Supporting information

Transition Metal Complexes Bearing NHC Ligands Substituted with Secondary Polyfluoroalkyl Groups.

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General Procedures

Temperature data were uncorrected. NMR spectra were recorded with a Varian MercuryPlus spectrometer or with an Agilent 400-MR DDR2 spectrometer. For the Varian MercuryPlus spectrometer, ^{1}H NMR spectra were recorded at 299.97 MHz, ^{13}C NMR spectra were recorded at 75.44 MHz using residual deuterated solvent signals as the internal standards, and ^{19}F NMR spectra were recorded at 282.23 MHz using CCl_3F as the internal standard. For the Agilent 400-MR DDR2 spectrometer, ^{1}H NMR spectra were recorded at 399.94 MHz, ^{13}C NMR spectra were recorded at 100.58 MHz and ^{19}F NMR spectra were recorded at 376.29 MHz. Chemical shifts are given in parts per million, coupling constants in Hertz. Mass spectra (ESI, APCI) were measured with a LCQ Fleet (Finnigan) instrument and HRMS spectra (ESI, APCI, FAB) with a LTQ Orbitrap XL (Thermo Fisher Scientific) or ZAB-EQ (VG Analytical) instrument. Melting points were measured by Electrothermal IA 9100 instrument.
All reactions were performed in a dry inert atmosphere (Ar) in oven-dried flasks. In the reactions including ruthenium or palladium, solids were introduced into the reaction flasks in a glove box.

Syntheses

2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptane-1,1-diol (7).
An oven-dried round-bottom flask was charged with aluminium powder (0.304 g, 11.2 mmol), lead(II) bromide (0.082 g, 0.22 mmol) and DMF (23 mL). Under a sonication, perfluorohexyl iodide (**6**, 5.00 g, 11.2 mmol) was added to the mixture dropwise. The resulting heterogeneous mixture was sonicated for 2 h and then poured into 10% hydrochloric acid (50 mL). The solids were filtered off and the filtrate was extracted with diethyl ether (3 × 50 mL), combined organic extracts were washed with water (3 × 30 mL) and dried with anhydrous $MgSO_4$. The solvent was removed on a rotary vacuum evaporator (40 °C, 30 min, 65 kPa) and the crude product was purified by sublimation using a

Kugelrohr apparatus (110-130 °C, 101 kPa) yielding diol **7** (2.31 g, 56.3%, white powder). ^{1}H NMR (299.97 MHz, acetone-d_6): δ 5.43 (t, $^{3}J_{H-F}$ = 7.6 Hz, 1H, $CH(OH)_2$), 6.40 (d, $^{3}J_{H-H}$ = 7.3 Hz, 2H, $CH(OH)_2$) ppm. ^{19}F NMR (282.23 MHz, acetone-d_6): δ -80.6 (t, ^{4}JF-F = 10 Hz, 3F, CF_3), -121.6 (bs, 2F, CF_2), -121.9 (bs, 2F, CF_2), -122.3 (bs, 2F, CF_2), -125.7 (bs, 2F, CF_2), -127.4 (bs, 2F, CF_2) ppm.

Attempted preparation of bis[1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-yl)-4,5-dihydroimidazol-2-ylidene]silver(I) bis(tetrafluoroborato)argentate (22).

Imidazolium salt **21** (20 mg, 0,025 mmol), silver(I) oxide (3,2 mg, 0,014 mmol), powdered molecular sieves 4Å (25 mg) and acetonitrile (1.6 mL) were placed into a foil-covered flask. The reaction mixture was stirred for 48h at room temperature. Filtration and evaporation of solvent on a rotary vacuum evaporator (50 °C, 1 h, 8 kPa) yielded crude reaction mixture, which according to analysis with ^{1}H a ^{19}F NMR spectroscopy contained mainly starting imidazolium salt **21** with small amount of admixtures.

Copies of ^{1}H, ^{19}F and ^{13}C NMR Spectra

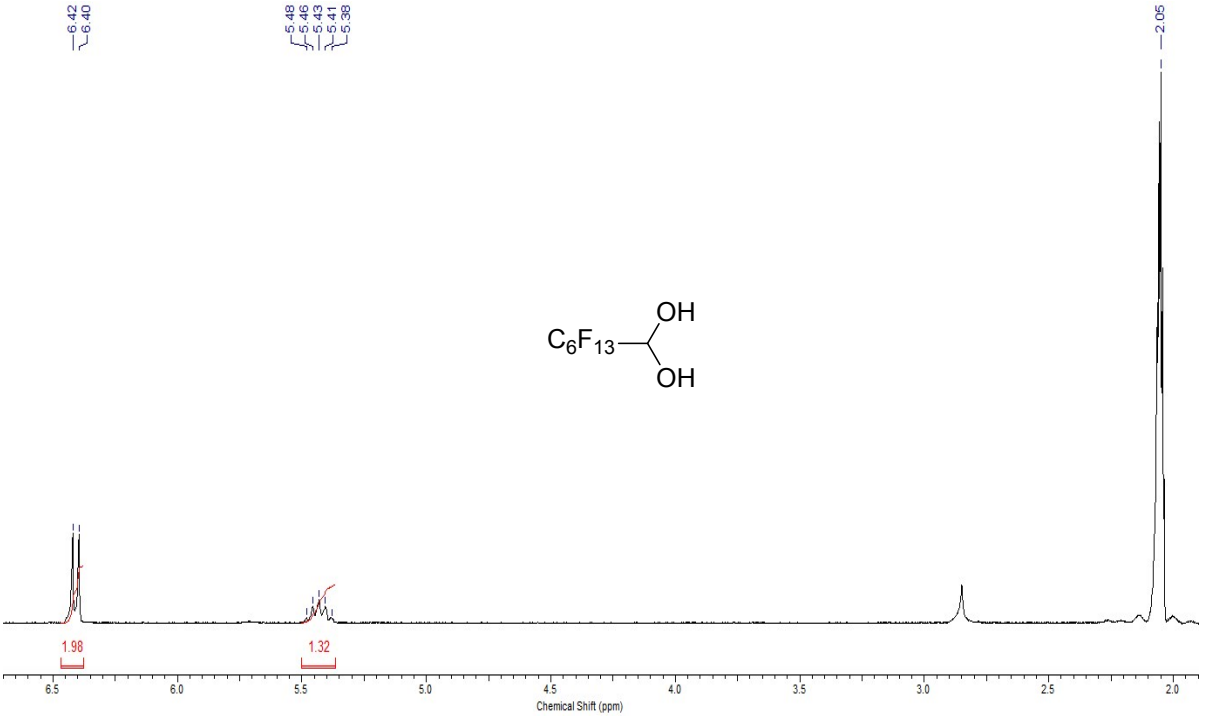


Figure S1. ^{1}H NMR spectrum, 299.97 MHz, acetone-d_6, 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-heptane-1,1-diol (**7**).

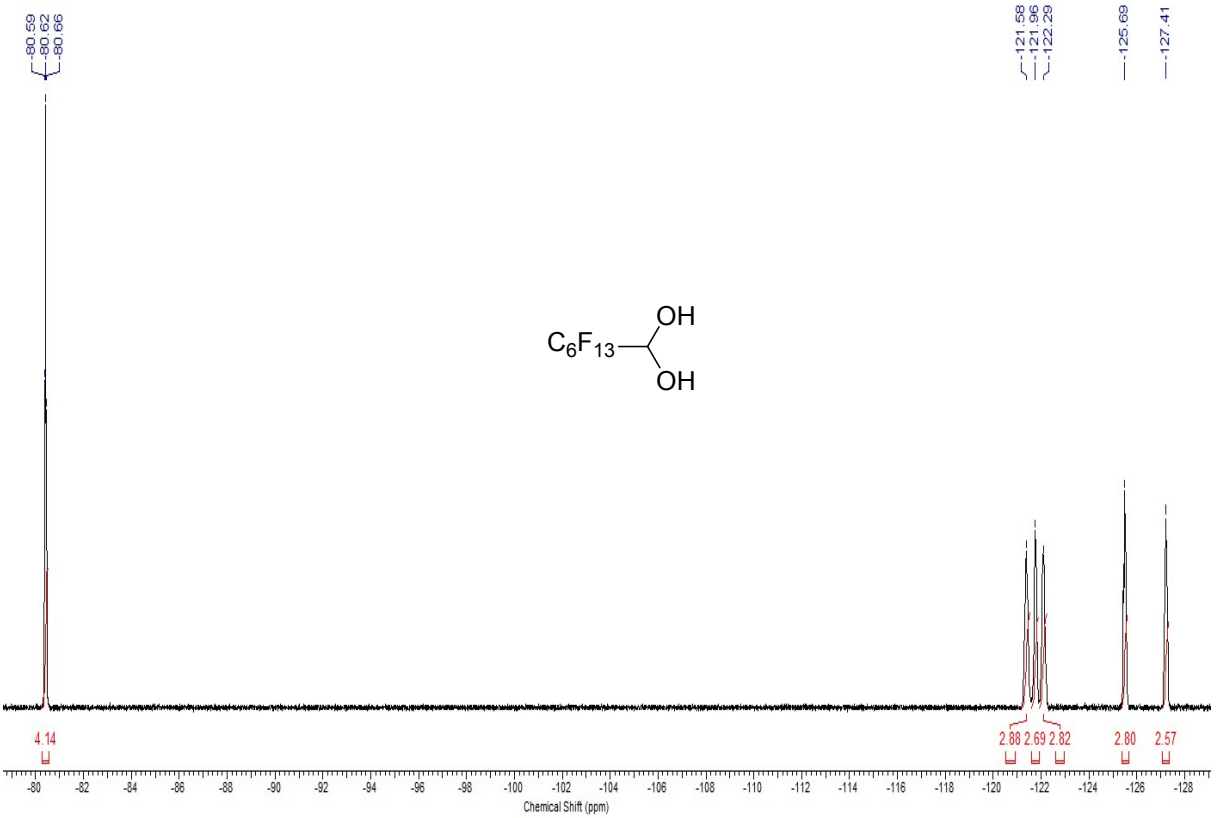


Figure S2. ^{19}F NMR spectrum, 282.23 MHz, acetone-d_6, 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-heptane-1,1-diol (**7**).

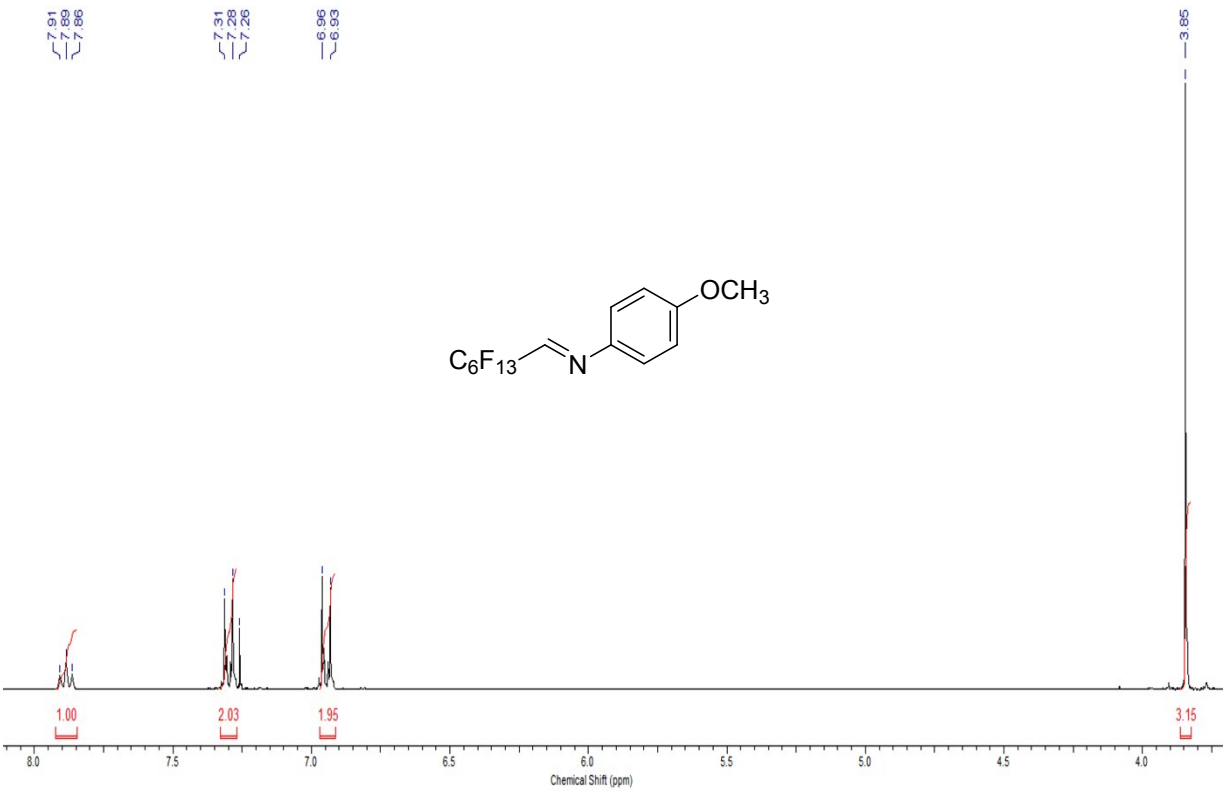


Figure S3. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-*N*-(4-methoxyphenyl)heptan-1-imine (**8**).

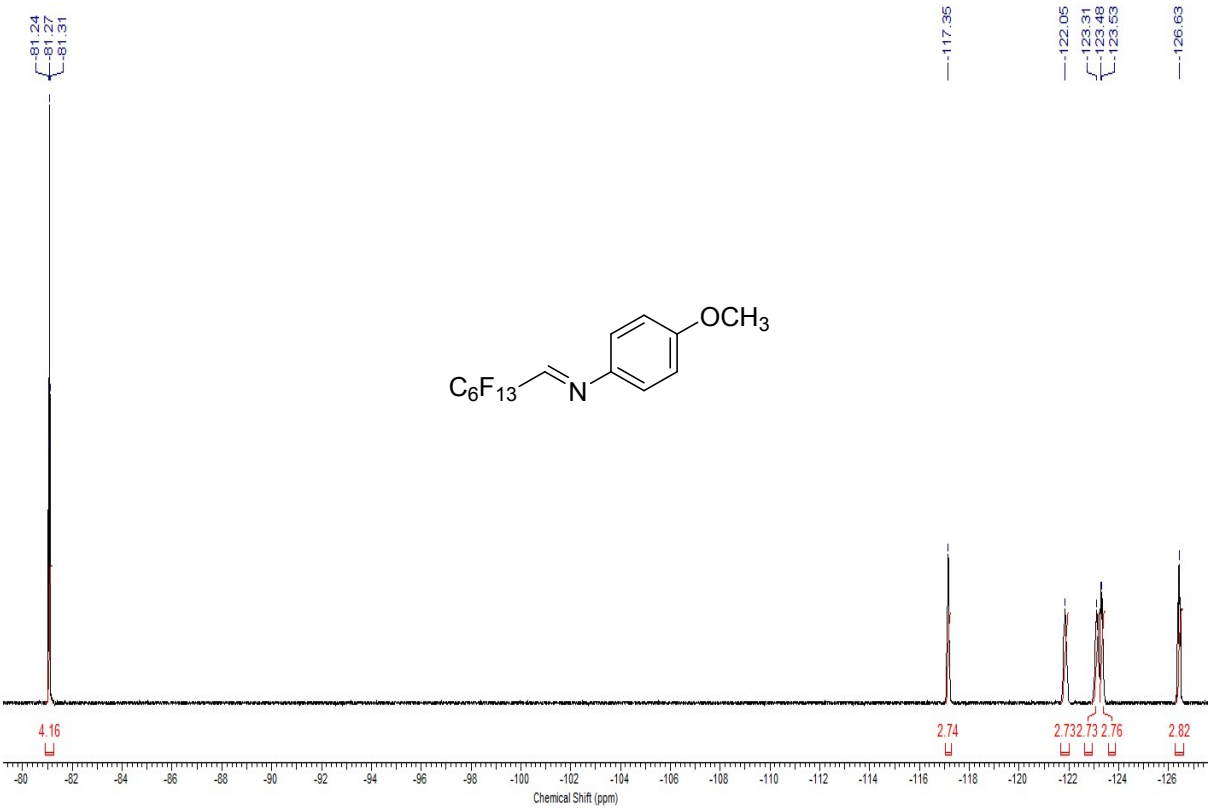


Figure S4. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-*N*-(4-methoxyphenyl)heptan-1-imine (**8**).

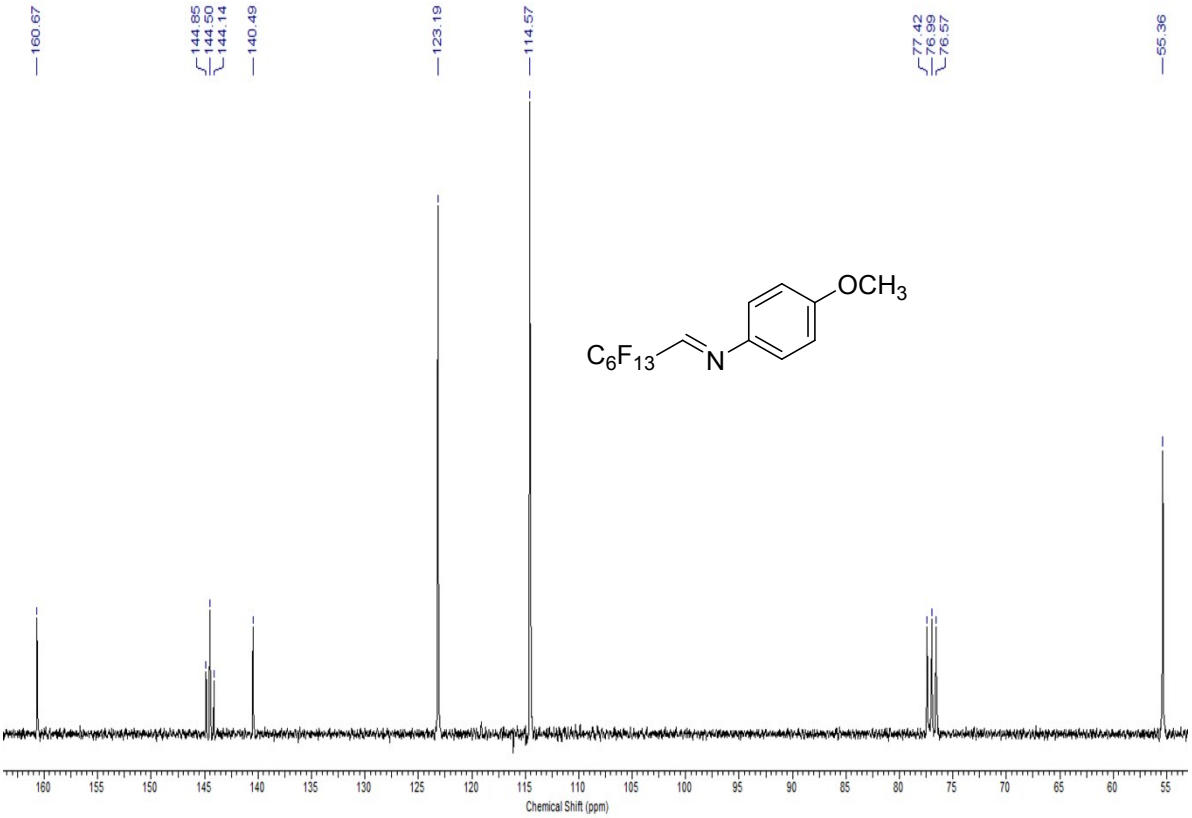


Figure S5. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, 2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoro-*N*-(4-methoxyphenyl)heptan-1-imine (**8**).

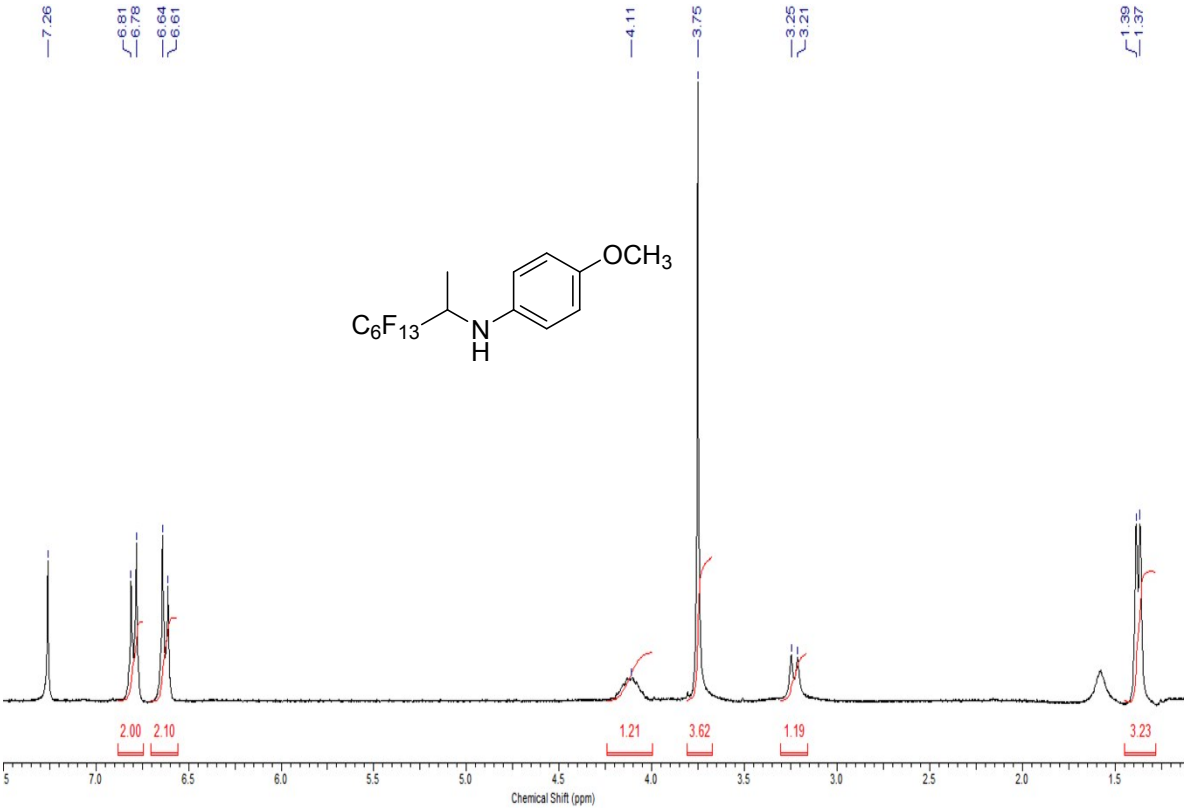


Figure S6. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, 4-methoxy-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-yl)aniline (**9**).

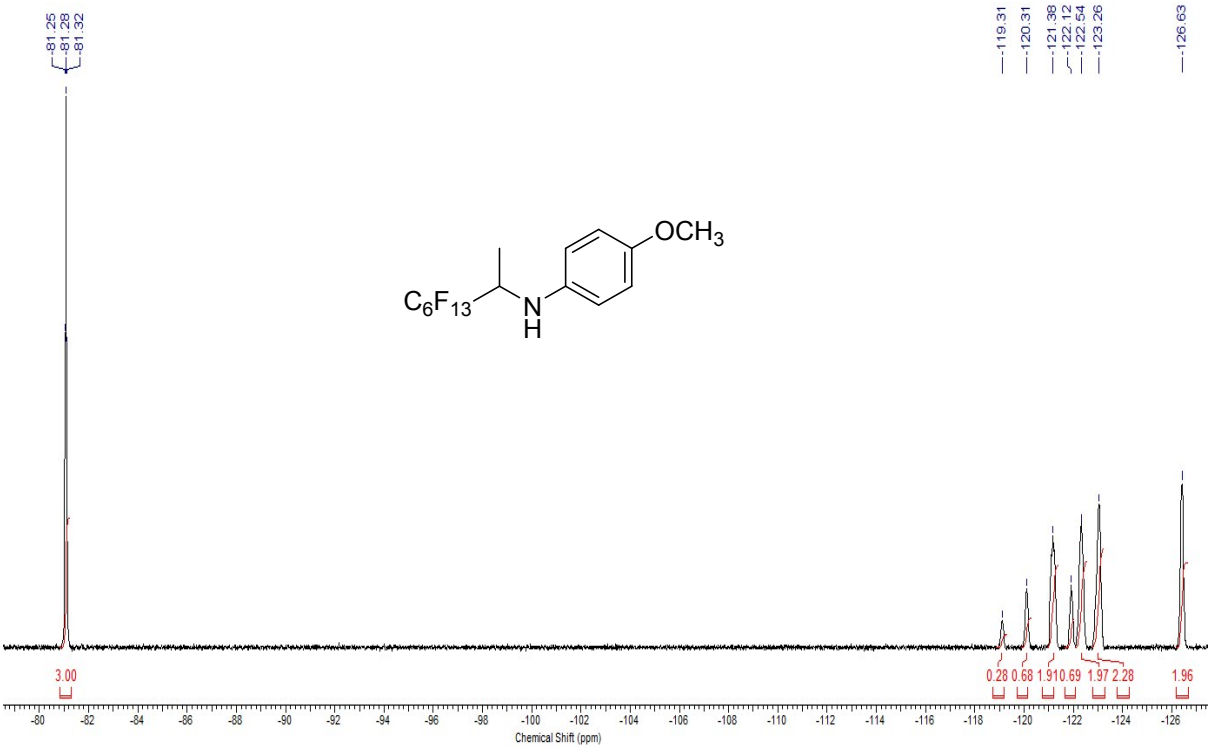


Figure S7. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, 4-methoxy-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-trideca-fluorooctan-2-yl)aniline (**9**).

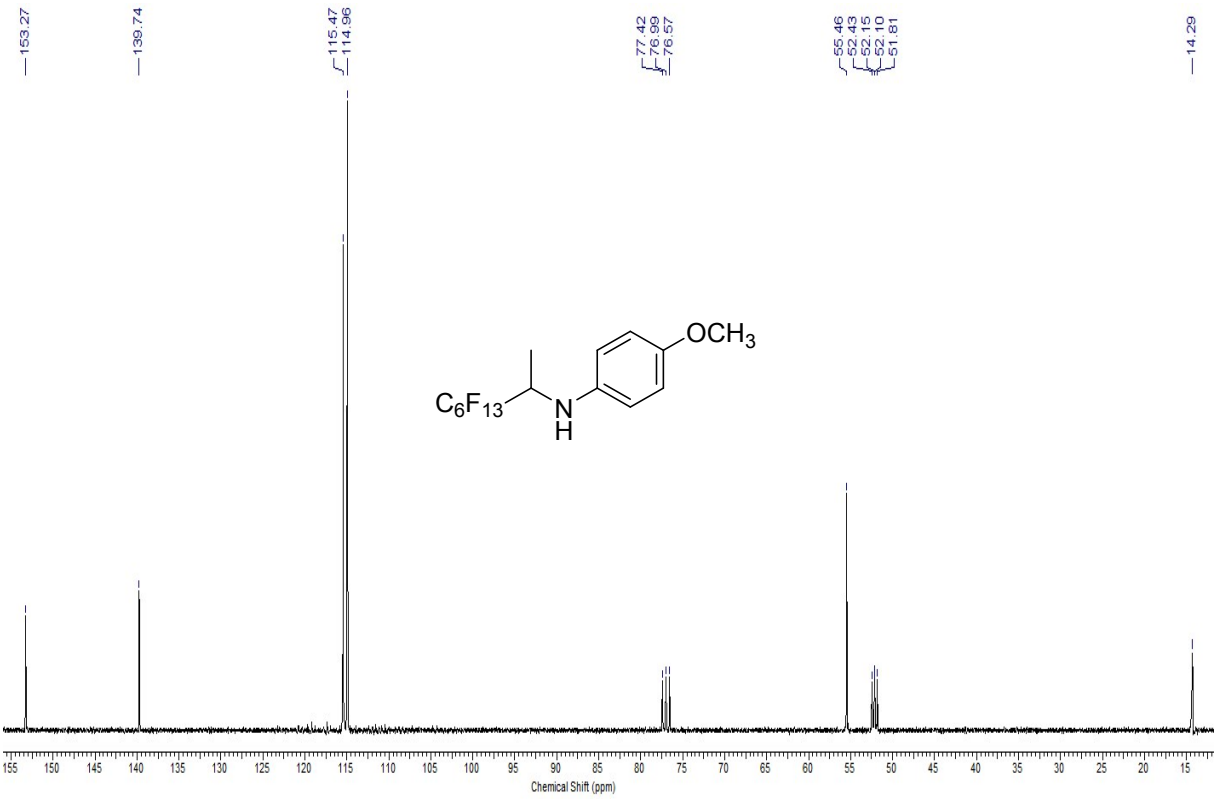


Figure S8. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, 4-methoxy-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-trideca-fluorooctan-2-yl)aniline (**9**).

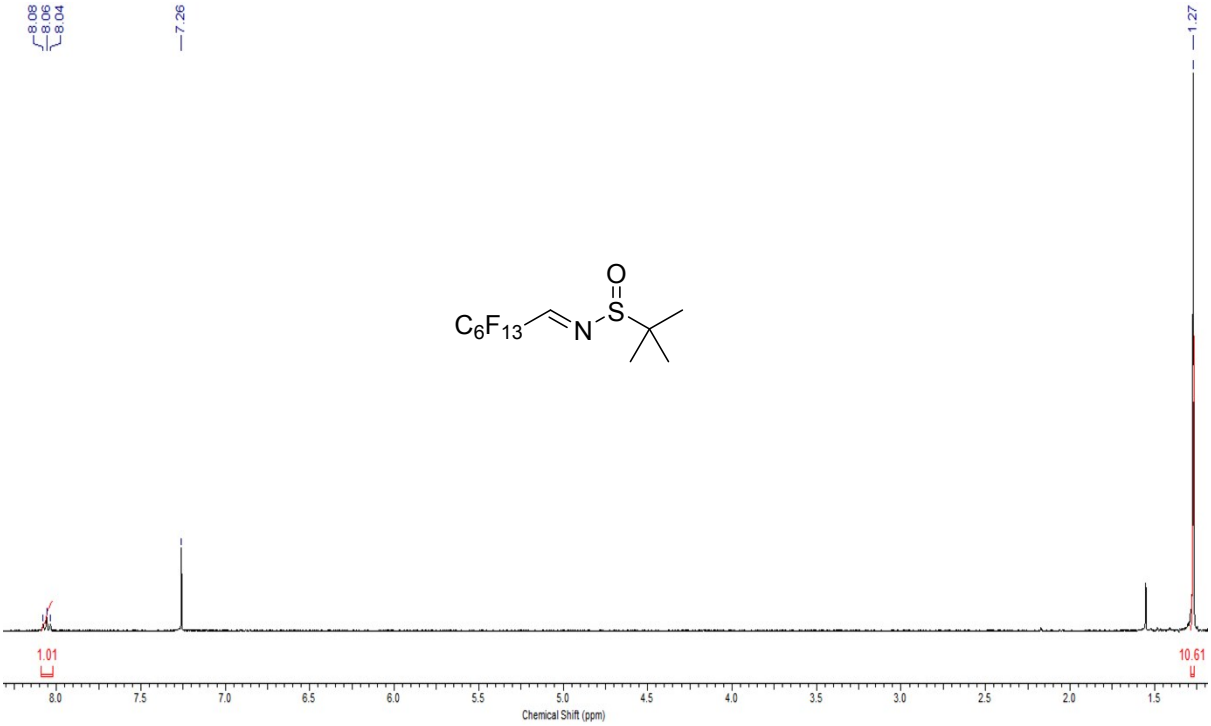


Figure S9. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, 2-methyl-*N*-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptylidene)propane-2-sulfinamide (**11**).

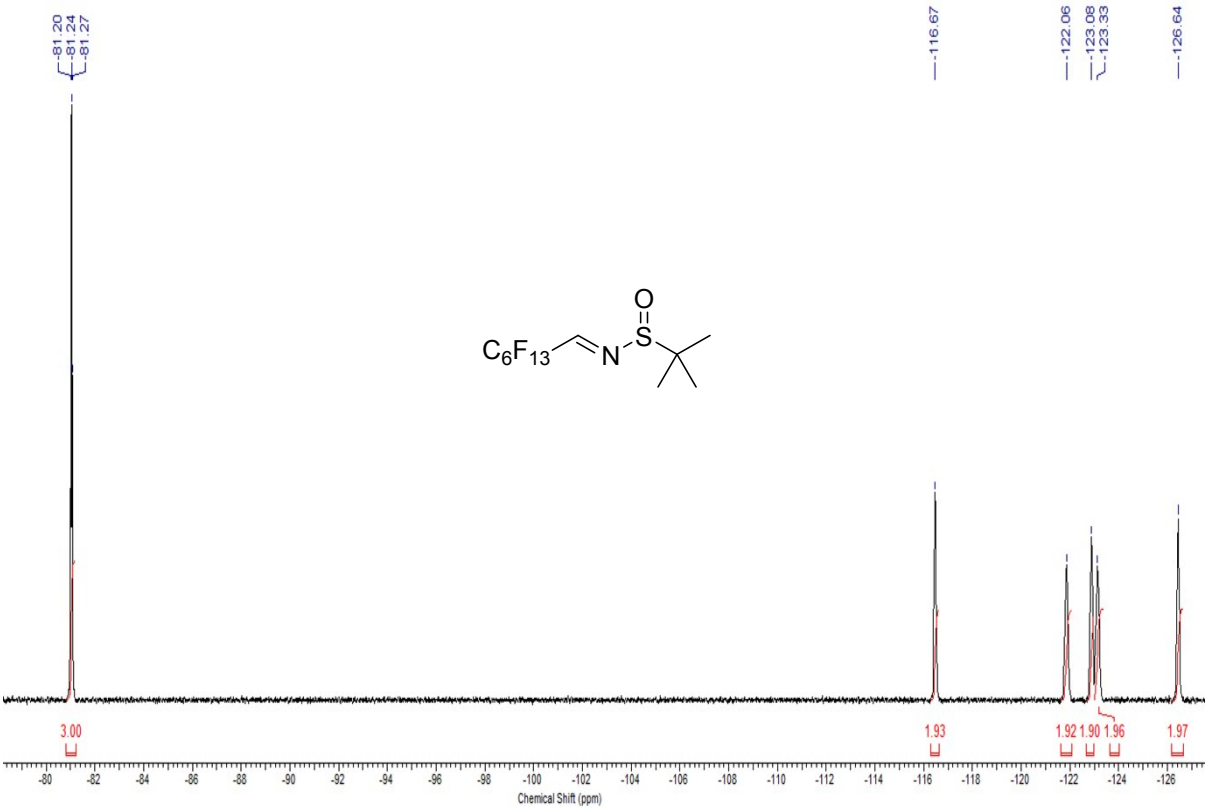


Figure S10. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, 2-methyl-*N*-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptylidene)propane-2-sulfinamide (**11**).

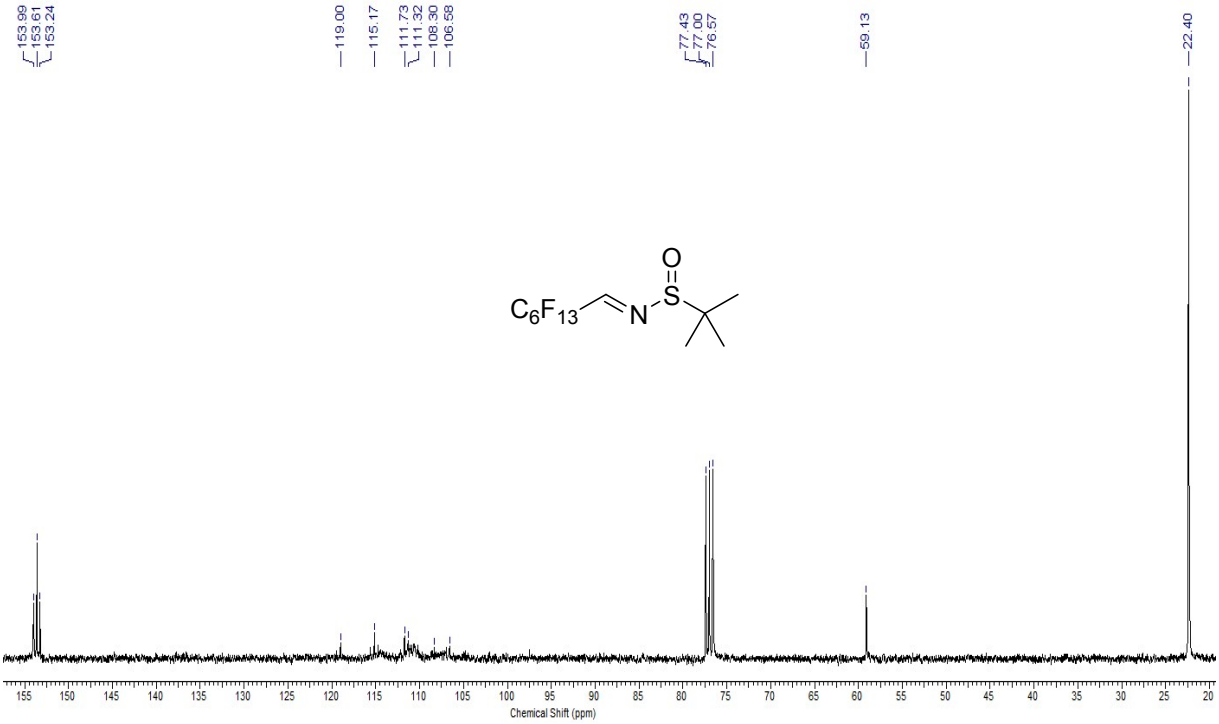


Figure S11. ^{13}C NMR spectrum, 75.44MHz, $CDCl_3$, 2-methyl-*N*-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptylidene)propane-2-sulfinamide (**11**).

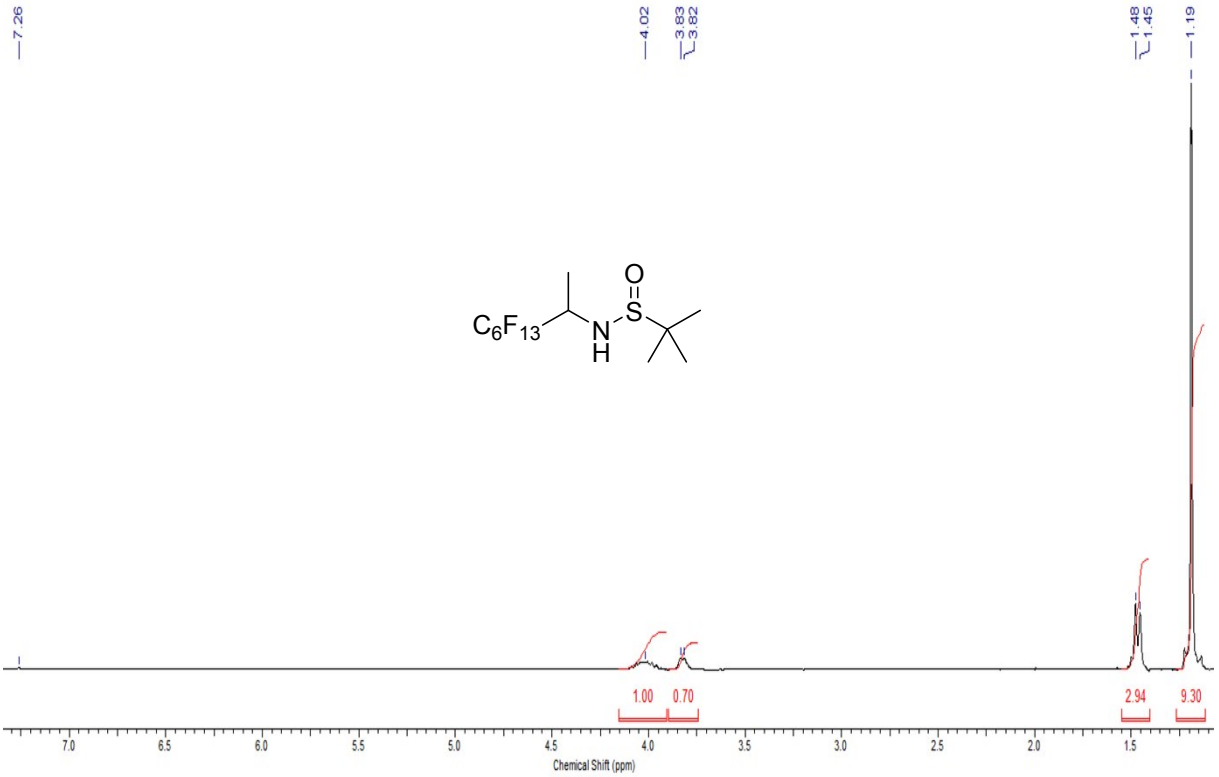


Figure S12. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, 2-methyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-yl)propane-2-sulfinamide (**12**).

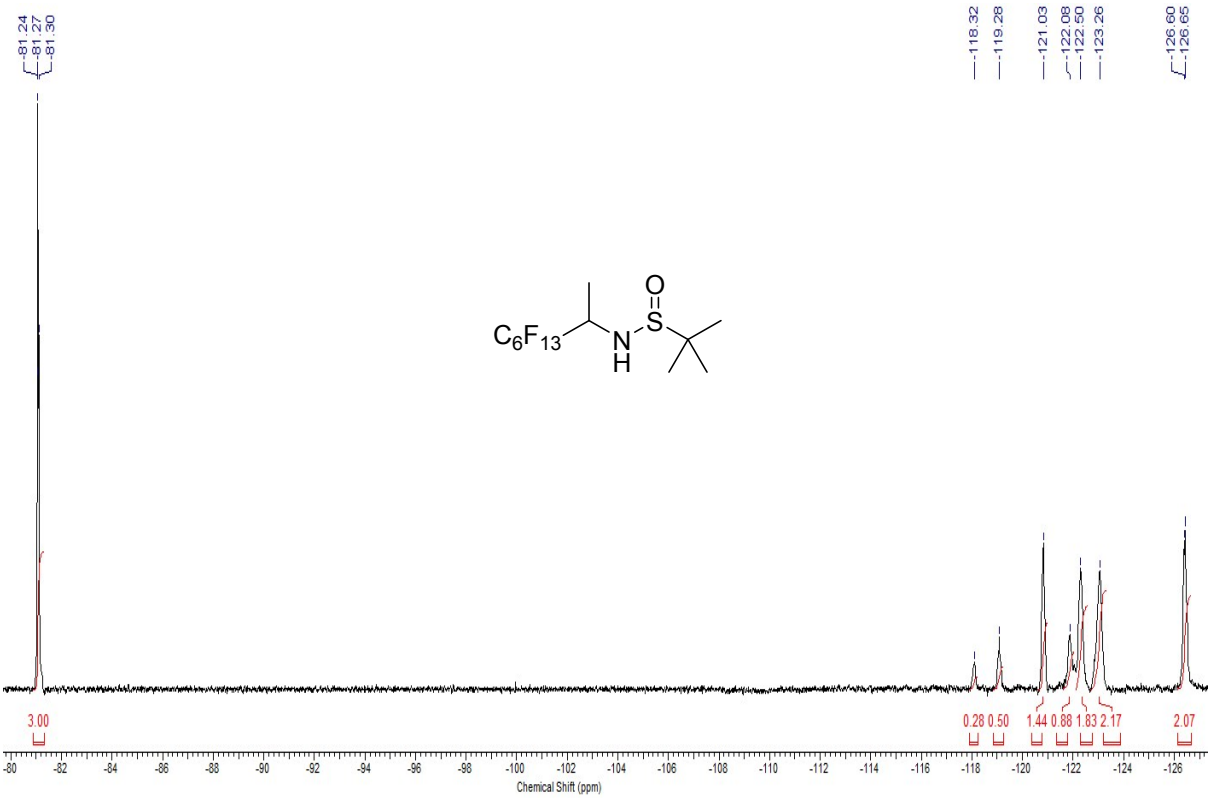


Figure S13. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, 2-methyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-trideca-fluorooctan-2-yl)propane-2-sulfinamide (**12**).

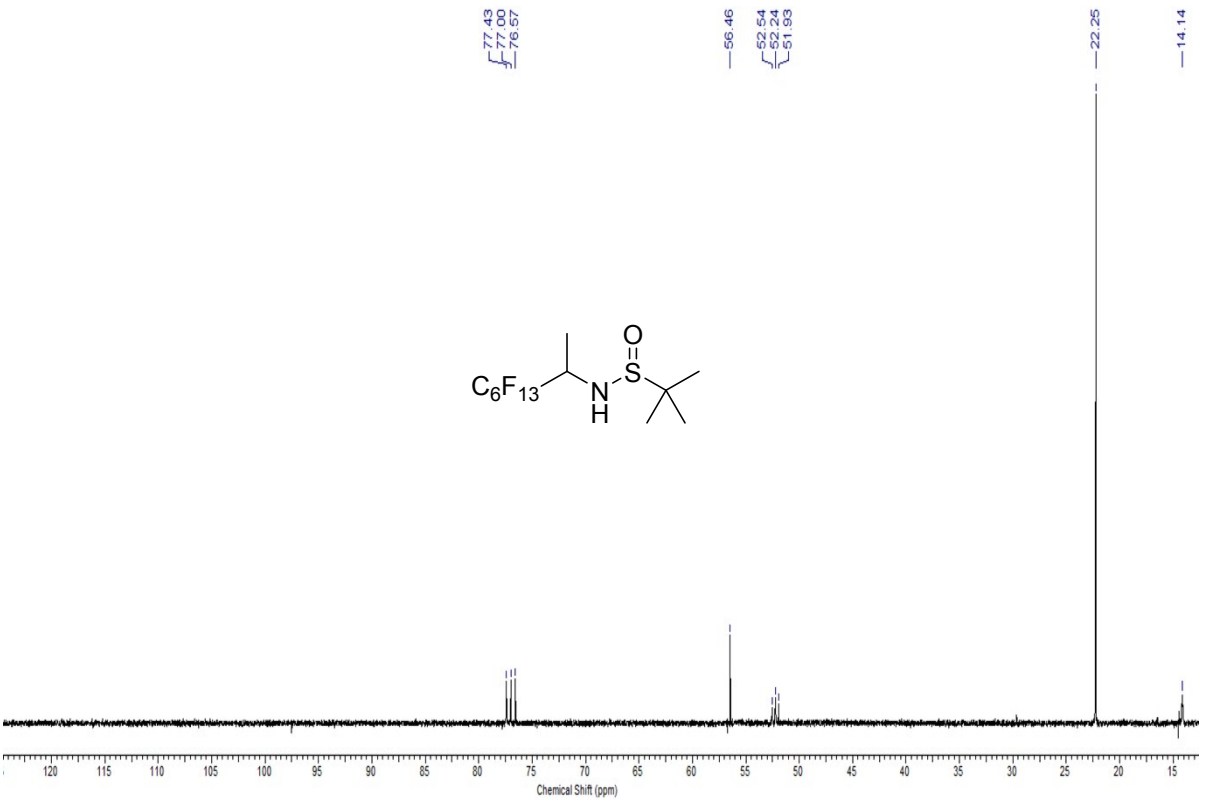
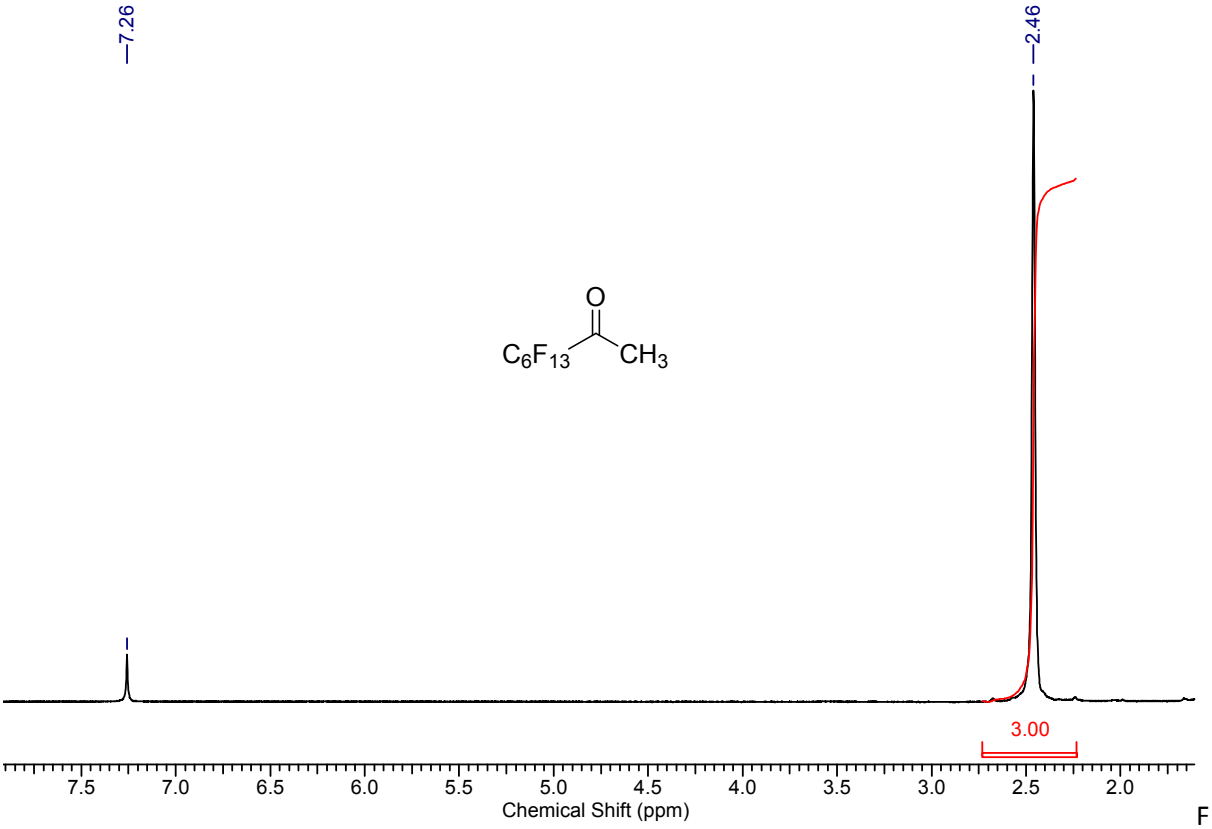


Figure S14. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, 2-methyl-*N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-trideca-fluorooctan-2-yl)propane-2-sulfinamide (**12**).



igure S15. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-one (**14**).

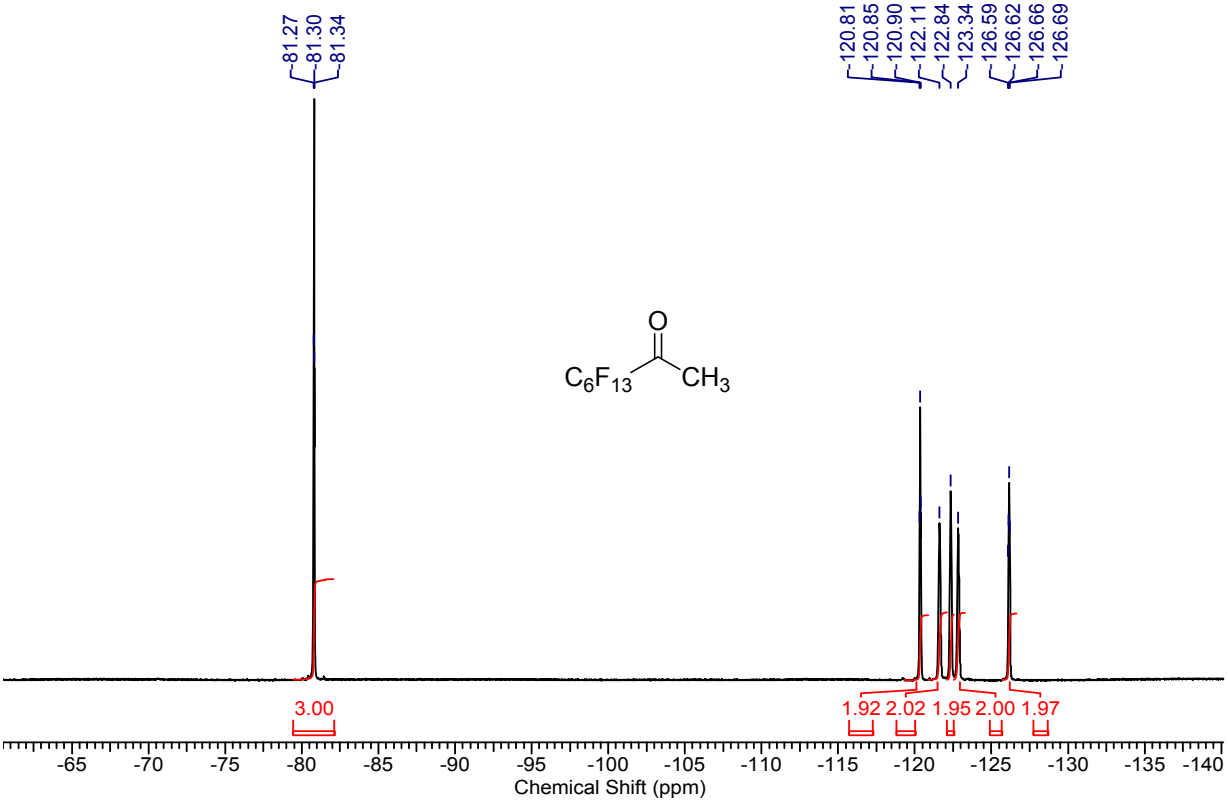


Figure S16. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-one (**14**).

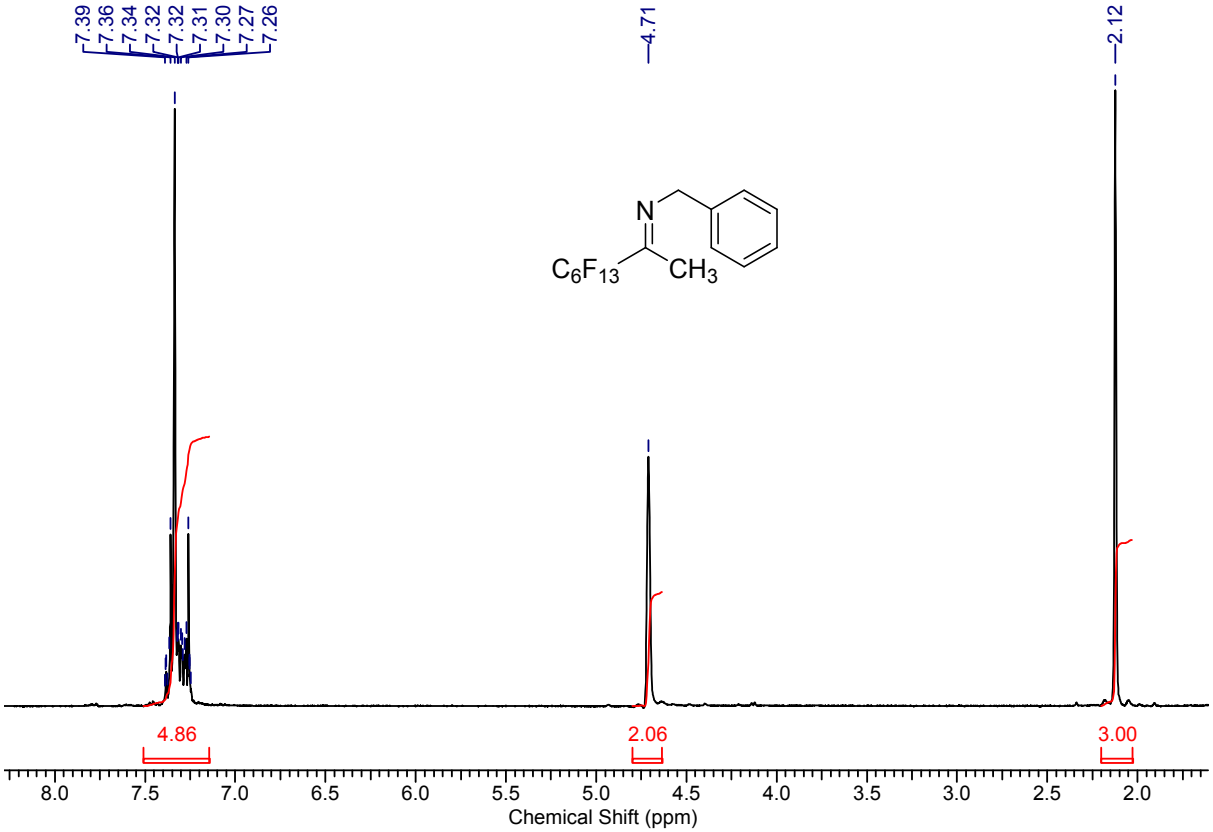


Figure S17. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, *N*-benzyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-imine (**15**).

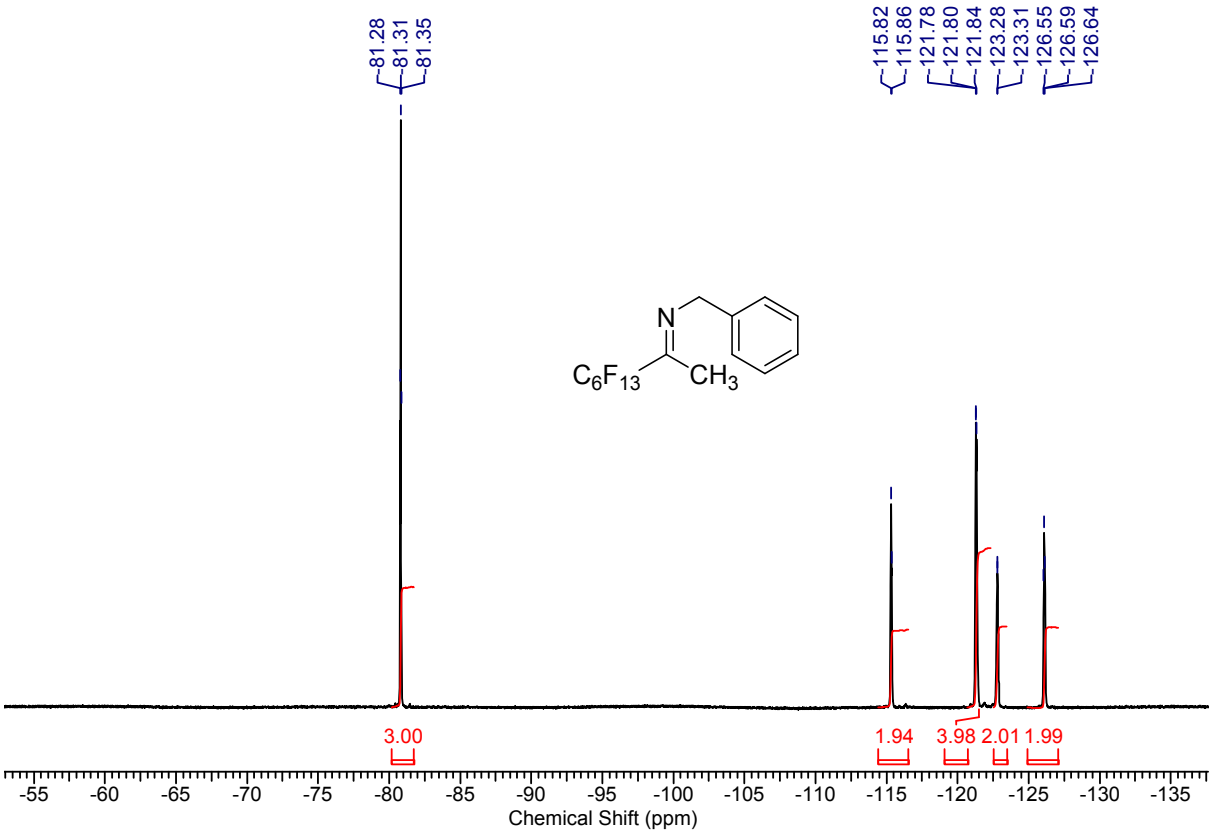


Figure S18. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, *N*-benzyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-imine (**15**).

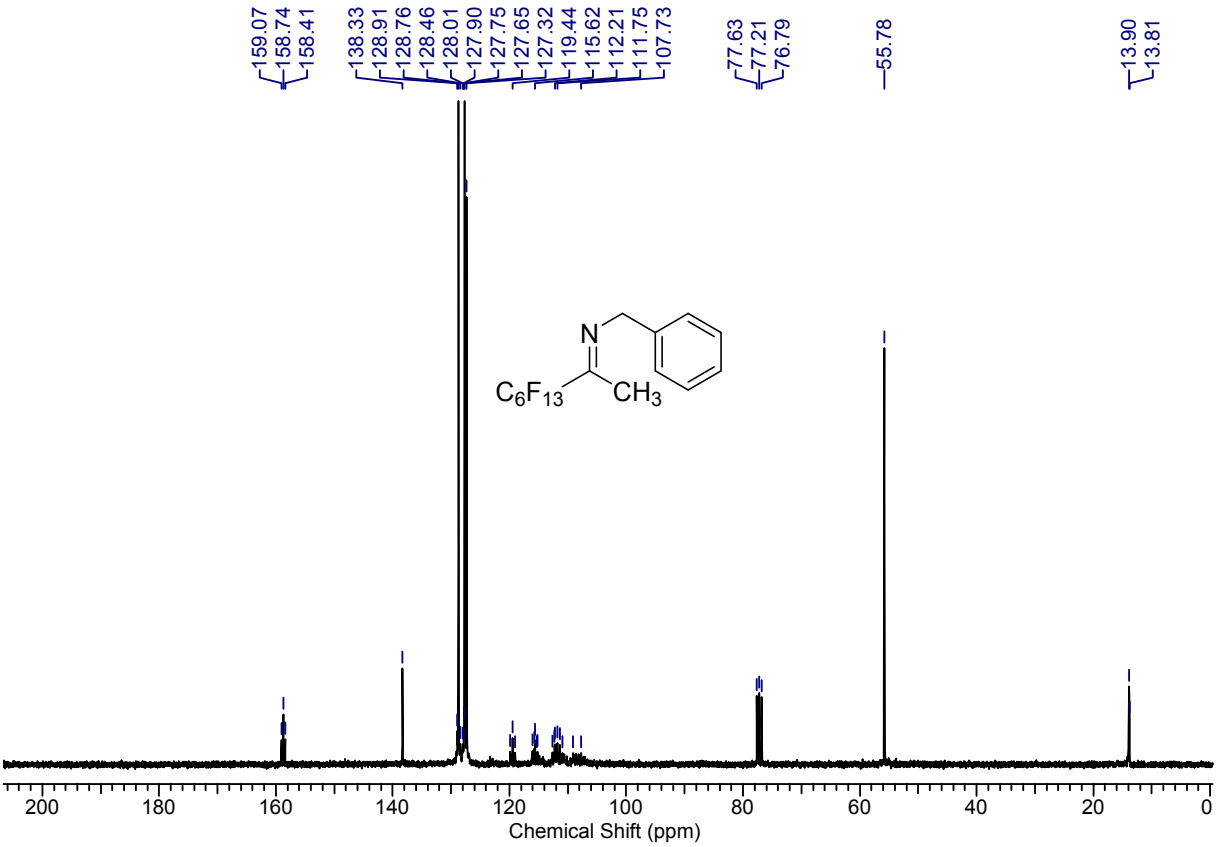


Figure S19. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, *N*-benzyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-imine (**15**).

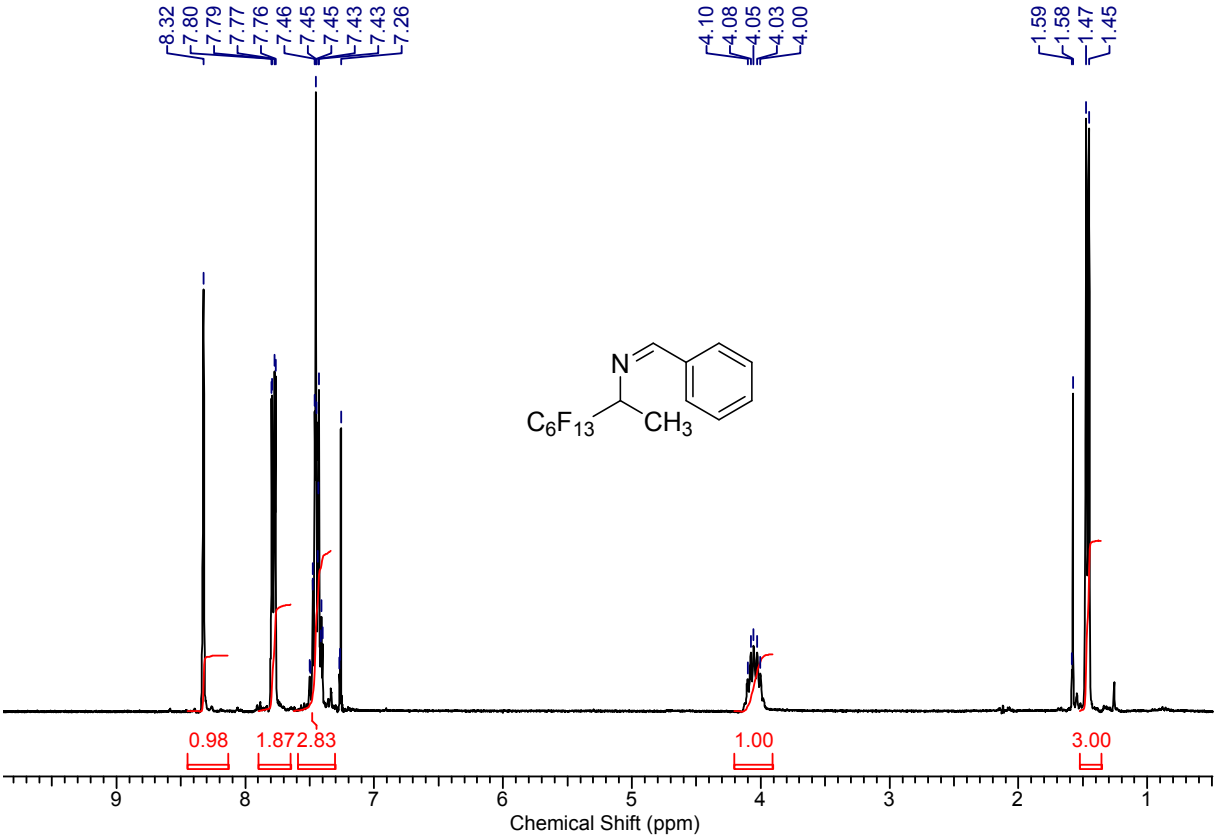


Figure S20. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, *N*-benzylidene-3,3,4,4,5,5,6,6,7,7,8,8,8-trideca-fluorooctan-2-amine (**16**).

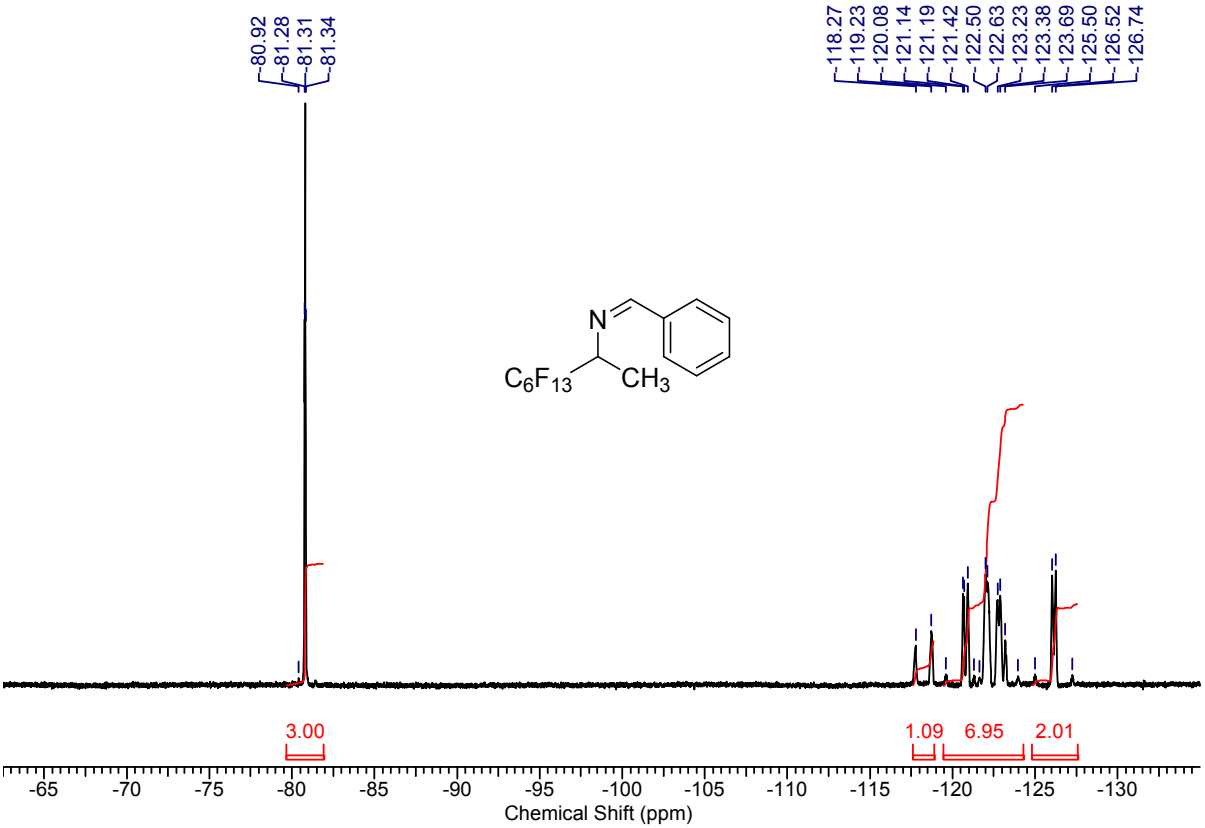


Figure S21. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, *N*-benzylidene-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-amine (**16**).

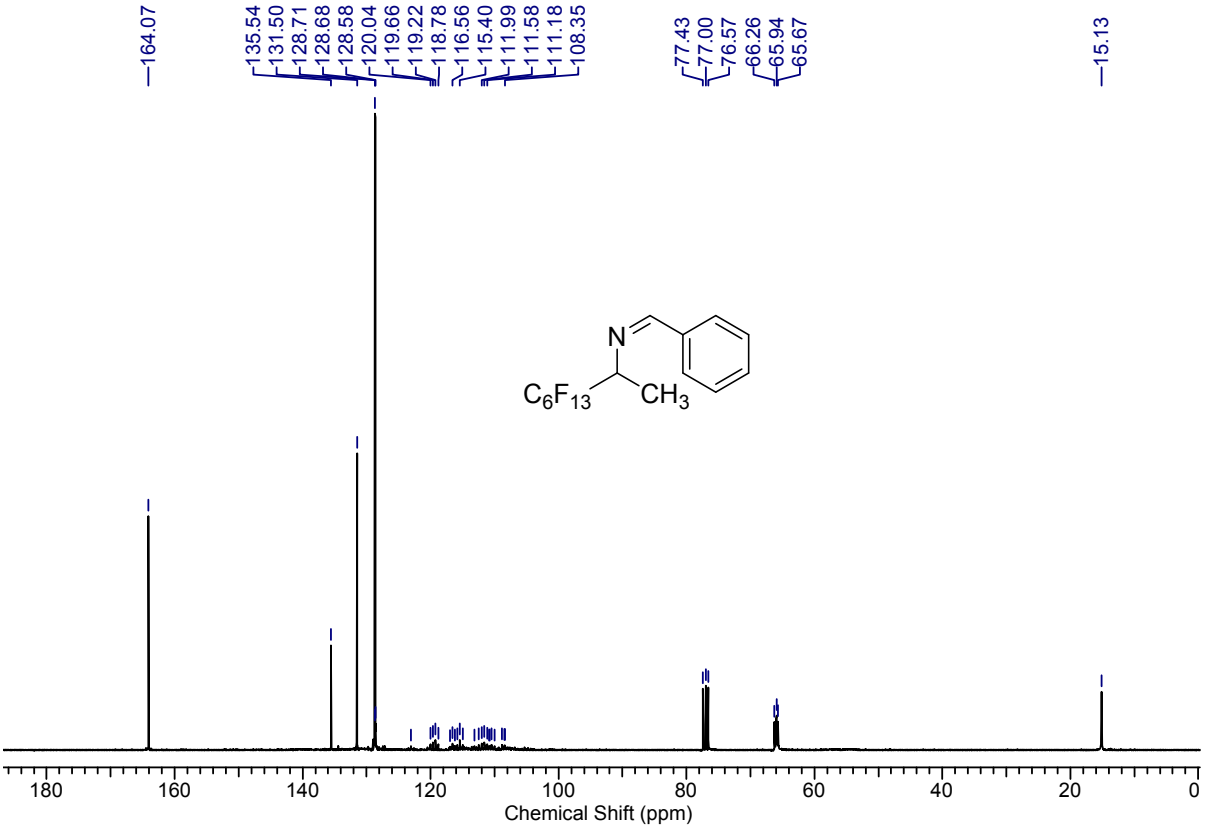


Figure S22. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, *N*-benzylidene-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-amine (**16**).

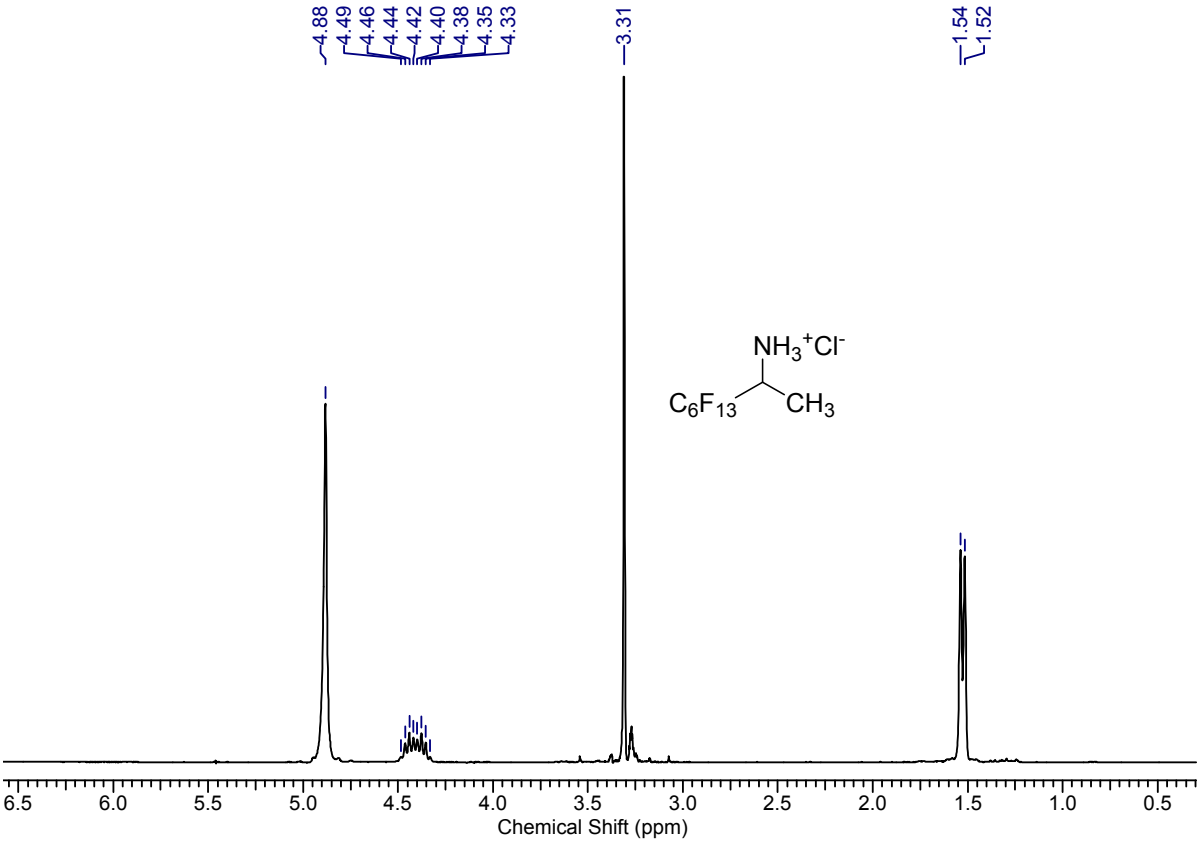


Figure S23. ^{1}H NMR spectrum, 299.97 MHz, CD_3OD, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-ammonium chloride (**10.HCl**).

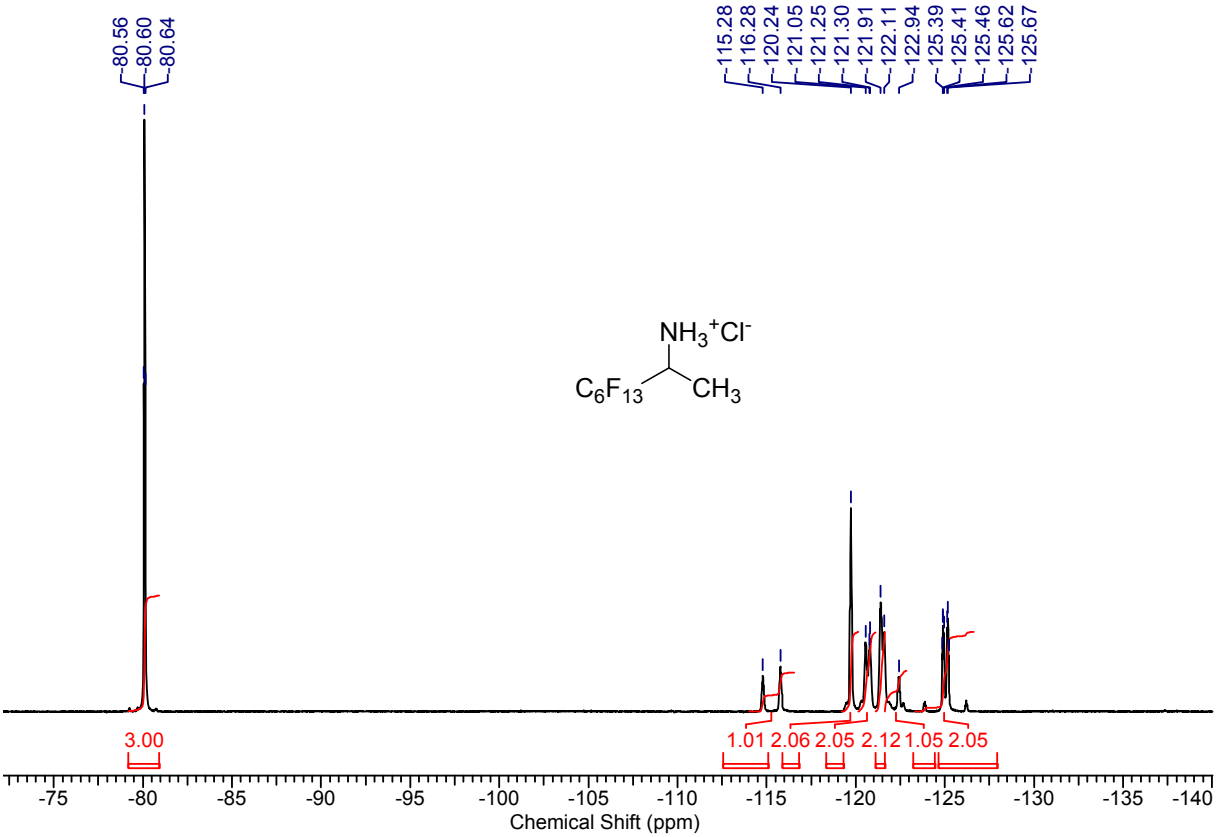


Figure S24. ^{19}F NMR spectrum, 282.23 MHz, CD_3OD, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-ammonium chloride (**10.HCl**).

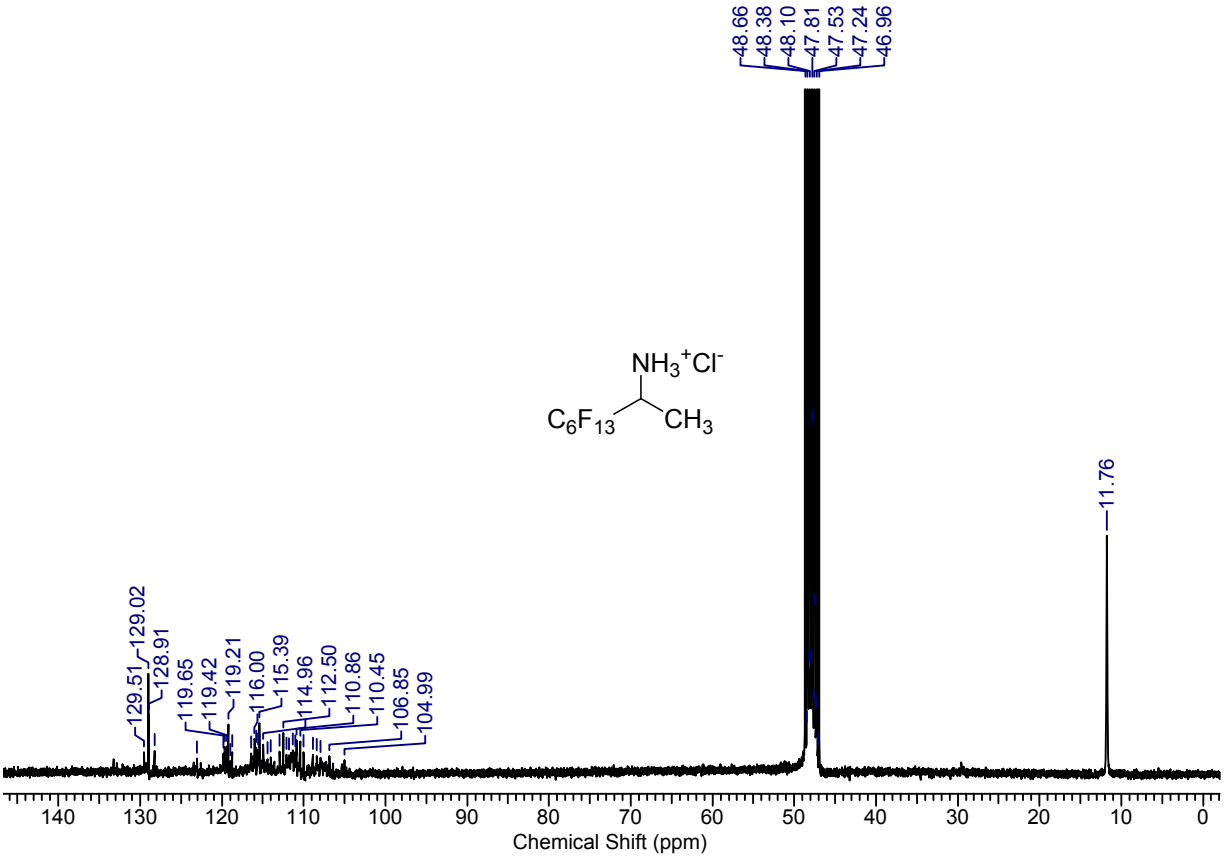


Figure S25. ^{13}C NMR spectrum, 282.23 MHz, CD_3OD, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-ammonium chloride (**10.HCl**).

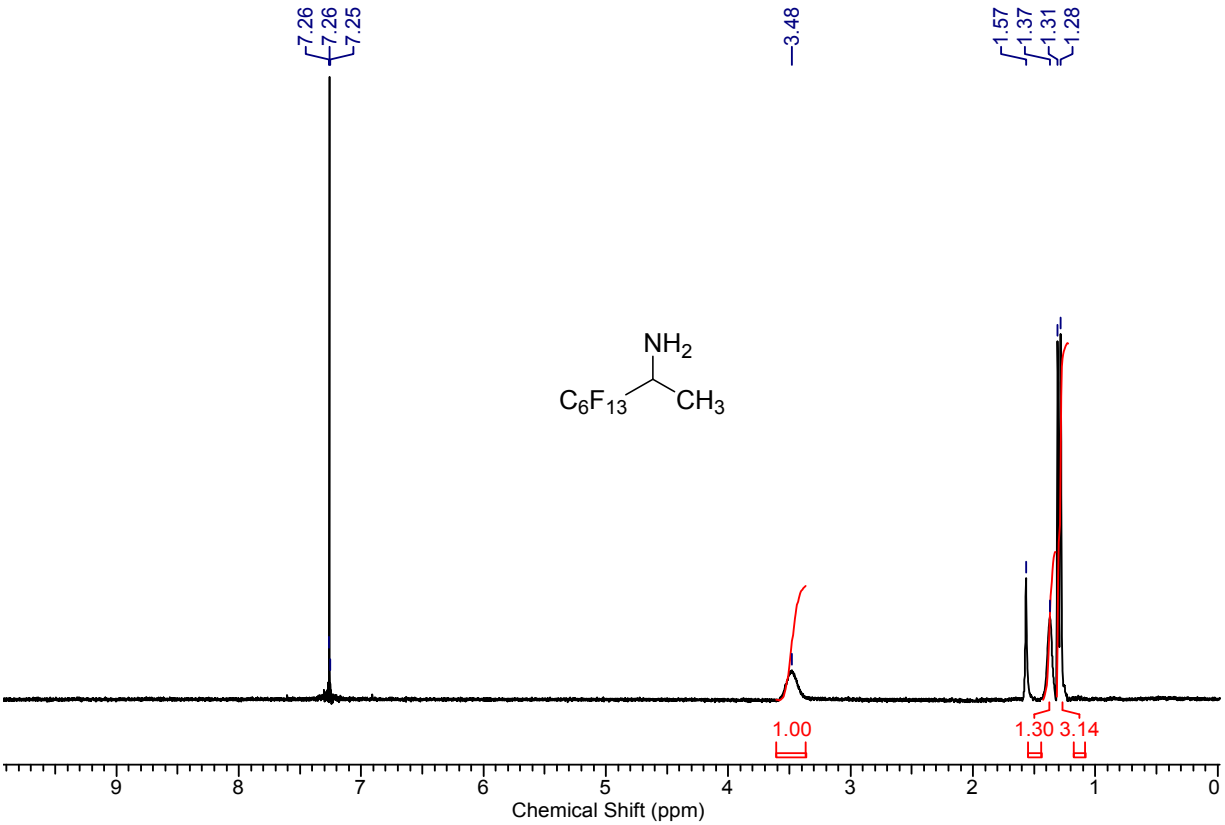


Figure S26. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-amine (**10**).

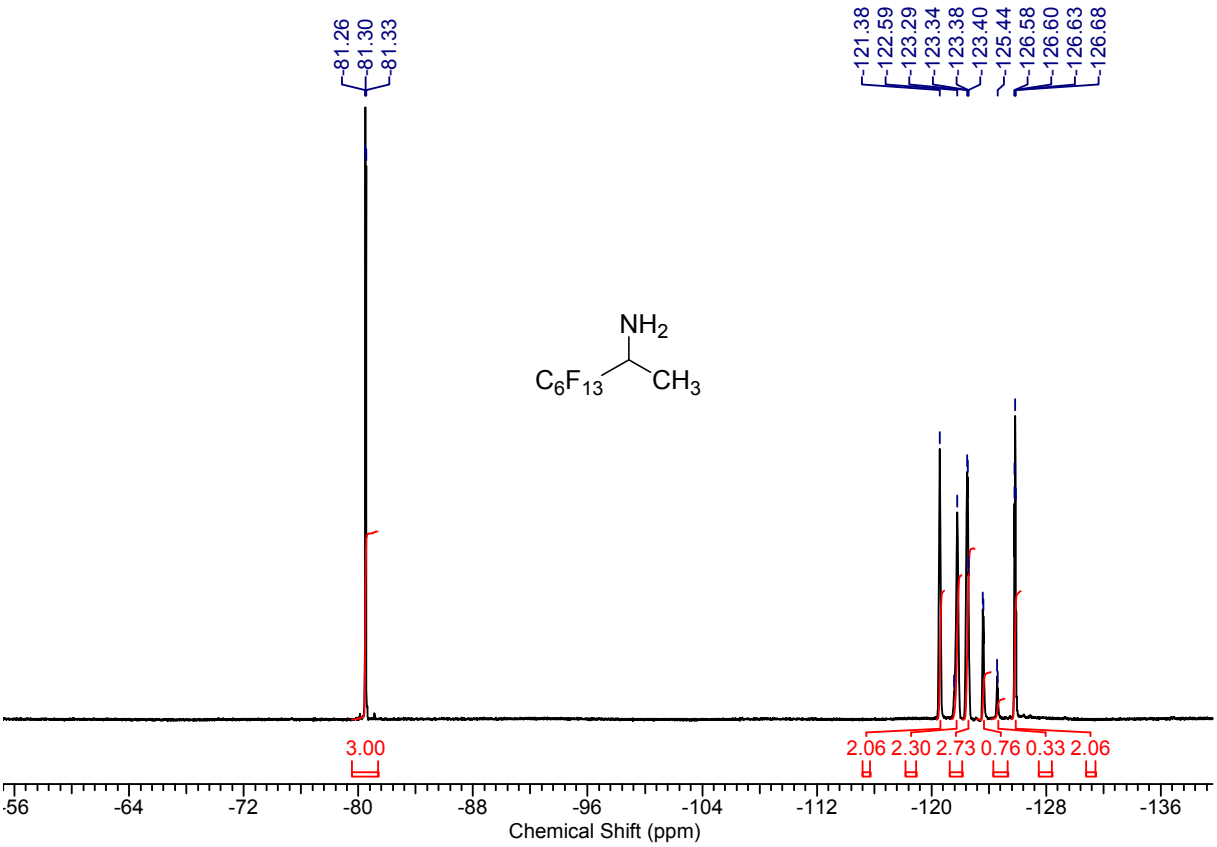


Figure S27. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-amine (**10**).

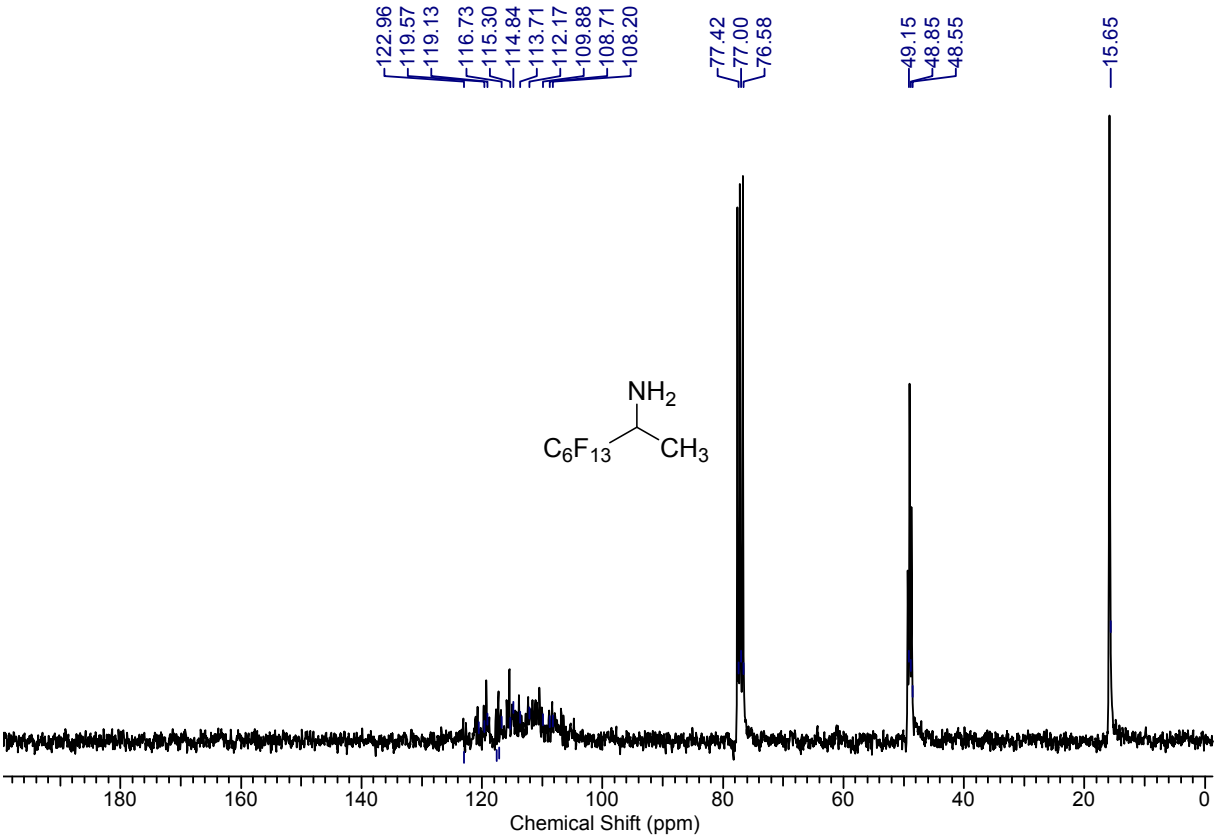


Figure S28. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-amine (**10**).

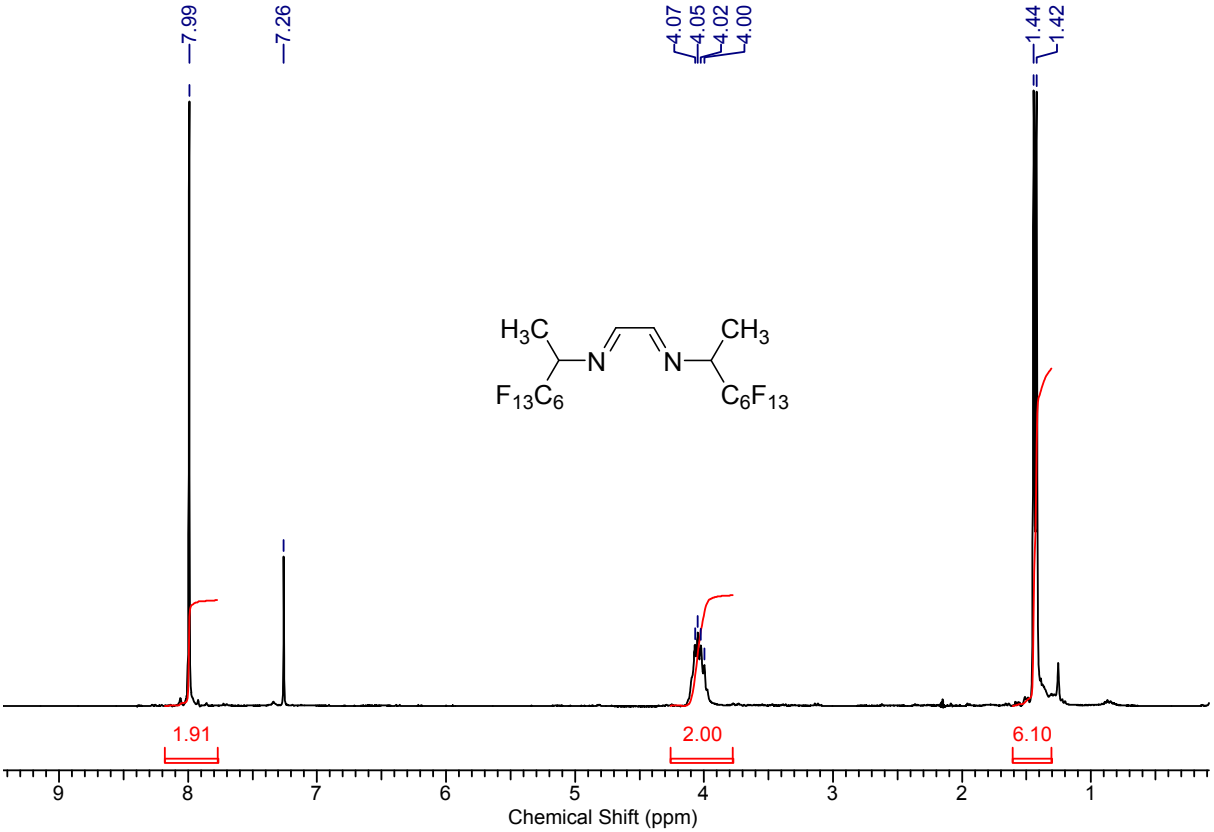


Figure S29. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, *N,N'*-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)ethane-diylidenediamine (**17**).

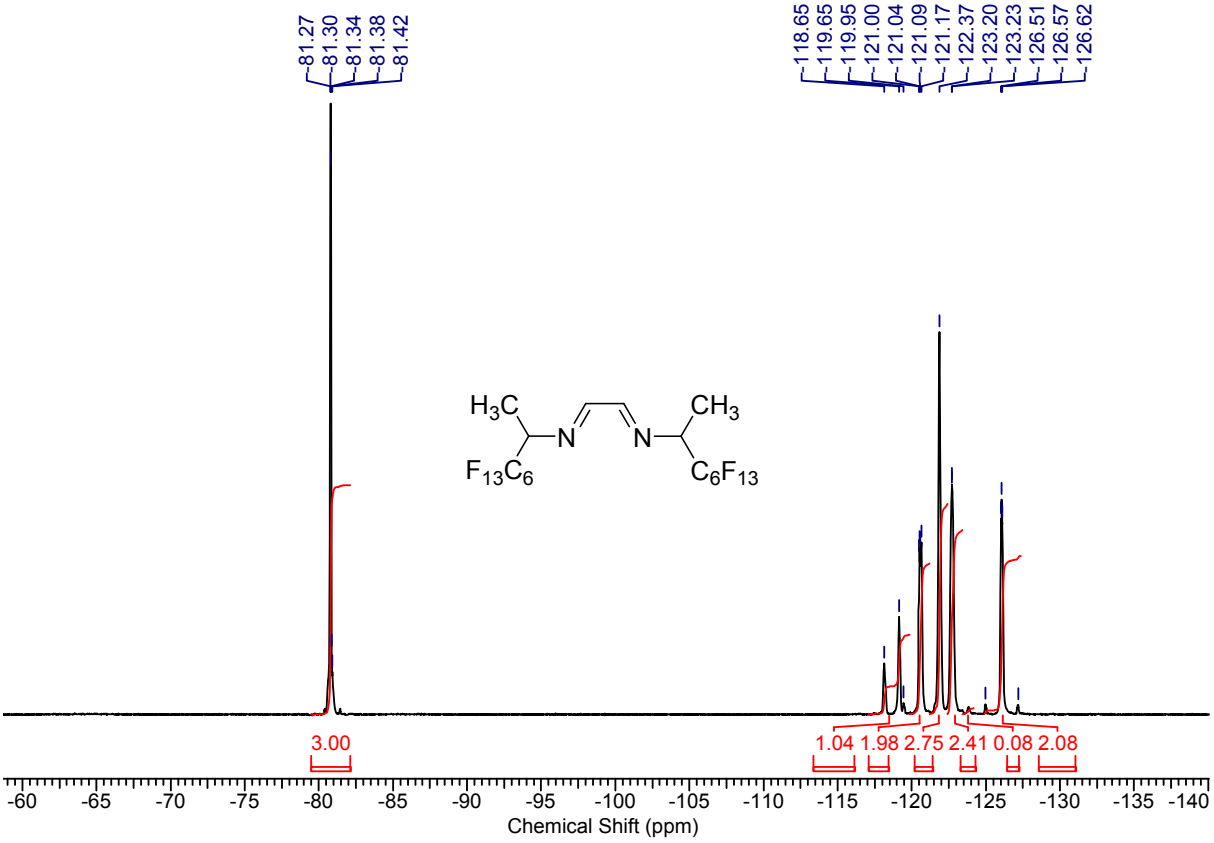


Figure S30. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, *N,N'*-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)ethane-diylidenediamine (**17**).

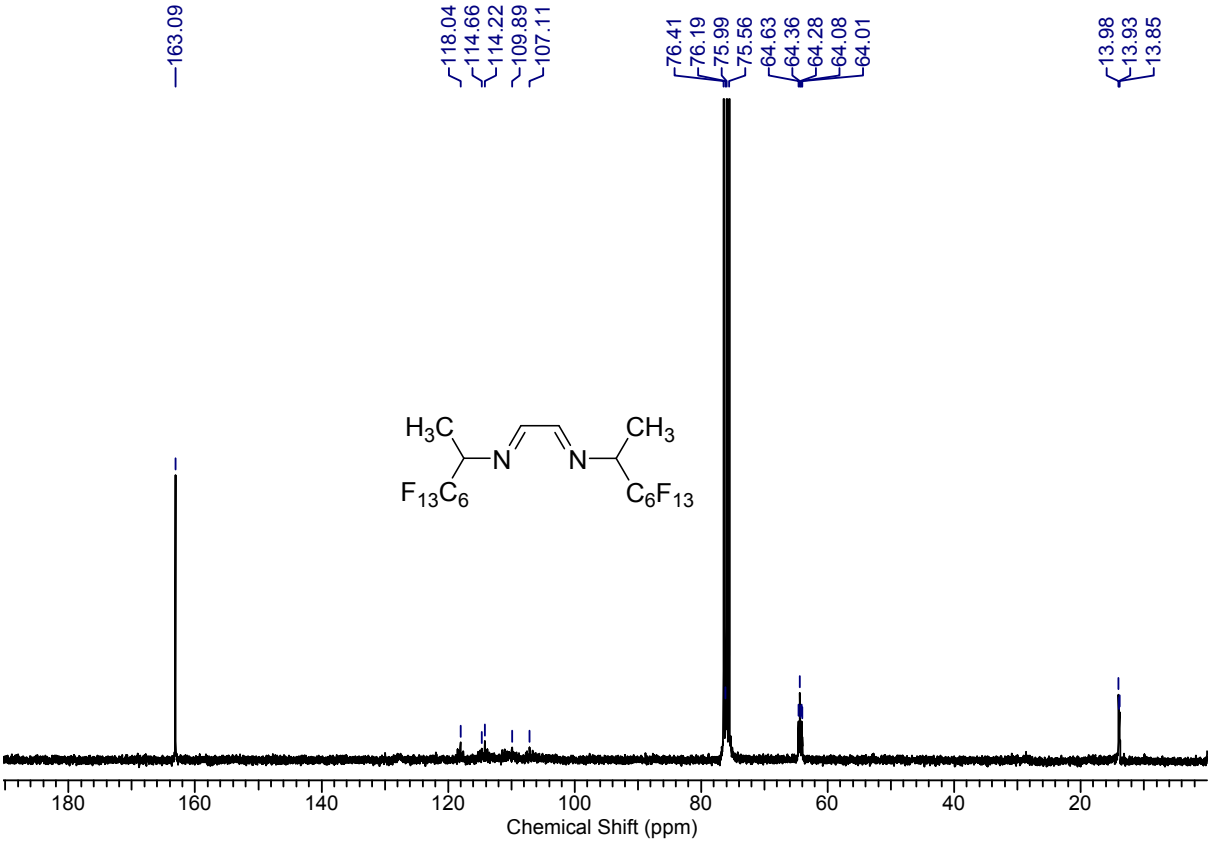


Figure S31. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, *N,N'*-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)ethane-diylidenediamine (**17**).

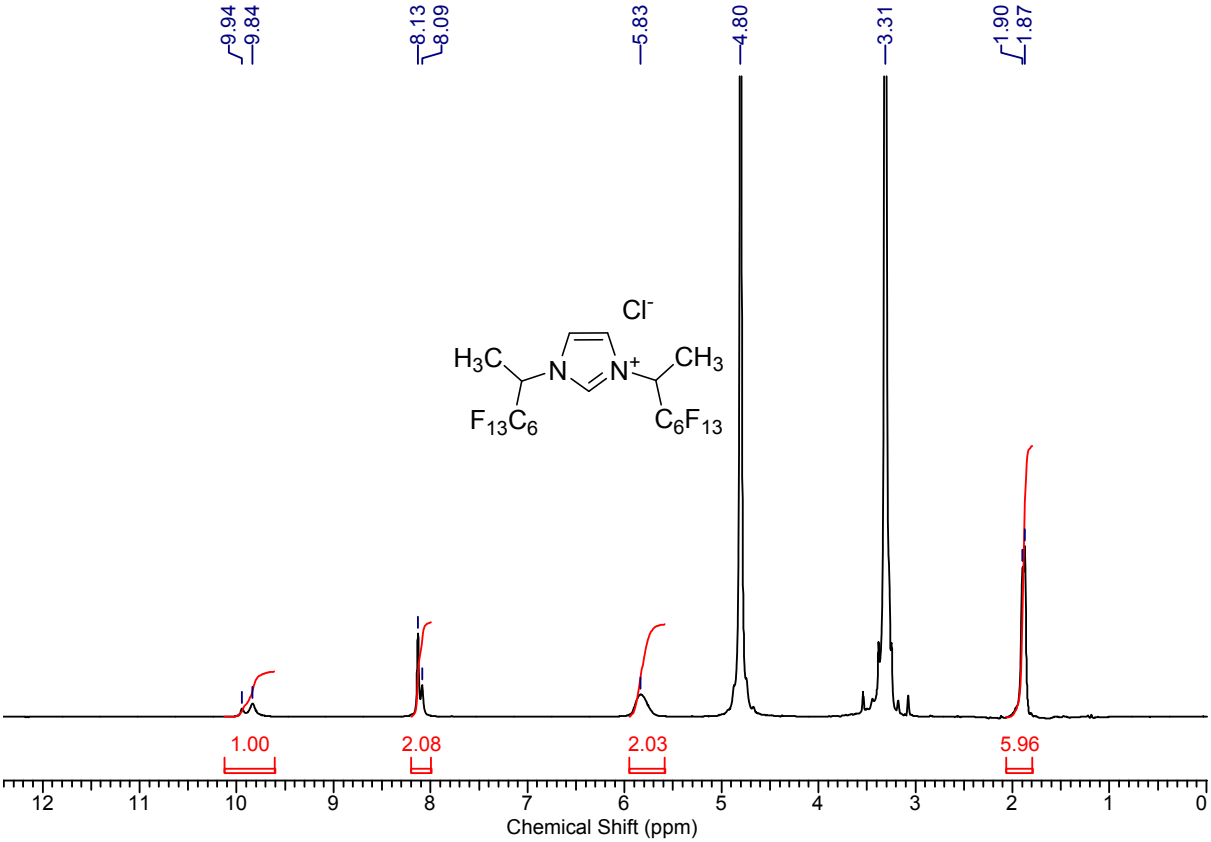


Figure S32. ^{1}H NMR spectrum, 299.97 MHz, CD_3OD, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-imidazolium chloride (**18**).

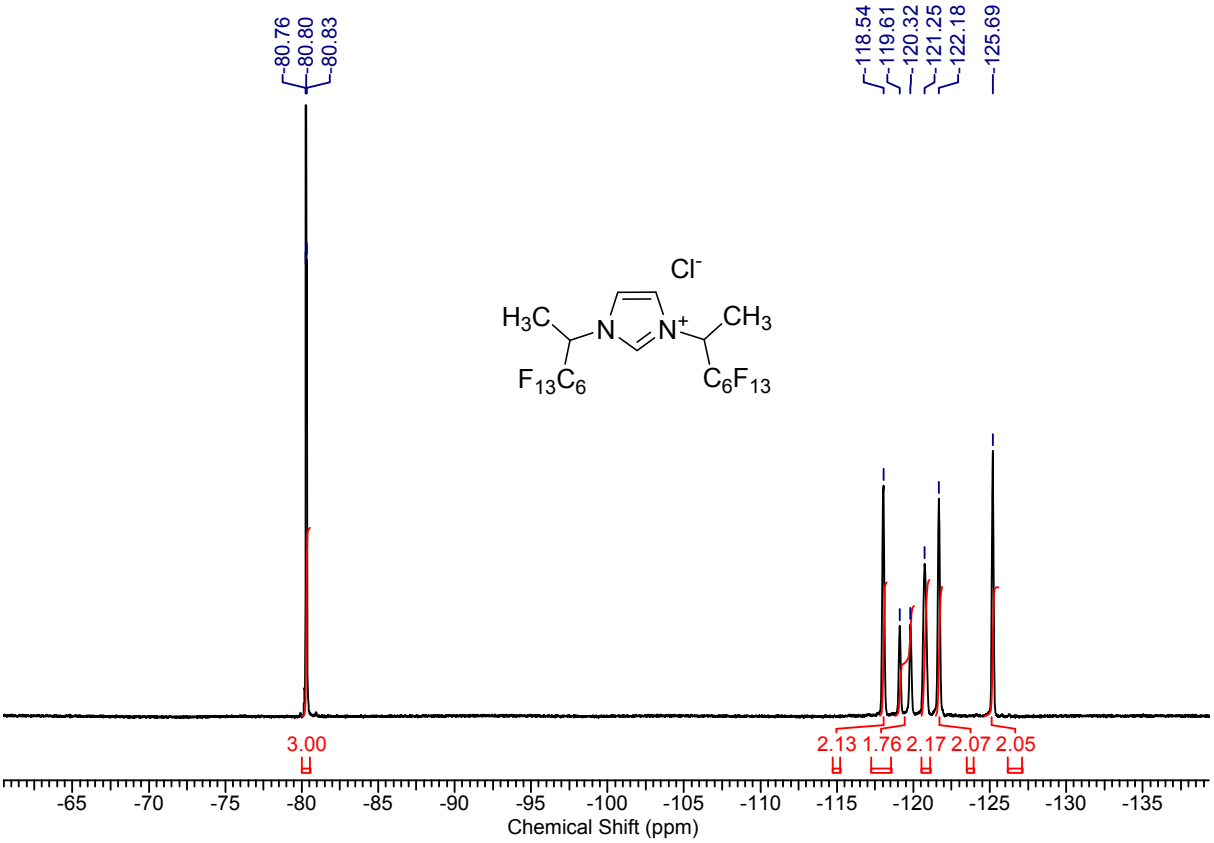


Figure S33. ^{19}F NMR spectrum, 282.23 MHz, CD_3OD, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-imidazolium chloride (**18**).

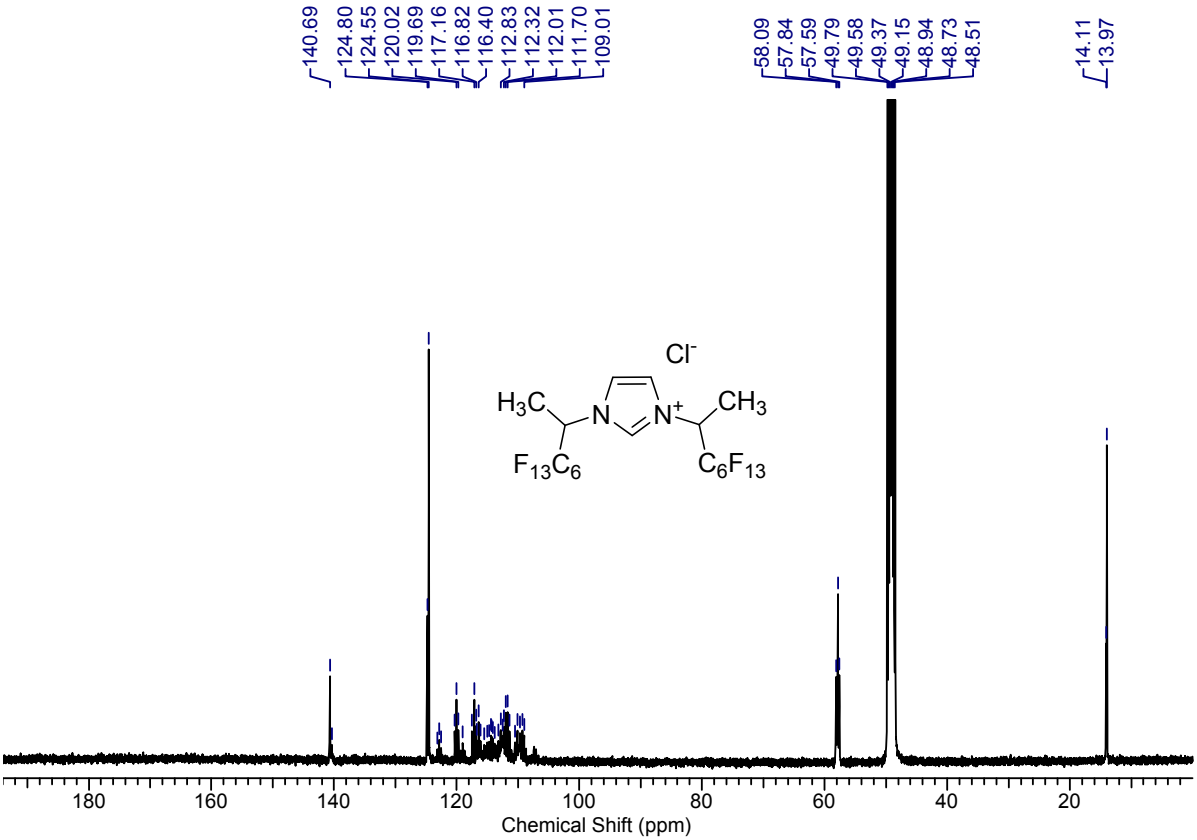


Figure S34. ^{13}C NMR spectrum, 75.44 MHz, CD_3OD, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-imidazolium chloride (**18**).

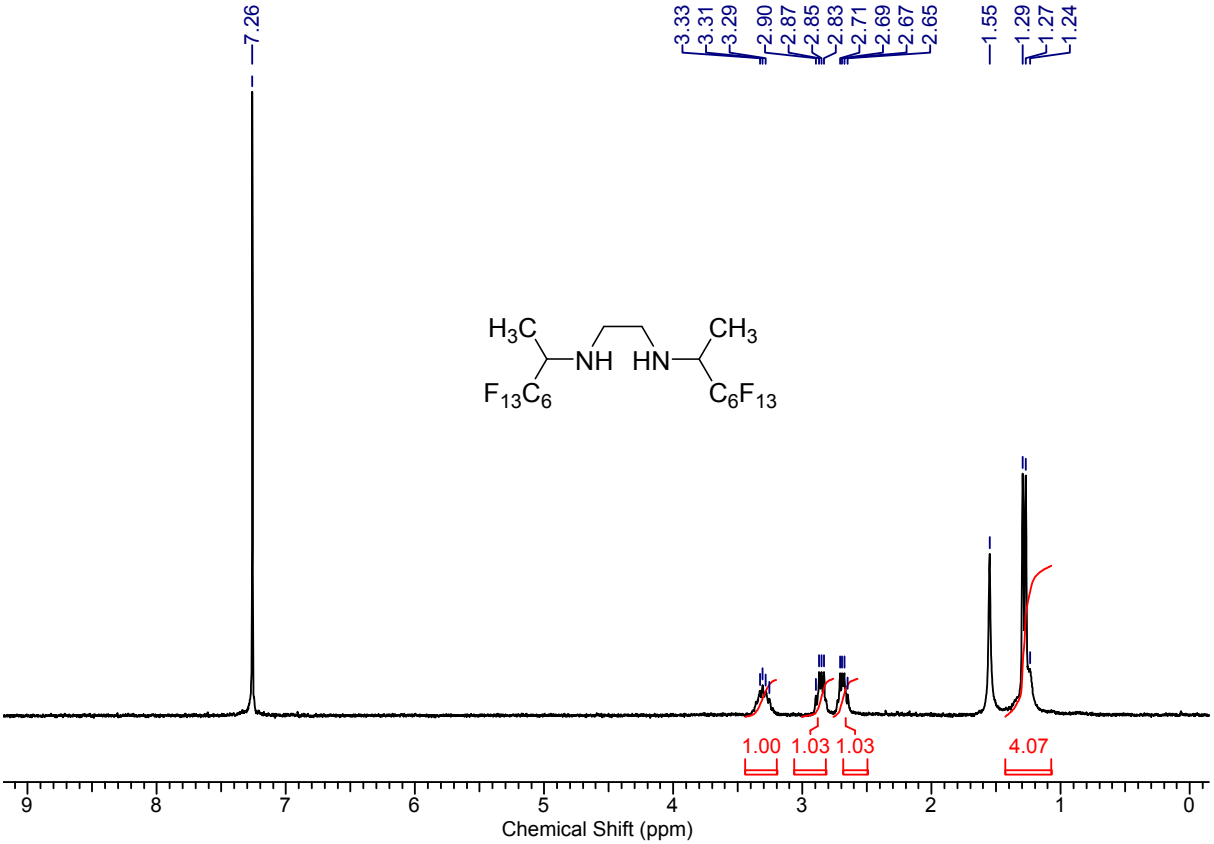


Figure S35. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, *N,N′*-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)ethane-1,2-diamine (**19**).

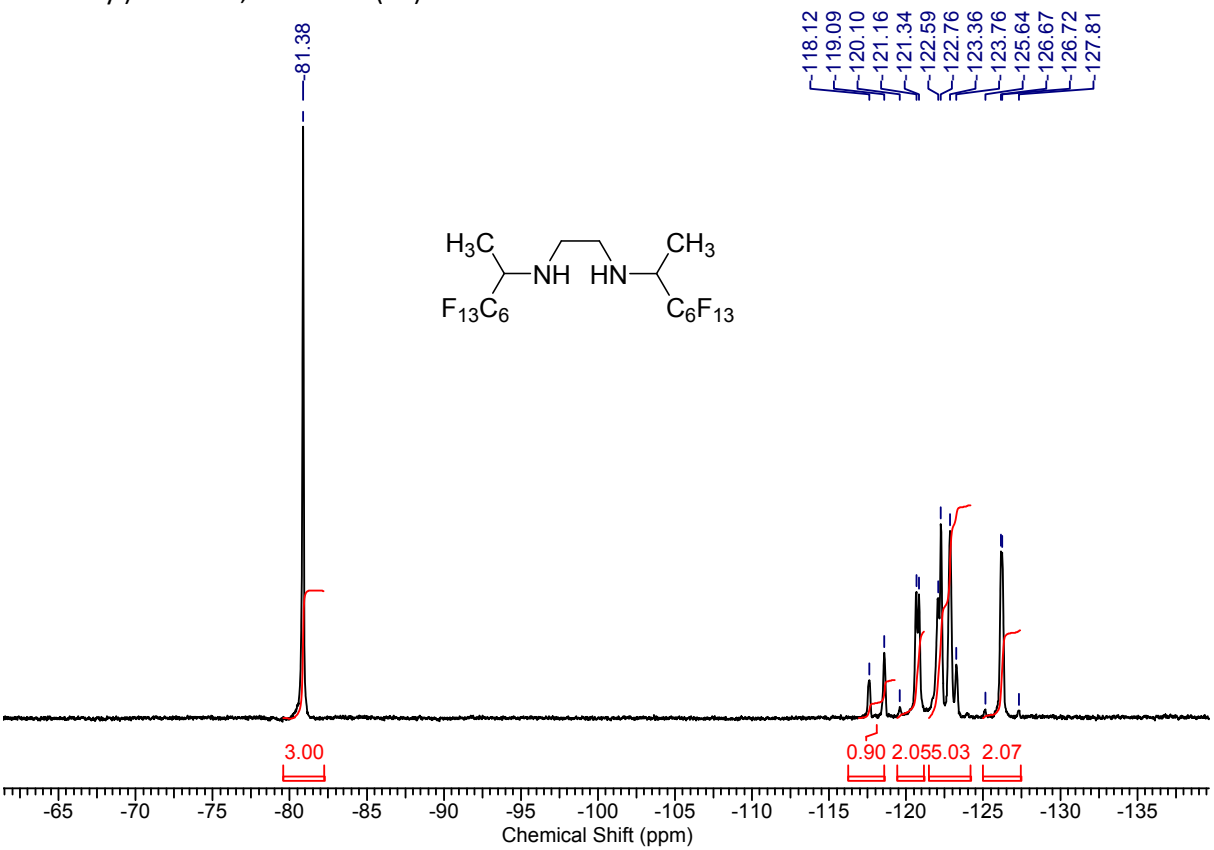


Figure S36. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, *N,N′*-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)ethane-1,2-diamine (**19**).

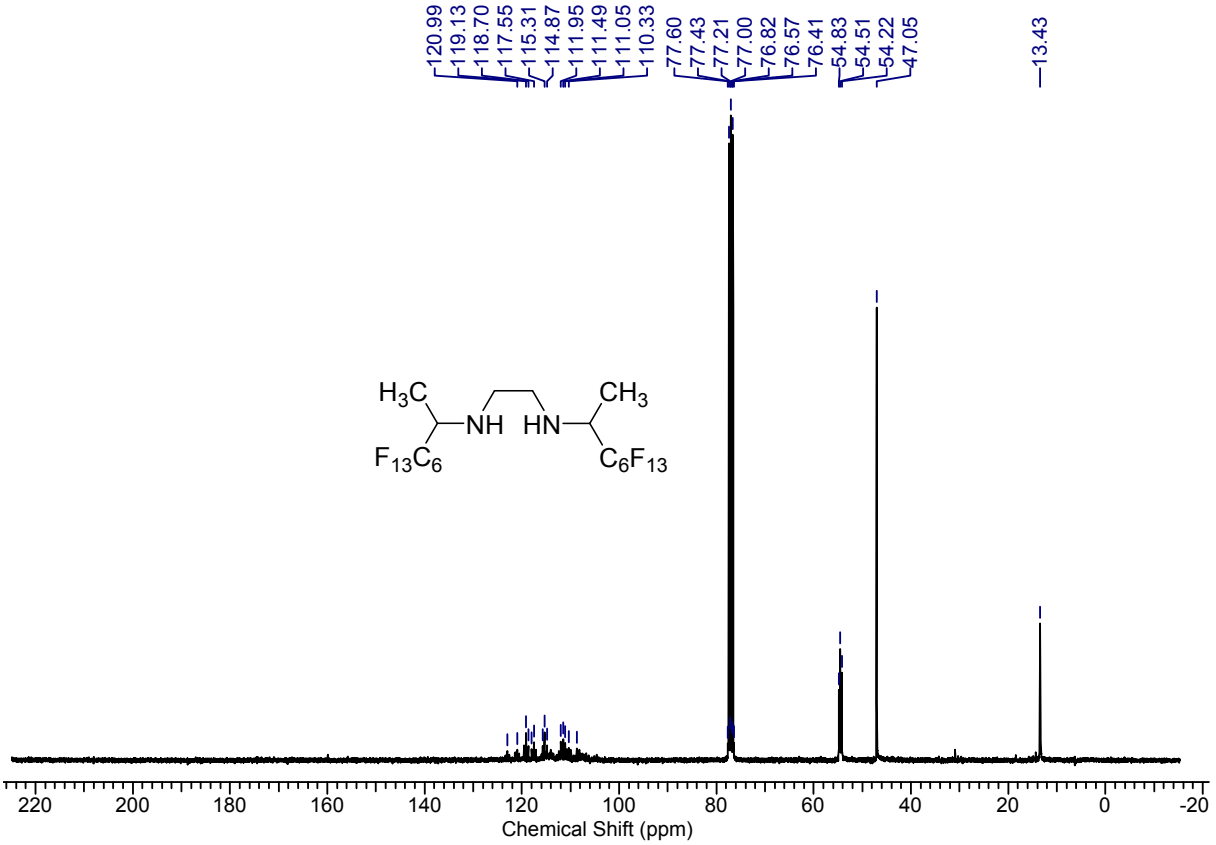


Figure S37. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, *N,N'*-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)ethane-1,2-diamine (**19**).

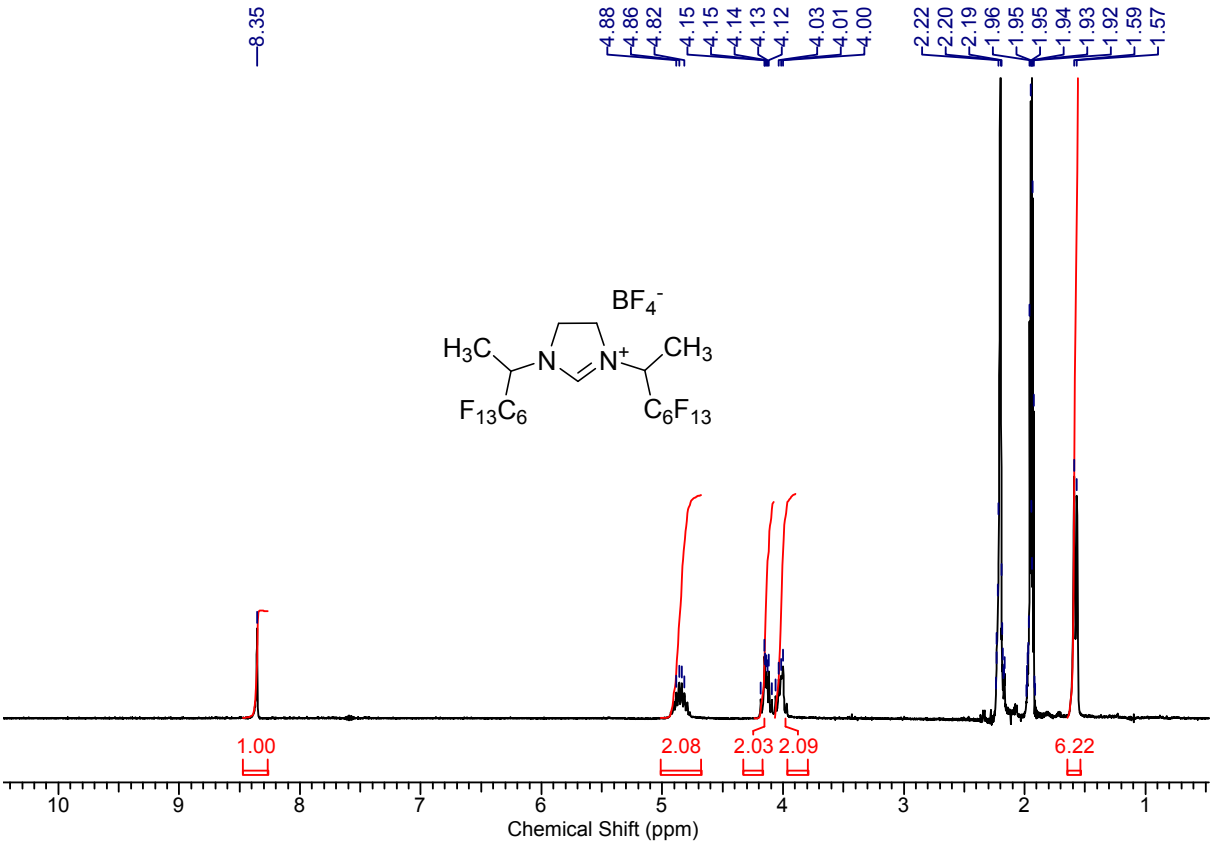


Figure S38. ^{1}H NMR spectrum, 299.97 MHz, CD_3CN, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-4,5-dihydroimidazolium tetrafluoroborate (**20**).

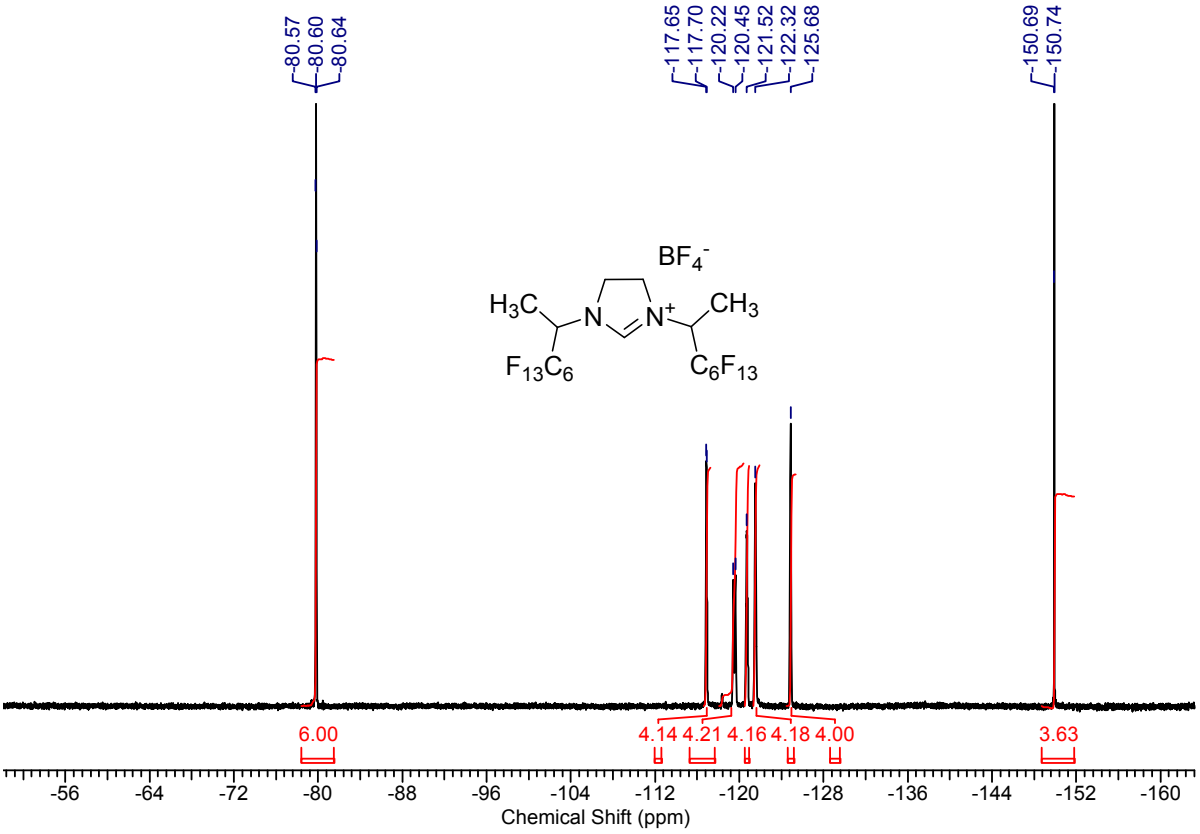


Figure S39. ^{19}F NMR spectrum, 282.23 MHz, CD_3CN, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-4,5-dihydroimidazolium tetrafluoroborate (**20**).

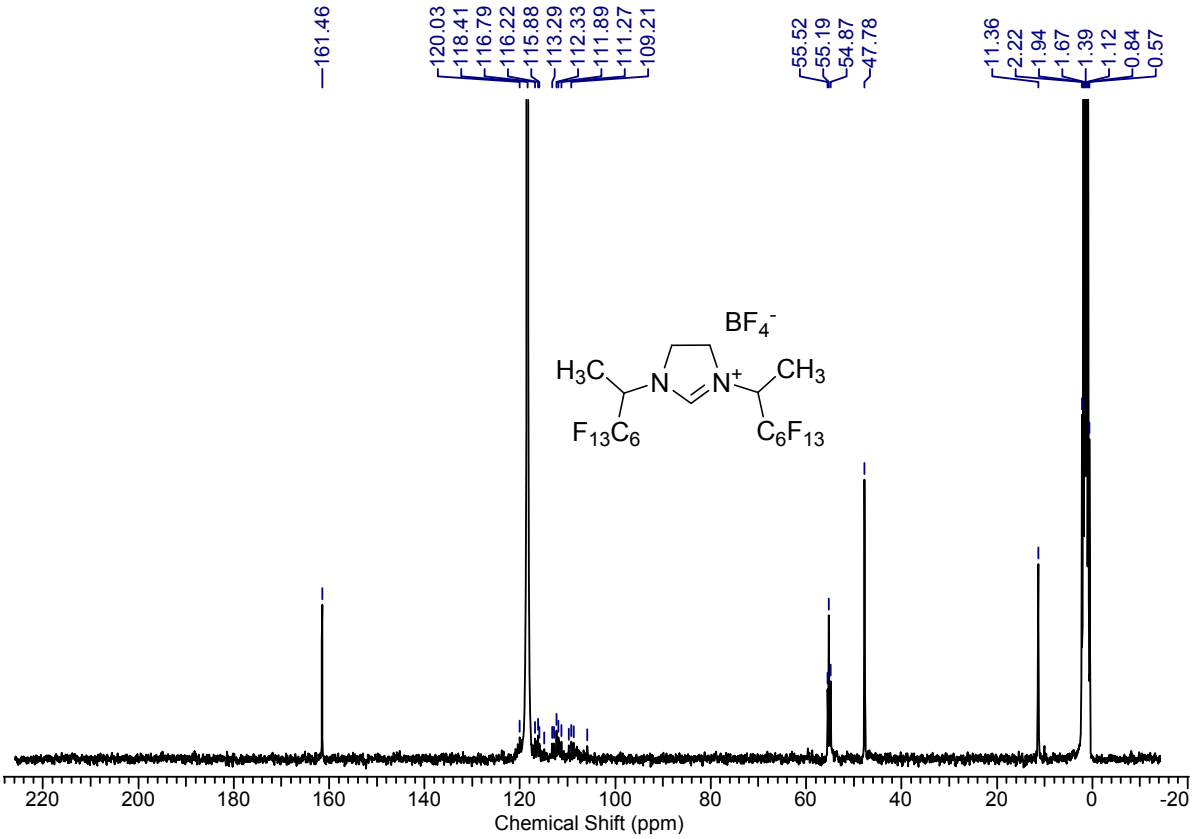


Figure S40. ^{13}C NMR spectrum, 75.44 MHz, CD_3CN, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-4,5-dihydroimidazolium tetrafluoroborate (**20**).

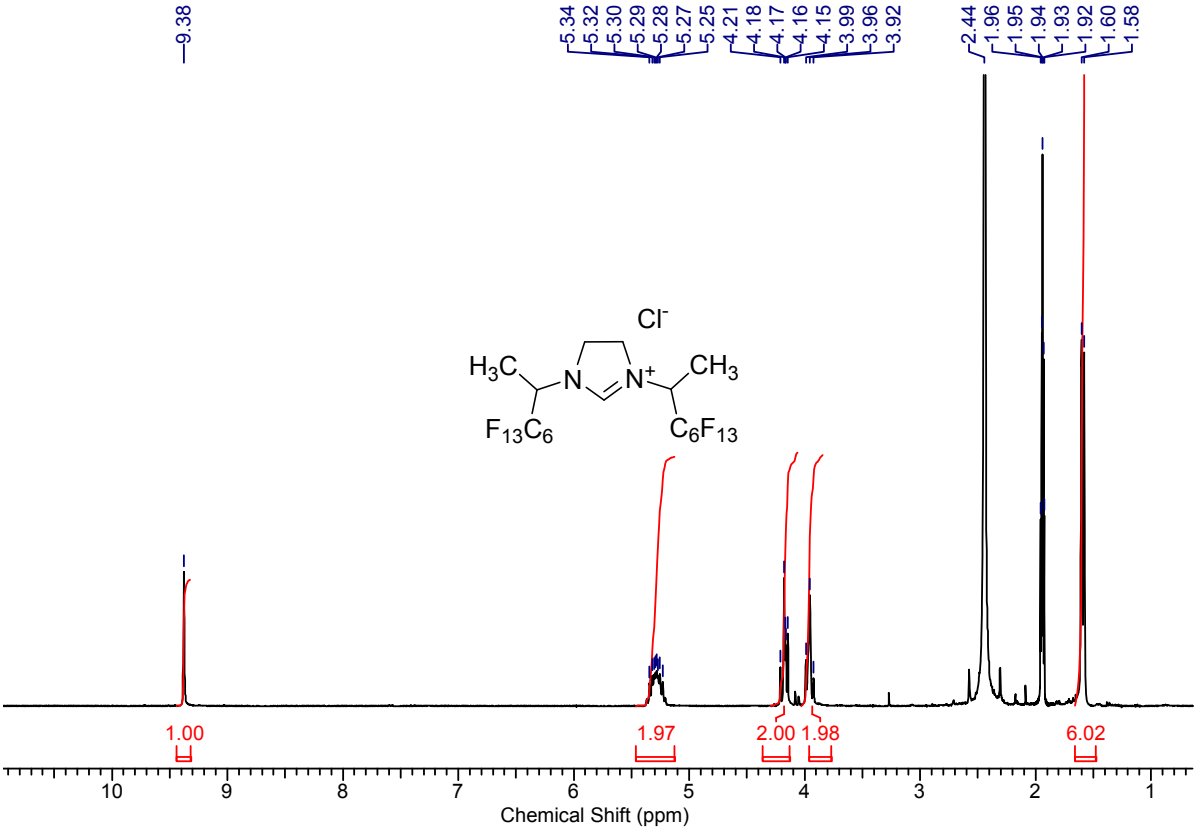


Figure S41. ^{1}H NMR spectrum, 299.97 MHz, CD_3CN, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-4,5-dihydroimidazolium chloride (**21**).

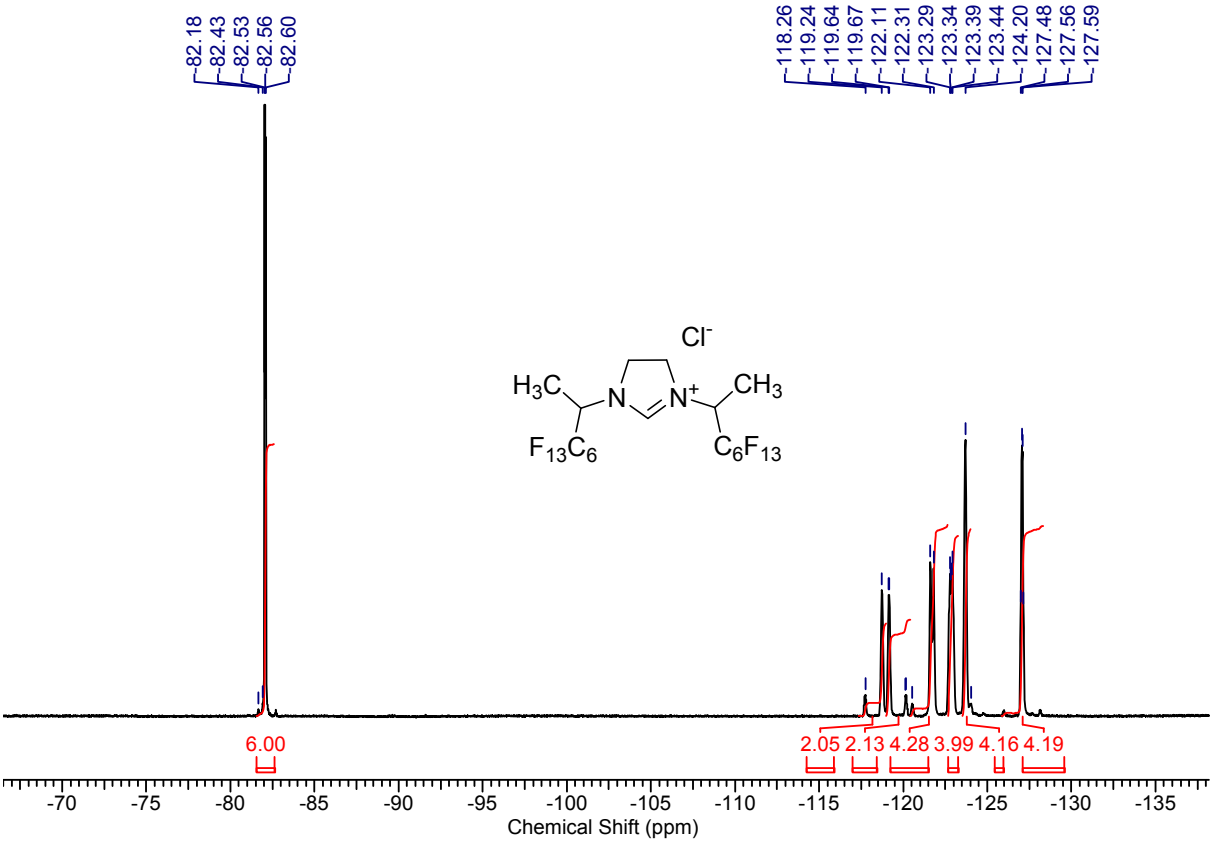


Figure S42. ^{19}F NMR spectrum, 282.23 MHz, CD_3OD, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-4,5-dihydroimidazolium chloride (**21**).

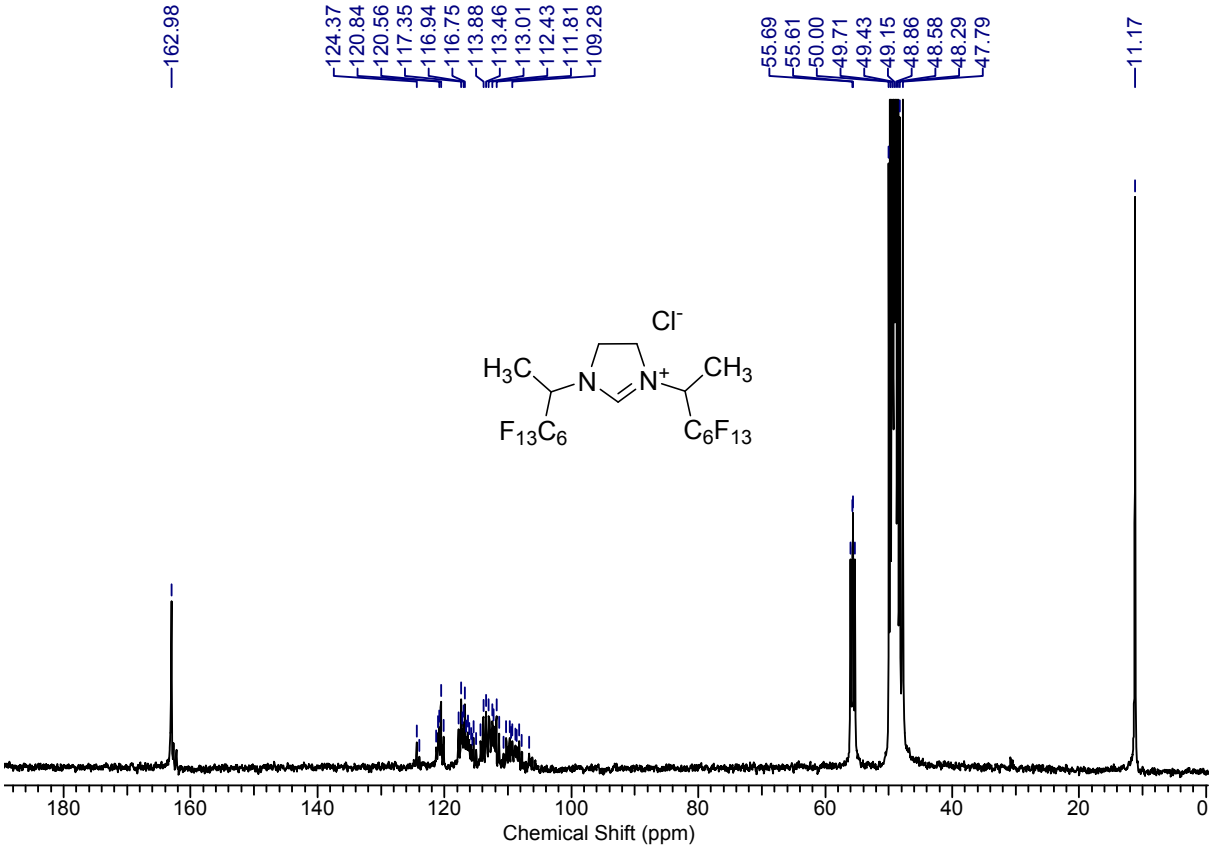


Figure S43. ^{13}C NMR spectrum, 75.44 MHz, CD_3OD, 1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-4,5-dihydroimidazolium chloride (**21**).

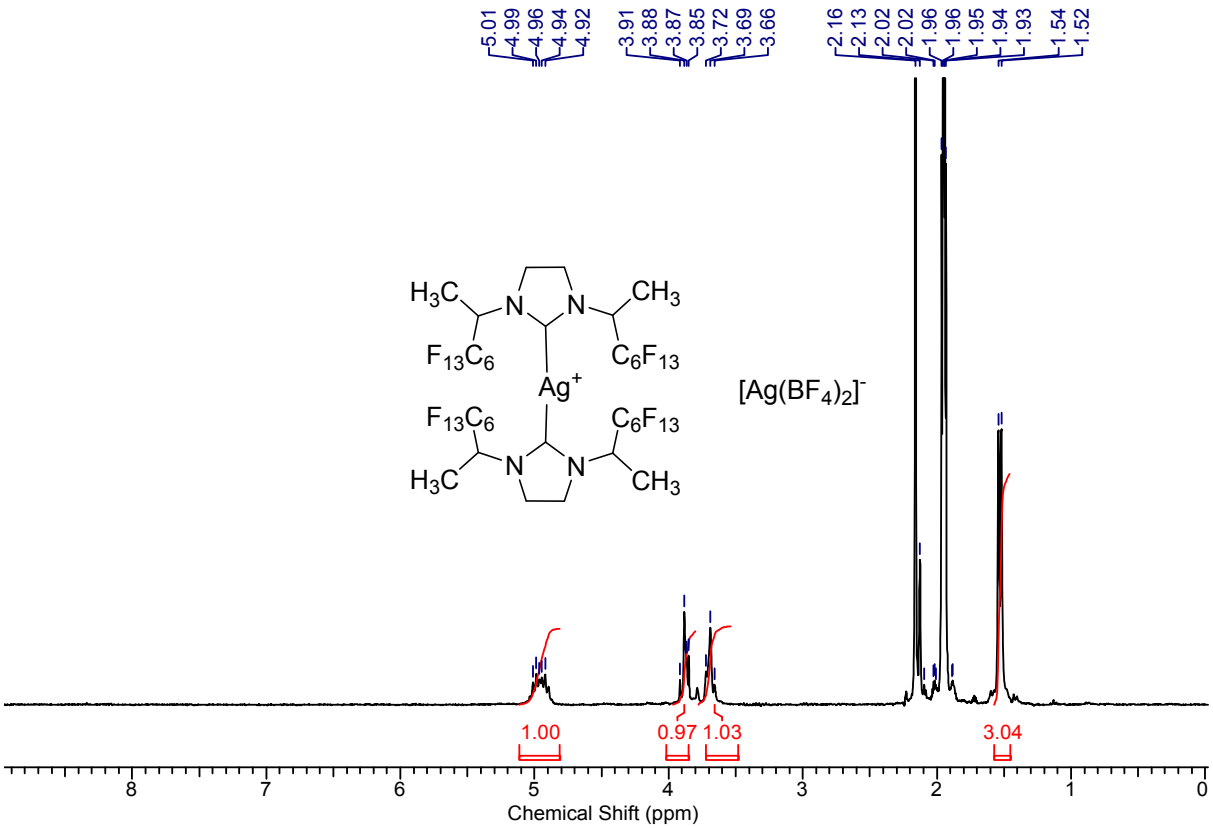


Figure S44. ^{1}H NMR spectrum, 299.97 MHz, CD_3CN, bis[1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)imidazolidin-2-ylidene]silver(I) bis(tetrafluoroborato)argentate (**23**).

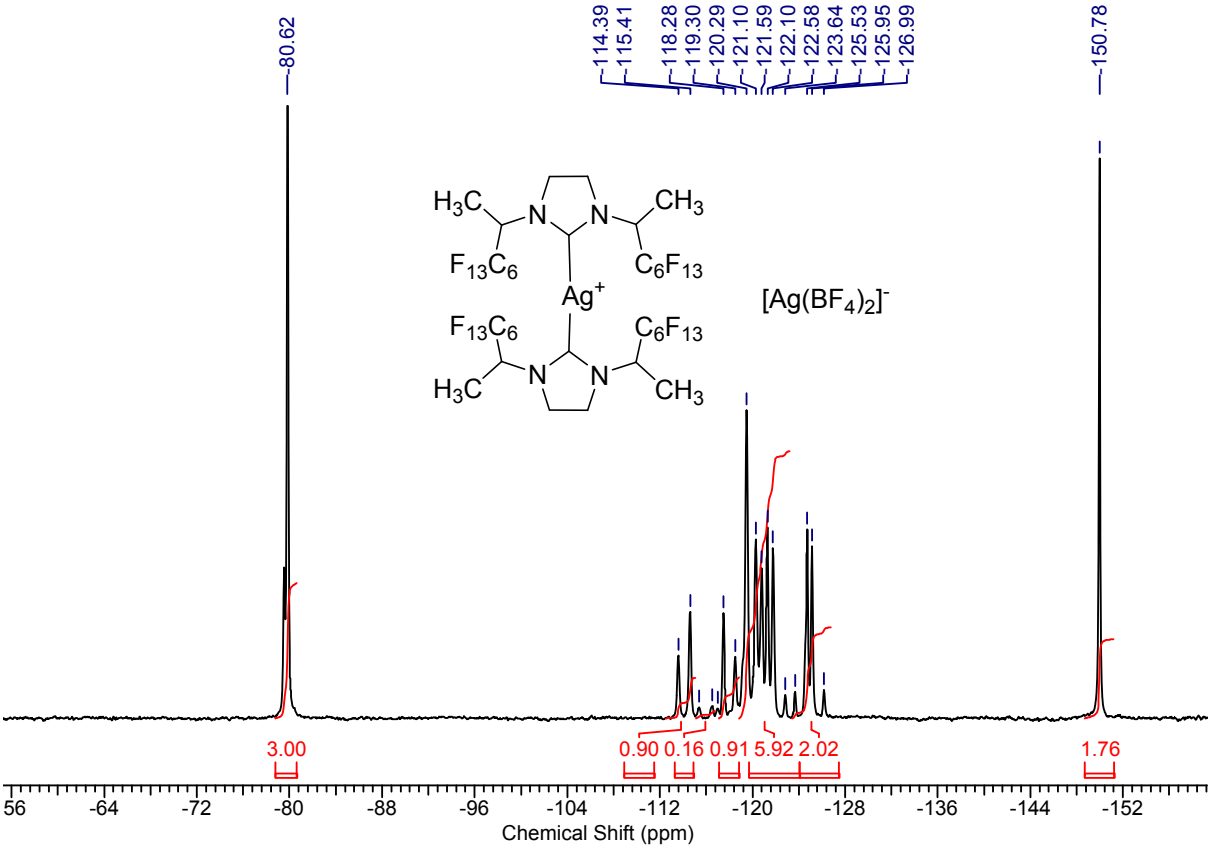


Figure S45. ^{19}F NMR spectrum, 282.23 MHz, CD_3CN, bis[1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)imidazolidin-2-ylidene]silver(I) bis(tetrafluoroborato)argentate (**23**).

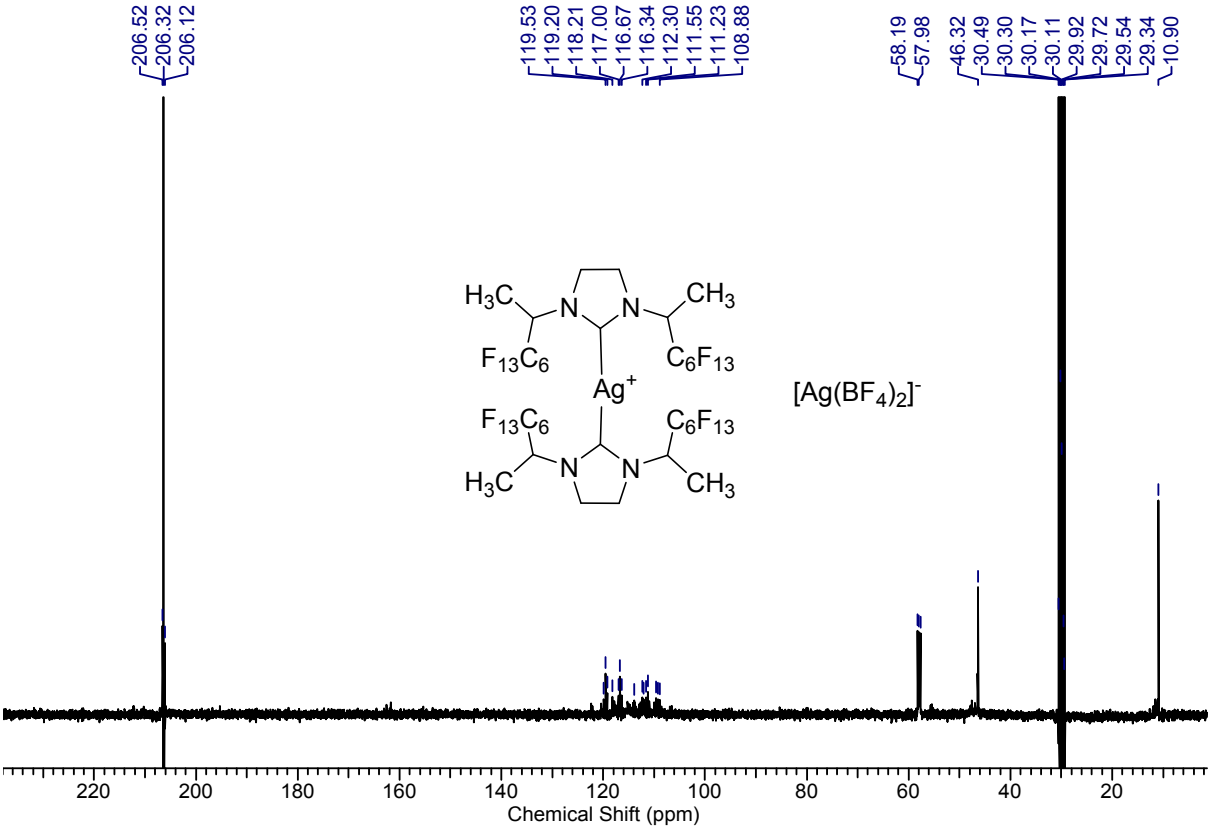


Figure S46. ^{13}C NMR spectrum, 75.44 MHz, acetone-d_6, bis[1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-trideca-fluorooctan-2-yl)imidazolidin-2-ylidene]silver(I) bis(tetrafluoroborato)argentate (**23**).

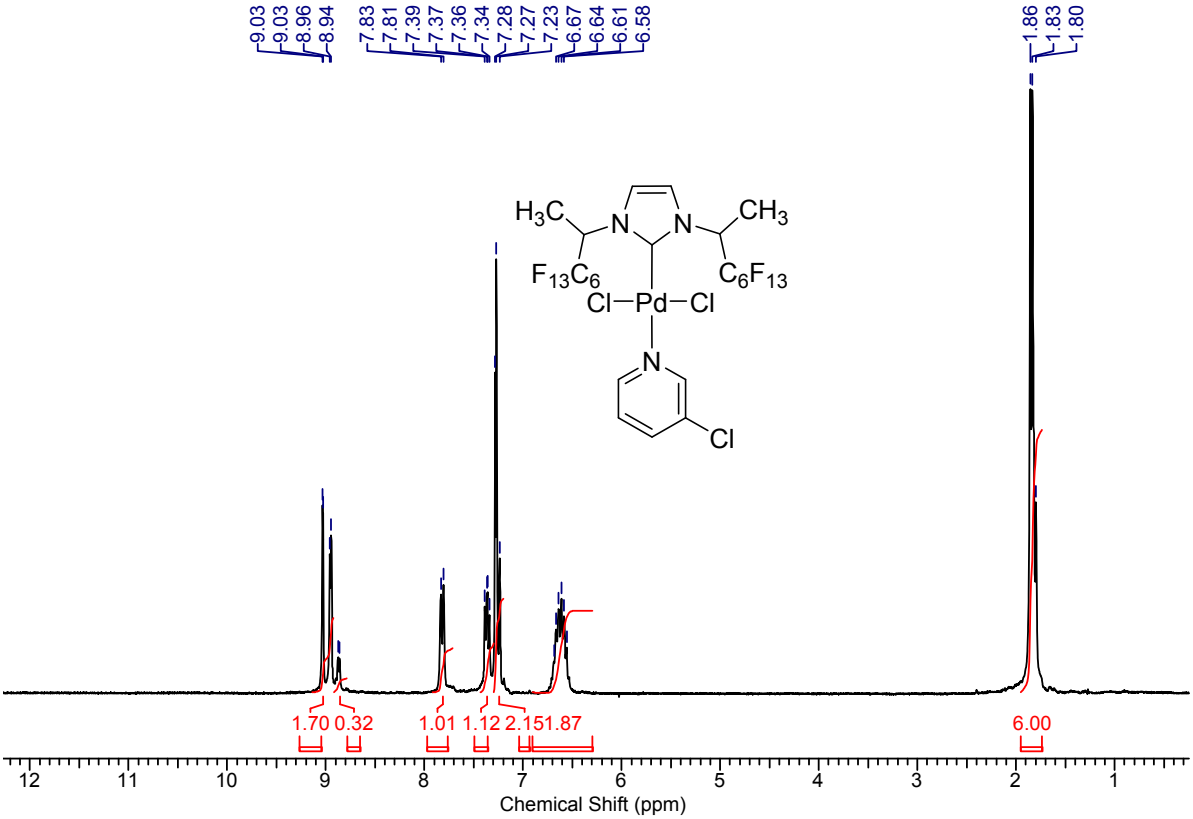


Figure S47. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, [1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-1,3-dihydroimidazol-2-ylidene](dichloro)(3-chloropyridine)palladium(II) (**24**).

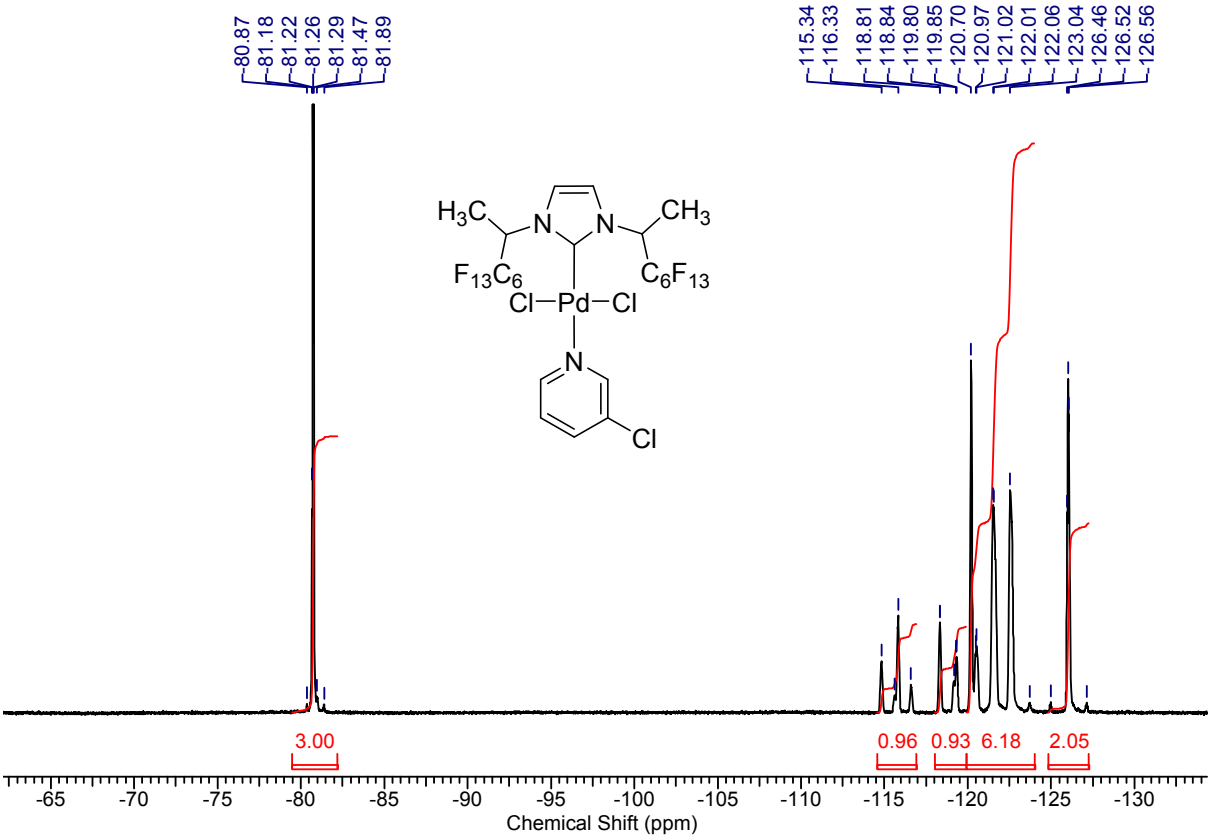


Figure S48. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, [1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-1,3-dihydroimidazol-2-ylidene](dichloro)(3-chloropyridine)palladium(II) (**24**).

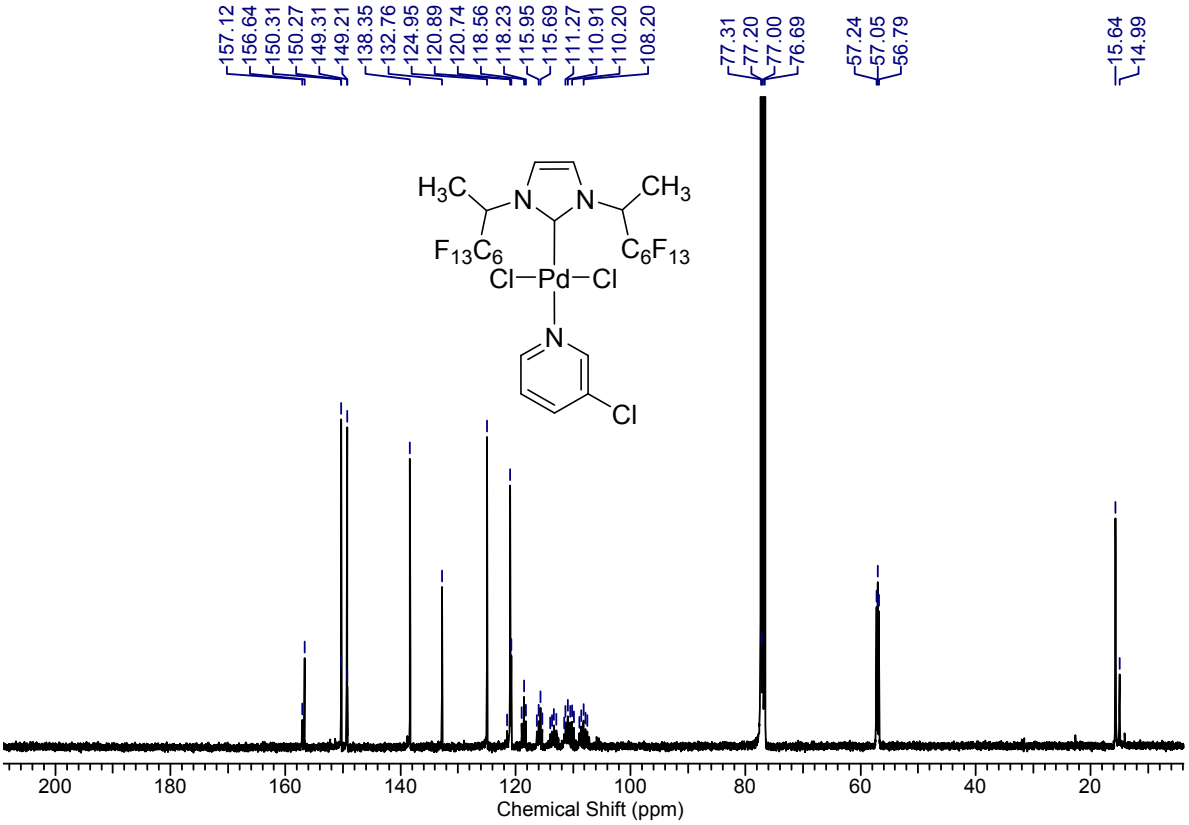


Figure S49. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, [1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-1,3-dihydroimidazol-2-ylidene](dichloro)(3-chloropyridine)palladium(II) (**24**).

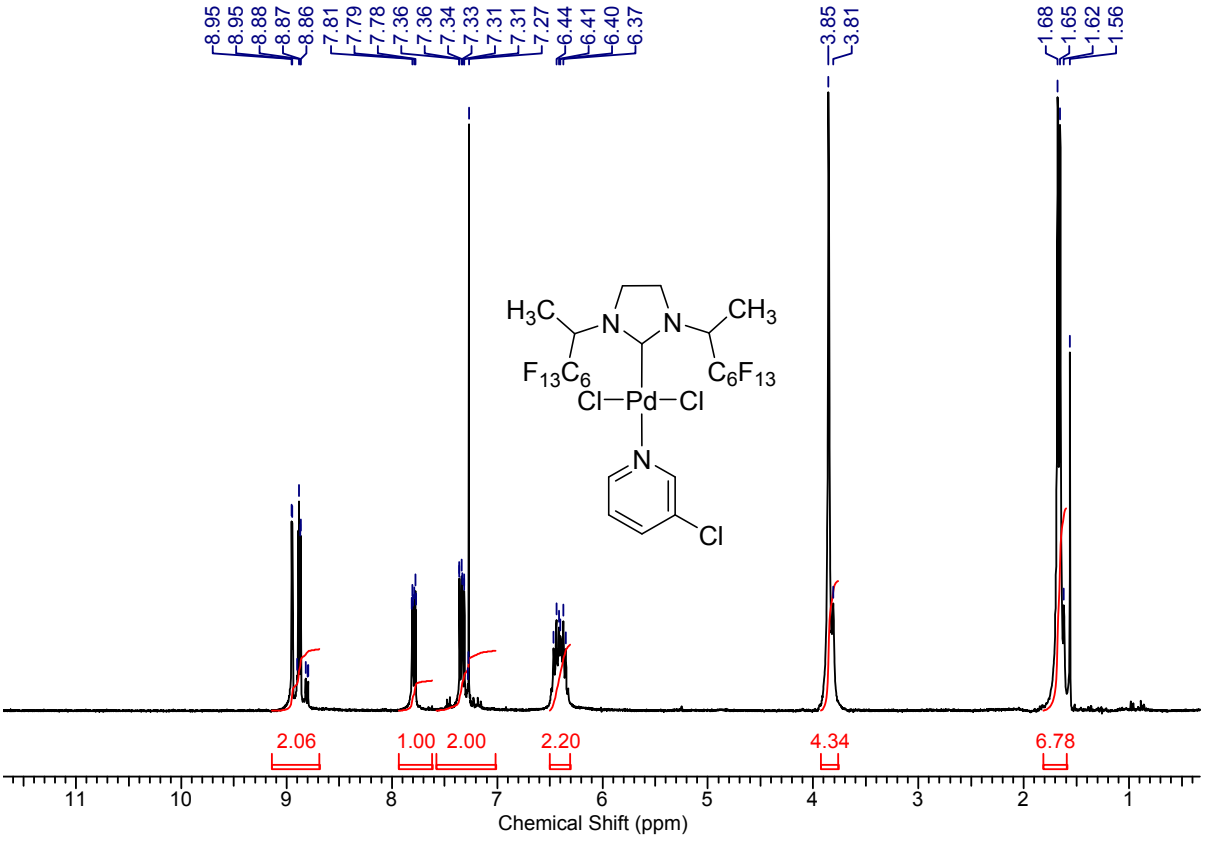


Figure S50. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, [1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)imidazolidin-2-ylidene](dichloro)(3-chloropyridine)palladium(II) (**25**).

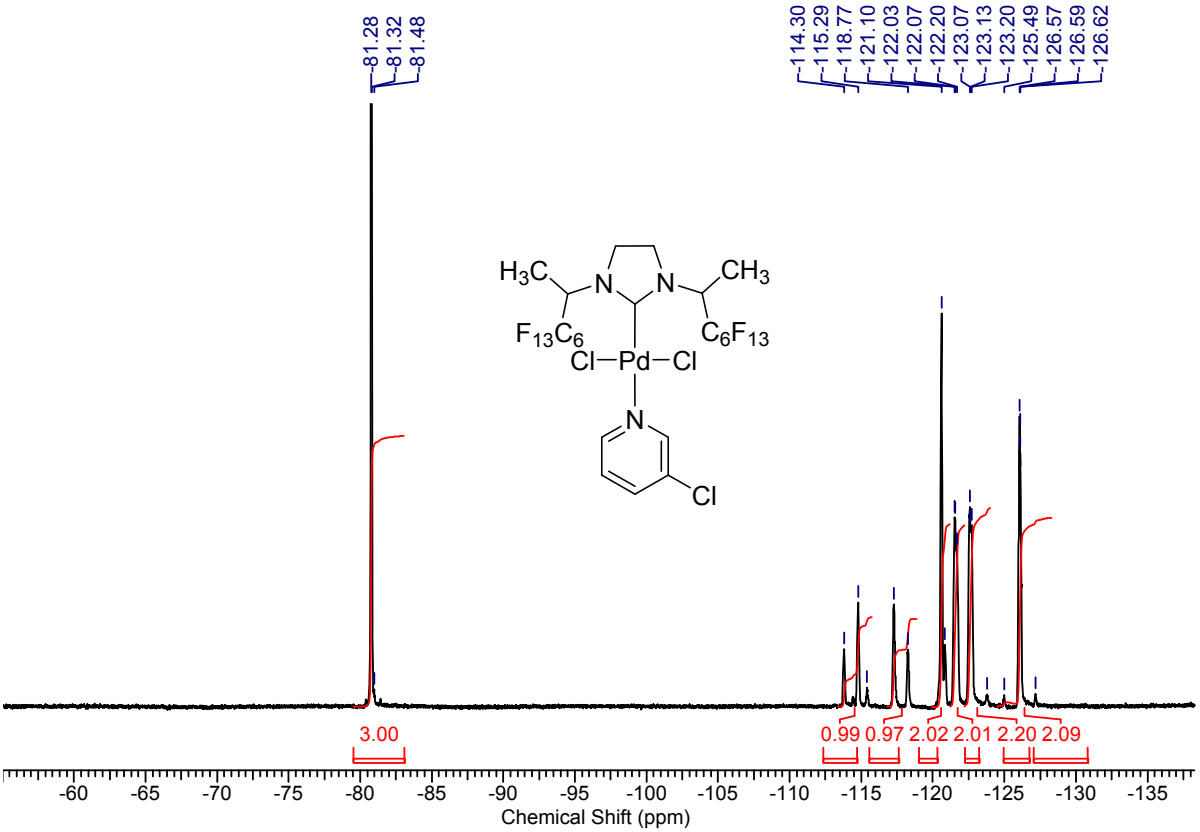


Figure S51. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, [1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)imidazolidin-2-ylidene](dichloro)(3-chloropyridine)palladium(II) (**25**).

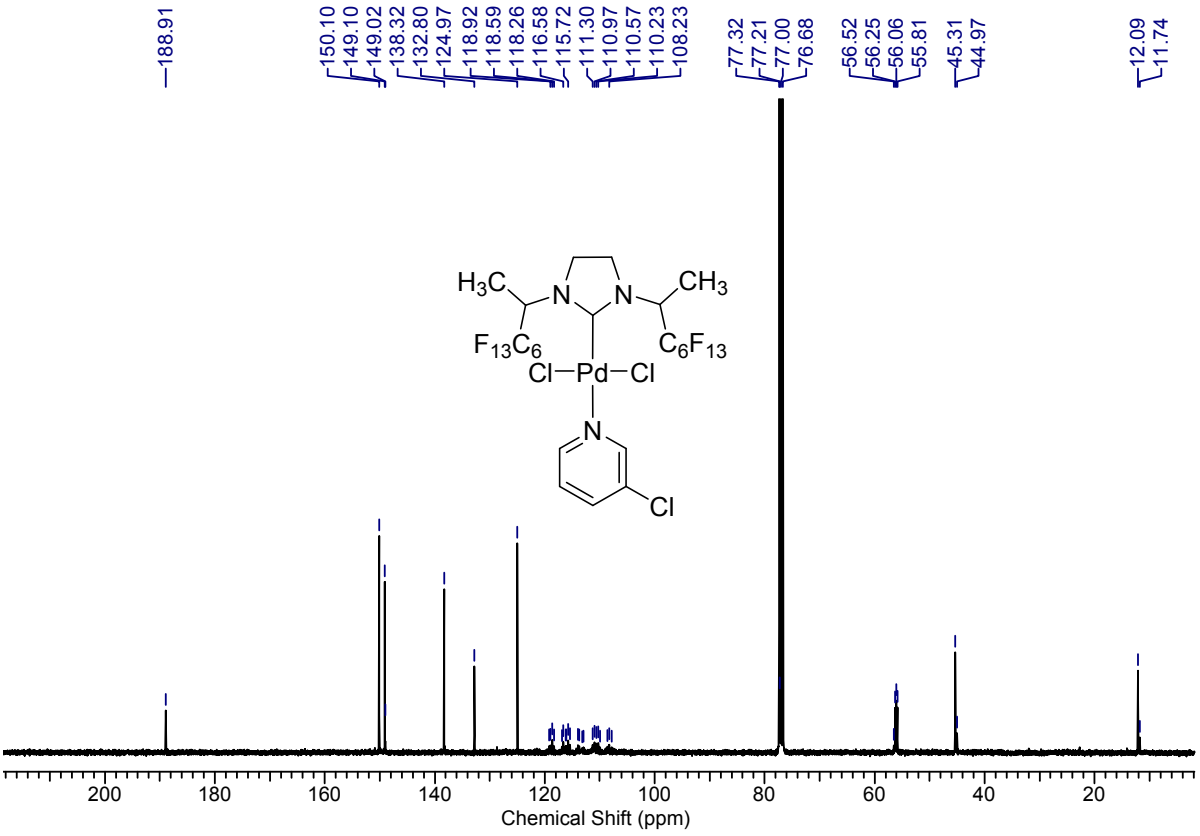


Figure S52. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, [1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)imidazolidin-2-ylidene](dichloro)(3-chloropyridine)palladium(II) (**25**).

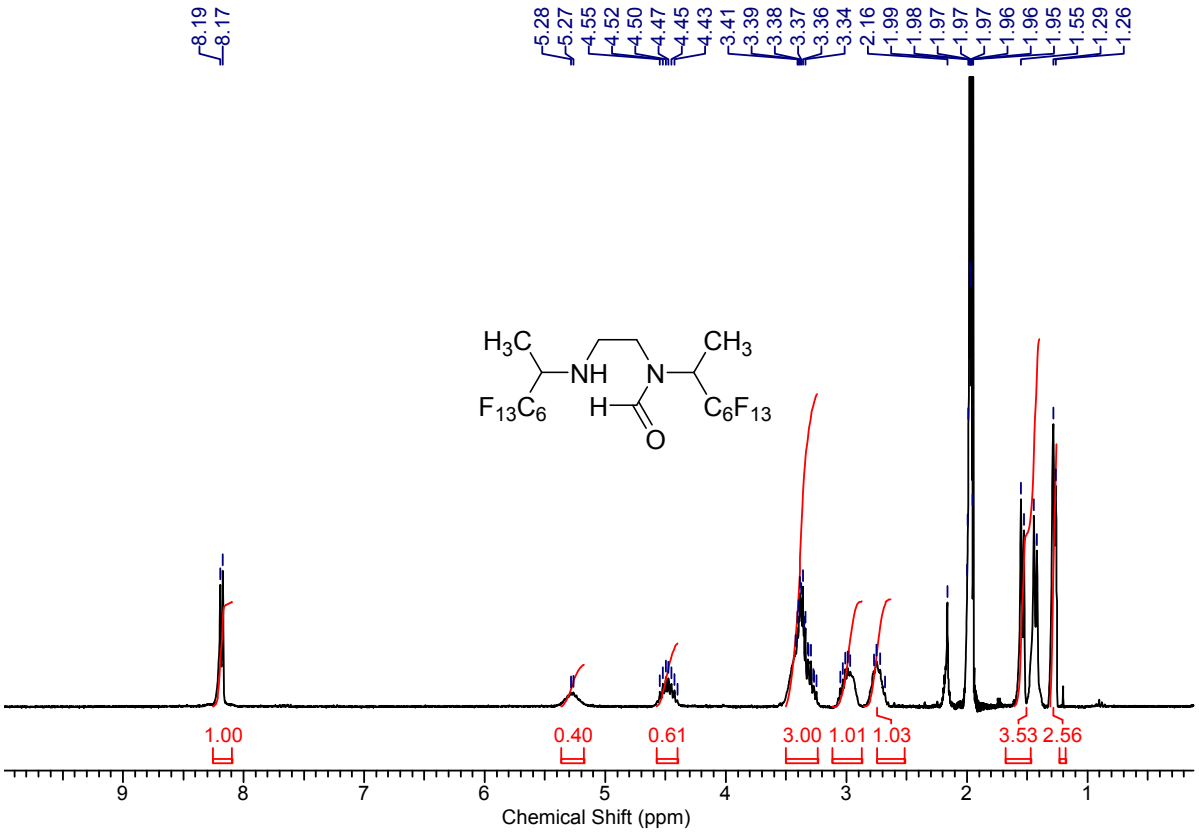


Figure S53. ^{1}H NMR spectrum, 299.97 MHz, CD_3CN, *N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-yl)-*N*-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-yl)ethyl]formamide (**26**).

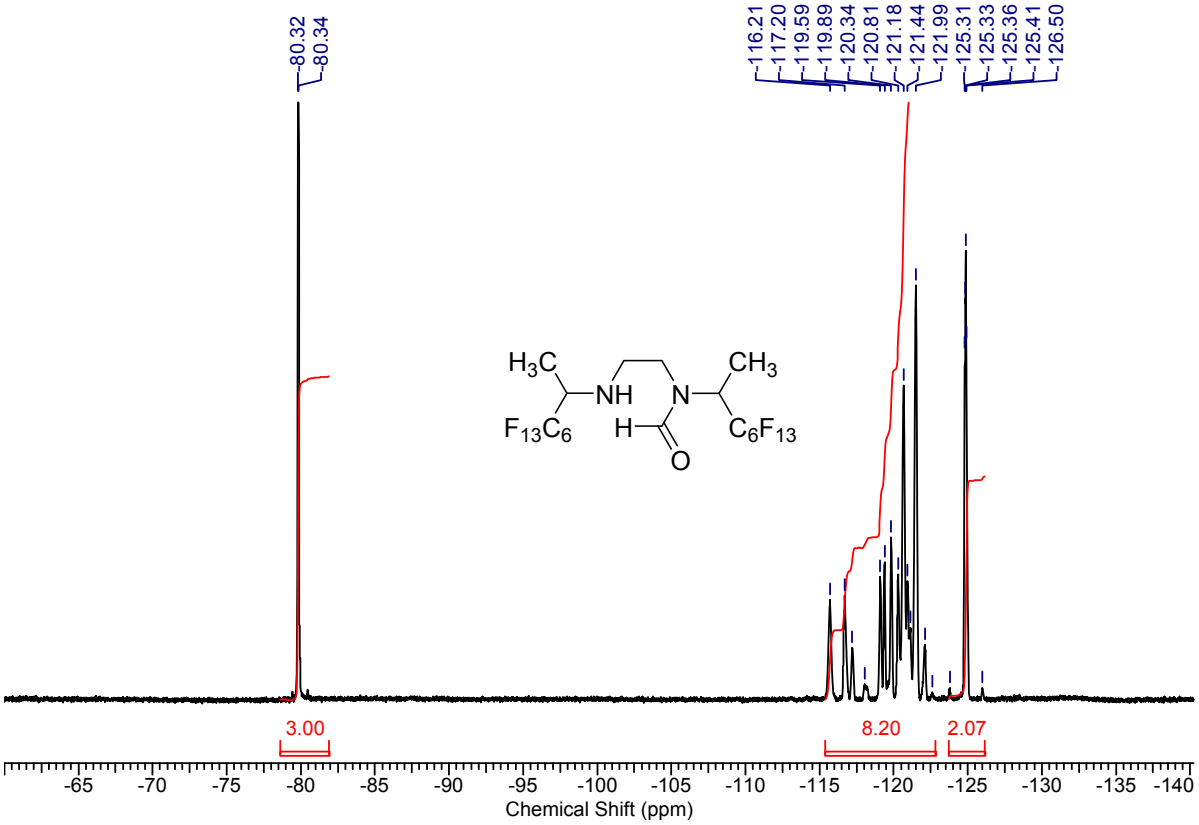


Figure S54. ^{19}F NMR spectrum, 282,23 MHz, CD_3CN, *N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-yl)-*N*-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-yl)ethyl]formamide (**26**).

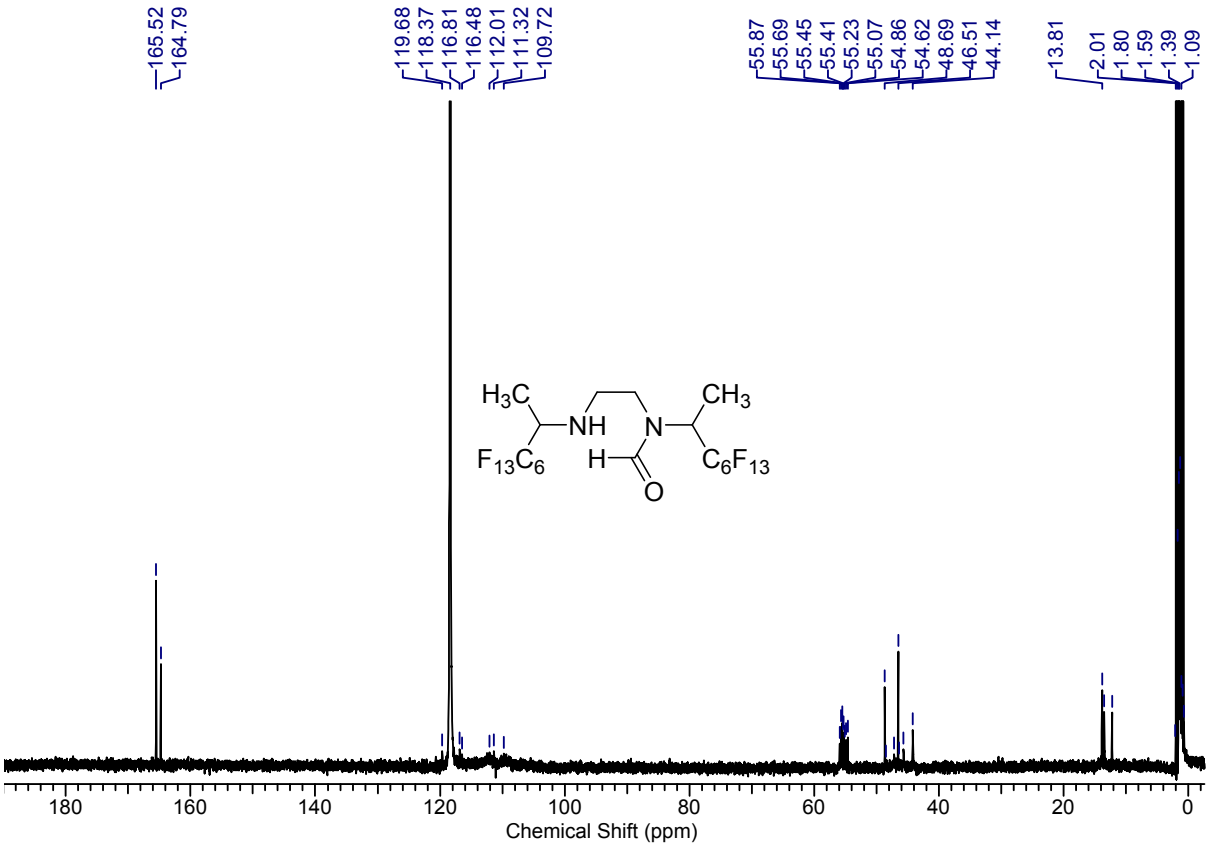


Figure S55. ^{13}C NMR spectrum, 75.44 MHz, CD_3CN, *N*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-yl)-*N*-[2-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-2-yl)ethyl]formamide (**26**).

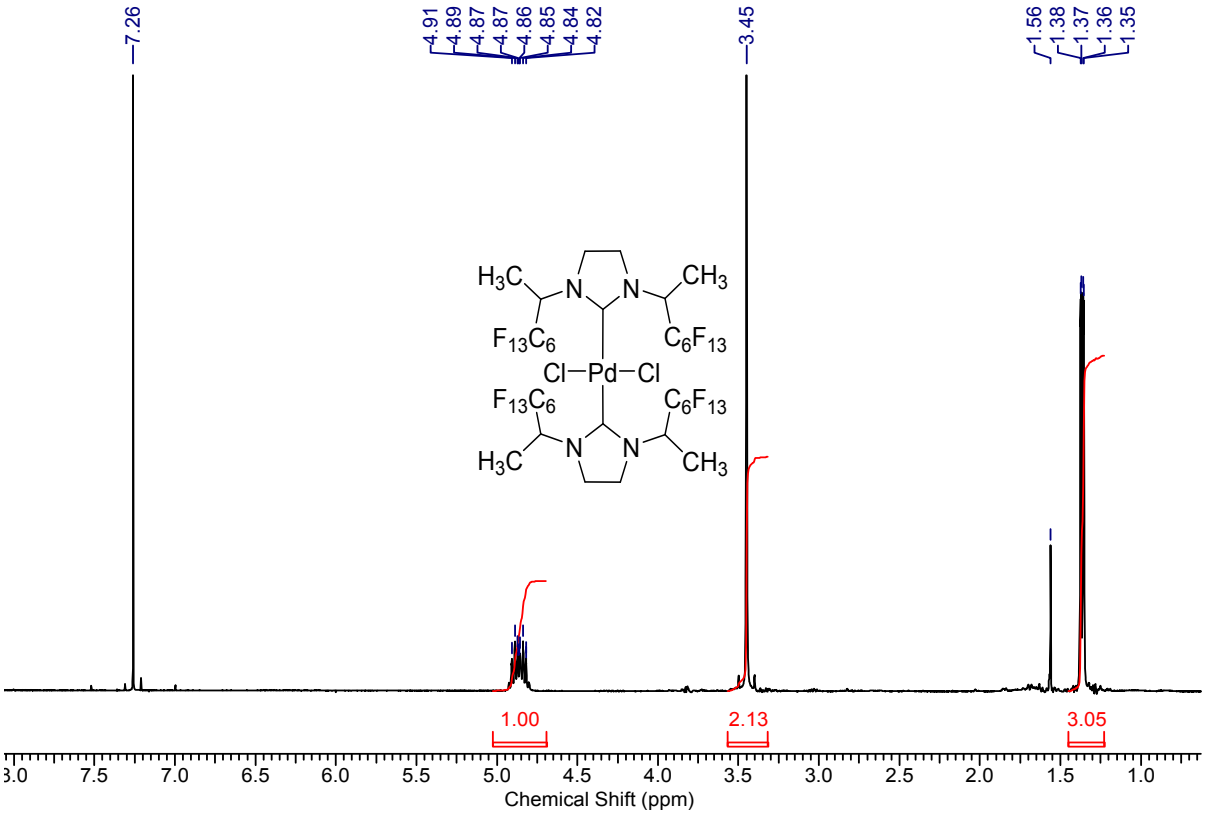


Figure S56. ^{1}H NMR spectrum, 299.97 MHz, $CDCl_3$, bis[1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-imidazolidin-2-ylidene]dichloropalladium (**27**).

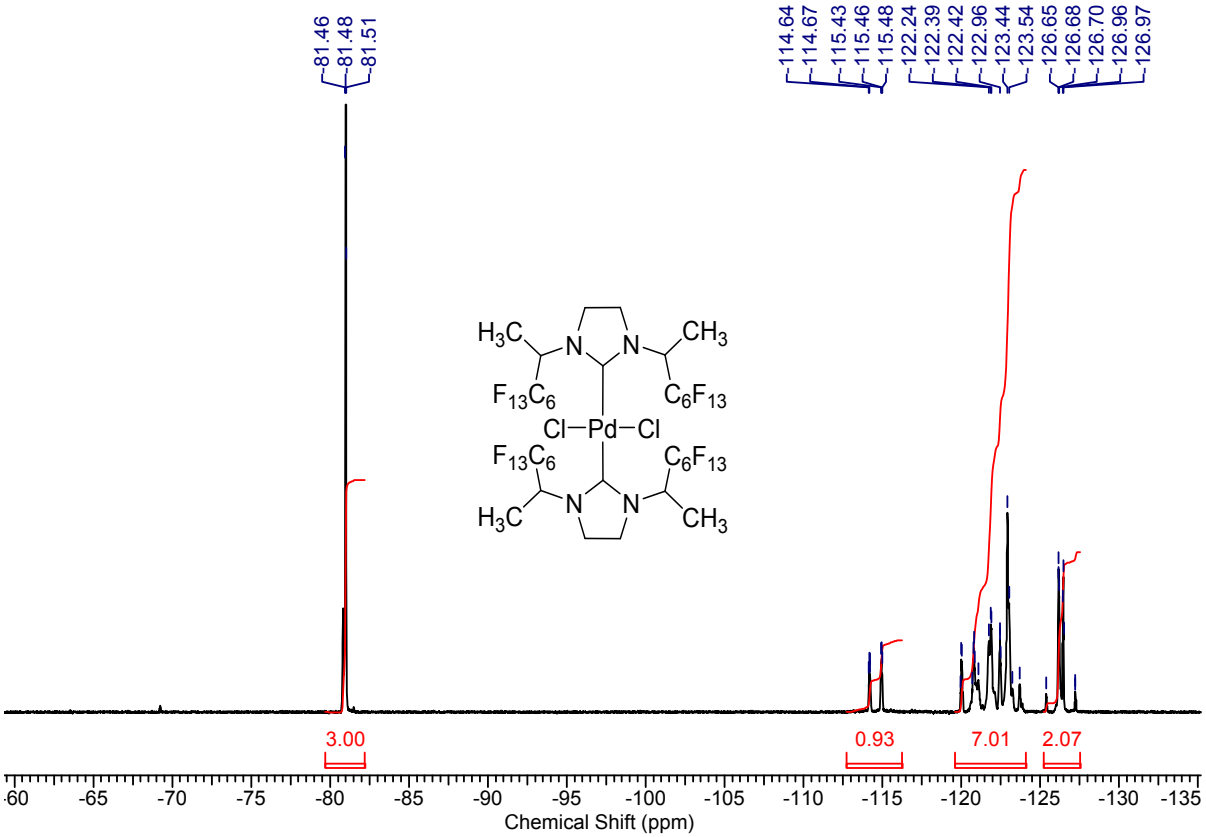


Figure S57. ^{19}F NMR spectrum, 282.23 MHz, $CDCl_3$, bis[1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-imidazolidin-2-ylidene]dichloropalladium (**27**).

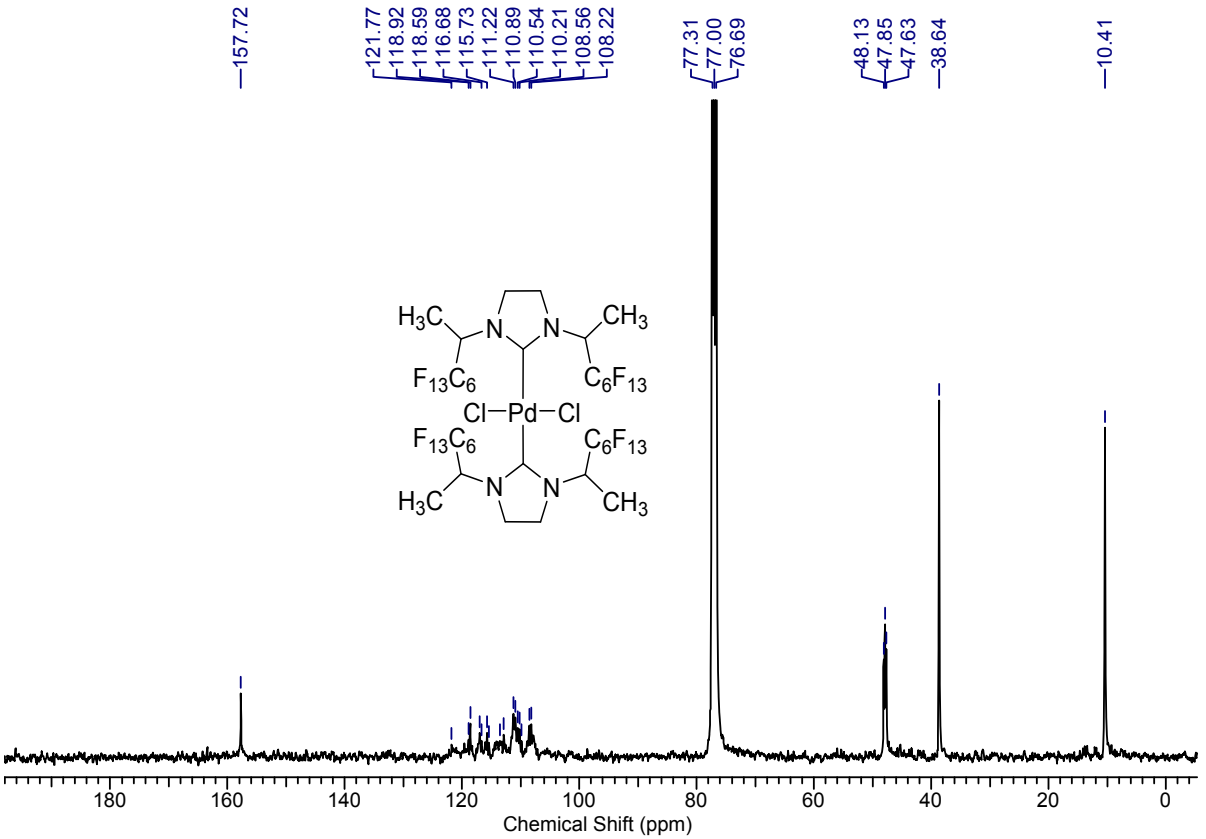


Figure S58. ^{13}C NMR spectrum, 75.44 MHz, $CDCl_3$, bis[1,3-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octan-2-yl)-imidazolidin-2-ylidene]dichloropalladium (**27**).