Supporting information

Naphthyl and Biphenyl *para*-substituted POCOP-Ni(II) Pincer Complexes as Efficient Catalysts in C-S Cross-Coupling Reactions

Luis E. López-Robledo,[a] Evelin E. Ortiz-Fuentes,[a] Ernesto Rufino-Felipe,[a] Juan S. Serrano-García,[a] Antonino Arenaza-Corona,[a] Simon Hernandez-Ortega,[a] Hugo Valdes,[b] Lucero Gonzalez-Sebastian,[c] Viviana Reyes-Marquez,[d] and David Morales-Morales[a,*]

[a]Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad de México, CP 04510, México. [b]Departamento de Química Orgánica y Química Inorgánica, Universidad de Alcalá, Campus Universitario, Alcalá de Henares, Madrid, C.P. 28805, Spain. [c]Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco No. 186, Ciudad de México, C.P. 09340, México. [d]Departamento de Ciencias Químico-Biológicas, Universidad de Sonora, Luis Encinas y Rosales s/n, Hermosillo 83000, Sonora, México.

*Fax: +52-5556162217; Tel: +52-5556224514
*E-mail: damor@unam.mx (D. Morales-Morales)

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NMR Spectra of complexes

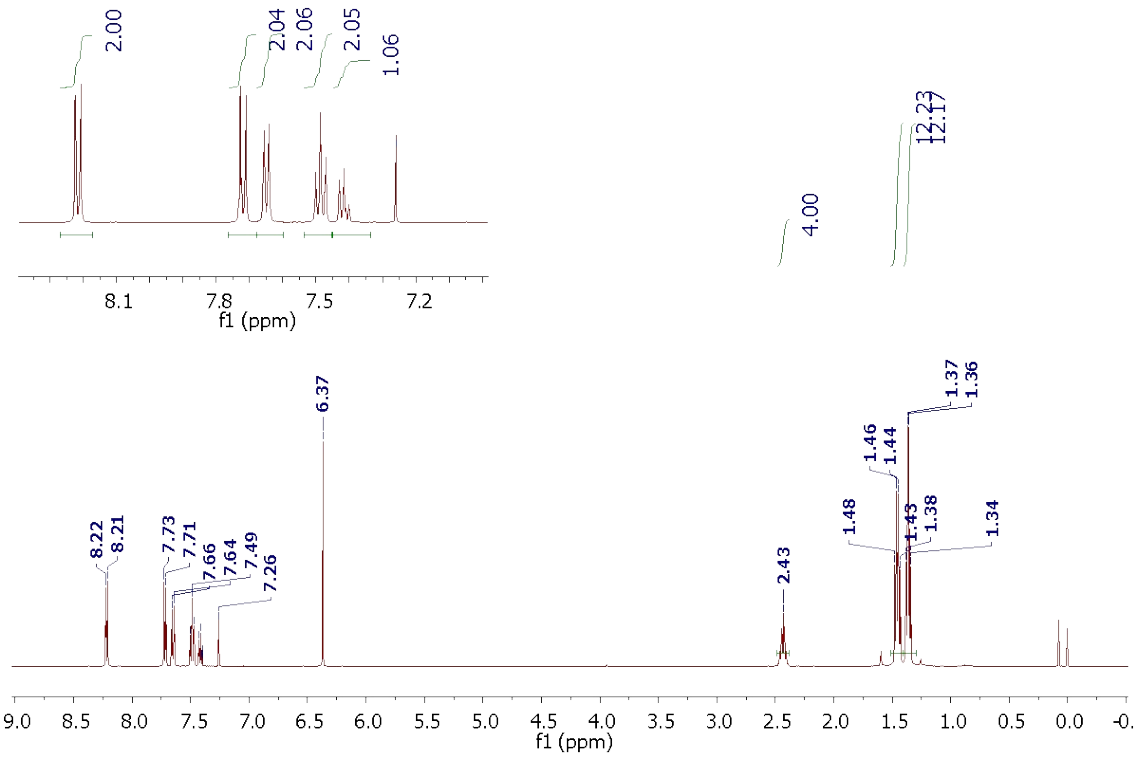

Figure S1. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of complex **4**

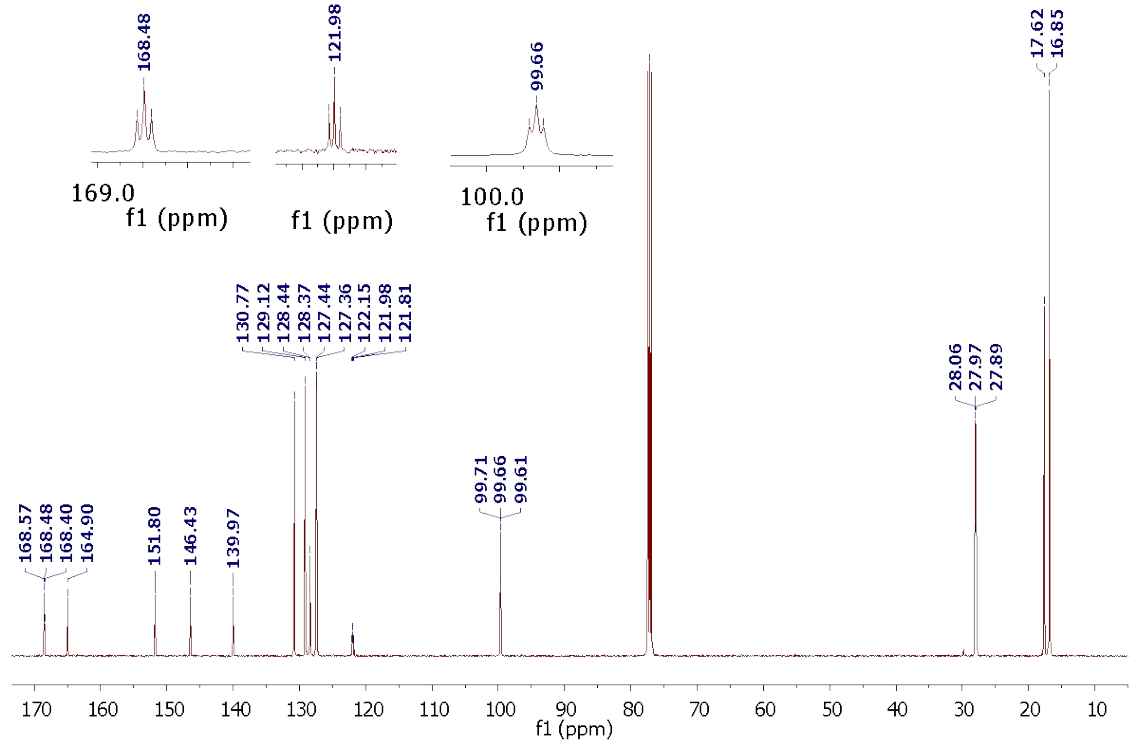

Figure S2. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of complex **4**

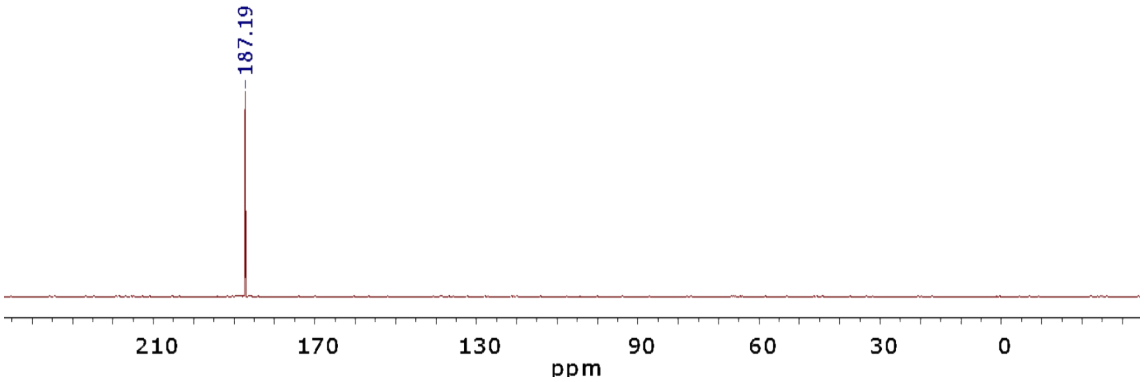

Figure S3. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) spectrum of complex **4**

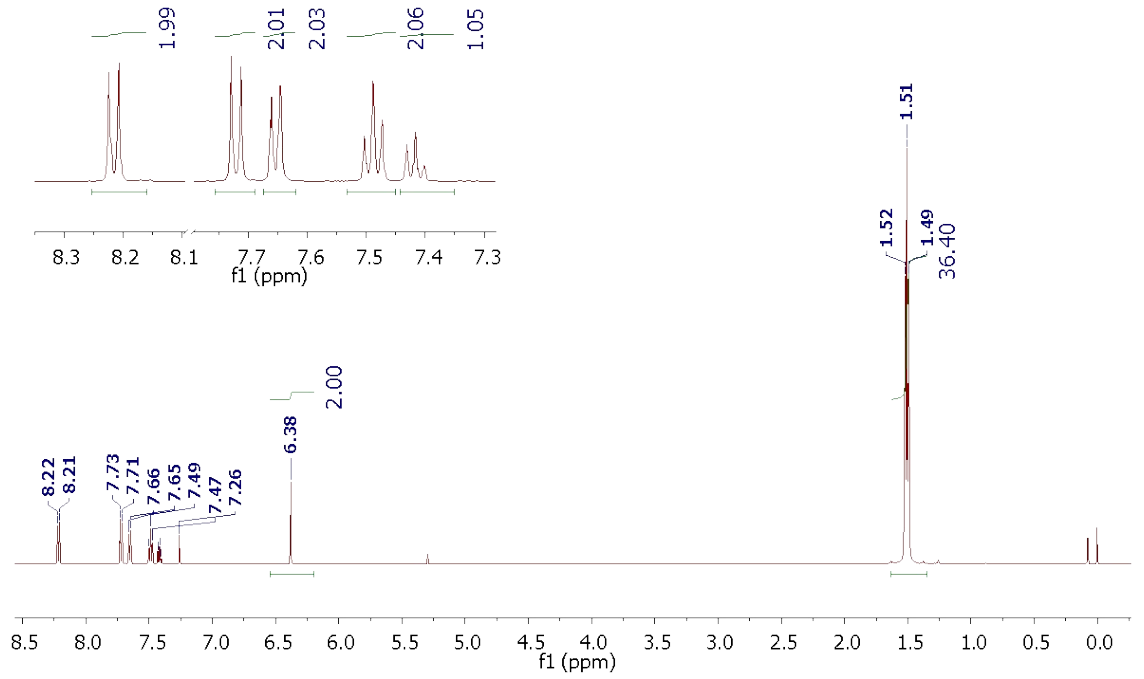

Figure S4. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of complex **5**

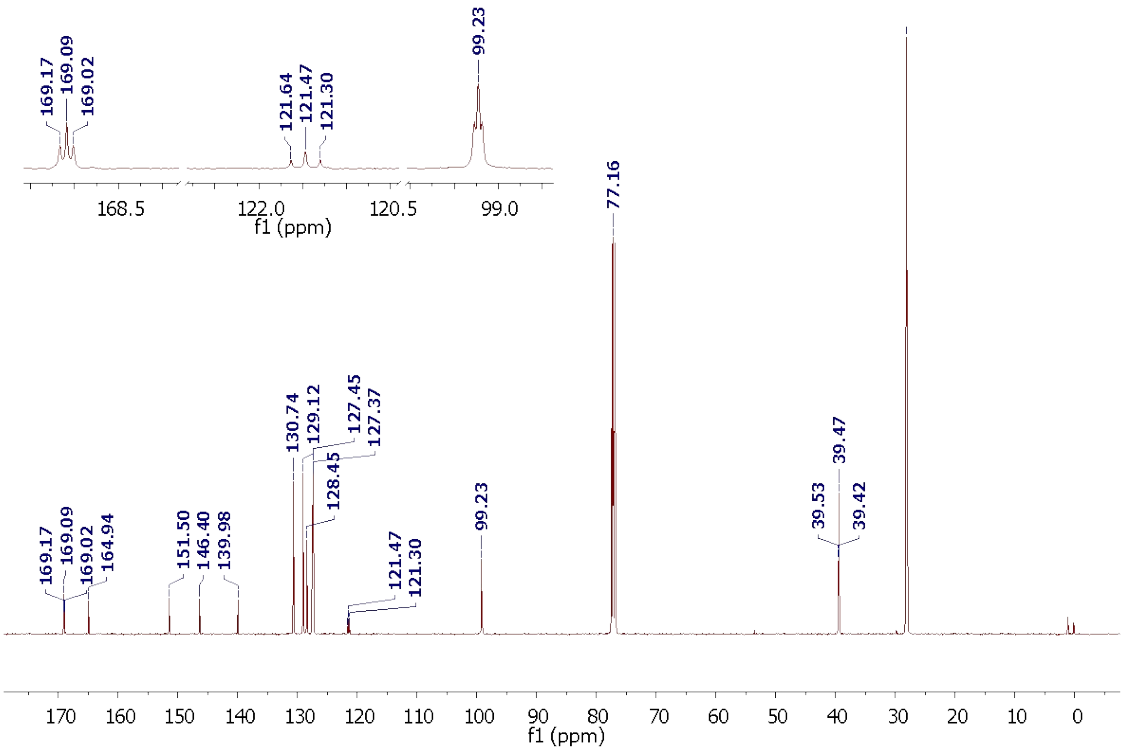

Figure S5. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of complex **5**

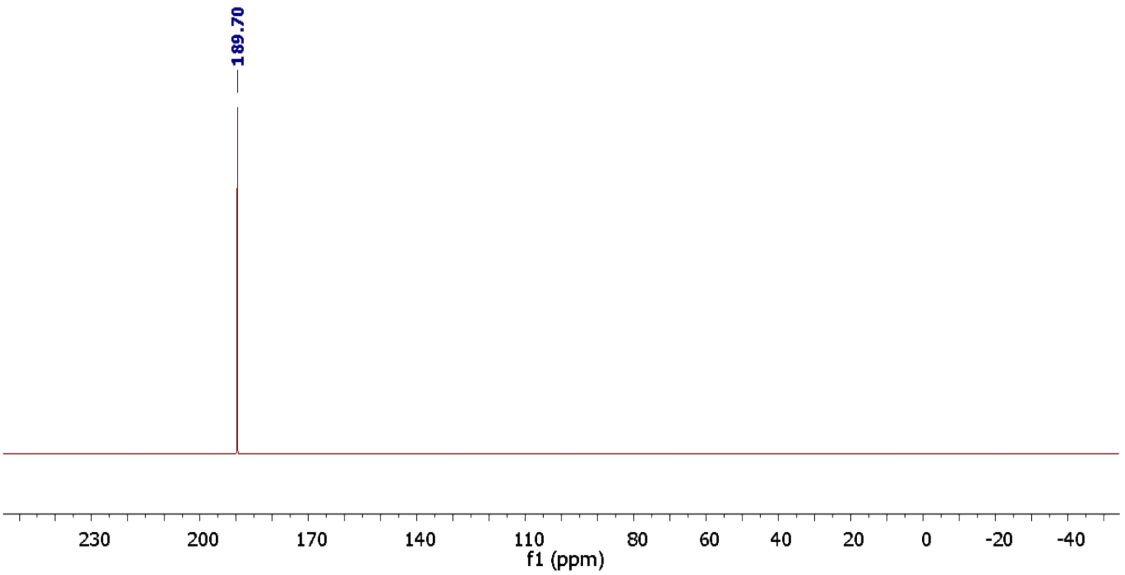

Figure S6. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) spectrum of complex **5**

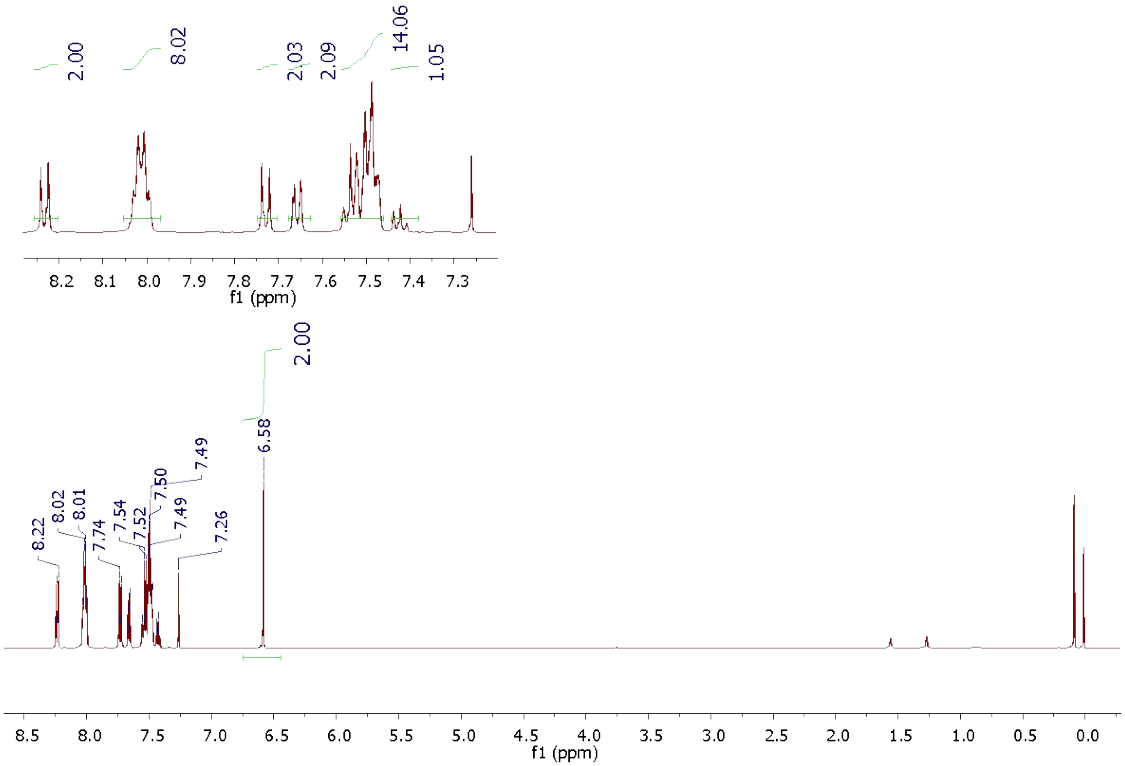

Figure S7. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of complex **6**

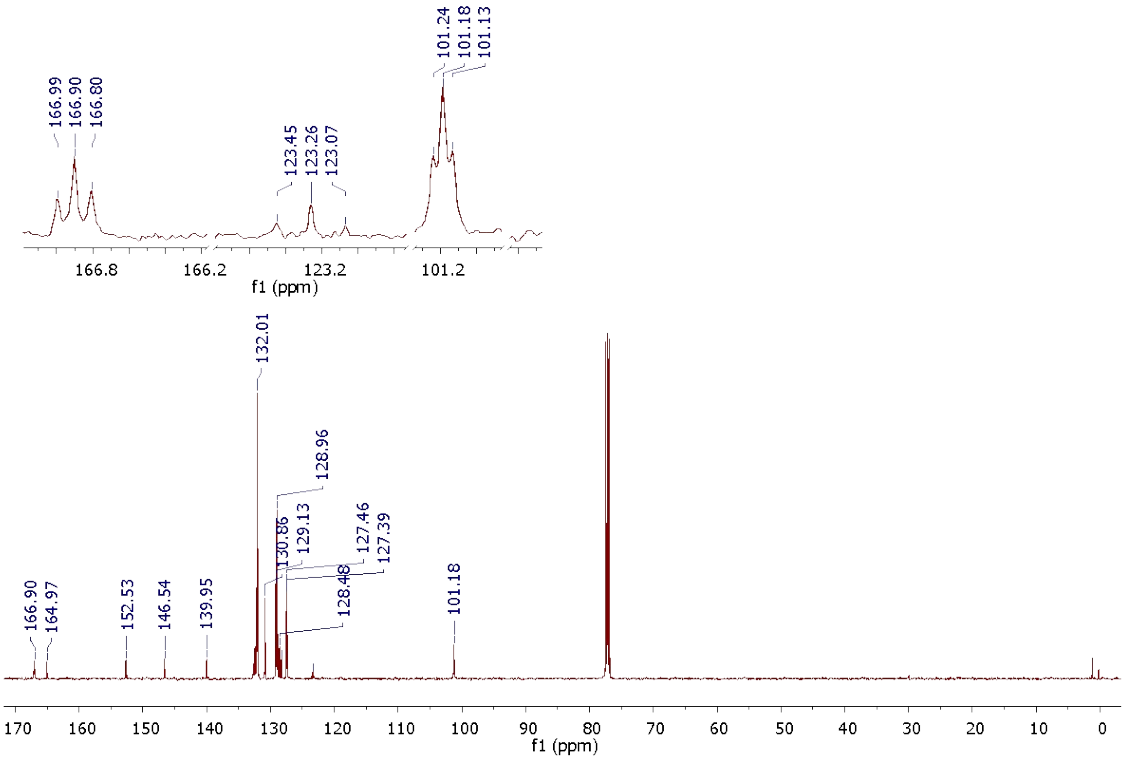

Figure S8. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of complex **6**

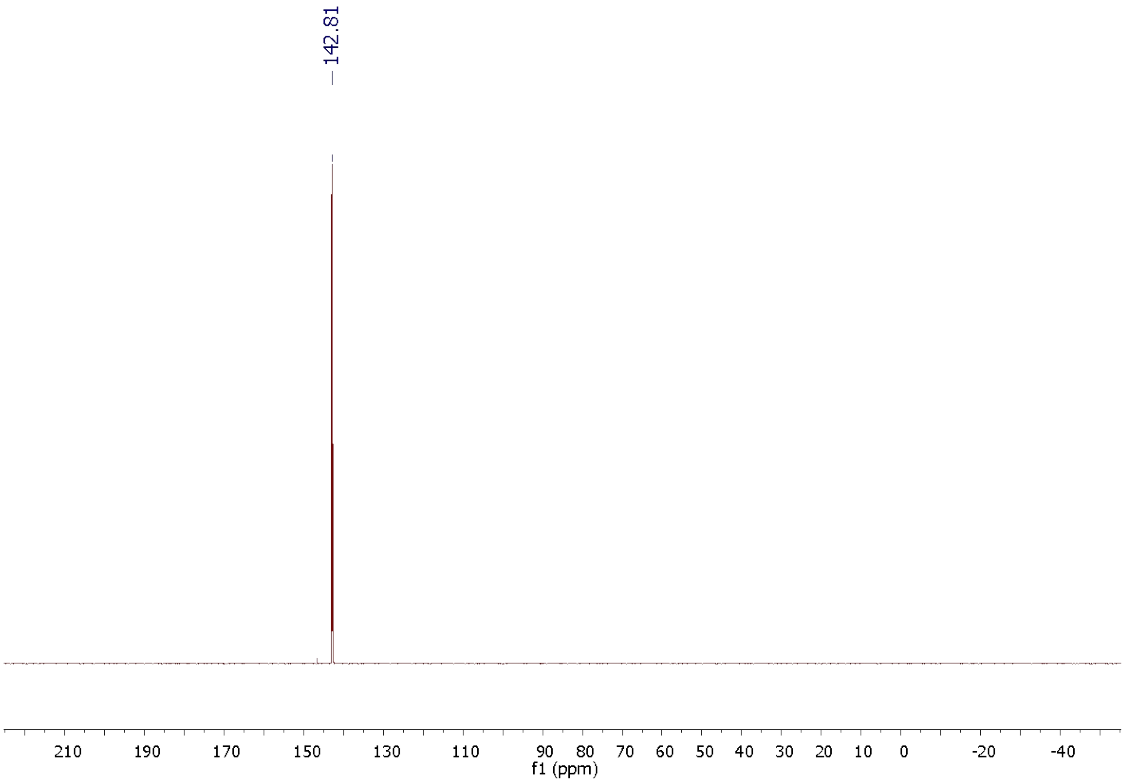

Figure S9. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) spectrum of complex **6**

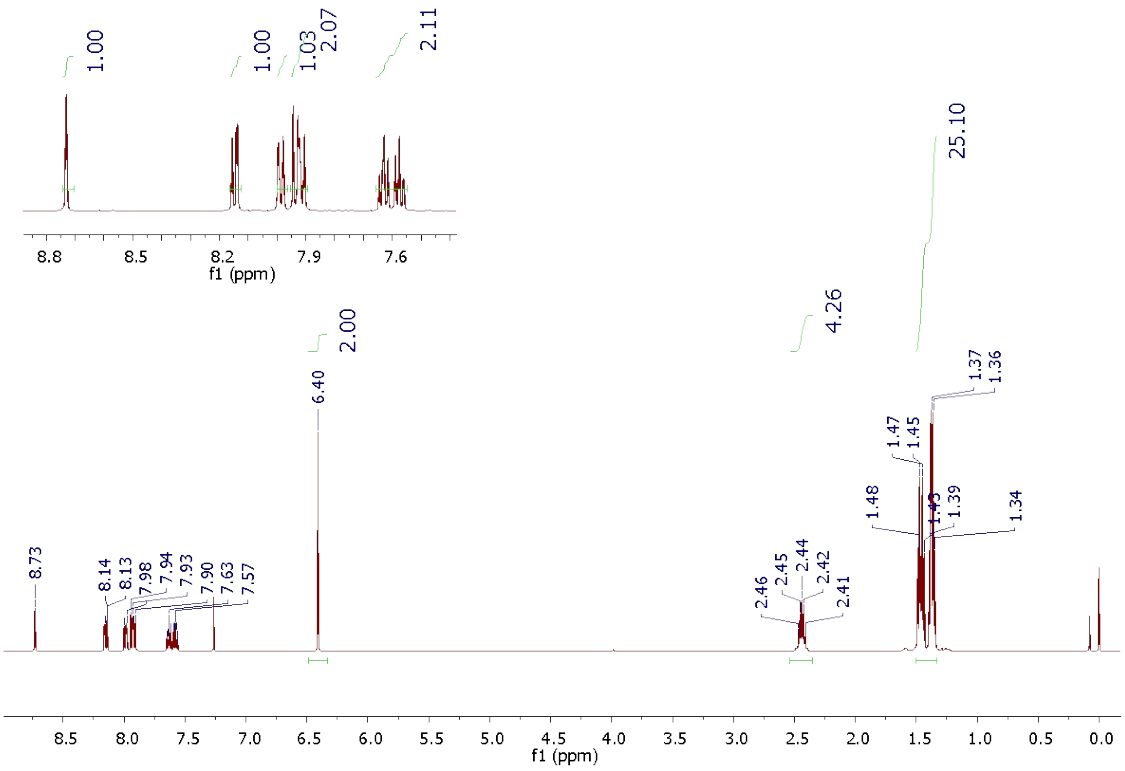

Figure S10. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of complex **7**

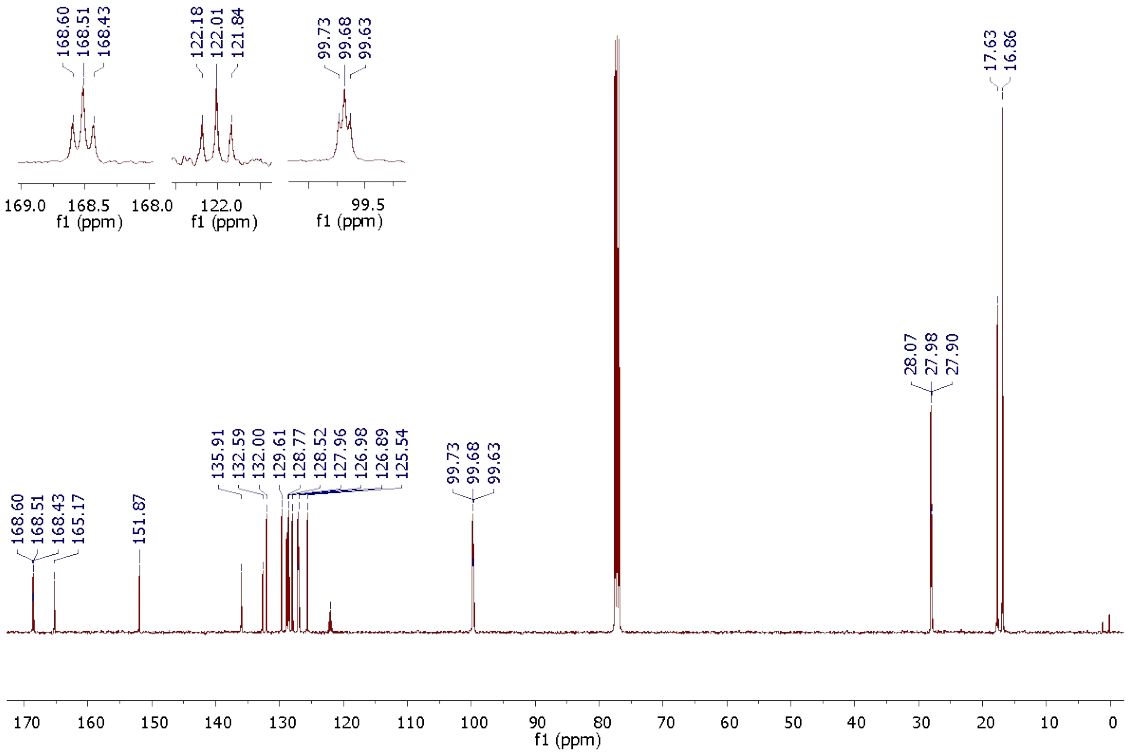

Figure S11. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of complex **7**

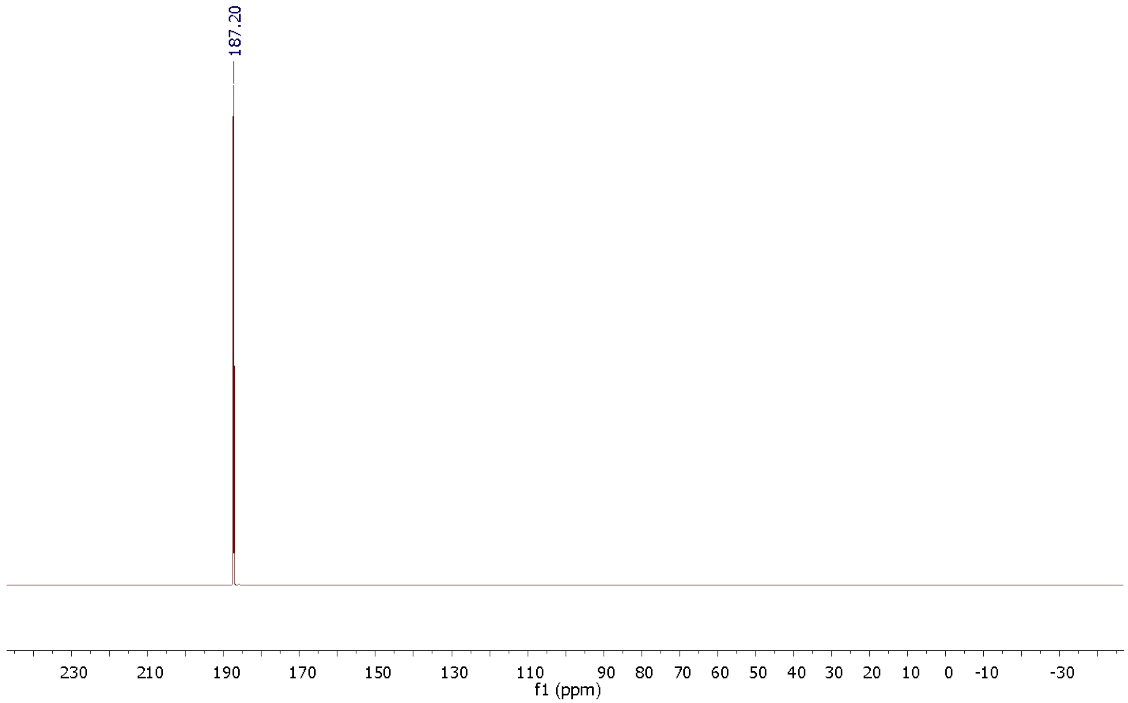

Figure S12. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) Spectrum of complex **7**

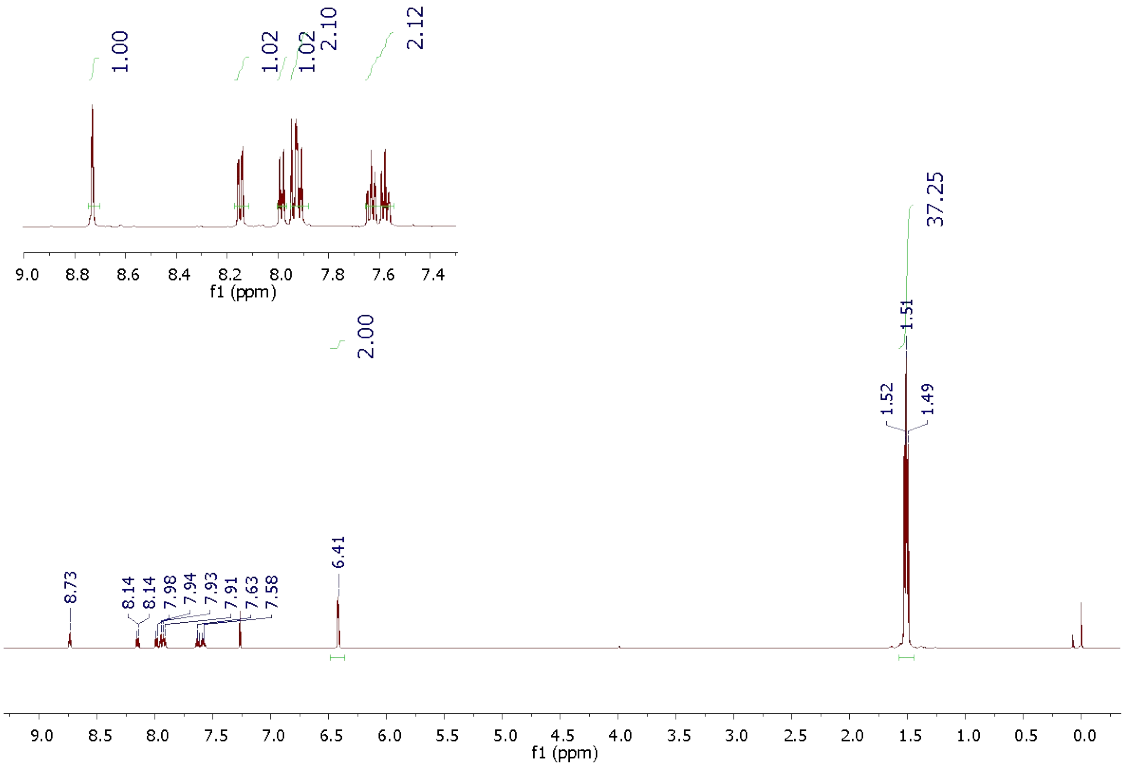

Figure S13. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of complex **8**

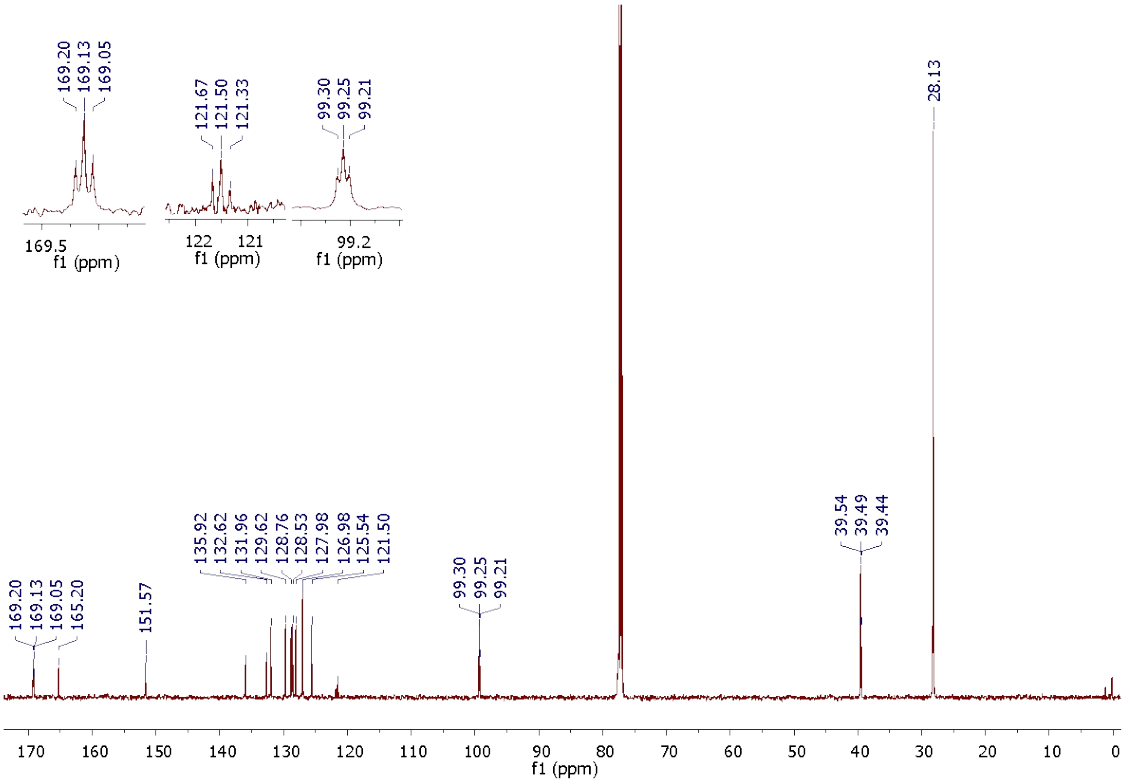

Figure S14. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) Spectrum of complex **8**

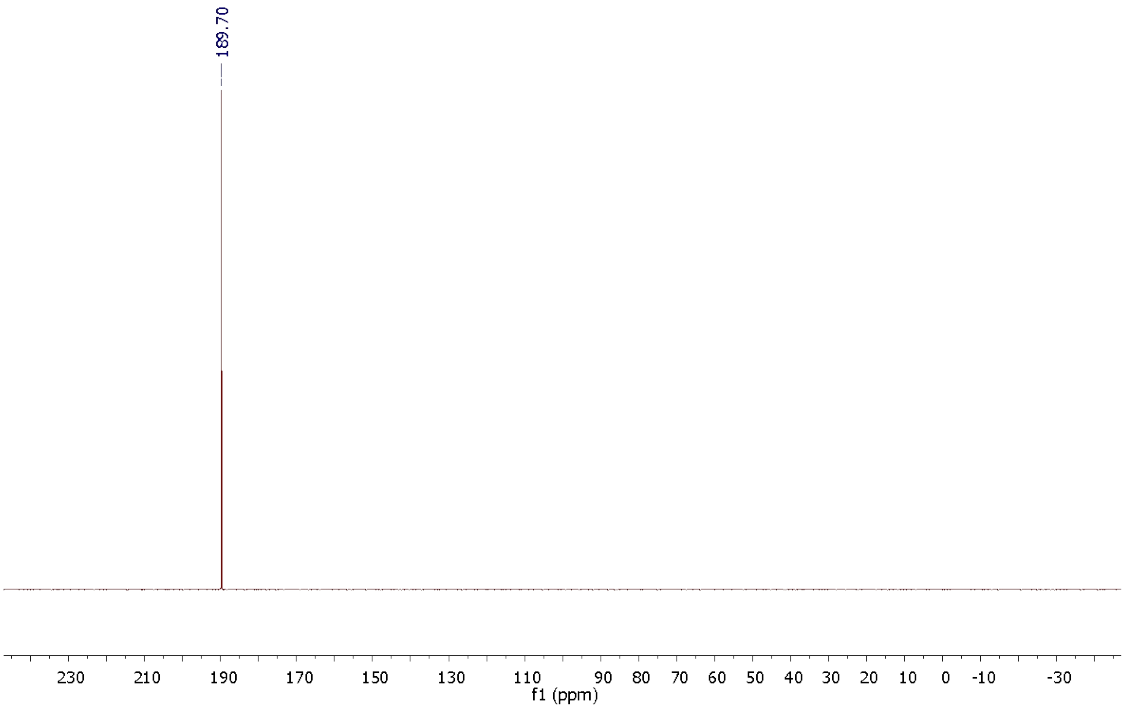

Figure S15. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) Spectrum of complex **8**

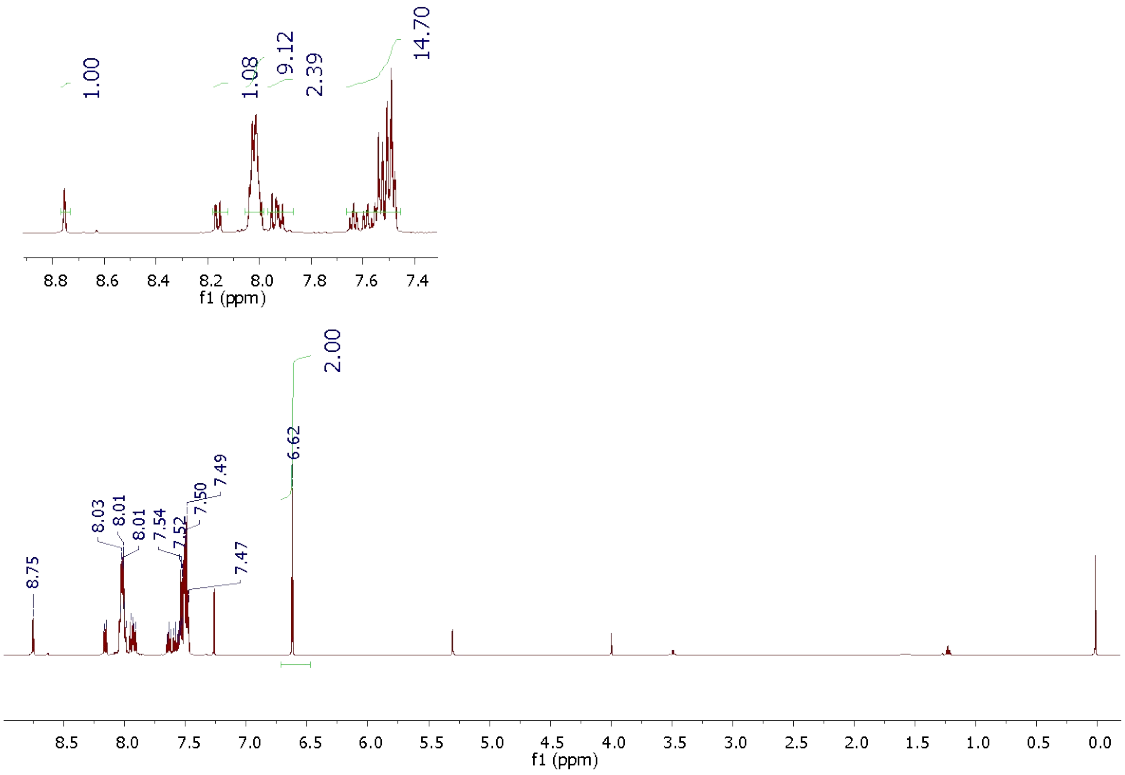

Figure S16. ^{1}H NMR ($CDCl_3$, 500 MHz) Spectrum of complex **9**

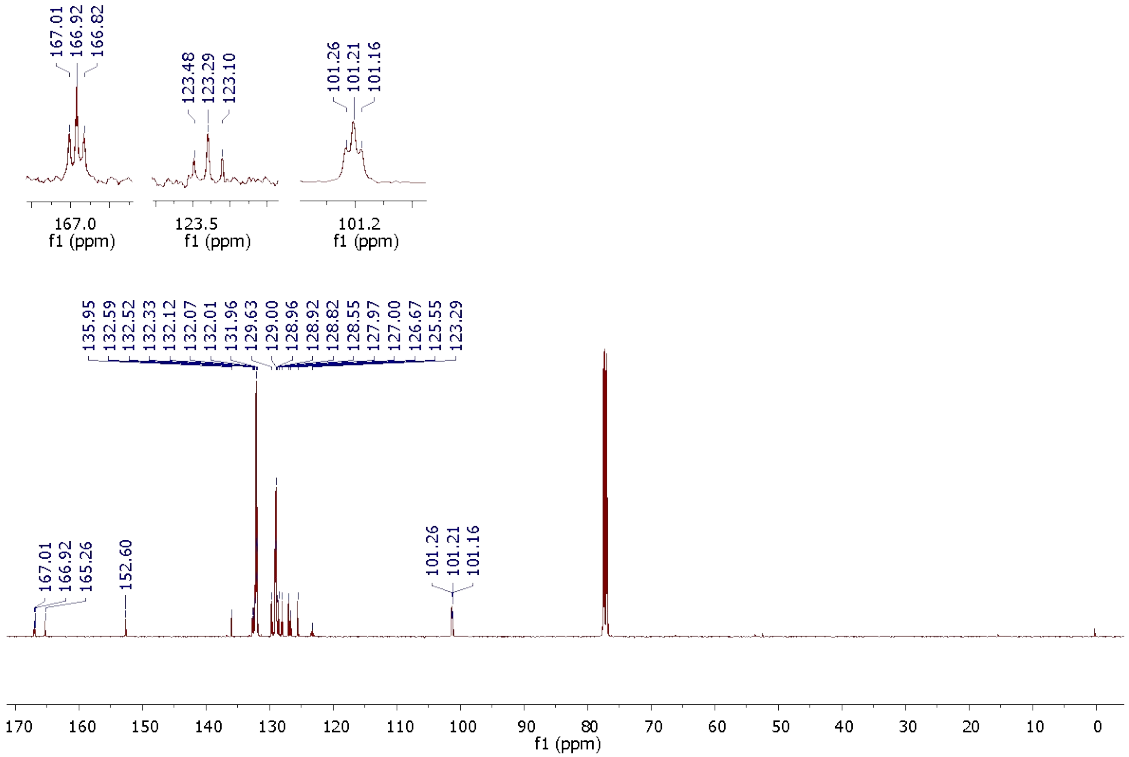

Figure S17. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of complex **9**

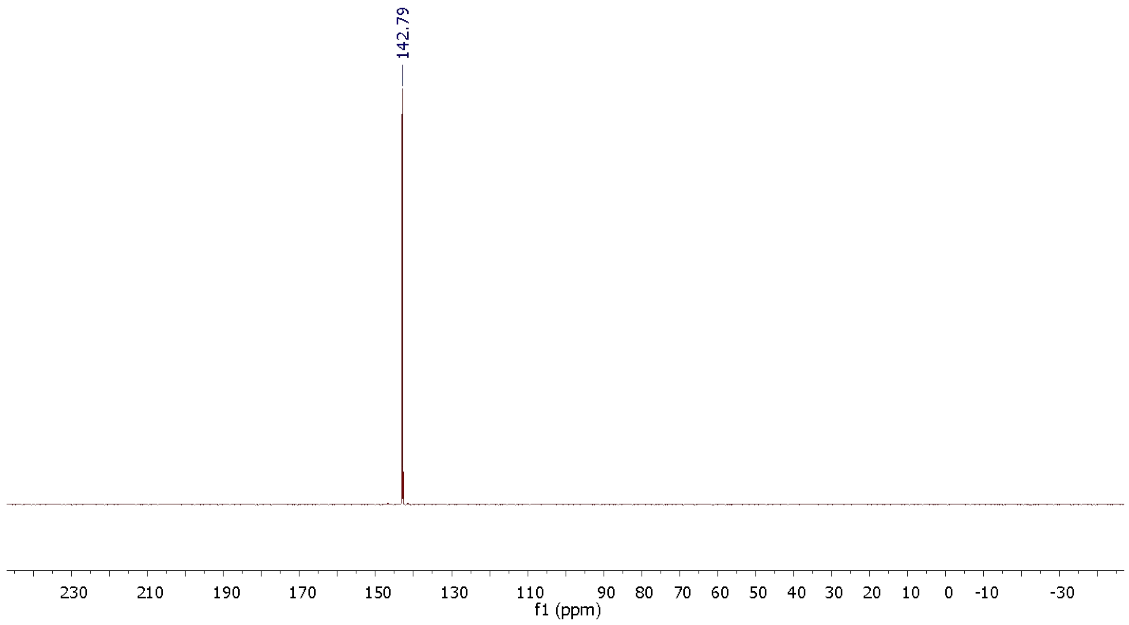

Figure S18. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) spectrum of complex **9**

ATR-FTIR spectra of complexes

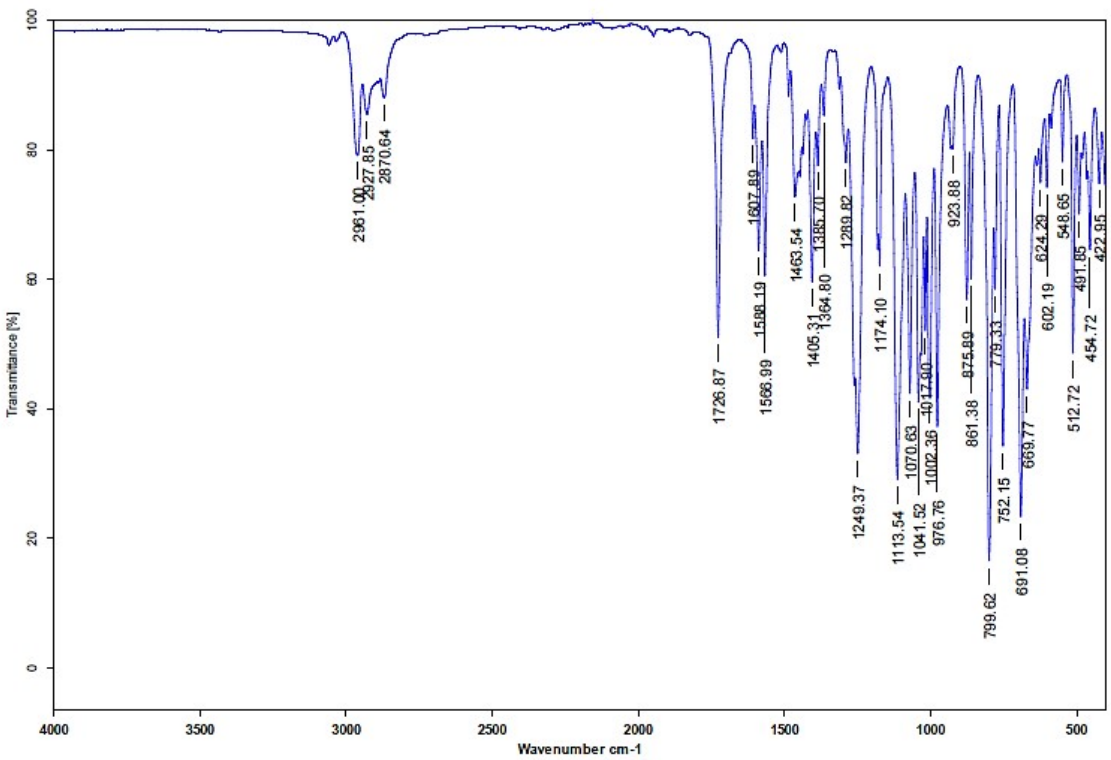

Figure S19. ATR-FTIR spectrum of complex **4**

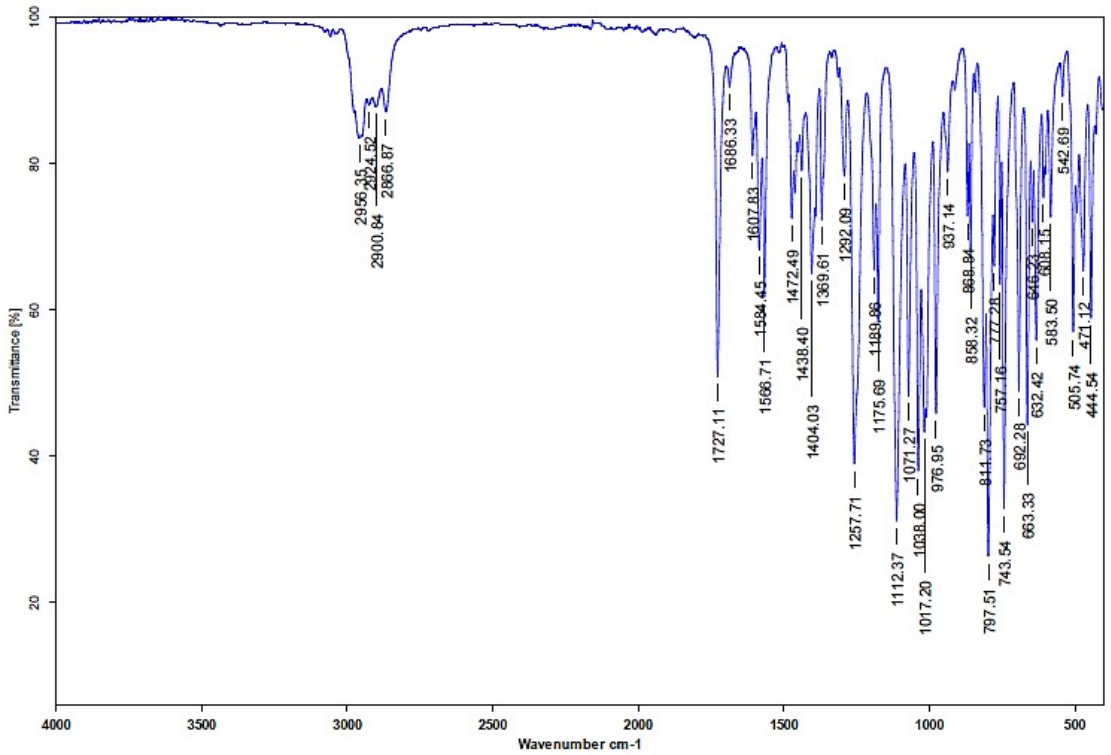

Figure S20. ATR-FTIR spectrum of complex **5**

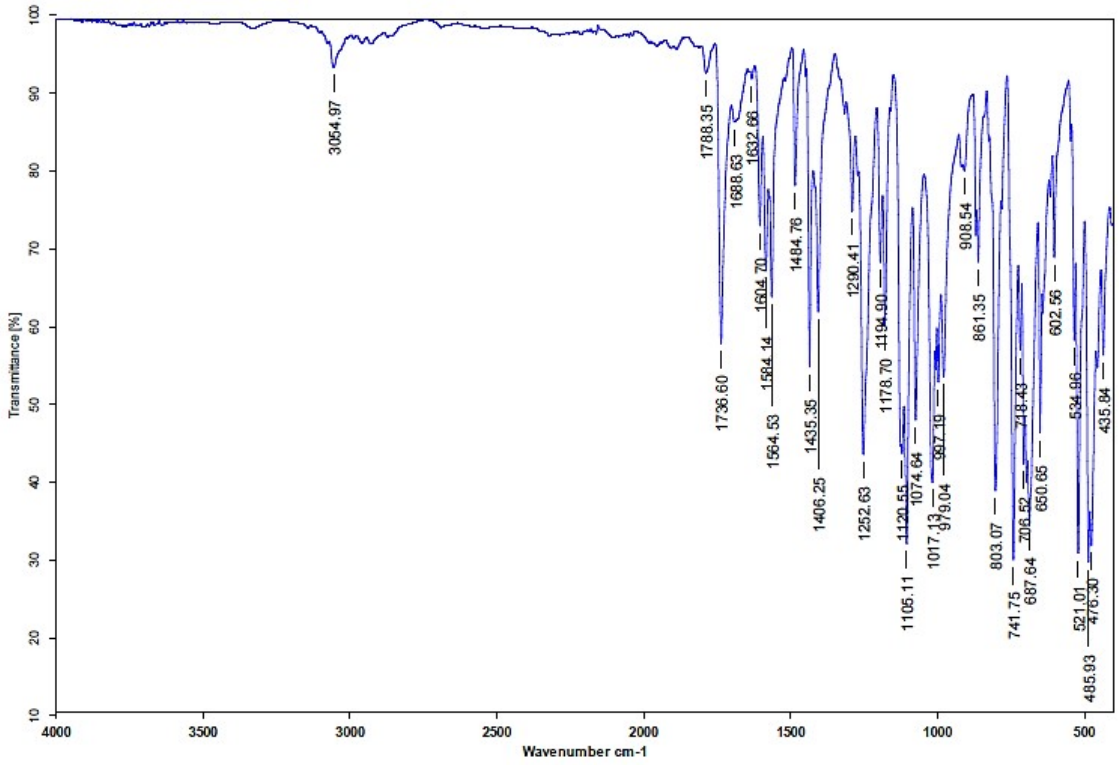

Figure S21. ATR-FTIR spectrum of complex **6**

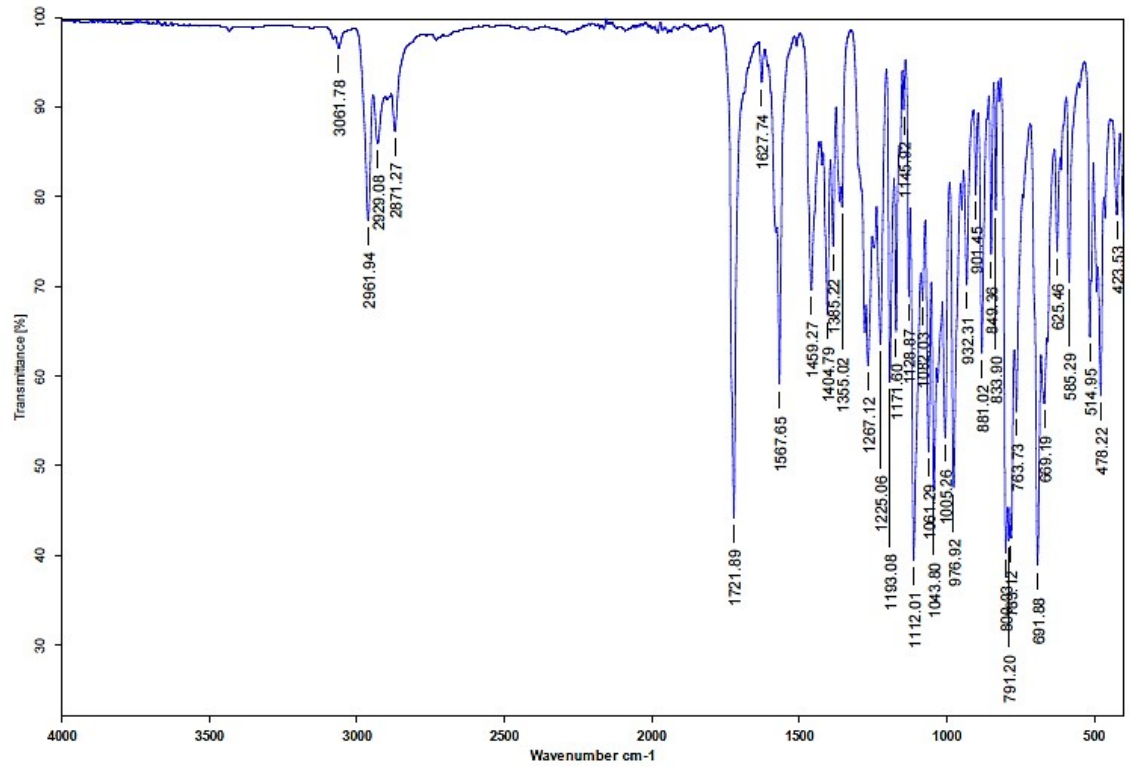

Figure S22. ATR-FTIR spectrum of complex **7**

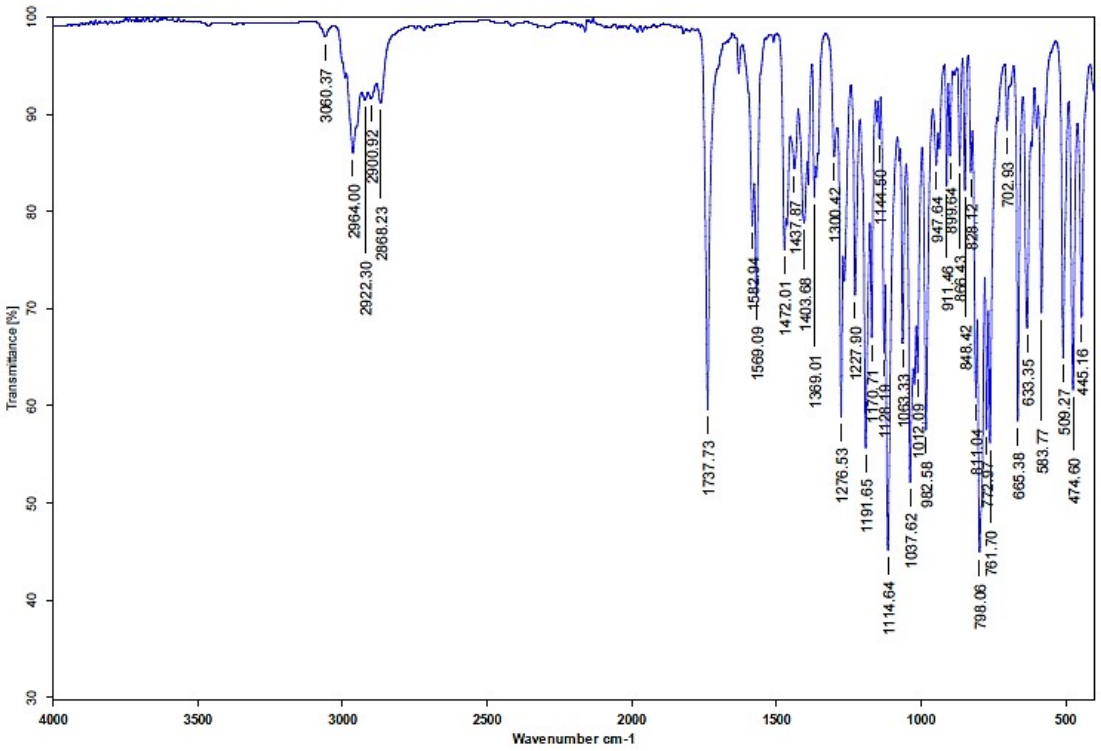

Figure S23. ATR-FTIR spectrum of complex **8**

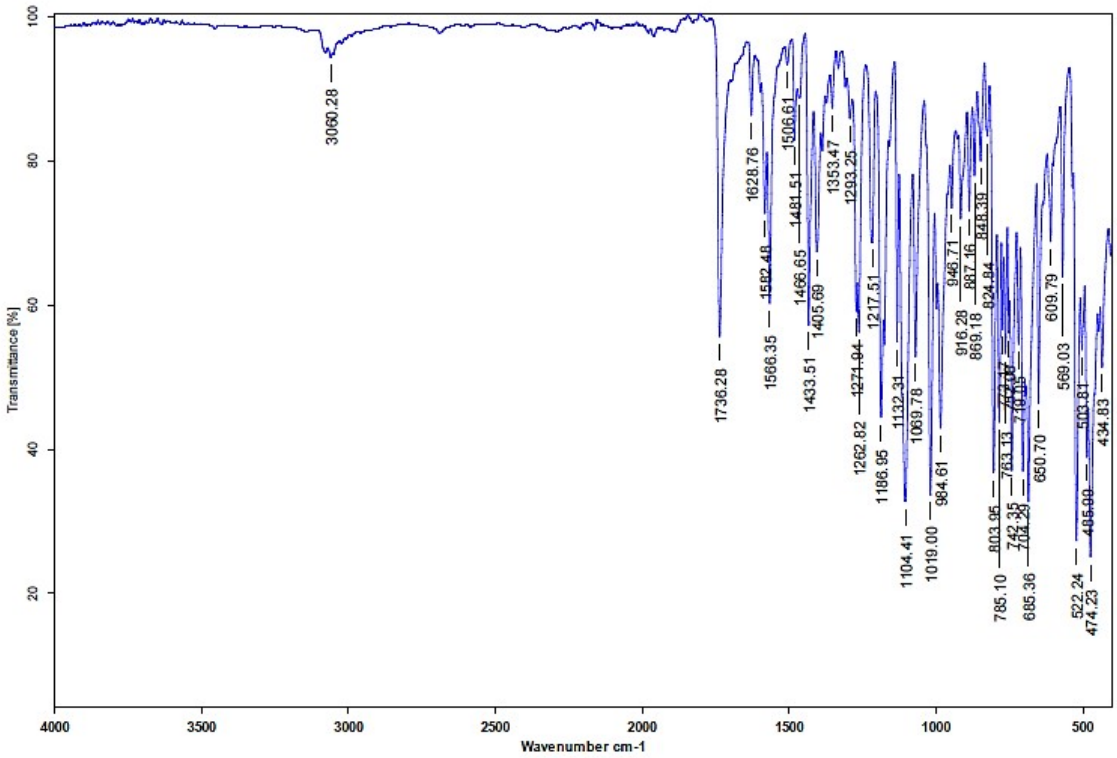

Figure S24. ATR-FTIR spectrum of complex **9**

Table S1. Crystallographic data of compounds **4**, **8** and **9**.

Complex	**4**	**8**	**9**
Empirical formula	$[C_{31}H_{39}ClNiO_4P_2][CHCl_2]$	$[C_{66}H_{90}Cl_2Ni_2O_8P_4][\ C_7H_8]$	$C_{41}H_{29}Cl\ NiO_4P_2$
Formula weight	716.65	1415.71	741.74
T(K)	150(2)	199(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	27.1448(13)	8.0438(2)	9.1360(4)
b (Å)	9.4225(4)	28.5592(10)	29.4452(16)
c (Å)	27.3977(12)	16.4261(5)	12.7283(7)
α (°)	90	90	90
β (°)	92.154(2)	102.7660(10)	94.484
γ (°)	90	90	90
V (Å^3)	7002.6(5)	3680.20(19)	3413.6(3)
Z	8	2	4
ρ_{Calc} (Mg m^{-3})	1.360	1.278	1.443
μ(mm^{-1})	0.908	0.723	0.784
F(000)	2992	1500	1528
Crystal size (mm^3)	0.404 x 0.258 x 0.202	0.407 x 0.221 x 0.104	0.398 x 0.202 x 0.161
Wavelength (Å)	0.71073	0.71073	0.71073
2θ range for data collection	2.286 to 25.401°	2.489 to 25.401°	2.624 to 25.369°
Index ranges	-32<=h<=28, -11<=k<=11, -33<=l<=32	-9<=h<=9, -34<=k<=34, -19<=l<=19	-11<=h<=11, -31<=k<=35, -15<=l<=15
Reflections collected	49360	45956	35264
Independent reflections	12842 [R(int) = 0.0281]	6769 [R(int) = 0.0540]	6251 [R(int) = 0.0304]
Data/restraints/parameters	12842 / 0 / 773	6769 / 235 / 508	6251 / 0 / 442
Goodness-of-fit (GOF) on F^2	1.170	1.068	1.116
Final *R* indices [$I \geq 2\sigma(I)$]	R1 = 0.0592, wR2 = 0.1280	R1 = 0.0502, wR2 = 0.0971	R1 = 0.0436, wR2 = 0.0882
Final *R* indices [all data]	R1 = 0.0701, wR2 = 0.1333	R1 = 0.0768, wR2 = 0.1090	R1 = 0.0561, wR2 = 0.0948
Largest difference peak/hole (e Å^{-3})	0.948 and -0.732	0.496 and -0.350	0.383 and -0.224

Table S2. Selected distances and angles of compounds **4**, **8** and **9**.

Bond	C-Ni (Å)	P-Ni (Å)	Ni-Cl (Å)	C-Ni-Cl (º)	P-Ni-P (º)
4	1.885(3)	2.1623(11)	2.2030(10)	178.96(12)	164.23(4)
	1.884(4)	2.1649(11)	2.2022(10)	178.56(13)	164.26(4)
		2.1587(11)			
		2.1640(12)			
8	1.882(3)	2.1870(9)	2.2049(9)	179.03(10)	163.37(4)
		2.1934(9)			
9	1.880(3)	2.1533(8)	2.1829(8)	176.79(8)	163.83(3)
		2.1680(7)			

Table S3. Principal interactions in the molecular structure of compounds.

Compound	**Interaction**	**Distance (Å)** **D-X⋯A**	**Distance (Å)** **D⋯A**	**Angle (°)** **D-X⋯A**	**Symmetry Operation**
4	H41-Cg	2.996	3.736	131.72	½-x, ½+y, 1.5-z
	H16-Cg	2.921	3.643	129.87	1-x, 1-y, 1-z
	H58-O8	2.537	3.322	140.16	-1/2+x, ½-y, -1/2+z
	H64B-O8	2.288	3.262	167.45	x, y, z
	H63A-O4	2.264	3.157	149.47	x, y, z
8	H21C-O4	2.618	3.488	147.93	-x, 1-y, 1-z
	H17B-Cg	3.60	3.835	137.04	1-x, 1-y, 1-z
9	H4-Cg	3.261	3.954	133.05	-x, 1-y, 2-z
	H6-Cg	2.969	3.802	149.75	1-x, 1-y, 1-z
	H37-Cl	2.907	3.530	125.56	1-x, 1-y, 1-z
	H24-Cg	2.814	3.633	147.55	½-x, -1/2+y, 1.5-z