Supporting Information

Synthesis and Structural Studies of Cu(I) Methylthiosalicylate Complexes and their Catalytic Application in Thiol-Yne Click Reaction

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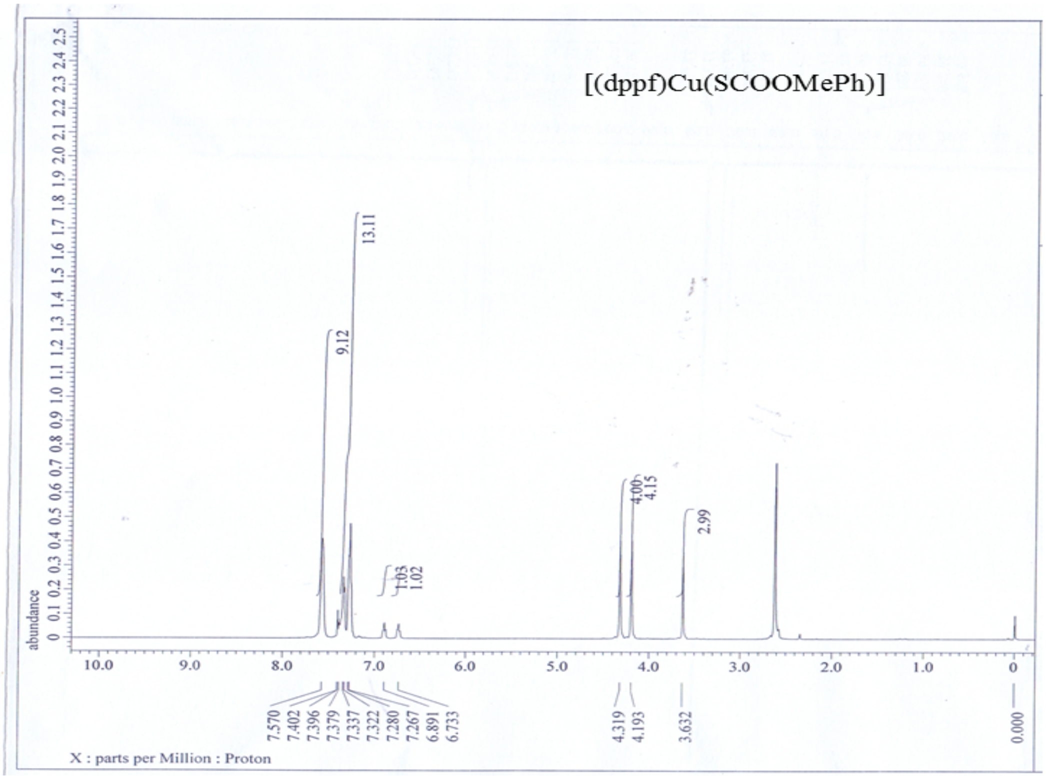
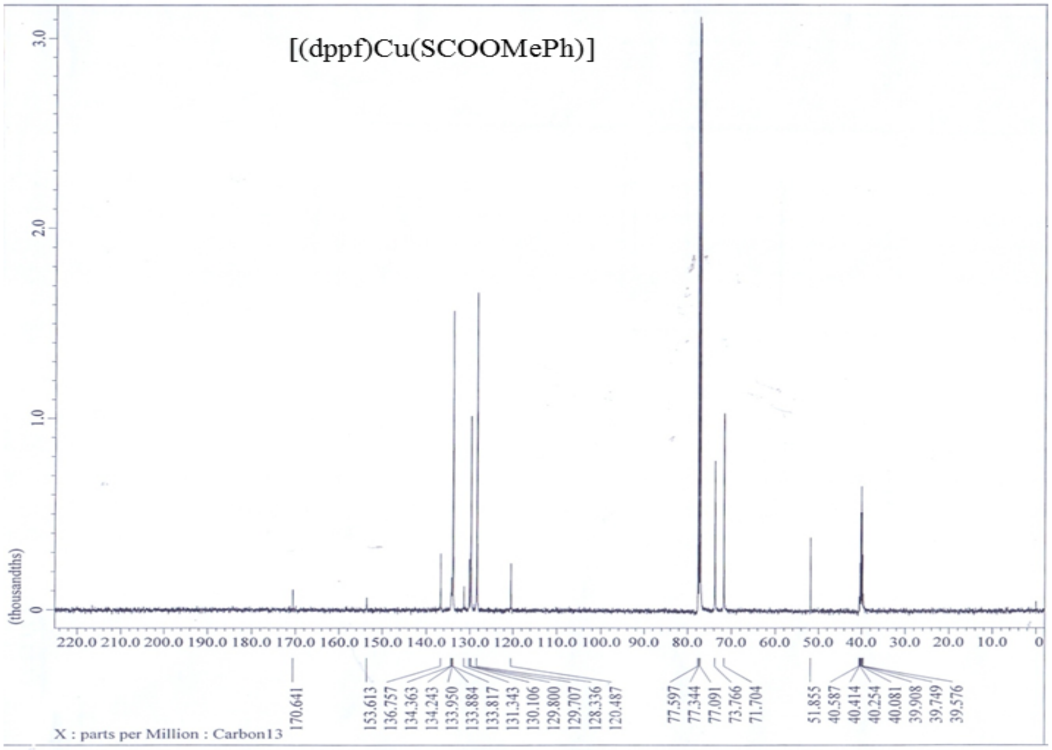
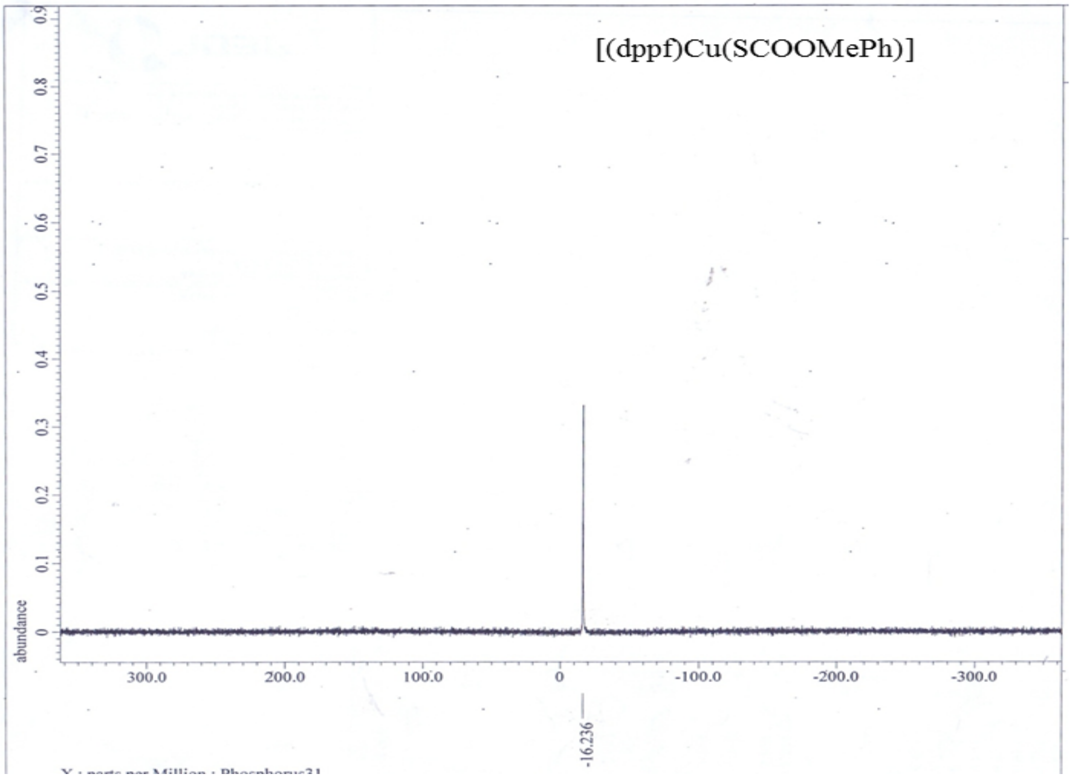
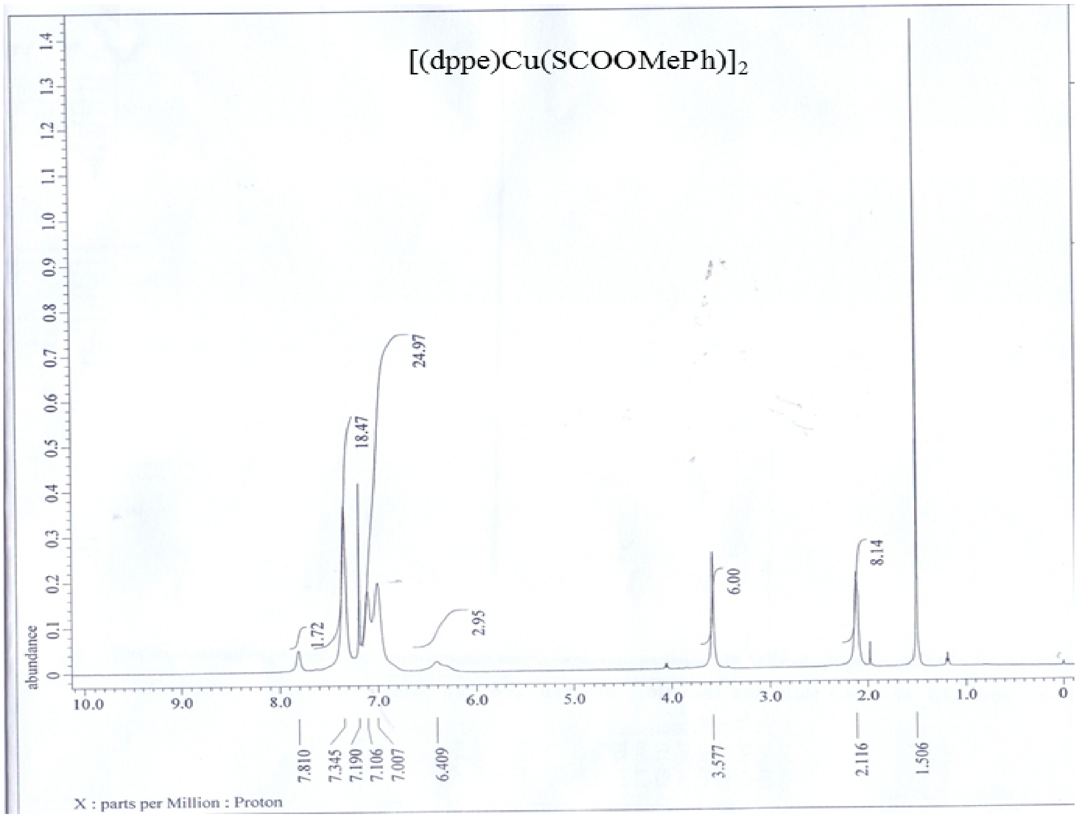
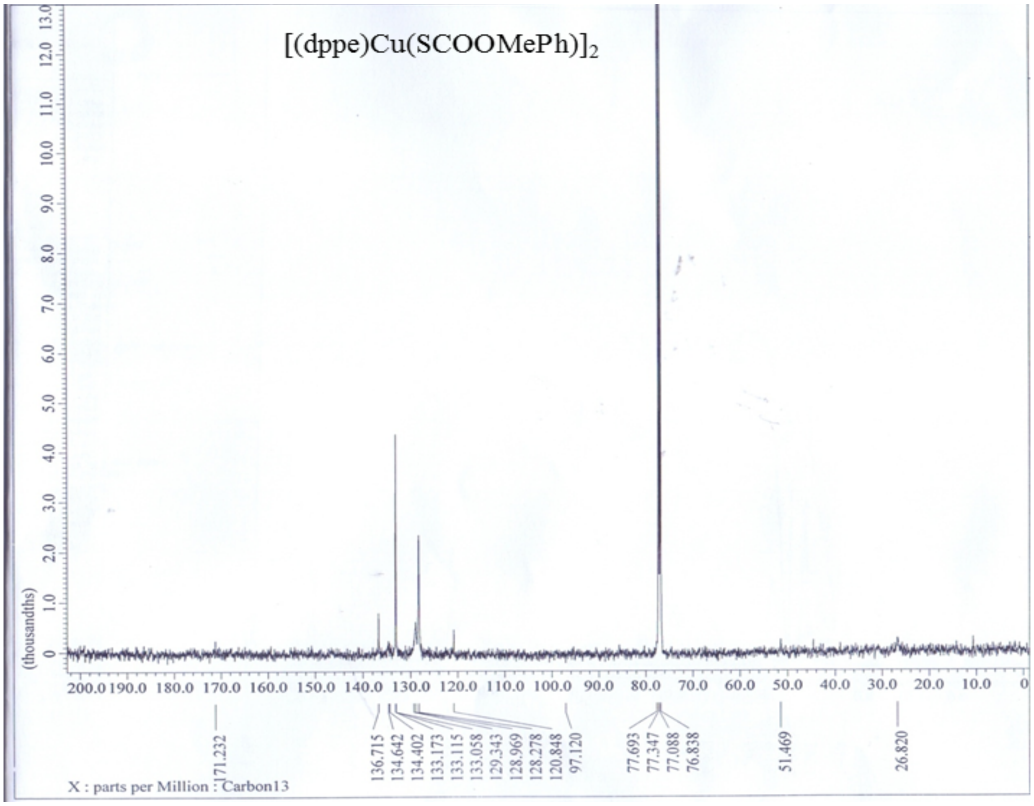
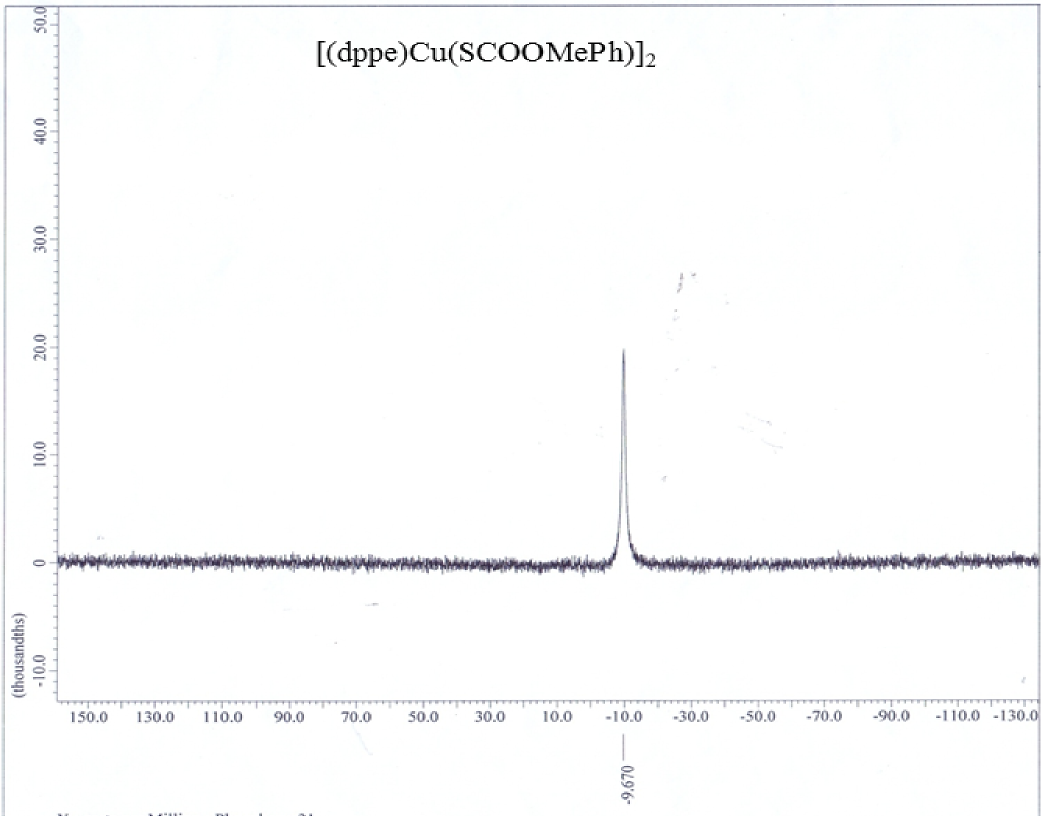

[(dppf)Cu(SCOOMePh)]
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5
13.11
9.12
1.03
1.02
4.00
4.15
2.99
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.570
7.402
7.396
7.379
7.337
7.322
7.280
7.267
6.891
6.733
4.319
4.193
3.632
0.000
X : parts per Million : Proton

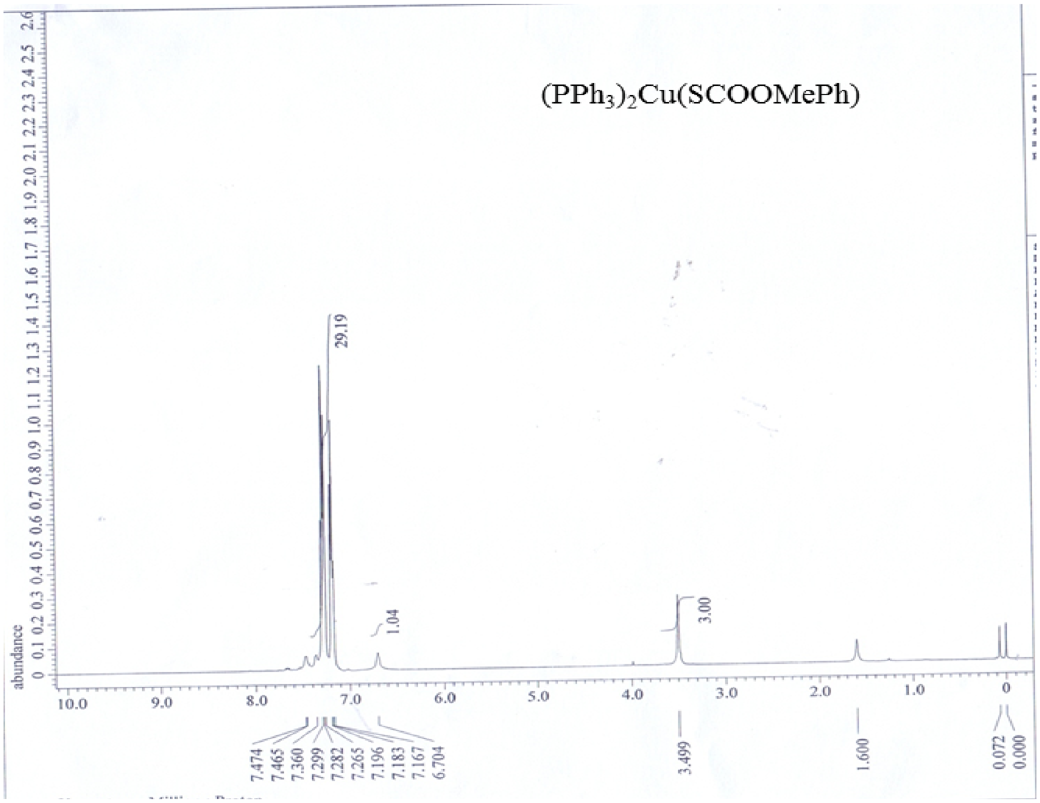

[(dppf)Cu(SCOOMePh)]
(thousandths)
0 1.0 2.0 3.0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
170.641
153.613
136.757
134.363
134.243
133.950
133.884
133.817
131.343
130.106
129.800
129.707
128.336
120.487
77.597
77.344
77.091
73.766
71.704
51.855
40.587
40.414
40.254
40.081
39.908
39.749
39.576
X : parts per Million : Carbon13


[(dppf)Cu(SCOOMePh)]
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
300.0
200.0
100.0
0
-100.0
-200.0
-300.0
-16.236
X : parts per Million : Phosphorus31


[(dppe)Cu(SCOOMePh)]$_2$
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.72
18.47
24.97
2.95
6.00
8.14
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.810
7.345
7.190
7.106
7.007
6.409
3.577
2.116
1.506
X : parts per Million : Proton


[(dppe)Cu(SCOOMePh)]$_2$
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
171.232
136.715
134.642
134.402
133.173
133.115
133.058
129.343
128.969
128.278
120.848
97.120
77.693
77.347
77.088
76.838
51.469
26.820
X : parts per Million : Carbon13


[(dppe)Cu(SCOOMePh)]$_2$
(thousandths)
-10.0
0
10.0
20.0
30.0
40.0
50.0
150.0 130.0 110.0 90.0 70.0 50.0 30.0 10.0 -10.0 -30.0 -50.0 -70.0 -90.0 -110.0 -130.0
-9.670


(PPh3)2Cu(SCOOMePh)
abundance
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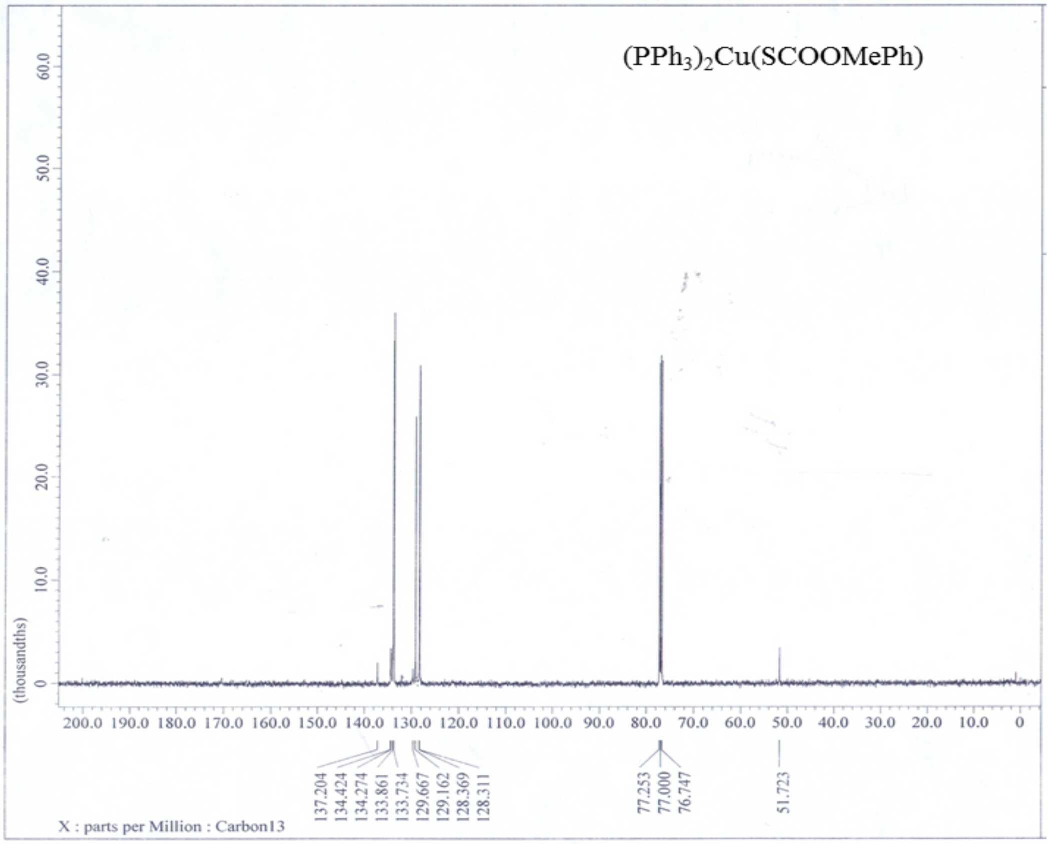
29.19
1.04
3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0
7.474
7.465
7.360
7.299
7.282
7.265
7.196
7.183
7.167
6.704
3.499
1.600
0.072
0.000


(PPh3)2Cu(SCOOMePh)
(thousandths)
0 10.0 20.0 30.0 40.0 50.0 60.0
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
137.204
134.424
134.274
133.861
133.734
129.667
129.162
128.369
128.311
77.253
77.000
76.747
51.723
X : parts per Million : Carbon13

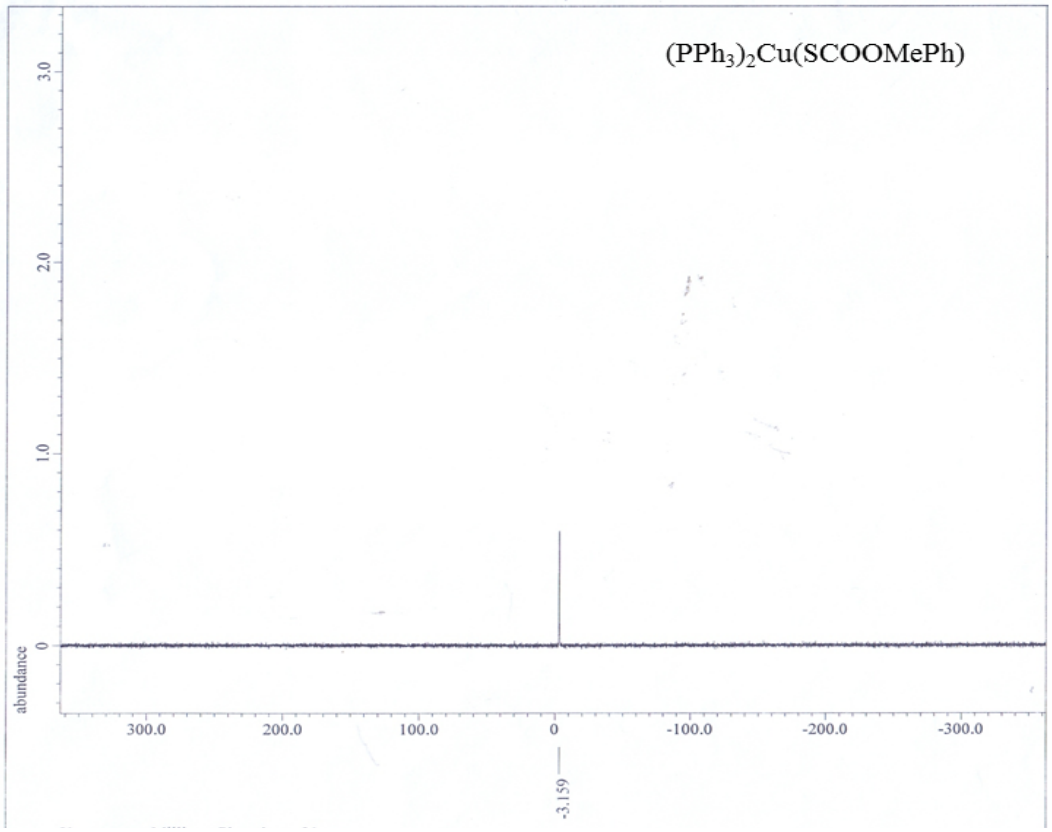


Figure SI 1. Scanned **^{1}H**, **^{13}C,** and **^{31}P-**NMR spectra of **1**, **2,** and **3 respectively.**

Mass Spectrum of [Phenyl(styryl)sulfane] with catalyst 1

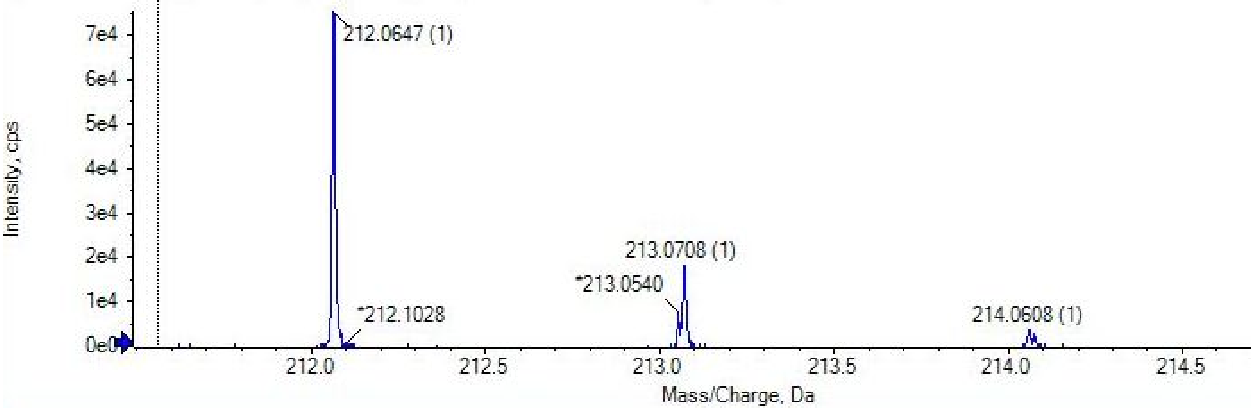


Figure SI 2. Mass Spectrum of **[Phenyl(styryl)sulfane].**

HPLC data of [Phenyl(styryl)sulfane] with catalyst 1.

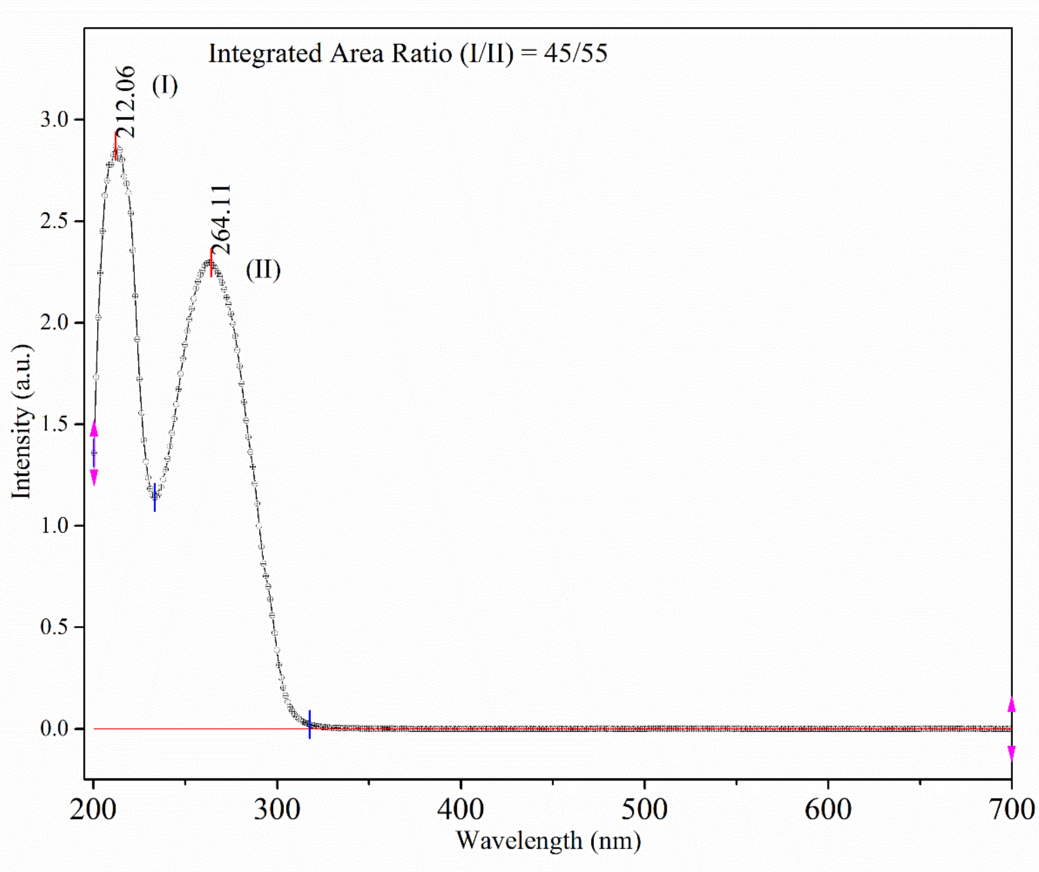


Figure SI 3. HPLC graph of **[Phenyl(styryl)sulfane].**

Hirshfeld Surface Analysis

Hirshfeld surface for the complexes **1**-**3**, mapped over $d_{norm,}$ shape index and curvedness are shown in Figure SI 4.

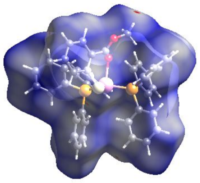
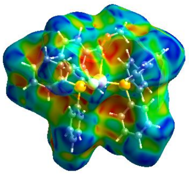
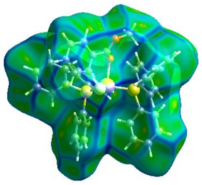
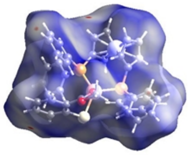
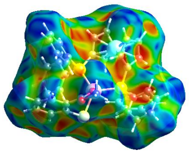
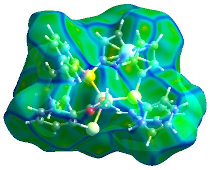
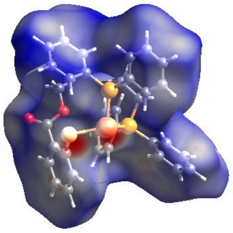
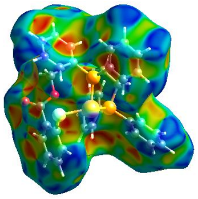
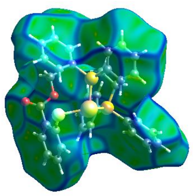
d norm	**Shape index**	**Curvedness**
		
1 (a)	**1 (b)**	**1 (c)**
		
2 (a)	**2 (b)**	**2 (c)**
		
3 (a)	**3 (b)**	**3 (c)**

Figure SI 4. $d_{norm,}$ shape index and curvedness of complex **1-3.**

Percentage contributions of various types of intermolecular interaction in fingerprints such as H···H, C···H, S···H, O···H and C···C, are shown as a bar graph (Figure SI 5). The 2D fingerprint plot presented in Figure SI 5, provides a summary of each combination of de and di across the surface of the molecule.

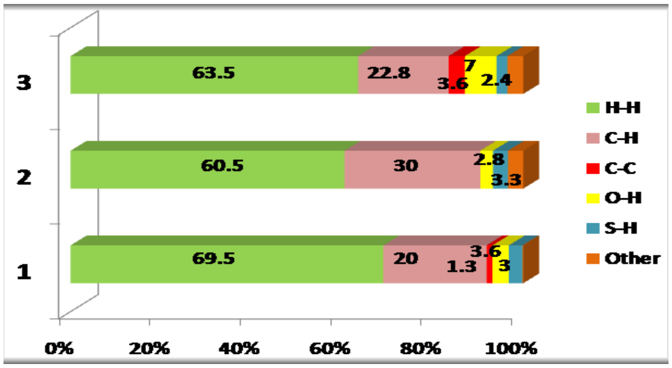
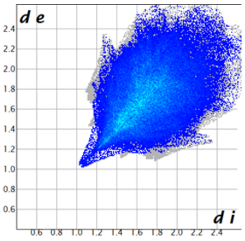
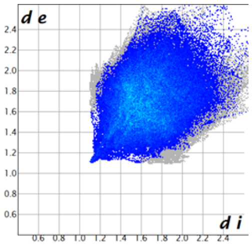
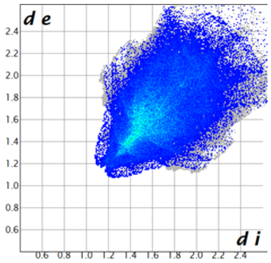
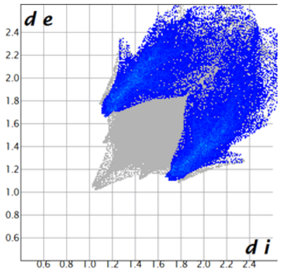
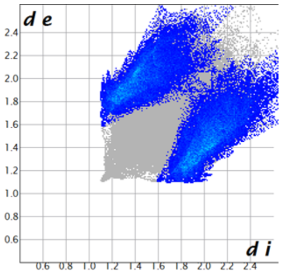
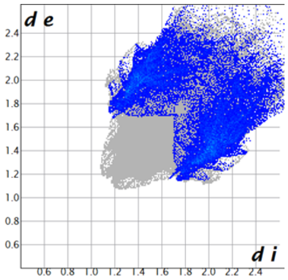


Figure SI5 . Relative contributions of various intermolecular contacts to the Hirshfeld surface area in complex **1**-**3**.

Hirshfeld 2D fingerprint plot of 1 and 2.

		1	2	3
1.	**H···H**	 **69.1%**	 **60.5%**	 **63.5%**
2.	**C···H**	 **22.8%**	 **33%**	 **20%**

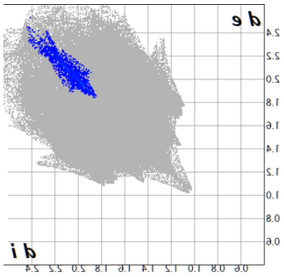
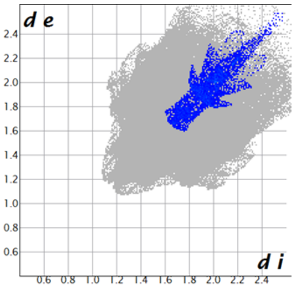
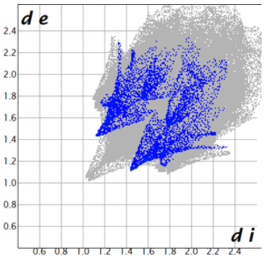
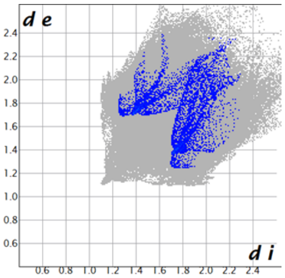
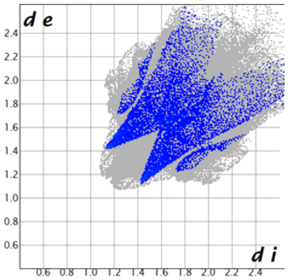
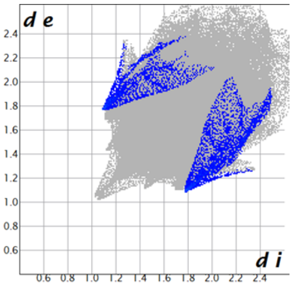
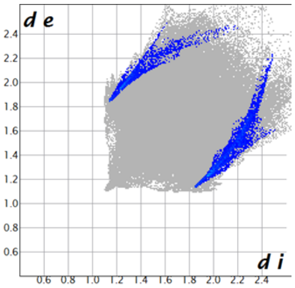
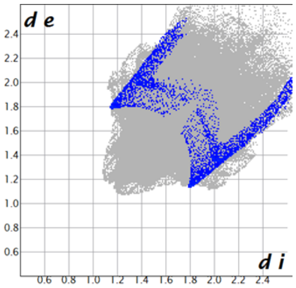
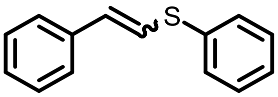
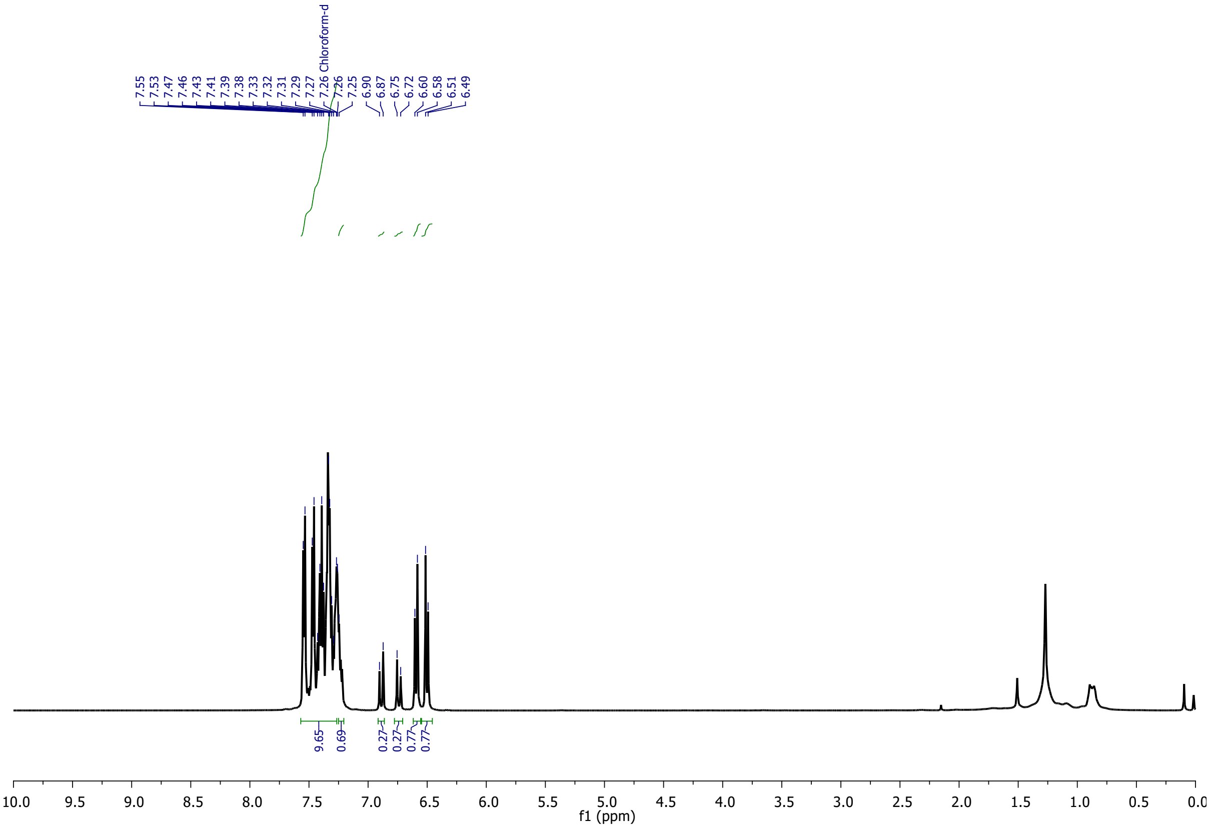
3.	C···C	 1.3%	Nil	 3.6%
4.	O···H	 3.6%	 2.8%	 7%
5.	S···H	 3.0%	 3.3%	 2.4%

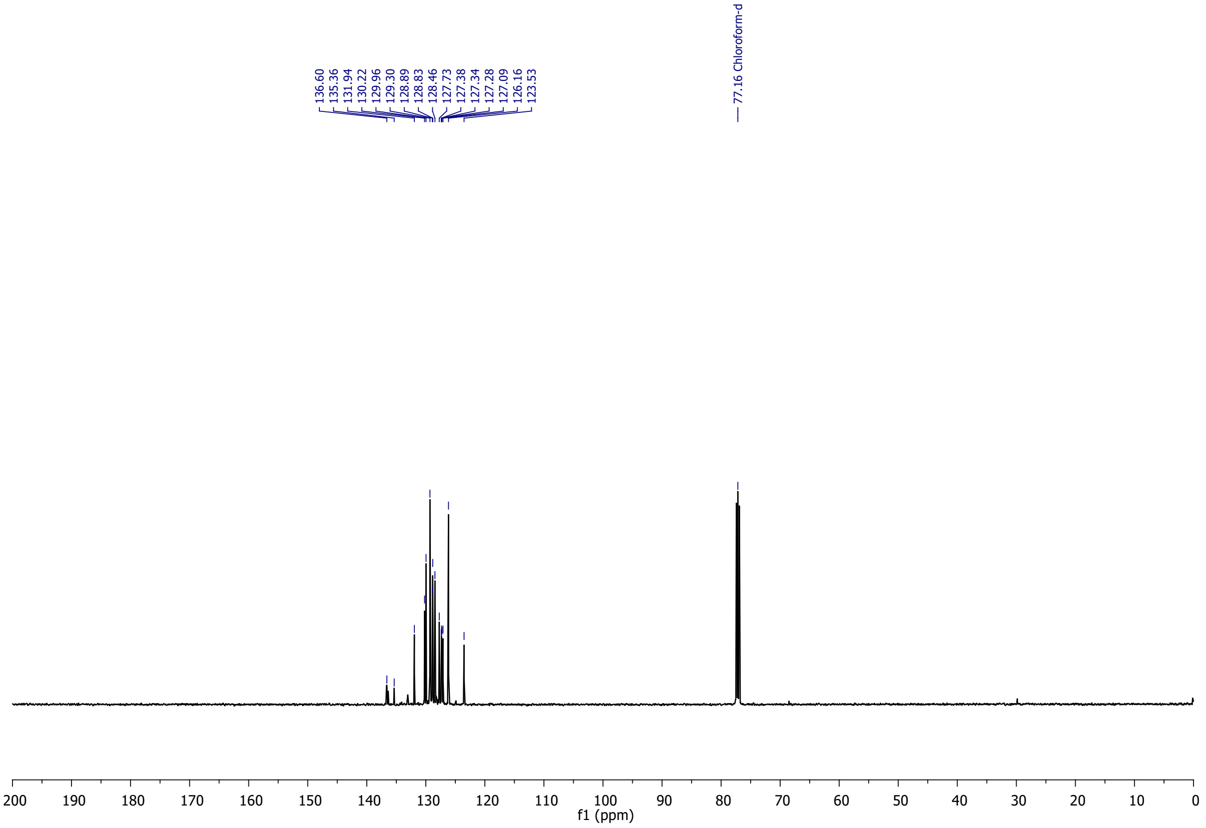
Figure SI 6. The Hirshfeld 2D fingerprint plots of **1**, **2** and **3**.

NMR spectra of catalyzed product:

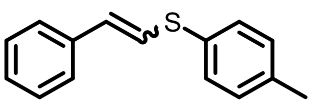
(1) Phenyl(styryl)sulfane: ^{1}H and ^{13}C

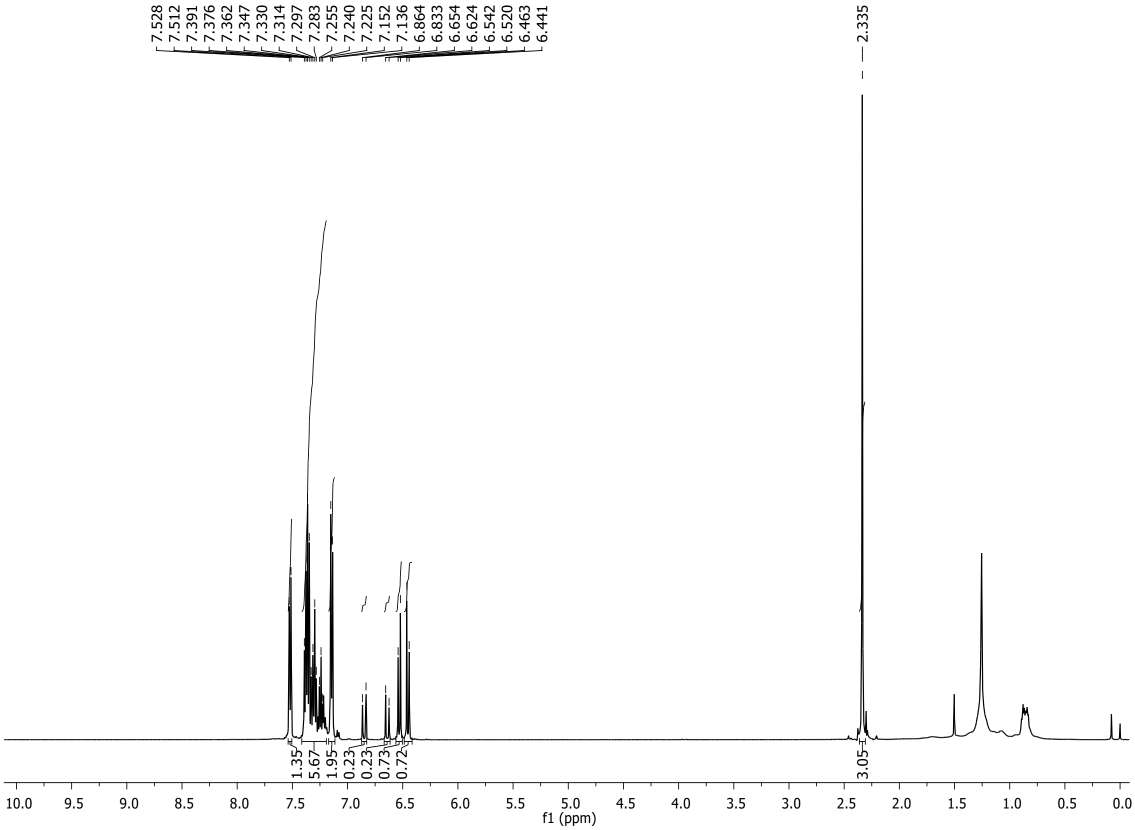


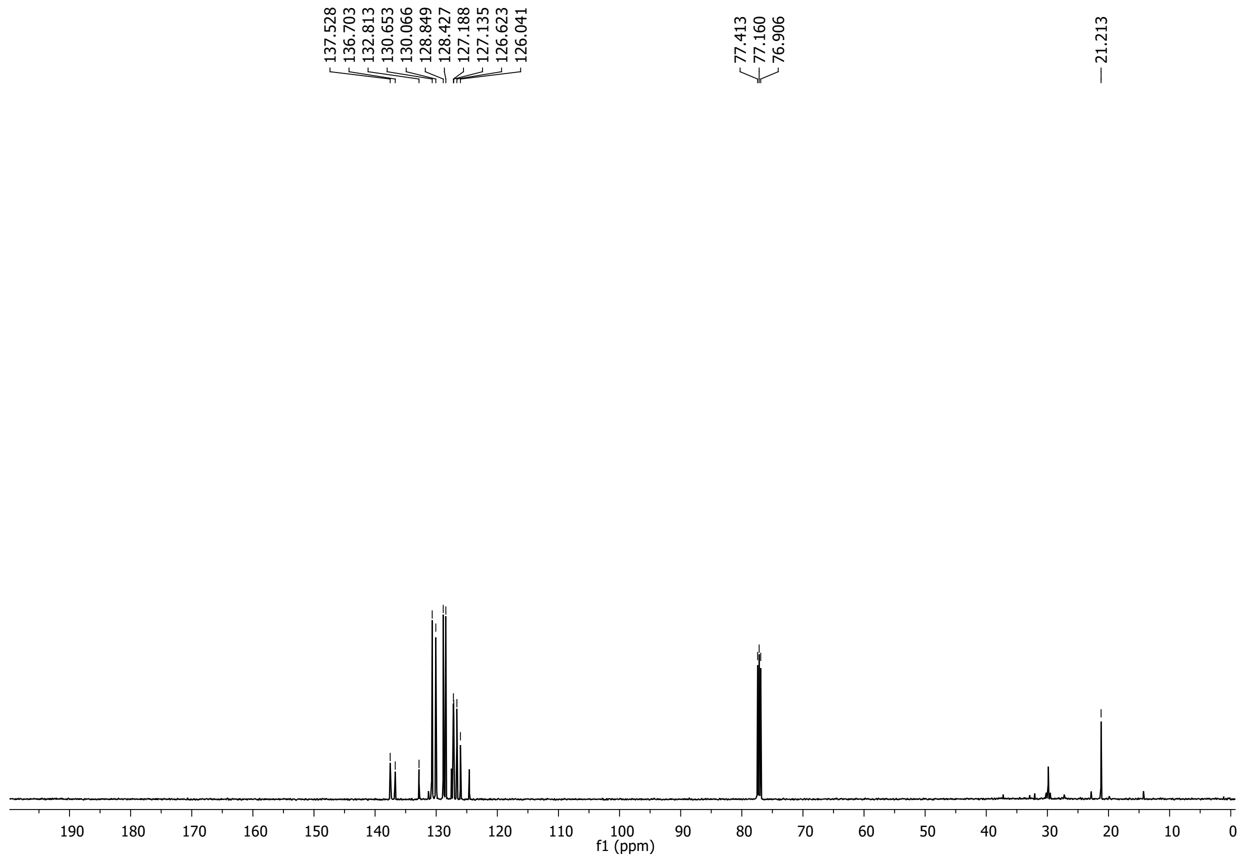

7.55
7.53
7.47
7.46
7.43
7.41
7.39
7.38
7.33
7.32
7.31
7.29
7.27
7.26 Chloroform-d
7.26
7.25
6.90
6.87
6.75
6.72
6.60
6.58
6.51
6.49
9.65
0.69
0.27
0.27
0.77
0.77
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


136.60
135.36
131.94
130.22
129.96
129.30
128.89
128.83
128.46
127.73
127.38
127.34
127.28
127.09
126.16
123.53
77.16 Chloroform-d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

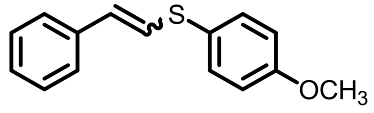
(2) Styryl(*P*-tolyl)sulfane: ^{1}H and ^{13}C

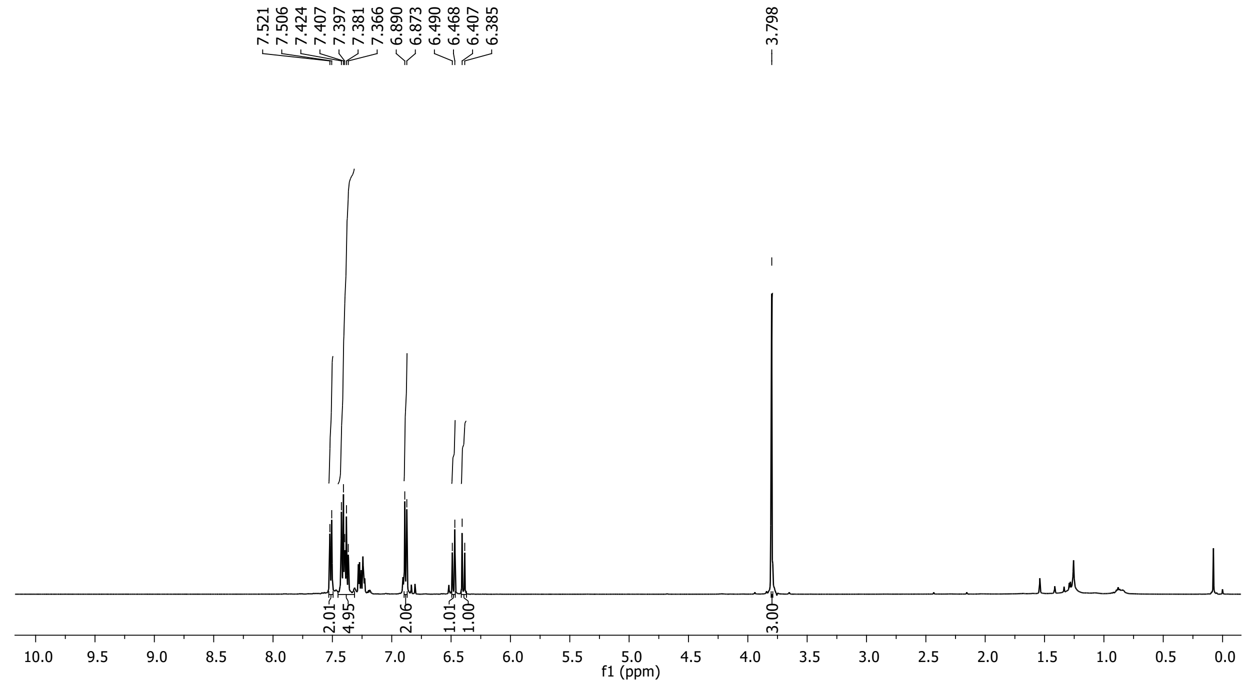


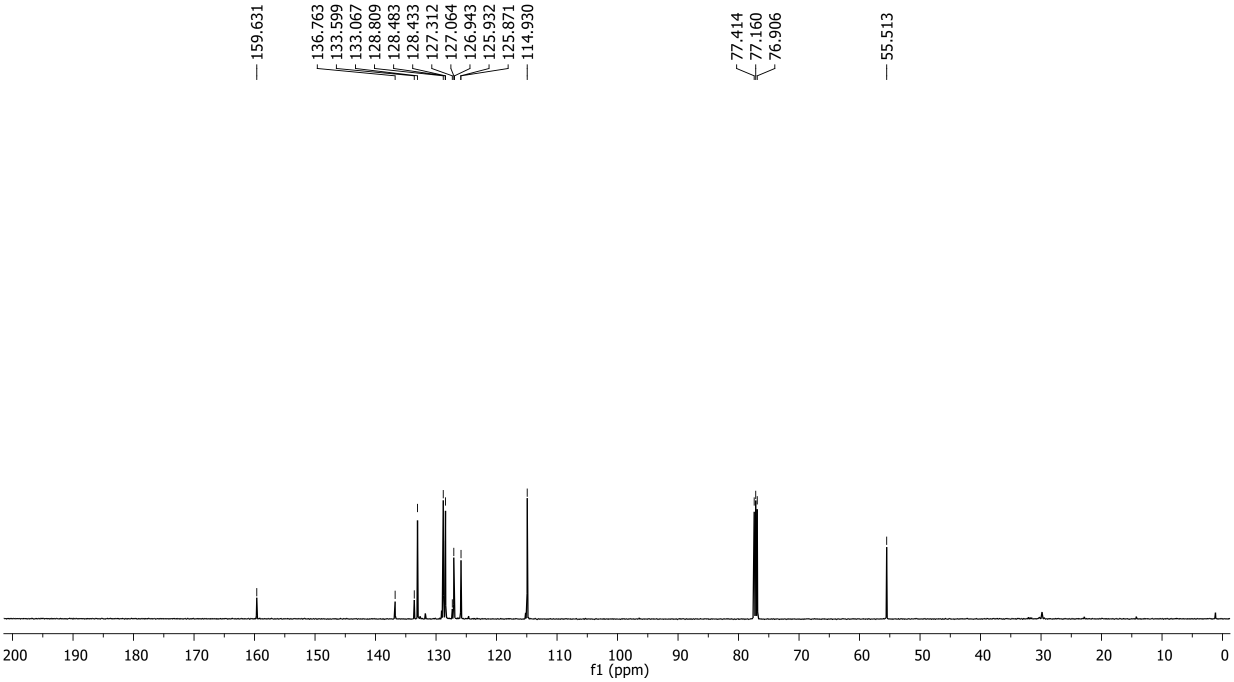




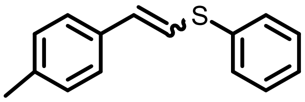
(3) (4-methoxyphenyl)(styryl)sulfane:

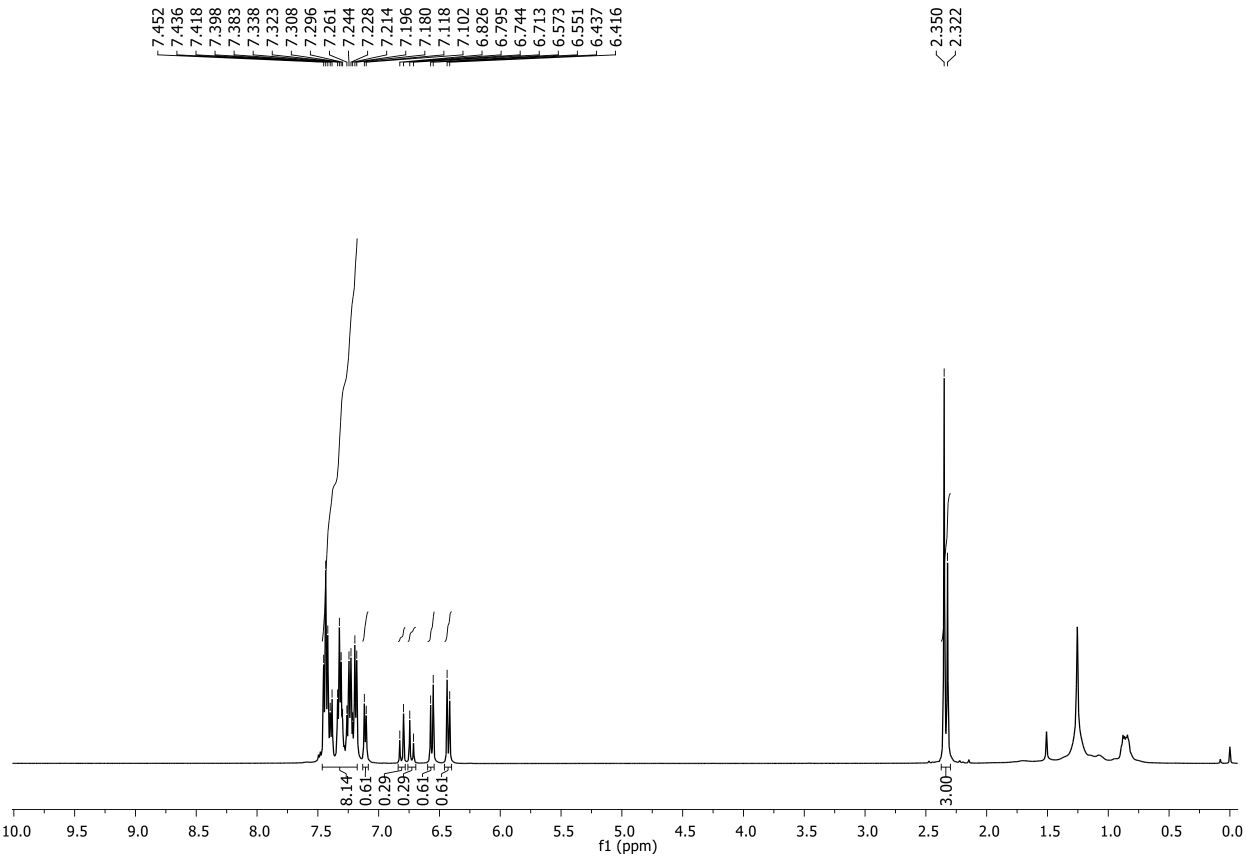


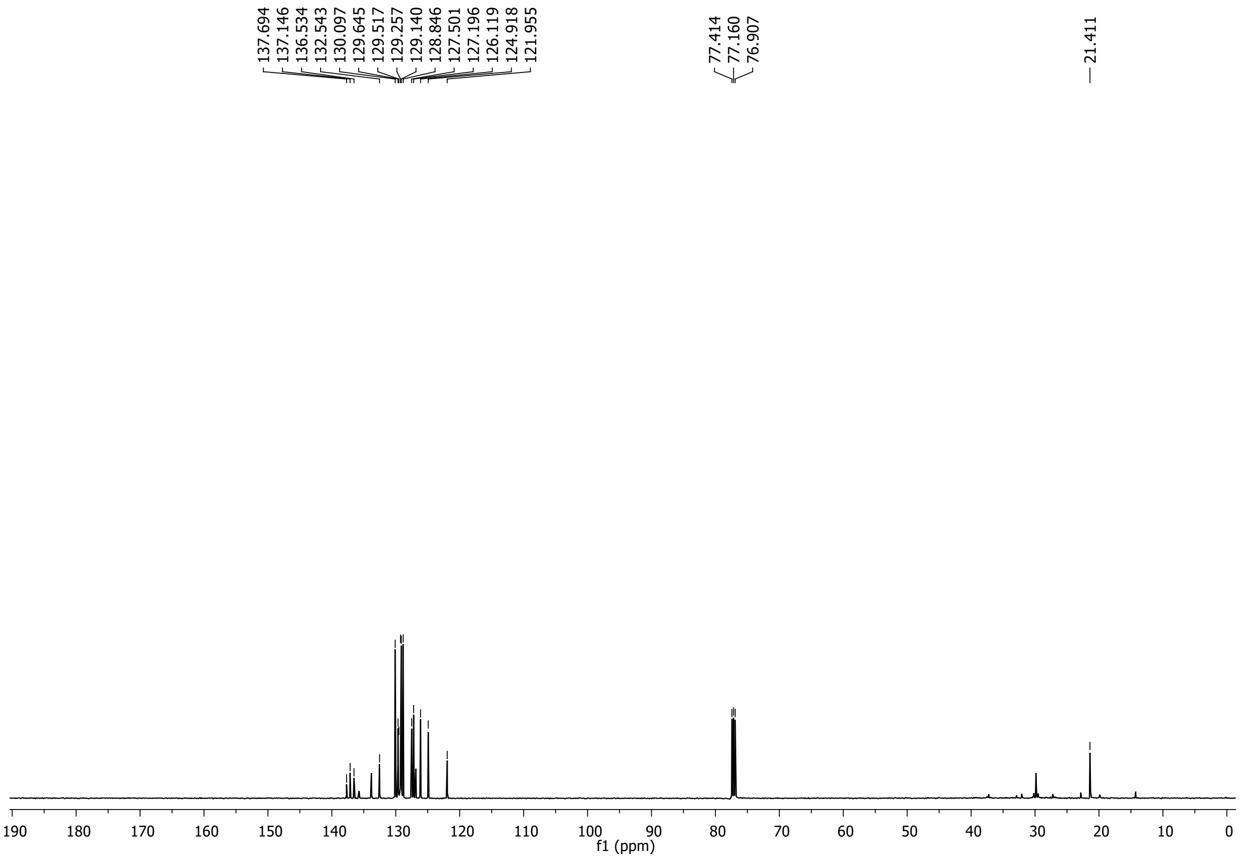




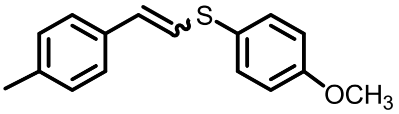
(4) (4-methylstyryl)(phenyl)sulfane:

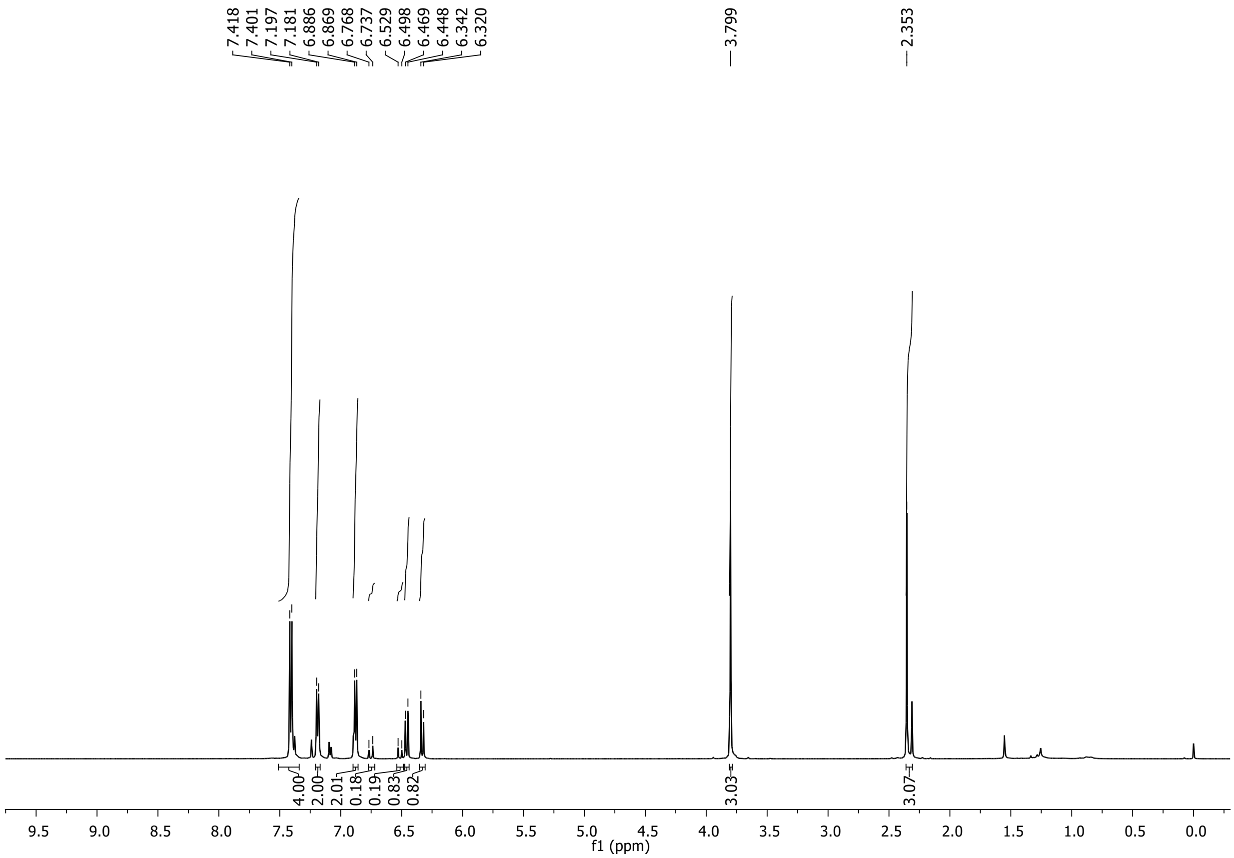



7.452
7.436
7.418
7.398
7.383
7.338
7.323
7.308
7.296
7.261
7.244
7.228
7.214
7.196
7.180
7.118
7.102
6.826
6.795
6.744
6.713
6.573
6.551
6.437
6.416
2.350
2.322
8.14
0.61
0.29
0.29
0.61
0.61
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



(5) (4-methoxyphenyl)(4-methylstyryl)sulfane:





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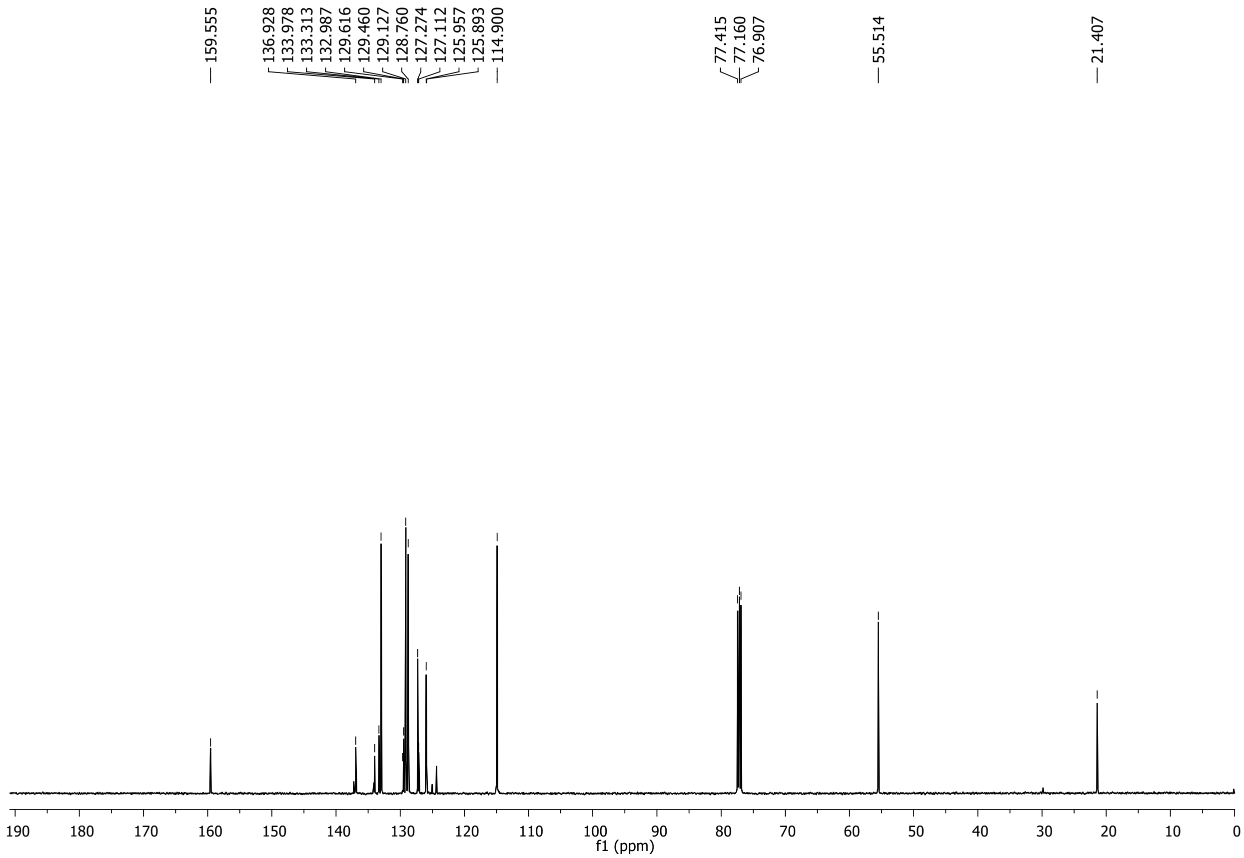
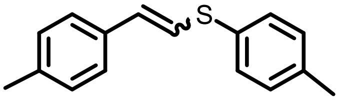
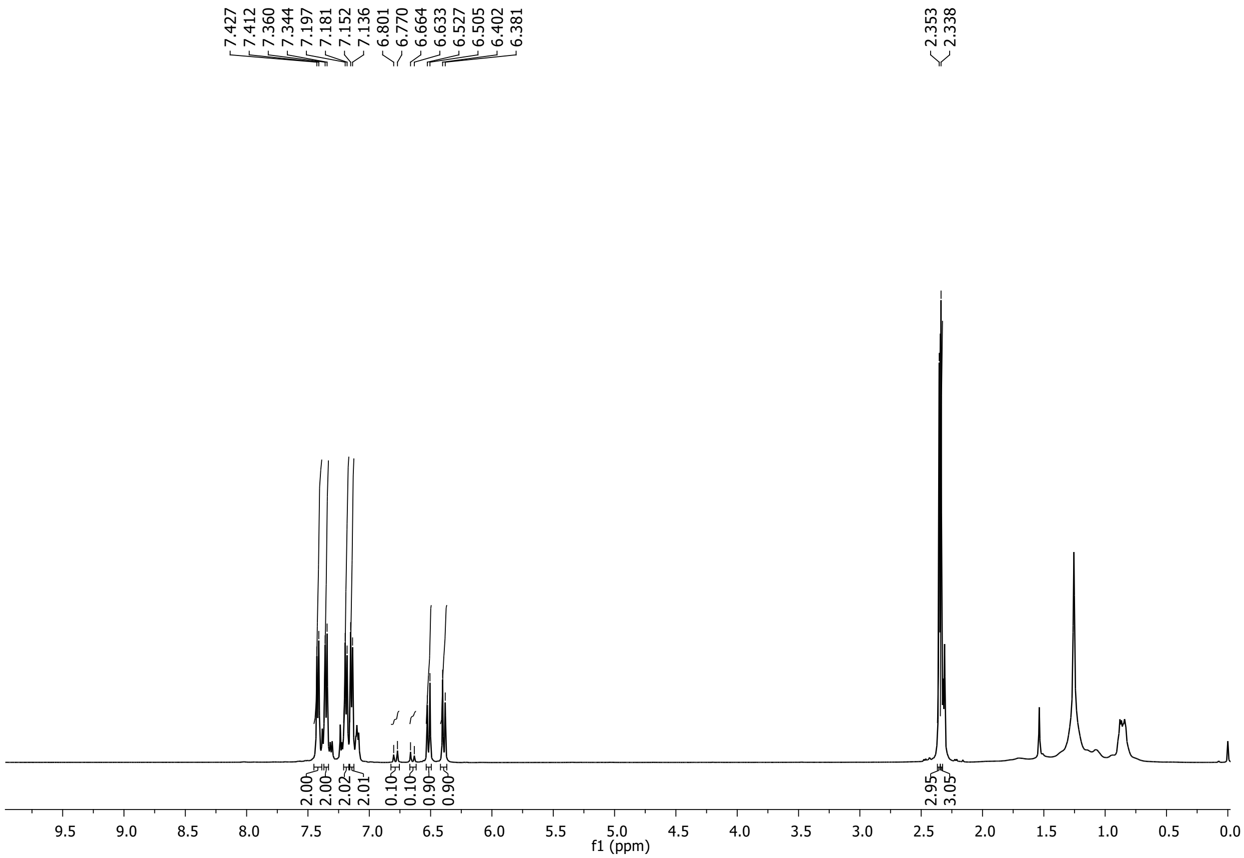
7.401
7.197
7.181
6.886
6.869
6.768
6.737
6.529
6.498
6.469
6.448
6.342
6.320
3.799
2.353
4.00
2.00
2.01
0.18
0.19
0.83
0.82
3.03
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



(6) (4-methylstyryl)(*P*-tolyl)sulfane:

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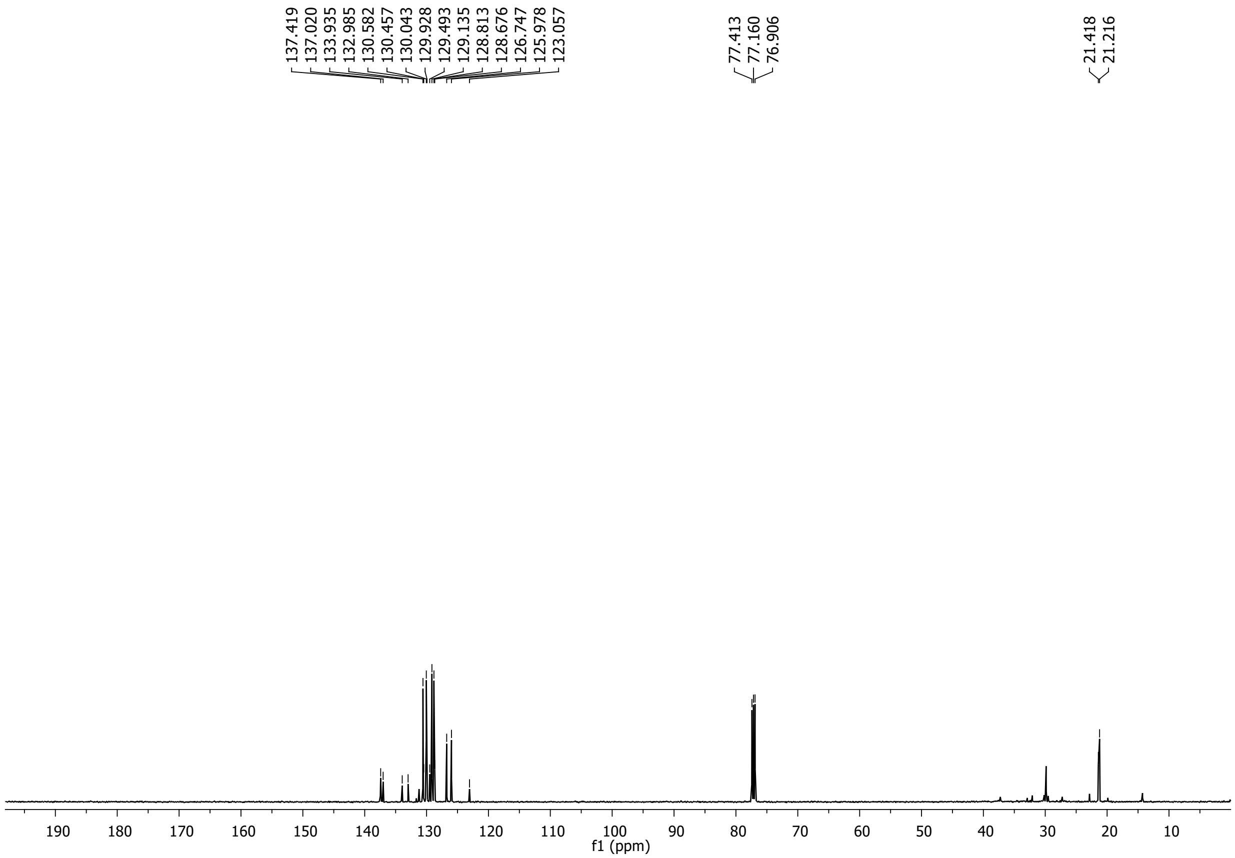
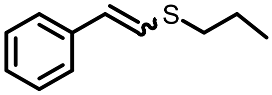
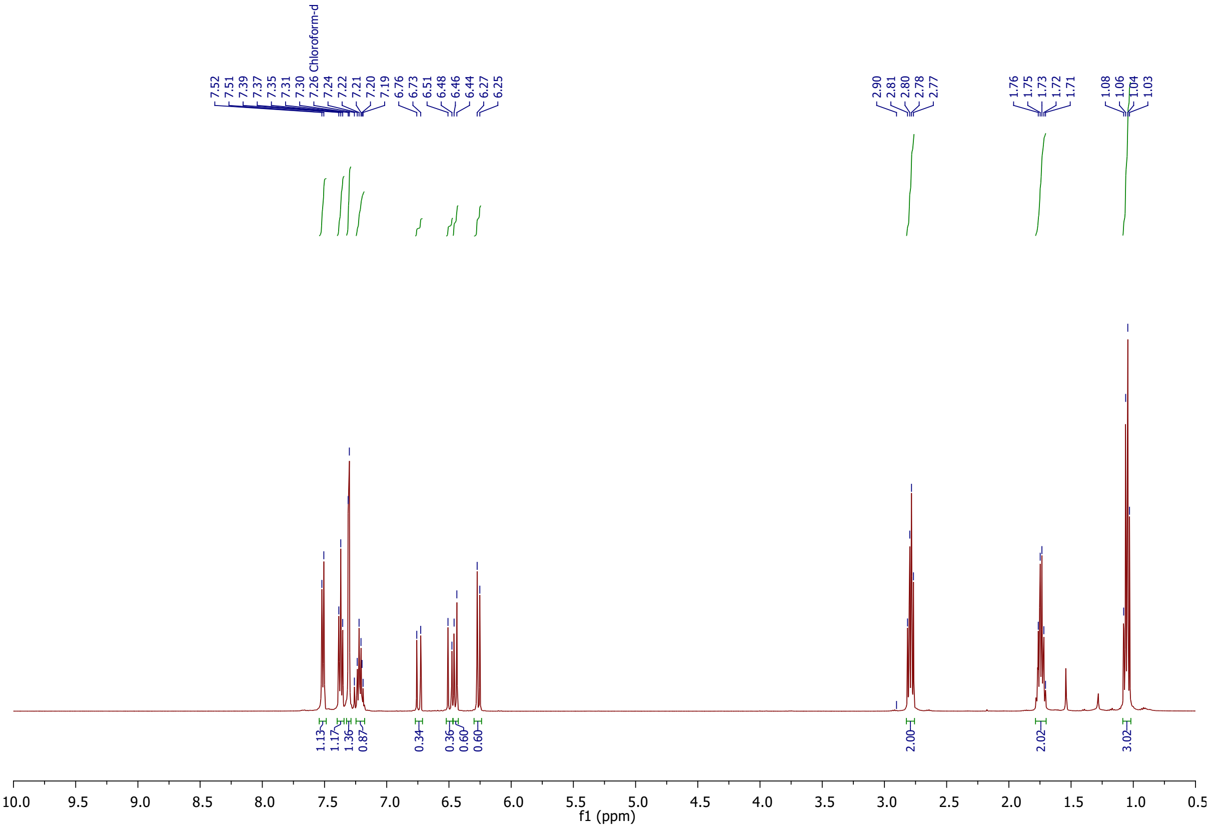
7.412
7.360
7.344
7.197
7.181
7.152
7.136
6.801
6.770
6.664
6.633
6.527
6.505
6.402
6.381
2.353
2.338
2.00
2.00
2.02
2.01
0.10
0.10
0.90
0.90
2.95
3.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

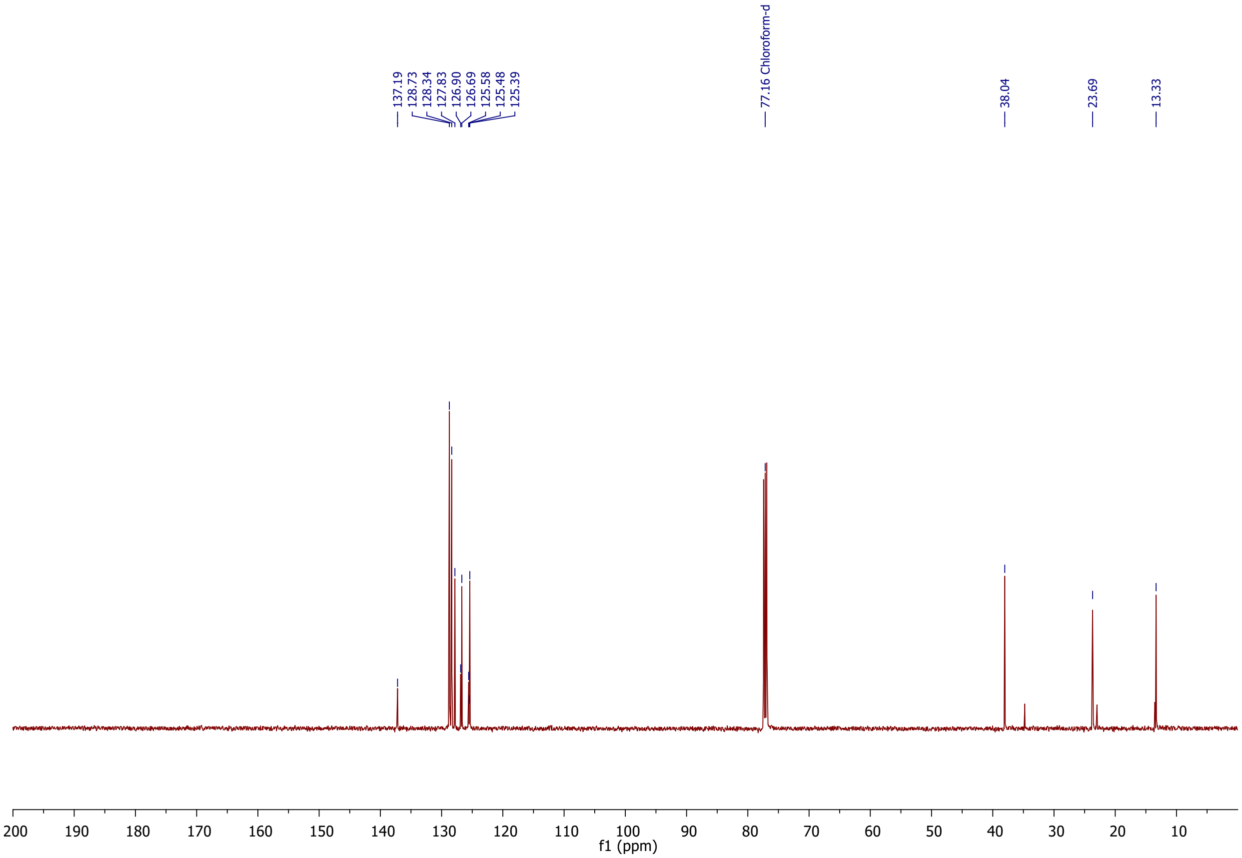


(7) Propyp(styryl)sulfane:

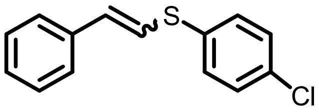


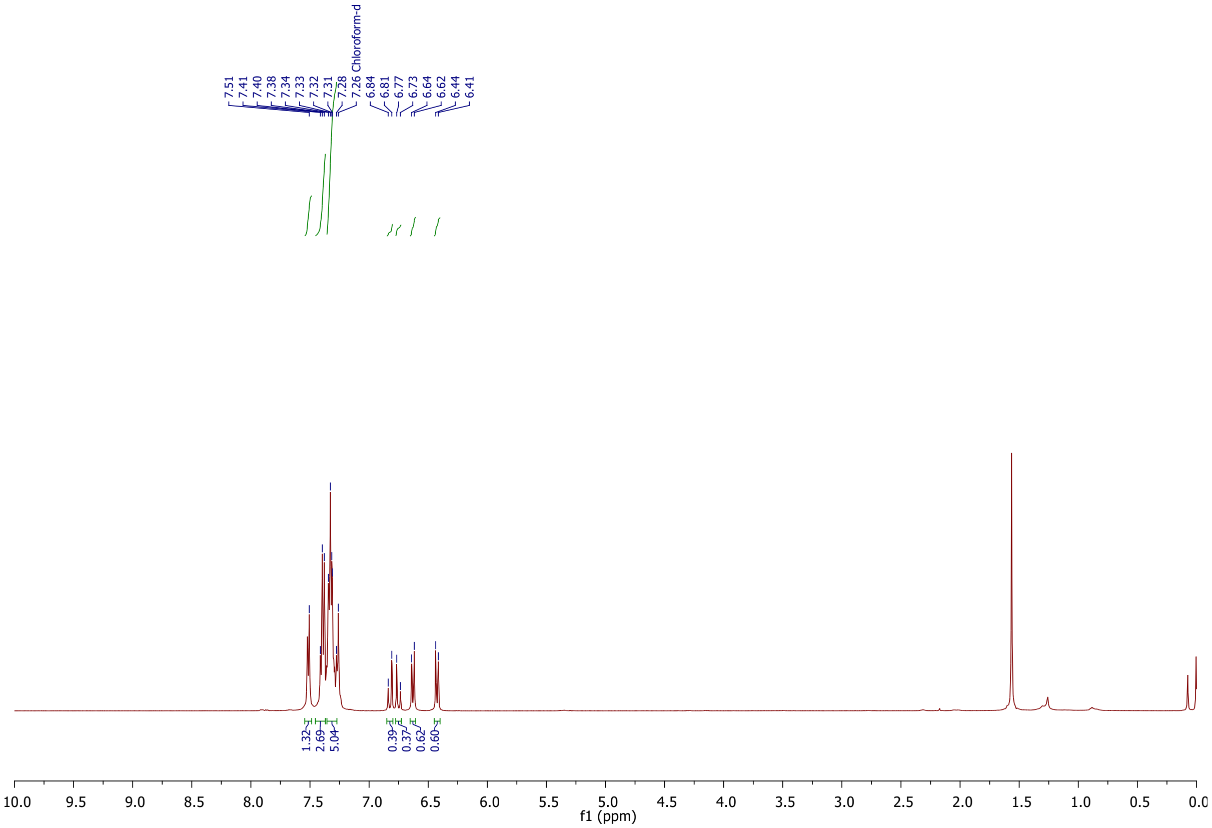
21

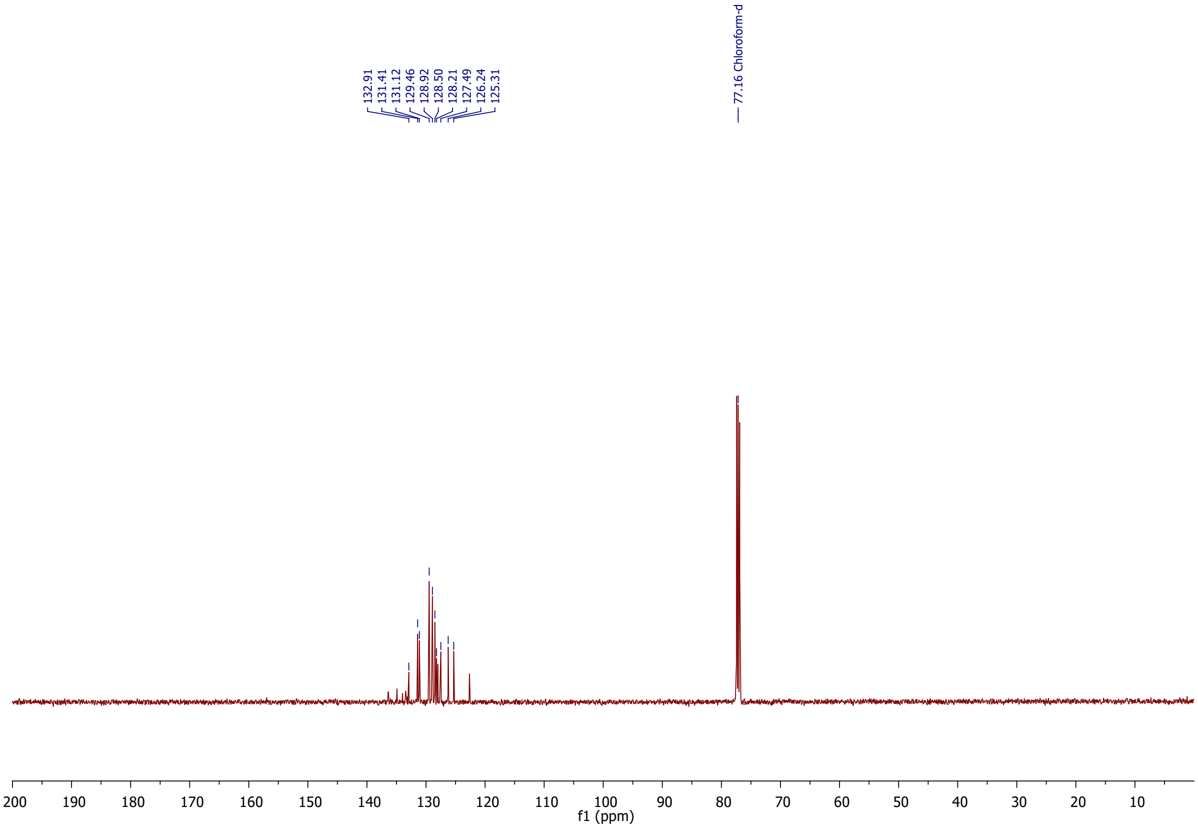

7.52
7.51
7.39
7.37
7.35
7.31
7.30
7.26 Chloroform-d
7.24
7.22
7.21
7.20
7.19
6.76
6.73
6.51
6.48
6.46
6.44
6.27
6.25
2.90
2.81
2.80
2.78
2.77
1.76
1.75
1.73
1.72
1.71
1.08
1.06
1.04
1.03
1.13
1.17
1.36
0.87
0.34
0.36
0.60
0.60
2.00
2.02
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



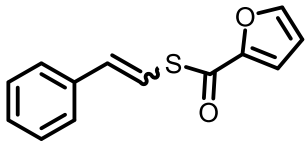
(8) (4-chlorophenyl)(styryl)sulfane:

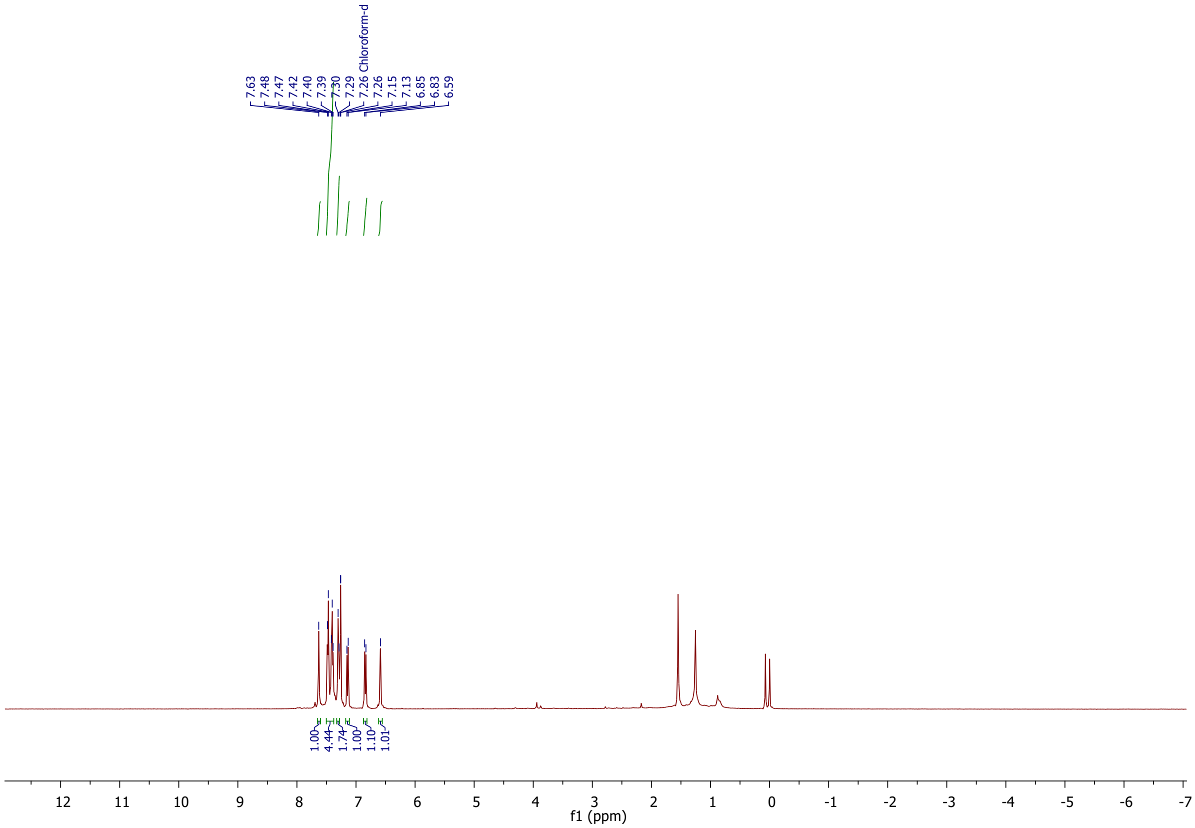



7.51
7.41
7.40
7.38
7.34
7.33
7.32
7.31
7.28
7.26 Chloroform-d
6.84
6.81
6.77
6.73
6.64
6.62
6.44
6.41
1.32
2.69
5.04
0.39
0.37
0.62
0.60
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



(9) (S-styryl)furane-2-carbothioate:




7.63
7.48
7.47
7.42
7.40
7.39
7.30
7.29
7.26 Chloroform-d
7.26
7.15
7.13
6.85
6.83
6.59
1.00
4.44
1.74
1.00
1.10
1.01
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
f1 (ppm)

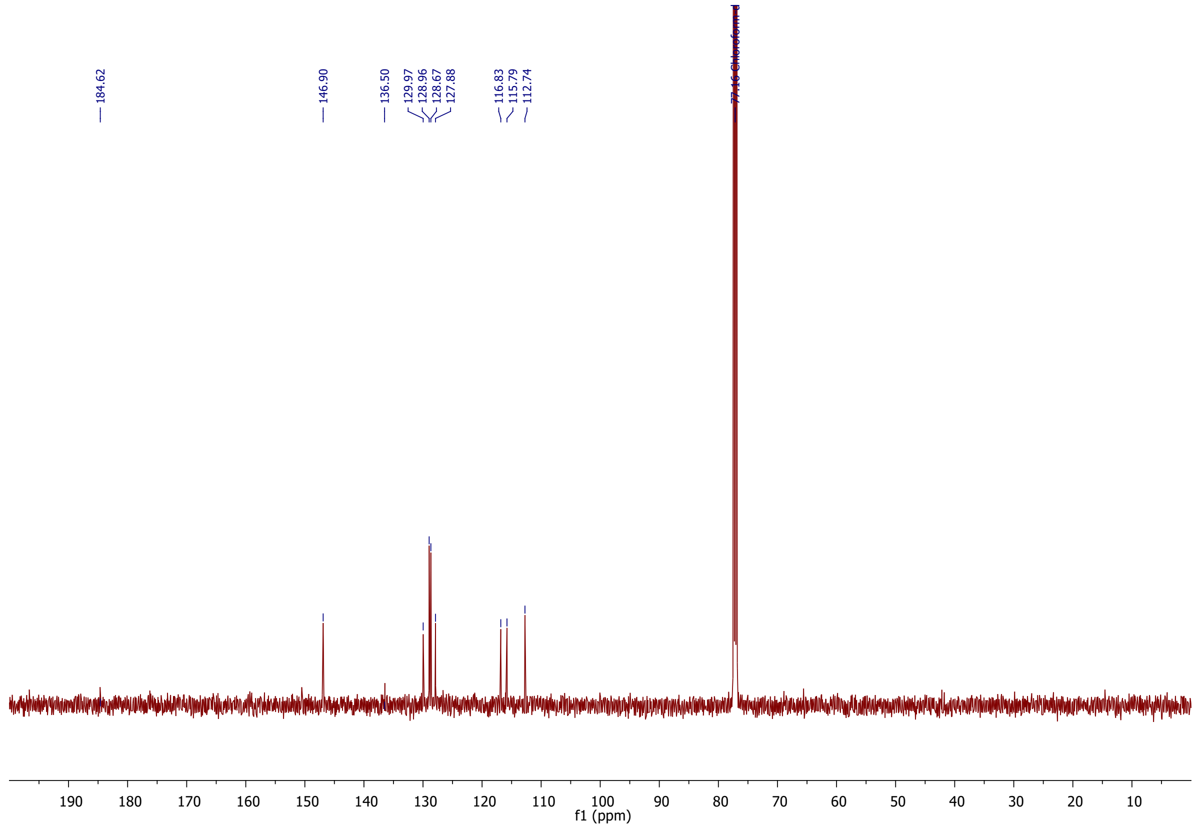


Figure SI 7. 1H and 13C spectra of catalytic products.

X-ray Crystallography:

X-ray intensity data of 42833 reflections (of which 7431 unique) for **1**, 12813 reflections (of which 3907 unique) for **2**, and 15943 reflections (of which 6944 unique) for **3** were collected at 293(2) K. The cell dimensions were determined by the least-squares fit method. The intensities were measured by ϕ and ω scan mode for ranges 2.241 to 25.999^o for **1**, 2.081 to 21.202^o for **2,** 3.467 to 29.062 ^{o} for **3**. 6101, 2686 and 4806 for **1**, **2** and **3** reflections were treated as observed [I >2σ(I)] respectively. Scan width for data collection was 1^o for all, while the exposure times were 11.2, 7.6 and 8.3 sec. for **1**, **2** and **3**, respectively. Although, we used the best available crystal for data collection, we could not grow a good quality crystal of **2** even after several attempts. Thus, the observed intensities in the case of **2** were very weak due to poor crystal quality (Fig. SI. 8 – SI. 9).

Data were corrected for Lorentz and polarization factors. All the hydrogen atoms were geometrically fixed and allowed to ride on their parent carbon atoms. The final refinement cycles converged to an R = 0.0327 and wR (F2) = 0.0748 for **1**, R = 0.0752 and wR (F2) = 0.1828 for **2** and R = 0.0458 and wR (F2) = 0.0986 for **3**. Although, the R, wR and GoF values in the case of **2** are satisfactory there was some residual density near S1 which is not much expected, however, the value was not very high (1.38) and can be fully adjusted with a H atom only. No trace of any other atom (even with partial occupancy) in the residual density map was observable (Fig. SI. 10). When we placed a H atom on S1 the refined S1-H distance becomes 1.10 Å. However, under such a situation, the charge on Cu(1) needs some other anion to be balanced. As mentioned, already, there is no other anion present. Notably, NMR spectrum is also consistent with the deprotonated ligand bound to Cu(I). Under such circumstances, the only possibility is the appearance of diffraction ripples. Such diffraction ripples are commonly observed near heavy atoms. Although S1 is not the heaviest atom present, however, from the residual peak pairs (Q1 and Q3) it seems that these are also diffraction ripples.

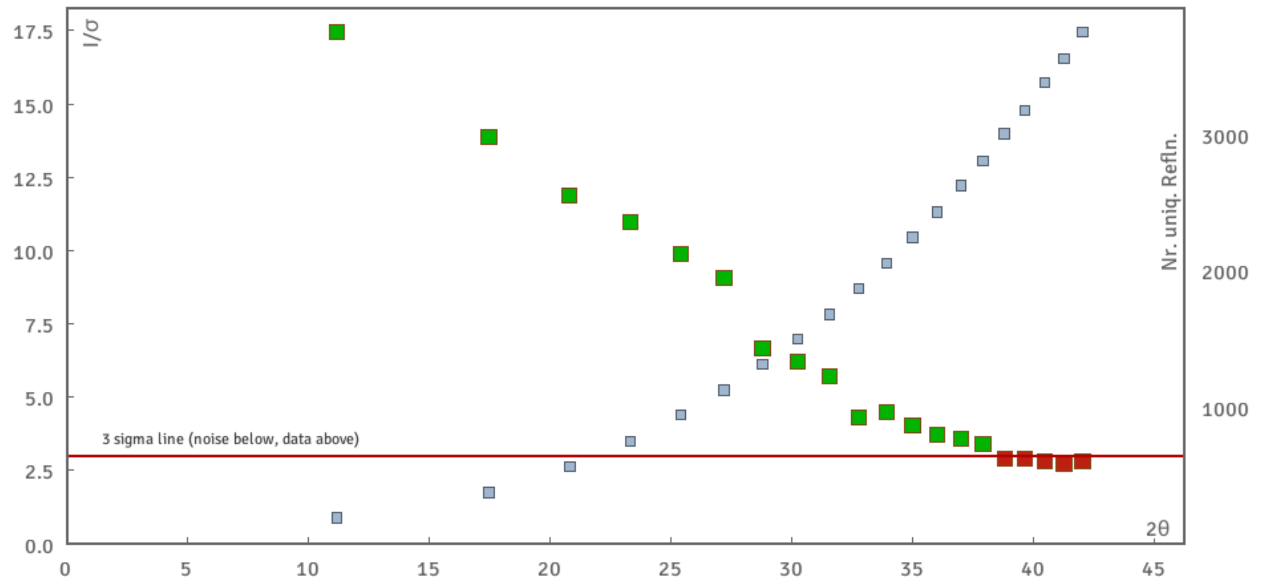


Fig. SI. 8 Plot of I/σ versus resolution

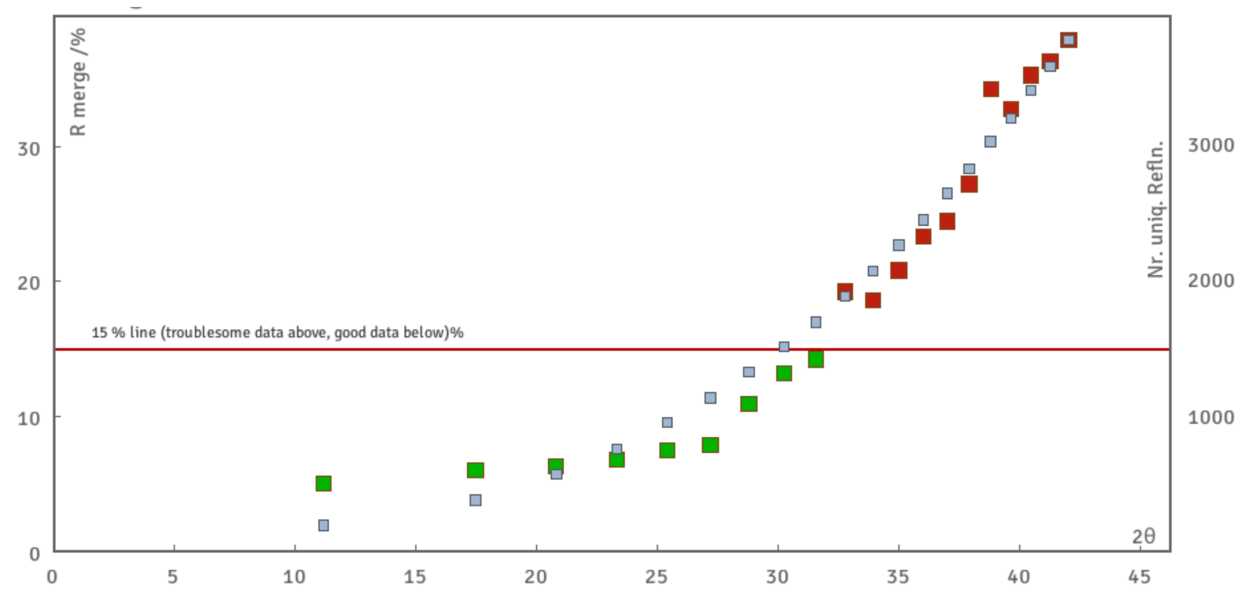


Fig. SI. 9 Plot of R_{merge} versus resolution

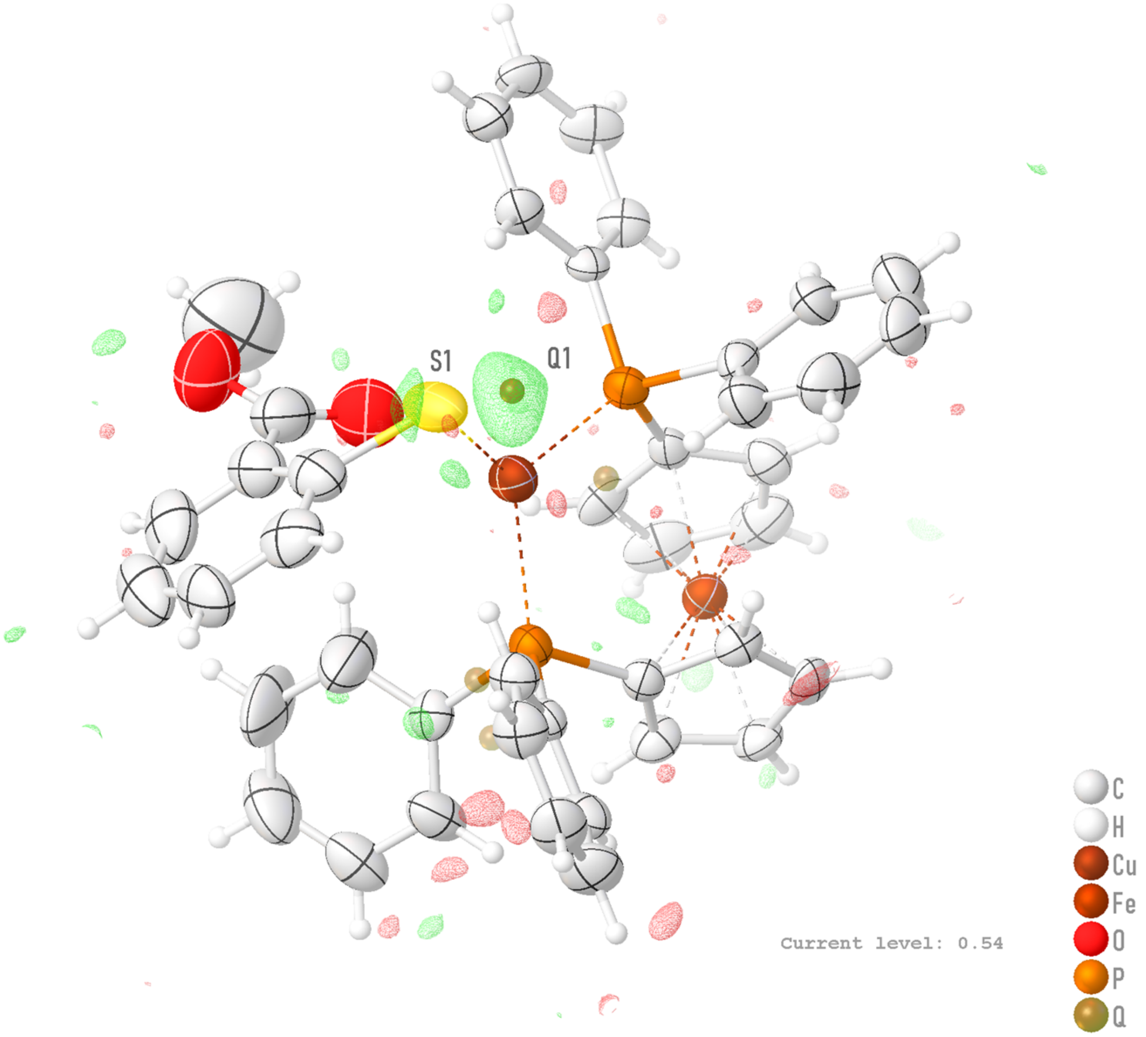


Fig. SI. 10 Molecular structure and residual electron density