Supporting Information

Novel non-symmetric POCOP-Ni(II) pincer complexes derived from 2,4-dihydroxybenzaldehyde

Jordi R.-Galindo [a], Jhon Sebastian Oviedo-Ortiz [b], Antonino Arenaza-Corona [a], Adrián Ruíz-Martínez [a], Juan S. Serrano-García [a], Simón Hernández-Ortega [a], Marcos Flores-Alamo [b], T. Keith Hollis[c] and David Morales-Morales [a,*] ‡

[a] Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Circuito Exterior, Coyoacán, CDMX, C.P. 04510, México

[b] Facultad de Química, Universidad Nacional Autónoma de México, CDMX 04510, México

[c] Department of Chemistry, Mississippi State University, MS, 39762, United States

‡ damor@unam.mx, Corresponding author

Table of Contents

1.	*Spectroscopic Data for Synthesis Optimization*	*S1*
2.	*Representative Spectroscopic Data for New Compounds*	*S5*
3.	*X-Ray and Supramolecular*	*S27*

1. Spectroscopic Data for Synthesis Optimization

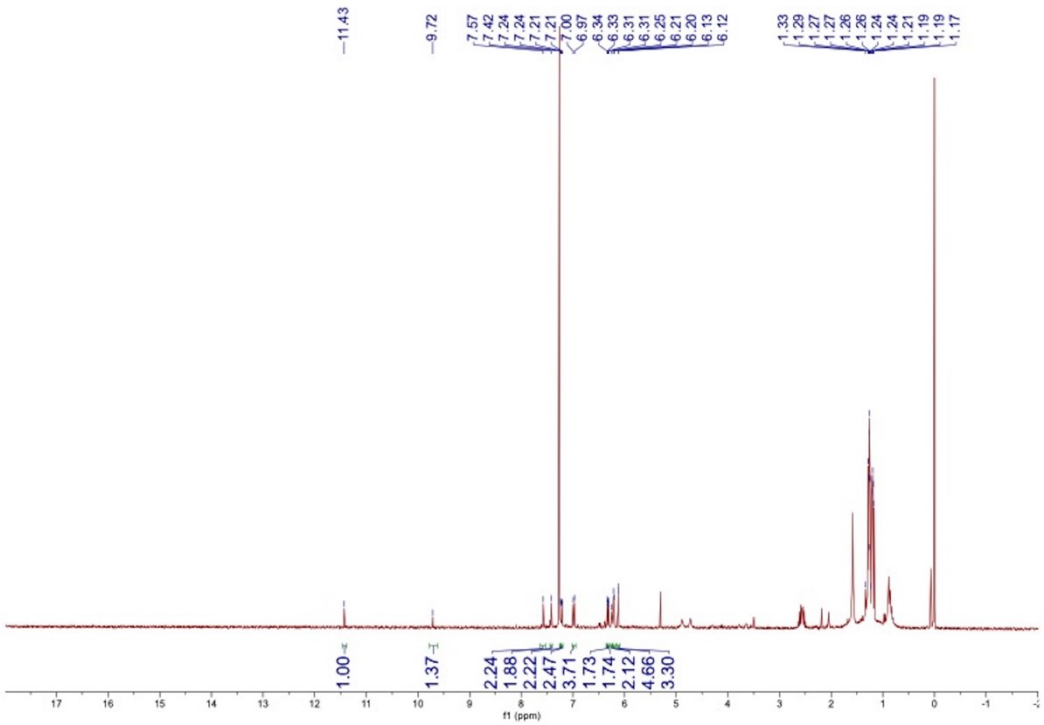

Figure S1. ^{1}H NMR spectrum (500 MHz) of attempted synthesis of **2a** in $CDCl_3$

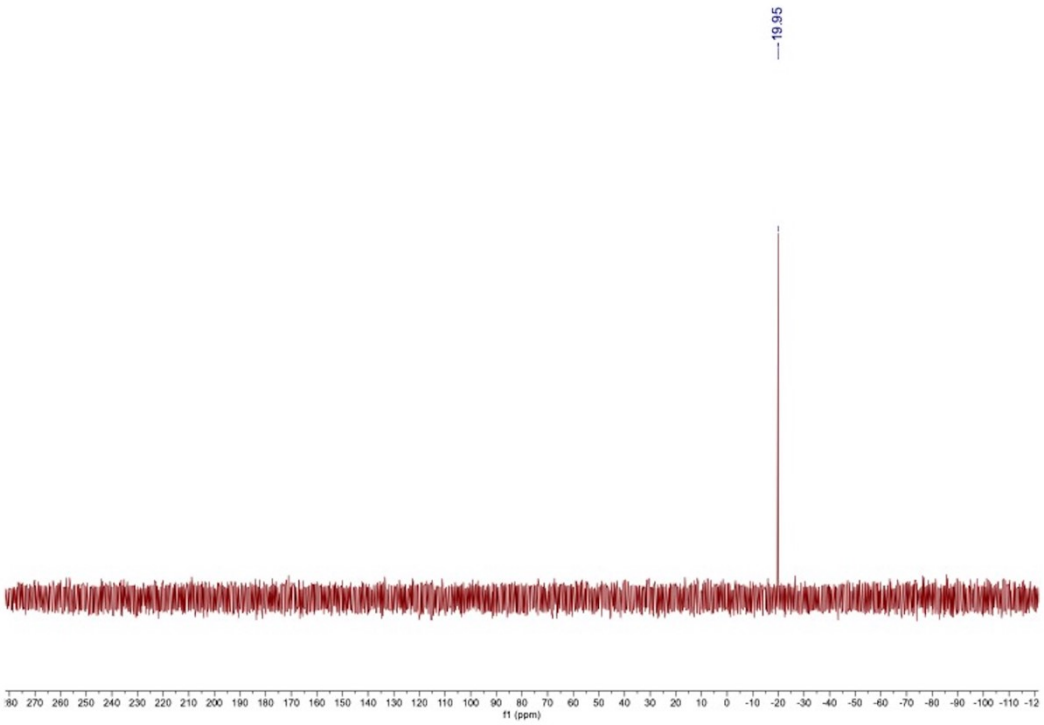

Figure S2. ^{31}P NMR spectrum (202 MHz) of attempted synthesis of **2a** in $CDCl_3$

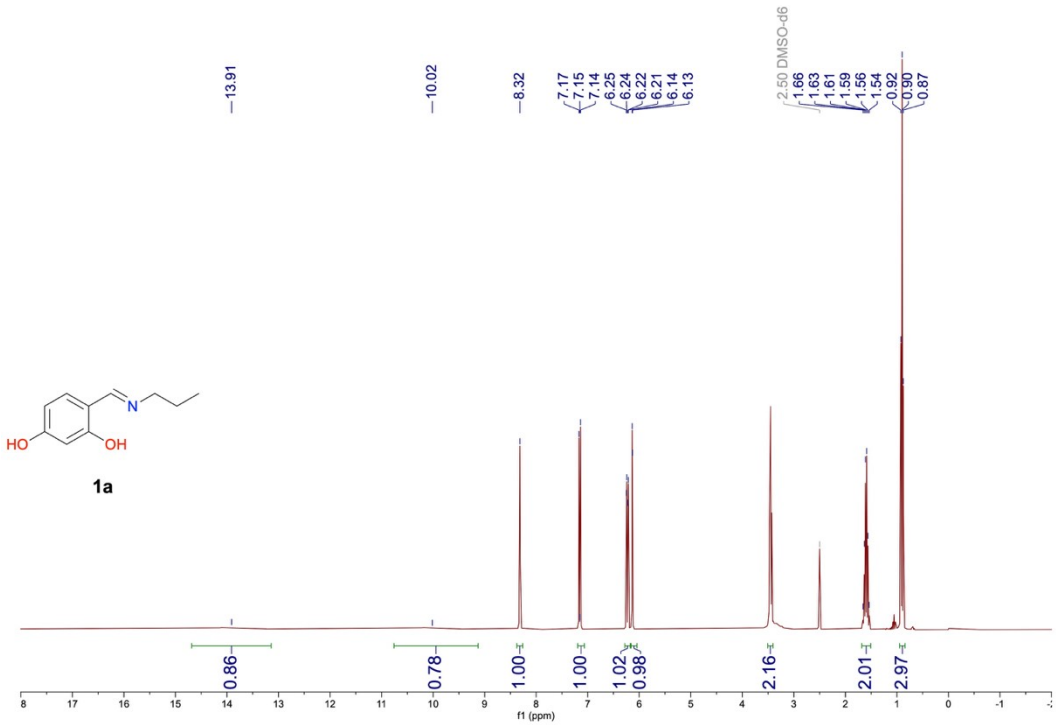

Figure S3. ^{1}H NMR spectrum (500 MHz) of **1a** in DMSO-d_6

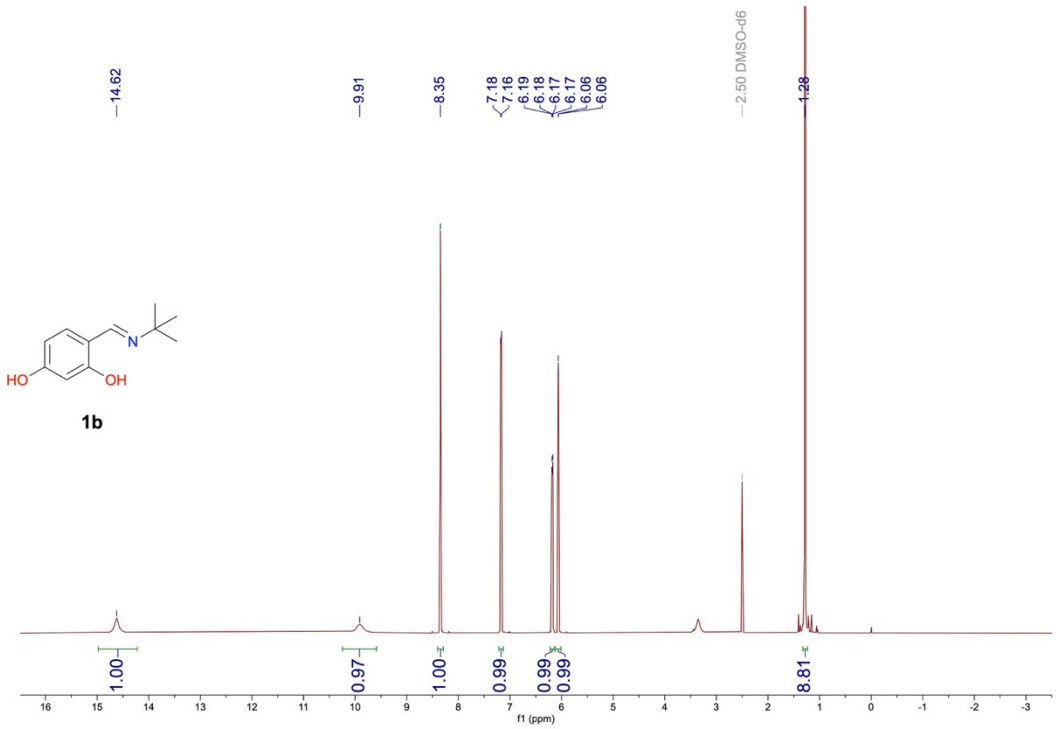

Figure S4. ^{1}H NMR spectrum (500 MHz) of **1b** in DMSO-d_6

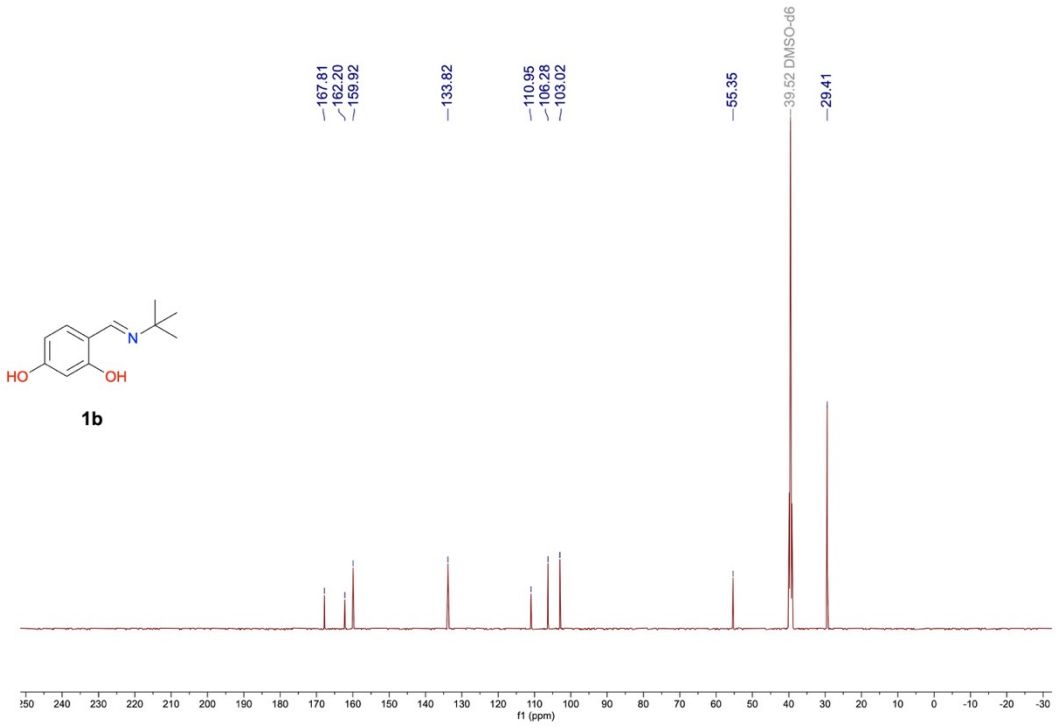

Figure S5. ^{13}C NMR spectrum (125 MHz) of **1b** in DMSO-d_6

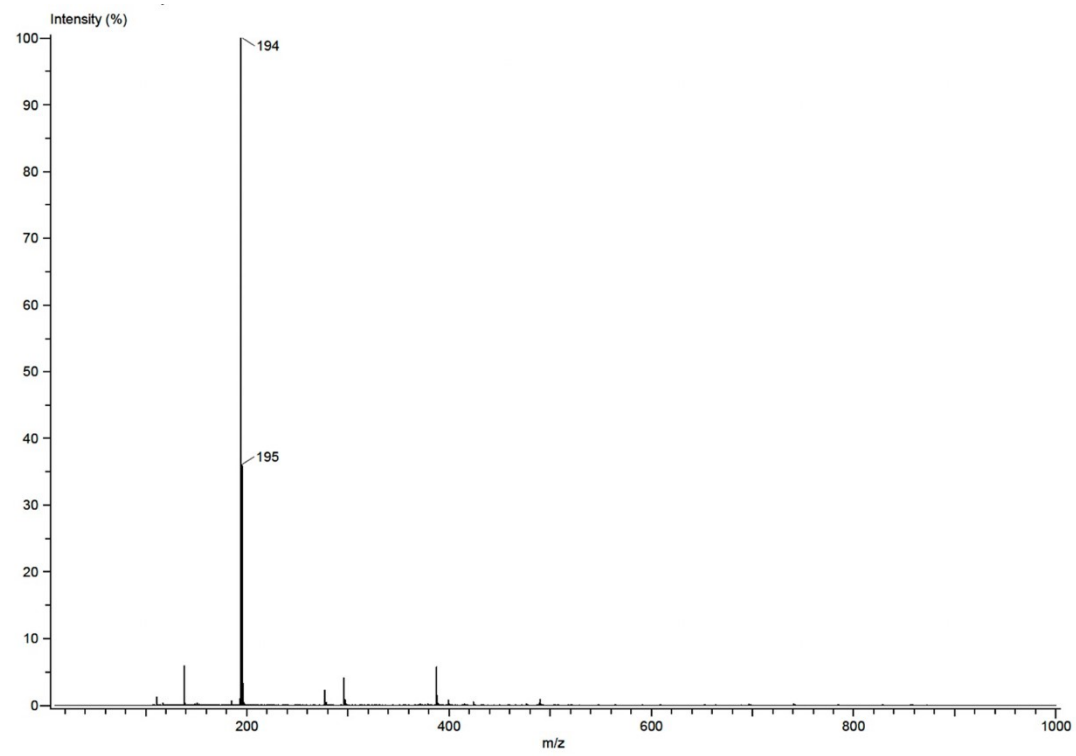

Figure S6. DART$^+$ mass spectrum of compound **1b**

2. Representative Spectroscopic Data for New Compounds

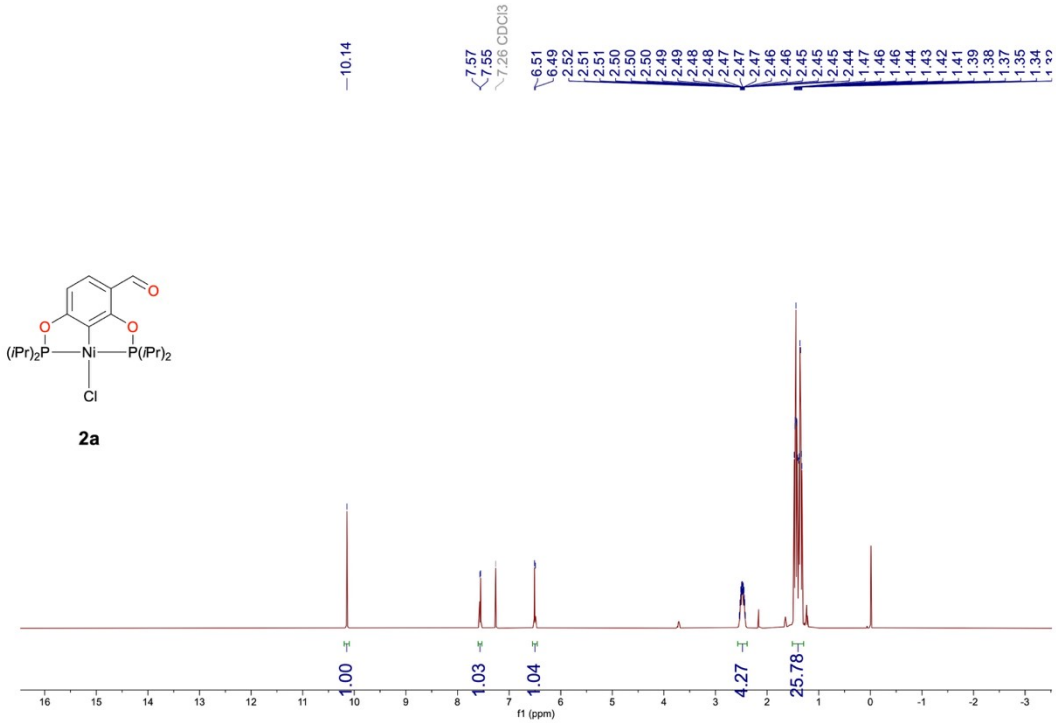

Figure S7. ^{1}H NMR spectrum (500 MHz) of **2a** in $CDCl_3$

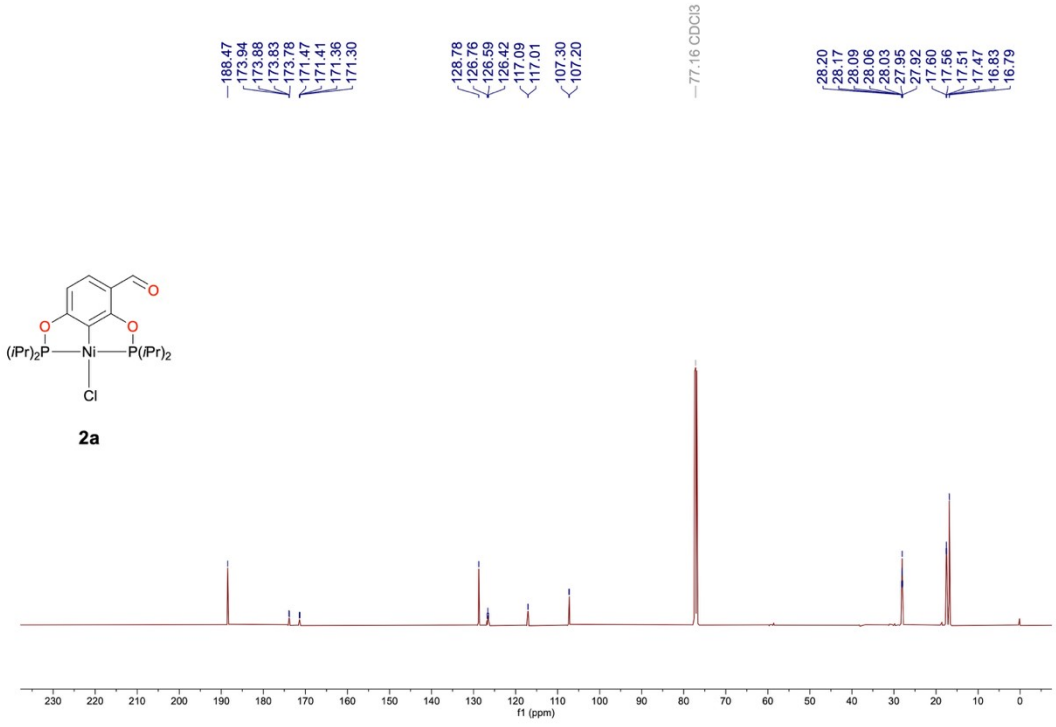

Figure S8. ^{13}C NMR spectrum (125 MHz) of **2a** in $CDCl_3$

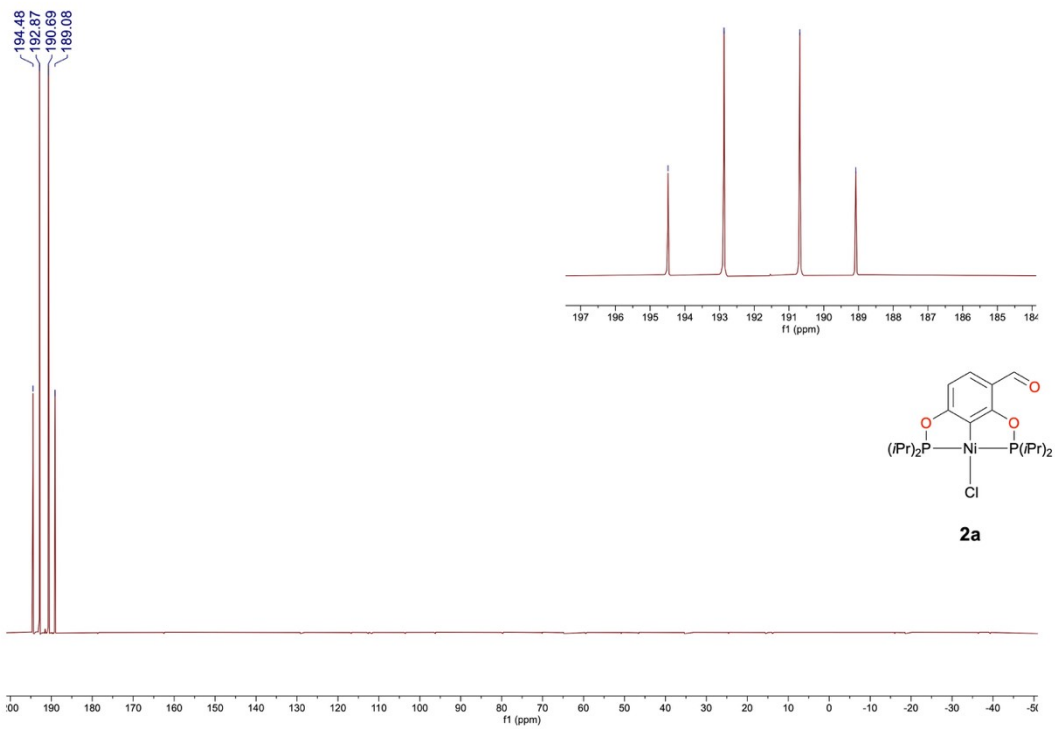

Figure S9. ^{31}P NMR spectrum (202 MHz) of **2a** in $CDCl_3$

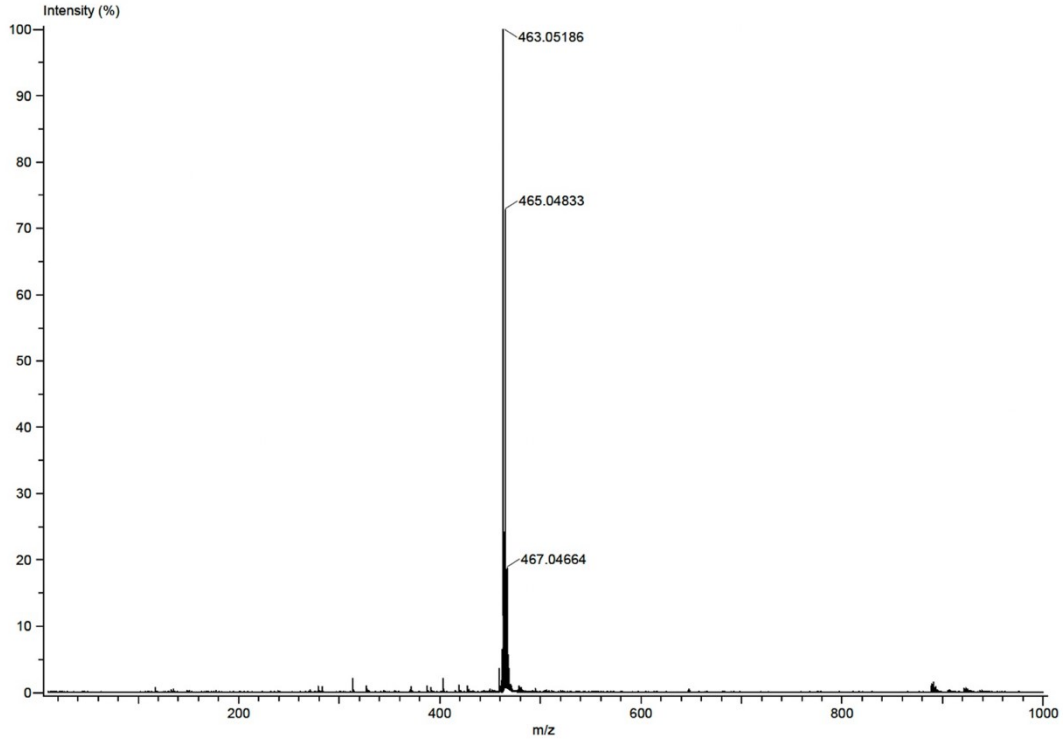

Figure S10. $DART^+$ mass spectrum of compound **2a**

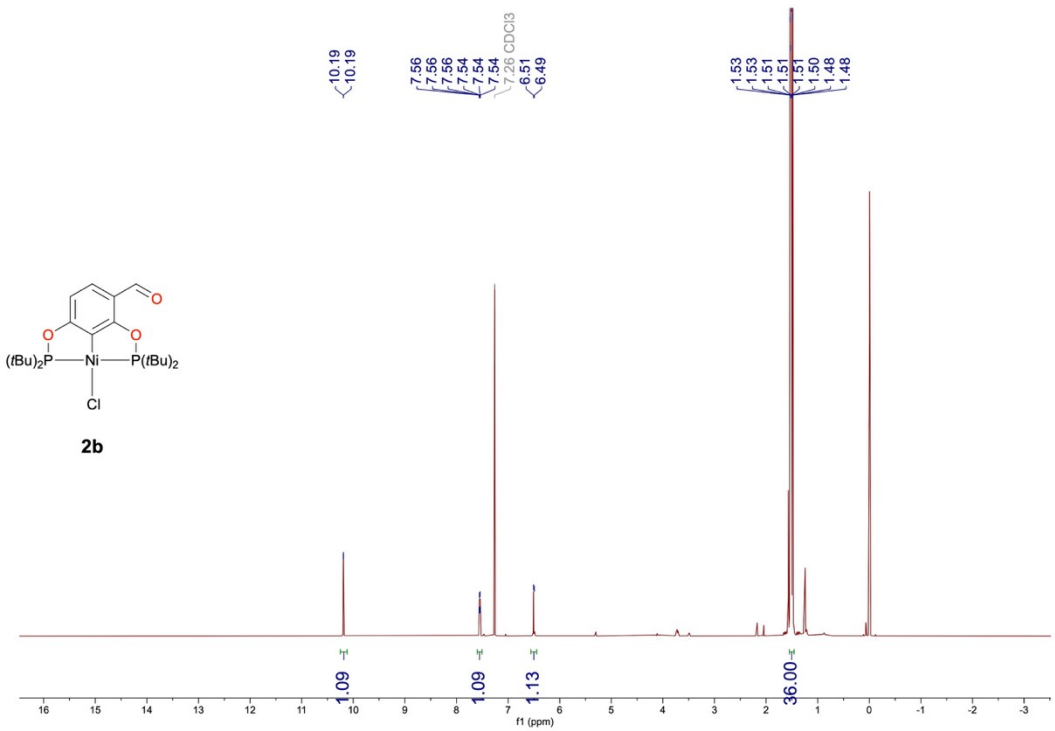

Figure S11. ^{1}H NMR spectrum (500 MHz) of **2b** in $CDCl_3$

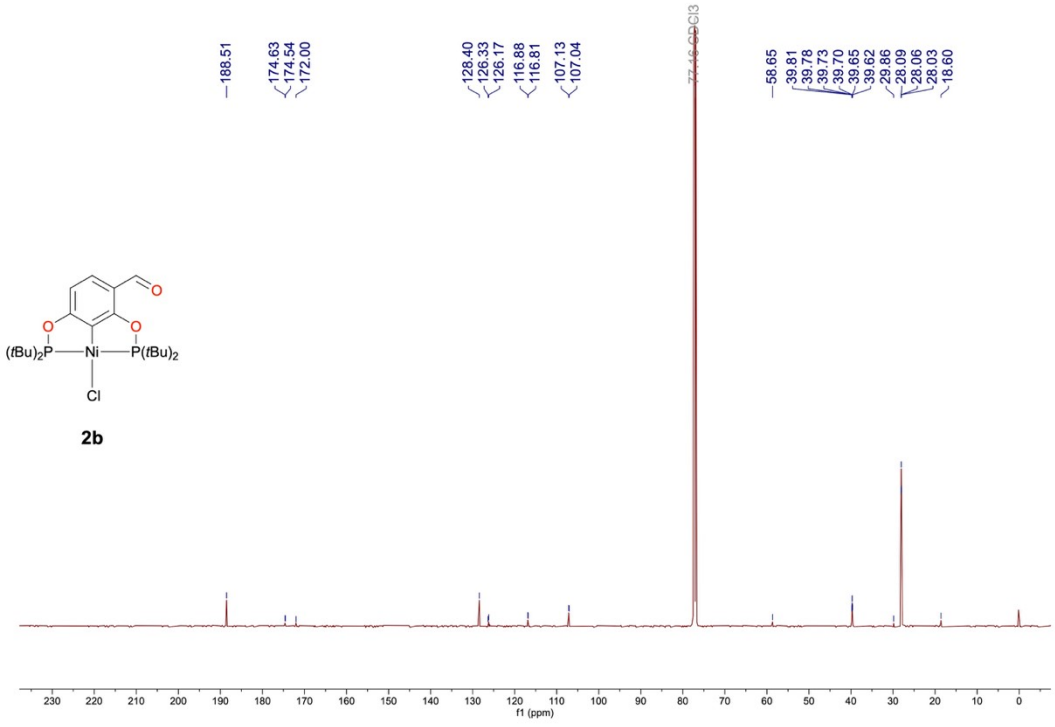

Figure S12. ^{13}C NMR spectrum (125 MHz) of **2b** in $CDCl_3$

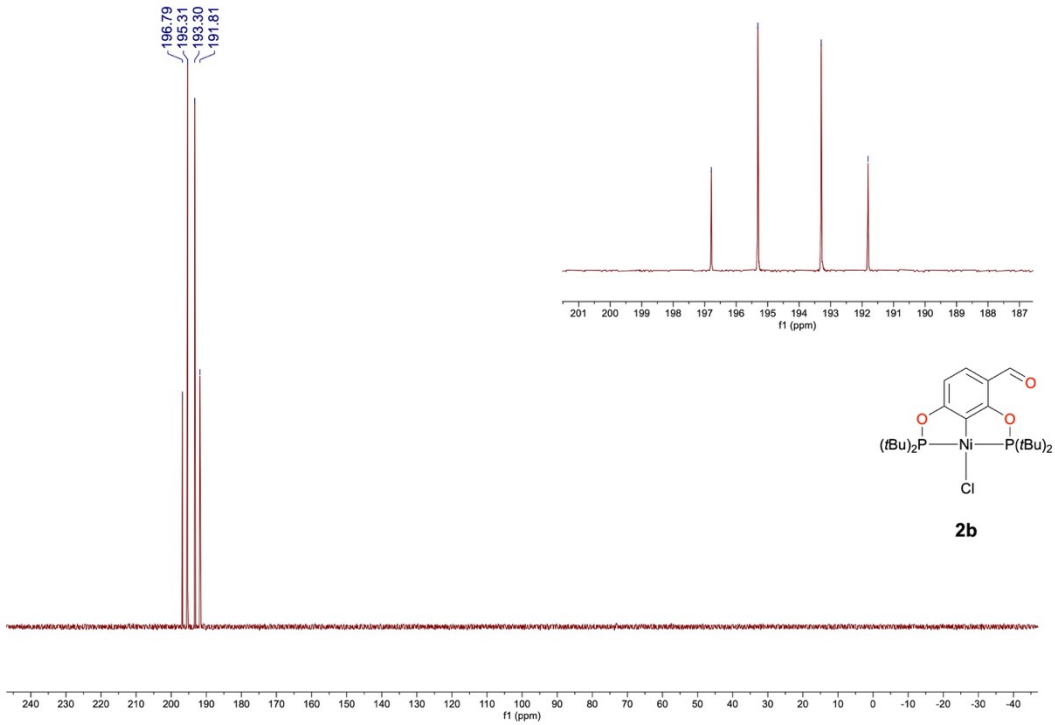

Figure S13. ^{31}P NMR spectrum (202 MHz) of **2b** in $CDCl_3$

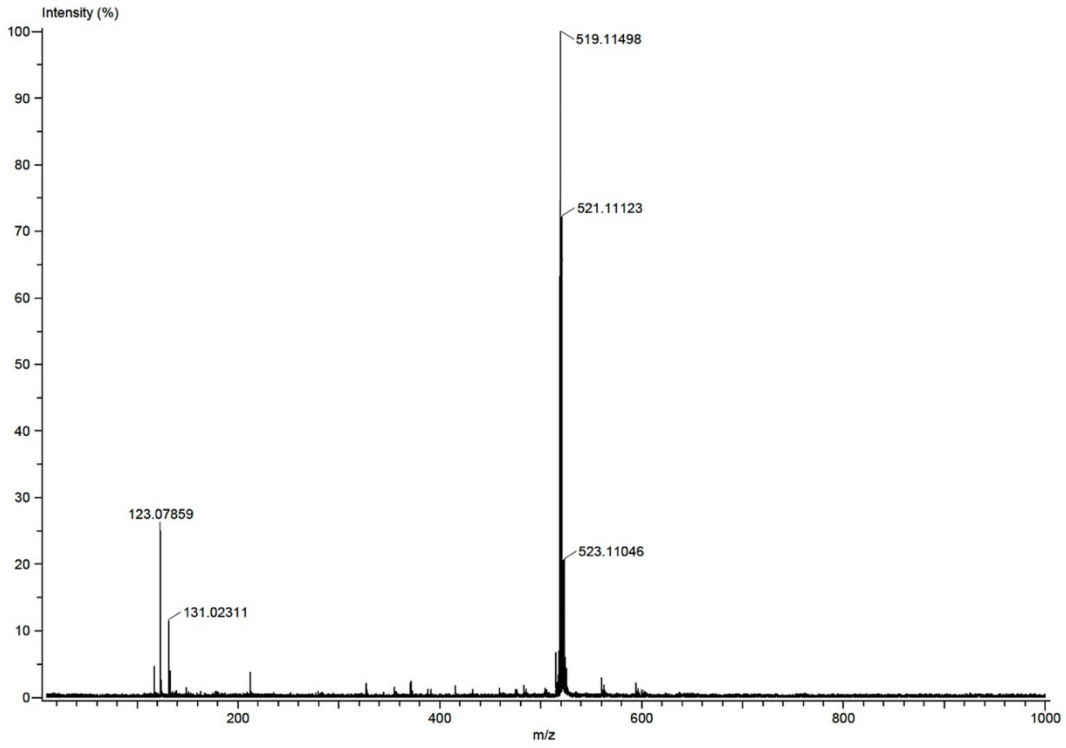

Figure S14. $DART^+$ mass spectrum of compound **2b**

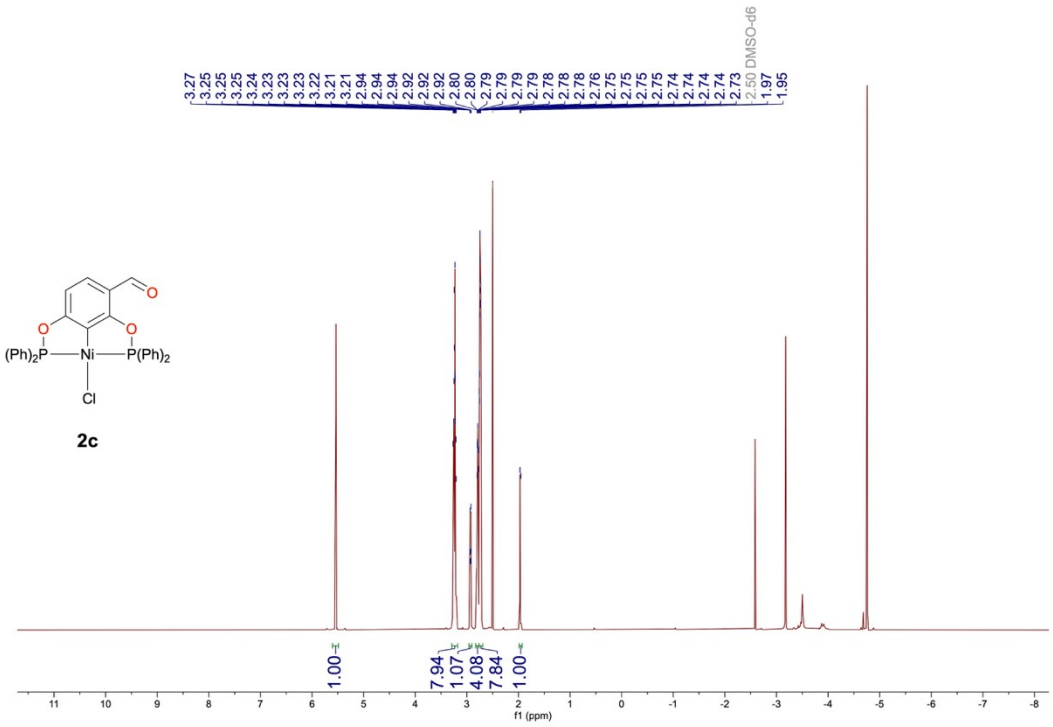

Figure S15. ^{1}H NMR spectrum (500 MHz) of **2c** in $CDCl_3$

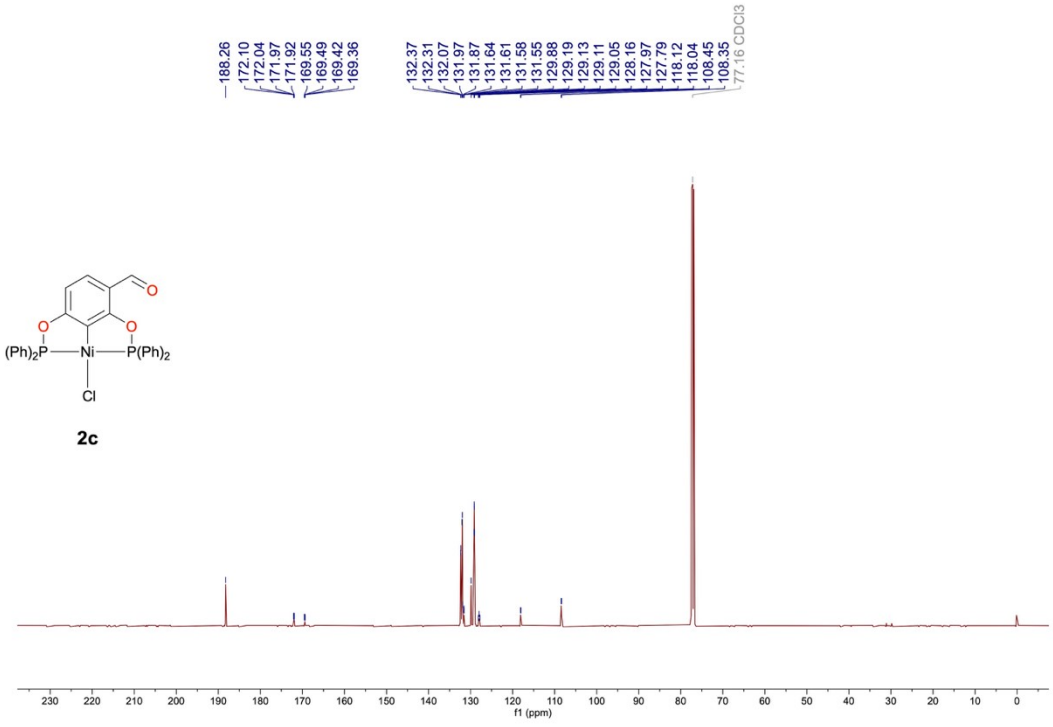

Figure S16. ^{13}C NMR spectrum (125 MHz) of **2c** in $CDCl_3$

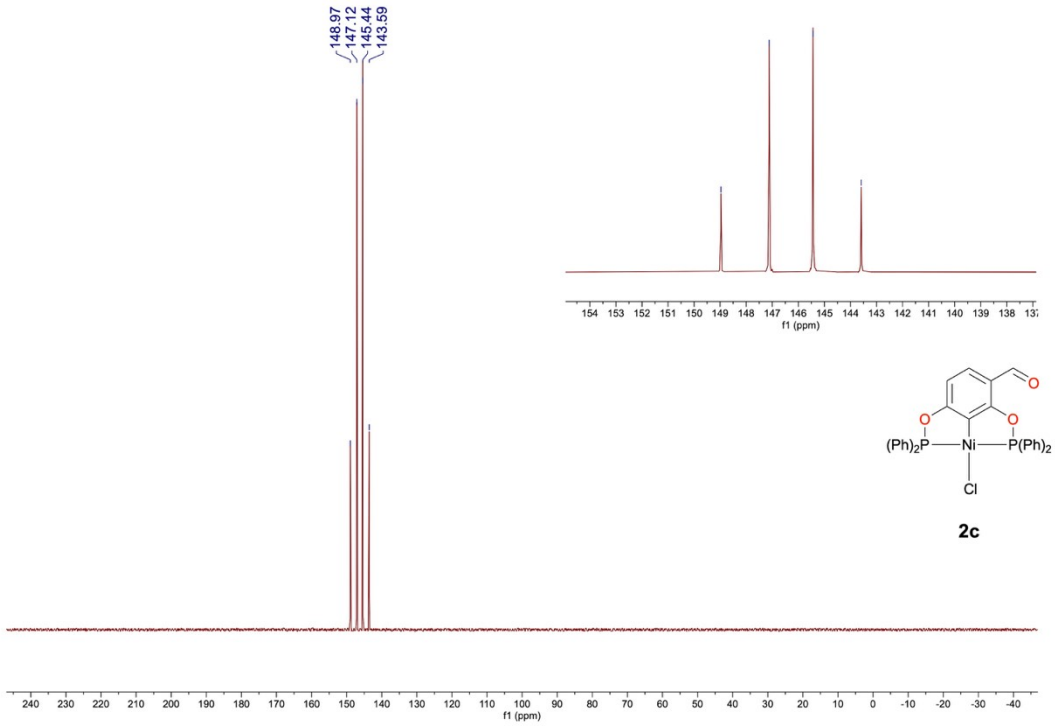

Figure S17. ^{31}P NMR spectrum (202 MHz) of **2c** in $CDCl_3$

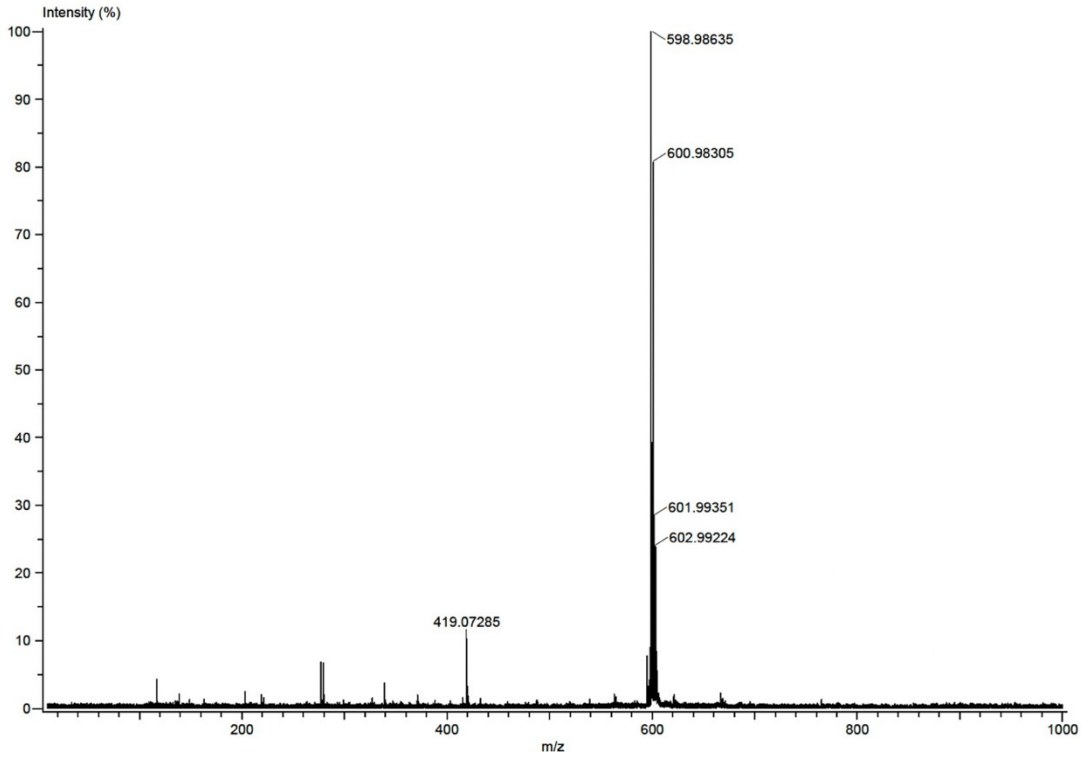

Figure S18. DART$^+$ mass spectrum of compound **2c**

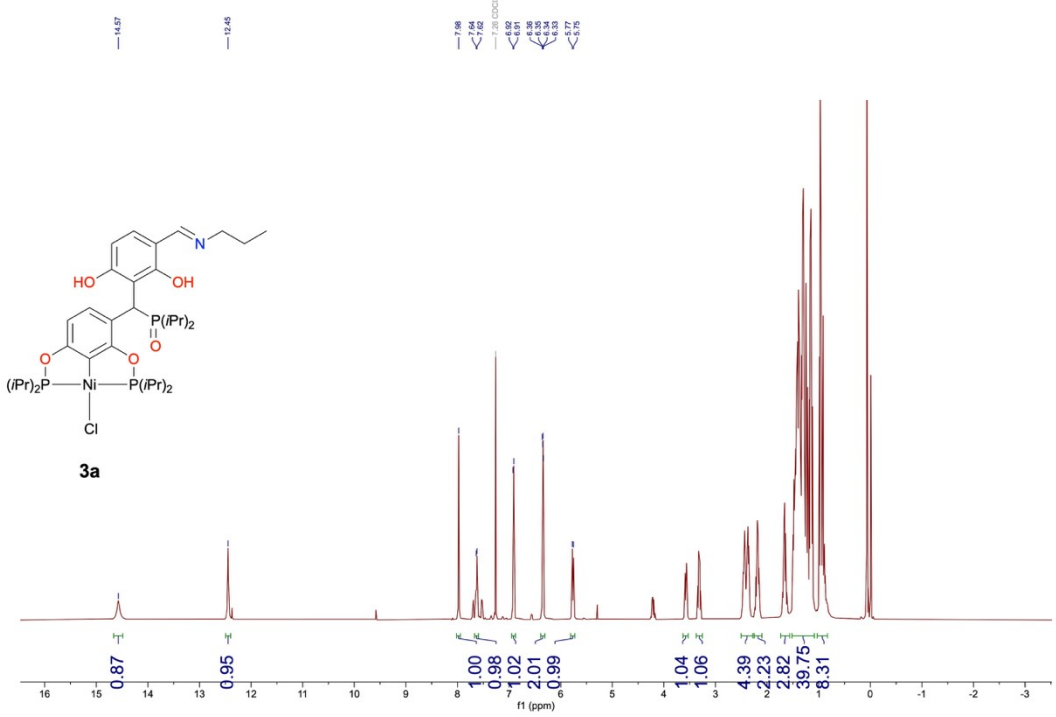

Figure S 19. ^{1}H NMR spectrum (500 MHz) of **3a** in $CDCl_3$

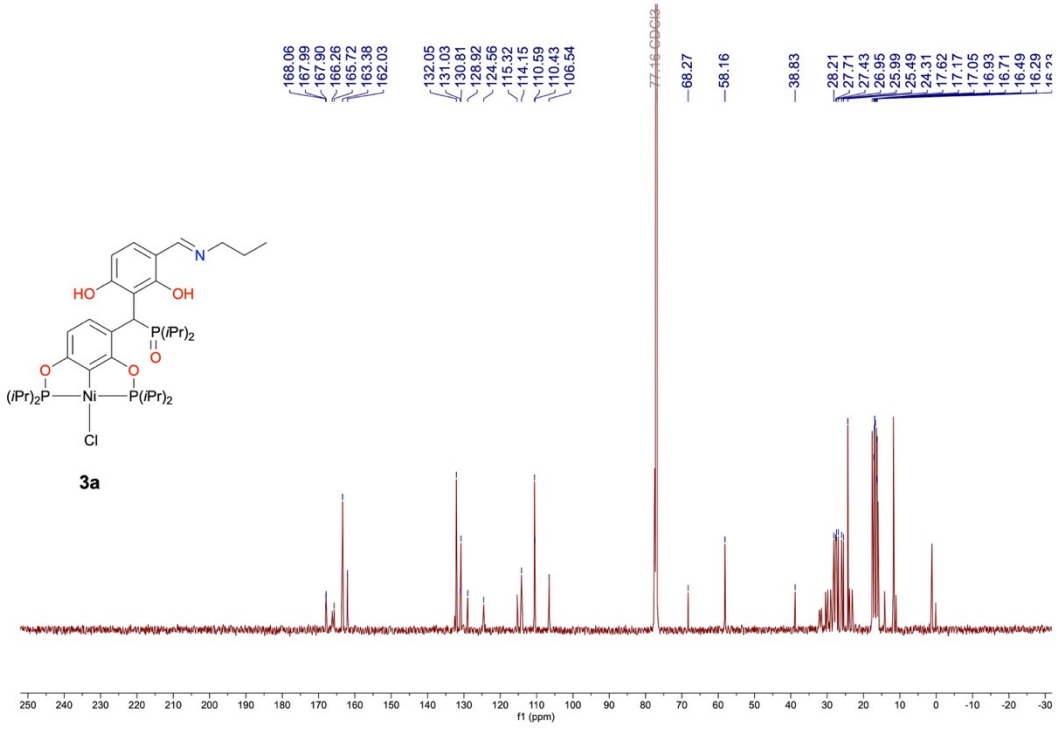

Figure S 20. ^{13}C NMR spectrum (125 MHz) of **3a** in $CDCl_3$

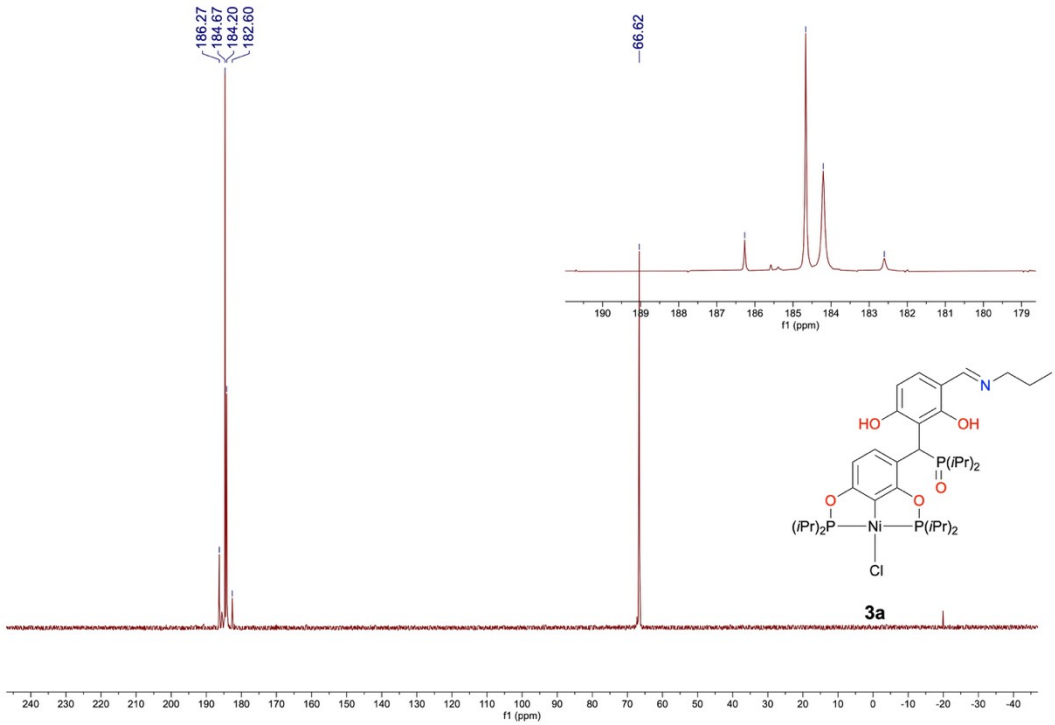

Figure S 21. ^{31}P NMR spectrum (202 MHz) of **3a** in $CDCl_3$

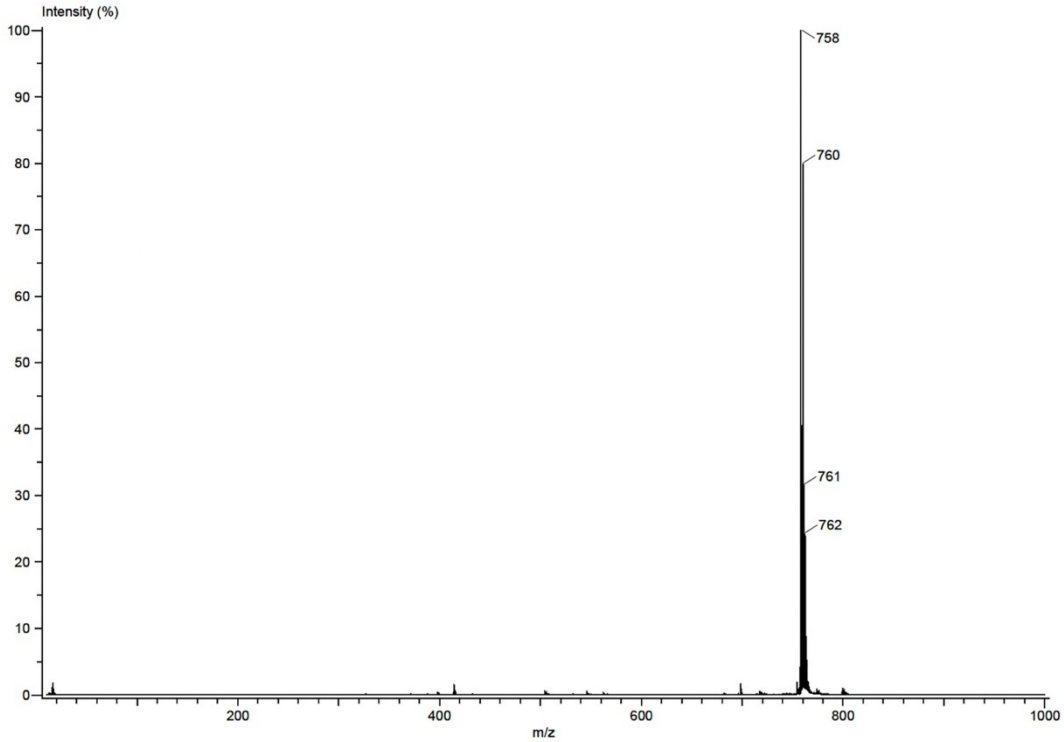

Figure S 22. $DART^+$ mass spectrum of compound **3a**

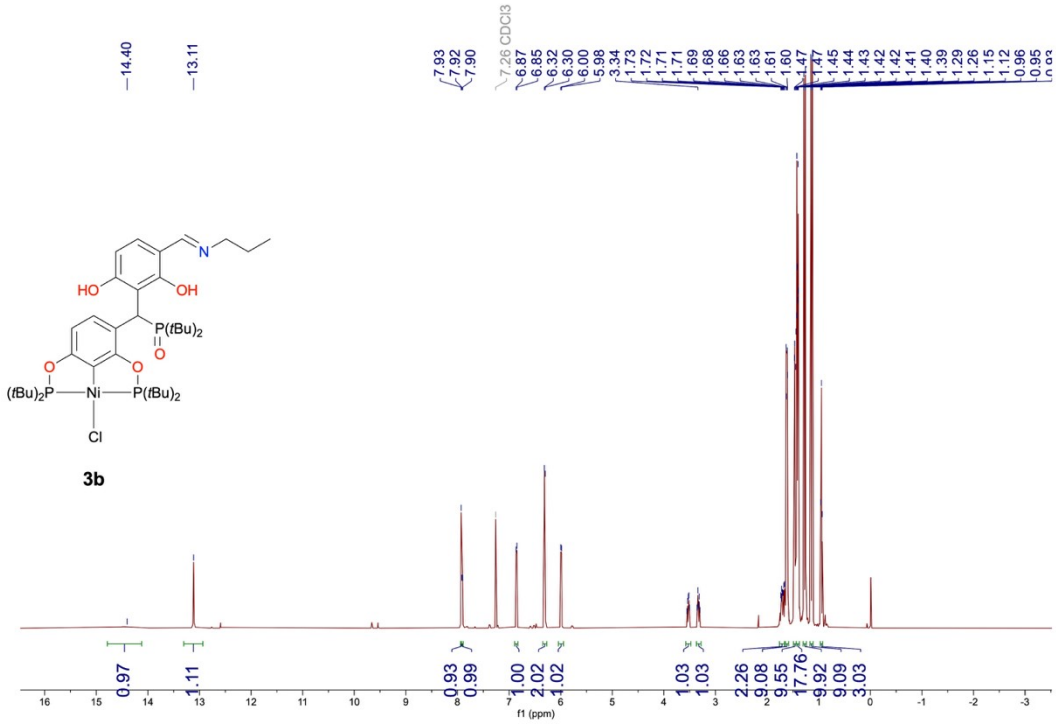

Figure S 23. ^{1}H NMR spectrum (500 MHz) of **3b** in $CDCl_3$

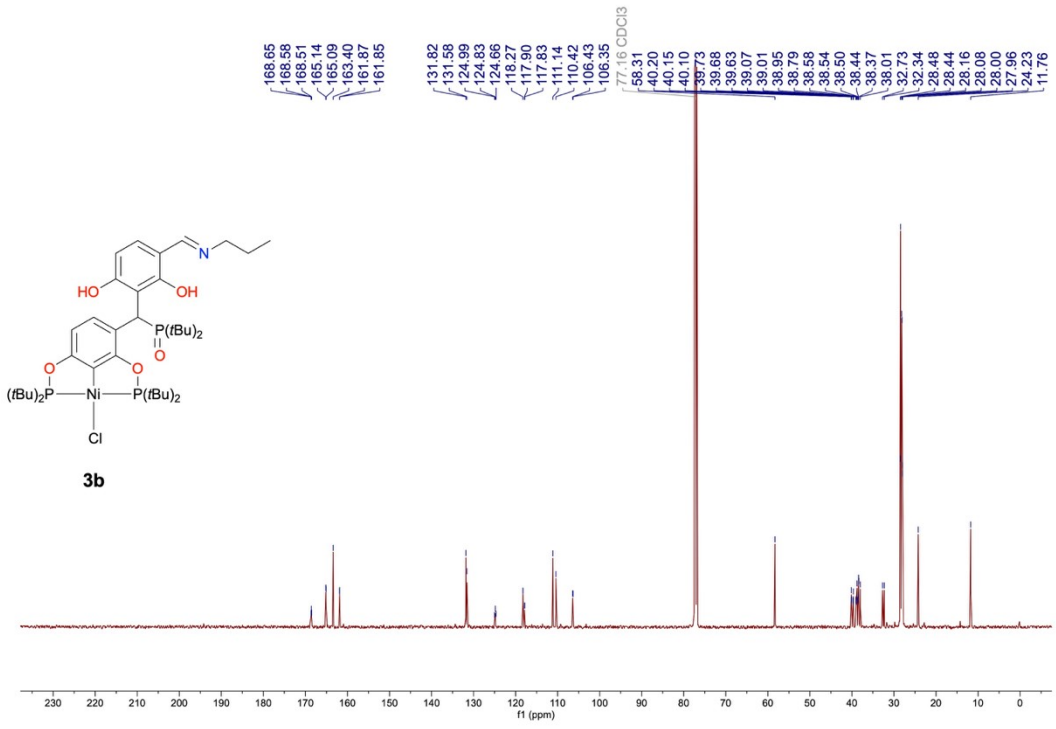

Figure S24. ^{13}C NMR spectrum (125 MHz) of **3b** in $CDCl_3$

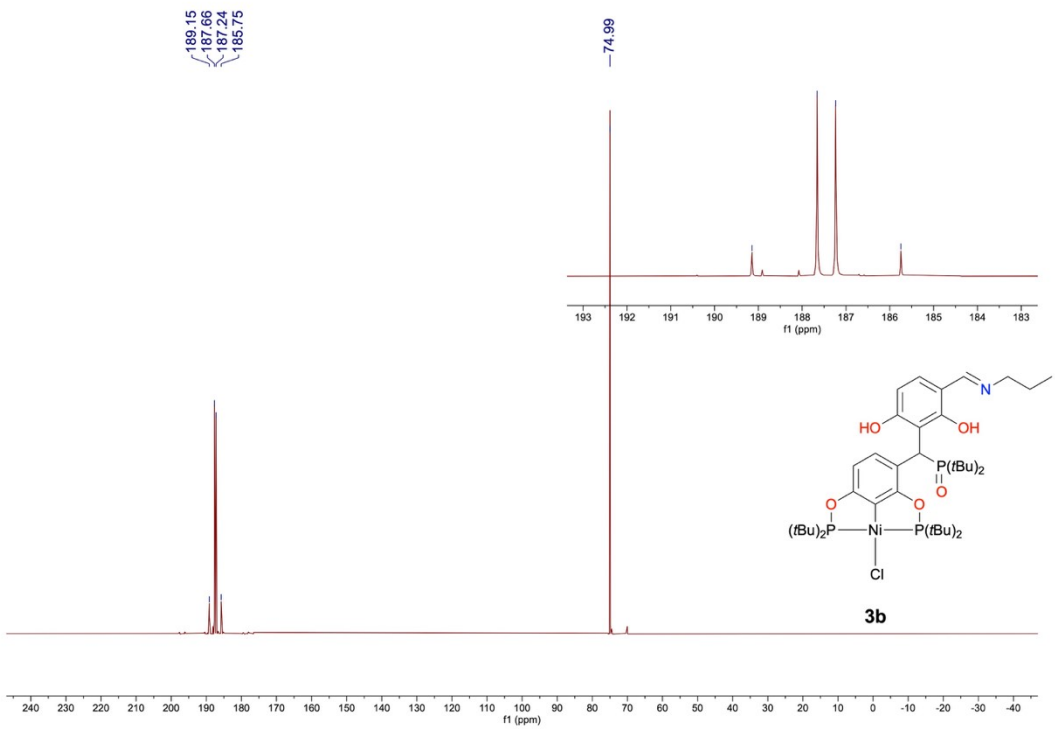

Figure S25. ^{31}P NMR spectrum (202 MHz) of **3b** in $CDCl_3$

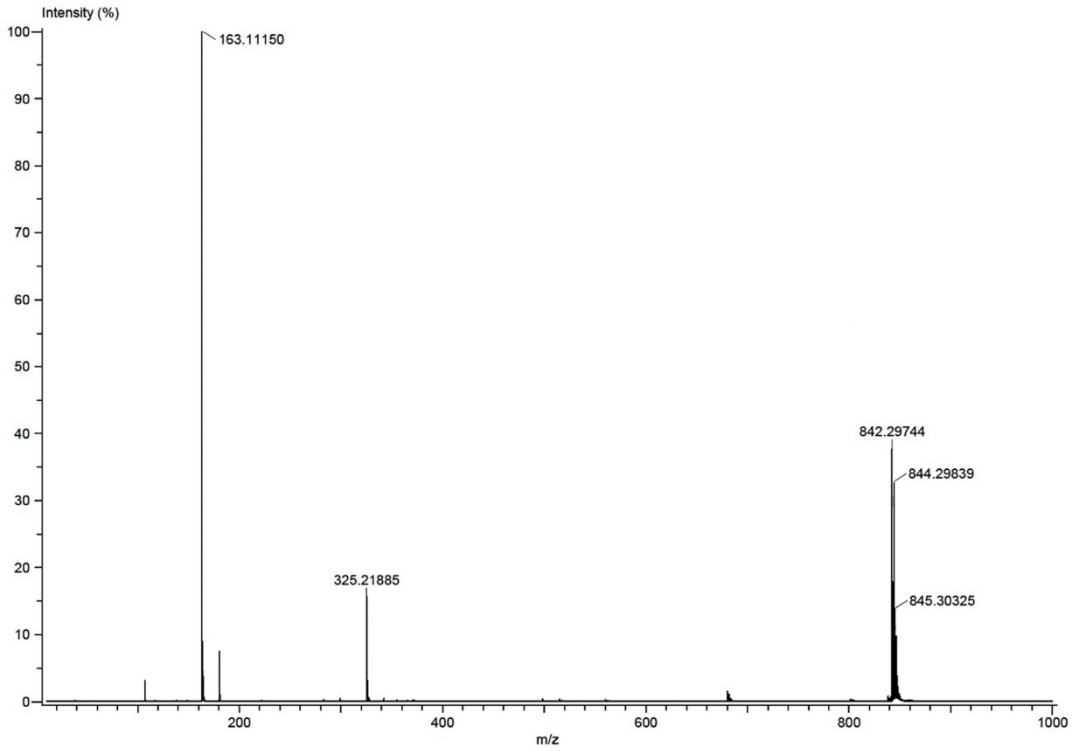

Figure S26. DART$^+$ mass spectrum of compound **3b**

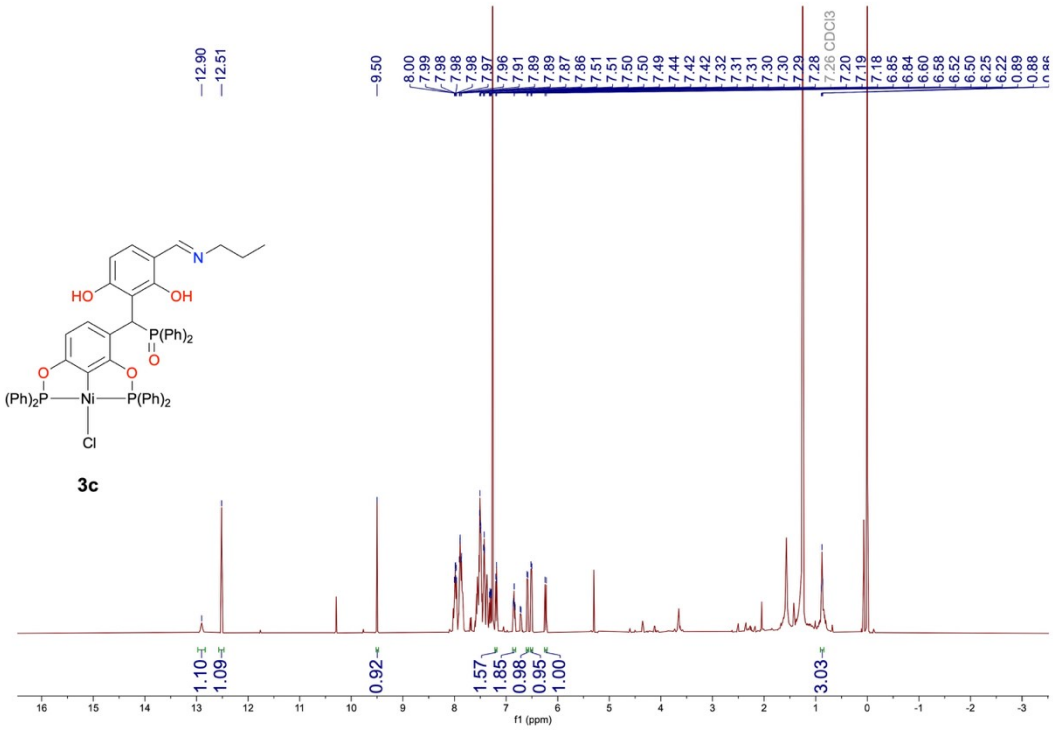

Figure S27. ^{1}H NMR spectrum (500 MHz) of **3c** in $CDCl_3$

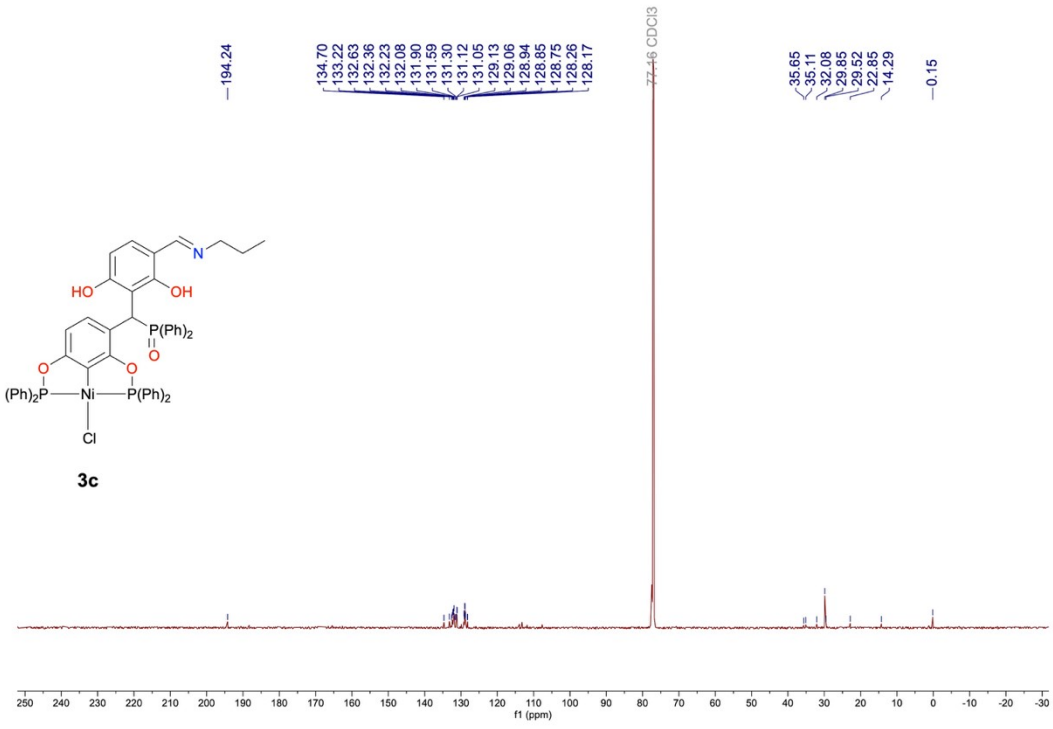

Figure S 28. ^{13}C NMR spectrum (125 MHz) of **3c** in $CDCl_3$

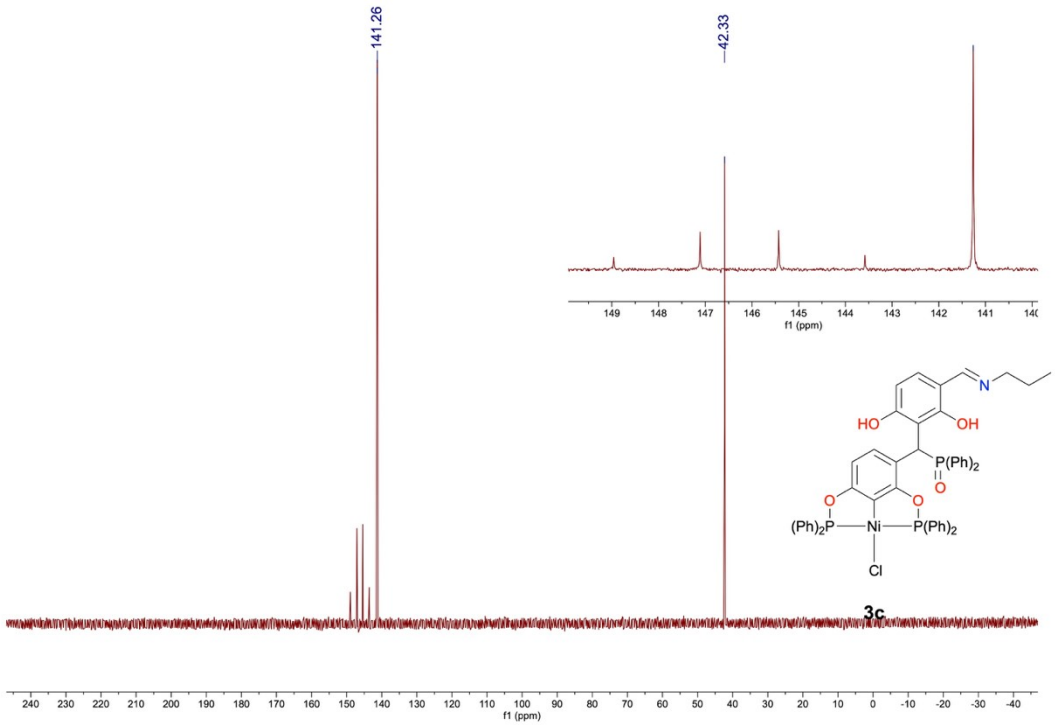

Figure S29. ^{31}P NMR spectrum (202 MHz) of **3c** in $CDCl_3$

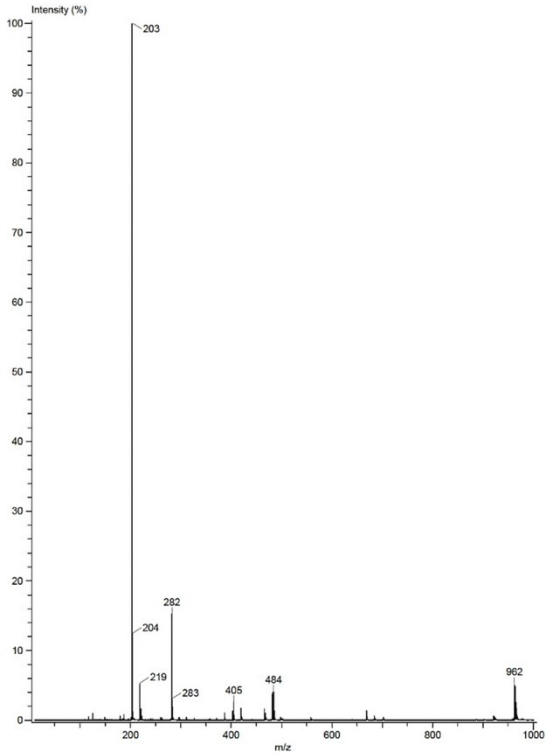

Figure S30. DART^{+} mass spectrum of compound **3c**

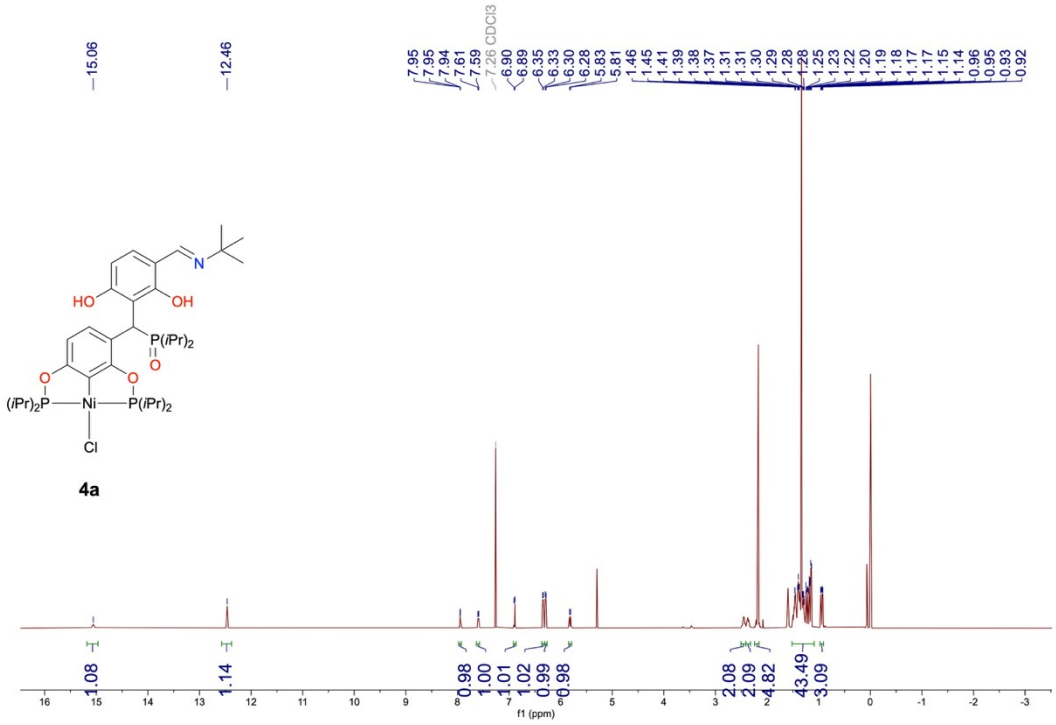

Figure S31. ^{1}H NMR spectrum (500 MHz) of **4a** in $CDCl_3$

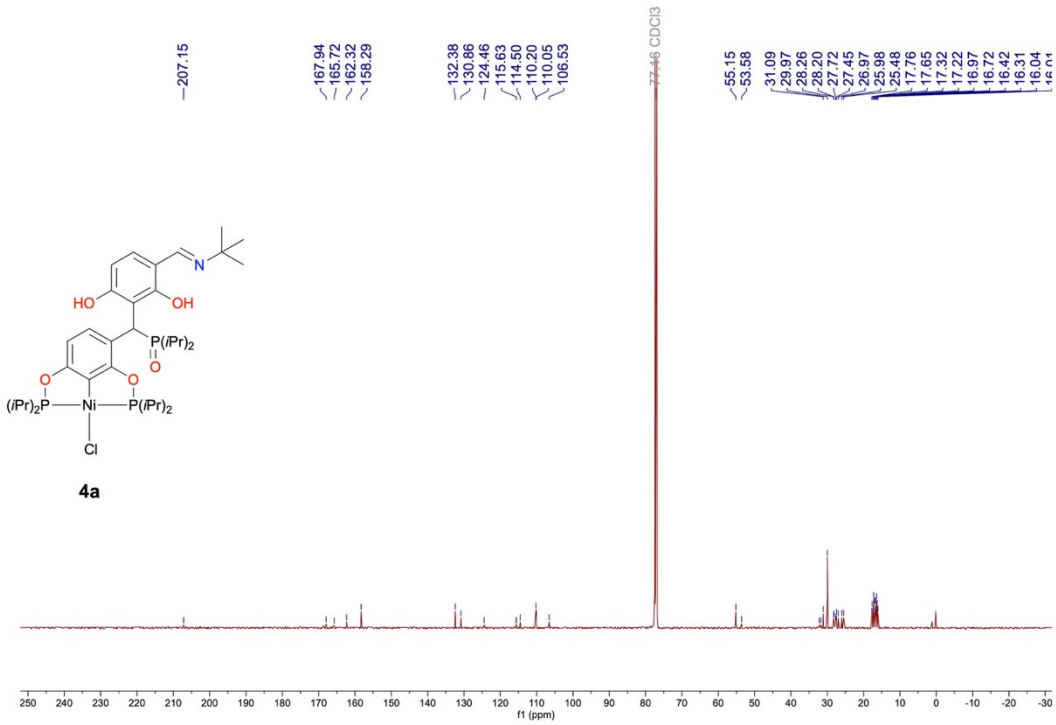

Figure S32. ^{13}C NMR spectrum (125 MHz) of **4a** in $CDCl_3$

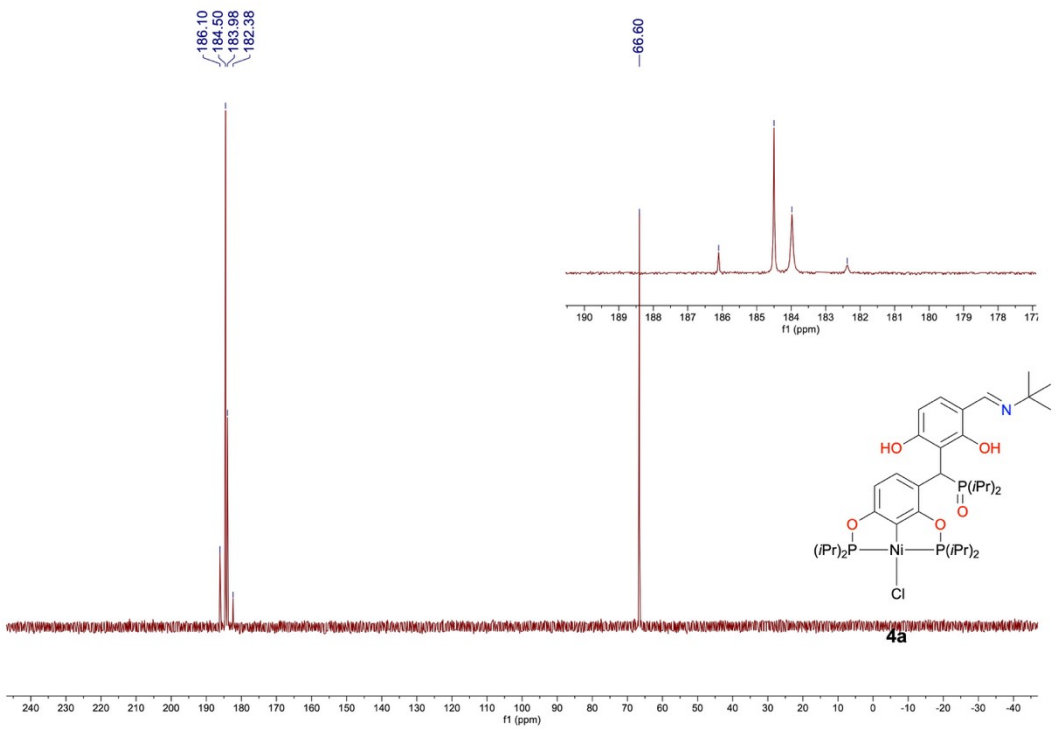

Figure S33. ^{31}P NMR spectrum (202 MHz) of **4a** in $CDCl_3$

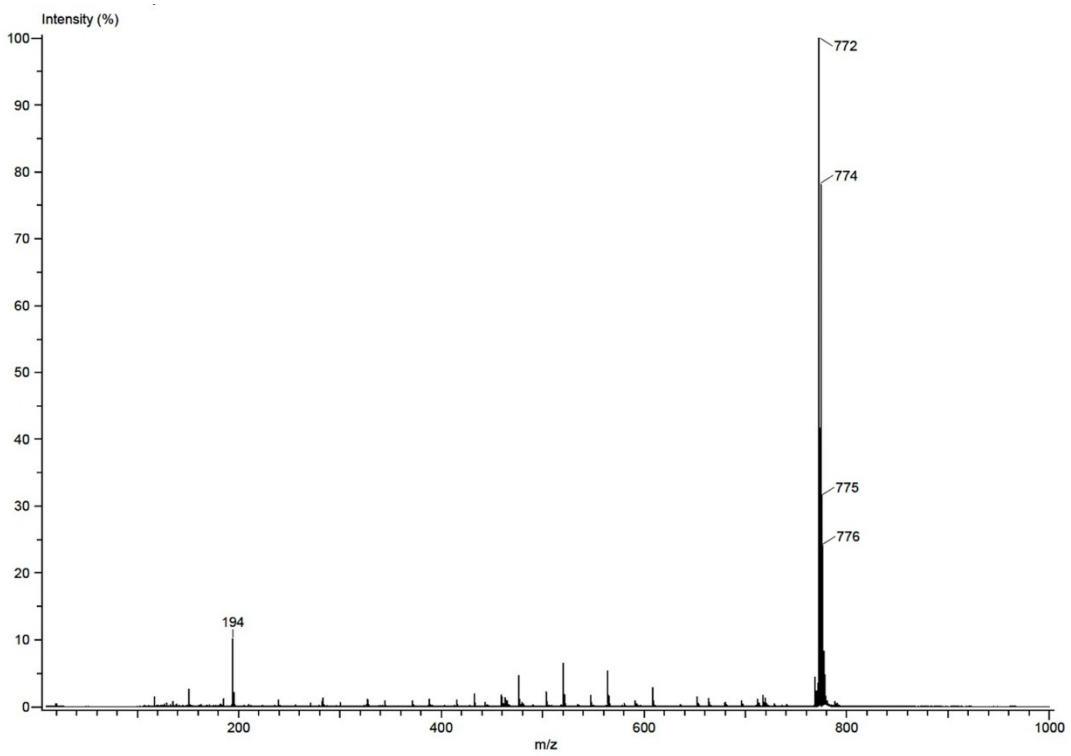

Figure S34. DART$^+$ mass spectrum of compound **4a**

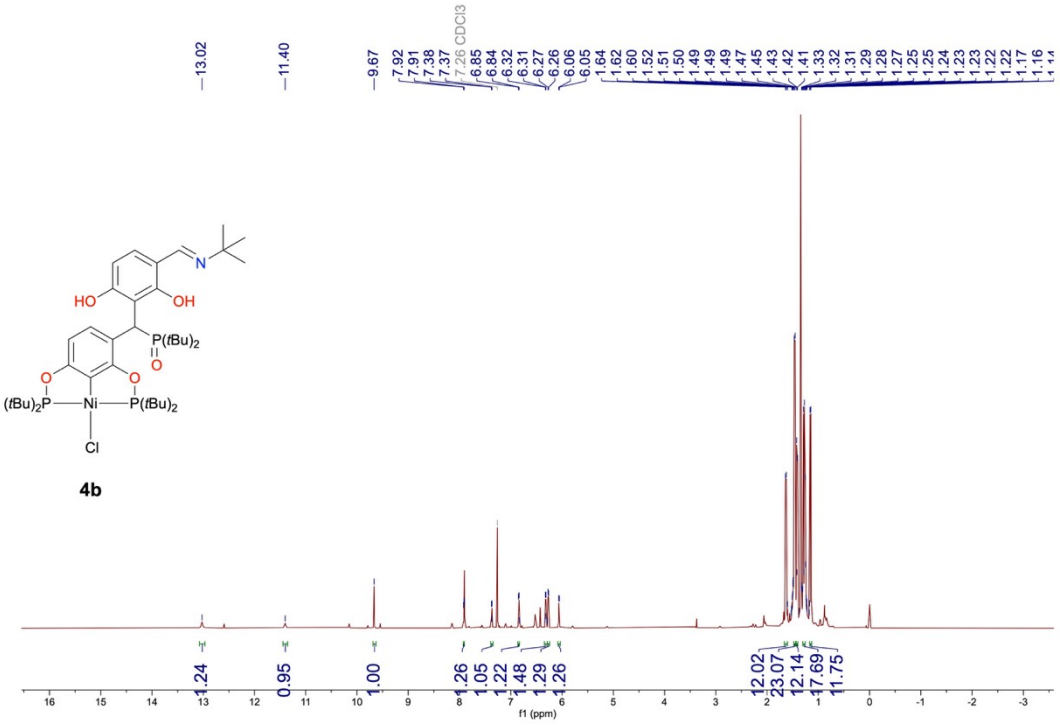

Figure S35. ^{1}H NMR spectrum (500 MHz) of **4b** in $CDCl_3$

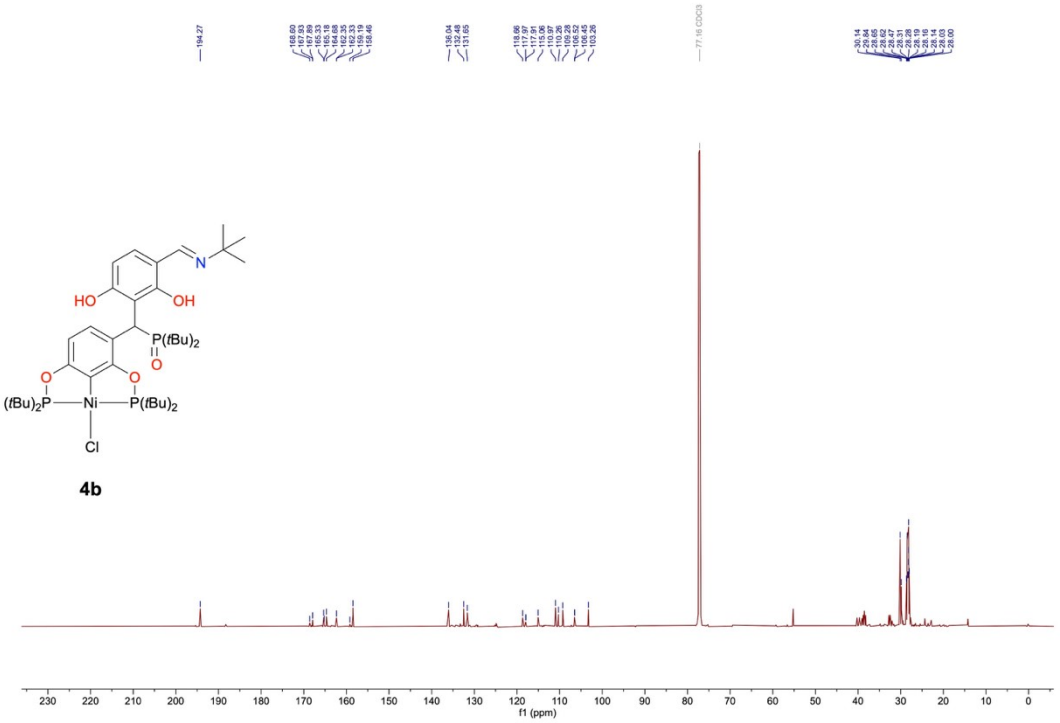

Figure S36. ^{13}C NMR spectrum (125 MHz) of **4b** in $CDCl_3$

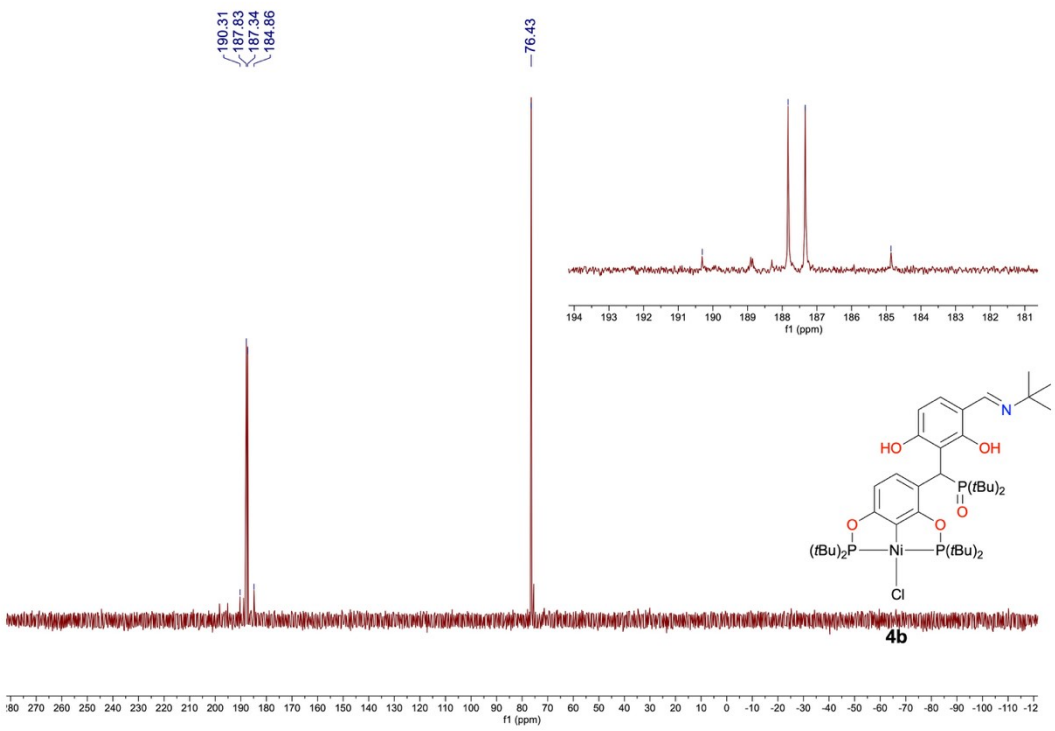

Figure S37. ^{31}P NMR spectrum (202 MHz) of **4b** in $CDCl_3$

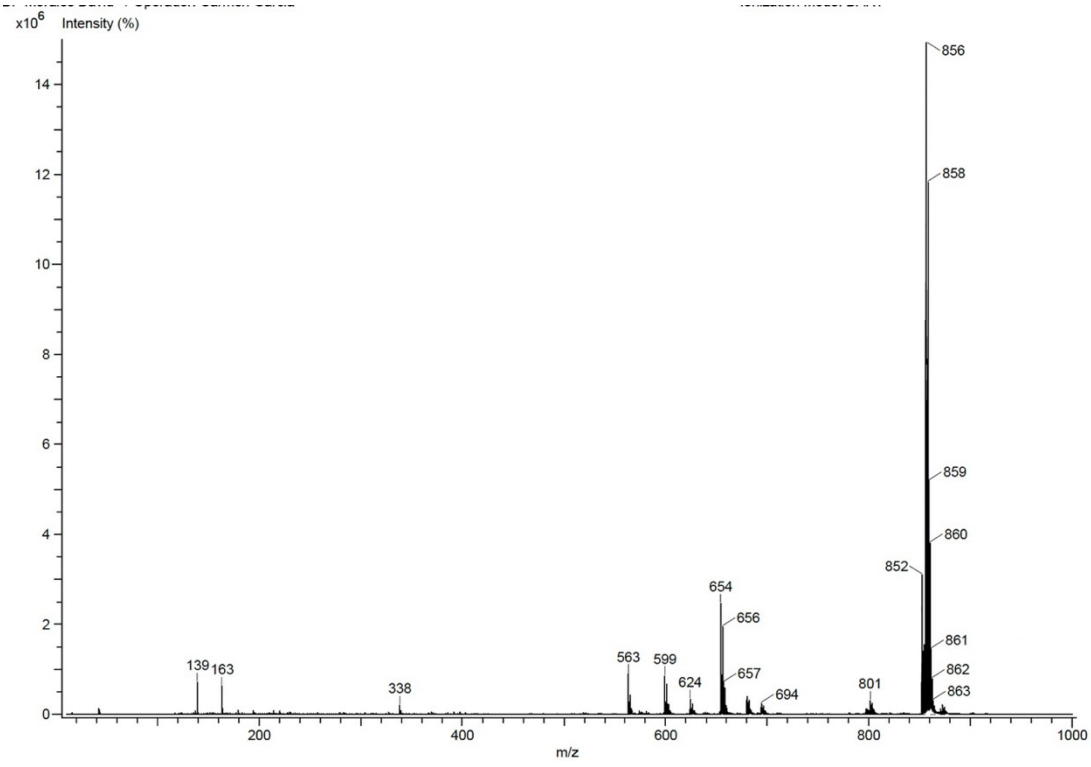

Figure S38. $DART^+$ mass spectrum of compound **4b**

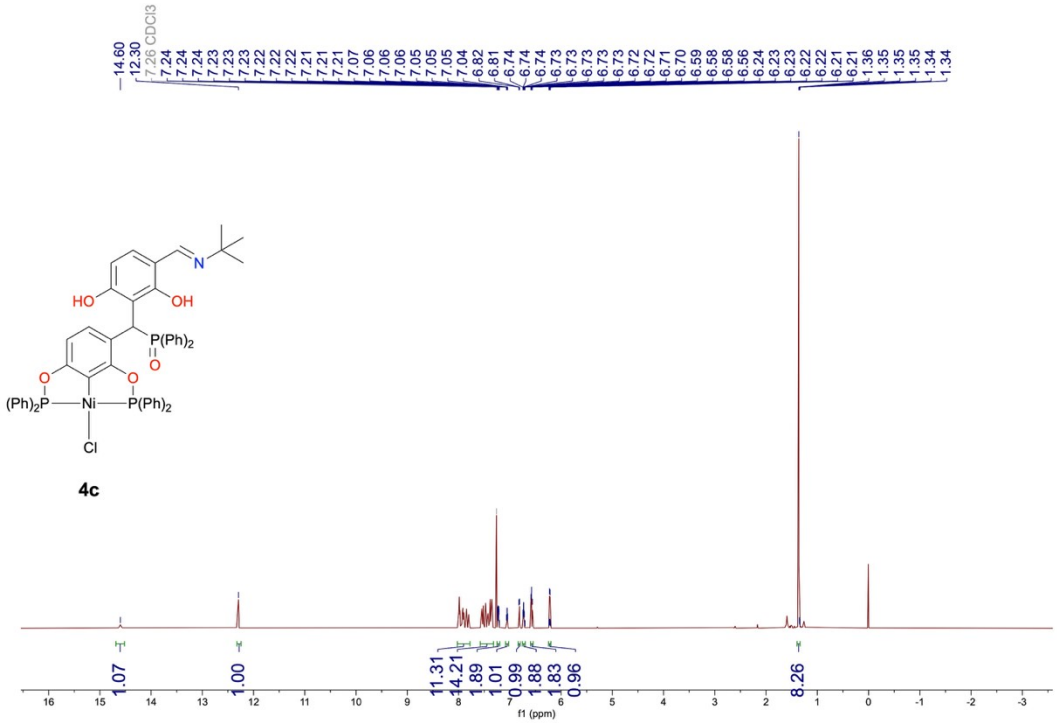

Figure S39. ^{1}H NMR spectrum (500 MHz) of **4c** in $CDCl_3$

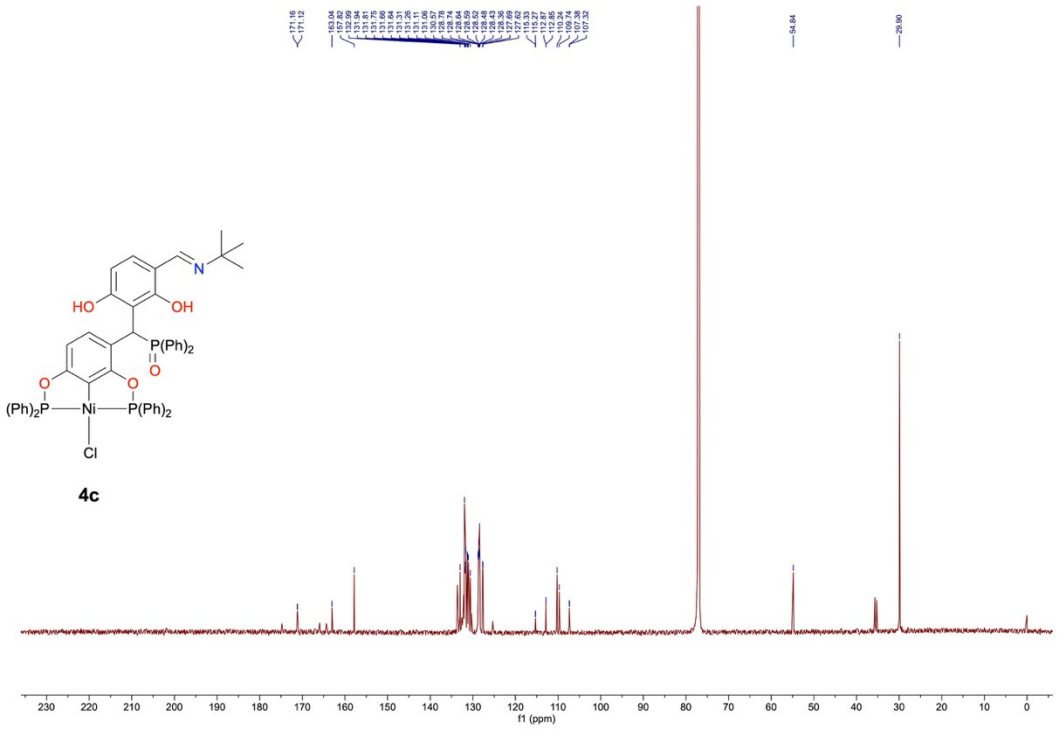

Figure S40. ^{13}C NMR spectrum (125 MHz) of **4c** in $CDCl_3$

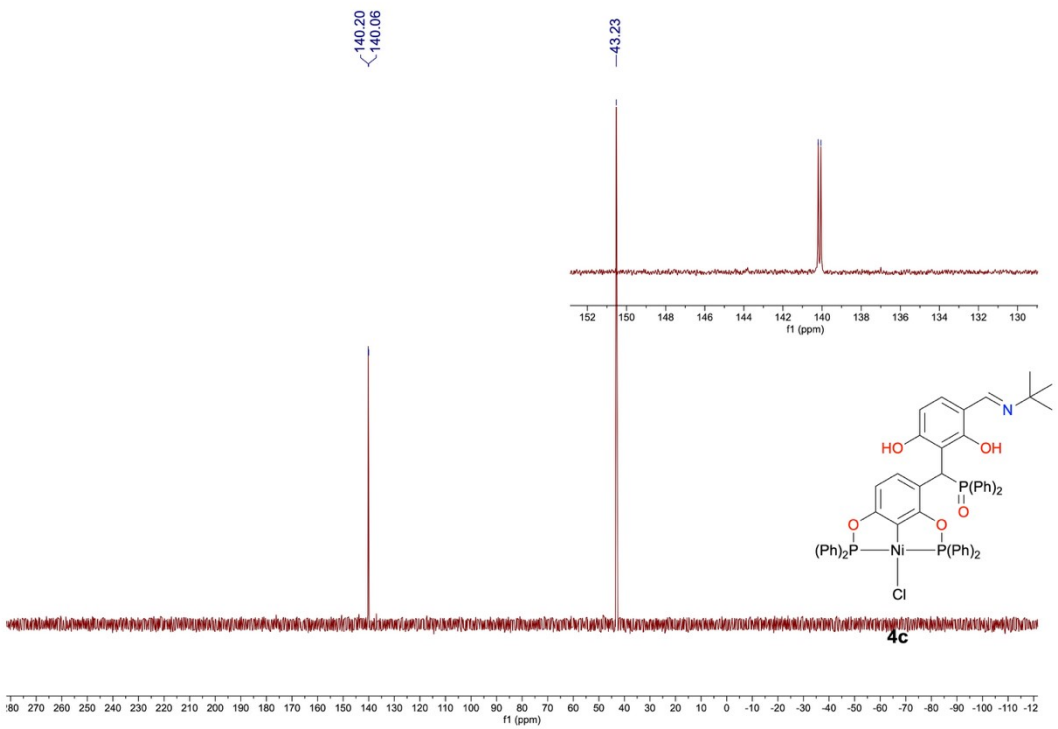

Figure S41. ^{31}P NMR spectrum (202 MHz) of **4c** in $CDCl_3$

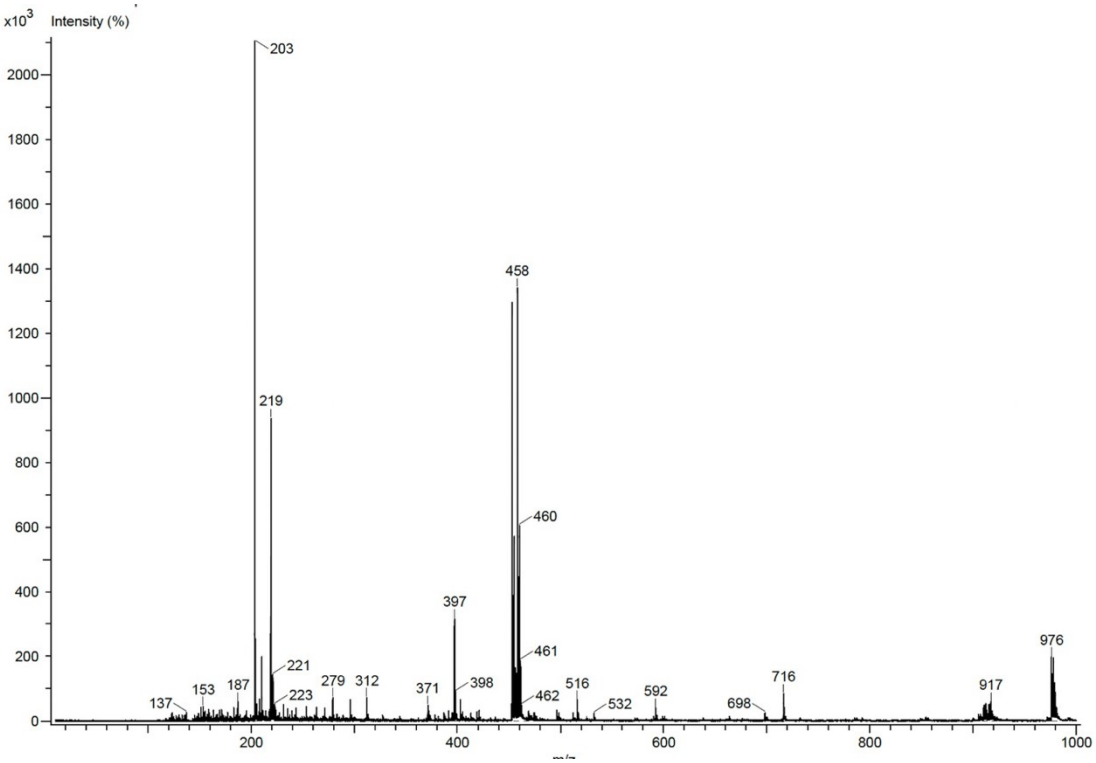

Figure S42. DART$^+$ mass spectrum of compound **4c**

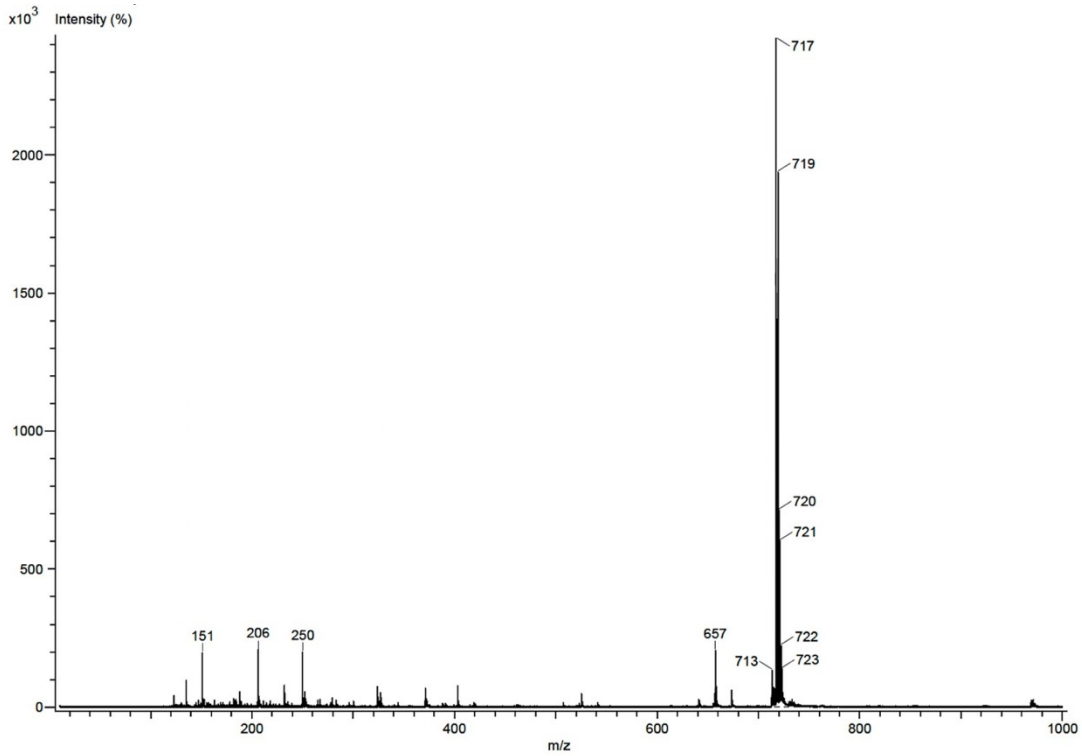

Figure S43. DART$^+$ mass spectrum of compound **5a**

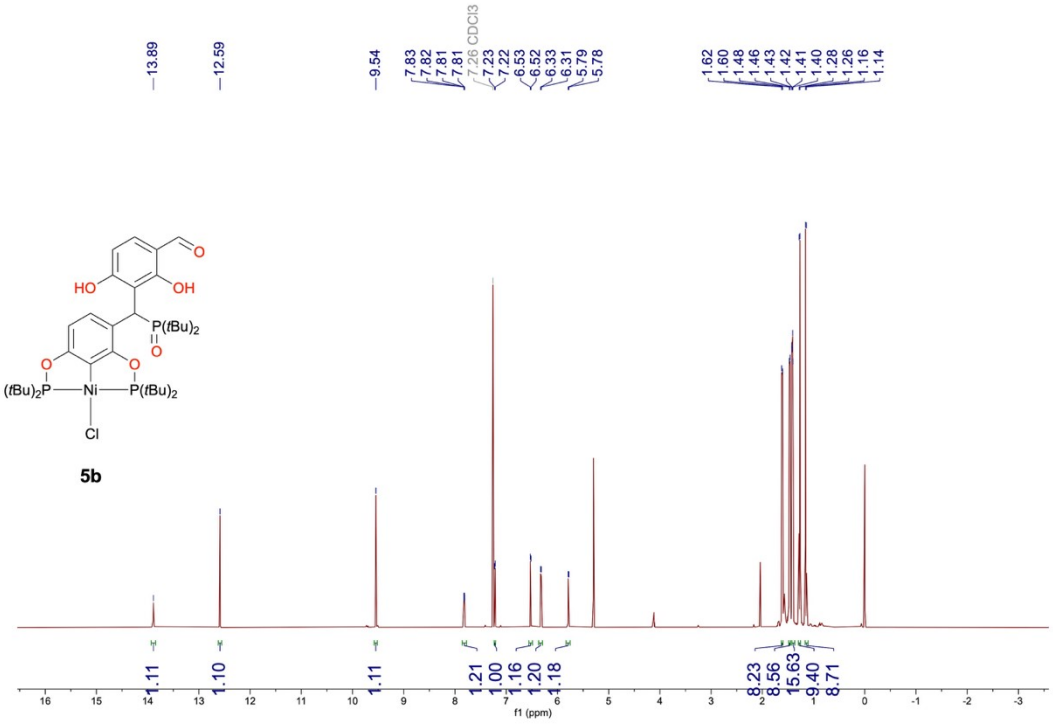

Figure S44. ^{1}H NMR spectrum (500 MHz) of **5b** in $CDCl_3$

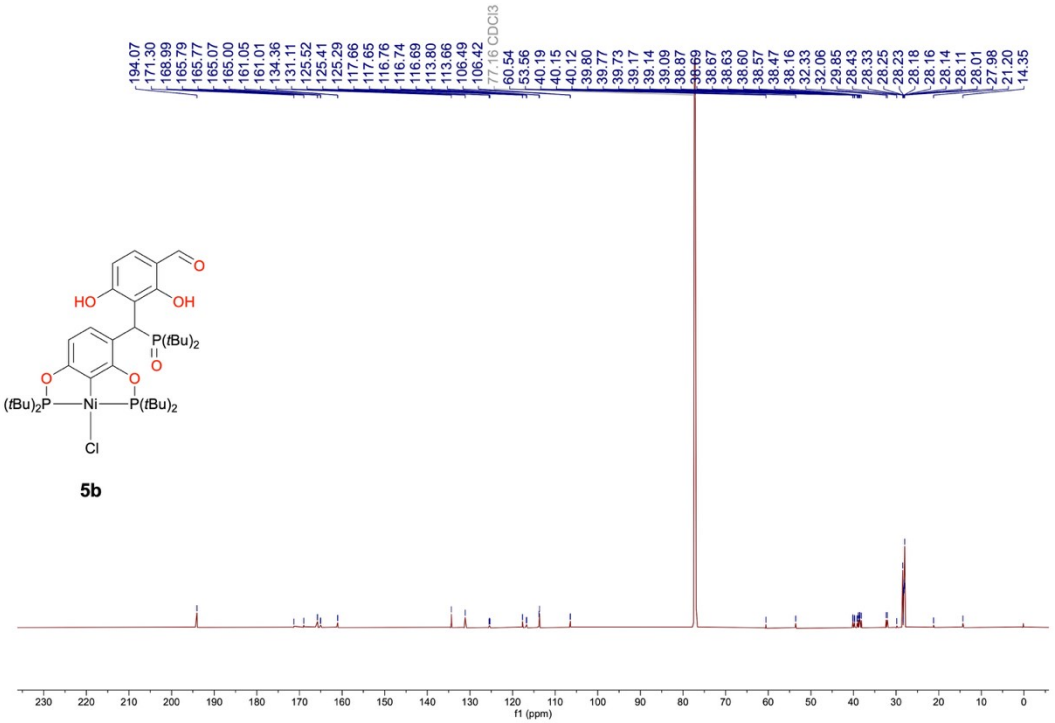

Figure S45. ^{13}C NMR spectrum (125 MHz) of **5b** in $CDCl_3$

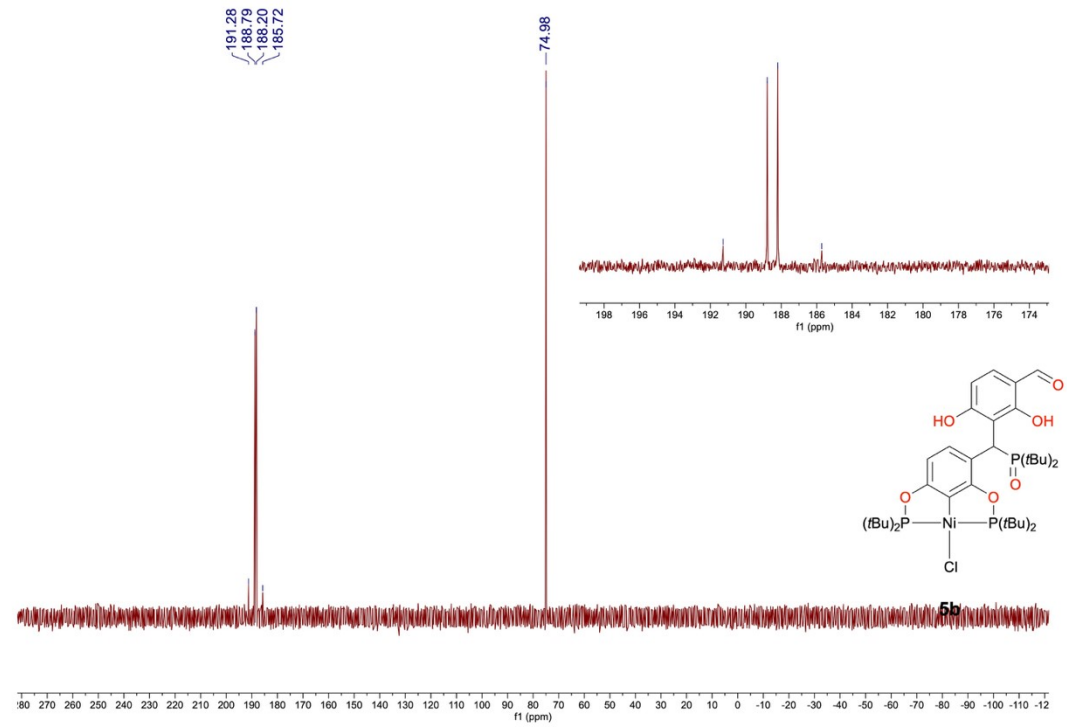

Figure S46. ^{31}P NMR spectrum (202 MHz) of **5b** in $CDCl_3$

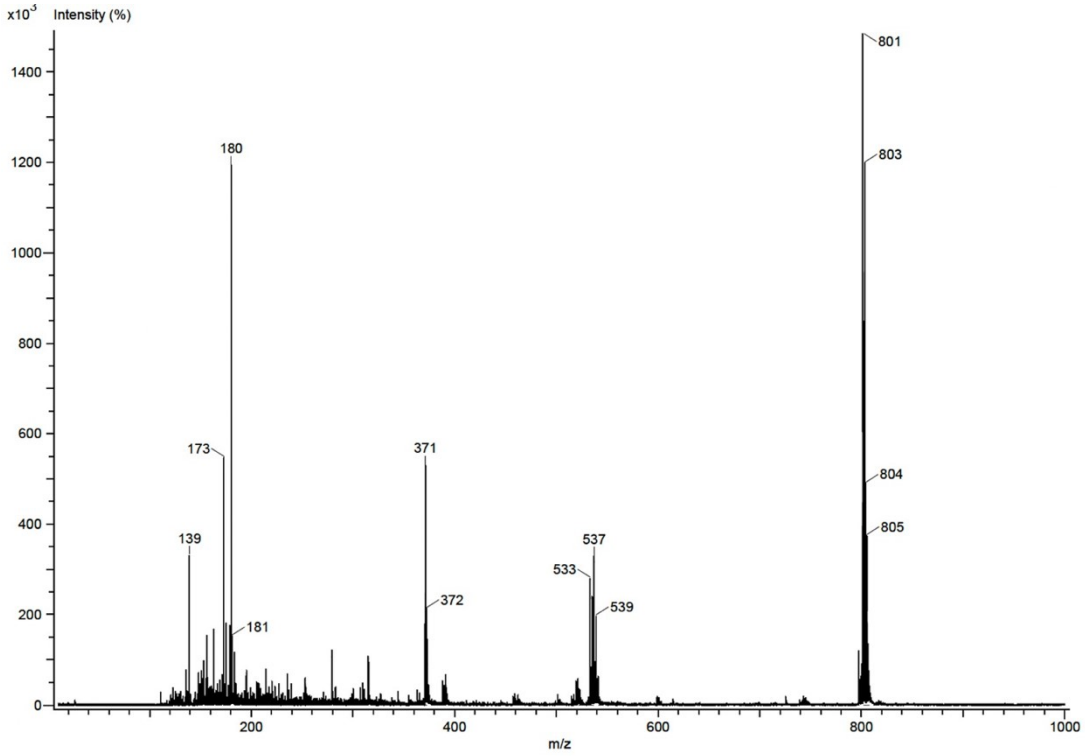

Figure S47. DART^{+} mass spectrum of compound **5b**

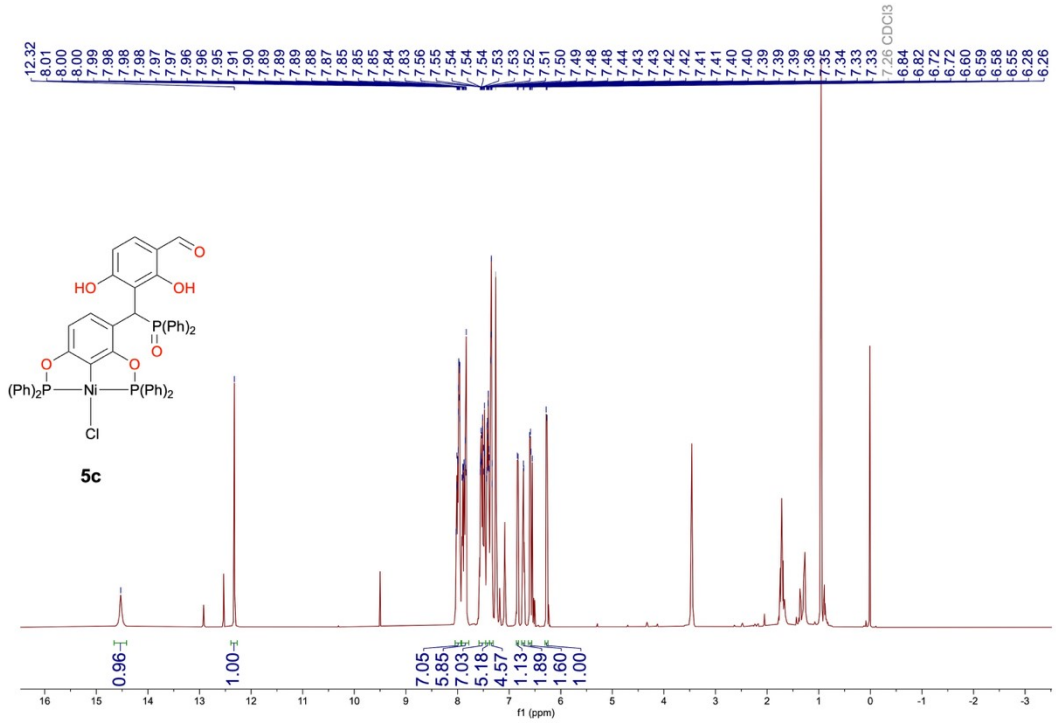

Figure S48. ^{1}H NMR spectrum (500 MHz) of **5c** in $CDCl_3$

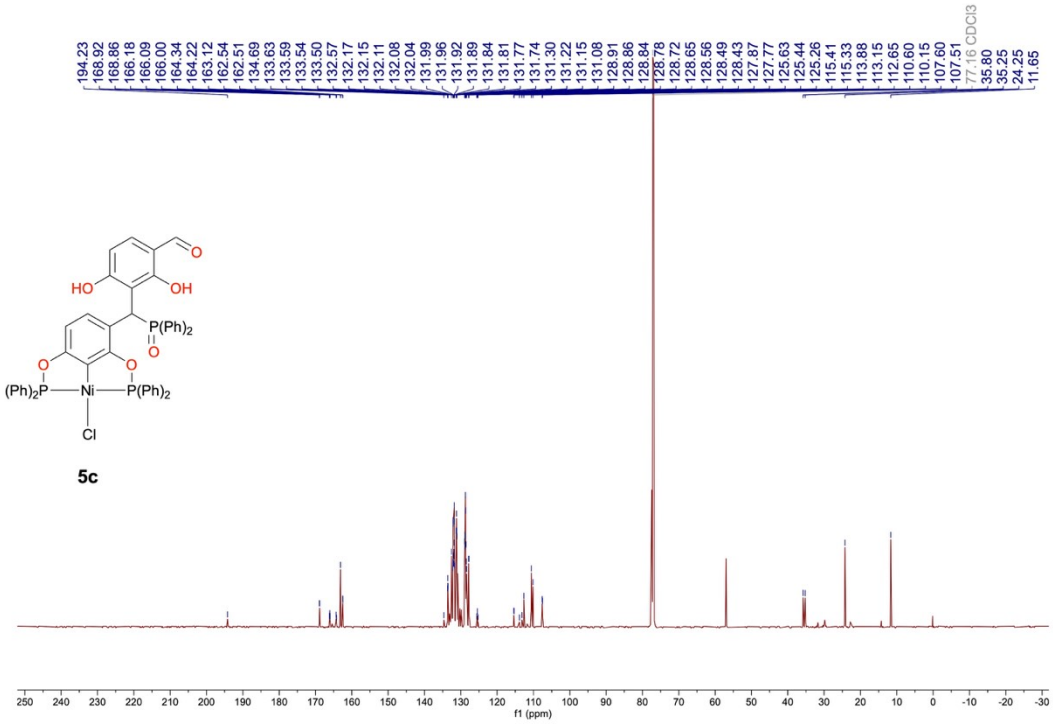

Figure S49. ^{13}C NMR spectrum (125 MHz) of **5c** in $CDCl_3$

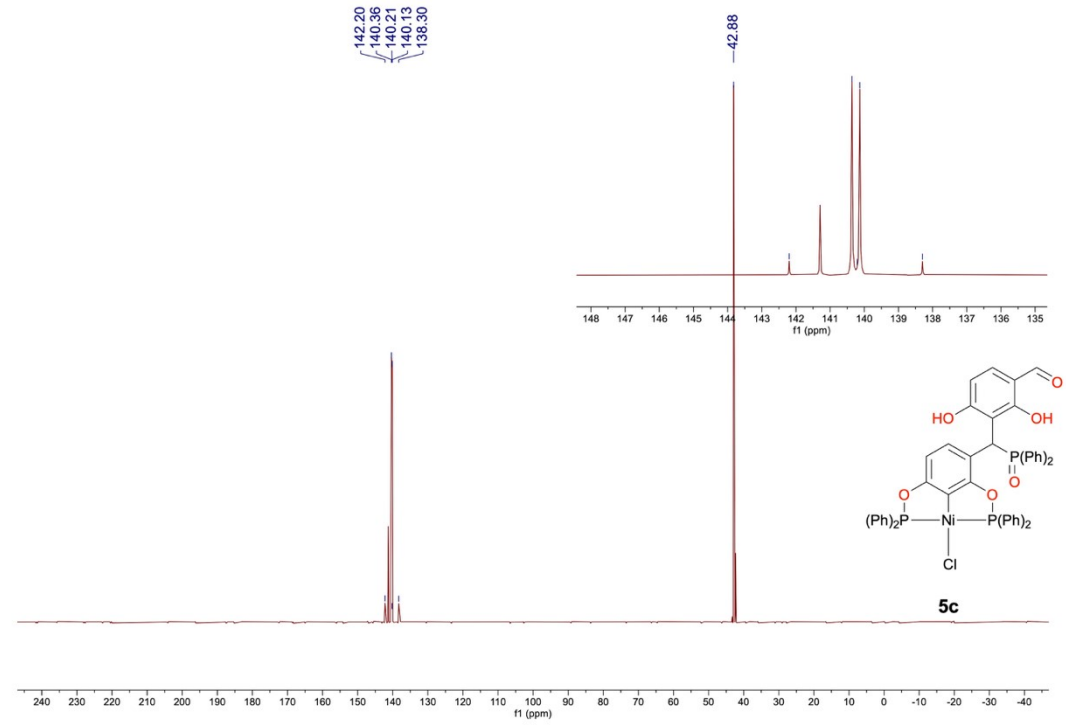

Figure S50. ^{31}P NMR spectrum (202 MHz) of **5c** in $CDCl_3$

3. X-Ray and Supramolecular

Table S1. Crystallographic data of compounds **1b** and **2c**

	1b	**2c**
Formula	$C_{11}H_{15}NO_2$	$C_{31}H_{23}ClNiO_3P_2$
Formula weight	193.24	599.59
Temperature (K)	100(2)	250(2)
Wavelength	1.54178	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	P-1
A (Å)	7.37910(10)	9.4058(3)
B (Å)	11.8651(2)	11.9319(4)
C (Å)	12.6163(2)	14.0770(4)
α (°)	90	96.6010(10)
β (°)	90	106.5490(10)
γ (°)	90	110.9160(10)
V ($Å^3$)	1104.60(3)	1372.58(8)
Z	4	2
δ_{cal} (g/cm^3)	1.162	1.451
μ (mm^{-1})	0.644	0.952
F (000)	416	616
Crystal size (mm^3)	0.600 x 0.444 x 0.407	0.361 x 0.277 x 0.154
Theta range (°)	5.117 to 68.339	2.418 to 25.394
Reflection collected	17736	17706
Data/restraints/parameters	2022 / 2 / 136	5045 / 0 / 343
Goodness-of-fit	1.038	1.150
Final R indices [I>2sigma(I)]	R1 = 0.0265, wR2 = 0.0699	R1 = 0.0576, wR2 = 0.0739

Table S2. Crystallographic data of compounds **3a**, **5b** and **5c**

	3a	**5b**	**5c**
Formula	$C_{35}H_{57}ClNNiO_5P_3$	$C_{38}H_{62}ClNiO_6P_3$	$C_{50}H_{38}ClNiO_6P_3$
Formula weight	758.88	801.94	921.87
Temperature (K)	250(2)	130(2)	130(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P-1	P21/n	P-1
a (Å)	10.7237(4)	9.5362(7)	9.3788(6)
b (Å)	10.8801(4)	22.0209(13)	12.1046(9)
c (Å)	17.5144(5)	21.058(2)	21.9764(16)
α (°)	101.438(2)	90	77.364(6)
β (°)	91.937(2)	92.733	86.101(5)
γ (°)	95.469(3)	90	68.500(7)

V ($Å^3$)	1990.88(12)	4417.1(6)	2264.9(3)
Z	2	4	2
δ_{cal} (g/cm^3)	1.266	1.206	1.352
μ (mm^{-1})	0.713	0.647	0.642
F (000)	808	1712	952
Crystal size (mm^3)	0.410 x 0.280 x 0.220	0.490 x 0.440 x 0.170	0.360 x 0.090 x 0.026
Theta range (°)	2.195 to 25.431	3.525 to 29.458	3.443 to 25.350
Reflection collected	26039	23834	21350
Data/restraints/parameters	7328 / 90 / 463	10499 / 0 / 460	8275 / 0 / 550
Goodness-of-fit on F^2	1.091	1.235	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0519, wR2 = 0.0975	R1 = 0.0511, wR2 = 0.1672	R1 = 0.0770, wR2 = 0.1827
Largest diff. peak and hole $e.Å^{-3}$	0.673 and -0.374	0.570 and -0.618	0.813 and -1.199

Table S3. Selected bonds and angles of compound **1b**

Compound	N-C(7)	N-C(8)	O(1)-C(2)	O(2)-C(4)	C(7)-N-C(8)
1b	1.303(2)	1.482(2)	1.302(2)	1.338(2)	127.3(1)

Table S4. Selected bond distances and angles for aldehyde complexes (2a-2c), and addition complexes (3a, 4a, 5b and 5c)

Compound	**Ni–C**	**Ni–P(1)**	**Ni–P(2)**	**Ni–Cl**	**C–Ni–Cl**	**P(1)–Ni–P(2)**
2c	1.879(3)	2.167(1)	2.139(1)	2.188(1)	176.4(1)	162.06(5)
3a	1.878(3)	2.1536(9)	2.1532(9)	2.1833(9)	178.05(10)	164.00(3)
5b	1.885(3)	2.1818(8)	2.1758(8)	2.2121(7)	178.77(9)	163.69(3)
5c	1.894(6)	2.1397(16)	2.1580(17)	2.1885(15)	176.98(18)	163.25(7)

Table S5. Principal interactions in the molecular structures of compounds 1b, 2a-2c, 3a, 4a, 5b and 5c

Comp.	**Interaction**	**D–X···A (Å)**	**D···A (Å)**	**D–X···A (°)**	**Symmetry operation**
1b	C7H7···O2	2.577	3.154(2)	119.45	1/2-x,1-y,-1/2+z
	C10H10A···O2	2.691	3.584(2)	151.78	1/2-x,1-y,-1/2+z

	O2H2···O1	1.666(1)	2.534(1)	171(2)	1/2+x,1.5-y,1-z
2c	C28H28···Cg[1]	3.511	3.980	113.47	-x,2-y,-z
	C5H5···Cg[2]	3.506	4.156	128.44	1-x,2-y,1-z
	C21H21···O3	2.674	3.359(5)	130.19	-x, 2-y, 1-z
	C22H22···Cl1	2.716	3.491(4)	140.3	1-x,2-y,1-z
	C23H23···Cl1	2.804	3.573(4)	139.8	-x,1-y,-z
3a	C7H7···O3	2.405	3.238	141.40	1+x,y,z
	C27H27B···O4	2.582	3.502	156.41	1-x,1-y,1-z
	C26H26···C5	2.647	3.531	156.76	1-x,1-y,1-z
	C16H16···Cl1	2.878	3.666	137.12	-1+x, y, z
5b	C8H8···O3	2.565	3.484(3)	162.84	2-x,2-y,1-z
5c	C16H16···Cl1	2.742	3.510	140.43	-1+x, y, z
	C10H10···Cl1	2.806	3.531	135.98	-1+x, y, z
	C23H23··· Cg[4]	2.616	3.382	140.01	-1+x, y, z
	O2H2···O3	1.735	2.522	160.65	1-x,1-y,1-z

Cg = Cg[3]= C1–C6; Cg[1]= C25–C30; Cg[2] = C19–C24; Cg[4]= C1, C2, C7, C9, C14, C15.

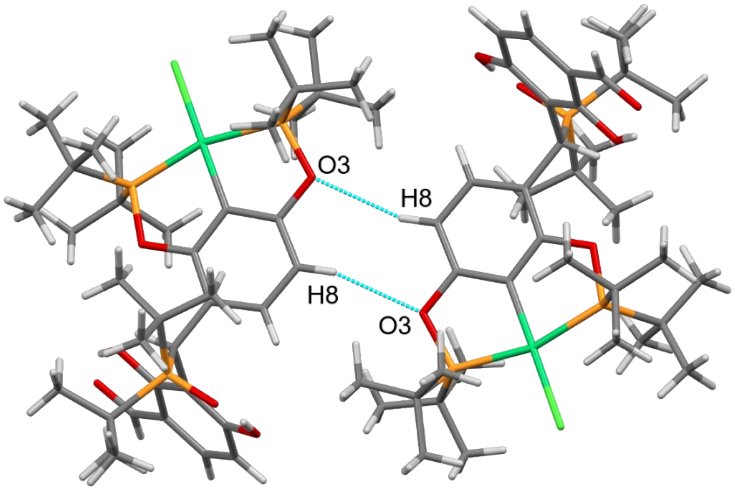

Figure S51. Tetrameric centrosymmetric of compound **5b**

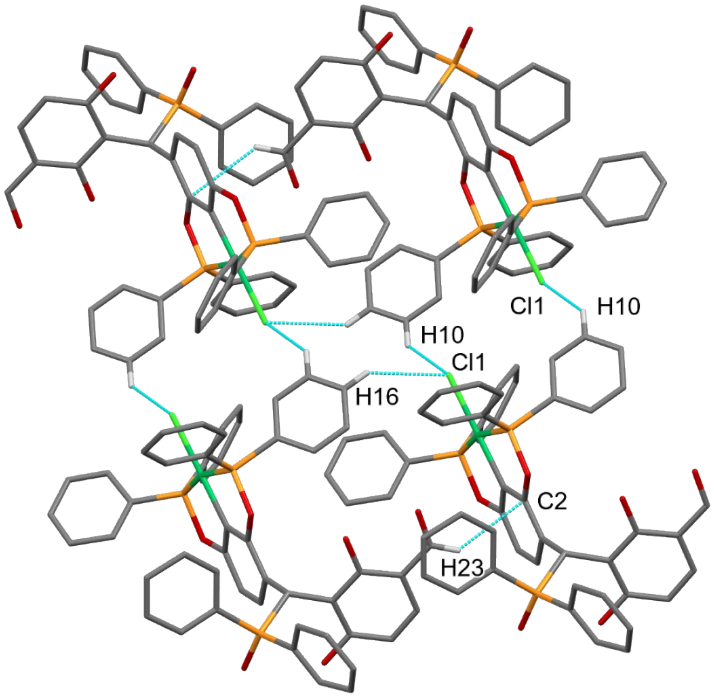

Figure S52. Tetrameric centrosymmetric of compound **5c**

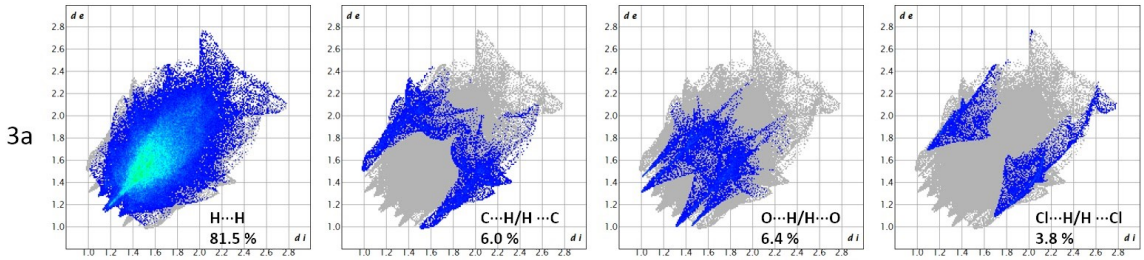

Figure S53. Individual contributions in fingerprints plots of compound **3a**.

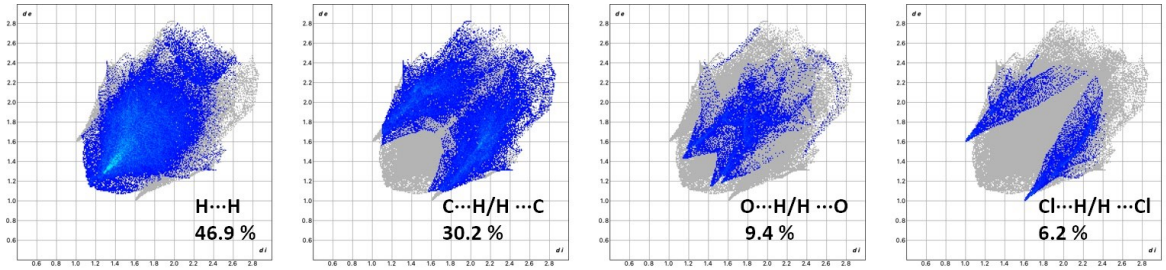

Figure S54. Individual contributions in fingerprints plots of compound **2c**

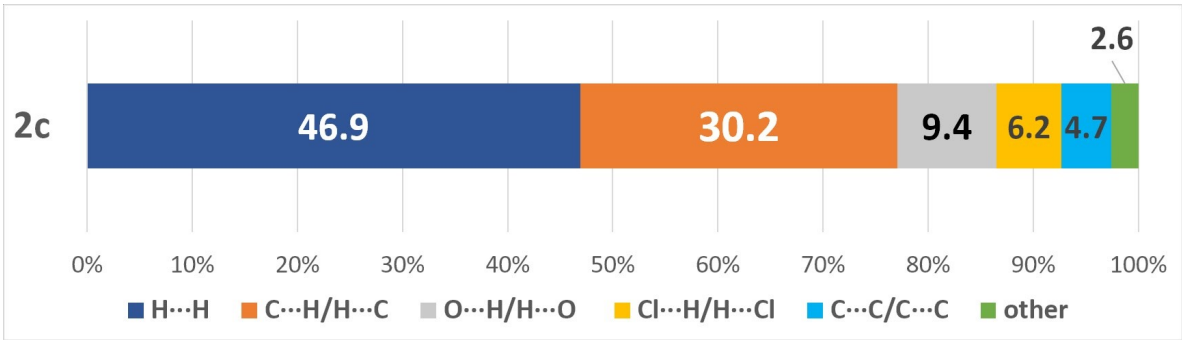

Figure S55. Individual contributions of compound **2c**

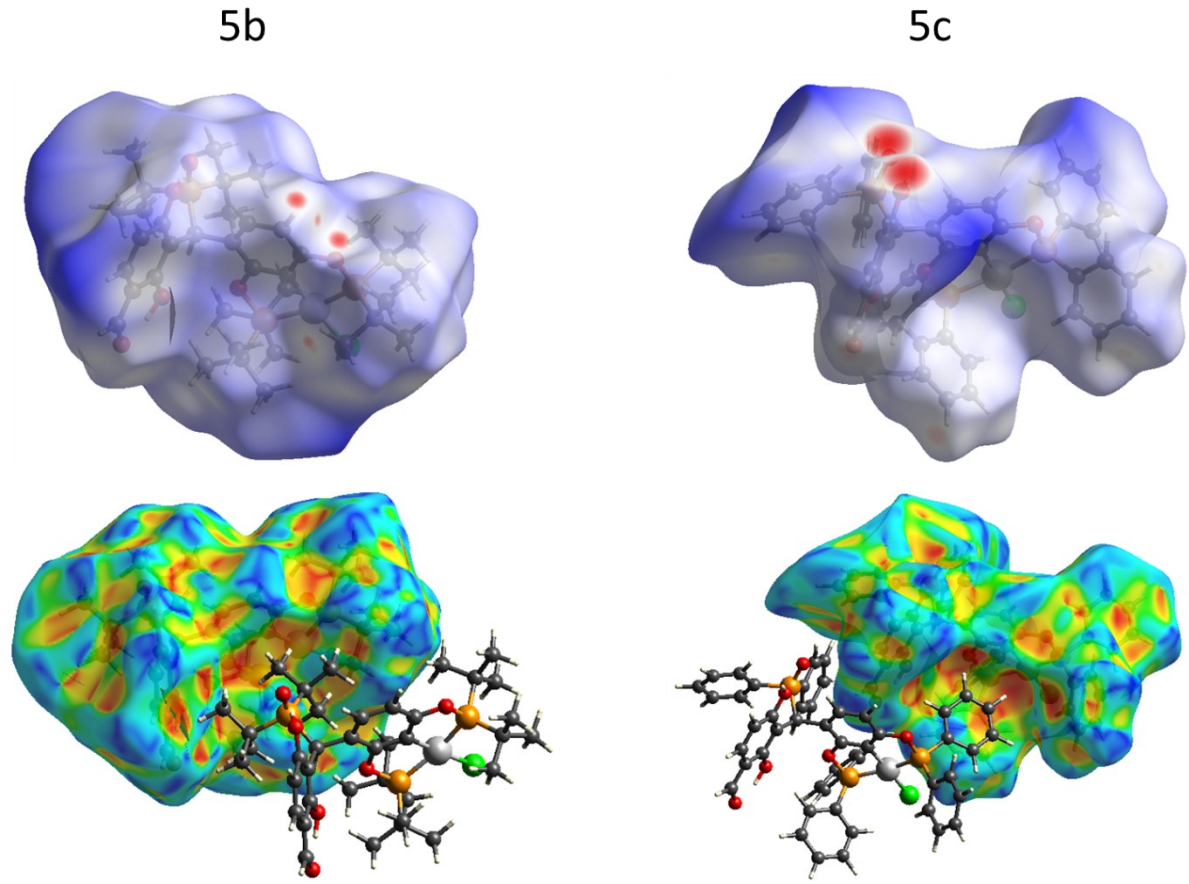

Figure S56. Hirshfeld surface of compound **5b** and **5c**. The top panel is mapped over d_{norm} and the bottom panel is over the shape index showing an intense orange-red spots indicating C-H···π interaction (left for **5b**) and a π···π (right for **5c**).

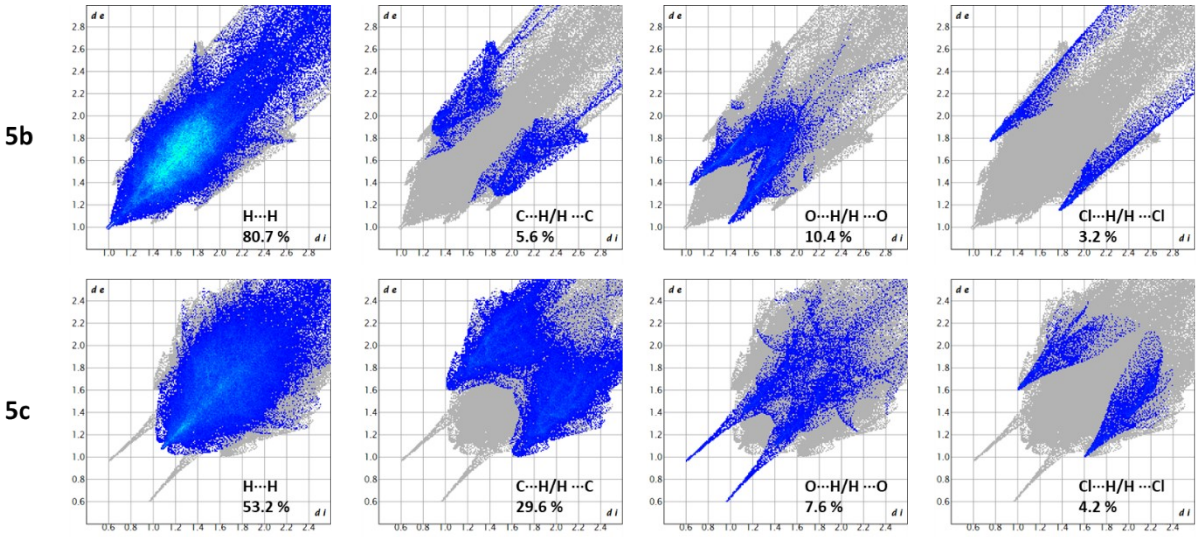

Figure S57. Individual contributions of contacts in fingerprint plots of compounds **5b** and **5c**.