A One-Pot Diastereoselective Self Assembly of C-Stereogenic Copper(I) Diphosphine Clusters

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Electronic Supporting Information

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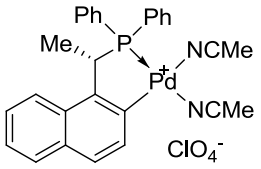
General Information

All reactions were carried out under a positive pressure of nitrogen using standard Schlenk technique. Solvents were purchased from their respective companies and used as supplied. Where necessary, solvents were degassed prior to use. A Low Temp Pairstirrer PSL-1800 was used for controlling low temperature reactions. Column chromatography was done on Silica gel 60 (Merck). Melting points were measured using SRS Optimelt Automated Point System SRS MPA100. Optical rotation were measured with JASCO P-1030 Polarimeter in the specified solvent in a 0.1 dm cell at 22.0^{o}C. NMR spectra were recorded on Bruker AV 300, AV 400 and AV 500 spectrometers. Chemical shifts were reported in ppm and referenced to an internal $SiMe_4$ standard (0 ppm) for ^{1}H NMR, chloroform-d (77.23 ppm) for ^{13}C NMR, and an external 85% H_3PO_4 for $^{31}P\{^{1}H\}$ NMR. All X-ray quality crystals were obtained *via* recrystallization from a dichloromethane solution layered with *n*-hexanes.

The palladacycle (*S*)-**8**[1] was prepared according to literature methods. All other reactants and reagents were used as supplied.



(*S*)-**8**

Caution! *Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.*

Preparation of Copper(I) Clusters 7a-c

To a solution of Ph_2PH (2.2 equiv) in toluene (10 mL) was added catalyst (*R*)- or (*S*)-**8** (6 mol %) and stirred for 10 minutes before cooling to -80^{o}C. Diunsaturated alkene (1.0 equiv) was added followed by NEt_3 (2.0 equiv) in toluene (1 mL) dropwise. The solution was stirred at -80^{o}C and the completion of the reaction was monitored by the disappearance of the phosphorous signal attributed to diphenylphosphine (-40 ppm) in the $^{31}P\{^{1}H\}$ NMR spectrum. Upon completion, the solution was allowed to room temperature. Volatiles were removed under reduced pressure. The crude product was redissolved in acetone (10 mL) and CuCl (2.0 equiv) was added. The mixture was refluxed overnight and on cooling, concentrated to give the crude complex, which was purified *via* silica gel column chromatography (DCM or 9 DCM : 1 EA) to afford white solid of the clusters **7a-c**.

7a

The hydrophosphination step was completed in 8 h. (72% yield based on Cu atoms). $[\alpha]_D$ = -48.6 (*c* 0.1, DCM). Mp: 206-208^{o}C. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ -1.2; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.03 (brs, 1H, Ar), 8.19-8.17 (m, 4H, Ar), 8.02-8.00 (m, 4H, Ar), 7.67-7.36 (m, 16H, Ar), 6.94-6.76 (m, 9H, Ar), 4.73-4.69 (m, 2H, PCHC*H*H), 4.59-4.54 (m, 2H, PC*H*CHH), 3.31 (dd, 2H, *J* = 18.1 Hz, 12.8 Hz, PCHCH*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.8 (d, 2C, $^{3}J_{PC}$ = 14.9 Hz, C=O), 140.1-128.0 (42C, Ar), 44.0 (d, 2C, $^{2}J_{PC}$ = 13.0 Hz, PCH*C*H$_2$), 38.9 (d, 2C, $^{1}J_{PC}$ = 25.5 Hz, P*C*H). HRMS (ESI, m/z (M + H)$^{+}$] calcd for

$C_{144}H_{121}O_6P_6Cu_6Cl_6$ 2727.1472, found 2727.1477. Elemental analysis calcd (%) for $C_{144}H_{121}O_6P_6Cu_6Cl_6$: C 63.44, H 4.44; found: C 63.48, H 4.49.

7b

The hydrophosphination step was completed in 45 h. (77% yield based on Cu atoms). $[\alpha]_D$ = +38.9 (*c* 0.1, DCM). Mp: 226-228°C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ -0.8; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.99 (brs, 1H, Ar), 8.15-8.11 (m, 4H, Ar), 7.99-7.95 (m, 4H, Ar), 7.68-7.64 (m, 4H, Ar), 7.38-7.33 (m, 6H, Ar), 6.97-6.85 (m, 13H, Ar), 4.68-4.63 (m, 2H, PCHC*H*H), 4.47-4.41 (m, 2H, PC*H*CHH), 3.30-3.24 (m, 2H, PCHCH*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 196.3 (2C, *C*=O), 166.7 (1C, *C*F), 164.7 (1C, *C*F), 140.1-115.4 (40C, Ar), 43.6 (2C, PCH*C*H_2), 38.8 (2C, P*C*H). HRMS (ESI, m/z (M + H)$^+$] calcd for $C_{144}H_{115}O_6P_6F_6Cu_6Cl_6$ 2835.0906, found 2835.0898.

7c

The hydrophosphination step was completed in 72 h. (72% yield based on Cu atoms). $[\alpha]_D$ = +44.5 (*c* 0.1, DCM). Mp: 249-251°C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ -1.0; ^1H NMR ($CDCl_3$, 500 MHz): δ 9.00 (brs, 1H, Ar), 8.18-8.14 (m, 4H, Ar), 7.88-7.86 (m, 4H, Ar), 7.67-7. 63 (m, 4H, Ar), 7.33-7. 32 (m, 6H, Ar), 7.12-7. 11 (m, 4H, Ar), 6.93-6.81 (m, 9H, Ar), 4.71-4.66 (m, 2H, PCHC*H*H), 4.46-4.41 (m, 2H, PC*H*CHH), 3.32 (dd, 2H, *J* = 17.1 Hz, 13.5 Hz, PCHCH*H*), 2.34 (s, 6H, C_6H_4C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 197.5 (2C, *C*=O), 143.6-128.0 (42C, Ar), 43.9 (2C, PCH*C*H_2), 38.8 (2C, P*C*H), 29.8 (1C, C_6H_4C*H*$_3$), 21.7 (1C, C_6H_4C*H*$_3$). HRMS (ESI, m/z (M + H)$^+$] calcd for $C_{150}H_{133}O_6P_6Cu_6Cl_6$ 2811.2415, found 2811.2430.

Preparation of Copper(I) Cluster 7d

The preparation is similar as above but THF was used in place of toluene.

7d

The hydrophosphination step was completed in 36 h. (89% yield based on Cu atoms). $[\alpha]_D$ = +42.0 (*c* 0.1, DCM). Mp: 265-268°C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ -0.6; ^1H NMR ($CDCl_3$, 300 MHz): δ 9.02 (brs, 1H, Ar), 8.15-8.10 (m, 4H, Ar), 7.73-7.67 (m, 4H, Ar), 7.44-7. 33 (m, 9H, Ar), 7.12-7. 05 (m, 7H, Ar), 6.93-6.83 (m, 3H, Ar), 6.23 (brs, 2H, Ar), 4.63-4.55 (m, 2H, PCHC*H*H), 4.19-4.08 (m, 2H, PC*H*CHH), 3.12-3.03 (m, 2H, PCHCH*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 186.3 (2C, C=O), 152.0 (2C, C(O)*C*-O), 146.8 (2C, O-*C*H=C), 139.7-128.2 (30C, Ar), 119.6 (2C, C(O)C=*C*H), 112.1 (2C, O-CH=*C*H), 43.0 (2C, PCH*C*H_2), 29.7 (2C, P*C*H). HRMS (ESI, m/z (M + H)$^+$] calcd for $C_{132}H_{109}O_{12}P_6Cu_6Cl_6$ 2667.0222, found 2667.0217.

Preparation of Copper(I) Cluster 7e

The preparation is similar as above but DCM was used as the solvent.

7e

The hydrophosphination step was completed in 12 h. (85% yield based on Cu atoms). $[\alpha]_D$ = -19.5 (*c* 0.1, DCM). Mp: 221-224°C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 2.4; ^1H NMR

($CDCl_3$, 300 MHz): δ 8.08-7.98 (m, 9H, Ar), 7.44-7.39 (m, 13H, Ar), 6.69-6.66 (m, 1H, Ar), 6.40 (brs, 1H, Ar), 4.71-4.64 (m, 2H, PC*H*), 4.49-4.45 (m, 2H, PCHC*H*), 3.04 (brs, 12H, CO_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.7 (4C, C=O), 137.9-127.6 (30C, Ar), 53.8 (2C, PCH*C*H), 52.3 (4C, CO_2CH_3), 44.1 (2C, P*C*H). HRMS (ESI, m/z (M + H)$^+$] calcd for $C_{126}H_{121}O_{24}P_6Cu_6Cl_6$ 2799.0549, found 2799.0552.

Preparation of Copper(I) Cluster 9

To a solution of Ph_2PH (2.2 equiv) in toluene (10 mL) was added catalyst (*R*)- or (*S*)-**8** (6 mol %) and stirred for 10 minutes before cooling to -80^{o}C. Diunsaturated alkene (1.0 equiv) was added followed by NEt_3 (2.0 equiv) in toluene (1 mL) dropwise. The solution was stirred at -80^{o}C and the completion of the reaction was monitored by the disappearance of the phosphorous signal attributed to diphenylphosphine (-40 ppm) in the $^{31}P\{^1H\}$ NMR spectrum. Upon completion, the solution was allowed to room temperature. Volatiles were removed under reduced pressure. The crude product was redissolved in acetone (10 mL) and $CuCl_2$ (2.0 equiv) was added. The mixture was refluxed overnight and on cooling, concentrated to give the crude complex, which was purified *via* silica gel column chromatography (DCM or 9 DCM : 1 EA) to afford white solid of the clusters **9**. 3% yield based on Cu atoms. $[\alpha]_D$ = +39.5 (*c* 0.1, DCM). Mp: 257-259^{o}C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 44.4; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.04-8.02 (m, 4H, Ar), 7.92-7.89 (m, 4H, Ar), 7.41-7.33 (m, 19H, Ar), 7.16 (t, 4H, ^3J = 7.7 Hz, 12.8 Hz, Ar), 7.05 (d, 2H, ^3J = 7.5 Hz, Ar), 6.79 (t, 1H, ^3J = 7.3 Hz, Ar), 4.91-4.90 (m, 2H, PCHC*H*H), 3.42-4.25 (m, 2H, PC*H*CHH), 3.07-2.96 (m, 2H, PCHCH*H*); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 198.0 (2C, C=O), 135.1-124.7 (42C, Ar), 48.0 (2C, PCH*C*H$_2$), 44.8 (2C, P*C*H). HRMS (ESI, m/z (M + H)$^+$] calcd for $C_{96}H_{81}O_4P_4Cu_4Cl_4$ 1818.1023, found 1818.1033.

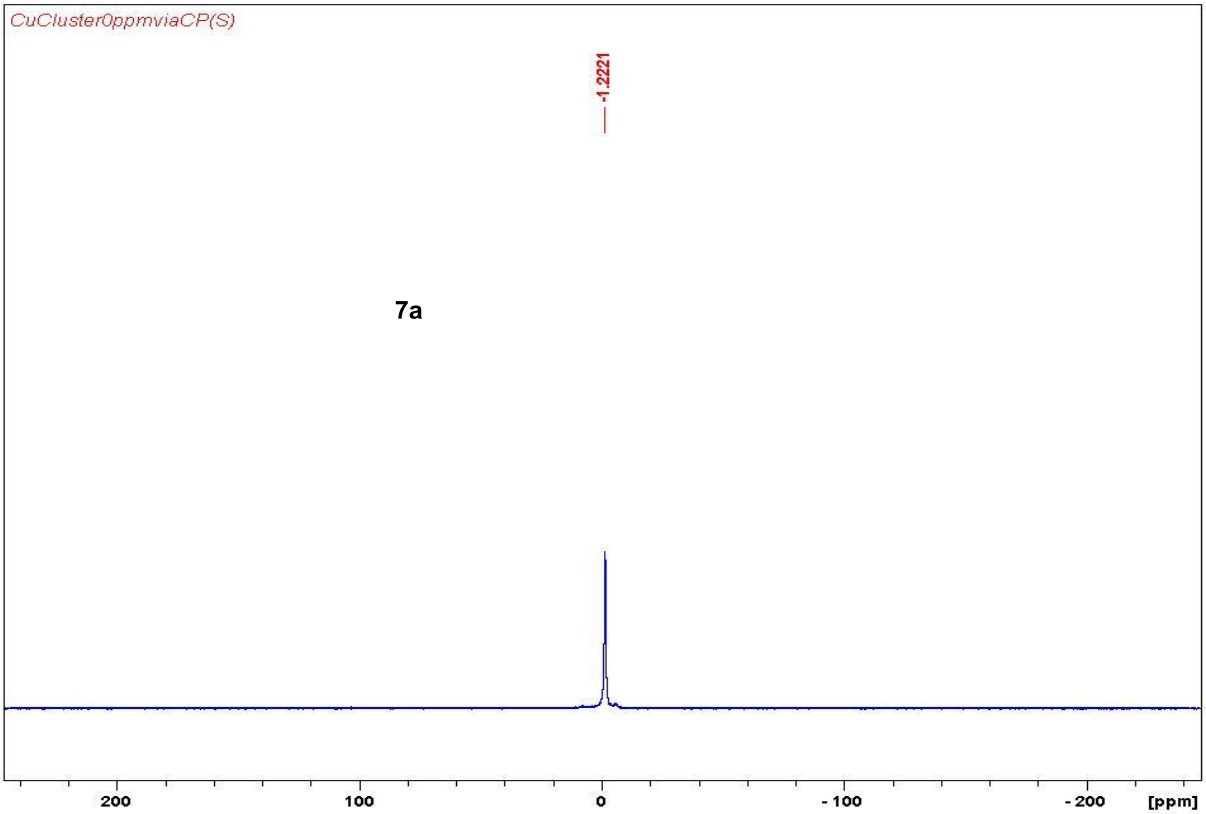
General Procedure for Catalytic Hydroboration

Under a nitrogen atmosphere, Cu(I) cluster **7a** (2.7 mg, 1.0 μmol, 1 mol %), base (10 mol %) and B_2pin_2 (27.9 mg, 0.11 mmol, 1.1 equiv.) in solvent (2 mL) was stirred for 10 mins. Enone (20.8 mg, 0.10 mmol, 1.0 equiv.) and MeOH (8.1 μL, 0.20 mmol, 2.0 equiv.) was added consecutively and stirred. The completion of the reaction was determined by TLC analysis and confirmed by ^{1}H NMR. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography to afford the desired product. The data were consistent with the literature.[2] The *ee* was determined on a Daicel Chiralpak AD-H column with n-hexane/2-propanol = 97/3, flow = 0.9 mL/min, wavelength = 210 nm. Retention times: 8.7 min, 12.4 min.

Reference

[1] Y. Huang, R. J. Chew, Y. Li, S. A. Pullarkat, P. H. Leung, *Org. Lett.* **2011**, *13*, 5862.

[2] Zhao, L.; Ma, Y.; He, F.; Duan, W.; Chen, J.; Song, C. *J. Org. Chem.* **2013**, *78*, 1677.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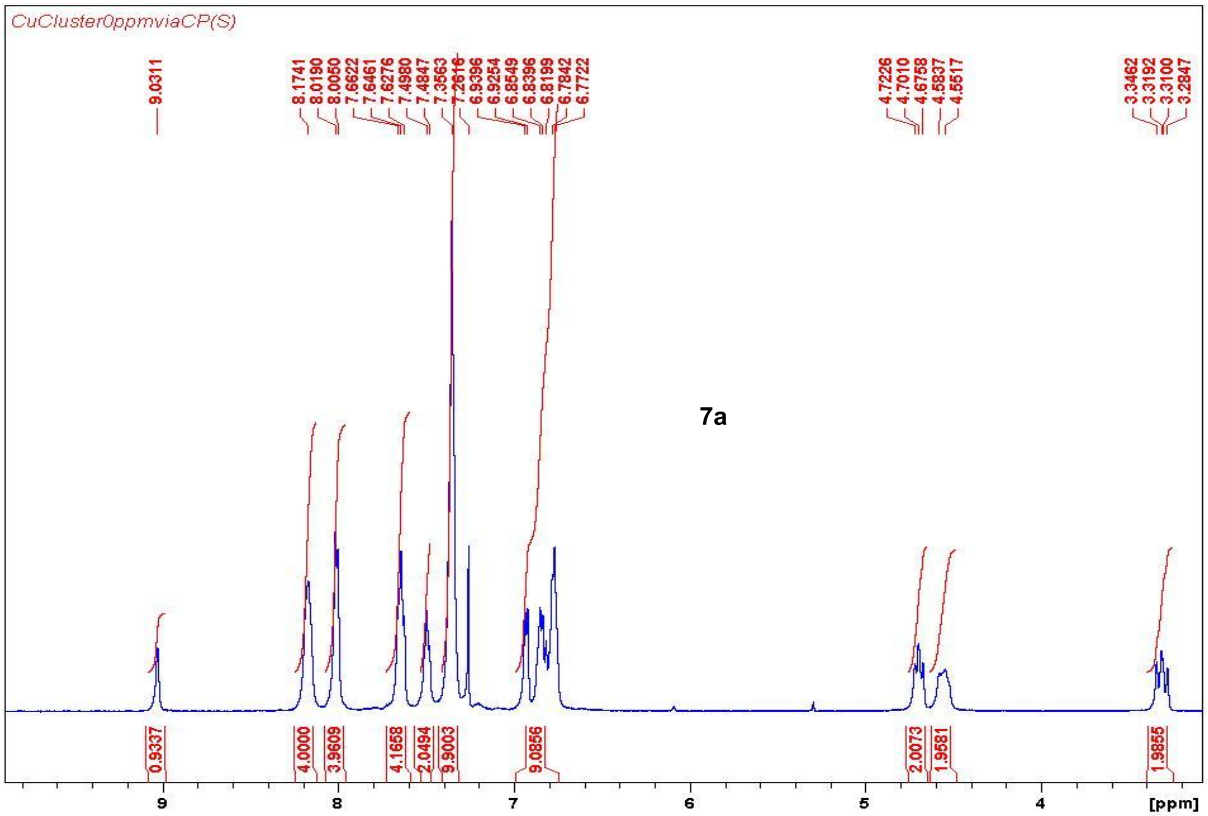
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4.6758
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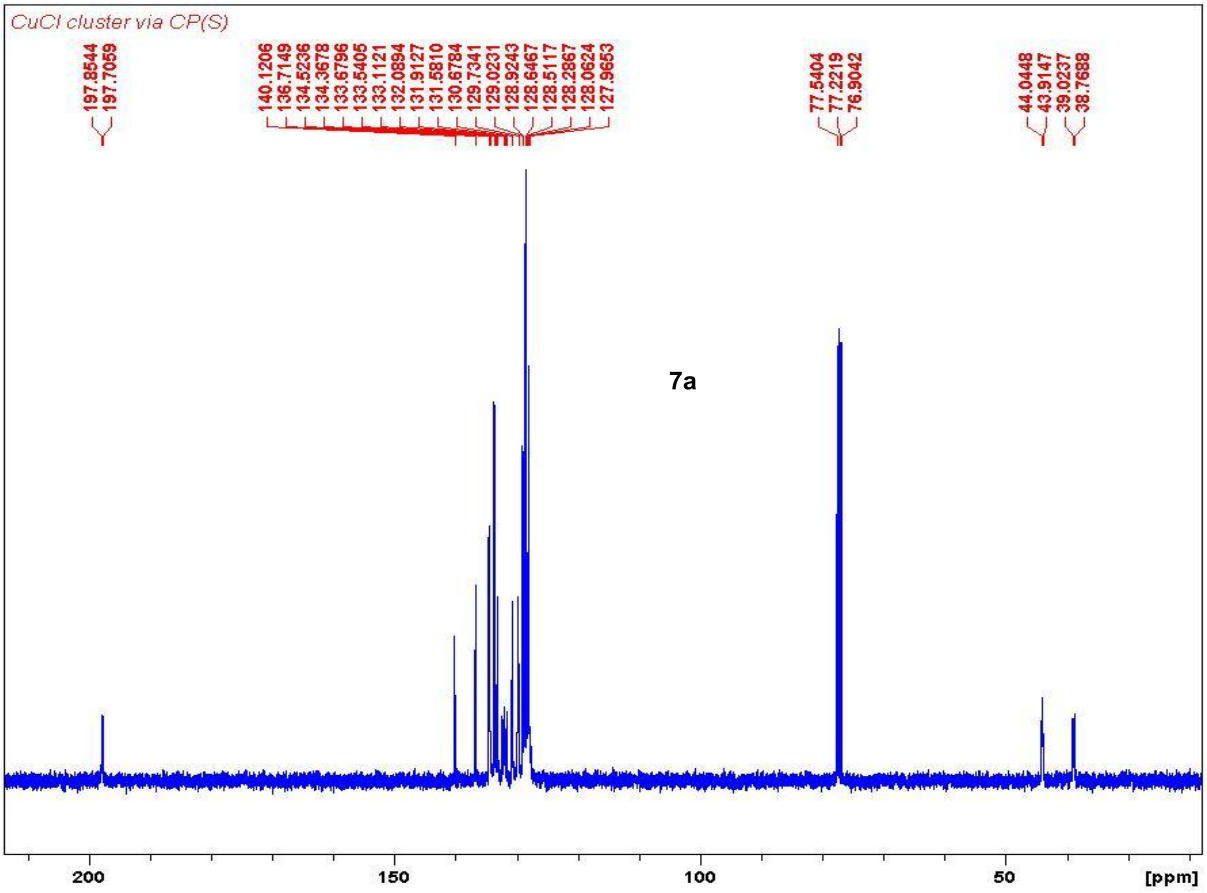
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129.0231
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128.6467
128.5117
128.2867
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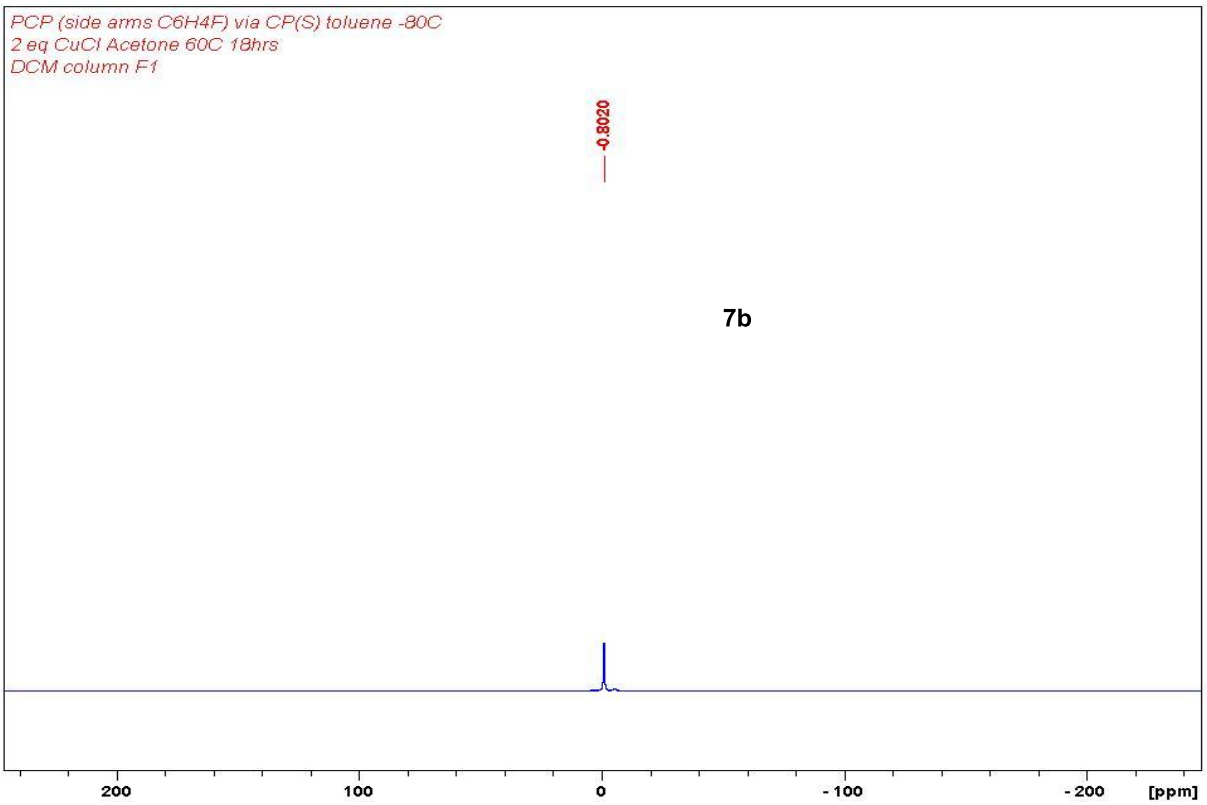
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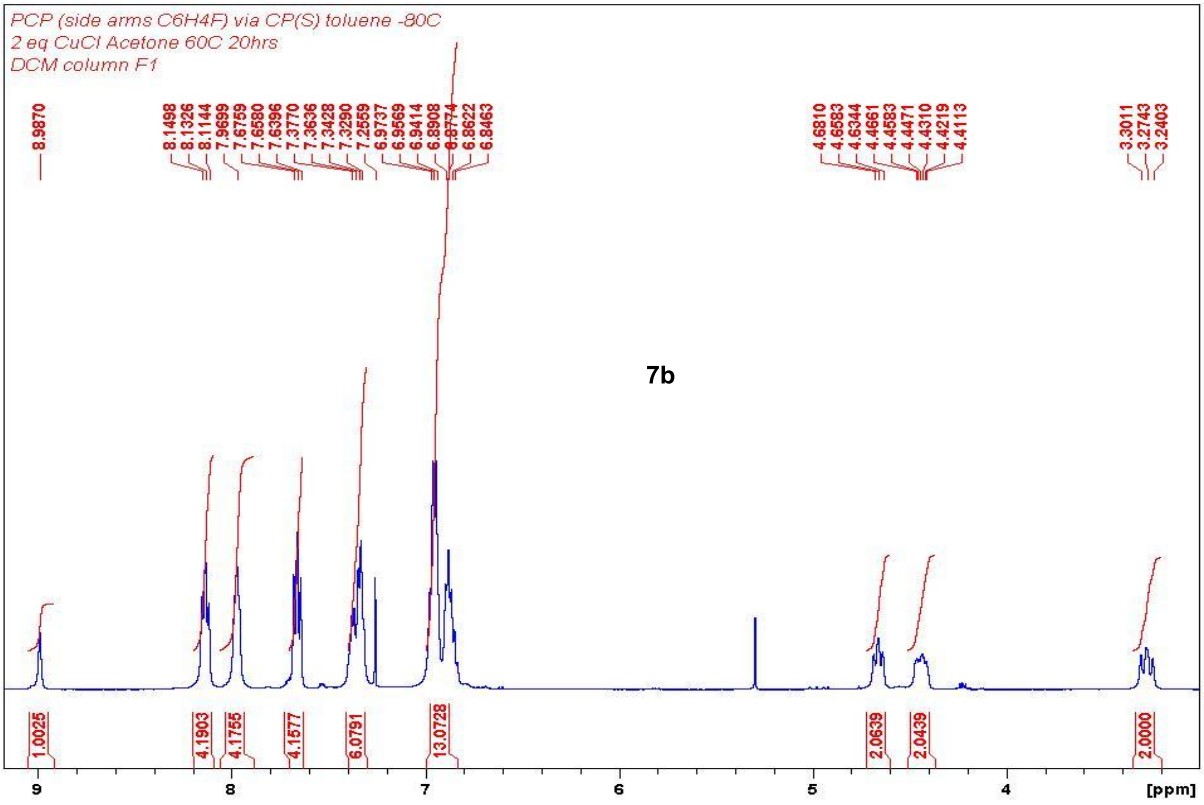
-200
[ppm]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6.8463
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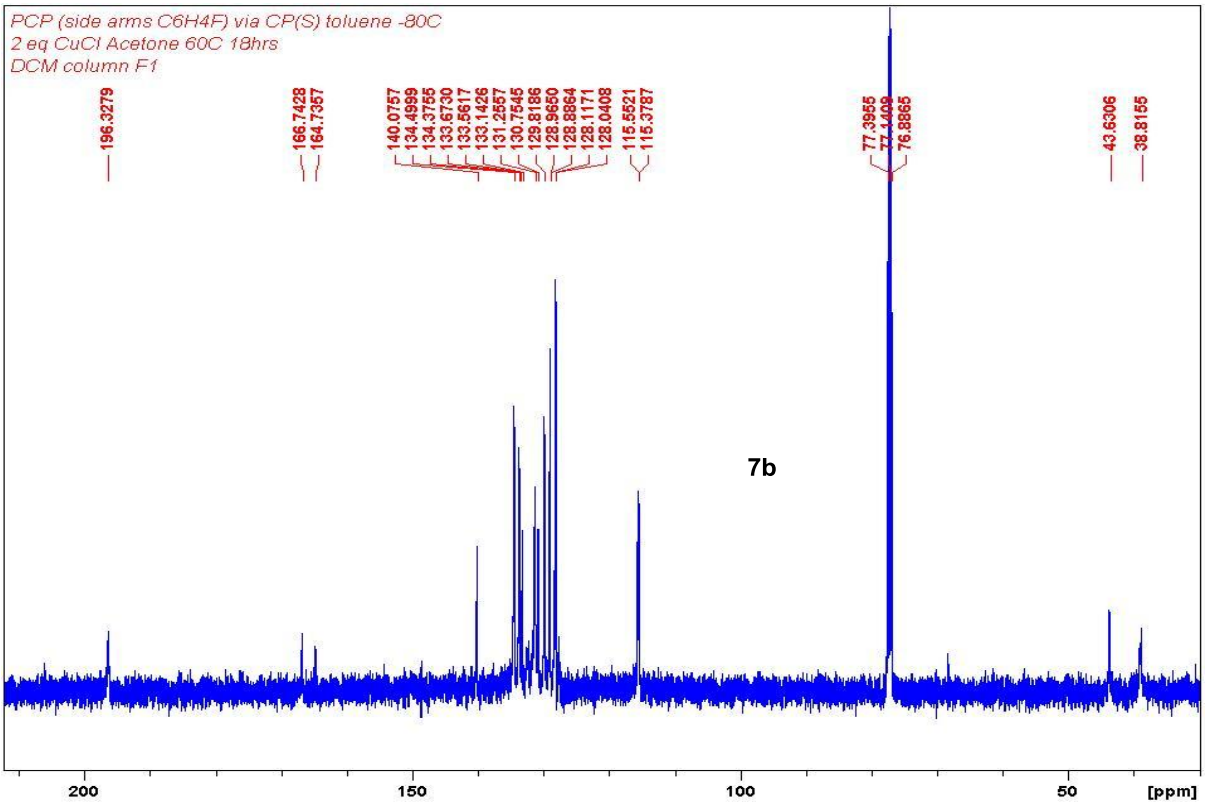
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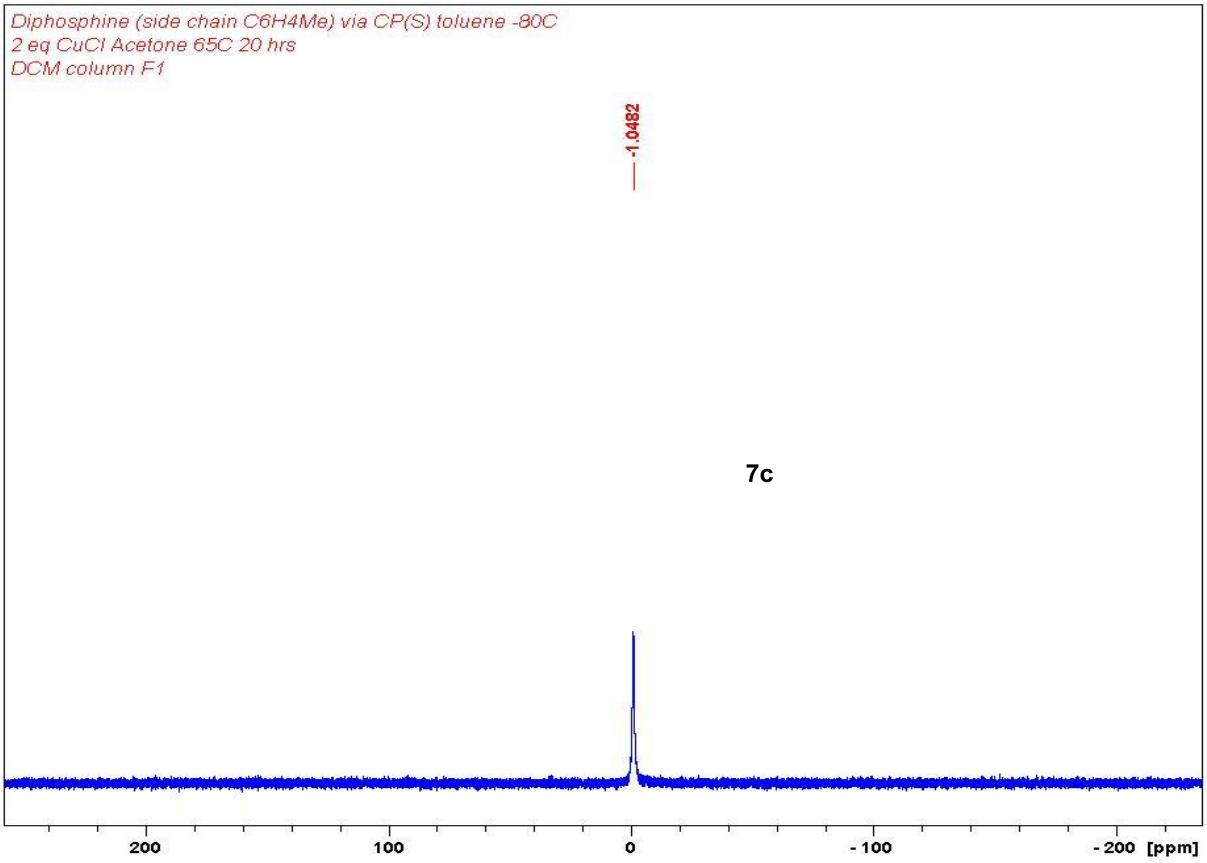
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0
- 100
- 200
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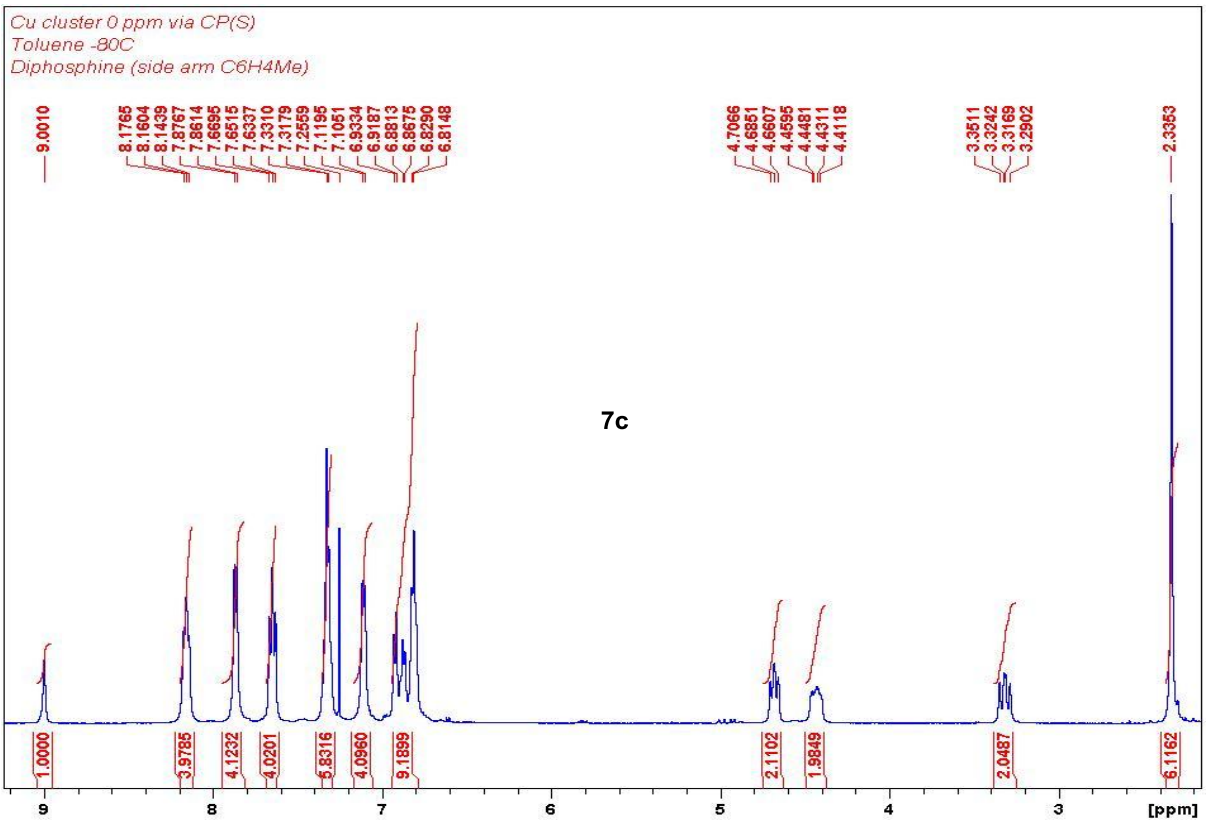
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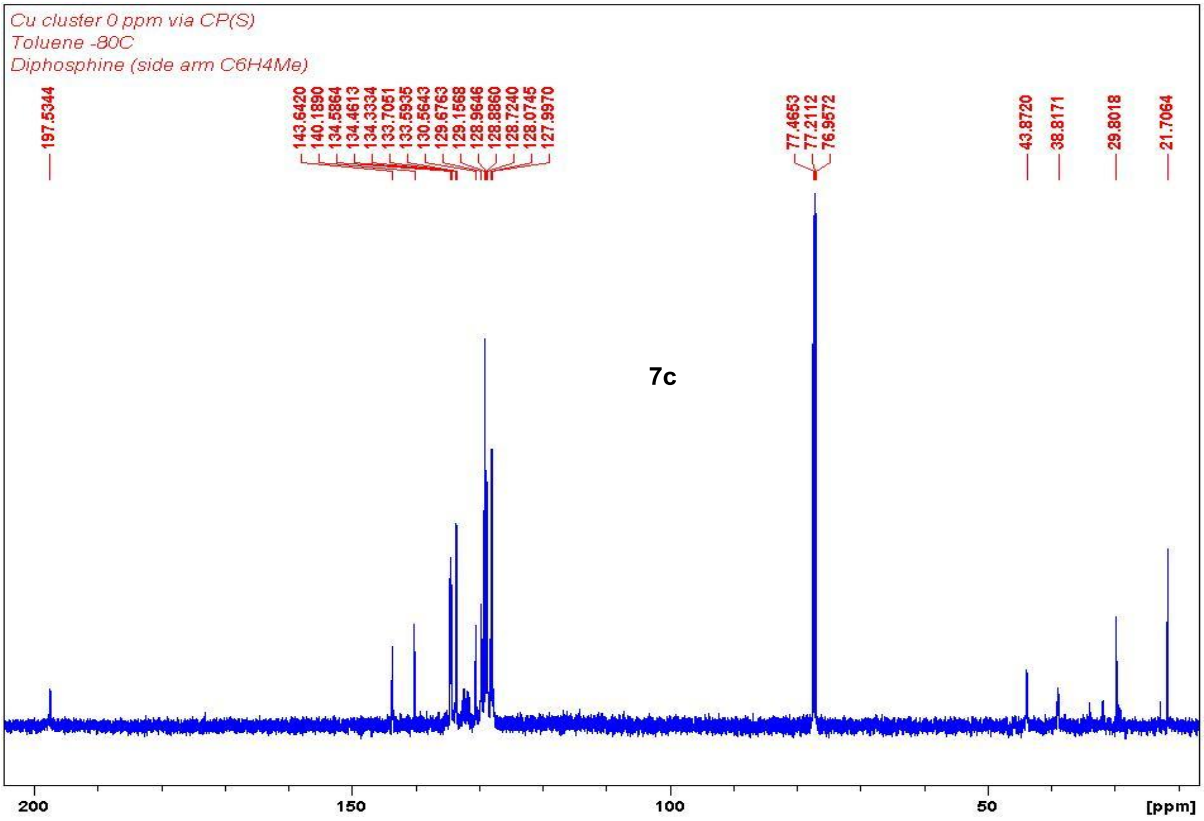
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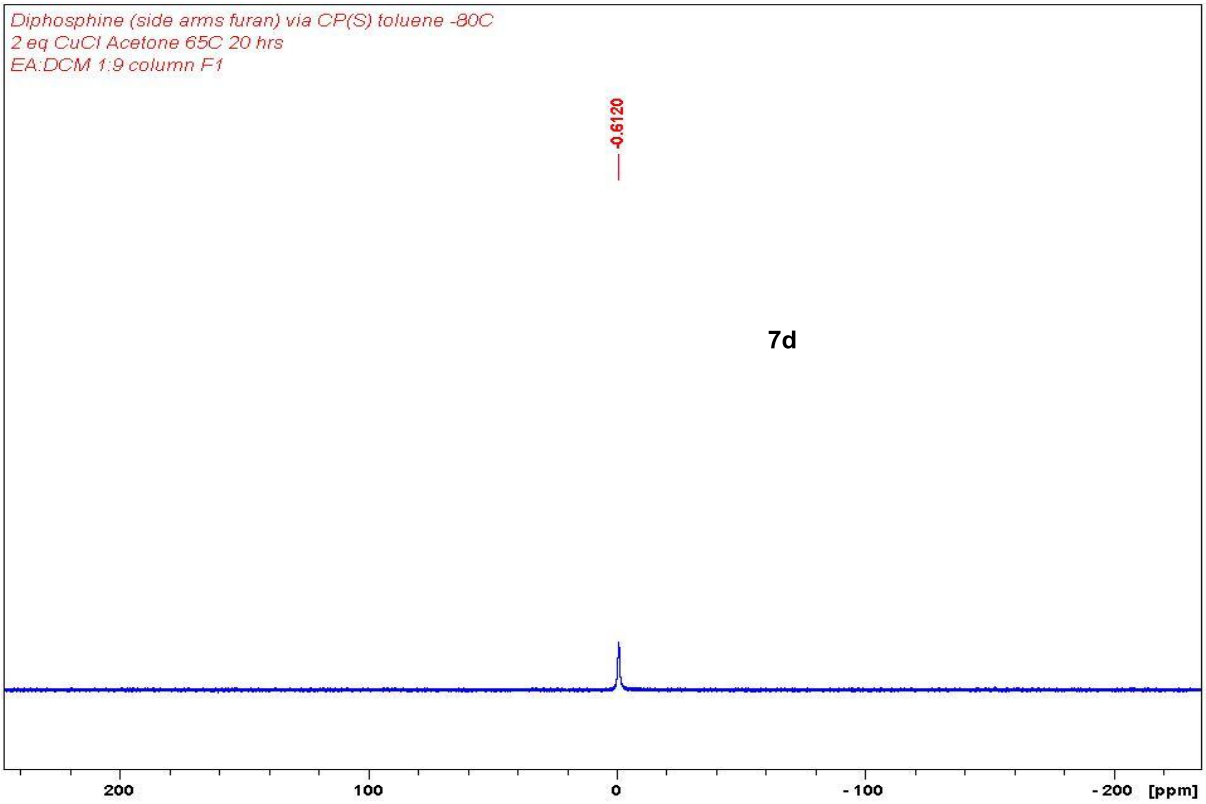
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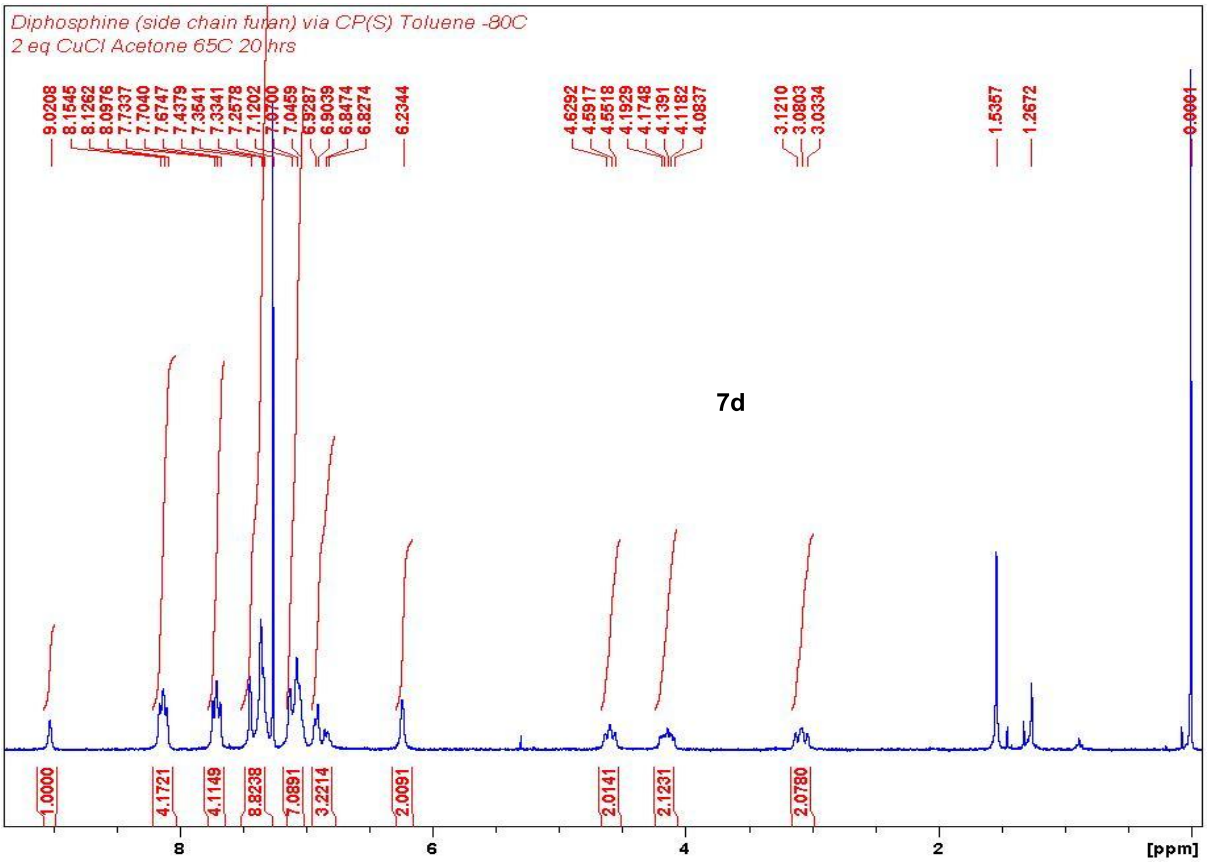
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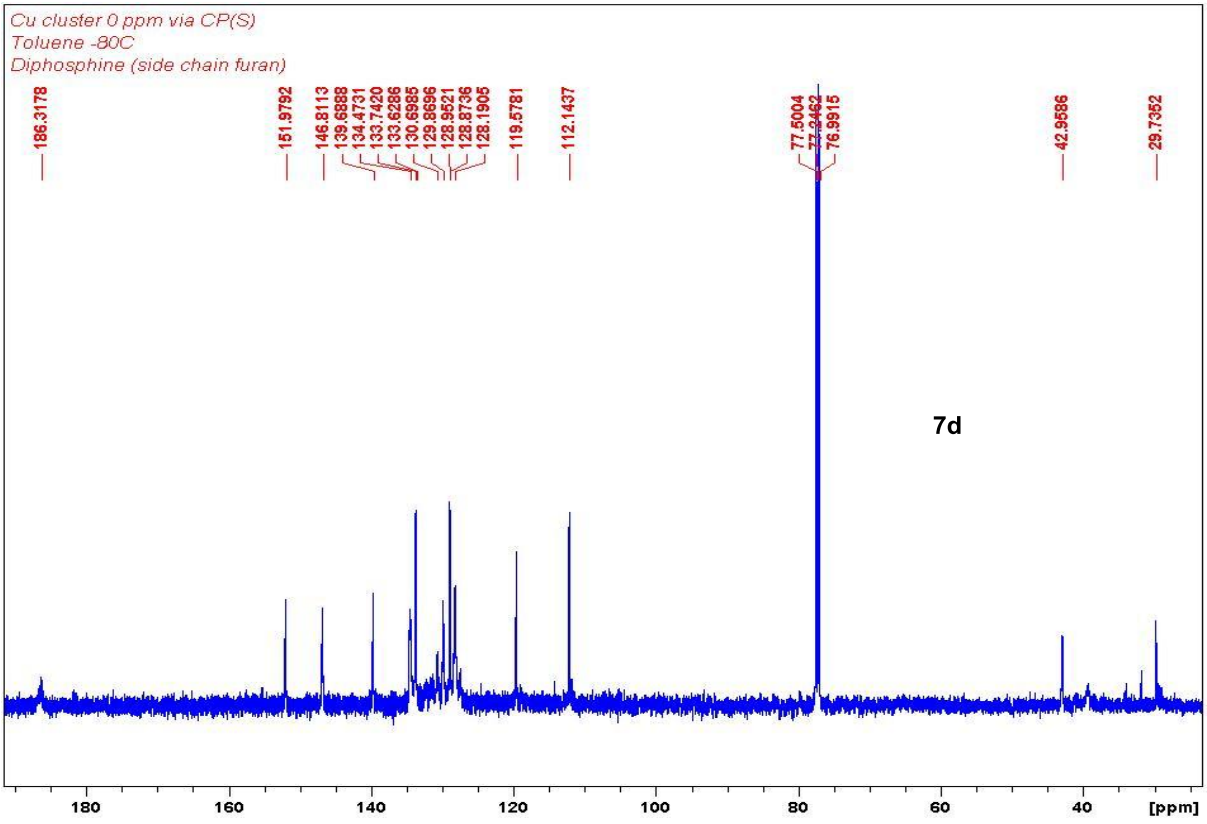
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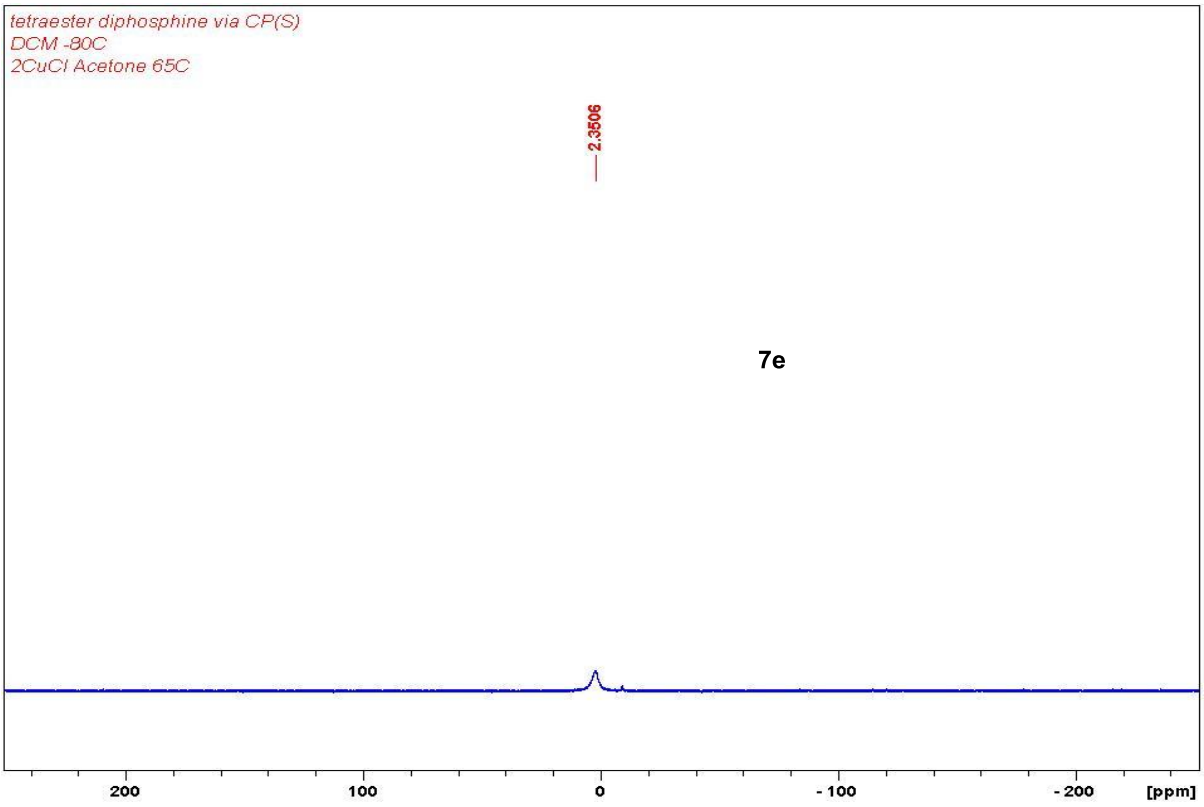
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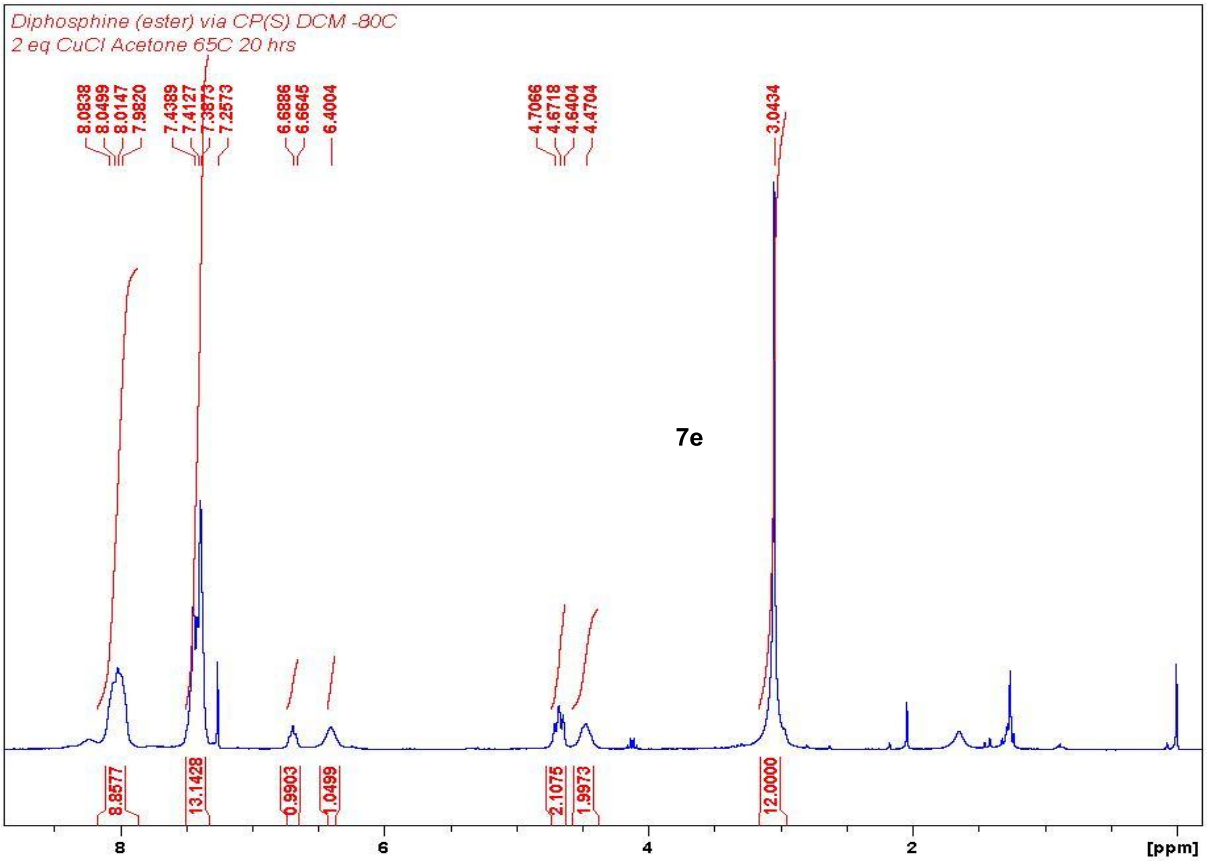
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2 eq CuCl Acetone 65C 20 hrs
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8.0499
8.0147
7.9820
7.4389
7.4127
7.3873
7.2573
6.6886
6.6645
6.4004
4.7066
4.6718
4.6404
4.4704
3.0434
7e
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2.1075
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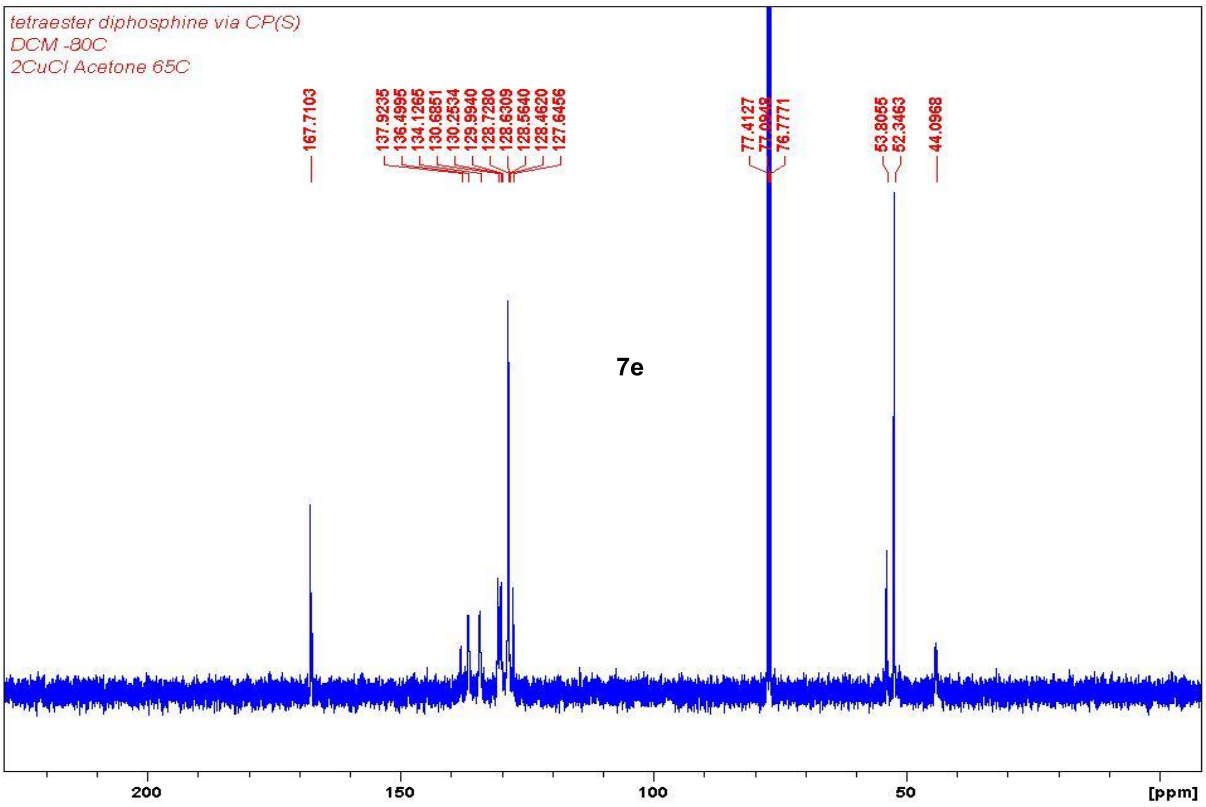
12.0000
8
6
4
2
[ppm]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DCM -80C
2CuCl Acetone 65C
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134.1265
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129.9940
128.7280
128.6309
128.5640
128.4620
127.6456
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76.7771
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52.3463
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7e
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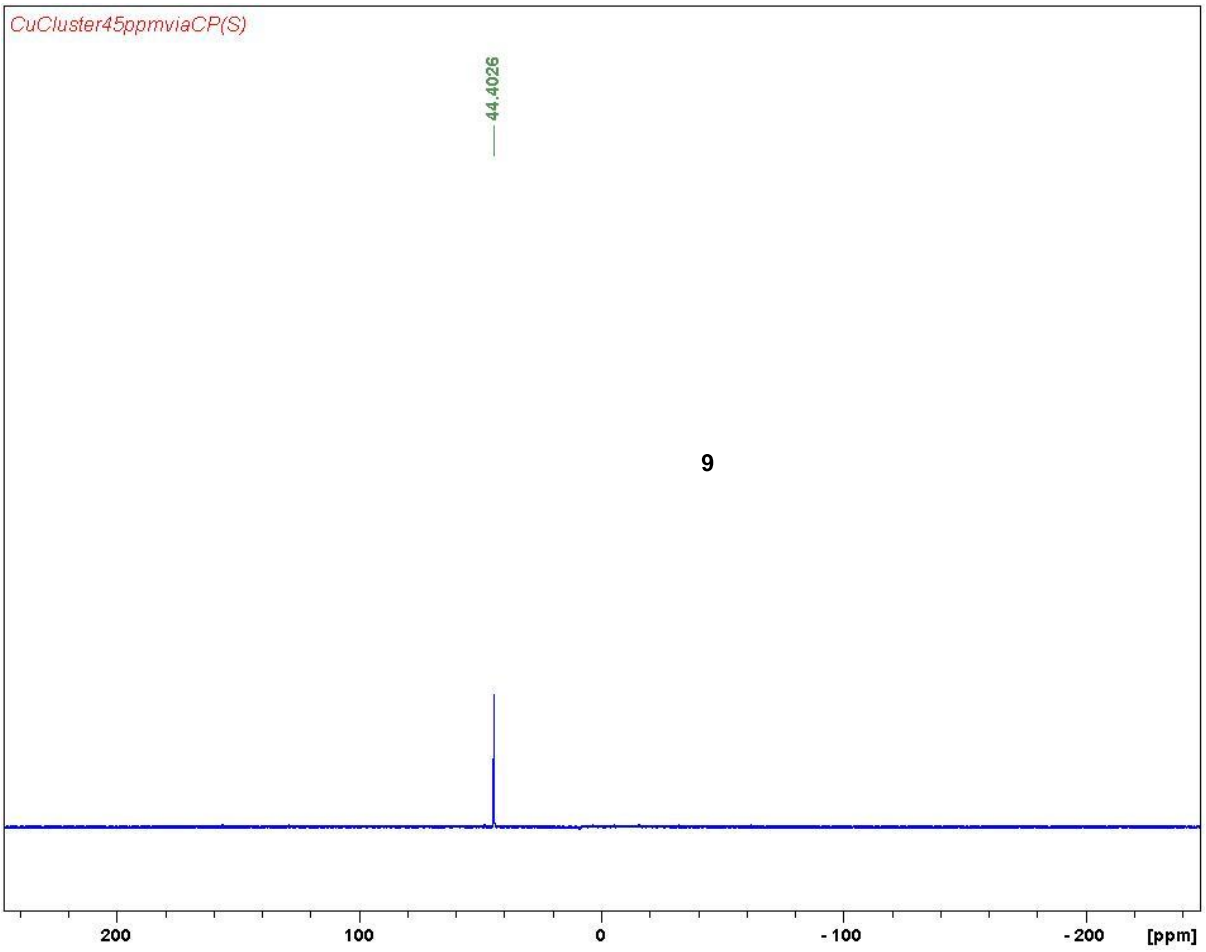
150
100
50
[ppm]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200
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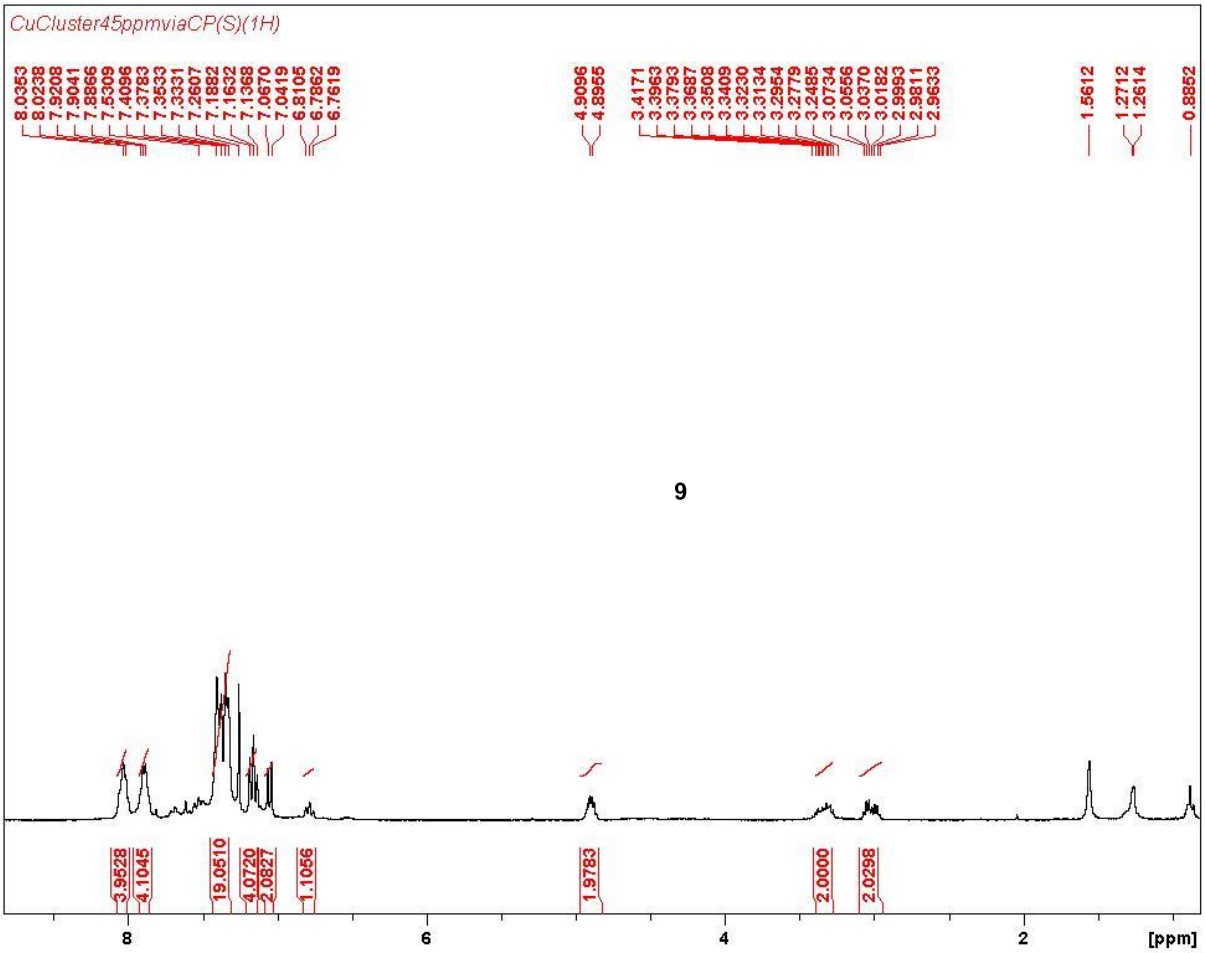
0
-100
-200
[ppm]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7.5309
7.4096
7.3783
7.3533
7.3331
7.2607
7.1882
7.1632
7.1368
7.0670
7.0419
6.8105
6.7862
6.7619
4.9096
4.8955
3.4171
3.3963
3.3793
3.3687
3.3508
3.3409
3.3230
3.3134
3.2954
3.2779
3.2485
3.0734
3.0556
3.0370
3.0182
2.9993
2.9811
2.9633
1.5612
1.2712
1.2614
0.8852
9
3.9528
4.1045
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1.9783
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2.0298
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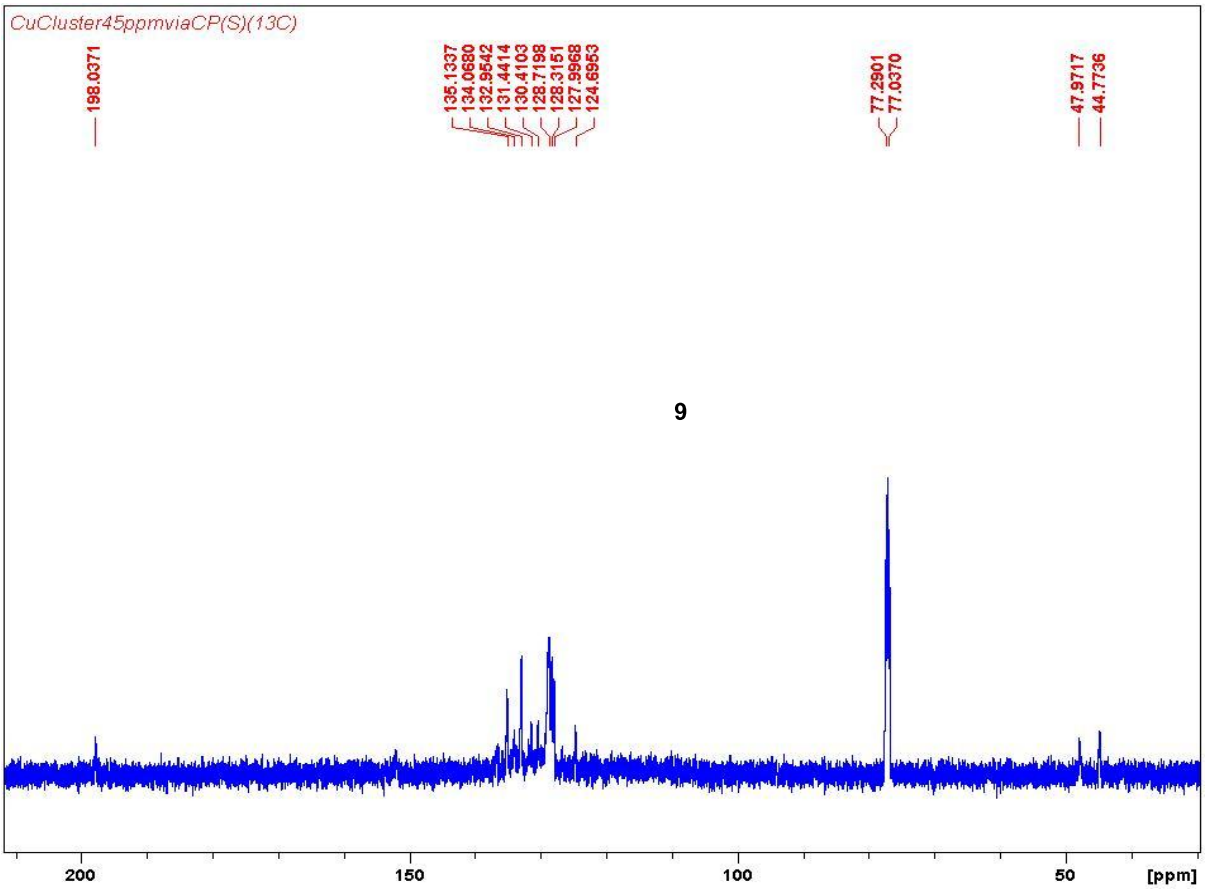
6
4
2
[ppm]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134.0680
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130.4103
128.7198
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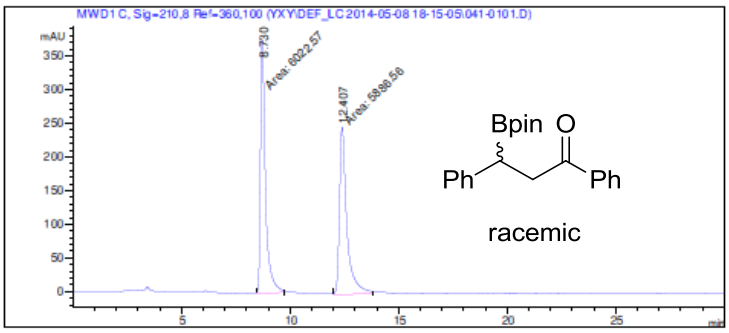
127.9968
124.6953
77.2901
77.0370
47.9717
44.7736
9
200
150
100
50
[ppm]

HPLC Spectra

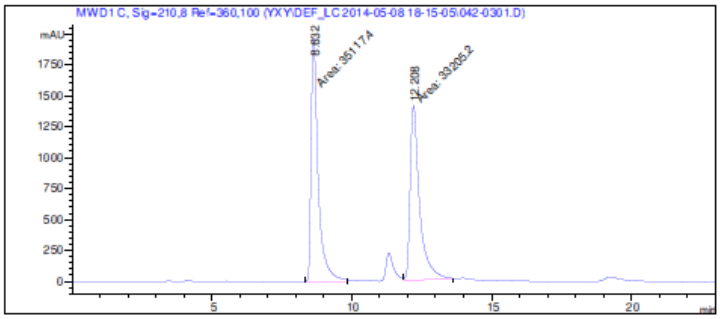
```
Sample Info     : Chalcone 1eq + B2pin2 1.1eq + Cs2CO3 10% + MeOH 2eq
                  Racemic
                  Eluant: 97H:3IPA Flow Rate: 0.9 mL/min Column: AD-H 23C

Additional Info : Peak(s) manually integrated
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.730 MM    0.2668 6022.56982  376.22086  50.5710
   2  12.407 MM    0.3946 5886.56006  248.62212  49.4290

Totals :                  1.19091e4   624.84297
```

Table 5 Entry 1.

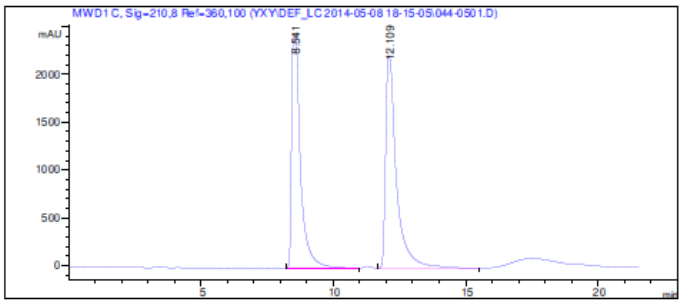
```
Sample Info     : Chalcone 1eq + B2pin2 1.1eq + Cs2CO3 10% + MeOH 2eq
                  1% CuCl cluster RT 1h THF
                  Eluant: 97H:3IPA Flow Rate: 0.9 mL/min Column: AD-H 23C

Additional Info : Peak(s) manually integrated
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.632 MM    0.2962 3.51174e4  1975.95789  51.3994
   2  12.208 MM    0.3924 3.32052e4  1410.25415  48.6006

Totals :                  6.83226e4  3386.21204
```

Table 5 Entry 2.

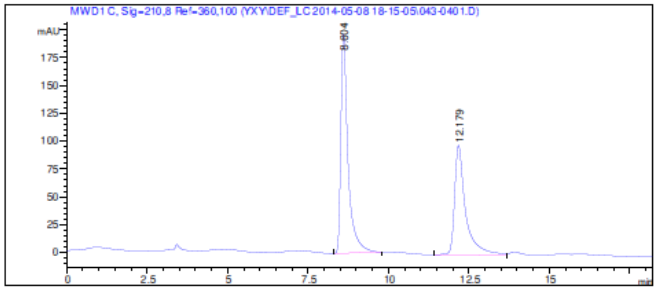
```
Sample Info     : Chalcone 1eq + B2pin2 1.1eq + Cs2CO3 10% + MeOH 2eq
                  1% CuCl cluster RT 1h DEE
                  Eluant: 97H:3IPA Flow Rate: 0.9 mL/min Column: AD-H 23C

Additional Info : Peak(s) manually integrated
```




```
                              Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.541 BV    0.3246 5.76537e4  2414.60400  47.8608
   2  12.109 VB    0.4204 6.28076e4  2217.89673  52.1392

Totals :                  1.20461e5  4632.50073
```

Table 5 Entry 3.

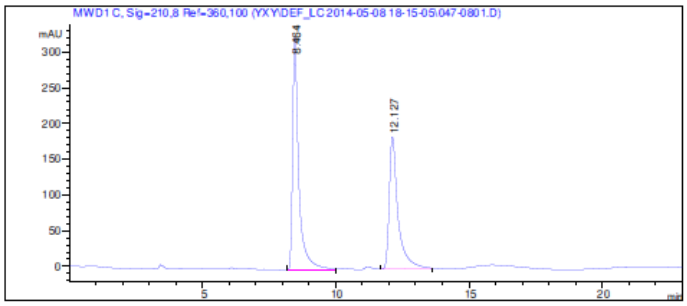
```
Sample Info     : Chalcone 1eq + B2pin2 1.1eq + Cs2CO3 10% + MeOH 2eq
                  1% CuCl cluster RT 2h EA
                  Eluant: 97H:3IPA Flow Rate: 0.9 mL/min Column: AD-H 23C

Additional Info : Peak(s) manually integrated
```




```
                              Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.604 BV    0.2265 3042.97852  196.69609  56.7813
   2  12.179 BV    0.3412 2316.14526   98.17410  43.2187

Totals :                  5359.12378  294.87019
```

Table 5 Entry 4.

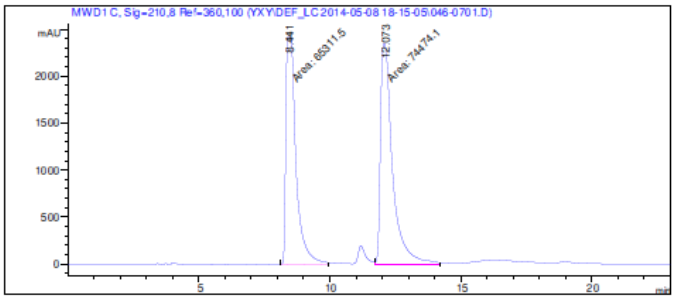
```
Sample Info      : Chalcone 1eq + B2pin2 1.1eq + KOtBu 10% + MeOH 2eq
                   1% CuCl cluster RT 0.5h EA
                   Eluant: 97H:3IPA Flow Rate: 0.9 mL/min Column: AD-H 23C

Additional Info : Peak(s) manually integrated
```




```
                              Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.464 BV    0.2341 5258.86377  326.16217  55.6017
   2  12.127 BB    0.3310 4199.24268  184.89804  44.3983

Totals :                  9458.10645  511.06021
```

Table 5 Entry 5.

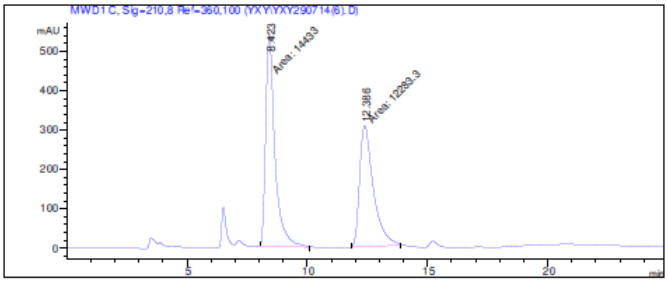
```
Sample Info      : Chalcone 1eq + B2pin2 1.1eq + Cs2CO3 10% + MeOH 2eq
                   1% CuCl cluster RT 1h DCM
                   Eluant: 97H:3IPA Flow Rate: 0.9 mL/min Column: AD-H 23C

Additional Info : Peak(s) manually integrated
```




```
                              Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.441 MM    0.4468 6.53115e4  2436.49878  46.7226
   2  12.073 MM    0.5278 7.44741e4  2351.66504  53.2774

Totals :                  1.39786e5  4788.16382
```

Table 5 Entry 6.

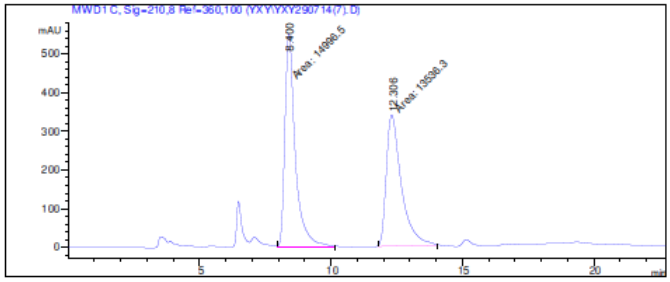
```
Sample Info      : chalcone + B2pin2 + Cs2CO3 10% + MeOH 2eq
                   1% CuCl cluster 7b RT EA 2h
                   Eluant: 97H:3IPA 0.9 mL/min
                   Column: AD-H 23C


Additional Info : Peak(s) manually integrated
-------------------------------------------------------------------------------
```




```
-------------------------------------------------------------------------------
                          Area Percent Report
-------------------------------------------------------------------------------

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.423 MM    0.4454 1.44330e4   540.04266  54.0232
   2  12.386 MM    0.6643 1.22833e4   308.16833  45.9768

Totals :                  2.67163e4   848.21100
```

Table 5 Entry 7.

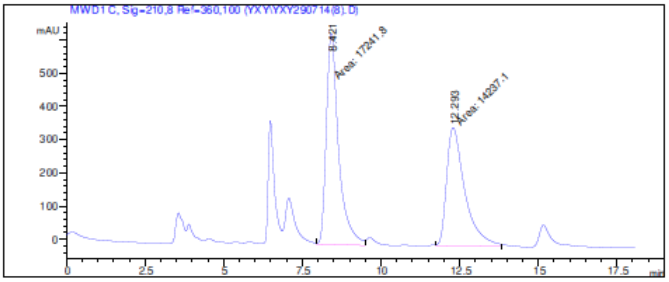
```
Sample Info      : chalcone + B2pin2 + Cs2CO3 10% + MeOH 2eq
                   1% CuCl cluster 7c RT EA 2h
                   Eluant: 97H:3IPA 0.9 mL/min
                   Column: AD-H 23C


Additional Info : Peak(s) manually integrated
-------------------------------------------------------------------------------
```




```
-------------------------------------------------------------------------------
                          Area Percent Report
-------------------------------------------------------------------------------

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.400 MM    0.4540 1.49965e4   550.57251  52.5589
   2  12.306 MM    0.6652 1.35363e4   339.17816  47.4411

Totals :                  2.85328e4   889.75067
```

Table 5 Entry 8.

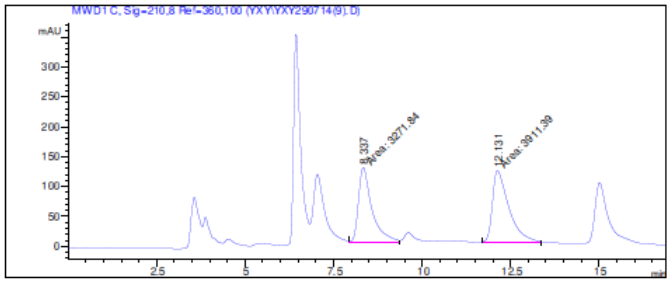
```
Sample Info      : chalcone + B2pin2 + Cs2CO3 10% + MeOH 2eq
                   1% CuCl cluster 7d RT EA 3h
                   Eluant: 97H:3IPA 0.9 mL/min
                   Column: AD-H 23C


Additional Info : Peak(s) manually integrated
-------------------------------------------------------------------------------
```




```
-------------------------------------------------------------------------------
                          Area Percent Report
-------------------------------------------------------------------------------

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.421 MM    0.4531 1.72418e4   634.19000  54.7726
   2  12.293 MM    0.6660 1.42371e4   356.30414  45.2274

Totals :                  3.14789e4   990.49414
```

Table 5 Entry 9.

```
Sample Info      : chalcone + B2pin2 + Cs2CO3 10% + MeOH 2eq
                   1% CuCl cluster 7e RT EA 2h
                   Eluant: 97H:3IPA 0.9 mL/min
                   Column: AD-H 23C


Additional Info : Peak(s) manually integrated
-------------------------------------------------------------------------------
```




```
-------------------------------------------------------------------------------
                          Area Percent Report
-------------------------------------------------------------------------------

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.337 MM    0.4395 3271.84058  124.06229  45.5483
   2  12.131 MM    0.5424 3911.39111  120.18320  54.4517

Totals :                  7183.23169  244.24548
```

NMR Spectra of Product formed between Diphosphine 5a and CuI

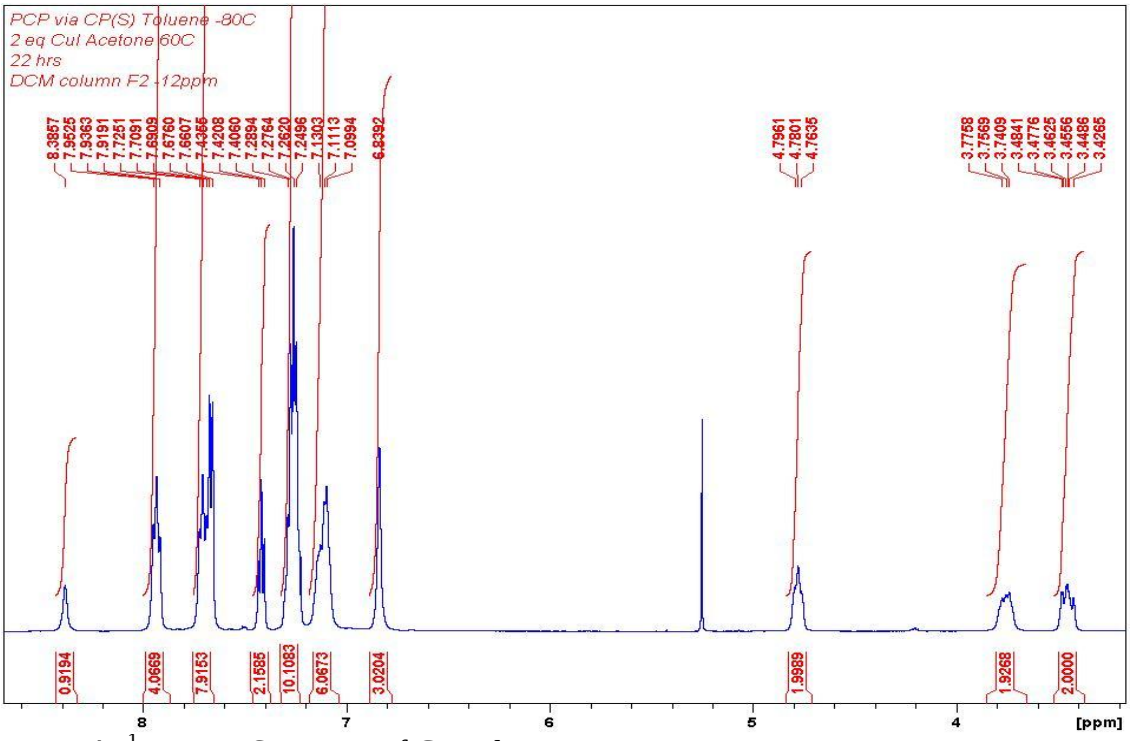


Figure A. ^{1}H NMR Spectrum of Complex.

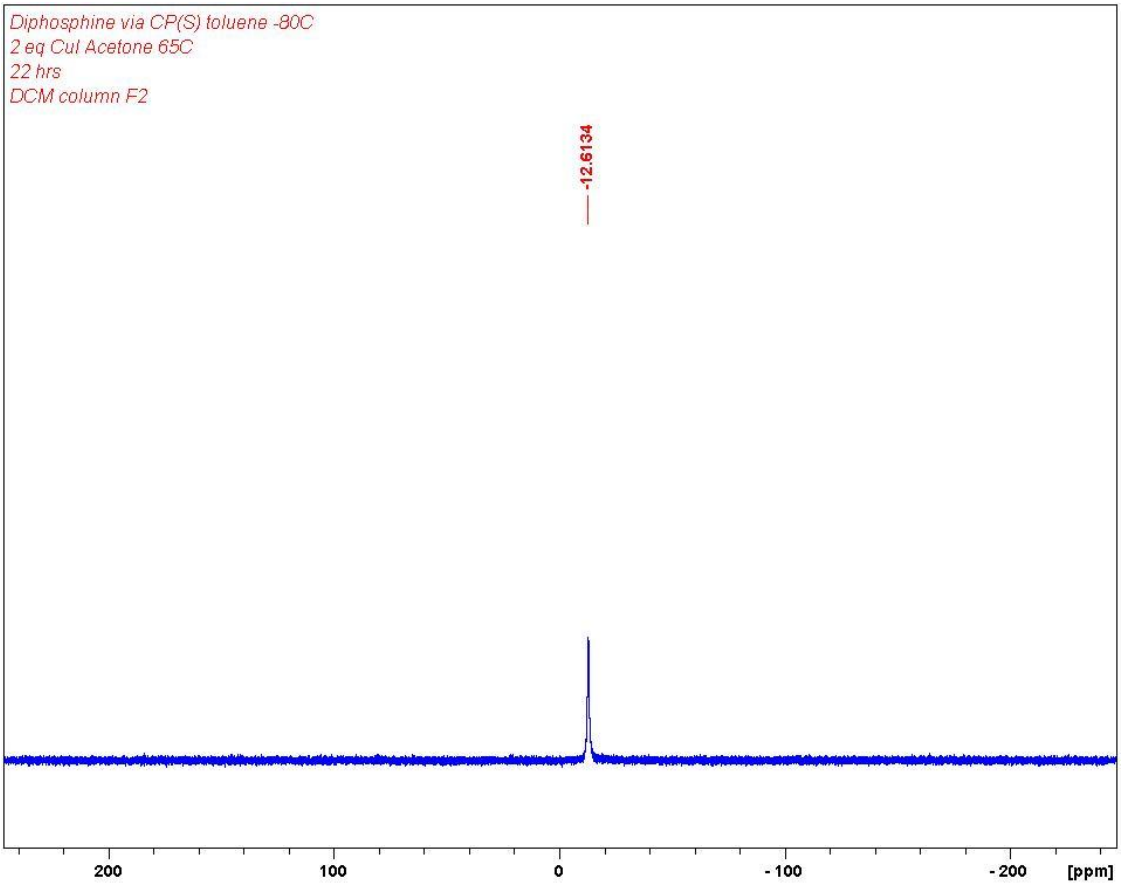


Figure B. $^{31}P\{^{1}H\}$ NMR Spectrum of Complex.

Determination of *ee* and *de* for Ligand 6

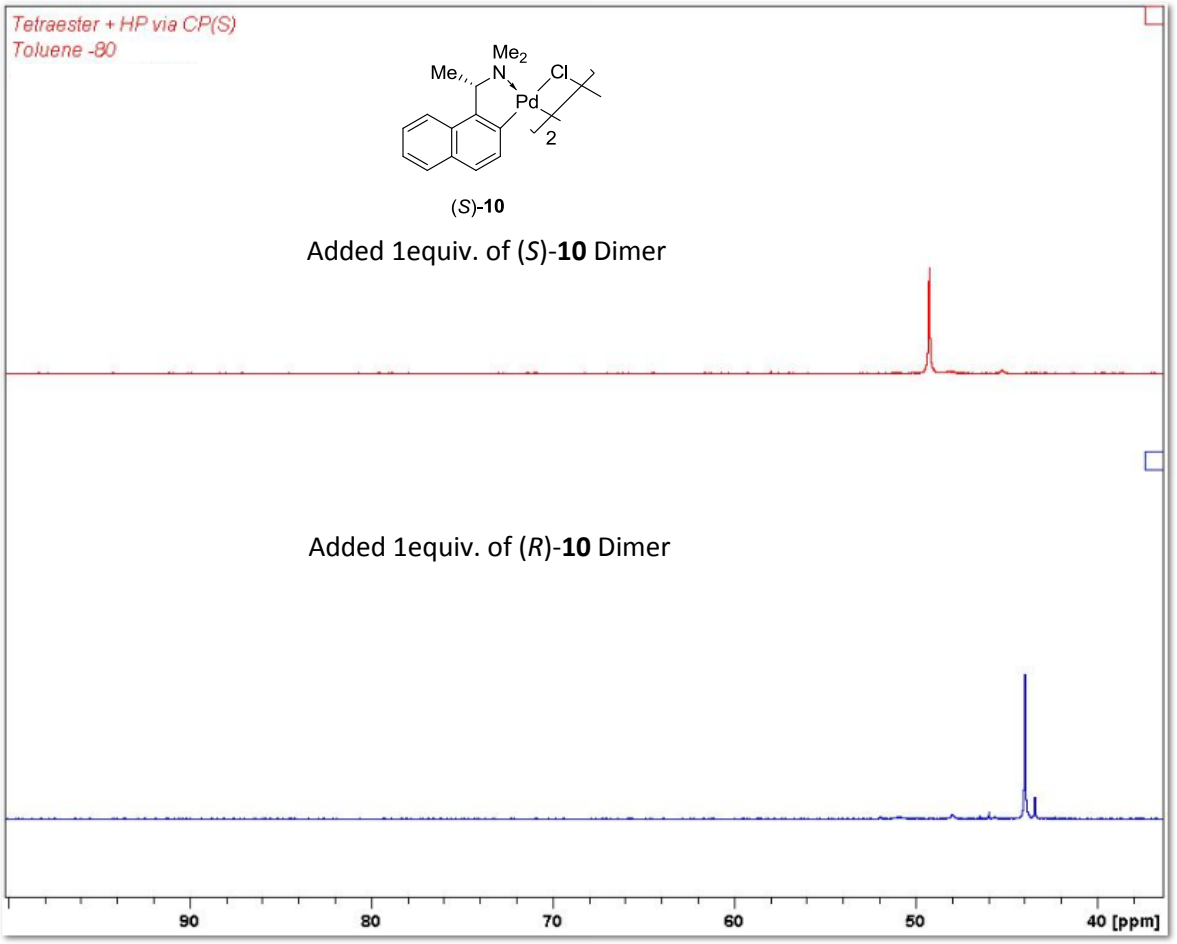


Figure C. Determination of *ee* and *de* for Ligand **6**.

The determination of enantio- and diastereo-selectivity was conducted in a same manner as previously reported.[1] Theoretically, 4 isomers may be formed *via* the double hydrophosphination reaction, and upon addition of a chiral derivatizing agent such as (*S*)-**10**, 3 phosphorous peaks may be observed in the case of a racemic mixture of isomers. However, we only observed the appearance of 1 major signal, indicating the optical purity of the P-H addition reaction. From the above spectra, we are able to calculate the *ee* and *de* of the resulting isomer. Hence we conclude that the *ee* and *de* of ligand **6** to be >99%.

X-Ray Structures of Clusters 7a-e

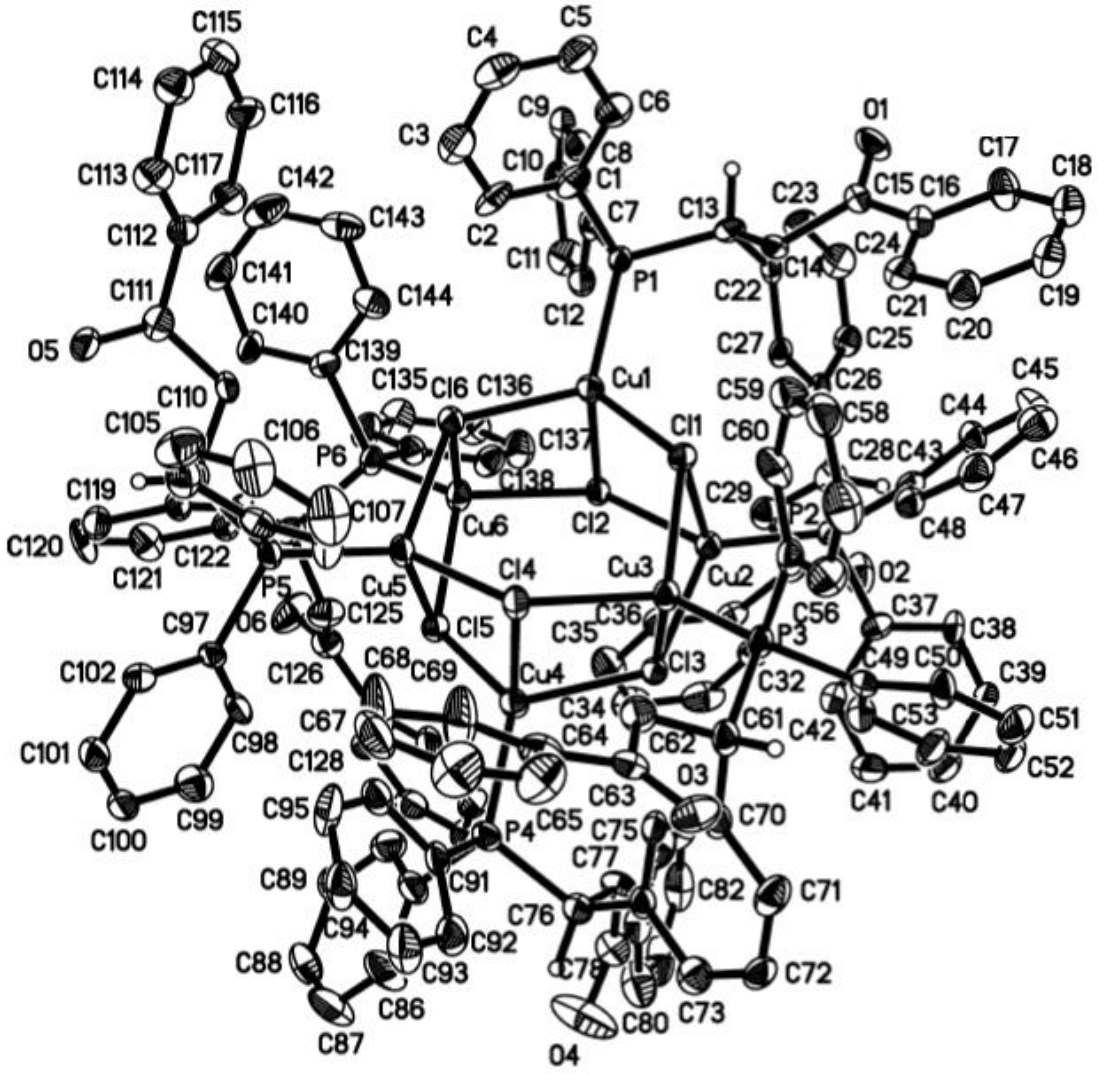


Figure D. X-Ray Structure of Cluster **7a**.

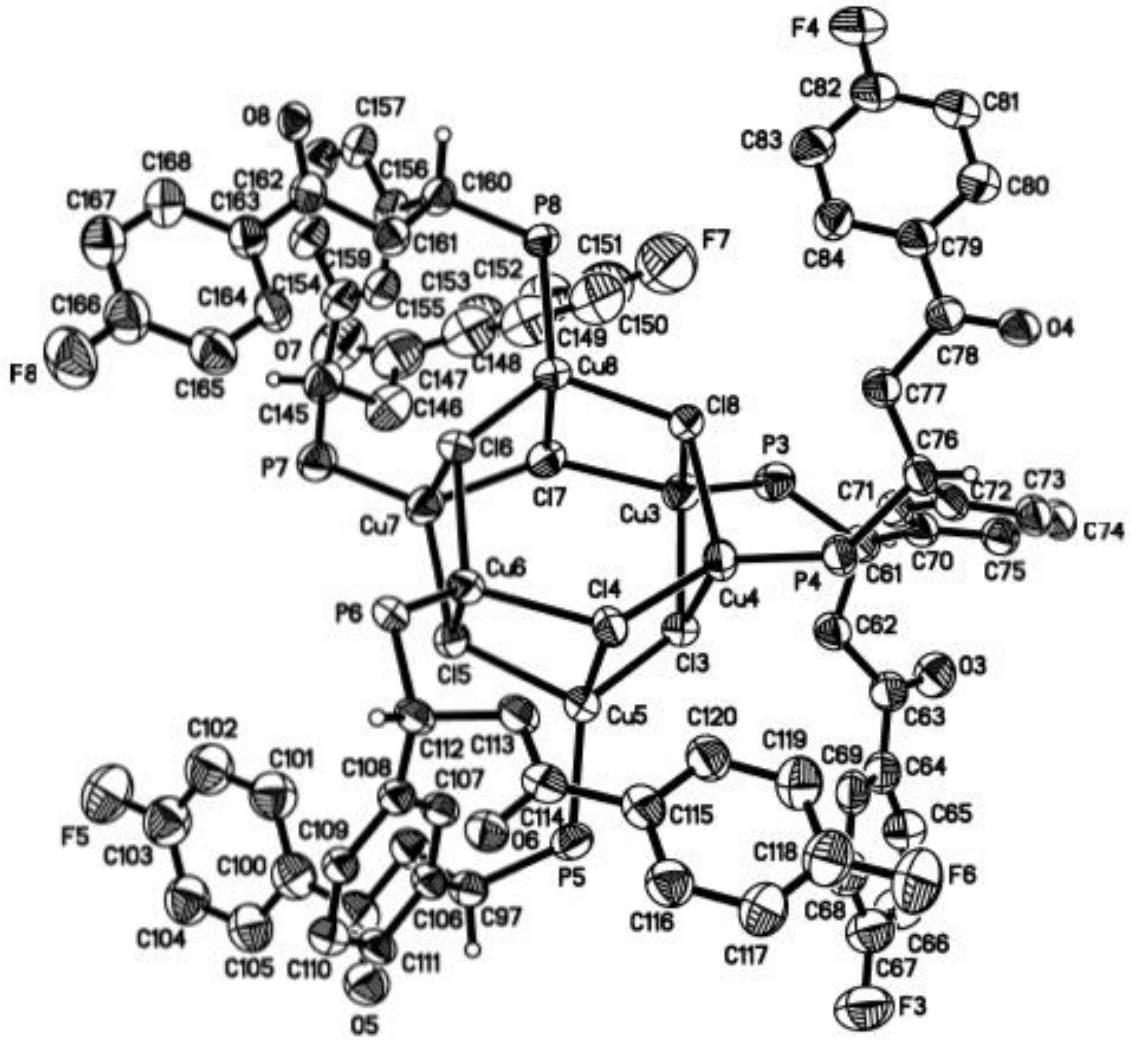


Figure E. X-Ray Structure of Cluster **7b**.

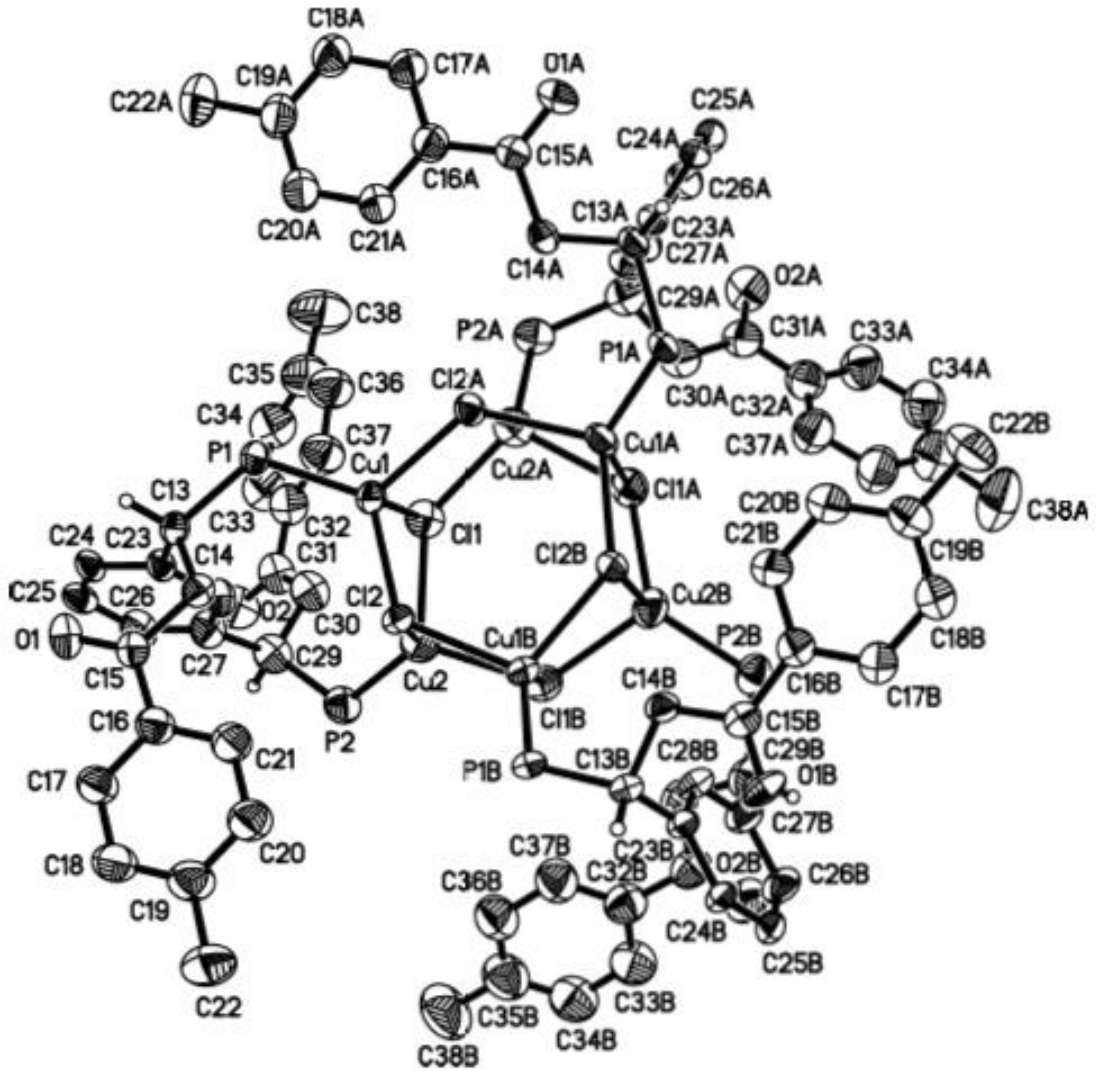


Figure F. X-Ray Structure of Cluster **7c**.

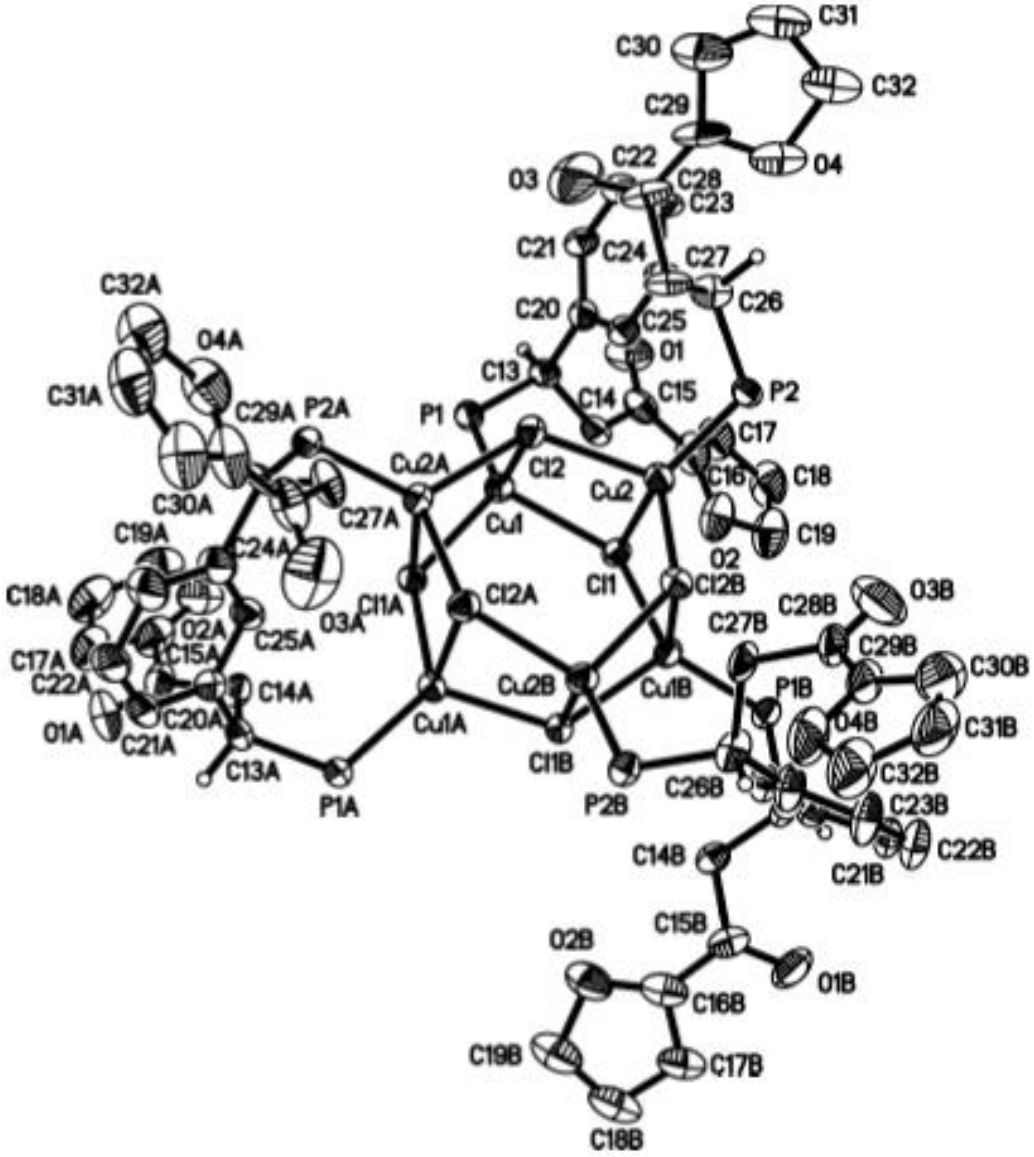


Figure G. X-Ray Structure of Cluster **7d**.

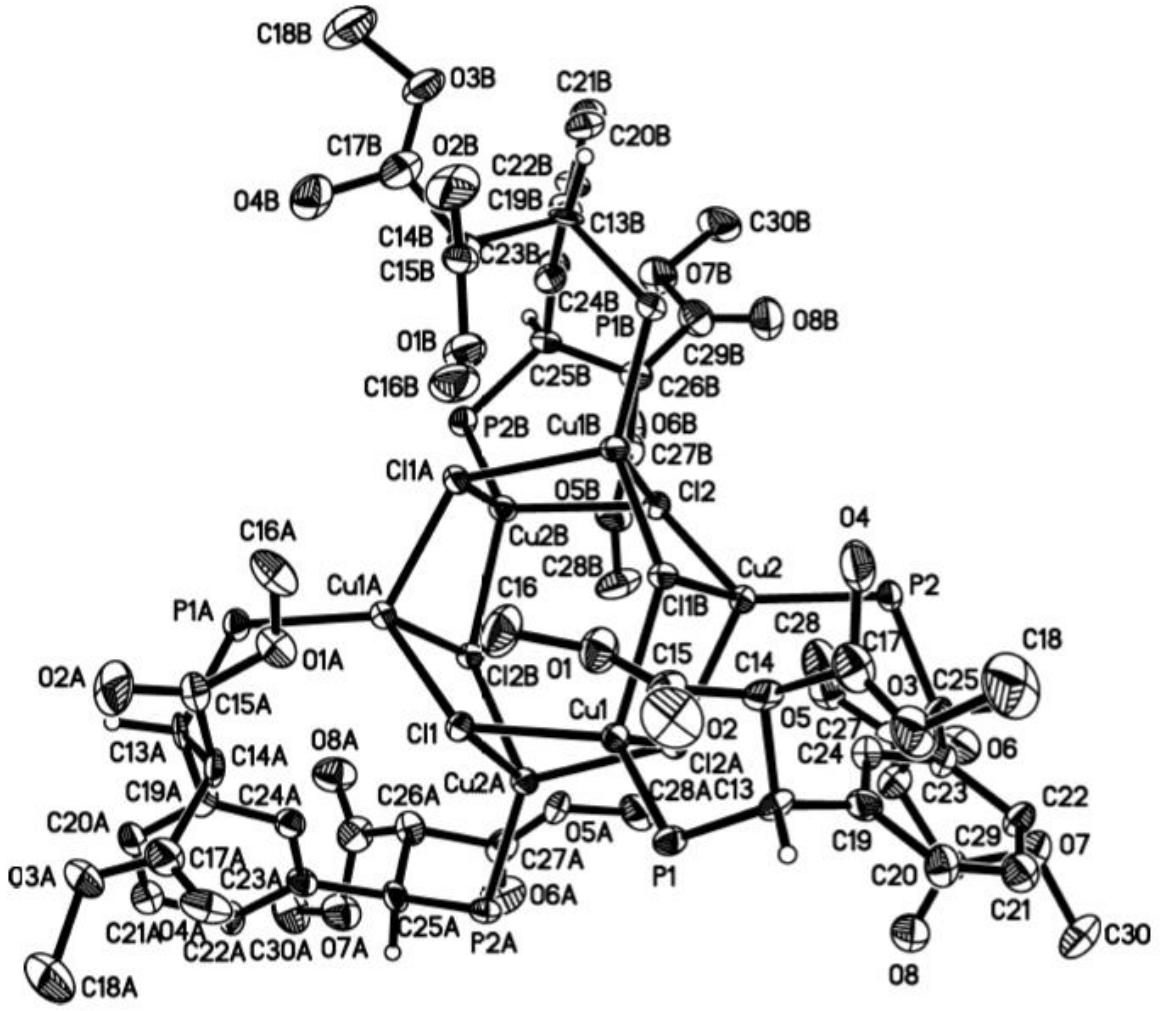


Figure H. X-Ray Structure of Cluster **7e**.

Crystallographic Data for Cluster 7a

Identification code	leung685	
Empirical formula	C150 H132 Cl18 Cu6 O6 P6	
Formula weight	3235.72	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 29.8580(18) Å	α= 90°.
	b = 17.4887(10) Å	β= 105.650(2)°.
	c = 28.7963(17) Å	γ = 90°.
Volume	14479.3(15) $Å^3$	
Z	4	
Density (calculated)	1.484 Mg/m^3	
Absorption coefficient	1.319 mm^{-1}	
F(000)	6600	
Crystal size	0.40 x 0.30 x 0.08 mm^3	
Theta range for data collection	1.64 to 30.59°.	
Index ranges	-40<=h<=42, -25<=k<=16, -41<=l<=34	
Reflections collected	78054	
Independent reflections	37663 [R(int) = 0.0739]	
Completeness to theta = 30.59°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9018 and 0.6205	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	37663 / 140 / 1713	
Goodness-of-fit on F^2	0.991	
Final R indices [I>2sigma(I)]	R1 = 0.0672, wR2 = 0.1511	
R indices (all data)	R1 = 0.1405, wR2 = 0.1983	
Absolute structure parameter	-0.005(11)	
Largest diff. peak and hole	2.497 and -1.244 $e.Å^{-3}$	

Crystallographic Data for Cluster 7b

Identification code	leung759s	
Chemical formula	C144.62H115.25Cl7.25Cu6F6O6P6	
Formula weight	2887.18	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.340 x 0.380 x 0.400 mm	
Crystal habit	colorless block	
Crystal system	trigonal	
Space group	R 3	
Unit cell dimensions	a = 33.8786(6) Å	α = 90°
	b = 33.8786(6) Å	β = 90°
	c = 42.7681(9) Å	γ = 120°
Volume	42511.0(18) Å3	
Z	12	
Density (calculated)	1.353 g/cm3	
Absorption coefficient	1.149 mm-1	
F(000)	17667	
Theta range for data collection	1.47 to 26.44°	
Index ranges	-40<=h<=41, -42<=k<=42, -53<=l<=53	
Reflections collected	95011	
Independent reflections	38828 [R(int) = 0.0676]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6960 and 0.6570	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	38828 / 14440 / 3501	
Goodness-of-fit on F2	1.031	
Δ/σmax	0.002	
Final R indices	24942 data; I>2σ(I)	R1 = 0.0720, wR2 = 0.1907
	all data	R1 = 0.1256, wR2 = 0.2329
Weighting scheme	w=1/[σ2(Fo2)+(0.1437P)2] where P=(Fo2+2Fc2)/3	
Absolute structure parameter	0.1(0)	
Largest diff. peak and hole	0.943 and -1.270 eÅ-3	
R.M.S. deviation from mean	0.216 eÅ-3	

Crystallographic Data for Cluster 7c

Identification code	leung758s_sq_s	
Chemical formula	C150H132Cl6Cu6O6P6	
Formula weight	2810.31	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.240 x 0.260 mm	
Crystal habit	colorless block	
Crystal system	cubic	
Space group	P 2 3	
Unit cell dimensions	a = 24.3499(19) Å	α = 90°
	b = 24.3499(19) Å	β = 90°
	c = 24.3499(19) Å	γ = 90°
Volume	14437.(3) Å3	
Z	4	
Density (calculated)	1.293 g/cm3	
Absorption coefficient	1.097 mm-1	
F(000)	5784	
Theta range for data collection	1.18 to 25.37°	
Index ranges	-29<=h<=6, -16<=k<=29, -29<=l<=21	
Reflections collected	33072	
Independent reflections	8840 [R(int) = 0.0788]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8100 and 0.7630	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	8840 / 2970 / 842	
Goodness-of-fit on F2	1.313	
Δ/σmax	0.001	
Final R indices	4823 data; I>2σ(I)	R1 = 0.1173, wR2 = 0.3159
	all data	R1 = 0.2083, wR2 = 0.3854
Weighting scheme	w=1/[σ2(Fo2)+(0.2000P)2] where P=(Fo2+2Fc2)/3	
Absolute structure parameter	0.0(0)	
Largest diff. peak and hole	1.094 and -1.032 eÅ-3	
R.M.S. deviation from mean	0.198 eÅ-3	

Crystallographic Data for Cluster 7d

Identification code	leung748s	
Chemical formula	C140H128.79Cl16Cu6O15P6	
Formula weight	3185.47	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.300 x 0.380 x 0.400 mm	
Crystal system	trigonal	
Space group	R 3	
Unit cell dimensions	a = 17.3752(10) Å	α = 90°
	b = 17.3752(10) Å	β = 90°
	c = 40.085(2) Å	γ = 120°
Volume	10480.3(14) Å3	
Z	3	
Density (calculated)	1.514 g/cm3	
Absorption coefficient	1.333 mm-1	
F(000)	4874	
Theta range for data collection	2.80 to 31.00°	
Index ranges	-24<=h<=23, -21<=k<=25, -58<=l<=58	
Reflections collected	45537	
Independent reflections	14843 [R(int) = 0.0684]	
Max. and min. transmission	0.6910 and 0.6180	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	14843 / 687 / 722	
Goodness-of-fit on F2	1.007	
Δ/σmax	0.003	
Final R indices	9863 data; I>2σ(I)	R1 = 0.0686, wR2 = 0.1828
	all data	R1 = 0.1080, wR2 = 0.2106
Weighting scheme	w=1/[σ2(Fo2)+(0.1211P)2] where P=(Fo2+2Fc2)/3	
Absolute structure parameter	0.0(0)	
Largest diff. peak and hole	1.287 and -0.992 eÅ-3	
R.M.S. deviation from mean	0.121 eÅ-3	

Crystallographic Data for Cluster 7e

Identification code	leung715s	
Chemical formula	C142H152Cl38Cu6O24P6	
Formula weight	4156.80	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal size	0.180 x 0.220 x 0.300 mm	
Crystal habit	colorless block	
Crystal system	trigonal	
Space group	R 3	
Unit cell dimensions	a = 29.118(3) Å	α = 90°
	b = 29.118(3) Å	β = 90°
	c = 16.8751(14) Å	γ = 120°
Volume	12390.8(18) Å3	
Z	3	
Density (calculated)	1.671 g/cm3	
Absorption coefficient	1.497 mm-1	
F(000)	6318	
Theta range for data collection	1.40 to 29.68°	
Index ranges	-40<=h<=40, -40<=k<=40, -22<=l<=23	
Reflections collected	77824	
Independent reflections	15493 [R(int) = 0.1246]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7744 and 0.6623	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	15493 / 2470 / 836	
Goodness-of-fit on F2	0.951	
Δ/σmax	0.001	
Final R indices	8256 data; I>2σ(I)	R1 = 0.0826, wR2 = 0.2082
	all data	R1 = 0.1317, wR2 = 0.2272
Weighting scheme	w=1/[σ2(Fo2)+(0.1236P)2+0.0000P] where P=(Fo2+2Fc2)/3	
Absolute structure parameter	0.1(0)	
Largest diff. peak and hole	0.645 and -1.841 eÅ-3	
R.M.S. deviation from mean	0.169 eÅ-3	

Crystallographic Data for Cluster 9

Identification code	leung690s	
Empirical formula	C96 H80 Cl4 Cu4 O4 P4	
Formula weight	1817.44	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.6496(9) Å	α= 64.969(3)°.
	b = 13.5286(9) Å	β= 80.065(4)°.
	c = 14.9416(10) Å	γ = 62.687(4)°.
Volume	2057.8(2) $Å^3$	
Z	1	
Density (calculated)	1.467 Mg/m^3	
Absorption coefficient	1.281 mm^{-1}	
F(000)	932	
Crystal size	0.24 x 0.10 x 0.08 mm^3	
Theta range for data collection	1.50 to 25.07°.	
Index ranges	-15<=h<=15, -16<=k<=16, -17<=l<=17	
Reflections collected	31644	
Independent reflections	7233 [R(int) = 0.0540]	
Completeness to theta = 25.07°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9045 and 0.7486	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7233 / 0 / 505	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0583, wR2 = 0.1620	
R indices (all data)	R1 = 0.0846, wR2 = 0.1949	
Largest diff. peak and hole	2.903 and -1.073 $e.Å^{-3}$	