Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

The Role of Ligand Electro-activity towards Phenyl acetylene Homocoupling Reaction by a Nickel(II) Complex of a Non-innocent *O*-amino phenol Ligand: A Mechanistic Insight

Mina Nasibipour [a], Elham Safaei [a,*], Marziyeh Sadat Masoumpour[b], Andrzej Wojtczak [c]

[a] Department of Chemistry, College of Sciences, Shiraz University, 71454, Shiraz, Iran.

[b] Nicolaus Copernicus University, Faculty of Chemistry, 87-100 Torun, Poland

Correspondence

Elham Safaei, Department of Chemistry, College of Sciences, Shiraz University, Shiraz, 71454, Iran

Email: e.safaei@shirazu.ac.ir

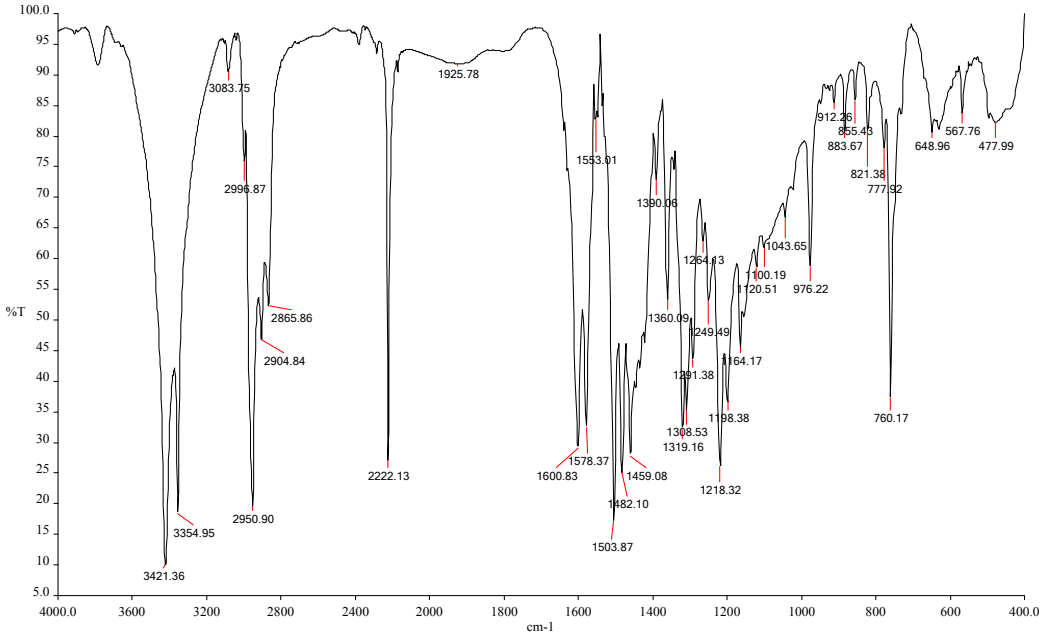


Figure S1 IR spectrum of H_2L^{NAP}

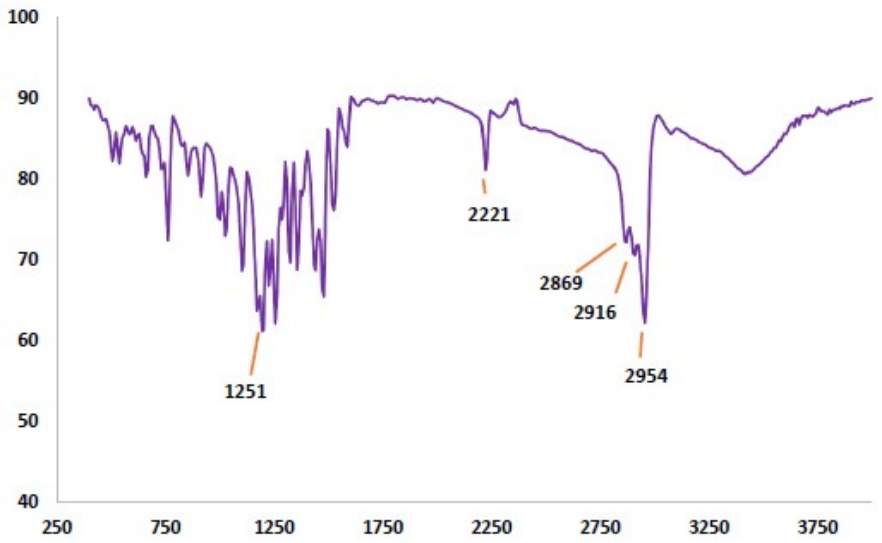


Figure S2 IR spectrum of $Ni^{II}L_2^{NIS}$

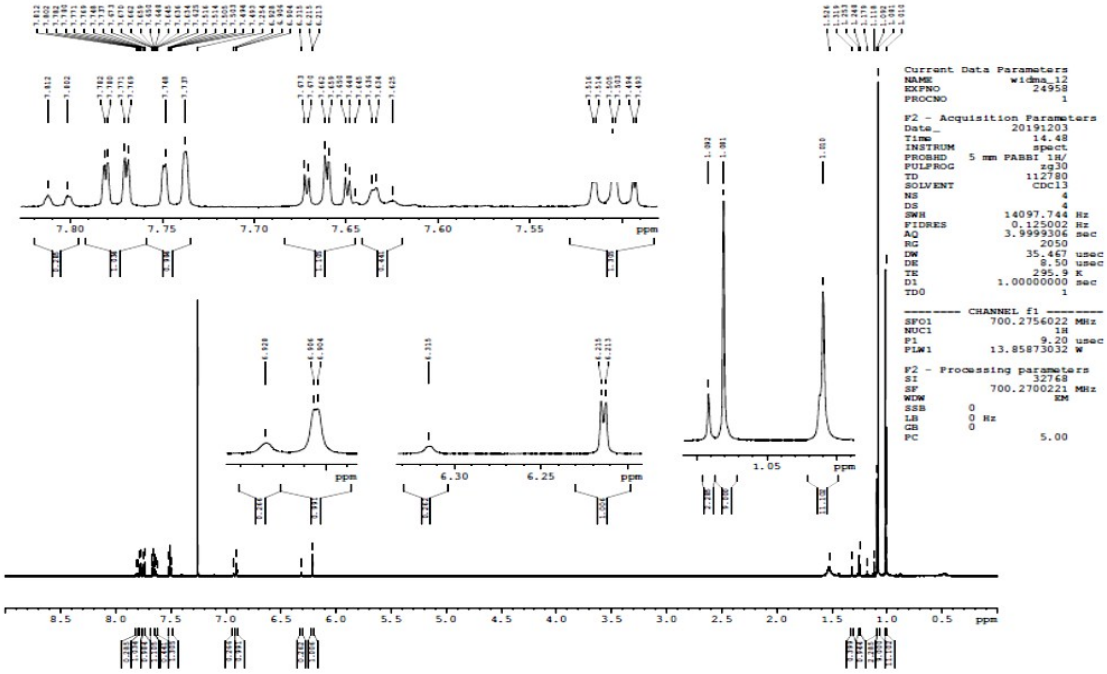


Figure S3 ^{1}H NMR spectrum of $Ni^{II}L_2^{NIS}$

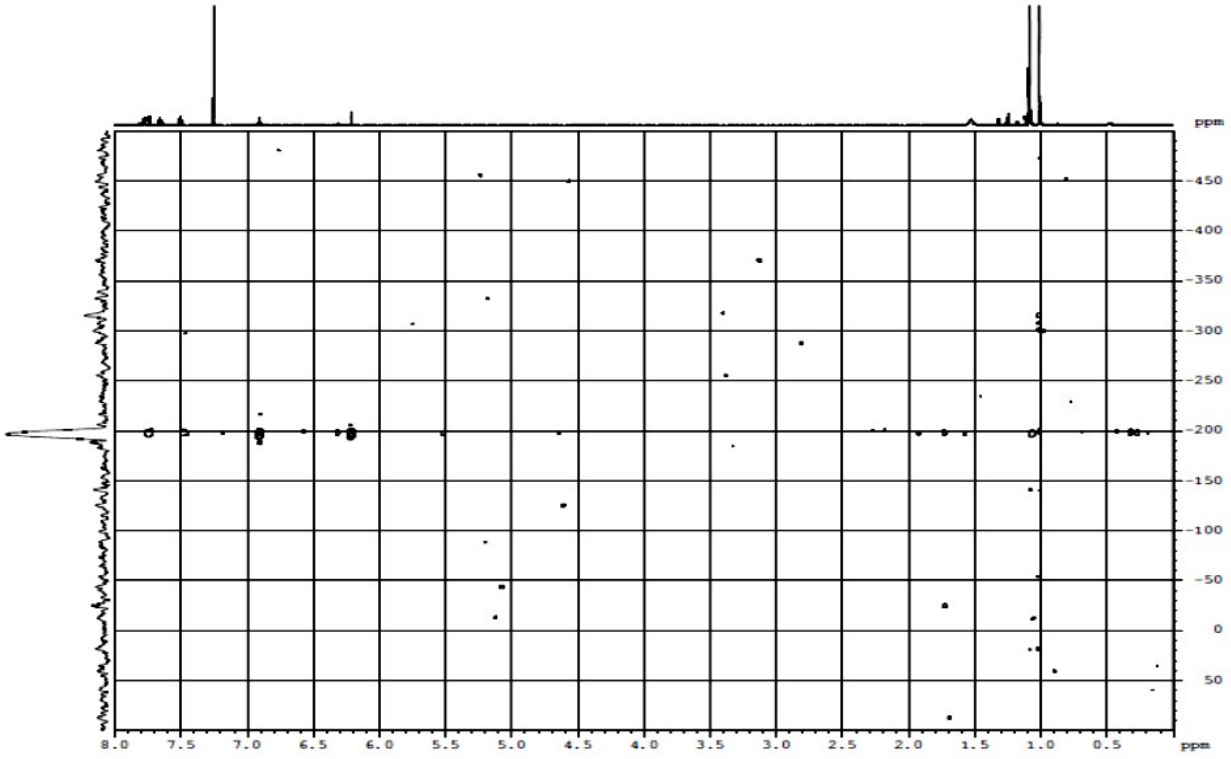


Figure S4 ^{15}N NMR spectrum of $Ni^{II}L_2^{NIS}$

Table S1 Crystallographic data for $Ni^{II}L_2^{NIS}$.

Empirical formula	C21 H24 N2 Ni0.50 O
Formula weight	349.78
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 16.469(2) b = 8.1558(8) c = 16.897(2) α= 90. β= 118.733(17) δ = 90.
Volume	1990.1(5)
Z	4
Temperature	293(2) K
Wavelength; Å	0.71073
Density (calculated)	1.167 Mg/m^3
Crystal size	0.529 x 0.356 x 0.122 mm^3
Absorption coefficient	0.525 mm^{-1}
F(000)	744
Theta range for data collection	2.412 to 28.446°.
Index ranges	-20<=h<=21, -10<=k<=10, -21<=l<=19
Reflections collected	13001
Independent reflections	4554 [R(int) = 0.0568]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Analytical
Max. and min. transmission	0.939 and 0.807
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4554 / 0 / 223
Goodness-of-fit on F^2	0.977
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1037
R indices (all data)	R1 = 0.0742, wR2 = 0.1146
Largest diff. peak and hole; $e.Å^{-3}$	0.357 and -0.252

Table S2. Selected bond lengths [Å] and angles [°] for $Ni^{II}L_2^{NIS}$.

Ni1-O1	O1-Ni1-O1#1
Ni1-O1#1	O1-Ni1-N1
Ni1-N1	O1#1-Ni1-N1
Ni1-N1#1	O1-Ni1-N1#1
O1-C1	O1#1-Ni1-N1#1
C1-C2	N1-Ni1-N1#1
C1-C6	C1-O1-Ni1
C2-C3	O1-C1-C2
C2-C14	O1-C1-C6
C3-C4	C2-C1-C6
C4-C5	C3-C2-C1
C4-C18	C3-C2-C14
C5-C6	C1-C2-C14
C6-N1	C2-C3-C4
N1-C7	C5-C4-C3
C7-C8	C5-C4-C18
C7-C12	C3-C4-C18
C8-C9	C4-C5-C6
C9-C10	N1-C6-C5
C10-C11	N1-C6-C1
C11-C12	C5-C6-C1
C12-C13	C6-N1-C7
C13-N2	C6-N1-Ni1
C14-C16	C7-N1-Ni1
C14-C17	C8-C7-C12
C14-C15	C8-C7-N1
C18-C19	C12-C7-N1
C18-C21	C9-C8-C7
C18-C20	C10-C9-C8
	C11-C10-C9
	C10-C11-C12
	C7-C12-C11

	C7-C12-C13
	C11-C12-C13
	N2-C13-C12
	C16-C14-C17
	C16-C14-C2
	C17-C14-C2
	C16-C14-C15
	C17-C14-C15
	C2-C14-C15
	C19-C18-C21
	C19-C18-C4
	C21-C18-C4
	C19-C18-C20
	C21-C18-C20
	C4-C18-C20
Symmetry transformations used to generate equivalent atoms: #1-x,-y,-z	

Table S3. Torsion angles [°] for $Ni^{II}L_2^{NIS}$.

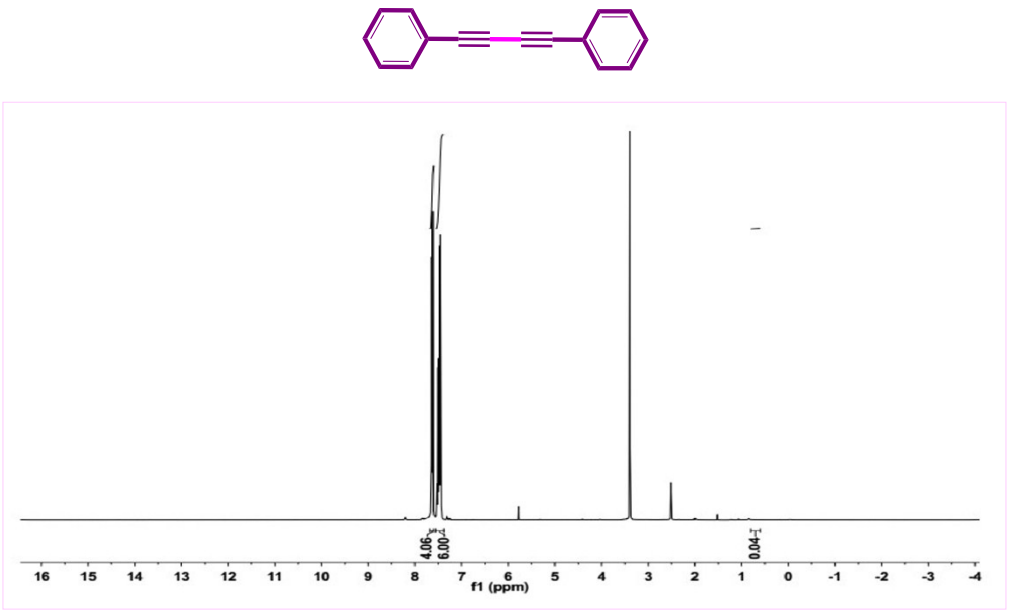
N(1)-Ni(1)-O(1)-C(1)	0.92(14)
N(1)#1-Ni(1)-O(1)-C(1)	-179.08(14)
Ni(1)-O(1)-C(1)-C(2)	-178.96(15)
Ni(1)-O(1)-C(1)-C(6)	-0.2(2)
O(1)-C(1)-C(2)-C(3)	179.02(19)
C(6)-C(1)-C(2)-C(3)	0.3(3)
O(1)-C(1)-C(2)-C(14)	-3.1(3)
C(6)-C(1)-C(2)-C(14)	178.12(19)
C(1)-C(2)-C(3)-C(4)	1.0(3)
C(14)-C(2)-C(3)-C(4)	-176.8(2)
C(2)-C(3)-C(4)-C(5)	-1.4(3)
C(2)-C(3)-C(4)-C(18)	179.9(2)
C(3)-C(4)-C(5)-C(6)	0.5(3)
C(18)-C(4)-C(5)-C(6)	179.0(2)
C(4)-C(5)-C(6)-N(1)	-178.0(2)

C(4)-C(5)-C(6)-C(1)	0.8(3)
O(1)-C(1)-C(6)-N(1)	-1.1(3)
C(2)-C(1)-C(6)-N(1)	177.79(17)
O(1)-C(1)-C(6)-C(5)	179.97(17)
C(2)-C(1)-C(6)-C(5)	-1.2(3)
C(5)-C(6)-N(1)-C(7)	-1.9(3)
C(1)-C(6)-N(1)-C(7)	179.18(16)
C(5)-C(6)-N(1)-Ni(1)	-179.34(16)
C(1)-C(6)-N(1)-Ni(1)	1.8(2)
O(1)-Ni(1)-N(1)-C(6)	-1.52(14)
O(1)#1-Ni(1)-N(1)-C(6)	178.47(14)
O(1)-Ni(1)-N(1)-C(7)	-178.79(16)
O(1)#1-Ni(1)-N(1)-C(7)	1.21(16)
C(6)-N(1)-C(7)-C(8)	-68.7(2)
Ni(1)-N(1)-C(7)-C(8)	108.40(19)
C(6)-N(1)-C(7)-C(12)	114.0(2)
Ni(1)-N(1)-C(7)-C(12)	-68.9(2)
C(12)-C(7)-C(8)-C(9)	0.4(3)
N(1)-C(7)-C(8)-C(9)	-176.91(19)
C(7)-C(8)-C(9)-C(10)	-0.1(3)
C(8)-C(9)-C(10)-C(11)	-0.6(4)
C(9)-C(10)-C(11)-C(12)	1.0(4)
C(8)-C(7)-C(12)-C(11)	0.1(3)
N(1)-C(7)-C(12)-C(11)	177.43(18)
C(8)-C(7)-C(12)-C(13)	179.59(18)
N(1)-C(7)-C(12)-C(13)	-3.1(3)
C(10)-C(11)-C(12)-C(7)	-0.8(3)
C(10)-C(11)-C(12)-C(13)	179.7(2)
C(3)-C(2)-C(14)-C(16)	111.0(2)
C(1)-C(2)-C(14)-C(16)	-66.6(3)
C(3)-C(2)-C(14)-C(17)	-128.8(2)
C(1)-C(2)-C(14)-C(17)	53.5(3)
C(3)-C(2)-C(14)-C(15)	-7.8(3)
C(1)-C(2)-C(14)-C(15)	174.5(2)
C(5)-C(4)-C(18)-C(19)	11.2(3)
C(3)-C(4)-C(18)-C(19)	-170.3(2)

C(5)-C(4)-C(18)-C(21)	-110.2(3)
C(3)-C(4)-C(18)-C(21)	68.4(3)
C(5)-C(4)-C(18)-C(20)	130.1(2)
C(3)-C(4)-C(18)-C(20)	-51.3(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z



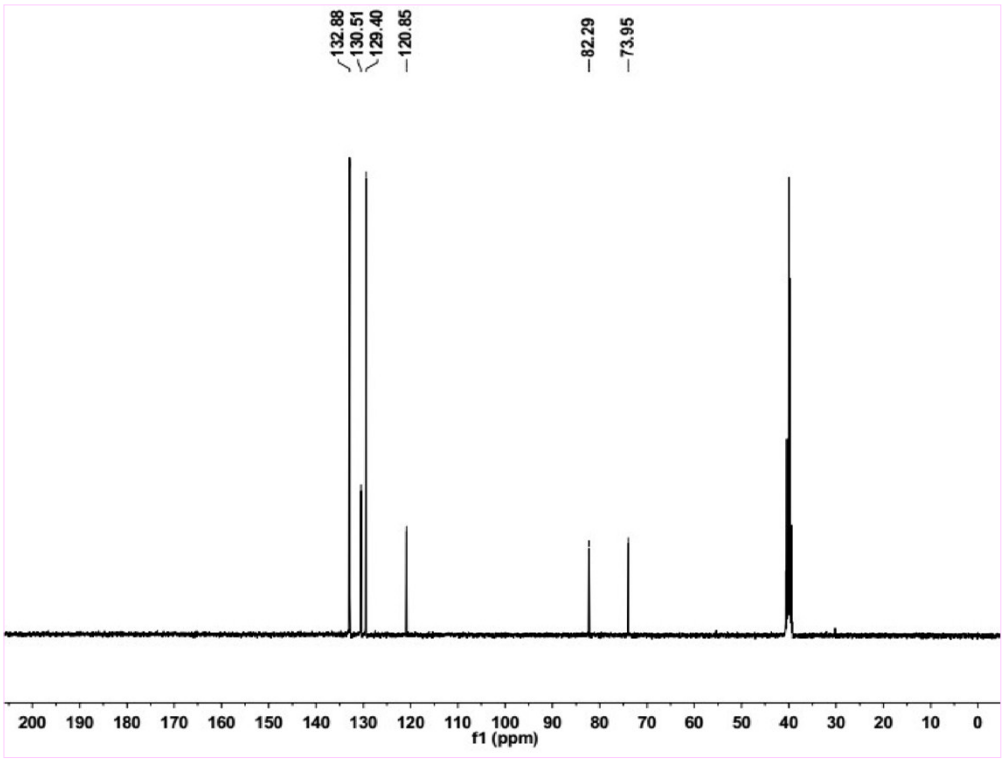
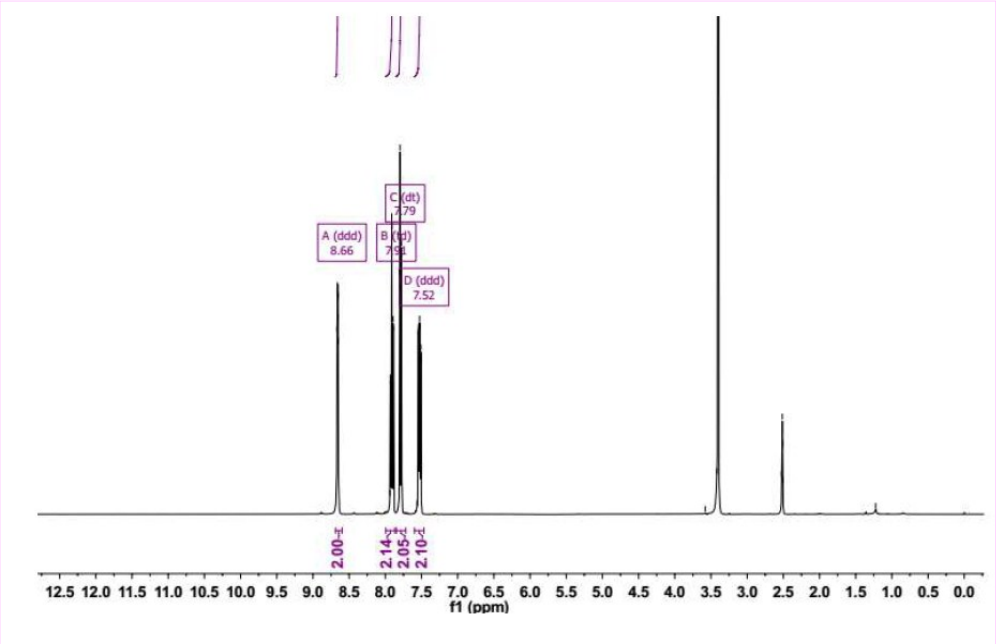


Figure S5 ^{1}H NMR and ^{13}C NMR spectrums of 1,4-diphenyl buta-1,3-diyne


A (ddd)
8.66
C (dt)
7.79
D (ddd)
7.52
2.00
2.14
2.05
2.10
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

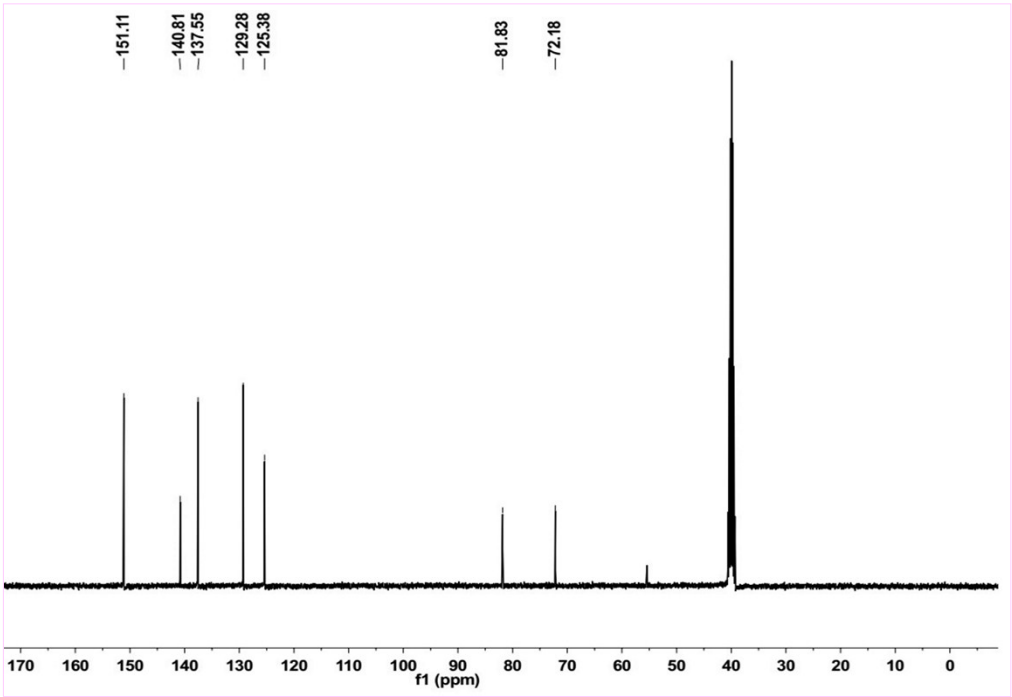
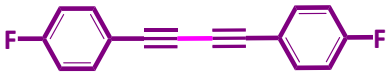

151.11
140.81
137.55
129.28
125.38
81.83
72.18
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Figure S6 ^{1}H NMR and ^{13}C NMR spectrum of 1,4-di(pyridin-2-yl)buta-1,3-diyne



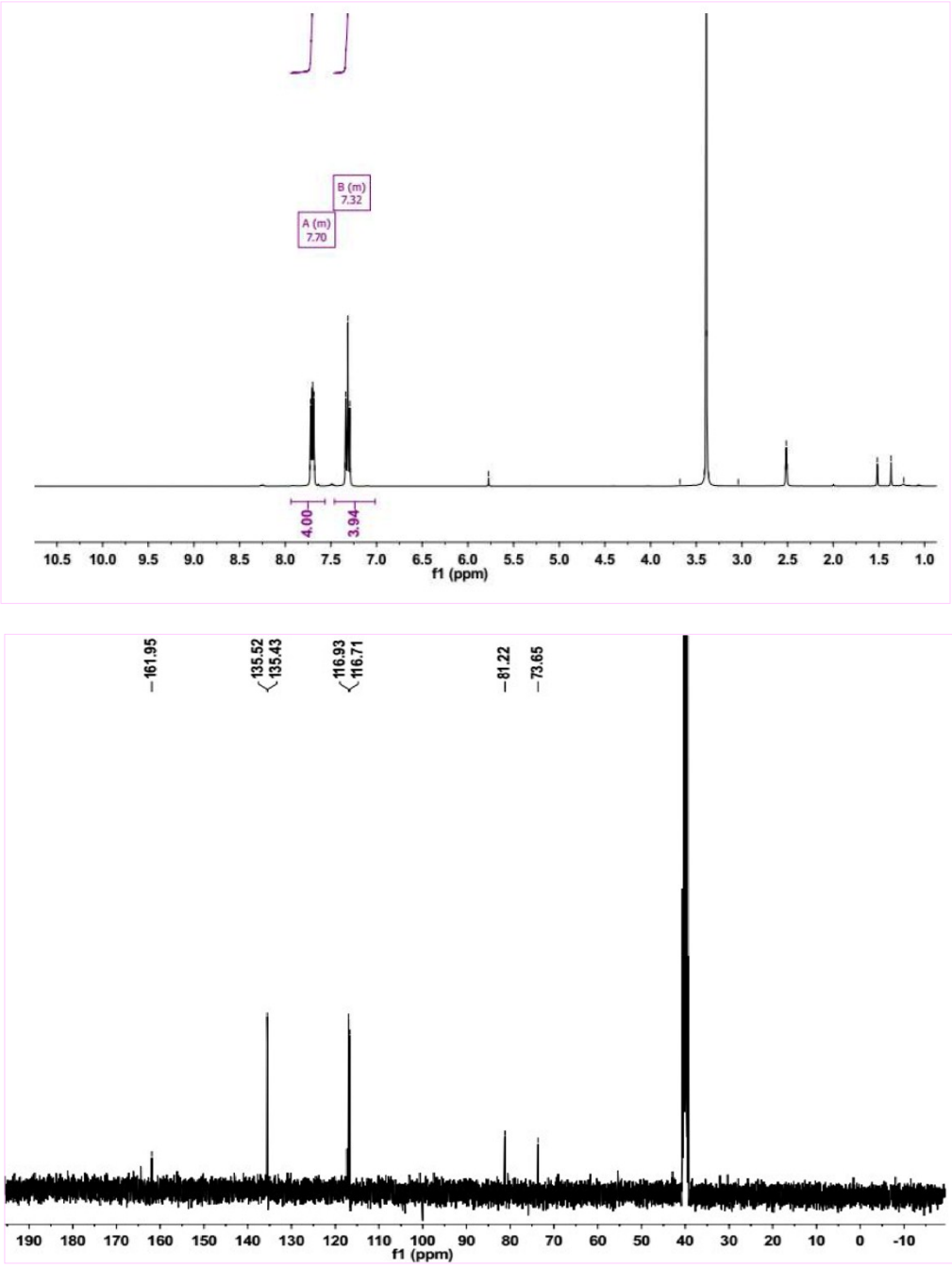
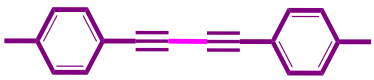
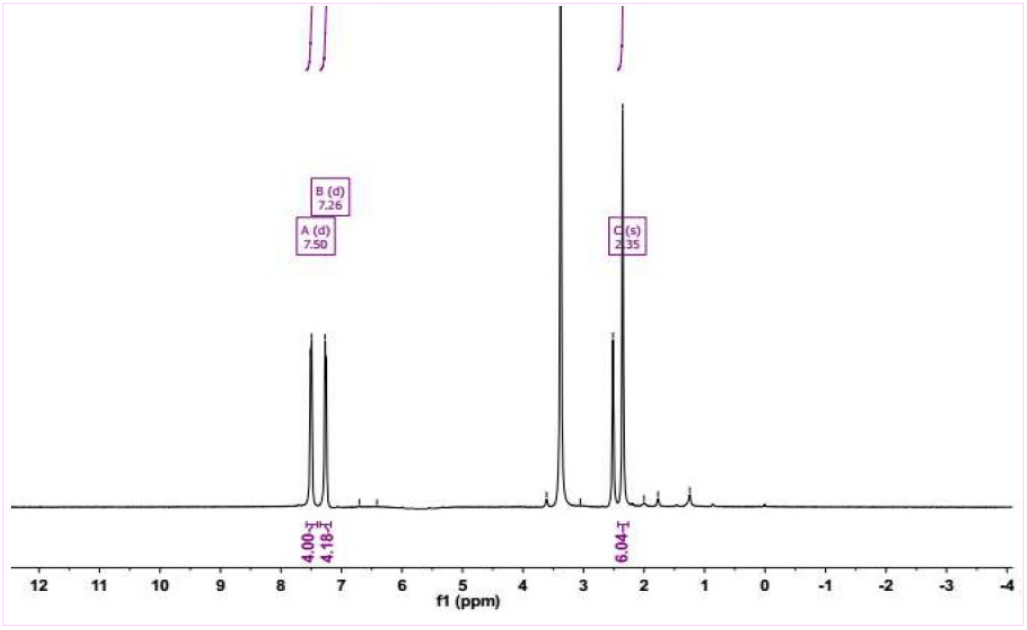


Figure S7 ^{1}H NMR and ^{13}C NMR spectrum of 1,4-*bis*(*p*-fluorophenyl)buta-1,3-diyne





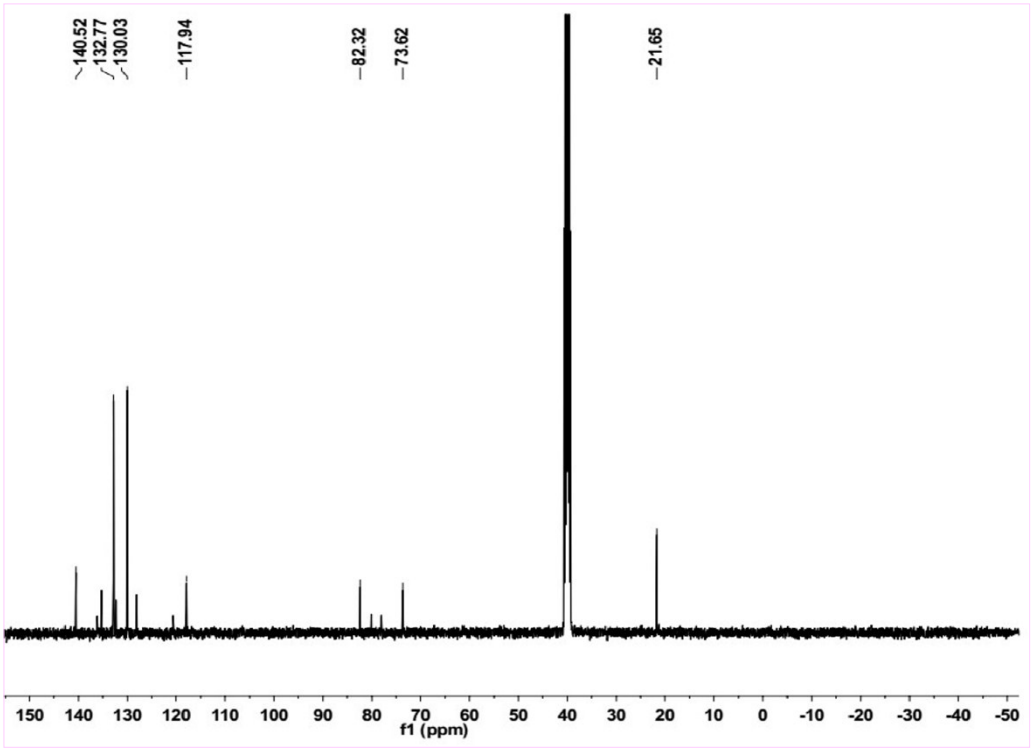
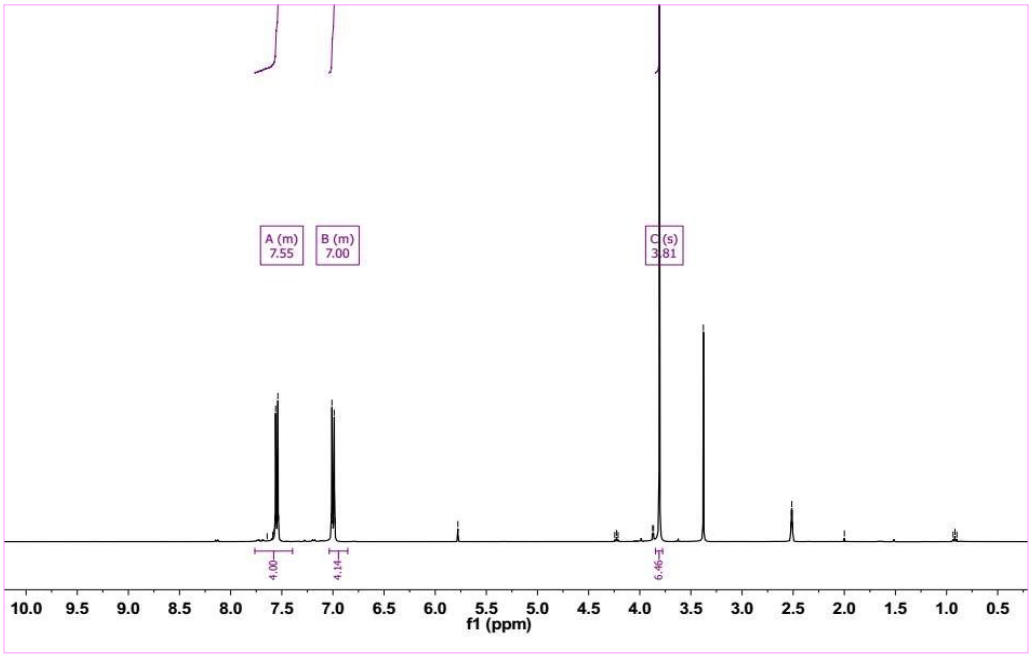


Figure S8 ^{1}H NMR and ^{13}C NMR spectrum of 1,4-*bis*(*p*-tolyl)buta-1,3-diyne



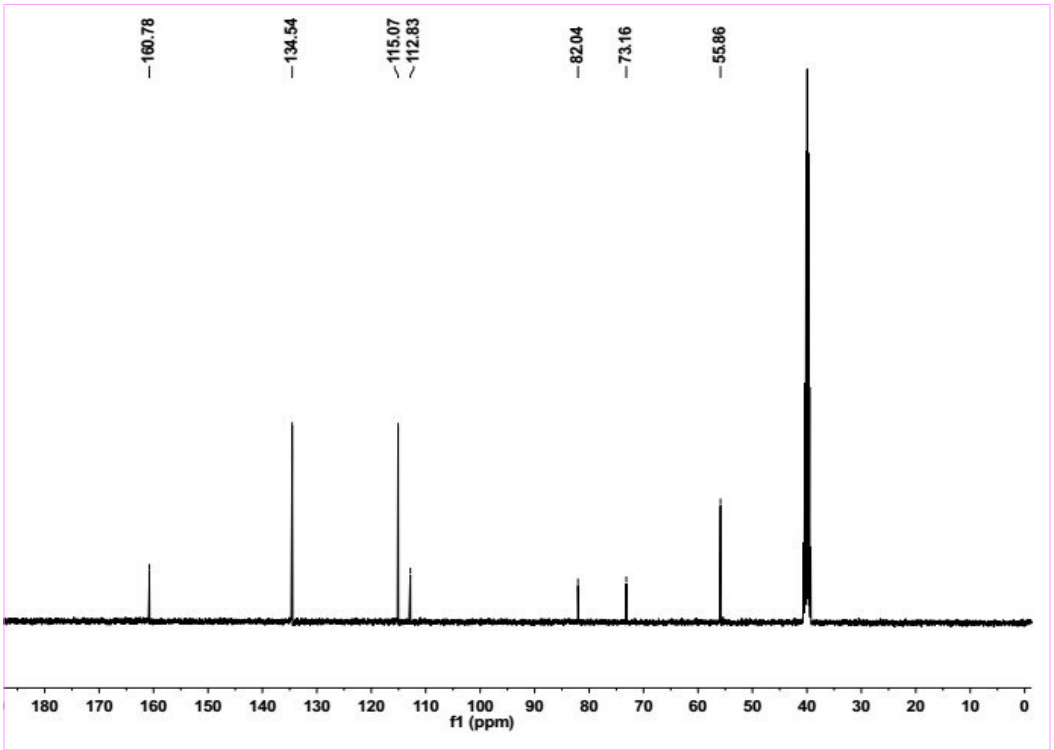
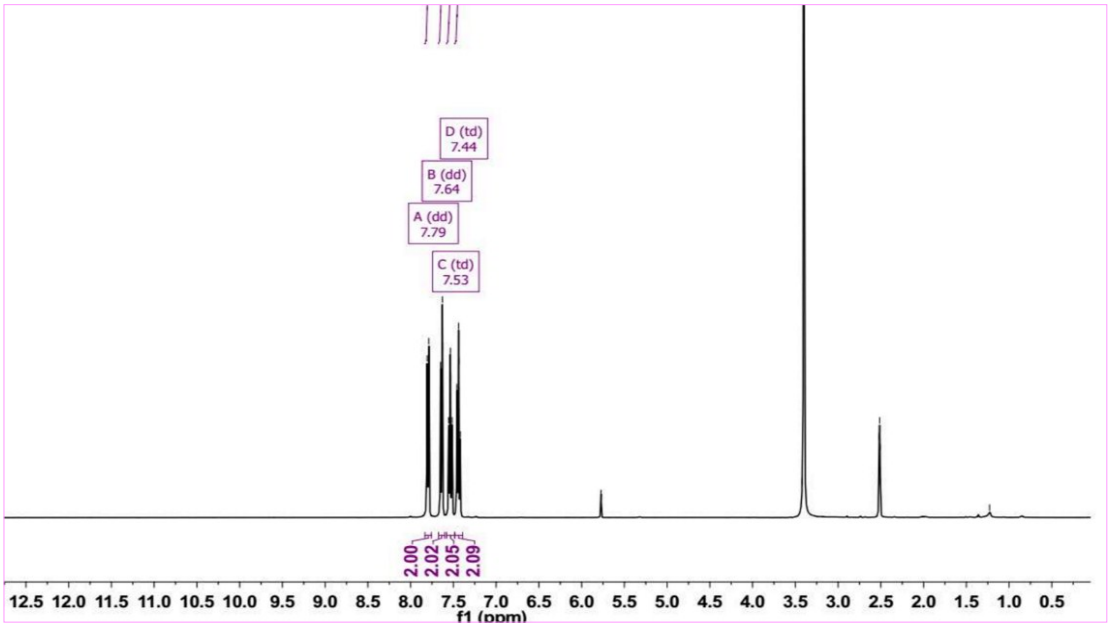


Figure S9 ^{1}H NMR and ^{13}C NMR spectrum of 1, 4-bis(4-methoxyphenyl)buta-1,3-diyne


Cl
Cl


D (td)
7.44
B (dd)
7.64
A (dd)
7.79
C (td)
7.53
2.00
2.02
2.05
2.09
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

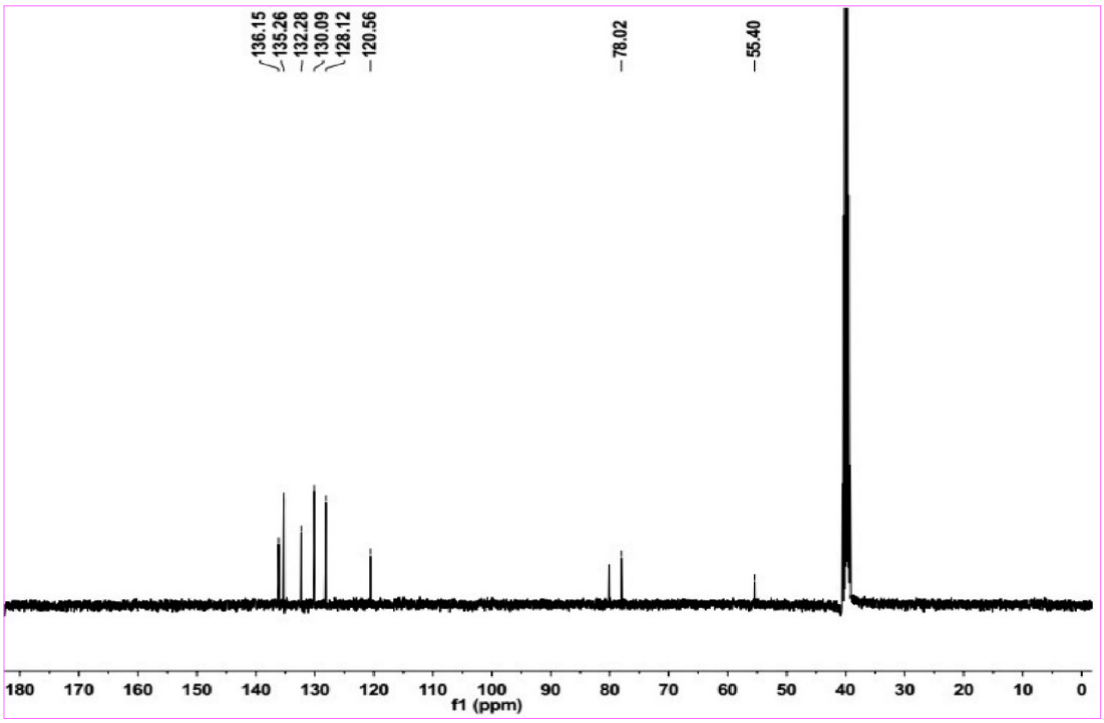

136.15
135.26
132.28
130.09
128.12
120.56
78.02
55.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Figure S10 ^{1}H NMR and ^{13}C NMR spectrum of 1,4-bis(2-chlorophenyl)buta-1,3-diyne