Supporting Information

Chemical Upcycling of Poly(bisphenol A carbonate) to Vinylene Carbonates through Organocatalysis

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1. General Information

All reagents and solvents were commercially available and used without any further purification. Poly(Bisphenol A carbonate) was purchased from Sigma Aldrech (M_w = 45,000 g.mol^{-1}, $Đ$ = 1.77). Nuclear magnetic resonance spectra were recorded on a Brüker DRX 300, Brüker ALS 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), Brüker ADVANCEIII 500, Brüker BBO probe, Brüker BBI probe (^{1}H: 500 MHz, ^{13}C: 125 MHz). Chemical shifts are given with reference to residual $CHCl_3$ central peaks: 7.26 ppm for proton, 77.16 ppm for carbon, respectively. J values are given in Hertz (Hz). Abbreviations are defined as follows: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quadruplet, hept = heptuplet, m = multiplet.

2. GC Method

GC method Gas chromatography (GC) analyses were performed using Schimadzu GC (GC-2025) apparatus equipped with a ZB-5-MS capillary column (30m length, 0.25 mm i.d., 0.50 µm film thickness). The carrier gas was N_2 at a total flow of 169.7 mL/min, a column flow at 1.65 mL/min and the injection mode is split (ratio 1:100). The column temperature was initially at 100°C for 1 min, and then was gradually increased to 260°C (25°C/min) and the temperature was kept at 260°C during 2.5 min. Finally, the temperature was increased to 315°C (45°C/min) and kept at 315°C during 5 min. The injector and FID temperature were respectively set at 300°C and 315°C.

3. General procedure for the preparation of vinylene carbonates from α-hydroxyketone and poly(bisphenol A carbonate)

The benzoin (1 mmol), poly(bisphenol A polycarbonate) (BPA-PC) (M_w = 45,000 g.mol^{-1}, $Đ$ = 1.77, 2 mmol of carbonate functionality based on the repeating unit), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (0.1 mmol, 10 mol %) and 2-MeTHF (2mL) were introduced into a (10 mL) sample tube. The reaction mixture was stirred at room temperature for 16 h. Ethyl acetate (5 mL) was added to the reaction mixture. The resulting mixture was washed three times with 1M NaOH (5 mL) and twice with brine (5 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography.

4. Scale-up procedure for the preparation vinylene carbonate from poly(bisphenol A carbonate)

Benzoin (10 mmol), poly(bisphenol A polycarbonate) (BPA-PC) (20 mmol of carbonate functionality based on the repeating unit), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (1 mmol, 10 mol %) and 2-MeTHF (40 mL) were introduced into a reaction flask. The reaction mixture was stirred at room temperature for 16 h. Ethyl acetate (50 mL) was added to the reaction mixture. The resulting mixture was washed three times with 1M NaOH (50 mL) and twice with brine (50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The crude vinylene carbonate was purified by recrystallization (EtOH). A solution of hydrochloric acid (5 M) was added to the aqueous layer until the pH reaches 1. The resulting mixture was extracted three times with ethyl acetate (50 mL). The resulting organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The crude bisphenol A was also purified by recrystallization (EtOH).

5. Procedures for the preparation vinylene carbonate from waste materials

Vinylene carbonates from a compact disk (CD)

A compact disk was cut into 1-2 cm pieces. Then, 508 mg of the CD (2 mmol of the monomer unit hypothesizing that the CD is composed of 100% PC-BPA) was introduced in a 10-mL reaction tube along with benzoin (1 mmol), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (0.1 mmol, 10 mol%) and 2-methylTHF (2mL). The reaction mixture was stirred at 50°C for 16 h. Ethyl acetate (5 mL) was added to the reaction mixture. The resulting mixture was washed three times with 1M NaOH (5 mL) and twice with brine (5 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The crude product was purified by recrystallization (EtOH) to give vinylene carbonate **2**. A solution of hydrochloric acid (5M) was added to the aqueous layer until the pH reaches 1. The resulting mixture was extracted three times with ethyl acetate (5 mL). The second organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. The crude bisphenol A was also purified by recrystallization (EtOH).

Vinylene carbonates from safety glasses

Used safety glasses were cut into small pieces (about 2 * 10 mm). The polycarbonate pieces (508 mg, 2 mmol of the monomer unit hypothesizing that the safety glasses are composed of 100% PC-BPA) were introduced in a 10-mL reaction tube and suspended in 2-methylTHF (2 mL). Benzoin (212 mg, 1 mmol) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (13.9 mg, 0.1 mmol, 10 mol%) were next introduced. The reaction tube was sealed and the reaction mixture was stirred at 50°C for 16 h. Ethyl acetate (10 mL) was added to the reaction mixture. The resulting mixture was washed three times with 1M NaOH (10 mL) and twice with brine (10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure to give a yellow oil. The crude product was purified by column chromatography (pentane/Et_2O 90:10) to give vinylene carbonate **2** (157 mg, 66%) as a yellowish solid. A solution of hydrochloric acid (5 M) was added to the aqueous layer until the pH reaches 1. The resulting mixture was extracted three times with ethyl acetate (10 mL). The combined organic layers were washed twice with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure to give BPA (177 mg, 78% yield based on the limiting reagent) as a slightly orange solid.

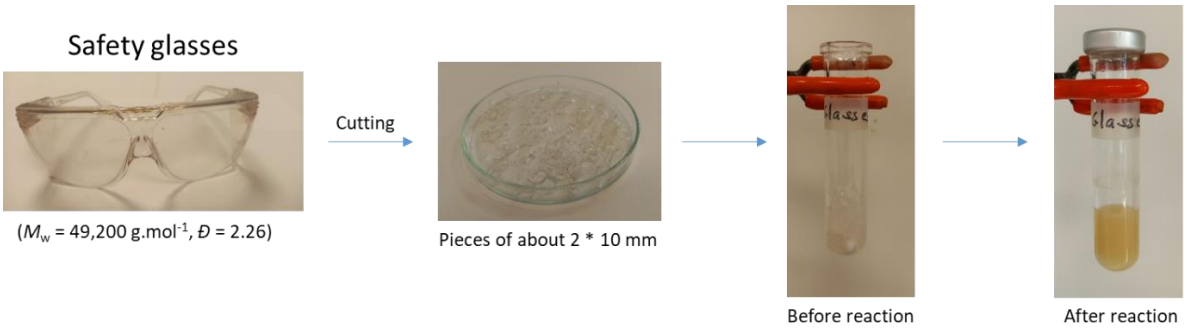


Figure S1. Depolymerisation of polycarbonate contained in safety glasses.

Vinylene carbonates from a polycarbonate plate

A polycarbonate plate was cut into small pieces (about 2 * 10 mm). Benzoin (212 mg, 1 mmol) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (13.9 mg, 0.1 mmol, 10 mol%) were introduced in a 10-mL reaction tube and dissolved in 2-methylTHF (4 mL). The polycarbonate pieces (508 mg, 2 mmol of the monomer unit hypothesizing that the safety glasses are composed of 100% PC-BPA) were progressively introduced in the tube. The reaction tube was sealed and the reaction mixture was stirred at 70°C for 24 h. Ethyl acetate (10 mL) was added to the reaction mixture. The resulting mixture was washed three times with 1M NaOH (10 mL) and twice with brine (10 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure to give a yellow oil. The crude product was purified by column chromatography (pentane/Et_2O 90:10) to give vinylene carbonate **2** (88 mg, 37%) as a yellowish solid. A solution of hydrochloric acid (5 M) was added to the aqueous layer until the pH reaches 1. The resulting mixture was extracted three times with ethyl acetate (10 mL). The combined organic layers were washed twice with brine (10 mL), dried over anhydrous $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure to give BPA (99 mg, 43% yield based on the limiting reagent) as a white solid.

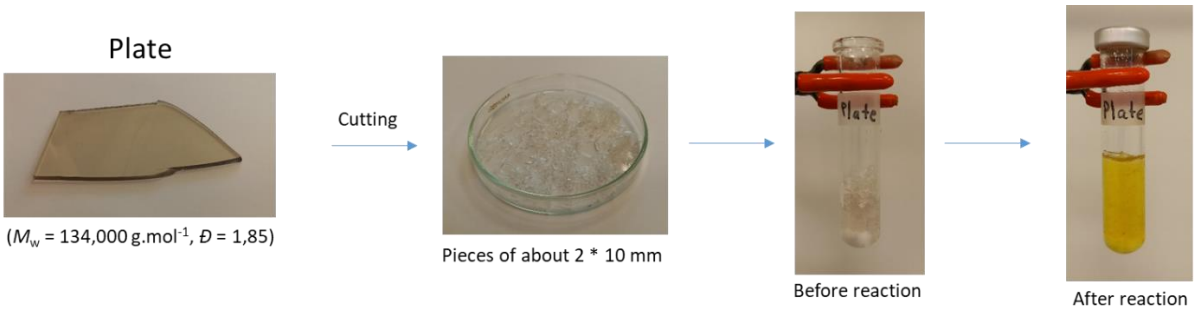
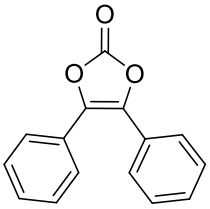
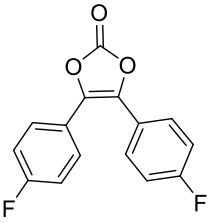


Figure S2. Depolymerisation of polycarbonate contained in a polycarbonate plate.

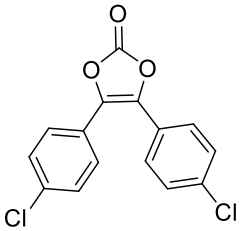
6. Characterization data of vinylene carbonates



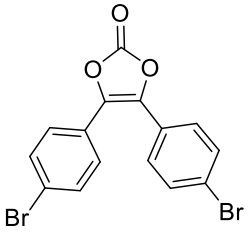
4,5-Diphenyl-1,3-dioxol-2-one (2). The title compound was prepared using benzoin (212 mg, 1 mmol), BPA-PC (508 mg, 2 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **2** (231 mg, 97%) as a white solid. Mp = 72-74 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H 7.61 – 7.49 (m, 4H), 7.48 – 7.38 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ_C 151.87 (C=O), 137.20 (2 Cq), 130.22 (2 CH^{Ar}), 129.10 (4 CH^{Ar}), 126.61 (4 CH^{Ar}), 125.67 (2 Cq). **MS (HRMS)**: $C_{15}H_{11}O_3$ $[M+H]^+$ Meas. m/z = 239.0702 for 239.0703, $C_{15}H_{10}NaO_3$ $[M+Na]^+$ Meas. m/z = 261.0522 for 261.0522, $C_{30}H_{20}NaO_6$ $[2M+Na]^+$ Meas. m/z = 499.1153 for 499.1152.



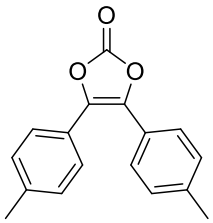
4,5-Bis(4-fluorophenyl)-1,3-dioxol-2-one (3). The title compound was synthesized from 4,4'-difluorobenzoin (248 mg, 1 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **3** (151 mg, 55%) as a white solid. Mp = 66 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H 7.57 – 7.48 (m, 4H), 7.16 – 7.07 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ_C 163.64 (d, $^{1}J_{C\text{-}F}$=252 Hz, 2 C_q-F), 151.47 (C=O), 136.22 (2 C_q), 128.80 (d, $^{3}J_{C\text{-}F}$ = 8.5 Hz, 4 CH), 121.69 (d, $^{4}J_{C\text{-}F}$= 3.5 Hz), 116.57 (d,$^{2}J_{C\text{-}F}$ = 22.2 Hz). **^{19}F NMR** (282 MHz, $CDCl_3$): δ_F -108.69 (s, 2 F_{Ar}). **MS (HRMS)**: $C_{15}H_8F_2NaO_3$ $[M+Na]^+$ Meas. m/z = 297.0331 for 297.0334, $C_{15}H_{10}F_2NaO_4$ $[M+Na+H_2O]^+$ Meas. m/z = 315.0436 for 315.0439.



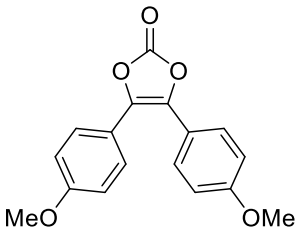
4,5-Bis(4-chlorophenyl)-1,3-dioxol-2-one (**4**). The title compound was synthesized from 4,4'-dichlorobenzoin (281 mg, 1 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure by following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **4** (209 mg, 68%) as a white solid. Mp = 141°C**. ^{1}H NMR** (300 MHz, $CDCl_3$): δ_H 7.51 – 7.45 (m, 4H), 7.43 – 7.38 (m, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ_C 151.25 (C=O), 136.51 (2 Cq), 129.63 (4 CH^{Ar}), 127.89 (4 CH^{Ar}), 123.86 (2 Cq). **MS (HRMS)**: $C_{15}H_9Cl_2O_3$ $[M+H]^+$ Meas. m/z = 306.9924 for 306.9923, $C_{15}H_8Cl_2NaO_3$ $[M+Na]^+$ Meas. m/z = 328.9742 for 328.9743, $C_{15}H_{10}Cl_2NaO_4$ $[M+Na+H_2O]^+$ Meas. m/z = 346.9849 for 346.9848.



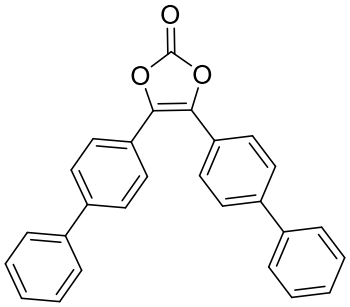
4,5-Bis(4-bromophenyl)-1,3-dioxol-2-one (5). The title compound was synthesized from 4,4'-dibromobenzoin (370 mg, 1 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **5** (329 mg, 83%) as a white solid. Mp = 152 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δH 7.57 (d, *J* = 8.6 Hz, 4H), 7.42 (d, *J* = 8.6 Hz, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ_C 151.21 (C=O), 136.63 (2 Cq), 132.59 (4 CH^{Ar}), 128.04 (4 CH^{Ar}), 124.78 (2 Cq), 124.32 (2 Cq). **MS (HRMS):** $C_{15}H_8Br_2NaO_3$ $[M+Na]^+$ Meas. m/z = 416.8732 for 416.8732.



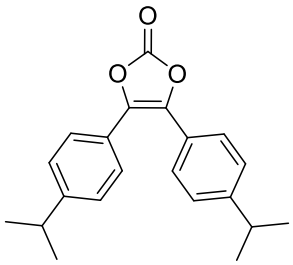
4,5-Di-p-tolyl-1,3-dioxol-2-one (6). The title compound was synthesized from 4,4'-dimethylbenzoin (240 mg, 1 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **6** (176 mg, 66%) as a white solid. Mp = 132 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H 7.47-7.42 (m, 4H), 7.23-7.18 (m, 4H), 2.39 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ_C 152.06 (C=O), 140.33 (2 Cq), 136.89 (2 Cq), 129.72 (4 CH^{Ar}), 126.46 (4 CH^{Ar}), 122.91 (2 Cq), 21.58 (2 CH_3). **MS (HRMS):** $C_{17}H_{15}O_3$ $[M+H]^+$ Meas. m/z = 267.1013 for 267.1016, $C_{17}H_{14}NaO_3$ $[M+Na]^+$Meas. m/z = 289.0833 for 289.0835, $C_{34}H_{28}NaO_6$ $[2M+Na]^+$ Meas. m/z = 555.1779 for 555.1778.



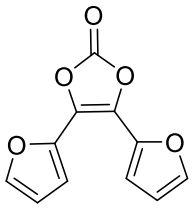
4,5-Bis(4-methoxyphenyl)-1,3-dioxol-2-one (7): The title compound was synthesized from 4,4'-dimethoxybenzoin (272 mg, 1 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **7** (194 mg, 65%) as a white solid. Mp = 143 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H = 7.47 (d, *J*=8.9 Hz, $4H^{Ar}$), 6.92 (d, *J*=8.9 Hz, $4H^{Ar}$), 3.84 (s, 6H, OCH_3).**^{13}C NMR** (75 MHz, $CDCl_3$): δ_C = 160.76 (2 OCq), 152.16 (C=O), 136.15 (2 Cq), 128.07 (4 CH), 118.15 (2 Cq), 114.52 (4 CH), 55.50 (2 OCH_3). **MS (HRMS)**: $C_{17}H_{15}O_5$ $[M+H]^+$ Meas. m/z = 299.0927 for 299.0914, $C_{17}H_{14}NaO_5$ $[M+Na]^+$ Meas. m/z = 321.0745 for 321.0733, $C_{34}H_{28}NaO_{10}$ $[2M+Na]^+$ Meas. m/z = 619.1592 for 619.1575.



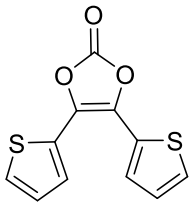
4,5-Di([1,1'-biphenyl]-4-yl)-1,3-dioxol-2-one (8). The title compared was prepared using 1,2-di([1,1'-biphenyl]-4-yl)-2-hydroxyethan-1-one), BPA-PC (508 mg, 2 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **8** (117 mg, 30%) as white powder. Mp= 85°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 7.73-7.59 (m, 12H, CH^{Ar}), 7.52-7.37 (m, 6H, CH^{Ar}). **^{13}C NMR** (75 MHz, $CDCl_3$) δ_C 143.02 (C=O), 140.0 (4 Cq), 137.17 (2 Cq), 129.14 (4 CH), 128.20 (2 CH), 127.77 (4 CH), 127.20 (4 CH), 127.06 (4 CH), 124.56 (2 Cq). **MS (HRMS)**: $C_{27}H_{19}O_3$ $[M+H]^+$ Meas. m/z = 391.1348 for 391.1329, $C_{54}H_{37}O_6$ $[2M+H]^+$ Meas. m/z = 781.2621 for 781.2585, $C_{54}H_{36}NaO_6$ $[2M+Na]^+$ Meas. m/z = 803.2442 for 803.2404.



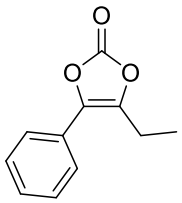
4,5-Bis(4-isopropylphenyl)-1,3-dioxol-2-one (9). The title compared was prepared using 2-hydroxy-1,2-bis(4-isopropylphenyl)ethan-1-one (296, 1 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **9** (225 mg, 70%) as colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 7.52–7.44 (m, 4H), 7.28–7.21 (m, 4H), 2.92 (hept, *J* = 6.9 Hz, 2H), 1.25 (d, *J* = 6.9 Hz, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ_C 151.19 (C=O), 136.98 (2 Cq), 130.33 (2 Cq), 127.15 (4 CH^{Ar}), 126.59 (4 CH^{Ar}), 123.29 (2 Cq), 34.23 (2 CH), 23.87 (4 CH_3). **MS (HRMS)** $C_{21}H_{22}NaO_3$ $[M+Na]^+$ Meas. m/z = 345.1456 for 345.1461, $C_{42}H_{44}NaO_6$ $[2M+Na]^+$ Meas. m/z = 667.3027 for 667.3030.



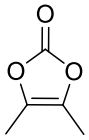
4,5-Di(furan-2-yl)-1,3-dioxol-2-one (10). The title compound was prepared using 1,2-di(furan-2-yl)-2-hydroxyethan-1-one (192 mg, 1 mmol), BPA-PC (508 mg, 2 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **10** (156 mg, 70%) as white powder. Mp = 140°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 7.58 (dd, *J* = 1.8, 0.8 Hz, 2H, CH^{Ar}), 6.91 (dd, *J* = 3.5, 0.8 Hz, 2H, CH^{Ar}), 6.57 (dd, *J* = 3.5, 1.8, 2H, CH^{AR}). **^{13}C NMR** (75 MHz, $CDCl_3$) δ_C 150.48 (C=O), 144.40 (2 CH), 140.05 (2 C_q), 128.98 (2 C_q), 112.06 (2 CH), 111.48 (2 CH). **MS (HRMS)**: $C_{11}H_7O_5$ $[M+H]^+$ Meas. m/z = 219.0288 for 219.0288; $C_{11}H_6NaO_5$ $[M+Na]^+$ Meas. m/z = 241.0107 for 241.0107.



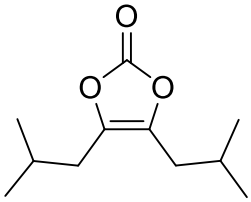
4,5-Di(thiophen-2-yl)-1,3-dioxol-2-one (11). The title compound was prepared using 2-hydroxy-1,2-di(thiophen-2-yl)ethan-1-one (224 mg, 1 mmol), BPA-PC (508 mg, 2 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **11** (138 mg, 55%) as a pink solid. Mp = 150°C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 7.49 (dd, *J* = 3.8, 1.3 Hz, $2H^{Ar}$), 7.47 (dd, *J* = 5.2, 1.3 Hz, $2H^{Ar}$), 7.14 (dd, *J* = 5.1, 3.7 Hz, $2H^{Ar}$). **^{13}C NMR** (75 MHz, $CDCl_3$) δ_C 150.74 (C=O), 132.37 (2 C_q), 128.40 (2 CH), 128.31 (2 CH), 127.88 (2 CH), 125.72 (2 C_q). **MS (HRMS)**: $C_{11}H_7O_3S_2$ $[M+H]^+$ Meas. m/z = 250.9828 for 250.983 ; $C_{11}H_6NaO_3S_2$ $[M+Na]^+$ Meas. m/z = 272.9647 for 272.9651.



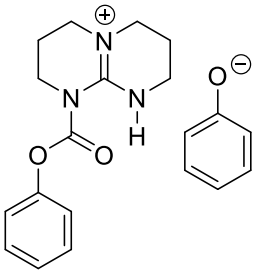
4-Ethyl-5-phenyl-1,3-dioxol-2-one (13). The title compound was prepared using 2-hydroxy-1-phenylbutan-1-one (164 mg, 1 mmol), BPA-PC (508 mg, 2 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **13** (124 mg, 65%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ_H 7.48-7.33 (m, $5H^{Ar}$), 2.73 (q, *J* = 7.5 Hz, 2H, CH_2), 1.30 (t, *J* = 7.5 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ_C 152.50 (C=O), 140.17 (C_q), 136.89 (C_q), 129.22 (CH), 129.11 (2 CH), 125.74 (Cq), 125.39 (2 CH), 18.60 (CH_2), 11.55 (CH_3).



4,5-Dimethyl-1,3-dioxol-2-one (14). The title compared was prepared using 3-hydroxybutan-2-one (88 mg, 1 mmol), BPA-PC (508 mg, 2 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give **14** (91 mg, 80%) as a white solid. Mp = 79-80 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H 2.02 (s, 6H, 2 CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ_C 153.27 (C=O), 134.85 (2 Cq), 9.04 (2 CH_3).



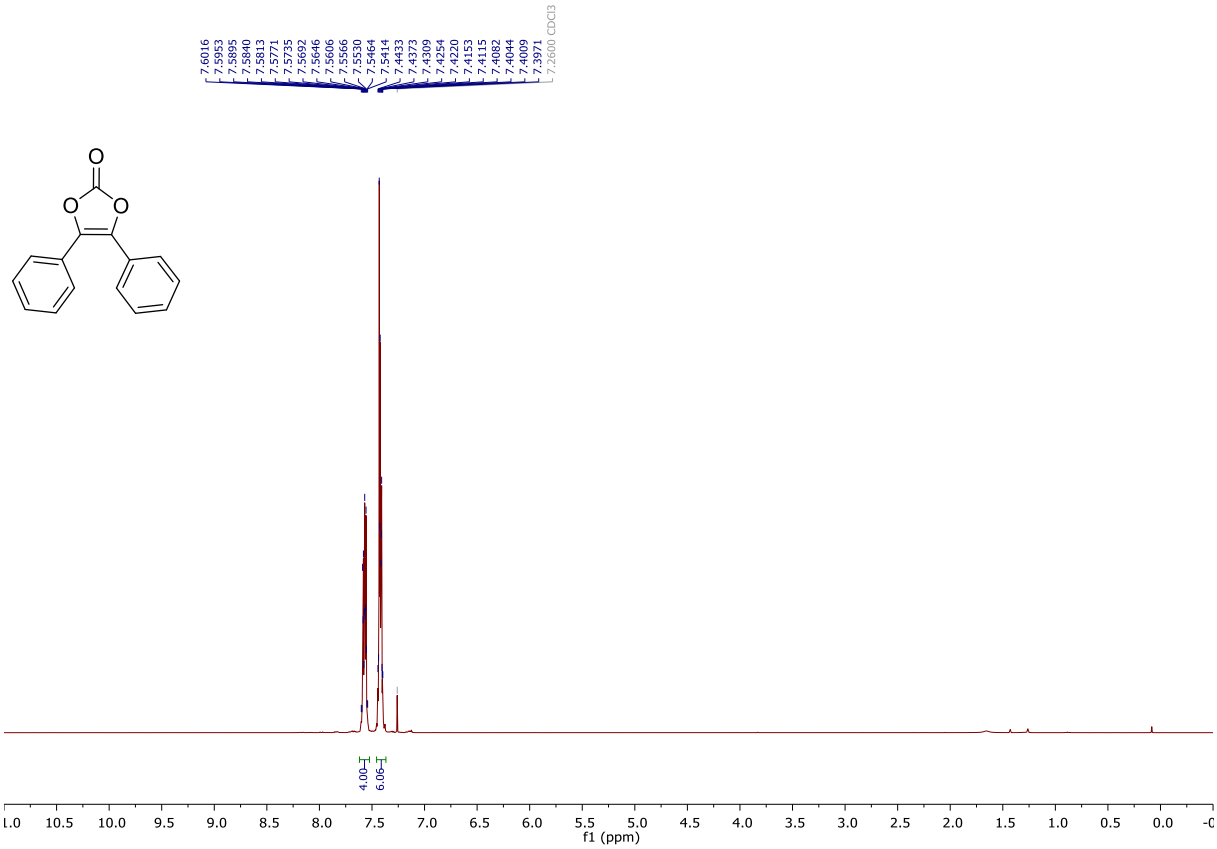
4,5-Diisobutyl-1,3-dioxol-2-one (15). The title compared was prepared using 5-hydroxy-2,7-dimethyloctan-4-one (172 mg, 1 mmol), BPA-PC (508 mg, 2 mmol), TBD (14 mg, 0.1 mmol, 10 mol%) and 2-methylTHF (2 mL) following the general procedure. The product was purified by flash chromatography (ether/pentane 10:90) to give to give **15** (149 mg, 75%) as a colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ_H 2.20 (d, *J* = 7.0 Hz, 4H, 2 $\underline{CH_2}$), 1.93 (thept, *J* = 6.5, 6.8 Hz, 2H, 2 CH), 0.94 (d, *J* = 6.7 Hz, 12H, 4 CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ_C 153.51 (C=O), 138.63 (2 Cq), 32.52 (2 CH), 26.74 (2 CH_2), 22.23 (4 CH_3). **MS (HRMS)**: $C_{11}H_{18}NaO_3$ $[M+Na]^+$ Meas. m/z = 221.1142 for 221.1148, $C_{22}H_{36}NaO_6$ $[2M+Na]^+$ Meas. m/z = 419.2392 for 419.2404.



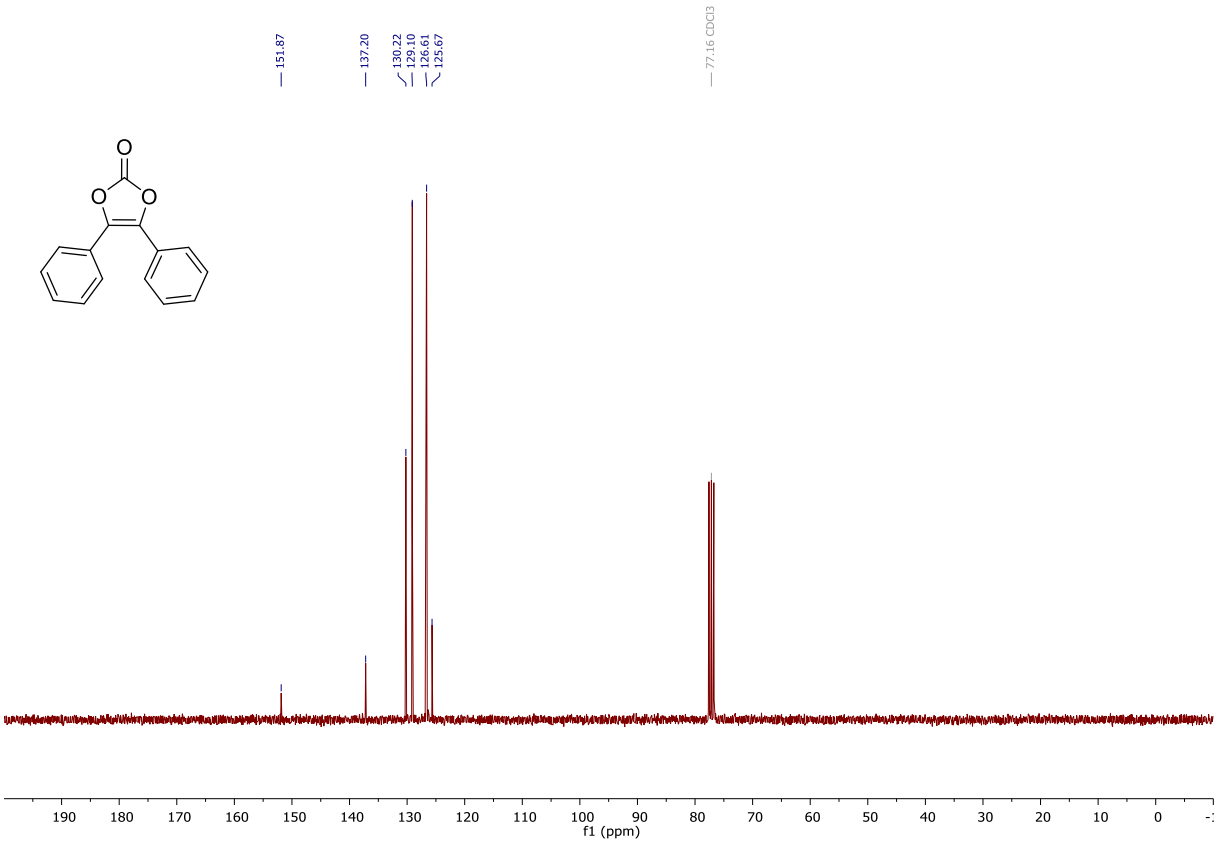
Diphenylcarbonate / TBD 1:1 adduct. The title compound was obtained by mixing 0.5 mL of a 0.2 M solution of diphenyl carbonate in d_6-DMSO with 0.5 mL of a 0.2 M solution of TBD in d_6-DMSO. The resulting solution was stirred at room temperature and a portion was transferred to an NMR tube. **^{1}H NMR** (300 MHz, d_6-DMSO) δ_H 9.52 (br s, 1H, NH), 7.26-7.18 (m, 1H), 7.17-7.07 (m, 5H), 6.79-6.67 (m, 4H), 3.62 (t, *J* = 6.4, 2H), 3.31 (t, *J* = 5.7, 2H), 3.18 (t, *J* = 5.8, 2H), 3.13 (t, *J* = 6.2, 2H), 1.92 (p, *J* = 6.3, 2H), 1.75 (p, *J* = 5.8, 2H). **^{13}C NMR** (75 MHz, d_6-DMSO) δ_C 157.77 (Cq), 152.76 (Cq), 151.27 (Cq), 145.79 (Cq), 129.27 (2 CH^{Ar} + CH^{Ar}), 125.20 (CH^{Ar}), 121.60 (2 CH^{Ar}), 118.38 (2 CH^{Ar}), 115.32 (2 CH^{Ar}), 47.87 (N-CH_2), 47.44 (N-CH_2), 43.71 (N-CH_2), 43.21 (N-CH_2), 23.42 (CH_2), 21.54 (CH_2).

7. NMR spectra of vinylene carbonates

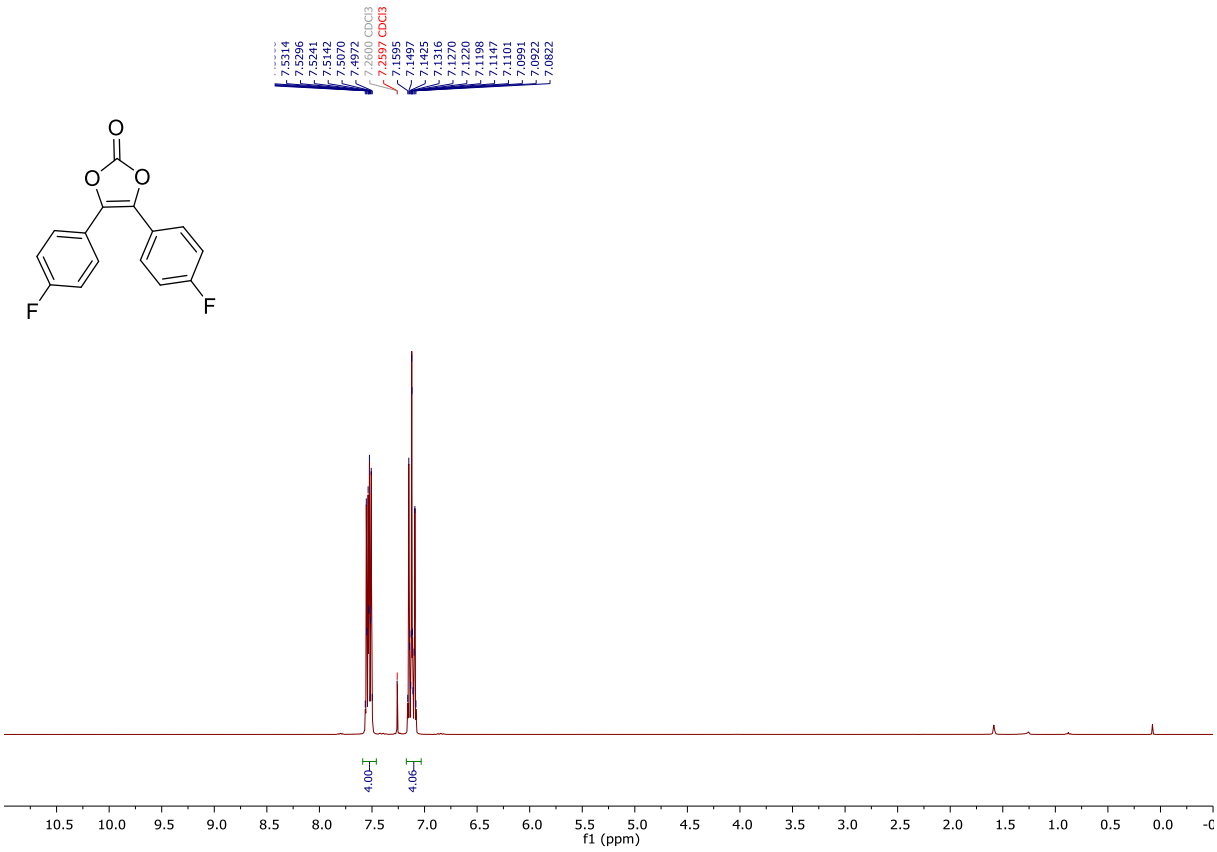
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-diphenyl-1,3-dioxol-2-one **(2)**.



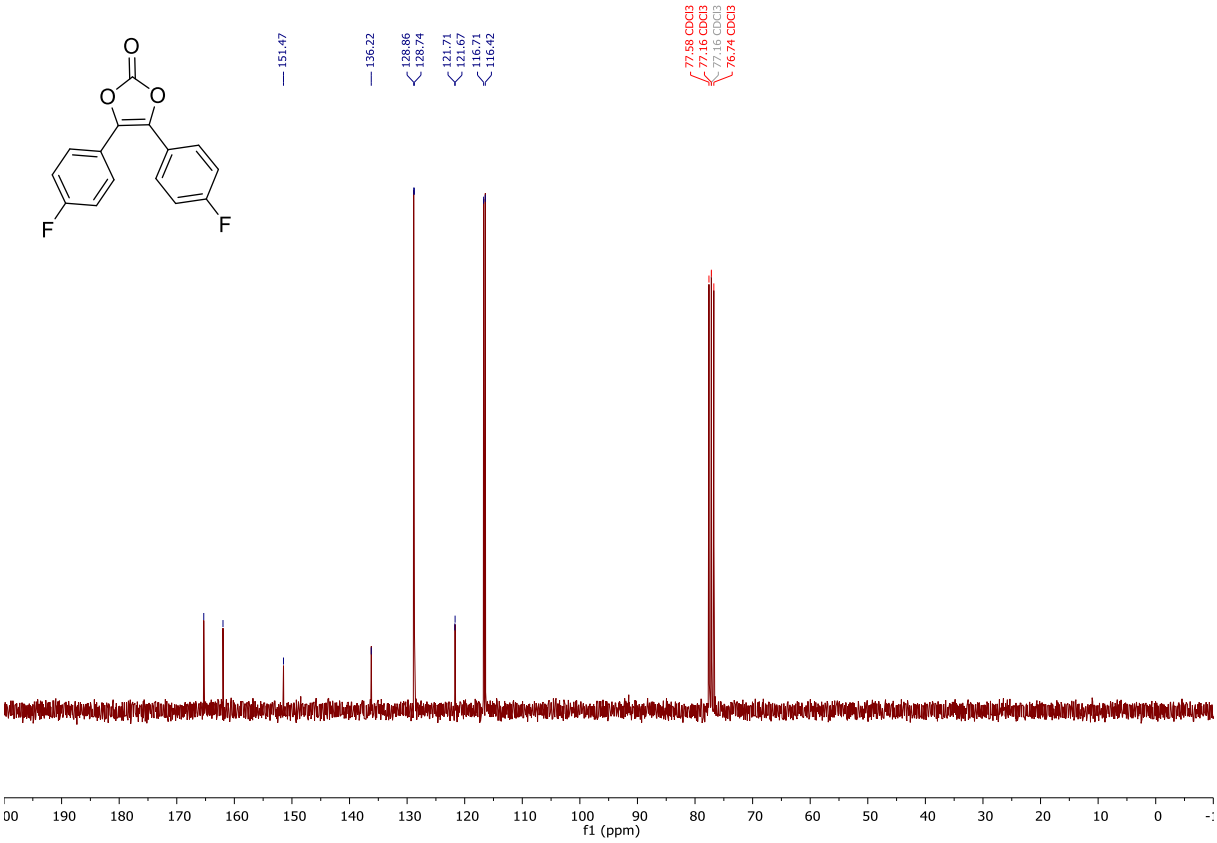
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-diphenyl-1,3-dioxol-2-one **(2)**.



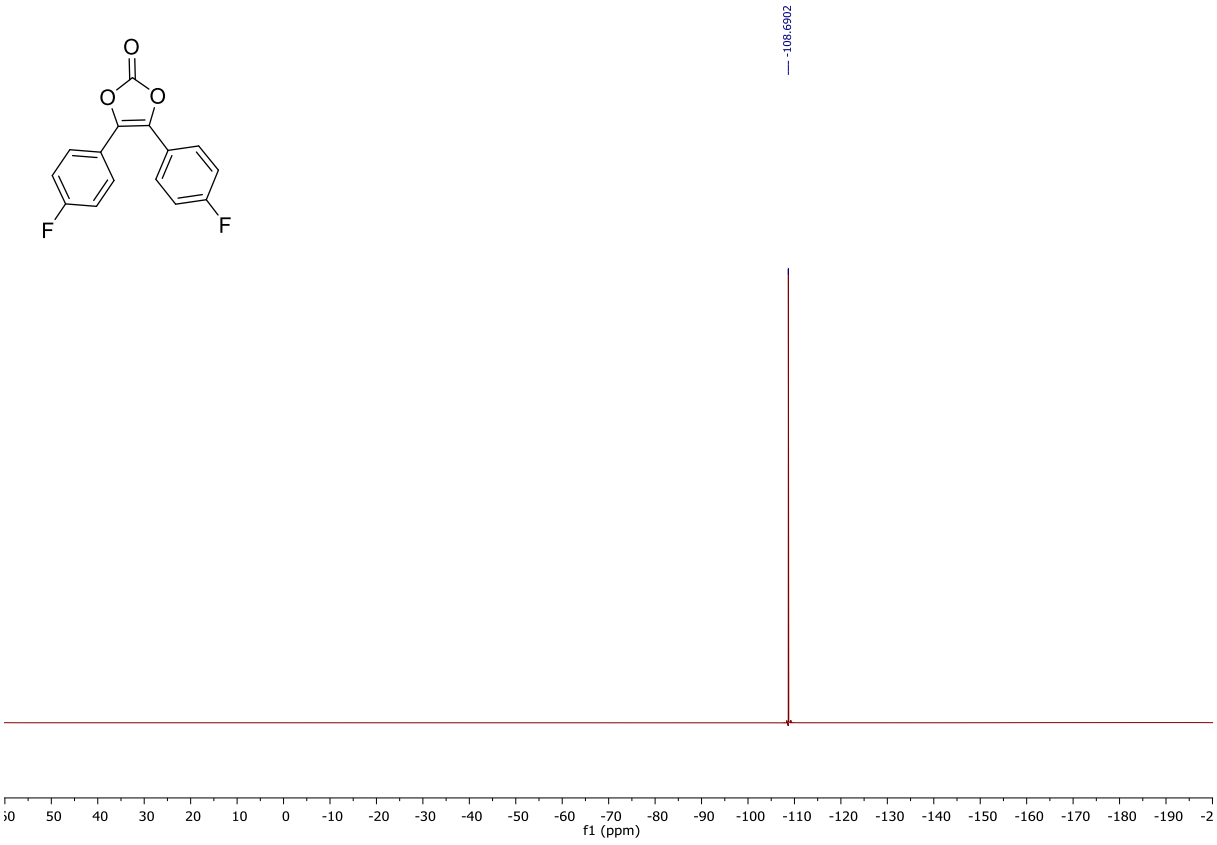
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-bis(4-fluorophenyl)-1,3-dioxol-2-one (**3**).



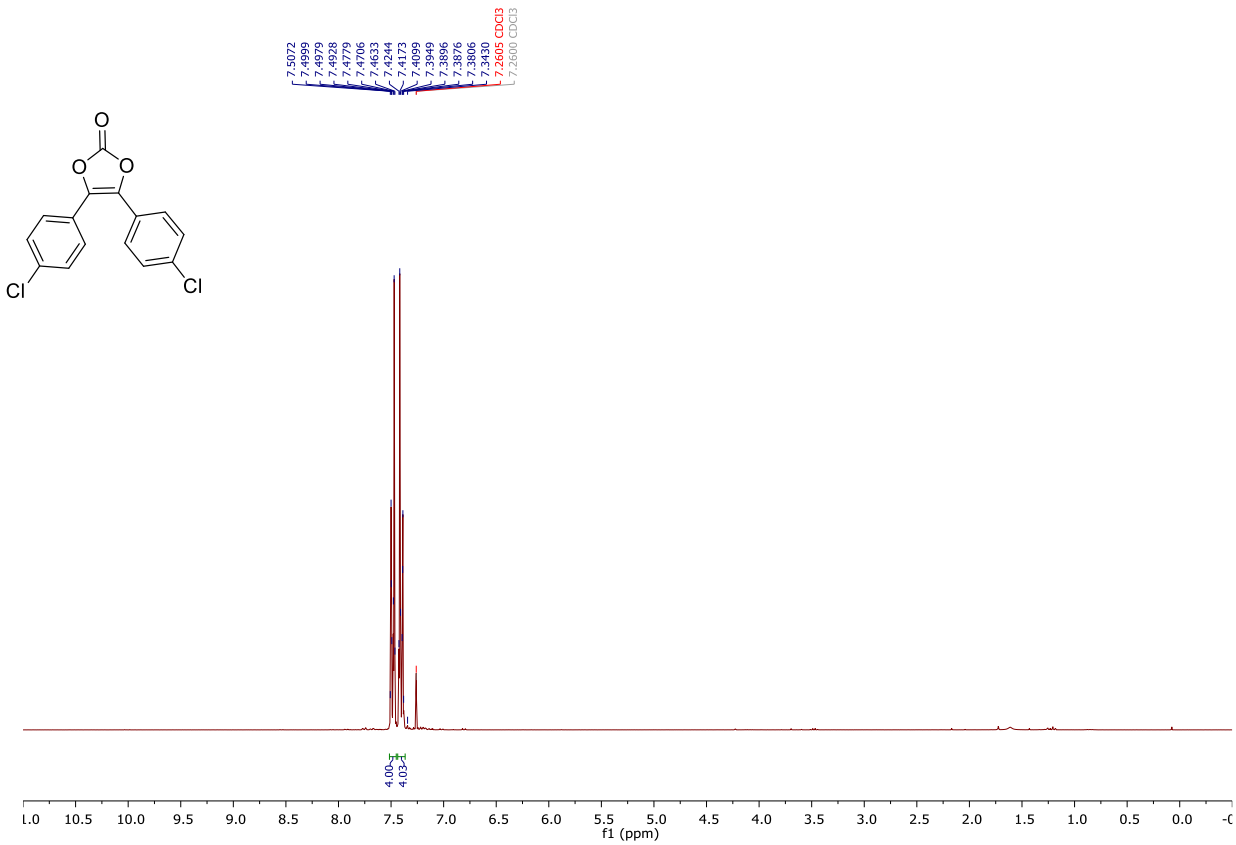
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-bis(4-fluorophenyl)-1,3-dioxol-2-one (**3**).



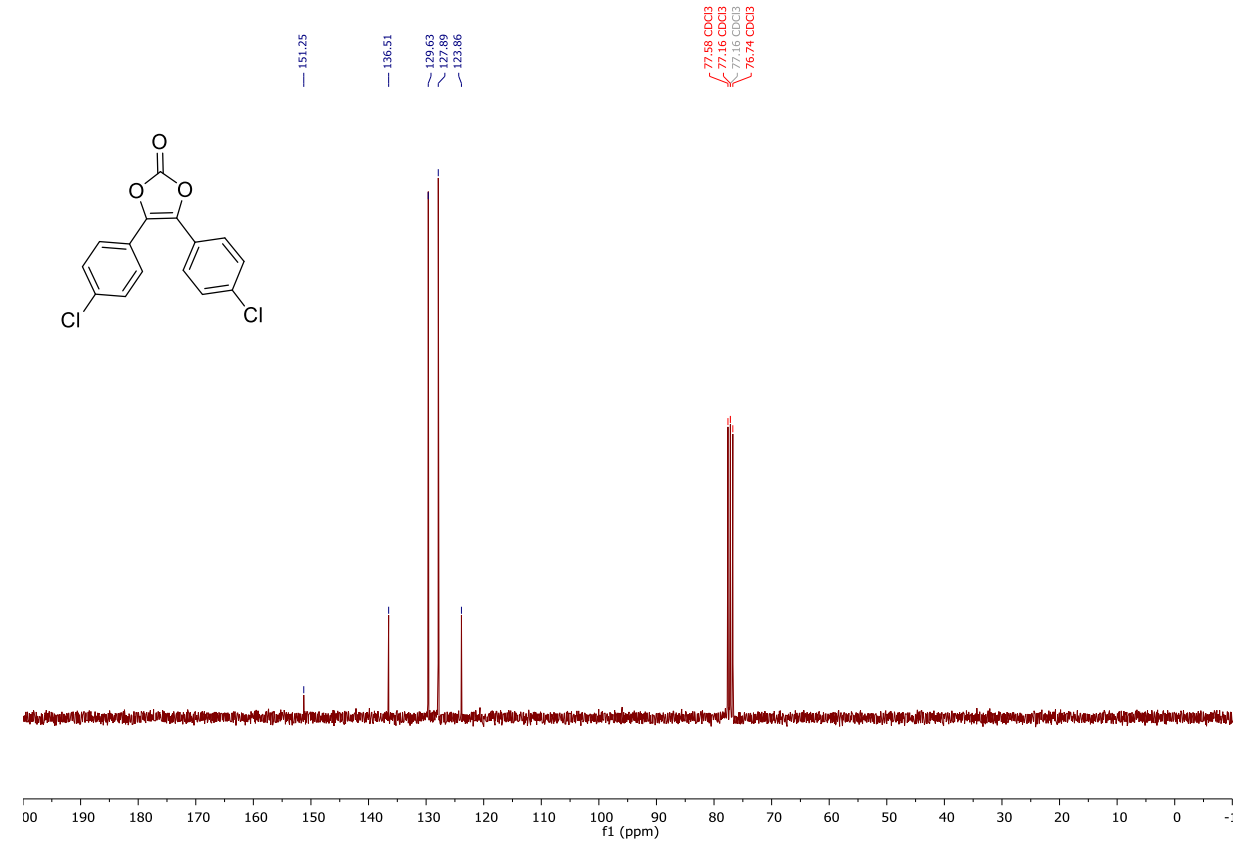
^{19}F NMR (282 MHz, $CDCl_3$) of 4,5-bis(4-fluorophenyl)-1,3-dioxol-2-one (**3**).



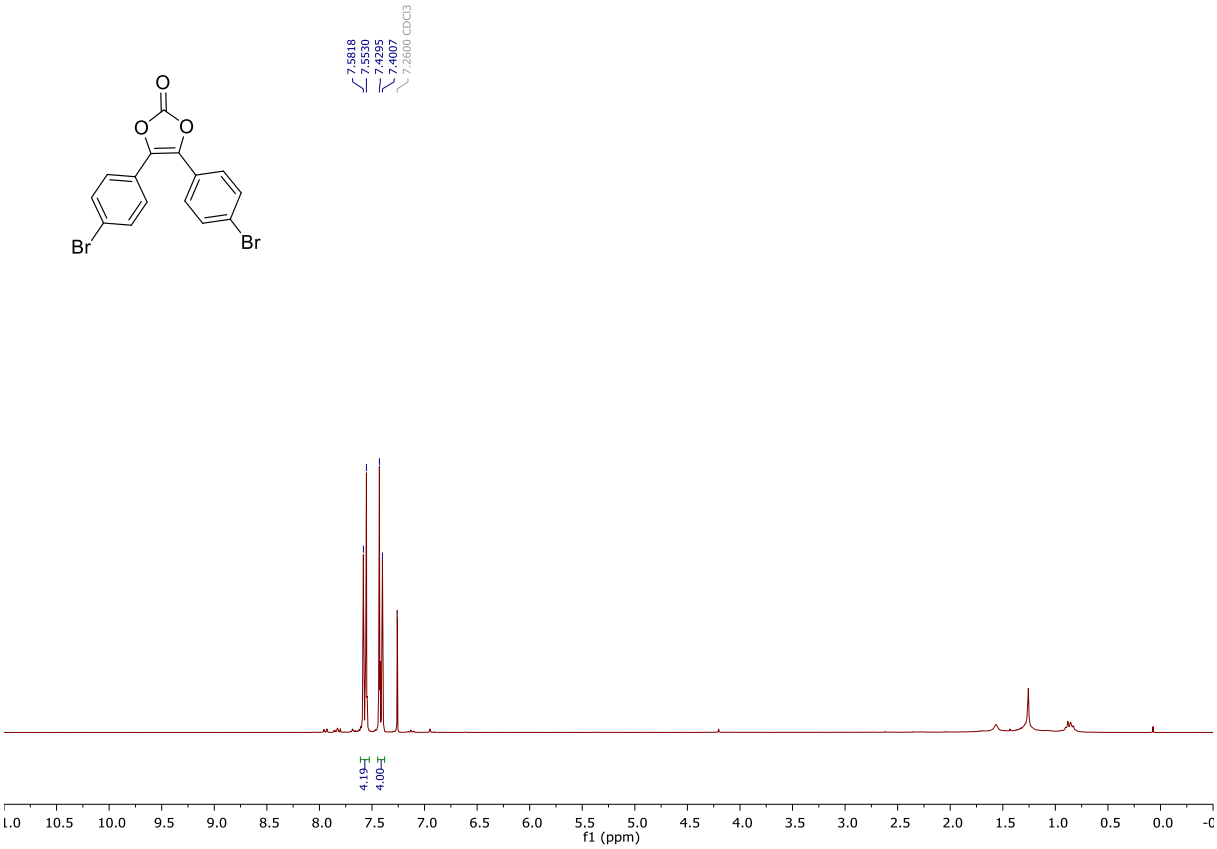
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-bis(4-chlorophenyl)-1,3-dioxol-2-one (**4**)



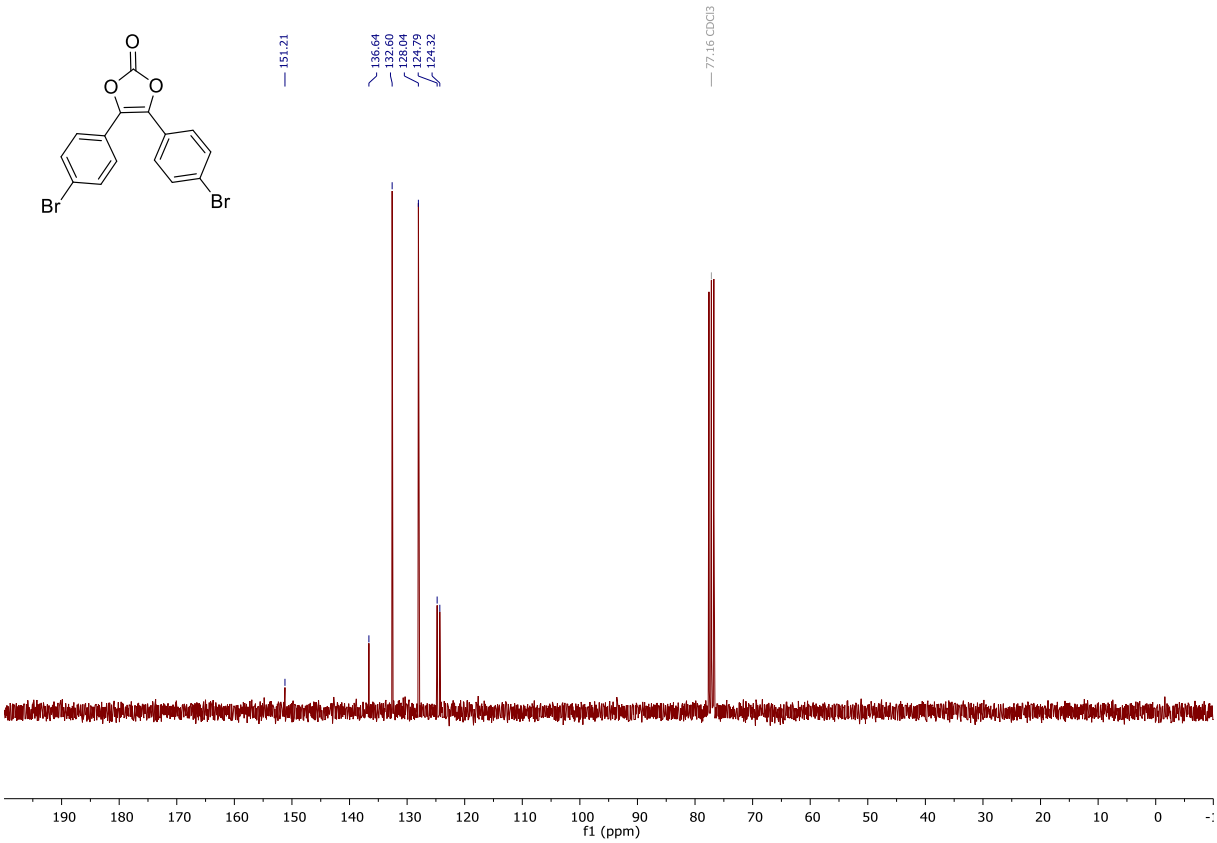
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-bis(4-chlorophenyl)-1,3-dioxol-2-one (**4**)



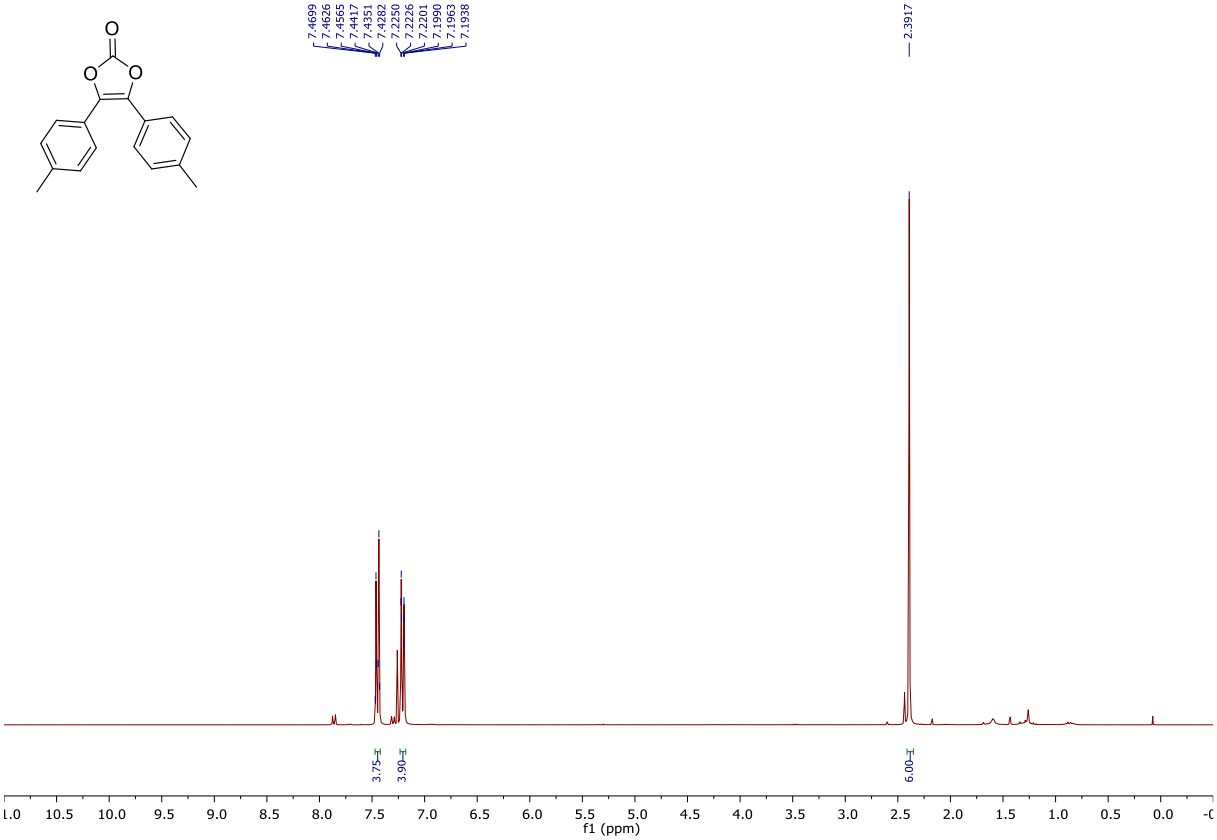
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-bis(4-bromophenyl)-1,3-dioxol-2-one **(5).**



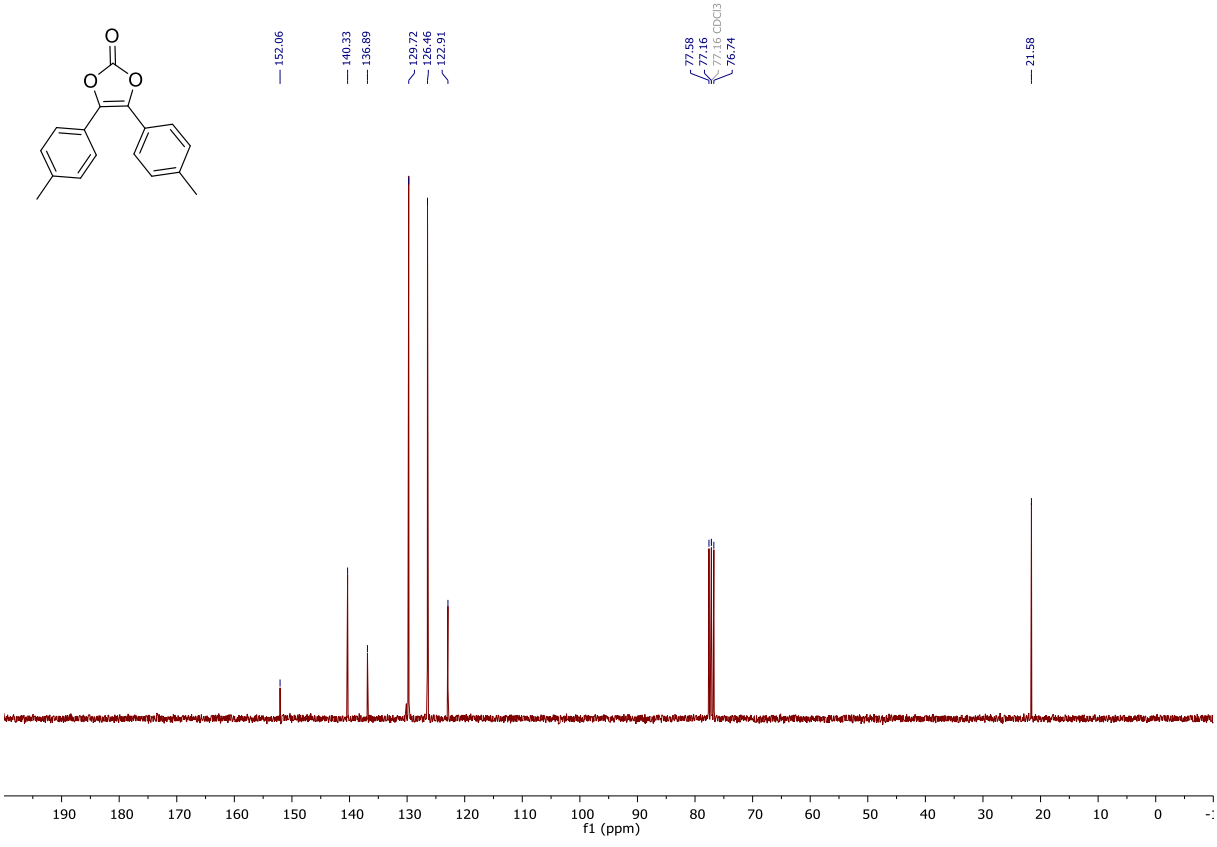
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-bis(4-bromophenyl)-1,3-dioxol-2-one **(5).**



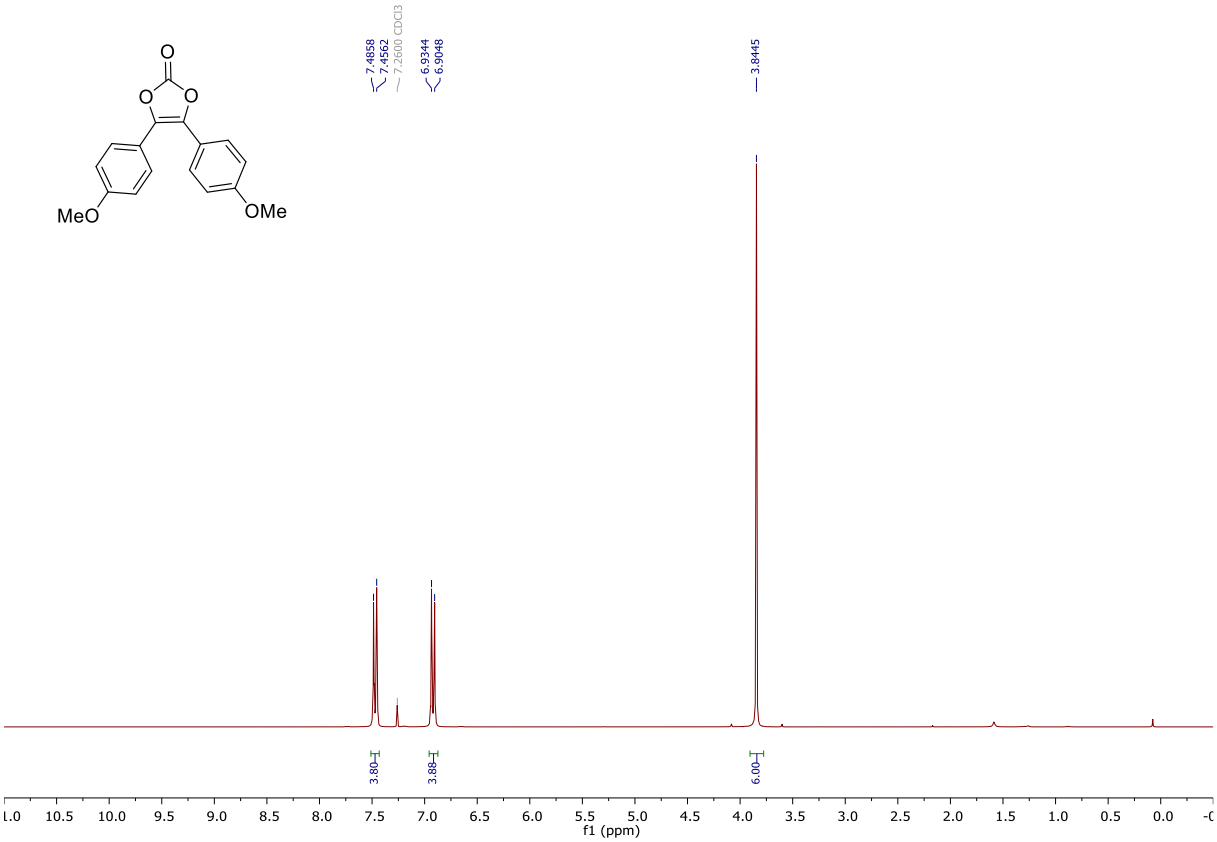
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-di-p-tolyl-1,3-dioxol-2-one **(6).**



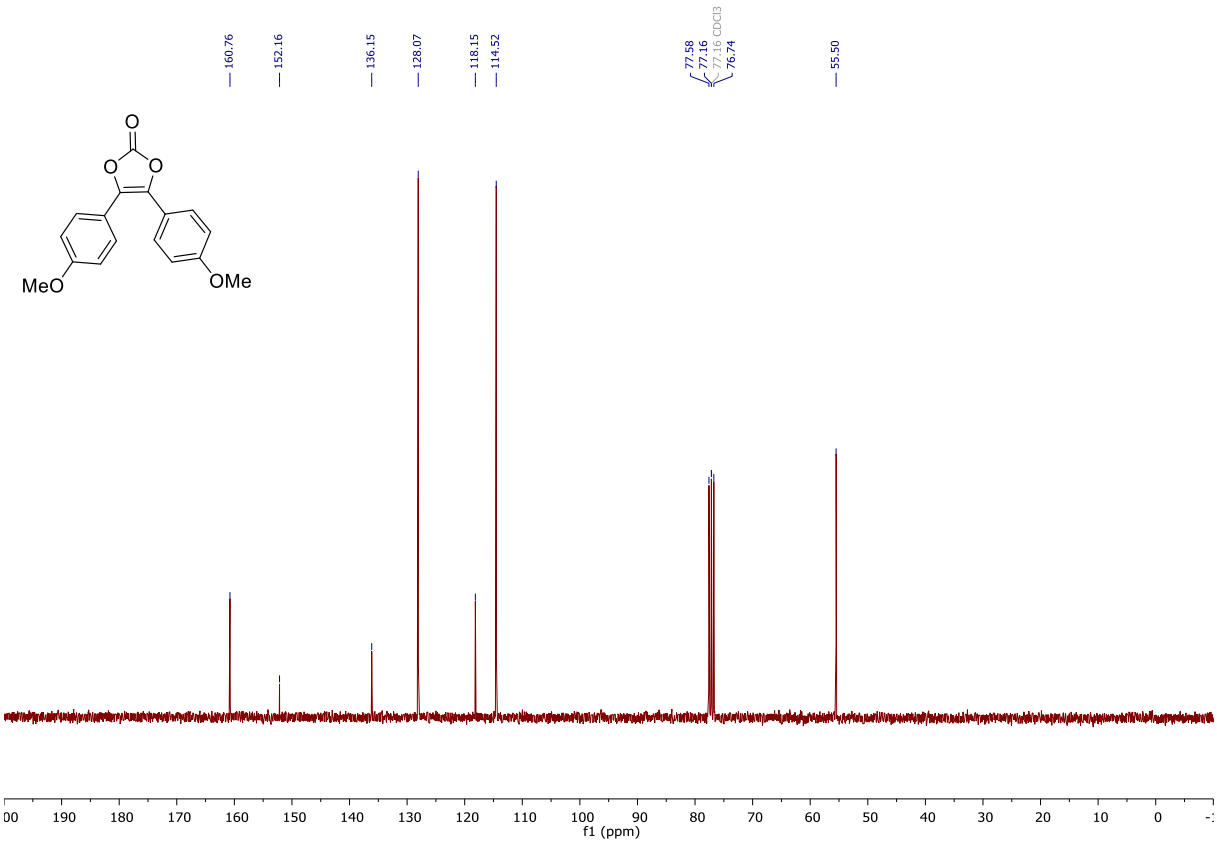
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-di-p-tolyl-1,3-dioxol-2-one **(6).**



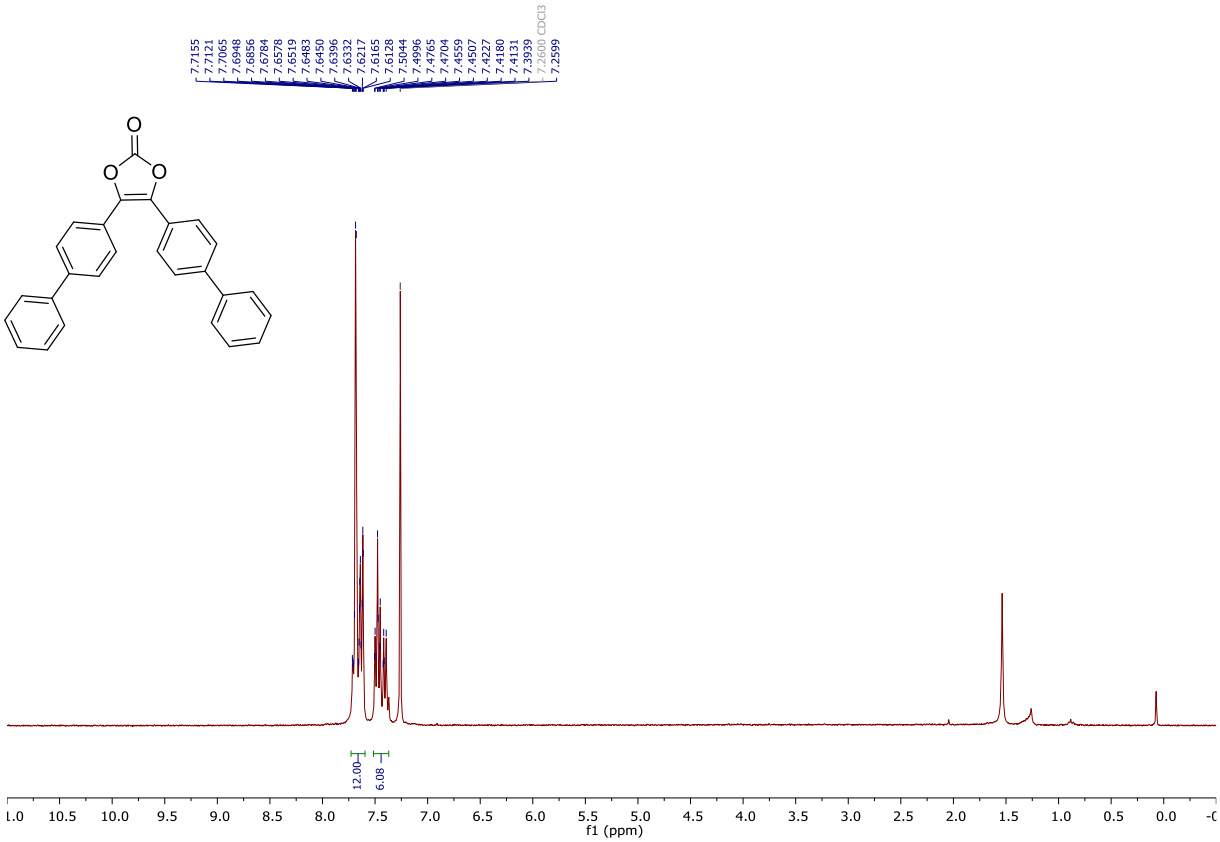
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-bis(4-methoxyphenyl)-1,3-dioxol-2-one **(7).**



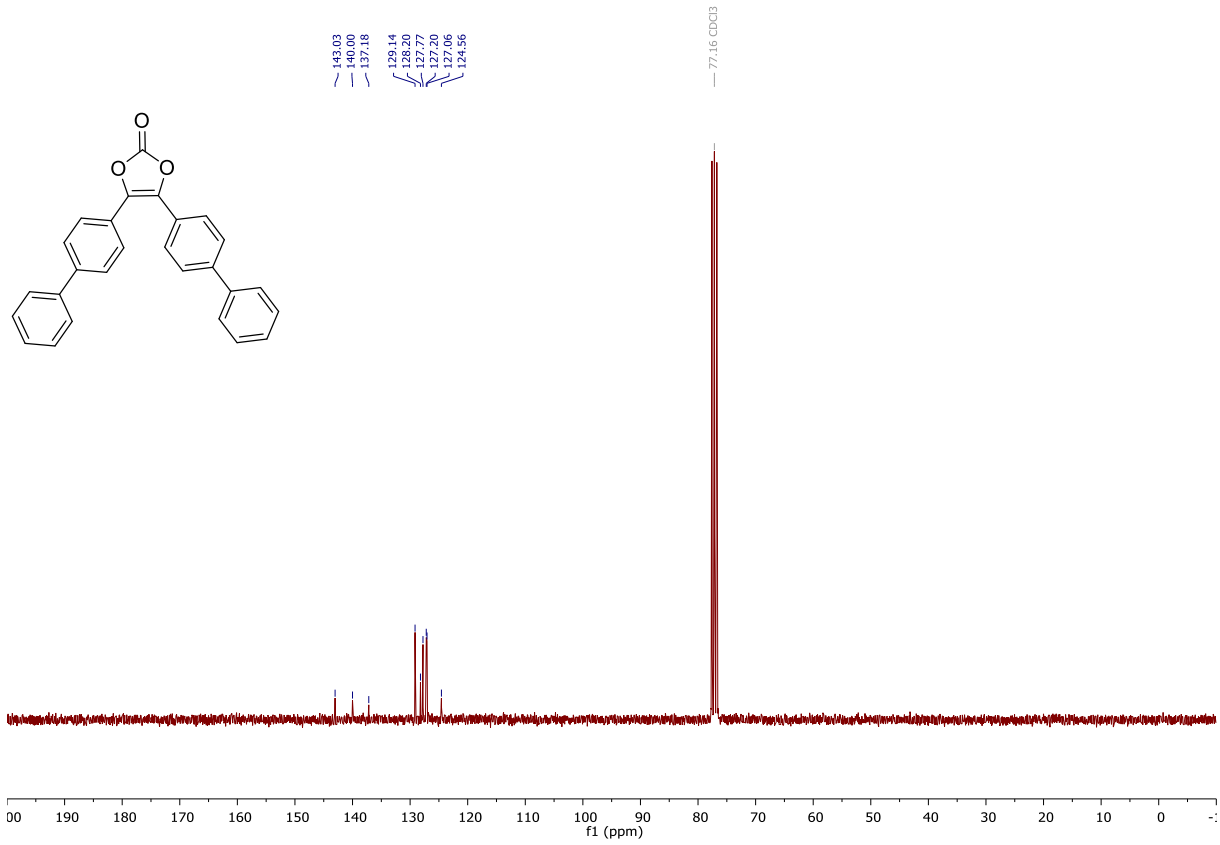
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-bis(4-methoxyphenyl)-1,3-dioxol-2-one **(7).**



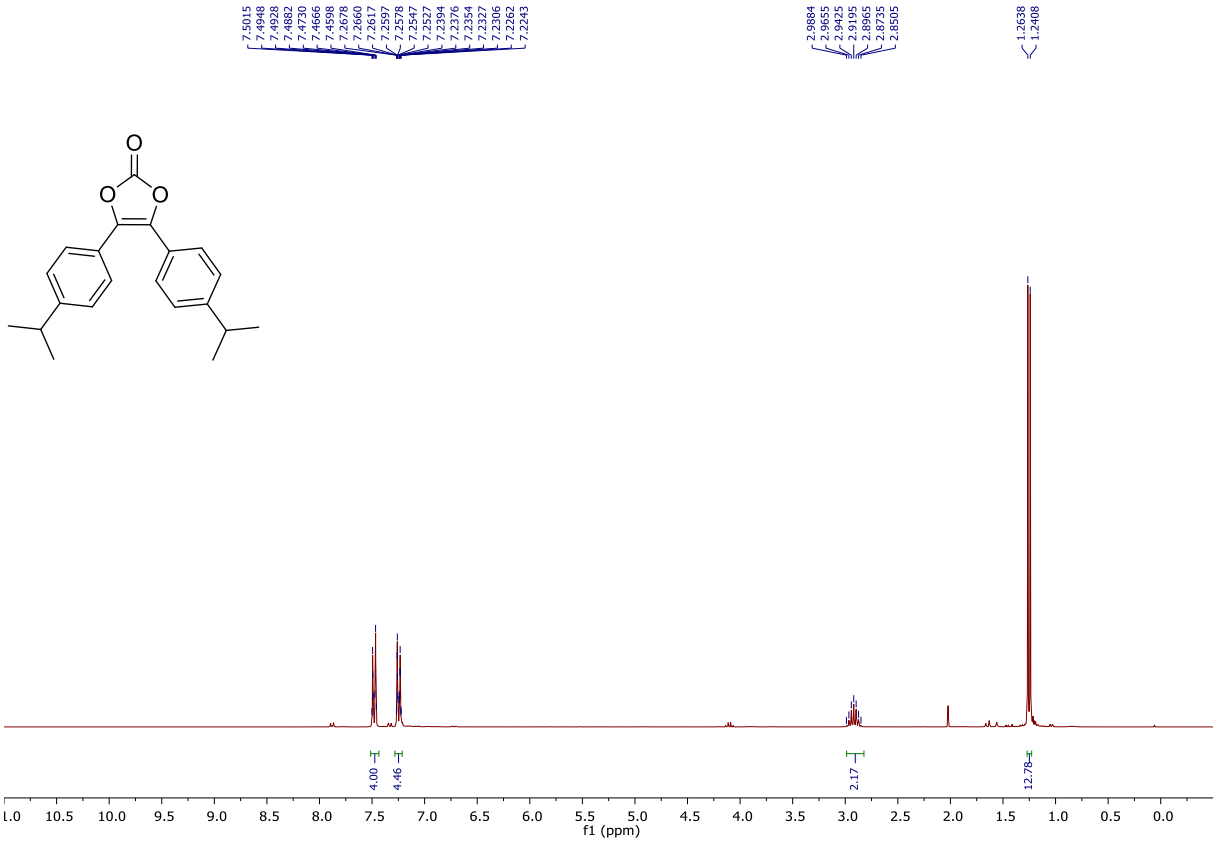
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-Di([1,1'-biphenyl]-4-yl)-1,3-dioxol-2-one **(8)**.



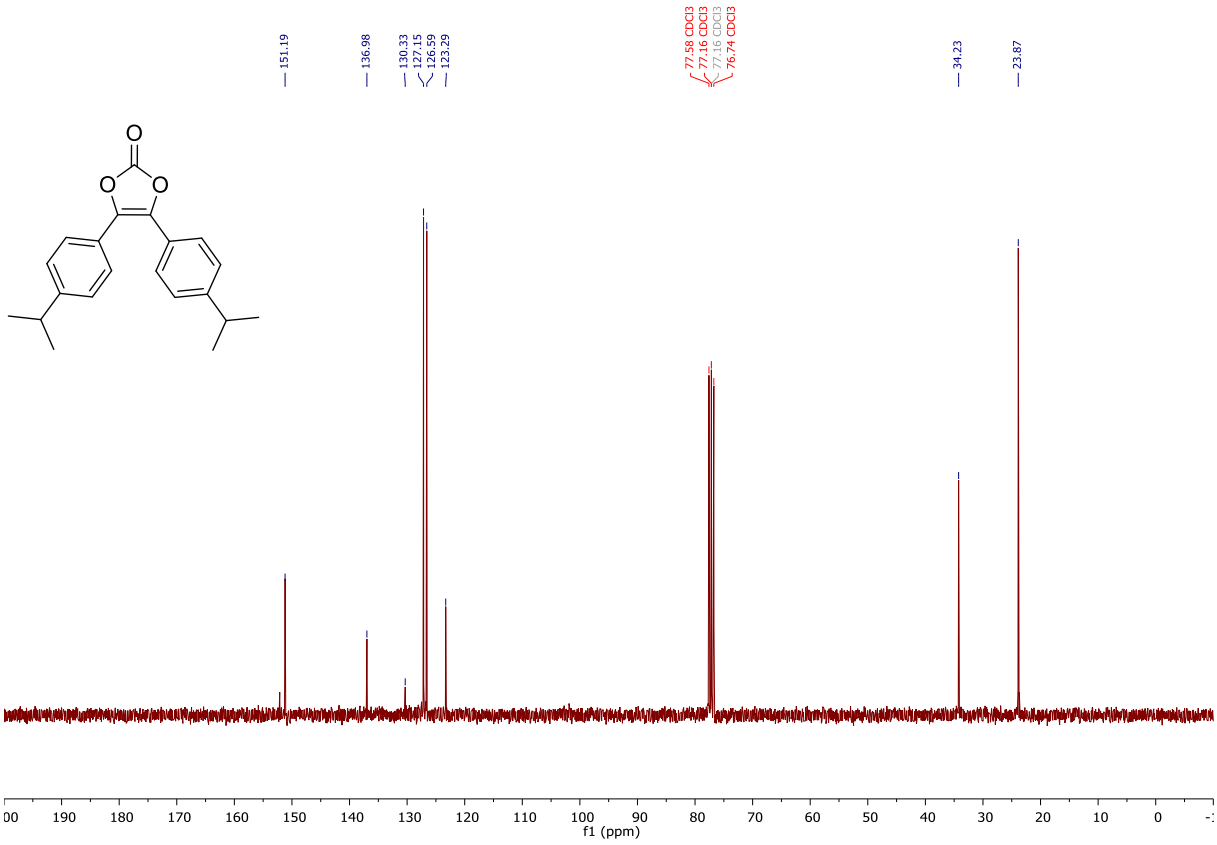
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-Di([1,1'-biphenyl]-4-yl)-1,3-dioxol-2-one **(8)**.



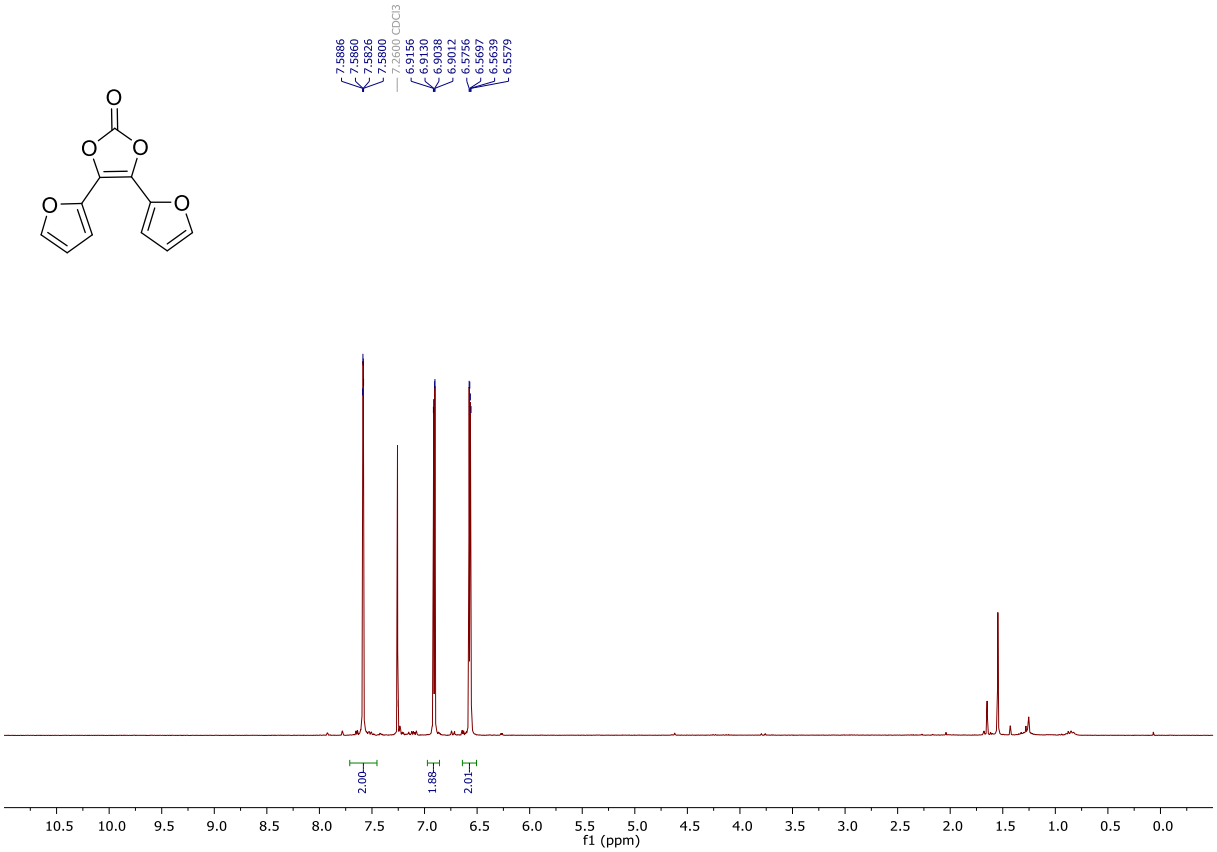
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-bis(4-isopropylphenyl)-1,3-dioxol-2-one (**9**).



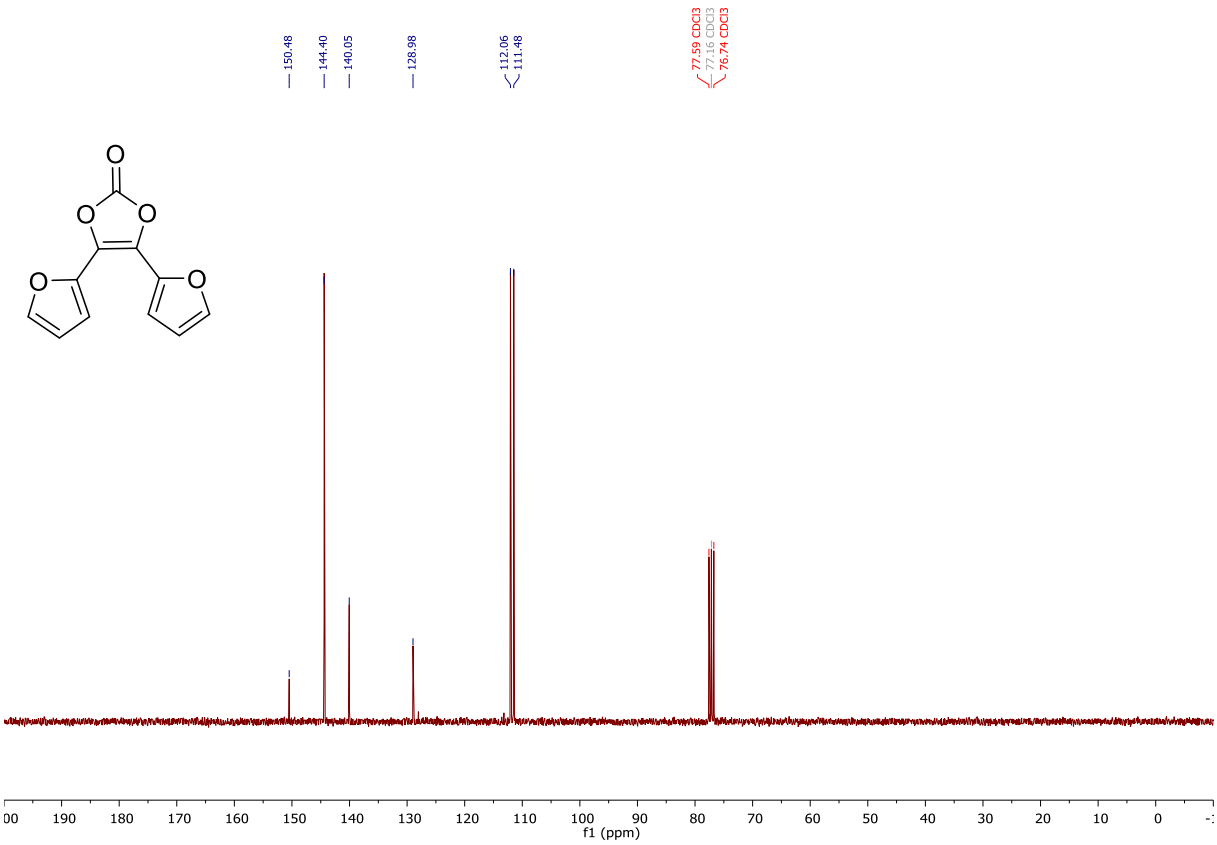
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-bis(4-isopropylphenyl)-1,3-dioxol-2-one (**9**).



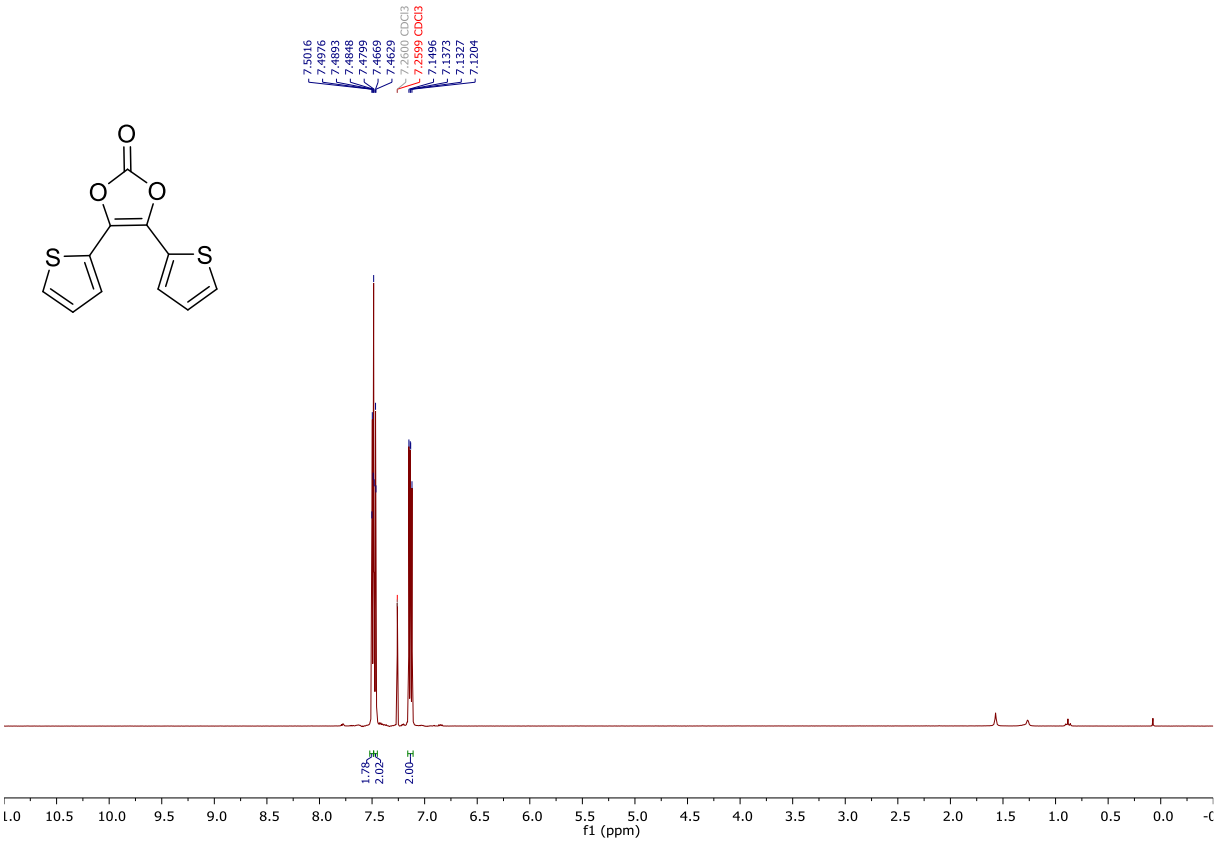
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-Di(furan-2-yl)-1,3-dioxol-2-one **(10).**



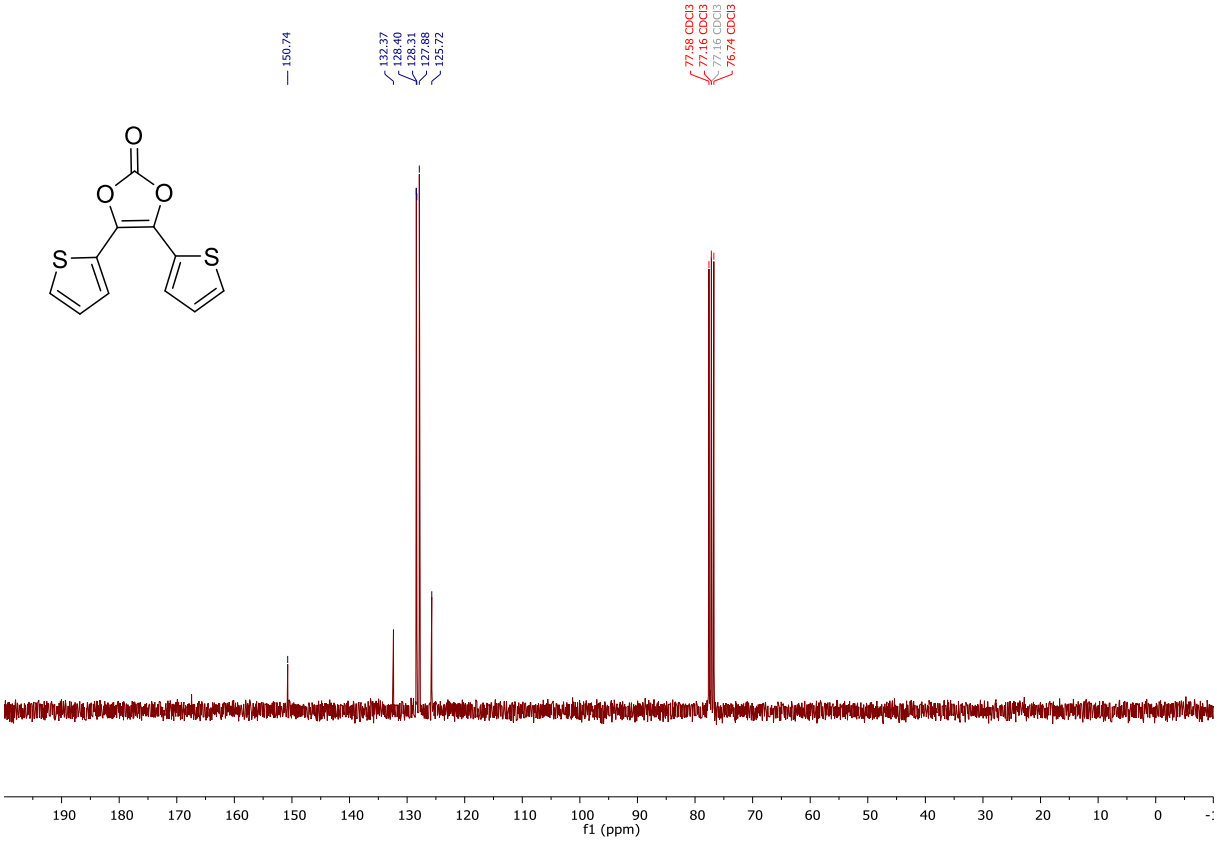
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-Di(furan-2-yl)-1,3-dioxol-2-one **(10).**



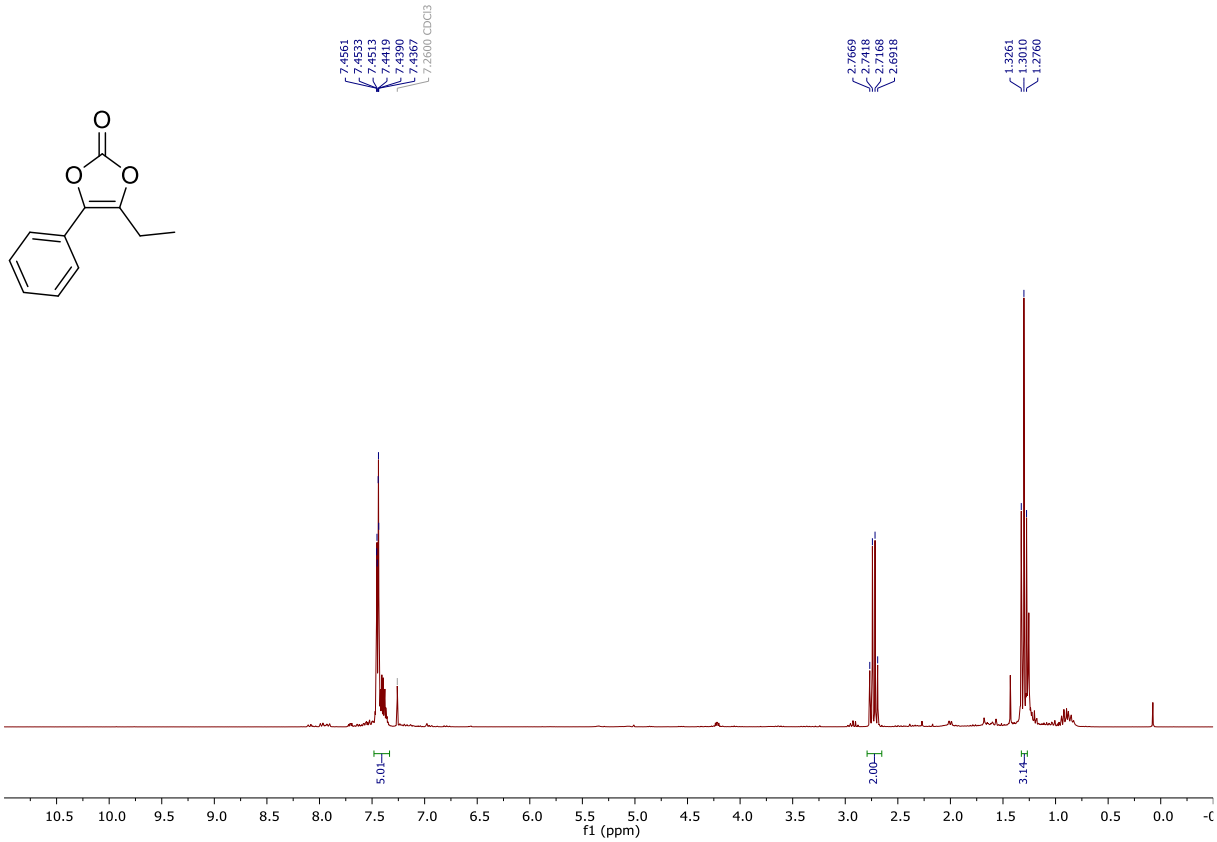
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-Di(thiophen-2-yl)-1,3-dioxol-2-one **(11).**



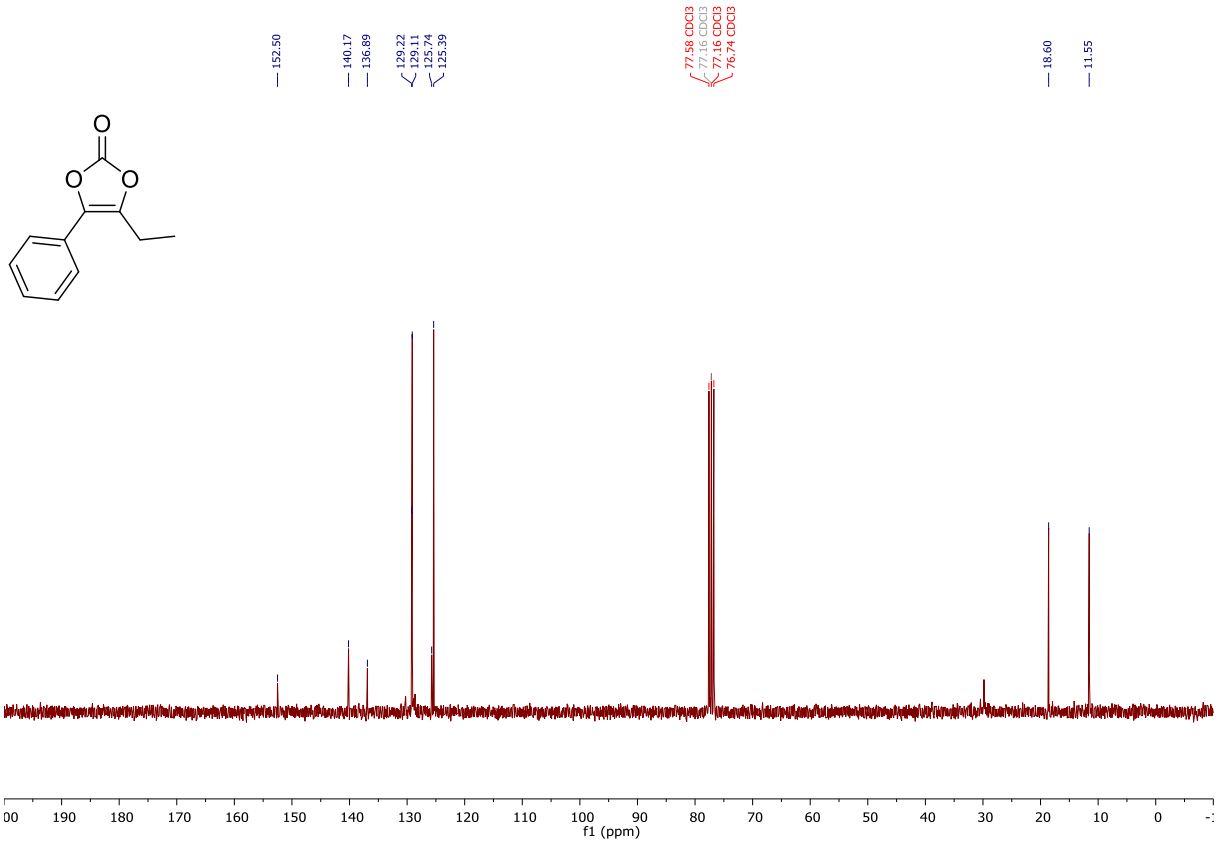
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-di(thiophen-2-yl)-1,3-dioxol-2-one **(11).**



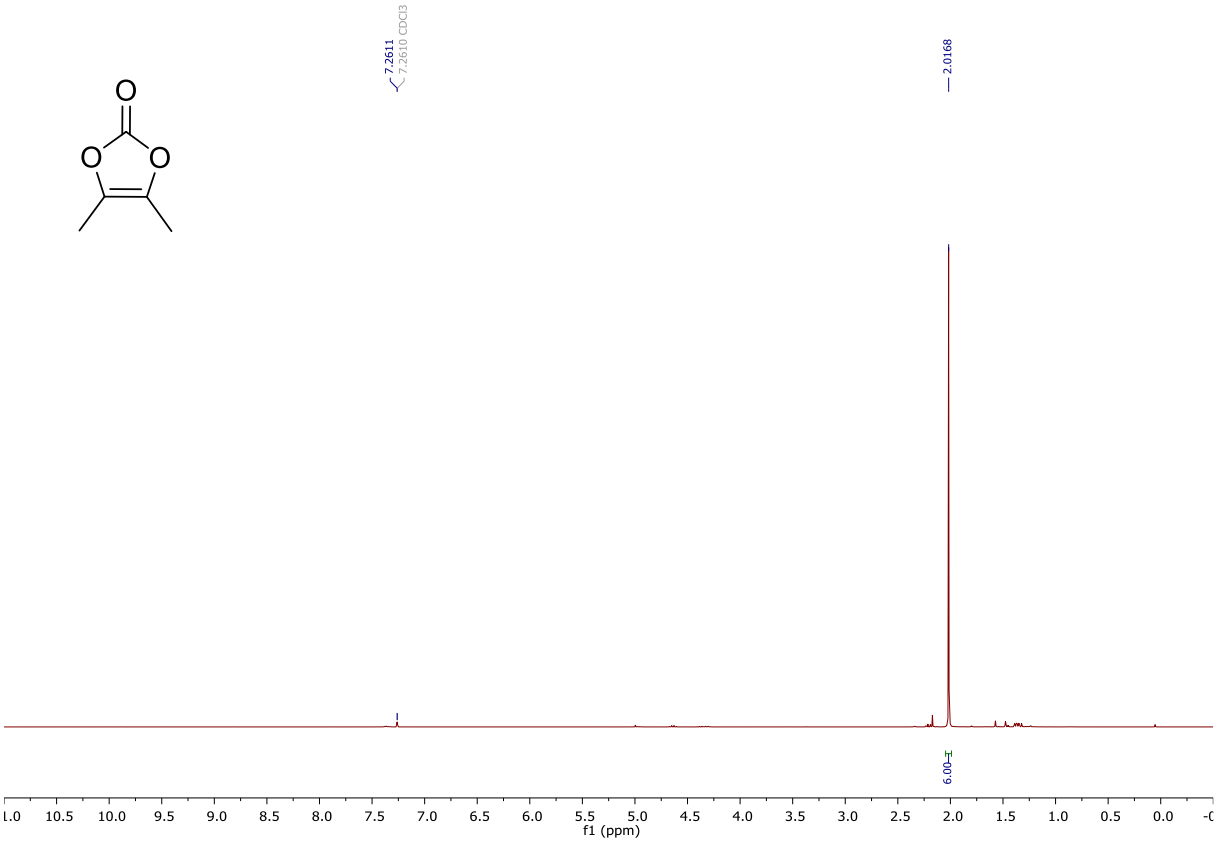
^{1}H NMR (300 MHz, $CDCl_3$) of 4-ethyl-5-phenyl-1,3-dioxol-2-one **(13).**



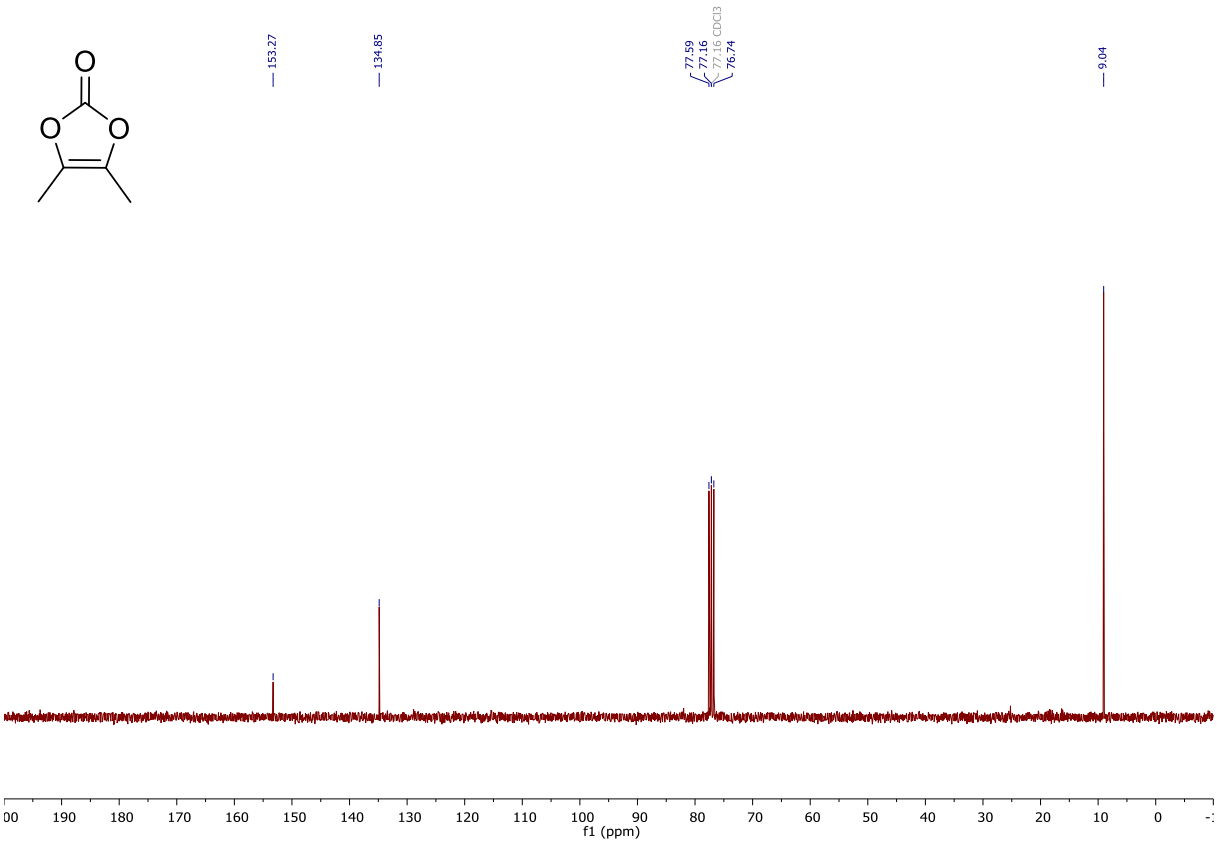
^{13}C-NMR (75 MHz, $CDCl_3$) of 4-ethyl-5-phenyl-1,3-dioxol-2-one **(13).**



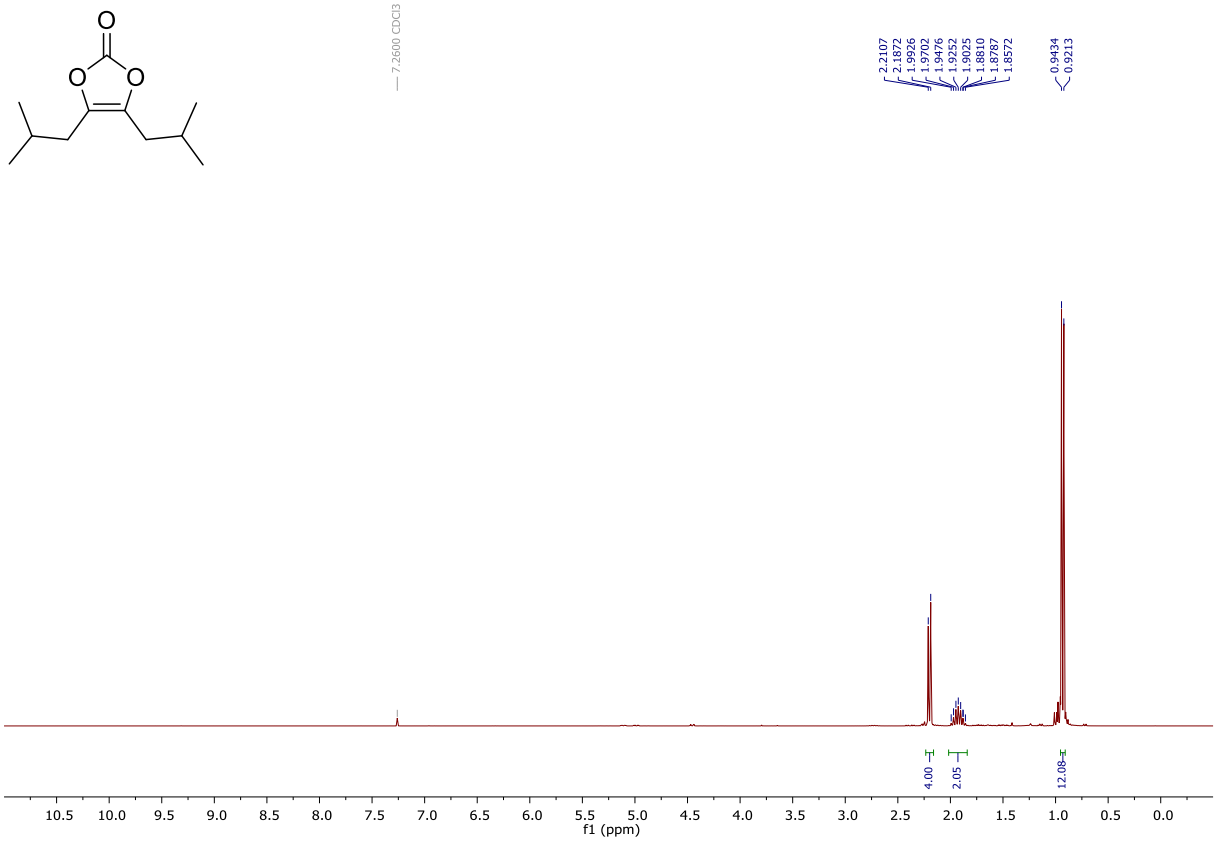
^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-dimethyl-1,3-dioxol-2-one **(14)**.



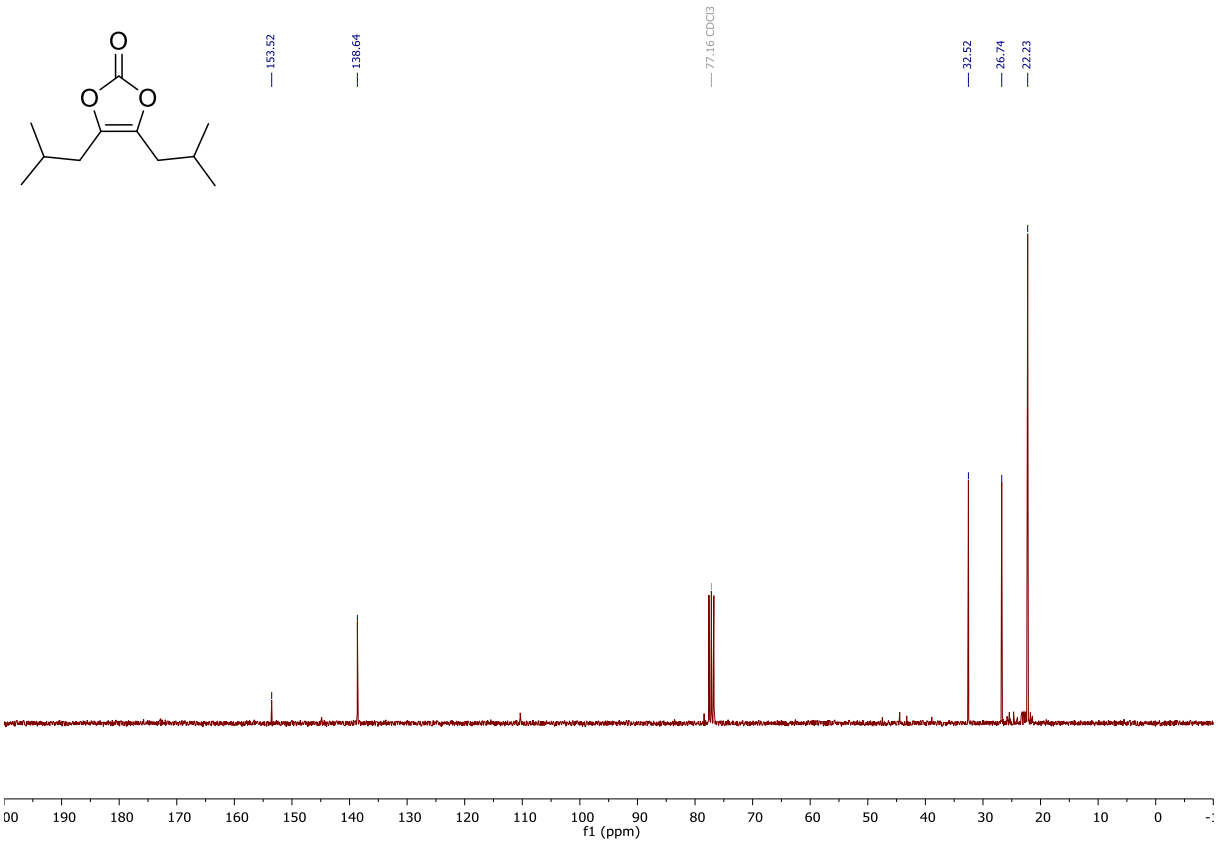
^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-dimethyl-1,3-dioxol-2-one **(14)**.



^{1}H NMR (300 MHz, $CDCl_3$) of 4,5-diisobutyl-1,3-dioxol-2-one **(15)**.



^{13}C-NMR (75 MHz, $CDCl_3$) of 4,5-diisobutyl-1,3-dioxol-2-one **(15)**.



8. NMR Mechanistic studies

8.1. NMR of benzoin / TBD mixtures

A 0.2 M mother solution of *benzoin* was prepared by dissolving 127.2 mg (0.6 mmol) of benzoin in 3 mL of d_6-DMSO.

A 0.2 M mother solution of *TBD* was prepared by dissolving 41.7 mg (0.3 mmol) of benzoin in 1.5 mL of d_6-DMSO.

Five (5) solutions of benzoin / TBD mixtures in d_6-DMSO were prepared as follows and the solutions were transferred in NMR tubes to record ^{1}H and ^{13}C NMR.

Benzoin		TBD		d_6-DMSO	Total volume	Molar benzoin / TBD ratio
Volume (mL)	n (mmol)	Volume (mL)	n (mmol)	Volume (mL)	(mL)	
0.5	0.1	0	0	0.5	1	**1 : 0**
0.5	0.1	0.125	0.025	0.375	1	**1 : 0.25**
0.5	0.1	0.25	0.05	0.25	1	**1 : 0.5**
0.5	0.1	0.375	0.075	0.125	1	**1 : 0.75**
0.5	0.1	0.5	0.1	0	1	**1 : 0**

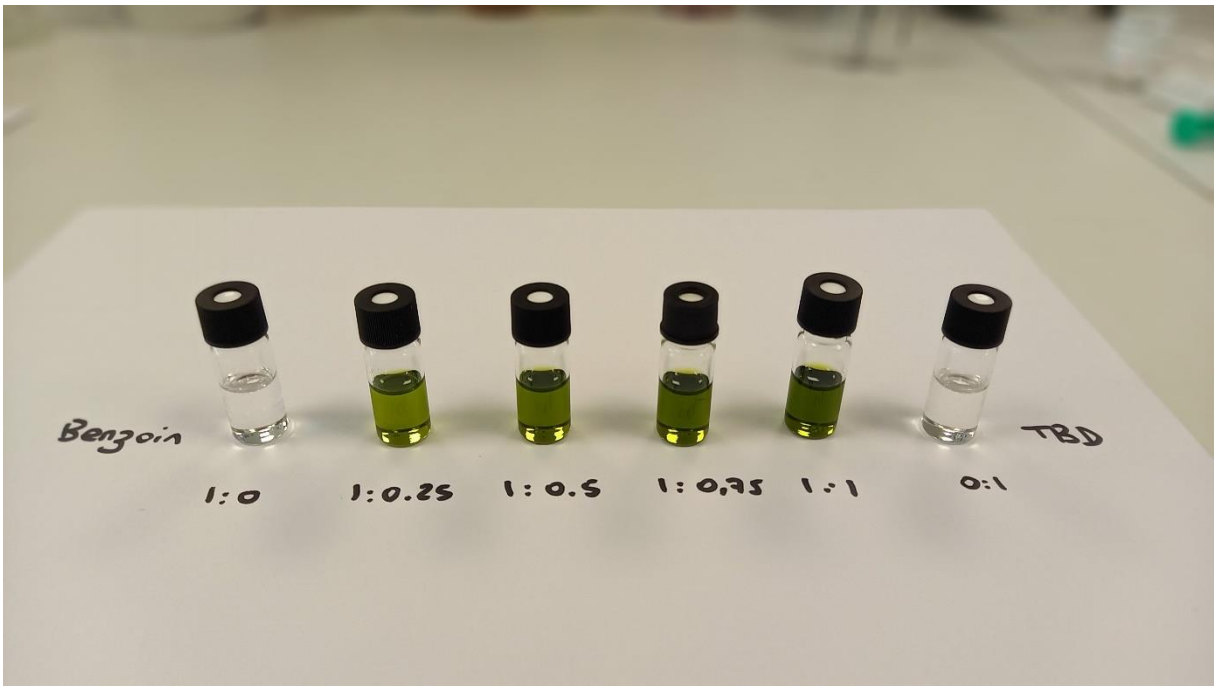


Figure S3. Picture of the solutions of benzoin / TBD mixtures in d_6-DMSO (before transferring to NMR tubes)

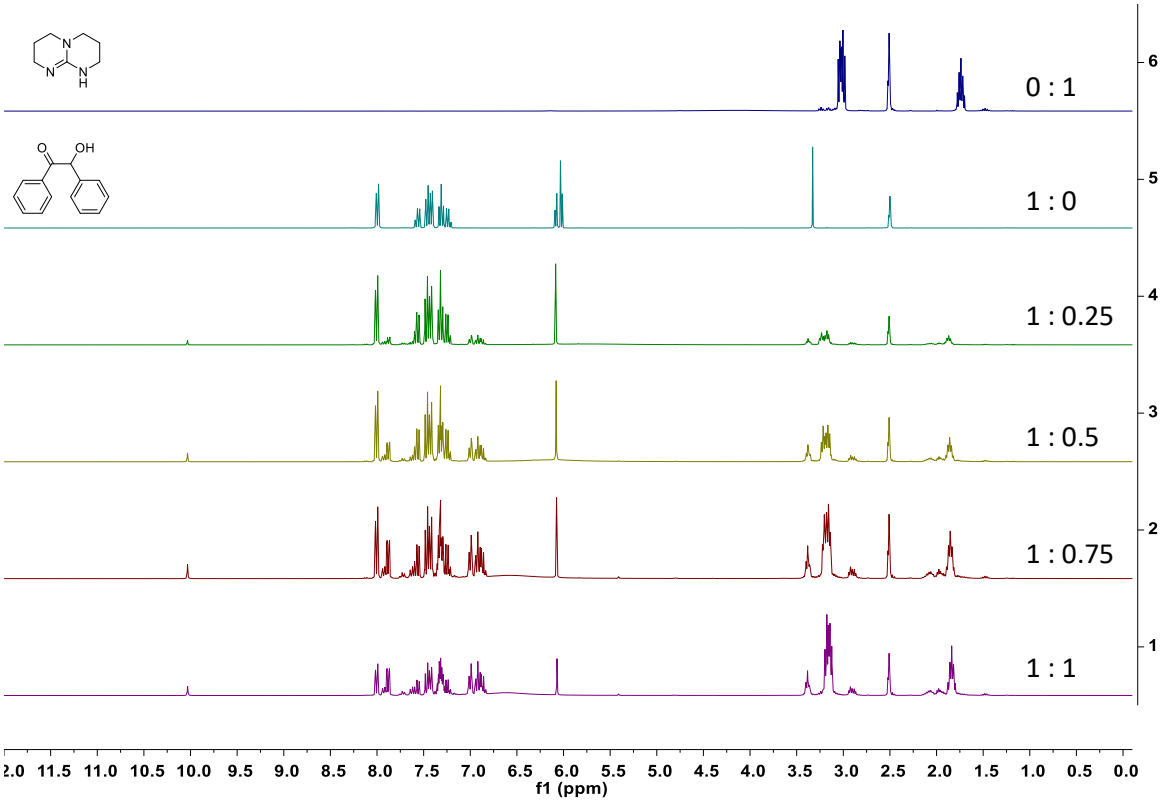


Figure S4. Superimposition of ^{1}H NMR (300 MHz, d_6-DMSO) spectra of benzoin / TBD mixtures.

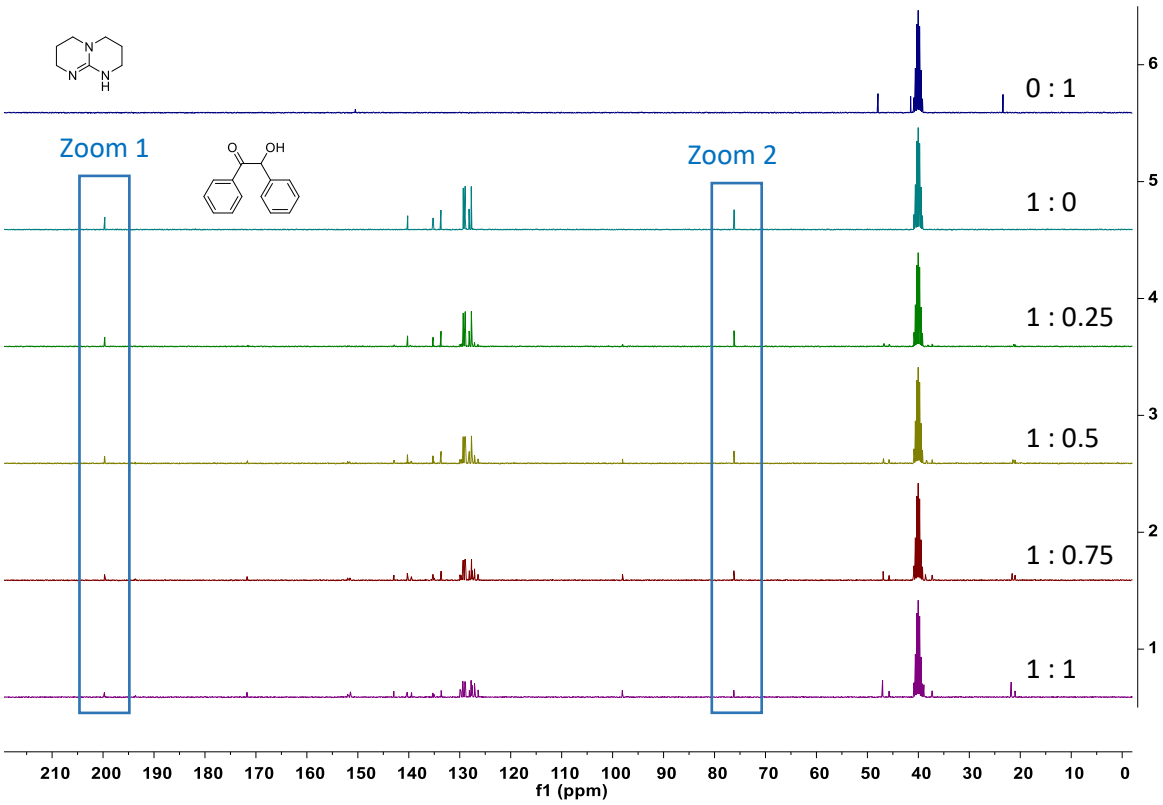


Figure S5. Superimposition of ^{13}C NMR (75 MHz, d_6-DMSO) spectra of benzoin / TBD mixtures.

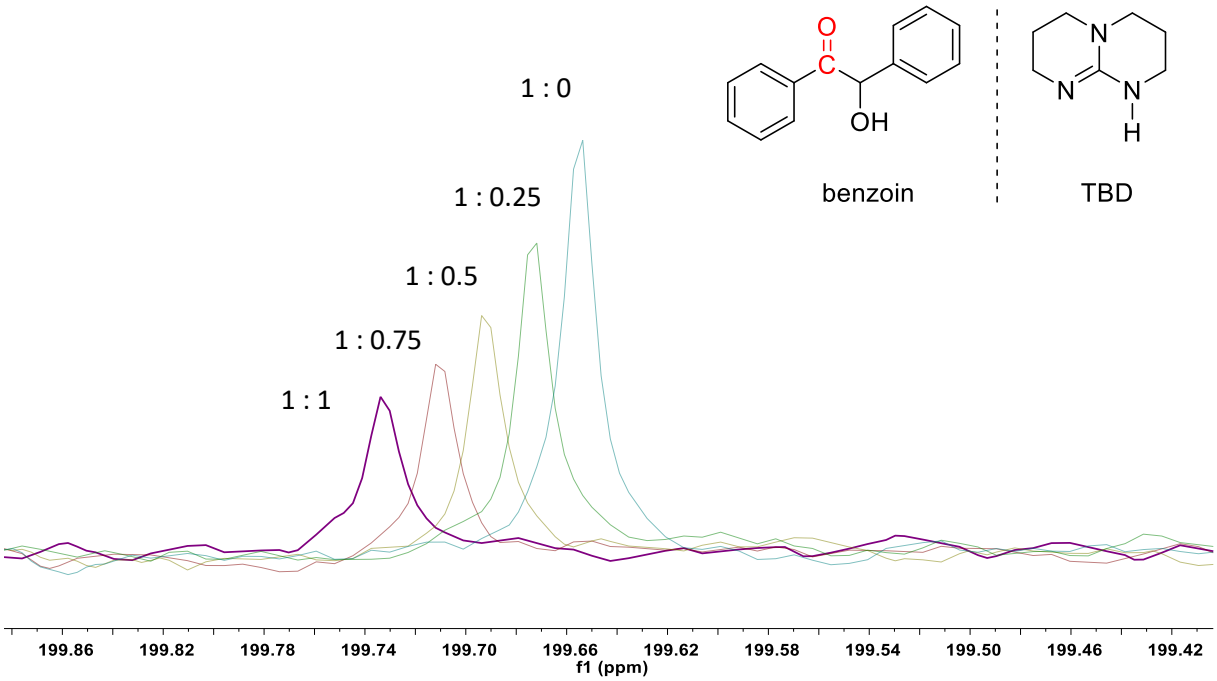


Figure S6. Superimposition of ^{13}C NMR (75 MHz, d_6-DMSO) spectra of benzoin / TBD mixtures (stacked, zoom 1 of the carbonyl region).

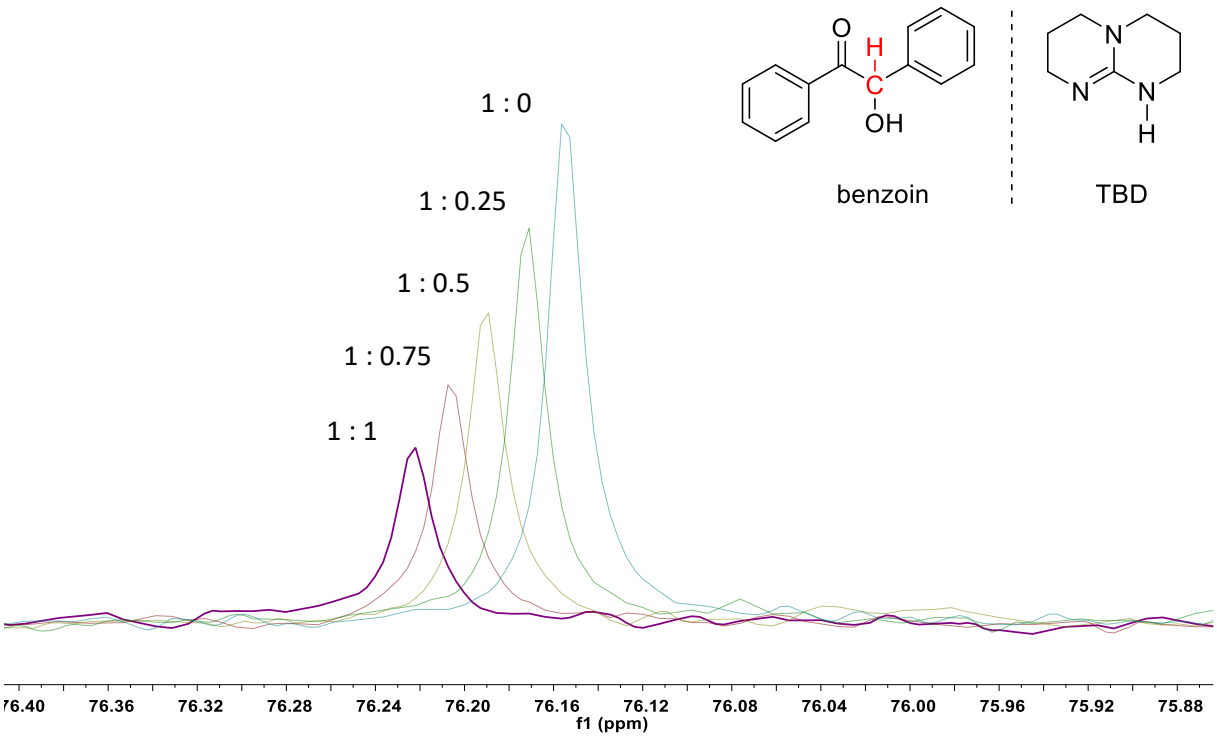


Figure S7. Superimposition of ^{13}C NMR (75 MHz, d_6-DMSO) spectra of benzoin / TBD mixtures (stacked, zoom 2 of the CH region).

8.2. NMR of diphenyl carbonate / TBD mixtures

A 0.2 M mother solution of *diphenyl carbonate* was prepared by dissolving 128.4 mg (0.6 mmol) of benzoin in 3 mL of d_6-DMSO.

A 0.2 M mother solution of *TBD* was prepared by dissolving 41.7 mg (0.3 mmol) of benzoin in 1.5 mL of d_6-DMSO.

Five (5) solutions of diphenyl carbonate / TBD mixtures in d_6-DMSO were prepared as follows and the solutions were transferred in NMR tubes to record ^{1}H and ^{13}C NMR.

Diphenyl carbonate		TBD		d_6-DMSO	Total volume	Molar benzoin / TBD ratio
Volume (mL)	n (mmol)	Volume (mL)	n (mmol)	Volume (mL)	(mL)	
0.5	0.1	0	0	0.5	1	**1 : 0**
0.5	0.1	0.125	0.025	0.375	1	**1 : 0.25**
0.5	0.1	0.25	0.05	0.25	1	**1 : 0.5**
0.5	0.1	0.375	0.075	0.125	1	**1 : 0.75**
0.5	0.1	0.5	0.1	0	1	**1 : 0**

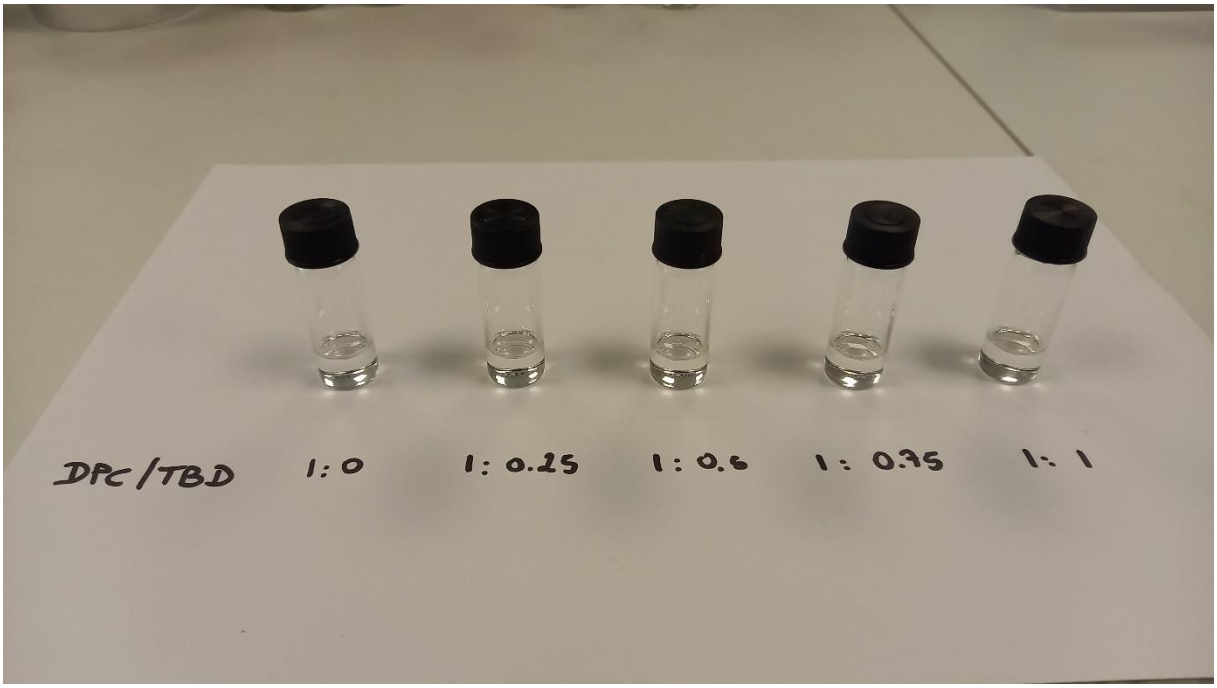


Figure S8. Picture of the solutions of diphenyl carbonate / TBD mixtures in d_6-DMSO (before transferring to NMR tubes)

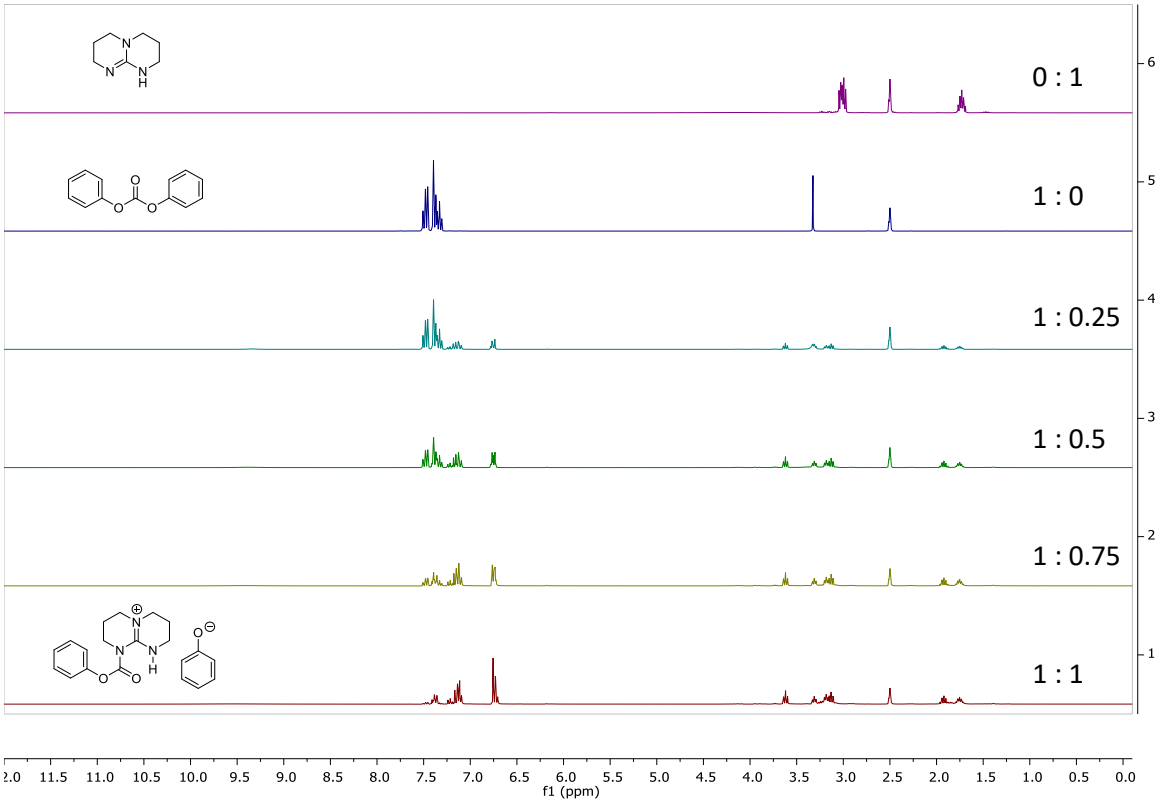


Figure S9. Superimposition of ^{1}H NMR (300 MHz, d_6-DMSO) spectra of diphenyl carbonate / TBD mixtures.

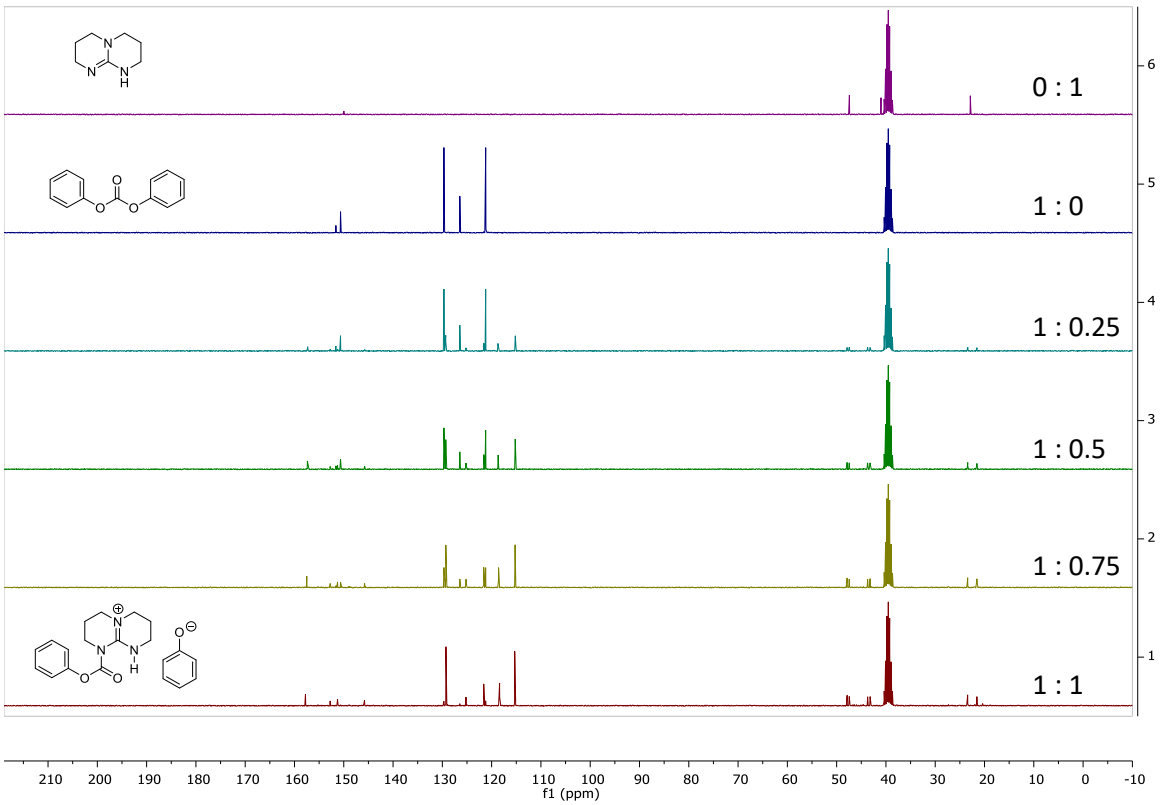
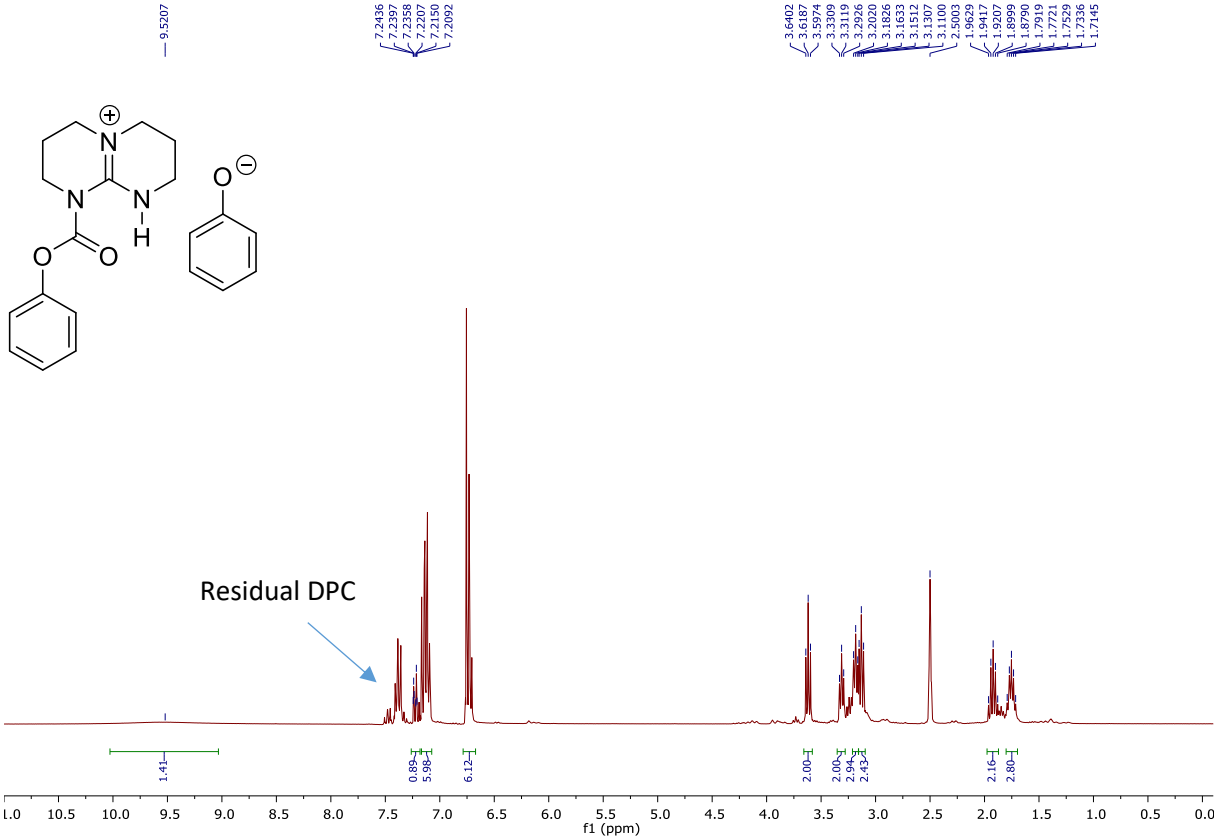
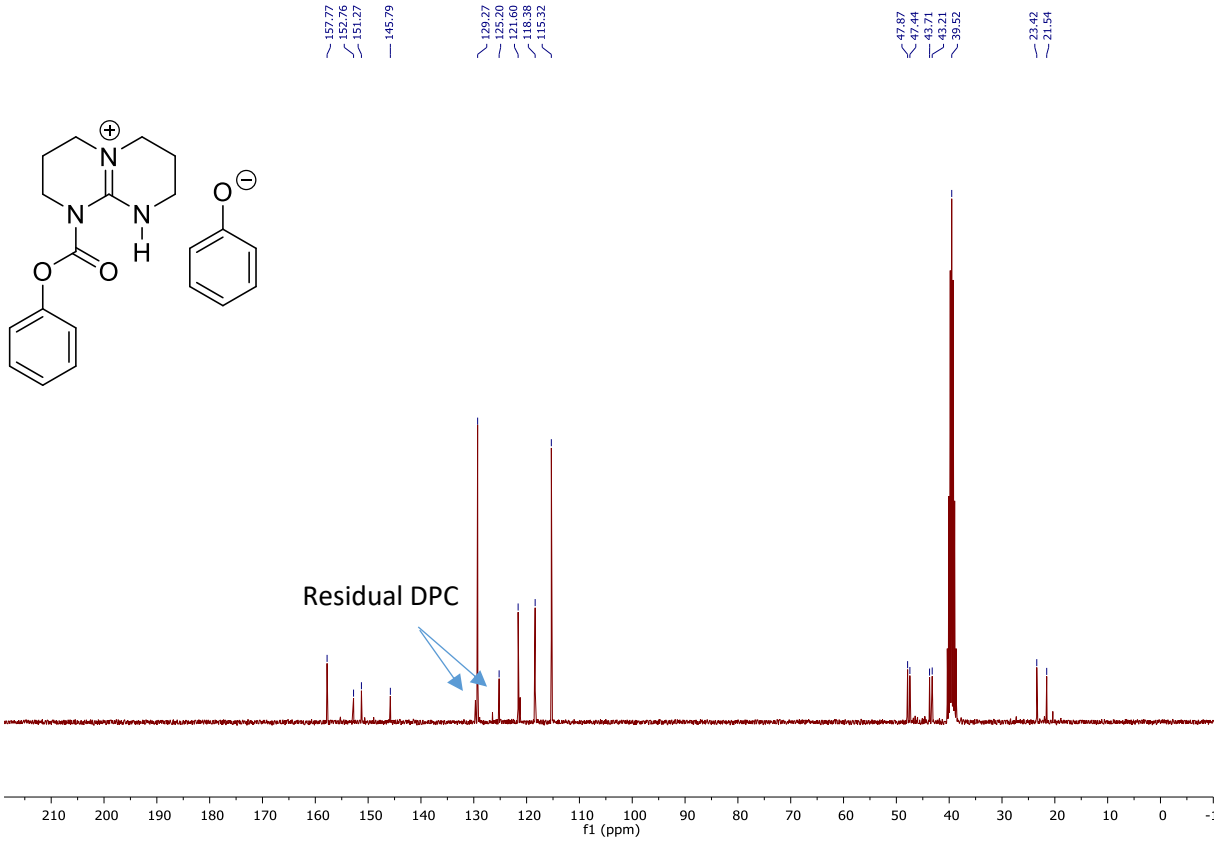


Figure S10. Superimposition of ^{13}C NMR (75 MHz, d_6-DMSO) spectra of diphenyl carbonate / TBD mixtures.

^{1}H NMR (300 MHz, d_6-DMSO) of diphenyl carbonate / TBD 1:1 adduct



^{13}C NMR (75 MHz, d_6-DMSO) of diphenyl carbonate / TBD 1:1 adduct



9. Mechanism proposal

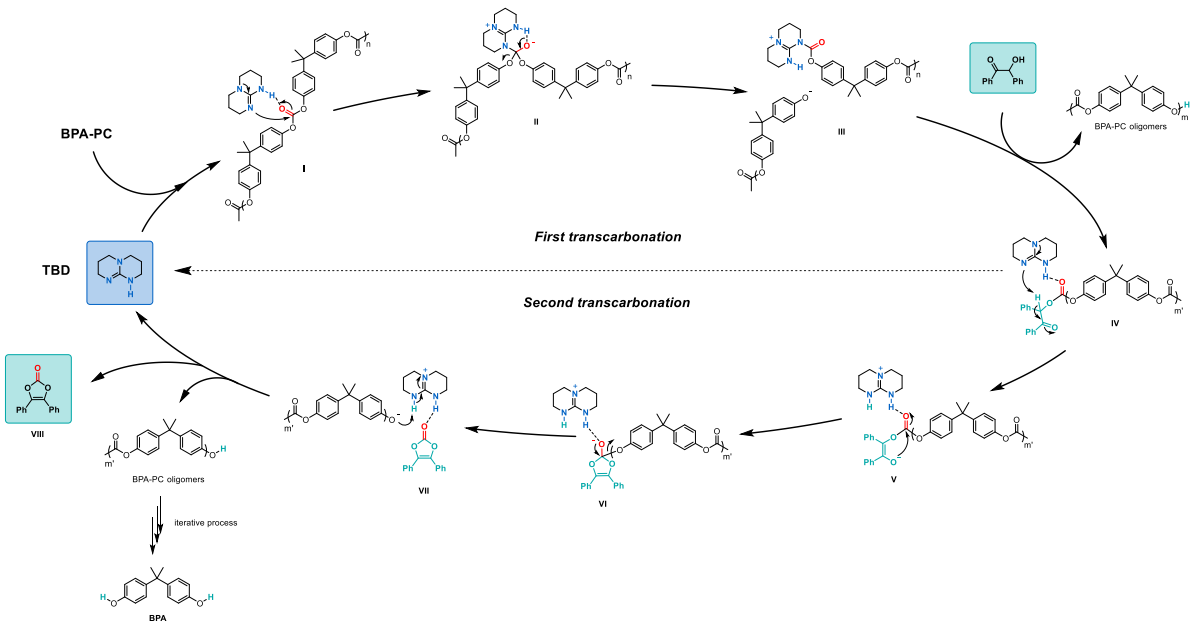


Figure S11. Mechanism proposal 1: Transcarbonation through carbonate activation (preferred).

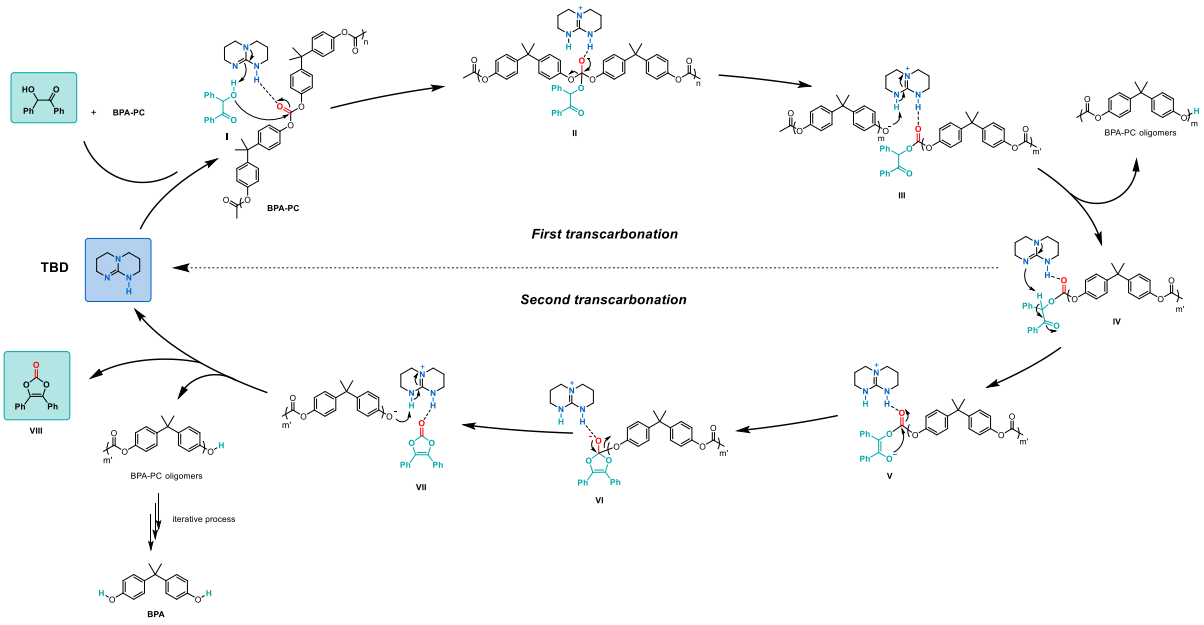


Figure S12. Mechanism proposal 2: Transcarbonation through dual (benzoin/carbonate) activation (alternative)

10. High-resolution mass spectrometry of vinylene carbonates

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_201204_12_KO-207.d		
Method	Tune_pos_Standard.m	Acquisition Date	12/4/2020 5:08:17 PM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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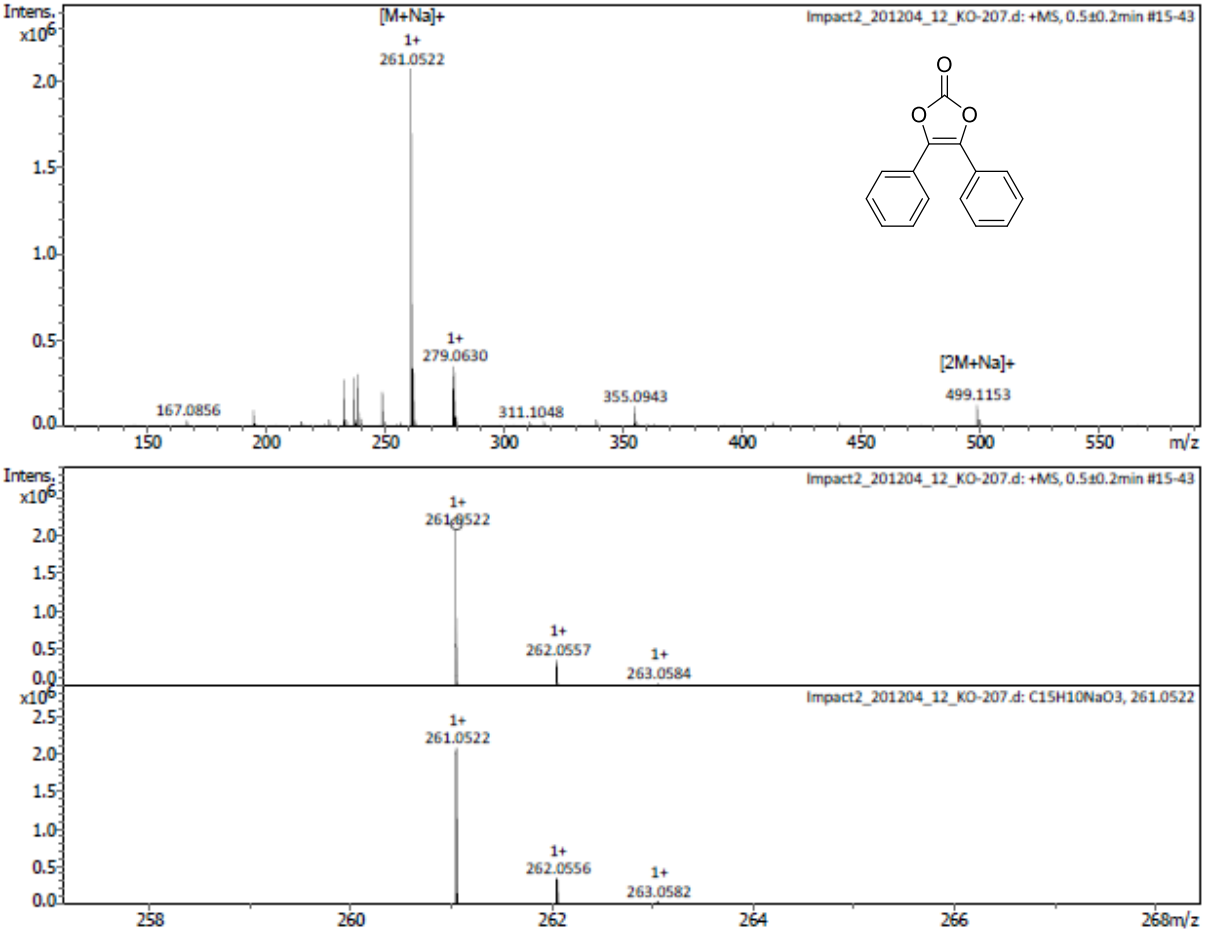
Scan End	1200 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
239.0702	C15H11O3	239.0703	C15H10O3	0.4	5.7	M+H	1+
261.0522	C15H10NaO3	261.0522		0.2	0.9	M+Na	1+
499.1153	C30H20NaO6	499.1152		-0.1	4.8	2M+Na	1+

Bruker Compass DataAnalysis 5.2 Page 1 of 1

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_210507_01_KO-338-2-P.d		
Method	Tune_pos_Standard.m	Acquisition Date	5/7/2021 8:45:05 AM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
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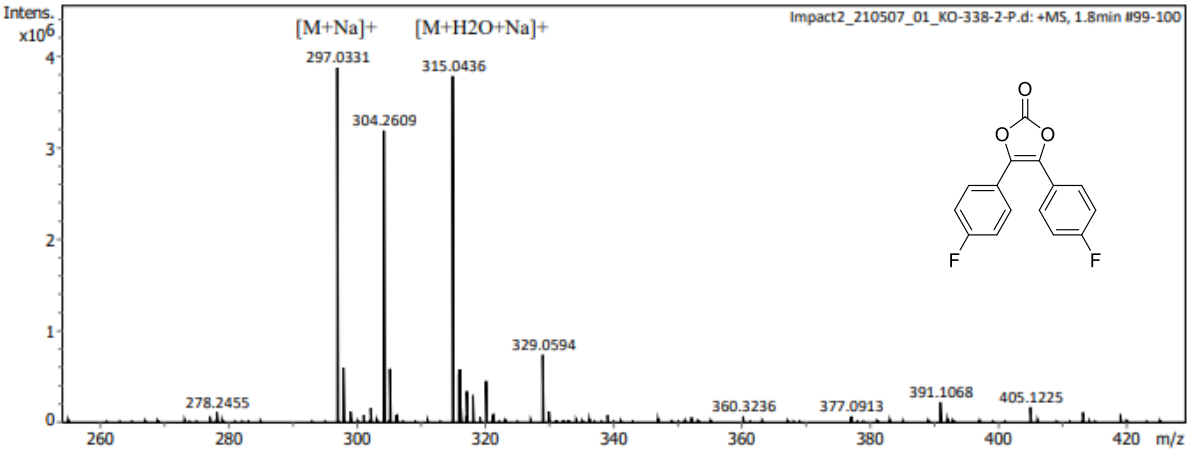
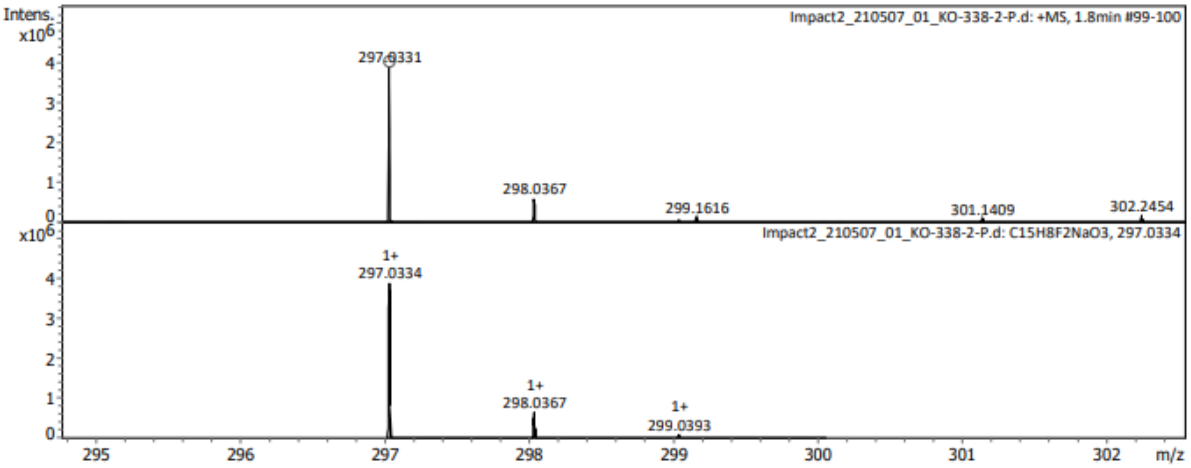
Scan End	1200 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source





Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
297.0331	C15H8F2NaO3	297.0334	C15H8F2O3	0.8	4.8	M+Na	1+
315.0436	C15H10F2NaO4	315.0439	C15H10F2O4	1.0	6.4	M+Na	1+

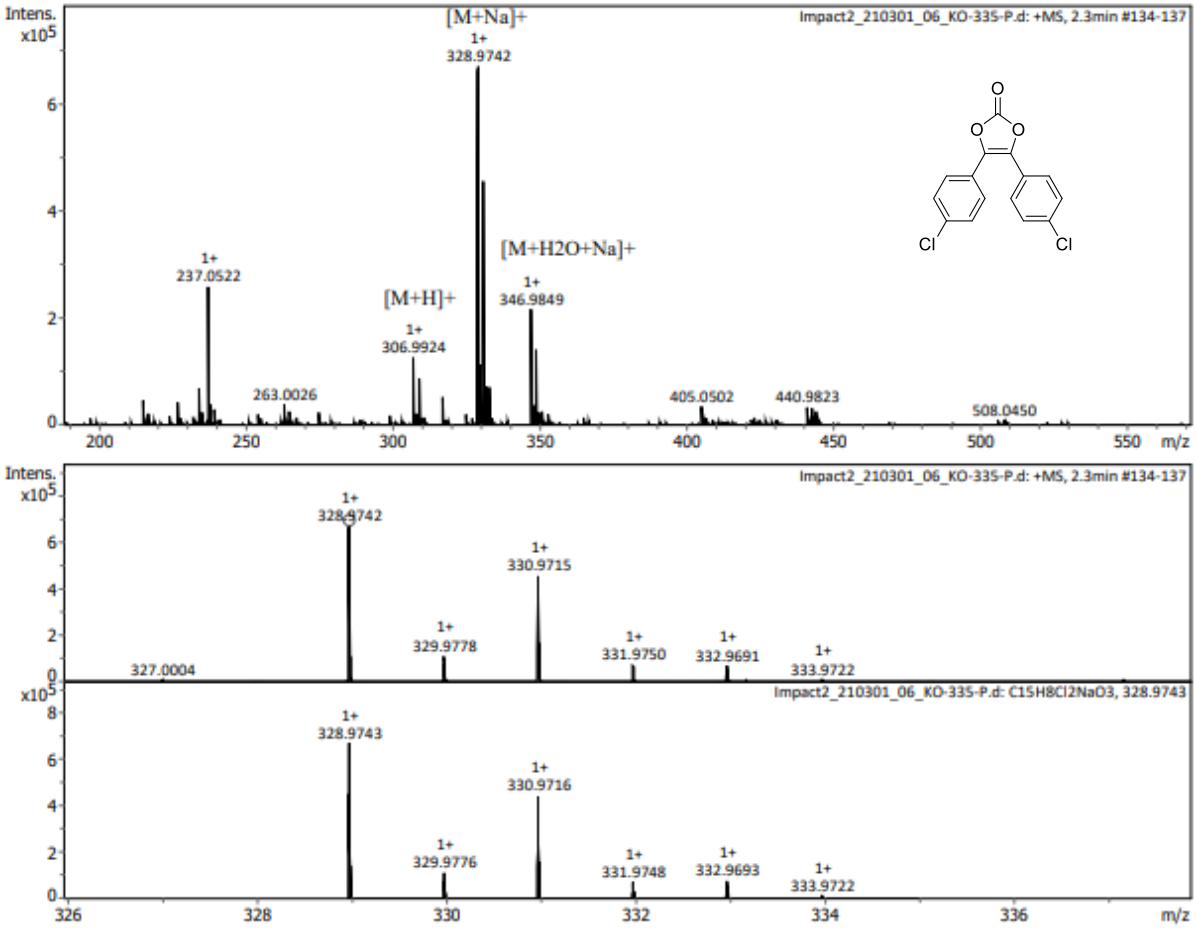
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_210301_06_KO-335-P.d		
Method	Tune_pos_Standard.m	Acquisition Date	3/1/2021 11:23:41 AM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	110 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
306.9924	C15H9Cl2O3	306.9923	C15H8Cl2O3	-0.3	10.7	M+H	1+
328.9742	C15H8Cl2NaO3	328.9743		0.1	10.0	M+Na	1+
346.9849	C15H10Cl2NaO4	346.9848	C15H10Cl2O4	-0.2	5.4	M+Na	1+

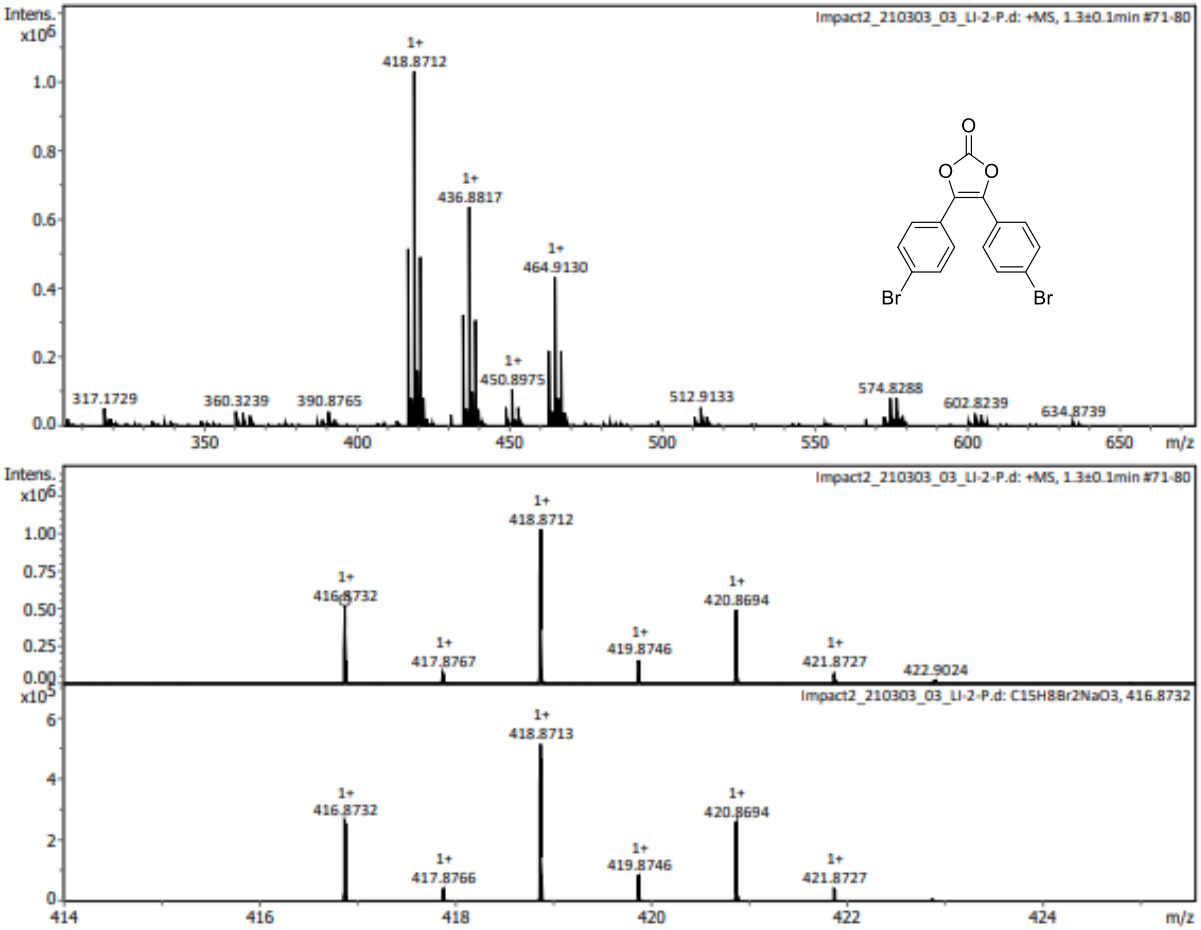
CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_210303_03_LI-2-P.d		
Method	Tune_pos_Standard.m	Acquisition Date	3/3/2021 8:27:07 AM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1200 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
416.8732	C15H8Br2NaO3	416.8732	C15H8Br2O3	0.2	10.5	M+Na	1+

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_210510_01_KO-397-P.d		
Method	Tune_pos_Standard.m	Acquisition Date	5/10/2021 10:42:13 AM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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Focus	Active	Set Capillary	1200 V	Set Dry Heater	200 °C
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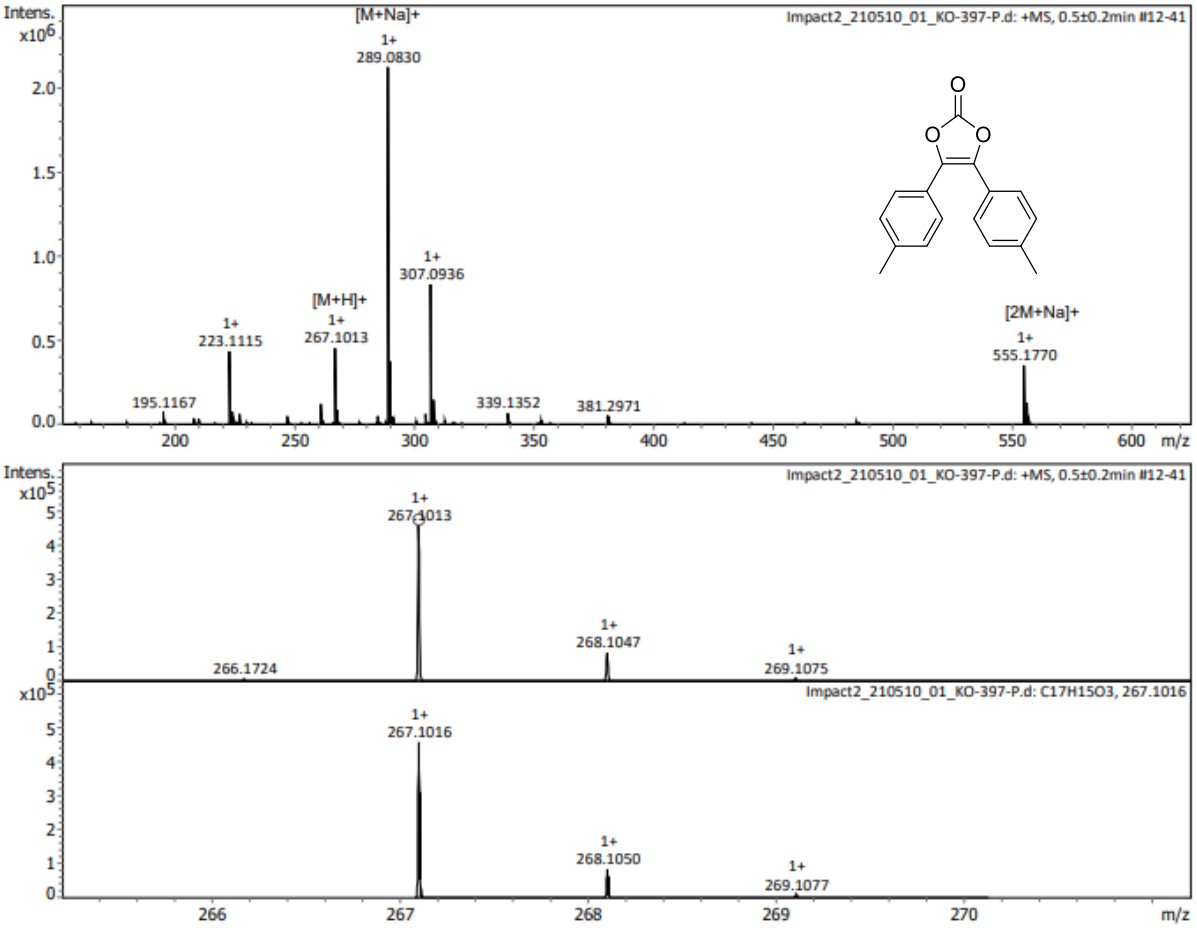
Scan End	1200 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
267.1013	C17H15O3	267.1016	C17H14O3	1.0	0.8	M+H	1+
289.0830	C17H14NaO3	289.0835		1.7	5.9	M+Na	1+
555.1770	C34H28NaO6	555.1778		1.5	5.3	2M+Na	1+

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_201204_13_KO-217.d		
Method	Tune_pos_Standard.m	Acquisition Date	12/4/2020 5:14:59 PM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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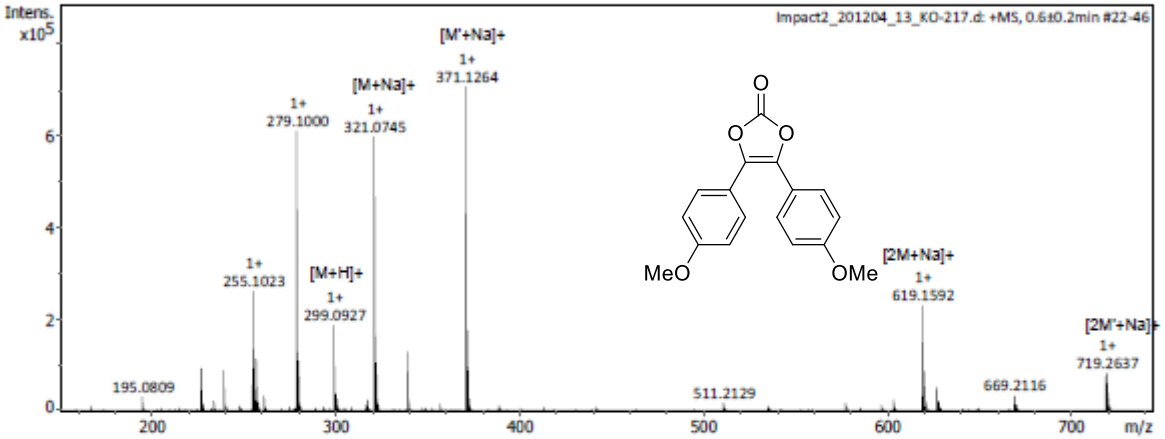
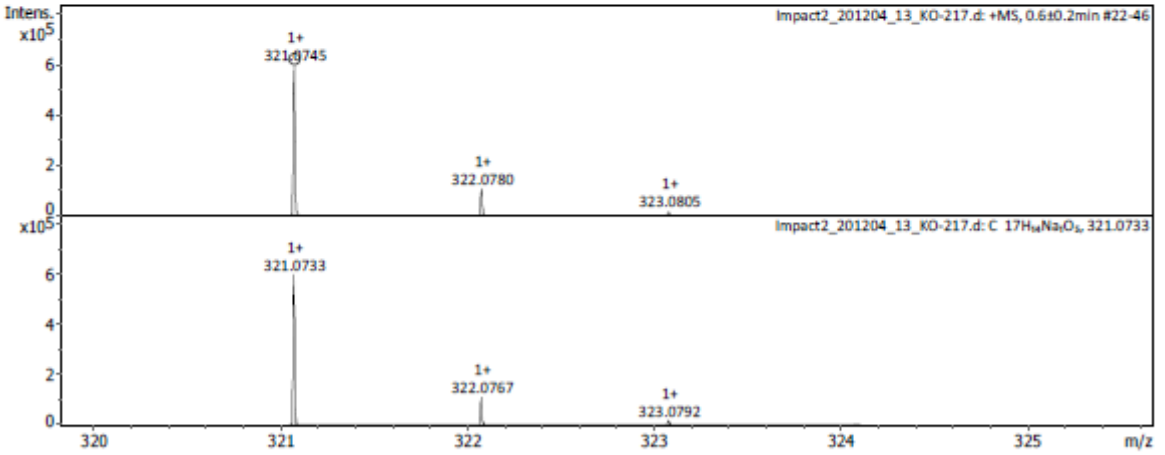
Scan End	1200 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source





Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
299.0927	C17H15O5	299.0914	C17H14O5	-4.2	18.2	M+H	1+
321.0745	C17H14NaO5	321.0733		-3.7	6.3	M+Na	1+
619.1592	C34H28NaO10	619.1575		-2.7	0.8	2M+Na	1+

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_210427_27_KO-378-P.d		
Method	Tune_pos_Standard.m	Acquisition Date	4/27/2021 6:06:11 PM
Comment		Instrument / Ser#	impact II 1825265.1 0081

Acquisition Parameter

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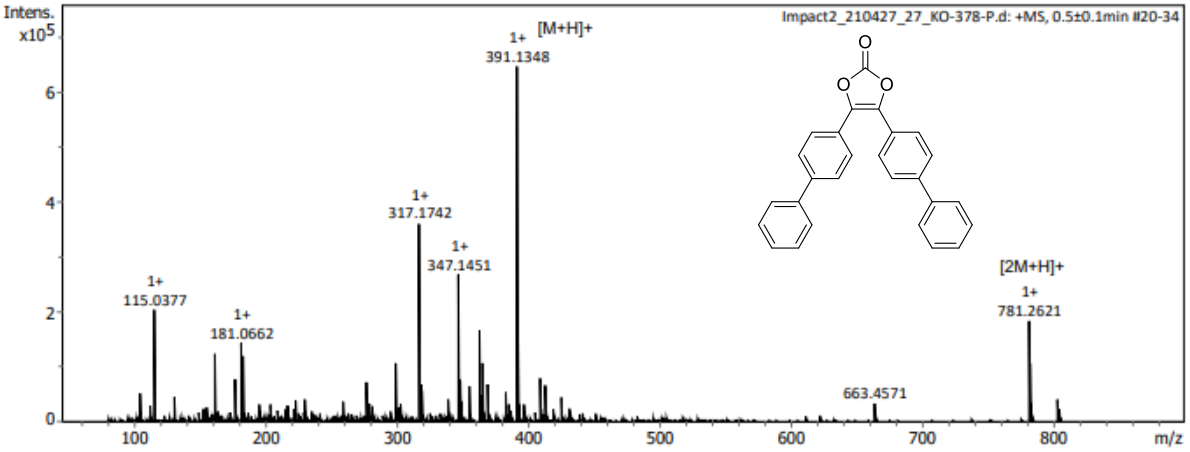
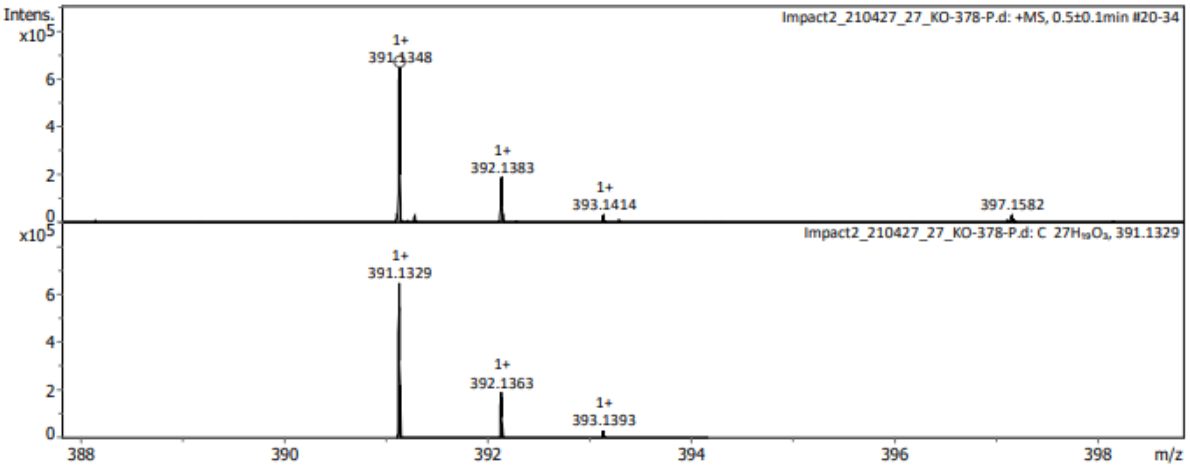
Scan End	1200 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source





Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
391.1348	C27H19O3	391.1329	C27H18O3	-5.0	3.2	M+H	1+
781.2621	C54H37O6	781.2585		-4.6	6.0	2M+H	1+
803.2442	C54H36NaO6	803.2404		-4.8	7.6	2M+Na	1+

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_210701_06_KO-446-p.d		
Method	Tune_pos_Standard.m	Acquisition Date	7/1/2021 6:09:30 PM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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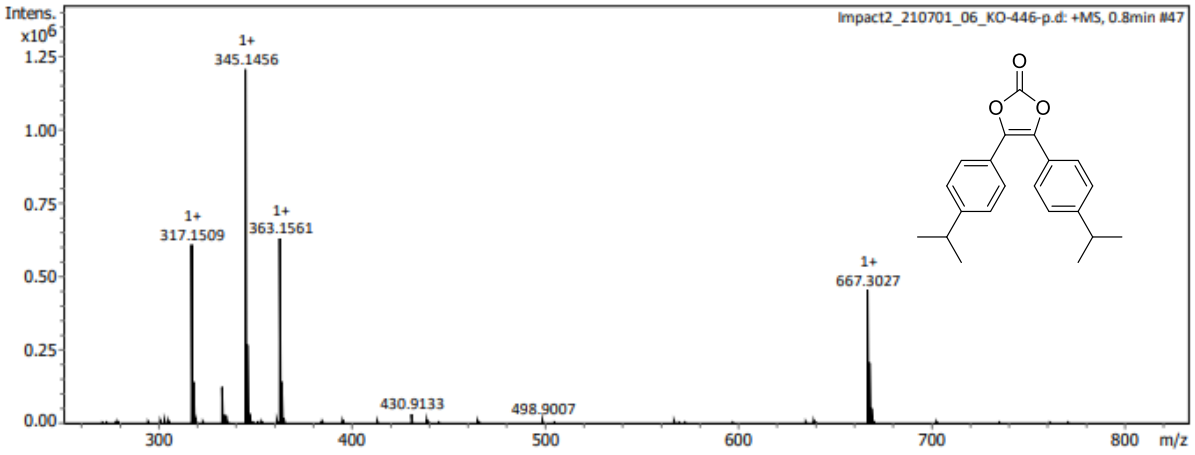
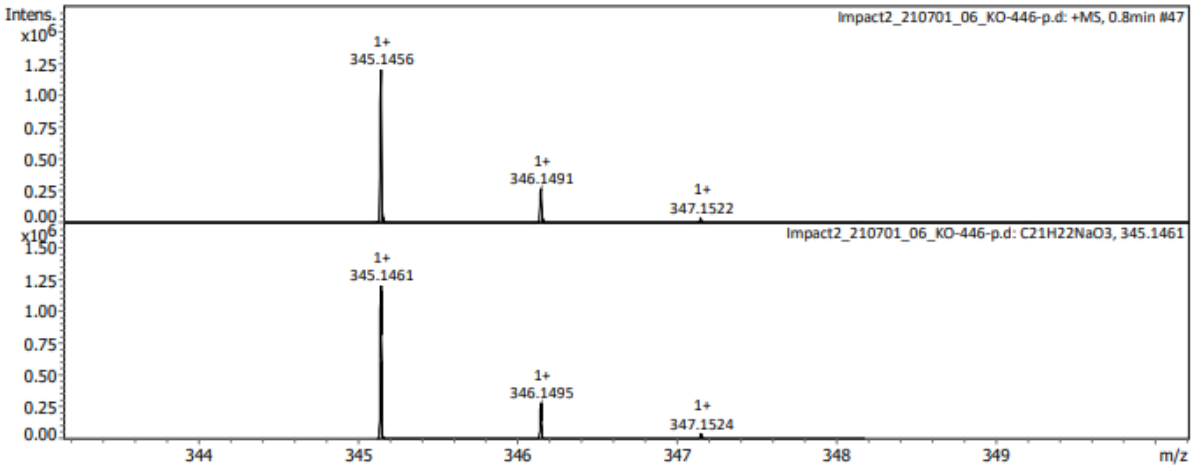
Scan End	1200 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source





Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
345.1456	C21H22NaO3	345.1461	C21H22O3	1.5	4.8	M+Na	1+
667.3027	C42H44NaO6	667.3030		0.5	2.5	2M+Na	1+

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_220603_04_MF-95.d		
Method	Tune_pos_Standard.m	Acquisition Date	6/3/2022 2:56:55 PM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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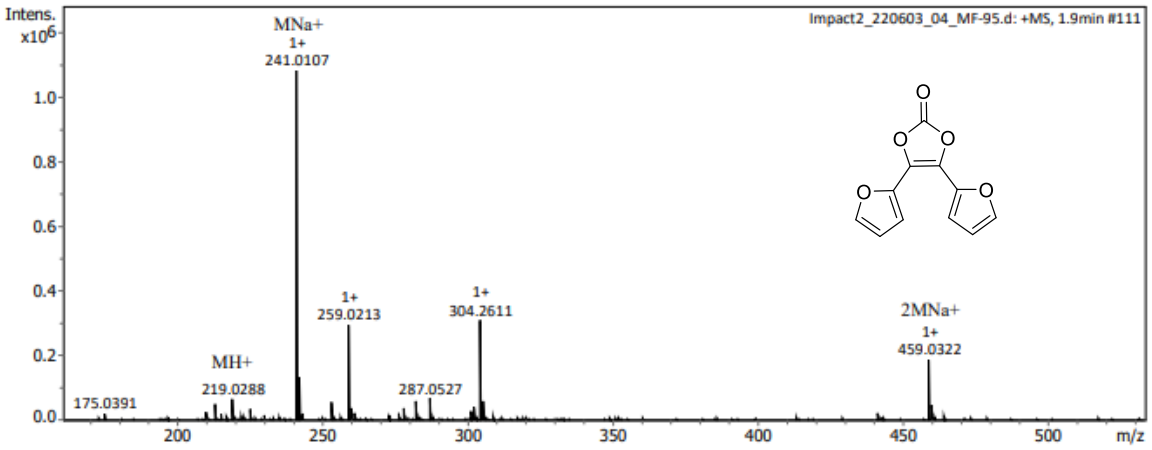
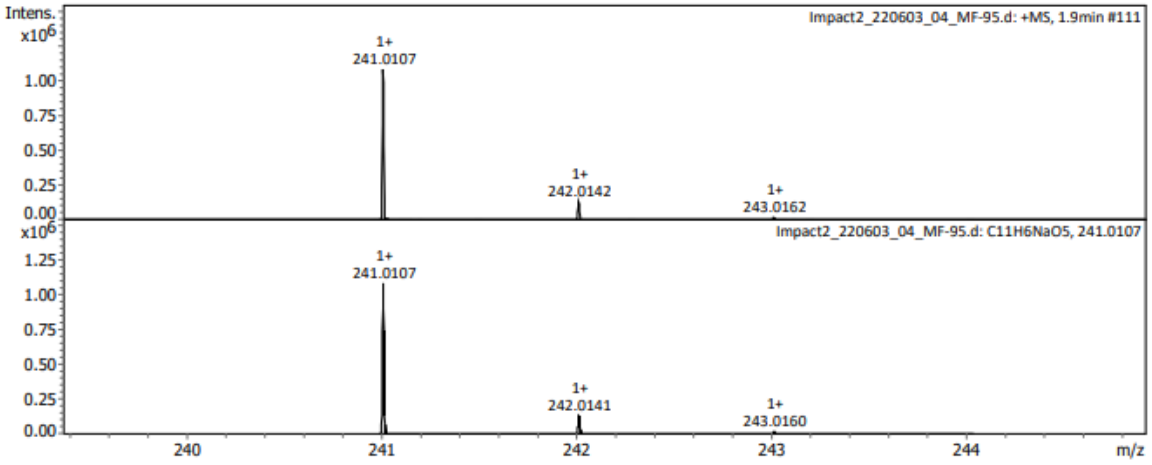
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source





Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
219.0288	C11H7O5	219.0288	C11H6O5	-0.1	5.0	M+H	1+
241.0107	C11H6NaO5	241.0107		0.0	1.0	M+Na	1+
459.0322	C22H12NaO10	459.0323		0.1	8.7	2M+Na	1+

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_220630_01_MF-97.d		
Method	Tune_pos_Standard.m	Acquisition Date	6/30/2022 10:22:54 AM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
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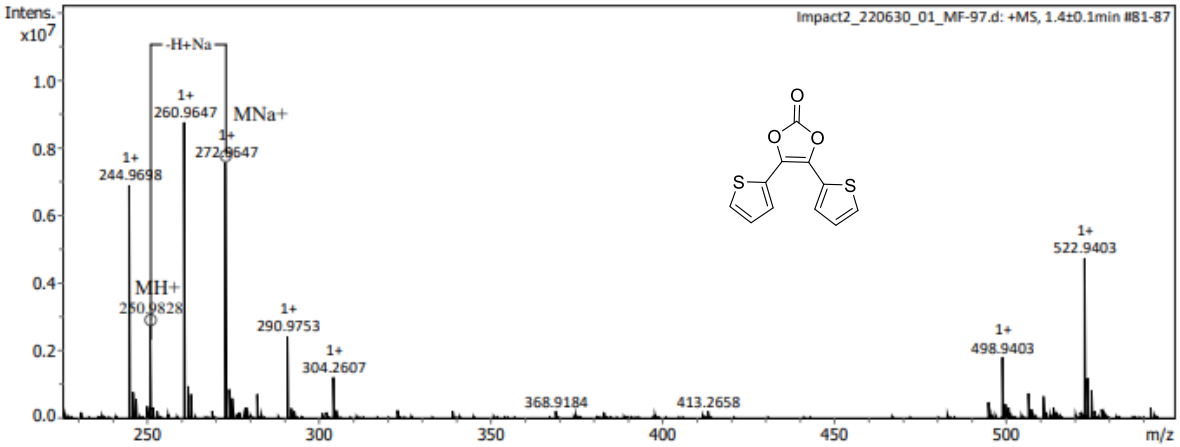
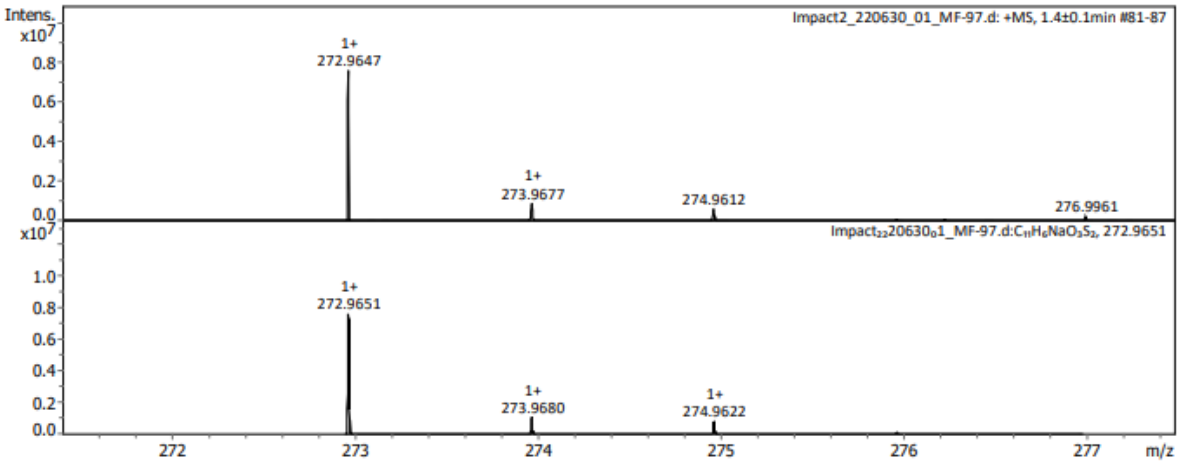
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source





Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
250.9828	C11H7O3S2	250.9831	C11H6O3S2	1.4	12.5	M+H	1+
272.9647	C11H6NaO3S2	272.9651		1.2	16.2	M+Na	1+

CENTRE COMMUN DE SPECTROMETRIE DE MASSE

Analysis Info

Analysis Name	Impact2_210401_05_KO-359-P.d		
Method	Tune_pos_Standard.m	Acquisition Date	4/1/2021 12:44:27 PM
Comment		Instrument / Ser#	impact II 1825265.10081

Acquisition Parameter

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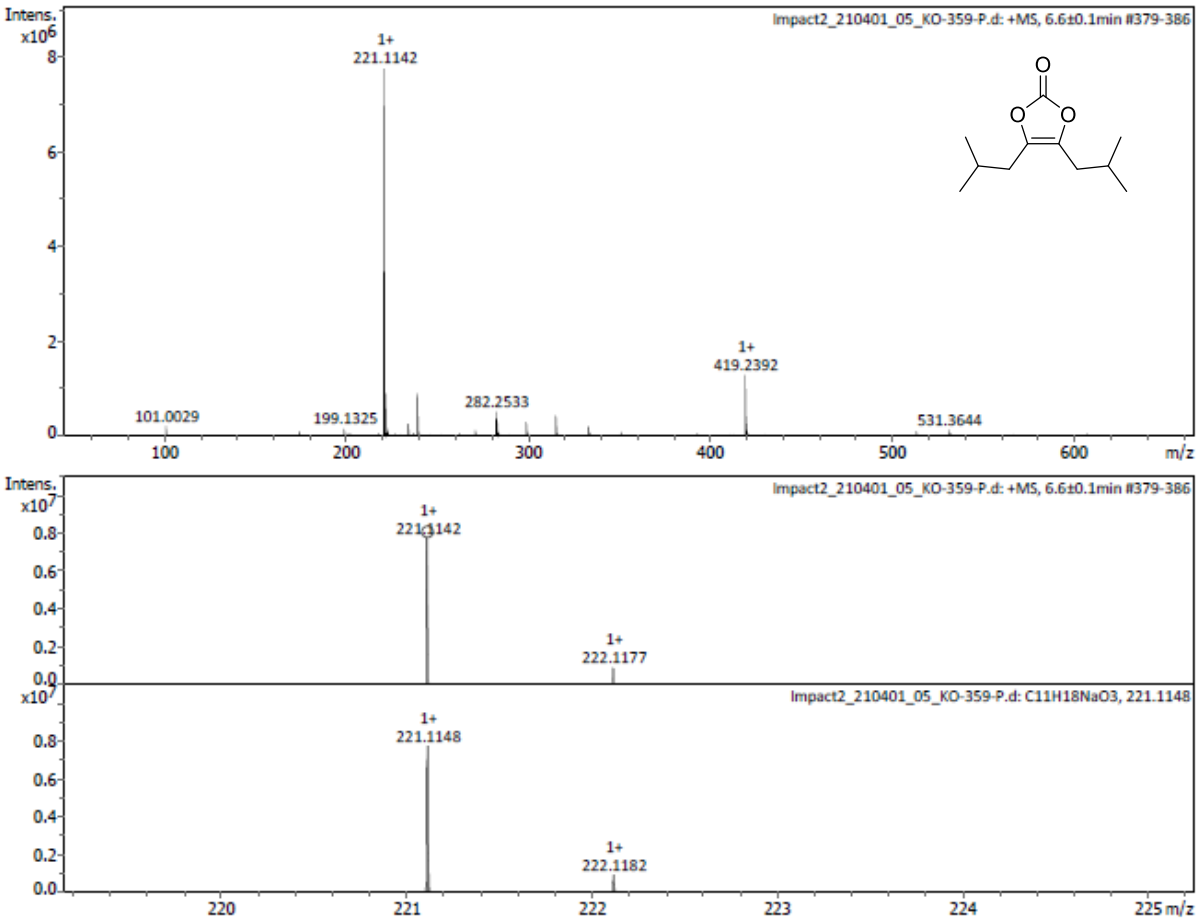
Scan End	1000 m/z	Set Collision Cell RF	750.0 Vpp	Set Divert Valve	Source



Meas. m/z	Ion Formula	m/z	Sum Formula	err [ppm]	mSigma	Adduct	z
221.1142	C11H18NaO3	221.1148	C11H18O3	3.0	3.4	M+Na	1+
419.2392	C22H36NaO6	419.2404		2.9	0.9	2M+Na	1+

11. Size-exclusion chromatography (SEC)

Molecular weight measurements were performed using a size exclusion chromatography (SEC) from Malvern Panalytical (Viscotek TDA). Stabilized THF was used as the mobile phase at a flow rate of 1 mL min^{-1} at 40 °C. Samples were injected at a concentration of about 3 mg mL^{-1} after filtration through a 0.45 µm PTFE membrane. Separation was performed on three Agilent mixed C columns (SDVB, 5 µm, 300 x 7.5 mm). Molecular weights were determined using a conventional calibration curve based on certified PS standards (Polymer Standards Service) from 470 to 2,500,000 g mol^{-1}. Omnisec 5.12 (Malvern Panalytical) software was used for data acquisition and processing.

SEC of commercially available BPA-PC (Sigma-Aldrich, M_w of about 45,000 g/mol).

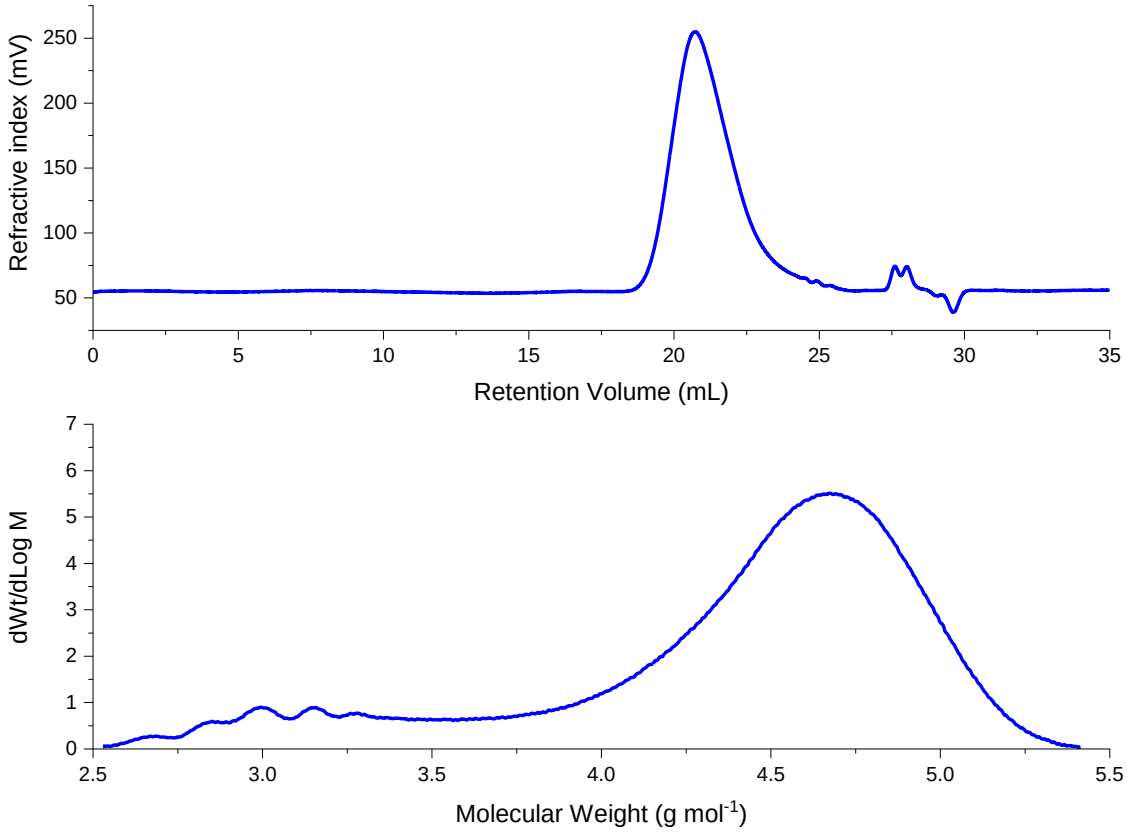


Figure S13. Chromatogram and molar mass distributions of commercially available BPA-PC obtained by SEC.

Sample Id	Mw (g mol^{-1})	Mn (g mol^{-1})
BPA-PC (Sigma-Aldrich)	42,560	7,290

Table S1. Average molecular weight values of commercially available BPA-PC (M_n, number average molecular weight and M_w, weight average molecular weight).

SEC of BPA-polycarbonate contained in CD, safety glasses and polycarbonate plate.

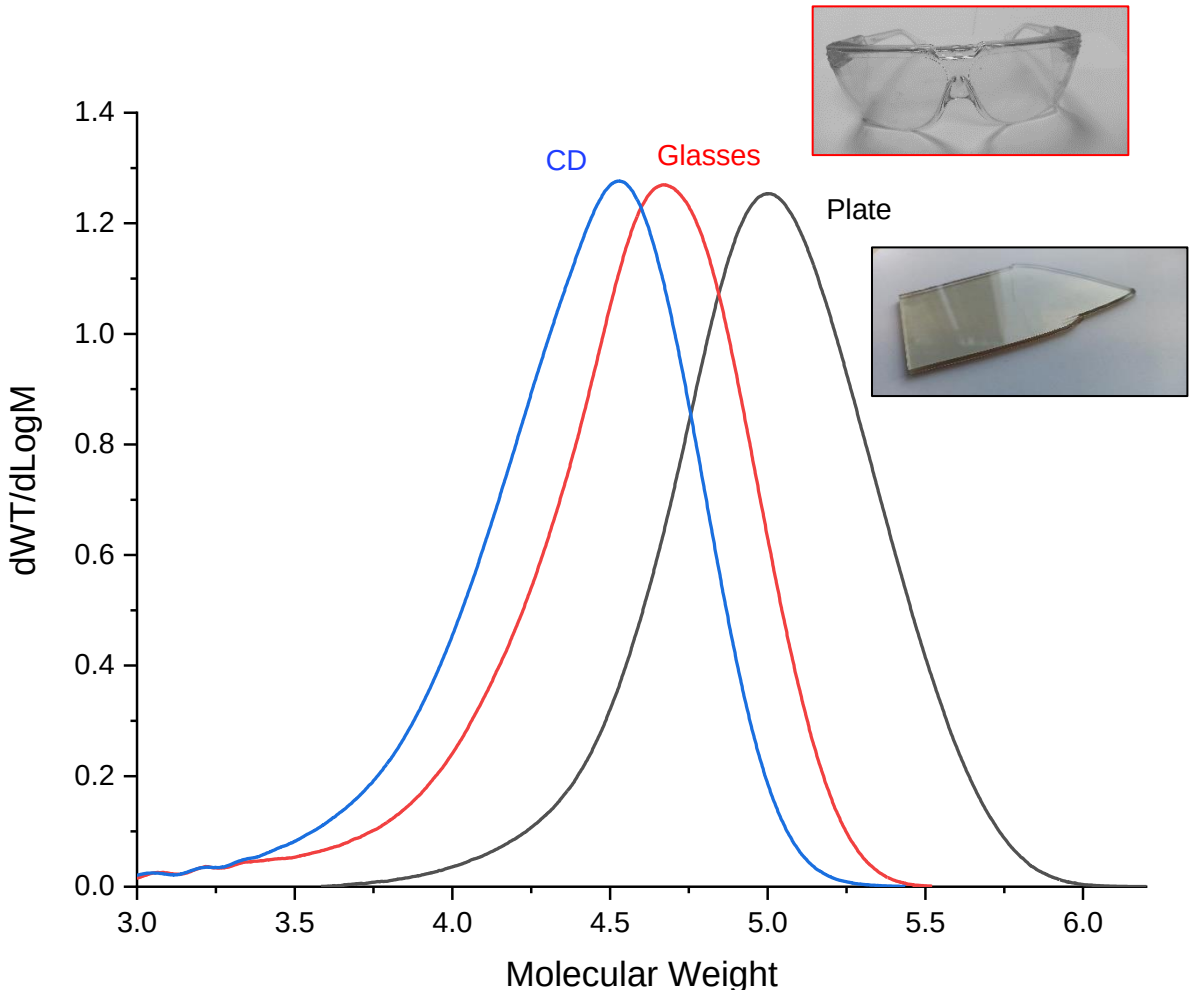


Figure S14. Molar mass distributions of BPA-polycarbonate contained in CD, safety glasses and polycarbonate plate obtained by SEC.

Sample Id	Mw (g mol^{-1})	Mn (g mol^{-1})
PC plate	133,986	72,545
PC glasses	49,163	21,704
PC CD	32,805	16,200

Table S2. Average molecular weight values of BPA-polycarbonate contained in CD, safety glasses and polycarbonate plate (M_n, number average molecular weight and M_w, weight average molecular weight).