Table S1

Crystallographic and structure refinement data for Na**4b** and complexes **5b, 5c, 5d** and **5f**.

Compound	**Na4b**	**5b**	**5c**	**5d**	**5f**
Formula	$C_{66}H_{36}B_2F_{36}N_{12}Na_2O_2$	$C_{35}H_{20}BCuF_{18}N_6$	$C_{32}H_{20}BCl_3CuF_9N_6$	$C_{32}H_{20}BCuF_{12}N_6$	$C_{35}H_{29}BCuF_9N_6O_3$
F_w	1780.67	940.92	840.24	790.89	824.97
Space group	*P*-1 (no. 2)	*P*-1 (no. 2)	$Pca2_1$ (no. 29)	$P2_1/n$ (no. 14)	$Pca2_1$ (no. 29)
T (K)	150(2)	110(2)	110(2)	110(2)	110(2)
λ (Å)	1.54178	1.54178	1.54178	1.54178	1.54178
a (Å)	11.2747(2)	11.2044(2)	17.33337(13)	10.98962(10)	17.25818(18)
b (Å)	12.5762(3)	13.9379(2)	14.29443(11)	13.10766(10)	14.28140(11)
c (Å)	14.4865(3)	24.6553(5)	27.03970(18)	21.50728(16)	28.1090(3)
α (°)	109.484(2)	74.7263(15)	90	90	90
β (°)	104.948(2)	83.9886(16)	90	91.0237(7)	90
γ (°)	102.991(2)	73.3009(16)	90	90	90
V (Å^3)	1758.61(7)	3555.92(12)	6699.64(8)	3097.59(4)	6928.05(12)
Z	1	4	8	4	8
ρ (calc) (g/cm^3)	1.681	1.758	1.666	1.696	1.582
μ (mm^{-1})	1.645	2.101	3.898	1.991	1.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22232, 6828, 6297	41528, 13786, 12647	46386, 12949, 12578	21696, 6055, 5644	55091, 13566, 12997
R_1/wR_2 [$I > 2\sigma(I)$]	0.0350/0.0867	0.0358/0.0927	0.0342/0.0938	0.0296/0.0776	0.0369/0.1027
R_1/wR_2 [all refl.]	0.0377/0.0891	0.0390/0.0952	0.0353/0.0947	0.0318/0.0792	0.0390/0.1043
GOF	1.022	1.020	1.039	1.040	1.055
□ρ_{max}, □ρ_{min} (e Å^{-3})	−0.27/0.28	−0.45/0.69	−0.36/0.57	−0.44/0.38	−0.47/0.49

Table S2

Crystallographic and structure refinement data for complexes **6b, 6c, 6d , 6f** and **Na4a'**.

Compound	**6b**	**6c**	**6d**	**6f**	**Na4a'**
Formula	$C_{34}H_{16}BCuF_{18}N_6O$	$C_{31}H_{16}BCl_3CuF_9N_6O$	$C_{31}H_{16}BCuF_{12}N_6O$	$C_{34}H_{25}BCuF_9N_6O_4$	$C_{30}H_{18}BF_9N_9NaO_7$
F_w	940.88	840.20	790.85	826.95	821.33
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$R3c$ (no. 161)	P-1 (no. 2)	$P2_1/n$ (no. 14)
T (K)	110(2)	110(2)	110(2)	110(2)	110(2)
λ (Å)	1.54178	1.54178	1.54178	1.54178	1.54178
a (Å)	13.54010(9)	26.7585(2)	13.98309(14)	14.7235(2)	9.32258(10)
b (Å)	26.17486(19)	15.10355(13)	13.98309(14)	14.8744(2)	23.3536(3)
c (Å)	19.93841(15)	17.27070(15)	29.4298(3)	16.4814(4)	15.70665(18)
α (°)	90	90	90	70.1798(18)	90
β (°)	97.7916(7)	108.8056(9)	90	88.5315(17)	97.3724(10)
γ (°)	90	90	120	89.3415(13)	90
V (Å^3)	7001.14(9)	6607.32(10)	4983.38(11)	3394.53(11)	3391.32(7)
Z	8	8	6	4	4
ρ (calc) (g/cm^3)	1.785	1.689	1.581	1.618	1.609
μ (mm^{-1})	2.158	3.978	1.881	1.805	1.422
Refl Obs	46290, 13733, 12422	47458, 12945, 11966	19972, 1992, 1984	39391, 14903, 12047	20217, 6614, 5643
R_1/wR_2 [$I > 2\sigma(I)$]	0.0332/0.0853	0.0300/0.0808	0.0201/0.0587	0.0428/0.1393	0.0374/ 0.0941
R_1/wR_2 [all refl.]	0.0374/0.0880	0.0333/0.0836	0.0202/0.0588	0.0538/0.1660	0.0459/ 0.1012
GOF	1.032	1.031	1.058	1.016	1.028
□ρ_{max}, □ρ_{min} (e Å^{-3})	−0.39/0.43	−0.49/0.42	−0.23/0.19	−0.48/0.62	-0.28/0.36

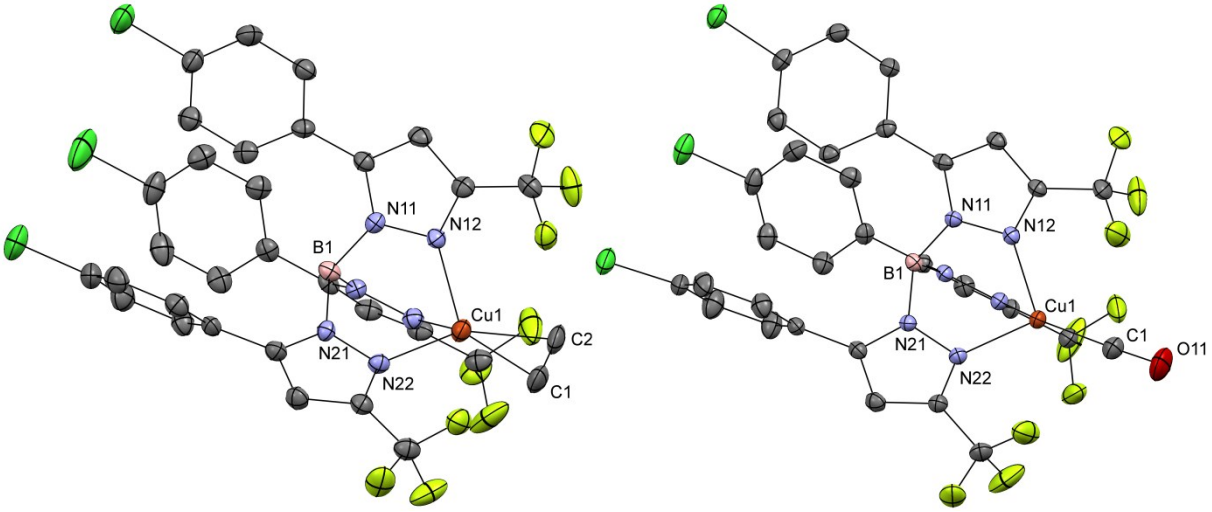


Figure S1. Crystal structures of **5c** (left) and **6c** (right) with displacement ellipsoids plotted at the 50% probability level at 110(2) K. For clarity hydrogen atoms and disordered fragments have been omitted.

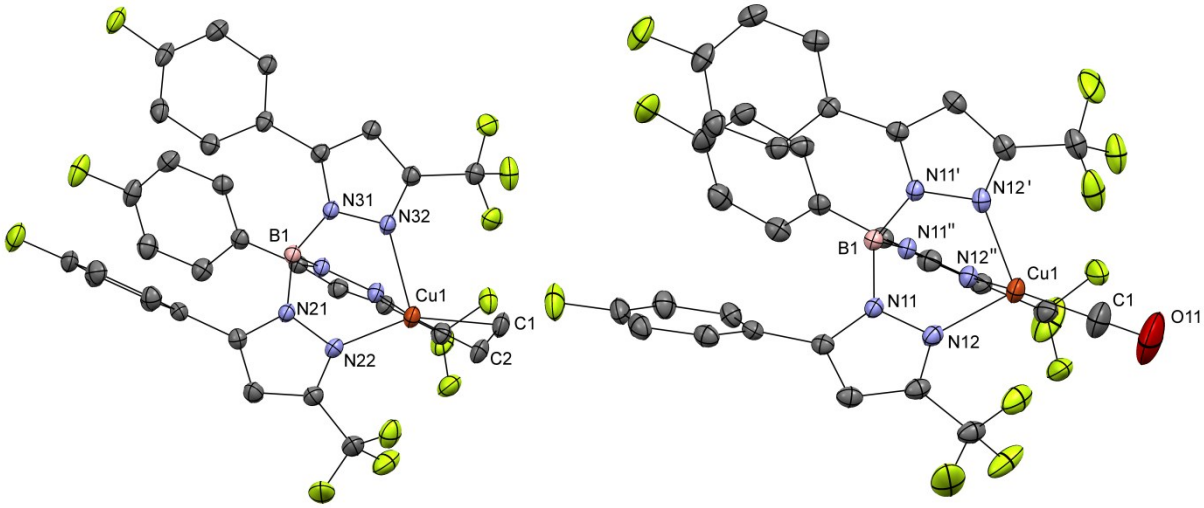


Figure S2. Crystal structures of **5d** (left) and **6d** (right) with displacement ellipsoids plotted at the 50% probability level at 110(2) K. For clarity hydrogen atoms and disordered fragments have been omitted. Symmetry operation ‘ = [1–y, x–y, z], “ = [1–x+y, 1–x, z].

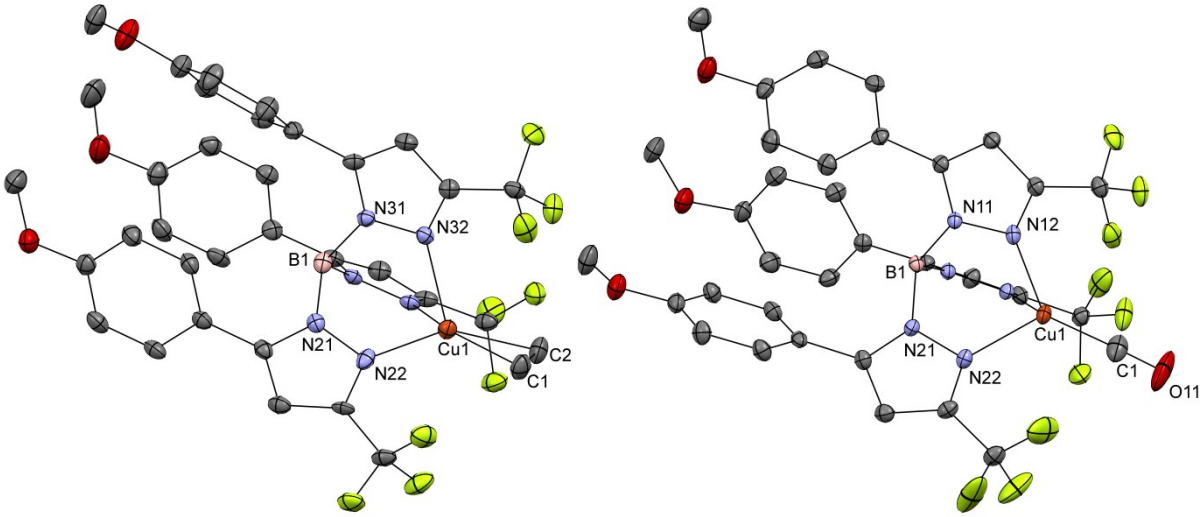
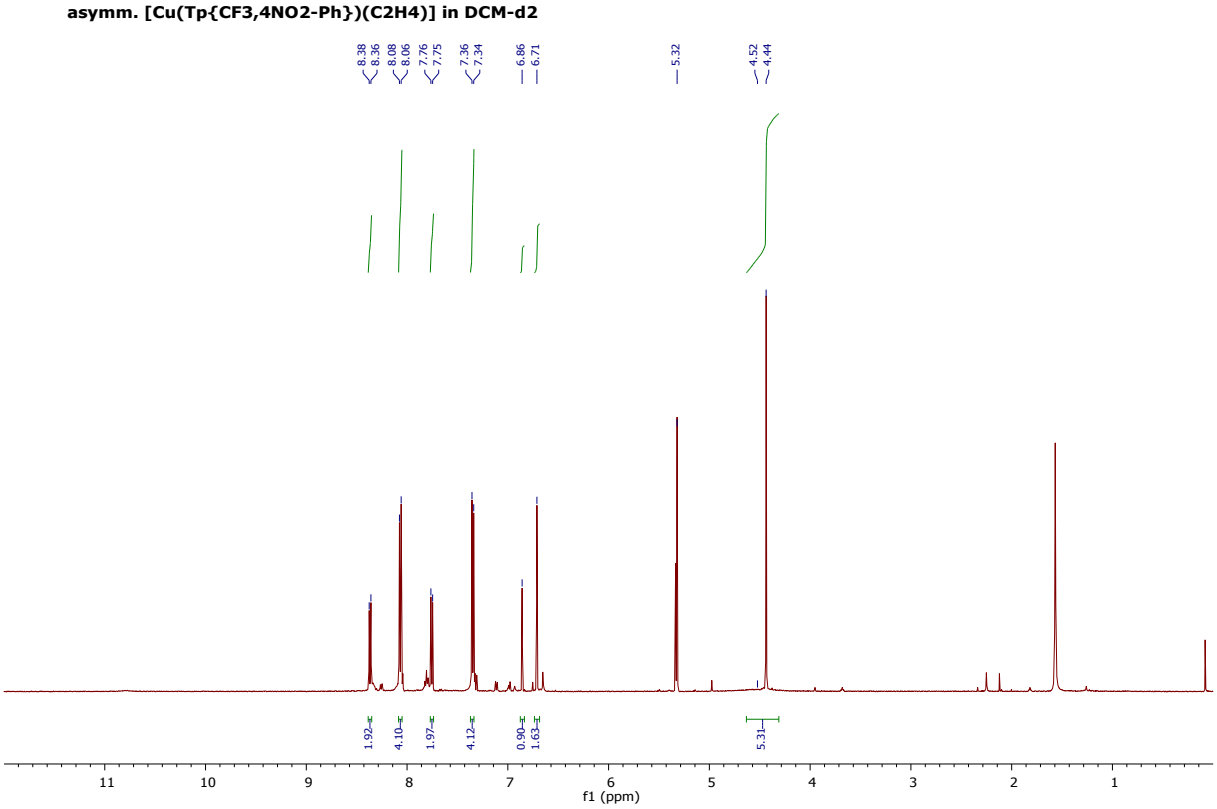
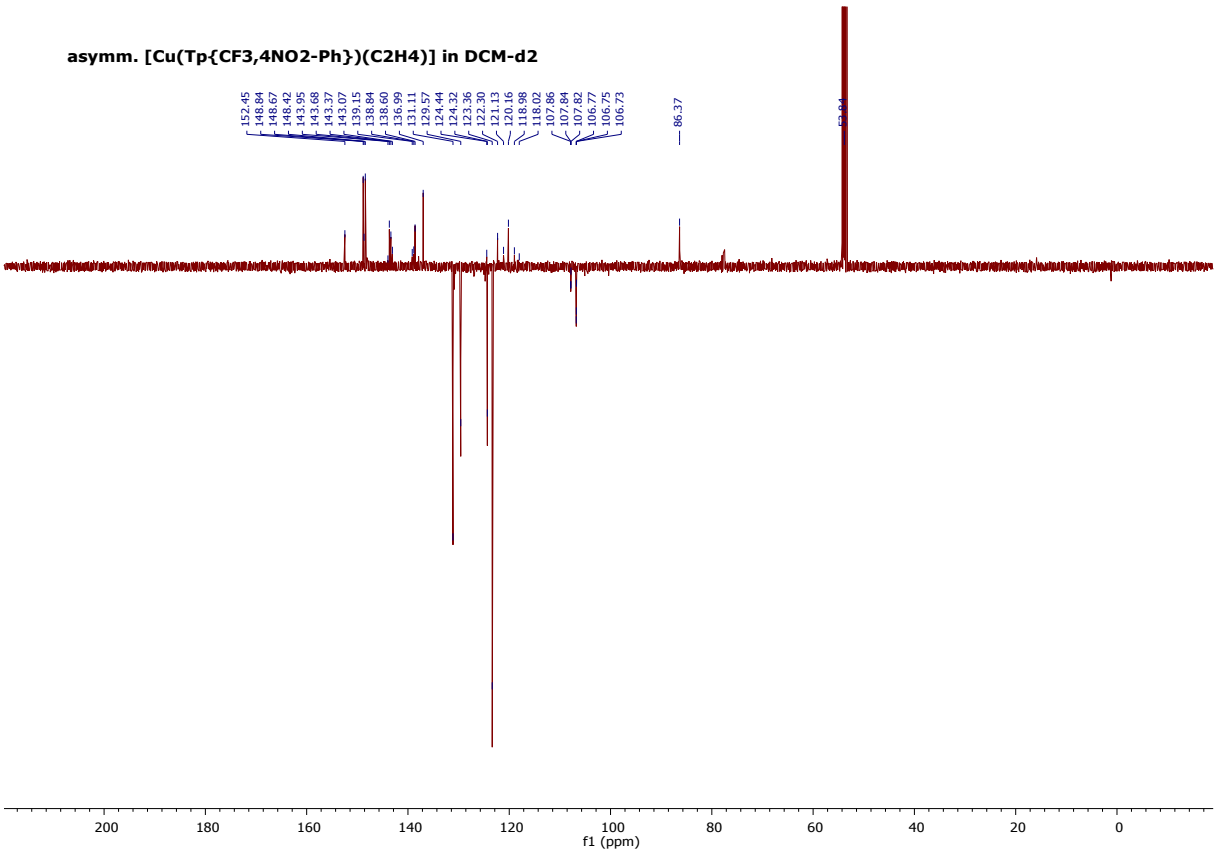
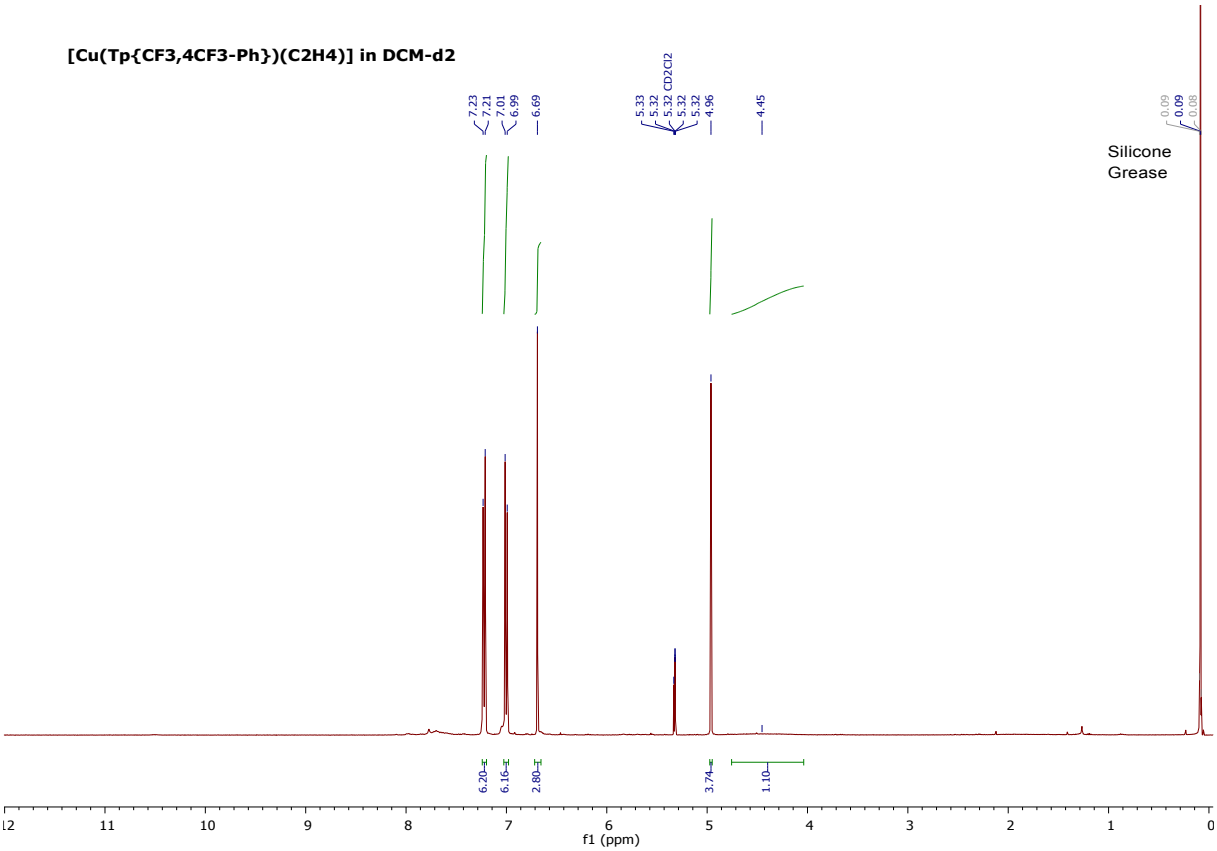


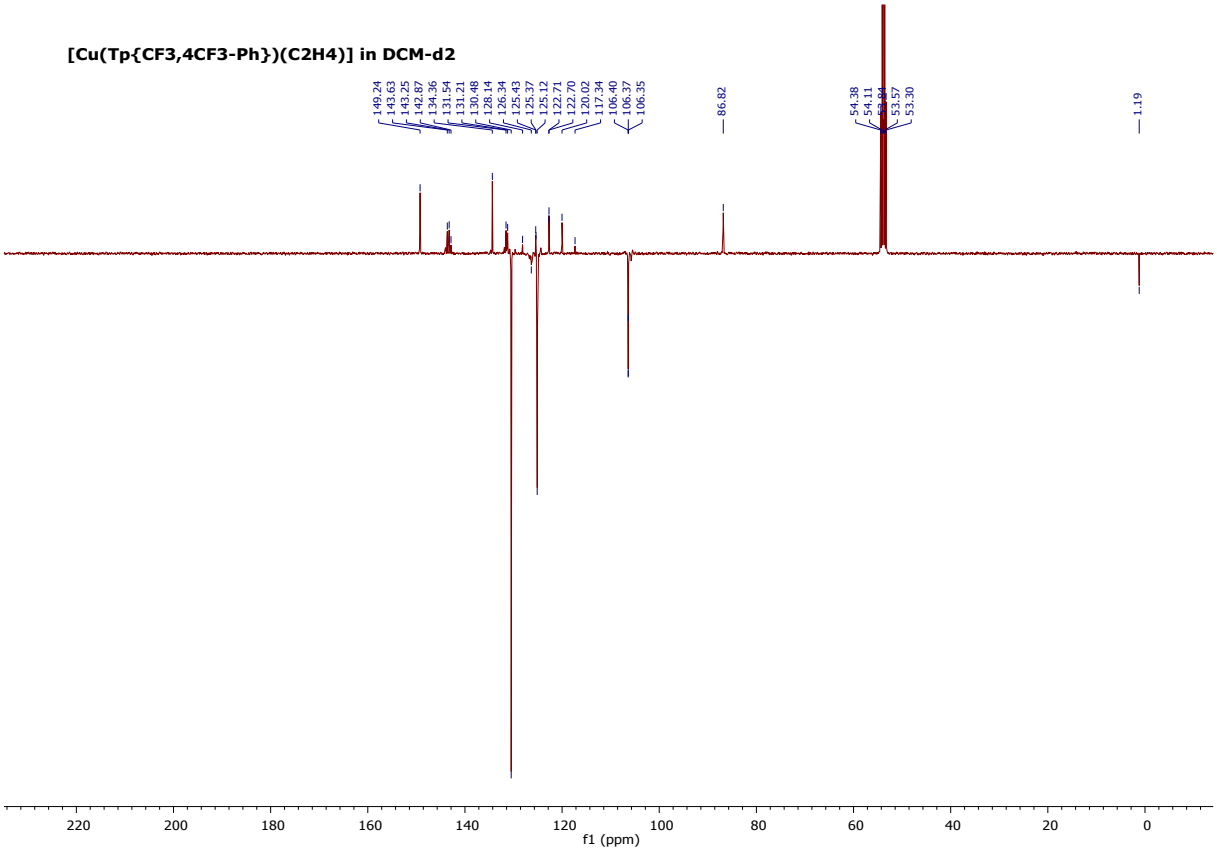
Figure S3. Crystal structures of **5f** (left) and **6f** (right) with displacement ellipsoids plotted at the 50% probability level at 110(2) K. For clarity hydrogen atoms and disordered fragments have been omitted.

^{1}H and ^{13}C NMR spectra of the copper compounds 5a', 5b-g, 6a', 6b-g

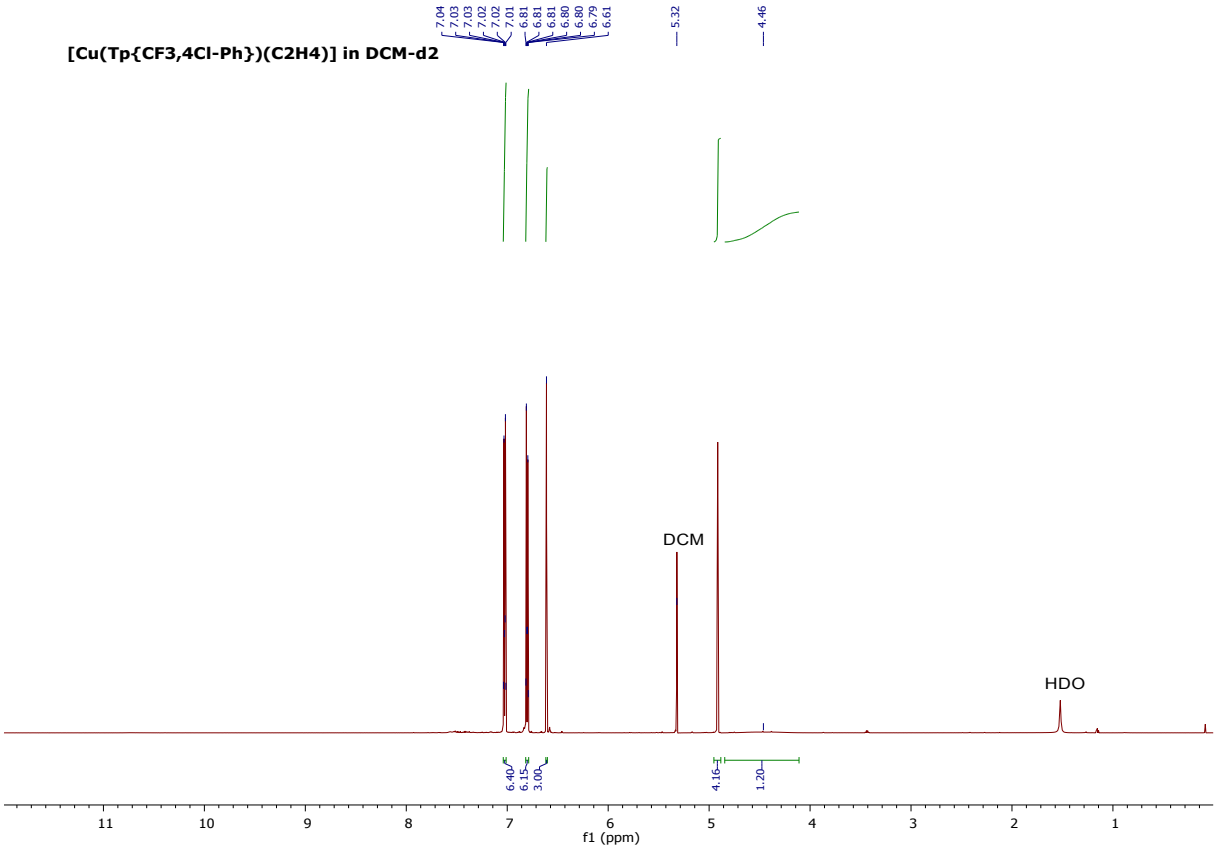




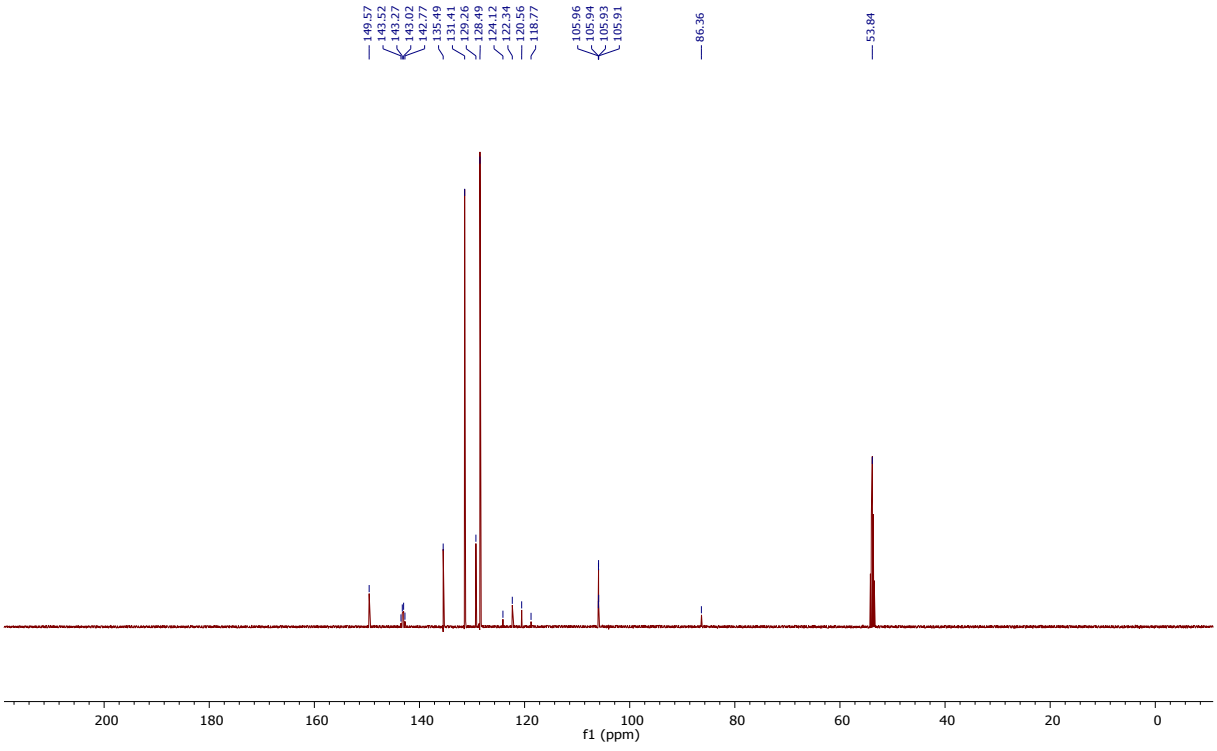

[Cu(Tp{CF3,4CF3-Ph})(C2H4)] in DCM-d2
7.23
7.21
7.01
6.99
6.69
5.33
5.32
5.32 CD2Cl2
5.32
5.32
4.96
4.45
0.09
0.09
0.08
Silicone
Grease
6.20
6.16
2.80
3.74
1.10
f1 (ppm)

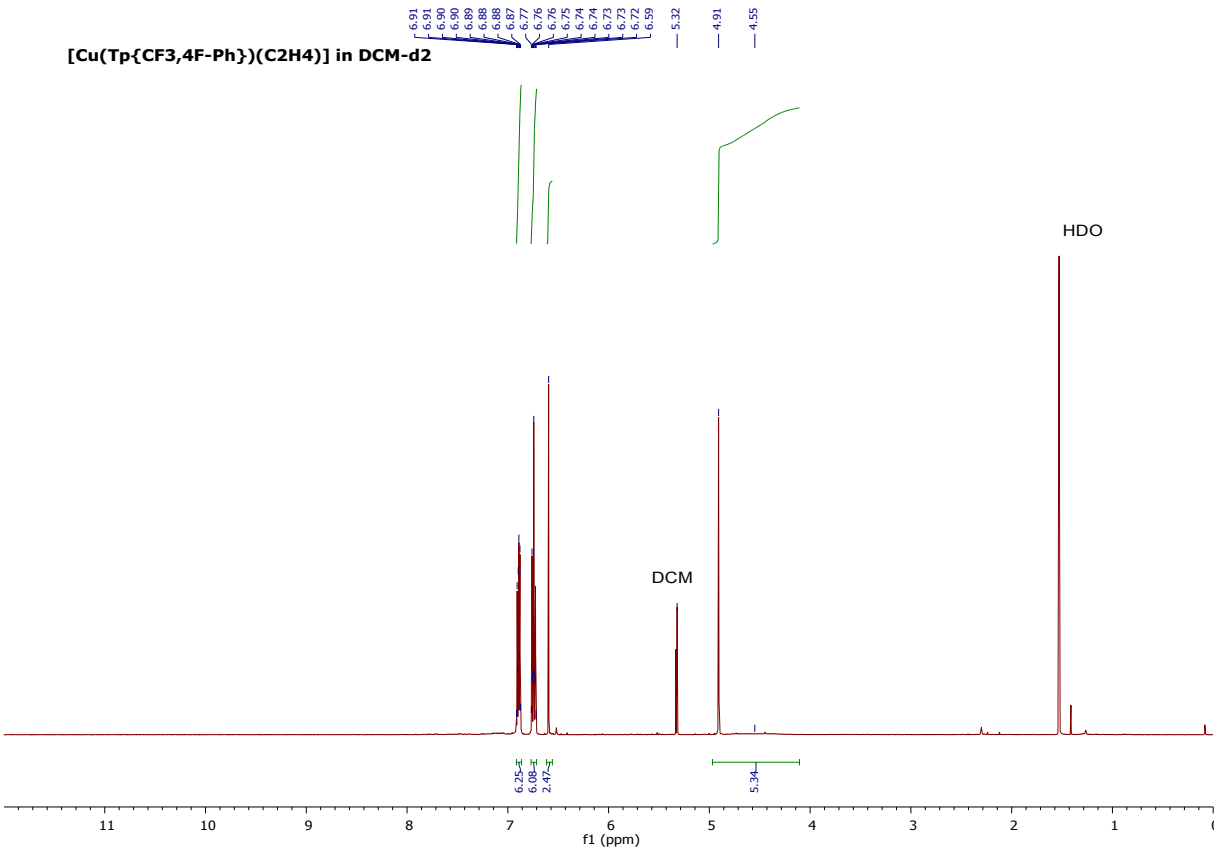

[Cu(Tp{CF3,4CF3-Ph})(C2H4)] in DCM-d2
149.24
143.63
143.25
142.87
134.36
131.54
131.21
130.48
128.14
126.34
125.43
125.37
125.12
122.71
122.70
120.02
117.34
106.40
106.37
106.35
86.82
54.38
54.11
53.84
53.57
53.30
1.19
f1 (ppm)

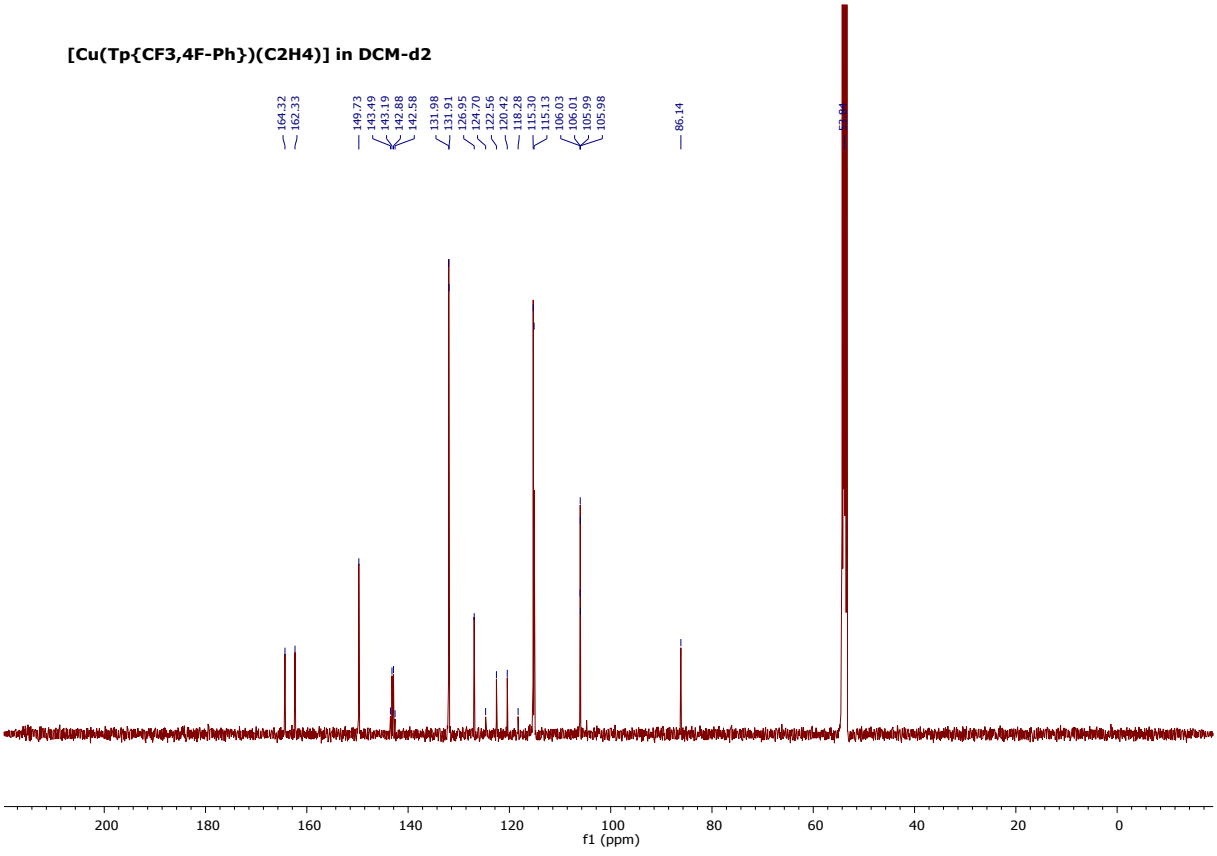
[Cu(Tp{CF3,4Cl-Ph})(C2H4)] in DCM-d2



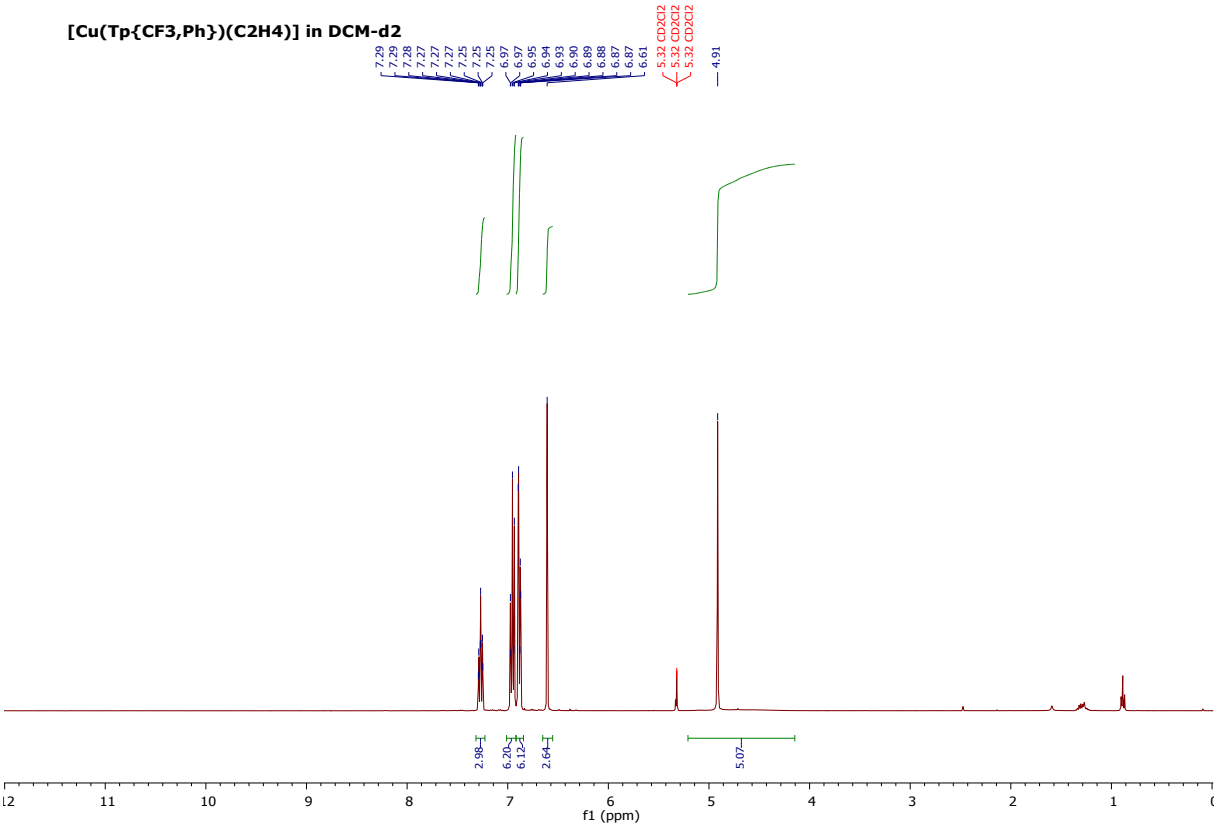
[Cu(Tp{CF3,4Cl-Ph})(C2H4)] in DCM-d2



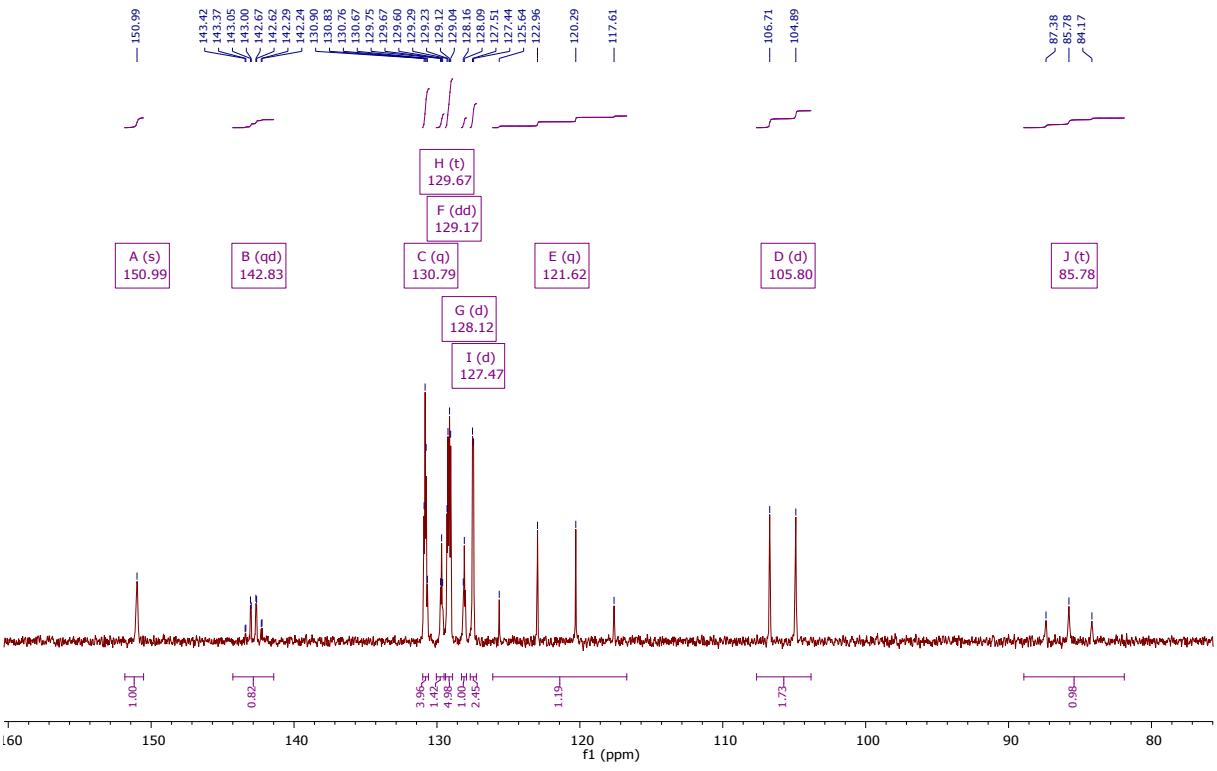

[Cu(Tp{CF3,4F-Ph})(C2H4)] in DCM-d2
6.91
6.91
6.90
6.90
6.89
6.88
6.88
6.87
6.77
6.76
6.76
6.75
6.74
6.74
6.73
6.73
6.72
6.59
5.32
4.91
4.55
HDO
DCM
6.25
6.08
2.47
5.34
11
10
9
8
7
6
5
4
3
2
1
f1 (ppm)

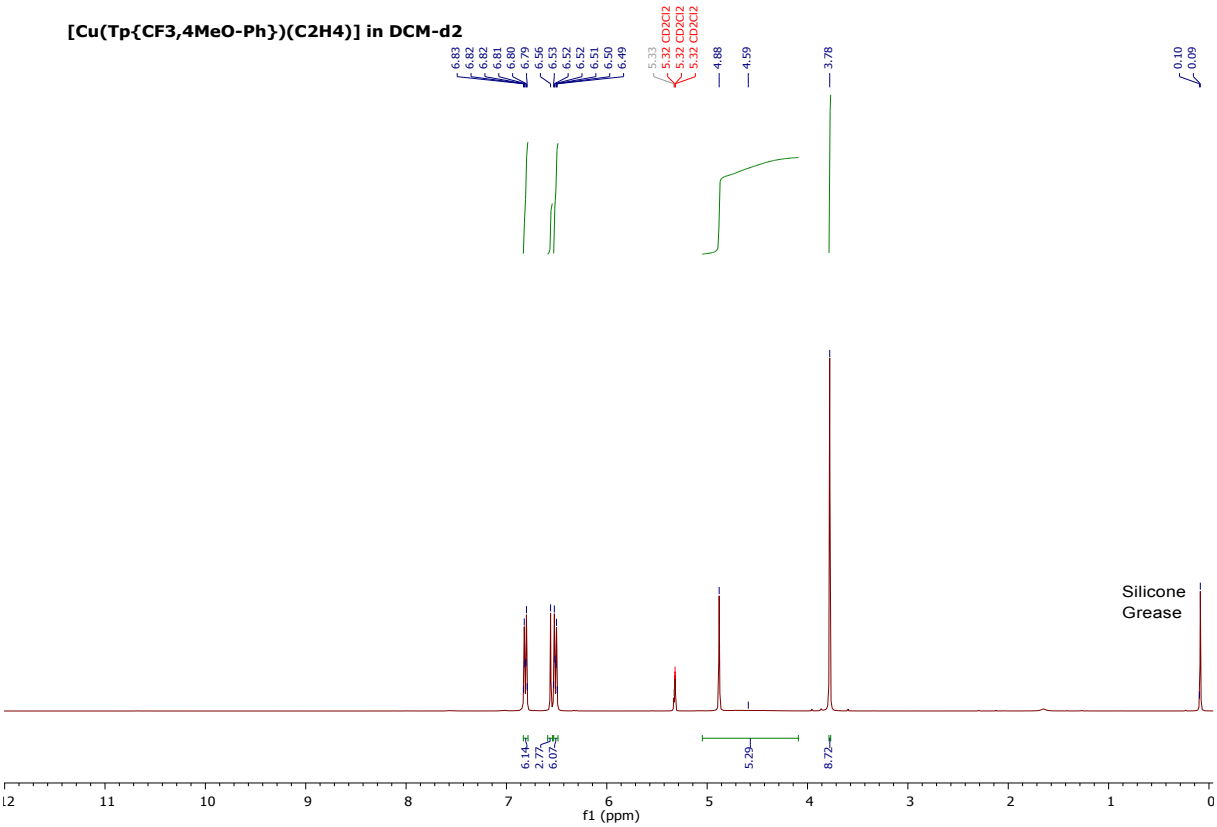

[Cu(Tp{CF3,4F-Ph})(C2H4)] in DCM-d2
164.32
162.33
149.73
143.49
143.19
142.88
142.58
131.98
131.91
126.95
124.70
122.56
120.42
118.28
115.30
115.13
106.03
106.01
105.99
105.98
86.14
53.84
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

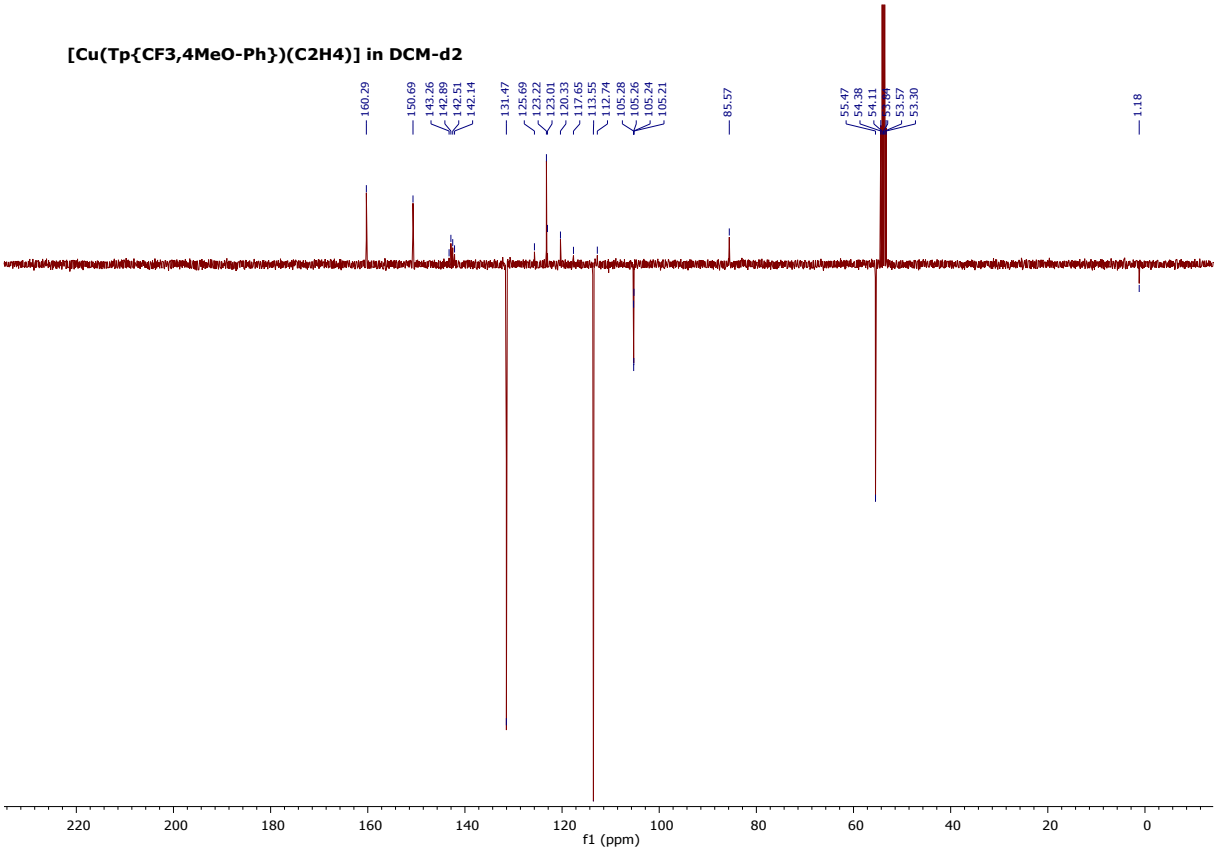
[Cu(Tp{CF3,Ph})(C2H4)] in DCM-d2

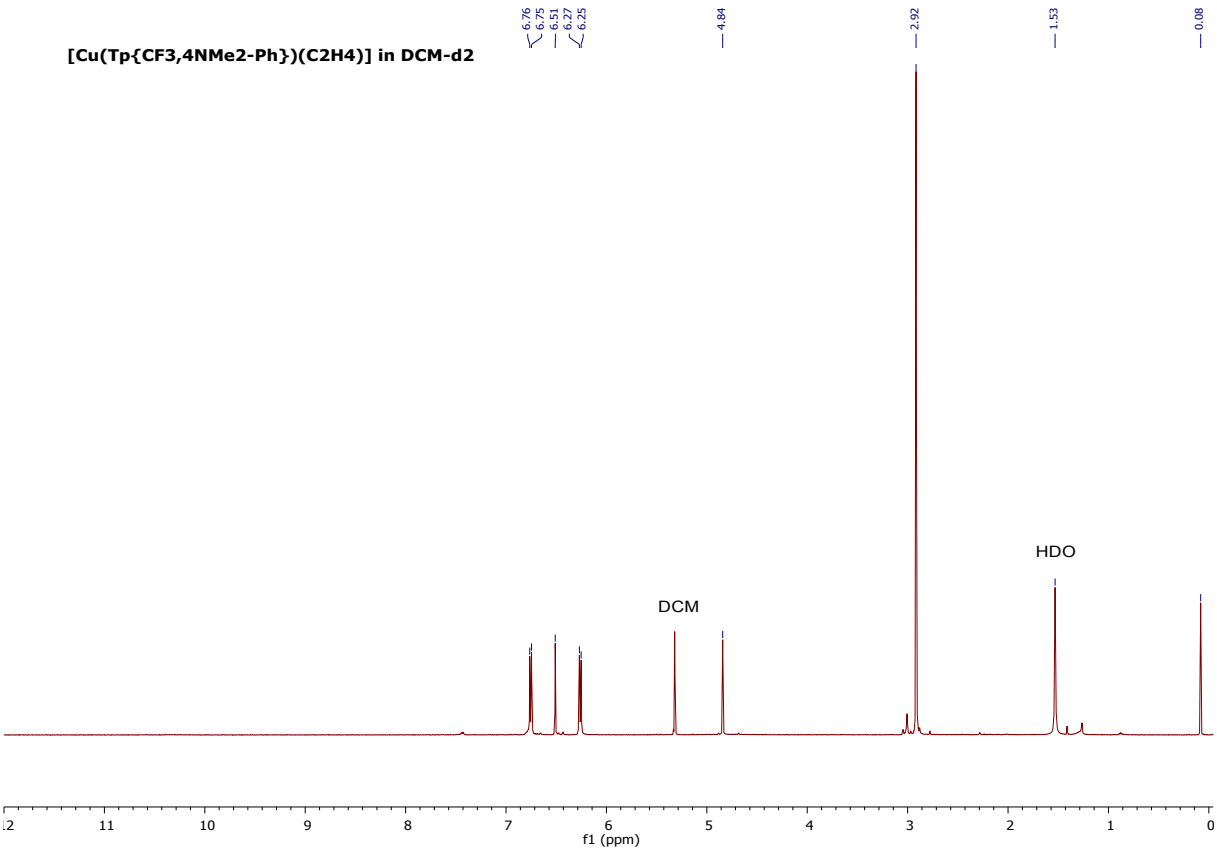


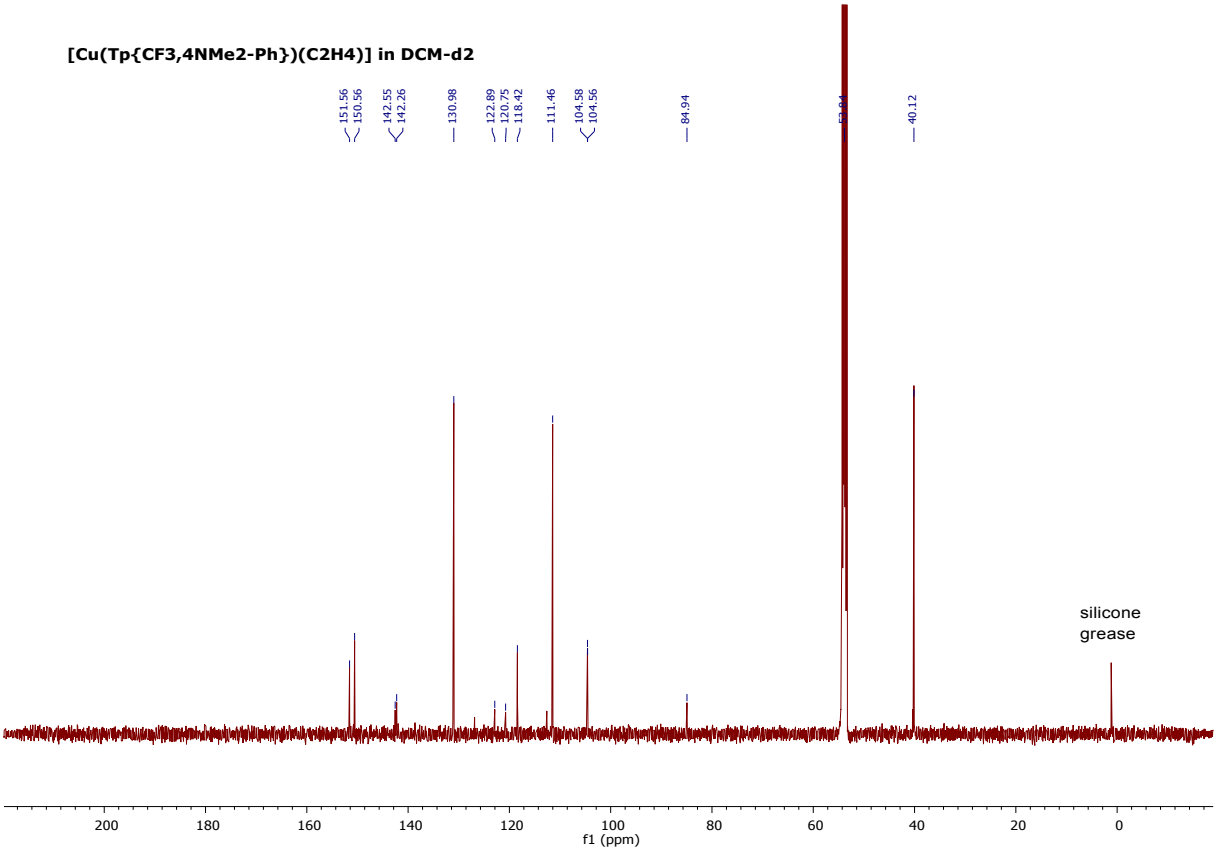
[Cu(Tp{CF3,Ph})(C2H4)] in DCM-d2



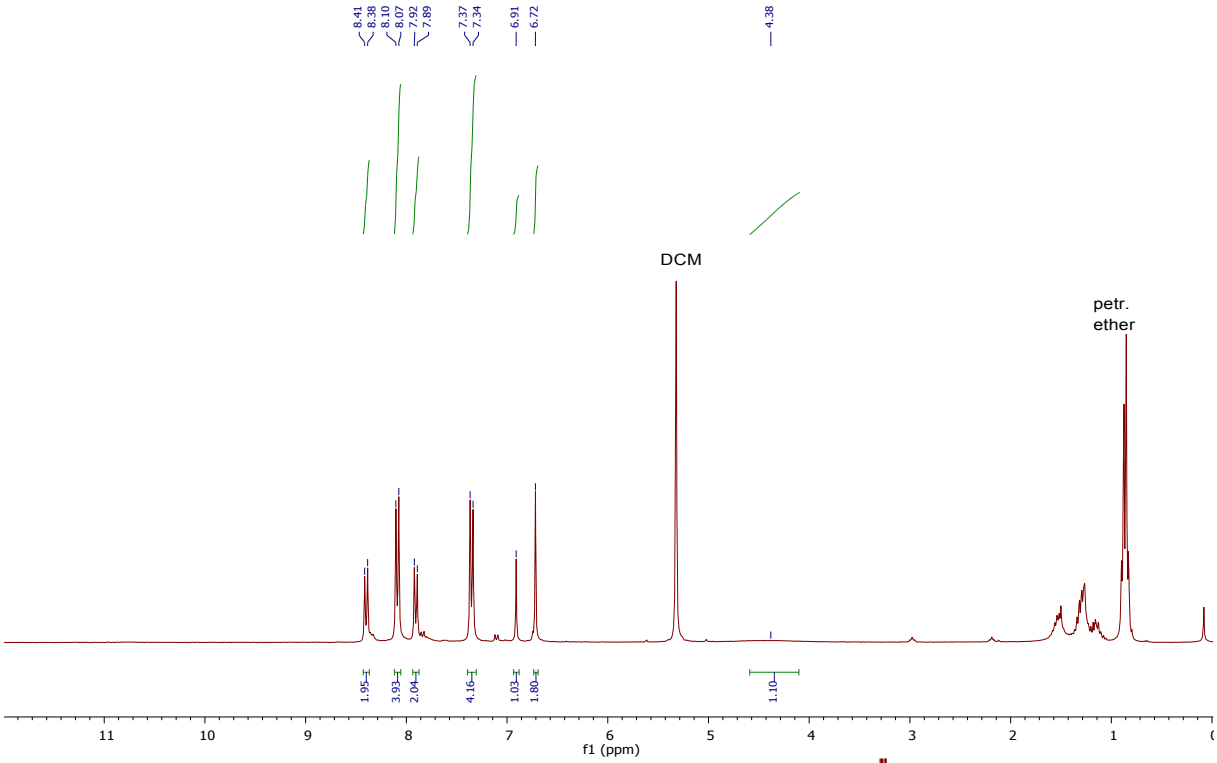

[Cu(Tp{CF3,4MeO-Ph})(C2H4)] in DCM-d2
6.83
6.82
6.82
6.81
6.80
6.79
6.56
6.53
6.52
6.52
6.51
6.50
6.49
5.33
5.32 CD2Cl2
5.32 CD2Cl2
5.32 CD2Cl2
4.88
4.59
3.78
0.10
0.09
Silicone
Grease
6.14
2.77
6.07
5.29
8.72
f1 (ppm)


[Cu(Tp{CF3,4MeO-Ph})(C2H4)] in DCM-d2
160.29
150.69
143.26
142.89
142.51
142.14
131.47
125.69
123.22
123.01
120.33
117.65
113.55
112.74
105.28
105.26
105.24
105.21
85.57
55.47
54.38
54.11
53.84
53.57
53.30
1.18
f1 (ppm)

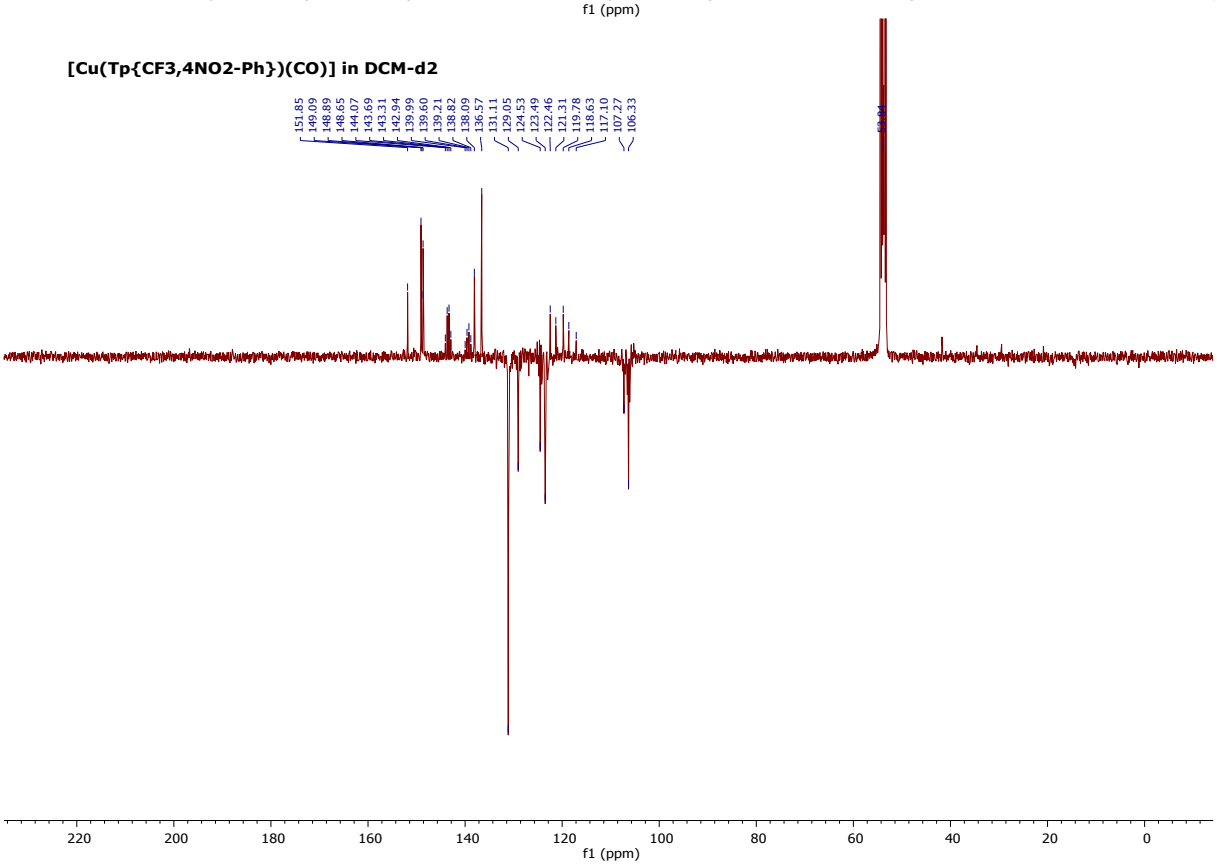

[Cu(Tp{CF3,4NMe2-Ph})(C2H4)] in DCM-d2
6.76
6.75
6.51
6.27
6.25
4.84
2.92
1.53
0.08
DCM
HDO
f1 (ppm)


[Cu(Tp{CF3,4NMe2-Ph})(C2H4)] in DCM-d2
151.56
150.56
142.55
142.26
130.98
122.89
120.75
118.42
111.46
104.58
104.56
84.94
40.12
silicone
grease
f1 (ppm)

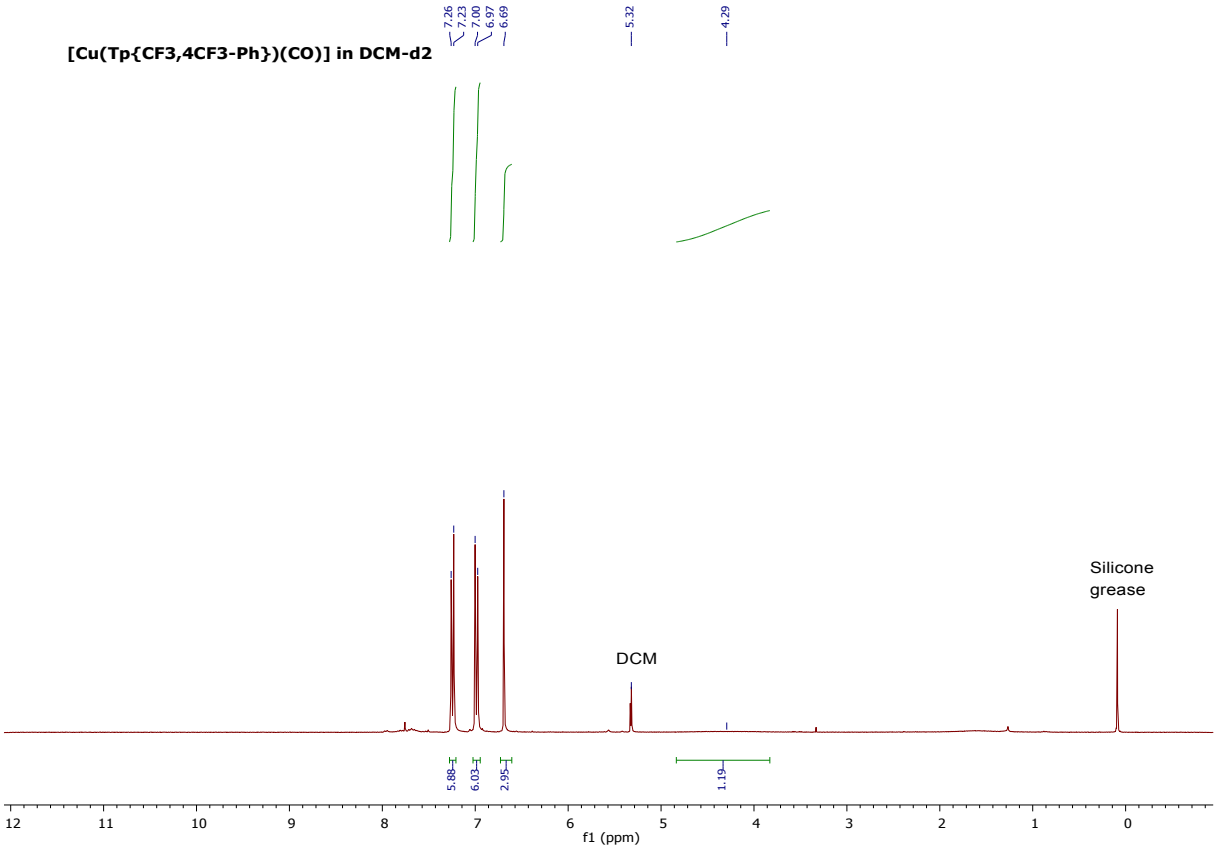
asymm. [Cu(Tp{CF3,4NO2-Ph})(CO)] in DCM-d2



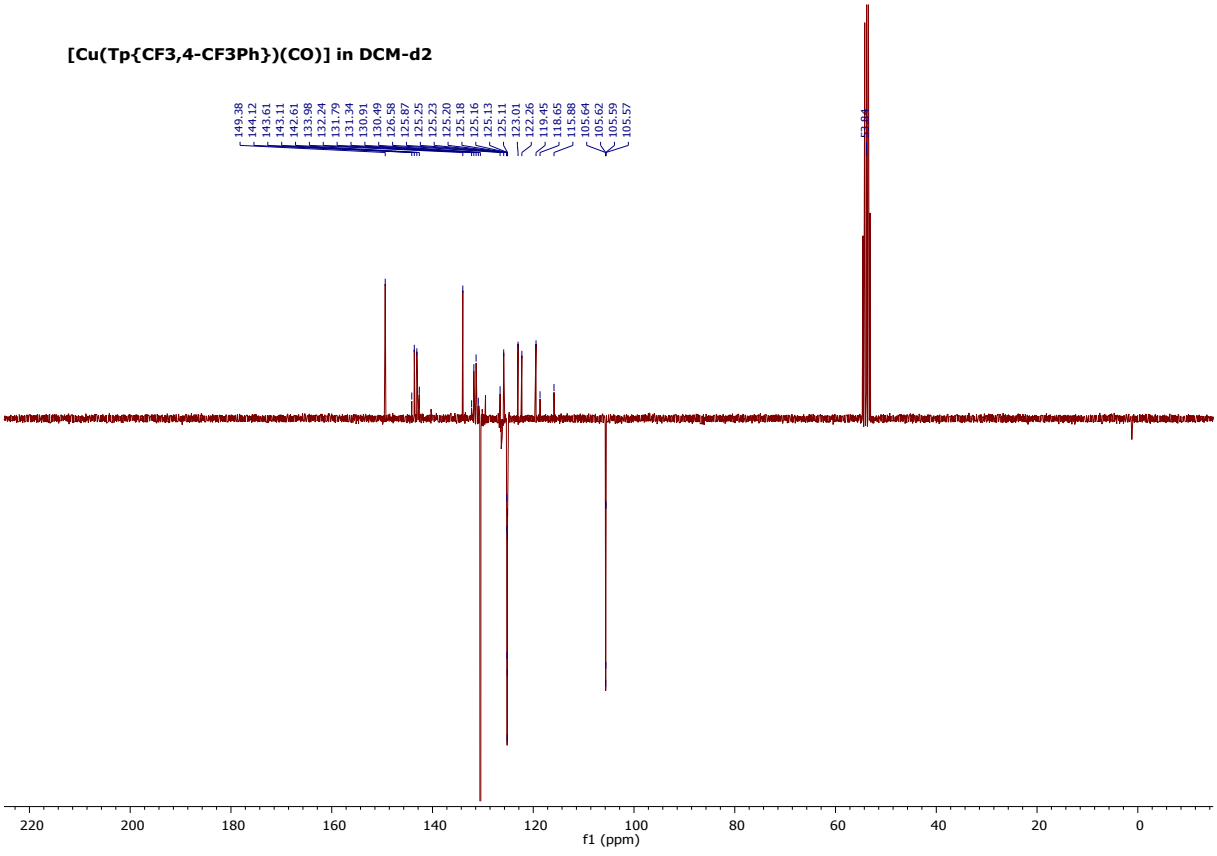
[Cu(Tp{CF3,4NO2-Ph})(CO)] in DCM-d2

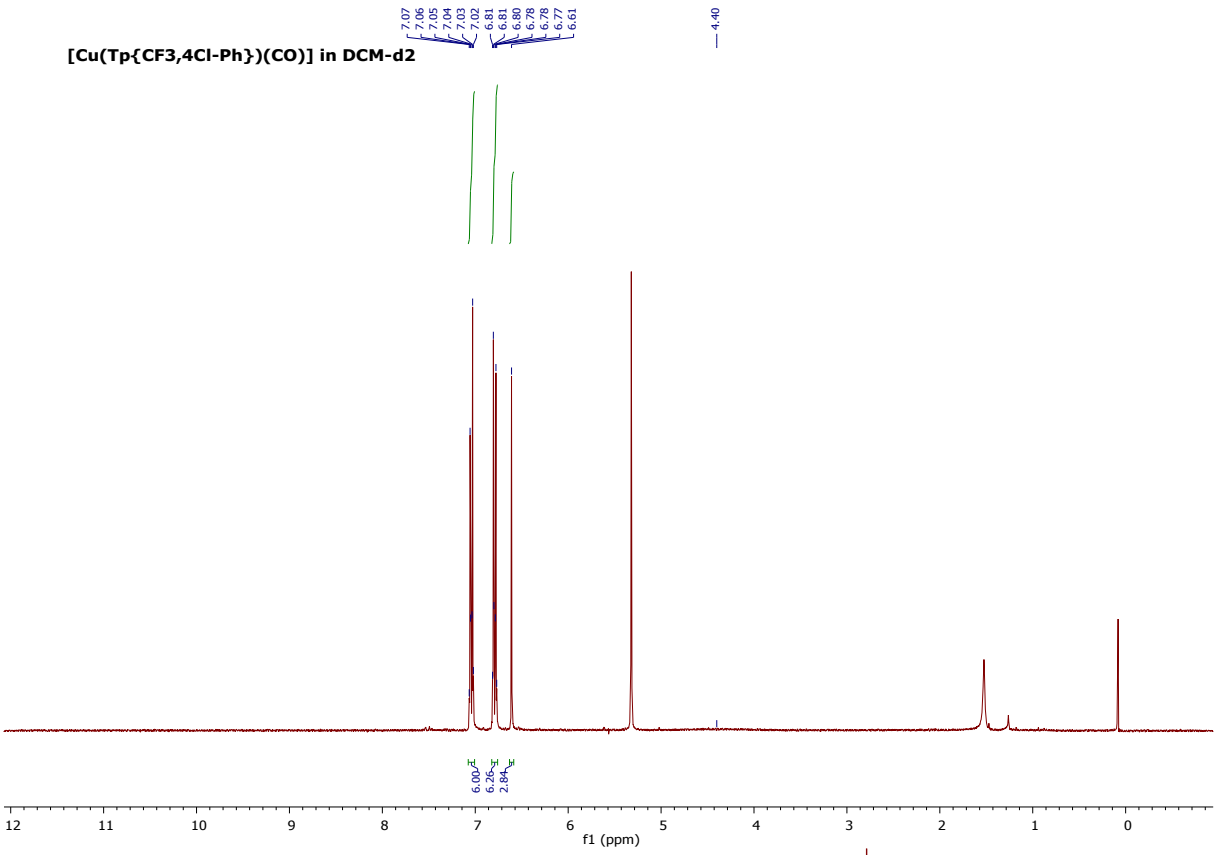


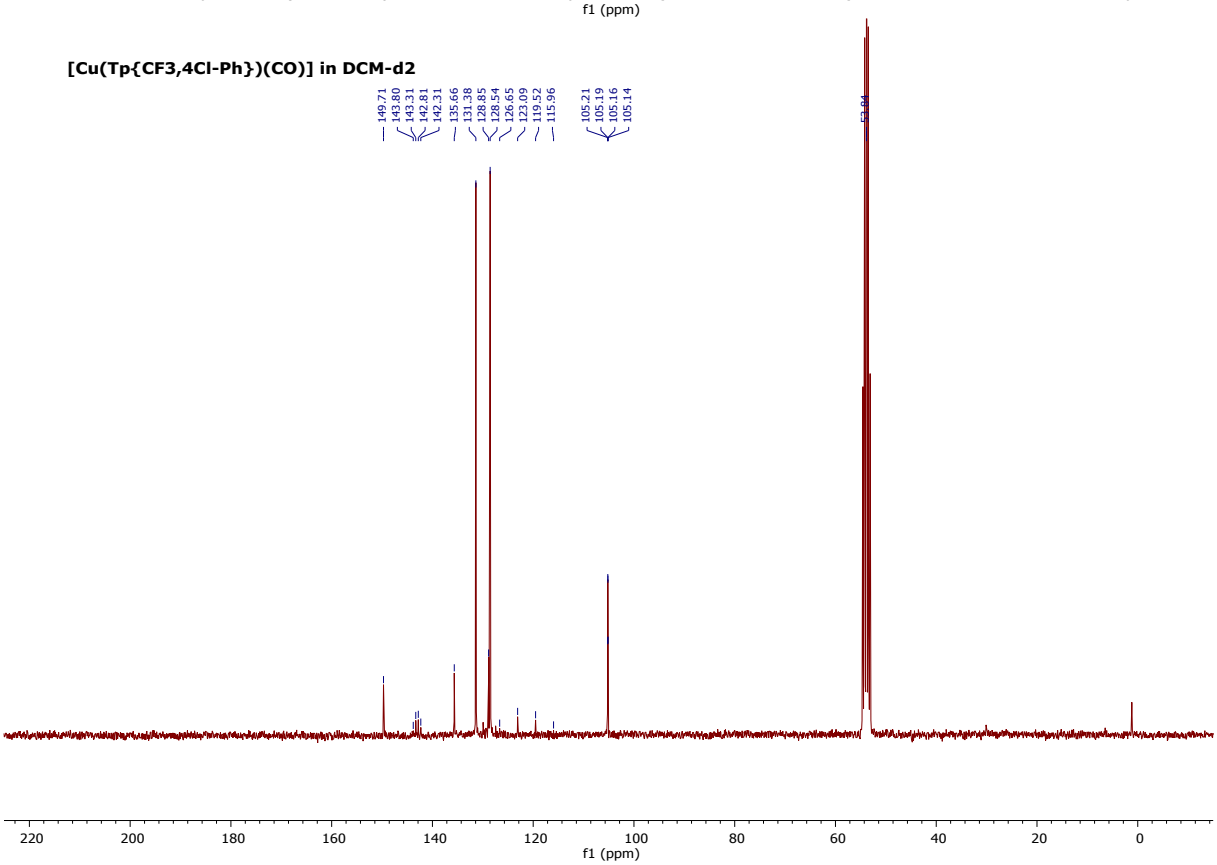
[Cu(Tp{CF3,4CF3-Ph})(CO)] in DCM-d2

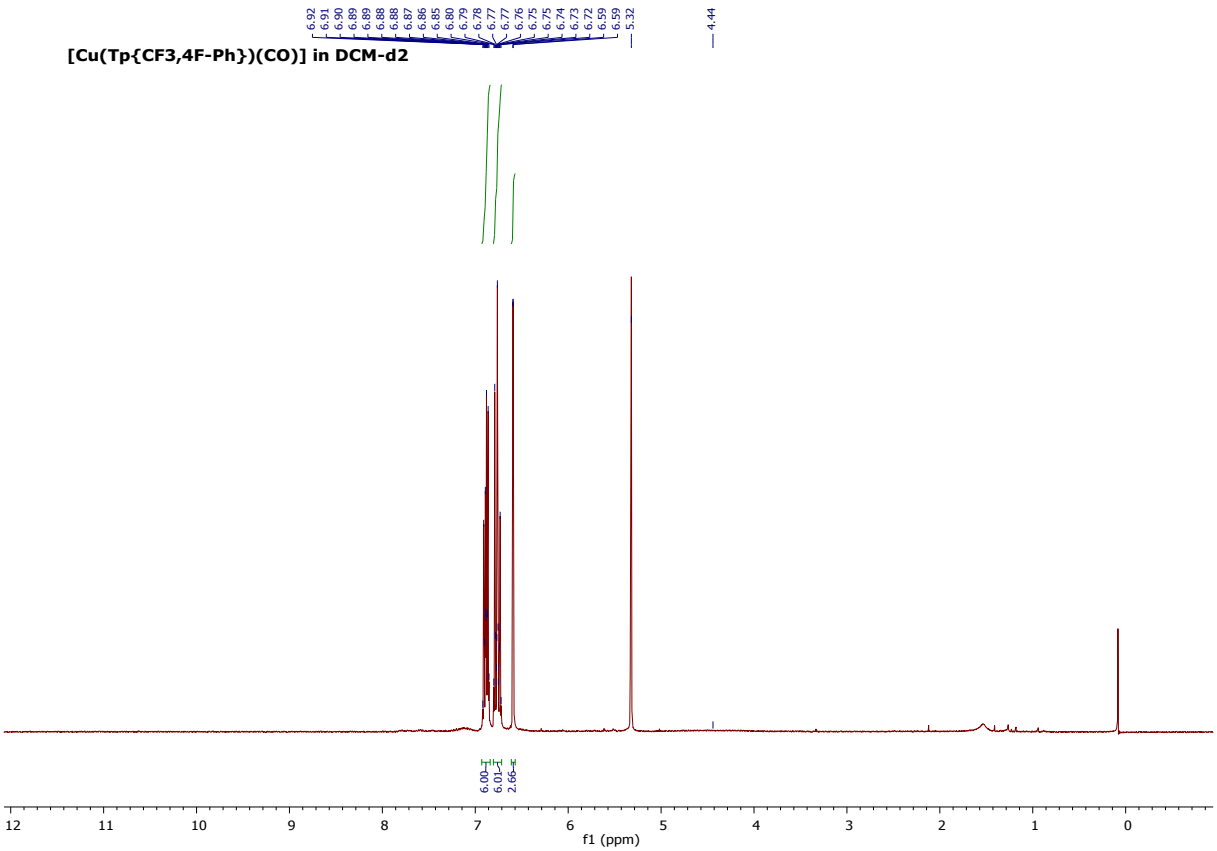


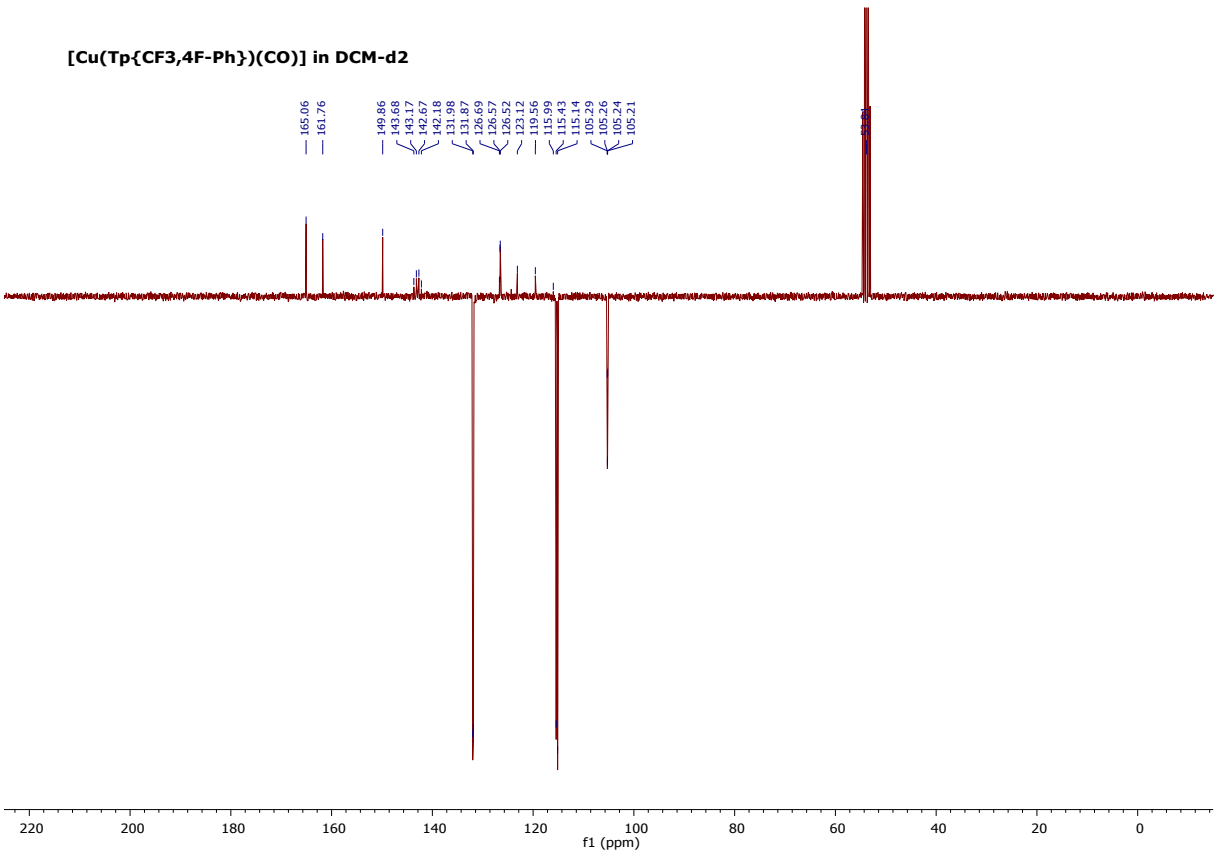
[Cu(Tp{CF3,4-CF3Ph})(CO)] in DCM-d2



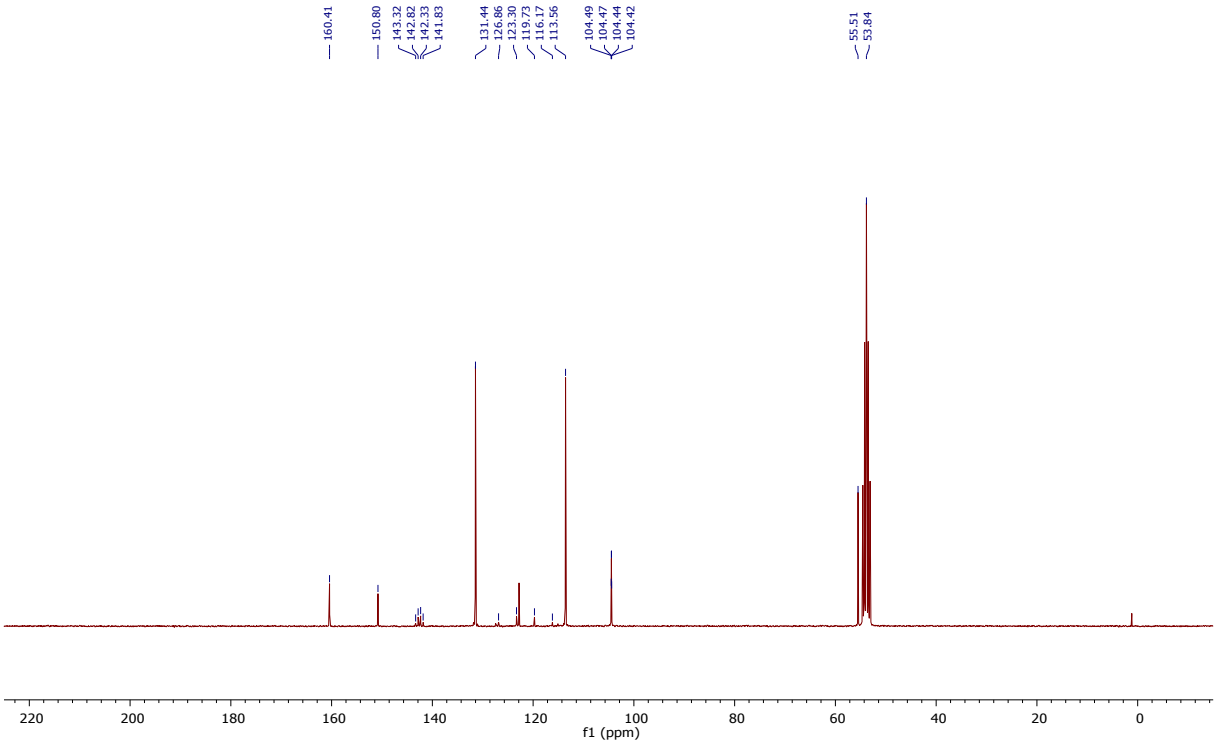

[Cu(Tp{CF3,4Cl-Ph})(CO)] in DCM-d2
7.07
7.06
7.05
7.04
7.03
7.02
6.81
6.80
6.78
6.78
6.77
6.61
4.40
6.00
6.26
2.84
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


[Cu(Tp{CF3,4Cl-Ph})(CO)] in DCM-d2
149.71
143.80
143.31
142.81
142.31
135.66
131.38
128.85
128.54
126.65
123.09
119.52
115.96
105.21
105.19
105.16
105.14
53.94
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

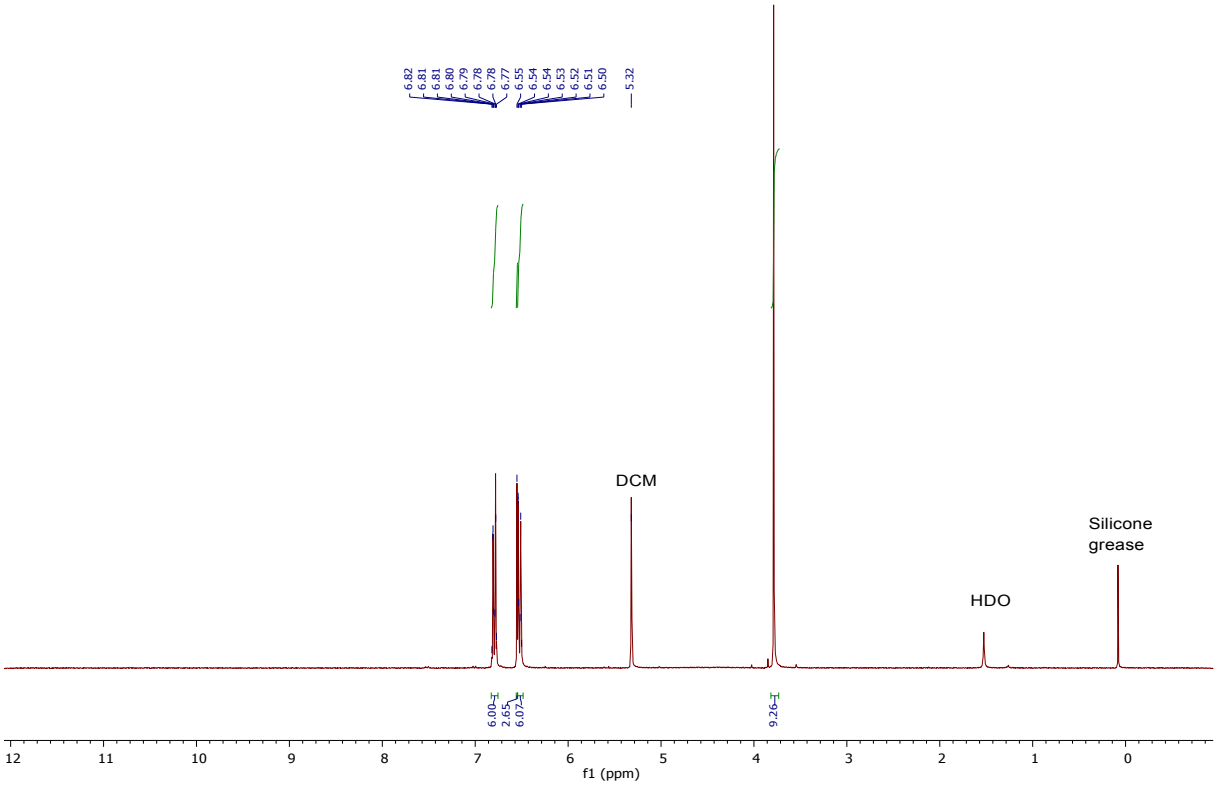

[Cu(Tp{CF3,4F-Ph})(CO)] in DCM-d2
6.92
6.91
6.90
6.89
6.89
6.89
6.88
6.88
6.87
6.86
6.85
6.80
6.79
6.78
6.77
6.77
6.76
6.75
6.75
6.74
6.73
6.72
6.59
6.59
5.32
4.44
6.00
6.01
2.66
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

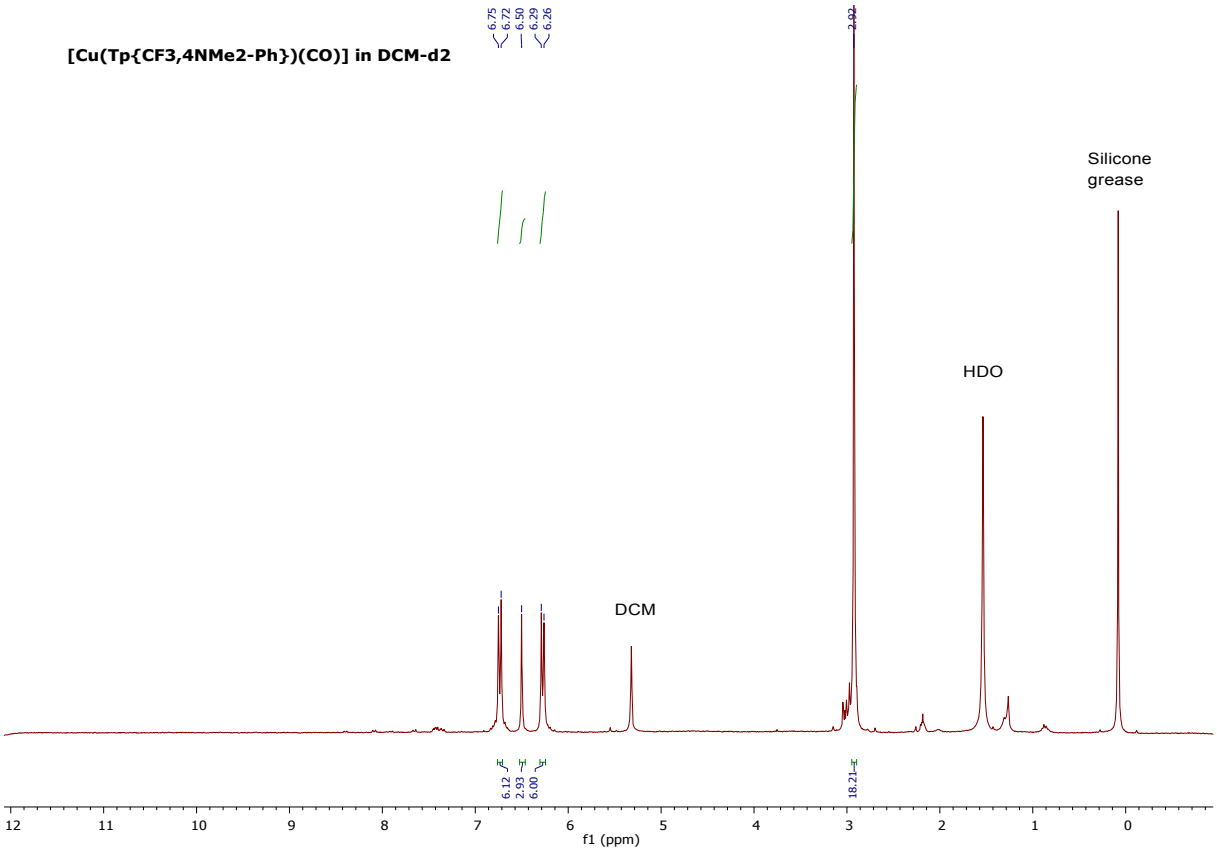

[Cu(Tp{CF3,4F-Ph})(CO)] in DCM-d2
165.06
161.76
149.86
143.68
143.17
142.67
142.18
131.98
131.87
126.69
126.57
126.52
123.12
119.56
115.99
115.43
115.14
105.29
105.26
105.24
105.21
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

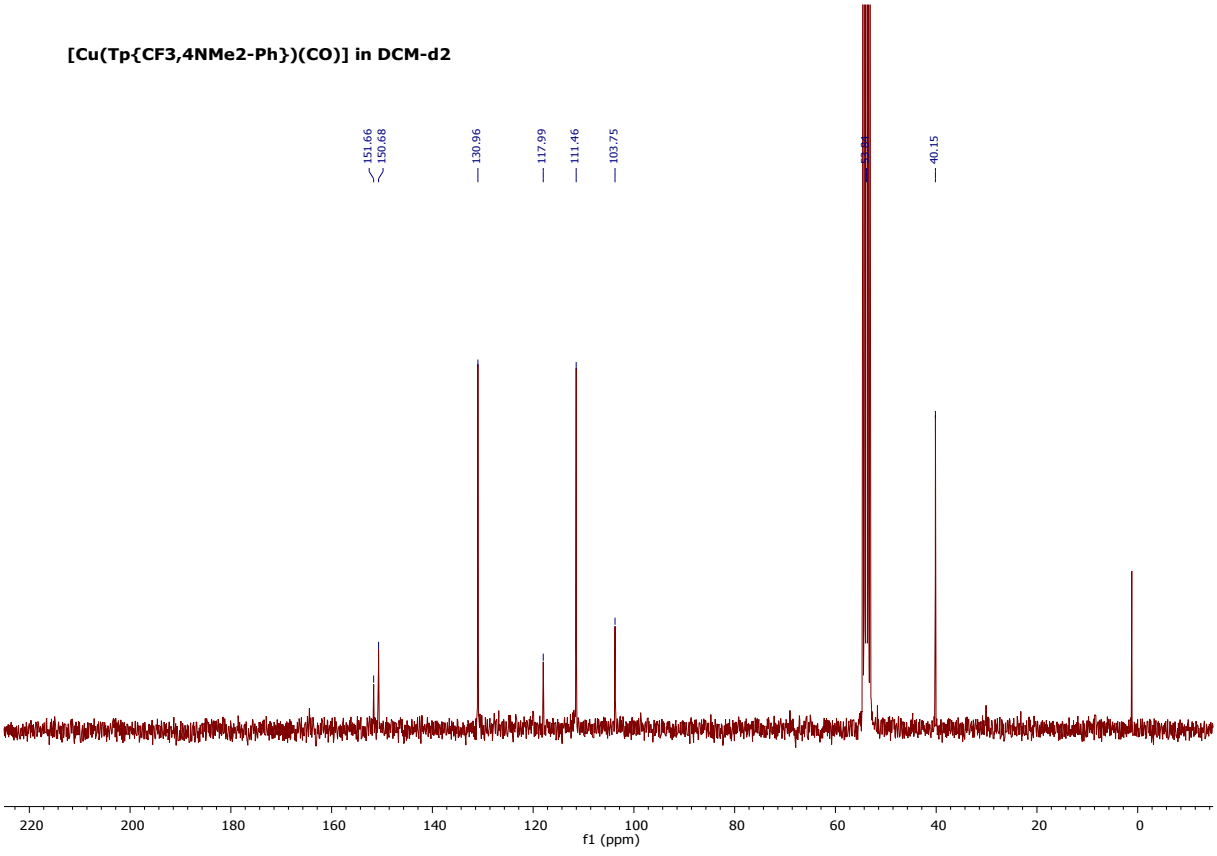
[Cu(Tp{CF3,4MeO-Ph})(CO)] in DCM-d2

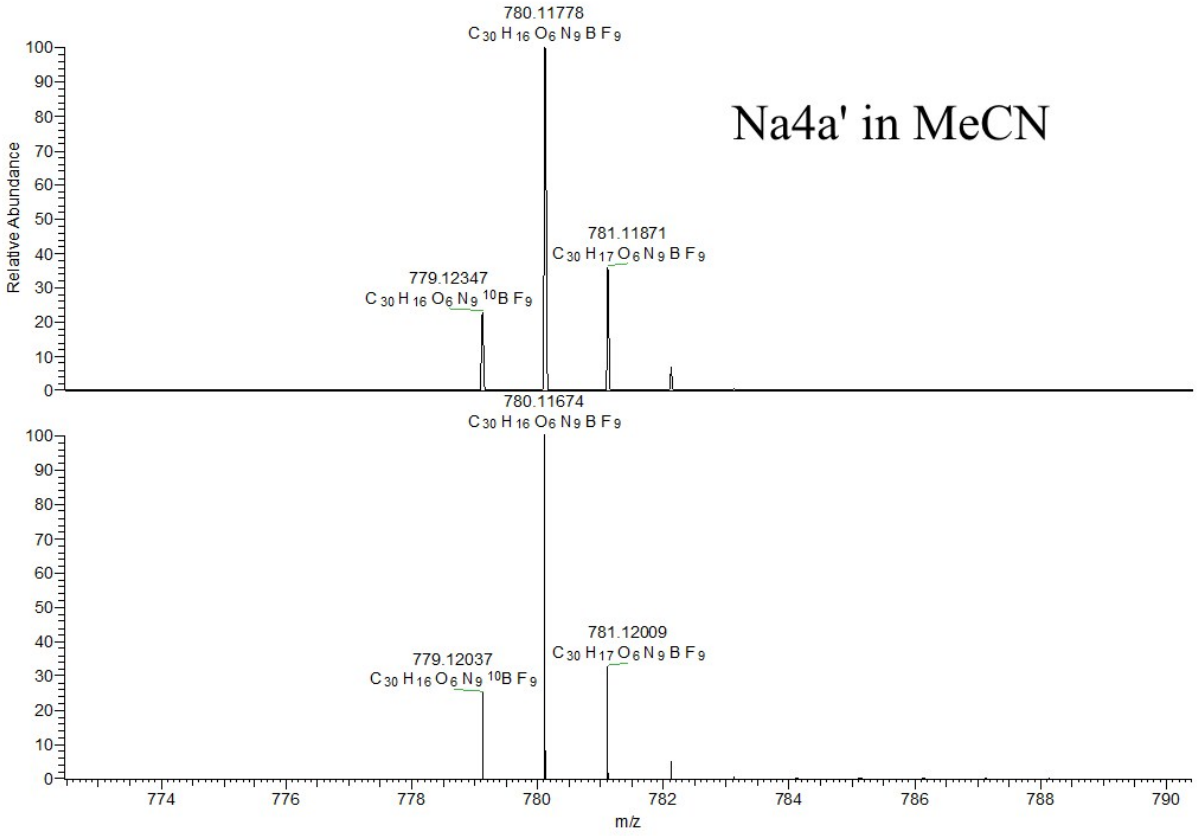


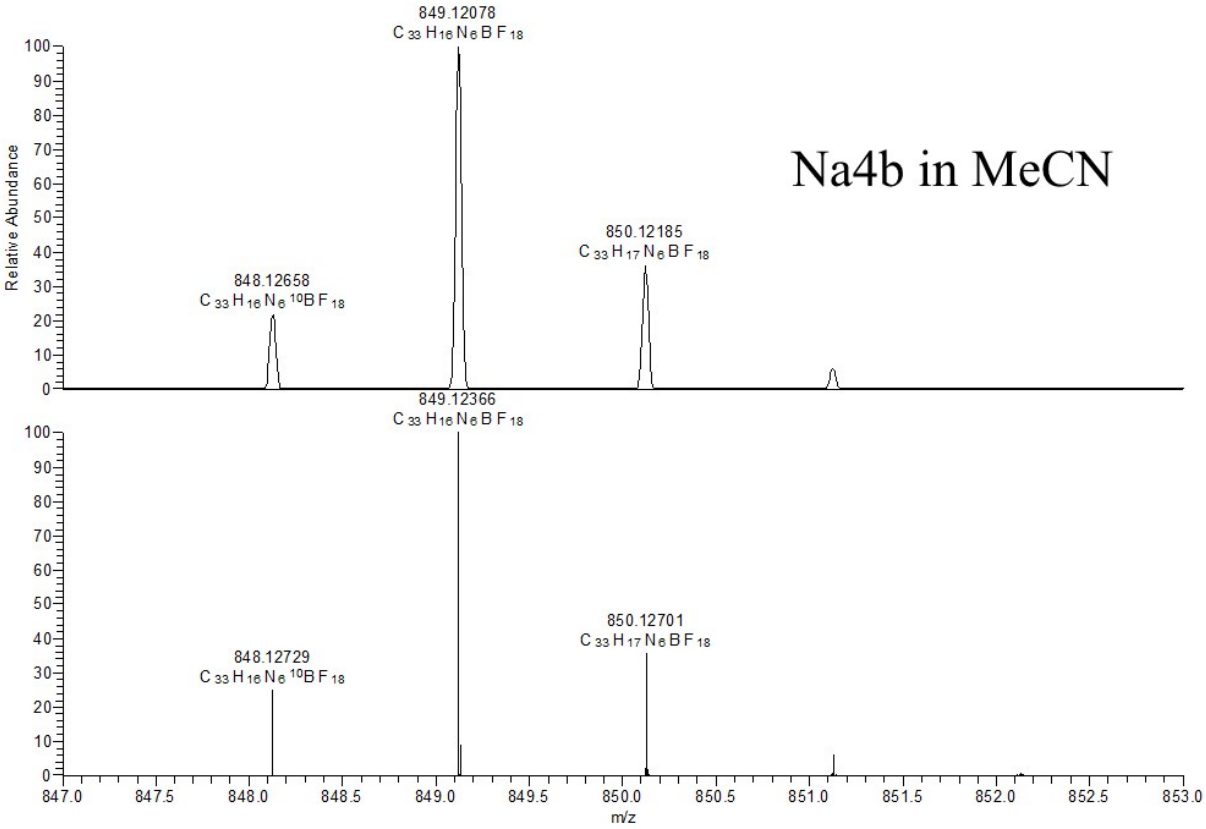
[Cu(Tp{CF3,4MeO-Ph})(CO)] in DCM-d2

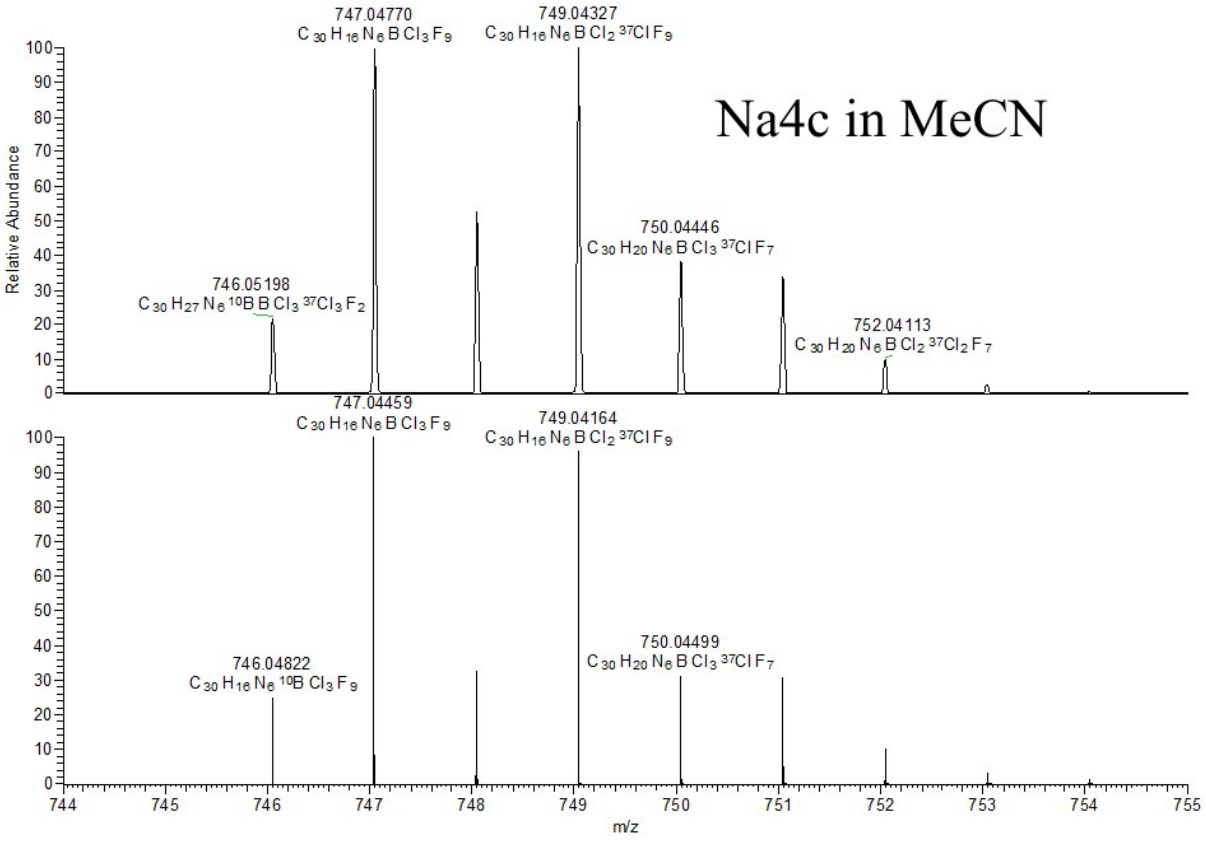


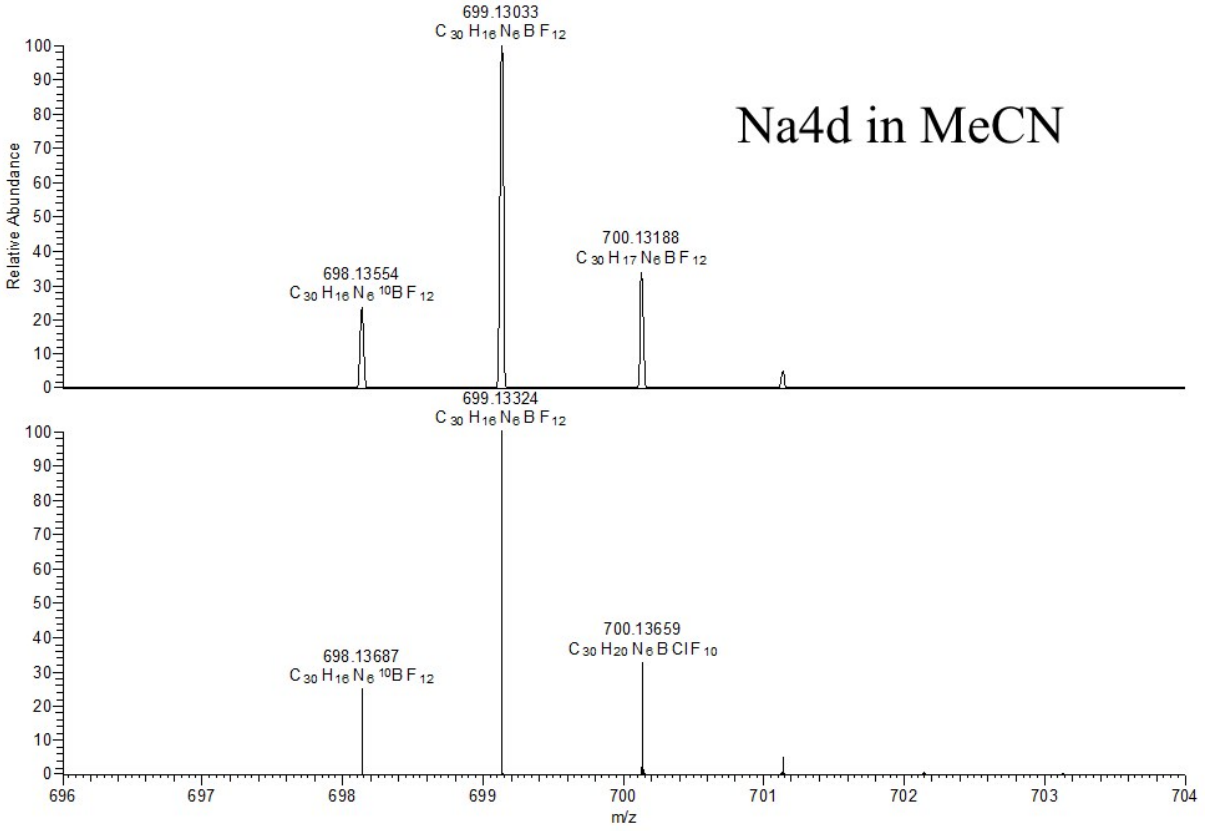

[Cu(Tp{CF3,4NMe2-Ph})(CO)] in DCM-d2
6.75
6.72
6.50
6.29
6.26
2.92
Silicone grease
HDO
DCM
6.12
2.93
6.00
18.21
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

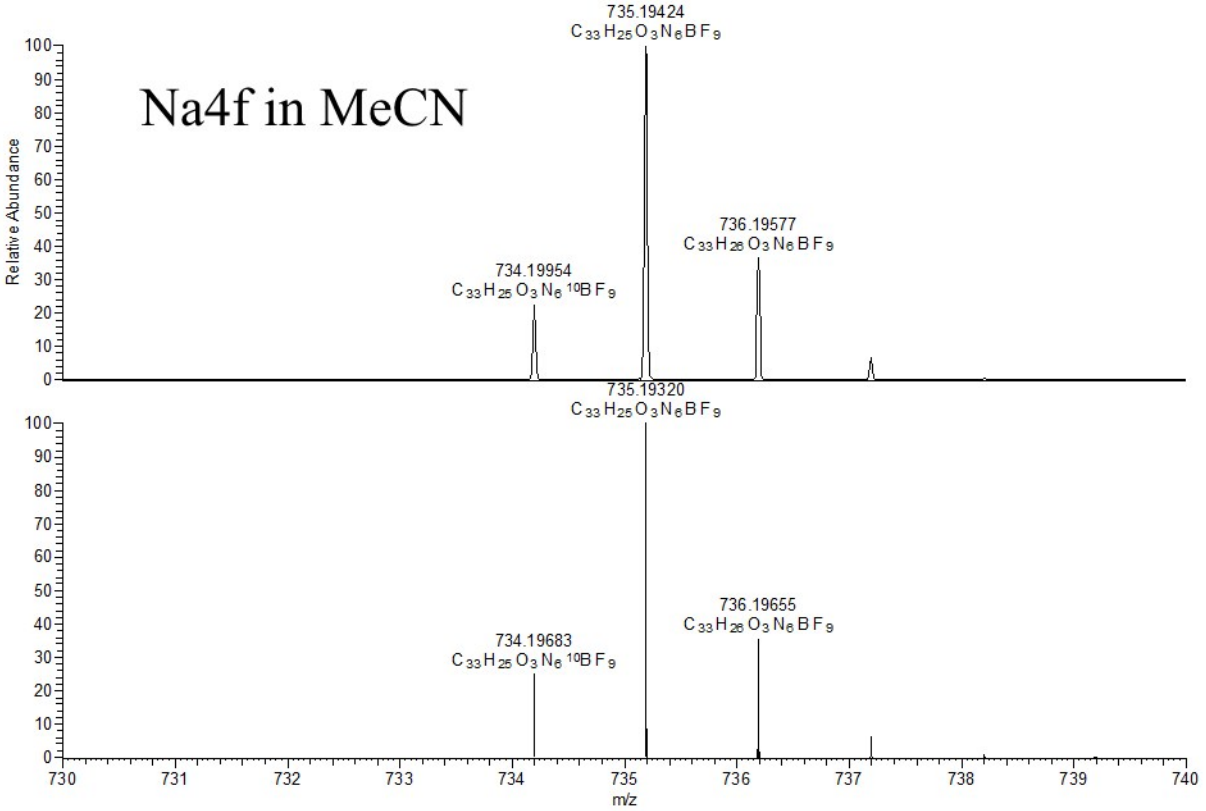

[Cu(Tp{CF3,4NMe2-Ph})(CO)] in DCM-d2
151.66
150.68
130.96
117.99
111.46
103.75
53.01
40.15
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

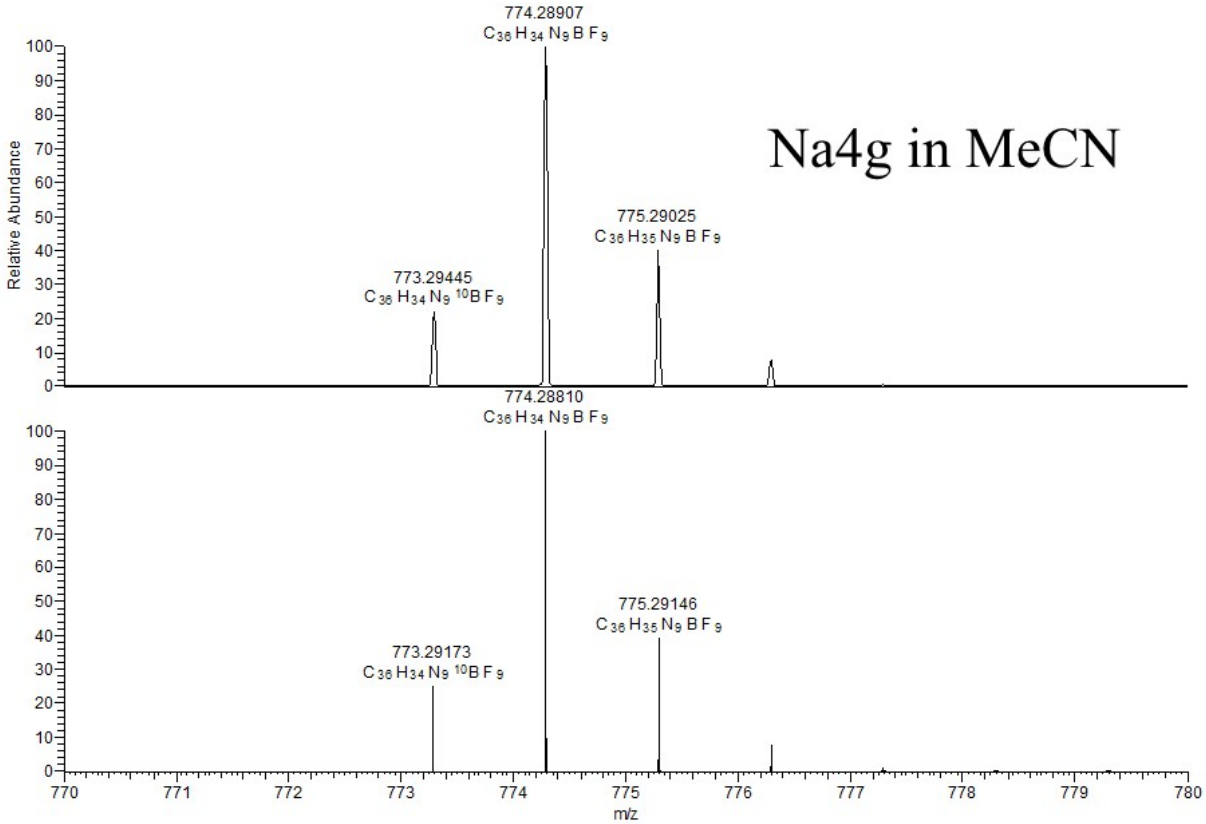

Na4a' in MeCN
780.11778
C30 H16 O6 N9 B F9
781.11871
C30 H17 O6 N9 B F9
779.12347
C30 H16 O6 N9 10B F9
780.11674
C30 H16 O6 N9 B F9
781.12009
C30 H17 O6 N9 B F9
779.12037
C30 H16 O6 N9 10B F9
Relative Abundance
m/z


Na4b in MeCN
849.12078
C33 H16 N6 B F18
850.12185
C33 H17 N6 B F18
848.12658
C33 H16 N6 10B F18
849.12366
C33 H16 N6 B F18
850.12701
C33 H17 N6 B F18
848.12729
C33 H16 N6 10B F18
Relative Abundance
m/z


Na4c in MeCN
747.04770
C 30 H 16 N 6 B Cl 3 F 9
749.04327
C 30 H 16 N 6 B Cl 2 37Cl F 9
750.04446
C 30 H 20 N 6 B Cl 3 37Cl F 7
746.05198
C 30 H 27 N 6 10B B Cl 3 37Cl 3 F 2
752.04113
C 30 H 20 N 6 B Cl 2 37Cl 2 F 7
747.04459
C 30 H 16 N 6 B Cl 3 F 9
749.04164
C 30 H 16 N 6 B Cl 2 37Cl F 9
750.04499
C 30 H 20 N 6 B Cl 3 37Cl F 7
746.04822
C 30 H 16 N 6 10B Cl 3 F 9
Relative Abundance
m/z


Na4d in MeCN
699.13033
C 30 H 16 N 6 B F 12
700.13188
C 30 H 17 N 6 B F 12
698.13554
C 30 H 16 N 6 10B F 12
699.13324
C 30 H 16 N 6 B F 12
700.13659
C 30 H 20 N 6 B Cl F 10
698.13687
C 30 H 16 N 6 10B F 12
Relative Abundance
m/z


Na4f in MeCN
735.19424
C33H25O3N6BF9
736.19577
C33H26O3N6BF9
734.19954
C33H25O3N6 10BF9
735.19320
C33H25O3N6BF9
736.19655
C33H26O3N6BF9
734.19683
C33H25O3N6 10BF9
Relative Abundance
m/z


Na4g in MeCN
774.28907
C36H34N9BF9
775.29025
C36H35N9BF9
773.29445
C36H34N9 10BF9
774.28810
C36H34N9BF9
775.29146
C36H35N9BF9
773.29173
C36H34N9 10BF9
Relative Abundance
m/z