Supporting Information

Strain-Release 2-Azaallyl Anion Addition/Borylation of [1.1.1]Propellane: Synthesis and Functionalization of Benzylamine Bicyclo[1.1.1]pentyl Boronates

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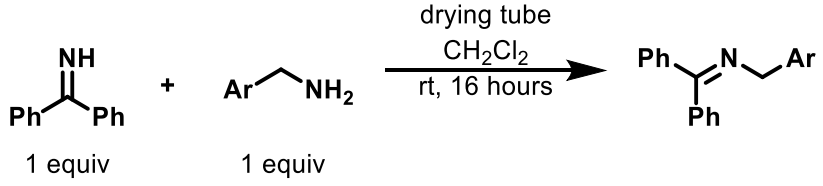
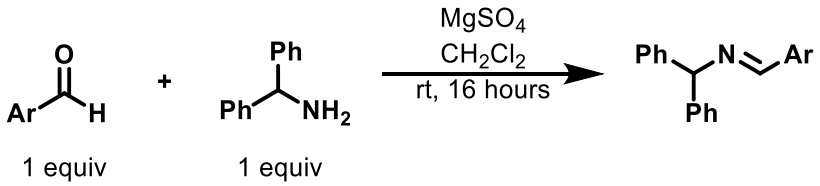
General Methods: All reactions were conducted under a nitrogen atmosphere in a glovebox with oven-dried glassware and standard Schlenk or vacuum line techniques unless otherwise noted. All solutions were handled under nitrogen and transferred via an Eppendorf brand pipetter. Anhydrous solvents were purchased from Sigma-Aldrich and directly used. Unless otherwise stated, reagents were commercially available and used as purchased. Chemicals were purchased from Sigma-Aldrich, Acros, or Alfa Aesar and solvents were purchased from Fisher Scientific. Reaction progress was monitored by thin-layer chromatography using glass-backed Silica Gel HL TLC Plates purchased from Sorbent Technologies and visualized by short-wave ultraviolet light. Reactions were performed in 4 mL vials purchased from Chemglass Life Sciences or in 10 mL microwave vials sealed with caps from Biotage. Flash chromatography was performed with silica gel (300-400 mesh, Silicycle) when SiO_2 as the stationary phase is indicated. Fully endcapped C_{18}-reversed phase silica gel was purchaesd as used from Sigma-Aldrich where stationary phase is indicated as such. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were obtained using a Brüker AM-500 Fourier-transform NMR spectrometer at 500 and 125, 600 and 150, or 400 and 100 MHz, respectively. ^{19}F spectra were obtained at 471 or 376 MHz. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using chemical ionization (CI) or electrospray ionization (ESI) in positive or negative mode, depending on the analyte.

General Procedure A for *N*-benzyl ketimine synthesis



Dichloromethane (0.4 M) is added to a round-bottomed flask. The benzylamine (1 equiv) and benzophenone imine (1 equiv) are then added and the flask is fitted with a drying tube ($CaCl_2$). The reaction mixture is stirred for 16 h at room temperature. The solvent is removed by rotary evaporation and the ketimine is used without further purification.

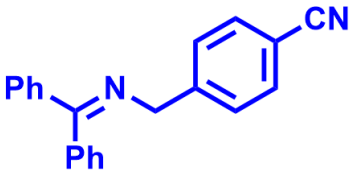
General Procedure B for aldimine synthesis



Under a nitrogen atmosphere,* a round-bottomed flask is charged with dichloromethane (0.4 M), the aryl aldehyde (1 equiv), benzhydrylamine (1 equiv), and magnesium sulfate (5 equiv). The reaction is stirred vigorously at room temperature for 16 h, and then filtered over a pad of Celite

which is rinsed once with dichloromethane. The organic layer is concentrated via rotary evaporation to give the aldimine, which is used without further purification.

*Many aryl aldehydes and benzhydrylamine are sensitive to air, so it is recommended to run this reaction under an inert atmosphere.

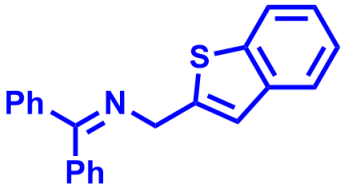


4-(((diphenylmethylene)amino)methyl)benzonitrile

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.70 (t, *J* = 7.3 Hz, 4H), 7.59-7.51 (m, 5H), 7.42-7.36 (m, 3H), 7.24 (m, 2H), 4.63 (s, 2H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 170.1, 147.7, 140.5, 137.4, 133.0, 131.2, 129.8, 129.7, 129.4, 129.3, 129.0, 128.4, 119.6, 111.1, 57.4 ppm.

HRMS calc'd for $[C_{21}H_{16}N_2+H]^+$ = 297.1391, found 297.1386.



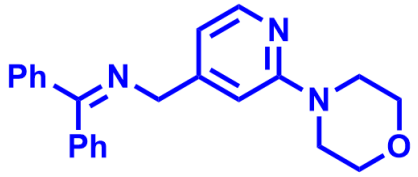
***N*-(benzo[b]thiophen-2-ylmethyl)-1,1-diphenylmethanimine**

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.88-7.76 (m, 1H), 7.73-7.71 (m, 3H), 7.58-7.52 (m, 3H), 7.45-7.38 (m, 3H), 7.31-7.26 (m, 4H), 7.16 (s, 1H), 4.81 (s, 2H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 169.8, 146.8, 141.1, 140.5, 140.4, 137.2, 131.2, 129.8, 129.4, 129.0, 128.5, 125.0, 124.5, 124.0, 132.1, 120.6, 53.9 ppm.*

*One peak not observed due to coincidental overlap.

HRMS calc'd for $[C_{22}H_{17}NS+H]^+$ = 328.1160, found 328.1155.

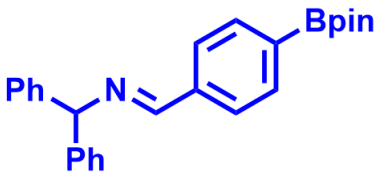


***N*-((2-morpholinopyridin-4-yl)methyl)-1,1-diphenylmethanimine**

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.07 (d, *J* = 5.0 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.57-7.50 (m, 3H), 7.43-7.36 (m, 3H), 7.24 (d, *J* = 6.7 Hz, 2H), 6.77 (s, 1H), 6.70 (d, *J* = 5.0 Hz, 1H), 4.48 (s, 2H), 3.71 (t, *J* = 5.0 Hz, 4H), 3.46 (t, *J* = 5.0 Hz, 4H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 169.8, 161.0, 152.1, 148.6, 140.6, 137.6, 131.1, 129.7, 129.6, 129.31, 129.0, 128.5, 114.0, 106.2, 67.3, 57.2, 46.5 ppm.

HRMS calc'd for $[C_{23}H_{23}N_3O+H]^+$ = 358.1919, found 358, 1918.



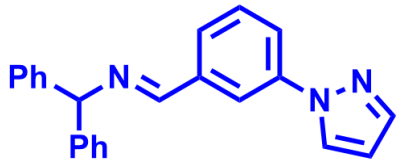
***N*-benzhydryl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanimine**

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.61 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 4H), 7.31 (t, *J* = 4.3 Hz, 4H), 7.22 (t, *J* = 7.3 Hz, 2H), 5.70 (s, 1H), 1.34 (s, 12H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 161.9, 145.5, 140.0, 135.8, 129.3, 128.54, 128.51, 127.8, 84.8, 78.9, 25.3 ppm.*

HRMS calc'd for $[C_{26}H_{28}BNO_2+H]^+$ = 398.2291, found 398.2285.

*An aromatic resonance is not observed due to quadrupolar relaxation from boron.



1-(3-(1H-pyrazol-1-yl)phenyl)-*N*-benzhydrylmethanimine

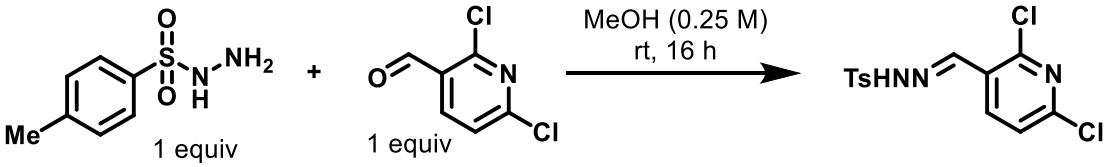
Prepared according to General Procedure B. The product was obtained as an orange solid.

^{1}H NMR (400 MHz, ($CDCl_3$): δ 8.46 (s, 1H), 8.18 (s, 1H), 7.98 (d, *J* = 2.4 Hz, 1H), 7.78 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.40-7.70 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.41-7.39 (m, 4H), 7.32 (t, *J* = 4.5 Hz, 4H), 7.25-7.22 (m, 2H), 6.48 (t, *J* = 1.9 Hz, 1H), 5.64 (s, 1H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.0, 143.7, 141.4, 140.6, 137.7, 129.7, 128.6, 127.8, 127.2, 127.0, 126.8, 121.5, 118.5, 107.9, 77.9 ppm.

HRMS calc'd for $[C_{23}H_{19}N_3+H]^+$ = 338.1657, found 338.1647.

Preparation of sulfonylhydrazone for the Barluenga reaction



***N*'-((2,6-dichloropyridin-3-yl)methylene)-4-methylbenzenesulfonohydrazide**

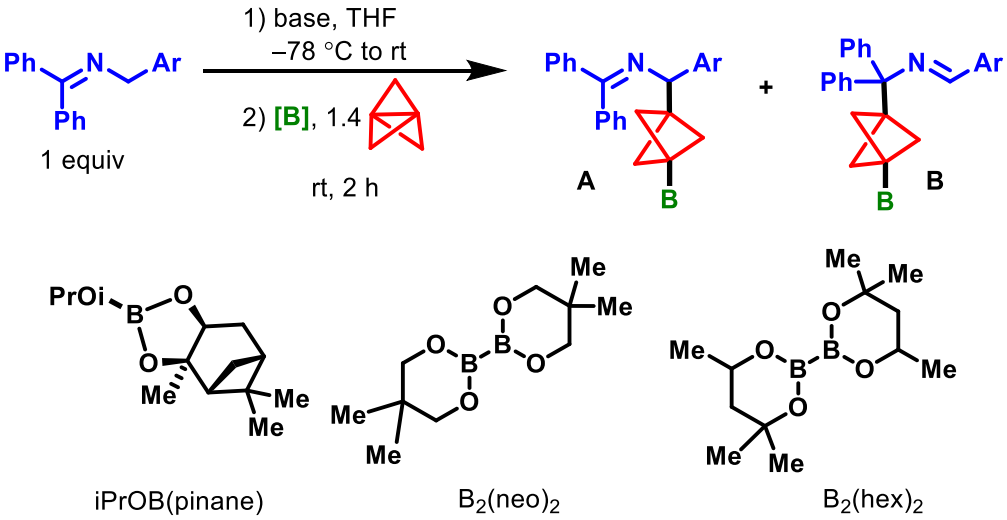
Prepared according to the literature procedure [*Org. Lett*. **2020**, *22*, 2271−2275]. The tosyl hydrazide (1 equiv) and aldehyde (1 equiv) were stirred in MeOH (0.25 M) under N_2, due to the air sensitivity of the aldehyde, for 16 h, over which time a white solid precipitated. The solid was collected via filtration on filter paper and dried under high vacuum to give the product which was used without further purification.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 10.6 (br s, 1H), 8.27-8.25 (m, 2H), 7.85-7.83 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 2.40 (s, 3H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 151.3, 149.3, 145.1, 141.3, 139.0, 137.3, 130.6, 128.6, 125.0, 21.5 ppm.

HRMS calc'd for $[C_{13}H_{11}Cl_2N_3O_2S+H]^+$ = 344.0027, found 344.0020.

Exploration of boron trapping reagents for the BCP



Entry	Conditions	% A / B (AY)
1	1.1 equiv *n*-BuLi, [B] = MeOBpin (2 equiv)	42 / 6 [B = Bpin]
2	1.1 equiv *n*-BuLi, [B] = B_2pin_2 (2 equiv)	46 / 4 [B = Bpin]
3	1.1 equiv *n*-BuLi, [B] = iPrOBpin (2 equiv)	56 / 8 [B = Bpin]
4[a]	1.1 equiv *n*-BuLi, [B] = iPrOB(pinane) (3 equiv)	60[b] / N/D [B = B(pinane)]
5	1.1 equiv *n*-BuLi , [Bpin] = $B_2(neo)_2$ (2 equiv)	46[c] / N/D [B = B(neo)]
6	1.1 equiv *n*-BuLi, [Bpin] = $B_2(hex)_2$	Not detected [B = B(hex)]

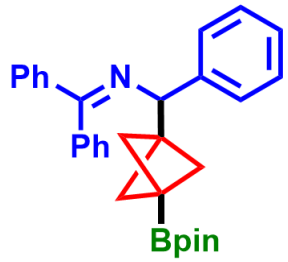
Table S1. Exploration of boronate ester electrophiles for the borylation reaction.

[a] iPrOB(pinane) was prepared according to *Org. Lett.* **2007**, *9*, 4315-4318 from (-)-pinane diol and isopropoxyborate.

[b] Despite this high AY and the stability of pinane diol-derived BCP boronate esters on silica gel, this substrate was not pursued for several reasons: (1) iPrOB(pinane) is not commercially available, (2) the high cost of (-)-pinane diol, (3) the ^{1}H NMR spectra of B(pinane)-derived BCP ketimines were difficult to interpret, and (4) lack of literature precedent for transition metal-catalyzed cross-coupling of B(pinane) esters, which are presumed to be even more reluctant to cross-couple than than pinacol boronate esters.

[c] The benzylamine BCP B(neo) ester was observed to oxidize rapidly to BCP-OH after handling in air atmosphere.

General Procedure C for the propellylation/borylation reaction: In a glovebox under nitrogen atmosphere, a 4 mL vial is charged with a stir bar and the ketimine (0.2 mmol, 1 equiv). THF (0.5 mL) is added via pipette at room temperature. In a second 4 mL vial, diisopropylamine (31 µL, 0.22 mmol, 1.1 equiv) is dissolved in 0.5 mL THF at room temperature. Both vials are capped with caps containing a septum. On a Schlenk line, under nitrogen atmosphere maintained by an inlet needle through the septum cap, the diisopropylamine solution is cooled in an ice bath. *n*-Butyllithium (0.13 mL of a 1.6 M solution in hexanes, 0.21 mmol, 1.05 equiv) is added dropwise. The solution is stirred for 1 minute, then removed from the ice bath and stirred one minute further at ambient temperature, producing a slightly yellow solution of LDA. The LDA solution is added via syringe dropwise to the ketimine solution under N_2, which has been cooled to -78 °C (dry ice/acetone), producing a deep purple solution. The resulting mixture is stirred for 10 minutes at -78 °C, then removed from the ice bath and stirred 10 minutes at ambient temperature. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (iPrOBpin [used as purchased from TCI America and stored in the glovebox to minimize hydrolysis], 0.2 mL, 1.0 mmol, 5 equiv) is added via syringe, followed immediately by [1.1.1]propellane as a stock solution [stored at -31 °C in the freezer of the glovebox] (0.28 mmol, 1.4 equiv). The reaction mixture is stirred vigorously for 2 – 24 hours and decolorizes from purple to a cloudy, white or off-white mixture. The vial is uncapped, exposed to air and 2 drops of water are added. The reaction mixture is diluted with ethyl acetate (2 mL) and transferred to a test tube. Next, 4 mL saturated brine are added to the test tube and shaken vigorously to wash the crude mixture. The organic layer is separated and the brine is washed with one further portion of ethyl acetate (2 mL). The combined organic layers are passed over a pad of $MgSO_4$/silica gel packed into a pipette. The filter cake is rinsed twice with 2 mL ethyl acetate. The combined organic layers are concentrated under reduced pressure to give a crude oil which is purified by flash chromatography on reversed-phase silica gel (C_{18}, fully endcapped).



1,1-diphenyl-*N*-(phenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (7a)

Compound **7a** was prepared according to General Procedure C, employing ketimine **4a** (54.2 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 16 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (90% → 95% MeCN/H_2O) to give a mixture of C1 and C3 isomers, a white solid, 61.1 mg, 66% overall yield. The ratio of C1:C3, 61:7, was determined by ^{1}H NMR and GC-MS of the purified reaction mixture.

^{1}H NMR (400 MHz, $(CD_3)_2CO$)*: δ 7.71 (d, *J* = 6.8 Hz 2H), 7.55-7.52 (m, 3H), 7.50-7.33 (m, 4H), 7.31 (d, *J* = 4.3 Hz, 4H), 7.25-7.21 (m, 1H), 7.11-7.10 (m, 2H), 4.36 (s, 1H), 1.63 (dd, *J* = 15.7, 6.2 Hz, 6H), 1.17 (s, 12H)** ppm.

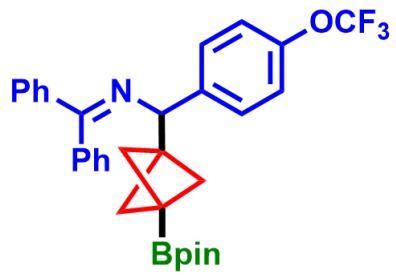
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)***: δ 166.4, 160.2, 145.6, 142.2, 140.4, 137.0, 130.4, 129.8, 129.5, 128.37, 128.32, 128.26, 128.22, 128.0, 127.59, 127.54, 126.5, 126.3, 83.2, 68.2, 50.6, 49.8, 48.7, 24.8 ppm.

HRMS calc'd for $[C_{31}H_{34}BNO_2]^+$ = 463.2683, found 463.2686 (C1 isomer). Integration of C1 and C3 in GC-MS found a C1:C3 ratio of 13.7:1, or 93% C1, 7% C3, corresponding to 61% and 5% isolated yield of C1 and C3, respectively. This ratio is confirmed by ^{1}H NMR.

*Due to overlap from C1 and C3 products, the aromatic region overintegrates to approximately 16 H. C1 isomer, the major product, should give 16 H, and an extra 1 H in this region is expected from the 7% C3 by 0.07 * 15 = 1.05 which is approx. 1 H. Overintegrated peaks are reported as observed.

**In the full spectrum singlet integrates to more than the expected value of 12H due to the presence of C3 isomer in the product mixture.

***Aromatic carbons of the C3 product, which is inseparable from C1, also appear in this spectrum, leading to more than the expected number of carbons for C1. The carbon shifts reported here are all carbons found in the spectrum of the C1/C3 mixture.



1,1-diphenyl-*N*-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (7b)

Compound **7b** was prepared according to General Procedure C, employing ketimine **4b** (83.3 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 16 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (80% → 95% MeCN/H_2O) to give the C1 isomer as a colorless oil, 74.6 mg, 70% overall yield.

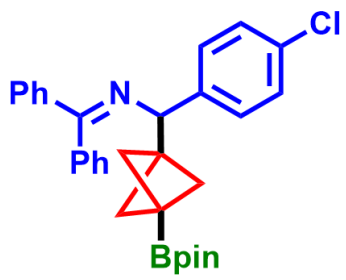
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (m, 2H), 7.43-7.42 (m, 3H), 7.38-7.31 (m, 5H), 7.12 (d, J = 4.8 Hz, 2H), 7.08-7.05 (m, 2H), 4.35 (s, 1H), 1.68 (dd, J = 12, 9.1 Hz, 6H), 1.20 (s, 12H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.9, 147.9, 141.0, 140.1, 136.8, 130.0, 129.5, 128.7, 128.5, 128.4, 128.14, 128.10, 120.66 (q, $J_{C\text{-}F}$ = 256 Hz), 120.65, 83.4, 67.5, 49.7, 48.5, 24.8 ppm.*

^{19}F NMR (376 MHz, $CDCl_3$) (unreferenced): δ -57.8 ppm.

HRMS calc'd for $[C_{32}H_{33}BF_3NO_3]^+$ = 547.2506, found 547.2513.

*A resonance is not observed due to quadrupolar relaxation from boron.



_N_-((4-chlorophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7c)

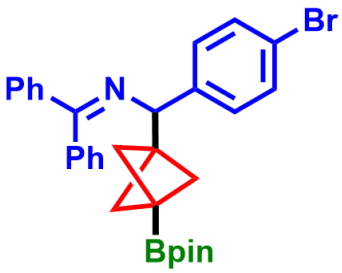
Compound **7c** was prepared according to General Procedure C, employing ketimine **4c** (61.2 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 16 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (80% → 95% MeCN/H_2O) to give exclusively the C1 isomer as a white solid, 60.0 mg, 60% overall yield.

^{1}H NMR (400 MHz, ($CDCl_3$): δ 7.61-7.59 (m, 2H), 7.33-7.31 (m, 3H), 7.29-7.22 (m, 3H), 7.17-7.16 (m, 4H), 6.97-6.95 (m, 2H), 4.21 (s, 1H), 1.59 (dd, *J* = 10.8, 9.4 Hz, 6H), 1.11 (s, 12H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.8, 140.8, 140.2, 136.8, 132.1, 129.9, 128.8, 128.6, 128.4, 128.3, 128.19, 128.11, 128.0, 83.3, 67.5, 49.7, 48.5, 24.8 ppm.*

HRMS calc'd for $[C_{31}H_{33}BClNO_2+H]^+$ = 498.2371, found 498.2372.

*A resonance is not observed due to quadrupolar relaxation from boron.



_N_-((4-bromophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7d)

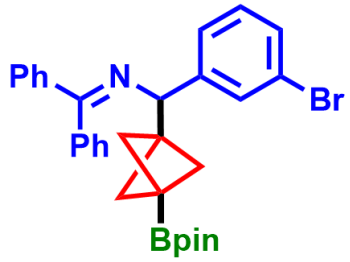
Compound **7d** was prepared according to General Procedure C, employing ketimine **4d** (70.0 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 21 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (70% → 95% MeCN/H_2O) to give exclusively the C1 isomer as a white solid, 62.1 mg, 57% overall yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.66 (m, 2H), 7.42-7.29 (m, 8H), 7.19-7.17 (d, 2H), 7.04-7.02 (m, 2H), 4.27 (s, 1H), 1.66 (dd, *J* = 10.4, 9.5 Hz, 6H), 1.18 (s, 12H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.9, 141.3, 140.2, 136.8, 131.1, 130.0, 129.2, 128.7, 128.47, 128.40, 128.1, 128.0, 120.3, 83.3, 67.6, 49.7, 48.4, 24.8 ppm.*

HRMS calc'd for $[C_{31}H_{33}BBrNO_2+H]^+$ = 542.1866, found 542.1850.

*A resonance is not observed due to quadrupolar relaxation from boron.



_N_-((3-bromophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7e)

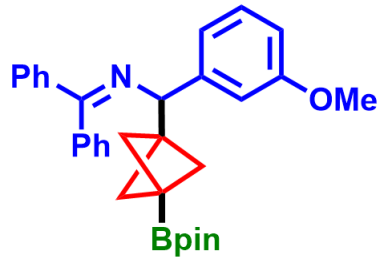
Compound **7e** was prepared according to General Procedure C, employing ketimine **4e** (70.1 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 16 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (80% → 95% MeCN/H_2O) to give the C1 isomer as white solid, 63.2 mg, 59% overall yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.68 (m, 2H), 7.50 (s, 1H), 7.43-7.32 (m, 7H), 7.23-7.21 (m, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.07-7.04 (m, 2H), 4.30 (s, 1H), 1.67 (dd, *J* = 12 Hz, 9.4 Hz, 6H), 1.19 (s, 12H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 168.3, 145.9, 141.0, 137.6, 131.13, 131.11, 131.0, 130.6, 129.6, 129.5, 129.4, 129.1, 128.9, 127.2, 122.8, 84.0, 68.5, 50.5, 49.2, 25.2 ppm.*

HRMS calc'd for $[C_{31}H_{33}BBrNO_2]^+$ = 541.1902. found 541.1926.

*A resonance is not observed due to quadrupolar relaxation from boron.



_N_-((3-methoxyphenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7f)

Compound **7f** was prepared according to General Procedure C, employing ketimine **4f** (60.3 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 16 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (80% → 95% MeCN/H_2O) to give a mixture of C1 and C3 isomers as a white solid, 55.5 mg, 56% overall yield. The ratio of C1:C3, 93:7, was determined by ^{1}H NMR and GC-MS of the purified reaction mixture.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (dd, *J* = 6.8, 1.4 Hz, 2H), 7.45-7.28* (m, 8H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.09-7.07 (m, 2H), 6.94 (s, br, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.75 (dd, *J* = 8.0, 2.1 Hz, 1H), 4.30 (s, 1H), 3.79 (s, 3H), 1.71 (dd, *J* = 12, 9.4 Hz, 6H), 1.19** (s, 13H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)***: δ 166.4, 160.1, 159.5, 145.6, 143.9, 140.4, 137.0, 129.8, 129.6, 129.5, 128.9, 128.7, 128.4, 128.2, 128.0, 127.6, 126.4, 121.5, 120.0, 113.3, 113.2, 112.3, 111.9, 83.4, 83.3, 68.1, 55.5, 55.2, 50.6, 49.9, 48.9, 48.7, 24.9 ppm.

IR (thin film): 3056, 2975, 2907, 2870, 1598 cm^{-1}.

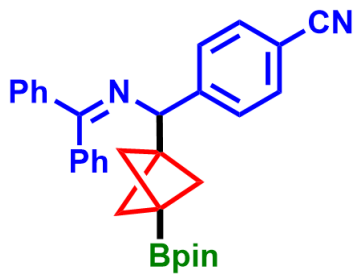
HRMS calc'd for $[C_{32}H_{36}BNO_3]^+$ = 493.2788, found 493.2786.

The ratio of C1:C3 was determined to be 13.9:1, or 93% C1, 7% C3, corresponding to 52% C1 and 3% C3 product in the purified mixture. The percentage of C3 as determined by GC-MS was 5, which is in fair agreement with the NMR determination.

*This multiplet integrates to more than the expected value of 6H due to the presence of C3 isomer in the product mixture.

**This singlet integrates to more than the expected value of 12H due to the presence of C3 isomer in the product mixture.

***Some carbons, but not all, of the C3 product, which is inseparable from C1, also appear in this spectrum, leading to more than the expected number of carbons for C1.



4-(((diphenylmethylene)amino)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)benzonitrile (7g)

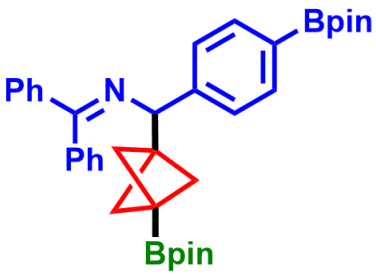
Compound **7g** was prepared according to General Procedure C, employing ketimine **4g** (59.3 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 16 hours at 80 °C. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (70% → 95% MeCN/H_2O) to give exclusively the C1 isomer, as a white solid, 39.8 mg, 40%.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.73-7.69 (m, 4H), 7.53-7.52 (m, 5H), 7.44-7.37 (m, 3H), 7.11-7.09 (m, 2H), 4.45 (s, 1H), 1.60 (dd, *J* = 13, 9.4 Hz, 6H), 1.15 (s, 12H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 168.7, 148.7, 140.9, 137.5, 132.9, 131.1, 129.67, 129.62, 129.47, 129.2, 129.1, 128.3, 119.7, 111.3, 84.0, 68.7, 50.5, 48.9, 25.1 ppm.*

HRMS calc'd for $[C_{32}H_{33}BN_2O_2+H]^+$ = 489.2713, found 489.2703.

*A resonance is not observed due to quadrupolar relaxation from boron.



1,1-diphenyl-N-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)methanimine (7h)

Compound **7h** was prepared according to General Procedure C, employing aldimine **4h'** (162.0 mg, 0.4 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 16 hours. The crude material was suspended in MeCN at room temperature, filtered on filter paper, and washed generously with MeCN to give the product as a white solid, 91.3 mg, 39%.

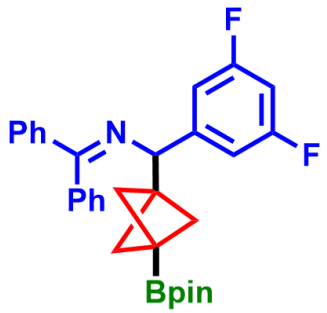
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.69 (m, 4H), 7.41-7.31 (m, 8H),* 7.06-7.03 (m, 2H), 4.33 (s, 1H), 1.69 (dd, *J* = 10, 9.6 Hz, 6H), 1.35 (s, 12H), 1.19 (s, 12H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.6, 145.6, 140.4, 137.0, 134.6, 129.8, 128.7, 128.3, 128.2, 128.0, 126.9, 83.7, 83.2, 68.5, 49.8, 48.6, 25.0, 24.9, 24.8 ppm.**

HRMS calc'd for $[C_{37}H_{45}B_2NO_4+H]^+$ = 590.3613, found 590.3595.

*****In the spectrum below, this signal integrates closer to 9H than the expected 8H. The product structure was confirmed by ^{13}C NMR and HRMS analysis despite this erroneous overintegration.

***Two resonances are not observed due to quadrupolar relaxation from boron.



***N*-((3,5-difluorophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7i)**

Compound **7i** was prepared according to General Procedure C, employing **4i** (61.5 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time on 0.2 mmol scale: 16 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (70% → 95% MeCN/H_2O) to give exclusively the C1 isomer as a pale yellow solid, 59.3 mg, 59% overall yield on 0.2 mmol scale, 73%.

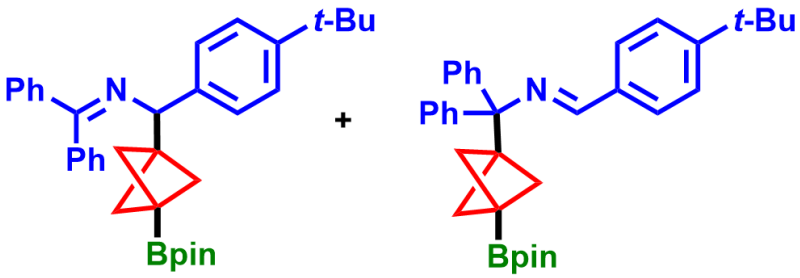
^{1}H NMR (600 MHz, ($CDCl_3$): δ 7.69-7.67 (m, 2H), 7.43-7.41 (m, 3H), 7.40-7.37 (m, 1H), 7.35-7.32 (m, 2H), 7.05-7.04 (m, 2H), 6.88-6.85 (m, 2H), 6.63 (tt, J = 8.9, 2.3 Hz, 1H), 4.29 (s, 1H), 1.67 (dd, J = 13, 9 Hz, 6H), 1.19 (s, 12H) ppm.

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 167.4, 162.9 (dd, $J_{C\text{-}F}$ = 246, 12 Hz), 146.3 (t, $J_{C\text{-}F}$ = 8.5 Hz), 139.9, 136.6, 130.2, 128.7, 128.57, 128.54, 128.1, 128.0, 110.1 (dd, $J_{C\text{-}F}$ = 20, 4.6 Hz), 101.87 (t, $J_{C\text{-}F}$ = 25 Hz), 83.4, 67.5, 49.7, 48.1, 24.8 ppm.*

^{19}F NMR (565 MHz, $CDCl_3$) (unreferenced): δ -110.84 ppm.

HRMS calc'd for $[C_{31}H_{32}BF_2NO_2+H]^+$ = 500.2572, found 500.2581.

*A resonance is not observed due to quadrupolar relaxation from boron.



_N_-((4-(*tert*-butyl)phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7j and 7j')

Compound mixture **7j** and **7j'** was prepared according to General Procedure C, employing ketimine **4j** (65.5 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 20 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (80% → 95% MeCN/H_2O) to give a C1:C3 mixture, 41.1 mg, 40% overall, 8.3:1 ratio, or 35% C1, 6% C3. The mixture was not further separable.

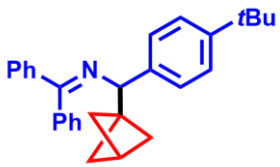
Note: Many peaks in the ^1H and ^{13}C NMR spectra of this isomeric mixture overlap, so the integrals are written as spectrally observed. See the full spectrum below for assignment of key peaks to each isomer, where possible.

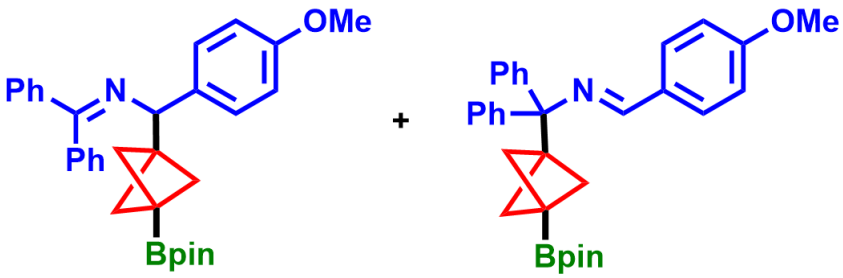
^1H NMR (400 MHz, $CDCl_3$): δ 7.69-7.66 (m, 2H), 7.44-7.39 (m, 4H), 7.34-7.32 (m, 9H), 7.09-7.07 (m, 2H), 4.30 (s, 1H, benzylic C-H of C1 isomer), 1.92 (s, BCP CH_2 x 3 (6H) of C3 isomer), 1.67 (dd, *J* = 13.2, 9.4 Hz, 6H, BCP CH_2 x 3 of C1 isomer), 1.33 (s, *tert*-butyl of C3 isomer, 9H), 1.29 (s, 9H, *tert*-butyl of C1 isomer), 1.18-1.17 (m, nominally 13.41 H, combined Bpin CH_3 of C1 and C3 isomer) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)*: δ 166.1, 149.1, 140.5, 139.2, 137.1, 129.7, 128.6, 128.35, 128.33, 128.2, 127.9, 127.1, 124.8, 83.3, 67.9, 49.8, 48.8, 34.5, 31.5, 24.8 ppm.

HRMS calc'd for $[C_{35}H_{42}BNO_2]^+$ = 519.3309, found 519.3303.

*Carbons from the C3 isomer are visible in this spectrum and are peak picked in the full spectrum below, but only carbons corresponding to the C1 isomer are assigned here. The C1 peaks are assigned as such based on peak intensity and analogy to BCP-H compound:





_N_-((4-methoxyphenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7k and 7k')

Compound mixture **7k** and **7k'** was prepared according to General Procedure C, employing ketimine **4k** (60.2 mg, 0.2 mmol 1 equiv) as the 2-azaallyl nucleophile and 2.8 equiv [1.1.1]propellane rather than 1.4 equiv. Reaction time: 20 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (80% → 95% MeCN/H_2O) to give a C1:C3 mixture, 62.6 mg, 63% overall, 3.4:1 C1:C3 mixture, or 49% C1, 14% C3.

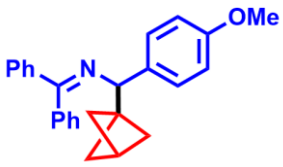
Note: Many peaks in the ^1H and ^{13}C NMR spectra of this isomeric mixture overlap, so the integrals are written as spectrally observed. See the full spectrum below for assignment of key peaks to each isomer, where possible.

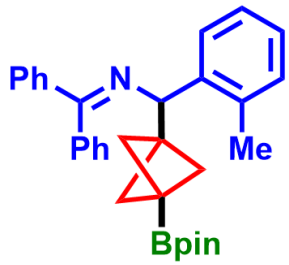
^1H NMR (400 MHz, $CDCl_3$): δ 7.68-7.66 (m, 2H), 7.44-7.19 (m, 13H), 7.07-7.04 (m, 2H), 6.83-6.80 (m, 2H), 4.26 (s, 1H), 3.83 (OC*H*$_3$ of C3 isomer), 3.77 (s, 3H), 1.92 (s, BCP CH_2 x 3 of C3 isomer), 1.67 (dd, *J* = 11.5, 9.1, 6H), 1.18 (s, 12H, Bpin CH_3 of C1), 1.17 (s, Bpin CH_3 of C3) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 166.1, 158.3, 140.4, 137.1, 134.6, 129.8, 128.6, 128.4, 128.3, 128.2, 128.0, 127.5, 113.4, 83.3, 67.5, 55.3, 49.7, 48.9, 24.8 ppm.

HRMS calc'd for [$C_{32}H_{36}BNO_3$] = 493.2503, found 493.2901.

*Carbons from the C3 isomer are visible in this spectrum and are peak picked in the full spectrum below, but only carbons corresponding to the C1 isomer are assigned here. The C1 peaks are assigned as such based on peak intensity and analogy to BCP-H compound:





1,1-diphenyl-*N*-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(*o*-tolyl)methyl)methanimine (7l and 7l')

Compound mixture **7l** and **7l'** was prepared according to General Procedure C, employing ketimine **4l** (54.5 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 17 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (70% → 90% MeCN/H_2O) to give a mixture of C1 and C3 isomers as a thick colorless oil, 67.0 mg, 70% overall yield.

^{1}H NMR (400 MHz, $(CD_3)_2CO$):* δ 7.72-7.69 (m, 3H), 7.53-7.21 (m, 8H), 7.19-7.15 (m, 1H), 7.09-7.03 (m, 4H), 4.67 (s, 1H), 1.90 (s, 3H), 1.63 (dd, *J* = 13, 9.3 Hz, 6H), 1.15 (12H)** ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)***: δ 166.3, 160.2, 145.8, 140.7, 140.3, 137.8, 137.5, 135.1, 134.5, 130.9, 129.9, 129.8, 129.7, 129.6, 128.5, 128.4, 128.2, 128.06, 128.01, 127.5, 126.3, 126.0, 125.9, 125.7, 83.2, 63.5, 51.5, 50.6, 49.8, 48.7, 24.8, 19.8, 19.3 ppm.

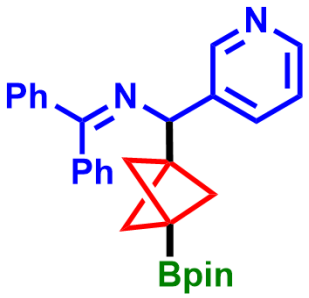
HRMS calc'd for $[C_{32}H_{36}BNO_2]^+$ = 477.2839, found 477.2832.

The ratio of C1:C3 was determined to be 10:1 by ^{1}H NMR and 9:1 by GC-MS, corresponding to 63% C1 and 7% C3 yields of product in the purified mixture.

*Aromatic protons from C1 and C3 overlap in 7-8 ppm region. Peaks corresponding to C3 products, if they are distinguishable from C1, are not noted here, but are labeled in full spectrum below.

**The 12 methyl protons of the Bpin fragment of C1 and C3 products overlap, so for this mixture this peak overintegrates to above 13H due to presence of 10% C3: 0.10*12 = 1.2 extra H, as seen in the spectrum.

***Some carbons, but not all, of the C3 product, which is inseparable from C1, also appear in this spectrum, leading to more than the expected number of carbons for C1. All carbons found are reported above.



1,1-diphenyl-*N*-(pyridin-3-yl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (7m)

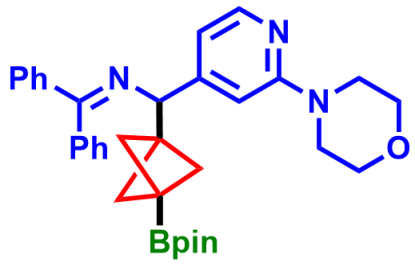
Compound **7m** was prepared according to General Procedure C, employing ketimine **4m** (54.5 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 24 hours. Reaction temperature: 60 °C. The standard workup was employed. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (50% → 90% MeCN/H_2O) to give the C1 isomer as a yellow solid, 38.4 mg, 41% overall yield.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.44 (s, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.0, 2H), 7.55-7.50 (m, 3H), 7.44-7.37 (m, 3H), 7.31 (t, *J* = 4.7 Hz, 1H), 7.71-7.70 (m, 2H), 4.41 (s, 1H), 1.62 (dd, *J* = 18, 8.5 Hz, 6H), 1.16 (s, 12H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.4, 148.9, 148.1, 139.9, 137.7, 136.7, 135.3, 130.1, 128.7, 128.59, 128.54, 128.1, 128.0, 123.3, 83.4, 65.8, 49.7, 48.4, 24.8 ppm.*

HRMS calc'd for $[C_{30}H_{33}BN_2O_2+H]^+$ = 465.2713, found 465.2684.

*A resonance is not observed due to quadrupolar relaxation from boron.



***N*-((2-morpholinopyridin-4-yl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7n)**

Compound **7n** was prepared according to General Procedure C, employing ketimine **4n** (71.5 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 24 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (70% → 95% MeCN/H_2O) to give exclusively the C1 isomer as a pale yellow solid, 44.4 mg, 40% overall yield.

^{1}H NMR (400 MHz, $CDCl_3$: δ 8.09-8.08 (m, 1H), 7.68-7.66 (m, 2H), 7.42-7.31 (m, 7H)*, 7.06-7.03 (m, 2H), 6.62-6.61 (m, 2H), 4.23 (s, 1H), 3.82 (t, *J* = 4.8 Hz, 4H), 3.46 (t, *J* = 4.9 Hz, 4H), 1.69 (s, 6H)**, 1.19 (s, 12H) ppm.

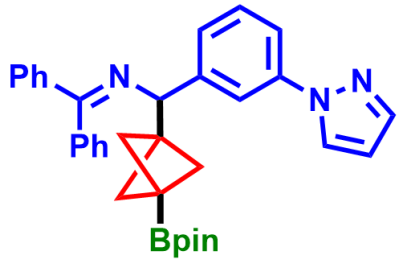
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.4, 160.0, 152.5, 147.5, 140.1, 136.7, 130.1, 128.7, 128.5, 128.4, 128.16, 128.12, 113.7, 105.7, 83.4, 67.7, 66.9, 49.9, 48.0, 46.0, 24.8 ppm.***

HRMS calc'd for $[C_{34}H_{40}BN_3O_3+H]^+$ = 550.3241, found 550.3224.

*Despite several attempts to prepare and analyze this compound, this multiplet region was found to integrate to 7-7.5 H rather than the expected 6 H. However, the ^{13}C NMR and HRMS were consistent with the proposed structure.

**This singlet is expected as a doublet of doublets, based on the same pattern in other spectra, but this pattern was poorly resolved in NMR spectroscopy.

***A resonance is not observed due to quadrupolar relaxation from boron.



***N*-((3-(1H-pyrazol-1-yl)phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7o)**

Compound **7o** was prepared according to General Procedure C, employing aldimine **4o'** (67.5 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 24 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (70% → 95% MeCN/H_2O) to give exclusively the C1 isomer, 58.2 mg, as an orange solid, 54%. Note: to load the column, the crude material was suspended in ~1 mL MeCN. It is presumed that the insoluble material was remaining **4o/4o'**.

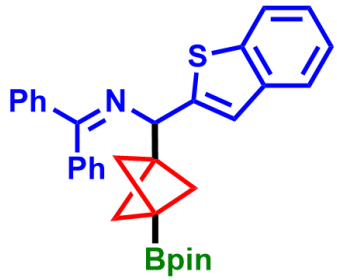
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 2.3 Hz, 1H), 7.71-7.69 (m, 3H), 7.61 (s, 1H), 7.56-7.54 (m, 1H), 7.42-7.40 (m, 3H), 7.39-7.25 (m, 6H), 7.08-7.06 (m, 2H), 6.43 (t, *J* = 2.0 Hz, 1H), 4.41 (s, 1H), 1.71 (dd, *J* = 12, 9.4 Hz, 6H), 1.18 (s, 12H) ppm.*

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 168.0, 144.8, 141.6, 141.2, 141.1, 137.7, 130.9, 130.0, 129.58, 129.50, 129.4, 129.0, 128.9, 127.8, 126.1, 118.6, 117.8, 108.3, 83.9, 68.9, 50.6, 49.3, 25.1 ppm.**

HRMS calc'd for $[C_{34}H_{36}BN_3O_2+H]^+$ = 530.2979, found 530.2967.

***The aromatic region of the ^{1}H NMR spectrum overintegrates by 1H, due to overlapping residual $CHCl_3$ signal. The ^{13}C NMR fully matches the expected product.

****A resonance is not observed due to quadrupolar relaxation from boron.



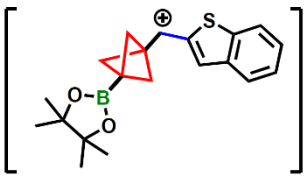
***N*-(benzo[b]thiophen-2-yl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7p)**

Compound **7p** was prepared according to General Procedure A, employing ketimine **4p** (65.4 mg, 0.2 mmol, 1 equiv) as the 2-azaallyl nucleophile. Reaction time: 40 hours. The crude material was purified by chromatography on reversed-phase C_{18}-endcapped silica gel (70% → 95% MeCN/H_2O) to give exclusively the C1 isomer as a pale yellow solid, 54.5 mg, 52% overall yield.

^{1}H NMR (400 MHz, ($(CD_3)_2CO$): δ 7.87-7.85 (m, 1H), 7.74-7.71 (m, 3H), 7.57-7.51 (m, 3H), 7.45-7.38 (m, 3H), 7.31 (td, *J* = 7.1, 1.3 Hz, 1H), 7.26 (td, *J* = 7.1, 1.3 Hz, 1H), 7.18-7.16 (m, 2H), 7.06 (s, 1H), 4.74 (s, 1H), 1.72 (s, 6H),*, 1.16 (s, 12H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$)**: δ 168.7, 147.7, 140.8, 140.7, 140.4, 137.2, 131.2, 129.7, 129.5, 129.1, 128.8, 124.9, 124.4, 124.1, 123.1, 119.9, 84.0, 65.7, 50.7, 48.8, 25.2 ppm.

HRMS calc'd for $[C_{33}H_{34}BNO_2S+H]^+$ = 520.2482, found 520.2457. Fragment analysis: parent peak, 520.2457, was found to have a major fragment of 339.1681, corresponding to C-N bond fragmentation of the C1 product: No fragment corresponding to C3 fragment found.

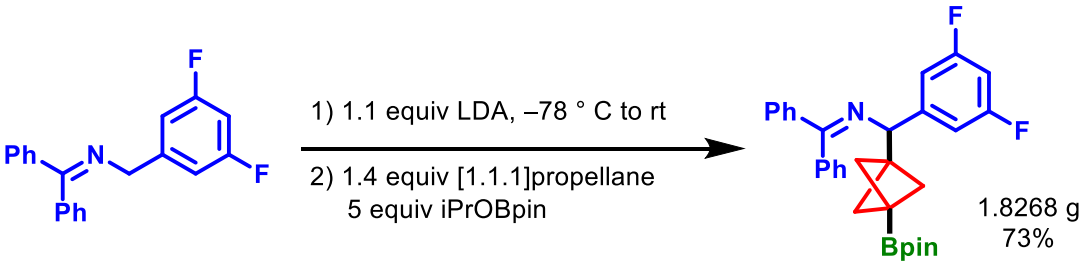


Exact Mass: 339.1585

*This multiplet is expected as a doublet of doublets based on the same pattern in other spectra, but this pattern is not resolved (appears as a triplet in the spectrum). The regioisomer assigned as C1 is supported by the singlet at 4.74 integrating to 1H (benzylic Ph_2C=N-C-*H*-(BCP)) as well as MS analysis (above).

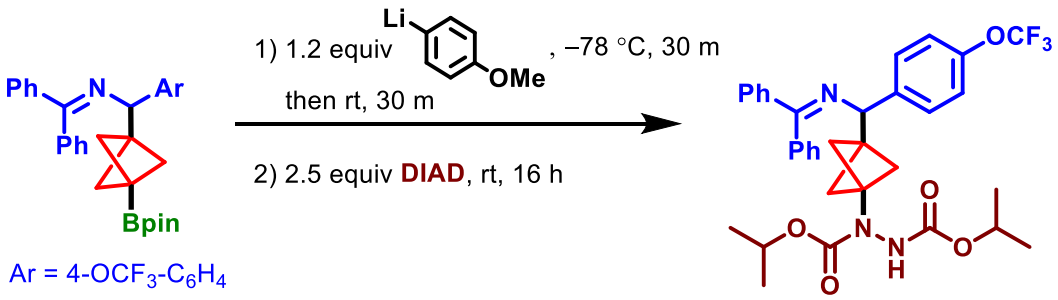
**A resonance is not observed due to quadrupolar relaxation from boron.

Gram-scale borylation/propellylation procedure



N-(3,5-difluorobenzyl)-1,1-diphenylmethanimine **7i** (1.536 g, 5.0 mmol, 1 equiv) is added to a 100 mL Schlenk flask under N_2 atmosphere. THF (12.5 mL) is added and the flask is chilled to -78 °C (dry ice/acetone). In a separate flask, diisopropylamine (iPr_2NH, 771 µL, 5.5 mmol, 1.1 equiv) is dissolved in 12.5 mL THF. The flask containing diisopropylamine is cooled to 0 °C. *n*-Butyllithium (1.6 M solution in hexanes, 3.27 mL, 1.05 equiv) was added to the diisopropylamine solution over approx. 2 mins, producing a clear, yellow solution. The solution is stirred 1 minute at 0 °C, then warmed to rt and stirred another minute. The solution is transferred via syringe to the flask containing *N*-benzyl ketimine and added dropwise, producing a bright purple azaallyl solution. At the end of LDA addition, the mixture is stirred for 10 minutes at -78 °C, then stirred 10 minutes further at room temperature. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (iPrOBpin; 5.10 mL, 25 mmol, 5 equiv) is added to the mixture in one portion, followed by [1.1.1]propellane as a stock solution in Et_2O (10 mL of 0.70 M stock solution, 1.4 equiv). The rxn mixture is stirred 48 hours at room temperature (after about 24 hours, the reaction mixture decolorized from purple to a pale yellow). At the end of the reaction period, the reaction mixture is poured into a separatory funnnel containing 30 mL water. The mixture is extracted with EtOAc (2x30 mL). The combined organic layers are washined with brine, then dried with $MgSO_4$. The drying agent is filtered over a cotton plug and the crude reaction mixture concentrated to a thick oil. To purify, the crude reaction mixture is dissolved in acetonitrile and loaded onto C_{18}-endcapped reversed-phase silica gel packed into a 25G Biotage SNAP cartridge (two sequential separations were done on the same catridge). The column is eluted with a gradient of 70 → 95% MeCN in H_2O and the second eluting peak is collected to give the product as 1.8268 g of a pale yellow solid, 73%.

C-N bond formation (Compound 10)



Under a nitrogen atmosphere in the glovebox, 4-bromoanisole (67.3 mg, 0.36 mmol, 1.2 equiv) is dissolved in 3 mL THF at room temperature in a Schlenk flask charged with a stir bar. On the Schlenk line, the solution is cooled to -78 °C. *n*-Butyllithium (0.23 mL of a 1.6 M solution in hexanes, 0.36 mmol, 1.2 equiv) is added dropwise producing a colorless solution. The mixture is stirred at this temperature for 1 hour. The BCP Bpin **7b** (164 mg, 0.3 mmol 1 equiv) is dissolved in 3 mL in the glovebox at room temperature and added dropwise to the 4-bromoanisole solution, producing a deep purple color. The mixture is stirred at -78 °C for 30 min then brought to ambient temperature and stirred 30 min further. Over the period of stirring at room temperature, the solution changes from deep purple to dark green in color. At room temperature, DIAD (146 µL, 0.75 mmol, 2.5 equiv as a solution in 0.5 mL THF) is then added dropwise, which changes the solution from dark green to orange in color. The mixture is stirred at ambient temperature for 16 h. After 16 h, sat'd. $NaHCO_3$ solution (9 mL) and ethyl acetate (10 mL) were added to the mixture and the layers were separated. The aqueous phase was extracted with ethyl acetate (2x10 mL). The organic layers were combined, washed with brine (10 mL), dried over Na_2SO_4, filtered over Celite, and concentrated under reduced pressure. The crude material was purified on SiO_2 using hexanes with 1.5% NEt_3 by volume to elute a yellow oil with unidentified impurities. A second round of chromatography was performed on C_{18}-endcapped reversed-phase silica gel using a gradient of 60 → 100% MeCN in H_2O to give a white solid, 45.5 mg, 24% yield, of the C-N coupled product.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69-7.68 (m, 2H), 7.44-7.43 (m, 3H), 7.40-7.38 (m, 1H), 7.35-7.32 (m, 4H), 7.14-7.13 (m, 2H), 7.04-7.03 (m, 2H), 6.40-6.25 (br s, 1H), 4.93-4.89 (m, 2H), 4.55 (s, 1H), 1.86 (m, 6H), 1.23-1.22 (m, 12H) ppm.*

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 167.4, 156.1, 148.1, 141.1, 139.8, 136.6, 130.2, 128.8, 128.7, 128.6, 128.4, 128.1, 128.0, 127.8, 120.7, 120.6 (q, $J_{C\text{-}F}$ = 256 Hz), 69.8, 65.0, 53.5, 51.6,** 39.7, 22.1, 22.0 ppm.

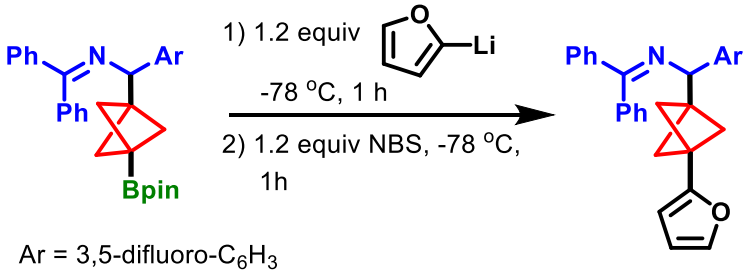
^{19}F NMR (376 MHz, $CDCl_3$) (unreferenced): δ -57.81 ppm.

LRMS calc'd for M^+ = $[C_{34}H_{36}F_3N_3O_5]^+$ = 623.2, found 580.2 [M^+-$CH(CH_3)_2$]. [*HRMS has not yet been obtained for this cpd.*]

*Rotamers of the 1,2-hydrazine dicarboxylate broaden lines in the ^{1}H NMR spectrum, leading to poor peak resolution.

**This signal appears very broad (see inset in full spectrum). This is attributed to coincident overlap of the two methine carbons of the isopropyl groups on the 1,2-hydrazine dicarboxylate.

Arylation (Compound 11)



This procedure is adapted from the literature [*Nature Chemistry* **2019**, 11, 117–122]. Under a nitrogen atmosphere in a 4 mL vial charged with a stir bar, furan (0.18 mmol, 13.1 uL, 1.2 equiv) was dissolved in 0.6 mL THF and cooled to -78 °C. *n*-Butyllithium (0.18 mmol, 0.11 mL of a 1.6 M solution in hexanes, 1.2 equiv) was added dropwise. The resulting mixture was warmed to room temperature and stirred for 1 hour, turning a pale yellow yellow. The furan solution was cooled back down to -78 °C. The ketimine BCP Bpin **7i** (74.8 mg, 0.15 mmol, 1 equiv) was dissolved in 0.5 mL THF and added to the furan solution and stirred 1 h at -78 °C, changing during this time period from a dark purple to a clear, orange solution. *N*-Bromosuccinimide (NBS, 32.0 mg, 0.18 mmol, 1.2 equiv) was added to the furan/BCP Bpin solution at -78 °C and stirred for 1 hour at this temperature. After this period, the flask was warmed to room temperature, uncapped, and quenched with saturated sodium thiosulfate solution (2 mL) under an air atmosphere, stirring for two minutes. The mixture was further diluted with water (10 mL) then extracted with ethyl acetate (3x2 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by flash chromatography on deactivated SiO_2 (3% NEt_3 in eluent by volume) using hexanes as the eluent; the crude mixture was poorly soluble in the eluent mixture, so several drops of ethyl acetate were used to facilitate dissolution. The product was obtained from column chromatography as a pale yellow solid, 66% yield (average of two runs).

Product R_f = 0.61 (10% EtOAc in hexanes)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74-7.73 (m, 2H), 7.46-7.45 (m, 3H), 7.43-7.41 (m, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.25 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.08-7.05 (m, 2H), 6.90 (d, *J* = 6.7 Hz, 2H), 6.68 (tt, *J* = 8.9, 2.3 Hz, 1H), 6.24 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.95 (dd, *J* = 3.1, 0.6 Hz, 1H), 4.46 (s, 1H), 1.88 (m, 6H)* ppm.

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 167.9, 162.9 (dd, $J_{C\text{-}F}$ = 247, 12 Hz), 154.4, 146.3 (t, $J_{C\text{-}F}$ = 4.6 Hz), 141.4, 139.7, 136.5, 130.4, 128.8, 128.69, 128.66, 128.2, 127.9, 110.2, 110.1 (dd, $J_{C\text{-}F}$ = 19.8, 4.8 Hz),** 105.1, 102.2, (t, $J_{C\text{-}F}$ = 25 Hz), 68.2, 50.8, 43.9, 36.3 ppm.

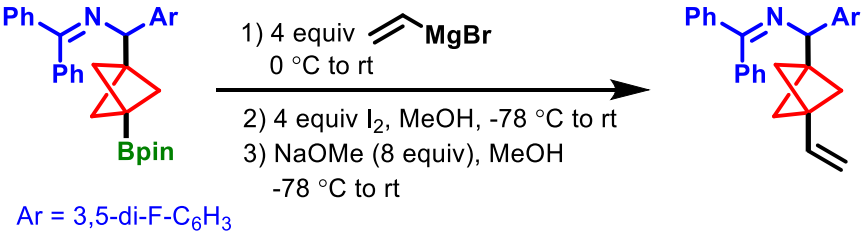
^{19}F NMR (376 MHz, $CDCl_3$) (unreferenced): δ -110.32 ppm.

HRMS calc'd for $[C_{29}H_{23}F_2NO+H]^+$ = 440.1826, found 440.1835.

*NMR for this molecule was obtained in both $CDCl_3$ and acetone-d_6 on a 400 and 600 MHz spectrometer, but no spectrum was obtained in which the expected doublet of doublets for the BCP CH_2 (c. δ 1.88) and the triplet of triplets at δ 6.68 were both resolved. In this spectrum, the expected dd at c. δ 1.88 is reported as a multiplet due to poor resolution.

**One peak of the dd at δ 110.1 overlaps with the furan carbon of δ 110.2 – this is evidently the case due to the height disparity of these two patterns but the peaks can nevertheless be assigned (see full spectrum below).

Zweifel olefination (Compound 12)



In the glovebox under a nitrogen atmosphere, the BCP Bpin **7i** (149.7 mg, 0.3 mmol, 1 equiv) is dissolved in 3 mL THF at room temperature, forming a slightly yellow, clear solution. On the Schlenk line using a needle under positive nitrogen pressure to maintain the inert atmosphere, the solution is cooled to 0 °C and vinylmagnesium bromide (1.2 mL of a 1.0 M solution in THF, 1.2 mmol, 4 equiv) is added dropwise. The Grignard reagent decolorizes upon mixing with reaction mixture, but as all the reagent is added, the solution gradually turns a deep purple. The mixture is stirred 5 minutes at 0 °C and then warmed to rt and stirred for 1 hour. The mixture is cooled to -78 °C and a solution of I_2 (152.2 mg, 1.2 mmol, 4 equiv) in MeOH (9 mL) is added dropwise. The reaction mixture is stirred for 15 minutes at this temperature, then warmed to room temperature for 1 hour. The reaction mixture is cooled again to -78 °C followed by the addition of NaOMe (129.7 mg, 2.4 mmol, 8 equiv) as a solution in 3 mL MeOH. The reaction mixture is stirred 10 minutes at this temperature then allowed to warm to rt and stirred 1 hour at room temperature. At the end of the reaction period, the mixture is opened to air atmosphere and quenched with saturated sodium thiosulfate aqueous solution (10 mL). The mixture is extracted twice with EtOAc and the combined organic layers are dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The reaction mixture is purified by flash chromatography on SiO_2 using 1.5% NEt_3 in hexanes by volume as the eluent to deliver 52.4 mg of a yellow oil, 44%.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.72-7.70 (m, 2H), 7.55-7.51 (m, 3H), 7.46-7.37 (m, 3H), 7.13-7.10 (m, 2H), 7.00-6.97 (m, 2H), 6.87 (tt, *J* = 9.4, 2.4 Hz, 1H), 5.88 (dd, *J* = 17, 10 Hz, 1H), 4.97 (dd, *J* = 10.9, 2.1 Hz, 1H), 4.93 (q, *J* = 2.1 Hz, 1H), 4.54 (s, 1H), 1.60 (dd, *J* = 13, 9.3 Hz, 6H) ppm.

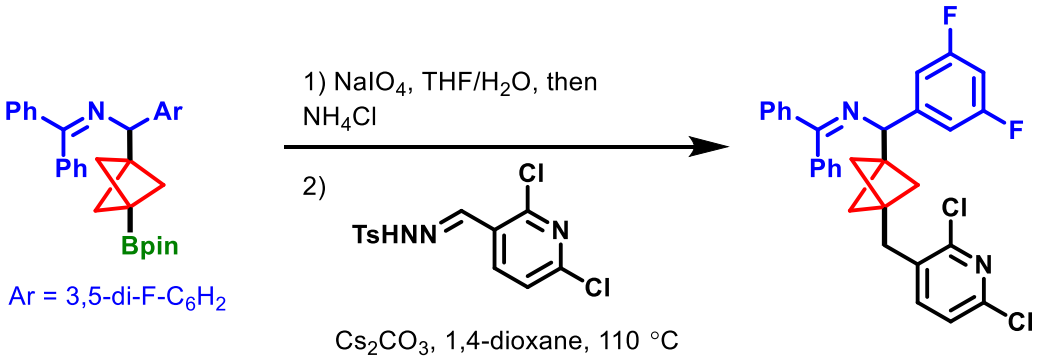
$^{13}C\{^{1}H\}$ NMR (125 MHz, ($CDCl_3$): δ 167.5, 162.9 (dd, J_{C-F} = 247, 13 Hz), 146.6 (t, J_{C-F} = 8.2 Hz), 139.8, 137.6, 136.6, 130.3, 128.7, 128.6, 128.1, 127.9, 114.8, 110.1 (dd, J_{C-F} = 21, 4.6 Hz), 102.0 (tt, J_{C-F} = 25 Hz), 66.5, 50.0, 42.7, 42.0 ppm*.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -111.55 ppm.

HRMS calc'd for $[C_{27}H_{23}F_2N+H]^+$ = 400.1877, found 400.1875.

*In $CDCl_3$ and $(CD_3)_2CO$, this compound presented one fewer than the expected number of carbons for the aromatic region. We attribute this to coincidental overlap of two carbons, owing to the consistency of all other data with the presented structure.

Barluenga-Valdés reaction



***N*-((3-((2,6-dichloropyridin-3-yl)methyl)bicyclo[1.1.1]pentan-1-yl)(3,5-difluorophenyl)methyl)-1,1-diphenylmethanimine (13)**

Under an air atmosphere, the BCP Bpin **7i** (109.9 mg, 0.22 mmol, 2.2 equiv) was added to a flask charged with a stir bar and dissolved in an approximately 4:1 mixture of THF/H_2O by volume (1.8 mL THF, 0.4 mL H_2O, 0.1 M overall) at room temperature. Sodium periodate ($NaIO_4$; 47.1 mg, 0.22 mmol, 2.2 equiv) is added and the mixture is stirred vigorously for 1 h, producing a slightly cloudy mixture. At the end of this period, 1.1 mL saturated aqueous NH_4Cl solution is added, and the mixture is stirred vigorously for 24 hours, producing a cloudy white suspension. The mixture is dumped into a separatory funnel with 5 mL brine and extracted twice with 5 mL EtOAc. The combined organic layers are dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude BCP boronic acid is used immediately in the coupling reaction.

Procedure adapted from *Org. Lett*. **2020,** *22*, 2271−2275. In the glovebox under a nitrogen atmosphere, the crude boronic acid mixture is dissolved in 0.4 mL 1,4-dioxane (0.25 M) and added to a microwave vial that is pre-charged with the sulfonylhydrazone (34.4 mg, 0.1 mmol, 1 equiv) and Cs_2CO_3 (48.8 mg, 0.15 mmol, 1.5 equiv) and a stir bar. The vial is capped and stirred for 18 hours at 110 °C. After this time, the reaction mixture is cooled to room temperature, the cap removed, the resulting solution filtered over a pad of $MgSO_4/SiO_2$ into an RBF and the pad rinsed with ethyl acetate (3x2 mL). The mixture is concentrated under reduced pressure to a

crude oil. The oil is purified by first eluting on SiO_2 with a gradient of 10 → 70% CH_2Cl_2 in hexanes with 1.5% NEt_3 by volume to give the product, mixed with small amounts of protodeboration product (approx. 3:1 ratio of desired product to protodeboration product). A second column on C_{18} reversed-phase silica gel, eluting with 60 → 100% MeCN in H_2O, gave the product as a yellow oil, 29.1 mg, 55%.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.69 (m, 3H), 7.53-7.49 (m, 3H), 7.43-7.36 (m, 4H), 7.08-7.07 (m, 2H), 6.96-6.91 (m, 2H), 6.84 (tt, *J* = 9.2, 2.4 Hz, 1H), 4.48 (s, 1H), 2.94 (s, 2H), 1.47 (dd, *J* = 14, 9.4 Hz, 6H) ppm.

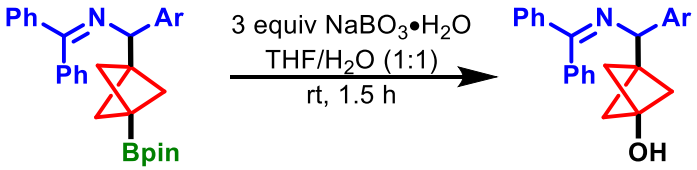
^{13}C{^{1}H} NMR (100 MHz, $(CDCl_3)$): δ 168.77, 163.8 (dd, J_{C-F} = 246, 12 Hz), 150.5, 148.1, 147.9 (t, J_{C-F} = 8.7 Hz), 143.7, 140.7, 137.3, 134.0, 131.2, 129.6, 129.4, 129.1, 128.6, 124.3, 110.9 (dd, J_{C-F} = 18, 6.8 Hz), 102.7 (t, J_{C-F} = 26 Hz), 67.0, 49.6, 44.2, 40.8, 35.6 ppm.*

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -111.55 ppm.

HRMS calc'd for $[C_{31}H_{24}Cl_2F_2N_2+H]^+$ = 533.1363, found 533.1356.

*Coincidental overlap of two aromatic carbons leads to 22 C presenting in this spectra, one fewer than the 23 C expected.

Oxidation of a ketimine BCP Bpin (Compound 14)



Ar = 3,5-difluoro-C_6H_3

The ketimine BCP Bpin **7i** (49.9 mg, 0.1 mmol, 1 equiv) was added to a 25 mL RBF charged with a stir bar. Then, THF (1 mL) and H_2O (1 mL) were added at room temperature. Sodium perborate monohydrate was next added in one portion (29.9 mg, 0.3 mmol, 3 equiv). The reaction mixture was white and cloudy throughout the reaction time period. The reaction was stirred for 90 minutes and followed by TLC. At the end of the reaction period, the reaction mixture was poured into 5 mL of water and extracted with ethyl acetate (2x5 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product mixture was purified on deactivated silica (3% NEt_3 by volume) using a 5→20% EA in hexanes gradient to obtain the product as a white solid, 30.4 mg, 78%.

Product R_f = 0.14 (10% EtOAc in hexanes)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70-7.68 (m, 2H), 7.45-7.40 (m, 4H), 7.37-7.34 (m, 2H), 7.03-7.02 (m, 2H), 6.85-6.84 (m, 2H), 6.67 (tt, *J* = 8.9, 2.0 Hz, 1H), 4.52 (s, 1H), 1.71 (dd, *J* = 11.5, 9.3 Hz, 6H) ppm.*

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 167.8, 162.9 (dd, J_{C-F} = 247, 12 Hz), 146.6 (t, J_{C-F} = 8.7 Hz), 139.7, 136.4, 130.4, 128.8, 128.7, 128.6, 128.2, 127.2, 110.1 (dd, J_{C-F} = 18, 6.6 Hz), 102.31 (t, J_{C-F} = 12.7 Hz), 64.6, 64.3, 52.4, 35.0.

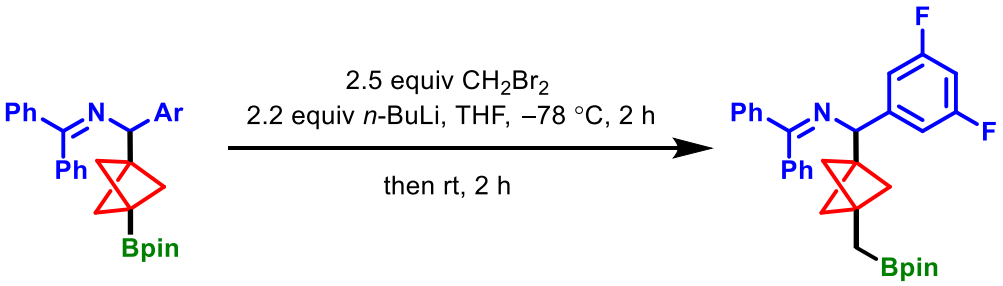
^{19}F NMR (376 MHz, $CDCl_3$) (unreferenced): δ -110.2 ppm.

HRMS calc'd for $[C_{25}H_{21}F_2NO+H]^+$ = 390.1669, found 390.1664.

*The O*H* of the alcohol is not observed in this NMR spectrum.

Unsuccessful transformations of the BCP Bpin

Methylene homologation



Ar = 3,5-di-F-C_6H_3

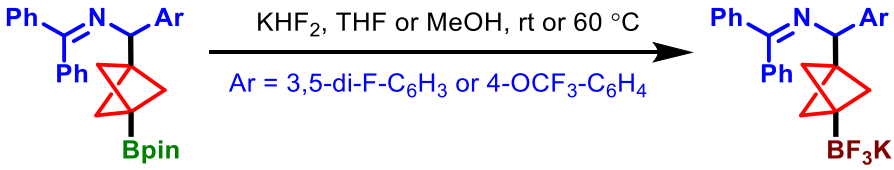
Angew. Chem. Int. Ed. **2020,** *59*, 1970-1974

62% AY with 25% SM remaining

The SM and homologation product were inseparable on SiO_2 and C_{18}-endcapped reversed-phase silica gel, so satisfactory characterization data could not be obtained.

The above result is representative of multiple attempts to improve the product yield by changing the stoichiometry of CH_2Br_2 and *n*-BuLi. Full conversion of Bpin SM could not be achieved.

Potassium trifluoroborate formation



Entry	Conditions	% BF_3K formed (AY)
1	40 equiv KHF_2, MeOH, rt, 4 h	62 (+ 13% BCP-OH)
2	40 equiv KHF_2, MeOH, rt, 24 h	35 (+ 32% BCP-OH)
3	40 equiv KHF_2, THF, 60 °C, 16 h	36
4	40 equiv KHF_2, THF, 60 °C, 72 h	26

Table S2. Representative examples of optimization of potassium trifluoroborate formation.

Initial investigations applying standard reaction conditions for trifluoroborate formation (5 equiv KHF_2, THF, room temperature) were unsuccessful, producing sluggish and incomplete conversion to trifluoroborates. Using excess KHF_2 (40 equiv) in MeOH solvent for 4 hours produced a 62% AY of the BF_3K product with 13% of the oxidation product (BCP-OH, Table S2, entry 1). Extending the reaction time to 24 hours gave an overall lower yield of the trifluoroborate product with an expectedly higher proportion of oxidation product 32% BCP-OH (entry 2). Similarly sluggish conversion at room temperature in THF was observed using excess

KHF_2 (not in table). However, elevating the temperature to 60 °C for either 16 or 72 hours gave poor yields of the product (entries 3 and 4) with significant portions of inseparable Bpin starting material remaining. From the above examples and further trials, we concluded that trifluoroborate formation on benzylamine BCP pinacol boronates was not viable under these conditions because pure trifluoroborate product could not be obtained.

Full optimization data for the arylation of BCP pinacol boronate esters

Initial HTE experimentation examined 6 Pd precatalysts, 4 solvents, and aq. Cs_2CO_3 base at 100 °C for 16 h reaction time. This screen revealed cataCXium A [Ad_2(*n*-Bu)P G2 precat) to be most effective for producing the desired arylation product among the ligands screened, and provided a starting point for bench-scale evaluation of temperature. We scaled up entry A1 of this screen (Table S3, entry 1, below), which produced the desired arylation product in 5% AY. Further increasing the reaction temperature to 120 °C improved the AY to 21% so this temperature was chosen for a broad screen of 24 Pd precats, 4 solvents, and 2 bases (Fig. S1, S34).

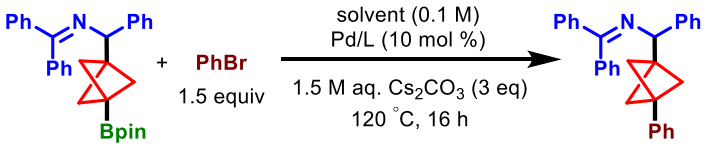


Plate 1 (96 rxns): 1.5 M aq. Cs_2CO_3 (3 equiv)

	1 2 3 4 5 6	7 8 9 10 11 12
A B C D	PhMe	CPME
E F G H	*t*-AmOH	DMAc

Cs2CO3	1	2	3	4	5	6	7	8	9	10	11	12
A					Y		Y	Y	Y	Y	Y	
B						Y						Y
C	Y	Y	Y			Y	Y	Y	Y		Y	Y
D	Y	Y		Y	Y	Y	Y	Y		Y	Y	Y
E	Y	Y	Y	Y	Y		Y	Y	Y	Y	Y	
F						Y	Y					Y
G	Y	Y	Y		Y	Y	Y	Y	Y		Y	Y
H	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y

Plate 2 (96 rxns): 2 M aq. KOH (4 equiv)

	1 2 3 4 5 6	7 8 9 10 11 12
A B C D	PhMe	CPME
E F G H	*t*-AmOH	DMAc

KOH	1	2	3	4	5	6	7	8	9	10	11	12
A	Y	Y	Y	Y	Y		Y	Y	Y	Y	Y	
B						Y						Y
C	Y	Y	Y		Y	Y	Y	Y	Y		Y	Y
D	Y	Y		Y	Y	Y	Y	Y		Y	Y	Y
E	Y	Y	Y	Y				Y	Y	Y		
F	Y					Y					Y	Y
G	Y	Y	Y		Y	Y	Y	Y	Y		Y	Y
H	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y

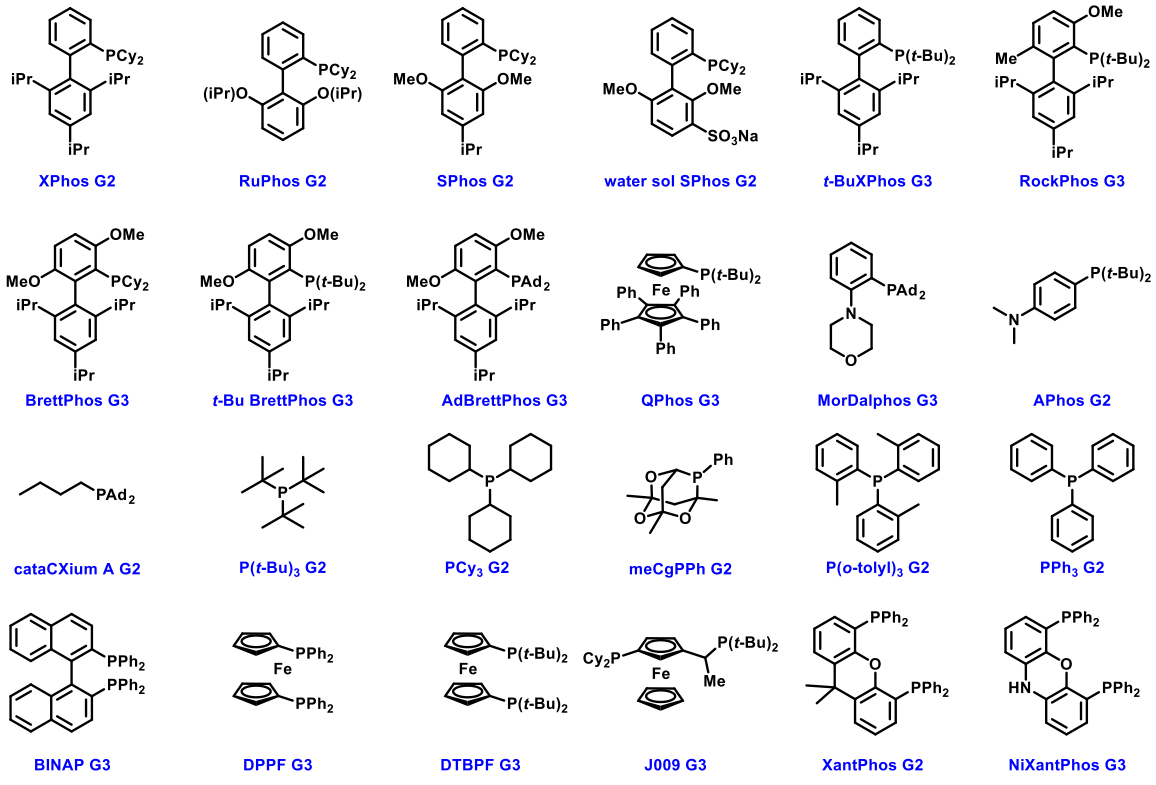
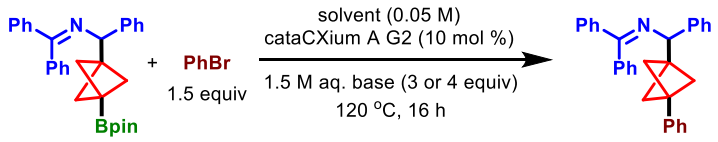


Figure S1. Top: results of two 96-well plate HTE screens, with yield of arylation product determined by LCAP (liquid chromatography area percent). Bottom: 24 Pd precatalysts

evaluated in this screen (presented in the order they appear in each quadrant of the 96 well plates).

From these 2 96-well experiments, cataCXium A was still the top performing ligand. Plate 1 (Cs_2CO_3), reaction C7 gave cleanest profile and highest conversion to product: 10 mol % Pd cataCXium A G2, 3 equiv. aq. Cs_2CO_3, 0.1 M in CPME showed 30% LCAP (42% conversion). Scaling this reaction up to bench-scale and extending reaction time to 24 h, a 43% AY using substrate **7i** was observed (Table S3, entry 3). From this exhaustive screen, cataCXium A was confirmed as the best ligand for the arylation reaction of those examined.

Further screening of 6 hydroxide, carbonate, and phosphate bases commonly used in Suzuki couplings was examined next in 4 solvents (Fig. S2). Of these bases and solvents, cesium hydroxide (CsOH) in CPME was the top performer. Bench-scale evaluation of this reaction showed 54% of the starting material remained with 27% AY of the arylation product, a decrease in yield from an otherwise equivalent reaction using Cs_2CO_3 base (Table S3, entry 3). Further bench-scale evaluation of four high-boiling ethereal solvents (diglyme, *n*-Bu_2O, CPME, and 1,4-dioxane) showed CPME to be the top performing solvent. Further, studying CuCl and CsF additives under the standard reaction conditions did not improve the yield; in the case of CuCl, the overall yield was slightly reduced. Thus, before continuing optimization of other parameters (Table S3, entries 4-11), cataCXium A, Cs_2CO_3 base, CPME solvent, and 120 °C reaction temperature were finalized as optimal parameters for arylation.



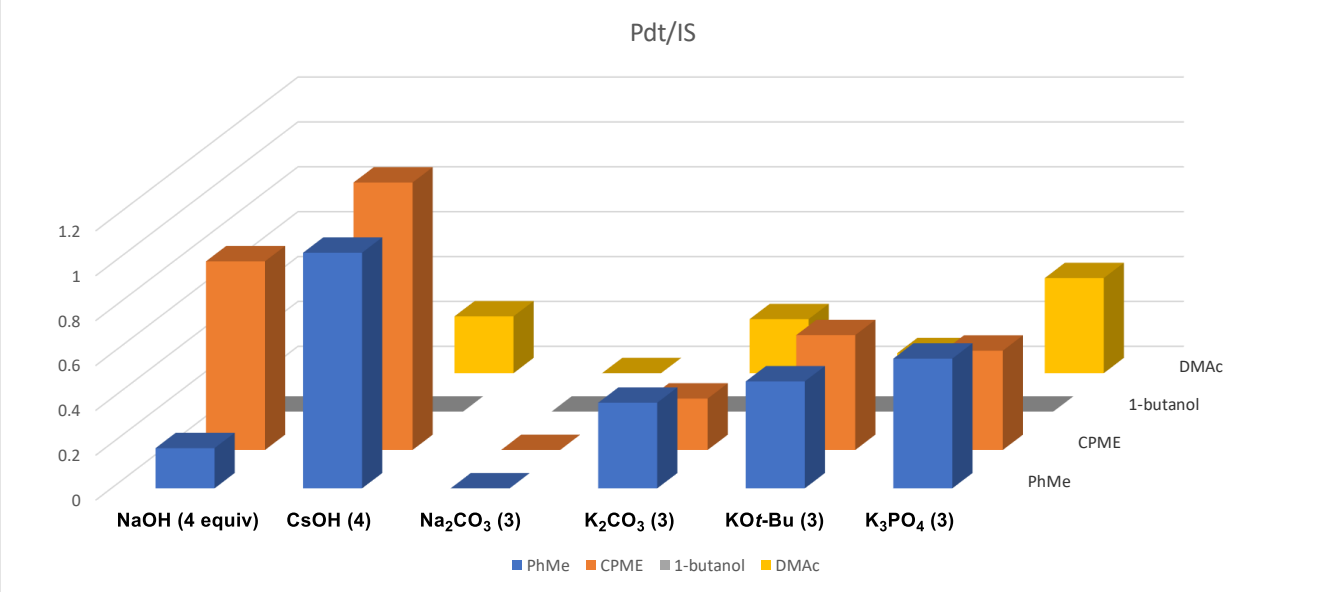
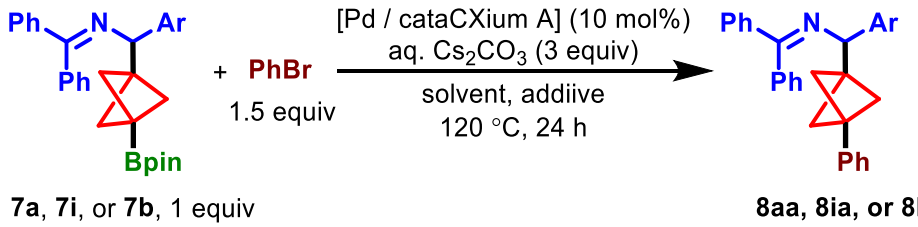


Figure S2. Evaluation of hydroxide, carbonate, and phosphate bases in 4 solvents for the arylation reaction.

A full optimization table (Table S3) and discussion is presented below. This table includes all entries from Table 2 of the main text.



7a, **7i**, or **7b**, 1 equiv

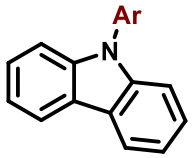
8aa, 8ia, or 8ba

Table S3. Optimization of the BCP Bpin cross-coupling reaction.

Entry	Substrate	Catalyst	Solv, add.	% **8**[a]	% **7** remaining[a]
1[b]	**7a**	Precat. G2	PhMe (0.1 M)	5	71
2	**7a**	Precat. G2	PhMe (0.1 M)	21	55
3	**7i**	Precat. G2	CPME (0.1 M)	43	46
4[c]	**7i**	Precat. G2	CPME (0.1 M)	46	24
5	**7i**	Precat. G2	CPME (0.4 M)	55	25
6	**7i**	Precat. G2	CPME (0.75 M)	54	9
7[d]	**7i**	$Pd(OAc)_2$ / cataCXium A (1:1)	CPME (0.4 M)	38	31
8	**7i**	$Pd(OAc)_2$ / cataCXium A (1:2)	CPME (0.4 M)	62	9
9	**7b**	$Pd(OAc)_2$ / cataCXium A (1:2)	CPME (0.4 M)	60	20
10	**7b**	**$Pd(OAc)_2$ / cataCXium A (1:2)**	**CPME (0.4 M), Cu_2O (1.0 equiv)**	**69 (53% IY)**	**18**
11	**7b**	$Pd(OAc)_2$ / cataCXium A (1:2)	CPME (0.4 M), Cu_2O (2.0 equiv)	56	8

[a] AY as determined by integration of the ^1H NMR spectrum against CH_2Br_2 internal standard. [b] Reaction performed at 100 °C, 0.1 M. [c] 1.5 equiv BCP Bpin, 1.0 equiv ArBr. [d] From this entry on, we switched from using Pd precatalysts due to the formation of *N*-arylated carbazole

side products (below) which form via *N*-arylation of the carbazole generated from the precatalyst. This impurity was inseparable from arylated BCP product in most cases.



Unsuccessful substrates in the arylation reaction

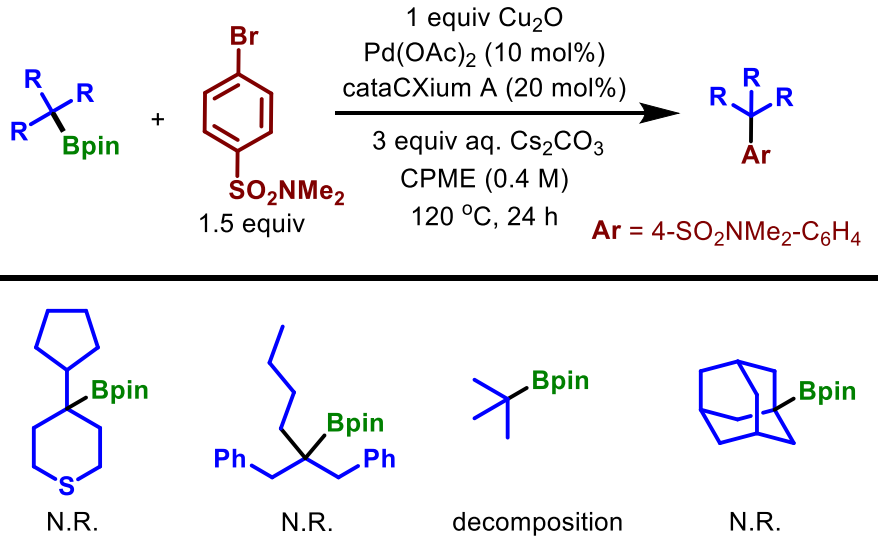


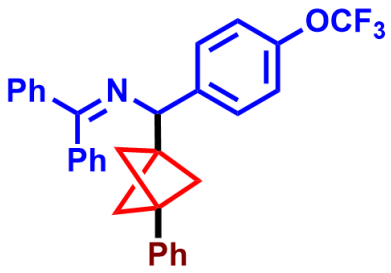
Figure S4. Substrates which did not produce any of the desired arylation product under the optimal conditions for coupling of benzylamine BCP pinacol boronates.

General procedure D for the arylation of BCP pinacol boronate esters: A 10 mL microwave vial is charged with a stir bar and the BCP Bpin (0.1 mmol, 1 equiv) and brought into a glovebox under nitrogen atmosphere. The vial is charged with $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 0.10 equiv), cataCXium A (7.2 mg, 0.02 mmol, 0.20 equiv), Cu_2O (14.8 mg, 0.1 mmol, 1.0 equiv) and the aryl bromide if it is a solid (0.15 mmol, 1.5 equiv). CPME (0.25 mL, 0.4 M) is then added, followed by the aryl bromide if it is a liquid and Cs_2CO_3 (0.2 mL of a 1.5 M aqueous solution, 3 equiv). The vial is sealed and brought out of the glovebox. The reaction is stirred and heated to 120 °C for 24 hours. At the end of the reaction period, the vial was cooled to room temperature, vented of pressure, uncapped, and diluted with EtOAc (~2 mL). The crude mixture is passed over a $MgSO_4/SiO_2$ plug (1:1 by volume) into an RBF. The flask is washed twice more with EtOAc (3x2 mL).* The organic layer is concentrated under reduced pressure. The reaction mixture is purified by flash chromatography on SiO_2, eluting with a hexanes/EtOAc mixture containing 1.5% (by volume) NEt_3.

*Alternatively, the reaction mixture can be worked up as the following: The reaction mixture is diluted with 5 mL EtOAc and the two layers were separated. The organic layer was washed with 5 mL brine, dried ($MgSO_4$), filtered and concentrated under reduced pressure.

Note on chromatography:

- All separations performed on a Biotage Isolera One System using a 10 g SNAP cartridge and 12-20 mL/min elution speed.
- The addition of 1.5% NEt_3 by volume is essential to separation of these mixtures. We found that deactivation using 3% NEt_3 eluted mixtures of protodeboration (BCP-H) and BCP arylation (BCP-Ar) products, due to degradation of remaining starting BCP Bpin starting material on the column (not all reactions could not be pushed to 100% consumption of starting material even with prolonged stirring).
- Using no NEt_3, or only using NEt_3 to wet pack the silica but not in the eluent mixture, gave no elution of any spots (total degradation of starting material and product on the silica gel).
- 1.5% NEt_3 permits the arylation product to elute from the column while permitting protodeboration/degradation of remaining BCP Bpin on silica. In some cases, co-elution of protodeboration product with the arylation product was observed but this can generally be optimized by adjusting the proportion of EtOAc in the gradient mixture.
- Purification by a second round of chromatography on reversed-phase SiO_2 was required for substrates which produced large proportions of homocoupled aryl halide (e.g. a biphenyl) that did not separate under the standard chromatography conditions.



1,1-diphenyl-*N*-((3-phenylbicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8ba)

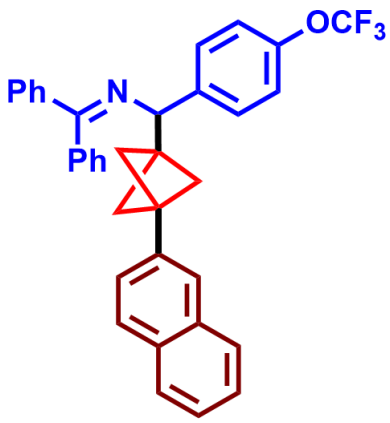
Prepared according to the General Procedure D for arylation on a 0.1 mmol scale. The crude reaction mixture was eluted on SiO_2 using 1.5% NEt_3 by volume in hexanes to obtain 26.4 mg of a yellow oil, 53%.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.75 (m, 2H), 7.56-7.49 (m, 5H), 7.46-7.37 (m, 3H), 7.31-7.29 (m, 2H), 7.27-7.23 (m, 2H), 7.18-7.13 (m, 5H), 4.63 (s, 1H), 1.84 (dd, J = 14, 9.4 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 168.3, 148.8 (d, J_{C-F} = 1.5 Hz), 142.69, 142.0, 141.0, 137.6, 131.1, 129.9, 129.66, 129.61, 129.4, 129.1, 129.0, 128.8, 127.3, 126.8, 121.7, 121.6 (q, J_{C-F} = 256 Hz), 67.2, 51.3, 43.6, 43.0 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.4 ppm.

HRMS calc'd for $[C_{32}H_{26}F_3NO+H]^+$ = 498.2044, found 498.2028.



***N*-((3-(naphthalen-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bb)**

Prepared according to General Procedure D for arylation on a 0.1 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 2% EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 37.4 mg of a clear colorless oil, 68%.

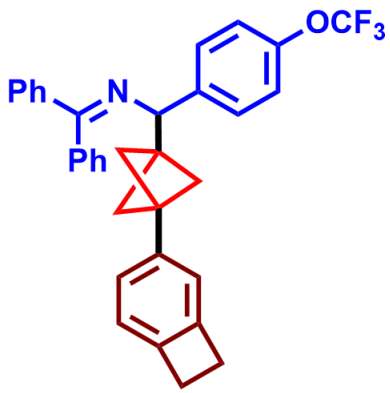
^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.82-7.75 (m, 5H), 7.64 (br s, 1H), 7.56-7.52 (m, 5H), 7.46-7.31 (m, 8H), 7.17-7.14 (m, 2H), 4.67 (s, 1H), 1.92 (dd, J = 14, 9.4 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.3, 148.1 (d, $J_{C\text{-}F}$ = 1.8 Hz), 141.2, 140.1, 138.7, 136.8, 133.4, 132.3, 130.2, 128.8, 128.7, 128.6, 128.5, 128.2, 128.0, 127.8, 127.7, 127.6, 126.1, 125.4, 124.6, 124.4, 120.7, 120.6 (q, $J_{C\text{-}F}$ = 256 Hz),* 66.4, 50.7, 43.1, 42.6 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.4 ppm.

HRMS calc'd for $[C_{36}H_{28}F_3NO+H]^+$ = 548.2201, found 548.2208.

*****The most downfield peak of this quartet coincidentally overlapped with the peak at 124.6 in such a way that prevented peak-picking in both $CDCl_3$ and $(CD_3)_2CO$ but can be seen in the full spectrum. The other peaks of the quartet are clearly visible.



_N_-((3-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bc)

Prepared according to General Procedure D for arylation using 1.5 equiv 4-bromobenzocyclobutene as the aryl halide (18.6 µL). The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 1% EtOAc in hexanes with 1.5% NEt_3 to obtain a single eluting peak as a mixture of BCP arylation product, BCP-H (e.g. protodeboration) product, and 3,3'-bi(bicyclo[4.2.0]octane-1,1',3,3',5,5'-hexaene), the homocoupling of the aryl bromide, as a mixture. A second chromatographic purification was performed on reversed-phase (C_{18}-endcapped) silica gel, using a gradient of 70 → 100% MeCN/H_2O, which separated these three spots and delivered the BCP arylation product as a clear, colorless oil, 16.3 mg, 31%.

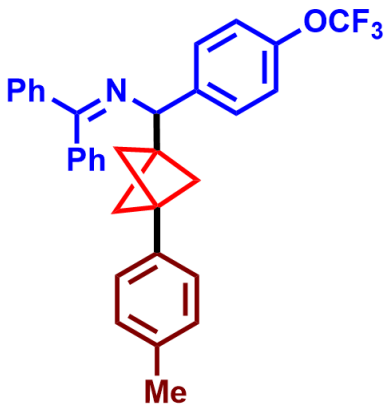
^{1}H NMR (400 MHz, ($(CD_3)_2CO$): δ 7.74-7.72 (m, 2H), 7.54-7.49 (m, 5H), 7.44-7.37 (m, 3H), 7.30 (d, J = 8 Hz, 2H), 7.15-7.12 (m, 2H), 6.98 (dd, J = 7.5, 1.4 Hz, 1H), 6.89 (t, J = 7.4 Hz, 2H), 4.62 (s, 1H), 3.06 (s, 4H), 1.80 (dd, J = 15, 9 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, ($CDCl_3$): δ 167.1, 148.0 (J_{C-F} = 1.4 Hz), 145.7, 143.9, 141.3, 140.1, 140.0, 136.8, 130.1, 128.79, 128.74, 128.56, 128.52, 128.1, 128.0, 124.5, 122.2, 120.7, 120.6 (d, J_{C-F} = 256 Hz),* 120.3, 66.4, 50.7, 43.3, 42.1, 29.45, 29.43 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.5 ppm.

HRMS calc'd for $[C_{34}H_{28}F_3NO+H]^+$ = 524.2201, found 524.2175.

*The downfield most peak of this quartet is expected at δ 124.4 but is coincident with the peak at δ 124.5. The center of the quartet and the J_{C-F} value was determined on the basis of visible peaks.



1,1-diphenyl-N-((3-(*p*-tolyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bd)

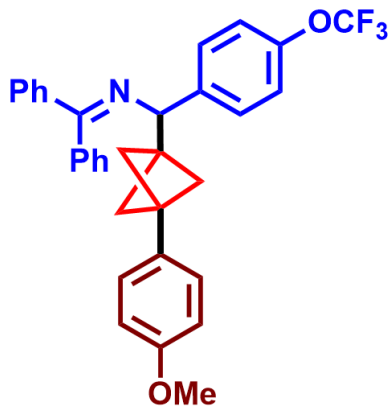
Prepared according to General Procedure D for arylation on a 0.3 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 1% EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 102.2 mg of a clear colorless oil, 67%.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.74-7.72 (m, 2H), 7.56-7.49 (m, 5H), 7.46-7.37 (m, 3H), 7.31-7.29 (m, 2H), 7.14-7.13 (m, 2H), 7.06 (s, 4H), 4.63 (s, 1H), 2.25 (s, 3H), 1.81 (dd, J = 14, 9.4 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 168.2, 148.8 (d, J_{C-F} = 1.8 Hz), 142.7, 141.0, 139.1, 137.6, 136.6, 131.1, 129.9, 129.66, 129.65, 129.60, 129.4, 129.0, 128.8, 126.8, 121.69, 121.64 (q, J_{C-F} = 256 Hz), 67.2, 51.3, 43.4, 43.0, 21.2 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.5 ppm.

HRMS calc'd for $[C_{33}H_{28}F_3NO+H]^+$ = 512.2201, found 512.2206.



_N_-((3-(4-methoxyphenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8be)

Prepared according to General Procedure D for arylation on a 0.1 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 1 % EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 29 mg of a thick, clear oil, 55%.

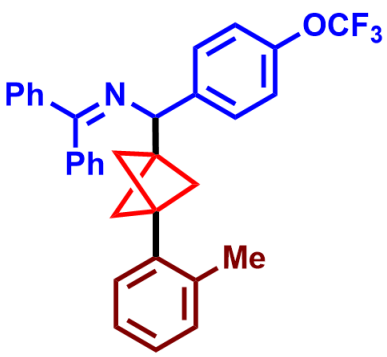
This product was also prepared under microwave irradiation conditions at 100 °C for 24 h. Following the standard workup as outline in General Procedure D and analysis of the crude reaction mixture using ^{1}H NMR against an internal standard, the AY was determined to be 73%, compared to 77% AY when the reaction is performed in an oil bath at 120 °C.

^{1}H NMR (600 MHz, $((CD_3)_2CO$): δ 7.73-7.72 (m, 2H), 7.56-7.49 (m, 5H), 7.43 (tt, J = 3.6, 1.3 Hz, 1H), 7.41-7.38 (m, 2H), 7.31-7.29 (m, 2H), 7.14-7.13 (m, 2H), 7.09 (dt, J = 8.7, 2.0 Hz, 2H), 6.82-6.80 (m, 2H), 4.62 (s, 1H), 3.73 (s, 3H), 1.80 (dd, J = 19, 9.4 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $((CD_3)_2CO$): δ 168.2, 159.5, 148.8 (d, J_{C-F} = 1.7 Hz), 142.7, 141.0, 137.6, 134.2, 131.1, 129.9, 129.65, 129.60, 129.4, 129.1, 128.8, 127.9, 121.69, 121.65 (q, J_{C-F} = 256 Hz), 144.4, 67.2, 55.5, 51.3, 43.2, 42.9 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.51 ppm.

HRMS calc'd for $[C_{33}H_{28}F_3NO_2+H]^+$ = 528.2150, found 528.2158.



1,1-diphenyl-*N*-((3-(o-tolyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bf)

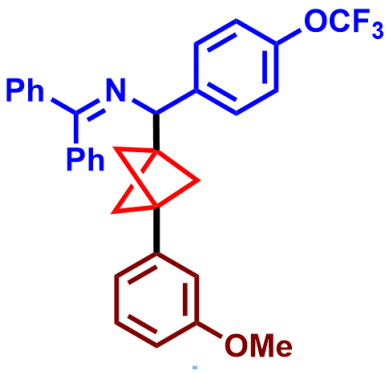
Prepared according to General Procedure D for arylation on a 0.2 mmol scale with the following modifications: a) Cu_2O additive is omitted from the reaction (AY was slightly higher without Cu_2O), b) performed in *n*-Bu_2O instead of CPME and c) run at 140 °C instead of 120 °C . The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 1.5 % EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 57.9 mg of a dark yellow oil, 57%.

^{1}H NMR (400 MHz, ($(CD_3)_2CO$): δ 7.75-7.73 (m, 2H), 7.54-7.50 (m, 5H), 7.44-7.37 (m, 3H), 7.32-7.30 (m, 2H), 7.15-7.13 (m, 2H), 7.08-7.02 (m, 4H), 4.64 (s, 1H), 2.29 (s, 3H), 1.95 (ddd, *J* = 16, 9.6, 1.2 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, ($(CD_3)_2CO$): δ 168.3, 148.8 (d, J_{C-F} = 1.8 Hz), 142.6, 141.0, 139.2, 137.6, 137.5, 131.3, 131.1, 129.9, 129.67, 129.62, 129.5, 129.1, 128.8, 128.5, 127.6, 126.6, 121.7, 121.6 (q, J_{C-F} = 256 Hz), 67.2, 51.4, 44.6, 44.2, 20.9 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.51 ppm.

HRMS calc'd for $[C_{33}H_{28}F_3NO+H]^+$ = 512.2201, found 512.2186.



***N*-((3-(3-methoxyphenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bg)**

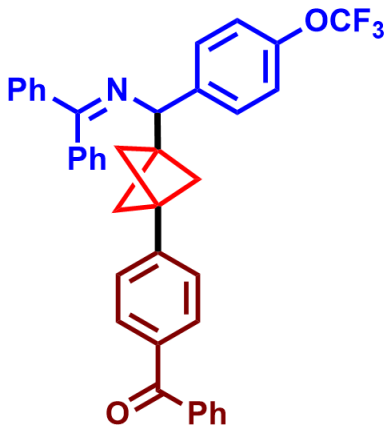
Prepared according to General Procedure D for arylation on a 0.1 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 1 % EtOAc in hexanes by volume with 1.5% NEt_3 to obtain 36.9 mg of an orange solid, 70%.

^{1}H NMR (400 MHz, ($(CD_3)_2CO$): δ 7.74-7.72 (m, 2H), 7.56-7.50 (m, 5H), 7.46-7.37 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.18-7.12 (m, 3H), 6.75-6.72 (m, 3H), 4.63 (s, 1H), 3.74 (s, 3H), 1.83 (dd, *J* = 14, 9.3 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, ($(CD_3)_2CO$): δ 168.3, 160.8, 148.8 (d, *J* = 1.4 Hz), 143.6, 142.6, 140.9, 137.5, 131.1, 130.1, 129.9, 129.65, 129.60, 129.4, 129.0, 128.8, 121.7, 121.6 (q, $J_{C\text{-}F}$ = 256 Hz), 119.1, 112.9, 112.3, 67.2, 55.5, 51.3, 43.6, 42.9 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.4 ppm.

HRMS calc'd for $[C_{33}H_{28}F_3NO_2+H]^+$ = 528.2150, found 528.2125.



4-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)phenyl)(phenyl)methanone (8bh)

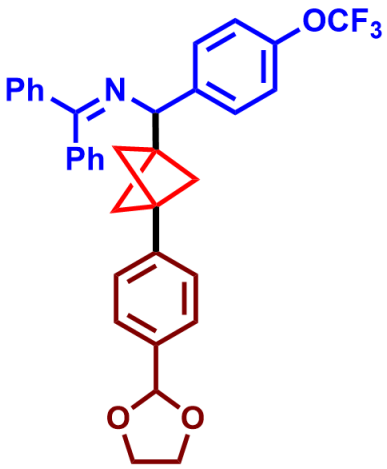
Prepared according to General Procedure D for arylation using 1.5 equiv 4-bromoacetophenone as the aryl halide (29.8 mg) with one modification: *Cu_2O additive is omitted from the reaction*. Assay yield (AY) against CH_2Br_2 internal standard with 1.0 equiv Cu_2O on a 0.1 mmol scale: 58% (average of 2 trials) BCP arylation product. Without Cu_2O, the AY was found to be 75% (0.2 mmol scale reaction). The reaction without Cu_2O was purified on SiO_2 using a gradient of 0 → 10% EtOAc in hexanes with 1.5% NEt_3 to deliver the 60.9 mg of a yellow oil, 50%.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.76 (m, 4H), 7.70-7.68 (m, 2H), 7.62 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.57-7.50 (m, 7H), 7.46-7.30 (m, 7H), 7.15-7.13 (m, 2H), 4.66 (s, 1H), 1.91 (dd, *J* = 15, 9.7 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 196.2, 168.5, 148.9 (d, J_{C-F} = 1.8 Hz), 146.7, 142.5, 140.9, 138.9, 137.5, 136.8, 133.2, 131.1, 130.8, 130.6, 129.9, 129.68, 129.65, 129.51, 129.36, 129.1, 128.8, 127.0, 121.7, 121.6 (q, J_{C-F} = 256 Hz), 67.1, 51.4, 43.5, 43.3 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.4 ppm.

HRMS calc'd for $[C_{39}H_{30}F_3NO_2+H]^+$ = 602.2307, found 602.2286.



_N_-((3-(4-(1,3-dioxolan-2-yl)phenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bi)

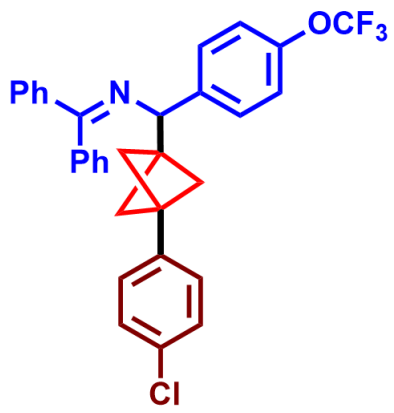
Prepared according to General Procedure D for arylation on a 0.1 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 1 % EtOAc in hexanes with 1.5% NEt_3 to obtain 31.5 mg of an orange solid, 55%.

^{1}H NMR (400 MHz, $((CD_3)_2CO$): δ 7.74-7.73 (m, 2H), 7.55-7.50 (m, 5H), 7.44 (tt, J = 7.2, 2.3 Hz, 1H), 7.39 (tt, J = 7.0, 1.3 Hz, 2H), 7.36-7.34 (m, 2H), 7.31-7.30 (m, 2H), 7.20-7.18 (m, 2H), 7.15-7.13 (m, 2H), 5.68 (s, 1H), 4.63 (s, 1H), 4.08-4.01 (m, 2H), 3.98-3.92 (m, 2H), 1.84 (ddd, J = 21, 9.5, 1.2 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (150 MHz, $((CD_3)_2CO$): δ 168.3, 148.8, 142.8, 142.6, 140.9, 137.8, 137.5, 131.1, 129.9, 129.6, 129.5, 129.4, 129.0, 128.8, 127.4, 126.6, 121.69, 121.62 (q, $J_{C\text{-}F}$ = 256 Hz) 103.4, 67.1, 65.9, 51.3, 43.4, 43.1 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.51 ppm.

HRMS calc'd for $[C_{35}H_{30}F_3NO_3+H]^+$ = 570.2256, found 570.2233.



***N*-((3-(4-chlorophenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bj)**

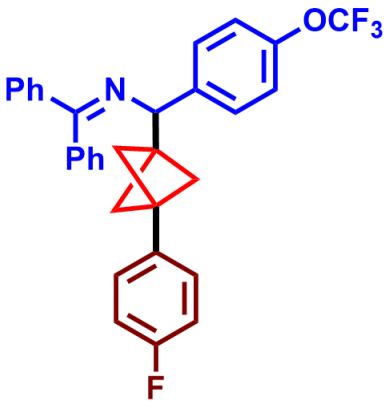
Prepared according to General Procedure D for arylation on a 0.3 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 1 % EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 107.0 mg of a thick, clear oil, 55%.

^{1}H NMR (600 MHz, $((CD_3)_2CO$): δ 7.74-7.72 (m, 2H), 7.55-7.50 (m, 5H), 7.44 (tt, *J* = 7.2, 1.3 Hz, 1H), 7.39 (tt, *J* = 7.6, 1.5 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.27 (dt, *J* = 8.5, 1.9 Hz, 2H), 7.18 (dt, *J* = 8.5, 2 Hz, 2H), 7.14-7.12 (m, 2H), 4.63 (s, 1H), 1.84 (ddd, *J* = 21, 9.5, 1.2 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (150 MHz, $((CD_3)_2CO$): δ 168.4, 148.8 (d, *J* = 1.4 Hz), 142.5, 140.98, 140.97, 137.5, 132.7, 131.1, 129.9, 129.66, 129.63, 129.4, 129.12, 129.10, 128.8, 128.7, 121.7, 121.6 (q, J_{C-F} = 256 Hz) 67.1, 51.3, 43.1, 43.09 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.4 ppm.

HRMS calc'd for $[C_{32}H_{25}ClF_3NO+H]^+$ = 532.1655, found 532.1658.



***N*-((3-(4-fluorophenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bk)**

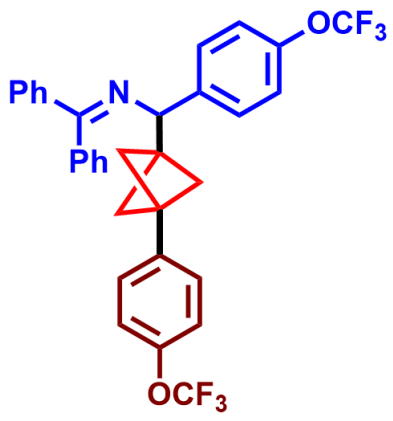
Prepared according to General Procedure D for arylation on a 0.3 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 1 % EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 105.4 mg of a thick, clear oil, 56%.

^{1}H NMR (600 MHz, $((CD_3)_2CO)$: δ 7.74-7.72 (m, 2H), 7.54-7.50 (m, 5H), 7.43 (tt, *J* = 7.2, 2.4 Hz, 1H), 7.39 (t, *J* = 7 Hz, 2H), 7.31-7.30 (m, 2H), 7.21 (m, 2H), 7.14-7.12 (m, 2H), 7.00 (tt, *J* = 8.9, 2.3 Hz, 2H), 4.63 (s, 1H), 1.84 (ddd, *J* = 21, 9.5, 1.2 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (150 MHz, $((CD_3)_2CO)$: δ 168.4, 162.6 (d, $J_{C\text{-}F}$ = 242 Hz), 148.8, 142.6, 140.9, 138.2 (d, $J_{C\text{-}F}$ = 3.7 Hz), 137.5, 131.1, 129.9, 129.66, 129.62, 129.4, 129.1, 129.8, 129.7, 121.7, 121.6 (d, $J_{C\text{-}F}$ = 256 Hz), 115.7 (d, $J_{C\text{-}F}$ = 21.6 Hz), 67.1, 51.4, 43.0, 42.9 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.5, -118.0 ppm.

HRMS calc'd for $[C_{32}H_{25}F_4NO+H]^+$ = 516.1950, found 516.1938.



1,1-diphenyl-*N*-((4-(trifluoromethoxy)phenyl)(3-(4-(trifluoromethoxy)phenyl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (8bl)

Prepared according to General Procedure D for arylation on a 0.3 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 1 % EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 126.5 mg of a thick, clear oil, 73%.

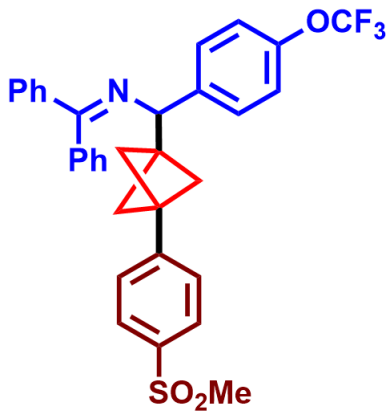
^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.75-7.72 (m, 2H), 7.56-7.49 (m, 5H), 7.46-7.37 (m, 3H), 7.32-7.29 (m, 4H), 7.22-7.20 (m, 2H), 7.15-7.12 (m, 2H), 4.64 (s, 1H), 1.87 (dd, *J* = 15, 9.4 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 168.4, 148.9 (d, $J_{C\text{-}F}$ = 1.9 Hz), 148.6 (d, $J_{C\text{-}F}$ = 1.8 Hz), 142.5, 141.4, 140.9, 137.5, 131.9, 129.9, 129.68, 129.64, 129.5, 129.1, 128.8, 128.7, 121.8, 121.7, 121.66 (q, $J_{C\text{-}F}$ = 256 Hz), 121.61 (q, $J_{C\text{-}F}$ = 256 Hz),* 67.1, 51.4, 43.1, 43.0 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.5, -58.6 ppm.

HRMS calc'd for $[C_{33}H_{25}F_6NO_2+H]^+$ = 582.1867, found 582.1832.

*****The most upfield peak of this quartet is clearly visible in the spectrum but wasn't peak-picked despite extensive scanning. All other peaks for the two -OCF_3 quartets were detected, which allowed coupling constants to be determined.



_N_-((3-(4-(methylsulfonyl)phenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bm)

Prepared according to General Procedure D for arylation on a 0.1 mmol scale with a modified workup: the reaction mixture was diluted with 1 mL EtOAc and 1 mL sat'd aq. NH_4Cl and then was stirred vigorously for 24 h. The two layers were separated and the organic layer was washed with 1 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 15 % EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 29 mg of a clear oil, 50%.

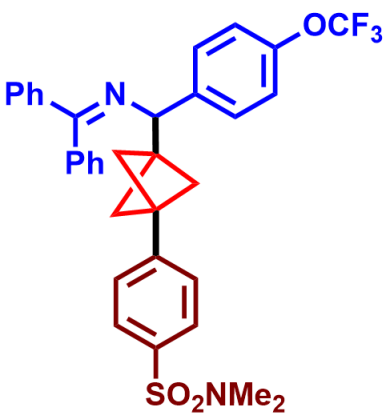
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 7.1 Hz, 2H), 7.49-7.43 (m, 3H), 7.43-7.29 (m, 7H), 7.17 (d, J = 8.2 Hz, 2H), 7.07-7.06 (m, 2H), 4.54 (s, 1H), 3.01 (s, 3H), 1.89 (dd, J = 13, 9.7 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (126 MHz, $((CD_3)_2CO$): δ 168.4, 148.7 (d, $J_{C\text{-}F}$ = 1.8 Hz), 147.7, 142.3, 140.8, 140.4, 137.4, 131.0, 129.8, 129.5, 129.5, 129.3, 128.9, 128.6, 128.1, 127.7, 121.6, 121.5 (q, $J_{C\text{-}F}$ = 256 Hz), 66.9, 51.3, 44.3, 43.218, 43.212*.

^{19}F NMR (471 MHz, $CDCl_3$) (unreferenced): δ -57.81 ppm.

HRMS calc'd for $[C_{33}H_{28}F_3NO_3S+H]^+$ = 576.1820, found 576.1810.

*****Two signals here, corresponding to a BCP carbon and the CH_3 of the $–SO_2CH_3$ group, are overlapping and could not be resolved in this spectrum, though they are both visible (see inset in full spectrum). The peaks are approximated manually in the report above.



4-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)-*N*,*N*-dimethylbenzenesulfonamide (8bn)

Prepared according to General Procedure D for arylation on a 0.1 mmol scale with a modified workup: the reaction mixture was diluted with 1 mL EtOAc and 1 mL sat'd aq. NH_4Cl and then was stirred vigorously for 24 h. The two layers were separated and the organic layer was washed with 1 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was eluted on SiO_2 using hexanes with 1.5% NEt_3 by volume to obtain 33 mg of slightly yellow oil, 55%.

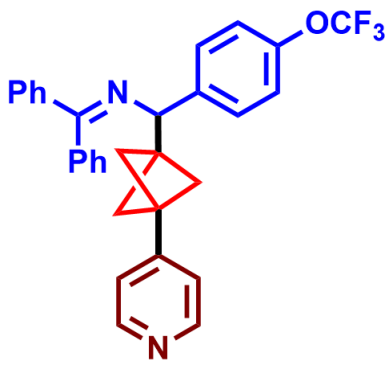
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 7.74-7.72 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.55-7.51 (m, 5H), 7.45-7.38 (m, 5H), 7.32-7.30 (m, 2H), 7.15-7.13 (m, 2H), 4.65 (s, 1H), 2.63 (s, 6H), 1.92 (dd, *J* = 19, 9.5 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2CO$): δ 168.4, 148.77 (d, J_{C-F} = 1.8 Hz), 146.9, 142.3, 140.8, 137.4, 134.6, 131.0, 129.8, 129.53, 129.51, 129.3, 128.9, 128.66, 128.63, 127.5, 121.6, 121.3 (q, J_{C-F} = 256 Hz), 68.9, 51.3, , 43.20*, 43.19, 38.1 ppm.

^{19}F NMR (471 MHz, $(CD_3)_2CO$ (unreferenced): δ -58.51 ppm.

HRMS calc'd for $[C_{34}H_{31}F_3N_2O_3S+H]^+$ = 605.2085, found 605.2068.

*****In the full spectrum, two peaks are clearly visible (see inset), and are reported here based on manual approximation of chemical shift.



1,1-diphenyl-*N*-((3-(pyridin-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bo)

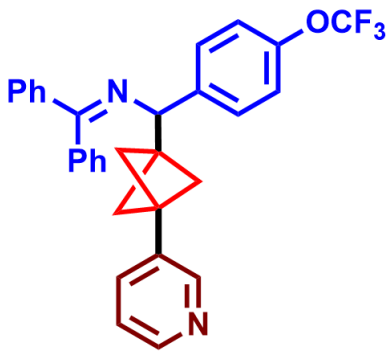
Prepared according to General Procedure D for arylation on a 0.3 mmol scale using 4 equiv (instead of standard 3 equiv) Cs_2CO_3 and 4-bromopyridine hydrochloride. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 50 % EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 100.2 mg of an orange solid, 67%.

^{1}H NMR (400 MHz, ($(CD_3)_2CO$): δ 8.45 (d, *J* = 5.8 Hz, 2H), 7.75-7.73 (m, 2H), 7.55-7.50 (m, 5H), 7.46-7.37 (m, 3H), 7.32-7.30 (m, 2H), 7.14-7.12 (m, 4H), 4.64 (s, 1H), 1.88 (dd, *J* = 15, 9.4 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, ($(CD_3)_2CO$): δ 168.6, 150.6, 150.0, 148.9 (d, *J* = 1.4 Hz), 142.4, 140.9, 137.5, 131.2, 130.0, 129.7, 129.6, 129.5, 129.1, 128.8, 122.1, 121.8, 121.6 (q, J_{C-F} = 256 Hz), 67.0, 51.1, 43.5, 42.6 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.44 ppm.

HRMS calc'd for $[C_{31}H_{25}F_3N_2O+H]^+$ = 499.1997, found 499.1978.



1,1-diphenyl-*N*-((3-(pyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bp)

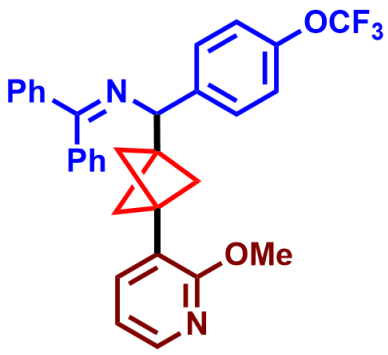
Prepared according to General Procedure D for arylation on a 0.1 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 20 % EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 18.9 mg of a clear oil, 38%.

^{1}H NMR (600 MHz, $((CD_3)_2CO$): δ 8.42 (m, 1H), 8.39 (dd, *J* = 4.7, 2.1 Hz, 1H), 7.74-7.72 (m, 2H), 7.57-7.50 (m, 6H), 7.44 (tt, *J* = 7.2, 2.3 Hz, 1H), 7.40 (m, 2H), 7.32-7.30 (m, 2H), 7.23 (ddd, *J* = 7.8, 4.7, 0.7 Hz, 1H), 7.15-7.13 (m, 2H), 4.64 (s, 1H), 1.91 (ddd, *J* = 22, 9.5, 1.3 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (125 MHz, $((CD_3)_2CO$): δ 168.5, 148.8, 148.79, 148.74, 142.5, 140.9, 137.5, 137.0, 134.2, 131.1, 129.9, 129.67, 129.63, 129.4, 129.1, 128.7, 123.9, 121.7, 121.6 (q, $J_{C\text{-}F}$ = 256 Hz), 67.1, 51.3, 43.6, 41.6 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.52 ppm.

HRMS calc'd for $[C_{31}H_{25}F_3N_2O+H]^+$ = 499.1997, found 499.1978.



***N*-((3-(2-methoxypyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bq)**

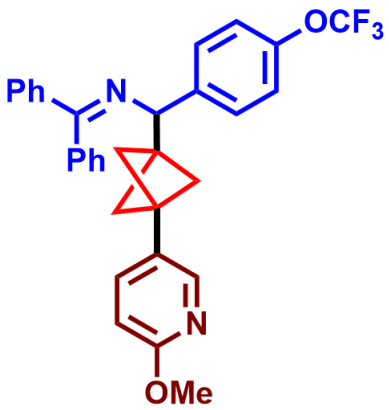
Prepared according to General Procedure D for arylation on a 0.1 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 0 → 10% EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 30.5 mg of a yellow oil, 58%.

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.97 (dd, *J* = 4.9, 1.8 Hz, 1H), 7.74-7.72 (m, 2H), 7.56-7.49 (m, 5H), 7.44-7.38 (m, 3H), 7.35-7.29 (m, 3H), 7.14-7.12 (m, 2H), 6.82 (dd, *J* = 7.1, 5 Hz, 1H), 4.62 (s, 1H), 3.85 (s, 3H), 1.89 (dd, *J* = 15, 9.3 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$): δ 168.31, 163.5, 148.5 (d, J_{C-F} = 1.8 Hz), 146.0, 142.6, 140.9, 137.5, 137.3, 131.1, 129.9, 129.65, 129.6, 129.4, 129.1, 128.8, 123.7, 121.7, 121.6 (q, *J* = 256 Hz), 117.5, 67.3, 53.3, 50.9, 44.5, 40.9 ppm.

^{19}F NMR (376 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.4 ppm.

HRMS calc'd for $[C_{32}H_{27}F_3N_2O_2+H]^+$ = 529.2103, found 529.2080.



_N_-((3-(6-methoxypyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8br)

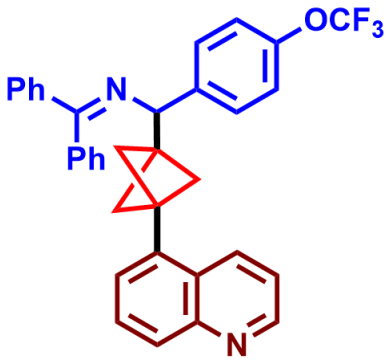
Prepared according to the general procedure for arylation on a 0.1 mmol scale with a modified workup the reaction mixture was diluted with 1 mL EtOAc and 1 mL sat'd aq. NH_4Cl and then was stirred vigorously for 24 h. The two layers were separated and the organic layer was washed with 1 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure.The crude reaction mixture was eluted on SiO_2 using hexanes with 1.5% NEt_3 by volume (column was performed twice) to obtain 17 mg of a clear oil, 32%.

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 7.95 (d, J = 2.3 Hz, 1H), 7.74-7.72 (m, 2H), 7.56-7.48 (m, 6H), 7.44-7.38 (m, 3H), 7.31-7.29 (m, 2H), 7.14-7.12 (m, 2H), 6.64 (d, J = Hz, 1H), 4.62 (s, 1H), 3.82 (s, 3H), 1.85 (dd, J = 19, 10 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2CO$): δ 168.2, 163.8, 148.7 (d, J_{C-F} = 1.8 Hz), 145.2, 142.4, 140.8, 137.6, 137.4, 131.0, 130.1, 129.8, 129.5, 129.4, 129.3, 128.9, 128.6, 121.58, 121.50 (q, J_{C-F} = 256 Hz), 110.8, 67.0, 53.3, 51.2, 43.3, 41.0 ppm.

^{19}F NMR (471 MHz, $(CD_3)_2CO$) (unreferenced): δ -58.52 ppm.

HRMS calc'd for $[C_{32}H_{27}F_3N_2O_2]^+$ = 529.2103, found 529.2090.



1,1-diphenyl-*N*-((3-(quinolin-5-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bs)

Prepared according to General Procedure D for arylation on a 0.3 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 10 → 60 % EtOAc in hexanes with 1.5% NEt_3 by volume to obtain 40.6 mg of yellow solid, 74%.

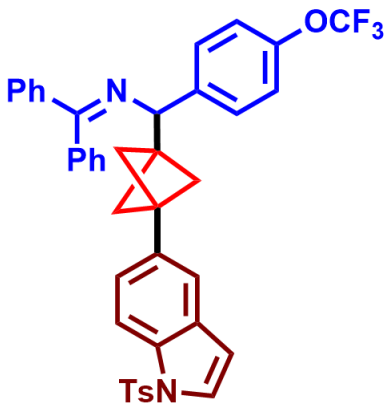
^{1}H NMR (400 MHz, ($(CD_3)_2CO$): δ 8.85 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.67-8.64 (m, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.77-7.75 (m, 2H), 7.61 (dd, *J* = 8.4, 7.1 Hz, 1H), 7.57-7.54 (m, 5H), 7.45-7.39 (m, 4H), 7.34-7.31 (m, 3H), 7.18-7.16 (m, 2H), 4.71 (s, 1H), 2.17 (ddd, *J* = 18, 9.5, 1.3 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (100 MHz, ($(CD_3)_2CO$): δ 168.5, 150.9, 149.9, 148.9, 142.5, 140.9, 138.3, 137.6, 134.0, 131.2, 130.0, 129.9, 129.7, 129.66, 129.63, 129.5, 129.1, 128.8, 128.1, 126.6, 121.79, 121.71, 121.6 (q, $J_{C\text{-}F}$ = 256 Hz),* 67.1, 52.6, 44.6, 40.0 ppm.

^{19}F NMR (376 MHz, ($(CD_3)_2CO$) (unreferenced): δ -58.46 ppm.

HRMS calc'd for $[C_{35}H_{27}F_3N_2O+H]^+$ = 549.2153, found 549.2135.

*The outer peaks of this quartet were not intense enough to be captured by NMR software but are clearly visible, so the coupling constant was calculated by hand.



1,1-diphenyl-*N*-((3-(1-tosyl-1H-indol-5-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bt)

Prepared according to General Procedure D for arylation on a 0.1 mmol scale with a modified workup the reaction mixture was diluted with 1 mL EtOAc and 1 mL sat'd aq. NH_4Cl and then was stirred vigorously for 24 h. The two layers were separated and the organic layer was washed with 1 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was eluted on SiO_2 using hexanes with 1.5% NEt_3 by volume (column was performed twice) to obtain 15 mg of a clear oil, 22%.

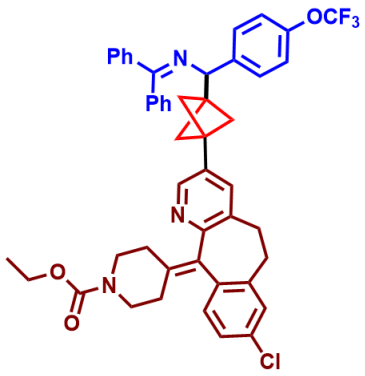
^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 7.88 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 9 Hz, 1H), 7.73-7.71 (m, 2H), 7.65 (d, *J* = 4 Hz, 1H), 7.54-7.49 (m, 5H), 7.45-7.29 (m, 8H), 7.18 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.14-7.12 (m, 2H), 6.70 (d, *J* = 3.5 Hz, 1H), 4.63 (s, 1H), 2.32 (s, 3H), 1.84 (dd, *J* = 15, 9 Hz, 6H) ppm.

^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2CO$): δ 168.2, 148.7 (q, J_{C-F} = 1.8 Hz), 146.3, 142.5, 140.8, 137.4 137.3, 136.0, 134.4, 131.9, 131.0, 130.9, 129.8, 129.5, 129.4, 129.3, 128.9, 128.6, 127.8, 127.7, 123.6, 121.56 (d, J_{C-F} = 0.8 Hz), 121.51 (q, J_{C-F} = 256 Hz),* 119.58, 113.9, 110.0, 67.0, 51.3, 43.5, 42.8, 21.3 ppm.

^{19}F NMR (471 MHz, $(CD_3)_2CO$ (unreferenced): δ -58.53 ppm.

HRMS calc'd for $[C_{41}H_{33}F_3N_2O_3S+H]^+$ = 691.2242, found 691.2221.

*The outer peaks of this quartet were not intense enough to be captured by NMR software but are clearly visible, so the coupling constant was calculated by hand.



ethyl -4-(8-chloro-3-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (8bu)

Prepared according to General Procedure D for arylation on a 0.1 mmol scale with a modified workup: the reaction mixture was diluted with 1 mL EtOAc and 1 mL sat'd aq. NH_4Cl and then was stirred vigorously for 24 h. The two layers were separated and the organic layer was washed with 1 mL brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography on SiO_2 using a gradient of 0 → 15% EtOAc in hexanes with 1.5% Et_3N by volume to give the product, as 39 mg of a white solid, 49%.

^{1}H NMR (500 MHz, $(CD_3)_2CO$): δ 8.19 (s, 1H), 7.72 (d, *J* = 7 Hz, 2H), 7.54-7.49 (m, 5H), 7.44-7.37 (m, 3H), 7.34 (s, 1H), 7.31-7.29 (m, 2H), 7.23-7.22 (m, 1H), 7.17-7.09 (m, 4H), 4.62 (s, 1H), 4.07 (q, *J* = 6Hz, 2H), 3.68 (m, 2H), 3.42-3.20 (m, 4H), 2.85-2.81 (m, 5H)*, 2.43-2.38 (m, 1H), 2.35-2.30 (m, 1H), 2.25-2.20 (m, 2H), 1.86 (dd, *J* = 15, 10 Hz, 6H), 1.20 (t, *J* = 7.5 Hz, 3H) ppm.

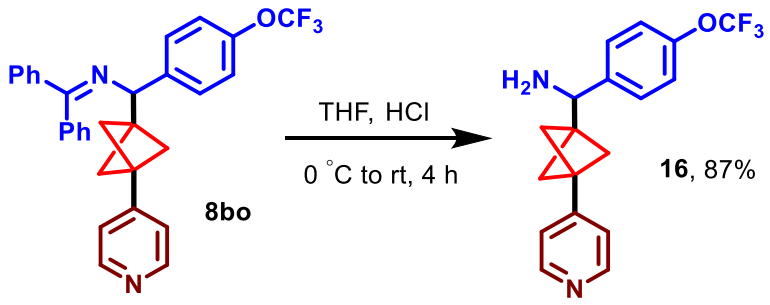
^{13}C{^{1}H} NMR (126 MHz, $(CD_3)_2CO$): δ 168.3, 156.1, 155.7, 148.7 (d, $J_{C\text{-}F}$ = 1.8 Hz), 145.2, 142.3, 141.3, 140.8, 139.4, 137.8, 137.4, 135.9, 135.5, 134.8, 133.5, 133.0, 131.4, 131.0, 129.8, 129.6, 129.5, 129.3, 128.9, 128.6, 126.6, 121.5, 121.4 (q, $J_{C\text{-}F}$ = 256 Hz), 66.9, 61.5, 51.2, 45.6, 45.5, 43.5, 41.2, 32.1, 31.9, 31.5, 31.35, 15.0 ppm.**

^{19}F NMR (471 MHz, $(CD_3)_2CO$ (unreferenced): δ -57.81 ppm.

HRMS calc'd for $[C_{48}H_{43}ClF_3N_3O_3+H]^+$ = 802.3023, found 802.2999.

***This peak is coincident with H_2O in the NMR solvent, leading to a larger than expected integration (expected: 2H, found 5H).

****37 C are expected but 39 signals are observed due to conformers of the seven-membered ring.



(3-(pyridin-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanamine (8bo)

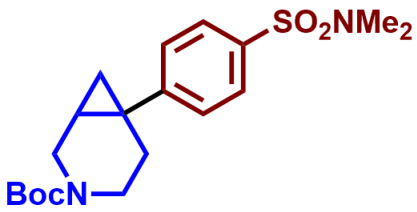
The BCP benzyl ketimine **8bo** (65.0 mg, 0.13 mmol, 1 equiv) is dissolved in 1.3 mL THF under air atmosphere and cooled in an ice bath. 1 M HCl (1.3 mL) is added dropwise and the mixture stirred 2 minutes. The reaction mixture is removed from the ice bath and stirred at room temperature for 4 hours. THF is removed under reduced pressure and the crude reaction mixture is transferred to a separatory funnel, diluting with deionized water to produce a homogenous aqueous layer. The aqueous layer is extracted with diethyl ether (5x10 mL) to remove all benzophenone. The aqueous layer is then basified with 1 M NaOH until basic as judged by pH paper, producing a cloudy white suspension. The aqueous layer is extracted with EtOAc (3x5 mL). The EtOAc layer is dried with $MgSO_4$, filtered, and concentrated under reduced pressure to an orange solid, 37.9 mg, 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 6.0 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 6.0 Hz, 2H), 4.14 (s, 1H), 1.86 (dd, *J* = 13, 9.3 Hz, 6H), 1.61 (br s, 2H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.7, 149.2, 148.3, 141.7, 127.9, 121.3, 120.8, 120.6 (q, $J_{C\text{-}F}$ = 256 Hz), 55.7, 49.6, 43.2, 40.8 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) (unreferenced): δ -57.87 ppm.

HRMS calc'd for $[C_{18}H_{17}F_3N_2O+H]^+$ = 335.1368, found 335.1371.



tert-butyl 6-(4-(*N*,*N*-dimethylsulfamoyl)phenyl)-3-azabicyclo[4.1.0]heptane-3-carboxylate (18a)

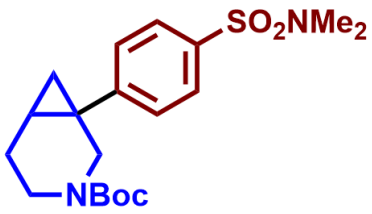
Prepared according to General Procedure D for arylation on a 0.2 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 20 → 80 % EtOAc in hexanes to obtain 72.0 mg of an off-white solid, 95%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66-7.71 (m, 2H), 7.35 – 7.41 (m, 2H), 3.78 (m, 2H), 3.41 (m, 1H), 3.17-3.33 (m, 1H), 2.69 (s, 6H), 2.13 (m, 2H), 1.61-1.69 (m, 1H), 1.47 (s, 9H), 1.06 (m, 1H), 0.95 (t, J = 5.5 Hz, 1H) ppm.*

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.1, 152.1, 132.9, 127.9, 127.5, 79.7, 41.8, 41.1, 40.5, 39.5, 37.9, 28.7, 28.5, 22.7, 19.8, 16.6 ppm.

HRMS calc'd for $[C_{19}H_{28}N_2O_4S+Na]^+$ = 403.1667, found 403.1675.

*****Boc rotamers broaden lines in the carbon NMR as well and lead to additional peaks, presumably from the rotamer, more than the expected 14 C.



***tert*-butyl 1-(4-(*N*,*N*-dimethylsulfamoyl)phenyl)-3-azabicyclo[4.1.0]heptane-3-carboxylate (18b)**

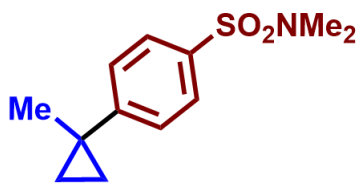
Prepared according to General Procedure D for arylation on a 0.2 mmol scale. The crude reaction mixture was eluted on SiO_2 using a gradient of 20 → 80 % EtOAc in hexanes to obtain 62.4 mg of an oily, colorless substance, 82%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.66 (m, 2H), 7.38 (d, *J* = 8.4, 2H), 4.12-4.04 (m, 1H), 3.54 (br s, 2H), 3.03-3.00 (m, 1H), 2.68 (s, 6H), 2.12-2.04 (m, 1H), 1.84 (br s, 1H), 1.45 (s, 9H), 1.37-1.35 (m, 1H), 1.10-1.07 (m, 1H), 0.83-0.80 (t, *J* = 5.9 Hz, 1H) ppm.*

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 155.0, 150.2, 133.2, 128.0, 79.8, 47.7, 46.5, 41.3, 40.4, 38.0, 28.5, 24.4, 22.5, 18.5, 17.8 ppm.

HRMS calc'd for $[C_{19}H_{28}N_2O_4S+Na]^+$ = 403.1667, found 403.1652.

*Owing to the presence of Boc group rotamers, many peaks in the proton NMR are very broad and are reported as broad singlet or multiplets. Boc rotamers broaden lines in the carbon NMR as well and lead to one additional peak, presumably from a rotamer, more than the expected 14 C.



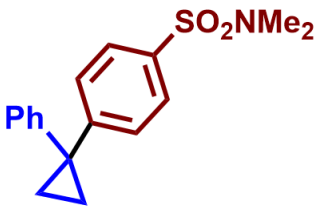
***N,N*-dimethyl-4-(1-methylcyclopropyl)benzenesulfonamide (18c)**

Prepared according to General Procedure D for arylation on a 0.1 mmol scale, using a ratio of 1.5 : 1.0 : 1.0 of RBpin : ArBr : Cu_2O. This ratio was chosen to give total consumption of the aryl bromide, which made purification easier. The crude reaction mixture was eluted on SiO_2 using a gradient of 10 → 60 % EtOAc in hexanes to obtain 16.7 mg of a yellow solid, 70%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.35, (d, *J* = 8.6 Hz, 2H), 2.69 (s, 6H), 1.44 (s, 3H), 0.95-0.90 (m, 2H), 0.89-0.84 (m, 2H) ppm.

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 152.7, 132.3, 127.8, 126.8, 38.0, 24.9, 19.6, 17.04. ppm.

HRMS calc'd for $[C_{12}H_{17}NO_2S+H]^+$ = 240.1058, found 240.1062.



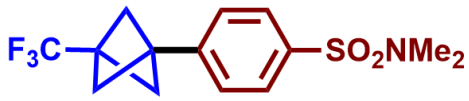
***N,N*-dimethyl-4-(1-phenylcyclopropyl)benzenesulfonamide (18d)**

Prepared according to General Procedure D for arylation on a 0.1 mmol scale, using a ratio of 1.5 : 1.0 : 1.0 of RBpin : ArBr : Cu_2O. The crude reaction mixture was eluted on SiO_2 using a gradient of 10 → 60 % EtOAc in hexanes to obtain 17.9 mg of a yellow solid, 59%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.62 (m, 2H), 7.34-7.22 (m, 7H), 2.69 (s, 6H), 1.43-1.40 (m, 2H), 1.36-1.33 (m, 2H) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 151.5, 144.1, 132.8, 129.2, 128.7, 128.2, 127.8, 126.8, 38.0, 30.0, 17.3 ppm.

HRMS calc'd for $[C_{17}H_{19}NO_2S+H]^+$ = 302.1214, found 302.1214.



_N,N_-dimethyl-4-(3-(trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)benzenesulfonamide (18e)

Prepared according to General Procedure D for arylation on a 0.1 mmol scale, using a reagent ratio of F_3C-BCP-Bpin (0.1 mmol, 1 equiv), aryl bromide, (0.15 mmol, 1.5 equiv) and Cu_2O (0.1 mmol, 1 equiv). The crude reaction mixture was eluted on SiO_2 using a gradient of 10 → 70 % EtOAc in hexanes to obtain 17.3 mg of a white solid, 54%.

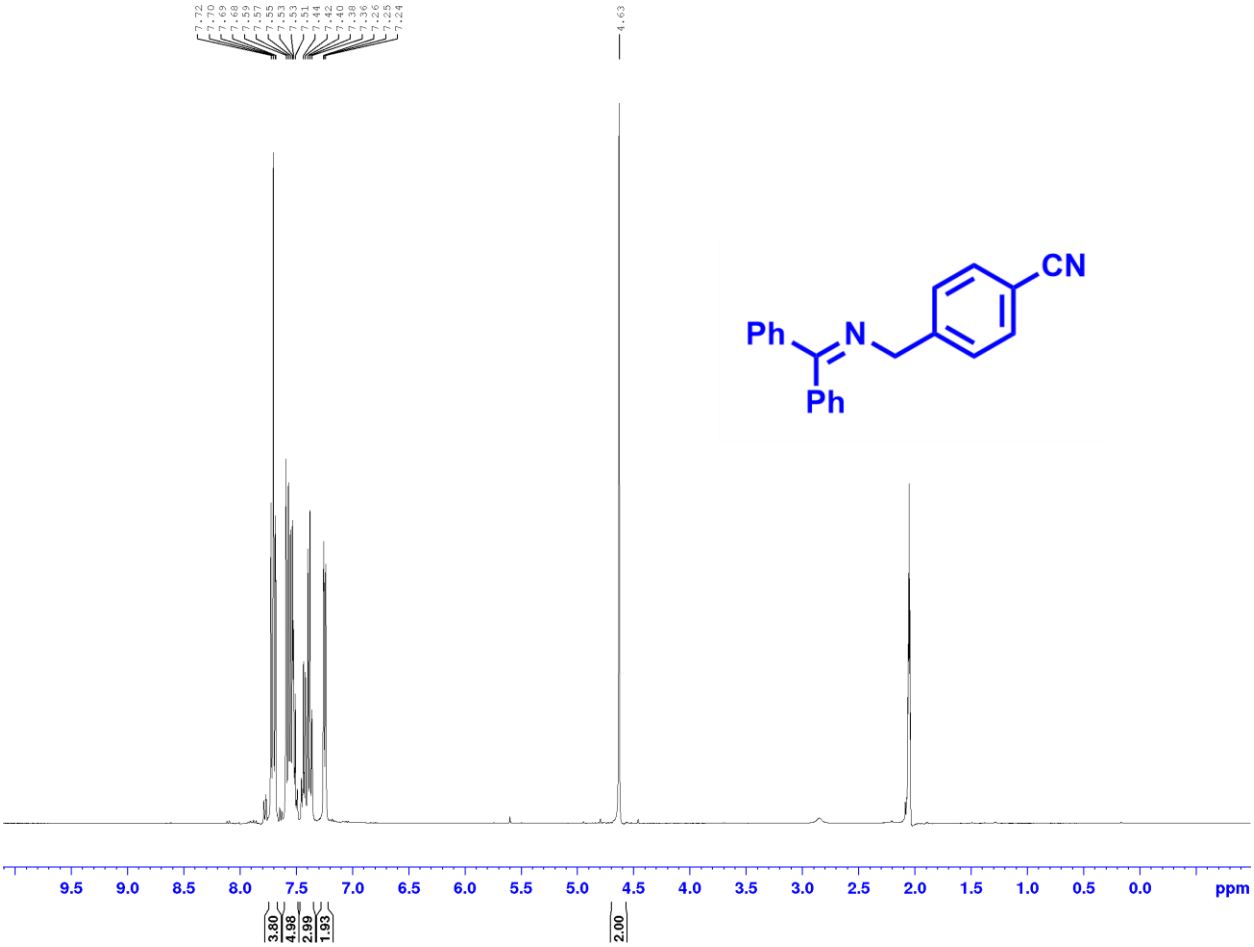
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.7 Hz, 2H), 2.70 (s, 6H), 2.30 (s, 6H) ppm.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.7, 134.5, 128.0, 126.9, 122.9 (q, $J_{C\text{-}F}$ = 275 Hz), 50.6, 41.1, 38.0, 36.7 (q, $J_{C\text{-}F}$ = 38 Hz) ppm.

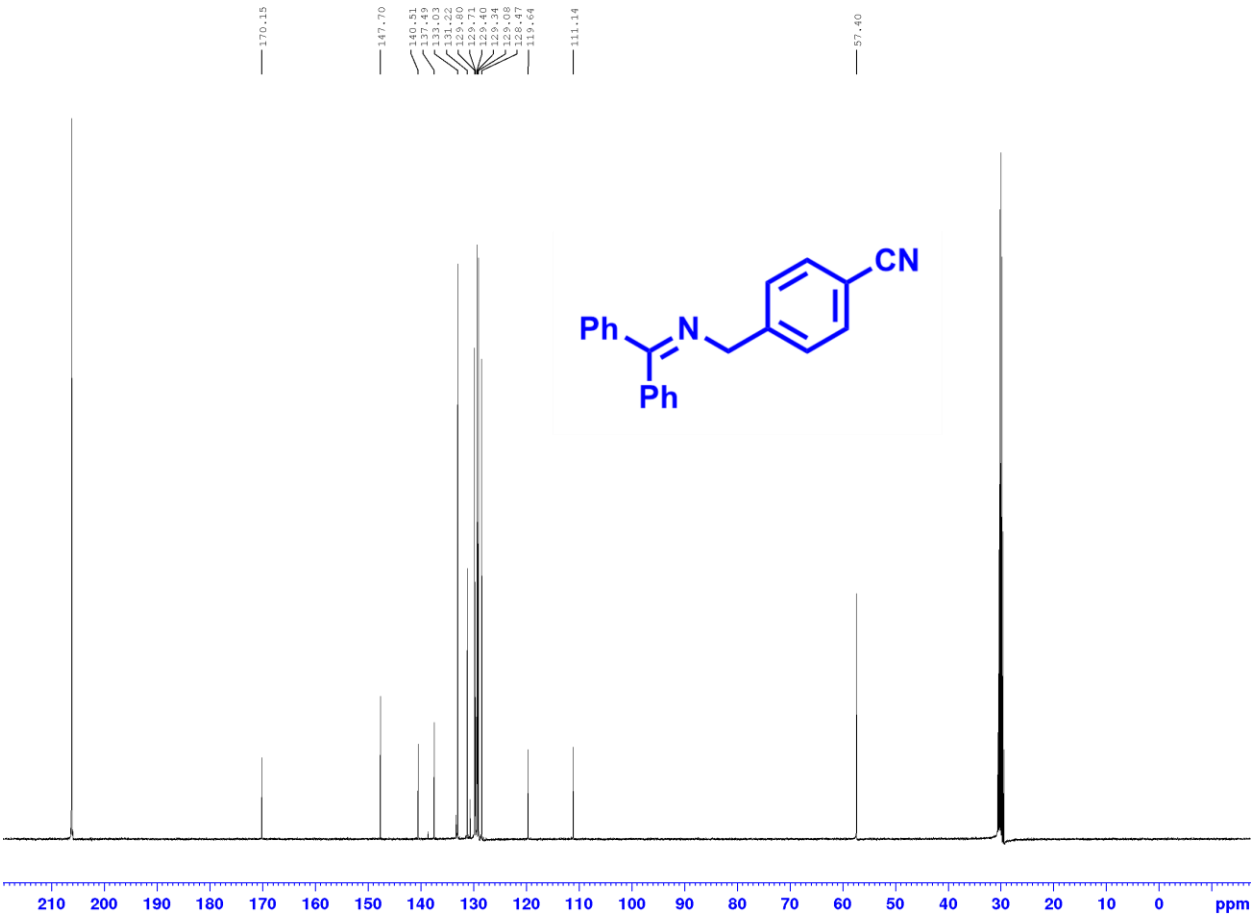
^{19}F NMR (376 MHz, $CDCl_3$ (unreferenced): δ -73.13 ppm.

HRMS calc'd for $[C_{14}H_{16}F_3NO_2S+H]^+$ = 320.0932, found 320.0925.

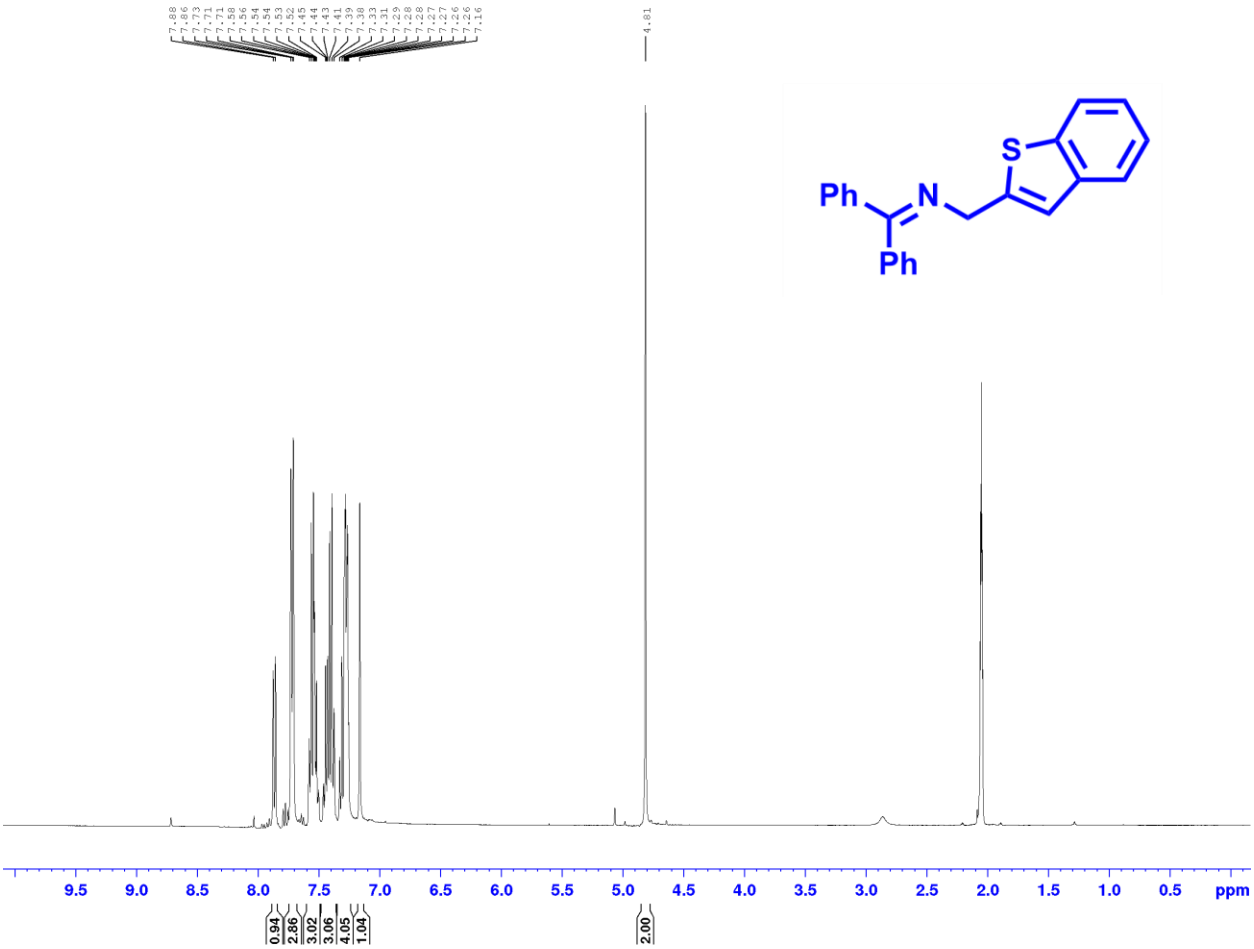
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **4-(((diphenylmethylene)amino)methyl)benzonitrile**



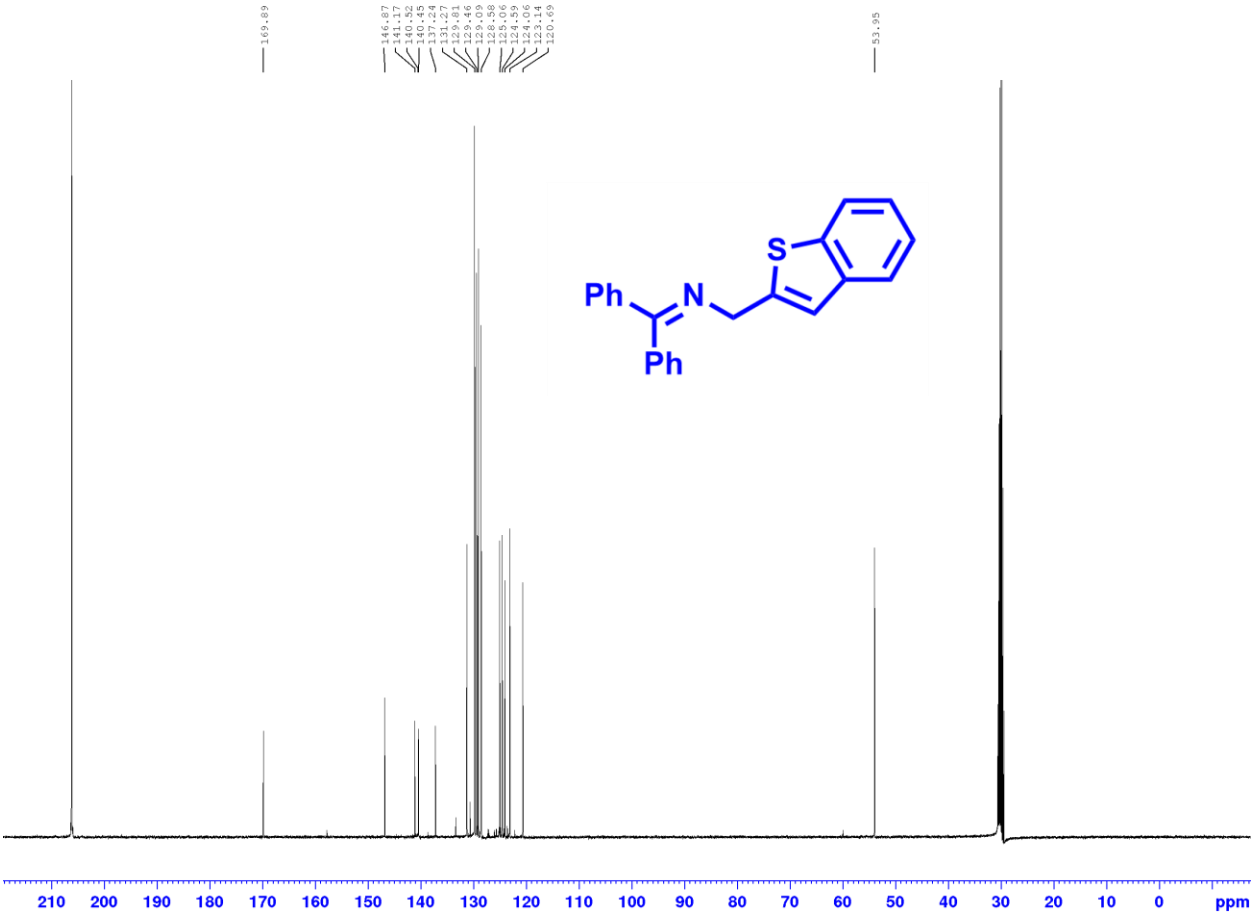
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of **4-(((diphenylmethylene)amino)methyl)benzonitrile**



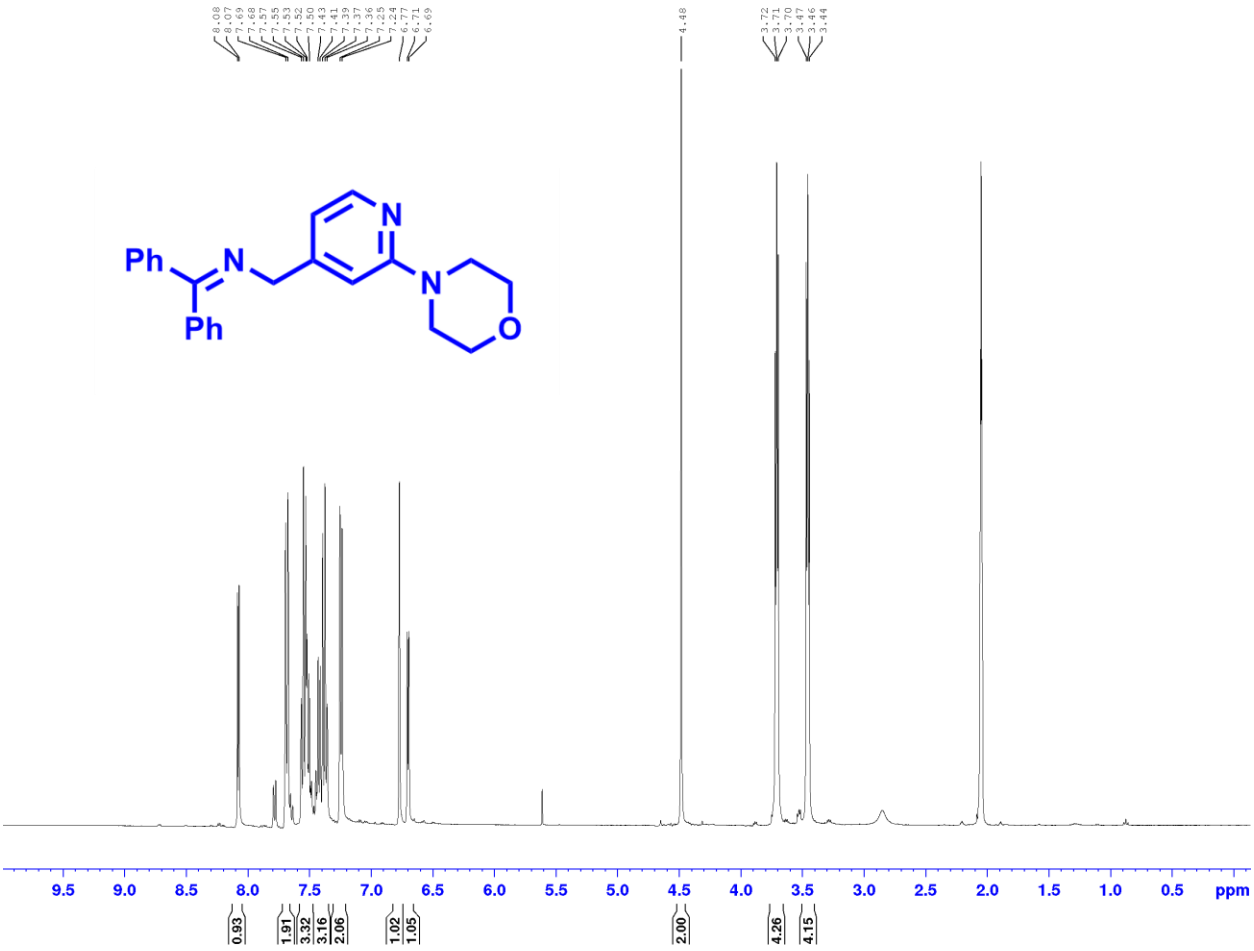
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N*-(benzo[b]thiophen-2-ylmethyl)-1,1-diphenylmethanimine**



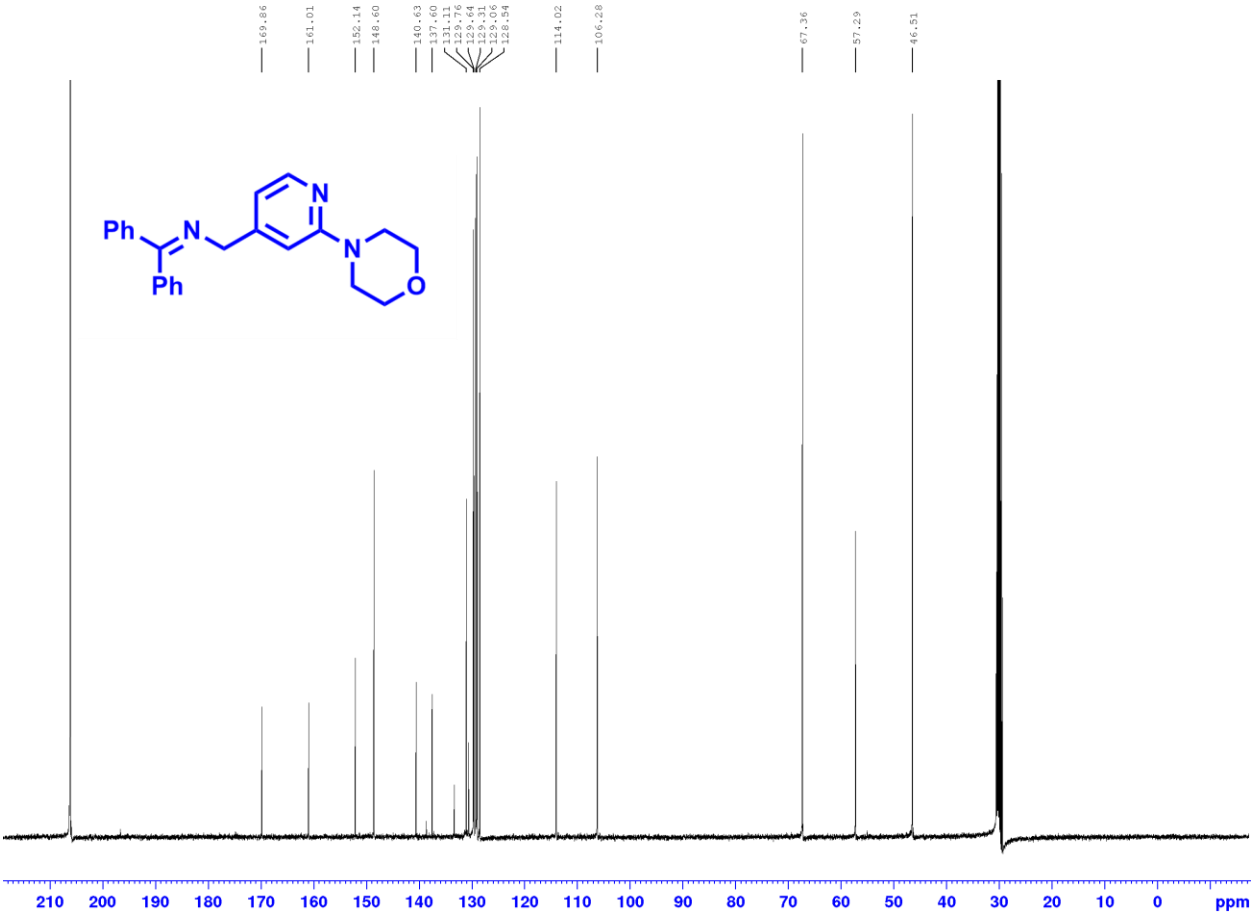
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N*-(benzo[b]thiophen-2-ylmethyl)-1,1-diphenylmethanimine**



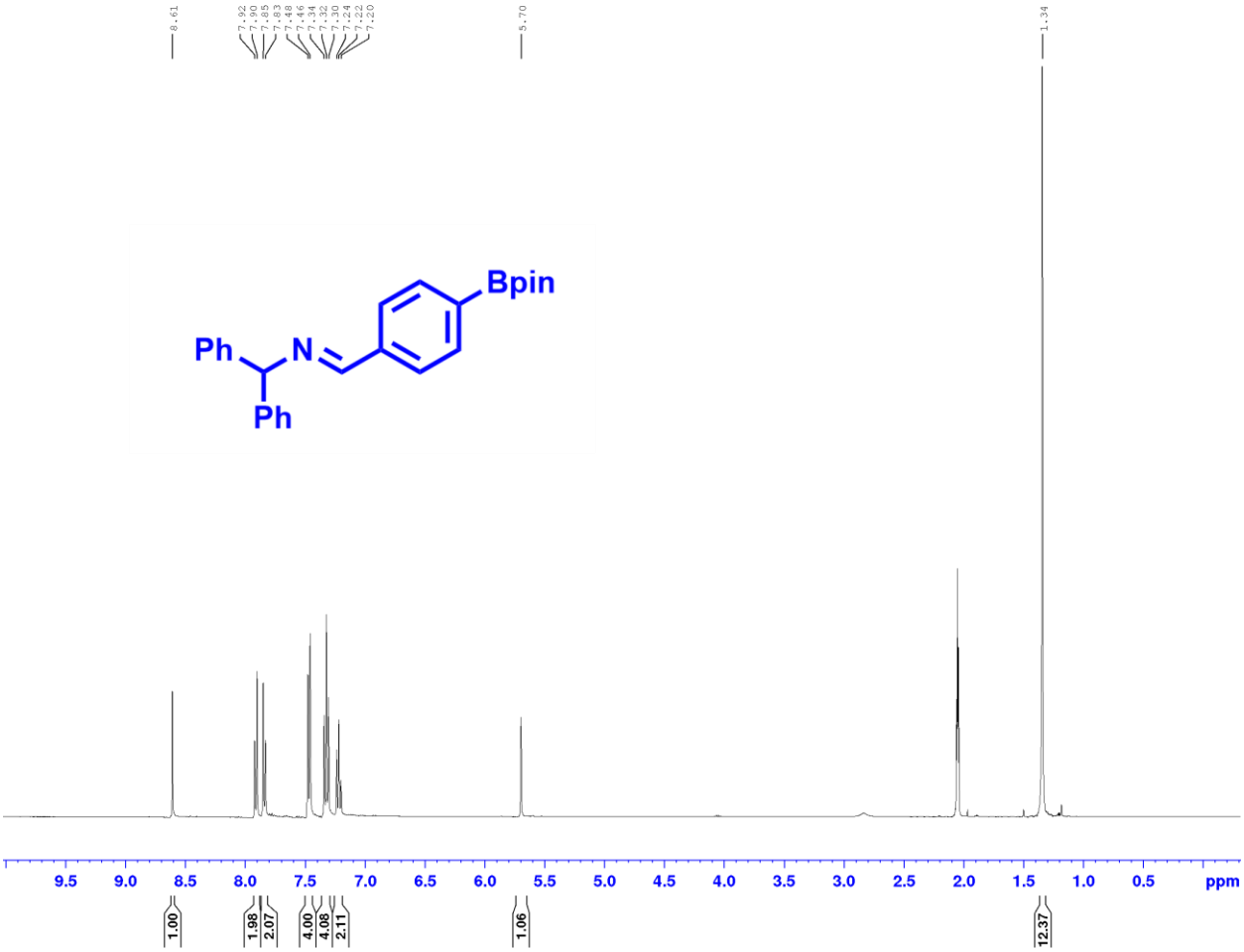
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N*-((2-morpholinopyridin-4-yl)methyl)-1,1-diphenylmethanimine**



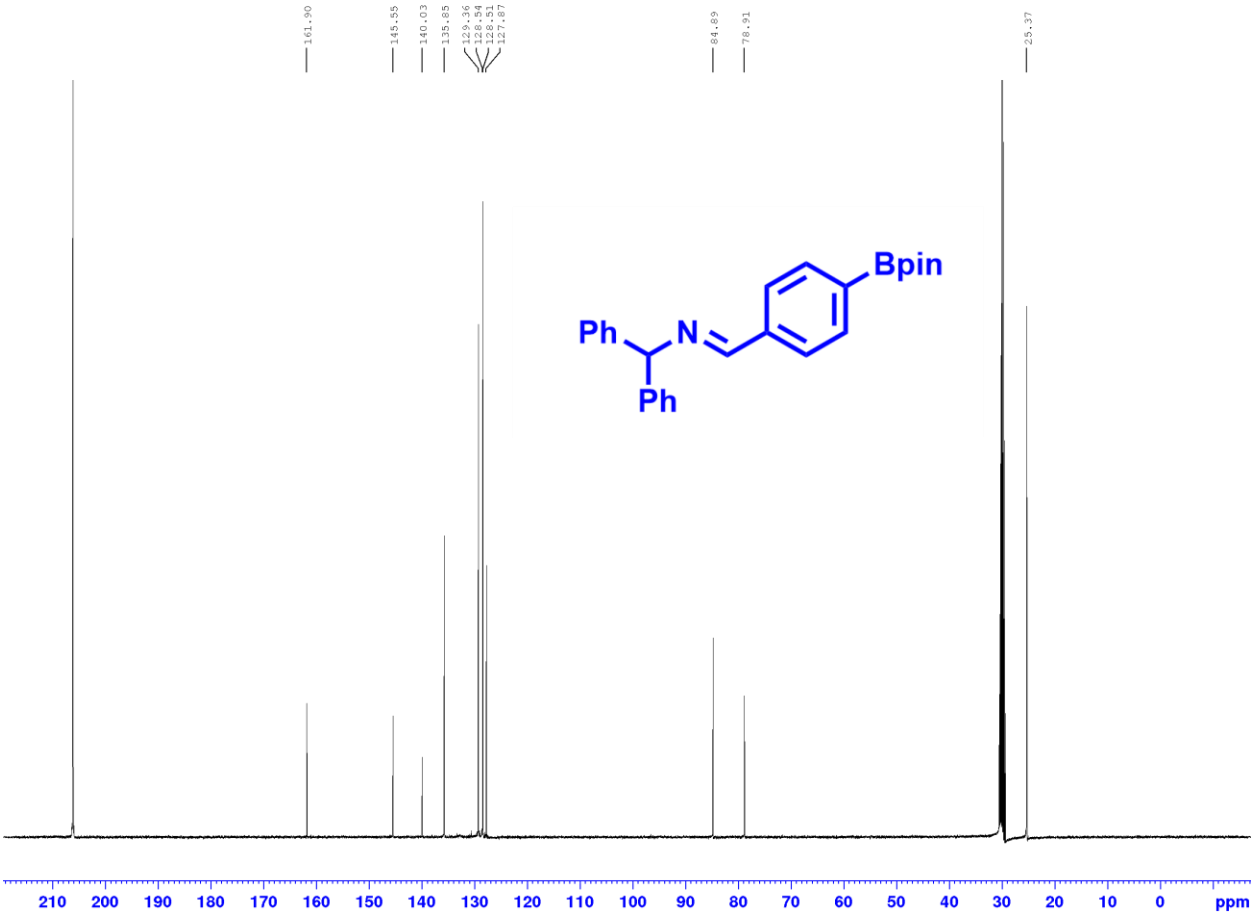
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N*-((2-morpholinopyridin-4-yl)methyl)-1,1-diphenylmethanimine**



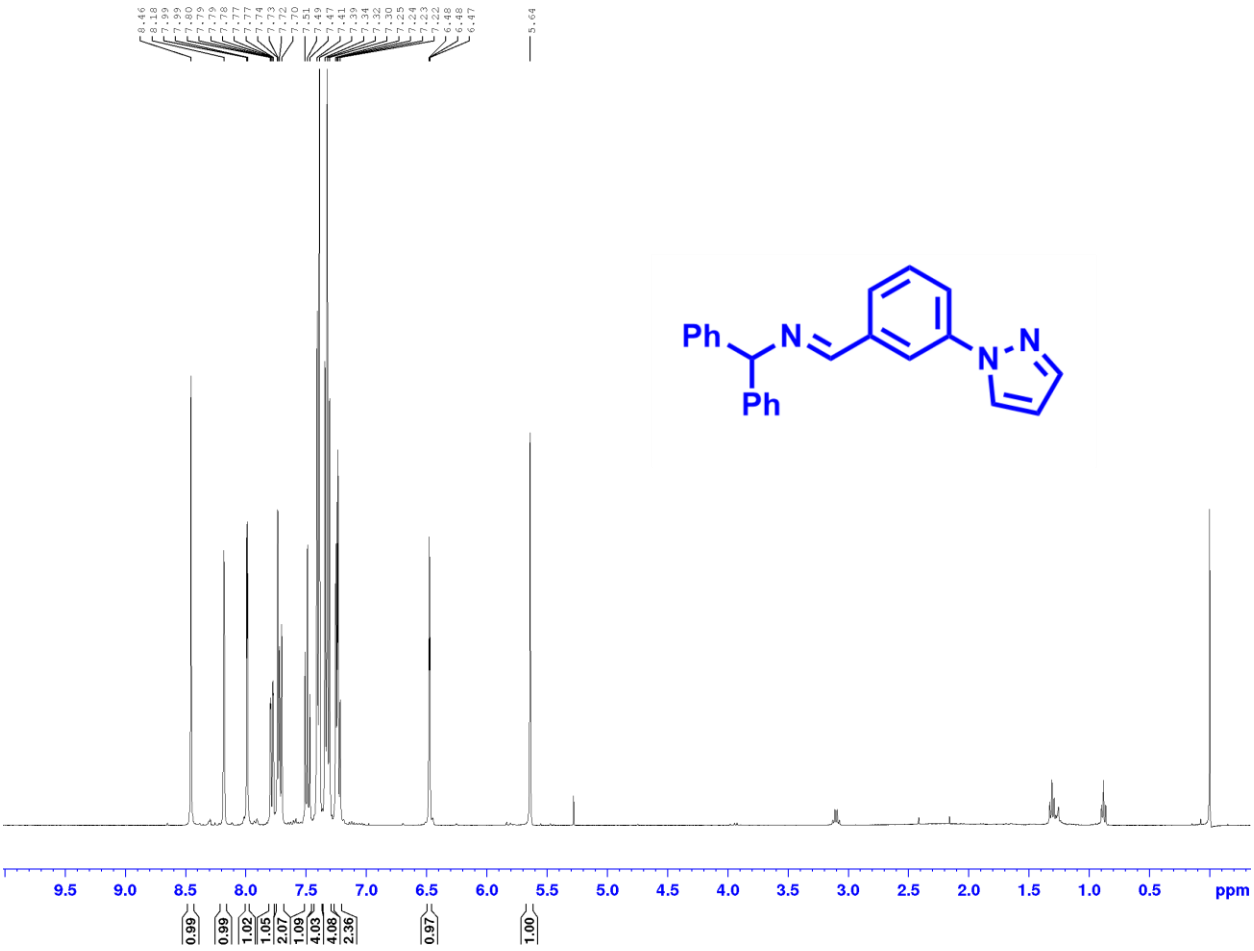
^{1}H NMR spectrum ((CD$_3$)$_2$CO, 400 MHz) of ***N*-benzhydryl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanimine**



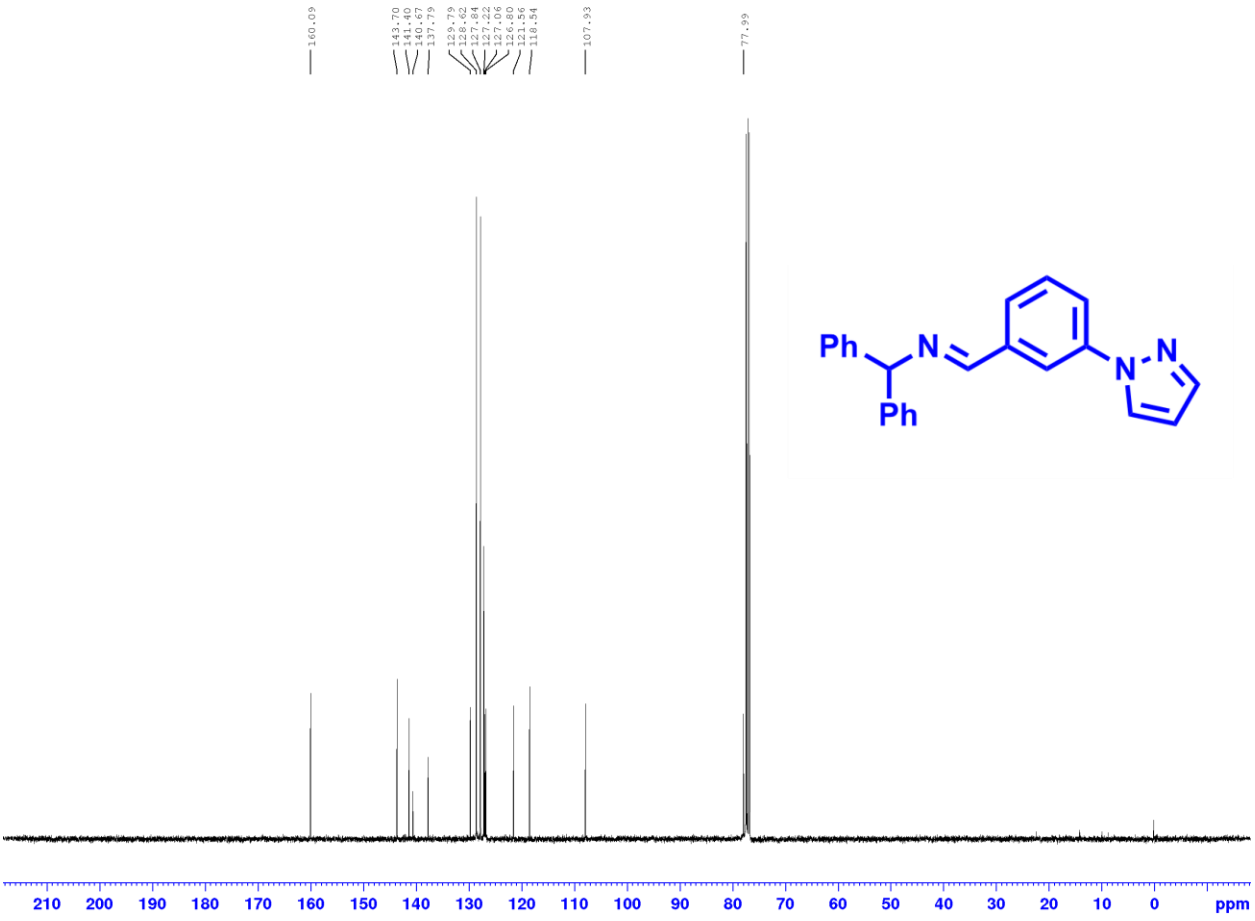
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N*-benzhydryl-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanimine**



^{1}H NMR spectrum ((CD$_3$)$_2$CO, 400 MHz) of **1-(3-(1H-pyrazol-1-yl)phenyl)-*N*-benzhydrylmethanimine**

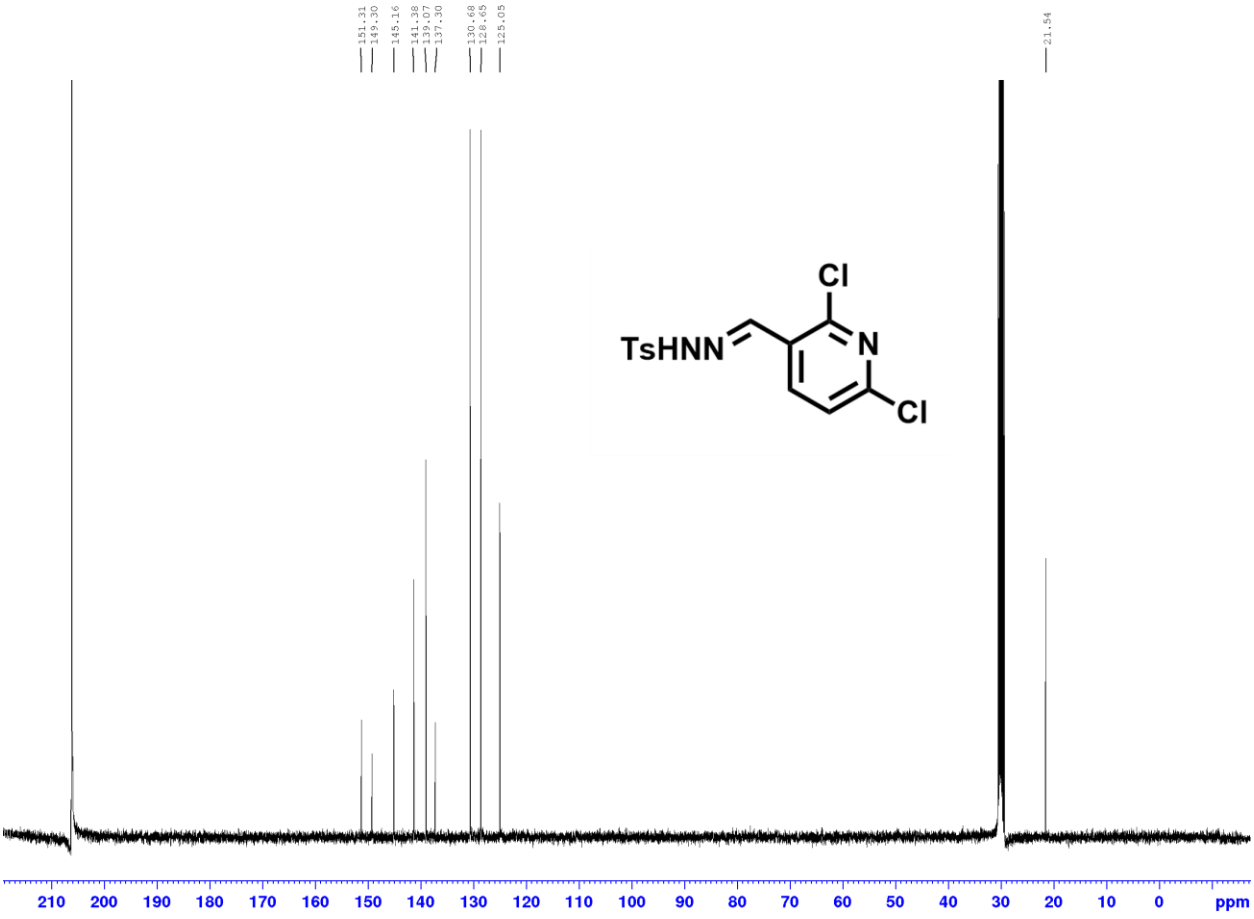


$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of **1-(3-(1H-pyrazol-1-yl)phenyl)-*N*-benzhydrylmethanimine**

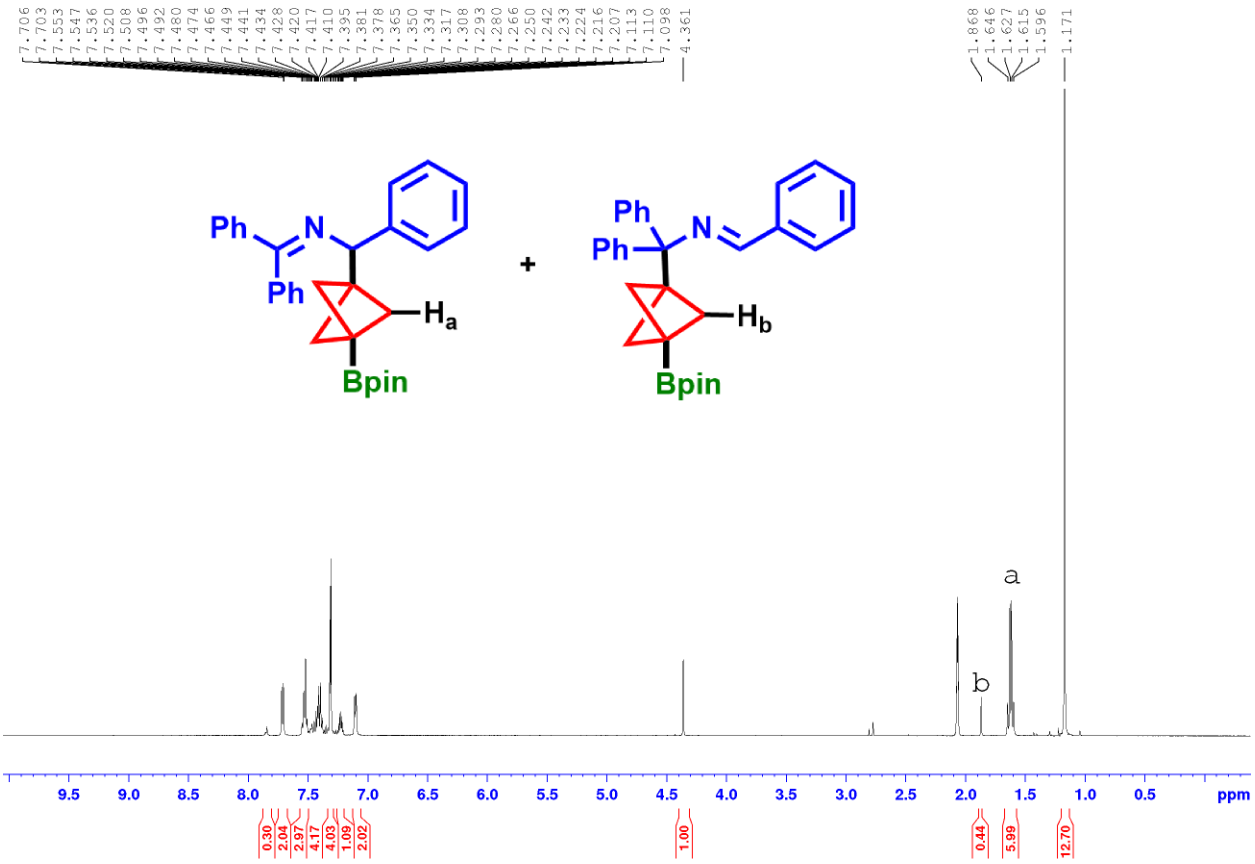


^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N*'-((2,6-dichloropyridin-3-yl)methylene)-4-methylbenzenesulfonohydrazide**

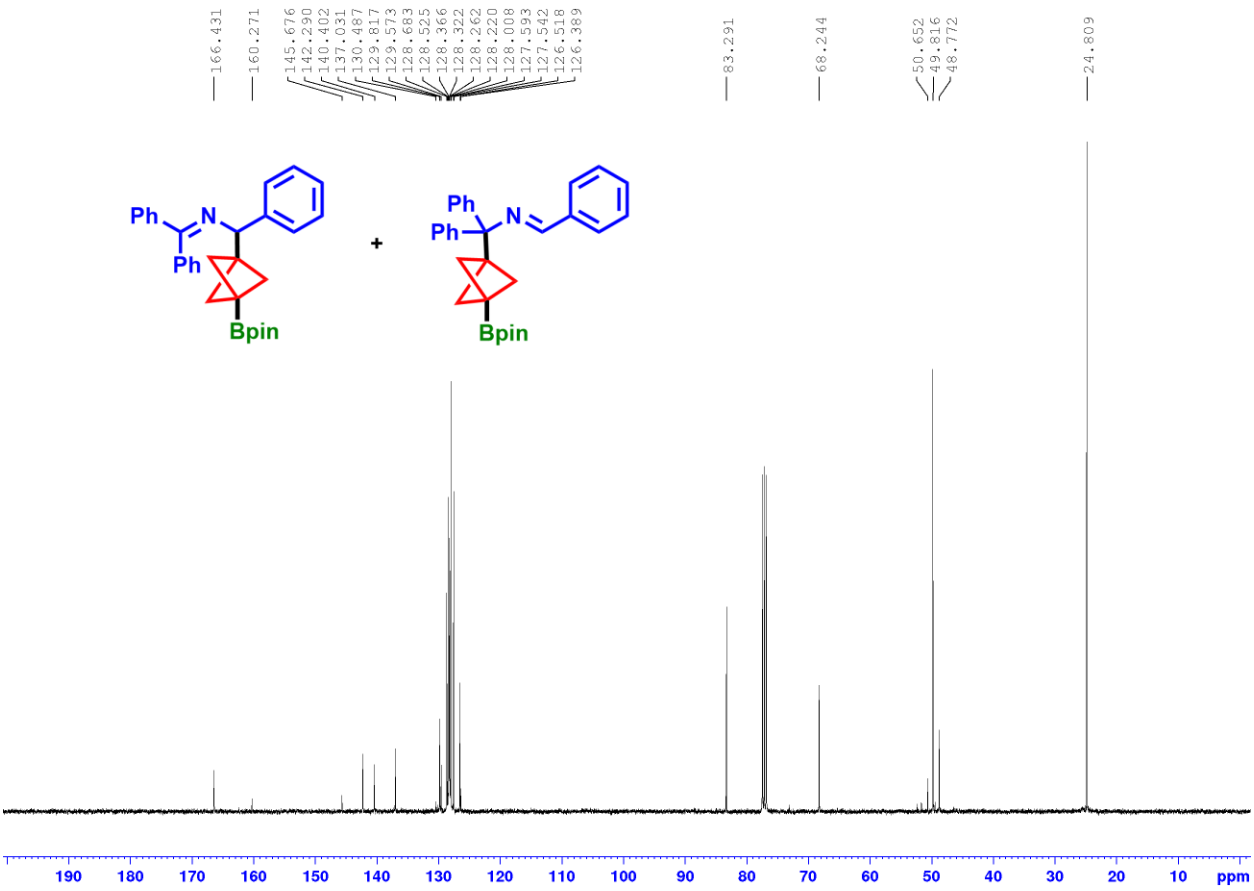
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N'*-((2,6-dichloropyridin-3-yl)methylene)-4-methylbenzenesulfonohydrazide**



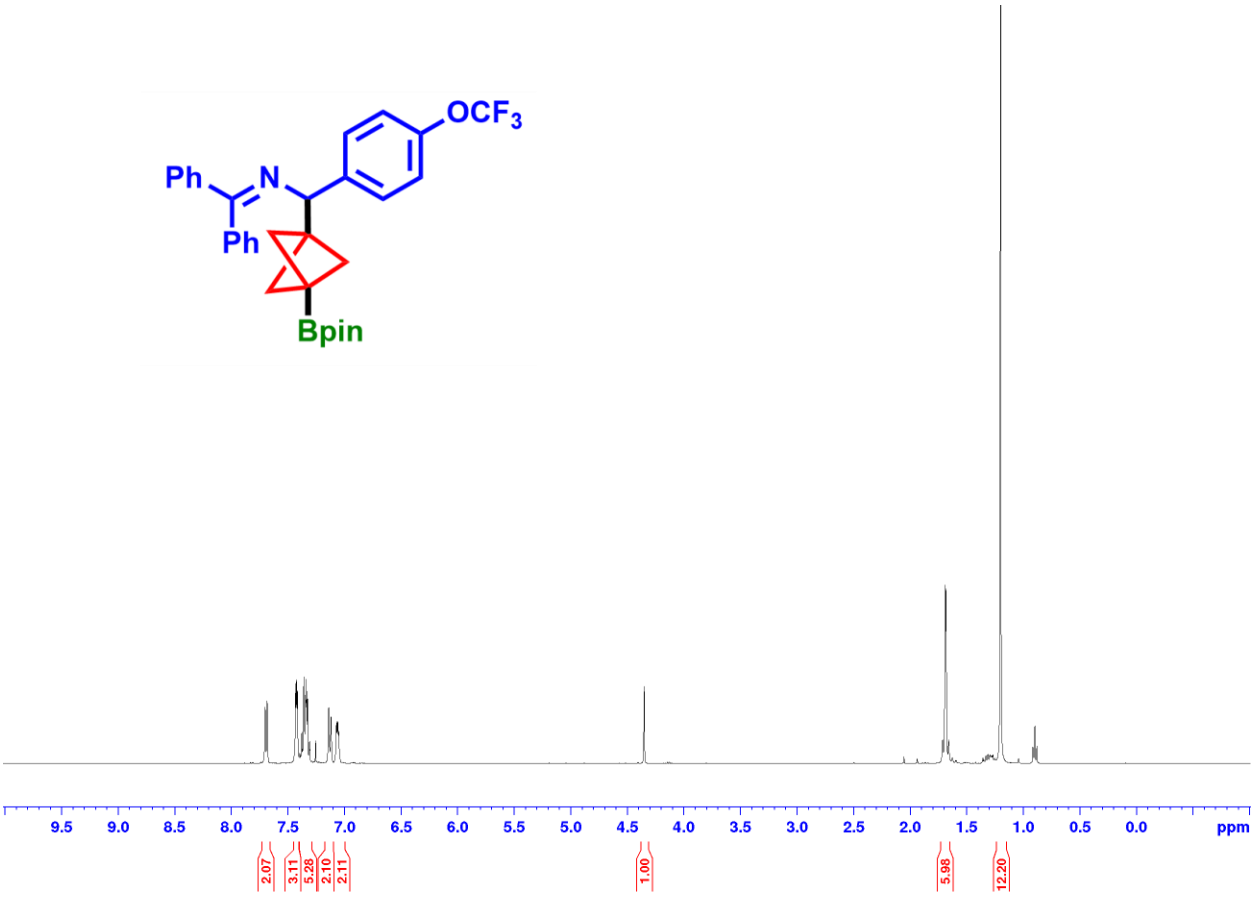
^{1}H NMR spectrum ((CD$_3$)$_2$CO, 400 MHz) **1,1-diphenyl-*N*-(phenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (7a)**



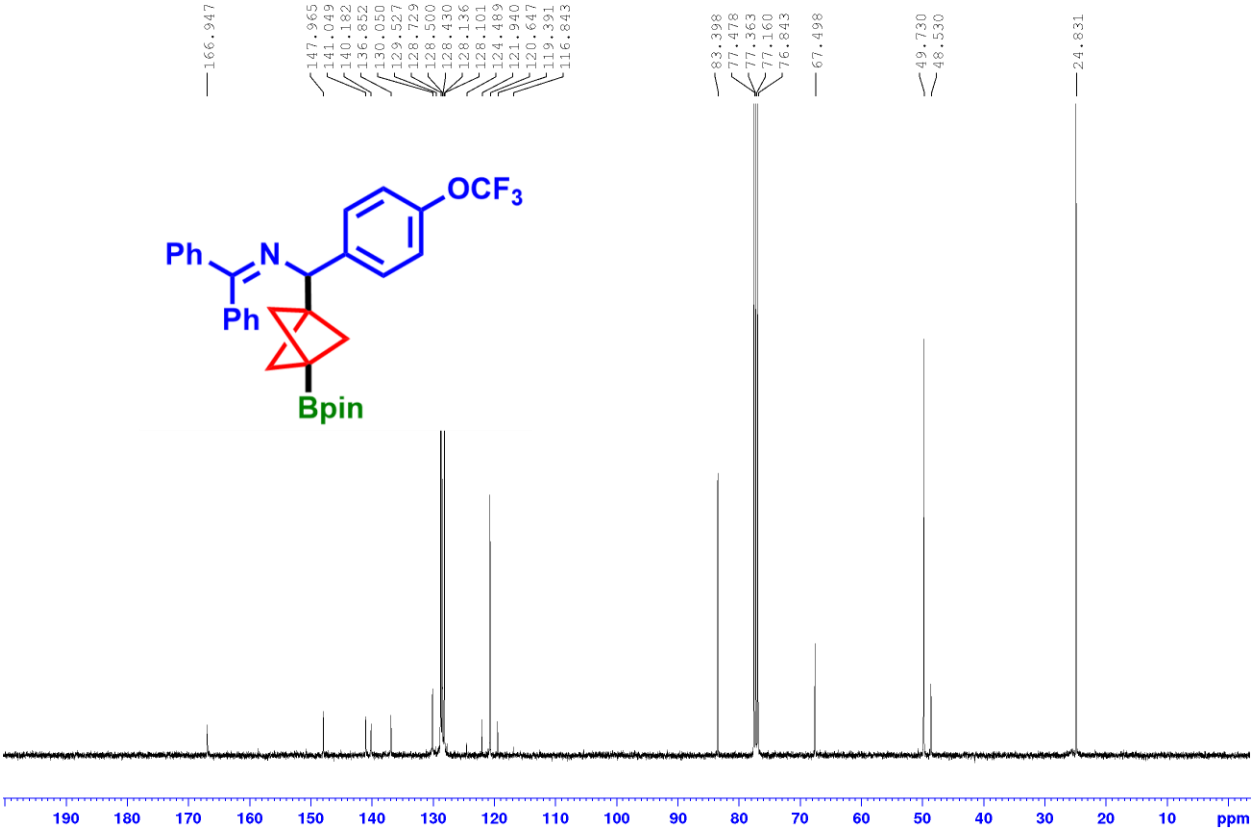
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of **1,1-diphenyl-*N*-(phenyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (7b)**



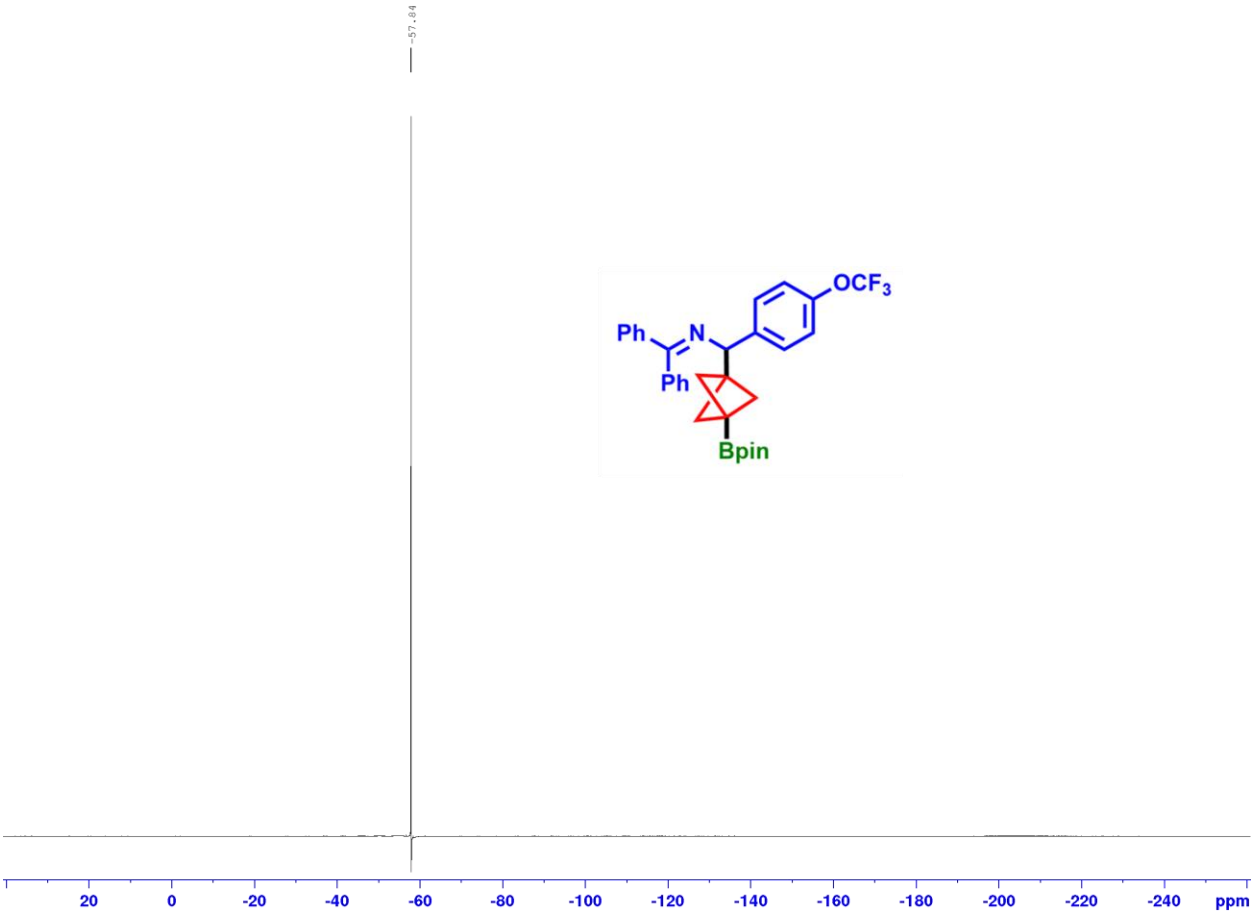
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **1,1-diphenyl-*N*-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (7b)**



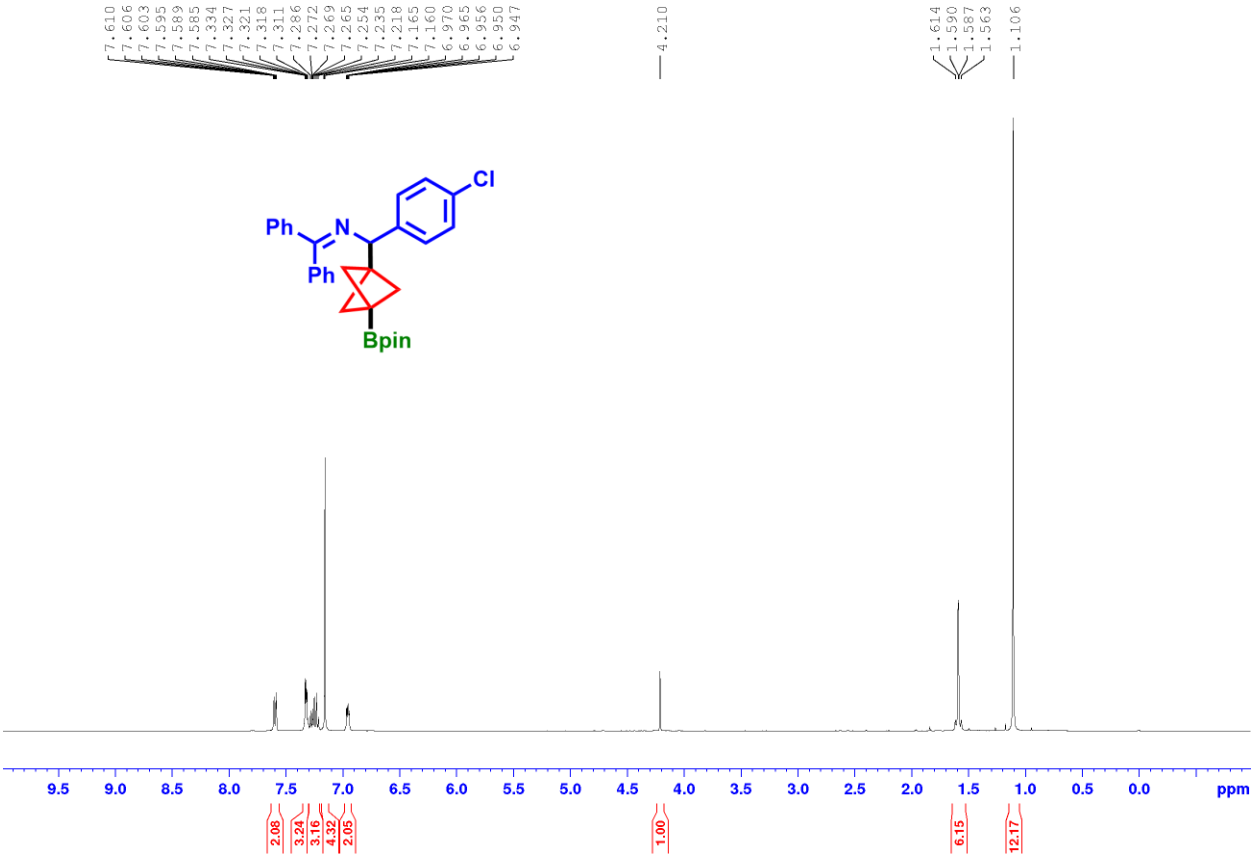
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of **1,1-diphenyl-*N*-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (7b)**



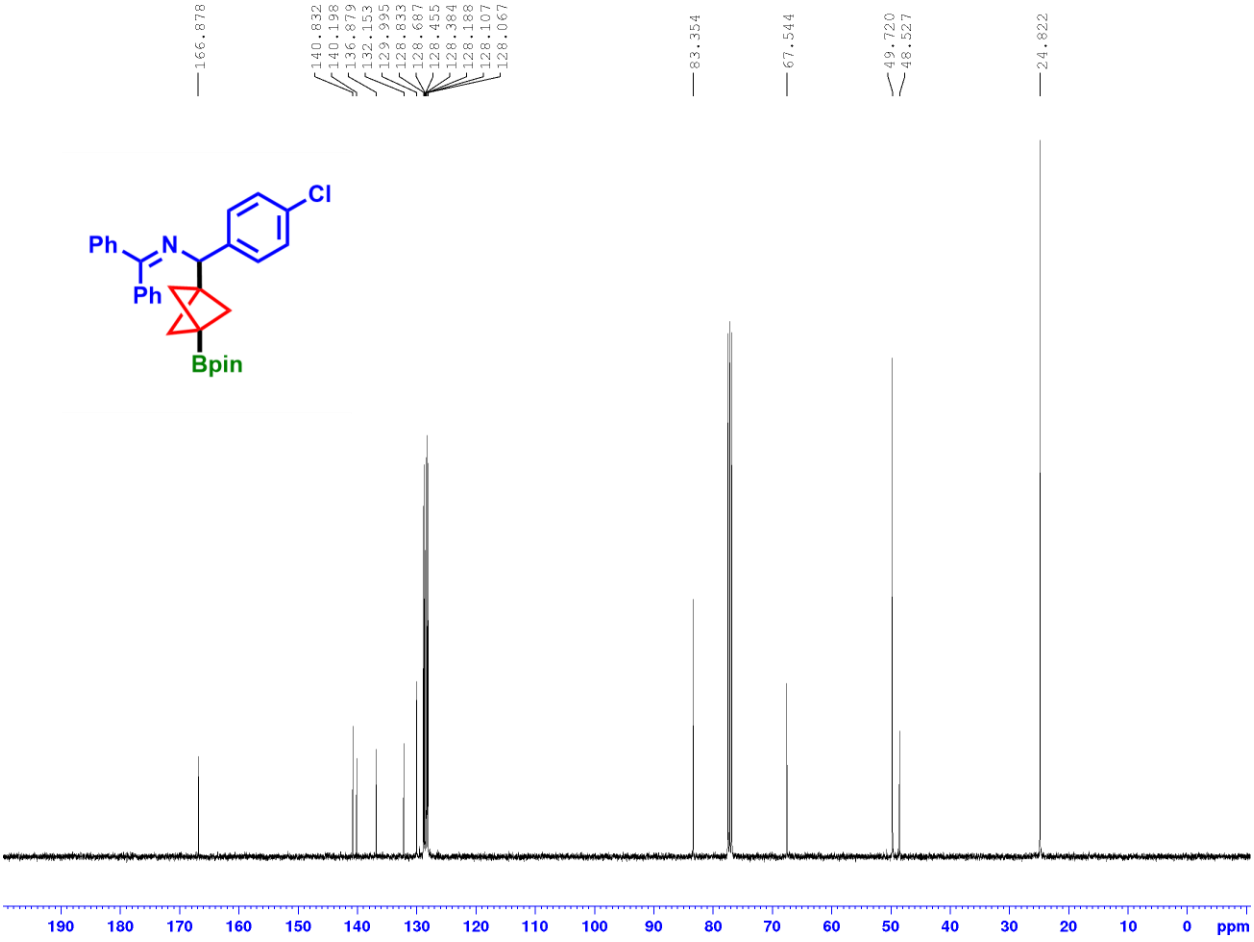
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 376 MHz) of **1,1-diphenyl-*N*-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (7b)**



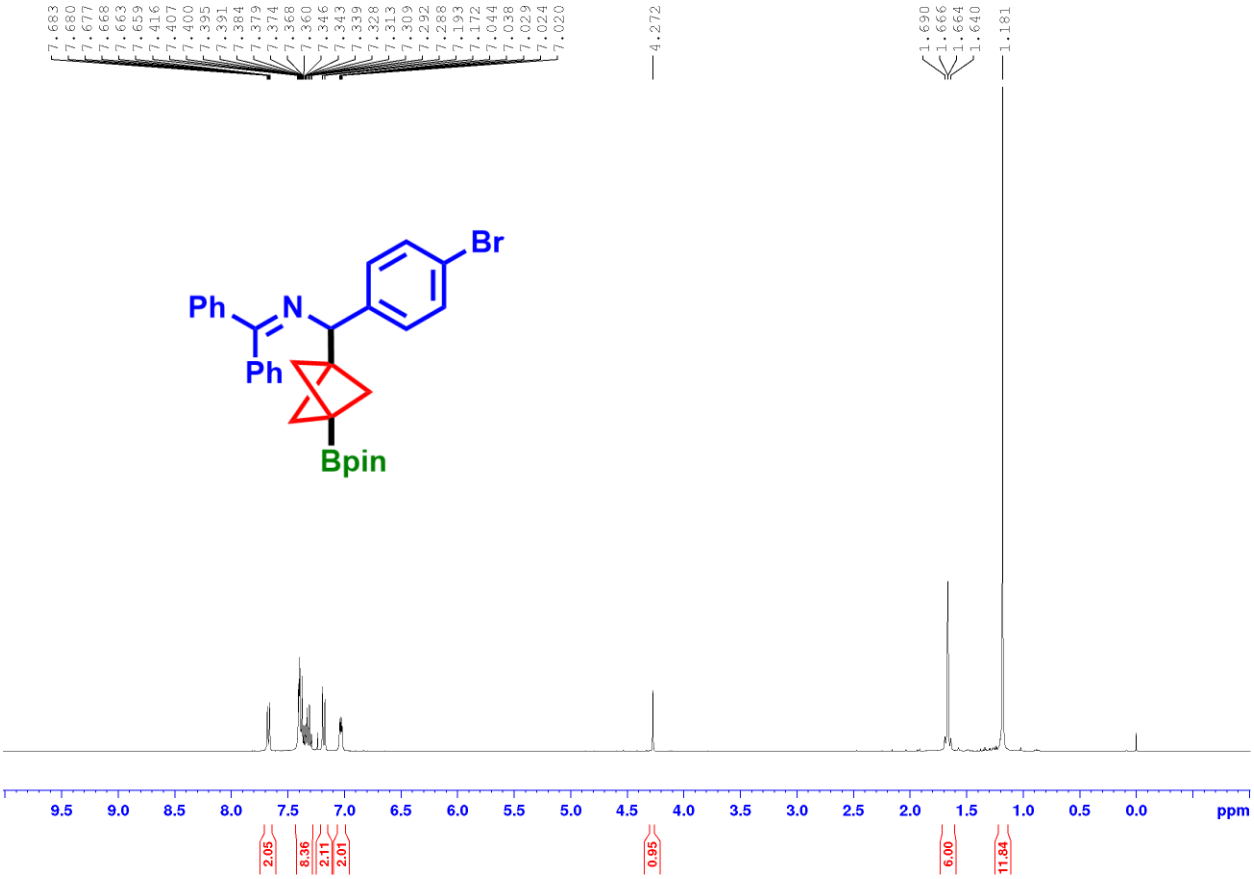
^{1}H NMR spectrum (($CDCl_3$, 400 MHz) of ***N*-((4-chlorophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7c)**



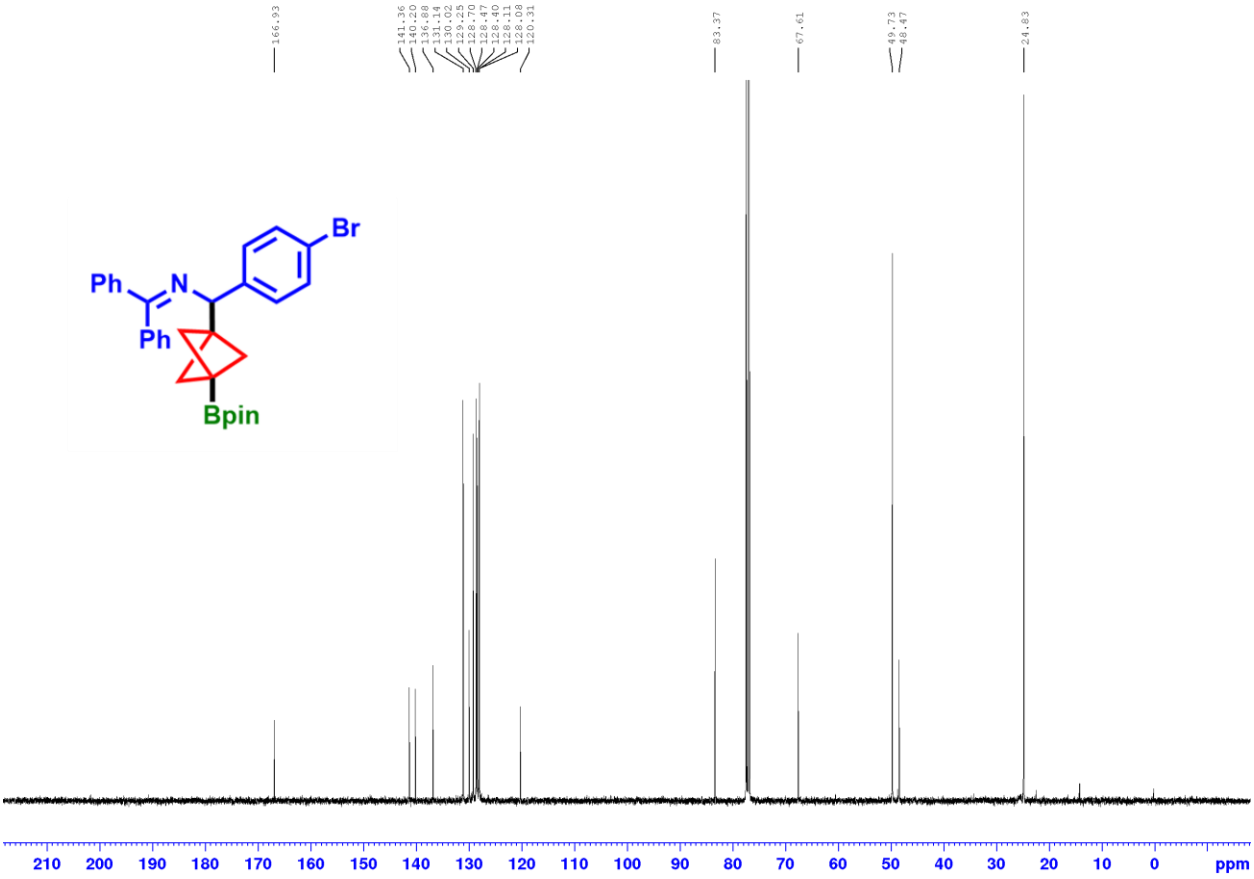
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of ***N*-((4-chlorophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7c)**



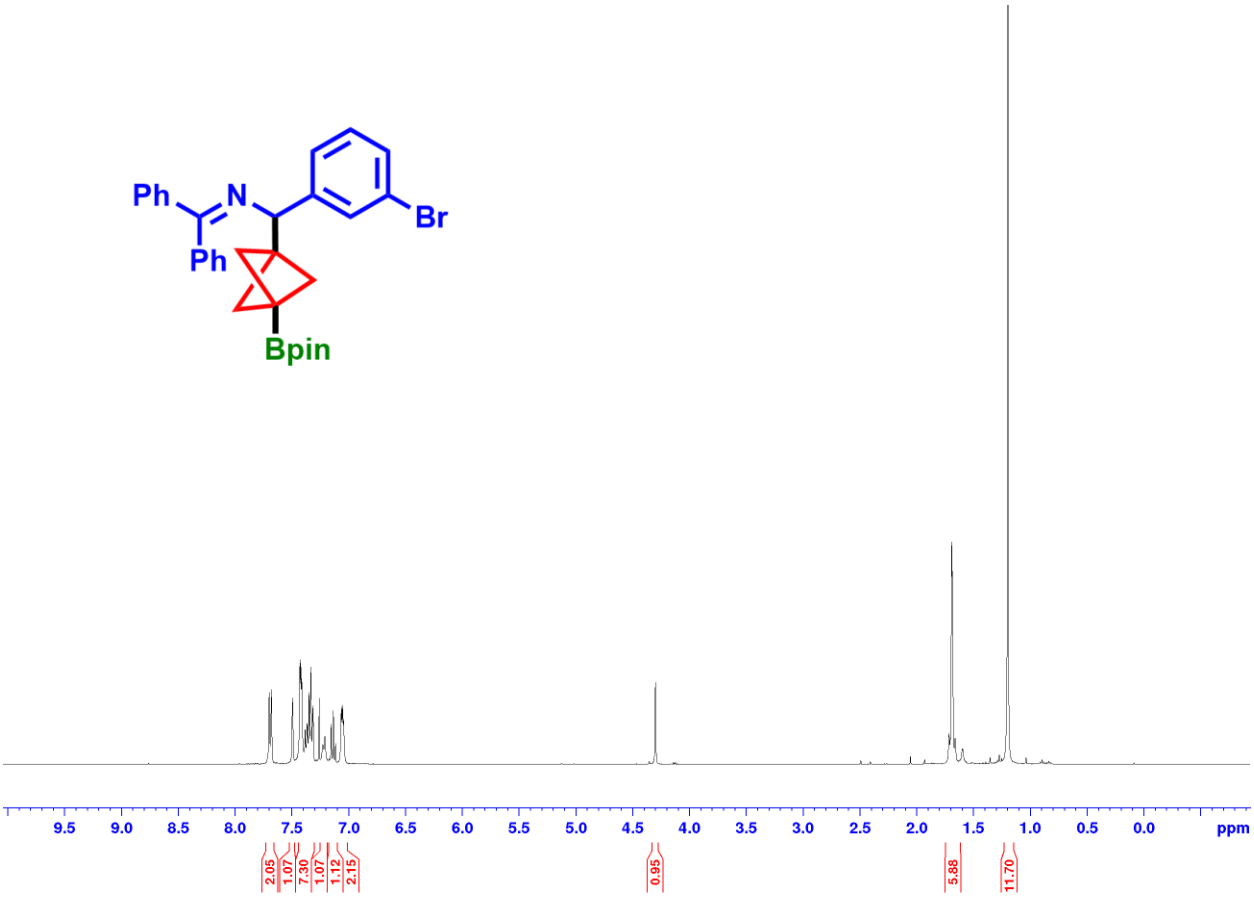
^{1}H NMR spectrum ((CDCl$_3$, 400 MHz) of ***N*-((4-bromophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7d)**



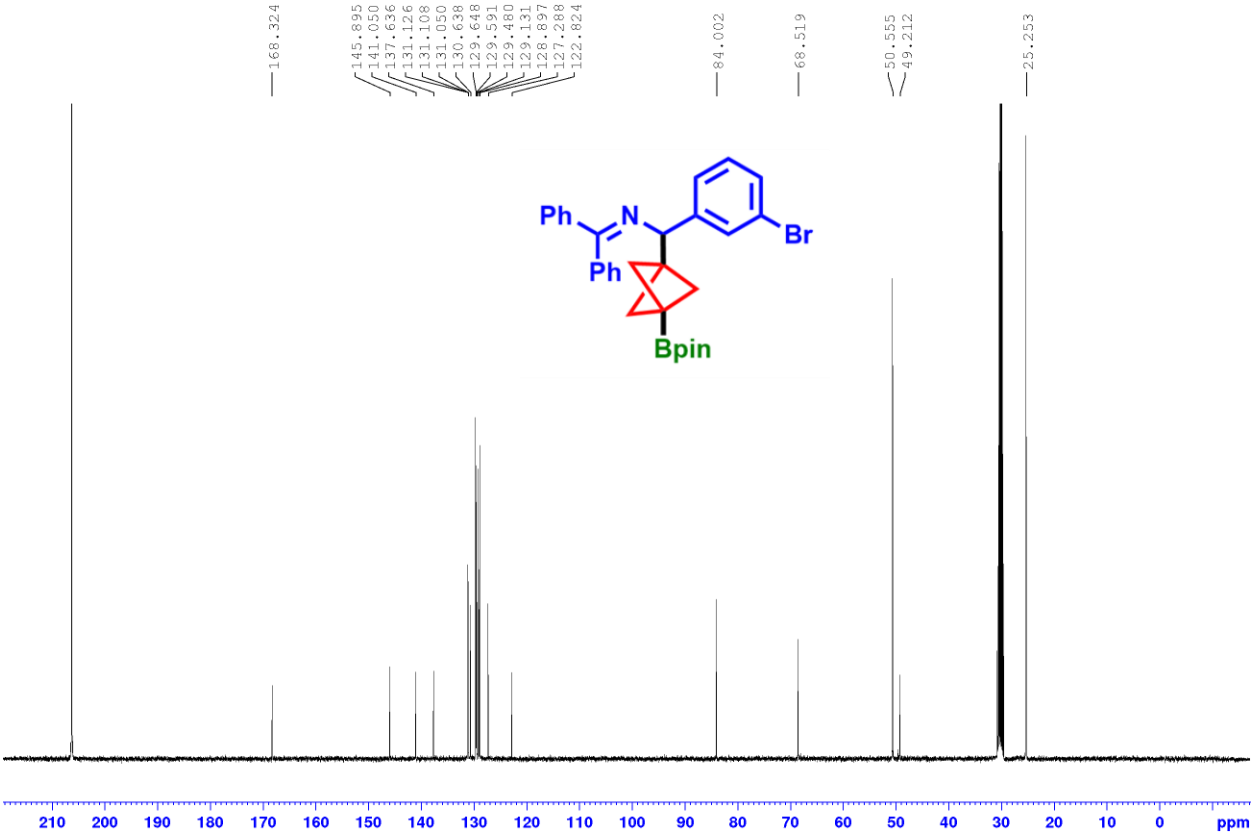
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of ***N*-((4-bromophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7d)**



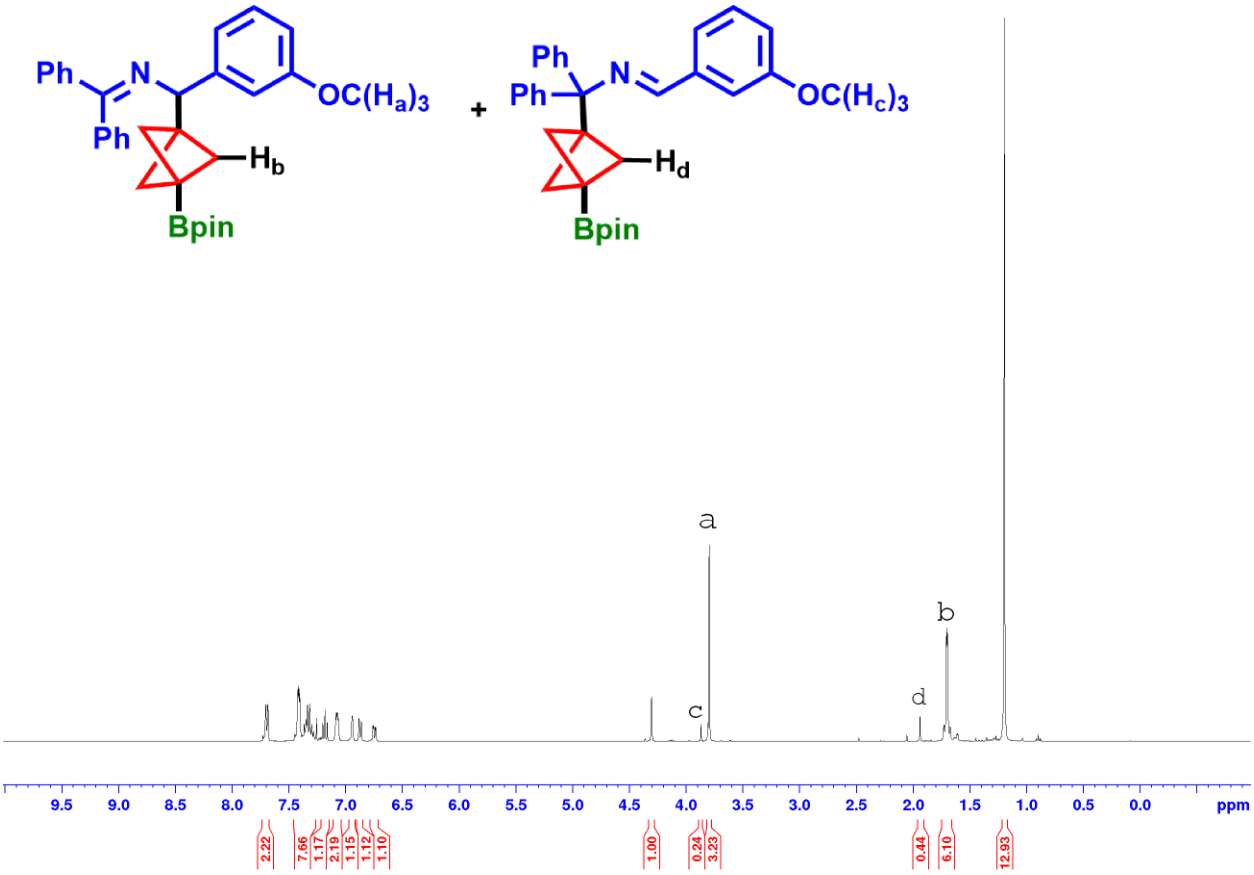
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ***N*-((3-bromophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7e)**



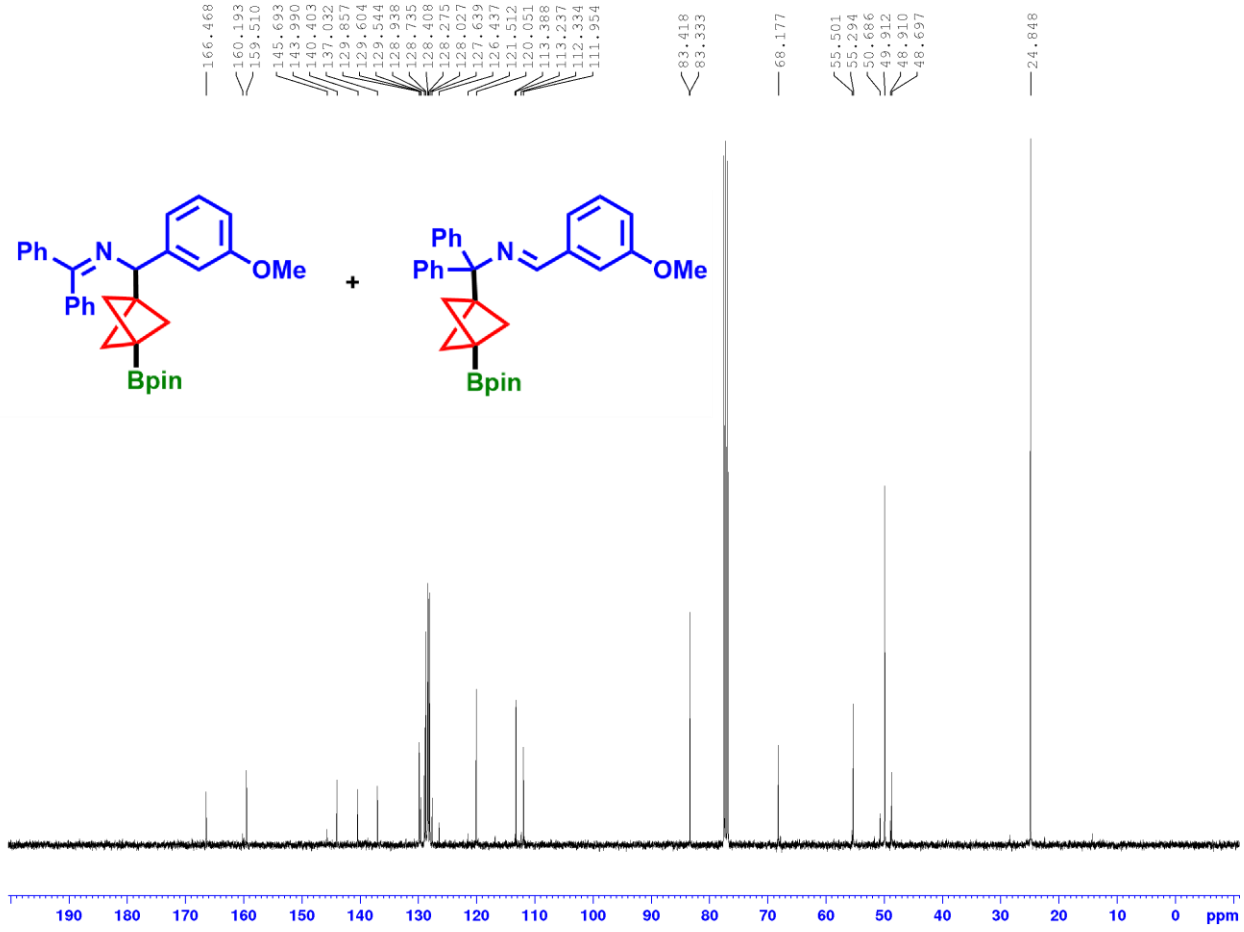
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of ***N*-((3-bromophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7e)**



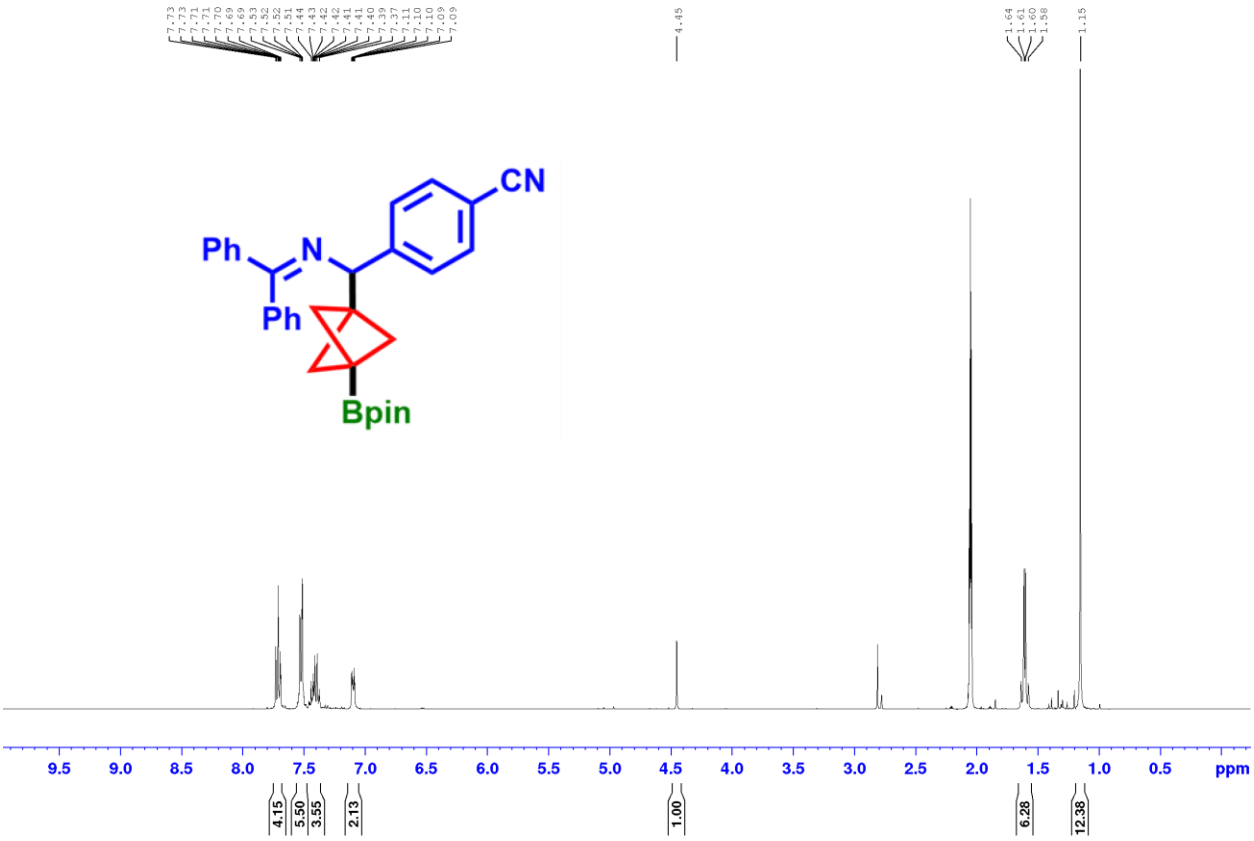
^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of ***N*-((3-methoxyphenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7f)**



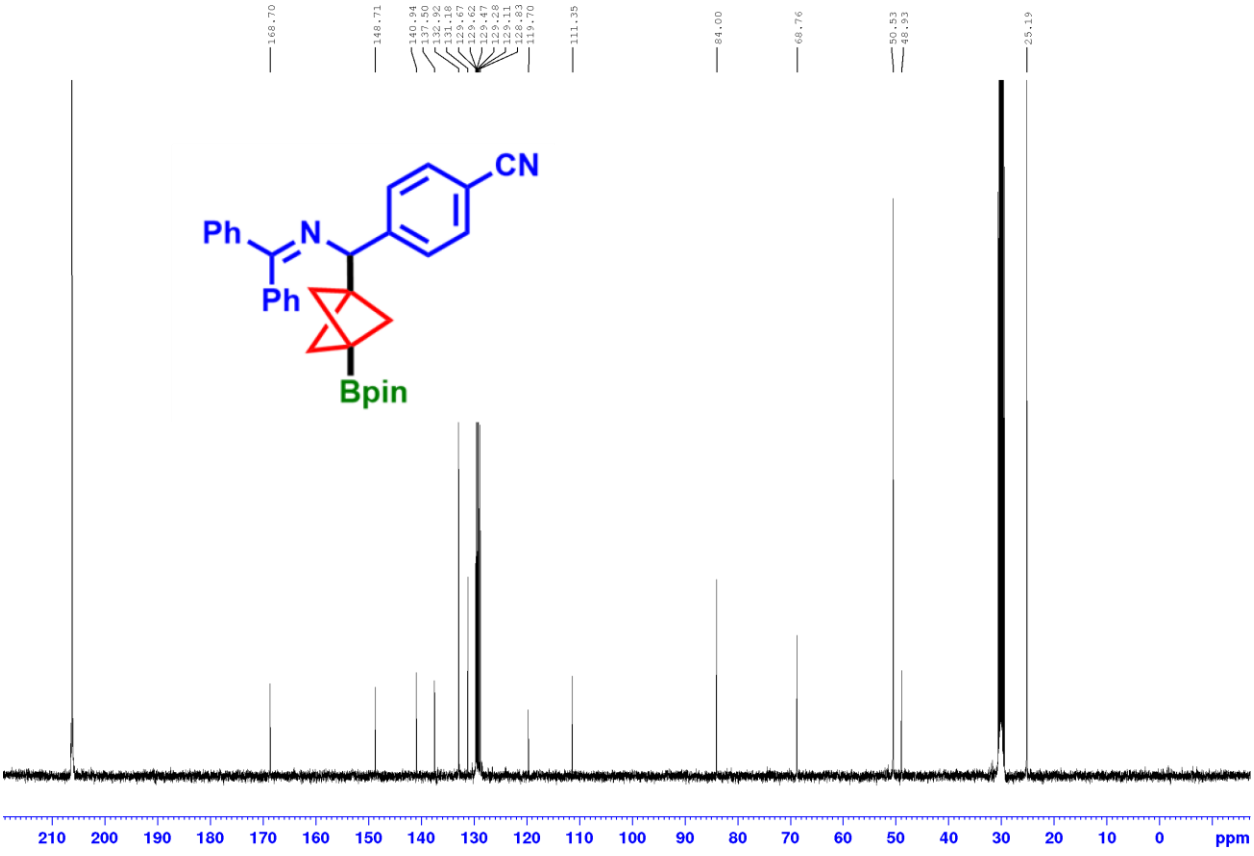
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of ***N*-((3-methoxyphenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7f)**



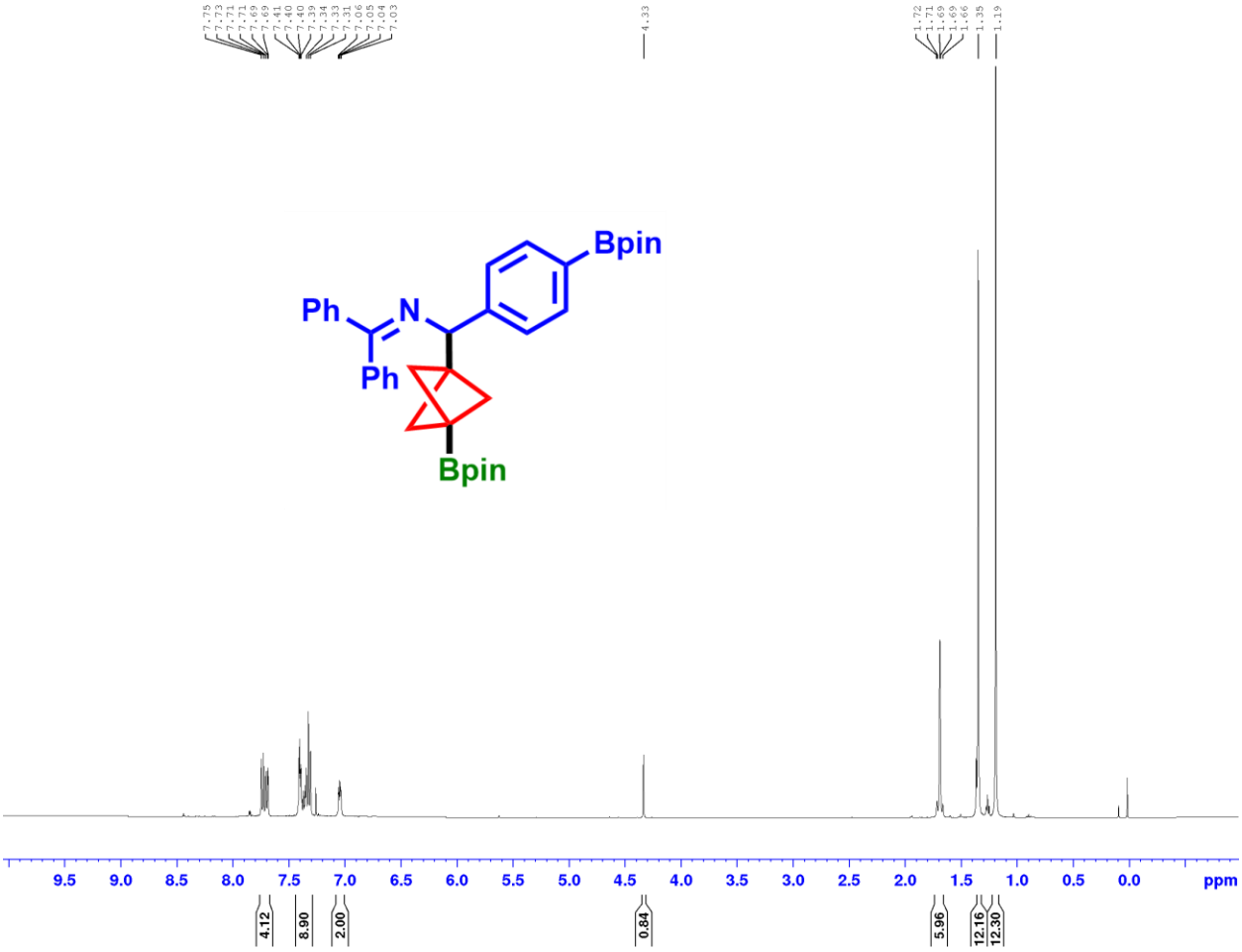
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **4-(((diphenylmethylene)amino)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)benzonitrile (7g)**



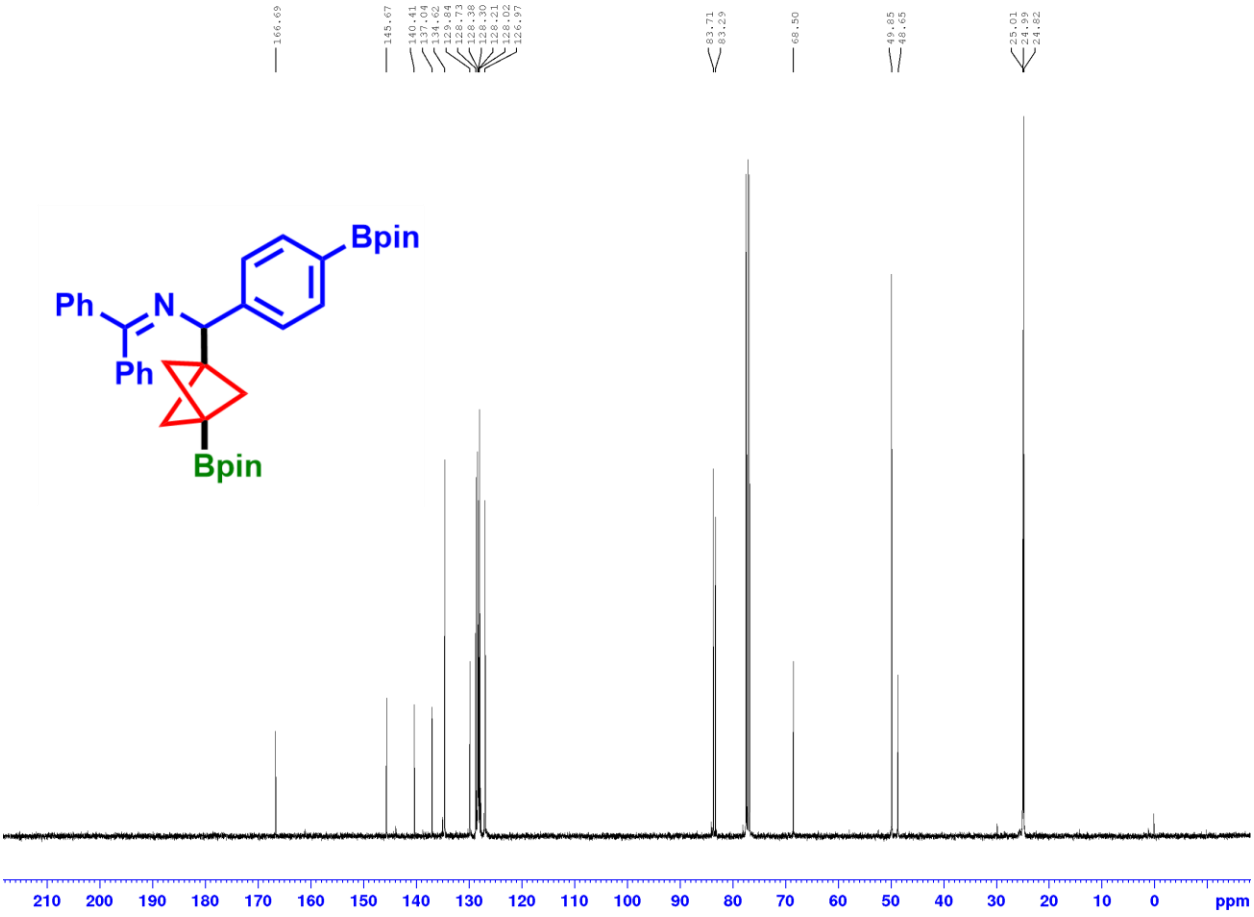
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$ 100 MHz) of **4-(((diphenylmethylene)amino)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)benzonitrile (7g)**



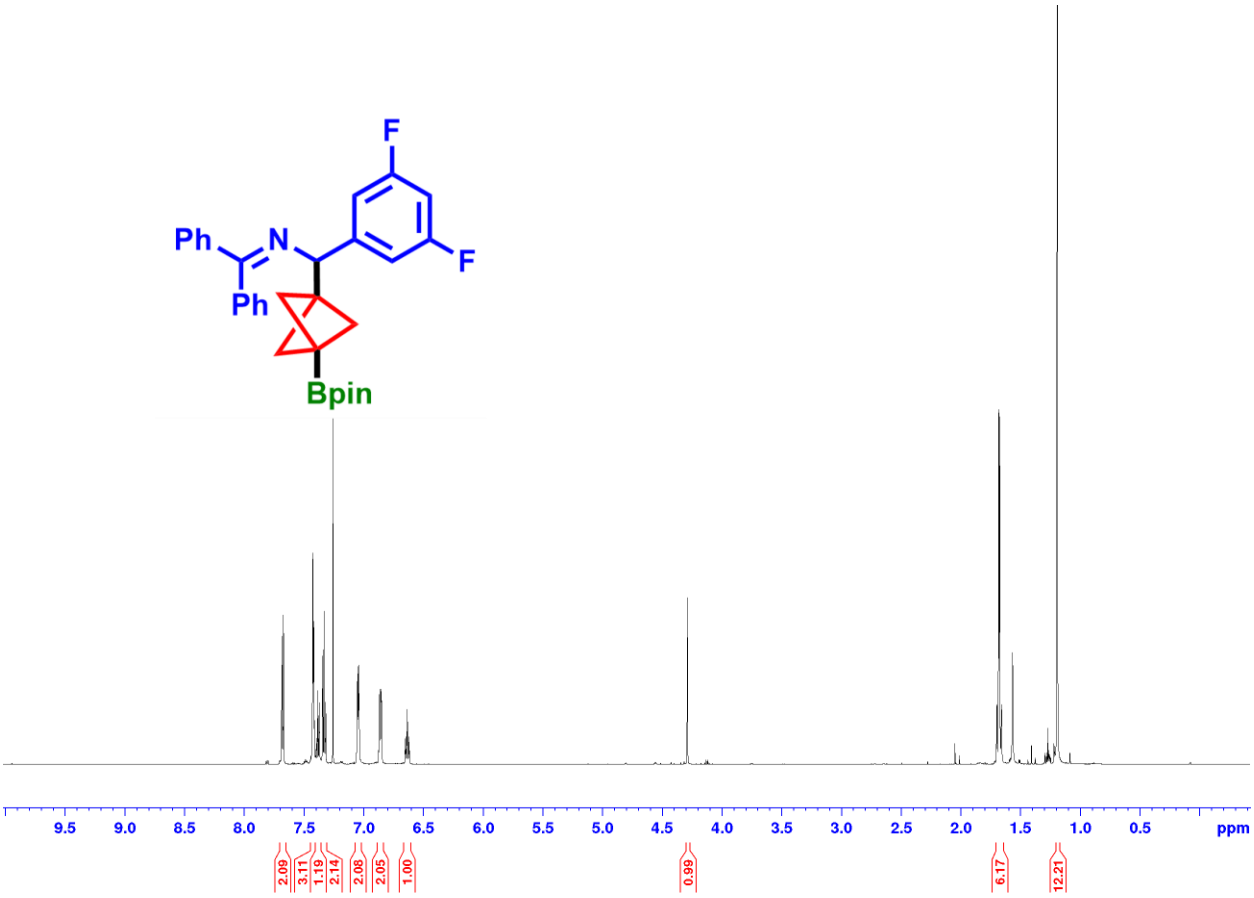
^{1}H NMR spectrum ((CDCl$_3$, 400 MHz) of **1,1-diphenyl-N-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)methanimine (7h)**



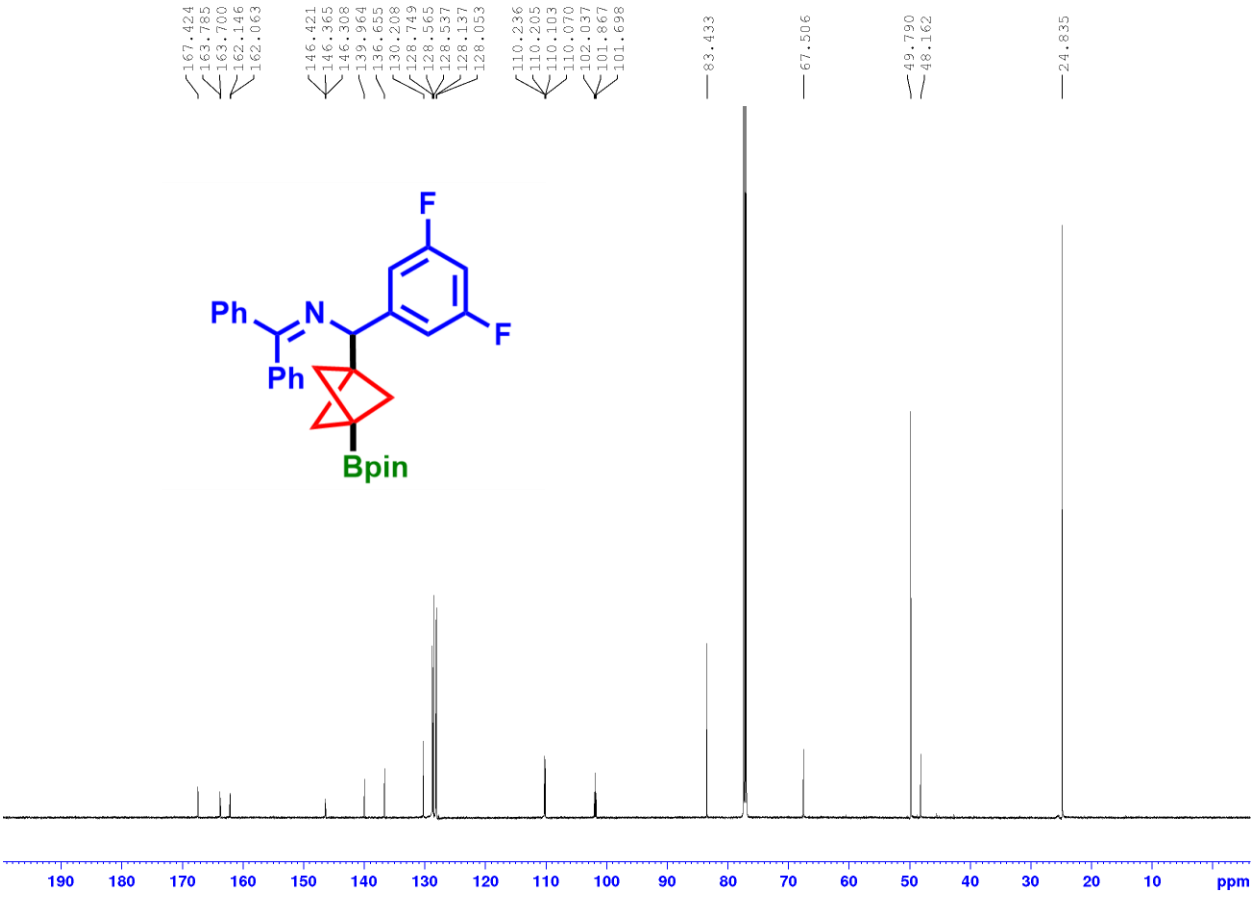
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of **1,1-diphenyl-N-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)methanimine (7h)**



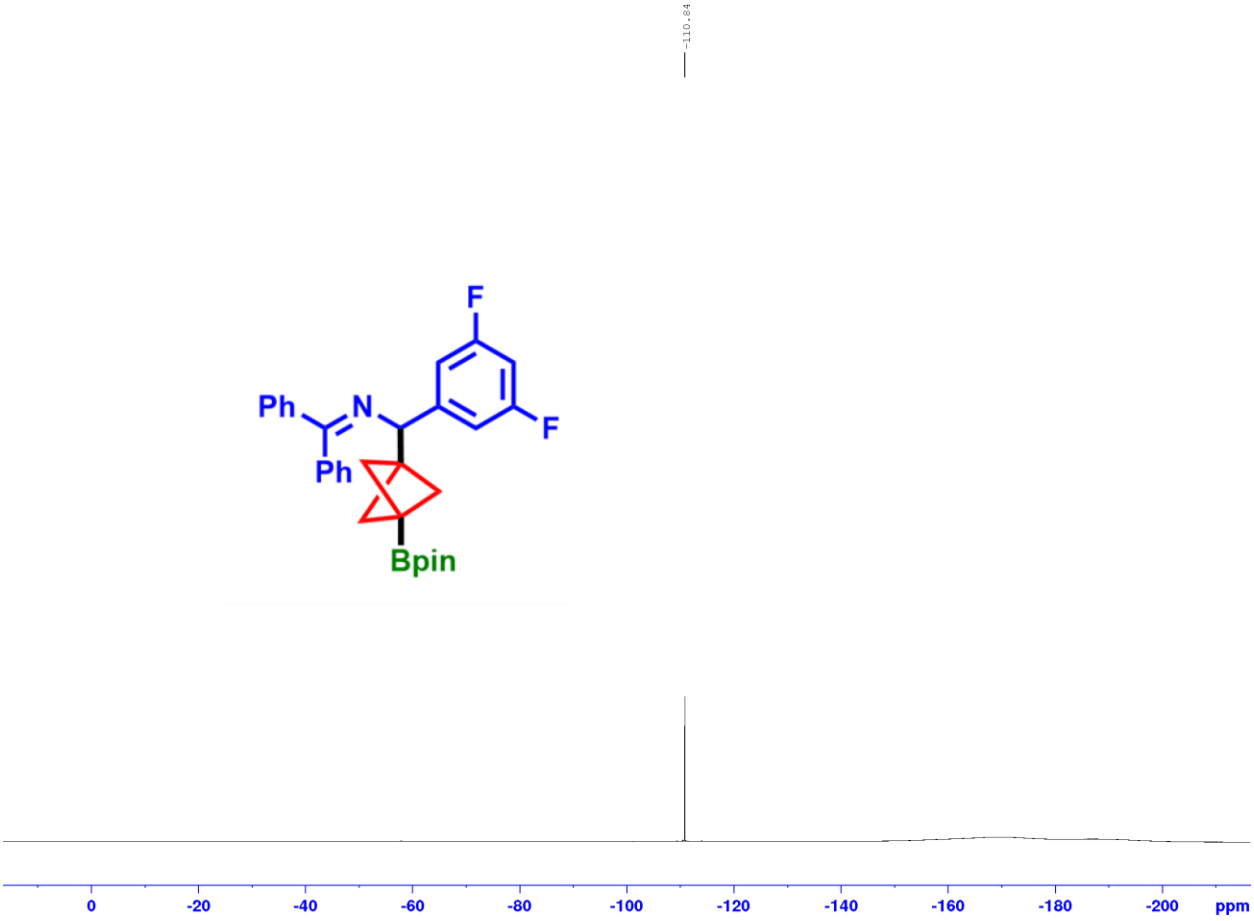
^{1}H NMR spectrum ((CDCl$_3$, 600 MHz) of ***N*-((3,5-difluorophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7i)**



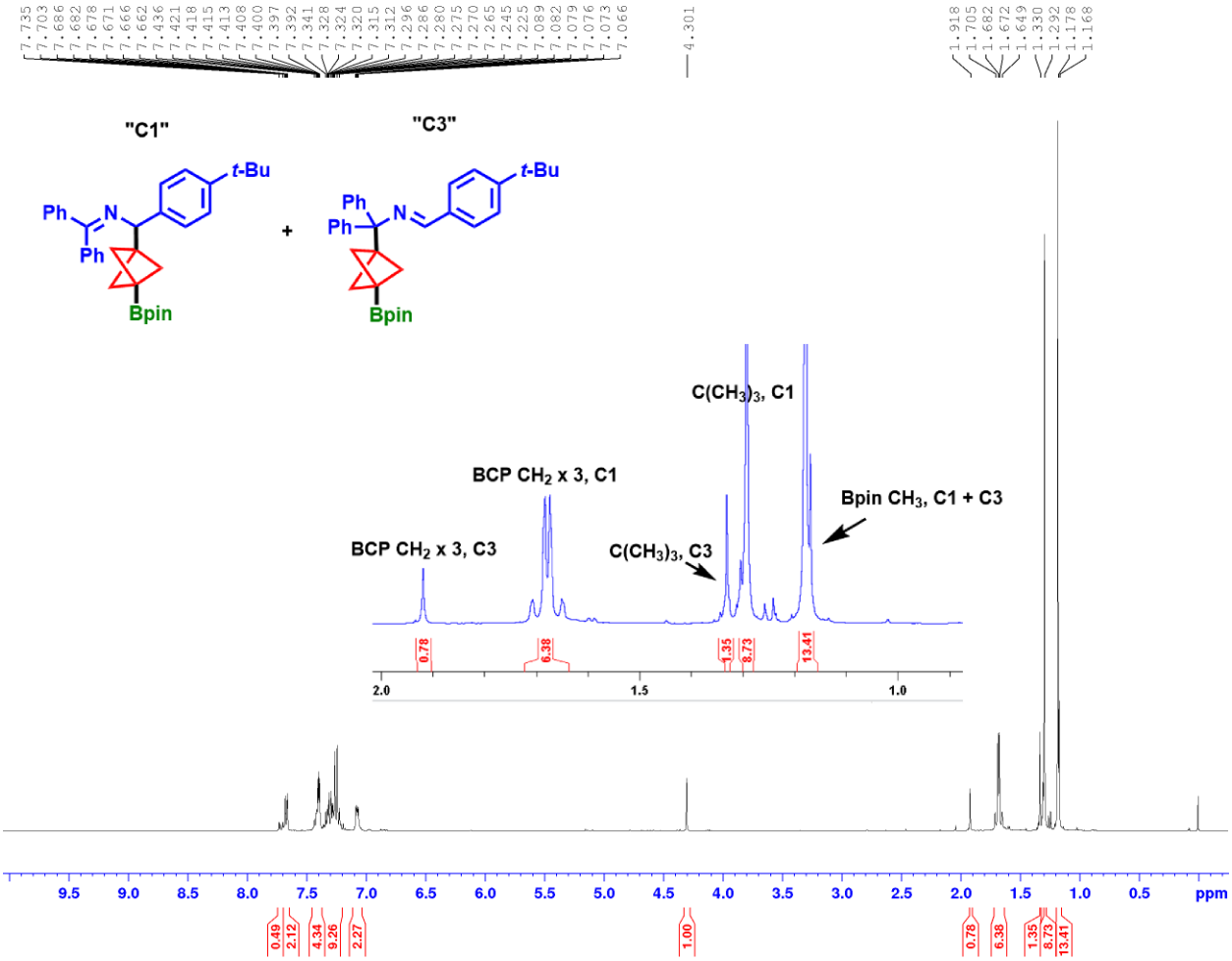
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***N*-((3,5-difluorophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7i)**



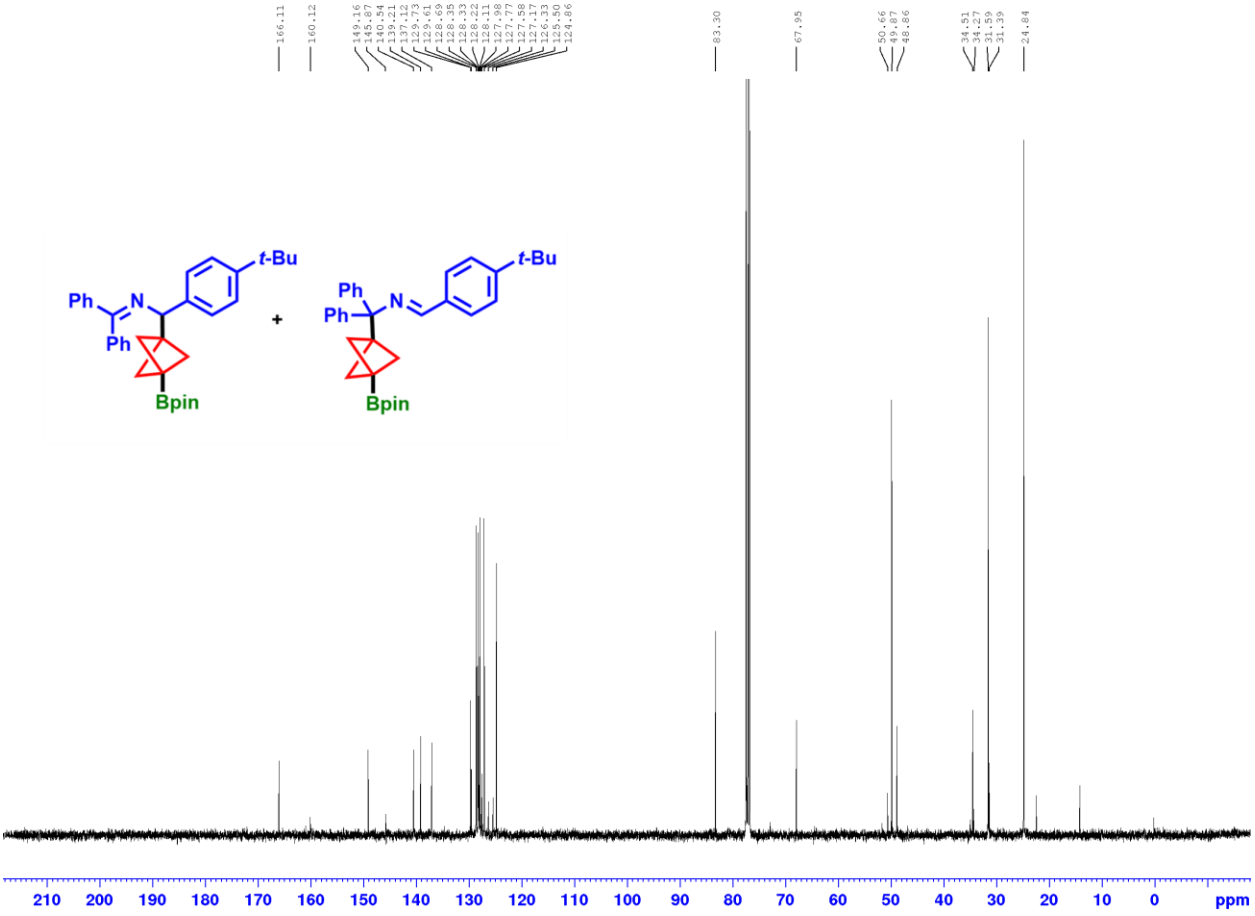
^{19}F NMR spectrum ($CDCl_3$, 565 MHz) of ***N*-((3,5-difluorophenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7i)**



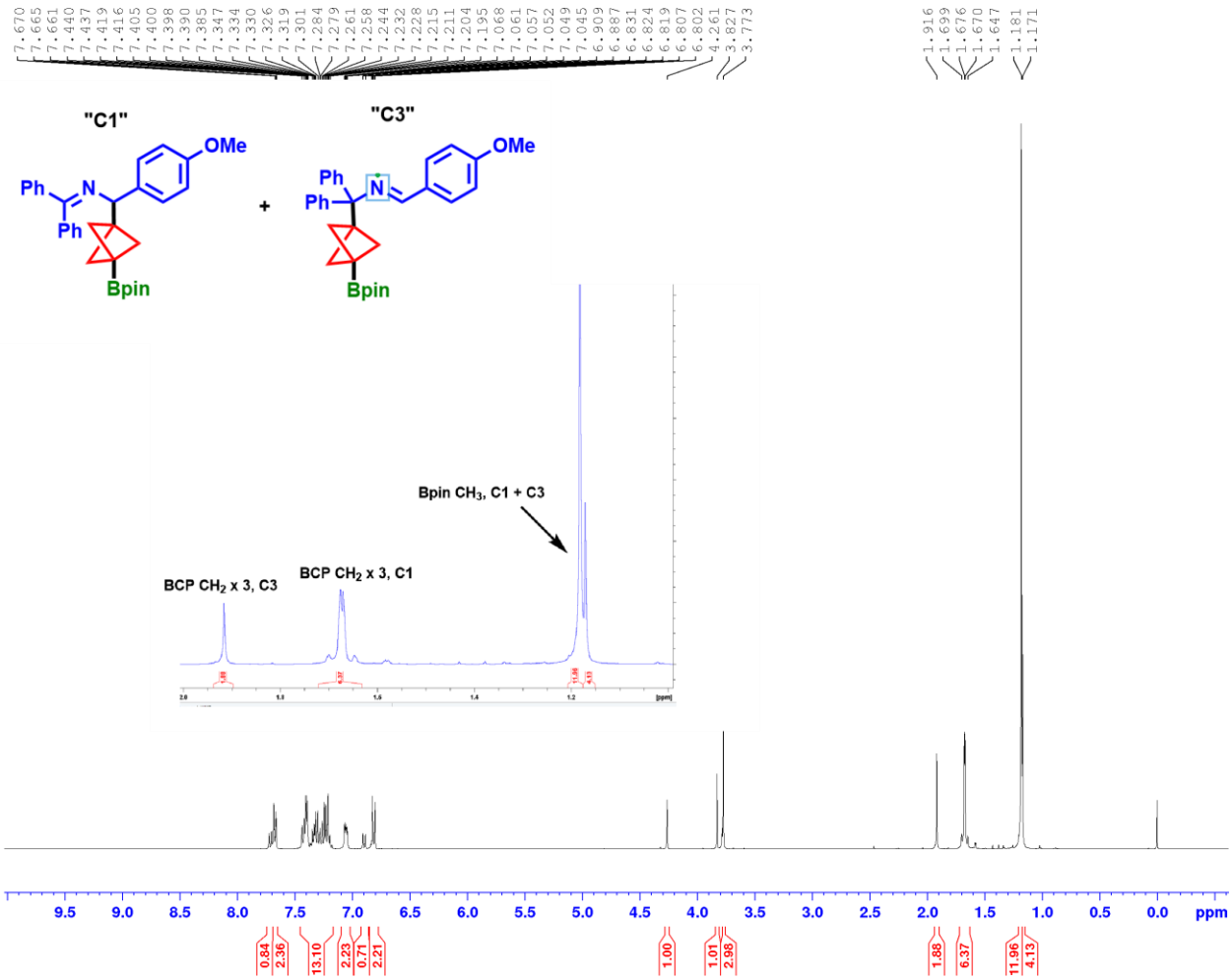
^{1}H NMR spectrum ((CDCl$_3$, 400 MHz) of ***N*-((4-(*tert*-butyl)phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7j and 7j')**



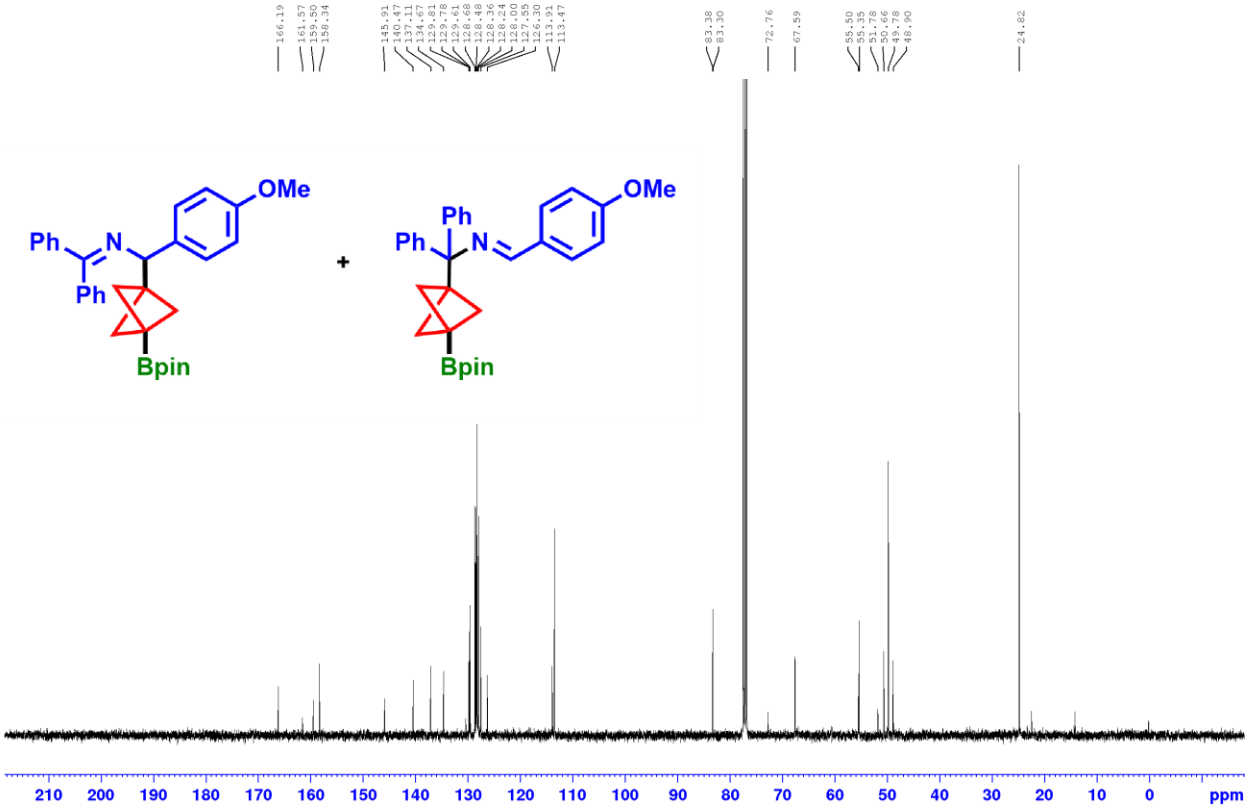
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of ***N*-((4-(*tert*-butyl)phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7j and 7j')**



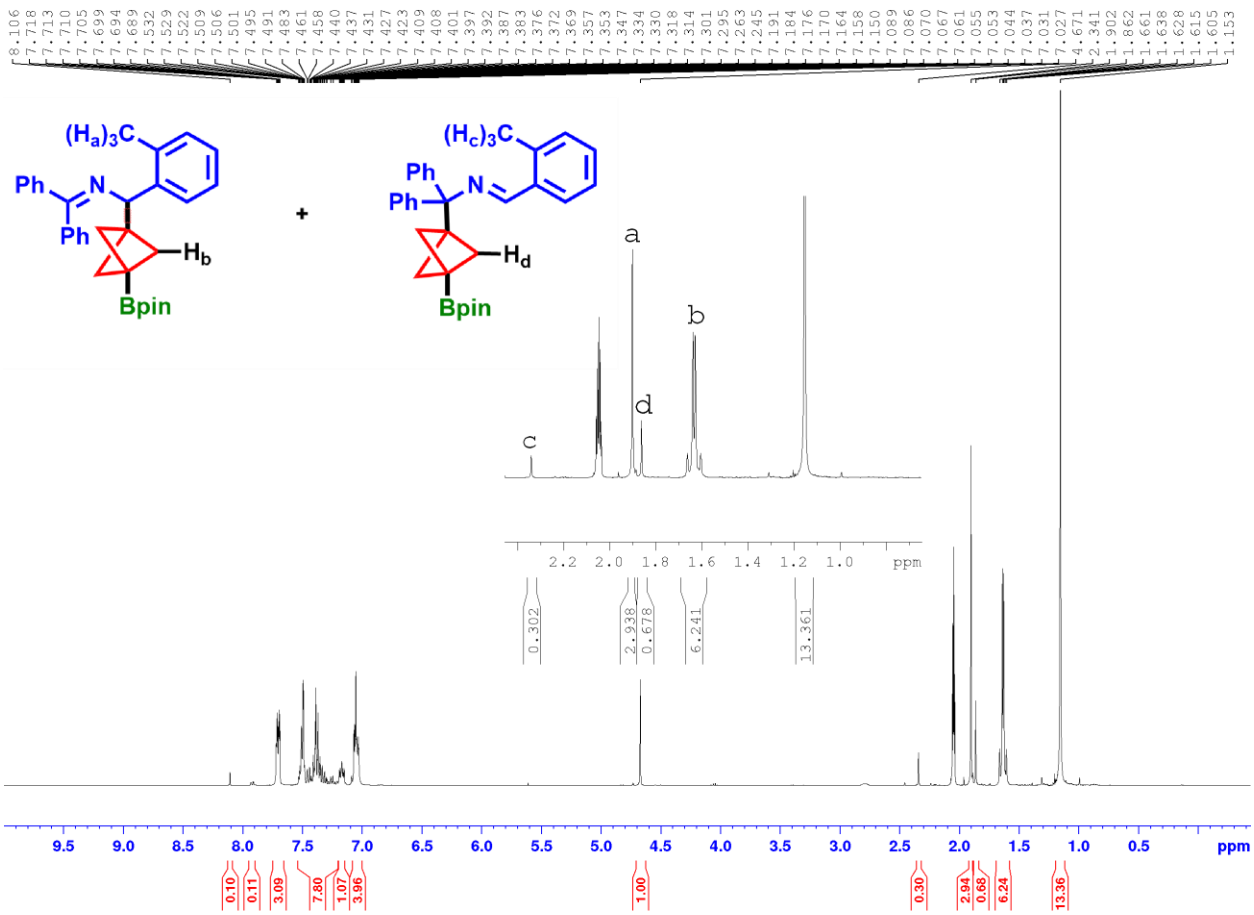
^{1}H NMR spectrum ((CDCl$_3$, 400 MHz) of ***N*-((4-methoxyphenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7k and 7k')**



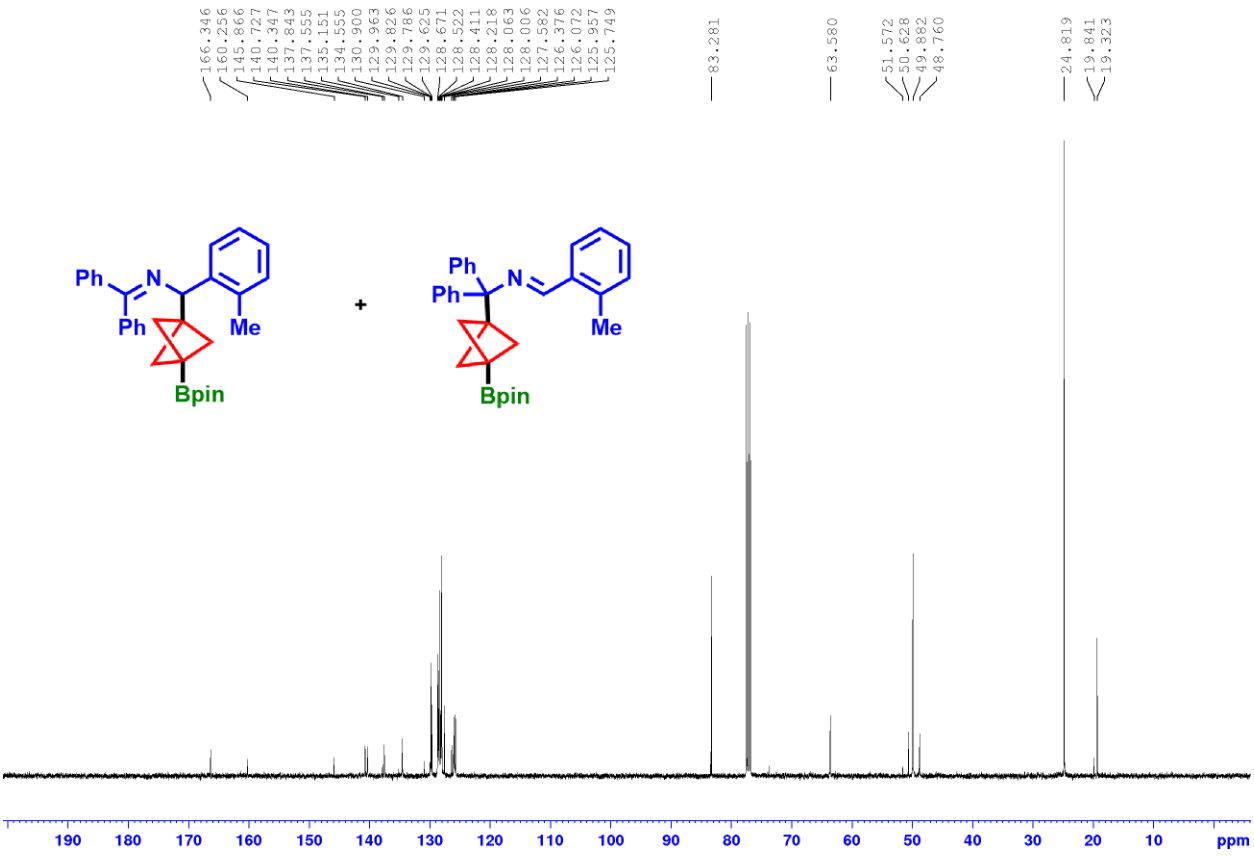
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of ***N*-((4-methoxyphenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7k and 7k')**



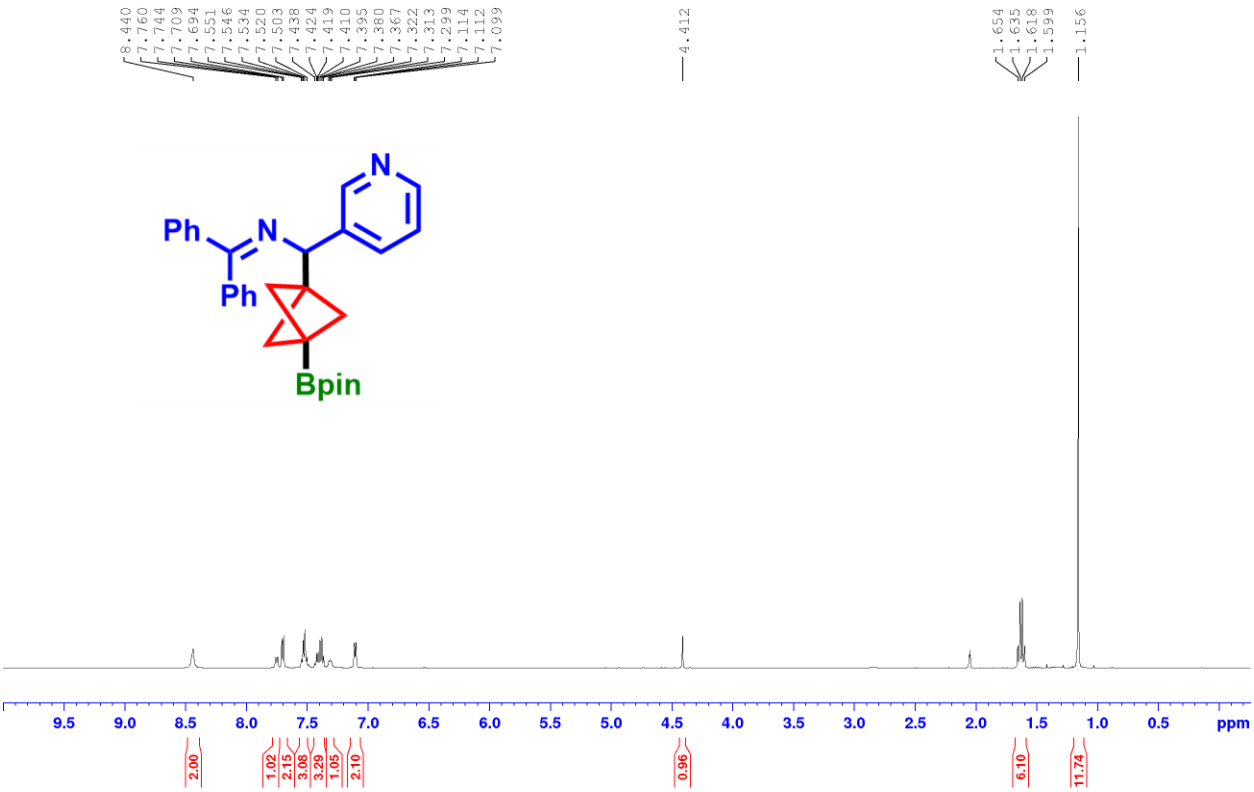
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **1,1-diphenyl-*N*-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(*o*-tolyl)methyl)methanimine (7l and 7l')**



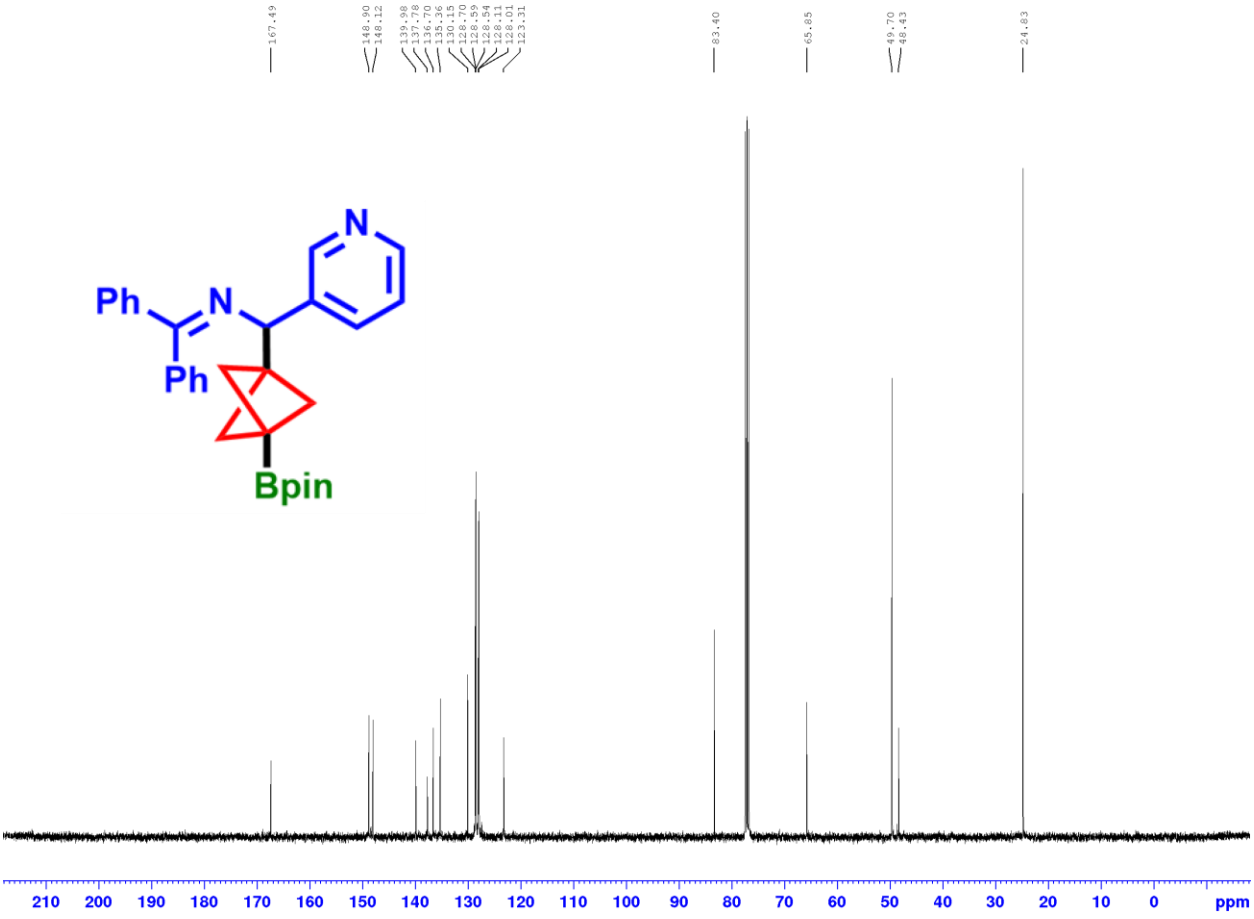
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of **1,1-diphenyl-*N*-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(*o*-tolyl)methyl)methanimine (7l and 7l')**



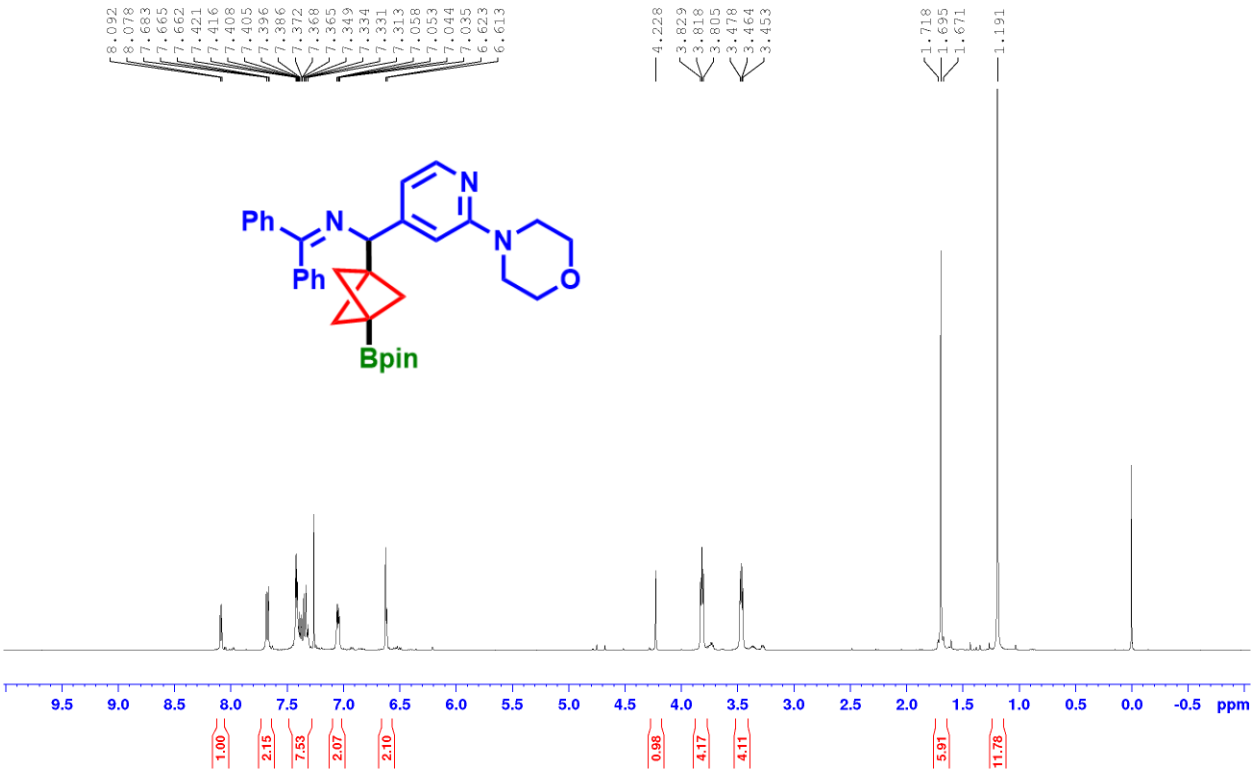
^{1}H NMR spectrum ((CD)$_3$CO, 400 MHz) of **1,1-diphenyl-*N*-(pyridin-3-yl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (7m)**



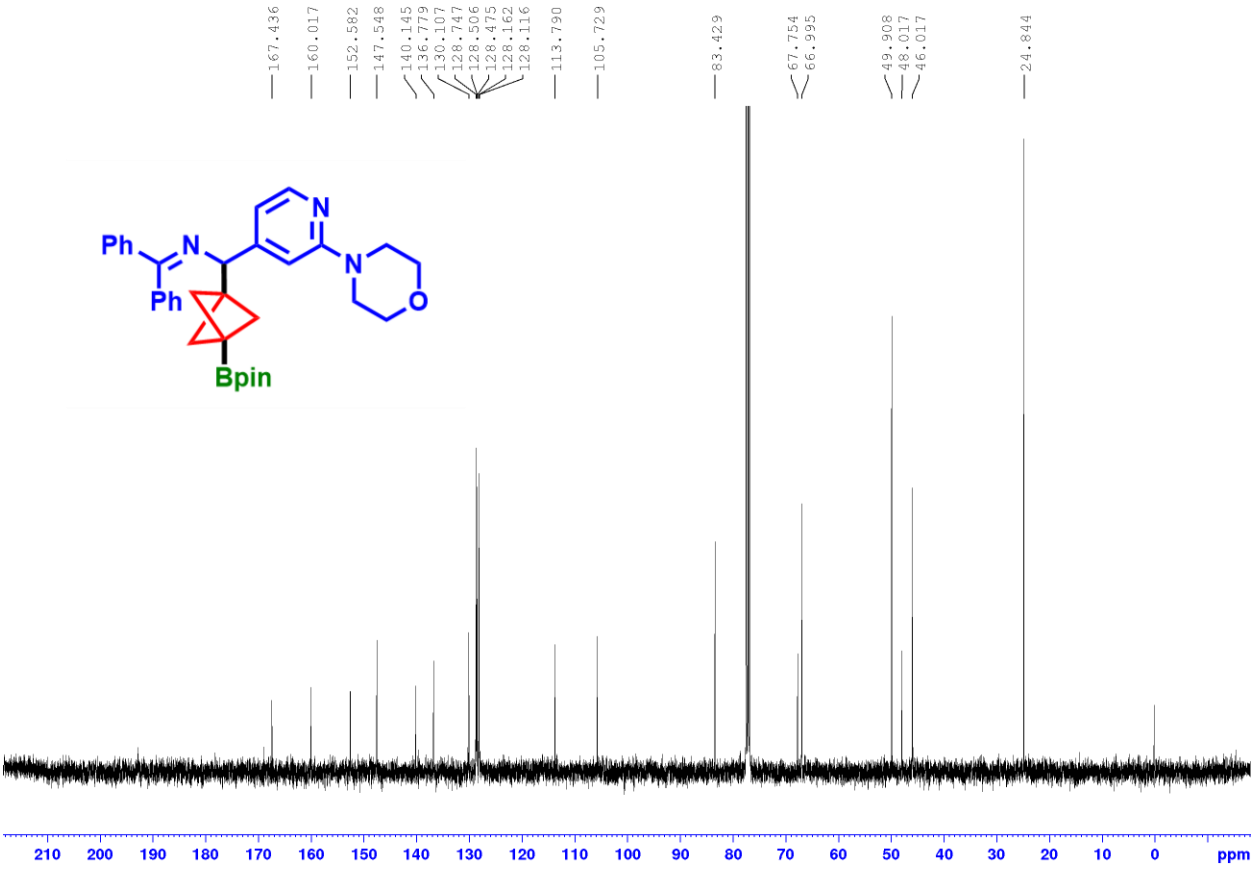
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of **1,1-diphenyl-*N*-(pyridin-3-yl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (7m)**



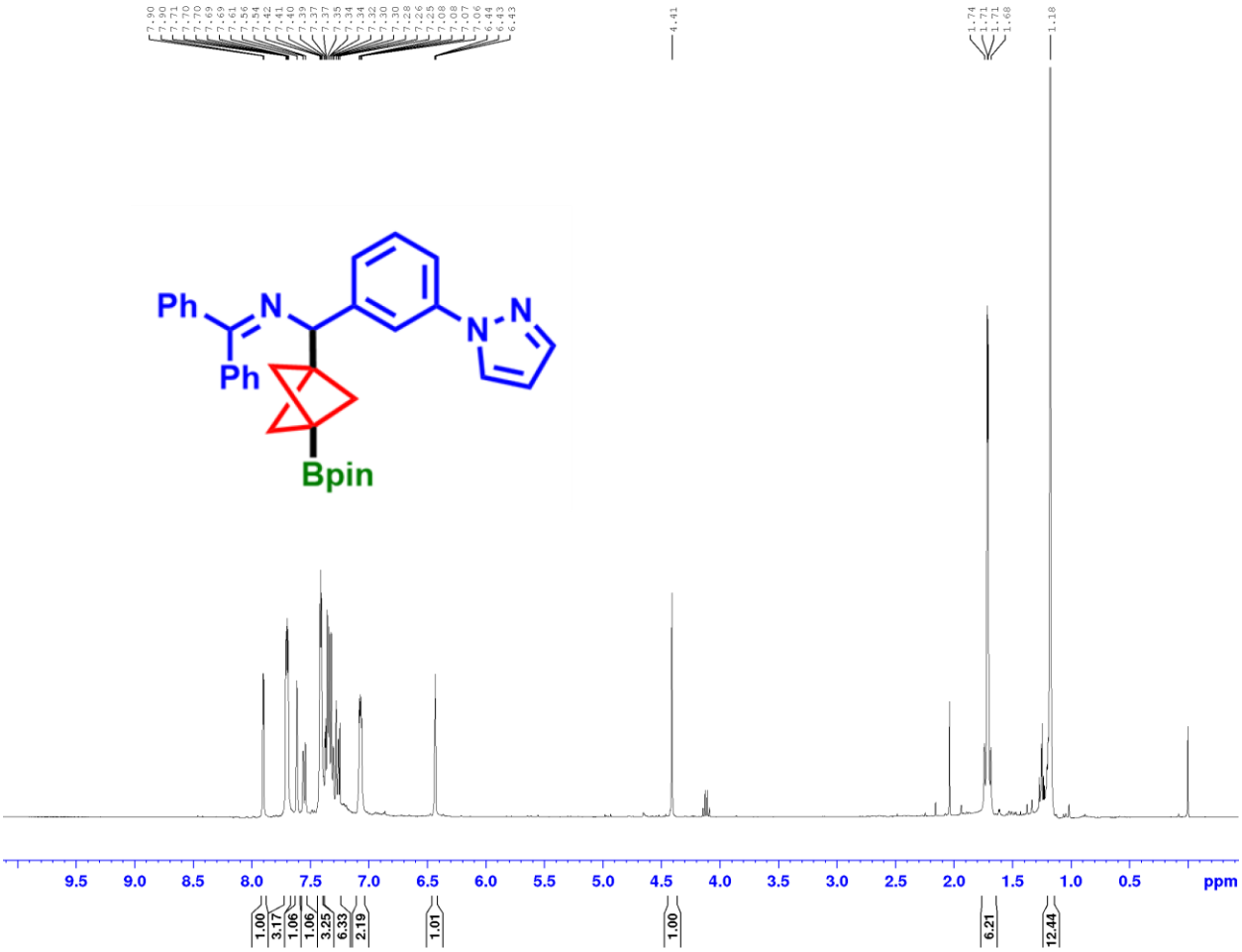
^{1}H NMR spectrum ((CDCl$_3$, 400 MHz) of ***N*-((2-morpholinopyridin-4-yl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7n)**



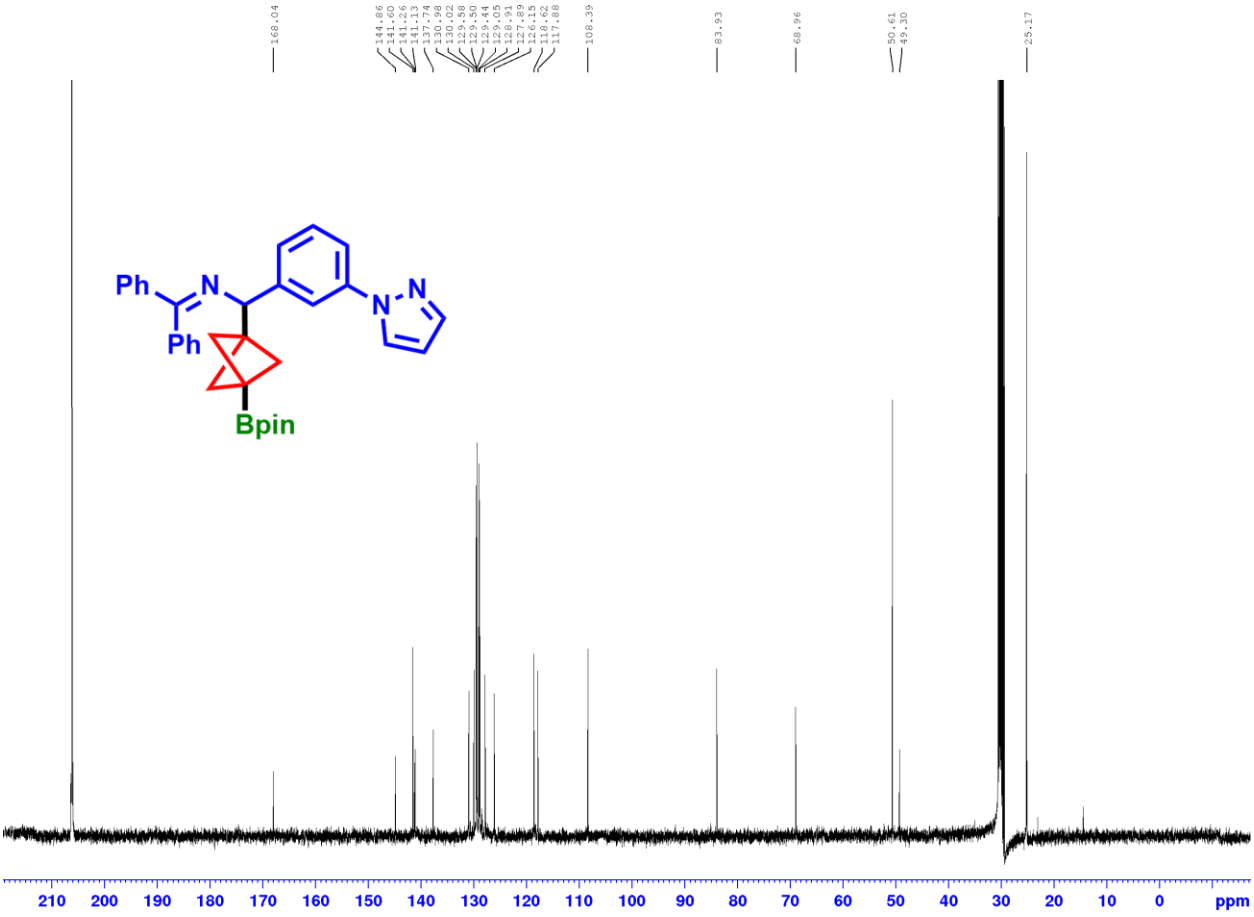
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***N*-((2-morpholinopyridin-4-yl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7n)**



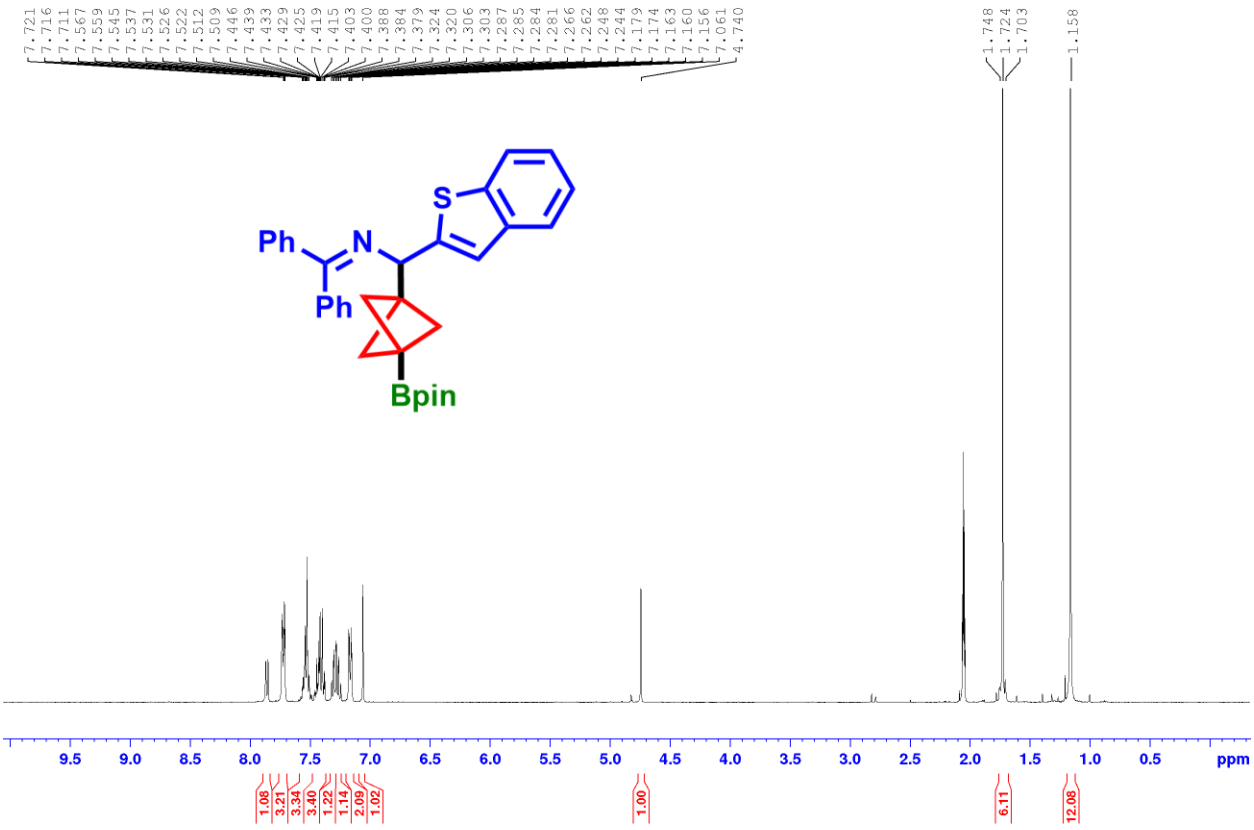
^{1}H NMR spectrum (400 MHz, ($CDCl_3$) of ***N*-((3-(1H-pyrazol-1-yl)phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7o)**



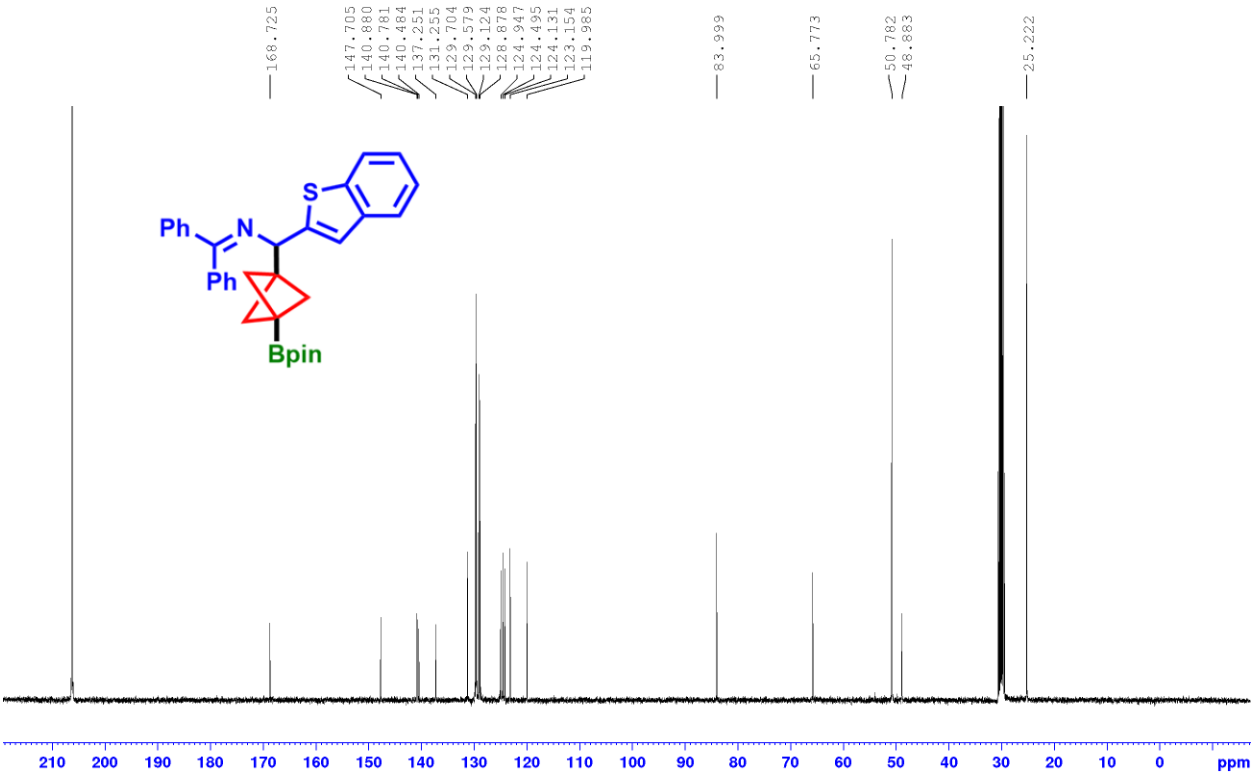
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $(CD_3)_2CO$) of ***N*-((3-(1H-pyrazol-1-yl)phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7o)**



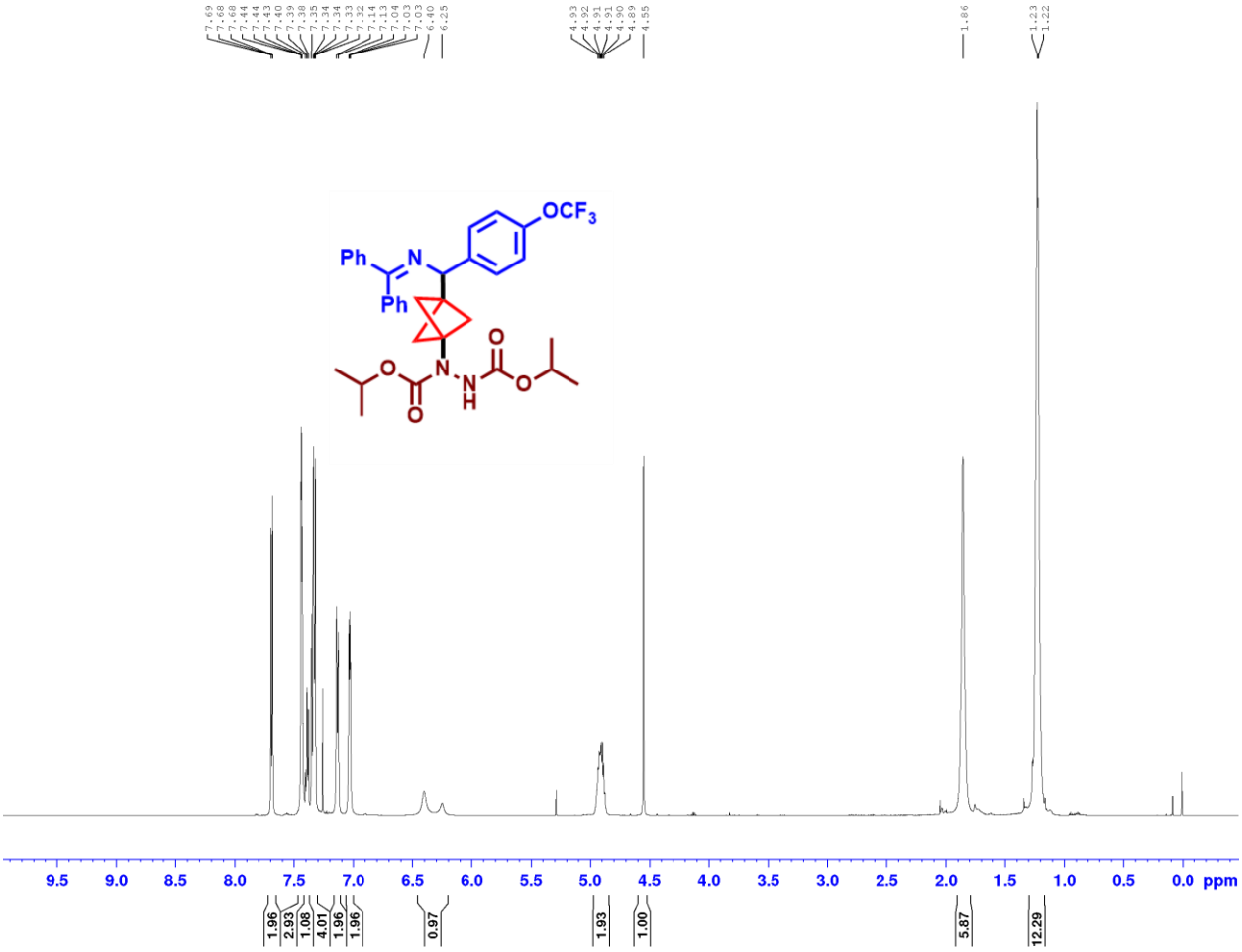
^{1}H NMR spectrum (((CD$_3$)$_2$CO, 400 MHz) of ***N*-(benzo[b]thiophen-2-yl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7p)**



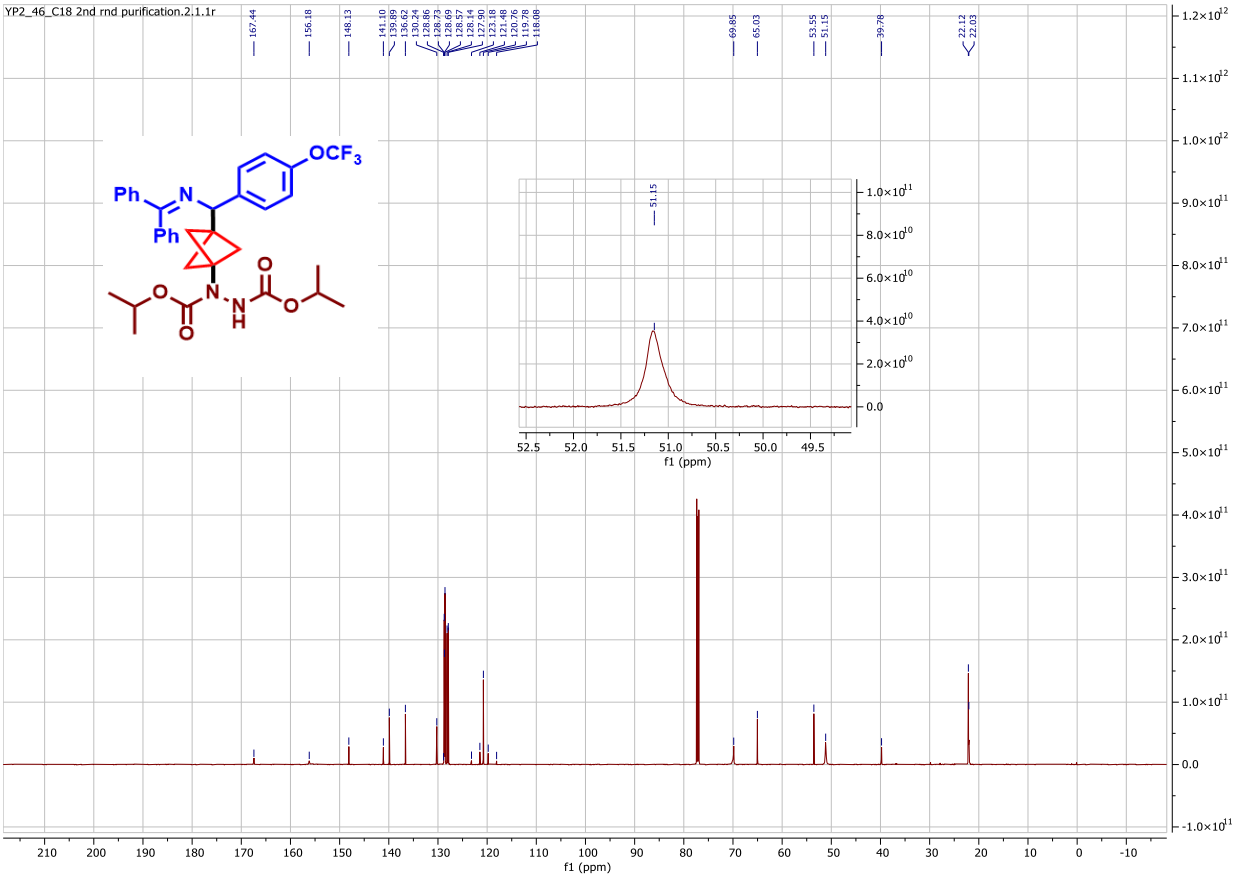
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N*-(benzo[b]thiophen-2-yl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (7p)**



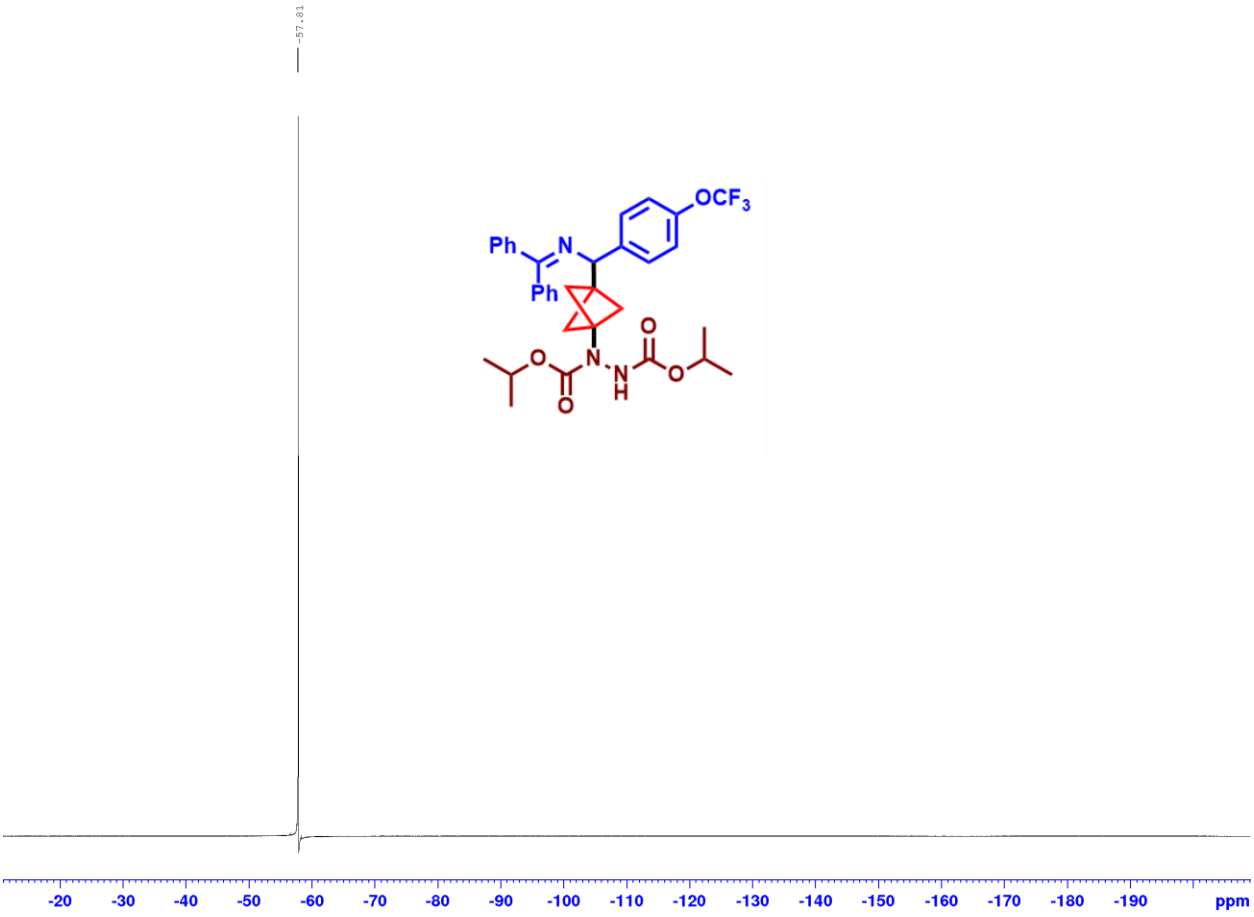
^{1}H NMR spectrum (((CD$_3$)$_2$CO, 600 MHz) of **diisopropyl -1-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)hydrazine-1,2-dicarboxylate (10)**



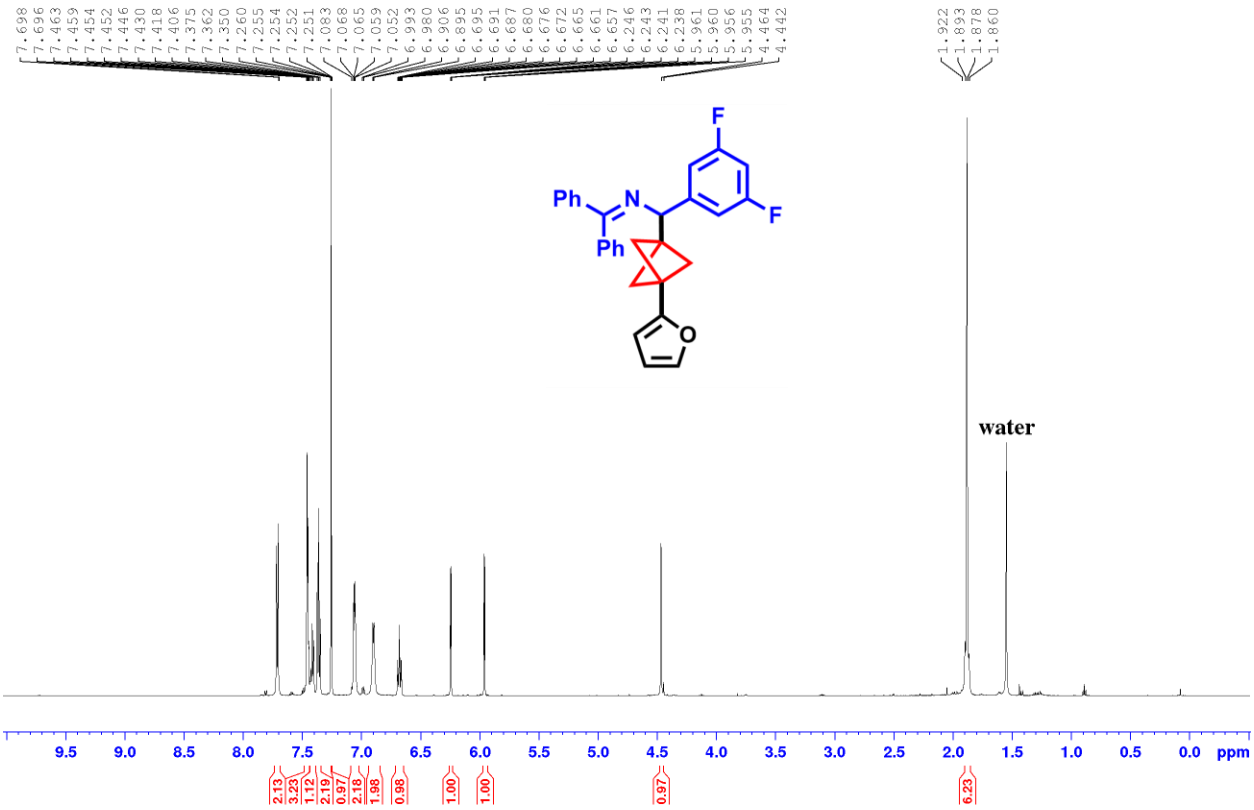
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 150 MHz) of **diisopropyl -1-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)hydrazine-1,2-dicarboxylate (10)**



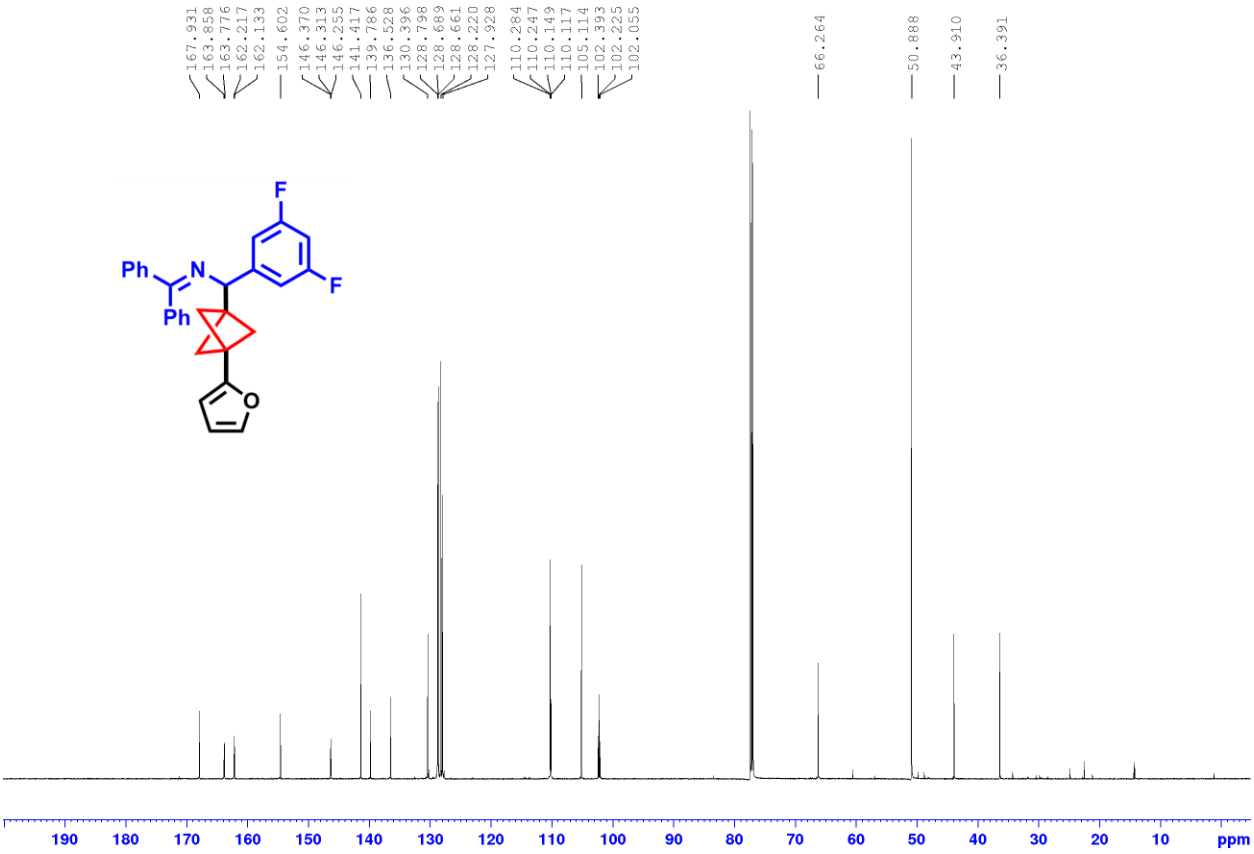
^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of **diisopropyl -1-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)hydrazine-1,2-dicarboxylate (10)**



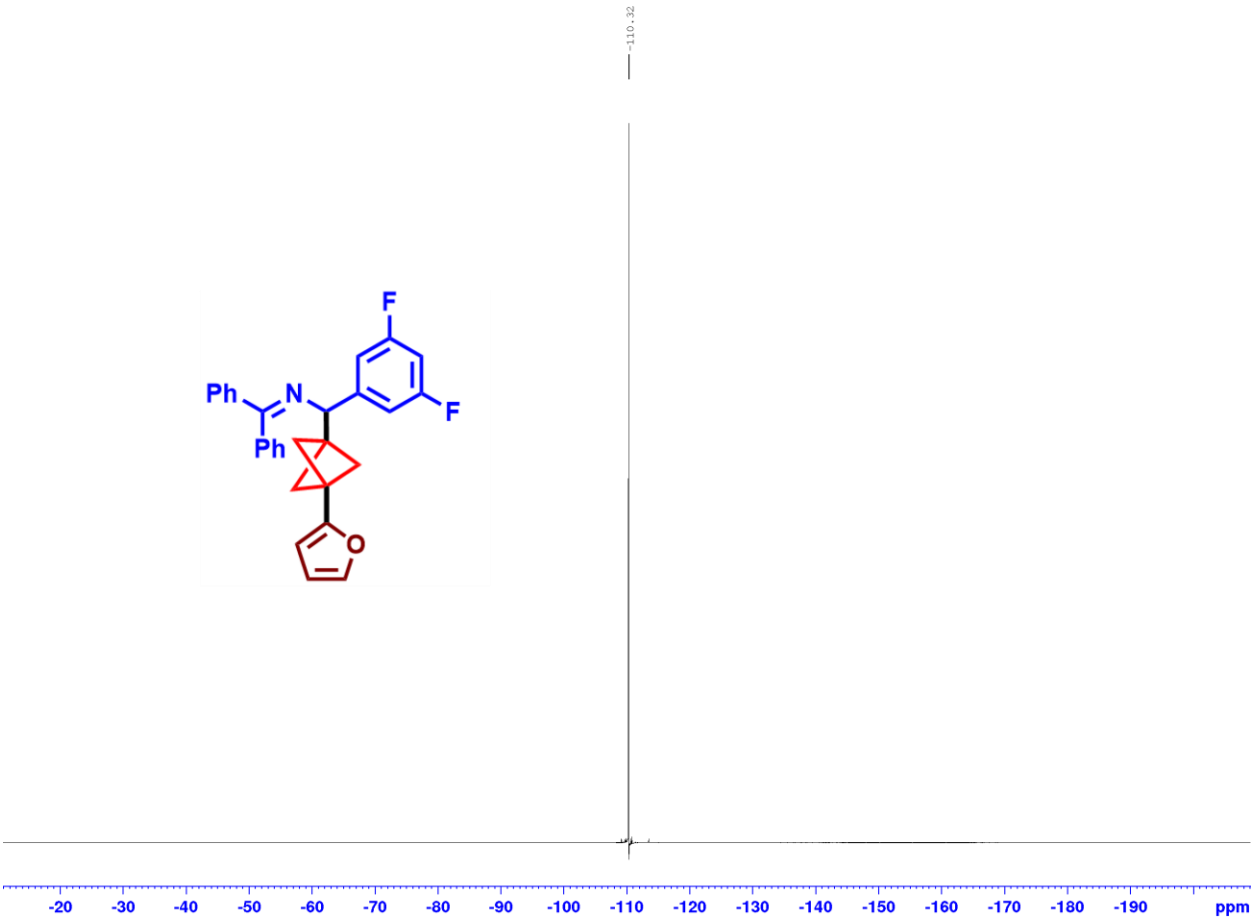
^{1}H NMR spectrum (($CDCl_3$, 600 MHz) of ***N*-((3,5-difluorophenyl)(3-(furan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (11)**



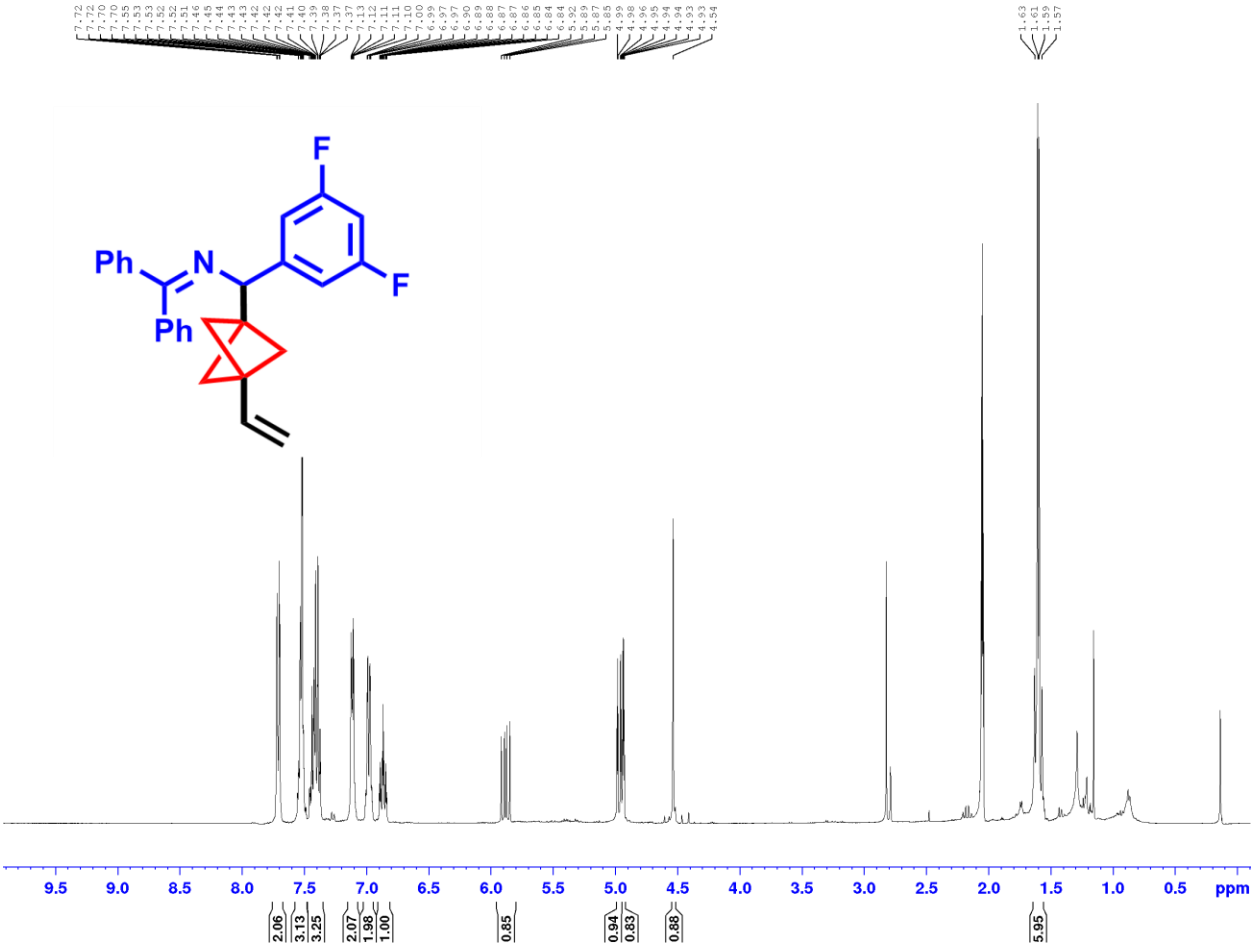
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz) of ***N*-((3,5-difluorophenyl)(3-(furan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (11)**



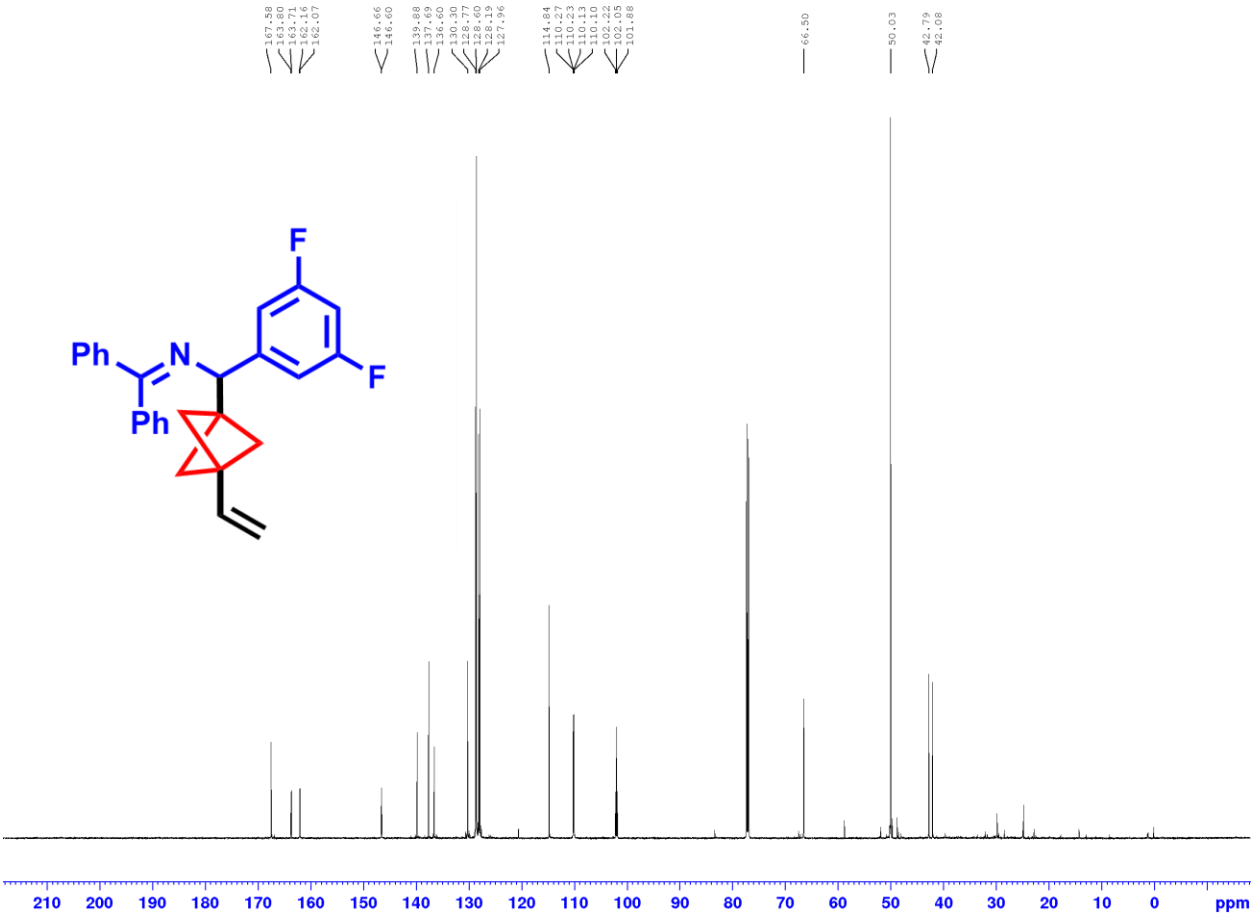
^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of ***N*-((3,5-difluorophenyl)(3-(furan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-1,1-diphenylmethanimine (11)**



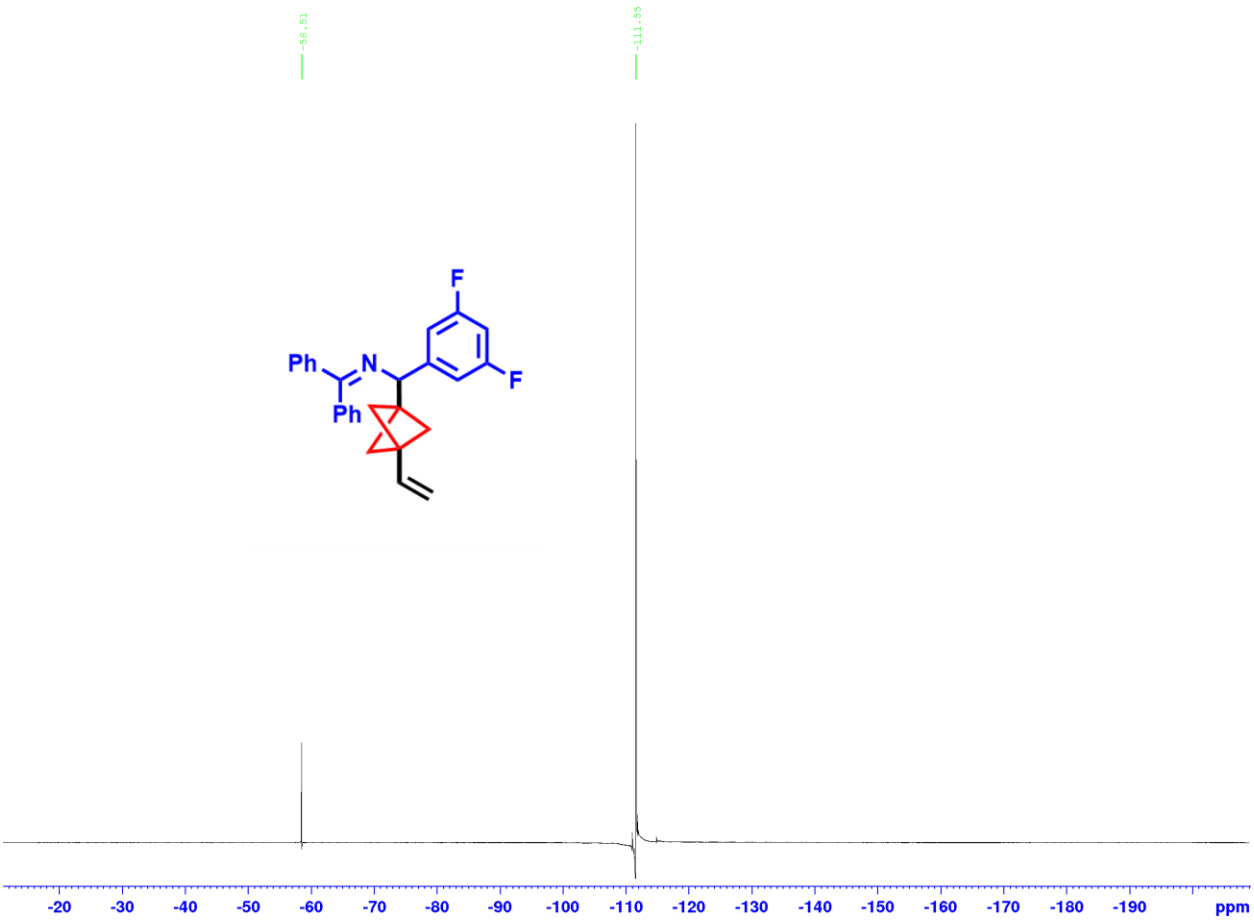
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **1,1-diphenyl-*N*-((4-(trifluoromethoxy)phenyl)(3-vinylbicyclo[1.1.1]pentan-1-yl)methyl)methanimine (12)**



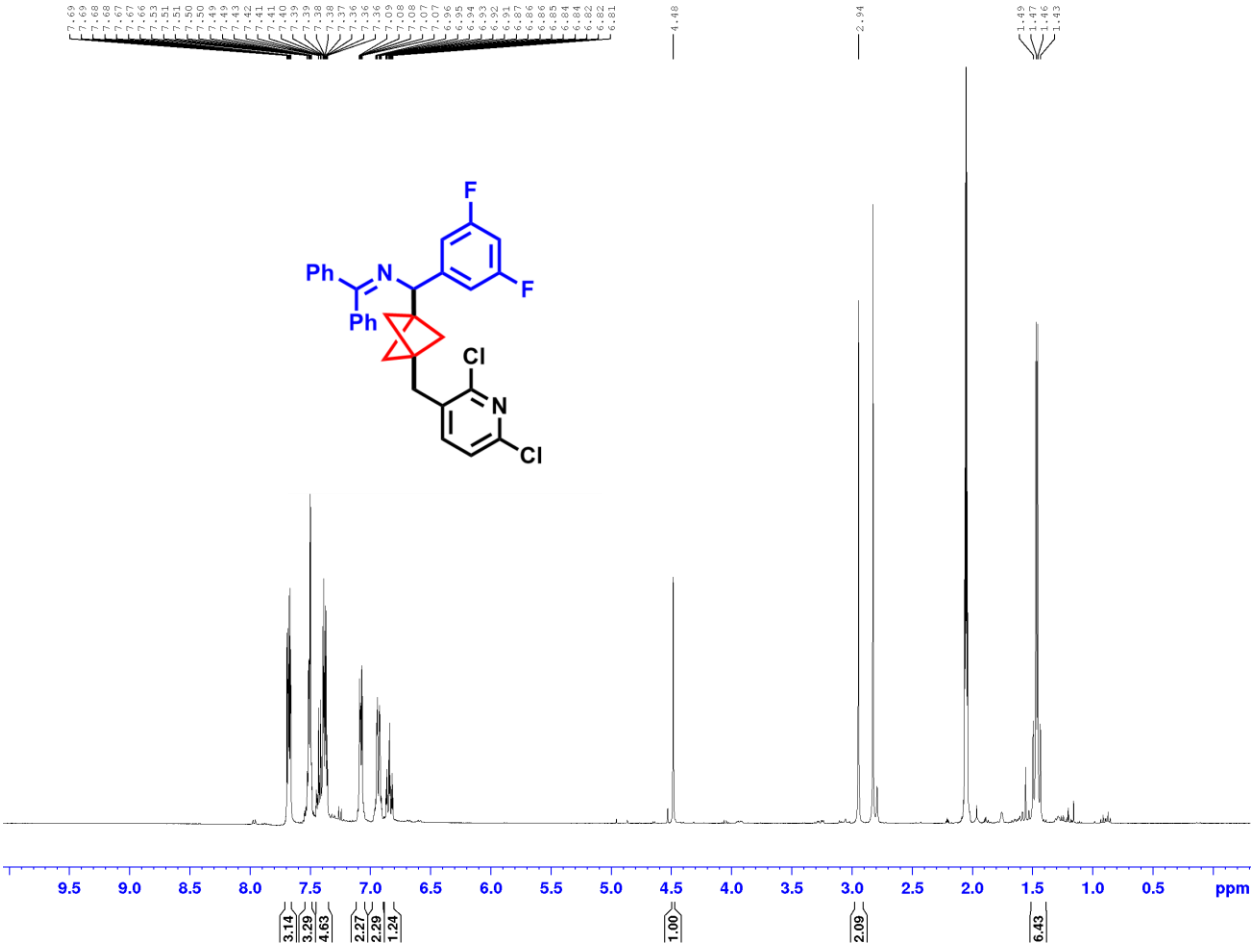
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 125 MHz) of **1,1-diphenyl-*N*-((4-(trifluoromethoxy)phenyl)(3-vinylbicyclo[1.1.1]pentan-1-yl)methyl)methanimine (12)**



^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of **1,1-diphenyl-*N*-((4-(trifluoromethoxy)phenyl)(3-vinylbicyclo[1.1.1]pentan-1-yl)methyl)methanimine (12)**



^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N*-((3-((2,6-dichloropyridin-3-yl)methyl)bicyclo[1.1.1]pentan-1-yl)(3,5-difluorophenyl)methyl)-1,1-diphenylmethanimine (13)**


7.69
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4.48
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9.5
9.0
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7.0
6.5
6.0
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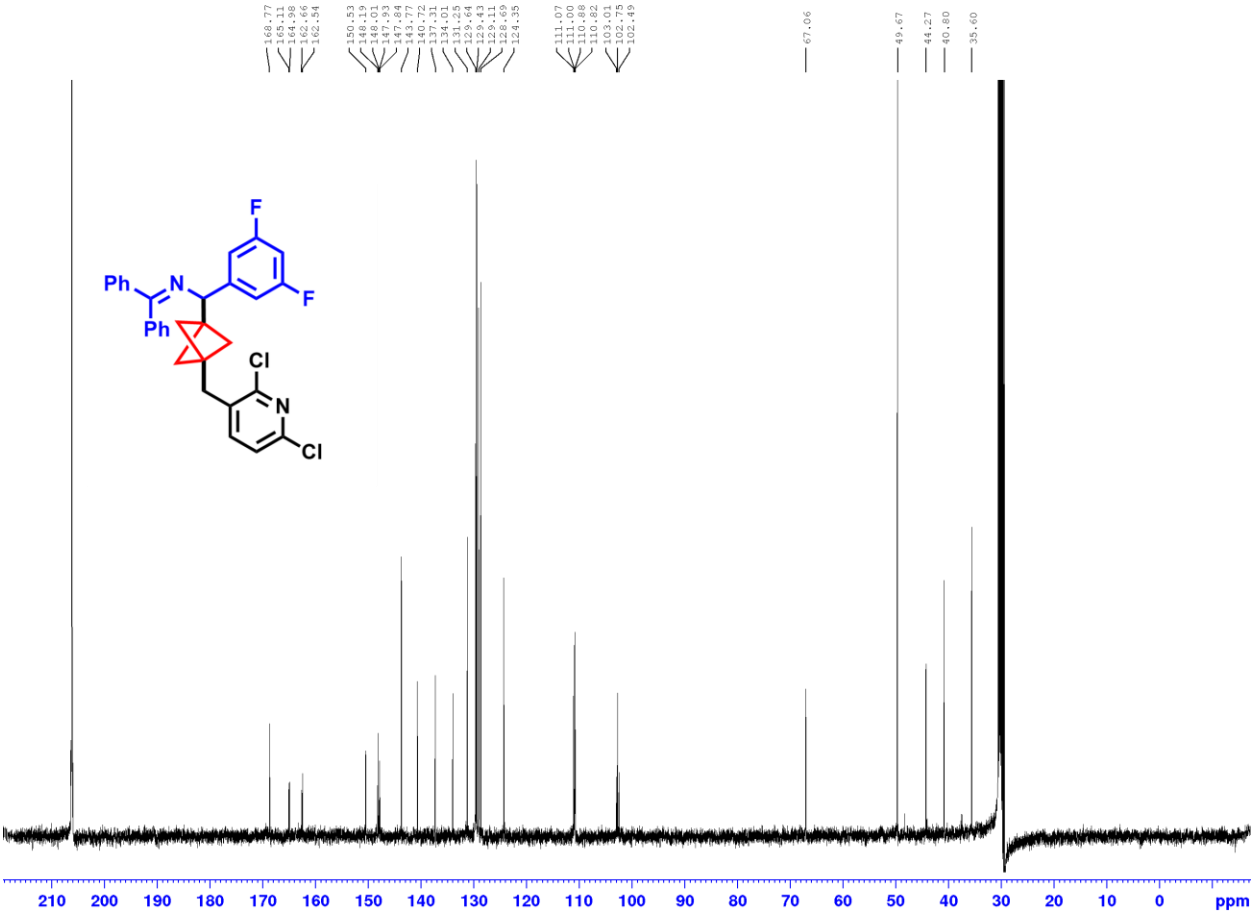
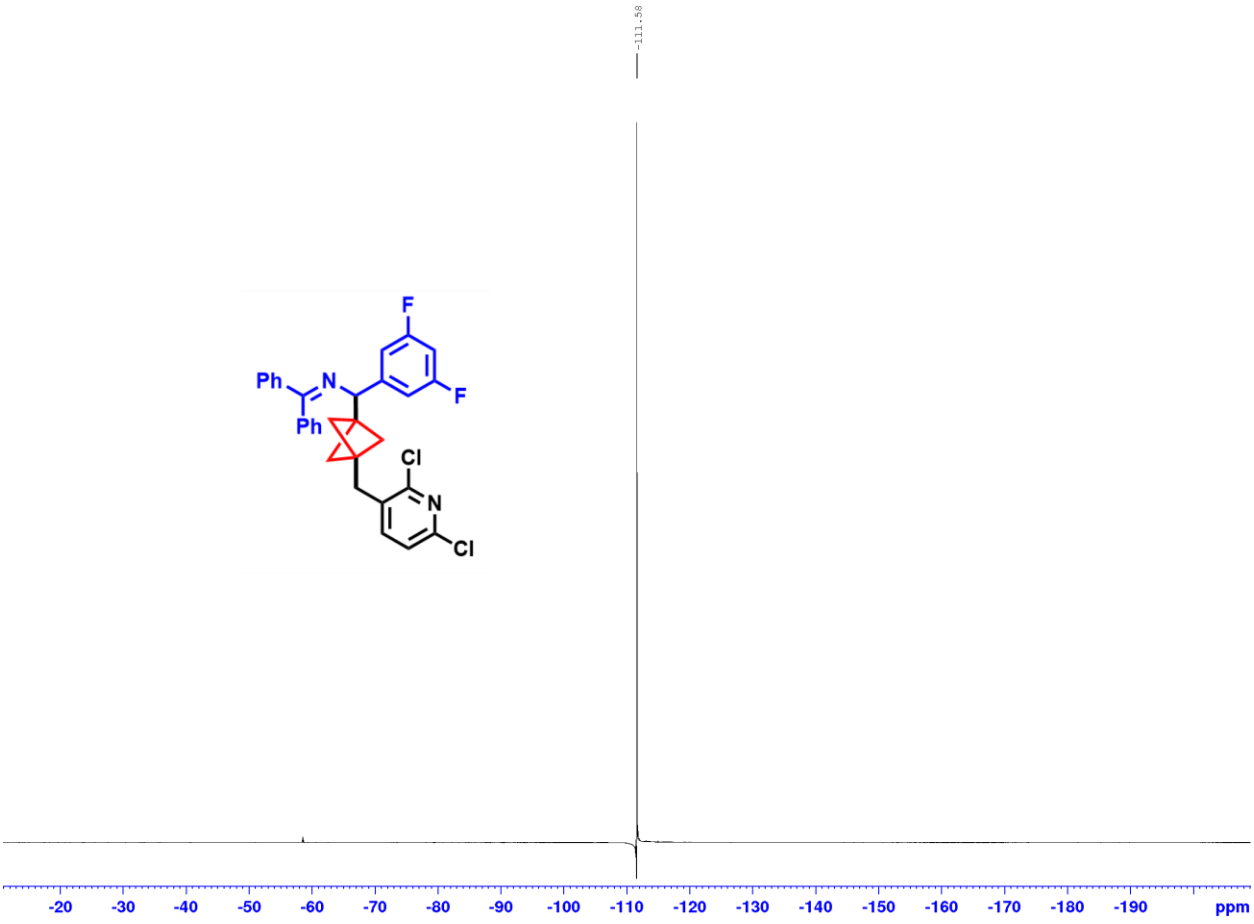
ppm
3.14
3.29
4.63
2.27
2.29
1.24
1.00
2.09
6.43

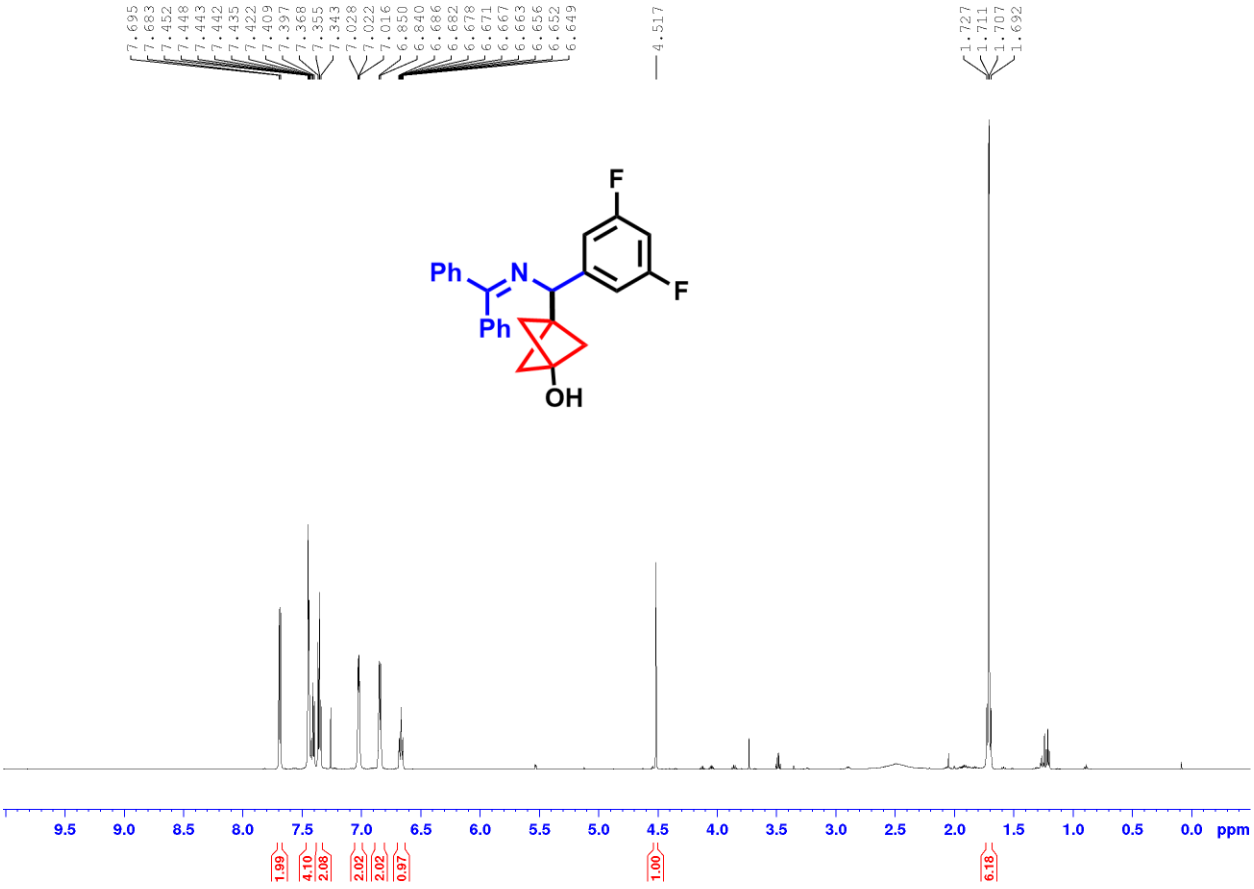
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N*-((3-((2,6-dichloropyridin-3-yl)methyl)bicyclo[1.1.1]pentan-1-yl)(3,5-difluorophenyl)methyl)-1,1-diphenylmethanimine (13)**



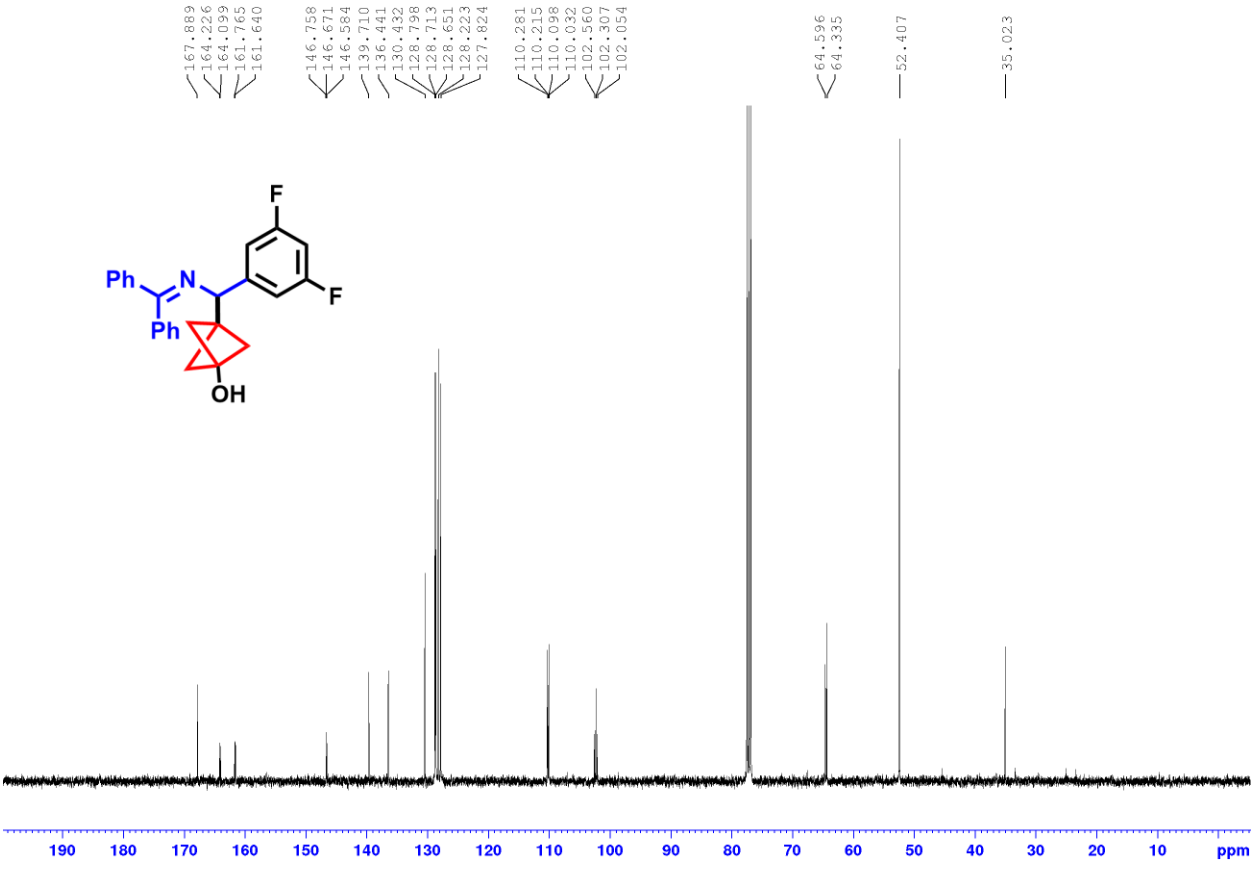
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of ***N*-((3-((2,6-dichloropyridin-3-yl)methyl)bicyclo[1.1.1]pentan-1-yl)(3,5-difluorophenyl)methyl)-1,1-diphenylmethanimine (13)**



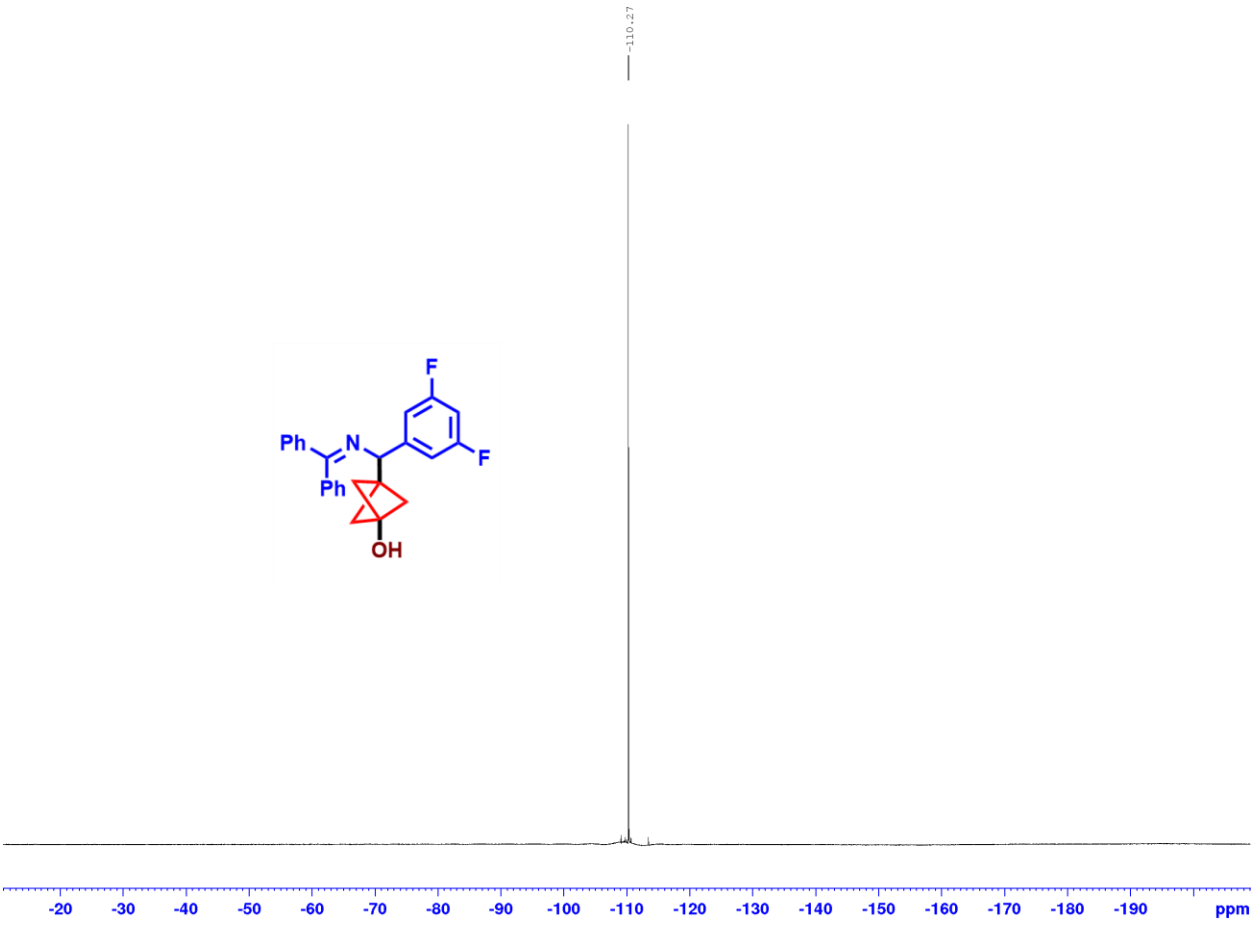
^{1}H NMR spectrum ((CDCl$_3$, 600 MHz) of **3-((3,5-difluorophenyl)((diphenylmethylene)amino)methyl)bicyclo[1.1.1]pentan-1-ol (14)**



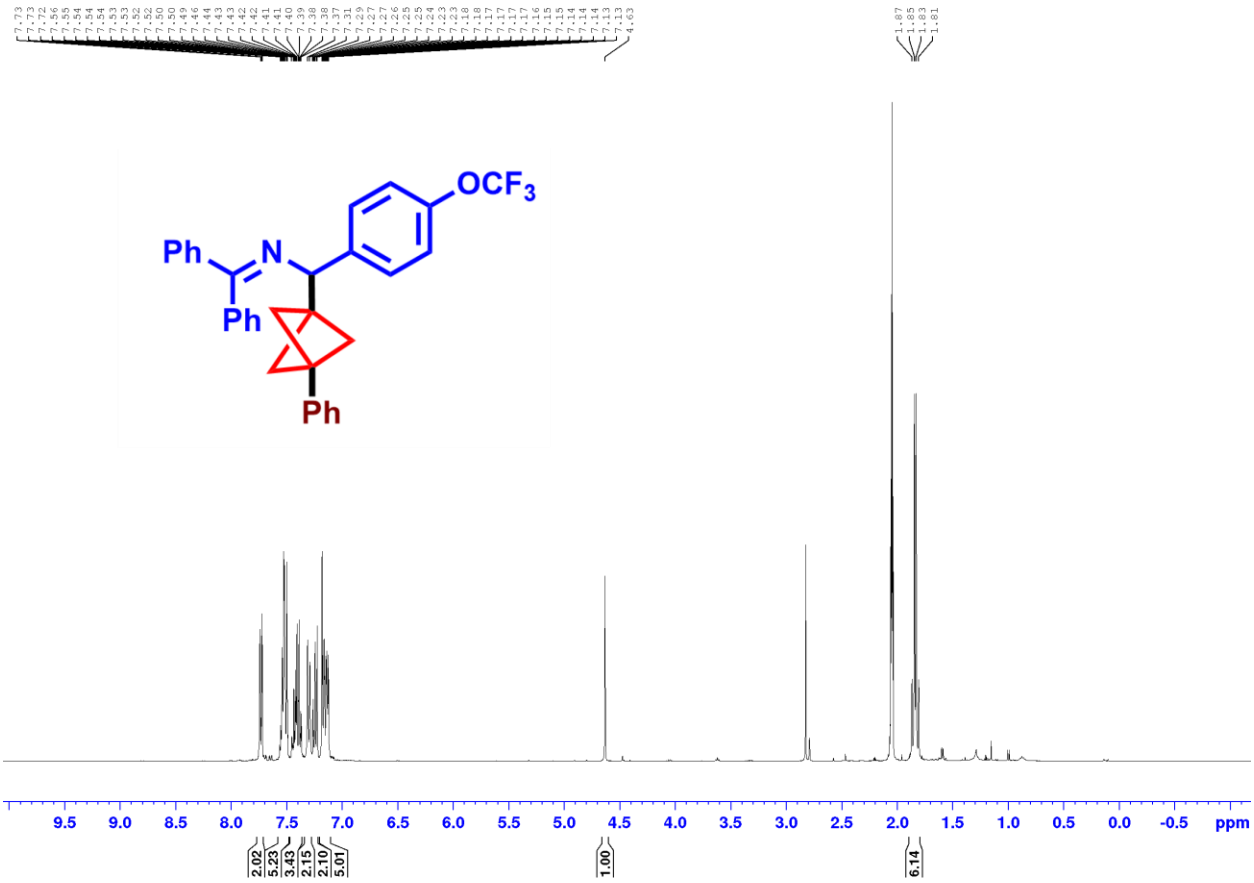
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of **3-((3,5-difluorophenyl)((diphenylmethylene)amino)methyl)bicyclo[1.1.1]pentan-1-ol (14)**



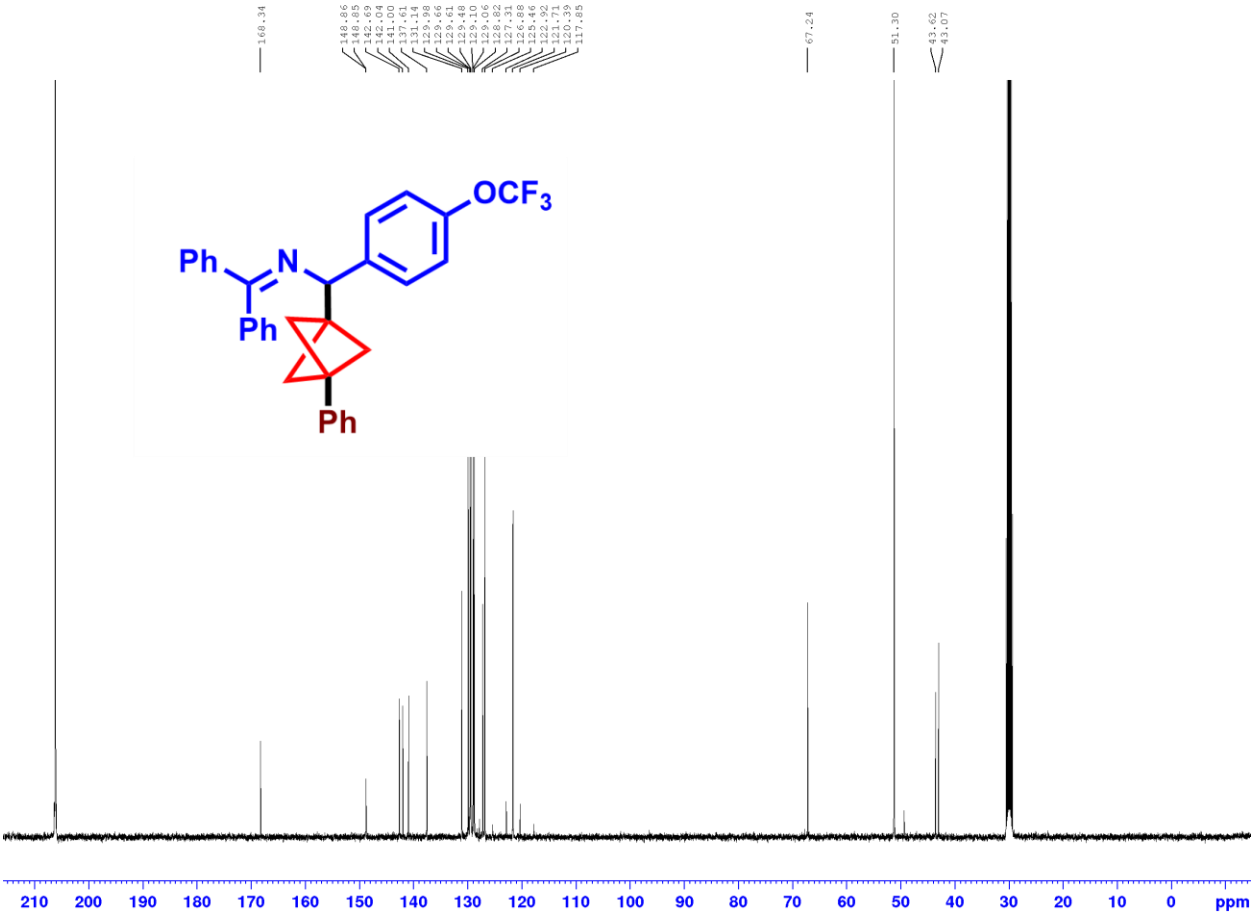
^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of **3-((3,5-difluorophenyl)((diphenylmethylene)amino)methyl)bicyclo[1.1.1]pentan-1-ol (14)**



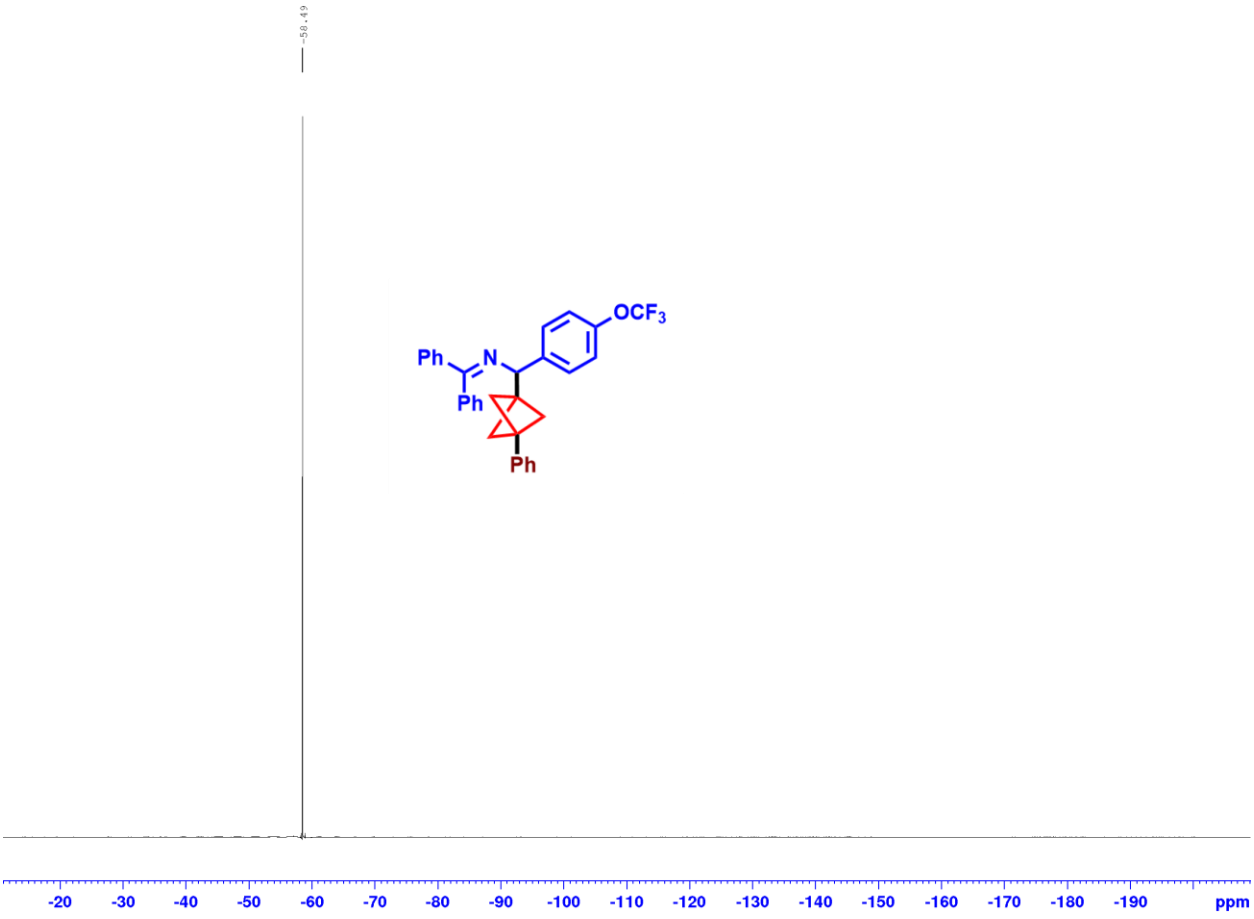
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **1,1-diphenyl-*N*-((3-phenylbicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8ba)**



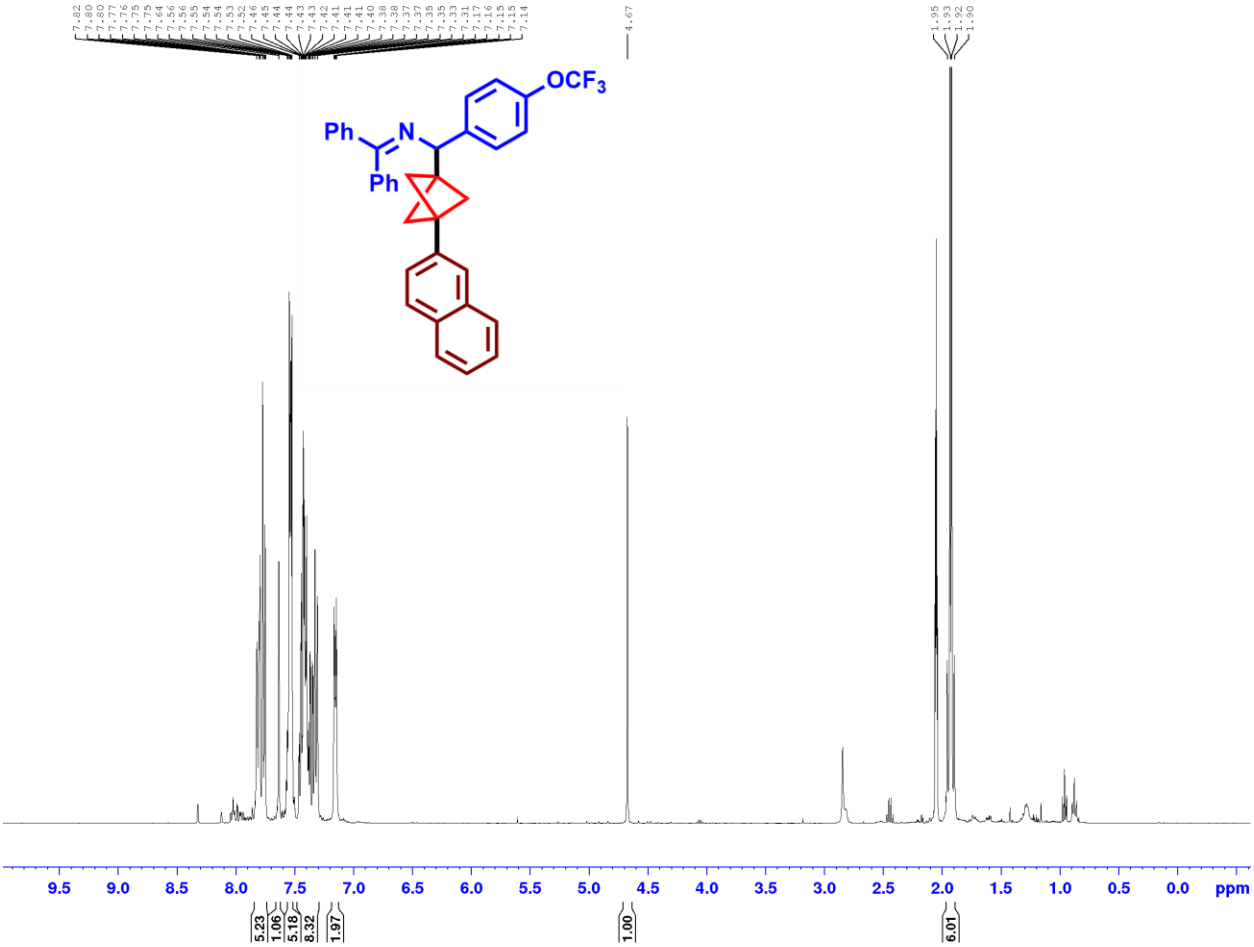
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of **1,1-diphenyl-*N*-((3-phenylbicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8ba)**



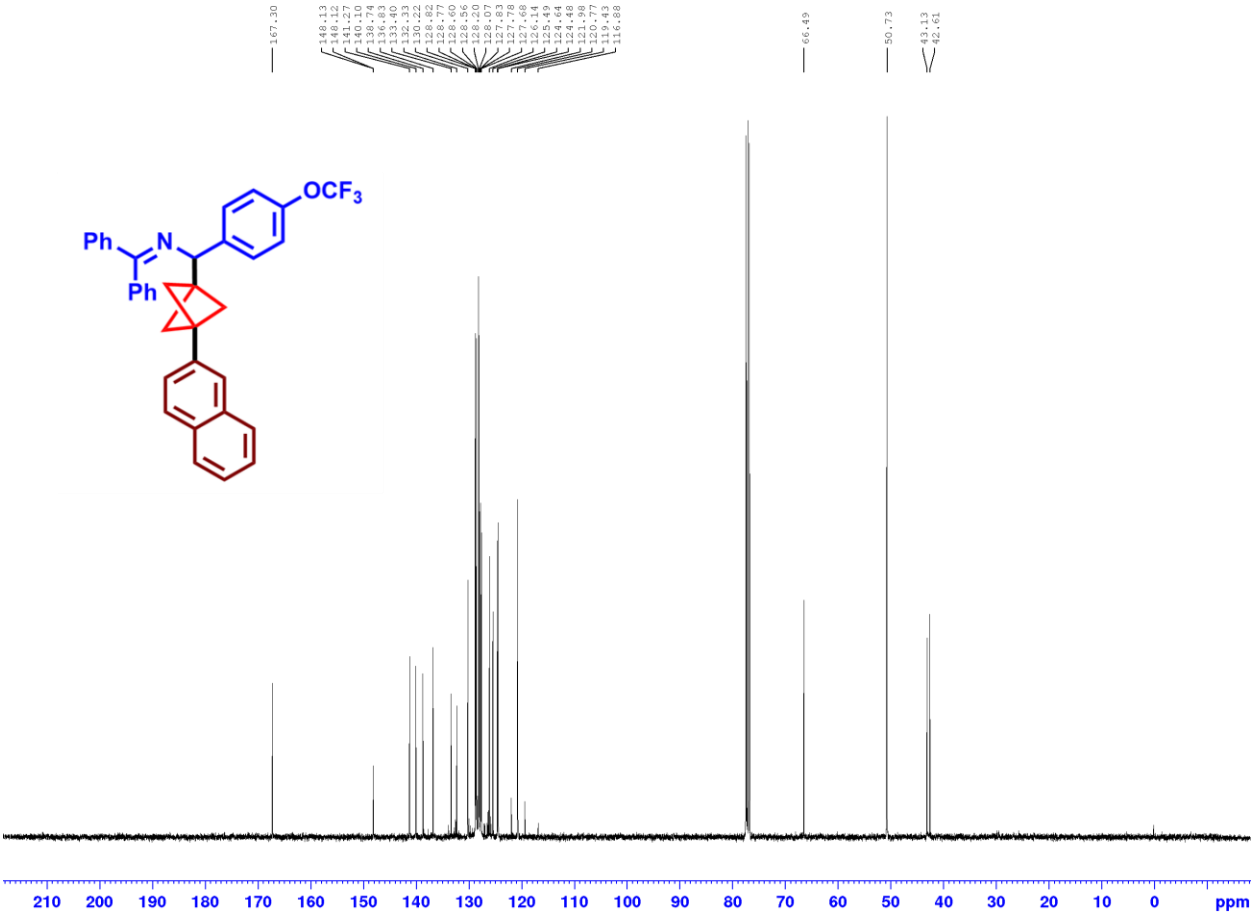
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of **1,1-diphenyl-*N*-((3-phenylbicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8ba)**



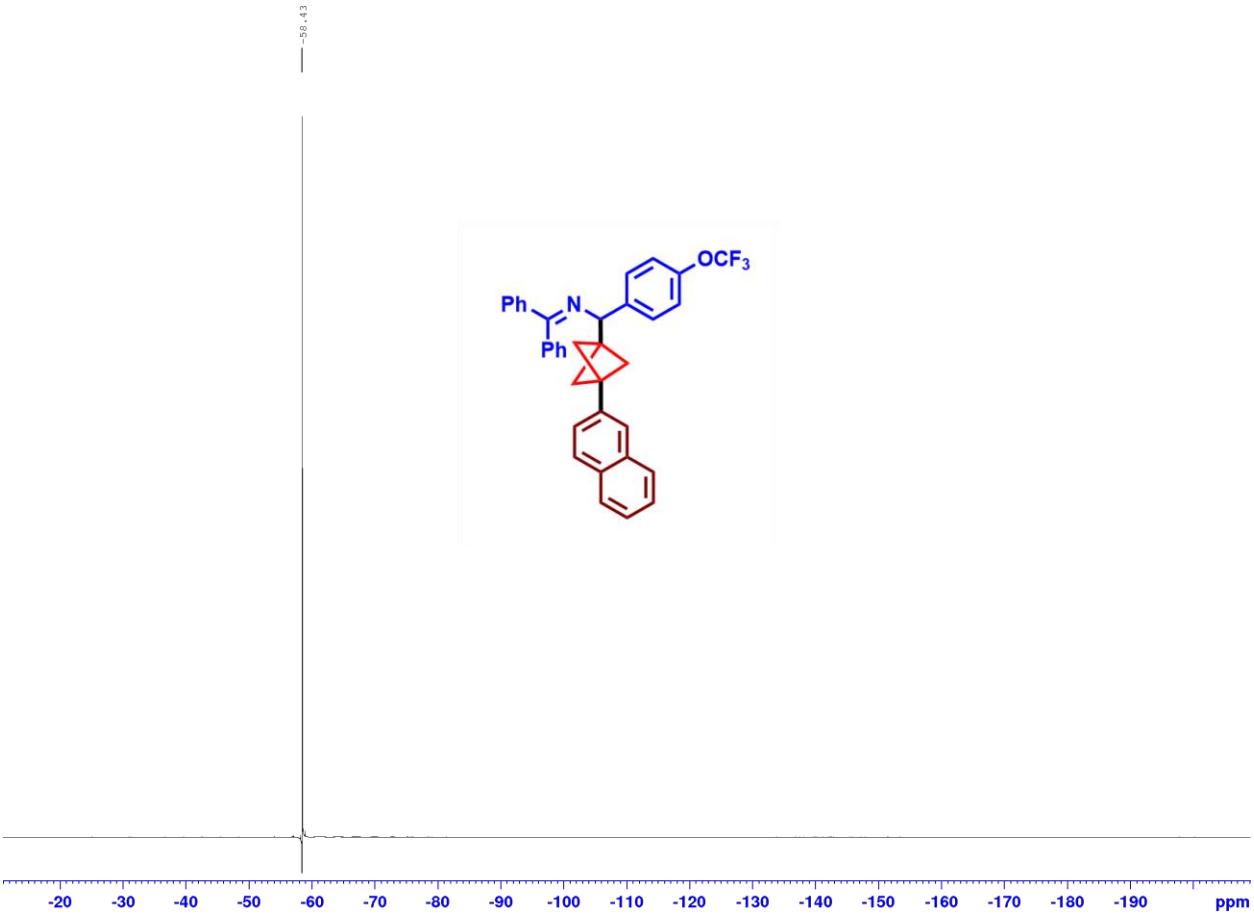
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N*-((3-(naphthalen-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bb)**



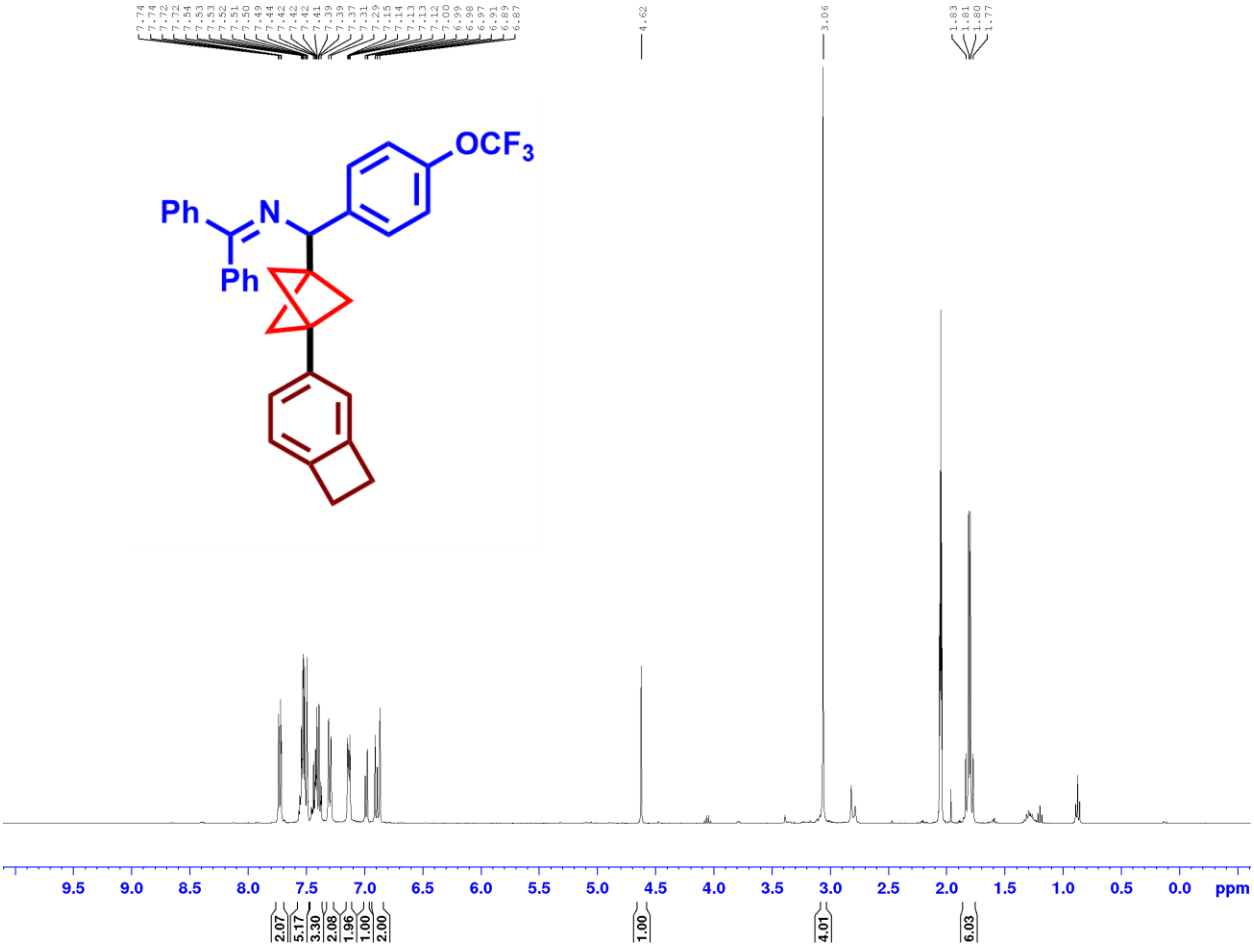
$^{13}C\{^{1}H\}$ NMR spectrum (($CDCl_3$ 100 MHz) of ***N*-((3-(naphthalen-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bb)**



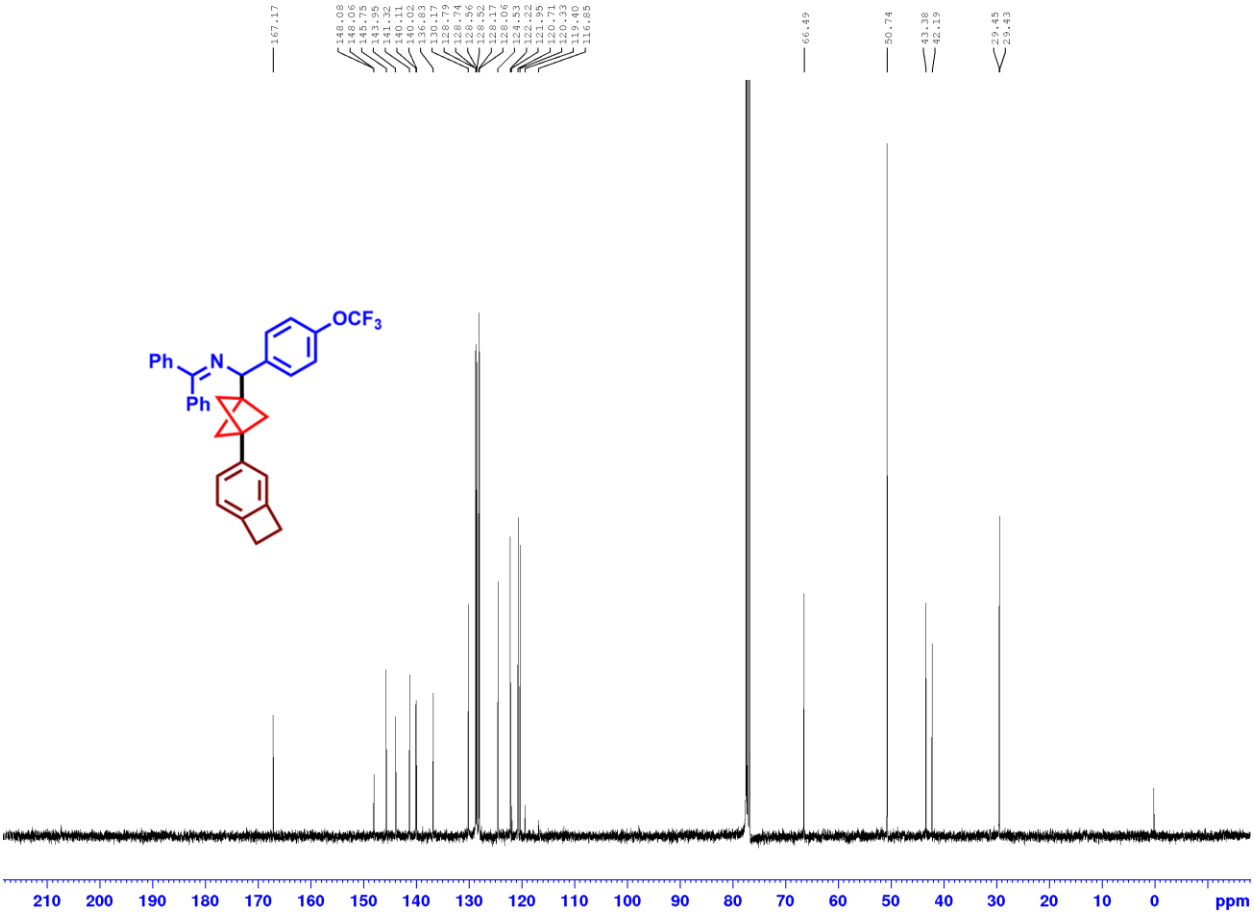
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of ***N*-((3-(naphthalen-2-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bb)**



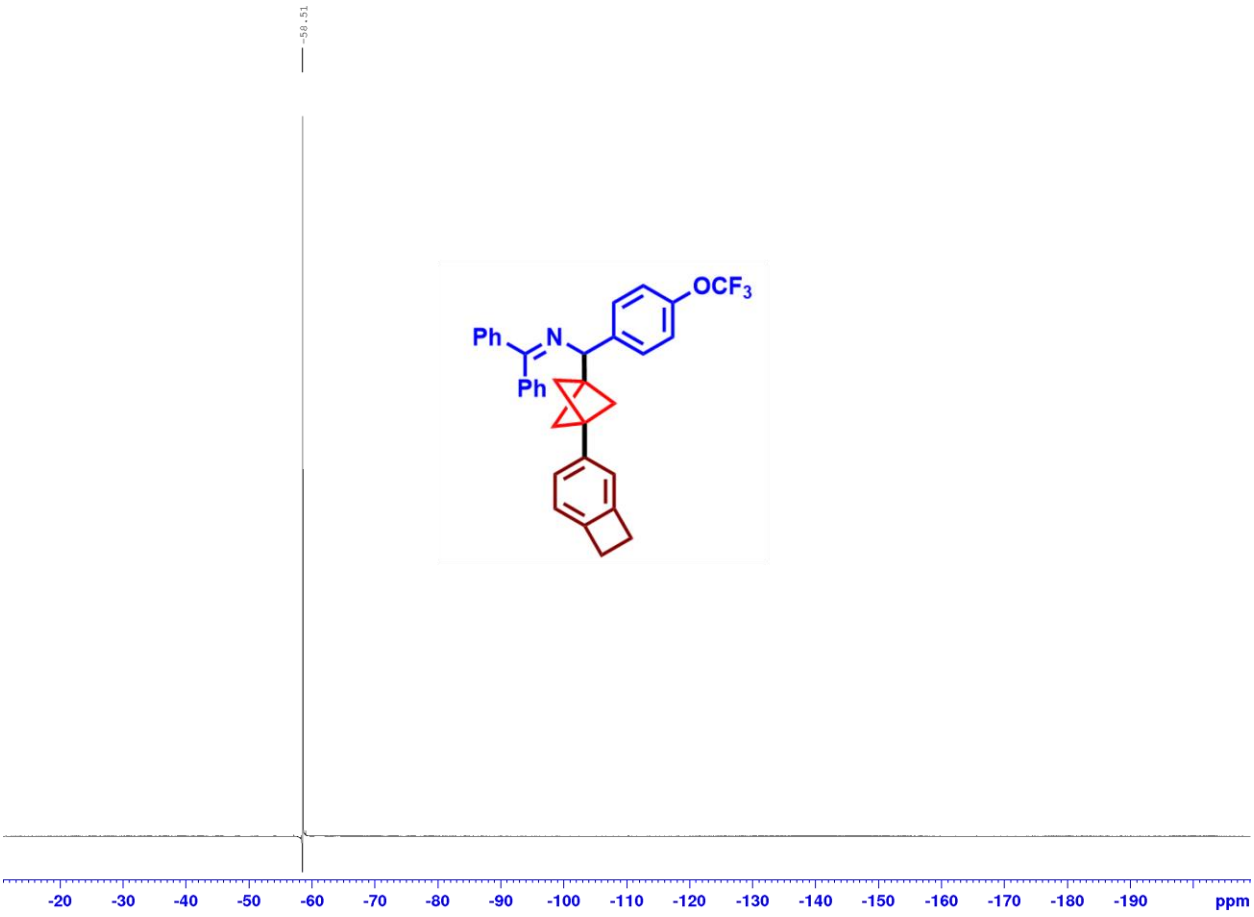
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N*-((3-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bc)**



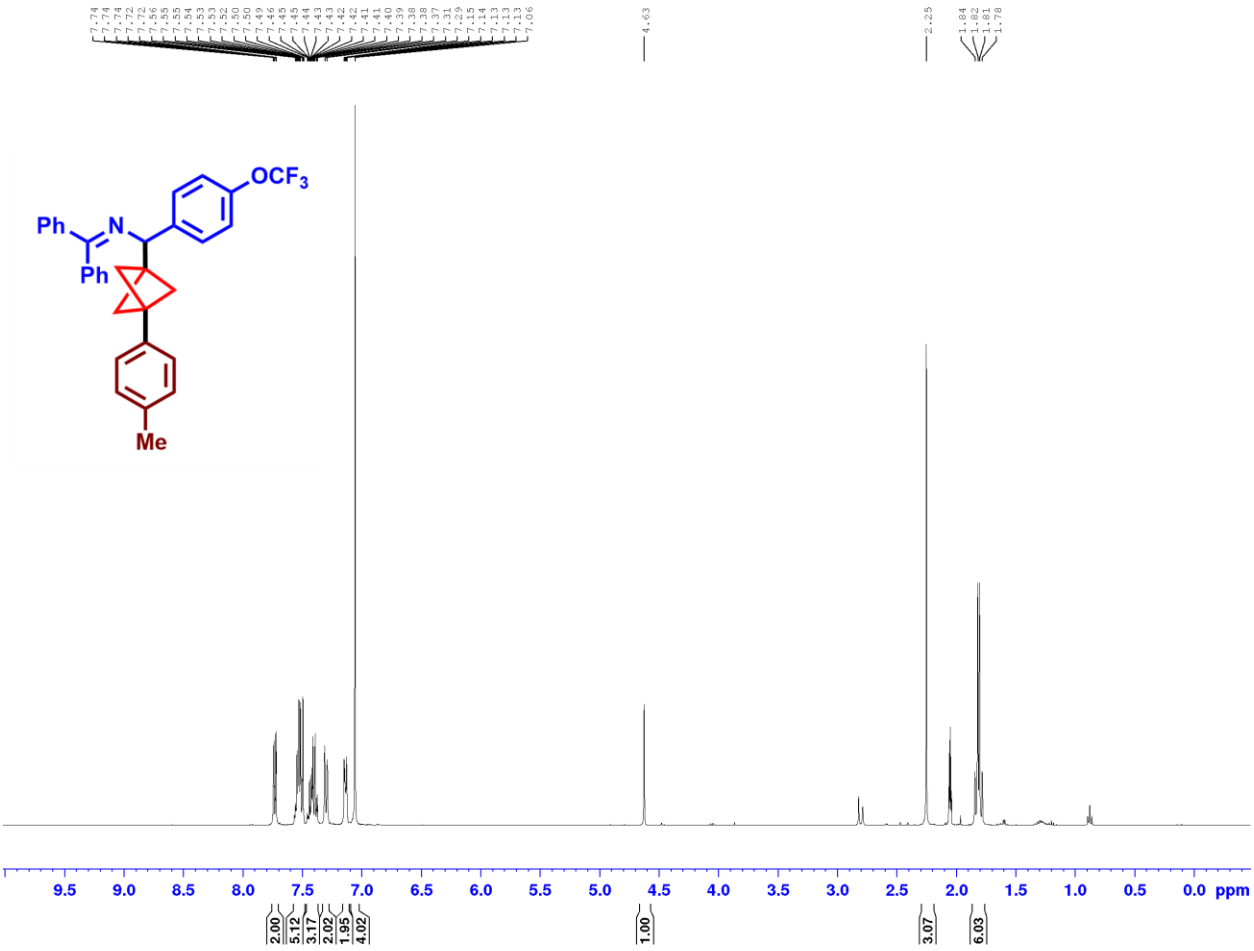
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N*-((3-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bc)**



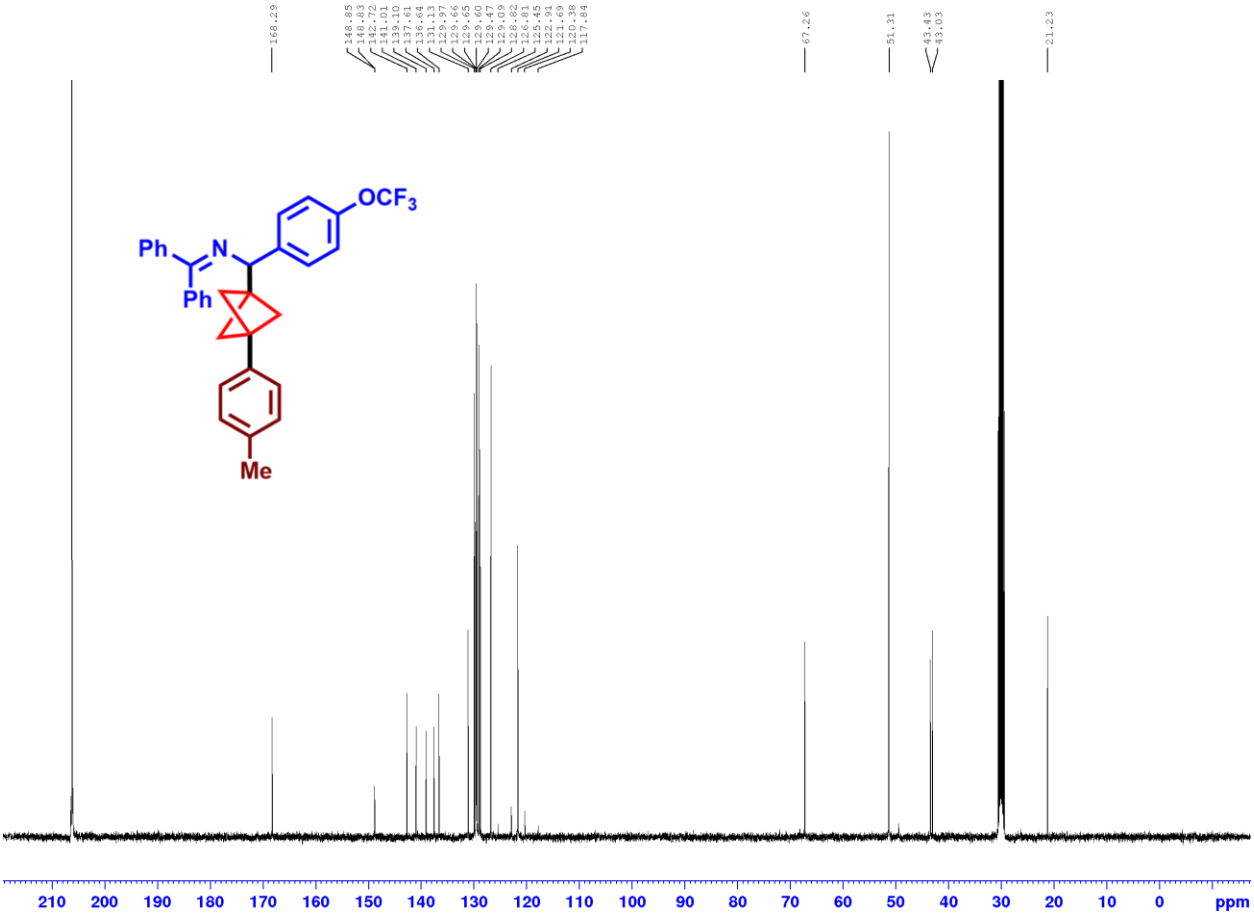
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of ***N*-((3-(bicyclo[4.2.0]octa-1,3,5-trien-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bc)**



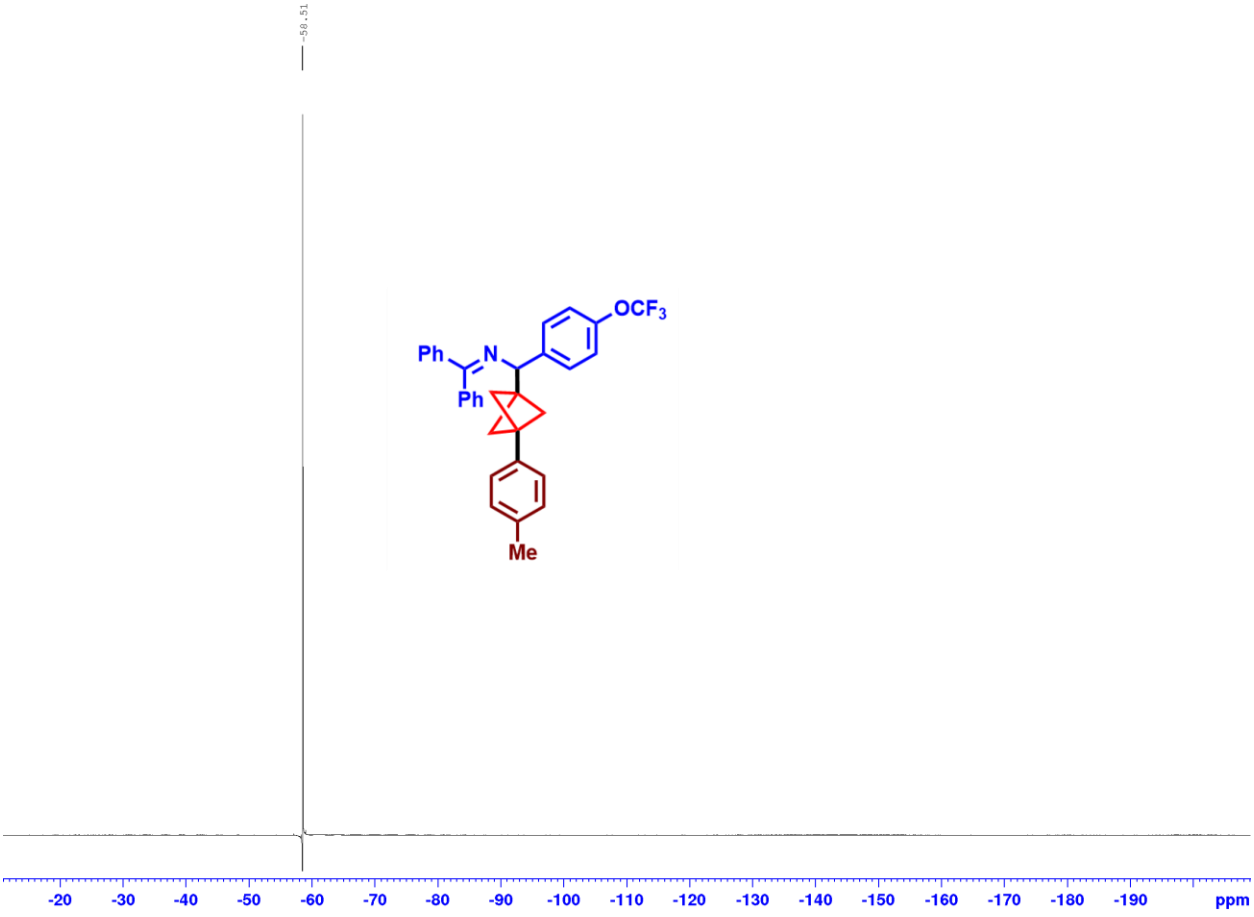
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **1,1-diphenyl-N-((3-(*p*-tolyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bd)**



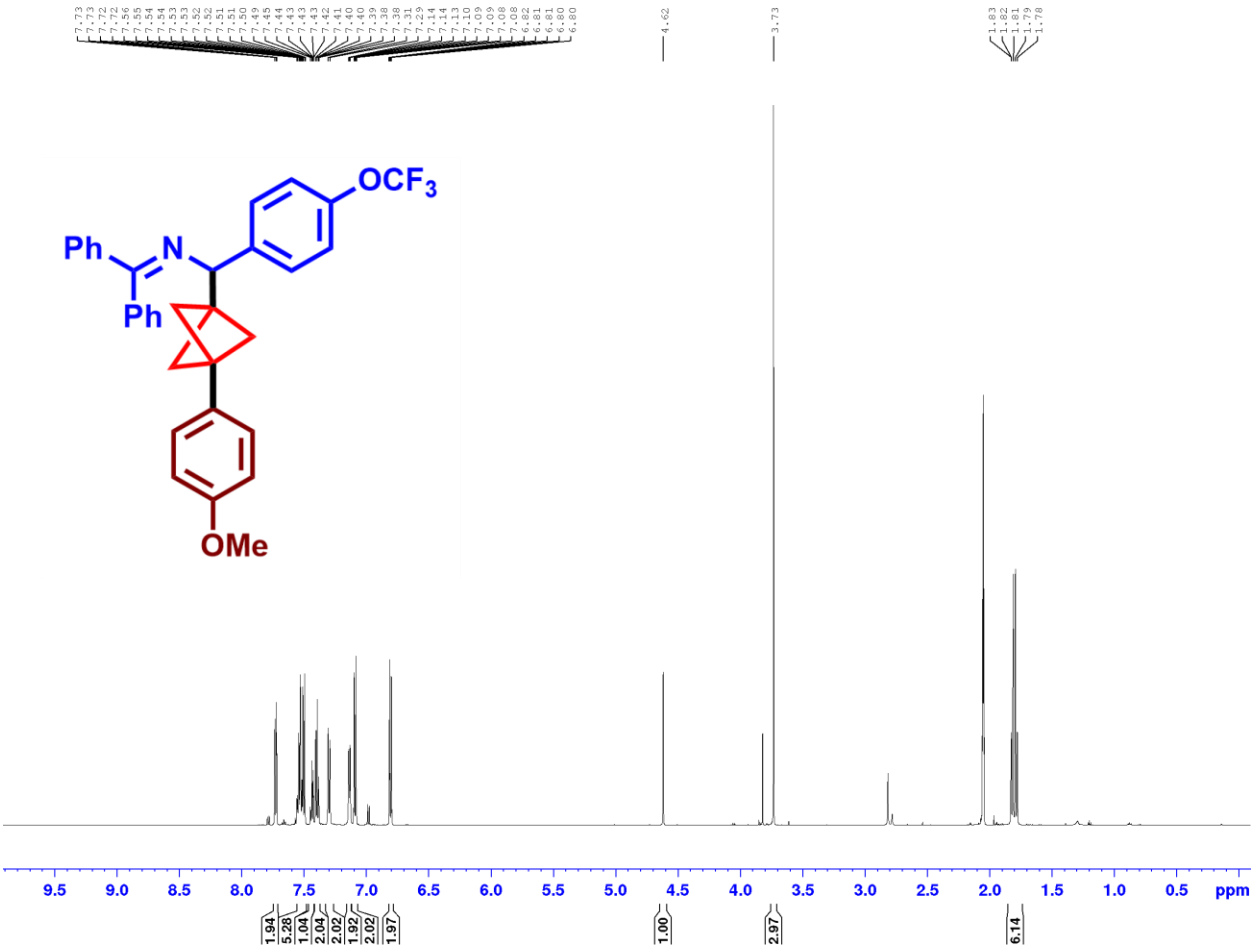
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of **1,1-diphenyl-N-((3-(*p*-tolyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bd)**



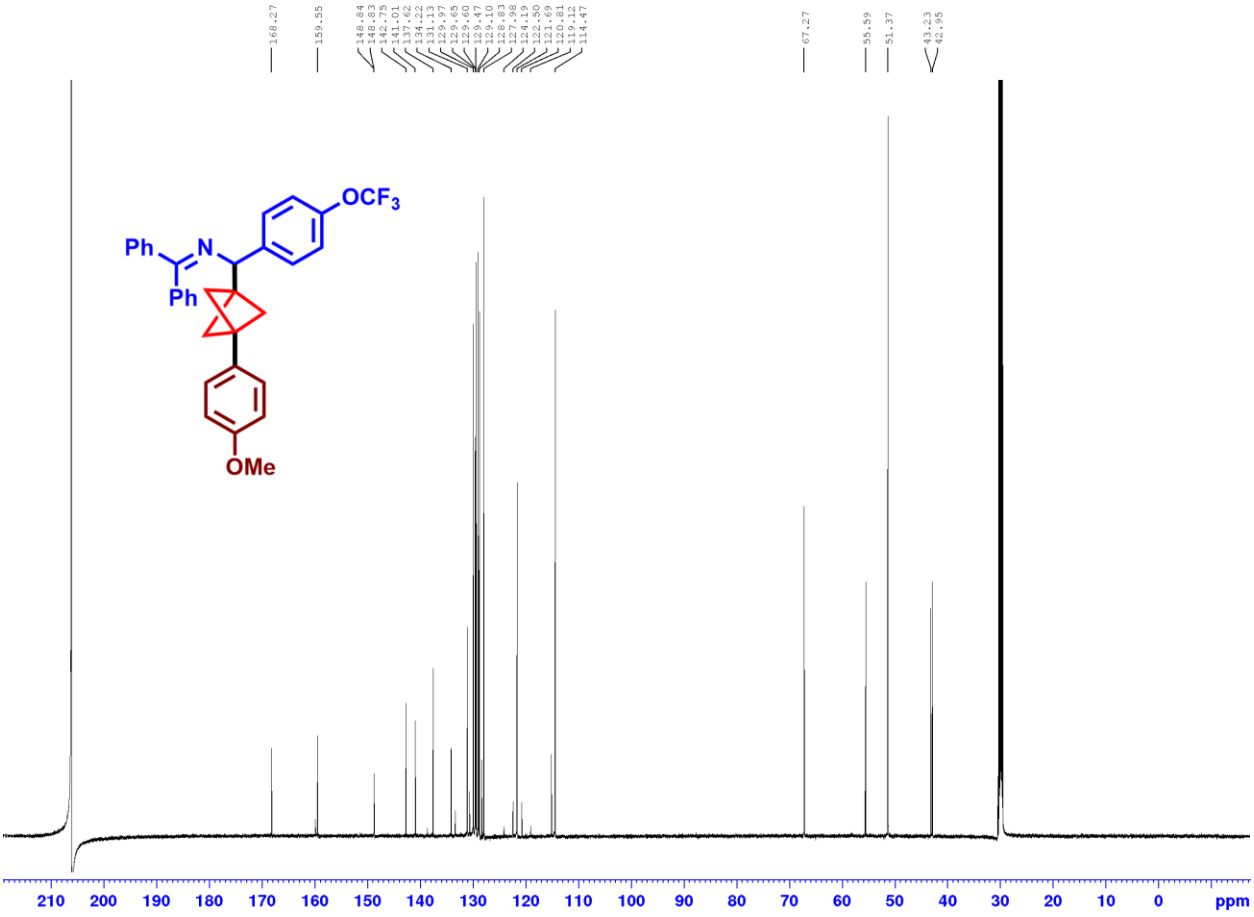
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of **1,1-diphenyl-N-((3-(*p*-tolyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bd)**



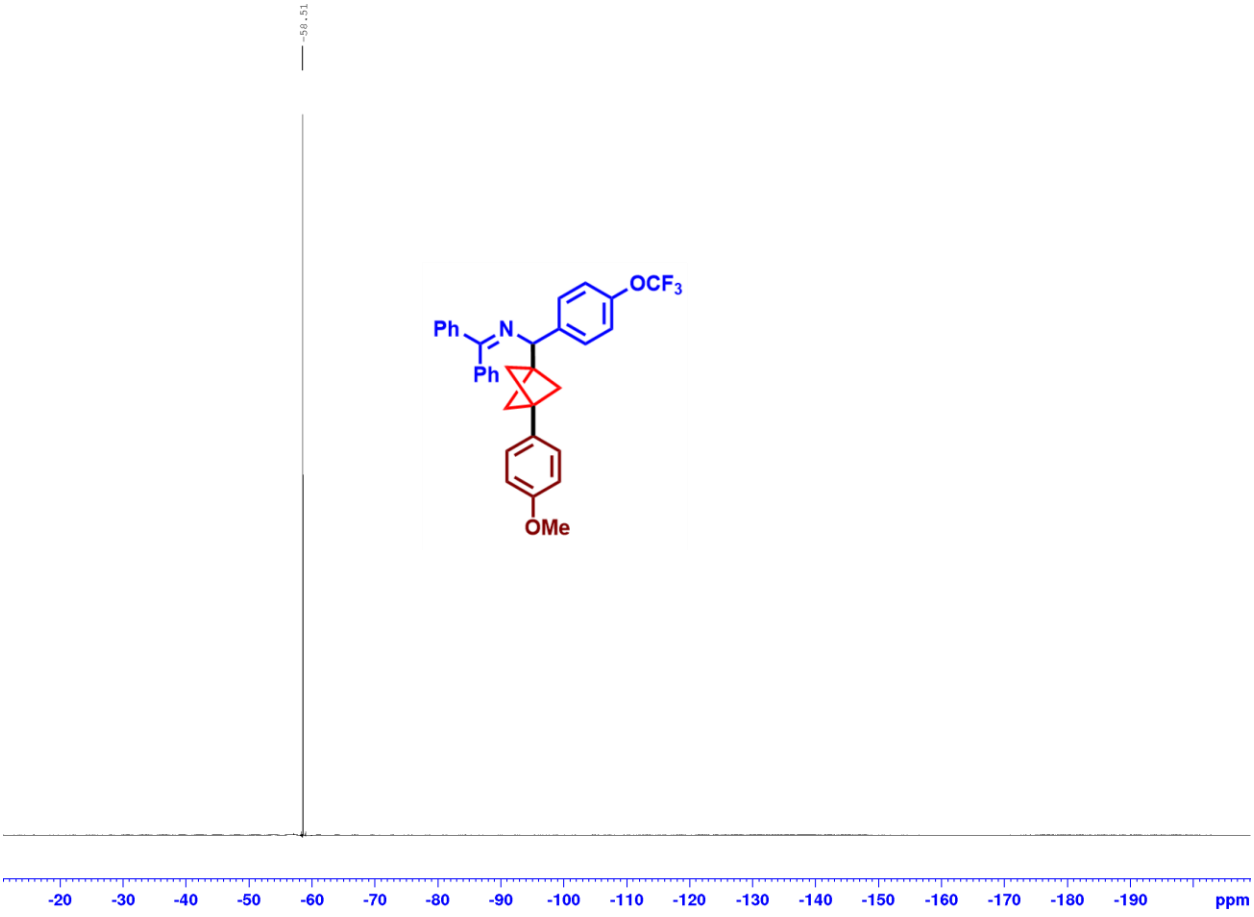
^{1}H NMR spectrum ($(CD_3)_2CO$, 600 MHz) of ***N*-((3-(4-methoxyphenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8be)**



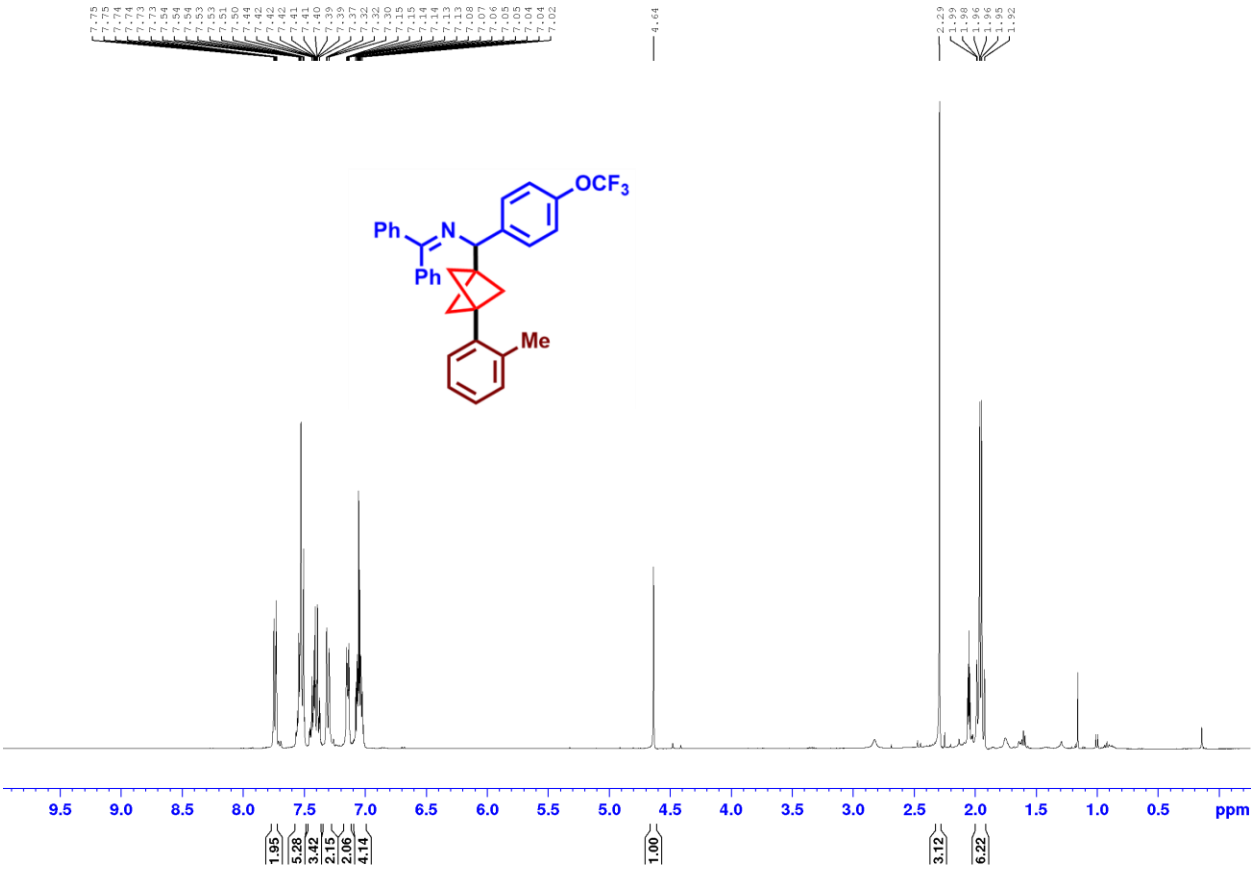
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 125 MHz) of ***N*-((3-(4-methoxyphenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8be)**



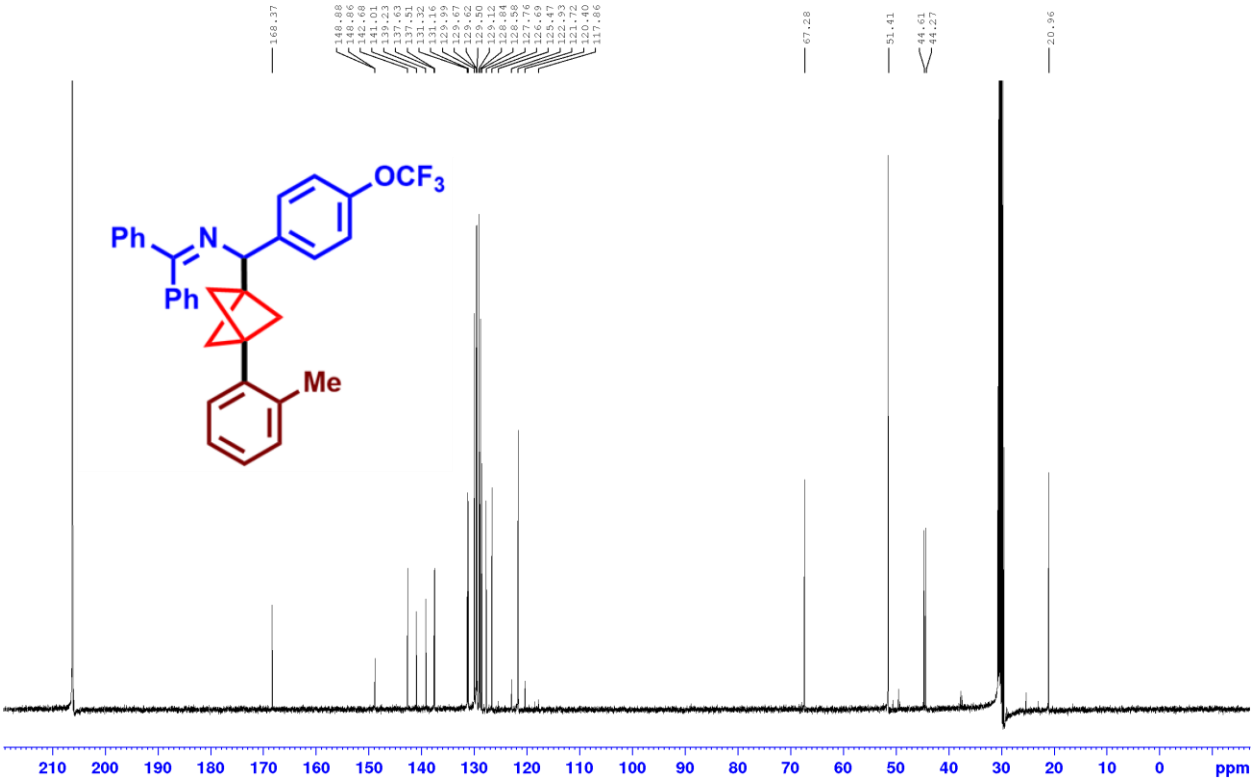
^{19}F NMR spectrum ($(CD_3)_2CO$, 565 MHz) of ***N*-((3-(4-methoxyphenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8be)**



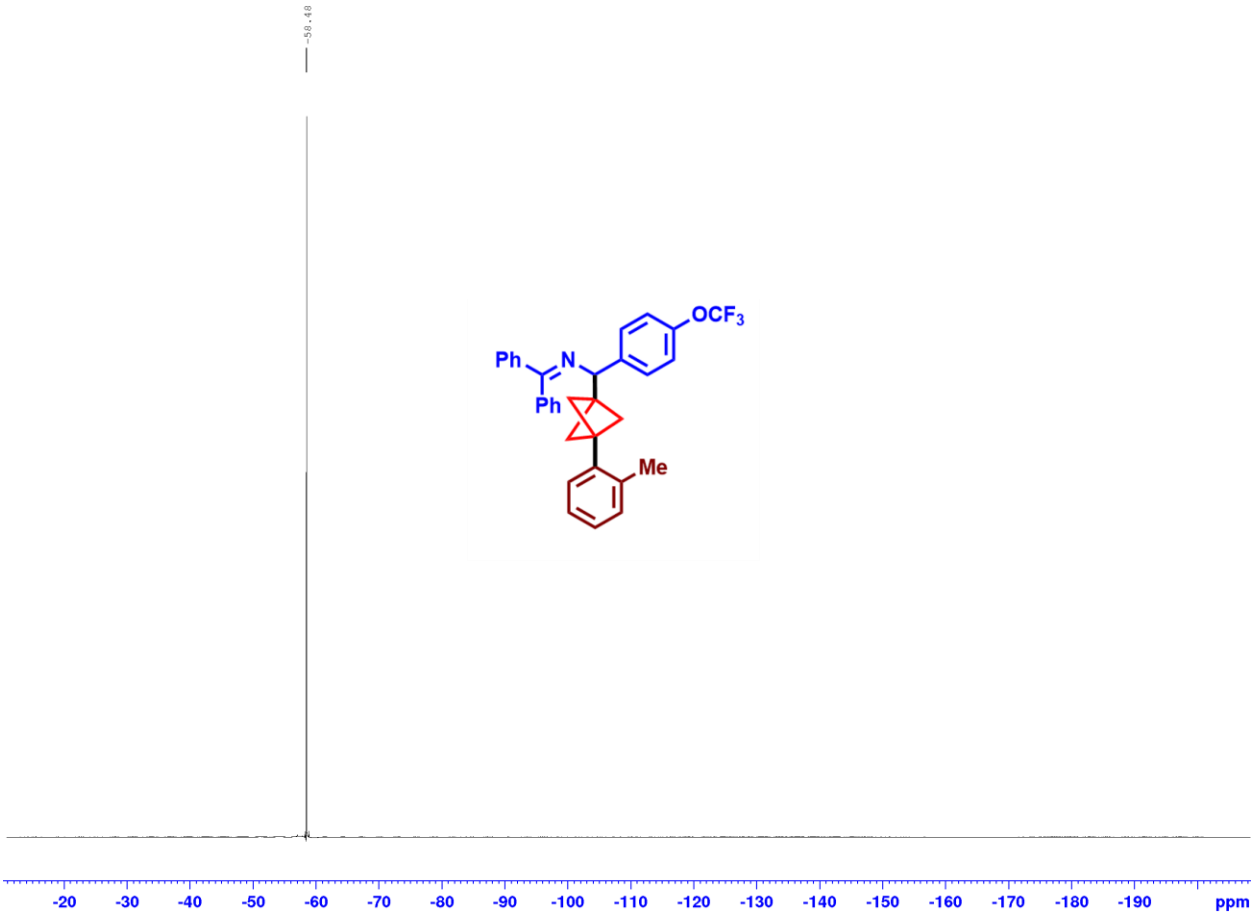
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **1,1-diphenyl-*N*-((3-(o-tolyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bf)**



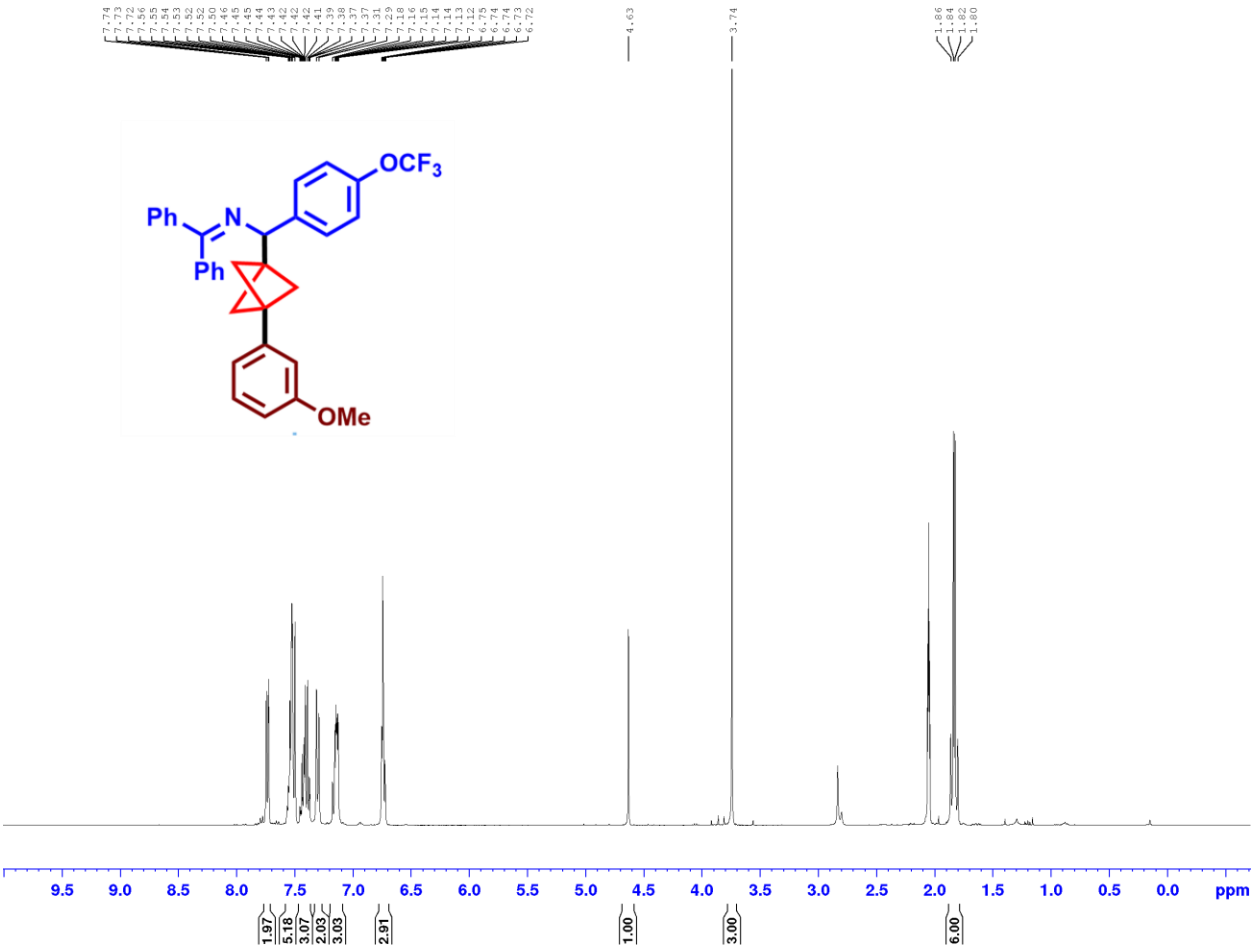
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of **1,1-diphenyl-*N*-((3-(o-tolyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bf)**



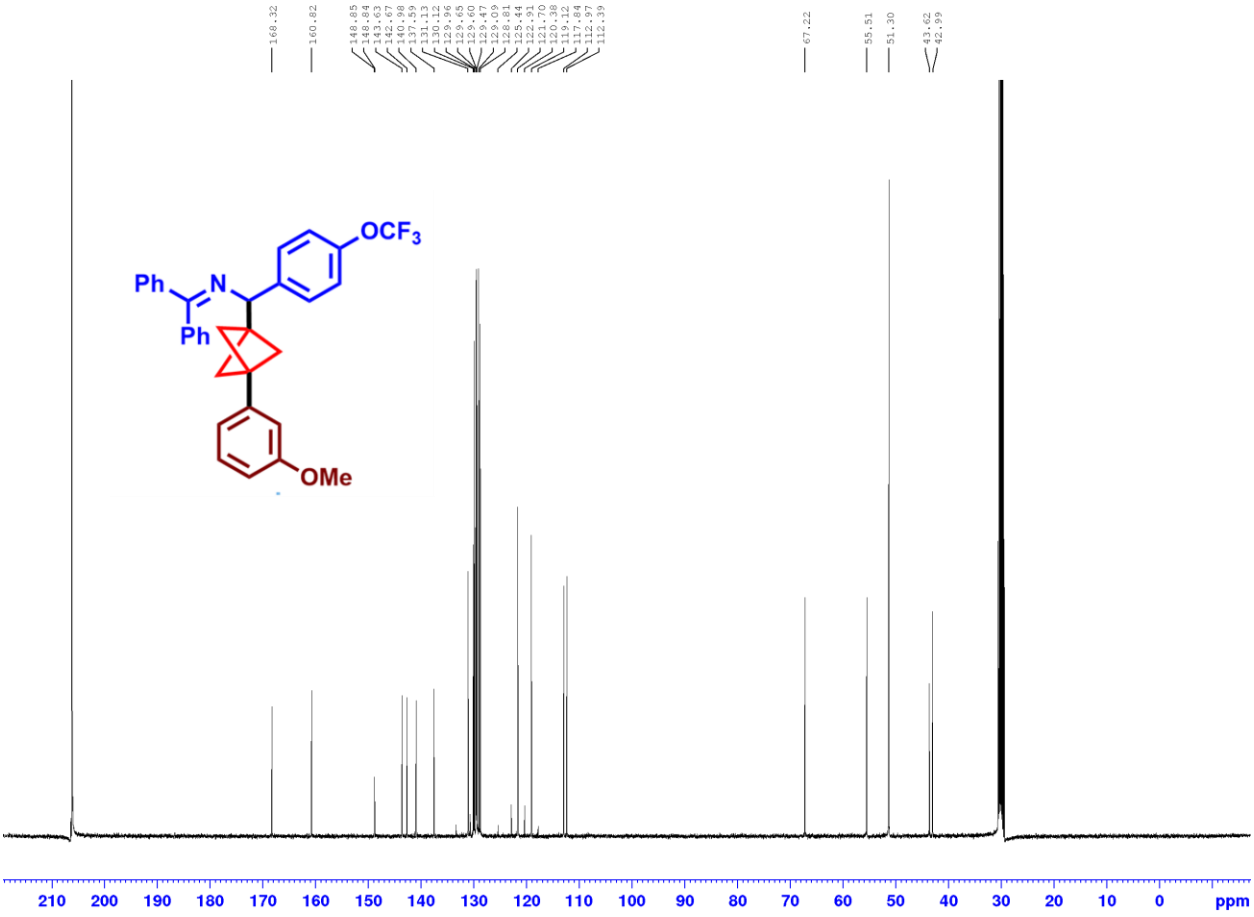
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of **1,1-diphenyl-*N*-((3-(o-tolyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bf)**



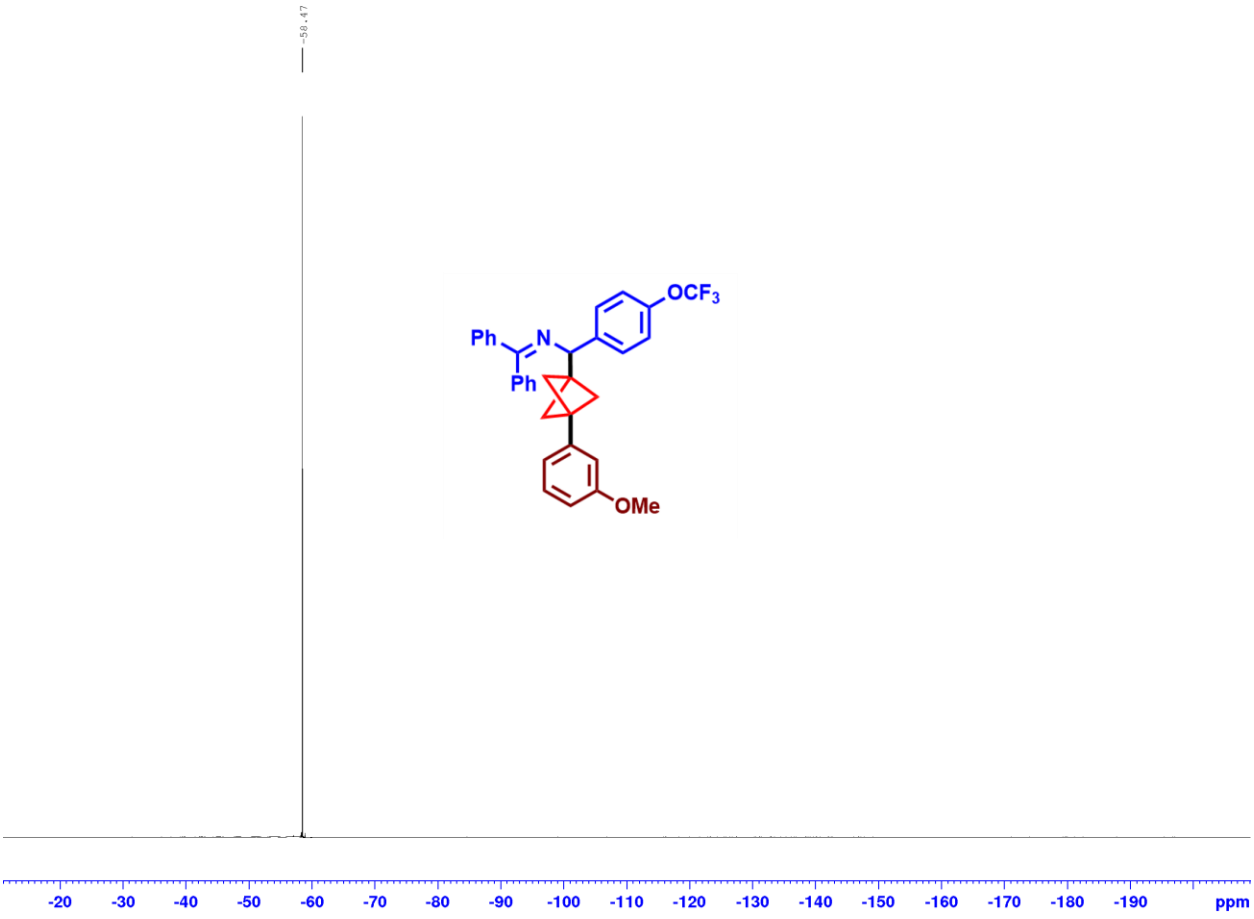
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N*-((3-(3-methoxyphenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bg)**



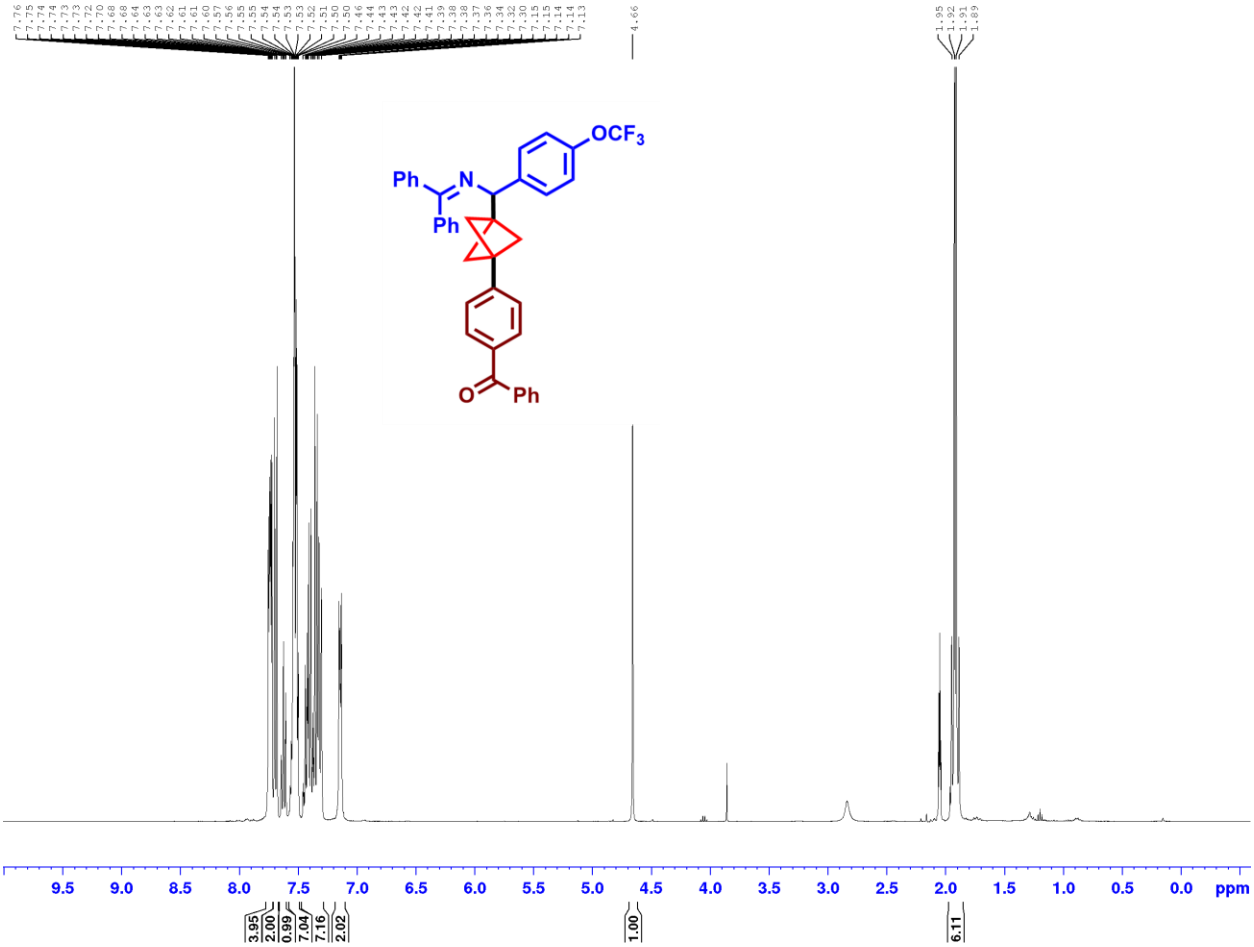
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N*-((3-(3-methoxyphenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bg)**



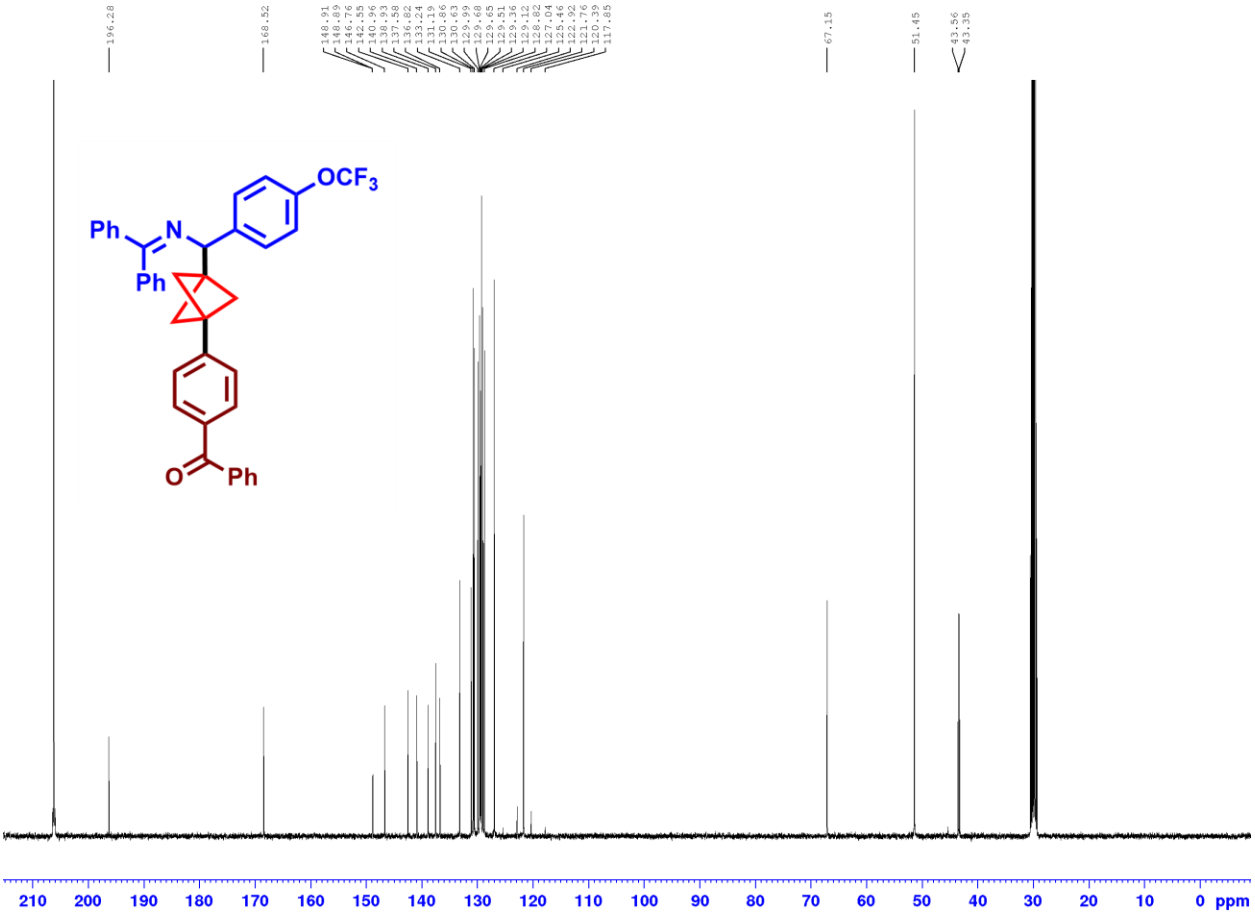
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of ***N*-((3-(3-methoxyphenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bg)**



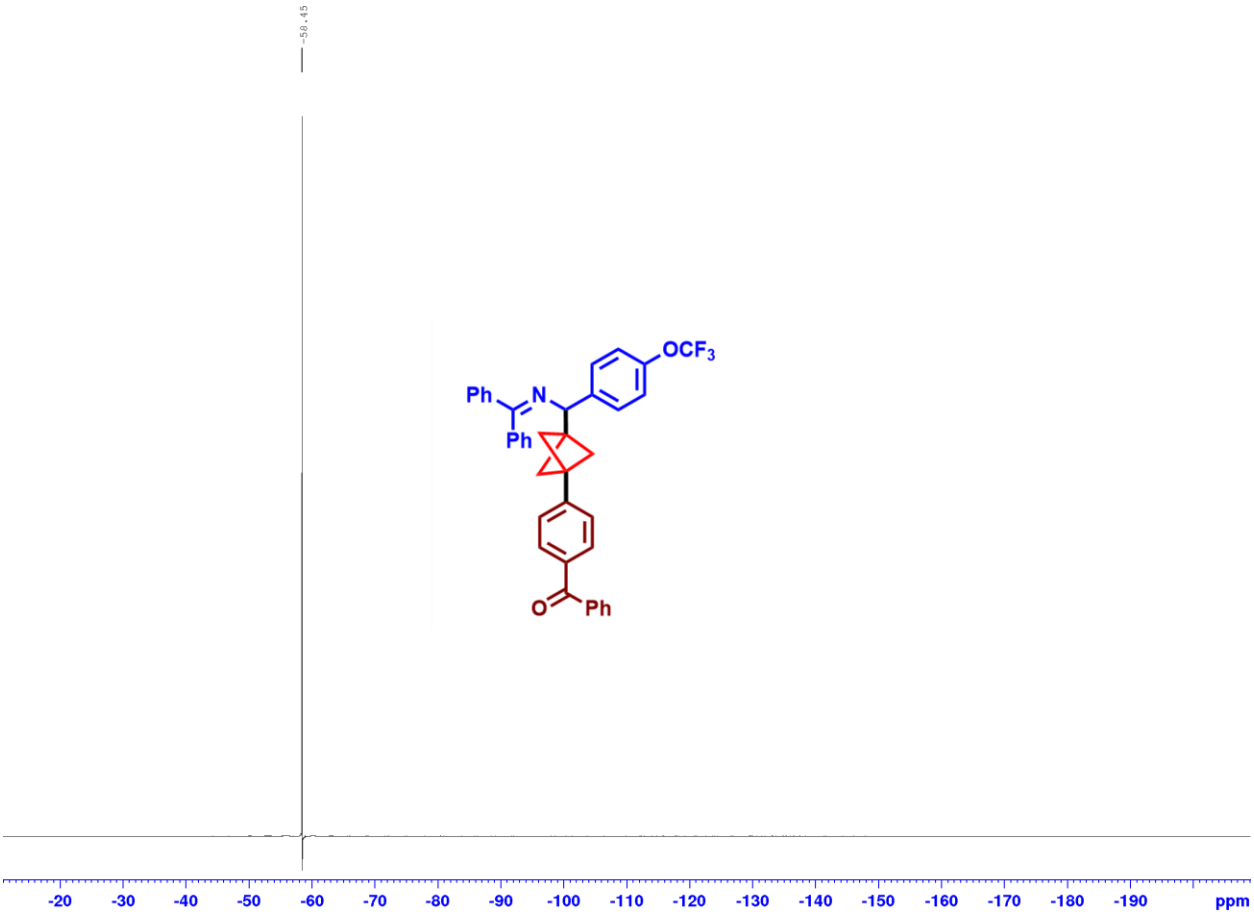
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **4-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)phenyl)(phenyl)methanone (8bh)**



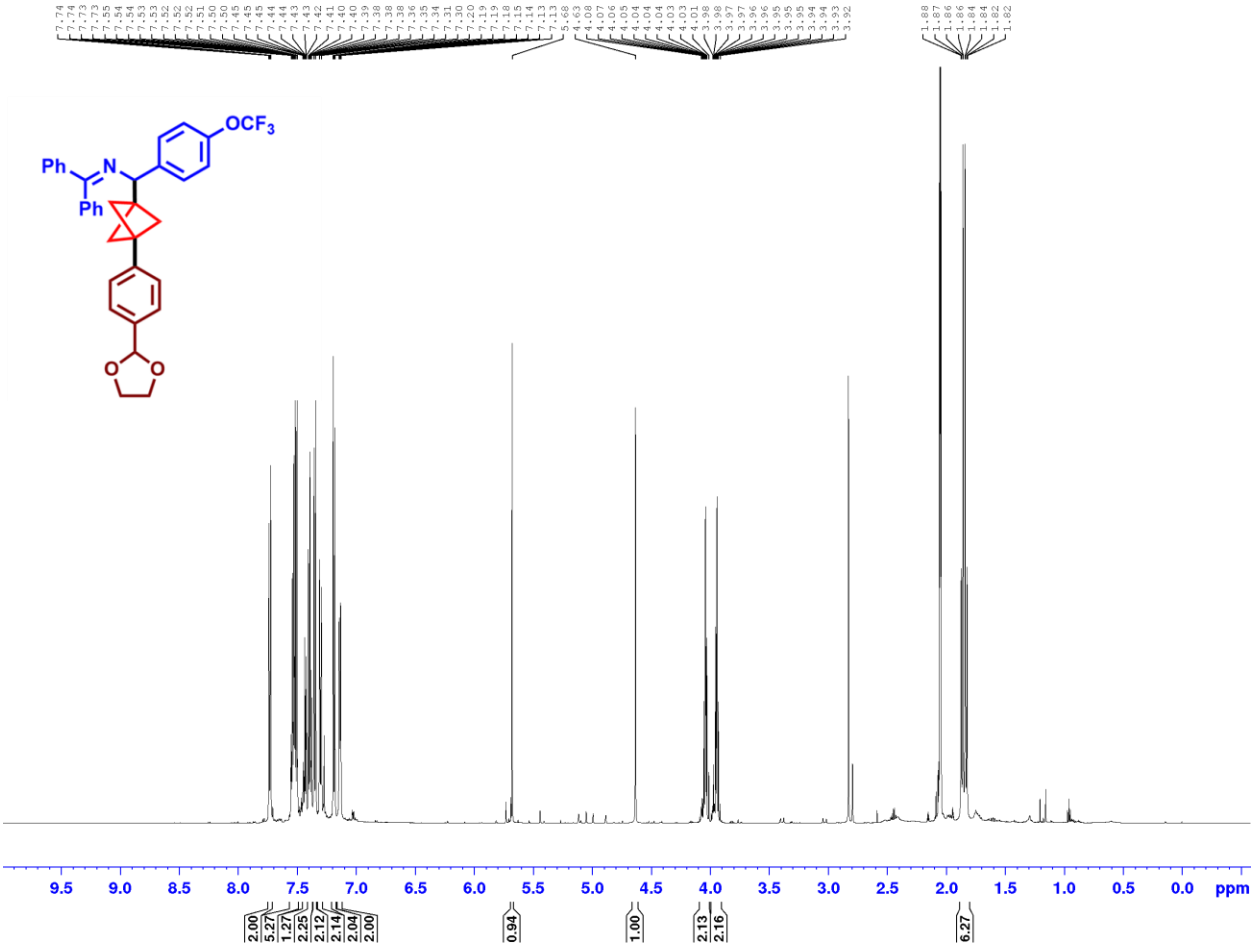
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of **4-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)phenyl)(phenyl)methanone (8bh)**



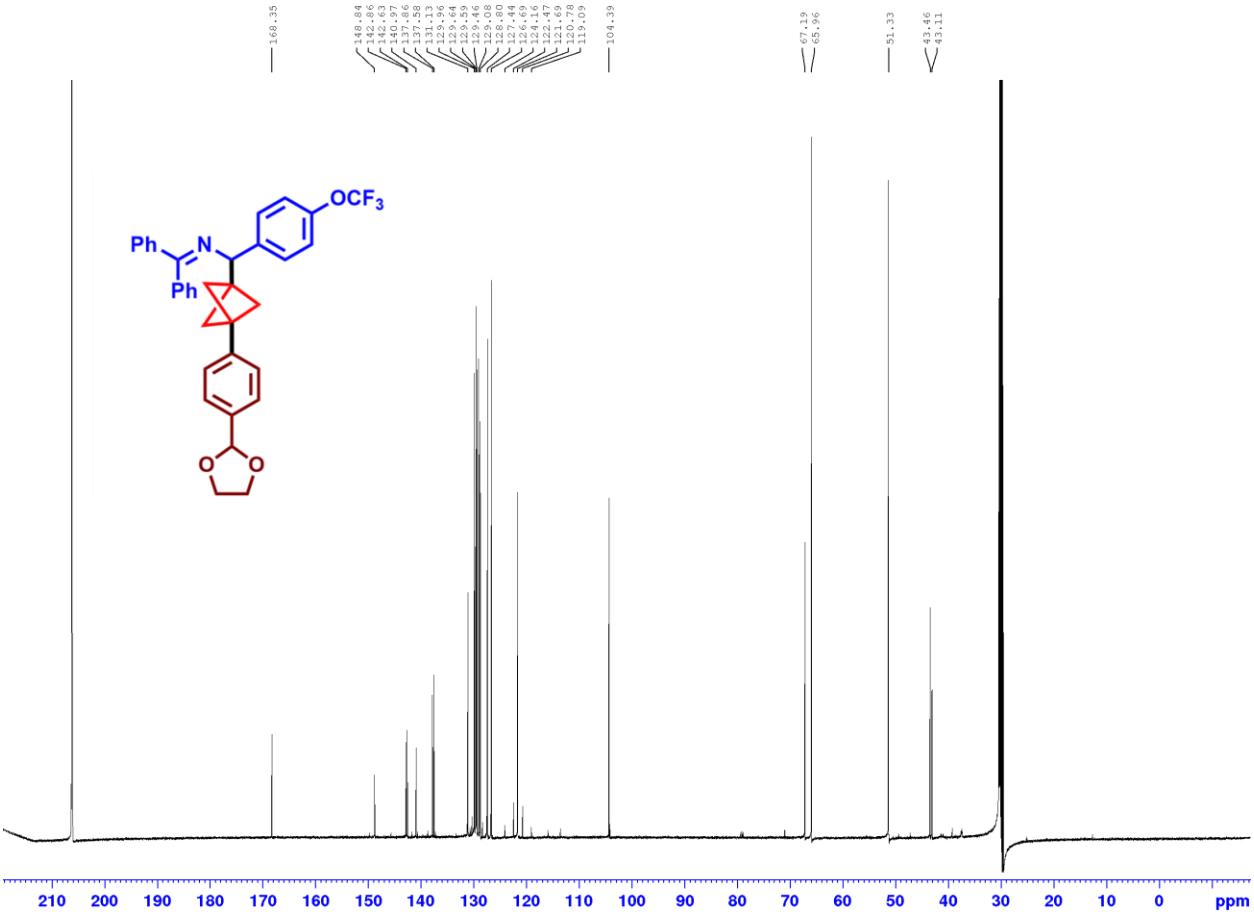
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of **4-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)phenyl)(phenyl)methanone (8bh)**



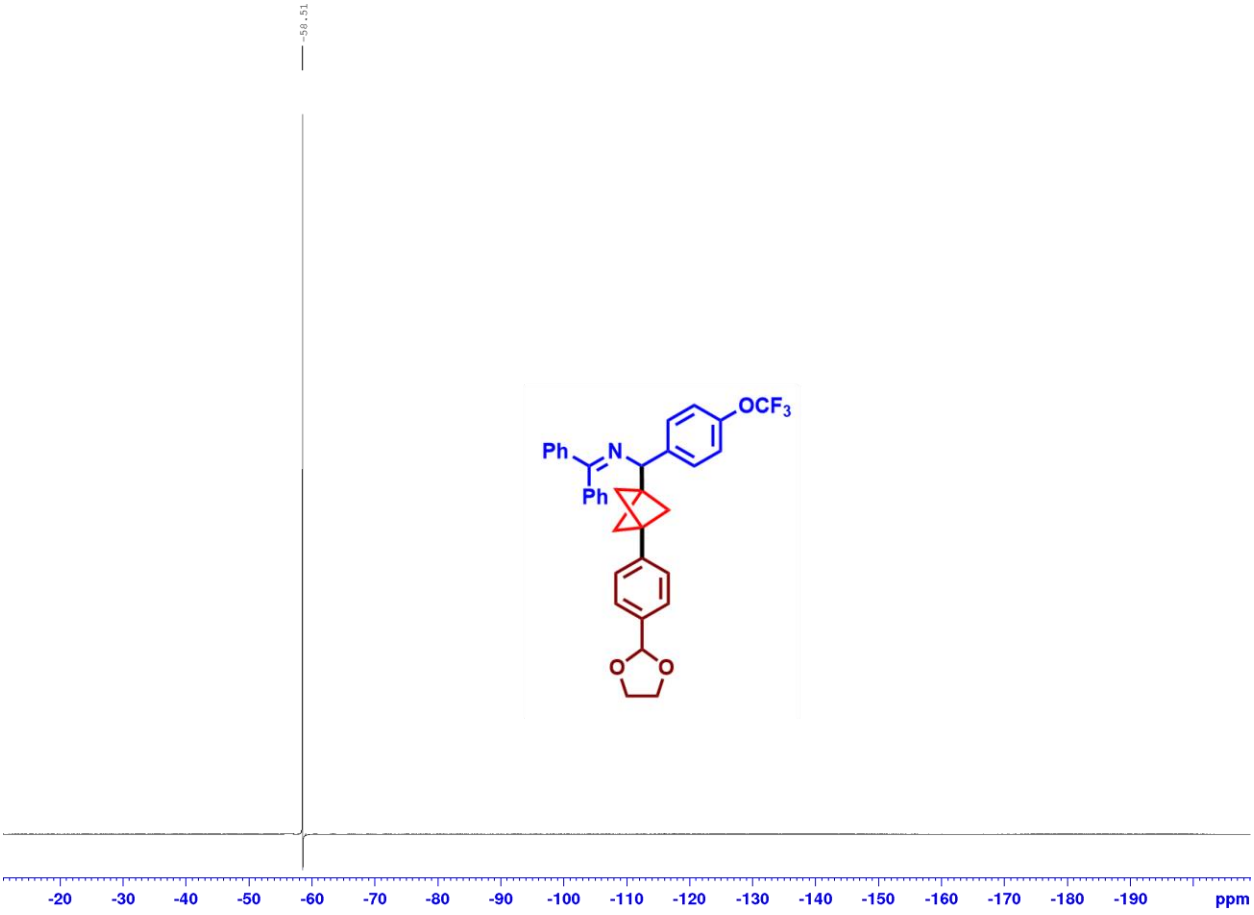
^{1}H NMR spectrum ($(CD_3)_2CO$, 600 MHz) of ***N*-((3-(4-(1,3-dioxolan-2-yl)phenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bi)**



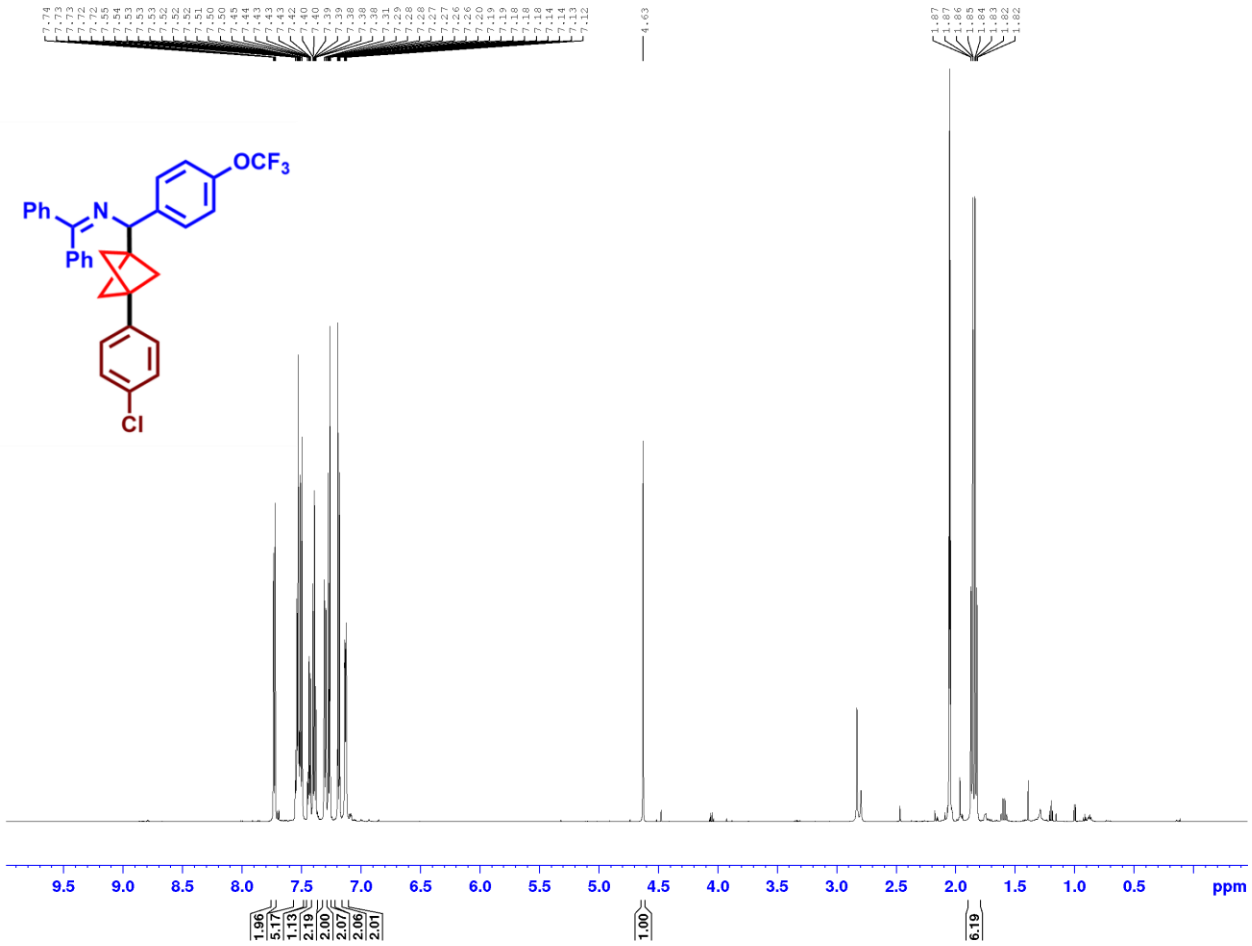
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 150 MHz) of ***N*-((3-(4-(1,3-dioxolan-2-yl)phenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bi)**



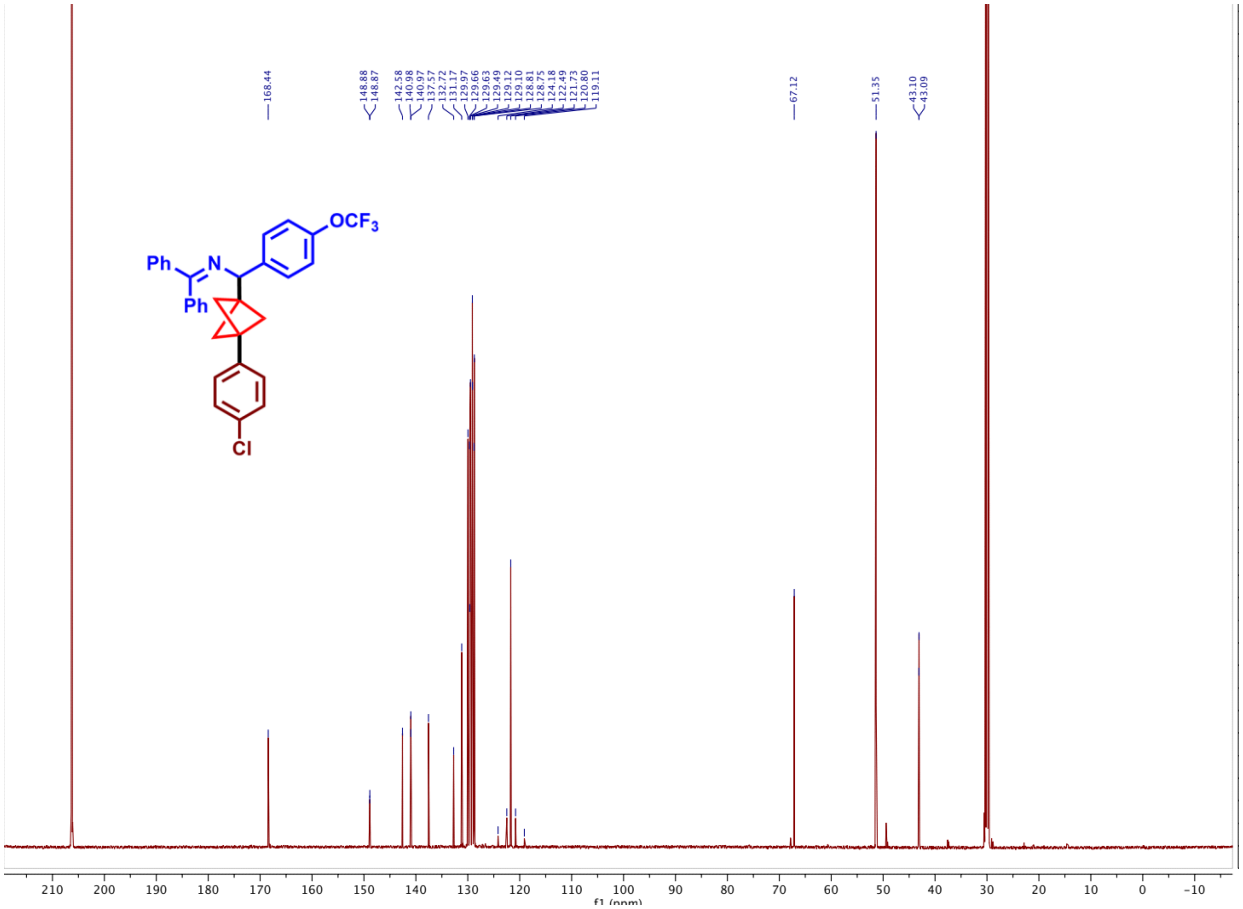
^{19}F NMR spectrum ($(CD_3)_2CO$, 565 MHz) of ***N*-((3-(4-(1,3-dioxolan-2-yl)phenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bi)**



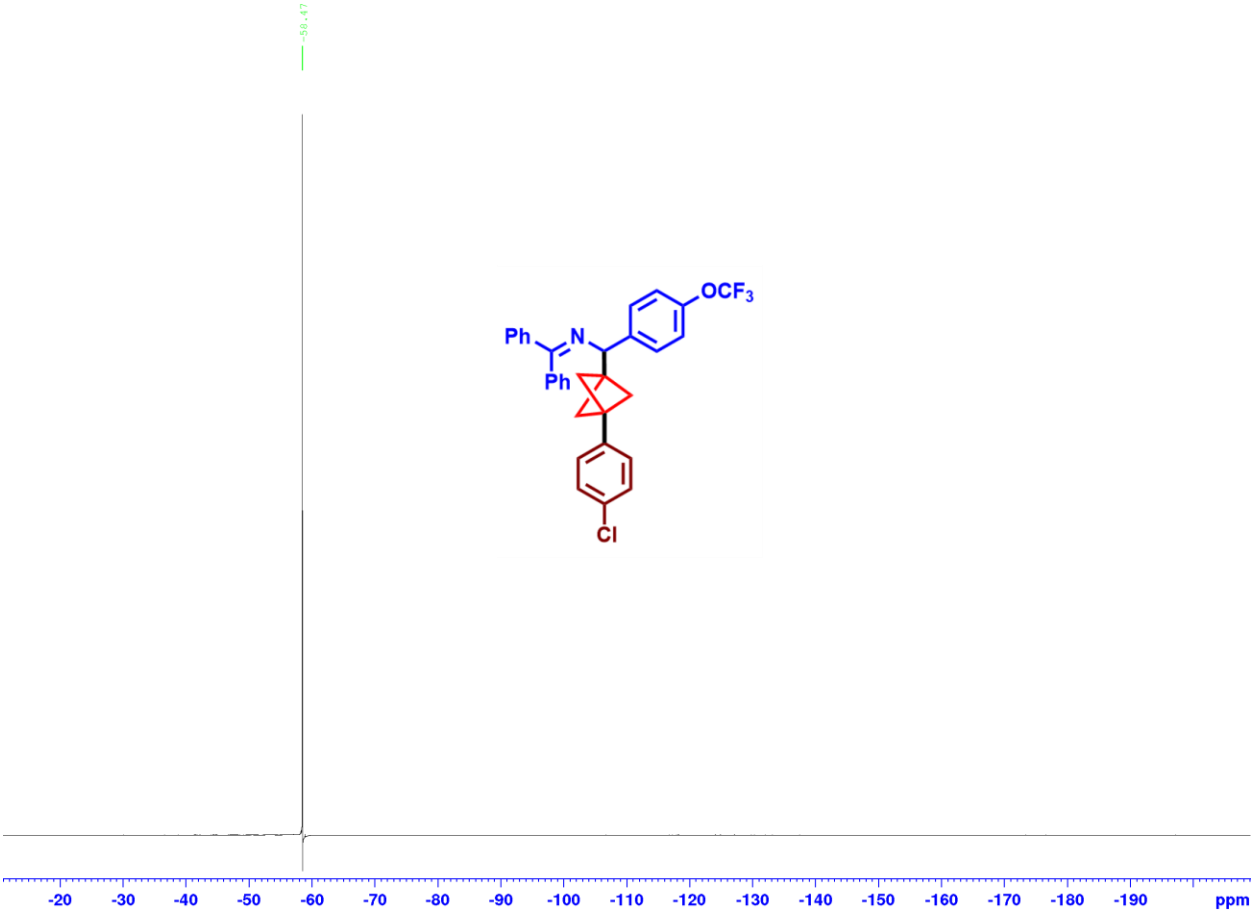
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N*-((3-(4-chlorophenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bj)**



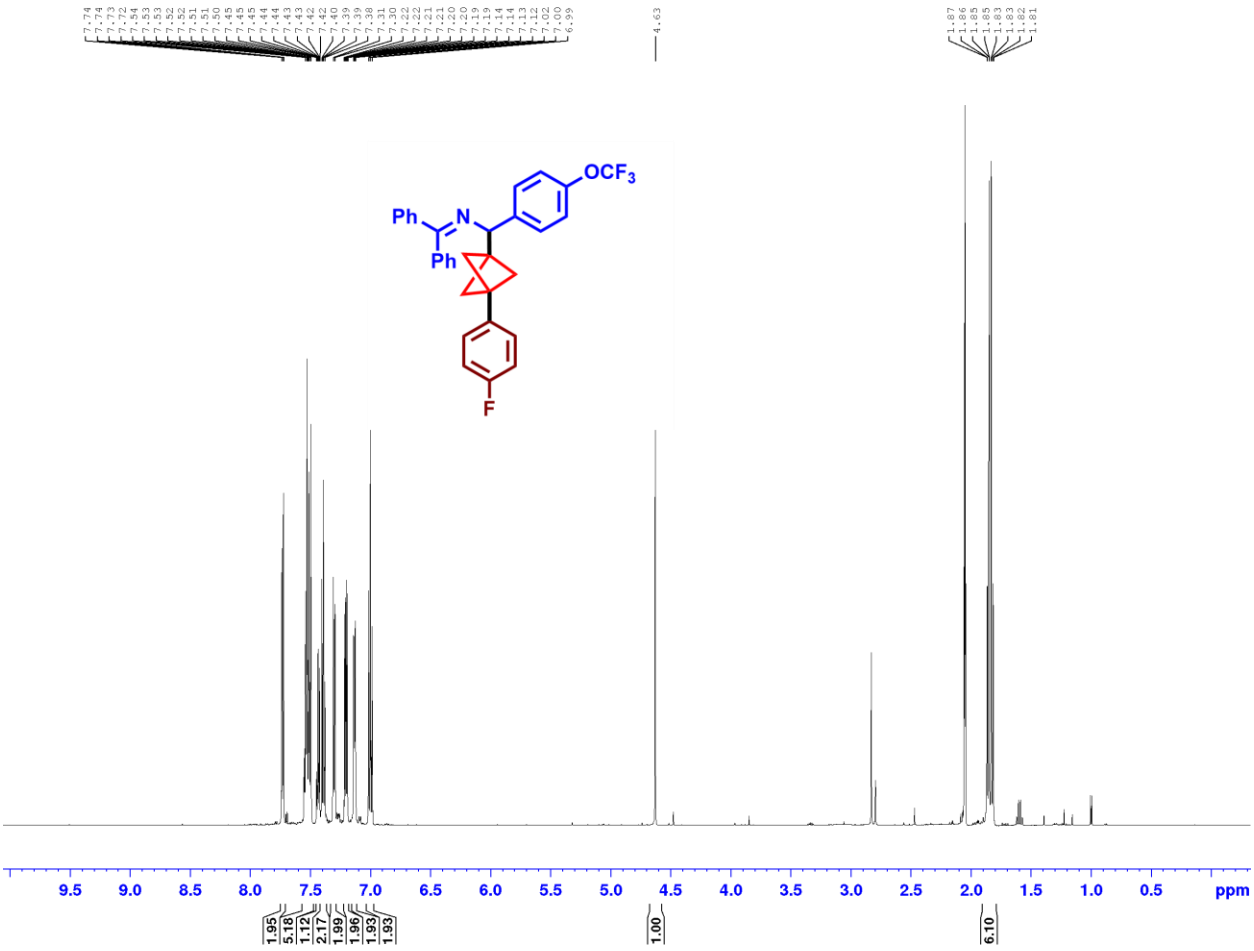
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N*-((3-(4-chlorophenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bj)**



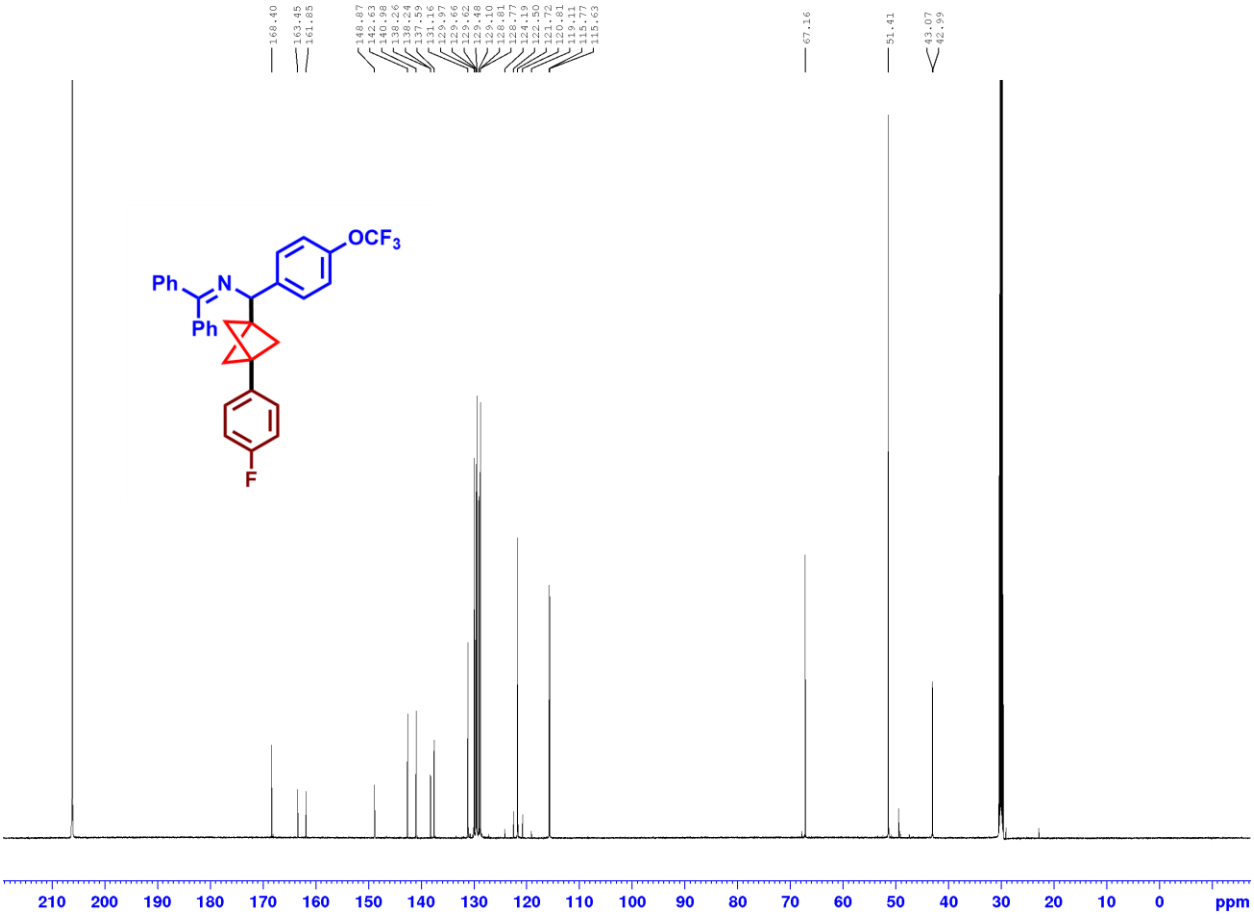
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of ***N*-((3-(4-chlorophenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bj)**



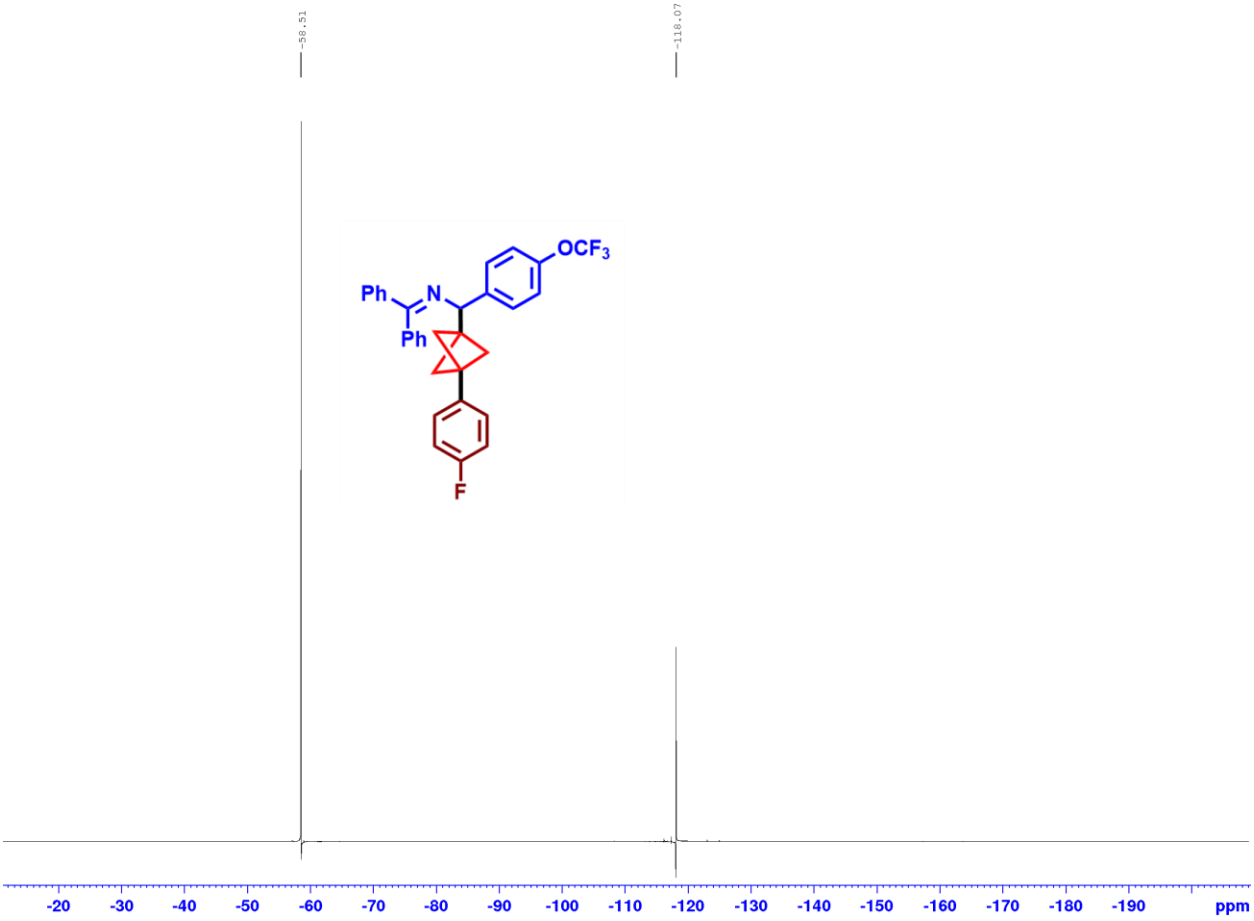
^{1}H NMR spectrum ($(CD_3)_2CO$, 600 MHz) of ***N*-((3-(4-fluorophenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bk)**



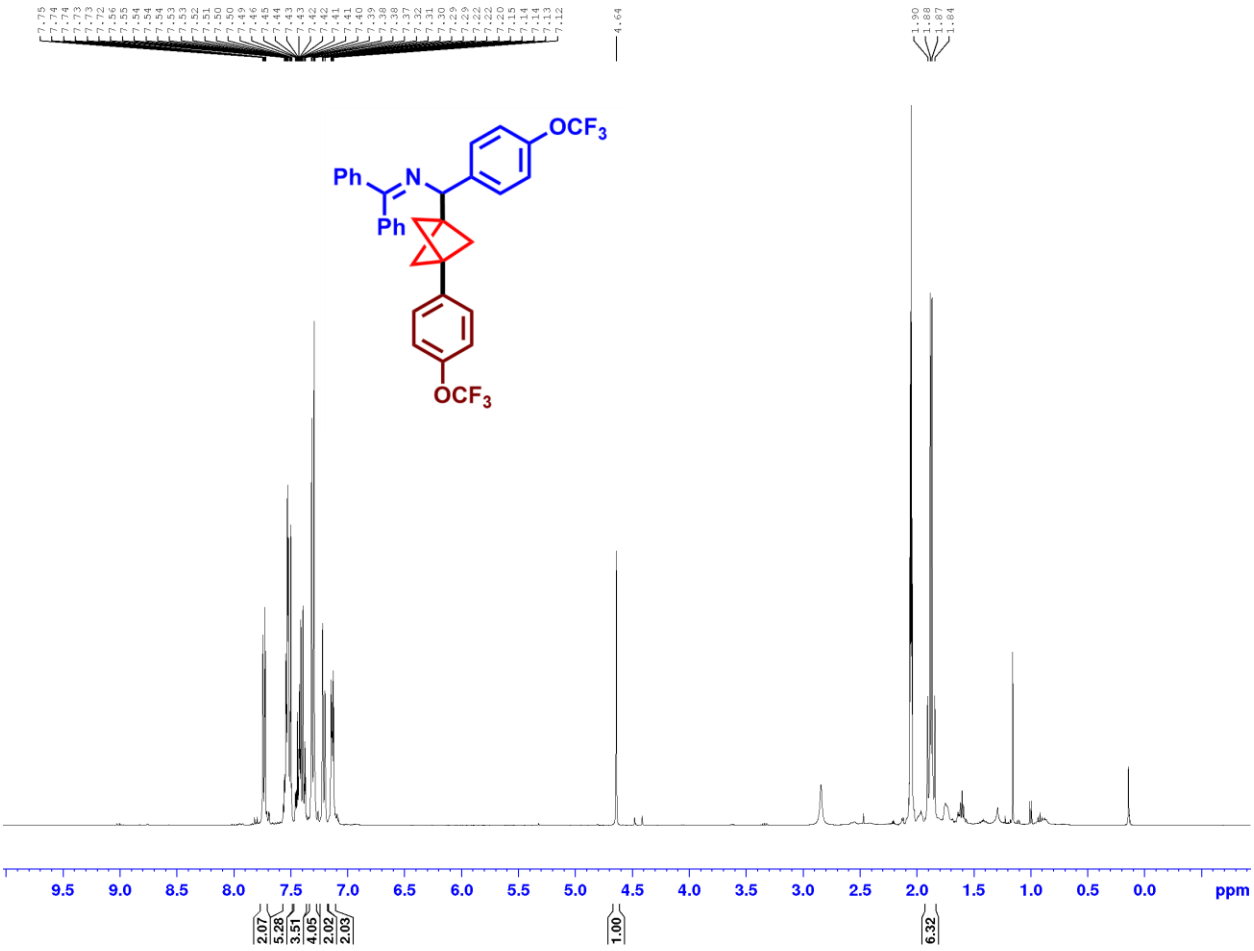
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 150 MHz) of ***N*-((3-(4-fluorophenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bk)**



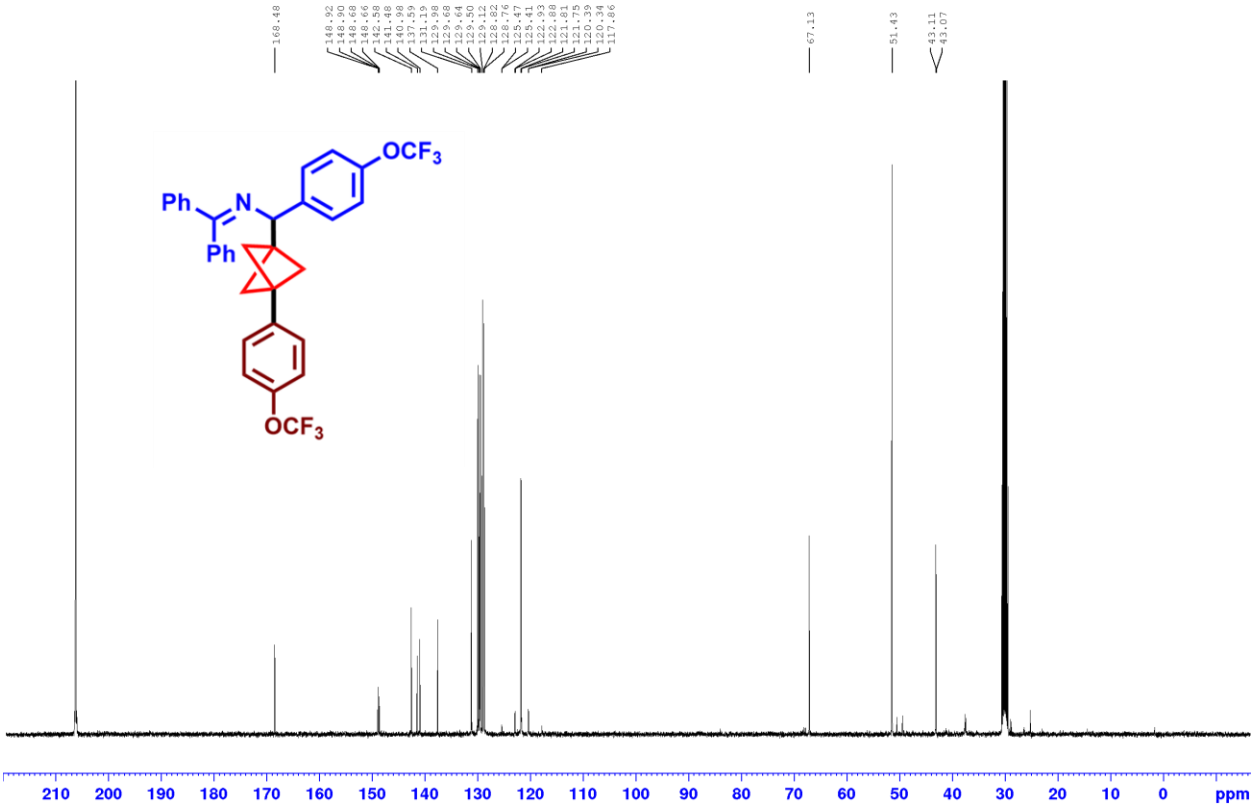
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of ***N*-((3-(4-fluorophenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bk)**



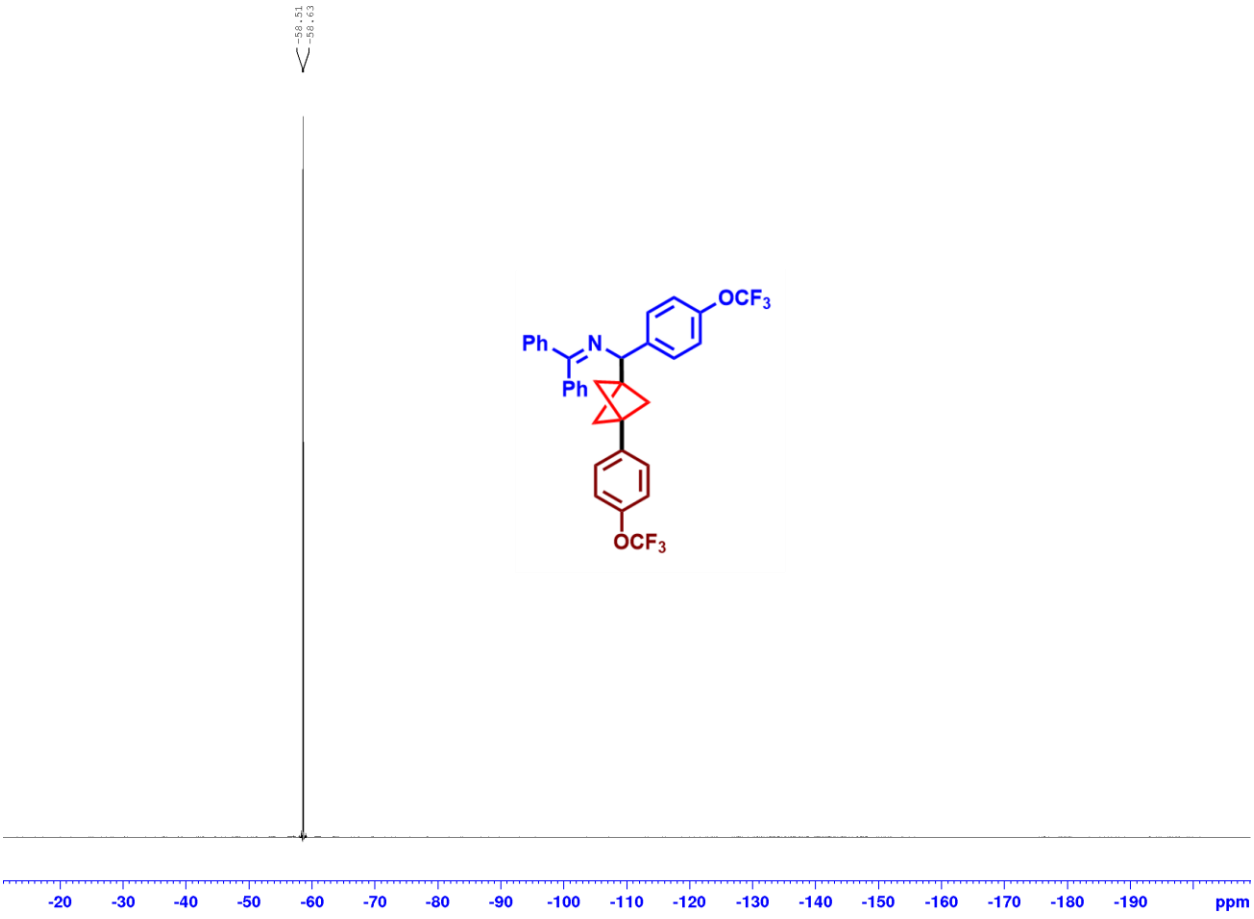
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **1,1-diphenyl-*N*-((4-(trifluoromethoxy)phenyl)(3-(4-(trifluoromethoxy)phenyl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (8bl)**



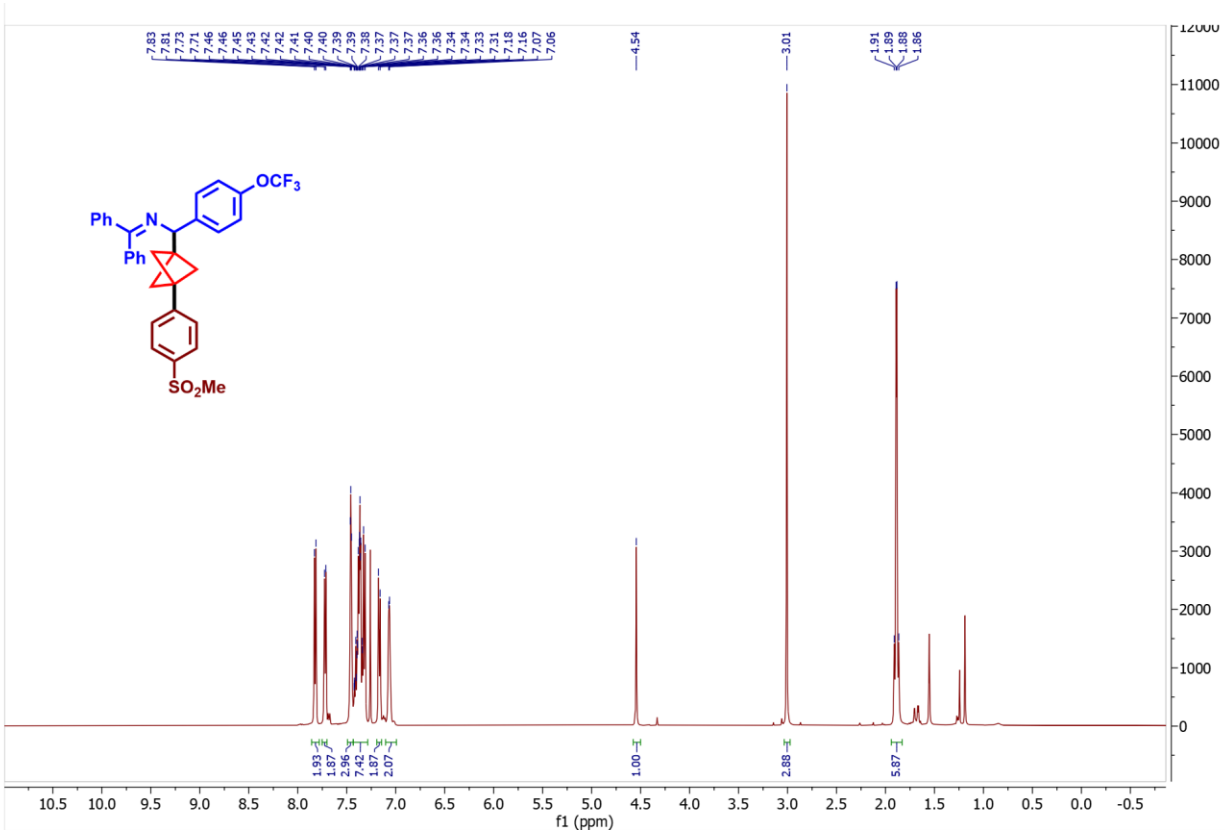
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of **1,1-diphenyl-*N*-((4-(trifluoromethoxy)phenyl)(3-(4-(trifluoromethoxy)phenyl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (8bl)**



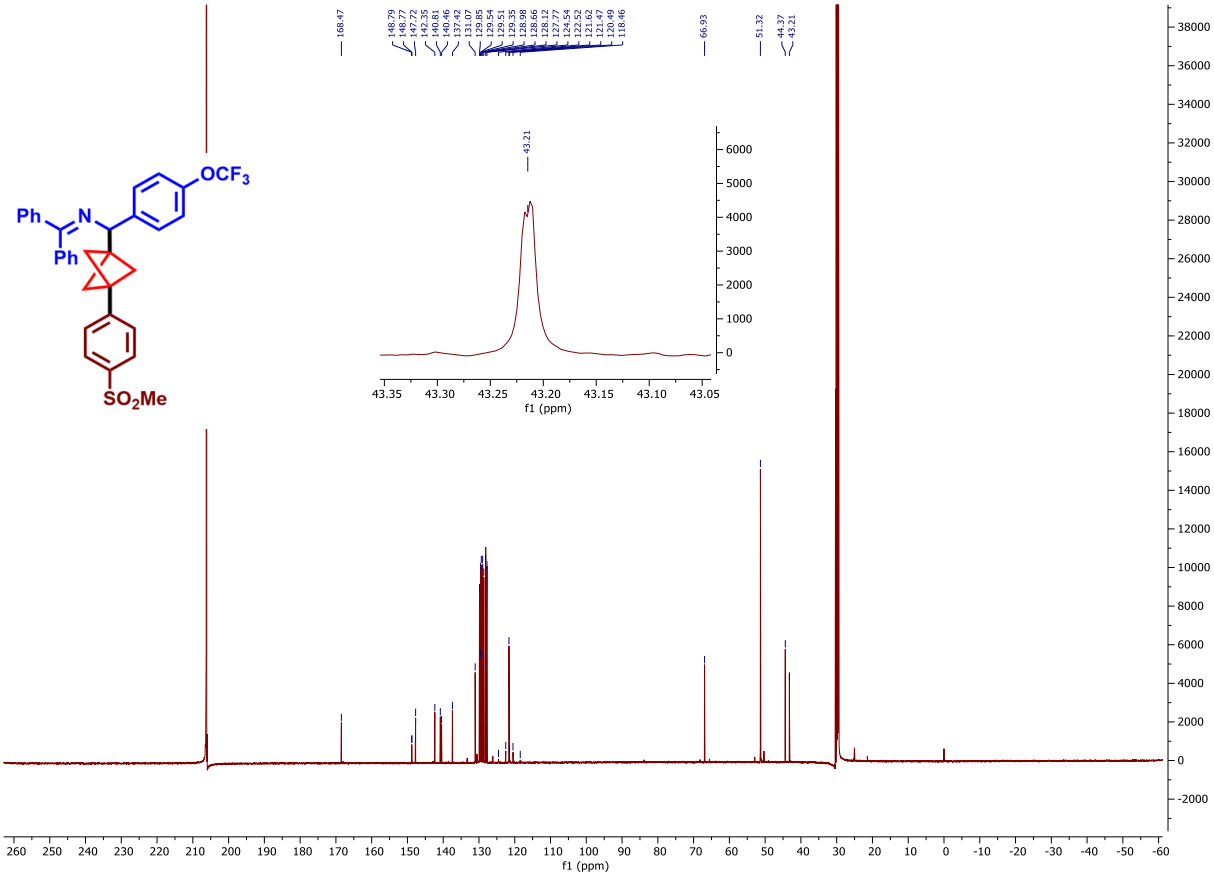
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of **1,1-diphenyl-*N*-((4-(trifluoromethoxy)phenyl)(3-(4-(trifluoromethoxy)phenyl)bicyclo[1.1.1]pentan-1-yl)methyl)methanimine (8bl)**



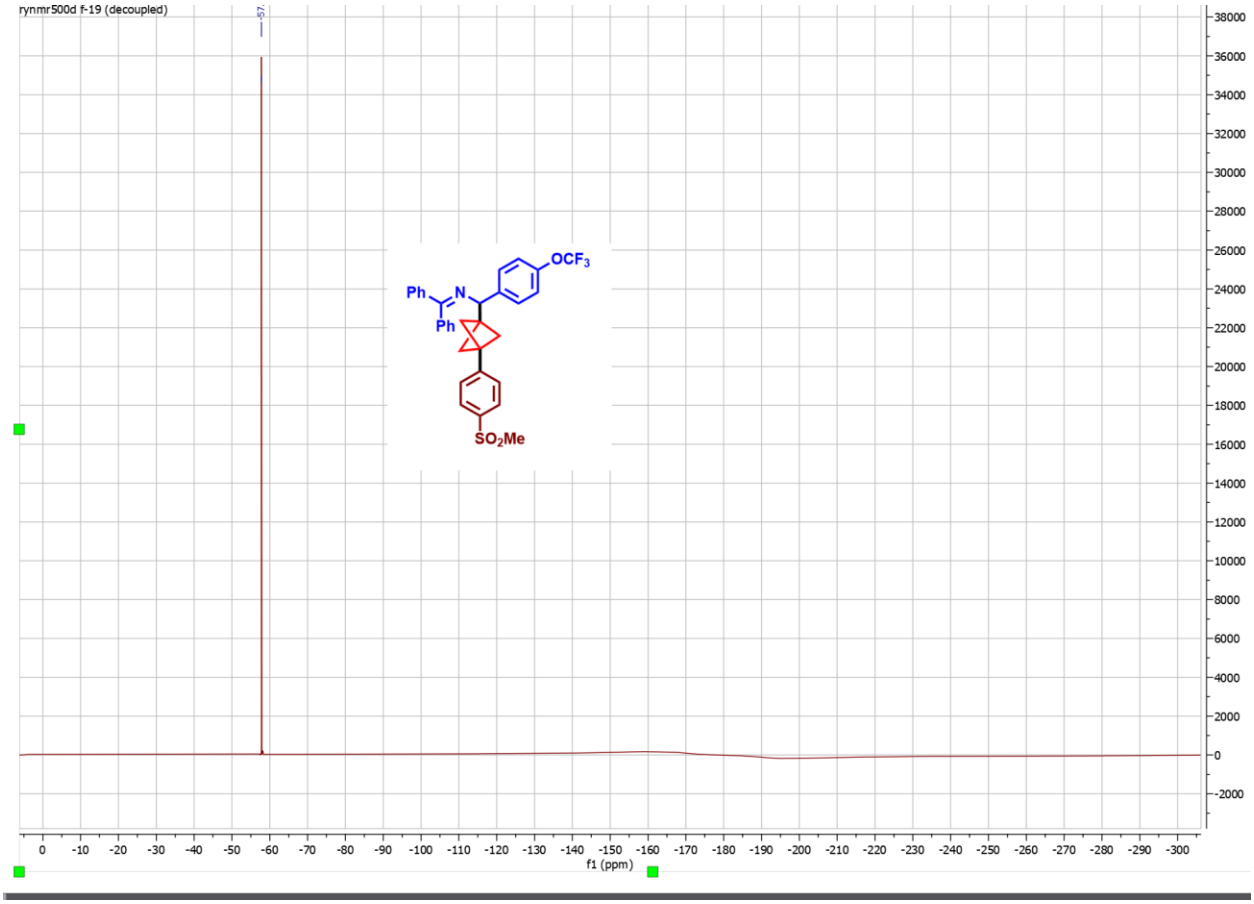
^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of ***N*-((3-(4-(methylsulfonyl)phenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bm)**



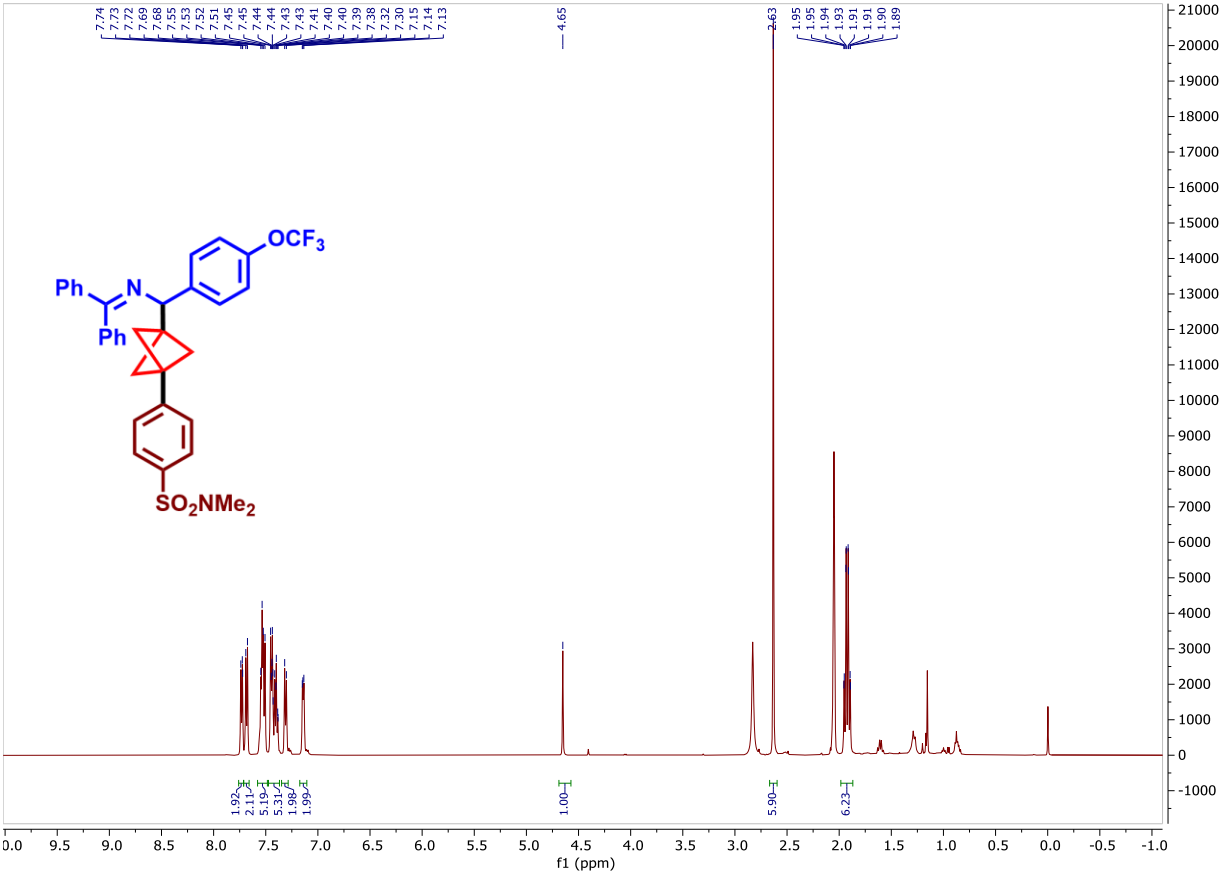
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 126 MHz) of ***N*-((3-(4-(methylsulfonyl)phenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bm)**



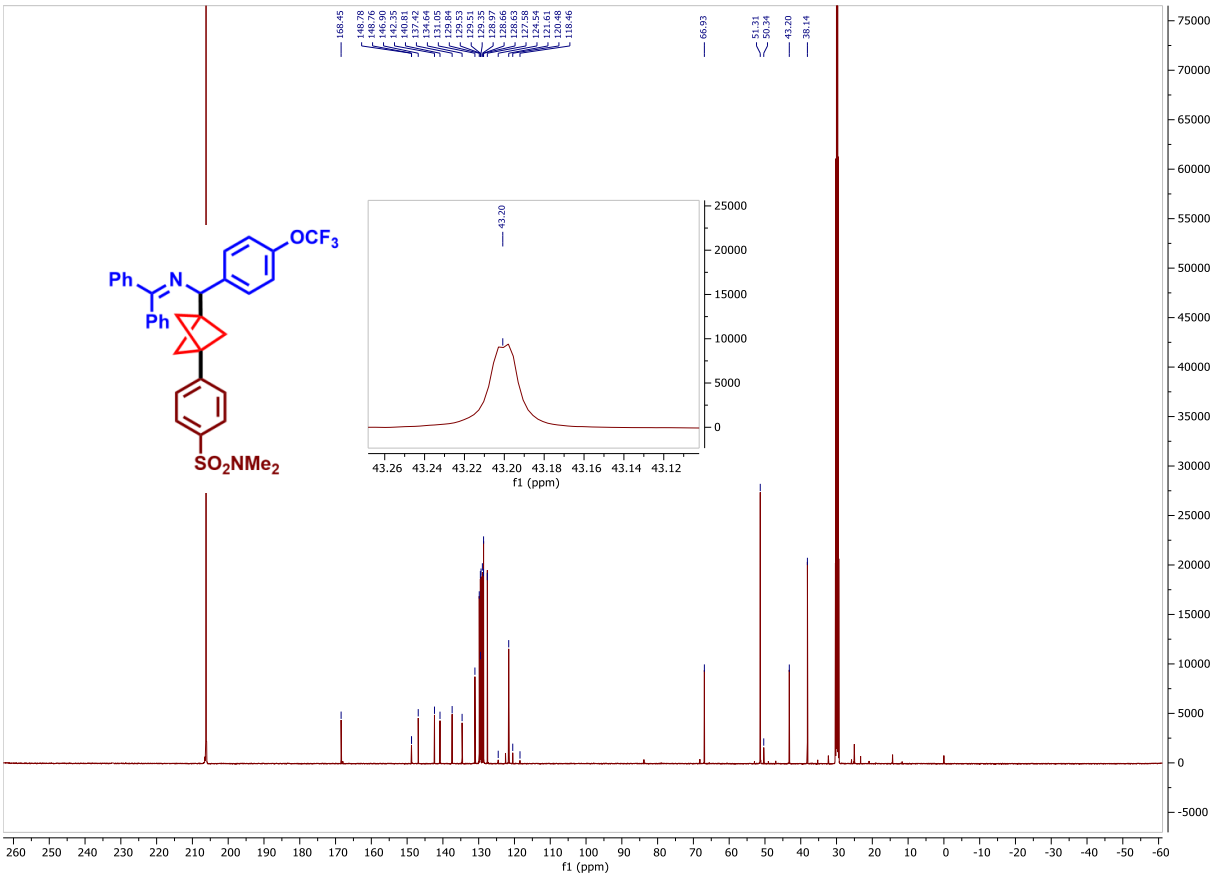
^{19}F NMR spectrum ($CDCl_3$, 471 MHz) of ***N*-((3-(4-(methylsulfonyl)phenyl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bm)**



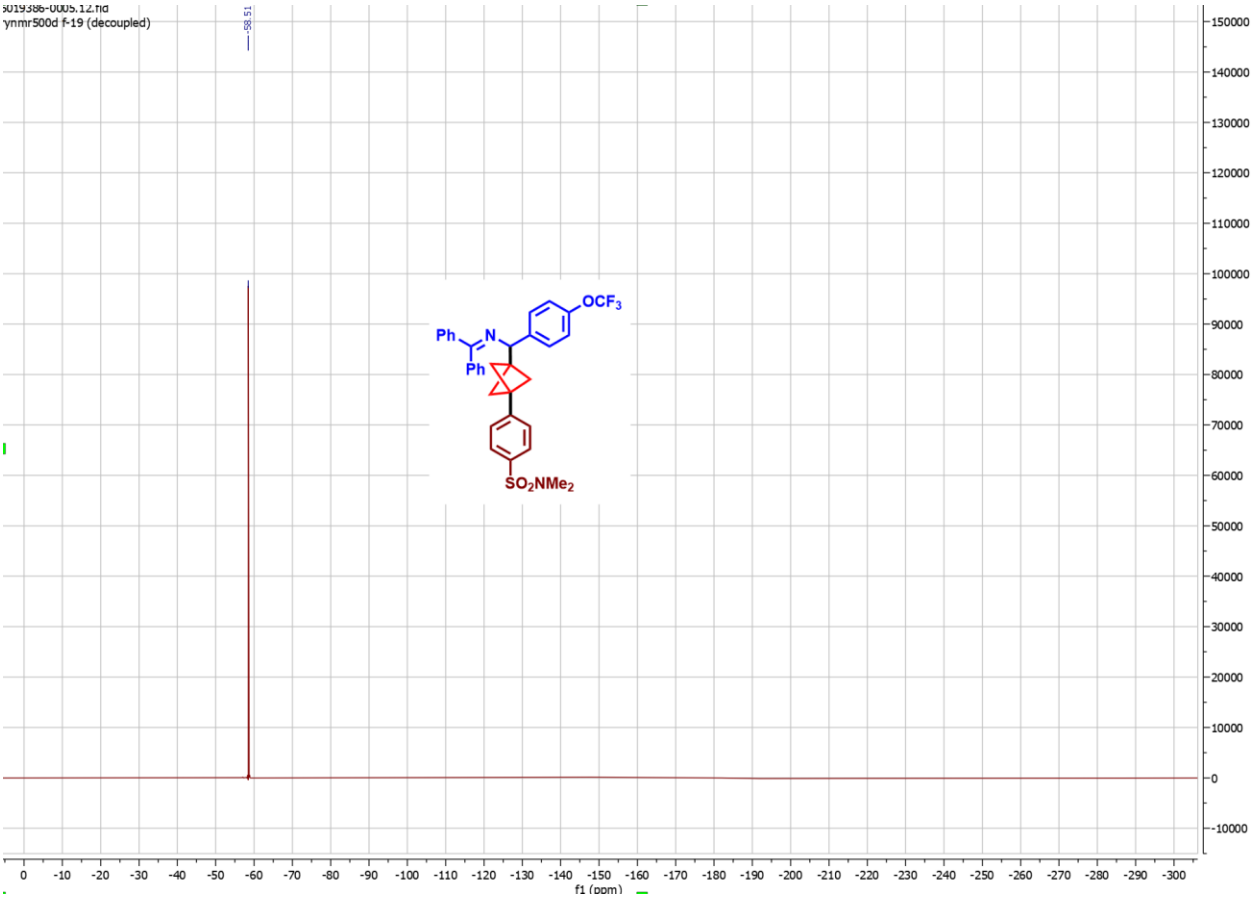
^{1}H NMR spectrum ($(CD_3)_2CO$, 500 MHz) of **4-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)-*N*,*N*-dimethylbenzenesulfonamide (8bn)**



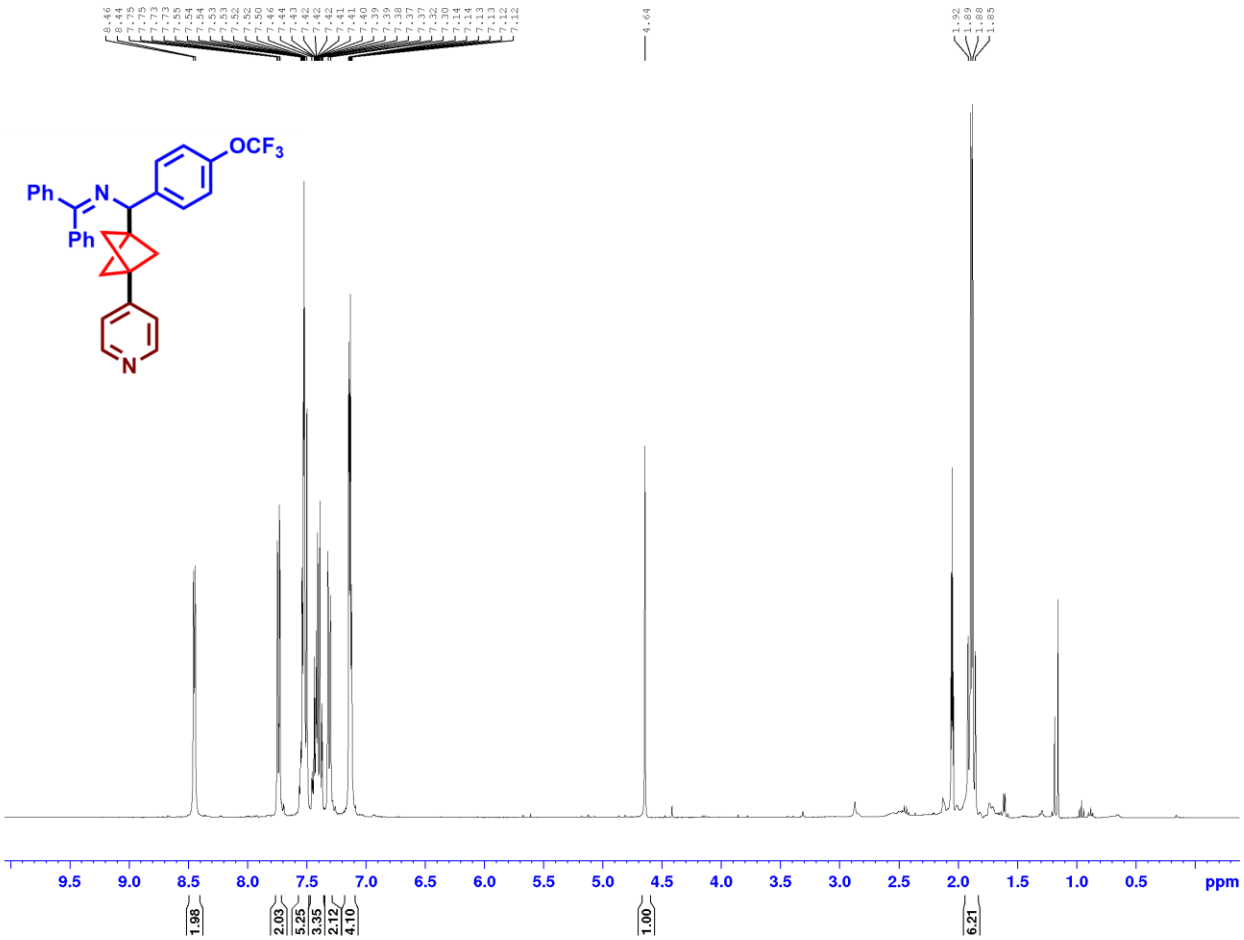
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, , 126 MHz) of **4-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)-*N*,*N*-dimethylbenzenesulfonamide (8bn)**



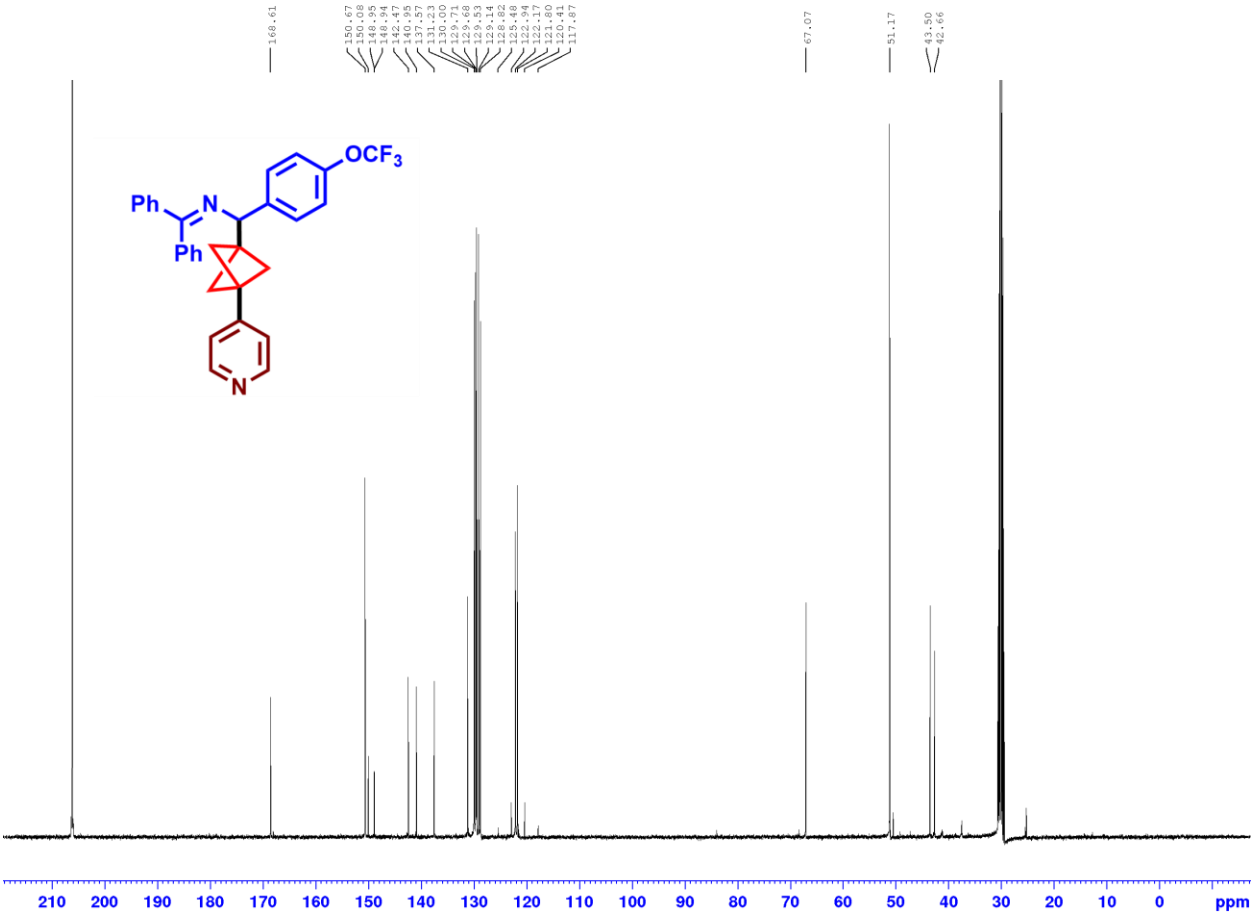
^{19}F NMR spectrum ($(CD_3)_2CO$, 471 MHz) of **4-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)-*N*,*N*-dimethylbenzenesulfonamide (8bn)**



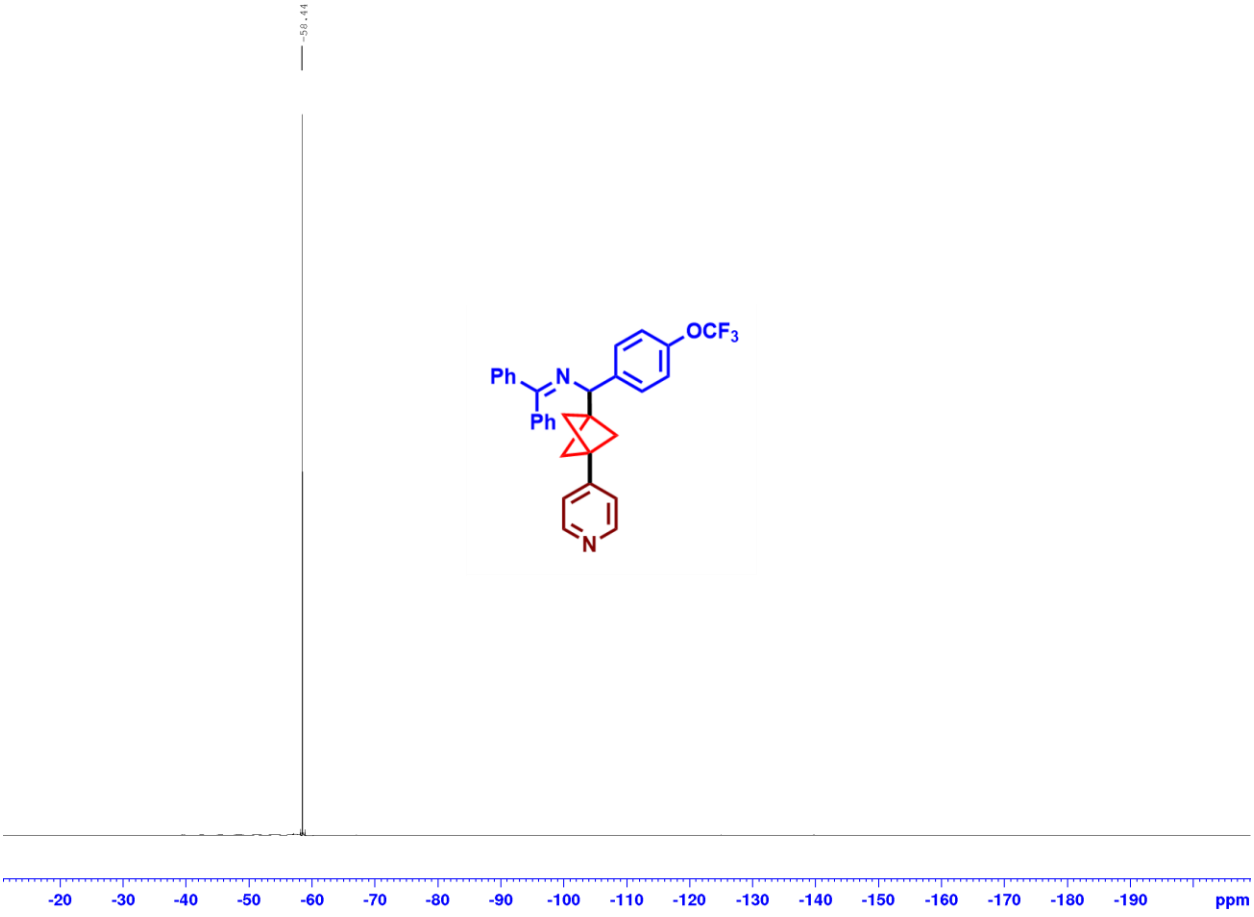
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **1,1-diphenyl-*N*-((3-(pyridin-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bo)**



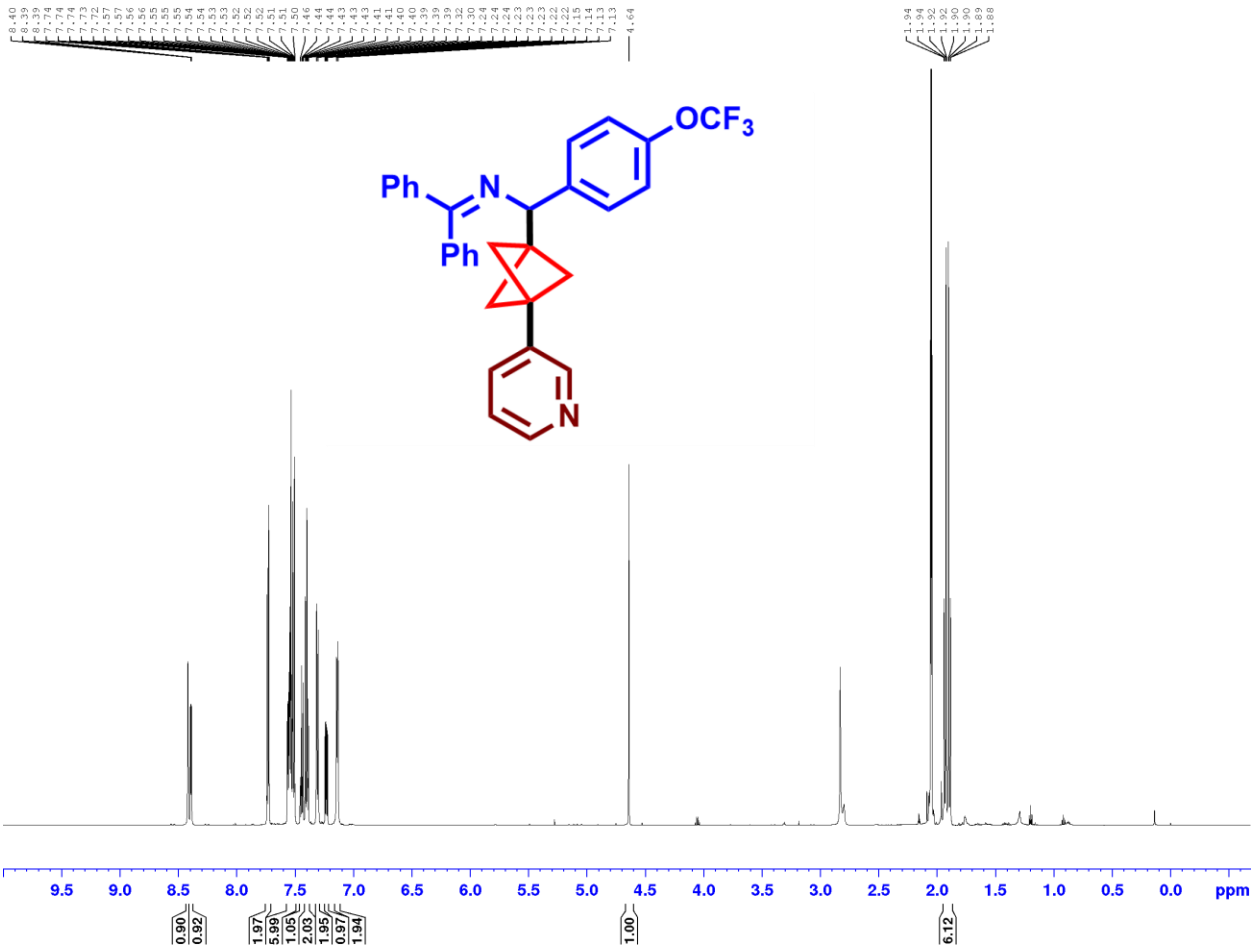
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of **1,1-diphenyl-*N*-((3-(pyridin-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bo)**



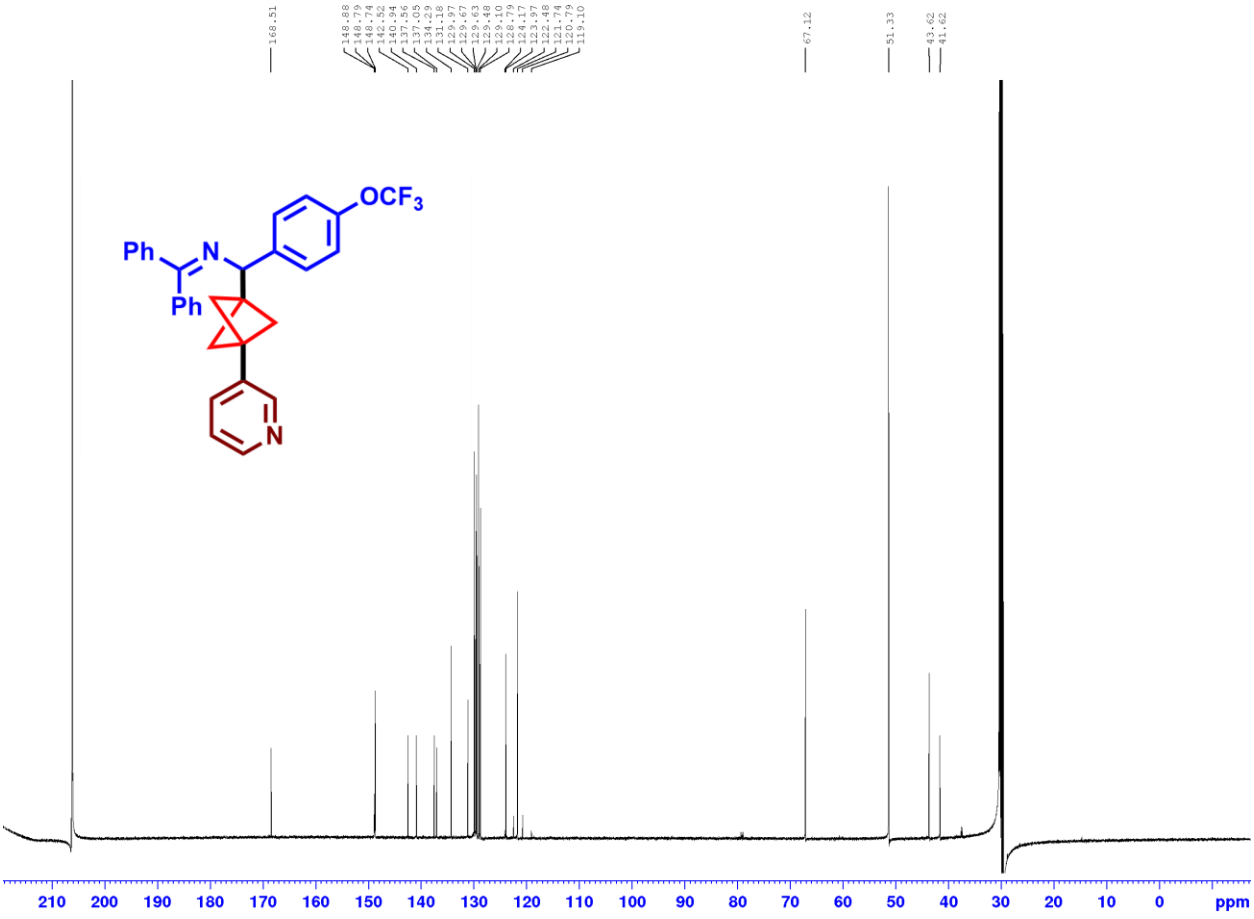
^{19}F NMR spectrum ($(CD_3)_2CO$, 371 MHz) of **1,1-diphenyl-*N*-((3-(pyridin-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bo)**



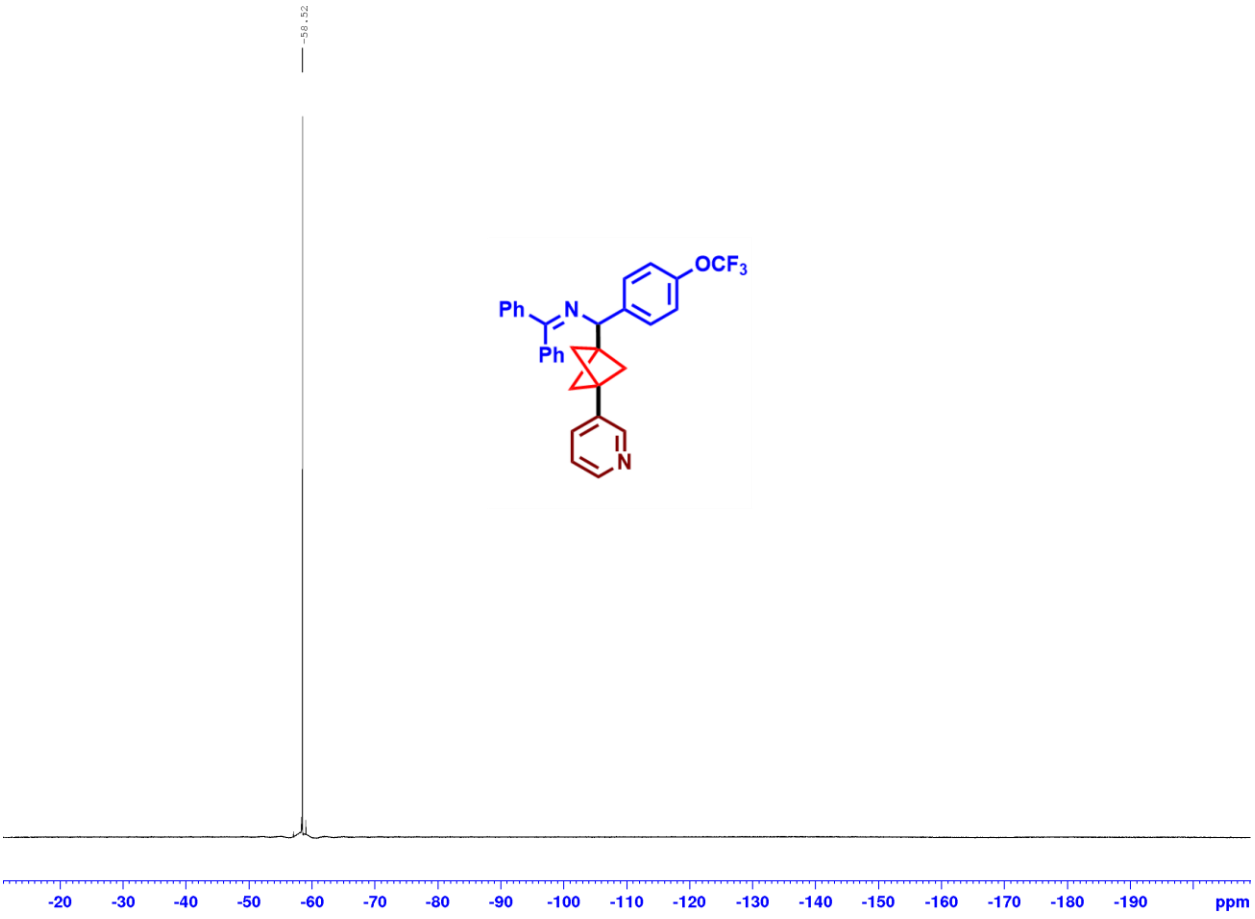
^{1}H NMR spectrum ($(CD_3)_2CO$, 600 MHz) of **1,1-diphenyl-*N*-((3-(pyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bn)**



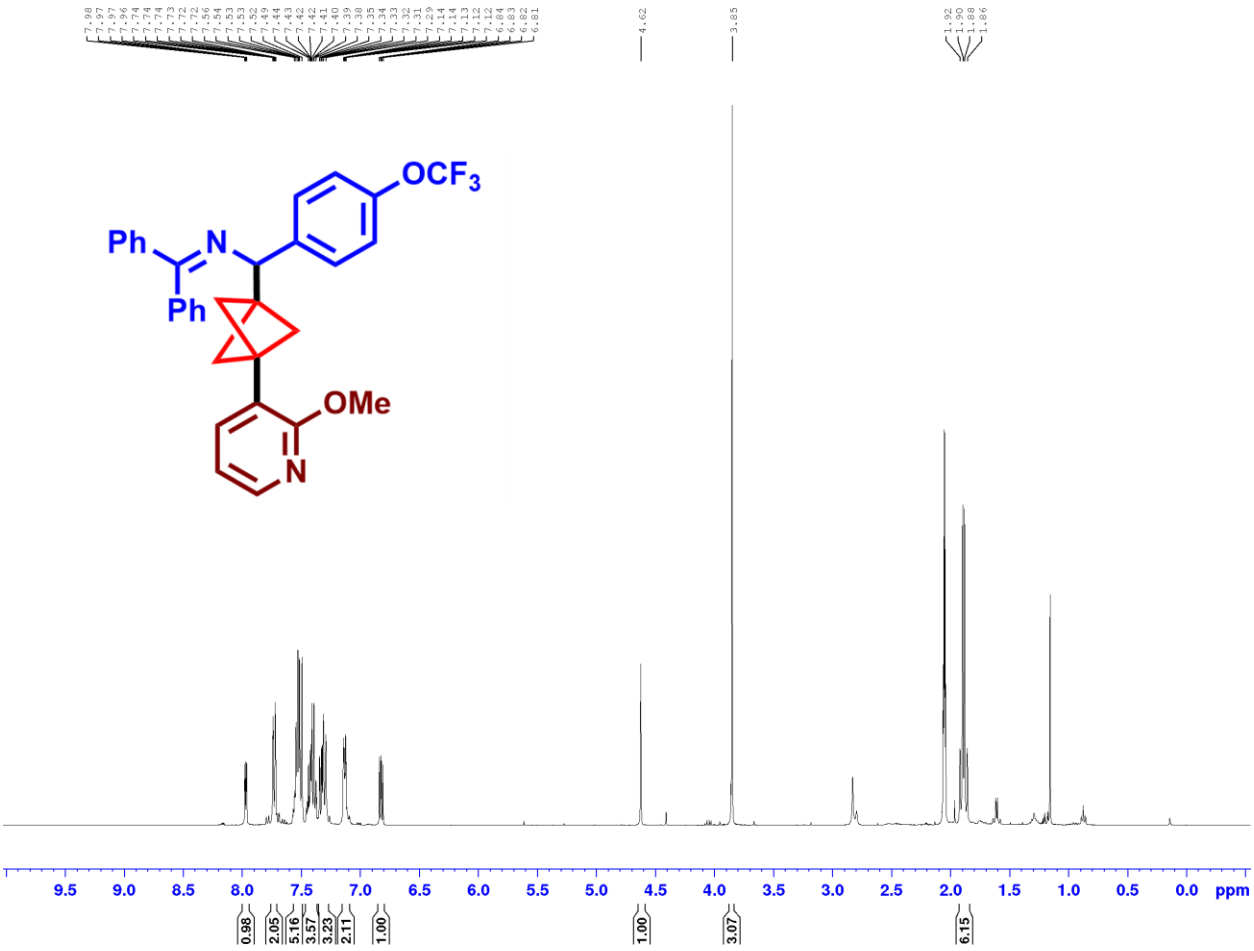
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 125 MHz) of **1,1-diphenyl-*N*-((3-(pyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bn)**



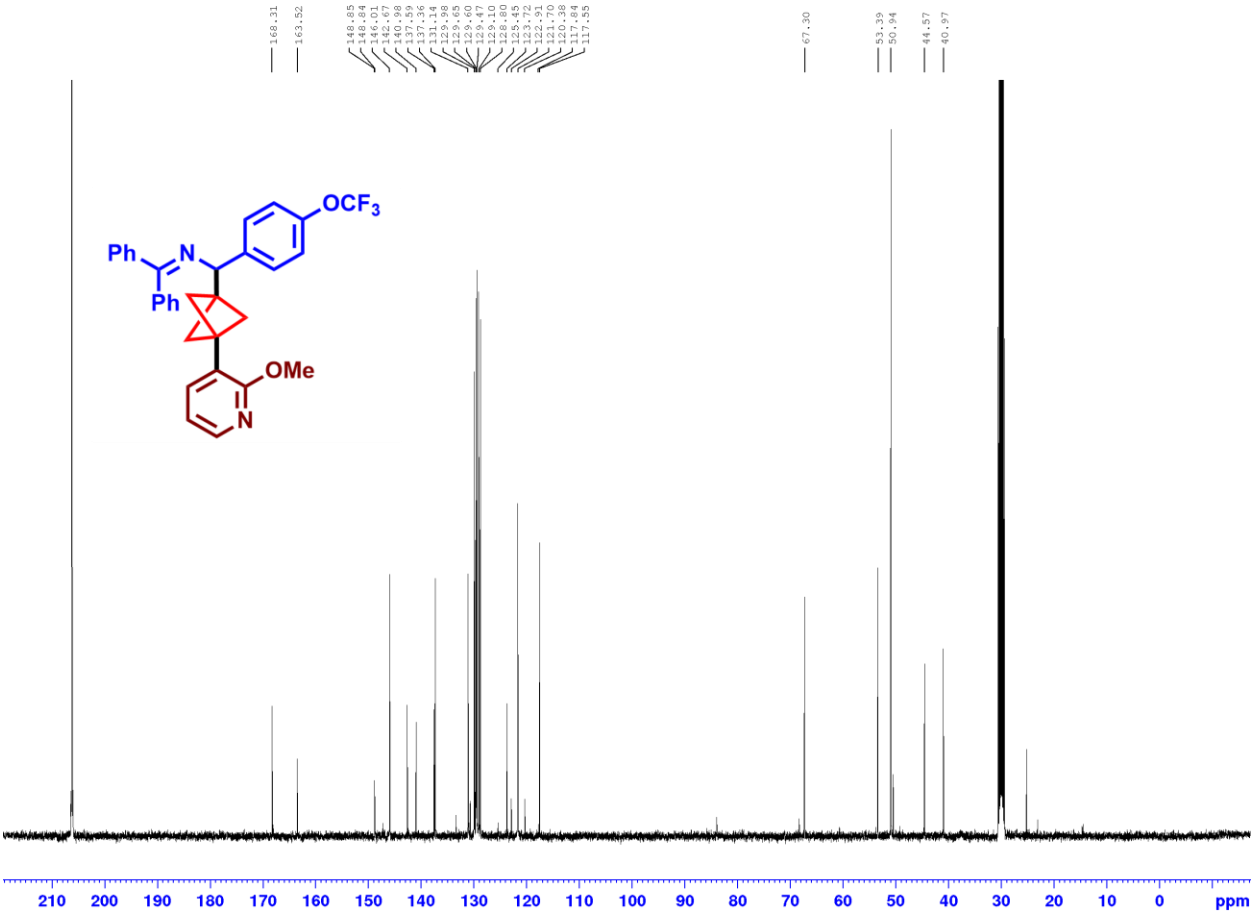
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of **1,1-diphenyl-*N*-((3-(pyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bn)**



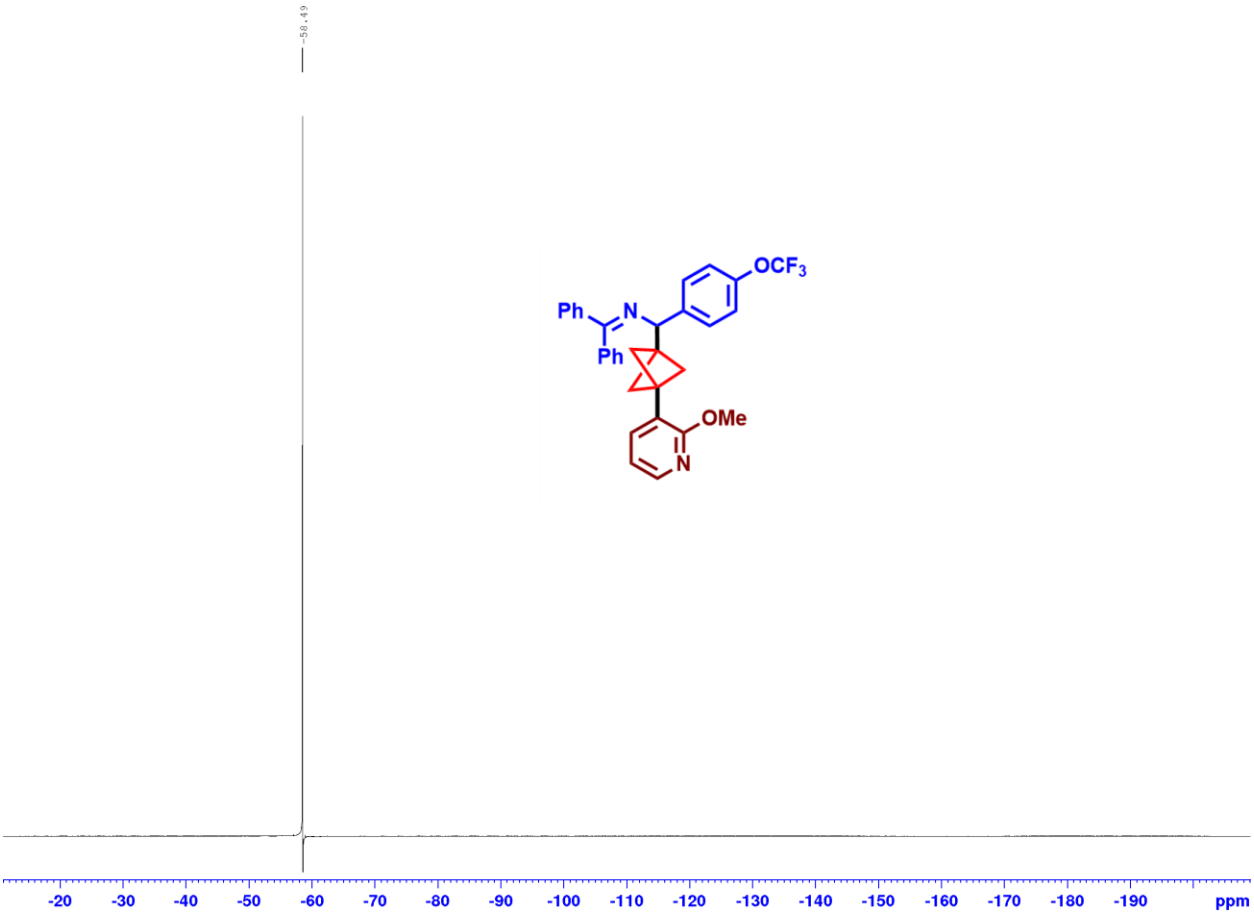
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N*-((3-(2-methoxypyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bq)**



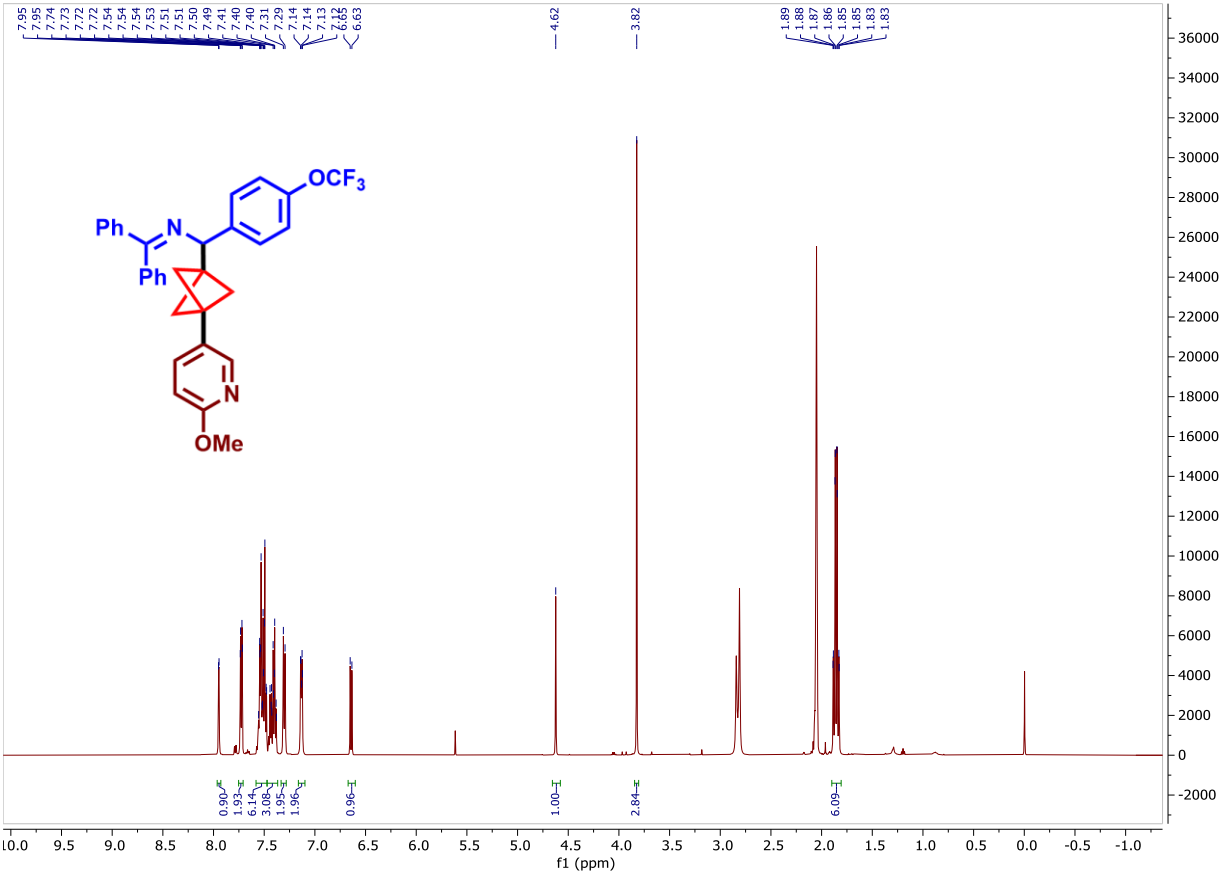
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of ***N*-((3-(2-methoxypyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bq)**



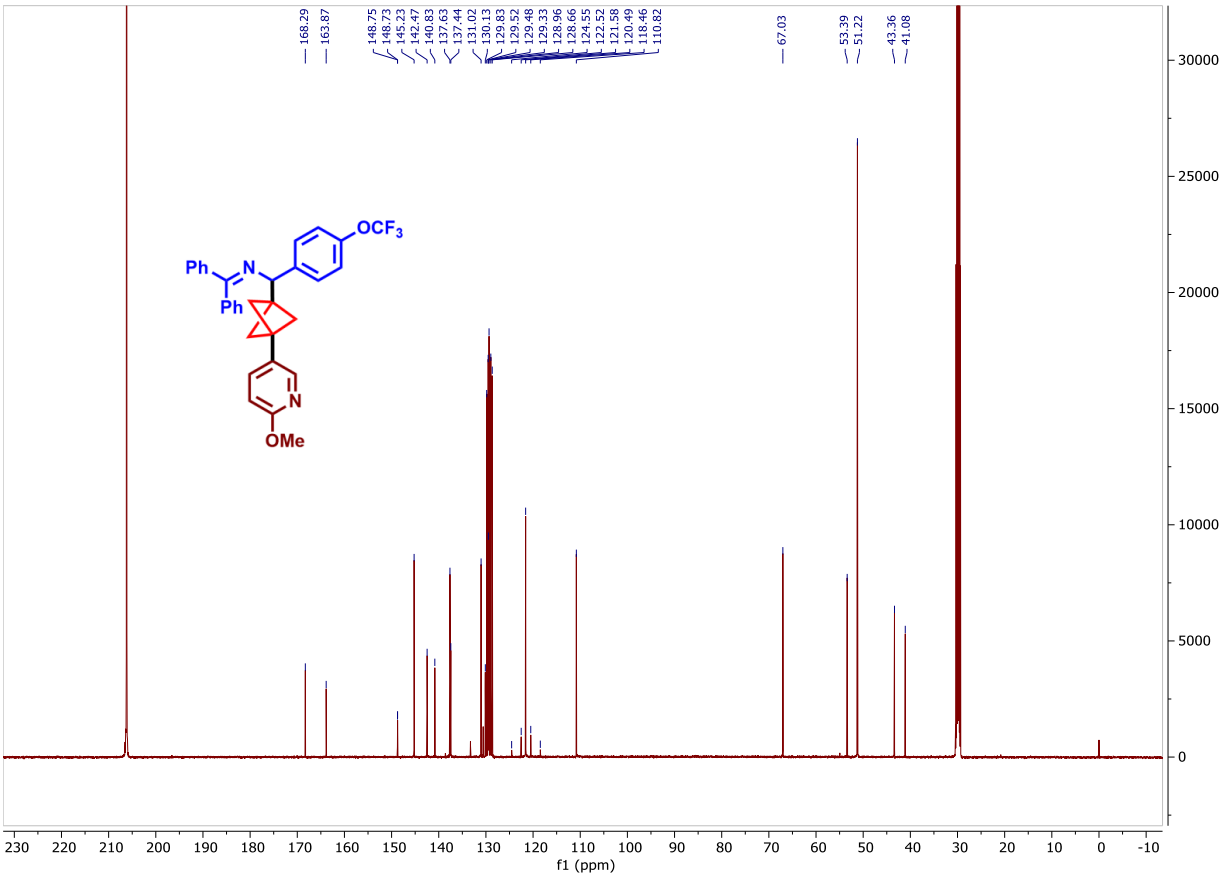
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of ***N*-((3-(2-methoxypyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8bq)**



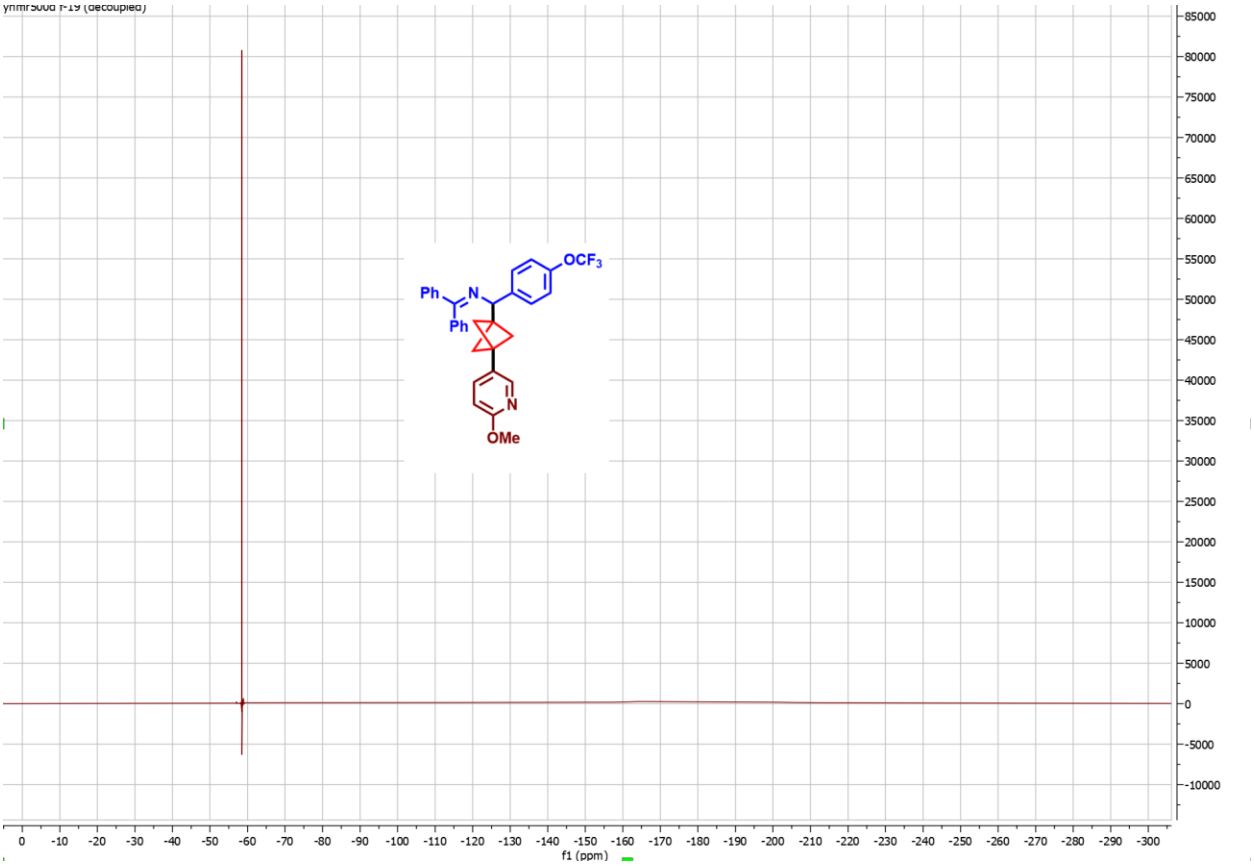
^{1}H NMR spectrum ($(CD_3)_2CO$, 500 MHz) of ***N*-((3-(6-methoxypyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8br)**



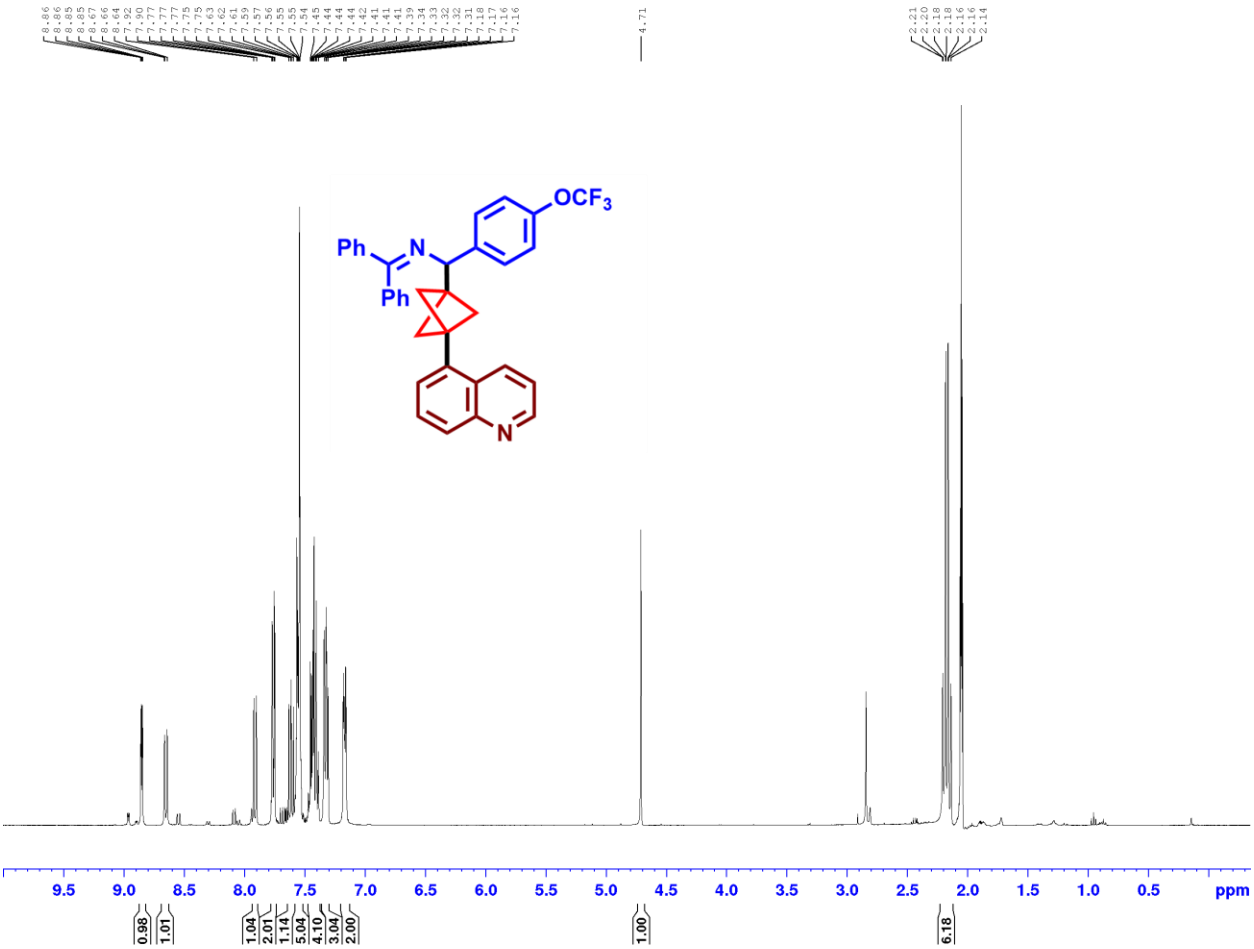
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 126 MHz) of ***N*-((3-(6-methoxypyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8br)**



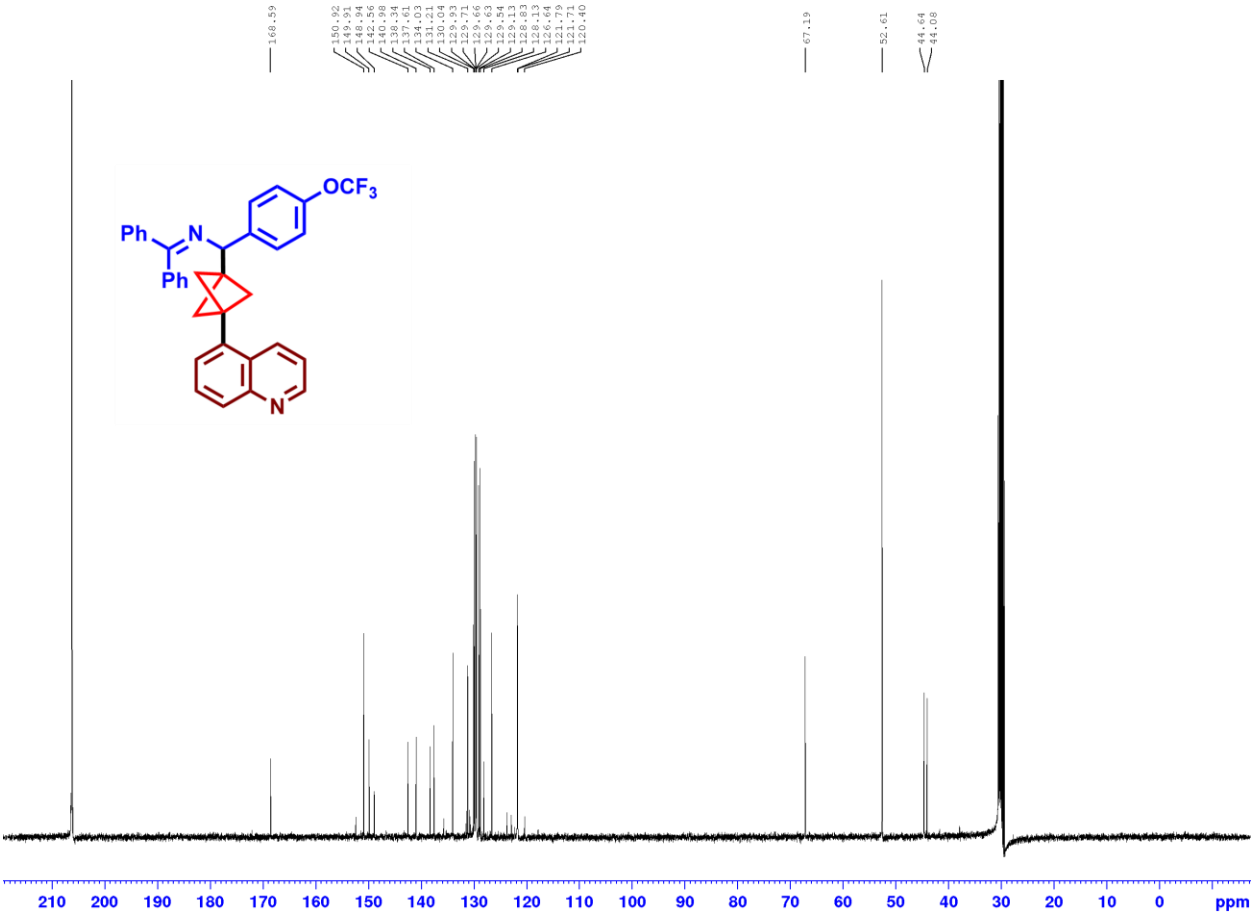
^{19}F NMR spectrum ($(CD_3)_2CO$, 471 MHz) of ***N*-((3-(6-methoxypyridin-3-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-1,1-diphenylmethanimine (8br)**



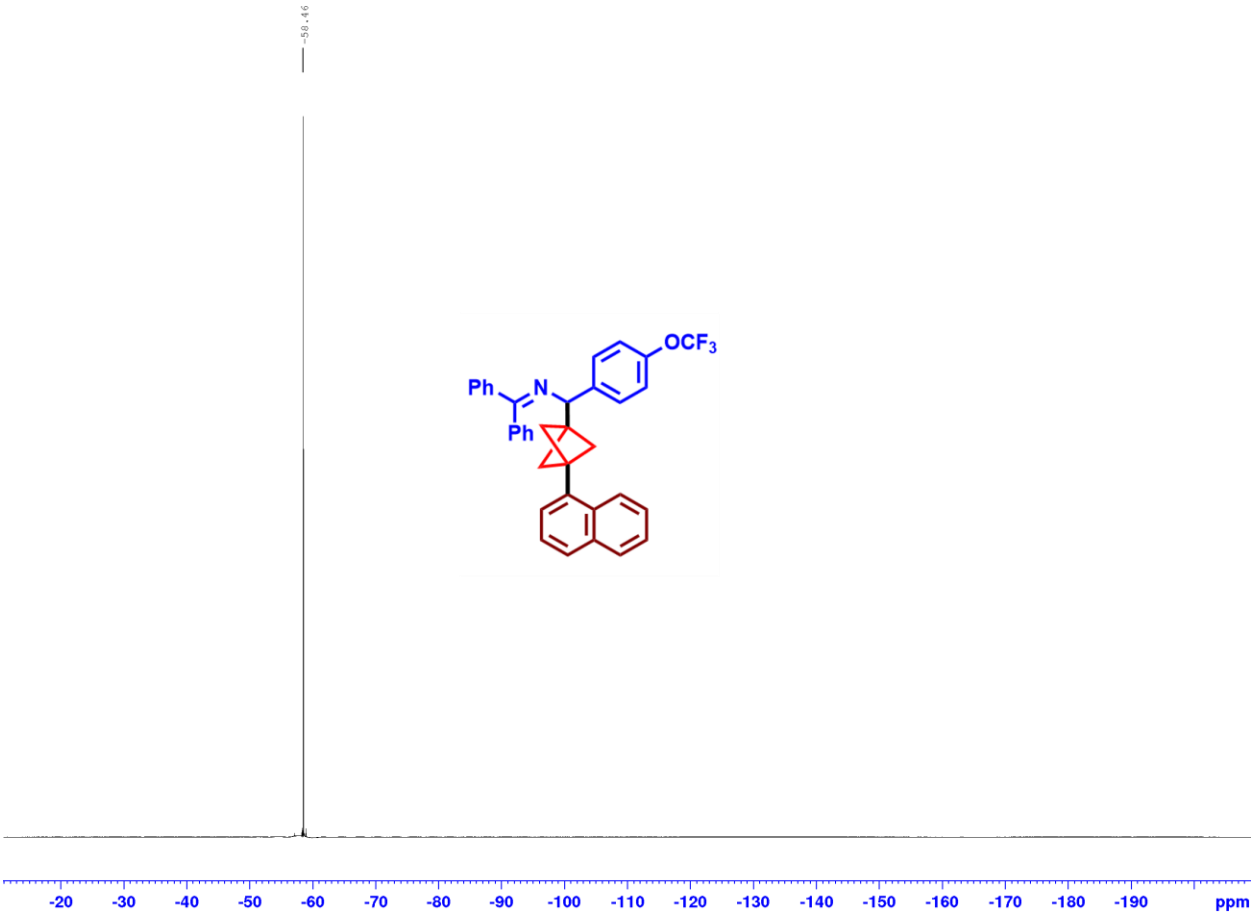
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of **1,1-diphenyl-*N*-((3-(quinolin-5-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bs)**



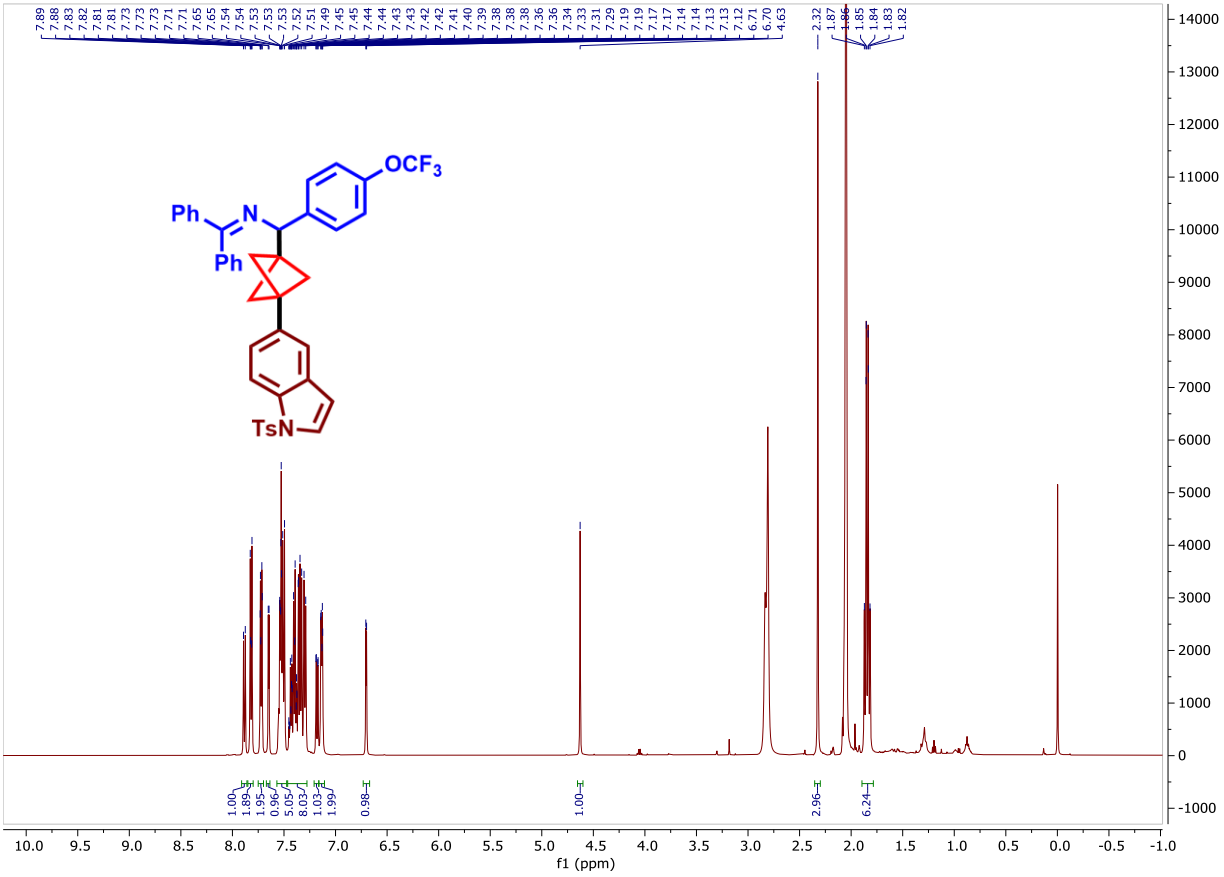
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) of **1,1-diphenyl-*N*-((3-(quinolin-5-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bs)**



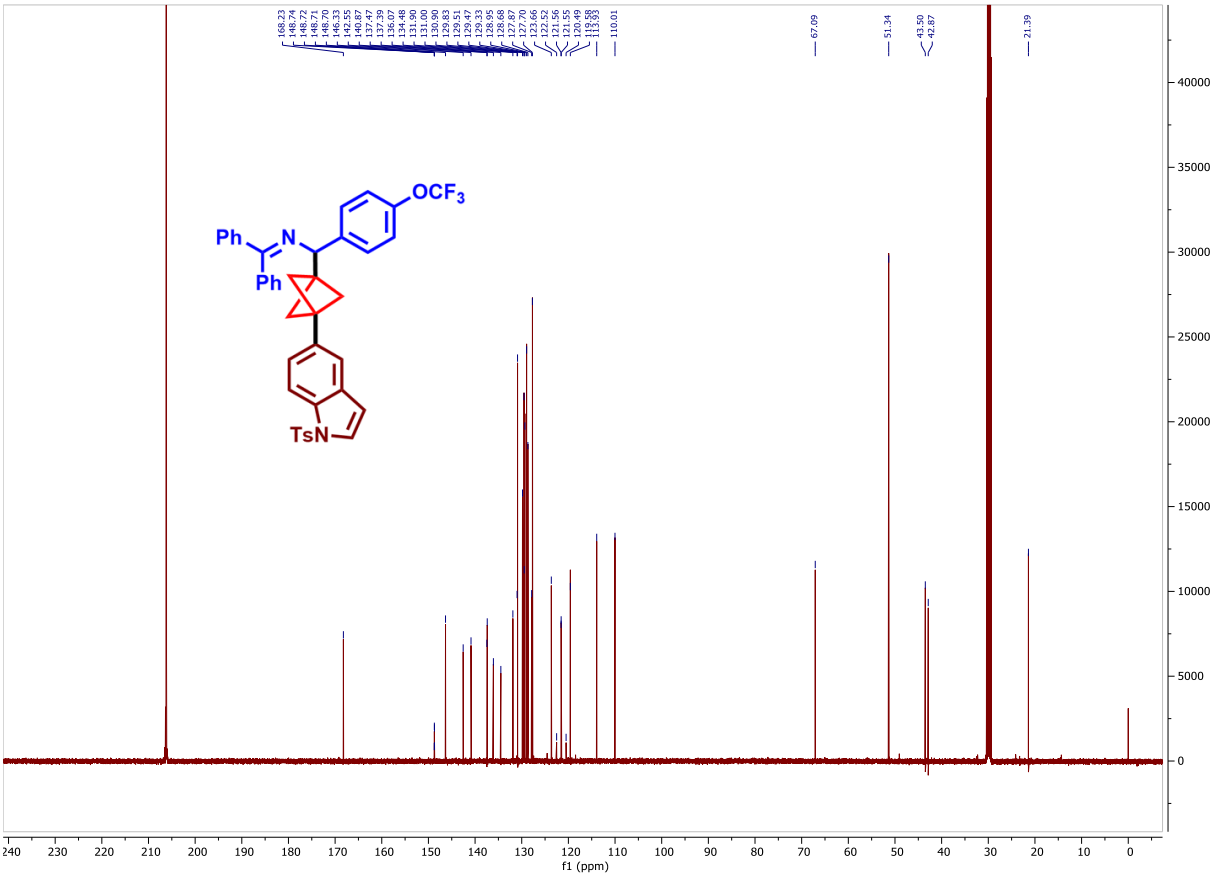
^{19}F NMR spectrum ($(CD_3)_2CO$, 376 MHz) of **1,1-diphenyl-*N*-((3-(quinolin-5-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bs)**



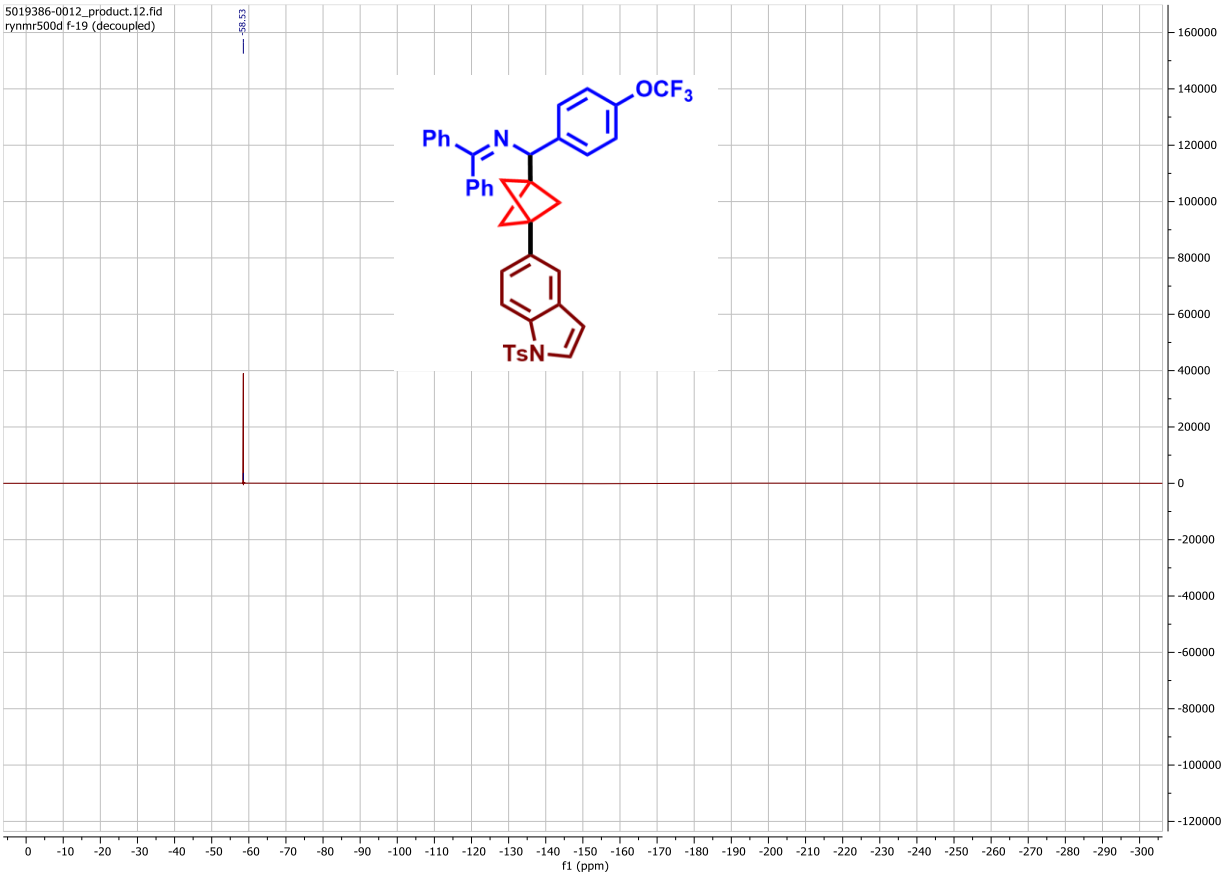
^{1}H NMR spectrum ($(CD_3)_2CO$, 500 MHz) of **1,1-diphenyl-*N*-((3-(1-tosyl-1H-indol-5-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bt)**



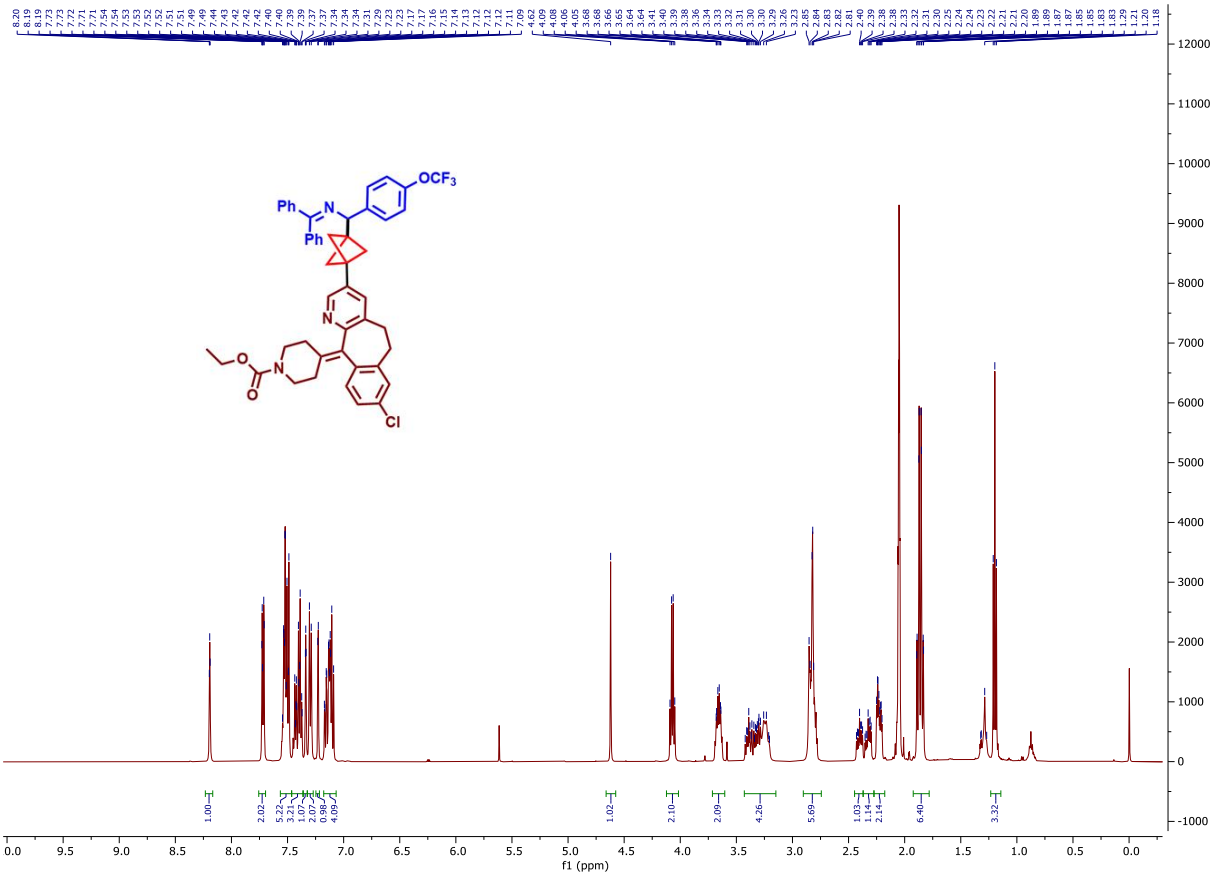
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 126 MHz) of **1,1-diphenyl-*N*-((3-(1-tosyl-1H-indol-5-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bt)**



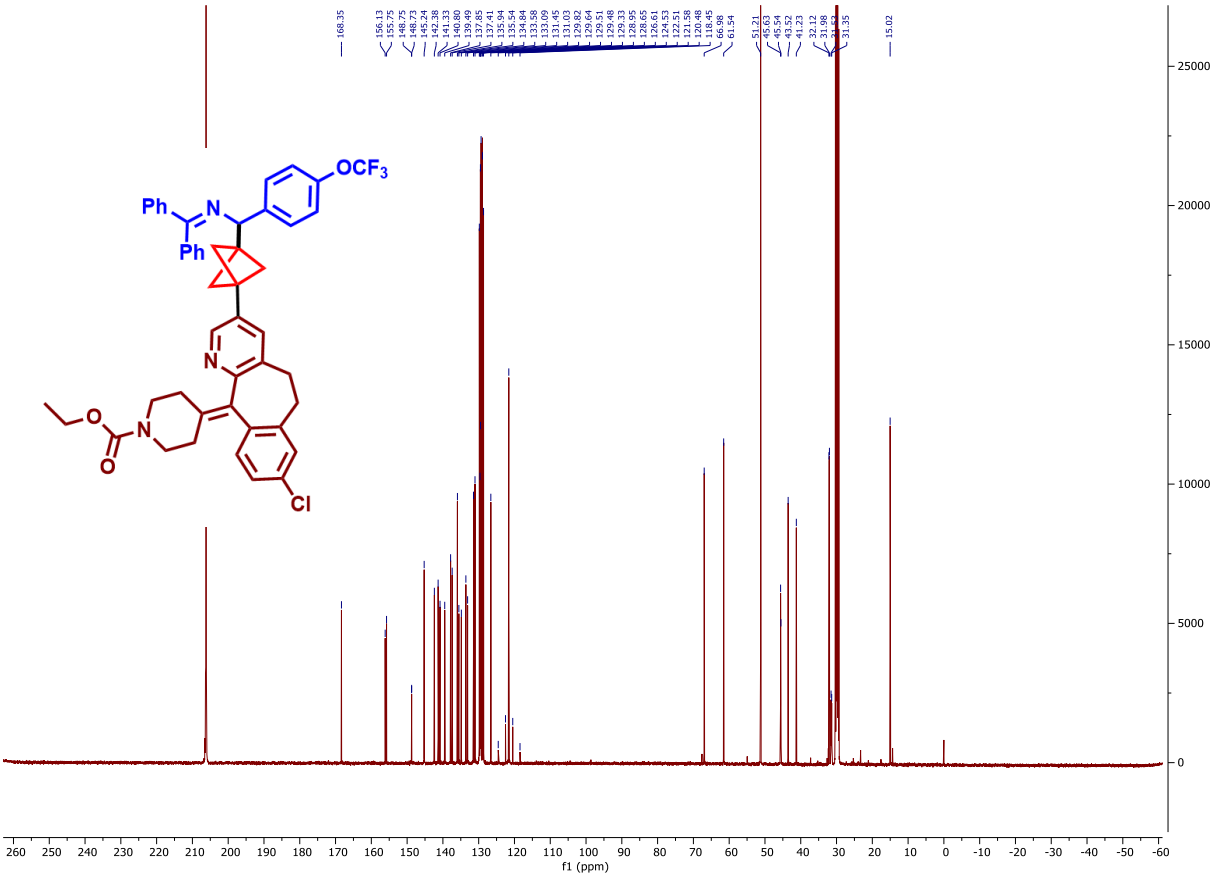
^{1}H NMR spectrum ($(CD_3)_2CO$, 500 MHz) of **1,1-diphenyl-*N*-((3-(1-tosyl-1H-indol-5-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methyl)methanimine (8bt)**



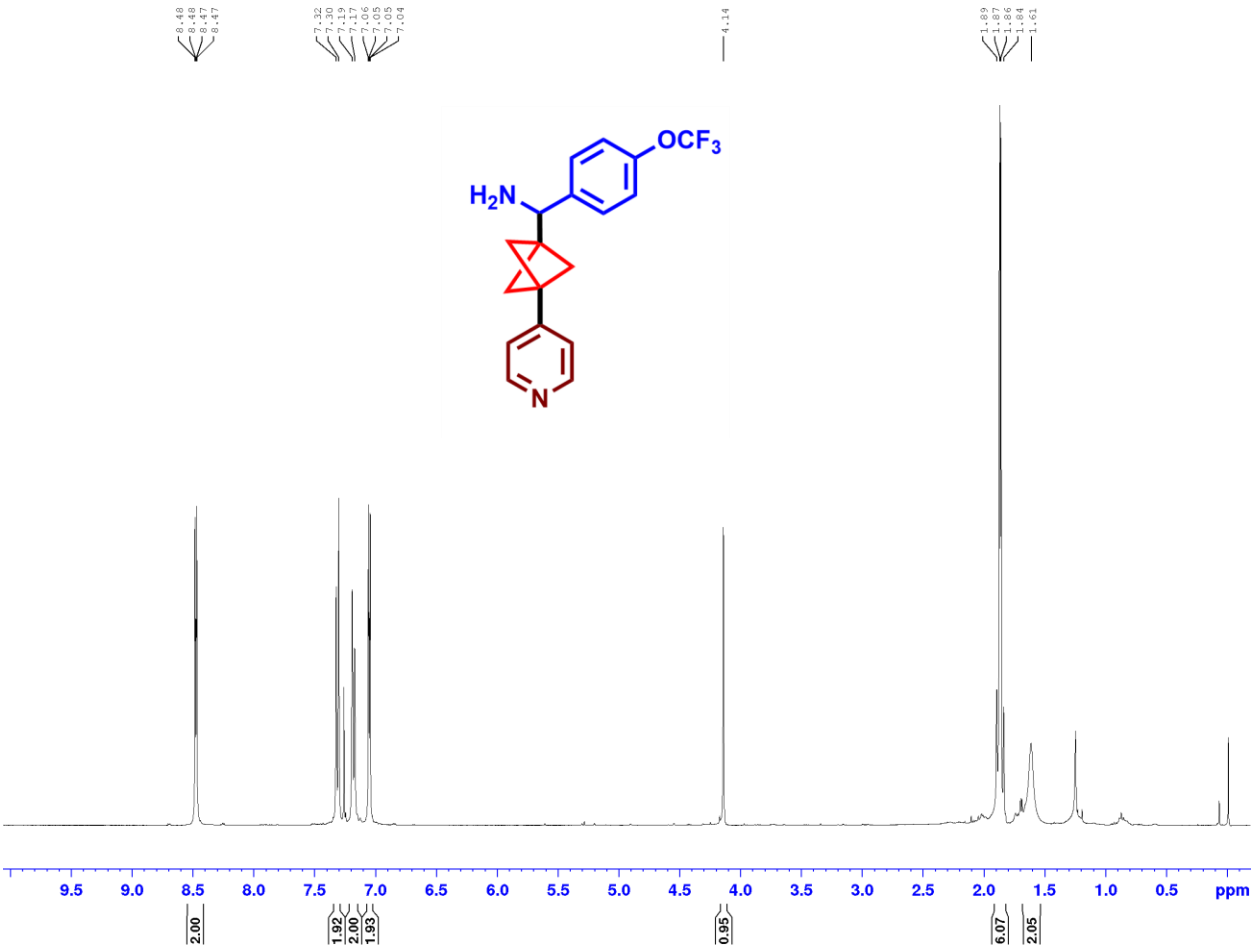
^{1}H NMR spectrum ($(CD_3)_2CO$, 500 MHz) of **ethyl -4-(8-chloro-3-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (8bu)**



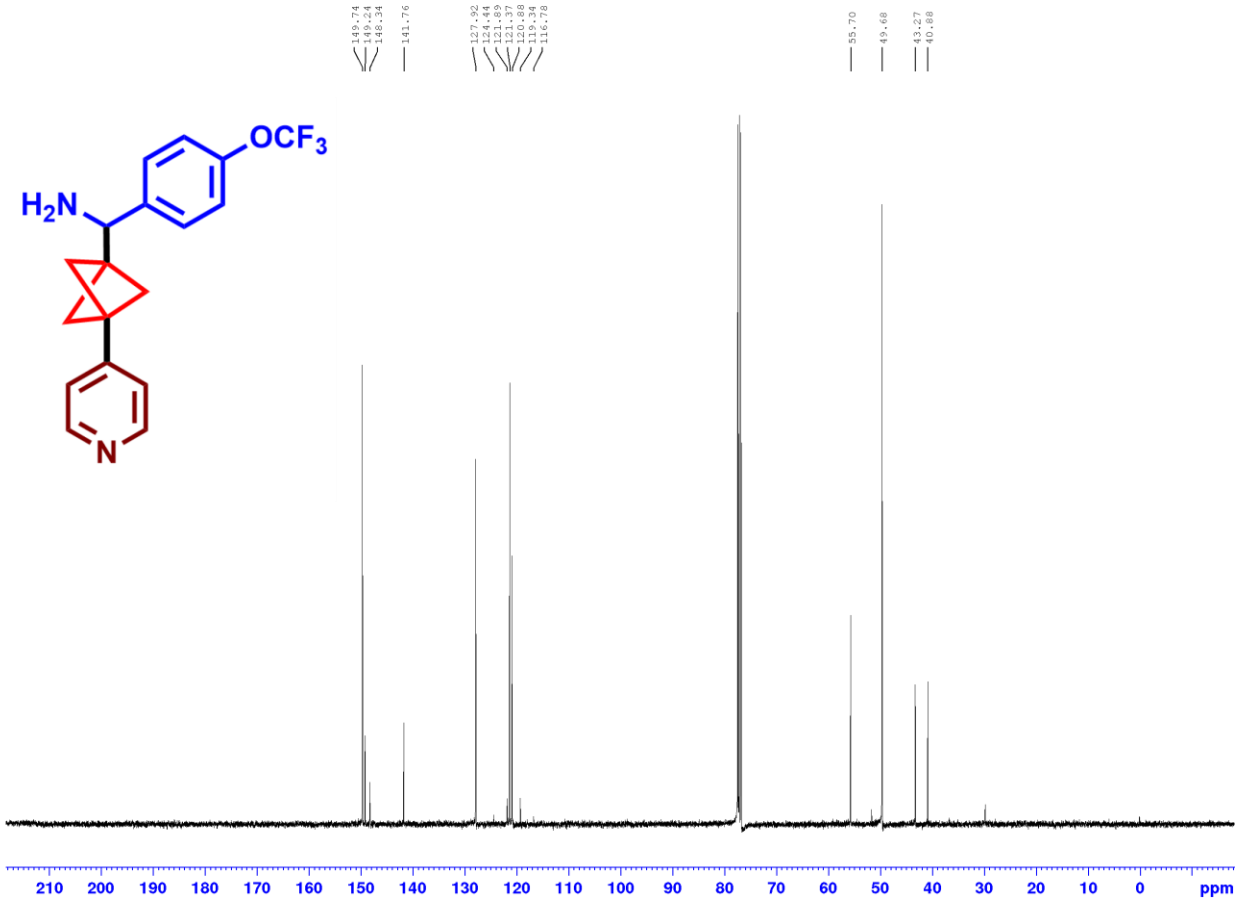
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 126 MHz) of **ethyl -4-(8-chloro-3-(3-(((diphenylmethylene)amino)(4-(trifluoromethoxy)phenyl)methyl)bicyclo[1.1.1]pentan-1-yl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidine-1-carboxylate (8bu)**



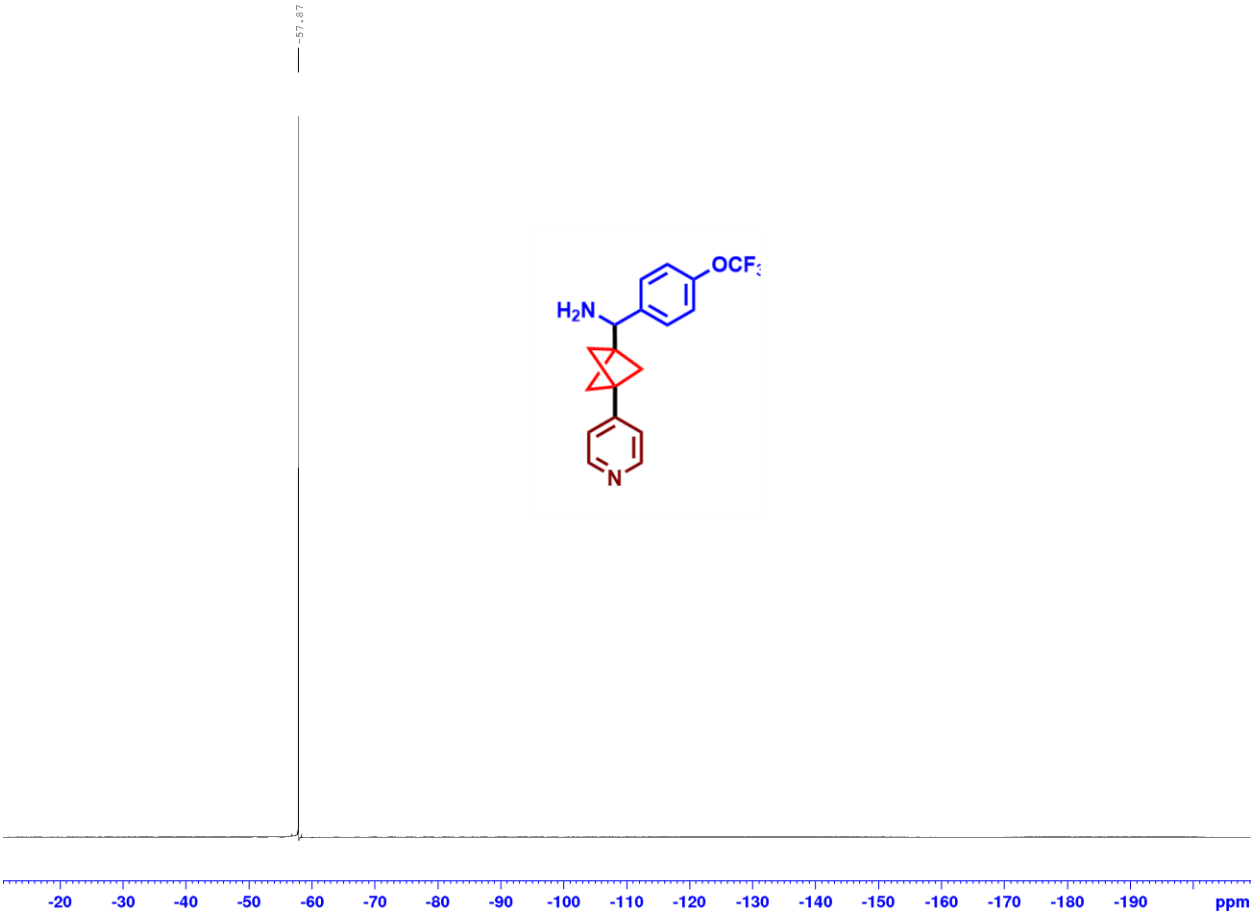
^{1}H NMR spectrum ((CDCl$_3$, 400 MHz) of **(3-(pyridin-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanamine (16)**



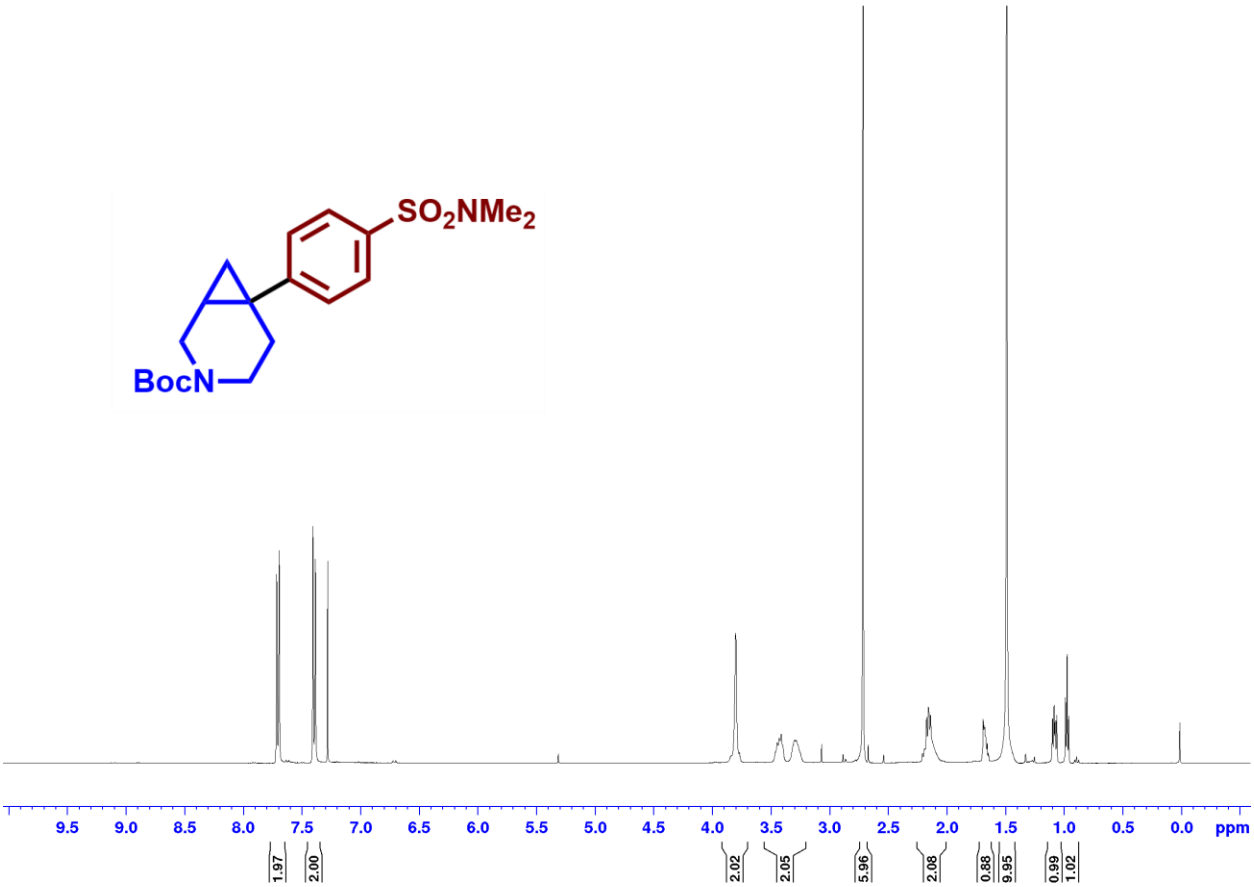
$^{13}C\{^{1}H\}$ NMR spectrum ($(CDCl_3$, 100 MHz) of **(3-(pyridin-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanamine (16)**



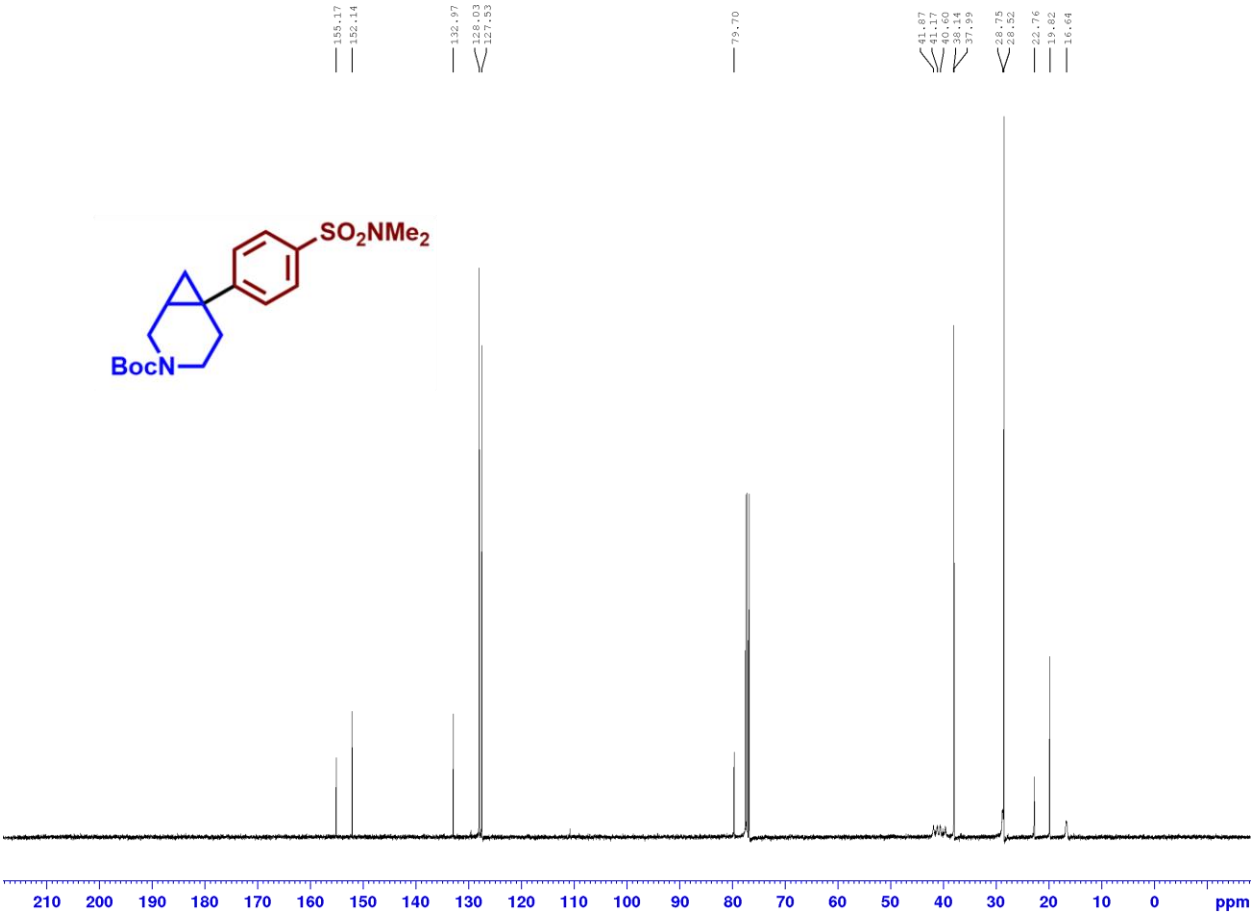
^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of **(3-(pyridin-4-yl)bicyclo[1.1.1]pentan-1-yl)(4-(trifluoromethoxy)phenyl)methanamine (16)**



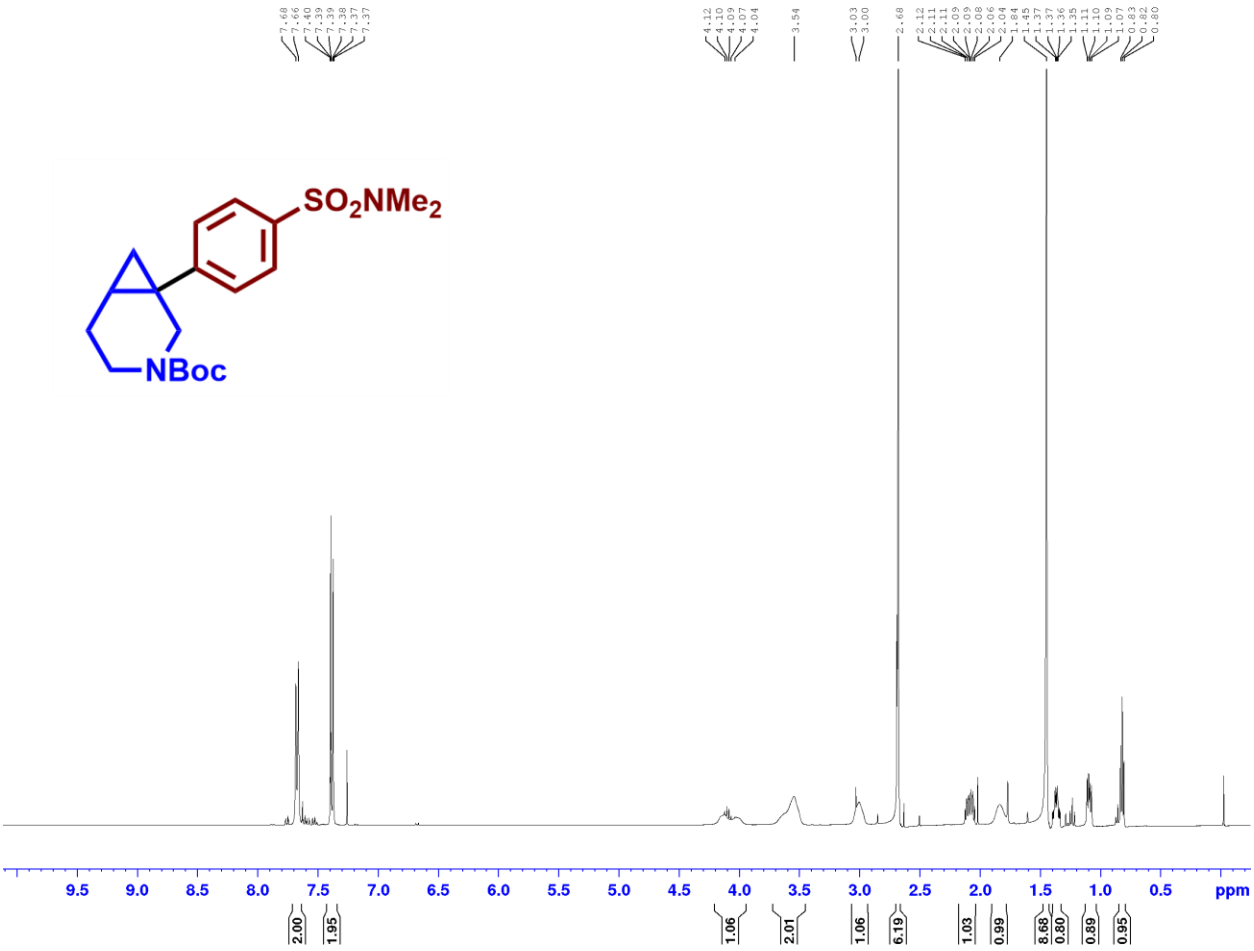
^{1}H NMR spectrum ((CDCl$_3$, 400 MHz) of ***tert*-butyl 6-(4-(*N*,*N*-dimethylsulfamoyl)phenyl)-3-azabicyclo[4.1.0]heptane-3-carboxylate (18a)**



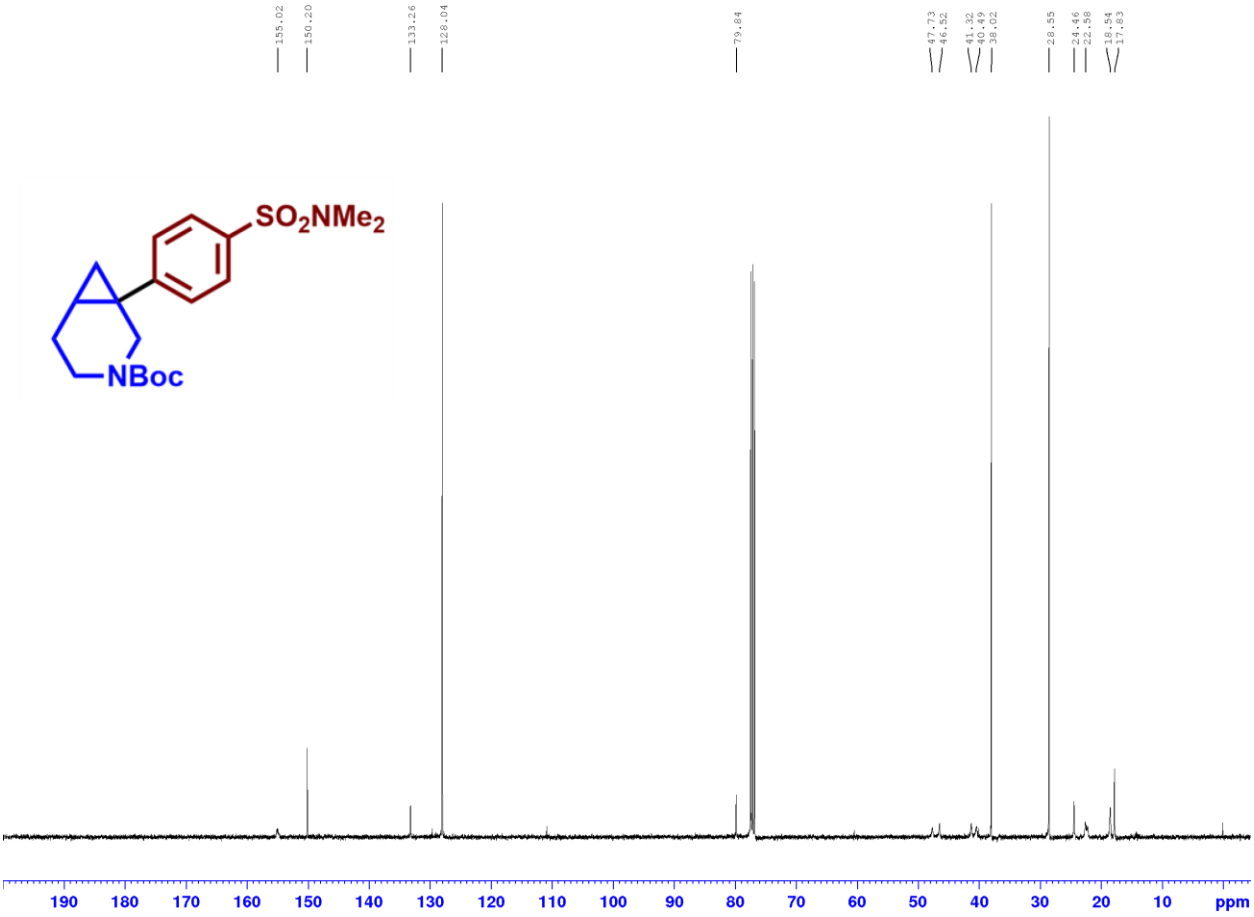
$^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz) of ***tert*-butyl 6-(4-(*N*,*N*-dimethylsulfamoyl)phenyl)-3-azabicyclo[4.1.0]heptane-3-carboxylate (18a)**



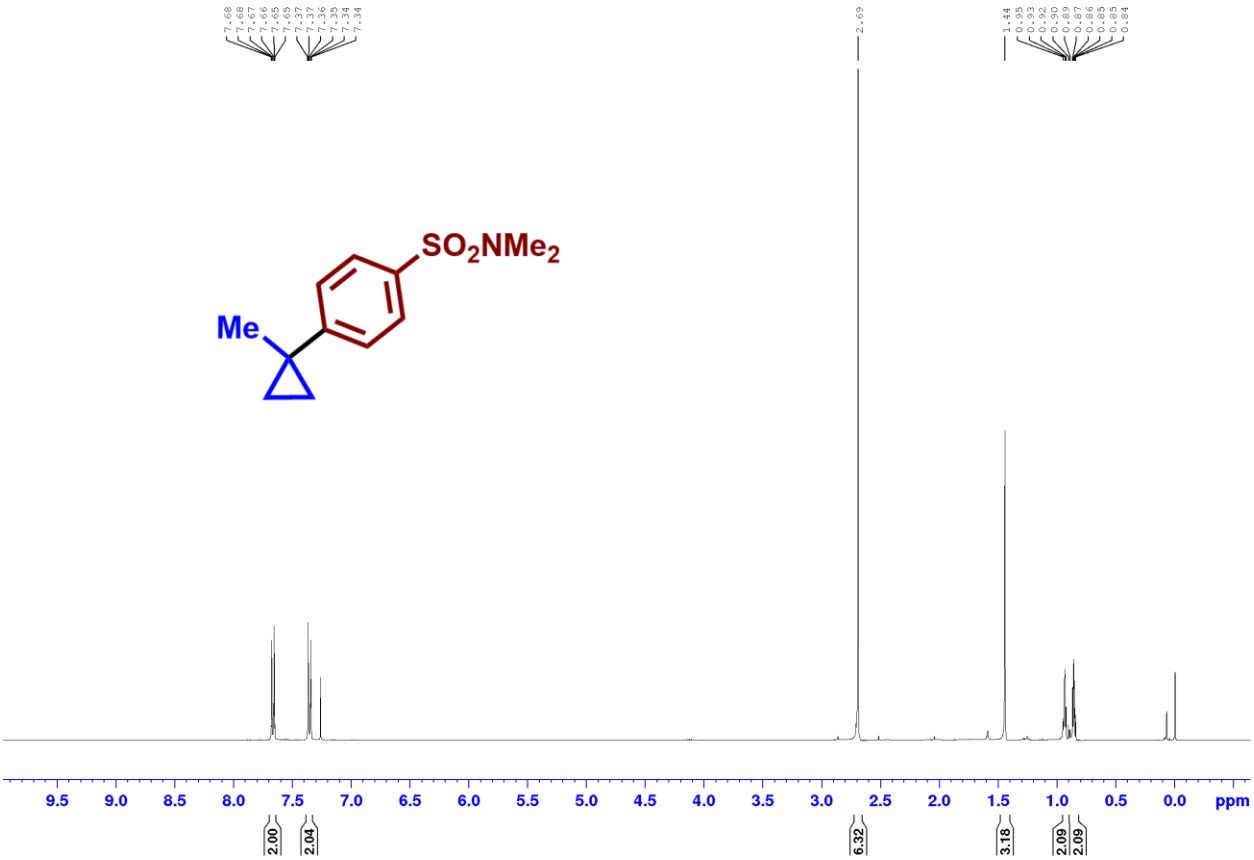
^{1}H NMR spectrum ((CDCl$_3$, 400 MHz) of ***tert*-butyl 1-(4-(*N*,*N*-dimethylsulfamoyl)phenyl)-3-azabicyclo[4.1.0]heptane-3-carboxylate (18b)**



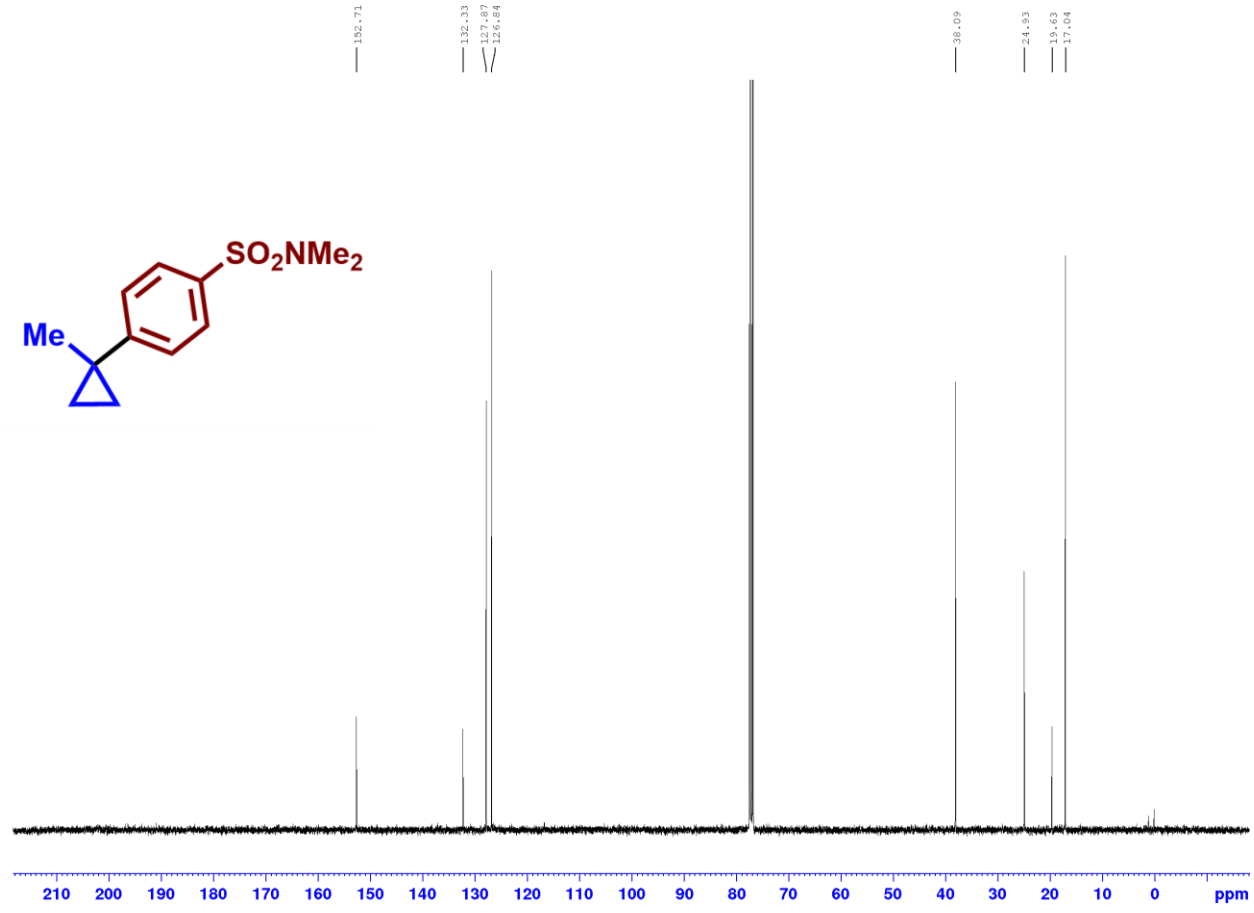
$^{13}C\{^{1}H\}$ NMR spectrum (($CDCl_3$, 100 MHz) of ***tert*-butyl 1-(4-(*N*,*N*-dimethylsulfamoyl)phenyl)-3-azabicyclo[4.1.0]heptane-3-carboxylate (18b)**



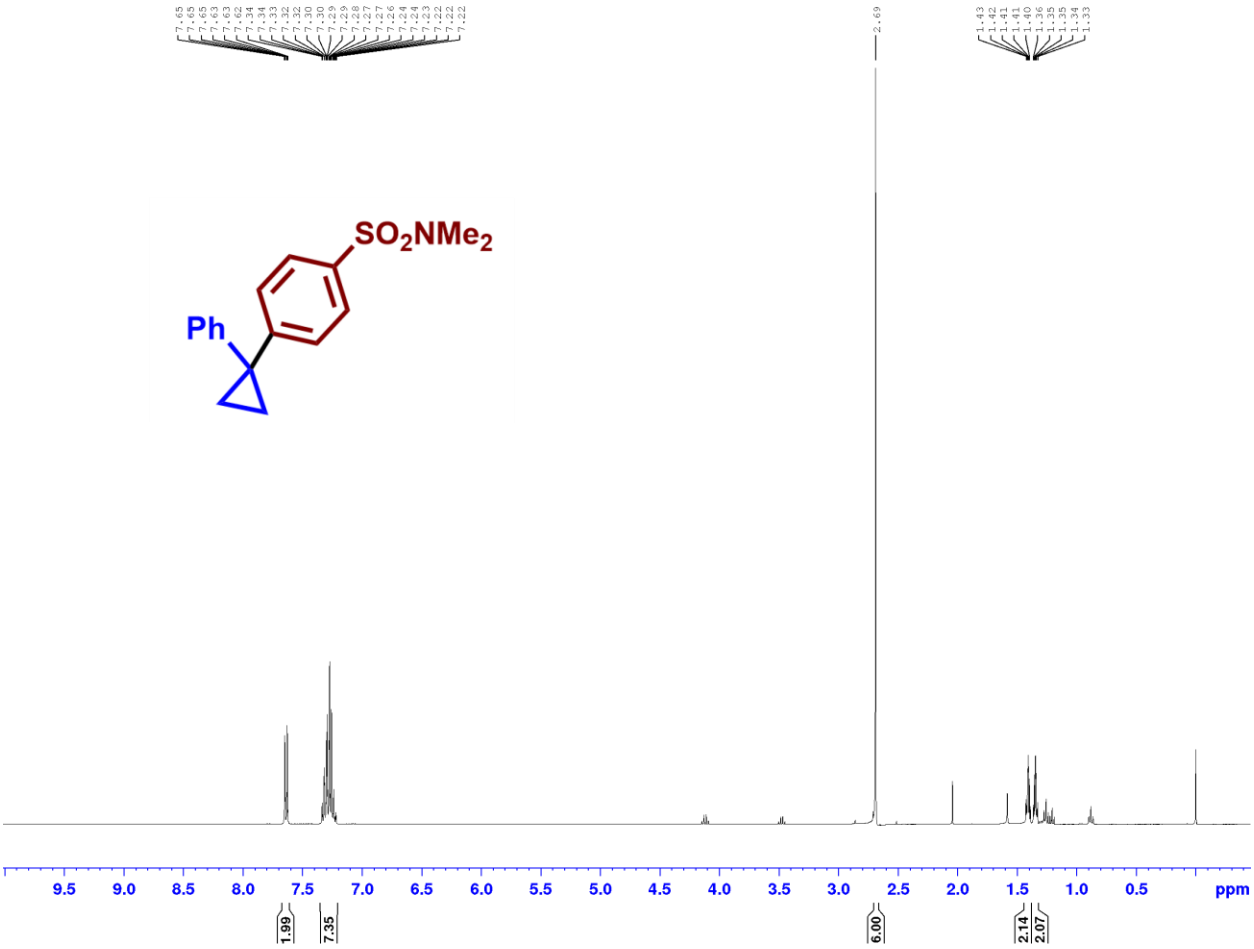
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N,N*-dimethyl-4-(1-methylcyclopropyl)benzenesulfonamide (18c)**



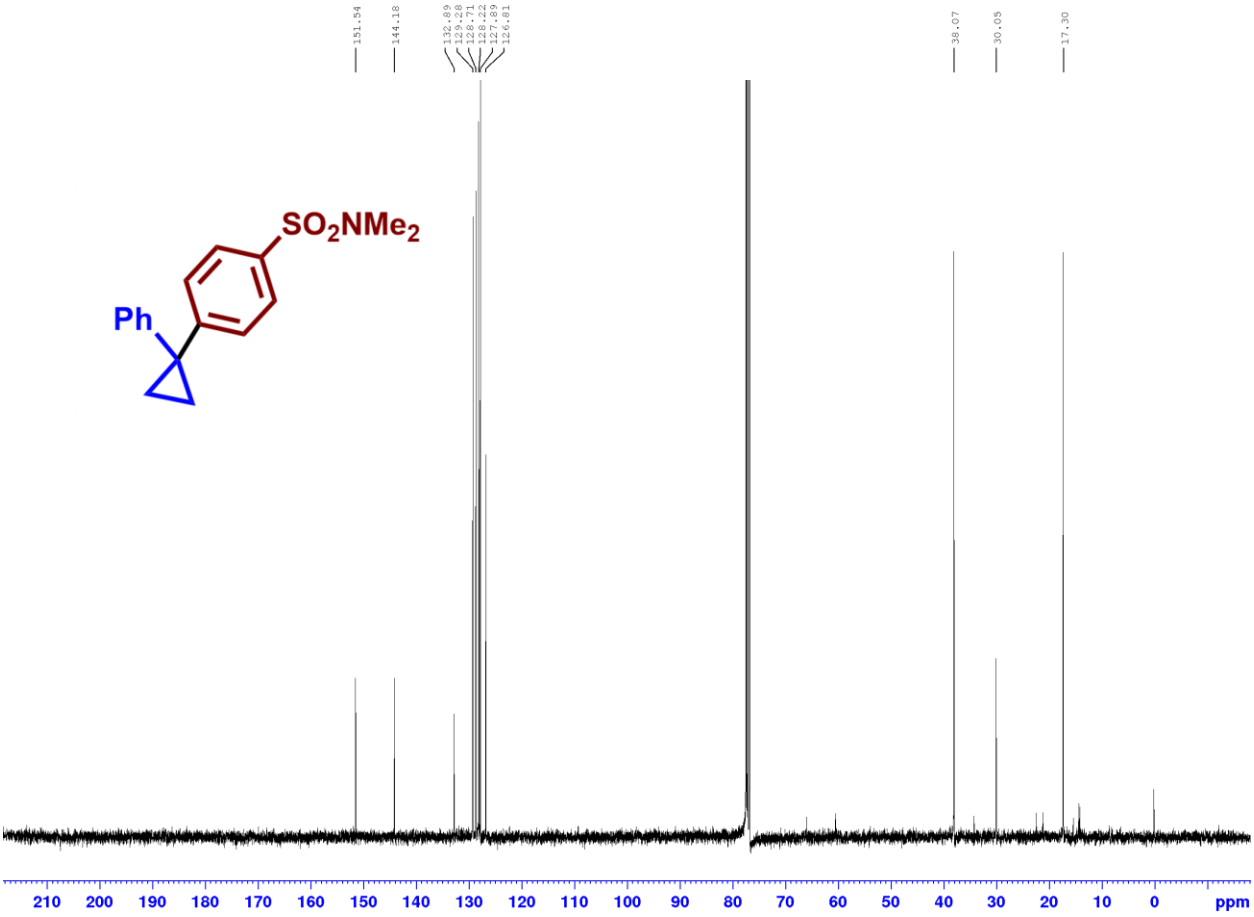
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) ***N,N*-dimethyl-4-(1-methylcyclopropyl)benzenesulfonamide (18c)**



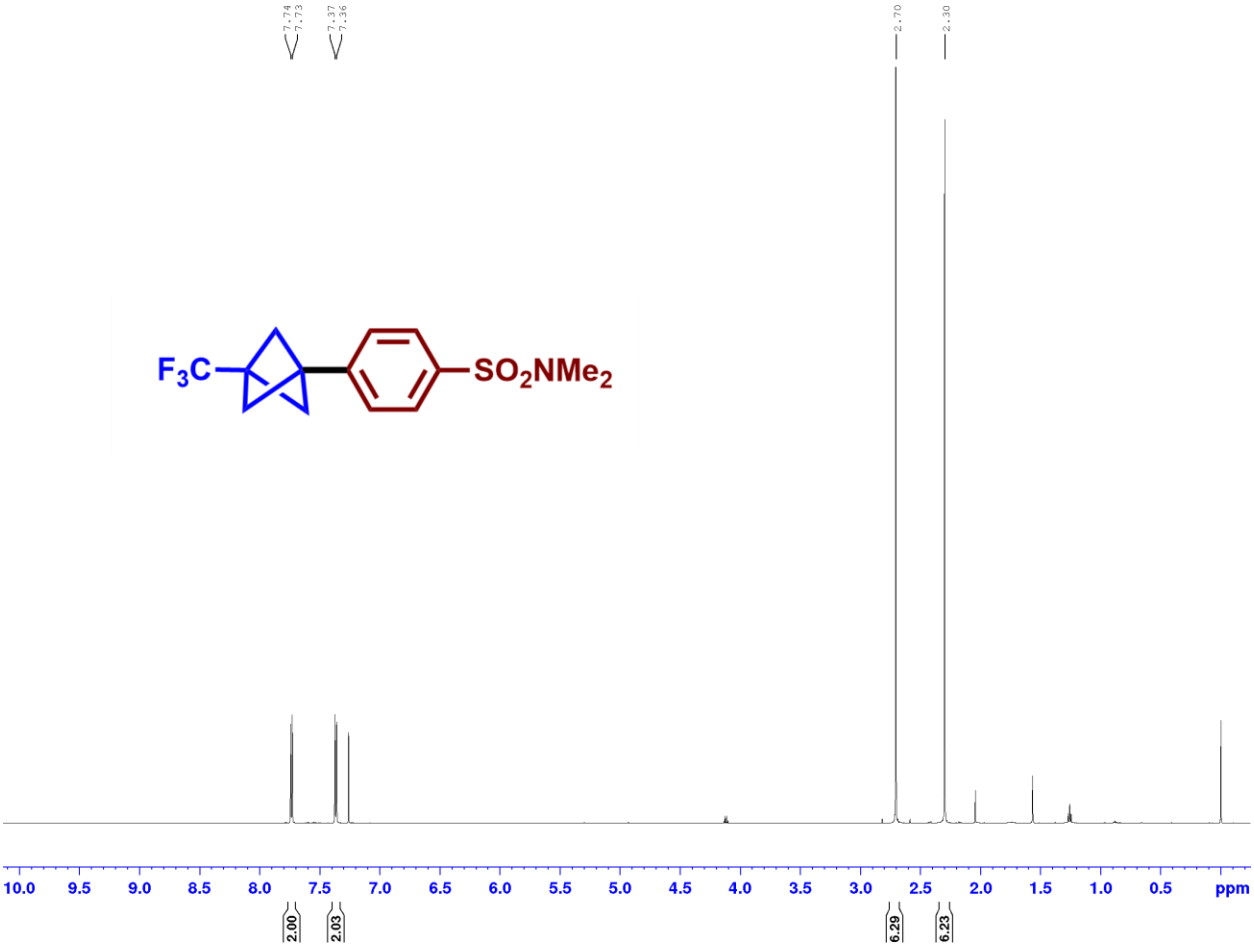
^{1}H NMR spectrum ($(CD_3)_2CO$, 400 MHz) of ***N,N*-dimethyl-4-(1-phenylcyclopropyl)benzenesulfonamide (18d)**



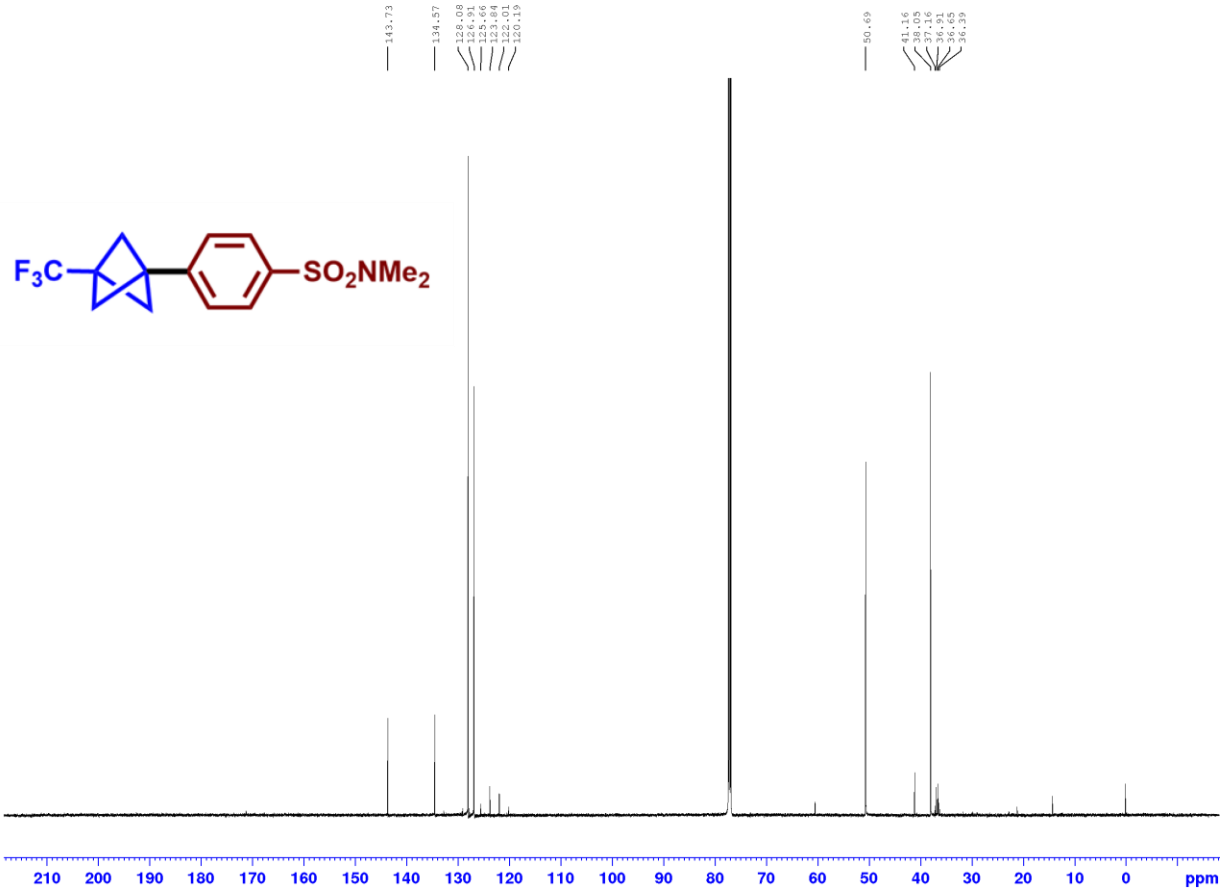
$^{13}C\{^{1}H\}$ NMR spectrum ($(CD_3)_2CO$, 100 MHz) ***N,N*-dimethyl-4-(1-phenylcyclopropyl)benzenesulfonamide (18d)**



^{1}H NMR spectrum ($CDCl_3$, 600 MHz) of ***N,N*-dimethyl-4-(3-(trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)benzenesulfonamide (18e)**



$^{13}C\{^{1}H\}$ NMR spectrum of $CDCl_3$, 126 MHz) of ***N,N*-dimethyl-4-(3-(trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)benzenesulfonamide (18e)**



^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of ***N,N*-dimethyl-4-(3-(trifluoromethyl)bicyclo[1.1.1]pentan-1-yl)benzenesulfonamide (18e)**