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$FeCl_3$-Catalyzed Dimerization/Elimination of 1,1-Diarylalkenes: Efficient Synthesis of Functionalized 4*H*-Chromenes

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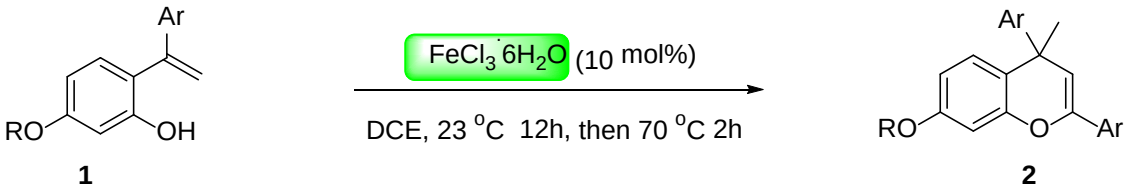
Contents:

1. General Information

^{1}H and **^{13}C NMR** spectra were recorded on a Bruker ACF300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26, acetone δ 2.05), carbon (chloroform δ 77.0, acetone δ 29.84) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in EI mode. All high resolution mass spectra (**HRMS**) were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (**TLC**), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or potassium permanganate solution followed by heating using a heat gun. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. The enantiomeric excess (**ee**) of products were determined by chiral phase HPLC analysis on SHIMAZU HPLC units or Agilent HPLC units, including the following instruments: pump, LC-20AD; detector, SPD-20A; column, Chiralcel OD-H.

All reactions were carried out under air atmosphere. All commercially available reagents were used as received for the reactions without any purification. All solvents were dried on alumina columns using a solvent dispensing system. 1,1-diarylalkenes[1] were synthesized following the reported procedure.

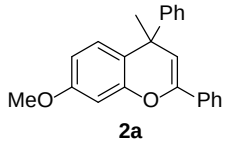
2. General Procedure for Dimerization/Elimination



1 **2**

To a vial equipped with a dried stir bar was added $FeCl_3 \cdot 6H_2O$ (0.02 mmol), 1,1-diarylalkenes **1** (0.20 mmol) and 1,2-dichloroethane (1 mL). The reaction mixture was allowed to stir at room temperature for 12 hours, and then was taken to 70 °C to stir for more 2 hours. The crude reaction mixture was concentrated under reduced pressure and directly purified by silica gel chromatography (ethyl acetate:hexanes = 1:50) to yield **2** in a pure form.

3. Analytical data for 2



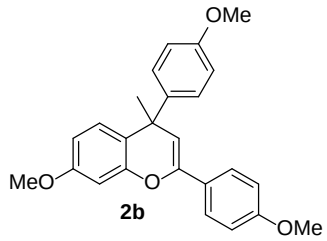
2a

Colorless oil, 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.46 – 7.41 (m, 4H), 7.39 – 7.32 (m, 3H), 7.25 – 7.19 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 6.61 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.50 (s, 1H), 3.84 (s, 3H), 1.90 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.80, 150.98, 150.09, 145.99, 134.18, 129.24, 128.38, 128.29, 128.15, 127.29, 125.97, 124.66, 120.94, 110.66, 107.38, 100.92, 55.34, 39.30, 30.45.

HRMS (ESI): m/z Calcd. for $[C_{23}H_{21}O_2, M+H]^+$: 329.1542; Found: 329.1550.



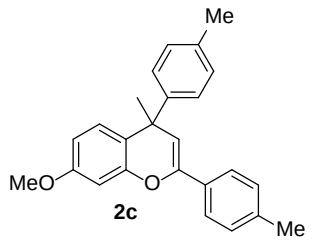
2b

Colorless oil, 72% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.66 (d, *J* = 2.6 Hz, 1H), 6.56 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.32 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 1.82 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 159.82, 158.71, 157.68, 151.00, 145.69, 142.78, 129.17, 128.32, 126.97, 126.02, 121.36, 113.71, 113.44, 110.52, 106.07, 100.90, 55.36, 55.32, 55.22, 38.61, 30.73.

HRMS (ESI): m/z Calcd. for $[C_{25}H_{25}O_4, M+H]^+$: 389.1753; Found: 389.1753.



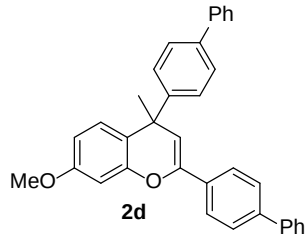
2c

Colorless oil, 92% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 2.6 Hz, 1H), 6.58 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.42 (s, 1H), 3.82 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H), 1.85 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.72, 151.02, 147.41, 145.95, 138.20, 135.45, 131.46, 129.18, 128.96, 128.83, 127.19, 124.56, 121.20, 110.57, 106.76, 100.89, 55.35, 38.92, 30.53, 21.20, 20.87.

HRMS (ESI): m/z Calcd. for $[C_{25}H_{25}O_2, M+H]^+$: 357.1855; Found: 357.1850.



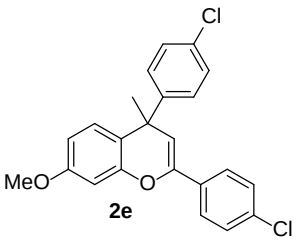
2d

Colorless oil, 70% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.66 – 7.64 (m, 4H), 7.60 – 7.55 (m, 4H), 7.53 – 7.41 (m, 6H), 7.41 – 7.31 (m, 2H), 6.97 (d, *J* = 8.6 Hz, 1H), 6.74 (d, *J* = 2.5 Hz, 1H), 6.62 (dd, *J* = 8.6, 2.5 Hz, 1H), 5.56 (s, 1H), 3.84 (s, 3H), 1.93 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.93, 151.05, 149.22, 145.89, 141.22, 140.81, 140.61, 138.89, 133.11, 129.27, 128.80, 128.70, 127.72, 127.45, 127.13, 127.04, 127.02, 126.93, 125.10, 120.85, 110.77, 107.39, 101.05, 55.40, 39.21, 30.51.

HRMS (ESI): m/z Calcd. for $[C_{35}H_{29}O_2, M+H]^+$: 481.2168; Found: 481.2168.



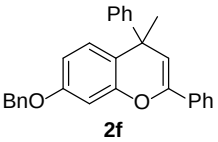
2e

Colorless oil, 64% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 – 7.62 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.29 (m, 2H), 7.29 – 7.24 (m, 2H), 6.84 (d, *J* = 8.6 Hz, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 6.59 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.39 (s, 1H), 3.82 (s, 3H), 1.84 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 159.02, 150.76, 148.48, 145.36, 134.35, 132.47, 131.97, 129.10, 128.69, 128.52, 128.28, 125.99, 120.22, 110.97, 107.23, 101.01, 55.40, 39.05, 30.39.

HRMS (ESI): m/z Calcd. for $[C_{23}H_{19}Cl_2O_2, M+H]^+$: 397.0762; Found: 397.0752.



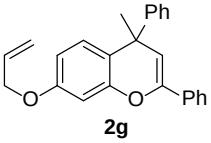
2f

Colorless oil, 78% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 – 7.72 (m, 2H), 7.48 – 7.46 (m, 2H), 7.45 – 7.39 (m, 6H), 7.37 – 7.31 (m, 4H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 1H), 6.79 (d, *J* = 2.6 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.49 (s, 1H), 5.08 (s, 2H), 1.89 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.03, 150.96, 150.06, 146.01, 136.89, 134.17, 129.30, 128.58, 128.39, 128.30, 128.17, 127.97, 127.49, 127.32, 125.99, 124.68, 121.26, 111.37, 107.37, 101.94, 70.14, 39.34, 30.47.

HRMS (ESI): m/z Calcd. for $[C_{29}H_{25}O_2, M+H]^+$: 405.1855; Found: 405.1852.



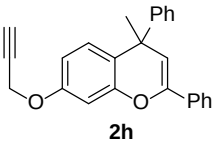
2g

Colorless oil, 85% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.43 – 7.39 (m, 4H), 7.37 – 7.29 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 6.60 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.08 (ddt, *J* = 17.3, 10.5, 5.3 Hz, 1H), 5.47 (s, 1H), 5.44 (dd, *J* = 17.3, 1.3 Hz, 1H), 5.31 (dd, *J* = 10.5, 1.3 Hz, 1H), 4.55 (dt, *J* = 5.3, 1.3 Hz, 2H), 1.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.82, 150.94, 150.08, 146.00, 134.19, 133.20, 129.24, 128.38, 128.30, 128.16, 127.31, 125.97, 124.67, 121.14, 117.66, 111.29, 107.38, 101.84, 68.95, 39.33, 30.46.

HRMS (ESI): m/z Calcd. for $[C_{25}H_{23}O_2, M+H]^+$: 355.1698; Found: 355.1700.



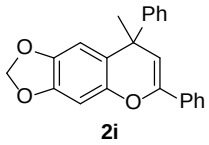
2h

Colorless oil, 66% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 – 7.70 (m, 2H), 7.44 – 7.37 (m, 4H), 7.37 – 7.28 (m, 3H), 7.19 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 2.6 Hz, 1H), 6.63 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.46 (s, 1H), 4.69 (d, *J* = 2.4 Hz, 2H), 2.55 (t, *J* = 2.4 Hz, 1H), 1.86 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.79, 150.95, 149.98, 146.06, 134.14, 129.37, 128.43, 128.32, 128.19, 127.33, 126.03, 124.71, 121.95, 111.27, 107.37, 102.19, 78.53, 75.61, 55.98, 39.38, 30.48.

HRMS (ESI): m/z Calcd. for $[C_{25}H_{21}O_2, M+H]^+$: 353.1542; Found: 353.1538.



2i

Colorless oil, 88% yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.69 (m, 2H), 7.46 – 7.37 (m, 4H), 7.36 – 7.31 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.67 (s, 1H), 6.40 (s, 1H), 5.90 (d, *J* = 1.3 Hz, 1H), 5.88 (d, *J* = 1.3 Hz, 1H), 5.40 (s, 1H), 1.86 (s, 3H).

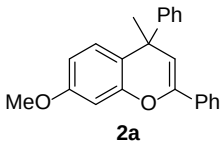
^{13}C NMR (125 MHz, $CDCl_3$): δ 149.89, 146.52, 146.06, 145.01, 143.65, 134.10, 128.38, 128.29, 128.21, 127.32, 126.09, 124.63, 120.56, 106.95, 106.23, 101.15, 97.98, 40.04, 30.40.

HRMS (ESI): m/z Calcd. for $[C_{23}H_{19}O_3, M+H]^+$: 343.1334; Found: 343.1340.

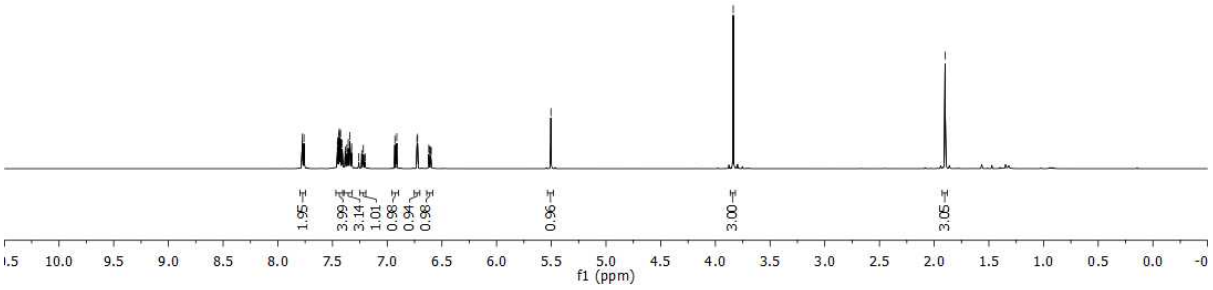
4. References

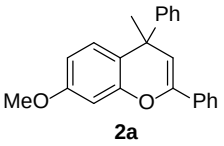
1 Z. Wang, F. Ai, Z. Wang, W. Zhao, G. Zhu, Z. Lin and J. Sun, *J. Am. Chem. Soc.*, 2015, **137**, 383.

5. NMR spectra of the products.



2a





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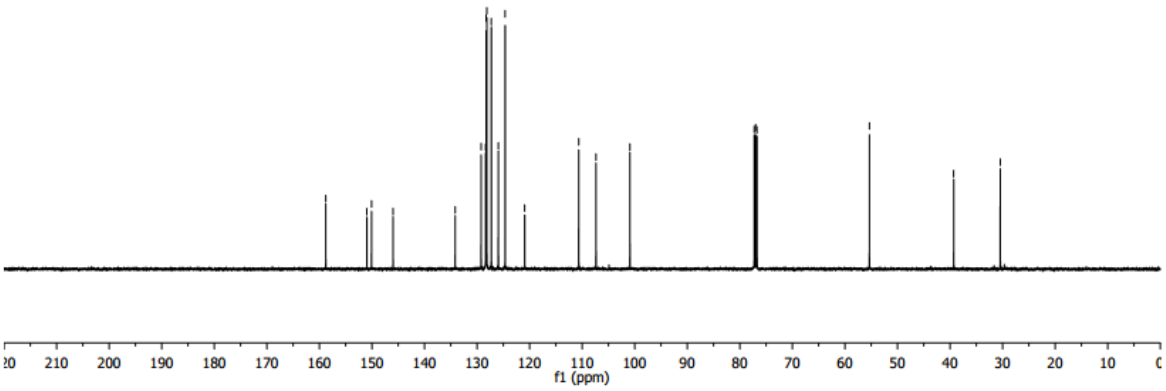

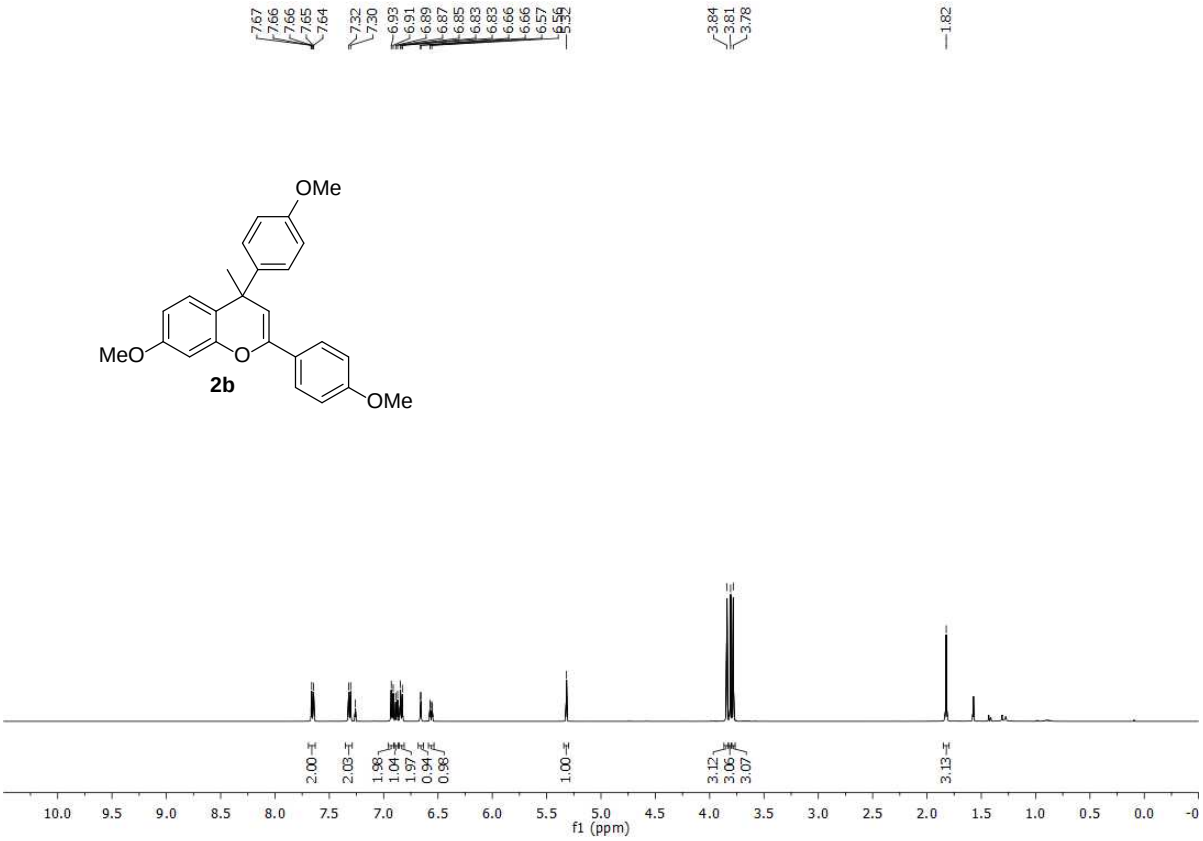
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3.78
1.82
OMe
MeO
O
OMe
2b
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0.98
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3.06
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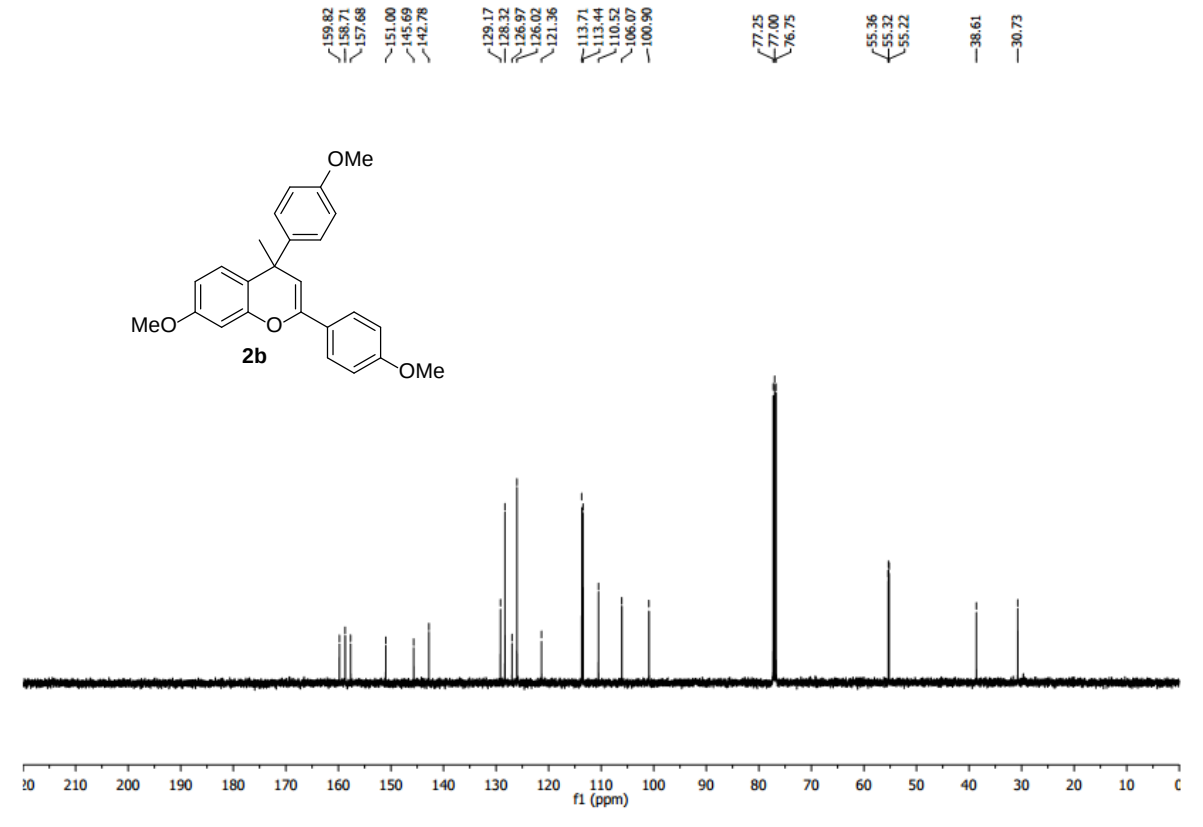
3.13
f1 (ppm)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MeO
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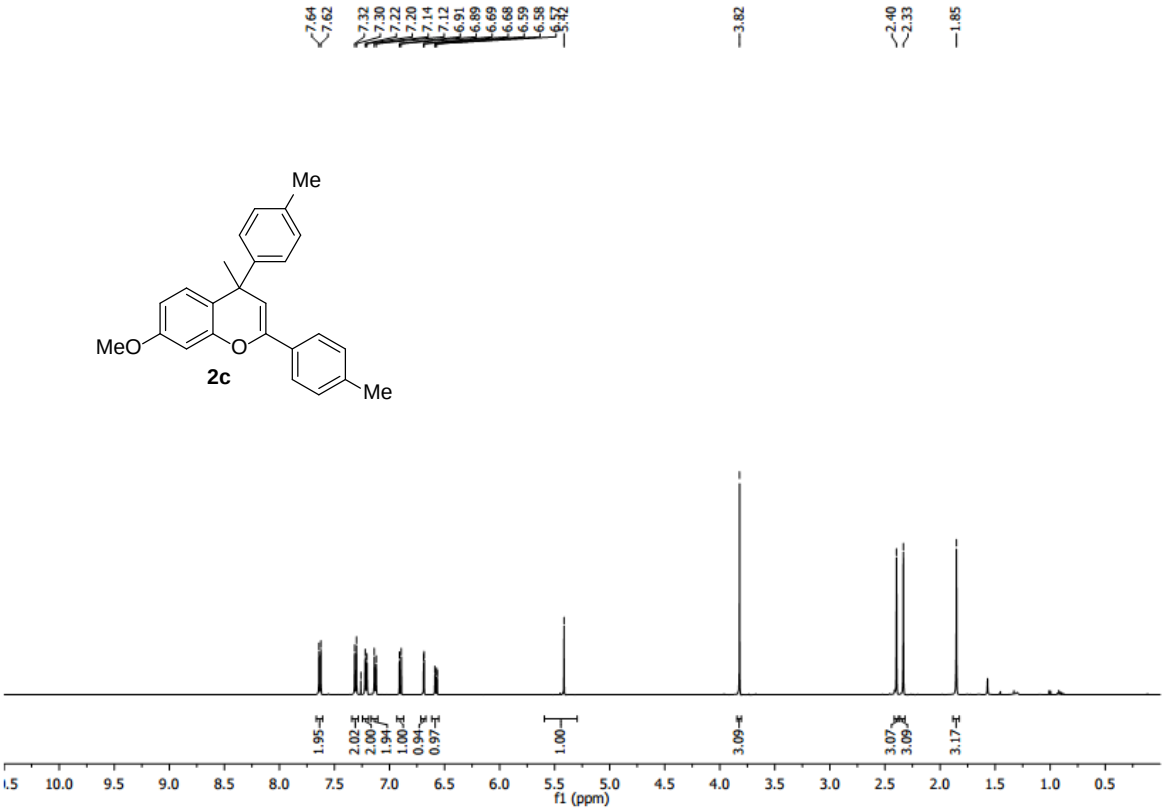
OMe
2b
f1 (ppm)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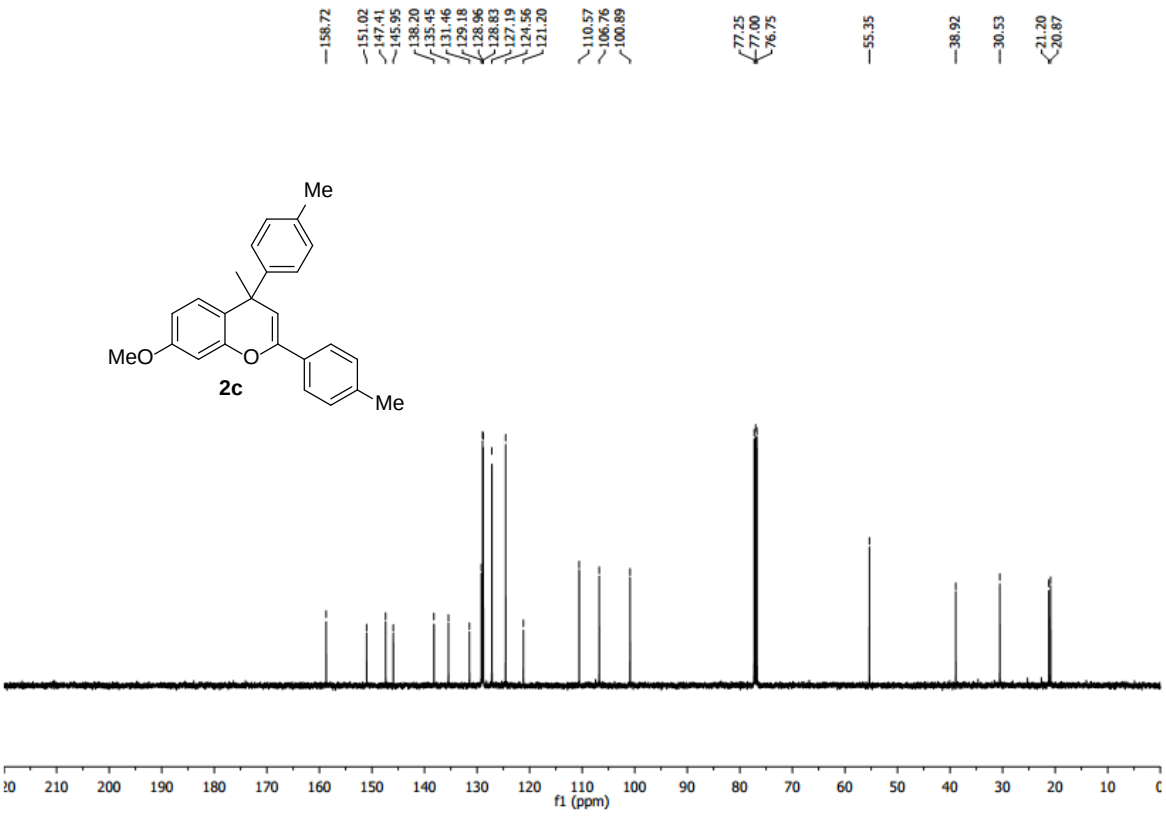
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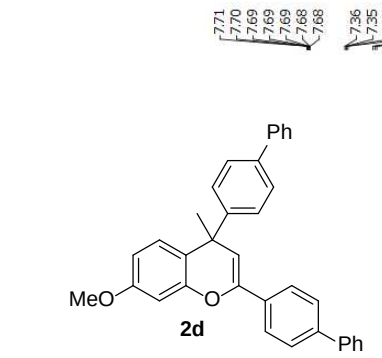
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Ph

2d

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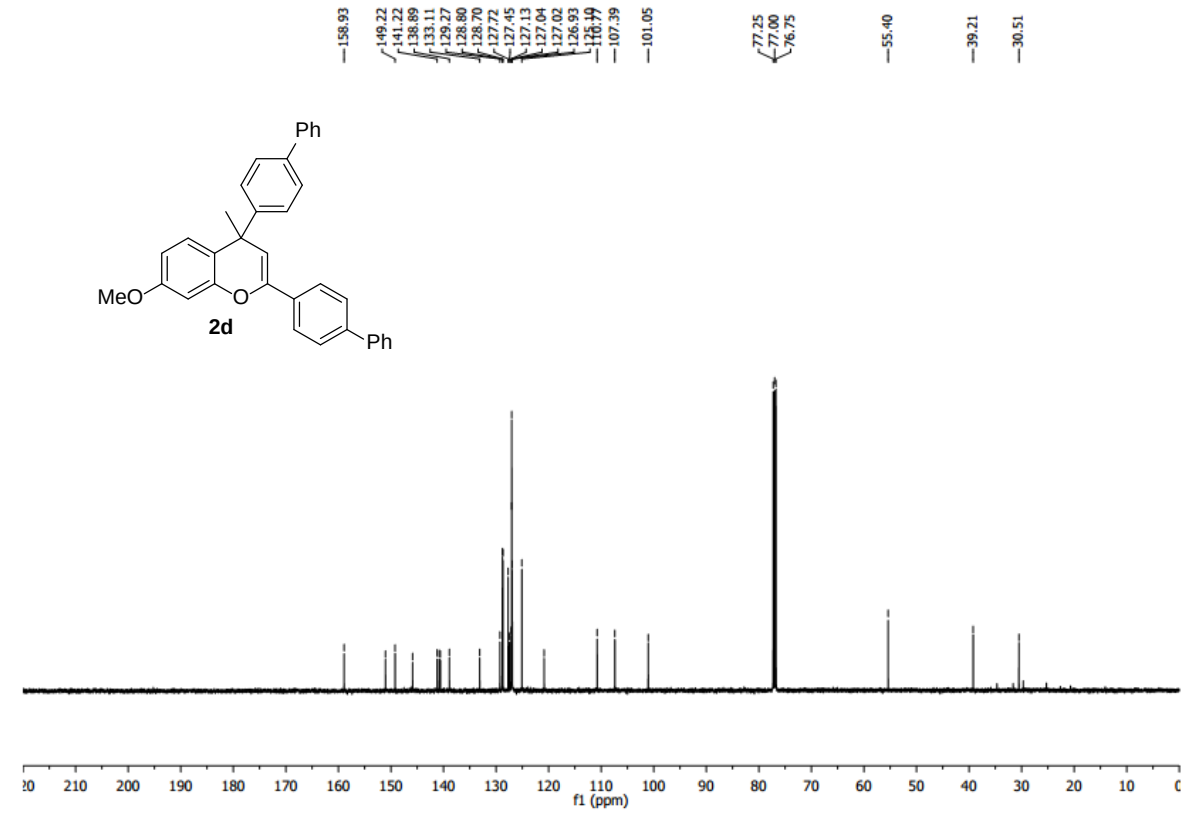
f1 (ppm)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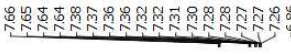
f1 (ppm)

Ph
MeO
O
Ph

2d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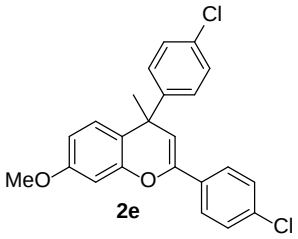
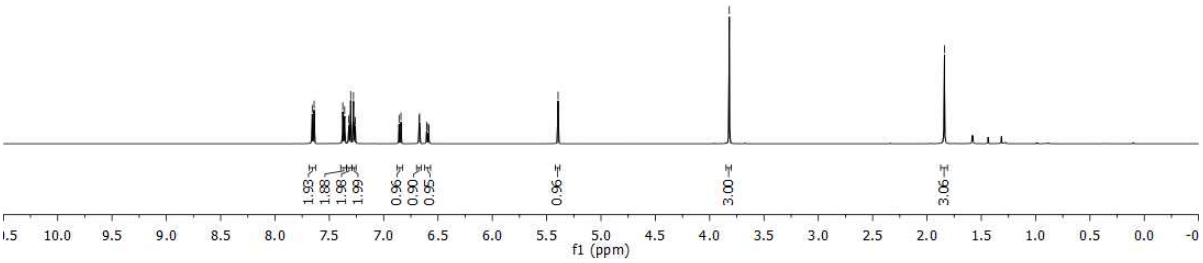
1.84


Cl
MeO
O
Cl

2e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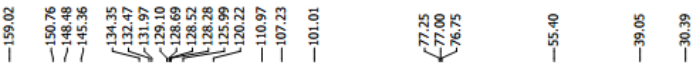
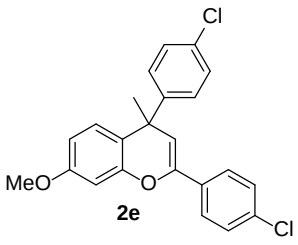
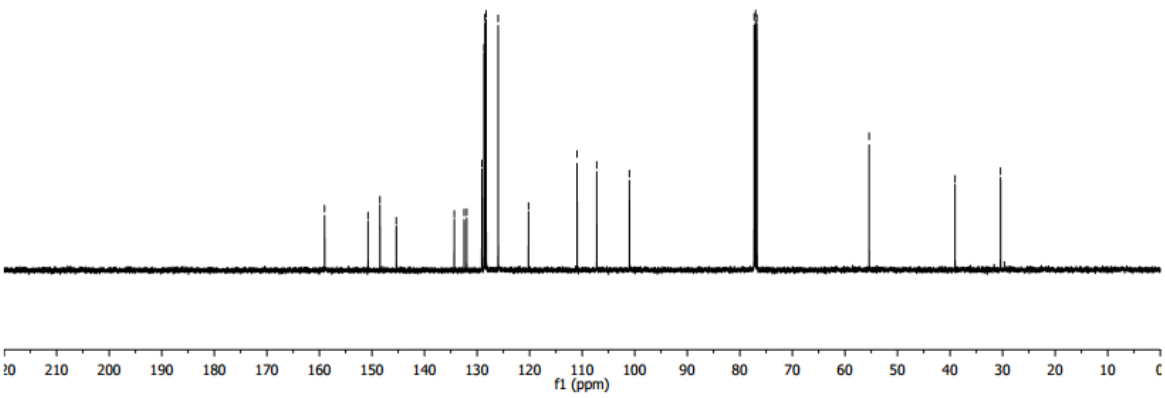
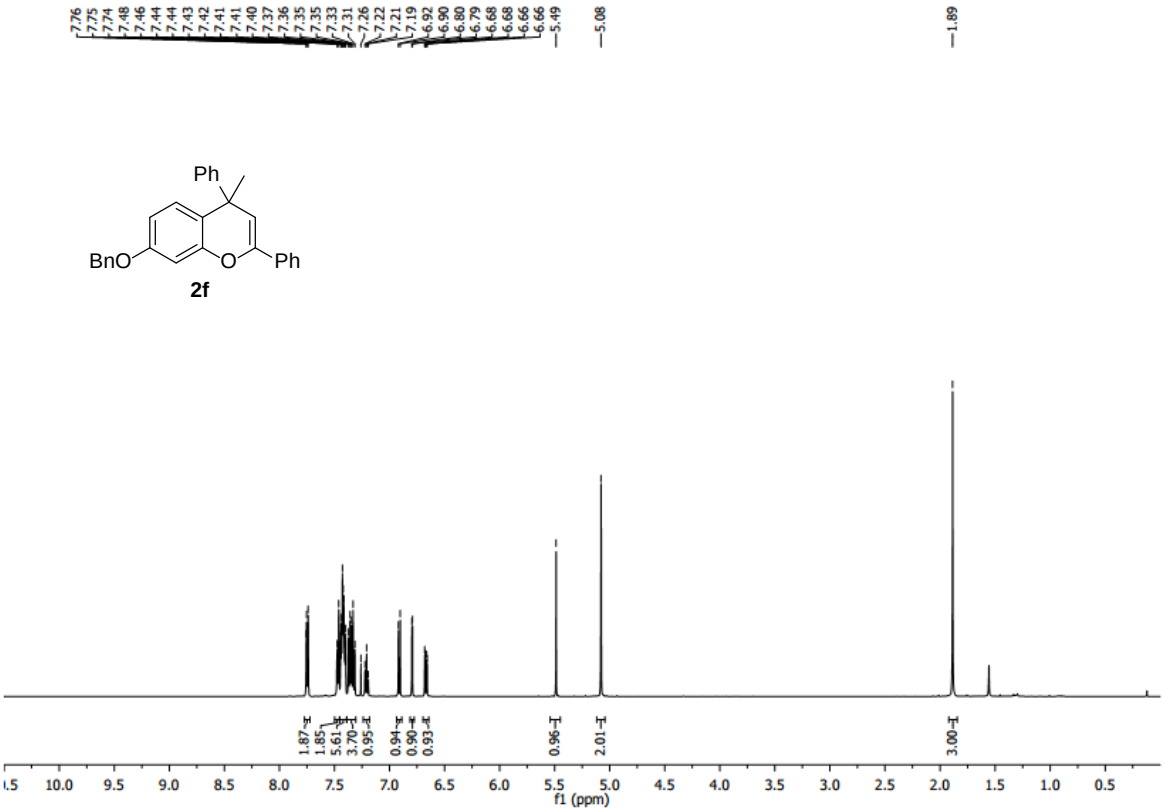
1.88
1.98
1.99
0.96
0.90
0.95
0.96
3.00
3.06
f1 (ppm)

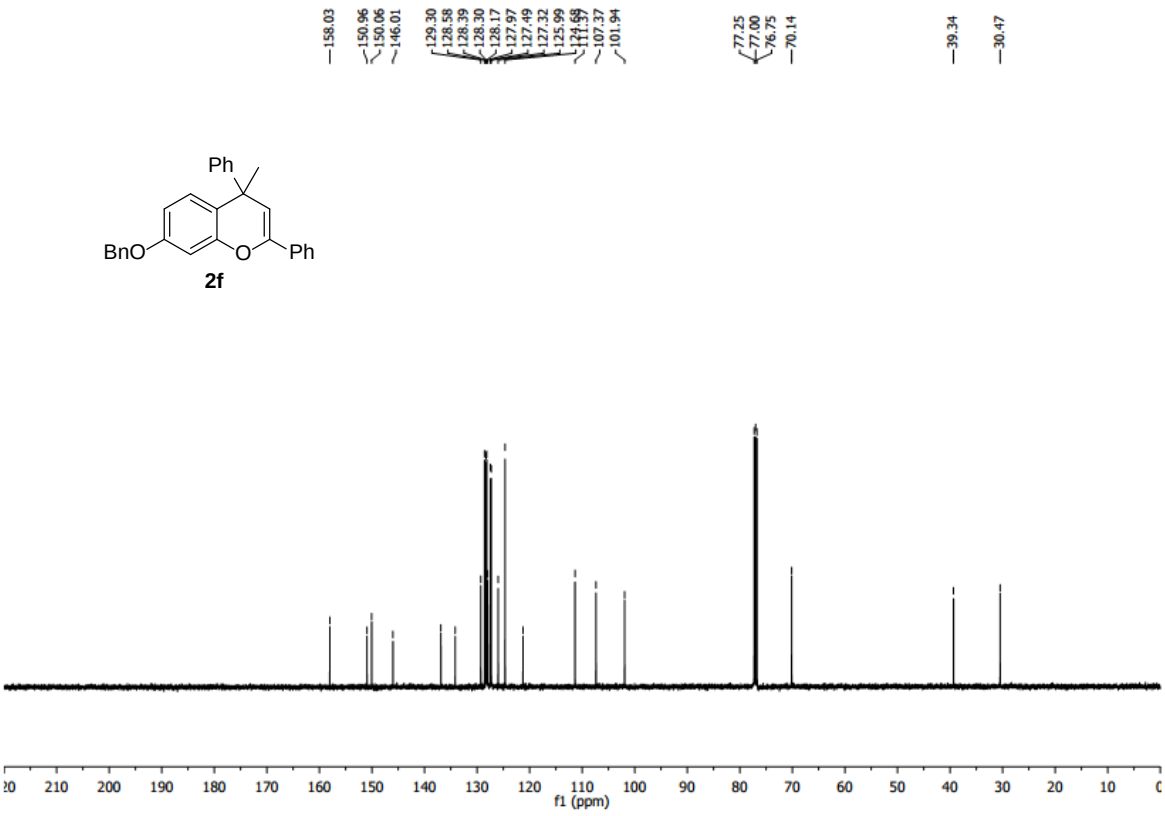

159.02
150.76
148.48
145.36
134.35
132.47
131.97
129.10
128.69
128.52
128.28
125.99
120.22
110.97
107.23
101.01
77.25
77.00
76.75
55.40
39.05
30.39


Cl
MeO
O
Cl

2e


f1 (ppm)


7.76
7.75
7.74
7.48
7.46
7.44
7.44
7.43
7.42
7.41
7.41
7.40
7.37
7.36
7.35
7.35
7.33
7.31
7.26
7.22
7.21
7.19
6.92
6.90
6.80
6.79
6.68
6.68
6.66
6.66
5.49
5.08
1.89
Ph
BnO
O
Ph
2f
1.87
1.85
5.61
3.70
0.95
0.94
0.90
0.93
0.96
2.01
3.00
f1 (ppm)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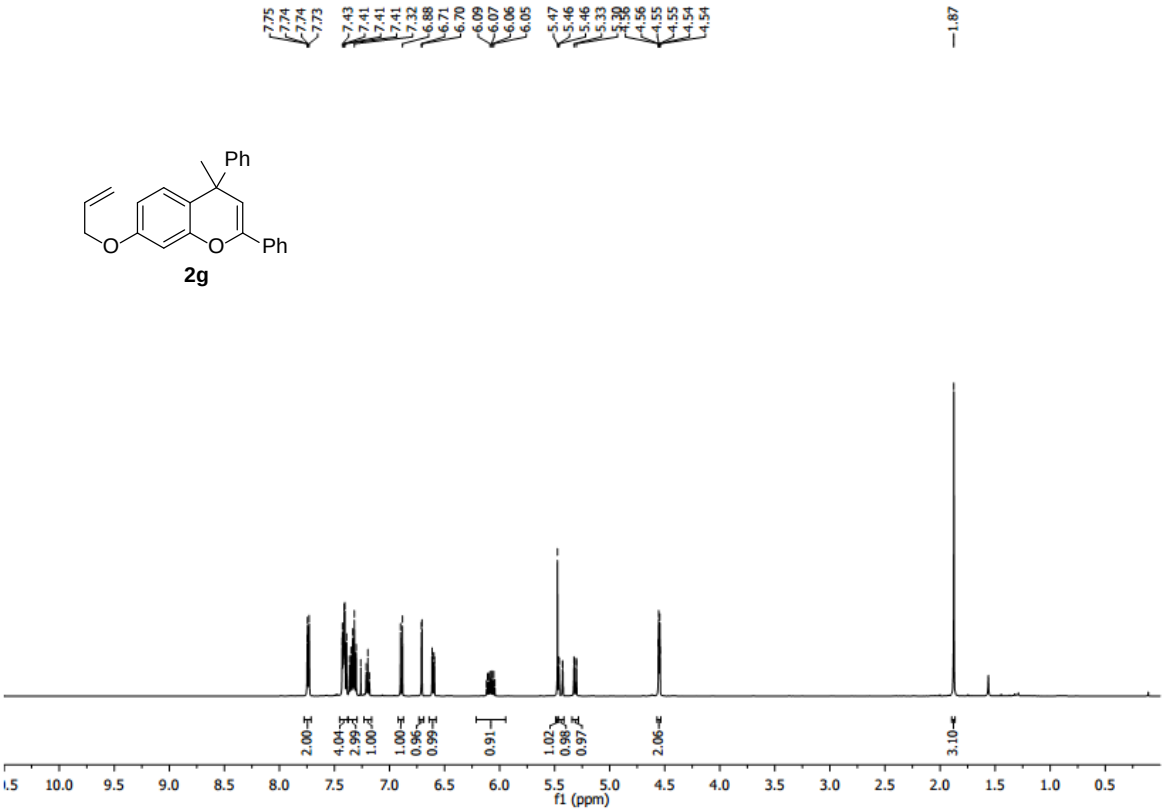
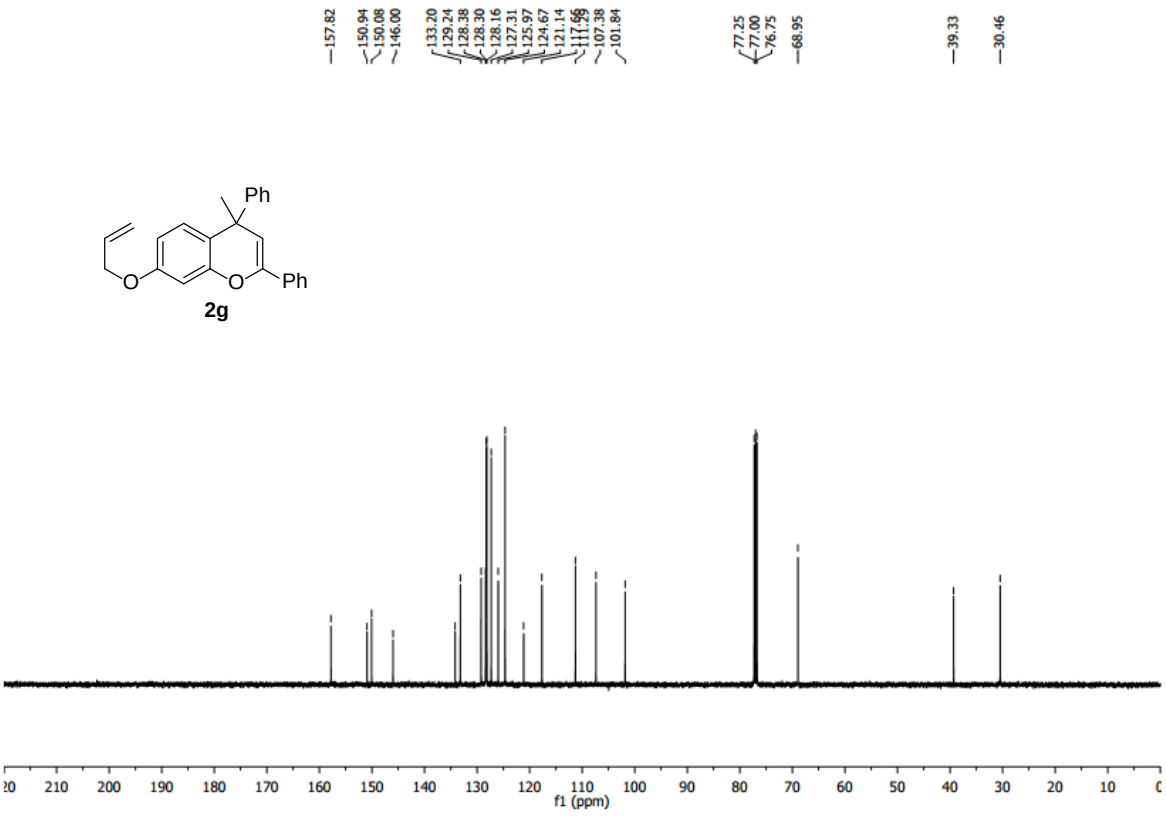
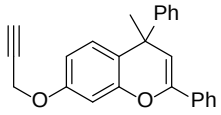
150.96
150.06
146.01
129.30
128.58
128.39
128.30
128.17
127.97
127.49
127.32
125.99
107.37
101.94
77.25
77.00
76.75
70.14
39.34
30.47
Ph
BnO
O
Ph
2f
f1 (ppm)

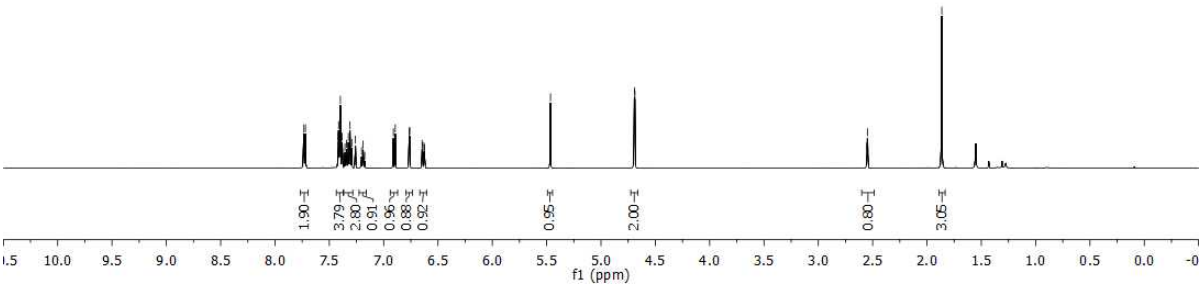

7.75
7.74
7.74
7.73
7.43
7.41
7.41
7.41
7.32
6.88
6.71
6.70
6.09
6.07
6.06
6.05
5.47
5.46
5.46
5.33
4.56
4.55
4.55
4.54
4.54
1.87
Ph
O
O
Ph
2g
2.00
4.04
2.99
1.00
1.00
0.96
0.99
0.91
1.02
0.98
0.97
2.06
3.10
f1 (ppm)


157.82
150.94
150.08
146.00
133.20
129.24
128.38
128.30
128.16
127.31
125.97
124.67
121.14
107.38
101.84
77.25
77.00
76.75
68.95
39.33
30.46
Ph
O
O
Ph
2g
f1 (ppm)

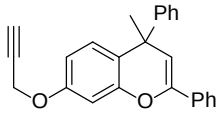

7.74
7.73
7.73
7.72
7.42
7.41
7.41
7.41
7.40
7.38
7.36
7.35
7.34
7.33
7.31
7.29
7.26
7.20
7.19
7.17
6.91
6.89
6.76
6.76
6.65
6.64
6.63
6.62
5.46
4.69
4.69
2.55
2.55
2.54
1.86


Ph
O
O
Ph

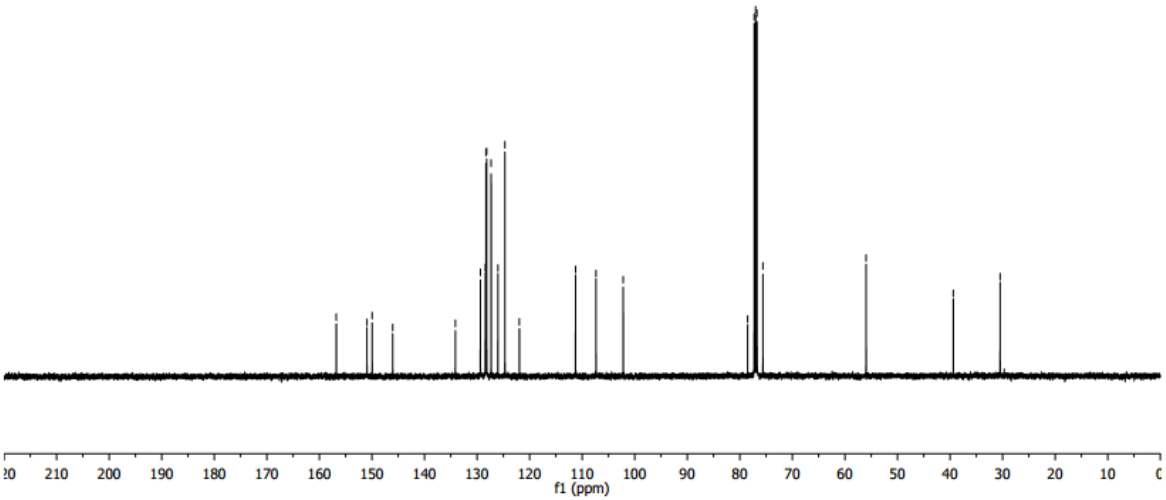
2h

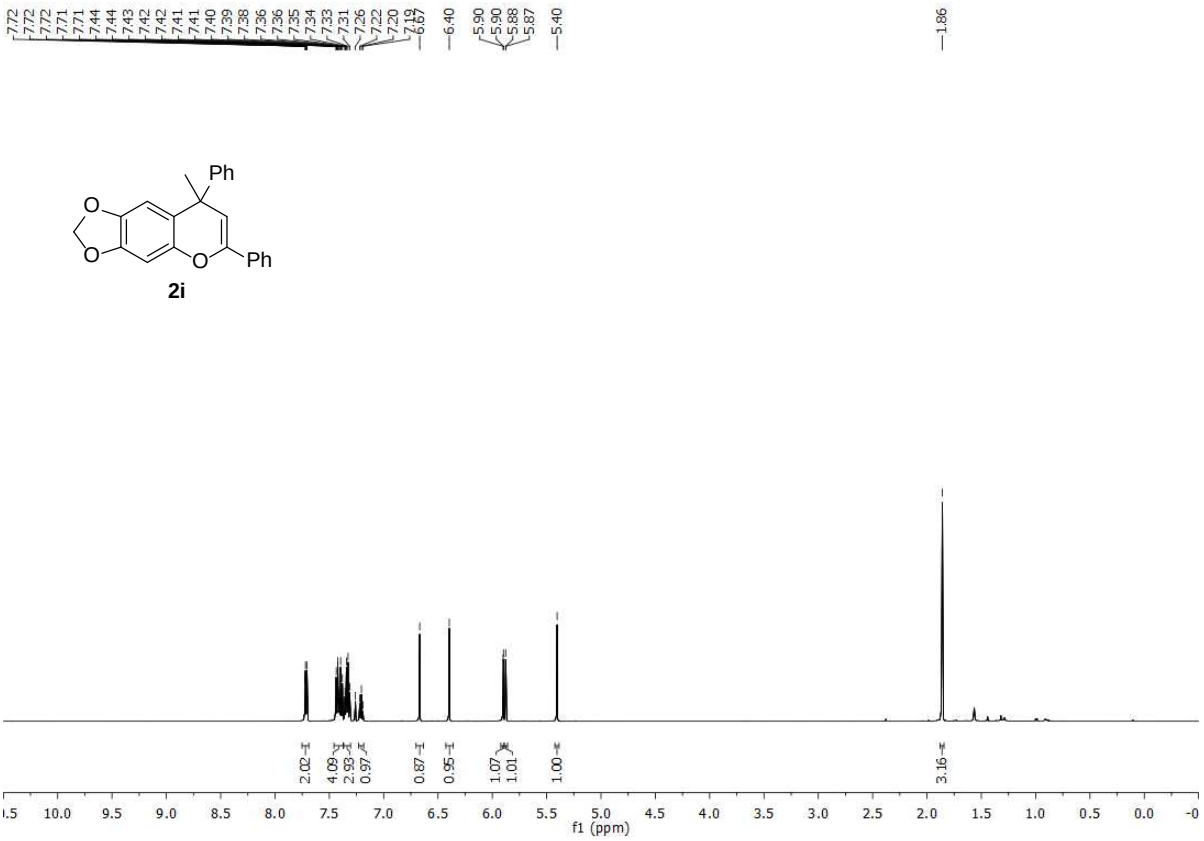

1.90
3.79
2.80
0.91
0.96
0.88
0.92
0.95
2.00
0.80
3.05
f1 (ppm)

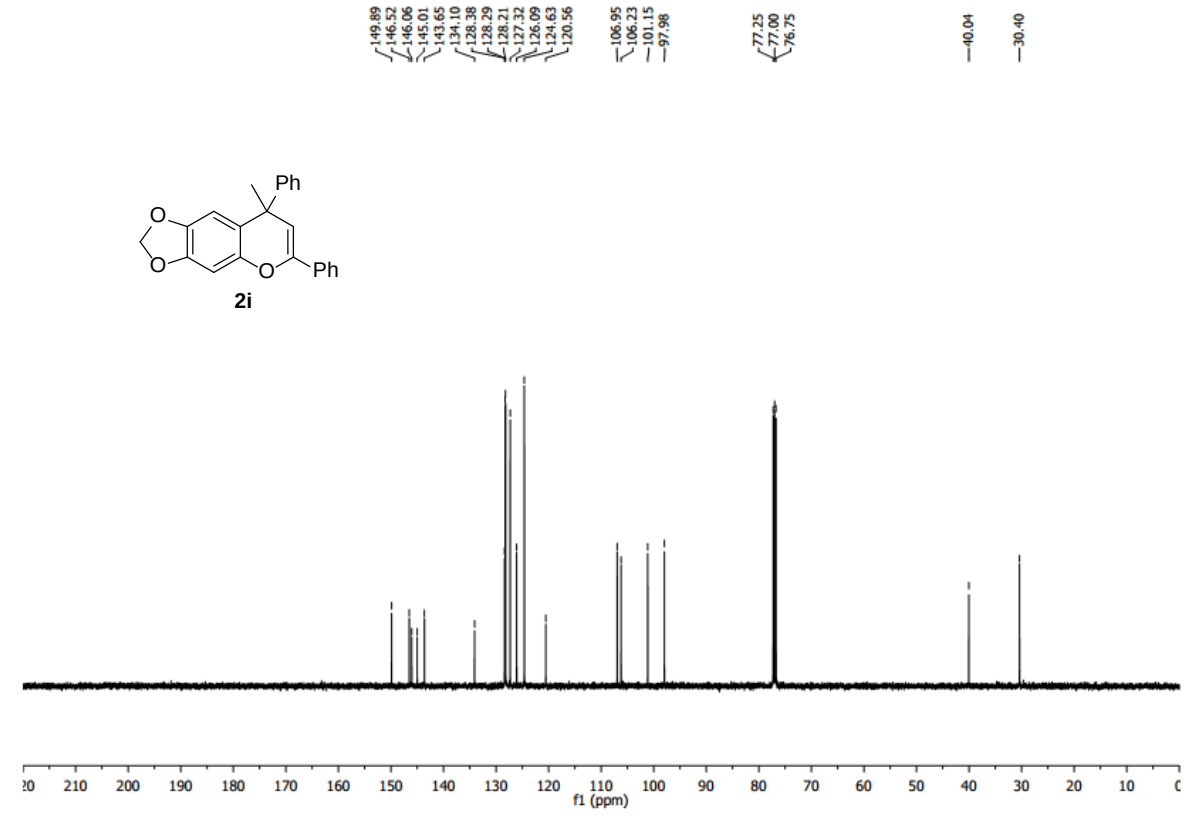

156.79
150.95
149.98
146.06
134.14
129.37
128.43
128.32
128.19
127.33
126.03
124.71
121.95
111.27
107.37
102.19
78.53
77.25
77.00
76.75
75.61
55.98
39.38
30.48


Ph
O
O
Ph

2h


f1 (ppm)


7.72
7.72
7.72
7.71
7.71
7.44
7.44
7.43
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.36
7.36
7.35
7.34
7.33
7.31
7.26
7.22
7.20
7.19
6.87
6.40
5.90
5.90
5.88
5.87
5.40
1.86
Ph
O
O
O
Ph
2i
2.02
4.09
2.93
0.97
0.87
0.95
1.07
1.01
1.00
3.16
f1 (ppm)


149.89
146.52
146.06
145.01
143.65
134.10
128.38
128.29
128.21
127.32
126.09
124.63
120.56
106.95
106.23
101.15
97.98
77.25
77.00
76.75
40.04
30.40
Ph
O
O
O
Ph
2i
f1 (ppm)