Supporting Information

An efficient $SeO_2/FeCl_3$ promoted acylation: intramolecular Friedel-Craft reaction leading to a one-pot synthesis of wrightiadione and its derivatives

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Contents

General: Unless otherwise stated, all chemicals and solvents were of analytical grade and used without further purification. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer and a JEOL JNM-ECP500 spectrometer with tetramethylsilane (TMS) as the internal standard. The chemical shifts were recorded in ppm and the following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet. Mass spectra were measured by an HP-1100 LC-MS spectrometer. X-Ray crystallography was performed on Rigaku R-AXIS RAPID/S imaging plate diffractometer. Flush column chromatography was performed by MERCK Silica gel 60. The progress of reactions was monitored by silica gel thin layer chromatography plates (MERCKTLC Silicagel 60 F_{254}).

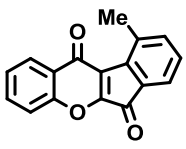
General procedure for the synthesis of compound 2

Under an Ar atmosphere, to a dichlorobenzene (3.0 mL) solution of 1 (0.2 mmol) were added SeO_2 (2.4 eq) and $FeCl_3$ (0.5 eq). The reaction mixture was stirred at 150℃for 12 h. After the reaction was complete (monitor with TLC), The reaction was quenched by adding sodium thiosulfate and the aqueous layer was extracted with CH_2Cl_2. The combined organic extract was washed with water and brine, and then dried over anhydrous $MgSO_4$. The solvent was evaporated and the obtained residue was purified by flash chromatography on silica gel (Hexane–EtOAc) to obtain pure product.

indeno[2,1-b]chromene-6,11-dione (2a, Wrightiadione)

(37.6 mg, 76%). Orange solid. mp: 242-243 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.46 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.23 (dd, *J* = 7.2, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 188.8, 175.3, 156.6, 140.9, 136.4, 135.4, 131.6, 129.1, 127.7, 127.5, 126.9, 126.8, 125.1, 124.2, 120.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_9O_3$ 249.0552 found 249.0546.

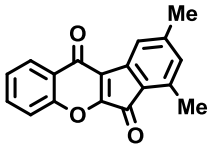
10-methylindeno[2,1-b]chromene-6,11-dione (2b)



(35.5 mg, 68%). Orange solid. mp: 262-265 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.94 (d, *J* = 7.2 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.61 (dd, *J* = 8.0， 0.8

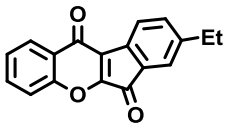
Hz, 1H), 7.45 (td, *J* = 8.0， 0.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 2.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.5, 175.6, 156.6, 156.4, 141.0, 140.3, 135.4, 134.6, 131.8, 126.5, 126.4, 126.2, 126.0, 124.9, 122.8, 120.0, 18.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{11}O_3$ 263.0708 found 263.0714.

7,9-dimethylindeno[2,1-b]chromene-6,11-dione (2c)



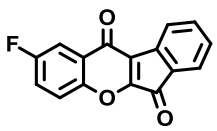
(39.8 mg, 72%). Orange solid. mp: 263-267 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.0 Hz, 1H), 7.87 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.53 (m, 2H), 6.83 (s, 1H), 2.55 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 189.9, 175.5, 156.6, 156.5, 144.3, 142.2, 138.3, 137.3, 136.3, 135.6, 126.4, 125.9, 125.6, 125.1, 124.1, 119.9, 21.5, 19.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}O_3$ 277.0865 found 277.0860.

8-ethylindeno[2,1-b]chromene-6,11-dione (2d)



(38.8 mg, 70%). Orange solid. mp: 264-268 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.81 – 7.73 (m, 2H), 7.65 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 190.1, 178.7, 157.6, 156.0, 138.7, 135.8, 132.4 131.9, 129.1, 126.2, 126.0, 125.6, 124.9, 121.9, 119.4, 116.2, 28.9, 15.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}O_3$ 277.0865 found 277.0872.

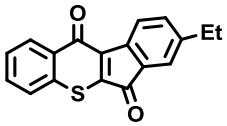
2-bromoindeno[2,1-b]chromene-6,11-dione (2e)



(36.2 mg, 68%). Orange solid. mp: 259-262 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.75(d, *J* = 8.0 Hz, 1H), 7.65 – 7.62 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.28 (dd, *J* = 7.6, 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 187.8, 174.1, 163.2 (d, J_{CF} = 15.0 Hz), 160.3, 158.6, 157.0, 152.1, 139.8, 135.8, 128.7,

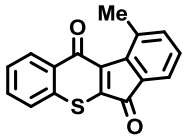
127.0, 124.6 (d, J_{CF} = 10.0 Hz), 123.0, 122.8 (d, J_{CF} = 8.0 Hz), 122.4 (d, J_{CF} = 5.0 Hz), 110.0 (d, J_{CF} = 15.0 Hz). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_8FO_3$ 267.0457 found 267.0464..

8-ethylindeno[2,1-b]thiochromene-6,11-dione (2f)



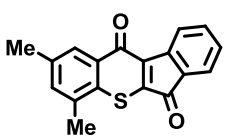
(45.5 mg, 77%). Red solid. mp: 197 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (d, *J* = 7.6 Hz, 1H), 8.10 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.66 – 7.58 (m, 2H), 7.46 (s, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.5, 177.8, 145.1, 142.7, 141.9, 138.2, 135.7, 134.8, 134.2, 131.9, 130.5, 129.0, 128.7, 128.4, 124.5, 124.0, 28.6, 15.2. HRMS (FAB) m/z: $[M+ H]^+$ calcd for $C_{18}H_{13}O_2S$ 293.0636, found 293.0630.

10-methylindeno[2,1-b]thiochromene-6,11-dione (2g)



(40.3 mg, 73%). Red solid. mp: 206 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.56 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 7.6Hz, 1H), 7.67 – 7.58 (m, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.16 (dd, *J* = 7.2 Hz, 7.6 Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.4, 177.3, 144.1, 142.6, 141.0, 140.3, 135.4, 134.6, 131.8, 131.3, 129.6, 128.4, 128.1, 122.8, 23.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{11}O_2S$ 279.0480, found 279.0475.

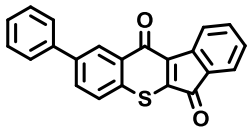
2,4-dimethylindeno[2,1-b]thiochromene-6,11-dione (2h)



(38.7 mg, 65%). Red solid. mp: 211 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (s, 1H),

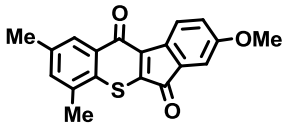
8.22 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.49 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.30 (s, 1H), 7.24 (dd, *J* = 7.6, 8.0 Hz, 1H), 2.53 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.5, 178.1, 144.3, 142.2, 138.3, 137.3, 136.3, 135.6, 134.7, 134.5, 132.3, 130.2, 128.2, 126.8, 124.5, 124.1, 21.2 19.6. HRMS (FAB) m/z: $[M + H]^+$ calcd for $C_{18}H_{13}O_2S$ 293.0636, found 293.0644.

2-phenylindeno[2,1-b]thiochromene-6,11-dione (2i)



(47.5 mg, 70%). Red solid. mp: 214-215 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.85 (d, *J* = 2.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.91 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 – 7.71 (m, 2H), 7.63 (d, *J* = 8.0Hz, 1H), 7.54 – 7.49 (m, 3H), 7.43 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.29 – 7.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 192.2, 177.8, 144.3, 143.1, 141.5, 138.9, 137.7, 135.7, 134.5, 134.3, 130.8, 130.1, 129.9, 129.2, 129.1, 129.0, 128.4, 127.2, 126.9, 126.8, 124.7, 124.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{13}O_2S$ 341.0636 found 341.0641.

8-methoxy-2,4-dimethylindeno[2,1-b]thiochromene-6,11-dione (2j)



(46.5 mg, 72%). Red solid. mp: 229℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31(s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.34 (s, 1H), 7.20 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 2.56 (s, 3H), 2.48 (s, 3H). HRMS (FAB) m/z: $[M + H]^+$ calcd for $C_{19}H_{15}O_3S$ 323.0742 found 323.0735. Due to the bad dissolution, this compound's ^{13}C NMR is unavailable.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) exp_159

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: exp_159

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Temperature:    293 K

                Calculated                Reported
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Space group     P 21/n                    P 1 21/n 1
Hall group      -P 2yn                    -P 2yn
Moiety formula  C18 H12 O2 S              C18 H12 O2 S
Sum formula     C18 H12 O2 S              C18 H12 O2 S
Mr              292.34                    292.34
Dx,g cm-3       1.400                     1.400
Z               4                         4
Mu (mm-1)       2.077                     2.077
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F000'           610.97
h,k,lmax        17,5,26                   17,5,25
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Tmin'           0.812

Correction method= # Reported T Limits: Tmin=0.507 Tmax=1.000
AbsCorr = MULTI-SCAN

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S = 1.030                 Npar= 191
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Click on the hyperlinks for more details of the test.

PLATON version of 04/06/2020; check.def file version of 02/06/2020

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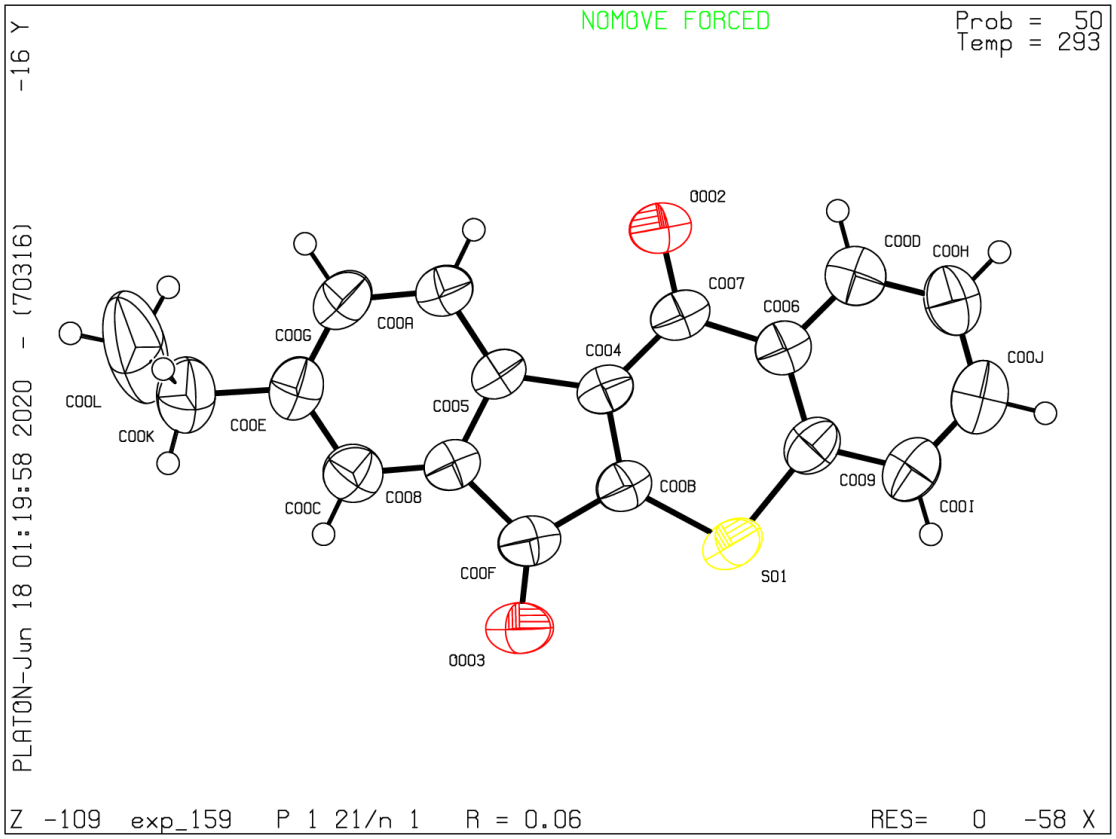

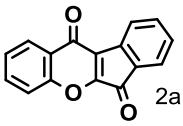
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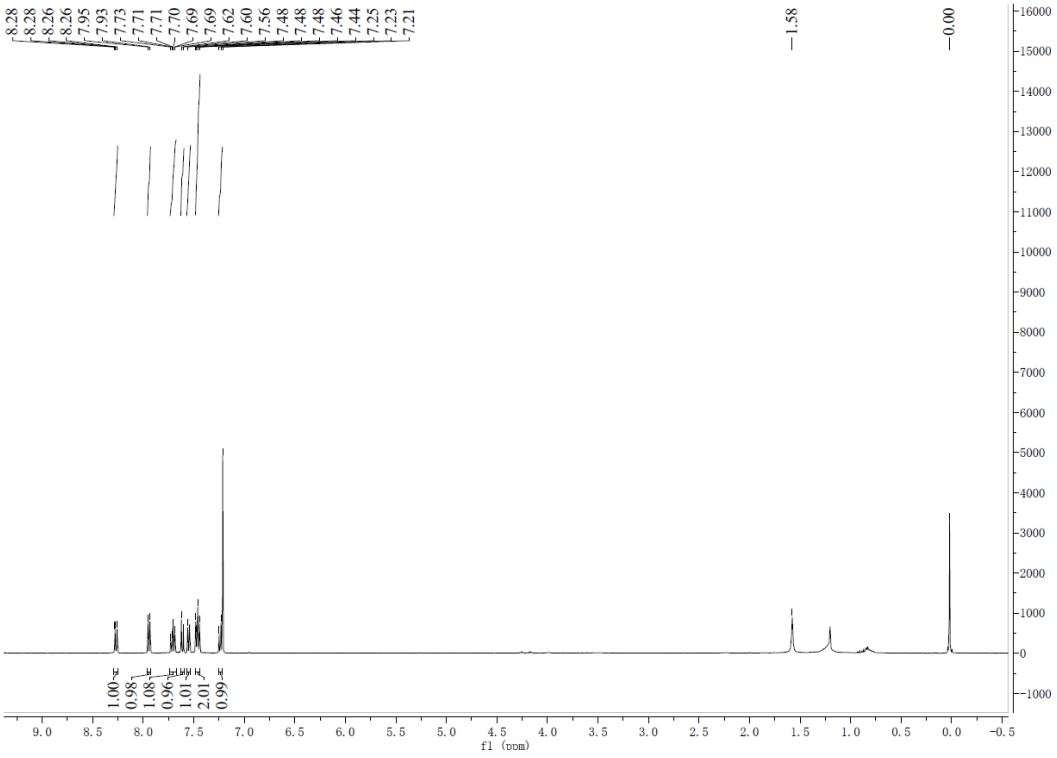
2a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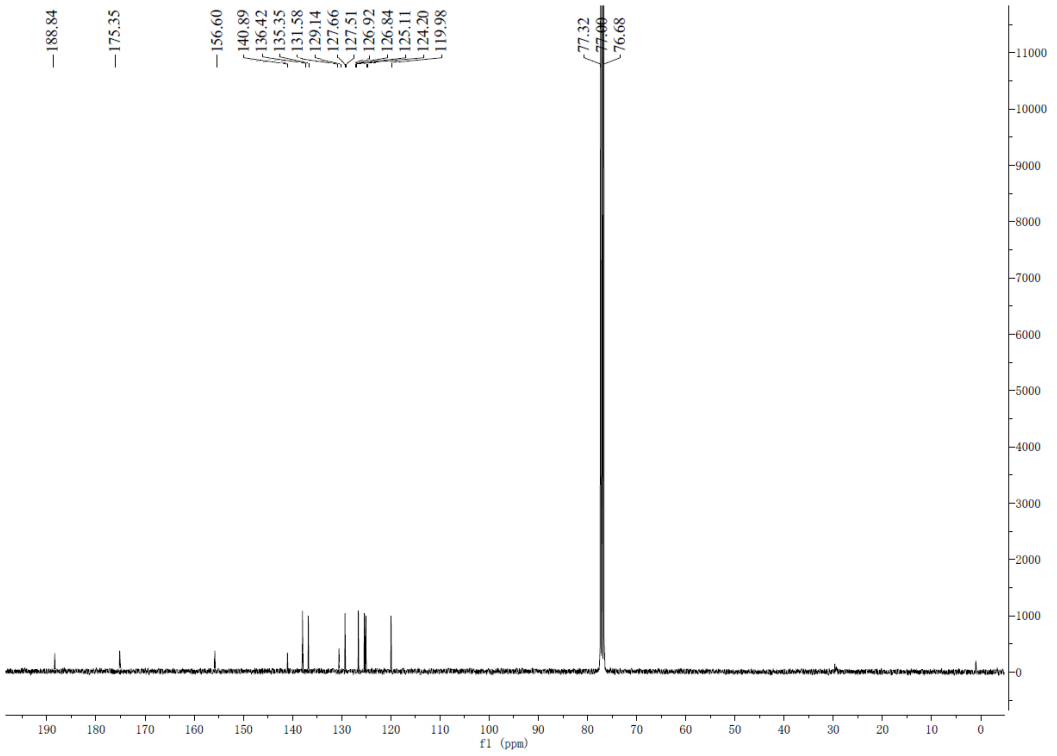
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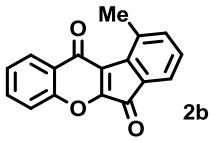
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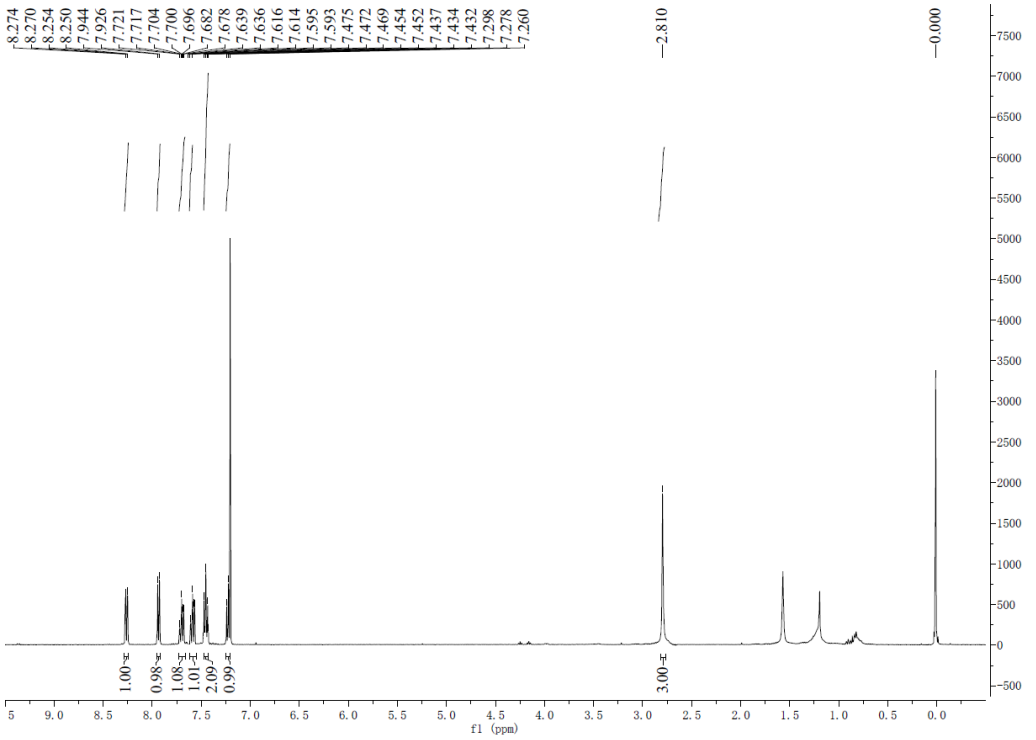
2b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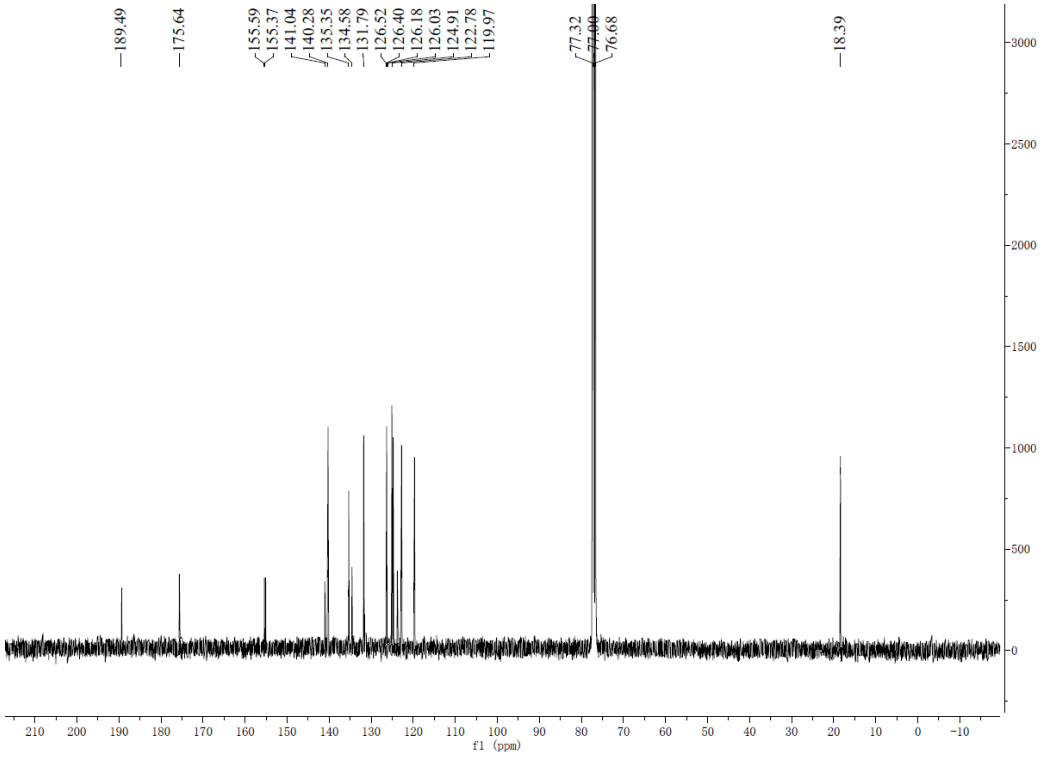
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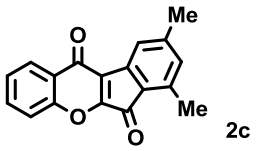
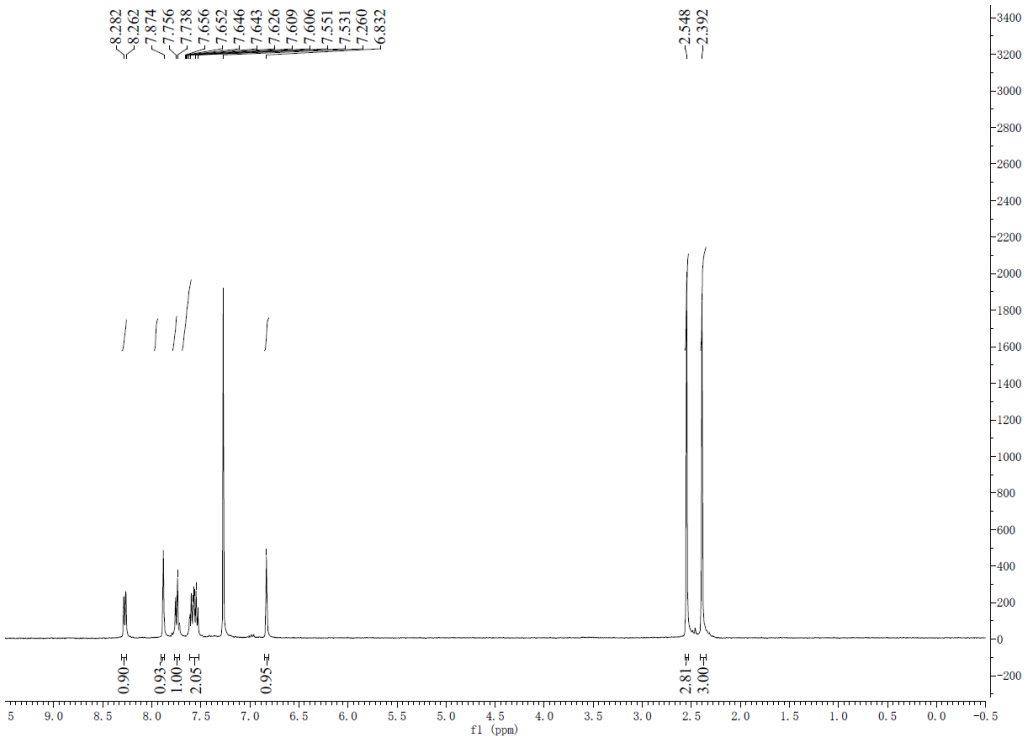

Me
O
O
Me
O

2c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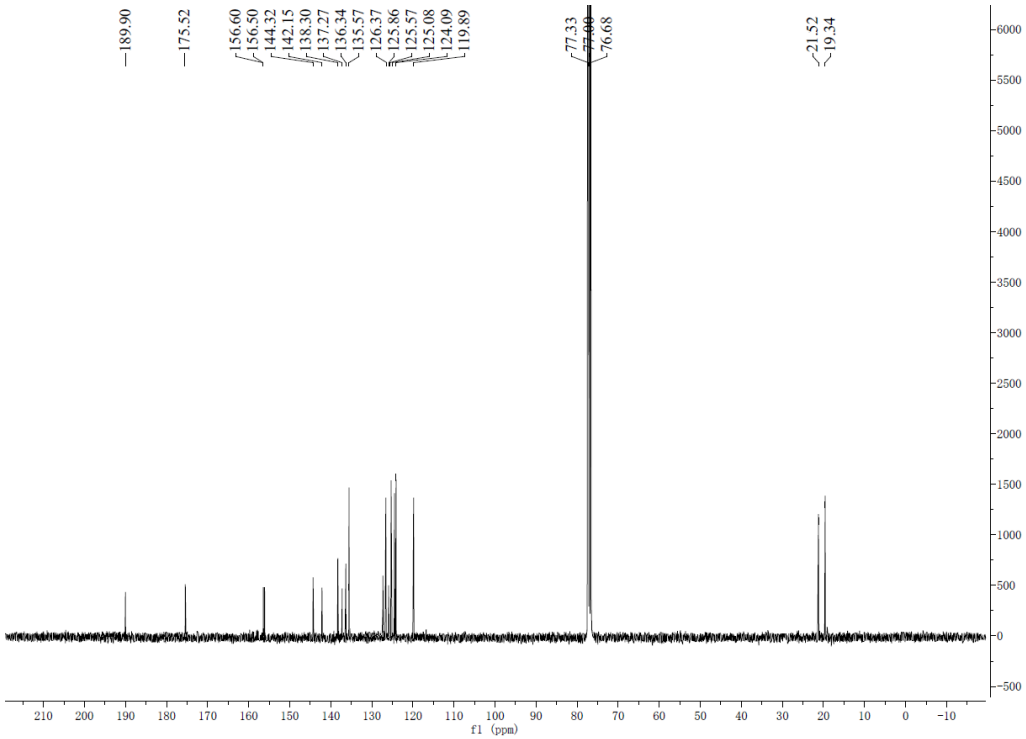
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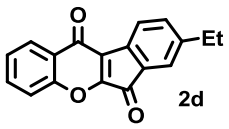
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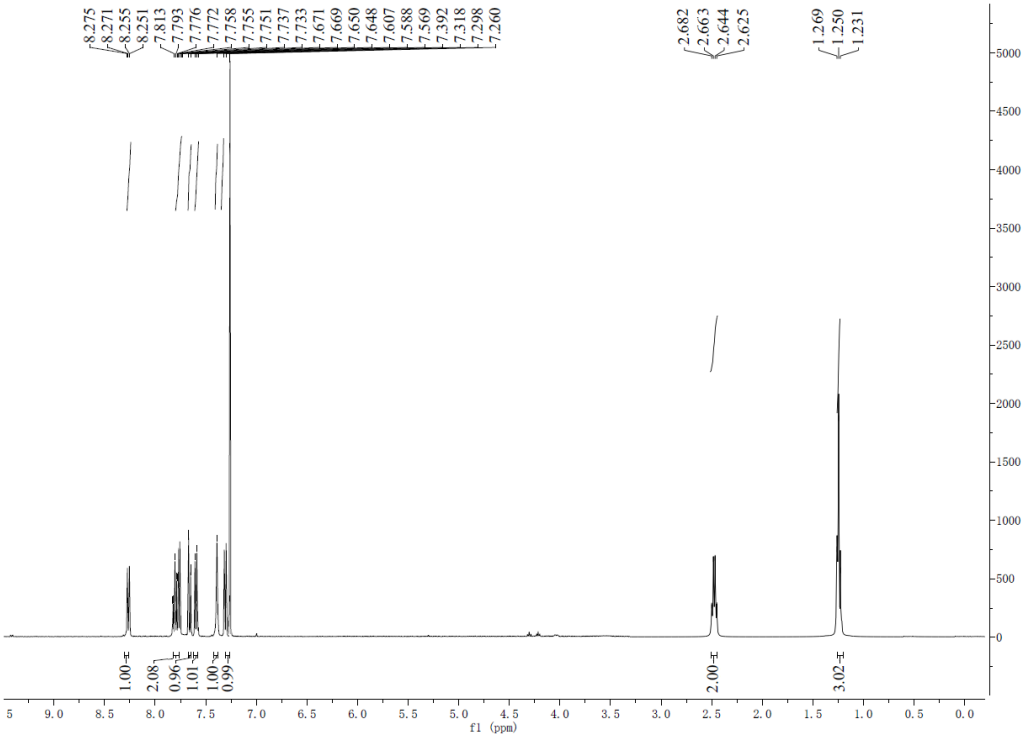
2d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2.682
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2.644
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1.250
1.231
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1.01
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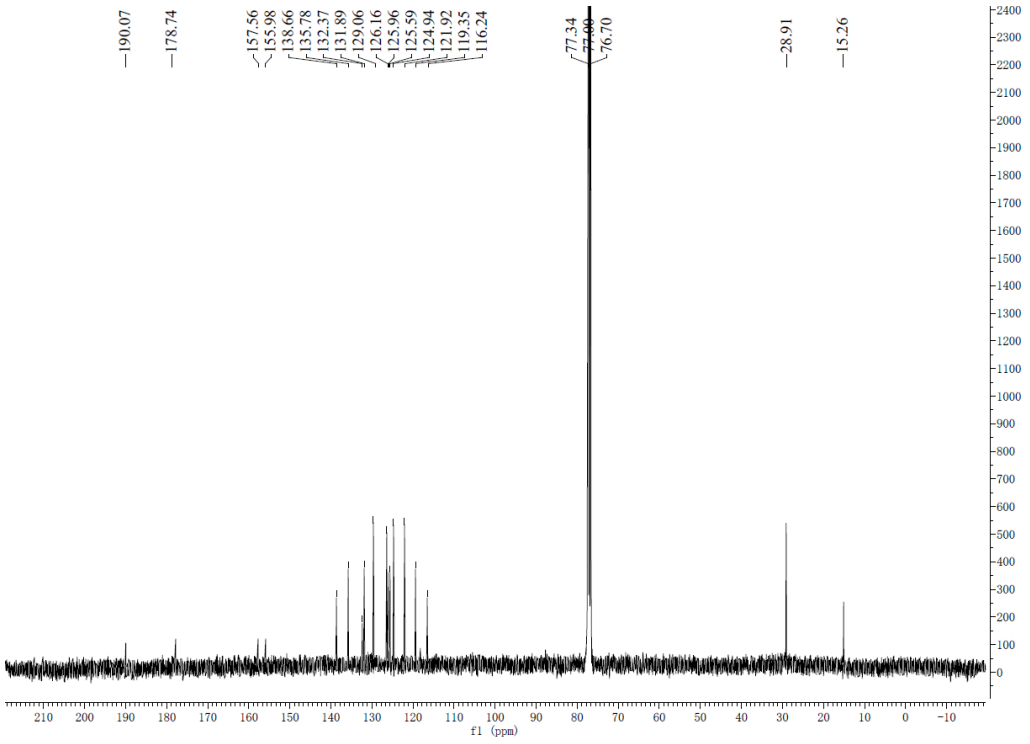
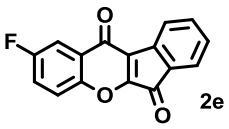
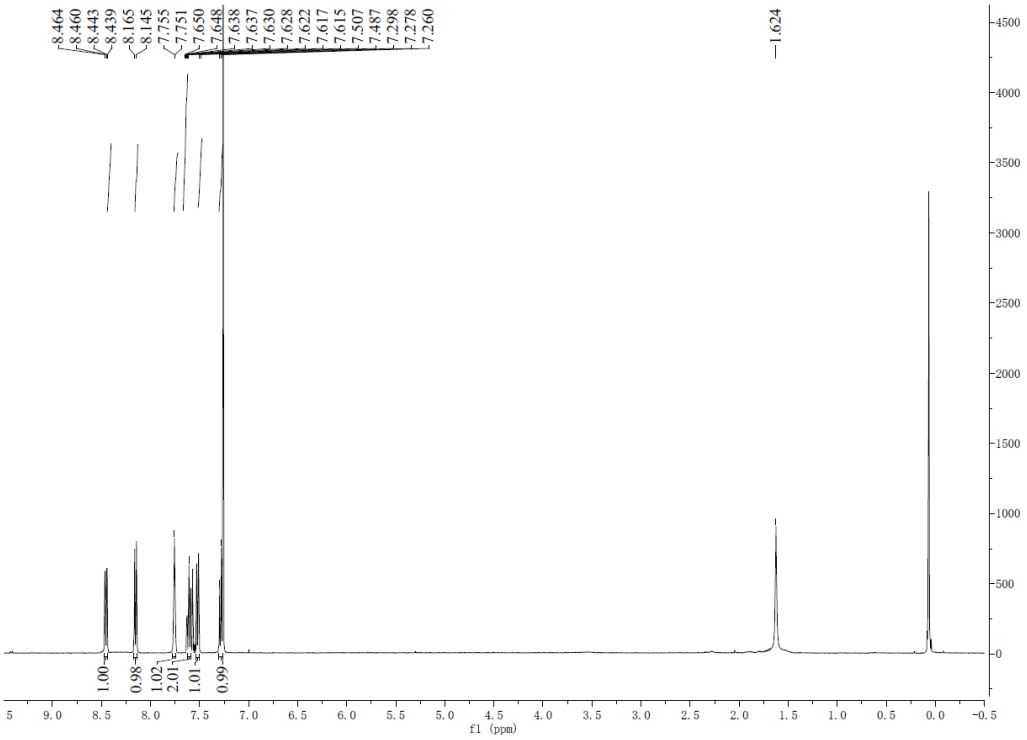
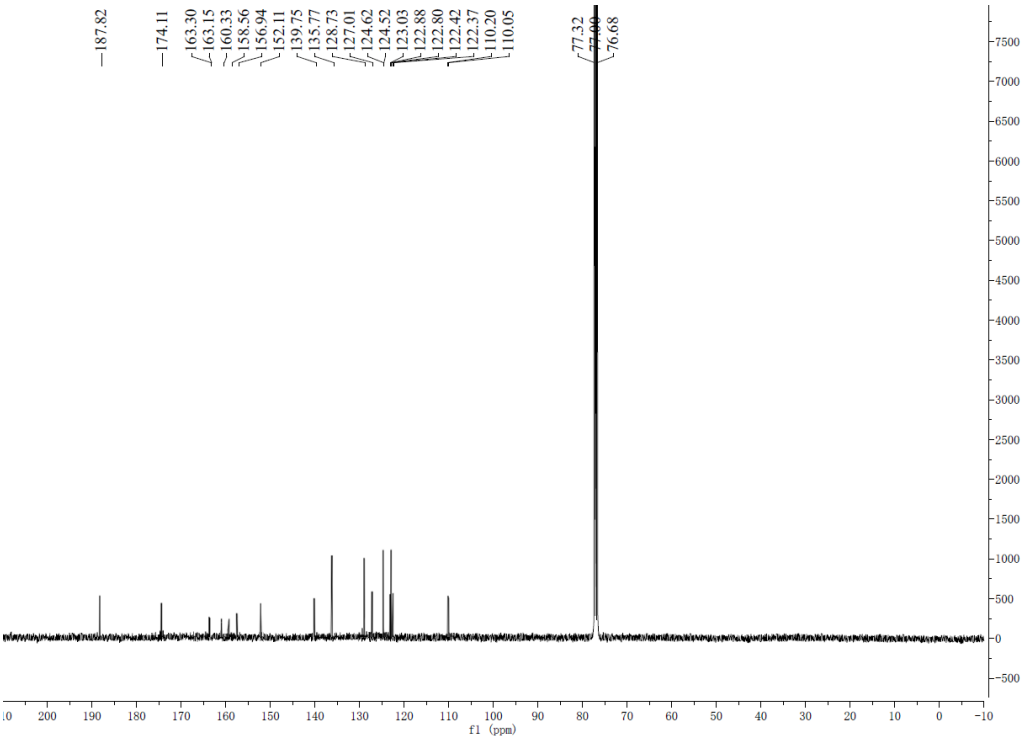
3.02
f1 (ppm)

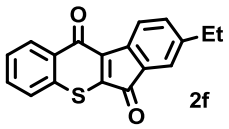

190.07
178.74
157.56
155.98
138.66
135.78
132.37
131.89
129.06
126.16
125.96
125.59
124.94
121.92
119.35
116.24
77.34
77.00
76.70
28.91
15.26
f1 (ppm)


F
O
O
O

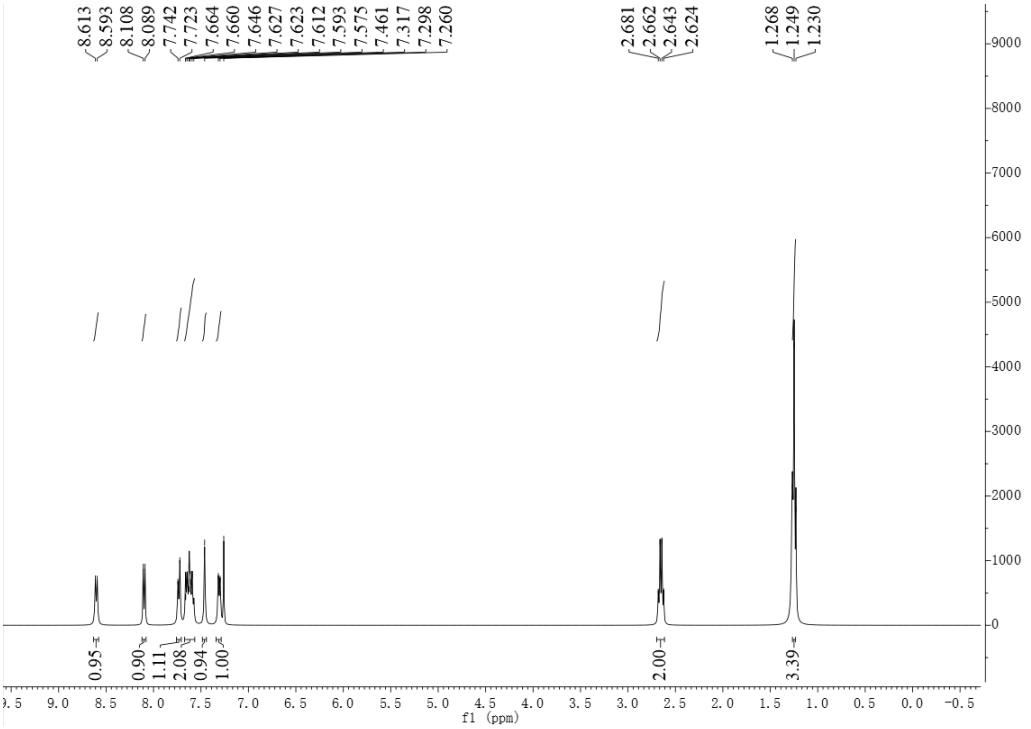
2e

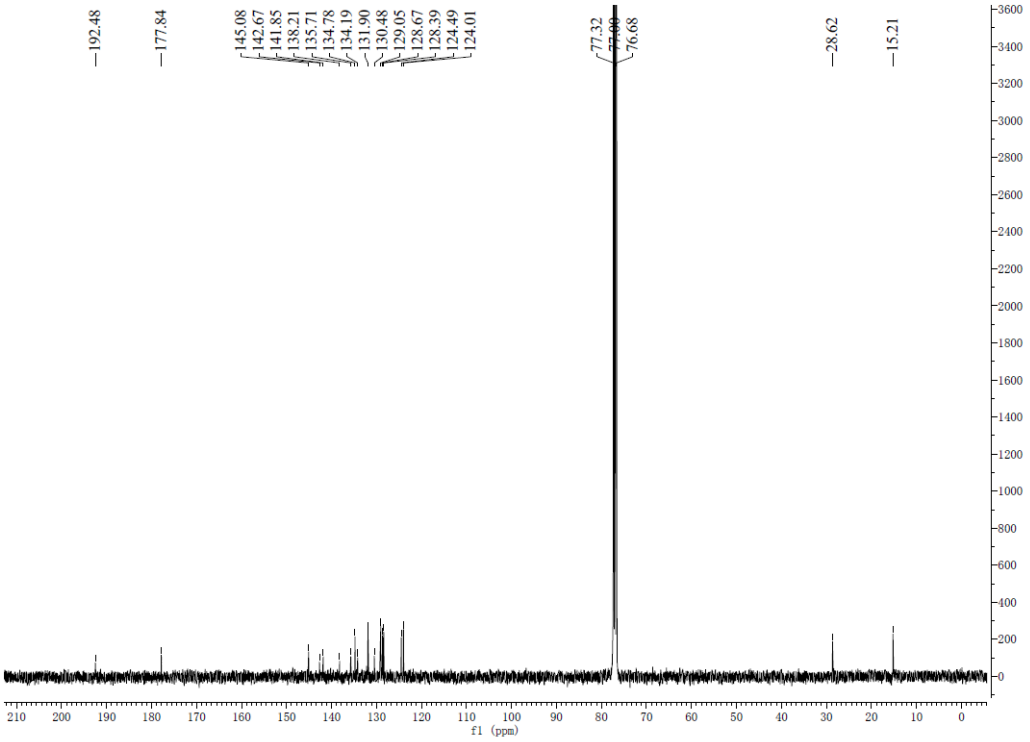

8.464
8.460
8.443
8.439
8.165
8.145
7.755
7.751
7.650
7.648
7.638
7.637
7.630
7.628
7.622
7.617
7.615
7.507
7.487
7.298
7.278
7.260
1.624
1.00
0.98
1.02
2.01
1.01
0.99
f1 (ppm)

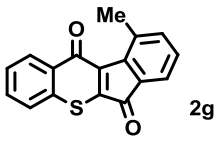

187.82
174.11
163.30
163.15
160.33
158.56
156.94
152.11
139.75
135.77
128.73
127.01
124.62
124.52
123.03
122.88
122.80
122.42
122.37
110.20
110.05
77.32
77.00
76.68
f1 (ppm)


O
Et
S
O

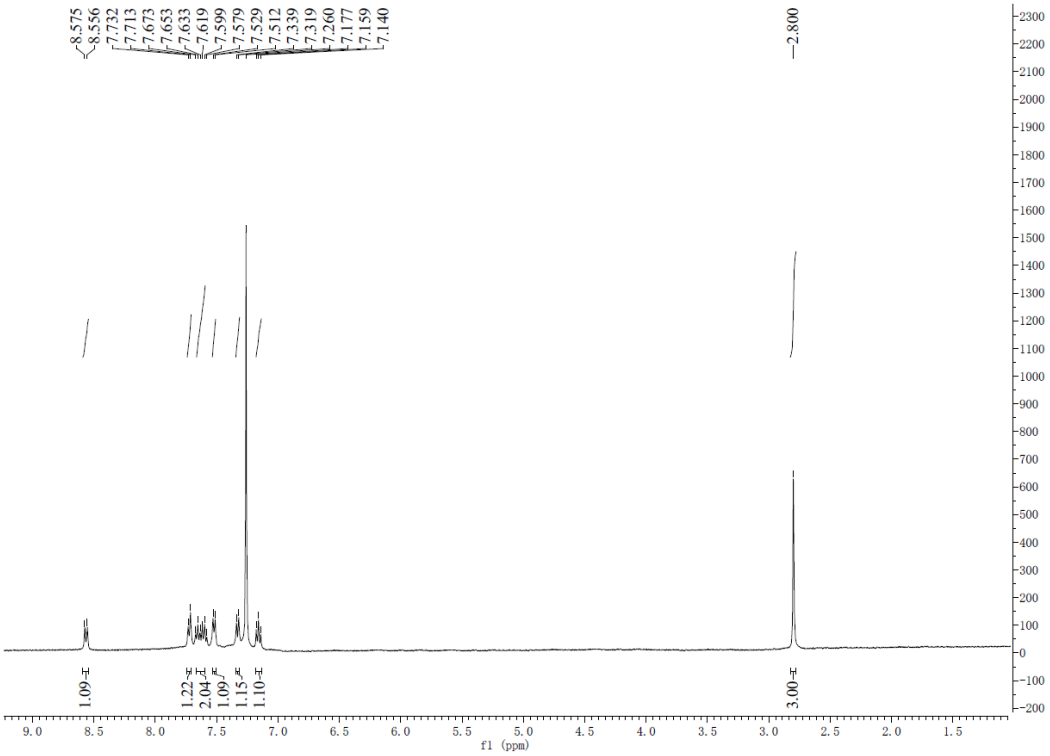
2f

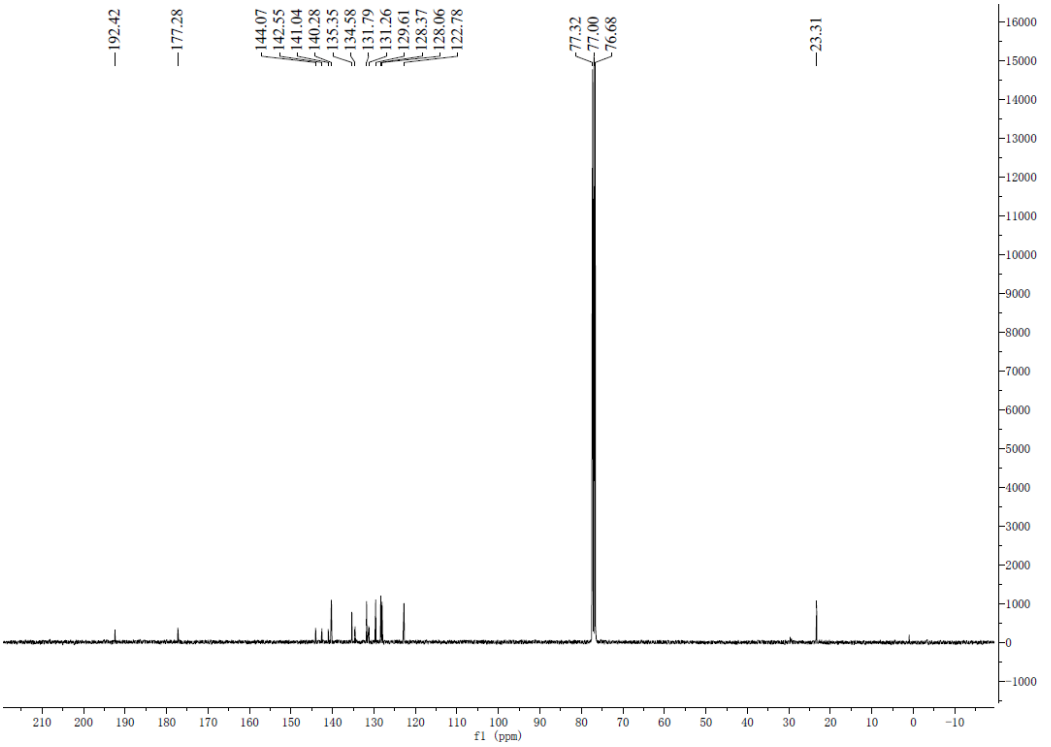

8.613
8.593
8.108
8.089
7.742
7.723
7.664
7.660
7.646
7.627
7.623
7.612
7.593
7.575
7.461
7.317
7.298
7.260
2.681
2.662
2.643
2.624
1.268
1.249
1.230
0.95
0.90
1.11
2.08
0.94
1.00
2.00
3.39
f1 (ppm)


192.48
177.84
145.08
142.67
141.85
138.21
135.71
134.78
134.19
131.90
130.48
129.05
128.67
128.39
124.49
124.01
77.32
77.00
76.68
28.62
15.21
f1 (ppm)


Me
O
S
O

2g


8.575
8.556
7.732
7.713
7.673
7.653
7.633
7.619
7.599
7.579
7.529
7.512
7.339
7.319
7.260
7.177
7.159
7.140
2.800
1.09
1.22
2.04
1.09
1.15
1.10
3.00
f1 (ppm)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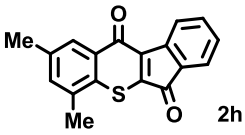
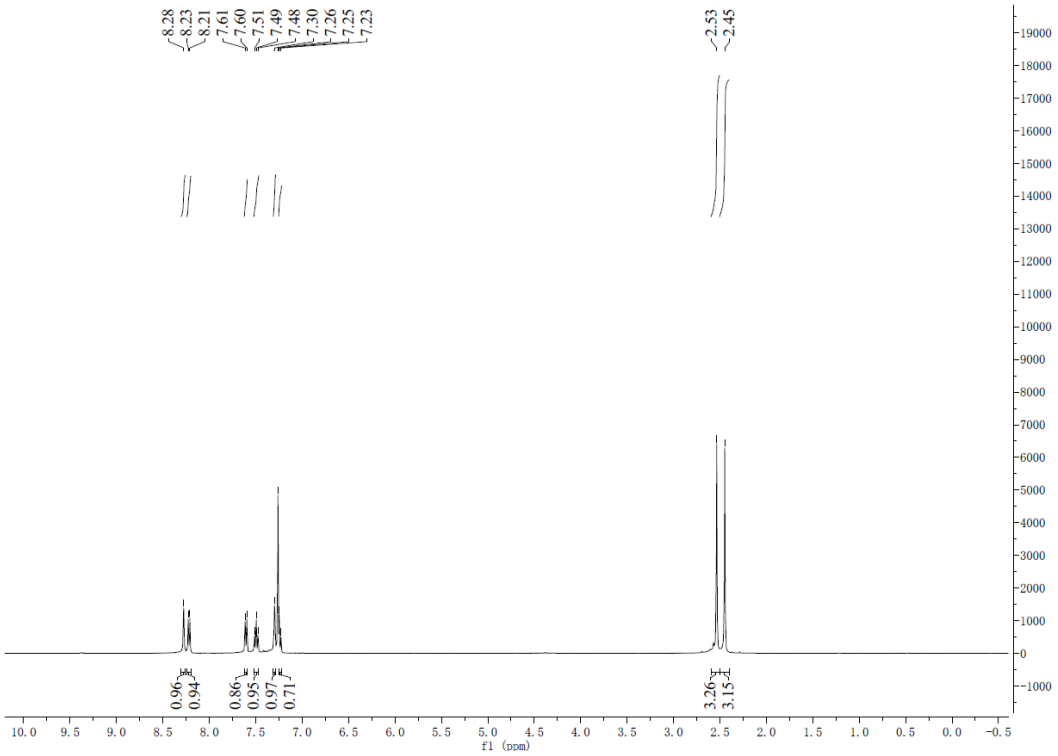
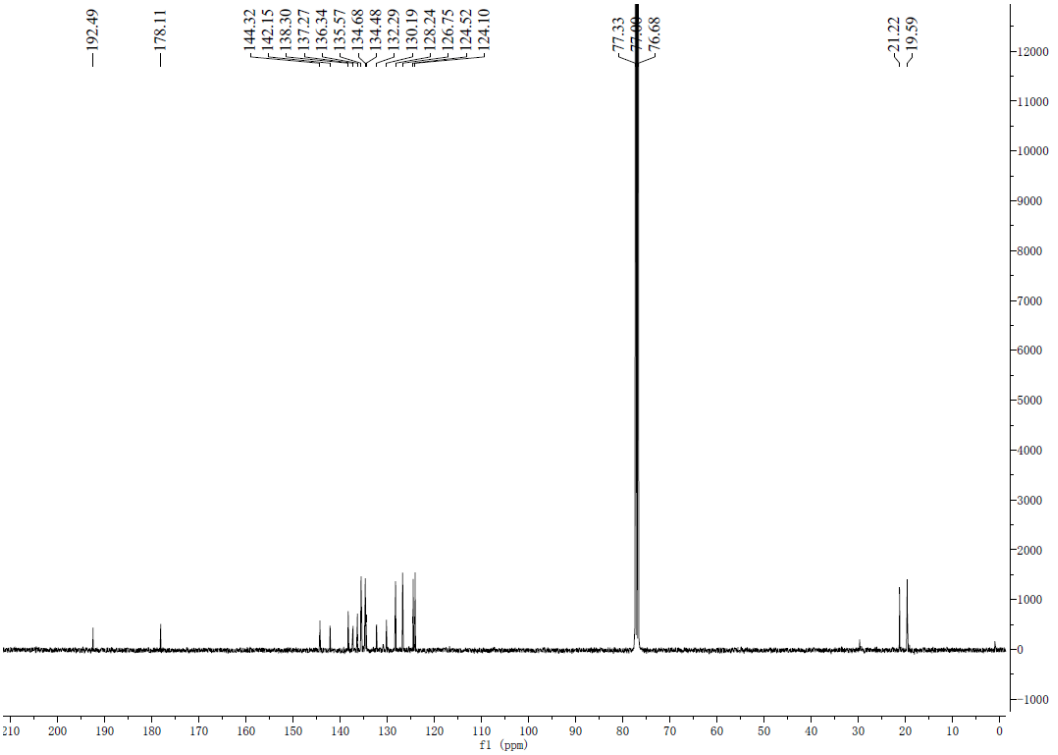
144.07
142.55
141.04
140.28
135.35
134.58
131.79
131.26
129.61
128.37
128.06
122.78
77.32
77.00
76.68
23.31
f1 (ppm)


Me
O
S
O
Me

2h


8.28
8.23
8.21
7.61
7.60
7.51
7.49
7.48
7.30
7.26
7.25
7.23
2.53
2.45
0.96
0.94
0.86
0.95
0.97
0.71
3.26
3.15
f1 (ppm)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178.11
144.32
142.15
138.30
137.27
136.34
135.57
134.68
134.48
132.29
130.19
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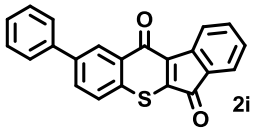
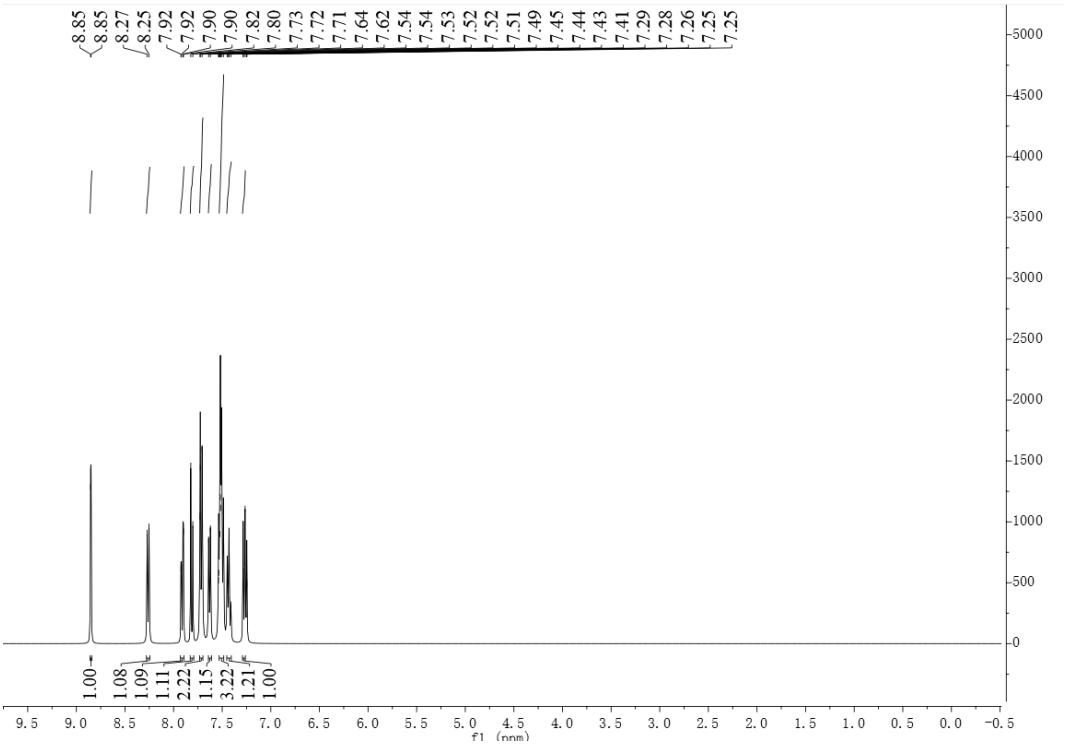
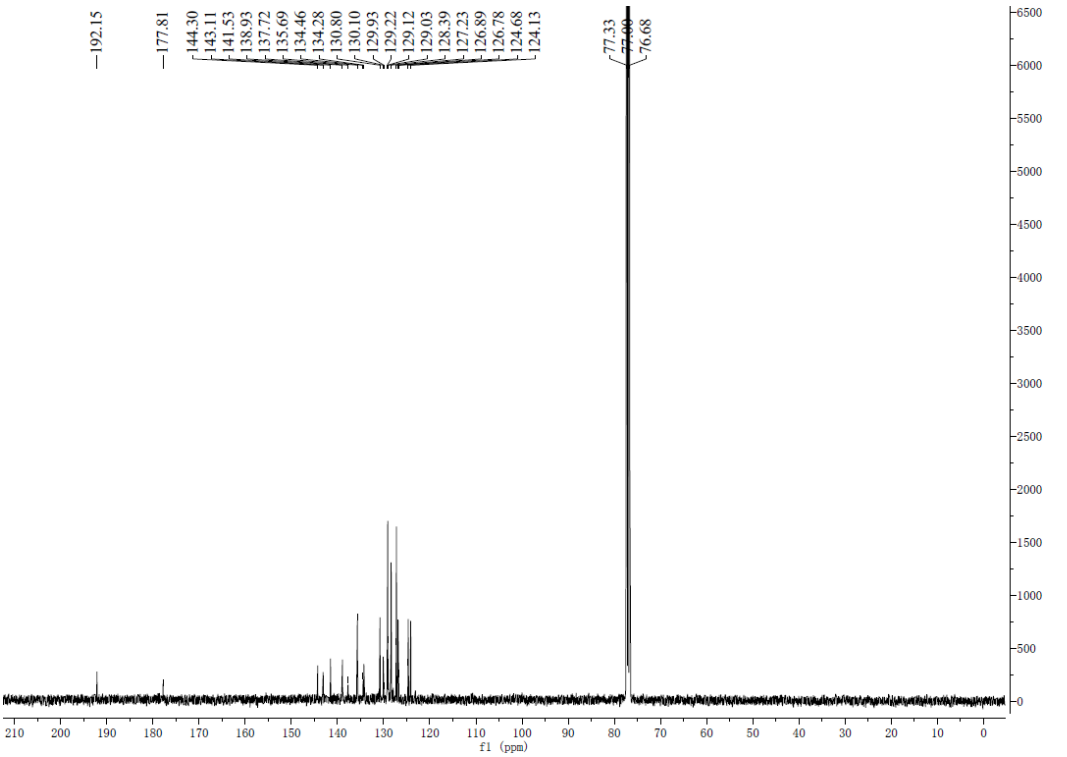
76.68
21.22
19.59
f1 (ppm)


O
S
O

2i


8.85
8.85
8.27
8.25
7.92
7.92
7.90
7.90
7.82
7.80
7.73
7.72
7.71
7.64
7.62
7.54
7.54
7.53
7.52
7.52
7.51
7.49
7.45
7.44
7.43
7.41
7.29
7.28
7.26
7.25
7.25
1.00
1.08
1.09
1.11
2.22
1.15
3.22
1.21
1.00
f1 (ppm)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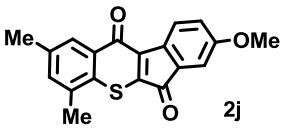
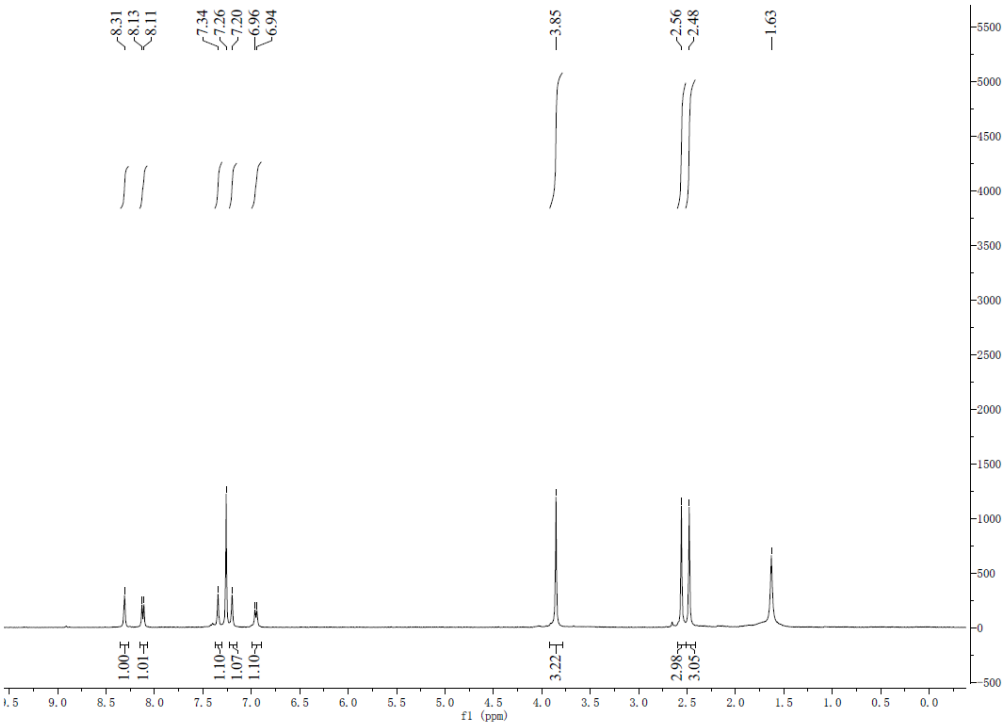
177.81
144.30
143.11
141.53
138.93
137.72
135.69
134.46
134.28
130.80
130.10
129.93
129.22
129.12
129.03
128.39
127.23
126.89
126.78
124.68
124.13
77.33
77.00
76.68
f1 (ppm)


O
Me
OMe
S
Me
O

2j


8.31
8.13
8.11
7.34
7.26
7.20
6.96
6.94
3.85
2.56
2.48
1.63
1.00
1.01
1.10
1.07
1.10
3.22
2.98
3.05
f1 (ppm)