Supporting Information

Making the Unconventional μ^2-P Bridging Binding Mode More Conventional in Phosphinine Complexes

Yuanfeng Hou,[a] Zhongshu Li,[a] Yaqi Li,[a] Peng Liu,[b] Cheng-Yong Su,*[a] Florian Puschmann,[c] and Hansjörg Grützmacher,*[a,c]*

a Lehn Institute of Functional Materials (LIFM), School of Chemistry, Sun Yat-Sen University, 510275 Guangzhou China.

b Guangdong Engineering and Technology Research Center for Advanced Nanomaterials, School of Environment and Civil Engineering, Dongguan University of Technology, Dongguan 523808, China.

c Department of Chemistry and Applied Biosciences, ETH Zürich, 8093 Zürich, Switzerland.

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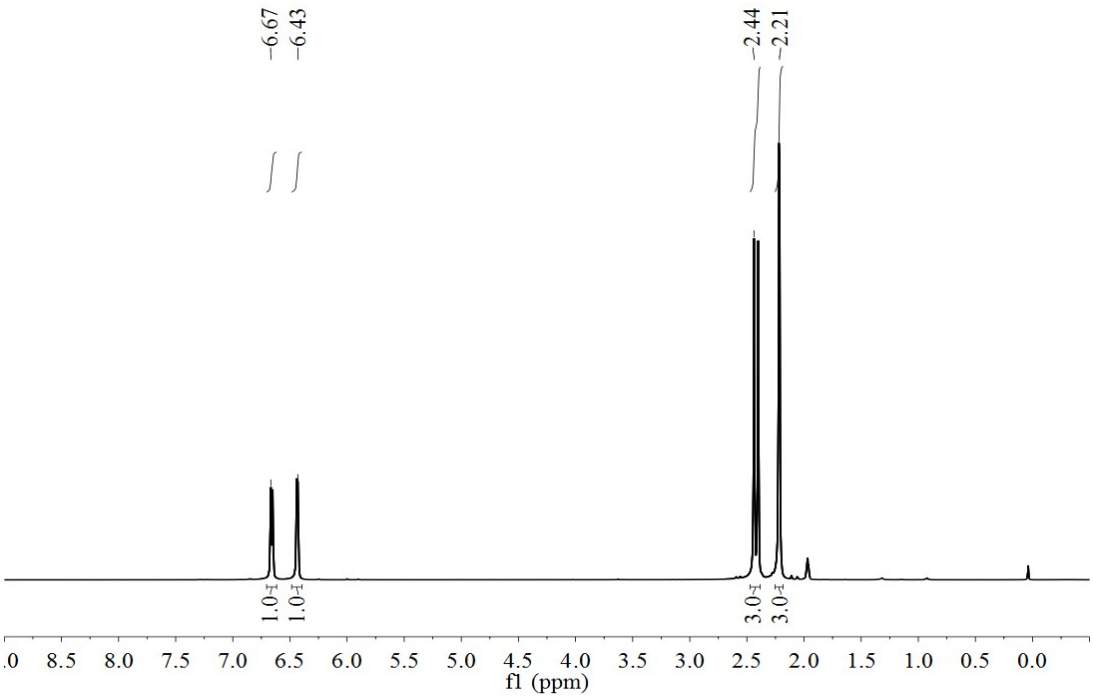

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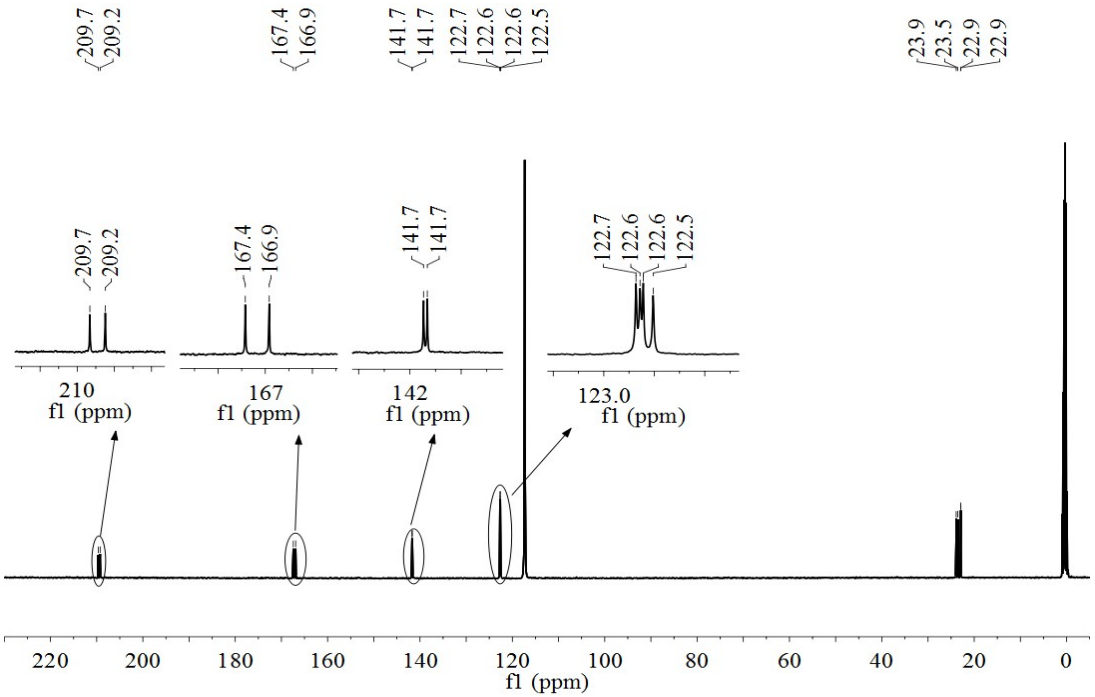

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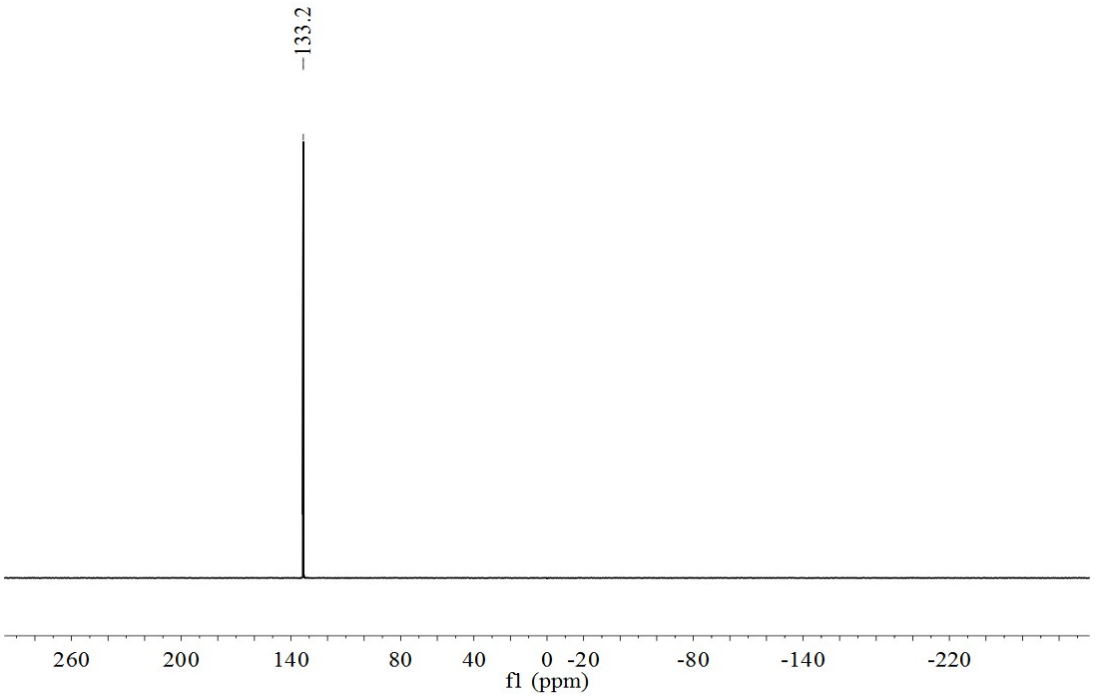

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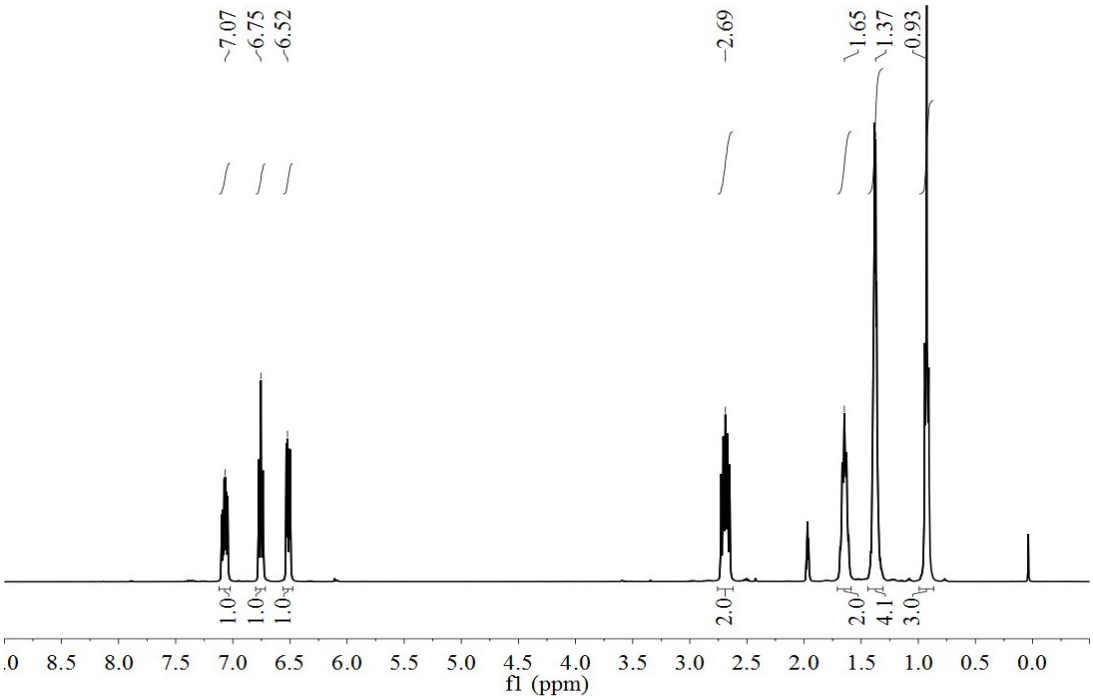

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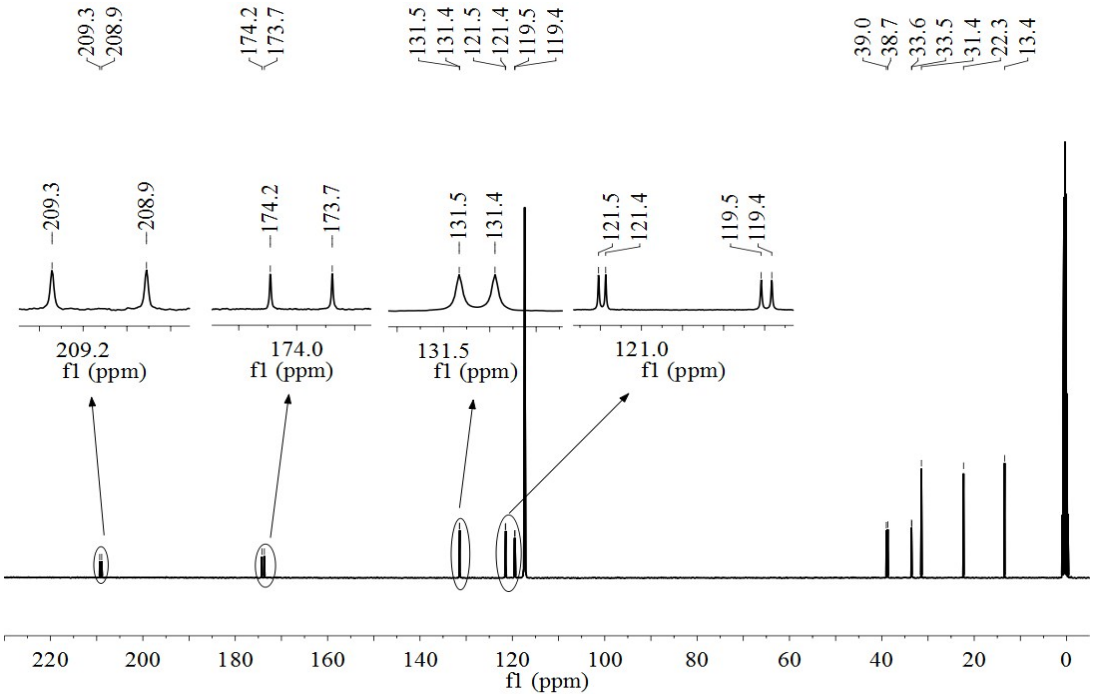

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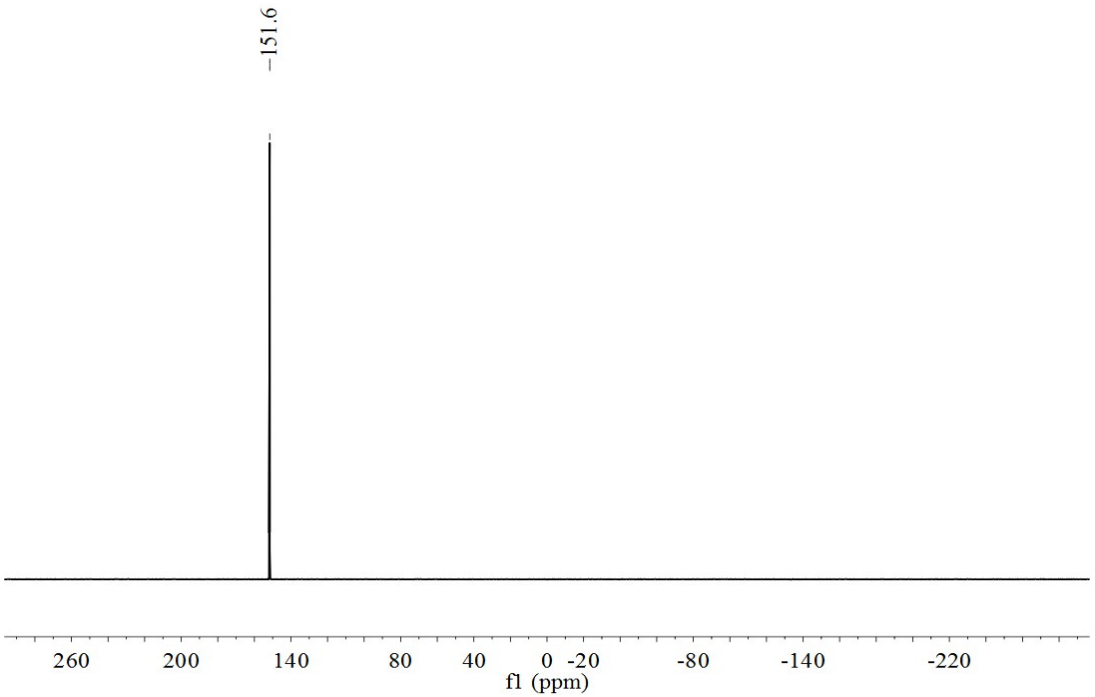

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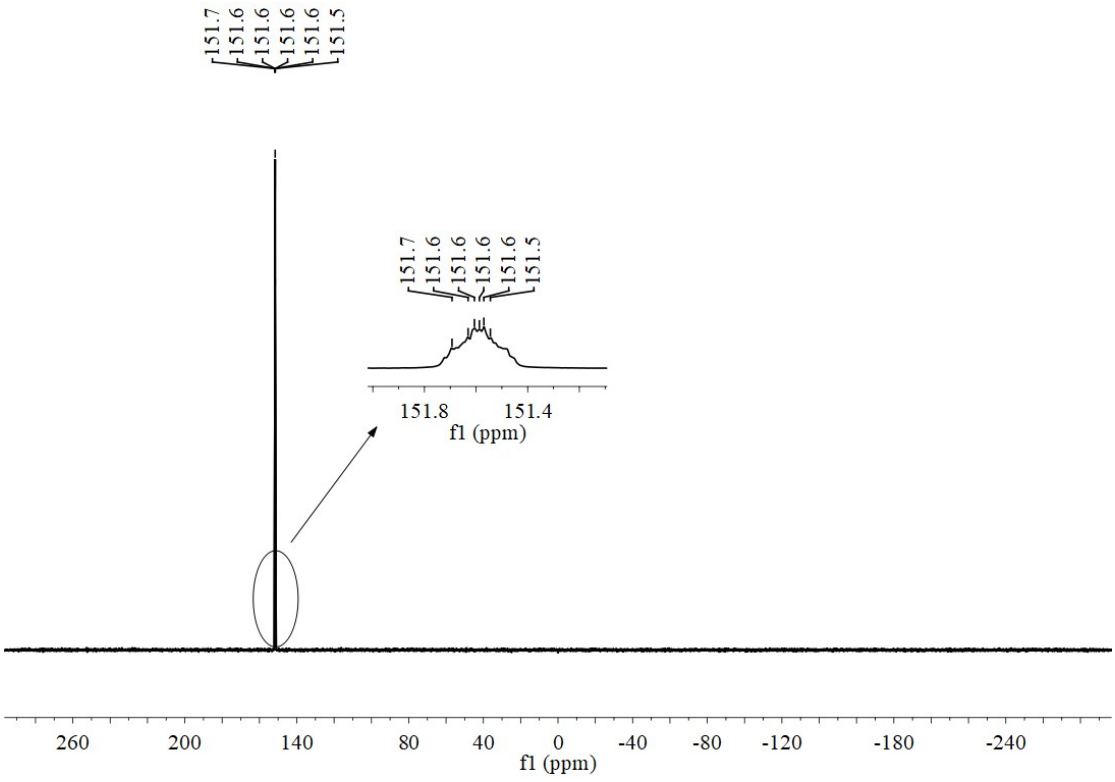

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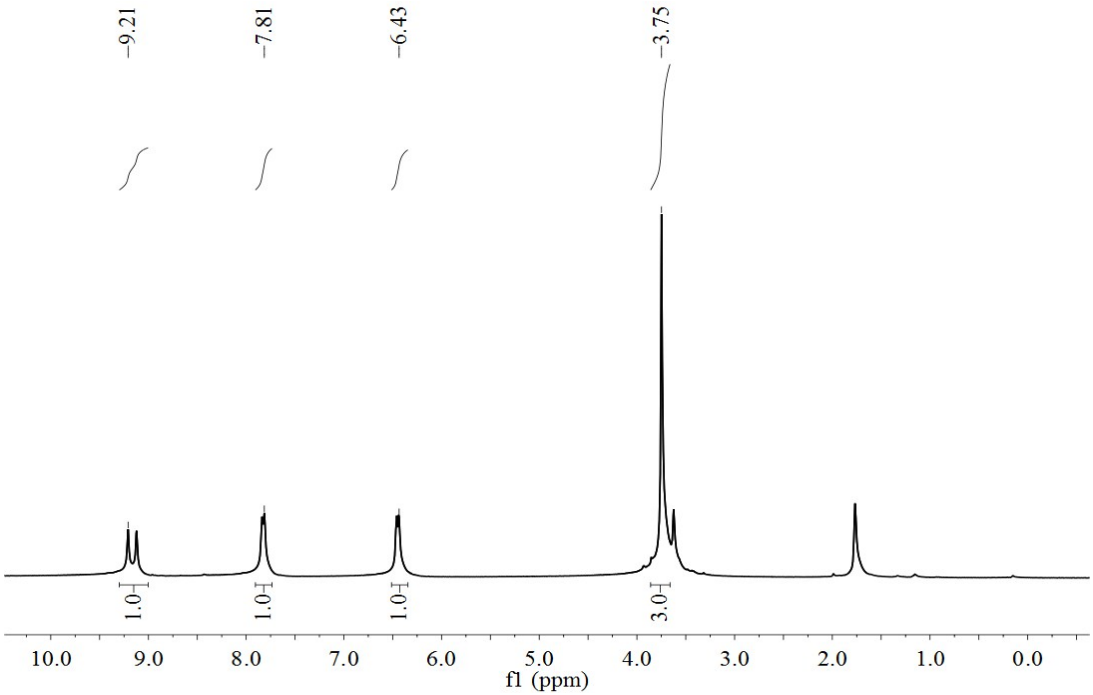

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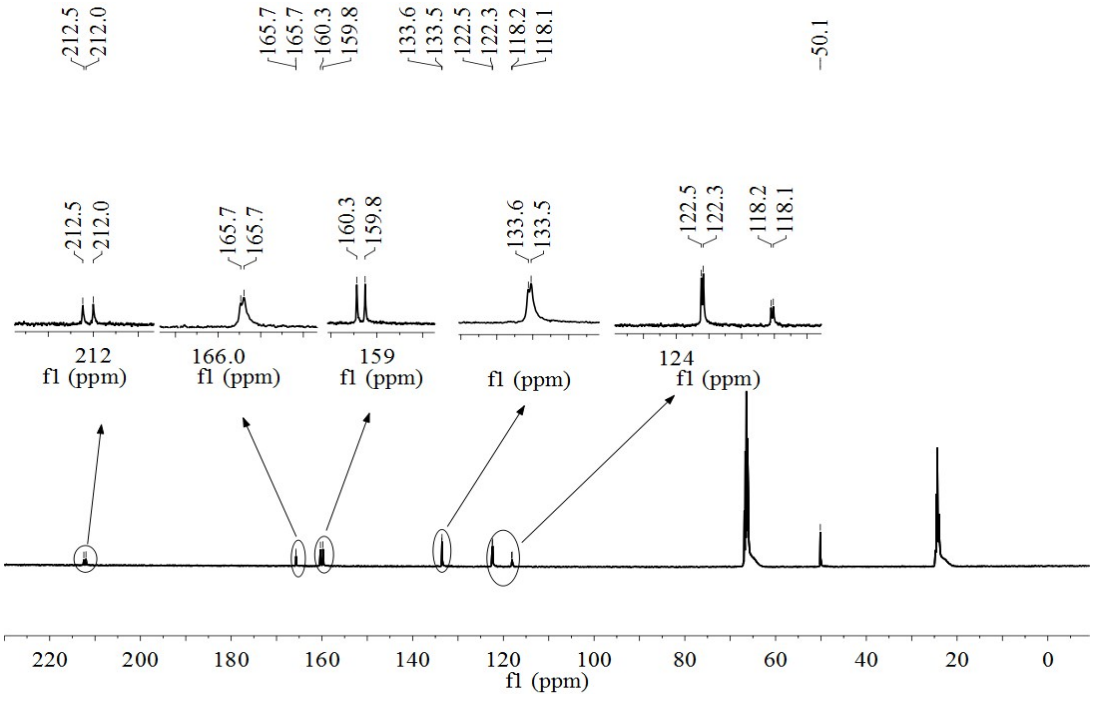

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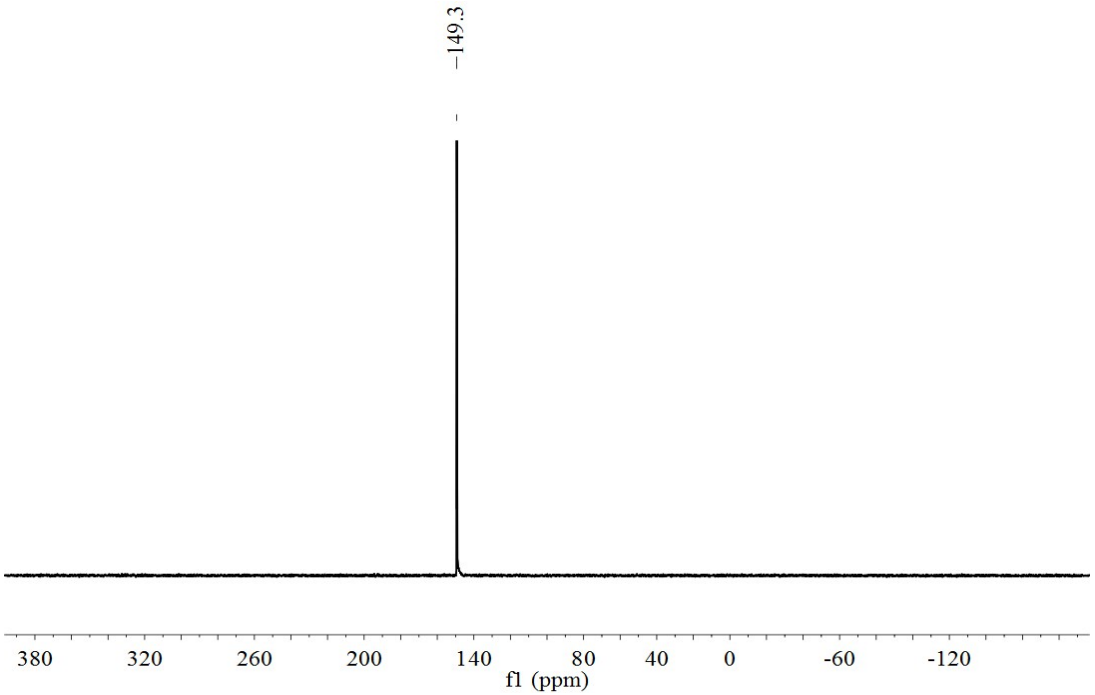

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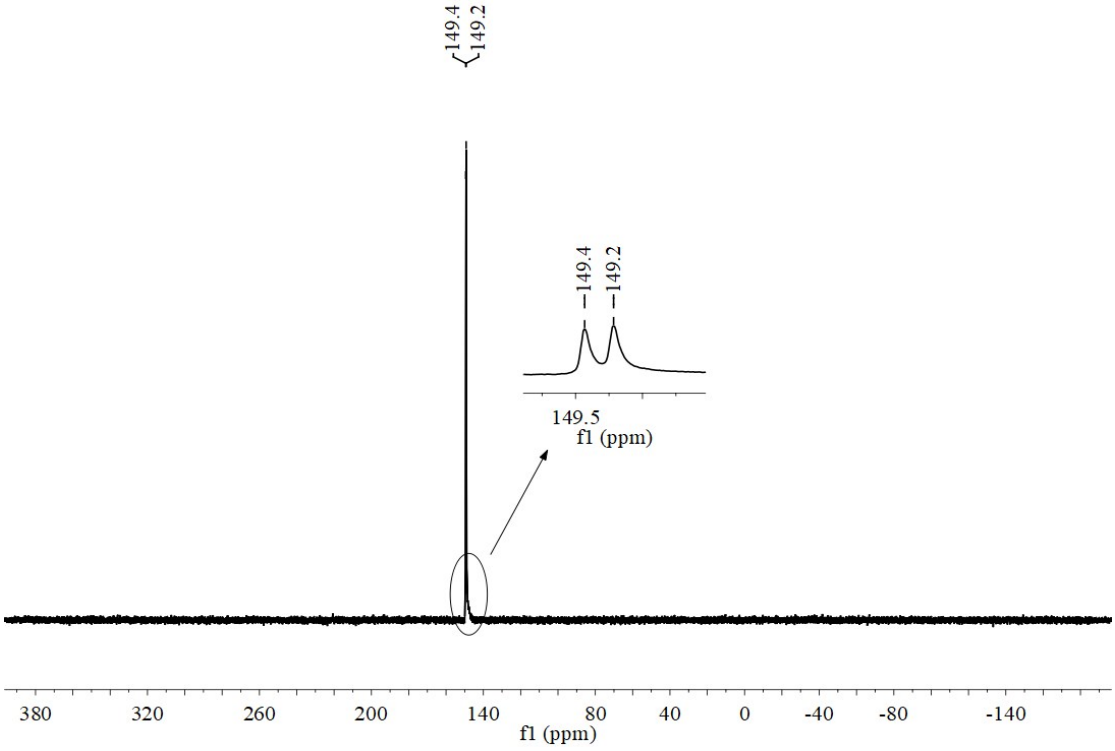

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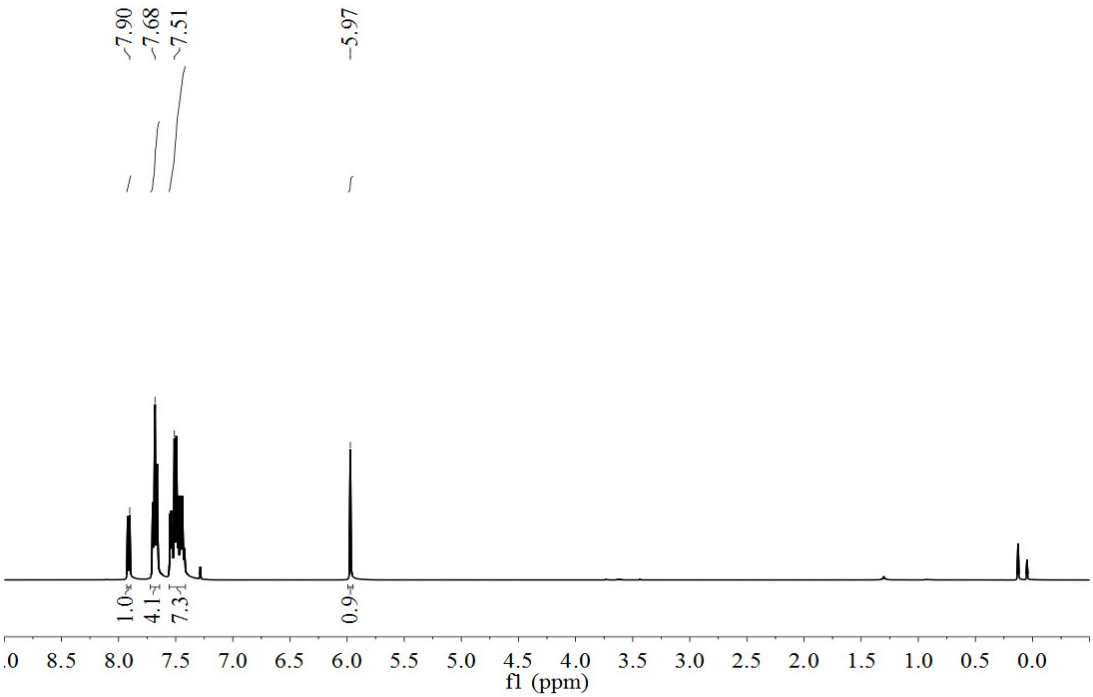

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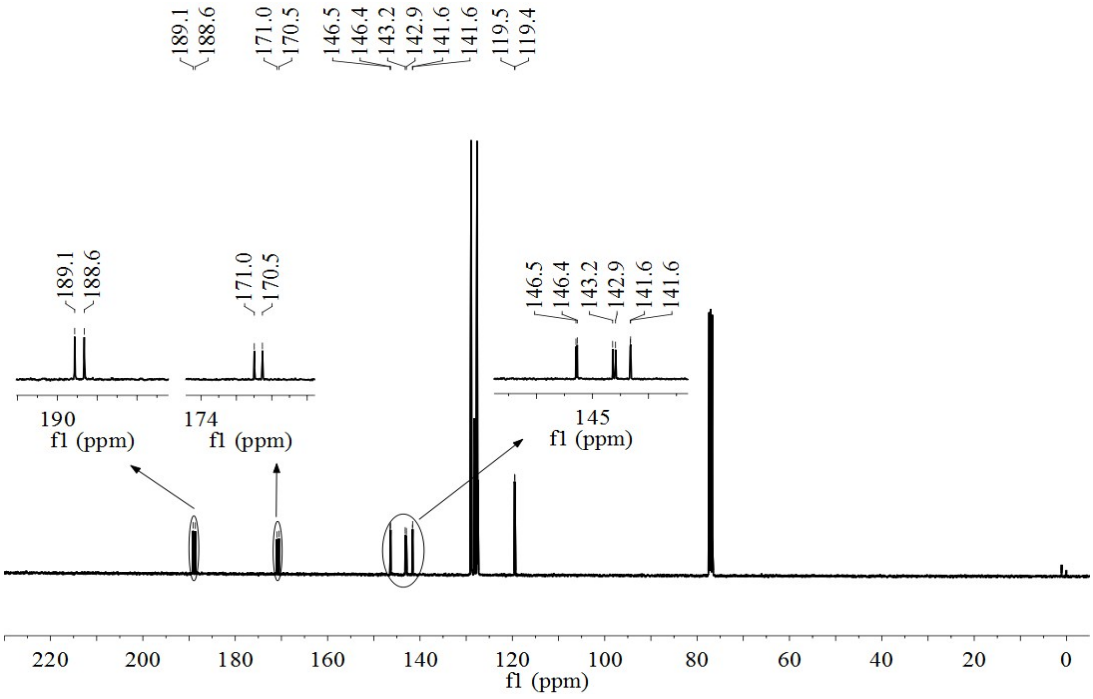

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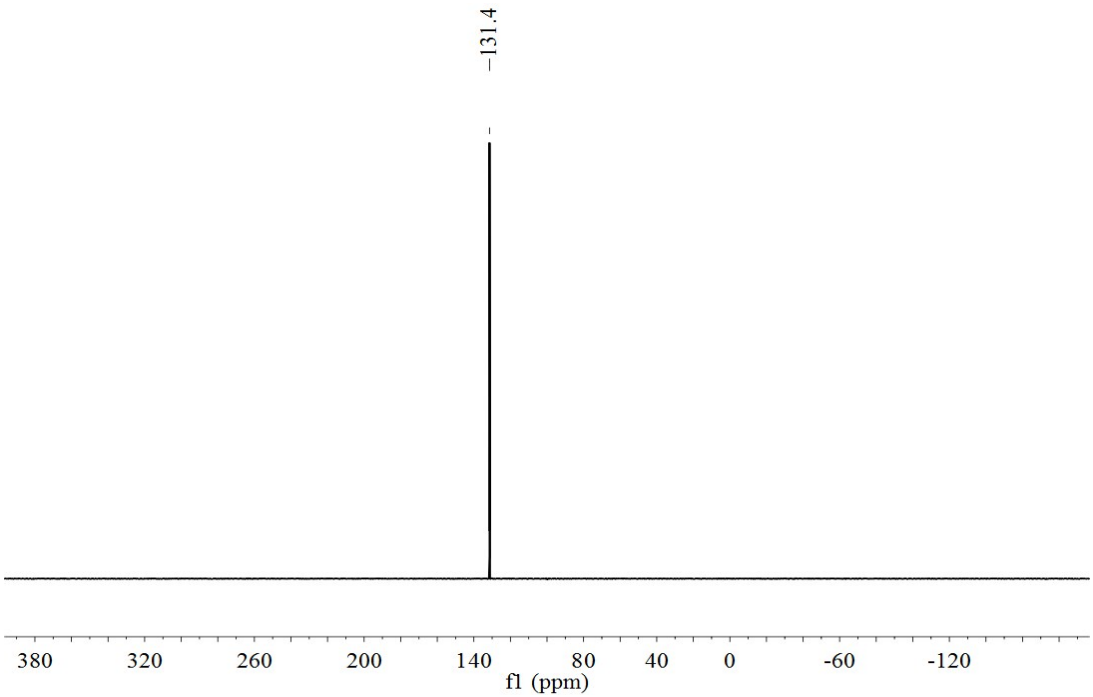

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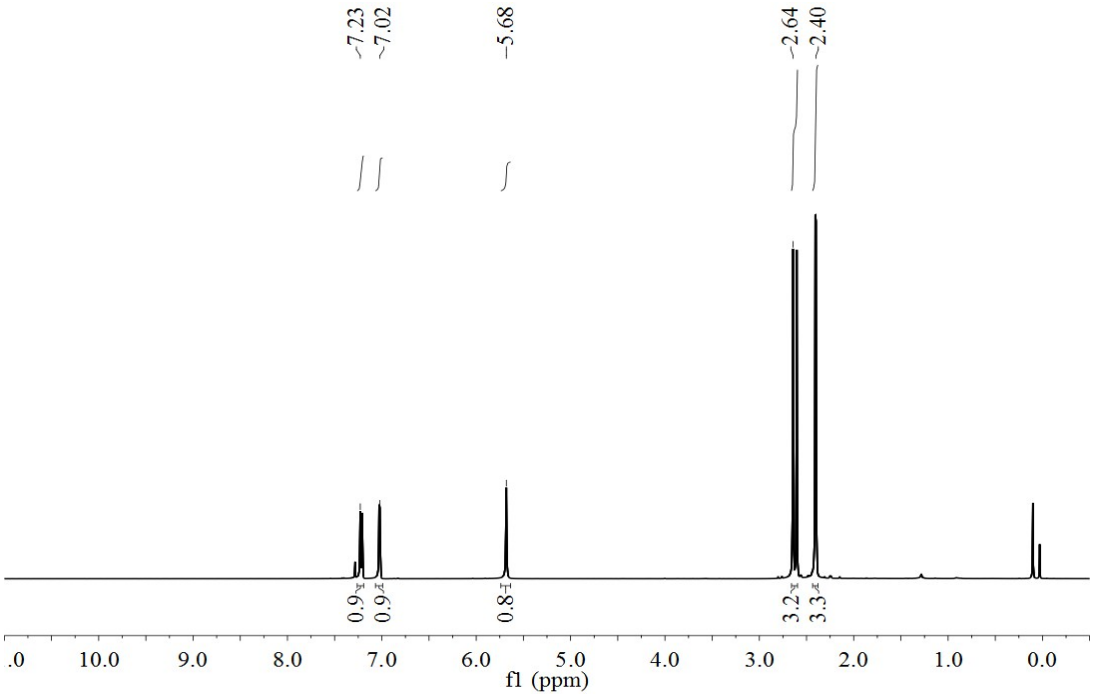

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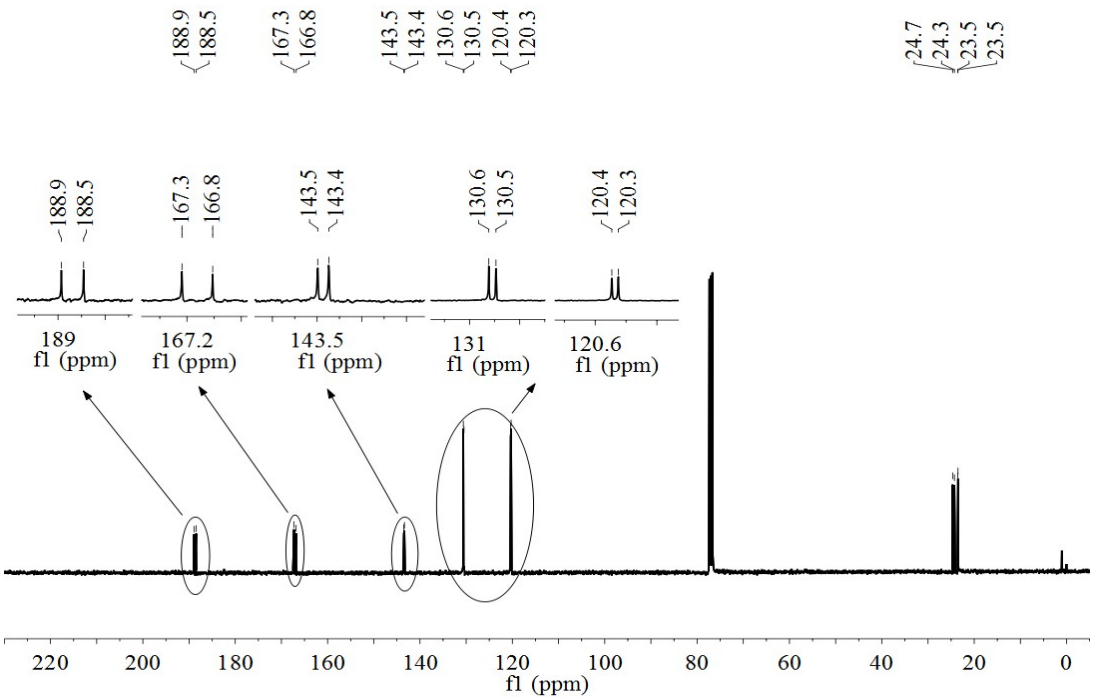

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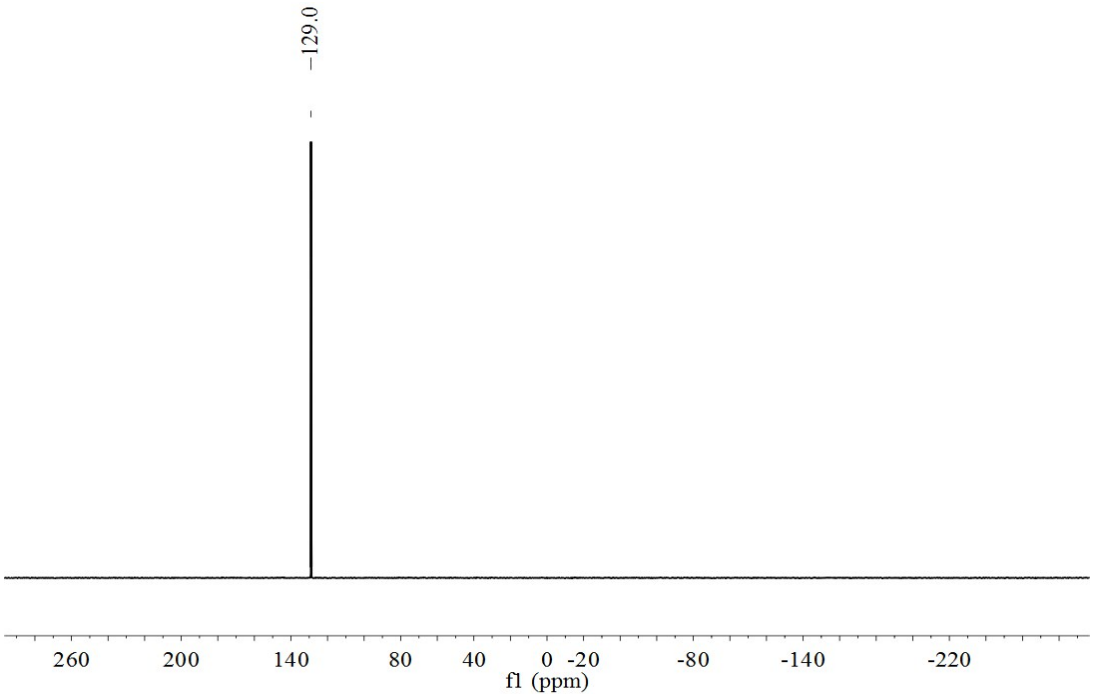

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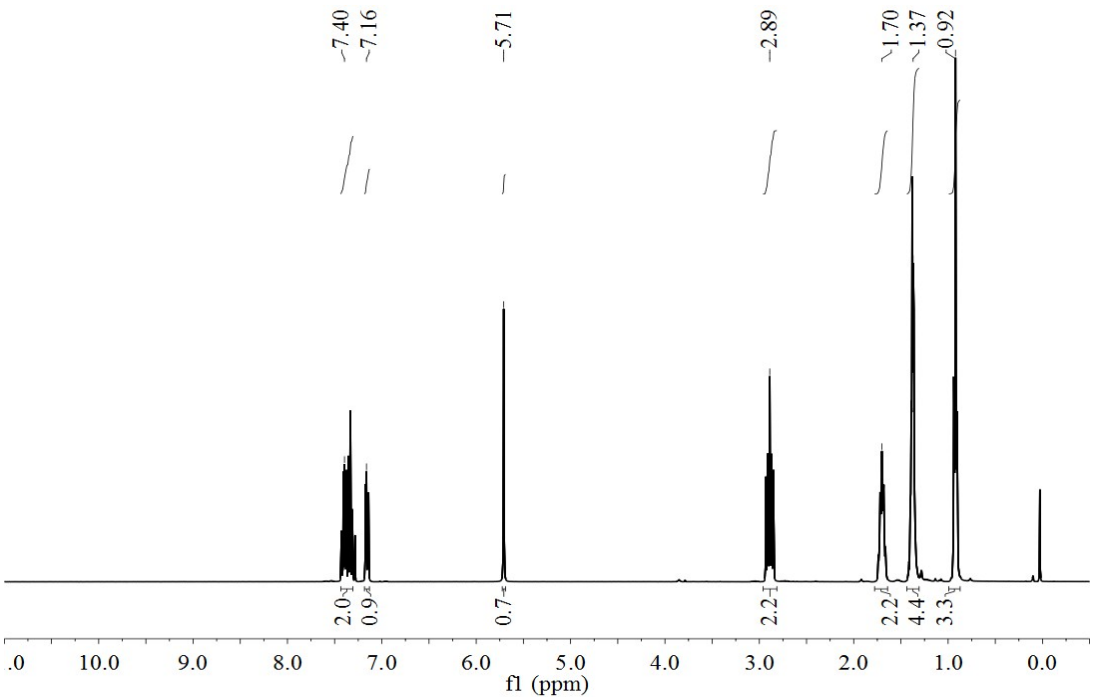

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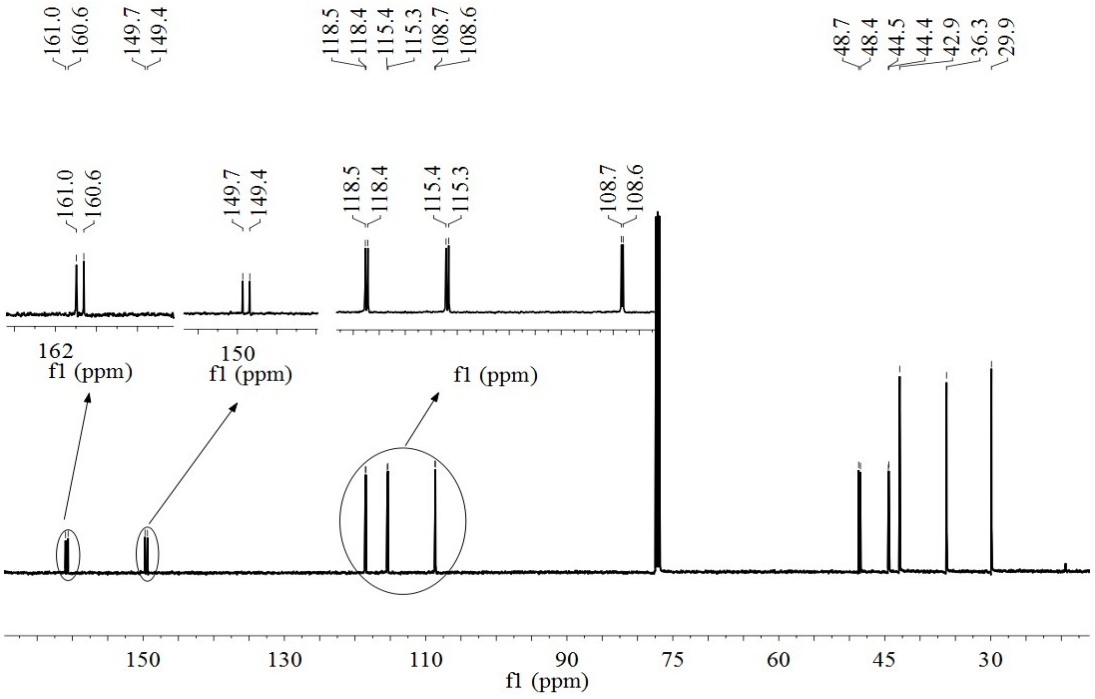

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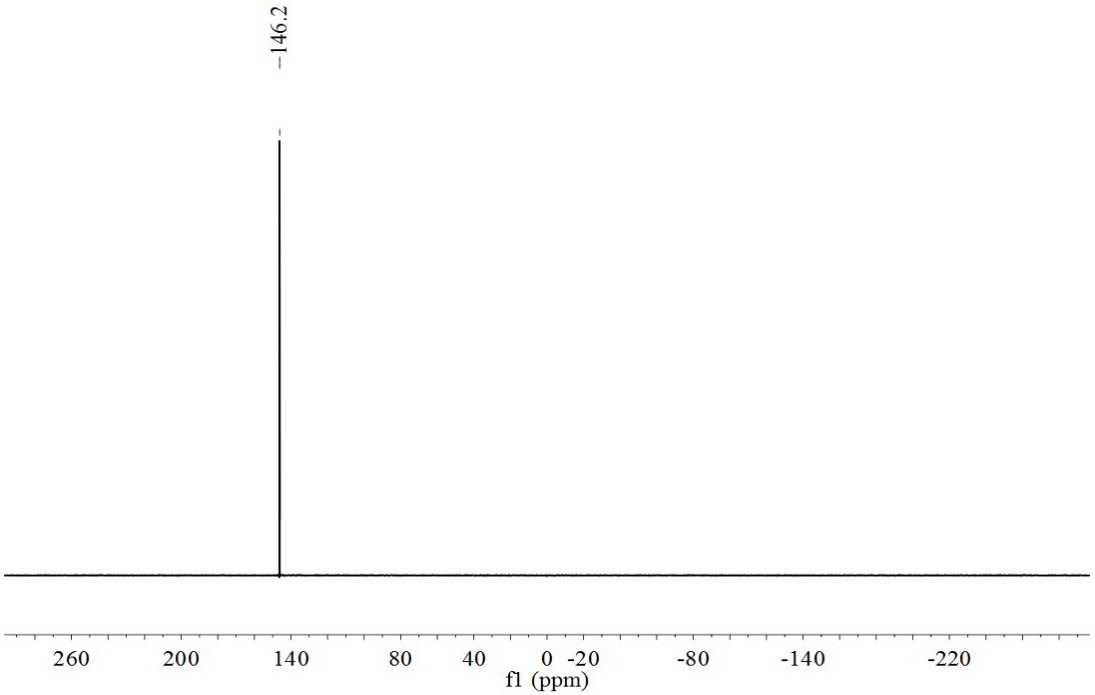

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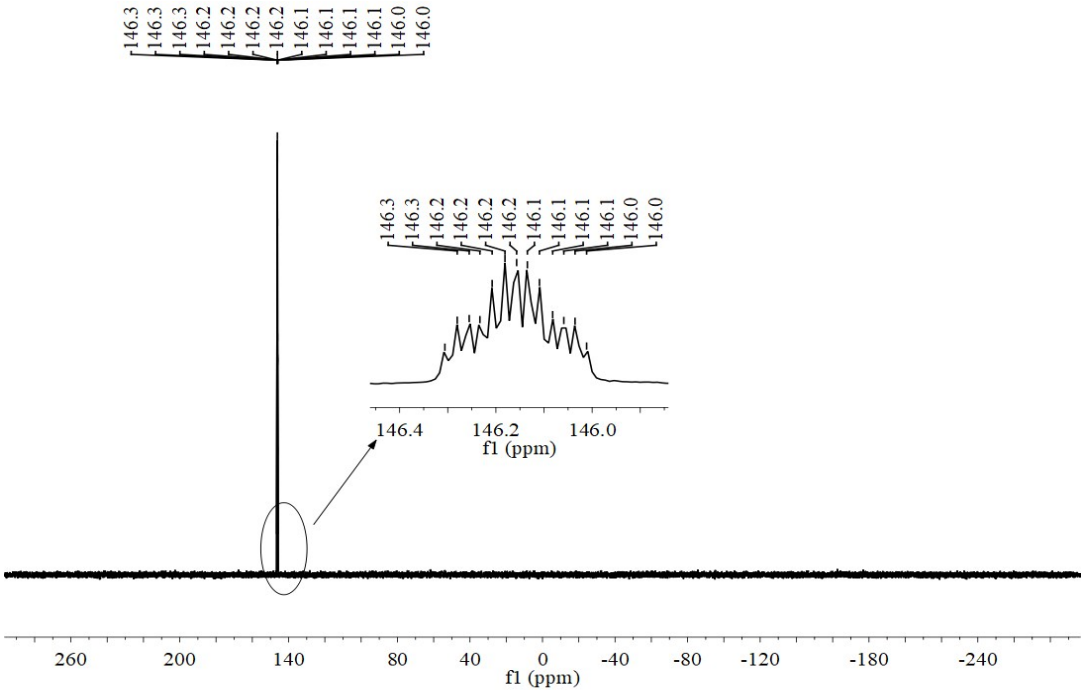

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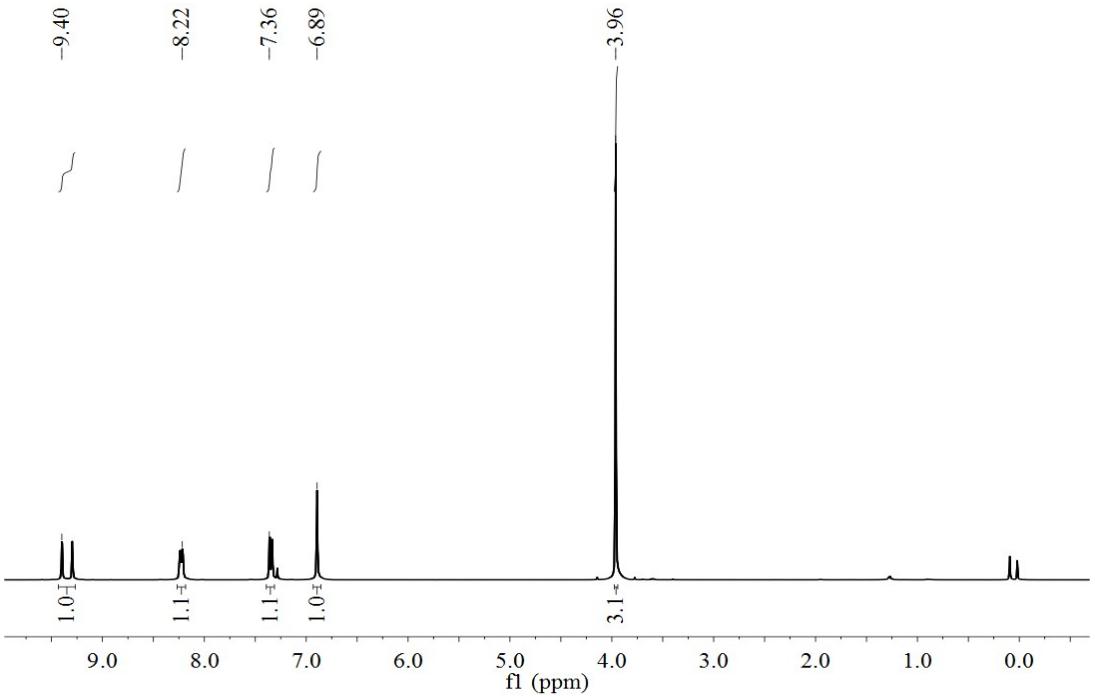

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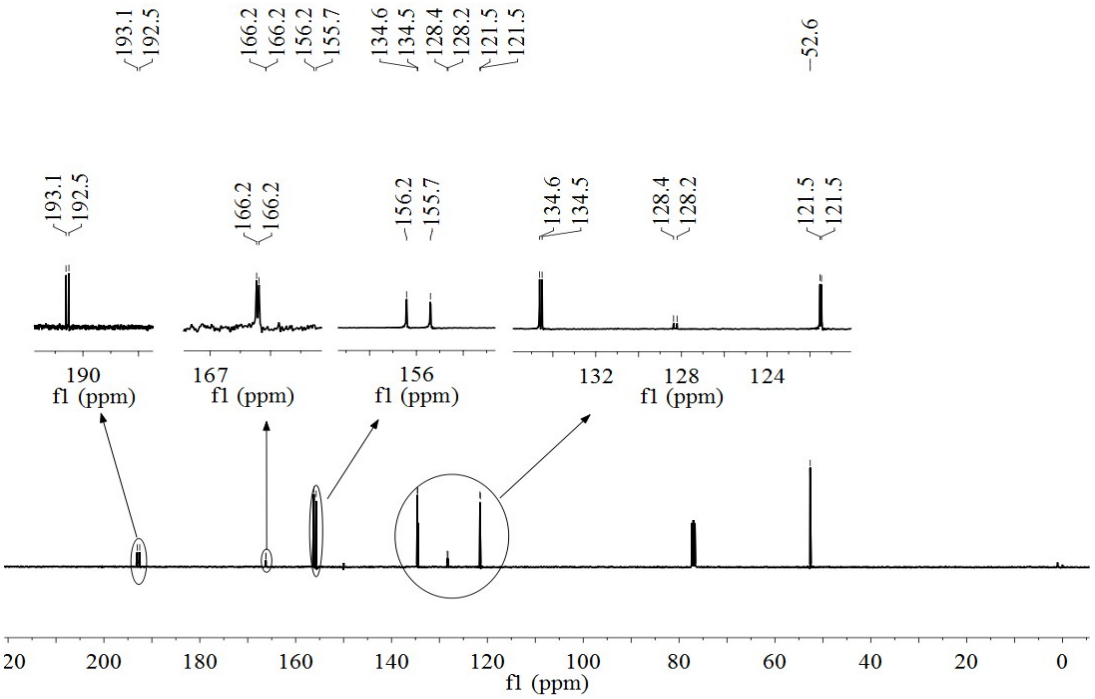

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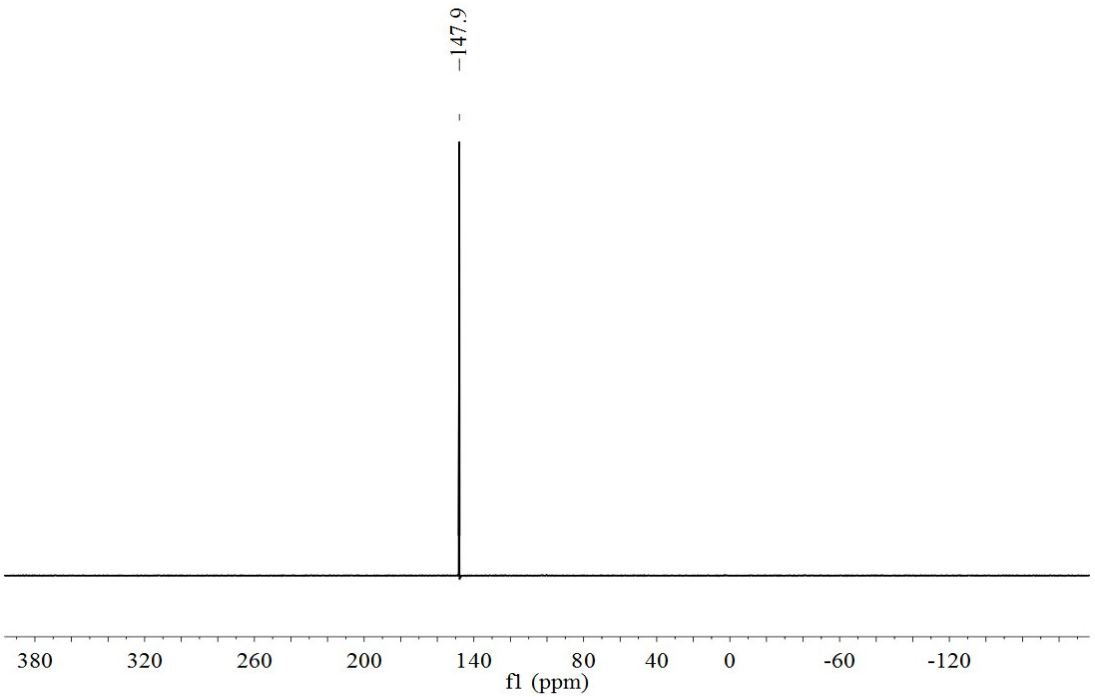

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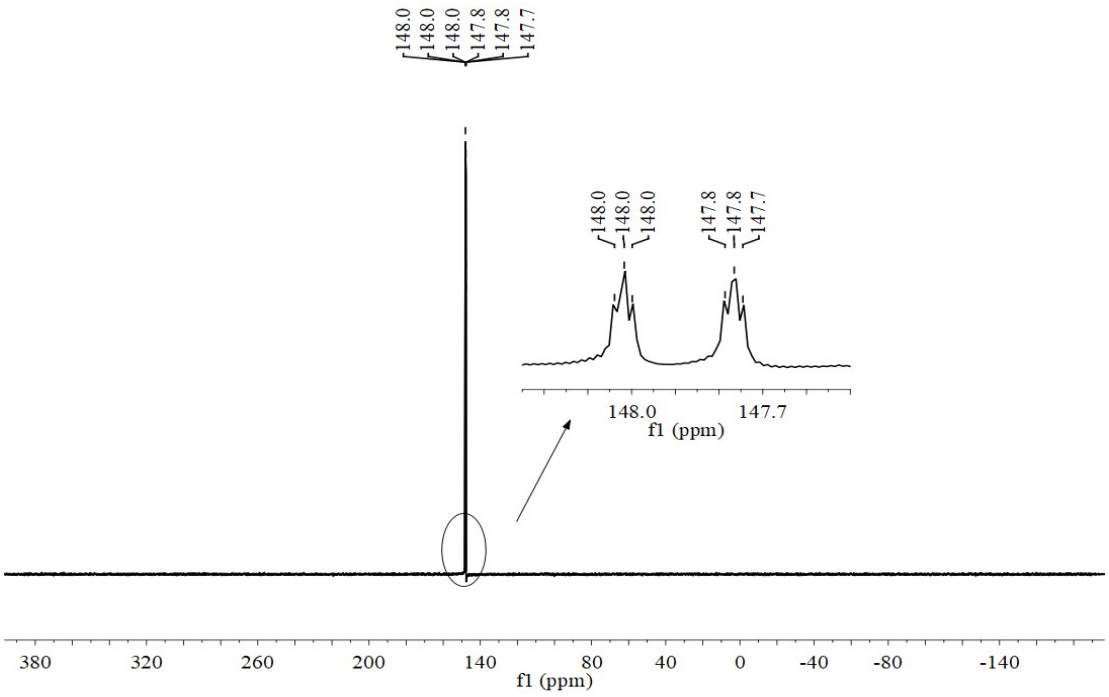

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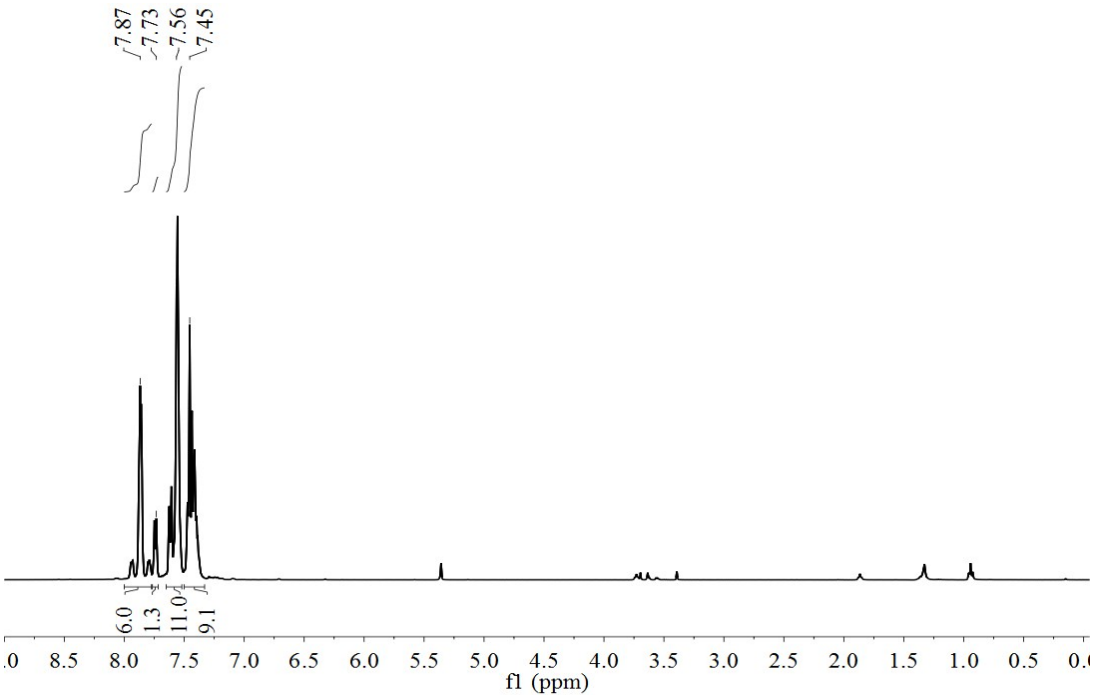

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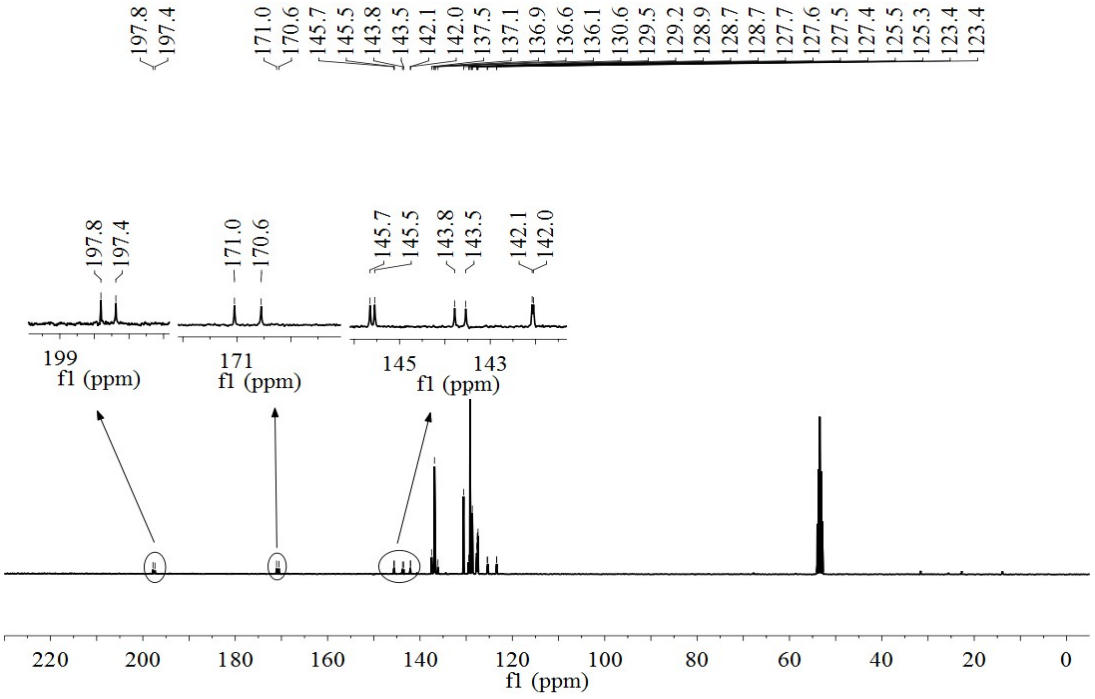

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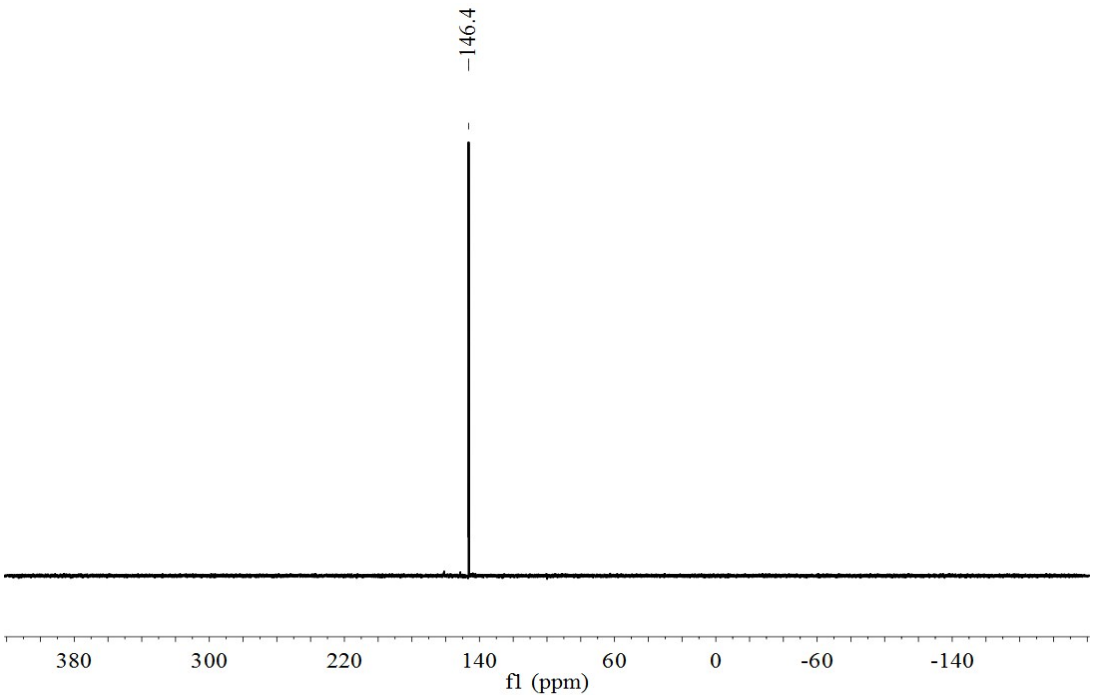

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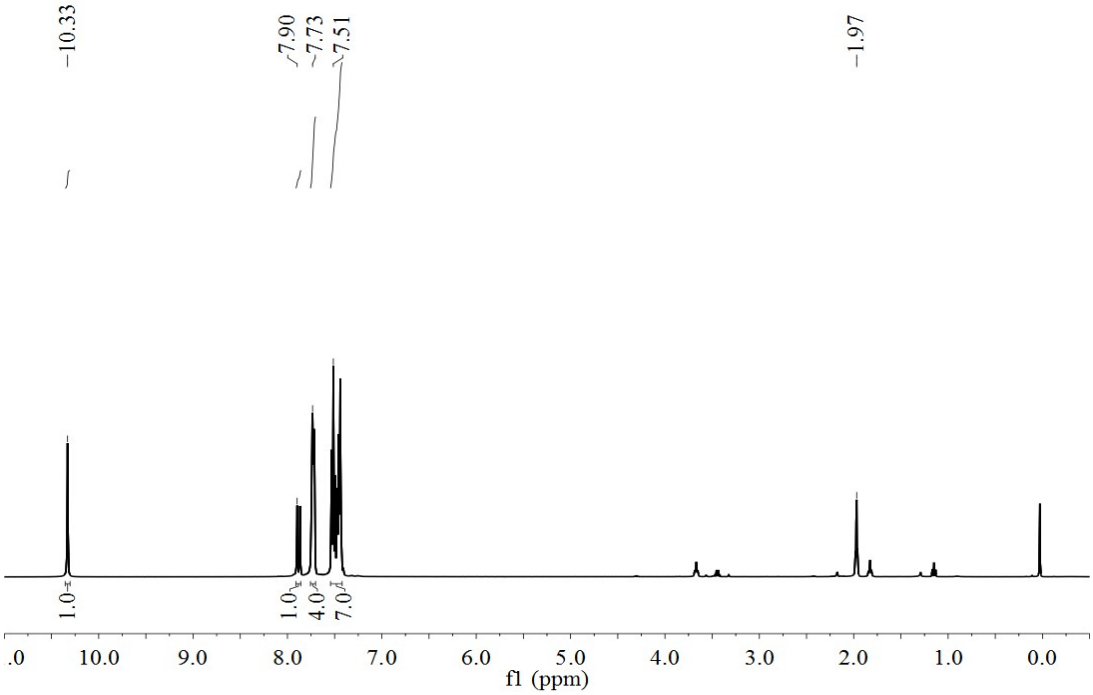

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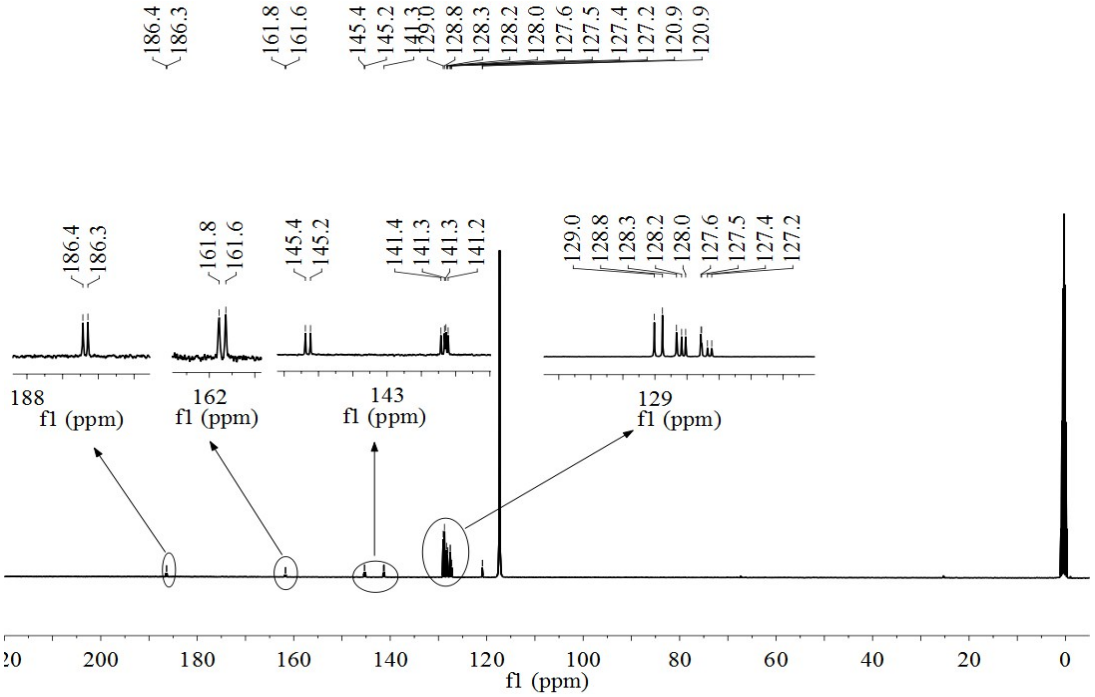

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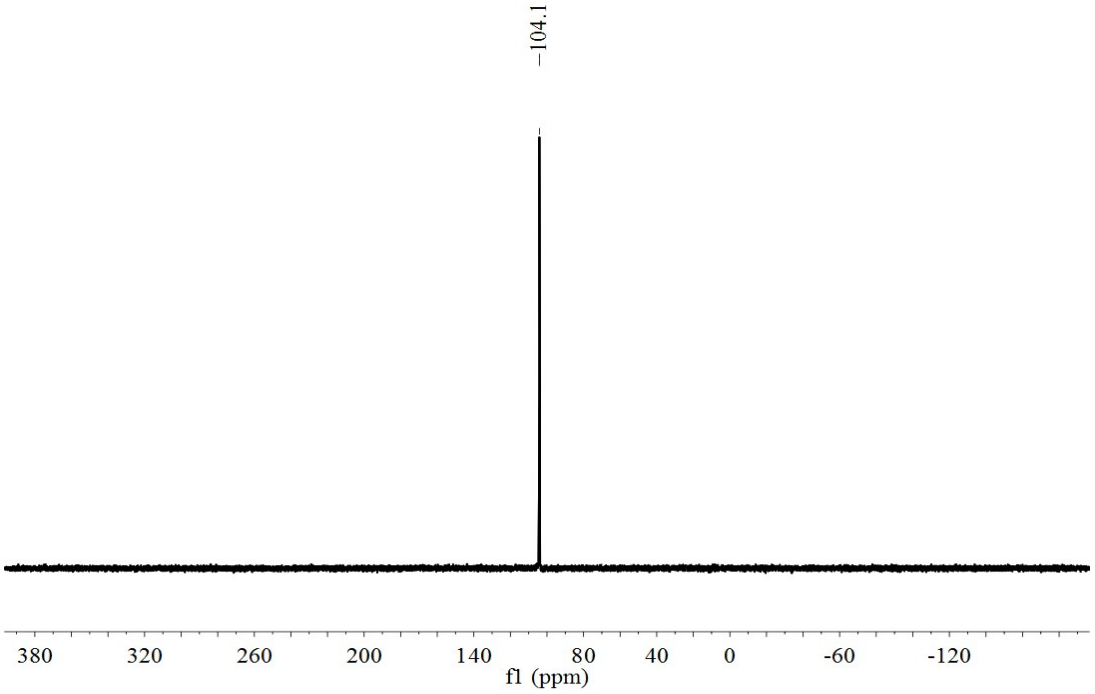

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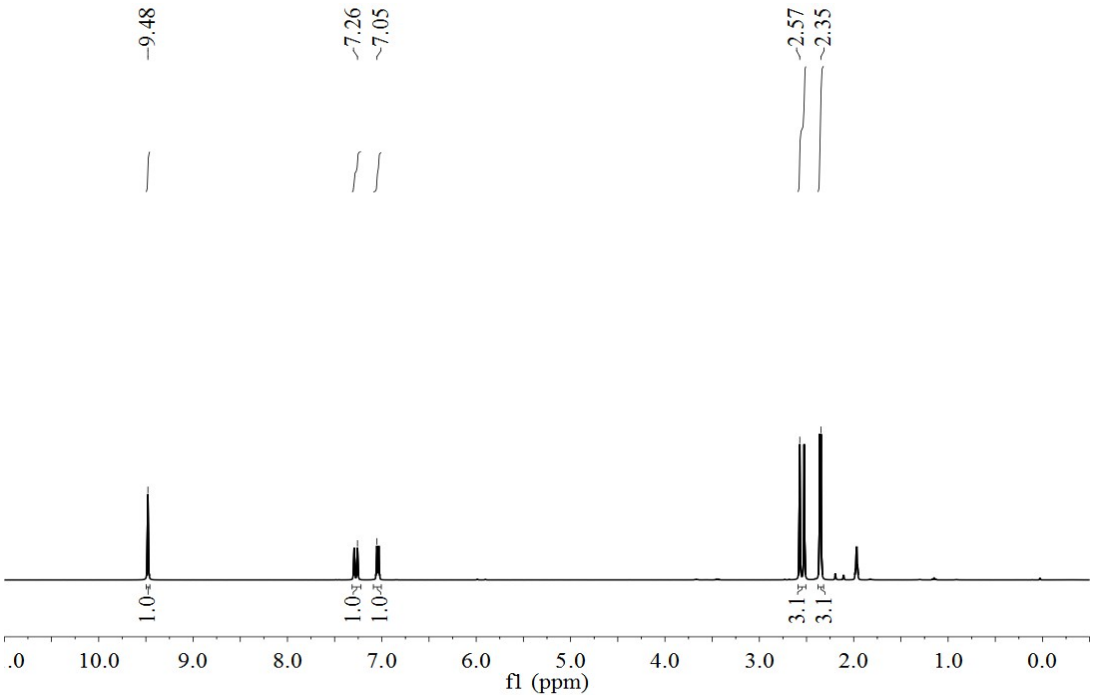

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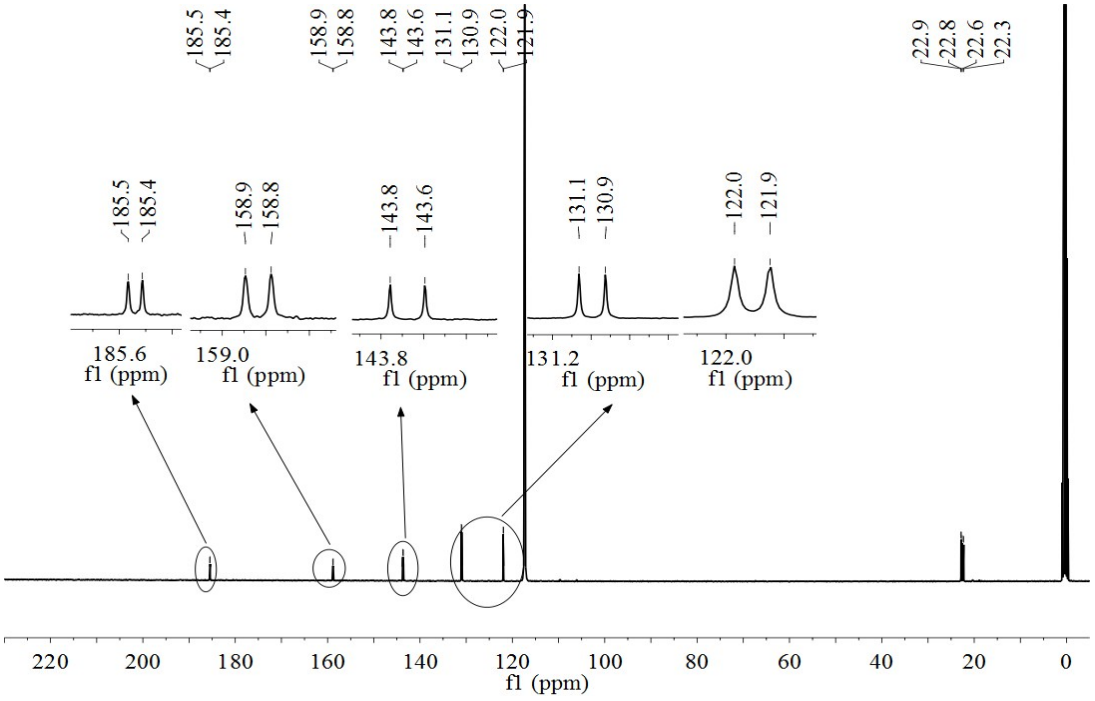

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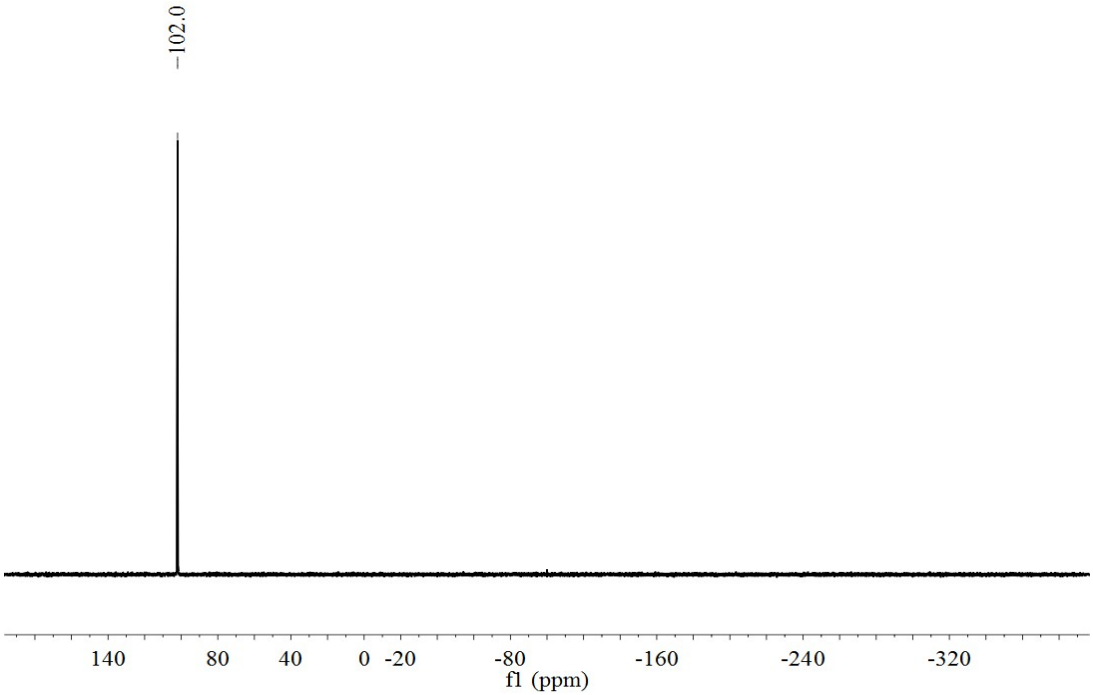

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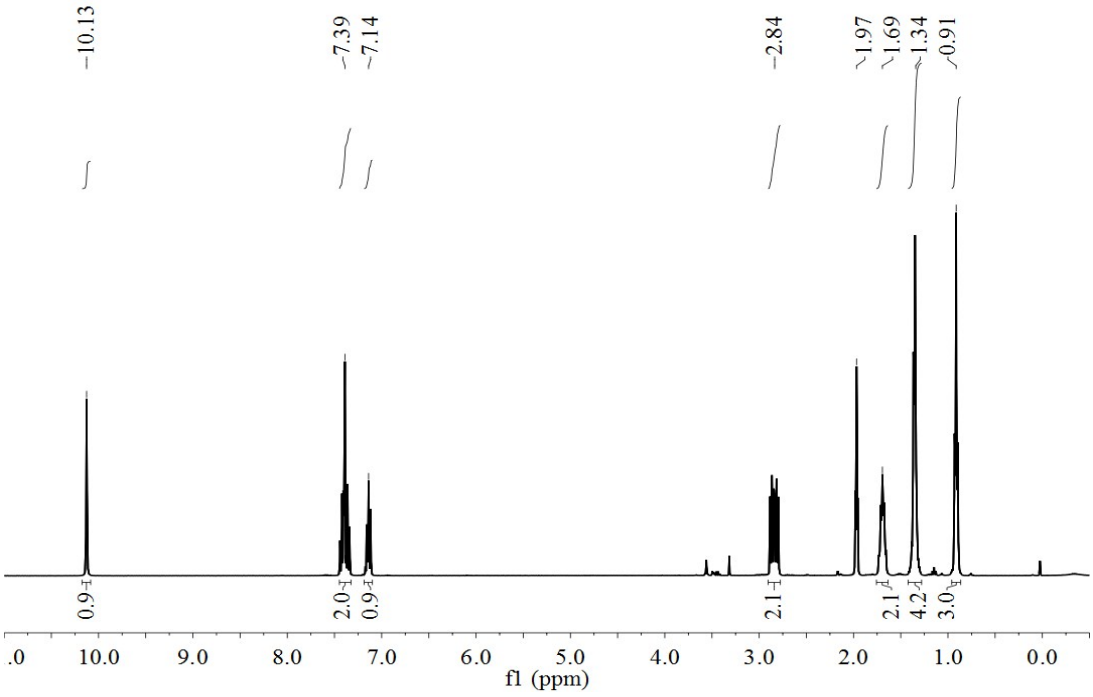

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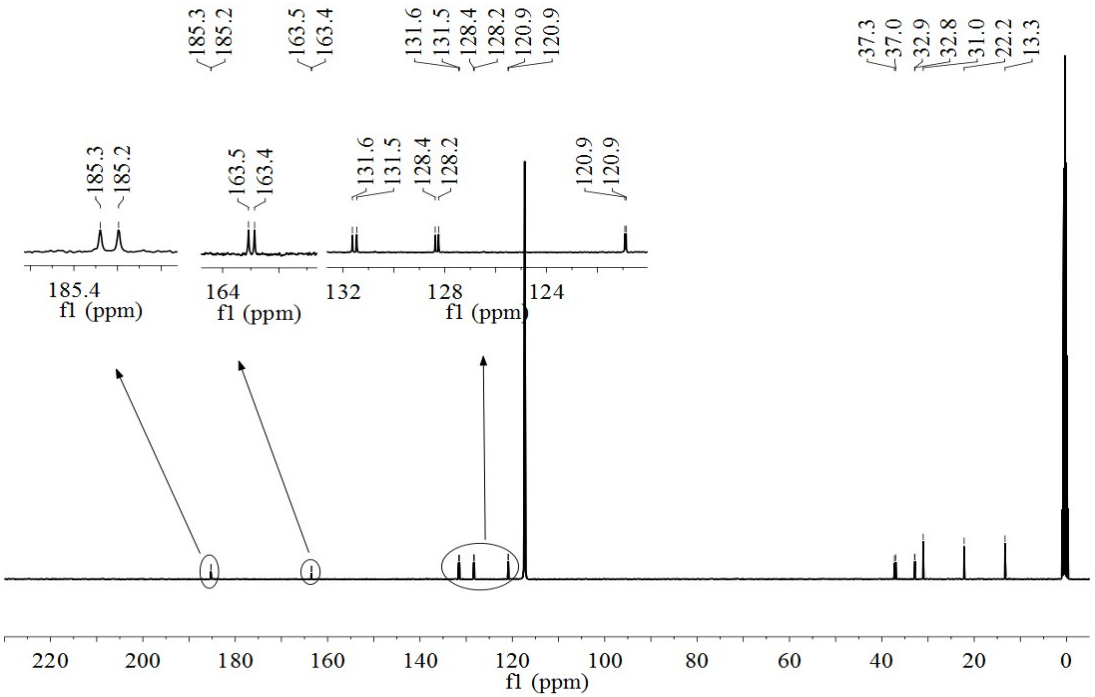

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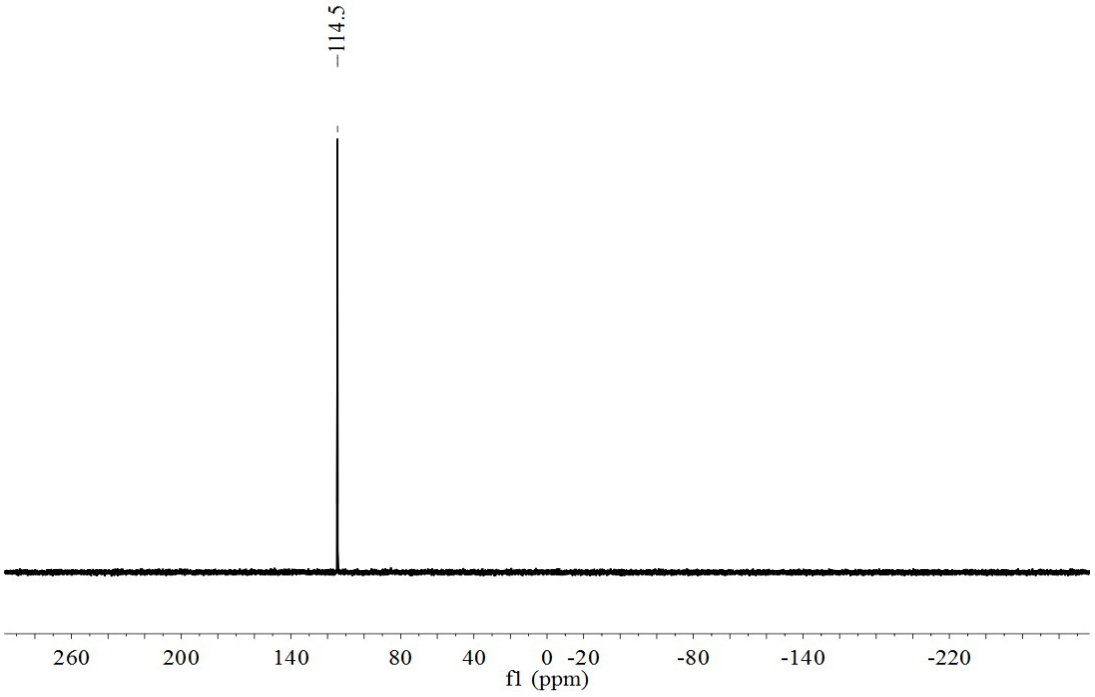

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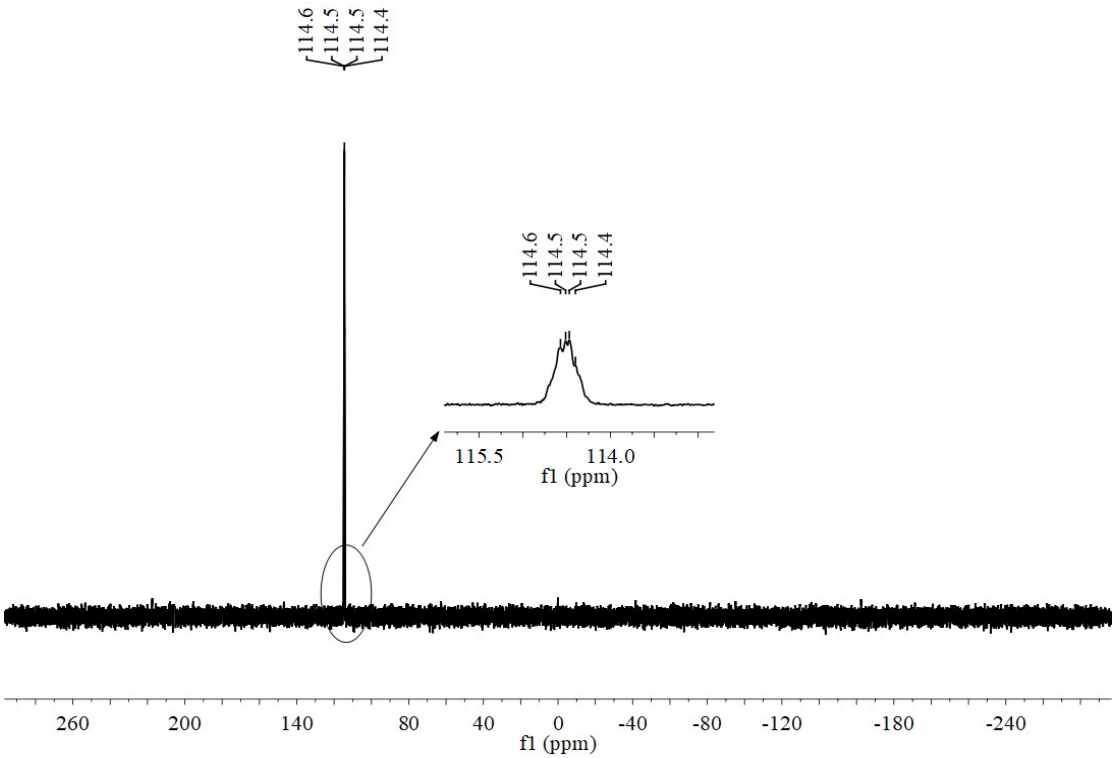
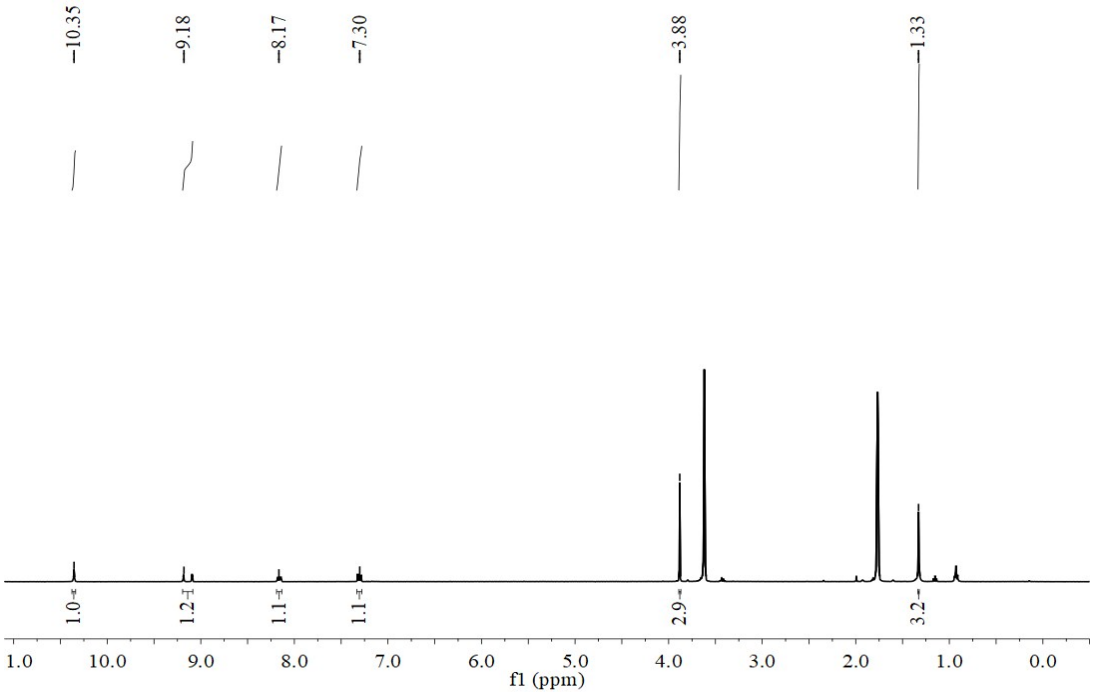


Figure S38. ^{31}P NMR spectrum of **4c** in CD_3CN.



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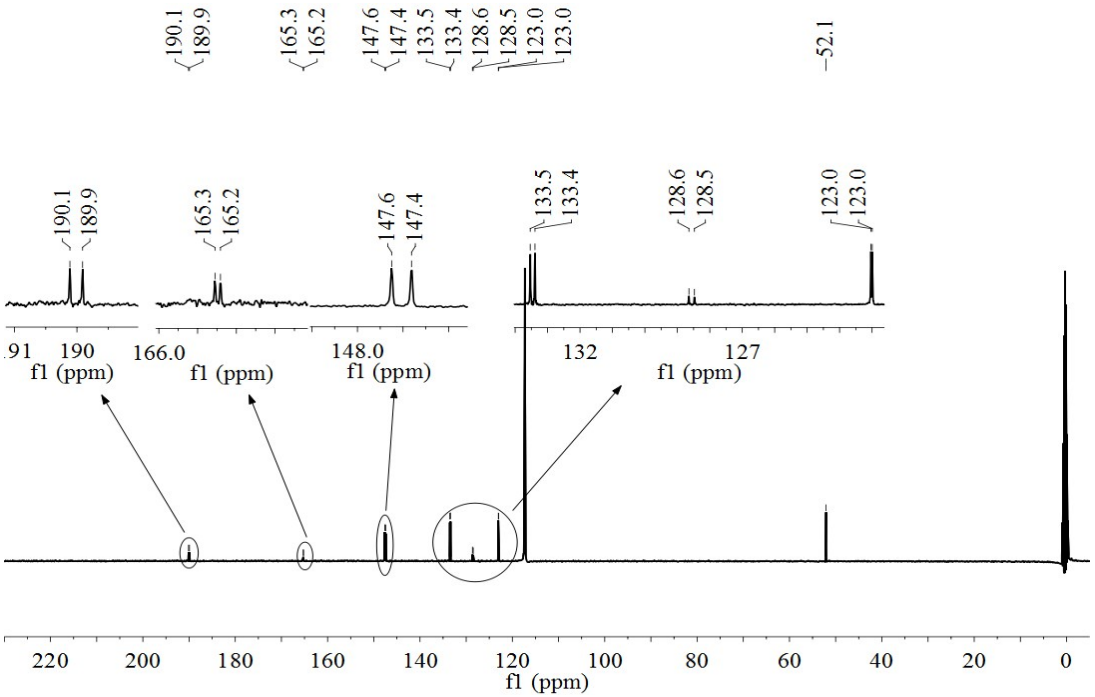

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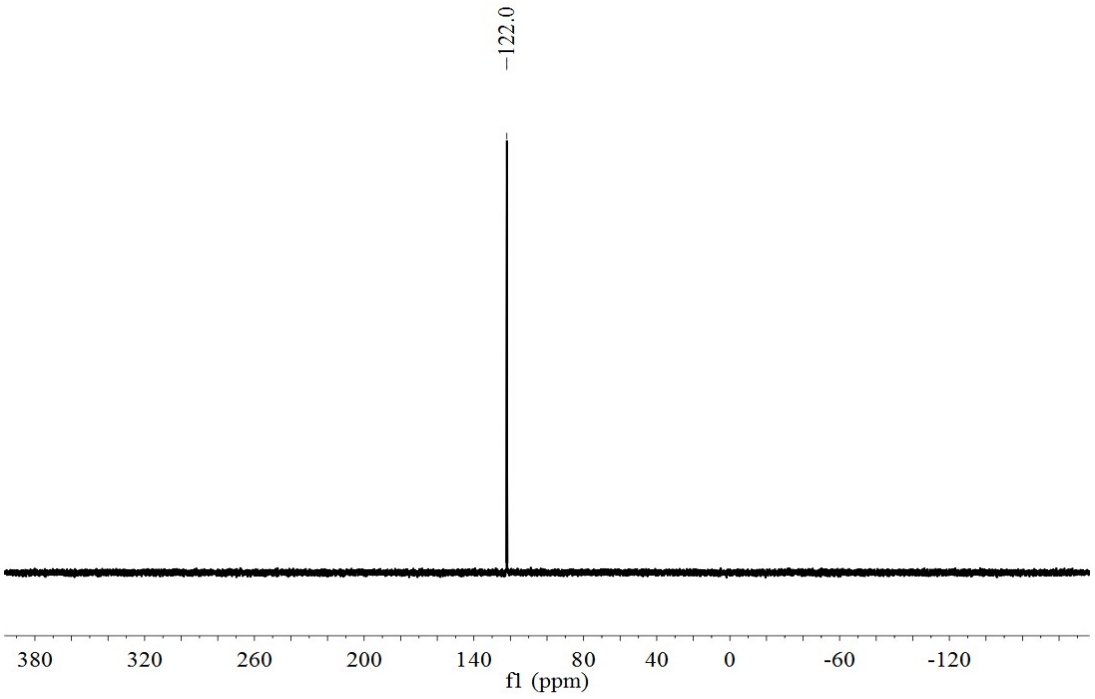

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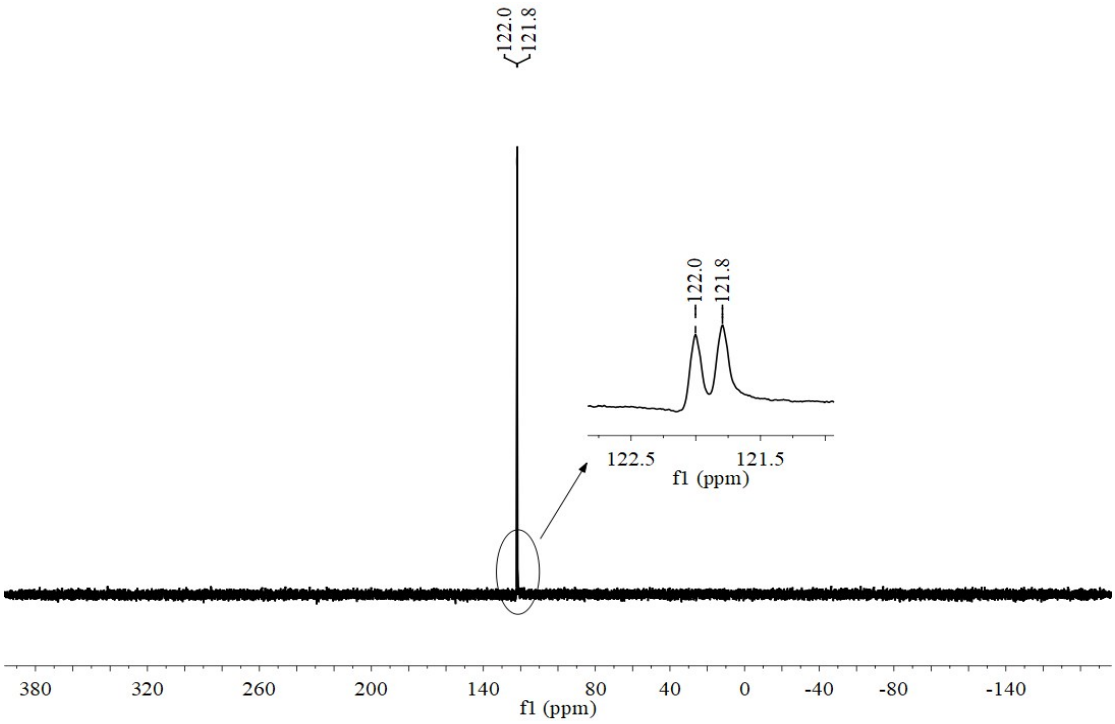


Figure S42. ^{31}P NMR spectrum of **4d** in CD_3CN.

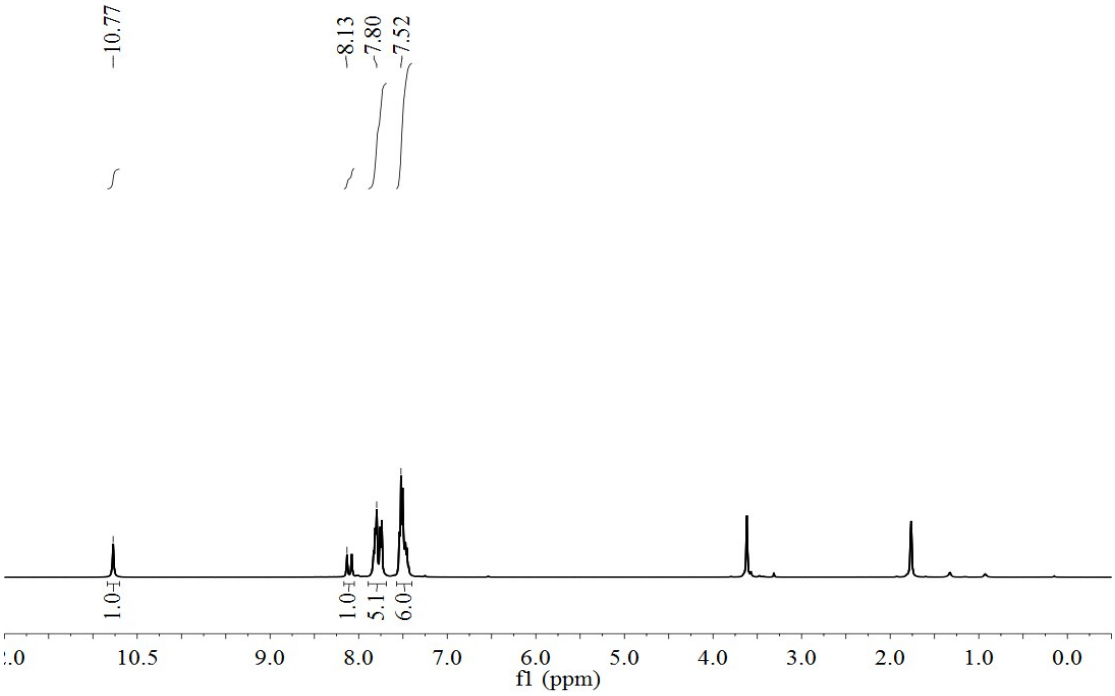
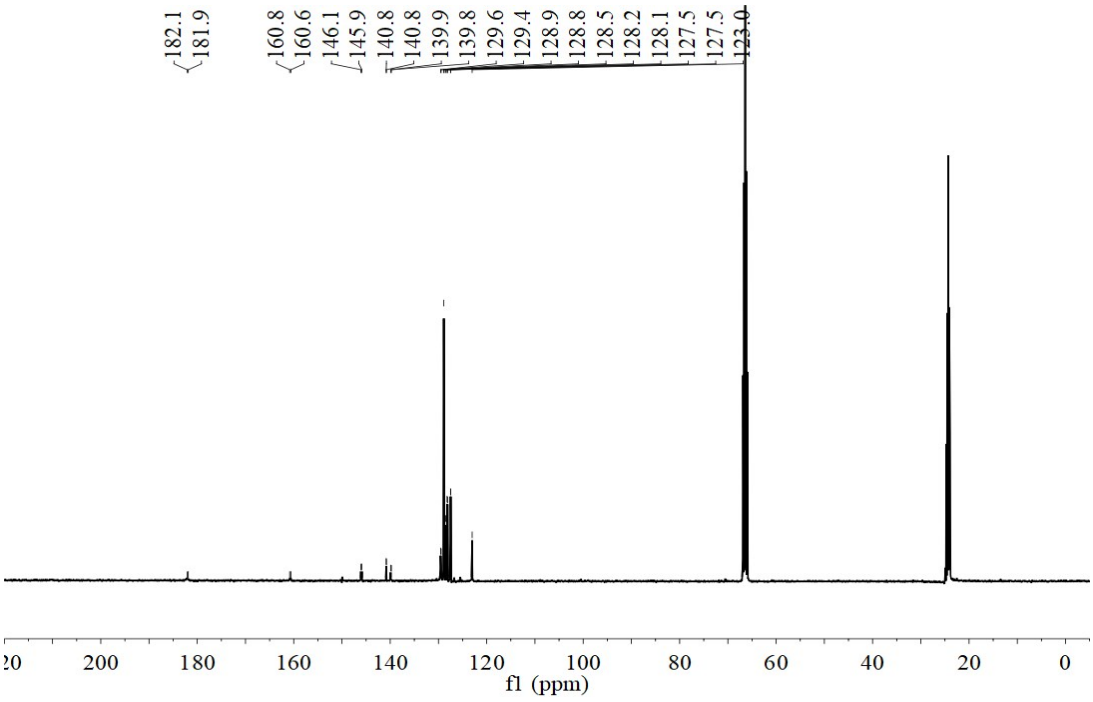


Figure S43. ^{1}H NMR spectrum of **6** in THF-D_8.



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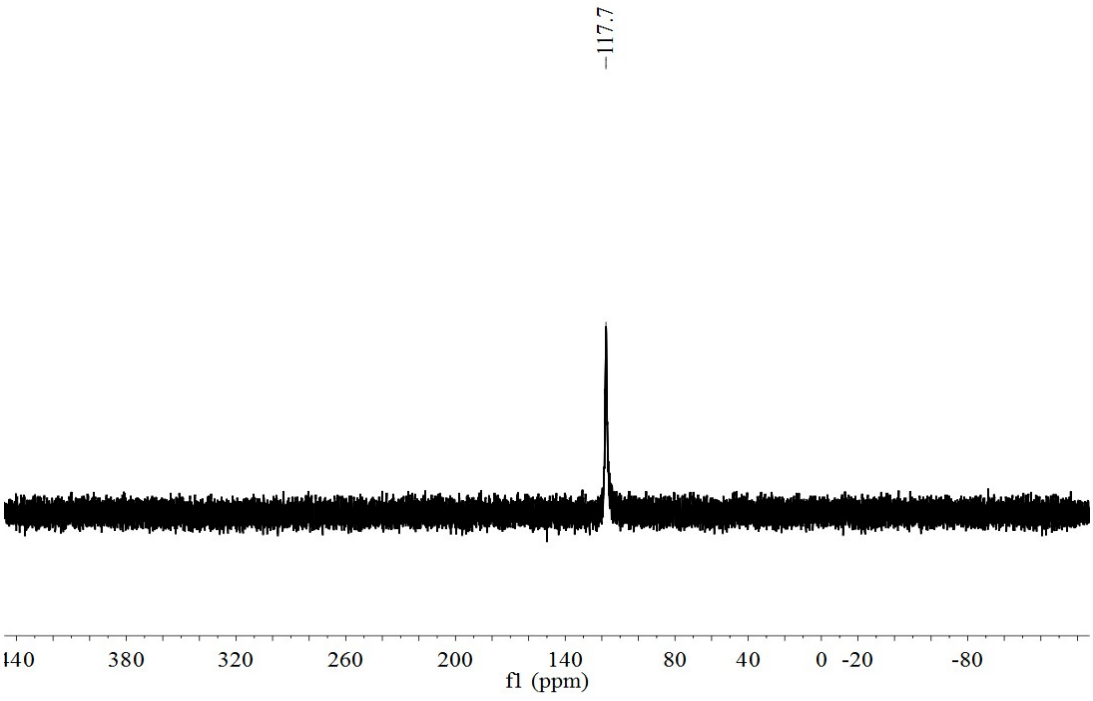


Figure S45. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in THF-D_8.

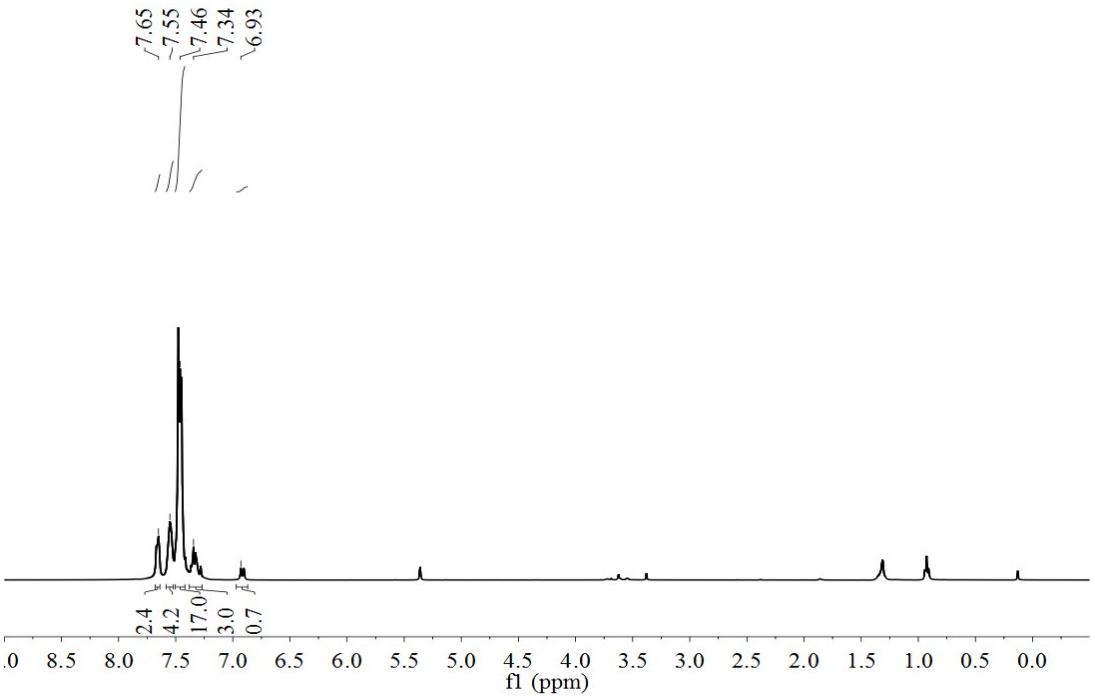


Figure S46. ^{1}H NMR spectrum of **7** in CD_2Cl_2.

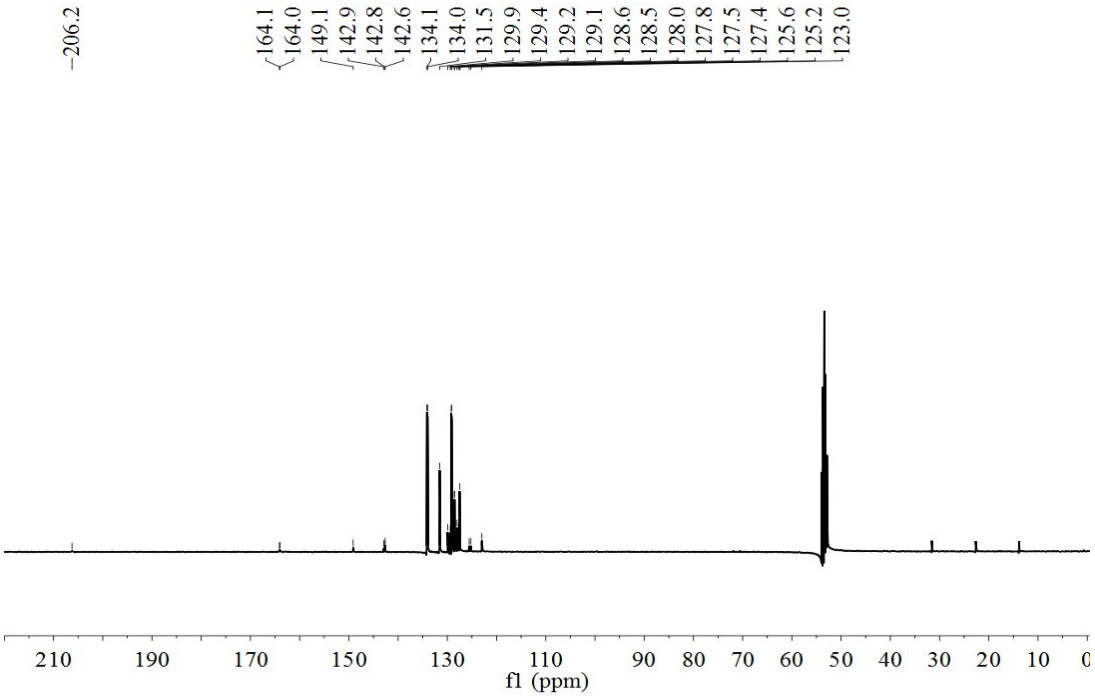


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in CD_2Cl_2.

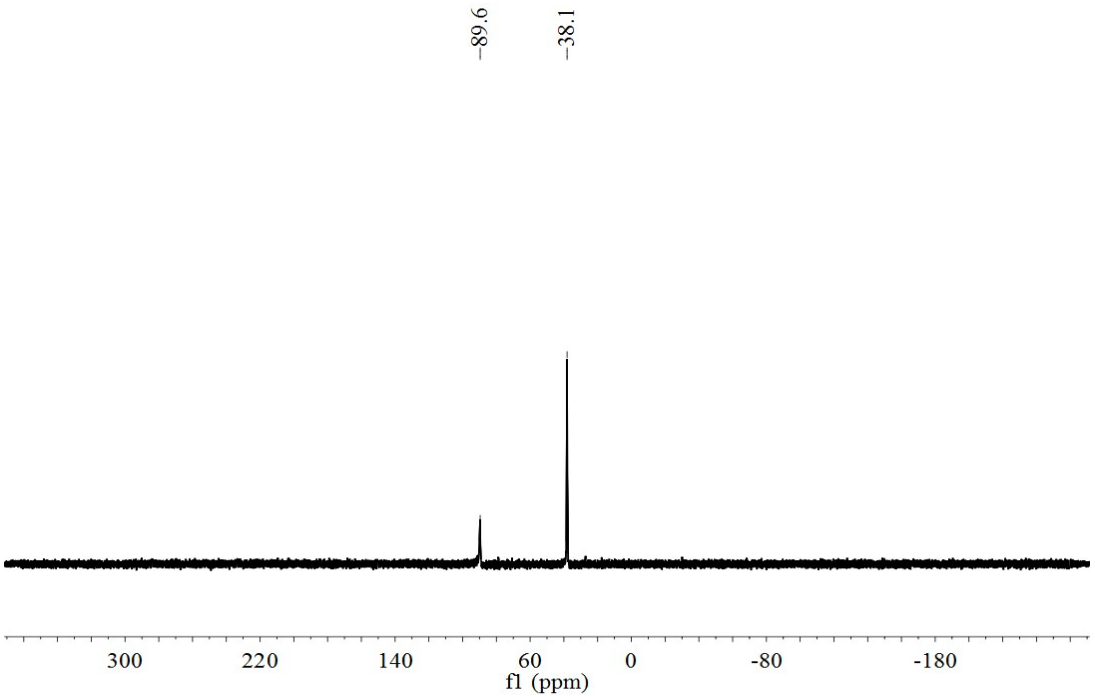


Figure S48. $^{31}P\{^{1}H\}$ NMR spectrum of **7** in CD_2Cl_2.

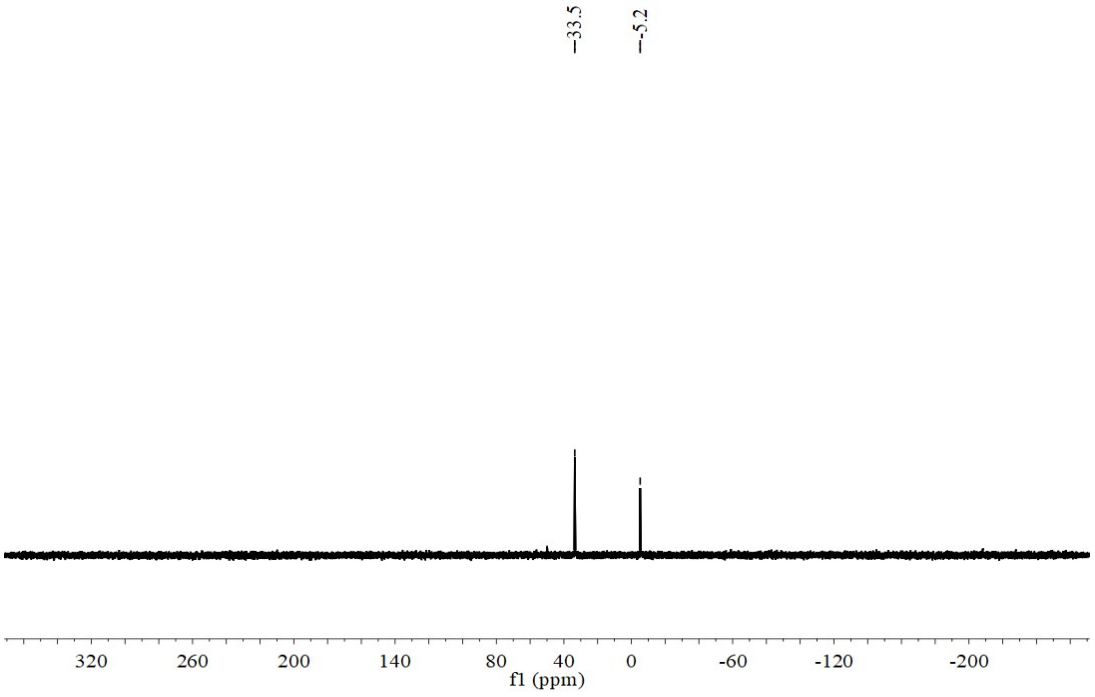


Figure S49. $^{31}P\{^{1}H\}$ NMR spectrum of **8** in THF-D_8.

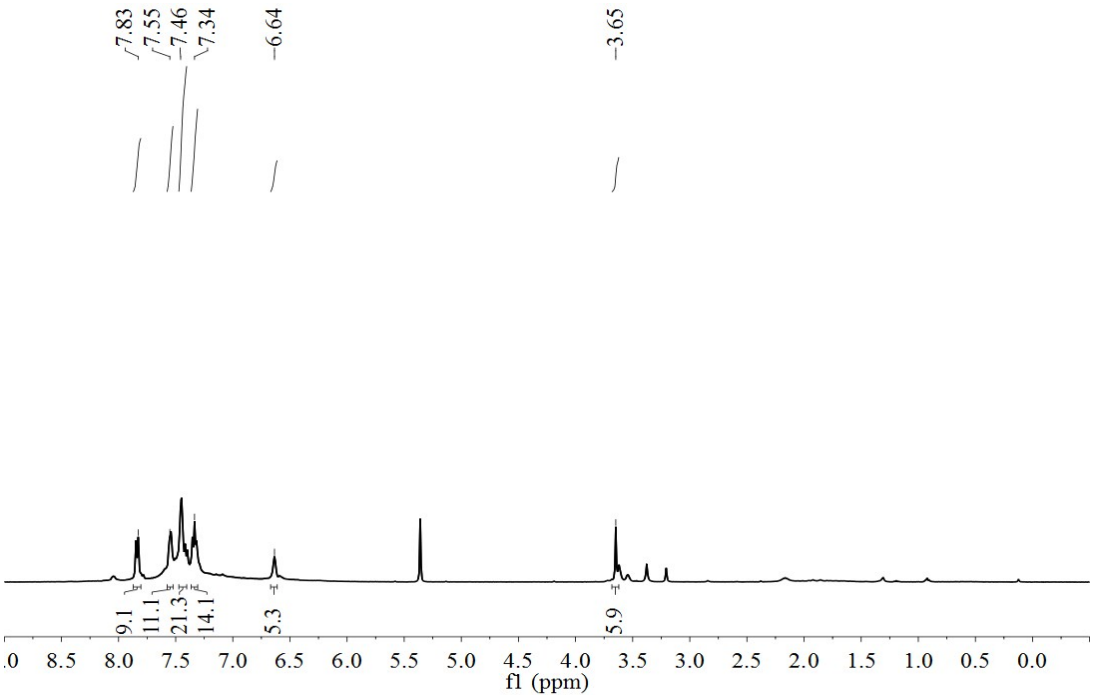


Figure S50. ^{1}H NMR spectrum of **9** in CD_2Cl_2.

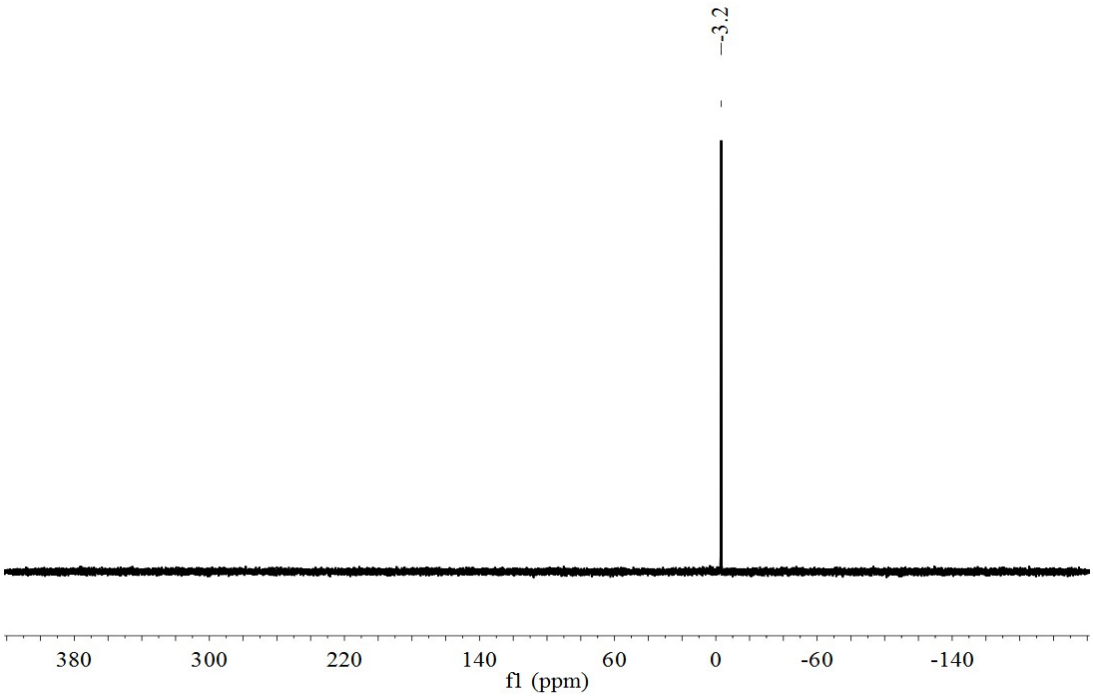


Figure S51. $^{31}P\{^{1}H\}$ NMR spectrum of **9** in CD_2Cl_2.

S2: X-Ray Diffraction Studies

These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, or by emailing data_request@ccdc.cam.ac.uk. The CCDC reference numbers are 1872113–1872122 (for **1a**, **3**, **4a-4d**, **5**, **6**, **7** and **9**)

Table S1. Crystal data and structure refinement for **1a**. (CCDC 1872122)

Empirical formula	$C_{62}H_{80}Na_2O_{15}P_2$
Formula weight	1173.18
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	27.5839(10)
b/Å	9.1559(2)
c/Å	28.1190(11)
α/°	90
β/°	121.726(5)
γ/°	90
Volume/Å^3	6040.4(4)
Z	4
ρ_{calc}g/cm^3	1.290
μ/mm^{-1}	1.339
F(000)	2496.0
Crystal size/mm^3	0.2 × 0.18 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.27 to 147.81
Index ranges	-34 ≤ h ≤ 33, -11 ≤ k ≤7, -34 ≤ l ≤ 34
Reflections collected	17565
Independent reflections	6005 [R_{int} = 0.0244, R_{sigma} = 0.0240]
Data/restraints/parameters	6005/0/379
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.0970
Final R indexes [all data]	R_1 = 0.0447, wR_2 = 0.1015
Largest diff. peak/hole / e Å^{-3}	0.68/-0.55

Table S2. Crystal data and structure refinement for **3**. (CCDC 1872113)

Empirical formula	$C_{35}H_{27}OPSn$
Formula weight	613.22
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.93270(10)

b/Å	18.4467(3)
c/Å	15.8535(2)
α/°	90
β/°	104.801(2)
γ/°	90
Volume/Å^3	2808.38(7)
Z	4
ρ_{calc}g/cm^3	1.450
μ/mm^{-1}	7.969
F(000)	1240.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.498 to 148.19
Index ranges	-11 ≤ h ≤ 12, -13 ≤ k ≤ 22, -19≤ l ≤ 18
Reflections collected	10059
Independent reflections	5500 [R_{int} = 0.0213, R_{sigma} = 0.0266]
Data/restraints/parameters	5500/0/343
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0788
Final R indexes [all data]	R_1 = 0.0314, wR_2 = 0.0802
Largest diff. peak/hole / e Å^{-3}	0.68/-0.71

Table S3. Crystal data and structure refinement for **4a**. (CCDC 1872121)

Empirical formula	$C_{17}H_{13}ClCuOP$
Formula weight	363.23
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.1019(13)
b/Å	3.8793(3)
c/Å	21.547(2)
α/°	90
β/°	97.229(9)
γ/°	90
Volume/Å^3	1418.2(2)
Z	4
ρ_{calc}g/cm^3	1.701
μ/mm^{-1}	4.916
F(000)	736.0

Crystal size/mm^3	0.12 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.208 to 146.176
Index ranges	-20 ≤ h ≤ 21, -4 ≤ k ≤ 3, -26 ≤ l ≤ 23
Reflections collected	4132
Independent reflections	2694 [R_{int} = 0.0638, R_{sigma} = 0.0785]
Data/restraints/parameters	2694/0/191
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0907, wR_2 = 0.2423
Final R indexes [all data]	R_1 = 0.1146, wR_2 = 0.2810
Largest diff. peak/hole / e Å^{-3}	1.85/-1.43

Table S4. Crystal data and structure refinement for **4b**. (CCDC 1872114)

Empirical formula	$C_{28}H_{36}Cl_2Cu_2O_4P_4$
Formula weight	758.43
Temperature/K	290.85(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.0889(4)
b/Å	9.7187(5)
c/Å	10.6284(5)
α/°	78.259(4)
β/°	87.754(4)
γ/°	80.431(4)
Volume/Å^3	806.66(7)
Z	1
ρ_{calc}g/cm^3	1.561
μ/mm^{-1}	5.293
F(000)	388.0
Crystal size/mm^3	0.21 × 0.18 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.498 to 146.494
Index ranges	-10 ≤ h ≤ 7, -11 ≤ k ≤ 8, -12 ≤ l ≤ 13
Reflections collected	4593
Independent reflections	3062 [R_{int} = 0.0353, R_{sigma} = 0.0369]
Data/restraints/parameters	3062/0/187
Goodness-of-fit on F^2	1.121
Final R indexes [I>=2σ (I)]	R_1 = 0.0555, wR_2 = 0.1528
Final R indexes [all data]	R_1 = 0.0571, wR_2 = 0.1545

Largest diff. peak/hole / e Å^{-3}	0.90/-0.84

Table S5. Crystal data and structure refinement for **4c**. (CCDC 1872120)

Empirical formula	$C_{40}H_{60}Cl_2Cu_2O_4P_4$
Formula weight	926.74
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.1382(8)
b/Å	11.4943(8)
c/Å	12.1632(7)
α/°	79.859(5)
β/°	71.565(6)
γ/°	66.823(7)
Volume/Å^3	1112.26(16)
Z	1
ρ_{calc}g/cm^3	1.384
μ/mm^{-1}	3.937
F(000)	484.0
Crystal size/mm^3	0.18 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.676 to 147.544
Index ranges	-11 ≤ h ≤ 10, -11 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	6787
Independent reflections	4298 [R_{int} = 0.0482, R_{sigma} = 0.0557]
Data/restraints/parameters	4298/0/239
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0503, wR_2 = 0.1304
Final R indexes [all data]	R_1 = 0.0563, wR_2 = 0.1397
Largest diff. peak/hole / e Å^{-3}	0.62/-0.70

Table S6. Crystal data and structure refinement for **4d**. (CCDC 1872118)

Empirical formula	$C_{18}H_{20}Cl_2Cu_2N_2O_6P_2$
Formula weight	620.28
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	7.3741(6)
b/Å	7.5275(7)

c/Å	11.8201(10)
α/°	78.770(7)
β/°	87.887(7)
γ/°	67.556(8)
Volume/Å^3	594.30(10)
Z	1
ρ_{calc}g/cm^3	1.733
μ/mm^{-1}	5.886
F(000)	312.0
Crystal size/mm^3	0.09 × 0.08 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.632 to 148.704
Index ranges	-8 ≤ h ≤ 9, -8 ≤ k ≤ 9, -14 ≤ l ≤ 9
Reflections collected	3417
Independent reflections	2282 [R_{int} = 0.0556, R_{sigma} = 0.0549]
Data/restraints/parameters	2282/0/148
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0636, wR_2 = 0.1843
Final R indexes [all data]	R_1 = 0.0689, wR_2 = 0.1994
Largest diff. peak/hole / e Å^{-3}	1.26/-1.60

Table S7. Crystal data and structure refinement for **5**. (CCDC 1872115)

Empirical formula	$C_{100}H_{78}Cl_2Cu_4O_4P_8$
Formula weight	1916.49
Temperature/K	200(2)
Crystal system	triclinic
Space group	P-1
a/Å	14.7461(6)
b/Å	15.0636(7)
c/Å	22.9640(7)
α/°	87.081(3)
β/°	75.816(3)
γ/°	63.403(4)
Volume/Å^3	4412.0(3)
Z	2
ρ_{calc}g/cm^3	1.443
μ/mm^{-1}	1.21
F(000)	1960.0
Crystal size/mm^3	0.2 × 0.1 × 0.02

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.26 to 49.42
Index ranges	$-16 \leq h \leq 17$, $-17 \leq k \leq 17$, $-27 \leq l \leq 27$
Reflections collected	37364
Independent reflections	15031 [R_{int} = 0.0839, R_{sigma} = 0.175]
Data/restraints/parameters	15031/0/1013
Goodness-of-fit on F^2	0.890
Final R indexes [I>=2σ (I)]	R_1 = 0.0584, wR_2 = 0.1155
Final R indexes [all data]	R_1 = 0.1298, wR_2 = 0.1288
Largest diff. peak/hole / e Å^{-3}	1.49/-0.98

Table S8. Crystal data and structure refinement for **6**. (CCDC 1872116)

Empirical formula	$C_{19}H_{16}AuClNOP$
Formula weight	537.71
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.7694(3)
b/Å	7.3282(3)
c/Å	38.4557(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3598.57(18)
Z	8
ρ_{calc}g/cm^3	1.985
μ/mm^{-1}	17.610
F(000)	2048.0
Crystal size/mm^3	0.22 × 0.2 × 0.13
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.312 to 132.014
Index ranges	$-14 \leq h \leq 15$, $-4 \leq k \leq 8$, $-45 \leq l \leq 40$
Reflections collected	7089
Independent reflections	3130 [R_{int} = 0.0416, R_{sigma} = 0.0430]
Data/restraints/parameters	3130/0/219
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0491, wR_2 = 0.1287
Final R indexes [all data]	R_1 = 0.0589, wR_2 = 0.1388
Largest diff. peak/hole / e Å^{-3}	2.61/-2.44

Table S9. Crystal data and structure refinement for **7**. (CCDC 1872119)

Empirical formula	$C_{35}H_{27}AuOP_2$
Formula weight	722.47
Temperature/K	149.98(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.7949(4)
b/Å	11.5285(6)
c/Å	11.9802(5)
α/°	87.576(4)
β/°	84.280(4)
γ/°	71.512(4)
Volume/Å^3	1406.85(11)
Z	2
ρ_{calc}g/cm^3	1.706
μ/mm^{-1}	11.107
F(000)	708.0
Crystal size/mm^3	0.13 × 0.11 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.416 to 146.866
Index ranges	$-8 \le h \le 13$, $-13 \le k \le 14$, $-14 \le l \le 14$
Reflections collected	8375
Independent reflections	5385 [R_{int} = 0.0595, R_{sigma} = 0.0773]
Data/restraints/parameters	5385/0/352
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0490, wR_2 = 0.1211
Final R indexes [all data]	R_1 = 0.0550, wR_2 = 0.1281
Largest diff. peak/hole / e Å^{-3}	2.31/-1.53

Table S10. Crystal data and structure refinement for **9**. (CCDC 1872117)

Empirical formula	$C_{92}H_{77}Au_6Cl_5O_5P_5S$
Formula weight	2808.49
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.31190(10)
b/Å	21.8107(2)
c/Å	28.8693(2)
α/°	90

β/°	99.0770(10)
γ/°	90
Volume/Å^3	9520.55(13)
Z	4
ρ_{calc}g/cm^3	1.959
μ/mm^{-1}	19.613
F(000)	5276.0
Crystal size/mm^3	0.2 × 0.18 × 0.16
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.102 to 148.902
Index ranges	-17 ≤ h ≤ 19, -26 ≤ k ≤ 27, -35 ≤ l ≤ 34
Reflections collected	170600
Independent reflections	19015 [R_{int} = 0.0620, R_{sigma} = 0.0242]
Data/restraints/parameters	19015/0/1000
Goodness-of-fit on F^2	1.119
Final R indexes [I>=2σ (I)]	R_1 = 0.0666, wR_2 = 0.1710
Final R indexes [all data]	R_1 = 0.0700, wR_2 = 0.1722
Largest diff. peak/hole / e Å^{-3}	3.33/-1.70

S3. DFT calculations

Geometry optimizations were performed using the Gaussian 09 optimizer.[1] All geometry optimizations were computed using the functional BP86[2] the BP86/def2-TZVPP level of theory.[3] At each of the optimized structures vibrational analysis was performed to ensure that the geometry corresponds to an energy minimum. The atomic partial charges and NRT calculations have been estimated with the natural bond orbital (NBO)[4] method using NBO 6.0.[5]

phosphinine

C	-0.37003200	1.33734900	0.00000500
C	-0.37011800	-1.33730700	0.00000600
C	1.02029500	-1.22769900	0.00000100
C	1.69224200	-0.00004400	-0.00000500
C	1.02036300	1.22765400	0.00000100
H	-0.80747600	2.33957400	0.00001300
H	1.61932900	-2.14306100	0.00000300
H	2.78375000	-0.00006700	-0.00001300
H	1.61945800	2.14297600	0.00000500
P	-1.49093100	0.00002400	-0.00000500
H	-0.80759500	-2.33950000	0.00001500

phosphini-2-ol

C	1.38212100	-1.02225800	0.00001100
C	-0.97240500	0.27039900	0.00000300
C	-0.19512500	1.43357900	-0.00001200
C	1.19920200	1.41985900	-0.00000600
C	1.96018500	0.24325700	0.00001100
H	2.03781400	-1.89721000	0.00002100
H	-0.72448200	2.39035300	-0.00002300
H	1.72055700	2.37881800	-0.00001400
H	3.04955300	0.32823700	0.00002600
P	-0.32617800	-1.37230000	-0.00001300

O	-2.33243000	0.46485000	0.00001500
H	-2.77519600	-0.40351000	0.00002800

phosphinin-2-olate

C	1.37427200	-0.99361000	0.00000200
C	-1.13052200	0.26932100	0.00001100
C	-0.26639100	1.43510500	-0.00000600
C	1.12104200	1.43975400	-0.00000400
C	1.93187700	0.28374500	0.00000600
H	2.06311700	-1.84937300	0.00000300
H	-0.79968200	2.39510800	-0.00001200
H	1.62455100	2.41453400	-0.00000500
H	3.02080500	0.40555200	0.00001300
P	-0.33196100	-1.39395000	-0.00000500
O	-2.38888000	0.36719200	0.00000300

phosphinin-2-olate [Na(18-crown-6)(H_2O)]$^+$

P	-1.63700700	2.07213400	0.31762100
Na	0.75950200	-0.82272800	-0.04594400
O	-2.06630900	-1.51997300	-1.84821100
O	0.49470600	-0.31154500	-2.54603000
O	-2.31243400	-2.54018500	0.95966800
O	2.98858100	-0.96180200	-1.29184300
O	2.64967900	-0.92870600	1.58752700
O	-0.10117500	-1.16125000	2.38923100
O	0.97187400	1.41863700	0.25922100
C	0.59847400	3.76272200	0.35240200
H	1.68701900	3.89280700	0.34836700
C	-1.61848500	4.86668700	0.40714600
H	-2.15726600	5.81735400	0.44369200
C	-0.21012600	4.89111600	0.39794600
C	-2.33338800	3.67594000	0.37165200
C	0.14253200	2.40640600	0.30650900
C	-1.89587800	-0.42887500	-2.76426600
H	-1.94069500	0.52967800	-2.21405100
H	-2.70587000	-0.44355400	-3.51967800
C	3.64961800	-0.12873600	0.93911100
H	4.53880800	-0.02553000	1.59261000
H	3.23430100	0.87376000	0.73111300
C	1.76695600	-0.16496200	-3.18250600
H	1.72101900	0.65104200	-3.92941800
H	2.04399100	-1.10143900	-3.70347000
C	2.11425900	-0.29342200	2.75379400
H	1.73121900	0.70720500	2.48542100
H	2.90037700	-0.18886900	3.52723100
C	4.05482200	-0.84074700	-0.34199300
H	4.91740300	-0.31821100	-0.79597400
H	4.35755000	-1.87236900	-0.10842400
C	-0.56407600	-0.55201000	-3.47135600
H	-0.45518000	-1.55333400	-3.93312200
H	-0.53425800	0.20031800	-4.28334400
C	0.99503300	-1.14783800	3.30985300
H	1.34702900	-2.18029400	3.49687400
H	0.66995100	-0.71268000	4.27441000
C	-2.44648500	-1.55638100	1.99823000
H	-3.39552600	-1.72858400	2.54144900
H	-2.45509300	-0.53178900	1.58429900
C	-3.23226200	-1.34933900	-1.03215900
H	-4.14151500	-1.36124400	-1.66700900
H	-3.18386100	-0.36809800	-0.52472700
C	2.81067300	0.18240400	-2.14097400
H	3.76167900	0.42214900	-2.65432600
H	2.47620800	1.05690300	-1.55342000
C	-3.34325000	-2.49349500	-0.03530500
H	-4.33382700	-2.43551800	0.45432500
H	-3.28029700	-3.45574100	-0.56487000
C	-1.29345400	-1.69135400	2.96922900
H	-1.54322000	-1.12435900	3.88693300
H	-1.15116000	-2.75294800	3.25085700
H	0.28361800	5.86679700	0.42858300
H	-3.42745900	3.72659800	0.38259400
O	0.02868900	-3.06717000	-0.52800500
H	-0.51021000	-2.77698200	-1.29004300
H	-0.65282900	-3.09781400	0.17785800

6H

Au	-1.07010600	-0.11968800	-0.00013700
P	1.14132200	-0.29021700	-0.00083600
Cl	-3.32345000	0.14202500	0.00077200
C	4.23934900	-0.19763600	0.00068800
O	1.61920000	2.37600200	-0.00035900
H	0.64253200	2.30593000	0.00069000
C	2.23356000	-1.62149500	-0.00003900
C	3.55536200	1.01958400	0.00049500
H	4.12110200	1.95448800	0.00079800
C	2.16063600	1.12866400	0.00001400
C	3.61587600	-1.45288000	0.00049200

H	4.24382600	-2.34597900	0.00081200
H	1.79771400	-2.62153900	-0.00021600
H	5.32972700	-0.16412400	0.00110100

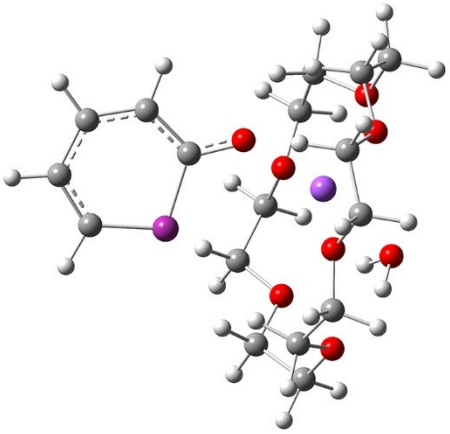
7H

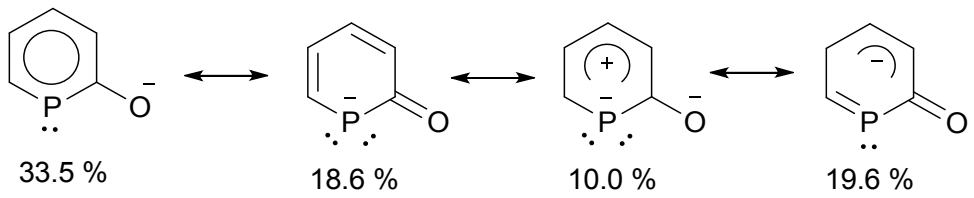
Au	0.99969500	-0.09319200	-0.09142100
P	3.22070900	0.10419700	0.48903700
P	-1.24196700	-0.18990300	-0.70424300
O	-1.73452000	2.41196100	-0.09729900
C	-2.09563700	-1.61942300	-0.11175000
C	-4.05626700	-0.31008400	0.60134100
C	-3.37615600	-1.54675600	0.37587600
H	-3.90505000	-2.47057900	0.62210300
C	-3.54908900	0.94961200	0.38773300
H	-4.14828200	1.82312900	0.66200700
C	-2.20009400	1.26745300	-0.06228600
H	-5.07038100	-0.37498500	1.00572500
H	-1.61649800	-2.59224300	-0.24606000
H	3.63076300	1.32583200	1.07967000
H	3.75162100	-0.79119800	1.45176500
H	4.24036600	-0.01273200	-0.49198800

8H

Au	-1.76688500	-0.40993400	-0.07482100
P	-3.51212800	-1.91510000	0.06050100
P	0.10178200	1.00159900	-0.12355100
O	-0.18682400	1.87946400	2.43843800
C	0.09754800	1.98470500	-1.62682700
C	-0.01102200	4.13338200	-0.39887000
C	0.06269800	3.34242200	-1.60430100
H	0.10112800	3.88719700	-2.55096500
C	-0.07070800	3.66680600	0.88307500
H	-0.12800400	4.37102300	1.71754800
C	-0.07728200	2.26054700	1.27853600
H	-0.02195800	5.21813800	-0.53503500
H	0.17159900	1.44552800	-2.57342700
H	-4.36416100	-2.07306400	-1.06051400
H	-3.20572500	-3.27588800	0.31057200
H	-4.49083700	-1.71028600	1.06406200
Au	1.82467900	-0.44905800	-0.01393800
Cl	3.53027200	-1.98015600	0.05225500

NRT calculation of $[Na(18\text{-crown-}6)(H_2O)]^+[PC_5H_4\text{-}O]^-$





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