Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

From π-expanded coumarins to π-expanded pentacenes

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General information

All chemicals were used as received unless otherwise noted. Reagent grade solvents (MeCN, CH_2Cl_2, hexane, toluene) were distilled prior to use. All reported NMR spectra were recorded on 500 MHz spectrometer unless otherwise noted. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. UV-vis absorption spectra were recorded in THF. Chromatography was performed on silica (Kieselgel 60, 200-400 mesh) and dry column vacuum chromatography (DCVC) was performed on preparative thin layer chromatography silica (Merck 107747). Mass spectra were obtained via EI or electrospray MS. Electronic absorption spectra were collected on a UV-VIS absorption spectrometer Lambda 35 (Perkin Elmer, Rodgau, Germany). The spectra were corrected with solvent absorption spectra. Steady-state fluorescence emission spectra were collected on an FLS920-stm spectrometer (Edinburgh Instruments, Livingstone, United Kingdom). The spectra were corrected for the detector response. Fluorescence decays were also acquired on the FLS920-stm spectrometer using Time Correlated Single Photon Counting (TCSPC) technique with a sub-nanosecond pulsed LED (EPLED 320) as an excitation source. Fluorescence decay times were determined from the decays using the least squares fitting method. The fitting was assumed to be correct when the goodness-of-fit value χ^2 was lower than 1.2. Fluorescence quantum yields were measured on a C9920-02G absolute QY measurement system from Hamamatsu (Hamamatsu Photonics Deutschland GmbH, Herrsching am Ammersee, Germany). All measurements were executed using 3ml quartz cuvette (Hellma GmbH, Jena, Germany) with 1 cm light path. All measurements were executed for samples with OD below 0.15.

Typical procedure.

To a mixture of di-*O*-benzoyl-1,5-dihydroxyantraquinone (480mg, 1 mmol) and K_2CO_3 (1.38g, 10 mmol) in 10 ml of DMSO, 6 mmol of derivative of phenylacetic acid methyl ester was added under an argon atmosphere and the resulting suspension was stirred at 100 °C for 1 hour. Acetic acid (0.6 mL), followed by 300 ml of water were added and the resulting suspension was cooled down. The precipitate was filtered off and washed with ethanol. Recrystallization from $CHCl_3$/EtOH gave pure biscoumarin.

3,7-Diphenylbenzo[*de*]chromeno[4,5-*gh*]chromene-2,8-dione (7)

Green-yellowish precipitate, 321 mg, 73% yield. M. p. > 300°C ($CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.48-7.51 (m, 6H, Ph), 7.42-7.45 (m, 4H, Ph), 7.35 (dd, *J* = 8.1 Hz, *J* = 1.0 Hz, 2H, Ar), 7.18 (t, *J* = 8.1 Hz, 2H, Ar), 7.09 (dd, *J* = 8.1 Hz, *J* = 1.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 118.3, 118.7,126.1, 127.1, 127.7, 129.3, 129.6, 129.8, 130.1, 135.6, 138.6, 151.8, 161.4. HRMS (EI): m/z calculated for $C_{30}H_{16}O_4$ $[M^{\cdot+}]$ = 440.1049; found: 440.1052. R_f (DCM): 0.52

1,7-Bis(4-methoxyphenyl)benzo[1,2,3-de:4,5,6-d'e']dichromene-2,8-dione (8)

Yellow-orange precipitate, 270 mg, 54% yield. M. p. > 300 °C ($CHCl_3$/MeOH). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 (d, *J* = 8.0 Hz, 4H, Ar), 7.33 (d, *J* = 4.7 Hz, 2H, Ar), 7.16-7.23 (br. m, 4H, Ar), 3.89 (s, 3H, Me),HRMS (ESI): m/z calculated for $C_{32}H_{20}O_6$ $[M+H^+]$ = 501.1338; found: 501.1332. R_f($CHCl_3$/AcOEt, 29:1): 0.67.

1,7-Bis(3,4-dimethoxyphenyl)benzo[1,2,3-de:4,5,6-d'e']dichromene-2,8-dione (9)

Orange solid, 364 mg, 83% yield. M. p. >300 °C ($CHCl_3$/MeOH). ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33 (dd, *J* = 7.7, *J* = 1.4 Hz, 2H, Ar), 7.21 (t, *J* = 8.0 Hz, 2H, Ar), 7.18 (dd, *J* = 8.2, *J* = 1.4 Hz, 2H, Ar), 6.92-7.01 (m, 6H, Ar), 3.95 (s, 6H), 3.83 (s, 6H). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 161.6, 151.6, 150.0, 149.9, 138.2, 129.7, 127.8, 127.8, 126.8, 125.6, 122.9, 118.8, 118.0, 113.0, 112.0, 56.1, 56.0. HRMS (ESI): m/z calculated for $C_{34}H_{24}O_8$ $[M+Na^+]$ = 583.1369; found: 583.1375. R_f(Acetone/DCM, 1:19): 0.42.

1,7-Di(thiophen-2-yl)benzo[1,2,3-de:4,5,6-d'e']dichromene-2,8-dione (10).

After crystallization from $CHCl_3$, the resulting precipitate was loaded on the column and chromatographed on silica gel (DCM/hexanes 1:2, then DCM). After solvent removal, **10** was recrystallized from DCM/EtOH to give red crystals (217mg ,48%).

^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.61 (dd, *J* = 5.2 Hz, *J* = 1.2 Hz, 2H, Ar), 7.38 (dd, *J* = 4.4 Hz, *J*=1.2 Hz, 2H, Ar), 7.37 (dd, *J* = 4.7, *J* = 1.1 Hz, 2H, Ar), 7.30 (t, *J* = 7.8 2H, Ar), 7.26 (dd, *J* = 3.6 Hz, *J* = 1.2 Hz, 2H, Ar), 7.61 (dd, *J* = 5.2 Hz, *J* = 3.6 Hz, 2H, Ar). ^{13}C NMR (CD_2Cl_2, 151 MHz): δ 173.6, 151.4, 136.0, 130.3, 130.0, 129.2, 127.9, 127.7, 126.4, 118.1, 111.3. HRMS (EI): m/z calculated for $C_{26}H_{12}O_4S_2^{+\cdot}$=452.0177; found: 452.0192. R_f (Acetone/DCM, 1:49): 0.54.

1,7-bis(4-fluorophenyl)benzo[1,2,3-de:4,5,6-d'e']dichromene-2,8-dione (11). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40-7.44 (d, *J* = 4.7 Hz, 4H, Ar), 7.36 (dd, *J* = 8.2 Hz, *J* = 0.9 Hz 2H, Ar), 7.23 (t, *J* = 8.1 Hz 2H, Ar), 7.19 (t, *J* = 8.6 Hz 4H, Ar), 3.89 (s, *J* = 8.2 Hz, *J* = 0.9 Hz 2H, Me),

Light yellow solid, 253 mg, 53% yield. M. p. > 300 °C. HRMS (EI): m/z calculated for $C_{30}H_{14}O_4F_2$ [$M^{\cdot+}$] = 476.0860; found: 476.0865. R_f (DCM): 0.65.

1,7-Bis(3,4- hexyloxyphenyl)benzo[1,2,3-de:4,5,6-d'e']dichromene-2,8-dione (**13**) 1,7-bis(3,4-bis(hydroxy)phenyl)benzo[1,2,3-de:4,5,6-d'e']dichromene-2,8-dione (250 mg, 0.5 mmol) was dissolved in Acetone (100 mL) and K_2CO_3 (345 mg, 2,5 mmol), KI (50 mg, 0.3 mmol), bromohexane (660 mg, 4mmol) were added. After 12 hours at 70°C reaction was filtered through a pad of silica. DCVC (silica, Acetone) and crystallization from DCM/MeOH afforded **13** as orange crystals (394 mg, 94%) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32(dd, *J* = 13.1, *J* = 2.3 Hz, 2H, Ar), 7.18-7.21 (m, 4H, Ar), 6.96 (s, 4H, Ar), 6.92 (s, 2H, Ar), 4.07 (s, 4H, Ar), 3.88-4.01 (br s, 4H, Hexyl), 1,87 (m, 4H, Hexyl), 1,77 (m, 4H, Hexy)1.29-1.58 (m, 32H, Hexyl), 0.93 (t, *J* = 6.9 Hz, 6, Hexyl) 0.89 (t, *J* = 7.1 Hz, 6, Hexyl). ^{13}C NMR ($CDCl_3$, 151 MHz): δ 161.6, 151.6, 150.2, 149.9, 138.2, 129.7, 127.9, 127.7, 126.9, 125.7, 123.0, 118.8, 117.9, 115.5, 114.0, 69.4, 69.1, 31.6, 31.6, 29.2, 29.1, 25.7, 25.6, 22.6, 22.6, 14.0, 14.0. M. p. > 300 °C. HRMS (EI): m/z calculated for $C_{30}H_{14}O_4F_2$ [$M^{\cdot+}$] =840.4601; found: 840.4608. R_f (DCM): 0.7.

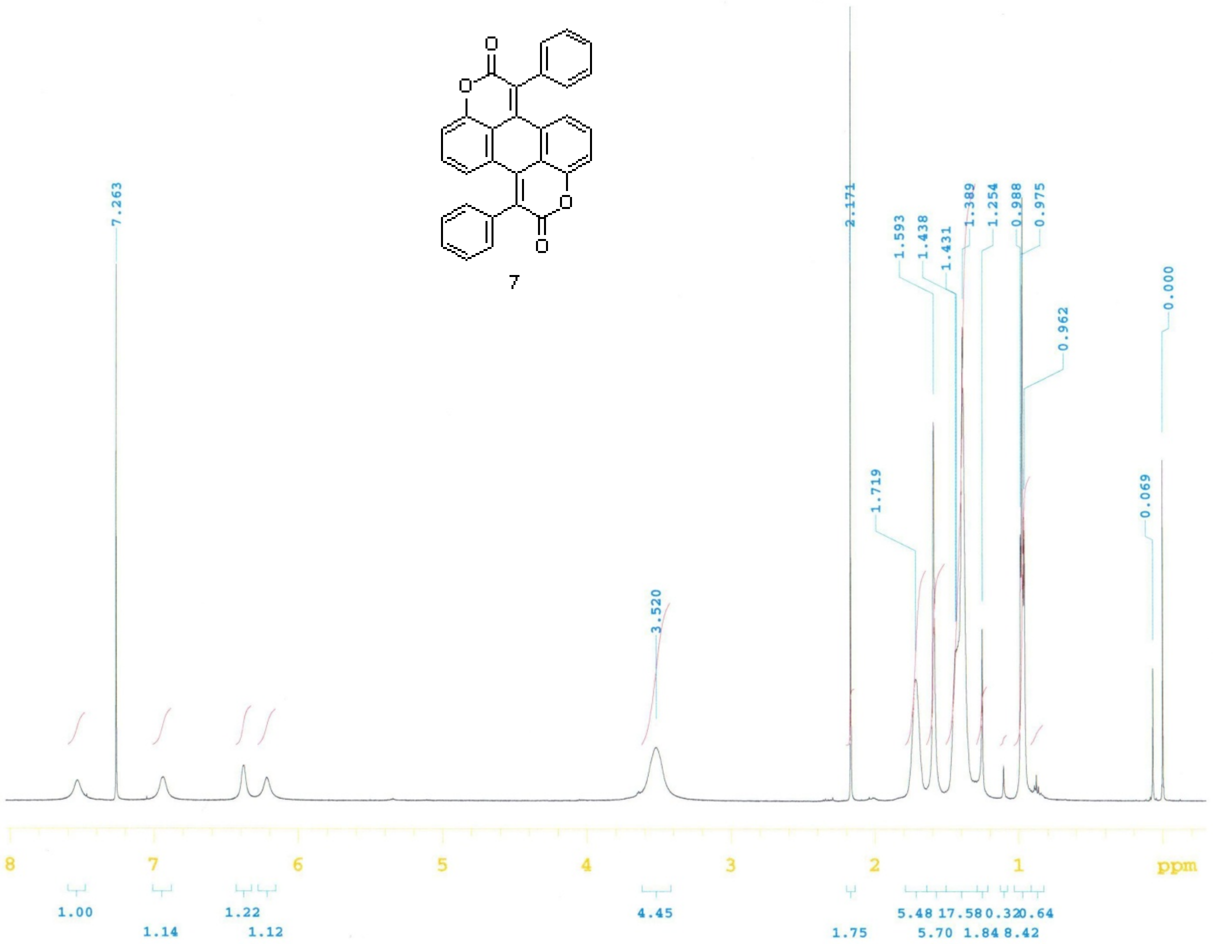
4,5,12,13-Tetrakis(hexyloxy)pentaceno[5,6,7-cdef:12,13,14-c'd'e'f']dichromene-2,10-dione (14)

Method A. 1,7-bis(3,4-bis(hexyloxy)phenyl)benzo[1,2,3-de:4,5,6-d'e']dichromene-2,8-dione (**13**, 420 mg, 0.5 mmol) was dissolved in dry DCM (150 mL) and $FeCl_3$ (810 mg, 5 mmol) was added, followed by catalytic amount of $BF_3 \cdot Et_2O$ (100 μL). After 30 minutes at room temperature reaction was filtered through a pad of silica. DCVC (silica, DCM/AcOEt 4:1) and crystallization from DCM/MeOH afforded **14** as red crystals (367 mg, 88%)

M. p. >300 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.53 (br s, 2H, Ar), 6.94 (br s, 2H, Ar), 6.38(br s, 2H, Ar), 6.22 (br s, 2H, Ar), 3.52 (br s, 8H, Hexyl), 3.52 (br s, 8H, Hexyl), 1.2-1.8 (m, 32H, Hexyl), 0.98 (t, J = 6.6 Hz, 12H, Hexyl). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ 207, 157.8, 149.1, 148.8, 146.3, 125.0, 124.3, 122.9, 122.3, 121.9, 117.1, 115.6, 109.0, 108.8, 106.3, 101.2, 67.6, 32.1, 32.0, 29.4, 29.4, 25.9, 25.8, 22.7, 14.1. HRMS (EI): m/z calculated for $C_{54}H_{60}O_8$ [$M^{\cdot+}$] = 836.4288; found: 836.4310.

Method B

1,7-Bis(3,4-bis(hexyloxy)phenyl)benzo[1,2,3-de:4,5,6-d'e']dichromene-2,8-dione (**13**, 440mg, 0.5 mmol) was dissolved in THF (300ml) and photoirradiated (365 nm, ordinary laboratory UV lamp) for 24h at room temperature. The reaction volume was reduced to around 50 ml and the resulting precipitate was filtered off and washed with THF to give pure **7** (230 mg, 53%).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0.962
0.069
0.000
8
7
6
5
4
3
2
1
ppm
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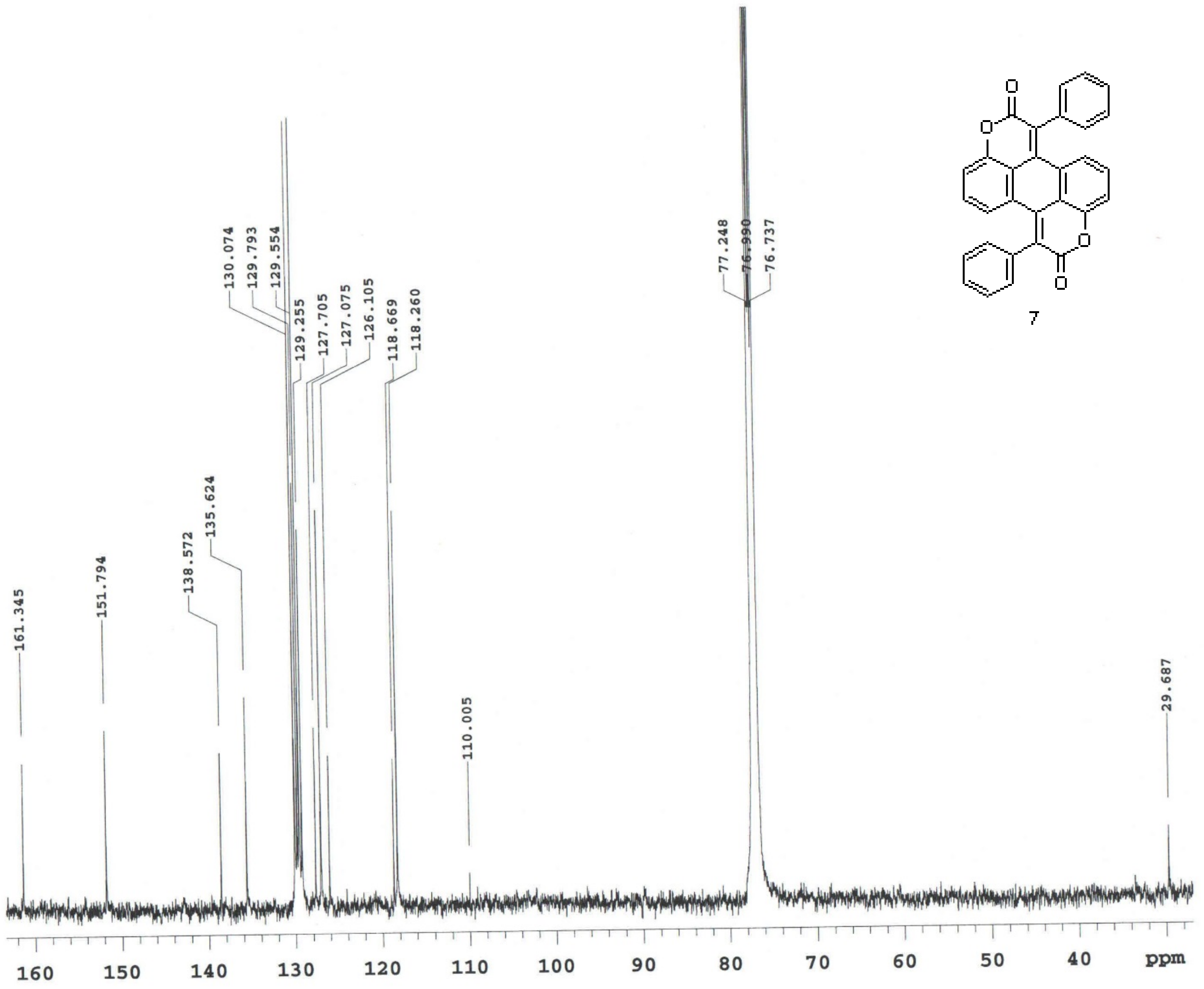

7

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118.260
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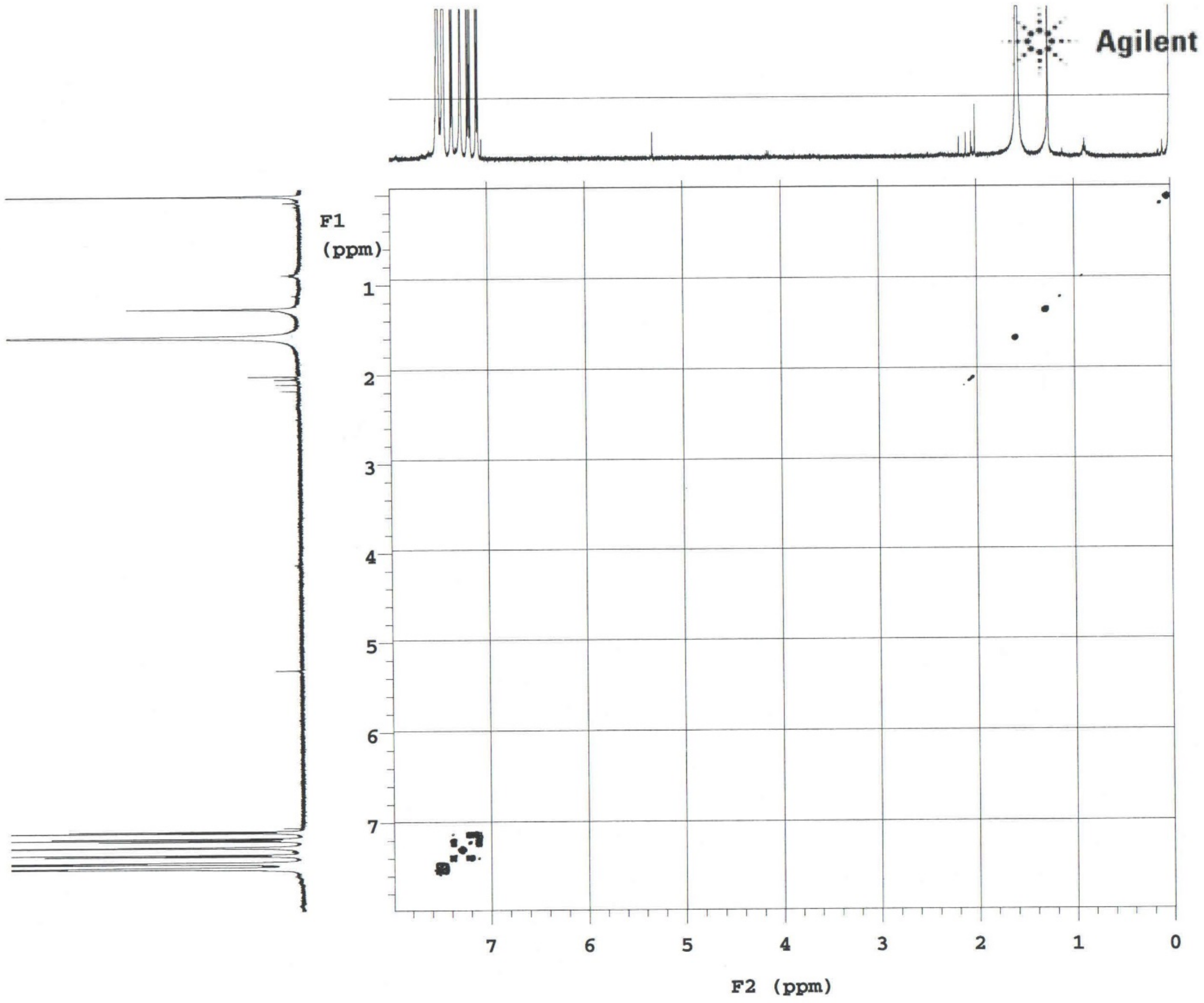
O
O
O



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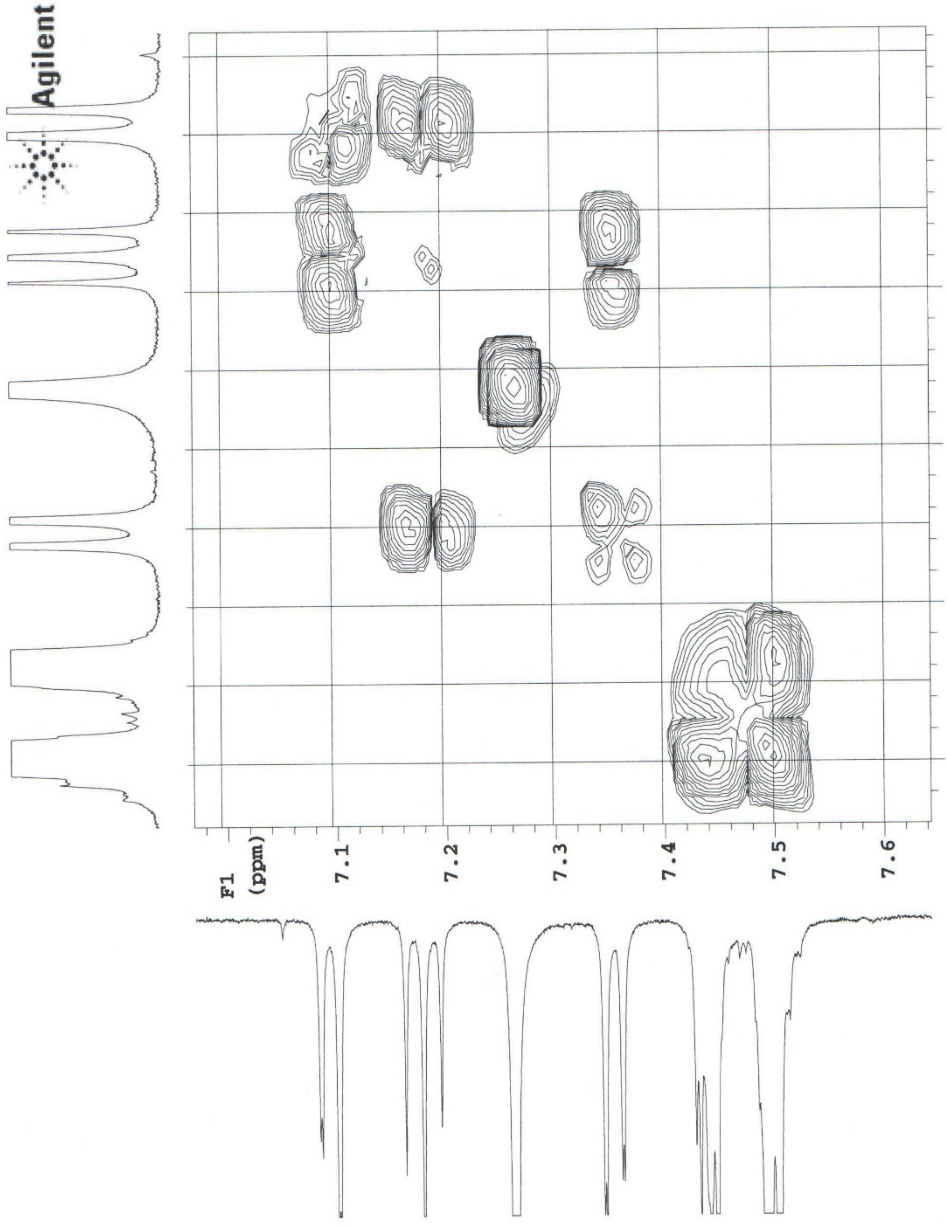

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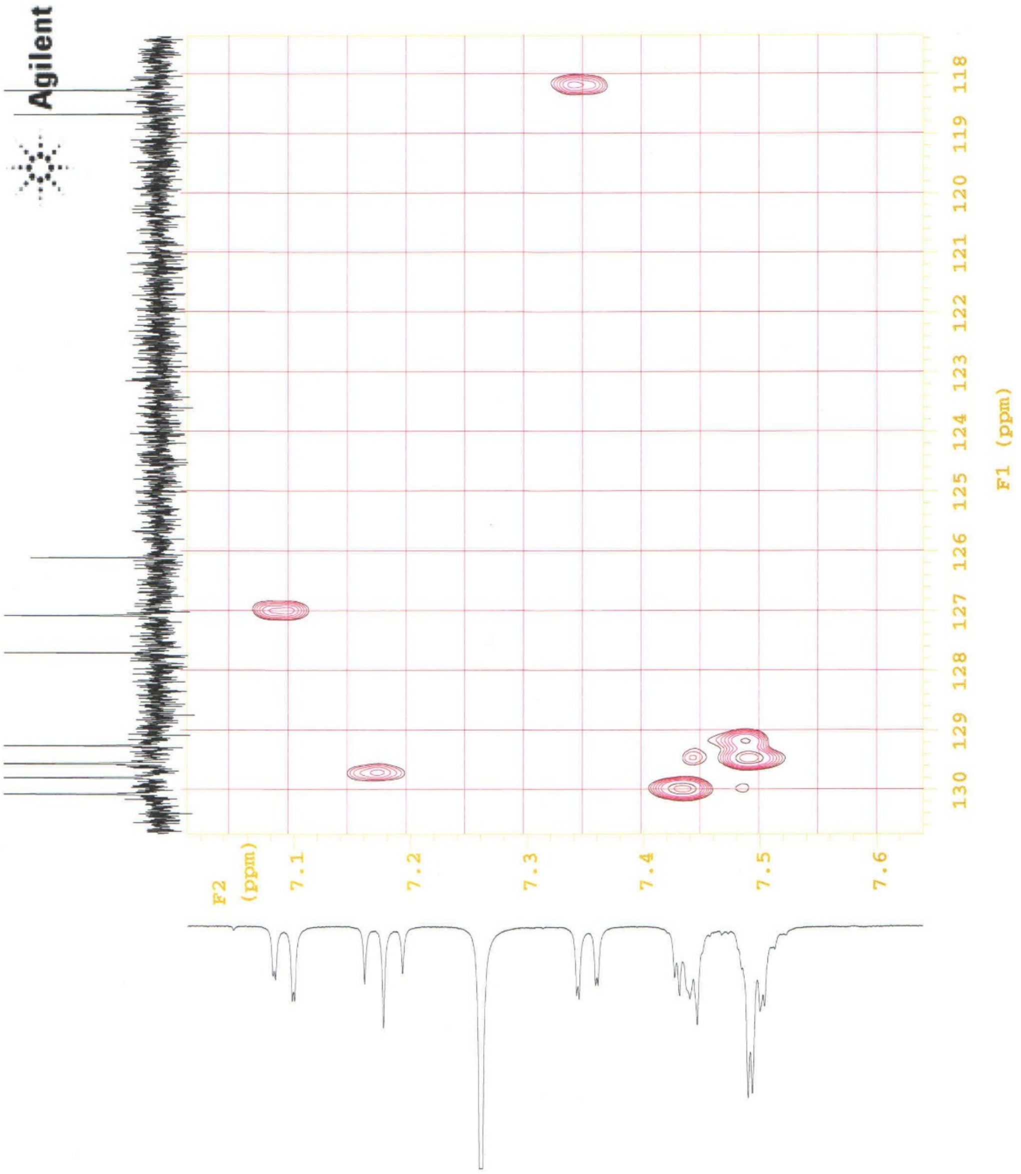Agilent
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7.3
7.4
7.5
7.6

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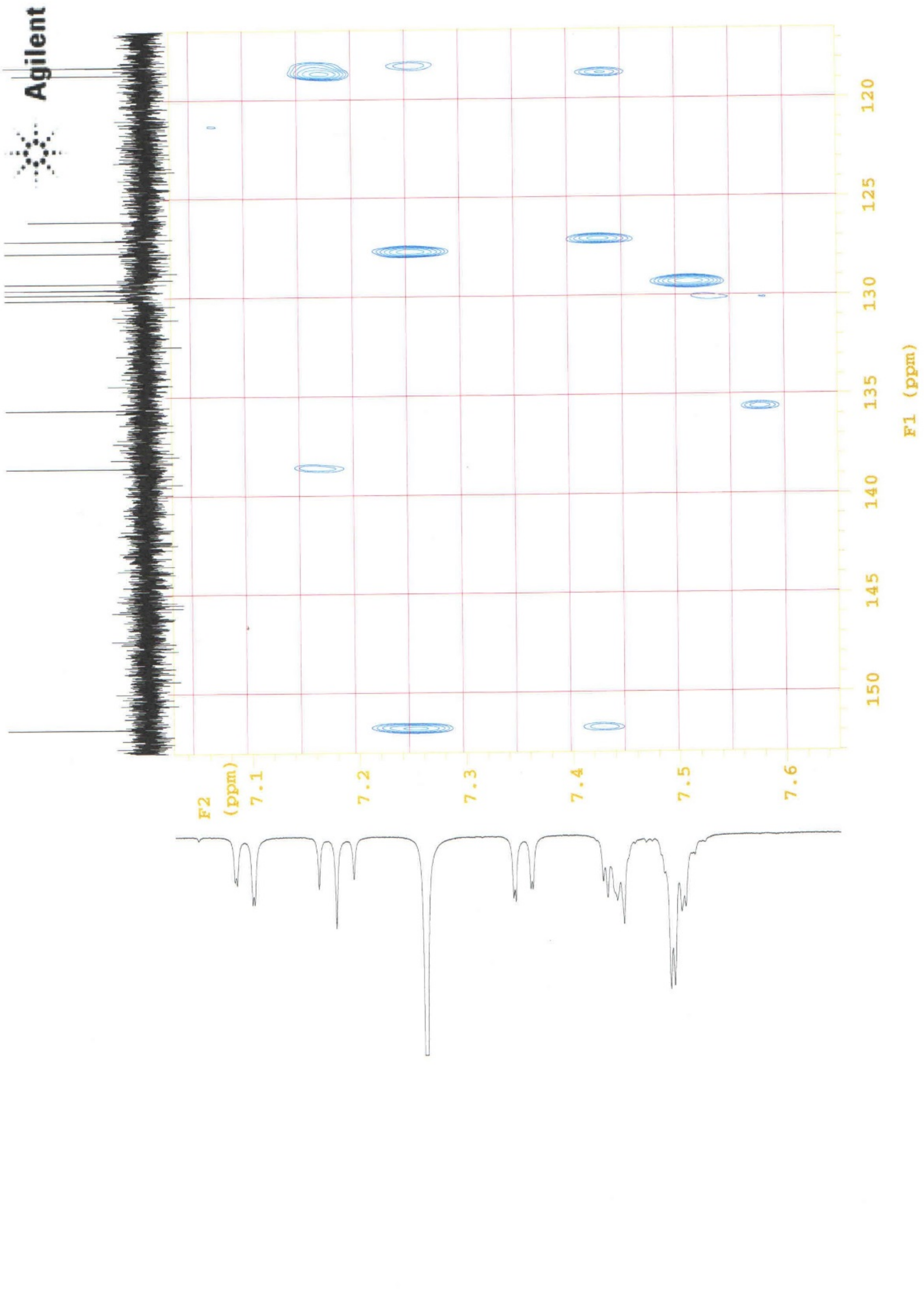

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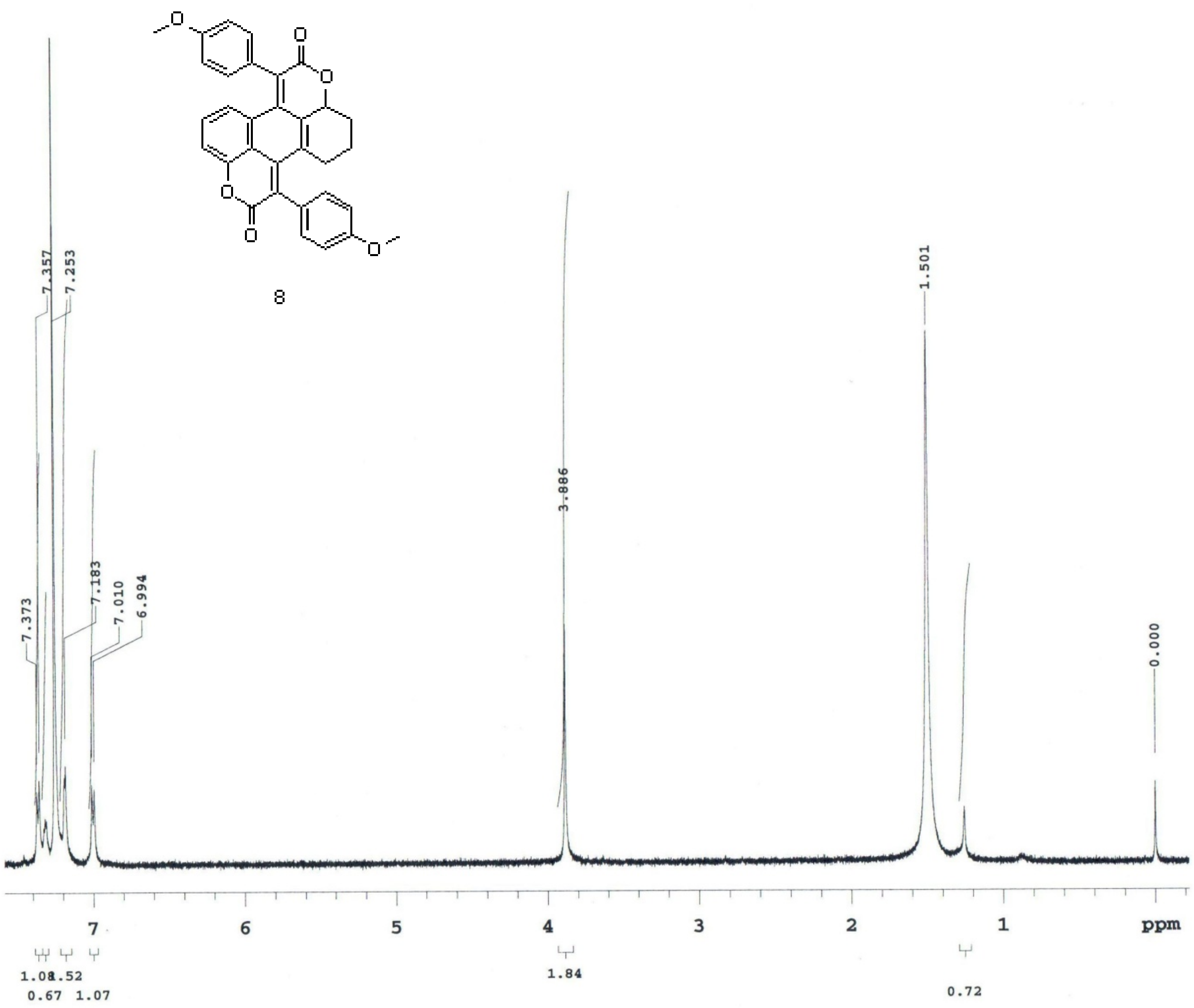
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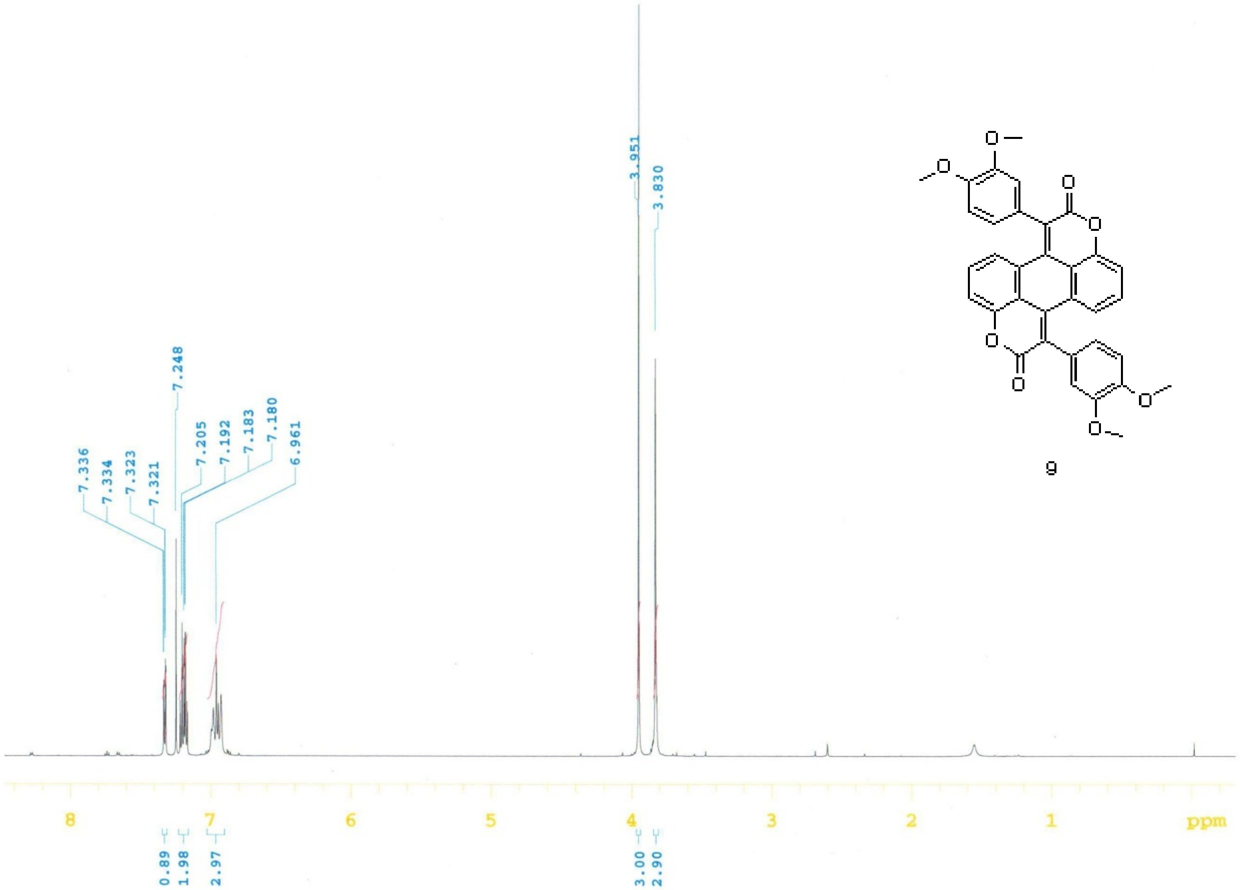
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2.97
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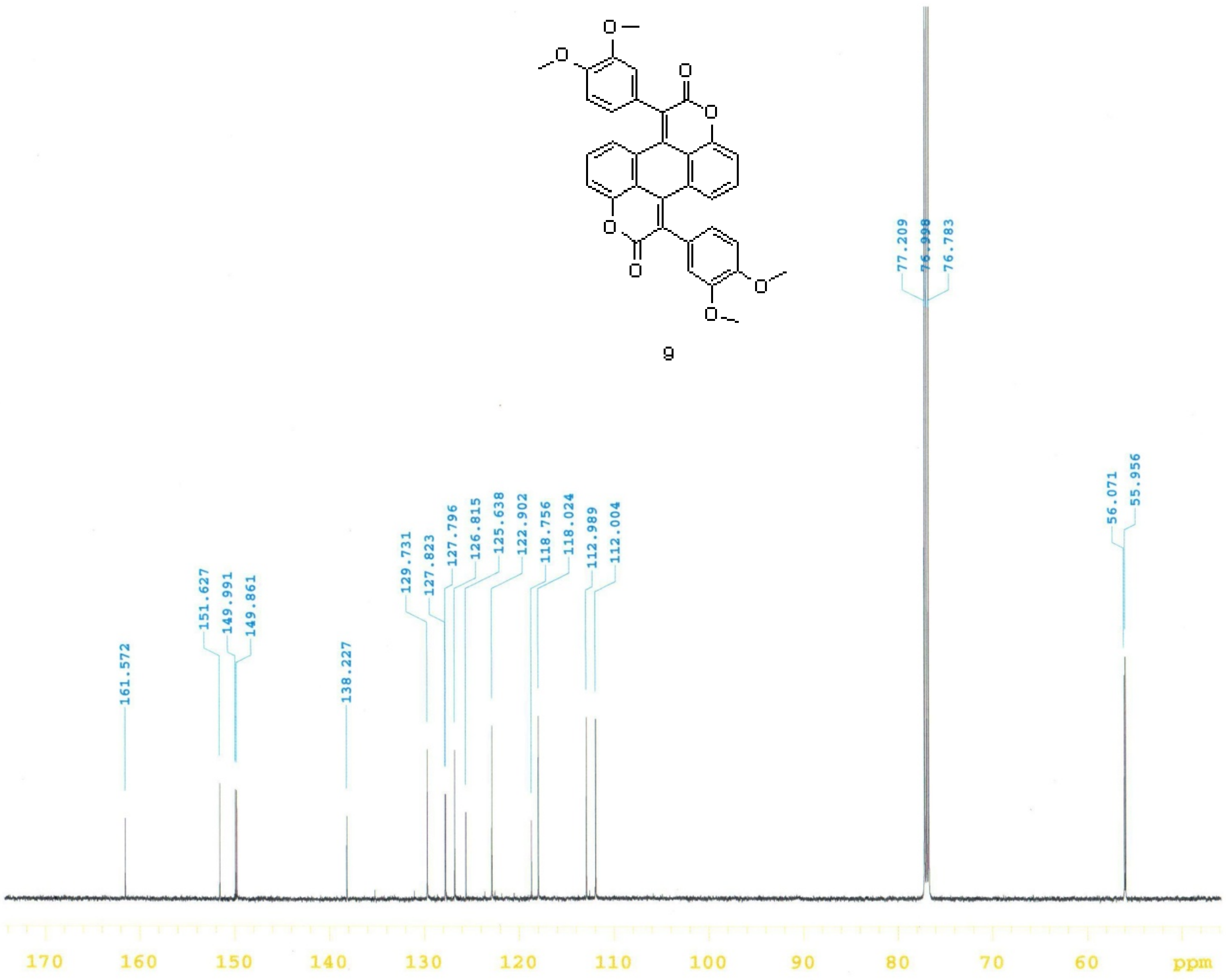
2.90
O
9



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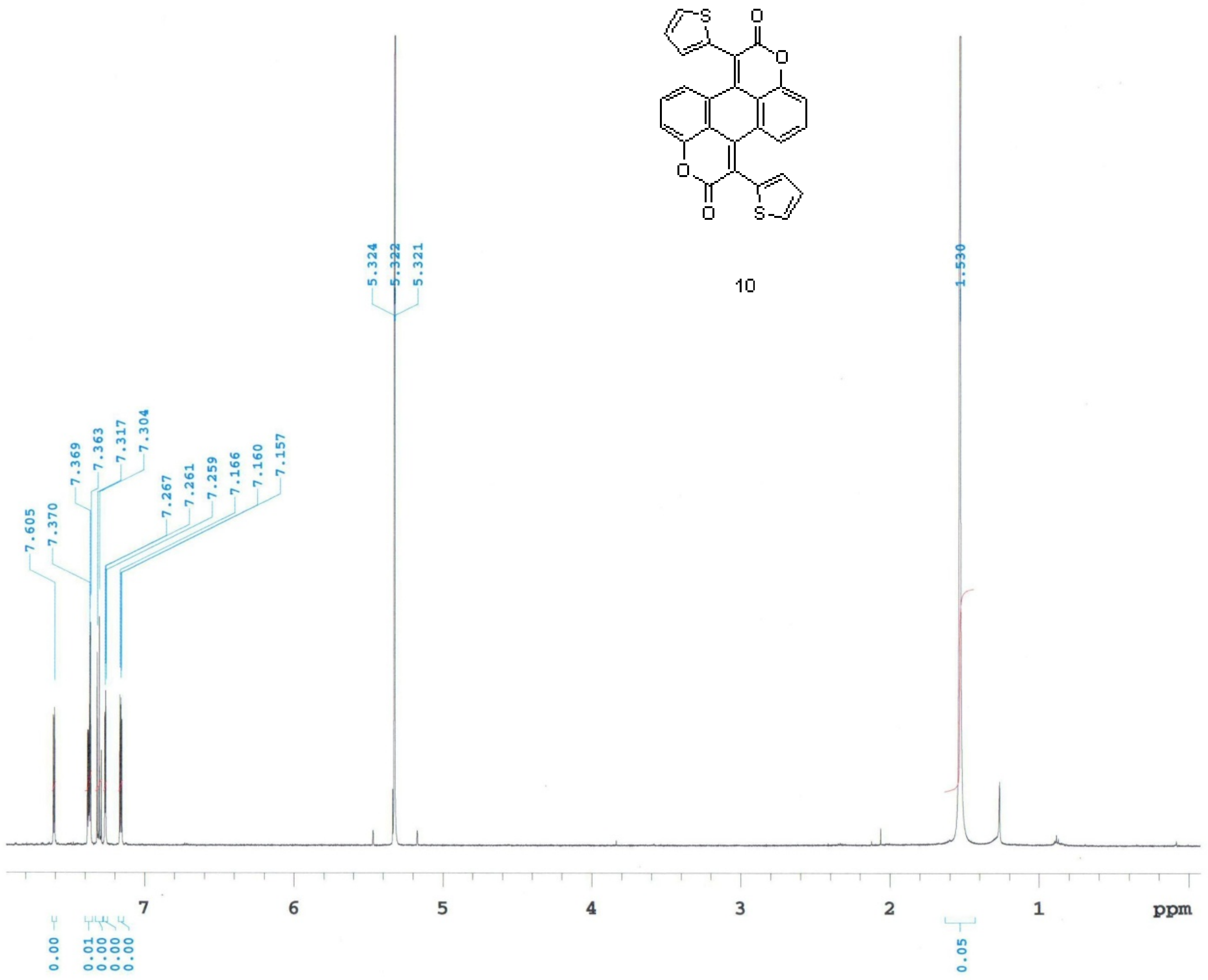

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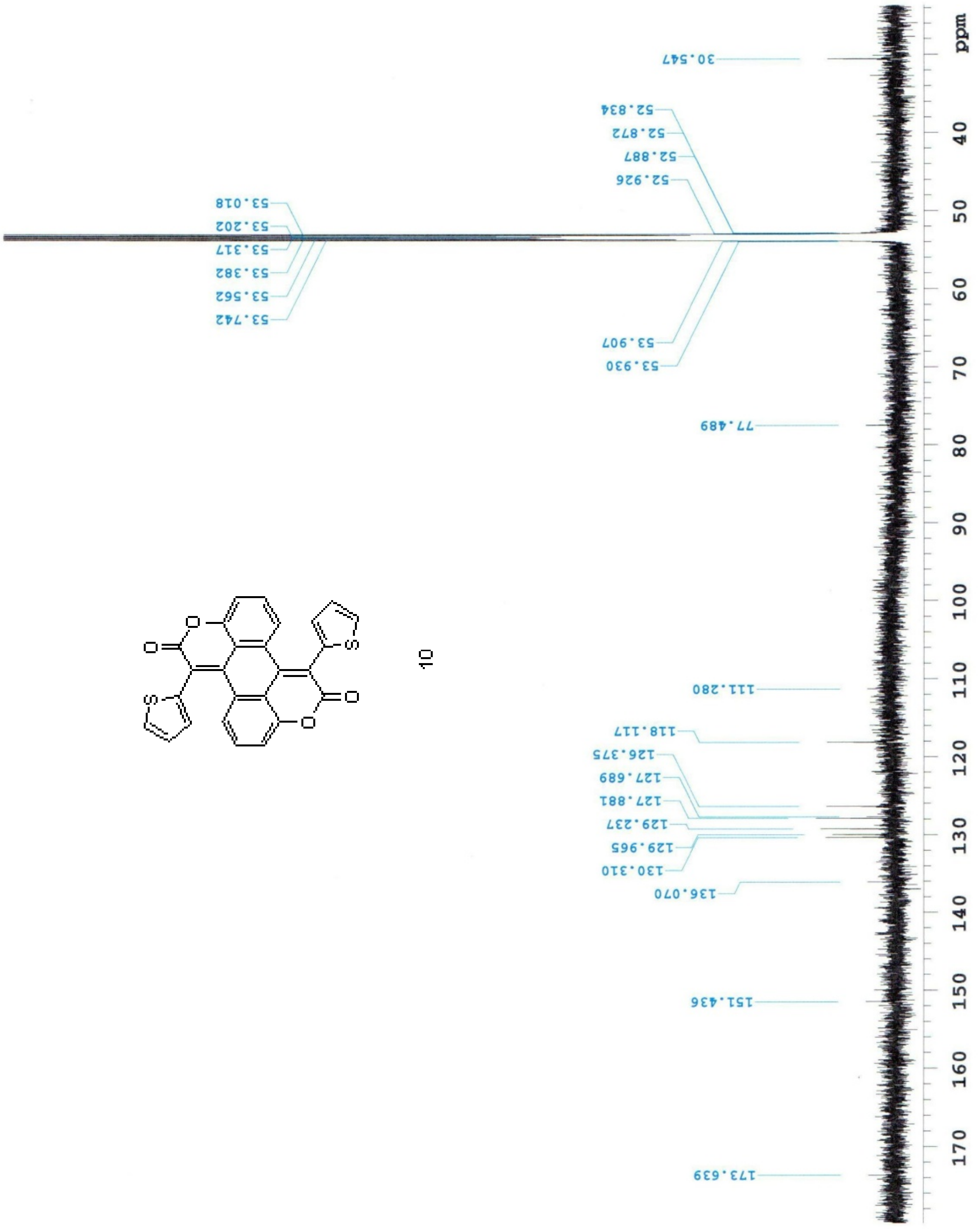
S



10

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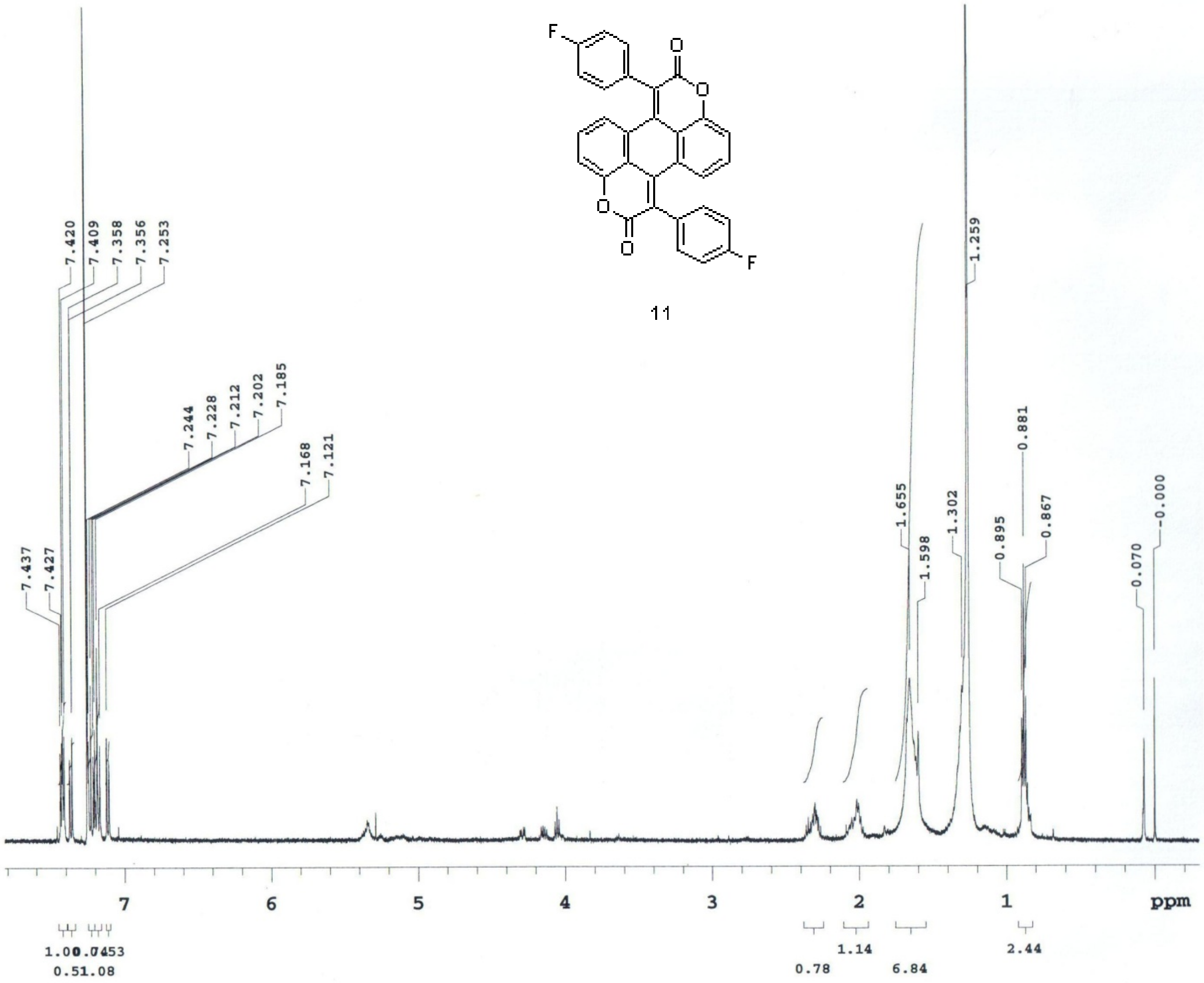

11

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7.168
7.121
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1.302
1.259
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0.881
0.867
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F
O
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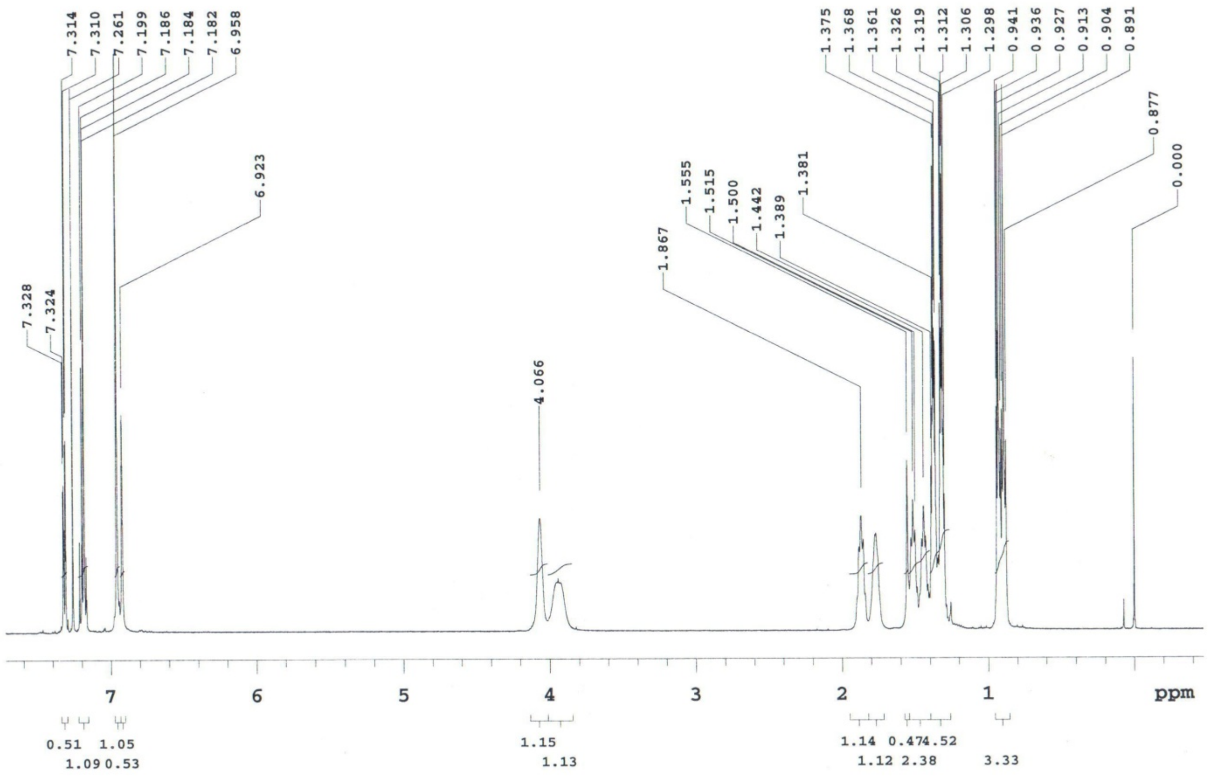
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1.515
1.500
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1.375
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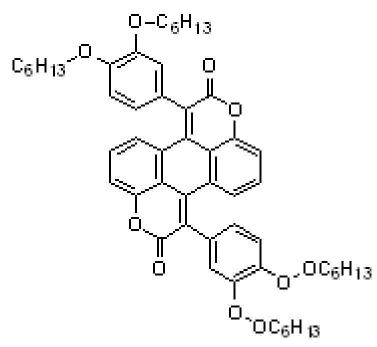
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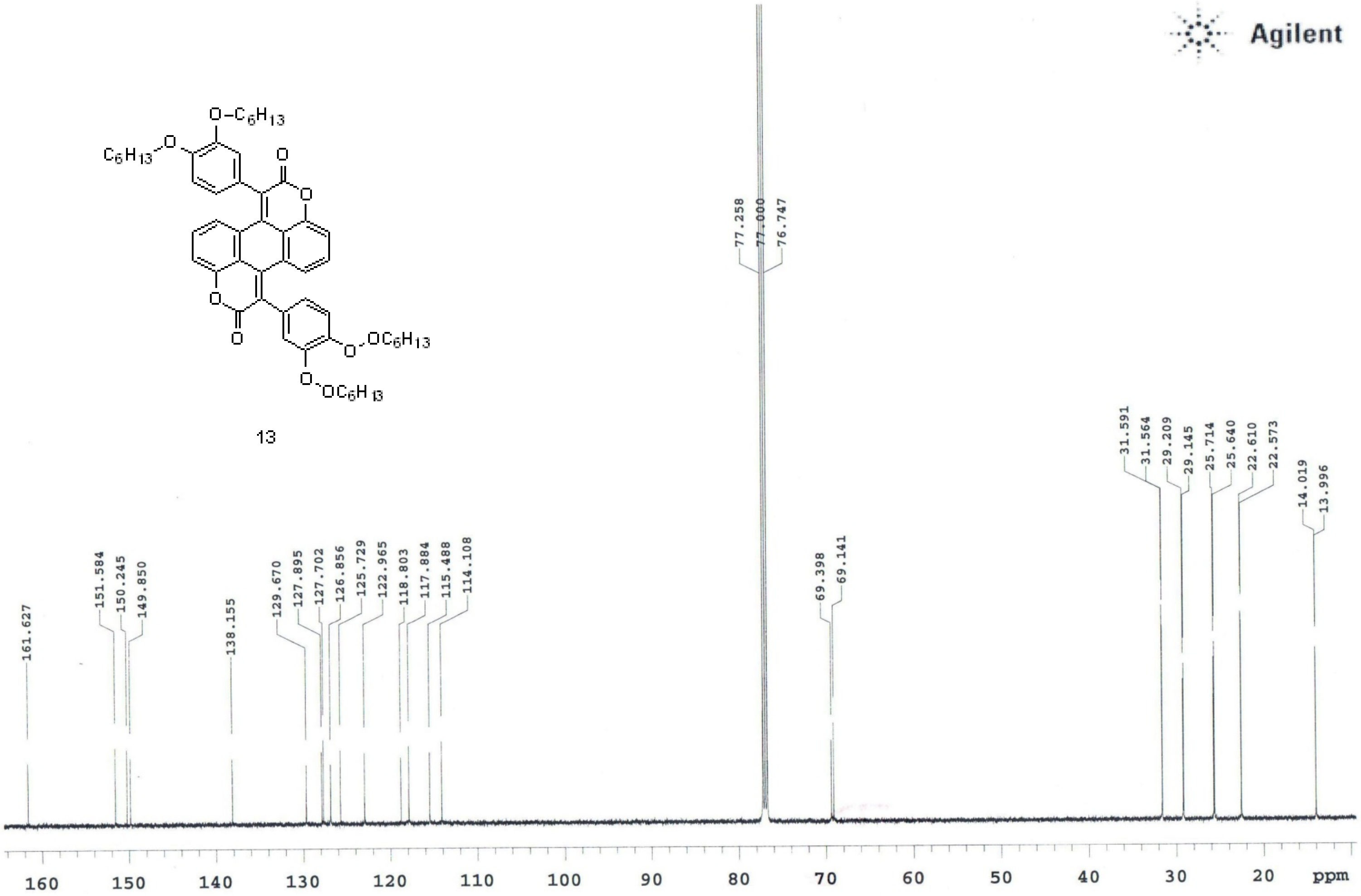
C6H13-O
OC6H13
OC6H13

13

Agilent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C6H13O
O
O
O
O
OC6H13
OC6H13
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129.670
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127.702
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77.000
76.747
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22.610
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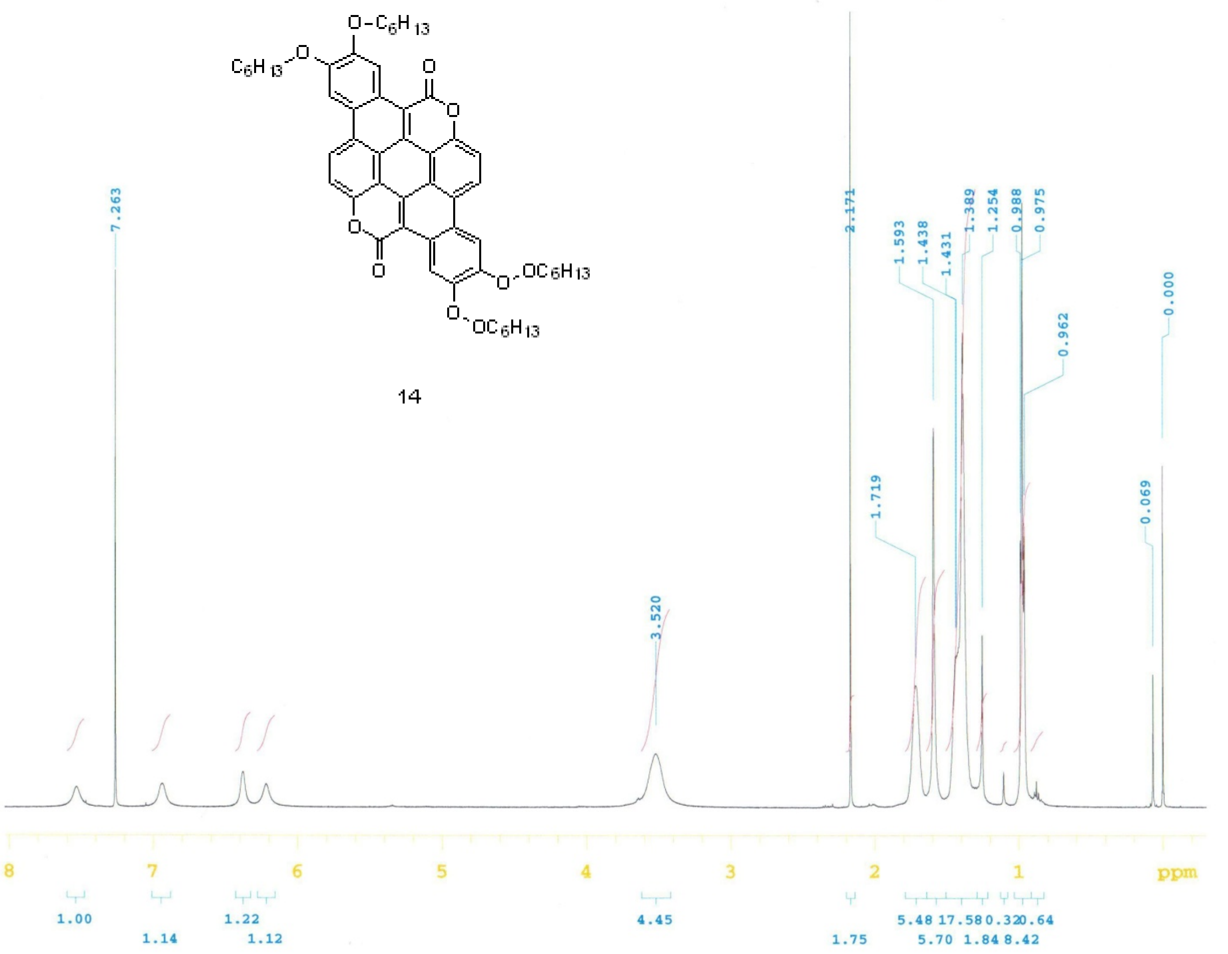
20
ppm

13


14

O-C6H13
C6H13-O
O-OC6H13
O-OC6H13
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1.389
1.254
0.988
0.975
0.962
0.000
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0.069
3.520
8
7
6
5
4
3
2
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ppm
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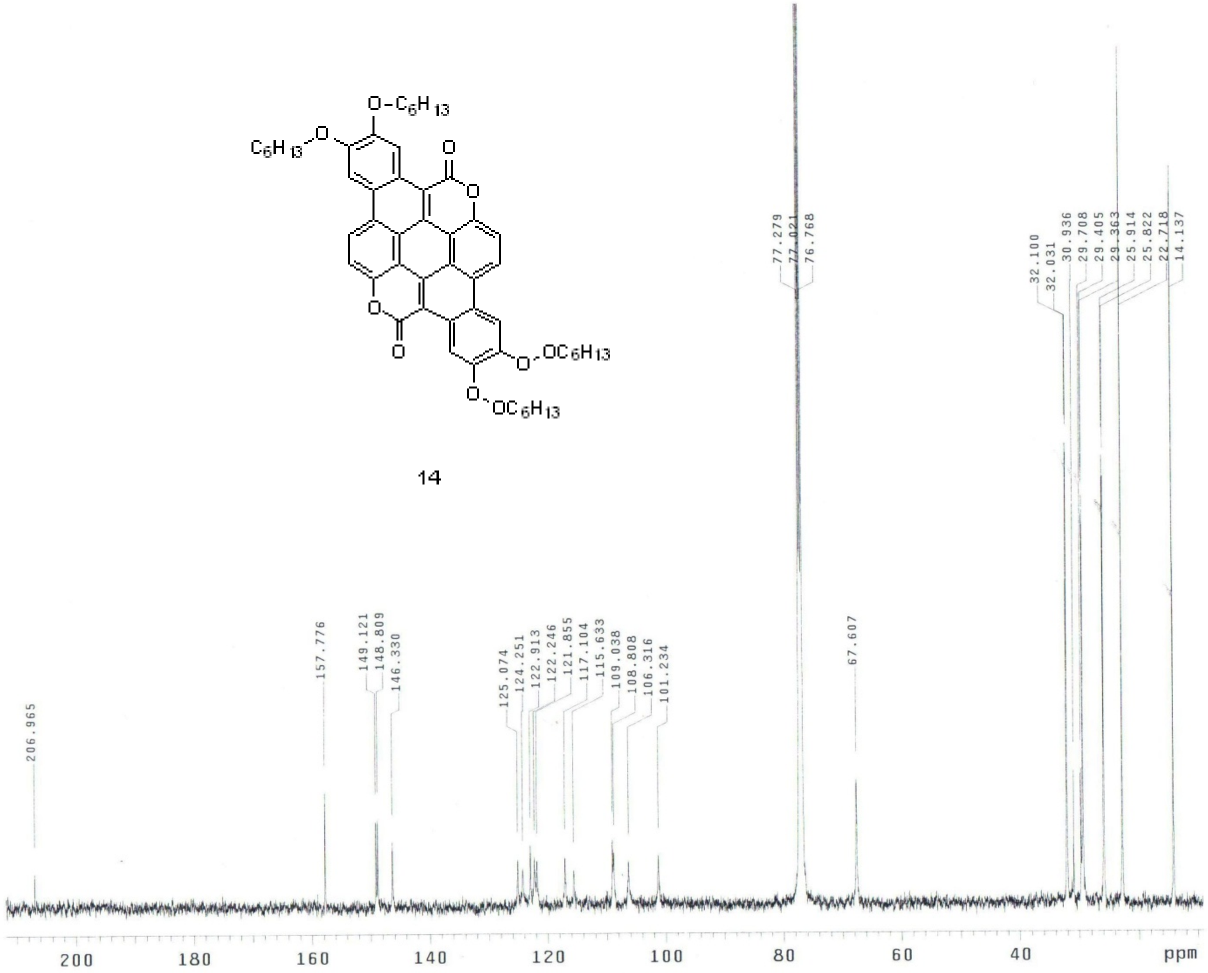

14

$O-C_6H_{13}$
$C_6H_{13}O$
OC_6H_{13}
OC_6H_{13}
O
O
O
O
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157.776
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148.809
146.330
125.074
124.251
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122.246
121.855
117.104
115.633
109.038
108.808
106.316
101.234
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77.021
76.768
67.607
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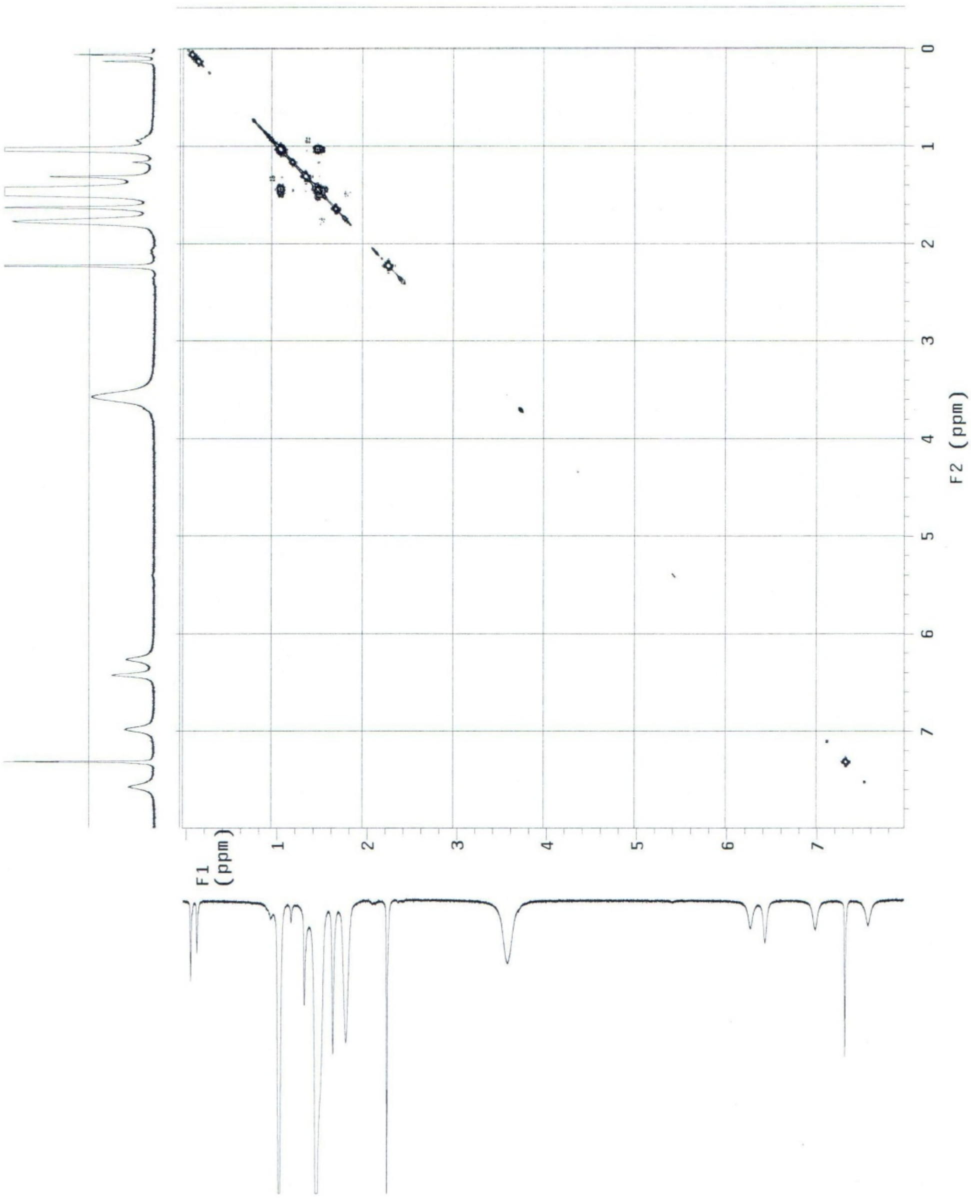
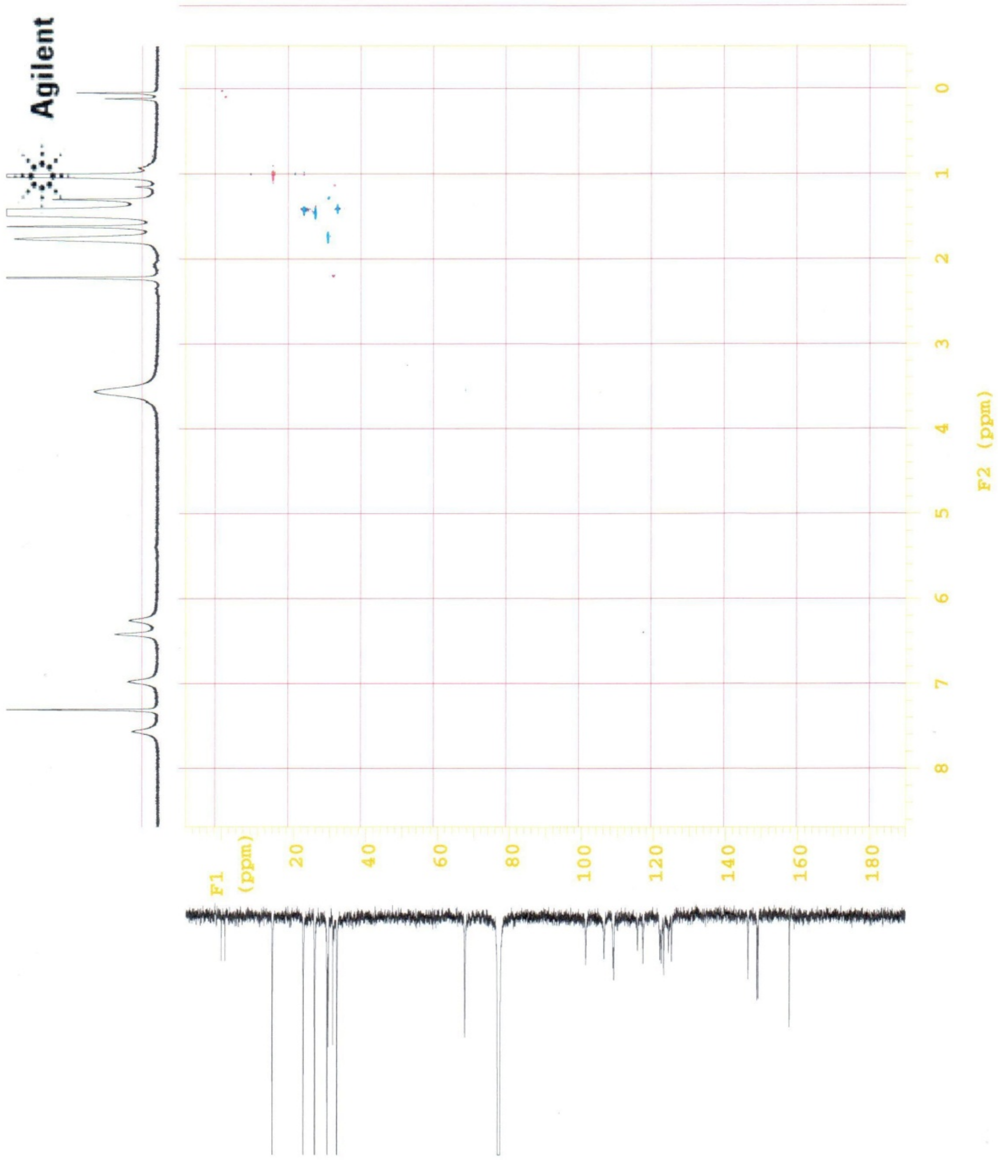


(**14**)COSY



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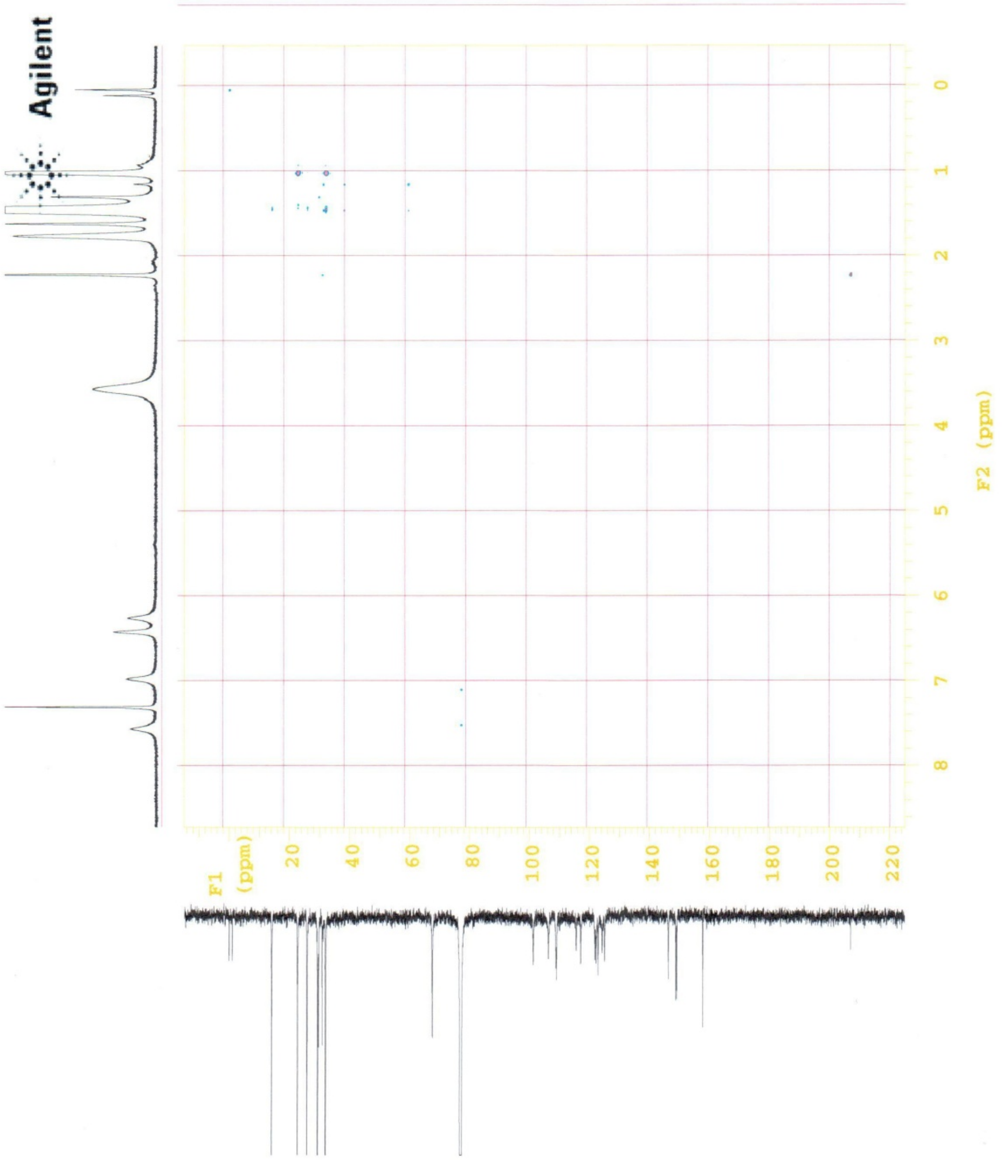
Agilent
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2
3
4
5
6
7
8
F1 (ppm)
20
40
60
80
100
120
140
160
180
200
220

(**14**) HMBC