Electronic Supplementary Material (ESI) for Dalton Transactions.

Pyridinium-Phosphonium Dications: Highly Electrophilic Phosphorus-based Lewis Acid Catalysts

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Supporting Information

This PDF file includes:

1. Spectroscopic Data (in some instances pentane impurities arise from trace contamination of the NMR solvent)

1.1 NMR Spectra of (*o*-NC_5H_4)PF_2Ph_2 (1).

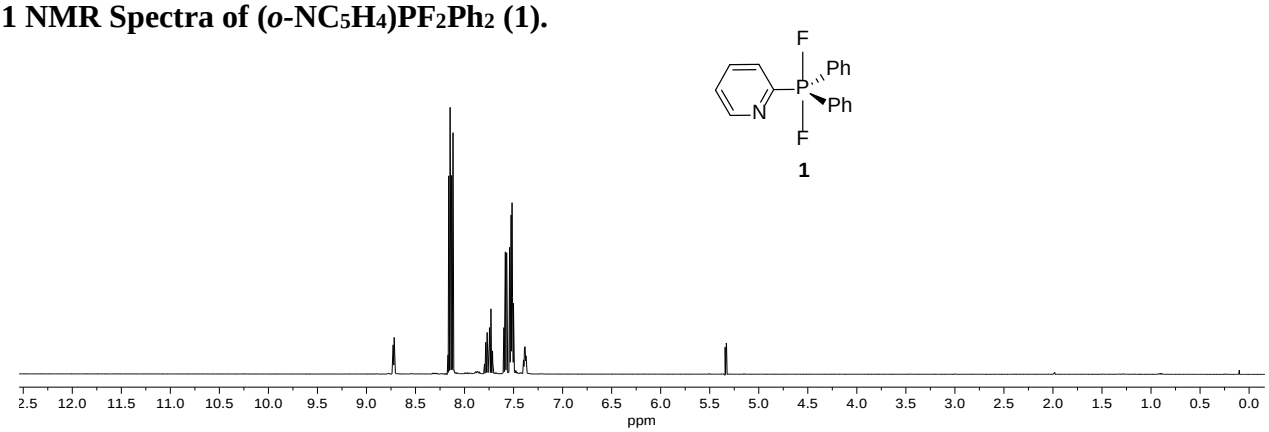


Figure S1. ^{1}H NMR spectrum (CD_2Cl_2) of (*o*-NC_5H_4)PF_2Ph_2 (**1**).

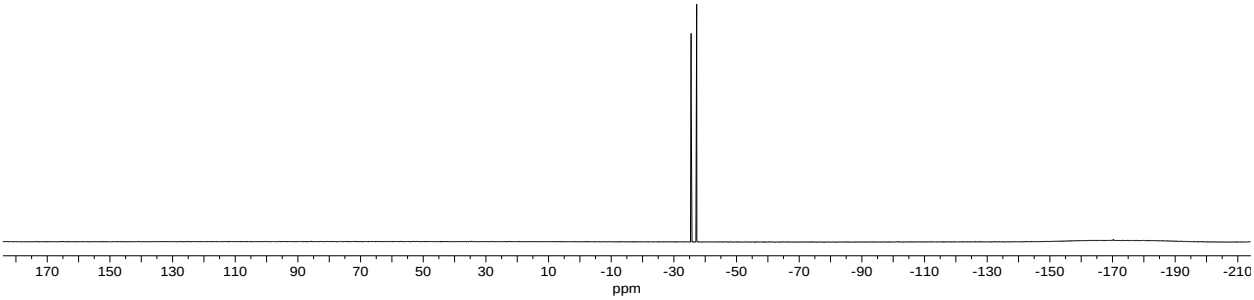


Figure S2. ^{19}F NMR spectrum (CD_2Cl_2) of (*o*-NC_5H_4)PF_2Ph_2 (**1**).

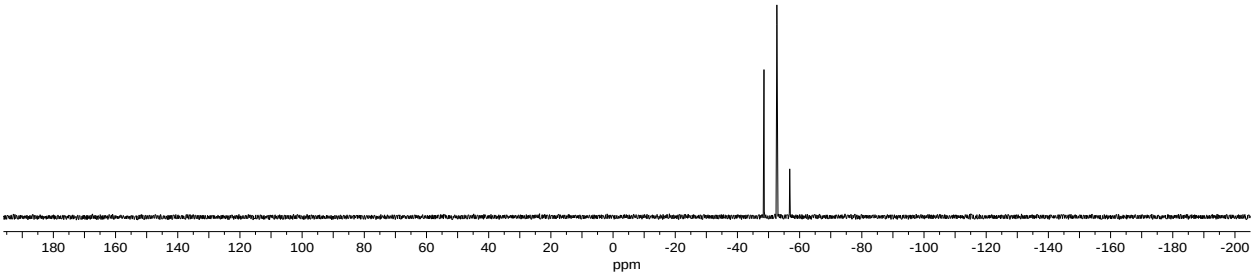


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of (*o*-NC_5H_4)PF_2Ph_2 (**1**).

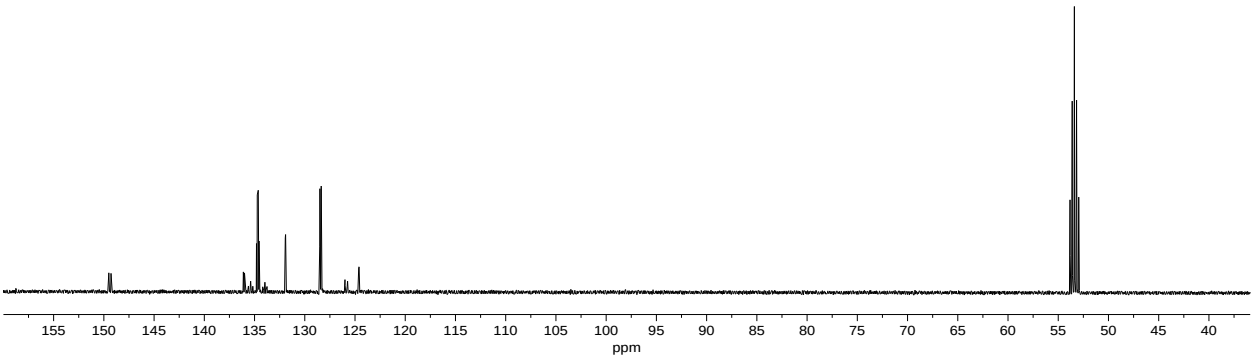
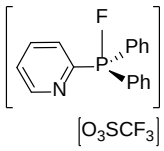


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of (o-NC_5H_4)PF_2Ph_2 (**1**).

1.2 NMR Spectra of [(o-NC_5H_4)$PFPh_2$][O_3SCF_3] (2a).



2a

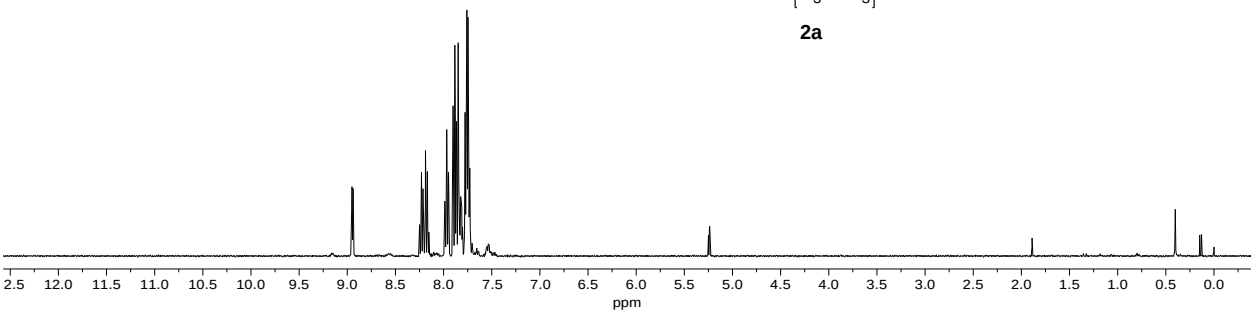


Figure S5. ^{1}H NMR spectrum (CD_2Cl_2) of [(o-NC_5H_4)$PFPh_2$][O_3SCF_3] (**2a**).

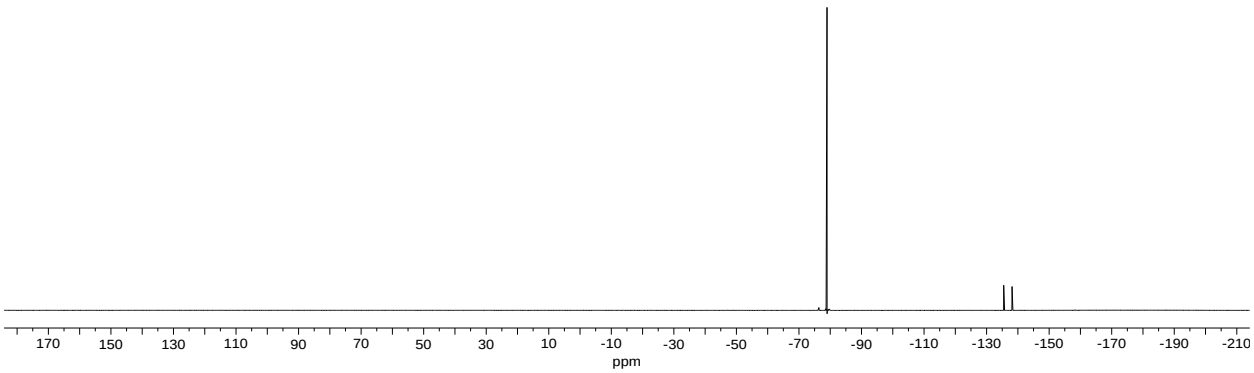


Figure S6. ^{19}F NMR spectrum (CD_2Cl_2) of [(o-NC_5H_4)$PFPh_2$][O_3SCF_3] (**2a**).

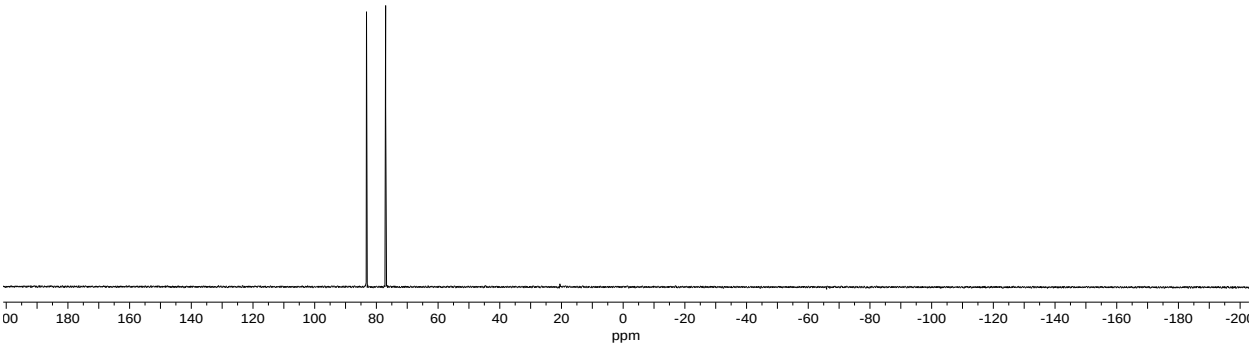


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-NC_5H_4)$PFPh_2$][O_3SCF_3] (**2a**).

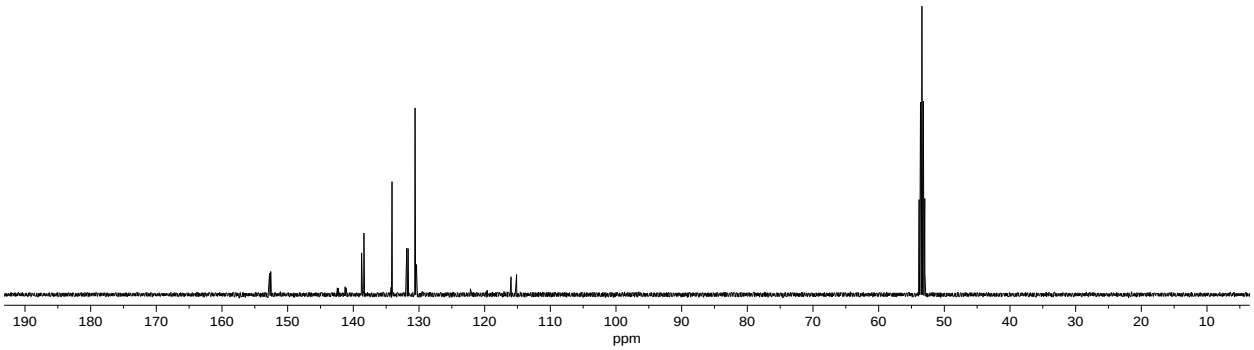
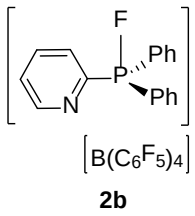


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-NC_5H_4)$PFPh_2$][O_3SCF_3] (**2a**).

1.3 NMR Spectra of [(*o*-NC_5H_4)$PFPh_2$][$B(C_6F_5)_4$] (2b).



2b

Figure S9. ^{1}H NMR spectrum (C_6D_5Br) of [(*o*-NC_5H_4)$PFPh_2$][$B(C_6F_5)_4$] (**2b**).

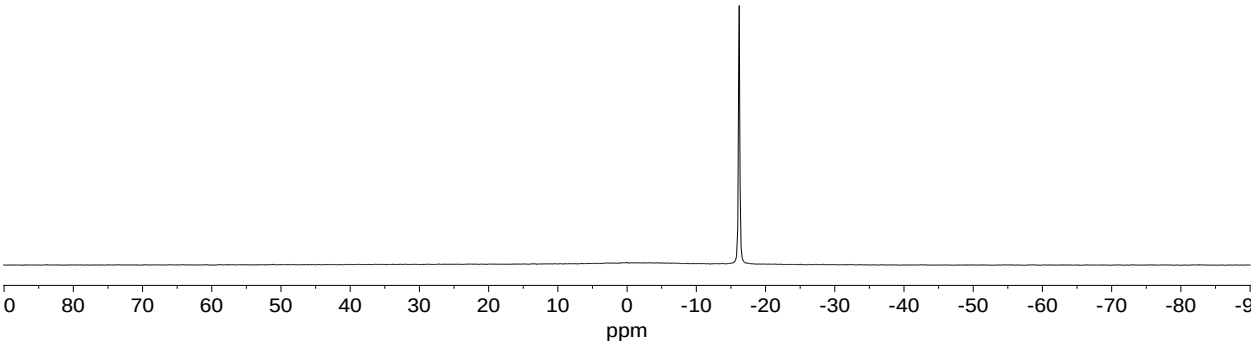


Figure S10. $^{11}B\{^{1}H\}$ NMR spectrum (C_6D_5Br) of [(*o*-NC_5H_4)$PFPh_2$][$B(C_6F_5)_4$] (**2b**).

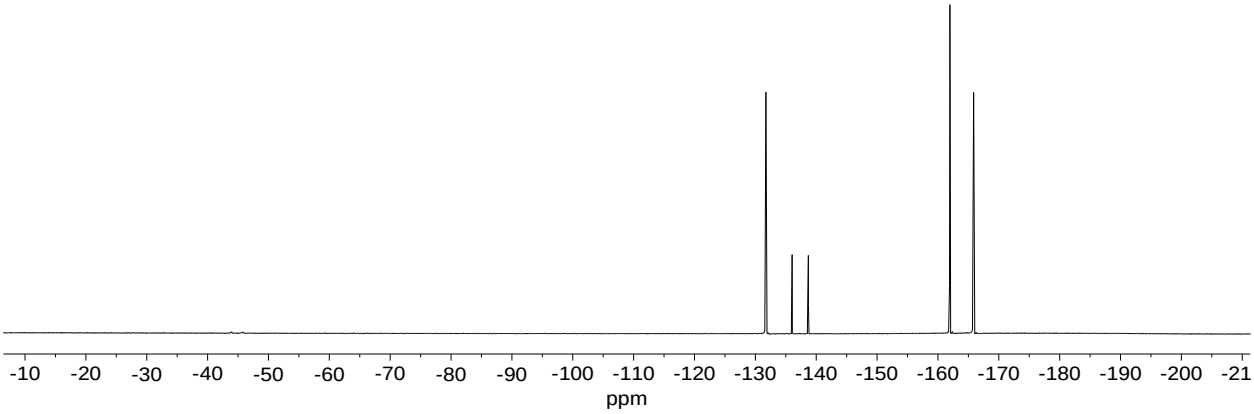


Figure S11. ^{19}F NMR spectrum (C_6D_5Br) of [(*o*-NC_5H_4)$PFPh_2$][$B(C_6F_5)_4$] (**2b**).

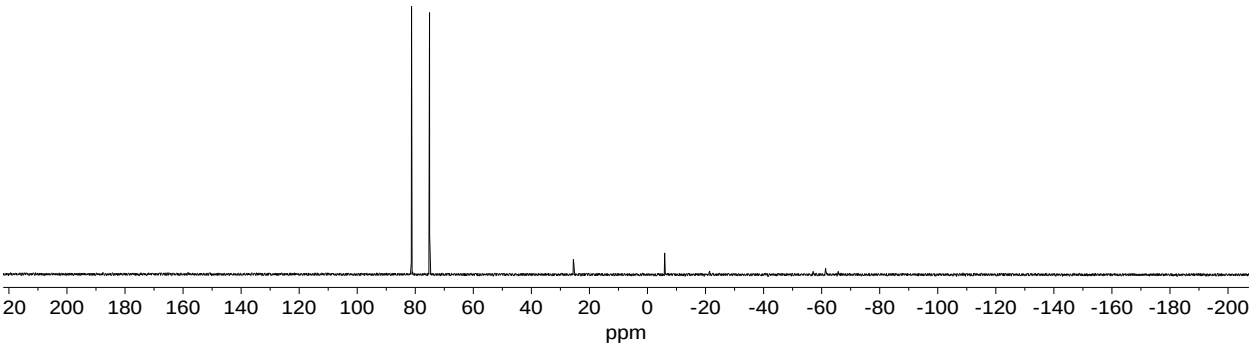


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_5Br) of [(*o*-NC_5H_4)$PFPh_2$][$B(C_6F_5)_4$] (**2b**).

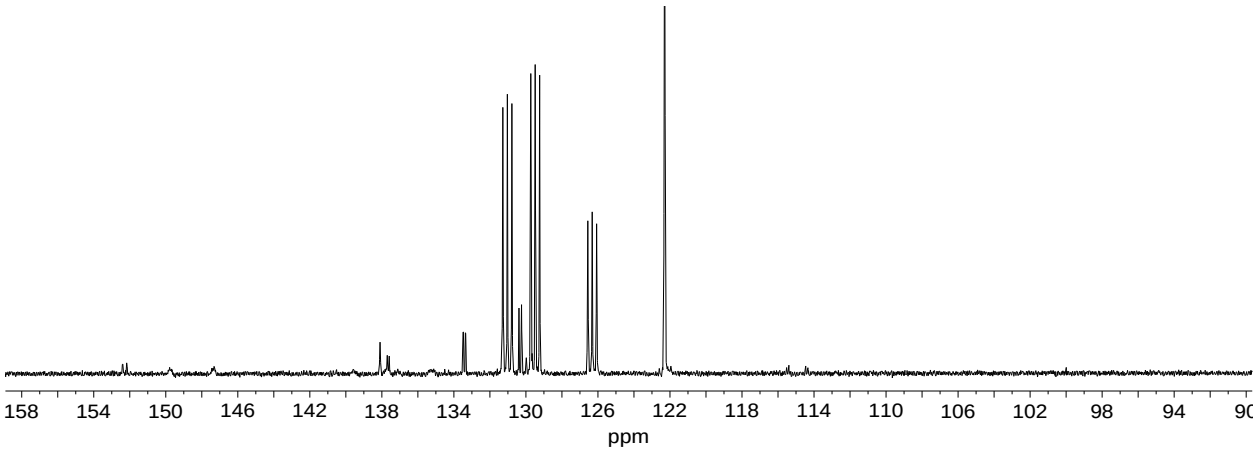


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_5Br) of [(*o*-NC_5H_4\)$PFPh_2$][$B(C_6F_5)_4$] (**2b**).

1.4 Reaction of 2b with one equivalent of Et_3SiH

Triethyl silane (Et_3SiH, 5.5 µL, 0.03 mmol, 1.0 eq.) was added to a solution of **2b** (31.5 mg, 0.03 mmol, 1.0 eq.) in CD_2Cl_2 (0.6 mL). The reaction mixture was left at ambient temperature for 3 h and then monitored with multi-nuclear NMR spectroscopy. The reaction mixture was transferred to a vial and the solvent/volatiles were removed *in vacuo* to remove the triethylsilylfluoride (Et_3SiF) side product.

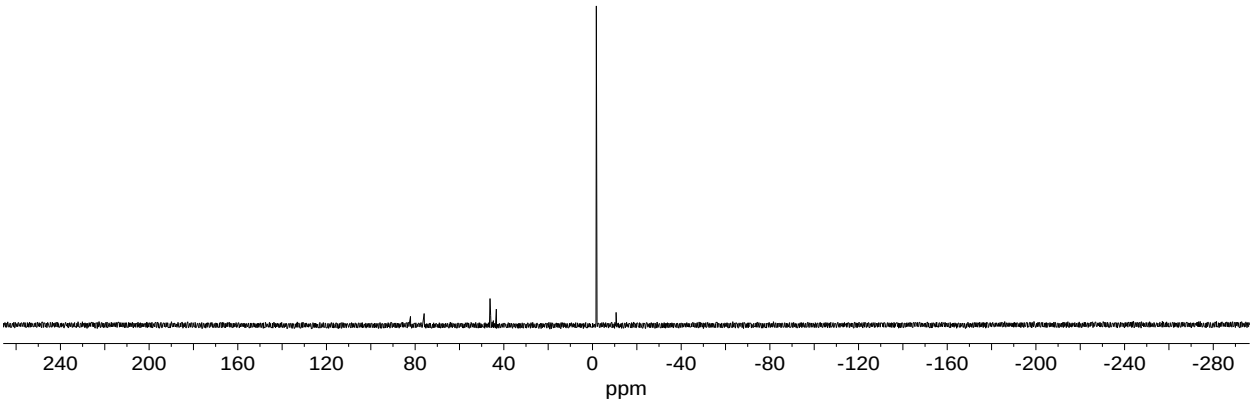


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of the crude reaction mixture.

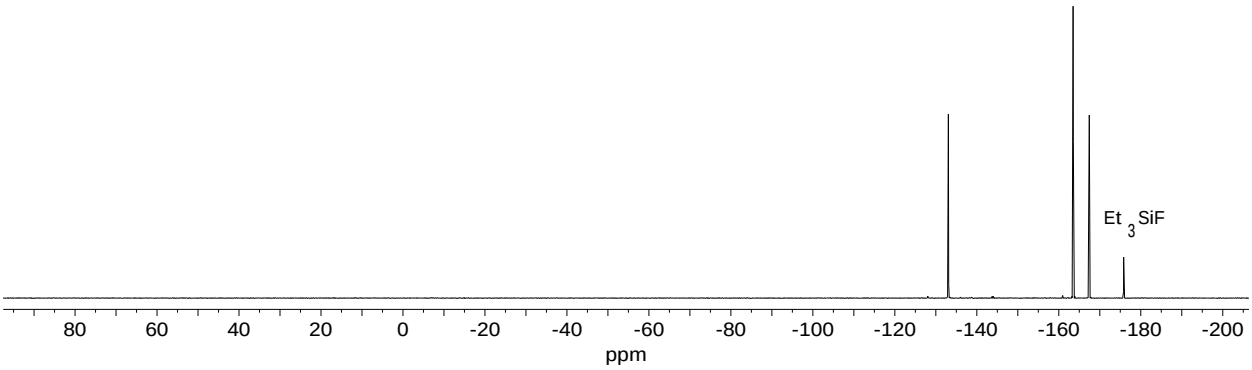


Figure S15. ^{19}F NMR spectrum (CD_2Cl_2) of the crude reaction mixture.

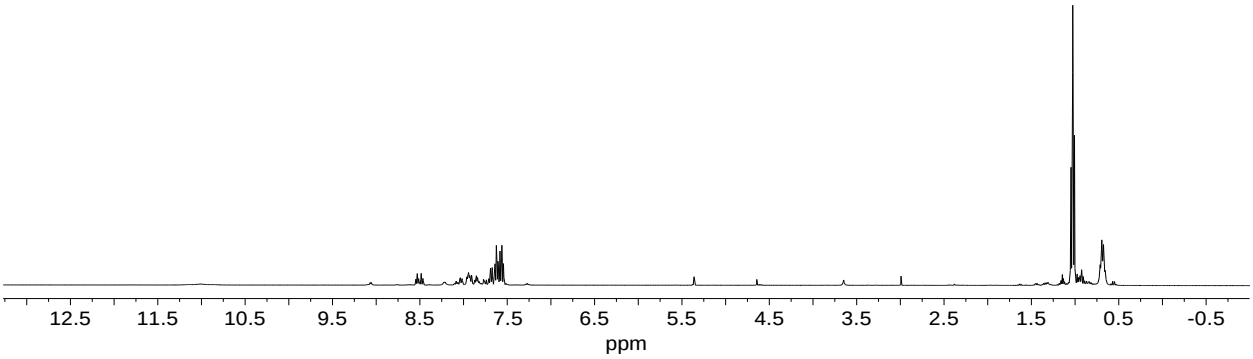


Figure S16. ^{1}H NMR spectrum (CD_2Cl_2) of the crude reaction mixture.

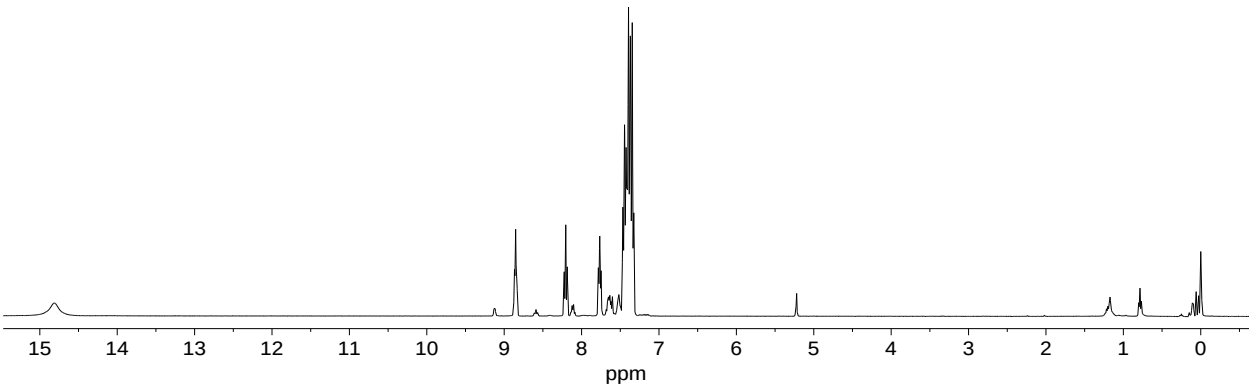


Figure S17. ^{1}H NMR spectrum(CD_2Cl_2) of the product after drying *in vacuo*.

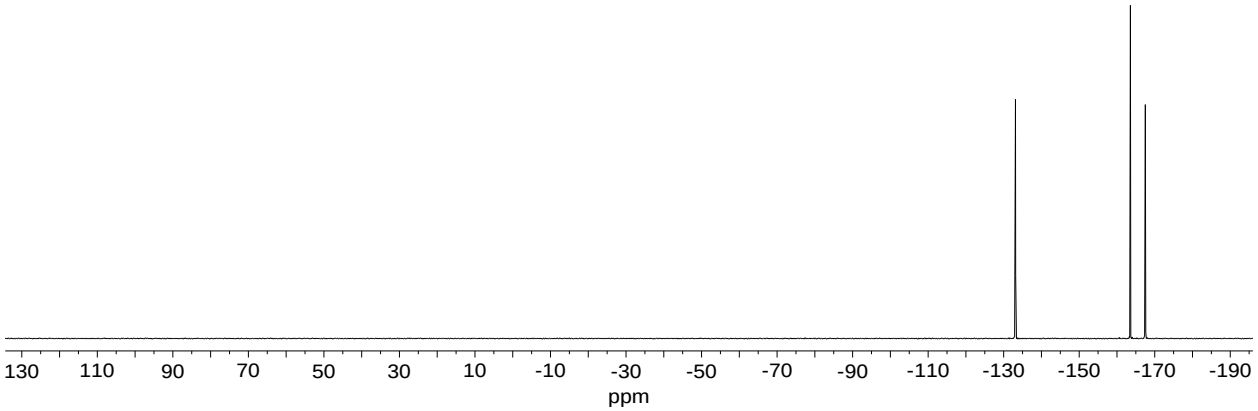
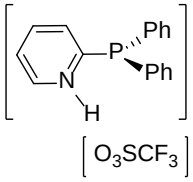


Figure S18. ^{19}F NMR spectrum (CD_2Cl_2) of the product after drying *in vacuo*.

1.5 NMR Spectra of [(*o*-HNC_5H_4)PPh_2][O_3SCF_3].



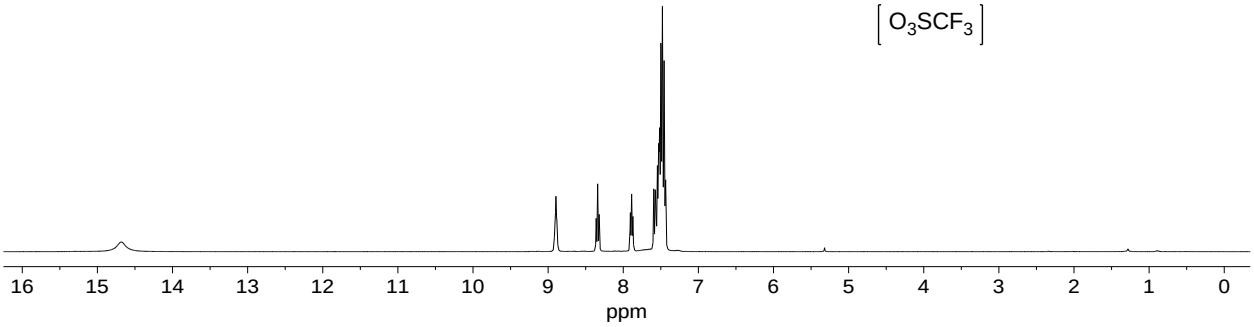


Figure S19. ^{1}H NMR spectrum (CD_2Cl_2) of [(*o*-HNC_5H_4)PPh_2][O_3SCF_3].

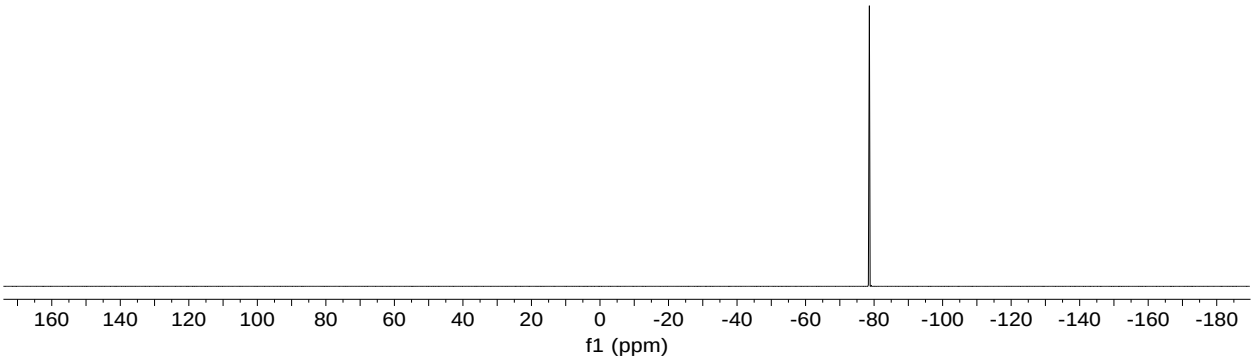


Figure S20. ^{19}F NMR spectrum (CD_2Cl_2) of [(*o*-HNC_5H_4)PPh_2][O_3SCF_3].

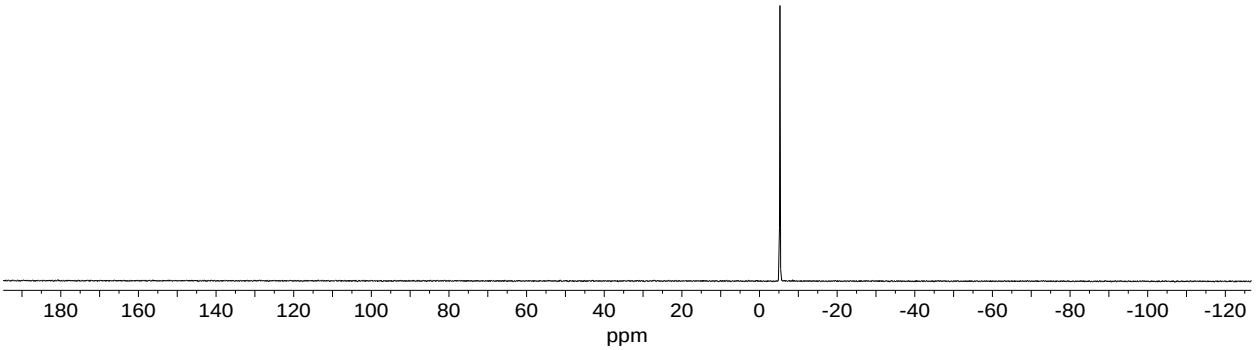


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-HNC_5H_4)PPh_2][O_3SCF_3].

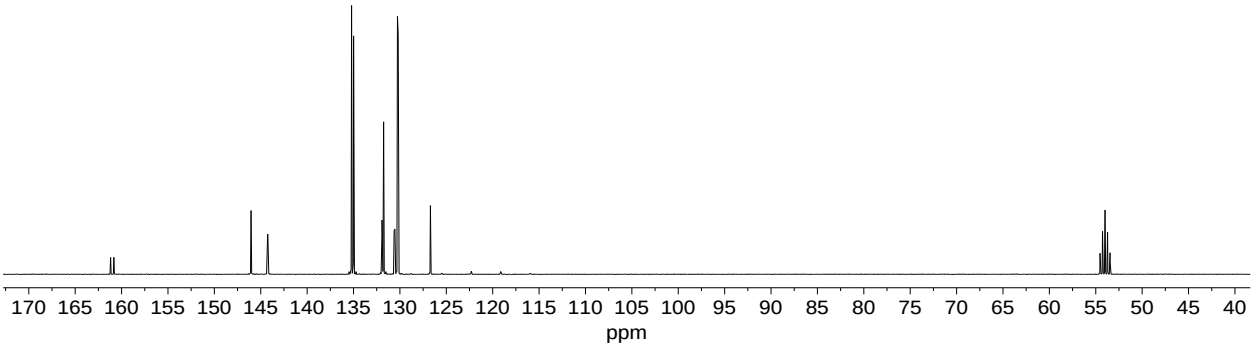
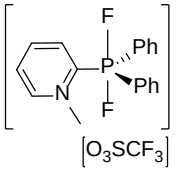


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-HNC_5H_4)PPh_2][O_3SCF_3].

1.6 NMR Spectra of [(*o*-$MeNC_5H_4$)PF_2Ph_2][O_3SCF_3] (3).



3

Figure S23. ^{1}H NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)PF_2Ph_2][O_3SCF_3] (**3**).

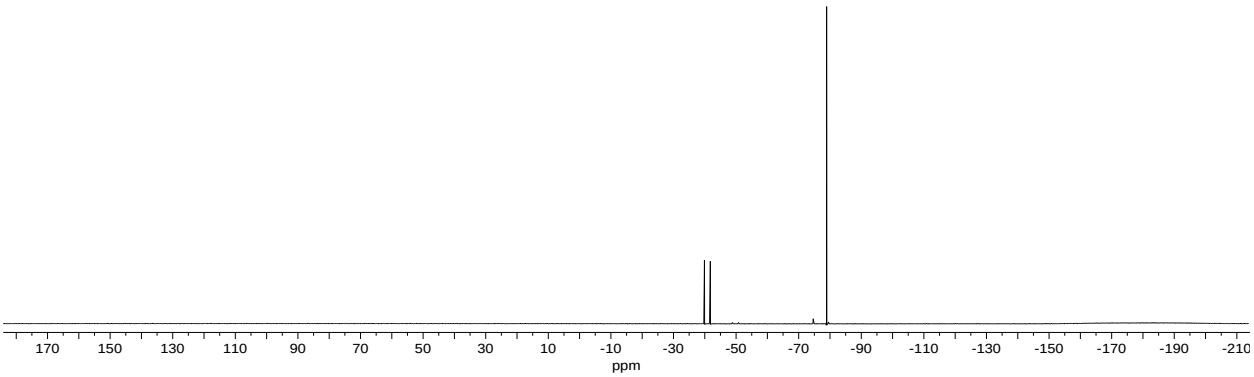


Figure S24. ^{19}F NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)PF_2Ph_2][O_3SCF_3] (**3**).

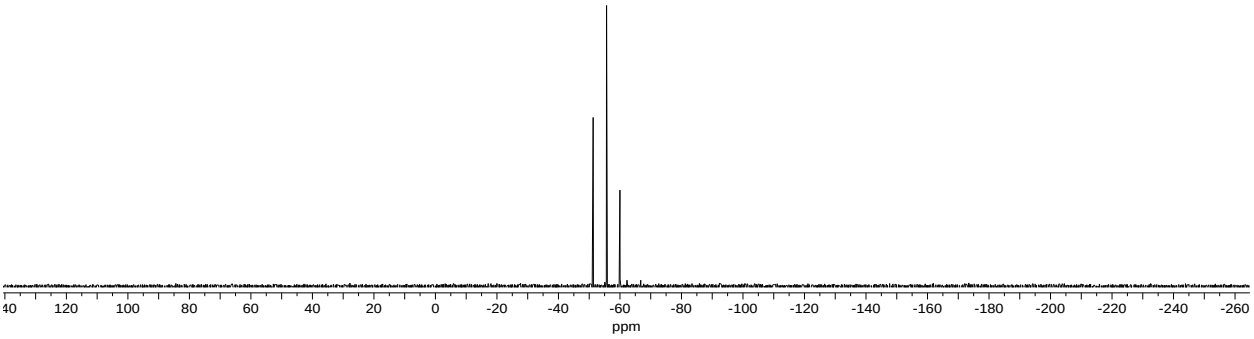


Figure S25. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)PF_2Ph_2][O_3SCF_3] (**3**).

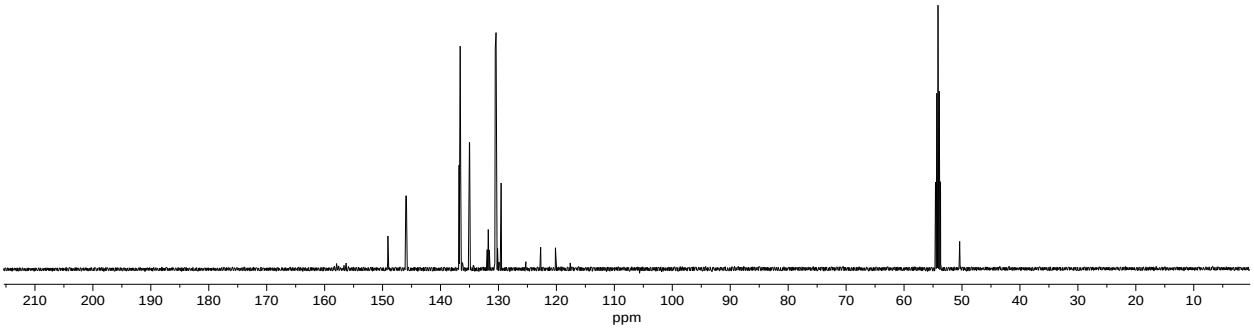
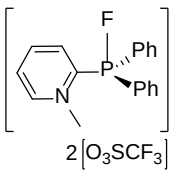


Figure S26. $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)PF_2Ph_2][O_3SCF_3] (**3**).

1.7 NMR Spectra of [(*o*-$MeNC_5H_4$)$PFPh_2$][O_3SCF_3]$_2$ (4a).



4a

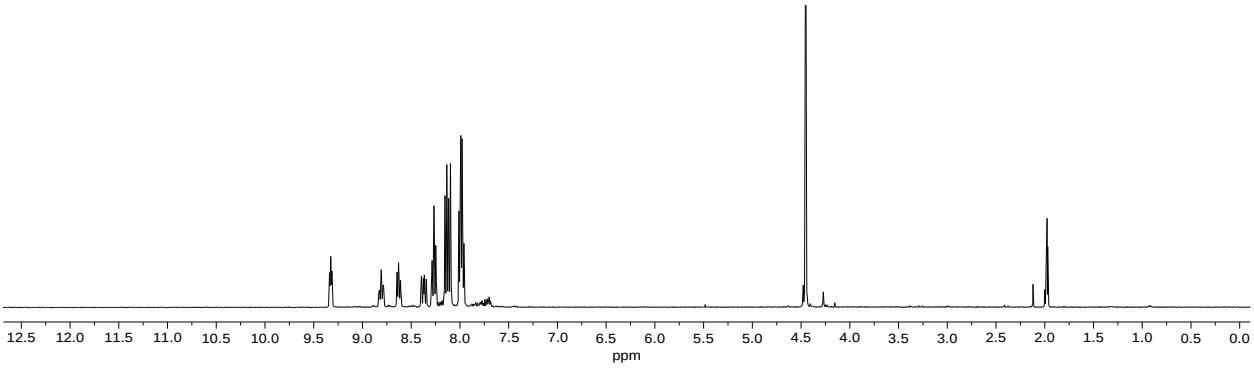


Figure S27. ^{1}H NMR spectrum (CD_3CN) of [(*o*-$MeNC_5H_4$)$PFPh_2$][O_3SCF_3]$_2$ (**4a**).

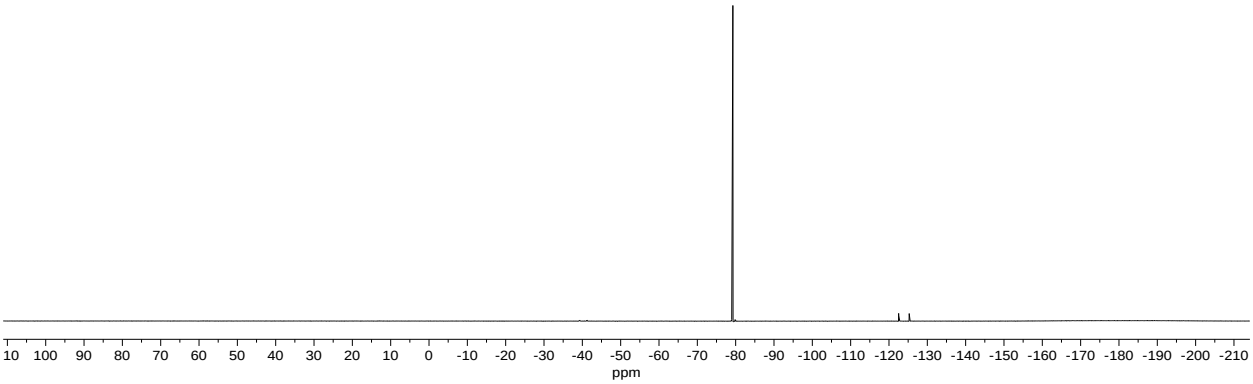


Figure S28. ^{19}F NMR spectrum (CD_3CN) of [(*o*-$MeNC_5H_4$)$PFPh_2$][O_3SCF_3]$_2$ (**4a**).

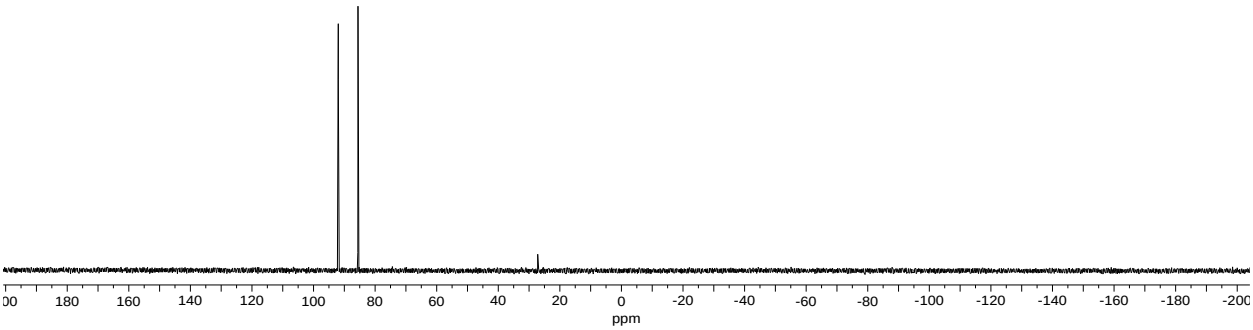


Figure S29. ^{31}P{^{1}H} NMR spectrum (CD_3CN) of [(*o*-$MeNC_5H_4$)$PFPh_2$][O_3SCF_3]$_2$ (**4a**).

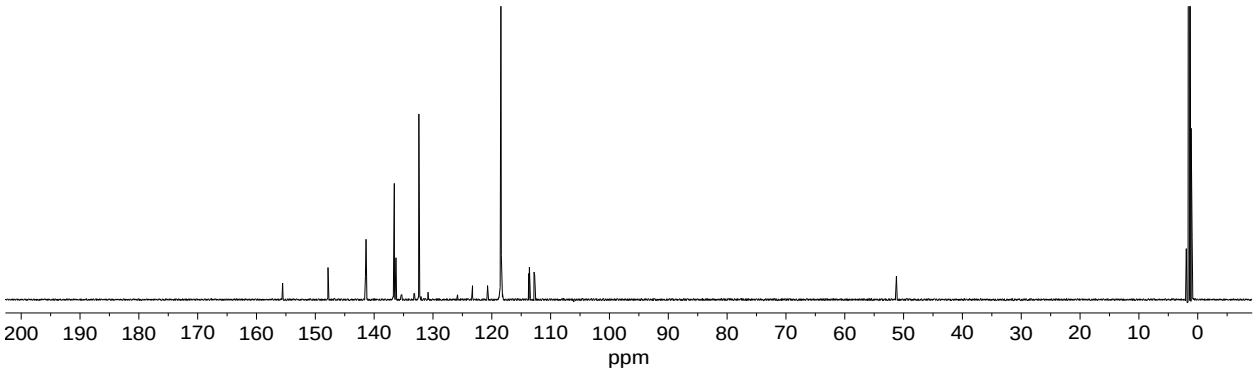
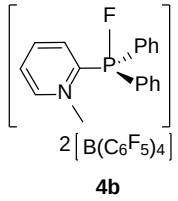


Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3CN) of $[(o\text{-}MeNC_5H_4)PFPh_2][O_3SCF_3]_2$ (**4a**).

1.8 NMR Spectra of $[(o\text{-}MeNC_5H_4)PFPh_2][B(C_6F_5)_4]_2$ (4b).



4b

Figure S31. ^{1}H NMR spectrum (CD_2Cl_2) of $[(o\text{-}MeNC_5H_4)PFPh_2][B(C_6F_5)_4]_2$ (**4b**).

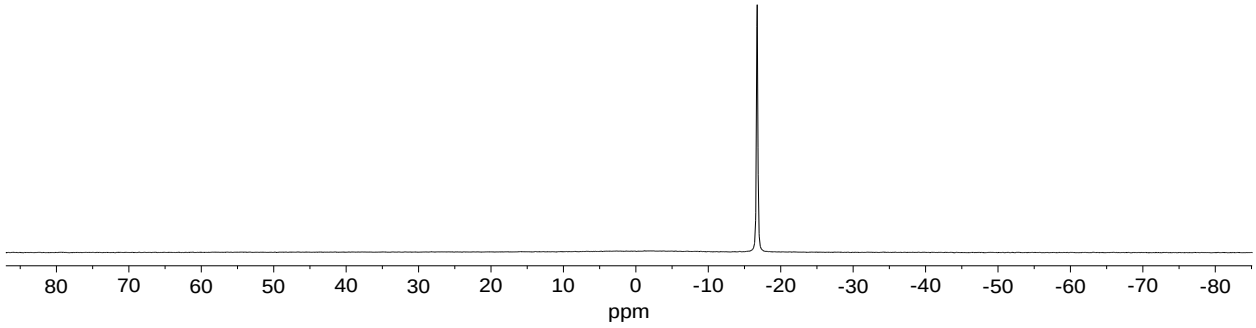


Figure S32. $^{11}B\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of $[(o\text{-}MeNC_5H_4)PFPh_2][B(C_6F_5)_4]_2$ (**4b**).

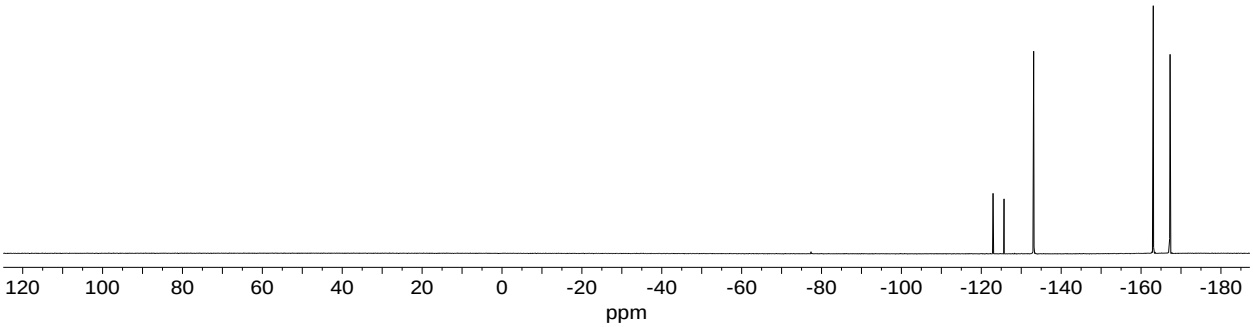


Figure S33. ^{19}F NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)$PFPh_2$][$B(C_6F_5)_4$]$_2$ (**4b**).

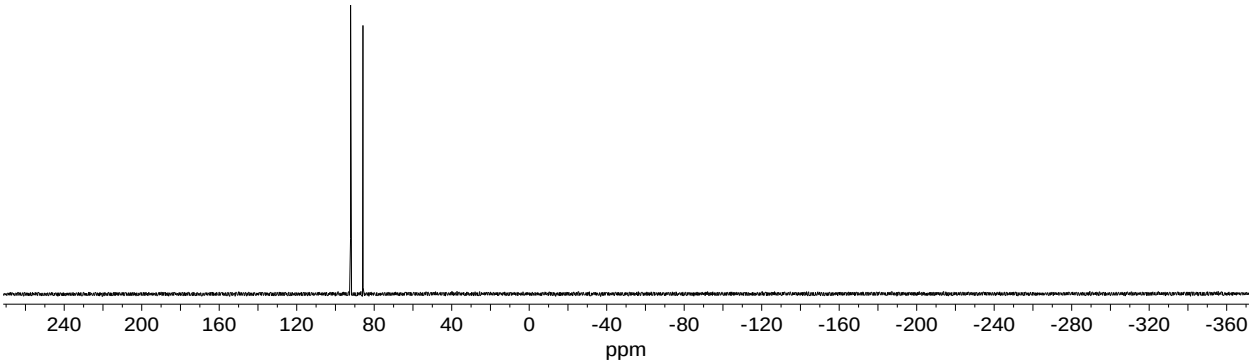


Figure S34. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)$PFPh_2$][$B(C_6F_5)_4$]$_2$ (**4b**).

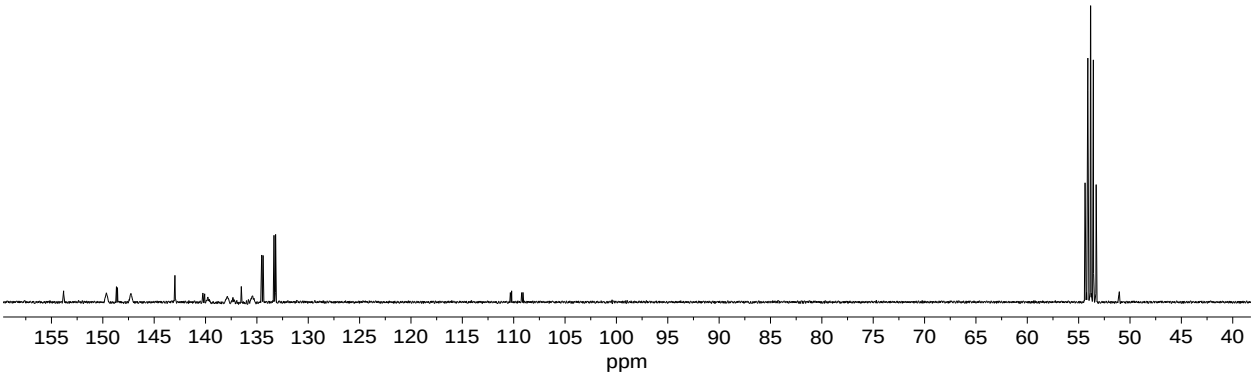
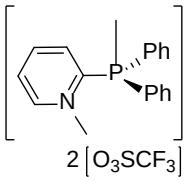


Figure S35. $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)$PFPh_2$][$B(C_6F_5)_4$]$_2$ (**4b**).

1.9 NMR Spectra of [(*o*-$MeNC_5H_4$)$P(CH_3)Ph_2$][O_3SCF_3]$_2$ (5a).



5a

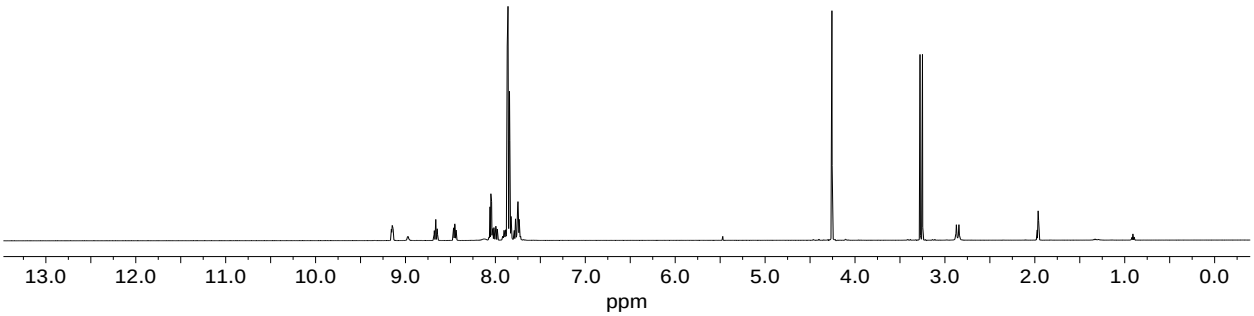


Figure S36. ^{1}H NMR spectrum (CD_3CN) of [(*o*-$MeNC_5H_4N$)P(CH_3)Ph_2][O_3SCF_3]$_2$ (**5a**).

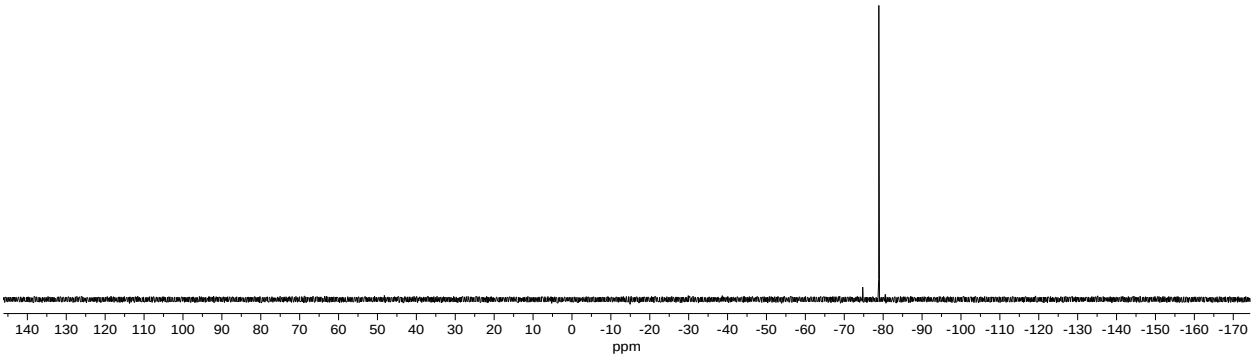


Figure S37. ^{19}F NMR spectrum (CD_3CN) of [(*o*-$MeNC_5H_4$)P(CH_3)Ph_2][O_3SCF_3]$_2$ (**5a**).

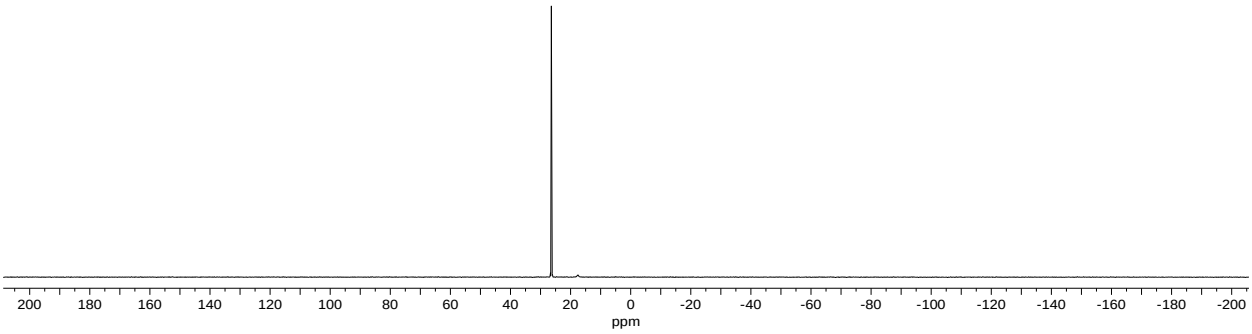


Figure S38. ^{31}P{^{1}H} NMR spectrum (CD_3CN) of [(*o*-$MeNC_5H_4$)P(CH_3)Ph_2][O_3SCF_3]$_2$ (**5a**).

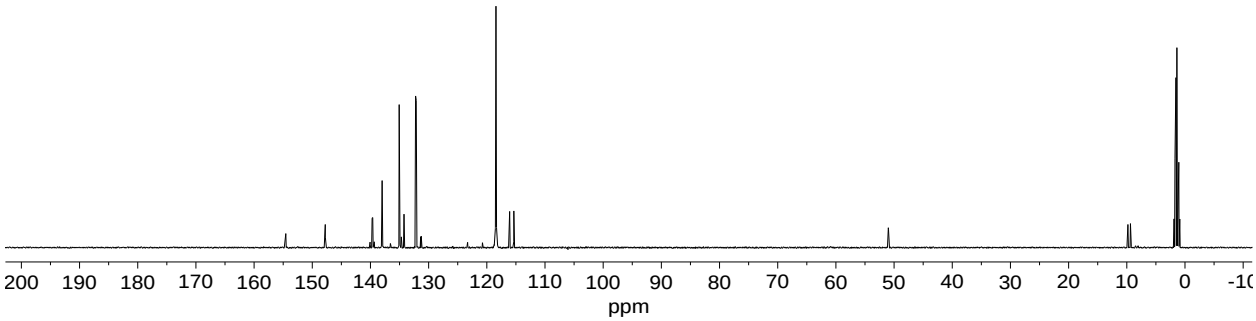


Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3CN) of $[(o\text{-}MeNC_5H_4)P(CH_3)Ph_2][O_3SCF_3]_2$ (**5a**).

1.10 NMR Spectra of $[(o\text{-}MeNC_5H_4)P(CH_3)Ph_2][B(C_6F_5)_4]_2$ (5b).

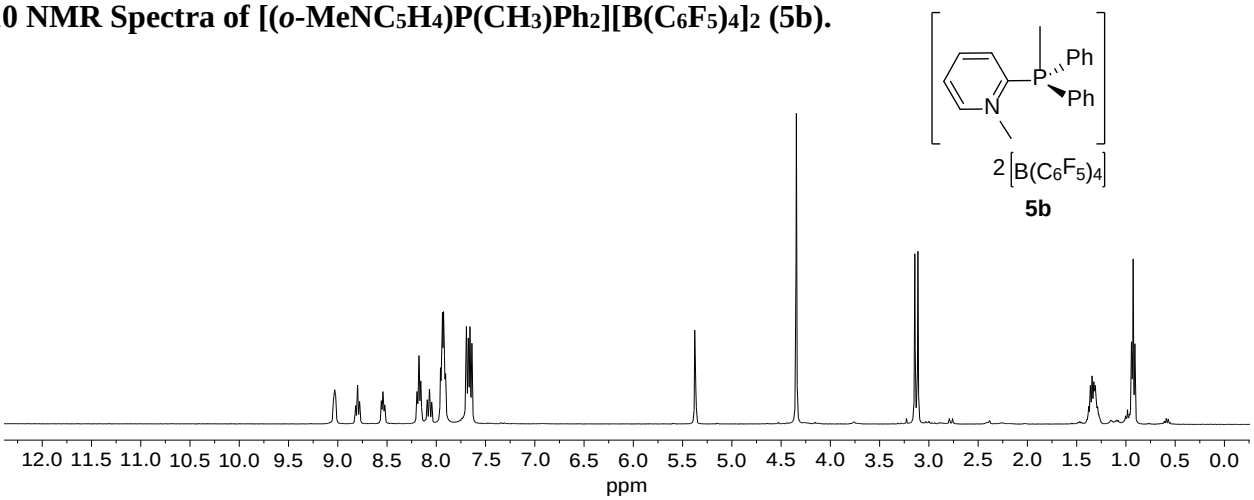


Figure S40. ^{1}H NMR spectrum (CD_2Cl_2) of $[(o\text{-}MeNC_5H_4)P(CH_3)Ph_2][B(C_6F_5)_4]_2$ (**5b**).

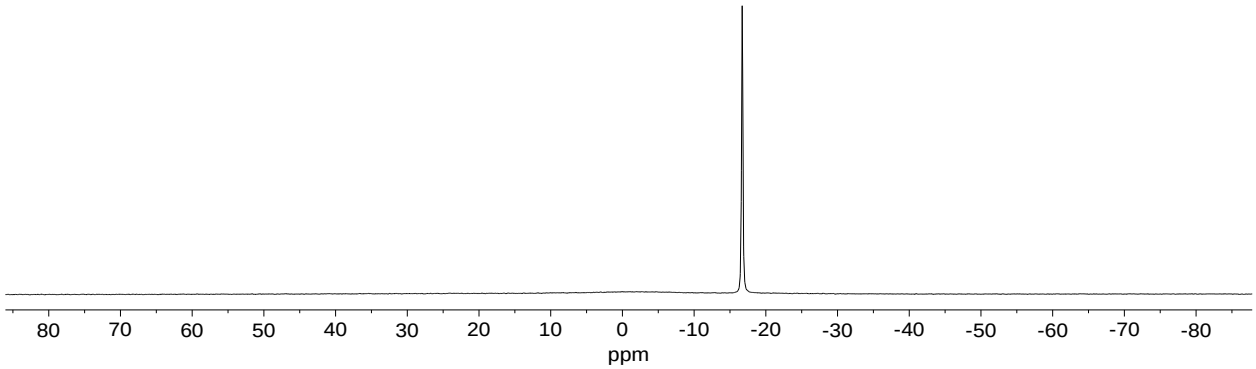


Figure S41. $^{11}B\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of $[(o\text{-}MeNC_5H_4)P(CH_3)Ph_2][B(C_6F_5)_4]_2$ (**5b**).

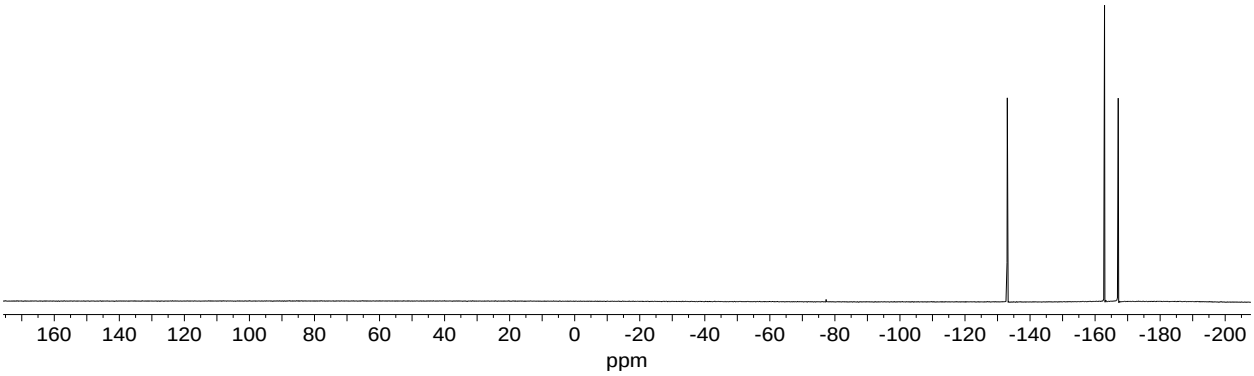


Figure S42. ^{19}F NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)$P(CH_3)Ph_2$][$B(C_6F_5)_4$]$_2$ (**5b**).

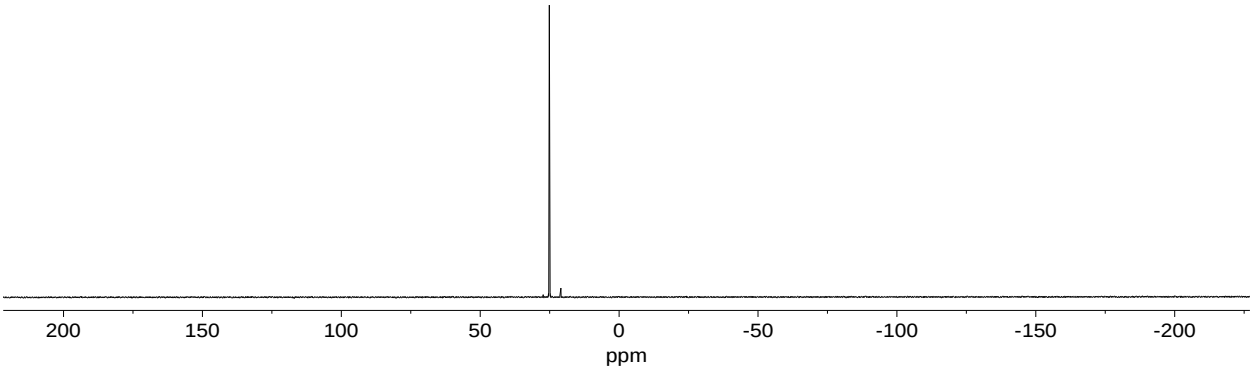


Figure S43. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)$P(CH_3)Ph_2$][$B(C_6F_5)_4$]$_2$ (**5b**).

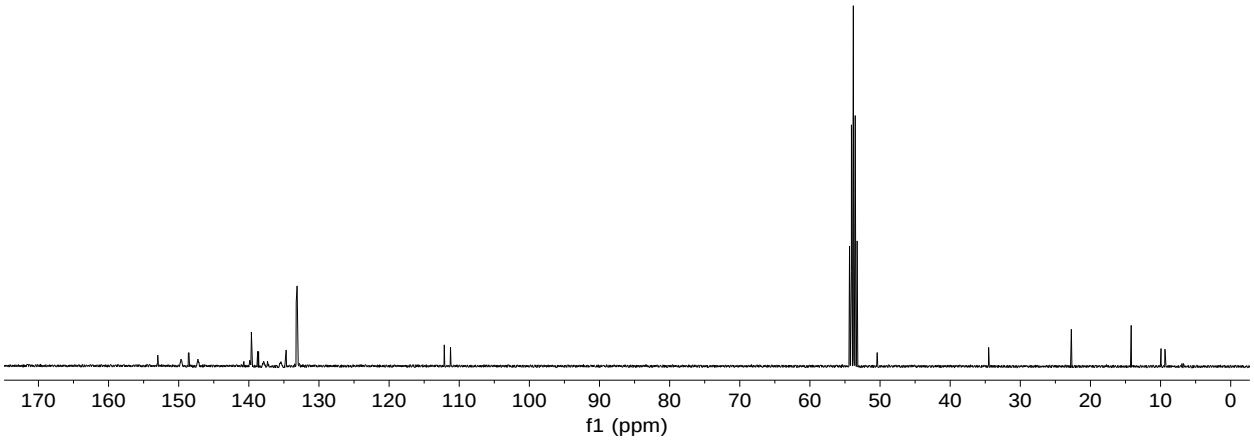
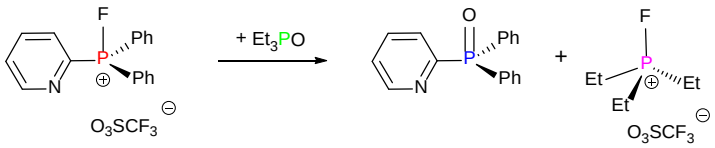


Figure S44. $^{13}C\{1H\}$ NMR spectrum (CD_2Cl_2) of [(*o*-$MeNC_5H_4$)$P(CH_3)Ph_2$][$B(C_6F_5)_4$]$_2$ (**5b**).

1.11 General Procedure for Gutmann-Beckett Tests

A solution of the phosphonium cation (0.07 mmol) in CD_2Cl_2 (0.6 mL) was added to a separate vial containing triethylphosphine oxide (Et_3PO, 0.07 mmol). The reaction mixture was investigated by multi-nuclear NMR spectroscopy after one hour at ambient temperature.

1.111 Reaction of [(*o*-NC_5H_4)$PFPh_2$][O_3SCF_3] (2a) with Et_3PO



$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 150.2 (d, ^1J(P,F) = 955 Hz, 1P; $[Et_3PF]^+$), 78.7 (d, ^1J(P,F) = 1000 Hz, 1P; [(*o*-NC_5H_4)$PFPh_2$]$^+$), 64.1 (s(br), 1P; Et_3PO), 19.7 ppm (s, 1P; (*o*-NC_5H_4)Ph_2P=O). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -79.0 (s, 3F; O_3SCF_3), -136.3 (d, ^1J(P,F) = 1000 Hz, 1F; [(*o*-NC_5H_4)$PFPh_2$]$^+$), -160.6 ppm (dm, ^1J(P,F) = 955 Hz, ^3J(F,H) = 15 Hz, 1F; $[Et_3PF]^+$).

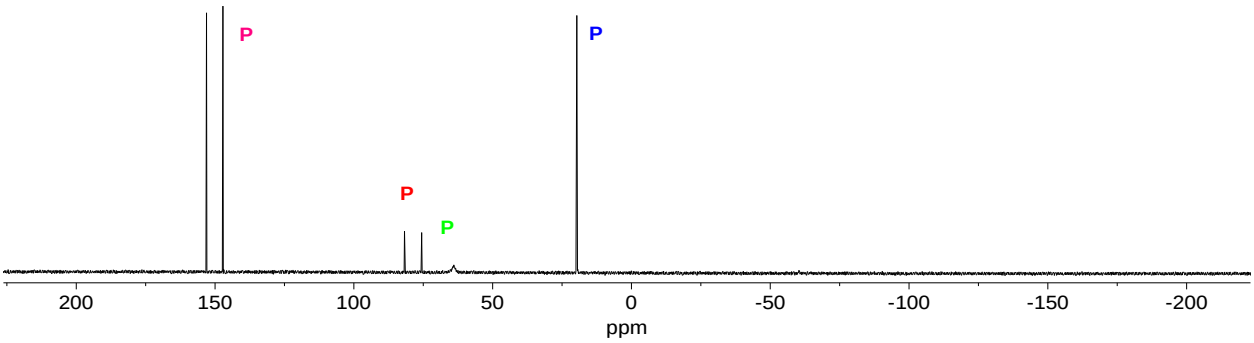


Figure S45. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2) of **2a** with one equivalent of Et_3PO.

1.112 Reaction of [(*o*-NC_5H_4)$PFPh_2$][$B(C_6F_5)_4$] (2b) with Et_3PO

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 148.1 (d, ^1J(P,F) = 965 Hz, 1P; $[Et_3PF]^+$), 76.8 (d, ^1J(P,F) = 995 Hz, 1P; [(*o*-NC_5H_4)$PFPh_2$]$^+$), 60.2 (s(br), 1P; Et_3PO), 20.0 ppm (s, 1P; (*o*-NC_5H_4)Ph_2P=O). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ – 133.7 (m(br), 8F; B(*o*-B_6F_5)$_4$), -134.0 (d, 1F; [(*o*-NC_5H_4)$PFPh_2$]$^+$), -159.0 (dm, ^1J(P,F) = 965 Hz, ^3J(F,H) = 15 Hz, $[Et_3PF]^+$), -163.7 (t, ^3J(F,F) = 20 Hz, 4F; B(*p*-C_6F_5)$_4$), -167.5 ppm (m(br), 8F; B(*m*-B_6F_5)$_4$).

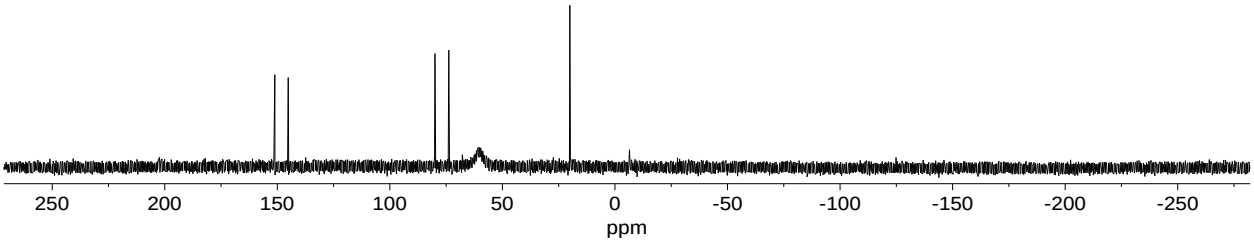


Figure S46. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **2b** with one equivalent of Et_3PO.

1.113 Reaction of [(*o*-$MeNC_5H_4$)$PFPh_2$][O_3SCF_3]$_2$ (4a) with Et_3PO

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 150.3 (d, ^{1}J(P,F) = 955 Hz, 1P; $[Et_3PF]^+$), 52.8 (s(br), 1P; Et_3PO), 27.8 (s, 1P; [(*o*-$MeNC_5H_4$)PPh_2=O]$^+$), -55.7 ppm (t, ^{1}J(P,F) = 700 Hz, 1P; **1**). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -40.95 (d, 2F; **1**), -79.0 (s, 6F; O_3SCF_3), -160.8 ppm (dm, ^{3}J(F,H) = 15 Hz, $[Et_3PF]^+$).

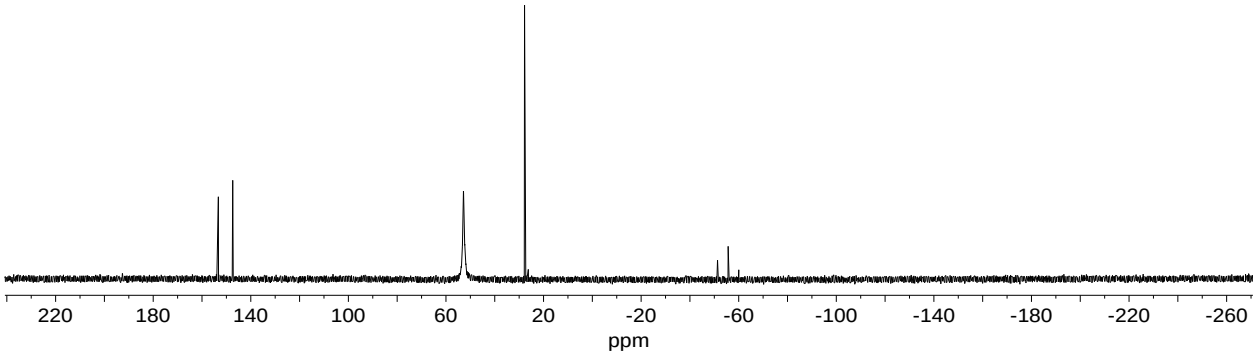


Figure S47. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **4a** with one equivalent of Et_3PO.

1.114 Reaction of [(*o*-$MeNC_5H_4$)$PFPh_2$][$B(C_6F_5)_4$]$_2$ (4b) with Et_3PO

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 147.7 (d, ^{1}J(P,F) = 981 Hz, 1P; $[Et_3PF]^+$), 27.9 ppm (s, 1P; [(*o*-$MeNC_5H_4$)PPh_2=O]$^+$). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ – 133.7 (m(br), 16F; B(*o*-$B_6F_5)_4$), -159.0 (dm, ^{3}J(F,H) = 15 Hz, 1F; $[Et_3PF]^+$), -163.7 (t, ^{3}J(F,F) = 20 Hz, 8F; B(*p*-$C_6F_5)_4$), -167.5 ppm (m(br), 16F; B(*m*-$B_6F_5)_4$).

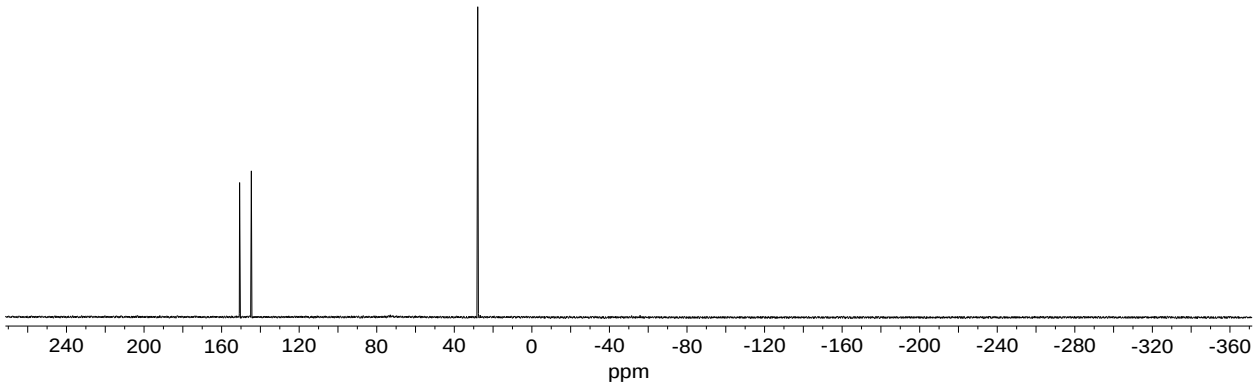


Figure S48. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **4b** with one equivalent of Et_3PO.

1.115 Reaction of [(*o*-$MeNC_5H_4$)$P(CH_3)Ph_2$][O_3SCF_3]$_2$ (5a) with Et_3PO

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 51.81 (s(br), 1P; Et_3PO), 26.16 ppm (s, 1P; **5a**). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -79.9 ppm (s, 6F; O_3SCF_3).

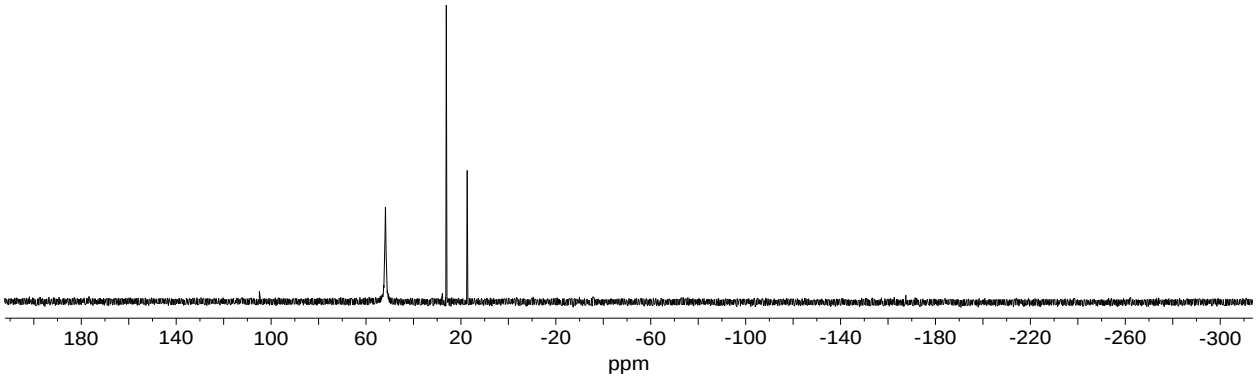


Figure S49. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **5a** with one equivalent of Et_3PO.

1.116 Reaction of [(*o*-$MeNC_5H_4$)$P(CH_3)Ph_2$][$B(C_6F_5)_4$]$_2$ (5b) with Et_3PO

$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 162 MHz, H_3PO_4): δ 55.1 (s(br), 1P; Et_3PO), 26.5 ppm (s, 1P; **5b**). **^{19}F NMR** (CD_2Cl_2, 377 MHz, $CFCl_3$): δ -133.0 (m(br), 16F; B(*o*-$B_6F_5)_4$), -163.0 (t, ^{3}J(F,F) = 20 Hz, 8F; B(*p*-$C_6F_5)_4$), -167.2 ppm (m(br), 16F; B(*m*-$B_6F_5)_4$).

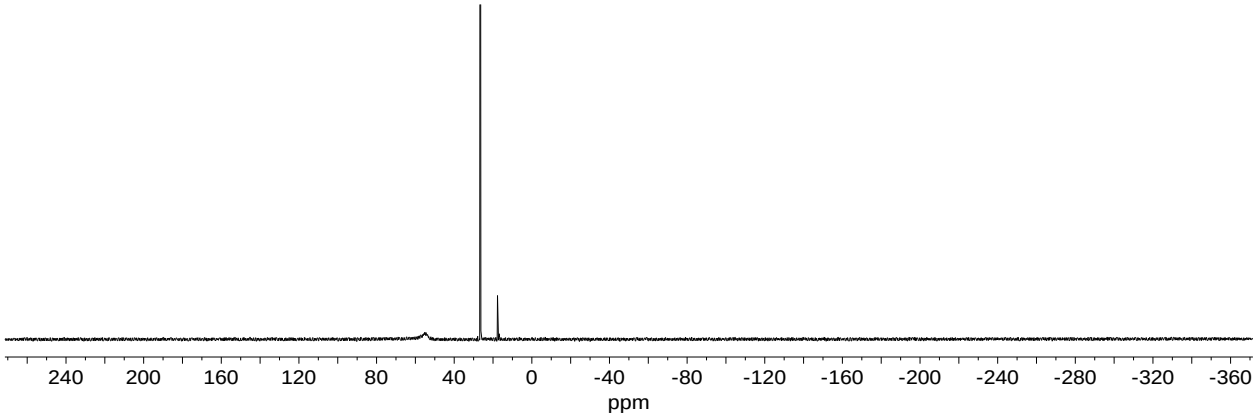


Figure S50. $^{31}P\{^{1}H\}$ NMR spectrum (CD_2Cl_2) of **5b** with one equivalent of Et_3PO.

1.12 General Procedure for the Catalysed Dimerization of 1,1-Diphenylethylene

In a 20 mL vial, a solution of the phosphonium catalyst (2 mol%) was prepared in 0.6 mL CD_2Cl_2. 1,1-diphenylethylene (0.2 mmol) was added at ambient temperature and the reaction mixture was transferred to a NMR tube. The sample was sealed, aggregated and allowed to react at ambient temperature for the desired time, giving 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene. For the reaction with catalyst **4b**, the reaction mixture was dried *in vacuo* and the solid was re-dissolved in 5 mL of *n*-pentane. The suspension was filtered through a celite plug and dried *in vacuo* to afford a white microcrystalline solid. (48.7 mg, 97% Yield). **^{1}H NMR** (C_6D_6, 400 MHz, Me_4Si): δ 1.5 (s, 3H; CH_3), 3.0 (d, ^{3}J(H,H) = 13 Hz, 1H; CH_2), 3.4 (d, ^{3}J(H,H) = 13Hz, 1H; CH_2), 6.89 - 7.23 ppm (m, 19H; Ar-H).**$^{13}C\{^{1}H\}$ NMR** (C_6D_6, 125 MHz, Me_4Si): δ 29.1 (s, 1C; CH_3), 51.5 (s, 1C; CH_2), 61.4 (s, 1C; CPh), 61.8 (s, 1C; CPh), 125.4 (s, 1C; Ph), 125.9 (s, 1C; Ph), 126.0 (s, 1C; Ph), 126.3 (s, 1C; Ph), 127.3 (s, 1C; Ph), 127.3 (s, 2C; Ph), 127.9 (s,

2C; Ph), 128.0 (s, 2C; Ph), 128.3 (s, 2C; Ph), 129.1 (s, 2C; Ph), 129.3 (s, 2C; Ph), 147.9 (s, 1C; Ph), 149.1 (s, 1C; Ph), 149.4 (s, 1C; Ph), 149.7 (s, 1C; Ph), 151.0 ppm (s, 1C; Ph).

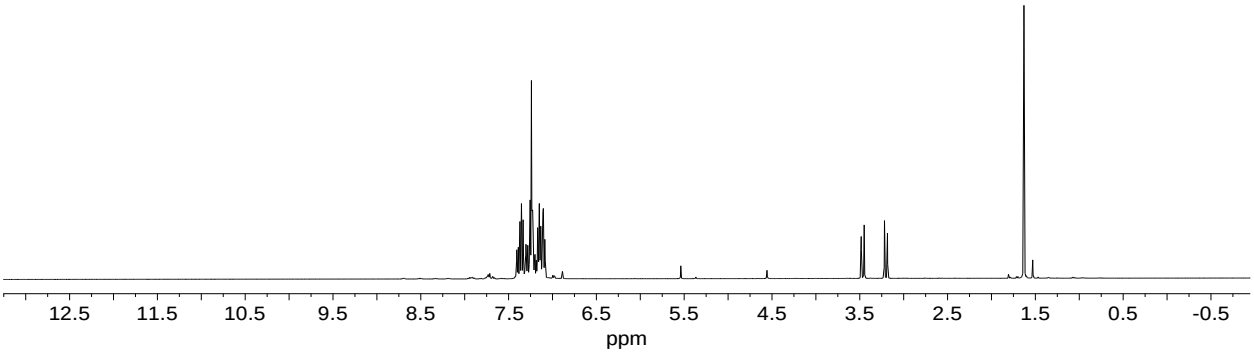


Figure S51. ^{1}H NMR spectrum (CD_2Cl_2) of catalysis with **4b**, t = <30 min.

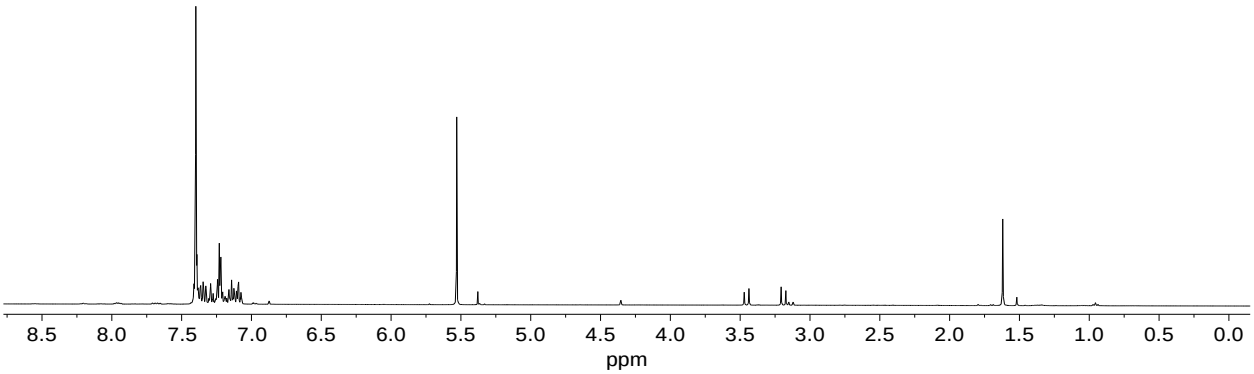


Figure S52. ^{1}H NMR spectrum (CD_2Cl_2) of catalysis with **5b**, t = 2.5 h.

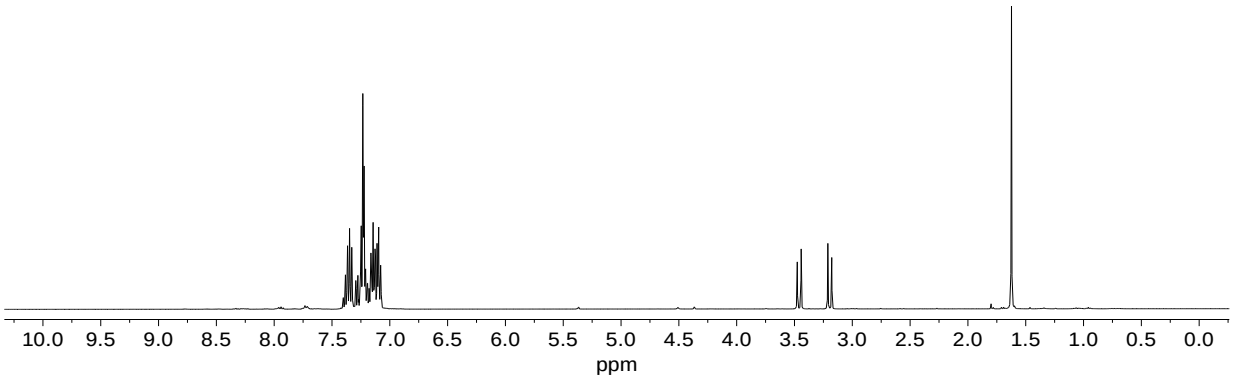


Figure S53. ^{1}H NMR spectrum (C_6D_6) of 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene.

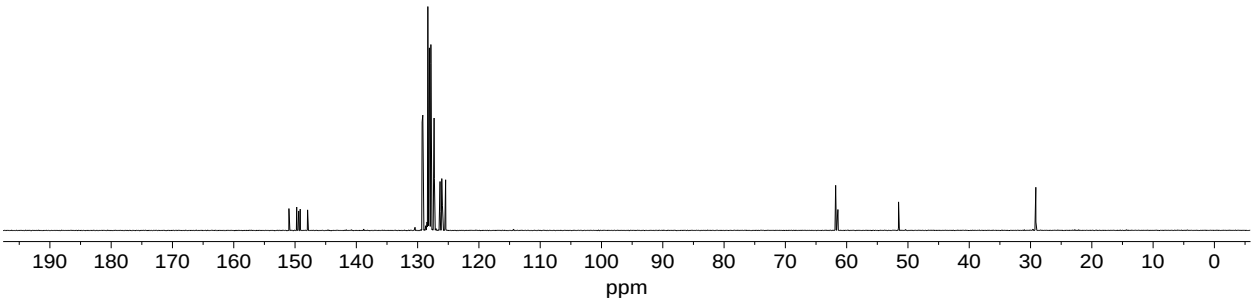


Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6) of 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene.

1.13 General Procedure for the Hydrodefluorination of 1-fluoropentane

In a 20 mL vial, a solution of the phosphonium catalyst (5 mol%) was prepared in 0.7 mL CD_2Cl_2. Triethyl silane (Et_3SiH, 0.04 mmol) was added at ambient temperature, the reaction was briefly stirred, and then 1-fluoropentane was added (0.04 mmol). Fluorobenzene (C_6H_5F, 0.03 mmol) was then added as an internal standard. The reaction mixture was transferred to a NMR tube and left at ambient temperature for 4 h, before being monitored by ^{19}F NMR spectroscopy. Conversions were determined from the proportion of Si-F bonds formed relative to C-F bonds consumed.

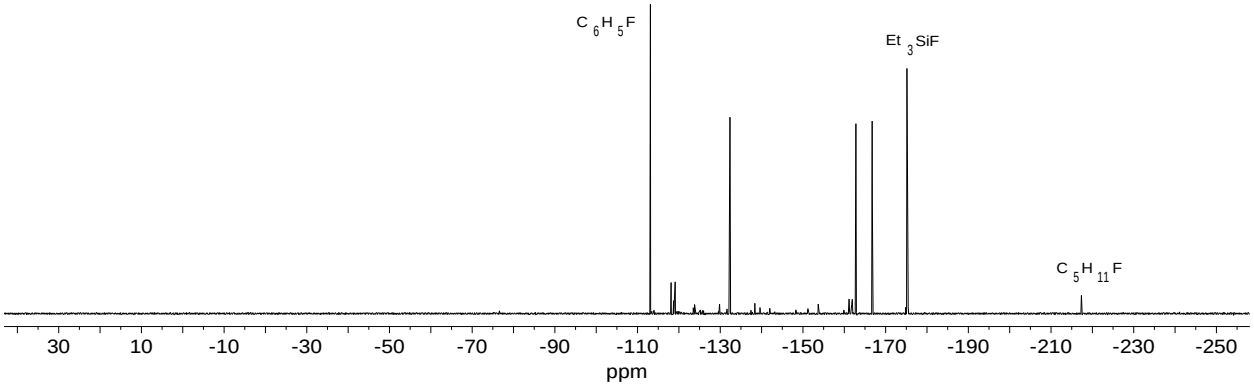


Figure S55. ^{19}F NMR spectrum (CD_2Cl_2) of hydrodefluorination catalysis with **4b**.

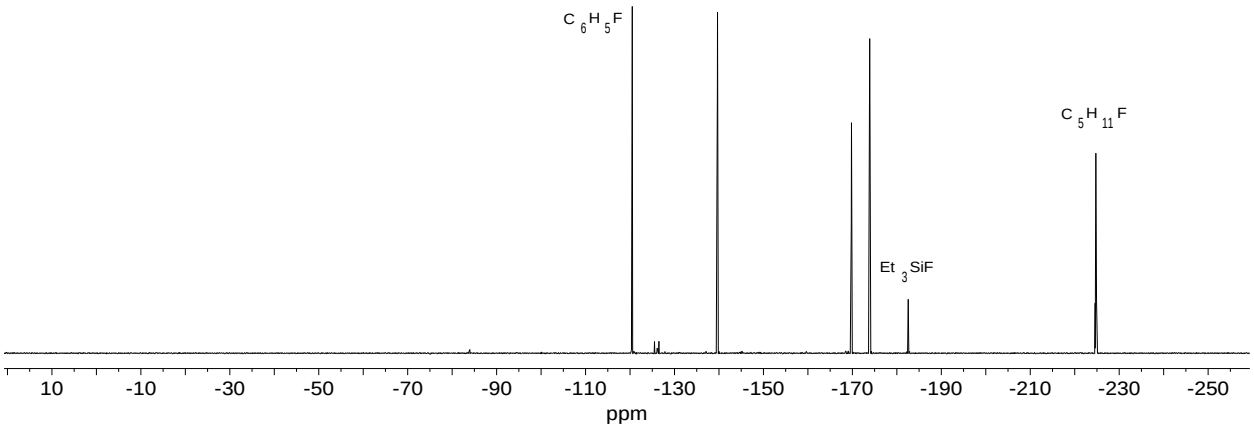


Figure S56. ^{19}F NMR spectrum (CD_2Cl_2) of hydrodefluorination catalysis with **5b**.

1.14 General Procedure for the Hydrosilylation of α-methylstyrene

In a 20 mL vial, a solution of the phosphonium catalyst (2 mol%) was prepared in 0.7 mL CD_2Cl_2. Triethyl silane (Et_3SiH, 0.05 mmol) was added at ambient temperature, the reaction mixture was briefly stirred, and then α-methylstyrene (0.05 mmol) was added. The mixture was transferred to a NMR tube and heated at 45 °C for 4 h. For the reaction with catalyst **4b**, the solvent volume was reduced *in vacuo* to *ca.* 1 mL. 3 mL of *n*-pentane was added and the suspension was filtered through a celite plug. The filtrate was dried *in vacuo*, giving colourless oil. (50 mg, 85% Yield). **^{1}H NMR (C_6D_5Br, 400 MHz, Me_4Si):** δ 0.2 (m, 6H; $SiCH_2CH_3$), 0.7 (t, ^3J(H,H) = 8 Hz, 9H; $SiCH_2CH_3$), 0.8 (m, 2H; CH_2), 1.0 (d, ^3J(H,H) = 7 Hz, 3H; CH_3), 2.7 (m, 1H; CH), 6.9 (m, 1H; *p*-Ph), 7.0 ppm (m, 4H; *o*- & *p*-Ph); **$^{13}C\{^1H\}$ NMR (C_6D_5Br, 125 MHz, Me_4Si):** δ 3.9 (s, 1C; $SiCH_2CH_3$), 7.7 (s, 1C; $SiCH_2CH_3$), 21.6 (s, 1C; CH_2), 26.8 (s, 1C; CH_3), 36.2 (s, 1C; CH), 125.9 (s, 1C; *p*-Ph), 126.7 (s, 2C; *o/m*-Ph), 128.4 (s, 2C; *o/m*-Ph), 149.8 ppm (s, 1C; *i*-Ph).

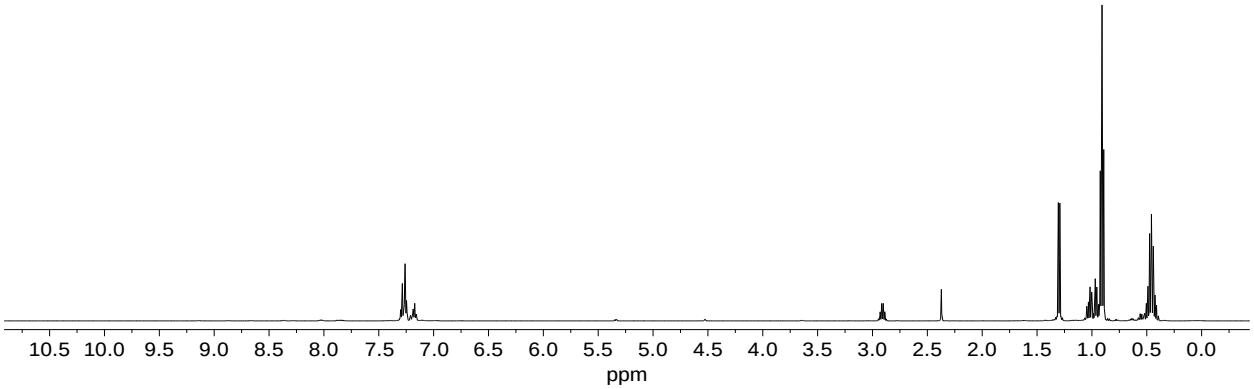


Figure S57. ^1H NMR spectrum (CD_2Cl_2) of crude mixture for hydrosilylation catalysis with **4b**.

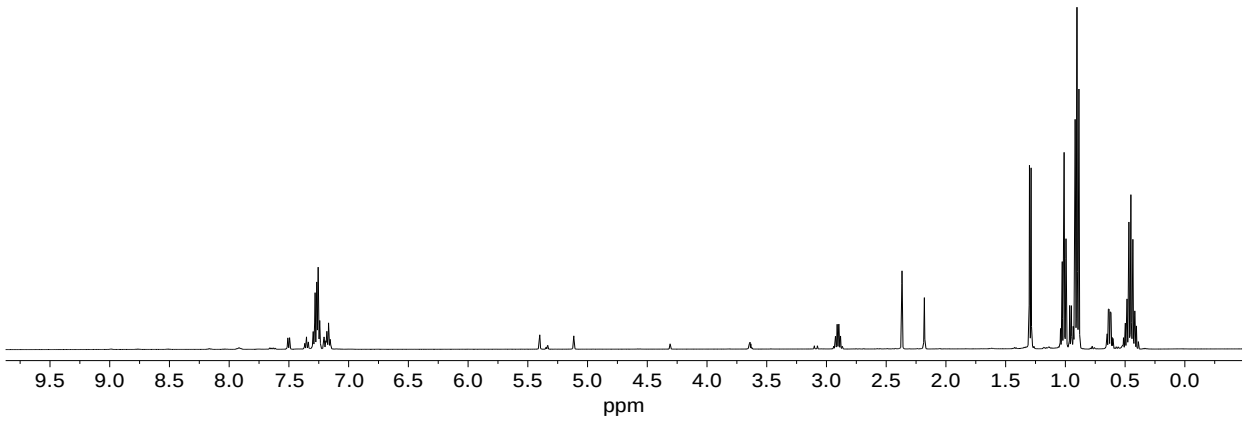


Figure S58. ^{1}H NMR spectrum (CD_2Cl_2) of hydrosilylation catalysis with **5b**.

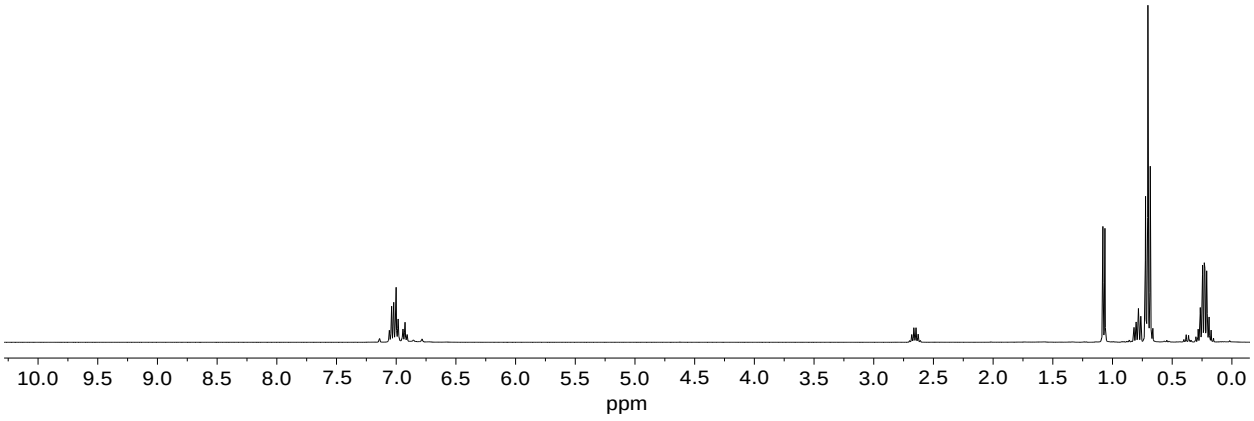


Figure S59. ^{1}H NMR spectrum (C_6D_5Br) of the isolated hydrosilylated product.

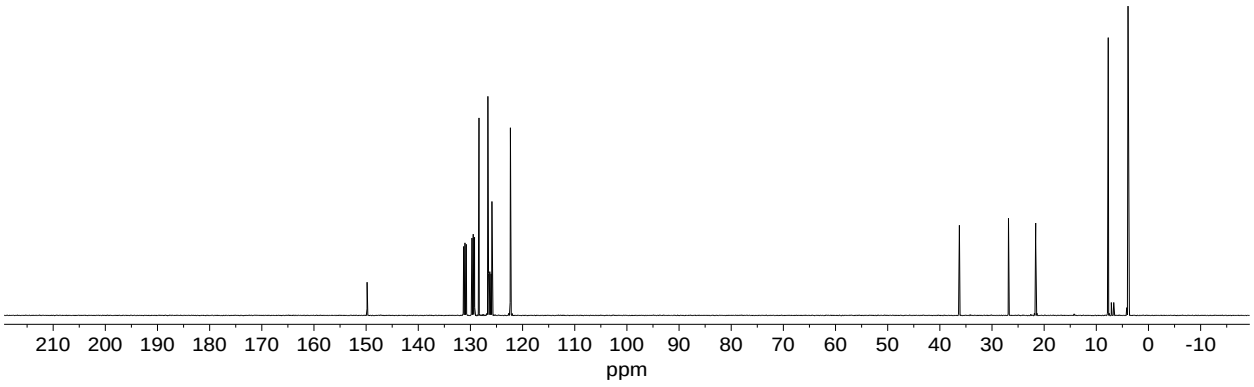


Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_5Br) of the isolated hydrosilylated product.

1.15 General Procedure for the Dehydrocoupling of Phenol with Et_3SiH

In a 20 mL vial, a solution of the phosphonium catalyst (2 mol%) was prepared in 0.7 mL CD_2Cl_2. Triethyl silane (Et_3SiH, 0.05 mmol) was added at ambient temperature, the reaction mixture was briefly stirred, and then added to a vial containing phenol (0.05 mmol). The mixture was transferred to a NMR

tube and heated at 50 °C for 24 h. For the reaction with catalyst **4b**, the solvent volume was reduced *in vacuo* to *ca.* 1 mL. 3 mL of *n*-pentane was added and the suspension was filtered through a celite plug. The filtrate was dried *in vacuo*, giving a colourless oil. (56 mg, 79% Yield). **^{1}H NMR (C_6D_5Br, 400 MHz, Me_4Si):** δ 0.5 (q, ^{3}J(H,H) = 8 Hz, 6H; CH_2), 0.8 (t, ^{3}J(H,H) = 8 Hz, 9H; CH_3), 6.72 (m, 3H; *p*-Ph & *o/m*-Ph), 7.0 ppm (m, 2H; *o/m*-Ph); **^{13}C{^{1}H} NMR (C_6D_5Br, 125 MHz, Me_4Si):** δ 5.2 (s, 3C; CH_2), 6.9 (s, 3C; CH_3), 120.0 (s, 2C; *o/m*-Ph), 121.4 (s, 1C; *p*-Ph), 129.5 (s, 2C; *o/m*-Ph), 155.7 ppm (s, 1C; *i*-Ph).

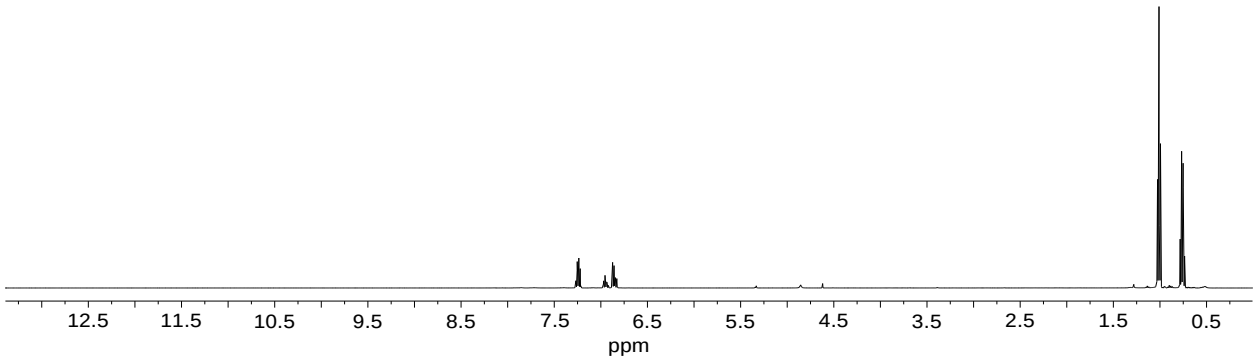


Figure S61. ^{1}H NMR spectrum (CD_2Cl_2) of dehydrocoupling catalysis with **4b**.

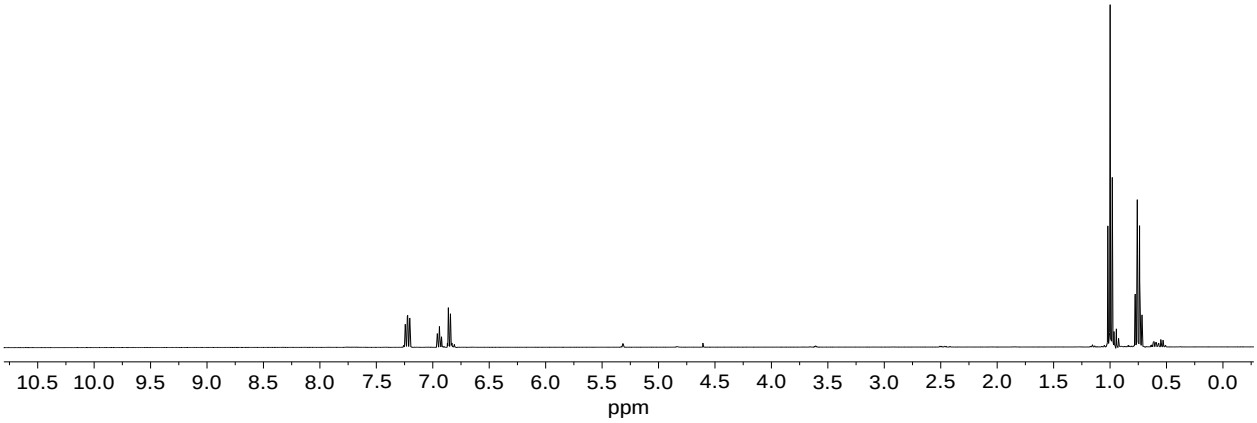


Figure S62. ^{1}H NMR spectrum (CD_2Cl_2) of dehydrocoupling catalysis with **5b**.

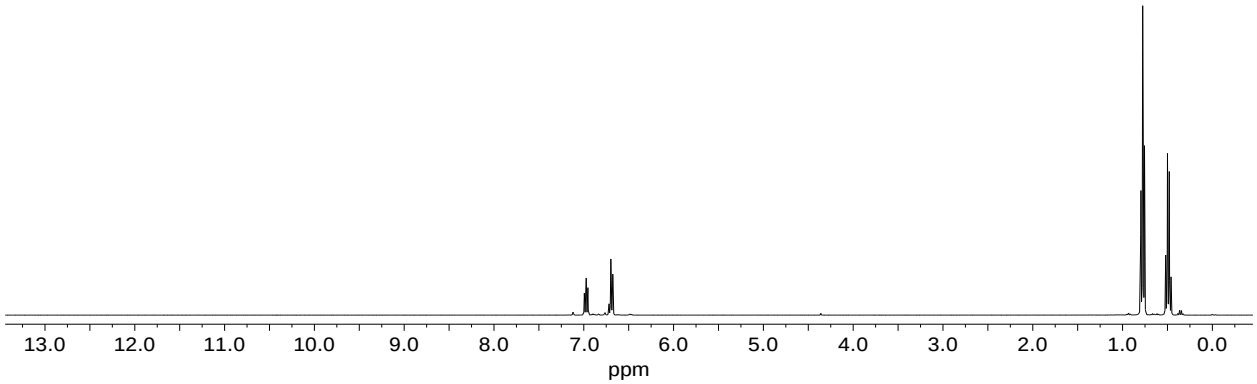


Figure S63. ^{1}H NMR spectrum (C_6D_5Br) of the triethyl(phenoxy)silane.

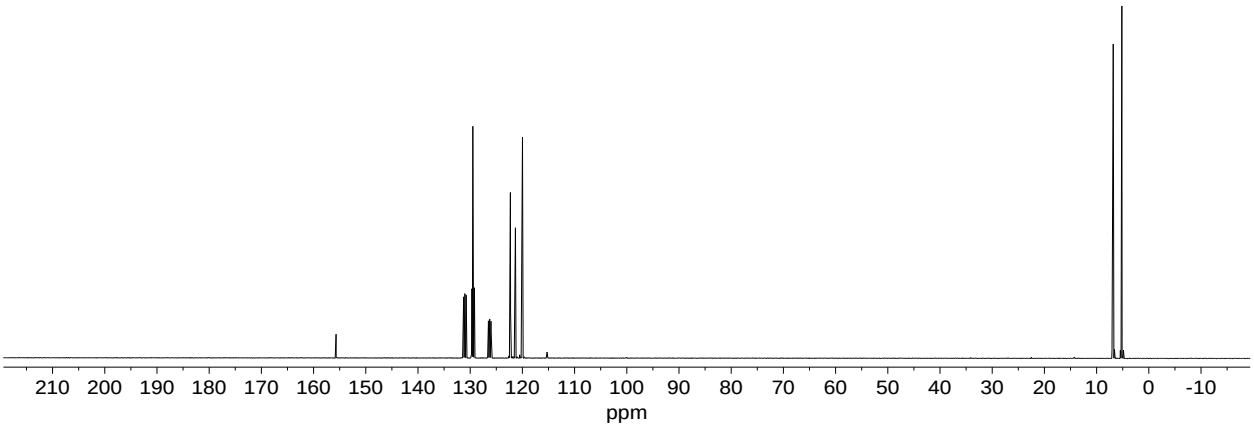


Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_5Br) of triethyl(phenoxy)silane.

1.16 General Procedure for the Hydrodeoxygenation of Benzophenone

In a 20 mL vial, a solution of the phosphonium catalyst (1 mol%) was prepared in 0.7 mL CD_2Cl_2. Triethyl silane (Et_3SiH, 0.04 mmol) was added at ambient temperature, the reaction was briefly stirred, and then the solution was added to a vial containing benzophenone (0.02 mmol). The reaction mixture was left to stir at ambient temperature for 2 h, before toluene (0.02 mmol) was added as an internal standard. The reaction mixture was transferred to a NMR tube and monitored by ^{1}H NMR spectroscopy. For catalysts **4b** and **5b**, the $^{31}P\{^{1}H\}$ NMR spectra were obtained after 5 h at ambient temperature to monitor possible catalyst decomposition.

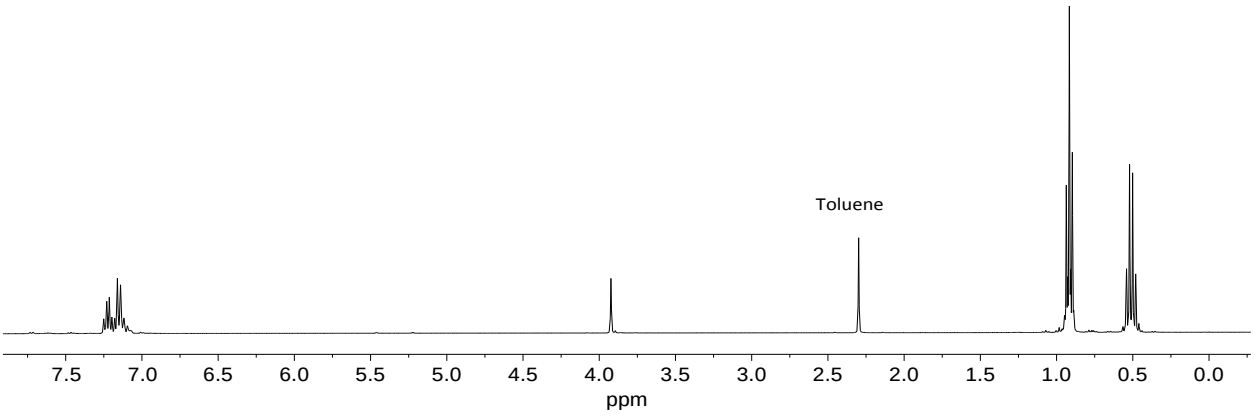


Figure S65. ^{1}H NMR spectrum (CD_2Cl_2) for the hydrodeoxygenation catalysis with **4b**.

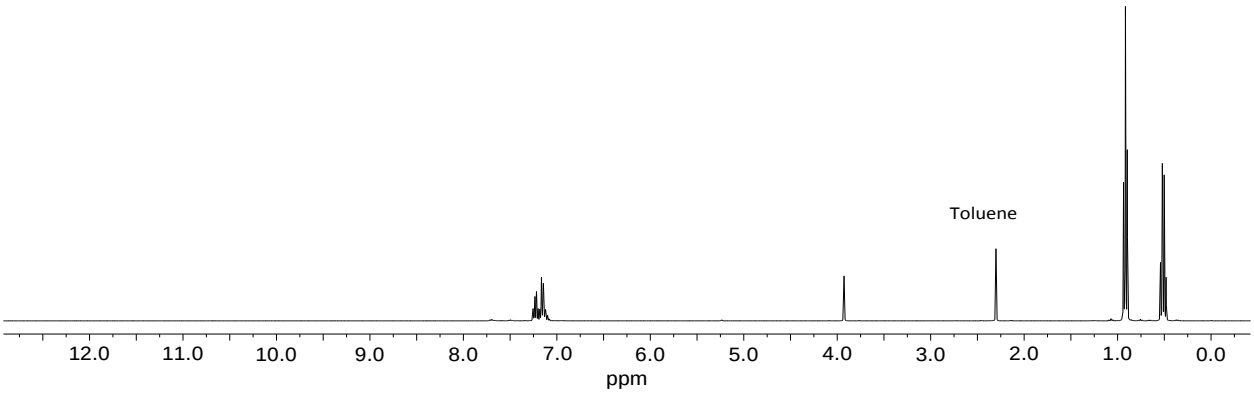


Figure S66. ^{1}H NMR spectrum (CD_2Cl_2) for the hydrodeoxygenation catalysis with **5b**.

2. Crystallographic Details

Table 1. Crystallographic data and details of the structure refinements of compounds [(*o*-$MeNC_5H_4$)PF_2Ph_2][O_3SCF_3] (**3**) and [(*o*-$MeNC_5H_4$)$PFPh_2$][O_3SCF_3]$_2$ (**4a**).

	3	**4a**
Formula	$C_{20}H_{19}C_{12}F_5NO_3PS$	$C_{20}H_{17}F_7NO_6PS_2$
M_r [g mol^{-1}]	550.29	595.44
Colour, habit	Block, colourless	Block, colourless
Crystal system	Monoclinic	Triclinic
Space group	P 2_1/n	P -1
a [Å]	9.2119(6)	8.157(5)
b [Å]	23.8207(2)	11.063(5)
c [Å]	11.1023(7)	14.545(5)
α [°]	90	71.127(5)
β [°]	105.486(3)	77.393(5)
γ [°]	90	84.080(5)
V [Å^3]	2347.8(3)	1211.3(10)
Z	4	2
T [K]	150(2)	150(2)
Crystal size [mm]	0.20x0.20x0.10	0.20x.0.20x0.10
ρ_c (Mg m^{-3})	1.557	1.633
F (000)	1120	604
θ_{min} [°]	1.71	1.51
θ_{max} [°]	32.49	32.63
Index range	$-13 \leq h \leq 13$ $-35 \leq k \leq 35$ $-13 \leq l \leq 16$	$-12 \leq h \leq 12$ $-16 \leq k \leq 16$ $-21 \leq l \leq 21$
μ [mm^{-1}]	0.497	0.378
Absorption correction	SADABS	SADABS
Reflections collected	33578	32906
Reflections unique	8440	8762

R_{int}	0.0299	0.0300
Parameters	298	335
GOOF	1.028	1.019
R1 [I>2σ(I)]	0.0444	0.0397
wR_2 (all data)	0.1192	0.1090