Supporting Information

Keto-coumarin Scaffold for Photoinitiators for 3D Printing and Photocomposites

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Figure S1. Free radical photopolymerization experiments for laser write upon laser diode irradiation: Characterization of the 3D written patterns by numerical optical microscopy; **(C) KC-C**/NPG (0.025%/0.125% w/w) in TMPTA (thickness = 2100 µm for **(b)**); **(D) Coum-B1**/Iod/NPG (0.03%/0.16%/0.16% w/w) in TMPTA (thickness = 1980 µm); **(E) KC-D**/NPG (0.04%/0.2% w/w) in TMPTA (thickness = 2090 µm); **(F) KC-E**/Iod/NPG (0.016%/0.083%/0.083% w/w) in TMPTA (thickness = 2110 µm); **(G) KC-E**/NPG (0.024%/0.118% w/w) in TMPTA (thickness = 1760 µm); **(H) KC-E**/EDB (0.018%/0.09% w/w) in TMPTA (thickness = 2240 µm); **(I) KC-F**/Iod/NPG (0.015%/0.077%/0.077% w/w) in TMPTA (thickness = 2220 µm); **(J) KC-G**/Iod/NPG (0.06%/0.3%/0.3% w/w) in TMPTA (thickness = 2090 µm); and **(K) KC-G**/NPG (0.06%/0.3% w/w) in TMPTA (thickness = 2490 µm); respectively.

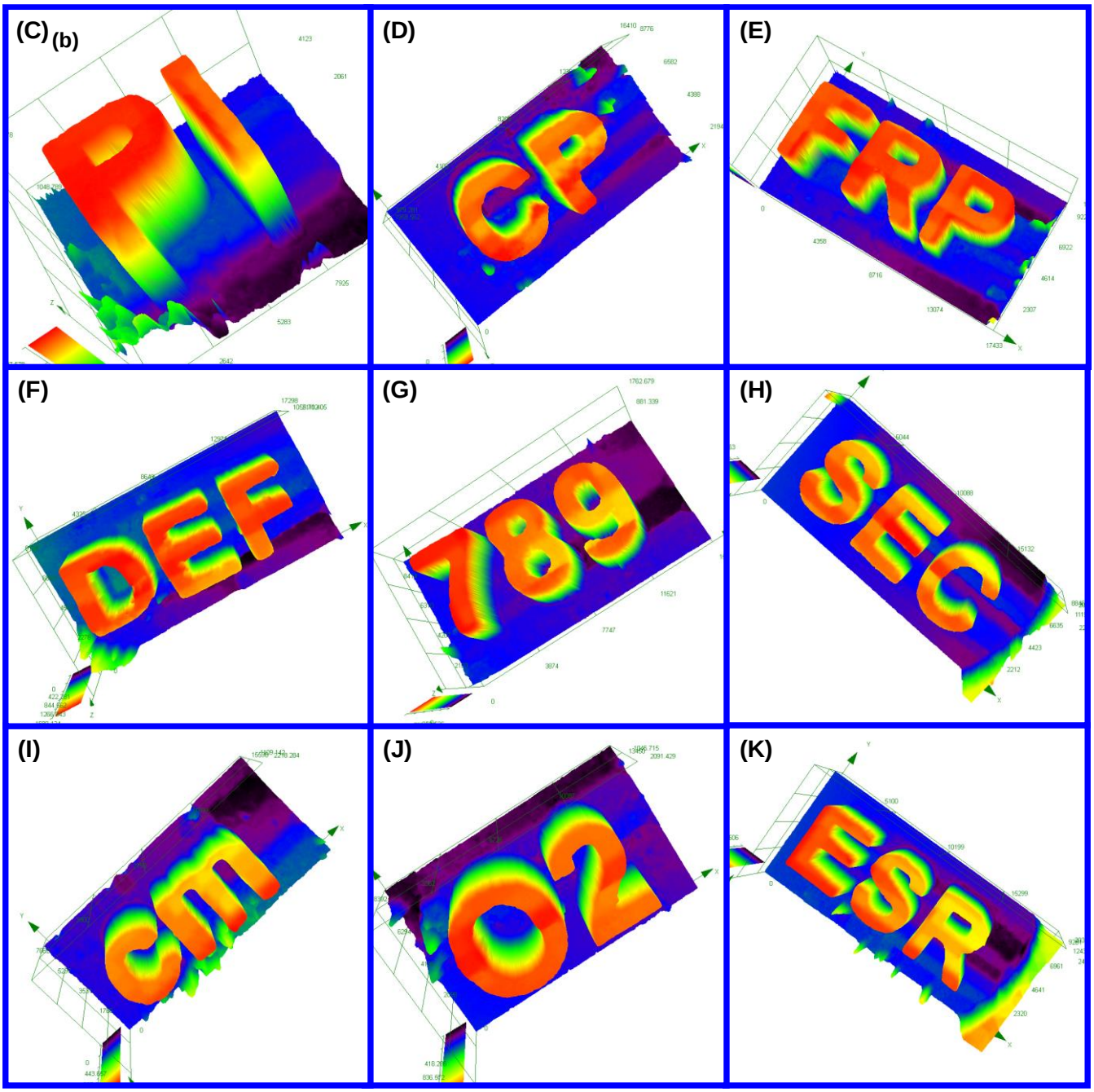


Figure S2. Photocomposites produced upon Near-UV light (LED @395 nm), Belt Speed = 2 m/min, using the free radical polymerization (FRP) in the presence of 50% glass fibers/50% acrylate resin (thickness = 2 mm for one layer of glass fibers) for different systems: **(6)** 0.2% **Coum-B1** + 1% Iod + 1%

NPG in TMPTA; **(7)** 0.2% **KC-G** + 1% Iod + 1% NPG in TMPTA; **(8)** 0.2% **KC-D** + 1% Iod + 1% NPG in TMPTA; **(9)** 0.2% **KC-E** + 1% Iod in TMPTA; and **(10)** 0.2% **KC-G** + 1% EDB in TMPTA.

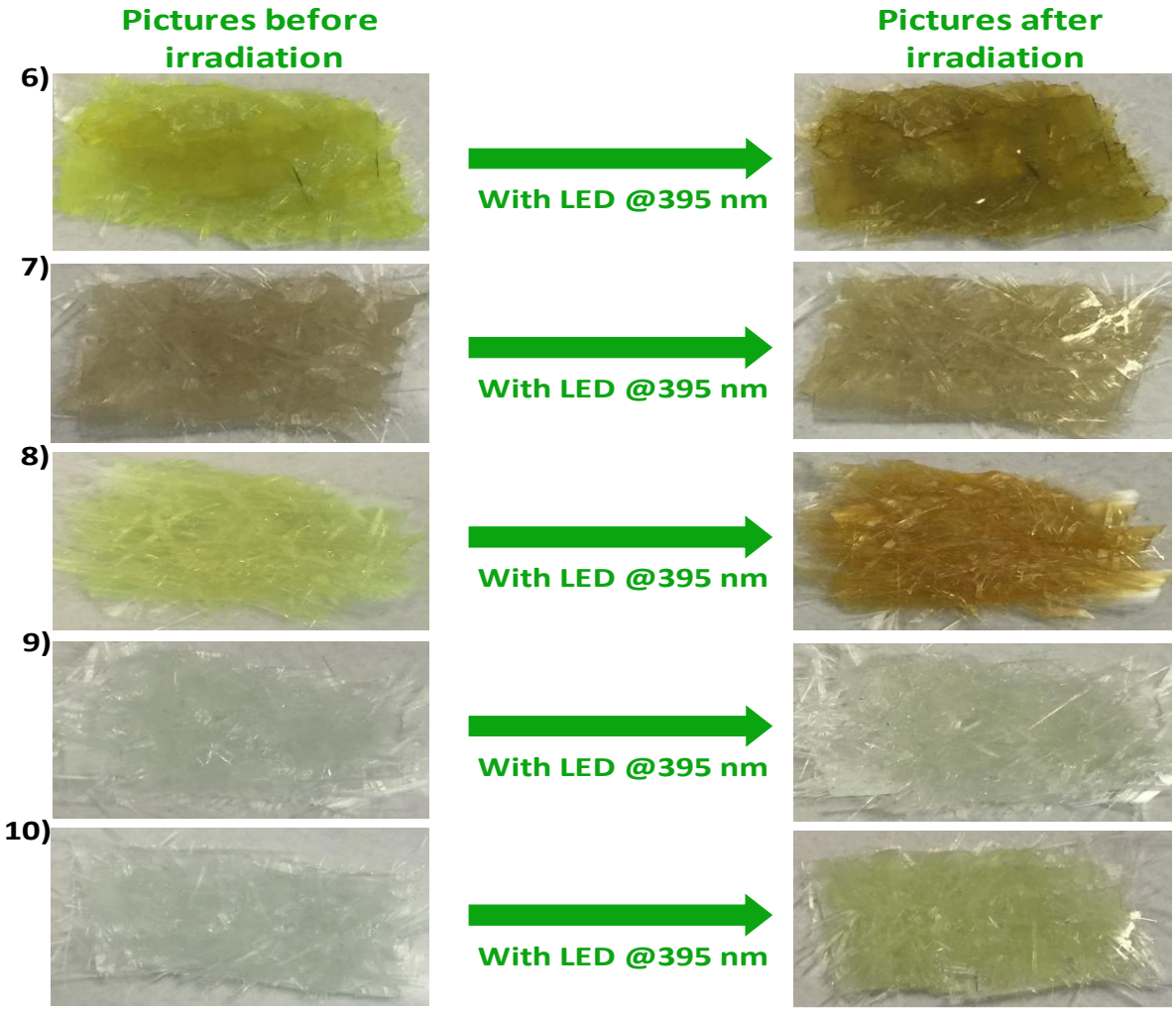
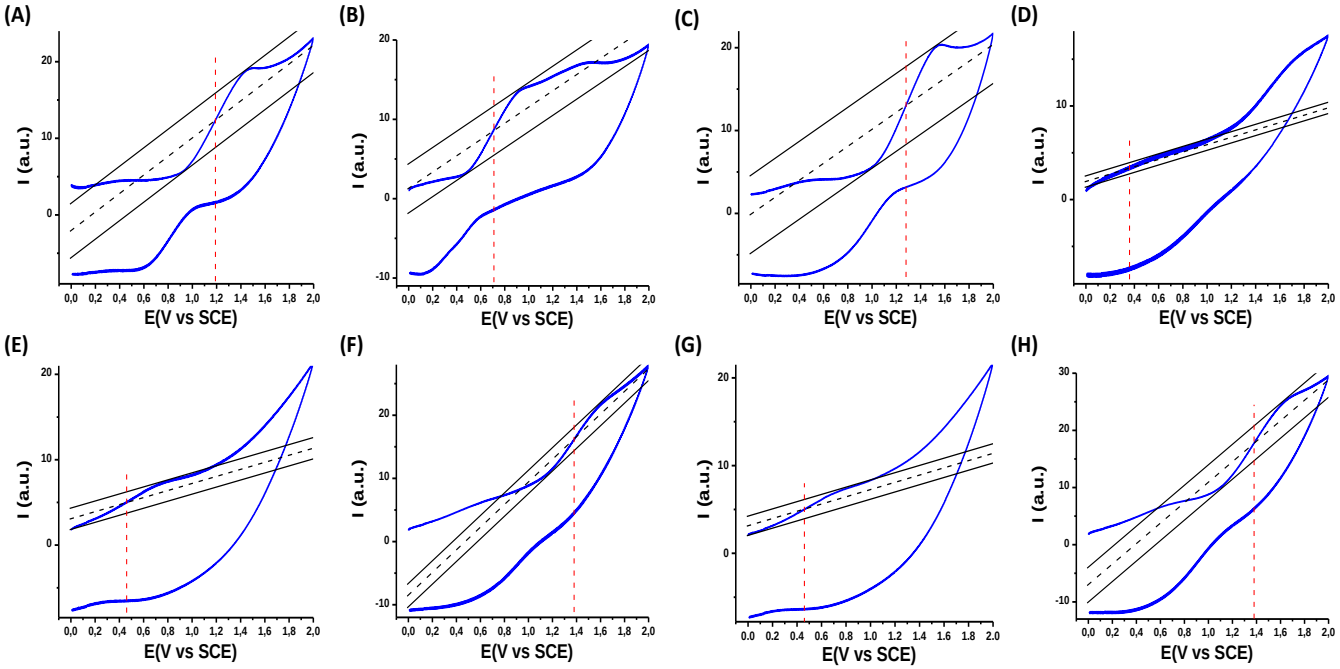


Table S1. Number of passes to be tack-free for impregnated glass fibers with **acrylate resin** using Near-UV conveyor (LED @395 nm), belt speed used = 2 $m.min^{-1}$.

One layer of glass fibers (50% glass fibers/50% acrylate resin)	**At the surface**	**On the bottom**
(1) 0.2% KC-E + 1% Iod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 1 pass
(2) 0.2% KC-E + 1% EDB in TMPTA	T.F. after 1 pass	T.F. after 1 pass
(3) 0.2% KC-F + 1% Iod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 1 pass
(4) 0.2% KC-C + 1% Iod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 1 pass
(5) 0.2% KC-E + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 1 pass
(6) 0.2% Coum-B1 + 1% Iod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 3-4 passes
(7) 0.2% KC-G + 1% Iod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 2-3 passes
(8) 0.2% KC-D + 1% Iod + 1% NPG in TMPTA	T.F. after 1 pass	T.F. after 1-2 passes
(9) 0.2% KC-E + 1% Iod in TMPTA	T.F. after 1 pass	T.F. after 3-4 passes
(10) 0.2% KC-G + 1% EDB in TMPTA	T.F. after 1 pass	T.F. after 2-3 passes

T.F.: Tack-free

Figure S3. Cyclic voltammetry experiments of the different Coumarins and Keto-coumarins investigated in this work: (A) **Coum-A1**; (B) **Coum-B1**; (C) **KC-C**; (D) **KC-D**; (E) **KC-E**; (F) **KC-F**; (G) **KC-G**; and (H) **KC-H**, respectively.

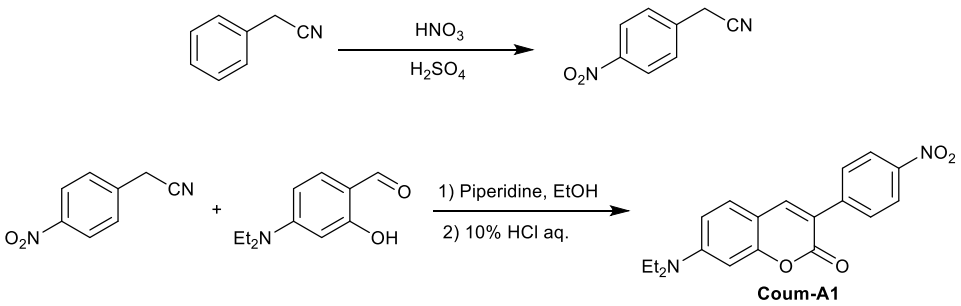

(A)
(B)
(C)
(D)
(E)
(F)
(G)
(H)
I (a.u.)
E(V vs SCE)

General methods and materials

^{1}H NMR spectra were recorded on Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: δ = 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, dd = double duplet, bs = broad signal, m = multiplet, quint = quintet), coupling constants (Hz). ^{13}C NMR spectra were recorded on Varian MR400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: δ = 77.0 ppm). LC-electrospray ionization mass spectra (ESI-MS) were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240-400 mesh silica gel. Purification on preparative thin layer chromatography was done on Merck TLC silica gel 60 F_{254}.

All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques. Synthesis grade solvents were used as purchased.

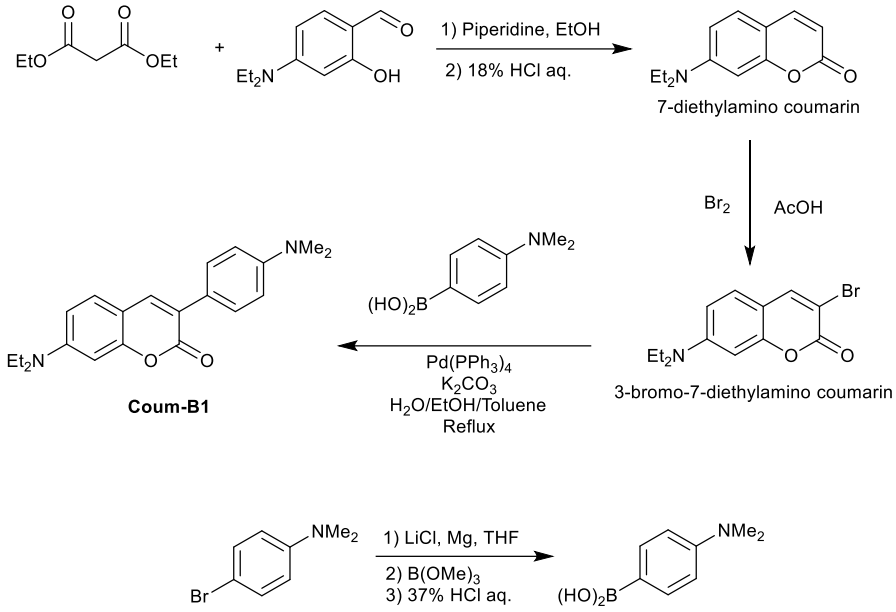
Synthesis of Coum-A1



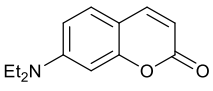
Coum-A1 was prepared according to reported procedure:[1] 4-diethylamino-salicyl aldehyde (1.2 mmol, 0.232 g) was dissolved in absolute ethanol (7 mL) under inert atmosphere. 2-(4-nitrophenyl)acetonitrile[2] (1.2 mmol, 0.200 g) was added to the solution followed by 5 drops of piperidine. The reaction mixture was stirred overnight, and the solvent was evaporated under reduce pressure to obtain a red solid. The solid was added to 10% HCl aq. (10 mL) and the suspension was refluxed for 6 hours. The mixture was cooled at room temperature, the result orange solid was filtered off and washed with water. The solid was purified by flash chromatography (SiO_2, cyclohexane:ethyl acetate 8:2) to obtain **Coum-A1** as orange solid (43%, 0.516 mmol, 0.174 g); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.26 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.83 (s, 1H), 7.36 (d, *J* = 8.9 Hz, 1H), 6.64 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.54 (d, *J* = 2.1 Hz, 1H), 3.46 (q, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 6H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ: 160.9, 156.7,

151.4, 146.7, 142.5, 142.1, 129.6, 128.6 (2C), 123.5 (2C), 117.7, 109.4, 108.7, 97.0, 45.0, 12.4; ESI-MS *m/z*: 339.2 $[M+H]^+$.

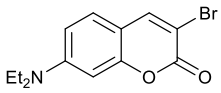
Synthesis of Coum-B1



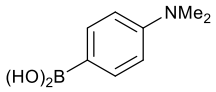
7-diethylaminocoumarin and 3-bromo-7-diethylaminocoumarin were prepared according to literature procedure.[3]



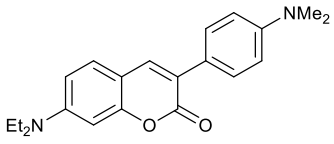
In a two necks round bottom flask under inert atmosphere were added 4-diethylamino salycilaldehyde (10 mmol, 2.2 g), absolute ethanol (20 mL), diethylmalonate (20 mmol, 3.2 g, 3.1 mL) and piperidine (1 mmol, 0.085 g, 99 µL). The solution was refluxed for 7 hours until disappearance of aldehyde, cooled at room temperature and the solvent was removed under reduced pressure. The residue was dissolved in DCM (20 mL), washed with 2 M HCl aq. (2 x 10 mL) and brine (2 x 10 mL). The organic phase was evaporated, the residue was suspended in 18% HCl aq. and refluxed for 2 hours. The solution was cooled at room temperature and 4M NaOH aq. was added until neutral pH. DCM (20 mL) was added and the two phases separated. The organic phase was washed with brine (2x 5 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure to obtain 7-diethylaminocoumarin as red solid (93%, 9.3 mmol, 2.02 g); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 9.3 Hz, 1H), 7.26 – 7.18 (m, 1H), 6.53 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.45 (d, *J* = 2.3 Hz, 1H), 6.00 (d, *J* = 9.3 Hz, 1H), 3.38 (q, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 6H).



To a solution of 7-diethylaminocoumarin (4.6 mmol, 0.998 g) in glacial acetic acid (10 mL) a solution of bromine (4.6 mmol, 0.735 g, 0.236 mL) in glacial acetic acid (5 mL) was added dropwise under stirring. After 30 minutes the solid was filtered and washed with water (3 x 10 mL) and dried under vacuum to give 3-bromo-7-diethylaminocoumarin in quantitative yield as orange solid.

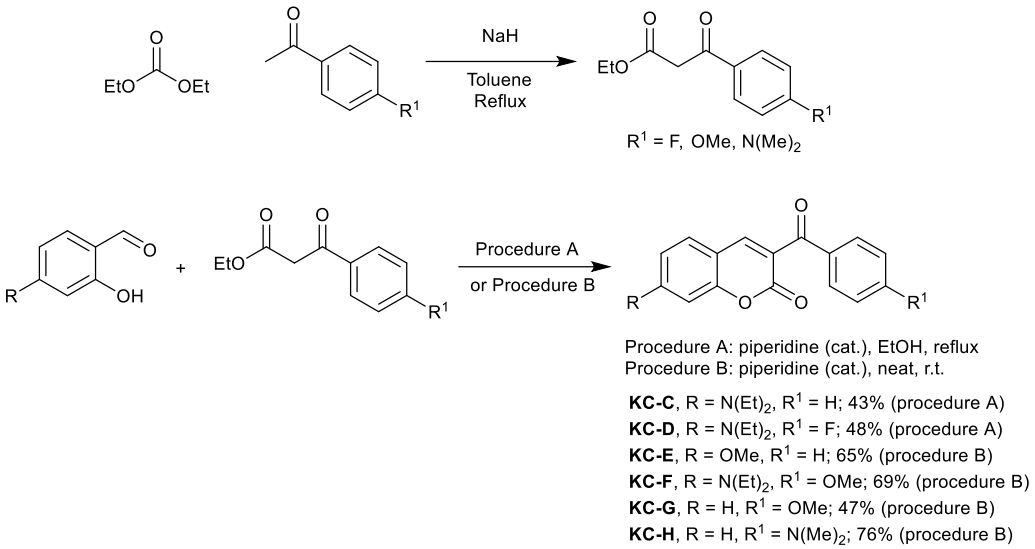


4-(dimethylamino)benzene boronic acid was prepared according to reported procedure[4]: to anhydrous LiCl under inert atmosphere, THF (2 mL), magnesium turnings (4.5 mmol, 100 mg) and DIBALH (1M in THF, 0.02 mmol) were added. A solution of 4-bromo-*N*,*N*-dimethylaniline (1.75 mmol, 350 mg) in THF (4 mL) was added dropwise to the mixture, and the reaction was stirred for 1 hours. The solution was cooled at 0°C, $B(OMe)_3$ (3.5 mmol, 364 mg, 0.391 mL) was added and the solution was stirred for 1 hour. 37% HCl aq. was slowly added until pH = 4 and the solution was stirred for 30 minutes. The mixture was extracted with AcOEt (3 x 10 mL), the organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure to obtain 4-(dimethylamino)benzene boronic acid as white solid (57% 1.0 mmol, 0.166 g); ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.11 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.07 (s, 6H).



To a degassed mixture of water:ethanol:toluene (10:5:5 mL) under inert atmosphere 3-bromo-7-diethylaminocoumarin (0.17 mmol, 0.050 g), $Pd(PPh_3)_4$ (0.008 mmol, 9.2 mg), 4-(dimethylamino) benzene boronic acid (0.34 mmol, 0.056 g) e K_2CO_3 (0.51 mmol, 0.070 g) were added. The mixture was refluxed for 7 hours, cooled at room temperature and the solvents were evaporated under reduced pressure. The reside was diluted with DCM (40 mL) and filtered through Celite®. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography (SiO_2, cyclohexane:ethyl acetate 95:5) to give **Coum-B1** (70%, 0.12 mmol, 0.040 g) as yellow solid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.63 (m, 3H), 7.30 (d, *J* = 8.8 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.59 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.54 (d, *J* = 2.0 Hz, 1H), 3.43 (q, *J* = 7.1 Hz, 4H), 2.99 (s, 6H), 1.22 (t, *J* = 7.1 Hz, 6H); ^{13}C-NMR (400 MHz, $CDCl_3$) δ: 162.0, 155.6, 150.1, 149.8, 137.9, 128.9 (2C), 128.4, 123.7, 121.2, 112.2 (2C), 109.5, 108.7, 97.2, 44.8 (2C), 40.5 (2C), 12.5 (2C); ESI-MS *m/z*: 337.2 $[M+H]^+$.

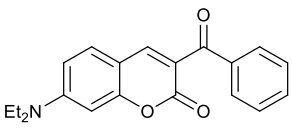
Synthesis of coumarins KC



Ethyl 3-(4'-substituted-phenyl)-3-oxopropionates were prepared according literature procedure: ethyl 3-(4'-fluorophenyl)-3-oxopropionate,[5] ethyl 3-(4'-methoxyphenyl)-3-oxopropionate,[6] ethyl 3-(4'-dimethylaminophenyl)-3-oxopropionate.[7]

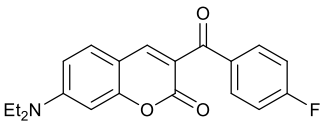
General Procedure A: To a solution of the salicylaldehyde derivative (2 mmol) in EtOH (25 mL), the ketoesters (2 mmol) and 10 drops of piperidine were added. The solution was refluxed for 1 hour and the disappearance of the starting materials was confirmed by TLC analysis. The mixture was cooled at room temperature and the solvent was removed under reduce pressure. The residue was subject of flash chromatography (SiO_2, cyclohexane:ethyl acetate 95:5) to give the desired product. Further recrystallization from ethanol improve the purity of the compound.

General procedure B: Piperidine (4 drops) was slowly added to a vial contain the salicylaldehyde derivative (2 mmol) and the ketoesters (2 mmol) under vigorous stirring. After disappearance of the starting material (1-3 hours) the mixture was diluted with DCM (15 mL) and washed with 1M HCl (2 x 5 mL). The organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure to obtain the desired product as red solid. Pure compounds were obtained after recrystallization from ethanol.

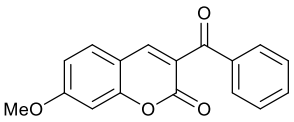


KC-C (43%, 0.86 mmol, 0.276 g):[7, 8] Prepared according to the general procedure A; ^{1}H NMR (401 MHz, $CDCl_3$) δ: 8.05 (s, 1H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 8.9 Hz, 1H), 6.59 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.47 (d, *J* = 2.3 Hz, 1H), 3.43 (q, *J* = 7.1 Hz, 4H), 1.21 (t, *J* = 7.1 Hz, 7H);

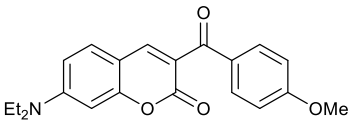
^{13}C NMR (101 MHz, $CDCl_3$) δ: 192.4, 159.9, 157.9, 152.5, 147.7, 137.8, 132.6, 130.9, 129.2 (2C), 128.1 (2C), 117.4, 109.5, 107.7, 96.9, 45.0 (2C), 12.4 (2C); ESI-MS *m/z*: 322.2 $[M+H]^+$.



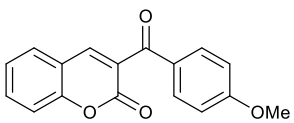
KC-D (48%, 0.96 mmol, 0.325 g): Prepared according to the general procedure A; ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.87 – 7.79 (m, 2H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.61 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.49 (d, *J* = 2.3 Hz, 1H), 3.44 (q, *J* = 7.1 Hz, 5H), 1.23 (t, *J* = 7.1 Hz, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 191.4, 165.7 (d, *J* = 254.0 Hz), 160.0, 158.5, 152.8, 148.0, 134.4, 132.1 (d, *J* = 9.3 Hz), 131.2, 117.8, 115.5 (d, *J* = 22.0 Hz), 109.8, 108.1, 97.1, 45.3, 12.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -105.9 (m, 1F); ESI-MS *m/z*: 340.3 $[M+H]^+$.



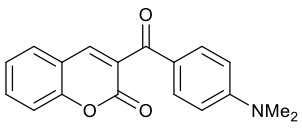
KC-E (43%, 1.3 mmol, 0.364 g):[7,8] Prepared according to the general procedure B; ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.88 – 7.80 (m, 2H), 7.63 – 7.54 (m, 1H), 7.52 – 7.41 (m, 3H), 6.90 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.86 (d, *J* = 2.3 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 192.0, 164.6, 158.7, 157.1, 146.4, 136.7, 133.4, 130.4, 129.5 (2C), 128.4 (2C), 122.9, 113.5, 111.9, 100.7, 56.0; ESI-MS *m/z*: 281.2 $[M+H]^+$.



KC-F (69%, 1.38 mmol, 0.484 g): Prepared according to the general procedure B; ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.60 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.50 (d, *J* = 2.3 Hz, 1H), 3.86 (s, 3H), 3.44 (q, *J* = 7.1 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 163.5, 159.9, 158.1, 152.3, 147.1, 131.9 (2C), 130.7, 130.4, 118.6, 113.6 (2C), 109.5, 107.9, 97.0, 55.5, 45.1, 12.5; ESI-MS *m/z*: 352.3 $[M+H]^+$.



KC-G (47%, 0.94 mmol, 0.263 g):[7, 9] Prepared according to the general procedure B; ^{1}H NMR (401 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.93 – 7.87 (m, 2H), 7.68 – 7.58 (m, 2H), 7.43 – 7.39 (m, 1H), 7.36 (td, *J* = 7.6, 1.1 Hz, 1H), 7.00 – 6.93 (m, 2H), 3.89 (s, 3H)**;** ^{13}C NMR (101 MHz, $CDCl_3$) δ: 189.8, 164.2, 158.7, 154.4, 144.5, 133.3, 132.1 (2C), 129.0, 129.0, 127.5, 124.9, 118.3 (2C), 116.9, 113.9, 55.5; ESI-MS *m/z*: 281.1 $[M+H]^+$.



KC-H (76%, 1.52 mmol, 0.446 g): Prepared according to the general procedure B; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.81 – 7.77 (m, 2H), 7.61 – 7.50 (m, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.27 (m, 1H), 6.72 – 6.51 (m, 2H), 3.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.8, 164.5, 154.4, 154.1, 143.4, 132.8, 132.3 (2C), 128.7, 128.4, 124.7, 123.2, 118.3, 116.8, 110.7 (2C), 40.0; ESI-MS *m/z*: 294.2 $[M+H]^+$.

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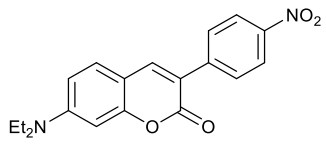
Copies of NMR spectra



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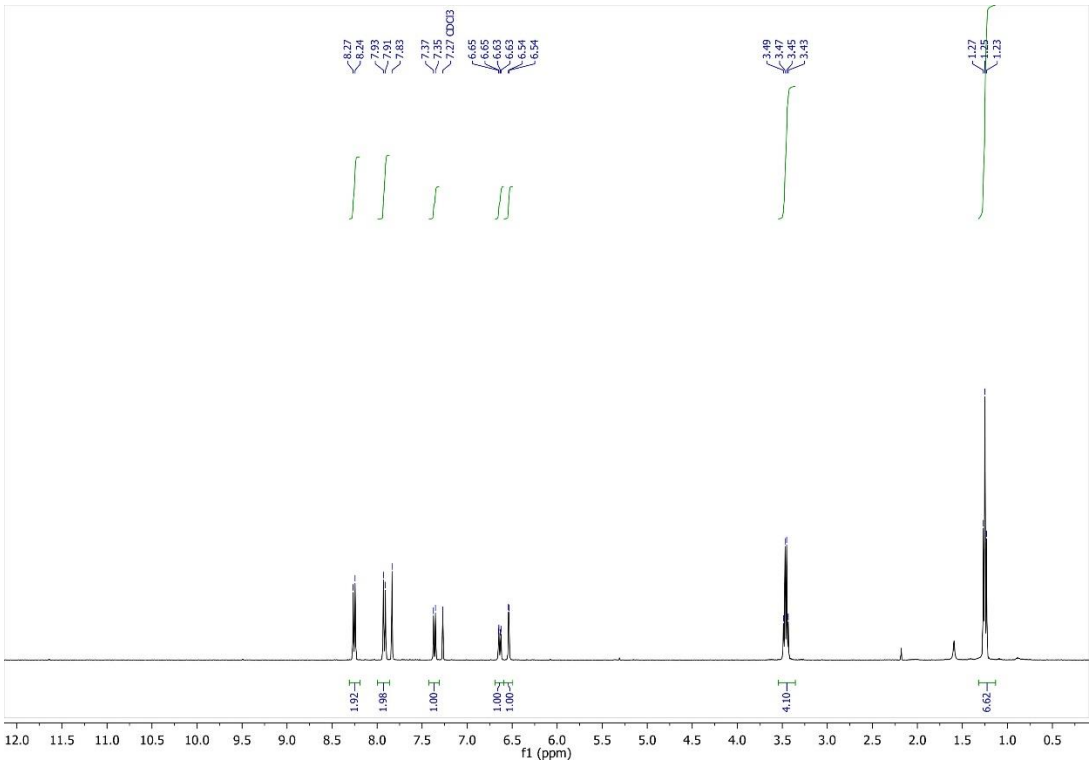

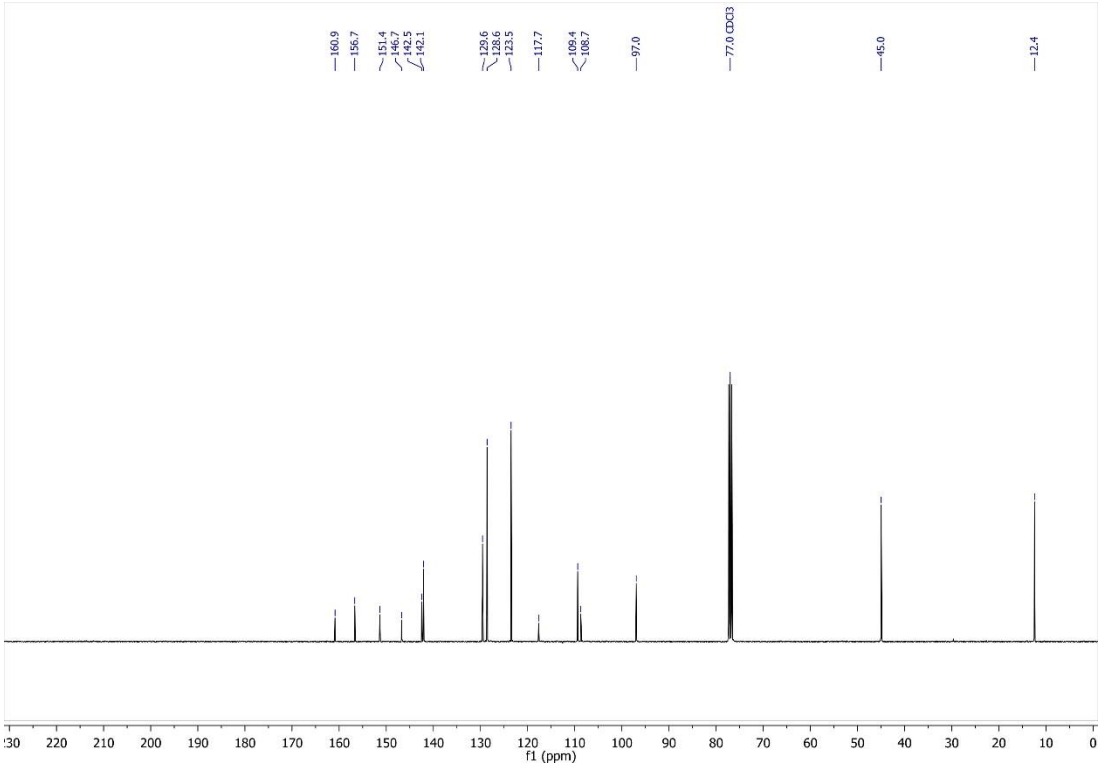

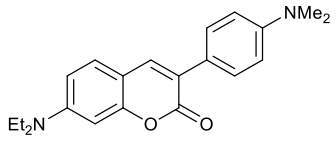
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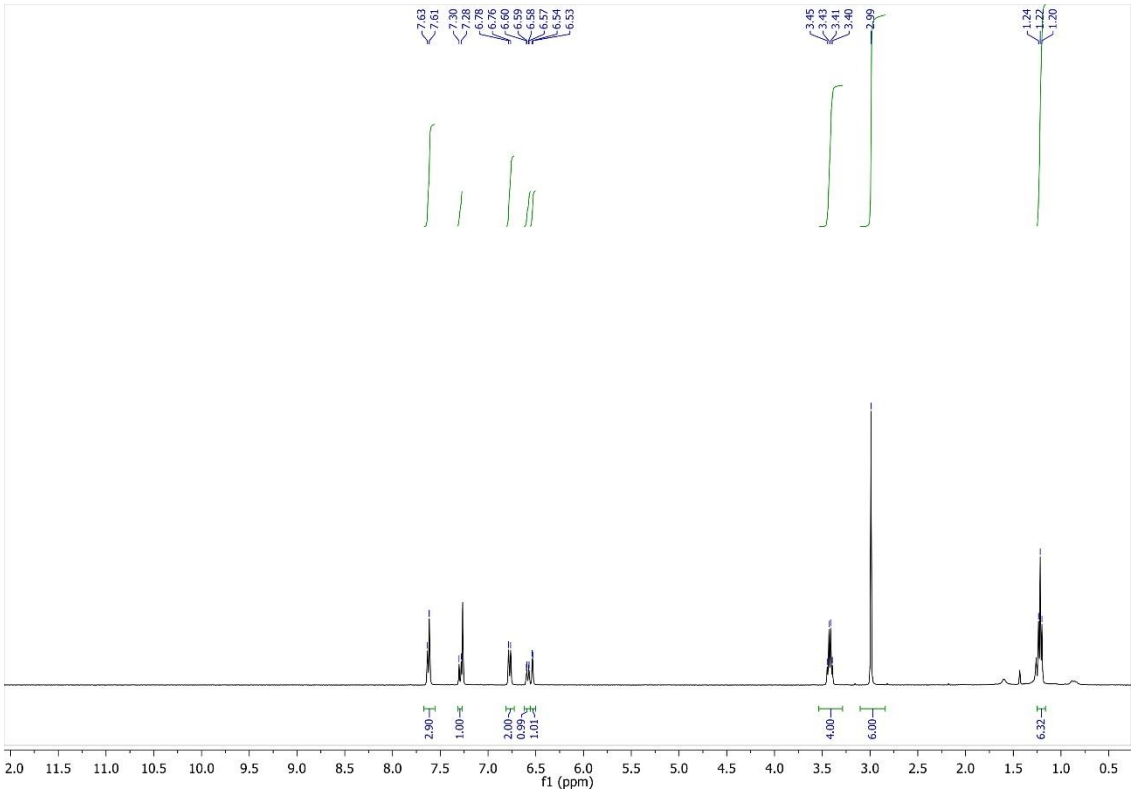
Et2N
O
O

Coum-B1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7.61
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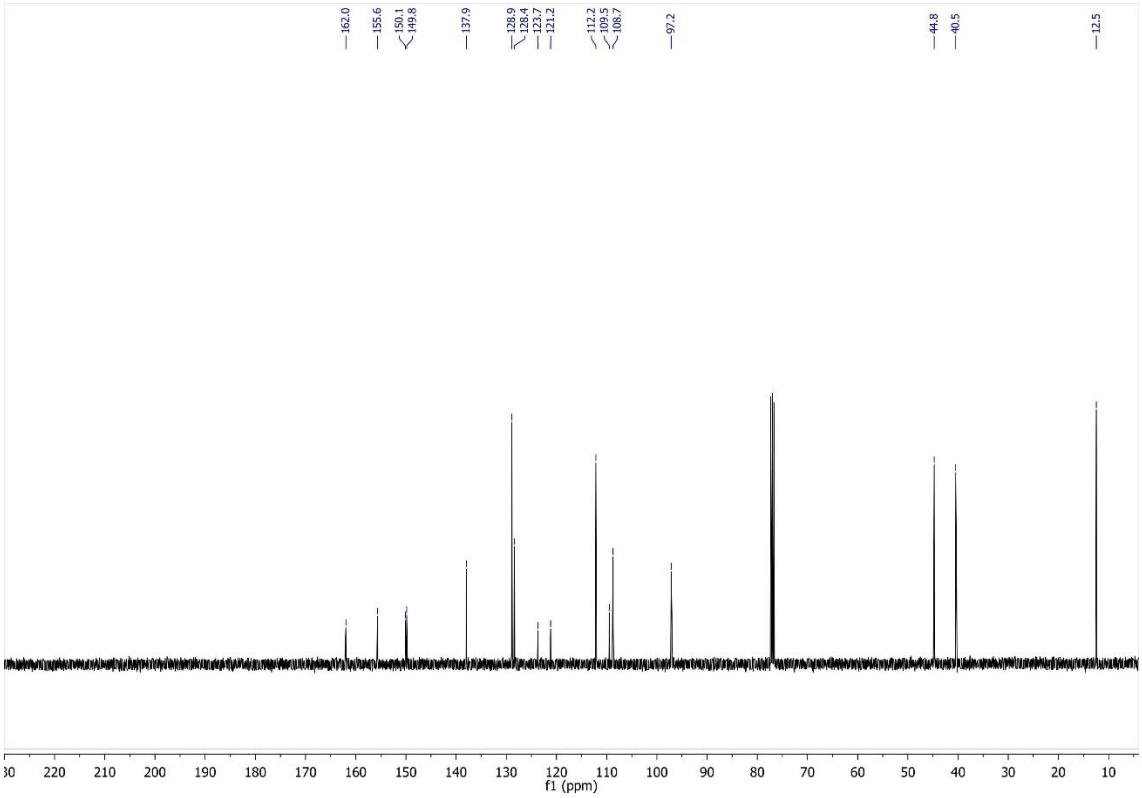
6.76
6.60
6.59
6.58
6.57
6.54
6.53
3.45
3.43
3.41
3.40
2.99
1.24
1.22
1.20
2.90
1.00
2.00
0.99
1.01
4.00
6.00
6.32
f1 (ppm)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109.5
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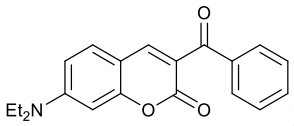
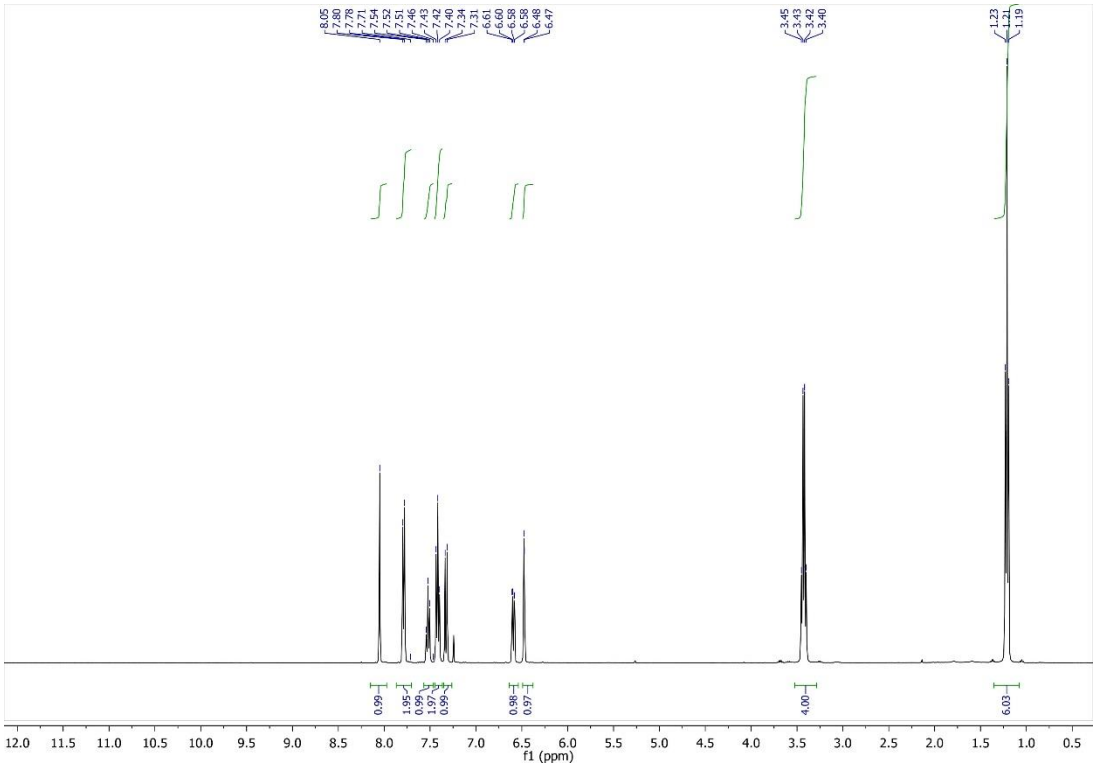
97.2
44.8
40.5
12.5
f1 (ppm)


O
Et2N
O
O

KC-C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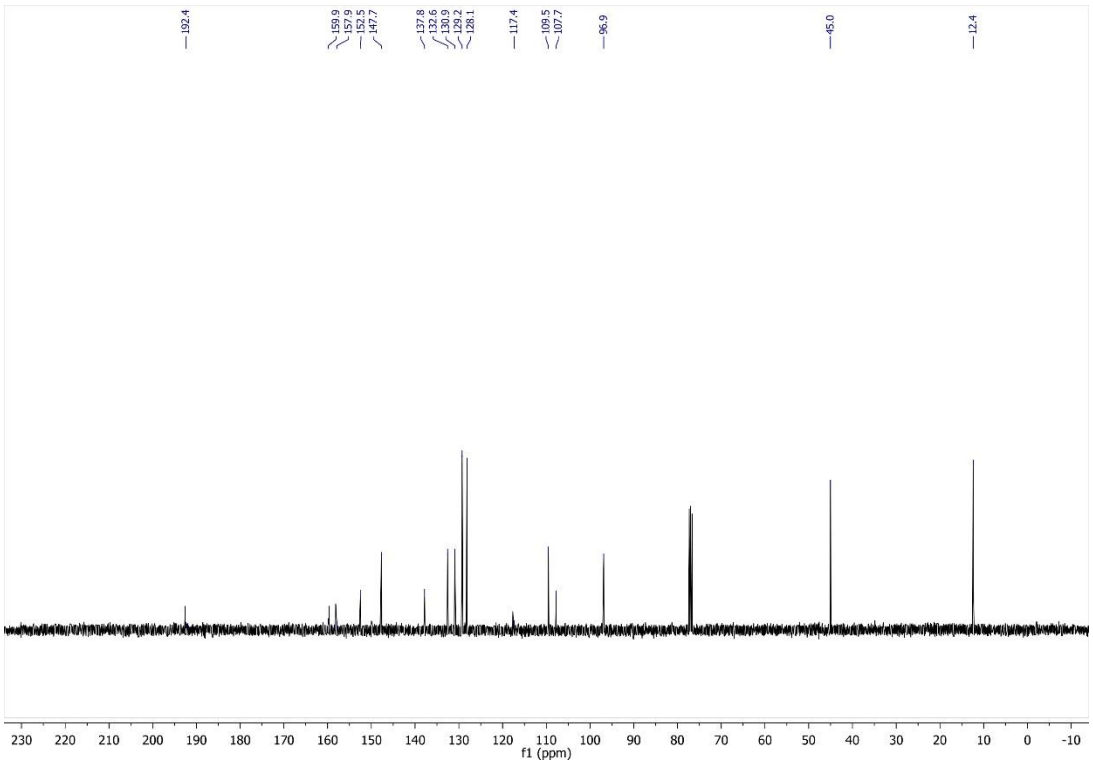
7.40
7.34
7.31
6.61
6.60
6.58
6.58
6.48
6.47
3.45
3.43
3.42
3.40
1.23
1.21
1.19
0.99
1.95
0.99
1.97
0.99
0.98
0.97
4.00
6.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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147.7
137.8
132.6
130.9
129.2
128.1
117.4
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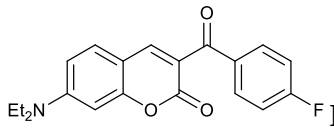
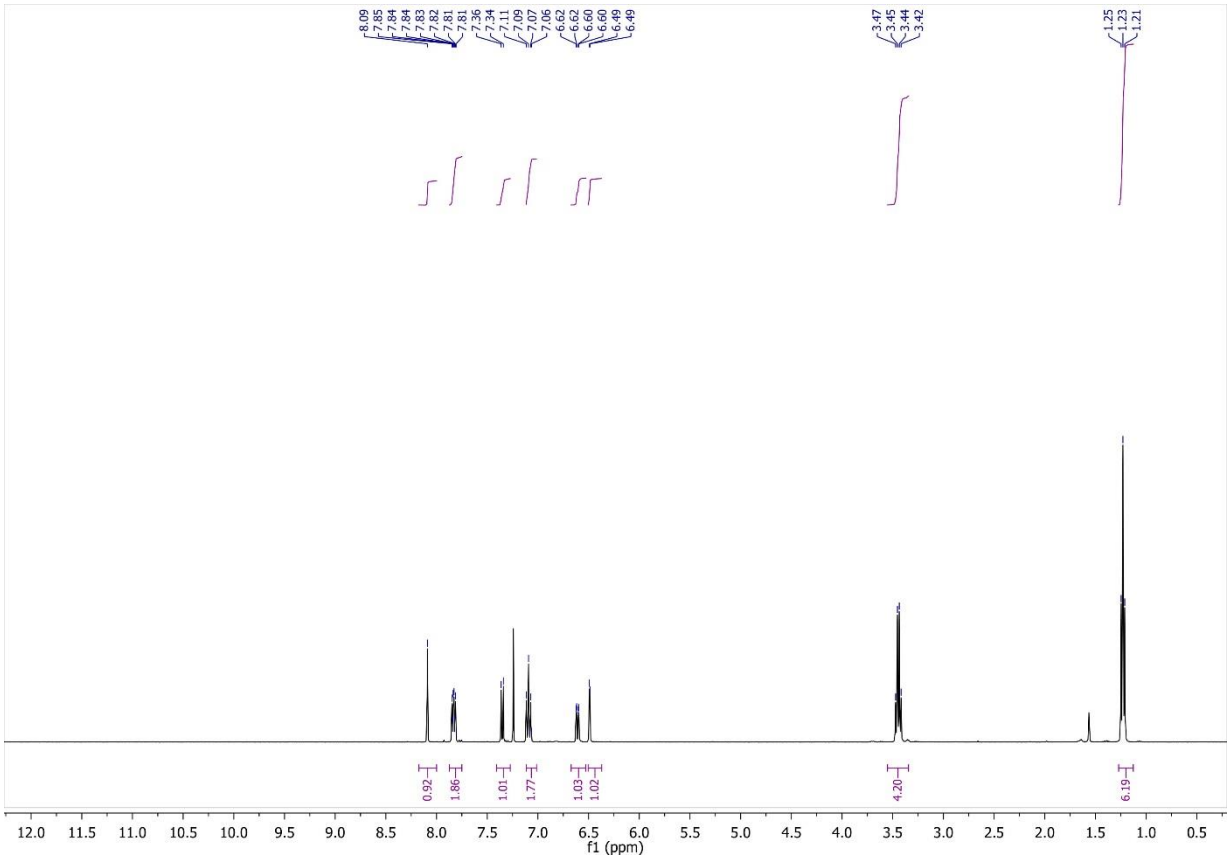
96.9
45.0
12.4
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
Et2N
O
O
F

KC-D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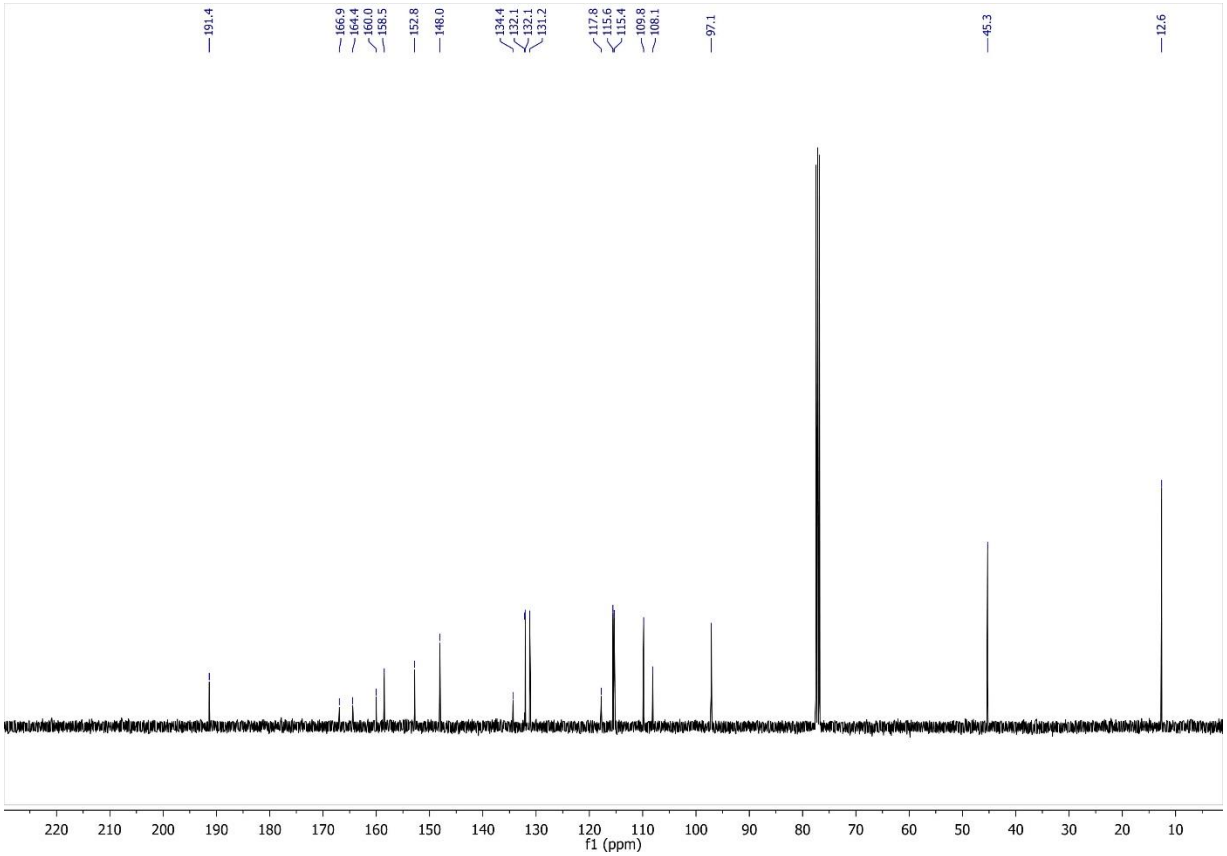
7.82
7.81
7.81
7.36
7.34
7.11
7.09
7.07
7.06
6.62
6.62
6.60
6.60
6.49
6.49
3.47
3.45
3.44
3.42
1.25
1.23
1.21
0.92
1.86
1.01
1.77
1.03
1.02
4.20
6.19
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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152.8
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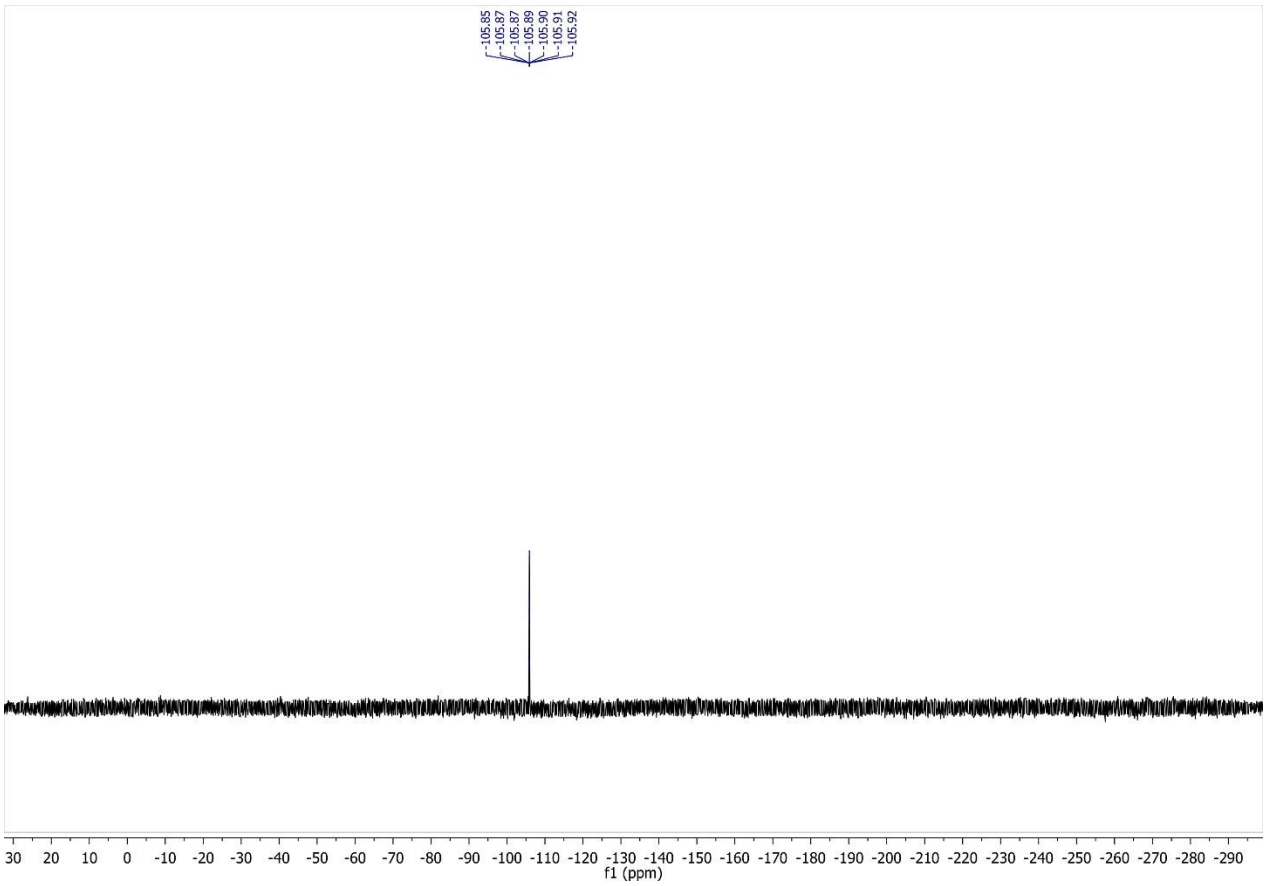
134.4
132.1
132.1
131.2
117.8
115.6
115.4
109.8
108.1
97.1
45.3
12.6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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-105.87
-105.87
-105.89
-105.90
-105.91
-105.92
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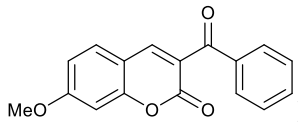
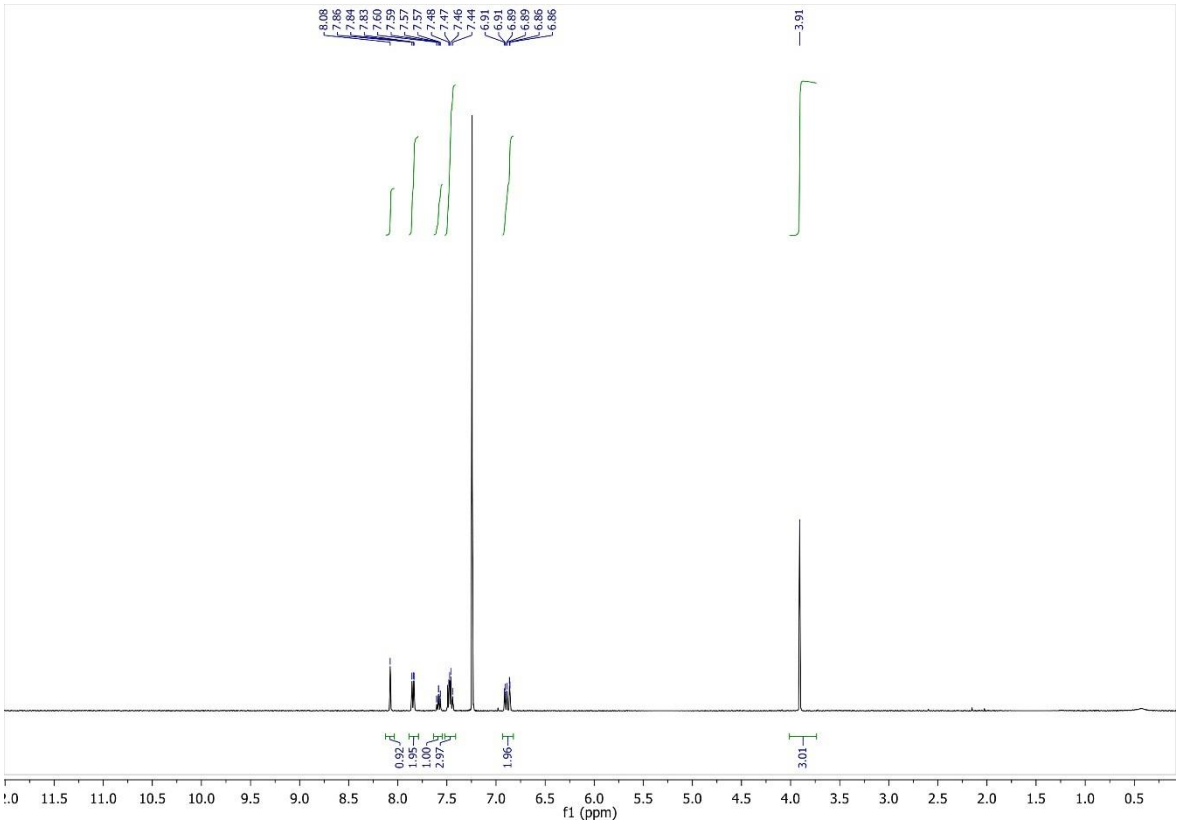
f1 (ppm)


O
MeO
O
O

KC-E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6.91
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1.00
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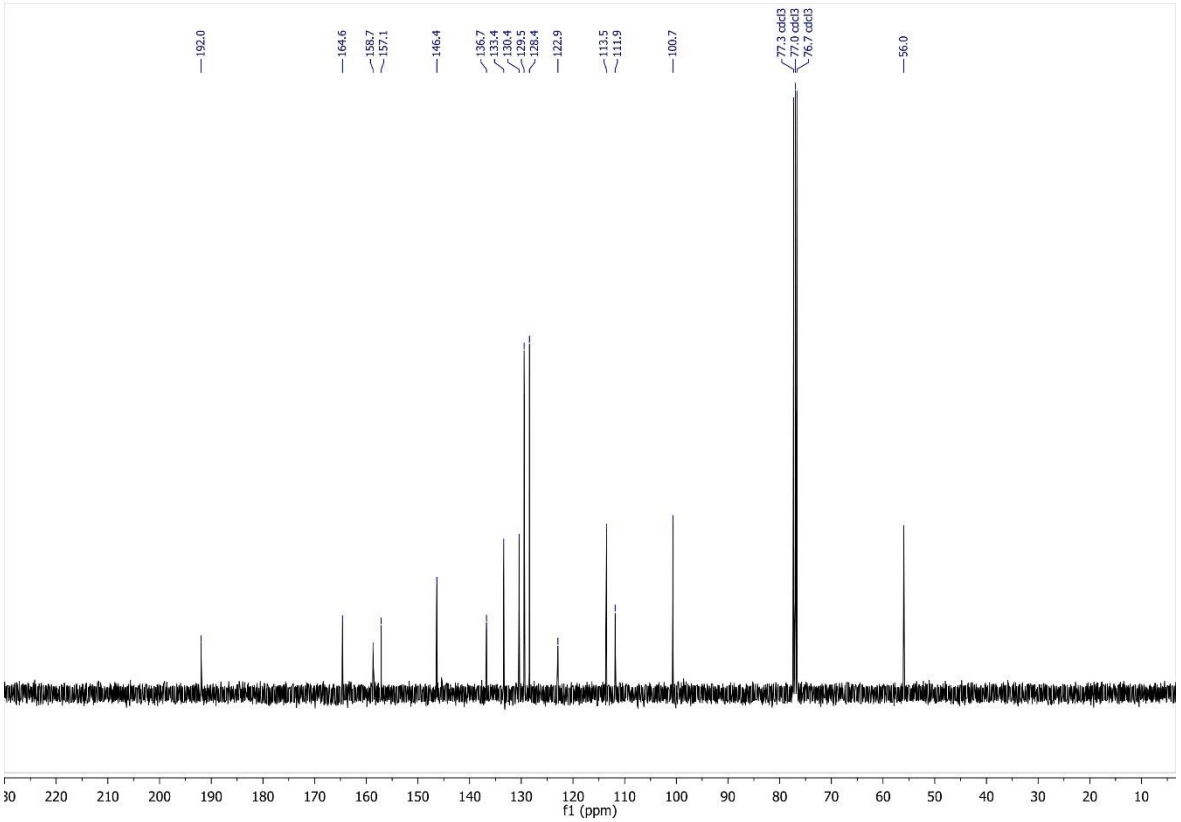
3.01
f1 (ppm)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158.7
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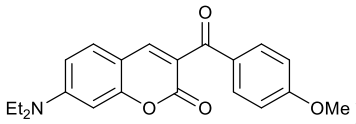
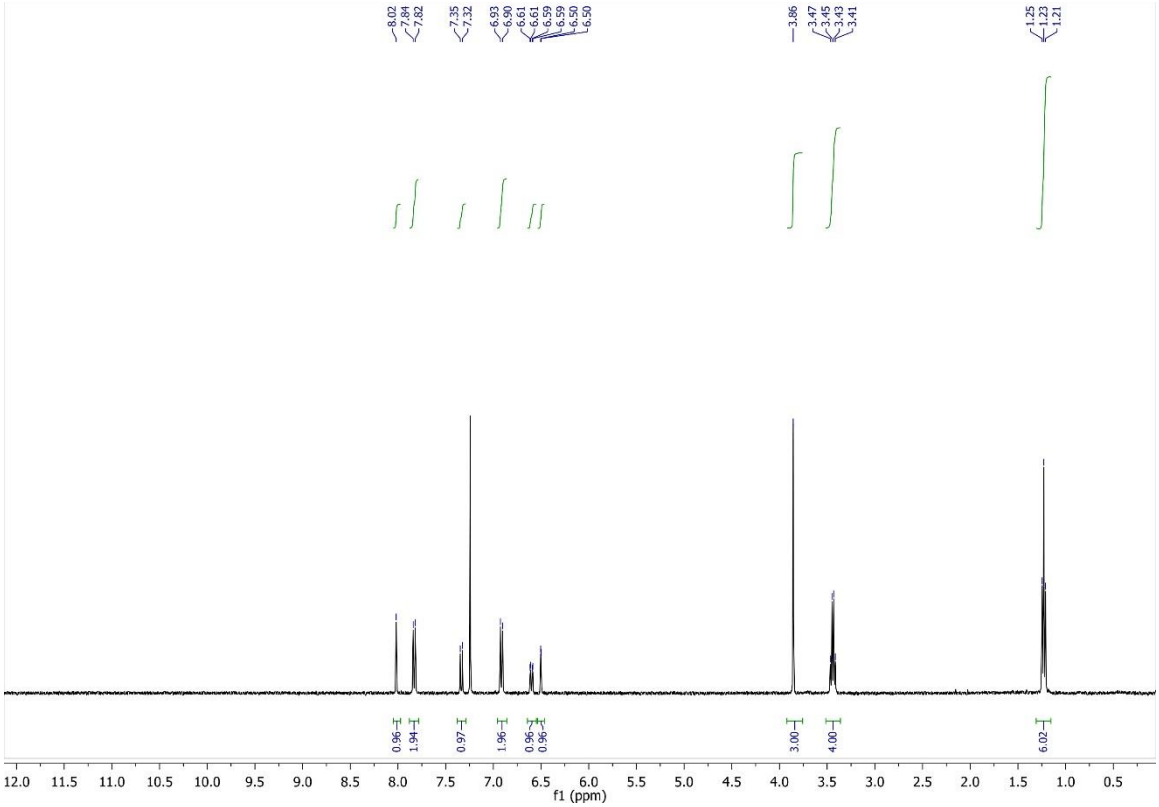
146.4
136.7
133.4
130.4
129.5
128.4
122.9
113.5
111.9
100.7
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
56.0
f1 (ppm)


O
Et2N
O
O
OMe

KC-F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6.50
6.50
3.86
3.47
3.45
3.43
3.41
1.25
1.23
1.21
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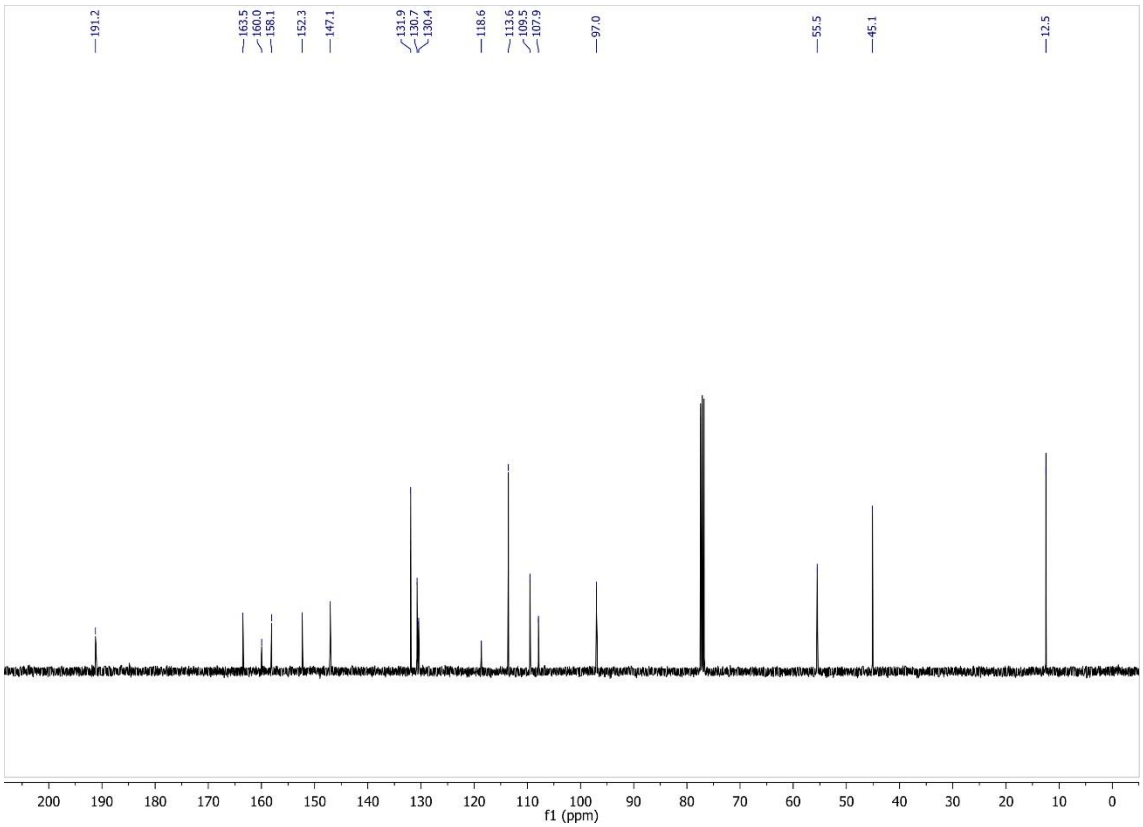
1.94
0.97
1.96
0.96
0.96
3.00
4.00
6.02
f1 (ppm)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152.3
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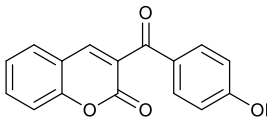
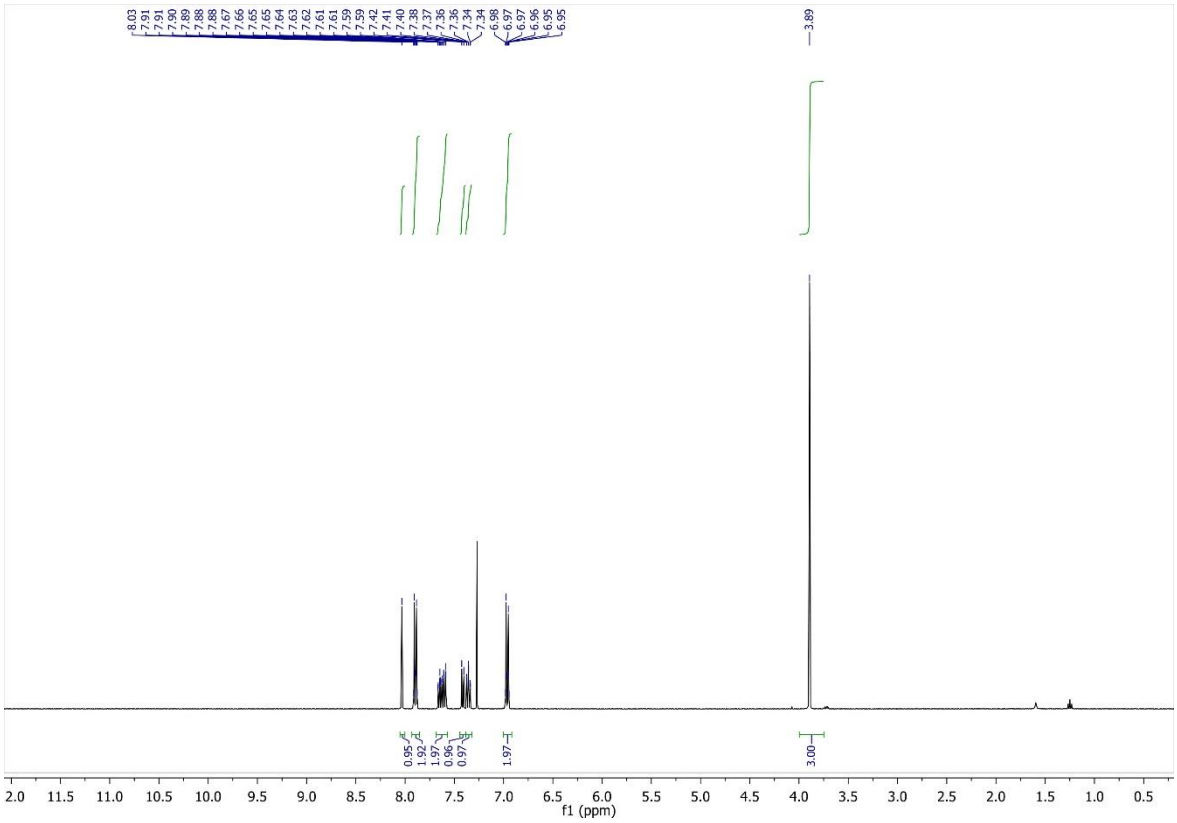
107.9
97.0
55.5
45.1
12.5
f1 (ppm)


O
O
O
OMe

KC-G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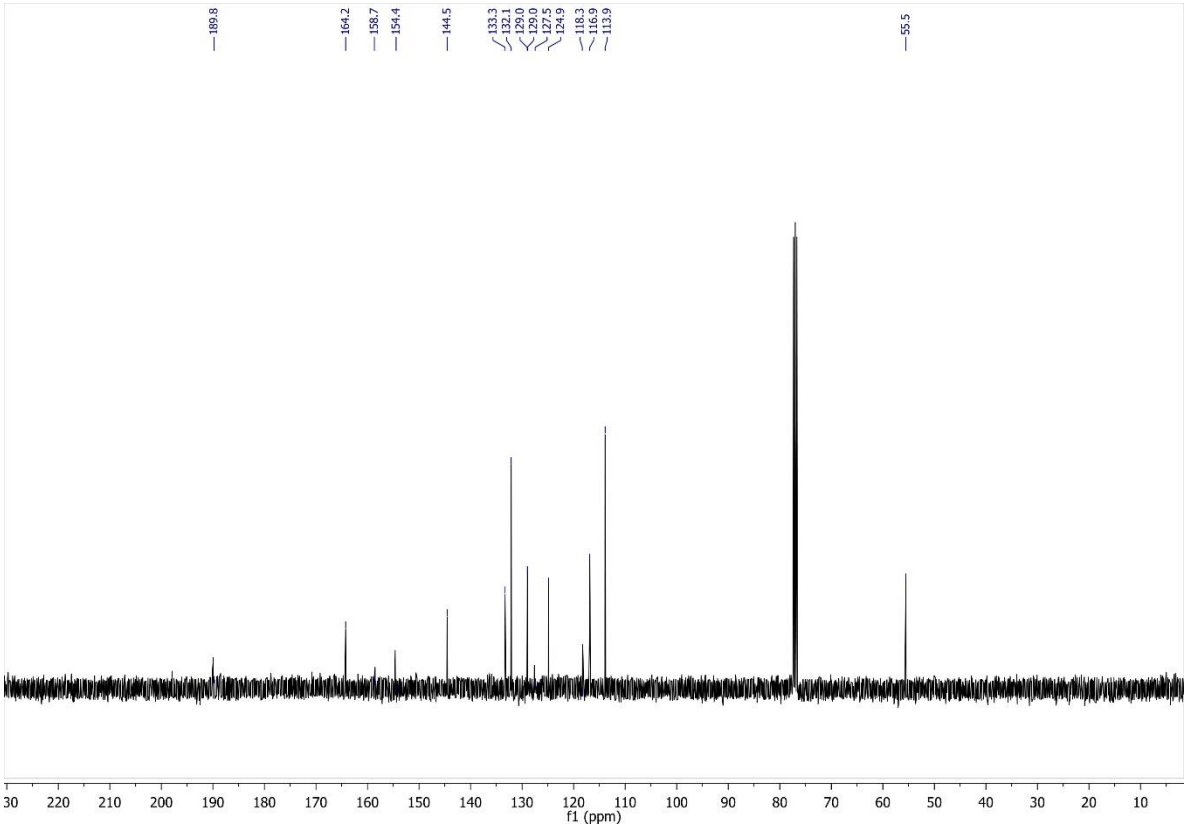
7.37
7.36
7.36
7.34
7.34
6.98
6.97
6.97
6.96
6.95
6.95
3.89
0.95
1.92
1.97
0.96
0.97
1.97
3.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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129.0
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124.9
118.3
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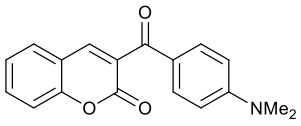
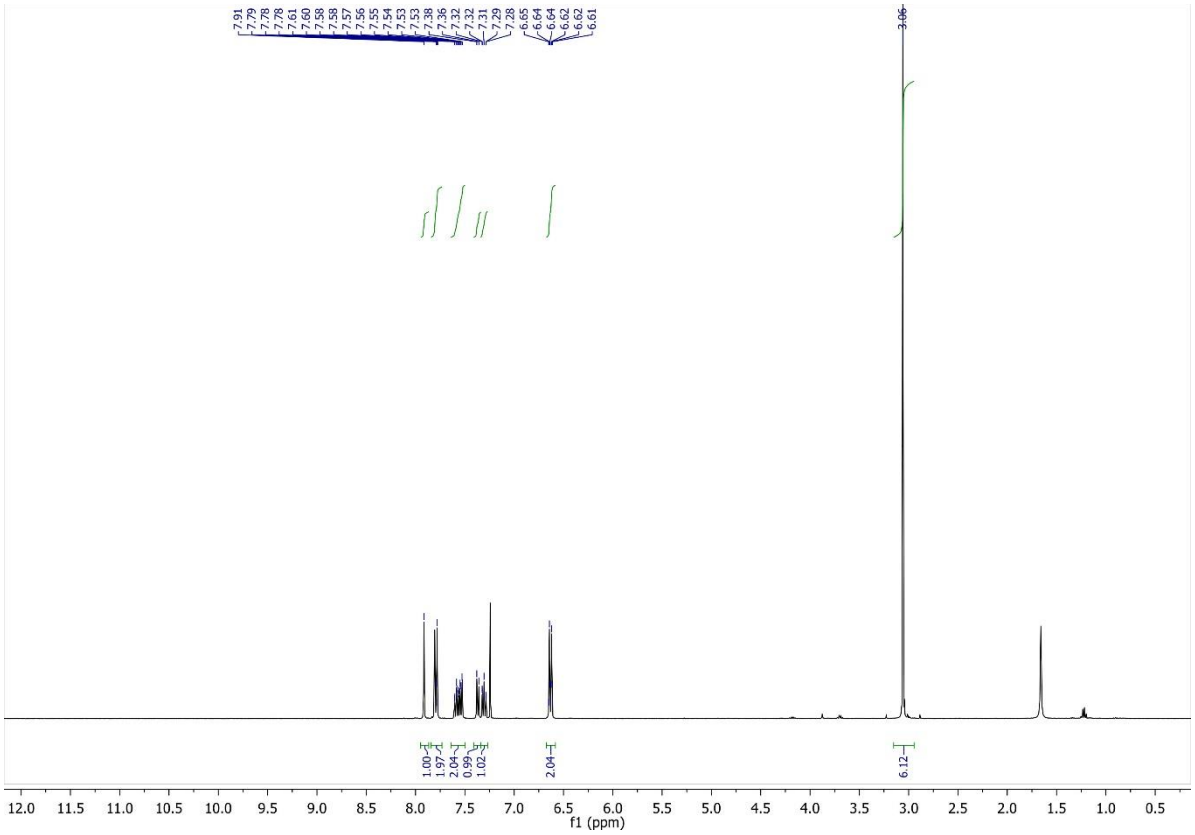
f1 (ppm)


O
O
O
NMe2

KC-H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7.31
7.29
7.28
6.65
6.64
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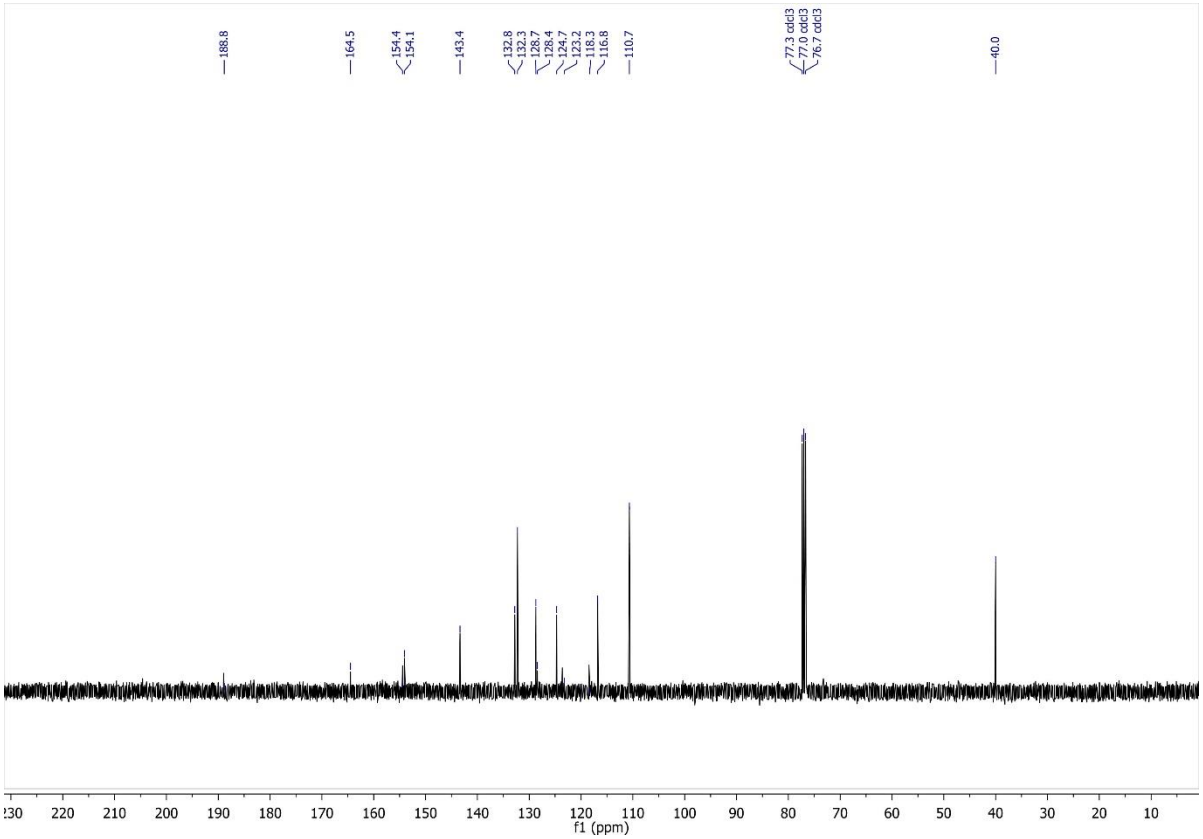
f1 (ppm)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154.1
143.4
132.8
132.3
128.7
128.4
124.7
123.2
118.3
116.8
110.7
77.3 cdcl3
77.0 cdcl3
76.7 cdcl3
40.0
f1 (ppm)