

Electronic Supporting Information

The Key-Intermediate in the Aminations of Saturated C-H Bonds: Synthesis, X-ray Characterization and Catalytic Activity of Ru(TPP)(NAr)₂ (Ar = 3,5-(CF₃)₂C₆H₃)

Simone Fantauzzi, Emma Gallo, Alessandro Caselli, Fabio Ragaini, Nicola Casati, Piero Macchi, and Sergio Cenini.

Experimental Section

General. Unless otherwise specified, all the reactions were carried out in nitrogen atmosphere employing standard Schlenk techniques and magnetic stirring. Benzene, cyclohexene and 1-octene were distilled over sodium-benzophenone and kept under nitrogen. All the other starting materials were commercial products and were used as received. 3,5-Bis(trifluoromethyl)phenyl azide,¹ Ru(TPP)CO² were synthesized by methods reported in the literature or using minor modifications of them.³ The purity of hydrocarbons and of the arylazide employed was checked by GC-MS or ¹H NMR analysis. NMR spectra were recorded at room temperature on a Bruker AC-300, on a Bruker Avance 300-DRX, operating at 300 MHz for ¹H, at 75 MHz for ¹³C and at 282 MHz for ¹⁹F, or on a Bruker Avance 400-DRX spectrometers, operating at 400 MHz for ¹H and at 100 MHz for ¹³C. Chemical shifts (ppm) are reported relative to TMS. The ¹H NMR signals of the compounds described in the following have been attributed by COSY and NOESY techniques. Assignments of the resonance in ¹³C NMR were made using the APT pulse sequence and HSQC and HMBC techniques. GC-MS analyses were performed on a Shimadzu QP5050A instrument. Infrared spectra were recorded on a Varian Scimitar FTS 1000 spectrophotometer. UV/Vis spectra were recorded on an Agilent 8453E instrument. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University.

Complex 1. 3,5-Bis(trifluoromethyl)phenyl azide (223 mg, 0.87 mmol) was added to a benzene (60 mL) suspension of Ru(TPP)(CO) (210 mg, 0.28 mmol). The resulting dark solution was refluxed under nitrogen for 4 hours until the complete consumption of Ru(TPP)(CO) (TLC, SiO₂, petroleum ether/CH₂Cl₂=7:3). The mixture was evaporated to dryness and the residue purified by chromatography (alumina, petroleum ether/dichloromethane = 8:2) (**1**, 230 mg, 70%) (Found: C, 61.34; H, 2.99; N, 7.55. Calcd for C₆₀H₃₄N₆F₁₂Ru: C, 61.70; H, 2.93; N, 7.20). λ_{max} (CH₂Cl₂)/nm 419 and 526 (log ε_M 5.03 and 4.00); ν_{max}(ATR)/cm⁻¹ 1014 (oxidation marker), 877 (imido band); ν_{max}(CH₂Cl₂)/cm⁻¹ 1016 (oxidation marker); ν_{max}(nujol)/cm⁻¹ 1016 (oxidation marker), 893, 878 (imido band);⁴ δ_H (300 MHz; CDCl₃) 8.87 (8 H, s, H_β), 8.08 (8 H, d, *J* 6.9 Hz, H_o), 7.83-7.76 (12 H,

m, H_{m-p}), 6.60 (2 H, s, H_{Ar}), 2.66 (4H, s, H_{Ar}); δ_{H} (300 MHz; C₆D₆) 9.00 (8 H, s, H _{β}), 8.17 (8 H, d, *J* 6.9 Hz, H _{α}), 7.62-7.58 (12 H, m, H_{m-p}), 6.58 (2 H, s, H_{Ar}), 2.95 (4 H, s, H_{Ar}); δ_{C} (75 MHz; CDCl₃) 151.9 (C), 142.5 (C), 141.9 (C), 134.6 (CH), 131.9 (CH), 129.7 (q, *J* 33.2 Hz, C-CF₃), 128.4 (CH), 127.2 (CH), 123.6 (C), 122.3 (q, *J* 271.7 Hz, CF₃), 118.1 (CH), 117.8 (CH); δ_{F} (282 MHz; CDCl₃) -64.06; δ_{F} (282 MHz; C₆D₆) -63.75; *m/z* (ESI) 1169 [M+1].

Synthesis of complex 2. Complex **1** (99 mg, 8.5·10⁻² mmol) was added to a benzene (15 mL) solution of 3,5-bis(trifluoromethyl)phenyl azide (217 mg, 8.4·10⁻¹ mmol) and cyclohexene (0.42 mL, 4.25 mmol). The resulting solution was stirred at 75 °C and the arylazide conversion was monitored by IR spectroscopy measuring the N₃ characteristic absorbance at 2116 cm⁻¹. After 4 hours (60% of ArN₃ conversion) the TLC analysis (alumina, petroleum ether/dichloromethane = 8:2) showed the complete consumption of **1**. The reaction mixture was concentrated to 2 mL and petroleum ether (20 mL) was added. The resulting suspension was filtered to eliminate a dark insoluble residue and concentrated to 10 mL. The resulting purple solid was collected by filtration and dried *in vacuo* (20 mg, 18%). The GC-MS analysis of the solution revealed the presence of the allylic amine *N*-(cyclohex-2-enyl)-3,5-bis(trifluoromethyl)benzenamine (Found: C, 65.20; H, 4.03; N, 6.20. Calcd for C₇₂H₅₂F₁₂N₆Ru: C, 65.01; H, 3.94; N, 6.32). λ_{max} (CH₂Cl₂)/nm 414 and 526 (log ϵ_{M} 4.80 and 3.92); ν_{max} (nujol)/cm⁻¹ 1013 (oxidation marker); ν_{max} (ATR)/cm⁻¹ 1008 (oxidation marker); δ_{H} (300 MHz; CDCl₃) 8.44 (8 H, s, H _{β}), 7.90-7.87 (8 H, m, H _{α}), 7.75-7.71 (12 H, m, H_{m-p}), 6.91 (2 H, s, H_{Ar}), 4.30-4.26 (2 H, m, CH-CH=CH), 2.85-2.82 (2 H, m, H_{Ar}), 2.61-2.59 (2 H, m, H_{Ar}), 1.60-1.54 (2 H, m, CH=CH-CH₂ overlapping with H₂O), 0.88-0.82 (2 H, m, CH=CH-CHH), 0.52-0.43 (2 H, m, CH=CH-CHH), 0.13-0.09 (2 H, m, CH₂-CHH-CH₂ overlapping with grease), -0.04-(-0.10) (2 H, m, CH₂-CHH-CH₂), -1.57-(-1.62) (2 H, m, N-CH-CHH), -1.91-(-1.95) (2 H, m, N-CH-CHH), -2.10-(-2.13) (2 H, m, N-CH); δ_{F} (282 MHz; CDCl₃) -63.25, -63.00; *m/z* (ESI) 1331 [M+1].⁵

7-(3,5-Bis(trifluoromethyl)phenyl)-1-methyl-7-aza-bicyclo[4.1.0]heptane.

3,5-bis(trifluoromethyl)phenyl azide (1.12 g, 4.39 mmol) was dissolved in 1-methyl-1-cyclohexene (10 mL). The resulting yellow solution was refluxed for 20 hours, the solvent evaporated *in vacuo* and the residue purified by flash-chromatography on deactivated silica using 10% Et₃N in petroleum ether during the packing of the column (eluent: petroleum ether / dichloromethane = 9:1) (60%). (Found: C, 55.95; H, 4.86; N, 4.51. Calcd for C₁₅H₁₅F₆N: C, 55.73; H, 4.68; N, 4.33). δ_{H} (300 MHz; CDCl₃) 7.42 (1 H, s, H_{Ar}), 7.22 (2 H, s, H_{Ar}), 2.28-2.26 (1 H, m, CH), 2.08-1.65 (4 H, m, CH₂), 1.63-1.35 (4 H, m, CH₂), 1.06 (3 H, s, CH₃); δ_{C} (75 MHz; CDCl₃) 153.5 (C), 132.4 (q, *J* 32.7

Hz, C-CF₃), 123.8 (q, *J* 270.8 Hz, CF₃), 120.6 (CH), 114.9 (CH), 45.6 (CH), 43.5 (C), 32.1 (CH₂), 24.5 (CH₂), 21.6 (CH₃), 20.7 (CH₂), 20.6 (CH₂); δ_F (282 MHz; CDCl₃) -63.41; *m/z* (EI) 323 [M⁺].

General procedure for catalytic reactions. In a typical run, **1** (15 mg, 1.28·10⁻² mmol) and 3,5-bis(trifluoromethyl)phenyl azide (160 mg, 6.27·10⁻¹ mmol) were added to a benzene (30 mL) solution of the hydrocarbon (3.2 mmol). The resulting solution was refluxed using a preheated oil bath. The consumption of the arylazide was monitored by TLC up to the point that its spot was no longer observable, and then by IR spectroscopy measuring the N₃ characteristic absorbance at 2116 cm⁻¹. The reaction was considered to be finished when the absorbance of the azide measured was below 0.03 (by using a 0.5 mm-thickness cell). The solution was then evaporated to dryness and analyzed by ¹H NMR with 2,4-dinitrotoluene as an internal standard (see Table 1 for yields). The residue was then purified by flash chromatography.

***N*-(cyclohex-2-enyl)-3,5-bis(trifluoromethyl)benzenamine.** *Method A:* By following the general procedure reported above, **1** (15.4 mg, 1.32·10⁻² mmol) and 3,5-bis(trifluoromethyl)phenyl azide (172.7 mg, 6.77·10⁻¹ mmol) were dissolved in a benzene solution of cyclohexene (340 μ L, 3.36 mmol). The same catalytic reaction was also performed by using **1** (15.0 mg, 1.28·10⁻² mmol), 3,5-bis(trifluoromethyl)phenyl azide (160.0 mg, 6.27·10⁻¹ mmol) and cyclohexene (30 mL) as solvent. Analytic data are in accord with the literature.⁶ *Method B:* complex **2** (17 mg, 1.28·10⁻² mmol) and 3,5-bis(trifluoromethyl)phenyl azide (166 mg, 6.51·10⁻¹ mmol) were added to a benzene (30 mL) solution of cyclohexene (0.325 ml, 3.21 mmol). The solution was refluxed for 18 hours, evaporated to dryness and analyzed by ¹H NMR with 2,4-dinitrotoluene as an internal standard (70%).

3,5-Bis(trifluoromethyl)-*N*-(3-methylcyclohex-2-enyl)benzenamine (A) + 3,5-bis(trifluoromethyl)-*N*-(2-methylcyclohex-2-enyl)benzenamine (B). By following the general procedure, **1** (15.0 mg, 1.28·10⁻² mmol) and 3,5-bis(trifluoromethyl)phenyl azide (168.0 mg, 6.59·10⁻¹ mmol) were dissolved in a benzene solution of 1-methyl-1-cyclohexene (380 μ L, 3.21 mmol) (**A/B** = 63:34). The same catalytic reaction was then performed by using **1** (15.2 mg, 1.30·10⁻² mmol), 3,5-bis(trifluoromethyl)phenyl azide (165.7 mg, 6.49·10⁻¹ mmol) and 1-methyl-1-cyclohexene (30 mL) as solvent (**A/B** = 56:44). Compounds **A** + **B** (Found: C, 56.09; H, 4.90; N, 4.67. Calcd for C₁₅H₁₅F₆N C, 55.73; H, 4.68; N, 4.33). δ_H (**A** isomer) (300 MHz; CDCl₃) 7.11 (1 H, s, H_{Ar}), 6.93 (2 H, s, H_{Ar}), 5.44-5.43 (1 H, m, CH=C-CH₃), 4.13 (1 H, br s, NH), 4.01 (1 H, br s, CHNH), 1.98-1.95 (2 H, m, CH₂), 1.88-1.83 (2 H, m, CH₂), 1.72 (3 H, s, CH₃), 1.71-1.64 (2 H, m, CH₂); δ_H (**B** isomer) (300 MHz; CDCl₃) 7.11 (1 H, s, H_{Ar}), 6.93 (2 H, s, H_{Ar}), 5.68-5.66 (1 H, m,

$CH=C-CH_3$), 4.13 (1 H, br s, NH), 3.84 (1 H, br s, $CHNH$), 2.04-2.02 (2 H, m, CH_2), 1.75 (3 H, m, CH_3), 1.70-1.56 (4 H, m, CH_2); δ_C (**A** isomer) (75 MHz; $CDCl_3$) 148.7 (C), 139.7 (C), 132.9 (q, J 30.9 Hz, $C-CF_3$), 124.0 (q, J 270.9 Hz, CF_3), 121.6 (CH), 112.5 (CH), 110.0 (CH), 48.7 (CH), 30.4 (CH₂), 28.5 (CH₂), 24.1 (CH₃), 20.0 (CH₂); δ_C (**B** isomer) (75 MHz; $CDCl_3$) 148.2 (C), 133.3 (C), 132.9 (q, J 30.9 Hz, $C-CF_3$), 127.2 (CH), 124.0 (q, J 270.9 Hz, CF_3), 112.2 (CH), 110.0 (CH), 51.4 (CH), 28.1 (CH₂), 25.5 (CH₂), 21.9 (CH₃), 18.2 (CH₂); δ_F (282 MHz; $CDCl_3$) -63.56; m/z (EI) 323 [M^+].

***N*-(3,5-bis(trifluoromethyl)phenyl)-1*H*-inden-1-amine.** By following the general procedure, **1** (15.0 mg, $1.28 \cdot 10^{-2}$ mmol) and 3,5-bis(trifluoromethyl)phenyl azide (164.9 mg, $6.46 \cdot 10^{-1}$ mmol) were dissolved in a benzene solution of indene (400 μ L, 3.43 mmol). The same catalytic reaction was then performed by using **1** (15.0 mg, $1.28 \cdot 10^{-2}$ mmol), 3,5-bis(trifluoromethyl)phenyl azide (160.5 mg, $6.29 \cdot 10^{-1}$ mmol) and indene (30 mL) as solvent (Found: C, 59.68; H, 3.38; N, 4.05. Calcd for $C_{17}H_{11}F_6N$: C, 59.48; H, 3.23; N, 4.08). δ_H (300 MHz; $CDCl_3$) 7.46 (1 H, d, J 7.5 Hz, H_{Ar}), 7.38-7.35 (2 H, m, H_{Ar}), 7.27-7.24 (1 H, m, H_{Ar}), 7.22 (1 H, s, H_{Ar}), 7.04 (2 H, s, H_{Ar}), 6.92 (1 H, dd, J 5.7 and 1.8 Hz, $CH=CH-CH$), 6.53 (1 H, d, J 5.7 and 1.8 Hz, $CH=CH-CH$), 5.16 (1 H, d, J 8.7 Hz, $CHNH$), 4.34 (1 H, d, J 8.7 Hz, NH); δ_C (75 MHz; $CDCl_3$) 148.5 (C), 144.0 (C), 143.2 (C), 135.3 (CH), 133.7 (CH), 132.8 (q, J 33.4 Hz, $C-CF_3$), 128.8 (CH), 126.4 (CH), 123.7 (q, J 273.0 Hz, CF_3), 123.4 (CH), 122.0 (CH), 112.8 (CH), 111.0 (CH), 61.2 (CH); δ_F (282 MHz; $CDCl_3$) -63.57; m/z (EI) 343 [M^+].

3,5-Bis(trifluoromethyl)-*N*-(2-methyl-1-phenylpropyl)benzenamine. By following the general procedure, **1** (15.2 mg, $1.30 \cdot 10^{-2}$ mmol) and 3,5-bis(trifluoromethyl)phenyl azide (166.0 mg, $6.51 \cdot 10^{-1}$ mmol) were dissolved in a benzene solution of isobutylbenzene (500 μ L, 3.18 mmol). The same catalytic reaction was then performed by using **1** (15.6 mg, $1.34 \cdot 10^{-2}$ mmol), 3,5-bis(trifluoromethyl)phenyl azide (170.8 mg, $6.70 \cdot 10^{-1}$ mmol) and isobutylbenzene (30 mL) as solvent (Found: C, 59.91; H, 4.92; N, 3.84. Calcd for $C_{18}H_{17}F_6N$: C, 59.83; H, 4.74; N, 3.88). δ_H (300 MHz; $CDCl_3$) 7.35-7.27 (5 H, m, H_{Ar}), 7.08 (1 H, s, H_{Ar}), 6.88 (2 H, s, H_{Ar}), 4.58 (1 H, d, J 5.7 Hz, NH), 4.15 (1 H, pst, J 6.3 Hz, $CHNH$), 2.12-2.05 (1 H, m, $CH(CH_3)_2$), 1.06 (3 H, d, J 6.9 Hz, CH_3), 0.94 (3 H, d, J 6.9 Hz, CH_3); δ_C (75 MHz; $CDCl_3$) 148.5 (C), 141.1 (C), 132.6 (q, J 32.4 Hz, $C-CF_3$), 129.0 (CH), 127.8 (CH), 127.4 (CH), 123.9 (q, J 270.9 Hz, CF_3), 112.8 (CH), 110.5 (br, CH), 64.3 (CH), 35.2 (CH), 20.0 (CH₃), 19.2 (CH₃); δ_F (282 MHz; $CDCl_3$) -63.60; m/z (EI) 361 [M^+].

3,5-Bis(trifluoromethyl)-*N*-(2-phenylpropan-2-yl)benzenamine. By following the general procedure, **1** (15.1 mg, $1.29 \cdot 10^{-2}$ mmol) and 3,5-bis(trifluoromethyl)phenyl azide (165.6 mg, $6.49 \cdot 10^{-1}$ mmol) were dissolved in a benzene solution of cumene (450 μ L, 3.23 mmol). The same catalytic reaction was then performed by using **1** (15.0 mg, $1.28 \cdot 10^{-2}$ mmol), 3,5-bis(trifluoromethyl)phenyl azide (169.4 mg, $6.64 \cdot 10^{-1}$ mmol) and cumene (30 mL) as solvent (Found: C, 58.70; H, 4.50; N, 3.97. Calcd for $C_{17}H_{15}F_6N$: C, 58.79; H, 4.35; N, 4.03). δ_H (400 MHz; $CDCl_3$) 7.48 (2 H, d, J 7.3 Hz, H_{Ar}), 7.38 (2 H, pst, J 7.3 Hz, H_{Ar}), 7.29 (1 H, t, J 7.3 Hz, H_{Ar}), 7.06 (1 H, s, H_{Ar}), 6.68 (2 H, s, H_{Ar}), 4.56 (1 H, s, NH), 1.71 (6 H, s, CH_3); δ_C (100 MHz; $CDCl_3$) 146.7 (C), 145.4 (C), 131.8 (q, J 32.4 Hz, C- CF_3), 128.9 (CH), 127.0 (CH), 125.2 (CH), 123.4 (q, J 270.9 Hz, CF_3), 114.0 (CH), 109.9 (CH), 56.2 (C), 30.3 (CH_3); δ_F (282 MHz; $CDCl_3$) -63.71; m/z (EI) 347 [M^+].

***N*-(3,5-bis(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-2-amine (A) and *N*-(3,5-bis(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-1-amine (B).** By following the general procedure, **1** (15.0 mg, $1.28 \cdot 10^{-2}$ mmol) and 3,5-bis(trifluoromethyl)phenyl azide (172.7 mg, $6.77 \cdot 10^{-1}$ mmol) were dissolved in a benzene solution of 1,2-dihydronaphthalene (400 μ L, 3.06 mmol). Compound **A** (Found: C, 60.80; H, 3.82; N, 4.00. Calcd for $C_{18}H_{13}F_6N$: C, 60.51; H, 3.67; N, 3.92). δ_H (300 MHz; $CDCl_3$) 7.26-7.13 (5 H, m, H_{Ar}), 6.95 (2 H, s, H_{Ar}), 6.65 (1 H, d, J 9.3 Hz, $CH=CH-CH(NH)$), 6.08 (1 H, dd, J 9.3 and 4.5 Hz, $CH=CH-CH(NH)$), 4.38 (1 H, dddd, J 8.4, 6.3, 6.3 and 4.5 Hz, $CH(NH)$), 4.16 (1 H, d, J 8.4 Hz, NH), 3.12 (1 H, dd, J 15.9 and 6.3 Hz, CH_2), 3.02 (1 H, dd, J 15.9 and 6.3 Hz, CH_2); δ_C (75 MHz; $CDCl_3$) 147.2 (C), 132.4 (q, J 32.8 Hz, C- CF_3 overlapping with another quaternary carbon), 129.9 (CH), 128.6 (CH), 127.8 (CH), 127.1 (CH, two signals overlaid), 126.6 (CH), 123.4 (q, J 270.8 Hz, CF_3), 112.1 (CH), 110.2 (CH), 46.4 (CH), 33.3 (CH_2); δ_F (282 MHz; $CDCl_3$) -63.17; m/z (EI) 357 [M^+]. Compound **B**. (Found: C, 60.61; H, 3.88; N, 3.97. Calcd for $C_{18}H_{13}F_6N$: C, 60.51; H, 3.67; N, 3.92). δ_H (400 MHz; $CDCl_3$) 7.34-7.24 (3 H, m, H_{Ar}), 7.19-7.17 (2 H, m, H_{Ar}), 7.01 (2 H, s, H_{Ar}), 6.62 (1 H, dt, J 9.6 and 1.6 Hz, $CH=CH-CH_2$), 6.02 (1 H, dt, J 9.6 and 4.3 Hz, $CH=CH-CH_2$), 4.76 (1 H, dt, J 8.6 and 6.3 Hz, $CH=NH$), 4.37 (1 H, d, J 8.6 Hz, NH), 2.64 (2 H, ddd, J 6.3, 4.3 and 1.6 Hz, CH_2); δ_C (100 MHz; $CDCl_3$) 147.7 (C), 134.5 (C), 133.3 (C), 132.6 (q, J 32.8 Hz, C- CF_3), 128.5 (CH), 128.0 (CH), 127.8 (CH), 126.9 (CH, two signals overlaid), 125.7 (CH), 123.5 (q, J 270.9 Hz, CF_3), 112.3 (CH), 110.3 (CH), 50.4 (CH), 29.4 (CH_2); δ_F (282 MHz; $CDCl_3$) -63.50; m/z (EI) 357 [M^+].

***N*-(3,5-bis(trifluoromethyl)phenyl)-1,2-dihydro-4-phenylnaphthalen-2-amine (A) and 1-(3,5-bis(trifluoromethyl)phenyl)-1a,2,3,7b-tetrahydro-7b-phenyl-1*H*-naphtho[2,1-*b*]azirine**

(B). By following the general procedure, **1** (15.2 mg, $1.30 \cdot 10^{-2}$ mmol) and 3,5-bis(trifluoromethyl)phenyl azide (164.9 mg, $6.46 \cdot 10^{-1}$ mmol) were dissolved in a benzene solution of 1-phenyl-3,4-dihydronaphthalene (600 μ L, 3.20 mmol). Compound **A** (Found: C, 66.65; H, 4.01; N, 3.18. Calcd for $C_{24}H_{17}F_6N$ C, 66.51; H, 3.95; N, 3.23). δ_H (300 MHz $CDCl_3$) 7.42-7.37 (5 H, m, H_{Ar}), 7.28-7.25 (3 H, m, H_{Ar}), 7.19 (1 H, s, H_{Ar}), 7.14-7.12 (1 H, m, H_{Ar}), 7.01 (2 H, s, H_{Ar}), 6.10 (1 H, d, J 4.6 Hz, $C(Ph)=CH-CH(NH)$), 4.51 (1 H, m, $CH(NH)$), 4.26 (1 H, d, J 8.9 Hz, NH), 3.22 (1 H, dd, J 15.4 and 5.7 Hz, CH_2), 3.05 (1 H, dd, J 15.4 and 7.2 Hz, CH_2); δ_C (75 MHz; $CDCl_3$) 147.8 (C), 142.5 (C), 139.8 (C), 134.2 (C), 134.1 (C), 133.0 (q, J 32.8 Hz, $C-CF_3$), 129.3 (CH), 128.8 (CH), 128.4 (CH), 128.3 (CH), 127.4 (CH), 126.8 (CH), 126.6 (CH), 123.9 (q, J 271.0 Hz, CF_3), 112.8 (CH), 110.8 (CH), 47.7 (CH), 34.7 (CH_2); δ_F (282 MHz; $CDCl_3$) -63.51; m/z (EI) 433 [M^+].

Compound **B** was isolated by chromatography in mixture with 1-phenylnaphthalene due to the very similar R_f values of these compounds in several solvents on both alumina and silica. The presence of 1-phenylnaphthalene was confirmed by GC-MS analysis. The 1H , ^{13}C , ^{19}F spectra of this mixture is reported. The 1H and ^{13}C NMR signals of **B** have been attributed by COSY, NOESY, HSQC and HMBC techniques.

3,5-Bis(trifluoromethyl)-*N*-(oct-1-en-3-yl)benzenamine (A) and (E/Z)-3,5-bis(trifluoromethyl)-*N*-(oct-2-enyl)benzenamine (B). By following the general procedure, **1** (16.2 mg, $1.39 \cdot 10^{-2}$ mmol) and 3,5-bis(trifluoromethyl)phenyl azide (172.7 mg, $6.77 \cdot 10^{-1}$ mmol) were dissolved in a benzene solution of 1-octene (570 μ L, 3.63 mmol). The same catalytic reaction was then performed by using **1** (14.9 mg, $1.28 \cdot 10^{-2}$ mmol), 3,5-bis(trifluoromethyl)phenyl azide (159.9 mg, $6.27 \cdot 10^{-1}$ mmol) and 1-octene (30 mL) as solvent. Compound **A** (Found: C, 57.02; H, 6.00; N, 4.06. Calcd for $C_{16}H_{19}F_6N$: C, 56.63; H, 5.64; N, 4.13). δ_H (300 MHz $CDCl_3$) 7.13 (1 H, s, H_{Ar}), 6.94 (2 H, s, H_{Ar}), 5.72 (1 H, ddd, J 17.2, 10.3 and 6.1 Hz, $CH=CH_2$), 5.23 (1 H, d, J 17.2 Hz, $CH=CH_2$), 5.20 (1H, d, J 10.3 Hz, $CH=CH_2$), 4.09 (1 H, d, J 6.9 Hz, NH), 3.87-3.83 (1 H, m, $CH(NH)$), 1.65-1.61 (2 H, m, CH_2), 1.36-1.30 (6 H, m, CH_2), 0.92 (3 H, pst, J 6.9 Hz, CH_3); δ_C (75 MHz; $CDCl_3$) 148.5 (C), 138.9 (CH), 132.6 (q, J 32.4 Hz, $C-CF_3$), 124.0 (q, J 270.8 Hz, CF_3), 116.4 (CH_2), 112.8 (CH), 110.4 (br, CH), 56.4 (CH), 36.1 (CH_2), 32.0 (CH_2), 25.9 (CH_2), 22.9 (CH_2), 14.4 (CH_3); δ_F (282 MHz; $CDCl_3$) -63.57; m/z (EI) 339 [M^+]. Compound **B** (E/Z = 63:37) (Found: C, 56.90; H, 5.85; N, 3.99. Calcd for $C_{16}H_{19}F_6N$: C, 56.63; H, 5.64; N, 4.13). δ_H (E isomer) (300 MHz; $CDCl_3$) 7.16 (1 H, s, H_{Ar}), 6.96 (2 H, s, H_{Ar}), 5.77-5.64 (1 H, m, $CH=CH$), 5.54-5.51 (1 H, m, $CH=CH$), 4.20 (1 H, br s, NH), 3.79-3.76 (2 H, m, CH_2), 2.09-2.05 (2 H, m, $CH_2CH=CH$), 1.40-1.20 (6 H, m, CH_2), 0.93-0.89 (3 H, m, CH_3); δ_H (Z isomer) (300 MHz; $CDCl_3$) 7.17 (1 H, s, H_{Ar}), 6.96 (2 H, s, H_{Ar}), 5.77-5.64 (1 H, m, $CH=CH$), 5.54-5.51 (1 H, m, $CH=CH$), 4.12 (1H, br s, NH),

3.84-3.81 (2 H, m, CH₂), 2.17-2.14 (2 H, m, CH₂CH=CH), 1.40-1.20 (6 H, m, CH₂), 0.93-0.89 (3 H, m, CH₃); δ_C (75 MHz; CDCl₃) 148.7 (C), 134.8 (CH), 134.7 (CH), 132.3 (m, C-CF₃), 125.0 (CH), 124.9 (CH), 112.0 (CH), 111.9 (CH), 110.1 (CH), 45.7 (CH₂), 40.8 (CH₂), 32.3 (CH₂), 31.5 (CH₂), 31.3 (CH₂), 29.1 (CH₂), 28.8 (CH₂), 27.6 (CH₂), 22.4 (CH₂), 14.0 (CH₃); δ_F (282 MHz; CDCl₃) - 63.55; m/z (EI) 339 [M⁺].

Crystallographic Experimentals and Data

Both complexes grow in needle shaped dark purple crystals. They were mounted on a Bruker SMART diffractometer equipped with an APEXII CCD detector and ω scans data at four different values of φ were collected at 150K (using an Oxford cryosystem nitrogen stream) and ambient temperature for complexes **1** and **2** respectively. APEXII was used to integrate the diffraction images after an initial cell was indexed. Data were empirically corrected for absorption using Sadabs,⁷ solved using SIR97⁸ and refined using SHELX-L 97,⁹ as included in the WinGX¹⁰ package. For complex **1** hydrogen atoms were constrained with a riding model and all the phenyl rings were constrained to a perfect hexagon using the AFIX66 command.

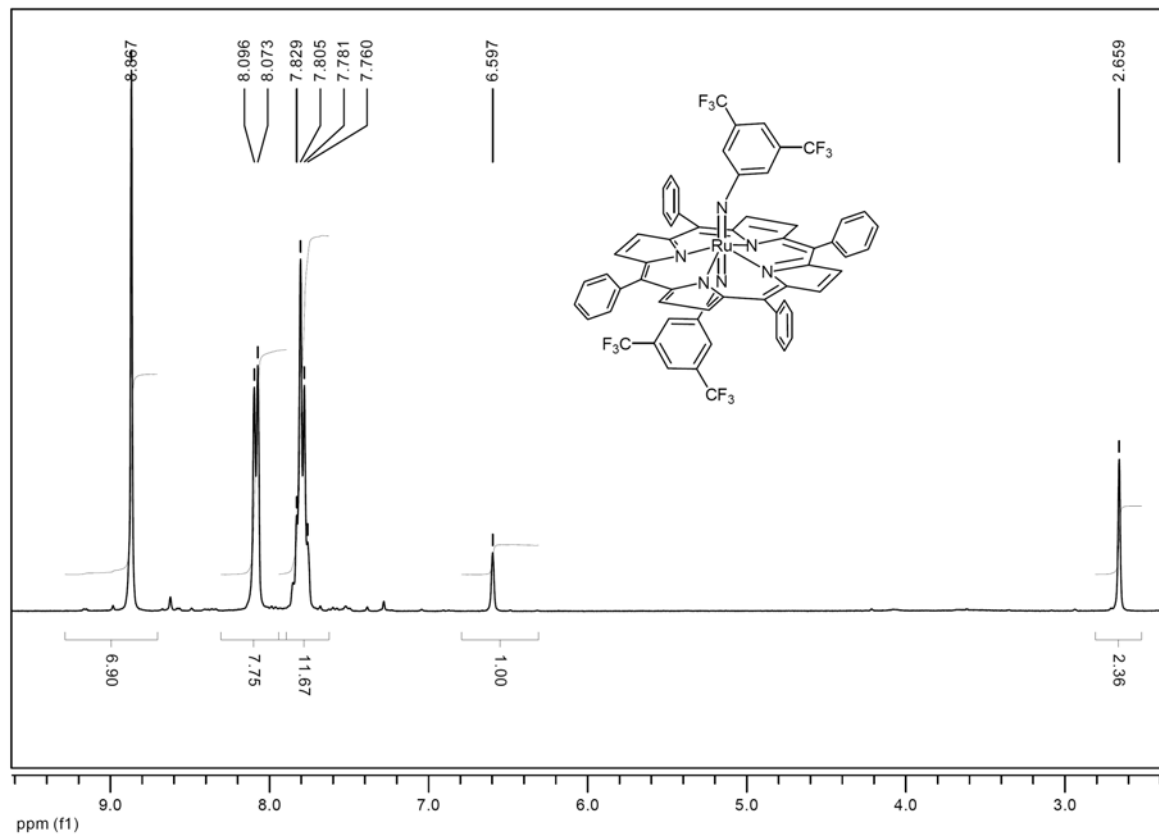
Crystal data for **1** (CCDC 720709): C₆₀H₃₄F₁₂N₆Ru, M = 1168, Triclinic, $a = 11.961(2)$, $b = 13.080(2)$, $c = 17.084(3)$ Å, $\alpha = 107.893(2)$, $\beta = 104.084(2)$, $\gamma = 93.677(2)$ °, $V = 2439.0(7)$ Å³, space group P-1 ($n^{\circ}2$), Z = 2, 19912 reflections measured, 7010 unique ($R_{\text{int}} = 0.0744$) which were used in all calculations. The final R(F) and wR(F²) were 0.0992 and 0.1156 (all data), 0.0476 and 0.0948 (for $I > 2\sigma(I)$).

For complex **2** hydrogen atoms were constrained with a riding model with the exception of the one bound to the first carbon of cyclohexene (C3 in fig. 2), that was located and refined. The cyclohexene moiety was disordered in two different positions with the double bond in two different sides. Two fragments have been refined with equal 0.5 occupation and constrained to be geometrically identical with the SAME command, forcing equal thermal parameters for related atoms and keeping pivotal atoms in the same positions. The CF₃ groups show some possible dynamical disorder which affects the accuracy of the thermal parameters.

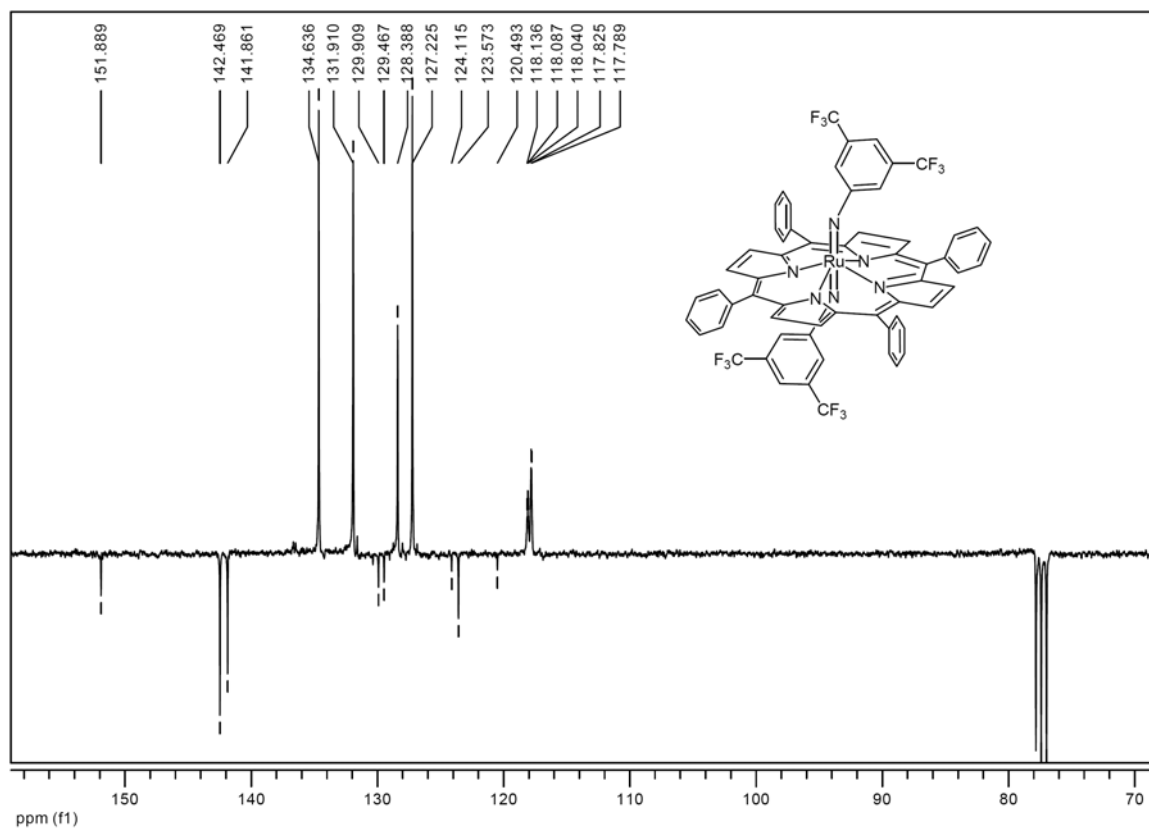
Crystal data for **2** (CCDC 720710): C₇₂H₅₂F₁₂N₆Ru, M = 1330.26, Triclinic, $a = 10.550(5)$, $b = 11.624(5)$, $c = 13.338(5)$ Å, $\alpha = 77.057(5)$, $\beta = 76.063(5)$, $\gamma = 75.063(5)$ °, $V = 1510.9(11)$ Å³, space group P-1 ($n^{\circ}2$), Z = 1, 14498 reflections measured, 5232 unique ($R_{\text{int}} = 0.0419$) which were used in all calculations. The final R(F) and wR(F²) were 0.0692 and 0.1454 (all data), 0.0559 and 0.1369 (for $I > 2\sigma(I)$).

NMR spectra.

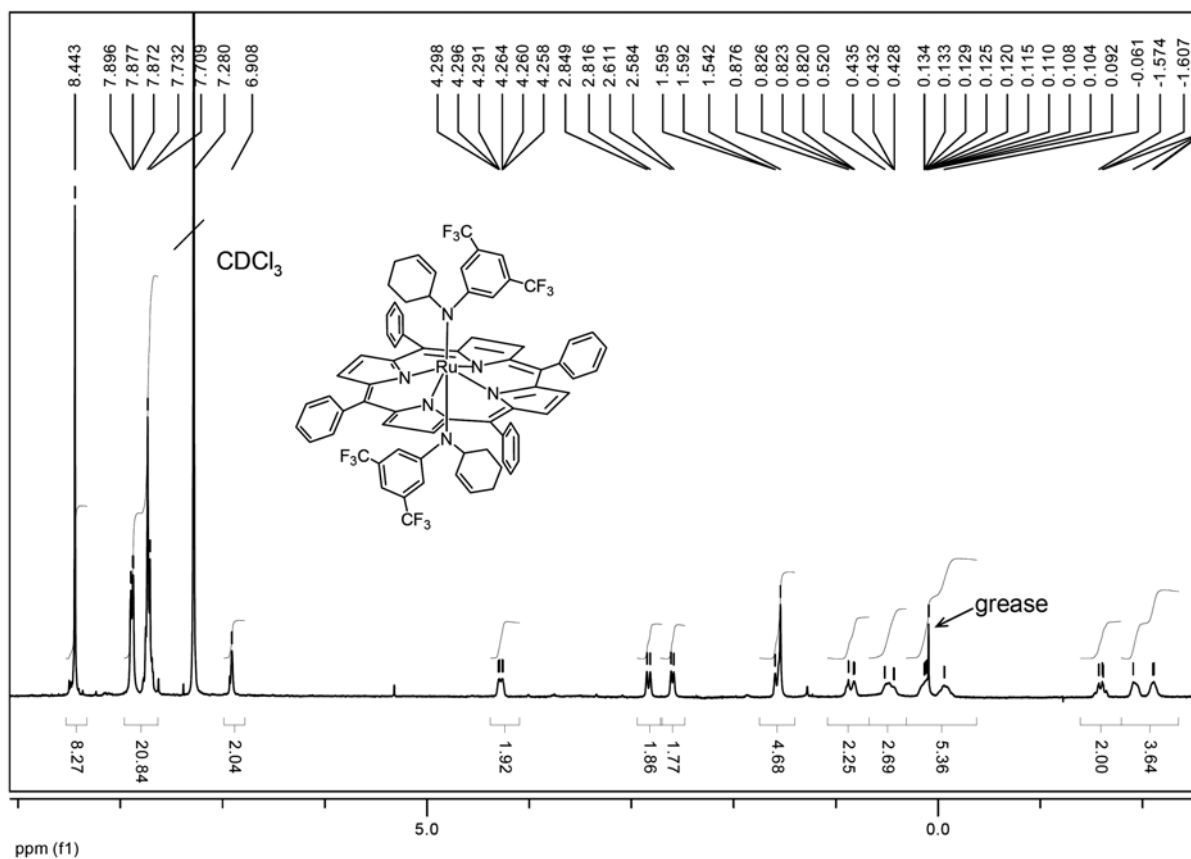
^1H NMR of complex **1** (CDCl_3).



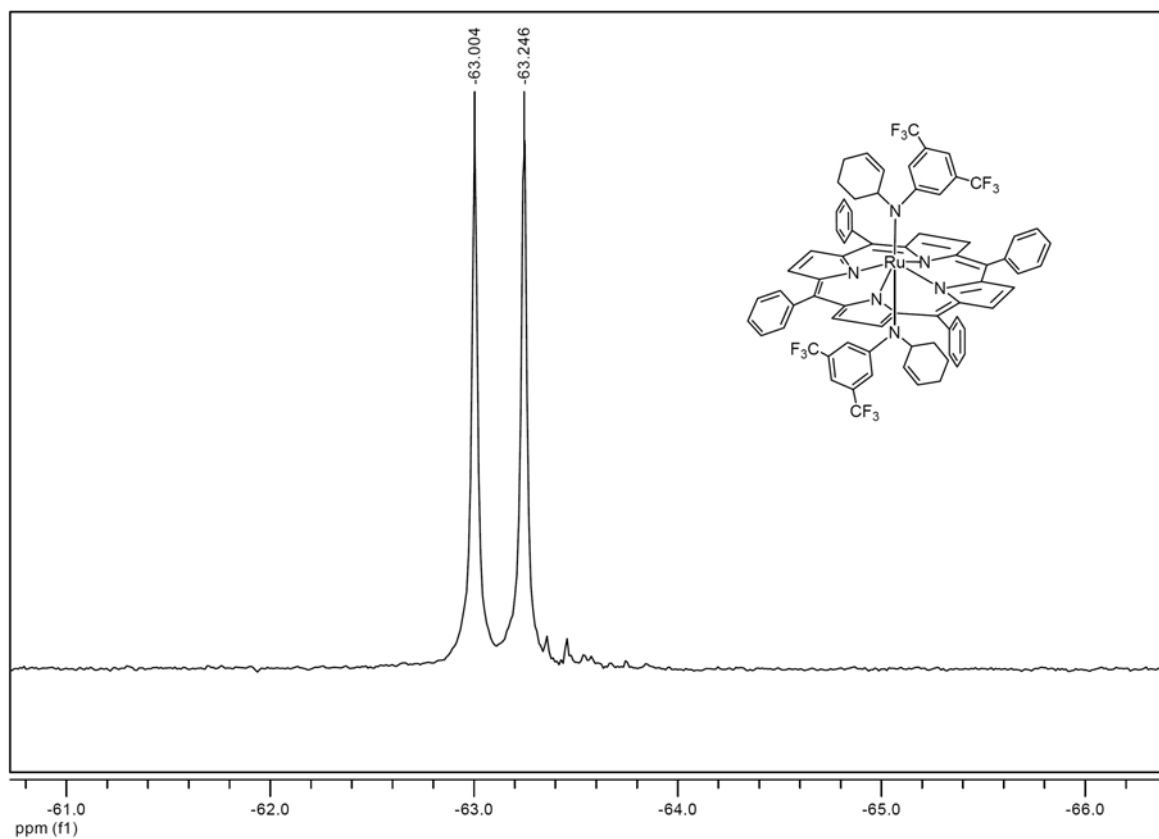
^{13}C NMR of complex **1** (CDCl_3).



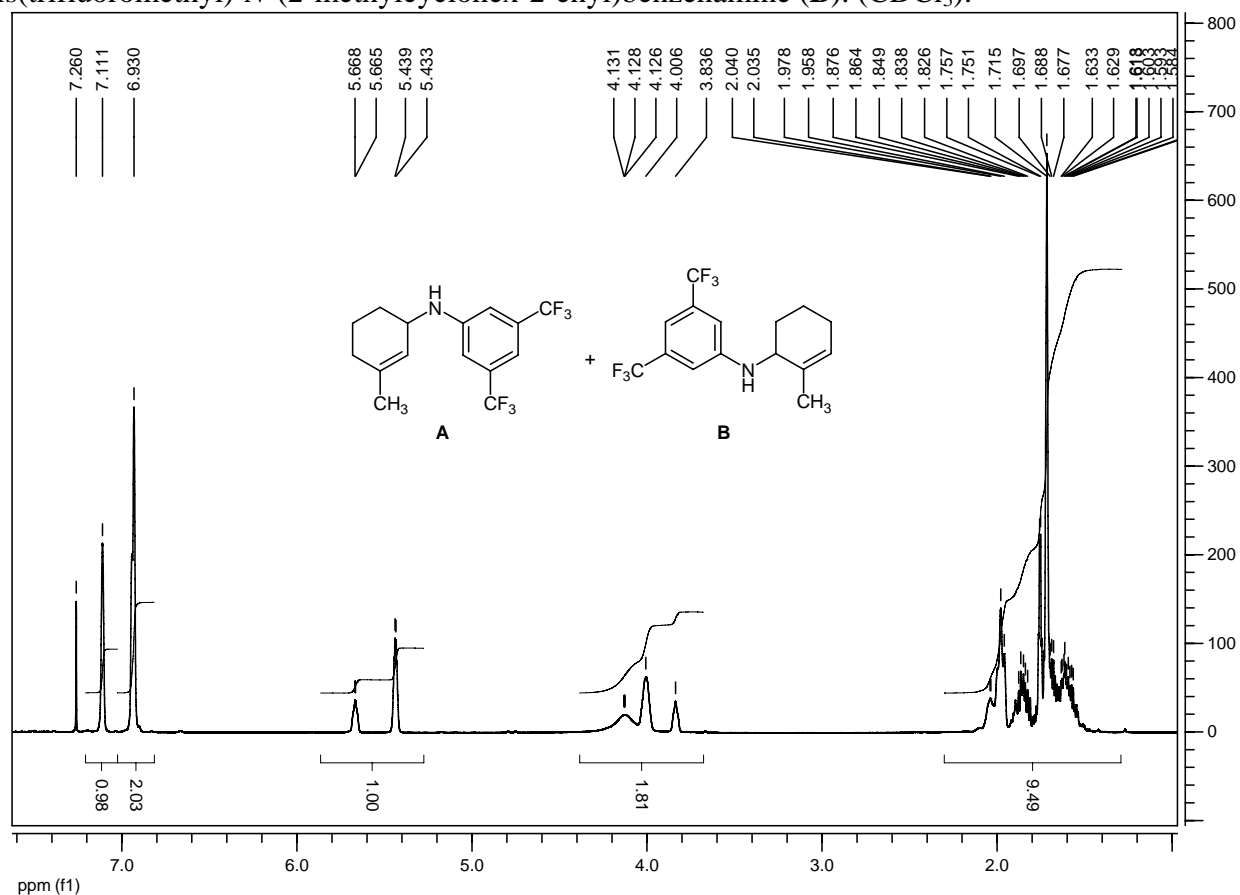
^1H NMR of complex **2** (CDCl_3).



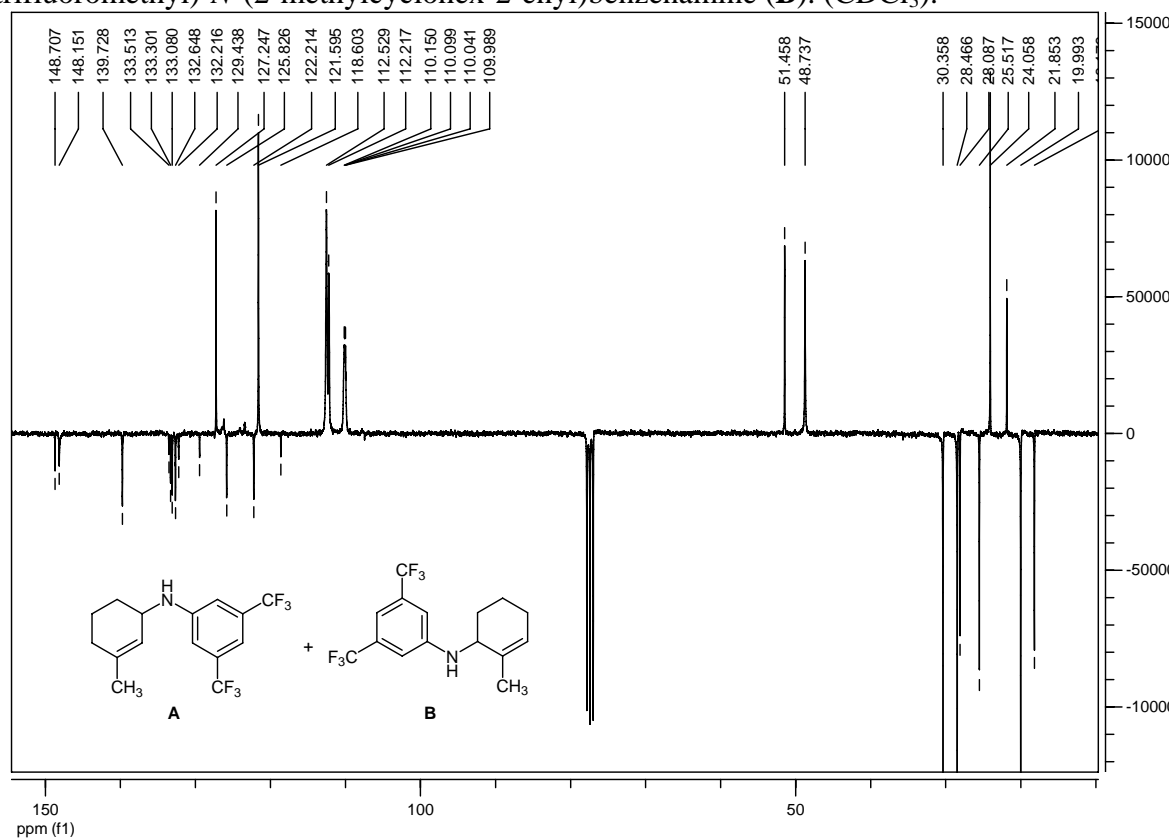
^{19}F NMR of complex **2** (CDCl_3).



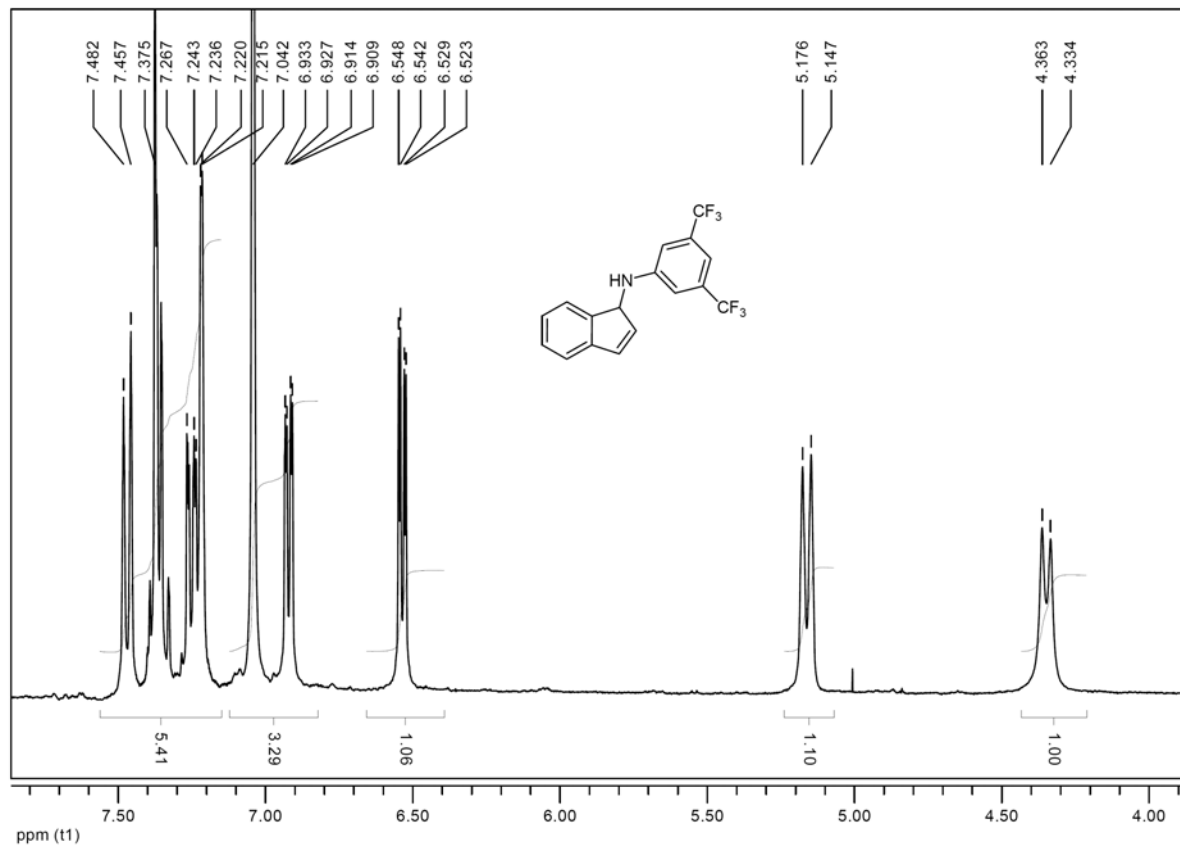
^1H NMR of 3,5-bis(trifluoromethyl)-*N*-(3-methylcyclohex-2-enyl)benzenamine (**A**) + 3,5-bis(trifluoromethyl)-*N*-(2-methylcyclohex-2-enyl)benzenamine (**B**). (CDCl_3).



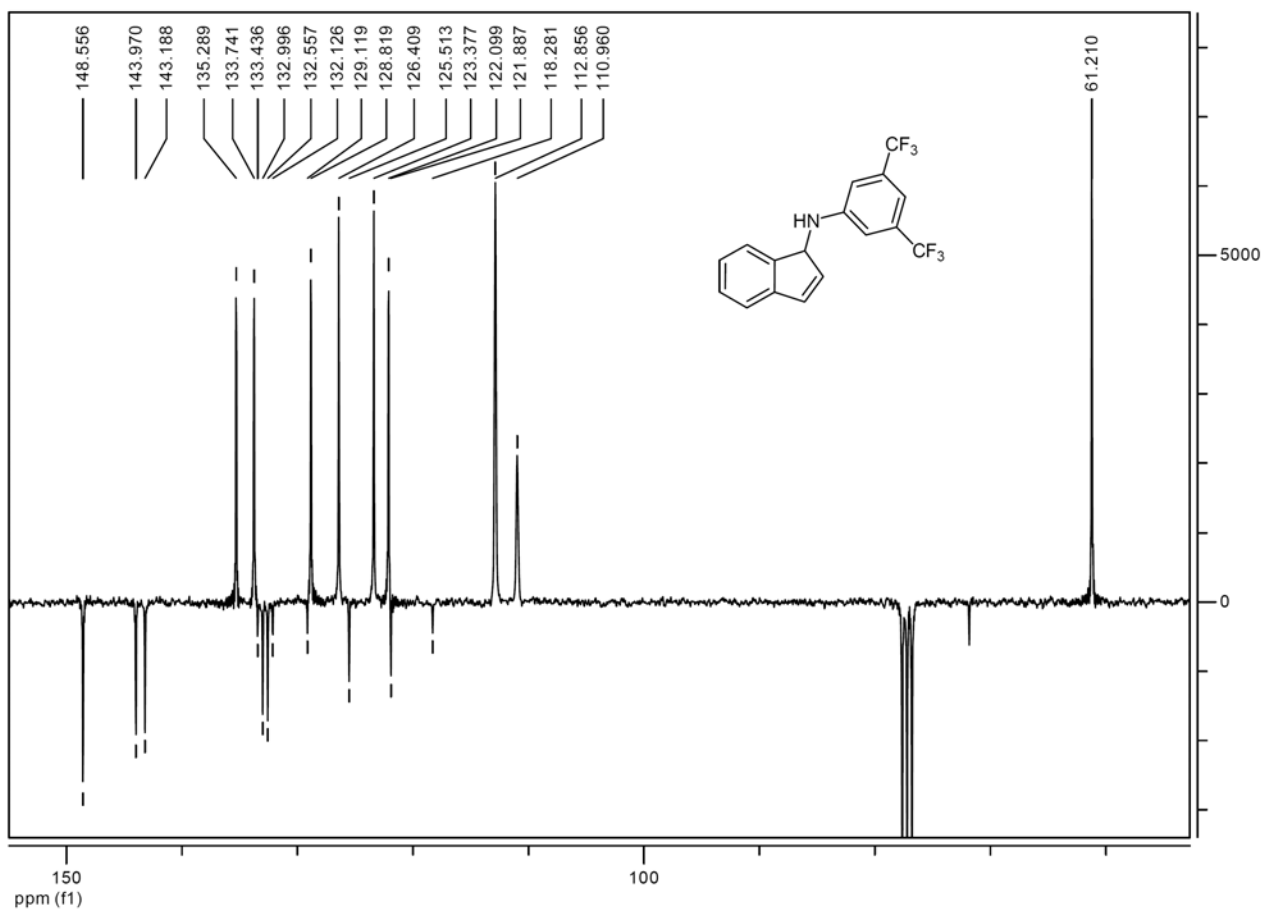
^{13}C NMR of 3,5-bis(trifluoromethyl)-*N*-(3-methylcyclohex-2-enyl)benzenamine (**A**) + 3,5-bis(trifluoromethyl)-*N*-(2-methylcyclohex-2-enyl)benzenamine (**B**). (CDCl_3).



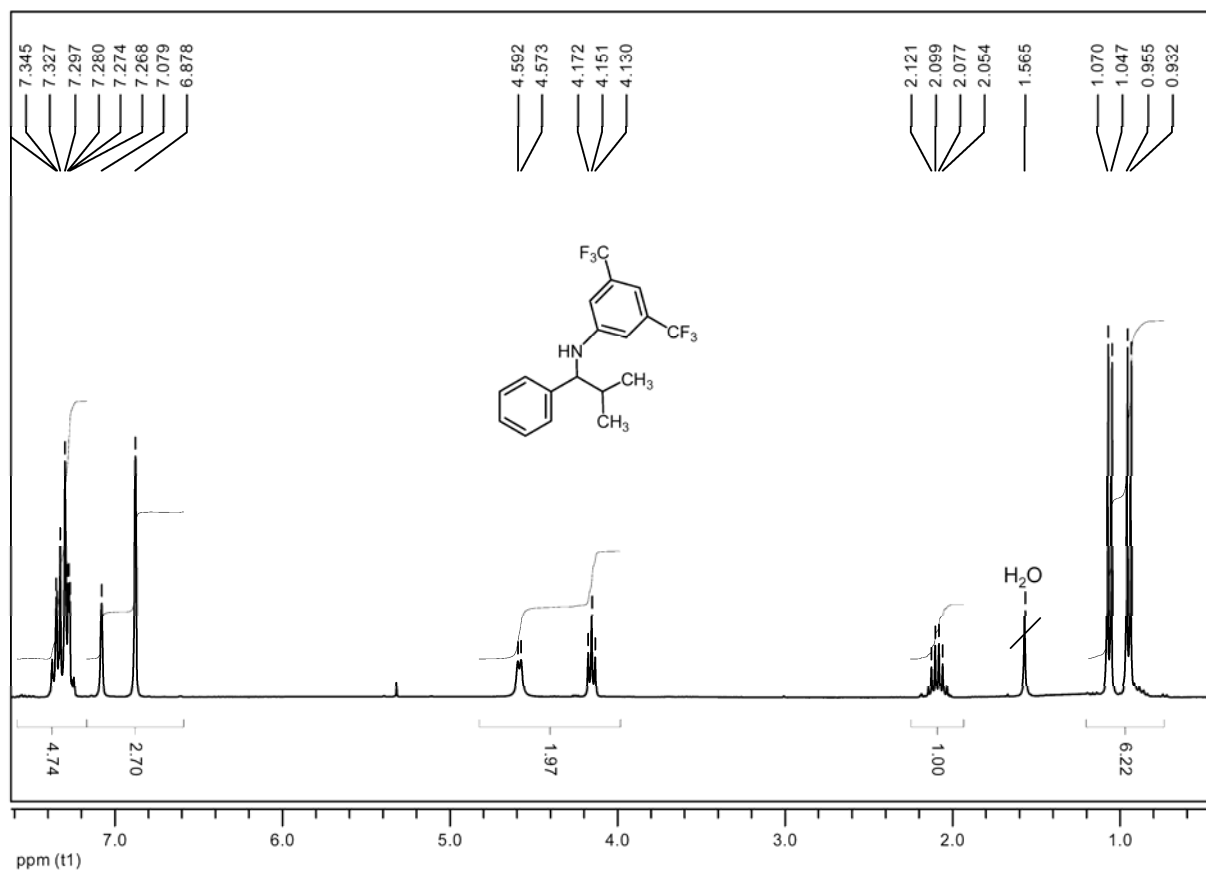
^1H NMR of *N*-(3,5-bis(trifluoromethyl)phenyl)-1*H*-inden-1-amine (CDCl_3).



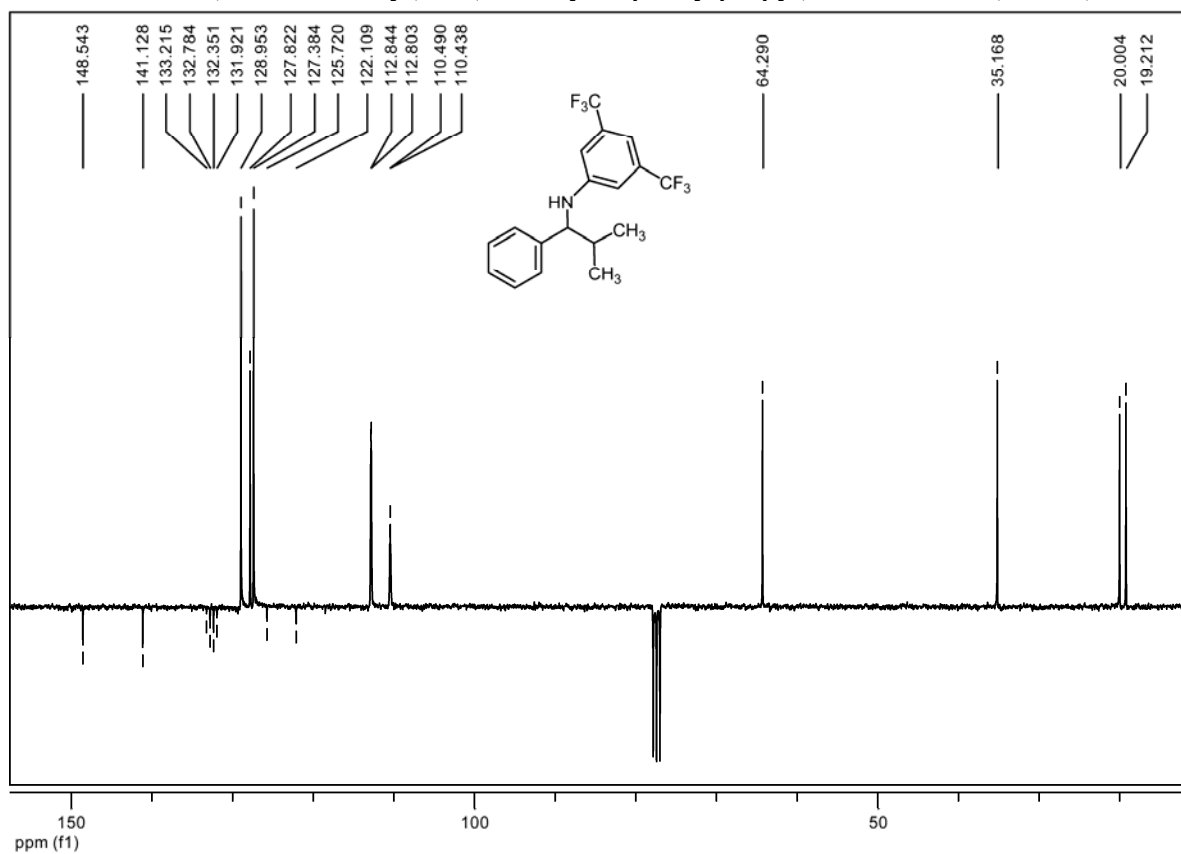
^{13}C NMR of *N*-(3,5-bis(trifluoromethyl)phenyl)-1*H*-inden-1-amine (CDCl_3).



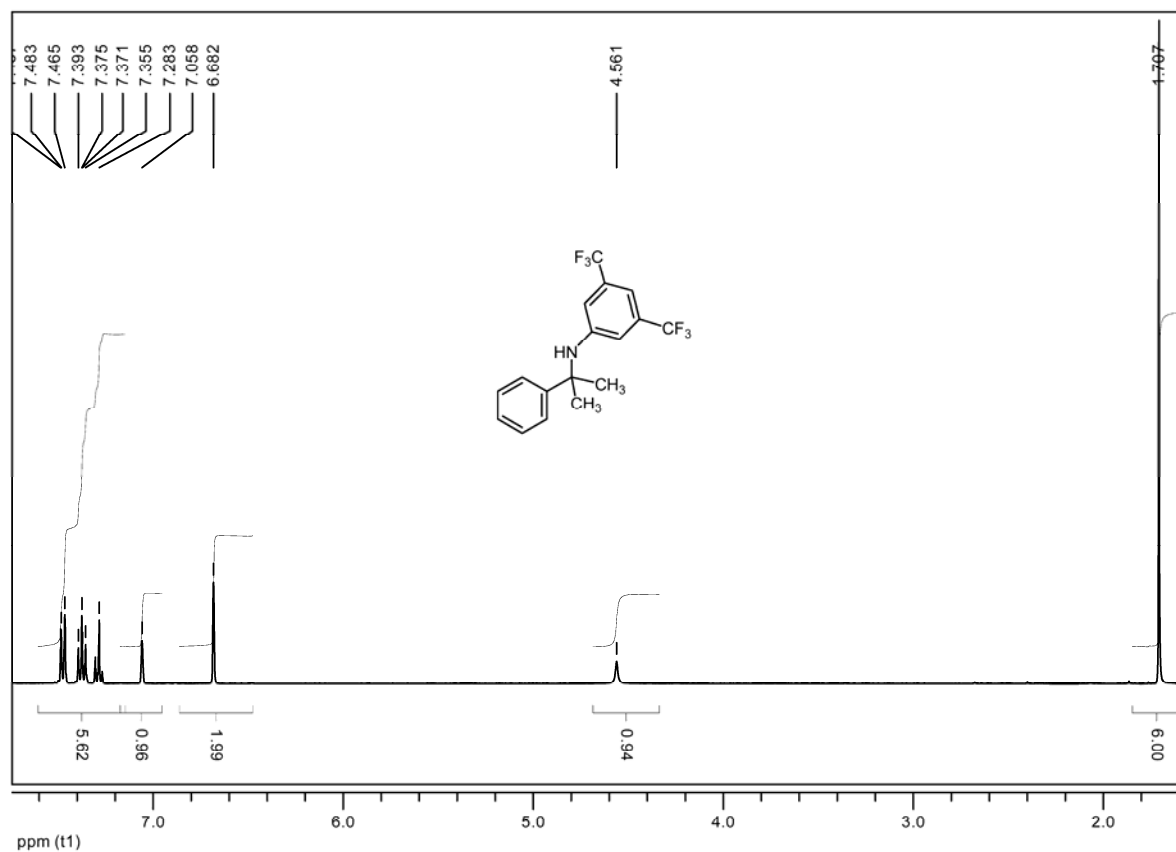
^1H NMR of 3,5-bis(trifluoromethyl)-*N*-(2-methyl-1-phenylpropyl)benzenamine (CDCl_3).



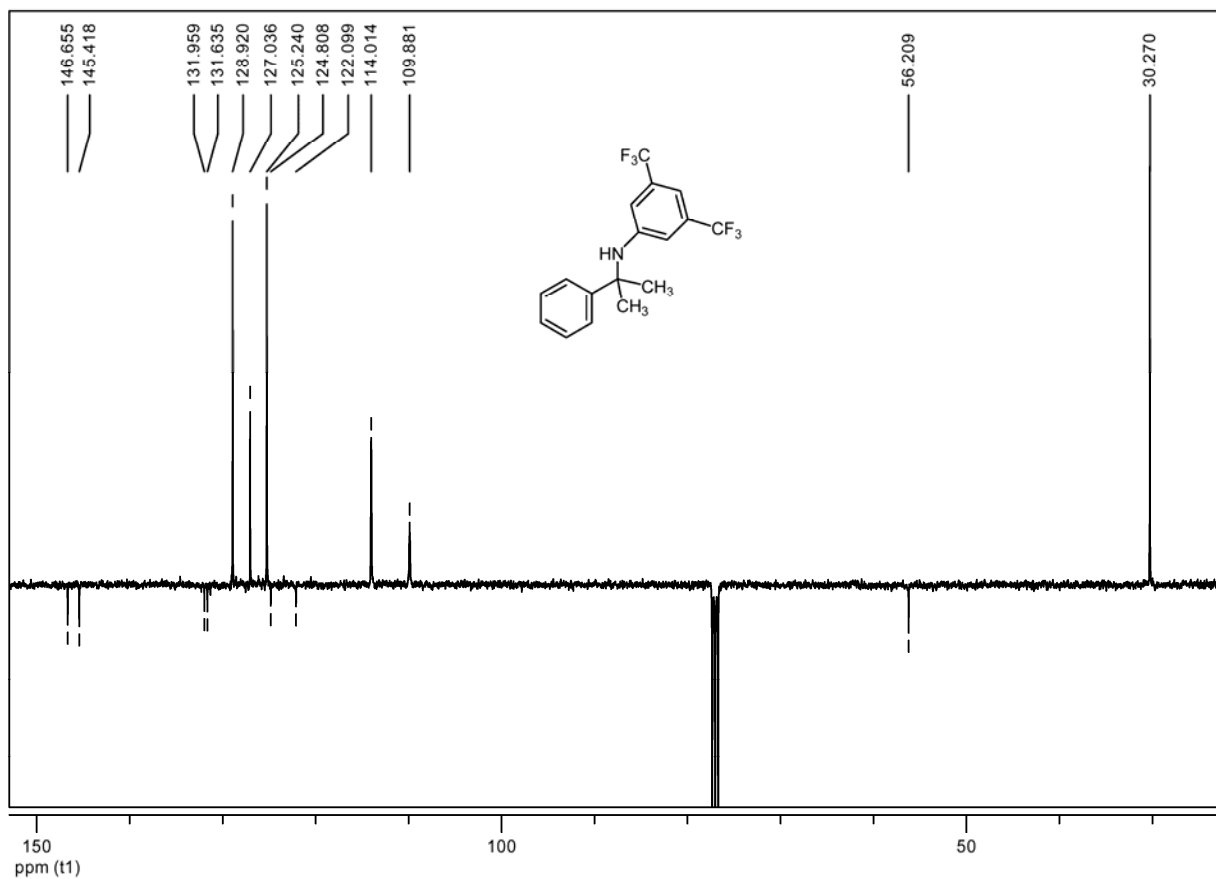
^{13}C NMR of 3,5-bis(trifluoromethyl)-*N*-(2-methyl-1-phenylpropyl)benzenamine (CDCl_3).



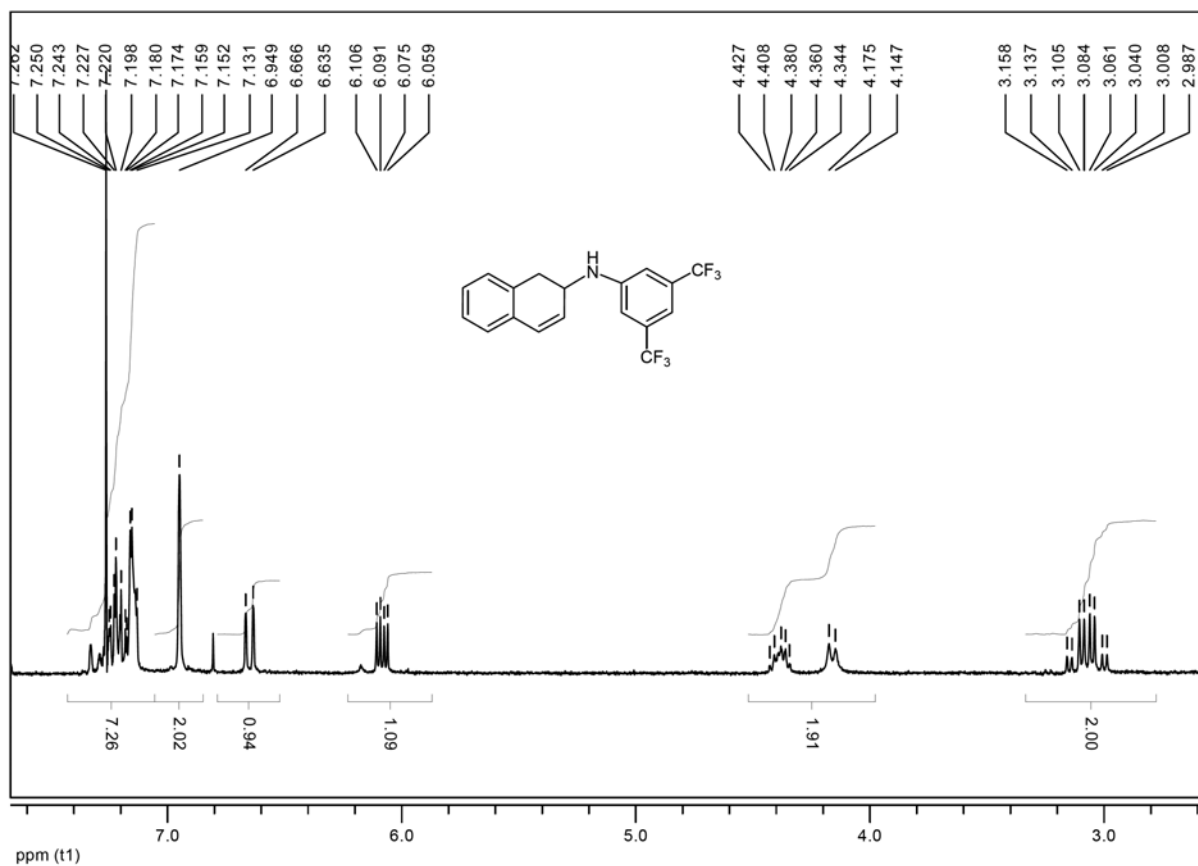
^1H NMR of 3,5-bis(trifluoromethyl)-*N*-(2-phenylpropan-2-yl)benzenamine (CDCl_3).



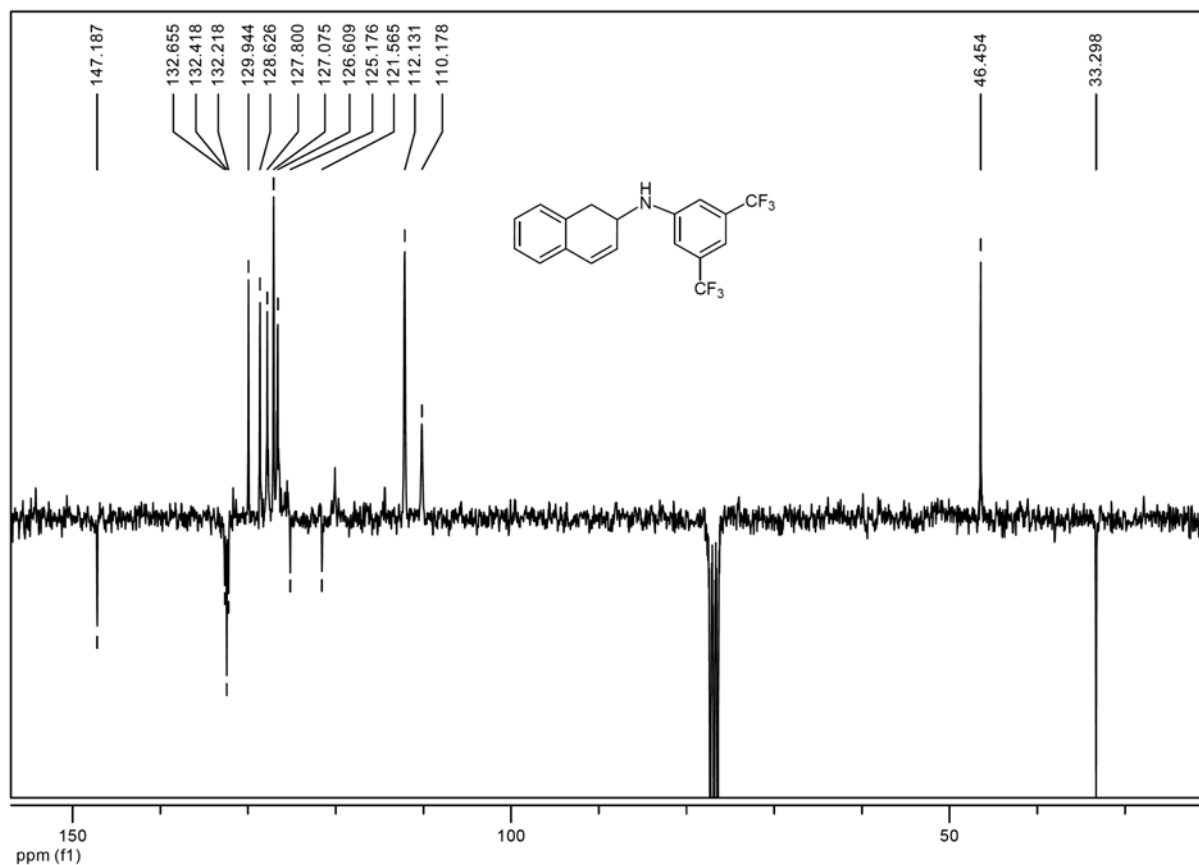
^{13}C NMR of 3,5-bis(trifluoromethyl)-*N*-(2-phenylpropan-2-yl)benzenamine (CDCl_3).



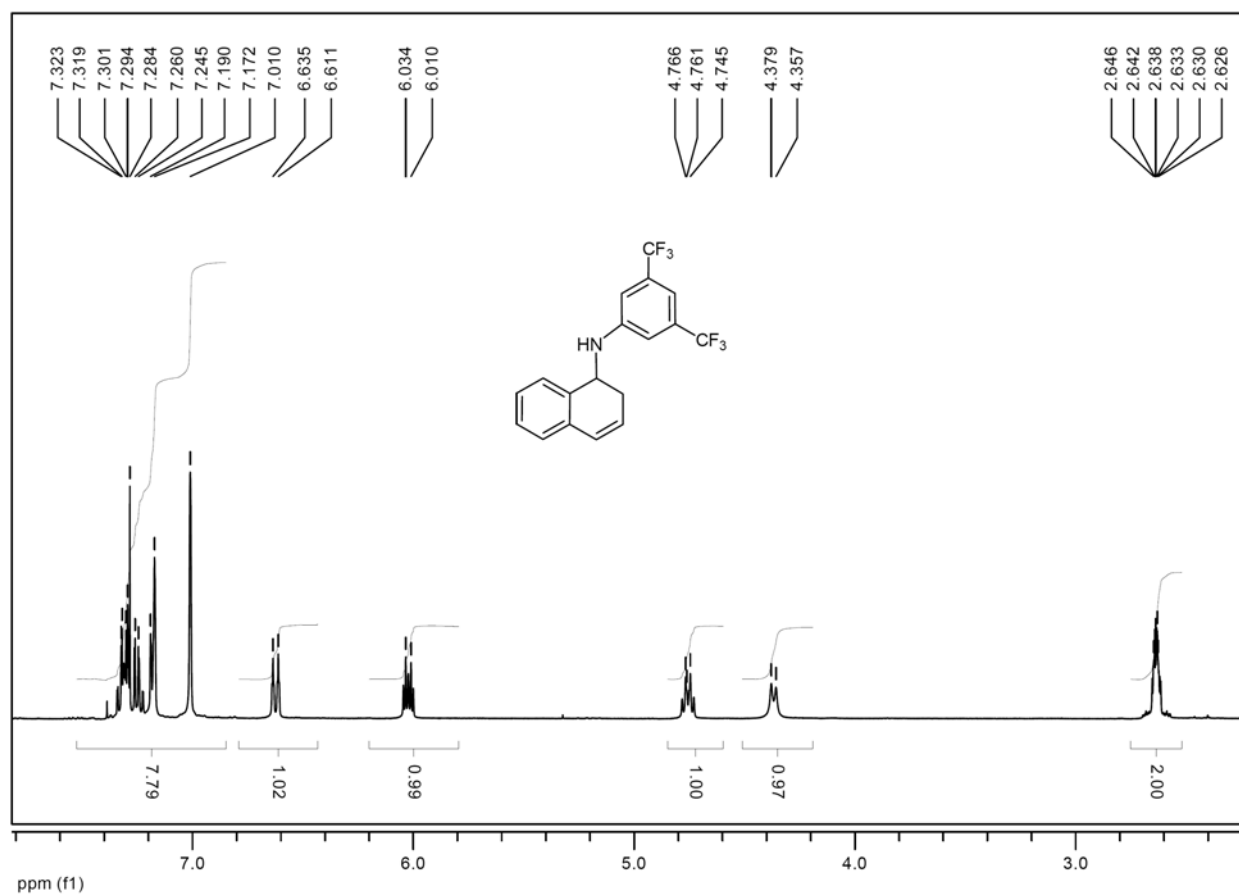
^1H NMR of *N*-(3,5-bis(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-2-amine (CDCl_3).



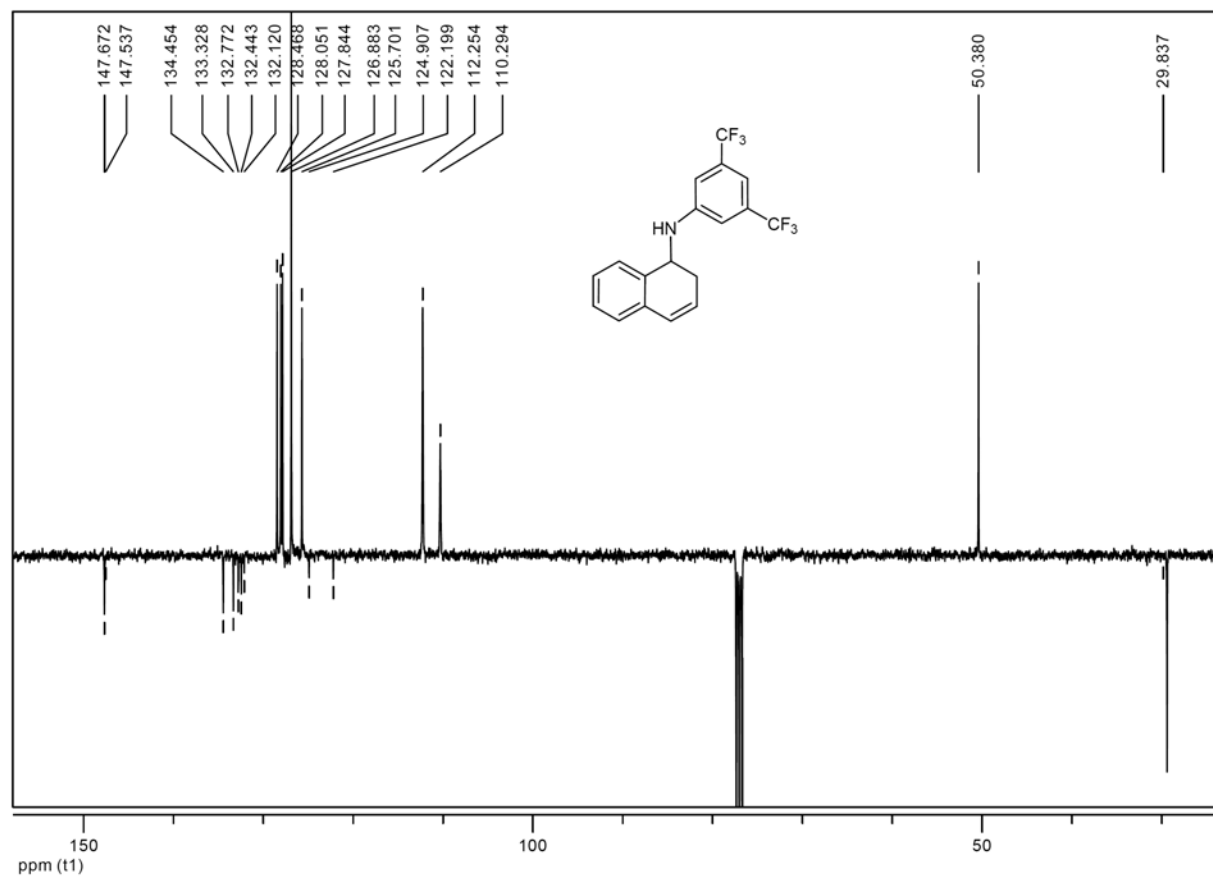
^{13}C NMR of *N*-(3,5-bis(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-2-amine (CDCl_3).



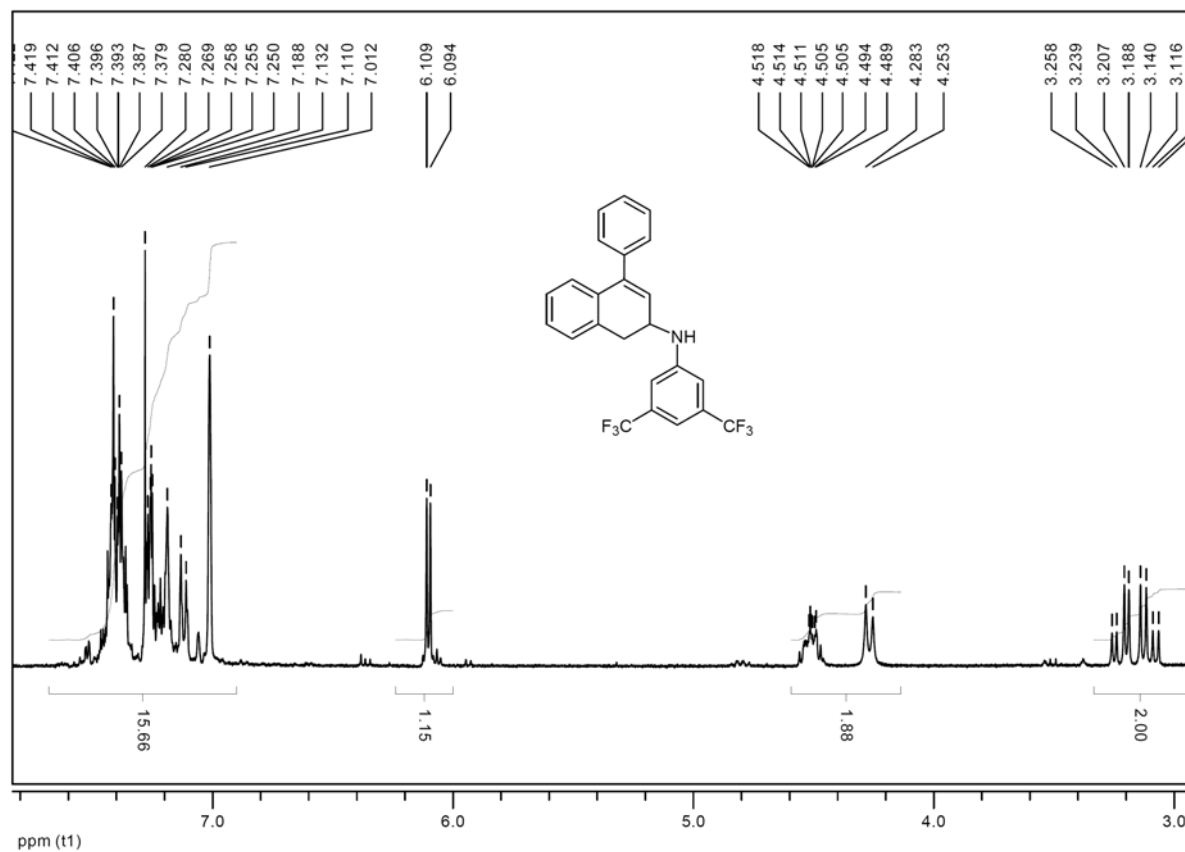
^1H NMR of *N*-(3,5-bis(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-1-amine (CDCl_3).



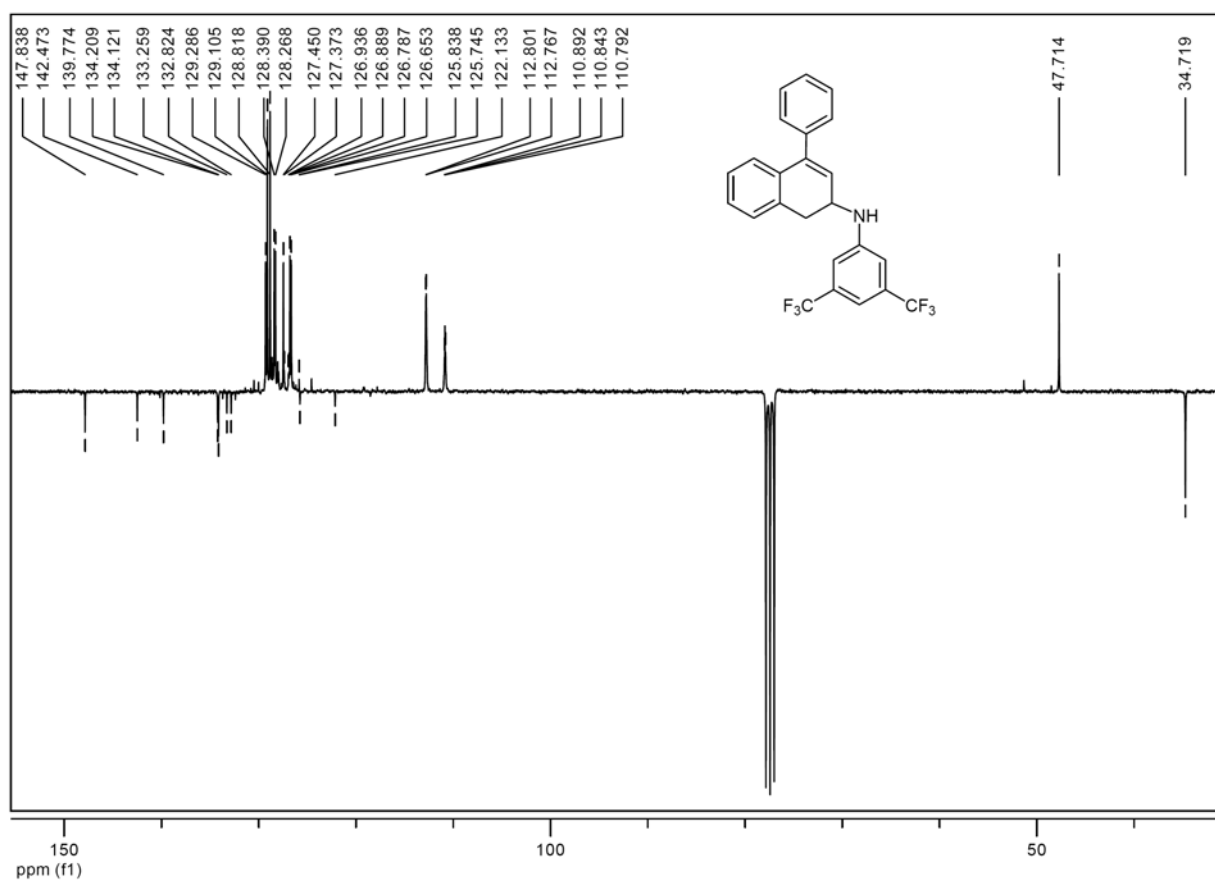
^{13}C NMR of *N*-(3,5-bis(trifluoromethyl)phenyl)-1,2-dihydronaphthalen-1-amine (CDCl_3).



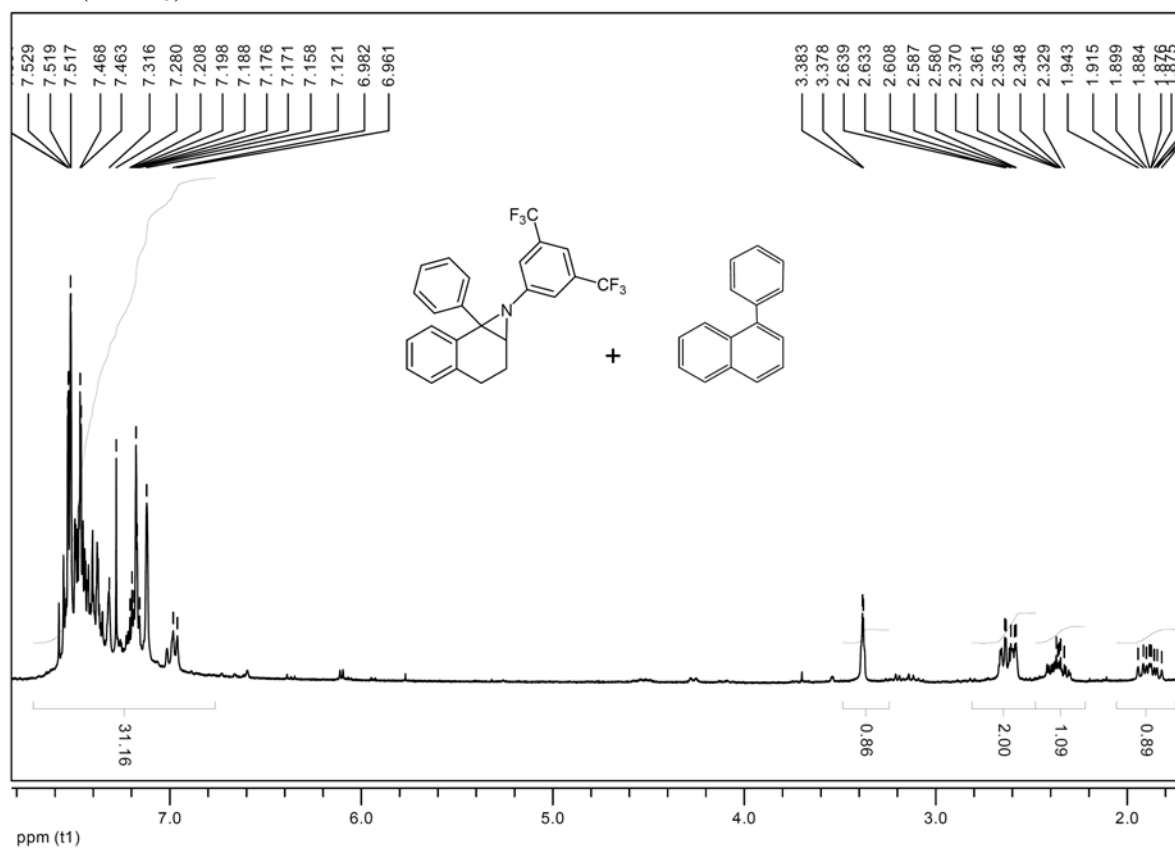
^1H NMR of *N*-(3,5-bis(trifluoromethyl)phenyl)-1,2-dihydro-4-phenylnaphthalen-2-amine (CDCl_3).



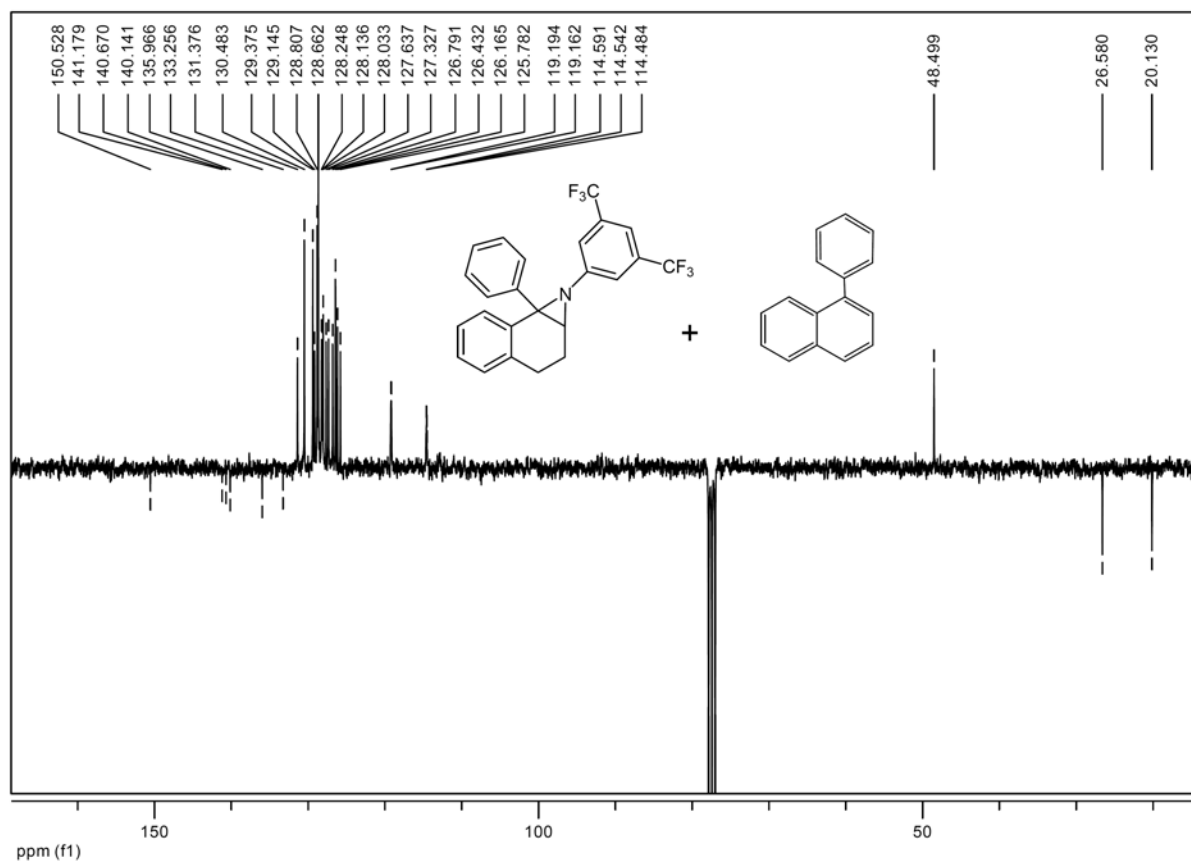
^{13}C NMR of *N*-(3,5-bis(trifluoromethyl)phenyl)-1,2-dihydro-4-phenylnaphthalen-2-amine (CDCl_3).



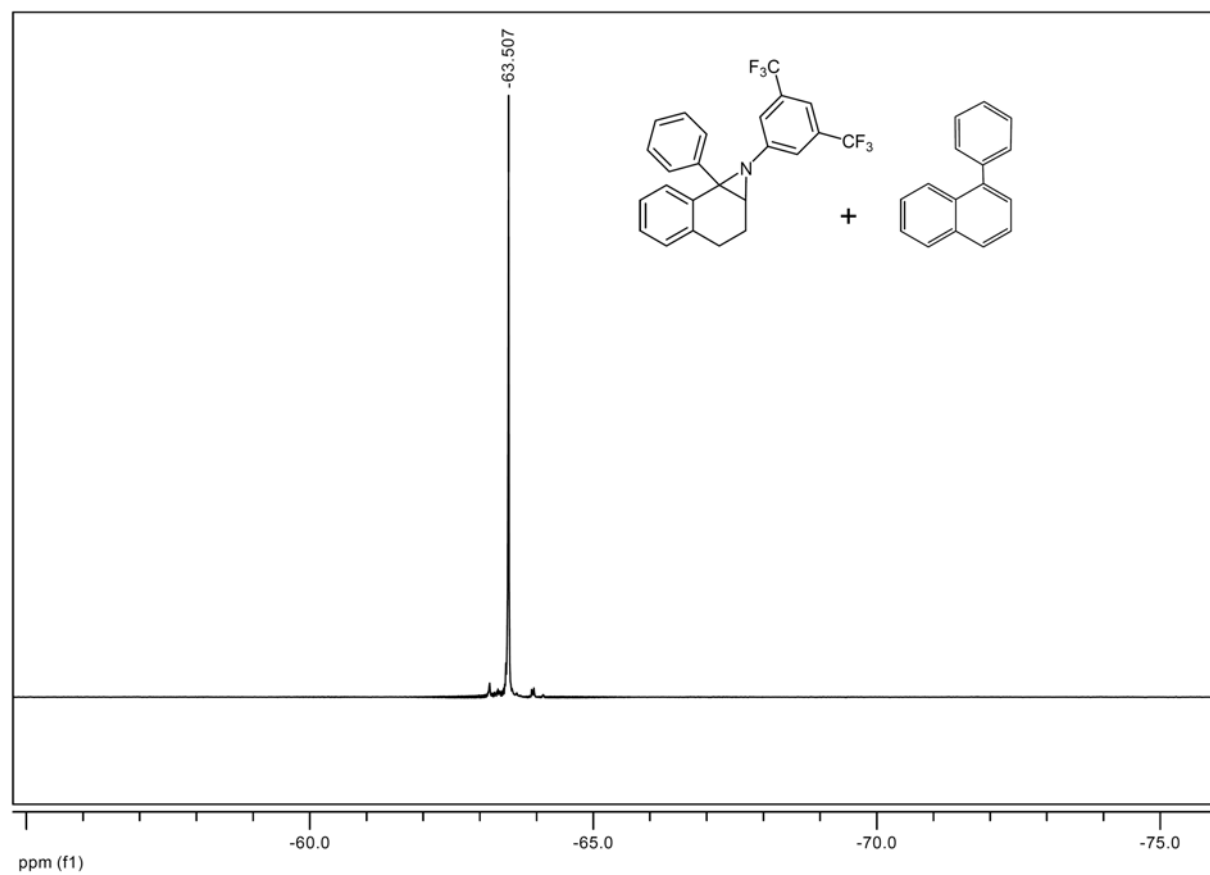
^1H NMR of 1-(3,5-bis(trifluoromethyl)phenyl)-1a,2,3,7b-tetrahydro-7b-phenyl-1H-naphtho[2,1-b]azirine (CDCl_3).



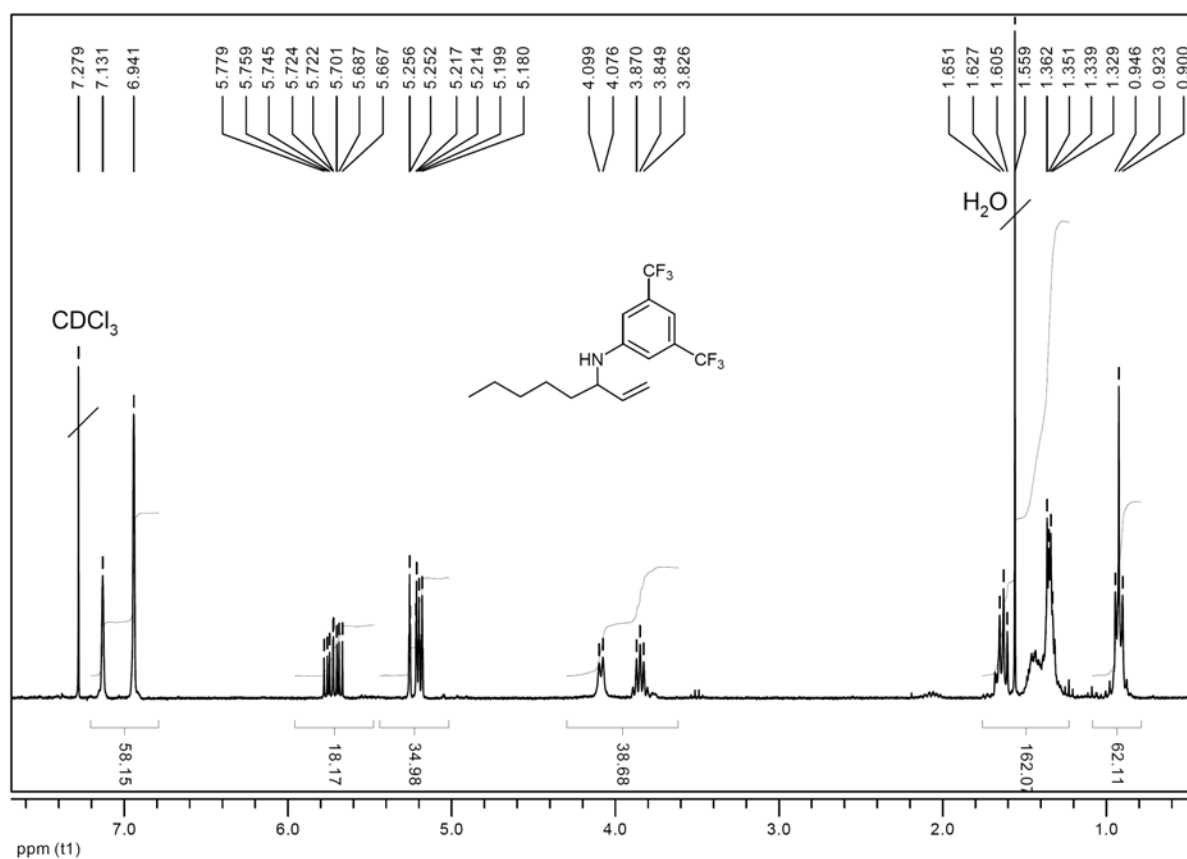
^{13}C NMR of 1-(3,5-bis(trifluoromethyl)phenyl)-1a,2,3,7b-tetrahydro-7b-phenyl-1H-naphtho[2,1-b]azirine (CDCl_3).



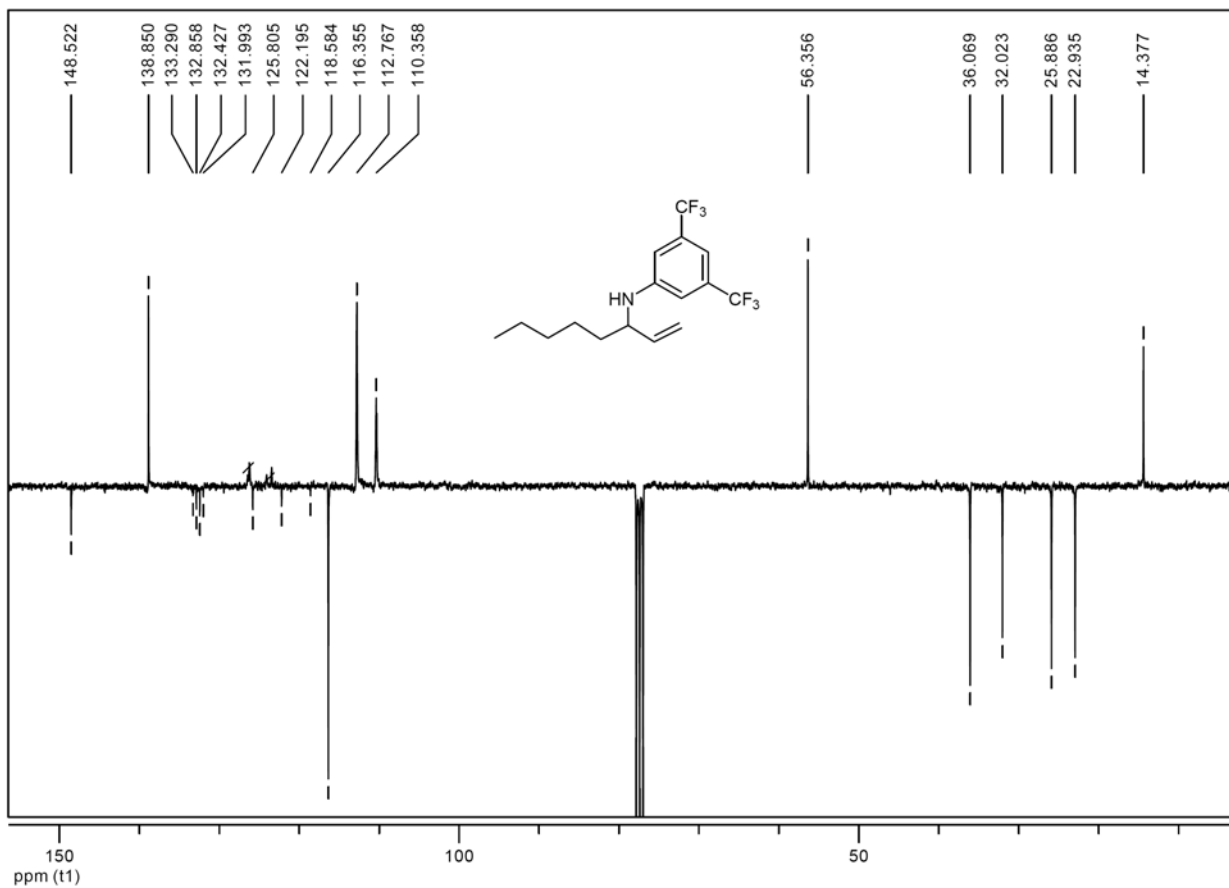
^{19}F NMR of 1-(3,5-bis(trifluoromethyl)phenyl)-1a,2,3,7b-tetrahydro-7b-phenyl-1*H*-naphtho[2,1-*b*]azirine (CDCl_3).



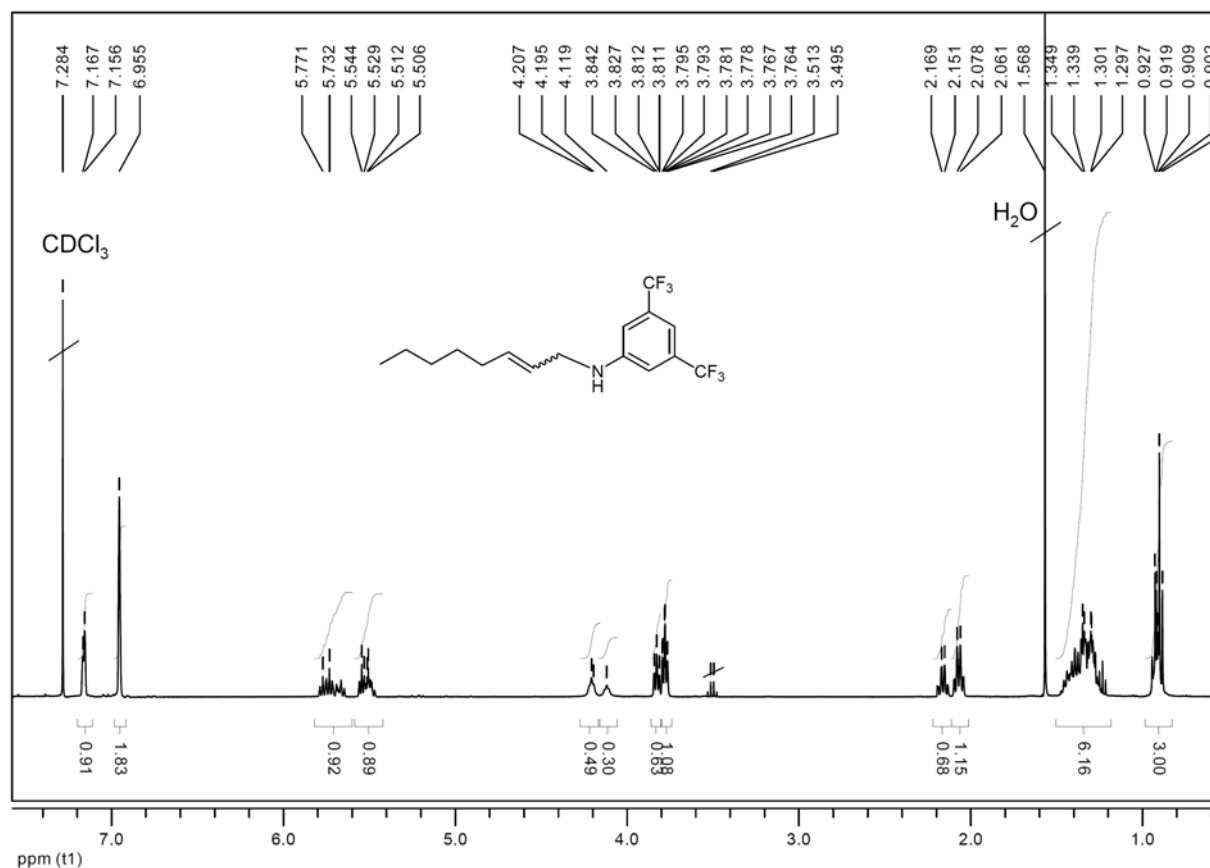
^1H NMR of 3,5-bis(trifluoromethyl)-*N*-(oct-1-en-3-yl)benzenamine (CDCl_3).



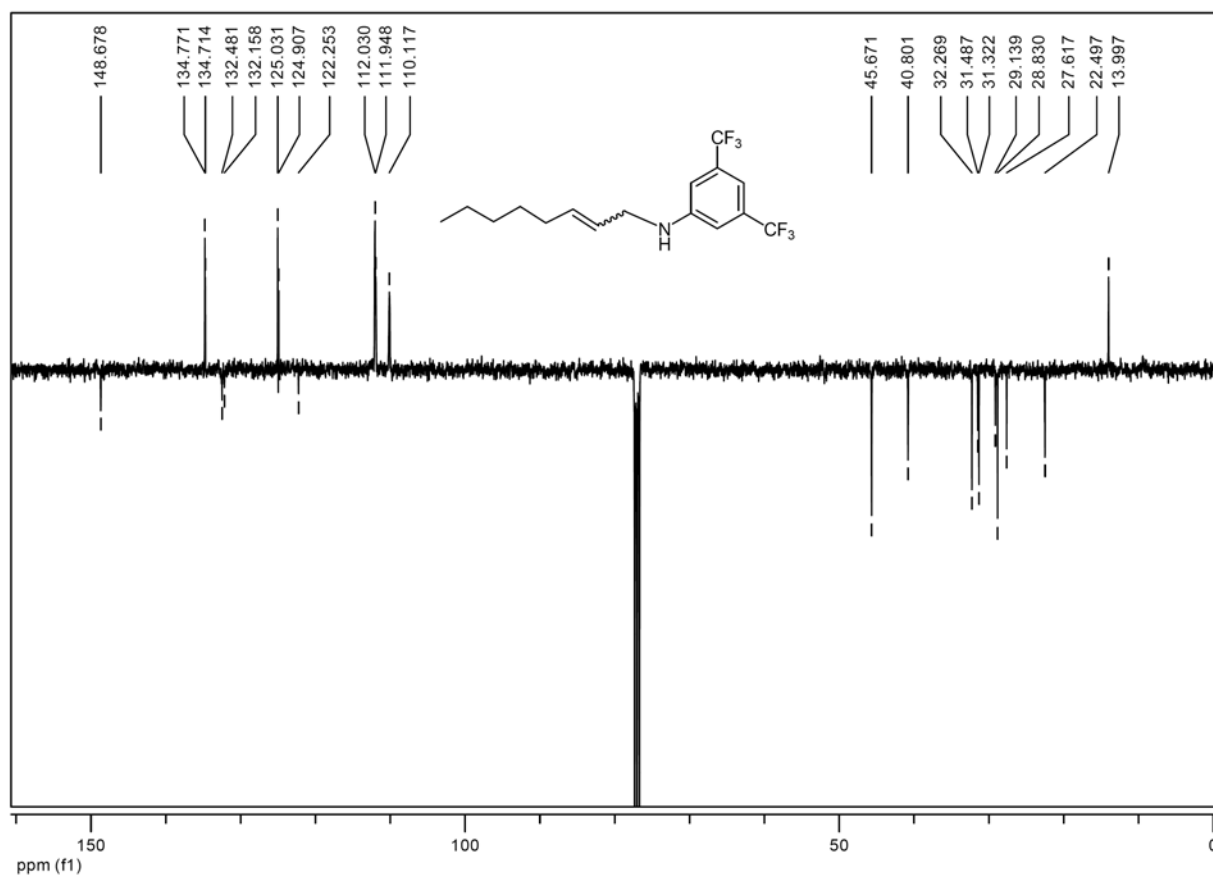
^{13}C NMR of 3,5-bis(trifluoromethyl)-*N*-(oct-1-en-3-yl)benzenamine (CDCl_3).



^1H NMR of E,Z mixture of 3,5-bis(trifluoromethyl)-N-(oct-2-enyl)benzenamine (CDCl_3).



^{13}C NMR of 3,5-bis(trifluoromethyl)-N-(oct-2-enyl)benzenamine (CDCl_3).



References.

- (1) M. Tanno, S. Sueyoshi and S. Kamiya, *Chemical & Pharmaceutical Bulletin*, 1982, **30**, 3125.
- (2) D. P. Rillema, J. K. Nagle, L. F. Jr. Barringer and T. J. Meyer, *J. Am. Chem. Soc.*, 1981, **103**, 56-61.
- (3) E. Gallo, A. Caselli, F. Ragaini, S. Fantauzzi, N. Masciocchi, A. Sironi and S. Cenini, *Inorg. Chem.*, 2005, **44**, 2039-2049.
- (4) C.-M. Che and W.-Y. Yu, *Pure Appl. Chem.*, 1999, **71**, 281-288.
- (5) The ^{13}C NMR spectrum is not reported because complex **2** partly decomposes during the experiment.
- (6) F. Ragaini, S. Cenini, F. Turra and A. Caselli, *Tetrahedron*, 2004, **60**, 4989-4994.
- (7) SADABS: Area-Detector Absorption Correction; Siemens Industrial Automation, Inc.: Madison, WI, 1996.
- (8) SIR97 - A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115-119.
- (9) SHELX-L 97 - Program for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- (10) WinGX 1.70.01 L. J. Farrugia, *J. Appl. Cryst.* 1999, **32**, 837-838.