Supporting Information

Synthesis of polychloromethylated and halogenated spiro[5,5]-trienones via deromative spirocyclization of biaryl ynones

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1. General considerations

All reactions were carried out under air. ^{1}H NMR ^{13}C NMR and ^{19}F NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz/100 MHz/377 NMR; or 600 MHz/151 MHz/565 NMR) in $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets) and m (multiplet). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI) or a Bruker maXis Impact + 1290 infinity.

2. Preparation of the starting materials

All of biaryl ynones (**1**) were prepared according to the reported methods (W.-C. Yang, M.-M. Zhang, Y. Sun, C.-Y. Chen and L. Wang, *Org. Lett.,* 2021, **23**, 6691).

3. General procedure for the synthesis of 3 and 4

General Procedure A (GP-A) for the synthesis of **3a**: A 15 mL Schlenk flask was charged with 1-[4'-methoxy(1,1'-biphenyl)-2-yl]alkynone (**1a**, 0.20 mmol), BPO (0.60 mmol), DCM (2.0 mL) and a magnetic stir bar. The reaction mixture was stirred at 100 ^{o}C for 12 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 15:1) to give the desired product **3a** in 77% yield.

General Procedure B (GP-B) for the synthesis of **4a**: A 20.0 mL sealable screw cap vial was charged with 1-[4'-methoxy(1,1'-biphenyl)-2-yl]alkynone (**1a**, 0.20 mmol), Eosin Y (10 mol%), PIDA (2 equiv) in PhCl:$CHCl_3$ (3:1, 2 mL). The reaction was placed under 5 W green LEDs irradiation and stirred for 48 h at room temperate under N_2. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1) to give the desired product **4a** in 47% yield.

General Procedure C (GP-C) for the synthesis of **4c**: A 15 mL Schlenk flask was charged with 1-[4'-methoxy(1,1'-biphenyl)-2-yl]alkynone (**1a**, 0.20 mmol), CuBr (5 mol%), TBHP (4 equiv), CH_2Br_2 (2.0 mL) and a magnetic stir bar. The reaction mixture was stirred at 120 ^{o}C for 16 h under air. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 15:1) to give the desired product **4c** in 80% yield.

4. Mechanism study

Free-radical inhibition and trapping experiment

A 15 mL Schlenk flask was charged with 1-[4'-methoxy(1,1'-biphenyl)-2-yl]alkynone (**1a**, 0.20 mmol), BPO (0.60 mmol), TEMPO or BHT (0.4 mmol), DCM (2.0 mL) and a magnetic stir bar. The reaction mixture was stirred at 100 °C for 12 h. After completion of the reaction, TLC detection showed that the reaction was completely inhibited and no desired product **3a** was found, indicating a radical pathway involved in the reaction. Meanwhile, the key intermediate dichloromethyl radical is captured by radical acceptor (acrylamide) and its corresponding product dichloromethylated oxindole was isolated in 51% yield.

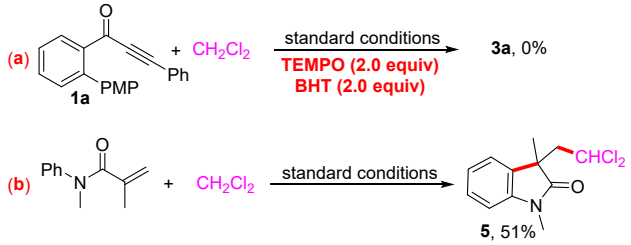
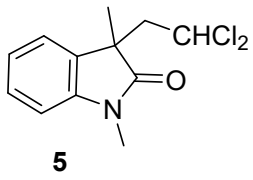


Figure S1. Control Experiments.

3-(2,2-dichloroethyl)-1,3-dimethylindolin-2-one (5)[1]

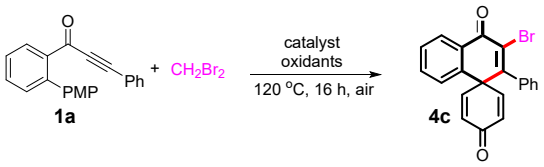


5

The product purified by flash column chromatography on silica gel (PE/ AcOEt = 30:1) to afford the **5** as a colorless liquid (26.2 mg, 51% yield). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 (td, *J* = 7.7, 1.1 Hz, 1H), 7.20 (dd, *J* = 7.3, 0.5 Hz, 1H), 7.10 (td, *J* = 7.6, 0.7 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 5.39 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.22 (s, 3H), 3.04 (dd, *J* = 14.9, 9.2 Hz, 1H), 2.71 (dd, *J* = 14.9, 4.1 Hz, 1H), 1.40 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 179.0, 143.4, 131.0, 128.6, 122.7, 122.6, 108.6, 69.6, 50.1, 47.2, 26.4, 25.4.

Refrence 1: M.-Z Lu and T.-P. Loh, *Org. Lett.*, 2014, **16**, 4698.

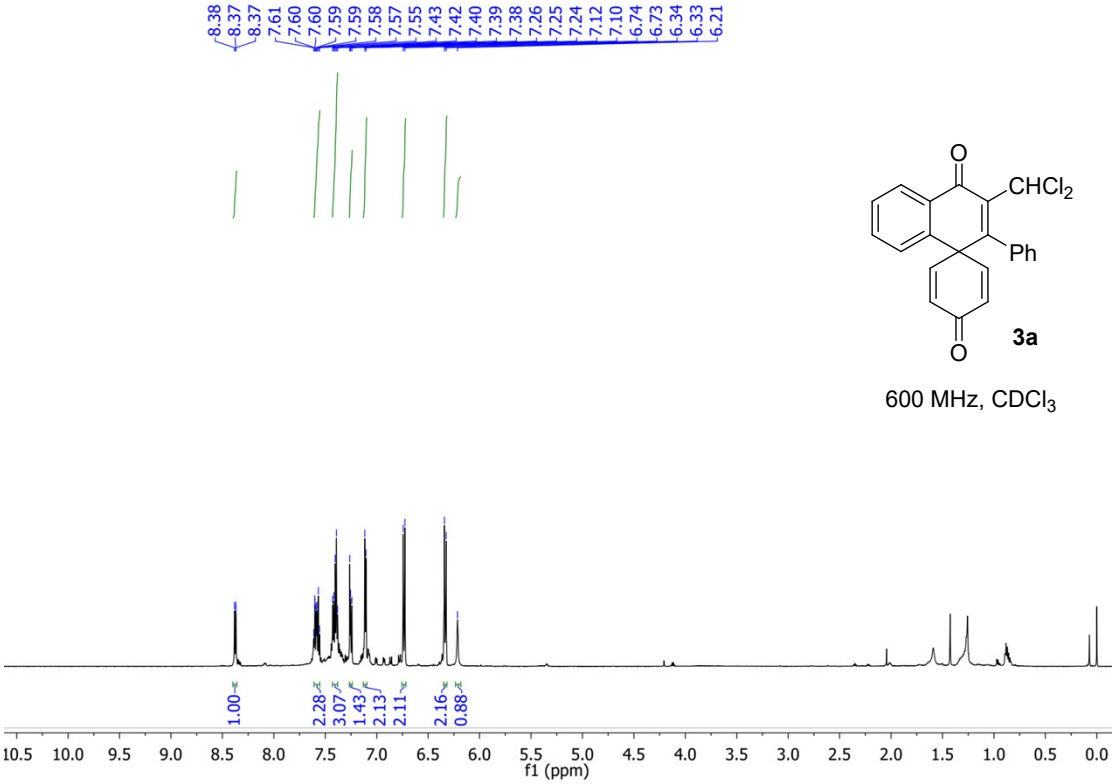
5. Optimization of the bromination reaction conditions[a]



Entry	Catalyst	Oxidant	Yield (%)[b]
1	CuBr	TBHP	80
2	CuBr	DTBP	12
3	CuBr	DCP	33
4	CuBr	$K_2S_2O_8$	trace
5	CuBr	$(NH_4)_2S_2O_8$	trace
6	CuBr	LPO	41
7	CuCl	TBHP	70
8	CuI	TBHP	67
9	CuO	TBHP	76
10	$Cu(OAc)_2$	TBHP	45
11	--	TBHP	trace
12	CuBr	--	trace

[a] Reaction conditions: **1a** (0.2 mmol), catalyst (5 mol%), oxidant (4 equiv) in CH_2Br_2 (2 mL) at 120 °C for 16 h under air; isolated yields.

6. ^{1}H NMR and ^{13}C NMR of the products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7.38
7.26
7.25
7.24
7.12
7.10
6.74
6.73
6.34
6.33
6.21
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CHCl2
Ph
O
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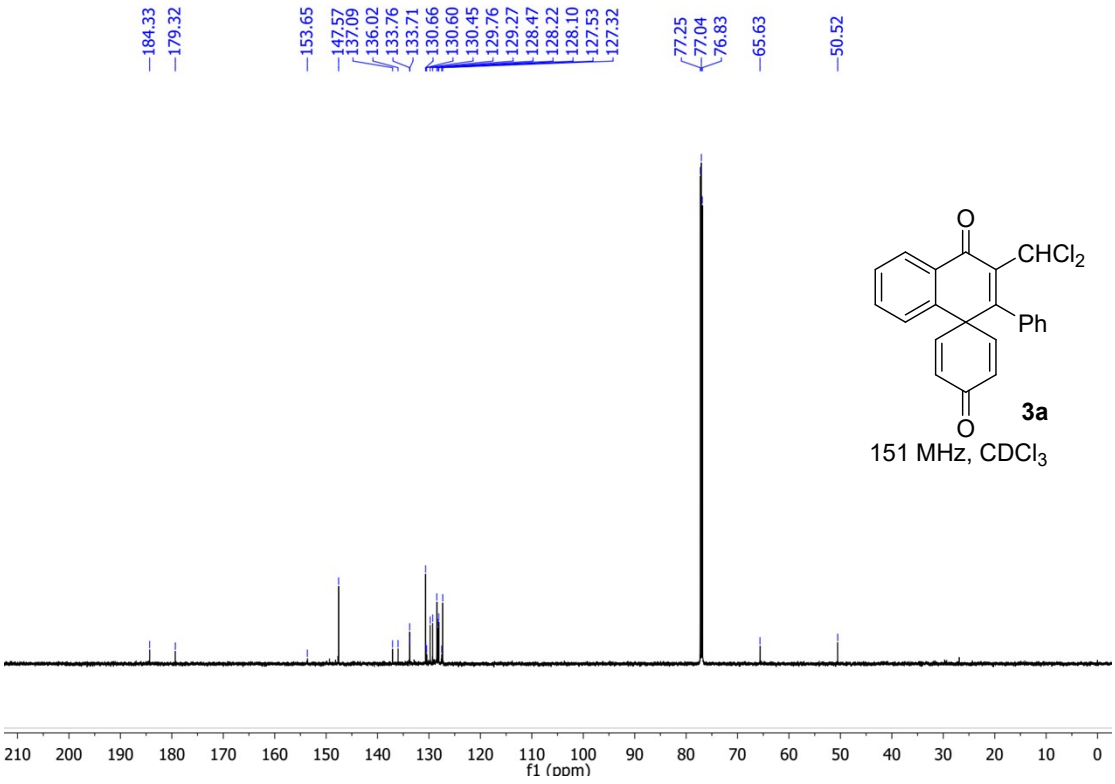
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128.10
127.53
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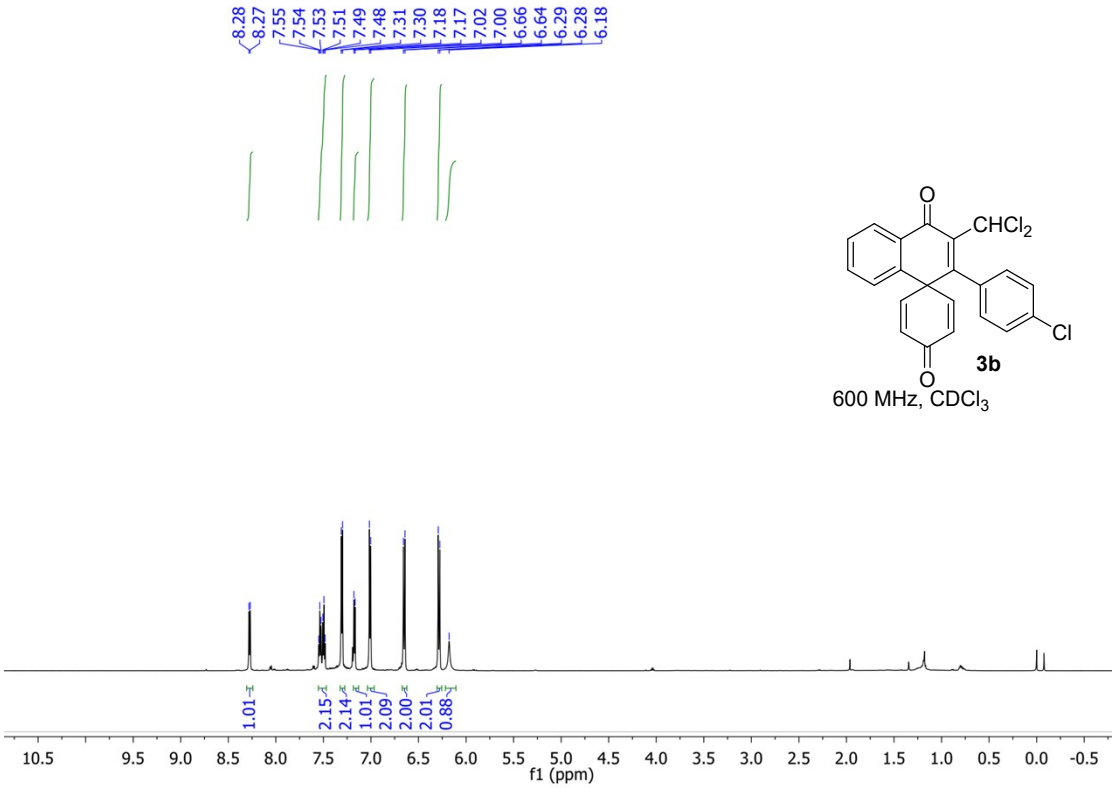
Ph
O
3a
151 MHz, CDCl3
f1 (ppm)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Cl
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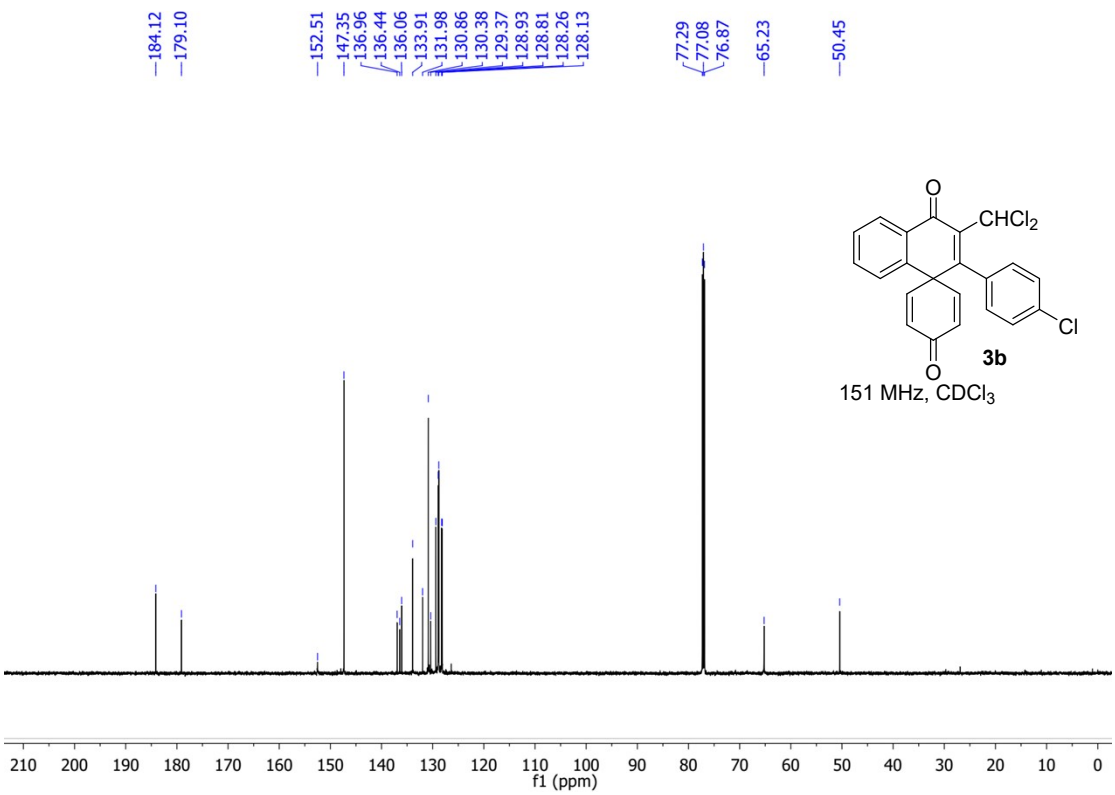
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Cl
O
3b
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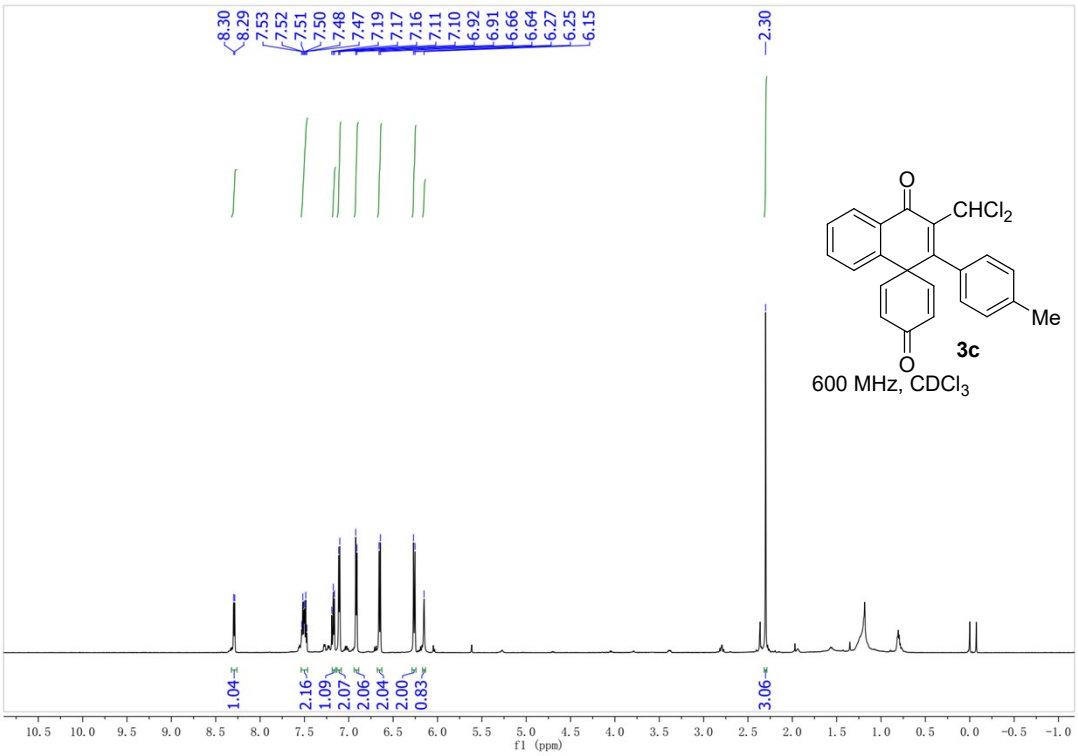
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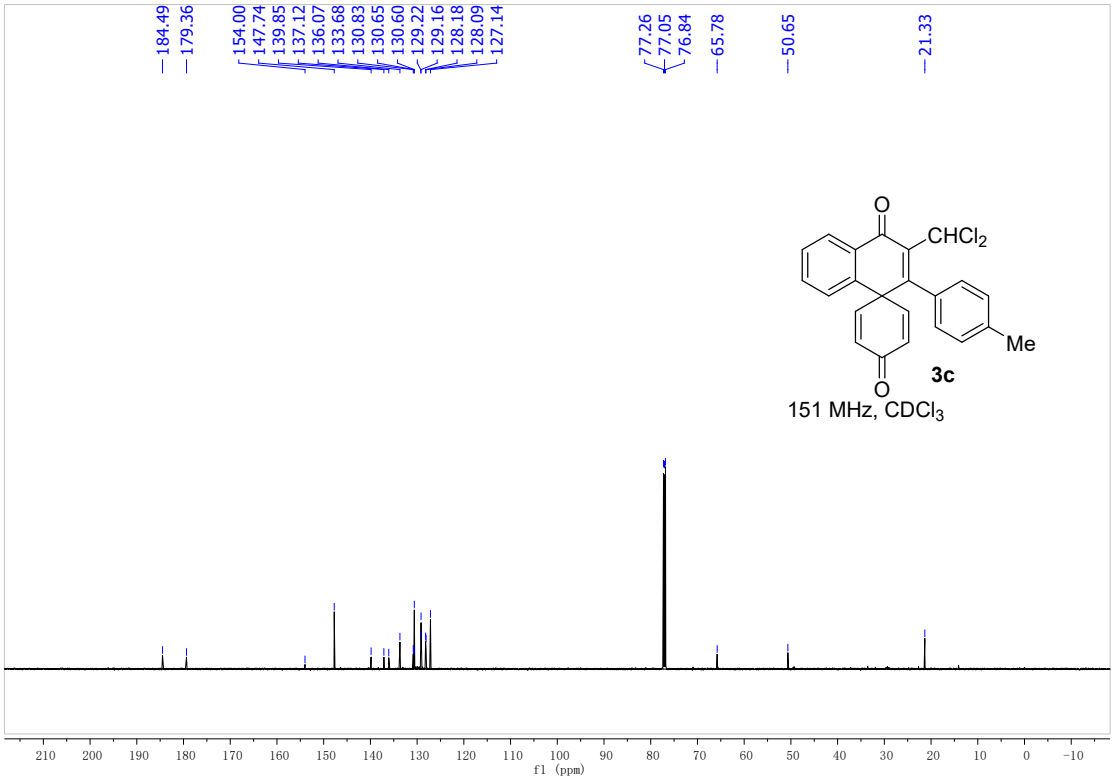
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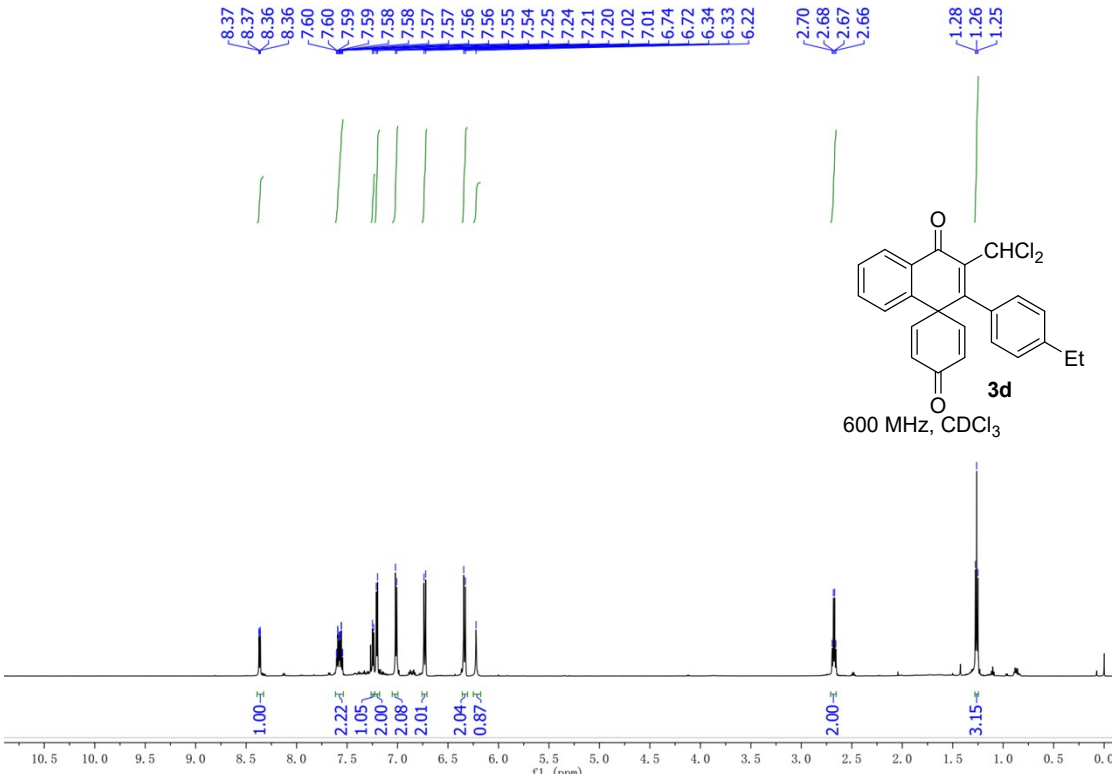
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Et
O
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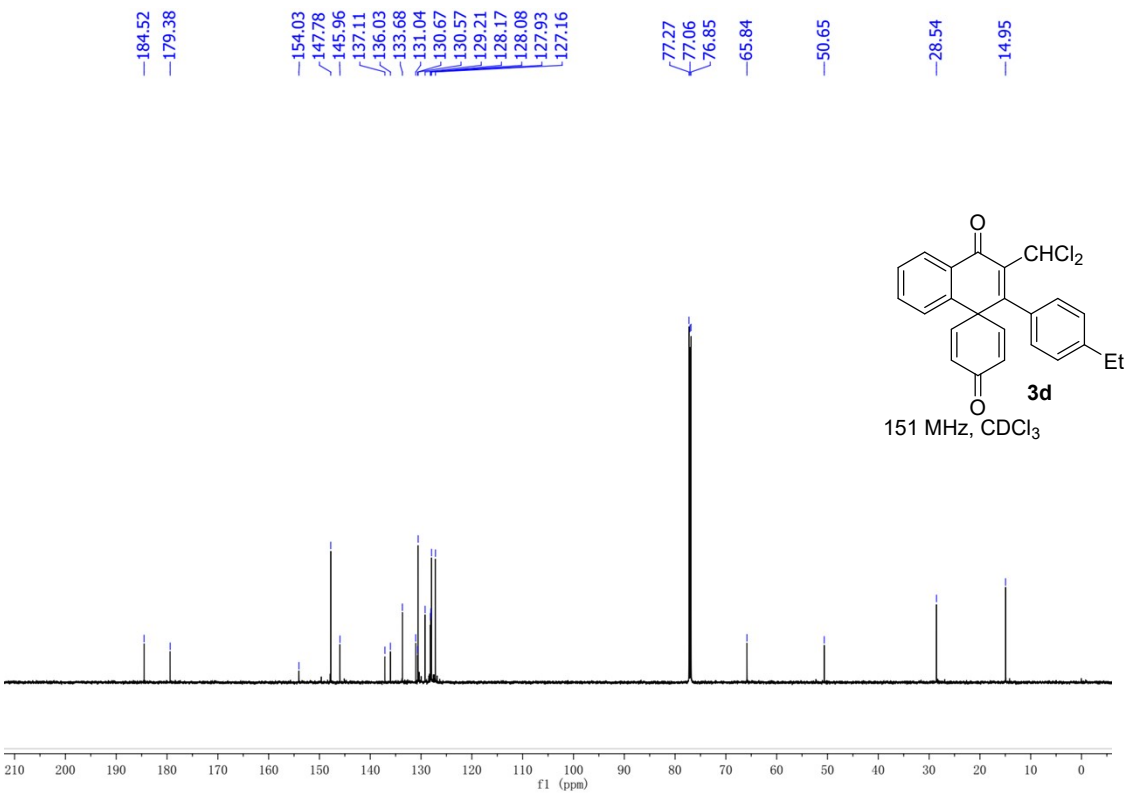
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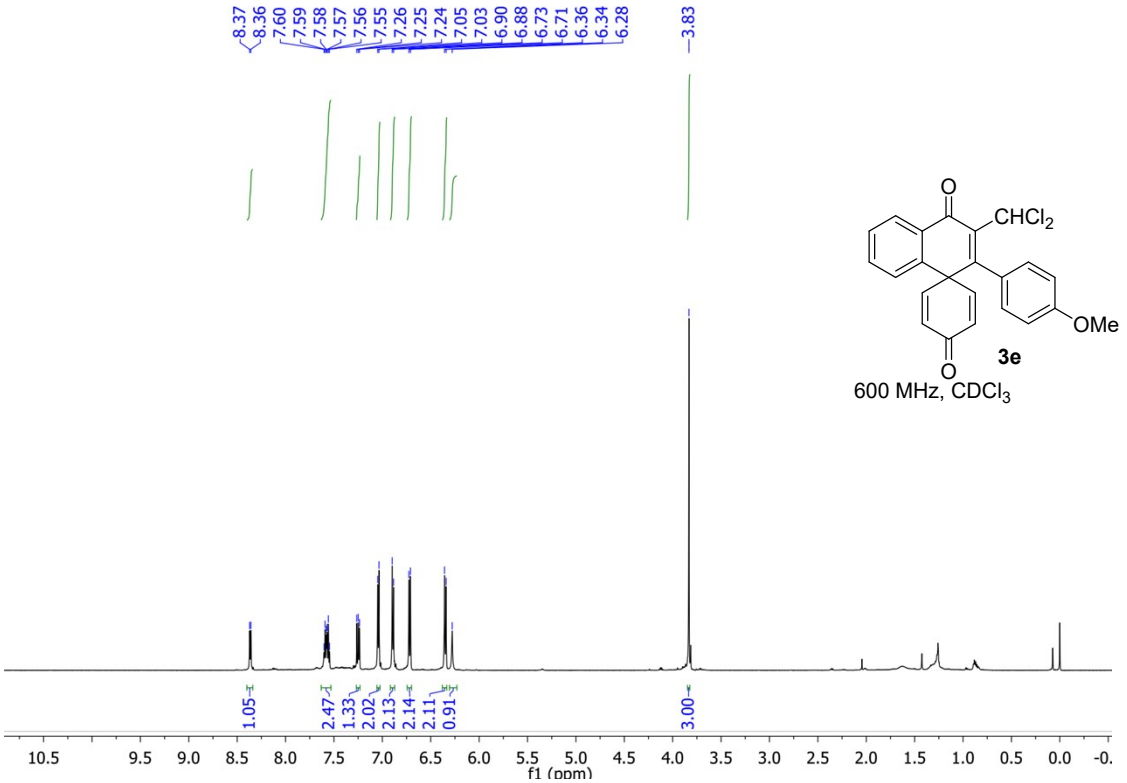
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OMe
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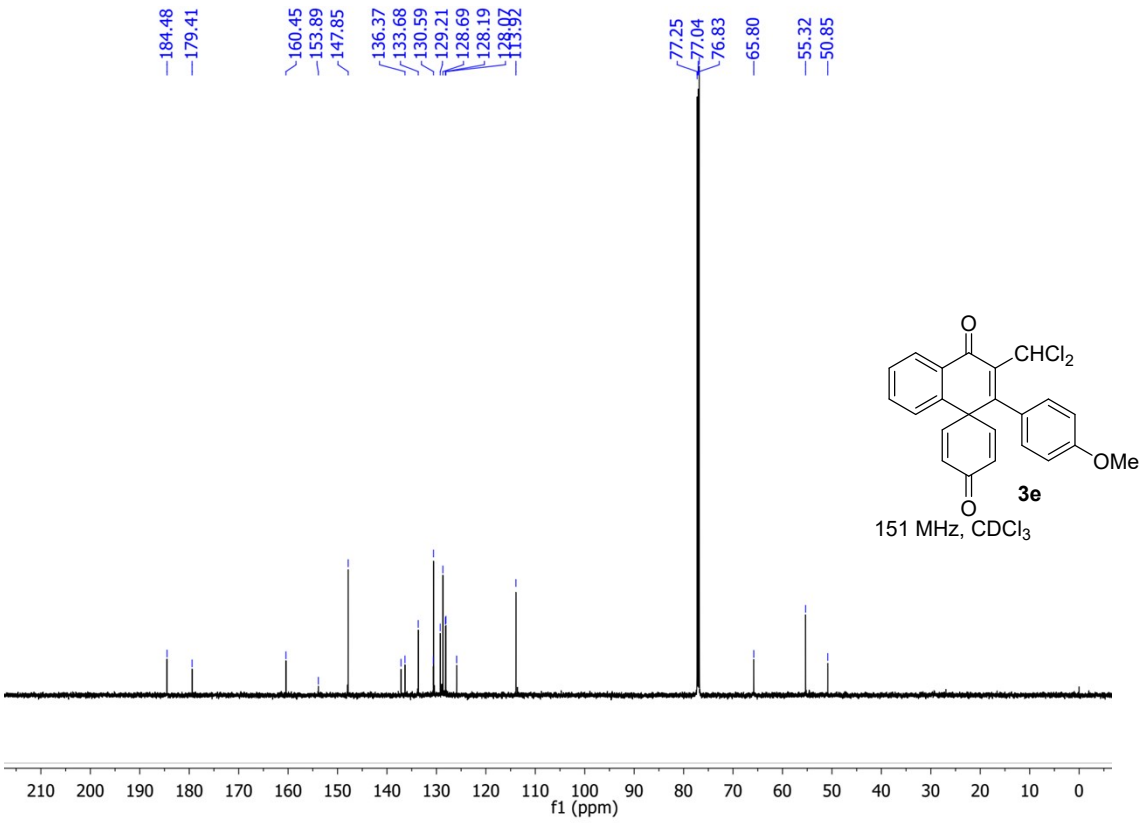
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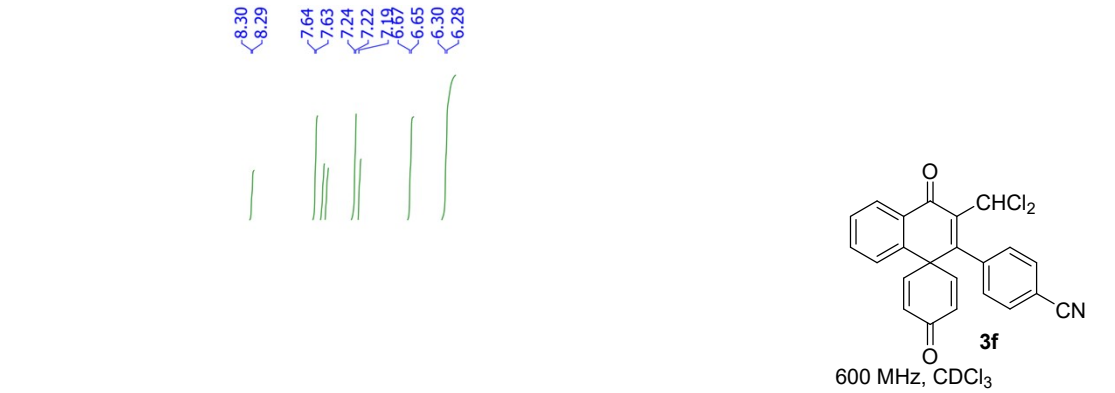
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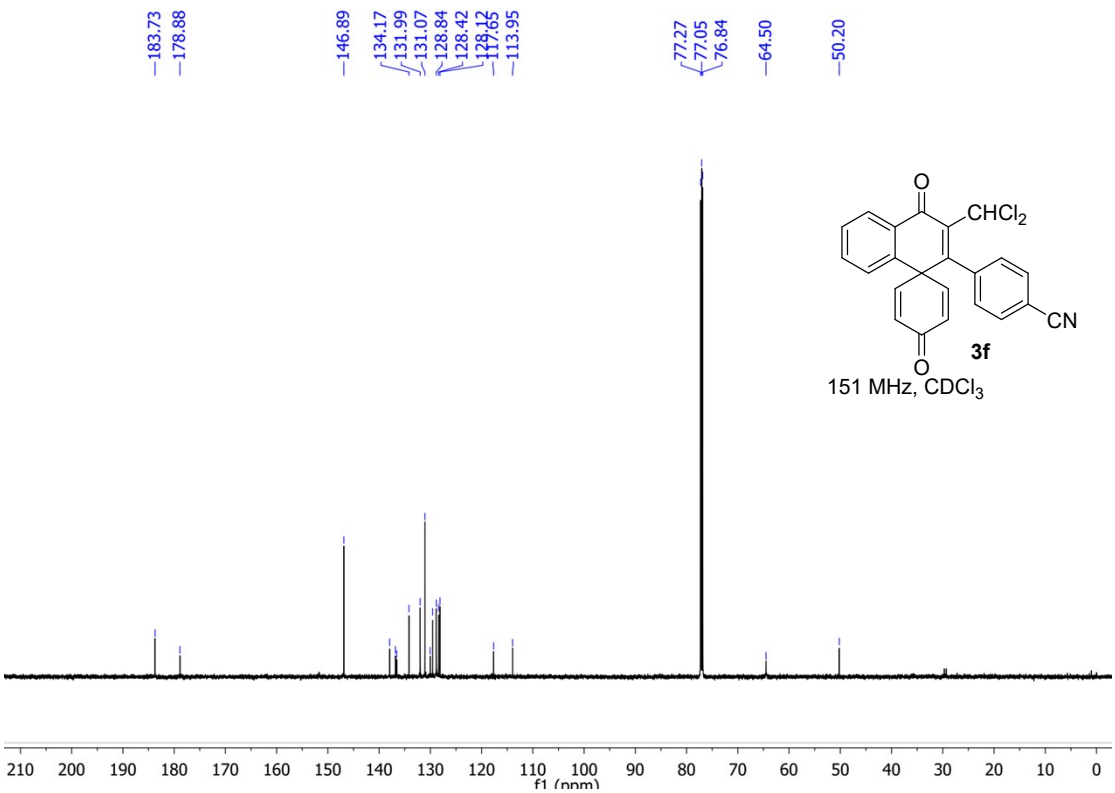
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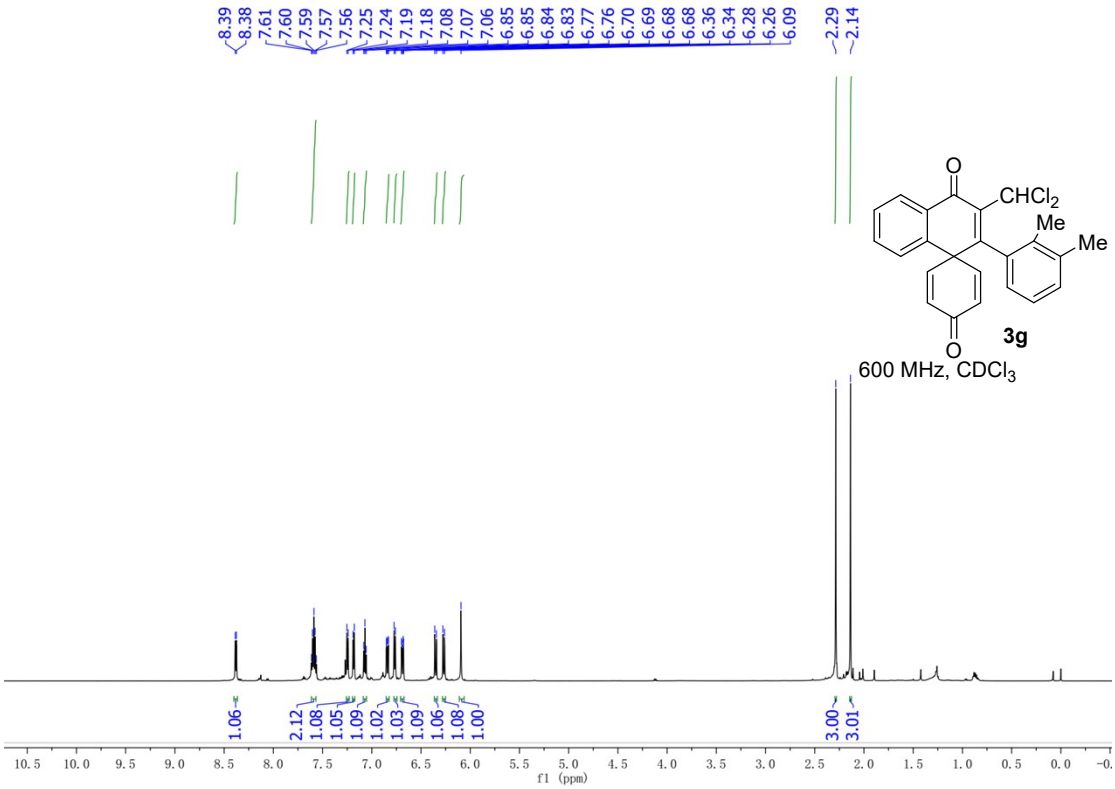
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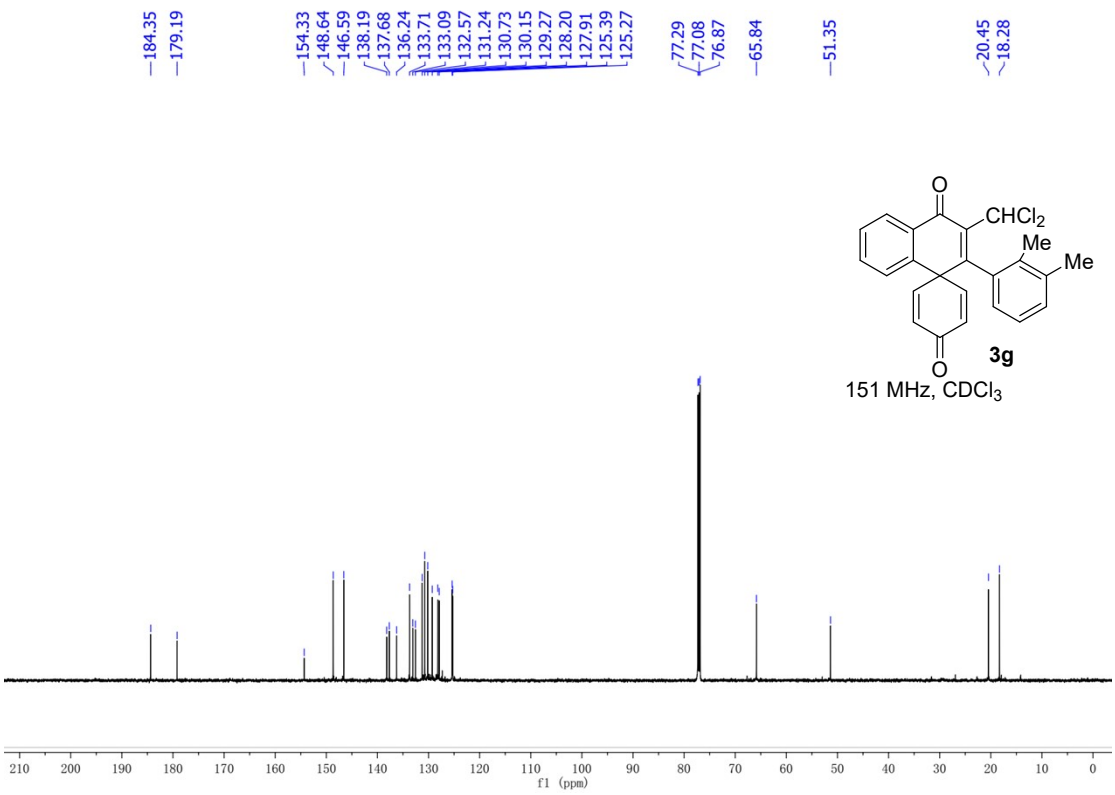
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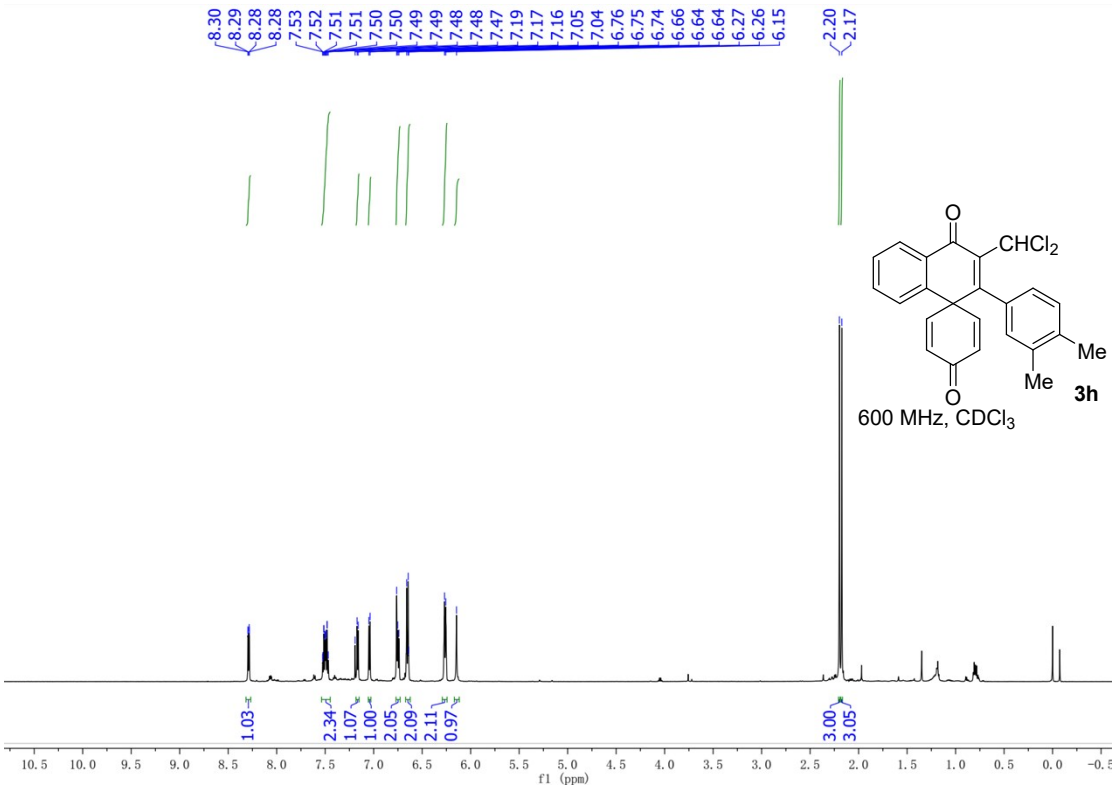
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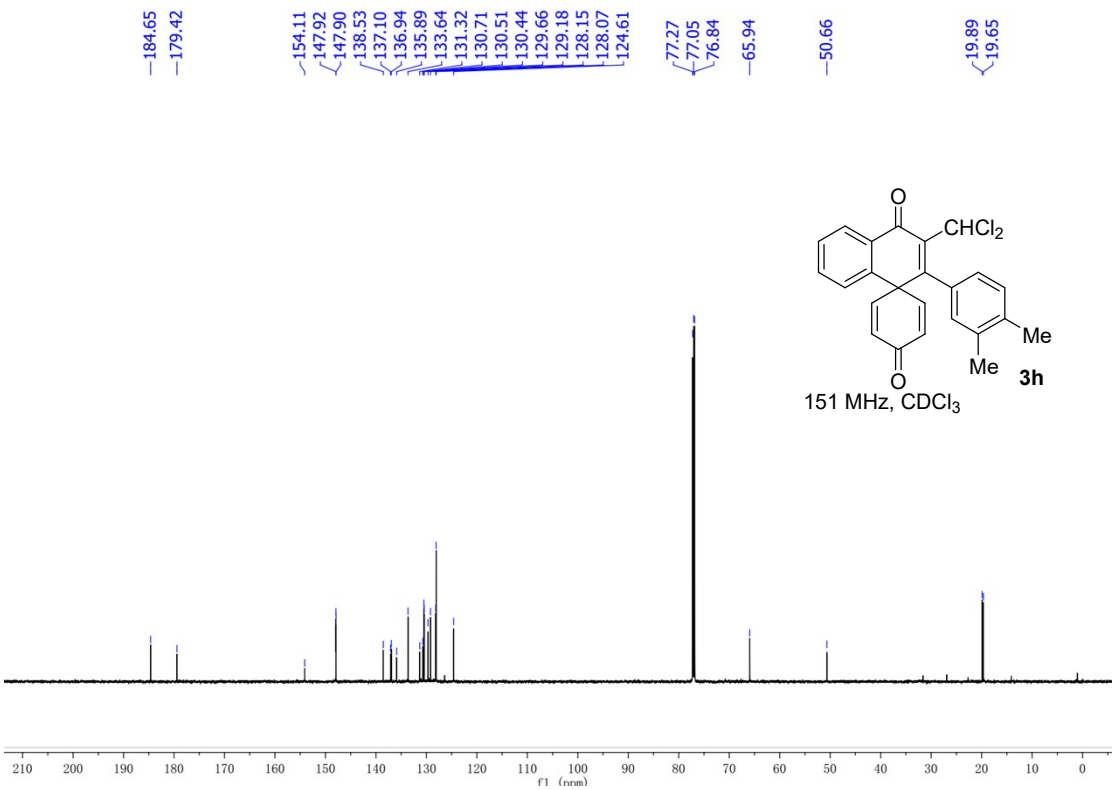
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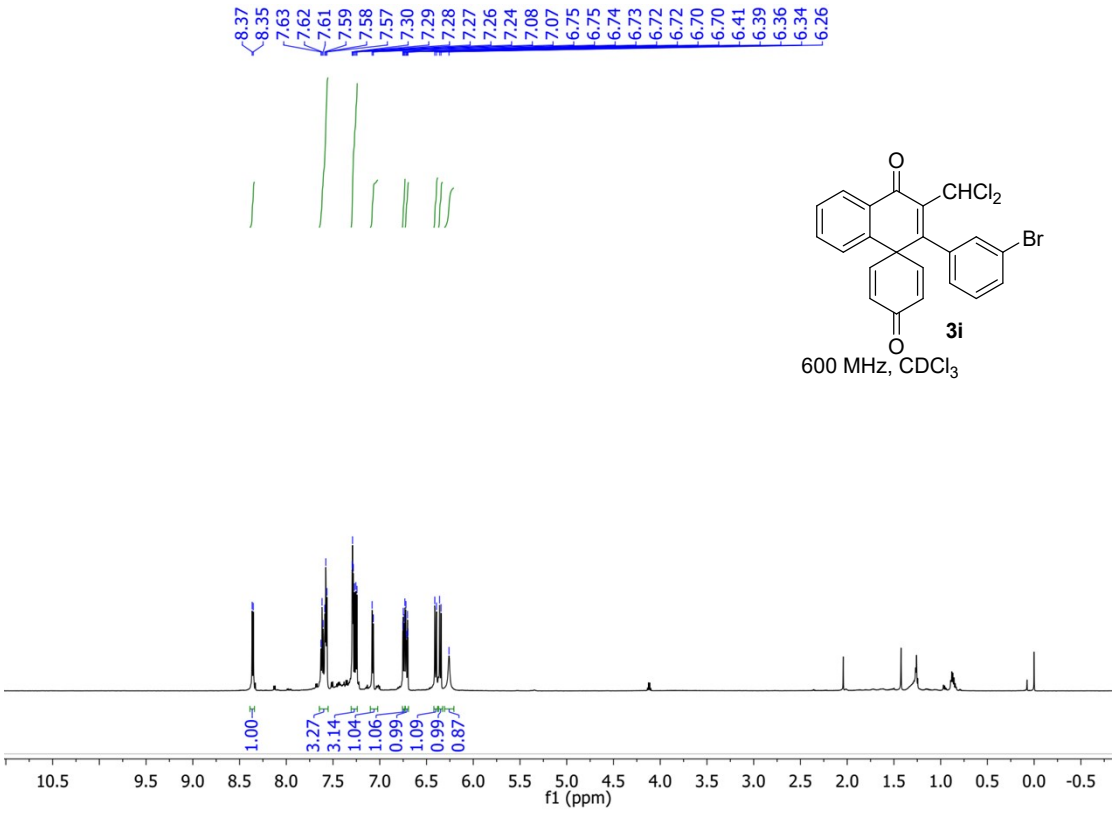
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Br
O
3i
600 MHz, CDCl3
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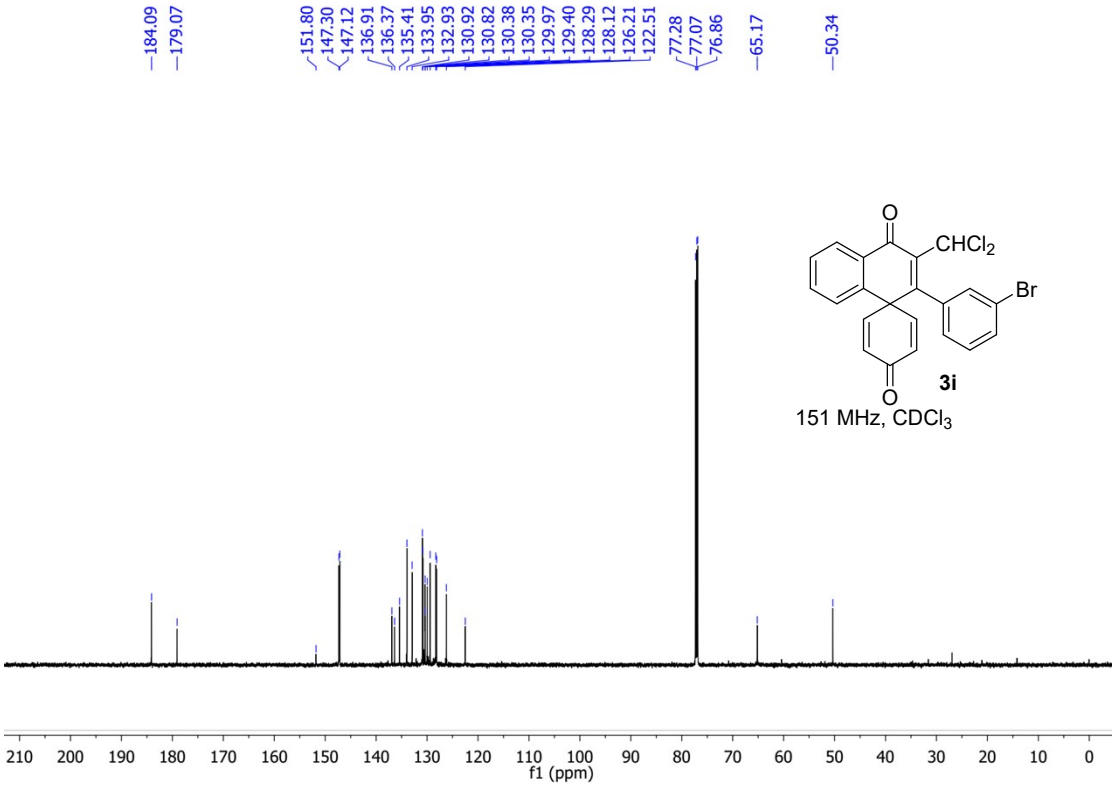
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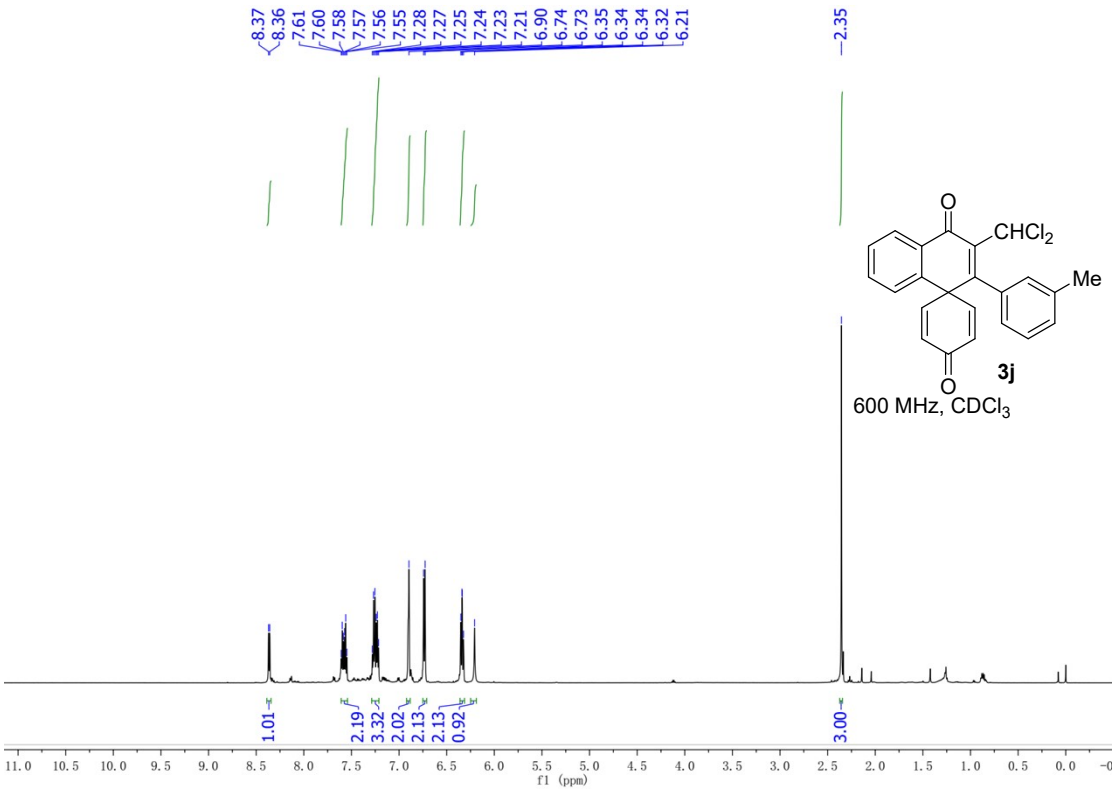
128.29
128.12
126.21
122.51
77.28
77.07
76.86
65.17
50.34
O
CHCl2
Br
O
3i
151 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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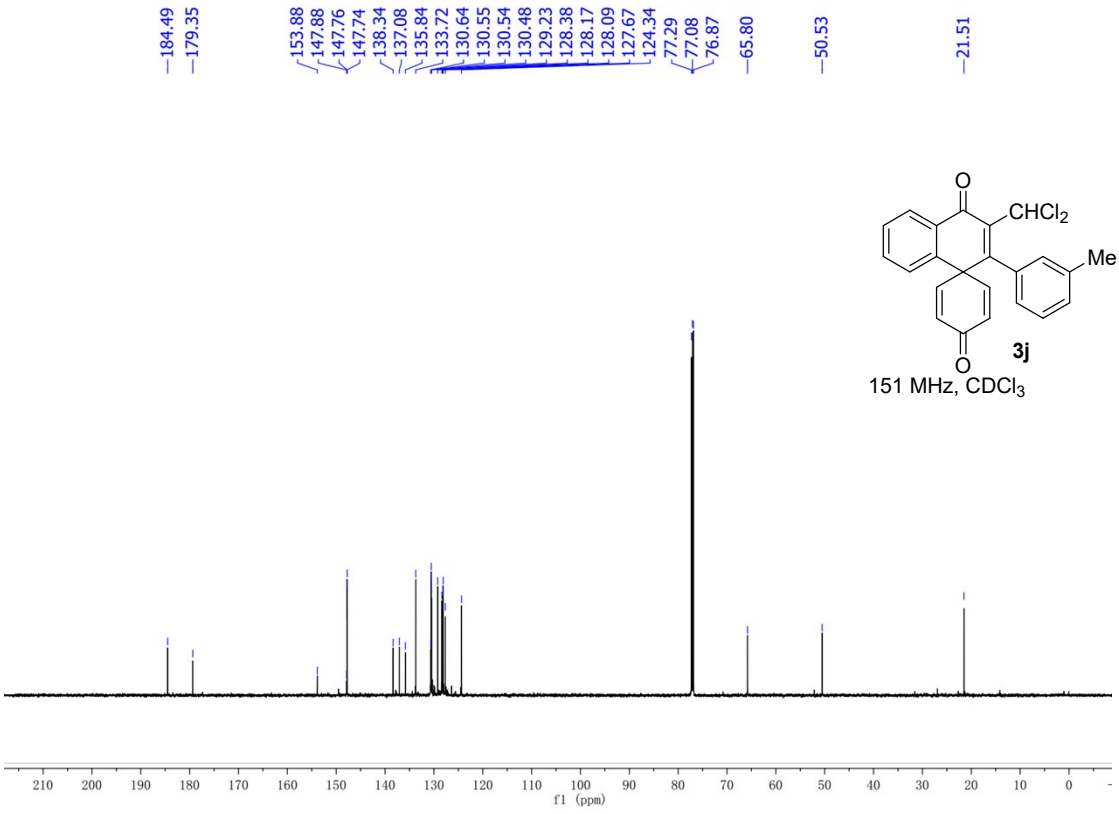
8.36
7.61
7.60
7.58
7.57
7.56
7.55
7.28
7.27
7.25
7.24
7.23
7.21
6.90
6.74
6.73
6.35
6.34
6.34
6.32
6.21
2.35
1.01
2.19
3.32
2.02
2.13
2.13
0.92
3.00
f1 (ppm)
O
CHCl2
Me
O
3j
600 MHz, CDCl3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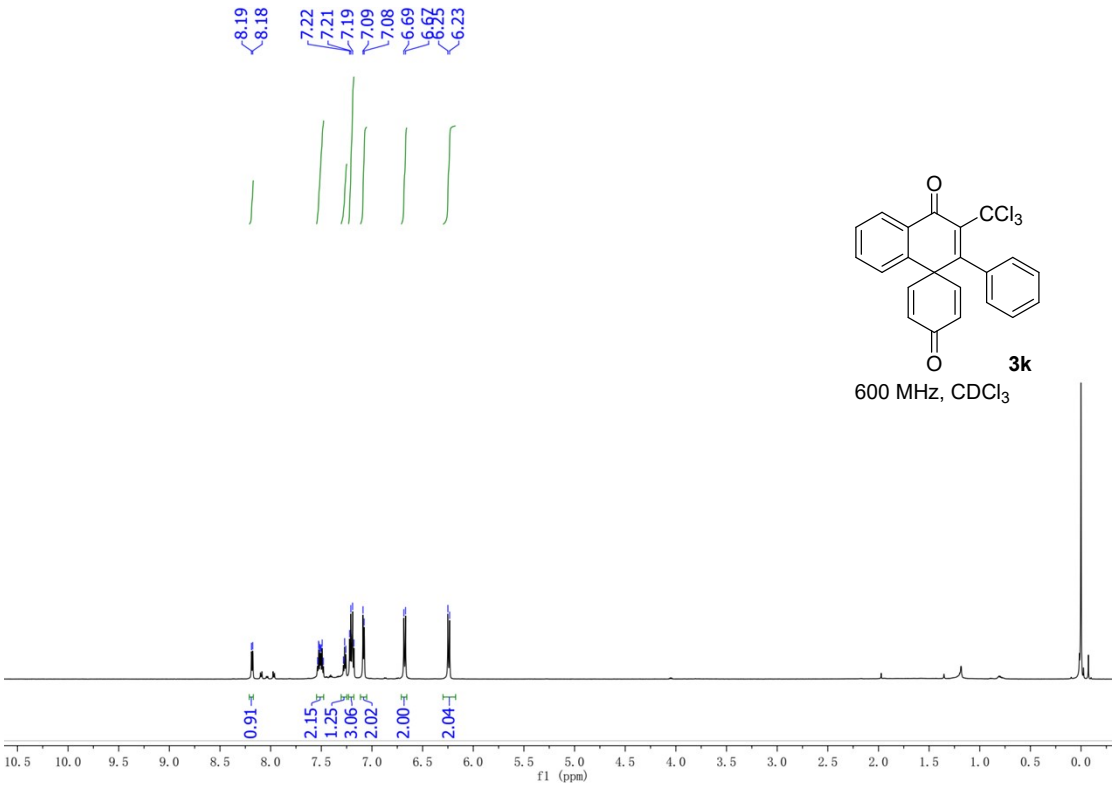
147.74
138.34
137.08
135.84
133.72
130.64
130.55
130.54
130.48
129.23
128.38
128.17
128.09
127.67
124.34
77.29
77.08
76.87
65.80
50.53
21.51
f1 (ppm)
O
CHCl2
Me
O
3j
151 MHz, CDCl3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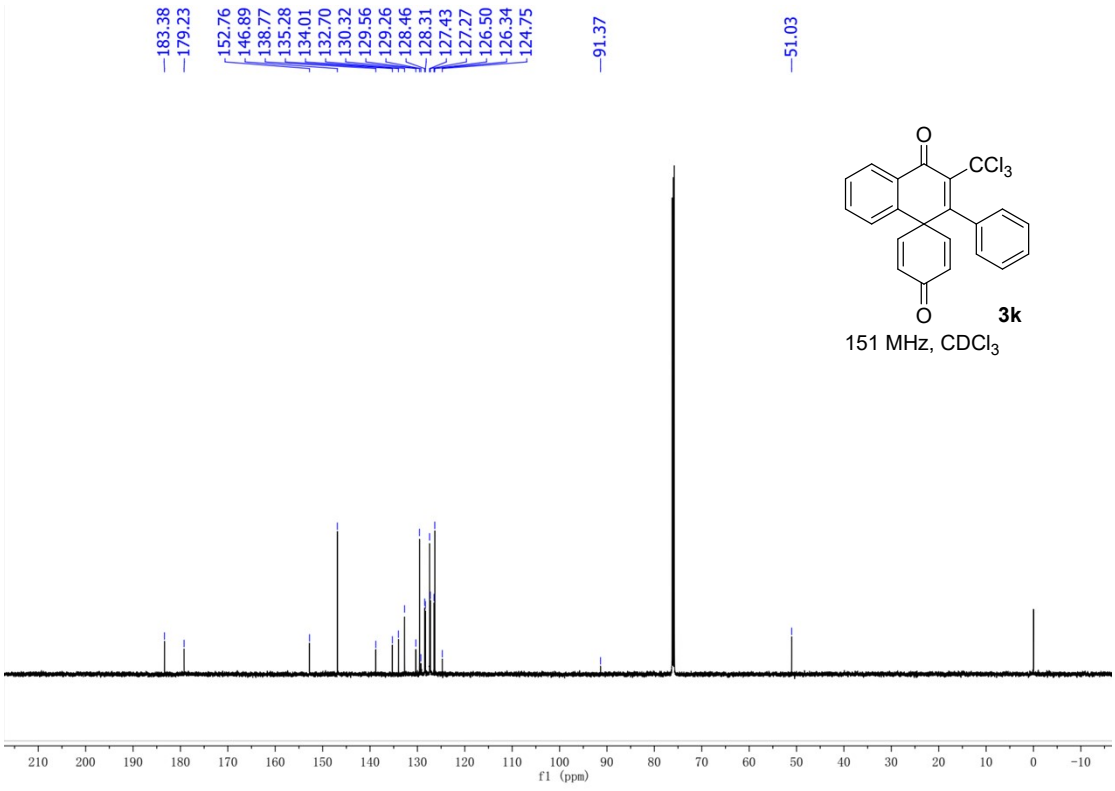
8.18
7.22
7.21
7.19
7.09
7.08
6.69
6.67
6.25
6.23
O
CCl3
O
3k
600 MHz, CDCl3
0.91
2.15
1.25
3.06
2.02
2.00
2.04
f1 (ppm)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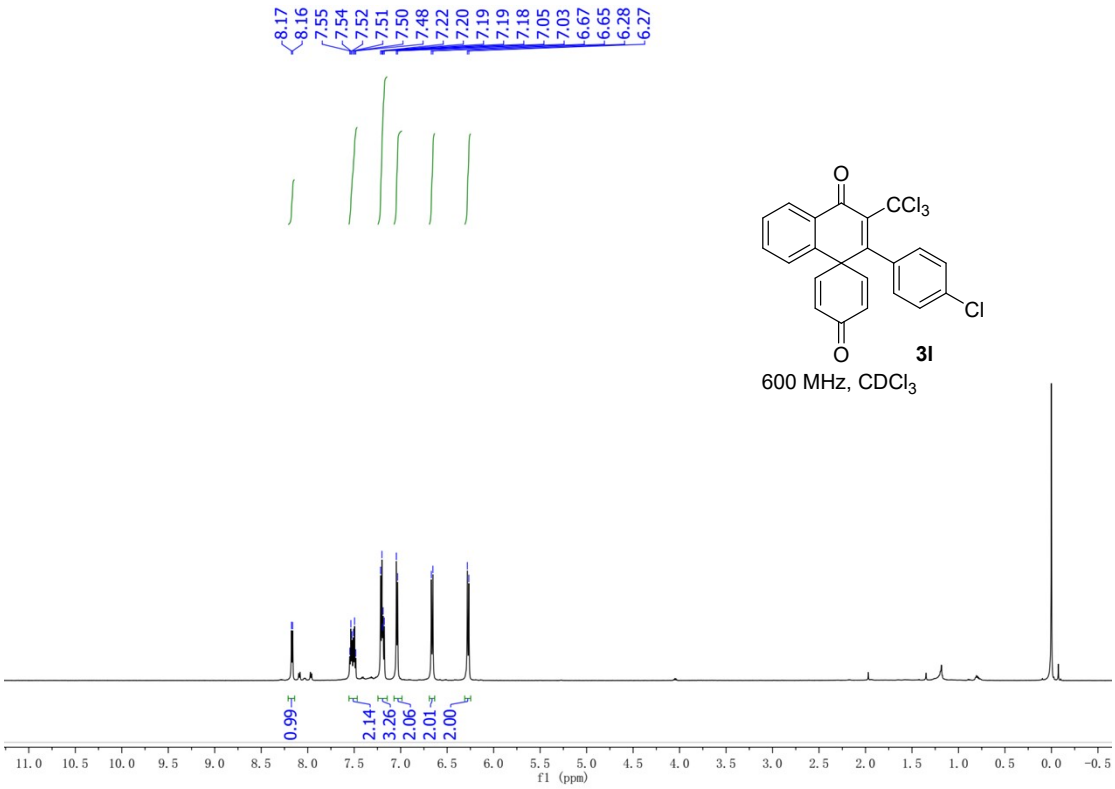
134.01
132.70
130.32
129.56
129.26
128.46
128.31
127.43
127.27
126.50
126.34
124.75
91.37
51.03
O
CCl3
O
3k
151 MHz, CDCl3
f1 (ppm)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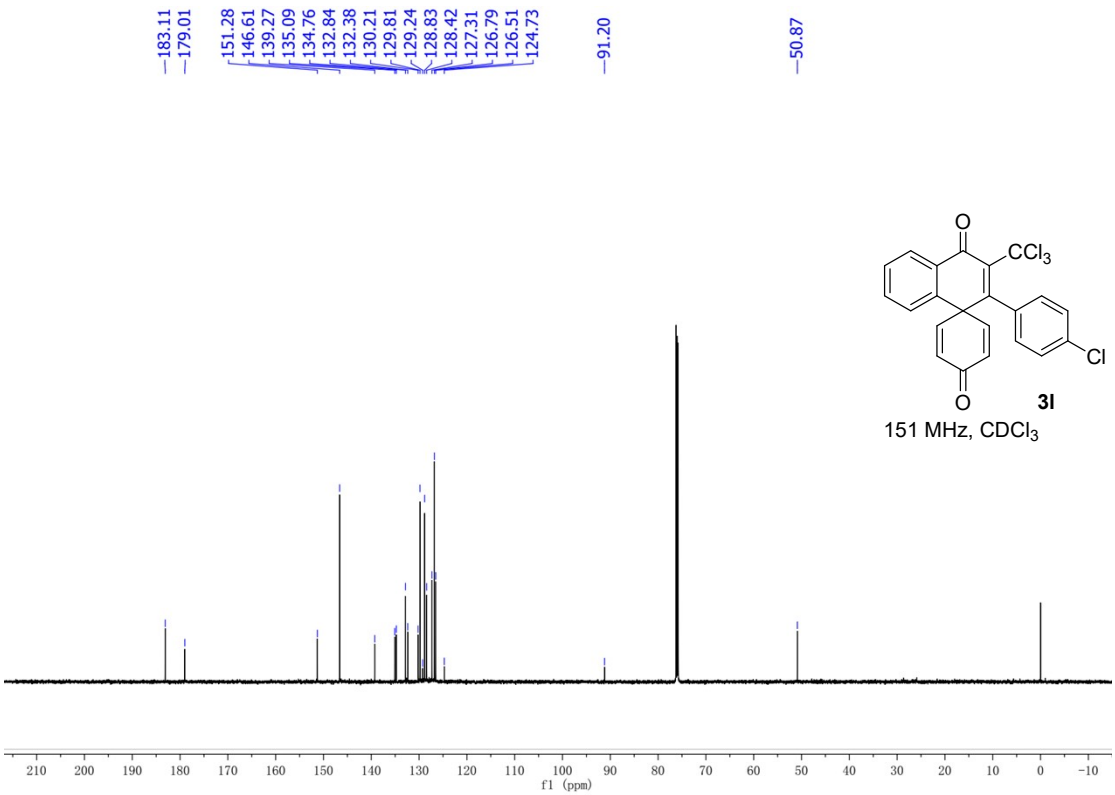
8.16
7.55
7.54
7.52
7.51
7.50
7.48
7.22
7.20
7.19
7.19
7.18
7.05
7.03
6.67
6.65
6.28
6.27
O
CCl3
Cl
O
3l
600 MHz, CDCl3
0.99
2.14
3.26
2.06
2.01
2.00
f1 (ppm)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179.01
151.28
146.61
139.27
135.09
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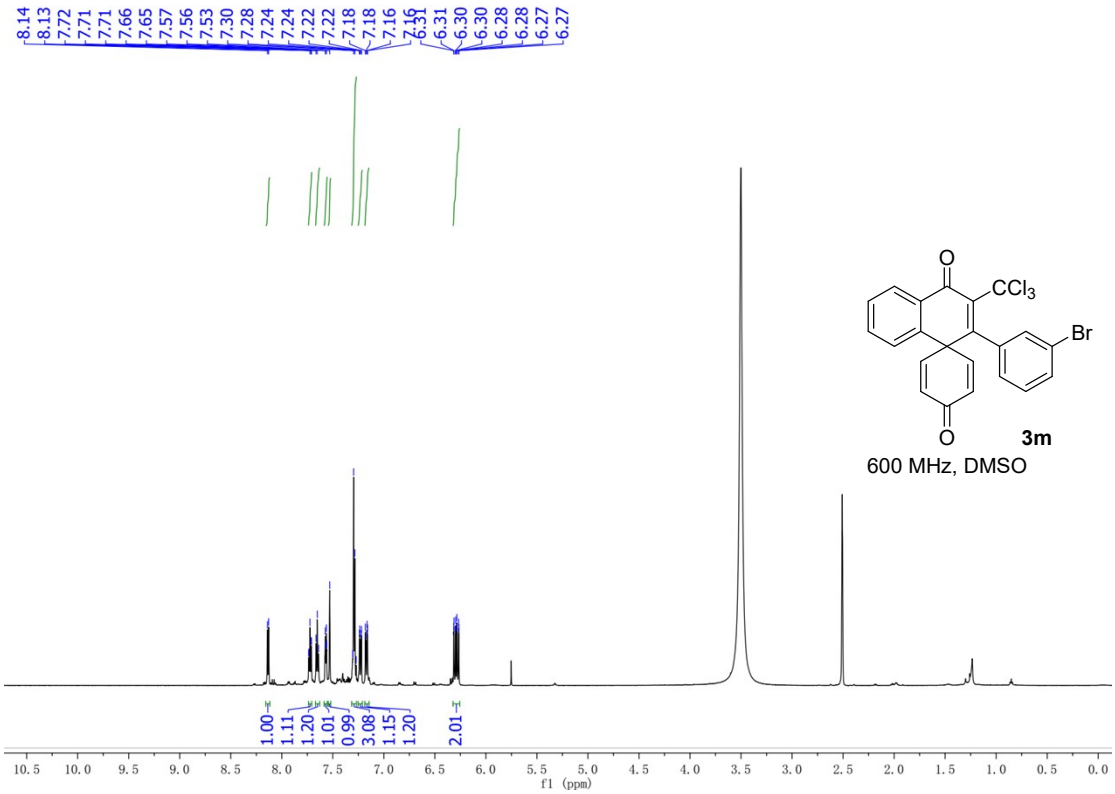
132.84
132.38
130.21
129.81
129.24
128.83
128.42
127.31
126.79
126.51
124.73
91.20
50.87
O
CCl3
Cl
O
3l
151 MHz, CDCl3
f1 (ppm)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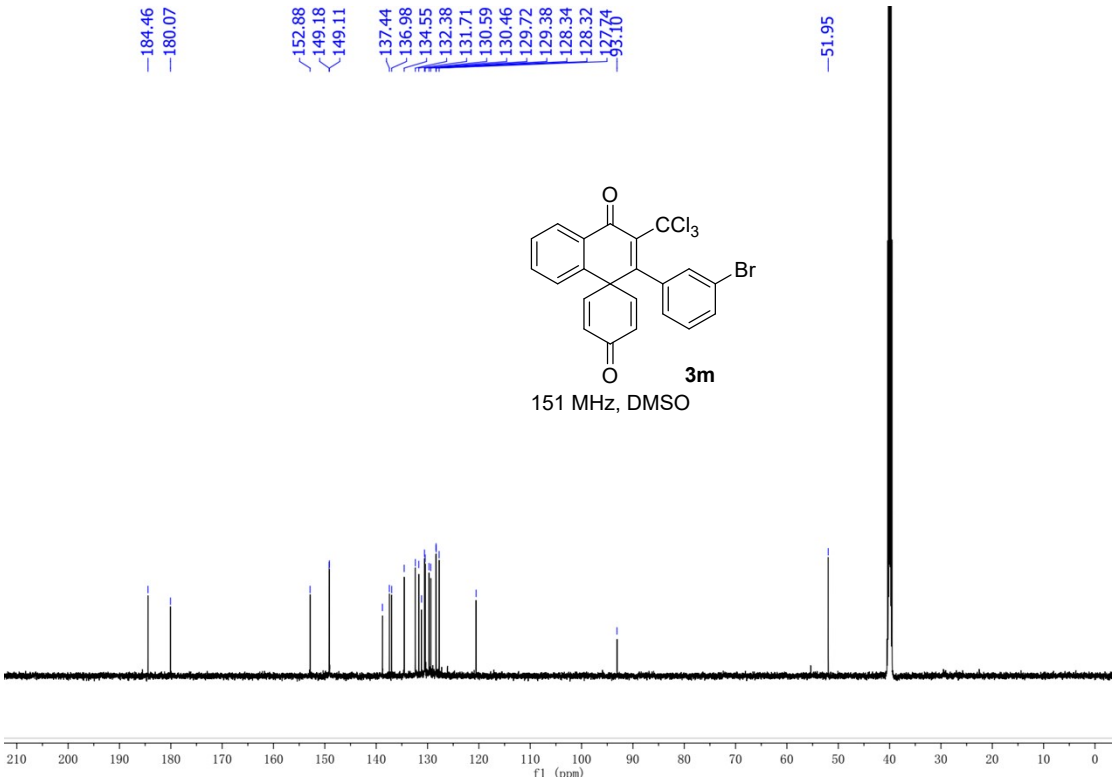
8.13
7.72
7.71
7.71
7.66
7.65
7.57
7.56
7.53
7.30
7.28
7.24
7.24
7.22
7.22
7.18
7.18
7.16
7.16
6.31
6.30
6.30
6.28
6.28
6.27
6.27
1.00
1.11
1.20
1.01
0.99
3.08
1.15
1.20
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
CCl3
Br
O
3m
600 MHz, DMSO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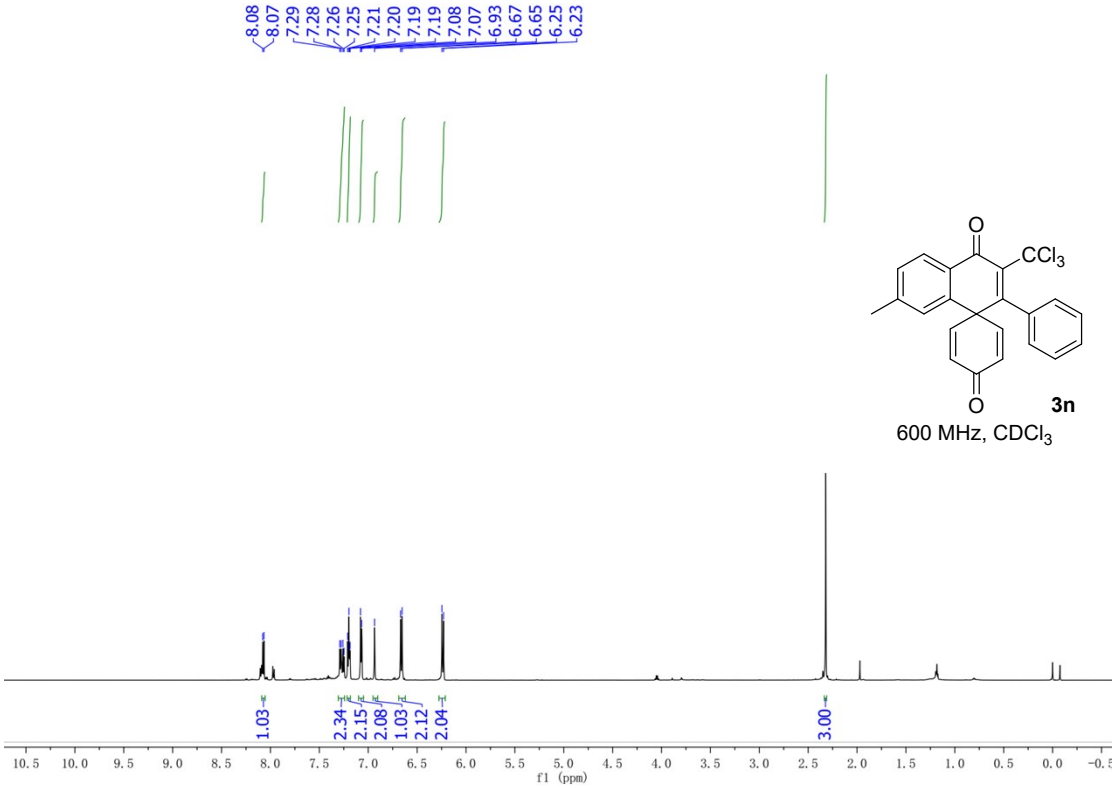
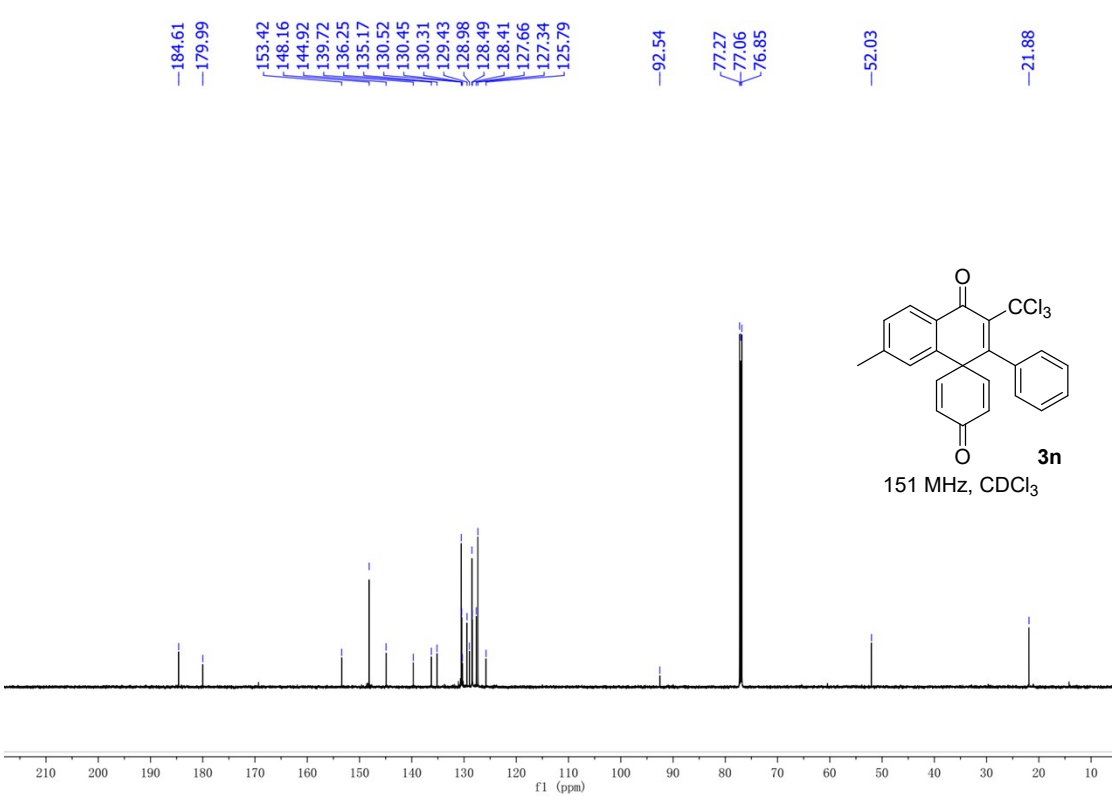
180.07
152.88
149.18
149.11
137.44
136.98
134.55
132.38
131.71
130.59
130.46
129.72
129.38
128.34
128.32
127.74
93.10
51.95
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
CCl3
Br
O
3m
151 MHz, DMSO


8.08
8.07
7.29
7.28
7.26
7.25
7.21
7.20
7.19
7.19
7.08
7.07
6.93
6.67
6.65
6.25
6.23
O
CCl3
O
3n
600 MHz, CDCl3
1.03
2.34
2.15
2.08
1.03
2.12
2.04
3.00
f1 (ppm)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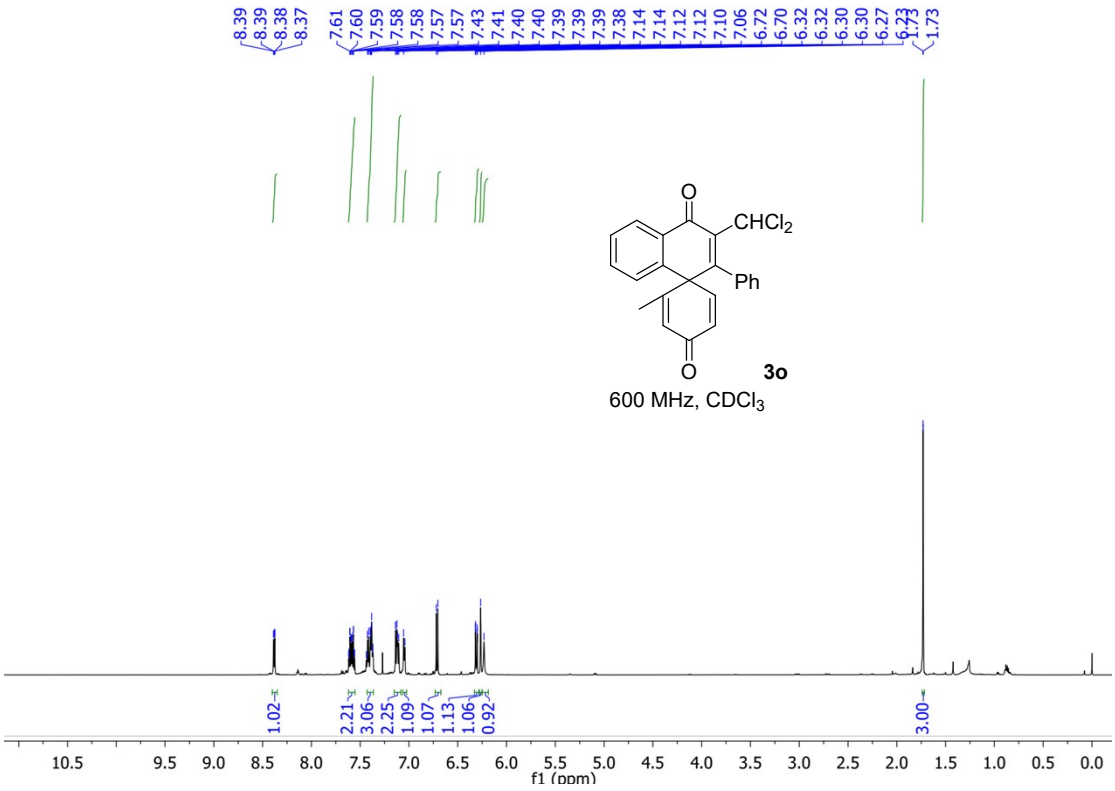
179.99
153.42
148.16
144.92
139.72
136.25
135.17
130.52
130.45
130.31
129.43
128.98
128.49
128.41
127.66
127.34
125.79
92.54
77.27
77.06
76.85
52.03
21.88
O
CCl3
O
3n
151 MHz, CDCl3
f1 (ppm)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8.39
8.38
8.37
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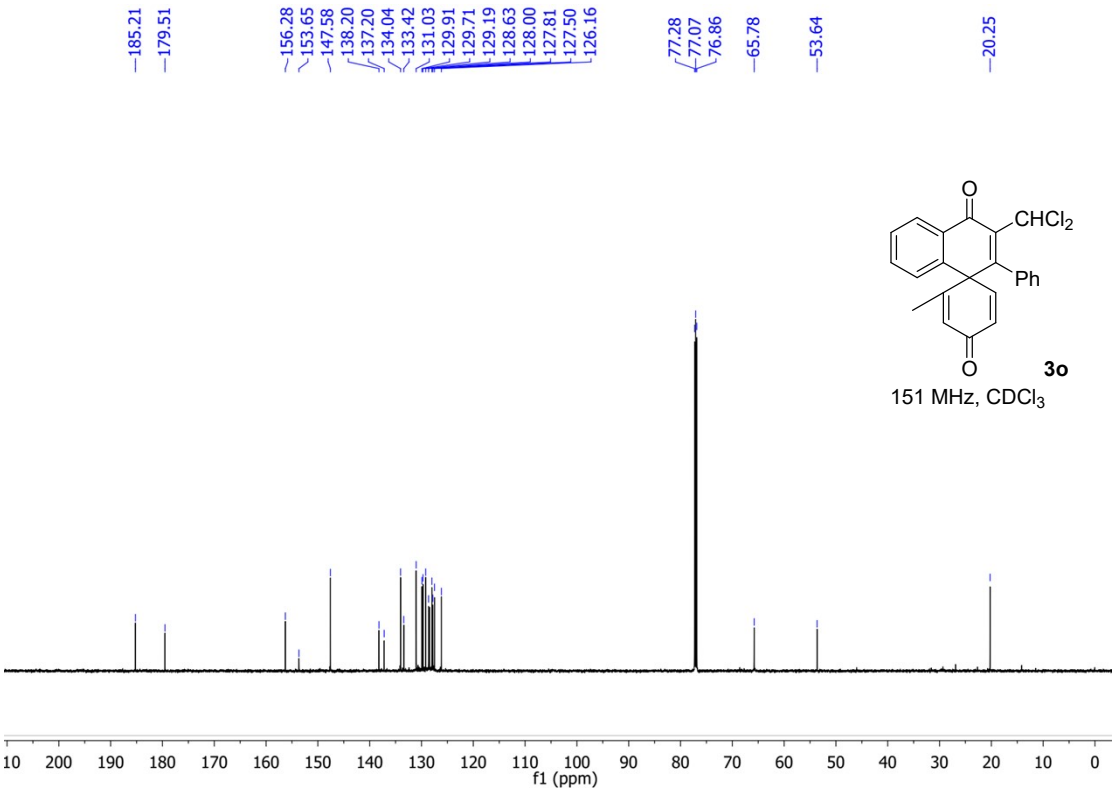
7.60
7.59
7.58
7.58
7.57
7.57
7.43
7.41
7.40
7.40
7.39
7.39
7.39
7.38
7.14
7.12
7.12
7.10
7.06
6.72
6.70
6.32
6.32
6.30
6.30
6.27
1.73
1.73
O
CHCl2
Ph
O
3o
600 MHz, CDCl3
1.02
2.21
3.06
2.25
1.09
1.07
1.13
1.06
0.92
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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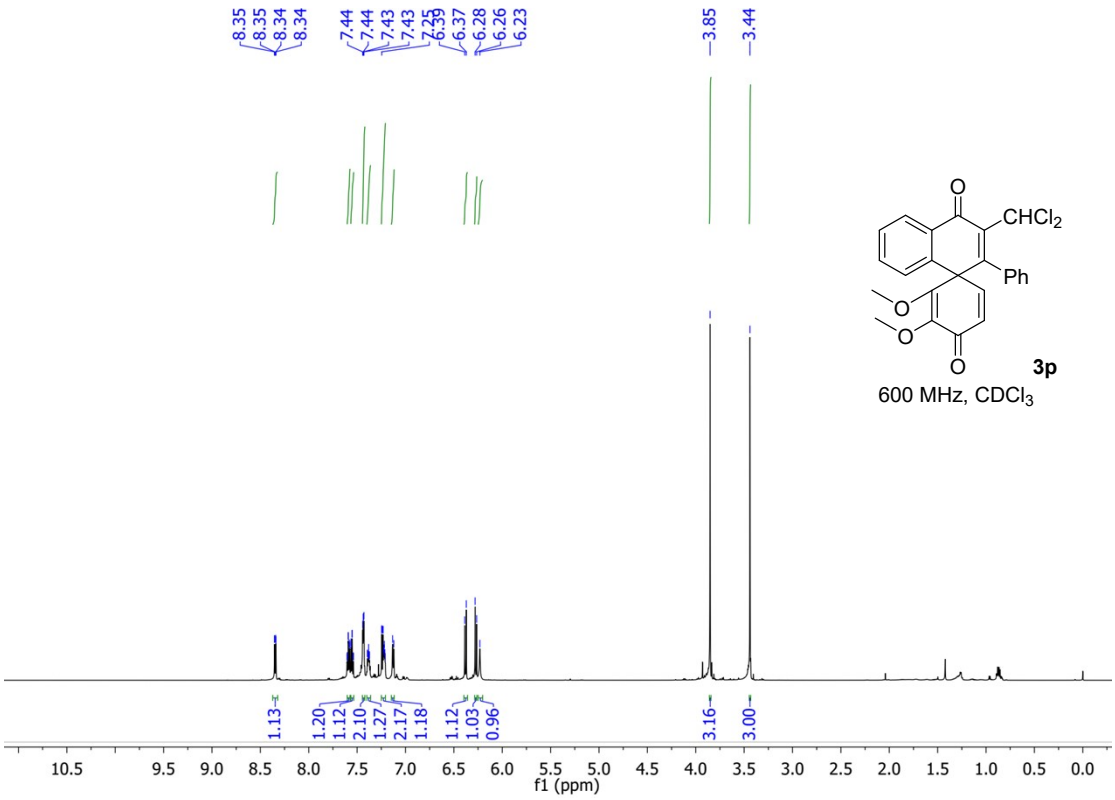
156.28
153.65
147.58
138.20
137.20
134.04
133.42
131.03
129.91
129.71
129.19
128.63
128.00
127.81
127.50
126.16
77.28
77.07
76.86
65.78
53.64
20.25
O
CHCl2
Ph
O
3o
151 MHz, CDCl3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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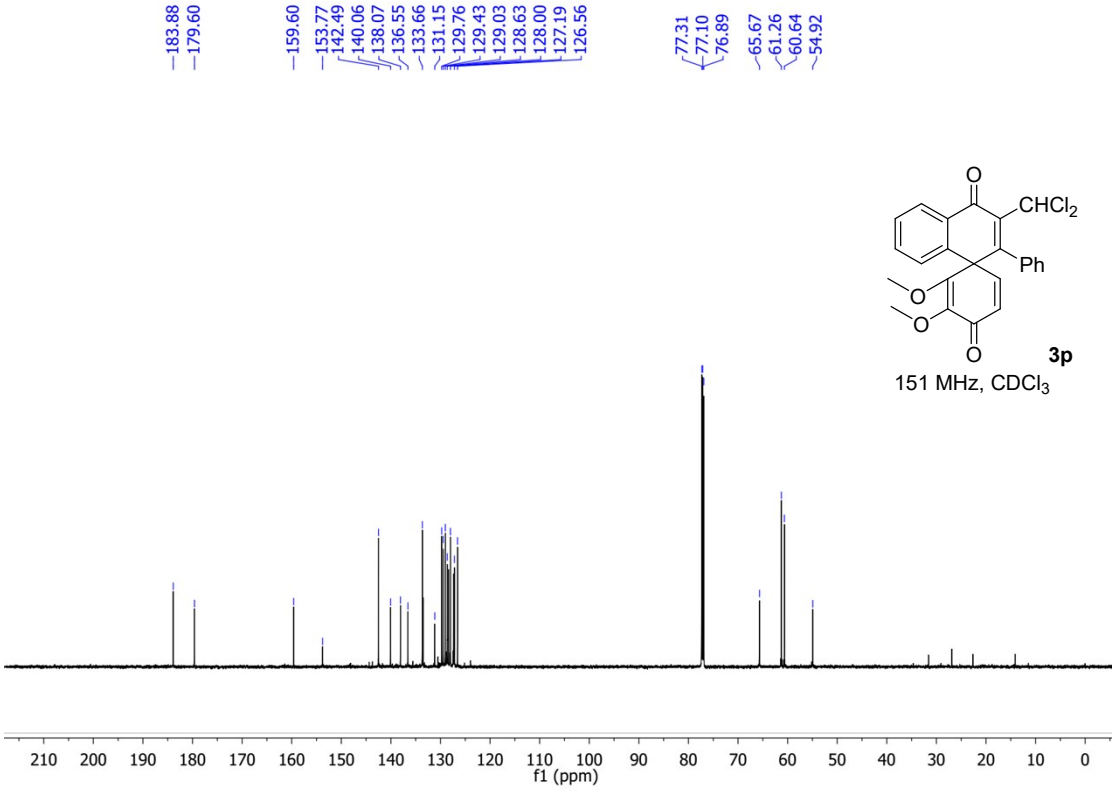
8.35
8.34
8.34
7.44
7.44
7.43
7.43
7.25
6.39
6.37
6.28
6.26
6.23
3.85
3.44
1.13
1.20
1.12
2.10
1.27
2.17
1.18
1.12
1.03
0.96
3.16
3.00
f1 (ppm)
CHCl2
Ph
O
O
O
O
3p
600 MHz, CDCl3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179.60
159.60
153.77
142.49
140.06
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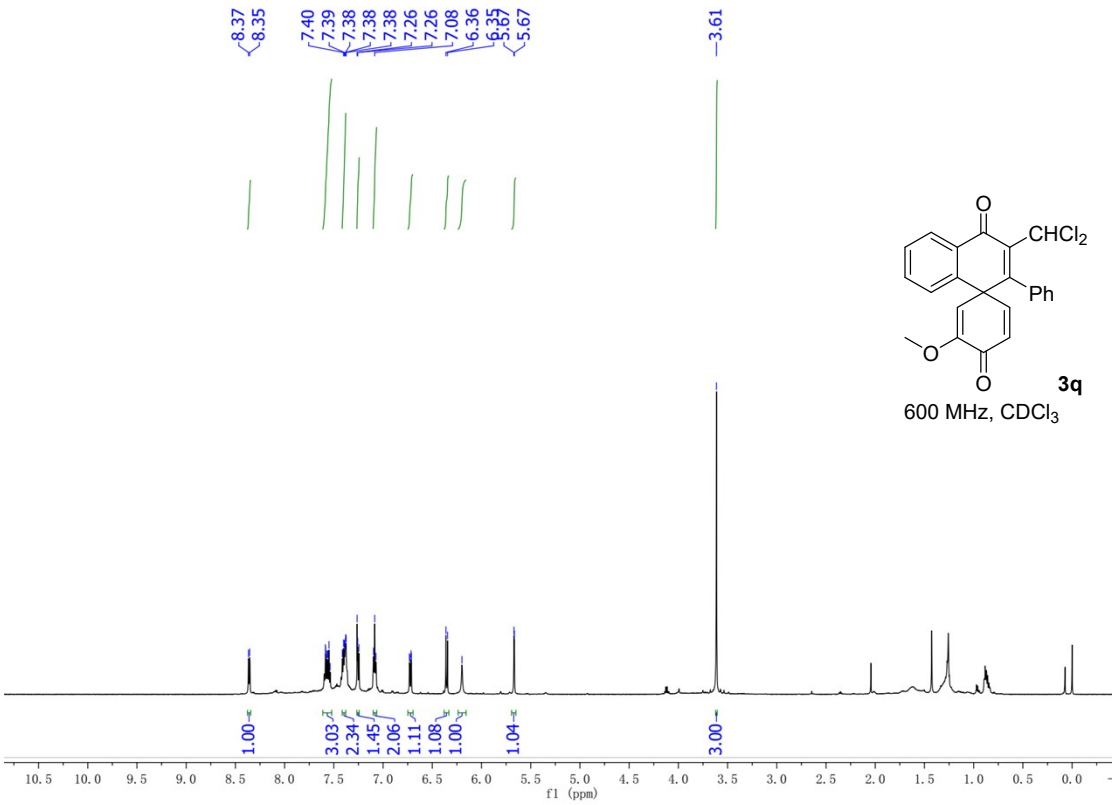
136.55
133.66
131.15
129.76
129.43
129.03
128.63
128.00
127.19
126.56
77.31
77.10
76.89
65.67
61.26
60.64
54.92
f1 (ppm)
CHCl2
Ph
O
O
O
O
3p
151 MHz, CDCl3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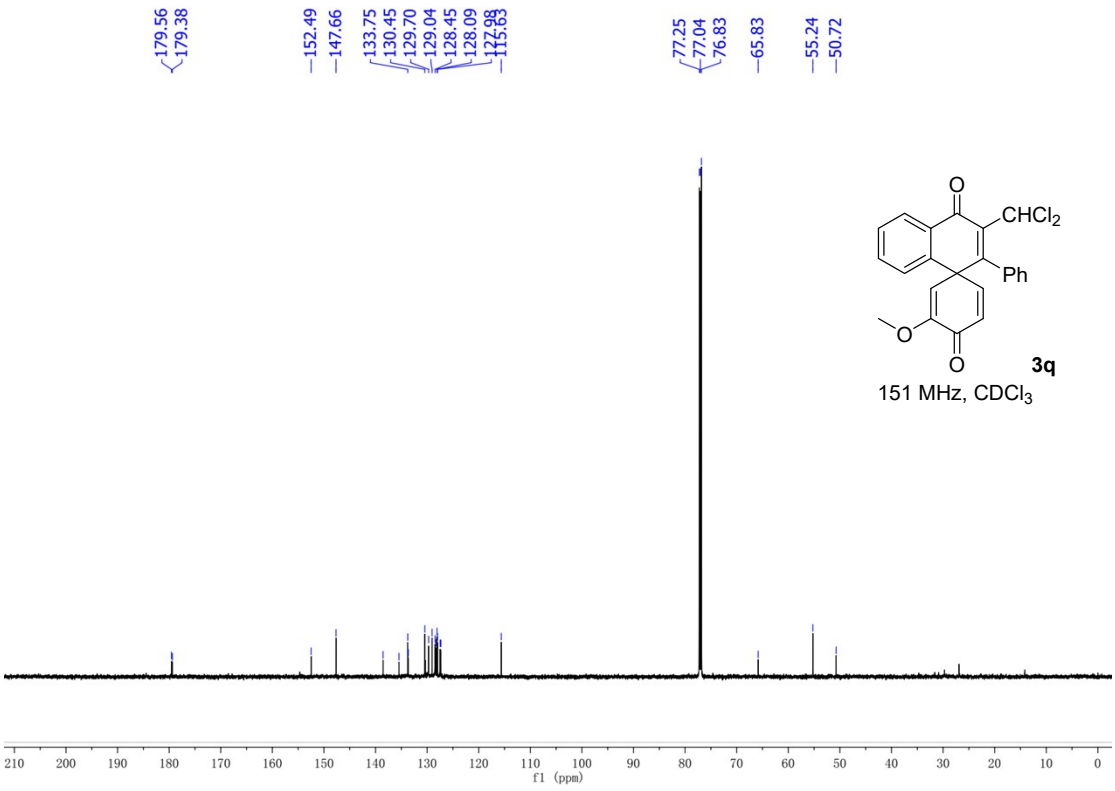
8.35
7.40
7.39
7.38
7.38
7.38
7.26
7.26
7.08
6.36
6.35
5.67
5.67
3.61
CHCl2
Ph
O
O
O
3q
600 MHz, CDCl3
1.00
3.03
2.34
1.45
2.06
1.11
1.08
1.00
1.04
3.00
f1 (ppm)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179.38
152.49
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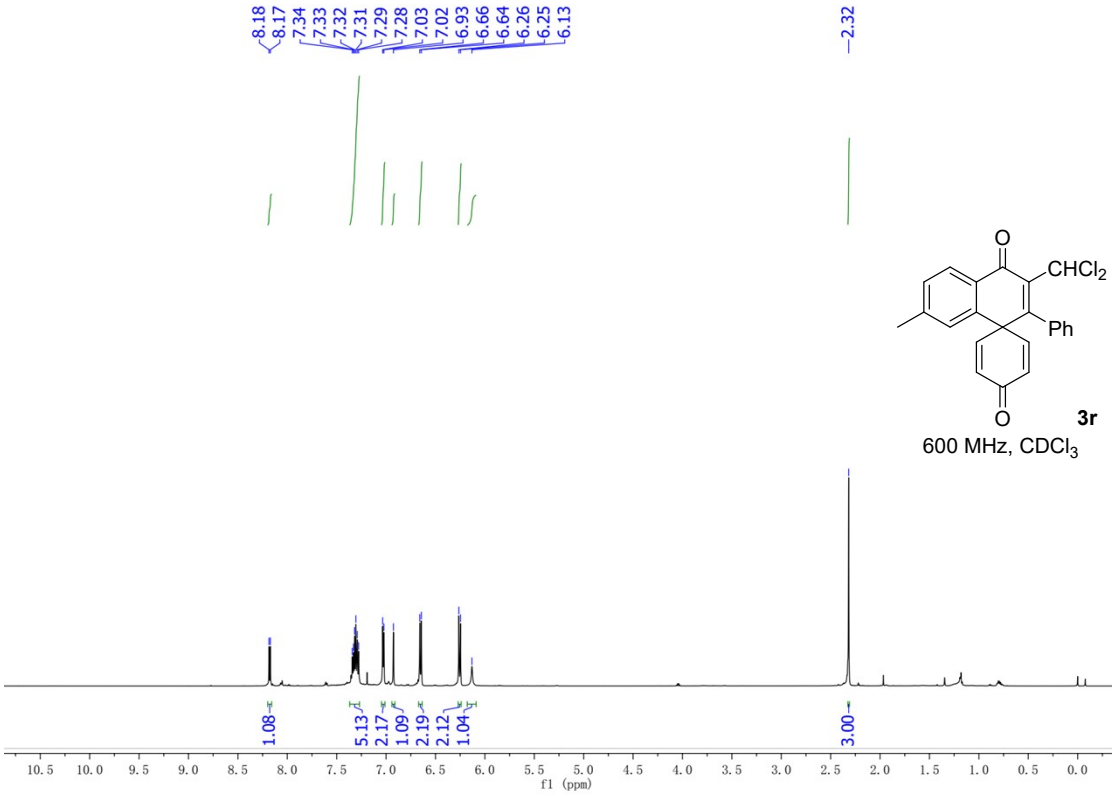
130.45
129.70
129.04
128.45
128.09
77.25
77.04
76.83
65.83
55.24
50.72
CHCl2
Ph
O
O
O
3q
151 MHz, CDCl3
f1 (ppm)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8.17
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7.31
7.29
7.28
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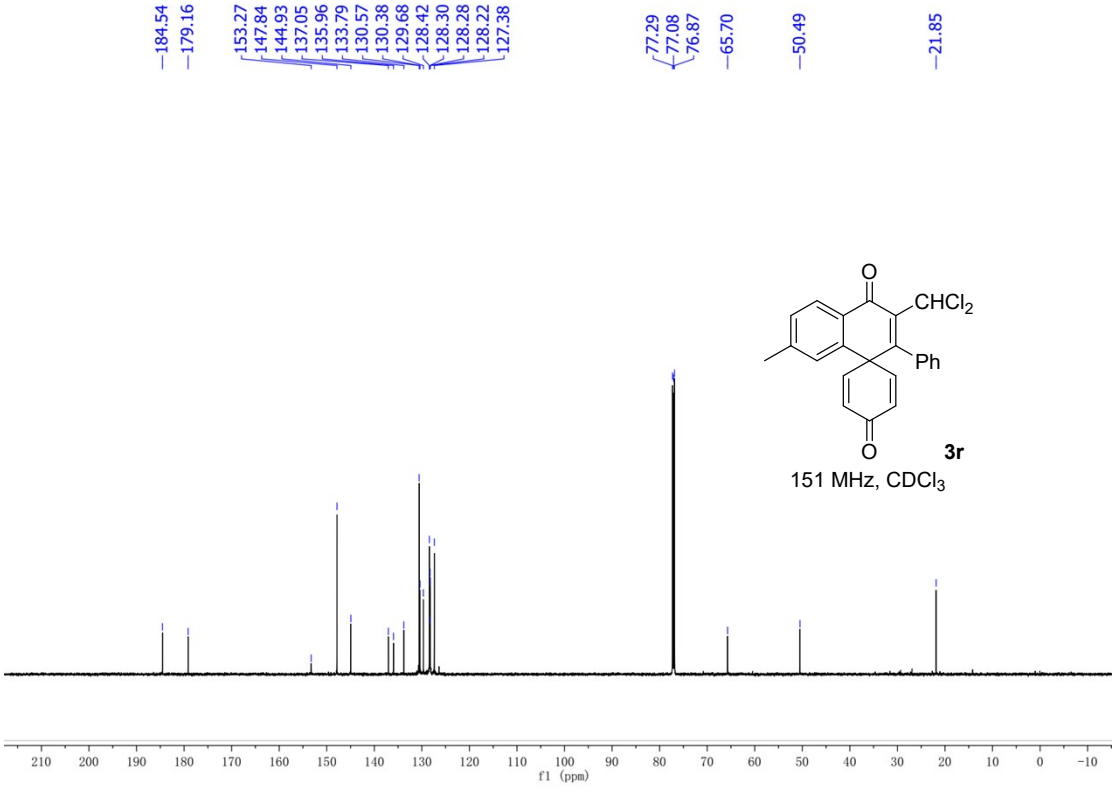
7.02
6.93
6.66
6.64
6.26
6.25
6.13
2.32
O
CHCl2
Ph
O
3r
600 MHz, CDCl3
1.08
5.13
2.17
1.09
2.19
2.12
1.04
3.00
f1 (ppm)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133.79
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130.38
129.68
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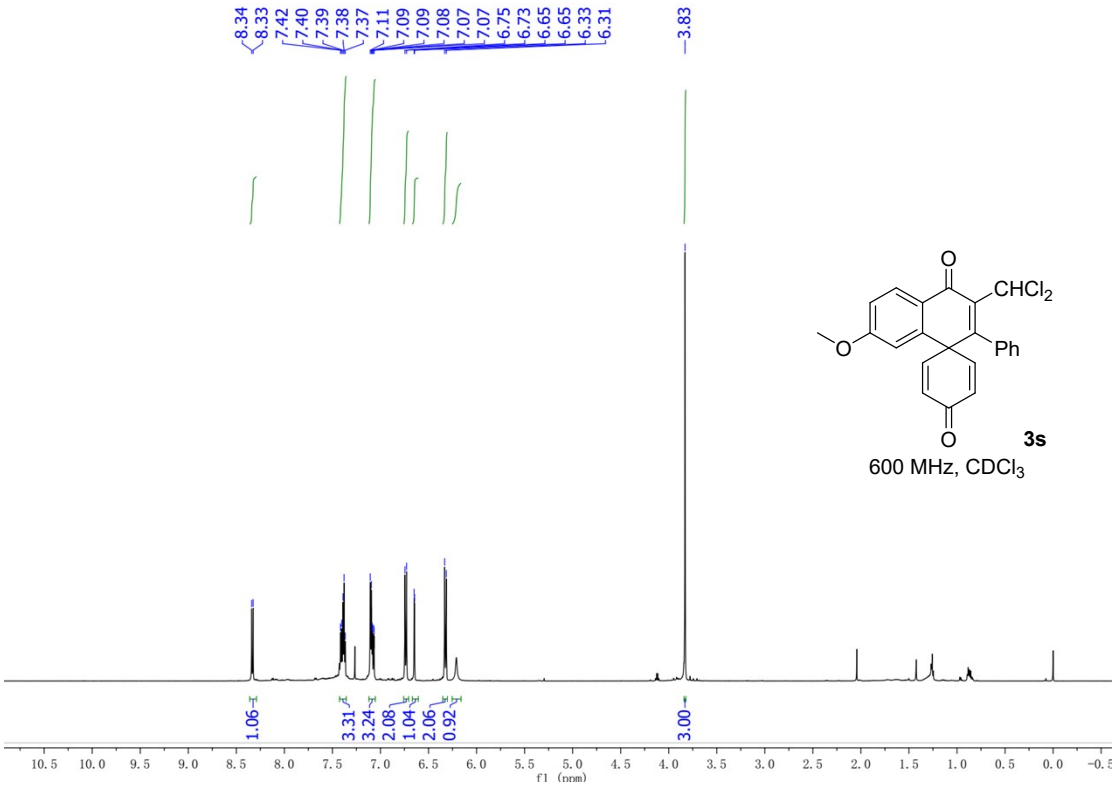
128.30
128.28
128.22
127.38
77.29
77.08
76.87
65.70
50.49
21.85
O
CHCl2
Ph
O
3r
151 MHz, CDCl3
f1 (ppm)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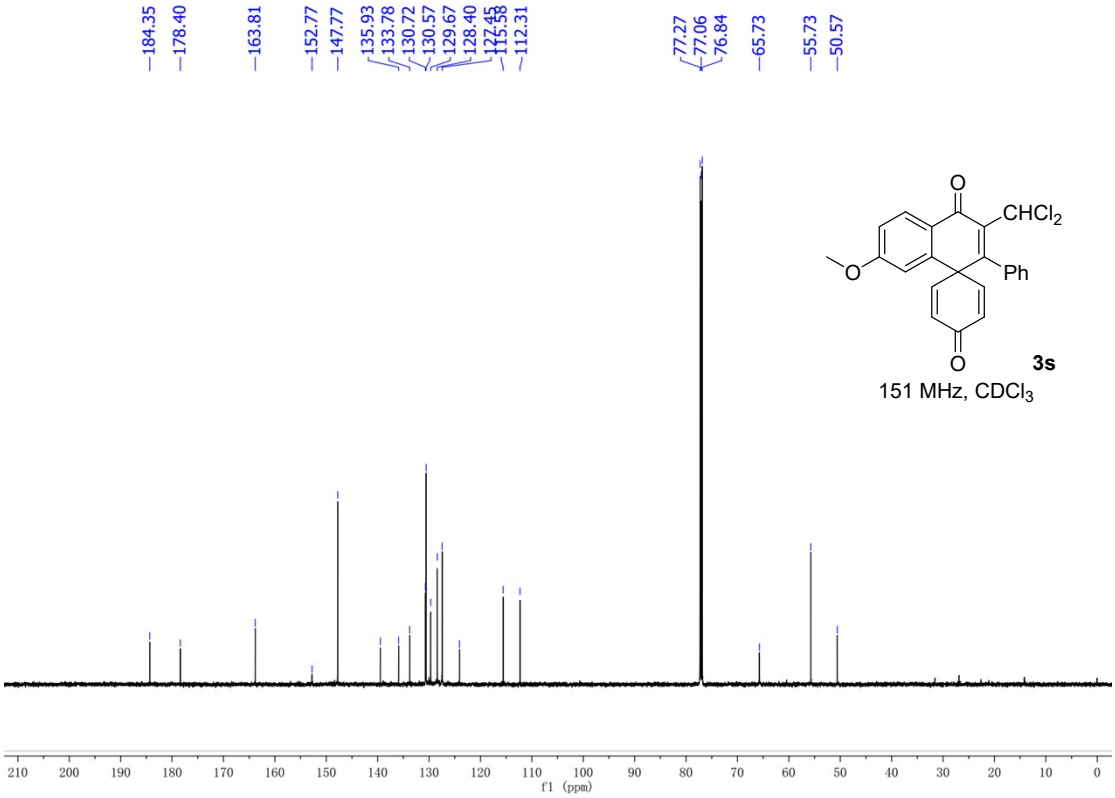
7.37
7.11
7.09
7.09
7.08
7.07
7.07
6.75
6.73
6.65
6.65
6.33
6.31
3.83
O
CHCl2
O
Ph
O
3s
600 MHz, CDCl3
1.06
3.31
3.24
2.08
1.04
2.06
0.92
3.00
f1 (ppm)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133.78
130.72
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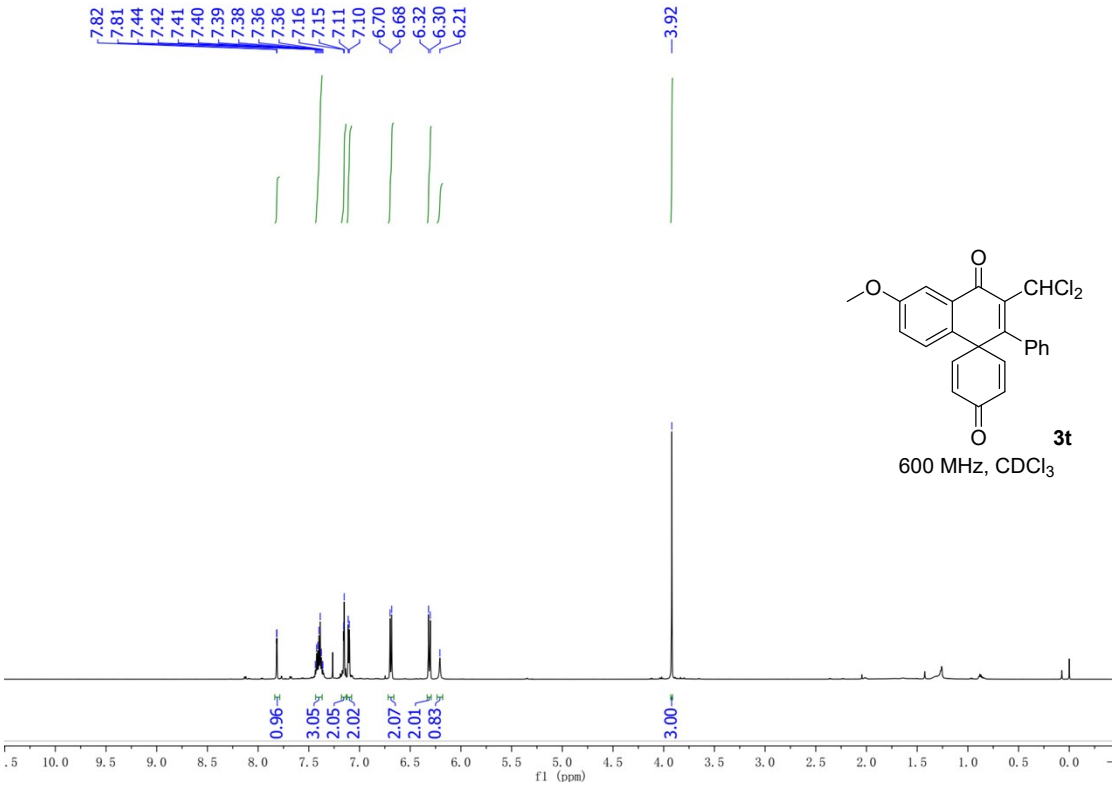
129.67
128.40
127.45
115.58
112.31
77.27
77.06
76.84
65.73
55.73
50.57
O
CHCl2
O
Ph
O
3s
151 MHz, CDCl3
f1 (ppm)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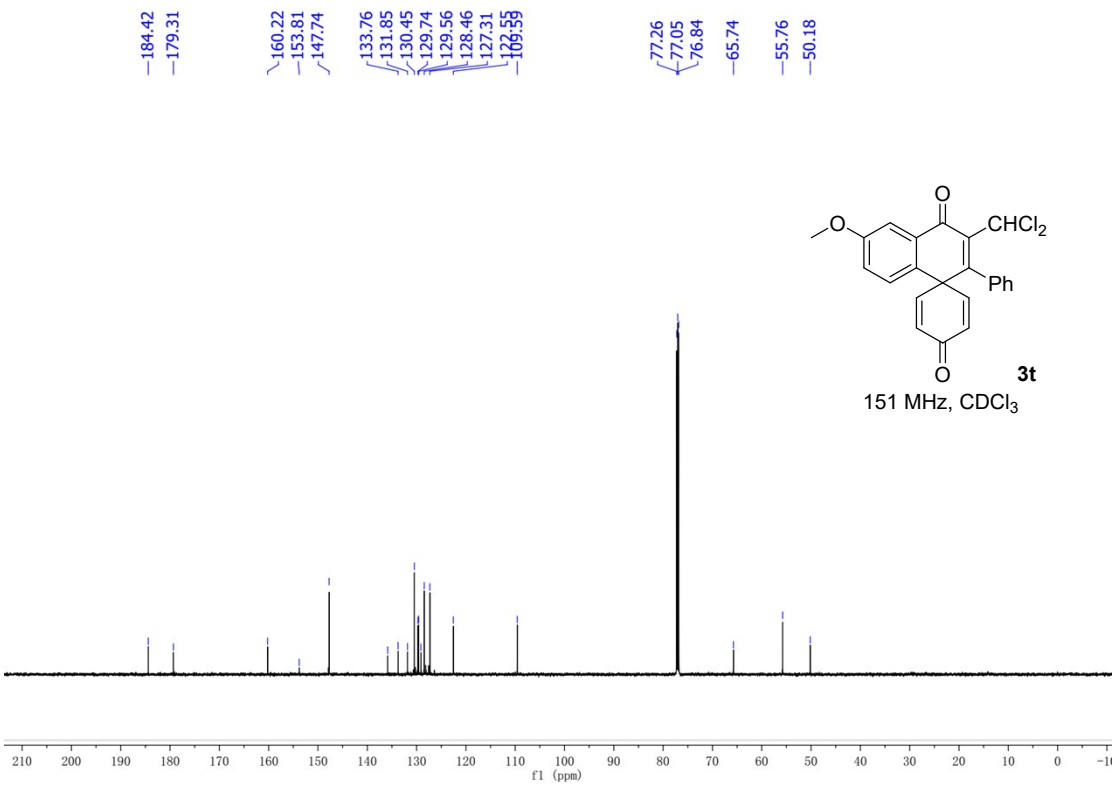
7.40
7.39
7.38
7.36
7.36
7.16
7.15
7.11
7.10
6.70
6.68
6.32
6.30
6.21
3.92
O
O
CHCl2
Ph
O
3t
600 MHz, CDCl3
0.96
3.05
2.05
2.02
2.07
2.01
0.83
3.00
f1 (ppm)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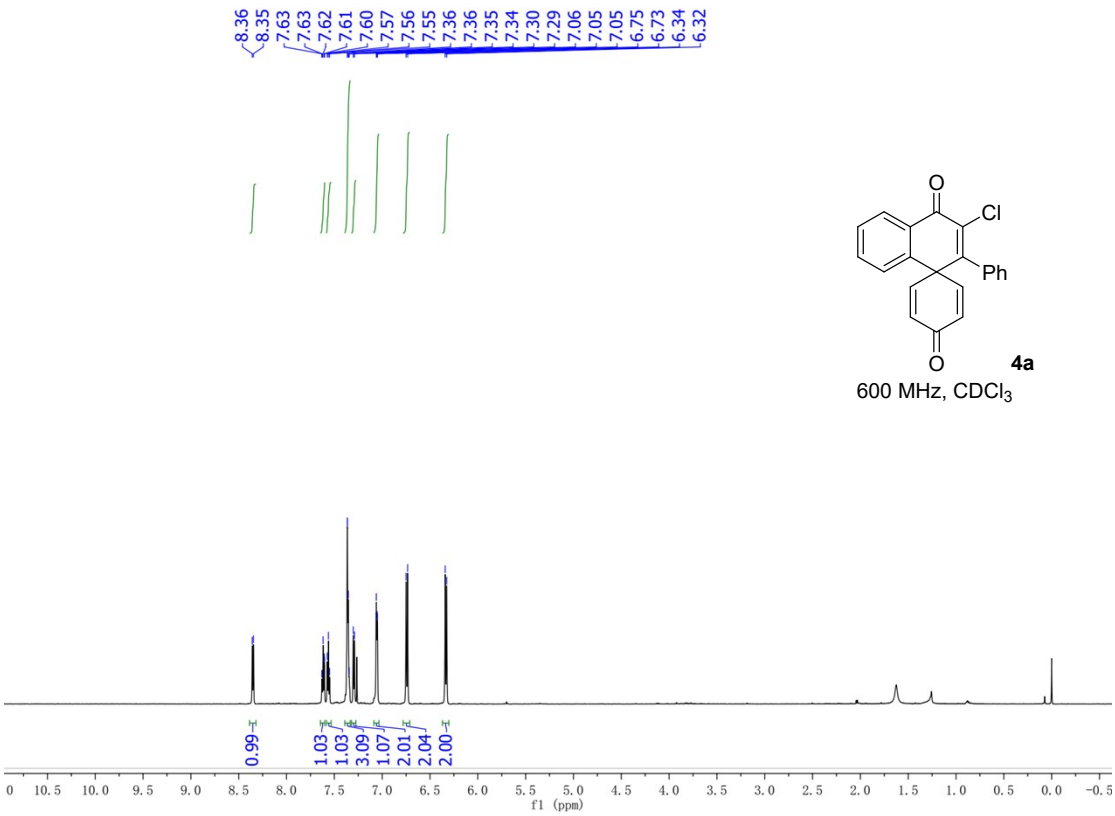
133.76
131.85
130.45
129.74
129.56
128.46
127.31
122.55
77.26
77.05
76.84
65.74
55.76
50.18
O
O
CHCl2
Ph
O
3t
151 MHz, CDCl3
f1 (ppm)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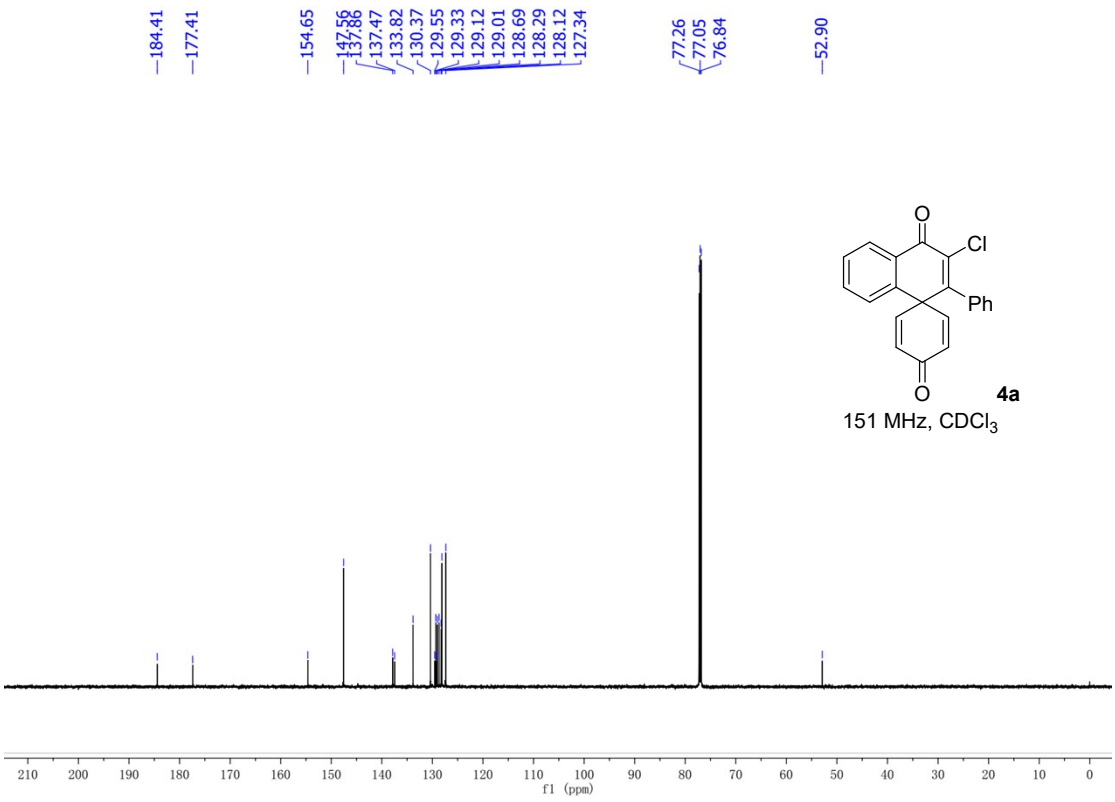
7.63
7.62
7.61
7.60
7.57
7.56
7.55
7.36
7.36
7.35
7.34
7.30
7.29
7.06
7.05
7.05
6.75
6.73
6.34
6.32
O
Cl
Ph
O
4a
600 MHz, CDCl3
0.99
1.03
1.03
3.09
1.07
2.01
2.04
2.00
f1 (ppm)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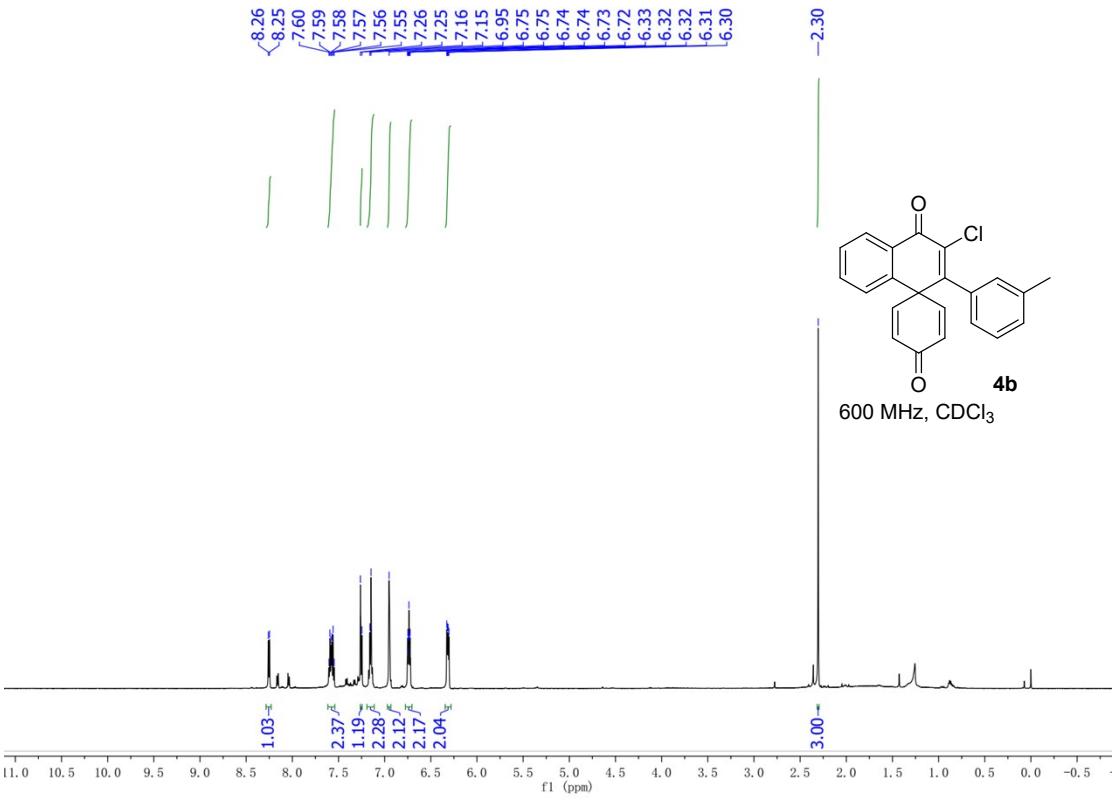
130.37
129.55
129.33
129.12
129.01
128.69
128.29
128.12
127.34
77.26
77.05
76.84
52.90
O
Cl
Ph
O
4a
151 MHz, CDCl3
f1 (ppm)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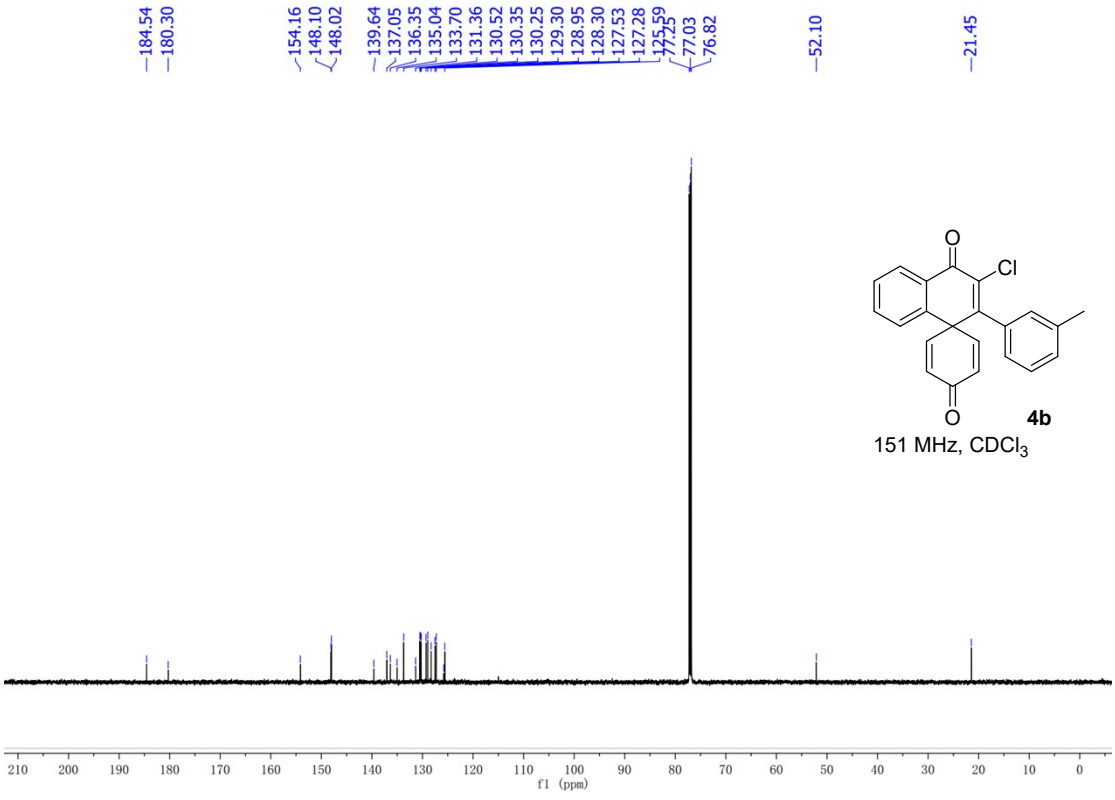
7.26
7.25
7.16
7.15
6.95
6.75
6.75
6.74
6.74
6.73
6.72
6.33
6.32
6.32
6.31
6.30
2.30
1.03
2.37
1.19
2.28
2.12
2.17
2.04
3.00
f1 (ppm)
Cl
O
O
4b
600 MHz, CDCl3


184.54
180.30
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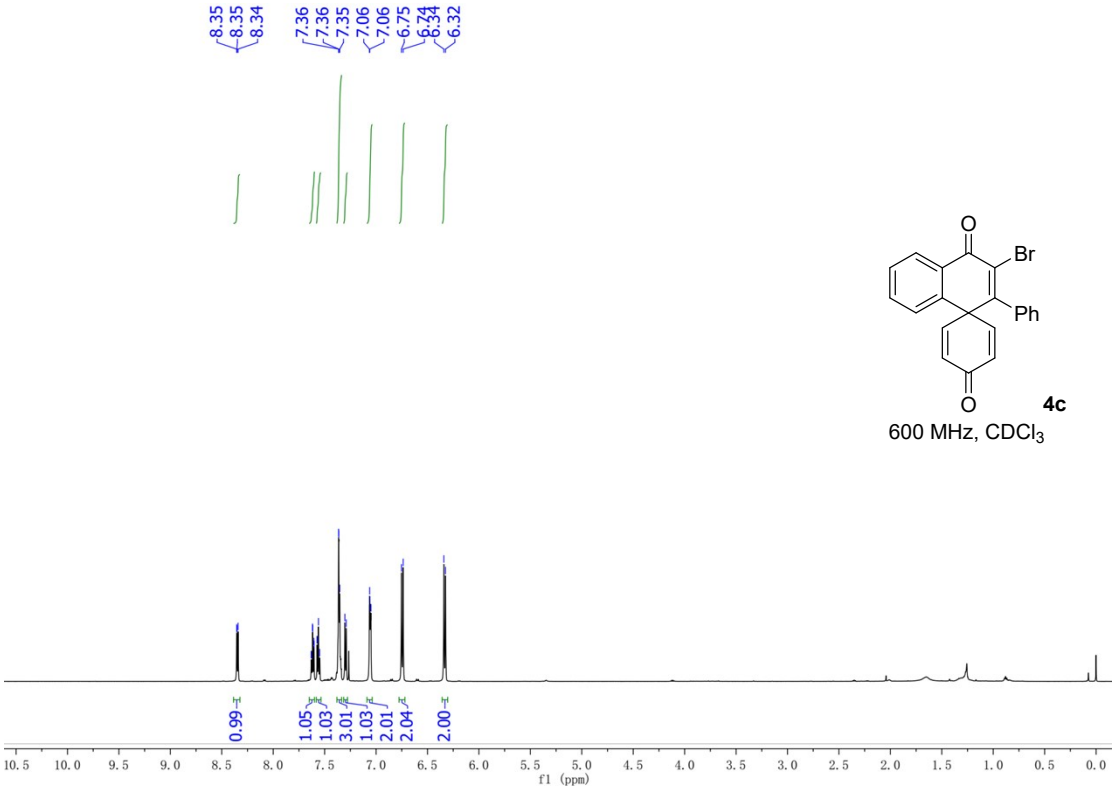
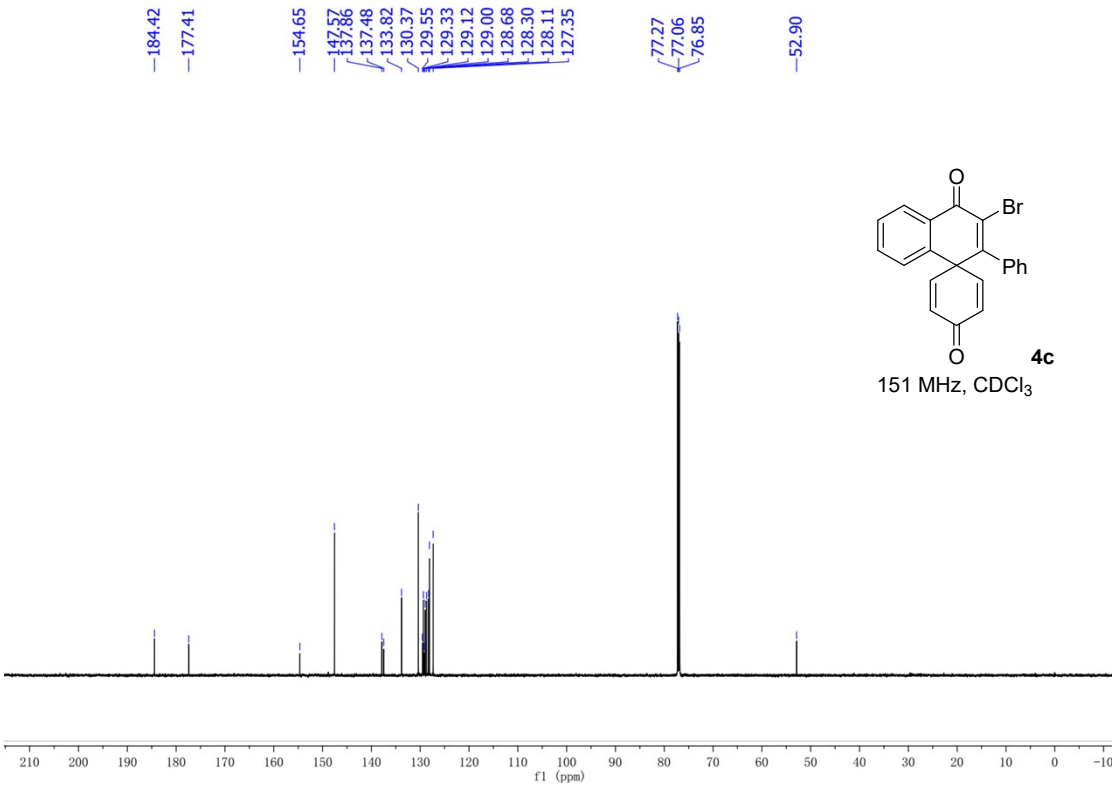
148.10
148.02
139.64
137.05
136.35
135.04
133.70
131.36
130.52
130.35
130.25
129.30
128.95
128.30
127.53
127.28
125.59
77.03
76.82
52.10
21.45
f1 (ppm)
Cl
O
O
4b
151 MHz, CDCl3


8.35
8.35
8.34
7.36
7.36
7.35
7.06
7.06
6.75
6.34
6.32
O
Br
Ph
O
4c
600 MHz, CDCl3
0.99
1.05
1.03
3.01
1.03
2.01
2.04
2.00
f1 (ppm)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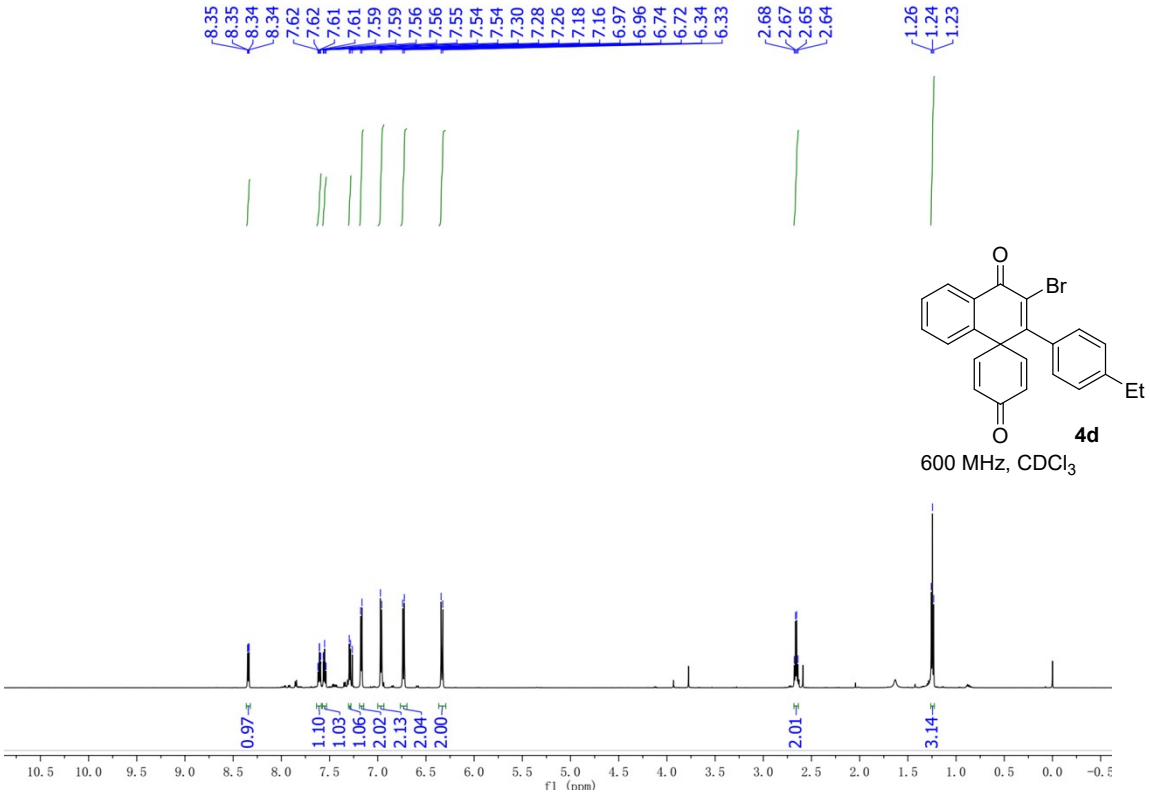
177.41
154.65
147.57
137.86
137.48
133.82
130.37
129.55
129.33
129.12
129.00
128.68
128.30
128.11
127.35
77.27
77.06
76.85
52.90
O
Br
Ph
O
4c
151 MHz, CDCl3
f1 (ppm)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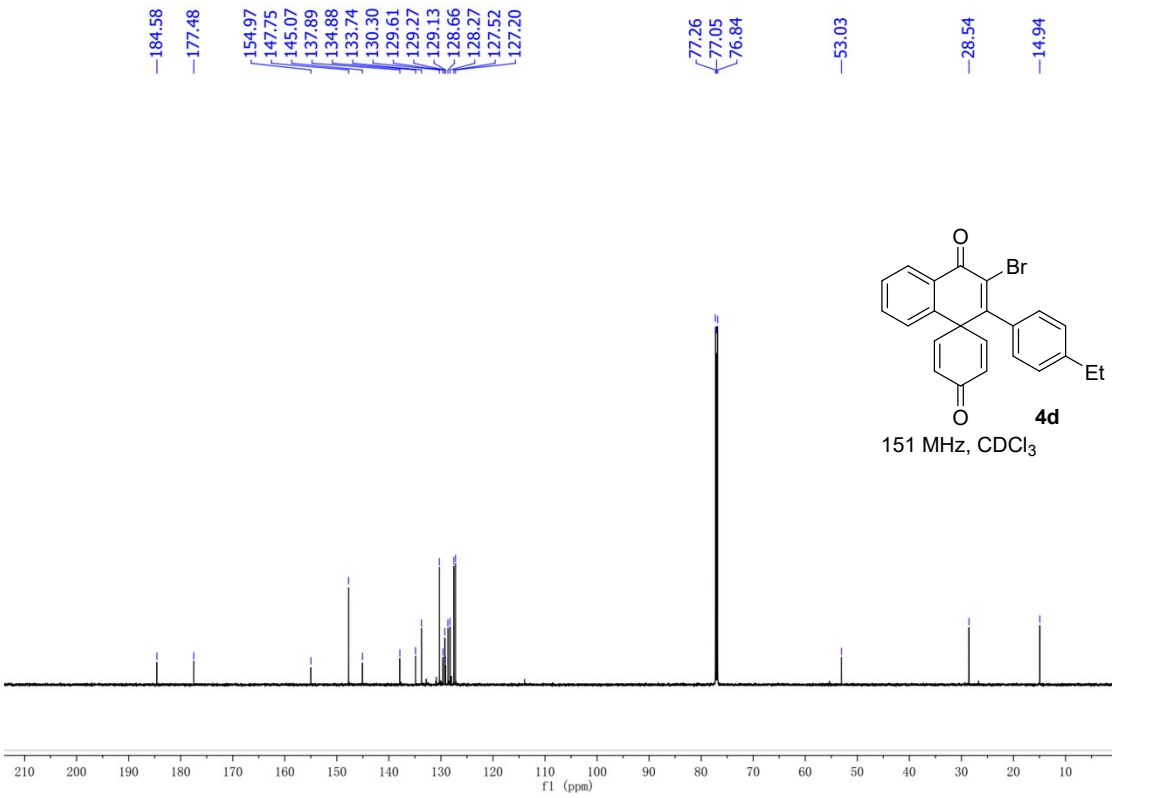
7.59
7.56
7.55
7.54
7.30
7.28
7.26
7.18
7.16
6.97
6.96
6.74
6.72
6.34
6.33
2.68
2.67
2.65
2.64
1.26
1.24
1.23
O
Br
Et
O
4d
600 MHz, CDCl3
0.97
1.10
1.03
1.06
2.02
2.13
2.04
2.00
2.01
3.14
f1 (ppm)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177.48
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147.75
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134.88
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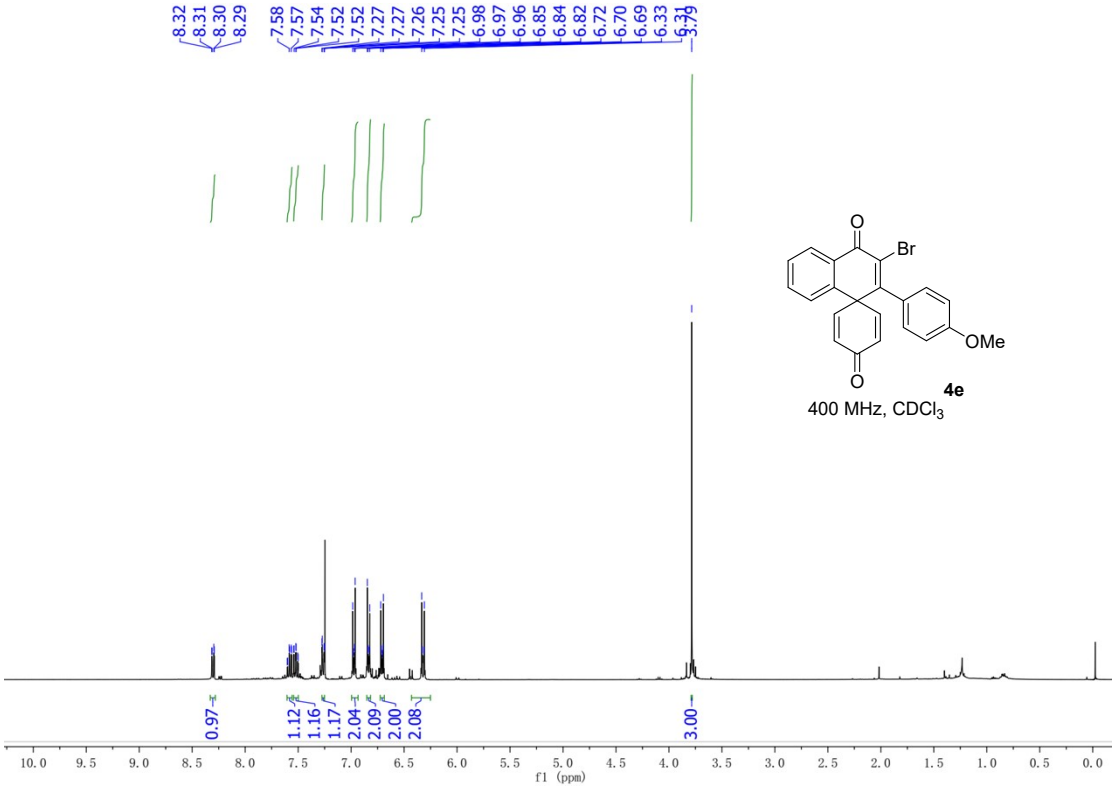
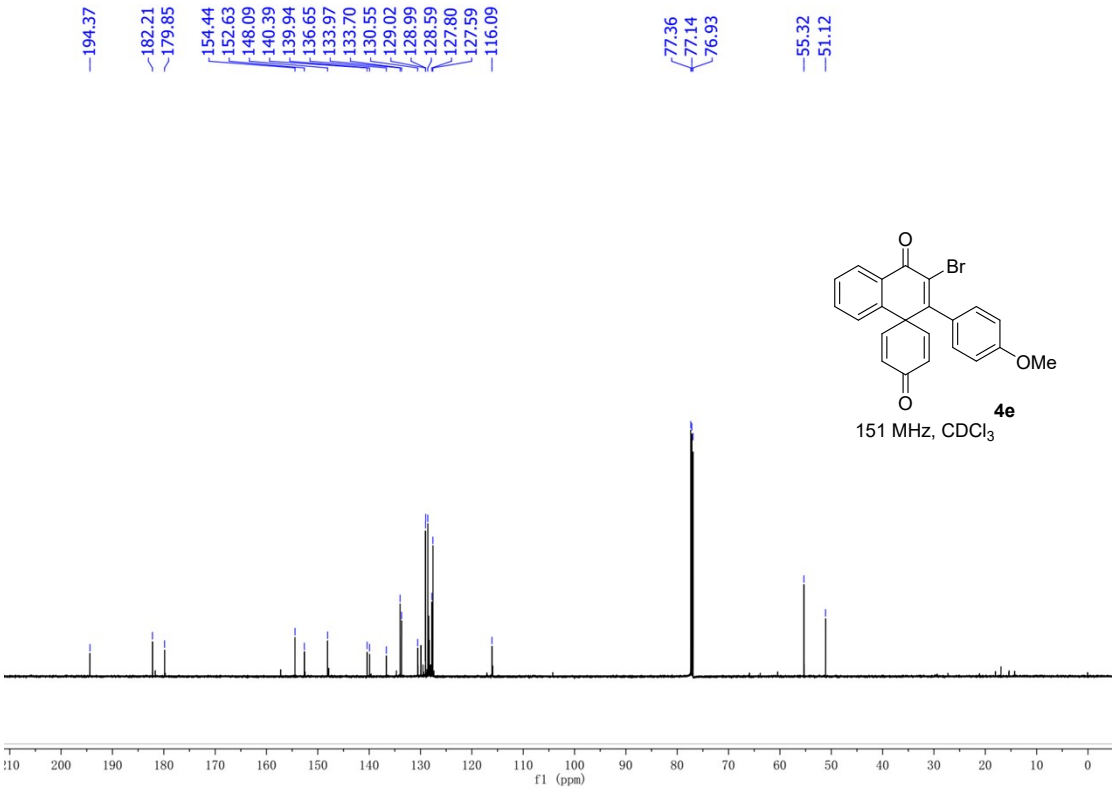
129.13
128.66
128.27
127.52
127.20
77.26
77.05
76.84
53.03
28.54
14.94
O
Br
Et
O
4d
151 MHz, CDCl3
f1 (ppm)



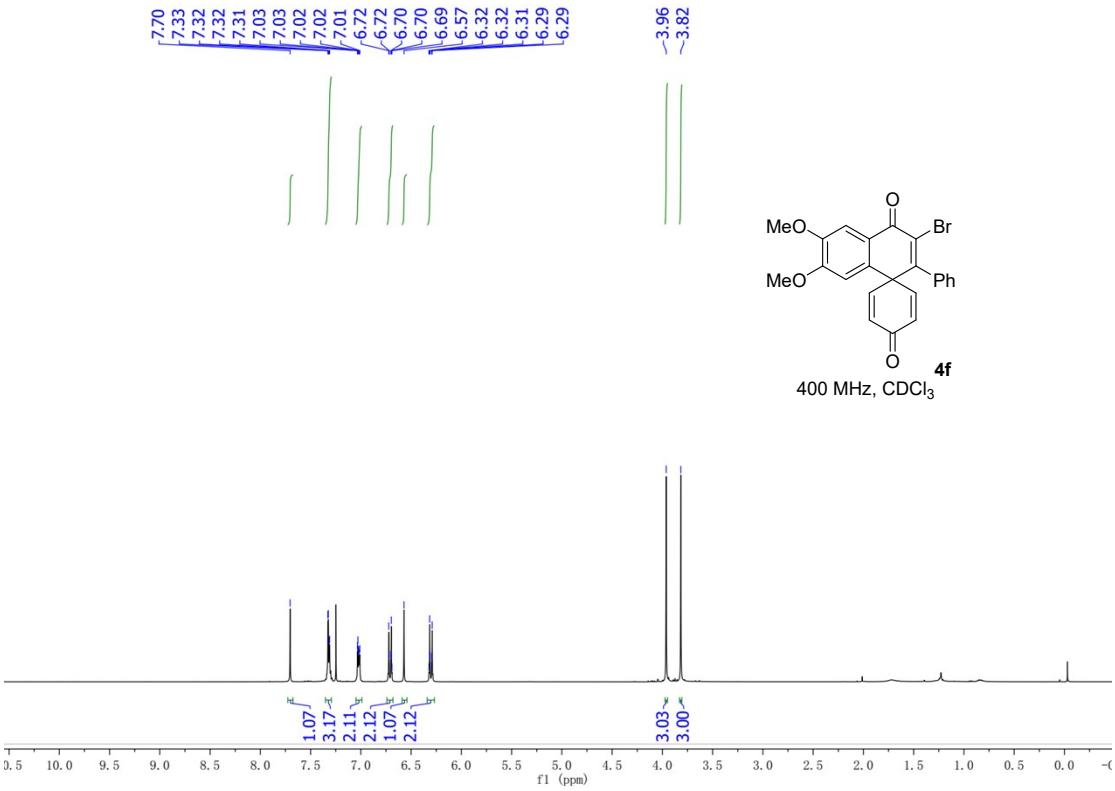
4e

400 MHz, $CDCl_3$



4e

151 MHz, $CDCl_3$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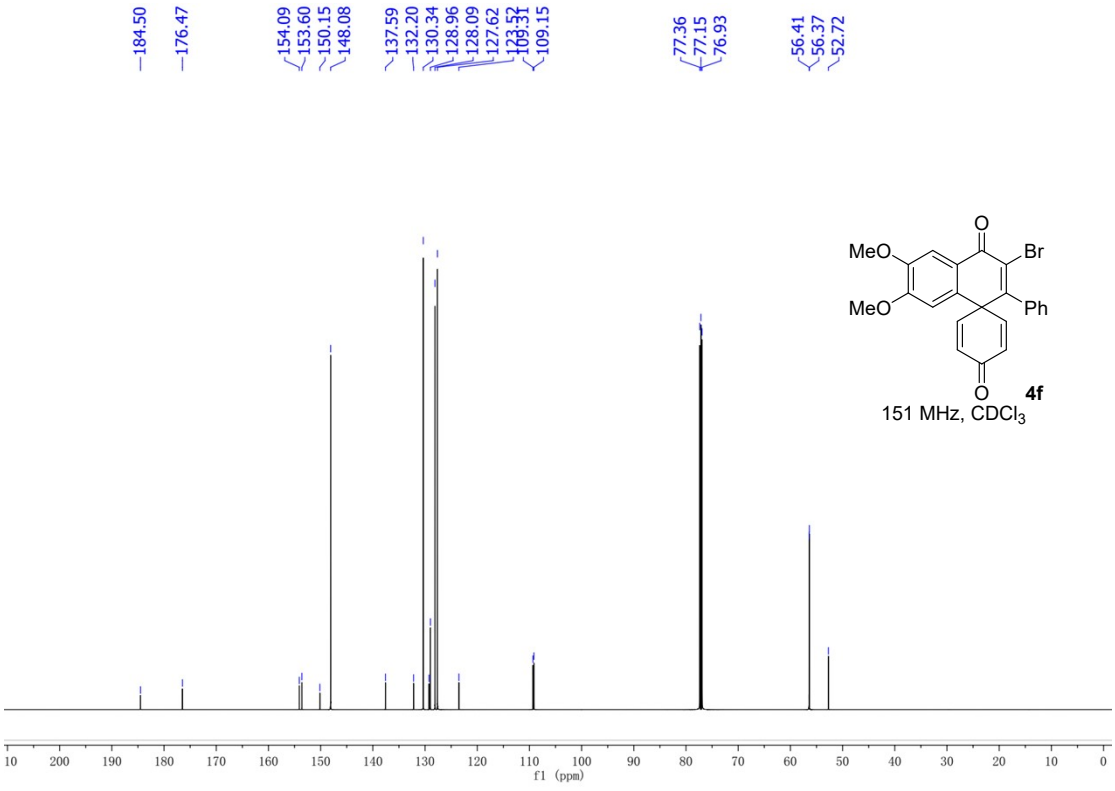
7.32
7.32
7.31
7.03
7.03
7.02
7.02
7.01
6.72
6.72
6.70
6.70
6.69
6.57
6.32
6.32
6.31
6.29
6.29
3.96
3.82
MeO
MeO
Br
Ph
O
O
4f
400 MHz, CDCl3
1.07
3.17
2.11
2.12
1.07
2.12
3.03
3.00
f1 (ppm)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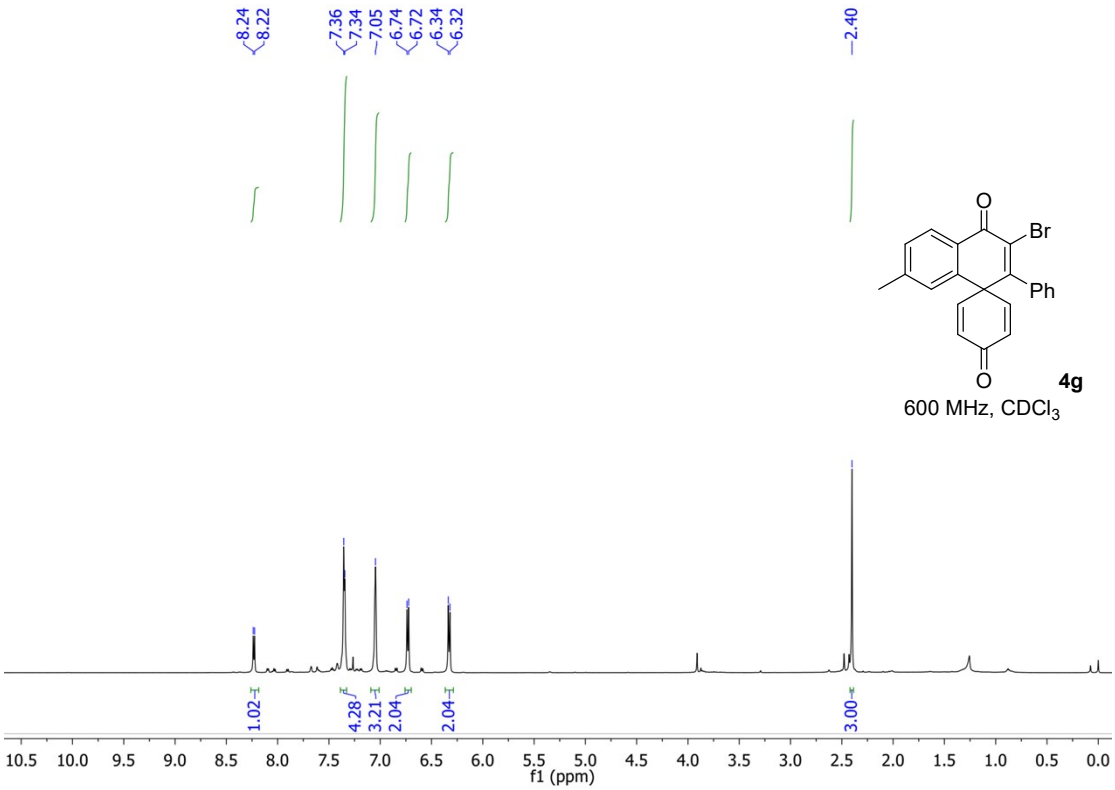
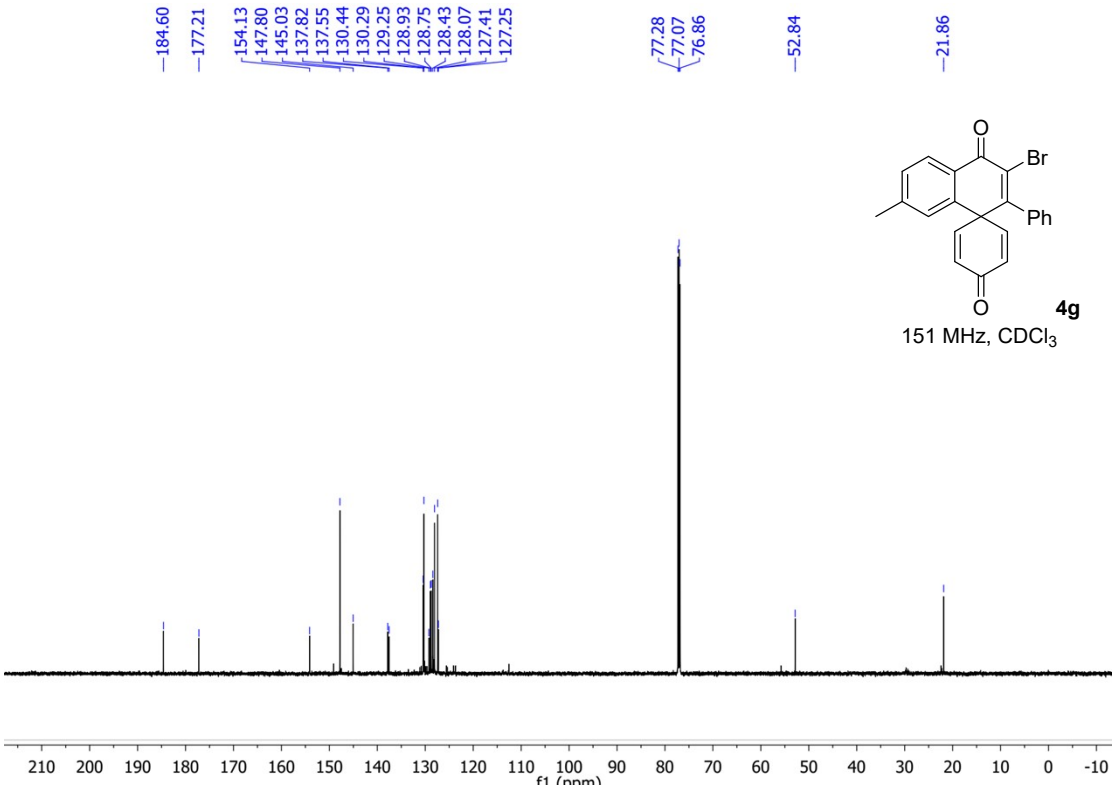
150.15
148.08
137.59
132.20
130.34
128.96
128.09
127.62
109.15
77.36
77.15
76.93
56.41
56.37
52.72
MeO
MeO
Br
Ph
O
O
4f
151 MHz, CDCl3
f1 (ppm)


8.24
8.22
7.36
7.34
7.05
6.74
6.72
6.34
6.32
2.40
O
Br
Ph
O
4g
600 MHz, CDCl3
1.02
4.28
3.21
2.04
2.04
3.00
10.5 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)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147.80
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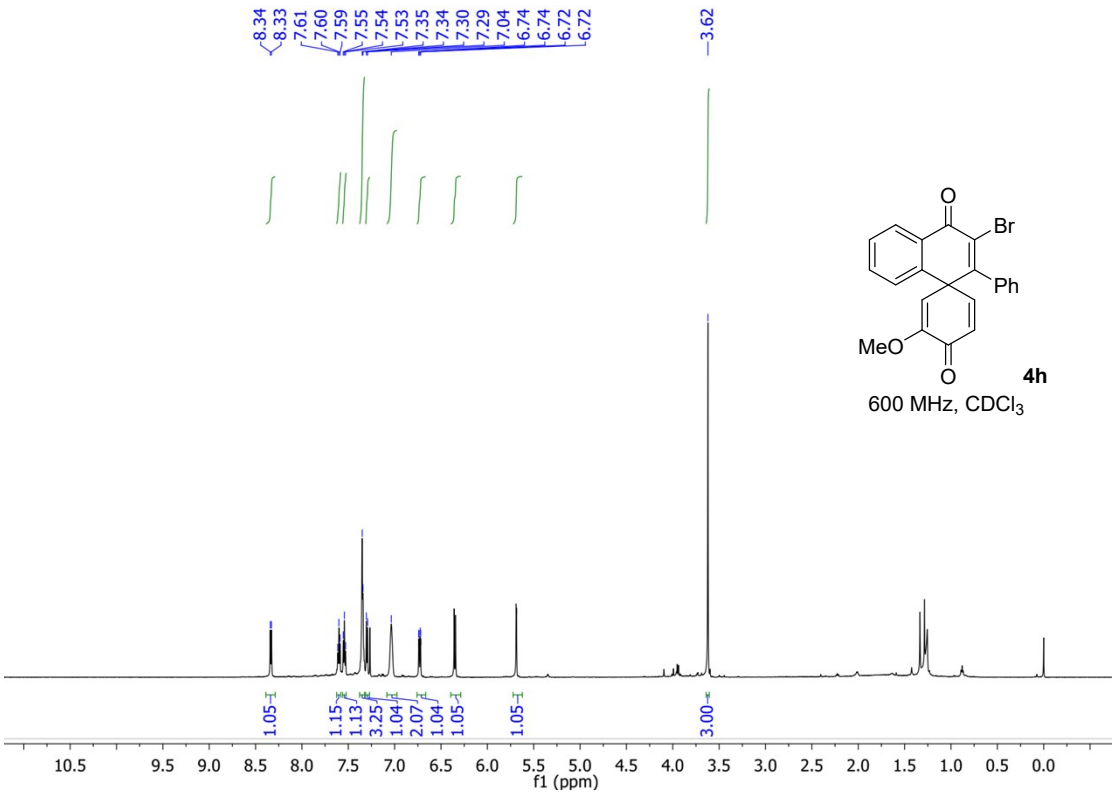
137.55
130.44
130.29
129.25
128.93
128.75
128.43
128.07
127.41
127.25
77.28
77.07
76.86
52.84
21.86
O
Br
Ph
O
4g
151 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.33
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7.59
7.55
7.54
7.53
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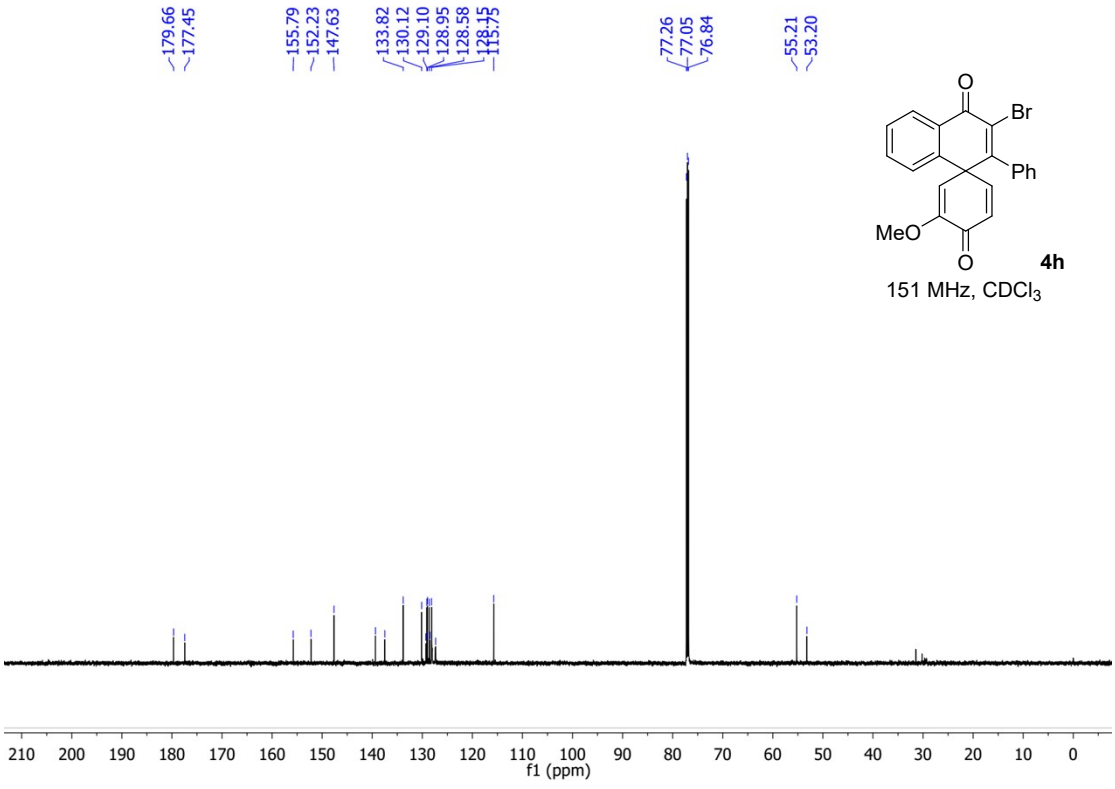
7.34
7.30
7.29
7.04
6.74
6.72
6.72
3.62
1.05
1.15
1.13
3.25
1.04
2.07
1.04
1.05
1.05
3.00
f1 (ppm)
O
Br
Ph
MeO
O
4h
600 MHz, CDCl3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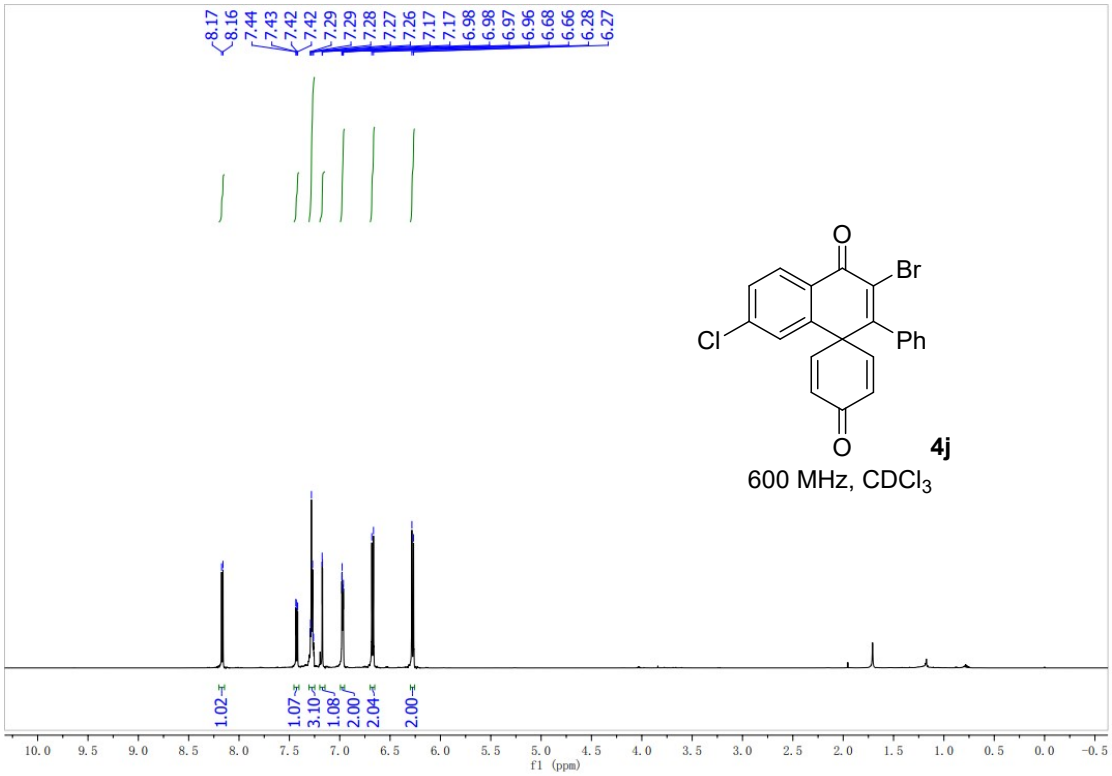
177.45
155.79
152.23
147.63
133.82
130.12
129.10
128.95
128.58
77.26
77.05
76.84
55.21
53.20
f1 (ppm)
O
Br
Ph
MeO
O
4h
151 MHz, CDCl3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8.16
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7.43
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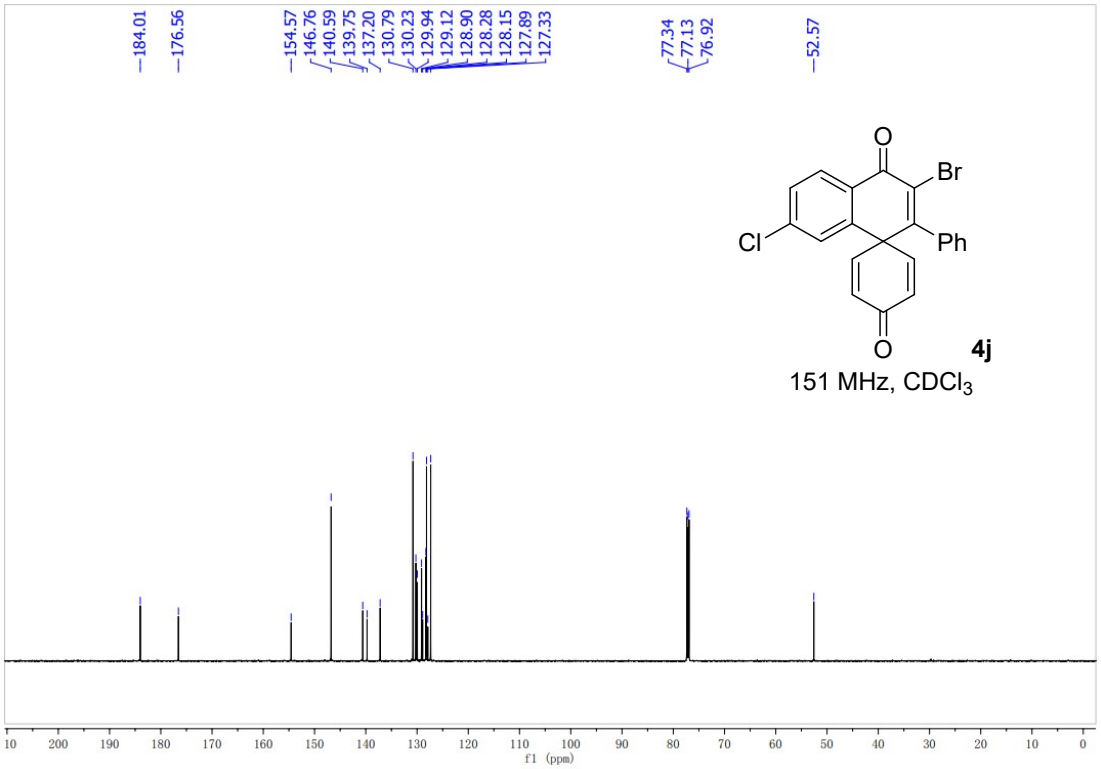
7.29
7.28
7.27
7.26
7.17
7.17
6.98
6.98
6.97
6.96
6.68
6.66
6.28
6.27
O
Br
Cl
Ph
O
4j
600 MHz, CDCl3
1.02
1.07
3.10
1.08
2.00
2.04
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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154.57
146.76
140.59
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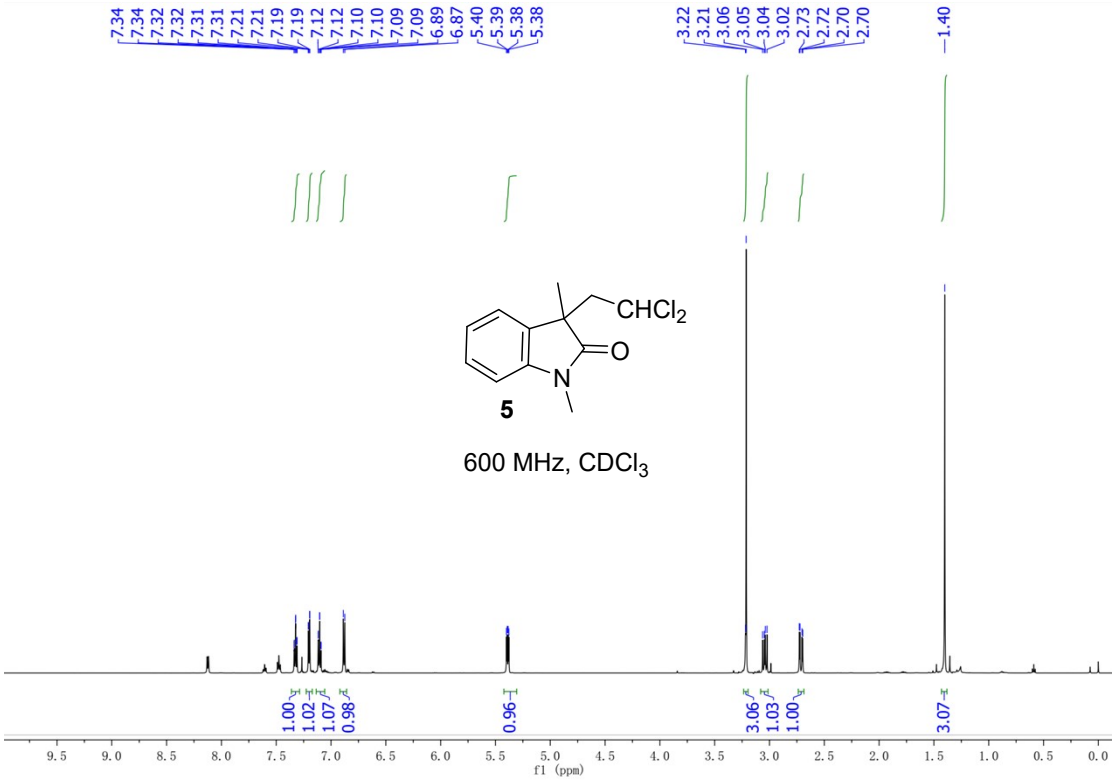
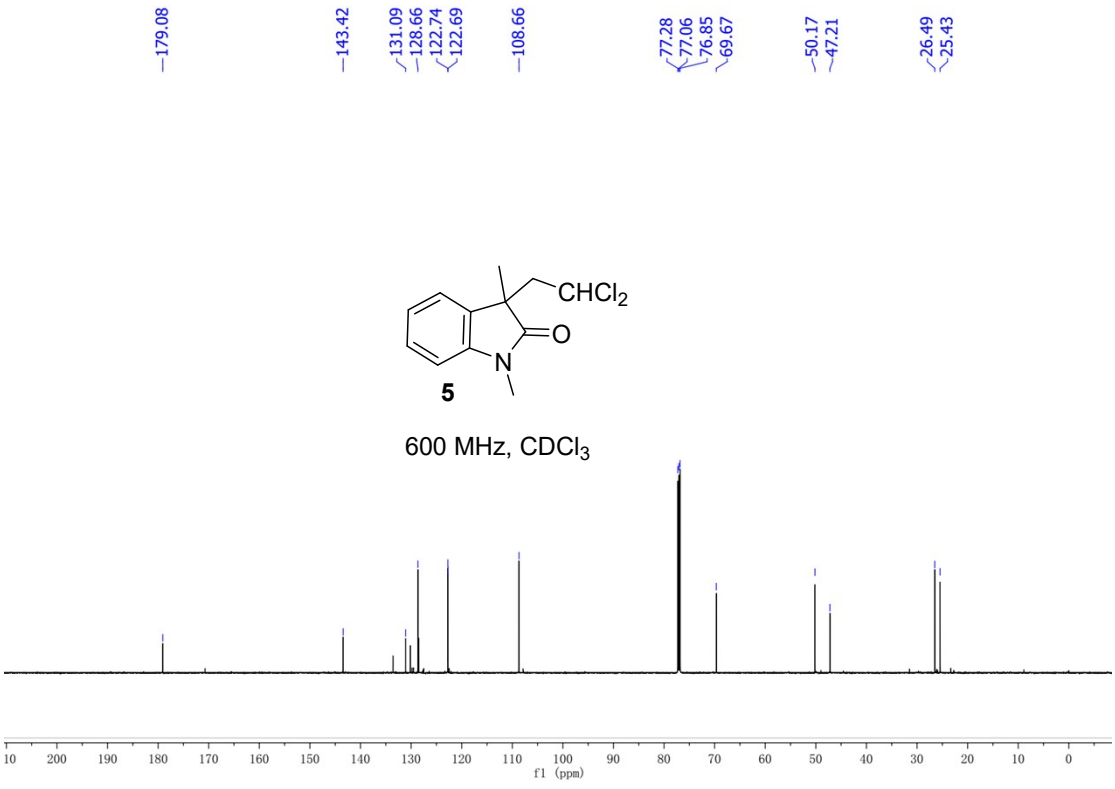
137.20
130.79
130.23
129.94
129.12
128.90
128.28
128.15
127.89
127.33
77.34
77.13
76.92
52.57
O
Br
Cl
Ph
O
4j
151 MHz, CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



5

600 MHz, $CDCl_3$



5

600 MHz, $CDCl_3$

7. X-Ray crystal structure of 4c (CCDC: 2174070)

General procedure for crystal culture of **4c**: To a test tube (25 mL) with added **4c** (36 mg), dichloromethane (0.5 mL) was added slowly to make it dissolve completely. After it dissolved, a mixture of petroleum ether (1.5 mL) and *n*-hexane (2.0 mL) was added. Then, the test tube was sealed with a rubber stopper, and connected to air with a syringe needle. Finally, the tube was put in a dry and ventilated place to make the organic solvent to volatilize slowly. After a few days, the crystal of **4c** was obtained. The X-ray crystal structure of **4c** was shown in Figure S4.

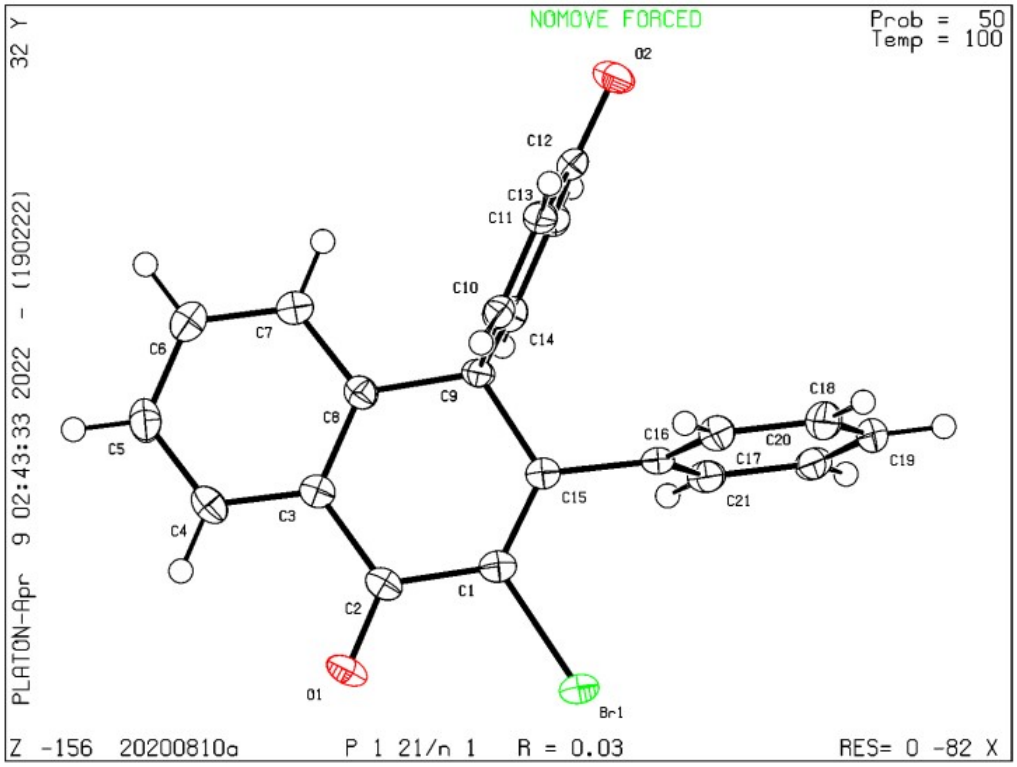


Figure S4 ORTEP diagram of **4c** with thermal displacement parameters drawn at 30% probability.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 20200810a

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 20200810a

```
Bond precision:   C-C = 0.0031 A          Wavelength=1.54184

Cell:             a=8.9293(2)     b=14.4901(3)         c=13.4949(4)
                  alpha=90        beta=109.131(3)      gamma=90
Temperature:      100 K

                 Calculated                Reported
Volume           1649.63(8)                1649.63(8)
Space group      P 21/n                    P 1 21/n 1
Hall group       -P 2yn                    -P 2yn
Moiety formula   C21 H13 Br O2             C21 H13 Br O2
Sum formula      C21 H13 Br O2             C21 H13 Br O2
Mr               377.21                    377.22
Dx,g cm-3        1.519                     1.519
Z                4                         4
Mu (mm-1)        3.469                     3.469
F000             760.0                     760.0
F000'            759.13
h,k,lmax         10,17,15                  10,17,15
Nref             2814                      2702
Tmin,Tmax        0.457,0.500               0.628,1.000
Tmin'            0.400

Correction method= # Reported T Limits: Tmin=0.628 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.960           Theta(max)= 65.087

R(reflections)= 0.0265( 2624)                    wR2(reflections)=
                                                 0.0732( 2702)
S = 1.062                Npar= 218
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