Supporting Information

for

DDQ-MEDIATED TANDEM SYNTHESIS OF FUNCTIONALIZED PYRANOCOUMARINS FROM 4-HYDROXYCOUMARINS AND 1,3-DIARYLALLYLIC COMPOUNDS

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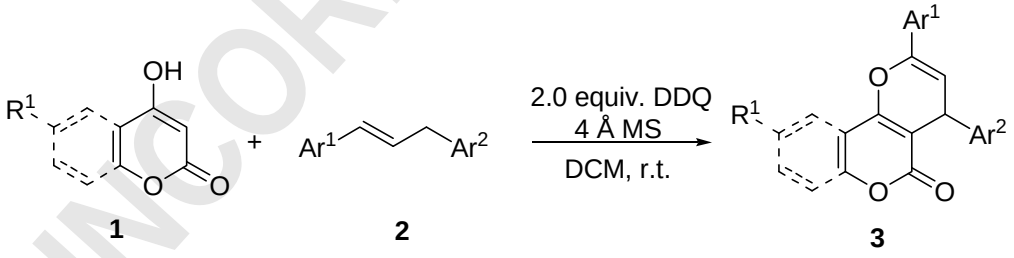
Contents

General Considerations

Column chromatography was carried out on silica gel (300-400 mesh) with mixed solvents (petroleum-ethyl acetate). CH_2Cl_2 was distilled from CaH_2. Infrared spectra was obtained on a FTIR spectrometer. NMR spectra was recorded for ^1H NMR at 400 MHz, for ^{13}C NMR at 100 MHz at 293 K unless otherwise noted. Chemical shifts are reported relative to residue peaks of the solvents either $CDCl_3$ (7.26 ppm for ^1H and 77.27 ppm for ^{13}C) or DMSO-d_6 (2.50 ppm for ^1H and 40.00 ppm for ^{13}C). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant, *J* (Hz) and integration. Low-resolution MS and HRMS were obtained using ESI ionization.

1b and **1c** were prepared according to the literature.[1] The diarylallylic compounds were prepared according to the literature.[2] **4a** was prepared according to the literature.[3] Other reagents were commercial available.

General Procedure for the Synthesis of 3

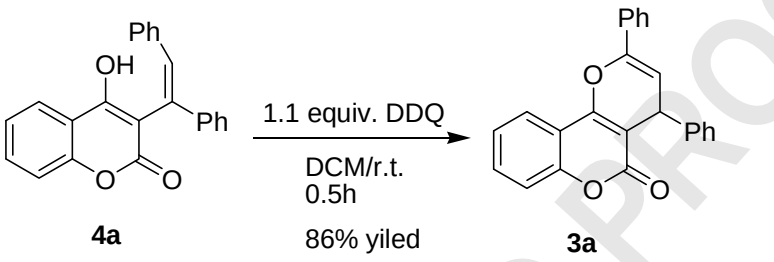


1 **2** **3**

A 10 mL round-bottom flask was charged with 4-hydroxycoumarin **1** (0.3 mmol), 1,3-diphenyl-1-propene **2** (0.25 mmol) and 4 Å MS (0.25 g) in CH_2Cl_2 (3 mL). Then DDQ (0.5 mmol) was added in portions during 15 min. The reaction mixture was stirred for the corresponding time, and then filtered through a Celite plug. The

filtrate was concentrated in vacuum, and the residue was purified by column chromatography with petroleum and ethyl acetate (10:1) as the eluent to give the corresponding product **3**.

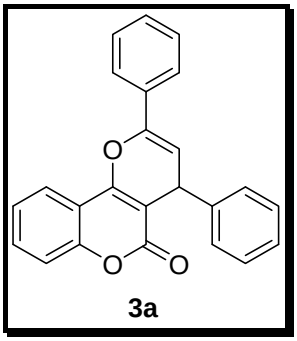
Procedure for the Synthesis of 3a from 4a



4a **3a**

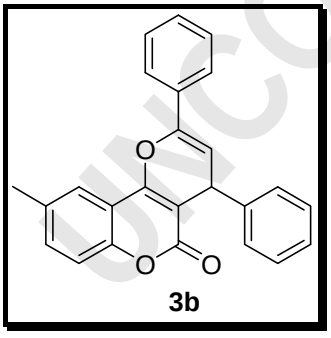
4a (0.5 mmol) was dissolved in CH_2Cl_2 (3 mL) in a 10 mL round-bottom flask and DDQ (0.6 mmol) was added in portions during 15mins. The mixture was stirred for additional 30 mins, and then filtered through a Celite plug. The filtrate was concentrated in vacuum, and the residue was purified by column chromatography with petroleum and ethyl acetate (10:1) as the eluent to give **3a**.

Characterization Data of 3



3a

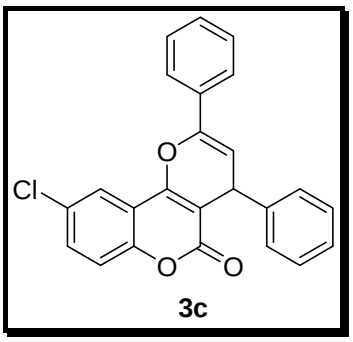
3a[4], white solid; m.p. 168-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1 H), 7.73 (d, J = 7.2 Hz, 2 H), 7.56 (m, 1 H), 7.47~7.30 (m, 9 H), 7.23 (m, 1 H), 5.84 (d, J = 4.8 Hz, 1 H), 4.70 (d, J = 4.8 Hz, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.42, 155.69, 152.69, 146.82, 143.49, 132.56, 131.96, 129.21, 128.63, 128.59, 128.43, 127.19, 124.61, 124.12, 122.63, 116.78, 114.50, 103.69, 103.62, 36.57 ppm; IR (KBr) ν 3026, 2918, 1720, 1632, 1610, 1492, 1387, 1270, 1169, 1012, 765, 692 cm^{-1}; MS (ESI) m/z 374.8 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{24}H_{16}O_3$ ($[M+Na]^+$), 375.0992; found, 375.0986.



3b

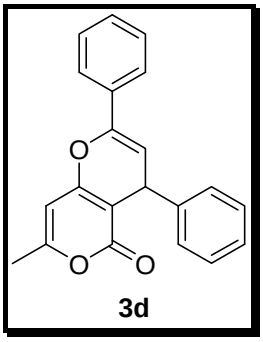
A white solid; m.p. 212-213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1 H), 7.60 (d, J = 6.4 Hz, 2 H), 7.48~7.36 (m, 9 H), 7.23 (d, J = 8.4 Hz, 1 H), 6.15 (d, J = 3.6 Hz 1 H), 5.77 (d, J = 4.4 Hz, 1 H), 2.43 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ

161.36, 158.85, 151.79, 138.29, 137.94, 135.32, 133.68, 133.66, 129.23, 128.88, 127.87, 127.79, 127.52, 127.38, 122.82, 120.11, 116.36, 114.80, 102.69, 78.77, 20.86 ppm; IR (KBr) *v* 3055, 3025, 1717, 1625, 1550, 1493, 1397, 1363, 1280, 1111, 1001, 765, 755, 702, 533 cm^{-1}; MS (ESI) m/z 389.02 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{25}H_{18}O_3$ ($[M+Na]^+$), 389.1148; found, 389.1141.



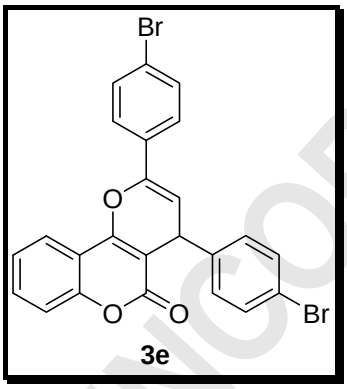
3c

A light yellow solid; m.p. 177-178 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.0 Hz 1 H), 7.60 (d, *J* = 6.8 Hz, 2 H), 7.53~7.46 (m, 4 H), 7.42~7.36 (m, 5 H), 7.29 (m, 1 H), 6.20 (d, *J* = 4.4 Hz, 1 H), 5.82 (d, *J* =4.4 Hz, 1 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.06, 158.12, 151.89, 137.83, 137.58, 134.93, 132.52, 129.50, 129.47, 129.00, 127.97, 127.94, 127.59, 127.40, 122.70, 120.74, 118.07, 116.07, 116.33, 79.05 ppm; IR (KBr) *v* 3059, 2925, 1721, 1625, 1544, 1480, 1391, 1156, 1114, 993, 760, 699 cm^{-1}; MS (ESI) m/z 409.2 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{24}H_{15}ClO_3$ ($[M+Na]^+$), 409.0602; found, 409.0594.



3d

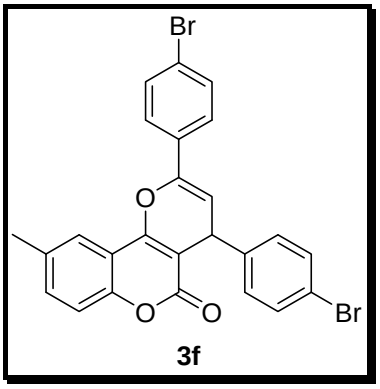
A yellow oil; ^{1}H NMR (400 MHz, CD_3SOCD_3) δ 7.45 (d, *J* = 8.0 Hz 2 H), 7.30~7.34 (m, 3 H), 7.25~7.18 (m, 5 H), 6.19 (s, 1 H), 6.10 (d, *J* = 4.4 Hz, 1 H), 5.67 (d, *J* = 4.4 Hz, 1 H), 2.14 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.64, 164.86, 159.51, 138.86, 138.08, 133.75, 129.36, 129.19, 127.96, 127.75, 127.71, 120.11, 100.16, 99.35, 77.72, 20.01 ppm; IR (film) *v* 3061, 2925, 1723, 1644, 1542, 1493, 1446, 1409, 1206, 1121, 998, 155, 699 cm^{-1}; MS (ESI) m/z 338.9 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{21}H_{16}O_3$ ($[M+Na]^+$), 339.0992; found, 339.0996



3e

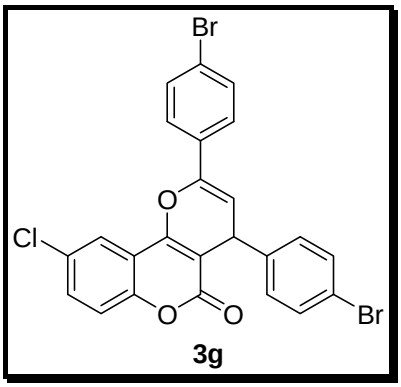
A white solid; m.p.158-159 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8 Hz, 1 H), 7.59~7.56 (m, 3 H), 7.50 (d, *J* = 7.6 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 8.4 Hz, 1 H), 7.28 (d, *J* = 7.6 Hz, 1 H), 7.21 (d, *J* = 7.6 Hz, 2 H), 6.11 (d, *J* = 4.0 Hz, 1 H), 5.73 (d, *J* = 4.0 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.33, 158.53, 153.56, 136.86, 136.58, 134.66, 132.98, 132.16, 131.10, 129.12, 129.06, 124.13,

123.60, 123.23, 122.07, 119.79, 116.71, 114.90, 102.34, 77.88 ppm; IR (KBr) *v* 3053, 1724, 1632, 1608, 1553, 1488, 1404, 1385, 1329, 1265, 1211, 1072, 1023, 999. 812, 756 cm^{-1}; MS (ESI) m/z 530.2 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{24}H_{14}Br_2O_3$ ($[M+Na]^+$), 530.9202; found, 530.9205.



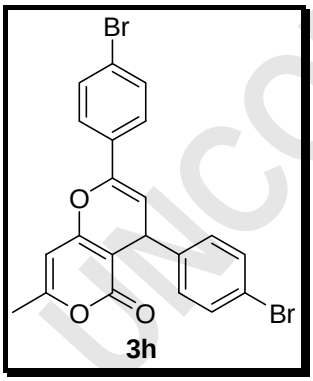
3f

A light yellow solid; m.p. 187-188 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.36 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1 H), 7.21~7.18 (m, 3 H), 6.07 (d, *J* = 4.4 Hz, 1 H), 5.69 (d, *J* = 4.4 Hz, 1 H), 2.40 (s, 3 H), ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.38, 158.72, 151.78, 136.96, 136.67, 134.76, 134.09, 133.92, 132.16, 131.06, 129.16, 129.05, 123.57, 122.76, 122.02, 119.68, 116.48, 114.52, 102.24, 77.91, 20.90 ppm; IR (KBr) *v* 3064, 2922, 1724, 1630, 1556, 1489, 1402, 1200, 1118, 1072, 1010, 814, 532 cm^{-1}; MS (ESI) m/z 544.8 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{25}H_{16}Br_2O_3$ ($[M+Na]^+$), 544.9358; found, 544.9345



3g

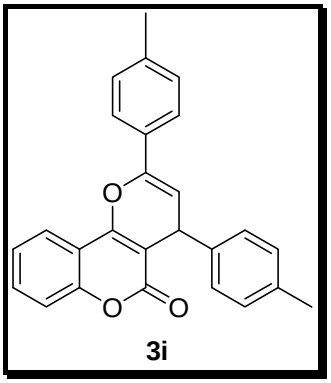
A light yellow solid; m.p. 185-186 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.4 Hz, 1 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 7.50 (m, 3 H), 7.41 (d, *J* = 8.4 Hz, 2 H), 7.27 (s, 1 H), 7.17 (d, *J* = 8.4 Hz, 2 H), 6.11 (d, *J* = 3.6 Hz, 1 H), 5.73 (d, *J* = 4.4 Hz, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.06, 157.96, 151.87, 136.48, 136.30, 134.37, 132.88, 132.27, 131.14, 129.72, 129.20, 129.04, 123.82, 122.63, 122.20, 120.32, 118.18, 116.03, 102.88, 77.18 ppm; IR (KBr) *v* 3064, 2922, 1724, 1630, 1556, 1489, 1402, 1267, 1200, 1117, 1072, 1009, 814, 772 cm^{-1}; MS (ESI) m/z 565.2 ($[M+Na]^+$); HRMS (ESI) calcd for $C_{24}H_{13}Br_2ClO_3$ ([M+Na]+), 564.9032.; found, 564.9065.



3h

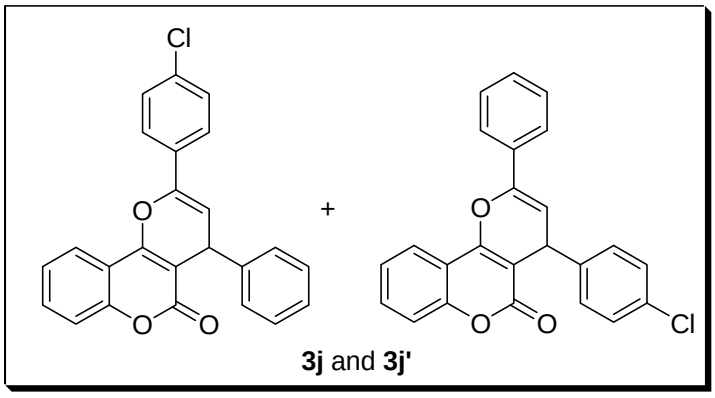
A white solid; m.p. 186-187 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 5.91 (m, 2 H), 5.55 (d, *J* = 4.4 Hz, 1 H), 2.25(s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ

166.40, 164.37, 159.96, 137.06, 136.39, 134.13, 132.07, 130.96, 129.21, 129.11, 123.47, 121.97, 118.55, 100.00, 99.34, 77.70, 20.29 ppm; IR (KBr) *v* 3097, 2924, 1718, 1641, 1541, 1487, 1406, 1205, 1007, 997, 827, 540cm^{-1}; MS (ESI) m/z 494.9 ([M+Na]$^{+}$); HRMS (ESI) calcd for $C_{21}H_{14}Br_2O_3$ ([M+Na]$^{+}$), 494.9202; found, 494.9199.



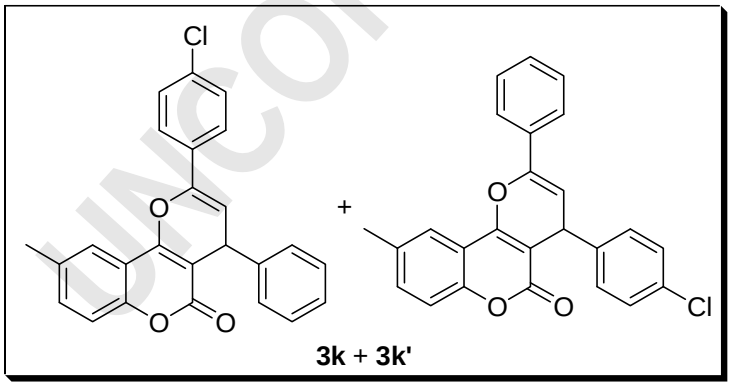
3i

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.0 Hz, 1 H), 7.65 (t, *J* = 8.0 Hz, 1 H), 7.46 (d, *J* = 7.6 Hz, 2 H), 7.36 (m, 2 H), 7.22 (m,4 H), 7.13 (d, *J* = 7.6 Hz, 2 H), 6.31 (d, *J* = 5.2 Hz, 1 H), 5.88 (d, *J* = 4.8 Hz, 1 H), 2.31 (s, 3 H), 2.28 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.94, 158.03, 153.29, 138.99, 137.08, 135.54, 135.37, 134.09, 133.48, 129.75. 128.65, 127.68, 124.81, 123.35, 121.11, 116.72, 115.14, 102.99, 77.81, 21.19, 21.16 ppm; IR (film) *v* 3028, 2924, 1731, 1614, 1573, 1493, 1398, 1327, 1266, 1177, 759 cm^{-1}; MS (ESI) m/z 403.1 ([M+Na]$^{+}$); HRMS (ESI) calcd for $C_{26}H_{20}O_3$ ([M+Na]$^{+}$), 403.1305; found, 403.1320.



3j and **3j'**

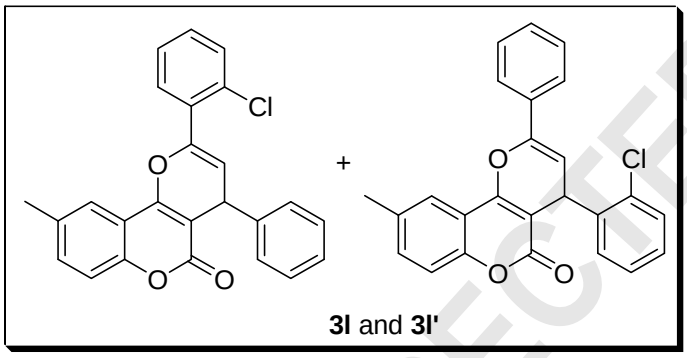
A white solid; m.p. 185-186 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (**3j**/**3j′** = 4:1) δ 7.86-7.81 (m, 1 H), 7.58-7.49 (m, 3 H), 7.44-7.24 (m, 9 H), 6.14 (d, *J* = 4.0 Hz, 0.8 H), 6.11 (d, *J* = 4.8 Hz, 0.2 H), 5.74-5.72 (m, 1 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.45, 158.61, 153.57, 137.99, 137.64, 136.34, 135.26, 134.16, 133.69, 132.74, 132.70, 129.32, 129.11, 128.93, 128.88, 128.77, 128.07, 127.94, 127.92, 127.38, 127.35, 123.98, 123.29, 123.15, 120.49, 119.51, 116.64, 116.61, 115.06, 102.31, 79.69, 77.85 ppm; IR (KBr) *v* 3034, 2870, 1719, 1624, 1492, 1106, 1022, 986, 759 cm^{-1}; MS (ESI) m/z 409.3 ([M+Na]$^{+}$); HRMS (ESI) calcd for $C_{24}H_{15}ClO_3$ ([M+Na]$^{+}$), 409.0602; found, 409.0598.



3k + **3k'**

A white solid; m.p. 172-173 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (**3k**/**3k′** = 7:3) δ 7.61-7.59 (m, 1 H), 7.55-7.49 (m, 2 H), 7.45-7.38 (m, 3 H), 7.35-7.30 (m, 4 H),

7.28-7.24 (m, 1 H), 7.20-7.18 (m,1 H), 6.11 (d, J = 4.4 Hz, 0.69 H), 6.08 (d, J = 4.4 Hz, 0.31 H), 5.72-5.70 (m,1 H), 2.39 (s, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.52, 161.14, 158.82, 158.70, 151.77, 138.09, 137.72, 136.65, 136.41, 135.75, 135.24, 134.27, 133.86, 133.82, 133.76, 133.74, 133.64, 129.31, 129.11, 128.93, 128.76, 128.05, 127.89, 127.43, 127.35, 122.84, 122.71, 120.38, 119.41, 116.41, 116.38, 114.67, 114.65, 102.23, 78.73, 20.83 ppm; IR (KBr) *v* 3066, 2924, 1721, 1632, 1560, 1492, 1400, 1120, 1007, 812, 727 cm^{-1}; MS (ESI) m/z 422.9 ([M+Na]$^+$); HRMS (ESI) calcd for $C_{25}H_{17}ClO_3$ ([M+Na]$^+$), 423.0758; found, 423.0751.



3l and **3l'**

A white solid; m.p. 198-199^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) (**3l**/**3l′** = 3:1) δ 7.65-7.63 (m, 2 H), 7.47-7.44 (m, 1 H), 7.36-7.29 (m, 8 H), 7.19 (d, J = 8.4 Hz, 1 H), 6.54 (d, J = 4.0 Hz, 1 H), 5.69 (d, J = 3.6 Hz, 1 H), 2.38 (s, 2.25 H), 2.36 (s, 0.75 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.42, 158.78, 151.78, 137.75, 135.67, 135.37, 133.80, 133.77, 133.57, 133.51, 133.11, 132.93, 130.29, 130.14, 129.87, 129.29, 128.94, 128.86, 127.87, 127.35, 127.24, 122.92, 122.79, 119.06, 116.36, 114.48, 102.54, 102.43, 75.39, 20.89, 20.83 ppm; IR (KBr) *v* 3057, 2926, 1723, 1627, 1556, 1493, 1397, 1285, 1202, 1114, 1009, 760, 698 cm^{-1}; MS (ESI) m/z 422.8 ([M+Na]$^+$); HRMS (ESI) calcd for $C_{25}H_{17}ClO_3$ ([M+Na]$^+$), 423.0753; found, 423.0751.

References:

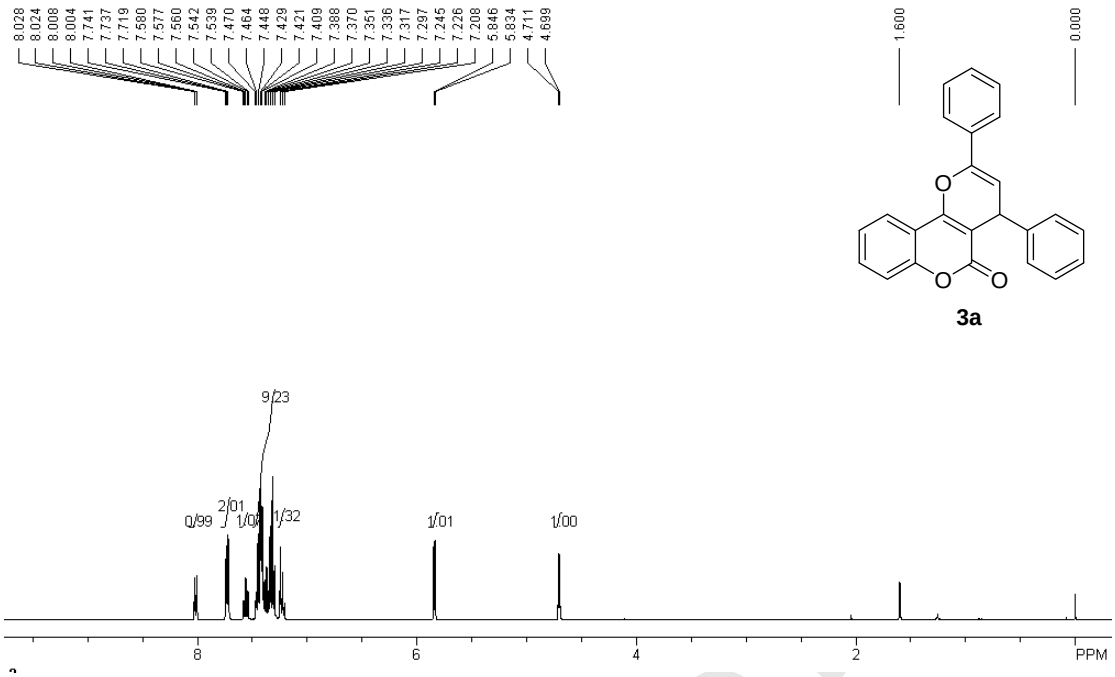
(1) Gong, D.-H.; Zhang, L.; Li, F.; Yuan, J.-Y.; Yuan, C.-Y. *Chinese Journal of Chemistry*. **2004**, *22*, 925.

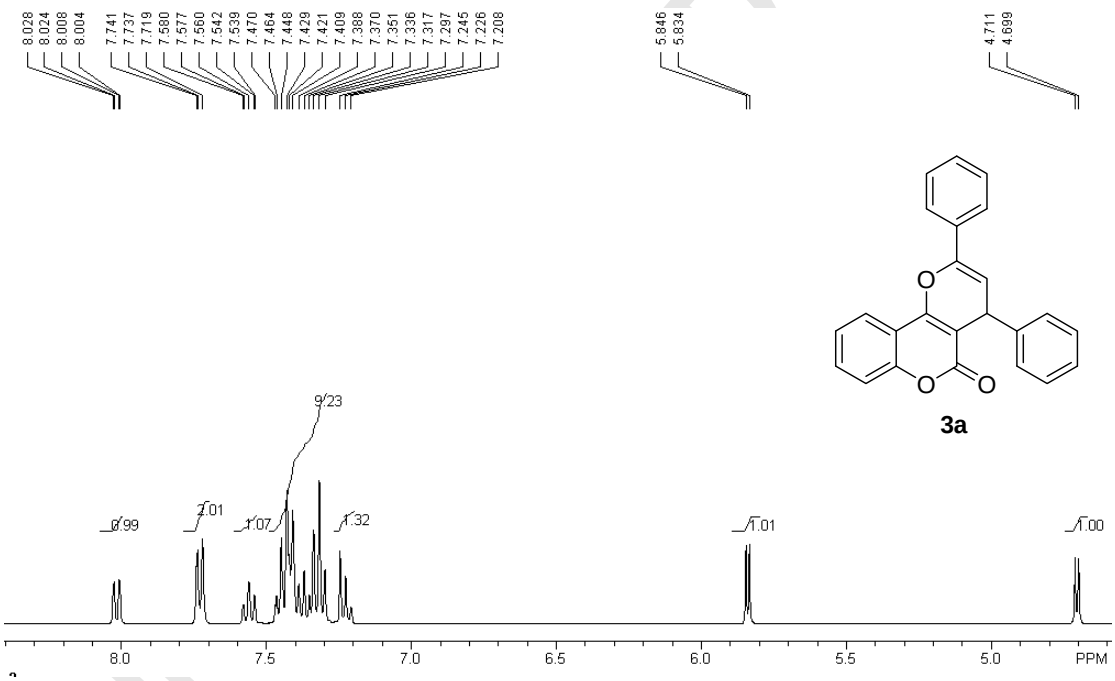
(2) Wang, J.-L.; Huang, W.; Zhang, Z.-X.; Xiang, X.; Liu, R.-T.; Zhou, X.-G. *The Journal of Organic Chemistry* **2009**, *74*, 3299.

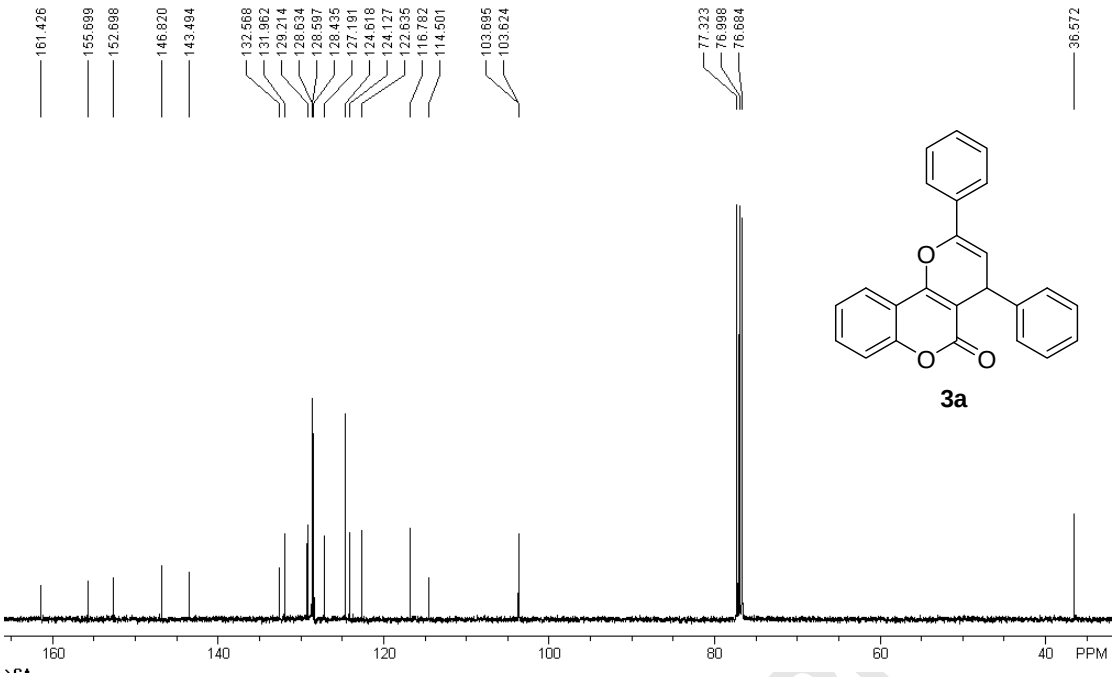
(3) Reddy, C. R.; Srikanth, B.; Narsimha R. N.; Shin, D. S. *Tetrahedron* **2008**, 64, 11666.

(4) Reisch, J. *Archiv der Pharmazie und Berichte der Deutschen Pharmazeutischen Gesellschaft* **1966**, *299*, 806.

Copies of ^{1}H and ^{13}CNMR Spectra of **3**



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120
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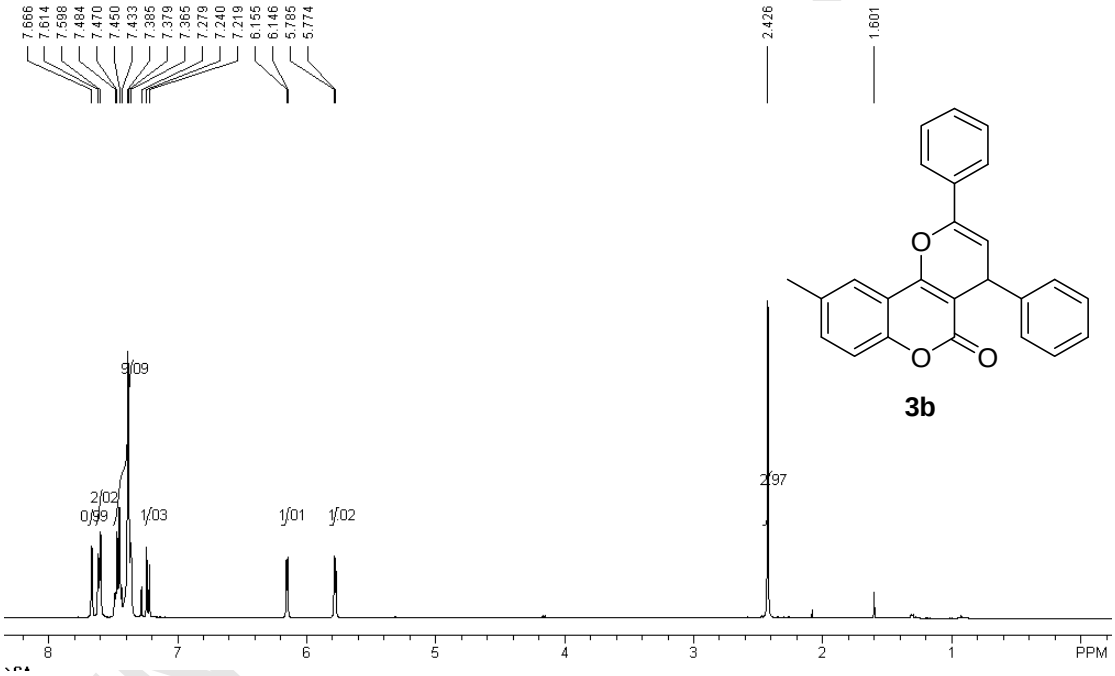
PPM

3a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6.146
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5.774
2.426
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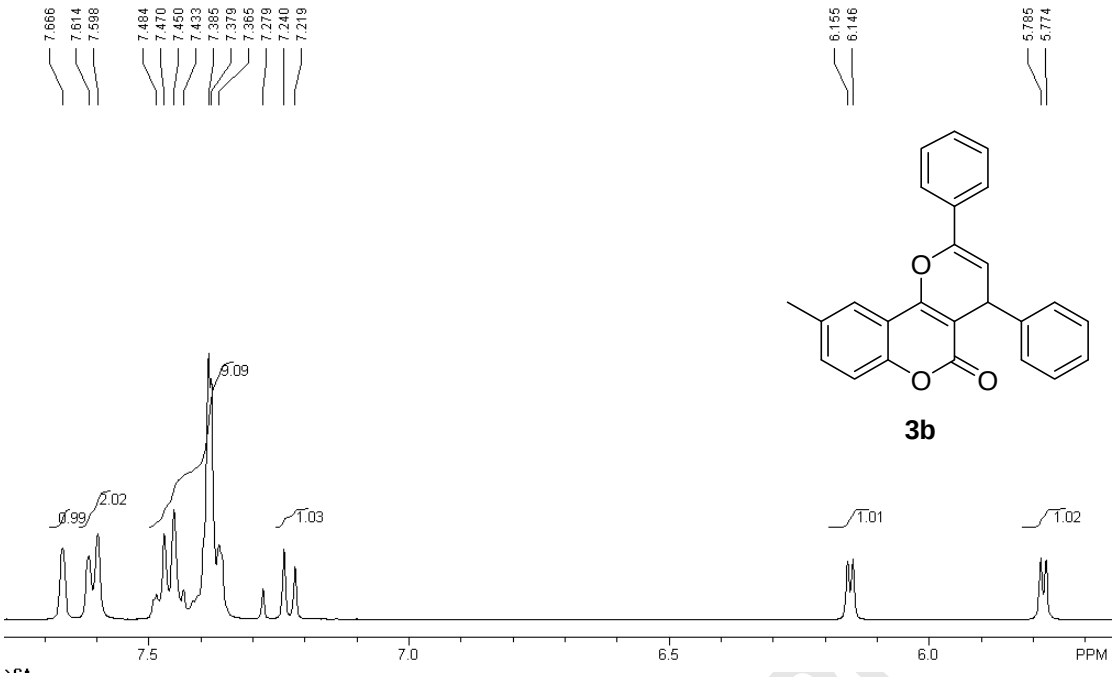
O
O
9.09
2.02
0.99
1.03
1.01
1.02
2.97
8
7
6
5
4
3
2
1
PPM

3b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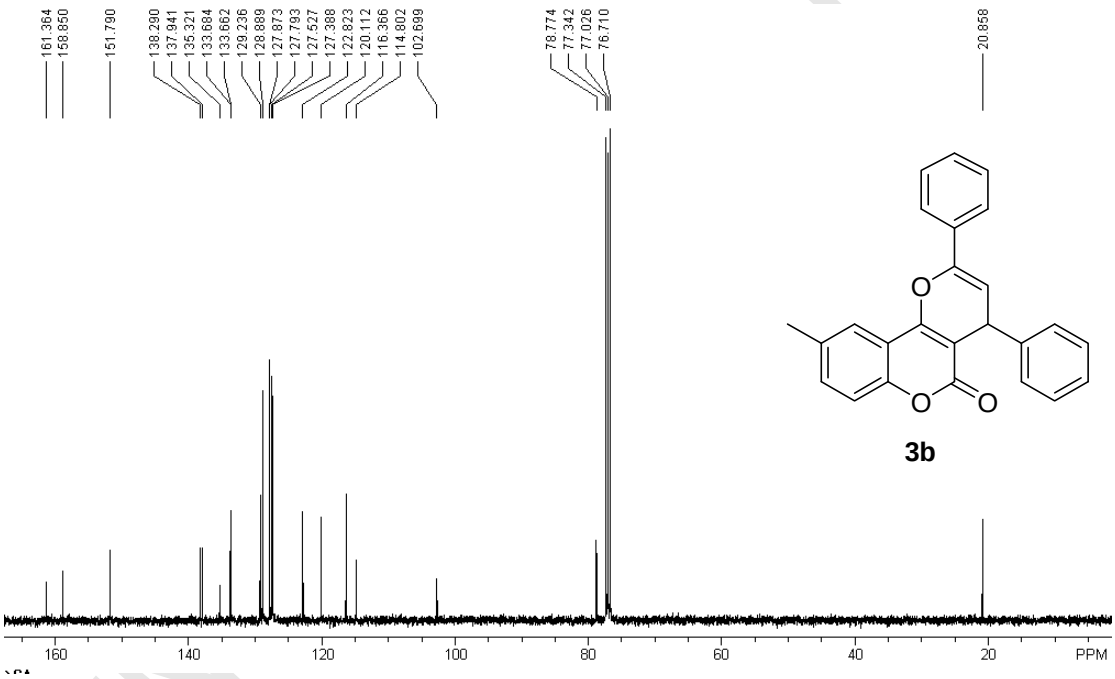
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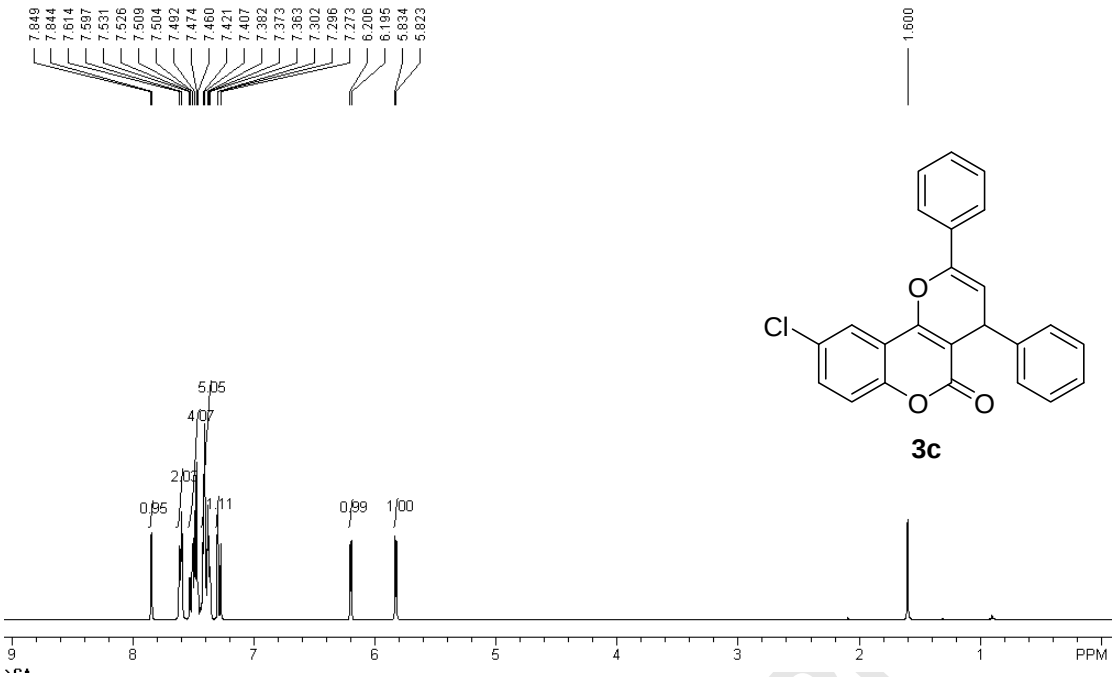
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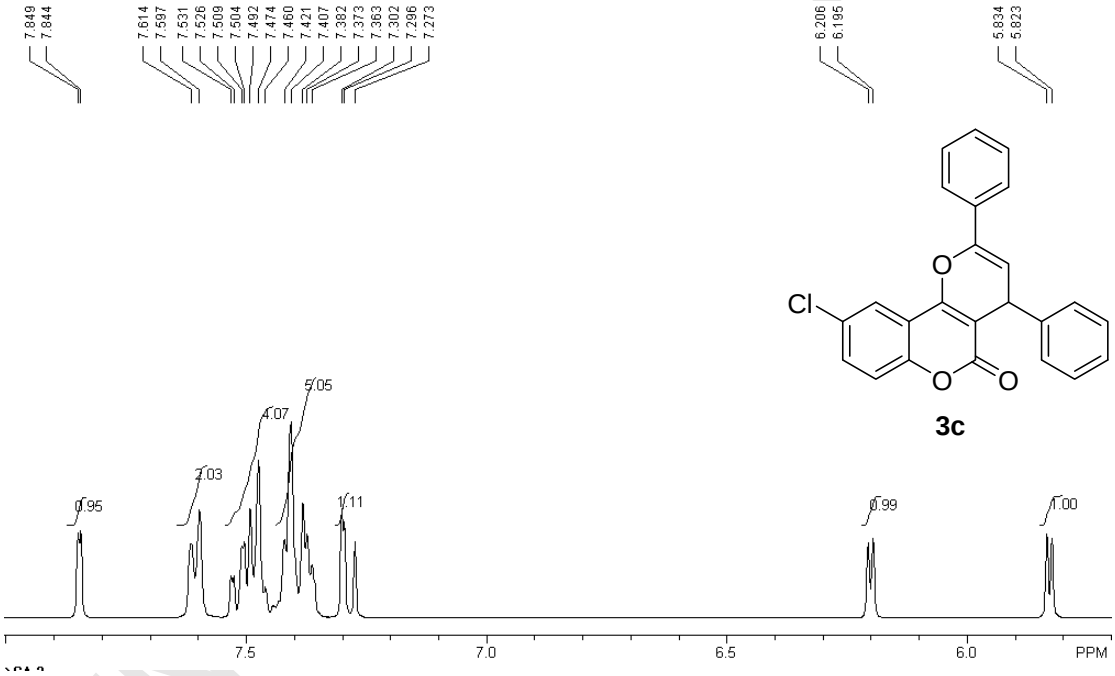
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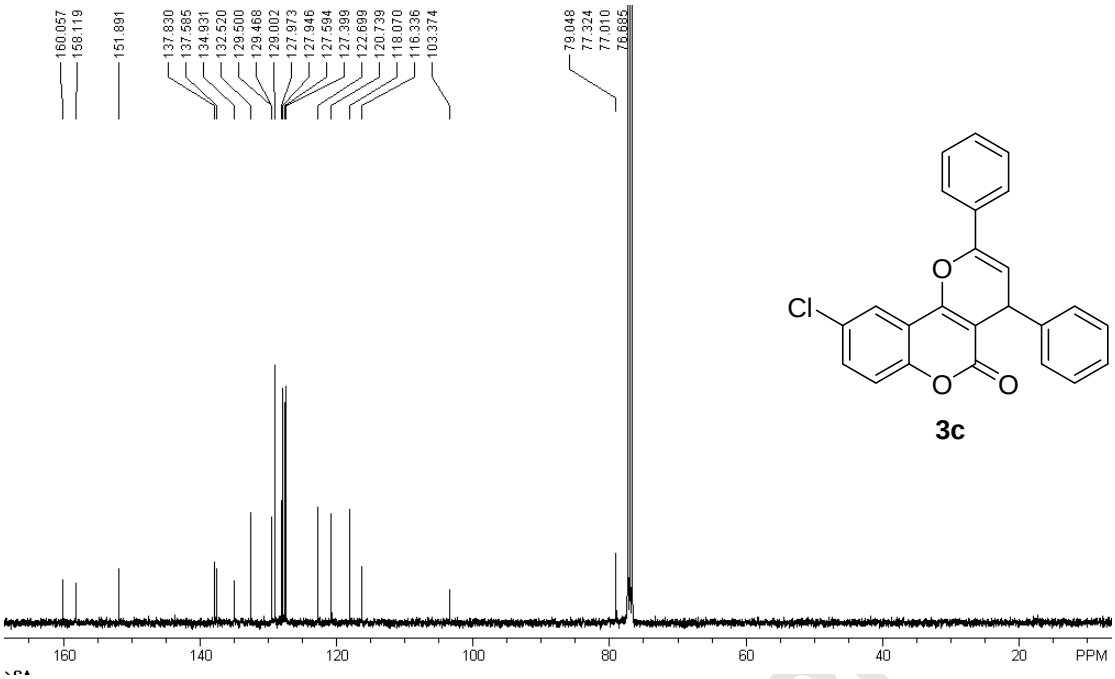
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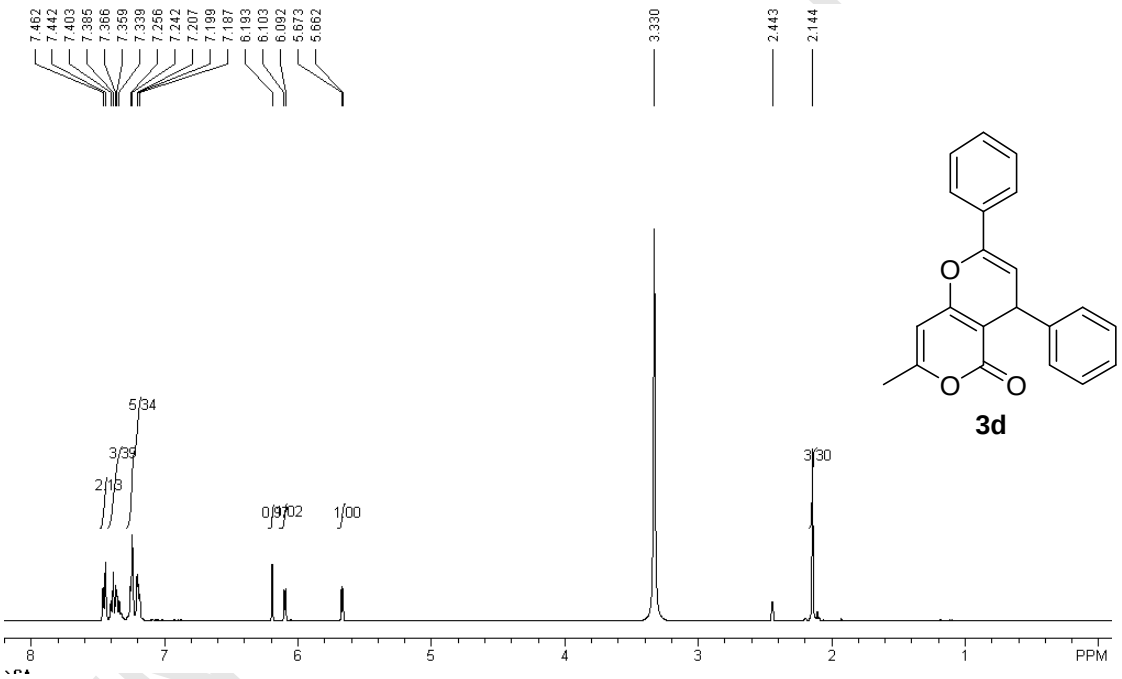
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3.330
2.443
2.144
5.34
3.39
2.13
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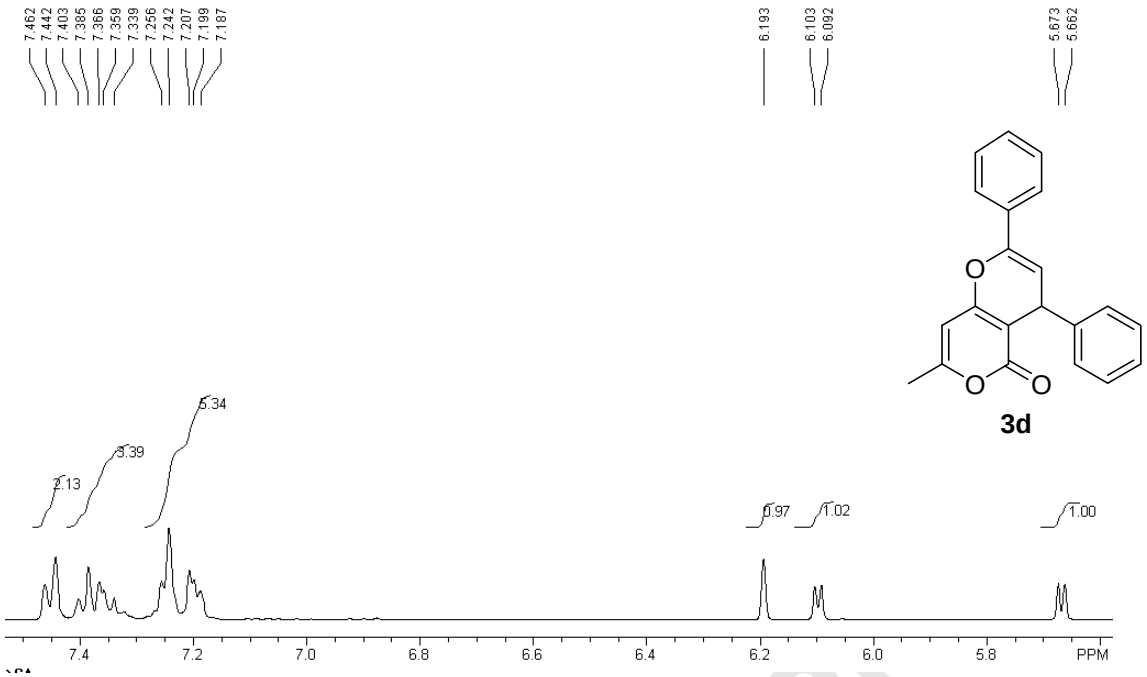
3d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O
O
O
3d
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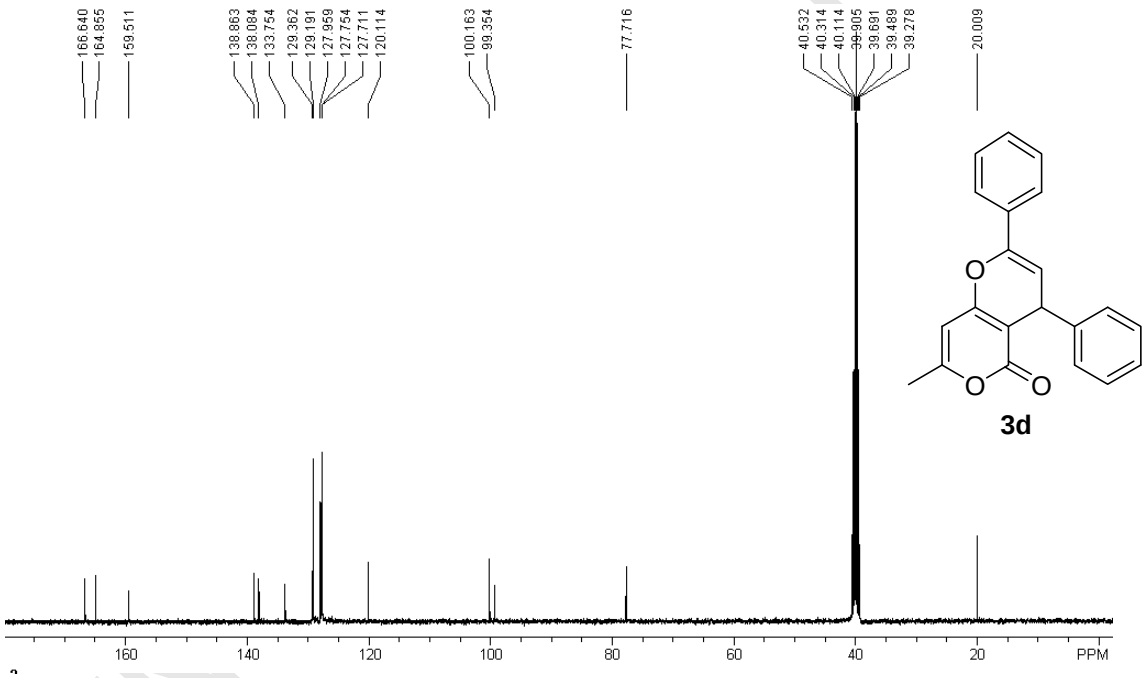
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O
3d
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120
100
80
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40
20
PPM


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7.580
7.560
7.510
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7.295
7.276
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7.202
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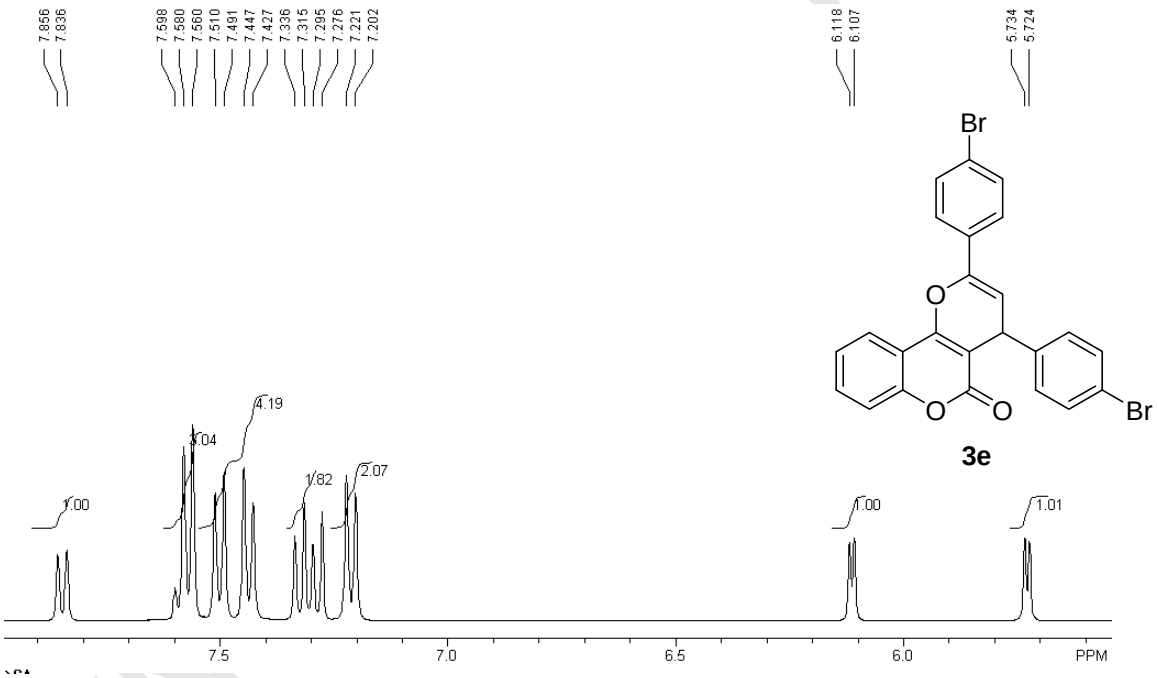
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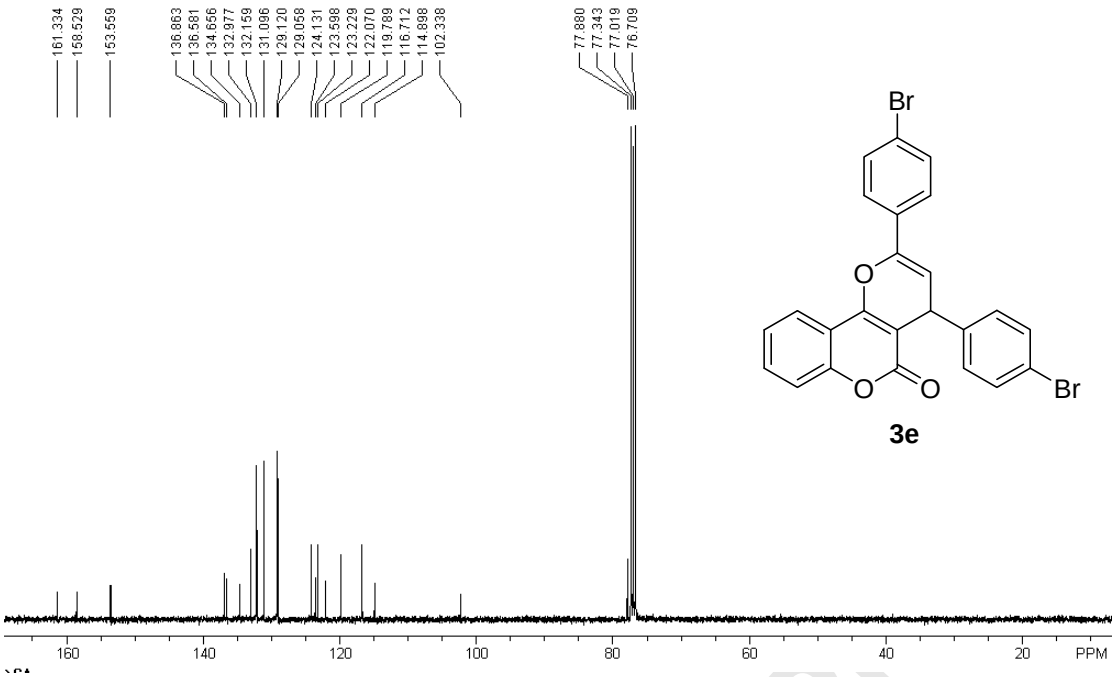
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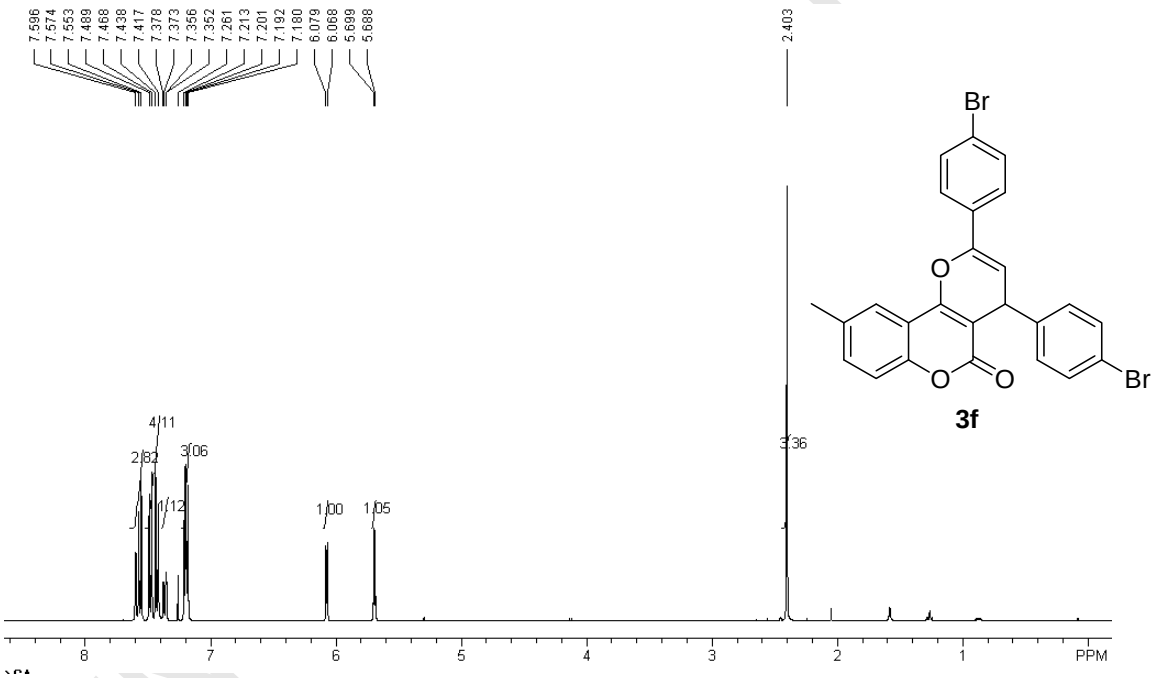
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7.192
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5.688
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Br
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O
O
Br
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1.05
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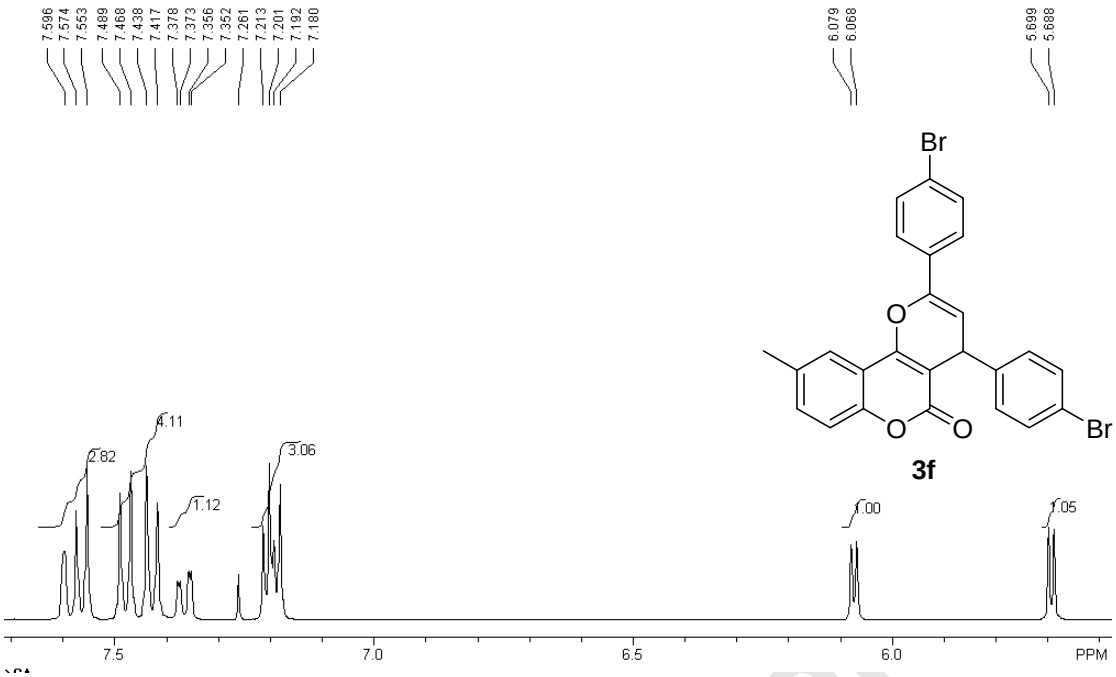
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7.192
7.180
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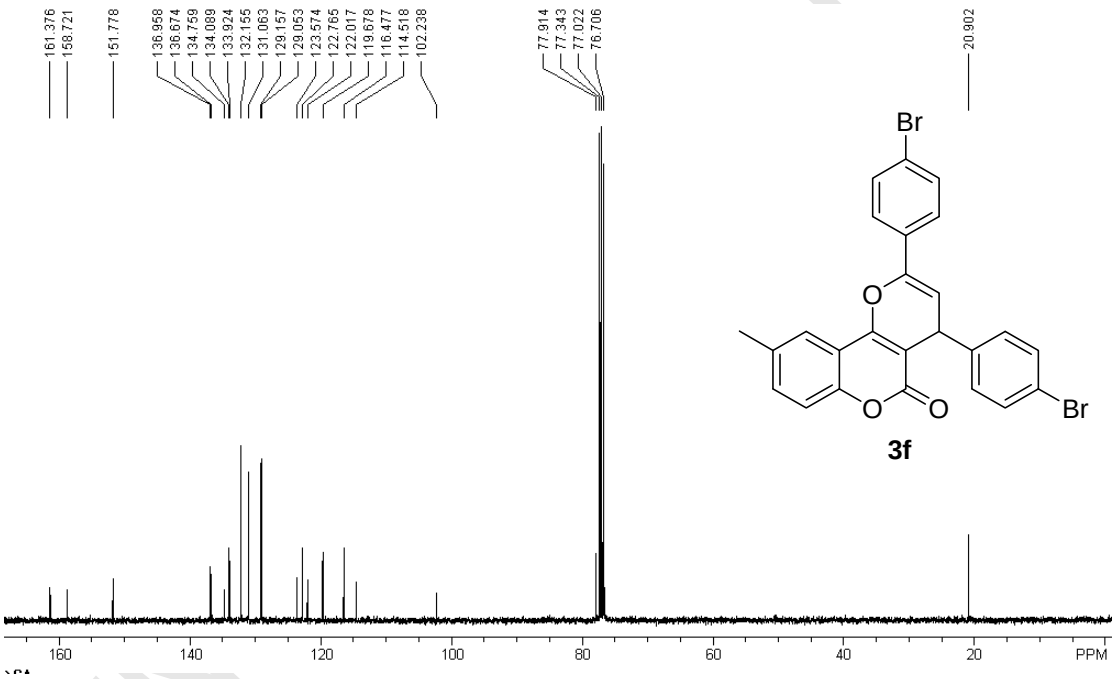
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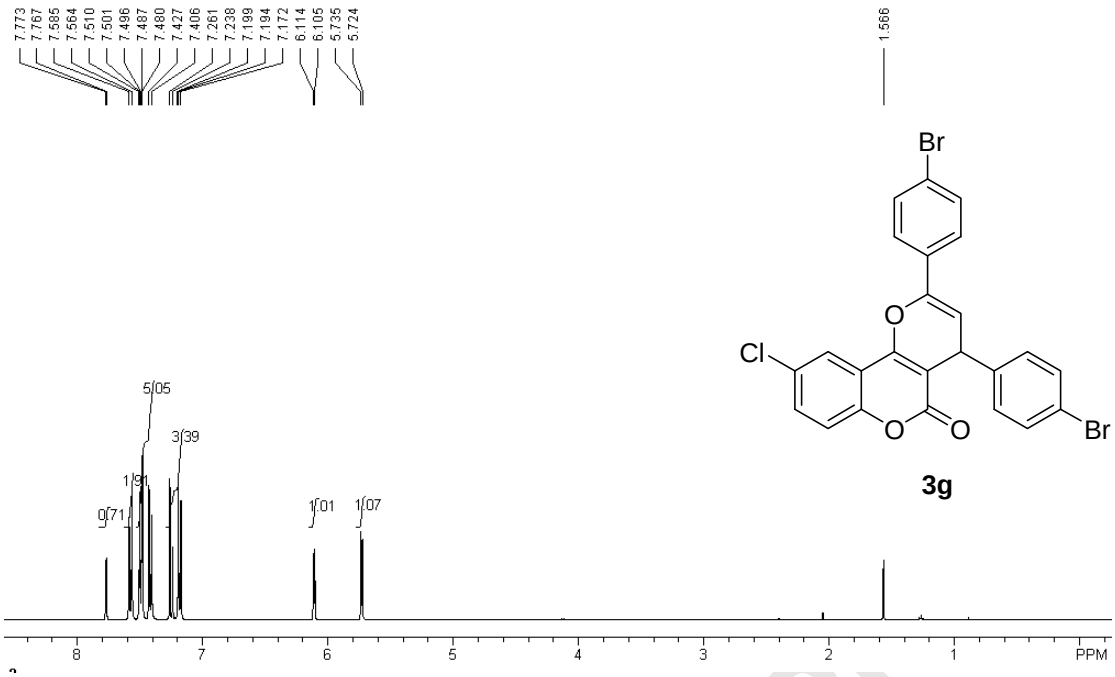
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7.172
6.114
6.105
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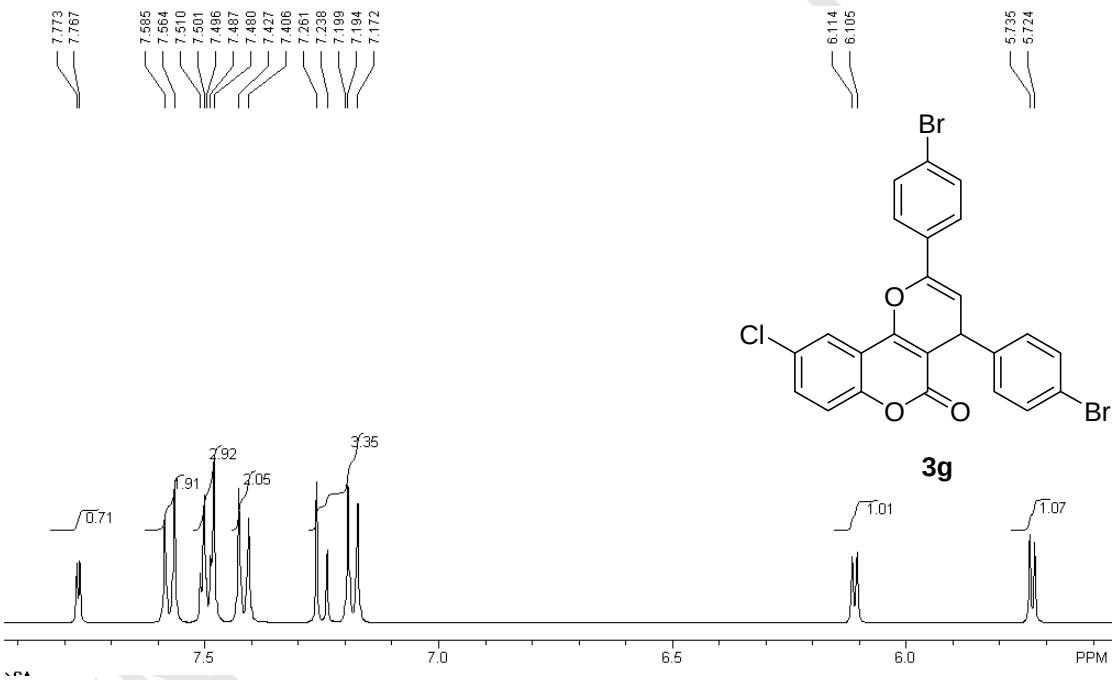
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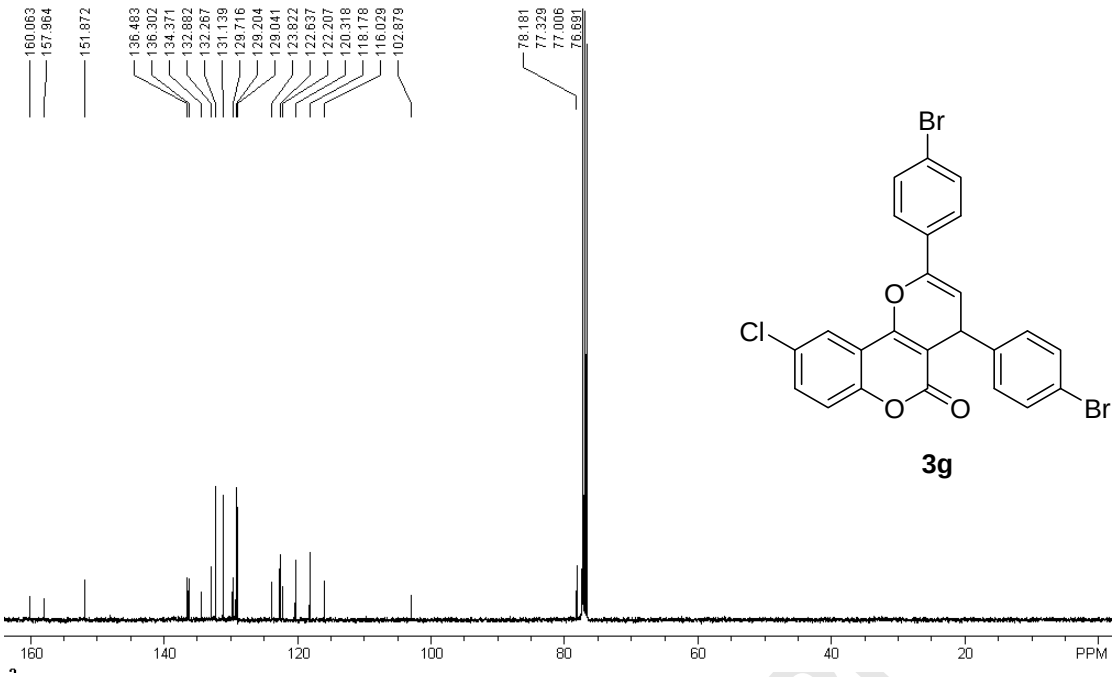
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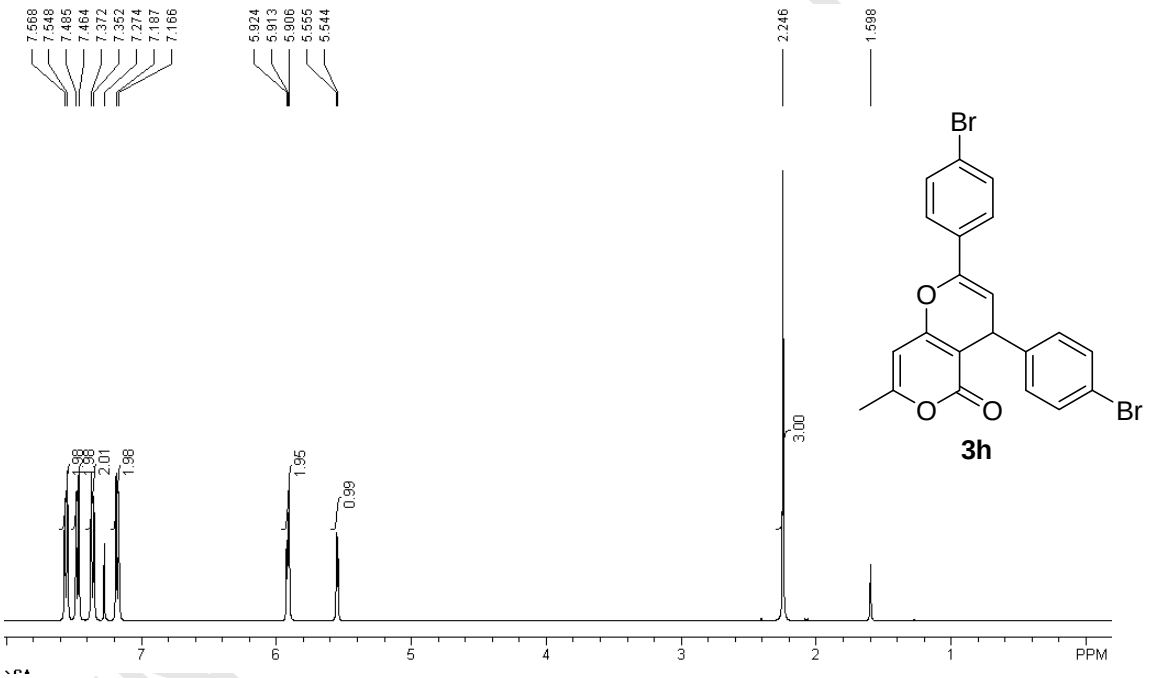
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5.544
2.246
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O
O
Br
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1.98
2.01
1.98
1.95
0.99
7
6
5
4
3
2
1
PPM

3h


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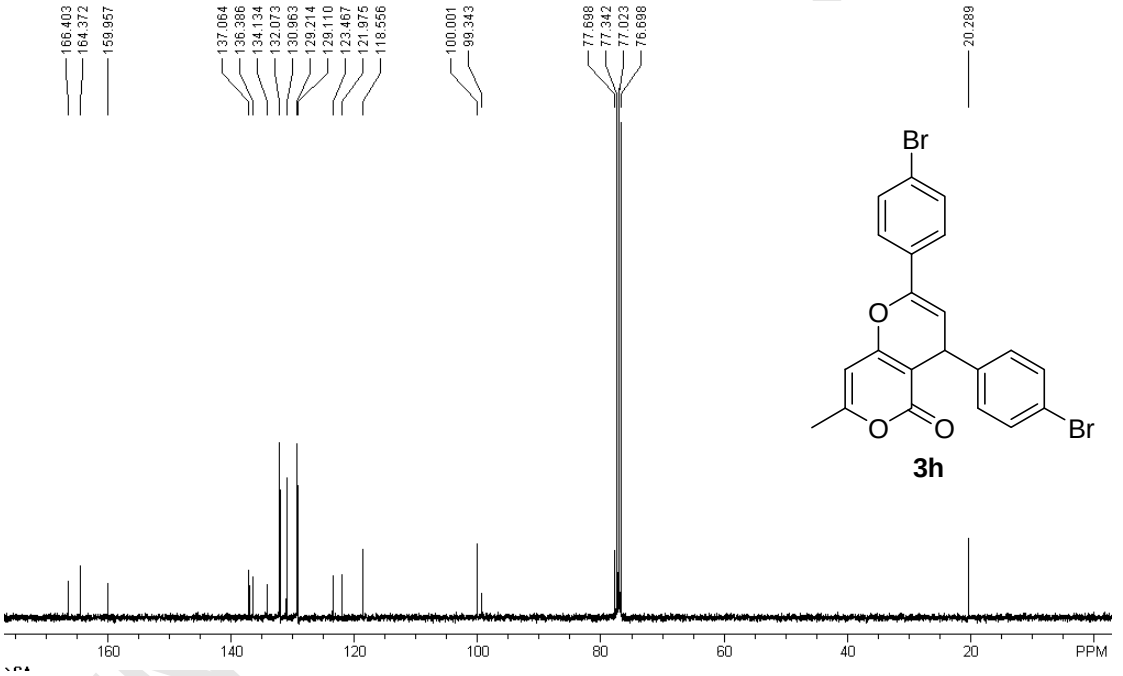
3h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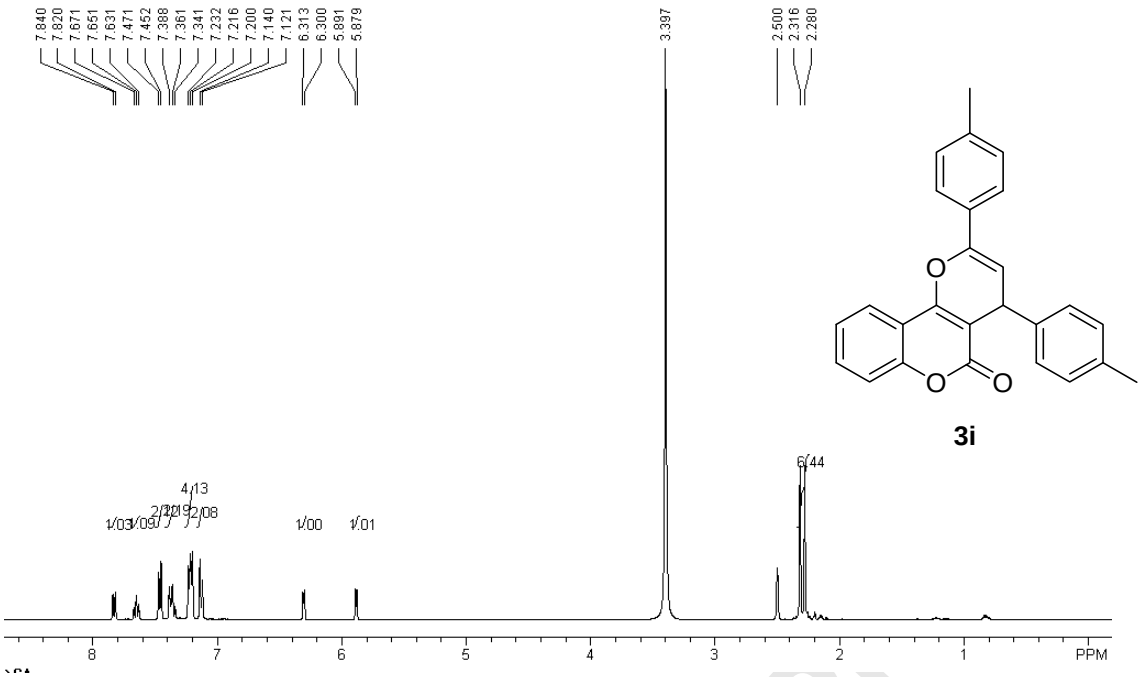
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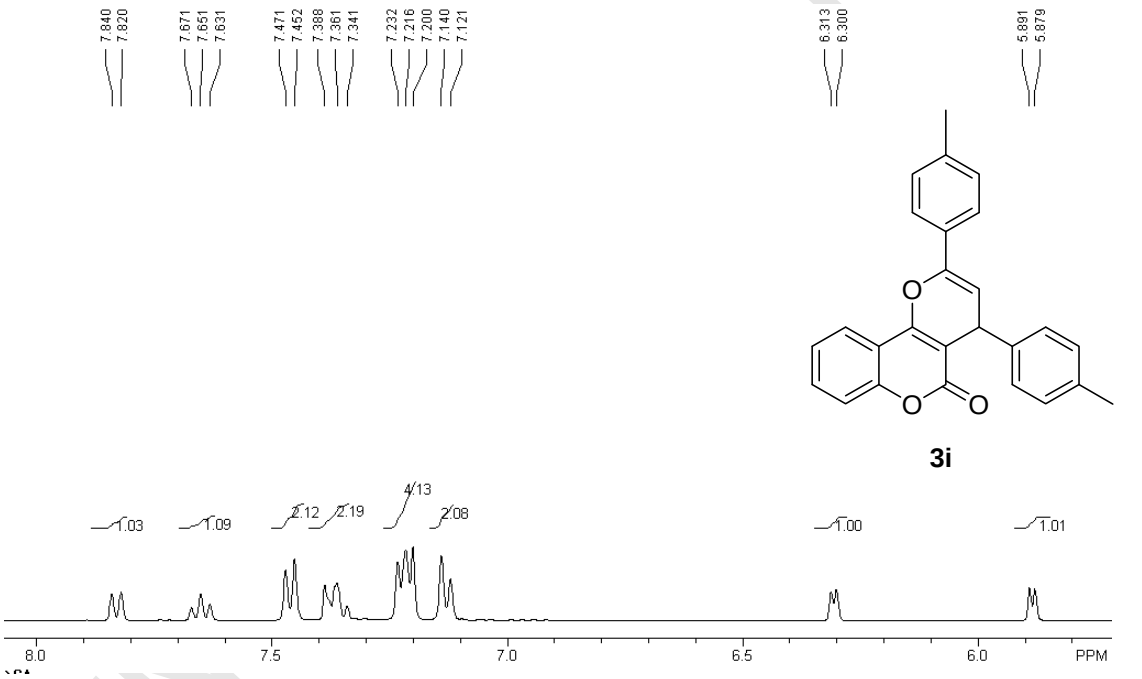
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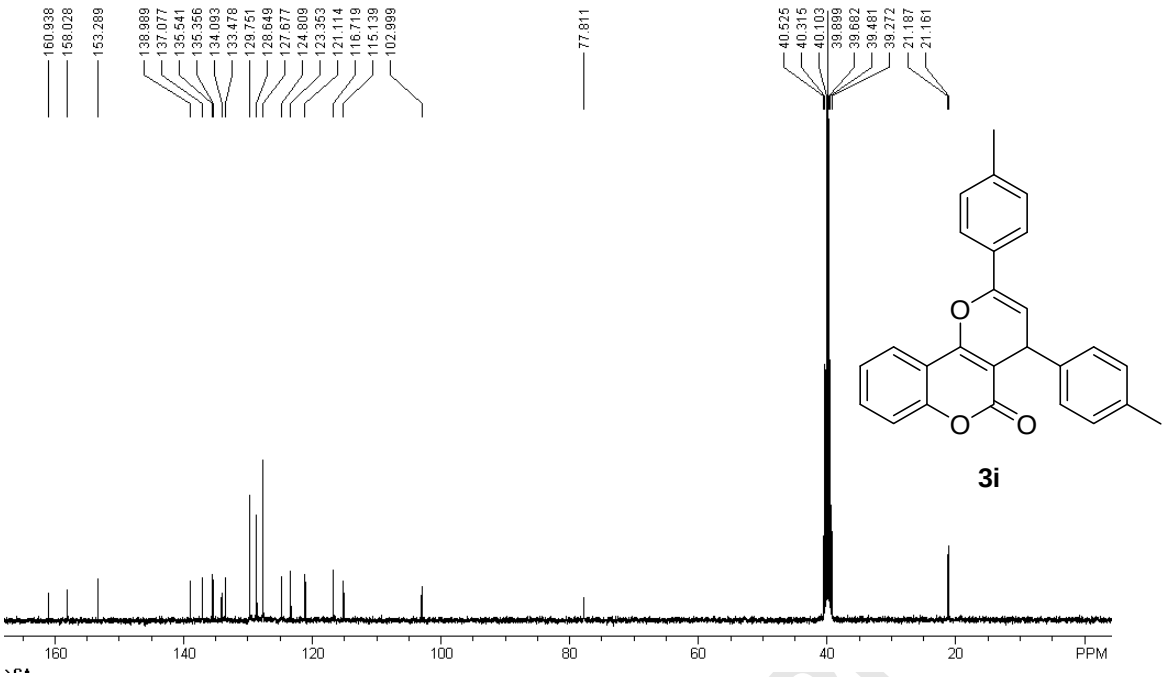
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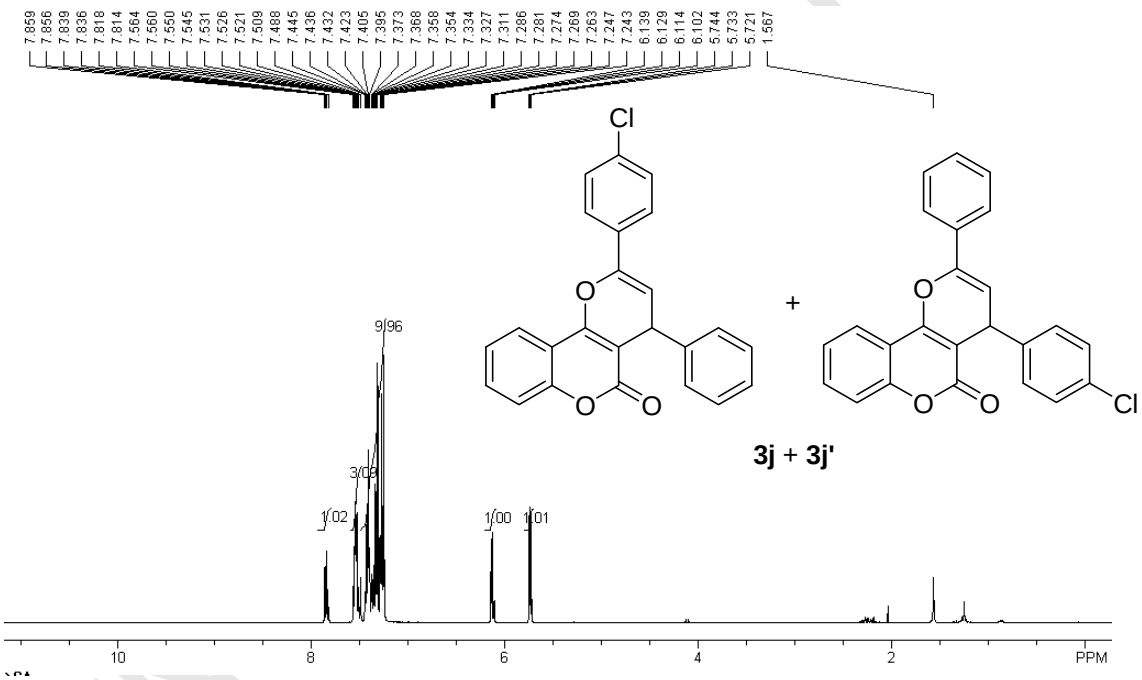
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6.129
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1.567
Cl
O
O
O
+
O
O
O
Cl
3j + 3j'
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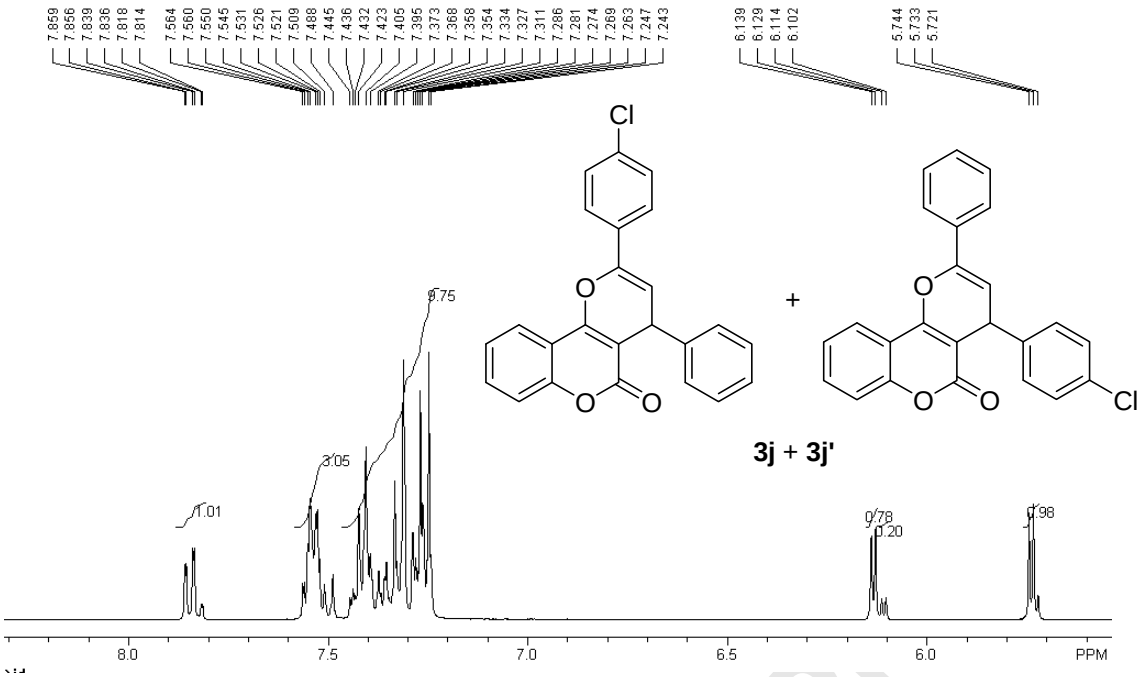
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O
+
O
O
O
Cl
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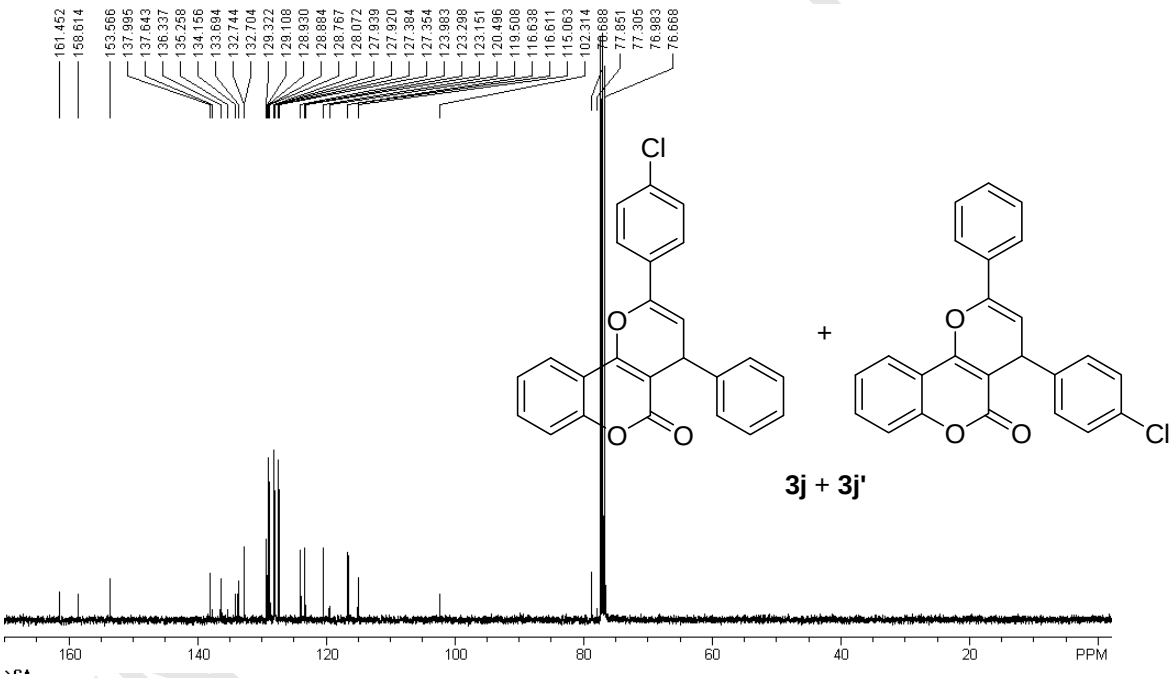
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115.063
102.314
76.688
77.851
77.305
76.983
76.668
Cl
O
O
O
+
O
O
O
Cl
3j + 3j'
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140
120
100
80
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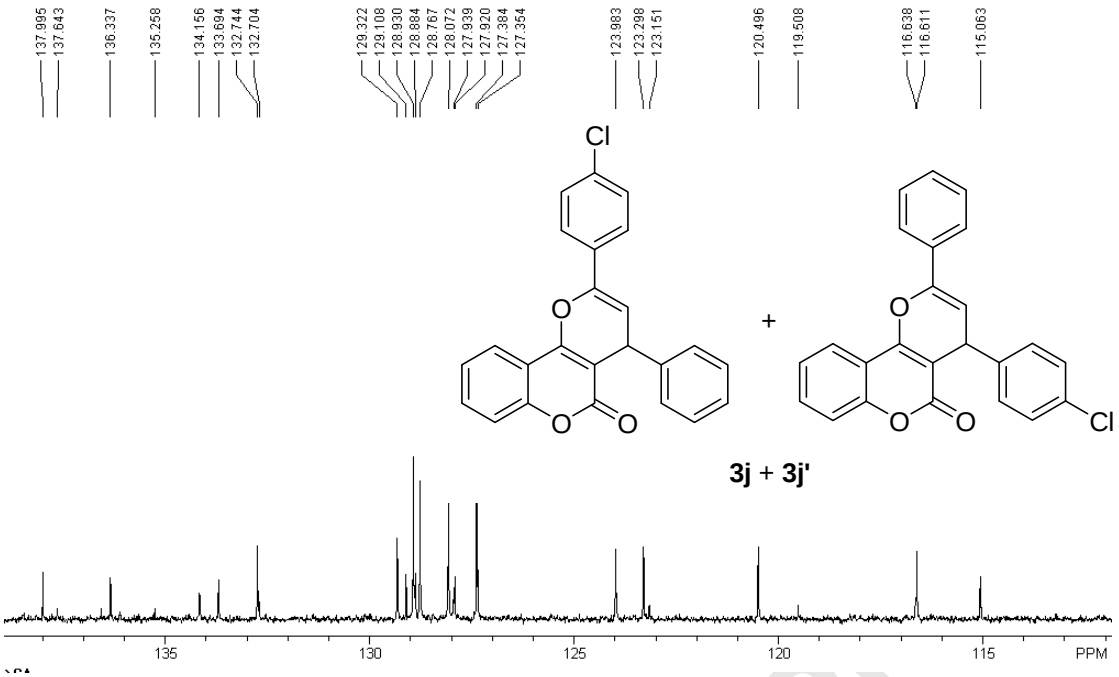
20
PPM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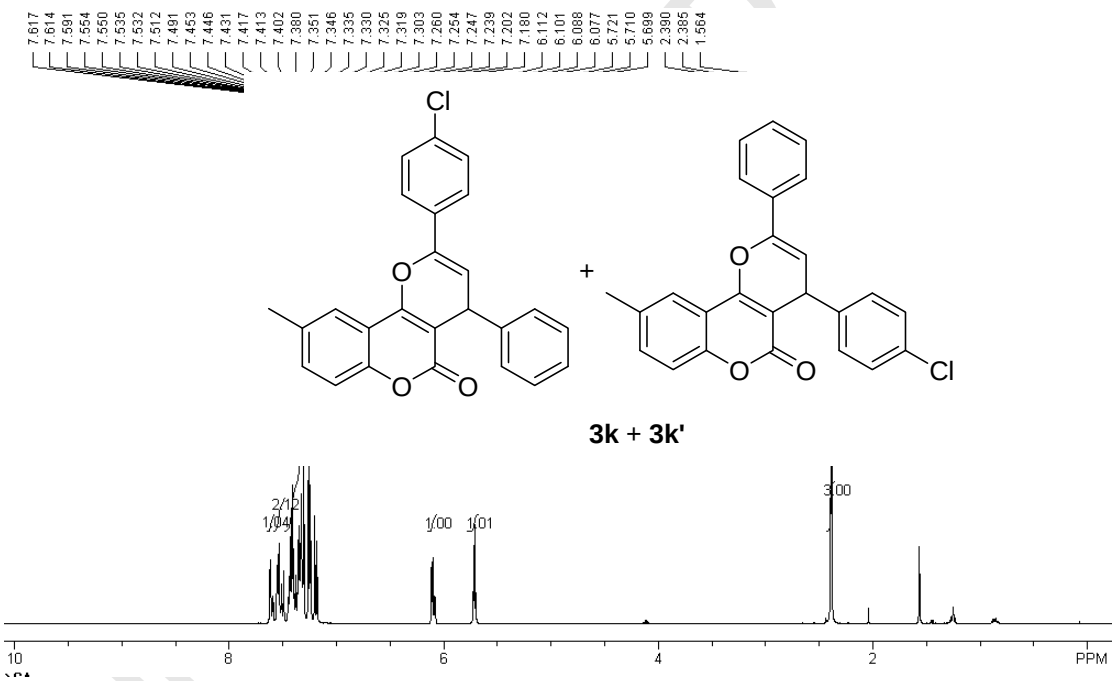
132.744
132.704
129.322
129.108
128.930
128.884
128.767
128.072
127.939
127.920
127.384
127.354
123.983
123.298
123.151
120.496
119.508
116.638
116.611
115.063
Cl
O
O
O
+
O
O
O
Cl
135
130
125
120
115
PPM

3j + **3j'**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7.550
7.535
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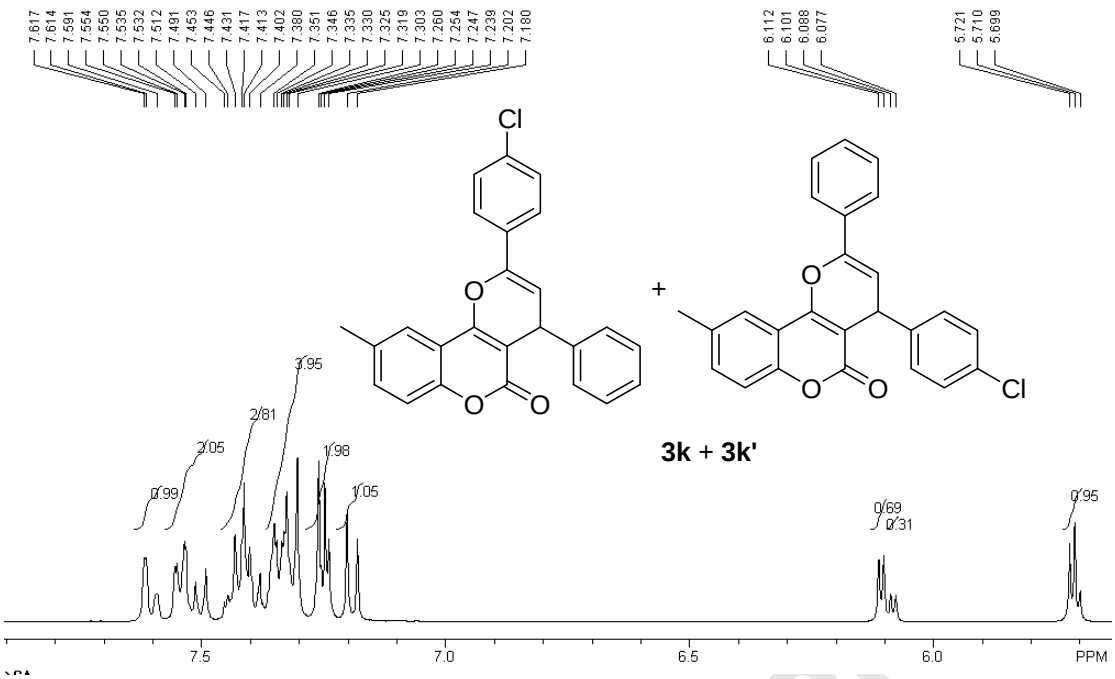
7.512
7.491
7.453
7.446
7.431
7.417
7.413
7.402
7.380
7.351
7.346
7.335
7.330
7.325
7.319
7.303
7.260
7.254
7.247
7.239
7.202
7.180
6.112
6.101
6.088
6.077
5.721
5.710
5.699
2.390
2.385
1.564
Cl
O
O
O
+
O
O
O
Cl
2.12
1.04
1.00
1.01
3.00
10
8
6
4
2
PPM

3k + **3k'**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7.417
7.413
7.402
7.380
7.351
7.346
7.335
7.330
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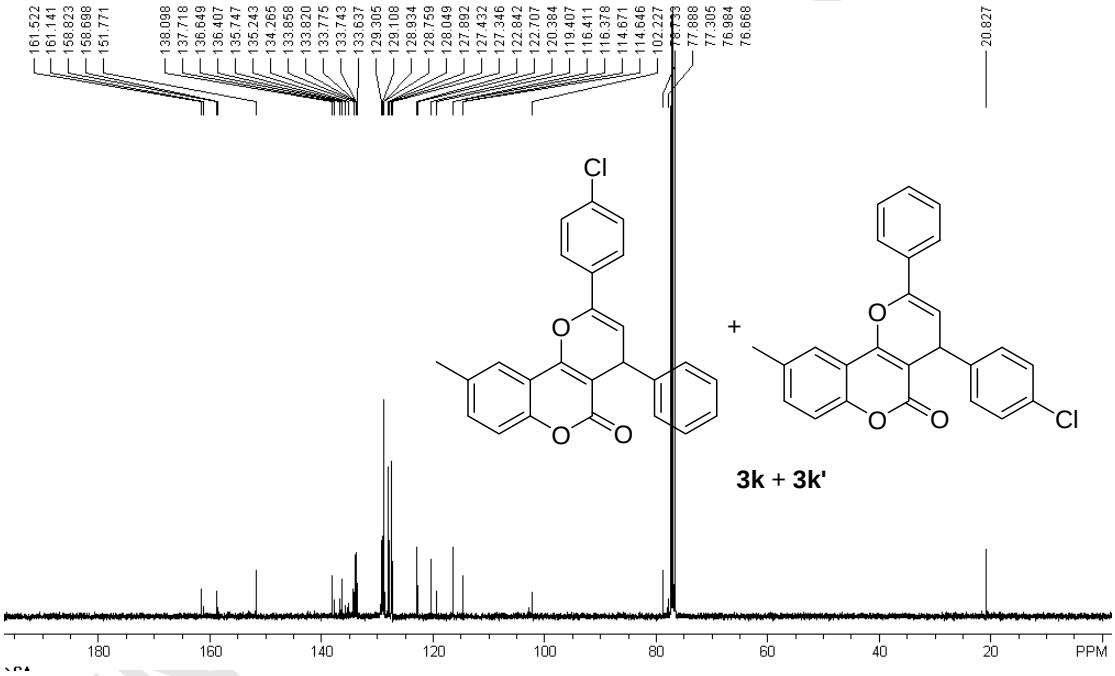
7.254
7.247
7.239
7.202
7.180
6.112
6.101
6.088
6.077
5.721
5.710
5.699
Cl
O
O
O
+
O
O
O
Cl
3.95
2.81
2.05
1.98
0.99
1.05
0.69
0.31
0.95
3k + 3k'
7.5
7.0
6.5
6.0
PPM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158.823
158.698
151.771
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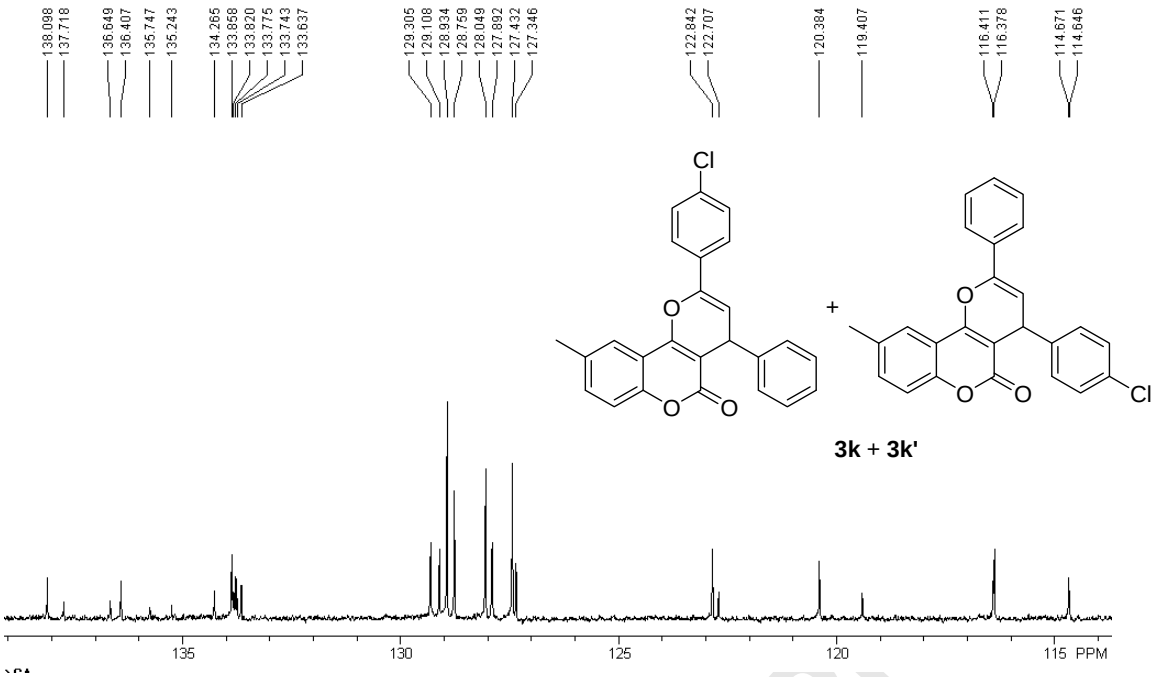
137.718
136.649
136.407
135.747
135.243
134.265
133.858
133.820
133.775
133.743
133.637
129.305
129.108
128.934
128.759
128.049
127.892
127.432
127.346
122.842
122.707
120.384
119.407
116.411
116.378
114.671
114.646
102.227
78.733
77.888
77.305
76.984
76.668
20.827
Cl
O
O
O
+
O
O
O
Cl
3k + 3k'
180
160
140
120
100
80
60
40
20
PPM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137.718
136.649
136.407
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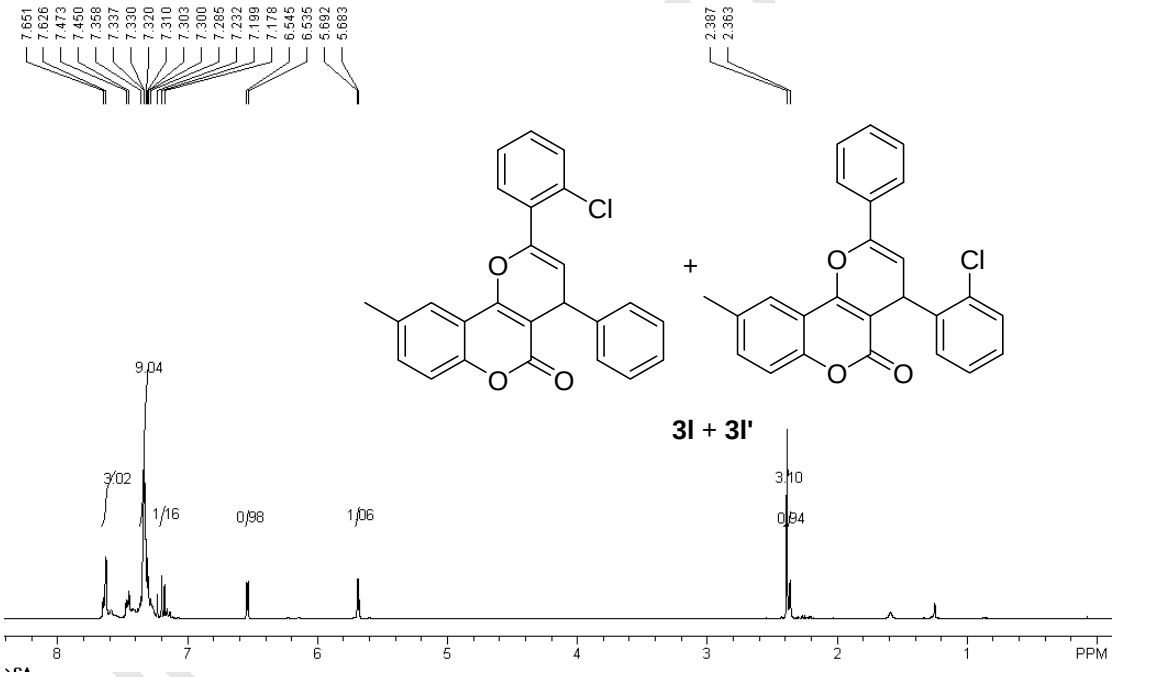
129.305
129.108
128.934
128.759
128.049
127.892
127.432
127.346
122.842
122.707
120.384
119.407
116.411
116.378
114.671
114.646
Cl
O
O
O
+
O
O
Cl
135
130
125
120
115 PPM

3k + **3k'**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7.450
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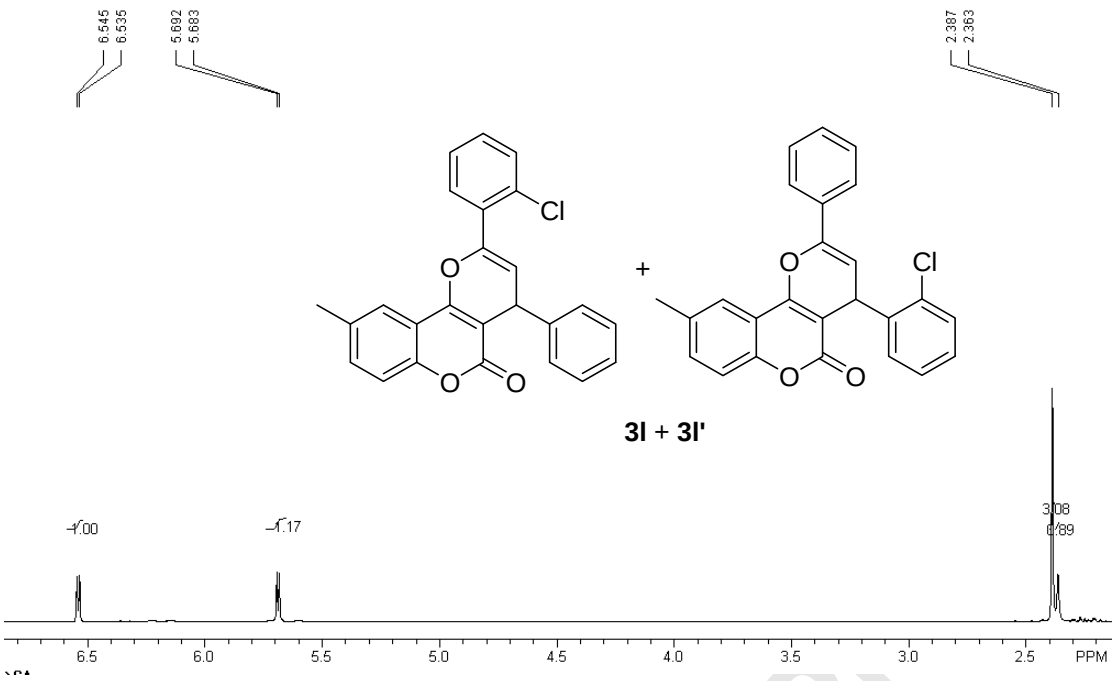
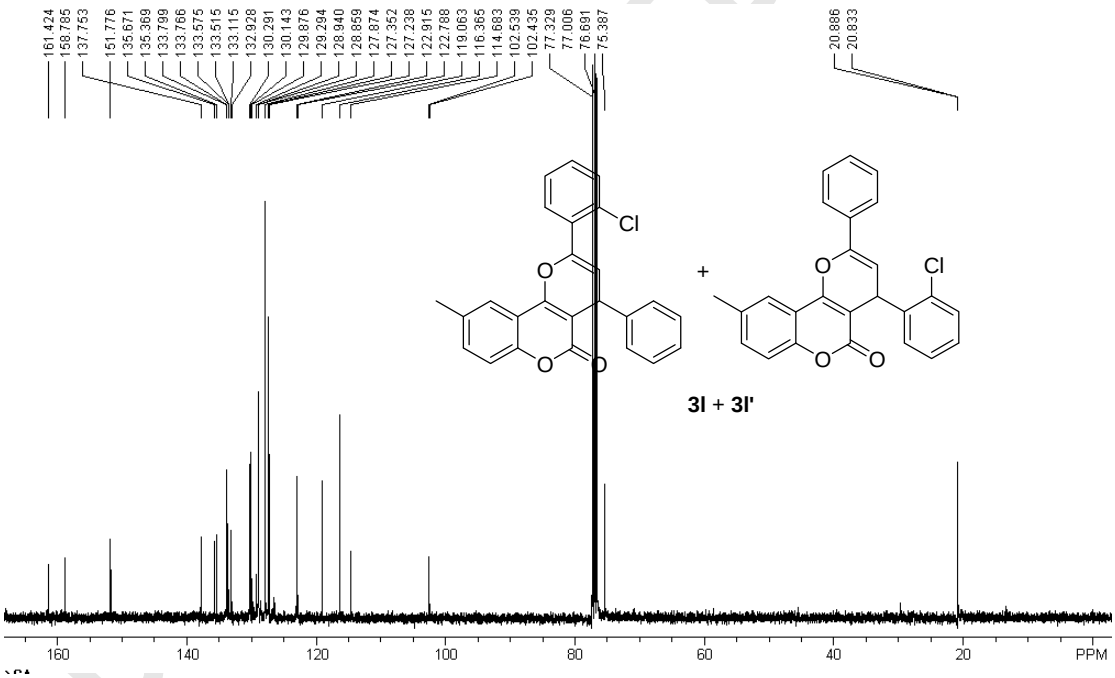
7.337
7.330
7.320
7.310
7.303
7.300
7.285
7.232
7.199
7.178
6.545
6.535
5.692
5.683
2.387
2.363
Cl
O
O
O
+
O
Cl
O
O
9.04
3.02
1.16
0.98
1.06
3.10
0.94
8
7
6
5
4
3
2
1
PPM

3l + **3l'**


6.545
6.535
5.692
5.683
2.387
2.363
Cl
O
O
O
+
Cl
O
O
O
3I + 3I'
1.00
1.17
3.08
0.89
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
PPM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133.766
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133.515
133.115
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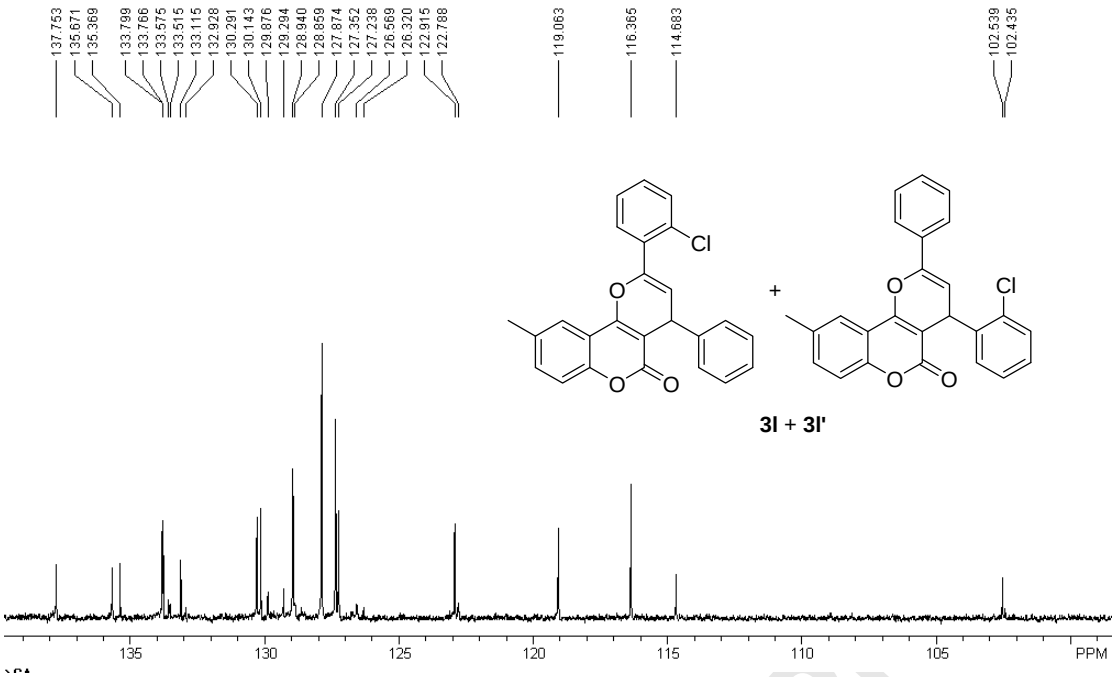
130.291
130.143
129.876
129.294
128.940
128.859
127.874
127.352
127.238
122.915
122.788
119.063
116.365
114.683
102.539
102.435
77.329
77.006
76.691
75.387
20.886
20.833
Cl
O
O
O
+
Cl
O
O
O
3I + 3I'
160
140
120
100
80
60
40
20
PPM



3l + **3l'**