Supporting information

Palladium-Catalysed Direct Arylation of Luminescent Bis-Cyclometalated Iridium (III) Complexes Incorporating *C^N*- or *O^O*-coordinating Thiophene-Based Ligands: an Efficient Method for Color Tuning

Kassem Beydoun,[‡a] Moussa Zaarour,[‡a] J. A. Gareth Williams,[b] Thierry Roisnel,[c] Vincent Dorcet,[c] Aurélien Planchat,[d] Abdou Boucekkine,[a] Denis Jacquemin,*[d,e] Henri Doucet,*[a] Véronique Guerchais*[a]

a K. Beydoun, M. Zaarour, Prof. A. Boucekkine, Dr. H. Doucet,* Dr. V. Guerchais*
UMR-CNRS 6226, Institut des Sciences Chimiques de Rennes
Campus de Beaulieu 35042 Rennes (France)
Tel: (+33)2-23-23-63-84
E-mail: henri.doucet@univ-rennes1.fr; veronique.guerchais@univ-rennes1.fr
‡These authors contributed equally to this work.

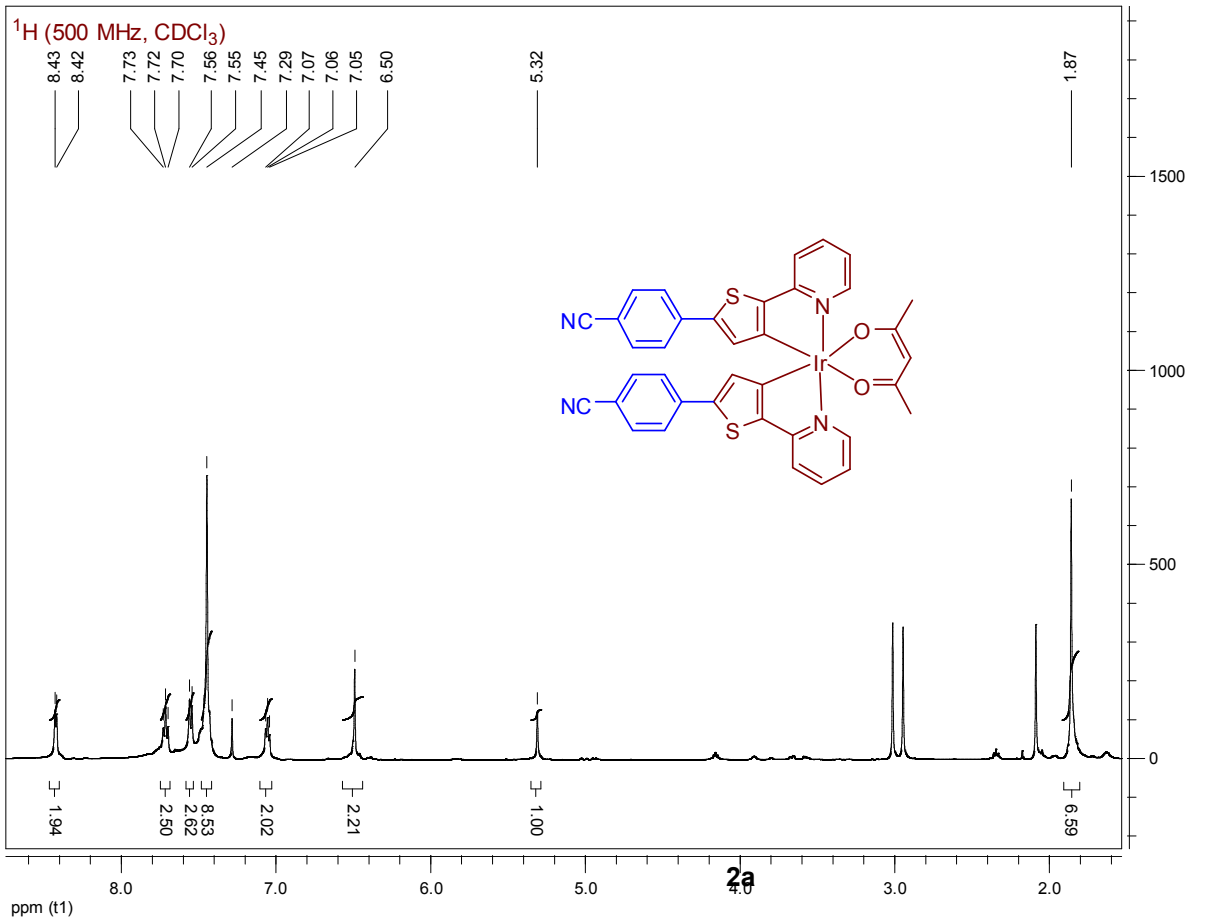
b J. A. G. Williams
Department of Chemistry, Durham University, South Road, Durham, UK DH1 3LE

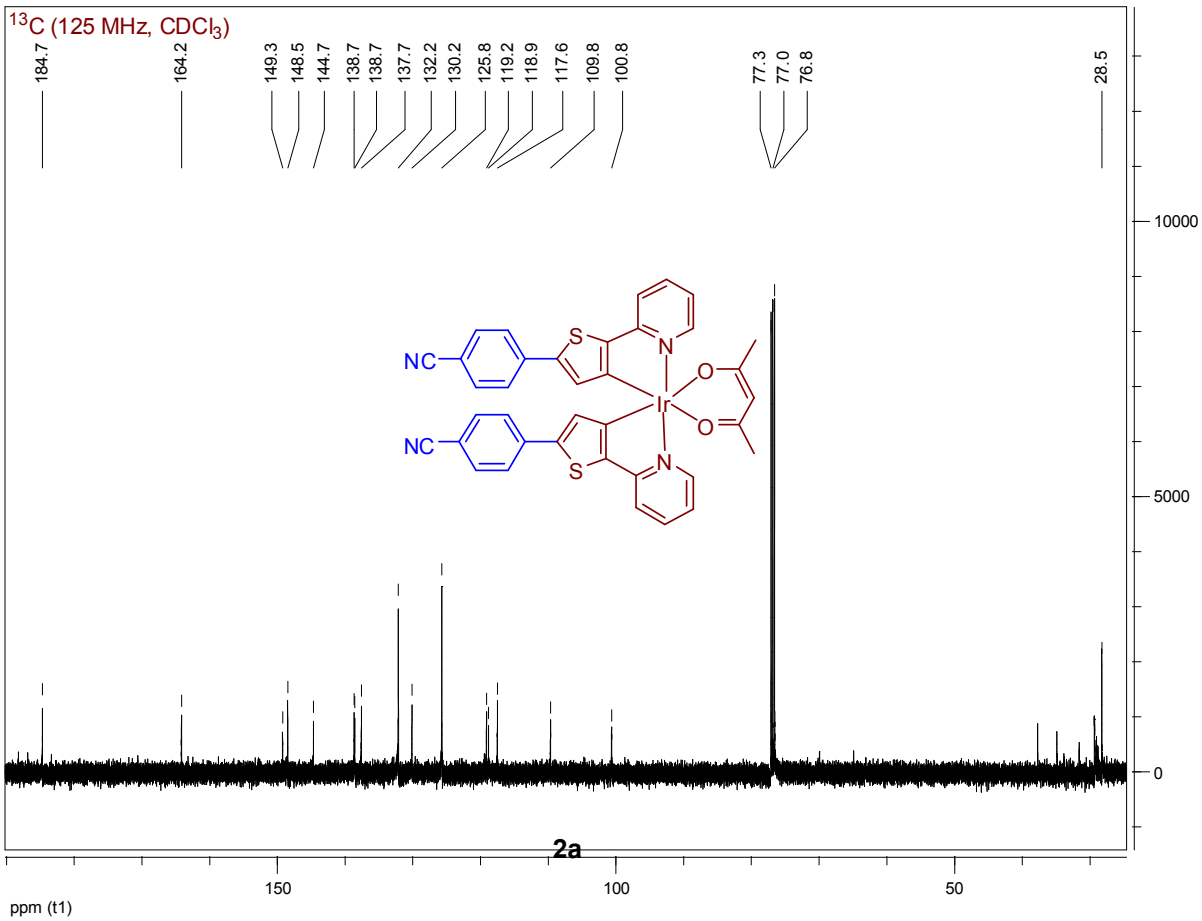
c T. Roisnel, V. Dorcet
Centre de Diffractométrie X, UMR-CNRS 6226, Institut des Sciences Chimiques de Rennes, Campus de Beaulieu 35042 Rennes (France)

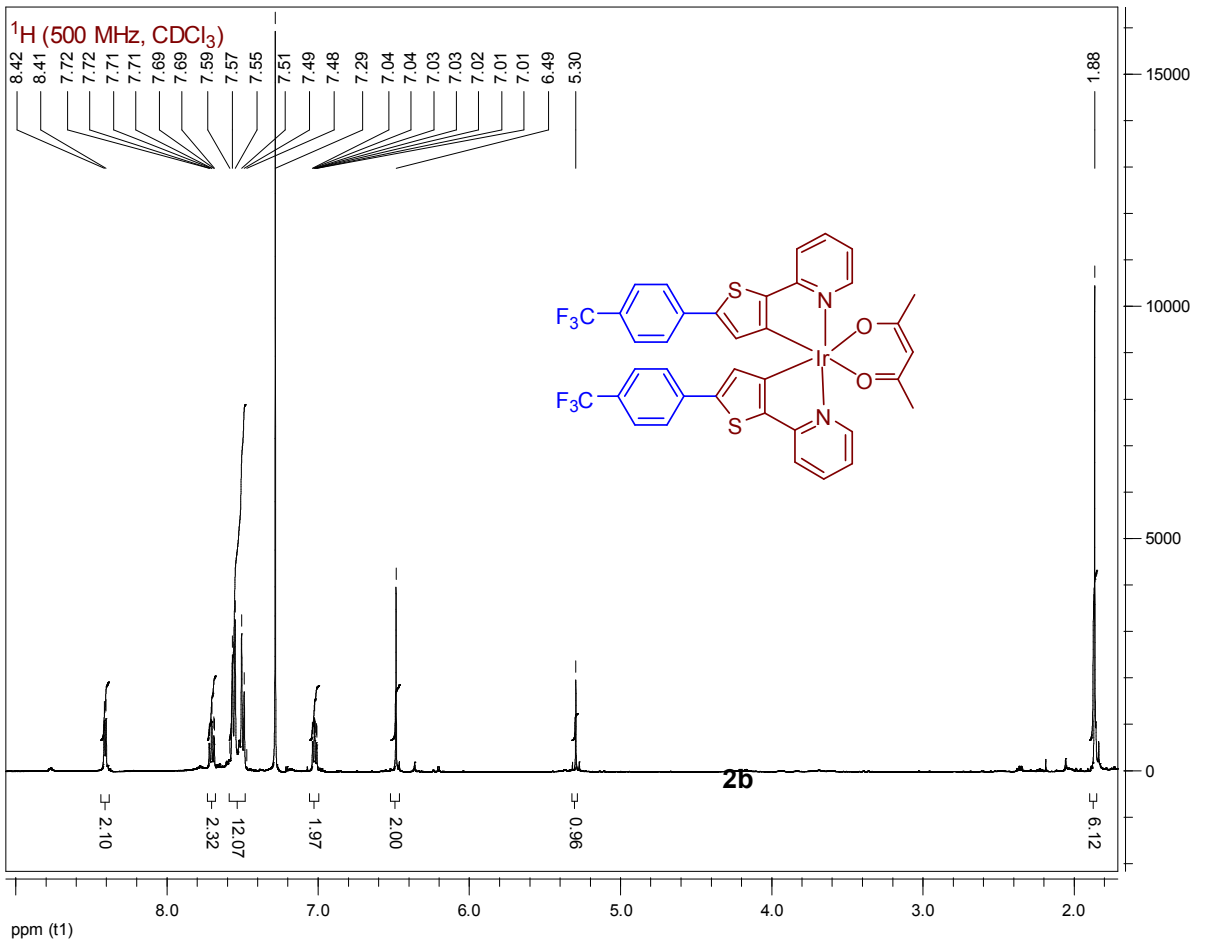
d A. Planchat, Prof. D. Jacquemin
UMR CNRS 6230, Université de Nantes, CEISAM, 2 rue de la Houssinière, 44322 Nantes cedex 3, France

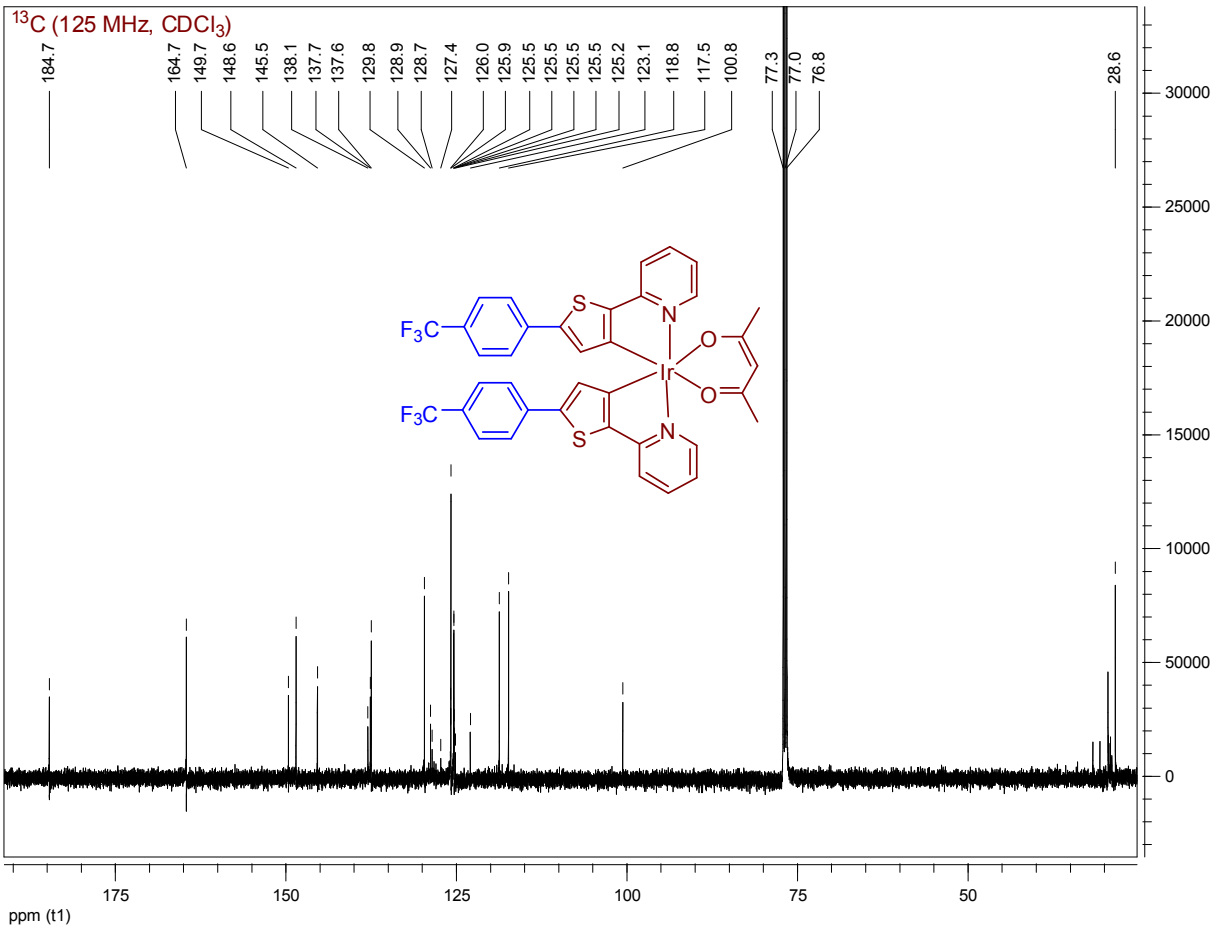
e Prof.D. Jacquemin
Institut Universitaire de France, 103 bd St Michel, 75005 Paris Cedex 5, France

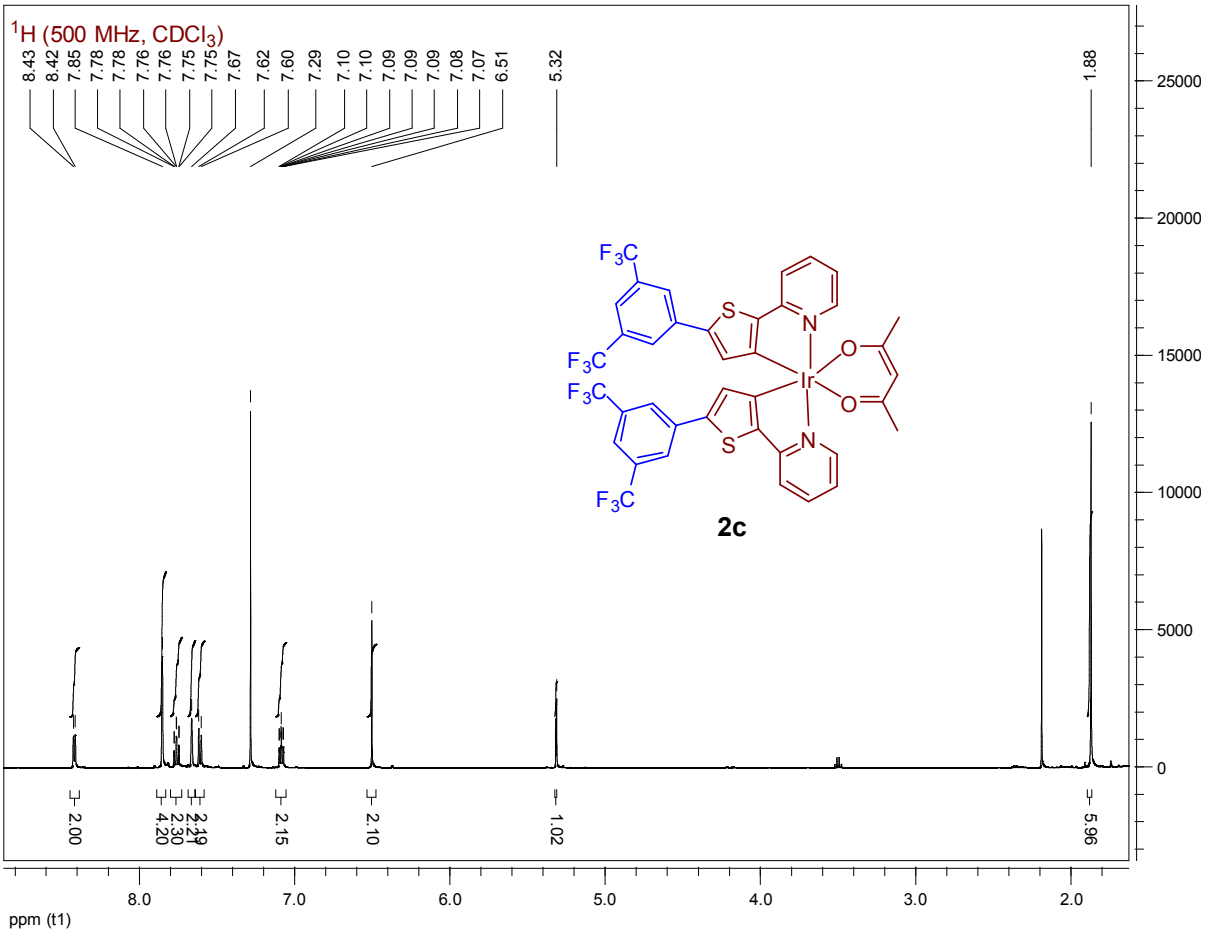
Contents

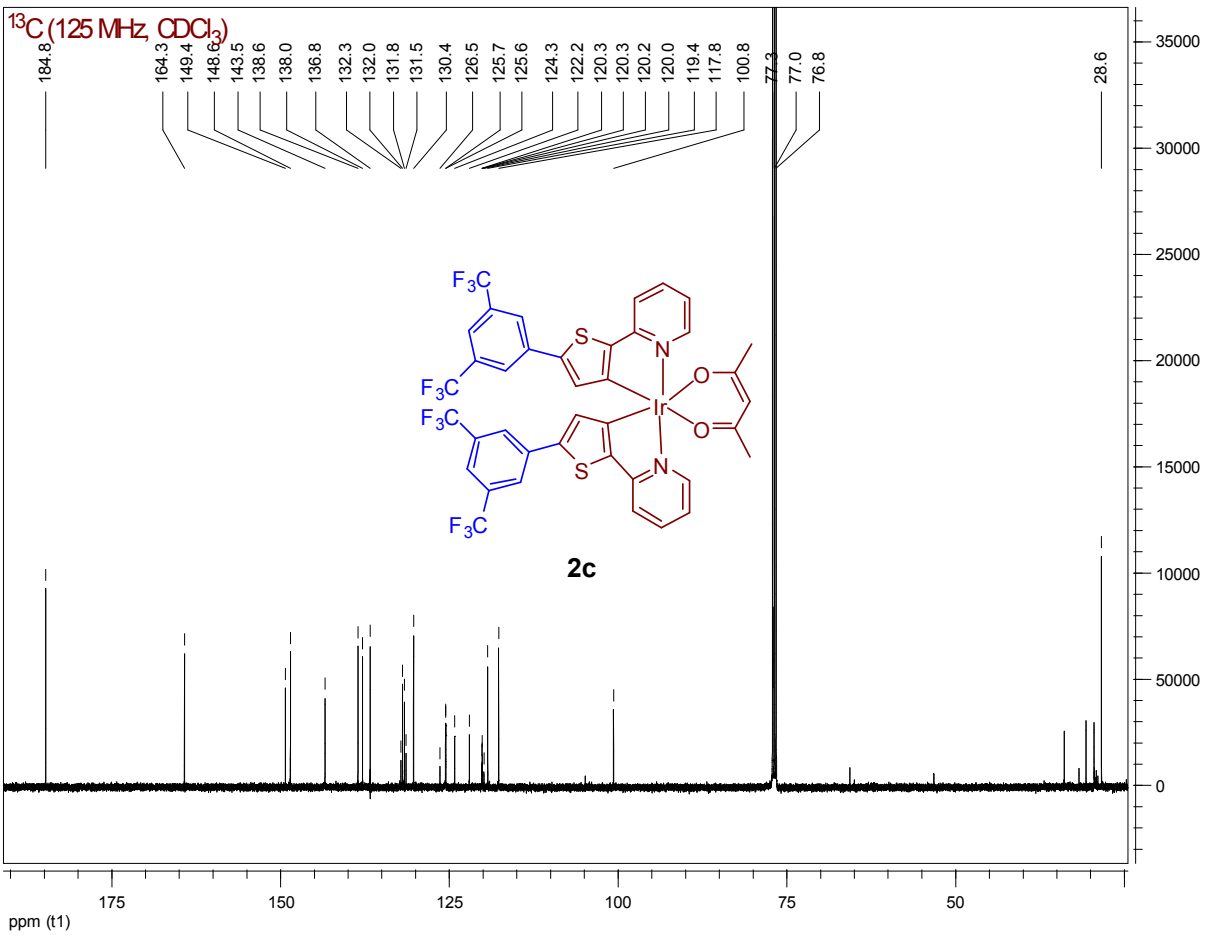

1H (500 MHz, CDCl3)
8.43
8.42
7.73
7.72
7.70
7.56
7.55
7.45
7.29
7.07
7.06
7.05
6.50
5.32
1.87
1.94
2.50
2.62
8.53
2.02
2.21
1.00
6.59
NC
NC
S
N
Ir
O
O
2a
ppm (t1)

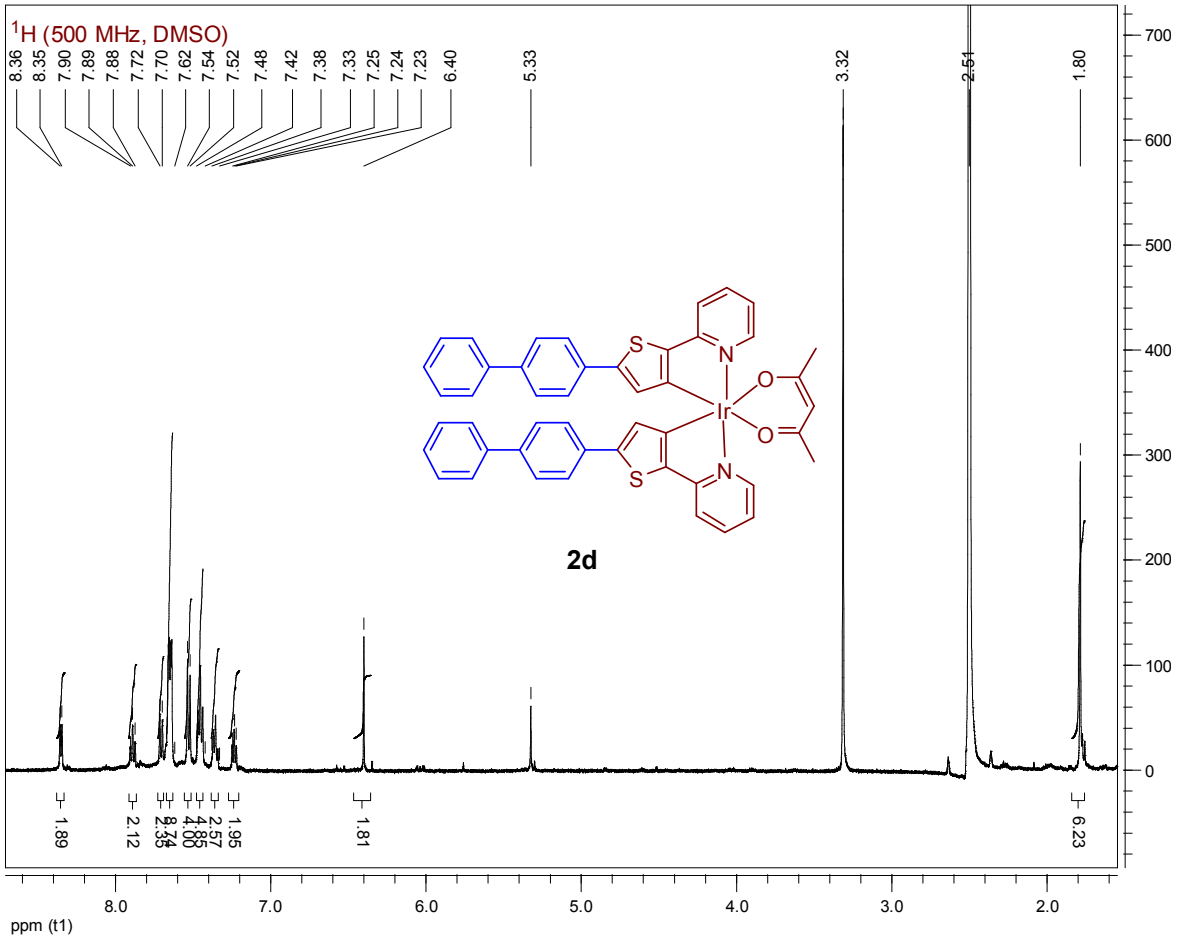

13C (125 MHz, CDCl3)
184.7
164.2
149.3
148.5
144.7
138.7
138.7
137.7
132.2
130.2
125.8
119.2
118.9
117.6
109.8
100.8
77.3
77.0
76.8
28.5
NC
NC
S
N
Ir
O
O
2a
ppm (t1)

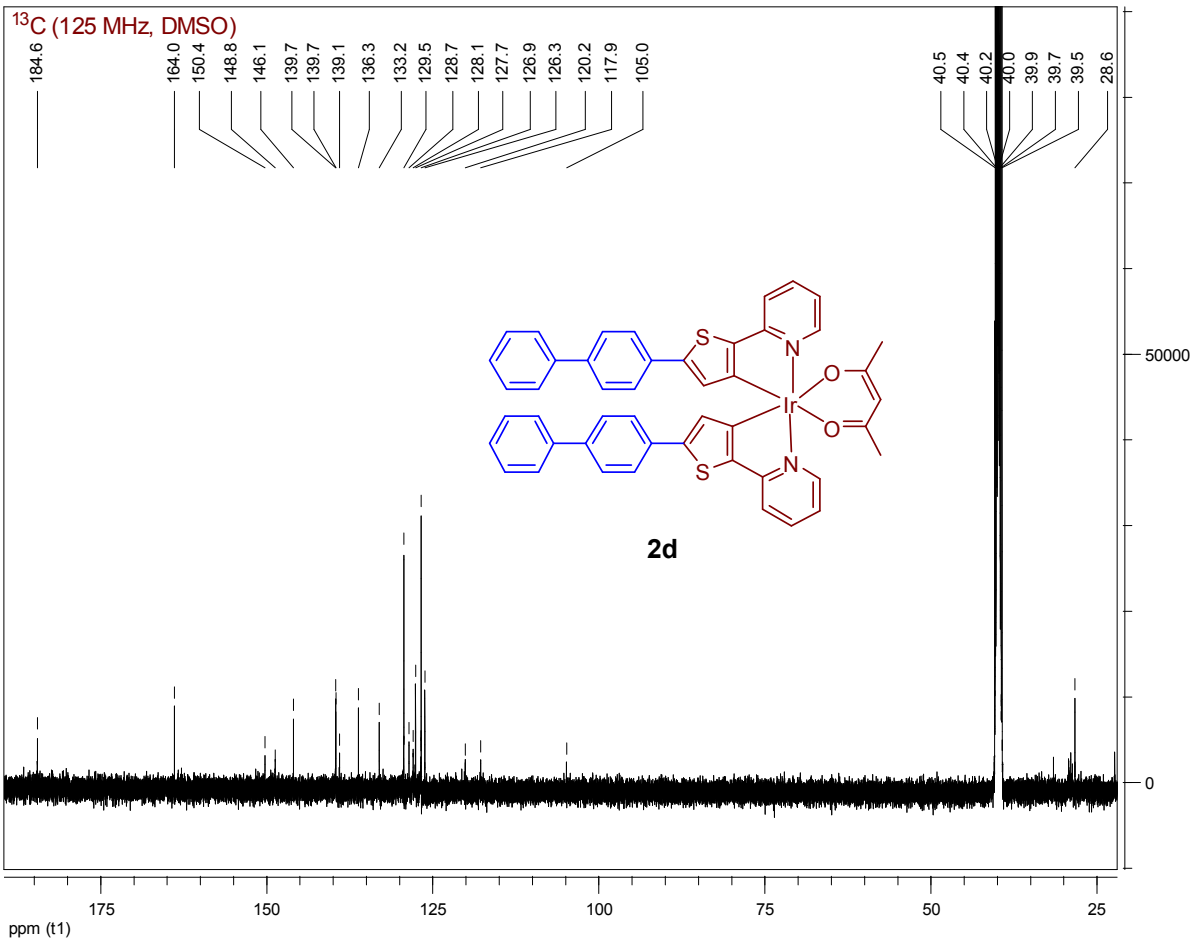

^{1}H (500 MHz, $CDCl_3$)
8.42 8.41 7.72 7.72 7.71 7.71 7.69 7.69 7.59 7.57 7.55 7.51 7.49 7.48 7.29 7.04 7.04 7.03 7.03 7.02 7.01 7.01 6.49 5.30
1.88
2.10 2.32 12.07 1.97 2.00 0.96 6.12
2b
ppm (t1)

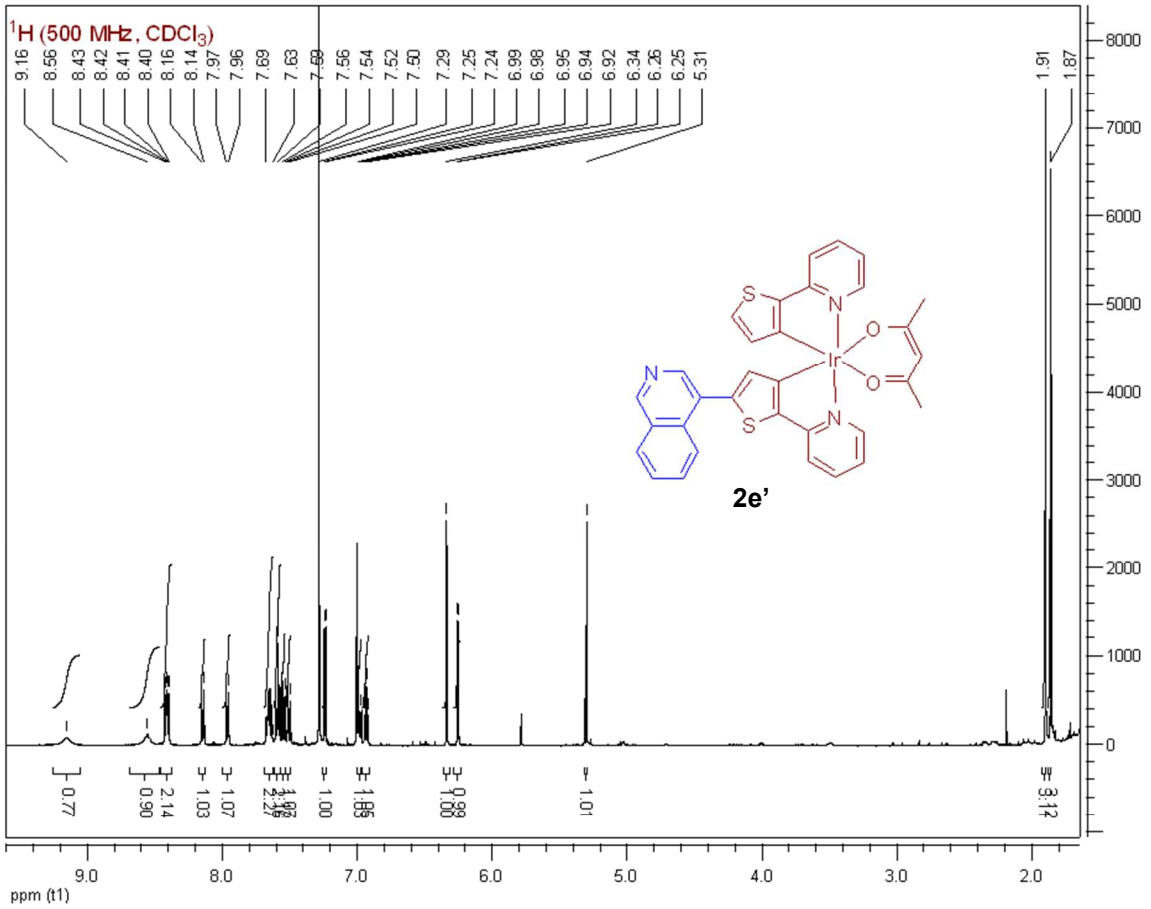

^{13}C (125 MHz, $CDCl_3$)
184.7 164.7 149.7 148.6 145.5 138.1 137.7 137.6 129.8 128.9 128.7 127.4 126.0 125.9 125.5 125.5 125.5 125.5 125.2 123.1 118.8 117.5 100.8 77.3 77.0 76.8 28.6
ppm (t1)


1H (500 MHz, CDCl3)
8.43
8.42
7.85
7.78
7.78
7.76
7.76
7.75
7.75
7.67
7.62
7.60
7.29
7.10
7.10
7.09
7.09
7.09
7.08
7.07
6.51
5.32
1.88
F3C
F3C
F3C
F3C
S
N
O
Ir
O
S
N
2c
2.00
4.20
2.30
2.29
2.15
2.10
1.02
5.96
ppm (t1)

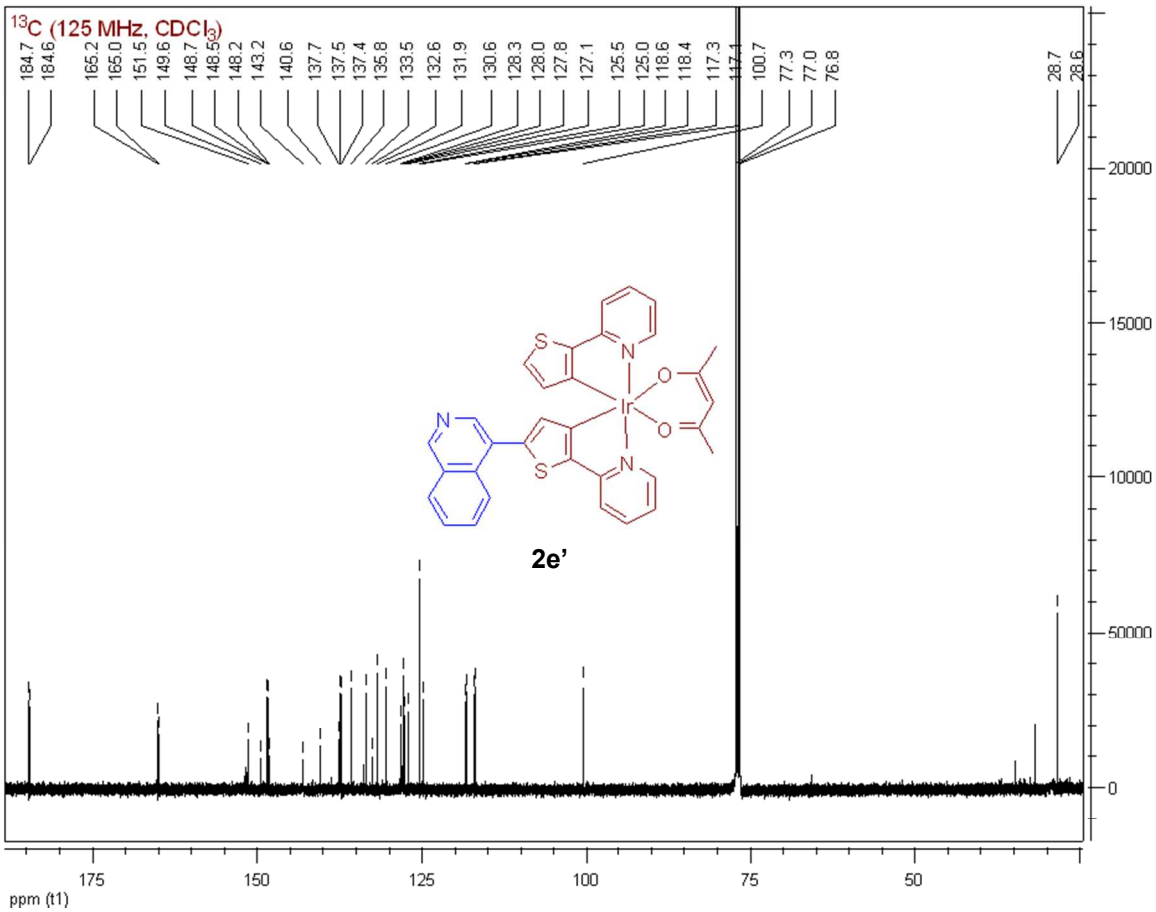

13C (125 MHz, CDCl3)
184.8
164.3
149.4
148.6
143.5
138.6
138.0
136.8
132.3
132.0
131.8
131.5
130.4
126.5
125.7
125.6
124.3
122.2
120.3
120.3
120.2
120.0
119.4
117.8
100.8
77.3
77.0
76.8
28.6
F3C
F3C
F3C
F3C
S
N
O
Ir
O
S
N
2c
ppm (t1)


1H (500 MHz, DMSO)
8.36
8.35
7.90
7.89
7.88
7.72
7.70
7.62
7.54
7.52
7.48
7.42
7.38
7.33
7.25
7.24
7.23
6.40
5.33
3.32
2.51
1.80
1.89
2.12
8.34
4.00
2.57
1.95
1.81
9.23
S
N
O
Ir
O
S
N
2d
700
600
500
400
300
200
100
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)

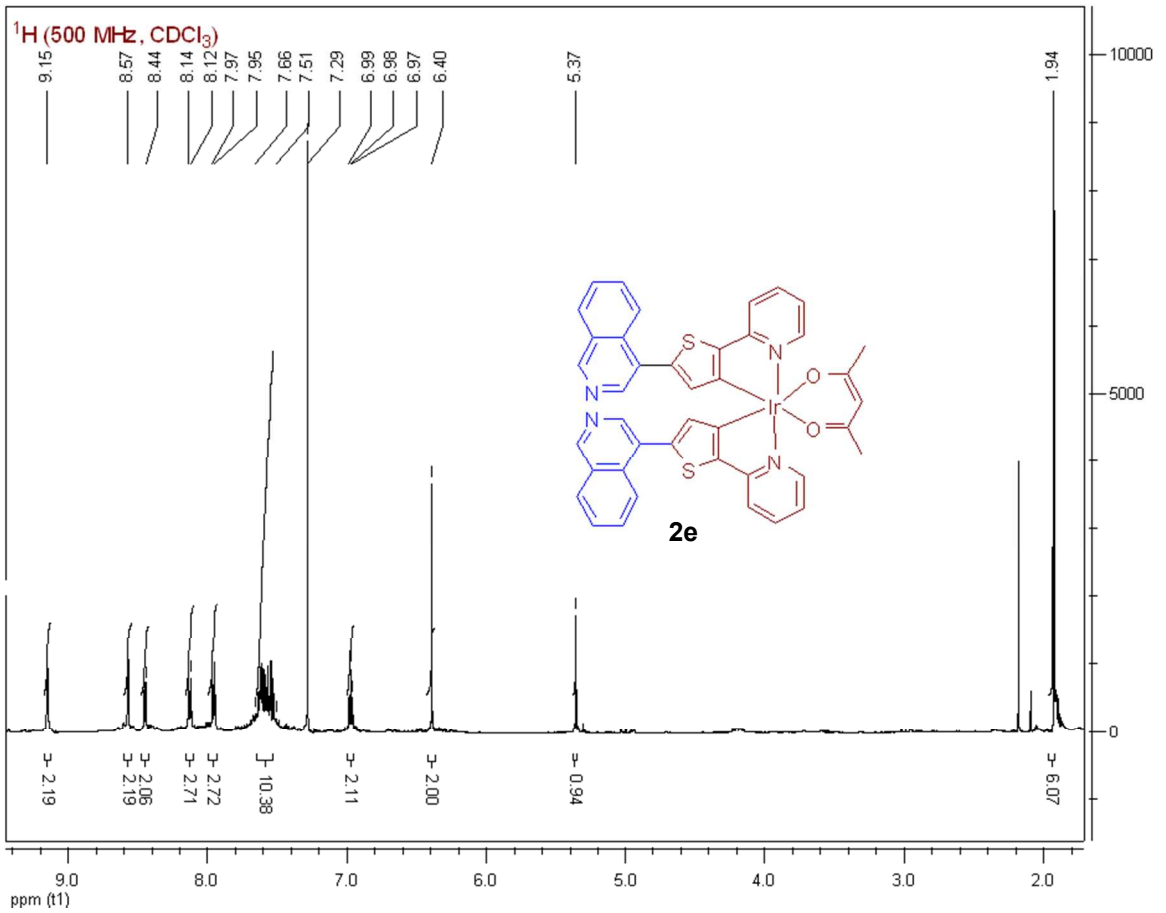

13C (125 MHz, DMSO)
184.6
164.0
150.4
148.8
146.1
139.7
139.7
139.1
136.3
133.2
129.5
128.7
128.1
127.7
126.9
126.3
120.2
117.9
105.0
40.5
40.4
40.2
40.0
39.9
39.7
39.5
28.6
S
N
O
Ir
O
S
N
2d
50000
0
175
150
125
100
75
50
25
ppm (t1)

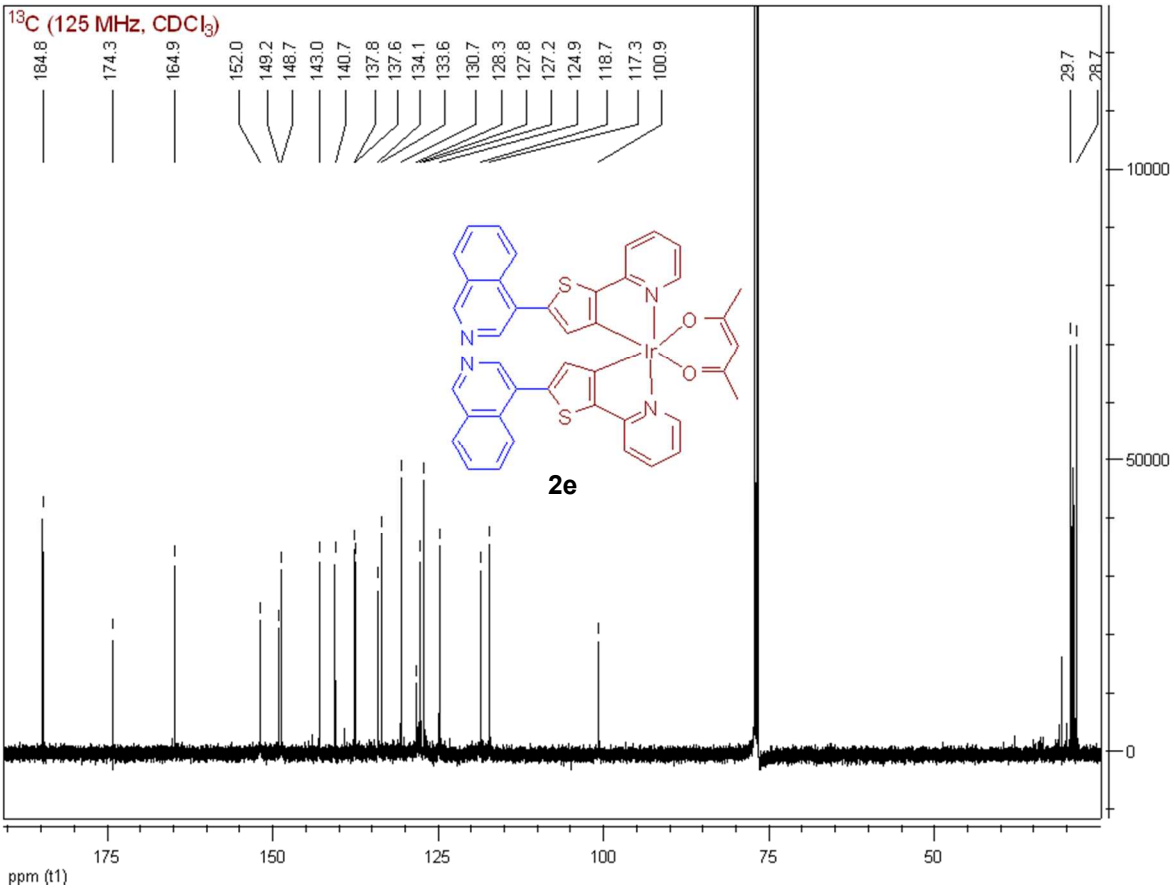

1H (500 MHz, CDCl3)
9.16
8.56
8.43
8.42
8.41
8.40
8.16
8.14
7.97
7.96
7.69
7.63
7.60
7.56
7.54
7.52
7.50
7.29
7.25
7.24
6.99
6.98
6.95
6.94
6.92
6.34
6.26
6.25
5.31
1.91
1.87
0.77
0.90
2.14
1.03
1.07
1.00
1.01
3.12
ppm (t1)

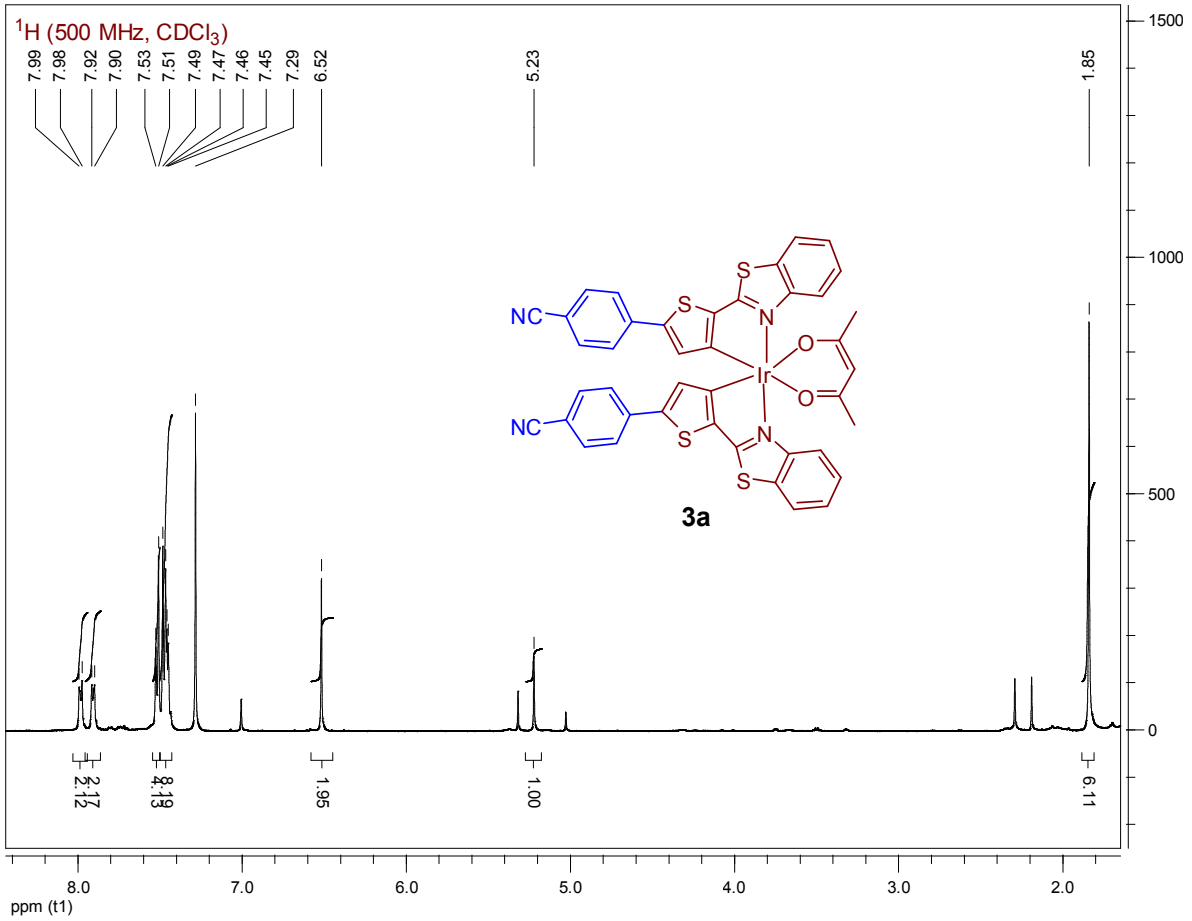
2e’

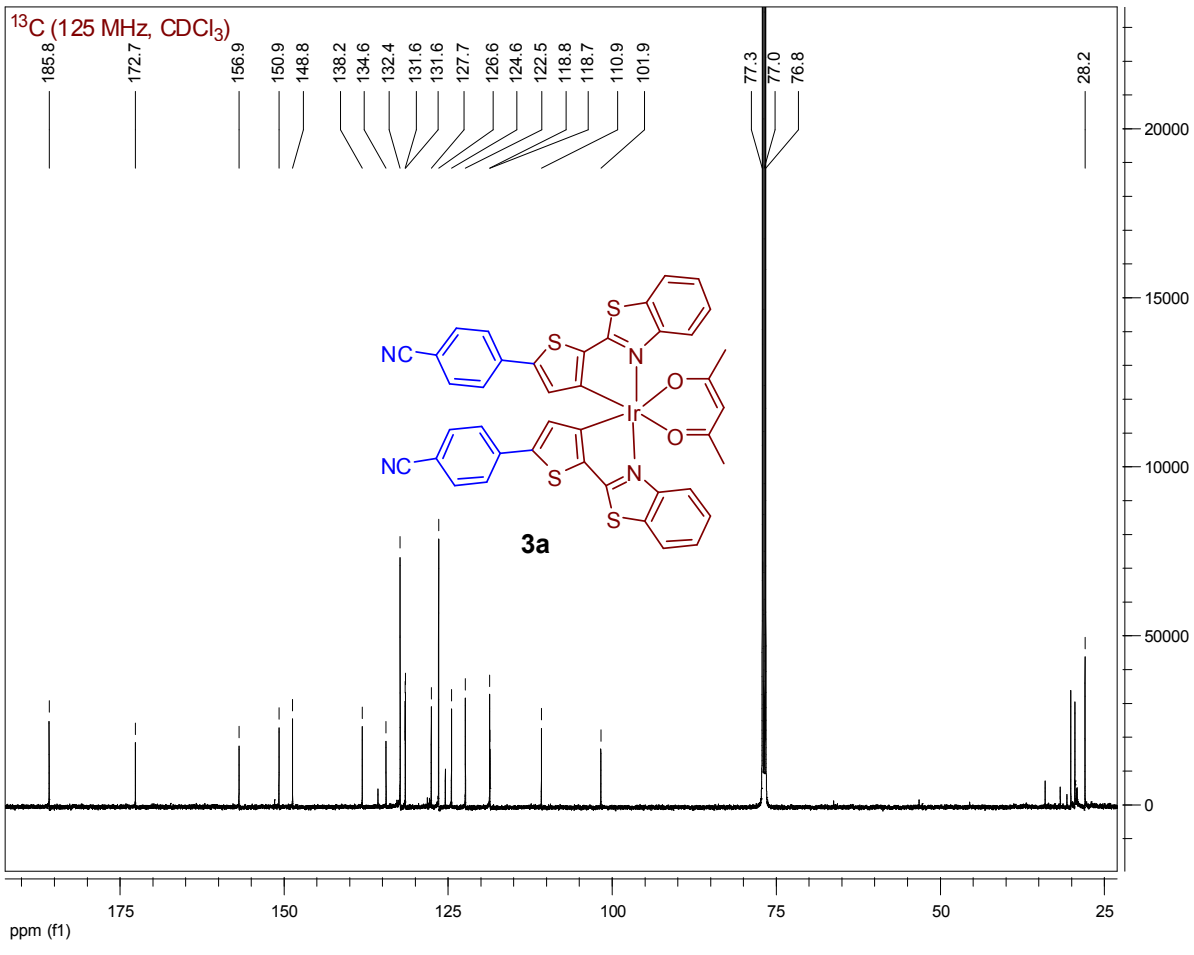

13C (125 MHz, CDCl3)
184.7
184.6
165.2
165.0
151.5
149.6
148.7
148.5
148.2
143.2
140.6
137.7
137.5
137.4
135.8
133.5
132.6
131.9
130.6
128.3
128.0
127.8
127.1
125.5
125.0
118.6
118.4
117.3
117.1
100.7
77.3
77.0
76.8
28.7
28.6
ppm (t1)

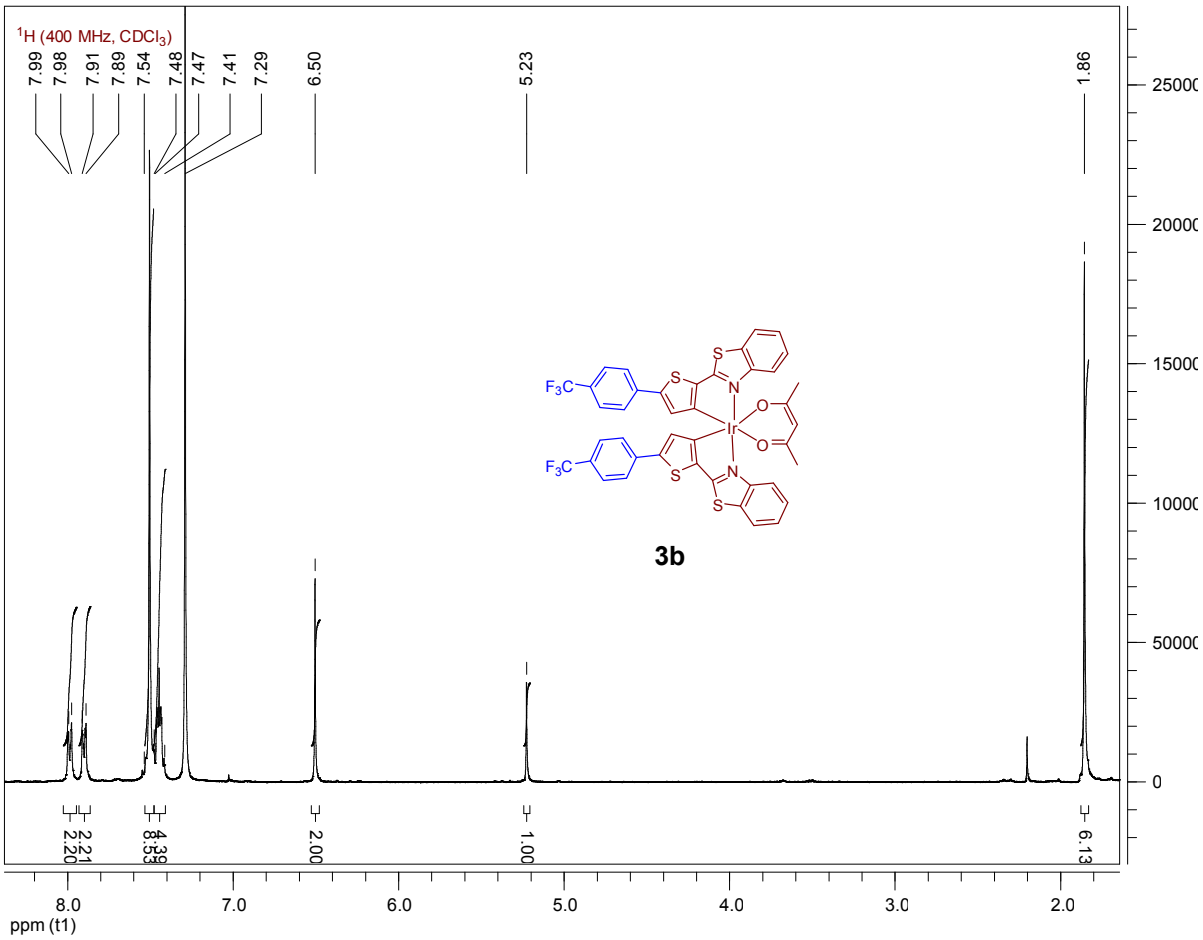
2e’

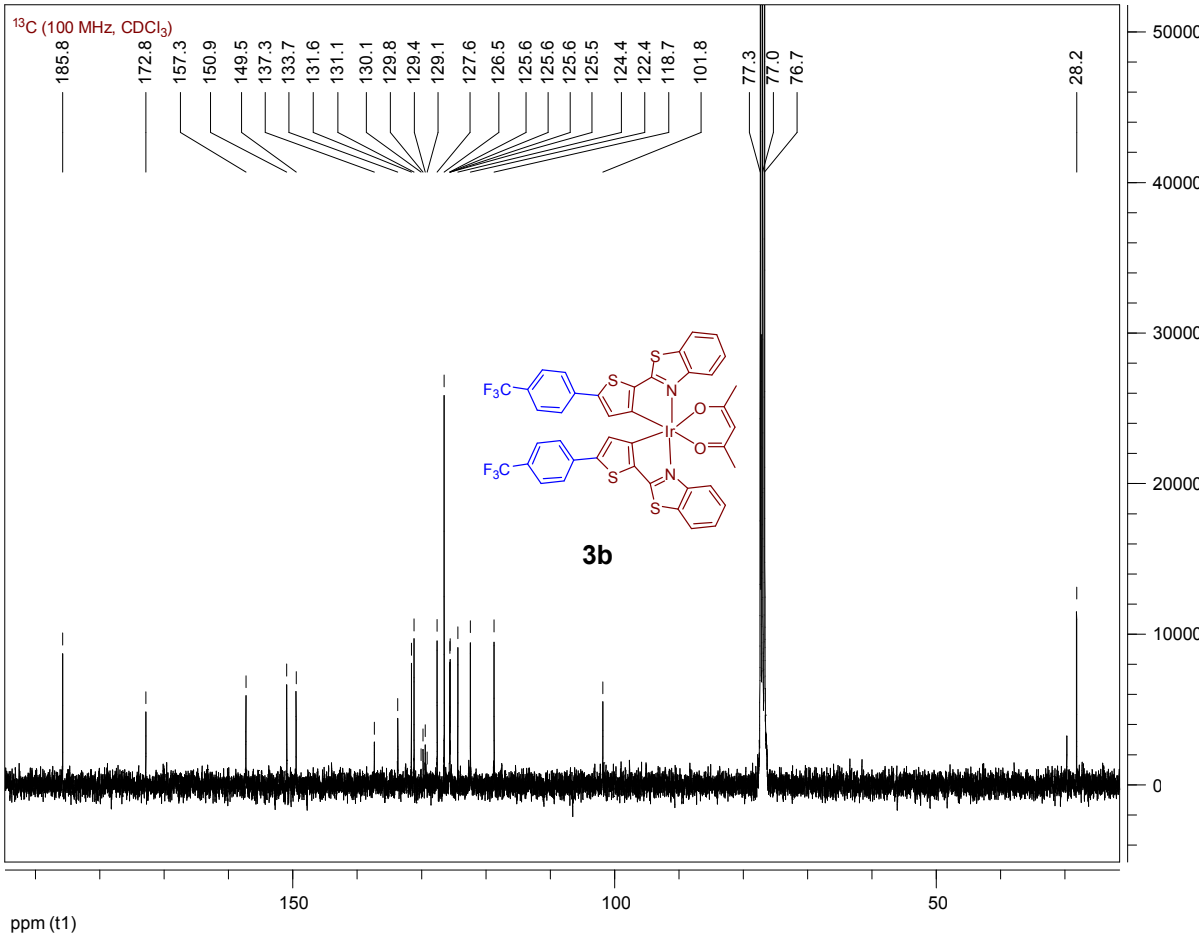

1H (500 MHz, CDCl3)
9.15
8.57
8.44
8.14
8.12
7.97
7.95
7.66
7.51
7.29
6.99
6.98
6.97
6.40
5.37
1.94
2.19
2.19
2.06
2.71
2.72
10.38
2.11
2.00
0.94
6.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
ppm (t1)
10000
5000
0
2e

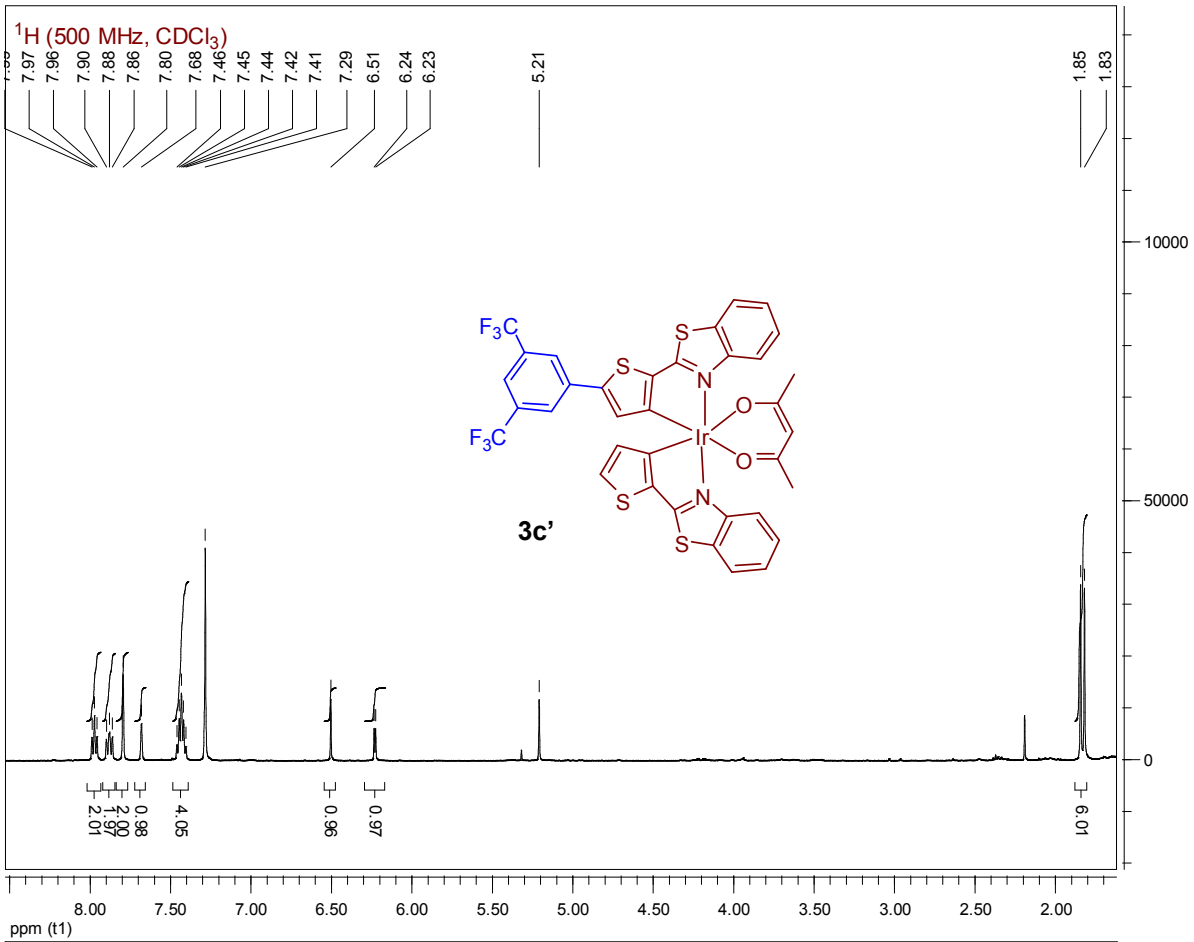

13C (125 MHz, CDCl3)
184.8
174.3
164.9
152.0
149.2
148.7
143.0
140.7
137.8
137.6
134.1
133.6
130.7
128.3
127.8
127.2
124.9
118.7
117.3
100.9
29.7
28.7
175
150
125
100
75
50
ppm (t1)
10000
50000
0
2e

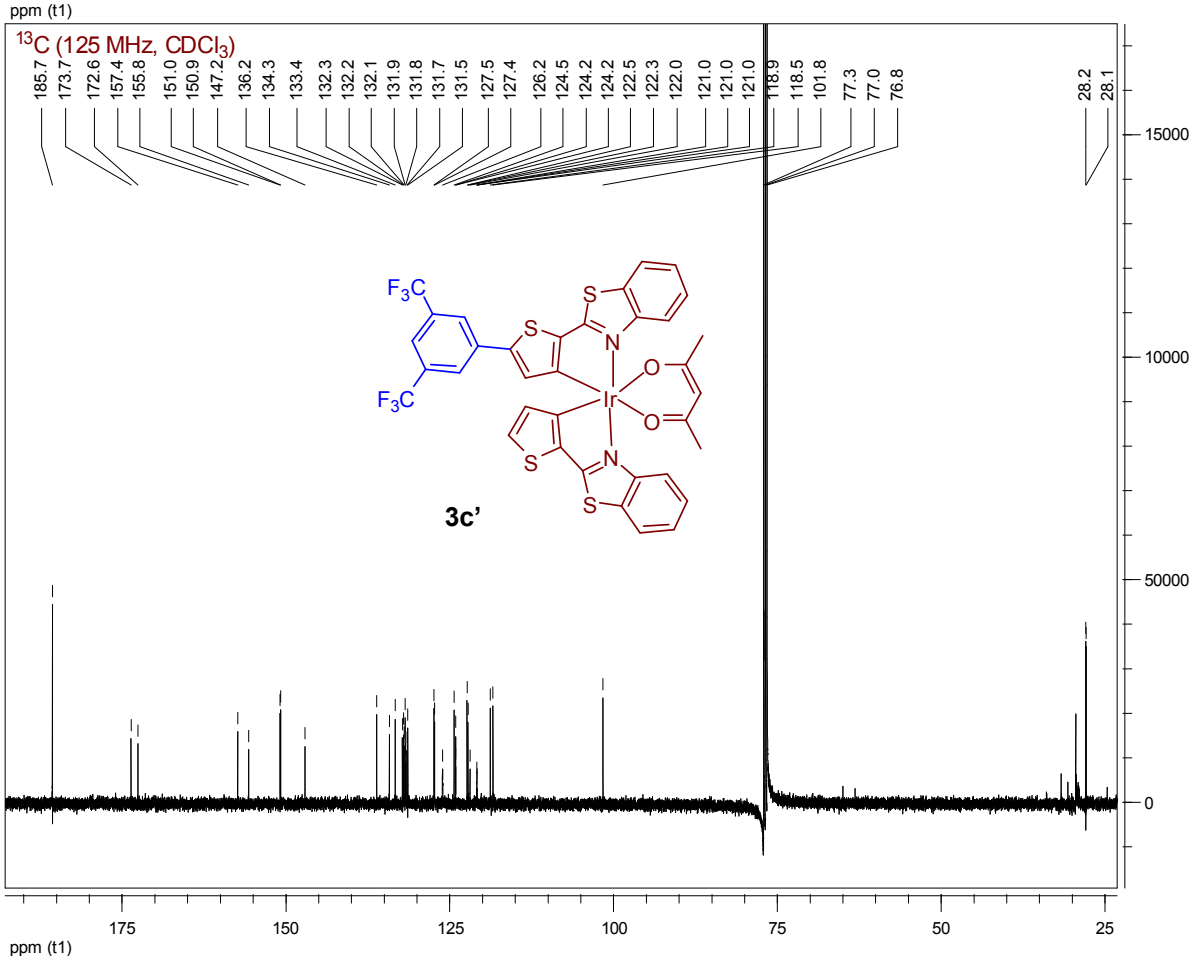

1H (500 MHz, CDCl3)
7.99
7.98
7.92
7.90
7.53
7.51
7.49
7.47
7.46
7.45
7.29
6.52
5.23
1.85
NC
NC
S
N
O
Ir
3a
2.12
8.19
1.96
1.00
6.11
ppm (t1)

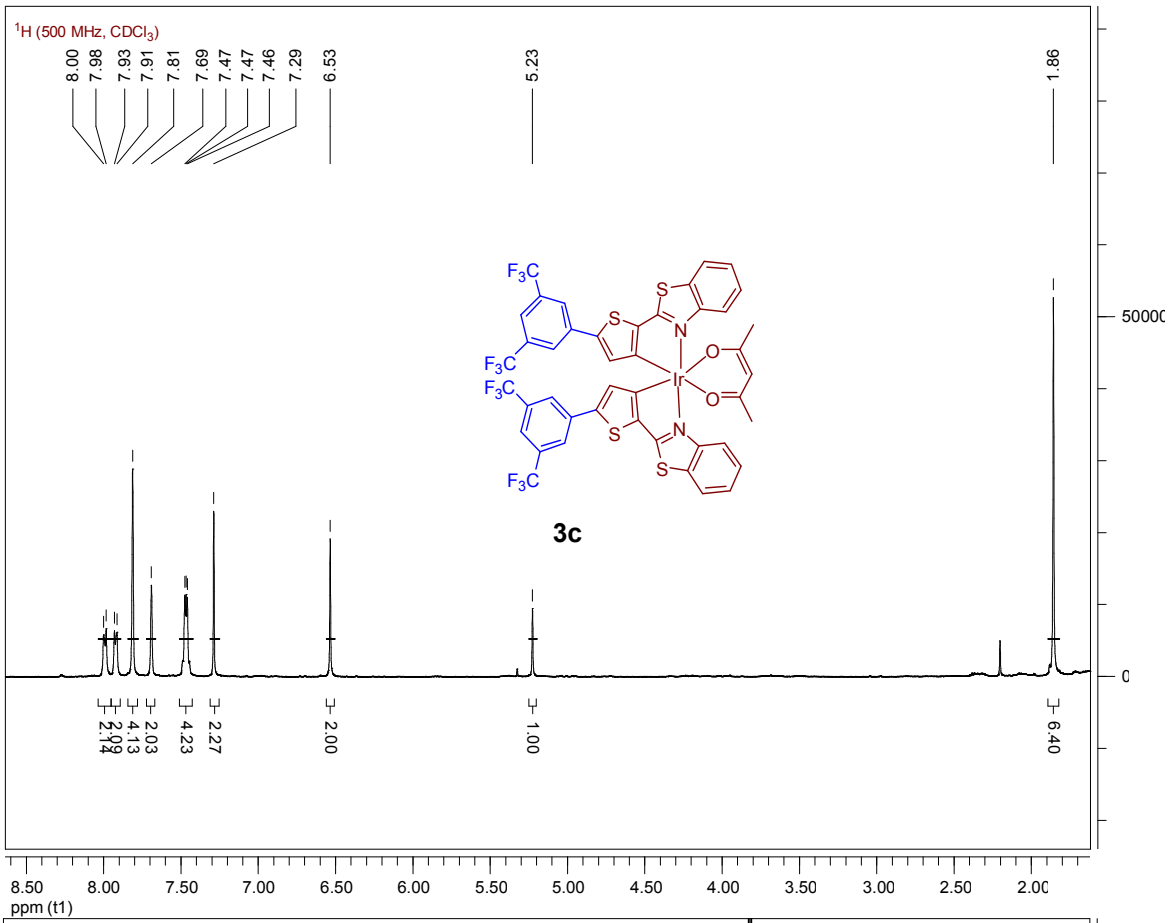

13C (125 MHz, CDCl3)
185.8
172.7
156.9
150.9
148.8
138.2
134.6
132.4
131.6
131.6
127.7
126.6
124.6
122.5
118.8
118.7
110.9
101.9
77.3
77.0
76.8
28.2
NC
NC
S
N
O
Ir
3a
ppm (f1)

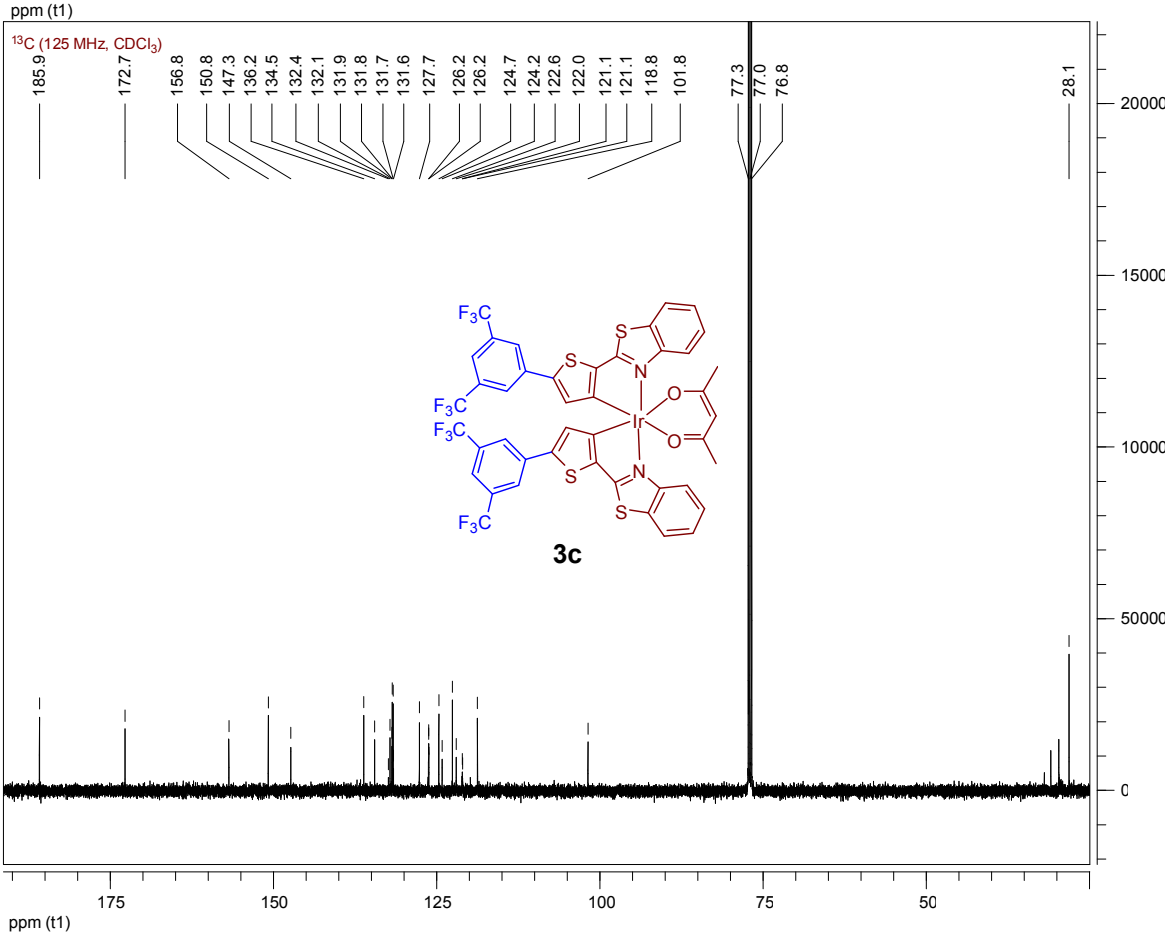

^{1}H (400 MHz, CDCl$_3$)
7.99
7.98
7.91
7.89
7.54
7.48
7.47
7.41
7.29
6.50
5.23
1.86
2.20
2.21
8.33
4.39
2.00
1.00
6.13
F$_3$C
S
N
Ir
O
3b
ppm (t1)

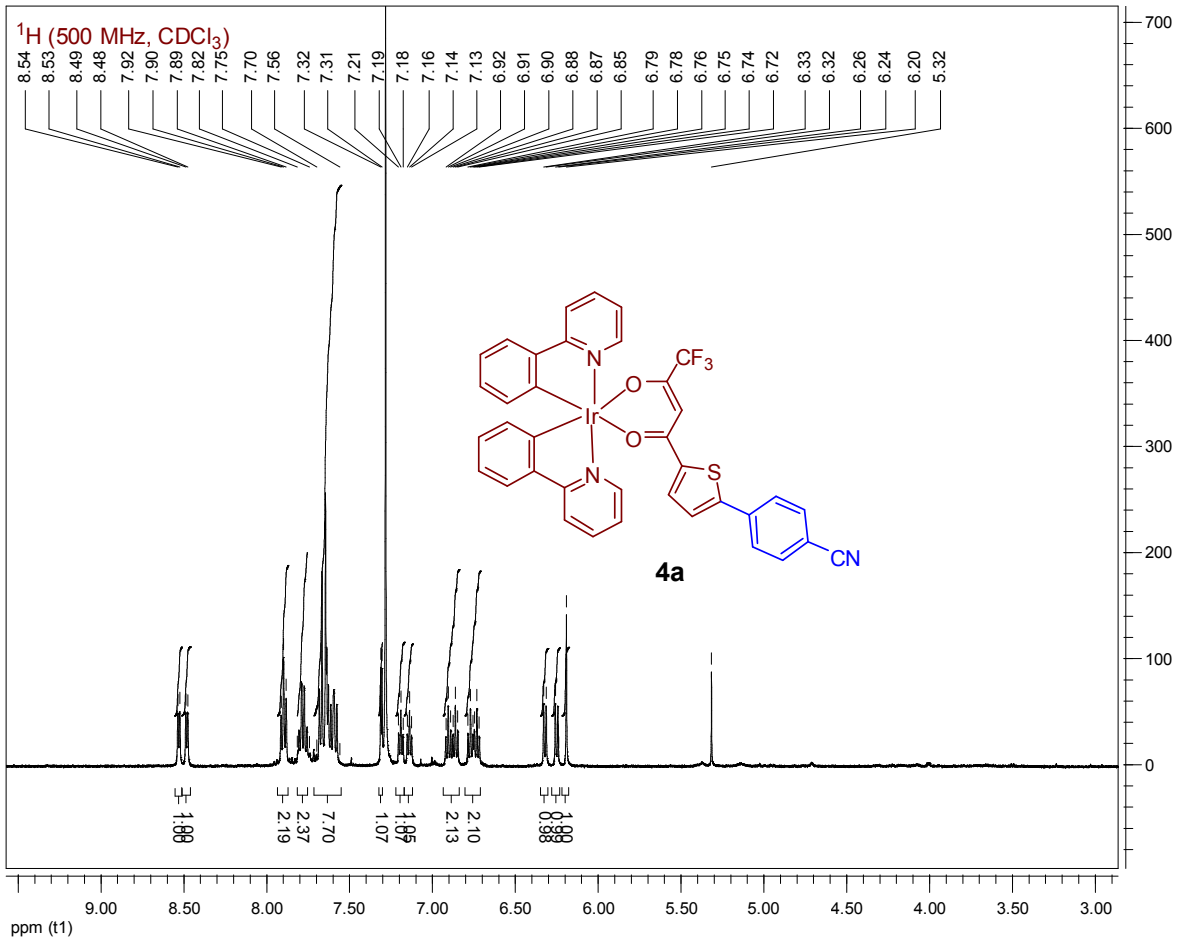

^{13}C (100 MHz, CDCl$_3$)
185.8
172.8
157.3
150.9
149.5
137.3
133.7
131.6
131.1
130.1
129.8
129.4
129.1
127.6
126.5
125.6
125.6
125.6
125.5
124.4
122.4
118.7
101.8
77.3
77.0
76.7
28.2
F$_3$C
S
N
Ir
O
3b
ppm (t1)

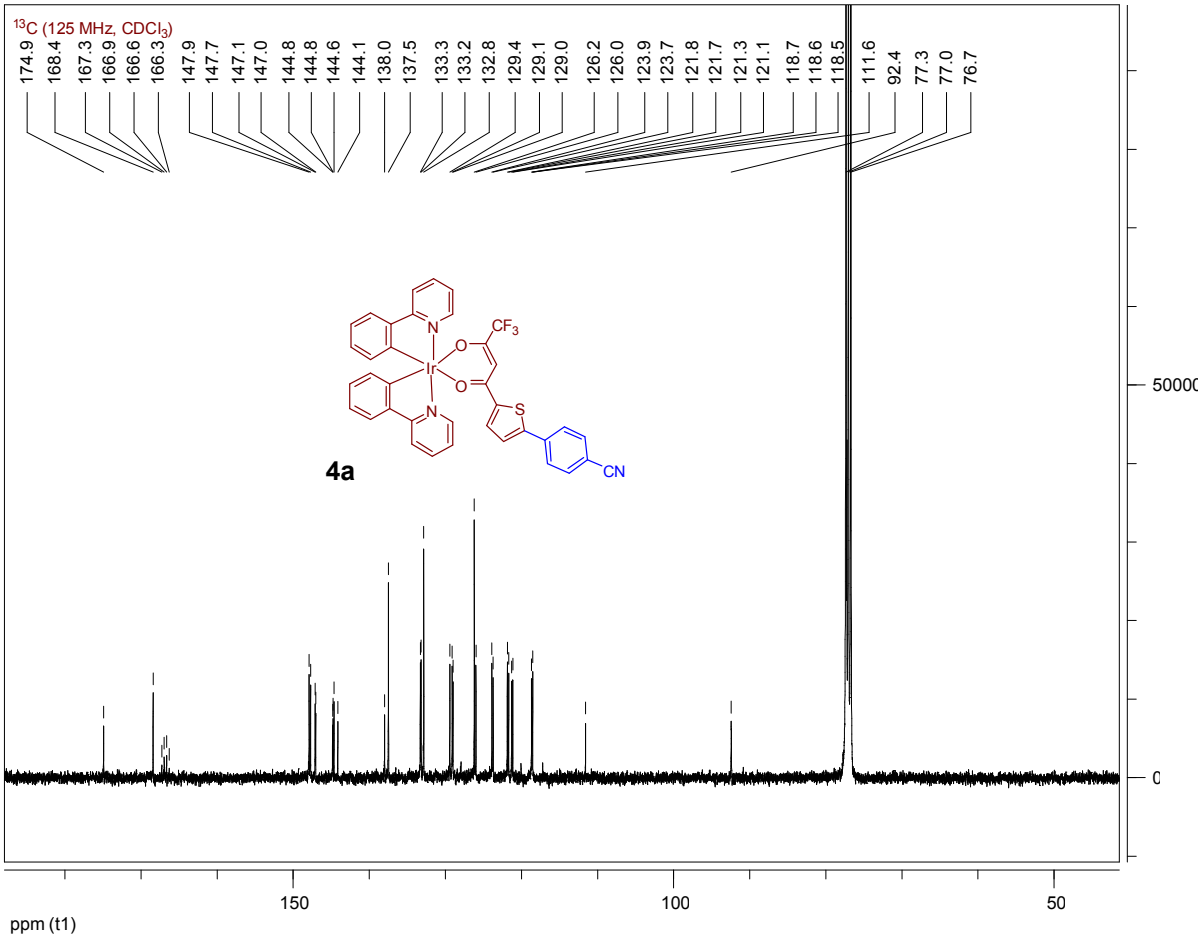

^{1}H (500 MHz, $CDCl_3$)
7.97
7.96
7.90
7.88
7.86
7.80
7.68
7.46
7.45
7.44
7.42
7.41
7.29
6.51
6.24
6.23
5.21
1.85
1.83
F_3C
F_3C
S
S
N
O
Ir
O
S
N
S
3c'
10000
50000
0
2.01
1.97
2.00
1.00
0.98
4.06
0.96
0.97
6.01
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
ppm (t1)

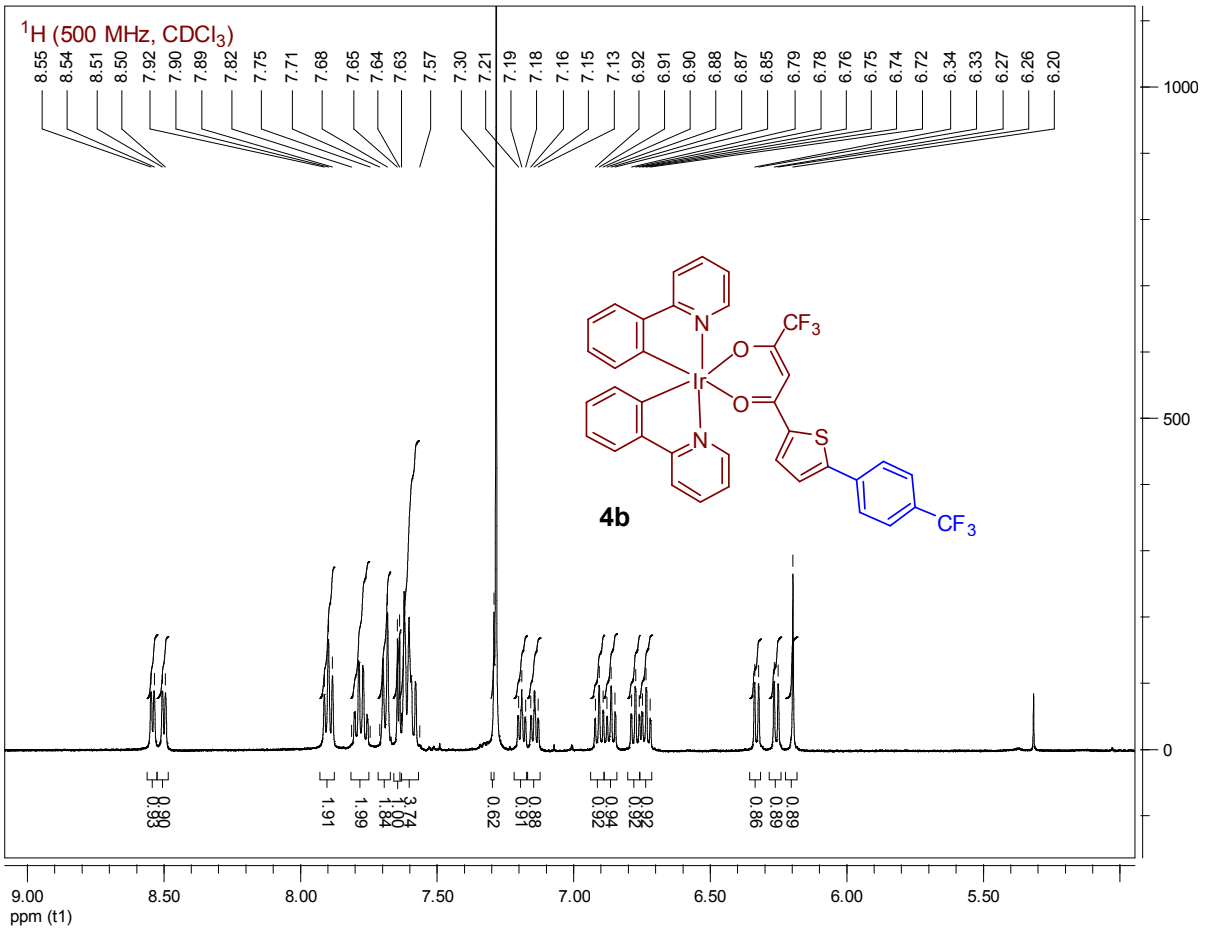

^{13}C (125 MHz, $CDCl_3$)
185.7
173.7
172.6
157.4
155.8
151.0
150.9
147.2
136.2
134.3
133.4
132.3
132.2
132.1
131.9
131.8
131.7
131.5
127.5
127.4
126.2
124.5
124.2
124.2
122.5
122.3
122.0
121.0
121.0
121.0
118.9
118.5
101.8
77.3
77.0
76.8
28.2
28.1
F_3C
F_3C
S
S
N
O
Ir
O
S
N
S
3c'
15000
10000
50000
0
175
150
125
100
75
50
25
ppm (t1)

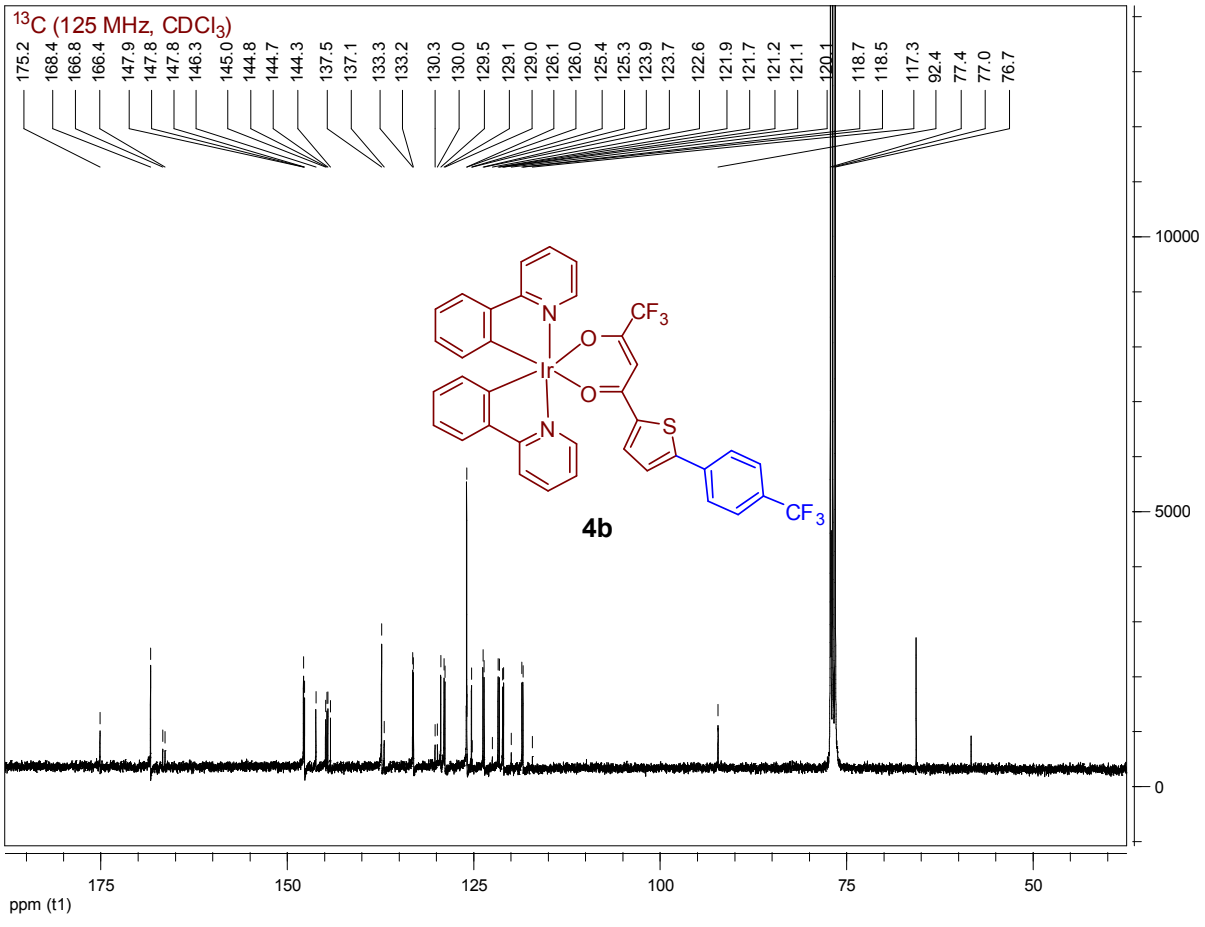

^{1}H (500 MHz, $CDCl_3$)
8.00
7.98
7.93
7.91
7.81
7.69
7.47
7.47
7.46
7.29
6.53
5.23
1.86
3c
2.14
2.09
4.13
2.03
4.23
2.27
2.00
1.00
6.40
ppm (t1)

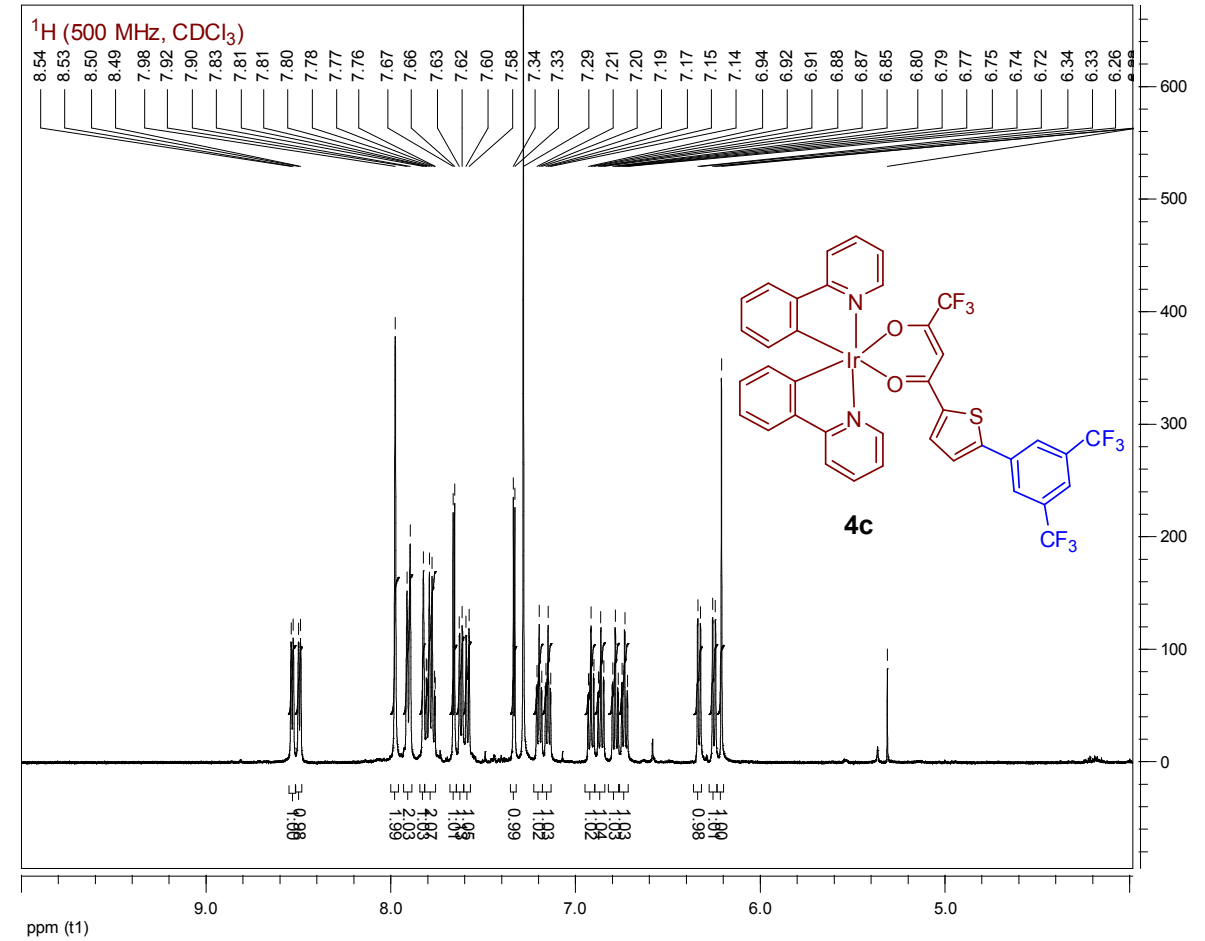

^{13}C (125 MHz, $CDCl_3$)
185.9
172.7
156.8
150.8
147.3
136.2
134.5
132.4
132.1
131.9
131.8
131.7
131.6
127.7
126.2
126.2
124.7
124.2
122.6
122.0
121.1
121.1
118.8
101.8
77.3
77.0
76.8
28.1
3c
ppm (t1)

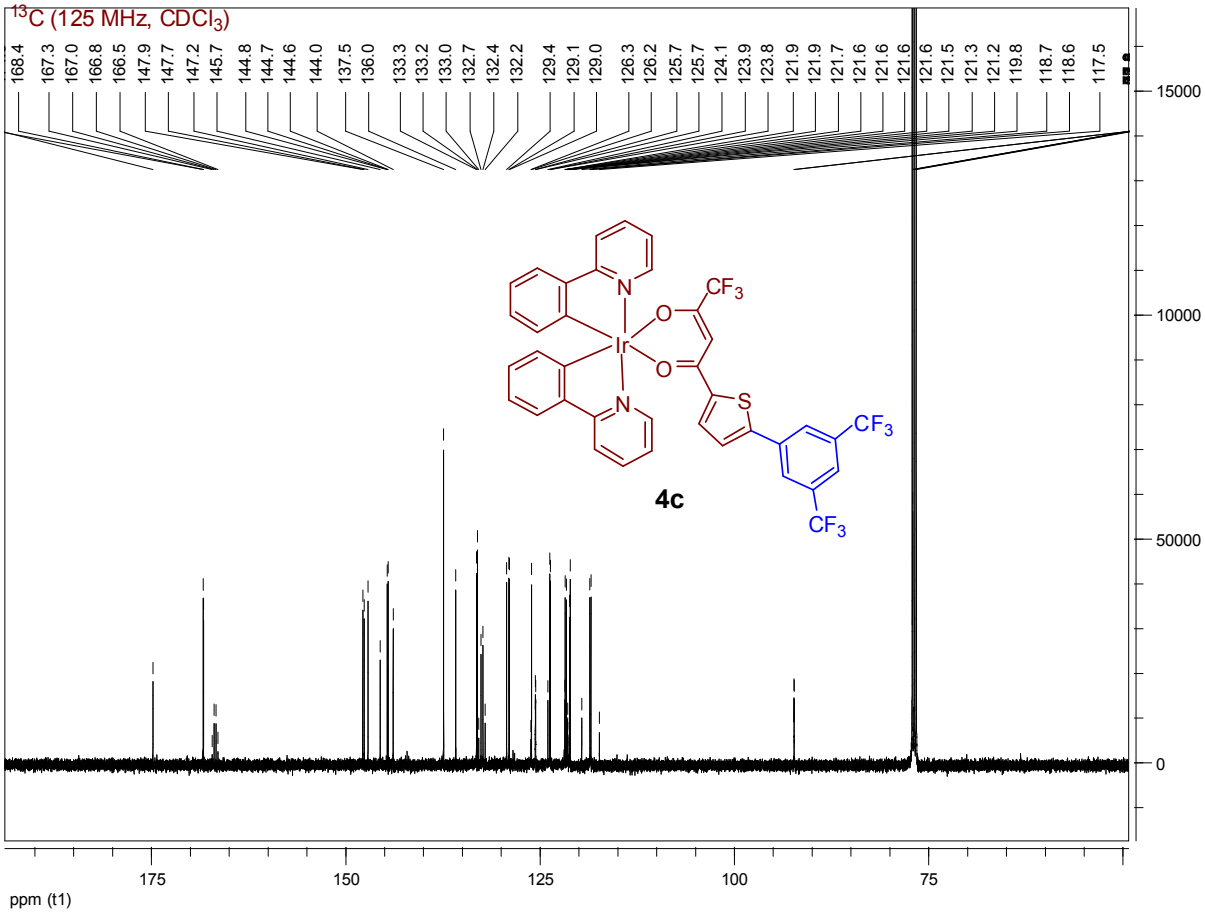

^{1}H (500 MHz, CDCl$_3$)
8.54 8.53 8.49 8.48 7.92 7.90 7.89 7.82 7.75 7.70 7.56 7.32 7.31 7.21 7.19 7.18 7.16 7.14 7.13 6.92 6.91 6.90 6.88 6.87 6.85 6.79 6.78 6.76 6.75 6.74 6.72 6.33 6.32 6.26 6.24 6.20 5.32
1.00 2.19 2.37 7.70 1.07 1.05 2.13 2.10 0.98 0.98 1.00
CF$_3$
N
O
Ir
S
CN
4a
ppm (t1)

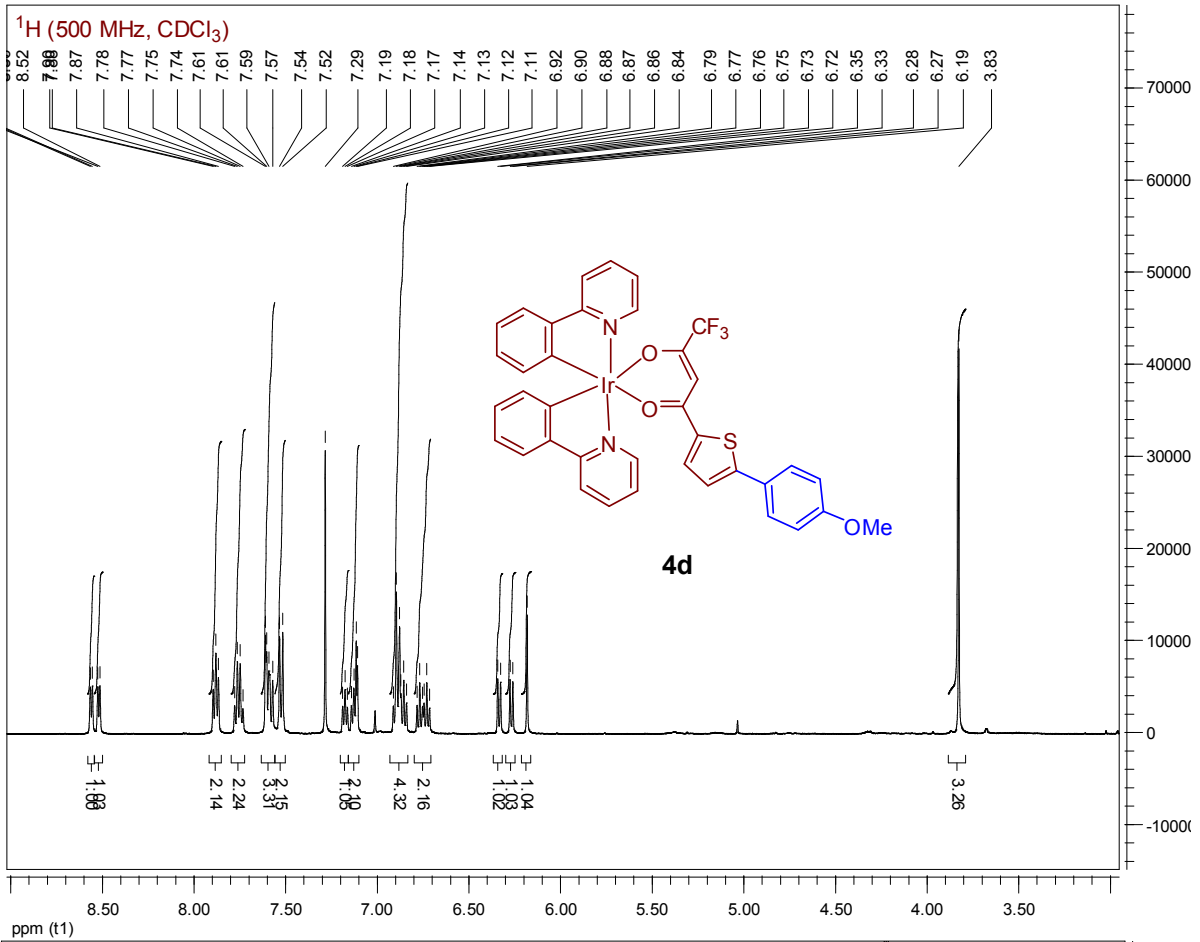

^{13}C (125 MHz, CDCl$_3$)
174.9 168.4 167.3 166.9 166.6 166.3 147.9 147.7 147.1 147.0 144.8 144.8 144.6 144.1 138.0 137.5 133.3 133.2 132.8 129.4 129.1 129.0 126.2 126.0 123.9 123.7 121.8 121.7 121.3 121.1 118.7 118.6 118.5 111.6 92.4 77.3 77.0 76.7
CF$_3$
N
O
Ir
S
CN
4a
ppm (t1)

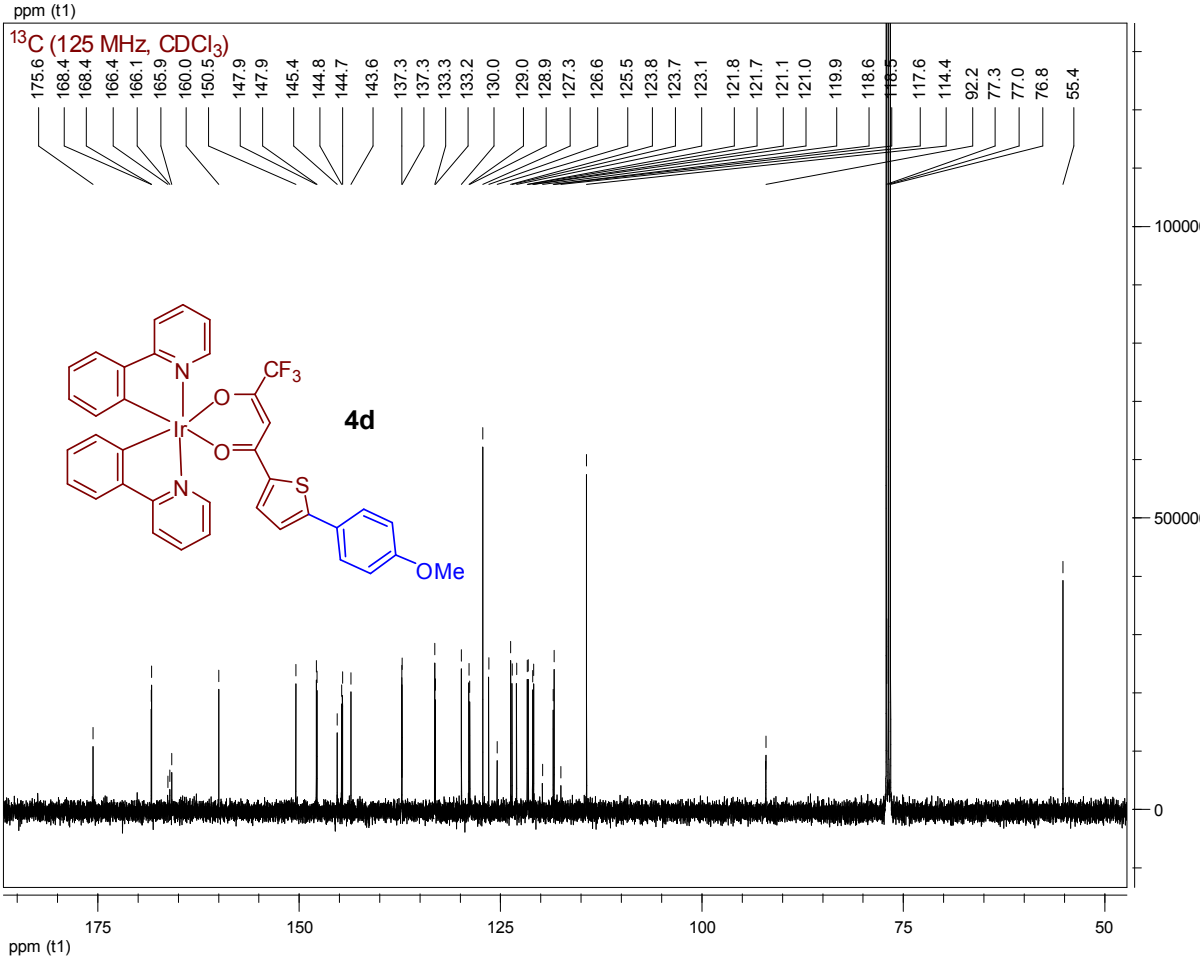

1H (500 MHz, CDCl3)
8.55 8.54 8.51 8.50 7.92 7.90 7.89 7.82 7.75 7.71 7.68 7.65 7.64 7.63 7.57 7.30 7.21 7.19 7.18 7.16 7.15 7.13 6.92 6.91 6.90 6.88 6.87 6.85 6.79 6.78 6.76 6.75 6.74 6.72 6.34 6.33 6.27 6.26 6.20
4b
0.88 1.91 1.99 3.74 0.62 0.88 0.91 0.92 0.94 0.92 0.86 0.89 0.89
9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50
ppm (t1)
1000 500 0

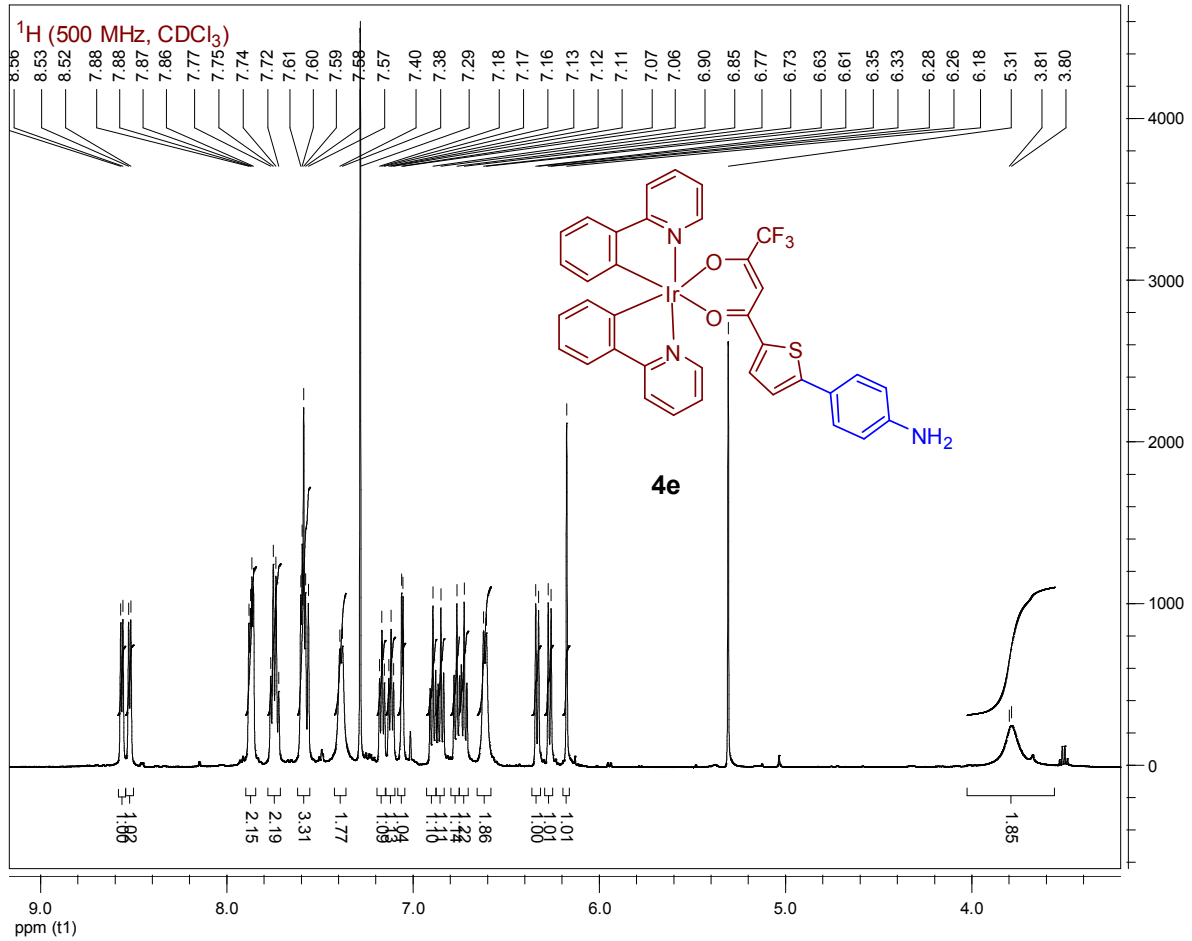

13C (125 MHz, CDCl3)
175.2 168.4 166.8 166.4 147.9 147.8 147.8 146.3 145.0 144.8 144.7 144.3 137.5 137.1 133.3 133.2 130.3 130.0 129.5 129.1 129.0 126.1 126.0 125.4 125.3 123.9 123.7 122.6 121.9 121.7 121.2 121.1 120.1 118.7 118.5 117.3 92.4 77.4 77.0 76.7
4b
175 150 125 100 75 50
ppm (t1)
10000 5000 0

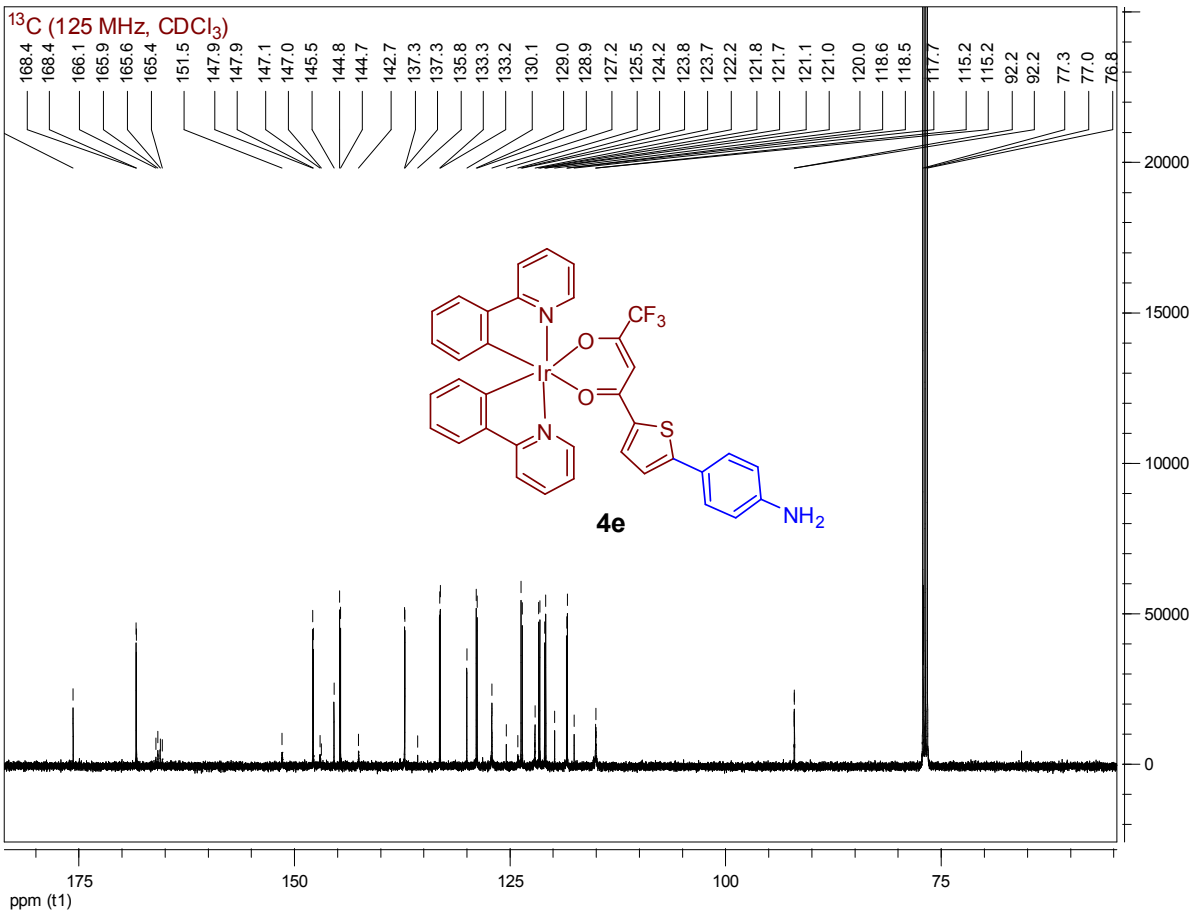

1H (500 MHz, CDCl3)
8.54 8.53 8.50 8.49 7.98 7.92 7.90 7.83 7.81 7.81 7.80 7.78 7.77 7.76 7.67 7.66 7.63 7.62 7.60 7.58 7.34 7.33 7.29 7.21 7.20 7.19 7.17 7.15 7.14 6.94 6.92 6.91 6.88 6.87 6.85 6.80 6.79 6.77 6.75 6.74 6.72 6.34 6.33 6.26
1.00 1.69 2.03 2.02 1.04 0.99 1.02 1.02 1.03 1.03 0.98 1.00
600
500
400
300
200
100
0
9.0
8.0
7.0
6.0
5.0
ppm (t1)
N
Ir
O
O
N
CF3
S
CF3
CF3
4c

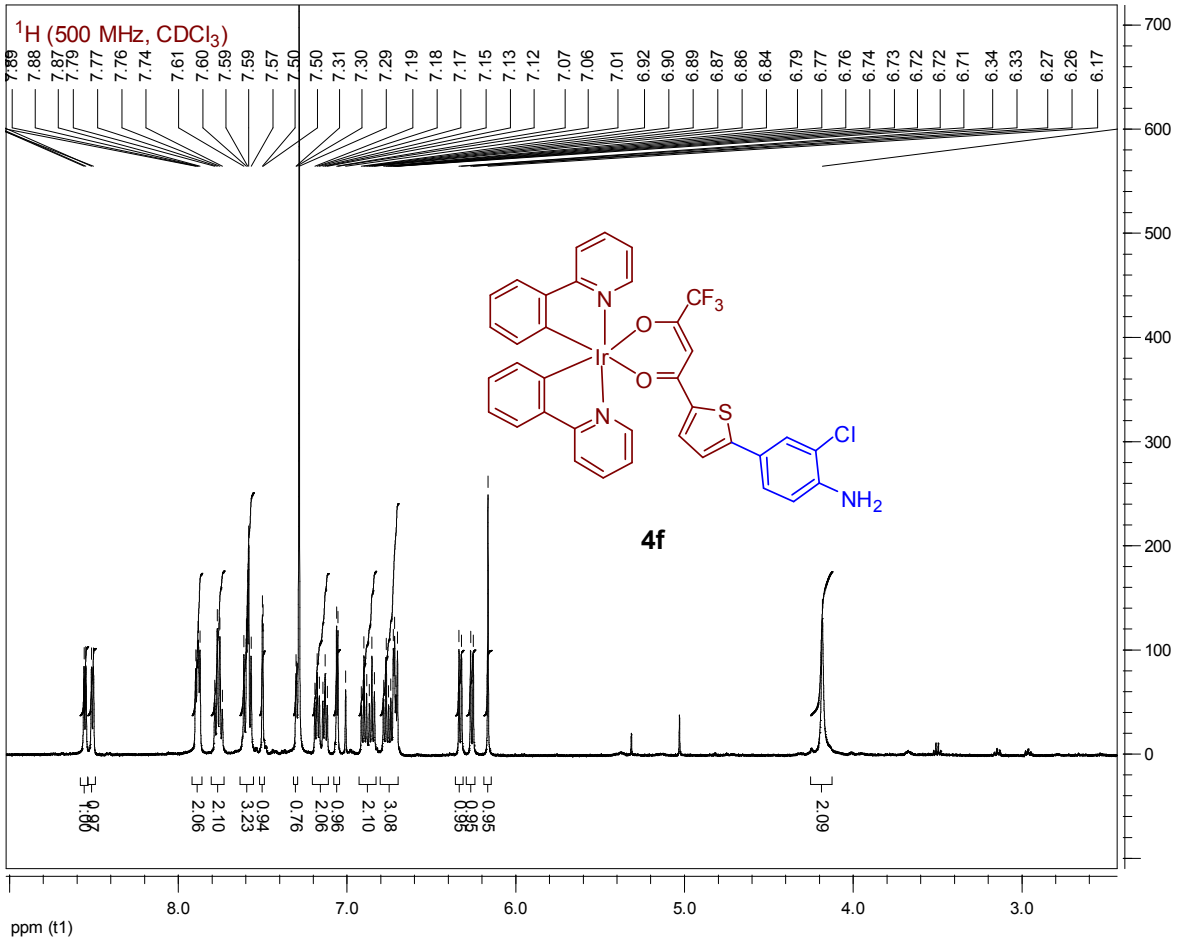

13C (125 MHz, CDCl3)
168.4 167.3 167.0 166.8 166.5 147.9 147.7 147.2 145.7 144.8 144.7 144.6 144.0 137.5 136.0 133.3 133.2 133.0 132.7 132.4 132.2 129.4 129.1 129.0 126.3 126.2 125.7 125.7 124.1 123.9 123.8 121.9 121.9 121.7 121.6 121.6 121.6 121.6 121.5 121.3 121.2 119.8 118.7 118.6 117.5
15000
10000
50000
0
175
150
125
100
75
ppm (t1)
N
Ir
O
O
N
CF3
S
CF3
CF3
4c

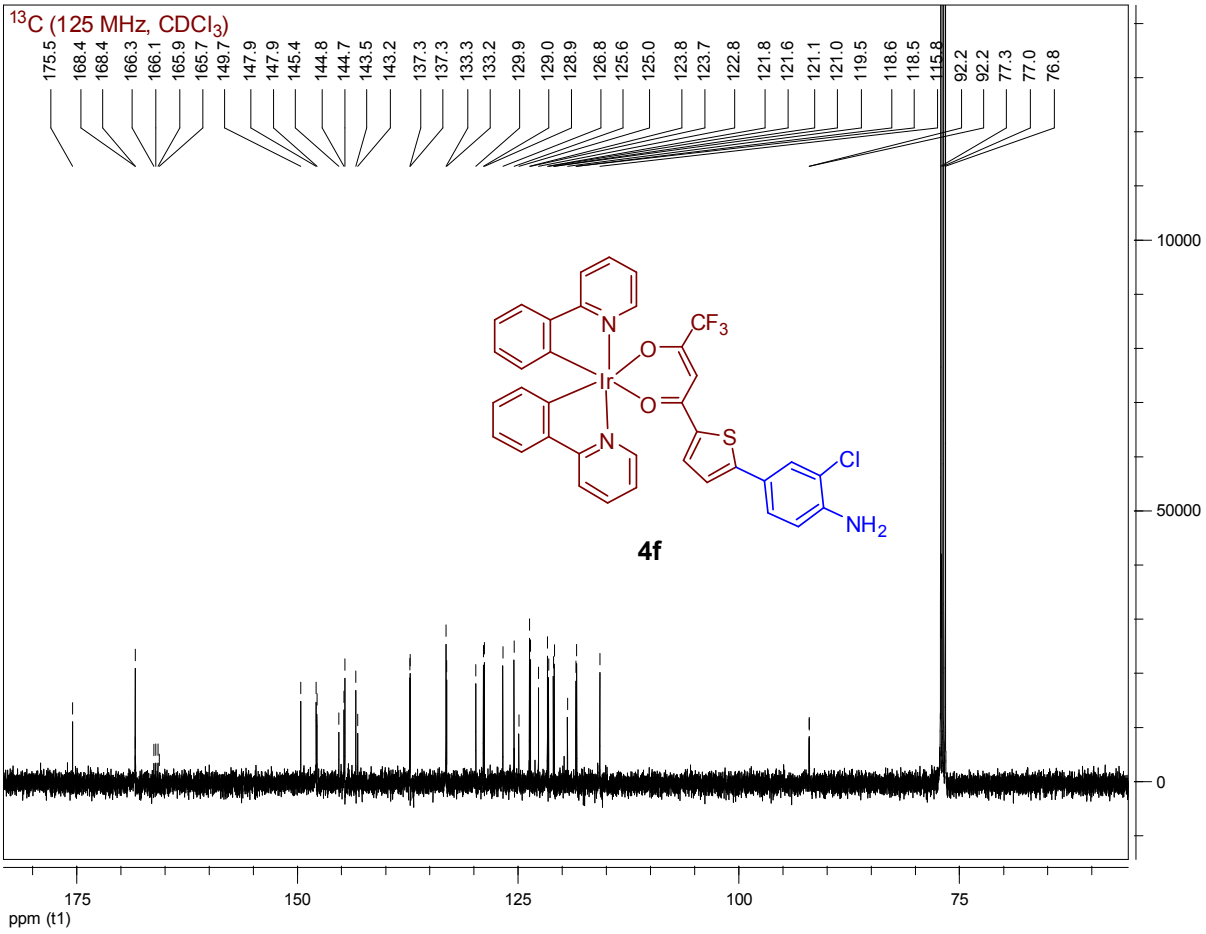

^{1}H (500 MHz, $CDCl_3$)
8.52
7.87
7.78
7.77
7.75
7.74
7.61
7.61
7.59
7.57
7.54
7.52
7.29
7.19
7.18
7.17
7.14
7.13
7.12
7.11
6.92
6.90
6.88
6.87
6.86
6.84
6.79
6.77
6.76
6.75
6.73
6.72
6.35
6.33
6.28
6.27
6.19
3.83
1.00
2.14
2.24
3.31
2.15
2.19
4.32
2.16
1.04
1.03
1.02
3.26
N
Ir
O
O
N
CF_3
O
S
OMe
4d
70000
60000
50000
40000
30000
20000
10000
0
-10000
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
ppm (t1)


^{13}C (125 MHz, $CDCl_3$)
175.6
168.4
168.4
166.4
166.1
165.9
160.0
150.5
147.9
147.9
145.4
144.8
144.7
143.6
137.3
137.3
133.3
133.2
130.0
129.0
128.9
127.3
126.6
125.5
123.8
123.7
123.1
121.8
121.7
121.1
121.0
119.9
118.6
118.5
117.6
114.4
92.2
77.3
77.0
76.8
55.4
N
Ir
O
O
N
CF_3
O
S
OMe
4d
10000
50000
0
175
150
125
100
75
50
ppm (t1)


1H (500 MHz, CDCl3)
8.56
8.53
8.52
7.88
7.88
7.87
7.86
7.77
7.75
7.74
7.72
7.61
7.60
7.59
7.58
7.57
7.40
7.38
7.29
7.18
7.17
7.16
7.13
7.12
7.11
7.07
7.06
6.90
6.85
6.77
6.73
6.63
6.61
6.35
6.33
6.28
6.26
6.18
5.31
3.81
3.80
CF3
O
Ir
O
N
N
S
NH2
4e
1.00
2.15
2.19
3.31
1.77
1.04
1.09
1.11
1.14
1.22
1.86
1.00
1.01
1.85
4000
3000
2000
1000
0
9.0
8.0
7.0
6.0
5.0
4.0
ppm (t1)


13C (125 MHz, CDCl3)
168.4
168.4
166.1
165.9
165.6
165.4
151.5
147.9
147.9
147.1
147.0
145.5
144.8
144.7
142.7
137.3
137.3
135.8
133.3
133.2
130.1
129.0
128.9
127.2
125.5
124.2
123.8
123.7
122.2
121.8
121.7
121.1
121.0
120.0
118.6
118.5
117.7
115.2
115.2
92.2
92.2
77.3
77.0
76.8
CF3
O
Ir
O
N
N
S
NH2
4e
20000
15000
10000
50000
0
175
150
125
100
75
ppm (t1)


1H (500 MHz, CDCl3)
4f
ppm (t1)


13C (125 MHz, CDCl3)
4f
ppm (t1)

Electrochemical data

General

Electrochemical studies in CH_2Cl_2, 0.15M $^nBu_4NPF_6$ were carried out under an argon blanket with an Autolab PGSTAT 30 potentiostat (Eco Chemie B.V., The Netherlands). Glassy carbon, sputtered platinum, and platinum wire were employed as working, counter, and reference electrodes, respectively.

Table S1. Electrochemical data for selected complexes of series 2 and 4 measured by cyclic voltammetry at 298 K in CH_2Cl_2 with $^nBu_4NPF_6$ as the supporting electrolyte scan rate = 200 mV s^{-1}. Values are given versus the Fc | Fc^+ couple under the same conditions.

Complex	E^{ox} / V (ΔE / mV)	E^{red} / V (ΔE / mV)
2a	0.45 (180)	–[(a)]
2b	0.29 (83)	–[(a)]
2c	0.40 (85)	–[(a)]
2d	0.78 (88)	–[(a)]
2e'	0.82 (90)	–[(a)]
4	1.01 (180)	–1.61 (170)
4a	0.51 (150)	–1.86 (120) –2.18 (150)
4b	0.55 (90)	–1.90 (170)
4c	0.49 (130)	–1.92 (130) –2.33 (200)
4e	0.47 (160) 0.72[(b)]	–2.12 (150)
4f	0.50 (120) 0.78[(b)]	–2.04 (130)

(a) No reduction wave observed within the accessible solvent window. *(b)* Irreversible.