Synthesis and reactivity of air stable Ni(II) complexes with isocyanides and dialkyldithiophosphate ligands: acyclic diaminocarbene formation

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Supplementary Information

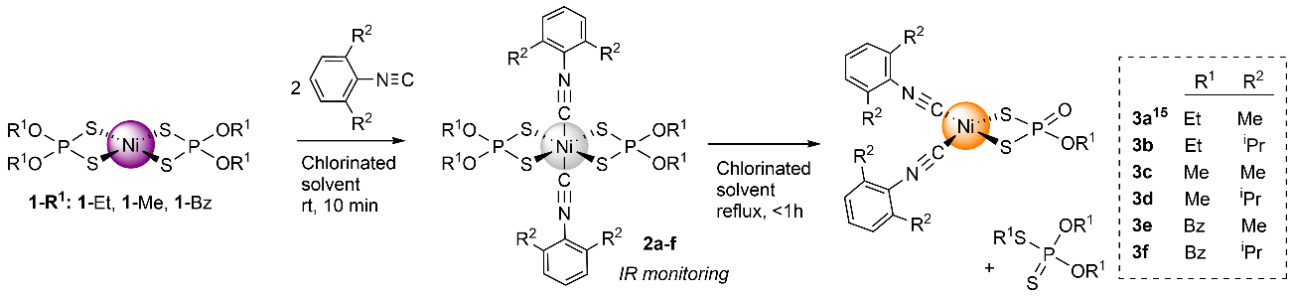
General protocol for the synthesis of $[Ni\{S_2P(OR^1)_2\}_2(CNXyl)_2]$, 3a-3f

One-pot preparation of $[Ni\{S_2P(OR)_2\}_2]$, 1-R.[1]

P_4S_{10} (0.224 g, 0.5 mmol) was dissolved in the alcohol (MeOH, EtOH, ^{i}PrOH, BzOH; 15 mL, excess) with magnetic stirring under N_2 in a round bottom flask equipped with a bubbler to purge the formed H_2S gas. Once the gas production had subsided, the solvent was evaporated under reduced pressure to *ca.* 80% volume to purge the dissolved H_2S gas. $NiCl_2.6H_2O$ (0.238 g, 1 mmol) was added, and the mixture was stirred vigorously to afford a purple solution which was filtered and concentrated under reduced pressure. Addition of hexane produced the precipitation of **1** as purple microcrystals which were recrystallised from CH_2Cl_2/hexane. **1-Me** Yield: 0.345 g, 92 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 97.95 ppm. **1-Et** Yield: 0.405 g, 94 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 92.66 ppm. **1-^{i}Pr** Yield: 0.457 g, 94 %. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 89.27 ppm **1-Cy** Yield: 0.595 g, 92%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 88.46 ppm. **1-Bz** Yield: 0.635 g, 94%. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 93.53 ppm.

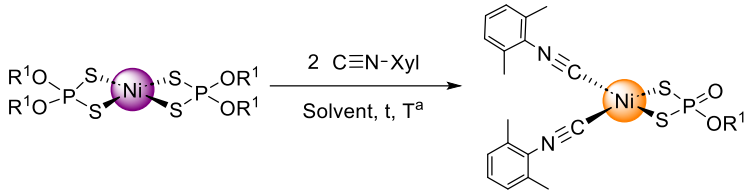
General synthesis of neutral diisocyanide alkylphosphate Ni(II) complexes (3a-3f).

To a solution of $[Ni\{S_2P(OR)_2\}_2]$ **1-R** (1 mmol) in dichloromethane (15 mL) was added *CNXyl* (0.266g, 2 mmol) or *CNAr* (0.374g, 2 mmol), and the octahedral **2n** complex was immediately detected by IR monitoring. The reaction conditions are detailed for each case (see below). The solvent was then evaporated in vacuo. The residue was washed with Et_2O (3 x 15 mL). The solid residue was recrystallized from CH_2Cl_2/ether. Slow evaporation gave **3a**[2]**-3f** as orange microcrystals. Dialkyl-thoate byproducts have not been isolated but they have been detected by ^1H and $^{31}P\{^1H\}$ NMR experiments. The data is in agreement with the literature.[3]



Scheme S1. Formation of neutral diisocyanide alkyldithiophosphate nickel (II) complexes. The formation of complexes **3a-f** was followed by FT-IR.

Table S1. Conditions[a] and yields for the reaction of dialkyldithiophosphate Ni(II) and two equivalents of isocyanide (CNXyl).



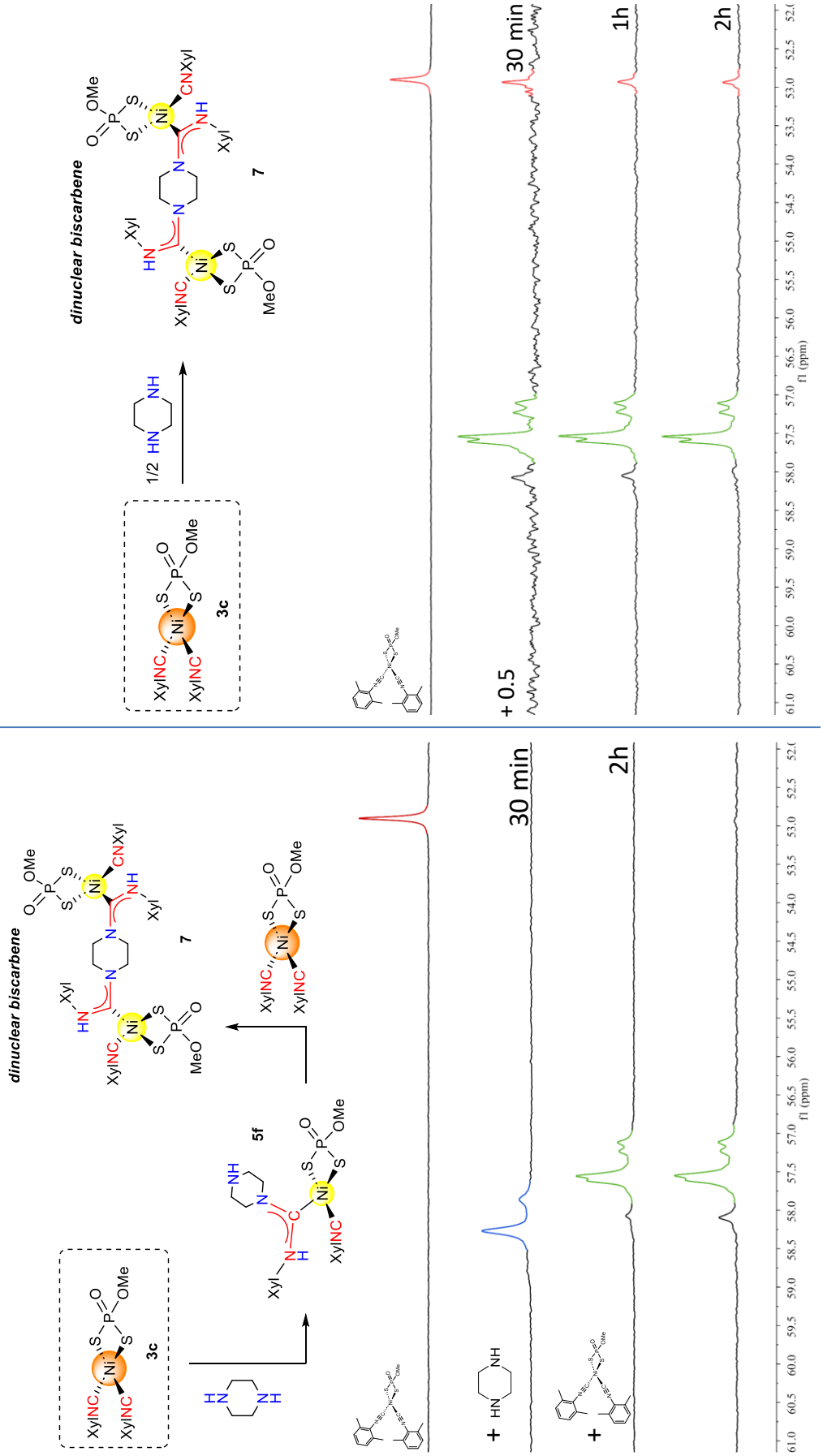
Entry	Solvent	R^1	Temperature	Time[b]	Yield (%)[c]
1	MeOH	Me	rt	24h	25
2	Toluene	Me	rt	24h	15
3	THF	Me	rt	24h	90
4	CH_2Cl_2	Me	rt	4h	90
5	CH_2Cl_2	Me	reflux	30 min	95
6	$CHCl_3$	Me	reflux	40 min	95
7	CH_2Cl_2	Me	MW 90°C	5 min	95
8	$C_2H_4Cl_2$	Et	reflux	5 days	80
9	CH_2Cl_2	Et	MW 140°C	40 min.	90
10	CH_2Cl_2	^{i}Pr, Cy, ^{t}Bu	MW 140 °C	2 h	n. r.

[a] General conditions: $[Ni\{(S_2POR)_2\}_2]$, 0.15 mmol; CNXyl, 0.3 mmol; solvent 20 mL.

[b] FT-IR monitoring in solution.

[c] Isolated product.

$^{31}P\{^{1}H\}$ NMR spectra monitoring of the reaction evolution of *bis* carbene bridge 7



^{1}H, ^{13}C {^{1}H}, ^{31}P{^{1}H} and bidimensional NMR spectra for neutral and cationic (carbene) complexes 3b-3f, 4a-4g, 5a-5g, 6a-6h and 7.

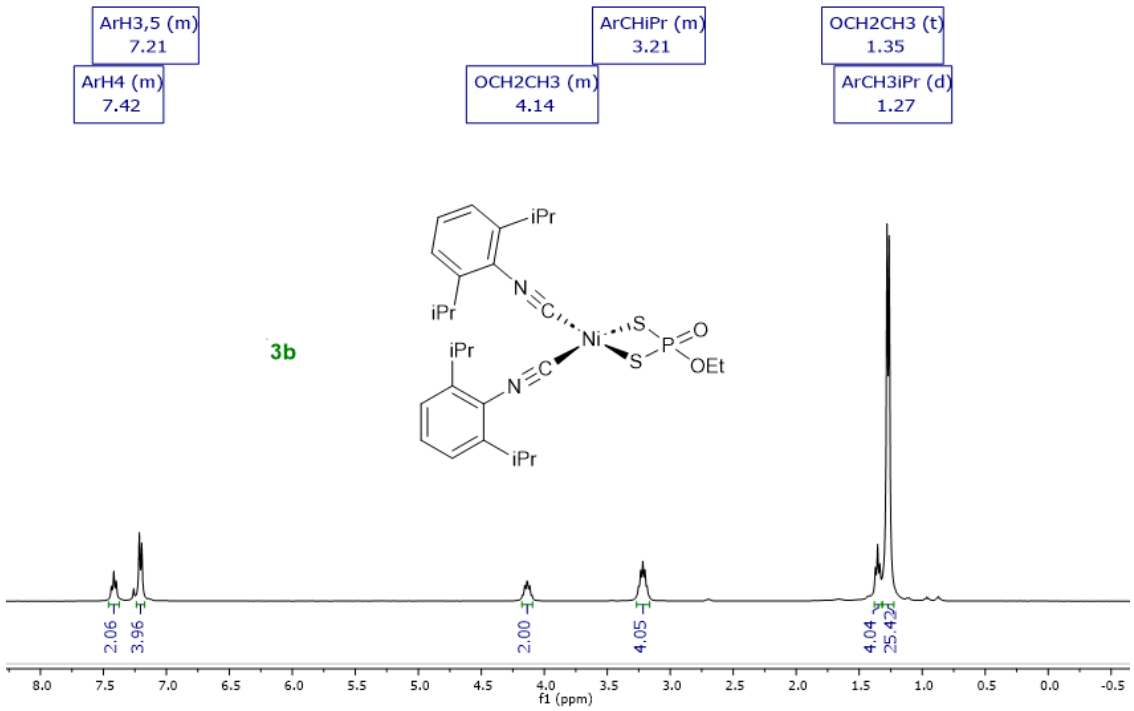


Figure S1. ^{1}H NMR ($CDCl_3$) of compound 3b, [Ni{$S_2P(O)(OEt)$}$(CNAr)_2$].

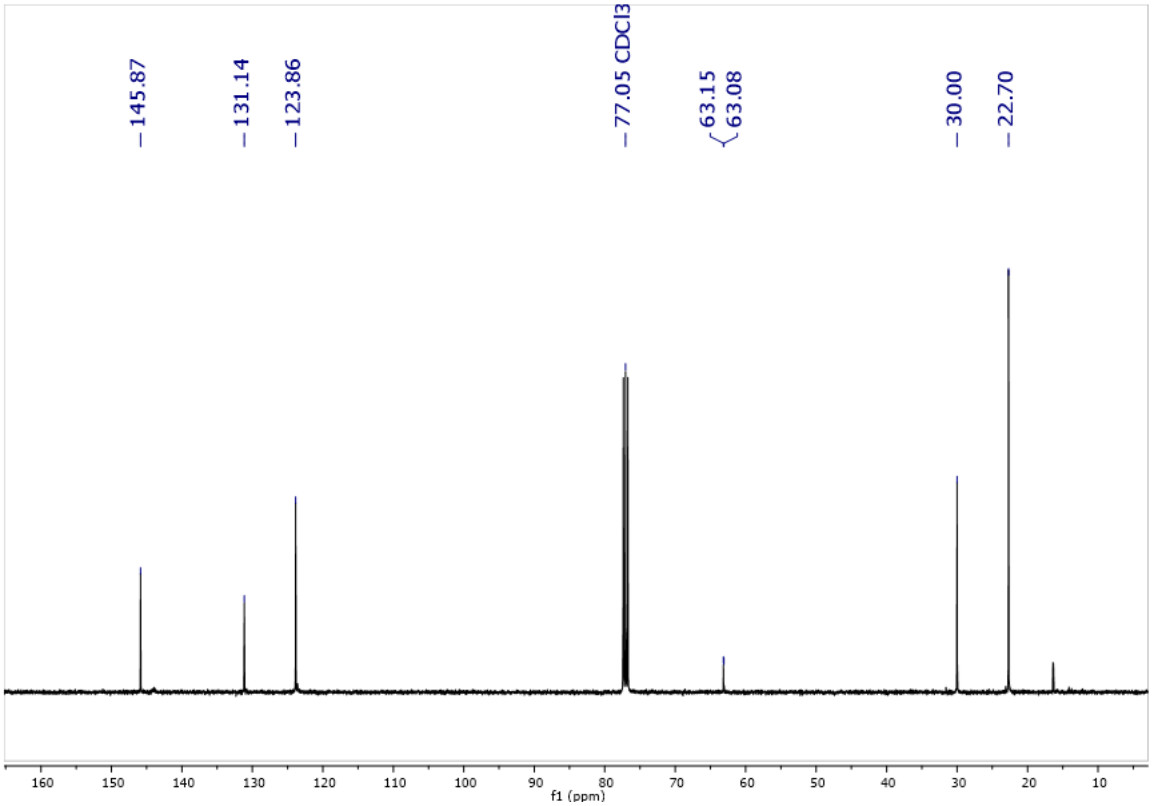


Figure S2. ^{13}C{^{1}H} NMR ($CDCl_3$) of compound 3b, [Ni{$S_2P(O)(OEt)$}$(CNAr)_2$].

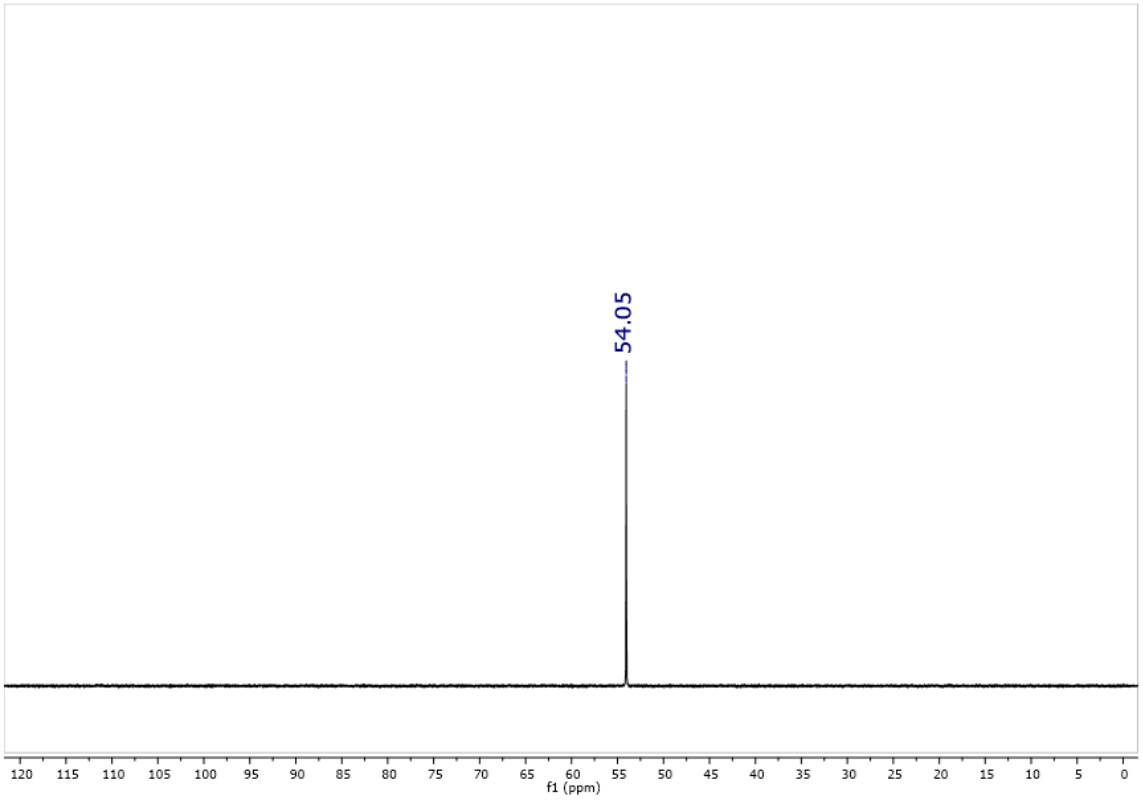


Figure S3. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 3b, $[Ni\{S_2P(O)(OEt)\}(CNAr)_2]$.

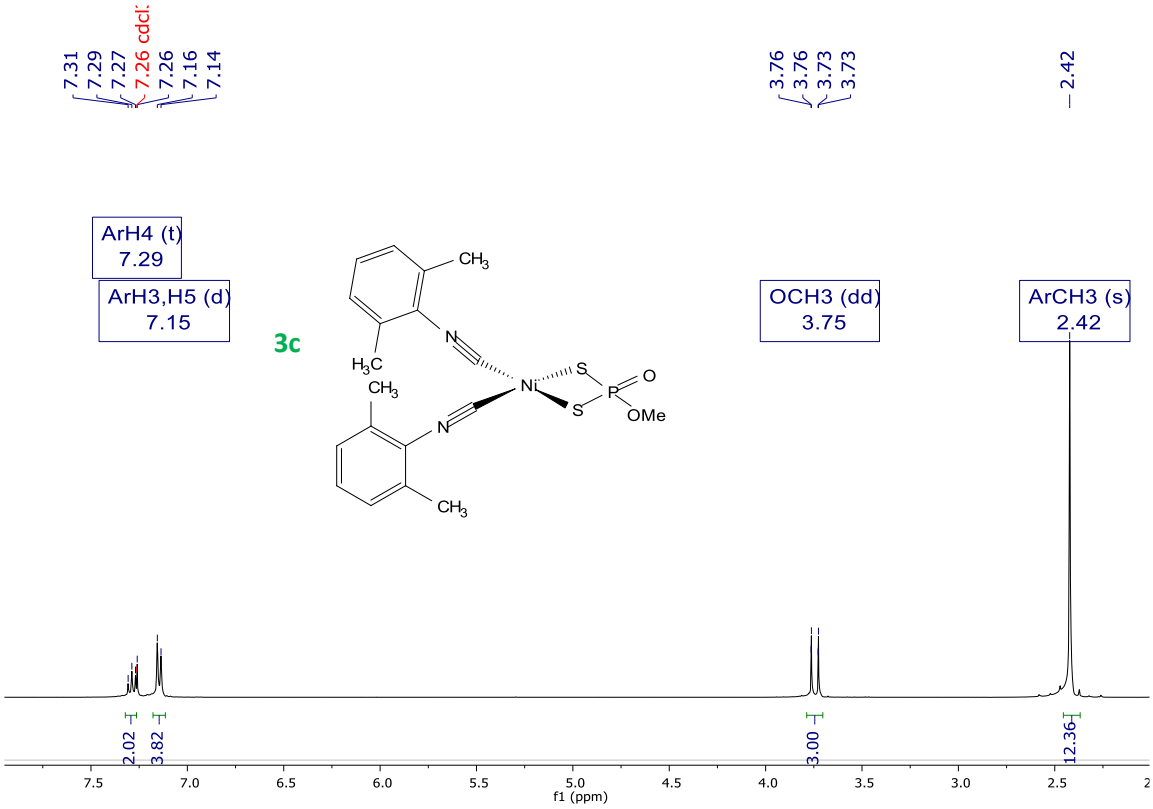


Figure S4. ^{1}H NMR ($CDCl_3$) of compound 3c, $[Ni\{S_2P(O)(OMe)\}(CNXyl)_2]$.

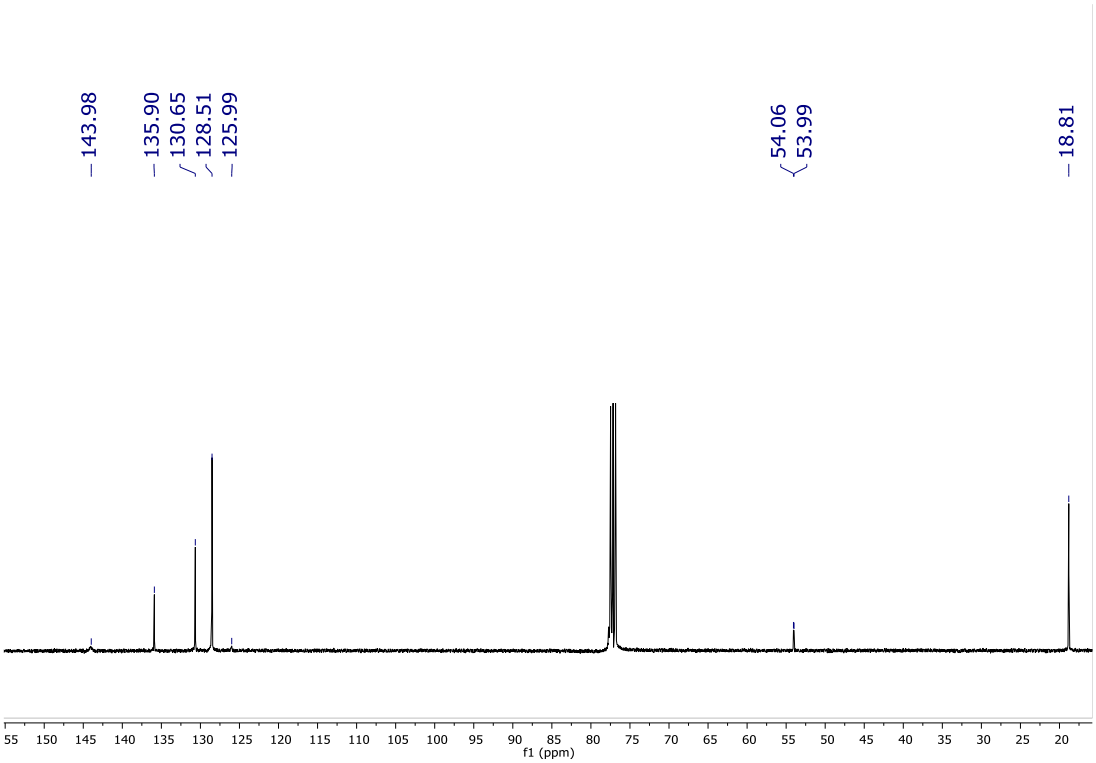


Figure S5. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 3c, [Ni{$S_2P(O)(OMe)$}$(CNXyl)_2$].

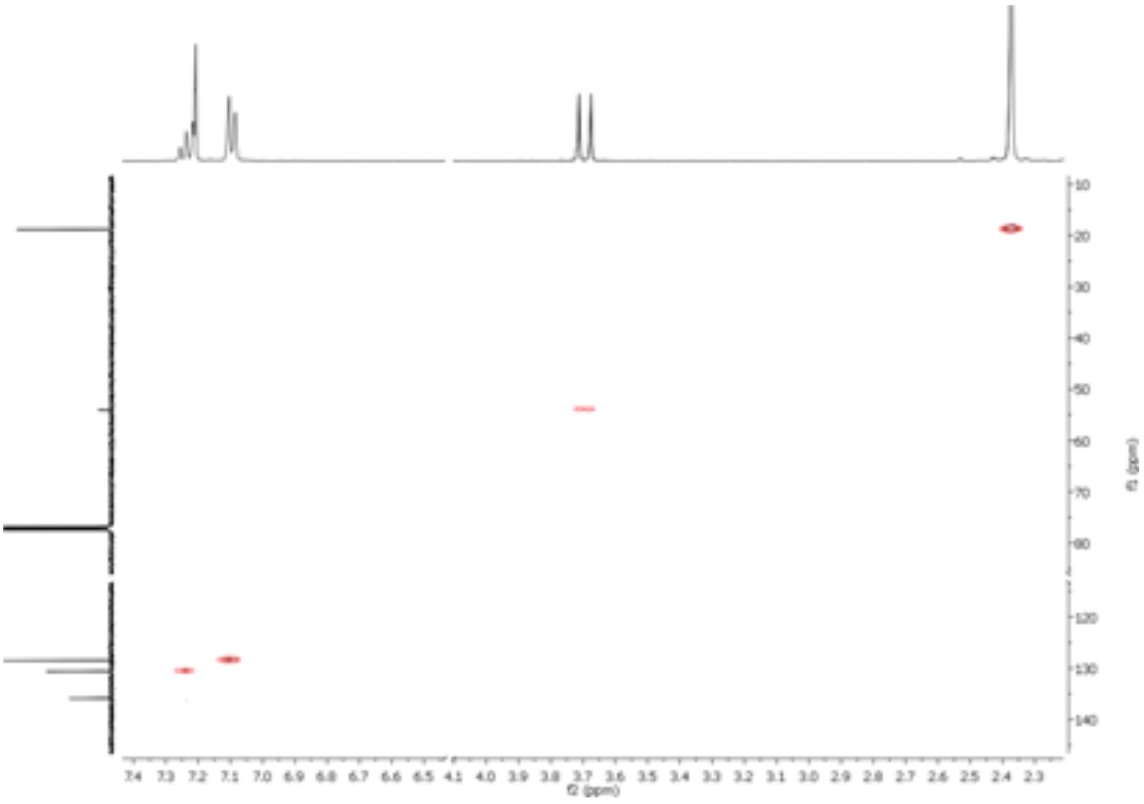


Figure S6. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 3c, [Ni{$S_2P(O)(OMe)$}$(CNXyl)_2$].

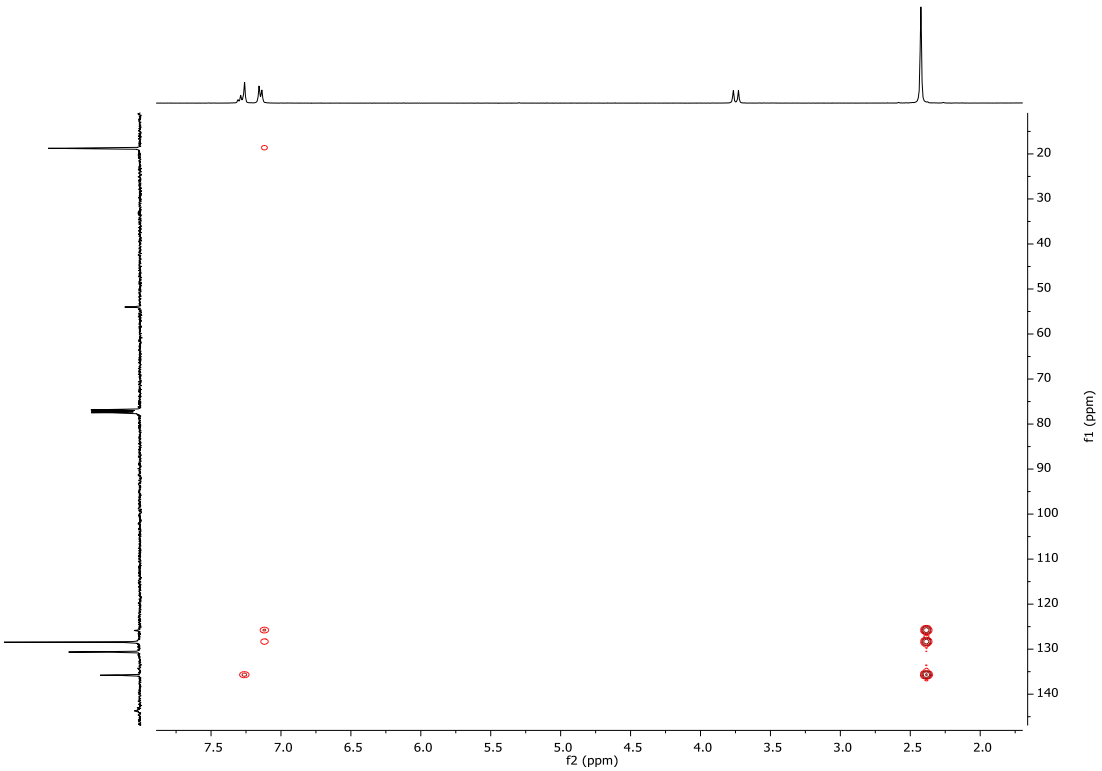


Figure S7. ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR ($CDCl_3$) of compound 3c, [Ni{$S_2P(O)(OMe)$}$(CNXyl)_2$].

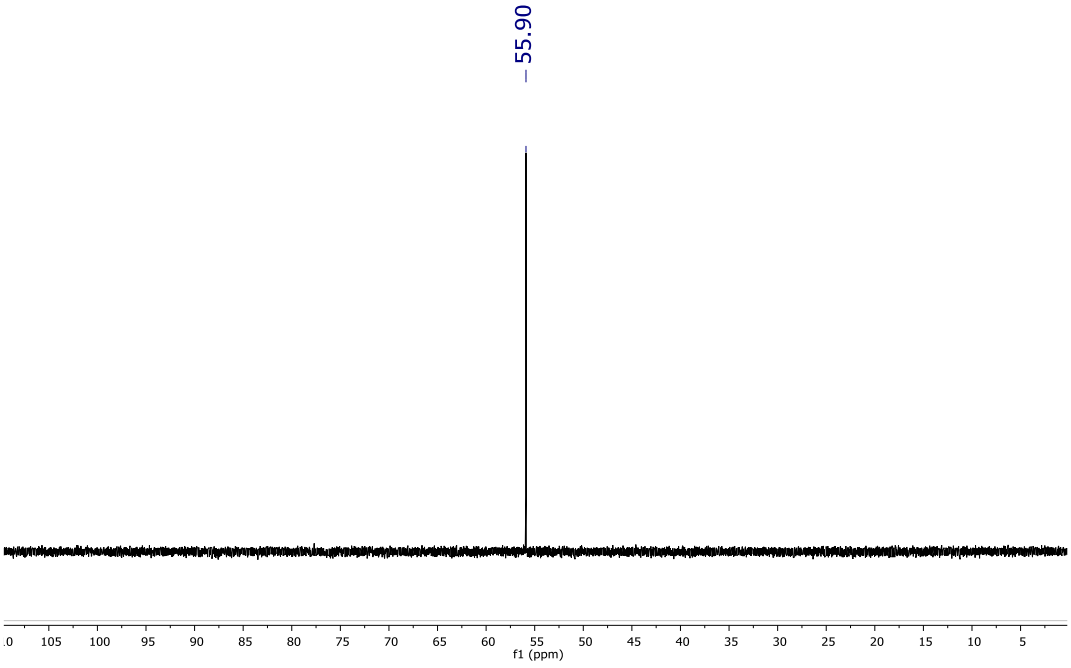


Figure S8. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 3c, [Ni{$S_2P(O)(OMe)$}$(CNXyl)_2$].

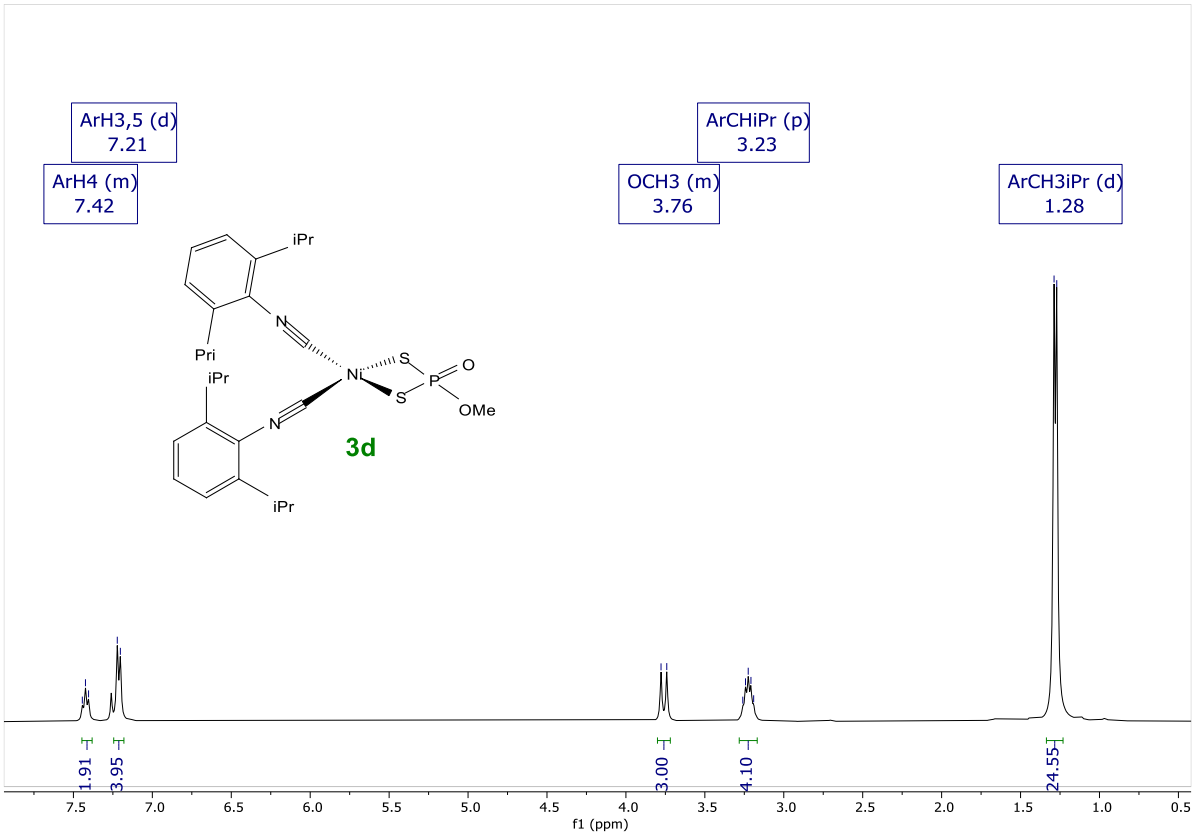


Figure S 9. ^{1}H NMR ($CDCl_3$) of compound 3d, [Ni{$S_2P(O)(OMe)$}$(CNAr)_2$].

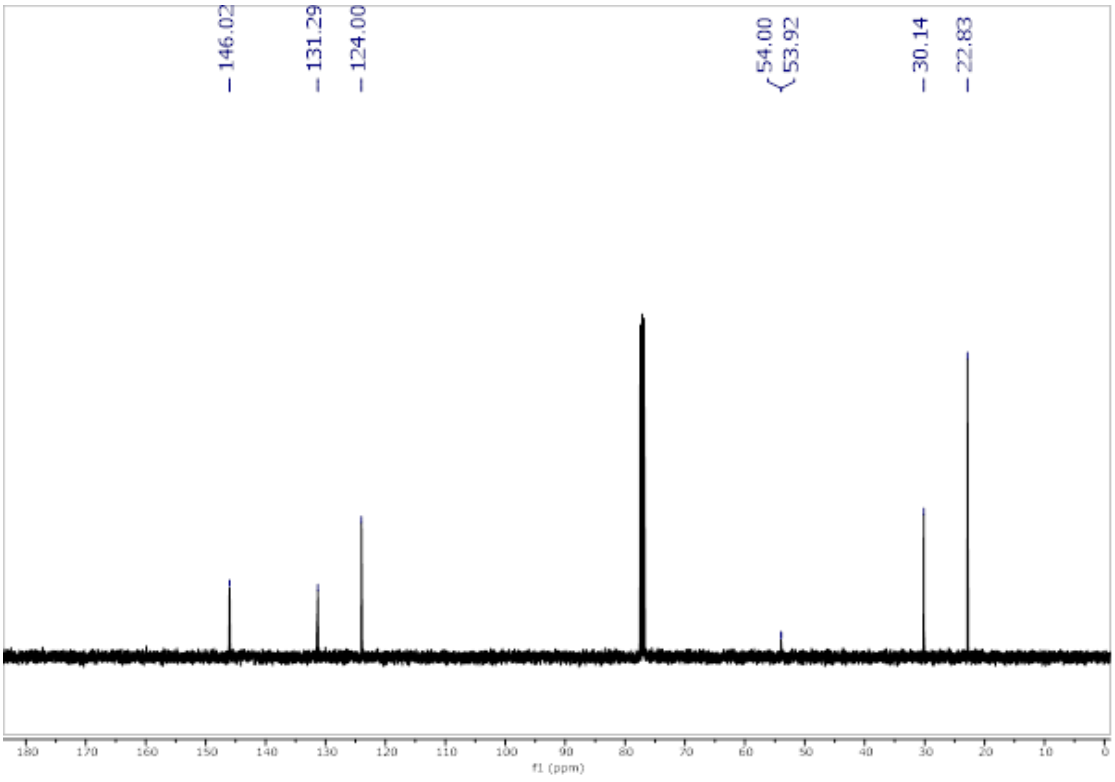


Figure S10. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 3d, [Ni{$S_2P(O)(OMe)$}$(CNAr)_2$].

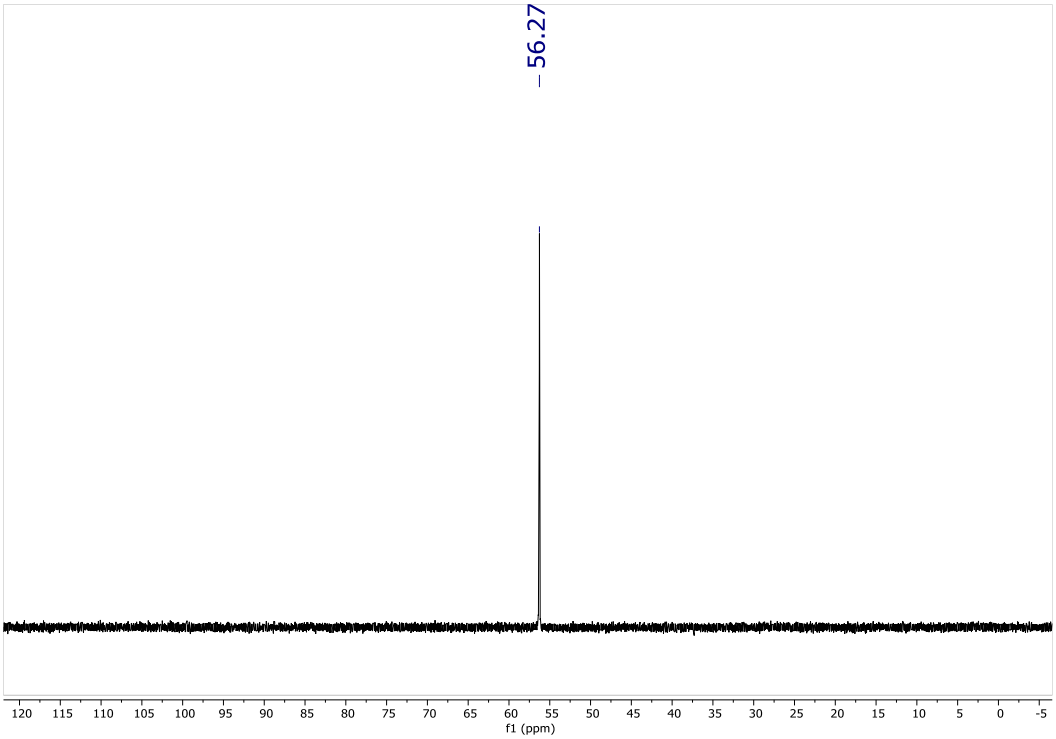


Figure S11. $^{31}P\{^{1}H\}$ NMR (CDCl3) of compound 3d, [Ni{S2P(O)(OMe)}(CNAr)2].

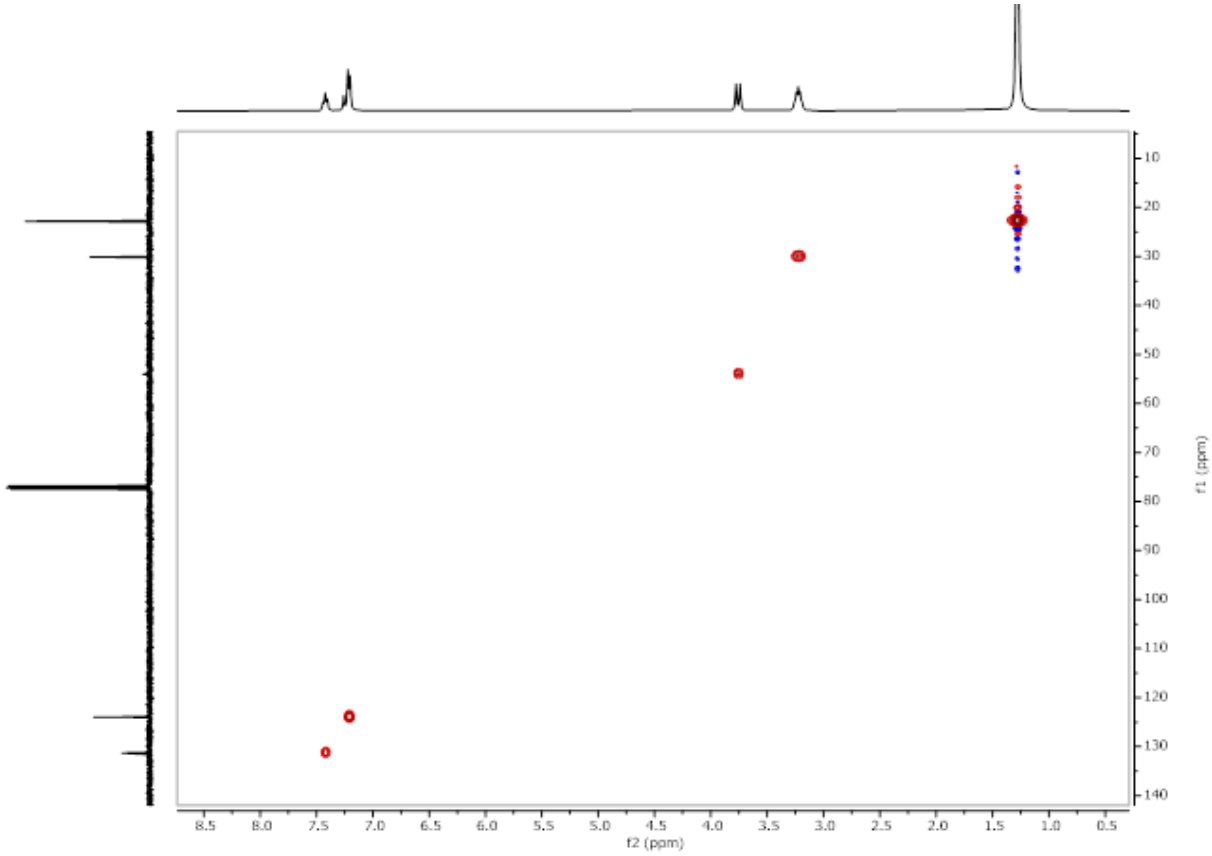


Figure S 12. ^{1}H-$^{13}C\{^{1}H\}$ HSQC ($CDCl_3$) of compound 3d, [Ni{S_2P(O)(OMe)}$(CNAr)_2$].

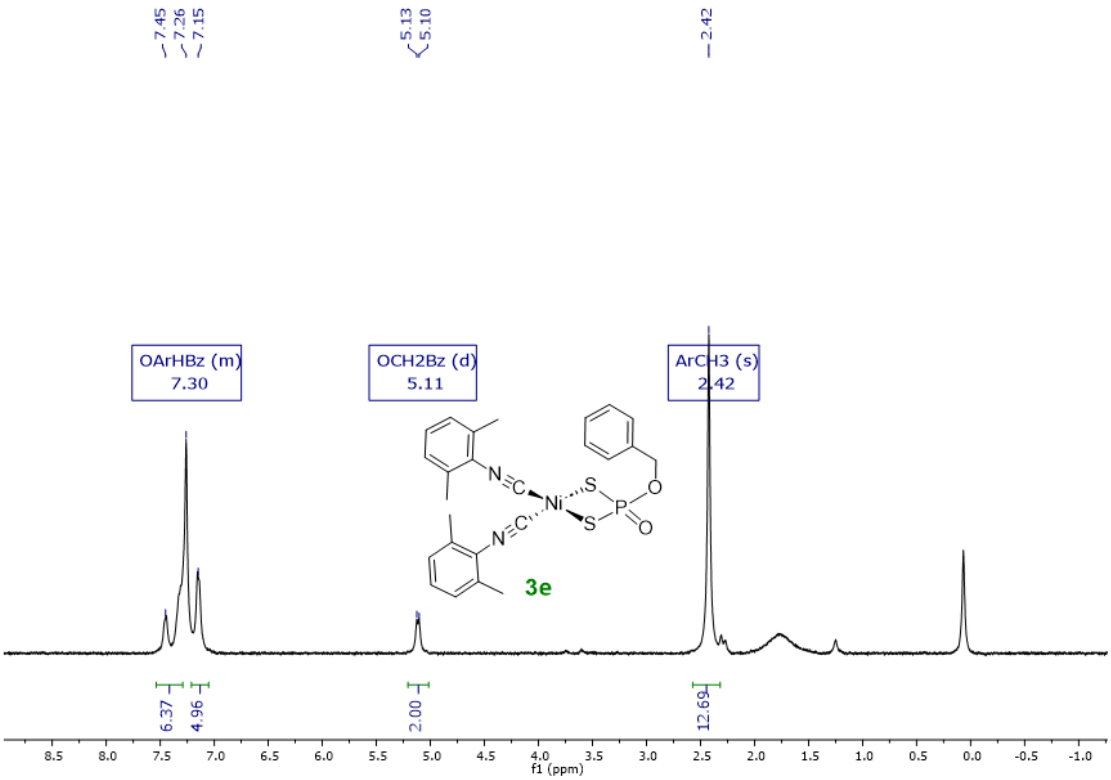


Figure S13. ^{1}H NMR ($CDCl_3$) of compound 3e, [Ni{$S_2P(O)(OBz)$}$(CNXyl)_2$].

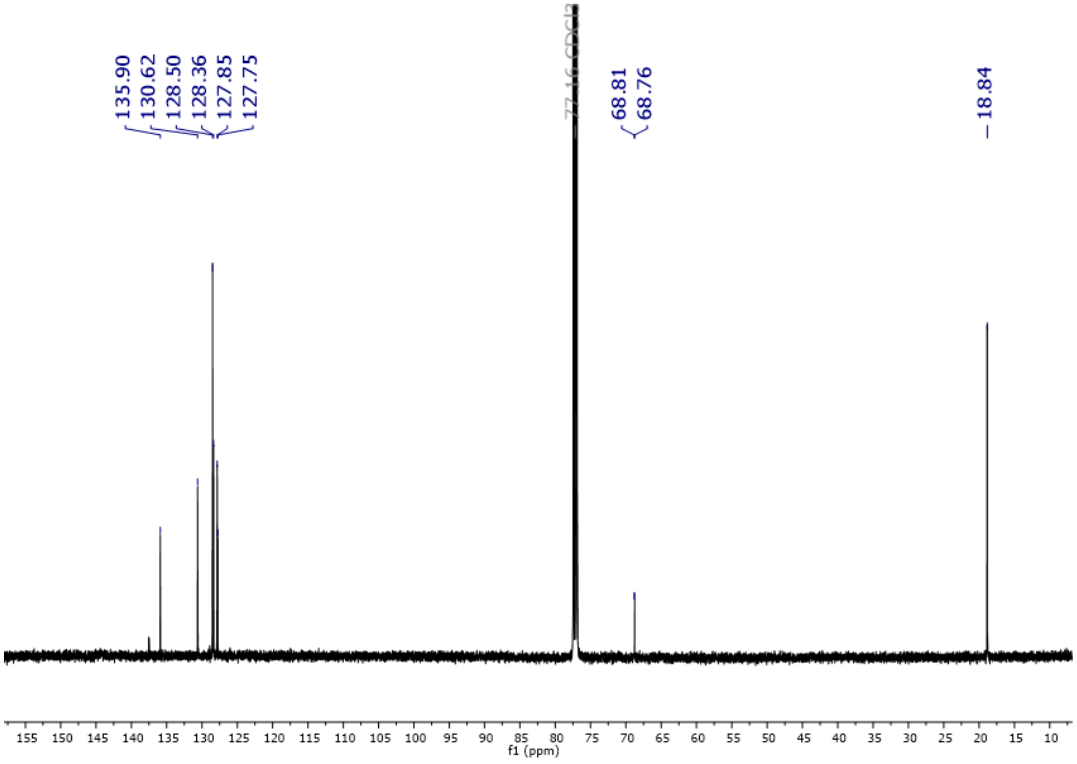


Figure S14. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 3e, [Ni{$S_2P(O)(OBz)$}$(CNXyl)_2$].

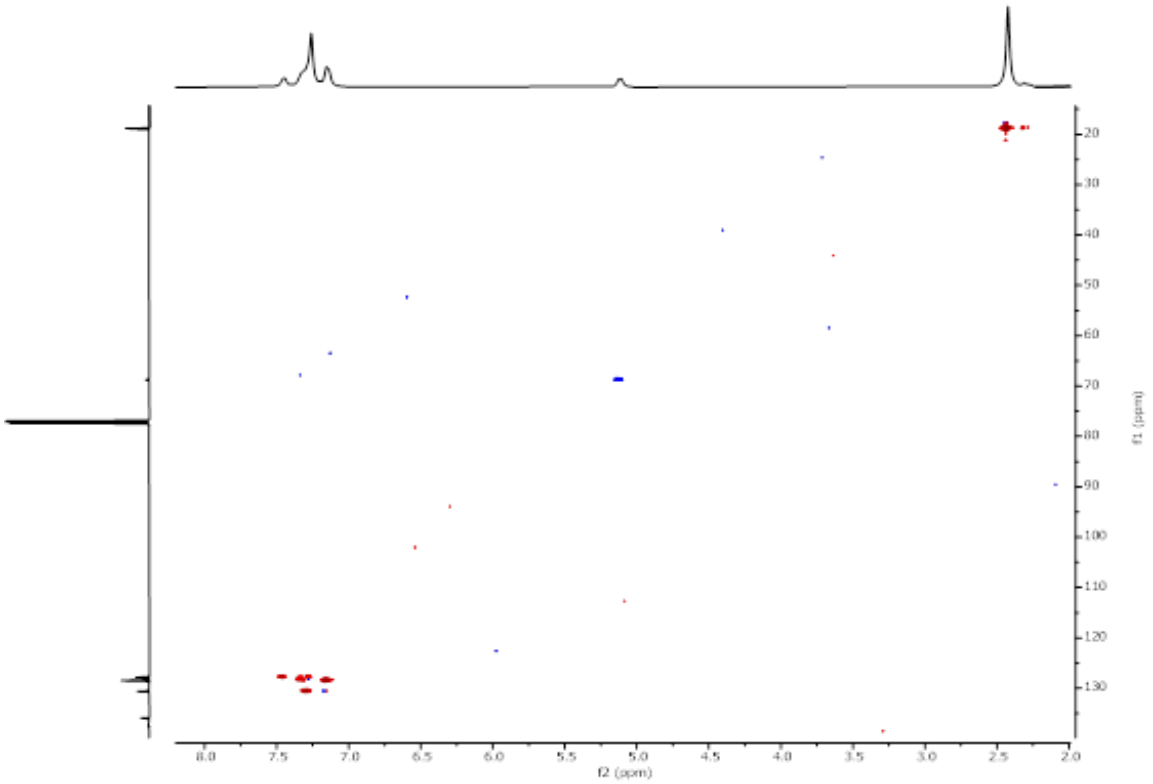


Figure S 15. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 3e, $[Ni\{S_2P(O)(OBz)\}(CNXyl)_2]$.

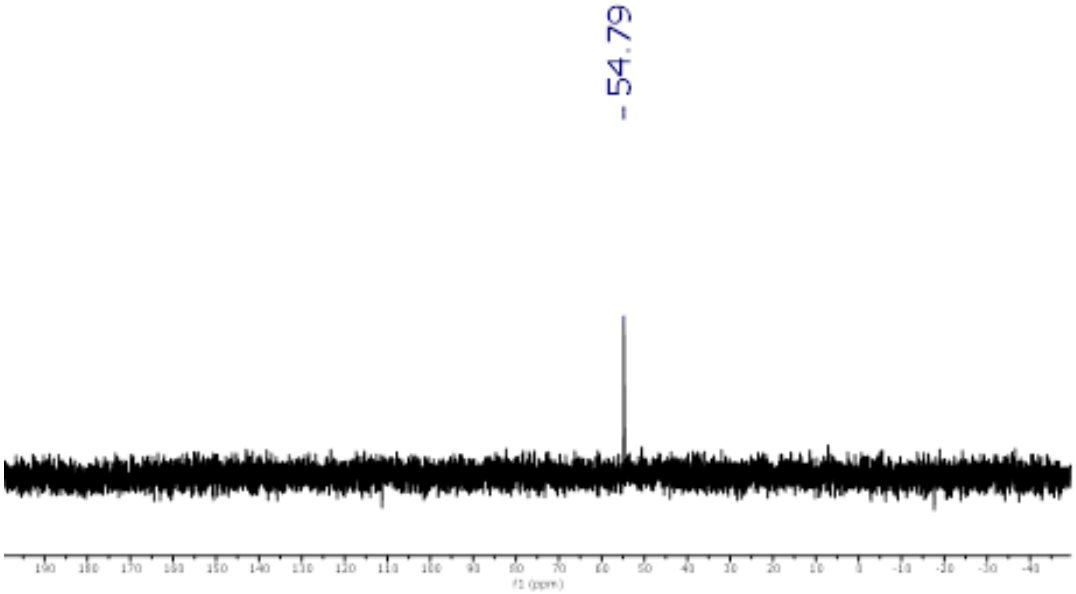


Figure S 16. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 3e, $[Ni\{S_2P(O)(OBz)\}(CNXyl)_2]$.

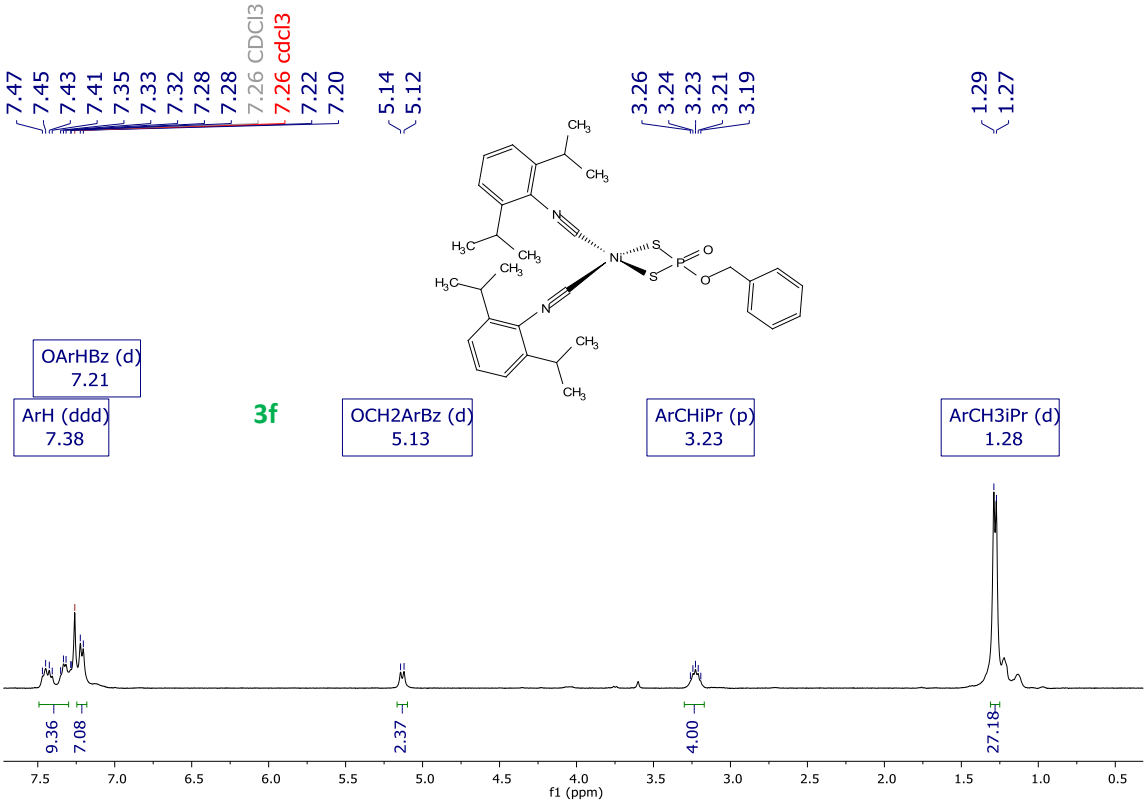


Figure S17. ^{1}H NMR ($CDCl_3$) of compound 3f, [Ni{$S_2P(O)(OBz)$}$(CNAr)_2$].

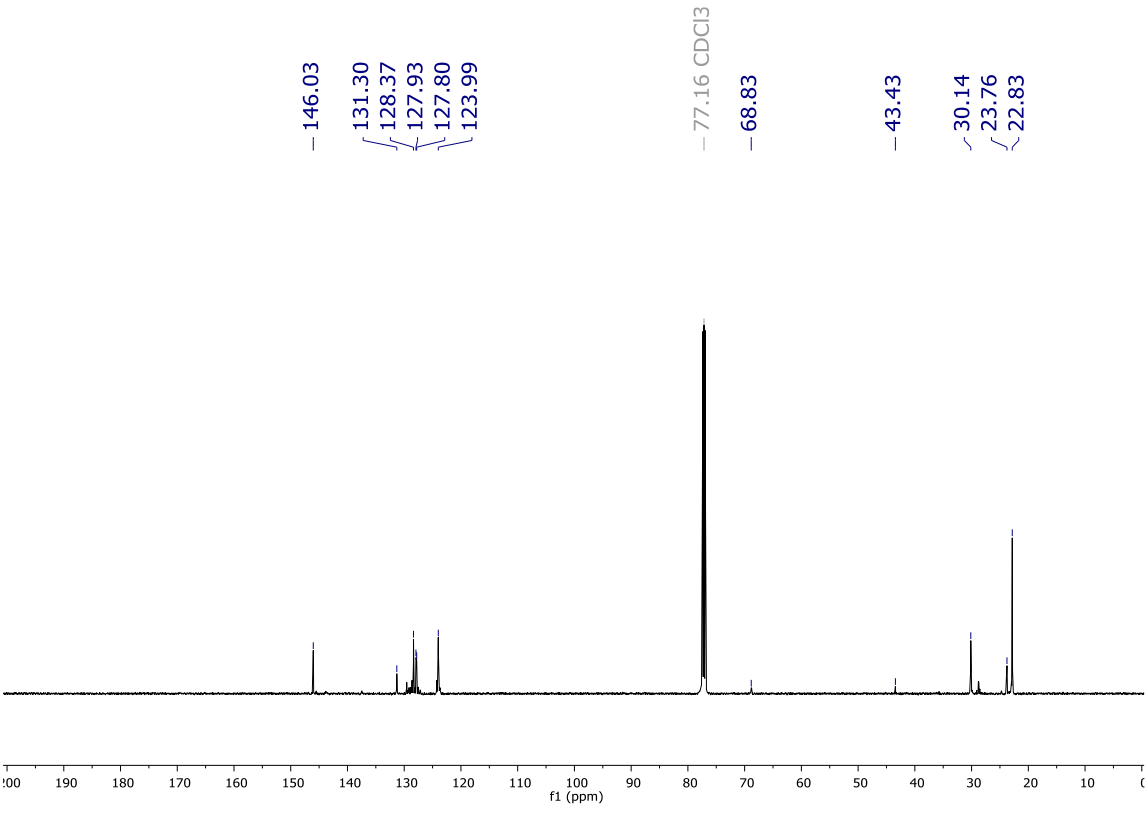


Figure S18. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 3f, [Ni{$S_2P(O)(OBz)$}$(CNAr)_2$].

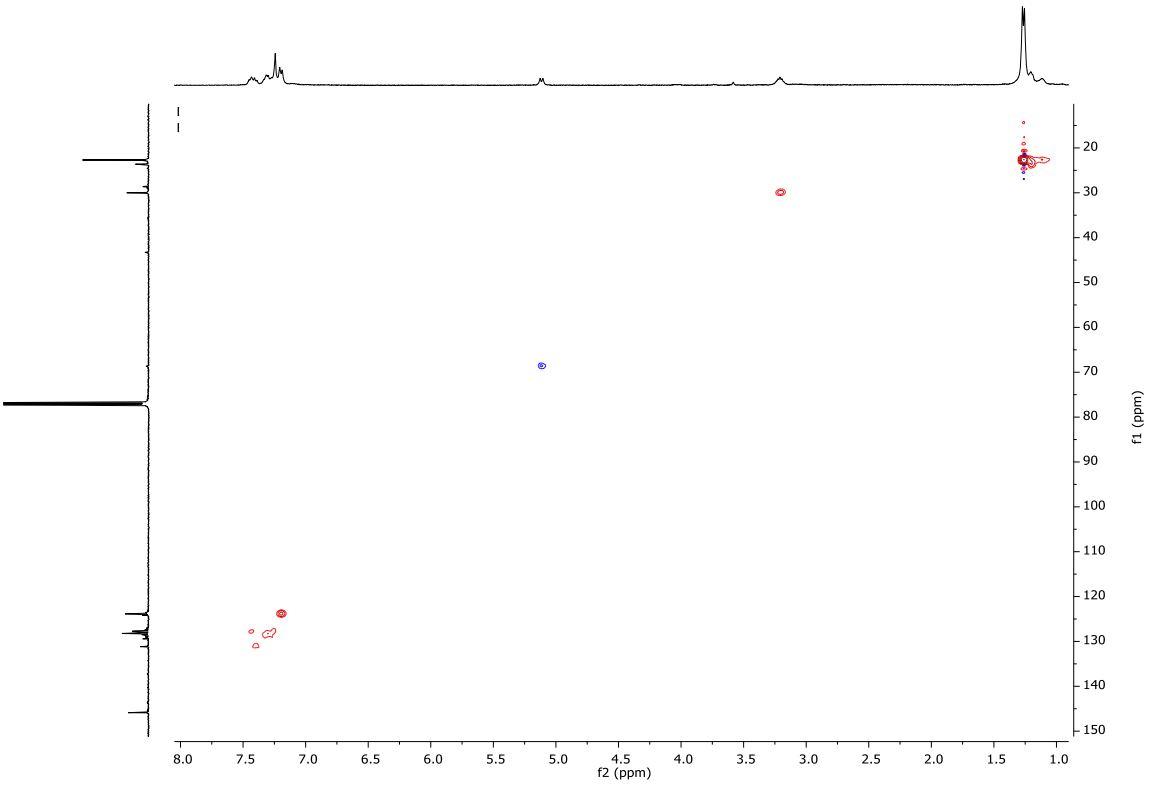


Figure S19. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 3f, [Ni{$S_2P(O)(OBz)$}$(CNAr)_2$].

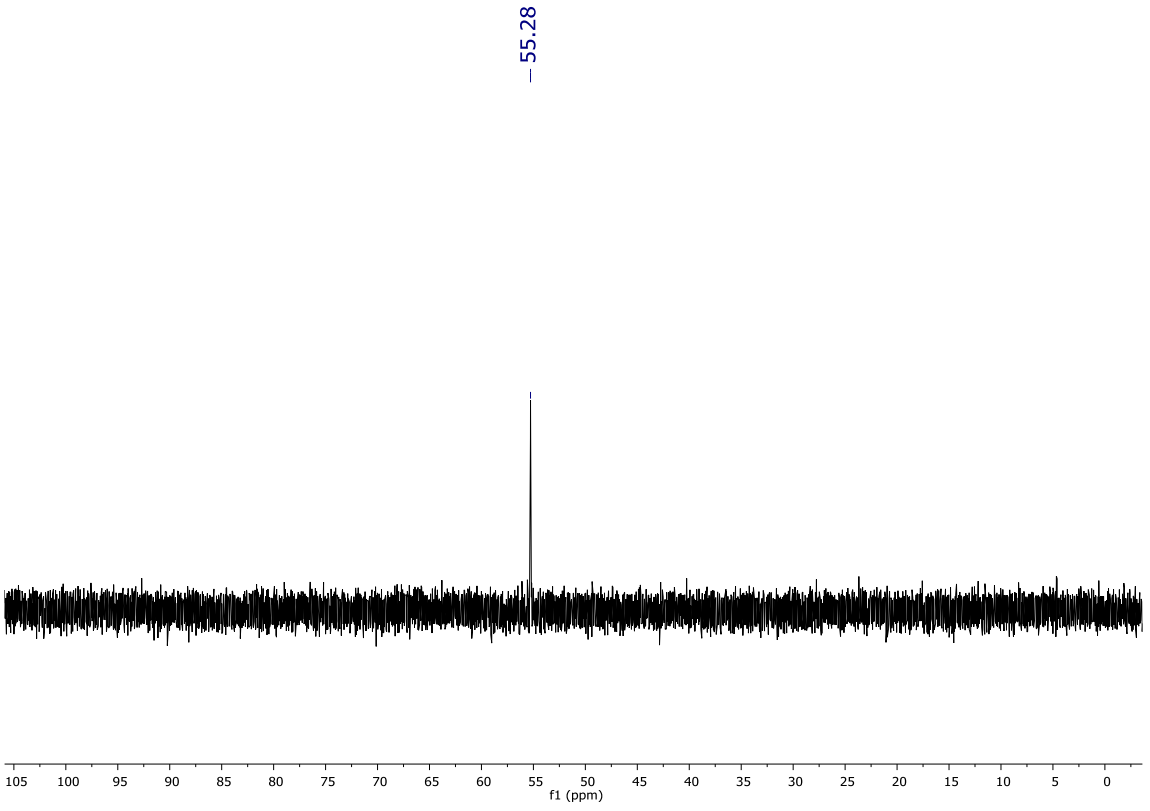


Figure S20. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 3f, [Ni{$S_2P(O)(OBz)$}$(CNAr)_2$].

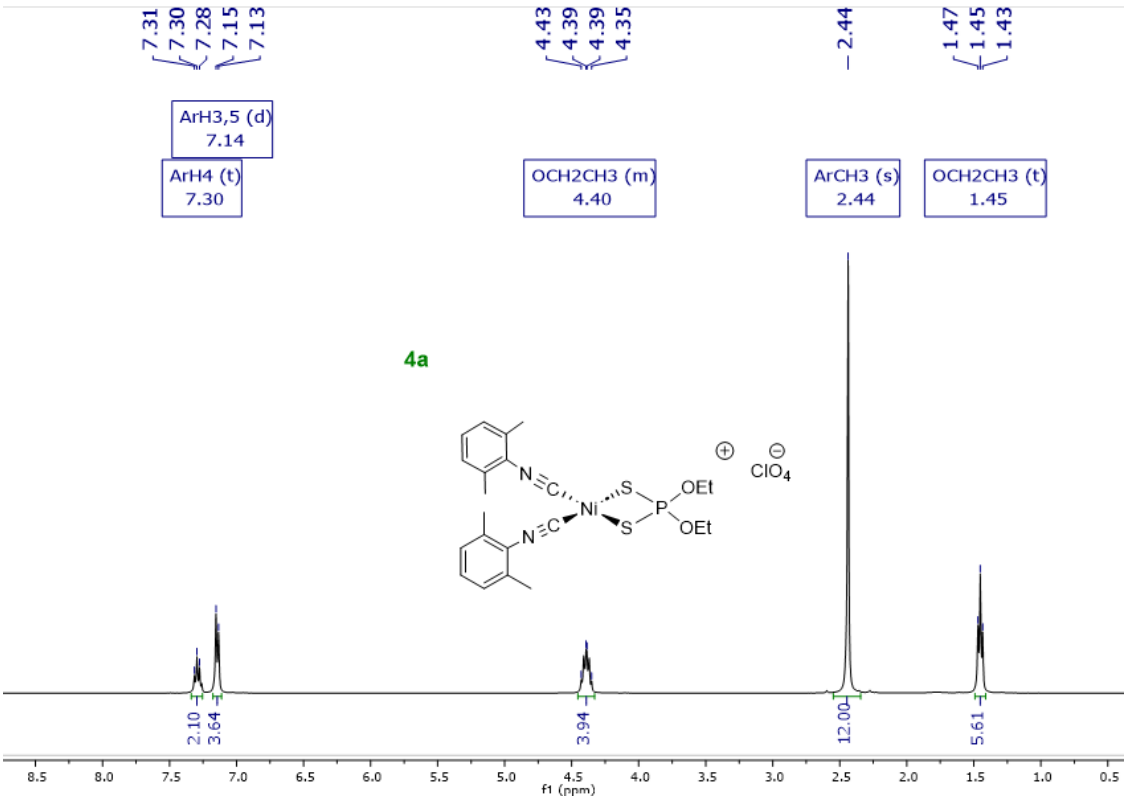


Figure S21. ^{1}H NMR ($CDCl_3$) of compound 4a, $[Ni\{S_2P(OEt)_2\}(CNXyl)_2]ClO_4$.

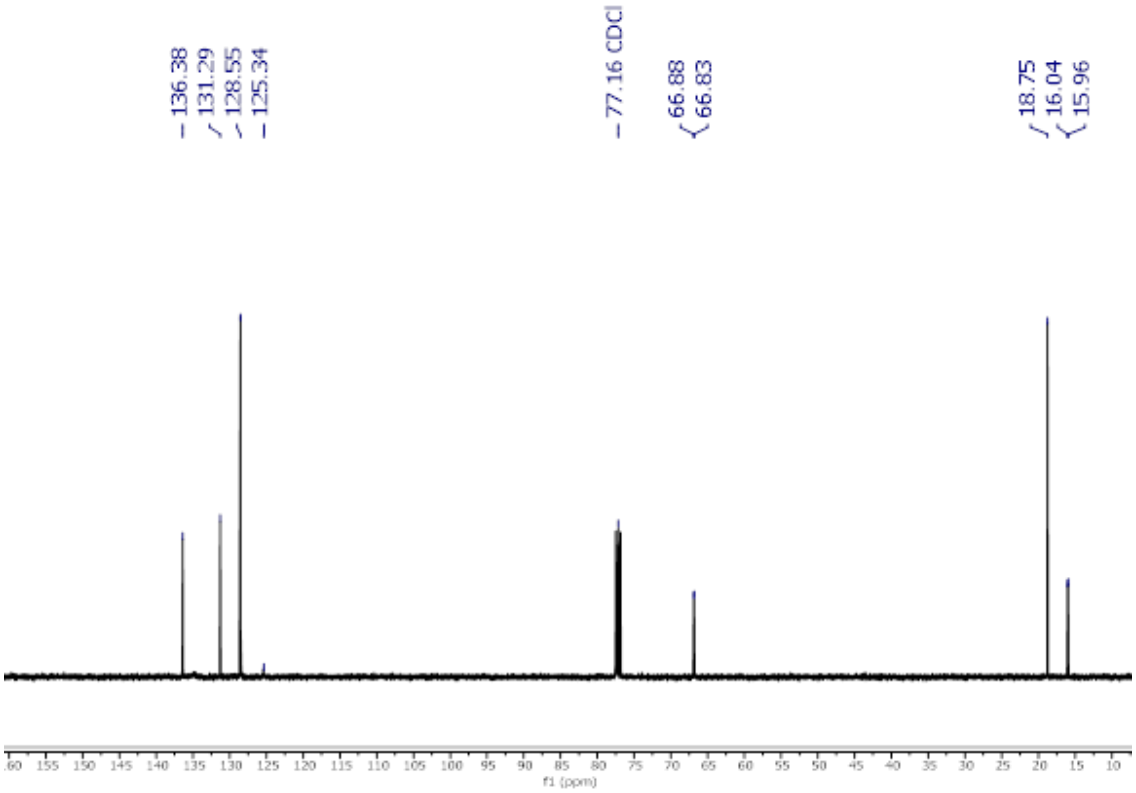


Figure S 22. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 4a, $[Ni\{S_2P(OEt)_2\}(CNXyl)_2]ClO_4$.

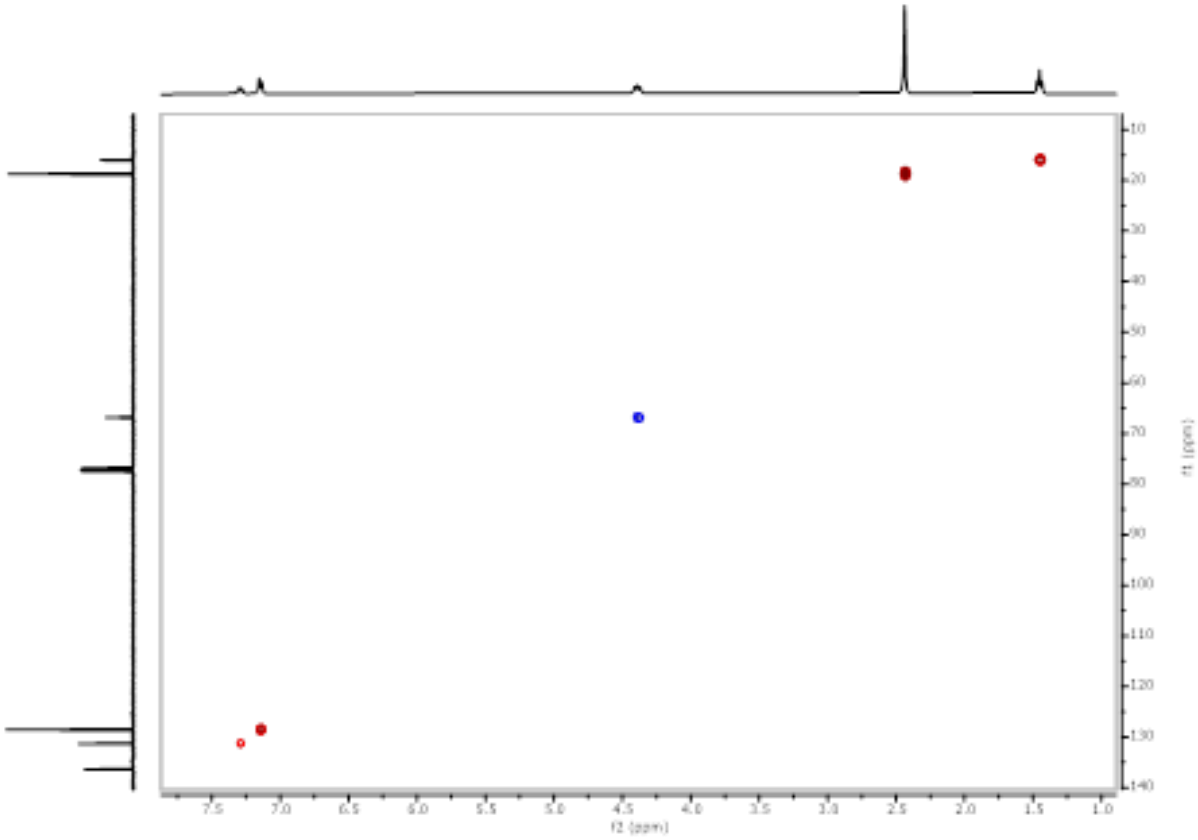


Figure S 23. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 4a, $[Ni\{S_2P(OEt)_2\}(CNXyl)_2]ClO_4$.

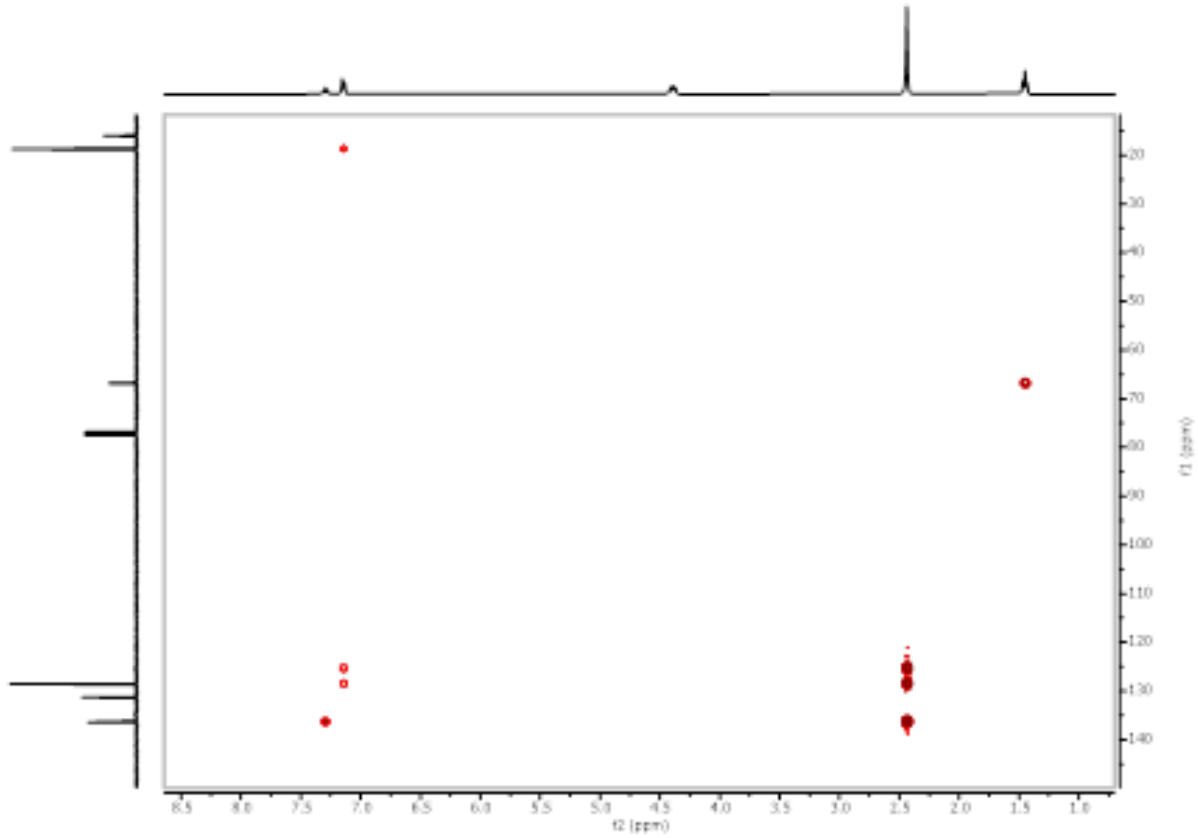


Figure S 24. ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR ($CDCl_3$) of compound 4a, $[Ni\{S_2P(OEt)_2\}(CNXyl)_2]ClO_4$.

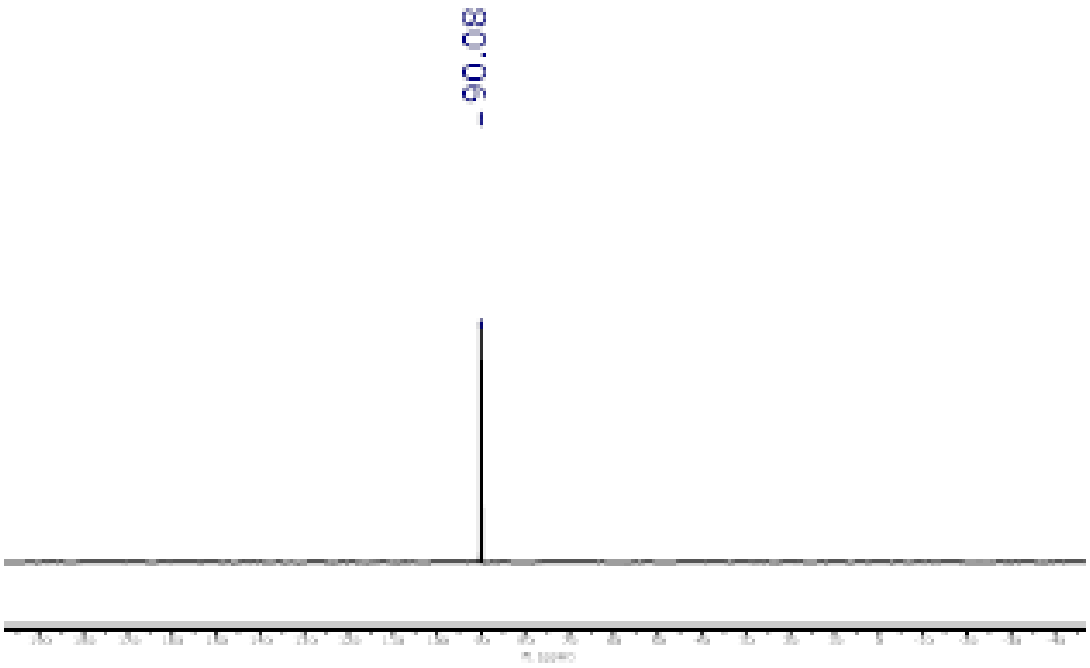


Figure S 25. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 4a, $[Ni\{S_2P(OEt)_2\}(CNAr)_2]ClO_4$.

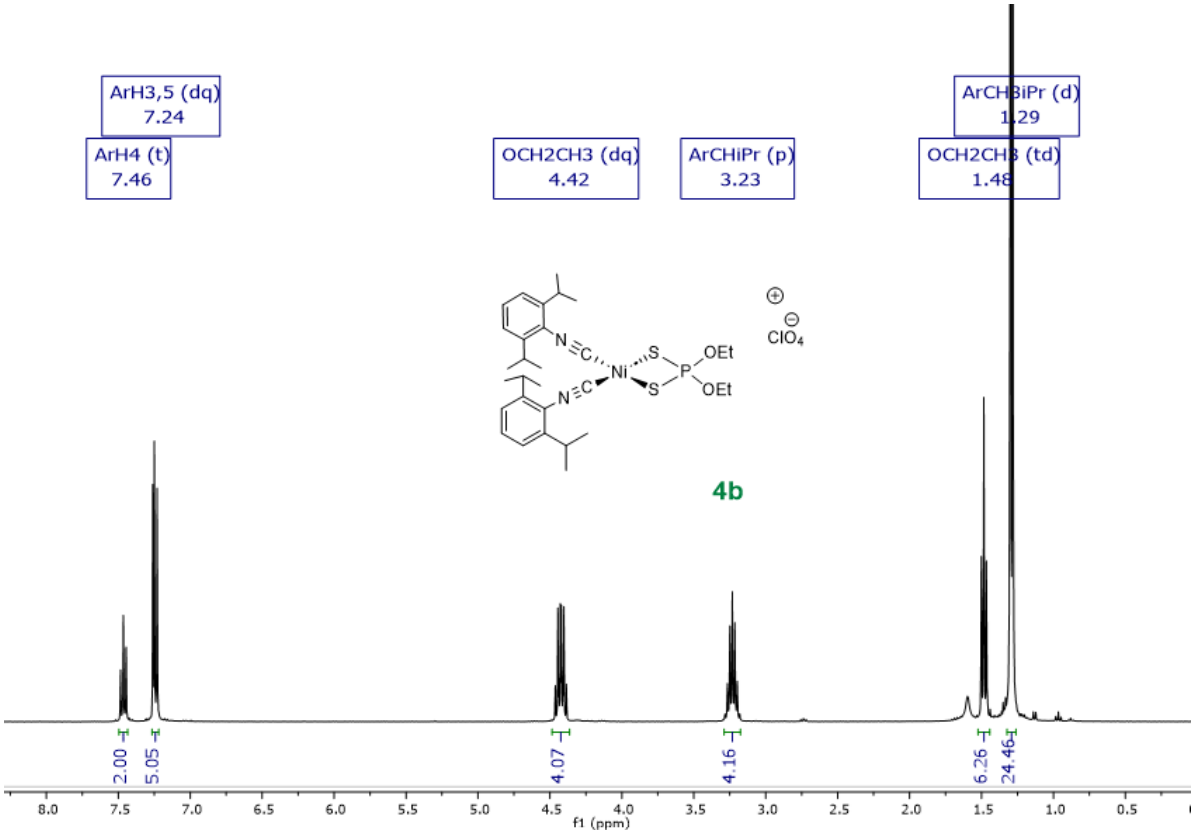


Figure S 26. ^{1}H NMR ($CDCl_3$) of compound 4b, $[Ni\{S_2P(OEt)_2\}(CNAr)_2]ClO_4$.

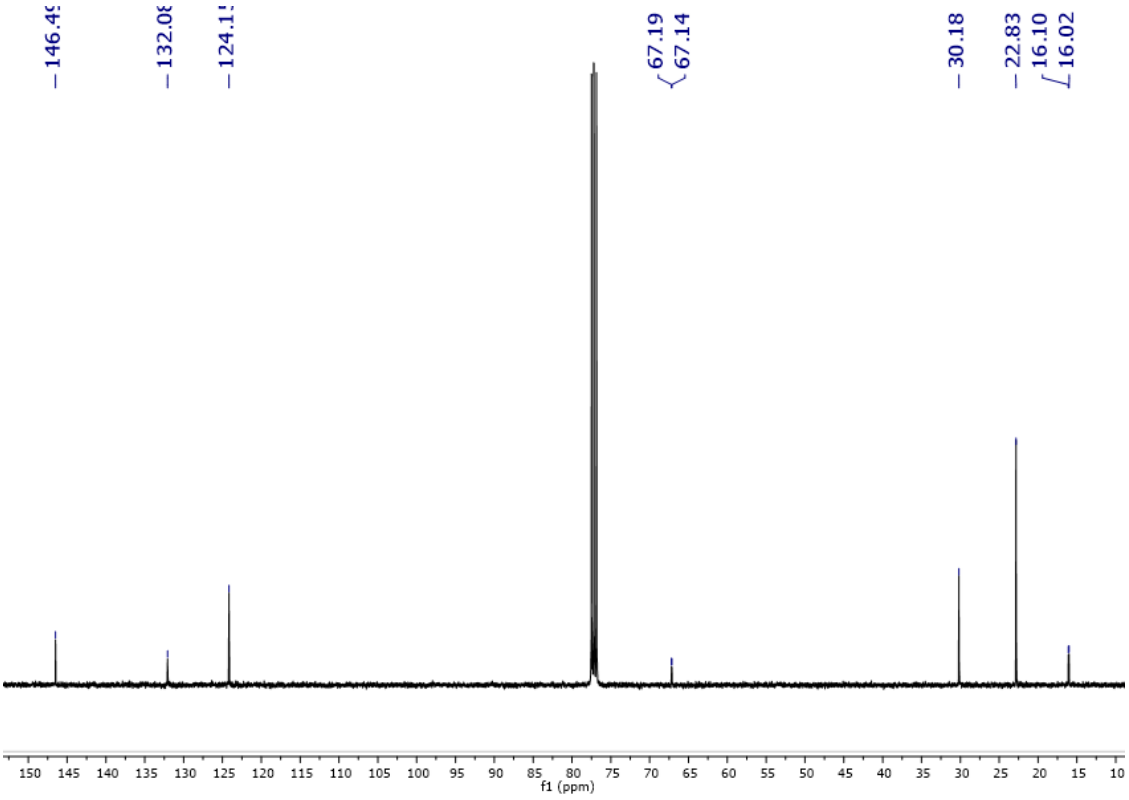


Figure S 27. $^{13}C\{^1H\}$ NMR ($CDCl_3$) of compound 4b, $[Ni\{S_2P(OEt)_2\}(CNAr)_2]ClO_4$.

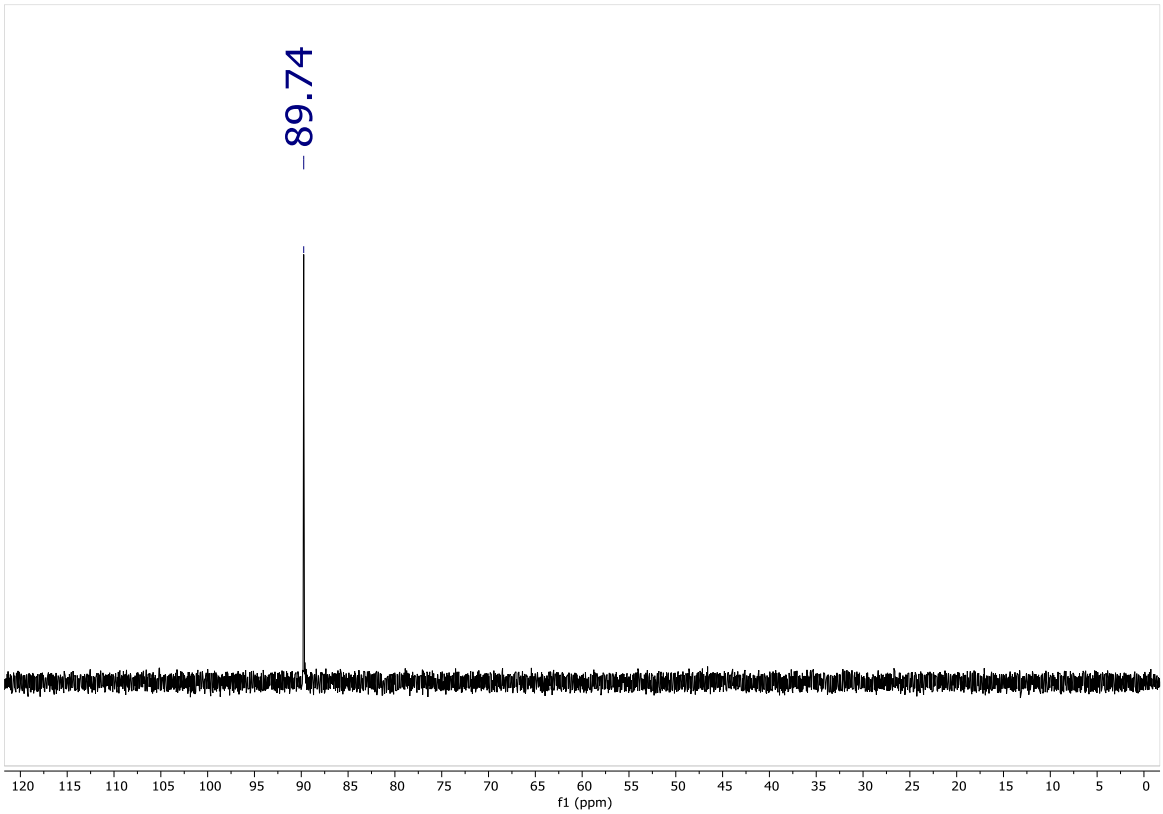


Figure S 28. $^{31}P\{^1H\}$ NMR ($CDCl_3$) of compound 4b, $[Ni\{S_2P(OEt)_2\}(CNAr)_2]ClO_4$.

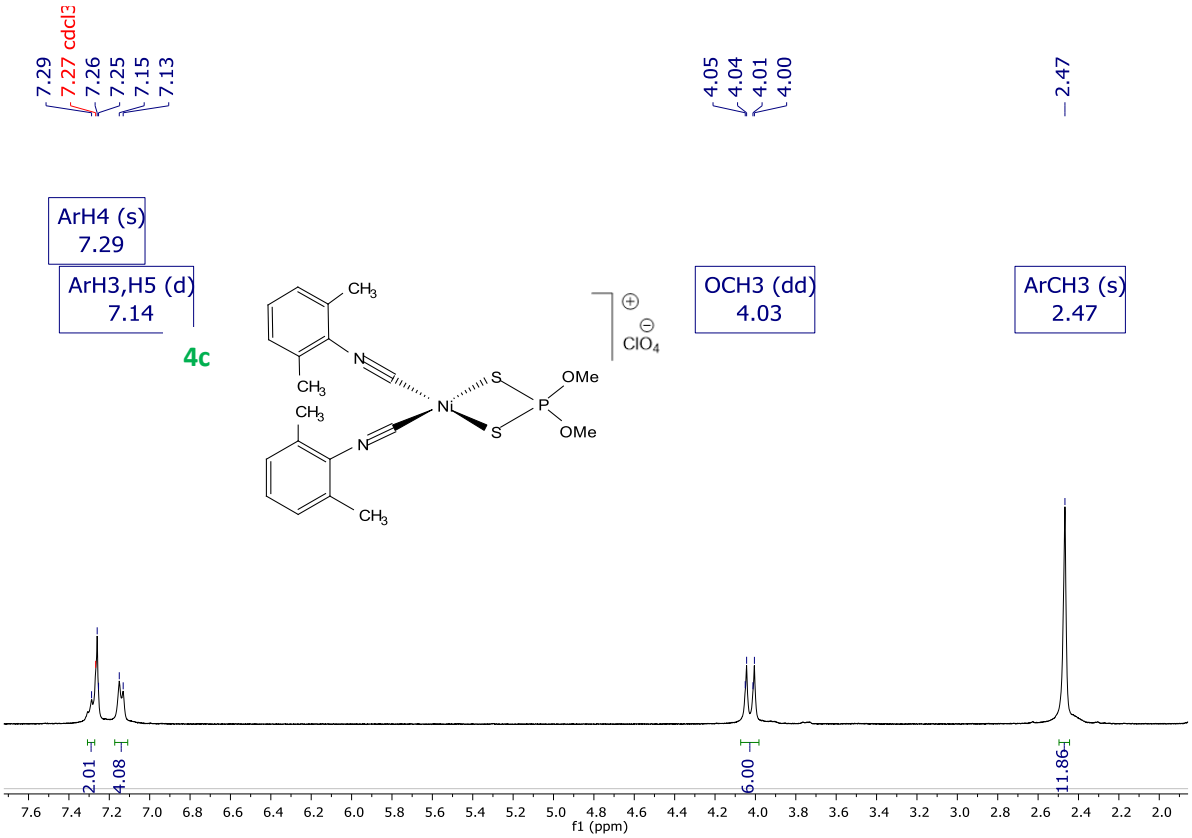


Figure S29. ^{1}H NMR ($CDCl_3$) of compound 4c, [Ni{$S_2P(OMe)_2$}$(CNXyl)_2$]ClO_4.

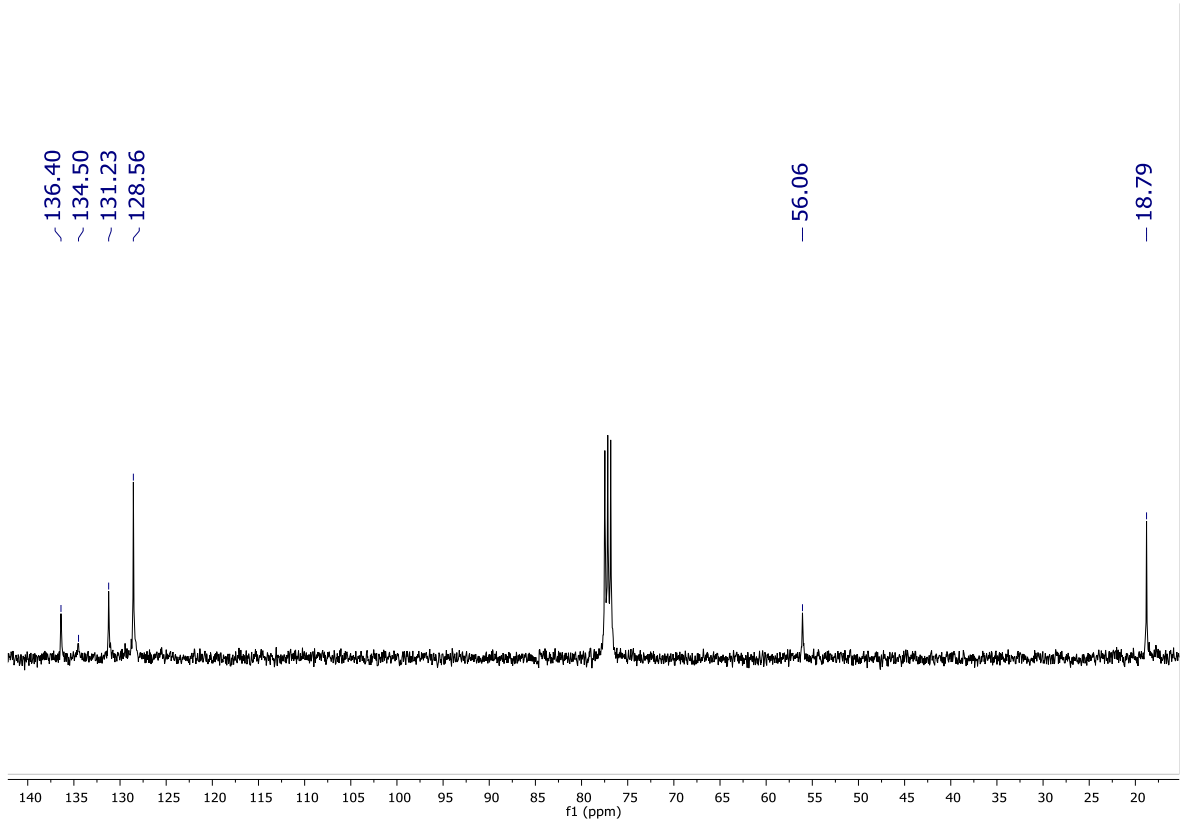


Figure S30. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 4c, [Ni{$S_2P(OMe)_2$}$(CNXyl)_2$]ClO_4.

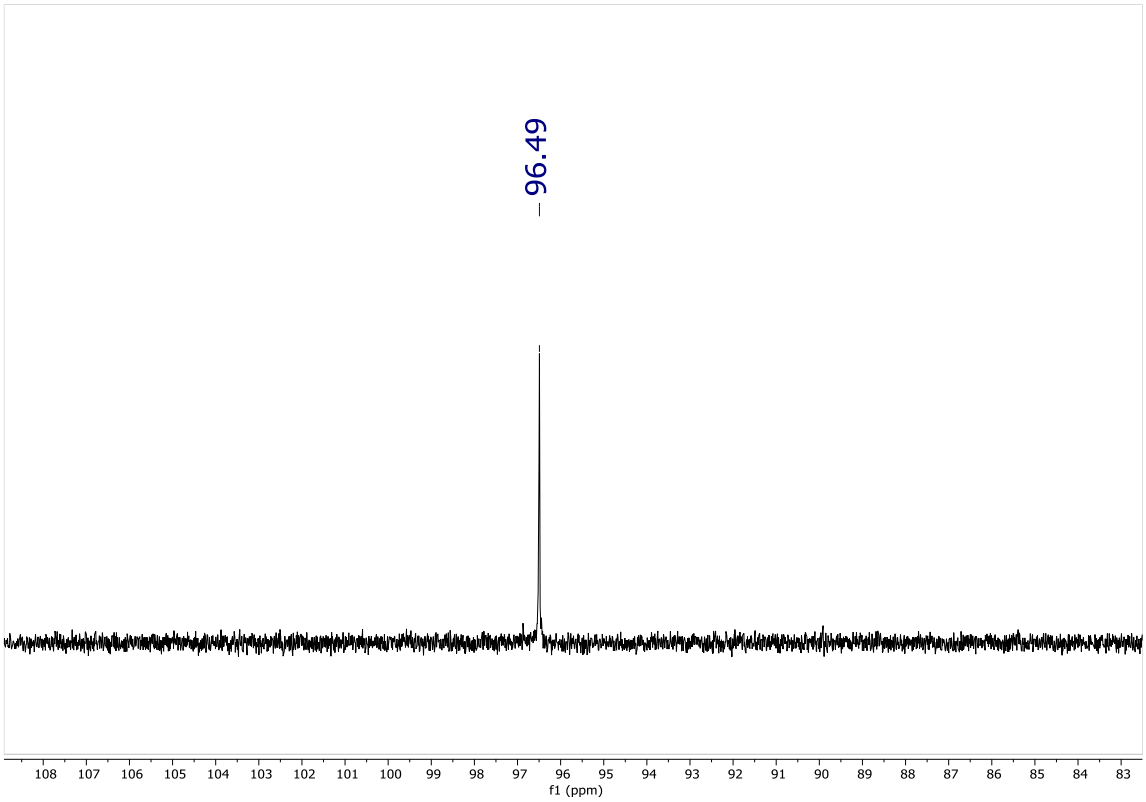


Figure S31. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 4c, $[Ni\{S_2P(OMe)_2\}(CNXyl)_2]ClO_4$.

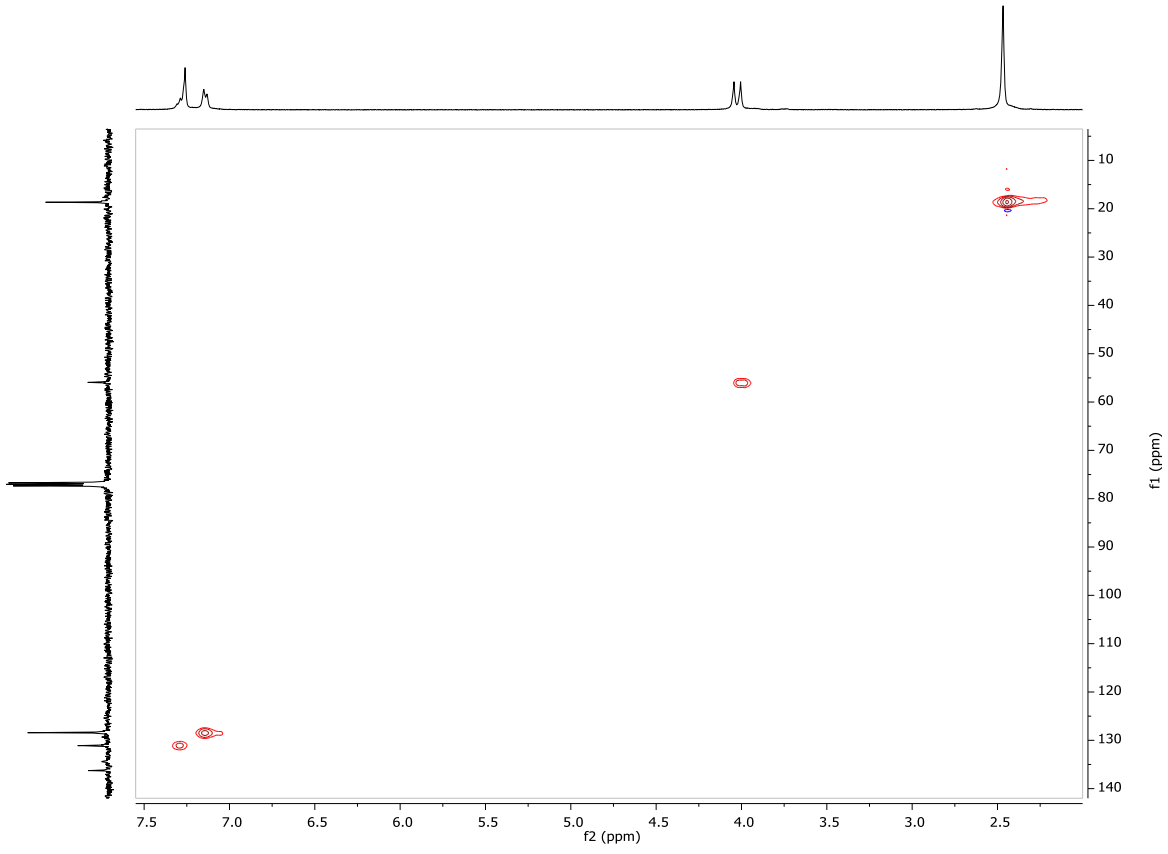


Figure S32. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 4c, $[Ni\{S_2P(OMe)_2\}(CNXyl)_2]ClO_4$.

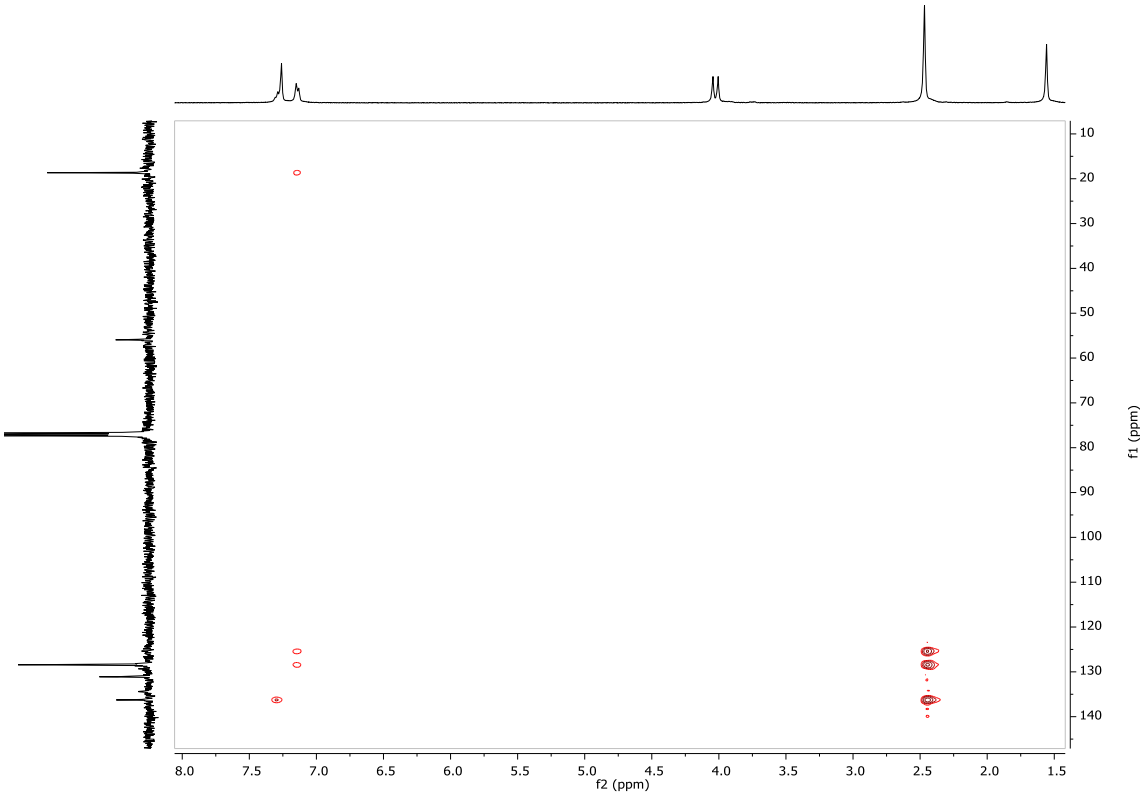


Figure S33. ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR ($CDCl_3$) of compound 4c, $[Ni\{S_2P(OMe)_2\}(CNXyl)_2]ClO_4$.

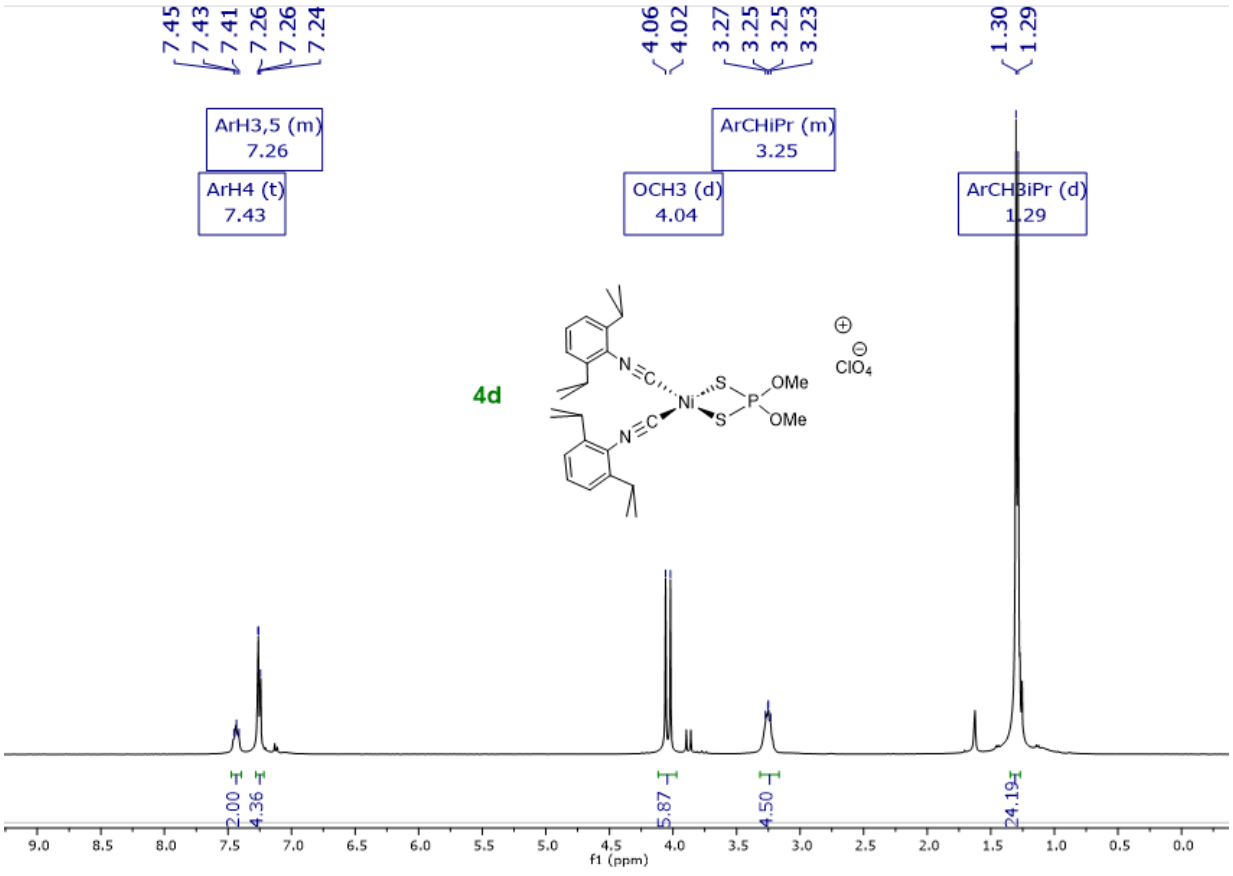


Figure S34. ^{1}H NMR ($CDCl_3$) of compound 4d, $[Ni\{S_2P(OMe)_2\}(CNAr)_2]ClO_4$.

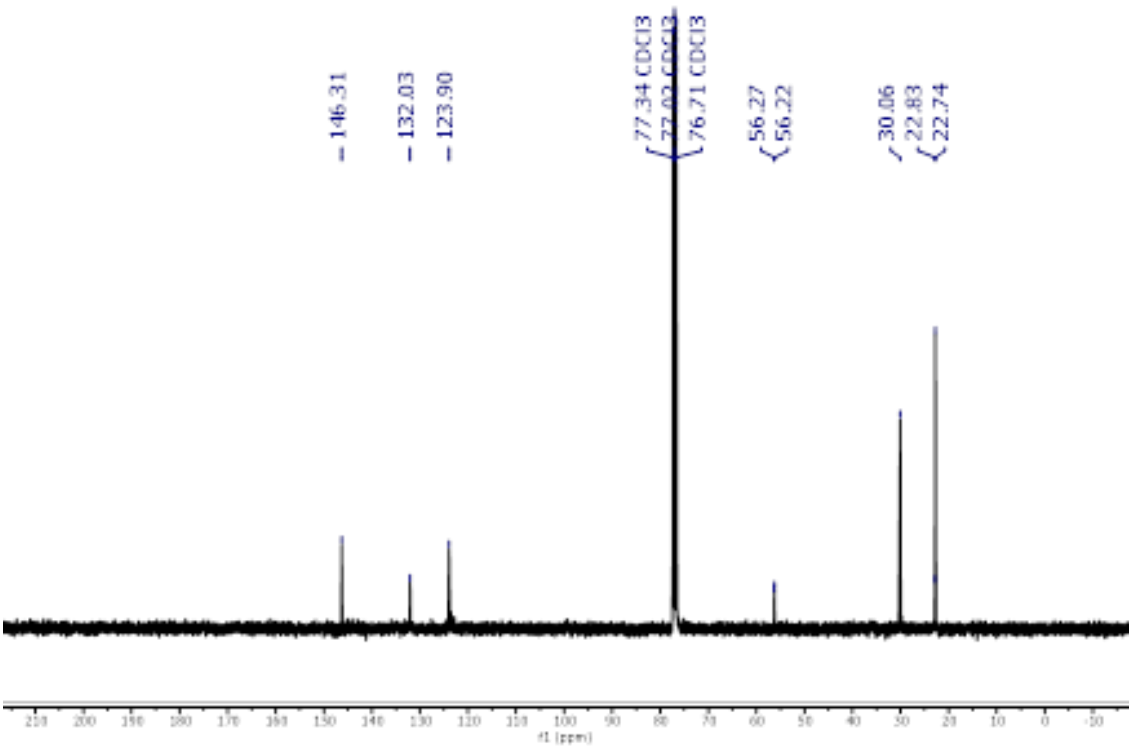


Figure S 35. ^{13}C {^{1}H} NMR ($CDCl_3$) of compound 4d, $[Ni\{S_2P(OMe)_2\}(CNAr)_2]ClO_4$.

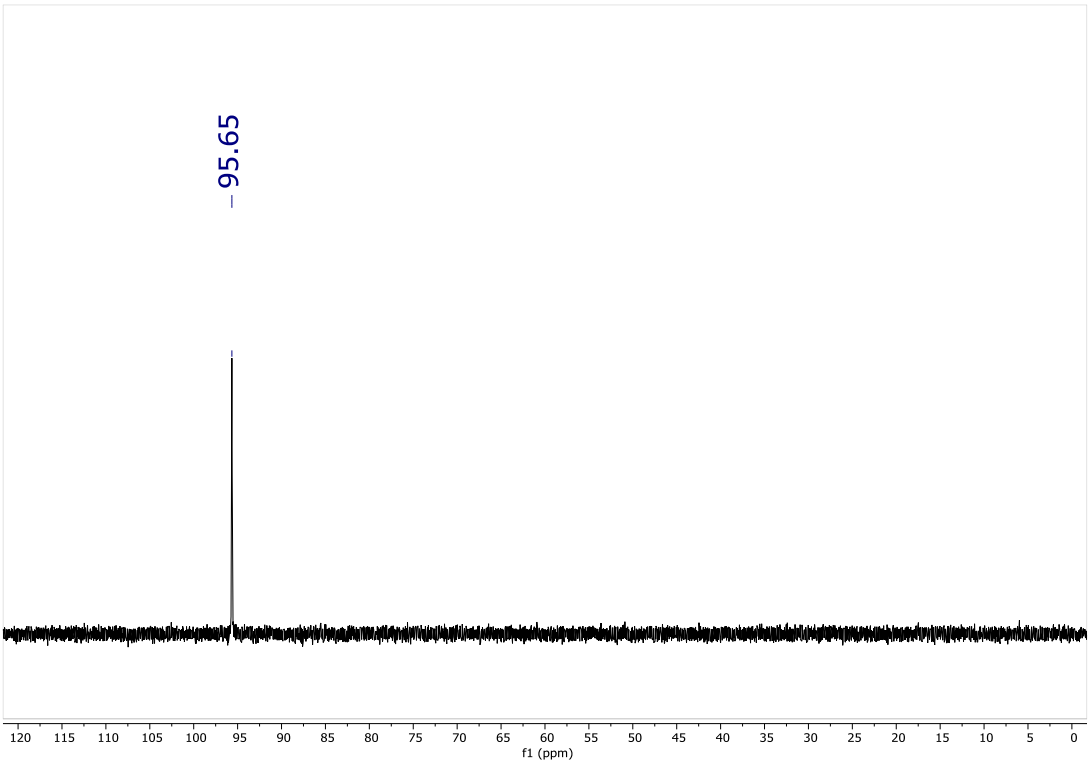


Figure S 36. ^{31}P {^{1}H} NMR ($CDCl_3$) of compound 4d, $[Ni\{S_2P(OMe)_2\}(CNAr)_2]ClO_4$.

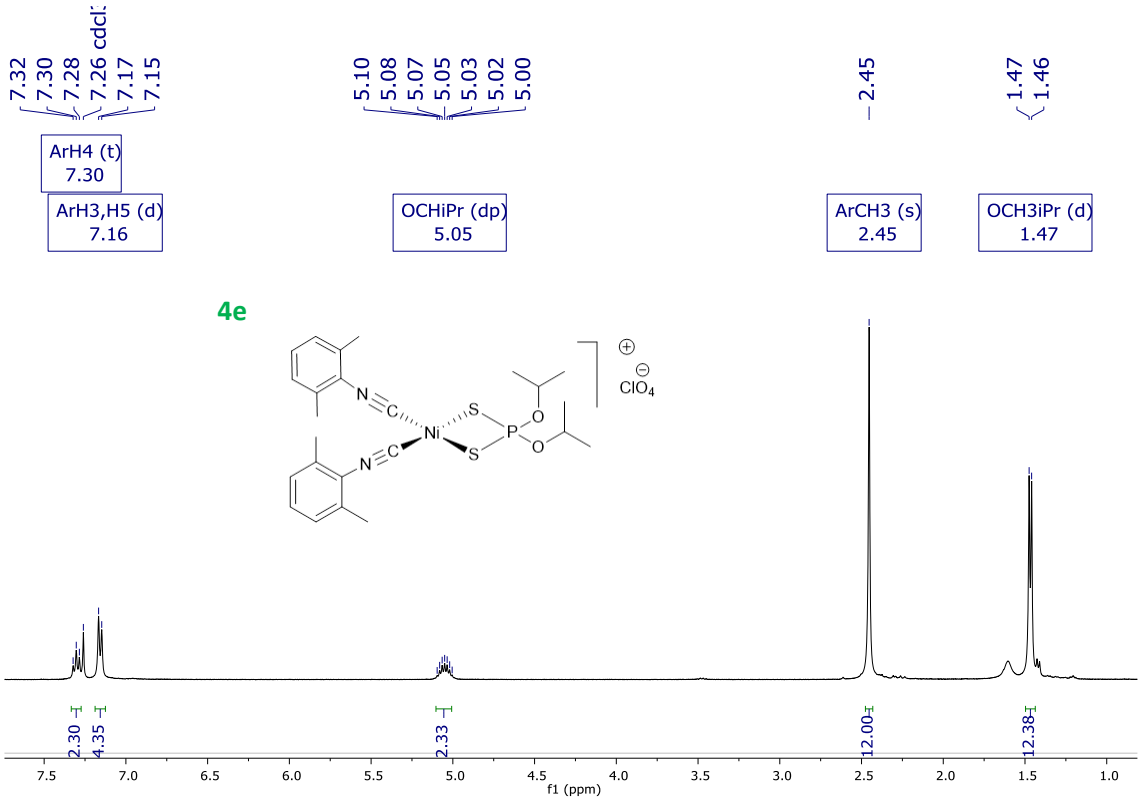


Figure S37. ^{1}H NMR (CDCl3) of compound 4e, [Ni{$S_2P(O^iPr)_2$}(CNXyl)$_2$]ClO_4.

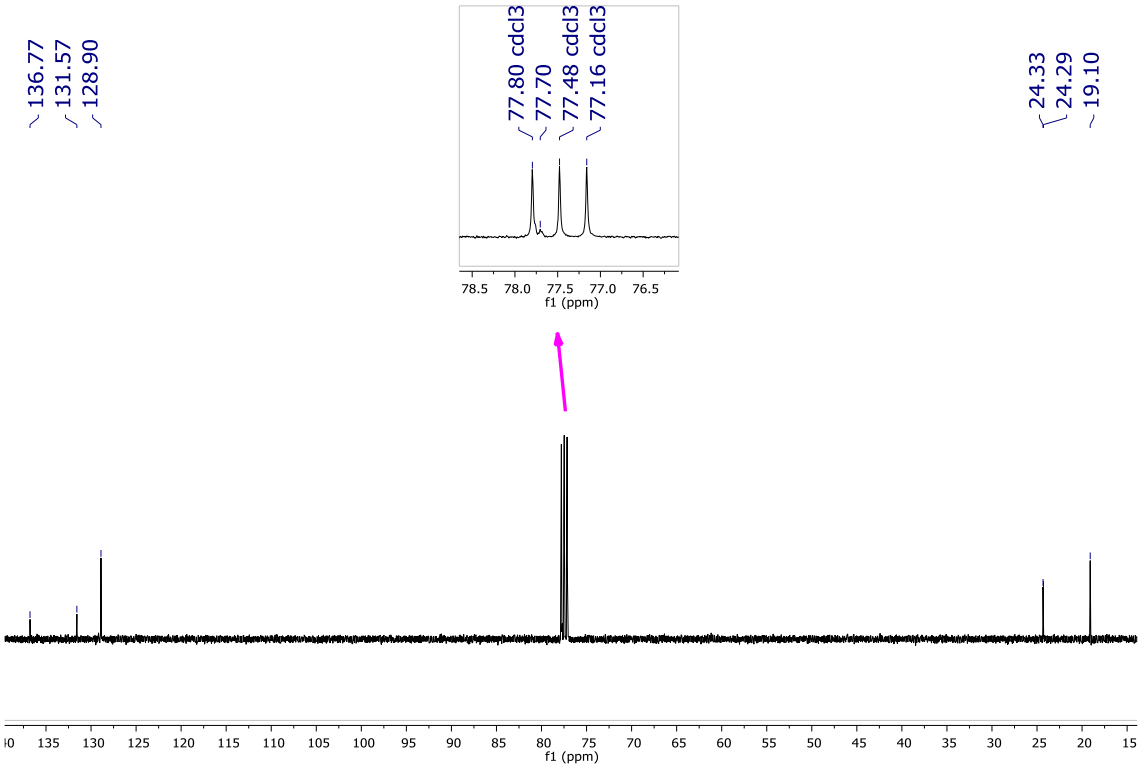


Figure S38. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 4e, [Ni{$S_2P(O^iPr)_2$}(CNXyl)$_2$]ClO_4.

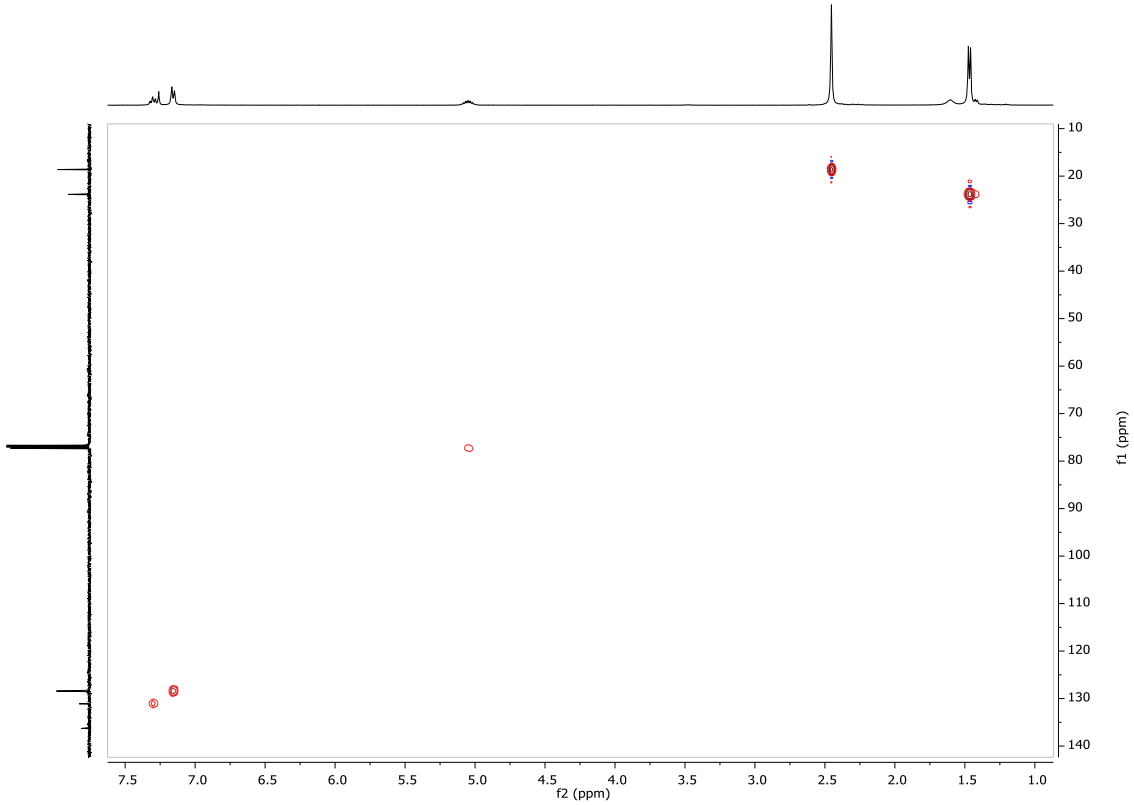


Figure S39. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 4e, $[Ni\{S_2P(O^iPr)_2\}(CNXyl)_2]ClO_4$.

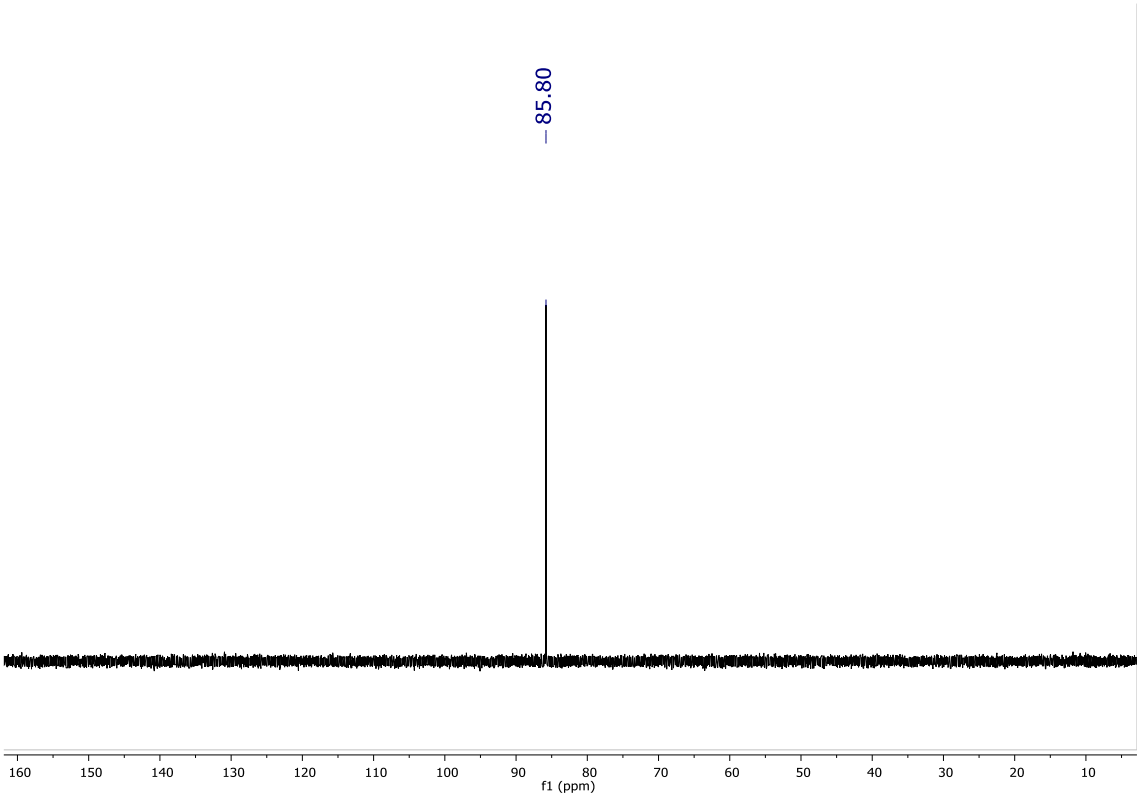


Figure S40. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 4e, $[Ni\{S_2P(O^iPr)_2\}(CNXyl)_2]ClO_4$.

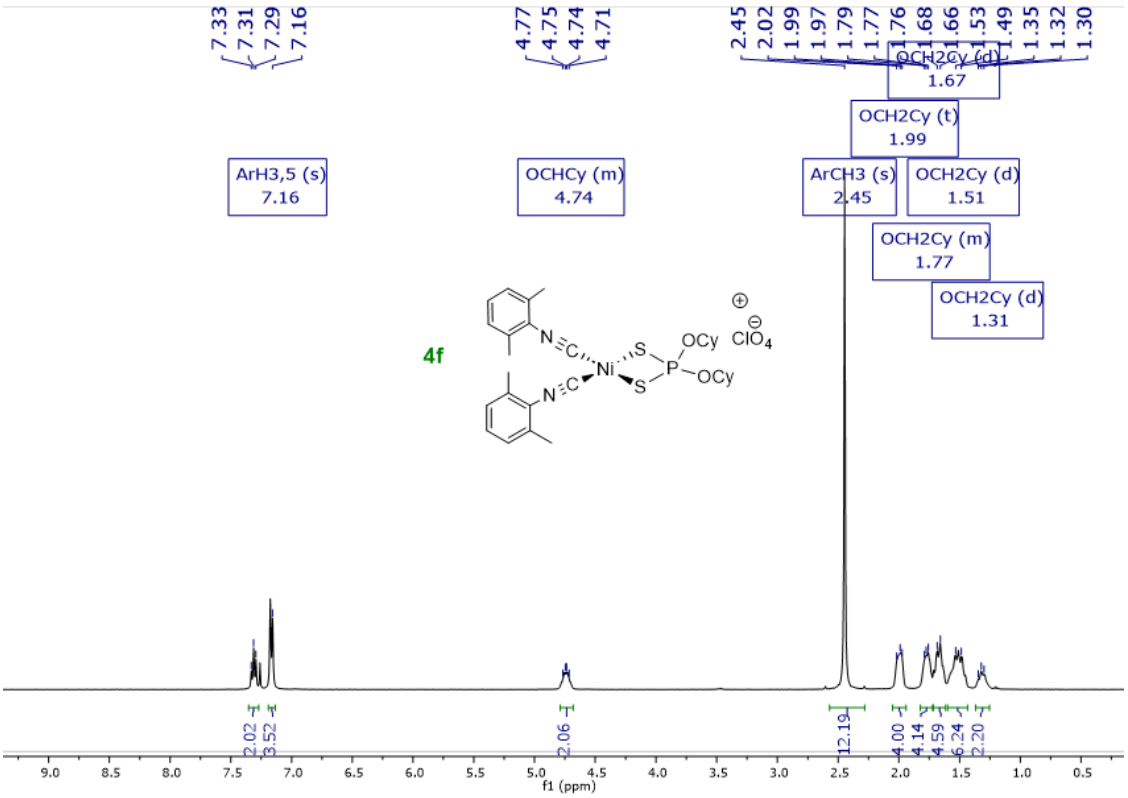


Figure S 41. ^{1}H NMR ($CDCl_3$) of compound 4f, $[Ni\{S_2P(OCy)_2\}(CNXyl)_2]ClO_4$

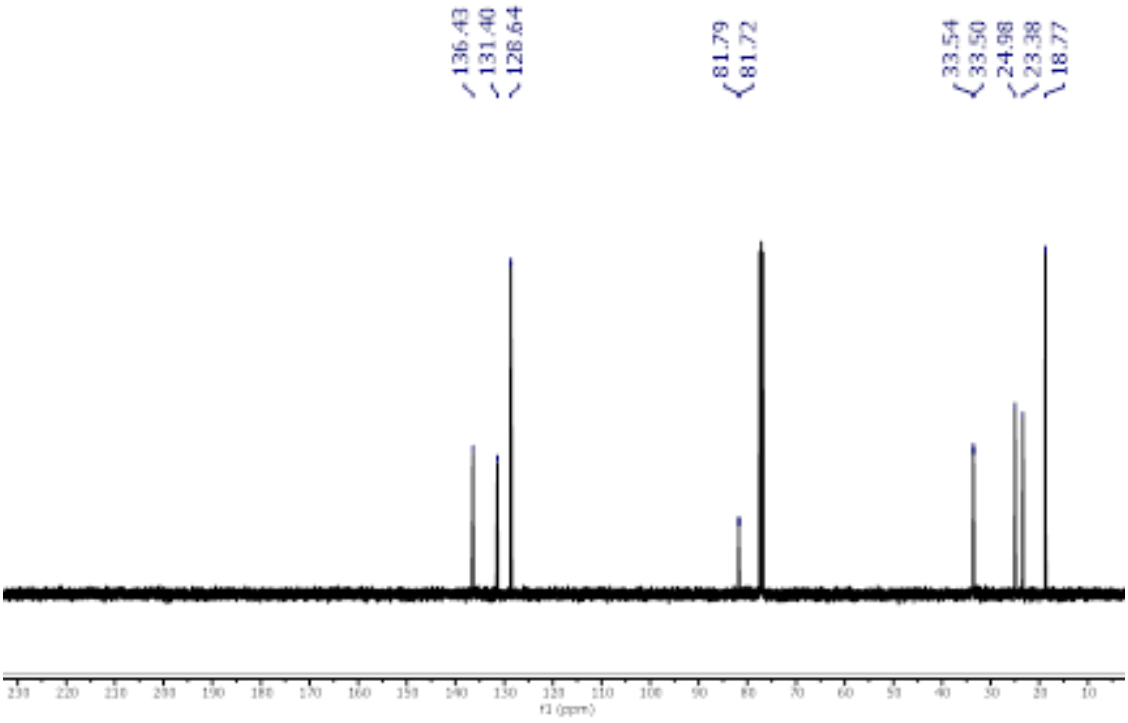


Figure S 42. ^{13}C {^{1}H} NMR ($CDCl_3$) of compound 4f, $[Ni\{S_2P(OCy)_2\}(CNXyl)_2]ClO_4$

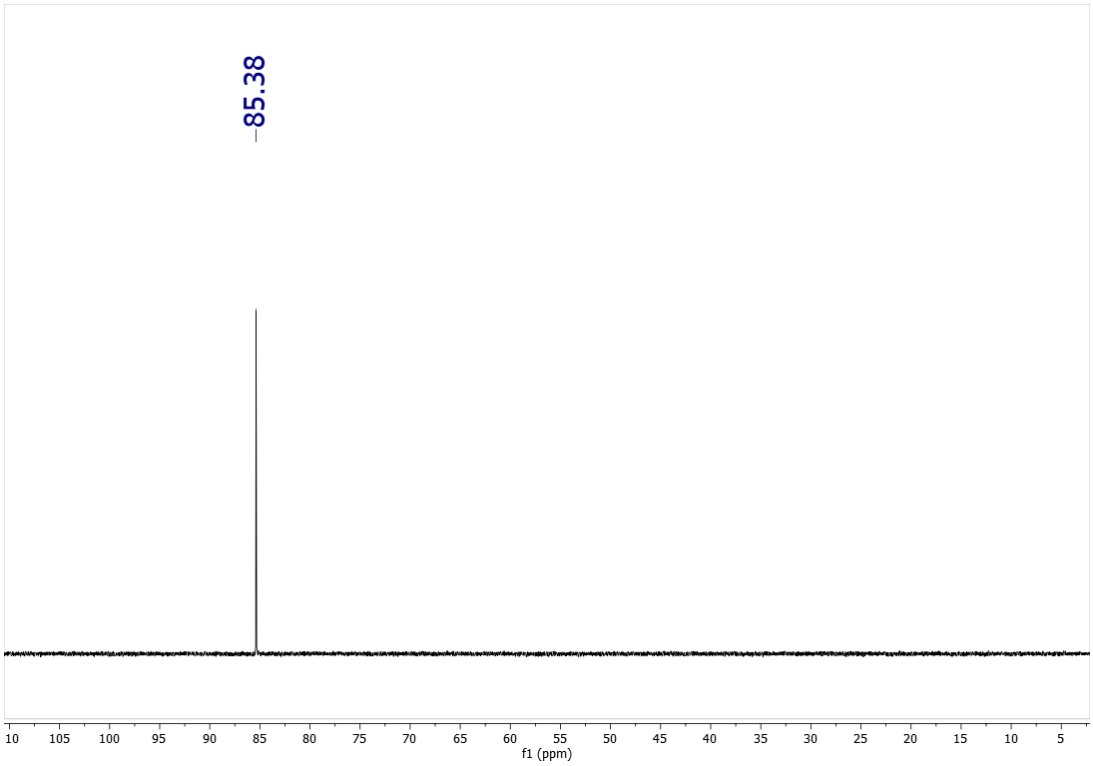


Figure S 43. ^{31}P {^{1}H} NMR ($CDCl_3$) of compound 4f, $[Ni\{S_2P(OCy)_2\}(CNXyl)_2]ClO_4$

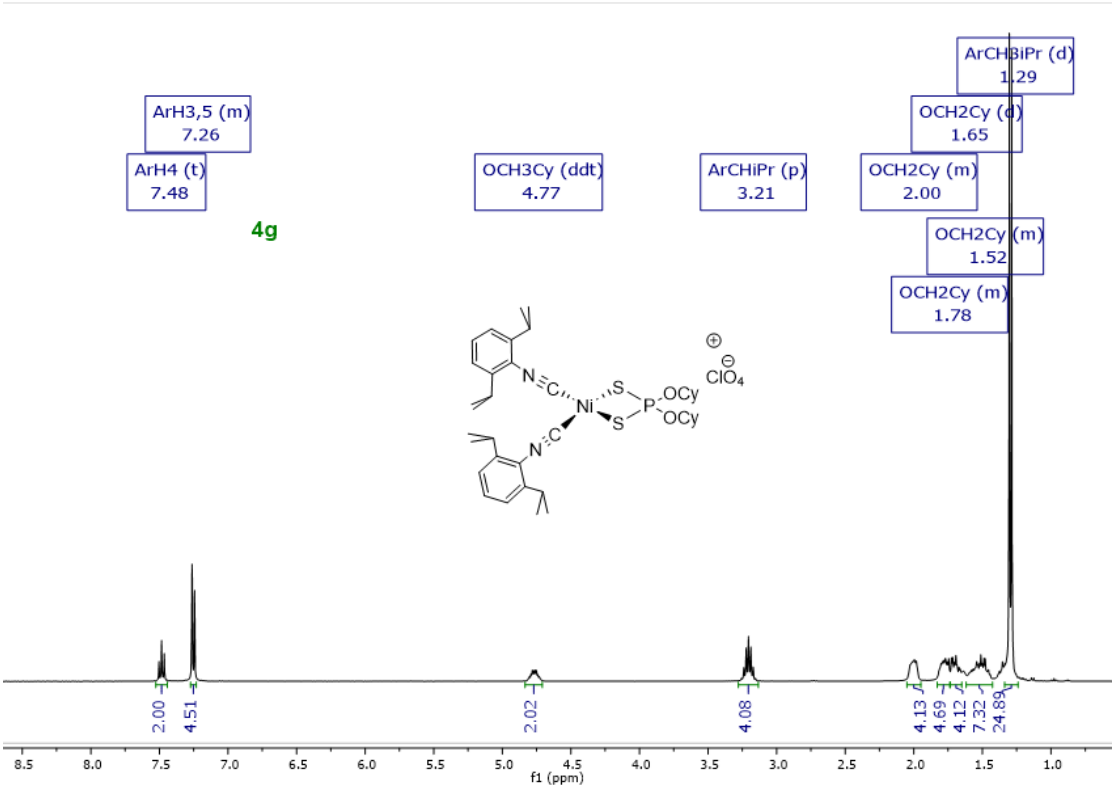


Figure S 44. ^{1}H NMR ($CDCl_3$) of compound 4g, $[Ni\{S_2P(OCy)_2\}(CNAr)_2]ClO_4$.

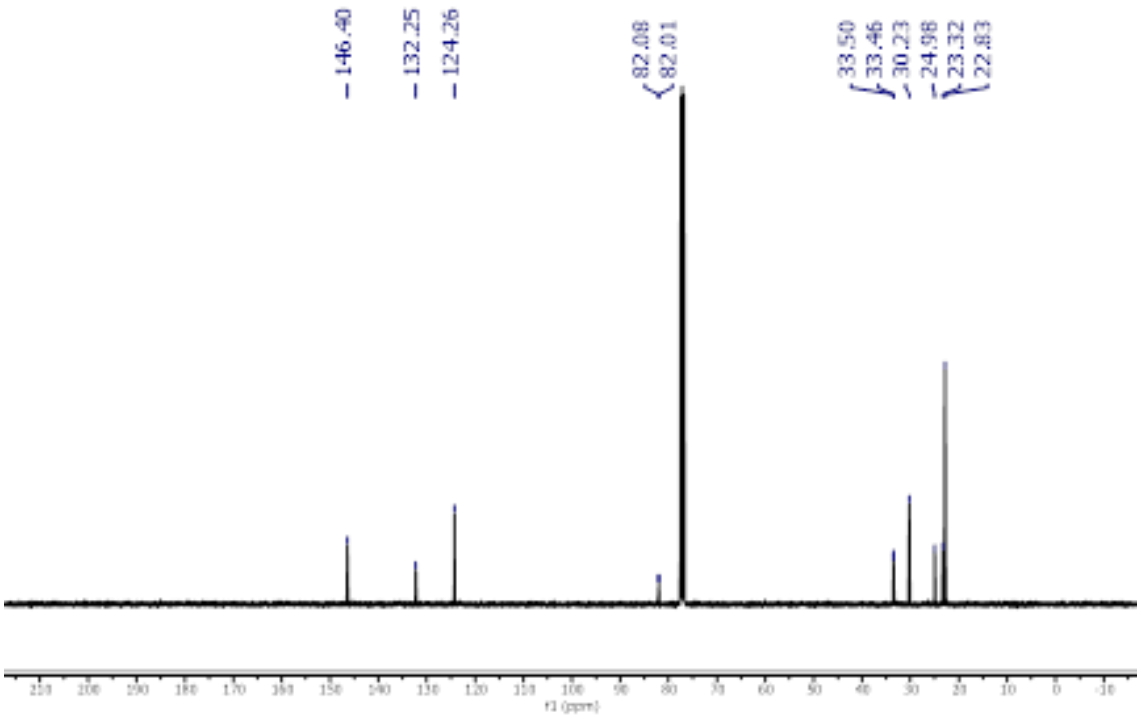


Figure S 45. ^{13}C {^{1}H} NMR ($CDCl_3$) of compound 4g, [Ni{$S_2P(OCy)_2$}$(CNAr)_2$]ClO_4

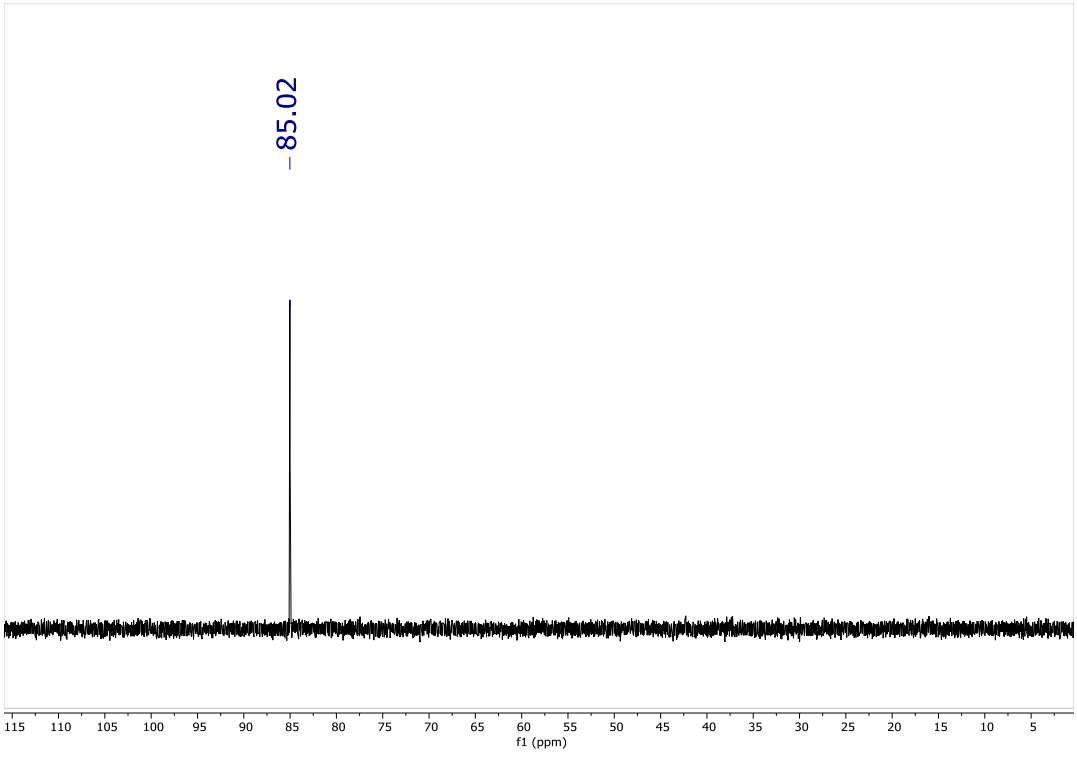


Figure S 46. ^{31}P {^{1}H} NMR ($CDCl_3$) of compound 4g, [Ni{$S_2P(OCy)_2$}$(CNAr)_2$]ClO_4

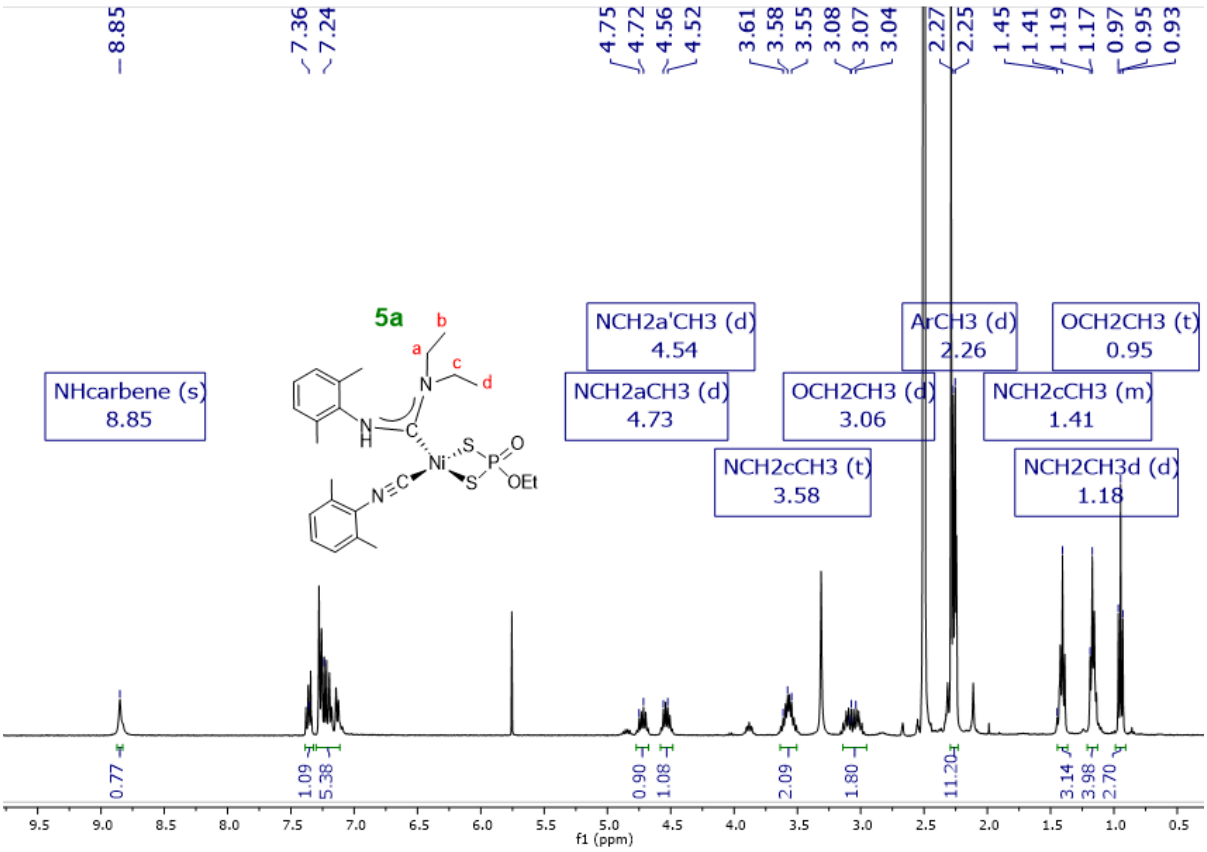


Figure S 47. ^{1}H NMR (DMSO-d6) of compound 5a, [Ni(S_2P(=O)(OEt)(CNXyl){C(NHXyl)(NEt_2)}].

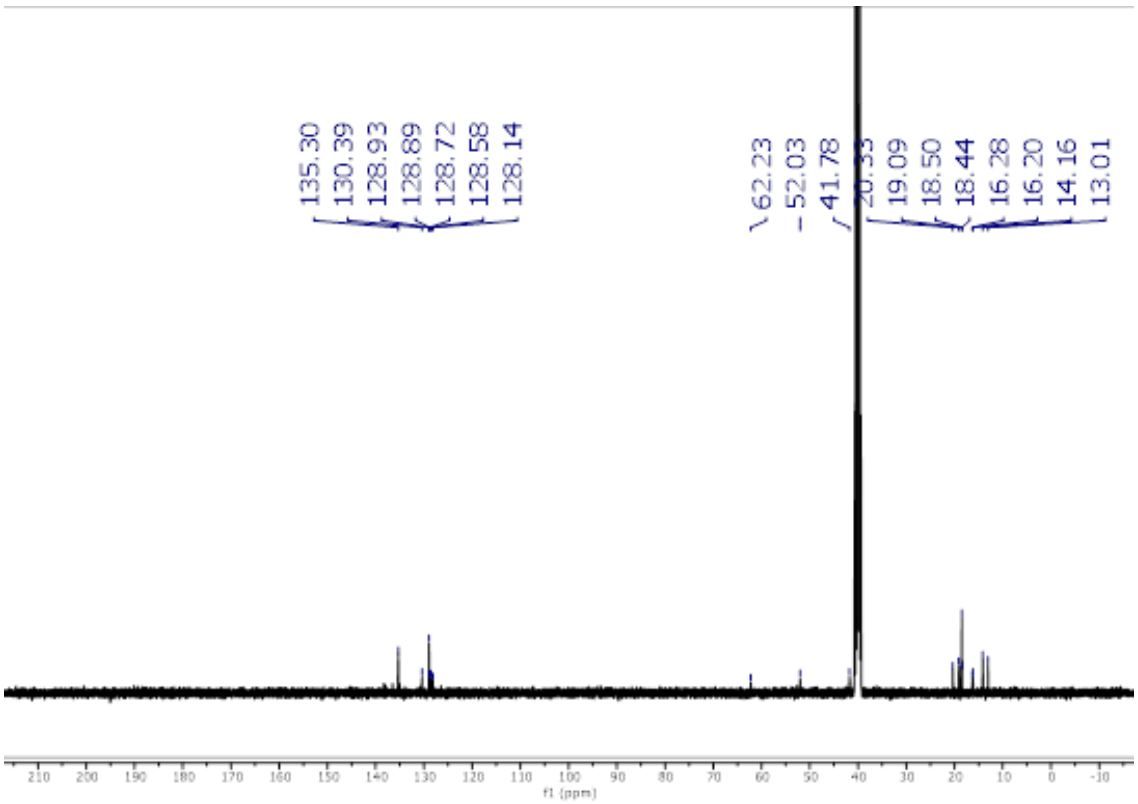


Figure S 48. ^{13}C{^{1}H} NMR (DMSO-d6) of compound 5a, [Ni(S_2P(=O)(OEt)(*CNXyl*){C(NHXyl)(NEt_2)].

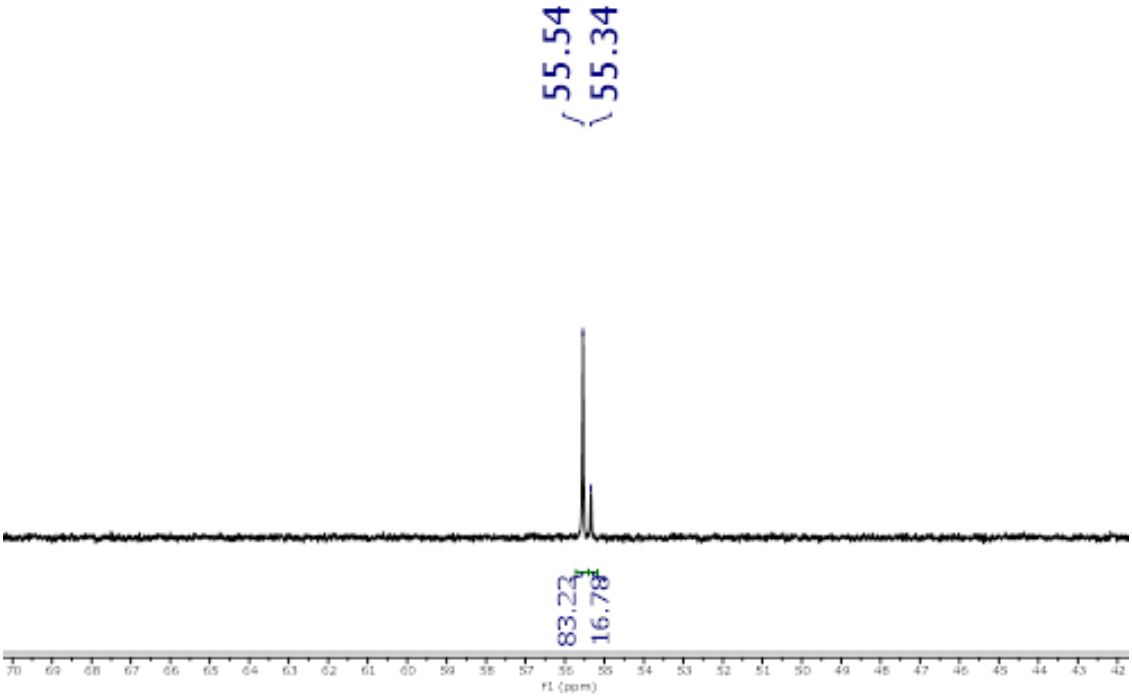


Figure S 49. $^{31}P\{^{1}H\}$ NMR (DMSO-d6) of compound 5a, [Ni(S_2P(=O)(OEt)(*CNXyl*){C(NHXyl)(NEt_2)}].

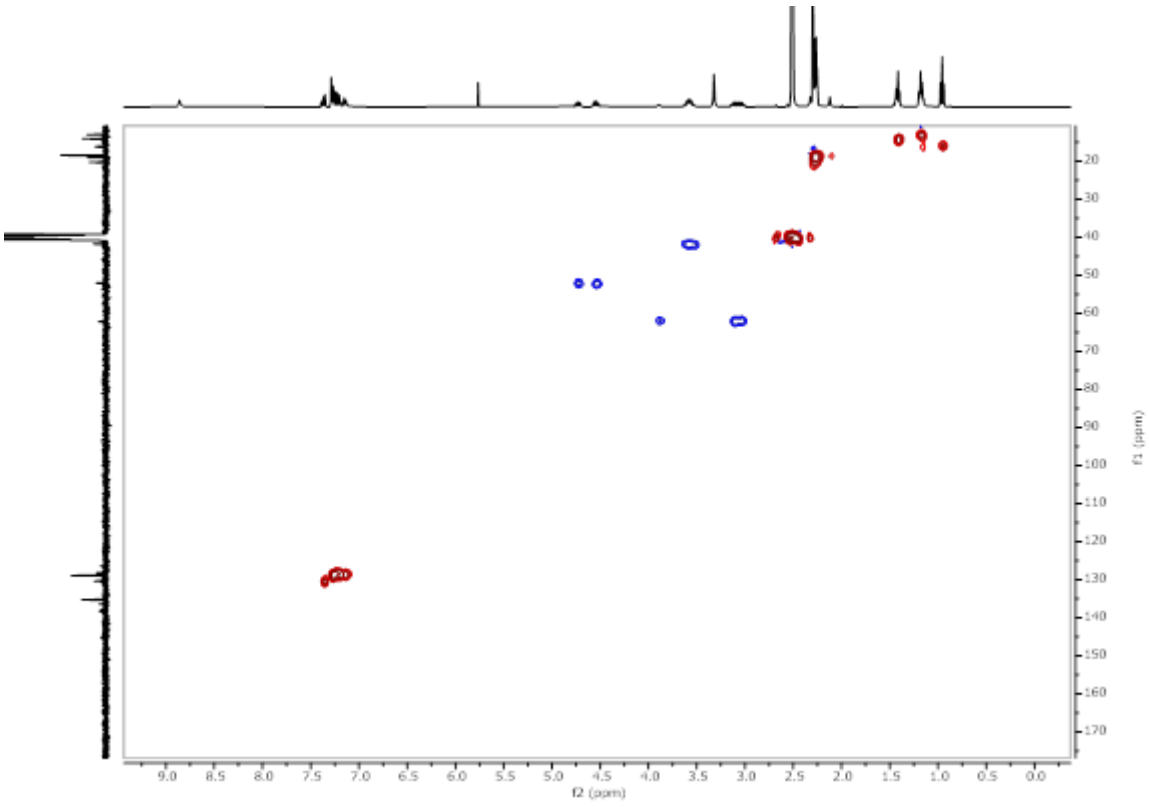


Figure S 50. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 5b, [Ni(S_2P(=O)(OEt)(CNXyl){C(NHXyl)(NEt_2)}].

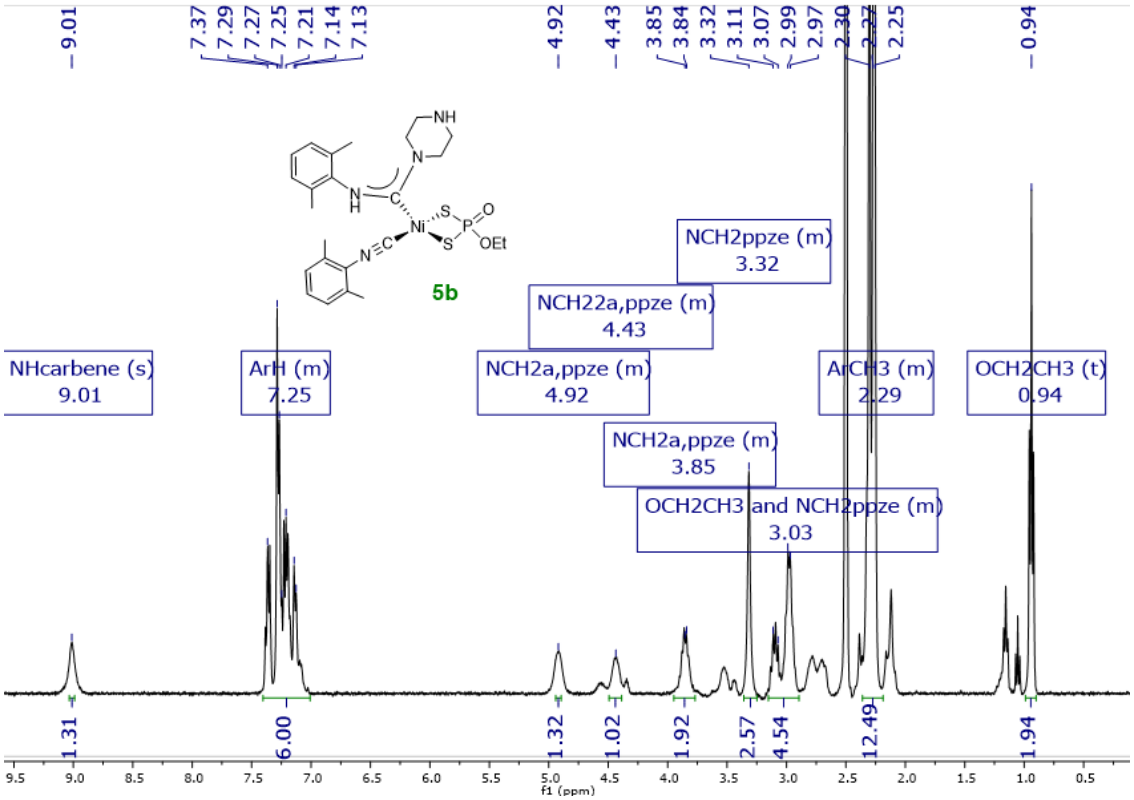


Figure S 51. ^{1}H NMR (DMSO-d6) of compound 5b, [Ni(S_2P(=O)(OEt)(CNXyl){C(NHXyl)(Nppze)}]

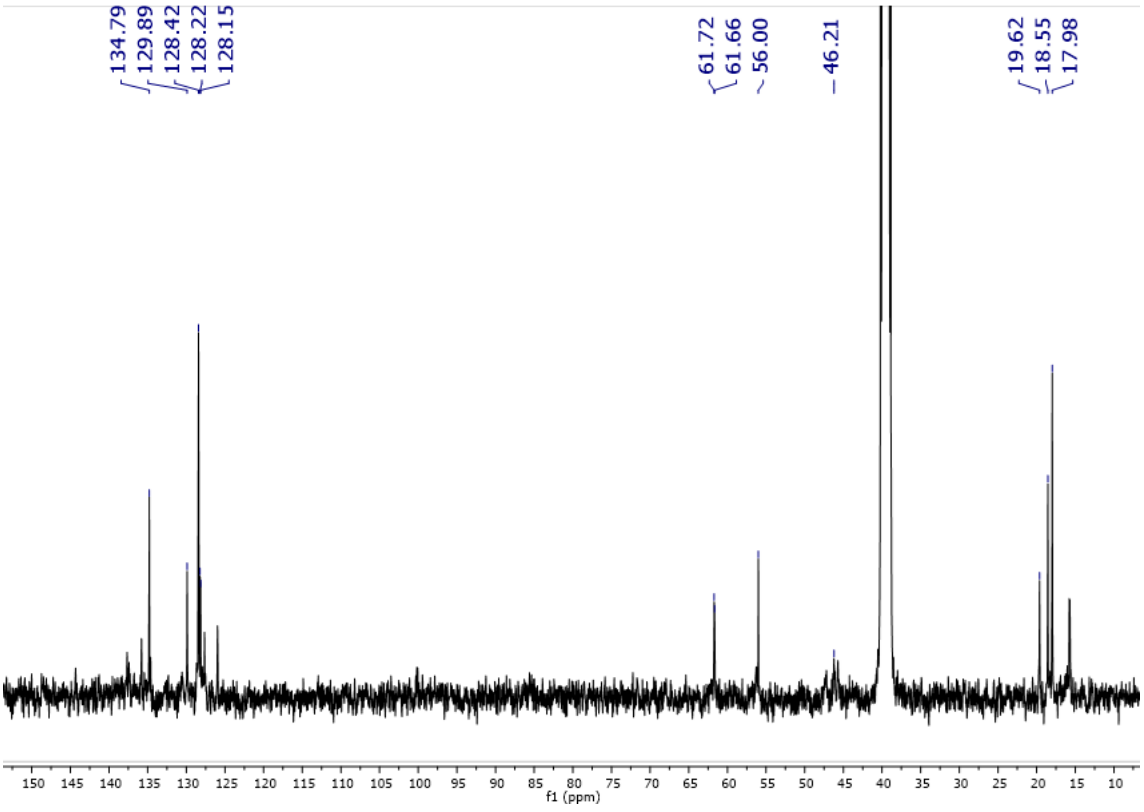


Figure S 52. ^{13}C{^{1}H} NMR (DMSO-d6) of compound 5b, [Ni(S_2P(=O)(OEt)(CNXyl){C(NHXyl)(Nppze)}]

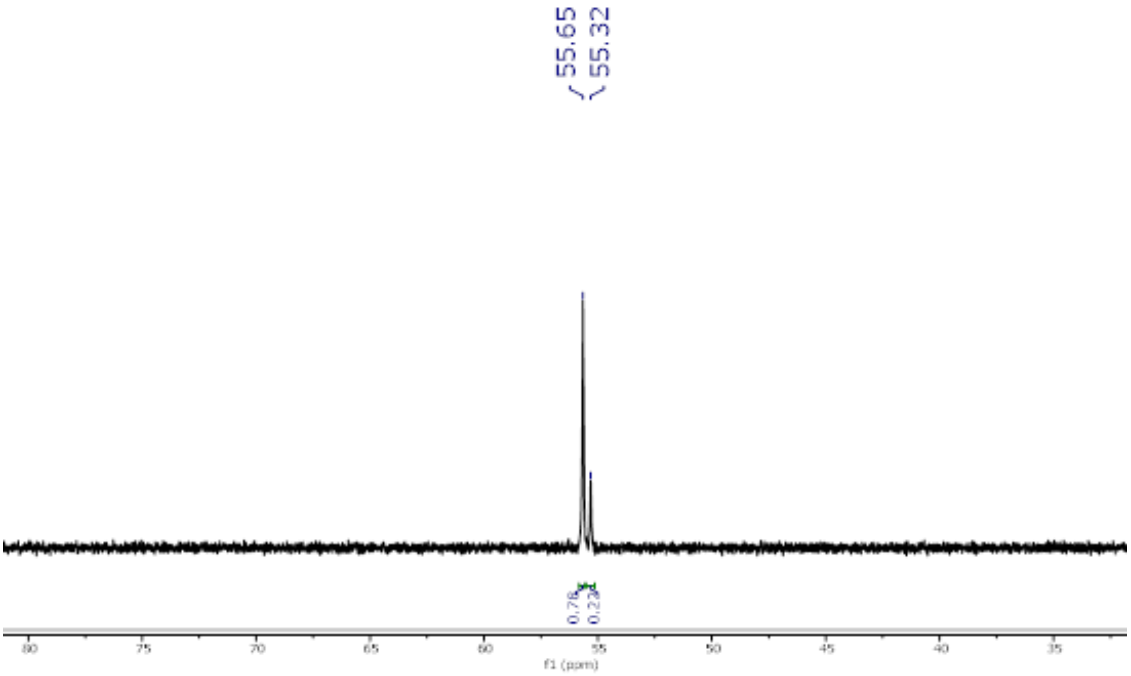


Figure S 53. $^{31}P\{^{1}H\}$ NMR (DMSO-d6) of compound 5b, [Ni(S_2P(=O)(OEt)(CNXyl){C(NHXyl)(NPpze)}]

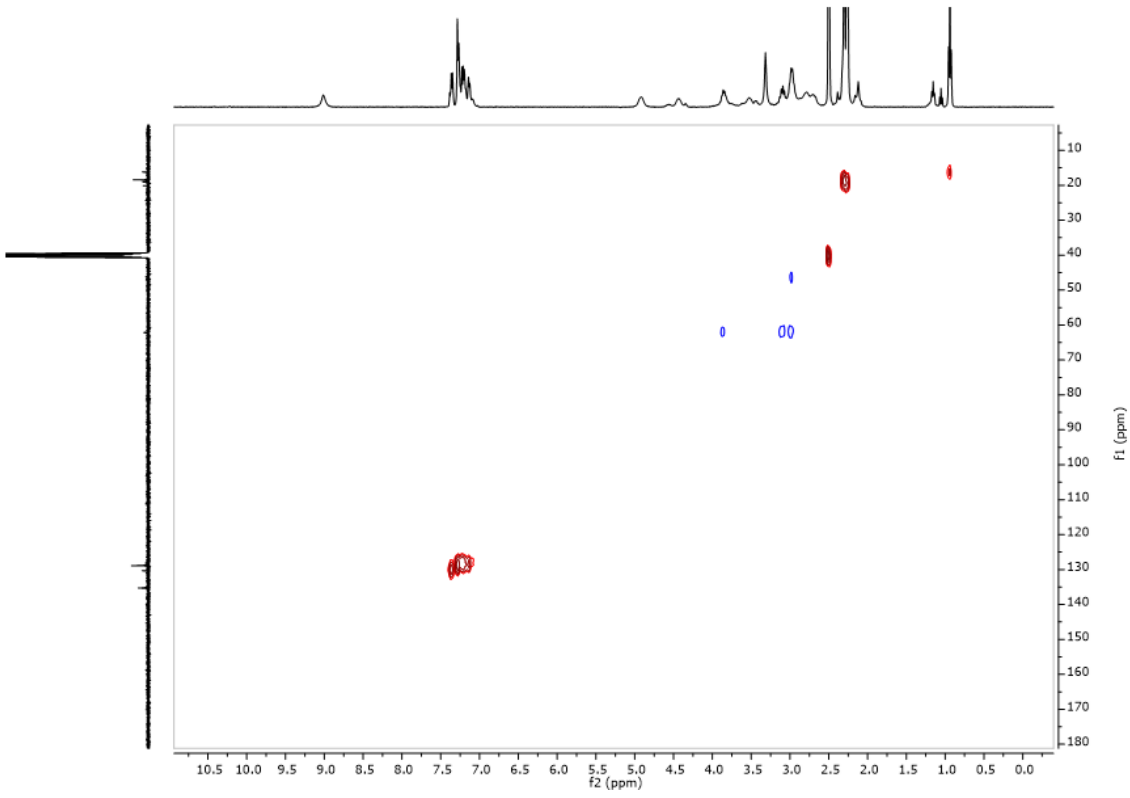


Figure S 54. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 5b, [Ni(S_2P(=O)(OEt)(CNXyl){C(NHXyl)(NPpze)}].

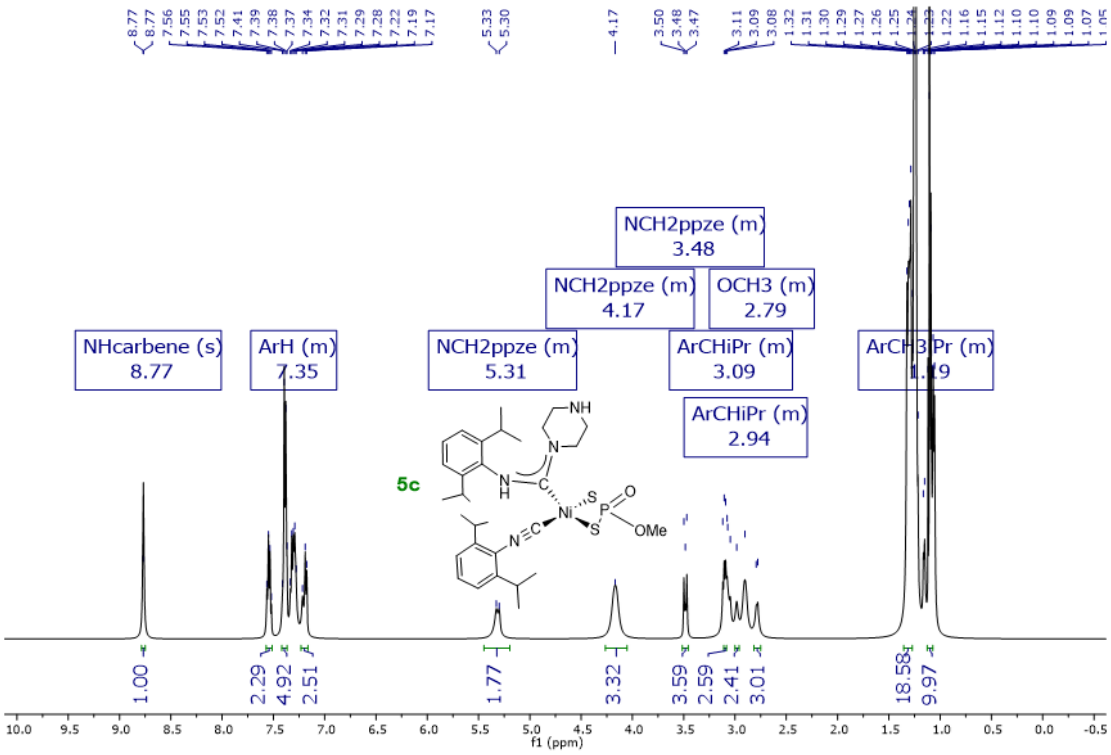


Figure S 55. ^{1}H NMR (DMSO-d6) of compound 5c, [Ni(S_2P(=O)(OMe)(CNAr){C(NHAr)(Nppze}]

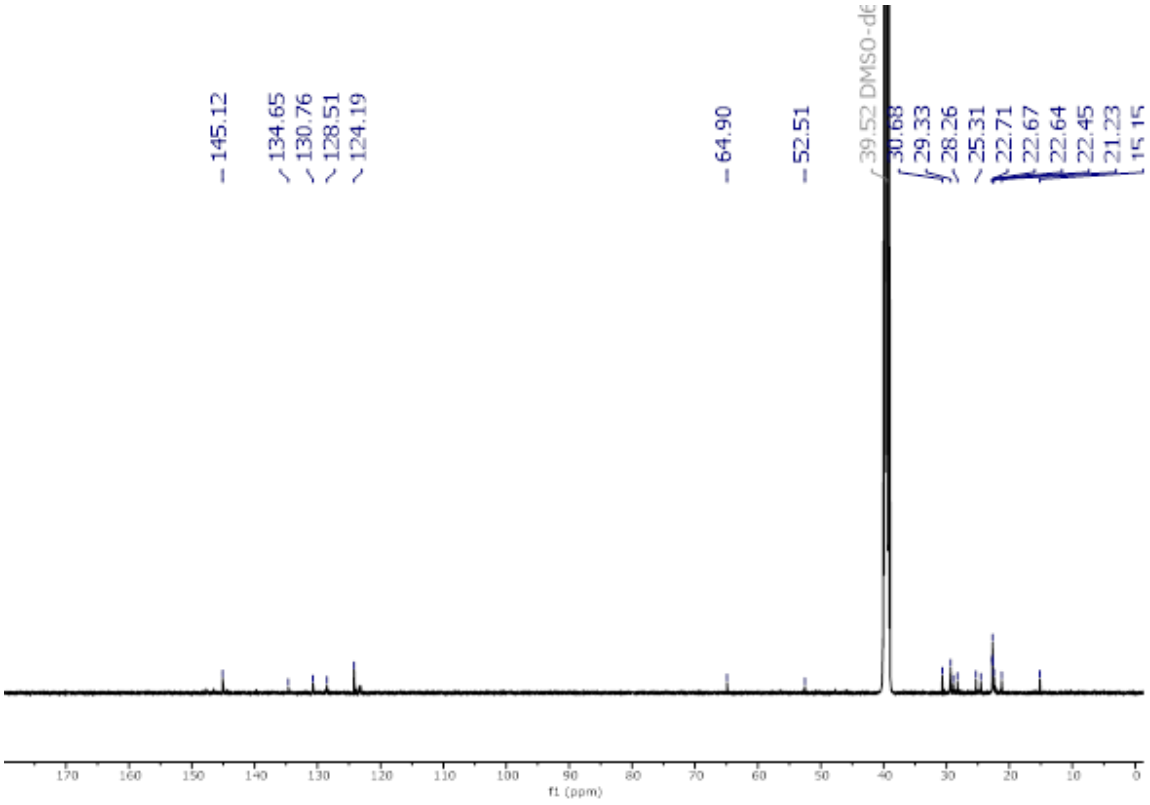


Figure S 56. ^{13}C {^{1}H} NMR (DMSO-d6) of compound 5c, [Ni(S_2P(=O)(OEt)(CNAr){C(NHAr)(Nppze)}].

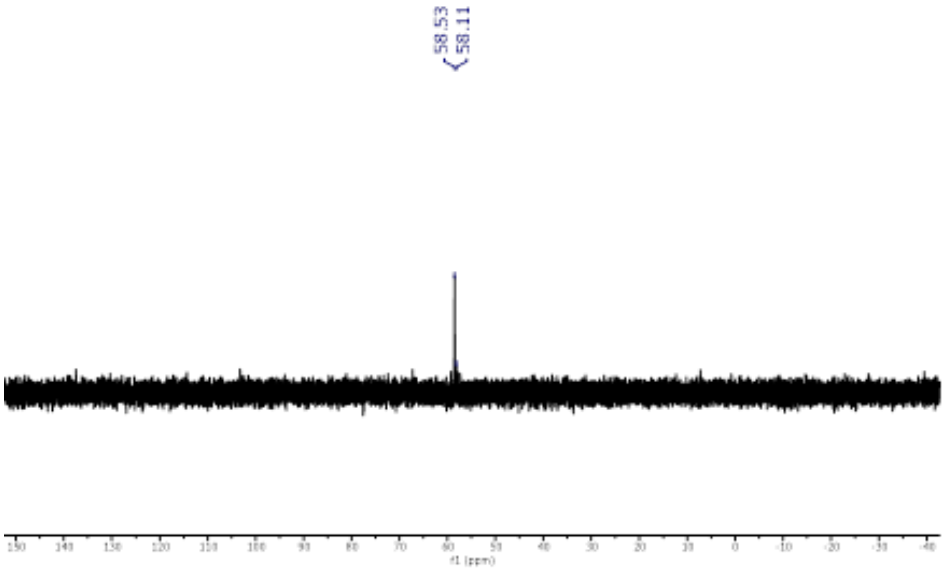


Figure S 57. ^{31}P {^{1}H} NMR (DMSO-d6) of compound 5c, [Ni(S_2P(=O)(OEt)(CNAr){C(NHAr)(Nppze)}]

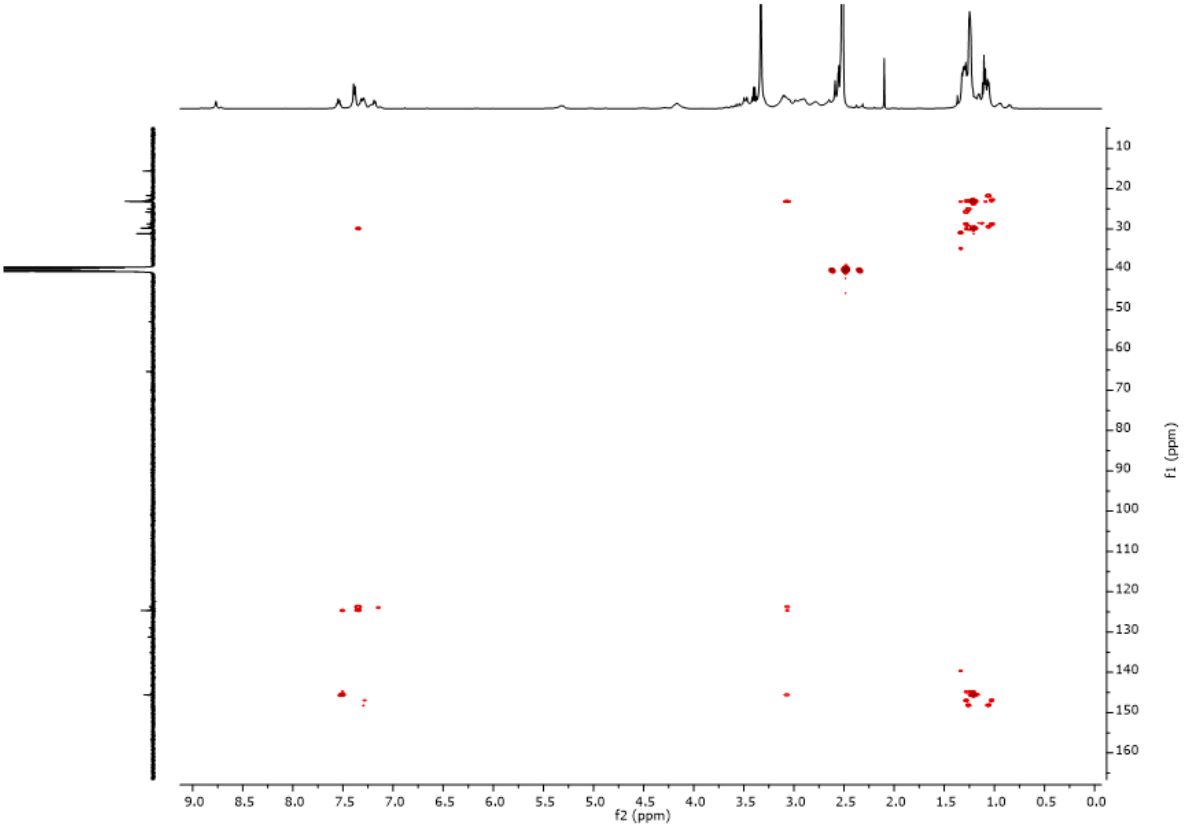


Figure S 58. ^{1}H-^{13}C{^{1}H} HMBC NMR ($CDCl_3$) of compound 5c, [Ni(S_2P(=O)(OMe)(CNAr){C(NHAr)(Nppze}].

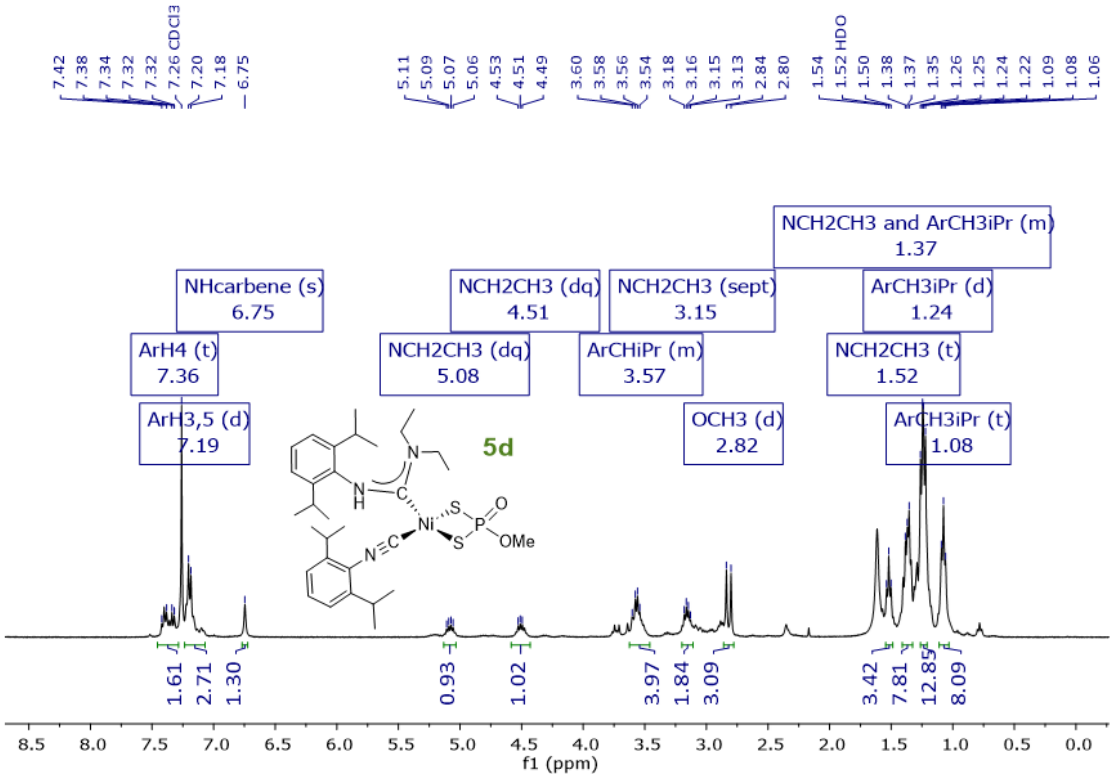


Figure S 56. ^{1}H NMR ($CDCl_3$) of compound 5d, [Ni(S_2P(=O)(OMe)(CNAr){C(NHAr)(NEt_2}].

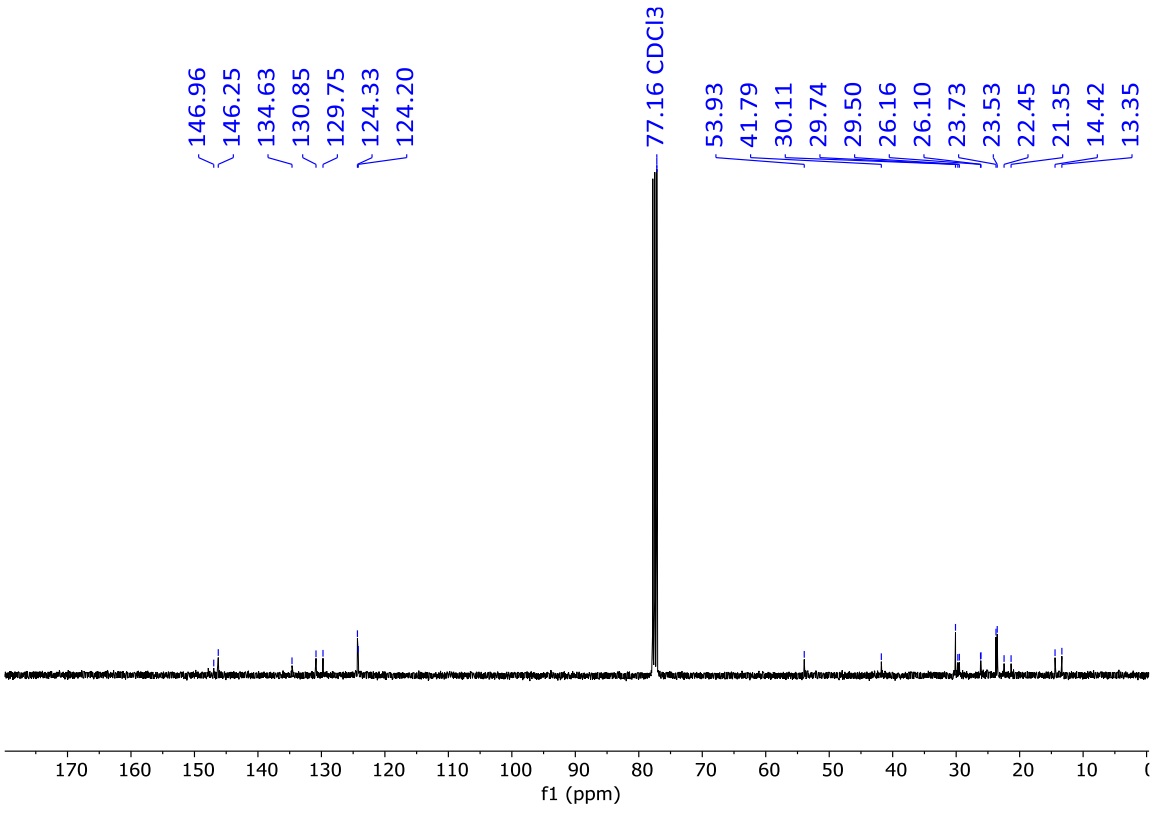


Figure S 57. ^{13}C NMR ($CDCl_3$) of compound 5d, [Ni(S_2P(=O)(OMe)(CNAr){C(NHAr)(NEt_2}].

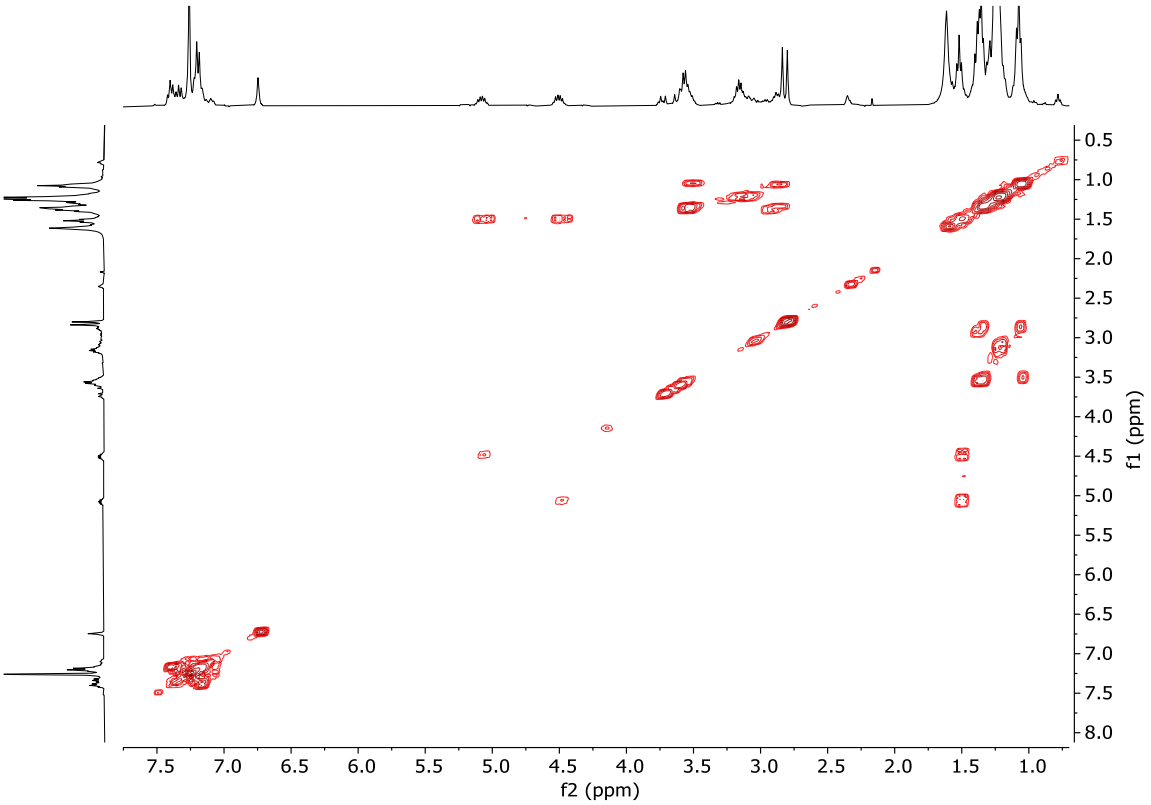


Figure S 58. ^{1}H-^{1}H COSY NMR (DMSO-*d6*) of compound 5d, [Ni(S_2P(=O)(OMe)(CNAr){C(NHAr)(NEt_2)}].

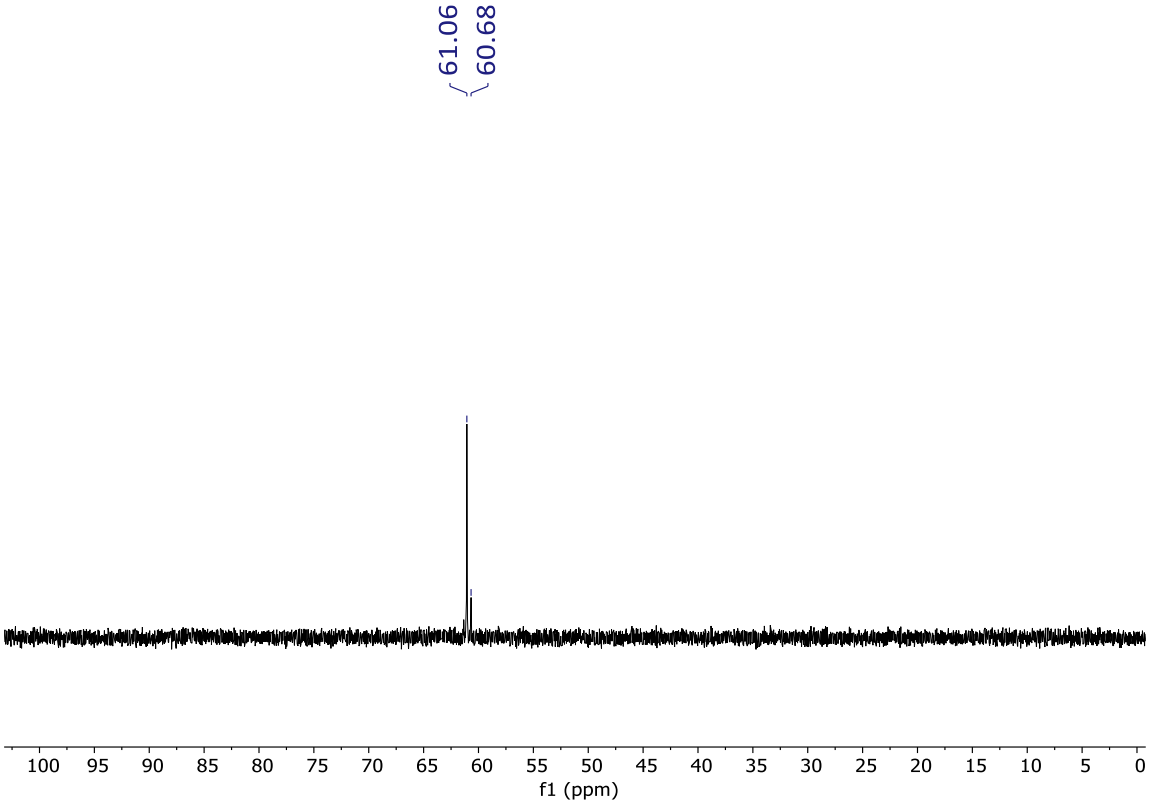


Figure S 59. ^{31}P {^{1}H} NMR ($CDCl_3$) of compound 5d, [Ni(S_2P(=O)(OEt)(CNAr){C(NHAr)(NEt_2)}]

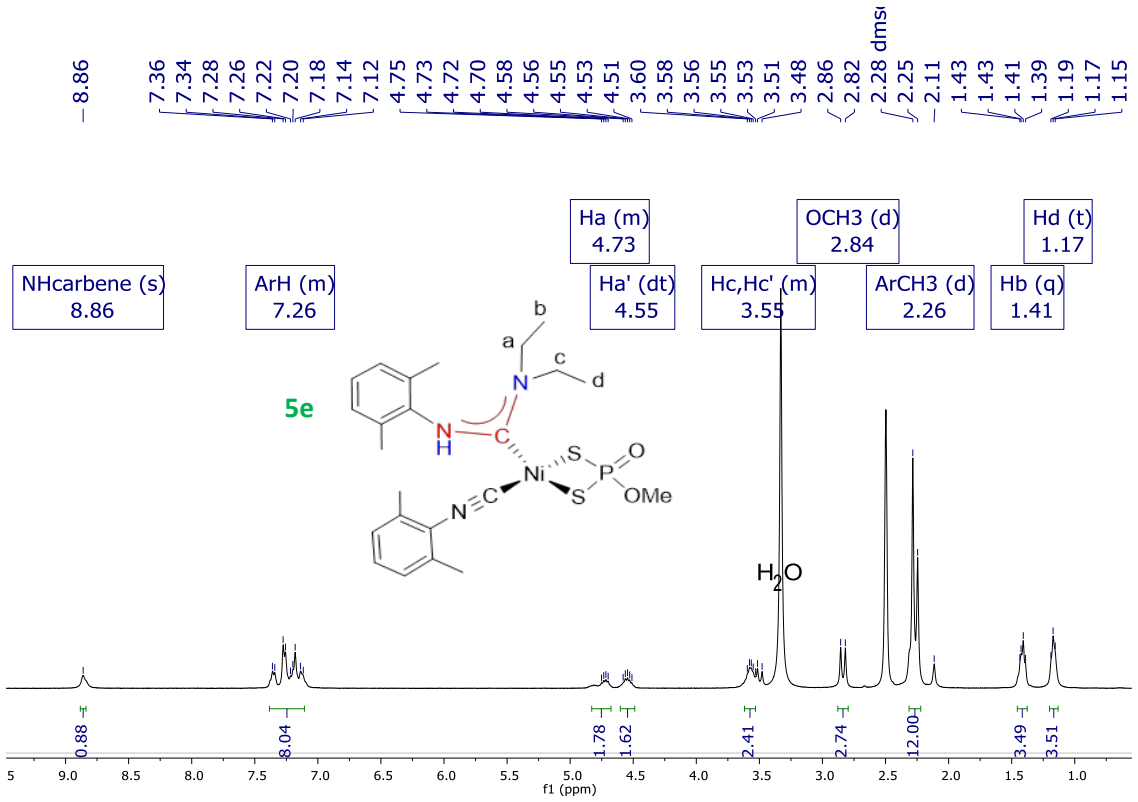


Figure S 60. ^{1}H NMR (DMSO-*d6*) of compound 5e, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(NEt_2)}].

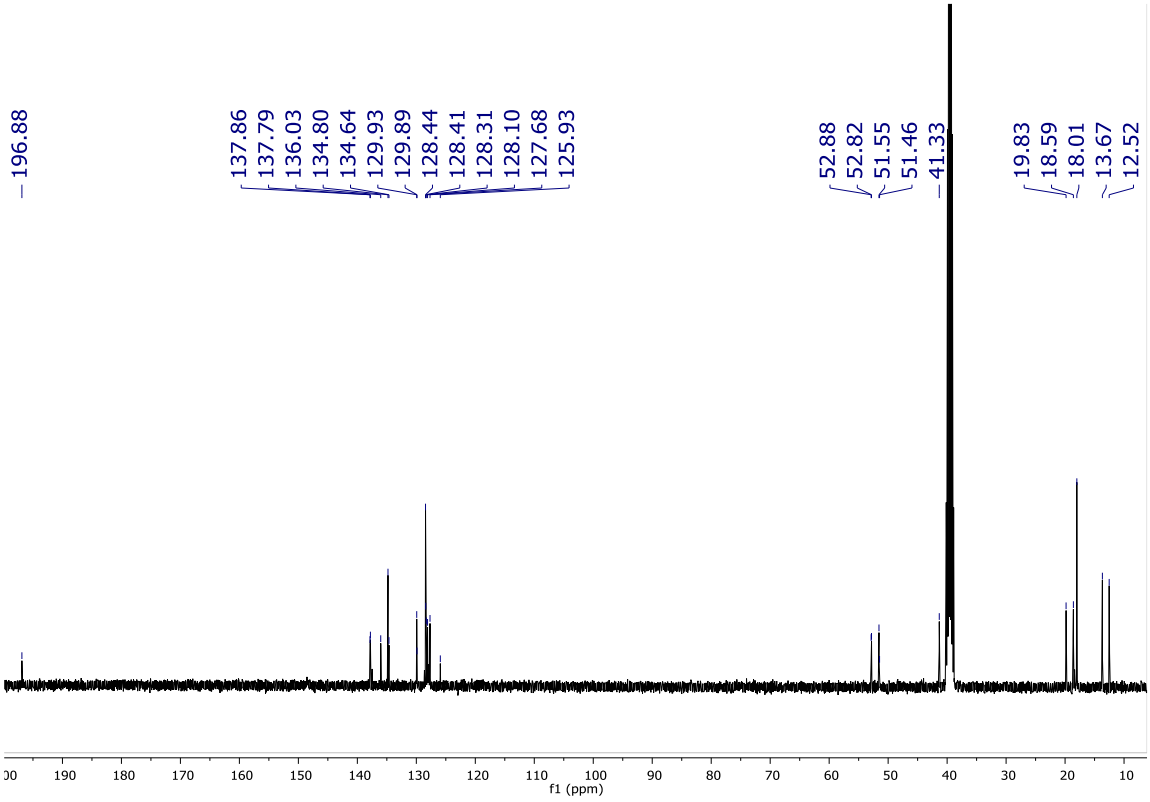


Figure S 61. ^{13}C{^{1}H} NMR (DMSO-*d6*) of compound 5e, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(NEt_2)}].

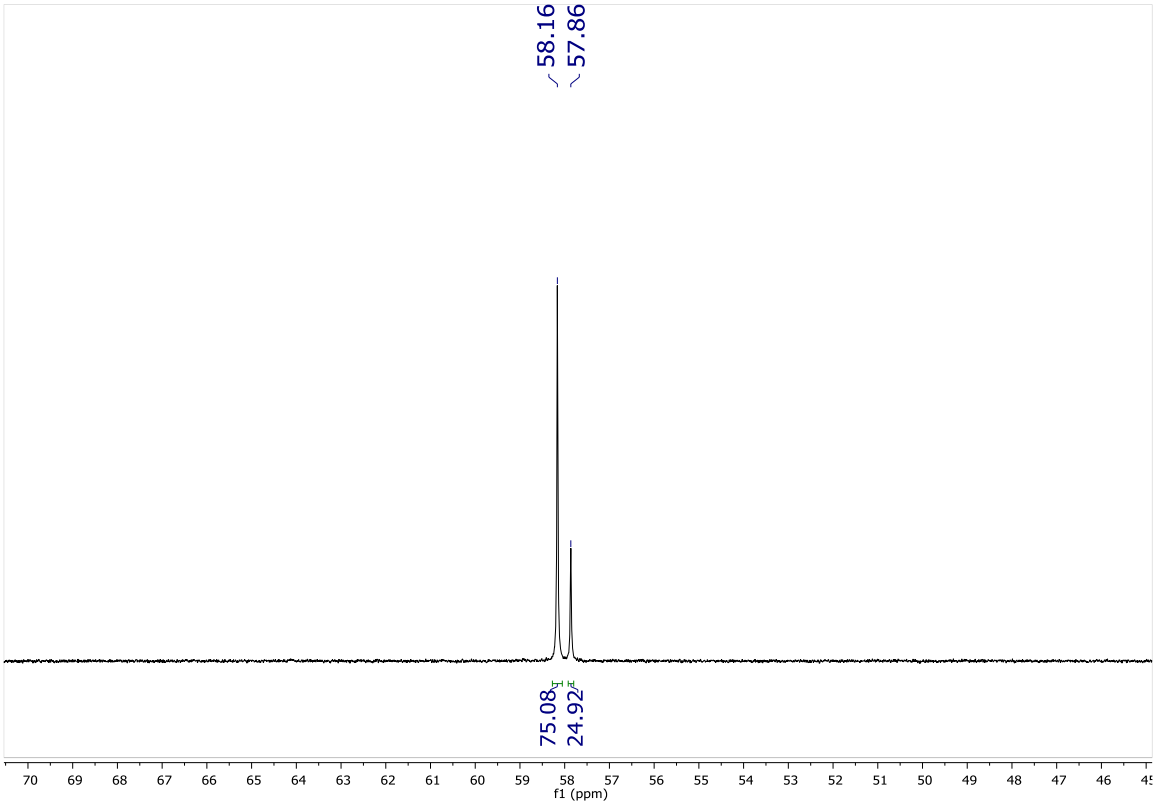


Figure S 62. $^{31}P\{^{1}H\}$ NMR (DMSO-*d6*) of compound 5e, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(NEt_2)}].

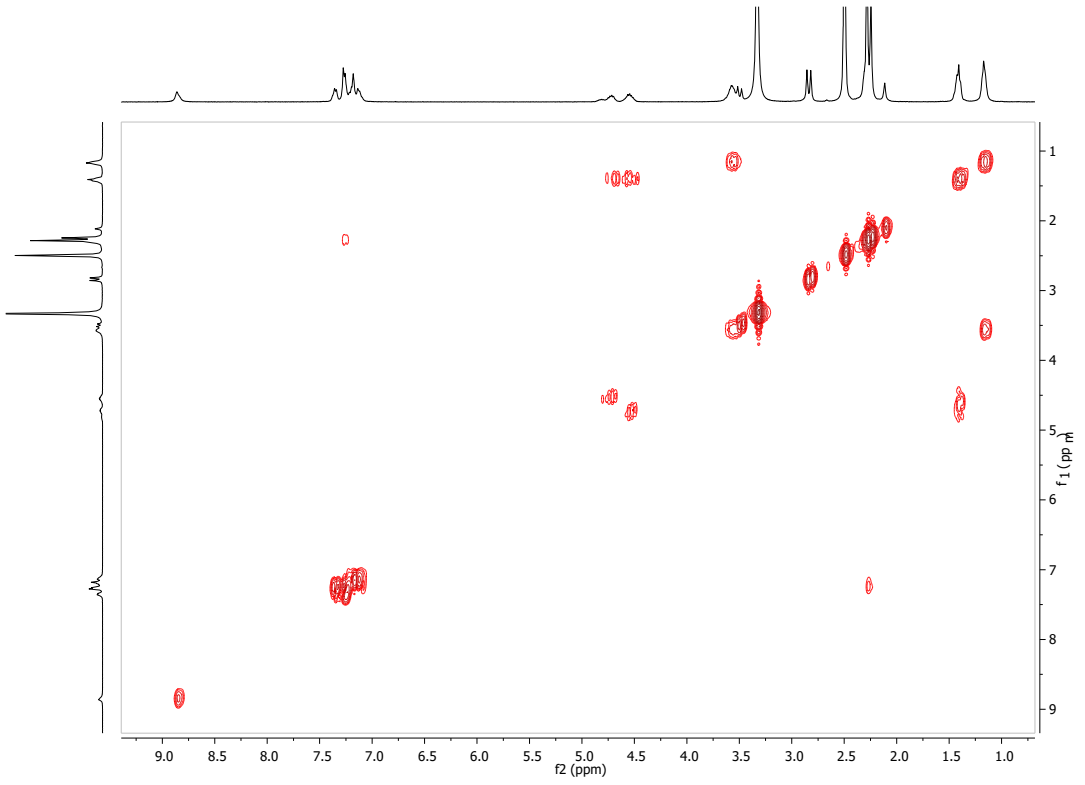


Figure S 63. ^{1}H-^{1}H COSY NMR (DMSO-*d6*) of compound 5e, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(NEt_2)}].

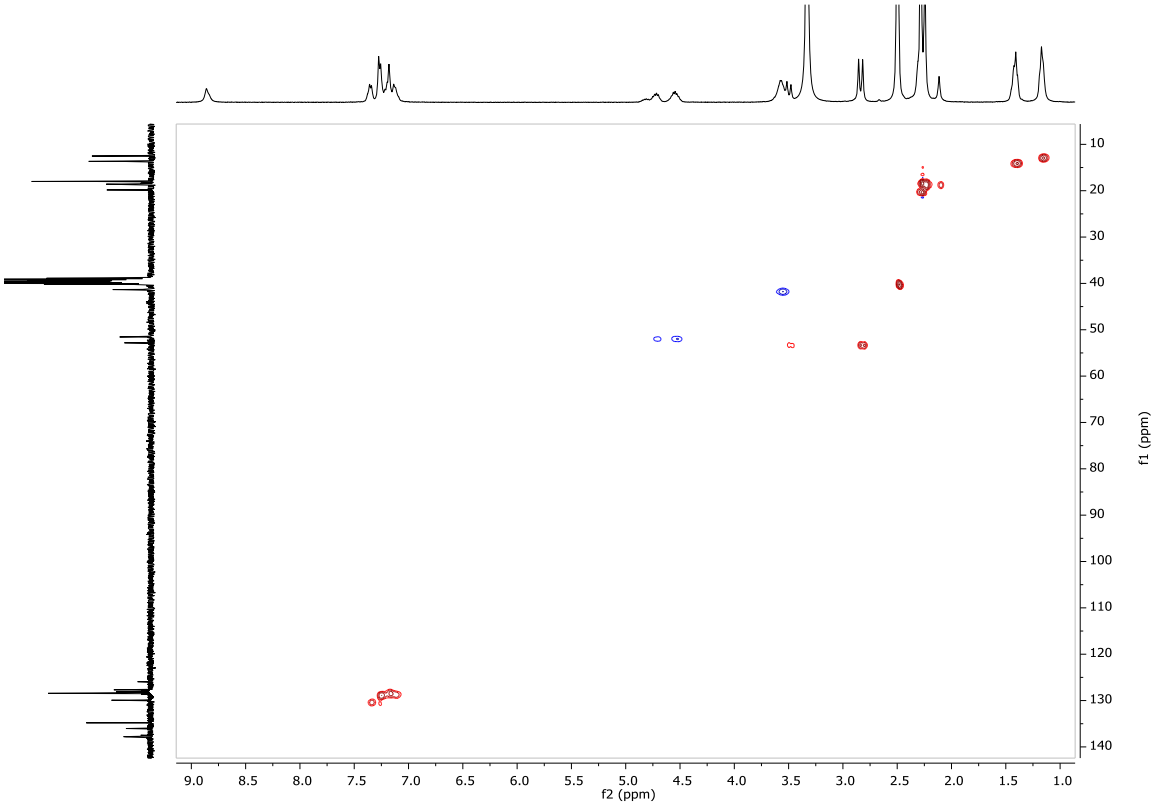


Figure S 64. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (DMSO-*d6*) of compound 5e, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(NEt_2)}].

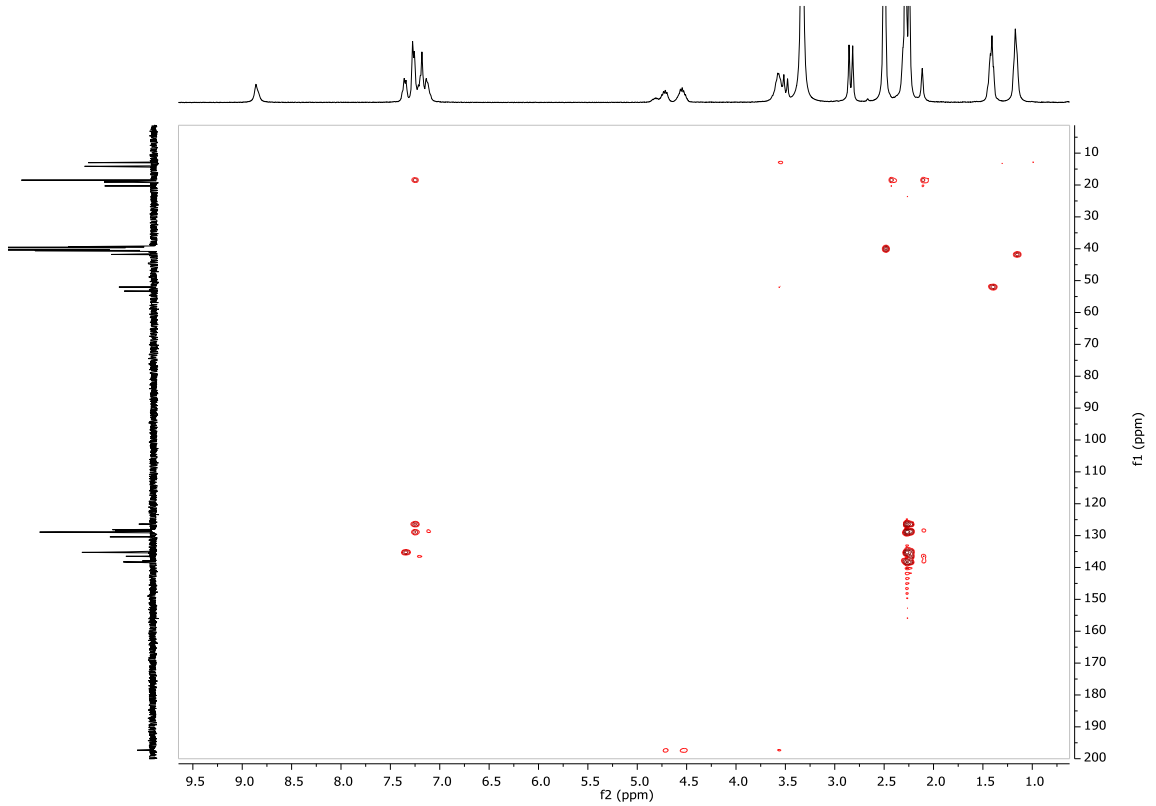


Figure S 65. ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR (DMSO-*d6*) of compound 5e, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(NEt_2)}].

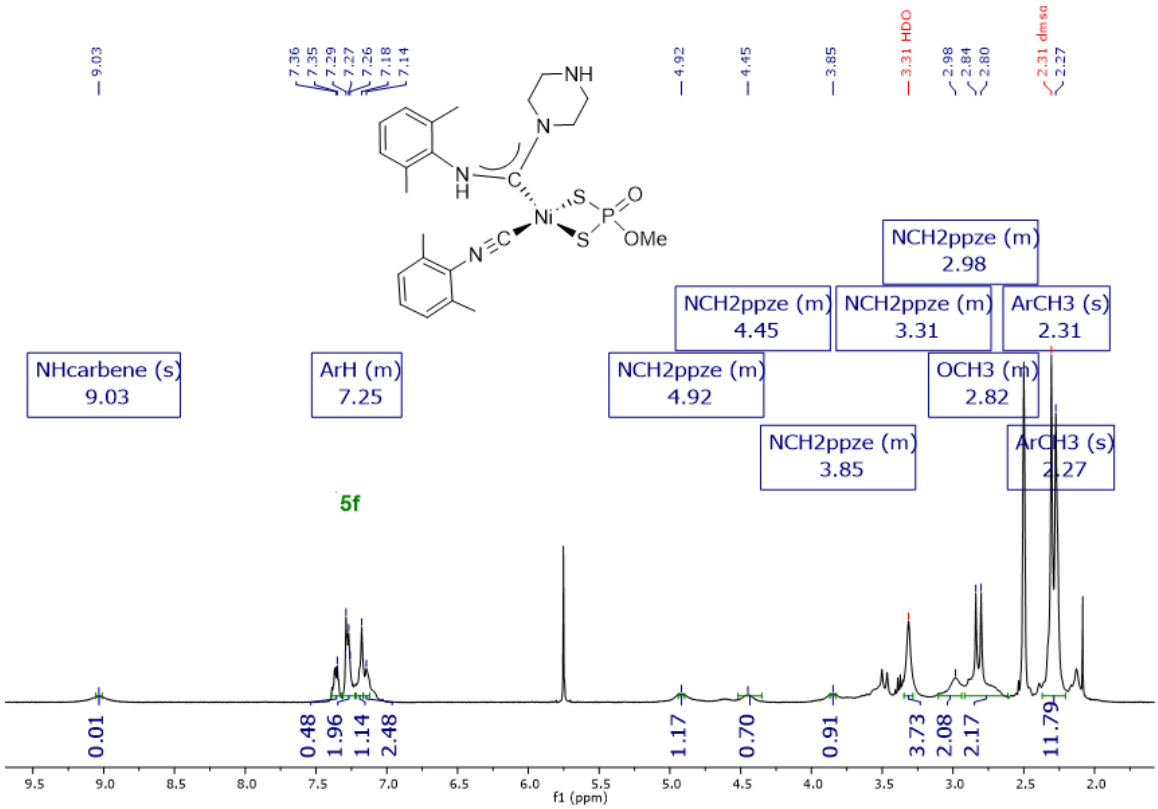


Figure S 66. ^{1}H NMR (DMSO-*d6*) of compound 5f, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(Nppze)}].

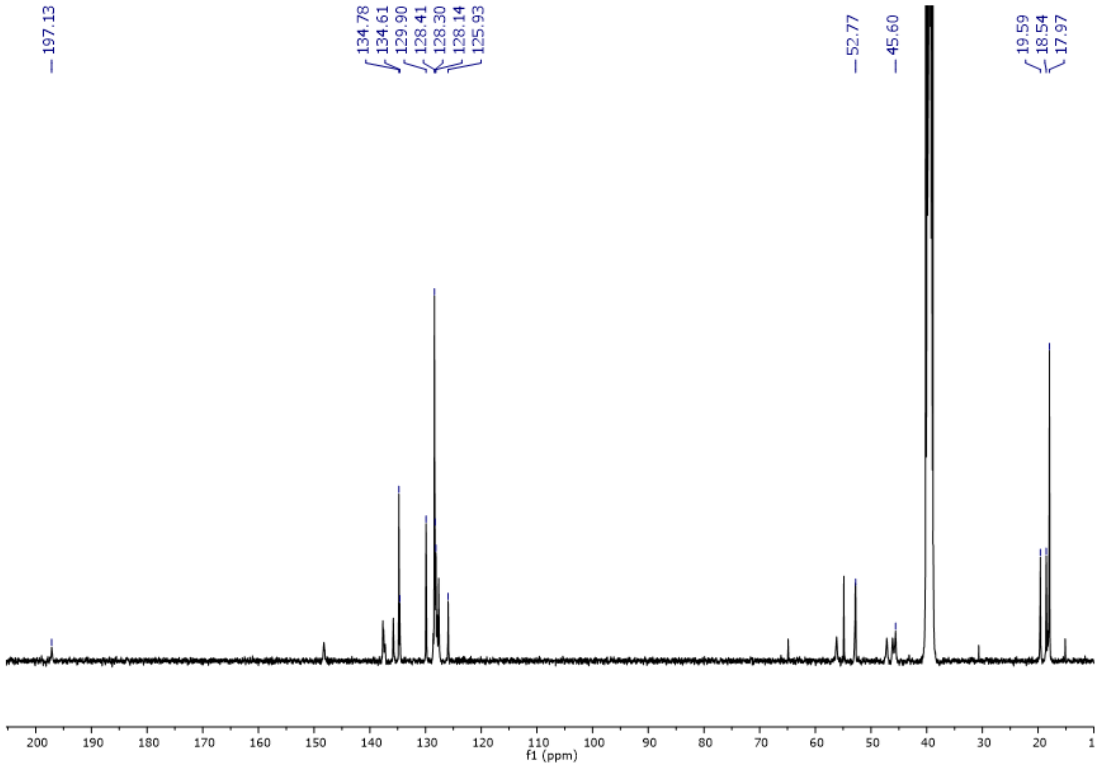


Figure S 67. ^{13}C{^{1}H} NMR (DMSO-*d6*) of compound 5f, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(Nppze)}].

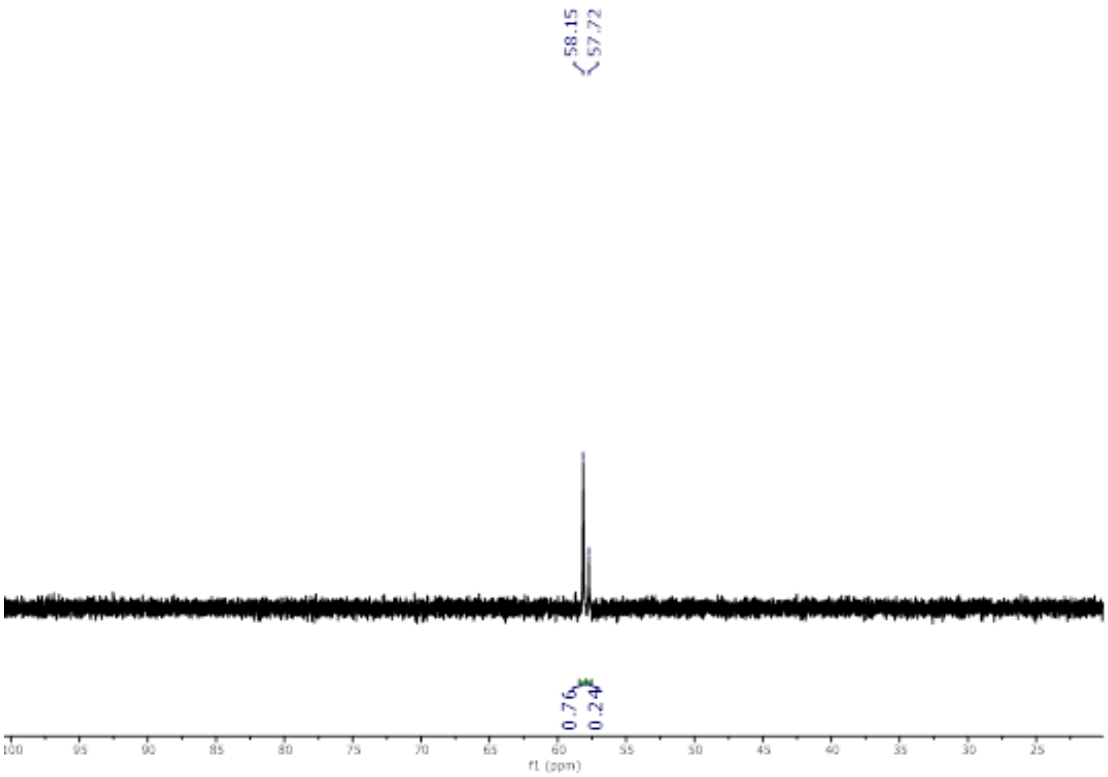


Figure S 68. $^{31}P\{^{1}H\}$ NMR (DMSO-*d6*) of compound 5f, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(Nppze)}].

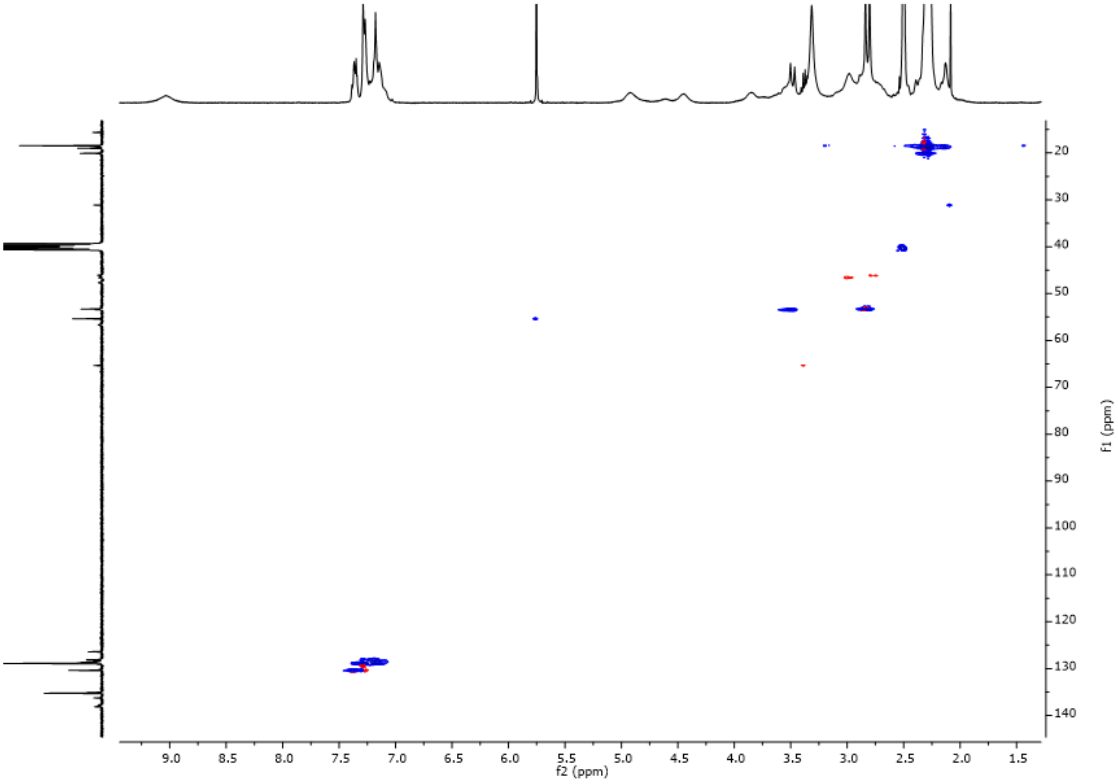


Figure S 69. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (DMSO-*d6*) of compound 5f, [Ni(S_2P(=O)(OMe)(CNXyl){C(NHXyl)(Nppze)}].

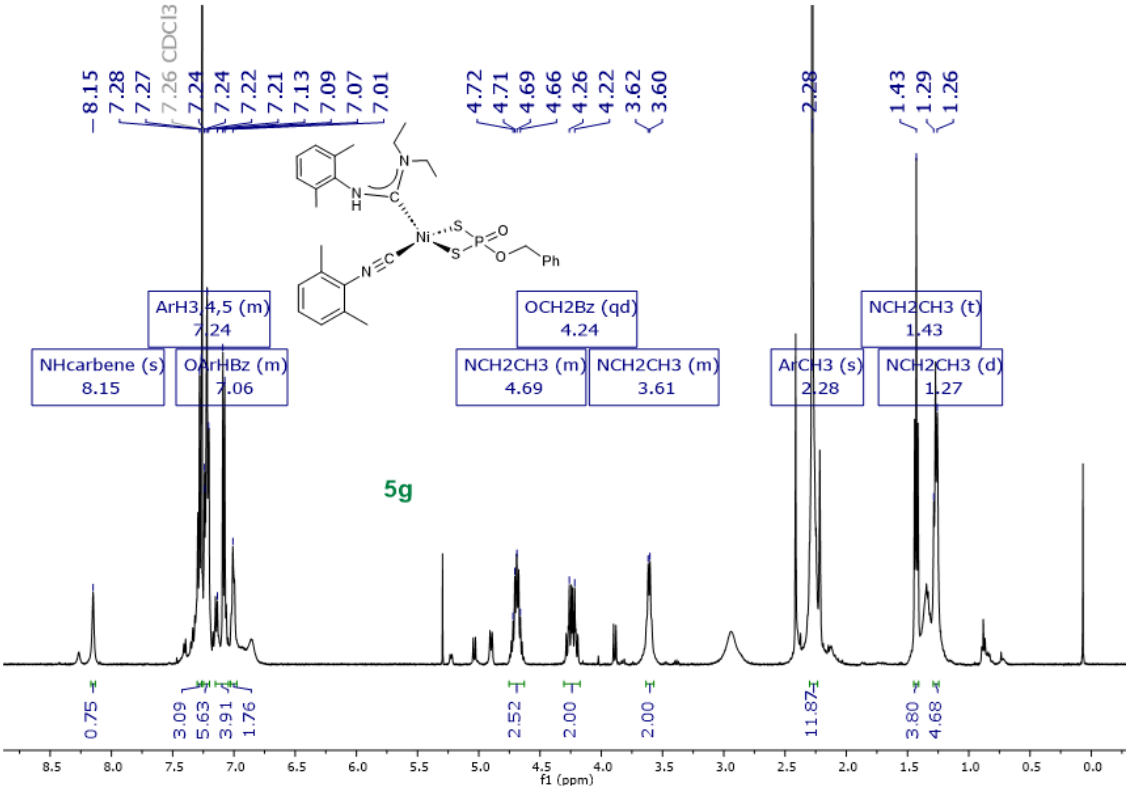


Figure S 70. ^{1}H NMR ($CDCl_3$) of compound 5g, [Ni{S_2P(=O)(OBz)}(CNXyl){C(NHXyl)(NEt_2)}].

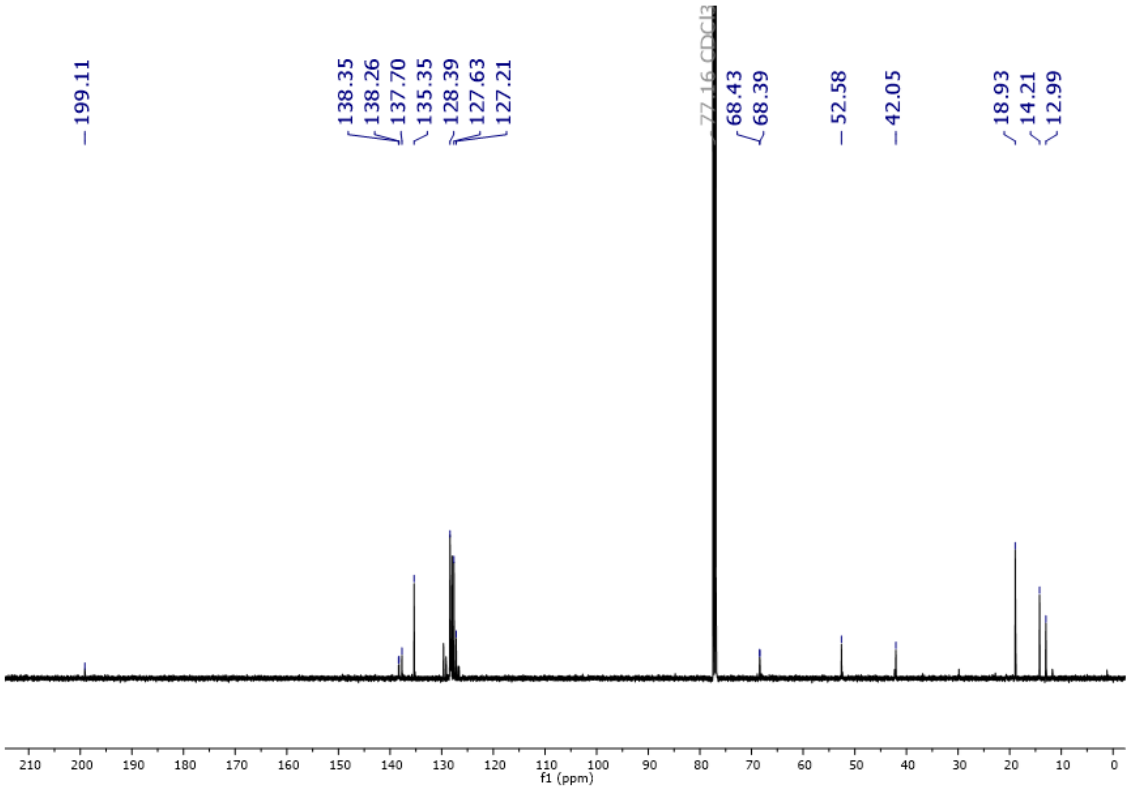


Figure S 71. ^{13}C{^{1}H} NMR ($CDCl_3$) of compound 5g, [Ni{S_2P(=O)(OBz)}(CNXyl){C(NHXyl)(NEt_2)}].

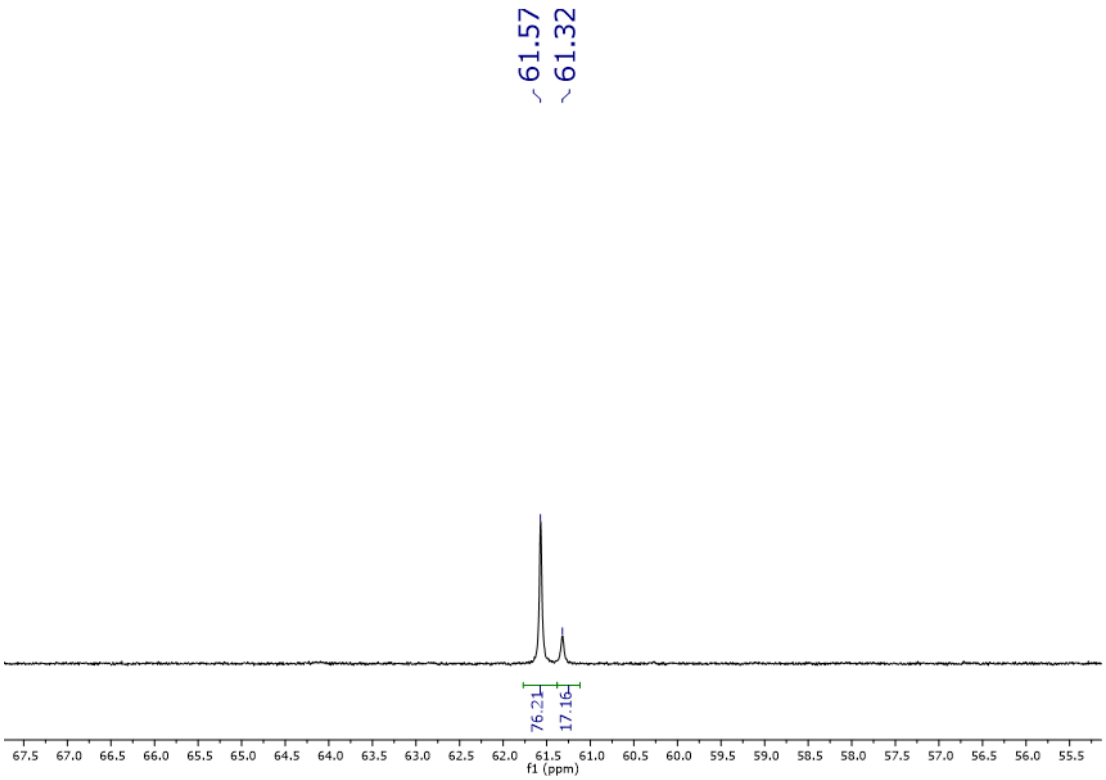


Figure S 72. $^{31}P\{^{1}H\}$ NMR (DMSO-*d6*) of compound 5g, [Ni{$S_2P(=O)(OBz)$}(CNXyl){C(NHXyl)(NEt_2)}].

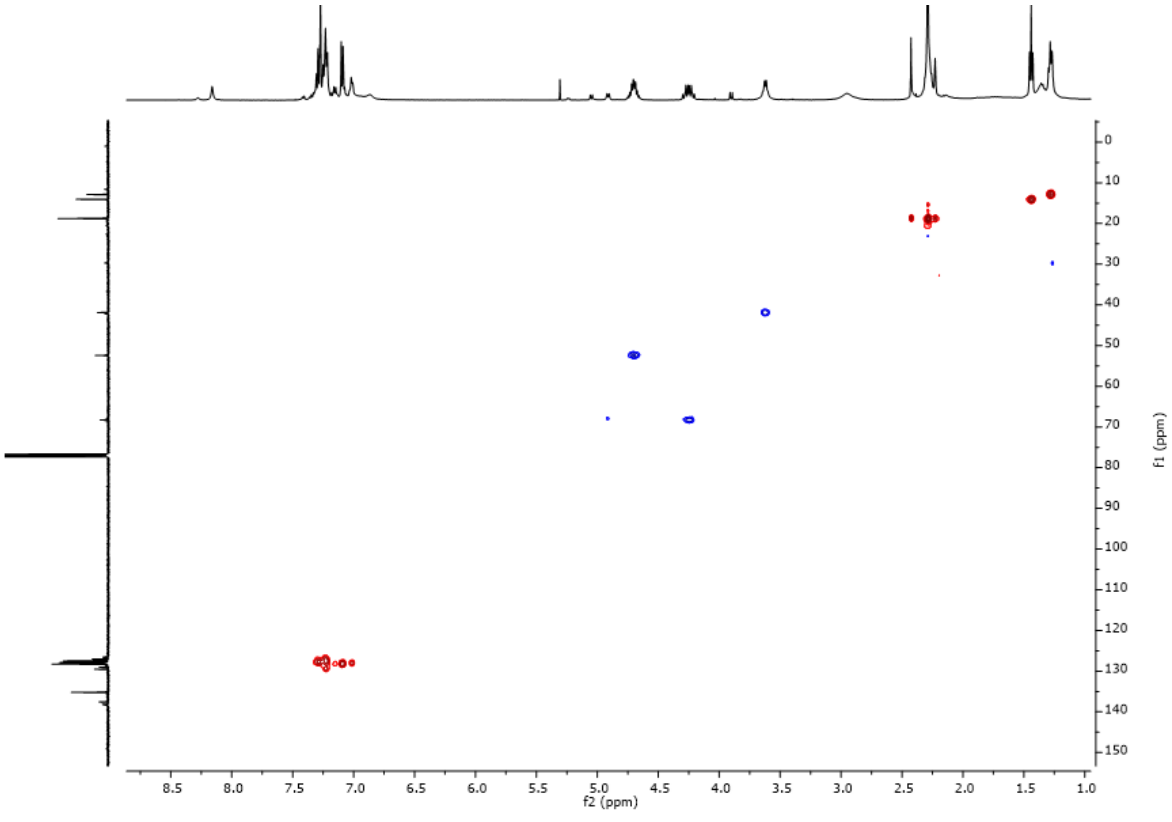


Figure S 73. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (DMSO-*d6*) of compound 5g, [Ni{$S_2P(=O)(OBz)$}(CNXyl){C(NHXyl)(NEt_2)}].

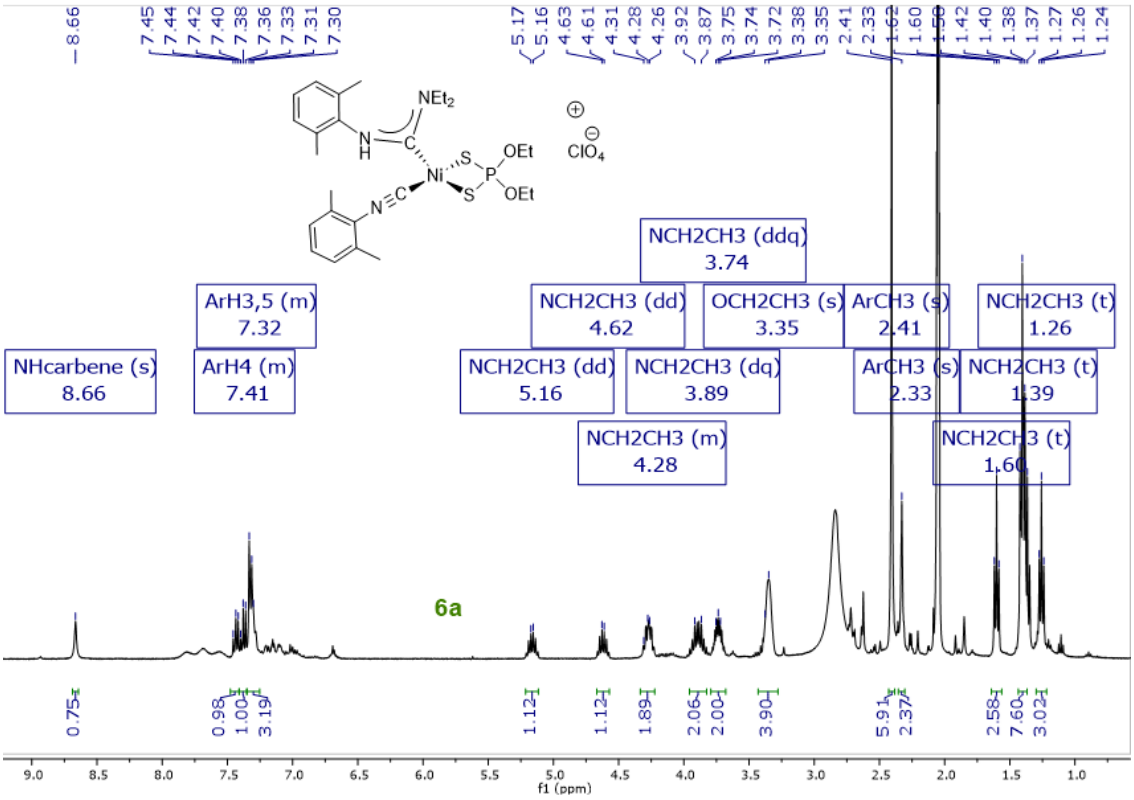


Figure S 74. ^{1}H NMR (Me_2CO-d6) of compound 6a, $[Ni(S_2P(OEt)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

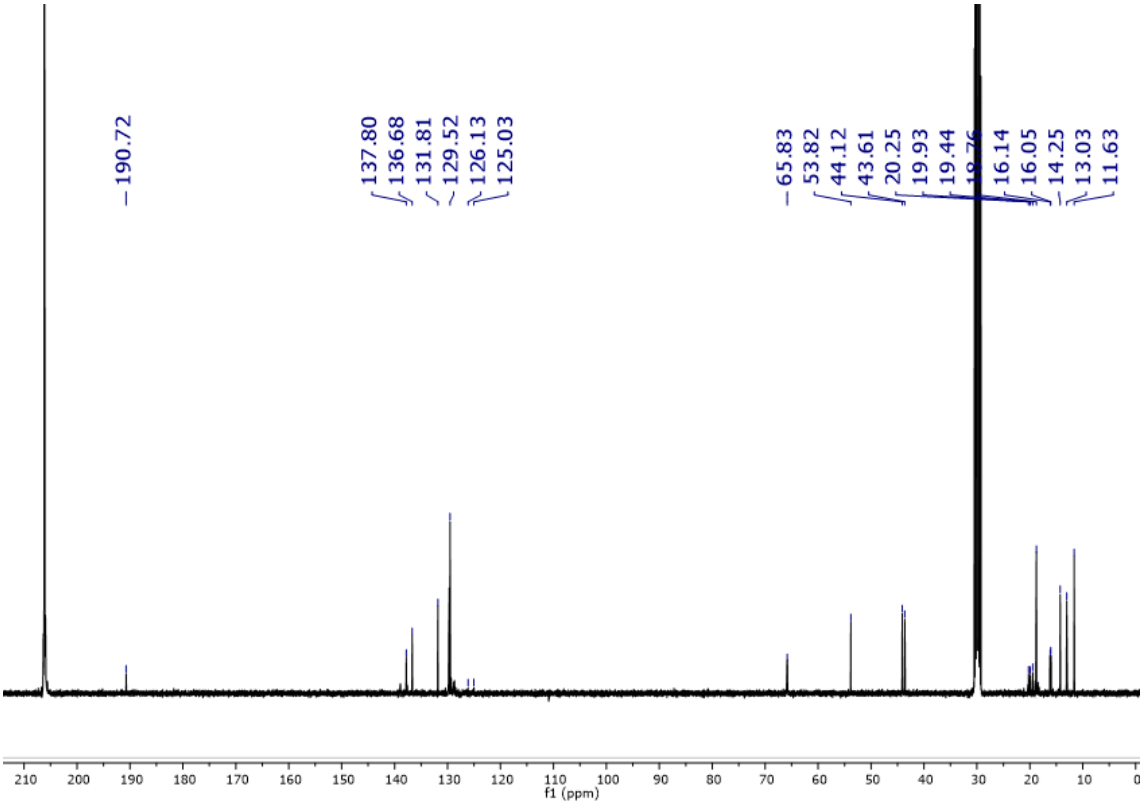


Figure S 75. $^{13}C\{^{1}H\}$ NMR (Me_2CO-d6) of compound 6a, $[Ni(S_2P(OEt)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

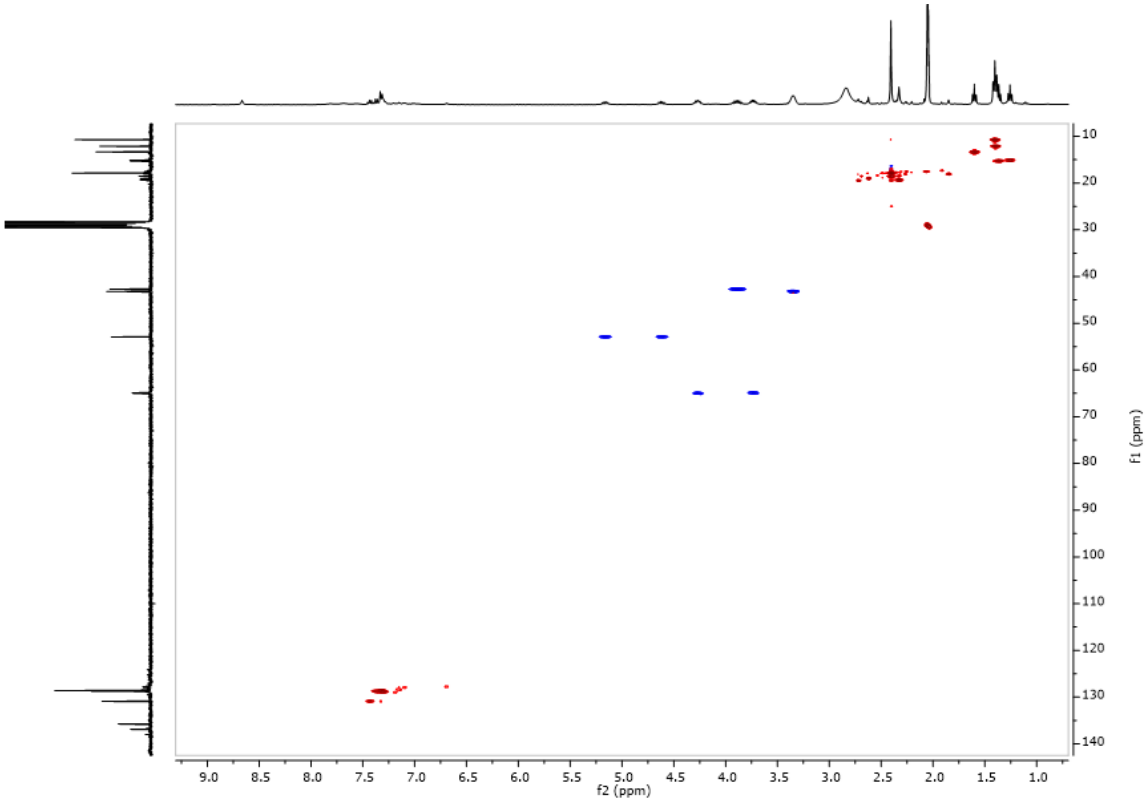


Figure S 76. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (Me_2CO-d6) of compound 6a, $[Ni(S_2P(OEt)_2(\mathit{CNXyl})\{C(NHXyl)(NEt_2)\}]ClO_4$.

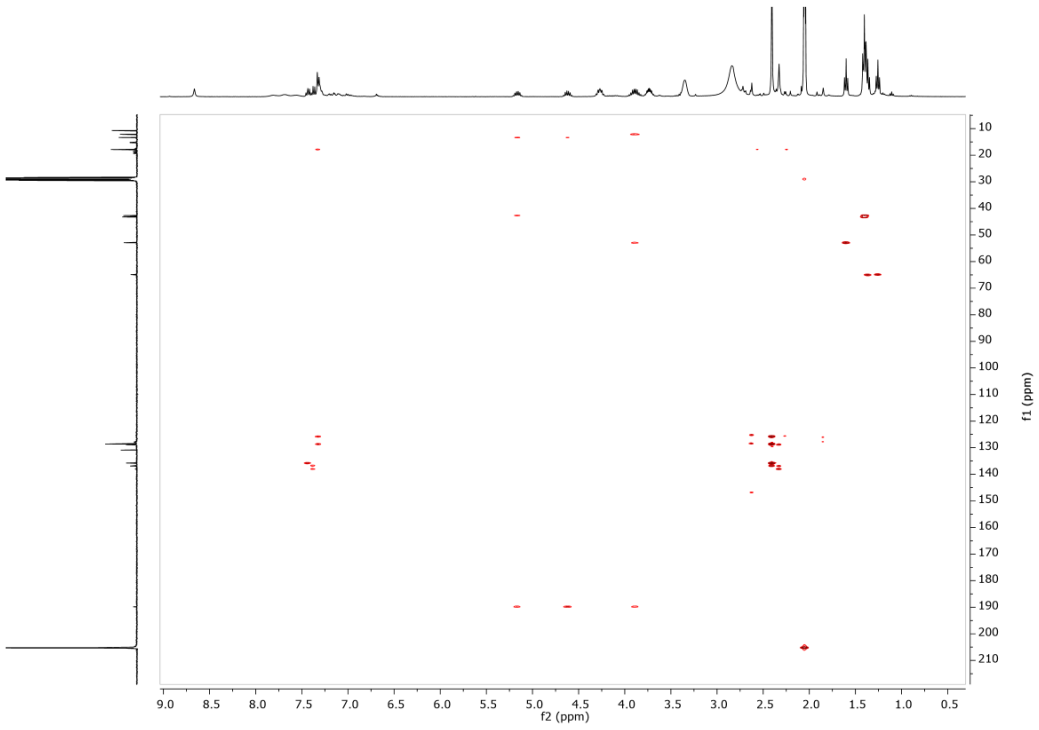


Figure S 77. ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR (Me_2CO-d6) of compound 6a, $[Ni(S_2P(OEt)_2(\mathit{CNXyl})\{C(NHXyl)(NEt_2)\}]ClO_4$

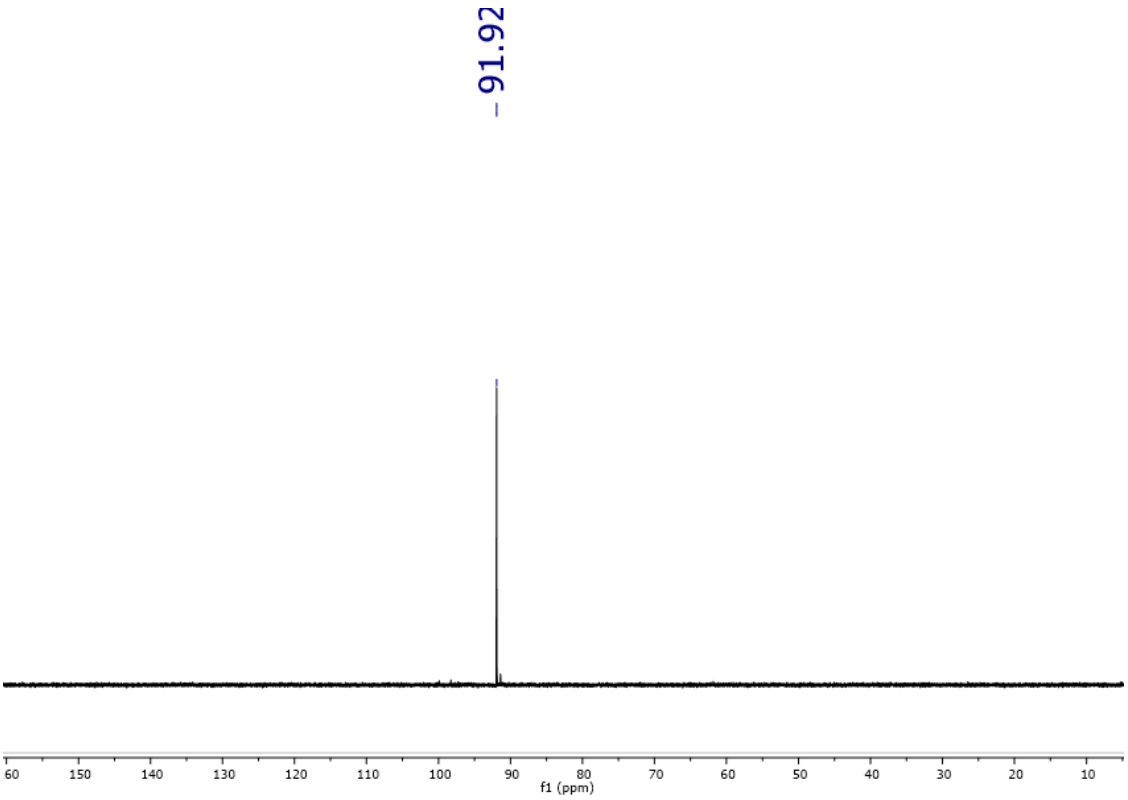


Figure S 78. $^{31}P\{^{1}H\}$ NMR (Me_2CO-d6) of compound 6a, $[Ni(S_2P(OEt)_2(\textit{CNXyl})\{C(NHXyl)(NEt_2)\}]ClO_4$.

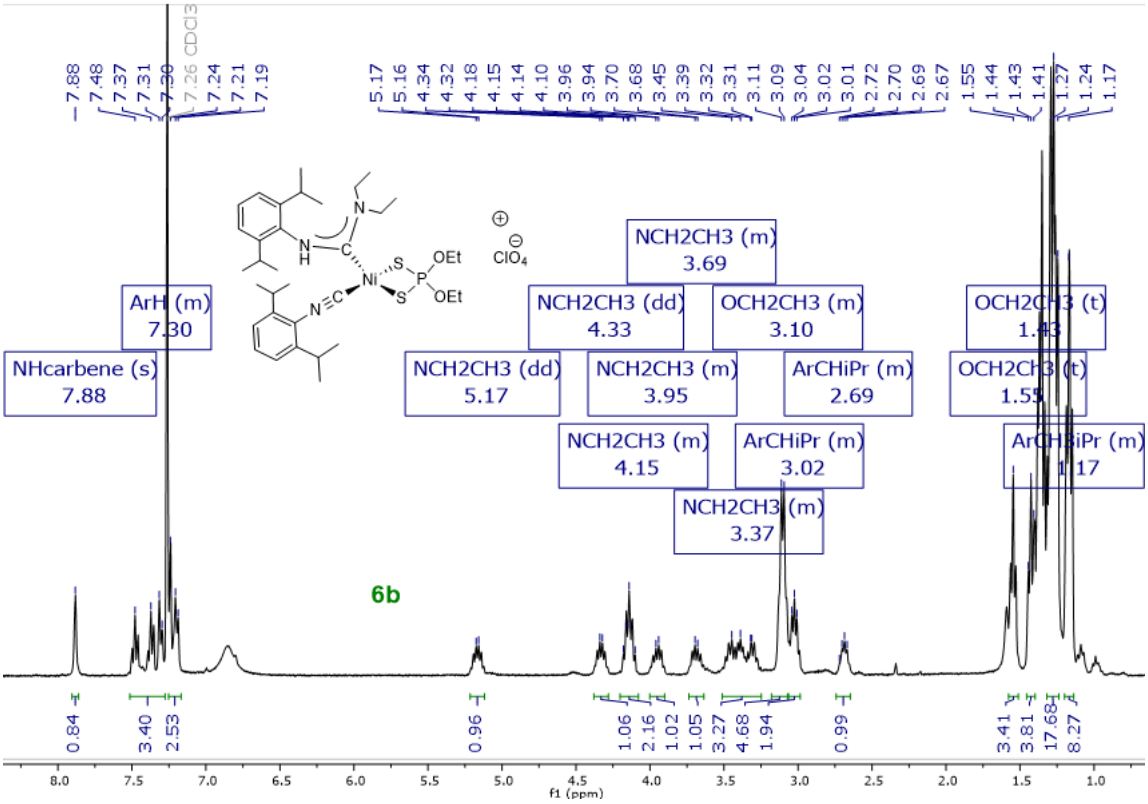


Figure S 79. ^{1}H NMR ($CDCl_3$) of compound 6b, $[Ni(S_2P(OEt)_2(CNAr)\{C(NHAr)(NEt_2)\}]ClO_4$.

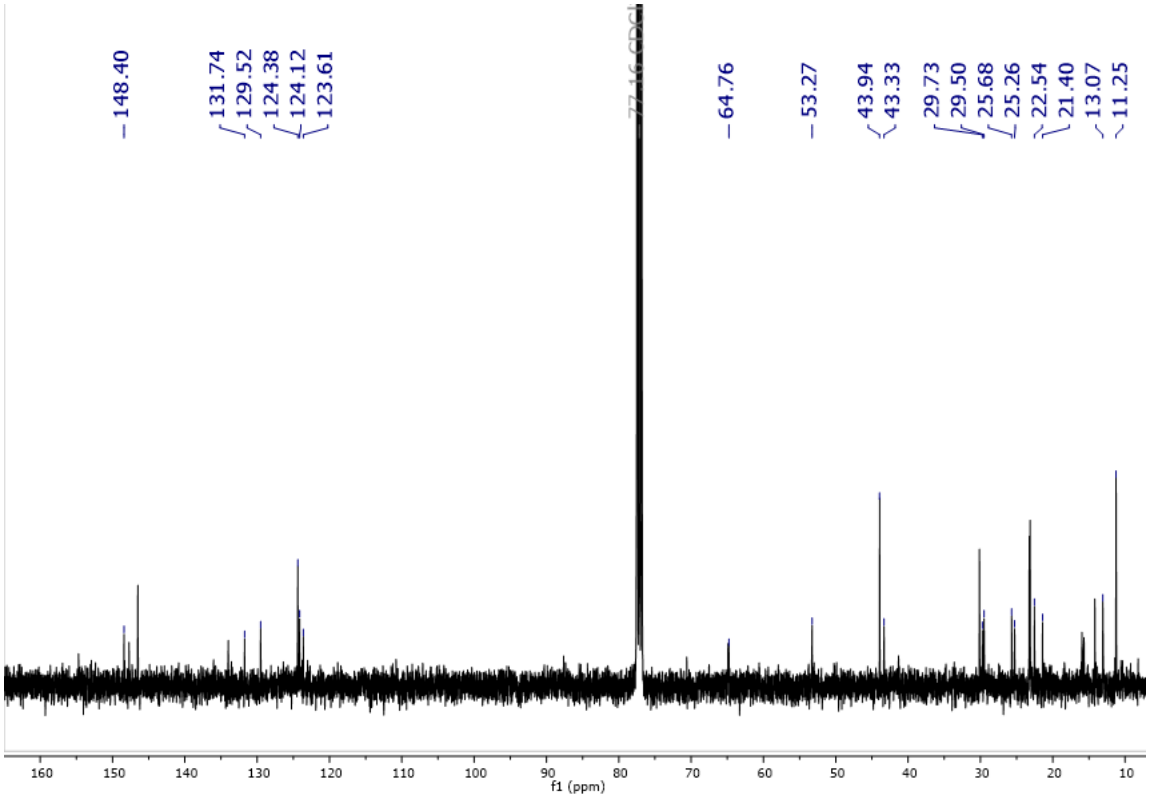


Figure S 80. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 6b, $[Ni(S_2P(OEt)_2(CNAr)\{C(NHAr)(NEt_2)\}]ClO_4$.

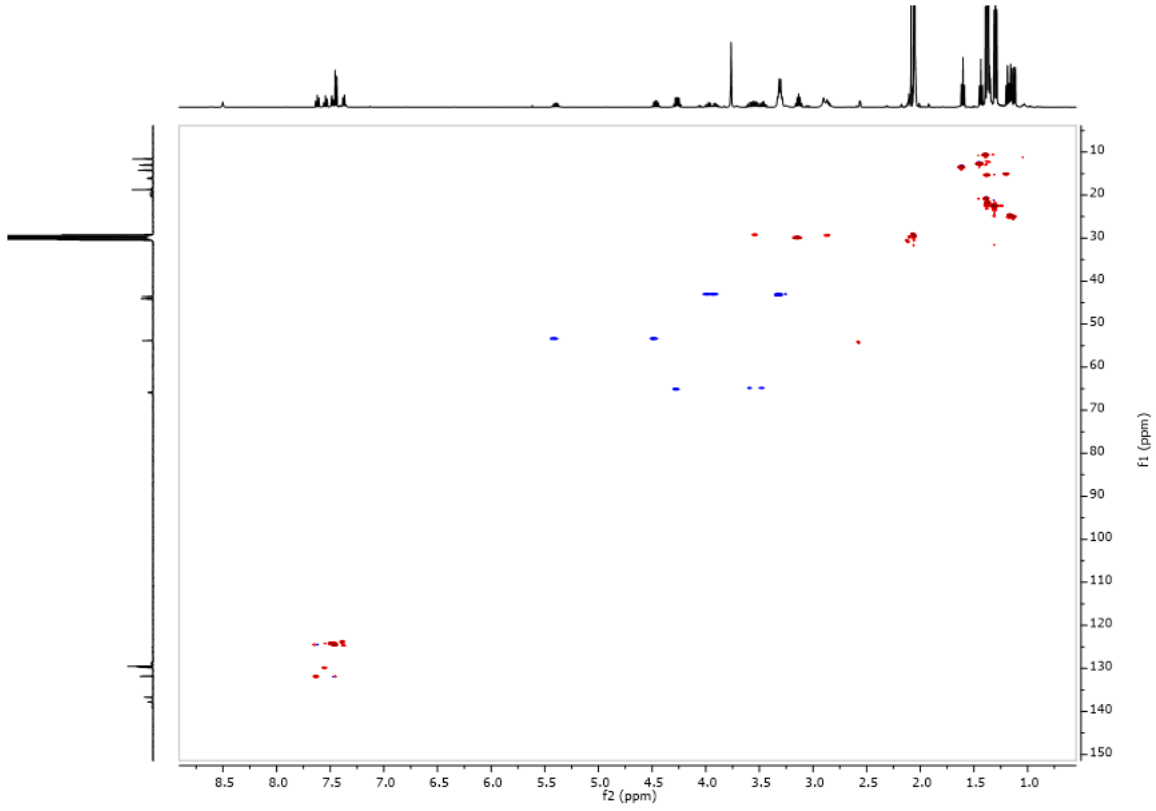


Figure S 81. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (Ac-d6) of compound 6b, $[Ni(S_2P(OEt)_2(CNAr)\{C(NHAr)(NEt_2)\}]ClO_4$.

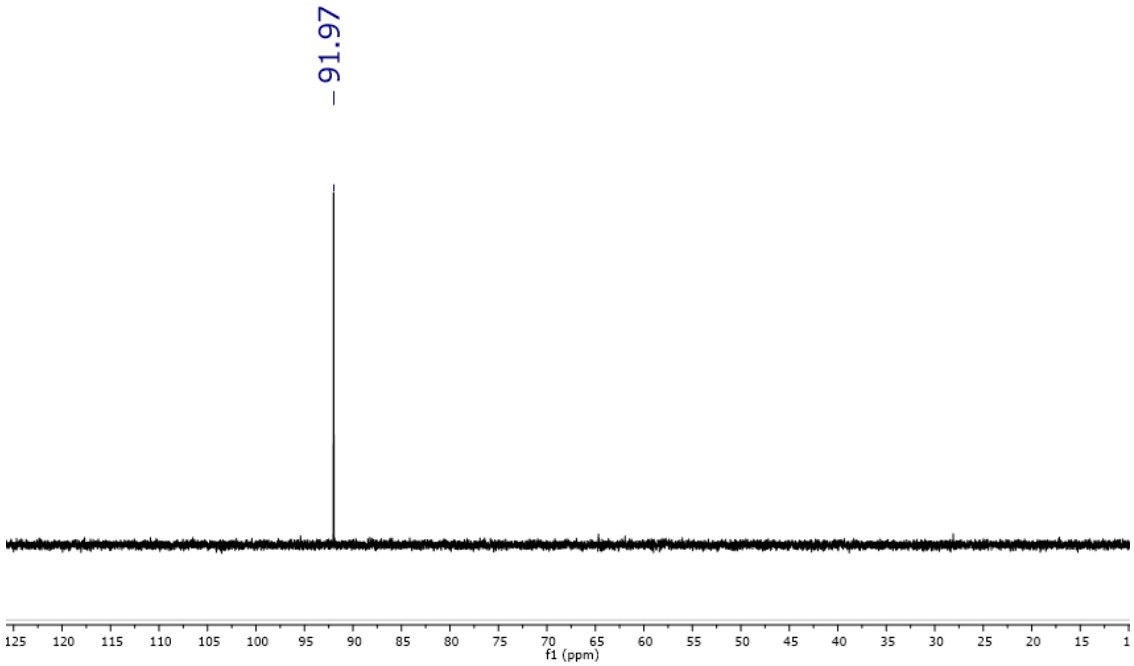


Figure S 82. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 6b, $[Ni(S_2P(OEt)_2(CNAr)\{C(NHAr)(NEt_2)\}]ClO_4$

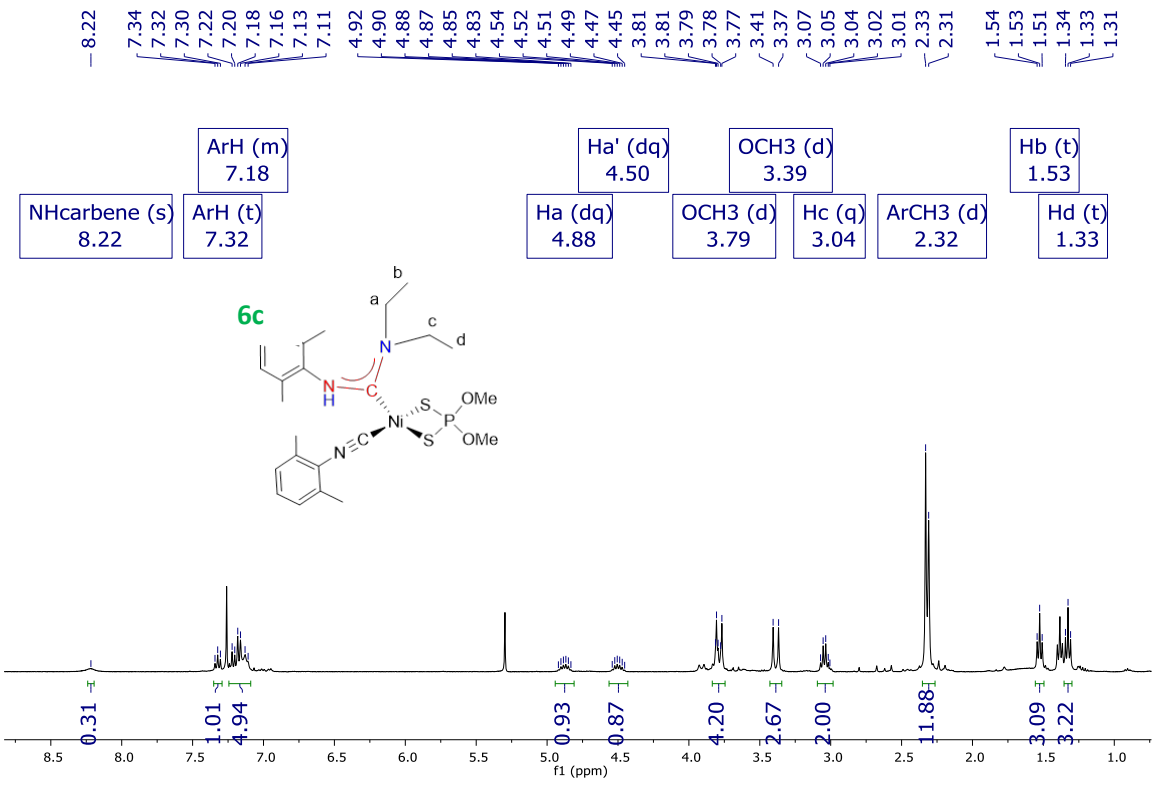


Figure S 83. ^{1}H NMR ($CDCl_3$) of compound 6c, $[Ni(S_2P(OMe)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

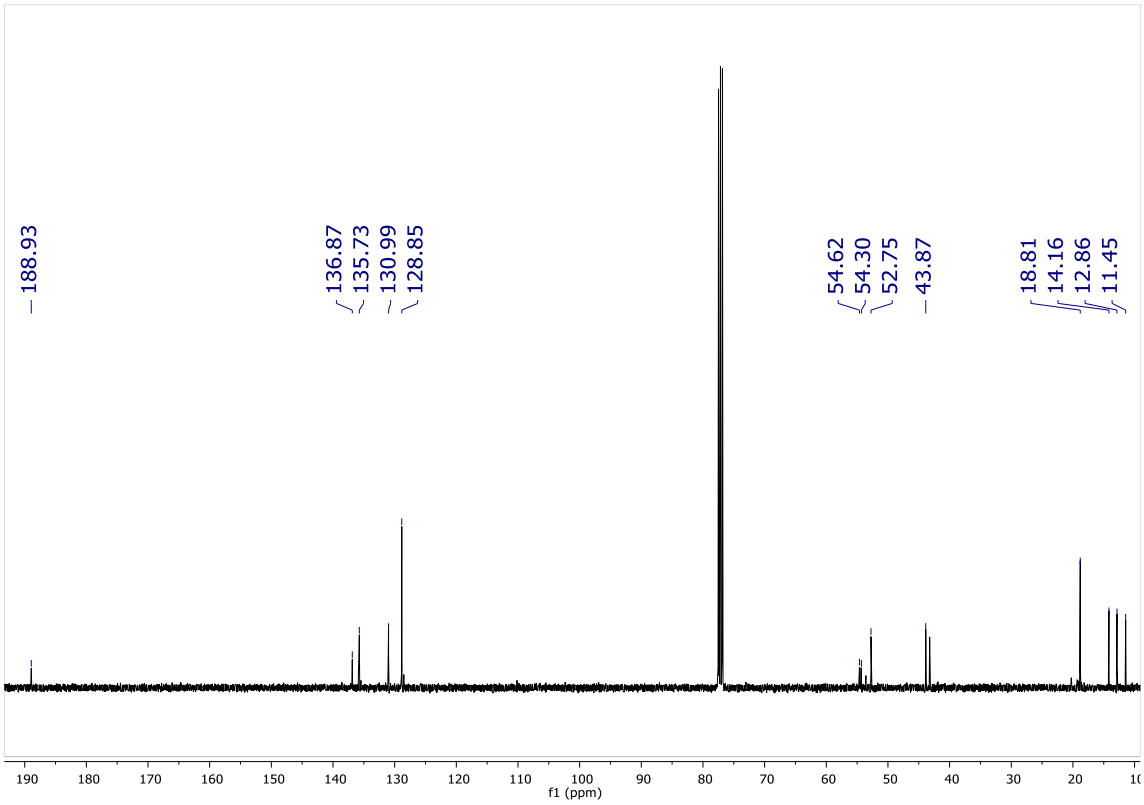


Figure S 84. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 6c, $[Ni(S_2P(OMe)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

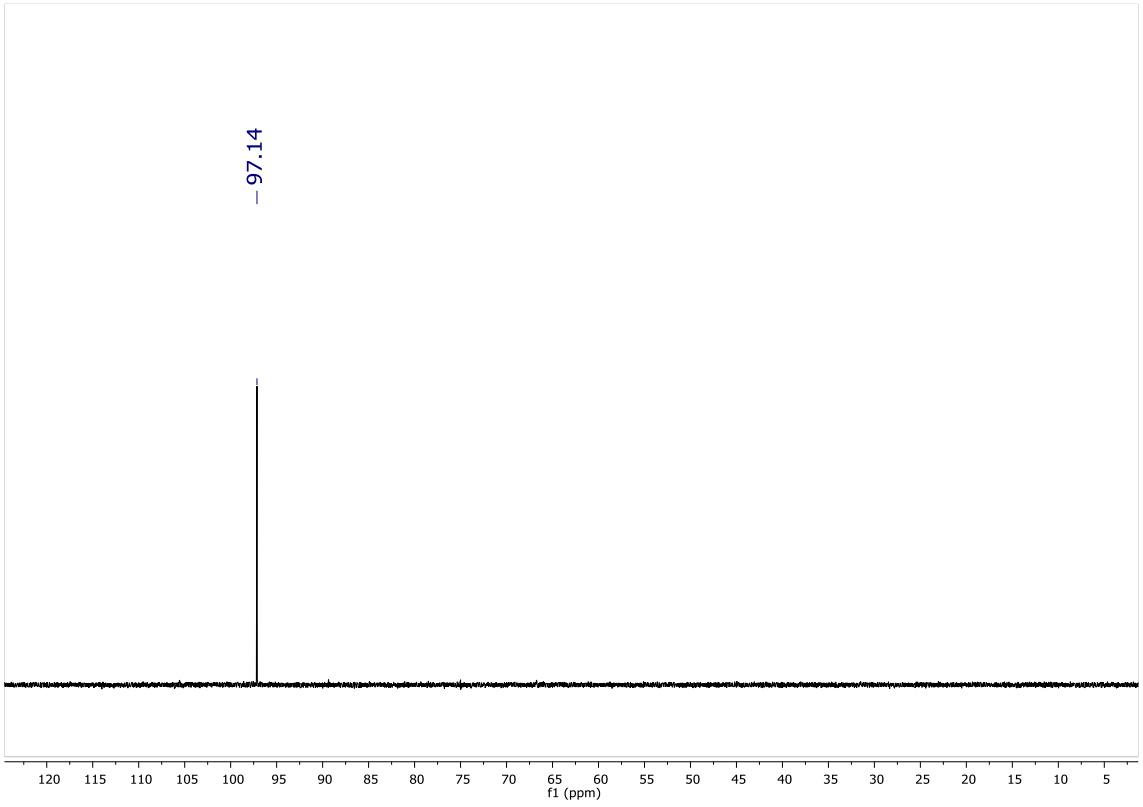


Figure S 85. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 6c, $[Ni(S_2P(OMe)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

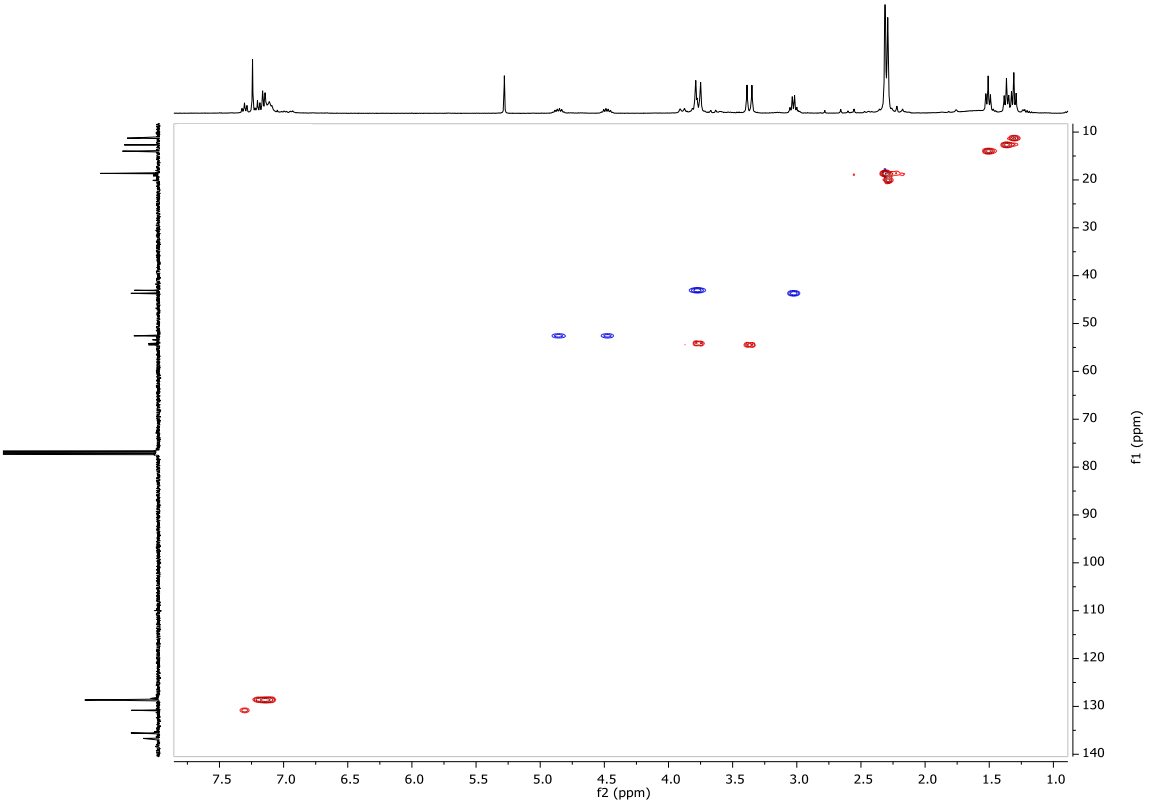


Figure S 86. ^{1}H-^{13}C{^{1}H} HSQC NMR ($CDCl_3$) of compound 6c, $[Ni(S_2P(OMe)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

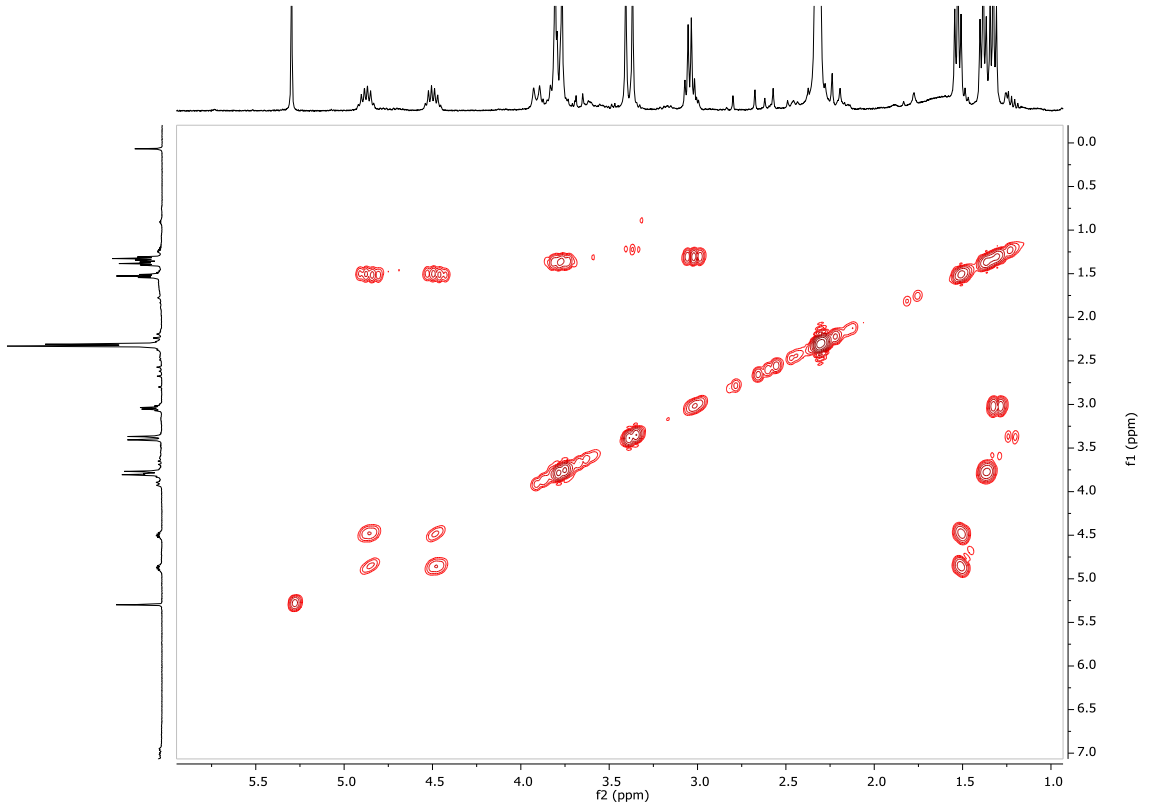


Figure S 87. ^{1}H-^{1}H COSY NMR ($CDCl_3$) of compound 6c, $[Ni(S_2P(OMe)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

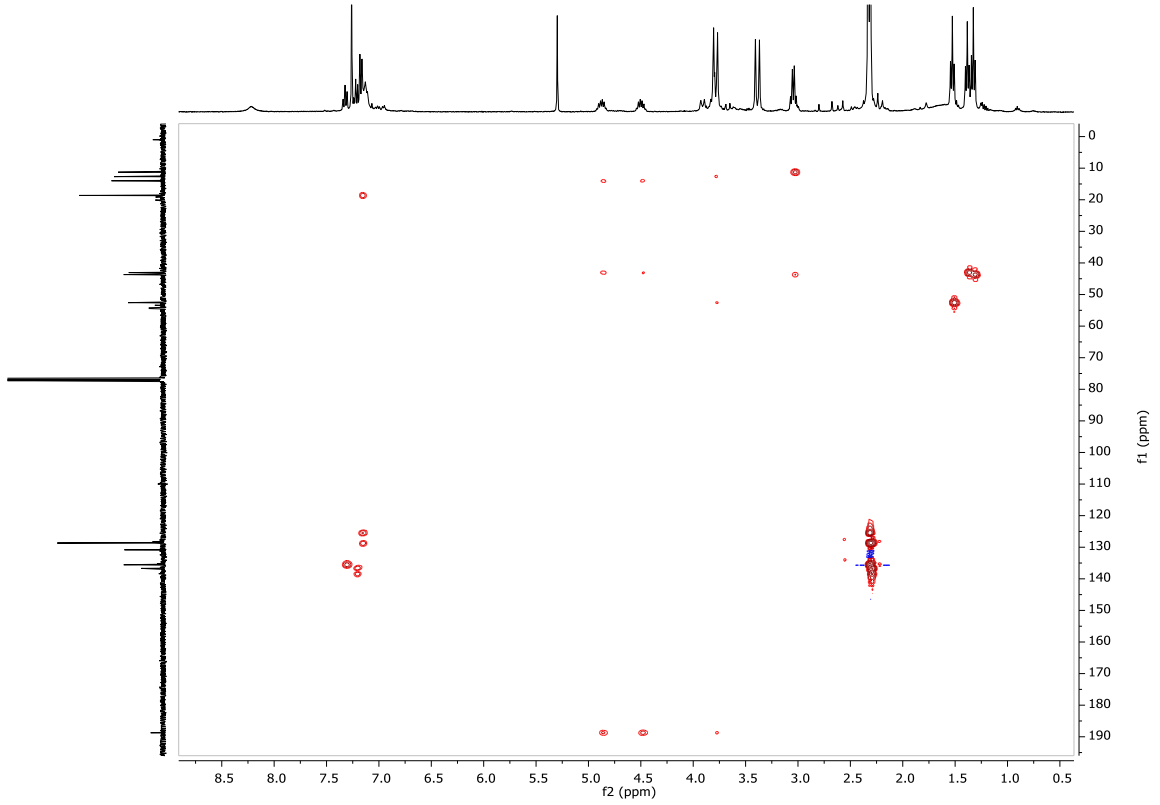


Figure S 88. ^{1}H-$^{13}C\{^{1}H\}$ HMBC NMR ($CDCl_3$) of compound 6c, $[Ni(S_2P(OMe)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

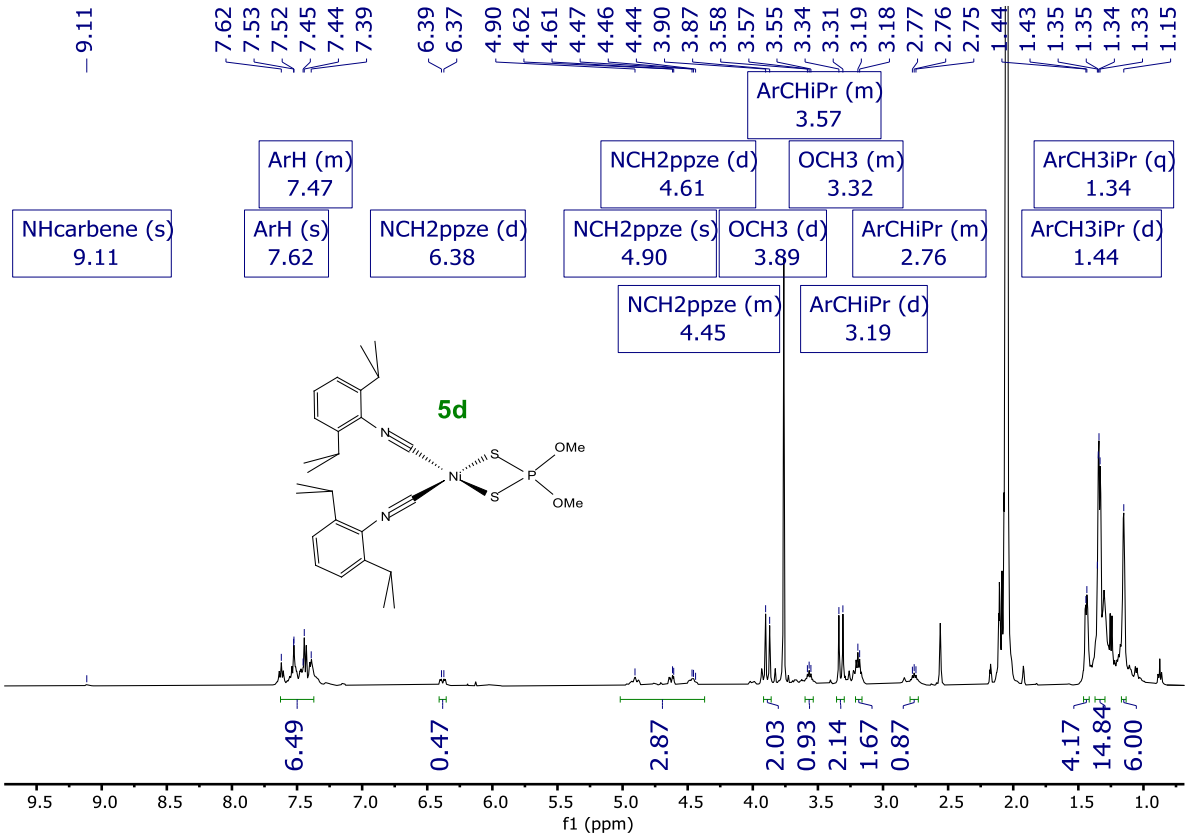


Figure S 89. ^{1}H NMR ($CDCl_3$) of compound 6d, $[Ni(S_2P(OMe)_2(CNAr)\{C(NHAr)(Nppze)\}]ClO_4$. Decomposition products are presented in the crude, preventing a perfect integration of the chemical shift.

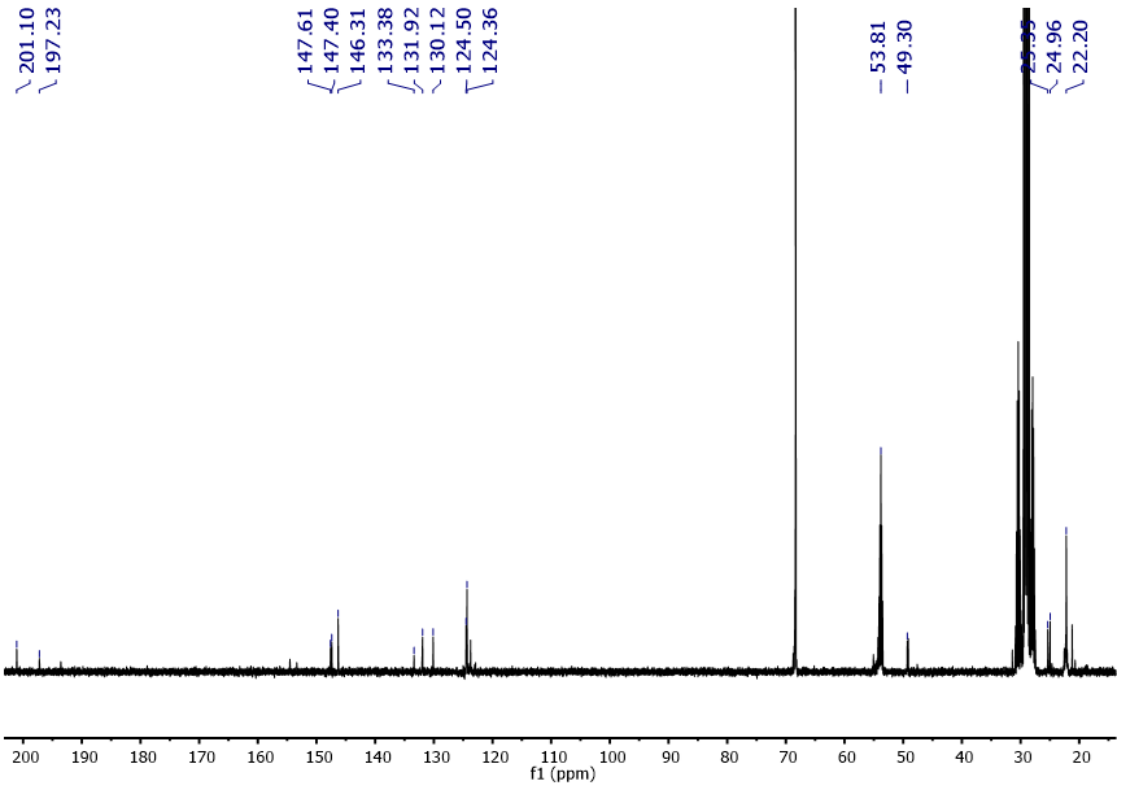


Figure S 90. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 6d, $[Ni(S_2P(OMe)_2(CNAr)\{C(NHAr)(Nppze)\}]ClO_4$.

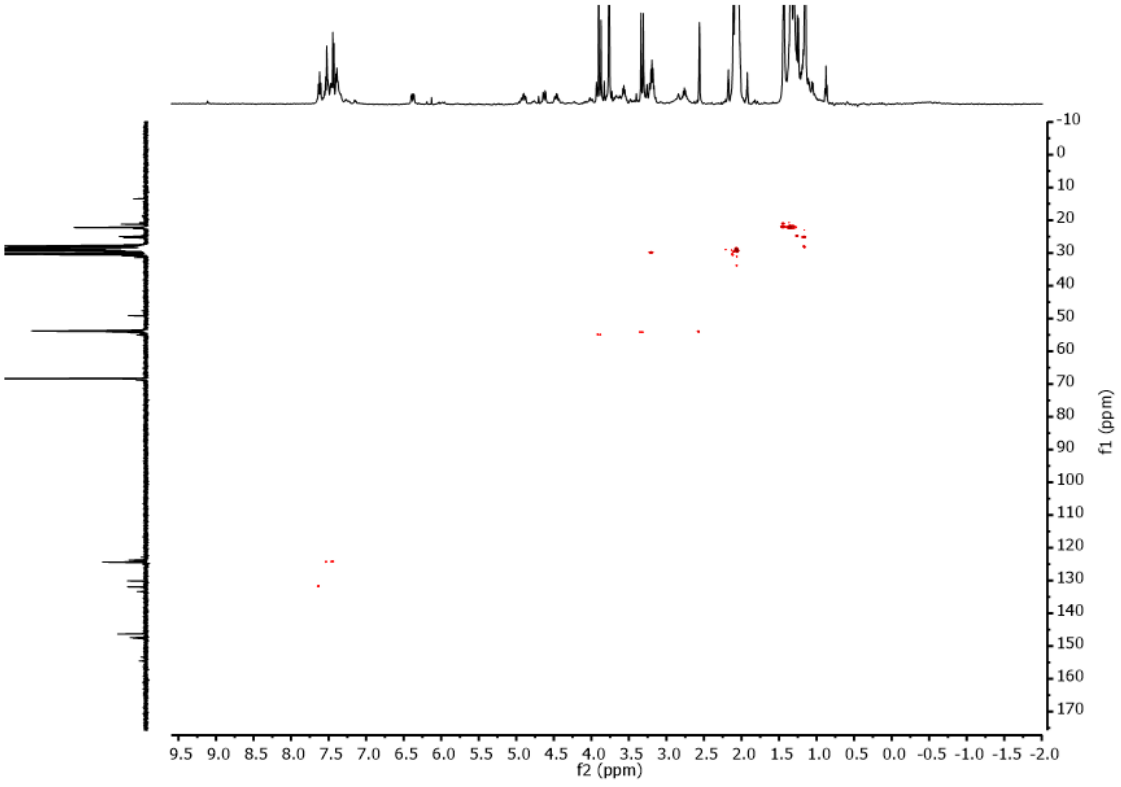


Figure S 91. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 6d, $[Ni(S_2P(OMe)_2(CNAr)\{C(NHAr)(Nppze)\}]ClO_4$.

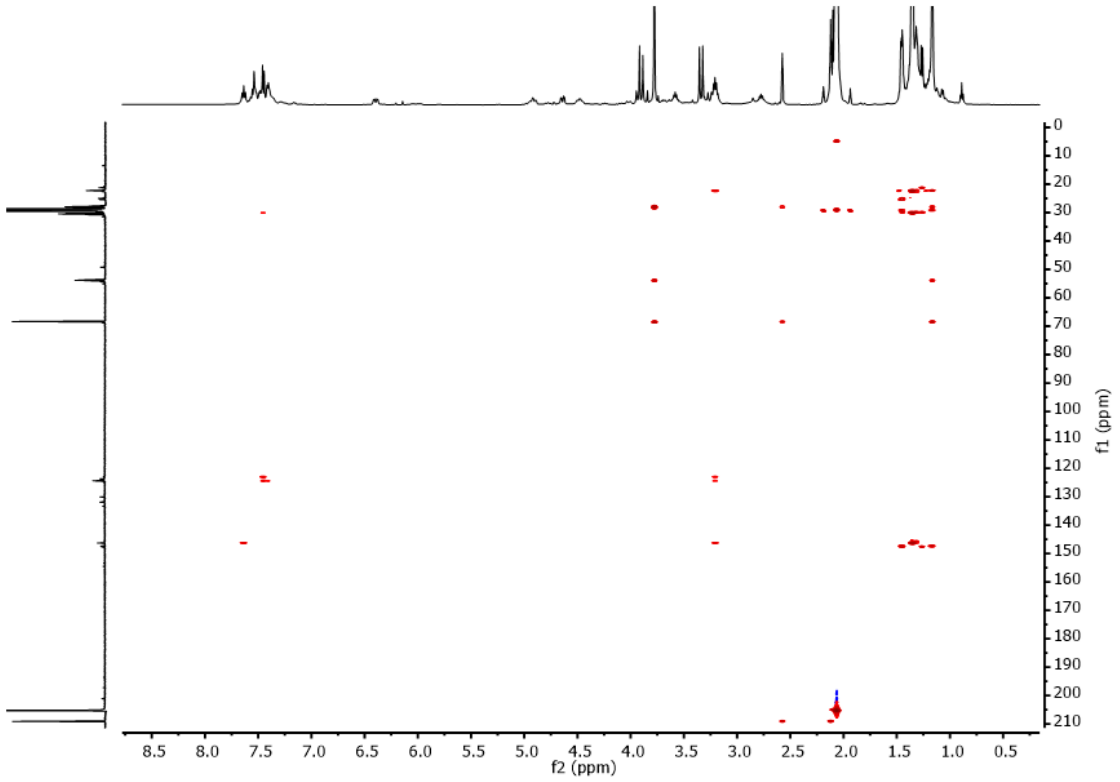


Figure S 92. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR ($CDCl_3$) of compound 6d, $[Ni(S_2P(OMe)_2(CNAr)\{C(NHAr)(Nppze)\}]ClO_4$.

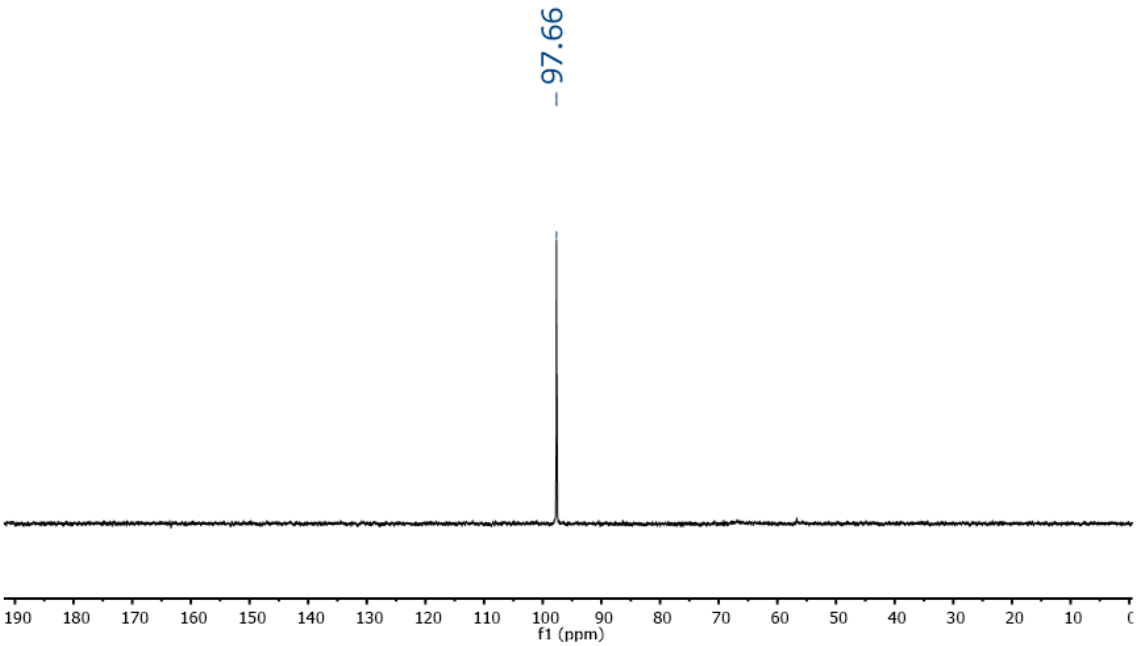


Figure S 93. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 6d, $[Ni(S_2P(OMe)_2(CNAr)\{C(NHAr)(Nppze)\}]ClO_4$.

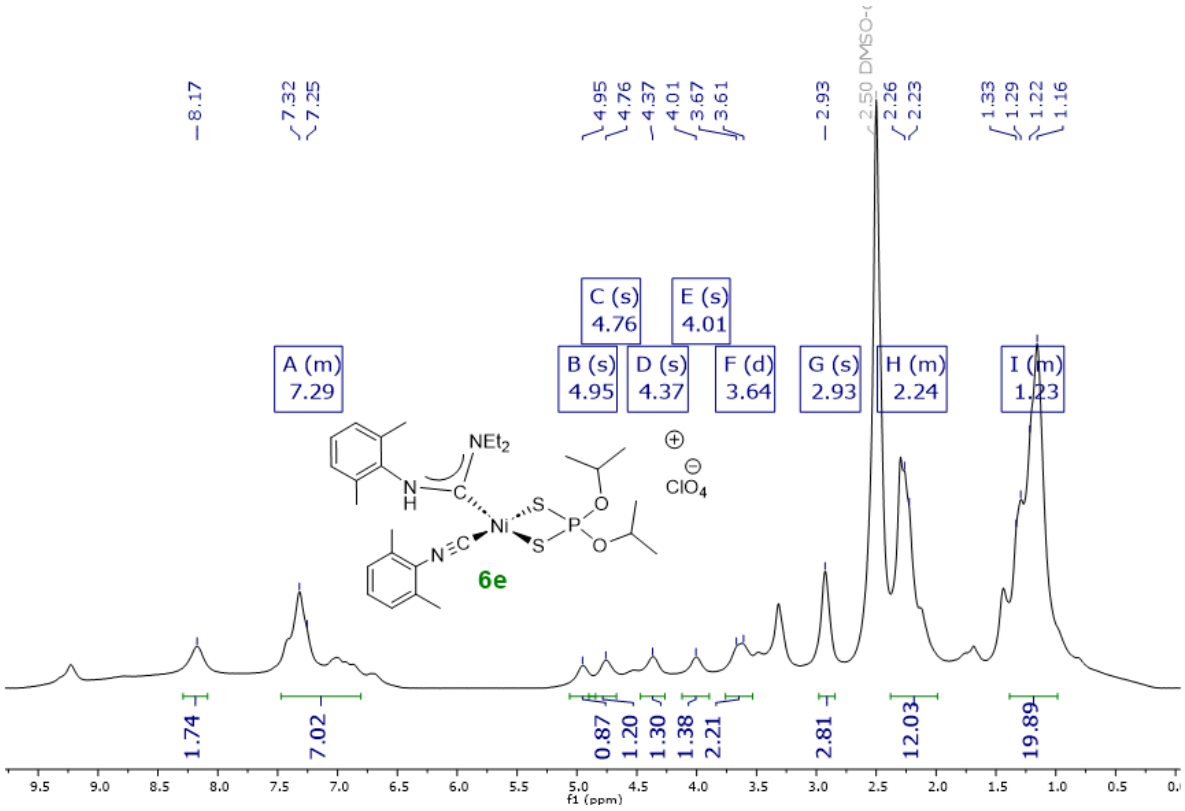


Figure S 94. ^{1}H NMR (DMSO-d6) of compound 6e, [Ni($S_2P(O^iPr)_2$(CNXyl){C(NHXyl)(NEt_2)}]ClO_4. Decomposition products are presented in the crude, preventing a perfect integration of the chemical shift.

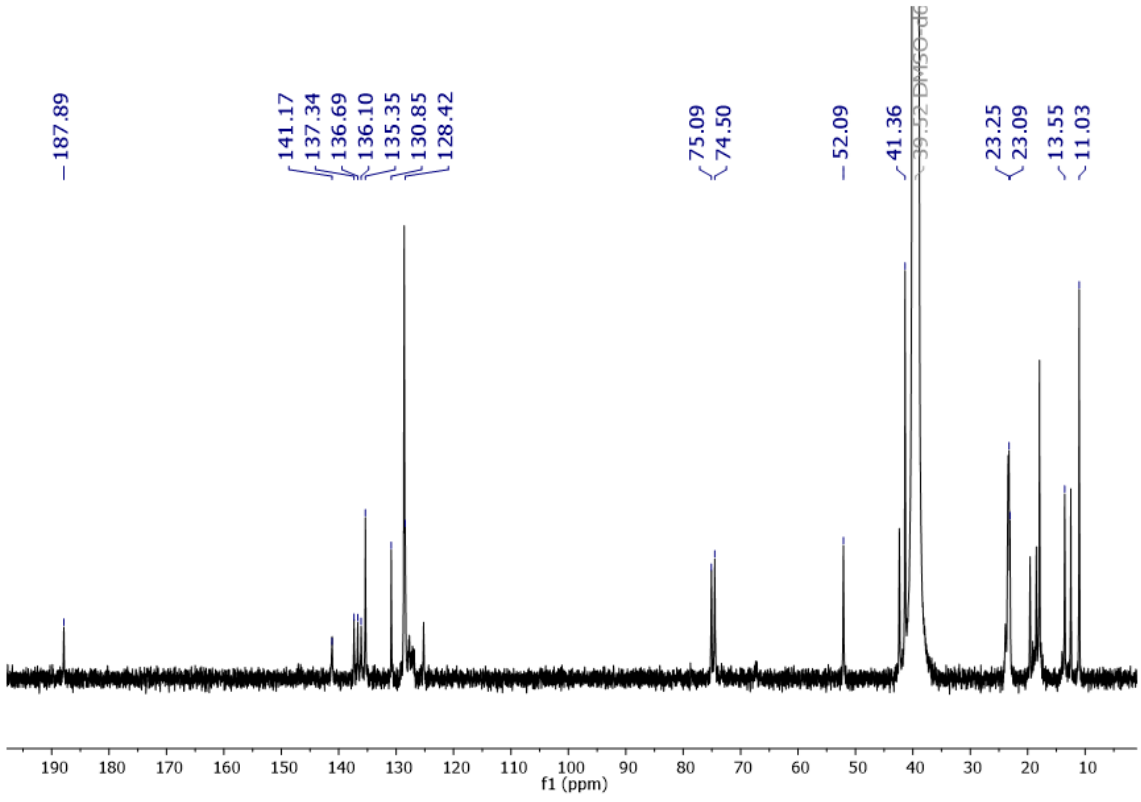


Figure S 95. ^{13}C {^{1}H} NMR (DMSO-d6) of compound 6e, [Ni($S_2P(O^iPr)_2$(CNXyl){C(NHXyl)(NEt_2)}]ClO_4.

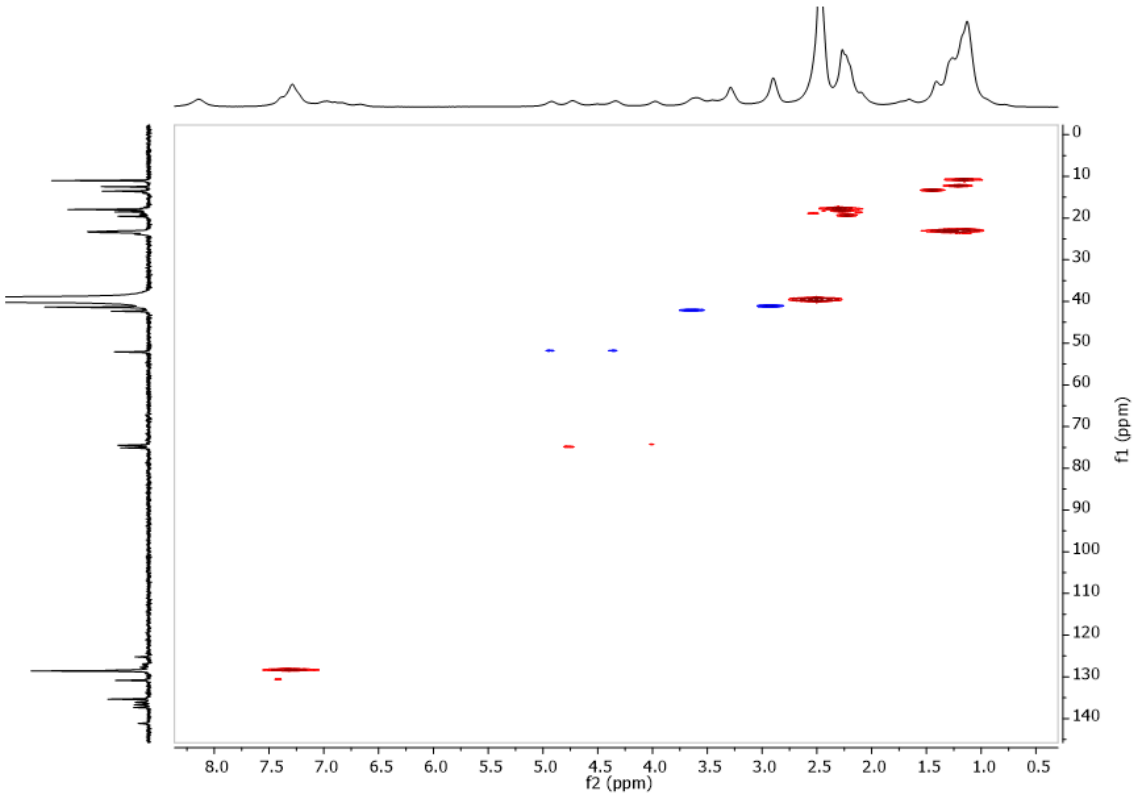


Figure S 96. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (DMSO-d6) of compound 6e, $[Ni(S_2P(O^iPr)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

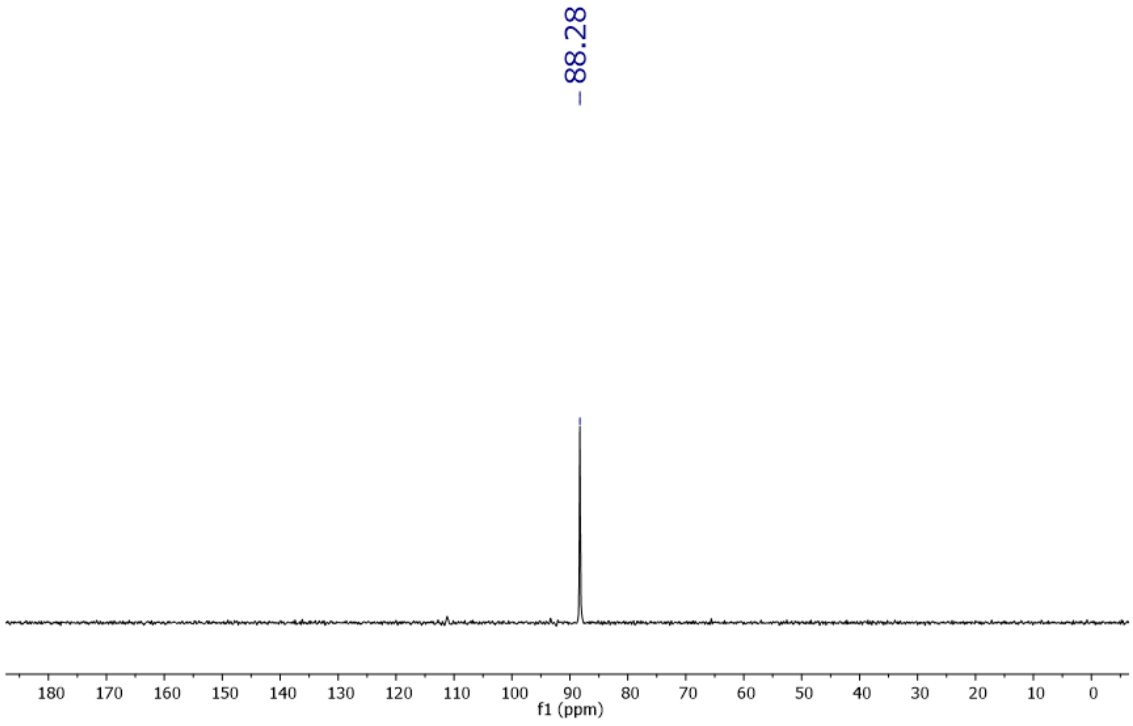


Figure S 97. $^{31}P\{^{1}H\}$ NMR (DMSO-d6) of compound 6e, $[Ni(S_2P(O^iPr)_2(CNXyl)\{C(NHXyl)(NEt_2)\}]ClO_4$.

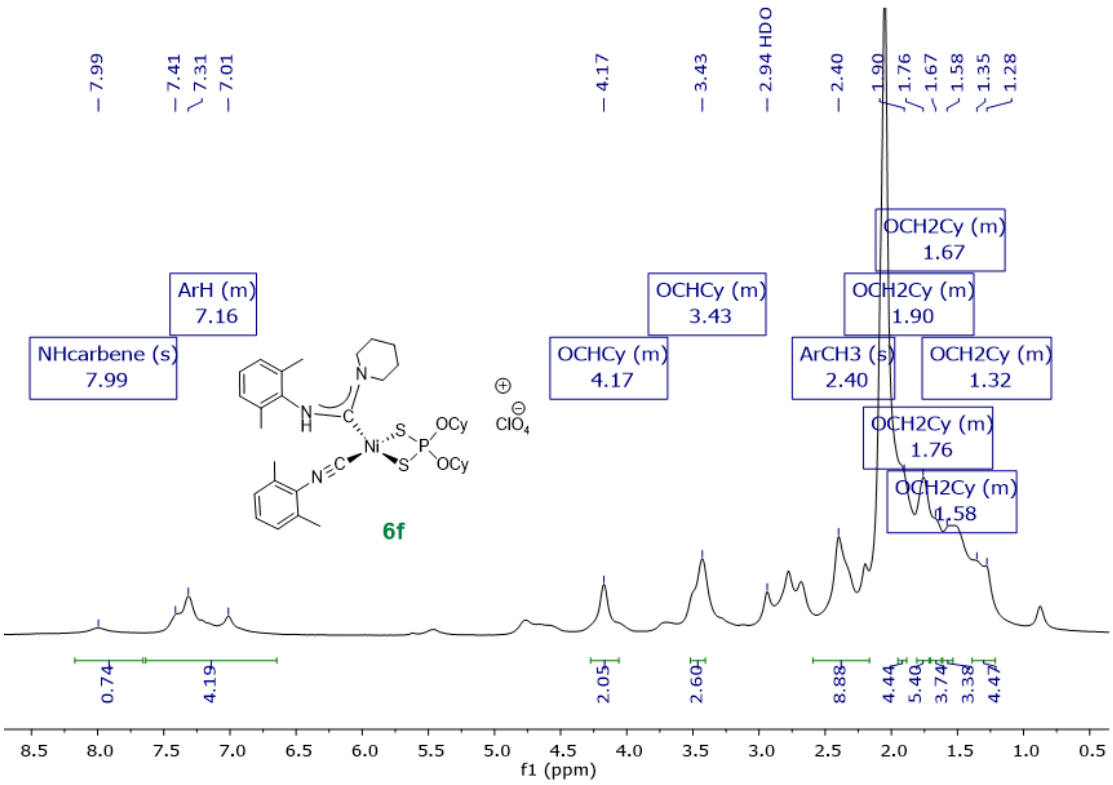


Figure S 98. ^{1}H NMR (Me_2CO-d6) of compound 6f, $[Ni(S_2P(OCy)_2(CNXyl)\{C(NHXyl)(Npip)\}]ClO_4$.

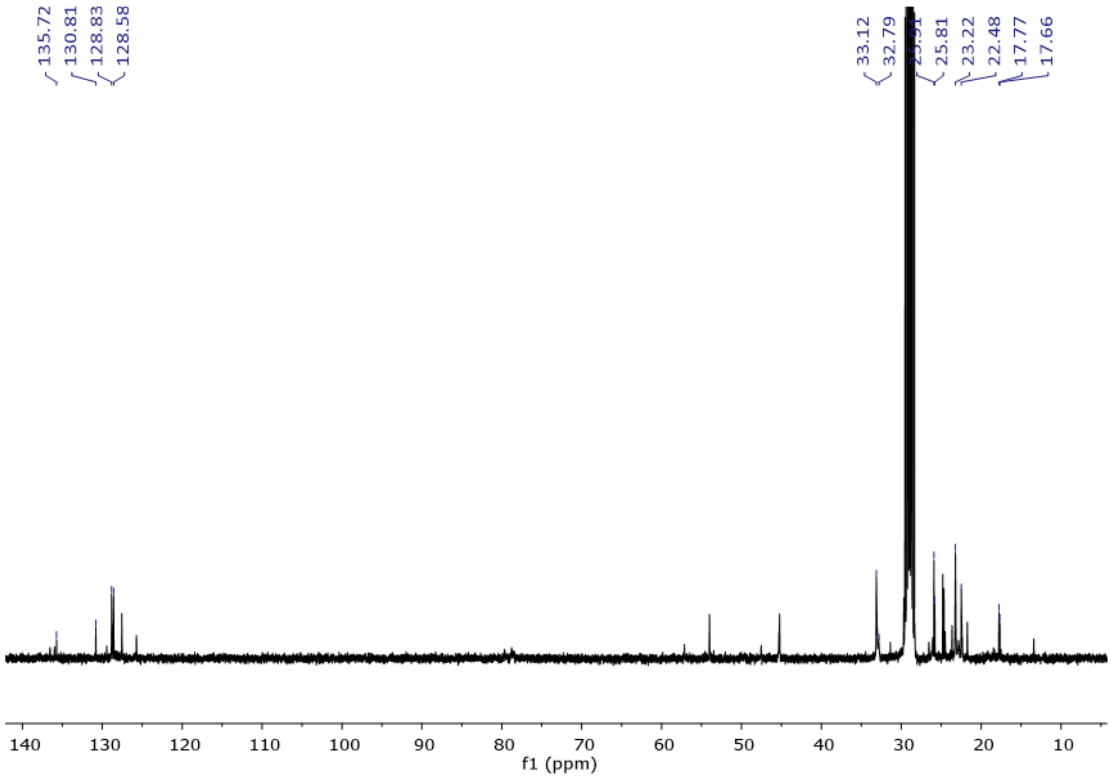


Figure S 99. ^{13}C {^{1}H} NMR (Me_2CO-d6) of compound 6f, $[Ni(S_2P(OCy)_2(CNXyl)\{C(NHXyl)(Npip)\}]ClO_4$.

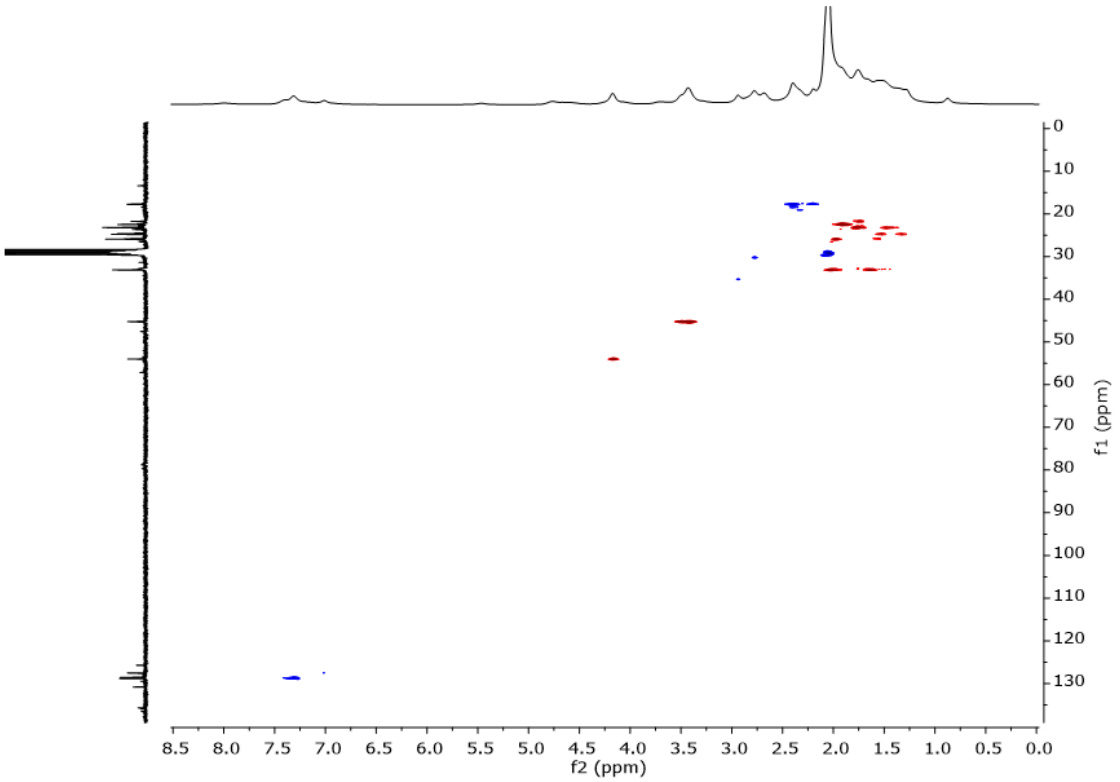


Figure S 100. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (Me_2CO-d6) of compound 6f, $[Ni(S_2P(OCy)_2(CNXyl)\{C(NHXyl)(Npip)\}]ClO_4$.

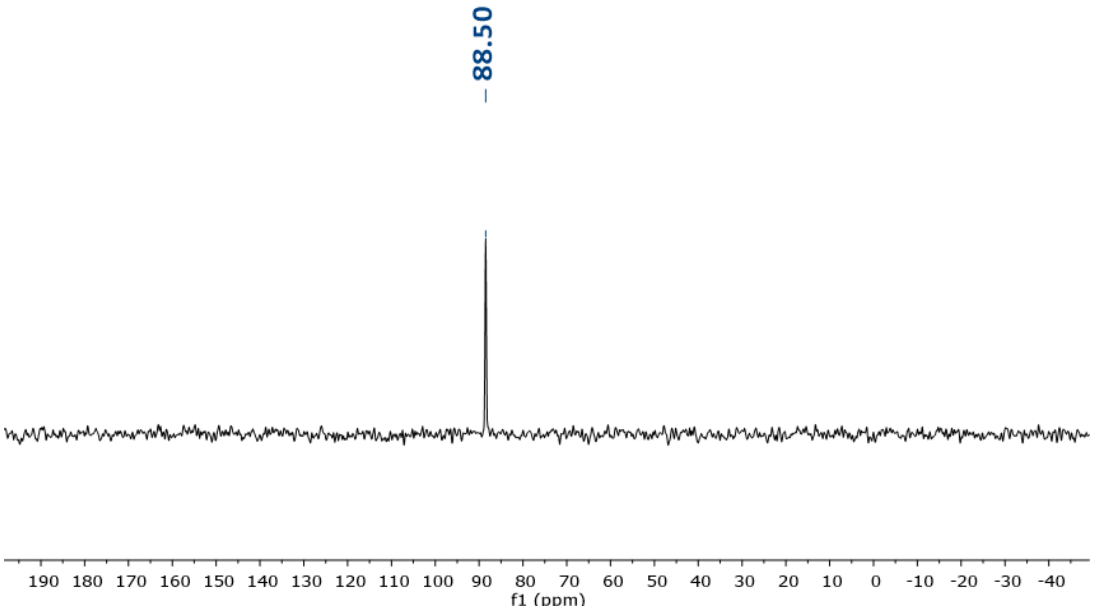


Figure S 101. $^{31}P\{^{1}H\}$ NMR (Me_2CO-d6) of compound 6f, $[Ni(S_2P(OCy)_2(CNXyl)\{C(NHXyl)(Npip)\}]ClO_4$.

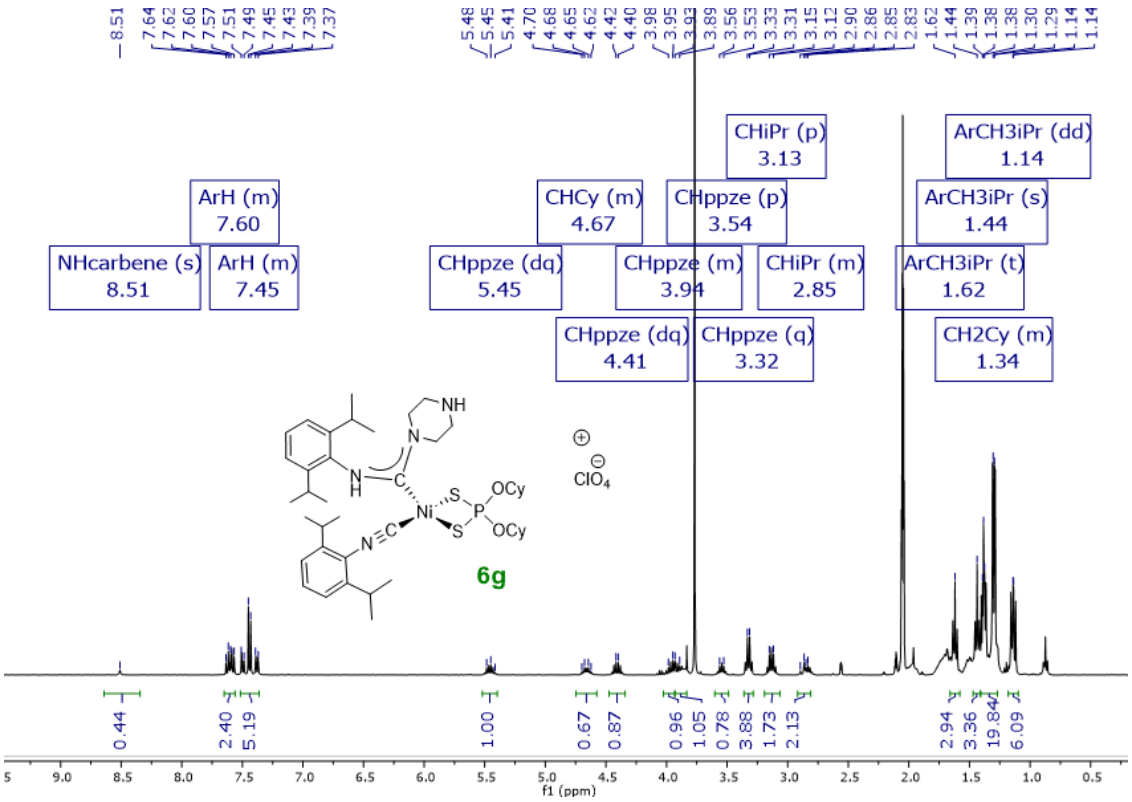


Figure S 102. ^{1}H NMR (Me_2CO-d6) of compound 6g, $[Ni(S_2P(OCy)_2(CNAr)\{C(NHAr)(NPpze)\}]ClO_4$.

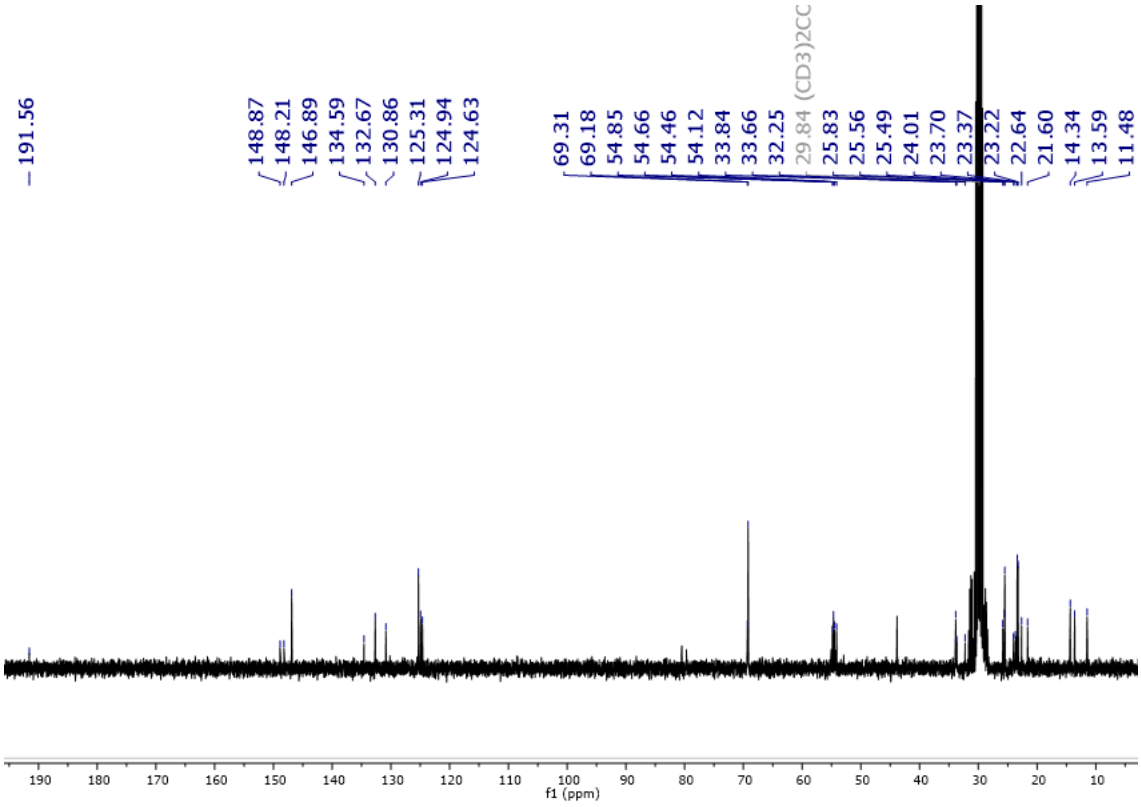


Figure S 103. ^{13}C {^{1}H} NMR (Me_2CO-d6) of compound 6g, $[Ni(S_2P(OCy)_2(CNAr)\{C(NHAr)(NPpze)\}]ClO_4$.

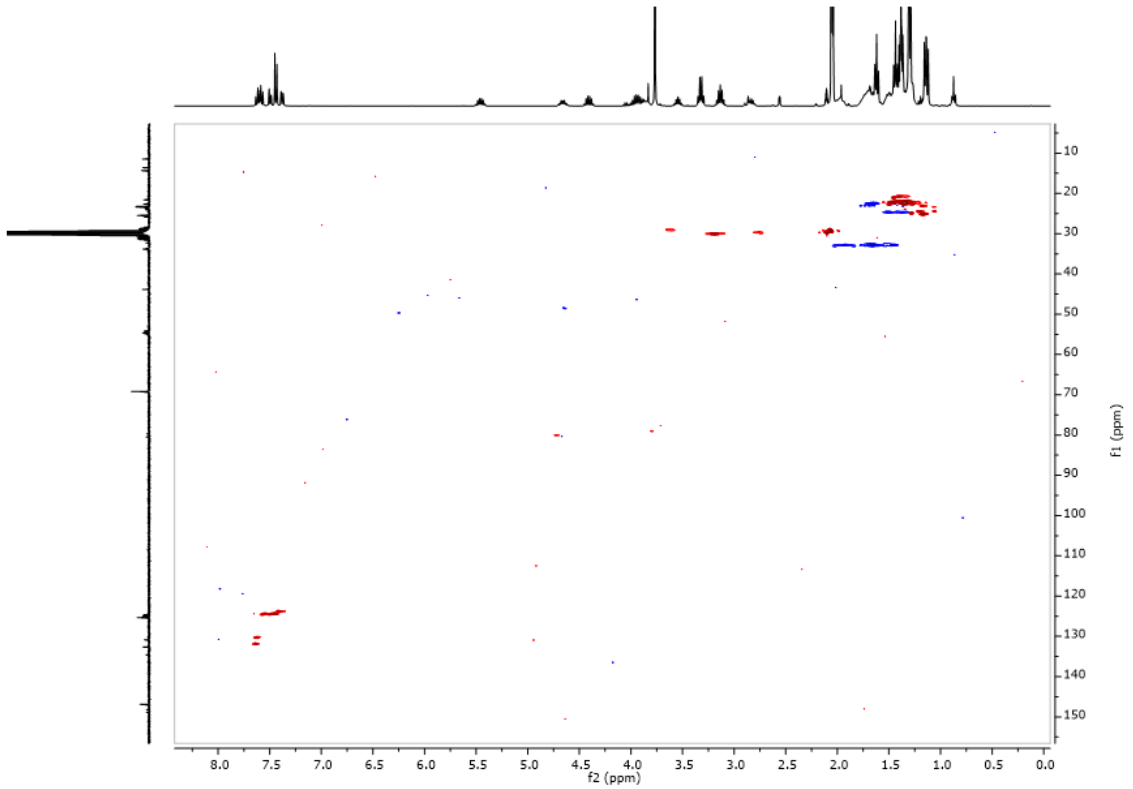


Figure S 104. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (Me_2CO-d6) of compound 6g, $[Ni(S_2P(OCy)_2(CNAr)\{C(NHAr)(NPpze)\}]ClO_4$.

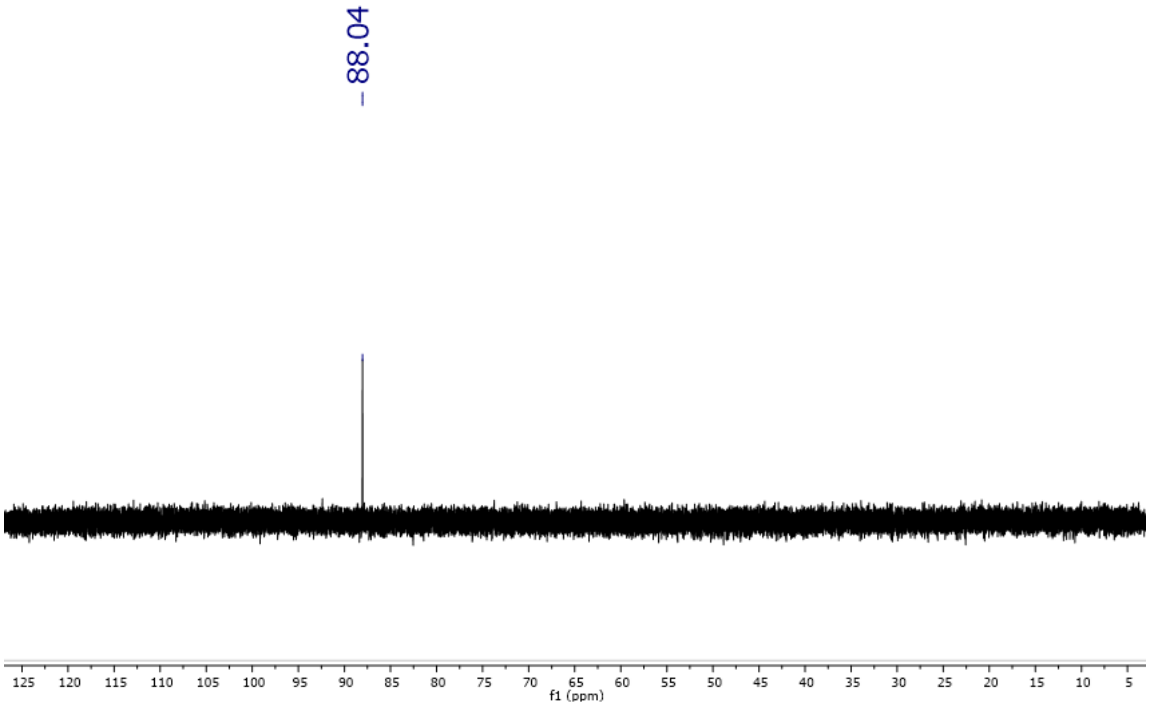


Figure S 105. $^{31}P\ \{^{1}H\}$ NMR (Me_2CO-d6) of compound 6g, $[Ni(S_2P(OCy)_2(CNAr)\{C(NHAr)(NPpze)\}]ClO_4$.

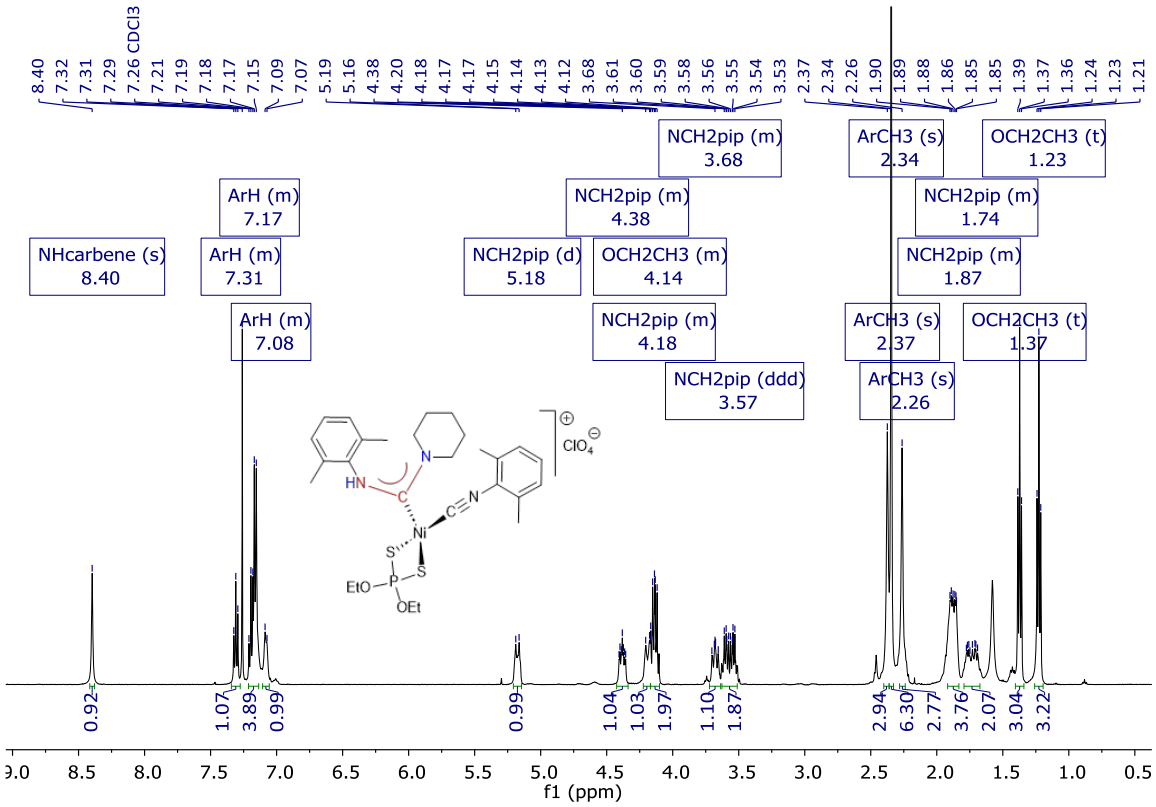


Figure S 106. ^{1}H NMR ($CDCl_3$) of compound 6h, $[Ni(S_2P(OEt)_2(CNXyl)\{C(NHXyl)(pip)\}]ClO_4$.

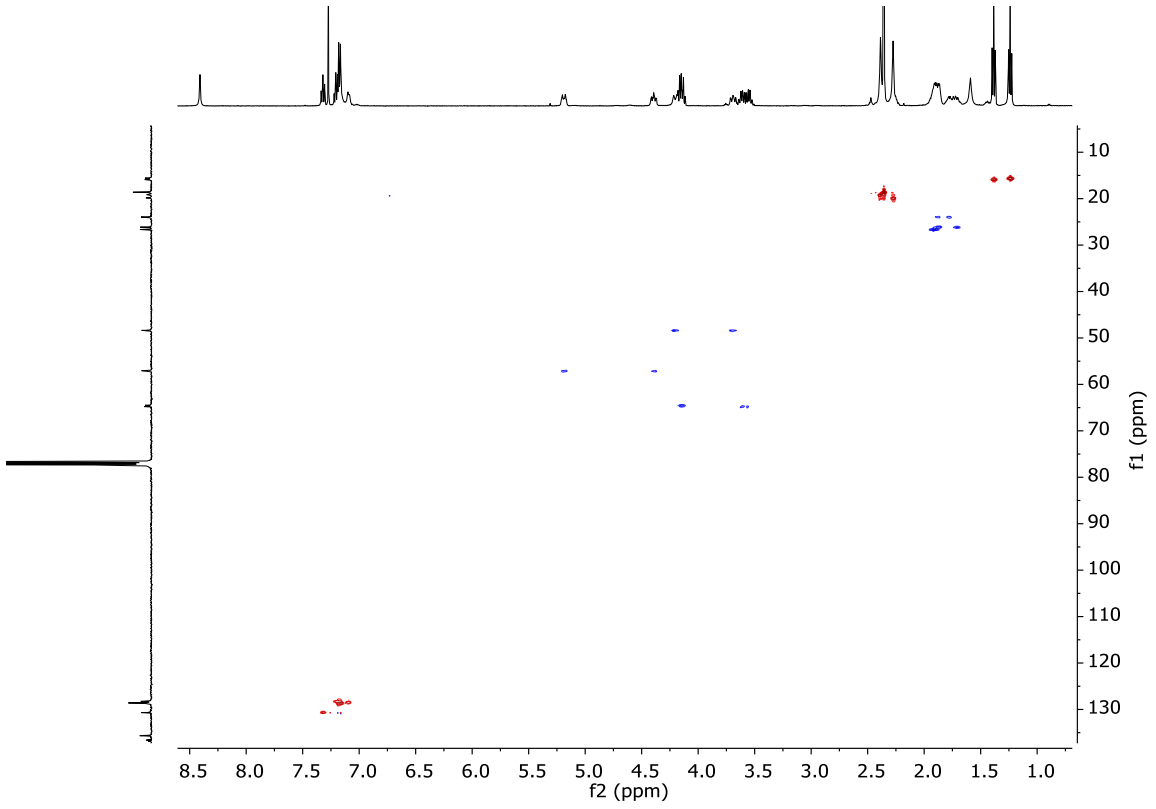


Figure S 107. ^{1}H-^{13}C{^{1}H} HSQC NMR ($CDCl_3$) of compound 6h, $[Ni(S_2P(OEt)_2(CNXyl)\{C(NHXyl)(pip)\}]ClO_4$.

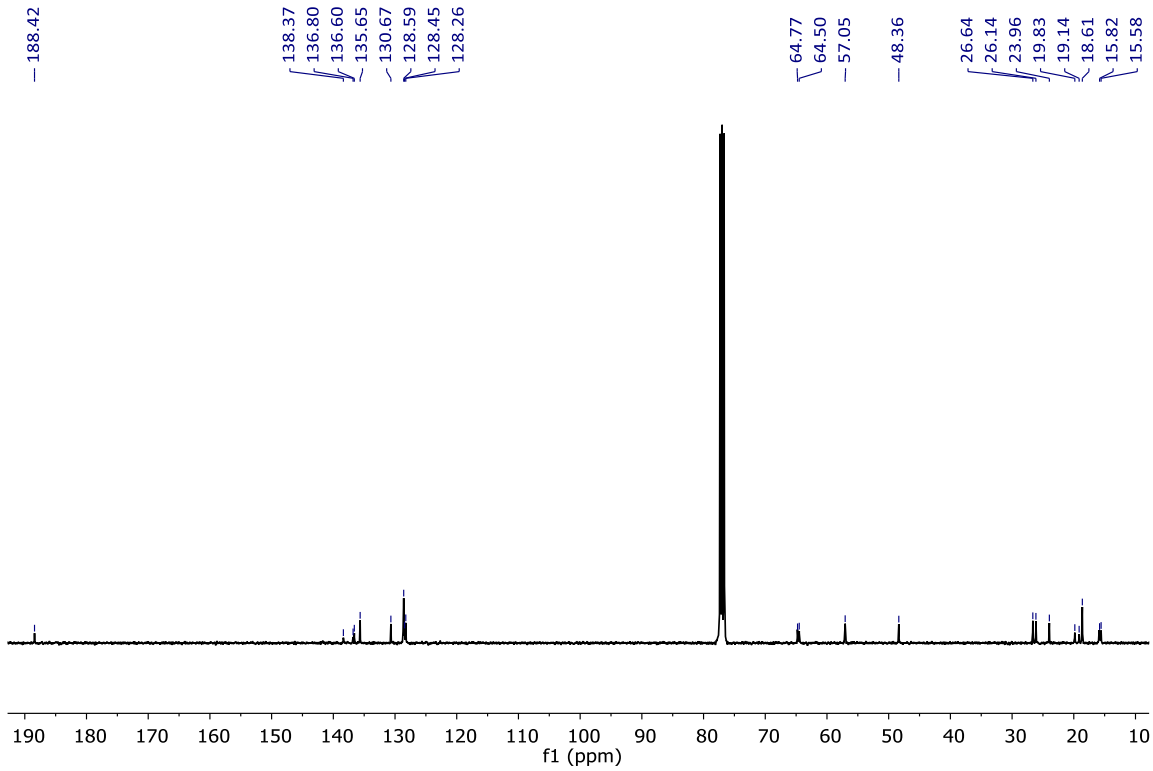


Figure S 108. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) of compound 6h, $[Ni(S_2P(OEt)_2(CNXyl)\{C(NHXyl)(pip)\}]ClO_4$.

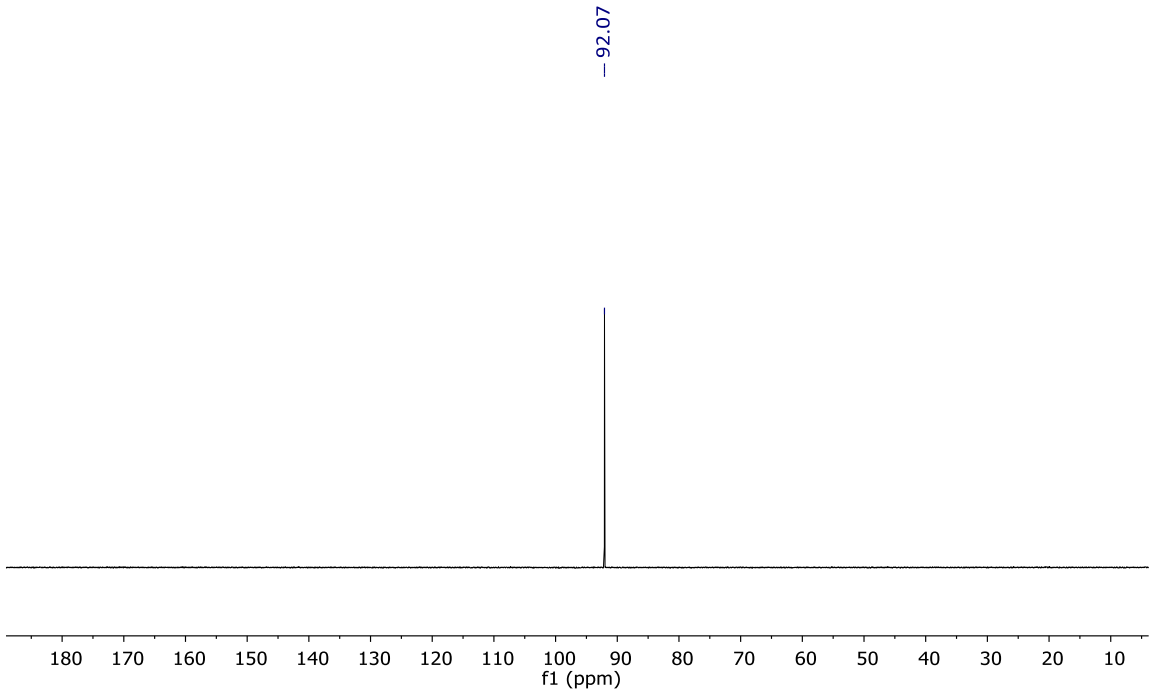


Figure S 109. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) of compound 6h, $[Ni(S_2P(OEt)_2(CNXyl)\{C(NHXyl)(pip)\}]ClO_4$.

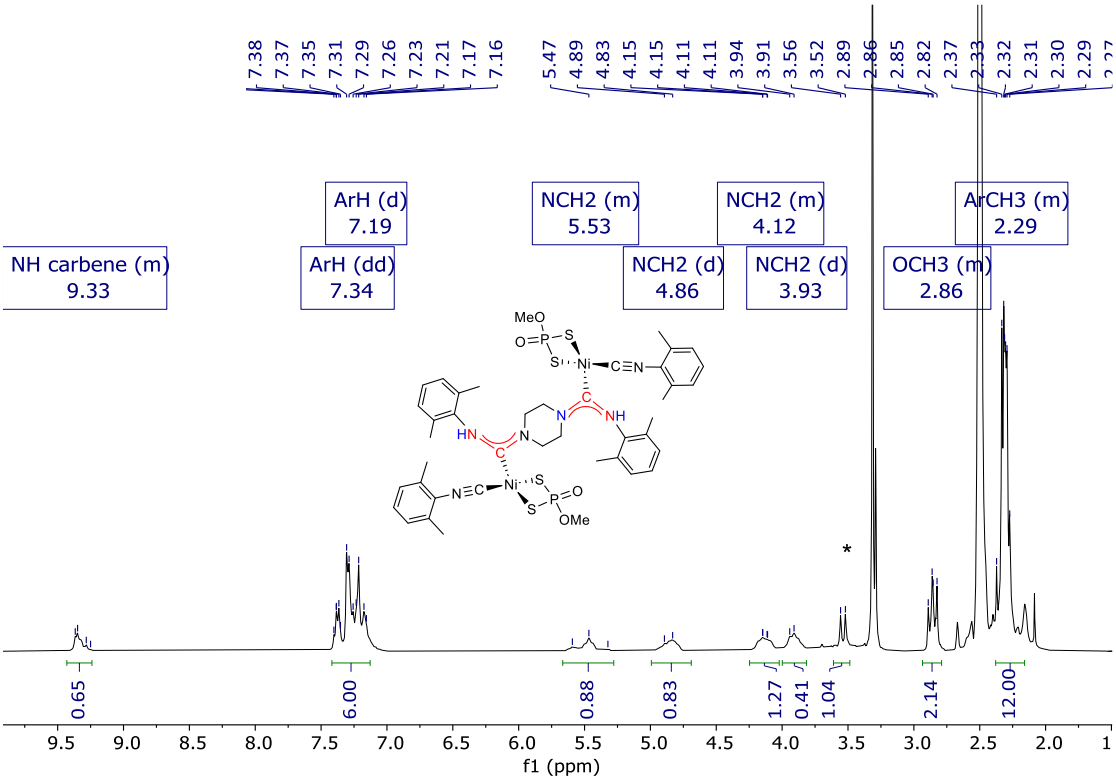


Figure S 110. ^{1}H NMR ($CDCl_3$) of compound 7, [{Ni(S_2P(=O)(OMe)(*CNXyl*)$_2$C(NHXyl)}$_2$($N_2C_4H_8$)}]. *Chemical shift of -*OCH_3* from the minor product (ratio Z/E, 77:23, see ^{31}P{^{1}H}).

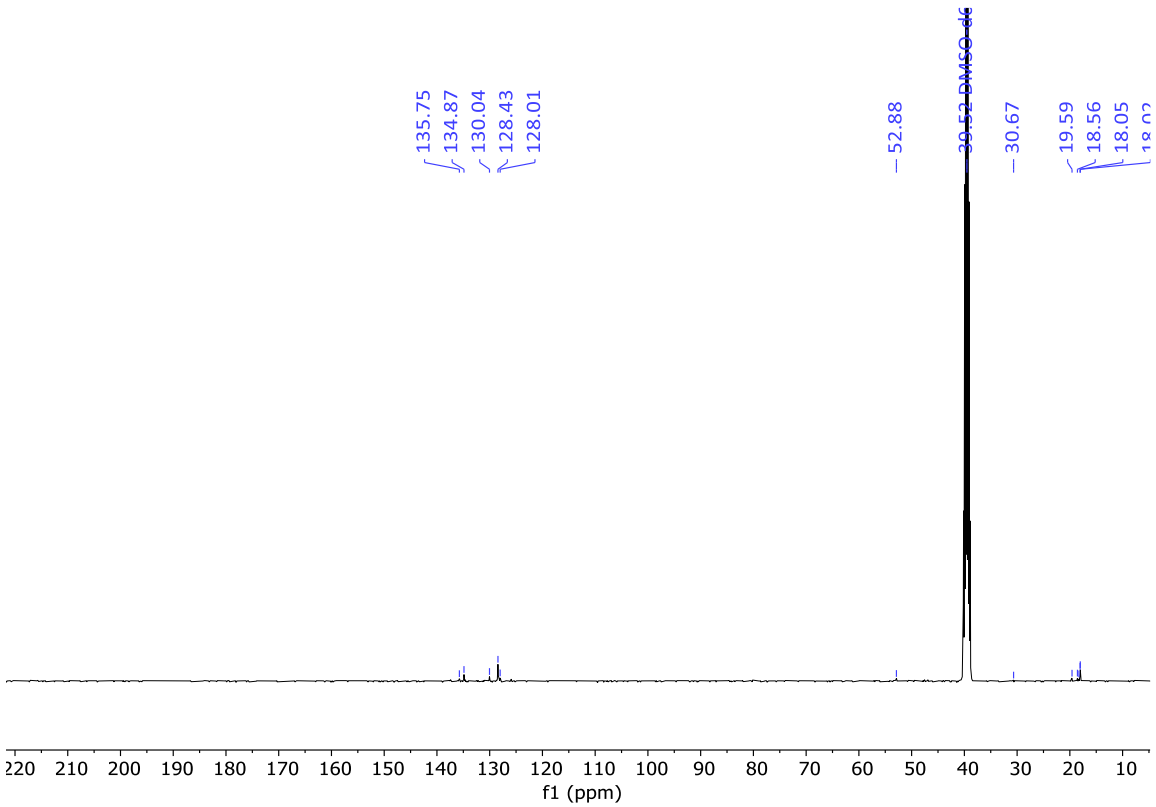


Figure S 111. ^{13}C {^{1}H} NMR (DMSO-d6) of compound 7, [{Ni(S_2P(=O)(OMe)(*CNXyl*)$_2$C(NHXyl)}$_2$($N_2C_4H_8$)}]. Chemical shift of C carbene is not observed due to the low solubility of the complex (spectrum was recorded with 35000 scans)

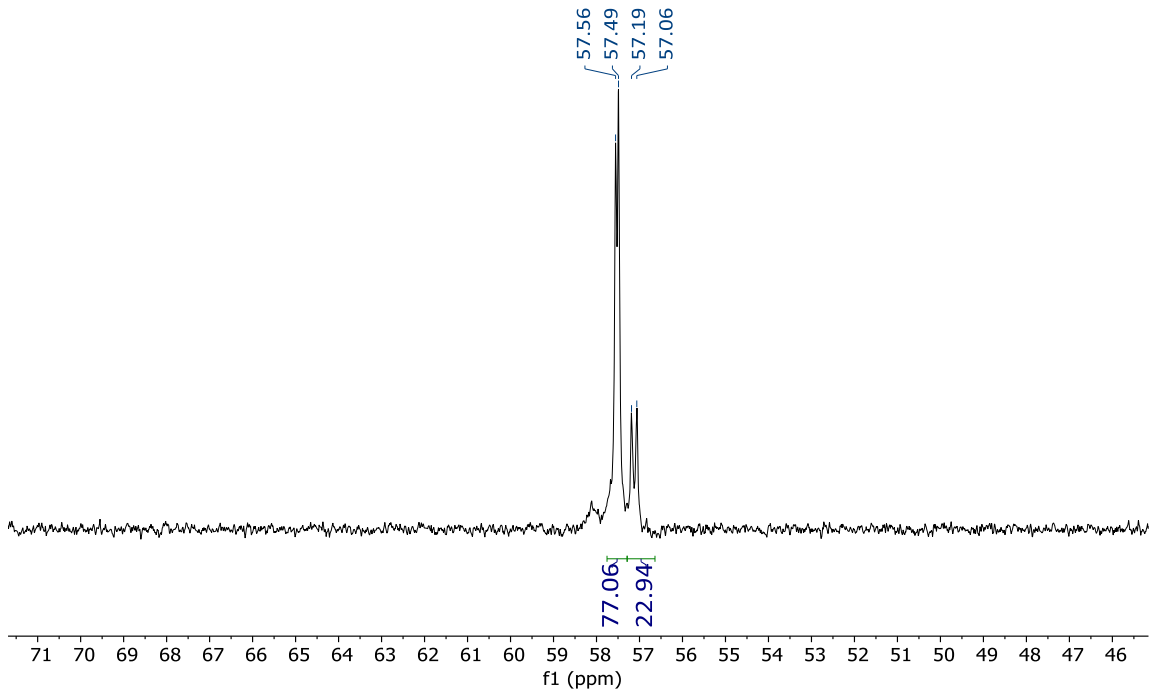


Figure S 112. $^{31}P\{^{1}H\}$ NMR (DMSO-d6) of compound 7, [{Ni(S_2P(=O)(OMe)(*CNXyl*)$_2$C(NHXyl)}$_2$($N_2C_4H_8$)}]. Ratio of isomers Z/E 77:23.

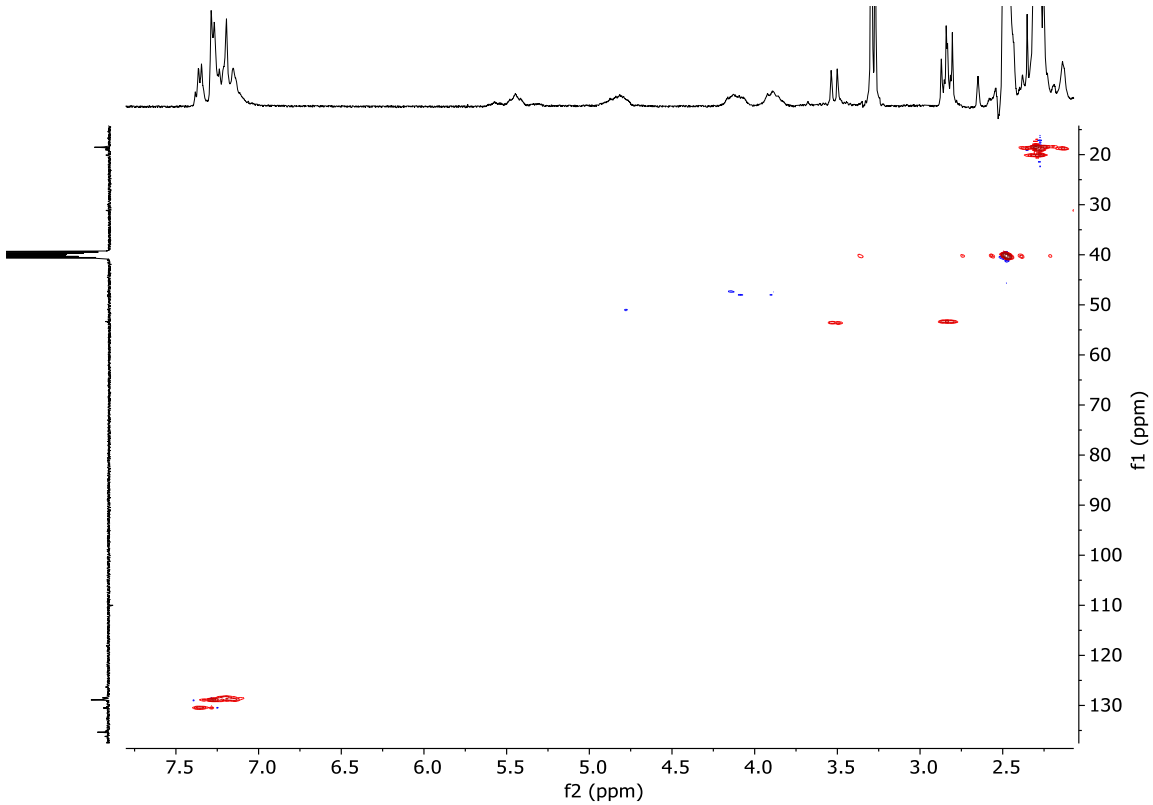


Figure S 113. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (DMSO-d6) of compound 7, [{Ni(S_2P(=O)(OMe)(CNXyl)$_2$C(NHXyl)}$_2$($N_2C_4H_8$)}].

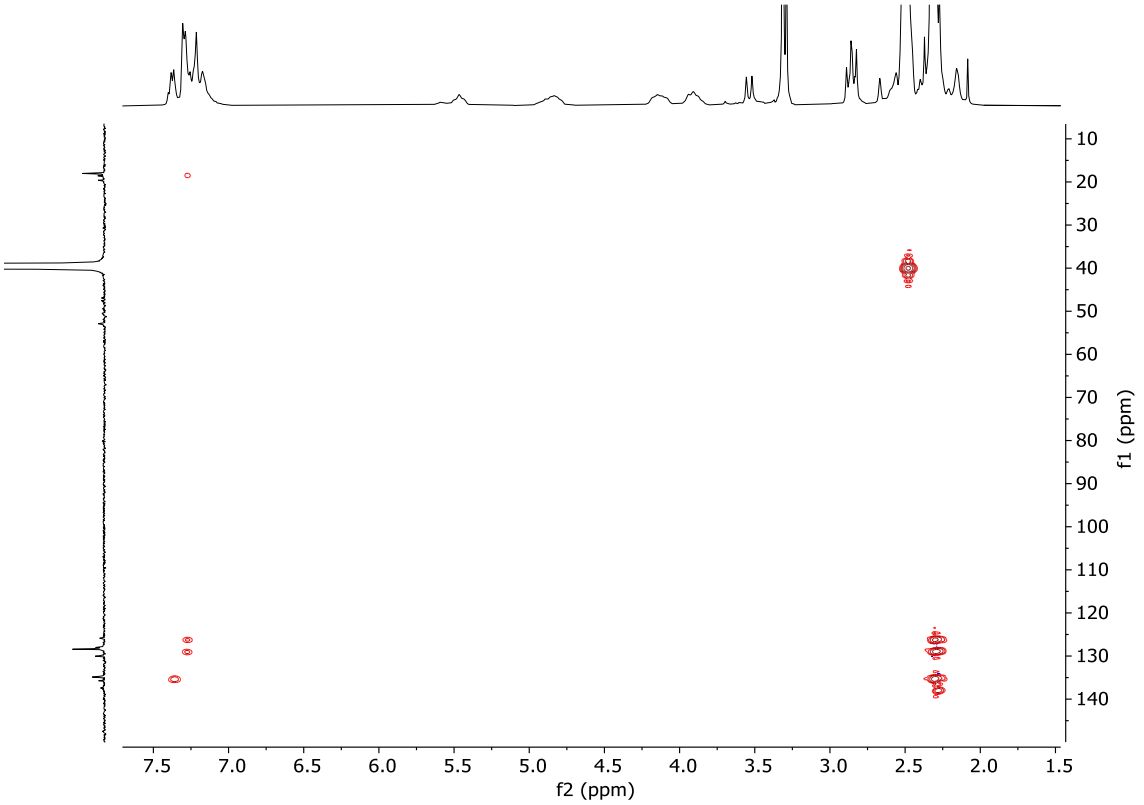
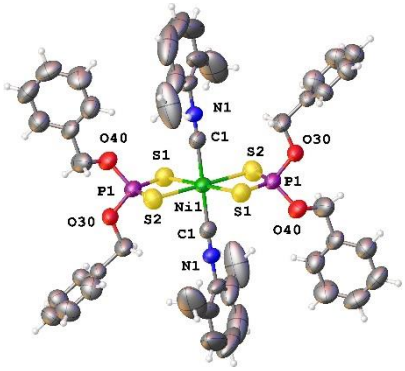
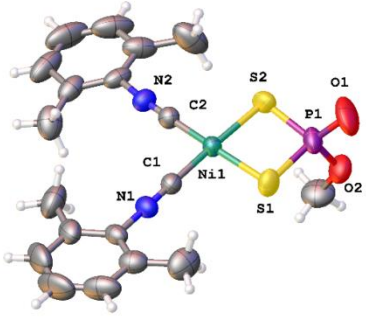


Figure S 114. ^{1}H-$^{13}C\{^{1}H\}$ HSQC NMR (DMSO-d6) of compound 7, $[\{Ni(S_2P(=O)(OMe)(CNXyl)_2C(NHXyl)\}_2(N_2C_4H_8)\}]$.

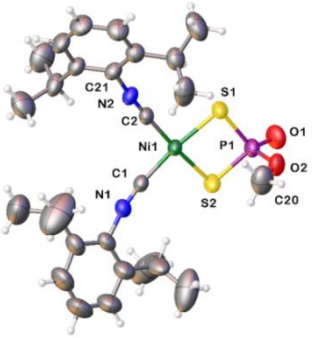
X-Ray Diffraction structures of neutral and cationic diisocyanide dithiophosphate Ni(II) complexes 2e, 3c, 3d, 3e, 4a, 4c, 4e, 4f, 5b, 5c, 5e, 6c, 6e, 6g, 6h, 7 and 8.



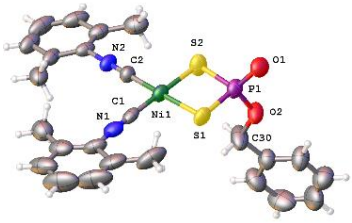
Compound 2e: $C_{46}H_{46}N_2NiO_4P_2S_4$ (M =939.74 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 11.1533(6) Å, b = 8.8012(8) Å, c = 24.1739(18) Å, β = 94.913(6)°, V = 2364.3(3) Å^3, Z = 2, T = 293(2) K, μ(MoKα) = 0.697 mm^{-1}, $Dcalc$ = 1.320 g/cm^3, 12866 reflections measured (5.734° ≤ 2Θ ≤ 59.31°), 5650 unique (R_{int} = 0.0543, R_{sigma} = 0.1019) which were used in all calculations. The final R_1 was 0.0670 (I > 2σ(I)) and wR_2 was 0.1975 (all data).. CCDC: 2308594



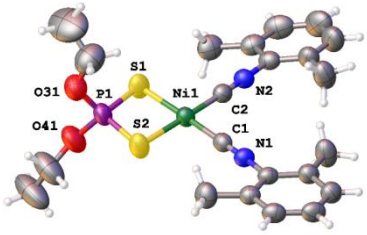
Compound 3c: $C_{19}H_{21}N_2O_2PS_2Ni$ (M =463.18 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 9.6257(4) Å, b = 22.5461(9) Å, c = 9.8951(3) Å, β = 95.047(3)°, V = 2139.14(14) Å^3, Z = 4, T = 293 K, μ(Mo Kα) = 1.193 mm^{-1}, $Dcalc$ = 1.438 g/cm^3, 11284 reflections measured (4.51° ≤ 2Θ ≤ 59.13°), 5057 unique (R_{int} = 0.0251, R_{sigma} = 0.0358) which were used in all calculations. The final R_1 was 0.0367 (I > 2σ(I)) and wR_2 was 0.0946 (all data). CCDC: 2298997



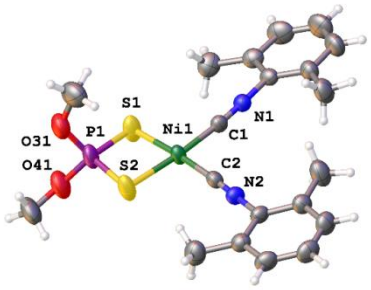
Compound 3d: $C_{27}H_{37}N_2NiO_2PS_2$ (M =575.38 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a= 13.8109(4) Å, b= 10.3758(3)Å, c= 21.4053(5)Å, β= 91.863(2)°, V= 3065.74(15)Å^3, Z= 4, T= 293K, μ(MoKα)= 0.846 mm^{-1}, $Dcalc$= 1.247 g/cm^3, 14802 reflections measured (4.362 ≤ 2Θ ≤ 59.586), 7266 unique (R_{int} = 0.0248, R_{sigma} = 0.0396) which were used in all calculations. The final R_1 was 0.0443 (I > 2σ(I)) and wR_2 was 0.1101 (all data). CCDC: 2298999



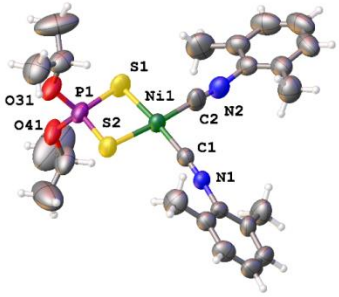
Compound 3e: $C_{25}H_{25}N_2NiO_2PS_2$ (M =539.27 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 14.2683(17) Å, b = 12.6497(7) Å, c = 14.8317(16) Å, β = 94.874(10)°, V = 2667.3(5) Å^3, Z = 4, T = 293(2) K, μ(Mo Kα) = 0.967 mm^{-1}, $Dcalc$ = 1.343 g/cm^3, 10091 reflections measured (4.984° ≤ 2Θ ≤ 49.454°), 4547 unique (R_{int} = 0.0543, R_{sigma} = 0.1063) which were used in all calculations. The final R_1 was 0.0579 (I > 2σ(I)) and wR_2 was 0.1390 (all data).CCDC: 2308595



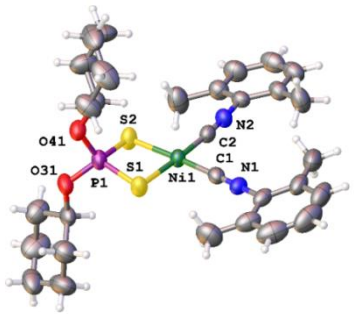
Compound 4a: $C_{22}H_{28}ClN_2NiO_6PS_2$ (M =605.71 g/mol): triclinic, space group P-1 (no. 2), a = 7.7849(4) Å, b = 9.6864(4) Å, c = 19.6397(10) Å, α = 100.452(4)°, β = 100.473(4)°, γ = 100.035(4)°, V = 1398.88(12) Å^3, Z = 2, T = 293(2) K, μ(MoKα) = 1.033 mm^{-1}, $Dcalc$ = 1.438 g/cm^3, 11919 reflections measured (4.324° ≤ 2Θ ≤ 59.548°), 6565 unique (R_{int} = 0.0203, R_{sigma} = 0.0344) which were used in all calculations. The final R_1 was 0.0697 (I > 2σ(I)) and wR_2 was 0.2320 (all data). CCDC: 2299006



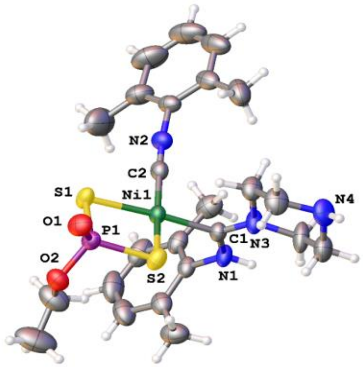
Compound 4c: $C_{20}H_{24}ClN_2NiO_6PS_2$ (*M* =577.66 g/mol): triclinic, space group P-1 (no. 2), *a* = 7.2158(3) Å, *b* = 10.0031(8) Å, *c* = 18.9825(10) Å, *α* = 99.859(5)°, *β* = 97.908(4)°, *γ* = 105.106(5)°, *V* = 1279.16(13) Å^3, *Z* = 2, *T* = 293 K, μ(MoKα) = 1.126 mm^{-1}, *Dcalc* = 1.500 g/cm^3, 9842 reflections measured (4.32° ≤ 2Θ ≤ 59.608°), 5964 unique (R_{int} = 0.0226, R_{sigma} = 0.0485) which were used in all calculations. The final R_1 was 0.0589 (I > 2σ(I)) and wR_2 was 0.1815 (all data). CCDC: 2299001



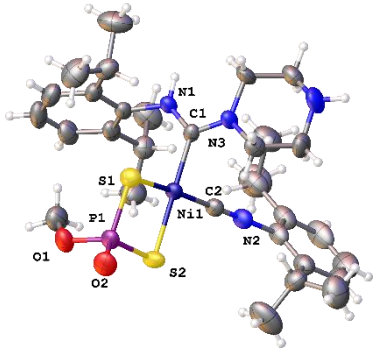
Compound 4e: $C_{24}H_{32}N_2O_6PS_2ClNi$ (*M* =633.76 g/mol): triclinic, space group P-1 (no. 2), *a* = 8.6853(3) Å, *b* = 11.9625(5) Å, *c* = 16.6919(6) Å, *α* = 93.616(3)°, *β* = 98.940(3)°, *γ* = 103.585(3)°, *V* = 1656.28(11) Å^3, *Z* = 2, *T* = 293(2) K, μ(Mo Kα) = 0.876 mm^{-1}, *Dcalc* = 1.271 g/cm^3, 14723 reflections measured (4.516° ≤ 2Θ ≤ 59.024°), 7756 unique (R_{int} = 0.0251, R_{sigma} = 0.0522) which were used in all calculations. The final R_1 was 0.0654 (I > 2σ(I)) and wR_2 was 0.1977 (all data). CCDC: 2299268



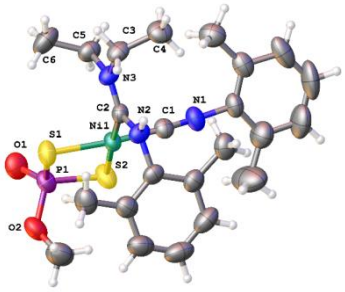
Compound 4f: $C_{30}H_{40}N_2O_6PS_2ClNi$ (*M* =713.89 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 17.7071(6) Å, *b* = 10.8206(4) Å, *c* = 21.3047(10) Å, *β* = 110.113(5)°, *V* = 3833.1(3) Å^3, *Z* = 4, *T* = 293(2) K, μ(Mo Kα) = 0.765 mm^{-1}, *Dcalc* = 1.237 g/cm^3, 19251 reflections measured (3.964° ≤ 2Θ ≤ 58.944°), 9105 unique (R_{int} = 0.0371, R_{sigma} = 0.0650) which were used in all calculations. The final R_1 was 0.0601 (I > 2σ(I)) and wR_2 was 0.1876 (all data). CCDC: 2299269



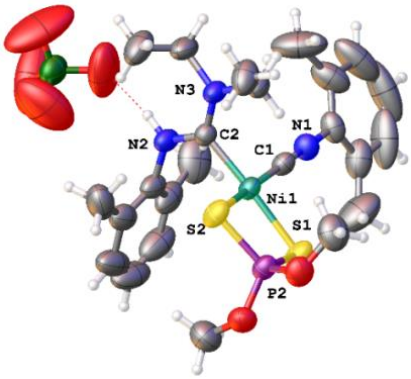
Compound 5b: $C_{25}H_{32}N_4O_2PS_2Ni$ (*M* =574.34 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 14.3103(5) Å, *b* = 15.1738(5) Å, *c* = 14.3126(5) Å, *β* = 100.034(3)°, *V* = 3060.32(19) Å^3, *Z* = 4, *T* = 293(2) K, μ(Mo Kα) = 0.849 mm^{-1}, *Dcalc* = 1.247 g/cm^3, 23465 reflections measured (4.43° ≤ 2Θ ≤ 59.718°), 7625 unique (R_{int} = 0.0351, R_{sigma} = 0.0439) which were used in all calculations. The final R_1 was 0.0384 (I > 2σ(I)) and wR_2 was 0.0976 (all data). CCDC: 2299273



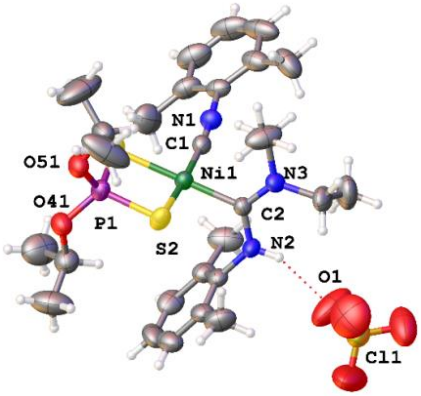
Compound 5c. $C_{31}H_{47}N_4NiO_2PS_2$ (*M* =661.52 g/mol): orthorhombic, space group Pbca (no. 61), *a* = 17.6491(10) Å, *b* = 21.2342(13) Å, *c* = 17.9976(8) Å, *V* = 6744.8(6) Å^3, *Z* = 8, *T* = 293(2) K, μ(Mo Kα) = 0.780 mm^{-1}, *Dcalc* = 1.303 g/cm^3, 25073 reflections measured (4.526° ≤ 2Θ ≤ 59.478°), 8204 unique (R_{int} = 0.0905, R_{sigma} = 0.1379) which were used in all calculations. The final R_1 was 0.0654 (I > 2σ(I)) and wR_2 was 0.1494 (all data). CCDC: 2299274



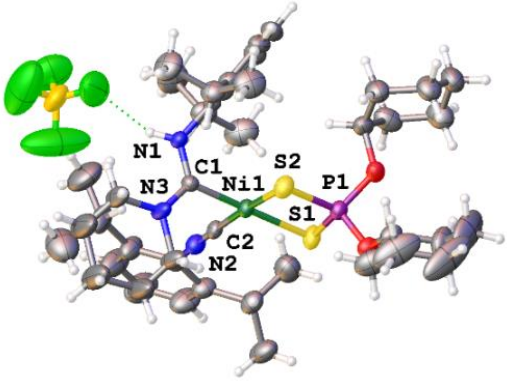
Compound 5e: $C_{23}H_{32}N_3NiO_2PS_2$ (*M* =536.31 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 14.1712(3) Å, *b* = 14.4321(4) Å, *c* = 14.8981(3) Å, *β* = 100.956(2)°, *V* = 2991.42(12) Å^3, *Z* = 4, *T* = 293 K, μ(MoKα) = 0.863 mm^{-1}, *Dcalc* = 1.191 g/cm^3, 16554 reflections measured (4.066° ≤ 2Θ ≤ 59.51°), 7189 unique (R_{int} = 0.0215, R_{sigma} = 0.0332) which were used in all calculations. The final R_1 was 0.0698 (I > 2σ(I)) and wR_2 was 0.2585 (all data). CCDC: 2299270



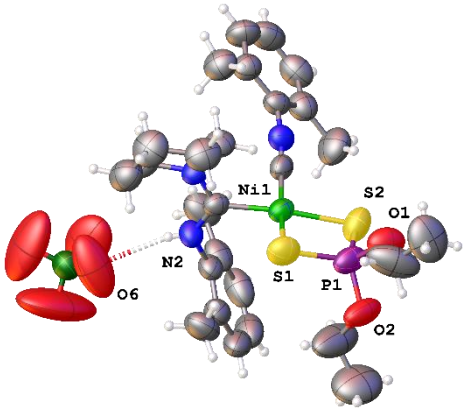
Compound 6c: $C_{24}H_{35}ClN_3NiO_6PS_2$ (*M* =650.80 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 10.8986(2) Å, *b* = 15.6526(3) Å, *c* = 18.4304(3) Å, *β* = 96.3167(16)°, *V* = 3124.97(9) Å^3, *Z* = 4, *T* = 293(2) K, μ(Mo Kα) = 0.931 mm^{-1}, *Dcalc* = 1.383 g/cm^3, 13800 reflections measured (4.448° ≤ 2Θ ≤ 57.516°), 7138 unique (R_{int} = 0.0234, R_{sigma} = 0.0413) which were used in all calculations. The final R_1 was 0.0503 (I > 2σ(I)) and wR_2 was 0.1517 (all data). CCDC: 2299288



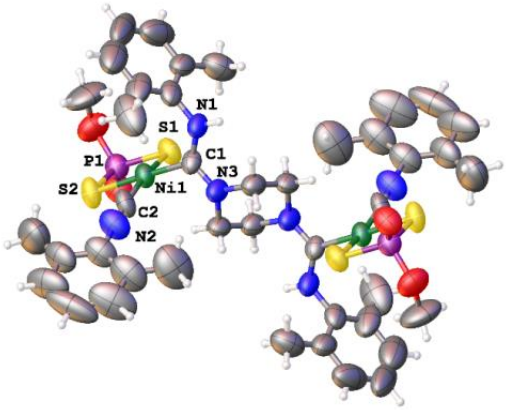
Compound 6e: $C_{28}H_{43}ClN_3NiO_6PS_2$ (*M* =706.90 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 9.2715(2) Å, *b* = 21.9434(4) Å, *c* = 18.2332(4) Å, *β* = 104.038(3)°, *V* = 3598.71(15) Å^3, *Z* = 4, *T* = 293(2) K, μ(Mo Kα) = 0.814 mm^{-1}, *Dcalc* = 1.305 g/cm^3, 41217 reflections measured (4.368° ≤ 2Θ ≤ 59.464°), 9086 unique (R_{int} = 0.0351, R_{sigma} = 0.0339) which were used in all calculations. The final R_1 was 0.0495 (I > 2σ(I)) and wR_2 was 0.1391 (all data).. CCDC: 2299303



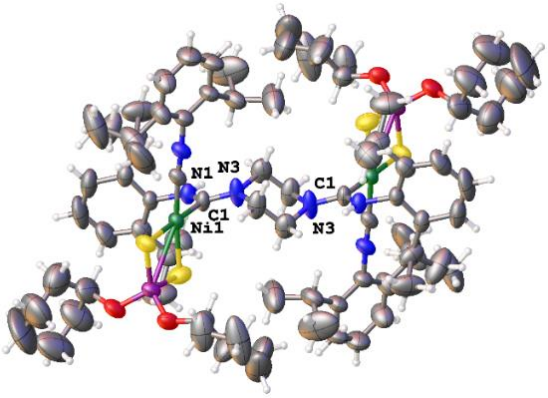
Compound 6g: $C_{43}H_{67}BF_4N_3NiO_2PS_2$ (*M* =898.60 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.1019(4) Å, *b* = 14.9066(6) Å, *c* = 17.7025(10) Å, *α* = 82.659(4)°, *β* = 89.705(4)°, *γ* = 86.302(4)°, *V* = 2377.2(2) Å^3, *Z* = 2, *T* = 293(2) K, μ(Mo Kα) = 0.582 mm^{-1}, *Dcalc* = 1.255 g/cm^3, 18610 reflections measured (4.484° ≤ 2Θ ≤ 59.212°), 11088 unique (R_{int} = 0.0303, R_{sigma} = 0.0664) which were used in all calculations. The final R_1 was 0.0678 (I > 2σ(I)) and wR_2 was 0.2042 (all data). CCDC: 2299286



Compound 6h: $C_{27}H_{39}ClN_3NiO_6PS_2$ (*M* =690.86 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.5858(5) Å, *b* = 19.6057(7) Å, *c* = 14.6622(5) Å, *β* = 112.736(4)°, *V* = 3336.8(2) Å^3, *Z* = 4, *T* = 293(2) K, μ(Mo Kα) = 0.876 mm^{-1}, *Dcalc* = 1.375 g/cm^3, 17174 reflections measured (6.806° ≤ 2Θ ≤ 59.354°), 7904 unique (R_{int} = 0.0295, R_{sigma} = 0.0484) which were used in all calculations. The final R_1 was 0.0766 (I > 2σ(I)) and wR_2 was 0.2393 (all data). CCDC: 2299289



Compound 7: $C_{42}H_{52}N_6Ni_2O_4P_2S_4$ (*M* =1060.53 g/mol): monoclinic, space group I2/a (no. 15), *a* = 15.8519(11) Å, *b* = 12.9097(15) Å, *c* = 25.918(2) Å, *β* = 102.398(8)°, *V* = 5180.2(8) Å^3, *Z* = 4, *T* = 293(2) K, μ(Mo Kα) = 0.996 mm^{-1}, *Dcalc* = 1.360 g/cm^3, 11394 reflections measured (4.108° ≤ 2Θ ≤ 49.472°), 4420 unique (R_{int} = 0.0762, R_{sigma} = 0.1059) which were used in all calculations. The final R_1 was 0.0717 (I > 2σ(I)) and wR_2 was 0.2072 (all data). CCDC: 2299483



Compound 8: $C_{80}H_{122}B_2F_8N_6Ni_2O_4P_2S_4$ (*M* =1713.05 g/mol): triclinic, space group P-1 (no. 2), *a* = 13.0354(7) Å, *b* = 13.3201(7) Å, *c* = 14.2399(5) Å, *α* = 90.782(4)°, *β* = 106.703(4)°, *γ* = 96.437(5)°, *V* = 2350.5(2) Å^3, *Z* = 1, *T* = 293(2) K, μ(Mo Kα) = 0.585 mm^{-1}, *Dcalc* = 1.210 g/cm^3, 22453 reflections measured (4.188° ≤ 2Θ ≤ 59.13°), 11134 unique (R_{int} = 0.0386, R_{sigma} = 0.0682) which were used in all calculations. The final R_1 was 0.0939 (I > 2σ(I)) and wR_2 was 0.3134 (all data). CCDC: 2300163

[1] Coldbery, D. E.; Fernelius, W. C.; Shamma, M.; Dwyer, F. P.; Hogarth, J. W.; Reid, I. K., Chromium(III) O,O'-Diethyl Dithiophosphate. In *Inorg. Synth.*, **1960**, 142-143.

[2] Boíllos, E.; Miguel, D., Alkyl Transfer Reactivity in the First Octahedral Isocyanide Complex of Nickel(II). *Organometallics* **2004,** *23* (11), 2568-2572.

[3] Paasivirta, J.; Simanainen, J.; Vesterinen, R.; Virkki, L., Three nuclei n.m.r. spectroscopy of dimethoate compounds. A large solvent effect on the ^{31}P-S-C-^{1}H vicinal coupling. *Organic Magnetic Resonance* **1977,** *9* (12), 708-711.