Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

C−H Nickellation of Phenol-Derived Phosphinites: Regioselectivity and Structures of Cyclonickellated Complexes

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1. General information and references

All 1D NMR spectra were recorded on a Bruker AV500 spectrometer and the HSQC experiments were recorded on a Bruker AV400 spectrometer, with access provided by Centre régional de résonance magnétique nucléaire de l'Université de Montréal.

The elemental analyses were performed by the Laboratoire d'Analyse Élementaire, Département de chimie, Université de Montreal, on a Fisons EA 1108, CHNS instrument.

All DFT calculations were performed using Gaussian16 Revision A03[1] on Grex cluster server from Westgrid computational facilities, with access provided by Compute Canada – Calcul Canada.

The crystallographic data for all resolved structures were collected either on a Bruker Microsource (Cu source) or a Bruker Venture Metaljet (Ga source) via the Bruker APEX II or APEX III[2] softwares. Cell refinement and data reduction were performed using SAINT[3]. An empirical absorption correction based on multiple measurements of equivalent reflections was applied using the SADABS program.[4] The space groups were confirmed by the XPREP[5] routine in APEX. The structures were solved in OLEX[6] using the SHELX[7] suite and refined by full-matrix least squares with SHEXL.[8] All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were set in calculated positions and refined as riding atoms, with thermal parameters being 1.5 times that of the carbon bearing the H in question. All ORTEPs were drawn using Platon[9].

[1] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[2] Bruker (2012). APEX2 / Bruker (2016) APEX3, Bruker AXS Inc., Madison, WI, USA.

[3] Bruker (2012). "SAINT Integration Software for Single Crystal Data", Bruker AXS Inc., Madison, WI, USA.

[4] Sheldrick, G. M., "Comparison of silver and molybdenum microfocus X-ray sources for single crystal structure determination", *J. Appl.Cryst.*, 2015, *48*, 3-10

[5] Bruker (2012). Data Preparation and Reciprocal Space Exploration Program, Bruker AXS Inc., Madison, WI, USA.

[6] A: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. "OLEX2: a complete structure solution, refinement and analysis program". *J. Appl. Cryst.* 2009, *42*, 339-341.

[7] Sheldrick, G. M., "SHELXT - Integrated space-group and crystal structure determination", *Acta Cryst.*, 2015, A71, 3-8.

[8] Sheldrick, G. M., Crystal structure refinement with SHELXL, *Acta Cryst.*, 2015, C71, 3-8.

[9] Spek, A. L., *Acta Cryst*., 2009, D65, 148-155

2. UV-vis Spectra for **1a** and **1a-NCMe**

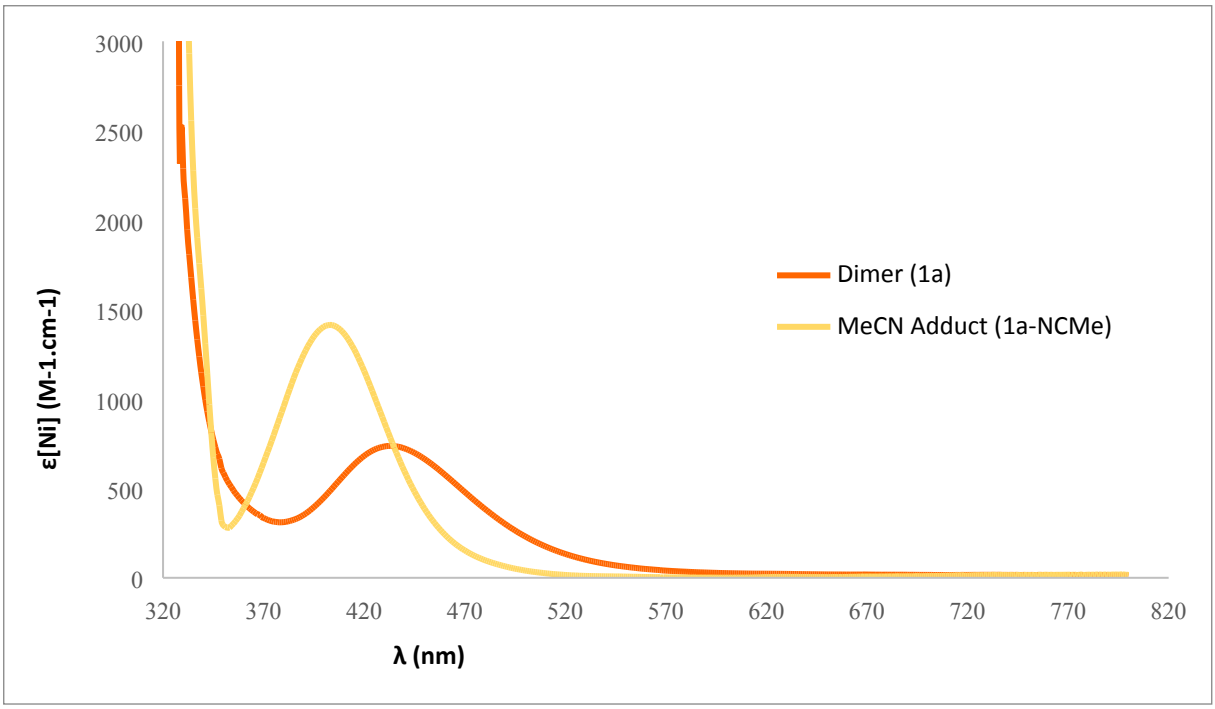

Figure S1: UV-vis spectra of the dimer derived from PhOP(i-Pr)$_2$ ([Dimer] = ½ [Ni] = 0.833 mM) and of the MeCN adduct ([Monomer] = 0.555 mM) generated by addition of 10 equiv of MeCN int toluene at 22 °C.

3. Estimation of K_{eq} for **1a** ⇌ **1a-NCMe**

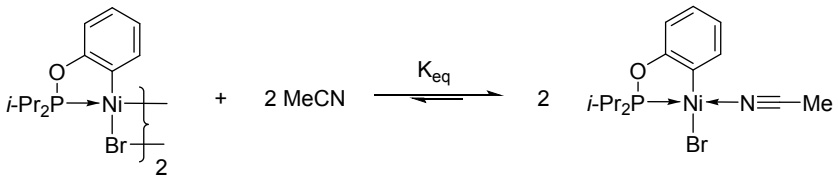

*Table S1: ^{31}P NMR estimation of the constants for equilibration of **1a** and **1a-NCMe***

eq$_{(MeCN)}$	%Dimer	%Monomer	[Dimer] (M)	[Monomer] (M)	[MeCN]$_{free}$ (M)	K_{eq}
0.5	0.7583	0.2417	0.0189575	0.012085	0.000415	4.5E+04
1	0.5276	0.4724	0.01319	0.02362	0.00138	2.2E+04
1.5	0.3746	0.6254	0.009365	0.03127	0.00623	2.7E+03
2	0.1887	0.8113	0.0047175	0.040565	0.009435	3.9E+03

4. NMR Spectra for compounds **1a-1f**, **1i-NCMe** and **1j-1k** in CD_3CN

1a

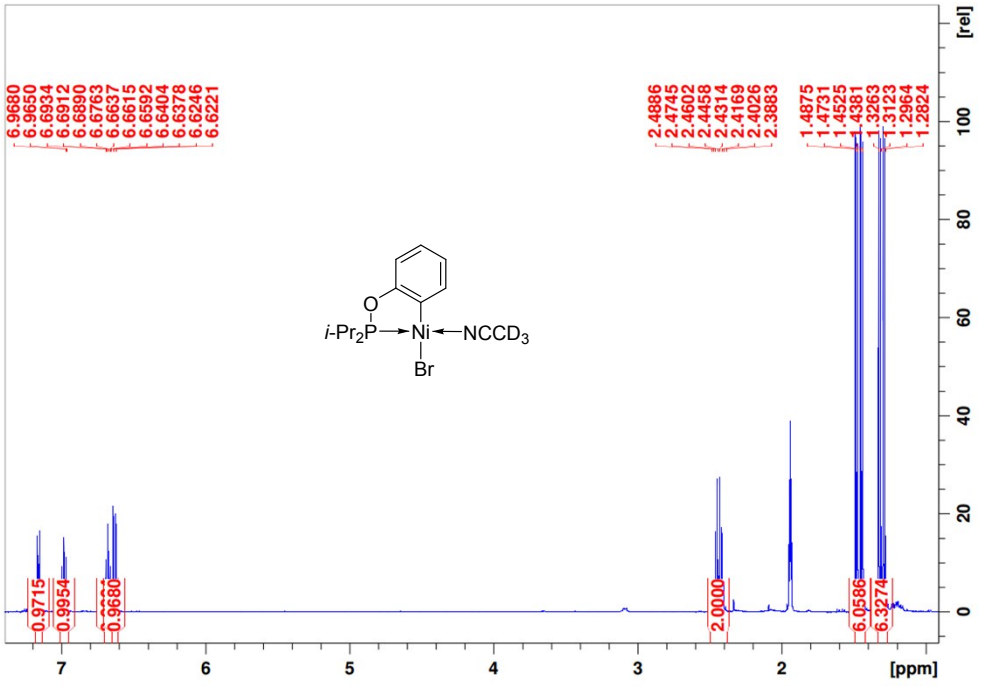

*Figure S2: Full ^{1}H NMR spectrum of **1a** in CD_3CN.*

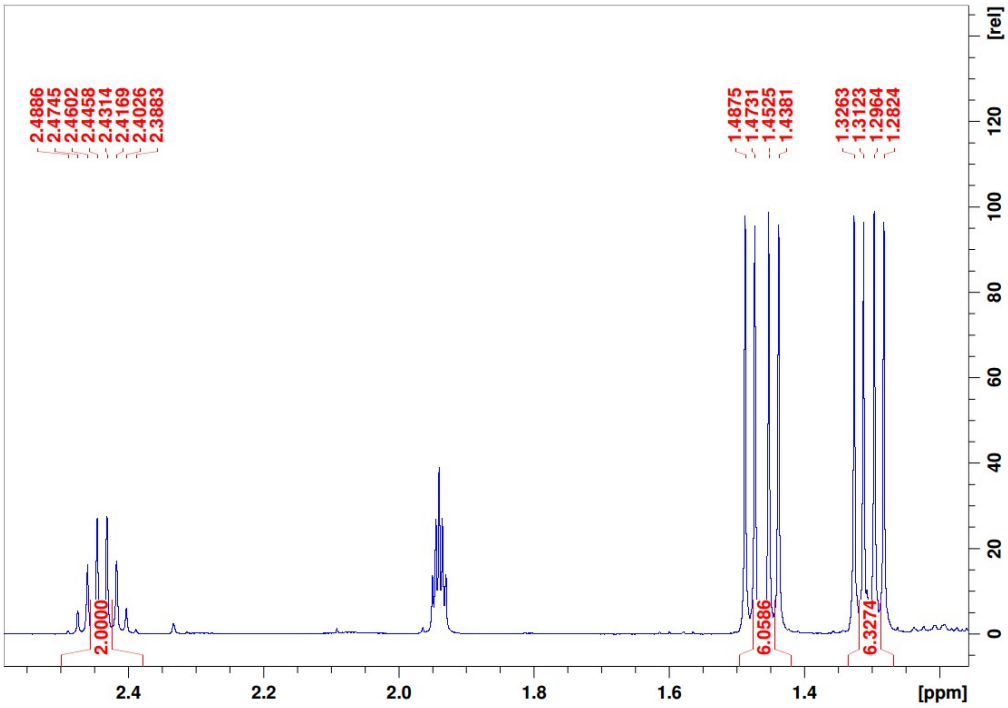

*Figure S3: ^{1}H NMR spectrum of **1a** in CD_3CN; focus on aliphatic region.*

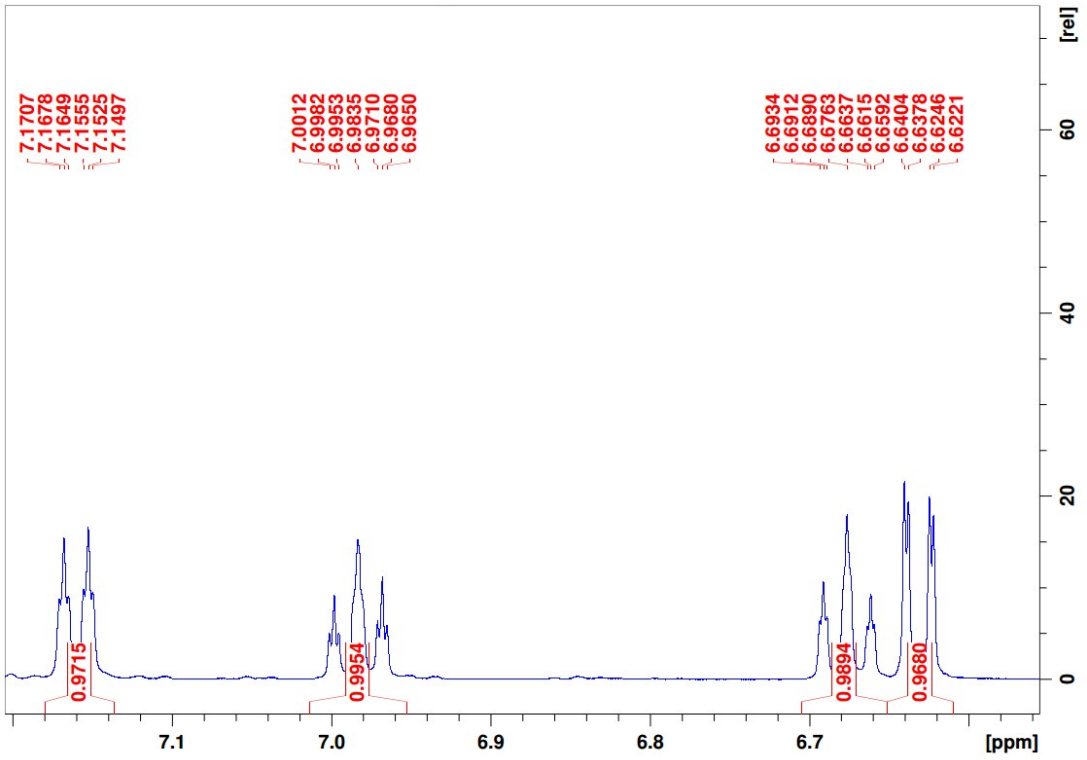

*Figure S4: ^{1}H NMR spectrum of **1a** in CD_3CN; focus on aromatic region.*

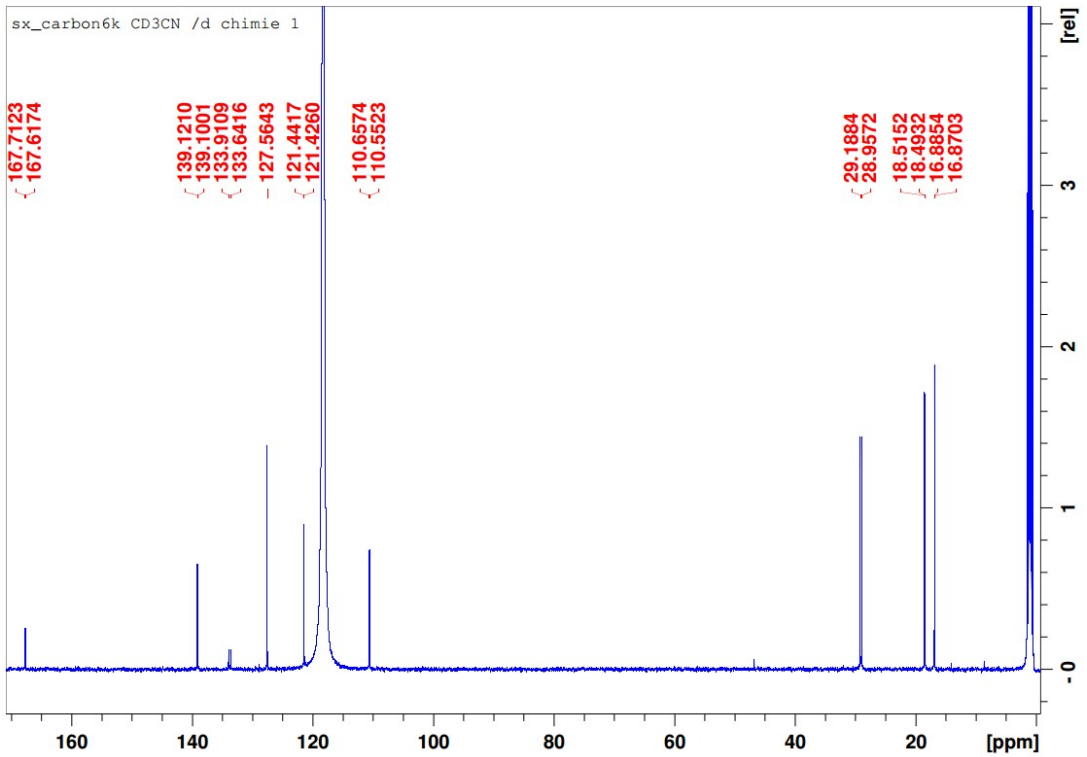

*Figure S5: Full $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in CD_3CN.*

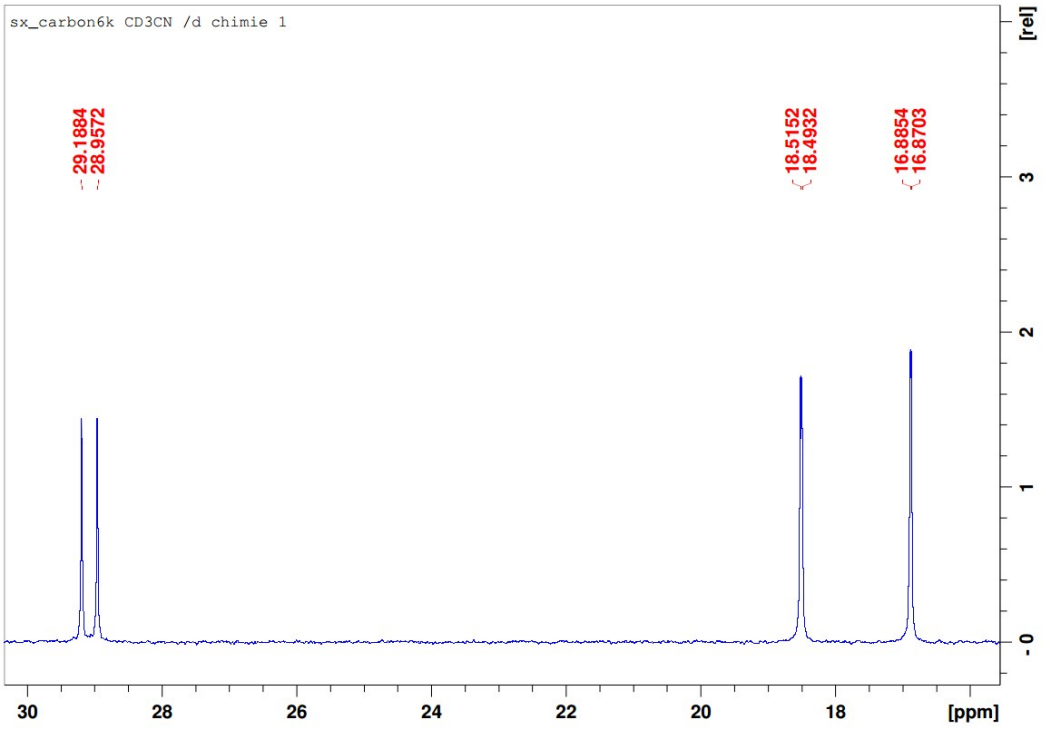

*Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in CD_3CN; focus on aliphatic region.*

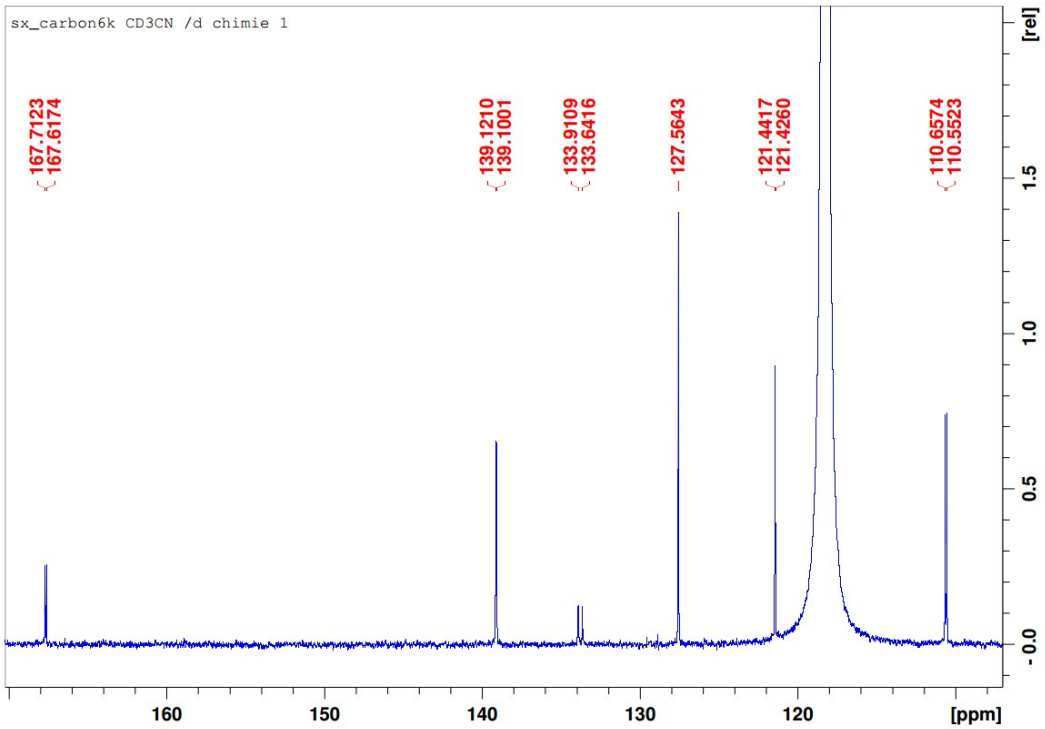

*Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in CD_3CN; focus on aromatic region.*

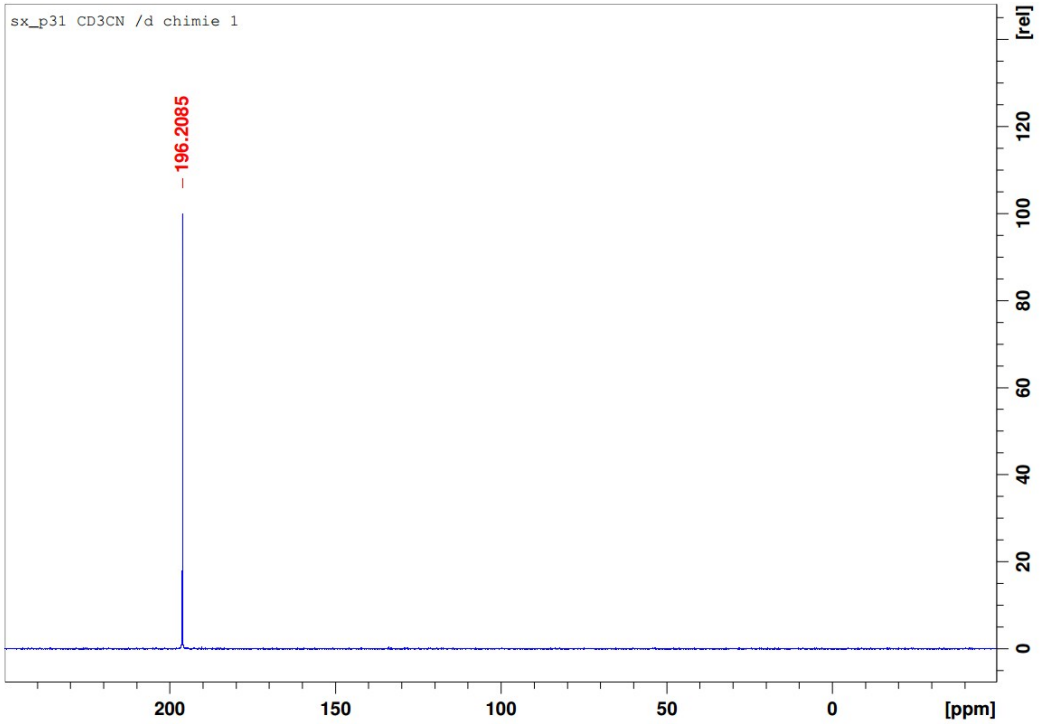

*Figure S8: $^{31}P\{^{1}H\}$ NMR spectrum of **1a** in CD_3CN.*

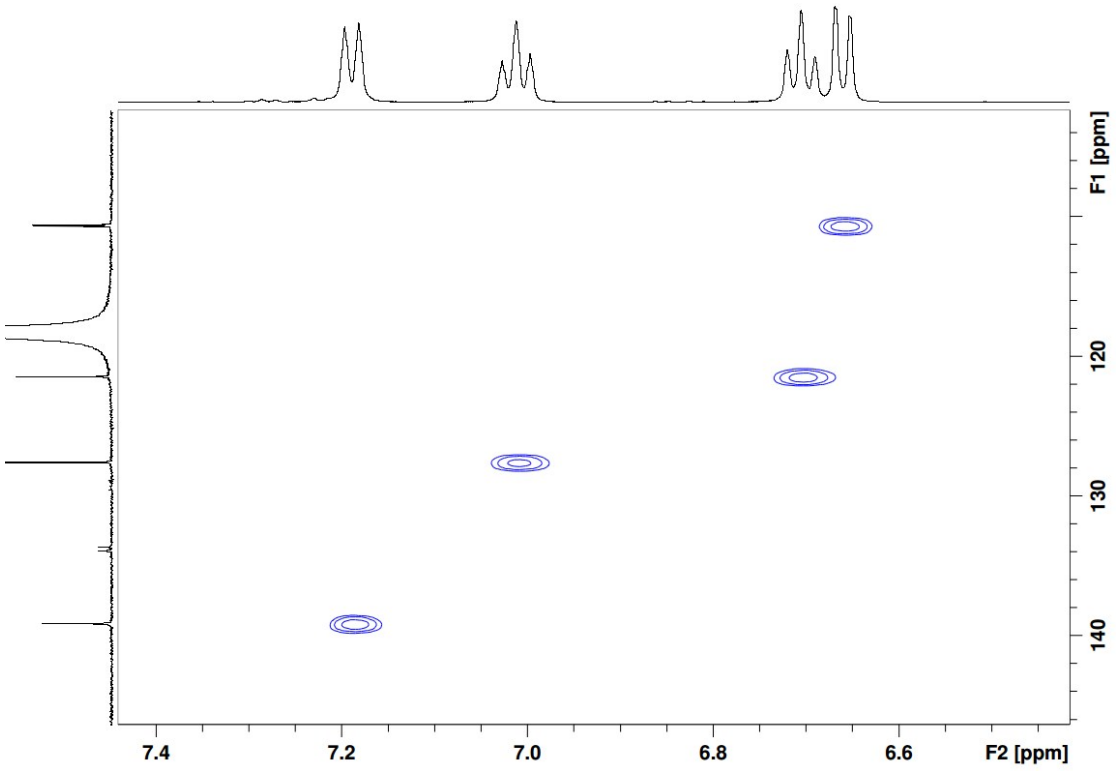

*Figure S9: HSQC spectrum of **1a** in CD_3CN; focus on aromatic region.*

1b+1b'

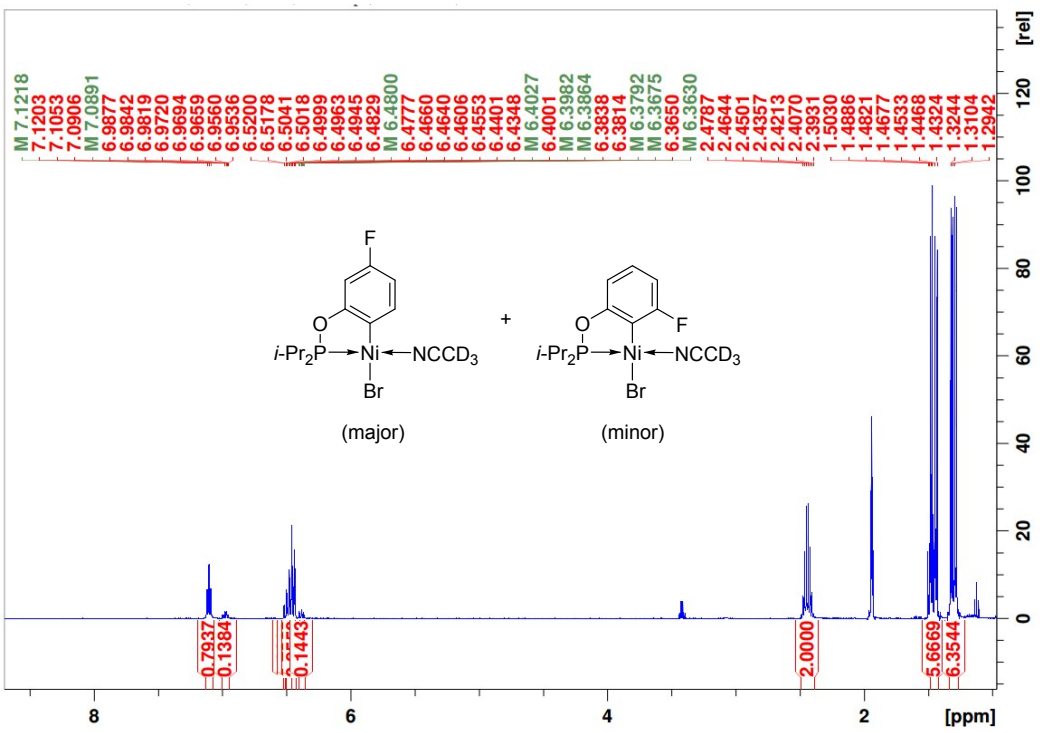

*Figure S10: Full ^{1}H NMR spectrum of **1b**(major)+**1b'**(minor) in CD_3CN.*

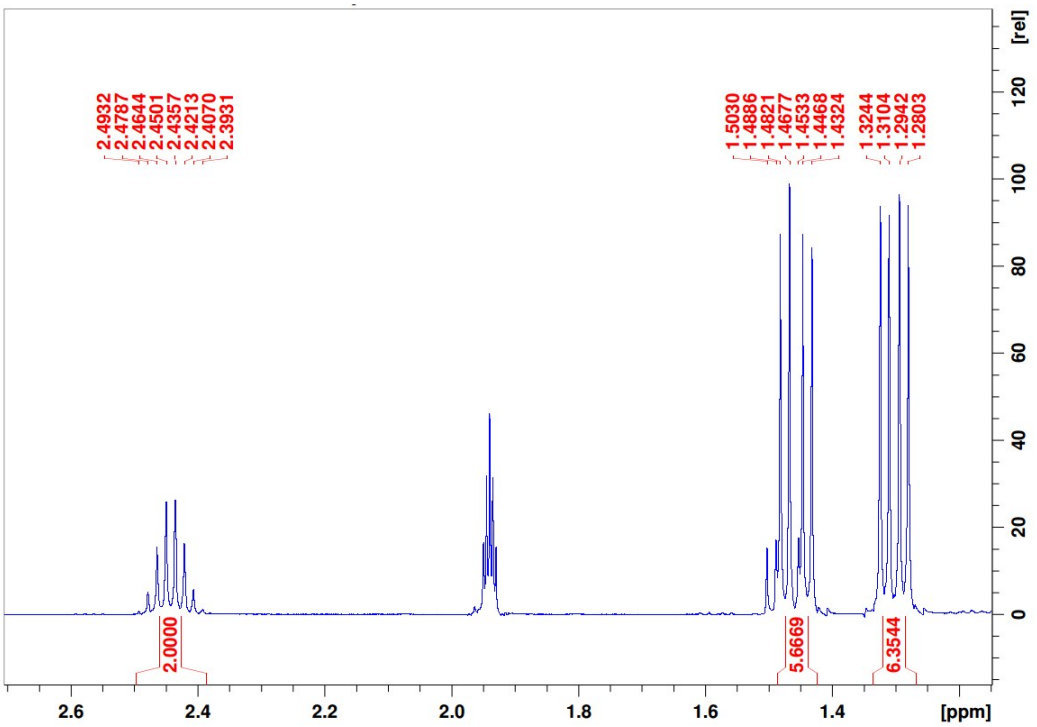

*Figure S11: ^{1}H NMR spectrum of **1b**+**1b'** in CD_3CN; focus on aliphatic region.*

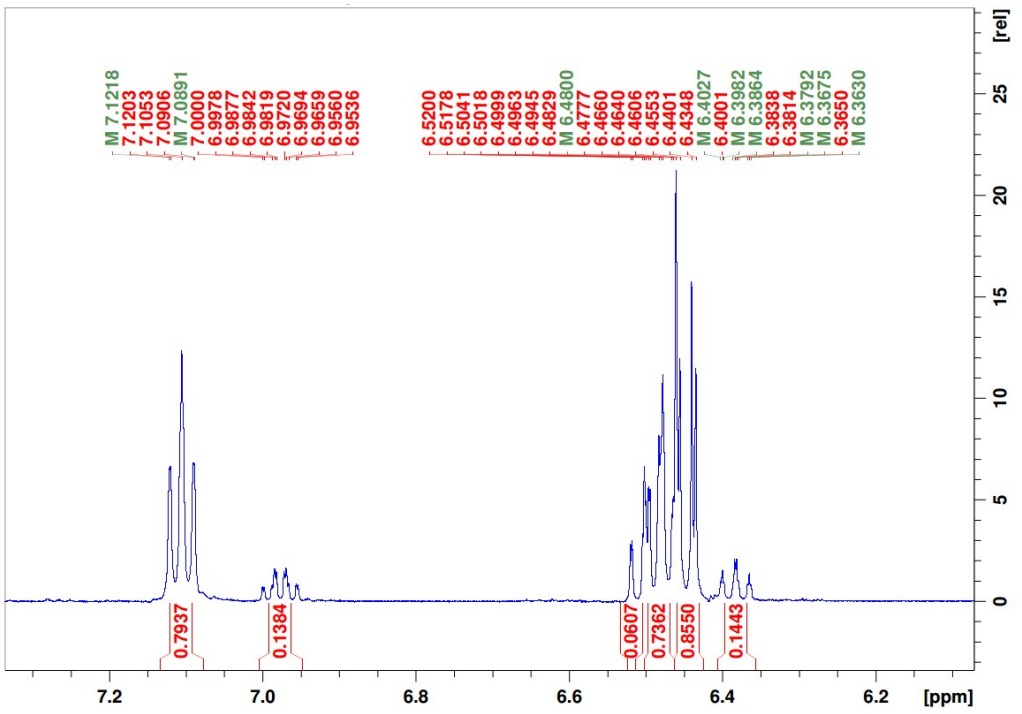

*Figure S12: ^{1}H NMR spectrum of **1b**+**1b'** in CD_3CN; focus on aromatic region.*

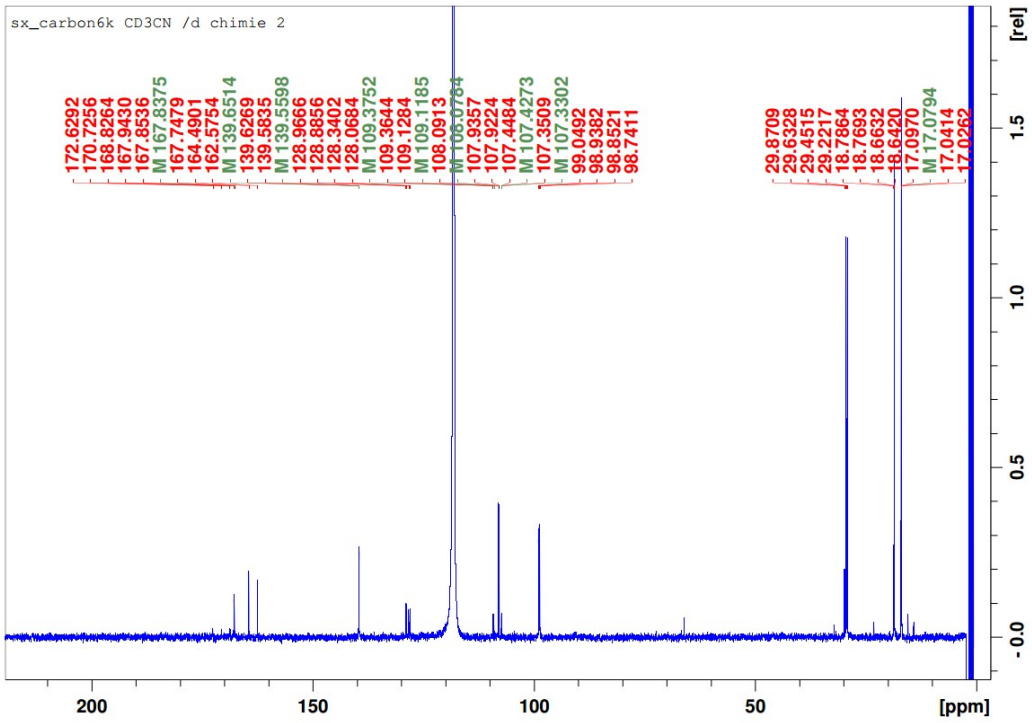

*Figure S13: Full $^{13}C\{^{1}H\}$ NMR spectrum of **1b**+**1b'** in CD_3CN.*

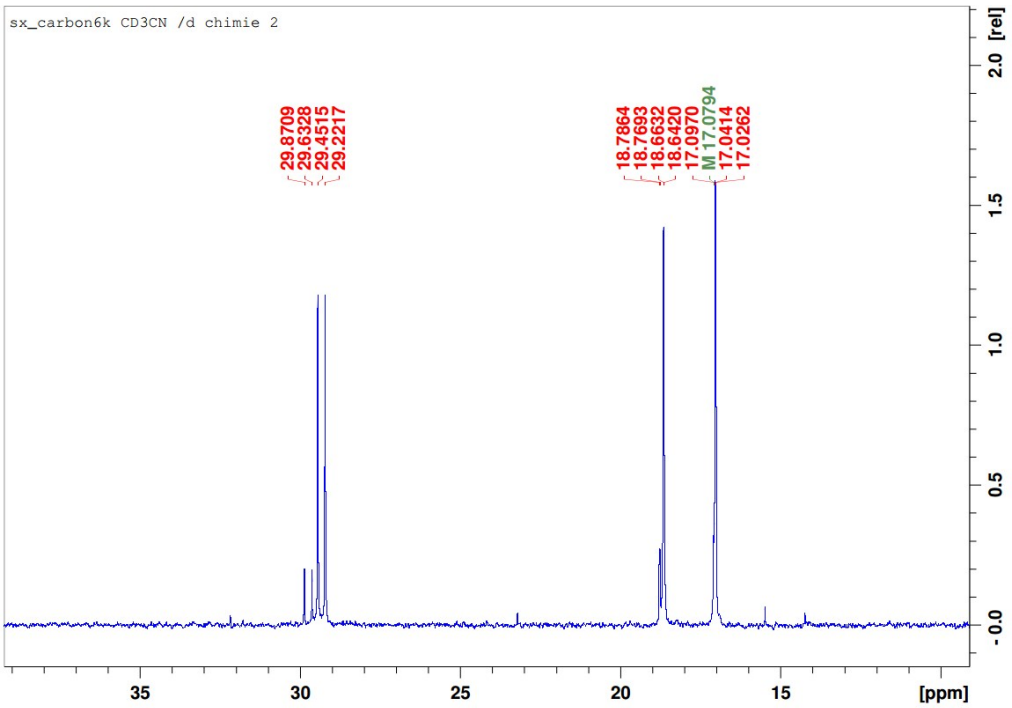

*Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum of **1b**+**1b'** in CD_3CN; focus on aliphatic region.*

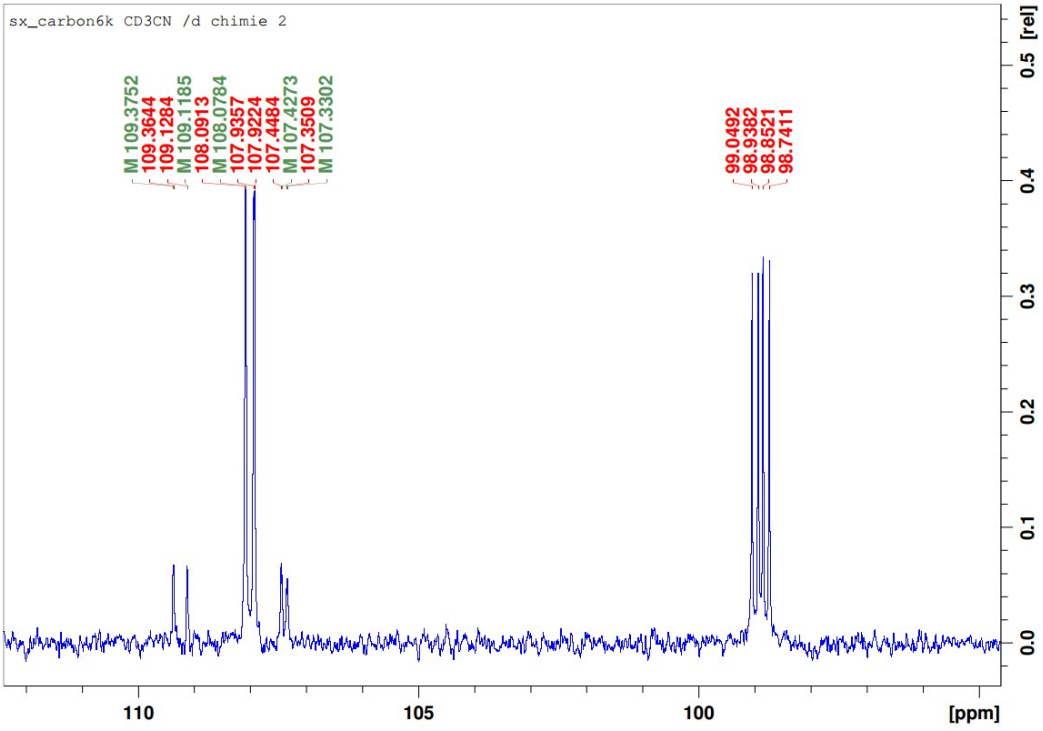

*Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of **1b**+**1b'** in CD_3CN; focus on aromatic region (I).*

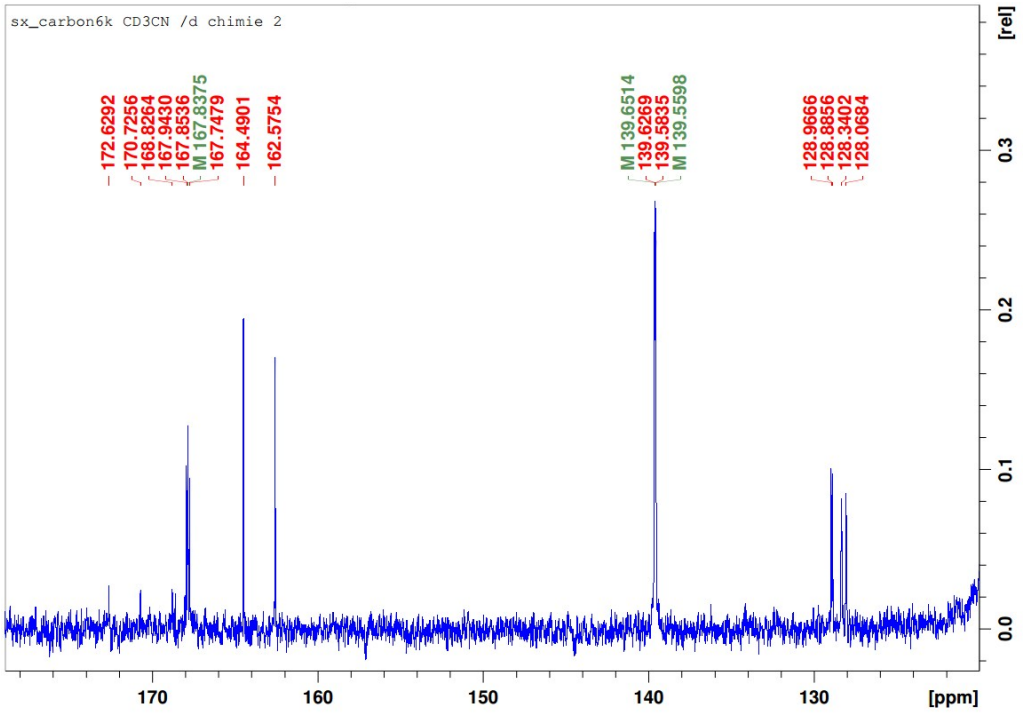

*Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of **1b**+**1b'** in CD_3CN; focus on aromatic region (II).*

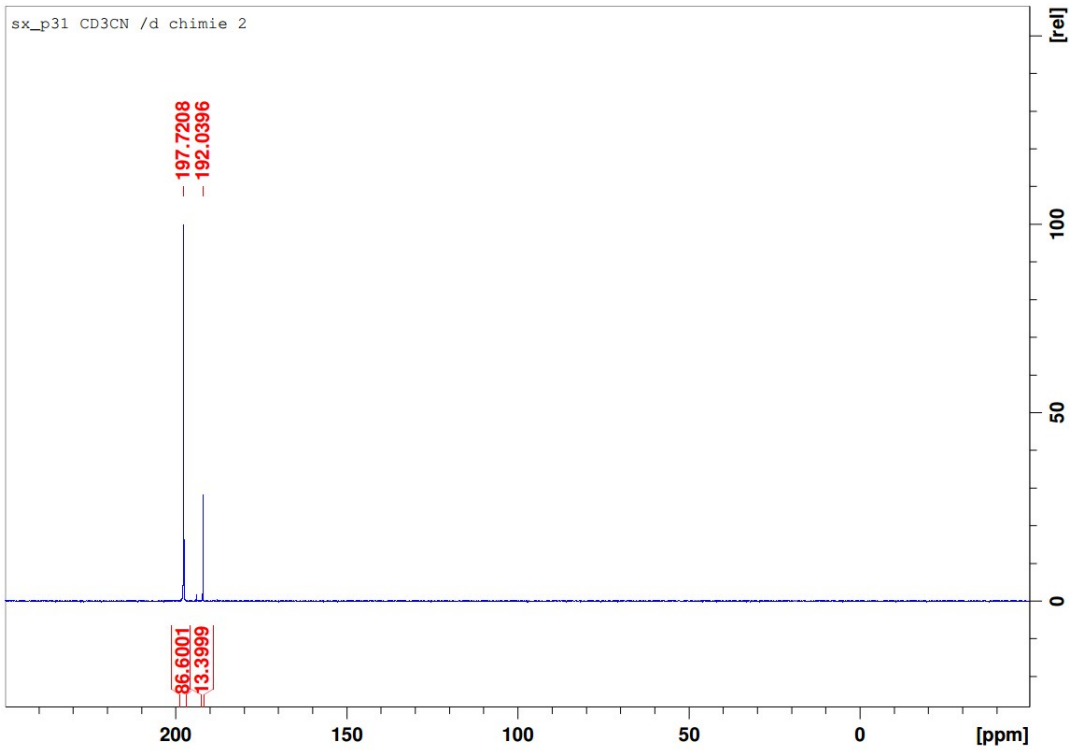

*Figure S17: $^{31}P\{^{1}H\}$ NMR spectrum of **1b**+**1b'** in CD_3CN.*

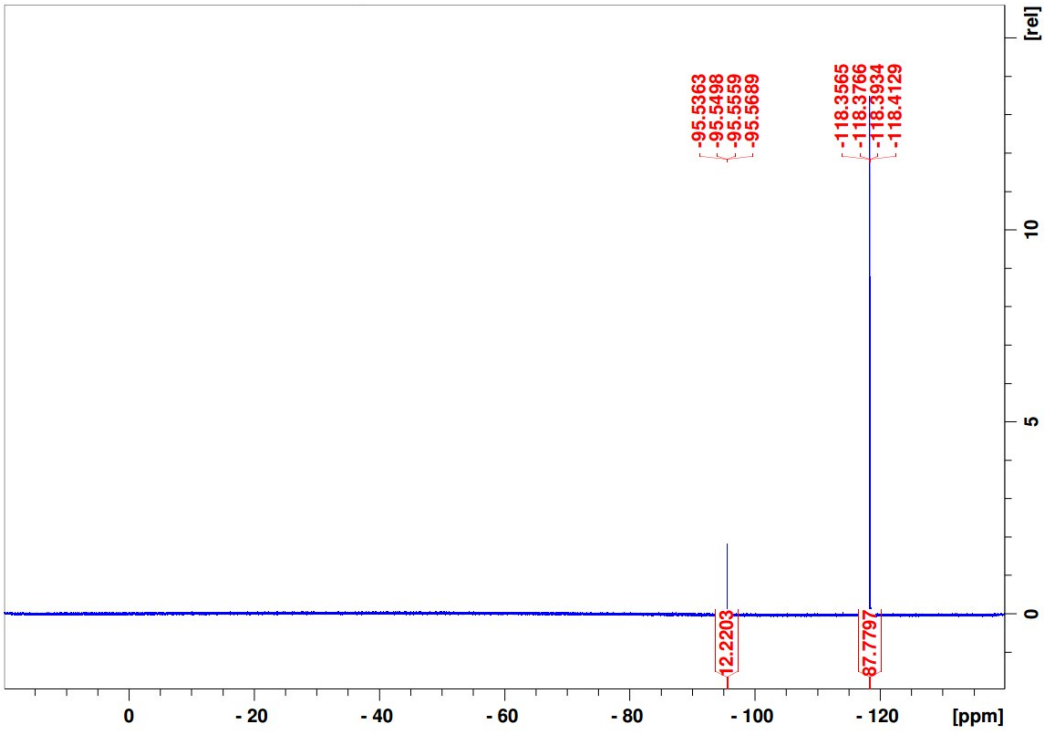

*Figure S18: ^{19}F NMR spectrum of **1b**+**1b'** in CD_3CN.*

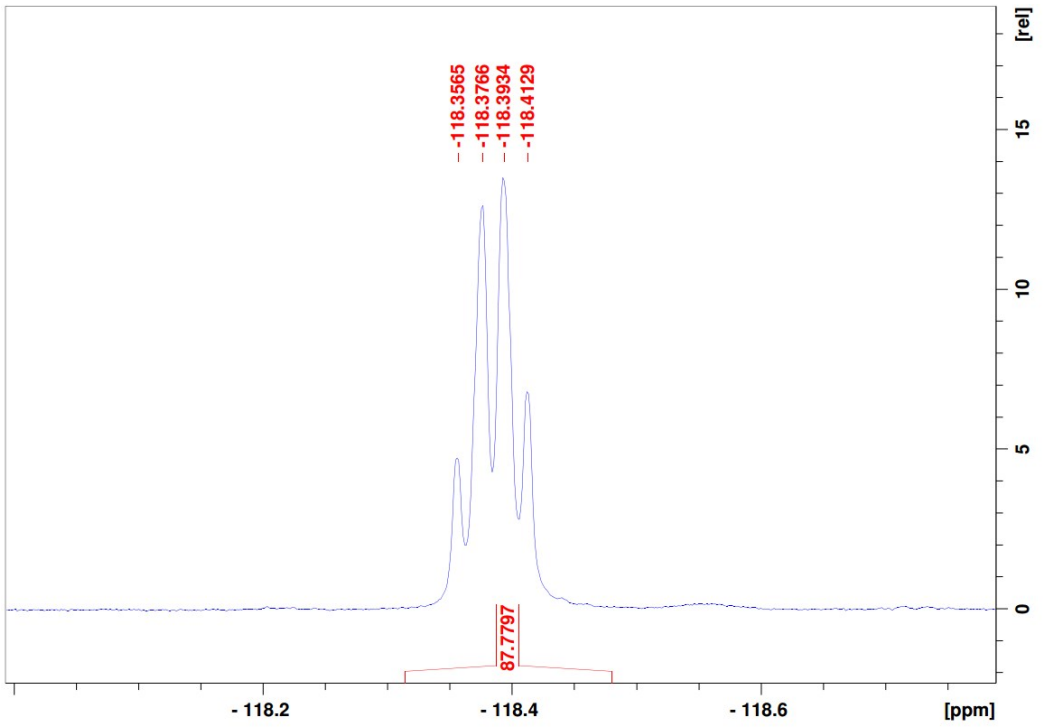

*Figure S19: ^{19}F NMR spectrum of **1b**+**1b'** in CD_3CN; focus on **1b**.*

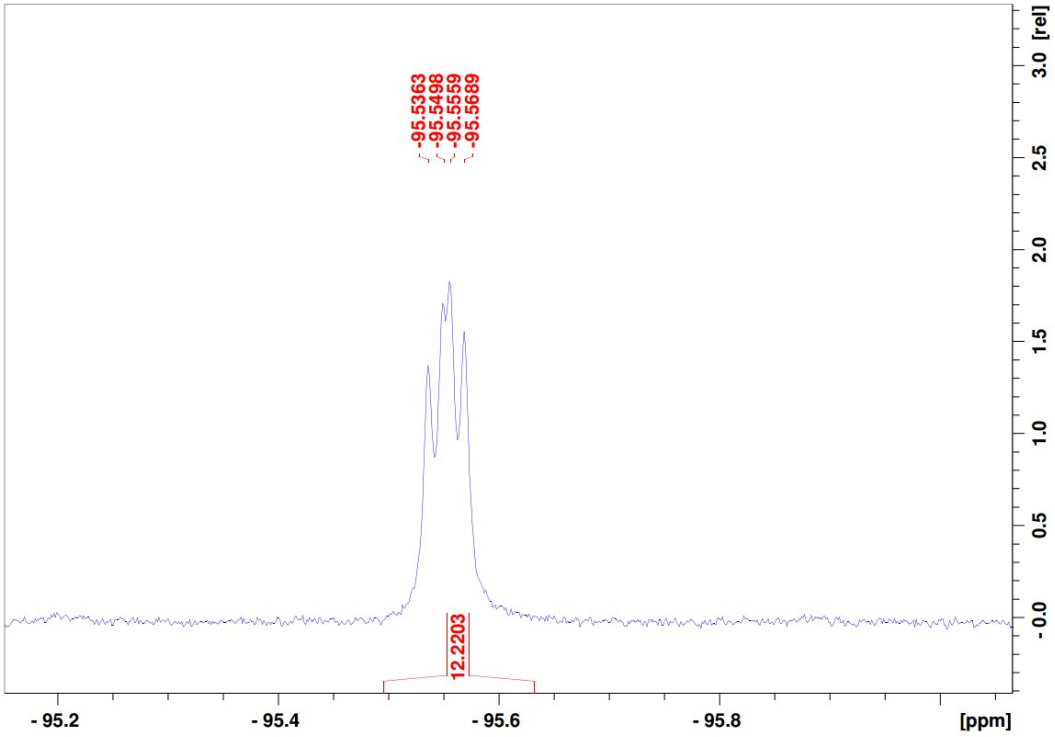

*Figure S20: ^{19}F NMR spectrum of **1b**+**1b'** in CD_3CN; focus on **1b'**.*

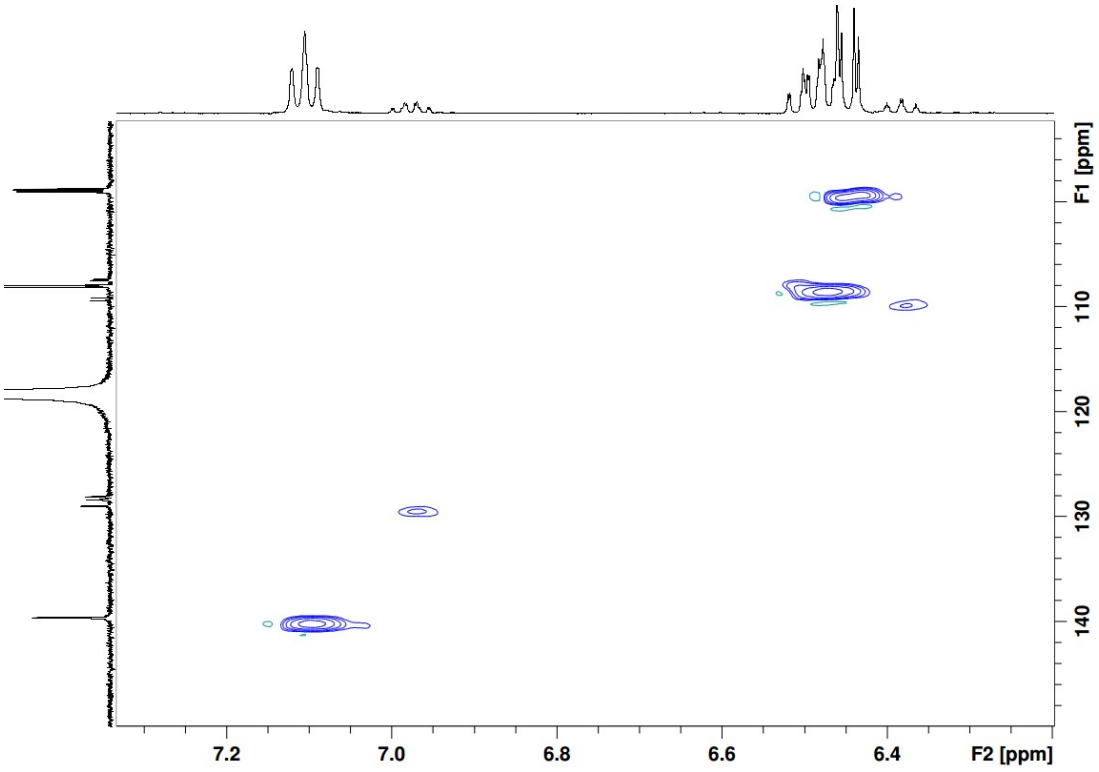

*Figure S21: HSQC spectrum of **1b**+**1b'** in CD_3CN; focus on aromatic region.*

1c

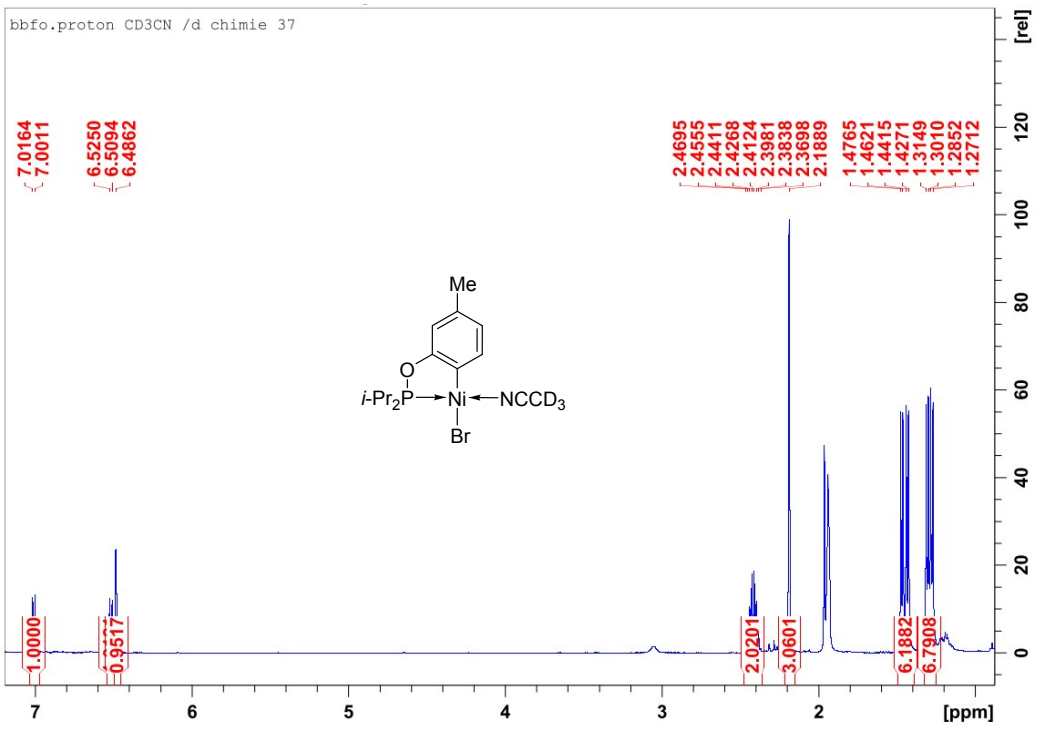

*Figure S22: Full ^{1}H NMR spectrum of **1c** in CD_3CN.*

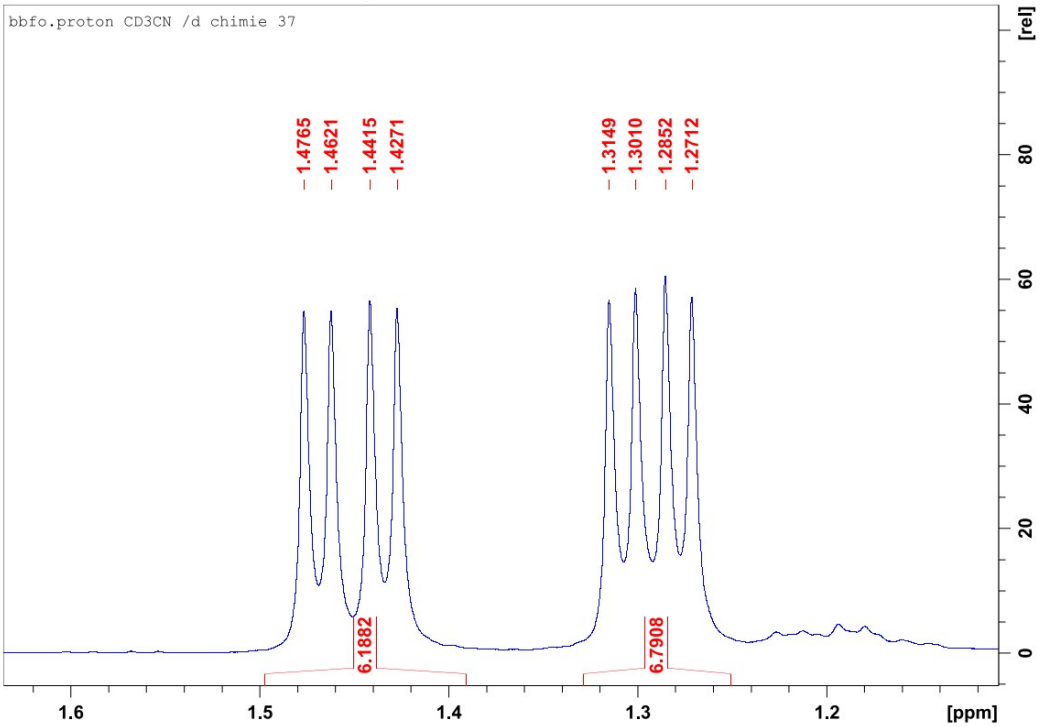

*Figure S23: ^{1}H NMR spectrum of **1c** in CD_3CN; focus on aliphatic region (I).*

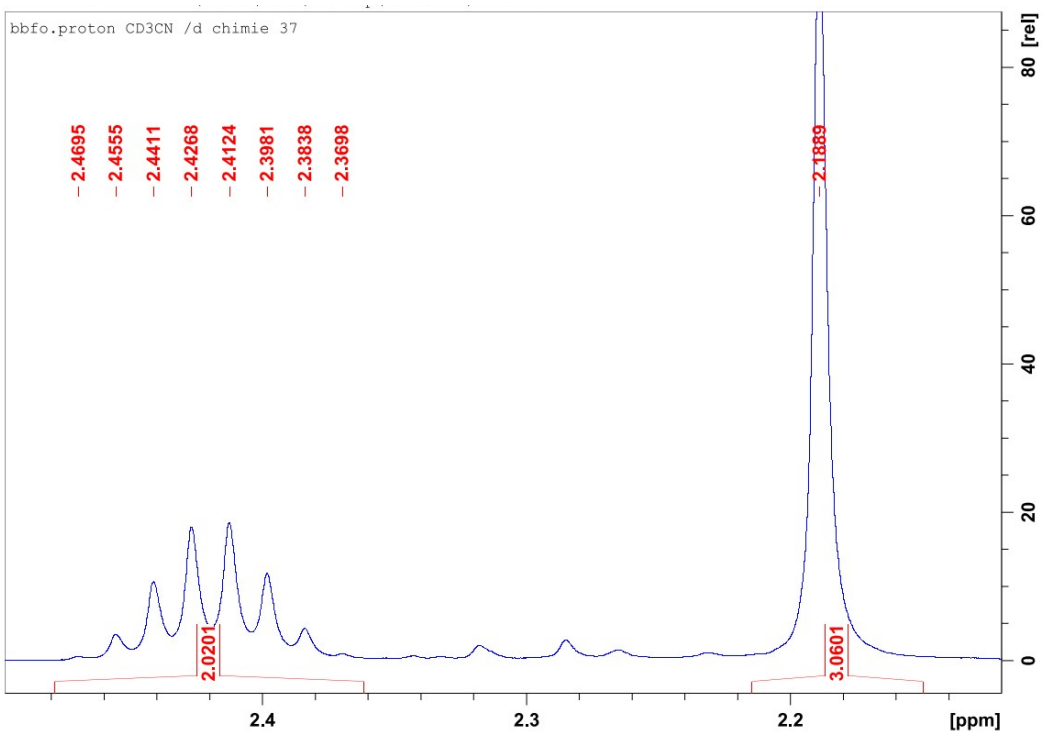

*Figure S24: ^{1}H NMR spectrum of **1c** in CD_3CN; focus on aliphatic region (II).*

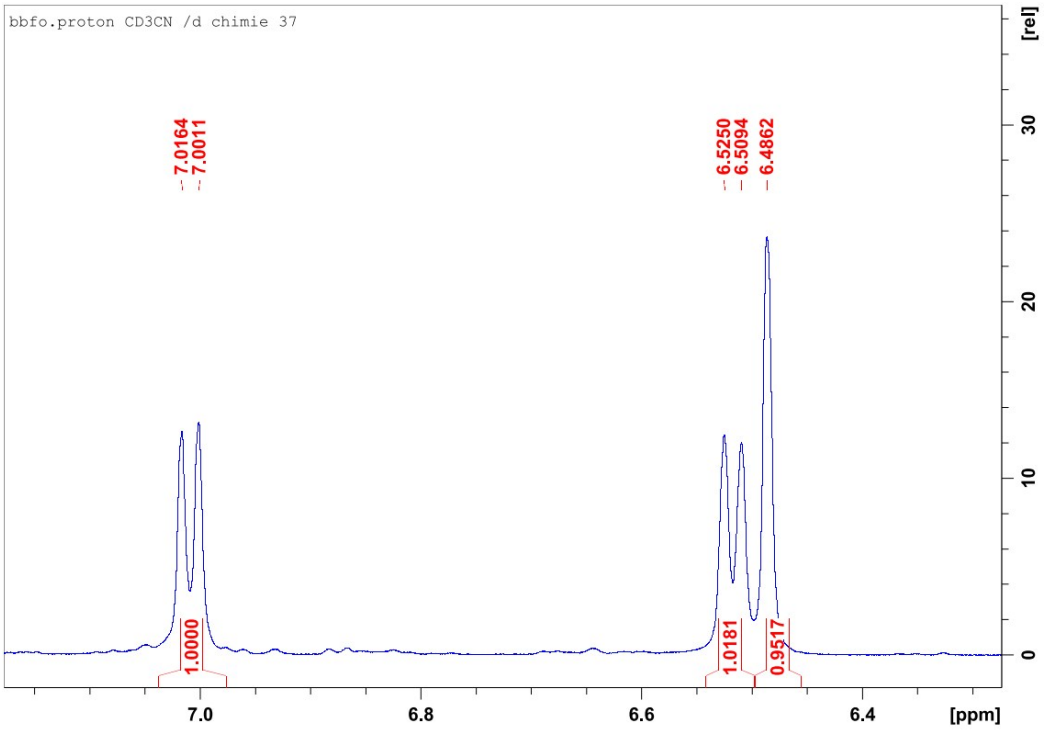

*Figure S25: ^{1}H NMR spectrum of **1c** in CD_3CN; focus on aromatic region.*

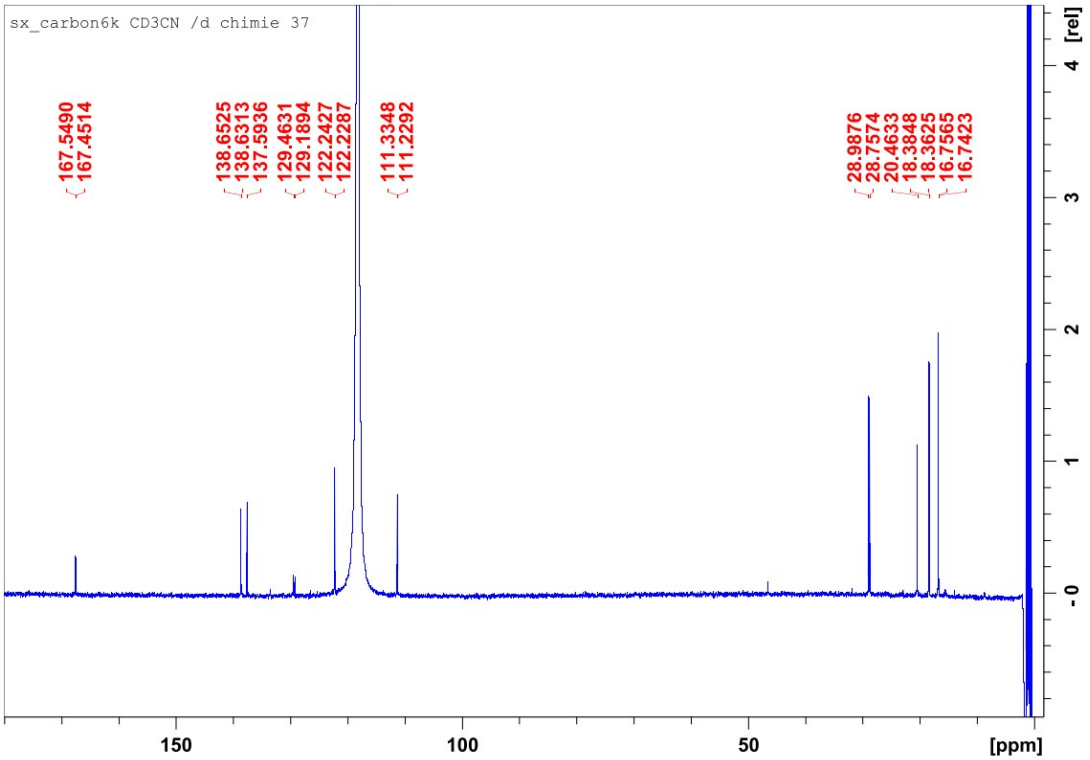

*Figure S26: Full $^{13}C\{^{1}H\}$ NMR spectrum of **1c** in CD_3CN.*

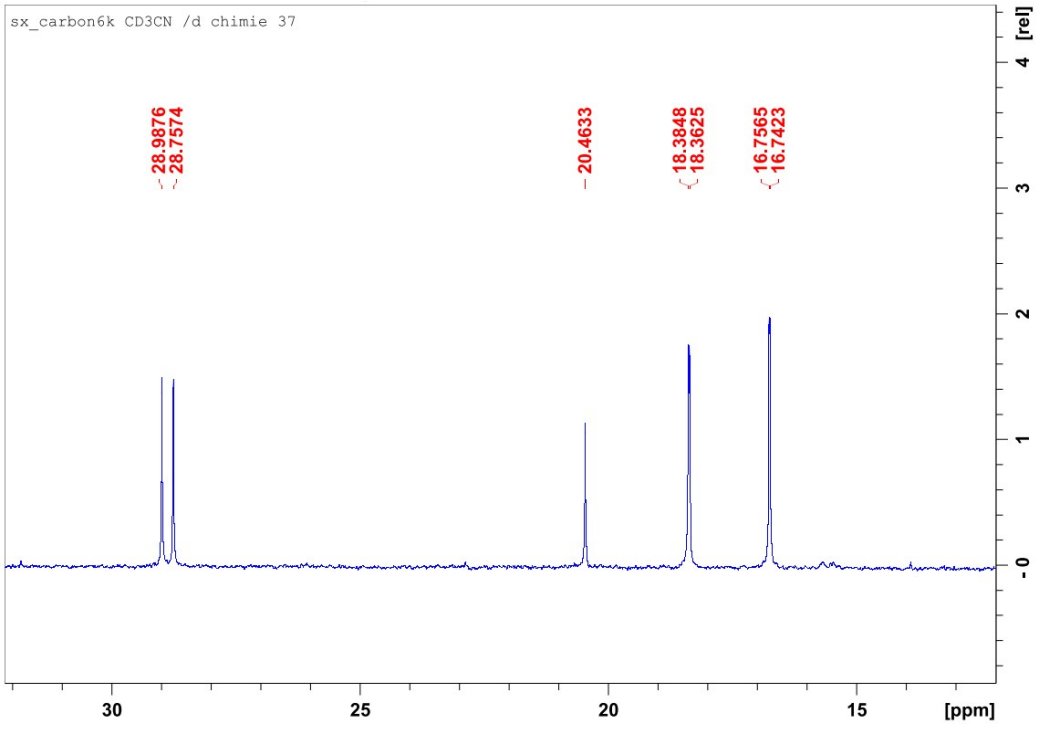

*Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum of **1c** in CD_3CN; focus on aliphatic region.*

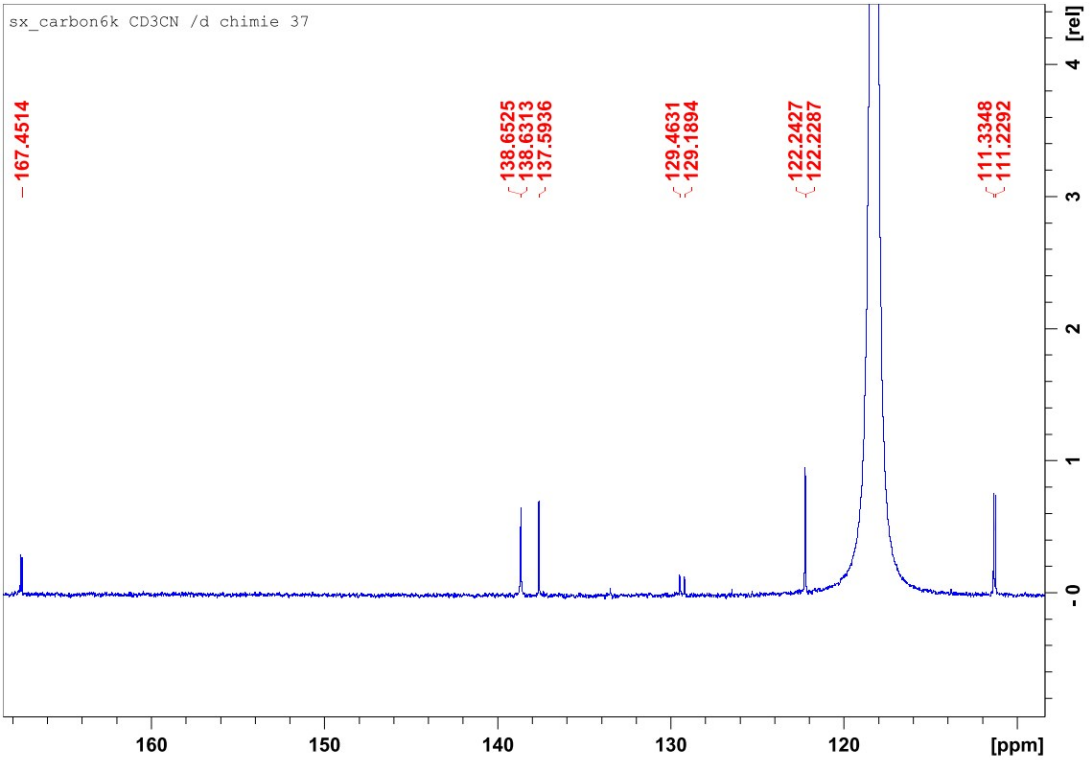

*Figure S28: $^{13}C\{^{1}H\}$ NMR spectrum of **1c** in CD_3CN; focus on aromatic region.*

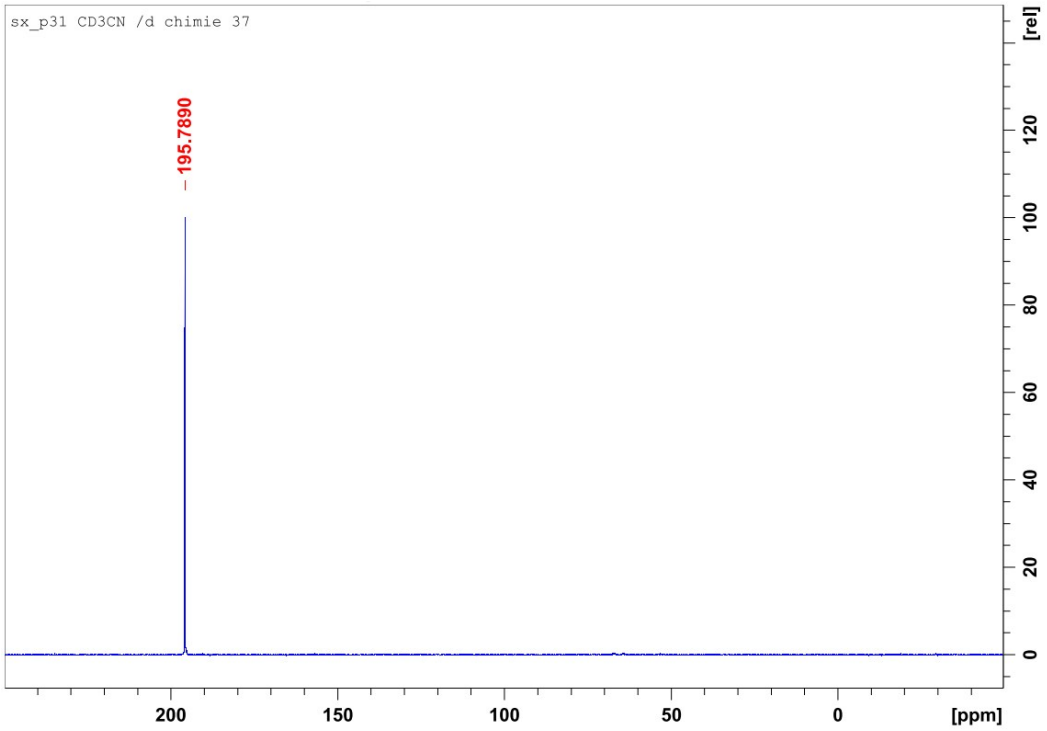

*Figure S29: $^{31}P\{^{1}H\}$ NMR spectrum of **1c** in CD_3CN.*

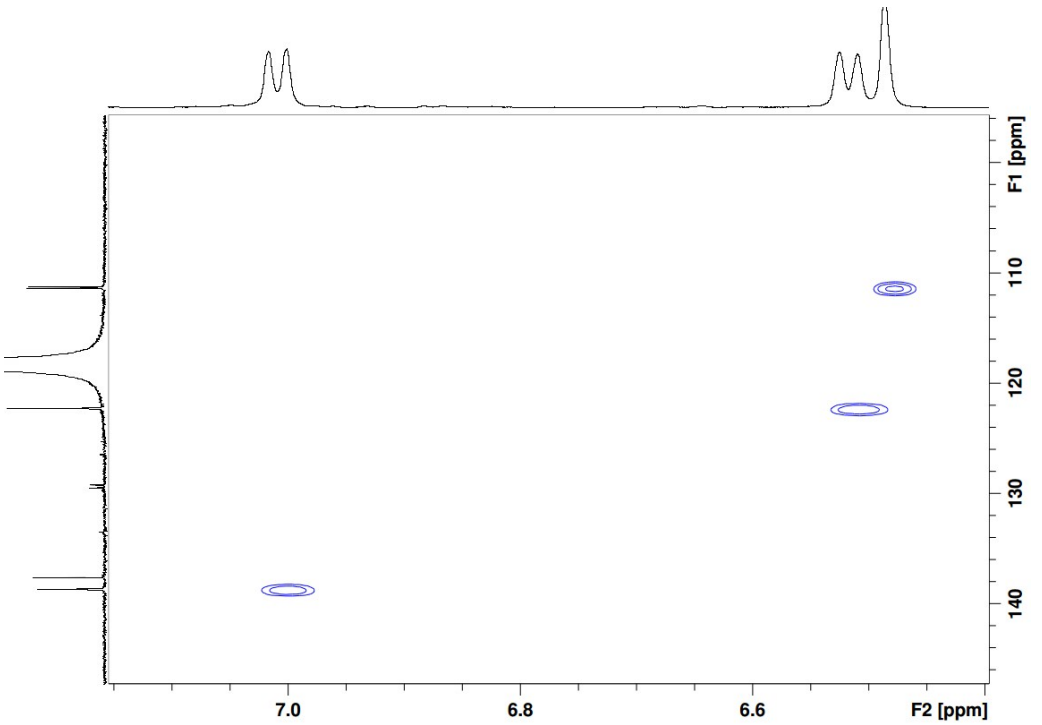

*Figure 30: HSQC spectrum of **1c** in CD_3CN.*

1d

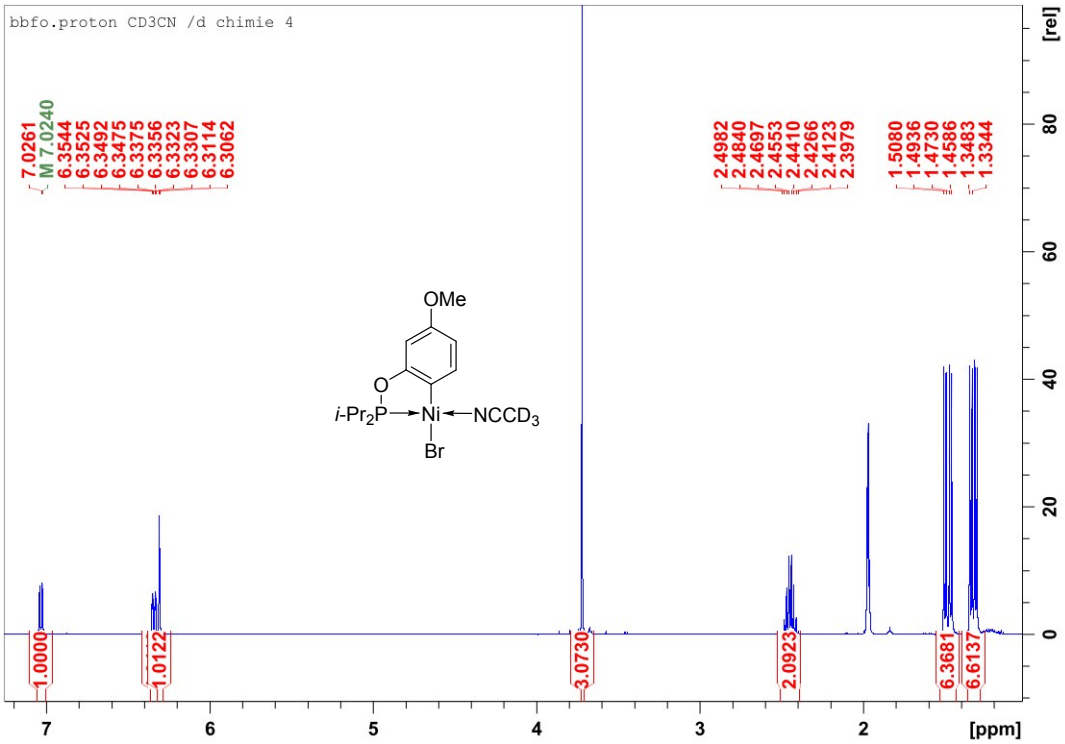

*Figure S31: Full ^1H NMR spectrum of **1d** in CD_3CN.*

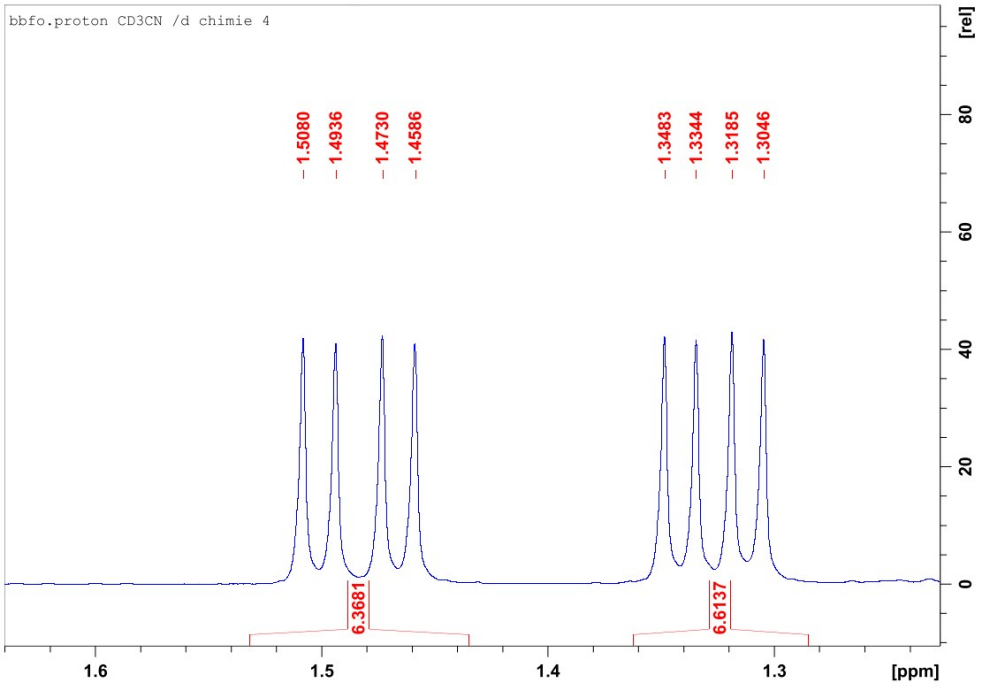

*Figure S32: ^{1}H NMR spectrum of **1d** in CD_3CN; focus on aliphatic region (I.)*

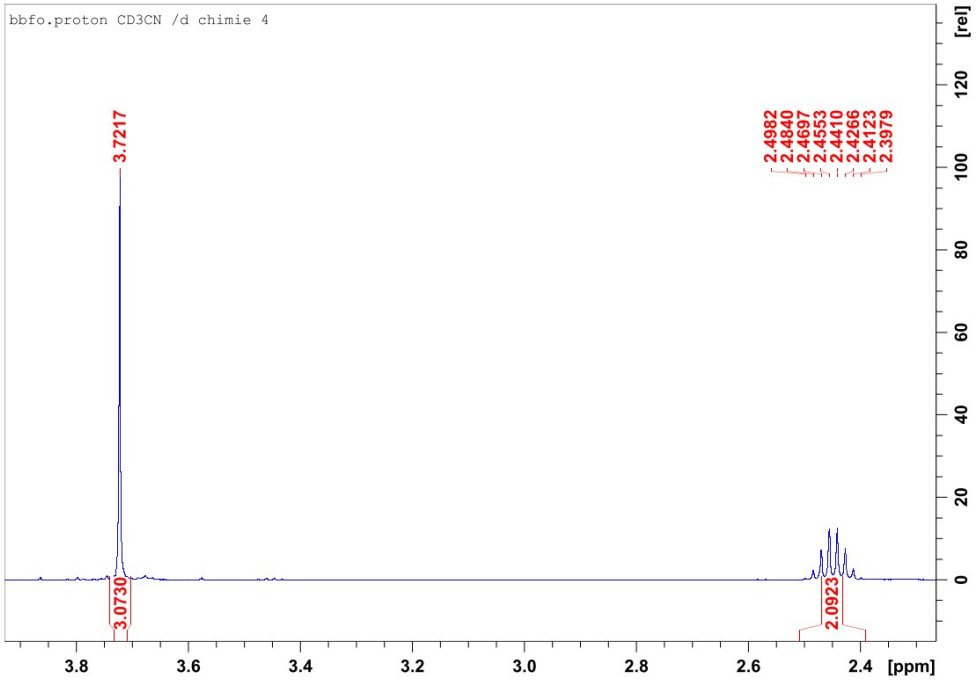

*Figure S33: ^{1}H NMR spectrum of **1d** in CD_3CN; focus on aliphatic region (II).*

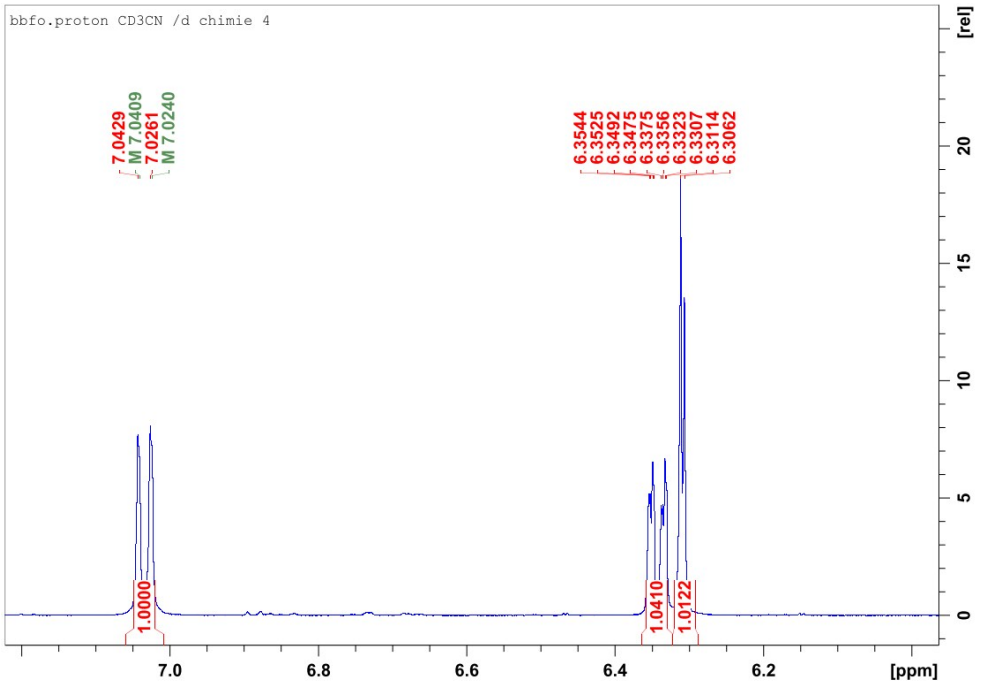

*Figure S34: ^{1}H NMR spectrum of **1d** in CD_3CN; focus on aromatic region.*

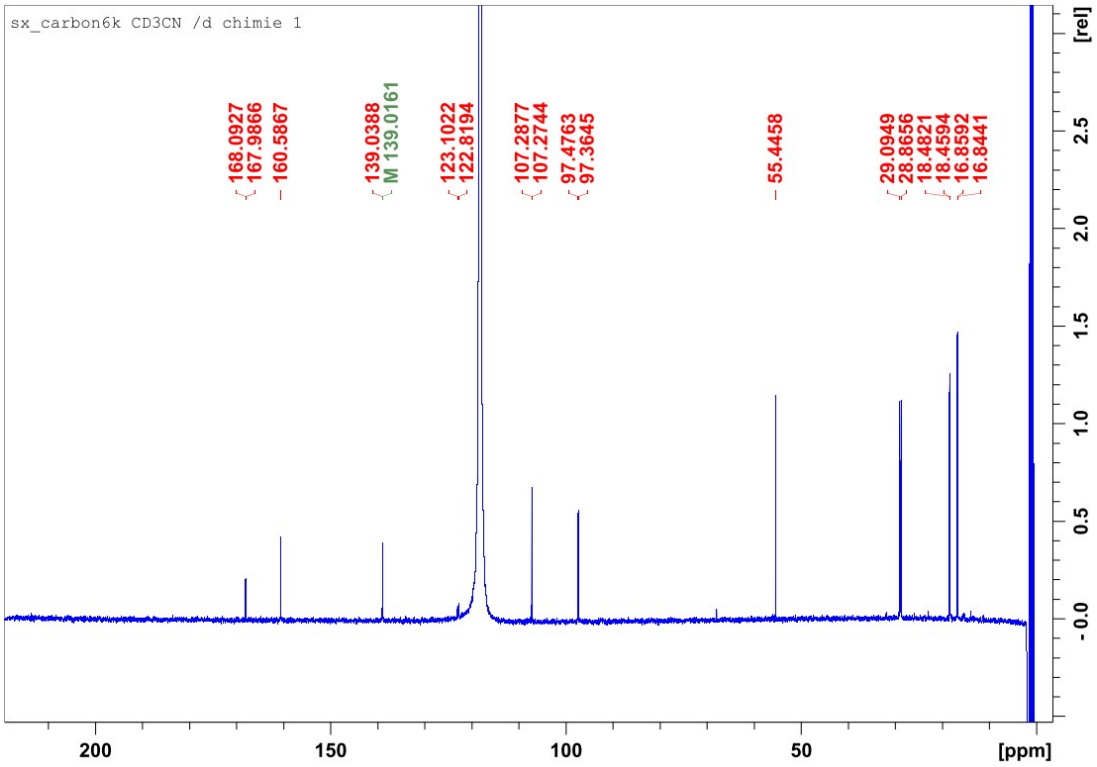

*Figure 35: Full $^{13}C\{1H\}$ NMR spectrum of **1d** in CD_3CN.*

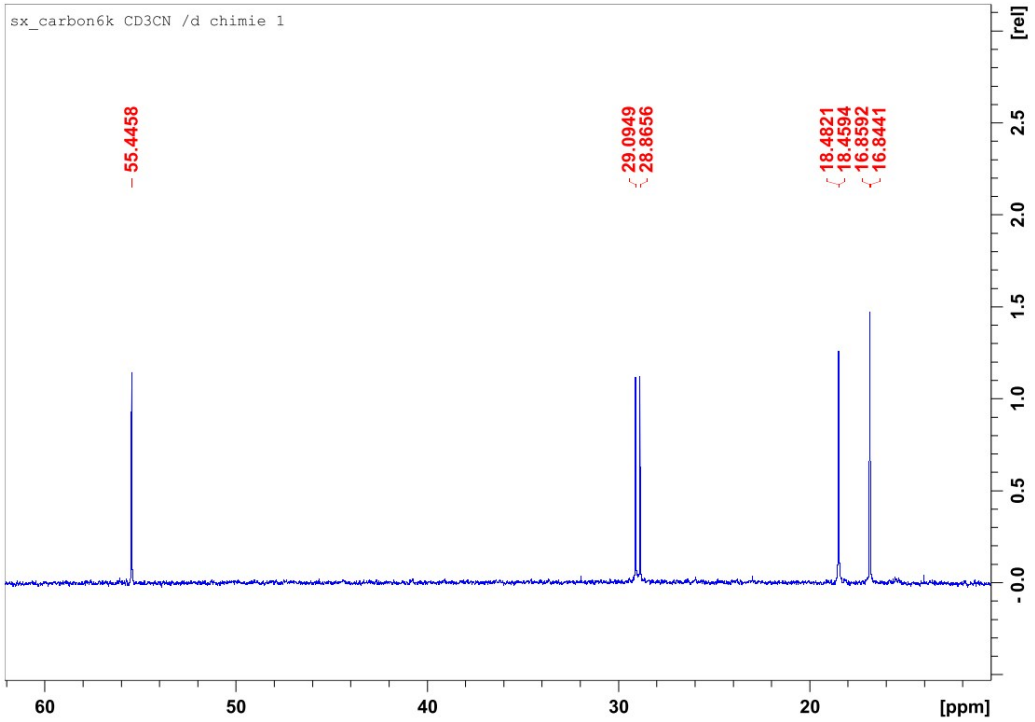

*Figure S36 $^{13}C\{^{1}H\}$ NMR spectrum of **1d** in CD_3CN; focus on aliphatic region.*

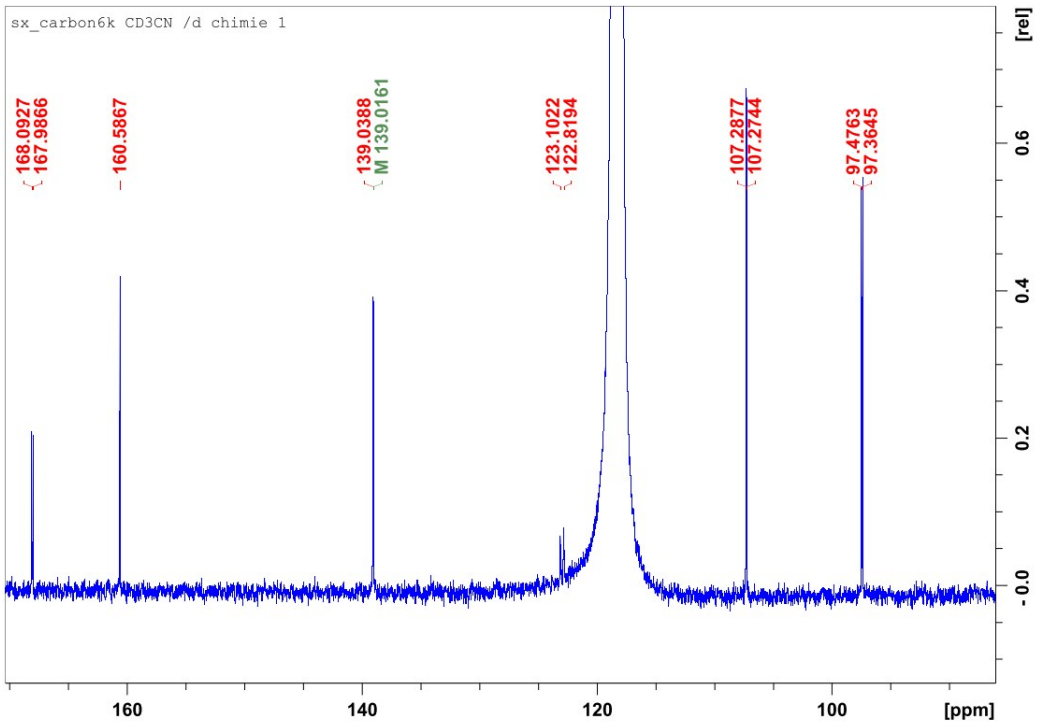

*Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of **1d** in CD_3CN; focus on aromatic region.*

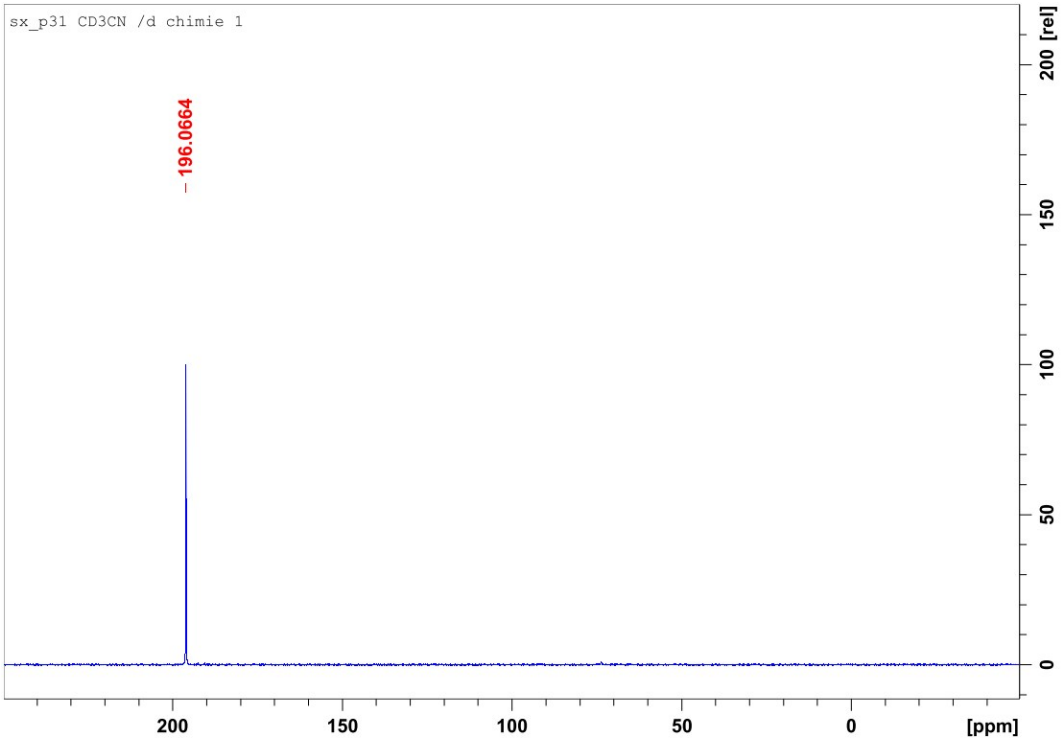

*Figure S38: $^{31}P\{^{1}H\}$ NMR spectrum of **1d** in CD_3CN.*

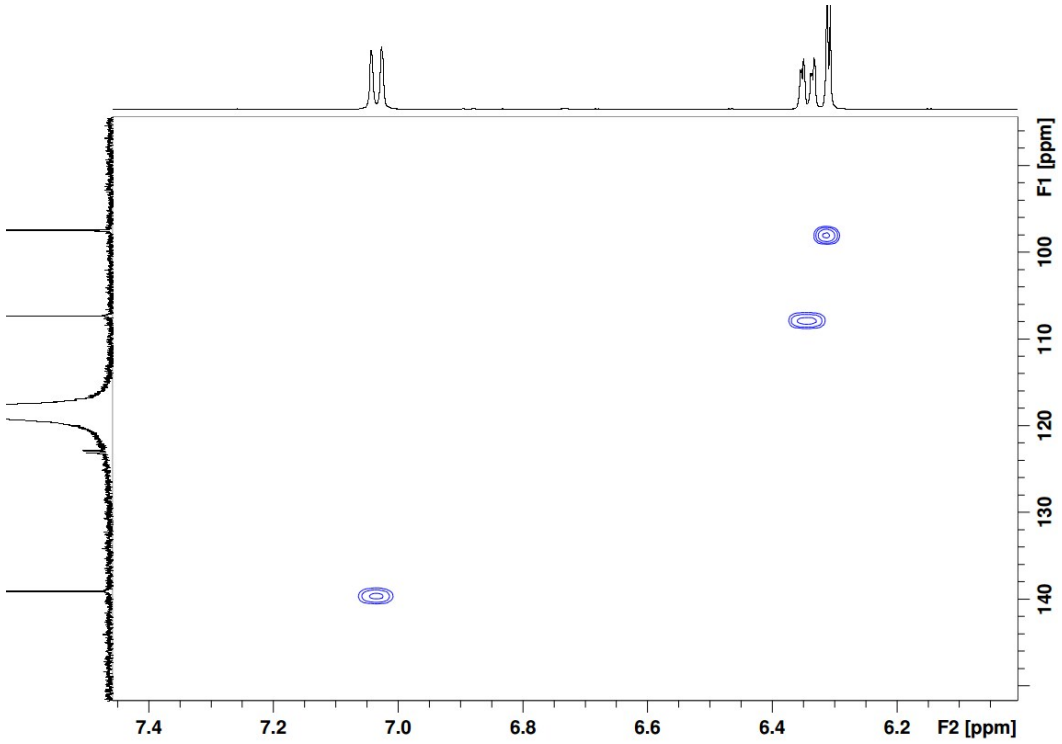

*Figure S39: HSQC spectrum of **1d** in CD_3CN; focus on aromatic region.*

1e

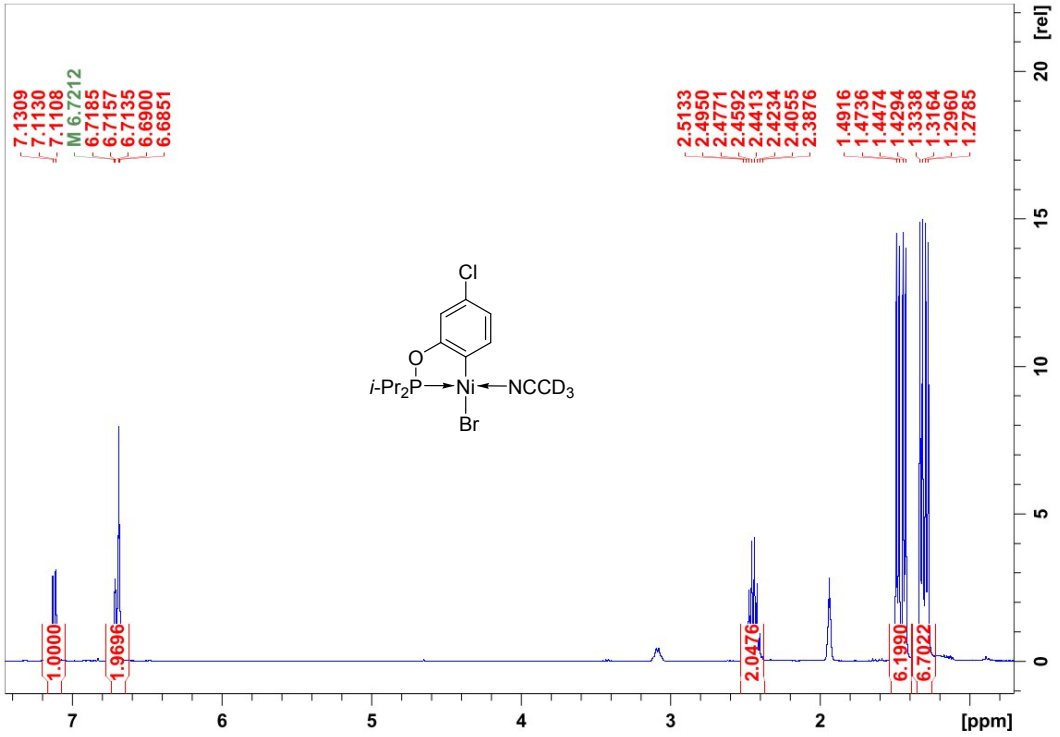

*Figure S40: Full ^{1}H NMR spectrum of **1e** in CD_3CN.*

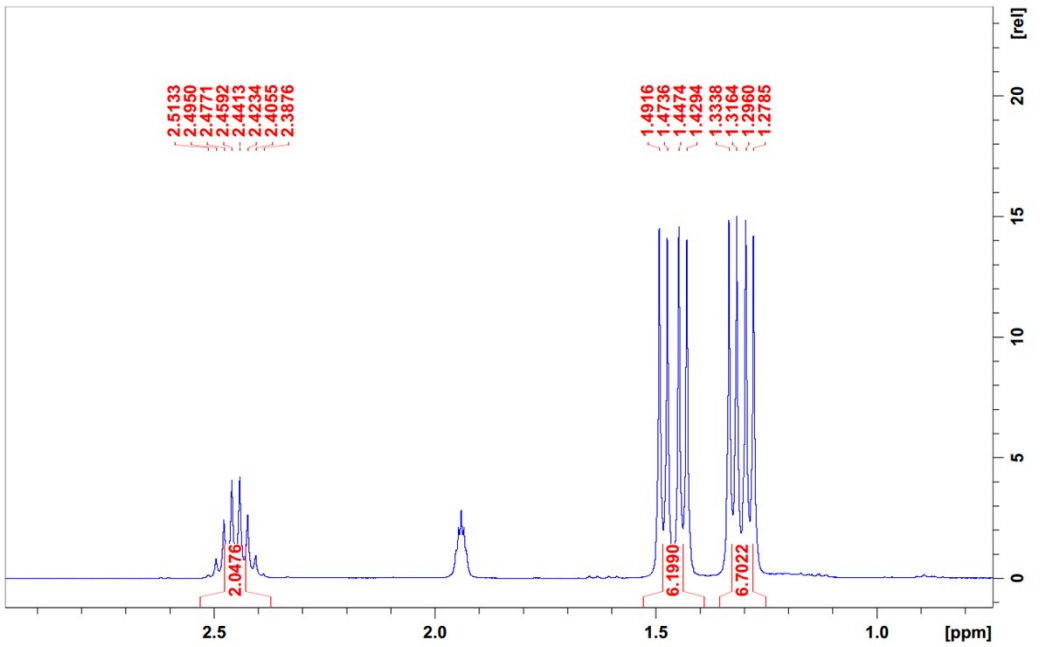

*Figure S41: ^{1}H NMR spectrum of **1e** in CD_3CN; focus on aliphatic region.*

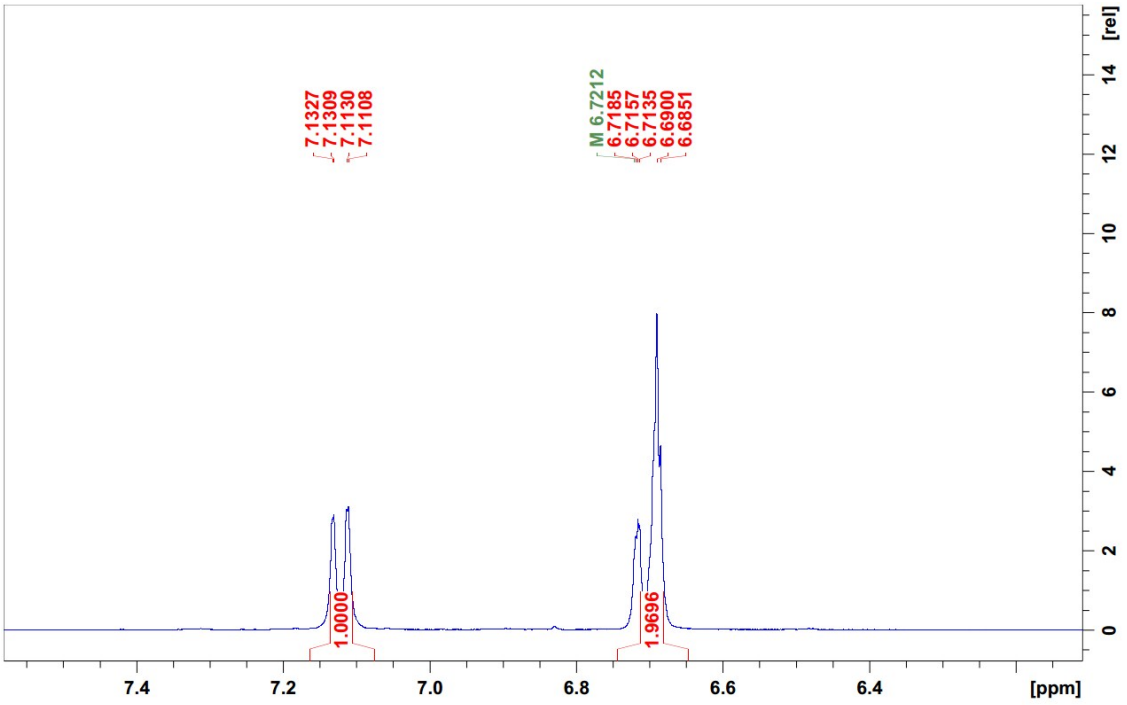

*Figure S42: ^{1}H NMR spectrum of **1e** in CD_3CN; focus on aromatic region.*

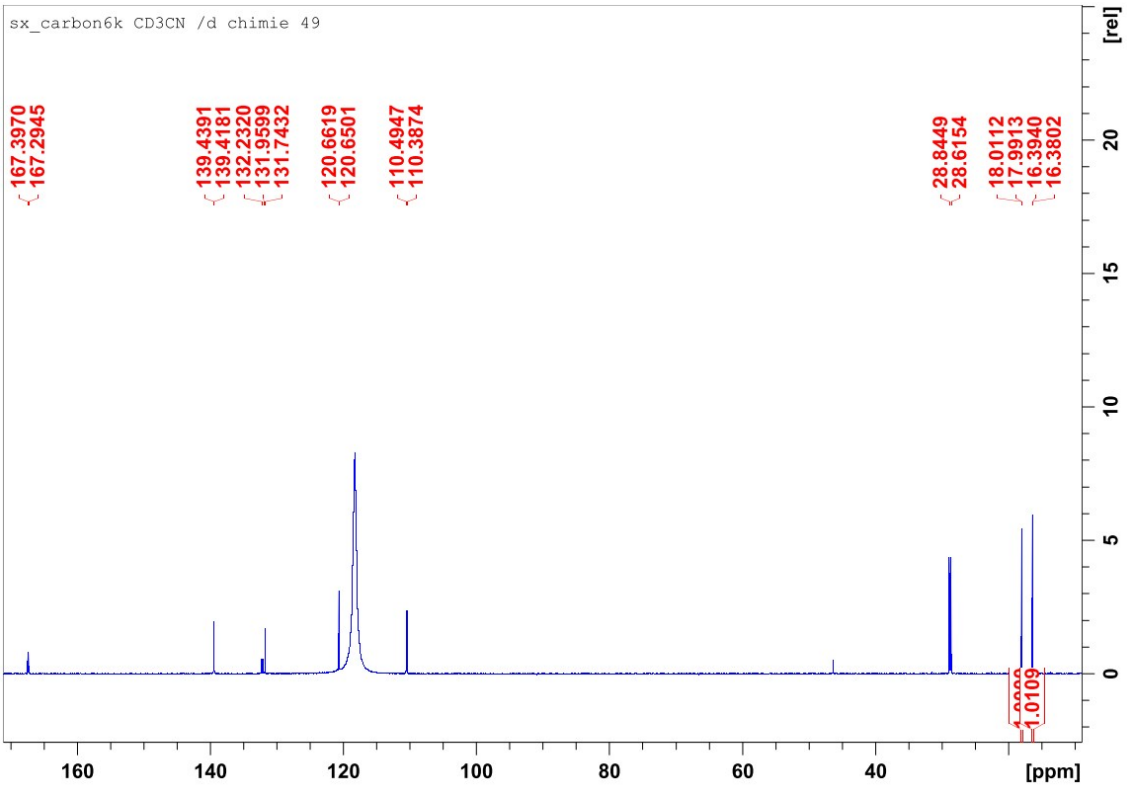

*Figure S43: Full $^{13}C\{^{1}H\}$ NMR spectrum of **1e** in CD_3CN.*

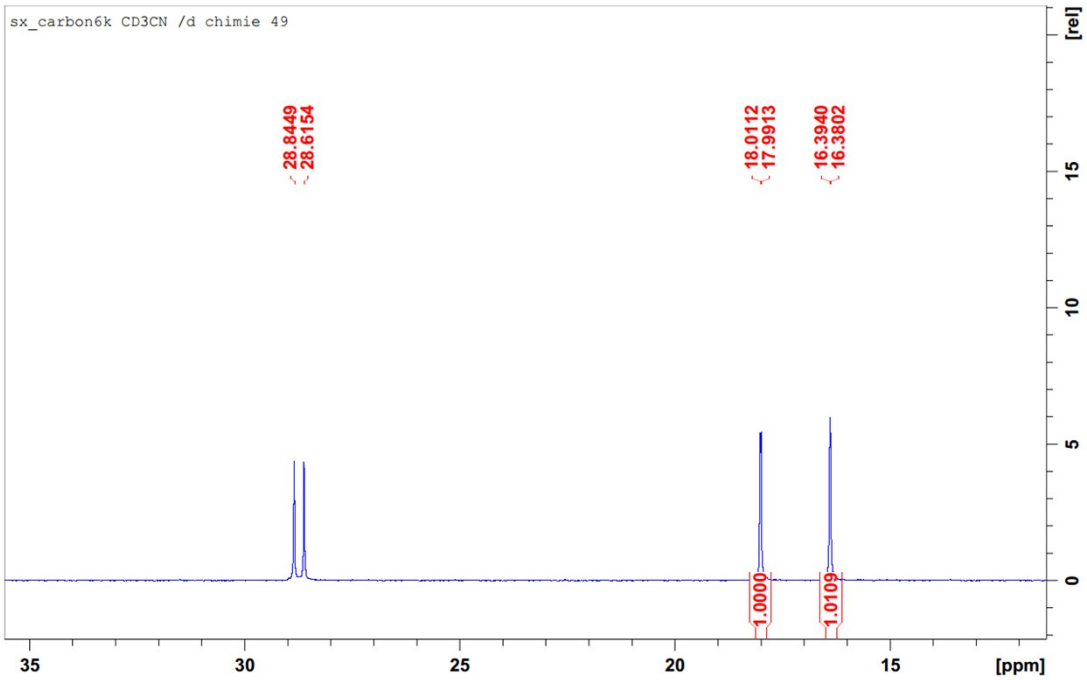

*Figure S44: $^{13}C\{^{1}H\}$ NMR spectrum of **1e** in CD_3CN; focus on aliphatic region.*

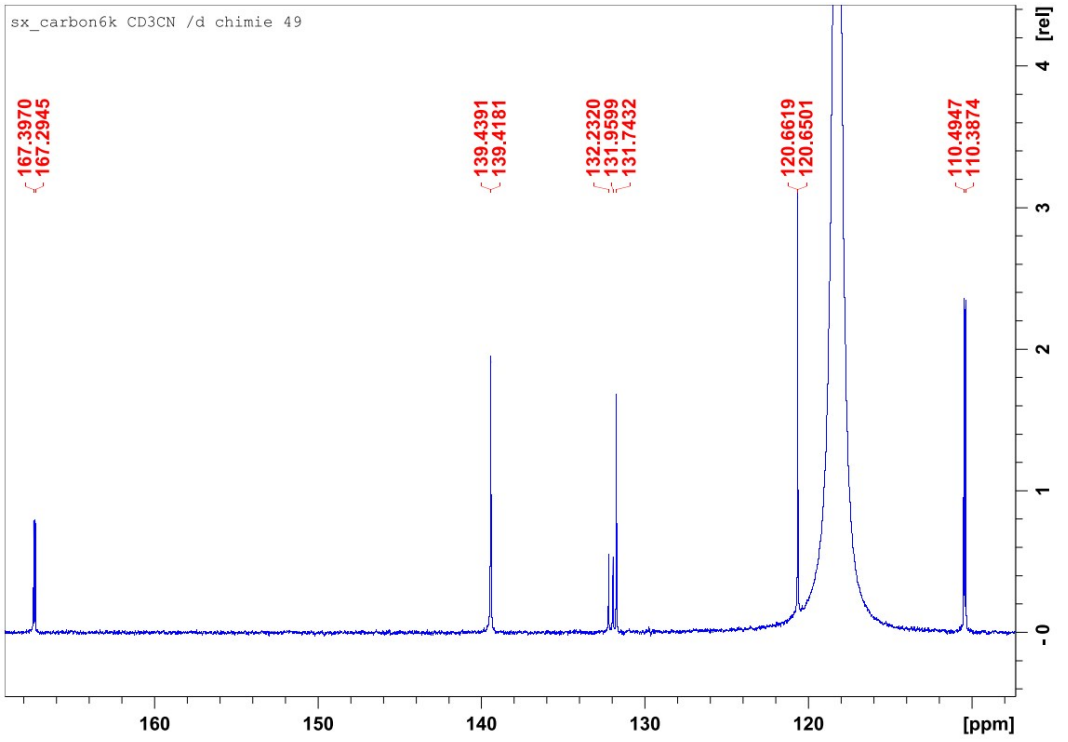

*Figure S45: $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in CD_3CN; focus on aromatic region.*

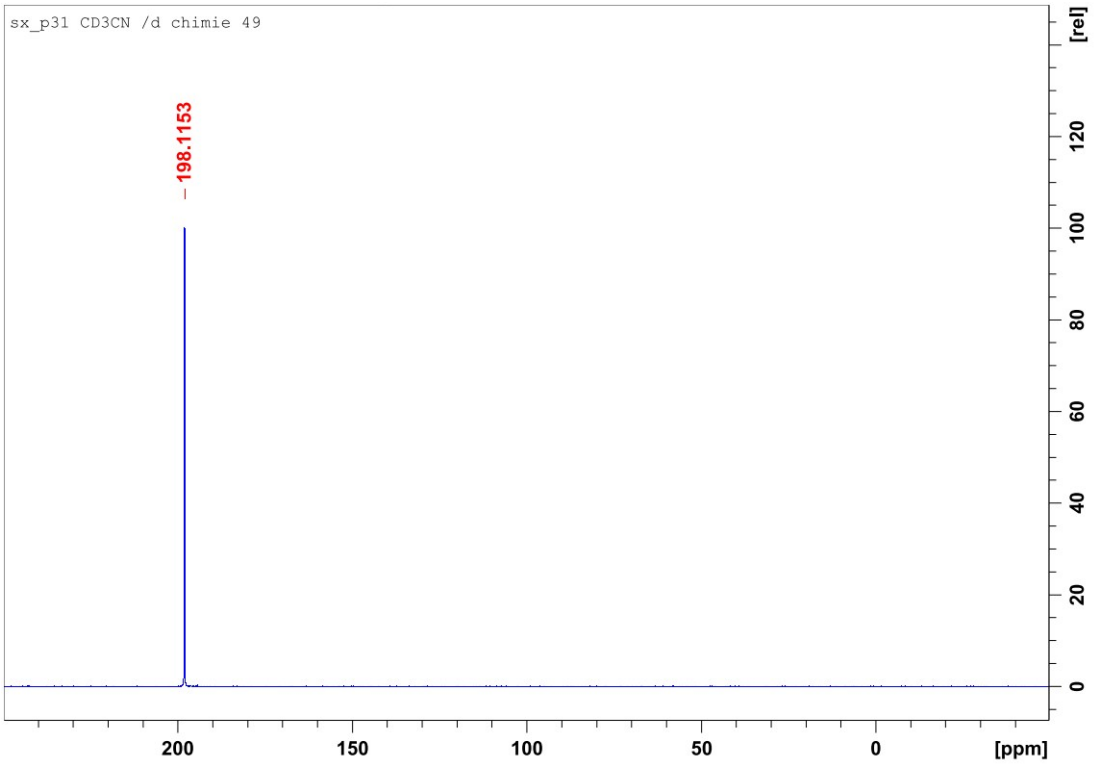

*Figure S46: $^{31}P\{^{1}H\}$ NMR spectrum of **1e** in CD_3CN.*

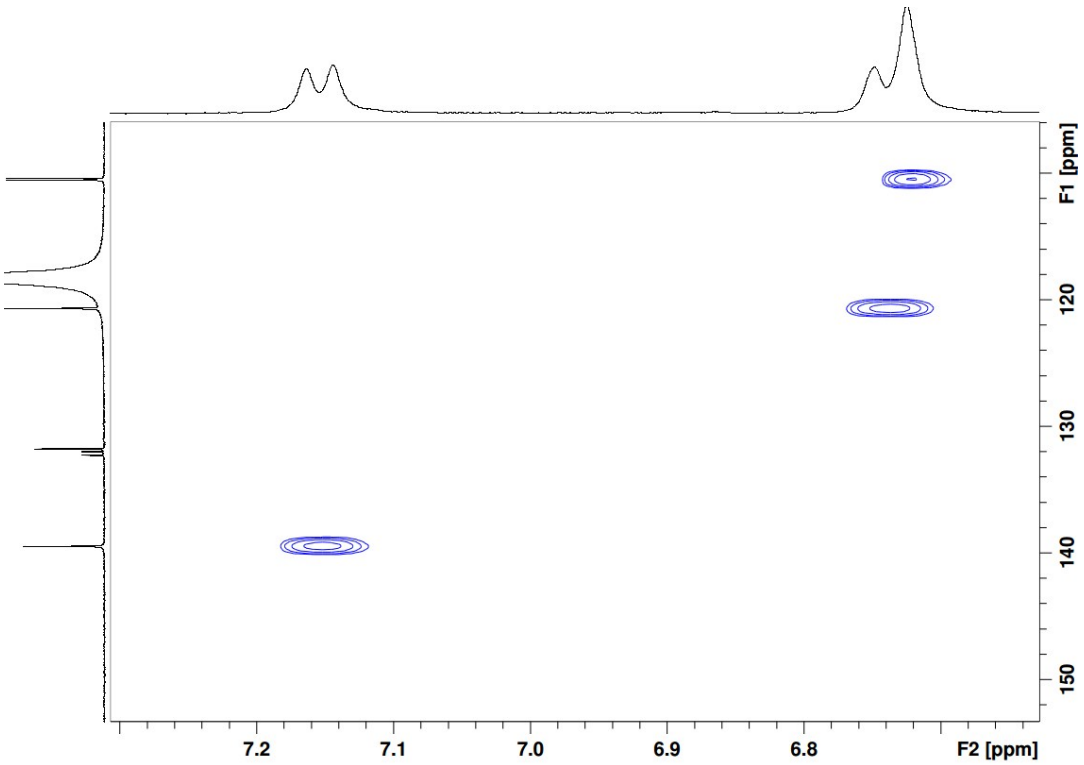

*Figure S47: HSQC spectrum of **1a** in CD_3CN; focus on aromatic region.*

1f

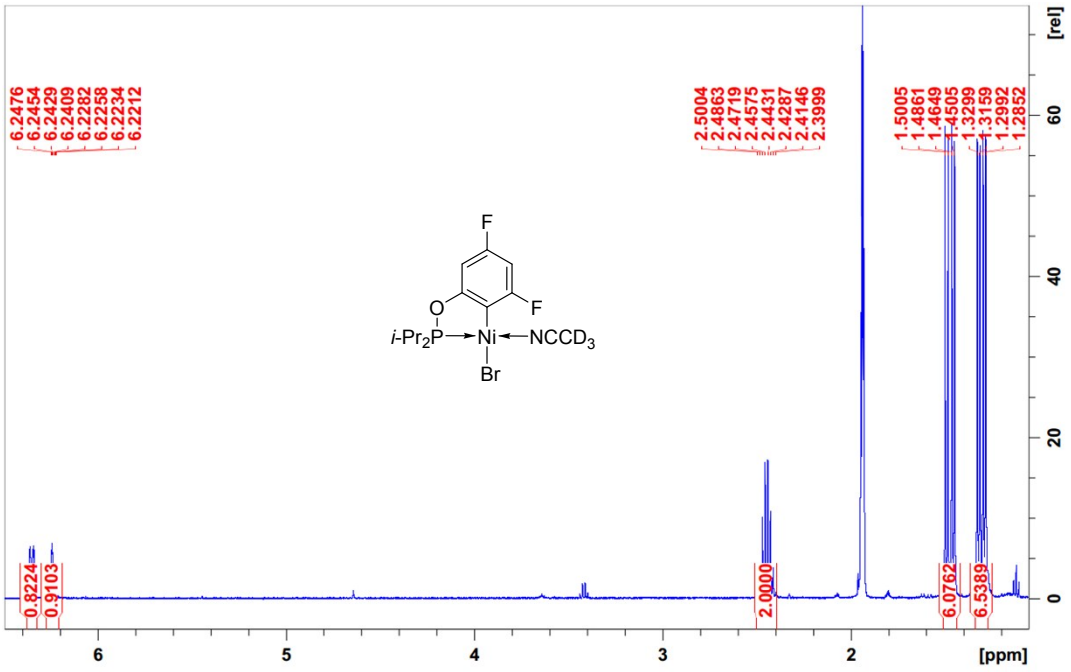

*Figure S48: Full ^{1}H NMR spectrum of **1f** in CD_3CN.*

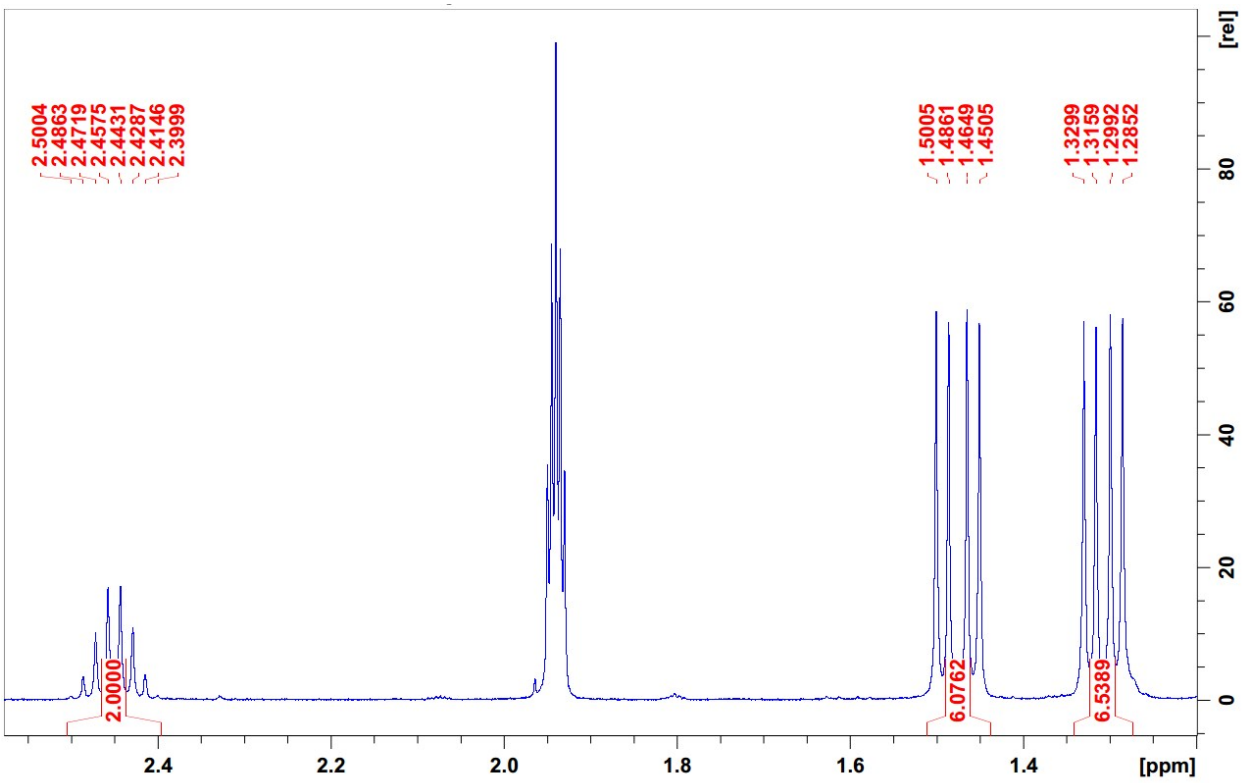

*Figure S49: ^{1}H NMR spectrum of **1f** in CD_3CN; focus on aliphatic region.*

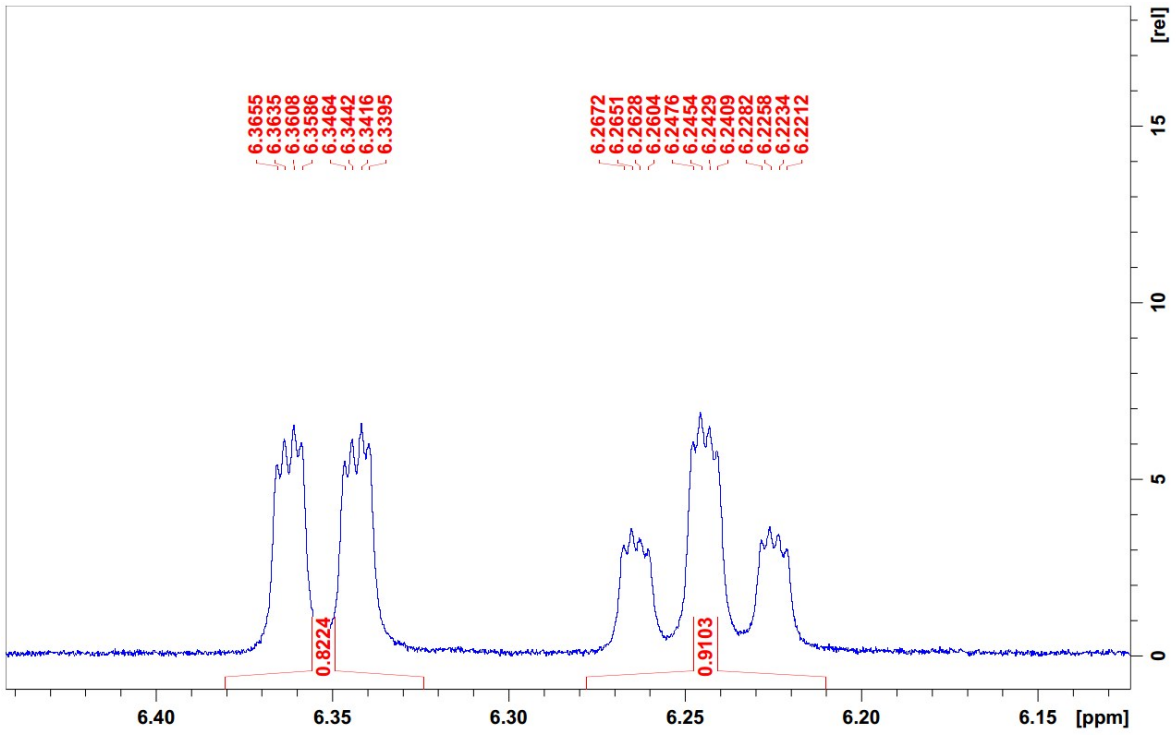

*Figure S50: ^{1}H NMR spectrum of **1f** in CD_3CN; focus on aromatic region.*

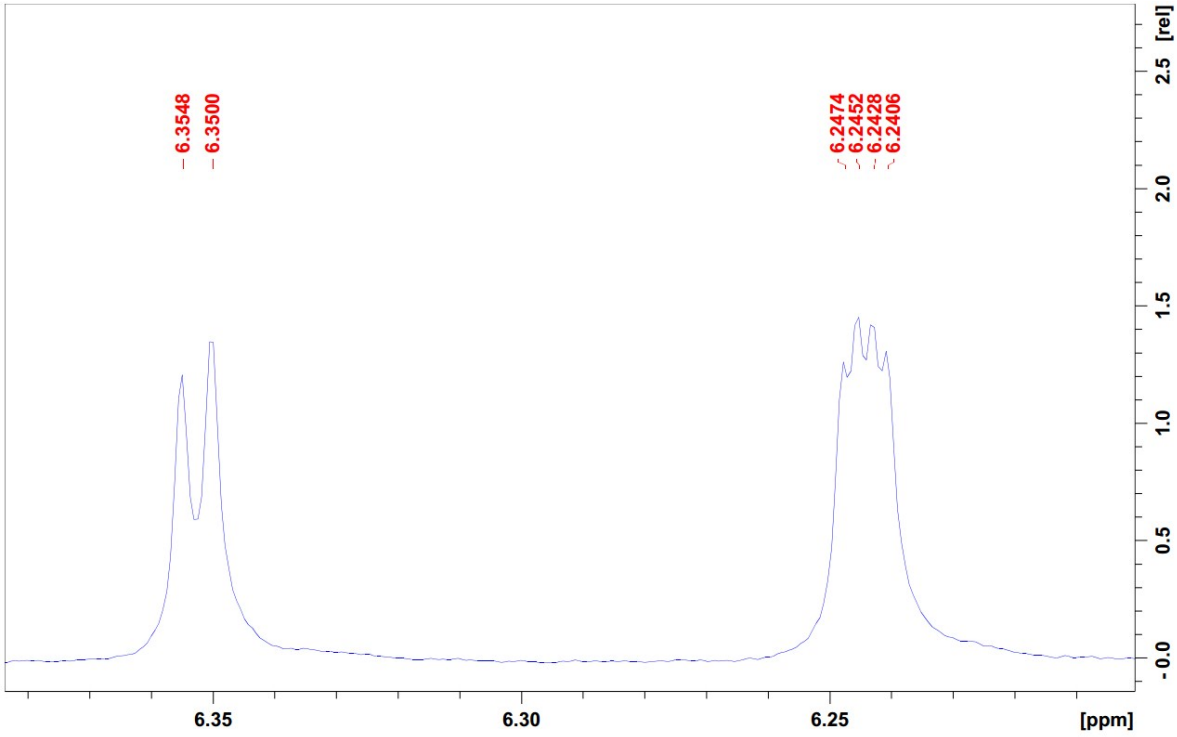

*Figure S51: $^{1}H\{^{19}F\}$ NMR spectrum of **1f** in CD_3CN; focus on aromatic region.*

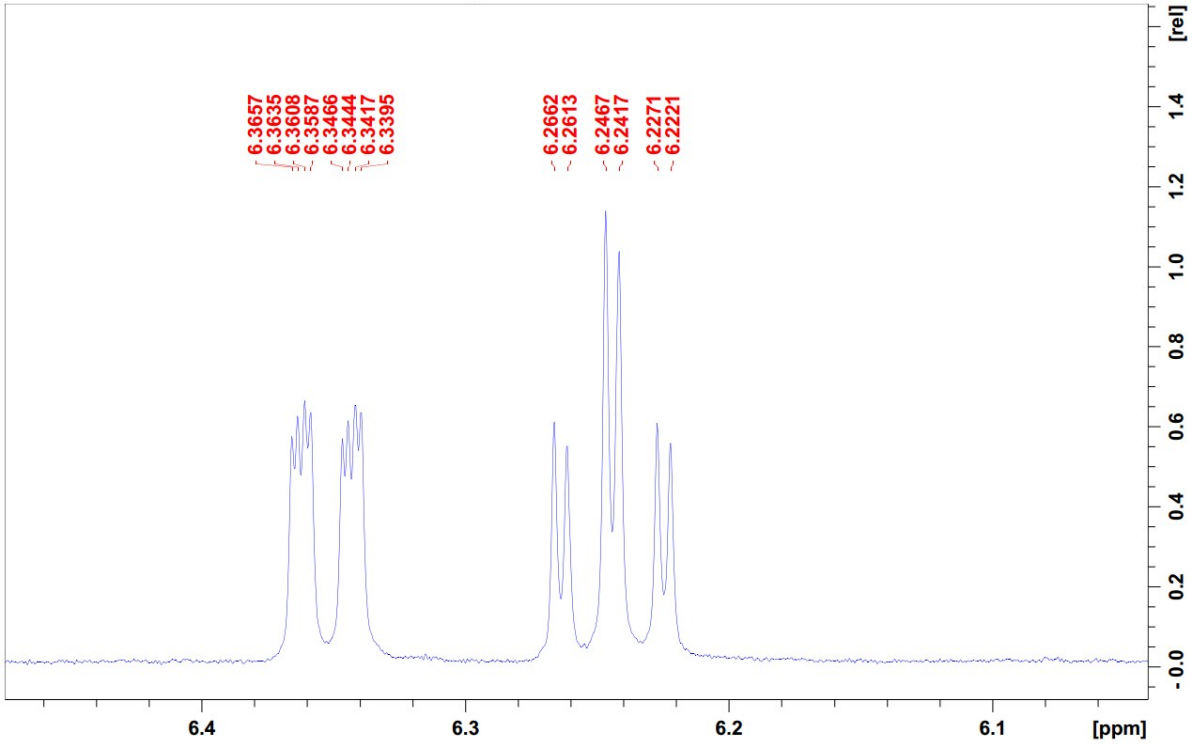

*Figure S52: $^{1}H\{^{19}F\}$ NMR spectrum of **1f** in CD_3CN; focus on aromatic region.*

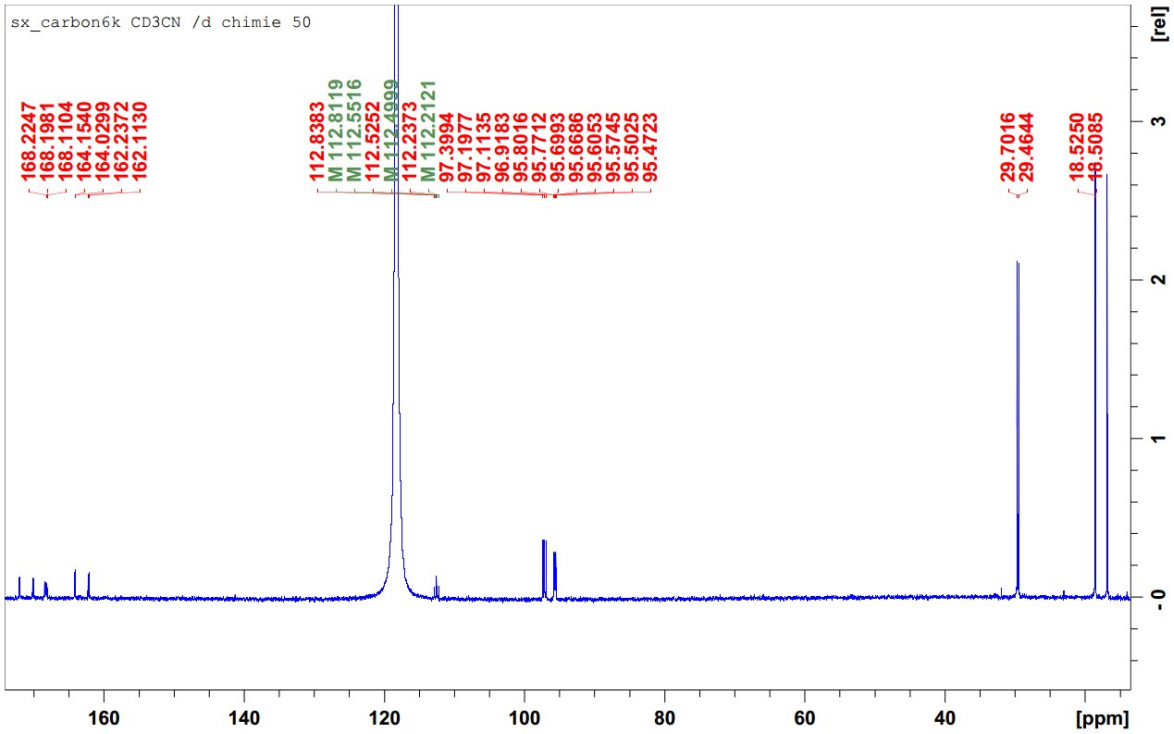

*Figure S53: Full $^{13}C\{^{1}H\}$ NMR spectrum of **1f** in CD_3CN.*

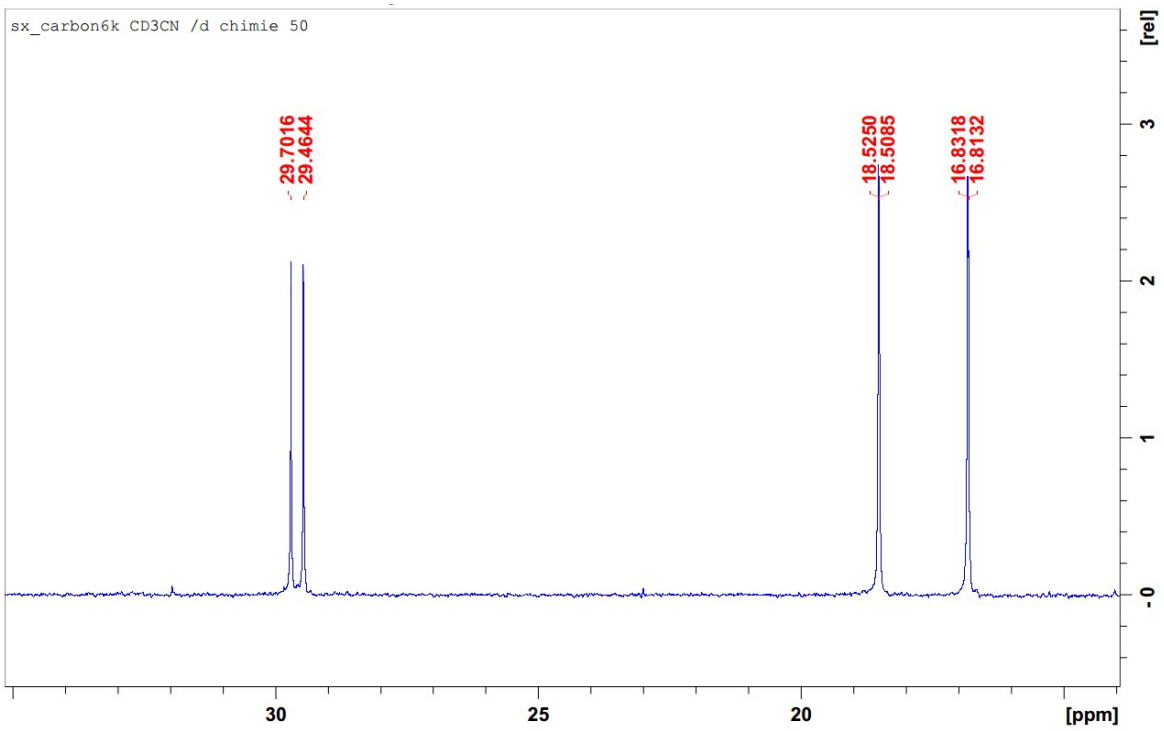

*Figure S54: $^{13}C\{^{1}H\}$ NMR spectrum of **1f** in CD_3CN; focus on aliphatic region.*

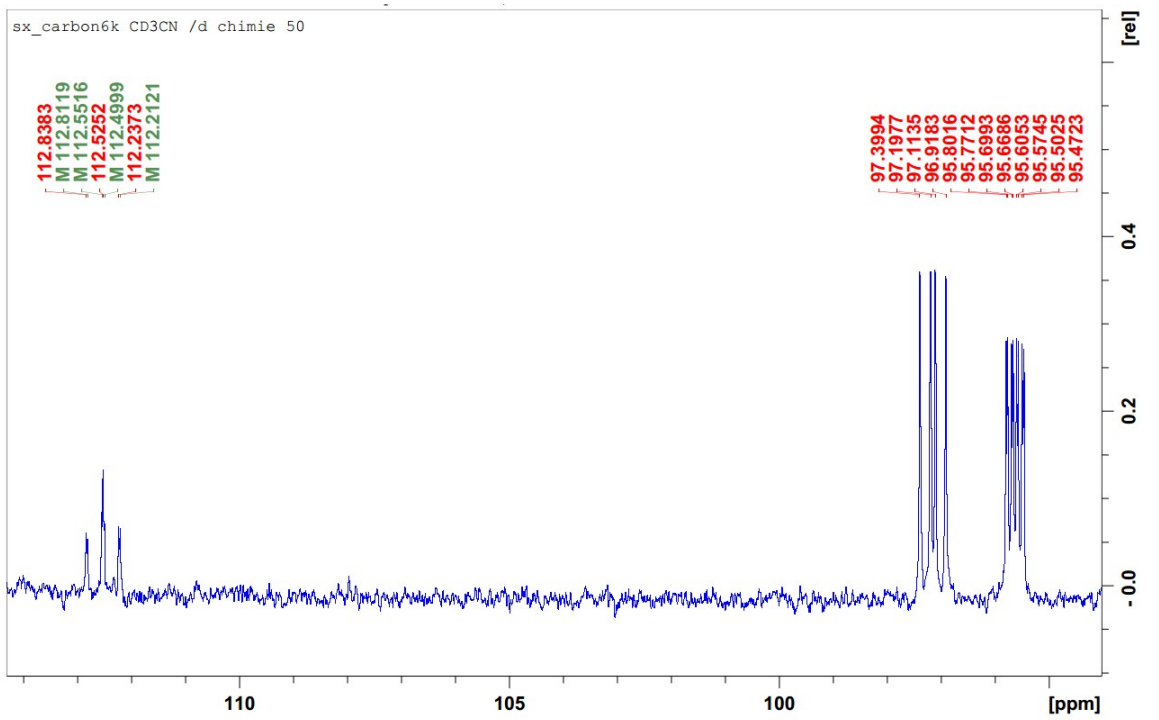

*Figure S55: $^{13}C\{^{1}H\}$ NMR spectrum of **1f** in CD_3CN; focus on aromatic region (I).*

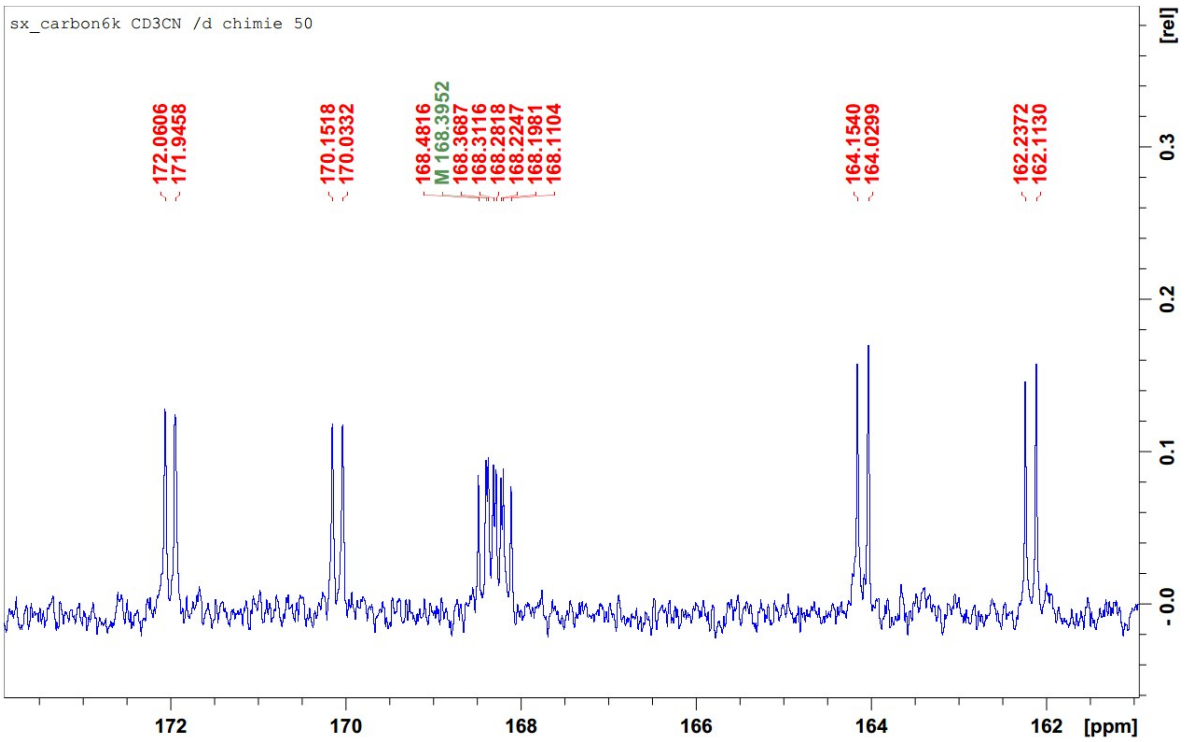

*Figure S56: $^{13}C\{^{1}H\}$ NMR spectrum of **1f** in CD_3CN; focus on aromatic region (II).*

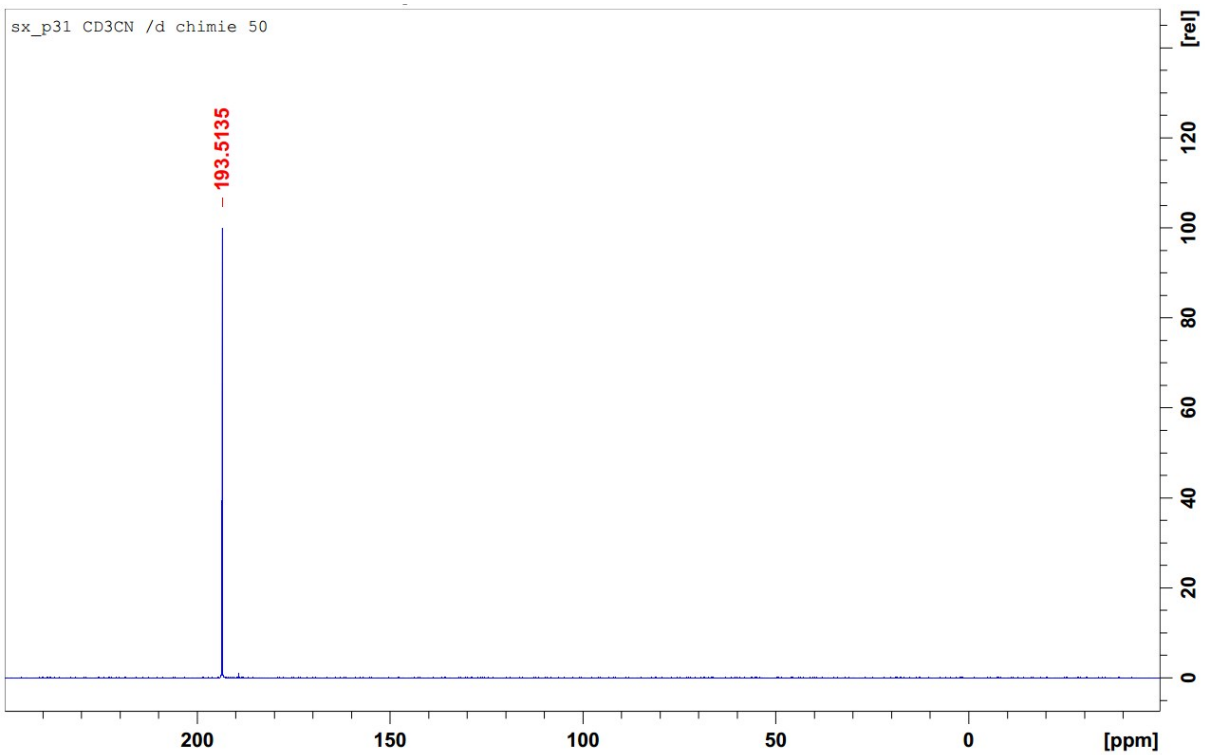

*Figure S57: $^{31}P\{^{1}H\}$ NMR spectrum of **1f** in CD_3CN.*

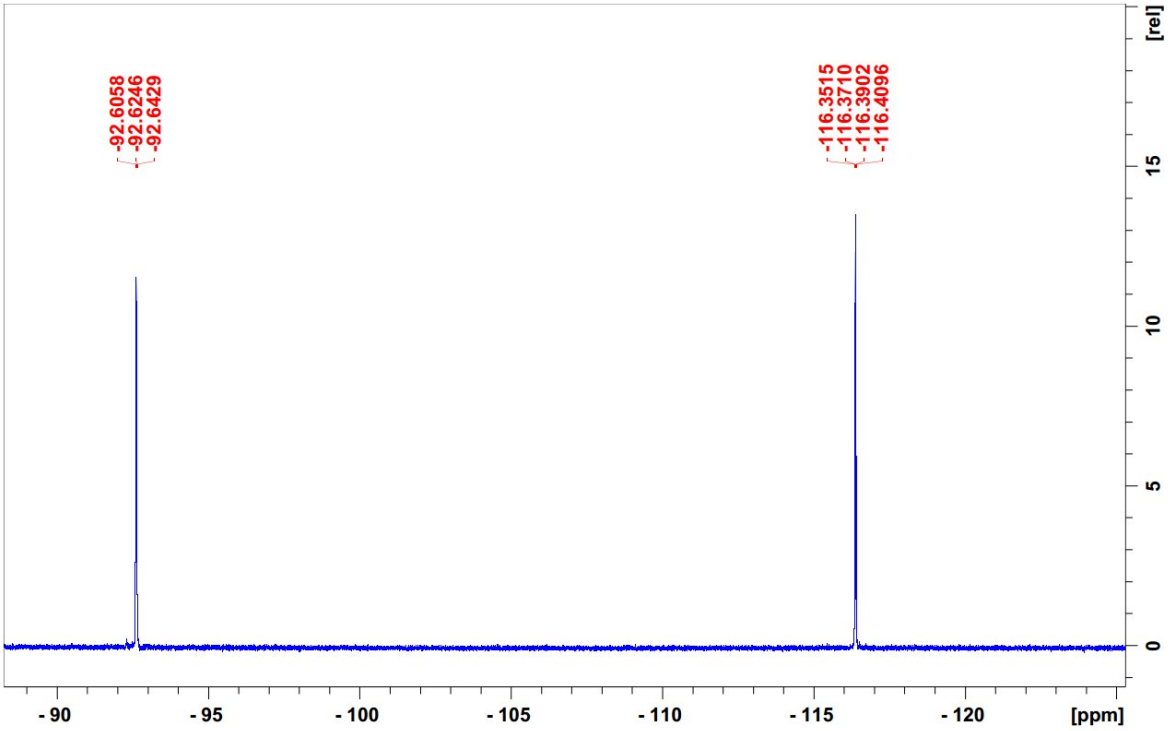

*Figure S58: $^{31}F\{^{1}H\}$ NMR spectrum of **1f** in CD_3CN.*

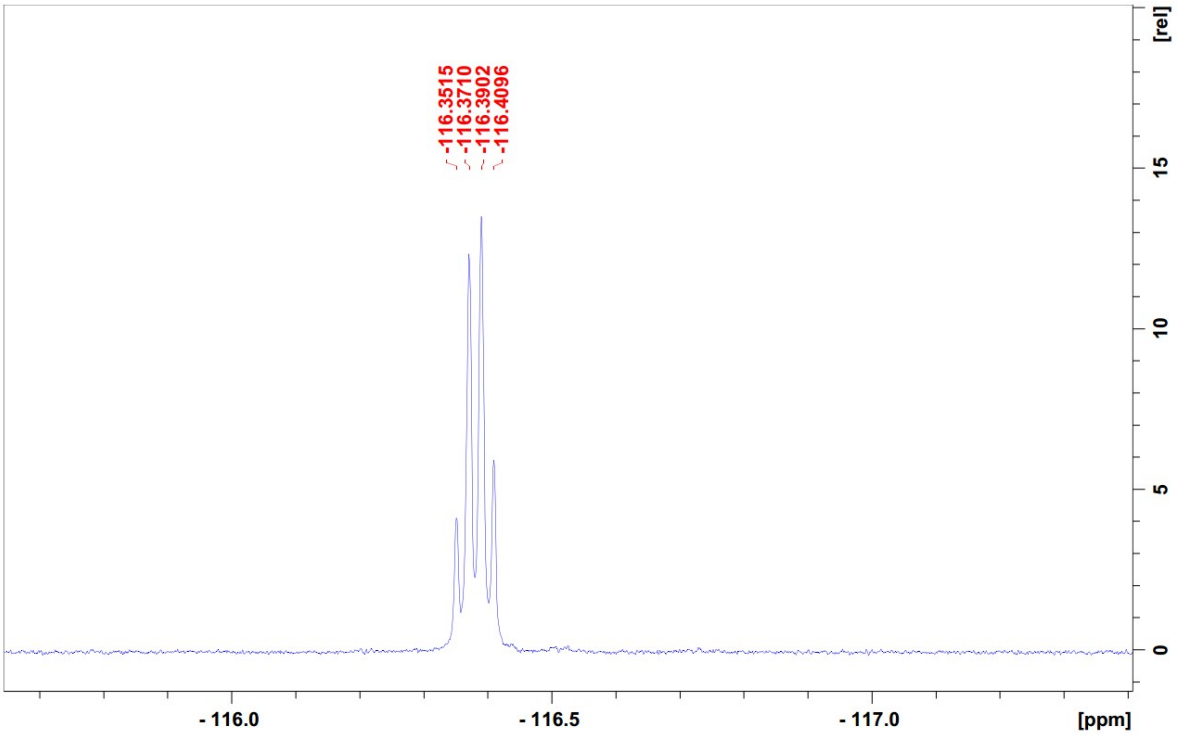

*Figure S59: $^{31}F\{^{1}H\}$ NMR spectrum of **1f** in CD_3CN; focus on $C5_{Ar}$-F.*

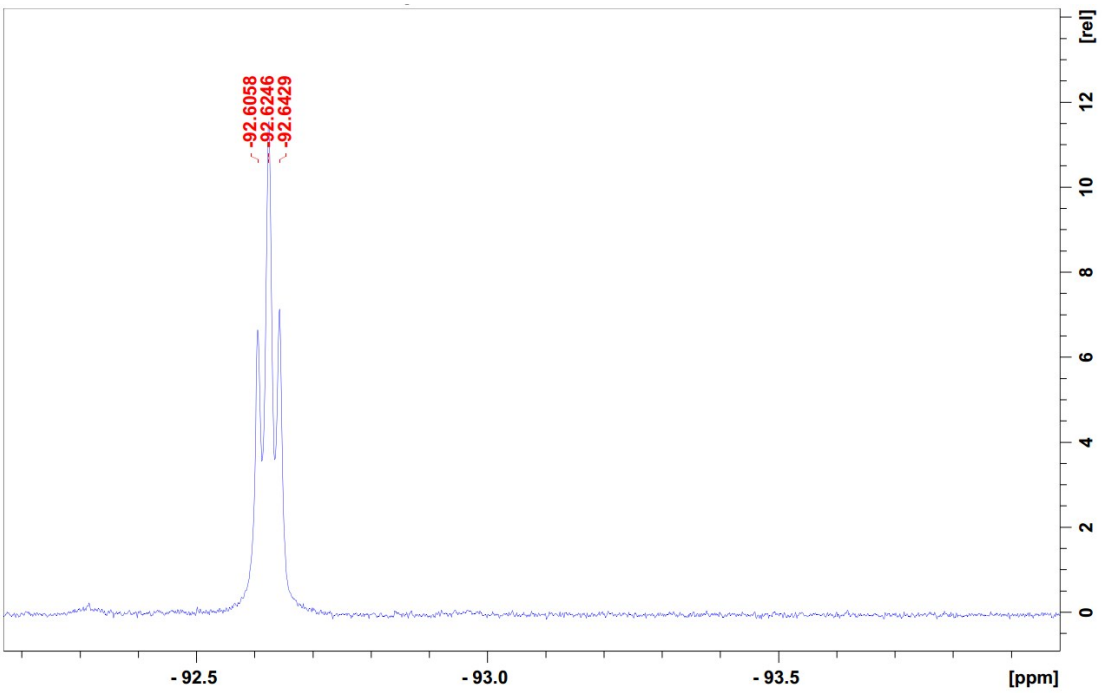

*Figure S60: $^{31}F\{^{1}H\}$ NMR spectrum of **1f** in CD_3CN; focus on $C3_{Ar}$-F.*

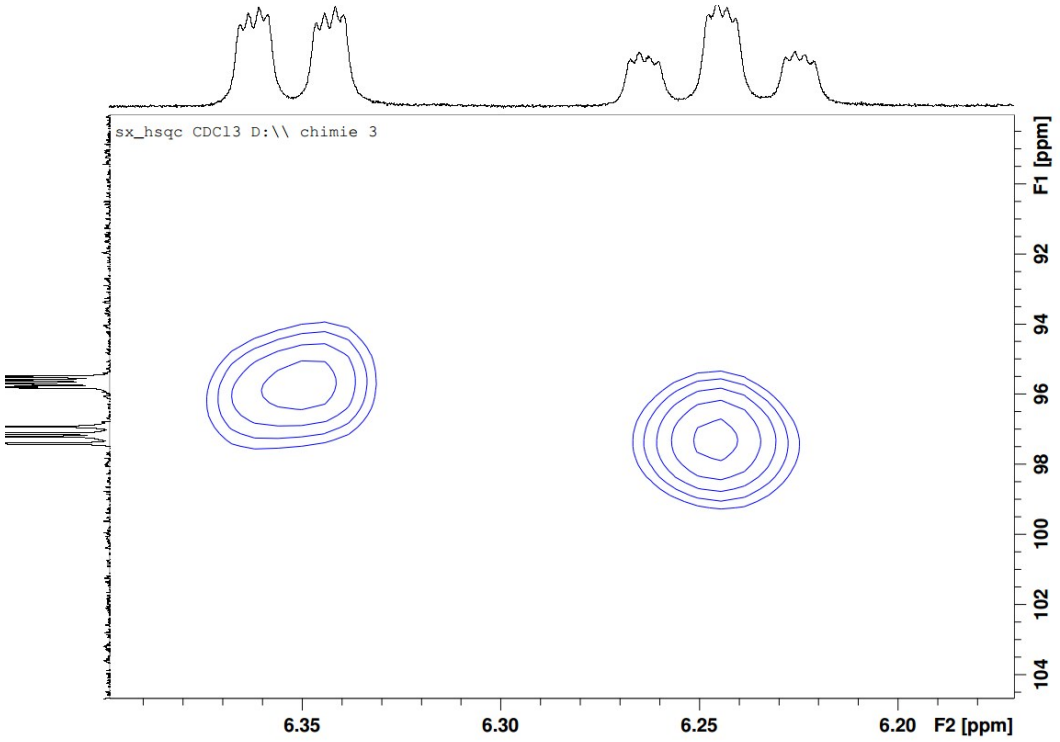

*Figure S61: HSQC spectrum of **1f** in CD_3CN; focus on aromatic region.*

1i-NCMe

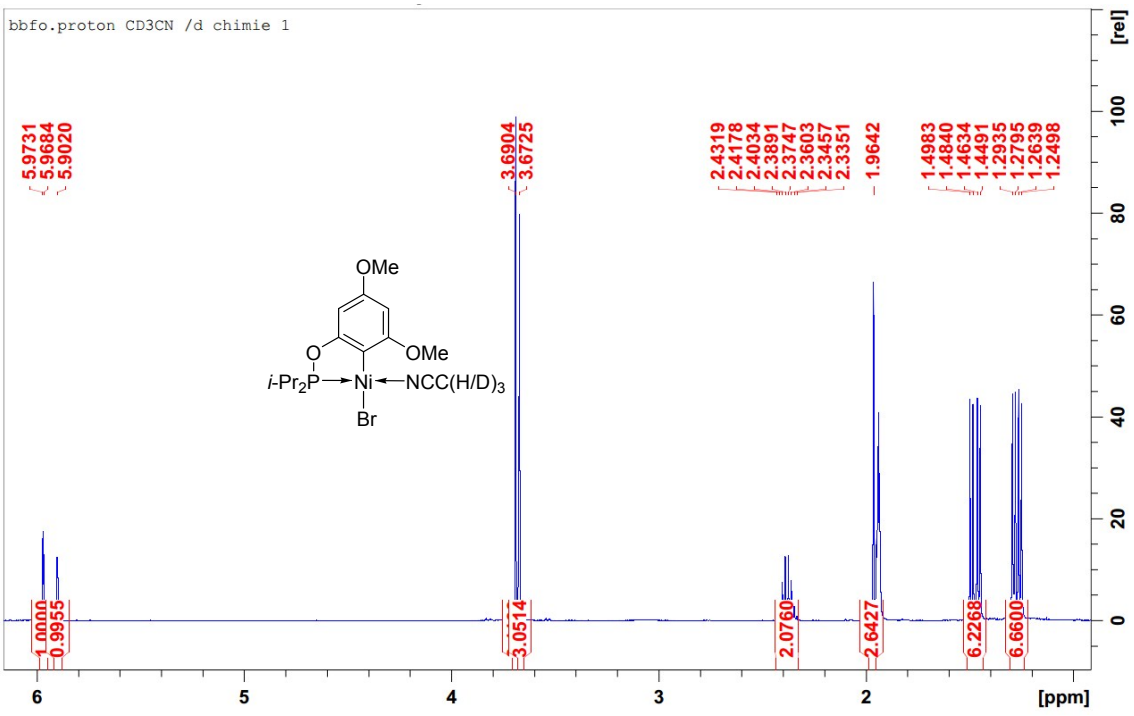

*Figure S62: Full ^{1}H NMR spectrum of **1i-NCMe** in CD_3CN.*

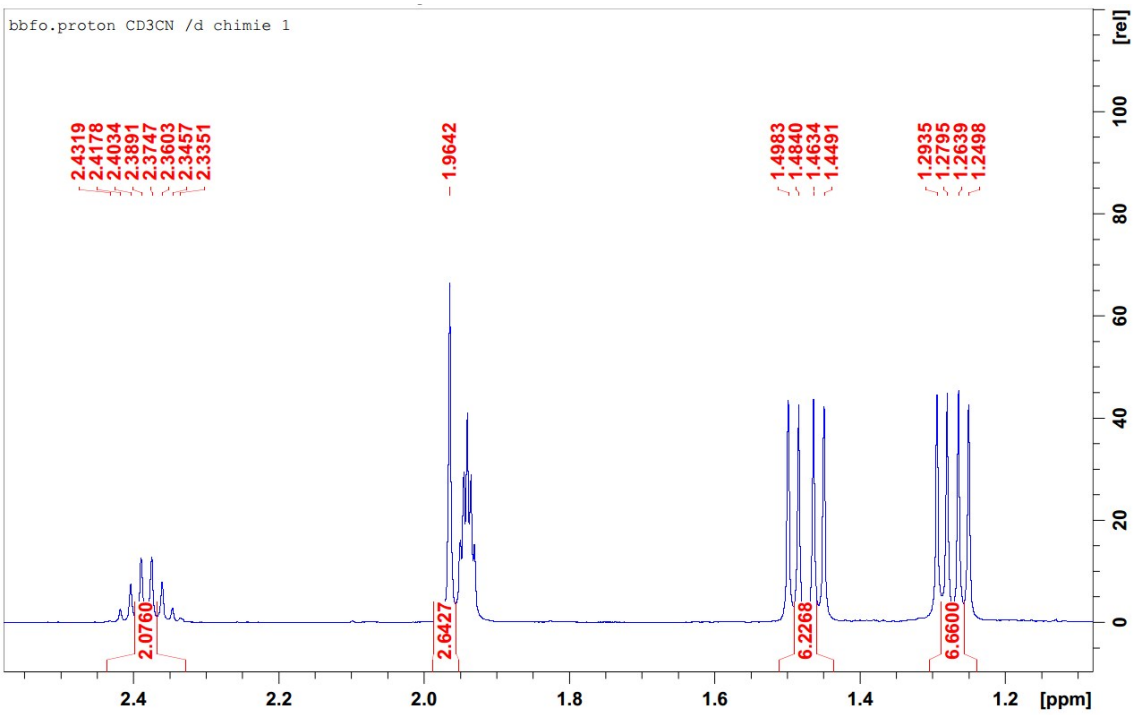

*Figure S63: ^{1}H NMR spectrum of **1i-NCMe** in CD_3CN; focus on aliphatic region.*

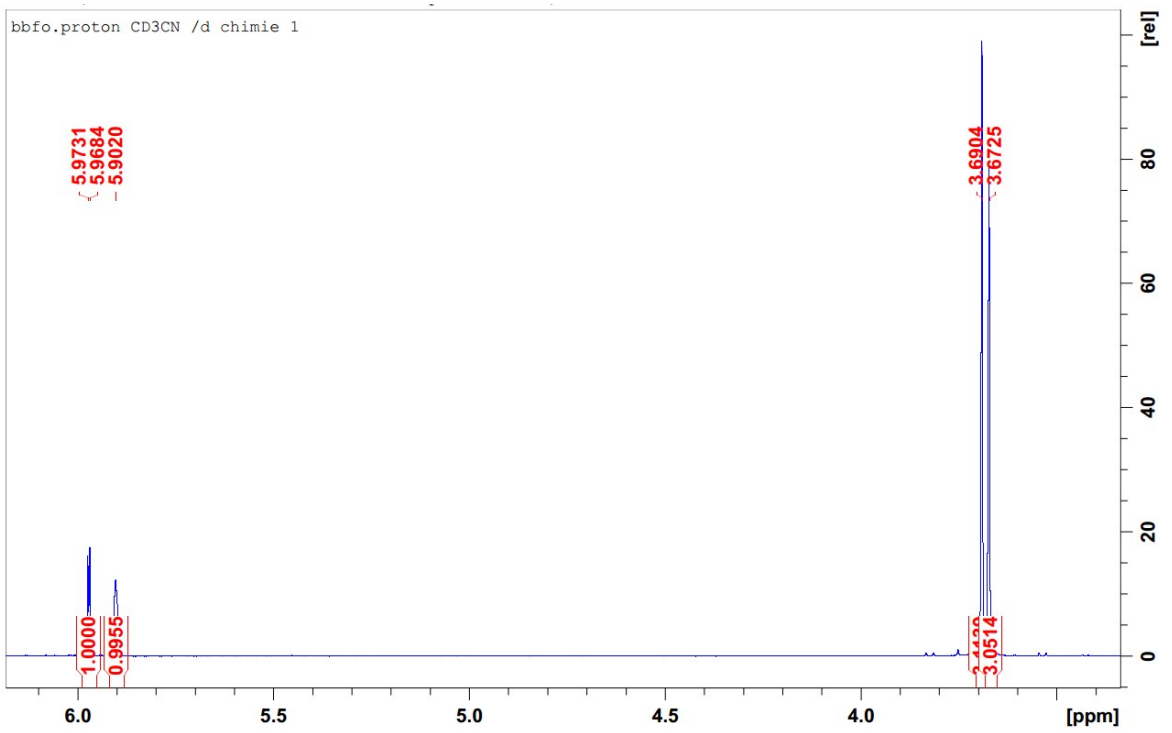

*Figure S64: ^{1}H NMR spectrum of **1i-NCMe** in CD_3CN; focus on O-CH_3 and aromatic region.*

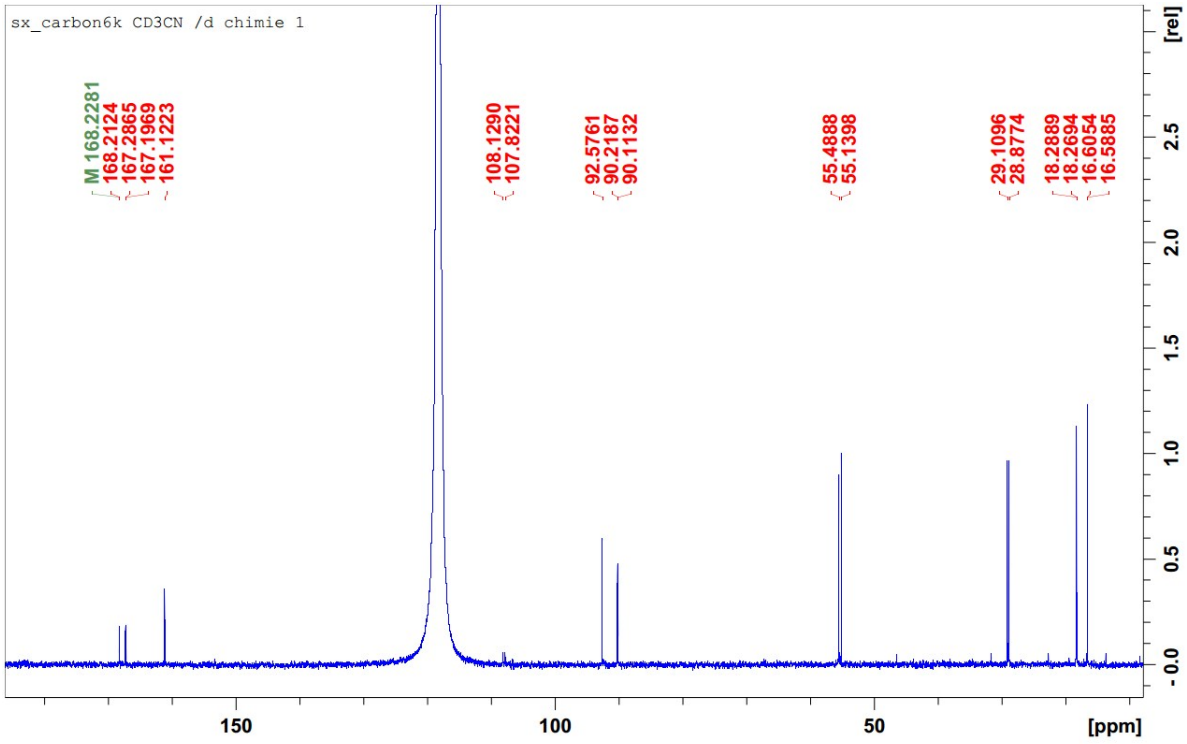

*Figure S65: Full $^{13}C\{^{1}H\}$ NMR spectrum of **1i-NCMe** in CD_3CN.*

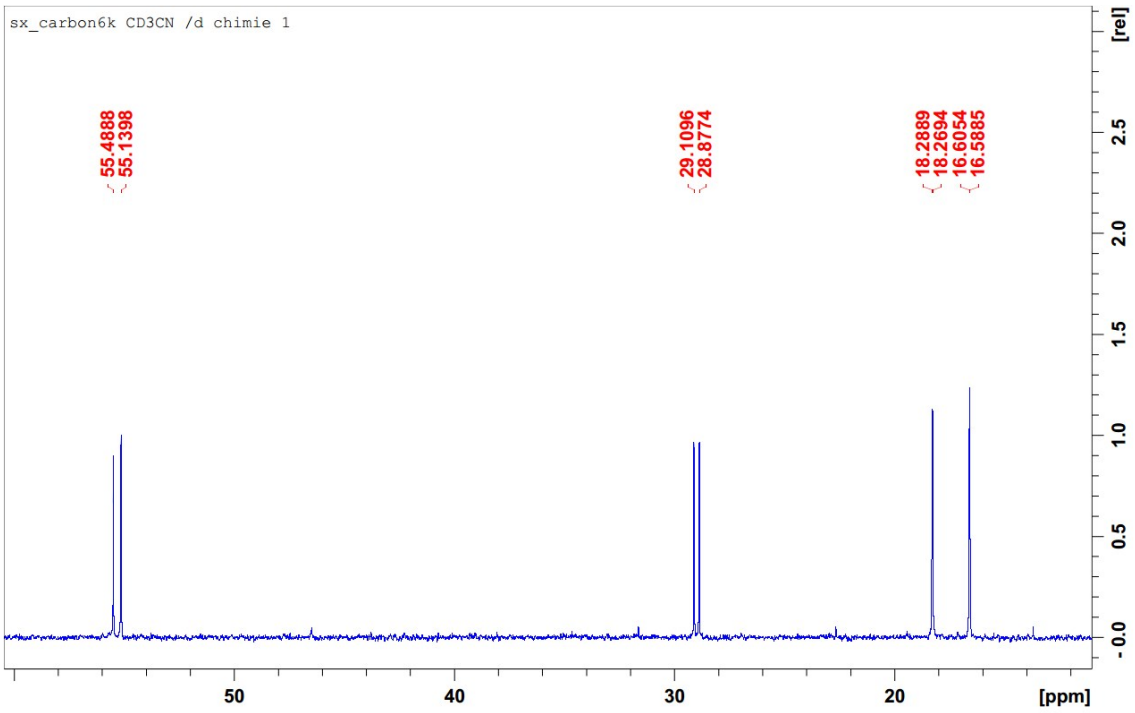

*Figure S66: $^{13}C\{^{1}H\}$ NMR spectrum of **1i-NCMe** in CD_3CN; focus on aliphatic region.*

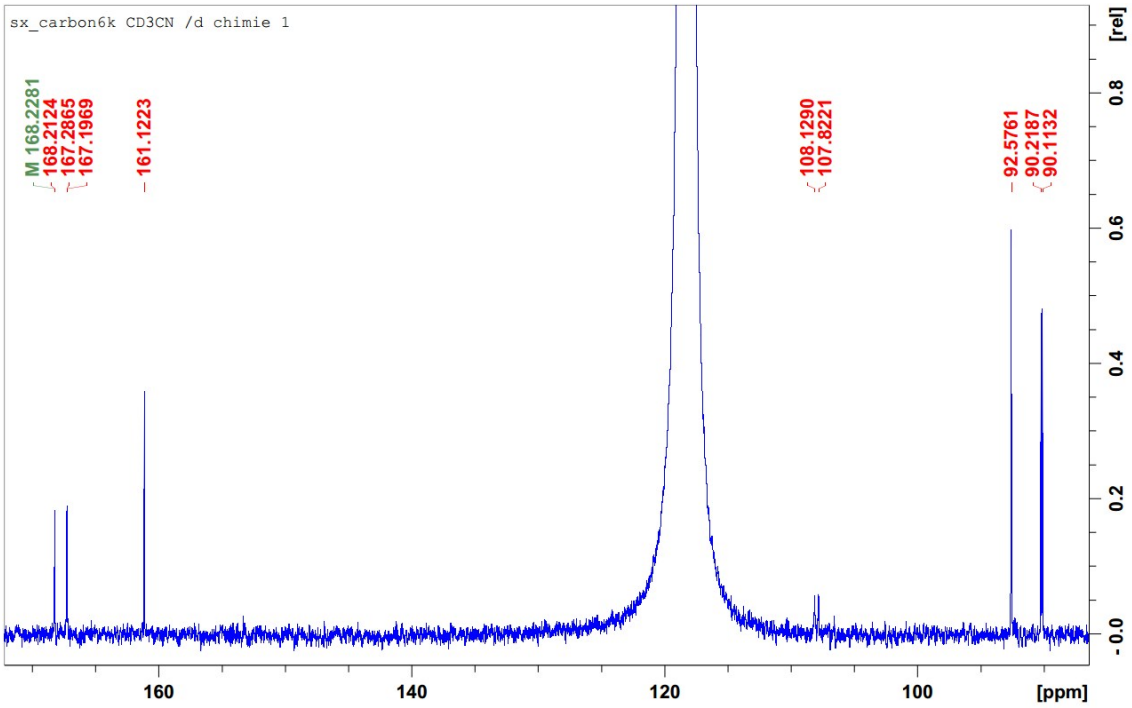

*Figure S67: $^{13}C\{^{1}H\}$ NMR spectrum of **1i-NCMe** in CD_3CN; focus on aromatic region.*

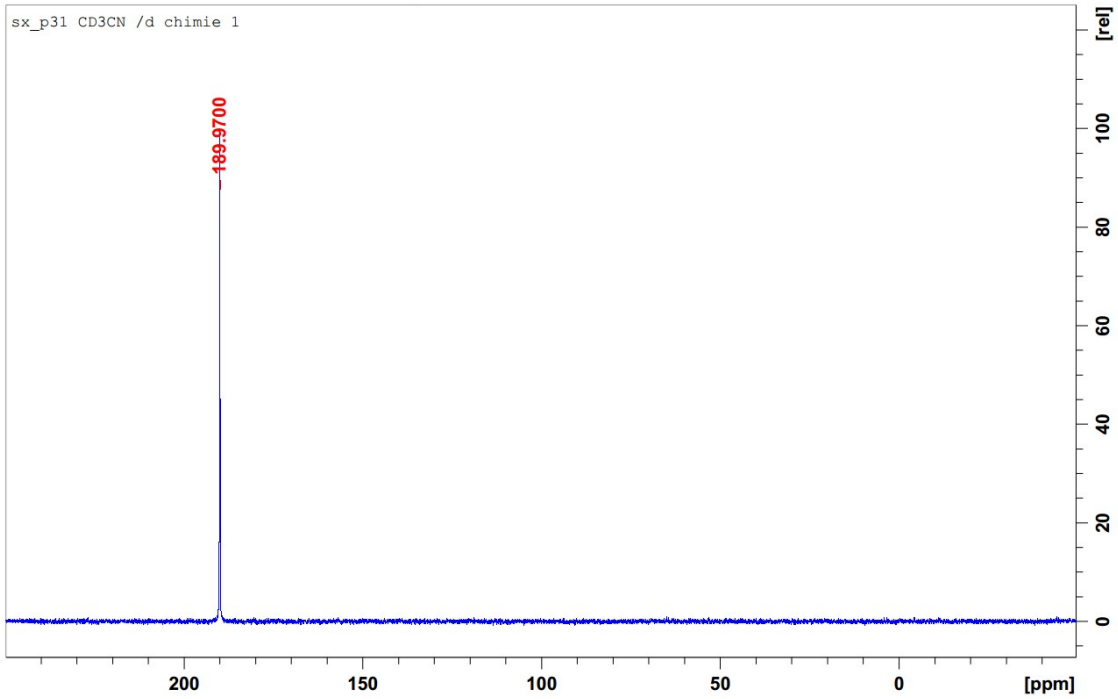

*Figure S68: $^{31}P\{^{1}H\}$ NMR spectrum of **1i-NCMe** in CD_3CN.*

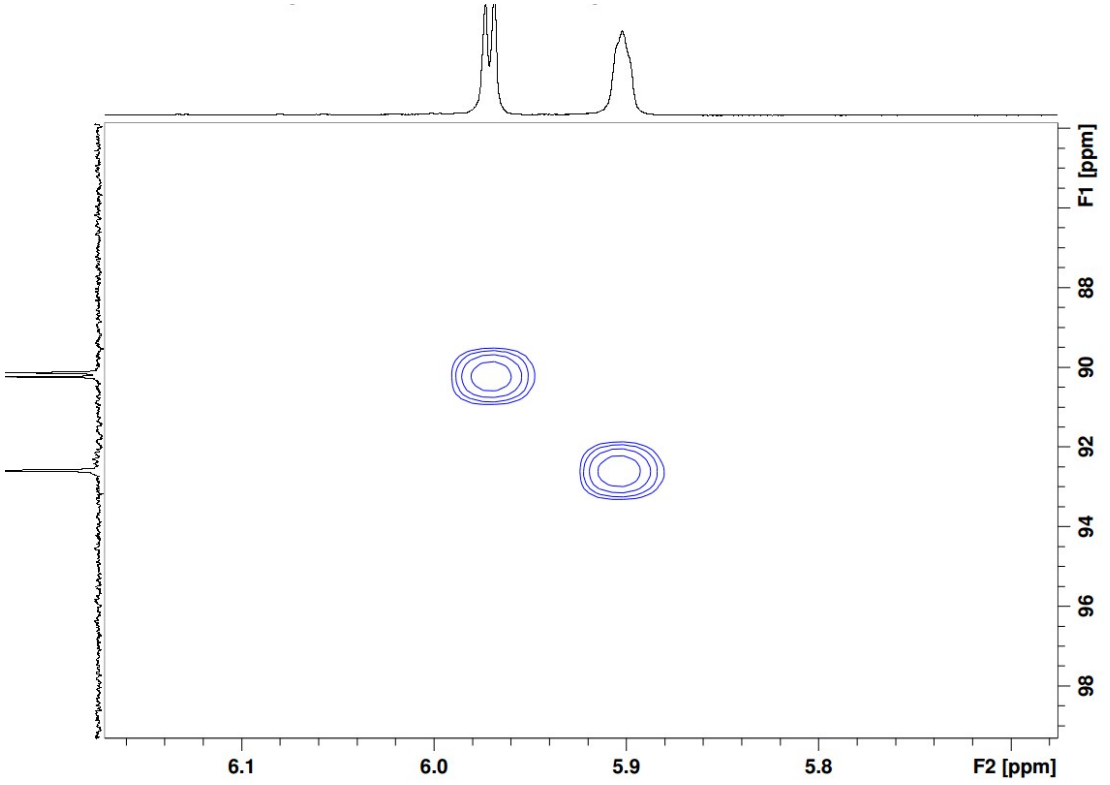

*Figure S69: HSQC spectrum of **1i-NCMe** in CD_3CN; focus on aromatic region.*

1j

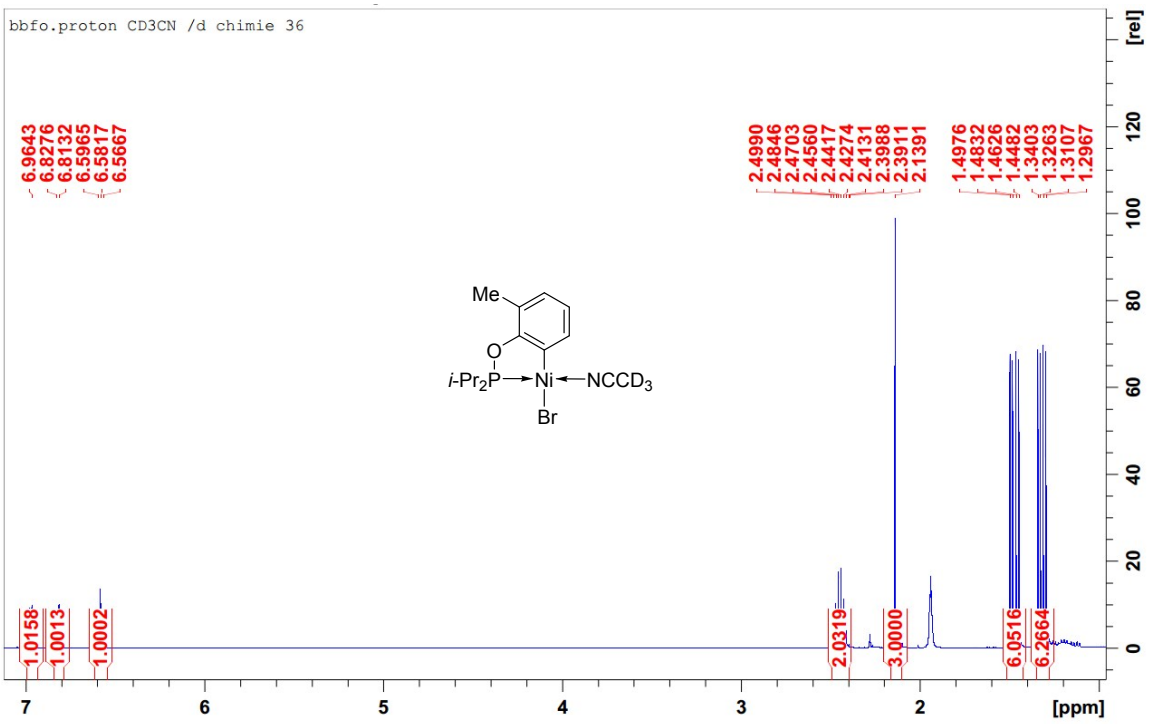

*Figure S70: Full ^{1}H NMR spectrum of **1j** in CD_3CN.*

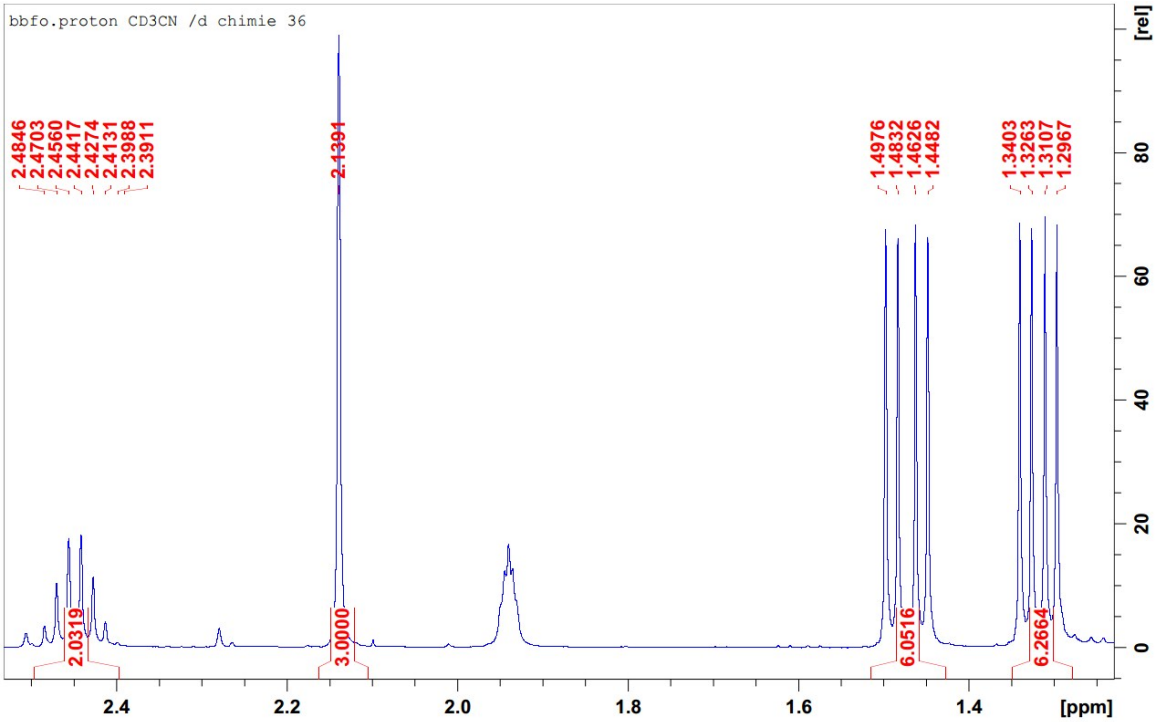

*Figure S71: ^{1}H NMR spectrum of **1j** in CD_3CN; focus on aliphatic region.*

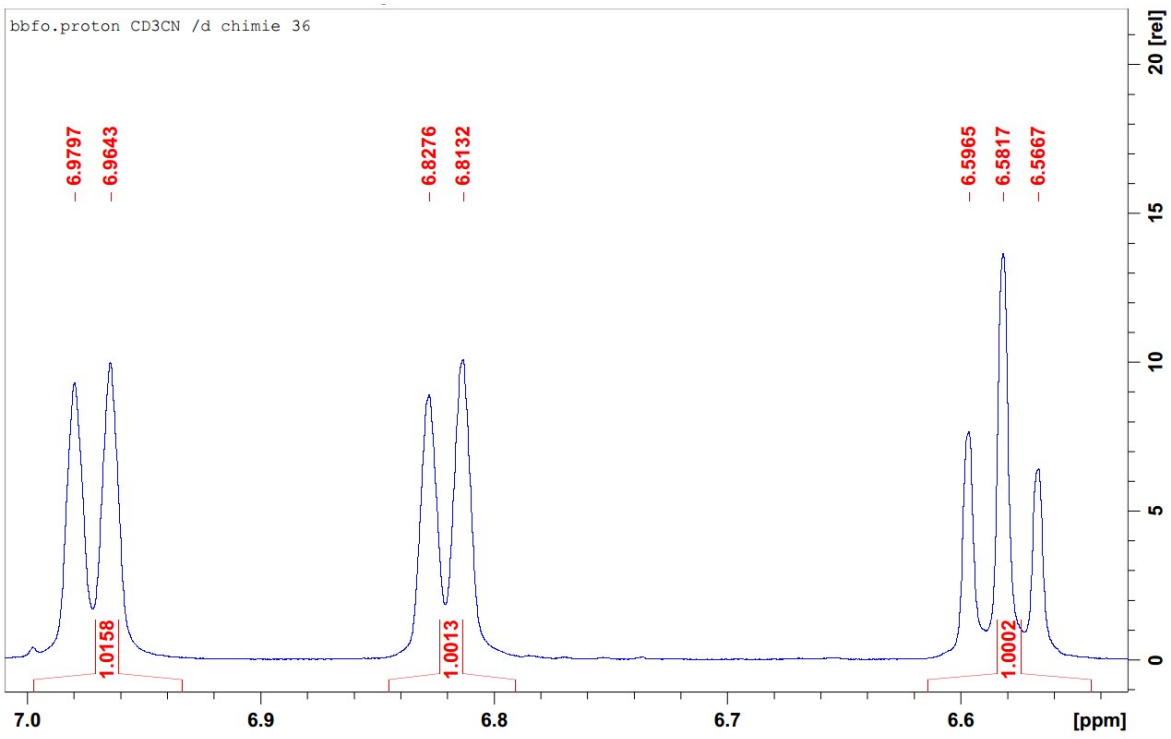

*Figure S72: ^{1}H NMR spectrum of **1j** in CD_3CN; focus on aromatic region.*

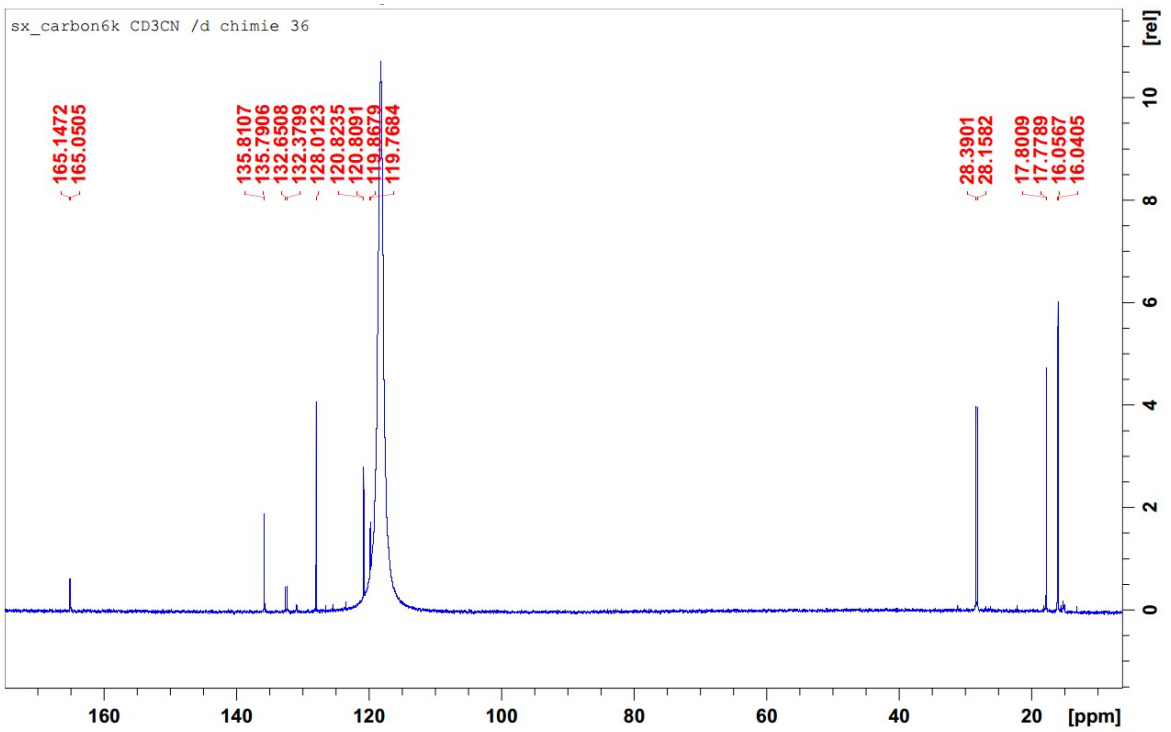

*Figure S73: Full $^{13}C\{^{1}H\}$ NMR spectrum of **1j** in CD_3CN.*

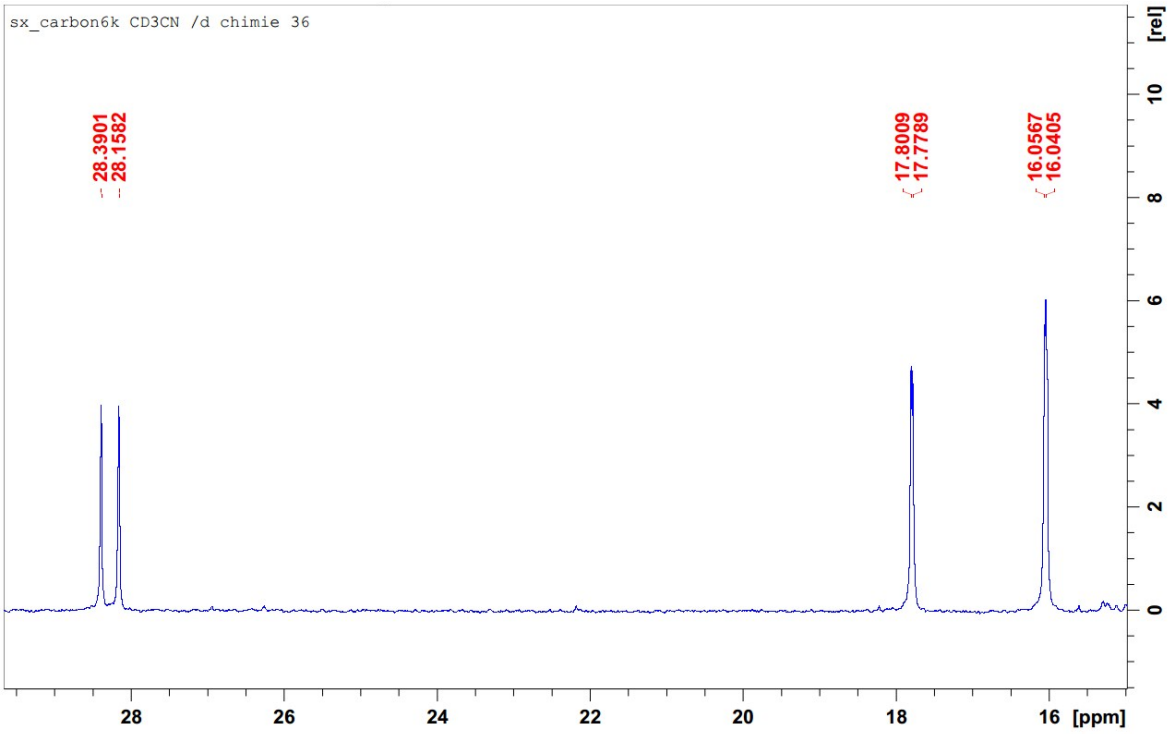

*Figure S74: $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in CD_3CN; focus on aliphatic region.*

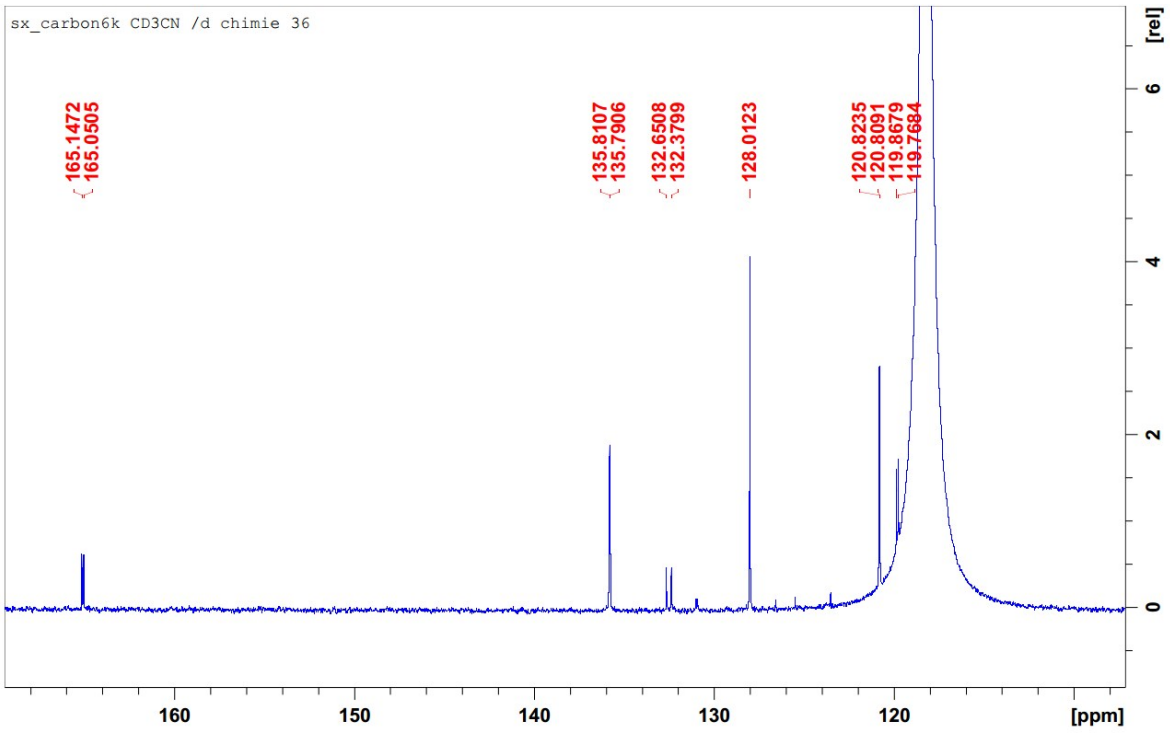

*Figure S75: $^{13}C\{^{1}H\}$ NMR spectrum of **1j** in CD_3CN; focus on aromatic region.*

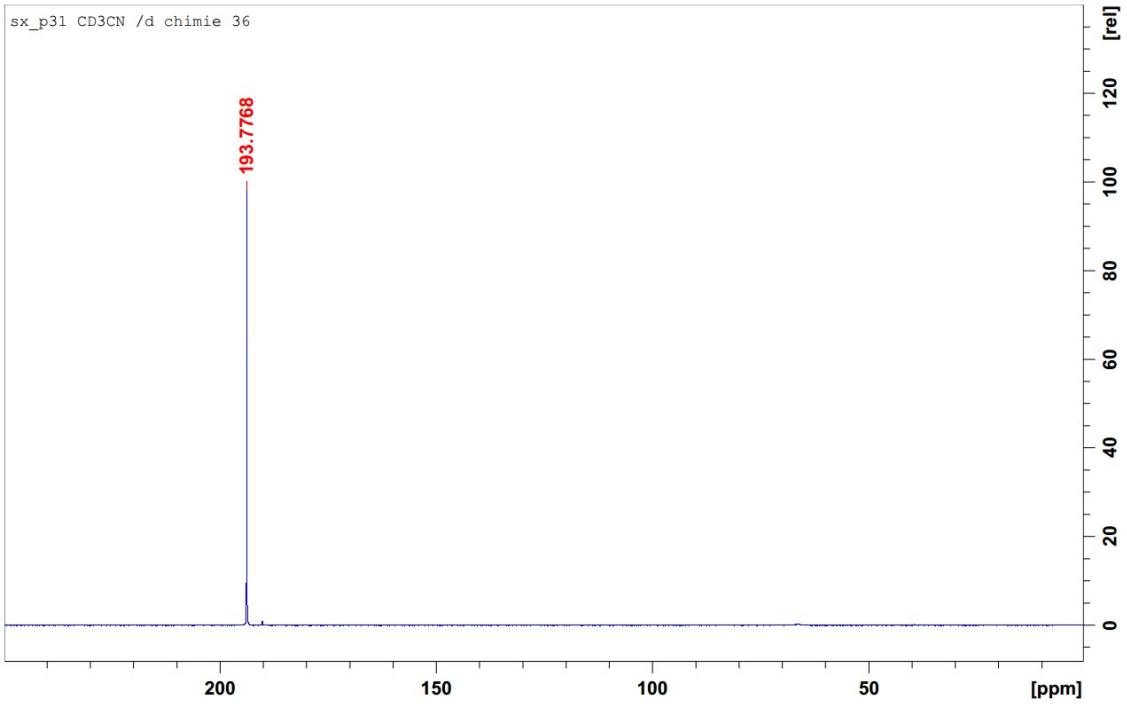

*Figure S76: $^{31}P\{^{1}H\}$ NMR spectrum of **1j** in CD_3CN.*

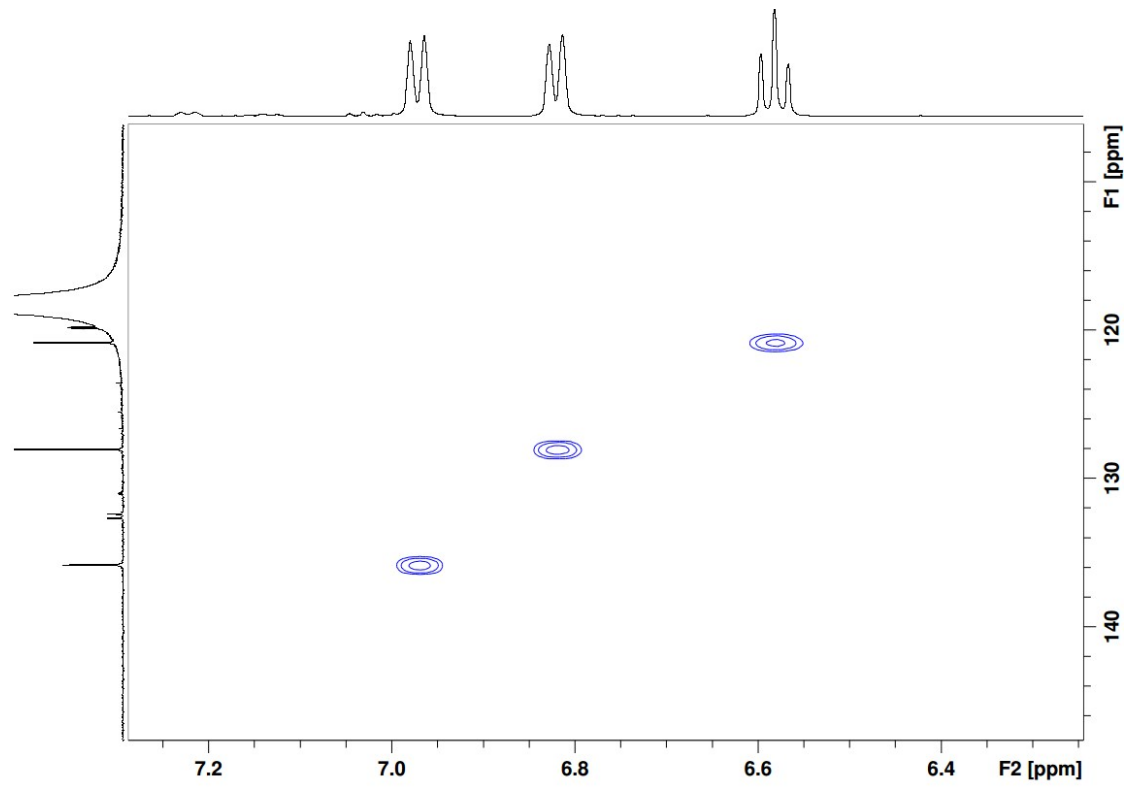

*Figure S77: HSQC spectrum of **1j** in CD_3CN; focus on aromatic region.*

1k

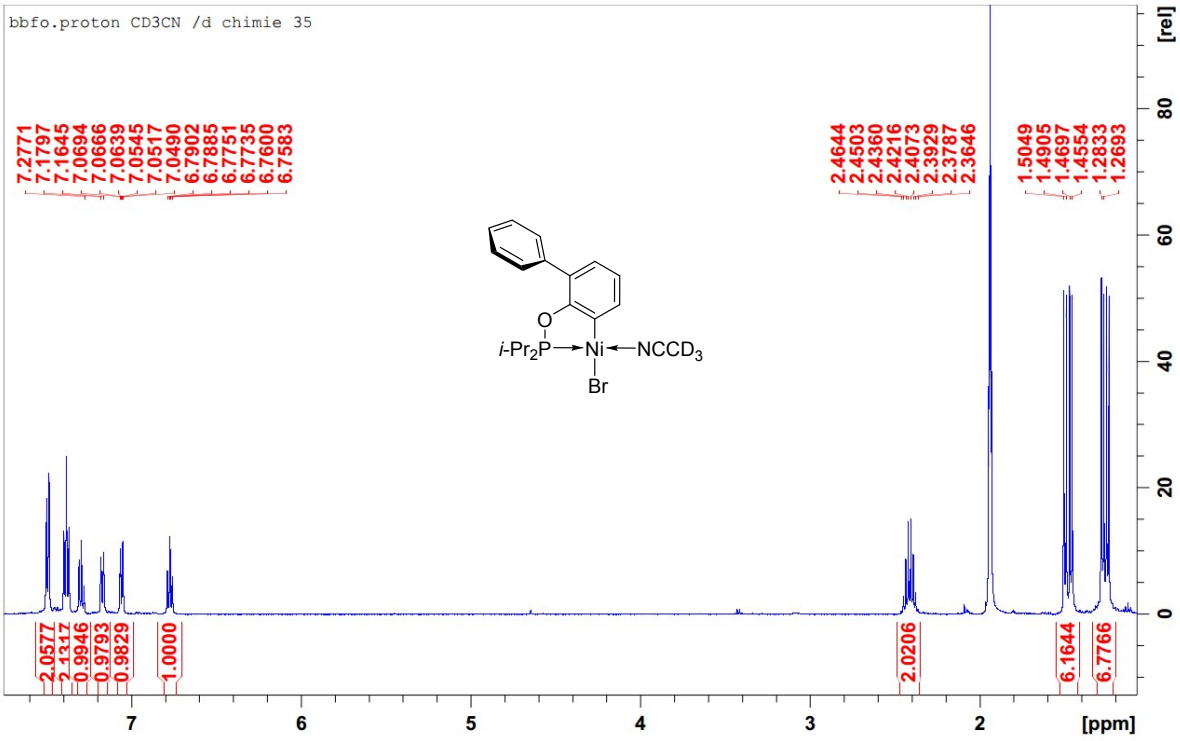

*Figure S78: Full ^{1}H NMR spectrum of **1k** in CD_3CN.*

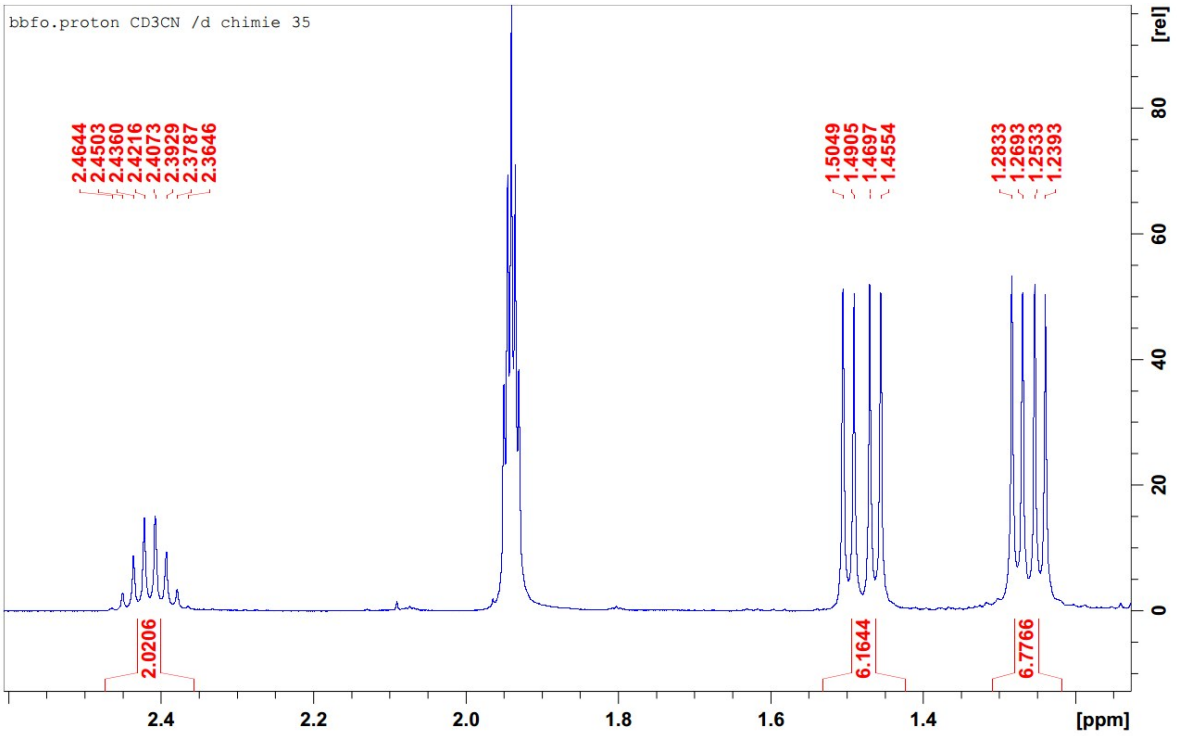

*Figure S79: ^{1}H NMR spectrum of **1k** in CD_3CN; focus on aliphatic region.*

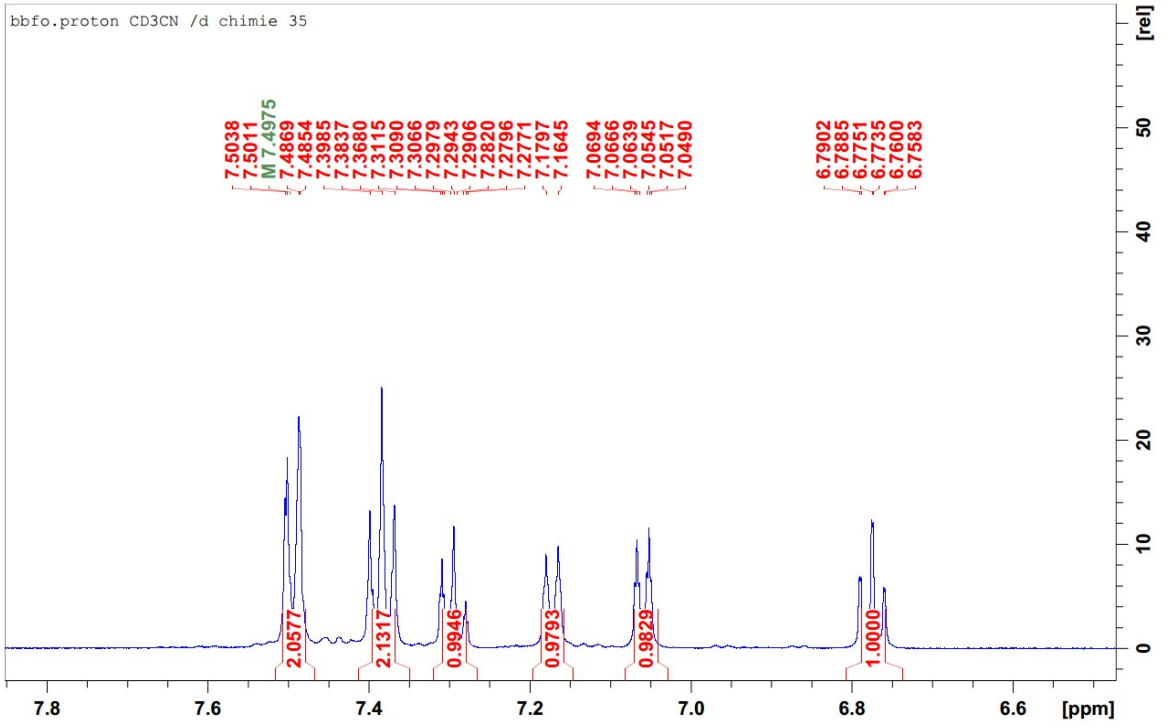

*Figure S80: ^{1}H NMR spectrum of **1k** in CD_3CN; focus on aromatic region.*

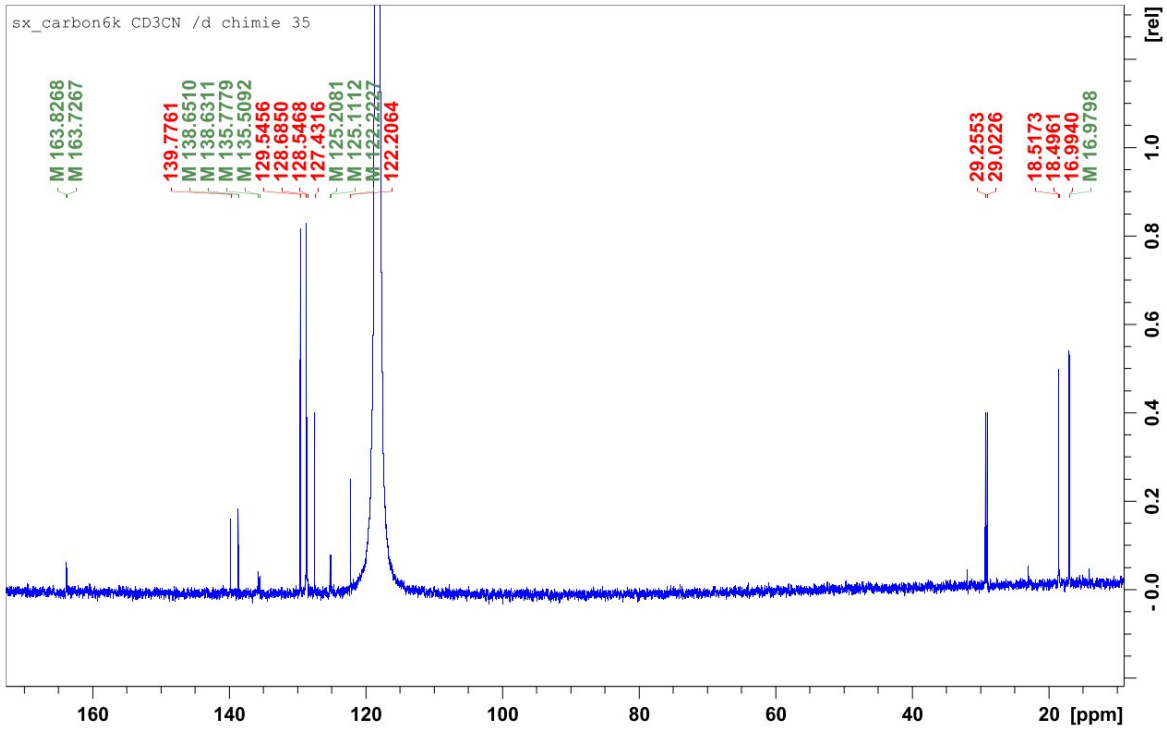

*Figure S81: Full $^{13}C\{^{1}H\}$ NMR spectrum of **1k** in CD_3CN.*

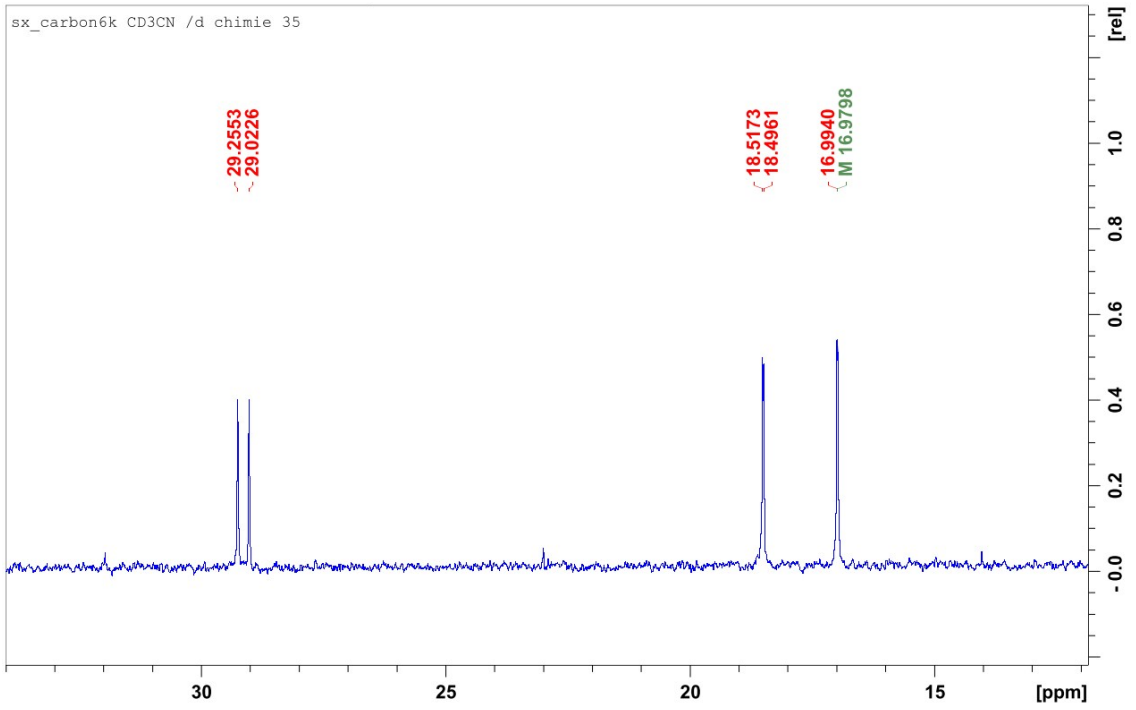

*Figure S82: $^{13}C\{^{1}H\}$ NMR spectrum of **1k** in CD_3CN; focus on aliphatic region.*

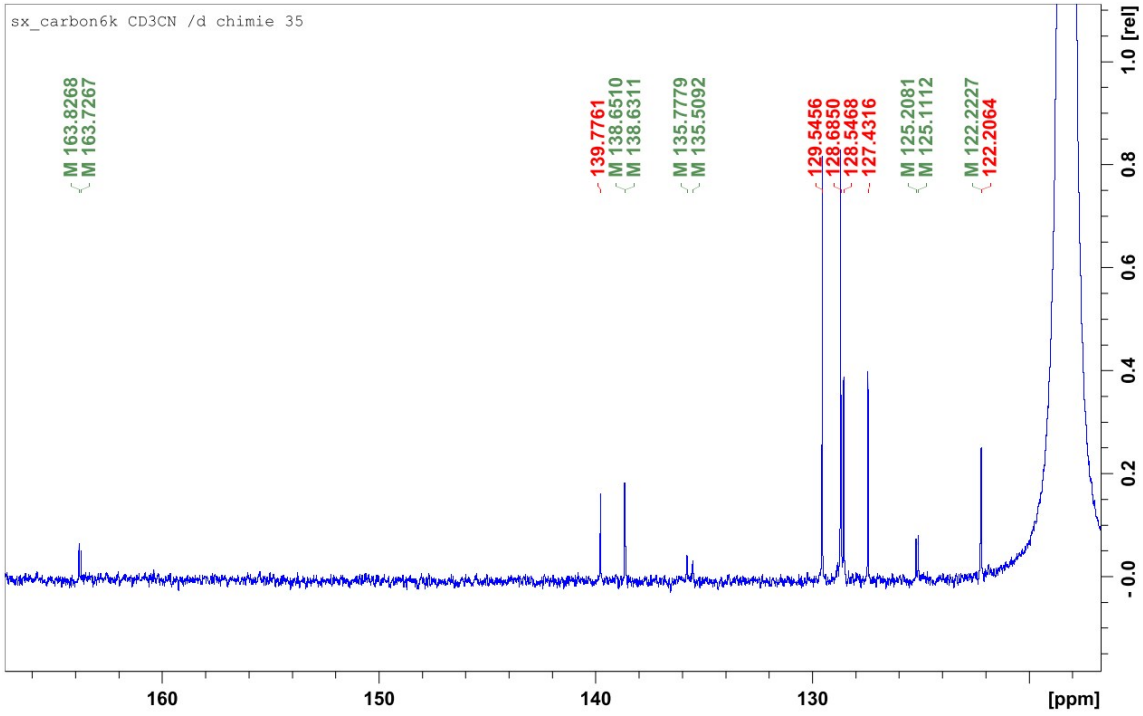

*Figure S83: $^{13}C\{^{1}H\}$ NMR spectrum of **1k** in CD_3CN; focus on aromatic region.*

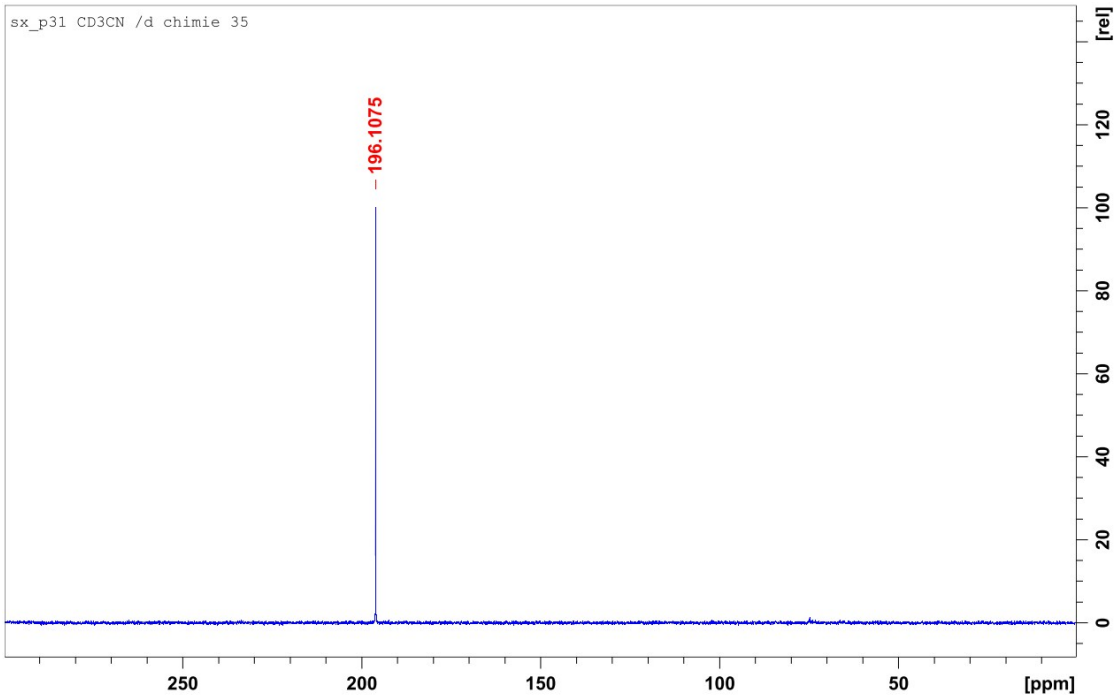

*Figure S84: $^{31}P\{^{1}H\}$ NMR spectrum of **1k** in CD_3CN.*

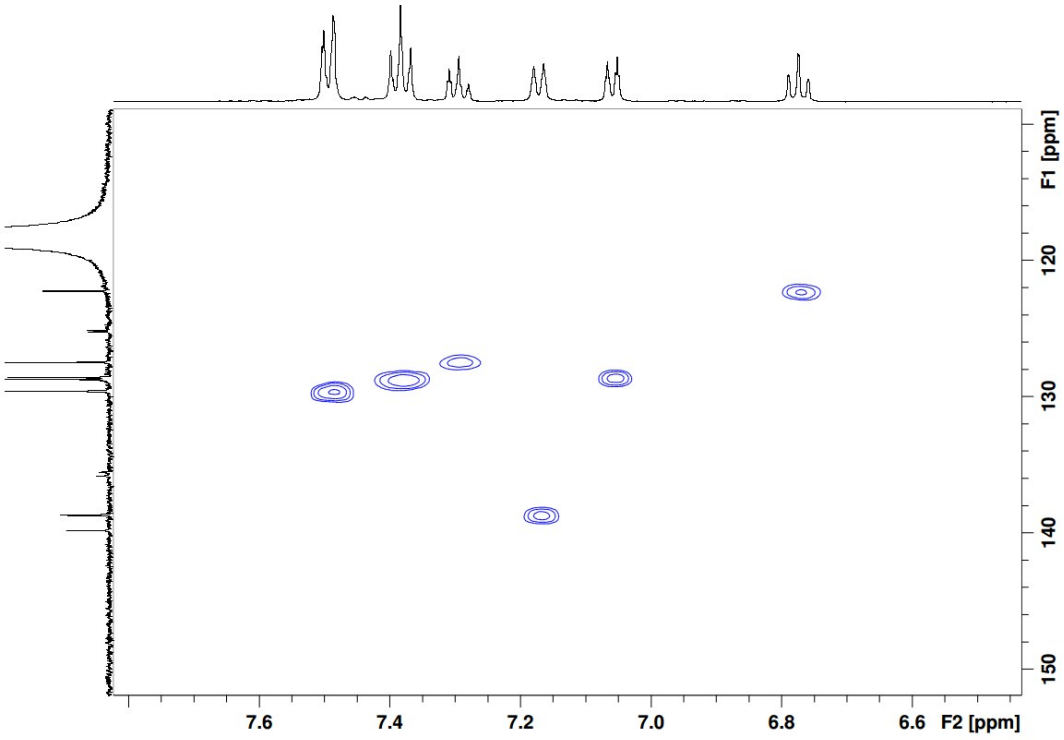

*Figure S85: HSQC spectrum of **1k** in CD_3CN; focus on aromatic region.*

5. Additional ORTEPs

1a-NCMe

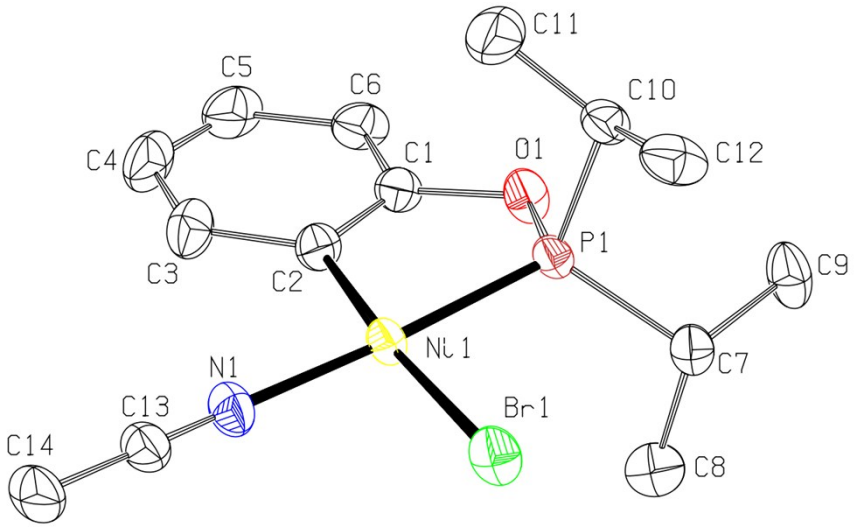

*Figure S86: Solid state structure of **1a-NCMe**. Thermal ellipsoids are shown at the 50% probability level; hydrogens are omitted for clarity.*

1b

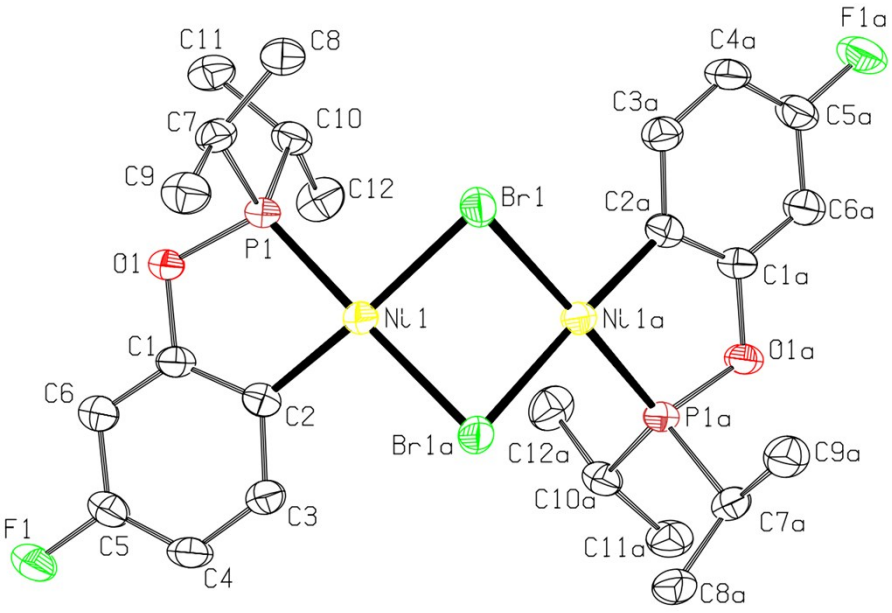

*Figure S87: Solid state structure of **1b**. Thermal ellipsoids are shown at the 50% probability level; hydrogens are omitted for clarity.*

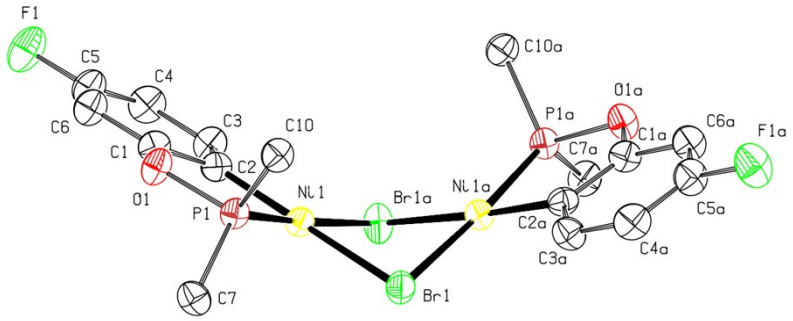

*Figure S88: Side view of **1b**. Thermal ellipsoids are shown at the 50% probability level; hydrogens and iso-propyl substituents are omitted for clarity.*

1c

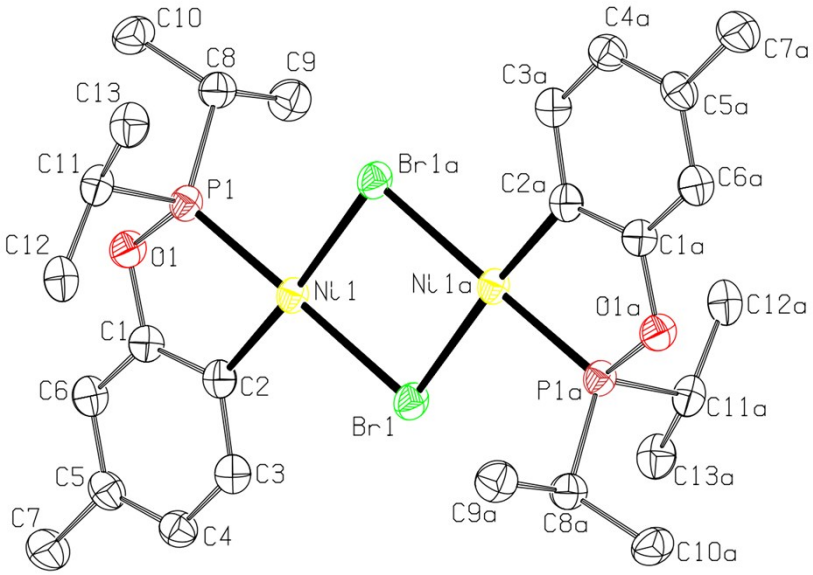

*Figure S89: Solid state structure of **1c**. Thermal ellipsoids are shown at the 50% probability level; hydrogens are omitted for clarity.*

1e

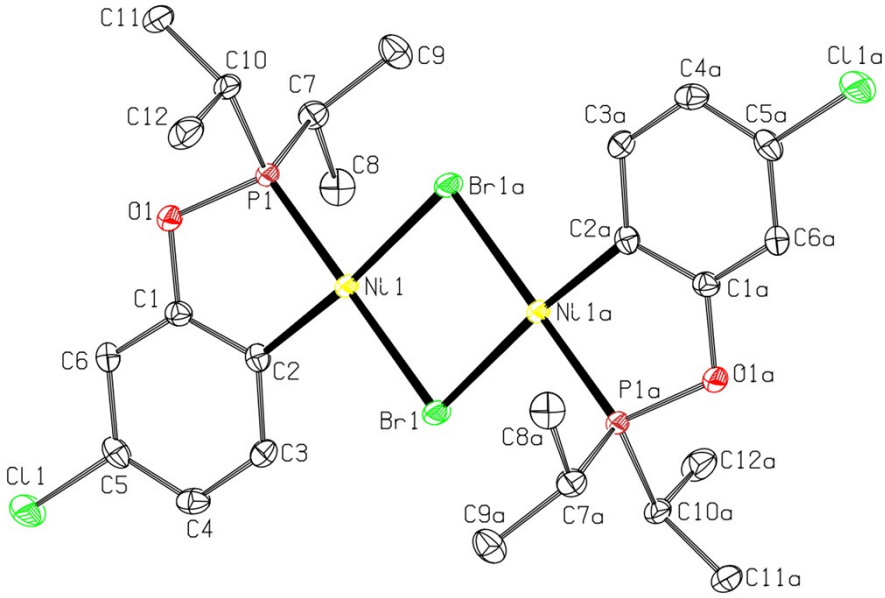

*Figure S90: Solid state structure of **1e**. Thermal ellipsoids are shown at the 50% probability level; hydrogens are omitted for clarity.*

1j

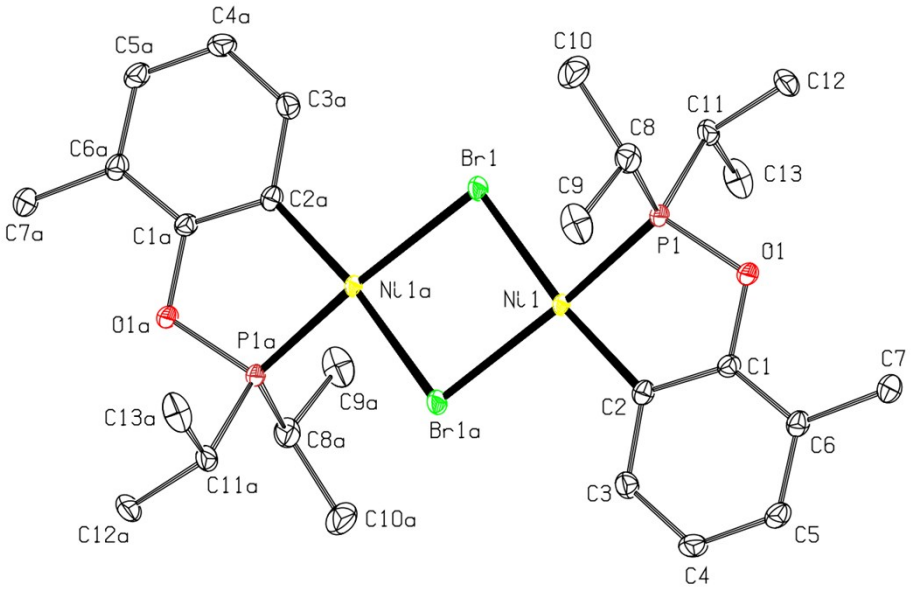

*Figure S91: Solid state structure of **1j**. Thermal ellipsoids are shown at the 50% probability level; hydrogens are omitted for clarity.*

6. Crystallographic data

*Table S2: Additional bond distances and angles around the nickel centre for compounds **1a**-**1e***

Compound	1a	1b	1c	1d	1e
***cis* Ni-Br**	2.3641 (7)	2.3781 (7)	2.3815 (5)	2.3875 (3)	2.3796 (5)
***trans* Ni-Br**	2.377	2.3736 (8)	2.39	2.3851 (3)	2.382
Ni-C2	1.914 (4)	1.911 (4)	1.920 (3)	1.9140 (17)	1.914 (2)
Ni-P1	2.0953 (10)	2.1056 (12)	2.0963 (7)	2.0985 (5)	2.0987 (7)
τ_4	0.059	0.056	0.042	0.116	0.036
Ni-Br-Ni	92.155	83.483	87.601	76.159 (10)	92.348
P1-Ni-C2	82.07 (12)	83.60 (13)	82.29(8)	82.97 (5)	82.38 (8)
C2-Ni-Br	97.61 (12)	93.87	97.39(8)	98.90 (5)	97.49 (8)
Br-Ni-Br	87.845	86.869	87.601	86.79 (1)	87.652
Br-Ni-P	92.619	92.56 (4)	92.739	92.297 (15)	92.483
trans C-Ni-Br	174.21	175.96 (13)	174.9	169.34 (5)	174.795
trans P-Ni-Br	176.19 (4)	175.853	178.82(3)	173.927 (17)	179.79 (3)

*Table S3: Additional bond distances and angles around the nickel centre for compounds **1f, 1j, 1k, 1a-NCMe** and **1i-NCMe***

Compound	1f	1j	1k	1a(NCMe)	1i-NCMe
***cis* Ni-Br**	2.386	2.392	2.393(2)	1.913 (2)	1.9149 (19)
***trans* Ni-Br**	2.3743(3)	2.3759(3)	2.390(2)	2.3533 (4)	2.3613 (4)
Ni-C2	1.9313(16)	1.9113(15)	1.919(12)	1.916 (2)	1.932 (2)
Ni-P1	2.1017(5)	2.0936(4)	2.104(3)	2.1018 (6)	2.1000 (6)
τ_4	0.10226258	0.05943898	0.0595666	0.0736048	0.2044153
Ni-Br-Ni	94.116	92.508	92.76(7)	x	x
P1-Ni-C2	82.41(5)	82.51(5)	81.5(4)	82.51 (7)	83.23 (6)
C2-Ni-Br	101.022	98.285	96.5(4)	96.03 (10)	100.20 (8)
Br-Ni-Br	85.884	87.492	86.51(7)	90.92 (7)	91.18 (6)
Br-Ni-P	90.636 (15)	92.931(13)	95.656	90.681 (19)	88.17 (2)
trans C-Ni-Br	173.04(5)	171.33(5)	175.9(4)	172.62 (7)	164.43 (6)
trans P-Ni-Br	172.198	179.948	175.36(12)	176.66 (6)	166.40 (6)

*Table S4: Crystal information for compounds **1b**-**1d***

	1b	**1c**	**1d**
chemical formula	$C_{24}H_{34}Br_2F_2Ni_2O_2P_2$	$C_{26}H_{40}Br_2Ni_2O_2P_2$	$C_{26}H_{40}Br_2Ni_2O_4P_2$
crystal colour	Orange	Orange	Orange
***Fw*; *F*(000)**	365.84; 1472	361.88; 736	755.76; 1536
***T* (K)**	100	100	100
wavelength (Å)	1.54178	1.54178	1.34139
space group	C_2/c	$P2_1/n$	$P2_1/c$
***a* (Å)**	12.7913(5)	11.1846(11)	24.6811(8)
***b* (Å)**	11.7694(5)	11.1021(11)	8.6173(3)
***c* (Å)**	19.0246(7)	12.8093(13)	15.0729(5)
α (deg)	90	90	90
β (deg)	103.6270(10)	109.753(3)	104.9950(10)
γ (deg)	90	90	90
Z	4	2	4
***V* (Å^3)**	2783.45(19)	1497.0(3)	3096.61(18)
ρ_{calcd} (g·cm^{-3})	1.746	1.606	1.621
μ (mm^{-1})	6.418	5.859	9.686
θ range (deg); completeness	5.175 − 72.160; 0.998	5.792 − 72.082; 0.999	1.612 − 60.765; 0.998
collected reflections; R_σ	55870; 0.0135	39328; 0.0209	52360; 0.0262
unique reflections; R_{int}	55870; 0.0400	39328; 0.0548	52360; 0.0421
R1[a]; wR2[b] [I > 2σ(I)]	0.0365; 0.1064	0.0358; 0.1020	0.0233; 0.0572
R1; wR2 [all data]	0.0367; 0.1065	0.0361; 0.1024	0.0244; 0.0601
GOF	1.271	1.093	1.067
largest diff peak and hole	0.739 and -0.473	1.233 and -0.699	0.682 and -0.532

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$
[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

*Table S5: Crystal information for compounds **1e**-**1f** and **1i-NCMe***

	1e	**1f**	**1i-NCMe**
chemical formula	$C_{24}H_{34}Br_2Cl_2Ni_2O_2P_2$	$C_{24}H_{32}Br_2F_4Ni_2O_2P_2$	$C_{16}H_{25}BrNNiO_3P$
crystal colour	Orange	Red	Orange
***Fw*; *F*(000)**	764.59; 768	383.84; 768	448.96; 920
***T* (K)**	100	100	100
wavelength (Å)	1.54178	1.54178	1.54178
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
***a* (Å)**	11.0573(3)	10.45540(10)	12.7532(3)
***b* (Å)**	11.0873(3)	12.15070(10)	13.1865(3)
***c* (Å)**	12.8018(3)	11.12550(10)	11.4773(3)
α (deg)	90	90	90
β (deg)	108.8690(10)	93.38	97.3600(10)
γ (deg)	90	90	90
Z	2	2	4
***V* (Å^3)**	1485.10(7)	1410.92(2)	1914.24(8)
ρ_{calcd} (g·cm^{-3})	1.710	1.807	1.558
μ (mm^{-1})	7.561	6.472	4.802
θ range (deg); completeness	5.814 − 72.041; 0.997	5.588 − 72.151; 0.997	3.494 − 72.162; 0.999
collected reflections; R_σ	58307; 0.0085	19280; 0.0112	3778; 0.0191
unique reflections; R_{int}	58307; 0.0272	19280; 0.0205	3778; 0.0504
R1[a]; wR2[b] [I > 2σ(I)]	0.0274; 0.0735	0.0200; 0.0506	0.0378; 0.1050
R1; wR2 [all data]	0.0275; 0.0735	0.0202; 0.0507	0.0386; 0.1061
GOF	1.128	1.158	1.083
largest diff peak and hole	0.642 and -0.427	0.352 and -0.339	1.643 and -0.485

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$
[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

*Table S6: Crystal information for compounds **1j**-**1k** and **1a-NCMe***

	1j	**1k**	**1a-NCMe**
chemical formula	$C_{26}H_{40}Br_2Ni_2O_2P_2$	$C_{36}H_{44}Br_2Ni_2O_2P_2$	$C_{14}H_{21}BrNNiOP$
crystal colour	Yellow	Orange	Yellow
***Fw*; *F*(000)**	1447.52; 736	847.89; 3456	388.91; 396
***T* (K)**	100	100	150
wavelength (Å)	1.34139	1.54178	1.34139
space group	$P2_1/n$	$P2_1$	P-1
***a* (Å)**	10.4265(2)	15.6693(4)	7.4137(4)
***b* (Å)**	14.2437(3)	12.3783(3)	9.6993(5)
***c* (Å)**	10.4603(2)	36.7303(10)	12.7577(7)
α (deg)	90	90	97.074(2)
β (deg)	105.6540(10)	91.6650(10)	101.279(2)
γ (deg)	90	90	111.252(2)
Z	2	8	2
***V* (Å^3)**	1495.86(5)	7121.2(3)	819.36(8)
ρ_{calcd} (g·cm^{-3})	1.607	1.582	1.576
μ (mm^{-1})	9.974	5.028	9.146
θ range (deg); completeness	4.678 − 60.586; 0.999	1.203 − 72.189; 0.996	3.145 − 60.638; 0.999
collected reflections; R_σ	23556; 0.0240	149169; 0.0532	19653; 0.0311
unique reflections; R_{int}	23556; 0.0422	149169; 0.0409	19653; 0.0502
R1[a]; wR2[b] [I > 2σ(I)]	0.0222; 0.0589	0.0489; 0.1295	0.0384; 0.1080
R1; wR2 [all data]	0.0224; 0.0592	0.0499; 0.1303	0.0389; 0.1087
GOF	1.102	1.034	1.251
largest diff peak and hole	0.578 and -0.630	1.878 and -0.698	0.630 and -1.540

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$
[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

7. Details on DFT optimizations

All DFT calculations were performed using Gaussian 16 on Grex server from Westgrid (provided by Compute Canada/Calcul Canada). Optimizations were carried out using 6-31g** for all light atoms (C, H, O P) and def2TZVP for Ni and Br basis sets. The M06 functional was exploited in implicit toluene solvent using the SMD model. Local minima were assessed by convergence and the absence of imaginary frequencies in the frequency calculation. The electronic energy was computed with def2TZVP for all atoms, from the optimized geometry. The thermal energy was calculated by the sum of the electronic energy and the thermal correction to Gibbs free energy outputted from the frequency calculations.

Calculations on the cyclometallated dimeric compounds **1a** and **1d** were carried out as follows. **1a** was optimized (a) from its crystal structure geometry, leading to a perfectly coplanar structure (dihedral angle Ni1-μ-Br1-μ-Br2-Ni2 = 180.00000°) and (b) from a bent geometry where the dihedral angle was set to 116° (in line with the solid state structure of **1d**), leading to a bent geometry with dihedral angle Ni1-μ-Br1-μ-Br2-Ni2 = 104°. **1d** was optimized (a) using structural parameters obtained from the crystal structure (bent conformation; dihedral angle of 102°) and (b) from the crystal structure unfolded to a coplanar structure (dihedral angle of 180°), leading to a nearly planar structure.

Calculations on model compounds featuring simplified Me_2POAr moieties were carried out as follows. The Me_2P analogue of the unsubstituted complex **1a** was called ModelPhenol. Three conformations were considered for the Me_2P analogue of complex **1d**: one with both methoxy methyls pointing towards C4 (ModelConf1), one with both Me pointing towards C6 (ModelConf2), and one with a Me pointing towards C4 and the other towards C6 (ModelConf3). For each of these models, optimizations were started from both a coplanar structure (derived from the crystal structure of **1a**) and a bent structure (derived from the crystal structure of **1d**). All optimizations starting from either a bent or a coplanar geometry ended up as bent compounds. Freezing the dihedral angle to 180° allowed us to find a planar local minimum for each compound, for the purposes of comparison. Only ModelConf2 could converge into a local coplanar minimum without requiring freezing; this model gave a structure featuring a dihedral angle of 178°.

In all six cases, the optimized bent structures were found to be lower in energy than the coplanar local minima, with stabilizations of 5.7 kJ/mol for **1a** and 6.5 kJ/mol for **1d**. It should be noted here that although the located minima are close to the global minimum, they could be local minima due to the rotation of the *i*-Pr groups. In the model compounds, stabilisations between the bent structures (absolute minimum) and the corresponding coplanar structures were as follows (all values in kJ/mol): ModelPhenol, 2.8; ModelConf1, 1.3; ModelConf2, 3.8; and ModelConf3, 3.3.

The transition state for flipping the dimer from one bent conformation to the other was found using the QST2 routine with input geometries coming from the optimized structures found with ModelPhenol and its mirror image leading to the structure bent the other way. This process yielded a nearly coplanar geometry as transition state, with one single imaginary frequency for which the vectors directed a bend towards one or the other faces of the dimer. The Internal Reaction Coordinate (IRC) confirmed the identity of the transition state as being the link between the two opposite bent structures. The energy of this transition state was found to be 11.6 kJ/mol higher than the optimized bent structures.

The possibility of an *s*-trans to s-*cis* isomerization suggested by a reviewer was also probed by performing DFT calculations on the model complex ModelPhenol. The geometry minimization of the s-*cis* isomer (ModelPhenolCis) led to a bent structure that was 10.0 kJ/mol higher in energy than the s-*trans* isomer. The mixed square planar-tetrahedral dinuclear species (ModelPhenolMix), which was proposed by a reviewer to be the intermediate/transition state for this isomerization, was computed as a triplet and found to be 68.3 kJ/mol higher than the *s-trans* bent dimer. The transition state leading to this intermediate was thus not investigated, as it should be much higher than the barrier required for the above described flipping mechanism.

Geometries of the optimized structures

a) Coplanar local minimum and bent optimized structures of **1a**

Table S7: Coordinates for optimized 1a-plane and 1a-bent

Plane structure				Bent structure			
Br	1.504573	-0.537126	-0.385582	Br	-0.424022	-1.557051	-1.804923
Ni	0.68079	0.966794	1.285711	Ni	1.359062	-0.350519	-0.725332
Br	-1.504573	0.537126	0.385582	Br	0.429147	1.617932	-1.756217
Ni	-0.68079	-0.966794	-1.285711	Ni	-1.316992	0.372456	-0.663208
P	0.073775	-2.343543	-2.737987	P	-2.795096	-0.820576	0.319267
P	-0.073775	2.343543	2.737987	P	2.804127	0.80899	0.339864
O	1.194955	2.76708	3.710688	O	3.524514	-0.212588	1.426931
O	-1.194955	-2.76708	-3.710688	O	-3.714906	0.21856	1.224856
C	2.355764	1.338085	2.167479	C	2.158646	-1.801728	0.253517
C	-0.749516	0.380589	4.519878	C	1.048679	1.573392	2.300641
H	0.184397	0.551881	5.070707	H	1.425365	0.78504	2.966128
H	-0.549489	-0.361314	3.737284	H	0.236288	1.156645	1.691081
H	-1.474105	-0.052468	5.219757	H	0.618069	2.365839	2.925274
C	3.524315	2.493926	4.004787	C	3.712269	-2.489256	2.038611
H	3.455868	3.160552	4.861401	H	4.445413	-2.1906	2.784384
C	-1.293539	1.685465	3.947163	C	2.167436	2.143163	1.435181
H	-2.195522	1.469041	3.354171	H	1.740153	2.891366	0.750512
C	3.5961	0.804497	1.797363	C	1.844253	-3.157231	0.088219
H	3.665433	0.140233	0.938774	H	1.124194	-3.451834	-0.672059
C	-1.620686	2.690512	5.04538	C	3.270869	2.772953	2.277098
H	-2.315452	2.238154	5.763686	H	2.835845	3.525978	2.945654
H	-2.093027	3.601716	4.660841	H	4.03467	3.274391	1.671701
H	-0.716756	2.978727	5.595956	H	3.766876	2.021916	2.904178
C	2.376999	2.185998	3.286042	C	3.119333	-1.520933	1.238792
C	4.76748	1.093509	2.497116	C	2.425633	-4.153636	0.872444
H	5.708927	0.654322	2.173198	H	2.149244	-5.19379	0.71156
C	4.732677	1.9371	3.601775	C	3.353166	-3.81958	1.853348
H	5.643178	2.165306	4.151667	H	3.80636	-4.59211	2.470789
C	-0.650213	4.001674	2.181331	C	4.270065	1.461793	-0.562815
H	-0.628716	4.607361	3.101745	H	4.983791	1.707968	0.239844
C	-2.059906	3.989272	1.606871	C	3.95765	2.709145	-1.377379
H	-2.358439	5.013217	1.350762	H	4.879057	3.08659	-1.837362
H	-2.805456	3.594073	2.307157	H	3.530803	3.520346	-0.775893
H	-2.109767	3.393108	0.687562	H	3.253953	2.485537	-2.188763
C	0.357441	4.566403	1.186866	C	4.856098	0.355864	-1.432113
H	0.371875	3.970568	0.26435	H	4.153315	0.068672	-2.225805
H	1.375685	4.586851	1.59202	H	5.100335	-0.54296	-0.854747
H	0.082577	5.593745	0.918143	H	5.777914	0.706804	-1.912007
C	-2.355764	-1.338085	-2.167479	C	-2.158997	1.804866	0.311433
C	0.749516	-0.380589	-4.519878	C	-4.542917	-0.575669	-1.775552
H	-0.184397	-0.551881	-5.070707	H	-5.028932	0.267229	-1.267034
H	0.549489	0.361314	-3.737284	H	-3.726461	-0.175103	-2.388661
H	1.474105	0.052468	-5.219757	H	-5.28127	-1.027793	-2.448678
C	-3.524315	-2.493926	-4.004787	C	-3.937017	2.477824	1.879836
H	-3.455868	-3.160552	-4.861401	H	-4.783715	2.177259	2.492723
C	1.293539	-1.685465	-3.947163	C	-4.051114	-1.610855	-0.769391
H	2.195522	-1.469041	-3.354171	H	-3.506119	-2.404393	-1.303123
C	-3.5961	-0.804497	-1.797363	C	-1.758472	3.147586	0.28537
H	-3.665433	-0.140233	-0.938774	H	-0.909689	3.442553	-0.327225
C	1.620686	-2.690512	-5.04538	C	-5.204182	-2.213397	0.024982
H	2.315452	-2.238154	-5.763686	H	-5.939252	-2.645759	-0.664912
H	2.093027	-3.601716	-4.660841	H	-4.882921	-3.010402	0.705199
H	0.716756	-2.978727	-5.595956	H	-5.716587	-1.444717	0.616046
C	-2.376999	-2.185998	-3.286042	C	-3.262154	1.521034	1.132424
C	-4.76748	-1.093509	-2.497116	C	-2.414237	4.130962	1.025522

H	-5.708927	-0.654322	-2.173198	H	-2.069915	5.161997	0.973267
C	-4.732677	-1.9371	-3.601775	C	-3.50409	3.797365	1.822598
H	-5.643178	-2.165306	-4.151667	H	-4.019613	4.560832	2.401253
C	0.650213	-4.001674	-2.181331	C	-2.314772	-2.038895	1.617477
H	0.628716	-4.607361	-3.101745	H	-3.244057	-2.146177	2.20075
C	2.059906	-3.989272	-1.606871	C	-1.890583	-3.397183	1.077957
H	2.358439	-5.013217	-1.350762	H	-1.707921	-4.078216	1.918446
H	2.805456	-3.594073	-2.307157	H	-2.647696	-3.86074	0.434512
H	2.109767	-3.393108	-0.687562	H	-0.957177	-3.322505	0.508203
C	-0.357441	-4.566403	-1.186866	C	-1.236763	-1.430663	2.507389
H	-0.371875	-3.970568	-0.26435	H	-0.289597	-1.33106	1.958222
H	-1.375685	-4.586851	-1.59202	H	-1.52138	-0.443889	2.892982
H	-0.082577	-5.593745	-0.918143	H	-1.051804	-2.085516	3.367783
$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9933.9727553 + 0.475031 = -9933.4977243 Ha				$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9933.9780433 + 0.478159 = - -9933.4998843 Ha			
$\Delta G_{bending}$ = -0.0021600 Ha = -5.67 kJ/mol							

b) Coplanar local minimum and bent optimized structures of **1d**

Table S8: Coordinates for optimized 1d-plane and 1d-bent

Plane structure				Bent structure			
Br	-0.304198	1.615779	-0.339206	Br	0.560944	1.544178	-2.101098
Br	0.304397	-1.616227	-0.336809	Br	-0.561129	-1.545744	-2.100197
Ni	-1.703448	-0.315135	-0.120295	Ni	1.292893	-0.466536	-0.994635
Ni	1.703554	0.314917	-0.120432	Ni	-1.292878	0.465527	-0.994782
P	-2.93224	-2.047282	0.119057	P	1.793232	-2.247127	0.074839
P	2.931982	2.047271	0.119458	P	-1.792464	2.246873	0.073837
O	-4.506298	-1.534021	0.133476	O	2.936743	-1.826505	1.198958
O	-7.255361	2.257455	0.057446	O	5.646492	1.674124	2.727035
C	-4.589573	-0.156842	0.057543	C	3.315742	-0.505838	1.066958
C	-3.401166	0.59025	-0.036261	C	2.720676	0.275431	0.058845
C	-3.58509	1.973477	-0.090509	C	3.199848	1.585713	-0.026529
H	-2.721171	2.631148	-0.158087	H	2.801023	2.253625	-0.786587
C	-4.843603	2.578881	-0.062335	C	4.174288	2.098599	0.833095
H	-4.913694	3.661799	-0.110177	H	4.502515	3.126948	0.71123
C	-5.985871	1.784374	0.024944	C	4.707936	1.283518	1.831268
C	-5.857302	0.395181	0.08797	C	4.276489	-0.039714	1.946438
H	-6.741503	-0.232598	0.160436	H	4.697381	-0.686539	2.711728
C	-7.434957	3.652059	-0.003735	C	6.122368	2.996101	2.641843
H	-6.965557	4.163239	0.849106	H	6.609816	3.194466	1.676524
H	-8.512873	3.829333	0.029928	H	6.86021	3.113739	3.439376
H	-7.035582	4.075651	-0.936408	H	5.318519	3.731147	2.792348
C	-2.865543	-2.985387	1.702274	C	2.662049	-3.602134	-0.819544
H	-3.805488	-3.560642	1.704111	H	3.079007	-4.225856	-0.012586
C	-2.8813	-1.997159	2.862564	C	3.80494	-3.010157	-1.635301
H	-1.963274	-1.394294	2.874215	H	3.420579	-2.359667	-2.432455
H	-2.939549	-2.538553	3.814813	H	4.381893	-3.814429	-2.108137
H	-3.735115	-1.311597	2.813634	H	4.493762	-2.42041	-1.02004
C	-1.6796	-3.935613	1.79018	C	1.727859	-4.434591	-1.686149
H	-1.650289	-4.662067	0.969177	H	0.889443	-4.864105	-1.125228
H	-1.732855	-4.500394	2.72903	H	2.286726	-5.264645	-2.13533
H	-0.730017	-3.386814	1.78908	H	1.312329	-3.836843	-2.506872
C	-2.928332	-3.257825	-1.265664	C	0.490585	-3.004706	1.134452
H	-1.916646	-3.692325	-1.260468	H	-0.283815	-3.348295	0.431565
C	-3.967697	-4.357326	-1.081446	C	1.021633	-4.180678	1.946157
H	-3.784755	-4.971931	-0.192642	H	1.361903	-5.013112	1.319607
H	-3.954689	-5.025632	-1.951306	H	0.226244	-4.563732	2.597323
H	-4.977011	-3.934777	-1.004656	H	1.854426	-3.872006	2.590212

C	-3.137272	-2.49825	-2.571801	C	-0.103578	-1.924159	2.032223
H	-4.11904	-2.007595	-2.588284	H	0.652605	-1.51852	2.717613
H	-3.097865	-3.192528	-3.419687	H	-0.915505	-2.34605	2.638098
H	-2.372049	-1.728217	-2.728027	H	-0.526943	-1.097748	1.448151
C	2.863347	2.985796	1.702348	C	-2.659538	3.602649	-0.821102
H	3.803491	3.560729	1.705335	H	-3.076857	4.226341	-0.014308
C	2.877196	1.997786	2.862851	C	-3.802024	3.01148	-1.638015
H	1.958854	1.395384	2.873499	H	-3.41725	2.361143	-2.435098
H	2.934569	2.539324	3.815071	H	-4.37825	3.816165	-2.111031
H	3.730718	1.311772	2.815076	H	-4.491585	2.421784	-1.02354
C	1.677608	3.936439	1.788487	C	-1.724248	4.435021	-1.686579
H	1.649639	4.662781	0.967341	H	-0.885934	4.863629	-1.124807
H	1.72979	4.501346	2.727322	H	-2.282289	5.265733	-2.135581
H	0.727842	3.387961	1.786209	H	-1.308525	3.83756	-2.50741
C	2.929662	3.257418	-1.2656	C	-0.489737	3.003282	1.134214
H	1.918004	3.692007	-1.261553	H	0.285255	3.346381	0.431737
C	3.139926	2.497521	-2.571328	C	0.103214	1.922176	2.032091
H	4.121686	2.006804	-2.586663	H	-0.653533	1.51713	2.717231
H	3.101467	3.191601	-3.419423	H	0.915408	2.343256	2.63818
H	2.374826	1.727495	-2.728174	H	0.525975	1.095456	1.448044
C	3.968929	4.356881	-1.080552	C	-1.020248	4.179557	1.945836
H	3.785217	4.971608	-0.191989	H	-1.359483	5.012381	1.319233
H	3.956787	5.025085	-1.950503	H	-0.2249	4.56184	2.597512
H	4.978131	3.934255	-1.002757	H	-1.853656	3.87146	2.589364
O	4.506048	1.534071	0.136072	O	-2.937285	1.827565	1.197127
O	7.255813	-2.256849	0.058207	O	-5.649416	-1.67086	2.725937
C	4.58957	0.156966	0.059182	C	-3.316619	0.506925	1.065882
C	3.401342	-0.590268	-0.035859	C	-2.721007	-0.275385	0.058904
C	3.585568	-1.973398	-0.091437	C	-3.200235	-1.585721	-0.02547
H	2.721823	-2.631176	-0.160188	H	-2.80083	-2.254455	-0.784511
C	4.844177	-2.578599	-0.063204	C	-4.175481	-2.097586	0.833847
H	4.914481	-3.661453	-0.11213	H	-4.503736	-3.126017	0.712774
C	5.986249	-1.783971	0.025495	C	-4.709893	-1.28138	1.83069
C	5.857384	-0.394862	0.089759	C	-4.278247	0.04186	1.94496
H	6.741433	0.233021	0.163189	H	-4.699609	0.689482	2.709319
C	7.435702	-3.651362	-0.004215	C	-6.125457	-2.992832	2.641689
H	6.965875	-4.163449	0.847845	H	-6.612091	-3.192118	1.676149
H	8.51363	-3.828473	0.029926	H	-6.864022	-3.109513	3.438695
H	7.036969	-4.074123	-0.937539	H	-5.321881	-3.727864	2.793673

$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -10162.988461 + 0.535439 = -10162.45302 Ha	$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -10162.99390 + 0.538414 = -10162.45549 Ha
$\Delta G_{bending}$ = -0.002469 Ha = -6.48 kJ/mol	

c) Coplanar local minimum and bent optimized structures of ModelPhenol

Table S9: Coordinates for optimized ModelPhenol-plane and ModelPhenol-bent

Plane structure				Bent structure			
Br	-0.184678	-1.64646	0.062125	Br	-0.45081	-1.598388	-1.7625
Ni	-1.720062	0.186585	0.026995	Ni	-1.303838	0.357053	-0.656494
Br	0.185931	1.64819	0.066747	Br	0.450795	1.598615	-1.762376
Ni	1.721321	-0.184808	0.032392	Ni	1.303827	-0.35692	-0.656486
P	3.045895	-1.840966	-0.058236	P	1.731753	-2.042345	0.553602
P	-3.048569	1.84016	-0.054453	P	-1.731888	2.04236	0.553716
O	-4.581961	1.253028	-0.194548	O	-3.016737	1.656871	1.516922
O	4.5858	-1.257656	-0.117728	O	3.016717	-1.657101	1.516752
C	-3.369348	-0.81163	0.011904	C	-2.754039	-0.419352	0.337136
C	-5.829065	-0.756803	-0.126897	C	-4.48679	-0.117119	2.061345
H	-6.731717	-0.157313	-0.218879	H	-4.952312	0.539043	2.793092
C	-3.465073	-2.204426	0.114159	C	-3.235531	-1.723052	0.162015
H	-2.562134	-2.803245	0.212715	H	-2.768889	-2.37355	-0.574278
C	-4.591381	-0.129885	-0.102098	C	-3.423258	0.351405	1.302037
C	-4.692906	-2.865294	0.093906	C	-4.306576	-2.219603	0.904494
H	-4.720734	-3.950108	0.17402	H	-4.653638	-3.236702	0.733747
C	-5.874695	-2.142889	-0.029435	C	-4.929835	-1.418849	1.855838
C	3.371176	0.81233	0.014864	C	2.754056	0.419276	0.337249
C	5.832975	0.75221	-0.079586	C	4.486952	0.116719	2.061255
H	6.736301	0.149755	-0.140288	H	4.952503	-0.53956	2.792878
C	3.466839	2.207537	0.077142	C	3.235623	1.722971	0.162233
H	2.562984	2.809735	0.140277	H	2.768951	2.373592	-0.573919
C	4.594284	0.127046	-0.060173	C	3.423312	-0.35164	1.301999
C	4.695616	2.866747	0.06152	C	4.306781	2.219351	0.904666
H	4.723137	3.953392	0.111452	H	4.653909	3.236442	0.734003
C	5.878714	2.140316	-0.018348	C	4.930078	1.418435	1.855845
C	-2.934871	2.98736	-1.451567	C	-2.242269	3.623442	-0.166001
H	-3.807955	3.650289	-1.456006	H	-2.59617	4.289129	0.629794
H	-2.023431	3.588443	-1.365819	H	-1.393142	4.087981	-0.67763
H	-2.899416	2.423602	-2.388473	H	-3.047008	3.459024	-0.888443
C	2.962158	-2.913927	-1.515855	C	2.242104	-3.623295	-0.166423
H	3.821012	-3.595115	-1.524941	H	2.596073	-4.289125	0.629228
H	2.035265	-3.496976	-1.49454	H	1.393014	-4.08778	-0.678152
H	2.97222	-2.301072	-2.422136	H	3.04684	-3.458671	-0.888825
C	3.096	-2.986015	1.345774	C	0.43493	-2.470399	1.745209
H	2.162898	-3.557964	1.391786	H	-0.435656	-2.873203	1.216482
H	3.940484	-3.67579	1.232375	H	0.812186	-3.213454	2.457447
H	3.208867	-2.419711	2.275146	H	0.126793	-1.569189	2.285809
C	-3.142852	2.90935	1.406327	C	-0.43505	2.47025	1.745381
H	-2.203077	3.459695	1.524342	H	0.435637	2.872907	1.216713
H	-3.970583	3.619821	1.297327	H	-0.812223	3.213366	2.4576
H	-3.304094	2.293205	2.296207	H	-0.127109	1.568989	2.286011
H	-6.834606	-2.654303	-0.047185	H	5.764371	1.802345	2.438835
H	6.839438	2.650319	-0.032041	H	-5.764036	-1.802895	2.43887
$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9619.6064987 + 0.263190 = -9619.3433087 Ha				$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9619.6027336 + 0.260489 = -9619.3422446 Ha			
$\Delta G_{bending}$ = -0.00106413 Ha = -2.79 kJ/mol							

d) Coplanar local minimum and bent optimized structures of ModelConf1

Table S10: Coordinates for optimized ModelConf1-plane and ModelConf1-bent

Plane structure				Bent structure			
Br	-0.558513	1.562276	0.012071	Br	0.859774	-1.528809	1.963661
Ni	-1.6325	-0.575607	0.002049	Ni	1.163251	0.63078	0.948209
Br	0.558577	-1.562311	-0.011981	Br	-0.842115	1.324872	2.110271
Ni	1.632493	0.575495	-0.001959	Ni	-1.159491	-0.726513	0.897415
P	2.549724	2.48794	-0.000841	P	-1.164018	-2.419534	-0.373276
P	-2.549831	-2.487986	0.001183	P	1.117979	2.410193	-0.197938
O	-4.185048	-2.274914	0.027402	O	2.46799	2.435359	-1.150804
O	4.184937	2.274888	-0.025582	O	-2.503621	-2.328919	-1.337628
C	-3.464314	0.015934	0.003457	C	2.751969	0.306108	-0.077855
C	-5.850876	-0.606518	0.015623	C	4.337205	1.139295	-1.77216
H	-6.614444	-1.379692	0.02481	H	4.635718	1.916099	-2.471077
C	-3.882948	1.347824	-0.010384	C	3.558801	-0.830421	0.022237
H	-3.144098	2.146293	-0.021573	H	3.284744	-1.622394	0.715907
C	-4.506825	-0.929016	0.015529	C	3.19854	1.272131	-0.999481
C	-5.22769	1.724496	-0.010872	C	4.72174	-1.004994	-0.731232
H	-5.483788	2.780022	-0.021522	H	5.309946	-1.90887	-0.600648
C	-6.216764	0.74143	0.002507	C	5.111095	-0.015421	-1.634118
C	3.464317	-0.016025	-0.003499	C	-2.743559	-0.289415	-0.094195
C	5.850884	0.606651	-0.014853	C	-4.337384	-0.93951	-1.858668
H	6.61439	1.379901	-0.02337	H	-4.65077	-1.648194	-2.620609
C	3.883011	-1.34788	0.009428	C	-3.52263	0.854924	0.095228
H	3.144257	-2.146454	0.019943	H	-3.235035	1.578684	0.854676
C	4.506812	0.929004	-0.014727	C	-3.207535	-1.164882	-1.094353
C	5.227815	-1.72443	0.00987	C	-4.674409	1.122206	-0.648457
H	5.484033	-2.779921	0.019889	H	-5.239241	2.027824	-0.446598
C	6.216816	-0.741257	-0.002679	C	-5.082086	0.220457	-1.631564
C	-2.264793	-3.583054	1.41691	C	1.161225	4.049868	0.569006
H	-2.939039	-4.445656	1.361117	H	1.322742	4.809113	-0.205087
H	-1.226388	-3.931392	1.411865	H	0.211887	4.245056	1.077995
H	-2.448239	-3.035099	2.345998	H	1.97407	4.095543	1.299777
C	2.301266	3.550656	1.446235	C	-1.280704	-4.097373	0.297957
H	2.972079	4.416026	1.392386	H	-1.454158	-4.808566	-0.517898
H	1.262338	3.89631	1.477288	H	-0.348988	-4.3537	0.812619
H	2.510758	2.981758	2.357102	H	-2.108159	-4.15173	1.011633
C	2.265628	3.582256	-1.417363	C	0.197447	-2.489291	-1.567836
H	1.2276	3.931717	-1.412385	H	1.139149	-2.684325	-1.043496
H	2.940803	4.44418	-1.362267	H	0.010742	-3.281213	-2.302662
H	2.448357	3.033467	-2.346098	H	0.27968	-1.525286	-2.08078
C	-2.302432	-3.549922	-1.446645	C	-0.236097	2.494953	-1.400336
H	-1.263198	-3.894523	-1.479297	H	-1.193479	2.594339	-0.876935
H	-2.972307	-4.415979	-1.392212	H	-0.087821	3.348824	-2.071924
H	-2.513749	-2.980847	-2.356981	H	-0.256552	1.569084	-1.984967
O	-7.548995	0.987074	0.003022	O	6.214071	-0.078334	-2.417343
O	7.549039	-0.986844	-0.003212	O	-6.176047	0.374377	-2.414635
C	-7.965871	2.331631	-0.010718	C	7.035228	-1.216318	-2.301571
H	-7.619589	2.858144	-0.91166	H	6.497889	-2.137541	-2.568862
H	-9.058644	2.319237	-0.008652	H	7.862334	-1.07584	-3.001774
H	-7.61632	2.877308	0.877467	H	7.444562	-1.323643	-1.286945
C	7.966006	-2.331382	0.009707	C	-6.967598	1.522296	-2.218916
H	9.058772	-2.318803	0.007734	H	-7.792829	1.456276	-2.932271
H	7.619639	-2.858459	0.910285	H	-7.381541	1.565303	-1.20143
H	7.616587	-2.876513	-0.878851	H	-6.404275	2.446077	-2.414343
$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9848.6184623 + 0.319498 = -9848.2989643 Ha				$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9848.6221453 + 0.322696 = -9848.2994493 Ha			
$\Delta G_{bending}$ = -0.00048501 Ha = -1.27 kJ/mol							

e) Coplanar local minimum and bent optimized structures of ModelConf2

Table S11: Coordinates for optimized ModelConf2-plane and ModelConf2-bent

Plane structure				Bent structure			
Br	0.437604	-1.598788	-0.06472	Br	0.694373	-1.885046	-1.795634
Ni	1.669889	0.449402	-0.023518	Ni	1.225644	0.348538	-1.070694
Br	-0.438559	1.601496	-0.03924	Br	-0.681421	1.08976	-2.360405
Ni	-1.670584	-0.447684	-0.020989	Ni	-1.22518	-0.727671	-0.882131
P	-2.73408	-2.282046	0.024305	P	-1.424168	-2.219297	0.606693
P	2.736425	2.282264	0.001519	P	1.359612	2.256147	-0.163529
O	4.346808	1.938658	0.11115	O	2.735806	2.287419	0.752601
O	-4.348502	-1.941754	-0.009361	O	-2.699505	-1.803248	1.574681
C	3.450238	-0.28354	-0.011364	C	2.755389	-0.001017	0.03432
C	5.883003	0.151405	0.082414	C	4.431067	0.894901	1.616171
H	6.671251	0.895948	0.138538	H	4.787459	1.757311	2.171147
C	3.766008	-1.649932	-0.066587	C	3.413086	-1.237417	0.140451
H	2.968155	-2.38706	-0.127037	H	3.043744	-2.090759	-0.424105
C	4.55711	0.570795	0.059484	C	3.314002	1.031921	0.79844
C	5.072236	-2.117449	-0.0462	C	4.533373	-1.419847	0.938635
H	5.292447	-3.181662	-0.087783	H	5.033717	-2.383612	0.999386
C	6.13879	-1.217533	0.030259	C	5.048268	-0.352979	1.6813
C	-3.45116	0.283641	0.006765	C	-2.744595	0.020967	0.018873
C	-5.885055	-0.154904	0.016107	C	-4.369254	-0.164223	1.872501
H	-6.673742	-0.901094	0.013505	H	-4.707059	-0.734818	2.73239
C	-3.766817	1.65105	0.025062	C	-3.407527	1.200413	-0.357432
H	-2.968462	2.39008	0.030268	H	-3.061036	1.756559	-1.225516
C	-4.558591	-0.572924	0.00481	C	-3.27778	-0.623801	1.142323
C	-5.073622	2.117257	0.03641	C	-4.501973	1.694862	0.337944
H	-5.29375	3.182211	0.048933	H	-5.004061	2.60827	0.027352
C	-6.140832	1.21494	0.031032	C	-4.986758	1.015139	1.459207
C	2.484163	3.432903	1.378091	C	0.045468	2.58174	1.042873
H	3.250868	4.21589	1.351392	H	0.259696	3.503529	1.59642
H	1.493346	3.892893	1.298946	H	-0.918378	2.671828	0.529135
H	2.547179	2.891292	2.326539	H	-0.014513	1.740109	1.74152
C	-2.565942	-3.310965	1.507133	C	-0.051745	-2.352188	1.782498
H	-3.284945	-4.137669	1.472714	H	-0.35102	-2.972781	2.635216
H	-1.549169	-3.714337	1.565525	H	0.815259	-2.800732	1.285993
H	-2.753174	-2.699592	2.395185	H	0.229226	-1.354141	2.133923
C	-2.544166	-3.441305	-1.355326	C	-1.81216	-3.929706	0.154126
H	-1.544285	-3.887651	-1.329274	H	-0.957158	-4.376326	-0.364044
H	-3.297564	-4.234034	-1.279996	H	-2.035301	-4.510643	1.056563
H	-2.667792	-2.907988	-2.302577	H	-2.679002	-3.944375	-0.513274
C	2.640686	3.32082	-1.48119	C	1.505797	3.789501	-1.114374
H	1.627847	3.724413	-1.586849	H	0.548839	4.017064	-1.594587
H	3.356853	4.147306	-1.406501	H	1.778054	4.609209	-0.439198
H	2.871537	2.714433	-2.362431	H	2.274758	3.680495	-1.884663
O	7.380068	-1.758589	0.046316	O	6.141355	-0.619704	2.433886
O	-7.382736	1.754786	0.042285	O	-6.054691	1.568672	2.080082
C	8.477239	-0.880547	0.124493	C	6.697596	0.435569	3.181658
H	8.458163	-0.283437	1.047695	H	5.989189	0.827832	3.925465
H	9.375722	-1.502529	0.126366	H	7.564439	0.024234	3.704545
H	8.519367	-0.200626	-0.738717	H	7.031835	1.261208	2.537077
C	-8.480545	0.874146	0.03722	C	-6.577661	0.903195	3.205127
H	-9.379558	1.495277	0.046415	H	-7.425458	1.498084	3.553605
H	-8.495046	0.24386	-0.863757	H	-6.932998	-0.106524	2.953964
H	-8.489109	0.225987	0.925537	H	-5.839473	0.829714	4.016793
$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9848.6182629 + 0.319331 = -9848.2989319 Ha				$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9848.6220184 + 0.321634 = -9848.3003844 Ha			
$\Delta G_{bending}$ = -0.0014525 Ha = -3.81 kJ/mol							

f) Coplanar local minimum and bent optimized structures of ModelConf3

Table S12: Coordinates for optimized ModelConf3-plane and ModelConf3-bent

Plane structure				Bent structure			
Br	0.478124	1.639666	0.013174	Br	0.815652	-0.842123	2.353836
Ni	1.634749	-0.453413	0.001085	Ni	1.210216	0.890733	0.732722
Br	-0.51553	-1.525114	-0.008995	Br	-0.731899	2.013107	1.641095
Ni	-1.672475	0.570143	0.003108	Ni	-1.174993	-0.288478	1.096187
P	-2.66661	2.443939	-0.007806	P	-1.250805	-2.262766	0.3374
P	2.633334	-2.324261	0.009121	P	1.260748	2.266382	-0.876504
O	4.258142	-2.041616	-0.050064	O	2.533665	1.860655	-1.850907
O	-4.291684	2.164952	0.043724	O	-2.630166	-2.410267	-0.562673
C	3.440686	0.213271	0.006957	C	2.740206	0.162948	-0.167
C	5.857526	-0.309612	-0.030369	C	4.287616	0.299511	-2.080652
H	6.619722	-1.082399	-0.055223	H	4.598985	0.791617	-2.998247
C	3.803934	1.568401	0.036778	C	3.482404	-0.937226	0.27005
H	3.032362	2.334743	0.064656	H	3.197035	-1.445144	1.188705
C	4.517263	-0.681314	-0.02379	C	3.199115	0.754055	-1.3594
C	5.126204	1.988911	0.031383	C	4.592472	-1.427975	-0.421309
H	5.383524	3.045347	0.053127	H	5.13035	-2.284743	-0.025524
C	6.160992	1.050319	-0.003645	C	4.994084	-0.807759	-1.604376
C	-3.47926	-0.09429	-0.001827	C	-2.763285	-0.091914	0.038323
C	-5.888848	0.430379	0.02706	C	-4.433186	-1.165597	-1.434835
H	-6.683382	1.171533	0.046179	H	-4.754002	-2.075154	-1.93353
C	-3.843206	-1.44197	-0.025104	C	-3.500366	1.095377	-0.100655
H	-3.072339	-2.209439	-0.046855	H	-3.16578	1.99631	0.408738
C	-4.559133	0.807574	0.022642	C	-3.283344	-1.194297	-0.65208
C	-5.171579	-1.87327	-0.02116	C	-4.656041	1.169835	-0.86484
H	-5.384921	-2.938201	-0.038512	H	-5.217199	2.097306	-0.95296
C	-6.199377	-0.931236	0.005909	C	-5.127283	0.038674	-1.538084
C	2.378799	-3.462051	-1.378078	C	1.534118	4.033175	-0.586687
H	3.101176	-4.284615	-1.320754	H	1.698495	4.542363	-1.543418
H	1.362439	-3.868517	-1.341618	H	0.658565	4.464574	-0.090472
H	2.510117	-2.924852	-2.322102	H	2.409798	4.170074	0.054615
C	-2.477463	3.482951	-1.480975	C	-1.342523	-3.712461	1.418417
H	-3.168424	4.332491	-1.430405	H	-1.572302	-4.600914	0.818709
H	-1.44838	3.853107	-1.543996	H	-0.382781	-3.854154	1.925727
H	-2.6931	2.888764	-2.374178	H	-2.124528	-3.567058	2.169359
C	-2.41366	3.578685	1.382073	C	0.062705	-2.651822	-0.850306
H	-1.396143	3.982627	1.349902	H	1.032032	-2.667112	-0.339676
H	-3.13383	4.403065	1.323026	H	-0.126904	-3.624833	-1.318636
H	-2.55023	3.040699	2.324891	H	0.09177	-1.874132	-1.621149
C	2.453325	-3.361694	1.484736	C	-0.15367	2.196527	-2.007297
H	1.423927	-3.729707	1.555466	H	-1.042237	2.602931	-1.51261
H	3.142299	-4.212642	1.43106	H	0.064011	2.775745	-2.91231
H	2.675747	-2.766119	2.375395	H	-0.354201	1.15465	-2.277551
O	7.421103	1.546208	-0.007872	O	6.048256	-1.197213	-2.360019
O	-7.520667	-1.229944	0.012411	O	-6.258335	0.202942	-2.26343
C	8.487398	0.628221	-0.044439	C	6.799088	-2.30286	-1.917382
H	8.464094	0.010131	-0.953653	H	6.189622	-3.21642	-1.864568
H	9.407369	1.217895	-0.043549	H	7.594587	-2.452649	-2.651446
H	8.489446	-0.031893	0.835061	H	7.254845	-2.120751	-0.933679
C	-7.884292	-2.589684	-0.00783	C	-6.76975	-0.916673	-2.946659
H	-8.9767	-2.62018	0.001348	H	-7.674197	-0.582306	-3.460681
H	-7.5235	-3.096187	-0.914539	H	-6.059483	-1.299667	-3.693553
H	-7.50758	-3.126937	0.87437	H	-7.034754	-1.730448	-2.256452
$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9848.6183918 + 0.320247 = -9848.2981448 Ha				$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9848.6220727 + 0.322662 = -9848.2994107 Ha			
$\Delta G_{bending}$ = -0.00126594 Ha = -3.23 kJ/mol							

g) Geometry of the transition state for the flipping

Table S13: Coordinates for the optimized transition state of ModelPhenol flipping

ModelPhenol – Transition state			
Br	-0.18607591	-1.64807091	0.04364467
Ni	-1.71931291	0.18668009	0.01022167
Br	0.18607509	1.64806609	0.04379567
Ni	1.71931209	-0.18668191	0.01019067
P	3.05429509	-1.83654291	-0.00462233
P	-3.05429391	1.83654409	-0.00443233
O	-4.57605391	1.25378709	-0.25000133
O	4.57605109	-1.25376291	-0.25017033
C	-3.36977591	-0.81090391	-0.01668833
C	-5.82662691	-0.75571991	-0.20142033
H	-6.72726491	-0.15615191	-0.31101533
C	-3.46786091	-2.20316891	0.09068767
H	-2.56710891	-2.80158591	0.20983767
C	-4.58938691	-0.12918991	-0.15485833
C	-4.69522491	-2.86376091	0.04744167
H	-4.72491891	-3.94838191	0.12959167
C	-5.87422391	-2.14164191	-0.10216833
C	3.36977509	0.81090409	-0.01663633
C	5.82662409	0.75573909	-0.20139533
H	6.72726209	0.15618209	-0.31105833
C	3.46786109	2.20315809	0.09087967
H	2.56711009	2.80156309	0.21009867
C	4.58938509	0.12920409	-0.15488633
C	4.69522409	2.86375509	0.04768867
H	4.72491909	3.94836809	0.12994767
C	5.87422209	2.14165109	-0.10200533
C	-2.91724891	3.11412509	-1.27998033
H	-3.81424091	3.74414309	-1.26427033
H	-2.03546891	3.73469109	-1.08855533
H	-2.81476791	2.64782709	-2.26414933
C	2.91723109	-3.11402291	-1.28026833
H	3.81422809	-3.74403491	-1.26463133
H	2.03546109	-3.73461291	-1.08887033
H	2.81472109	-2.64764891	-2.26439833
C	3.19632609	-2.75821091	1.55063667
H	2.25439909	-3.27683891	1.76089067
H	4.01038409	-3.48932591	1.48406567
H	3.40014409	-2.05634891	2.36550567
C	-3.19629391	2.75809209	1.55090067
H	-2.25436991	3.27672309	1.76116167
H	-4.01036691	3.48919809	1.48440767
H	-3.40007391	2.05616909	2.36572567
H	6.83360809	2.65310209	-0.13781533
H	-6.83361091	-2.65308891	-0.13802133

$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$
= -9619.60268 + 0.263779
= -9619.338898 Ha

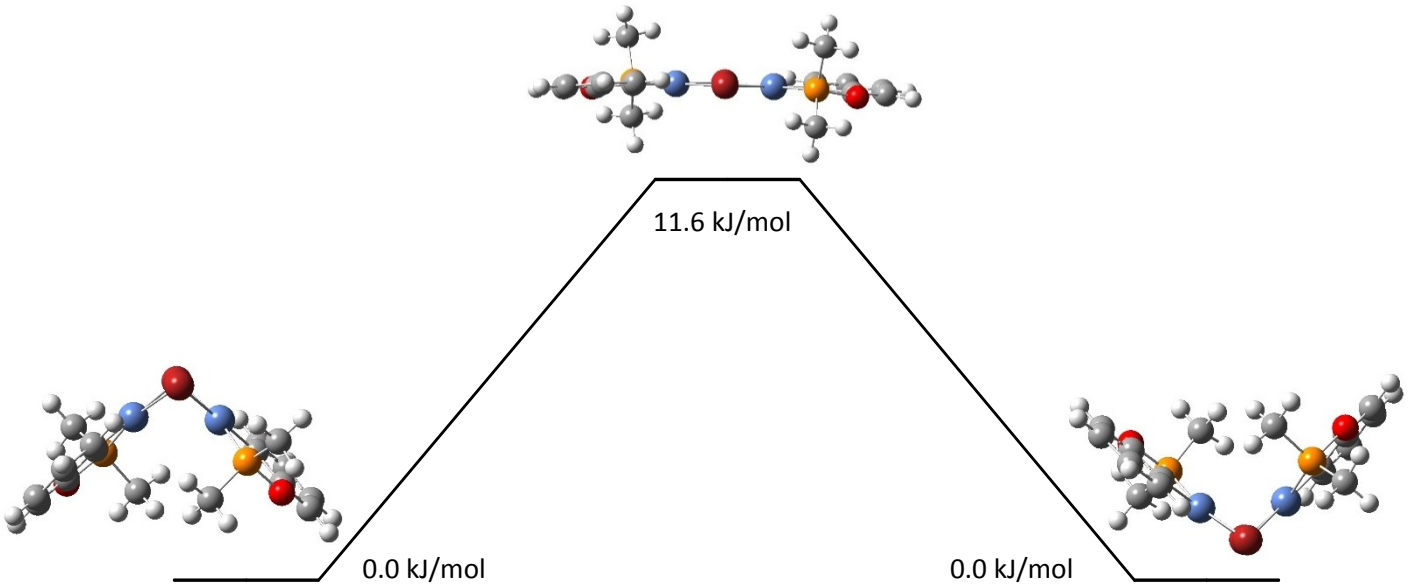

Figure S92: Proposed energy surface for the inversion of the bending in ModelPhenol

h) Geometry of the *s*-cis isomer and the mixed square planar-tetrahedral dinuclear intermediate

Table S14: Coordinates for the optimized transition state of ModelPhenol flipping

ModelPhenolCis				ModelPhenolMix			
Ni	-1.479321	-0.08185	-0.464563	Ni	-1.300403	0.735936	0.364086
Br	0.011471	1.401719	-1.560551	Ni	1.318597	0.400763	0.002088
Ni	1.474916	-0.102671	-0.457045	Br	0.222379	0.354496	2.190421
Br	-0.013023	-1.895791	-1.139416	Br	0.140462	2.513227	-0.499439
P	-2.747358	-1.460018	0.54016	P	-2.402239	0.846852	-1.452308
P	2.698325	-1.487157	0.59346	P	3.579312	0.319929	0.309392
O	3.868833	-0.631804	1.376982	O	3.984769	-0.952419	-0.678225
O	-4.060853	-0.6303	1.088401	O	-3.662337	-0.212123	-1.340868
C	2.805976	1.147271	0.157581	C	1.616371	-1.420519	-0.688673
C	4.840243	1.52284	1.496022	C	3.248242	-3.025031	-1.561909
H	5.60272	1.102221	2.147477	H	4.288069	-3.27001	-1.7677
C	2.850994	2.50393	-0.185585	C	0.608448	-2.347174	-0.97515
H	2.087508	2.920413	-0.837342	H	-0.427907	-2.106446	-0.722833
C	3.835482	0.702481	1.002621	C	2.928256	-1.804984	-0.977629
C	3.848385	3.353078	0.291993	C	0.896331	-3.579184	-1.561826
H	3.843179	4.401915	0.002599	H	0.094432	-4.281767	-1.779574
C	4.840814	2.865198	1.134996	C	2.216416	-3.909657	-1.860392
C	-2.775945	1.189391	0.181781	C	-2.6225	-0.59734	0.791883
C	-4.905513	1.562247	1.364039	C	-4.641792	-1.820866	0.090028
H	-5.753443	1.128571	1.889044	H	-5.393482	-1.991874	-0.676927
C	-2.691213	2.577321	0.017222	C	-2.671832	-1.316832	1.992497
H	-1.835723	3.006788	-0.497352	H	-1.91305	-1.14861	2.751788
C	-3.909387	0.730447	0.872155	C	-3.638907	-0.88749	-0.133634
C	-3.676026	3.438903	0.498827	C	-3.670899	-2.254818	2.247903
H	-3.571434	4.511047	0.345678	H	-3.67407	-2.790098	3.19508
C	-4.783989	2.933235	1.16977	C	-4.653631	-2.509437	1.297328
C	3.643766	-2.681282	-0.391256	C	4.090288	-0.263711	1.953157
H	4.343529	-3.228717	0.250886	H	5.145625	-0.559635	1.94859
H	2.961333	-3.389	-0.874276	H	3.932699	0.530069	2.692235
H	4.201635	-2.146282	-1.166207	H	3.472535	-1.124361	2.232292
C	-2.093257	-2.234034	2.045512	C	-1.53321	0.287784	-2.941436
H	-2.89614	-2.762198	2.57293	H	-2.247908	0.183072	-3.766194
H	-1.302391	-2.944382	1.781463	H	-0.760342	1.013673	-3.214824
H	-1.678093	-1.458719	2.697526	H	-1.054489	-0.678402	-2.746939
C	-3.507453	-2.825817	-0.376222	C	-3.23018	2.381401	-1.943396
H	-2.749268	-3.575146	-0.626476	H	-2.488386	3.124149	-2.252985
H	-4.288093	-3.290559	0.237182	H	-3.909869	2.173827	-2.778053
H	-3.950018	-2.446606	-1.302121	H	-3.801472	2.778799	-1.09924
C	1.984228	-2.477464	1.934074	C	4.871677	1.504539	-0.158505
H	1.385535	-3.290558	1.510622	H	4.851227	2.347922	0.540412
H	2.791619	-2.902966	2.541379	H	5.85781	1.027456	-0.12266
H	1.349406	-1.846661	2.564061	H	4.687861	1.882297	-1.168491
H	5.619058	3.525385	1.511559	H	2.449602	-4.869039	-2.317699
H	-5.55421	3.602553	1.546727	H	-5.43175	-3.244346	1.491473
$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9619.6022461 + 0.262749 = -9619.3394971 Ha				$E_{Gibbs} = E_{def2TZVP} + Corr_{EGibbs}$ = -9619.5757152 + 0.258432 = -9619.3172832 Ha			
$\Delta G_{s\text{-}cis} - \Delta G_{s\text{-}trans}$ = +0.00381164 Ha = +10.0 kJ/mol				$\Delta G_{mix\text{-}triplet} - \Delta G_{s\text{-}trans}$ = +0.02602554 Ha =+68.3 kJ/mol			