogen. The reaction was then heated to 60 °C and stirred under nitrogen overnight. The next day, TLC analysis indicated the incomplete consumption of starting material, so an additional 2 eq. (500 mg) dipinacolato diboron, 1.5 mol% (15 mg) $[Ir(OMe)(cod)]_2$ and 3 mol% (15 mg) 4,4′-di-tert-butyl-2,2′-bipyridine was added. The reaction was stirred at 70 °C for an additional 36 hours at which point full conversion was achieved. The reaction was then concentrated *in vacuo*, eluted through a silica plug with ethyl acetate, and concentrated under reduced pressure. The crude material (539 mg, 78 % yield, 1:2 ratio of a to b) was then used without further purification.
- **b)** The crude material from **a)** was added to a septum-capped 20 mL vial containing a premixed solution of 283 mg (1.56 mmol, 1 eq.) $Cu(OAc)_2$ and 152 mg sodium azide (2.34 mmol, 1.5 eq) in 10 mL methanol. A balloon filled with O_2 was then affixed and the reaction was heated to 55 °C overnight. After 16 hours, TLC analysis indicated the full consumption of starting material. The reaction was then filtered through celite and eluted with methanol and ethyl acetate. The resulting solution was then concentrated under reduced pressure. The resulting residue was then subjected to column chromatography on silica gel. The azide isomers **(1)** and **(2)** were isolable using a gradient of 0 to 30 % ethyl acetate in hexanes. Mixed fractions were resubjected to column chromatography using the same conditions to achieve full separation. The azides were isolated in 57 % total yield from unfunctionalized N,N-diethyl-2-isopropylbenzamide in a 7:3 ratio favoring isomer **(2)**.

4-azido-*N,N*-diethyl-2-isopropylbenzamide (1)



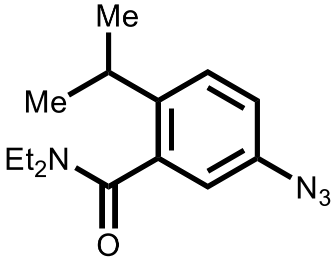
(1)

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 1H), 7.00 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 3.76 (dq, *J* = 14.2, 7.2 Hz, 1H), 3.39 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.13 (q, *J* = 7.1 Hz, 2H), 2.91 (hept, *J* = 6.9 Hz, 1H), 1.26 (t, *J* = 7.3 Hz, 3H), 1.22 (dd, *J* = 6.8, 3.4 Hz, 6H), 1.06 (t, *J* = 7.1 Hz, 3H).

^{13}**C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 169.79, 141.85, 137.77, 137.76, 127.57, 119.71, 115.99, 42.98, 38.76, 30.34, 24.83, 23.30, 14.10, 12.87. Inequivalency in the isopropyl carbons was observed as a result of hindered rotation.

HRMS: calcd for C14H21N4O$^+$ [M+H]$^+$ 261.1715, found 261.1714

5-azido-*N,N*-diethyl-2-isopropylbenzamide (2)



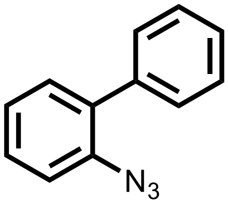
(2)

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 2.2 Hz, 1H), 6.87 (dd, *J* = 8.1, 2.3 Hz, 1H), 3.74 (dq, *J* = 14.3, 7.2 Hz, 1H), 3.38 (dq, *J* = 14.0, 7.1 Hz, 1H), 3.12 (q, *J* = 7.1 Hz, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 1.29 – 1.18 (m, 9H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}**C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 170.23, 147.43, 140.62, 133.13, 127.11, 116.64, 116.55, 42.99, 38.80, 30.76, 24.55, 23.16, 14.04, 12.86. Inequivalency in the isopropyl carbons was observed as a result of hindered rotation.

HRMS: calcd for C14H21N4O$^+$ [M+H]$^+$ 261.1715, found 261.1716.

2-azido-1,1'-biphenyl



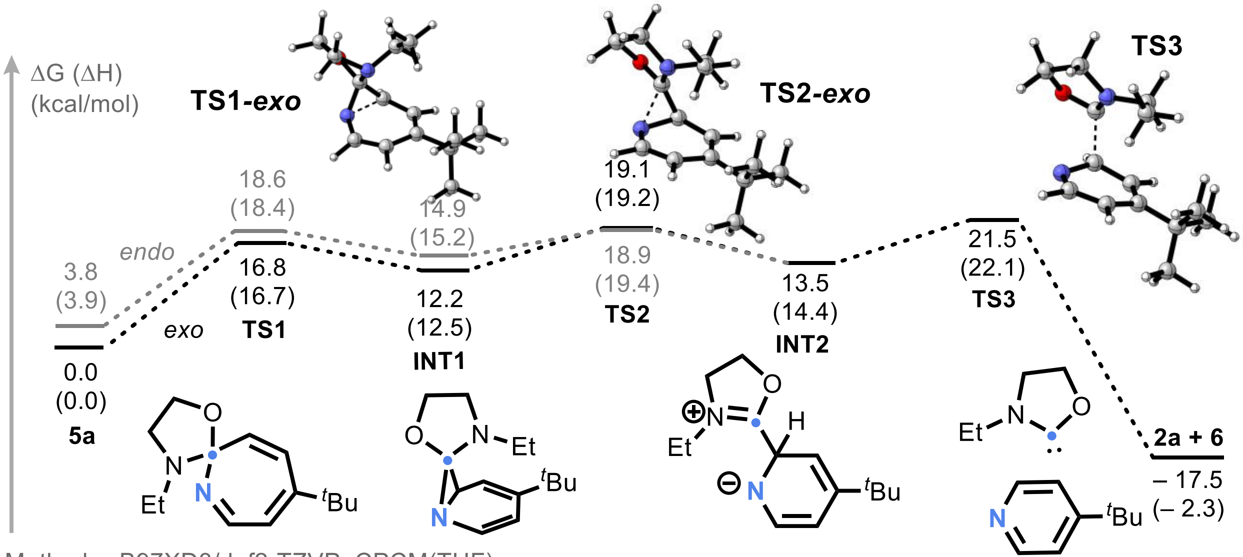
Synthesized according to general procedure A from [1,1’-biphenyl]-2-amine (535 mg, 3.2 mmol). Product was isolated as an orange liquid in 97 % yield (600 mg) after eluting through a plug of silica gel with hexanes.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 4H), 7.43 – 7.37 (m, 2H), 7.37 – 7.33 (m, 1H), 7.29 – 7.25 (m, 1H), 7.22 (td, *J* = 7.4, 1.1 Hz, 1H). Spectra match those previously reported.(*79*)

Computational Methods

Ground state geometries were preoptimized using CREST (*80*, *81*), and the lowest-energy conformer was further optimized to find ground state structures. Ground and transition state geometries were optimized with frequency calculations using density functional theory (DFT) in Orca 5.0 (*82–84*) at the BP86/def2-SVP level of theory utilizing an atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ).(*85–89*) This calculation made use of the nudged elastic band (NEB) technique to locate transition states along the IRC as implemented in the NEB-TS package in Orca 5.0.(*90*). A polarizable continuum solvation model (CPCM) in tetrahydrofuran (THF) was used to approximate the solvation shell. Single point energy calculations for all optimized structures were conducted using CPCM(THF) at the ωB97XD3/def2-TZVP level of theory utilizing the dispersion-corrected Head-Gordon ωB97X functional,(*91*) the Karlsruhe triple-zeta basis set,(*88*) the def2/J auxiliary basis set,(*89*) and Grimme's D3 zero-damping scheme,(*86*). Gibbs free energy and enthalpy were calculated following a frequency calculation at the single-point level of theory. All ground states and transition states were verified via frequency calculations; ground states were confirmed to have zero imaginary modes and transition states were all found to have a single imaginary mode. Transition states were confirmed to connect their neighboring intermediates along the IRC by distorting the transition state both directions along its imaginary mode and confirming that it relaxed to the same neighboring intermediates. The energy of **2a** + **6** was calculated at infinite separation in separate windows.

Reaction coordinate diagram reproduced from main text Figure 2D.



Method: ωB97XD3/def2-TZVP, CPCM(THF)

Table S1: Results of Functional and Basis Set Screening

Species Name	Functional/BasisSet	Free Energy (Hartrees)
01_SM_exo	wB97XD3_TZVP	-731.483
02_TS1_exo	wB97XD3_TZVP	-731.454
03_Int1_exo	wB97XD3_TZVP	-731.463
04_TS2_exo	wB97XD3_TZVP	-731.451
05_Int2_exo	wB97XD3_TZVP	-731.458
06_TS3_exo	wB97XD3_TZVP	-731.446
07_PDT_exo	wB97XD3_TZVP	-731.494
08_SM_endo	wB97XD3_TZVP	-731.477
09_TS1_endo	wB97XD3_TZVP	-731.452
10_Int1_endo	wB97XD3_TZVP	-731.459
11_TS2_endo	wB97XD3_TZVP	-731.45
12_Int2_endo	wB97XD3_TZVP	-731.46
13_TS3_endo	wB97XD3_TZVP	-731.445
14_PDT_endo	wB97XD3_TZVP	-731.493
01_SM_exo	TPSS_TZVP	-731.855
02_TS1_exo	TPSS_TZVP	-731.828
03_Int1_exo	TPSS_TZVP	-731.83
04_TS2_exo	TPSS_TZVP	-731.825
05_Int2_exo	TPSS_TZVP	-731.835
06_TS3_exo	TPSS_TZVP	-731.83
07_PDT_exo	TPSS_TZVP	-731.867
08_SM_endo	TPSS_TZVP	-731.85
09_TS1_endo	TPSS_TZVP	-731.824
10_Int1_endo	TPSS_TZVP	-731.825
11_TS2_endo	TPSS_TZVP	-731.824
12_Int2_endo	TPSS_TZVP	-731.836
13_TS3_endo	TPSS_TZVP	-731.83
14_PDT_endo	TPSS_TZVP	-731.866
01_SM_exo	PWPB95_TZVP	-731.109
02_TS1_exo	PWPB95_TZVP	-731.08
03_Int1_exo	PWPB95_TZVP	-731.085
04_TS2_exo	PWPB95_TZVP	-731.076
05_Int2_exo	PWPB95_TZVP	-731.083
06_TS3_exo	PWPB95_TZVP	-731.073
07_PDT_exo	PWPB95_TZVP	-731.116

08_SM_endo	PWPB95_TZVP	-731.104
09_TS1_endo	PWPB95_TZVP	-731.078
10_Int1_endo	PWPB95_TZVP	-731.082
11_TS2_endo	PWPB95_TZVP	-731.075
12_Int2_endo	PWPB95_TZVP	-731.084
13_TS3_endo	PWPB95_TZVP	-731.072
14_PDT_endo	PWPB95_TZVP	-731.115
01_SM_exo	PBE_TZVP	-730.776
02_TS1_exo	PBE_TZVP	-730.75
03_Int1_exo	PBE_TZVP	-730.752
04_TS2_exo	PBE_TZVP	-730.748
05_Int2_exo	PBE_TZVP	-730.758
06_TS3_exo	PBE_TZVP	-730.751
07_PDT_exo	PBE_TZVP	-730.784
08_SM_endo	PBE_TZVP	-730.771
09_TS1_endo	PBE_TZVP	-730.747
10_Int1_endo	PBE_TZVP	-730.748
11_TS2_endo	PBE_TZVP	-730.746
12_Int2_endo	PBE_TZVP	-730.759
13_TS3_endo	PBE_TZVP	-730.75
14_PDT_endo	PBE_TZVP	-730.783
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02_TS1_exo	M06-2x_TZVP_D3Zero	-731.333
03_Int1_exo	M06-2x_TZVP_D3Zero	-731.34
04_TS2_exo	M06-2x_TZVP_D3Zero	-731.328
05_Int2_exo	M06-2x_TZVP_D3Zero	-731.334
06_TS3_exo	M06-2x_TZVP_D3Zero	-731.324
07_PDT_exo	M06-2x_TZVP_D3Zero	-731.369
08_SM_endo	M06-2x_TZVP_D3Zero	-731.355
09_TS1_endo	M06-2x_TZVP_D3Zero	-731.331
10_Int1_endo	M06-2x_TZVP_D3Zero	-731.337
11_TS2_endo	M06-2x_TZVP_D3Zero	-731.328
12_Int2_endo	M06-2x_TZVP_D3Zero	-731.335
13_TS3_endo	M06-2x_TZVP_D3Zero	-731.323
14_PDT_endo	M06-2x_TZVP_D3Zero	-731.367

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04_TS2_exo	M06-2x_TZVP	-731.326
05_Int2_exo	M06-2x_TZVP	-731.331
06_TS3_exo	M06-2x_TZVP	-731.322
07_PDT_exo	M06-2x_TZVP	-731.366
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10_Int1_endo	M06-2x_TZVP	-731.335
11_TS2_endo	M06-2x_TZVP	-731.325
12_Int2_endo	M06-2x_TZVP	-731.333
13_TS3_endo	M06-2x_TZVP	-731.321
14_PDT_endo	M06-2x_TZVP	-731.364
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05_Int2_exo	M06_TZVP_D3Zero	-731.124
06_TS3_exo	M06_TZVP_D3Zero	-731.116
07_PDT_exo	M06_TZVP_D3Zero	-731.157
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10_Int1_endo	M06_TZVP_D3Zero	-731.124
11_TS2_endo	M06_TZVP_D3Zero	-731.116
12_Int2_endo	M06_TZVP_D3Zero	-731.124
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04_TS2_exo	M06_TZVP	-731.11
05_Int2_exo	M06_TZVP	-731.116
06_TS3_exo	M06_TZVP	-731.108
07_PDT_exo	M06_TZVP	-731.149

08_SM_endo	M06_TZVP	-731.134
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11_TS2_endo	M06_TZVP	-731.109
12_Int2_endo	M06_TZVP	-731.117
13_TS3_endo	M06_TZVP	-731.107
14_PDT_endo	M06_TZVP	-731.147

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04_TS2_exo	BP86_TZVP	-731.716
05_Int2_exo	BP86_TZVP	-731.727
06_TS3_exo	BP86_TZVP	-731.721
07_PDT_exo	BP86_TZVP	-731.754

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10_Int1_endo	BP86_TZVP	-731.714
11_TS2_endo	BP86_TZVP	-731.713
12_Int2_endo	BP86_TZVP	-731.727
13_TS3_endo	BP86_TZVP	-731.719
14_PDT_endo	BP86_TZVP	-731.752

01_SM_exo	B3LYP_TZVP	-731.287
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03_Int1_exo	B3LYP_TZVP	-731.258
04_TS2_exo	B3LYP_TZVP	-731.251
05_Int2_exo	B3LYP_TZVP	-731.262
06_TS3_exo	B3LYP_TZVP	-731.256
07_PDT_exo	B3LYP_TZVP	-731.3

08_SM_endo	B3LYP_TZVP	-731.281
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10_Int1_endo	B3LYP_TZVP	-731.253
11_TS2_endo	B3LYP_TZVP	-731.25
12_Int2_endo	B3LYP_TZVP	-731.263
13_TS3_endo	B3LYP_TZVP	-731.255
14_PDT_endo	B3LYP_TZVP	-731.299

01_SM_exo	B2PLYP_TZVP	-731.054
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05_Int2_exo	B2PLYP_TZVP	-731.027
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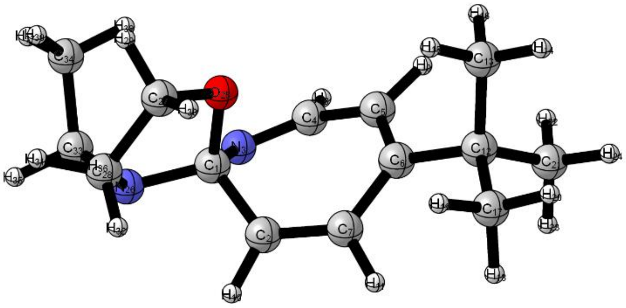
09_TS1_endo	B2PLYP_TZVP	-731.019
10_Int1_endo	B2PLYP_TZVP	-731.021
11_TS2_endo	B2PLYP_TZVP	-731.016
12_Int2_endo	B2PLYP_TZVP	-731.028
13_TS3_endo	B2PLYP_TZVP	-731.019
14_PDT_endo	B2PLYP_TZVP	-731.062

Coordinates for all optimized structures:

5a(endo)



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H	0.31507226477207	-2.92045039931146	1.32815309813584
H	-1.59942569486451	-1.55519695910399	1.77232701105623
H	0.76981500706076	-0.18988223514048	-2.62873278701801
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H	-3.62818551091668	0.39081158000012	-1.94997368572352
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C	-4.01185284256693	-1.16544951705960	0.28191283034918
H	-3.74337399781253	-1.82283992029904	1.13272613251491
H	-4.00981240265472	-1.78146554171818	-0.64076299029550
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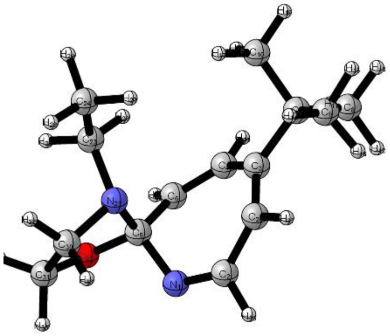
5a(exo)



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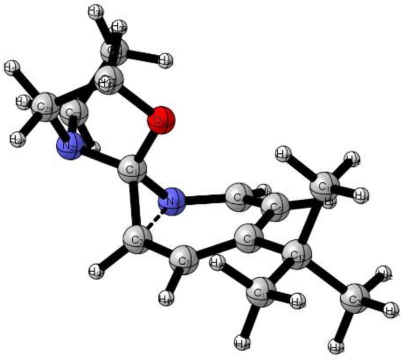

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H	-3.95789542716592	1.36129917330540	1.64815831029546
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H	-4.57219674494028	1.26311134626697	-0.75891607819076
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H	3.93832115124606	1.84629203667093	-0.90064408133113
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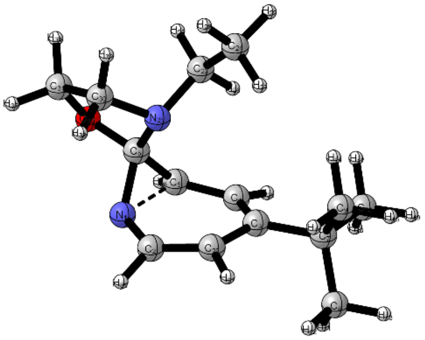
TS1(exo)



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C	-1.66641485173284	1.30677159135606	0.66961430330099
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C	0.93663826331612	1.25619332396940	-0.93839084486761
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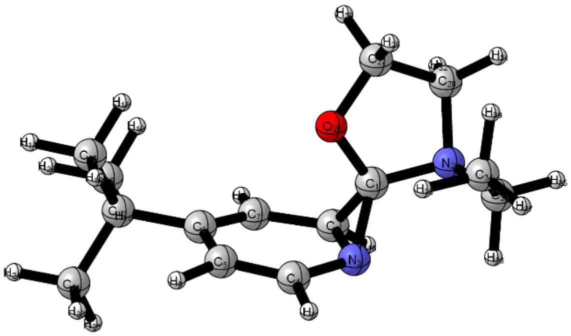
Int1(endo)



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H	-4.66138526934185	1.17257336431124	-0.78905858756678
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H	1.58140392620199	2.91011835321581	-0.01609895779575
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H	4.83371451647316	-1.21134947121088	1.50610932391504
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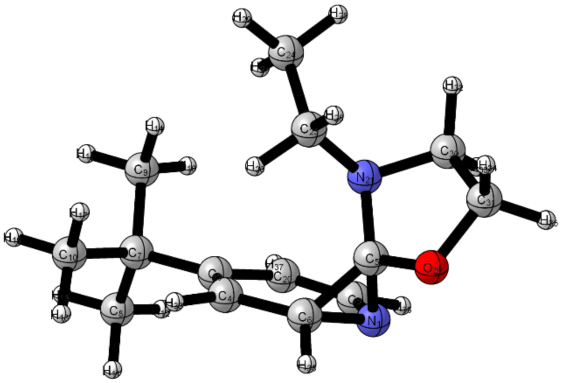
Int1(exo)



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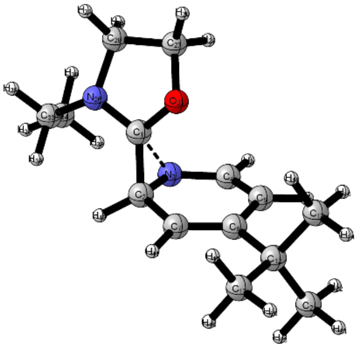
TS2(endo)



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C	0.22809571806613	-0.93685258214994	1.53103134573356
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H	1.01489351875369	-1.34396443115613	-1.67985902012084
H	-1.28345358676400	-0.45260653649053	-2.03375899037468
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C	-3.49287628563096	1.23422789196665	0.76232335062342
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H	-3.16176240127918	0.90800854945271	-1.96997630934927
H	-4.76326947755141	0.28182449677185	-1.46450713106800
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C	3.35261897143352	1.63910678406410	0.10515341481688
H	2.06078337035966	1.82711002625266	1.88880452237410
H	1.91515879610220	3.22619636926631	0.75199990398113
H	4.11036841493177	1.29016976264905	0.84015556732023
H	3.82759767676867	2.41656213753067	-0.53233785571815
C	3.70979741271890	-0.46046559618253	-1.28889762415285
C	4.36989636920288	-1.39322235356181	-0.26381215679835
H	4.48499209143829	0.07175491916718	-1.88240668781578
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H	5.01236007232245	-2.13416117240725	-0.78167690308337
H	3.59185711014223	-1.92780121019141	0.31412009887540
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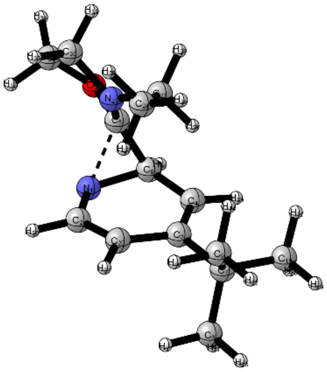
TS2(exo)



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C	-1.85843051348592	1.18846099946679	0.87164806532861
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C	2.28281974063244	-1.66248284075008	-0.91934197480110
C	2.89138915604067	-1.23681818802580	1.47382322196061
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H	4.66727036057074	-0.34830595934240	-0.41946658543913
H	1.42194346981972	-2.29464448530294	-0.62097579991816
H	3.17256188389832	-2.31822224561939	-1.02074854529871
H	2.06228091094545	-1.23569737845548	-1.91788853133274
H	2.05175325207553	-1.86466774891163	1.83590541995999
H	3.12885181603807	-0.49220934941027	2.26048664524179
H	3.77805683172172	-1.89176262705155	1.35208136723950
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C	-1.74659788616370	-1.18570019959780	0.09386649858757
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C	-3.92250252968307	1.77483915822855	0.28818747193904
H	-4.26229864236628	-0.40055297187003	0.03730397624848
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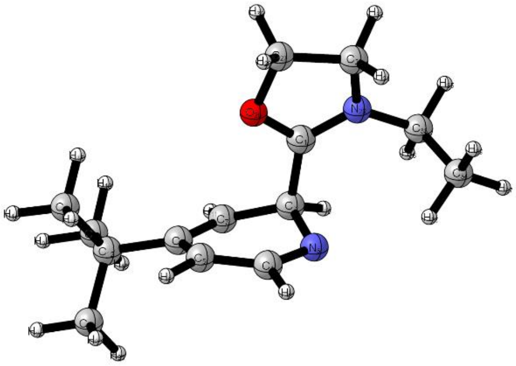
Int2(endo)



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C	0.18178192265934	-1.34095576585638	1.47466825165562
C	-1.04983284299158	-0.67954055643095	1.44168138510059
C	-1.62648255296713	-0.41033004710731	0.14015055187202
C	-0.82440513047089	-0.54403635577229	-0.96863889371857
H	0.50925879101771	-1.80931806826018	2.42644146496963
H	-1.64854740575723	-0.59362711195406	2.35973686512942
H	1.09278281014781	-1.27874370912525	-1.67660785615781
H	-1.21487469061021	-0.48466191540506	-1.99372078540235
C	-3.12448619962351	-0.06772377415888	0.04579154096826
C	-3.36933223438014	1.25148059873872	0.81767922675797
H	-4.44225119070089	1.53586698550428	0.77491801831343
H	-2.77462581238277	2.07868259823211	0.37737504281819
H	-3.08266858613051	1.15931918868621	1.88438512608873
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H	-3.45850611148818	-0.80090399474668	-2.00464983495777
H	-3.03455106481194	0.93958721125461	-1.91323948440856
H	-4.67044886974184	0.38724000766215	-1.42898842315339
C	-3.96515953036656	-1.20005466350627	0.68216766036291
H	-3.69655406291020	-1.35998158746520	1.74504748634033
H	-3.80354551871615	-2.15714260958323	0.14412534235226
H	-5.04782010381080	-0.95637657242040	0.63488350090022
O	0.93905776558538	1.47268486272677	0.14806353055135
N	2.80792581781803	0.58923501810843	-0.63865732516618
C	1.99101432950111	2.41588177409494	0.55457698743321
C	3.30506043031080	1.70584687658299	0.18766409546661
H	1.86787517281278	2.60458411985999	1.63579064144684
H	1.82383604068119	3.35154535772794	-0.01270799091309
H	3.84436411900061	1.31172894075470	1.07445930719481
H	3.99674549148442	2.34179998988896	-0.39817456142706
C	3.71518514144449	-0.38484165981160	-1.25089891889292
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H	4.51807470465603	0.19549422261208	-1.75017655611686
H	3.15056111021848	-0.90786099162226	-2.04598929687845
H	4.92518374472588	-2.11979233474959	-0.76402435491493
H	3.43358316734355	-1.91069700495776	0.24611950373476
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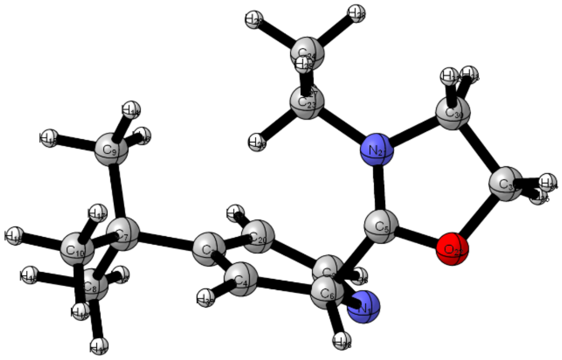
Int2(exo)



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C	0.65694661243185	0.70013501380822	1.33828030854637
C	-1.92059317815765	1.10363307566655	0.96672899203408
C	-0.50973693205050	1.65203288726076	1.25019834553021
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C	3.81223608164866	0.14167178263148	-0.24372761270735
C	2.25562092314110	-1.76968200586561	-0.78885892530702
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H	3.69734274130142	0.56918793212471	-1.25963761945026
H	4.68811773206043	-0.54122897105244	-0.25468983494194
H	1.36831529793412	-2.35706637110319	-0.47417844271932
H	3.12348278745698	-2.46116416626501	-0.83106029240996
H	2.06808096515218	-1.39565021181086	-1.81482880245897
H	1.90248630668710	-1.77272306229155	1.96527099674267
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H	3.63804807779151	-1.93911000989768	1.54532183830546
C	0.97150558717409	1.00274807413490	-1.04394850246152
N	-2.33499620572123	0.08833623272794	0.21395783954034
O	-2.91568807133558	1.92375960552890	1.30200713194013
C	-1.62227133997919	-1.15794438451713	-0.09481626055507
C	-1.52673312868591	-1.43985347985307	-1.59084942731632
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H	-0.61826317006144	-1.07089858414999	0.35848786898381
H	-0.95371403283531	-0.63209562723181	-2.08760392972496
H	-2.52377059573806	-1.53412303557170	-2.06744459017903
H	-0.98647139929526	-2.39454792207312	-1.74643670312442
C	-3.78963453302627	0.18777407411664	-0.03657562029077
C	-4.09299143922369	1.59243836468882	0.49819915125803
H	-4.30980204998382	-0.62315474491925	0.51654125029196
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H	1.48300038294102	0.76389895355477	-1.98711016581294
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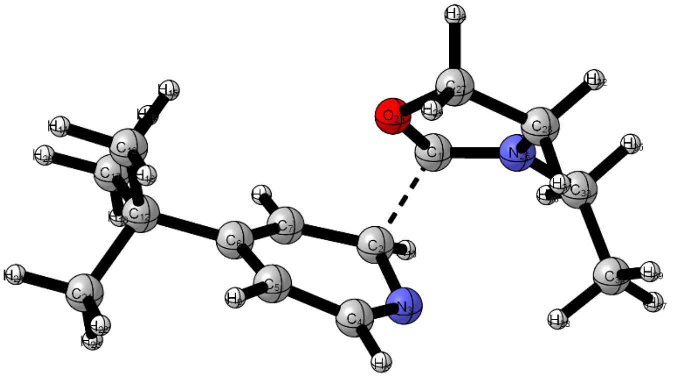
TS3(endo)



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C	0.27513176520092	-1.26462746494881	1.41522172750399
C	-0.99949789162497	-0.69089738452293	1.38524293692331
C	-1.63230809484130	-0.50318557702199	0.11051046830341
C	-0.86992471367051	-0.74481589082684	-1.01897876374300
H	0.70383939856443	-1.57586743174818	2.38849102560898
H	-1.53919933037626	-0.50802368608783	2.32569639991781
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H	-1.28753517994850	-0.64494979695875	-2.03063513581664
C	-3.10753448070043	-0.07285981290617	0.05237990643603
C	-3.22882289416224	1.32448068934752	0.70796852914516
H	-4.28232223805559	1.67456892736785	0.68443956993413
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H	-3.56926832553262	-0.96646011312268	-1.90798378802834
H	-3.06972614617378	0.75508356672223	-1.99220606731927
H	-4.69943904434659	0.32299312497280	-1.38659021050569
C	-3.97836855493204	-1.08650673613588	0.83208562011619
H	-3.66923574988193	-1.16272177107161	1.89353249982808
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H	-5.04486955402705	-0.77828628673040	0.81023013167495
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N	2.81990602982285	0.64007095246366	-0.67243334963673
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C	3.17618720907059	1.54905654054469	0.43730480602914
H	1.50601349708475	2.34275283371572	1.67851066543146
H	1.85629742126661	3.31528288815393	0.19266291637581
H	3.47445352141464	0.96140210899106	1.33184590129663
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H	4.98524936729821	-2.02736692385685	-0.87223752924289
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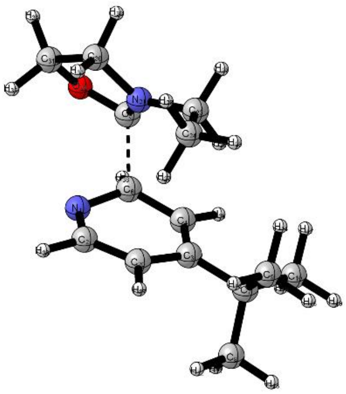
TS3(exo)



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H	3.63482172914941	0.61537110630241	-1.34439266927364
H	4.65812000961221	-0.51722031939954	-0.40067263151378
H	1.33003748107994	-2.31601505503842	-0.51508023173837
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H	1.98302451199807	-1.33752488201422	-1.86733794701912
H	1.95612258885570	-1.77410308571910	1.91031064646665
H	3.11730353525151	-0.45216912180752	2.26430124113824
H	3.67445372596824	-1.93322068046971	1.42593090556816
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H	-2.40281290720136	-1.64790619645760	-1.97739687515924
H	-0.94192308466407	-2.55109722734613	-1.48099383735461
C	-3.71305912821492	0.31322564744318	-0.30252458763382
C	-3.98530164766228	1.69935839783841	0.28964226060798
H	-4.44554575291633	-0.46039701985412	0.01574557548588
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H	-0.18302674658069	2.75452722780606	-1.77144661471866
H	1.36415896128065	0.82726428403282	-1.97299074429715
H	-0.58581421407125	2.19739551091947	2.33695484827793
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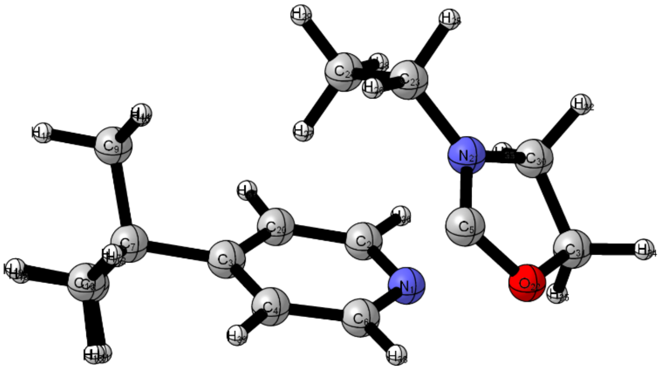

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C	0.80251857142239	0.80020120567365	1.08884882411398
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H	3.96754334107093	0.73397810906878	-1.43037358561286
H	4.97016528758098	-0.28820437682719	-0.35100341180513
H	1.71746048961203	-2.23710679011476	-0.61848373842083
H	3.49289205465680	-2.31888760801146	-0.87887201709264
H	2.47362993153829	-1.31837404048829	-1.96060159550763
H	2.18193377593050	-1.57776882470129	1.82943781391172
H	3.23753615776782	-0.17044396447540	2.19471753832674
H	3.93592918660494	-1.65365899983554	1.47697906213806
C	1.18995623371624	1.03249401304603	-1.26229166098382
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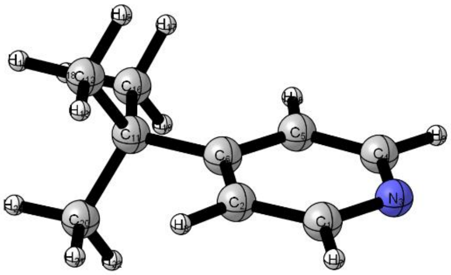
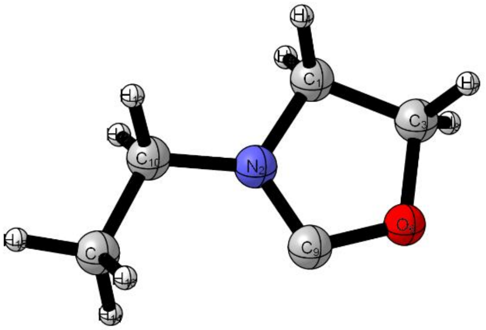
H	-1.64791542273655	-0.97557997753646	-1.72969991994903
H	-1.24631784625303	-2.63344578218904	-1.18871518604272
C	-3.67761210478863	0.69428683154174	-0.35143791405976
C	-3.88346790849309	1.83735184977832	0.64195920856860
H	-4.60837241278060	0.35927030592367	-0.85584791154122
H	-2.91805840672141	0.93930217176034	-1.11950856394604
H	-4.92078037033639	2.21798203159982	0.69421905343572
H	-3.17212708098286	2.66887107607336	0.47760572455251
H	-0.25479338714845	2.29423599546684	-2.28302292905961
H	1.74871061831923	0.82753989769622	-2.18776173257899
H	-0.93746533347720	1.88790706056415	1.80821225779371
H	1.03199877362299	0.40634397753206	2.08788312881702

2a



C	-1.79008603469844	-0.84749726611518	0.70034252335733
C	-0.65505750874216	-0.84560137429973	-0.12234079880394
N	-1.93086738145798	-0.06379086219537	1.78900052987385
C	-0.90193653404981	0.75515499485356	2.07216589941252
C	0.27705717558756	0.83061945546943	1.30970268101691
C	0.42765965097997	0.01397727502701	0.17113069910328
H	-2.63416965095453	-1.52130393560923	0.46621058412988
H	-0.62382774859228	-1.51979500903362	-0.99174293153648
H	-1.01477510622379	1.39828711726406	2.96403944091884
H	1.06524483122474	1.53078950293985	1.61780234406003
C	1.67680874417278	0.03224802717942	-0.72200157140235
C	1.25700208782568	0.43945098180351	-2.15549439992491
H	0.52410627994609	-0.27165790788364	-2.58645118611032
H	2.14443616942845	0.45857682405859	-2.82141786959998
H	0.79904798161631	1.44971980065286	-2.16097404443892
C	2.73508144127097	1.02835780369045	-0.21327935024138
H	2.34830518305809	2.06762253176715	-0.19752545319144
H	3.61743912995573	1.00890126197543	-0.88428199729034
H	3.08344901887205	0.77292718683550	0.80818338198839
C	2.29668314808677	-1.38603596432362	-0.74437432119667
H	1.58665155577665	-2.13829648747619	-1.14237116831833
H	2.59688632994260	-1.70273603881767	0.27543955883216
H	3.19967123697458	-1.39703791776259	-1.38924255063811

6

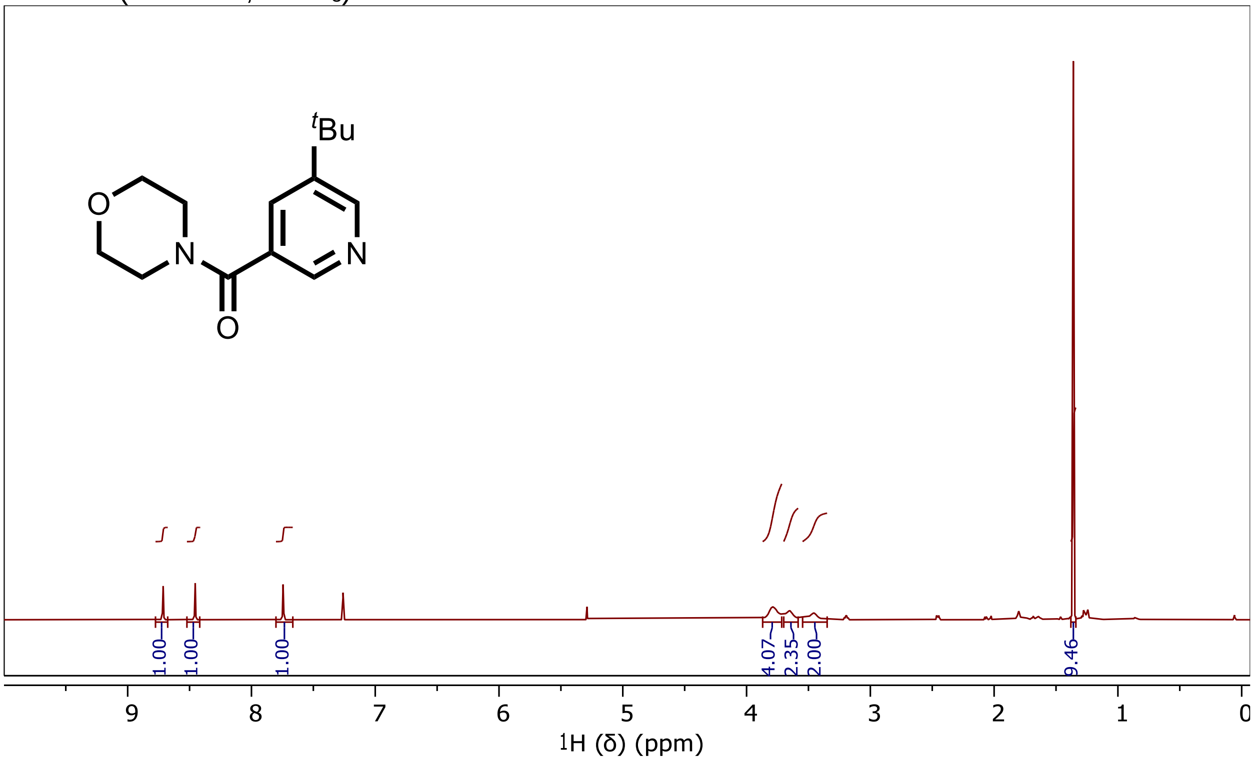


C	-4.70638028597950	1.67215322537420	0.04152243494276
N	-4.99755228866375	0.21700357889482	-0.01985785411814
C	-3.18861775820562	1.67430487784375	-0.14268631770069
H	-5.03618048838942	2.08677725897180	1.01687094568385
H	-5.25255064692879	2.20515779456271	-0.76454011989194
O	-2.84472107349857	0.23262665160990	-0.28628167525561
H	-2.63135209297648	2.06626216423203	0.72953313946694
H	-2.84798716450422	2.19295532174649	-1.05906873587575
C	-3.92710246009502	-0.56016282928651	-0.20582665056311
C	-6.38158007825187	-0.23174834004417	0.12153904148670
C	-6.55585206731972	-1.74269385821772	0.04024691249363
H	-6.98548494393656	0.27157142422329	-0.66710352940387
H	-6.76691195998132	0.15077211384185	1.09376241211837
H	-6.21199281536049	-2.13704985467860	-0.93582035574391
H	-7.62900915375972	-1.99176737545985	0.16338165331481
H	-5.97977472214885	-2.25786215361399	0.83335869904595

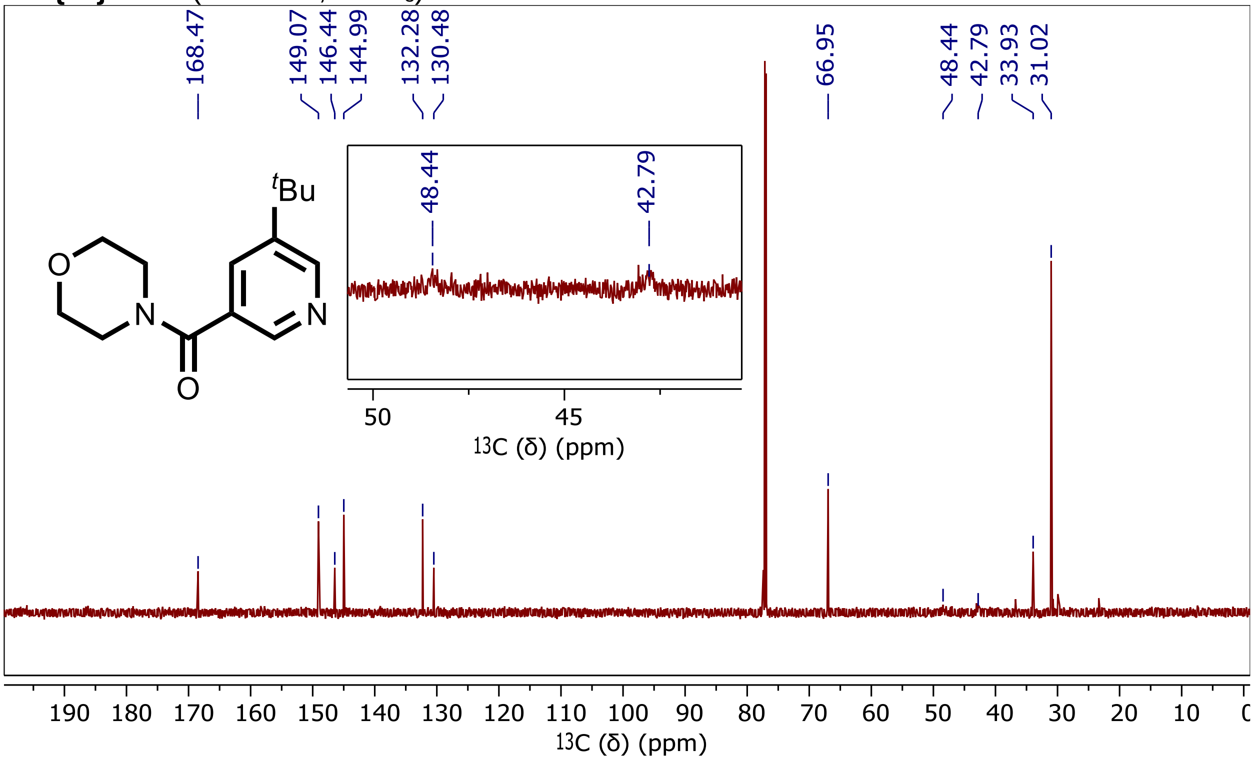
NMR Spectra for previously unreported compounds:

(5-(tert-butyl)pyridin-3-yl)(morpholino)methanone

^{1}H NMR (600 MHz, $CDCl_3$)

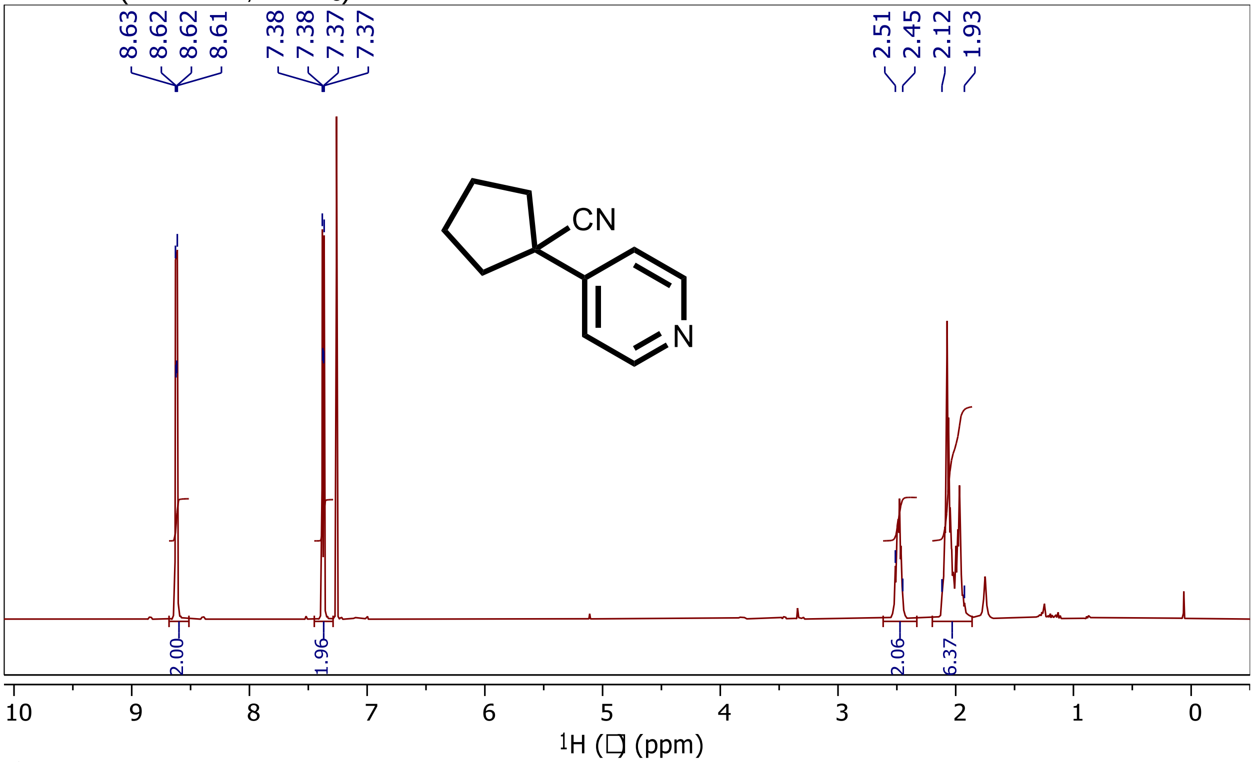


^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$)

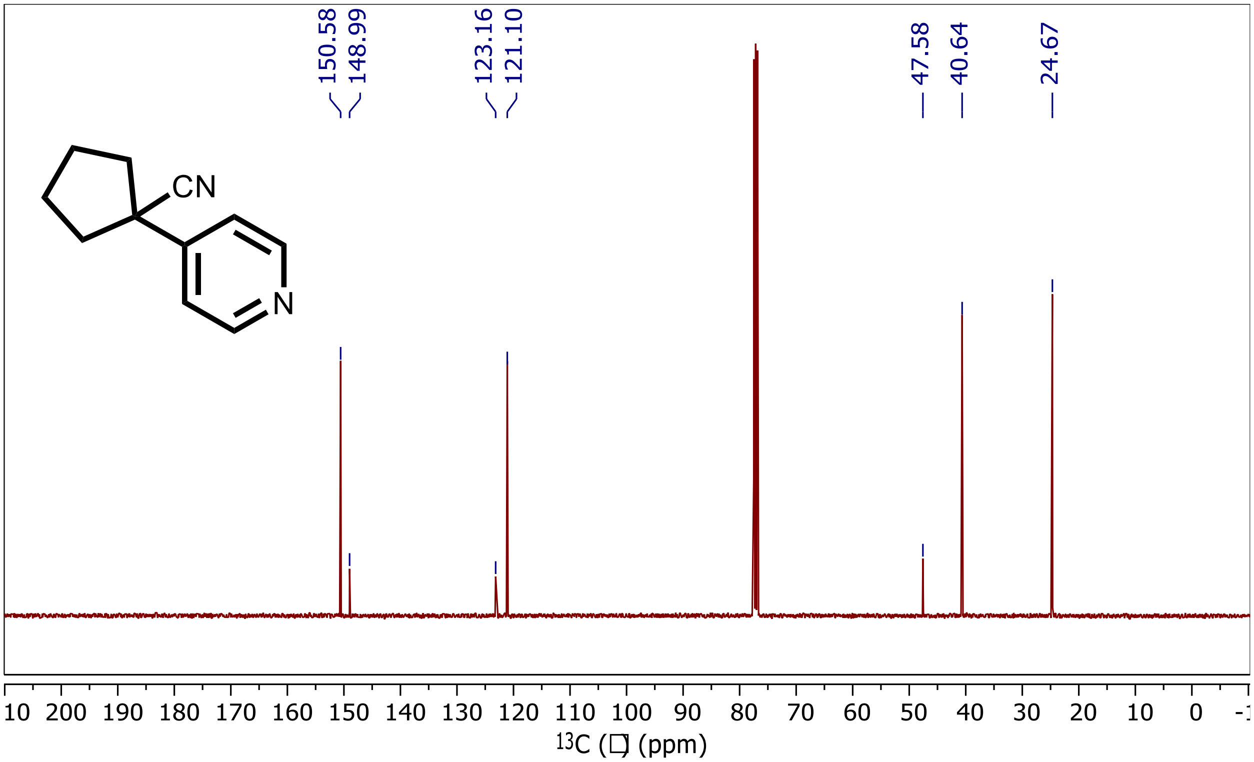


1-(pyridin-4-yl)cyclopentane-1-carbonitrile

^{1}H NMR (400 MHz, $CDCl_3$)

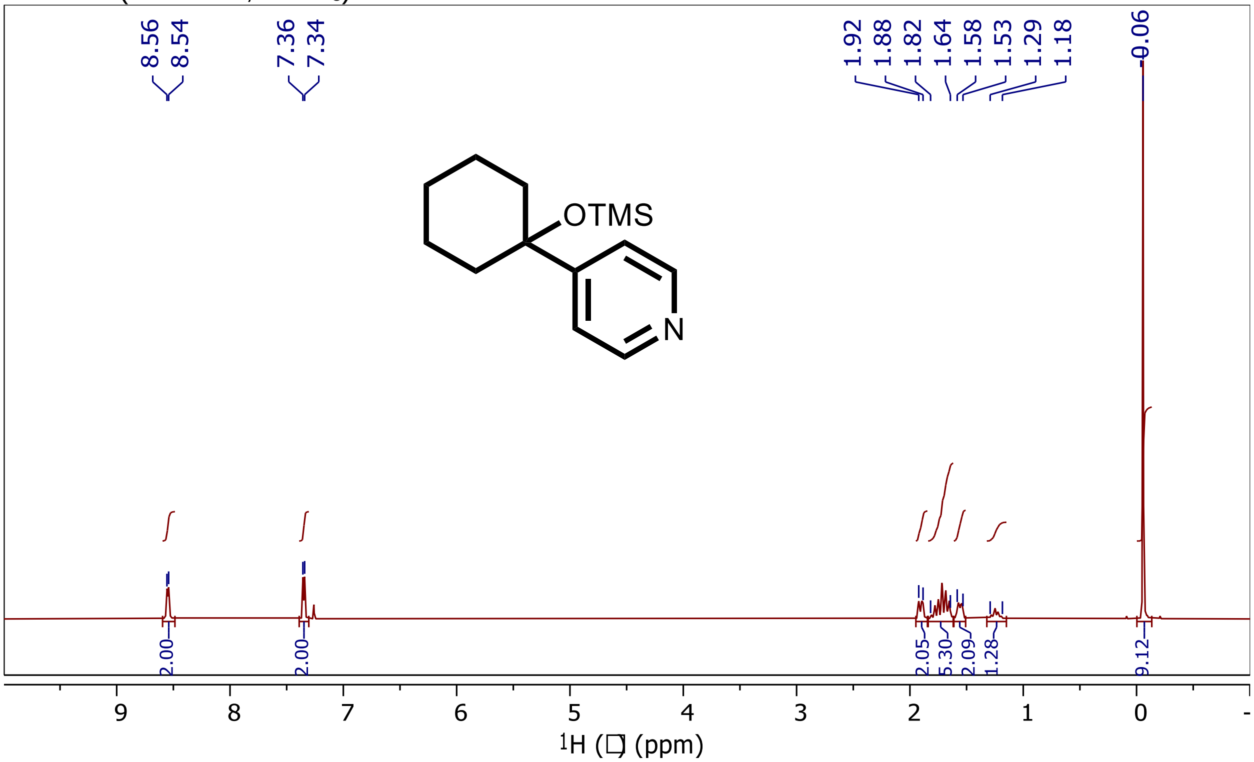


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

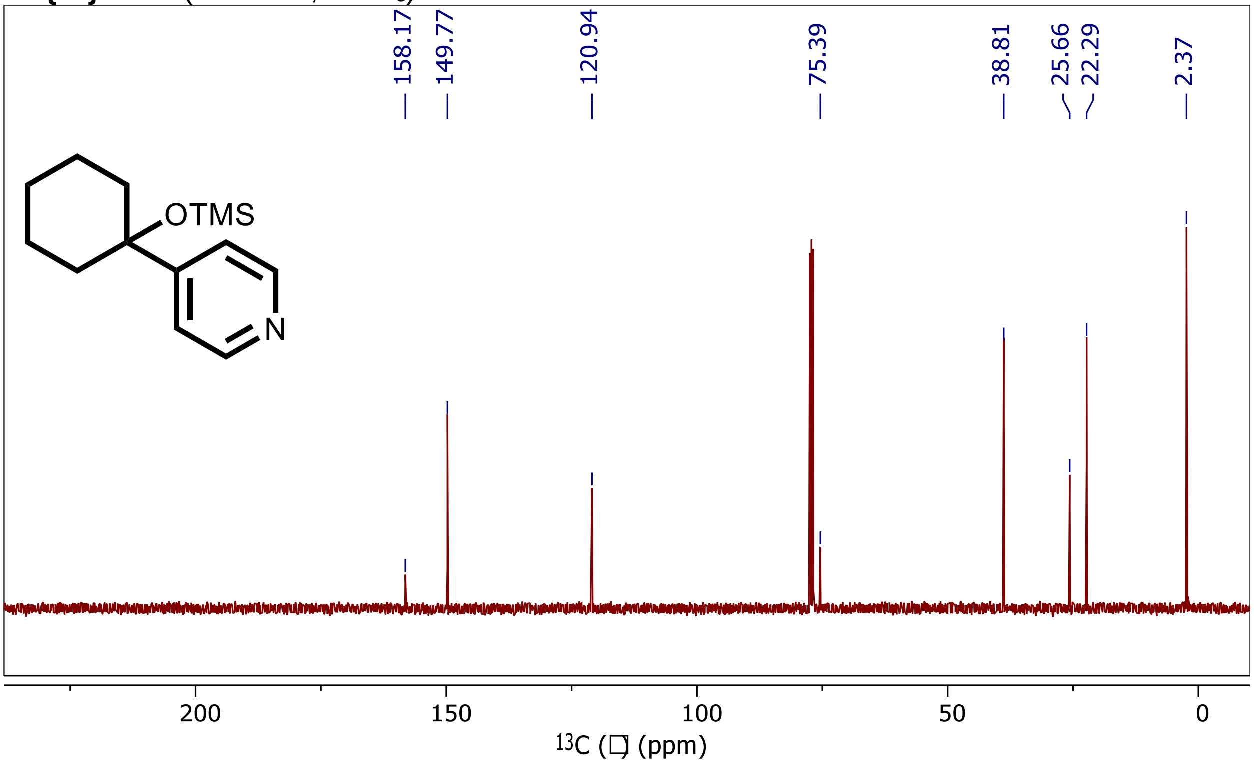


4-(1-((trimethylsilyl)oxy)cyclohexyl)pyridine

^{1}H NMR (400 MHz, $CDCl_3$)

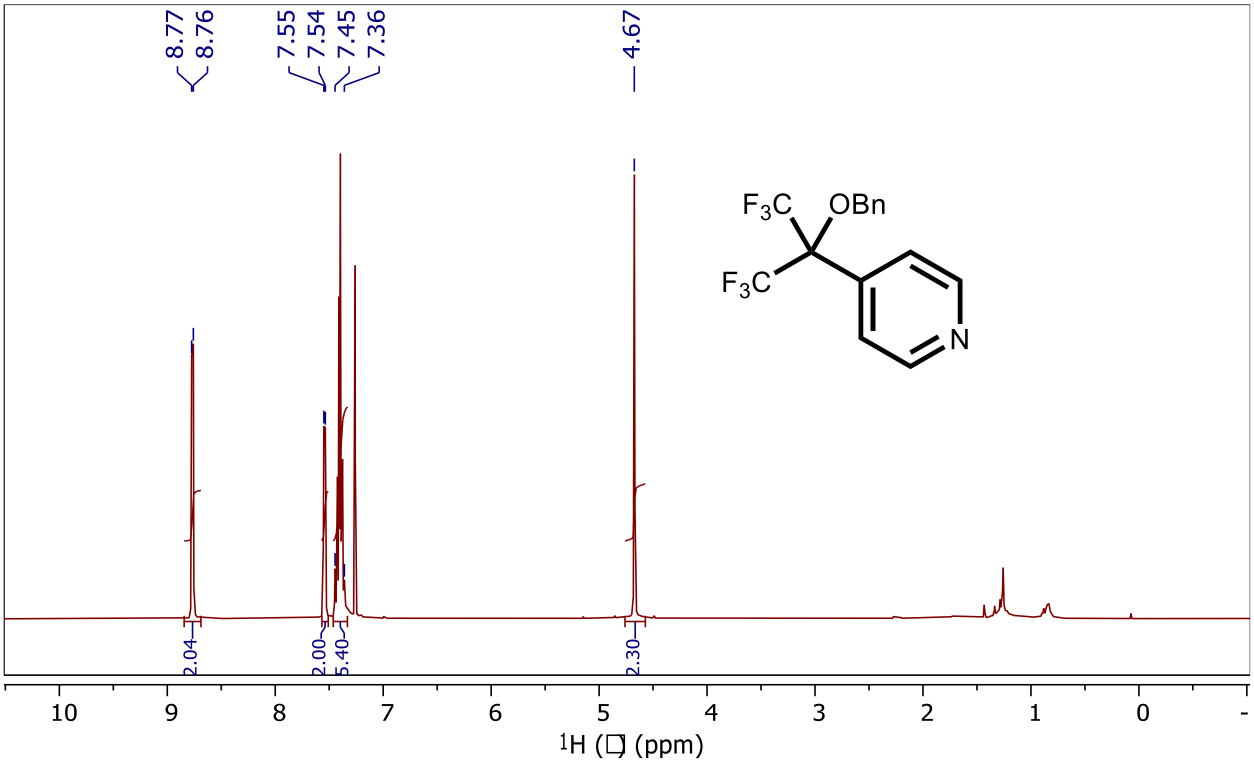


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

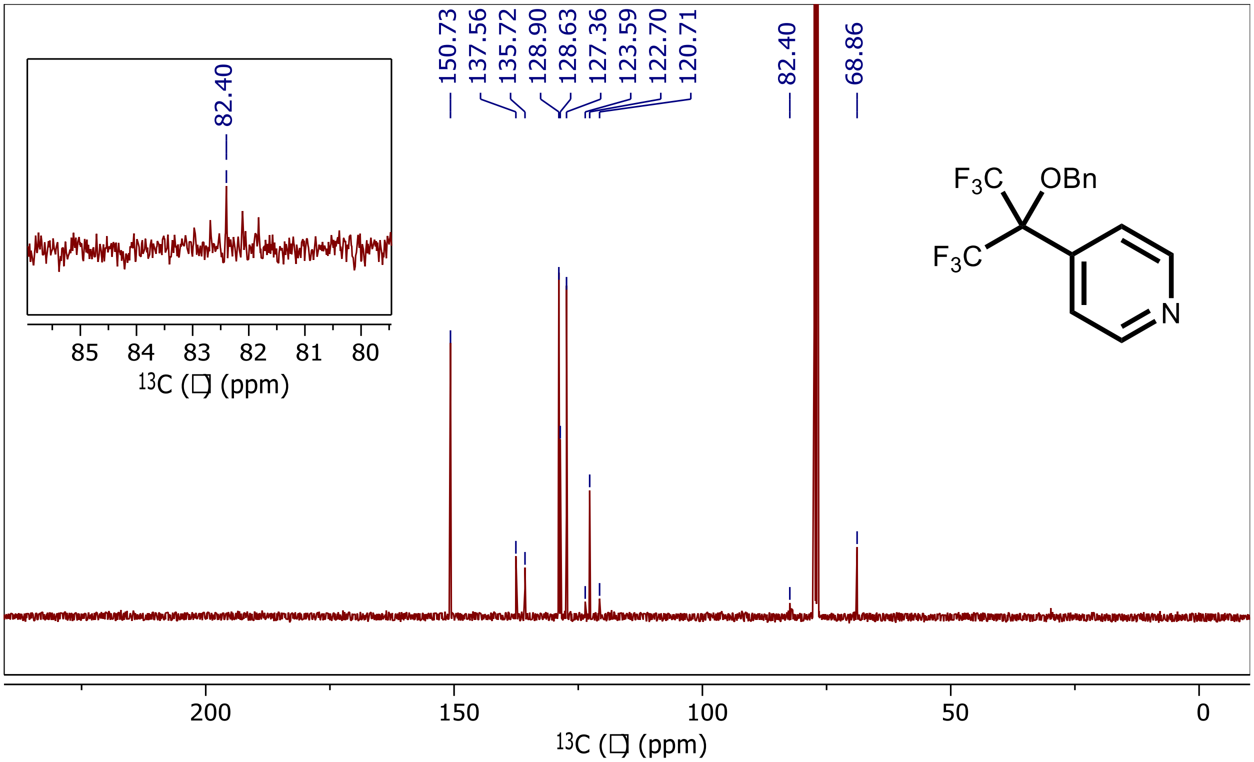


4-(2-(benzyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)pyridine

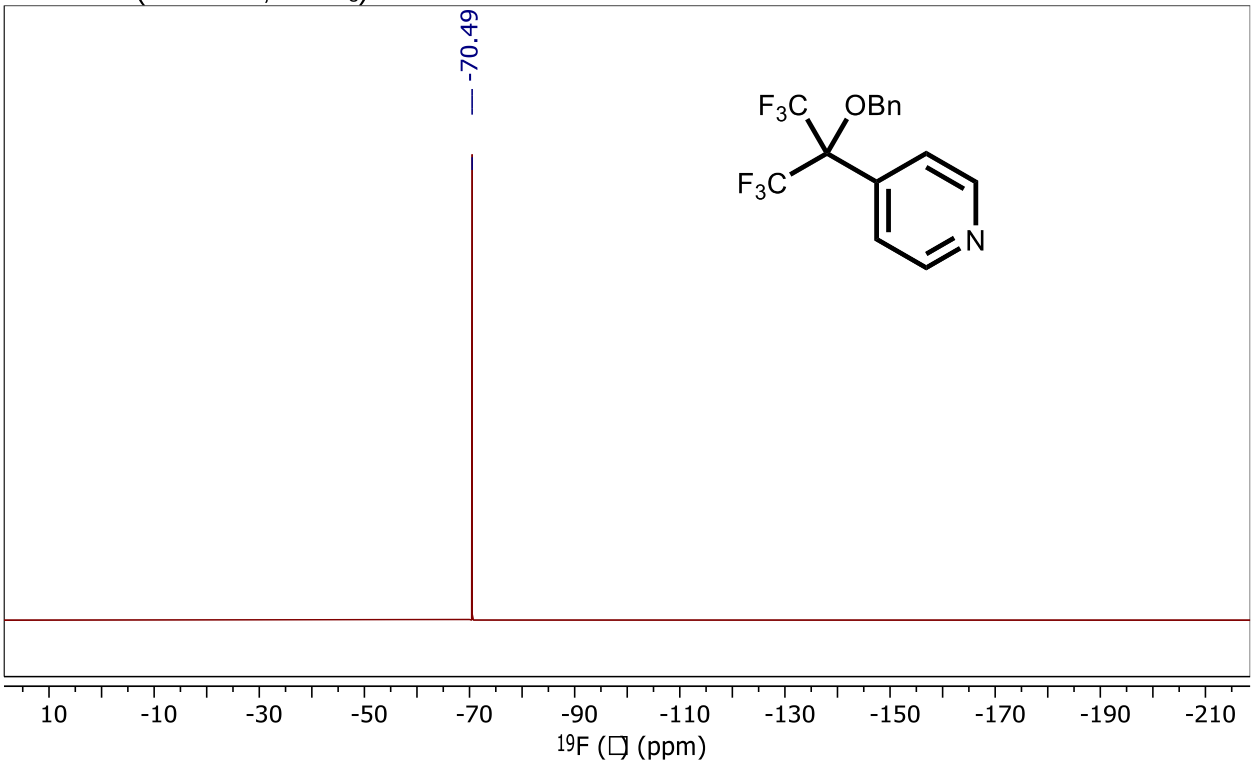
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)

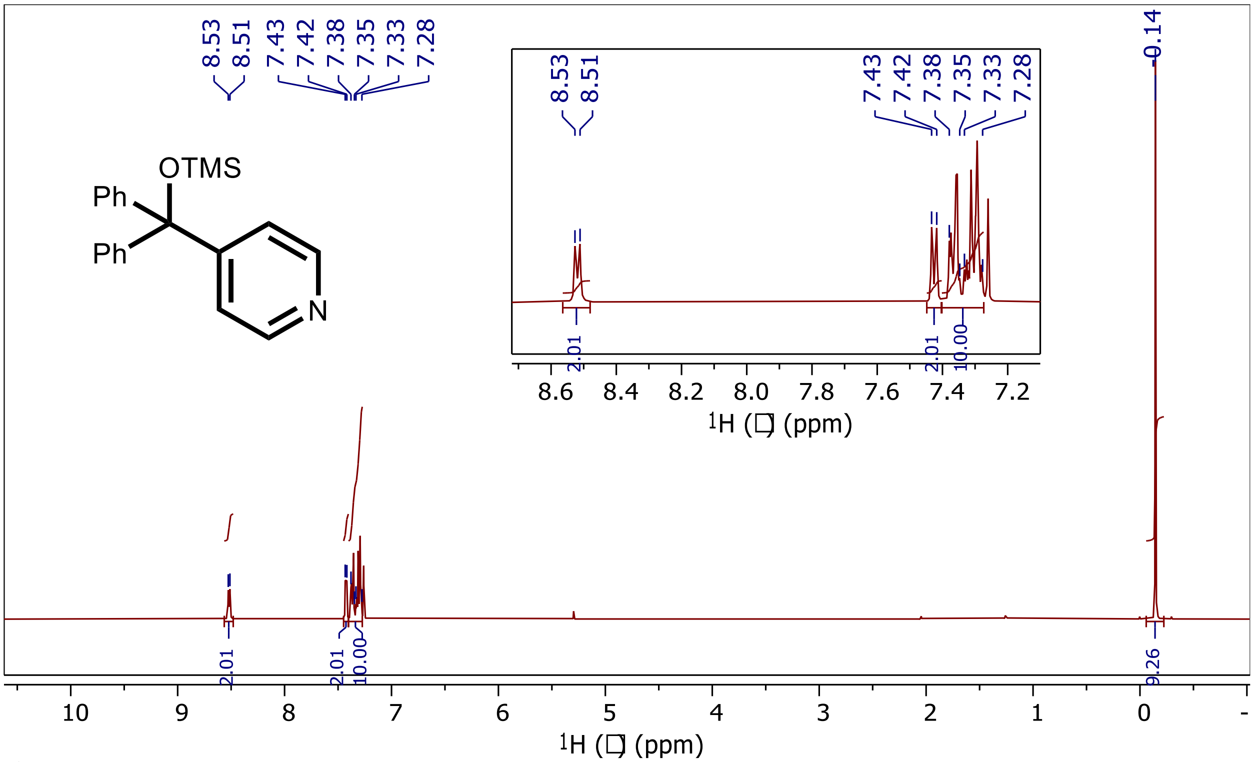


^{19}F NMR: (376 MHz, $CDCl_3$)

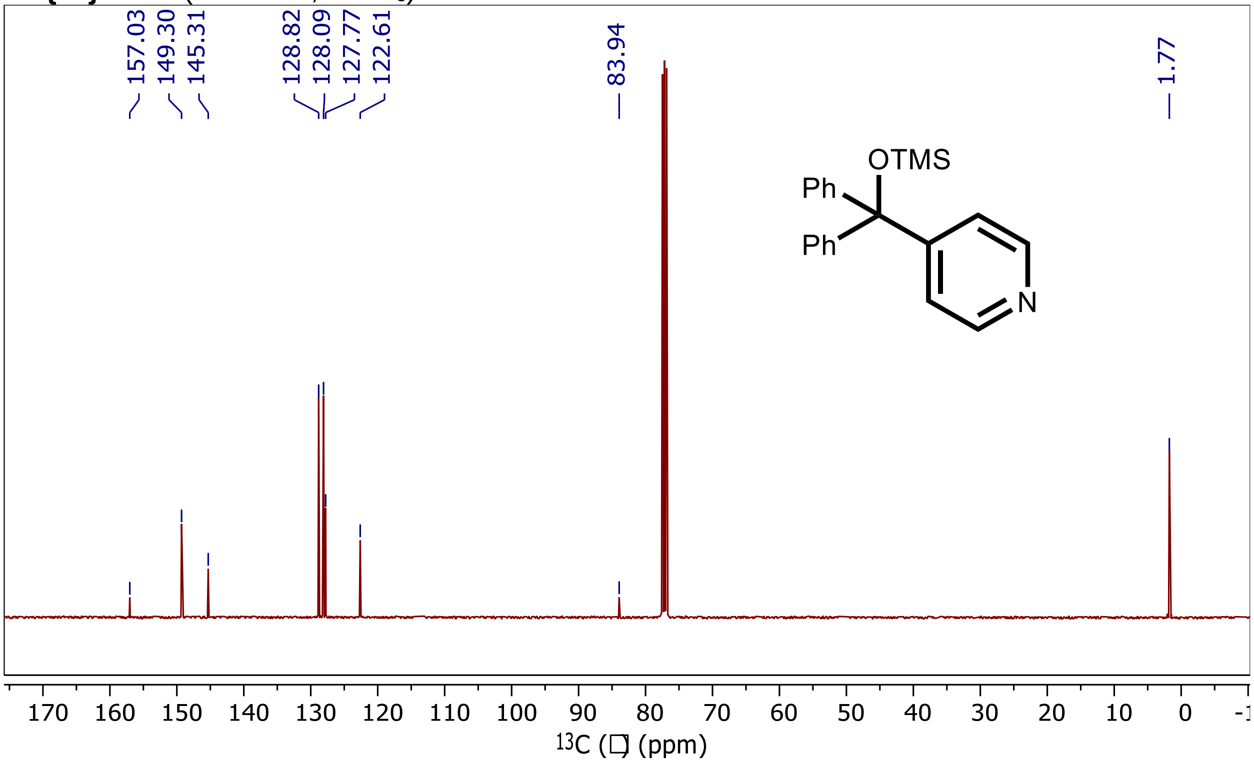


4-(diphenyl((trimethylsilyl)oxy)methyl)pyridine

^{1}H NMR (400 MHz, CDCl$_3$)

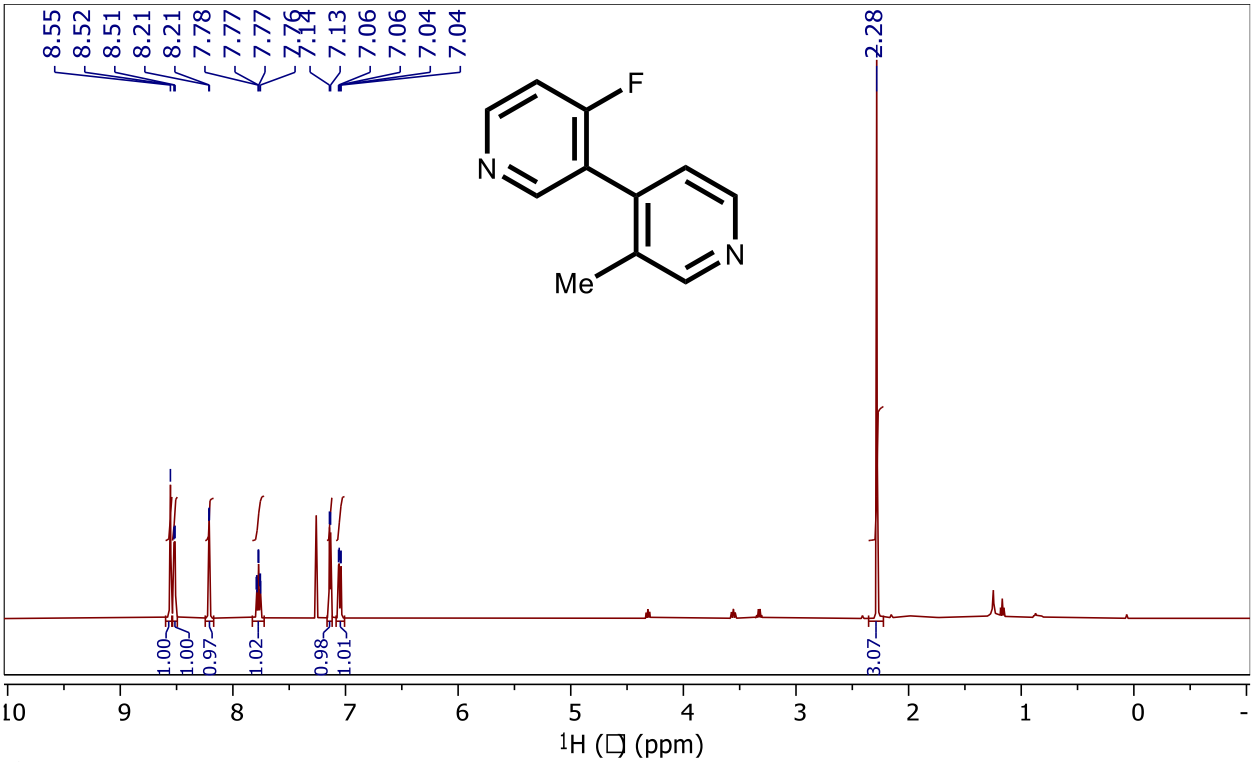


^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)

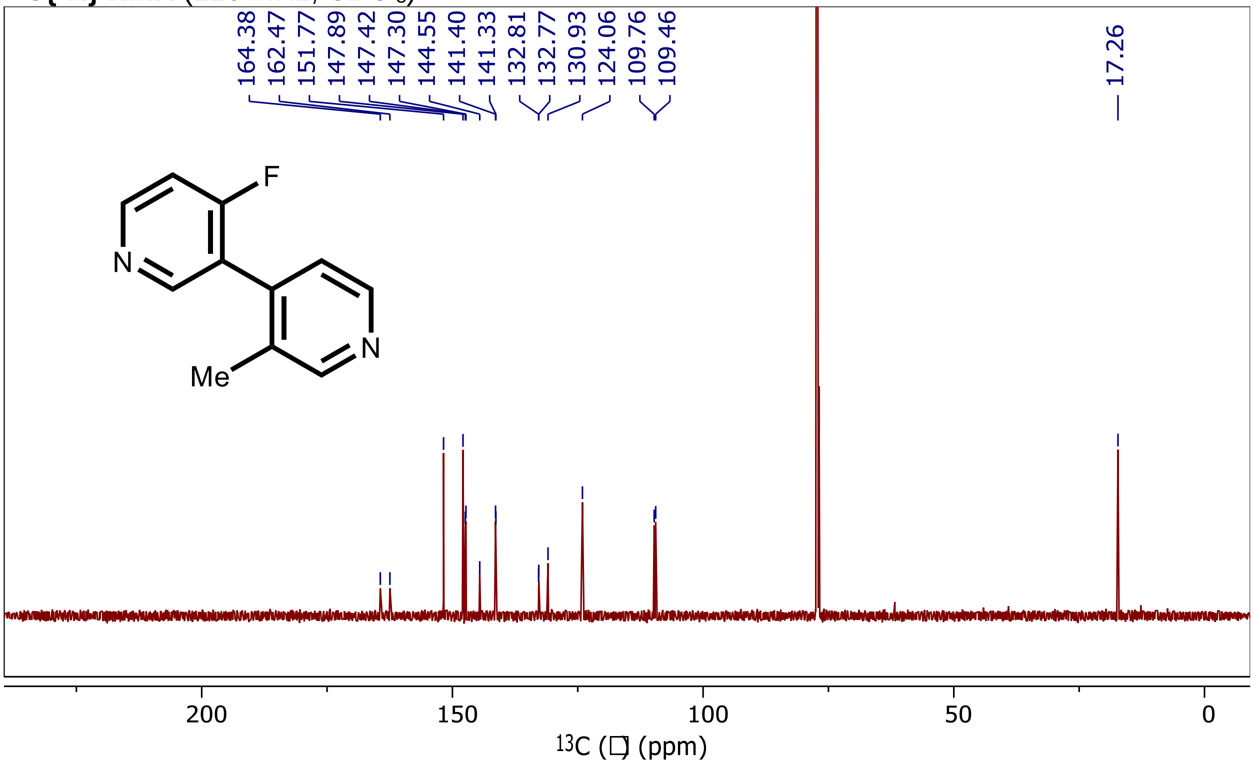


4-fluoro-3’-methyl-3,4’-bipyridine

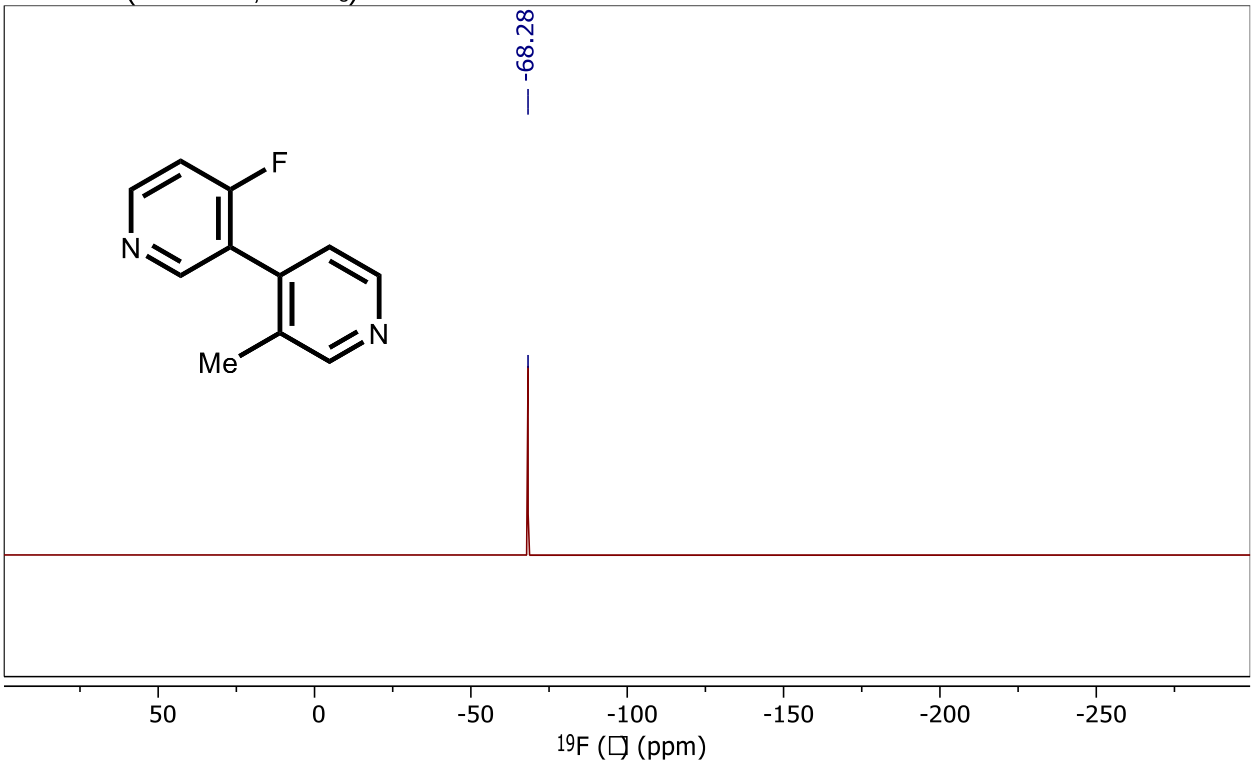
^{1}H NMR (500 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)

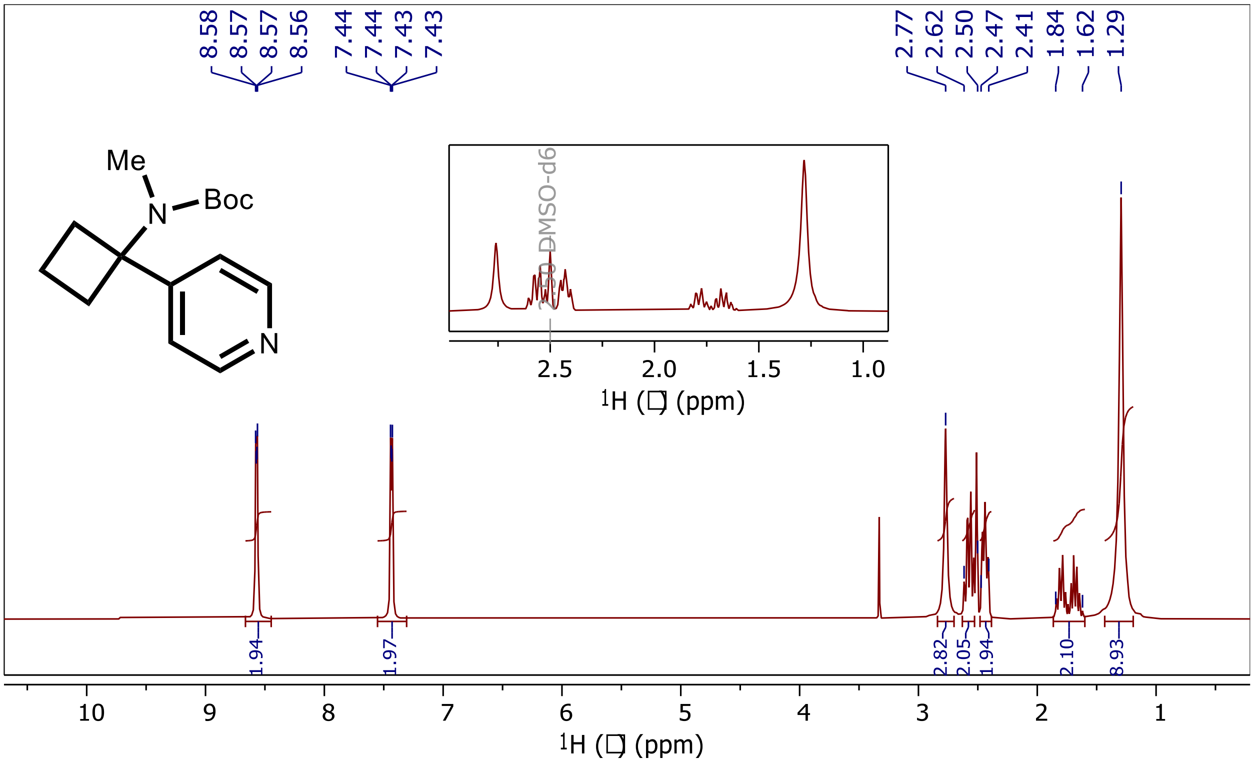


^{19}F NMR (470 MHz, $CDCl_3$)

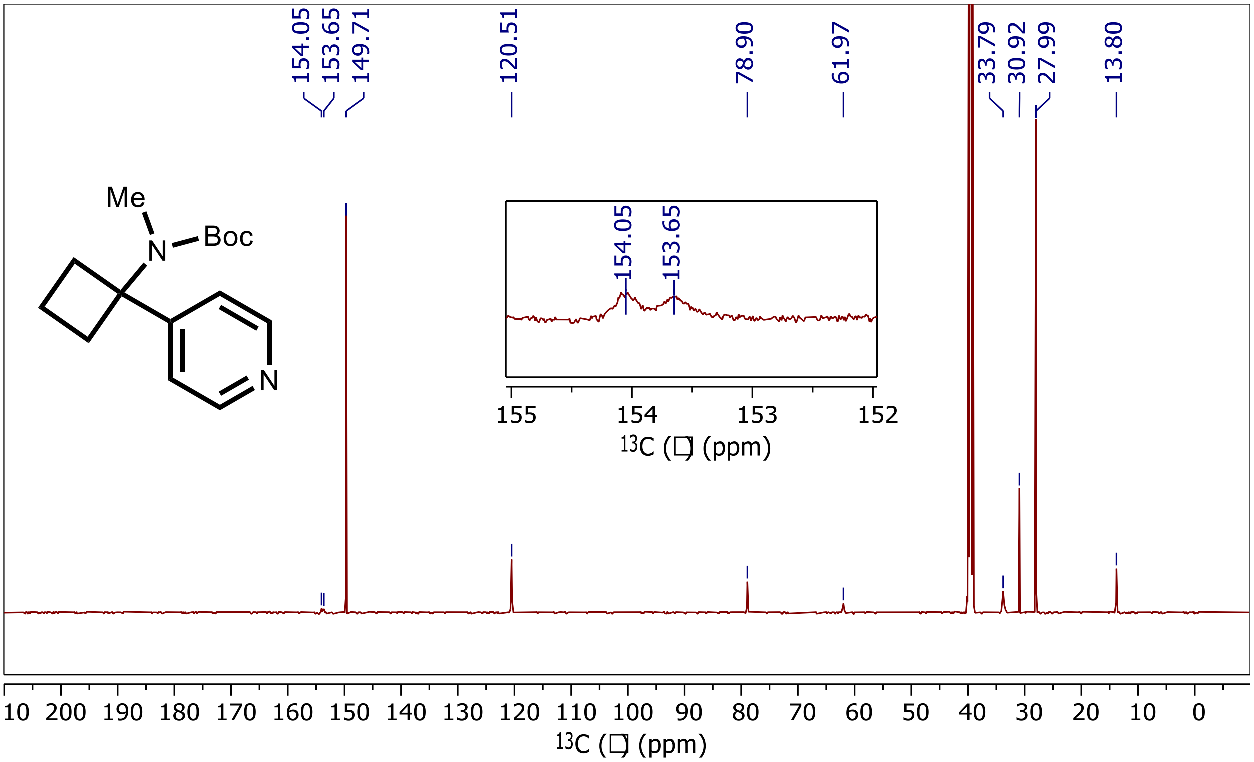


***tert*-butyl methyl(1-(pyridin-4-yl)cyclobutyl)carbamate**

^{1}H NMR (400 MHz, DMSO-*d6*)

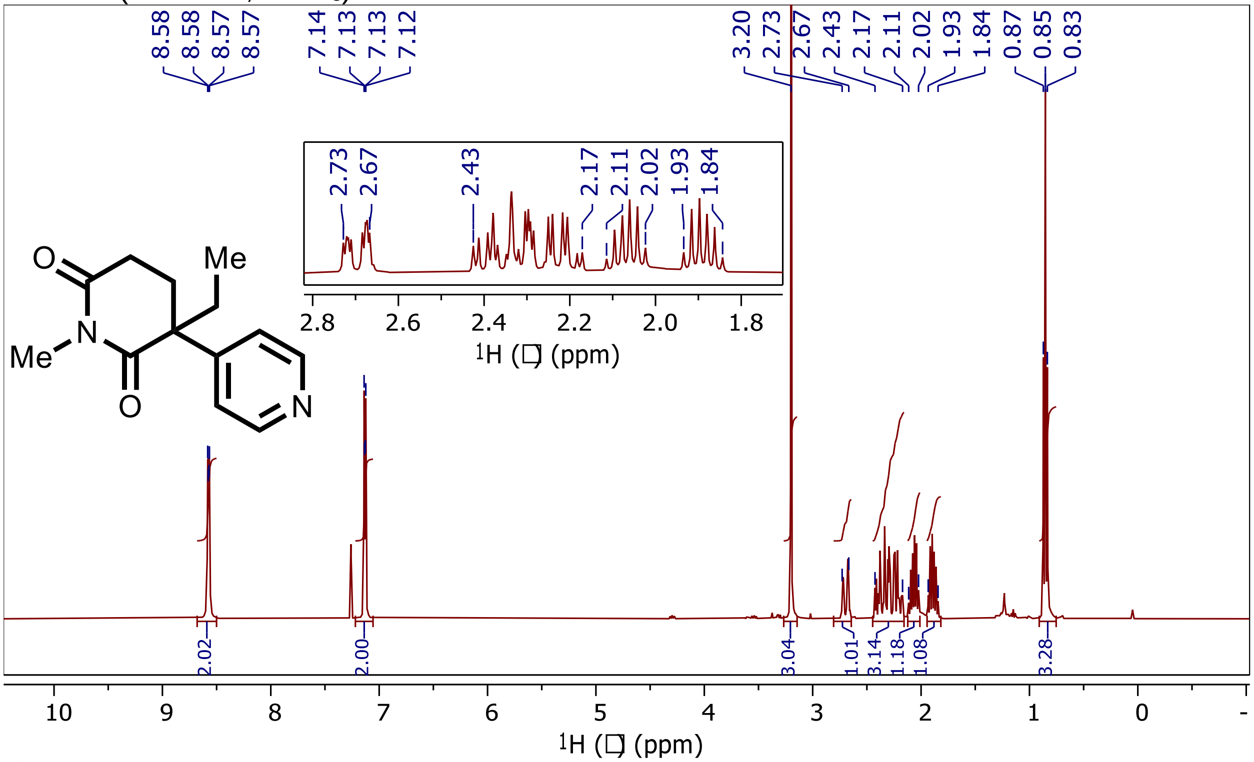


^{13}C{^{1}H} NMR (126 MHz, dmso-*d6*)

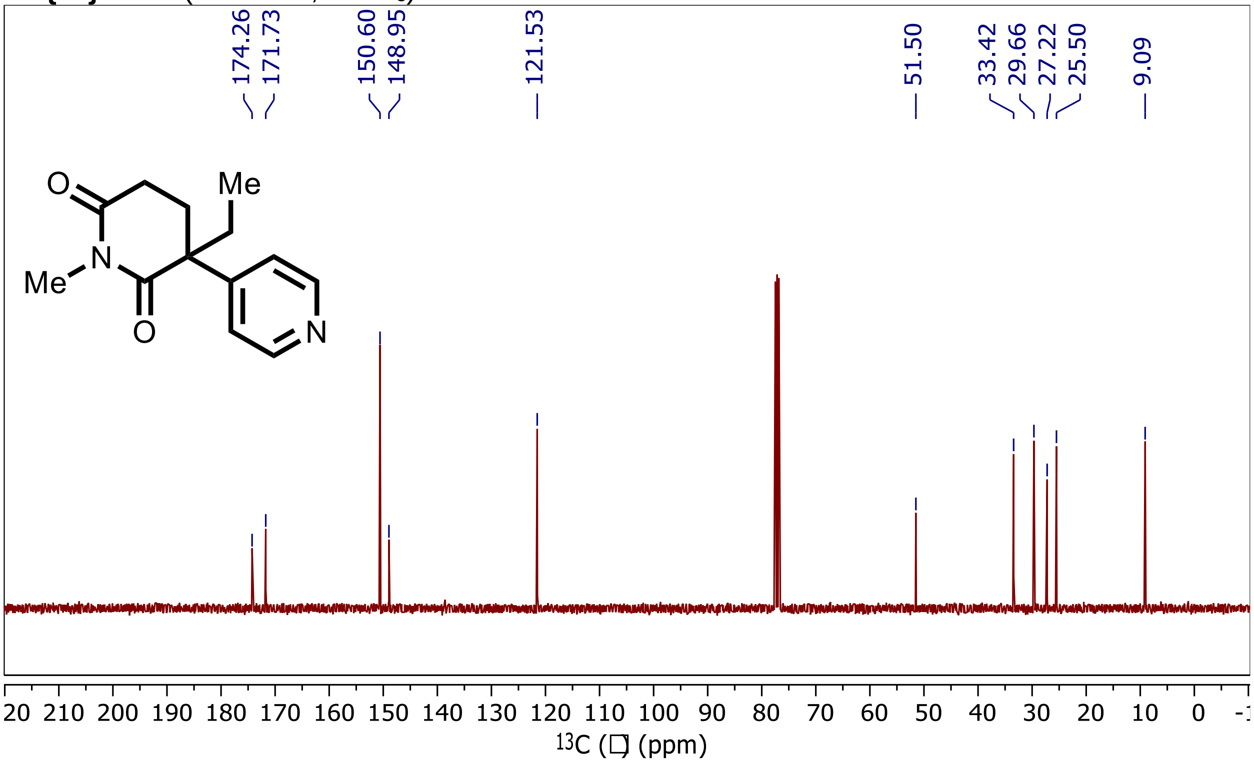


3-ethyl-1-methyl-3-(pyridin-4-yl)piperidine-2,6-dione

^{1}H NMR (400 MHz, $CDCl_3$)

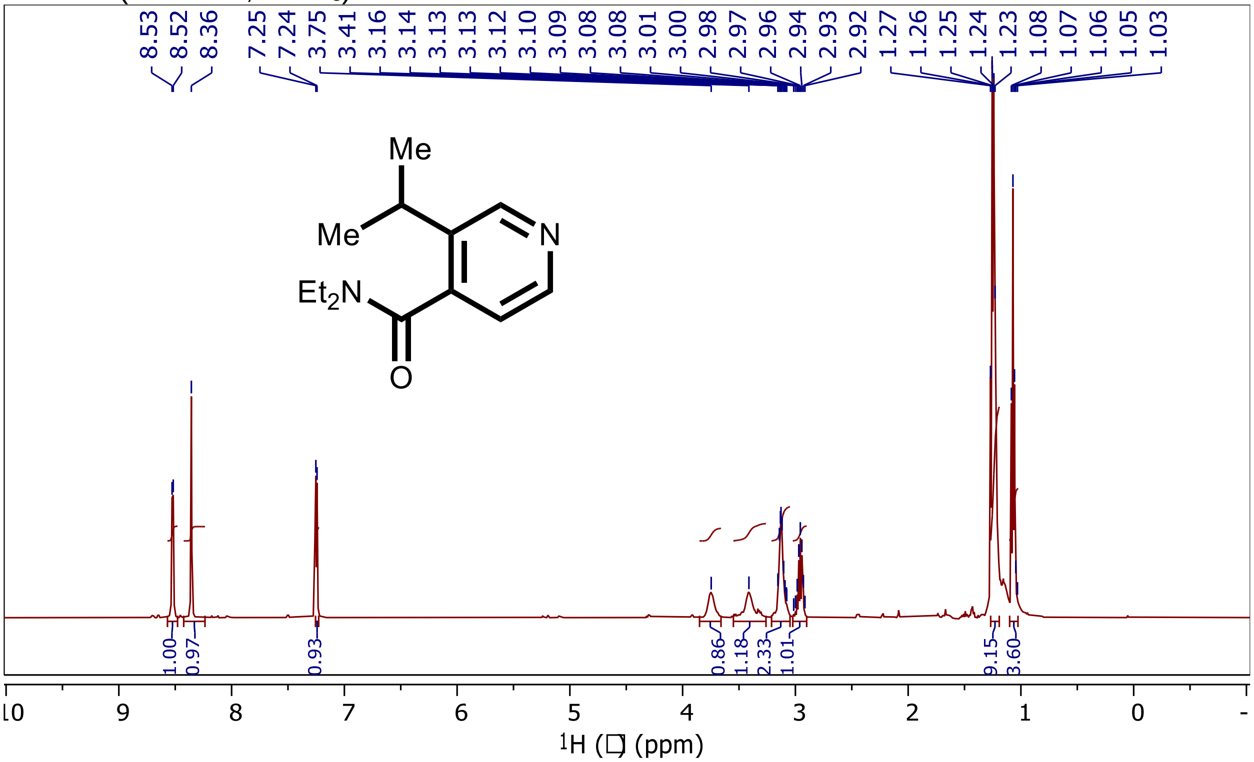


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

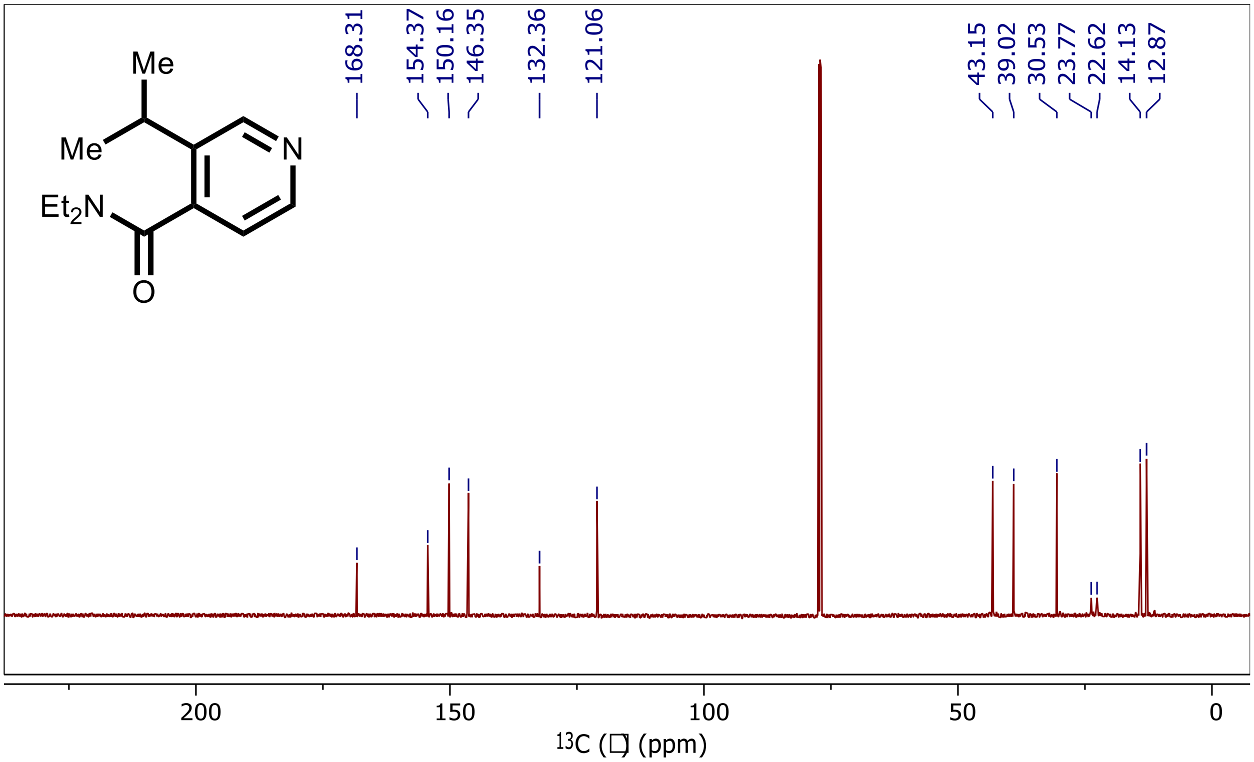


N,N-diethyl-3-isopropylisonicotinamide

^{1}H NMR (500 MHz, CDCl$_3$)

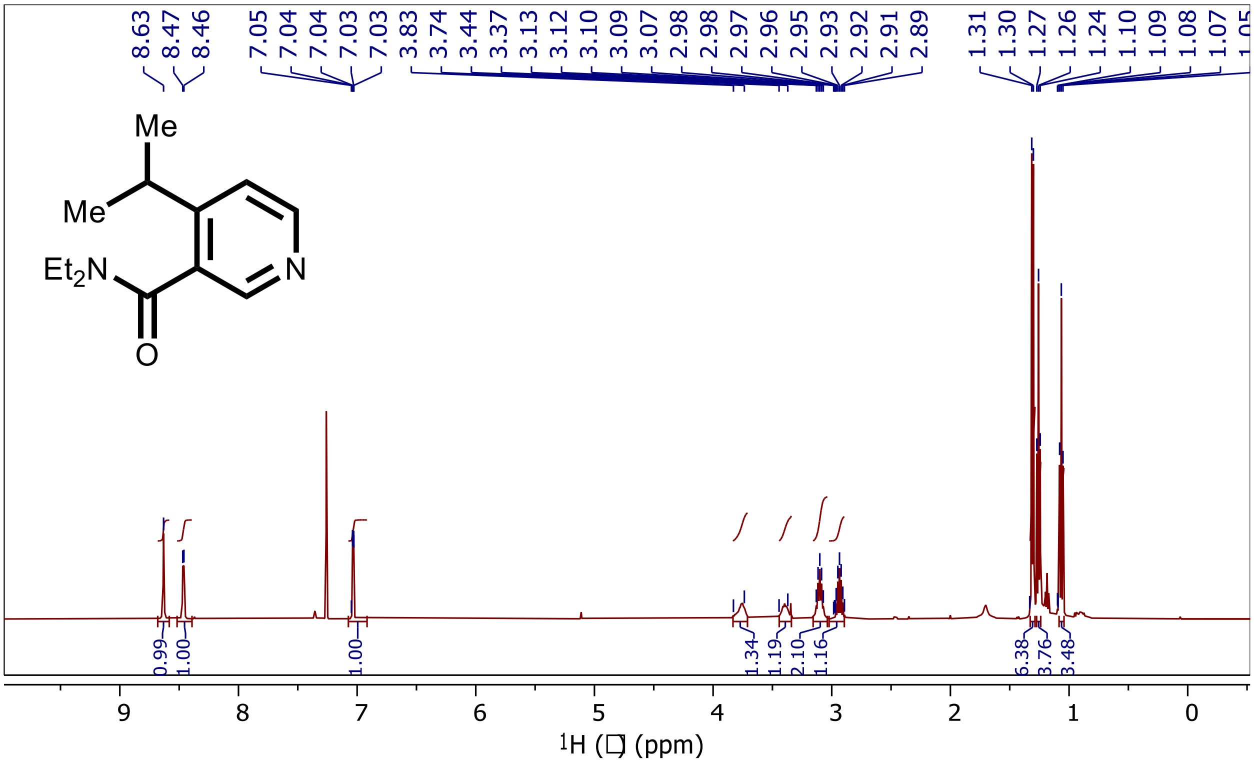


^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$)

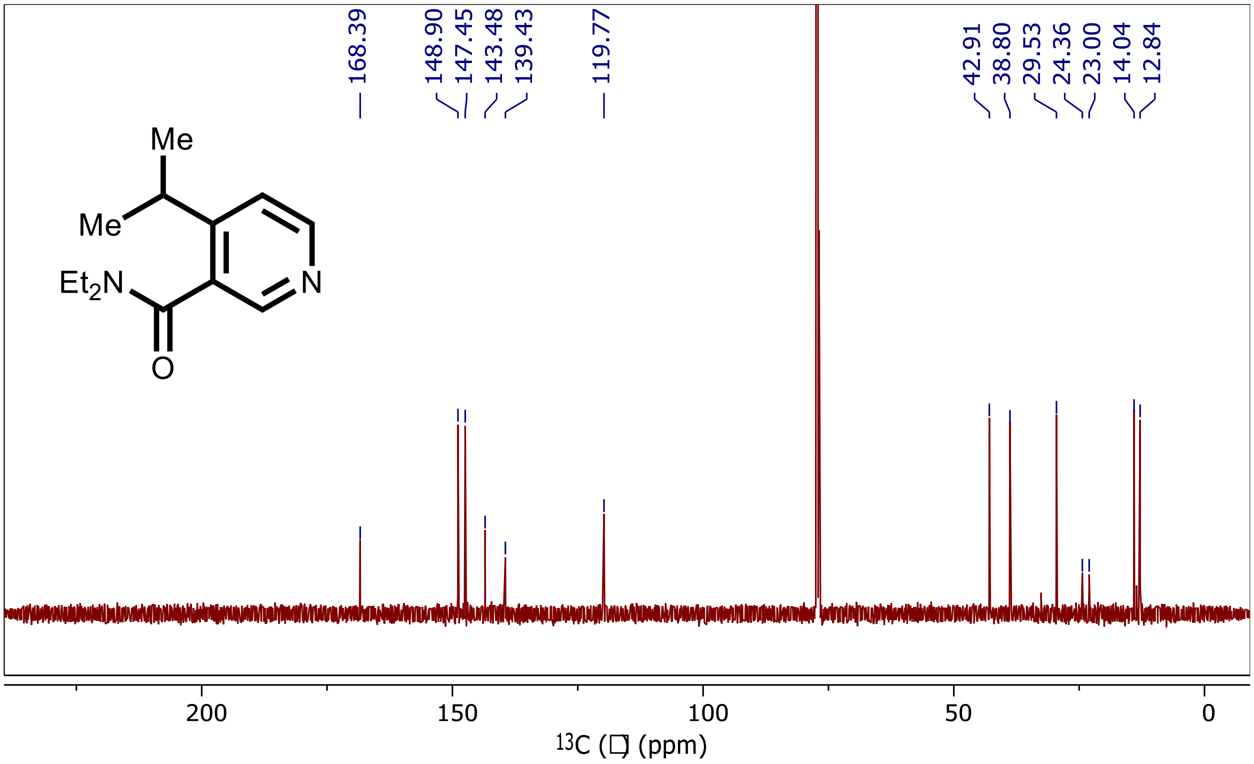


***N,N*-diethyl-4-isopropylnicotinamide**

^{1}H NMR (500 MHz, $CDCl_3$)

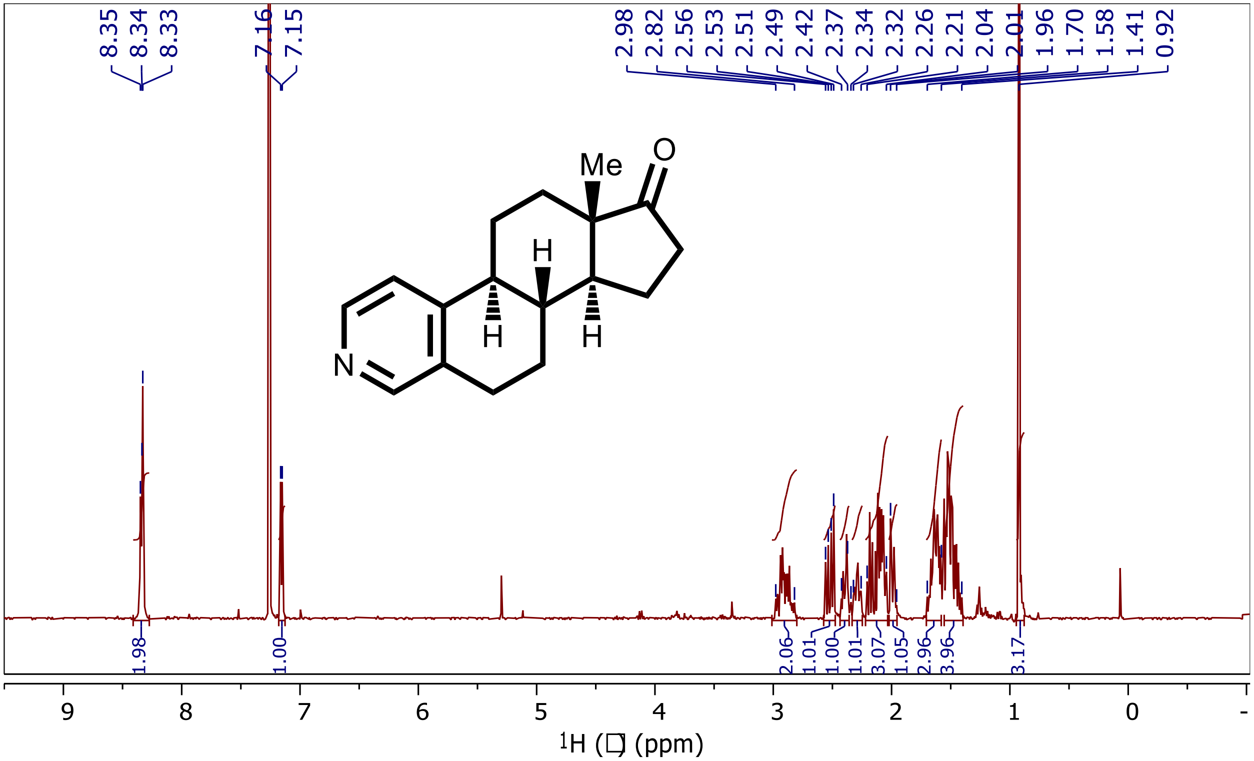


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

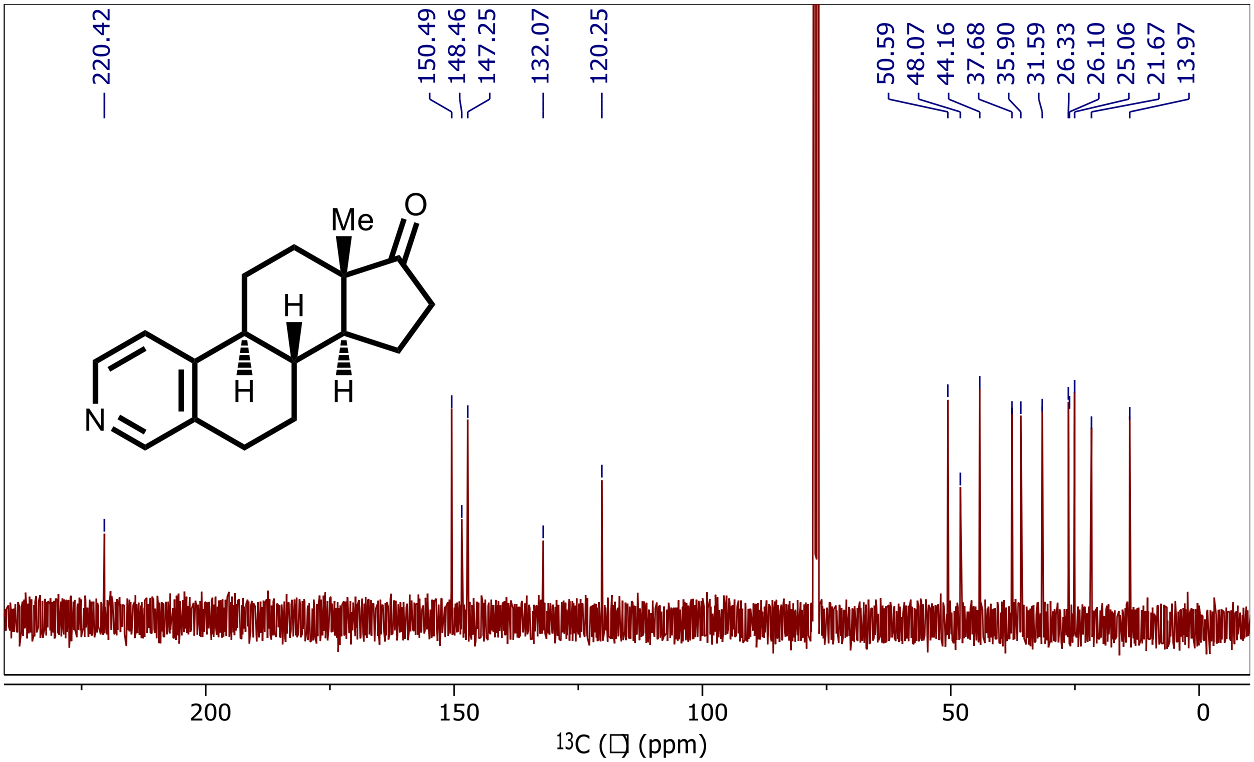


(4bS,6aS,9aS,9bR)-6a-methyl-4b,5,6,6a,8,9,9a,9b,10,11-decahydro-7H-indeno[5,4-f] isoquinolin-7-one

^{1}**H NMR** (400 MHz, CDCl$_3$)

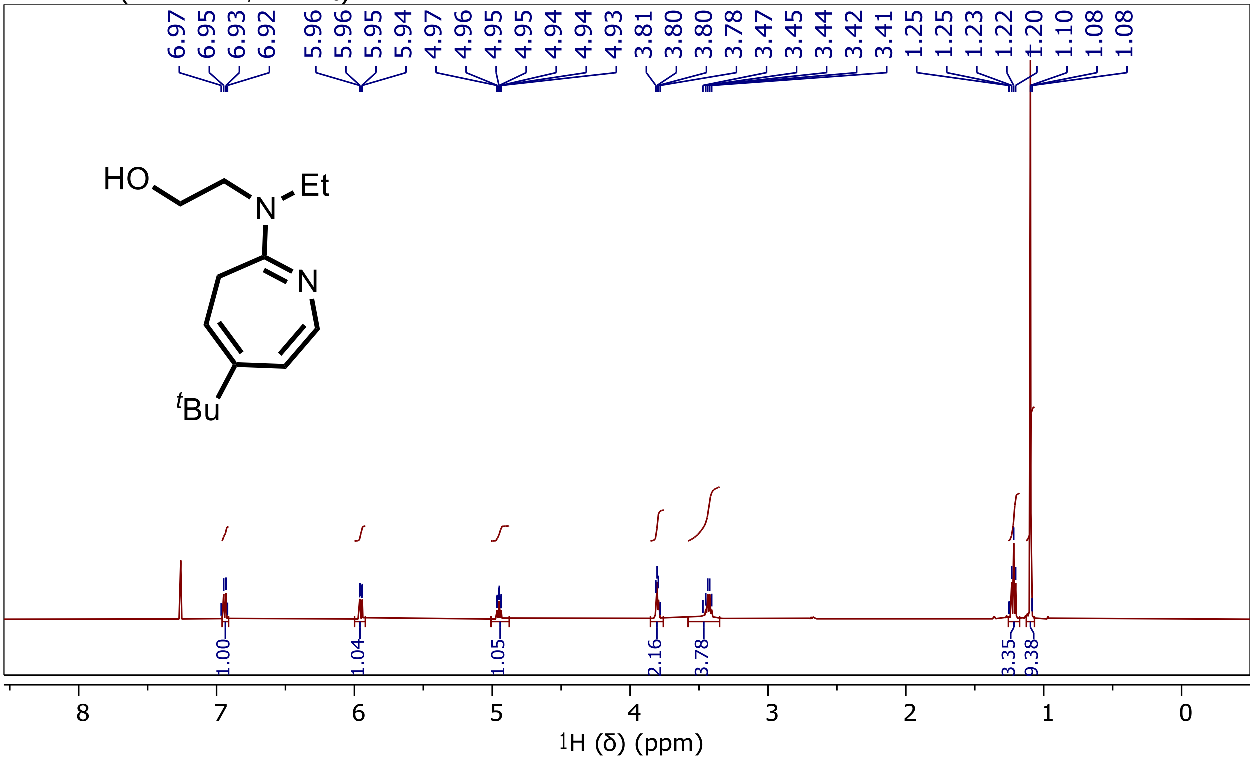


^{13}**C{^{1}H} NMR** (101 MHz, CDCl$_3$)

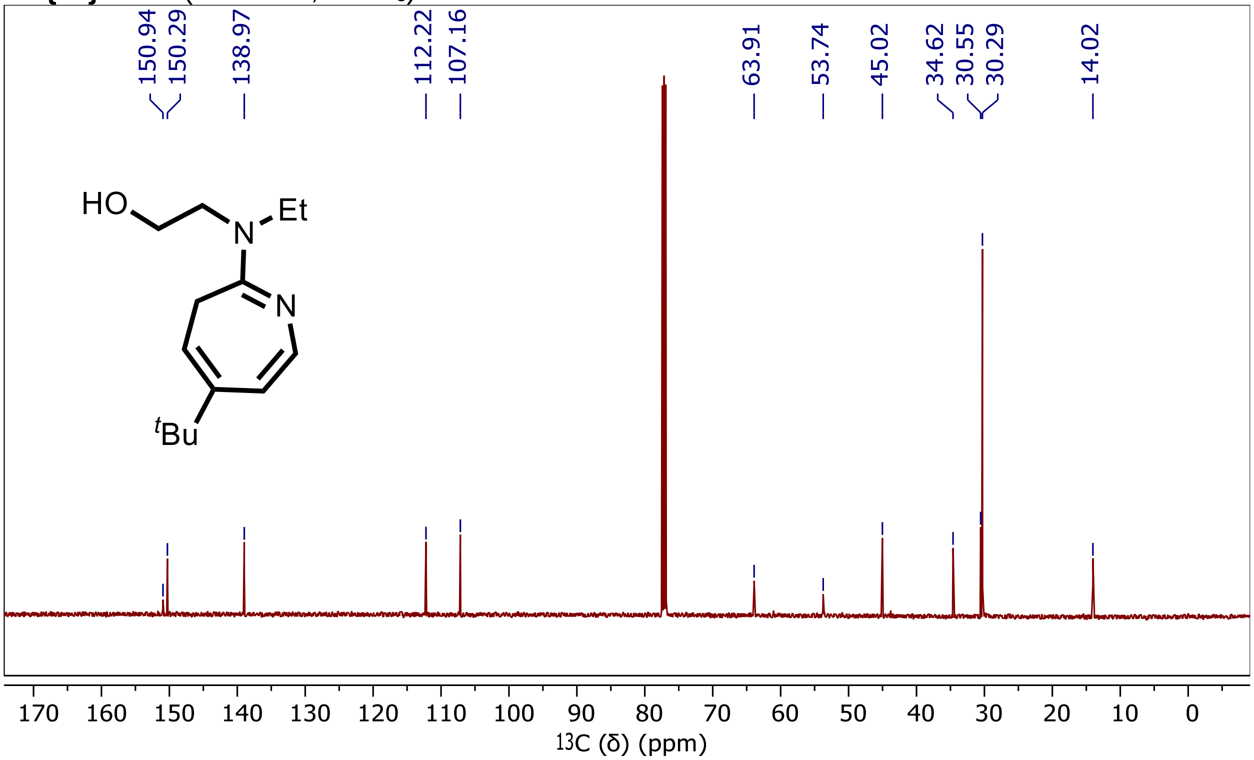


2-((5-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol

^{1}H NMR (500 MHz, CDCl$_3$)

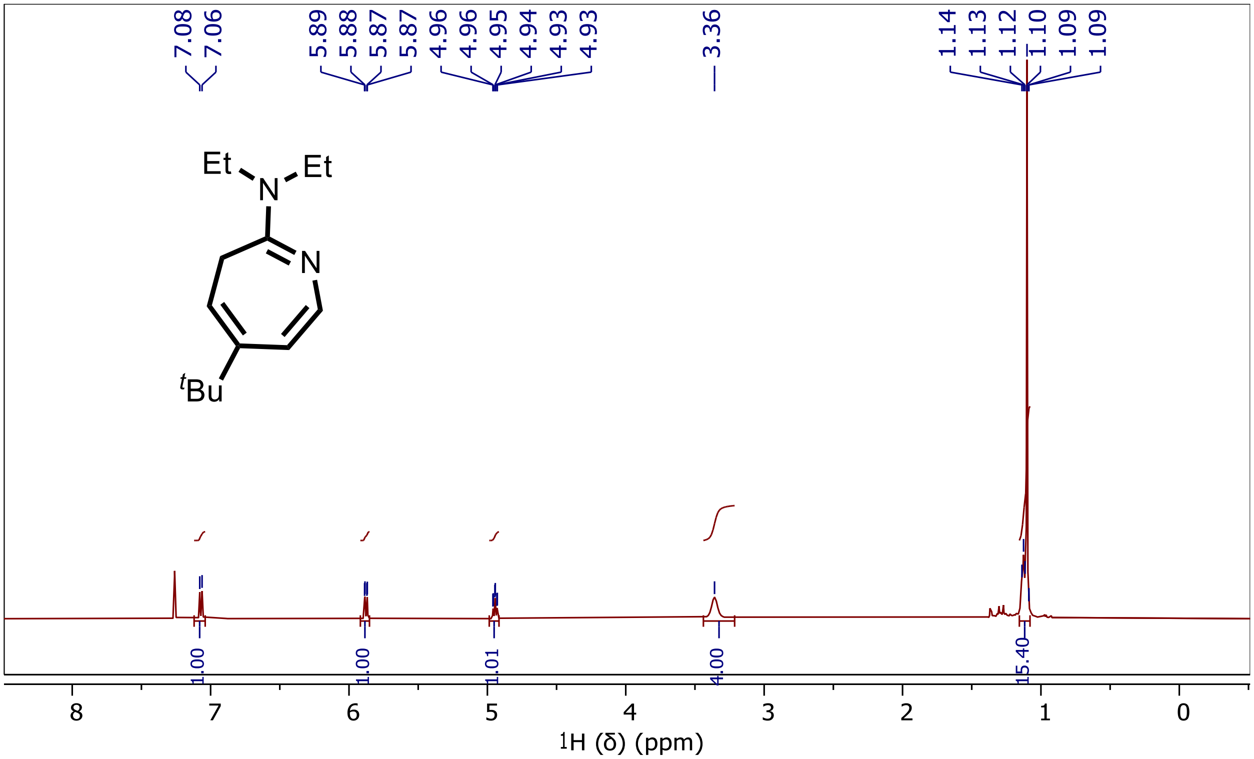


^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)

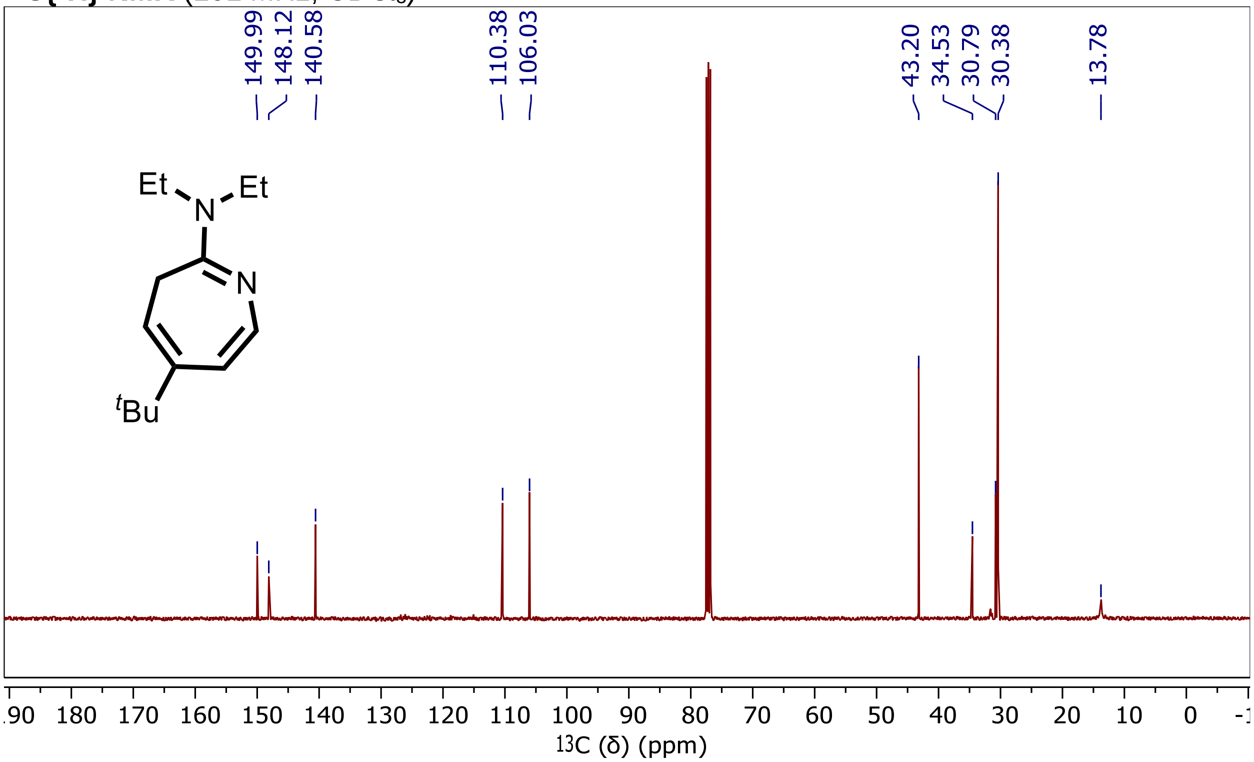


5-(tert-butyl)-N,N-diethyl-3H-azepin-2-amine

^{1}H NMR (500 MHz, CDCl$_3$)

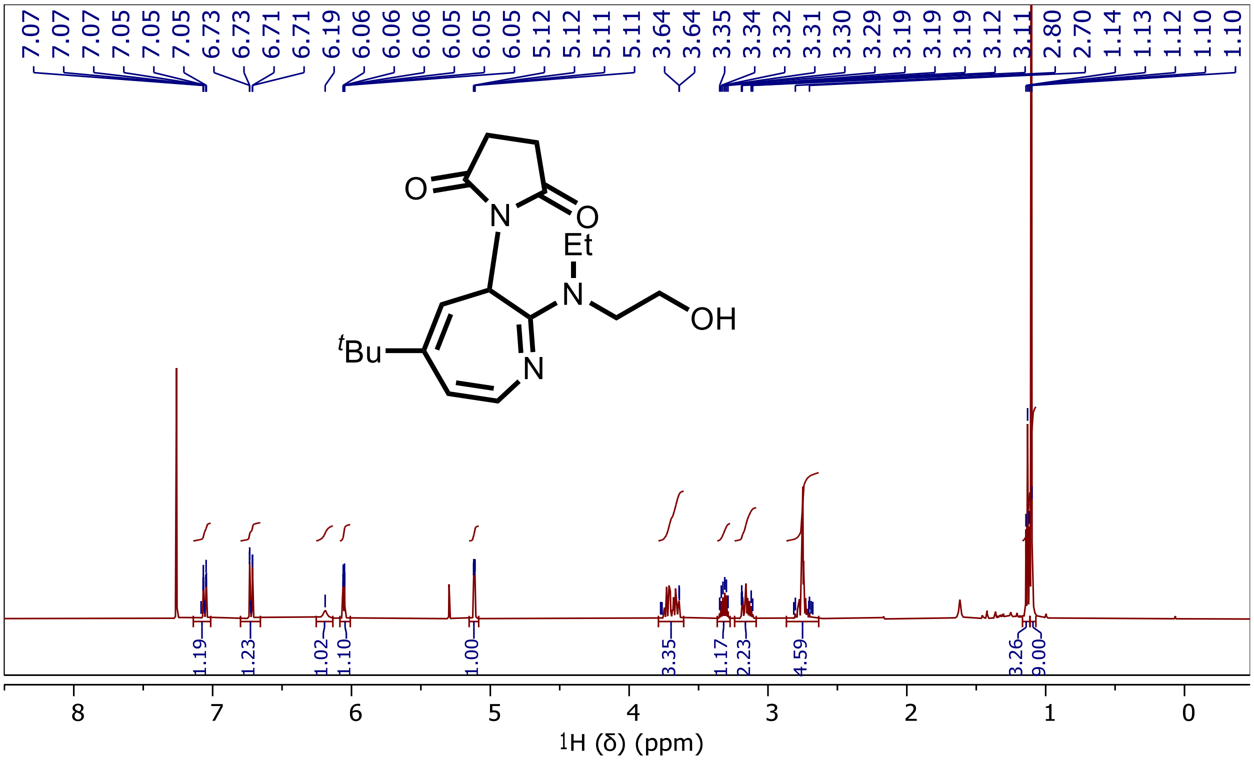


^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)

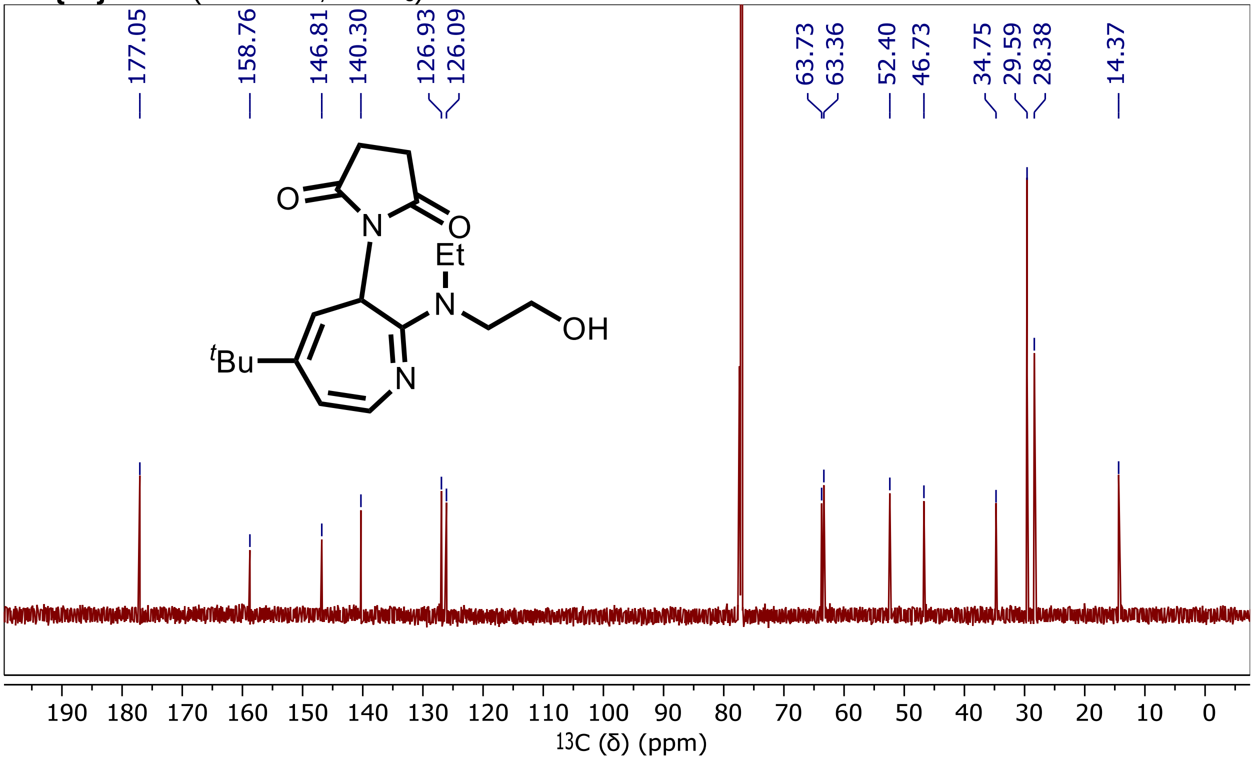


1-(5-(tert-butyl)-2-(ethyl(2-hydroxyethyl)amino)-3H-azepin-3-yl)pyrrolidine-2,5-dione

^{1}H NMR (600 MHz, CDCl$_3$)

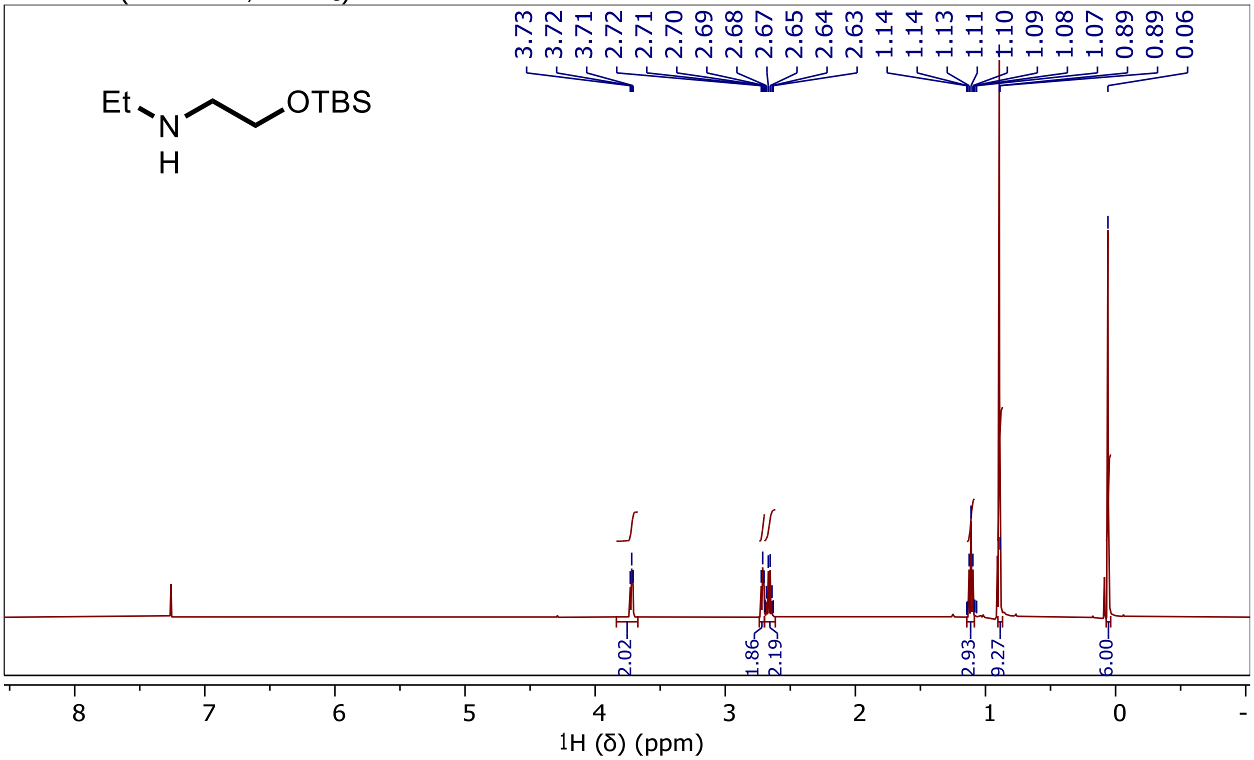


^{13}C {^{1}H} NMR (151 MHz, CDCl$_3$)

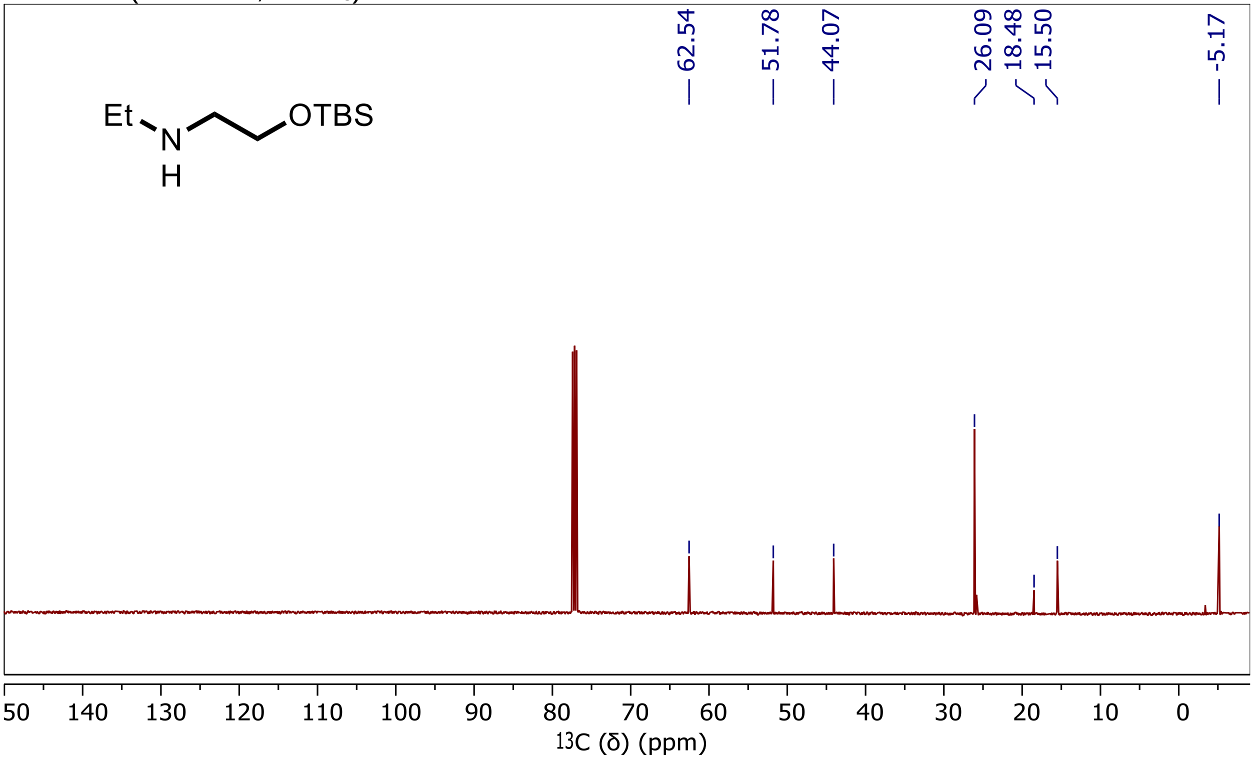


2-((tert-butyldimethylsilyl)oxy)-N-ethylethan-1-amine

^{1}H NMR (500 MHz, CDCl$_3$)

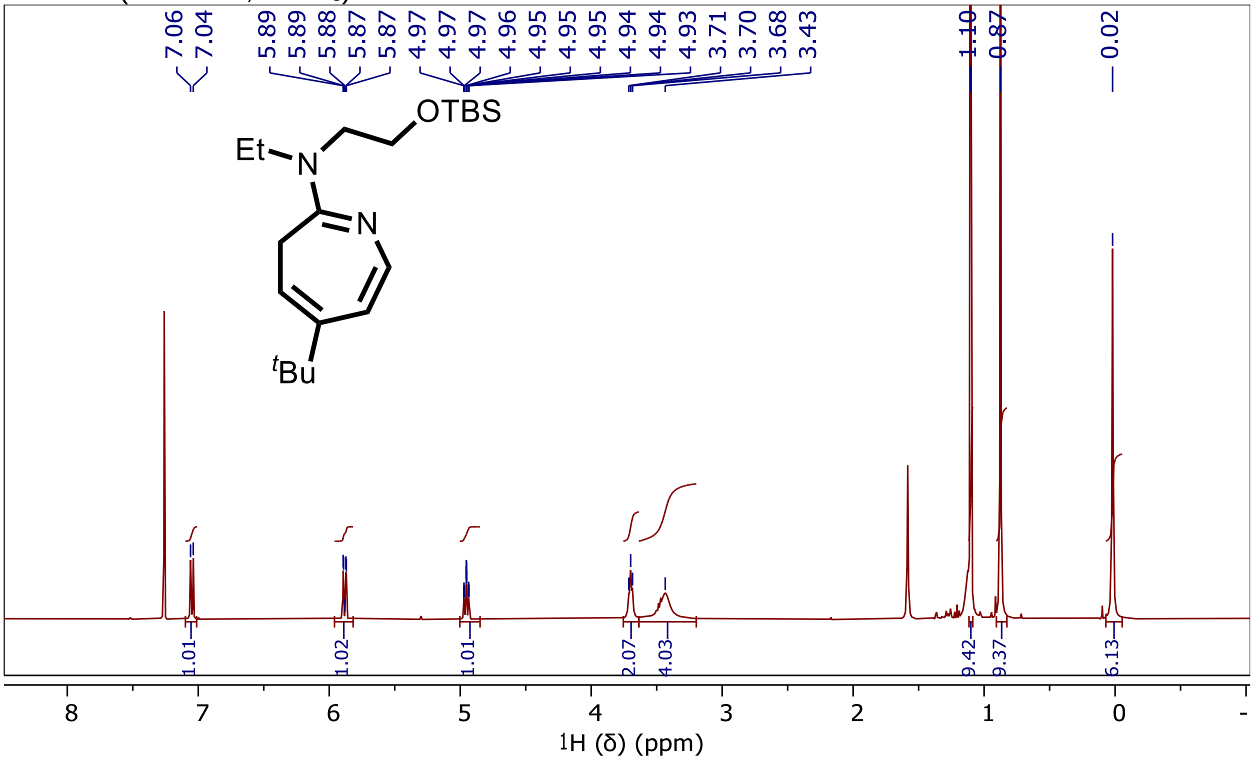


^{13}C NMR (126 MHz, CDCl$_3$)

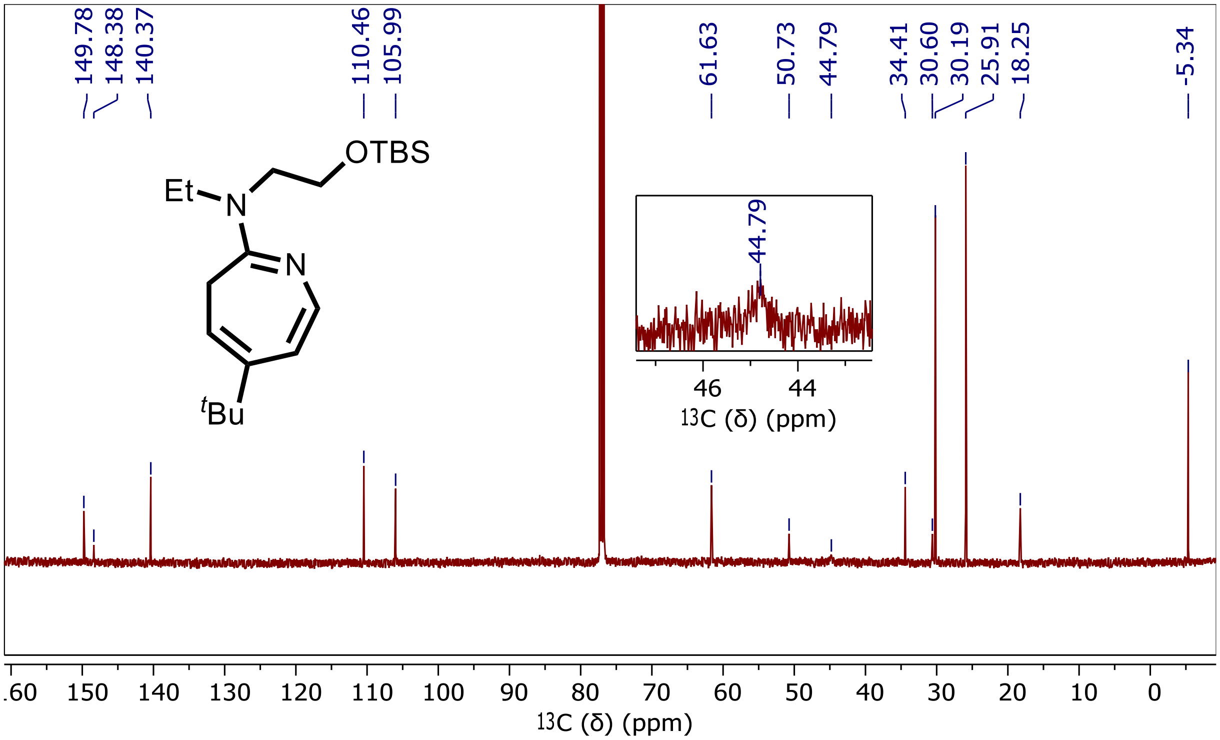


5-(tert-butyl)-N-(2-((tert-butyldimethylsilyl)oxy)ethyl)-N-ethyl-3H-azepin-2-amine

^{1}H NMR (400 MHz, CDCl$_3$)

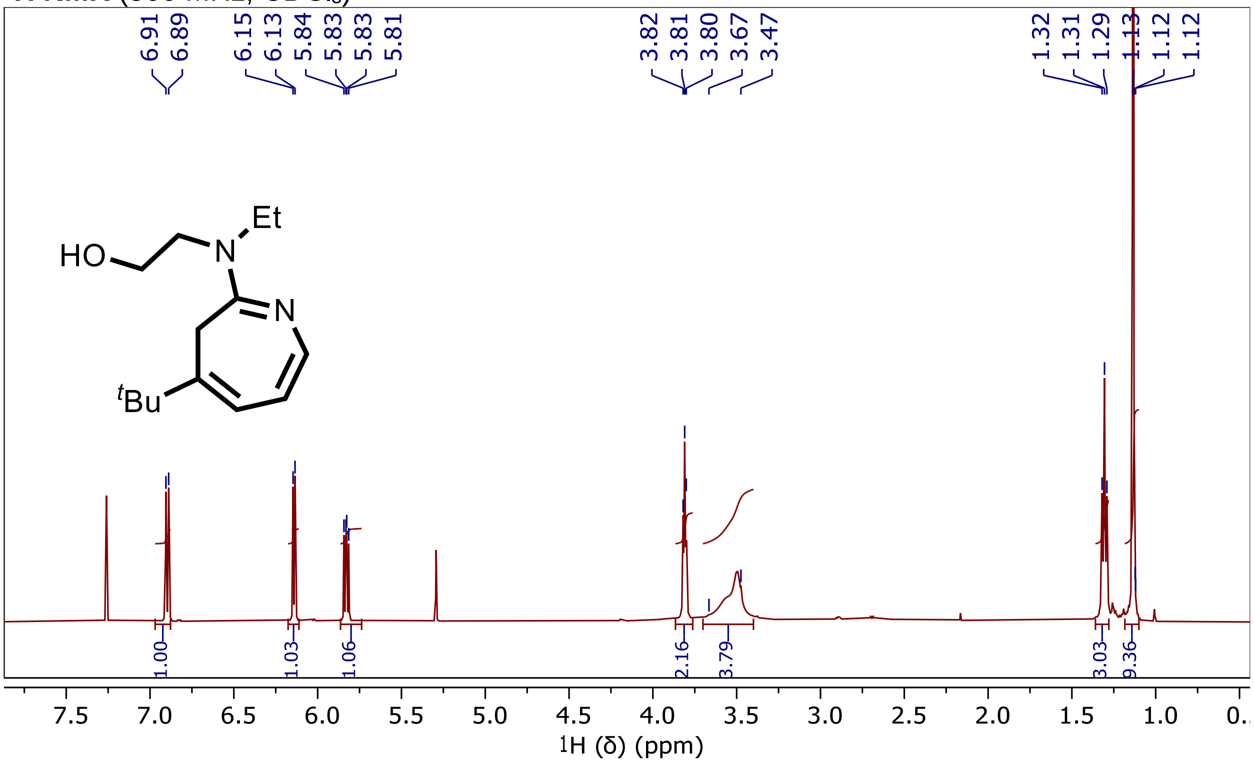


^{13}C {^{1}H} NMR (126 MHz, CDCl$_3$)

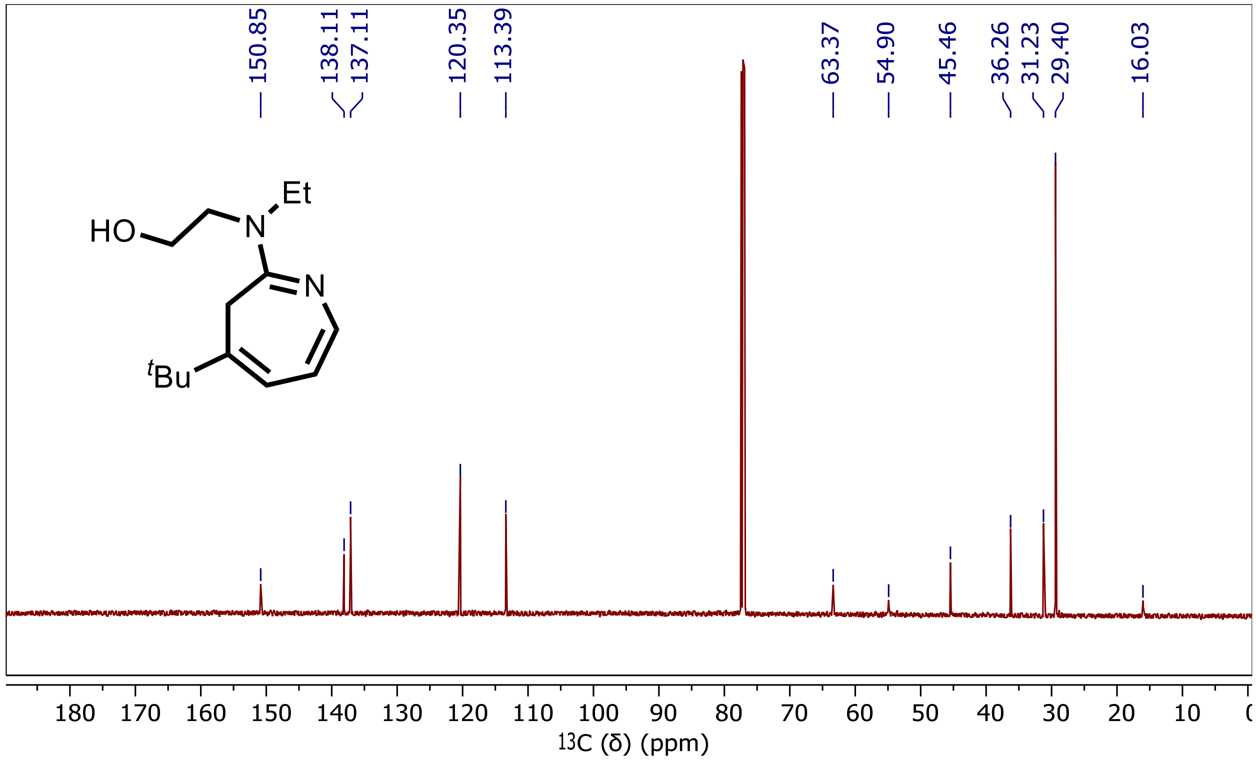


2-((4-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol

^{1}H NMR (500 MHz, CDCl$_3$)

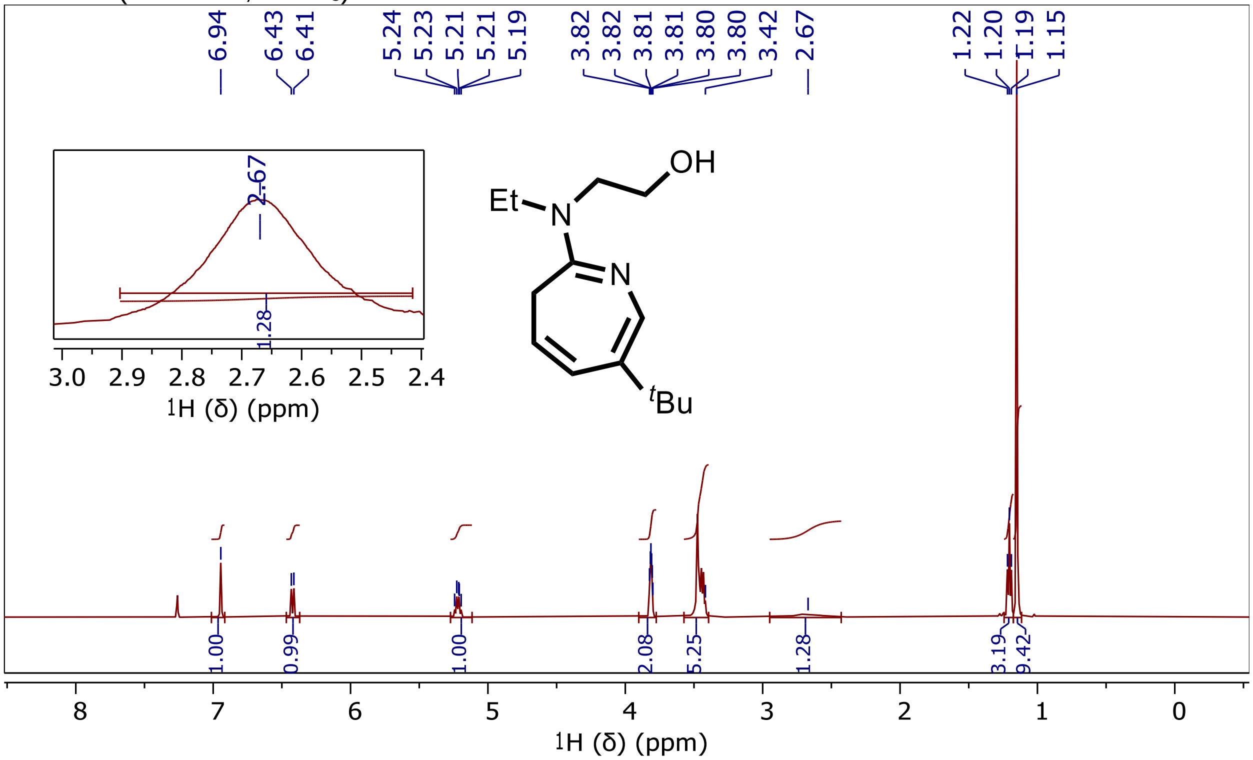


^{13}C {^{1}H} NMR (126 MHz, CDCl$_3$)

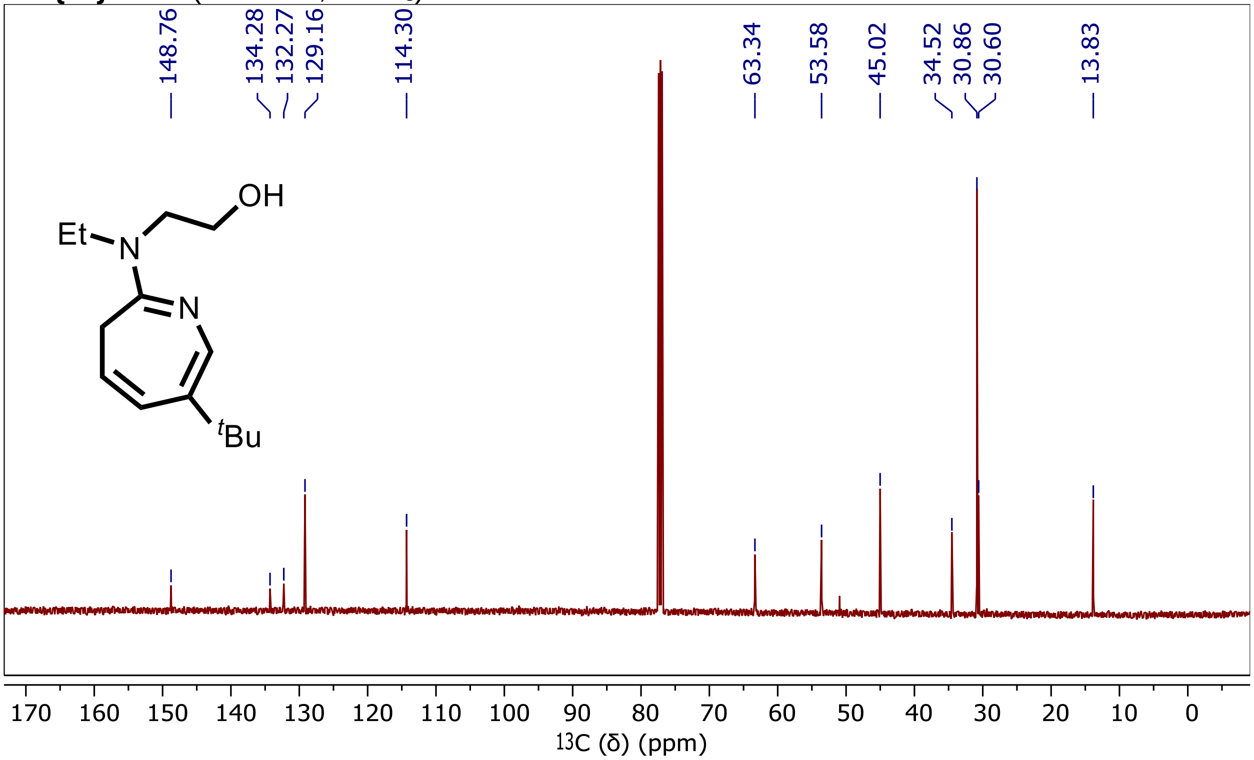


2-((6-(tert-butyl)-3H-azepin-2-yl)(ethyl)amino)ethan-1-ol

^{1}H NMR (500 MHz, $CDCl_3$)

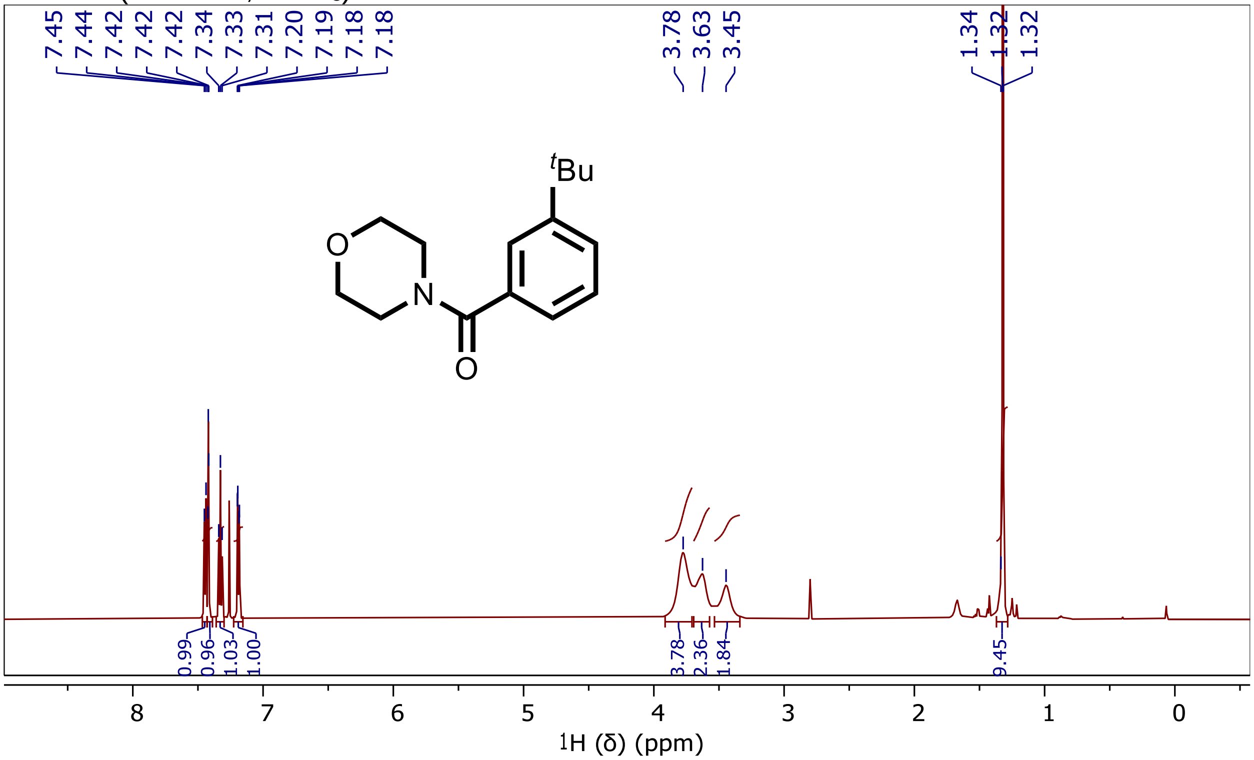


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

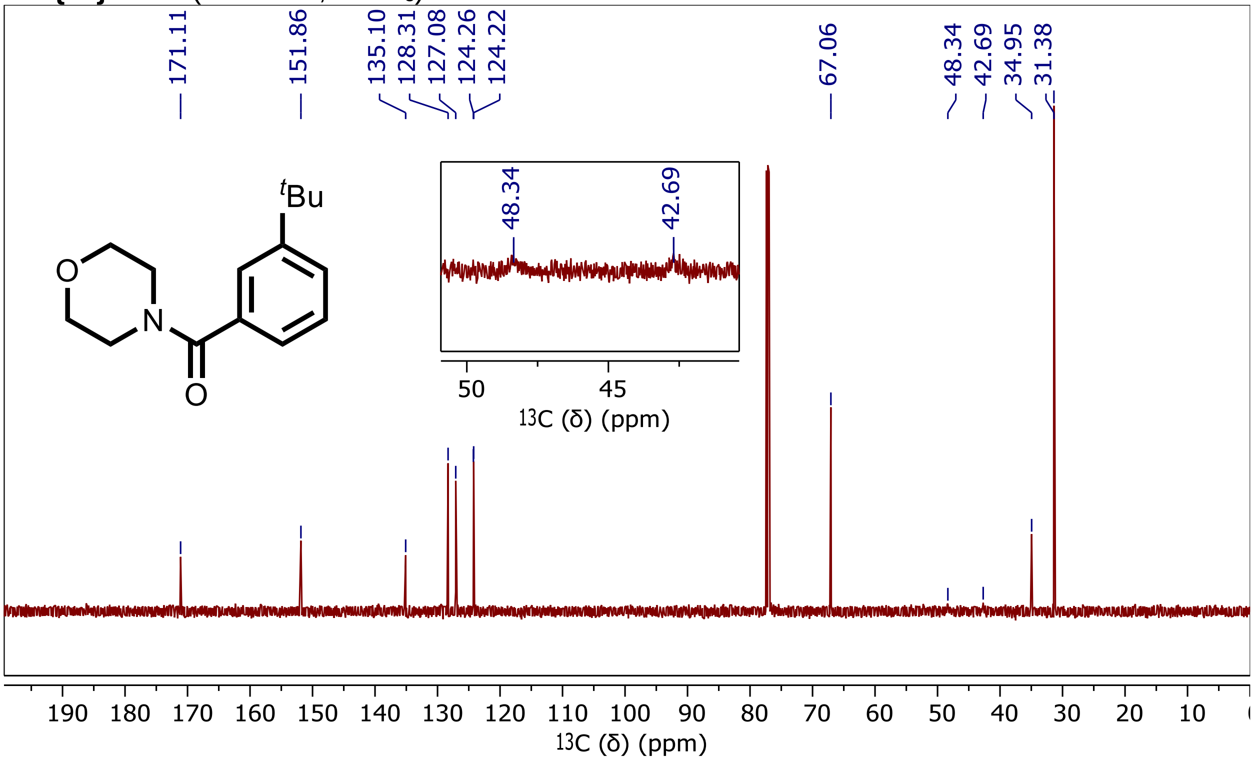


(3-(tert-butyl)phenyl)(morpholino)methanone

^{1}H NMR (600 MHz, $CDCl_3$)

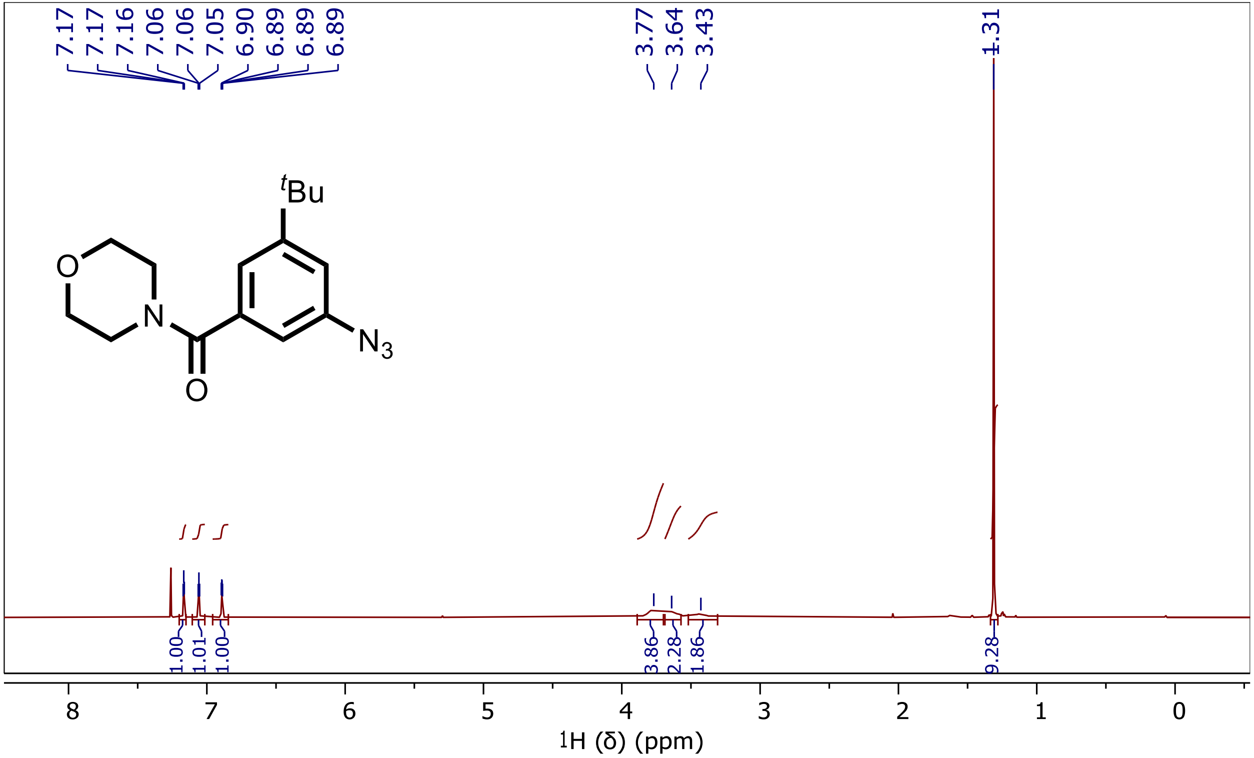


^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$)

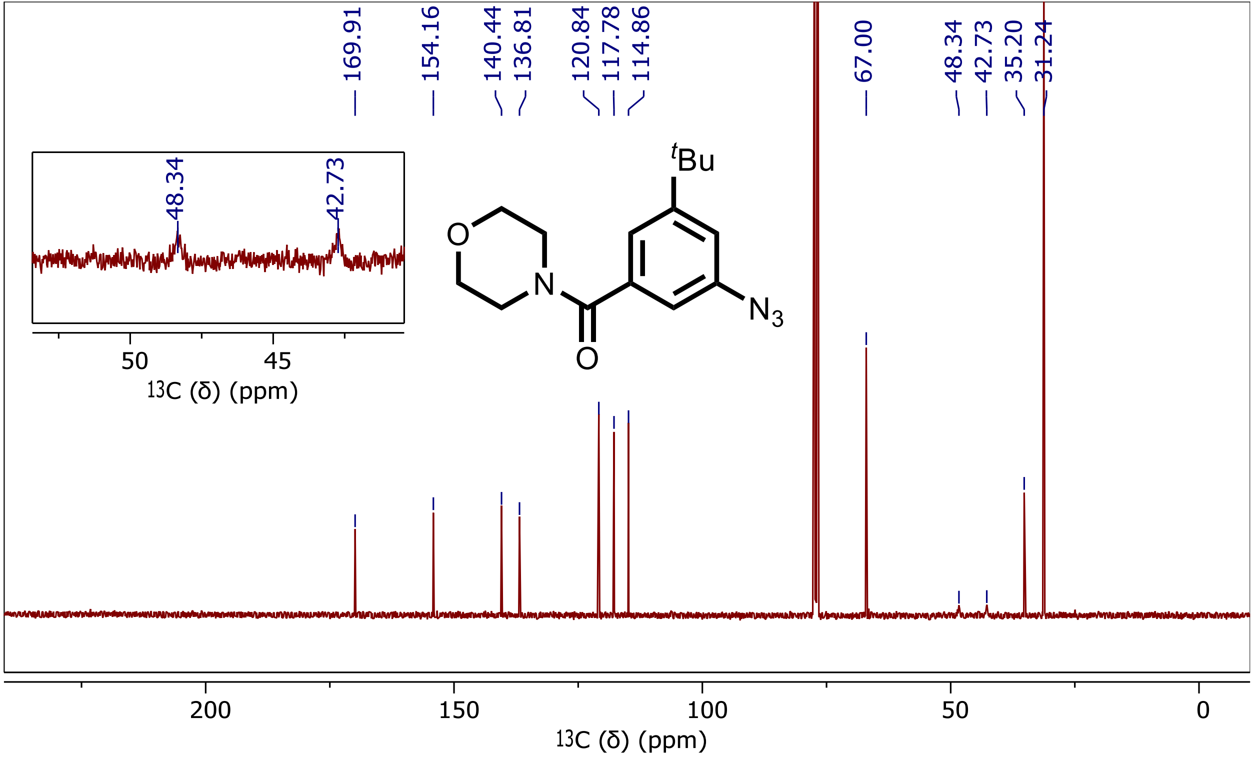


(3-azido-5-(tert-butyl)phenyl)(morpholino)methanone:

^{1}H NMR (400 MHz, $CDCl_3$)

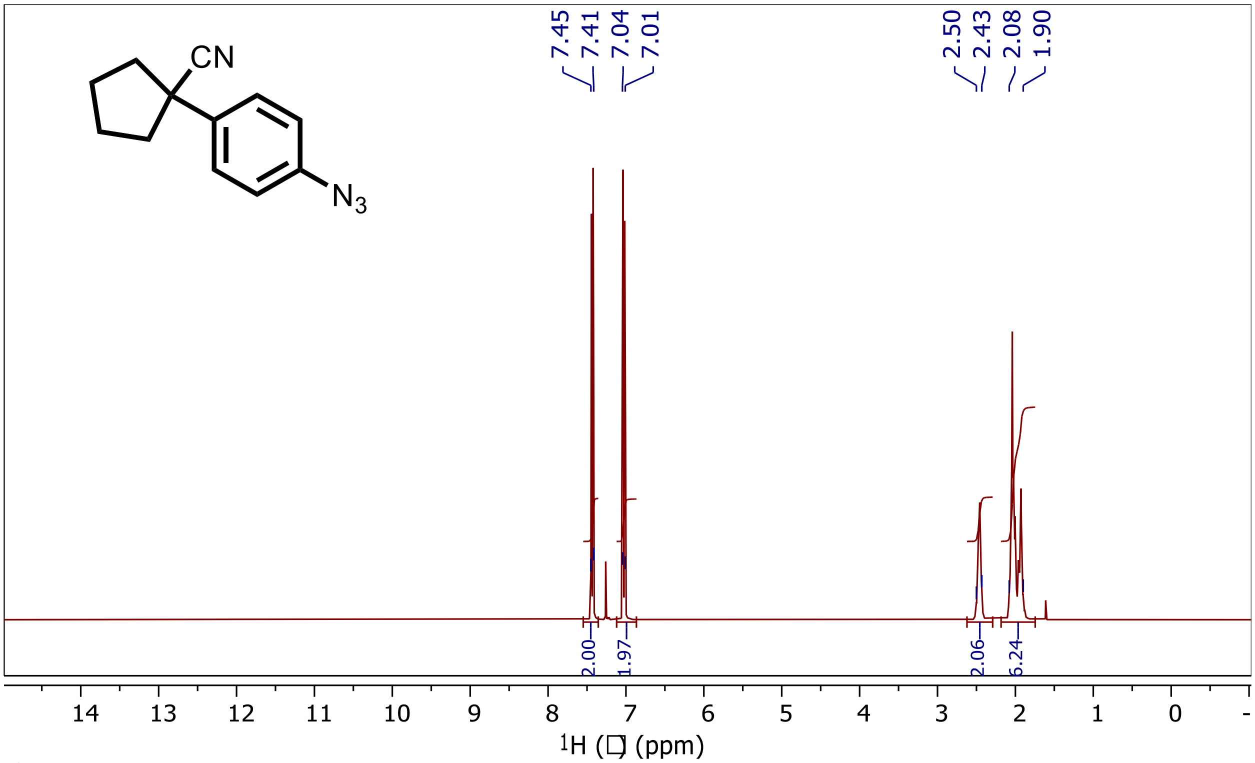


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)

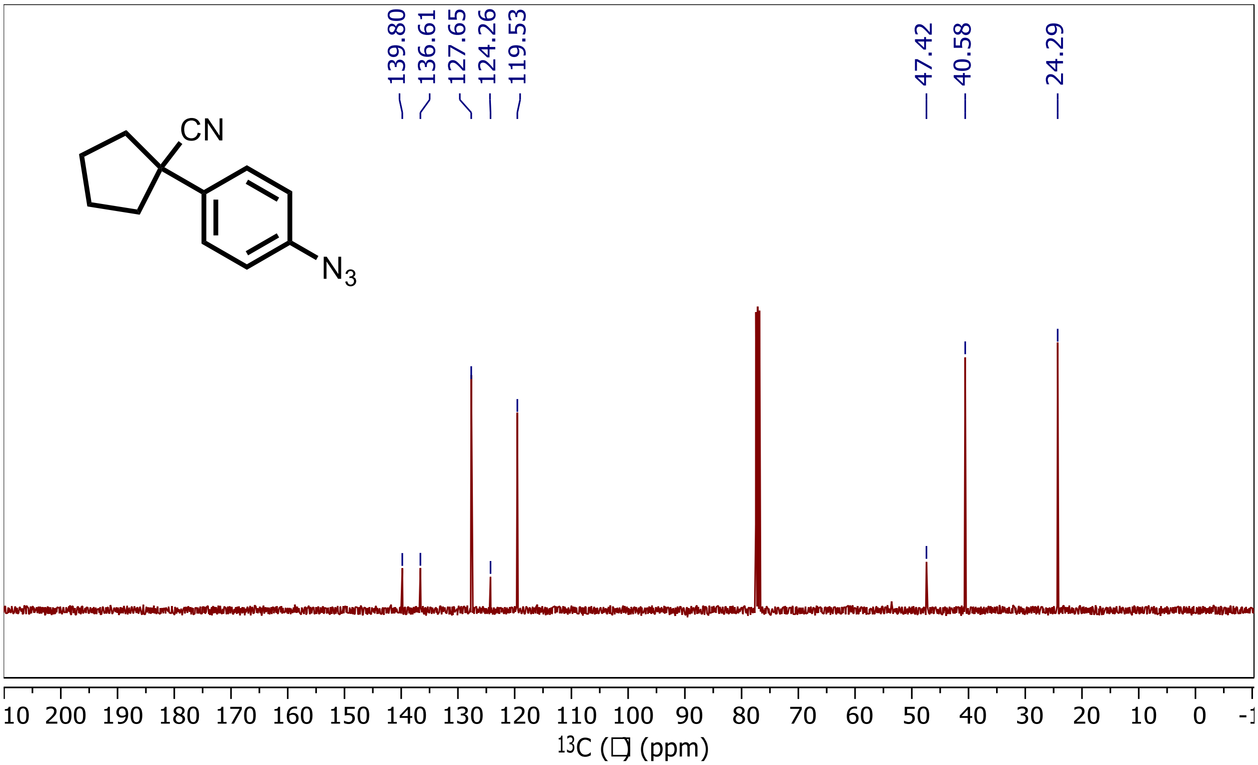


1-(4-azidophenyl)cyclopentane-1-carbonitrile

^{1}H NMR (400 MHz, $CDCl_3$)

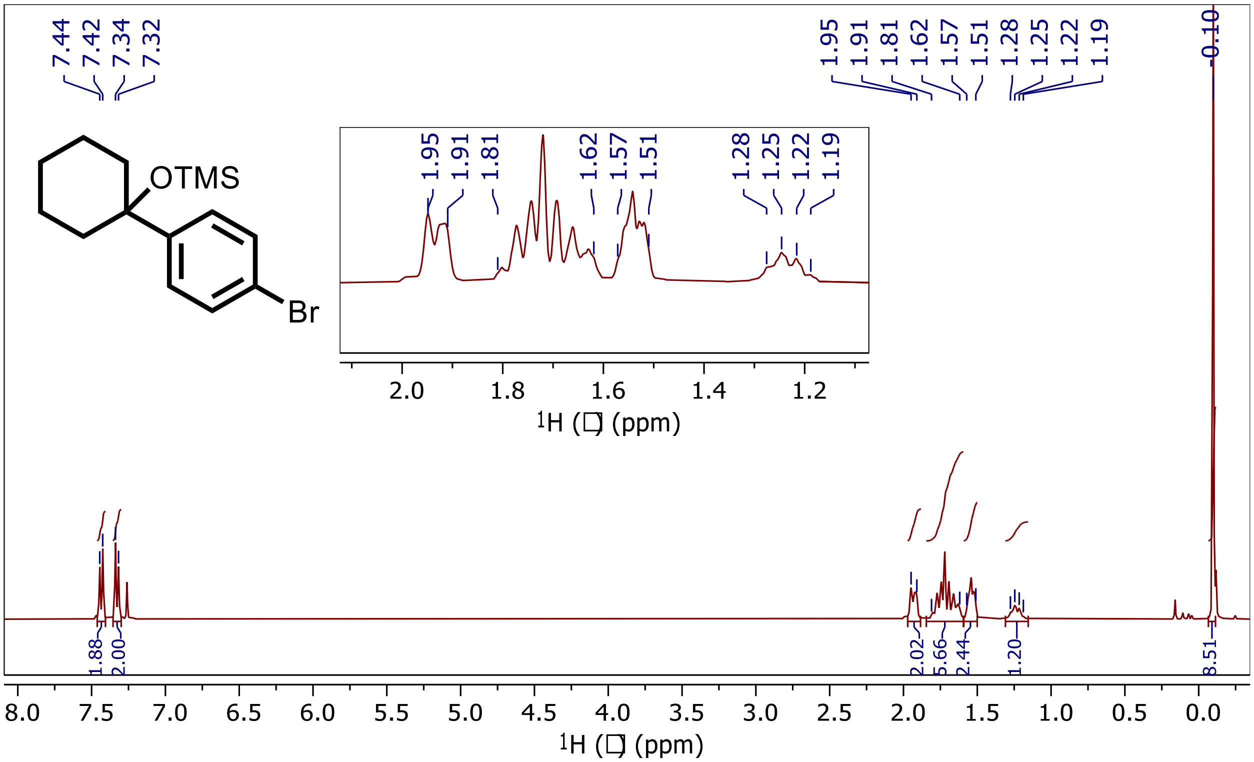


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

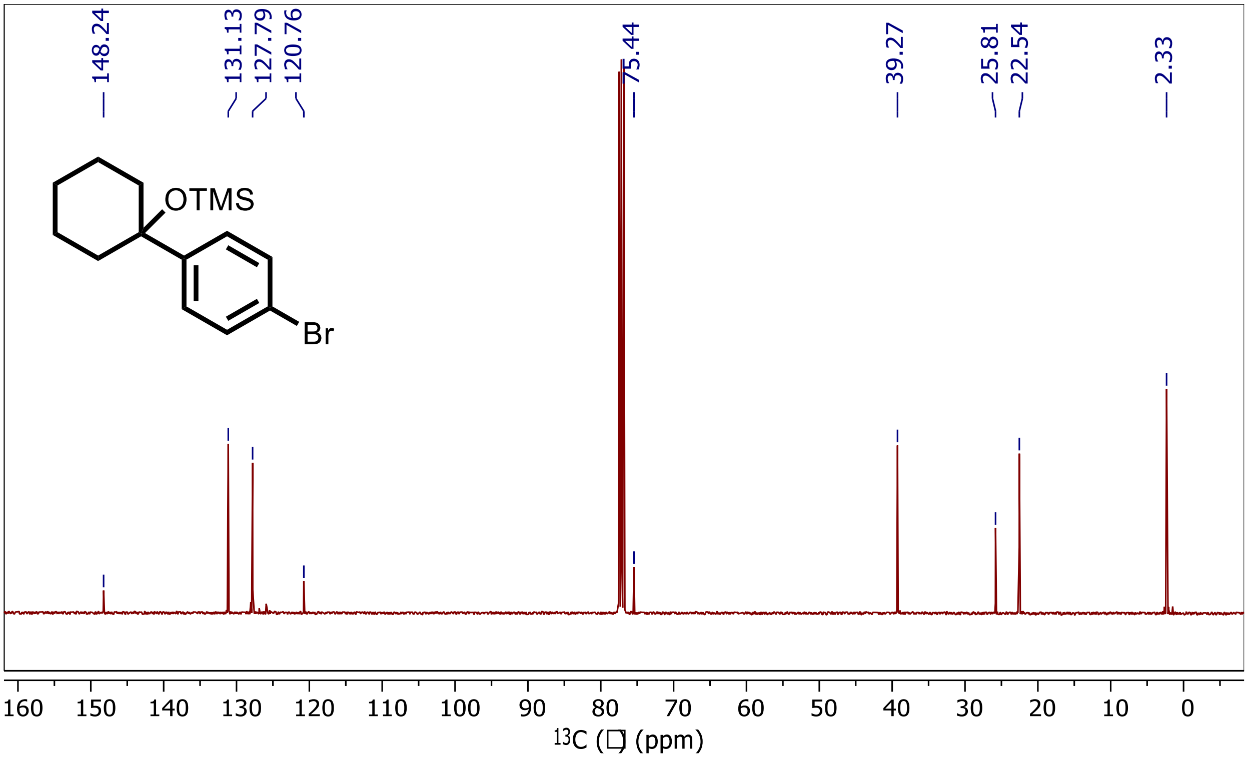


((1-(4-bromophenyl)cyclohexyl)oxy)trimethylsilane:

^{1}H NMR (400 MHz, $CDCl_3$)

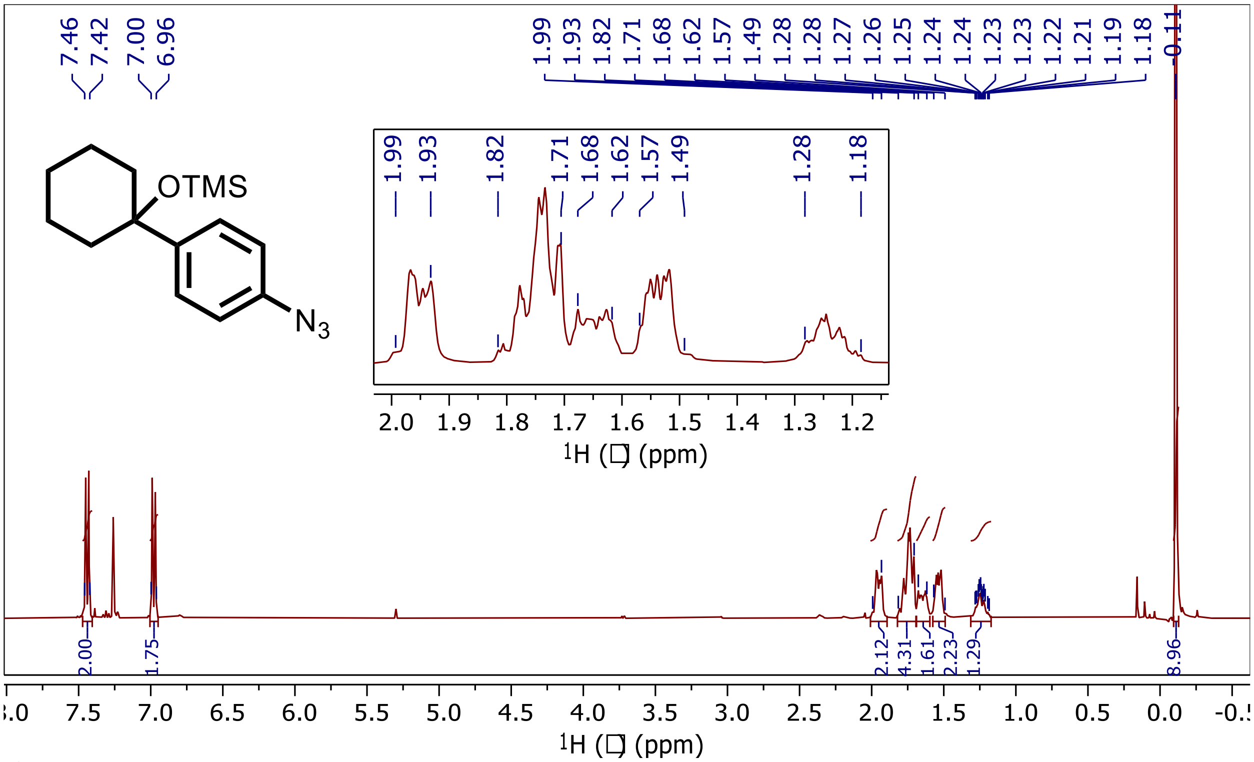


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

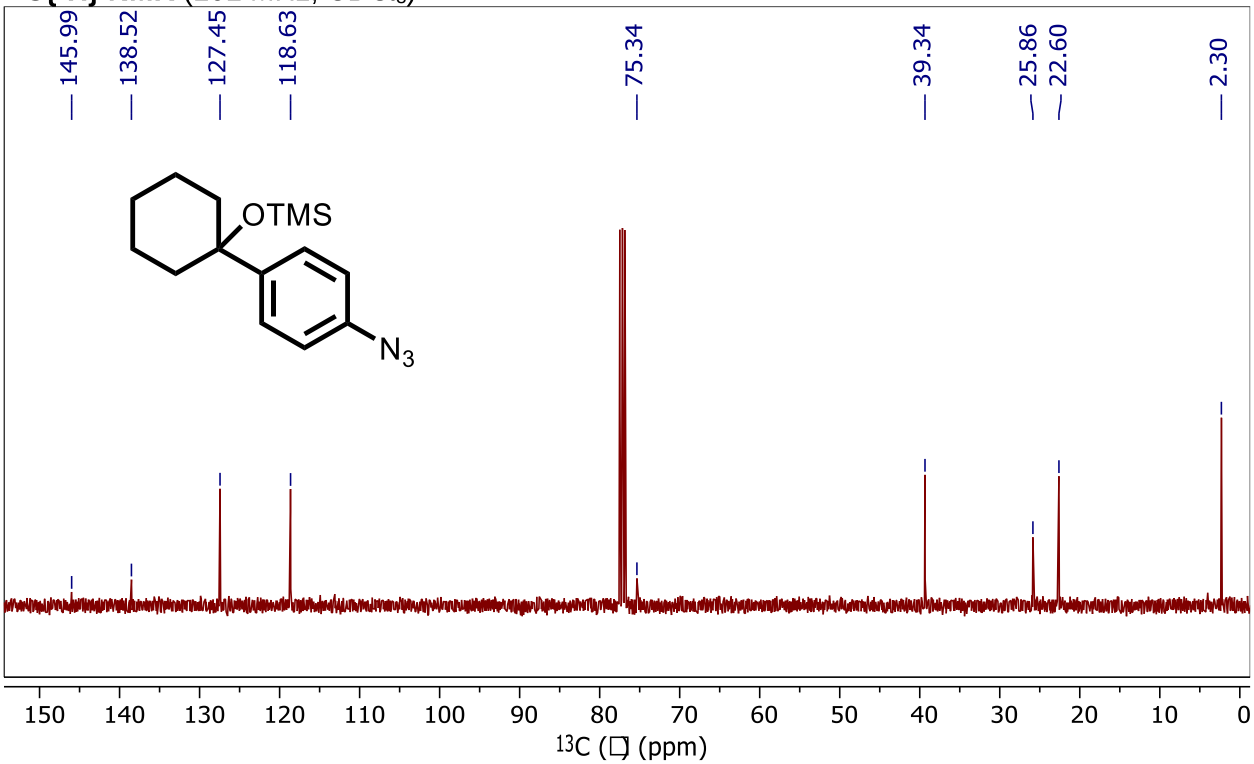


((1-(4-azidophenyl)cyclohexyl)oxy)trimethylsilane:

^{1}H NMR (400 MHz, CDCl$_3$)

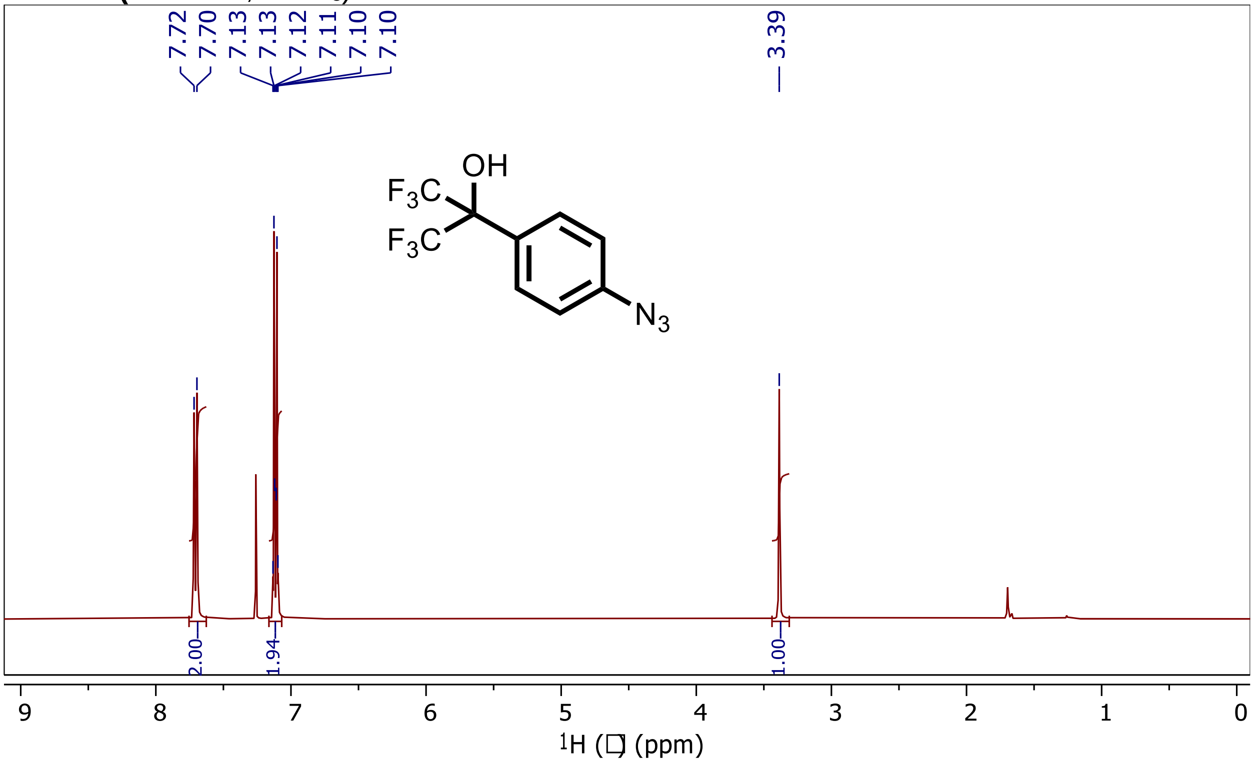


^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)

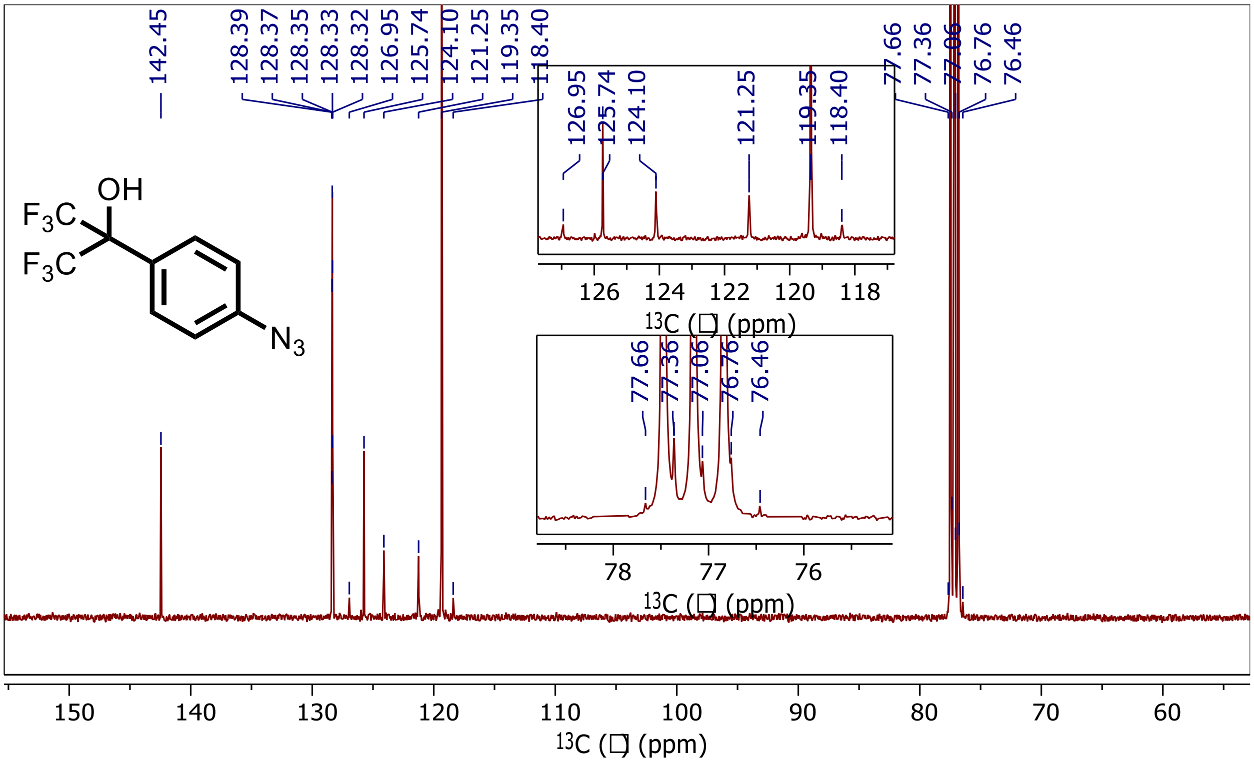


2-(4-azidophenyl)-1,1,1,3,3,3-hexafluoropropan-2-ol

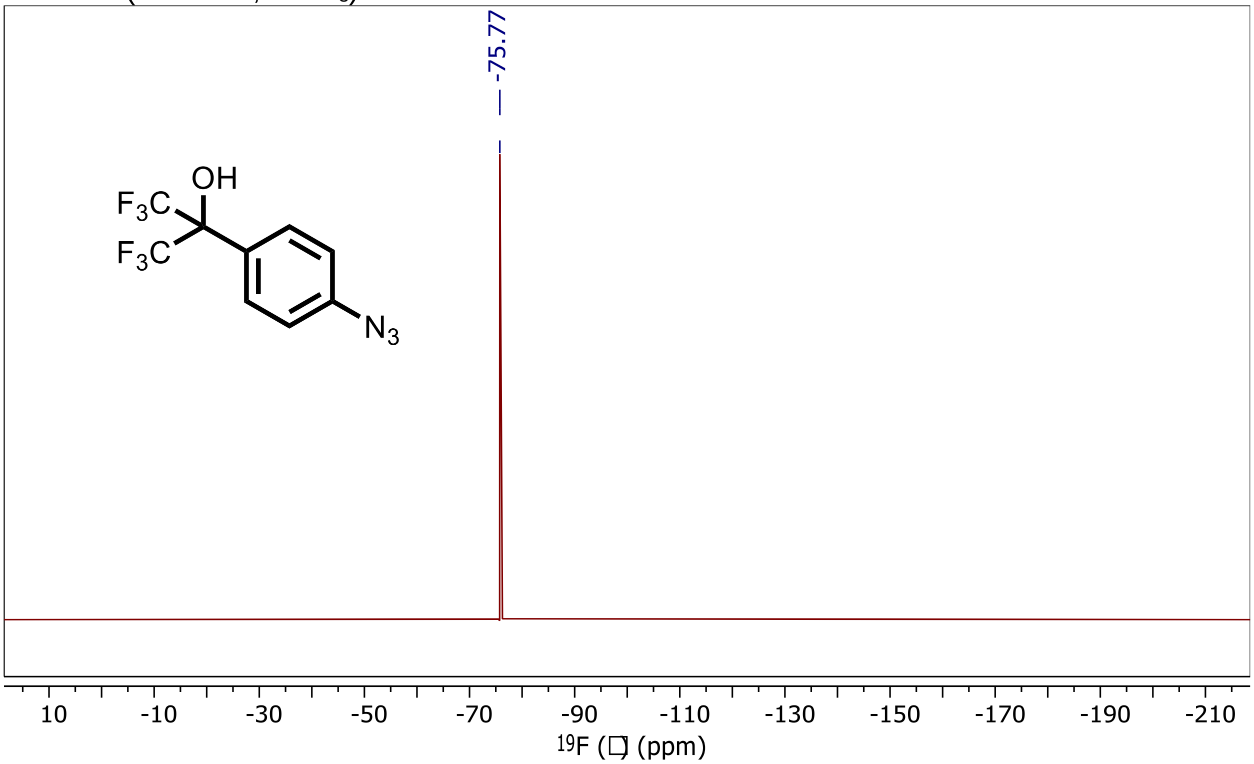
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

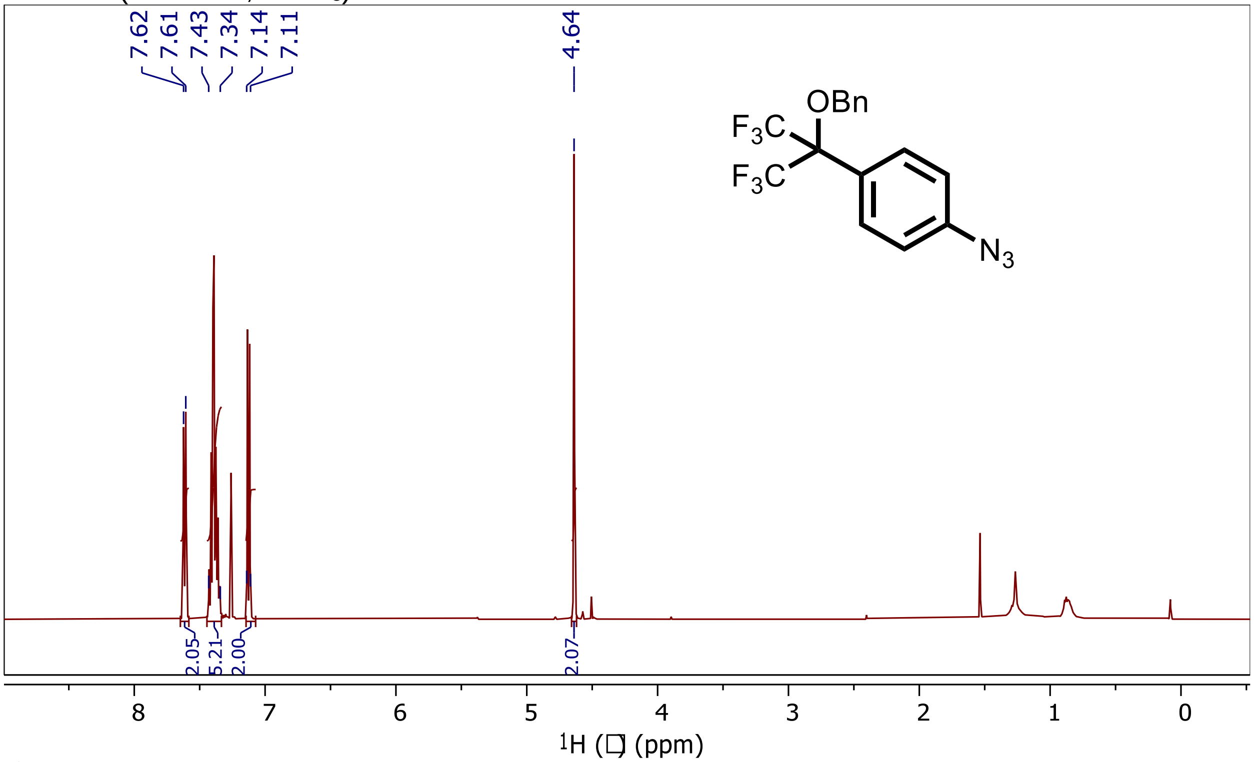


^{19}**F NMR** (376 MHz, $CDCl_3$)

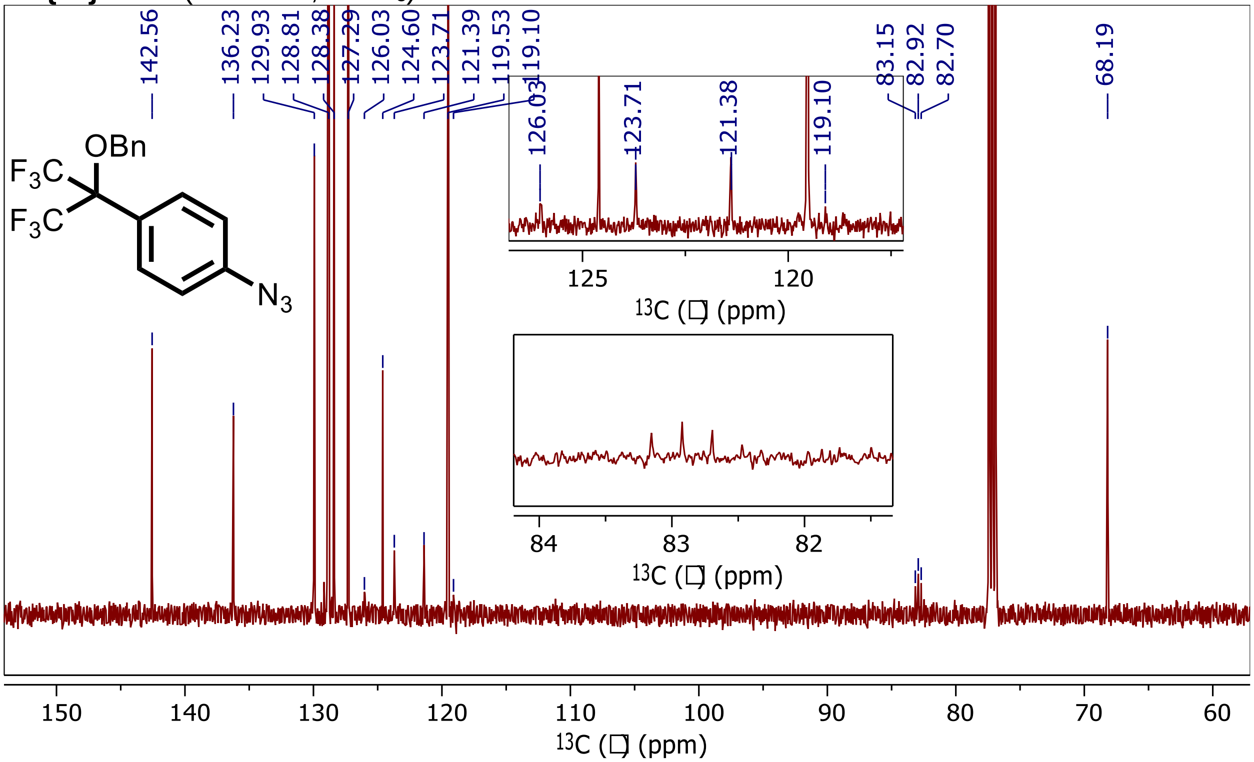


1-azido-4-(2-benzyloxy)-1,1,1,3,3,3-hexafluoropropan-2-yl)benzene

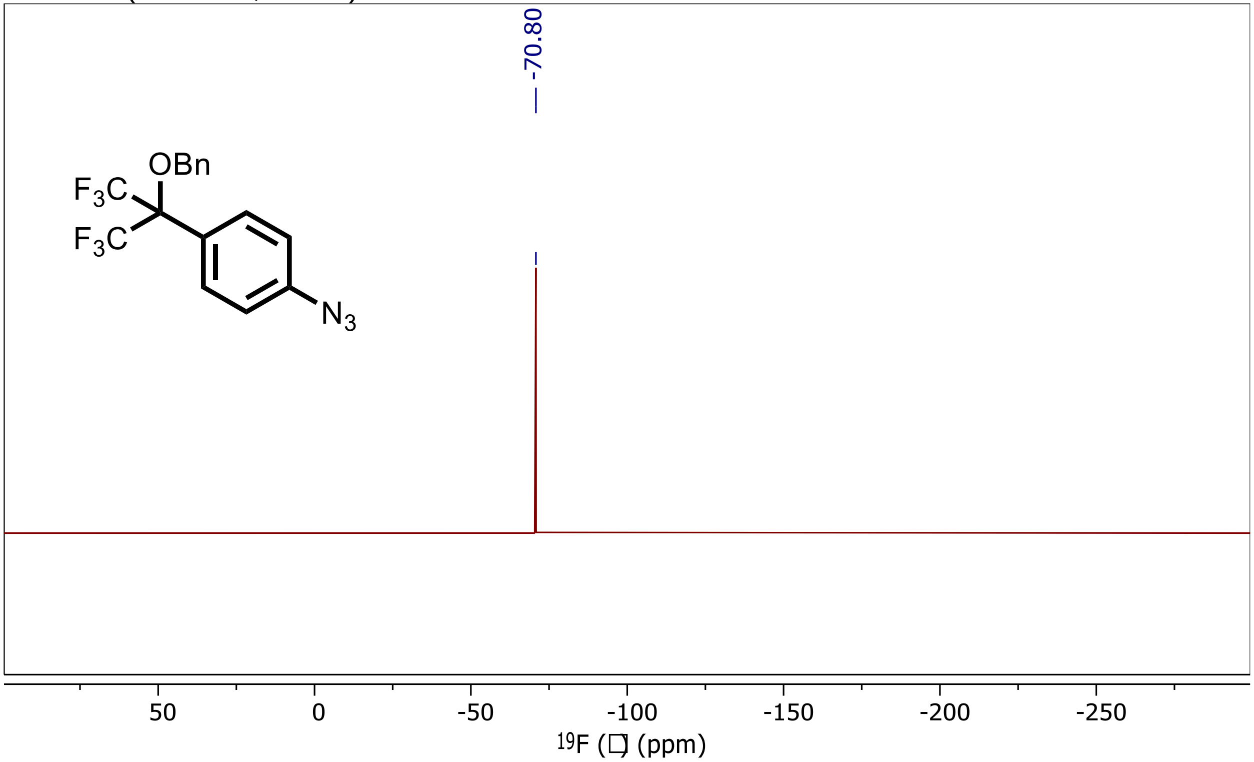
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

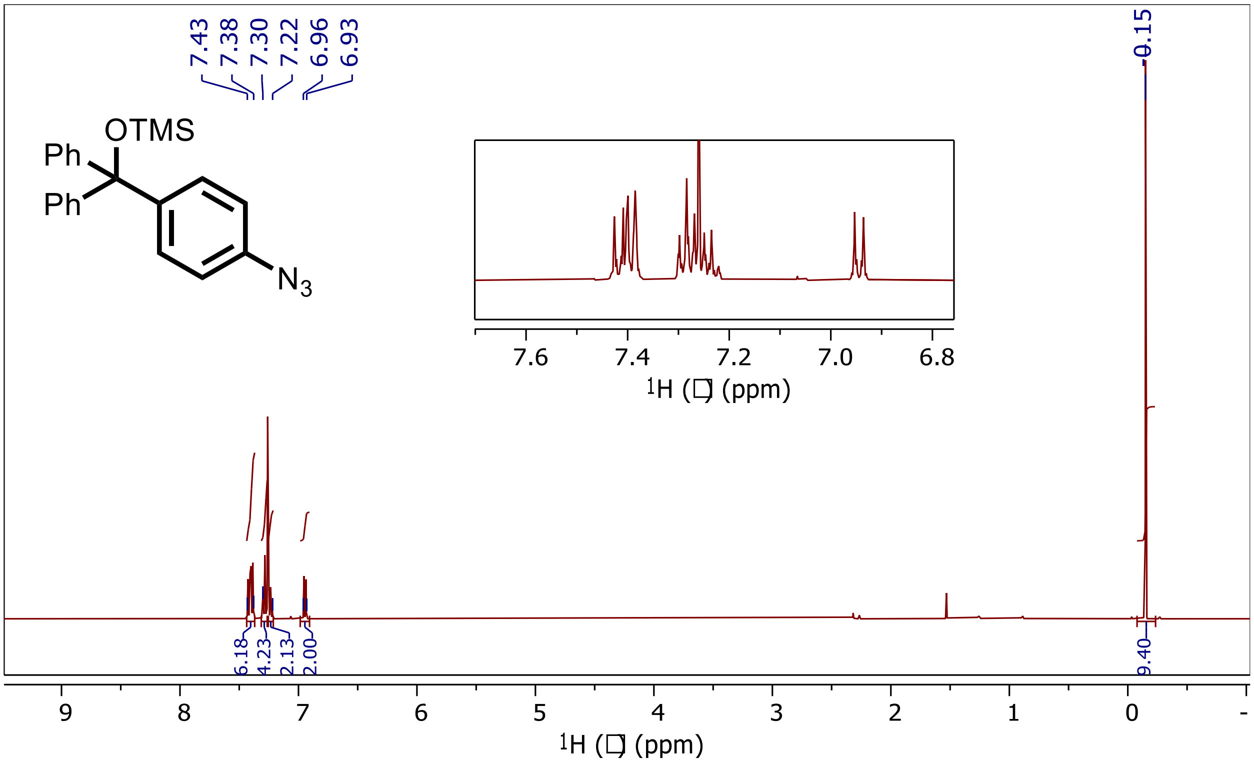


^{19}**F NMR** (470 MHz, $CDCl_3$)

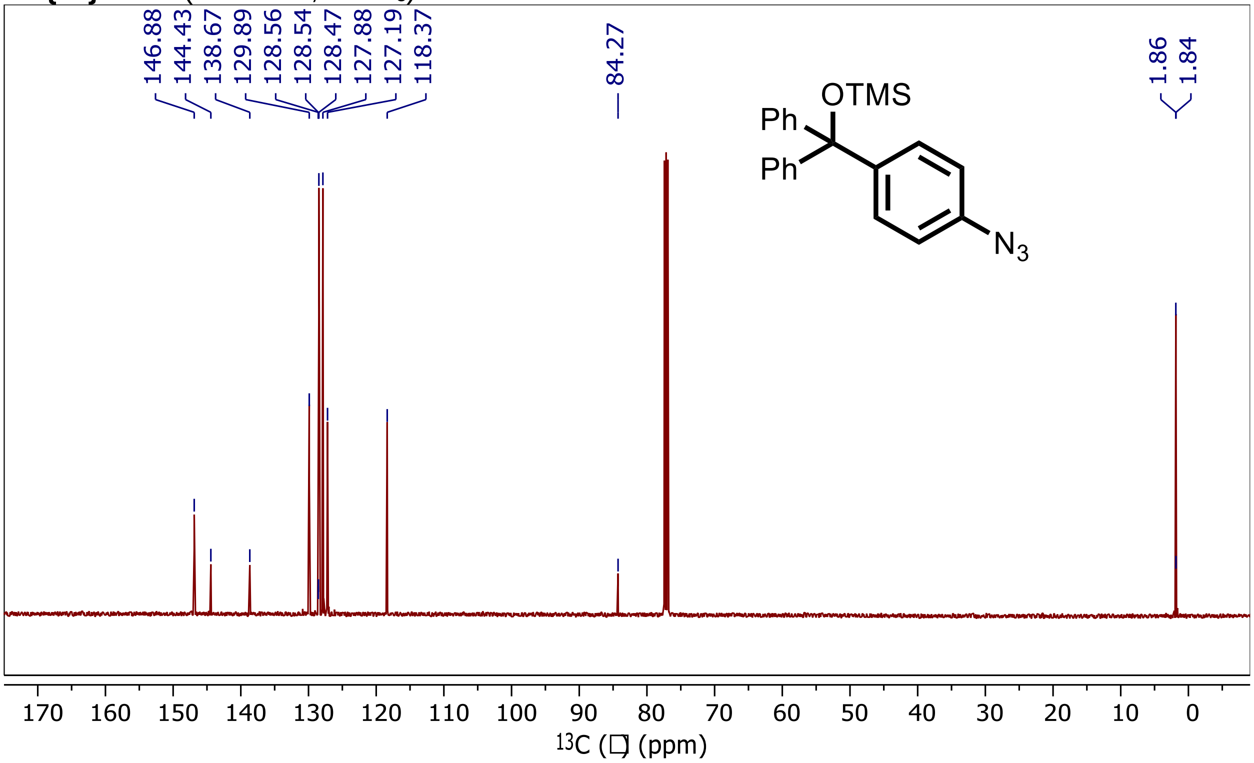


((4-azidophenyl)diphenylmethoxy)trimethylsilane:

^{1}H NMR (500 MHz, CDCl$_3$)

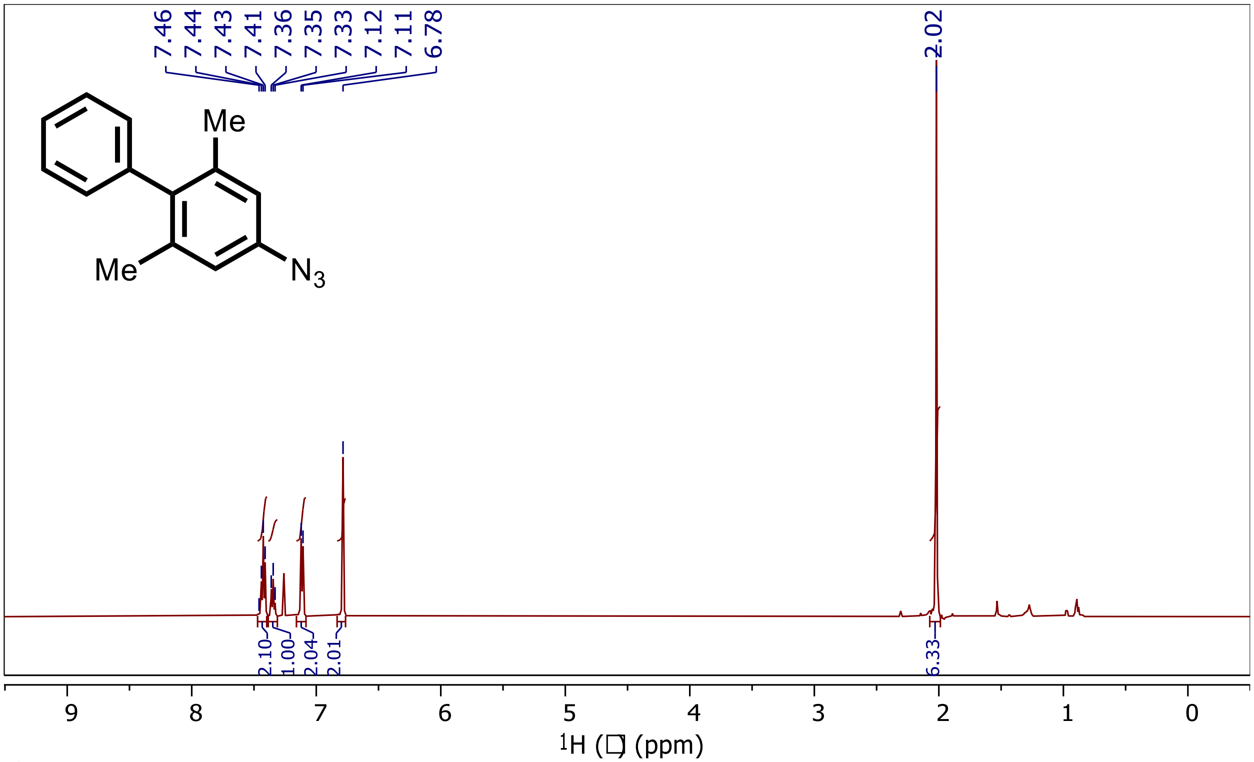


^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)

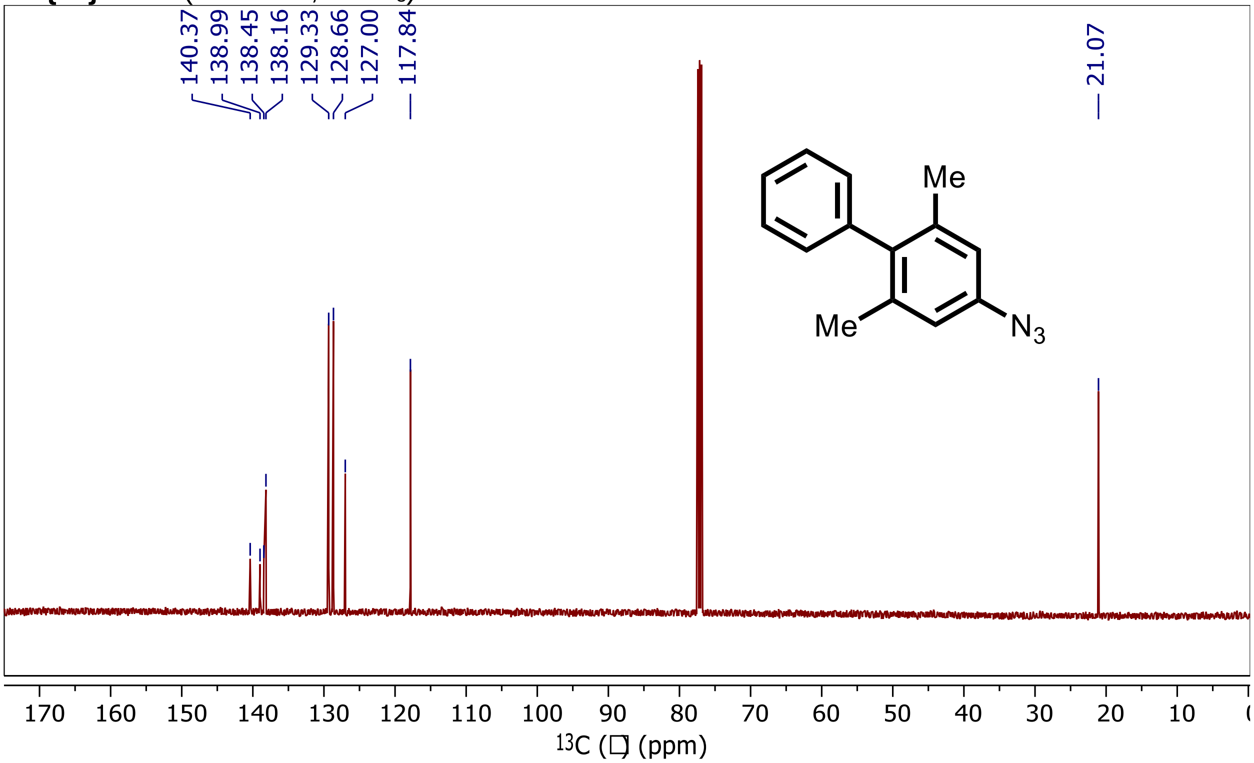


4-azido-2,6-dimethyl-1,1'-biphenyl

^{1}H NMR (500 MHz, $CDCl_3$)

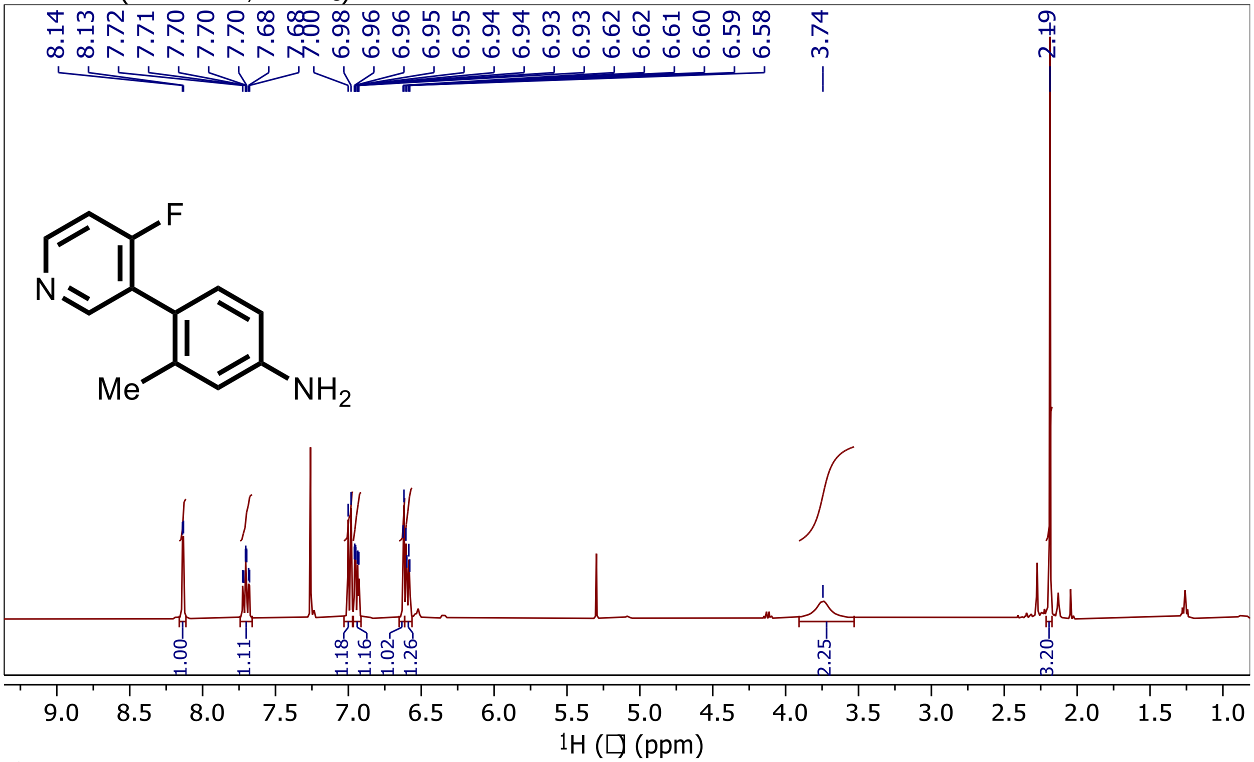


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

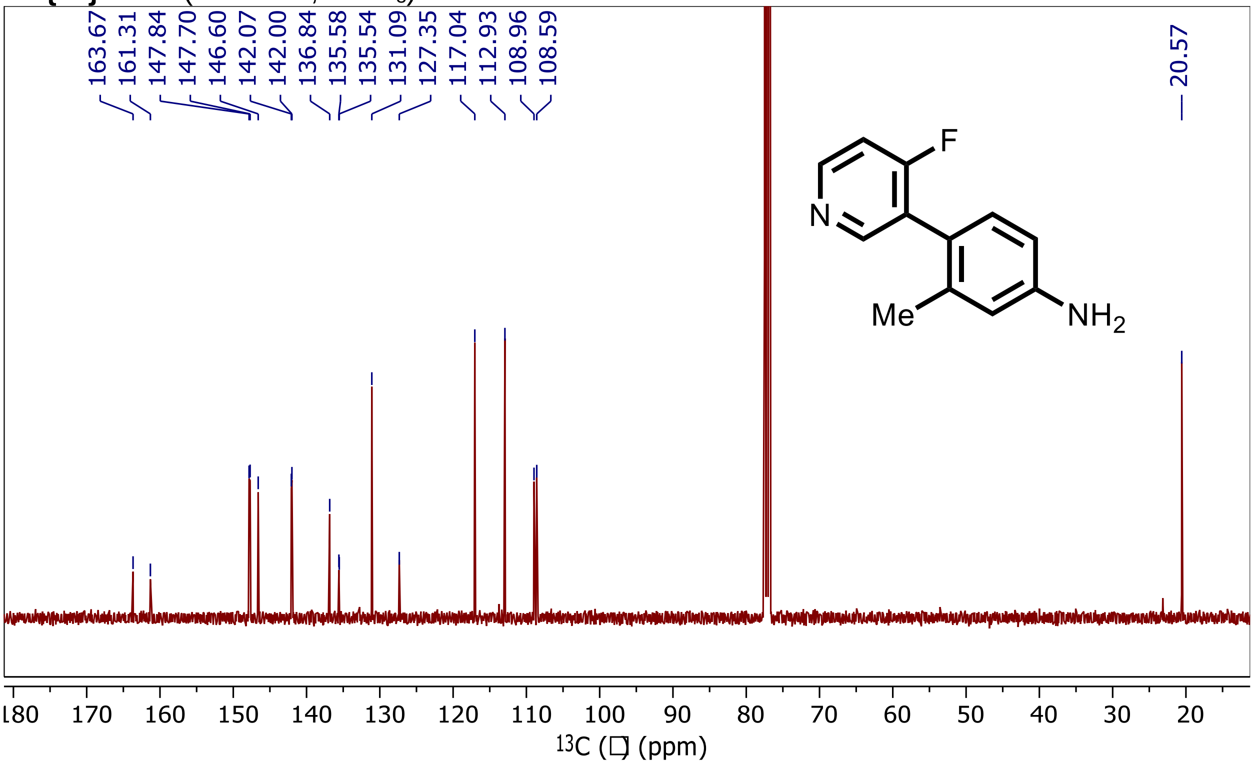


4-(4-fluoropyridin-3-yl)-3-methylaniline

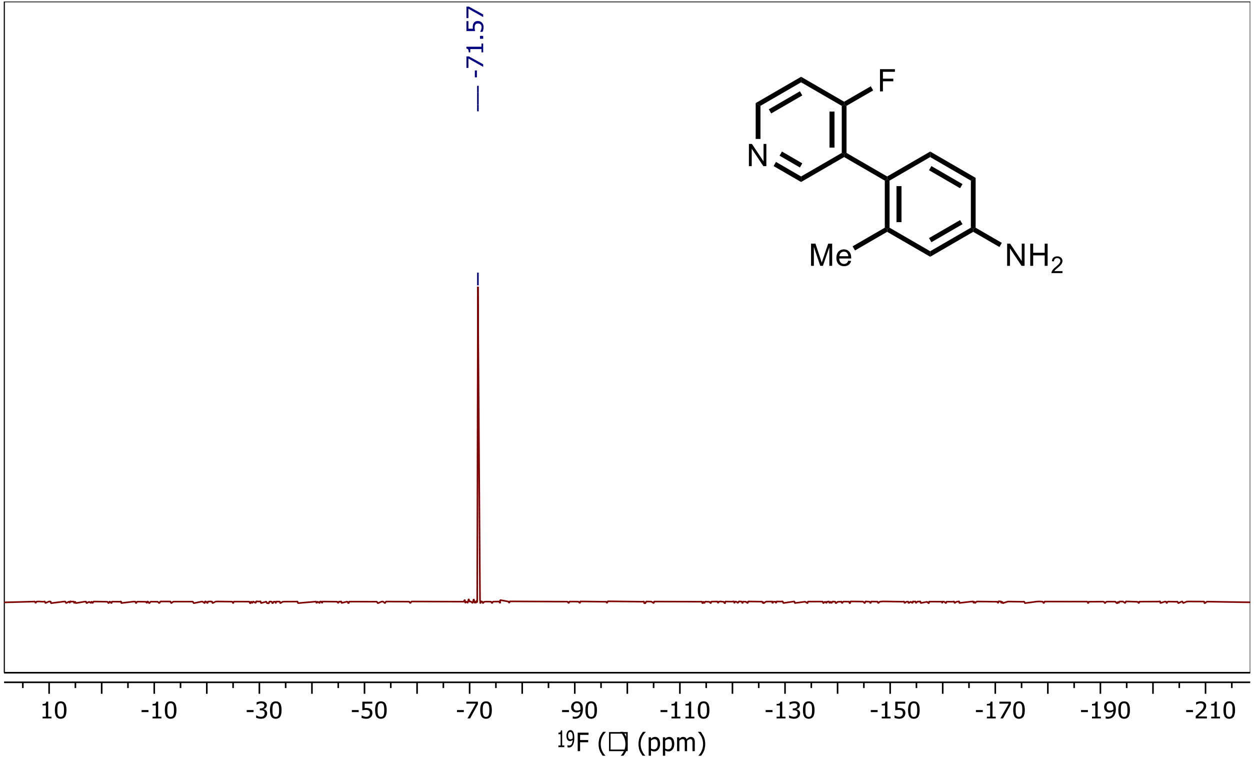
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

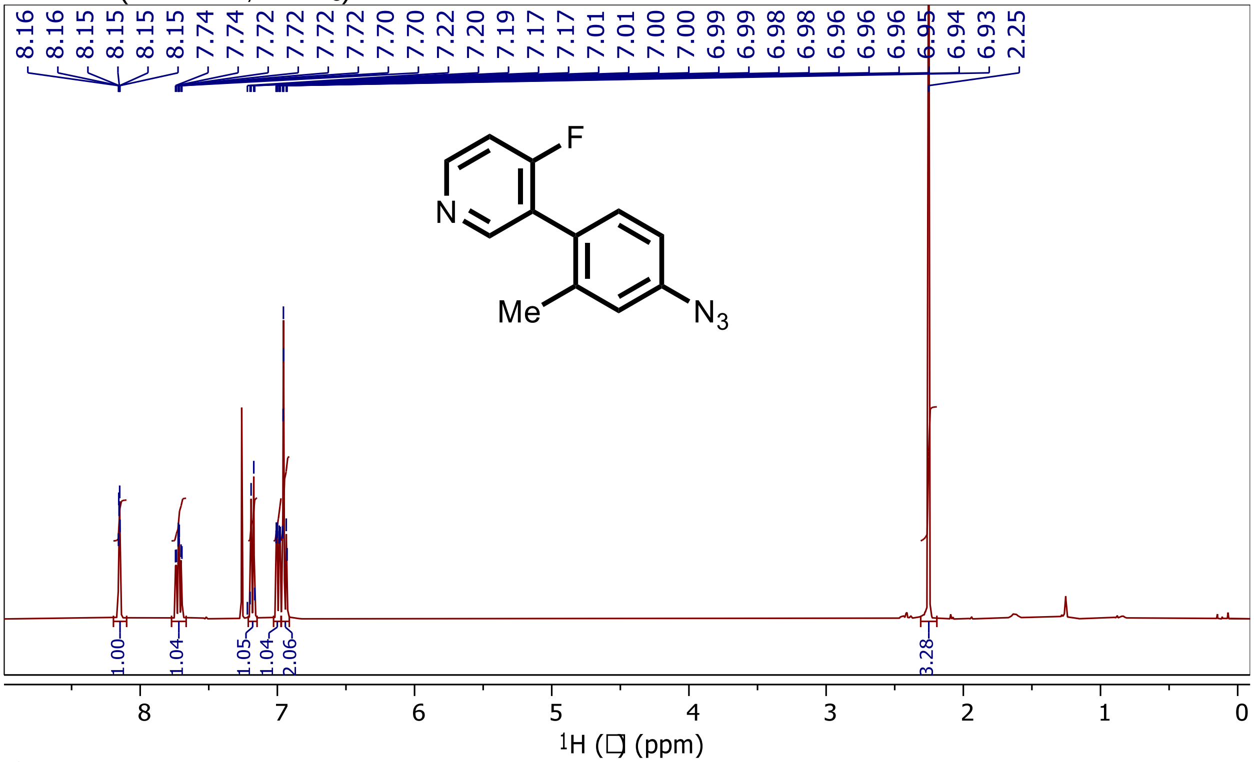


^{19}F NMR (376 MHz, $CDCl_3$)

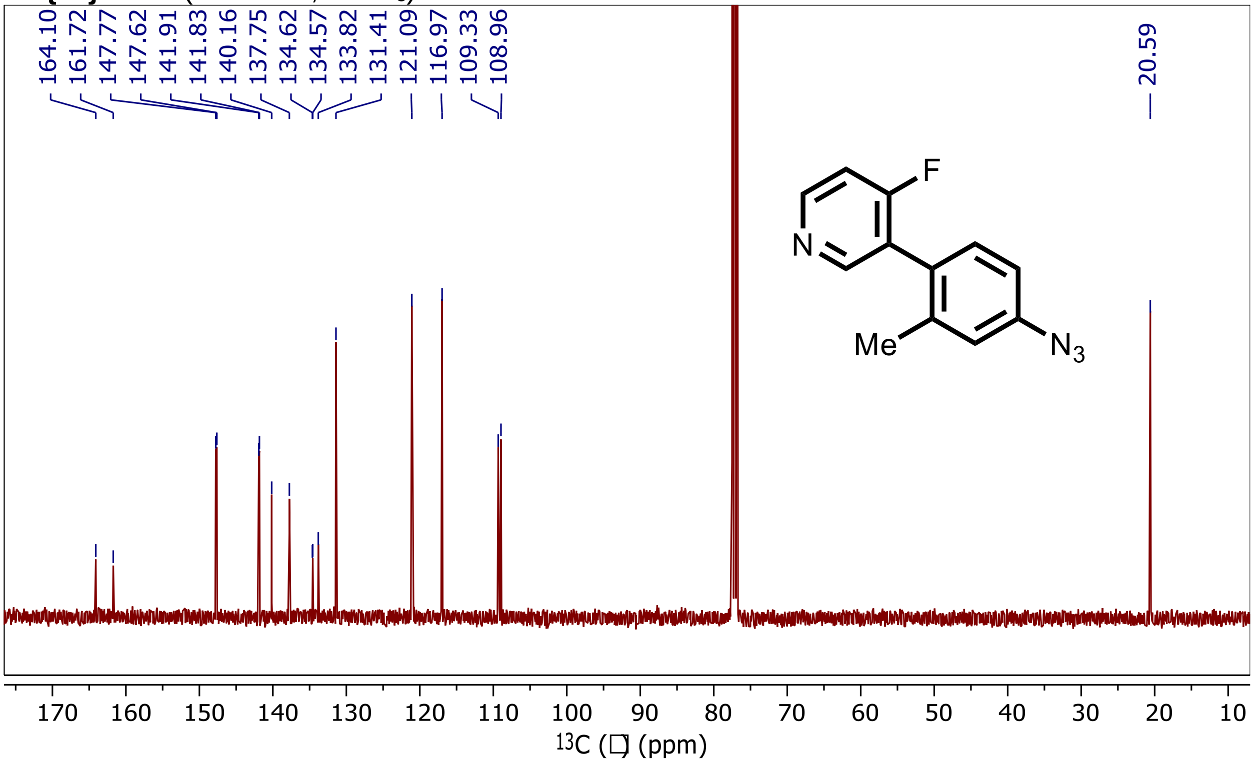


3-(4-azido-2-methylphenyl)-4-fluoropyridine

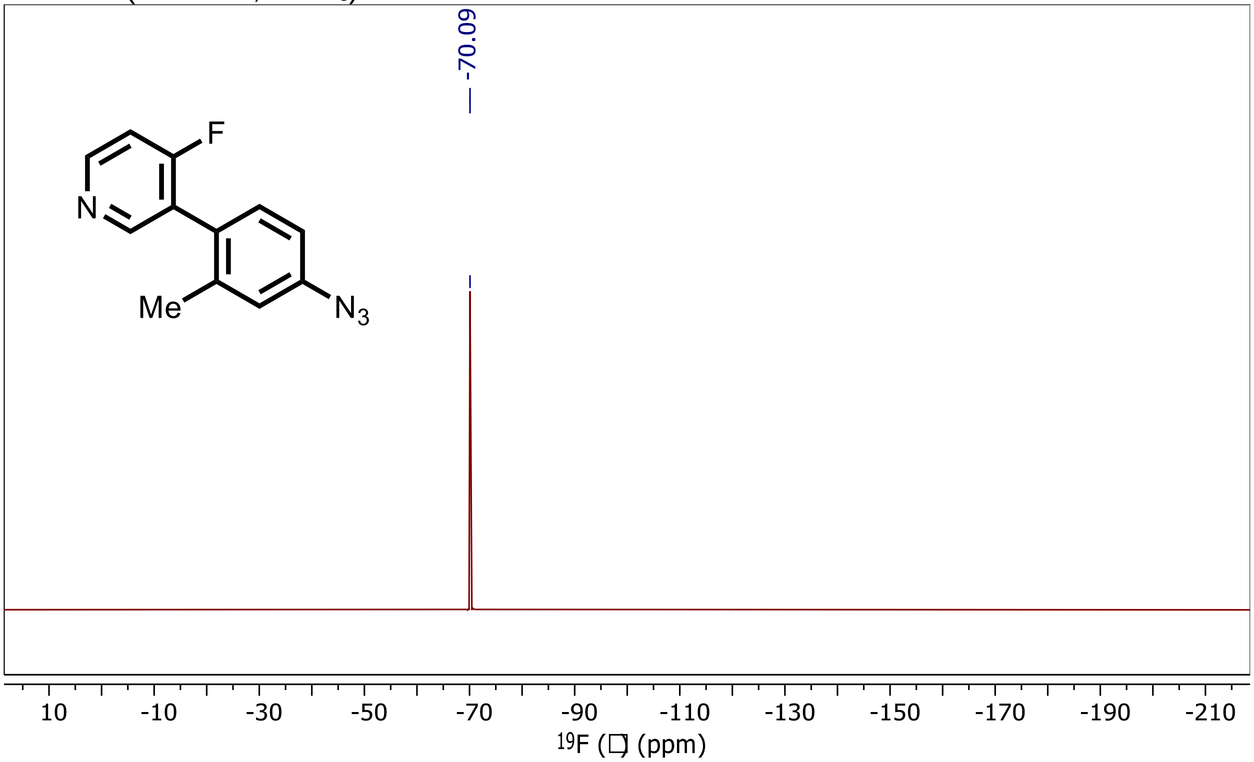
^{1}H NMR (400 MHz, CDCl$_3$)



^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)

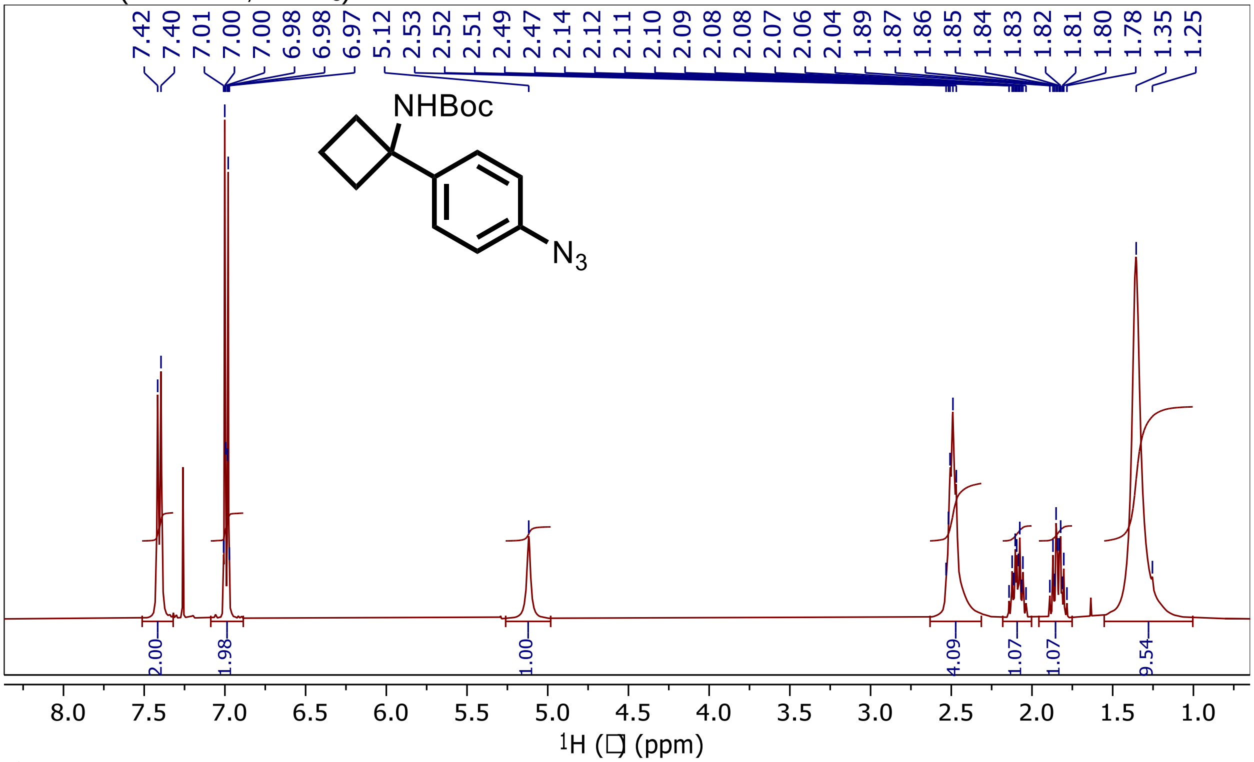


^{19}F NMR (376 MHz, $CDCl_3$)

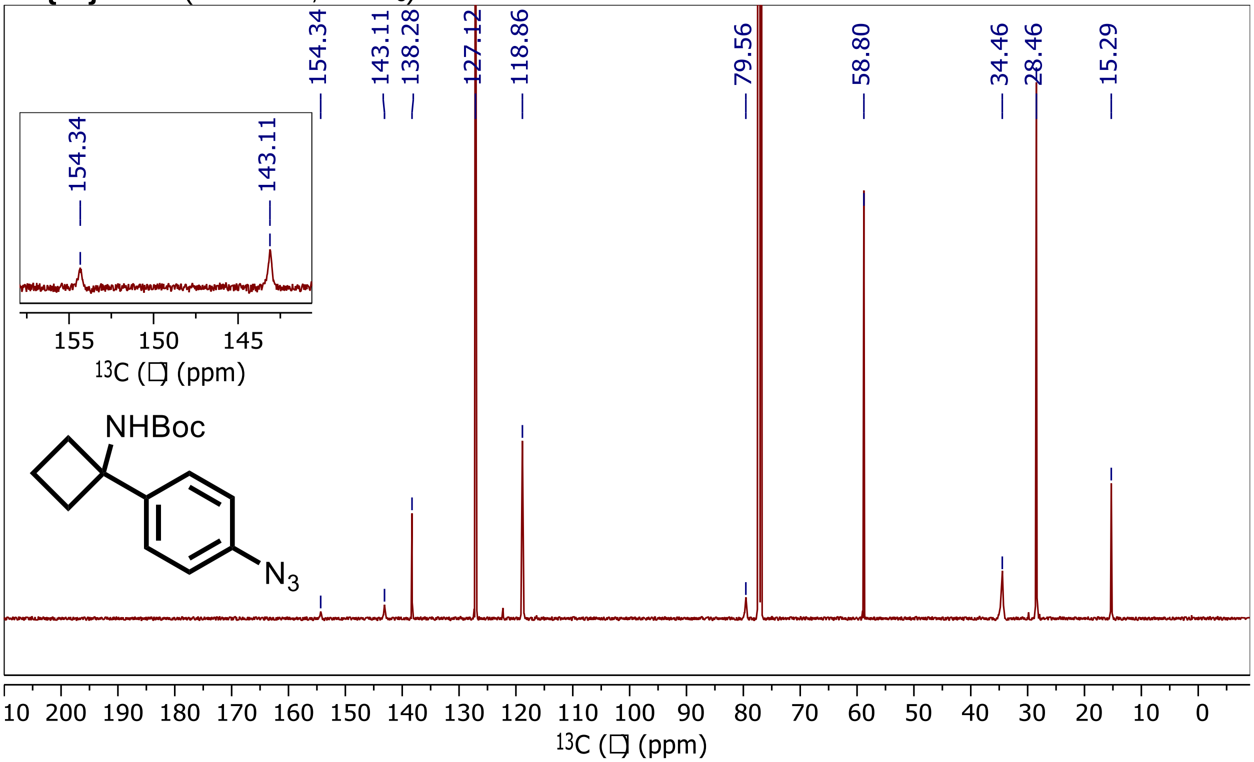


***tert*-butyl (1-(4-azidophenyl)cyclobutyl)carbamate**

^{1}H NMR (400 MHz, $CDCl_3$)

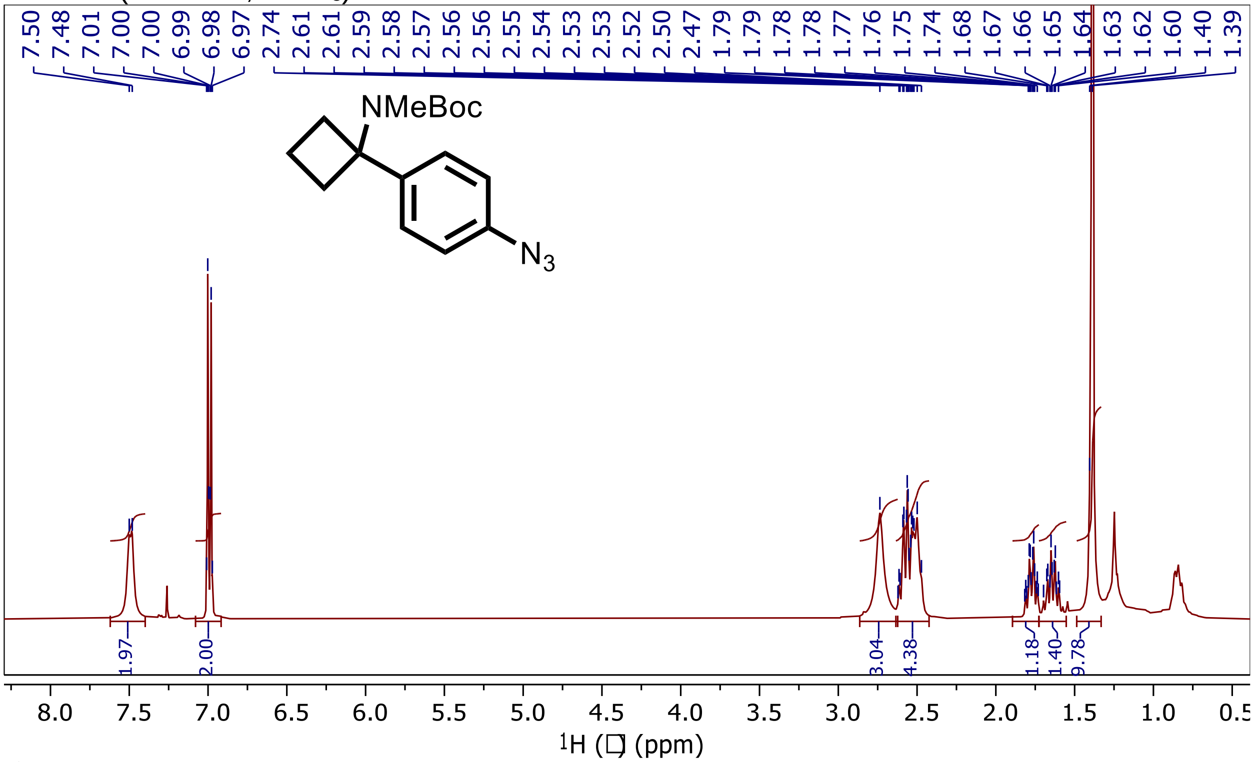


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)

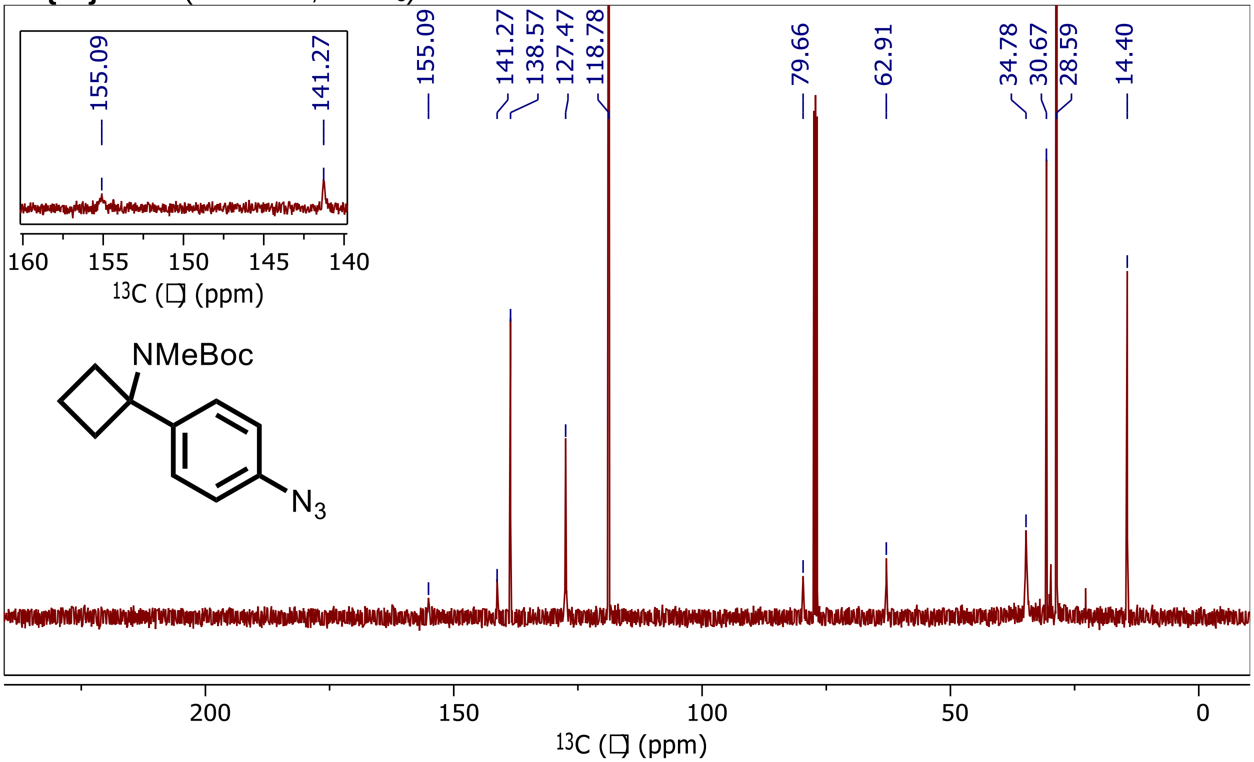


***tert*-butyl (1-(4-azidophenyl)cyclobutyl)(methyl)carbamate**

^{1}H NMR (400 MHz, CDCl$_3$)

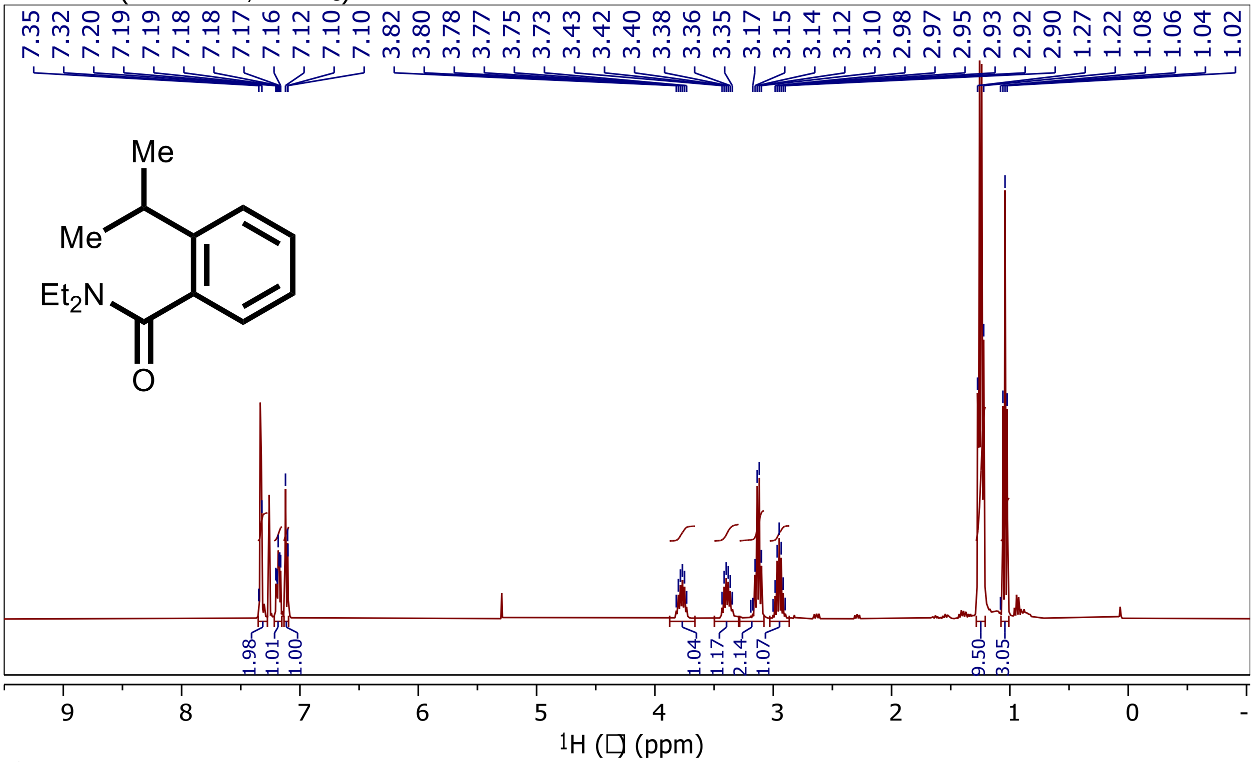


^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)

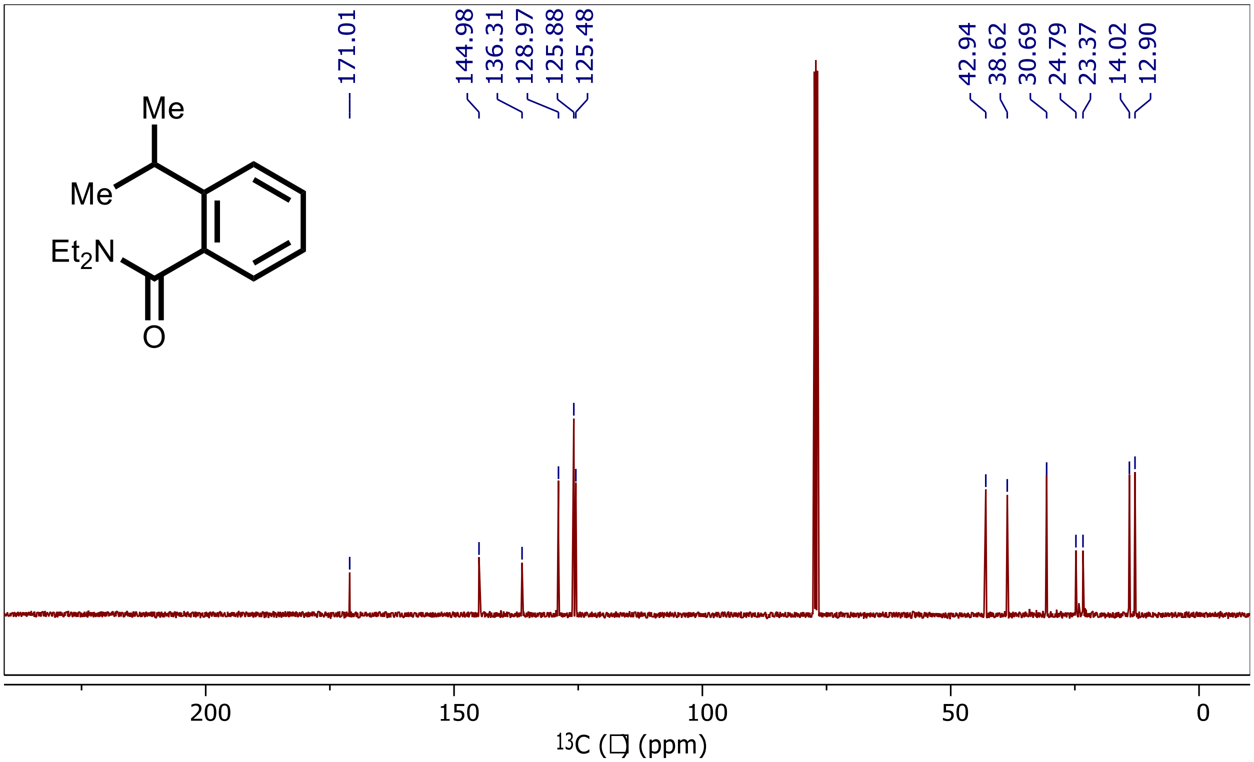


***N,N*-diethyl-2-isopropylbenzamide**

^{1}H NMR (400 MHz, $CDCl_3$)

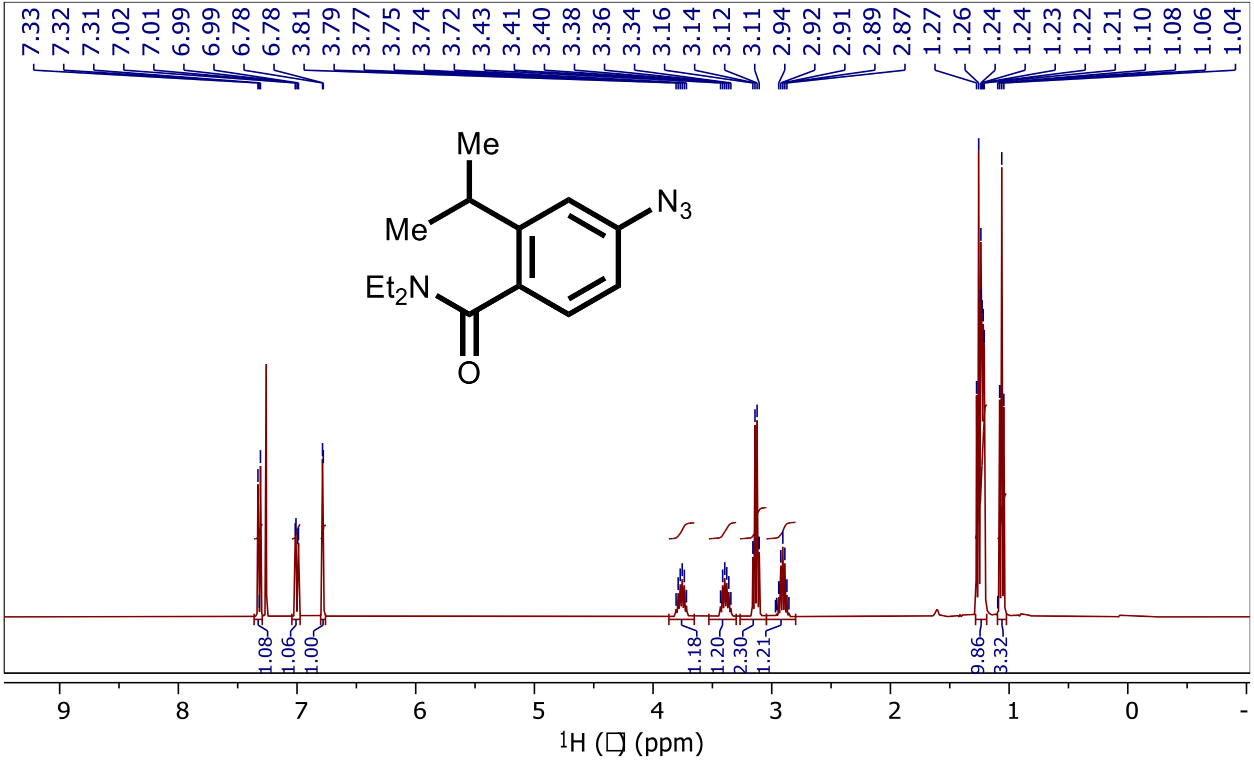


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)

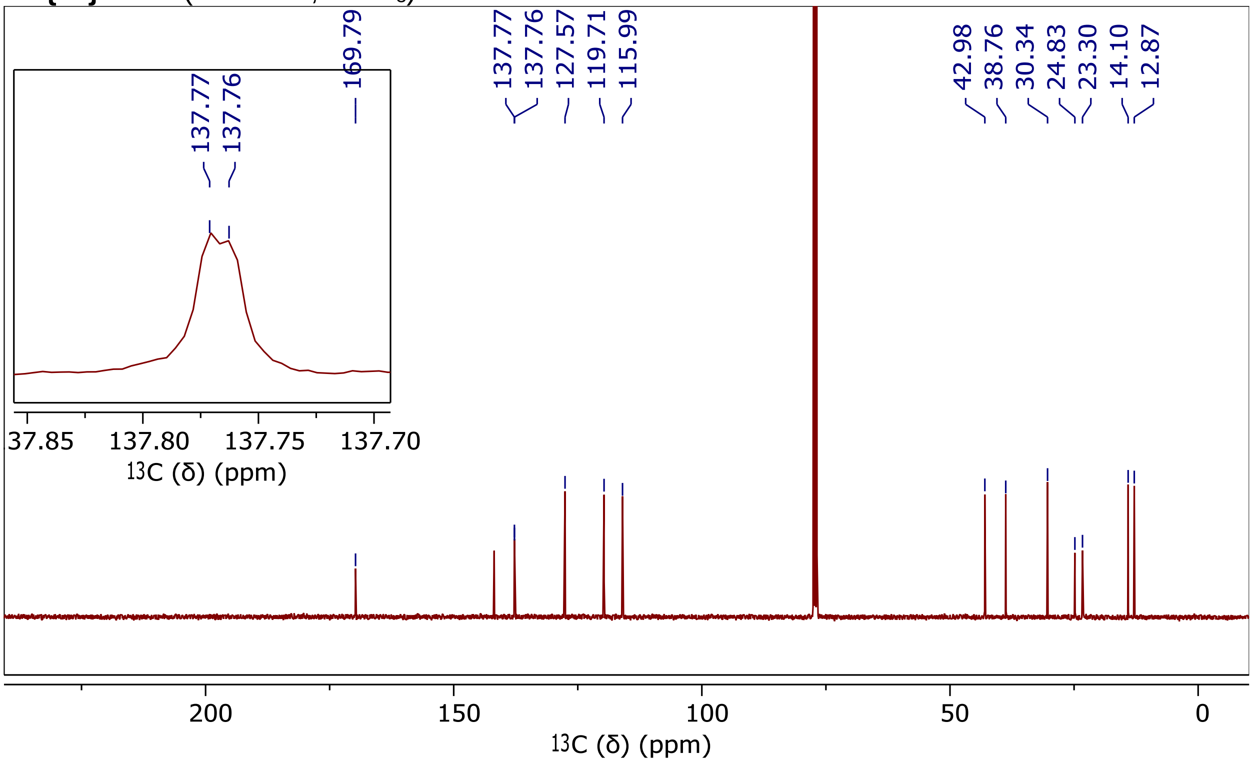


4-azido-*N,N*-diethyl-2-isopropylbenzamide

^{1}H NMR (400 MHz, CDCl$_3$)

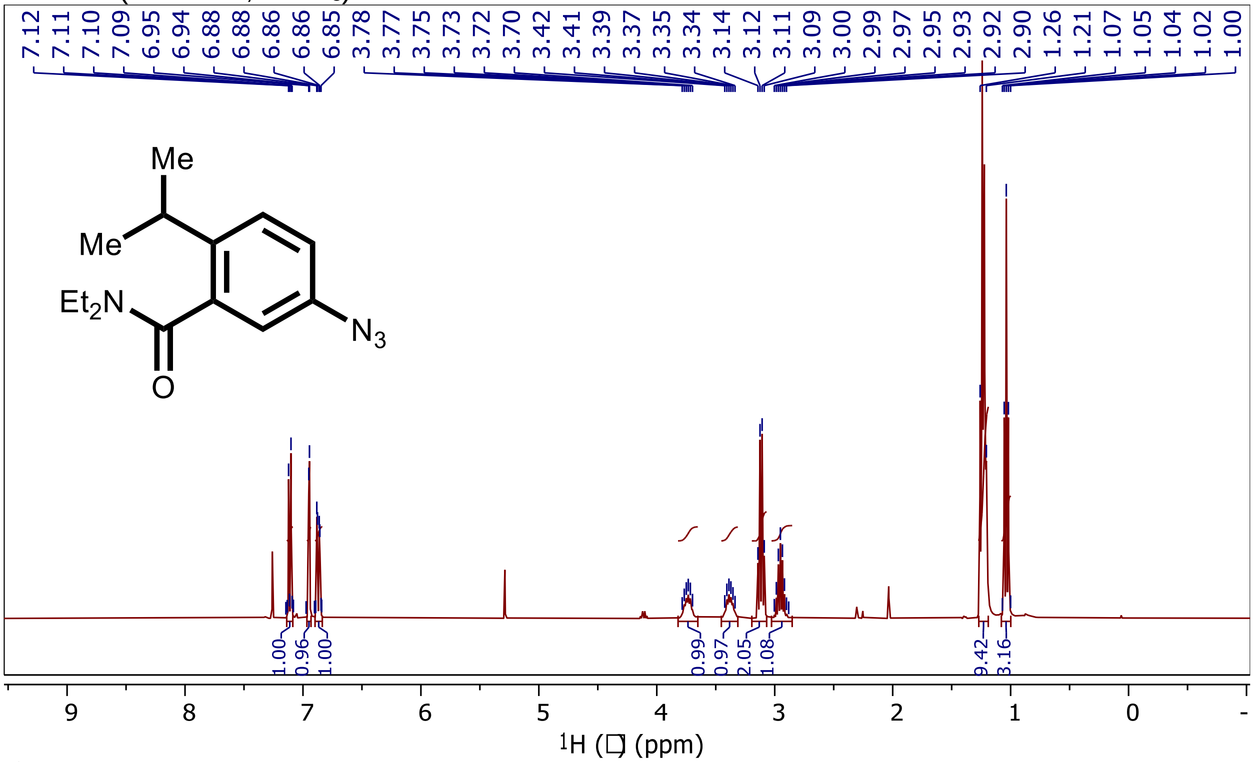


^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$)

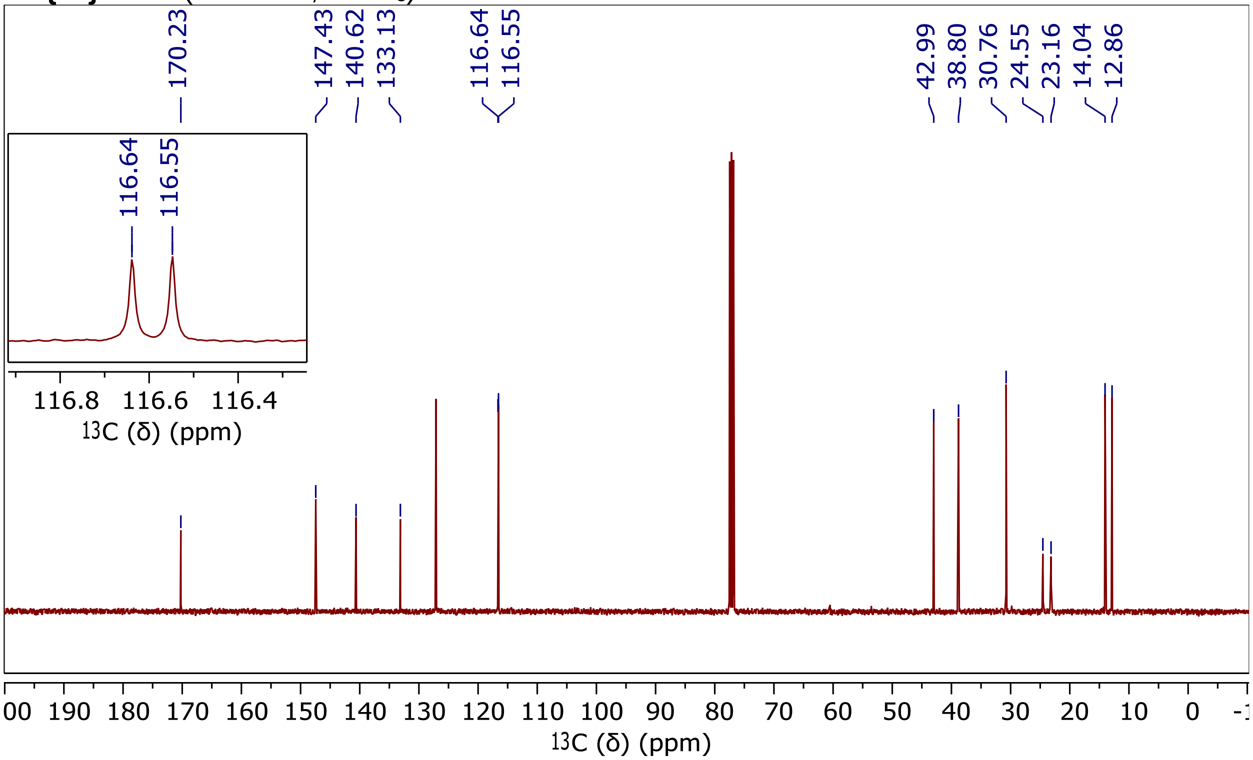


5-azido-N,N-diethyl-2-isopropylbenzamide

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)



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