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# Flex-activated CO Mechanochemical Production for Mechanical Damage Detection †

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## I. General experimental details:

All materials, unless otherwise stated, were purchased from commercial sources and utilised without further purification. 9,10-phenanthrenequinone was recrystallized in 1,4-dioxane prior to use. MMA precursor was filtered through basic alumina column to remove the polymerization inhibitor. Flash column chromatography was conducted with silica gel 60 (230-400 mesh) from Merck. For thin-layer chromatography, silica gel GF254 plates were used and visualized with a UV lamp (254 nm). All $^{1}H$ and $^{13}C$ NMR spectra were recorded using an AVANCE II 400 MHz Bruker spectrometer at the Technion NMR facilities. High-resolution mass spectrometry was performed in a Waters LCT Premier Mass Spectrometer (ESI) or a Bruker maxis impact with APCI solid probe. Thermal gravimetric analysis (TGA) was conducted on a TA instruments and done under $N_2$ at $5°C \cdot min^{-1}$. Raman spectra were obtained by using a confocal micro-Raman LabRam HR instrument from Horiba Scientific in backscattering geometry with a 50× objective mounted on an Olympus optical microscope. The excitation line was provided by VIS 532 nm laser (Torus, 100 mW) and a Peltier cooled charge-couple device (CCD) (1024 × 256 pixels) was used as detector. The calibration is initially made using a silicon reference at 520 $cm^{-1}$ which gives a peak position resolution of less than 1 $cm^{-1}$. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra were recorded on a JASCO 3600 FTIR spectrometer at room temperature. Ball milling was performed using a Retsch Cryomill cooled with liquid nitrogen. Fluorescent emission measurement was recorded by Jobin Yvon (Fluorolog-3) Fluorometer equipped with a temperature controlled holder 30 °C) after diluting the sample with $CHCl_3$. UV-Vis measurements were done in Thermo Evolution 220 Spectrophotomer after diluting the sample in $CHCl_3$.

## II. Synthesis procedures:

### Synthesis of 1,3-bis(4-methoxyphenyl)propan-2-one (1)

**1** is prepared according to literature procedure.[1] A solution of dicyclohexylcarbodiimide (DCC) (15.5 g, 75 mmol) and 4- (dimethyl amino) pyridine (DMAP) (0.92 g, 7.5 mmol) in $CH_3CN$ (550 mL) was stirred at 25 °C under argon. A solution of 4-methoxyphenylacetic acid (143 mmol) in $CH_3CN$ (300 mL) was added dropwise to the stirred solution. The resulting mixture was stirred at room temperature for 24 hours. The precipitated solid was removed by filtration. Volatiles from the filtrate were removed by evaporation under reduced pressure. The residue was purified from cold Et-OH to obtain the desired product (13.6 g, 70%). NMR in accordance

with the literature:[1] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.6 Hz, 4H), 6.85 (d, *J* = 8.7 Hz, 4H), 3.80 (s, 6H), 3.64 (s, 4H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 206.7, 158.8, 130.7, 126.2, 114.3, 55.41, 48.2.

**Synthesis of 1,3-bis(4-methoxyphenyl)-2H-cyclopenta[l]phenanthren-2-one (2)**

**2** is prepared according to literature procedure.[2] 1000 ml round-bottom flask equipped with a condenser and a dropping funnel, 9,10-phenanthrenequinone (12.6 g, 60 mmol) and **1** (13.6 g, 50 mmol) were suspended in MeOH (580 mL) and heated to reflux. Then, a solution of KOH (5.6 g, 100 mmol) in MeOH (98 mL) was added dropwise. After complete addition of the KOH solution, the reaction mixture was refluxed overnight and then cooled to room temperature. The precipitated solid was collected, washed with cold MeOH and dried to yield the desired product as a grey solid that was used for the next step without further purification. NMR in accordance with the literature:[2] $^{1}$H NMR (400 MHz, $CD_2Cl_2$) δ 7.82 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.29 (m, 6H), 6.97 (m, 6H), 3.86 (s, 3H). $^{13}$C NMR (101 MHz, $CD_2Cl_2$) δ 198.0, 160.3, 148.0, 134.1, 131.9, 131.7, 129.34, 128.8, 125.2, 125.0, 123.2, 114.7, 55.9.

**Synthesis of 9,14-bis(4-methoxyphenyl)-9,14-dihydro-9,14-methanobenzo[f]tetraphen-15-one (3)**

**3** was prepared according to literature procedure.[3,4] Product **2** (8.7 g, 19.6 mmol) and isoamyl nitrile (5.3 ml, 39.4 mmol) were dissolved in dichloroethane (DCE) (400 ml) in a three-necked round bottom flask which was fitted with a condenser and a dropping funnel. The solution was heated to 65°C. Anthranilic acid (3.2 g, 23.52 mmol) in DCE (250 ml) was added dropwise to the hot solution over a period of 30 min. After the addition was completed, the dark green solution changed to pale yellow. The mixture was further refluxed for 2 h and solvent was removed under reduced pressure. The residue was recrystallized from acetonitrile to give colorless crystals (3.5 g, 35%). NMR in accordance with the literature:[3] $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 8.3 Hz, 2H), 8.05 (m, 4H), 7.86 (d, J = 7.7 Hz, 2H), 7.56 (dd, J = 11.3, 4.1 Hz, 2H), 7.53 – 7.39 (m, 2H), 7.37 (dd, J = 11.3, 3.9 Hz, 2H), 7.21 (dd, J = 5.6, 3.1 Hz, 2H), 7.09 (m, 4H), 3.91 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 195.9, 159.2, 145.0, 142.2, 130.6, 127.2, 126.6, 126.2, 126.0, 126, 124.7, 123.6, 123.5, 77.48, 77.4, 77.2, 76.8, 66.2, 55.4.

**Synthesis of 9,14-bis(4-methoxyphenyl)benzo[f]tetraphene (3')**

**3'** was obtained by heating product **3** to 200°C using a heat gun. NMR in accordance with the literature[5]: $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.5 Hz, 2H), 8.01 – 7.93 (m, 2H), 7.55

(dd, *J* = 8.4, 0.6 Hz, 2H), 7.46 (m, 6H), 7.38 – 7.30 (m, 2H), 7.11 – 7.05 (m, 4H), 7.04 – 6.99 (m, 2H), 3.93 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.3, 134.9, 134.3, 134.0, 133.8, 132.2, 132.0, 131.7, 130.5, 129.1, 127.4, 126.9, 126.8, 126.0, 125.7, 123.5, 114.6, 55.5.

**Synthesis of 9,14-bis(4-hydroxyphenyl)-9,14-dihydro-9,14-methanobenzo[f]tetraphen-15-one (4)**

To a 250 mL round bottom flask, **3** (1.5 g, 2.9 mmol) was added and dissolved in dry dichloromethane (DCM) (180 mL). To this solution, boron tribromide solution (14 mL, 1 M in DCM) was added slowly while the reaction mixture was kept in an ice-bath. The solution was allowed to warm to room temperature and stirred for 15 h. The reaction was quenched by addition of water and the product was extracted into ethyl acetate (EtOAc). The organic layer was then washed with water, sat. $NaHCO_3$ (200 mL× 2) and again with water (200 mL×2). The organic layer was dried over $Na_2SO_4$ and the solvent was evaporated under reduced pressure. The received powder was farther purified by crystallization (acetone/hexane) to obtain clean yellow crystals. $^1$H NMR (400 MHz, DMSO) δ 9.68 (s, 2H), 8.87 (d, J = 8.4 Hz, 2H), 8.10 (dd, J = 5.6, 3.2 Hz, 2H), 7.95 (m, 2H), 7.72 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.1 Hz, 2H), 7.42 (t, J = 7.9 Hz, 2H), 7.26 (dd, J = 5.6, 3.1 Hz, 2H), 7.20 – 6.71 (m, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 206.5, 156.9, 144.3, 141.9, 129.9, 126.9, 126.4, 126.2, 125.0, 124.1, 123.5, 122.3, 65.4. HRMS (APCI) m/z (M+Na) calcd for $C_{35}H_{22}O_3Na$: 513.5, found: 513.1475.

**Synthesis of (15-oxo-9,14-methanobenzo[f]tetraphene-9,14-diyl)bis(4,1-phenylene) bis(2-methylacrylate) (5)**

In a dry round bottomed flask purged with Ar, diol **4** (0.5 g, 1.0 mmol), DCC (0.5 g, 2.2 mmol) and DMAP (25 mg, 0.2 mmol) were suspended in anhydrous $CH_3CN$ (50 ml). After stirring at room temperature for 30 minutes, methacrylic acid (0.4 mL, 2.2 mmol) was added to the reaction mixture. The temperature was increased to 45 $^o$C and the solution stirred for 48 hours. The precipitated solid was removed by filtration. Volatiles from the filtrate were removed by evaporation under reduced pressure. The crude product was purified by flash column chromatography (silica, 30% EtOAc/hexane) to yield a white powder (0.47 g, 72%). $^1$H NMR (400 MHz, $CD_2Cl_2$) δ 8.73 (d, J = 8.2 Hz, 2H), 8.26 – 8.02 (m, 4H), 7.79 (d, J = 8.2 Hz, 1H), 7.60 (dd, J = 14.5, 7.1 Hz, 1H), 7.51 (d, J = 5.5 Hz, 1H), 7.47 – 7.35 (m, 2H), 7.26 (d, J = 4.2 Hz, 2H), 6.40 (s, 1H), 5.82 (s, 1H), 2.10 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) 13C NMR (101 MHz, CDCl3) δ 194.56, 165.80, 150.54, 144.51, 141.81, 135.94, 130.55, 129.95, 127.48,

126.82, 126.77, 126.37, 126.14, 125.98, 123.62, 123.48, 66.46, 18.48.. HRMS (APCI) m/z ($M^+$) calcd for $C_{43}H_{30}O_5$: 627.21, found: 627.2189.

**Synthesis of benzo[f]tetraphene-9,14-diylbis(4,1-phenylene) bis(2-methylacrylate) (5')**

**5'** was obtained by heating product **5** to 200°C using a heat gun. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.24 (m, J = 7.9 Hz, 1H), 7.96 (dd, J = 6.6, 3.3 Hz, 1H), 7.61 – 7.55 (m, 4H), 7.52 (d, J = 8.4 Hz, 2H), 7.48 (dd, J = 6.6, 3.3 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 4H), 7.05 (dd, J = 11.3, 4.1 Hz, 2H), 6.47 – 6.40 (m, 2H), 5.85 – 5.79 (m, 2H), 2.13 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) 13C NMR (101 MHz, CDCl3) δ 165.91, 150.57, 139.11, 135.95, 134.50, 133.61, 131.10, 130.55, 127.47, 127.00, 126.64, 126.04, 125.95, 123.39, 122.33, 18.50. (APCI) m/z ($M^+$) calcd for $C_{42}H_{30}O_4$: 599.21, found: 599.2238.

## III. Polymerization of control PMMA network (6)

BPO (15 mg, 0.06 mmol), **3** (50 mg, 0.10 mmol), filtered MMA (1.0 mL, 9.4 mmol) and EGDMA (88 µL, 0.46 mmol) were combined in one vial and flushed with argon. Minimum amount of dry DCM was added to dissolve all components. Once the components were fully dissolved, DMA (6 µL, 0.05 mmol) was added. The solution was sealed and mixed for 5 minutes to increase viscosity and then injected into rectangular-shaped Teflon mold. The mold kept under inert atmosphere overnight to obtain a transparent yellow cross-linked polymer. Prior to any mechanical activation, the polymer was washed with DCM, $CDCl_3$ and acetone to remove unreacted component.

## IV. Polymerization of active PMMA network (7)

Benzoyl peroxide (BPO) (15 mg, 0.06 mmol), **5** (57 mg, 0.10 mmol), filtered methyl methacrylate (MMA) (1.0 mL, 9.4 mmol) and ethylene glycol dimethylacrylate (EGDMA) (88 µL, 0.46 mmol) were combined in one vial and flushed with argon. Minimum amount of dry DCM was added to dissolve all components. Once the components were fully dissolved, *N,N*-dimethylaniline (DMA) (6 µL, 0.05 mmol) was added. The solution was sealed and mixed for 5 minutes to increase viscosity and then injected into rectangular-shaped Teflon mold. The mold kept under inert atmosphere overnight to obtain a transparent yellow cross-linked polymer. Prior to any mechanical activation, the polymer was washed with DCM, chloroform ($CDCl_3$) and acetone to remove unreacted component.

## V. Mechanical activation via cryo-ball mill

Dry cross-linked material (50-100 mg) was inserted with 37 stainless steel balls (3/16 inches) into a 10 ml stainless steel grinding jar and milled for 3 h at 29 Hz under liquid nitrogen flow.

## VI. CoGEF

Initial modelling of the designed mechanophore was carried out *in silico* using the Constrained Geometries simulate External Force (CoGEF) method. The molecule was stressed by increasing the distance between terminal carbons with incremental steps of 0.1 Å. In each step the energy is calculated after the geometry of the molecule is minimized. These calculations were done using Spartan 14 at the B3LYP/631G* level of theory. The measurement showed a slow planarization of the bicyclic rings while increasing the distance between the terminal carbons (Fig. S1), until selective scission at the desired positions occurred, releasing the CO molecule. Force-bond angle just before scission: 49°.

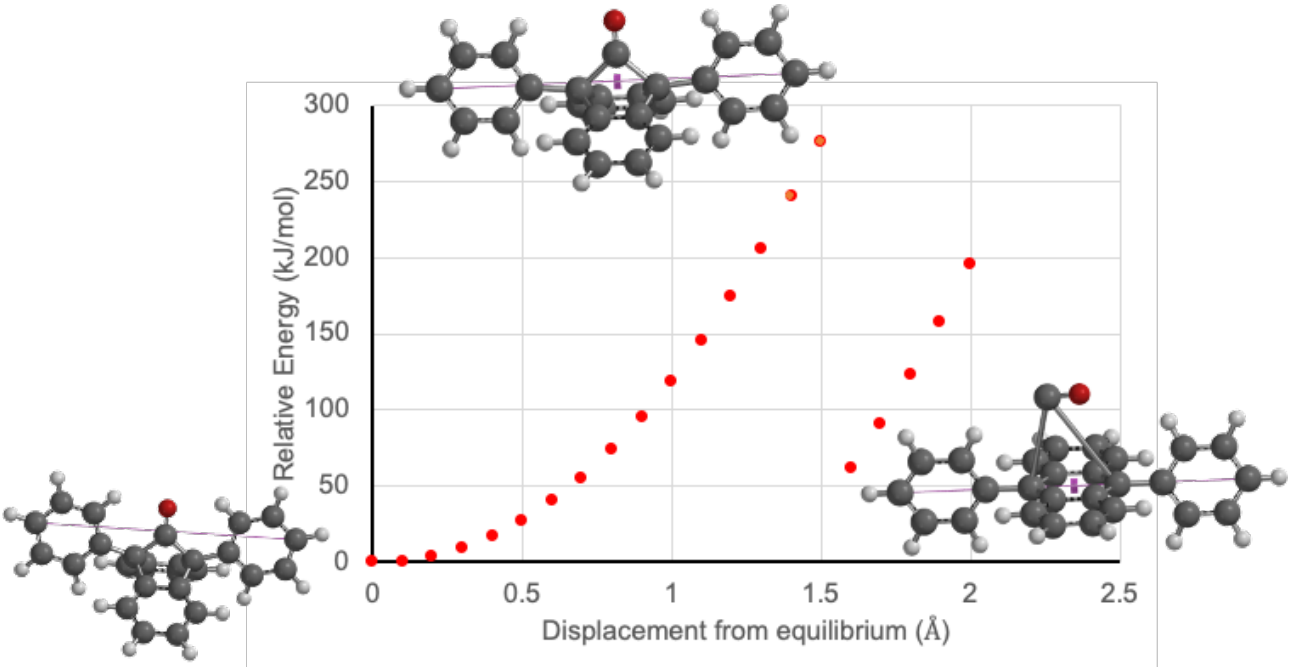



**Fig. S1** Plot of relative energy to displacement from equilibrium distance between terminal atoms.

## VII. NMR Characterization

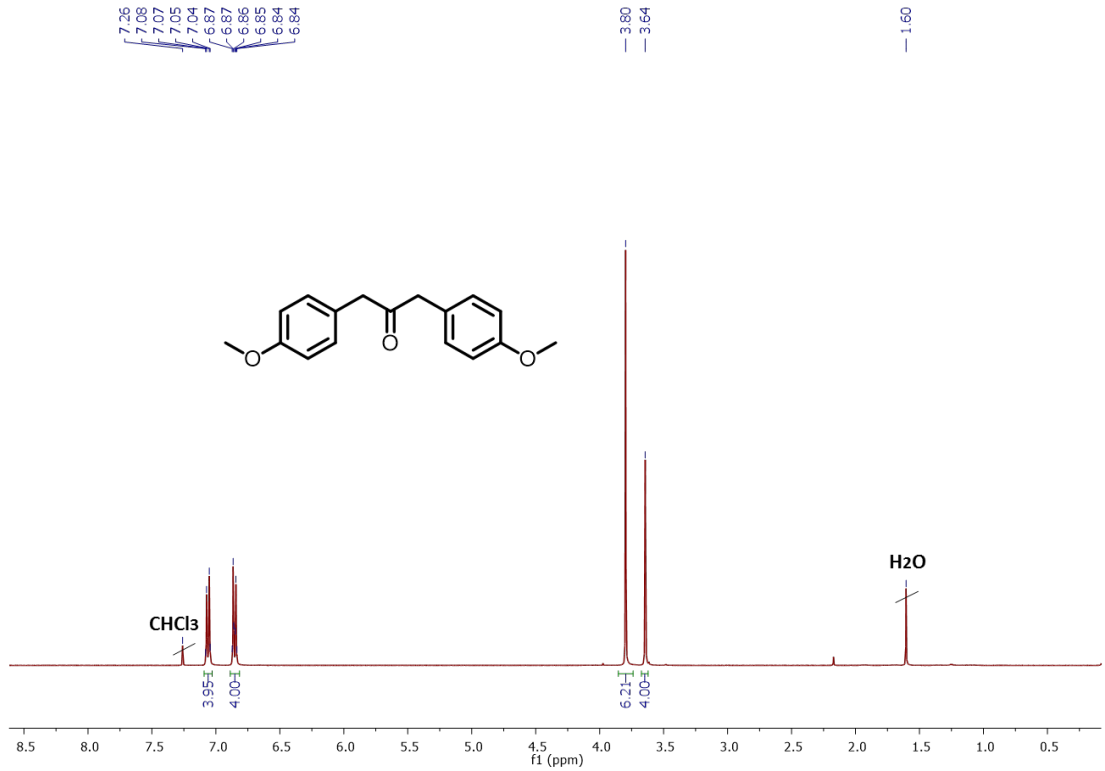



**Fig. S2** $^{1}$H NMR (400 MHz) of **1** in $CDCl_3$.

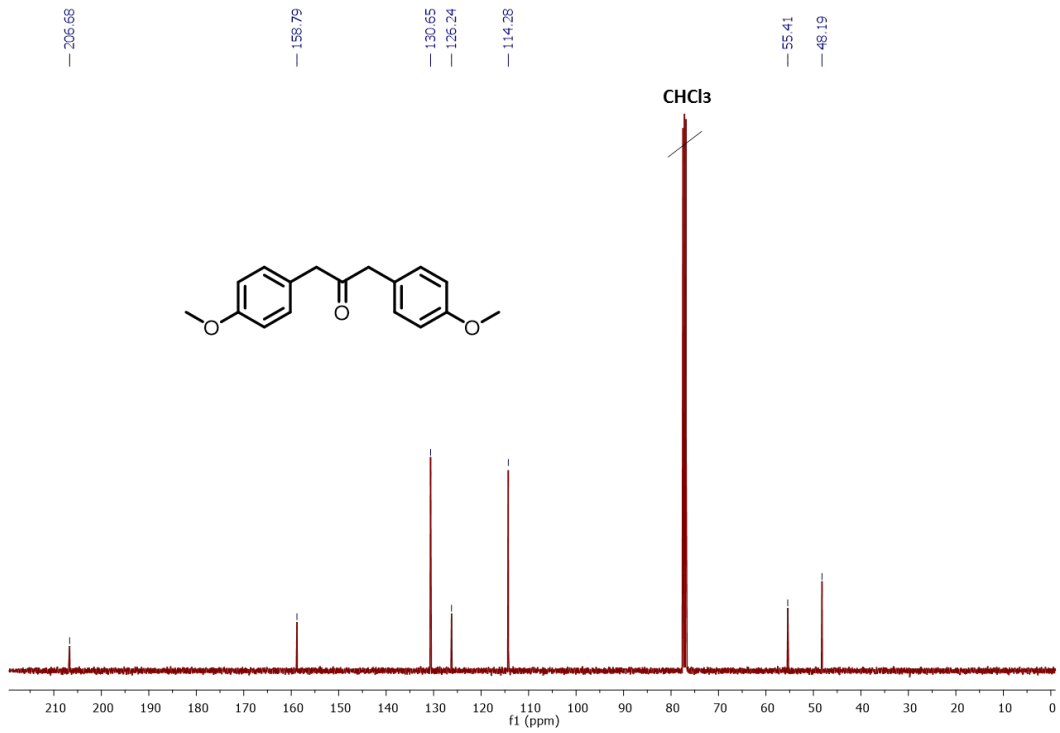



**Fig. S3** $^{13}$C NMR (101 MHz) of **1** in $CDCl_3$.

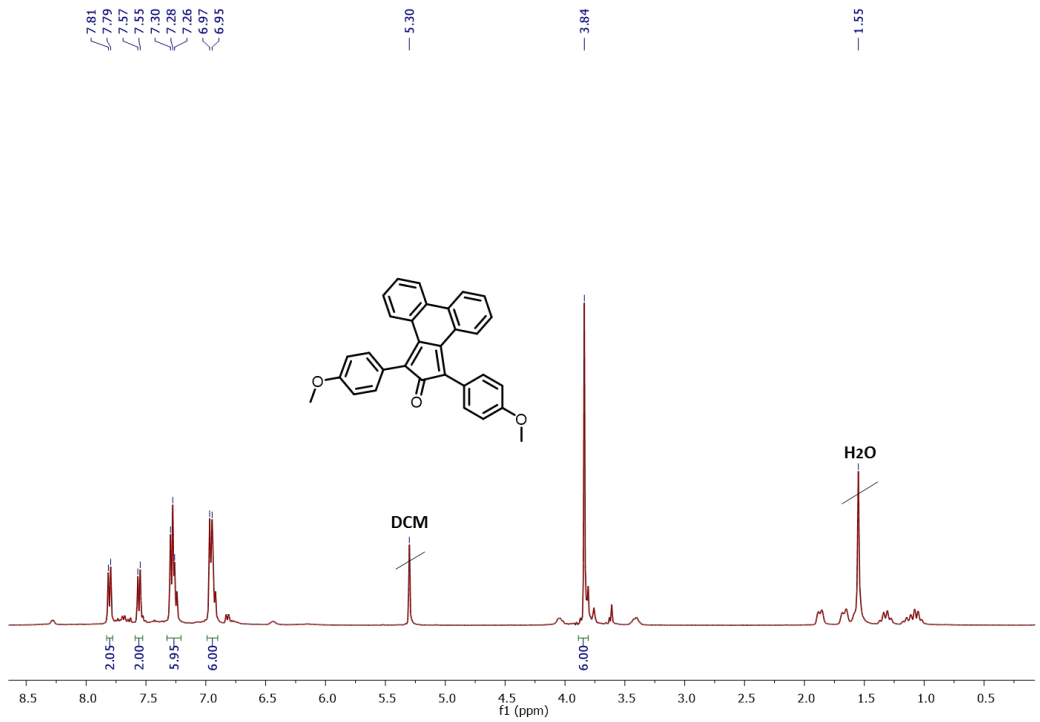



**Fig. S4** $^{1}$H NMR (400 MHz) of **2** in $CD_2Cl_2$.

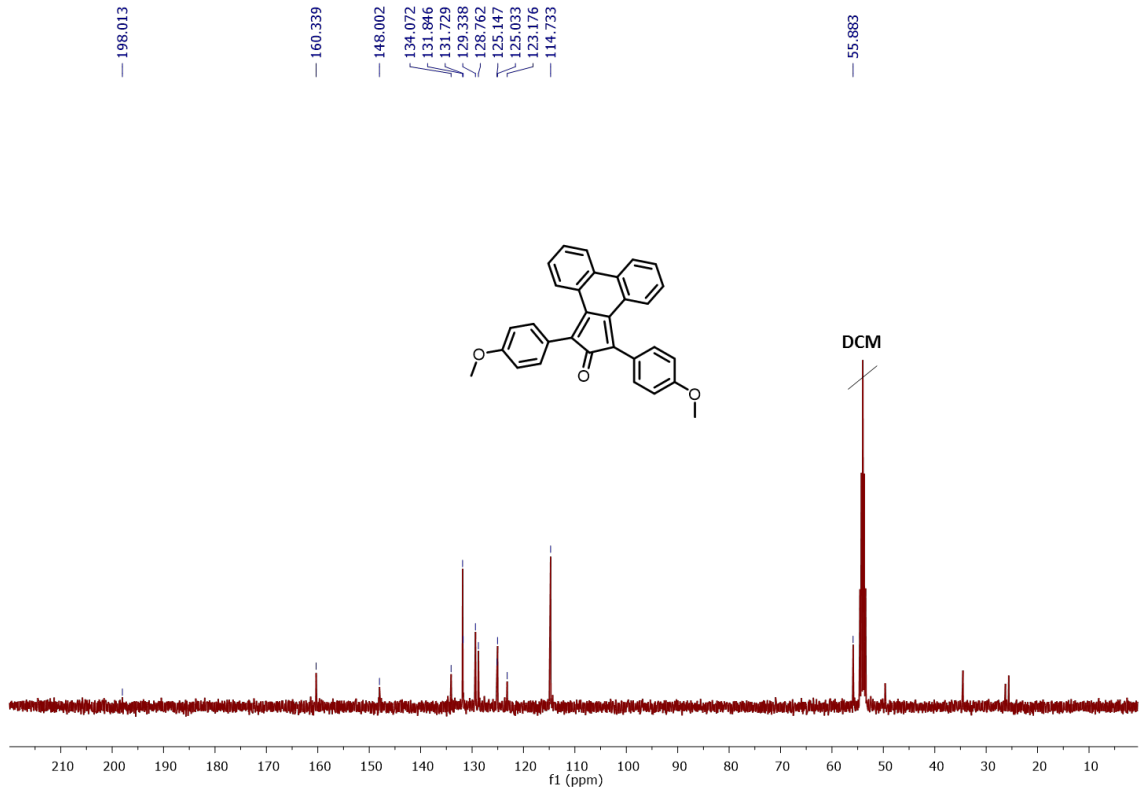



**Fig. S5** $^{13}$C NMR (101 MHz) of **2** in $CD_2Cl_2$.

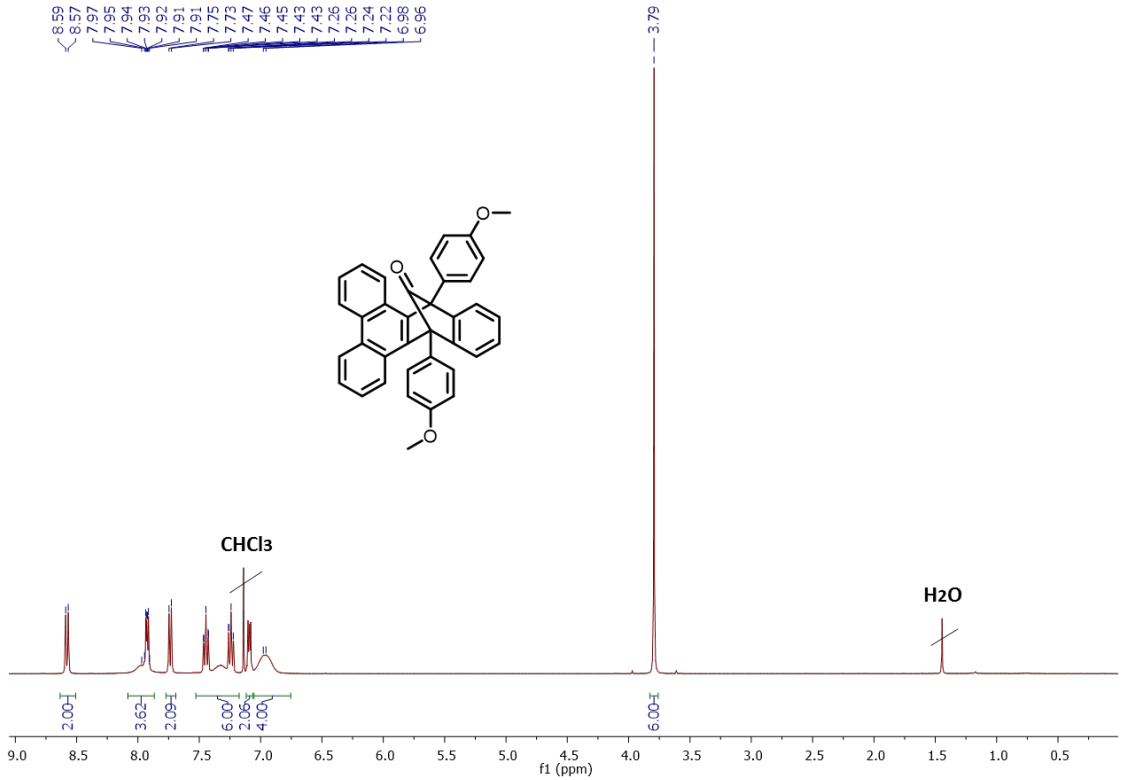



**Fig. S6** $^{1}$H NMR (400 MHz) of **3** in $CDCl_3$.

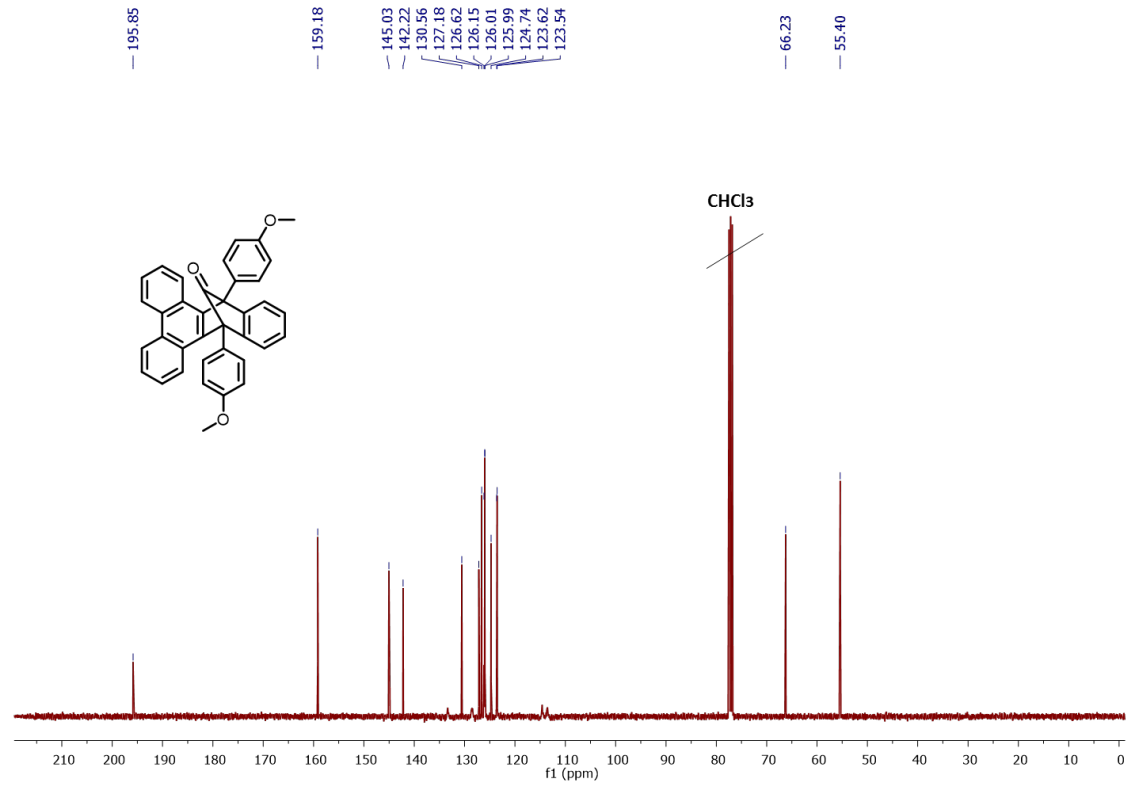



**Fig. S7** $^{13}$C NMR (101 MHz) of **3** in $CDCl_3$.

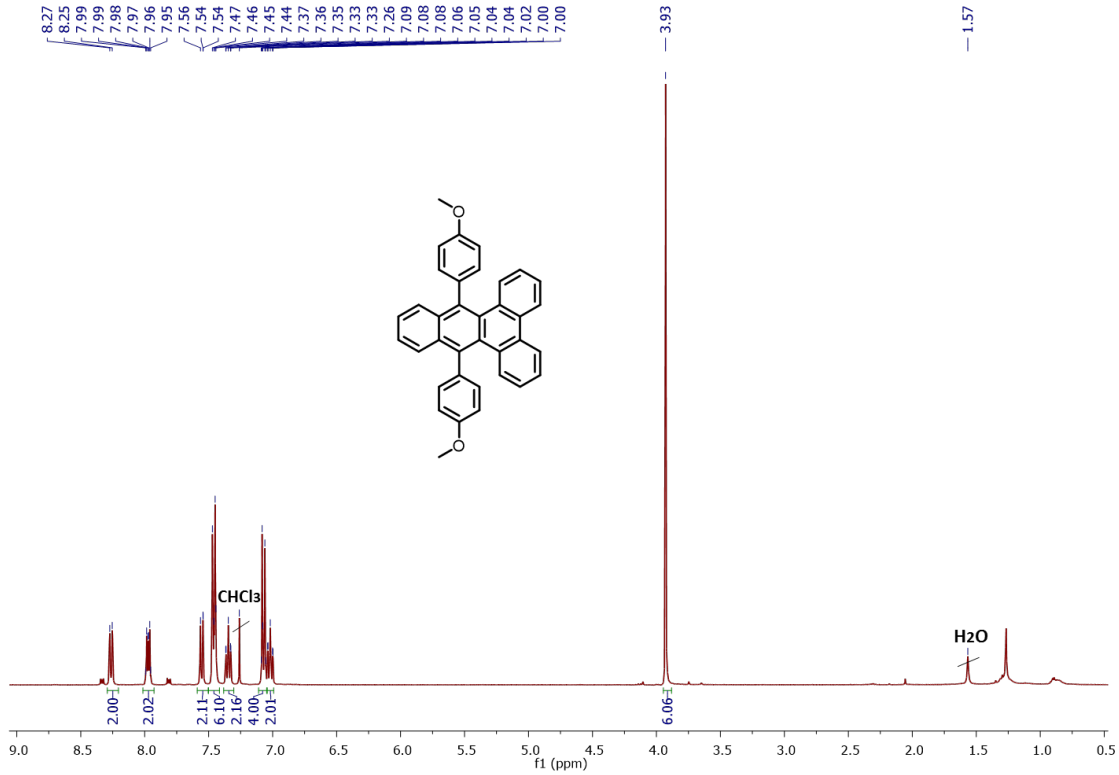



**Fig. S8** $^{1}$H NMR (400 MHz) of **3'** in $CDCl_3$.

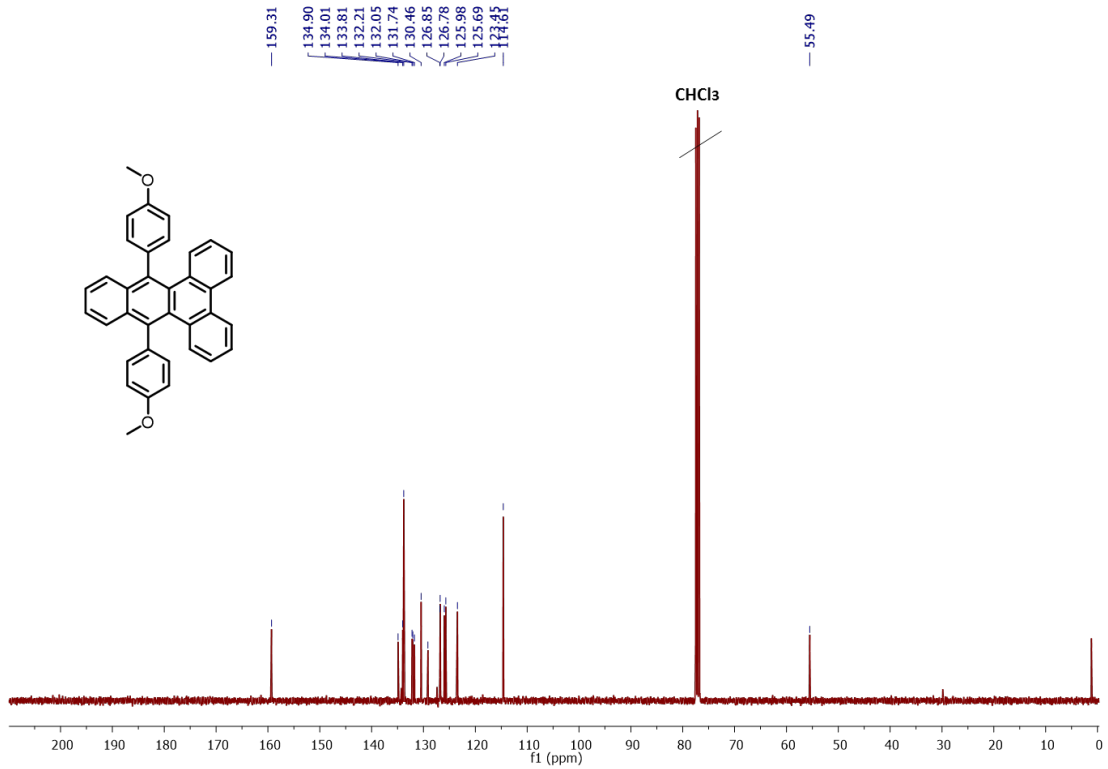



**Fig. S9** $^{13}$C NMR (101 MHz) of **3'** in $CDCl_3$.

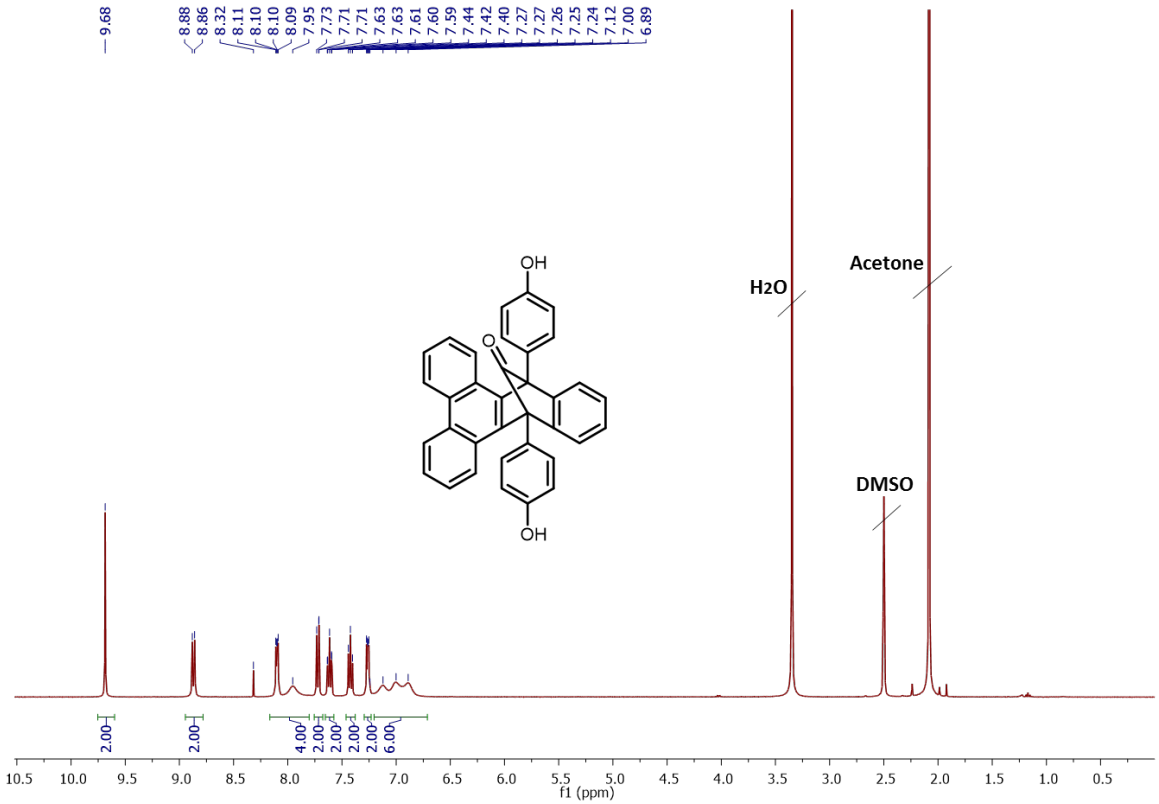



**Fig. S10** $^{1}$H NMR (400 MHz) of **4** in DMSO-d6.

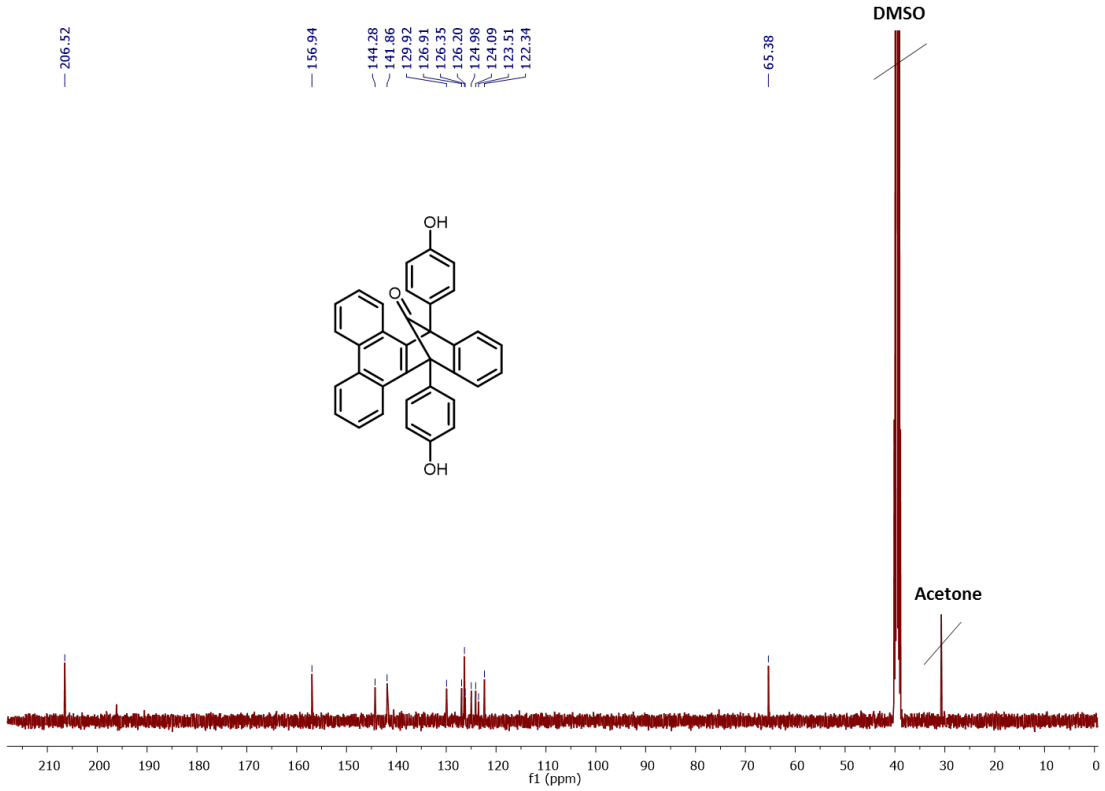



**Fig. S11** $^{13}$C NMR (101 MHz) of **4** in DMSO-d6.

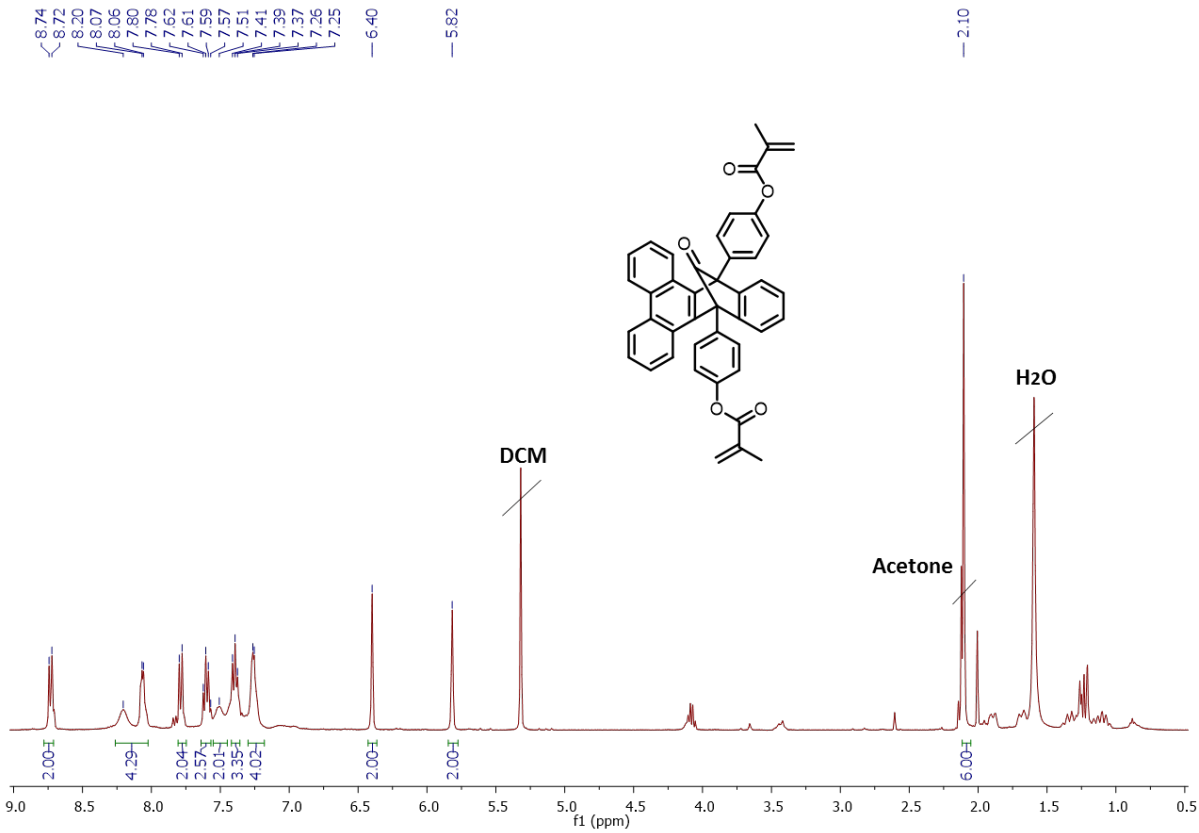



**Fig. S12** $^{1}$H NMR (400 MHz) of **5** in $CD_2Cl_2$.

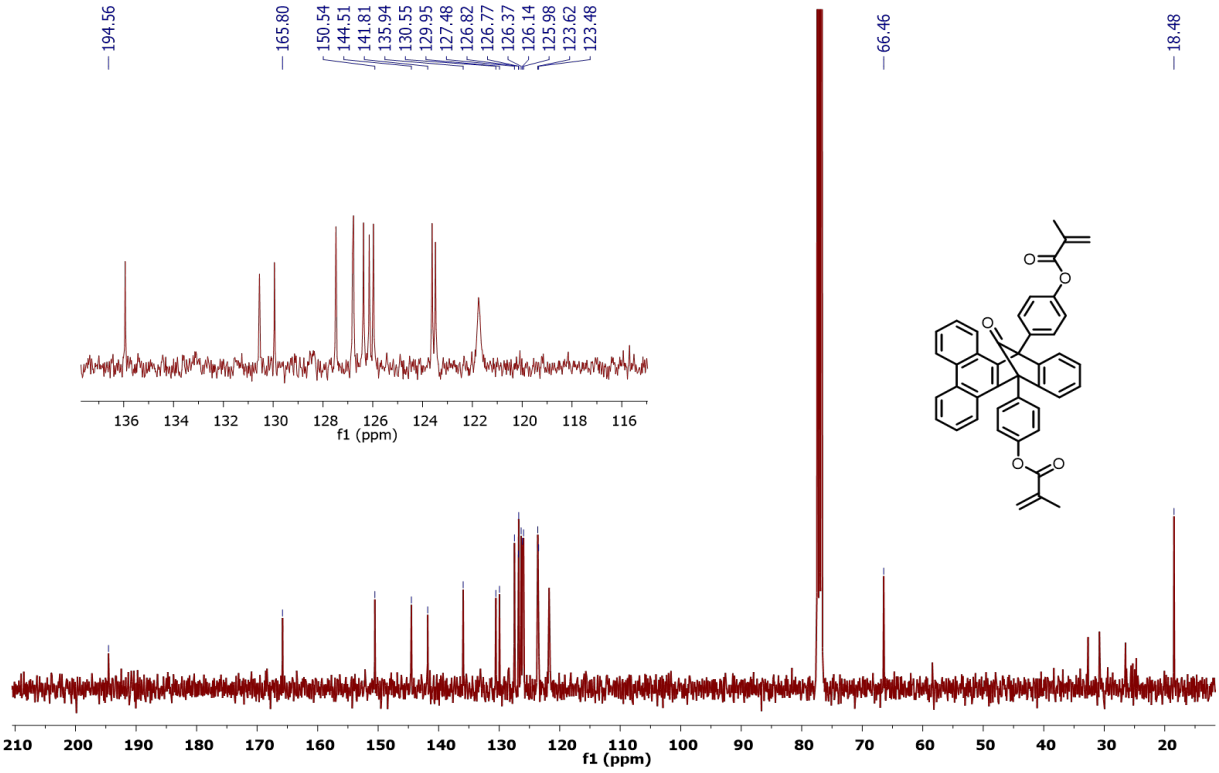



**Fig. S13** $^{13}$C NMR (101 MHz) of **5** in $CDCl_3$.

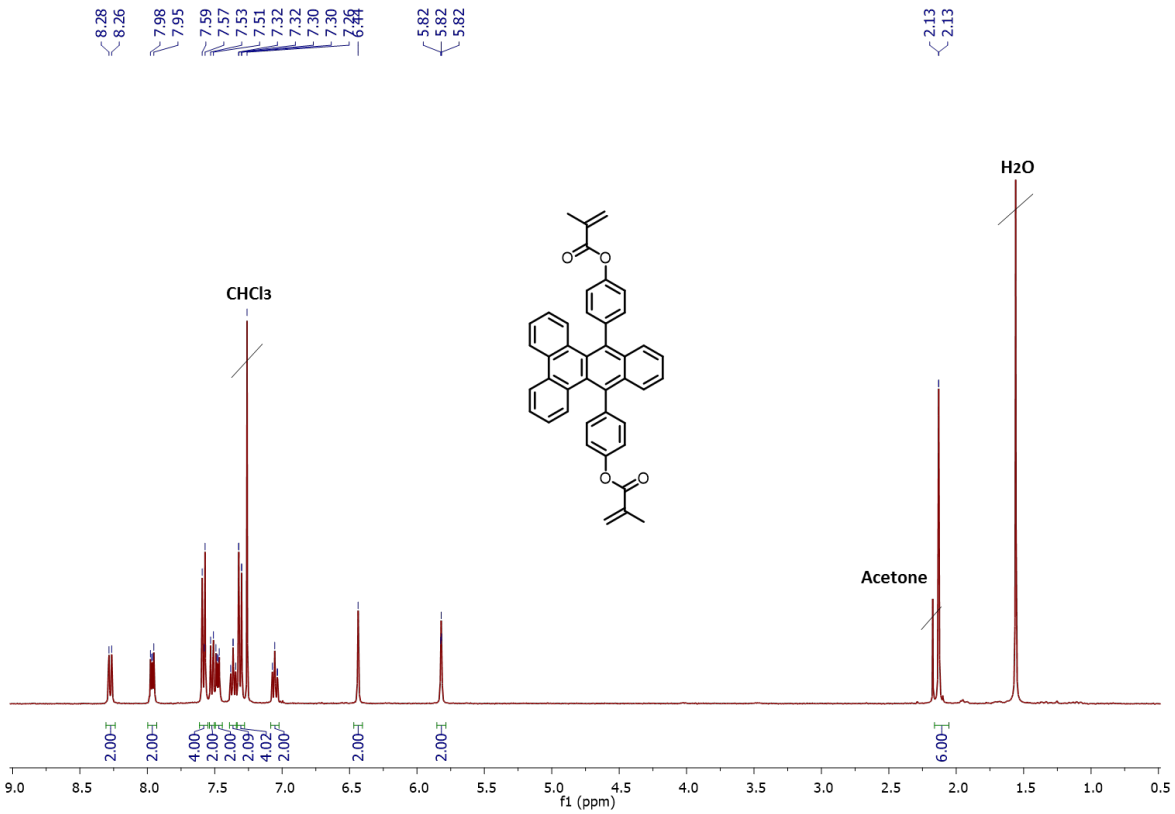



**Fig. S14** $^{1}$H NMR (400 MHz) of **5'** in $CDCl_3$.

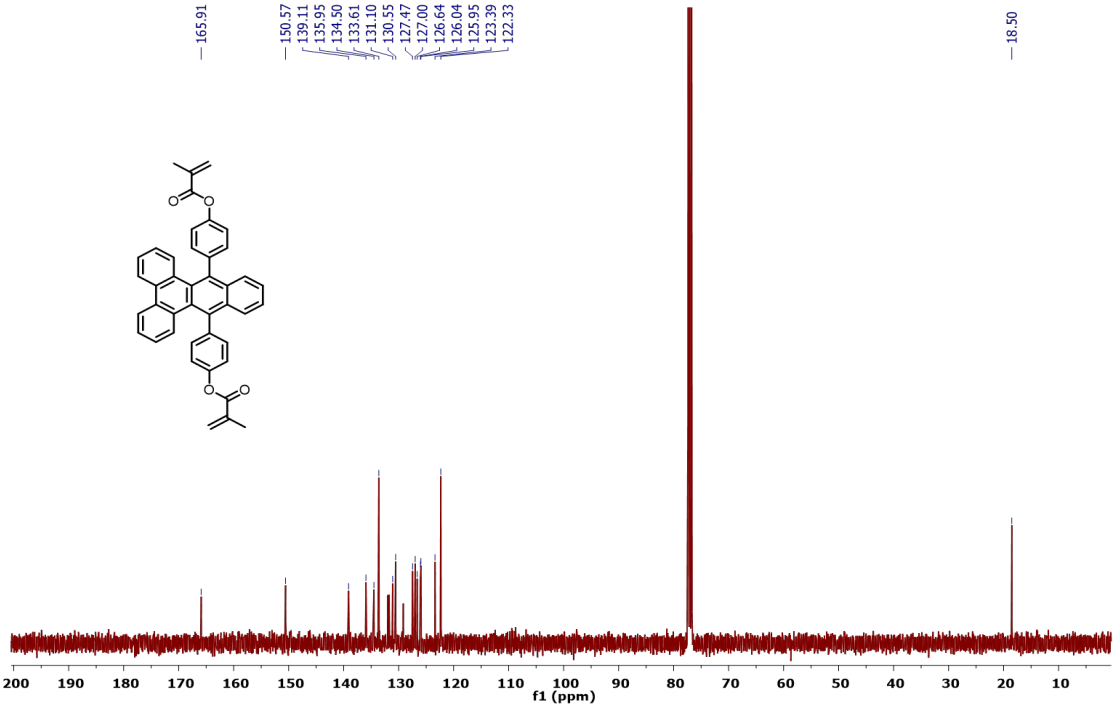



**Fig. S15** $^{13}$C NMR (101 MHz) of **5'** in $CDCl_3$.

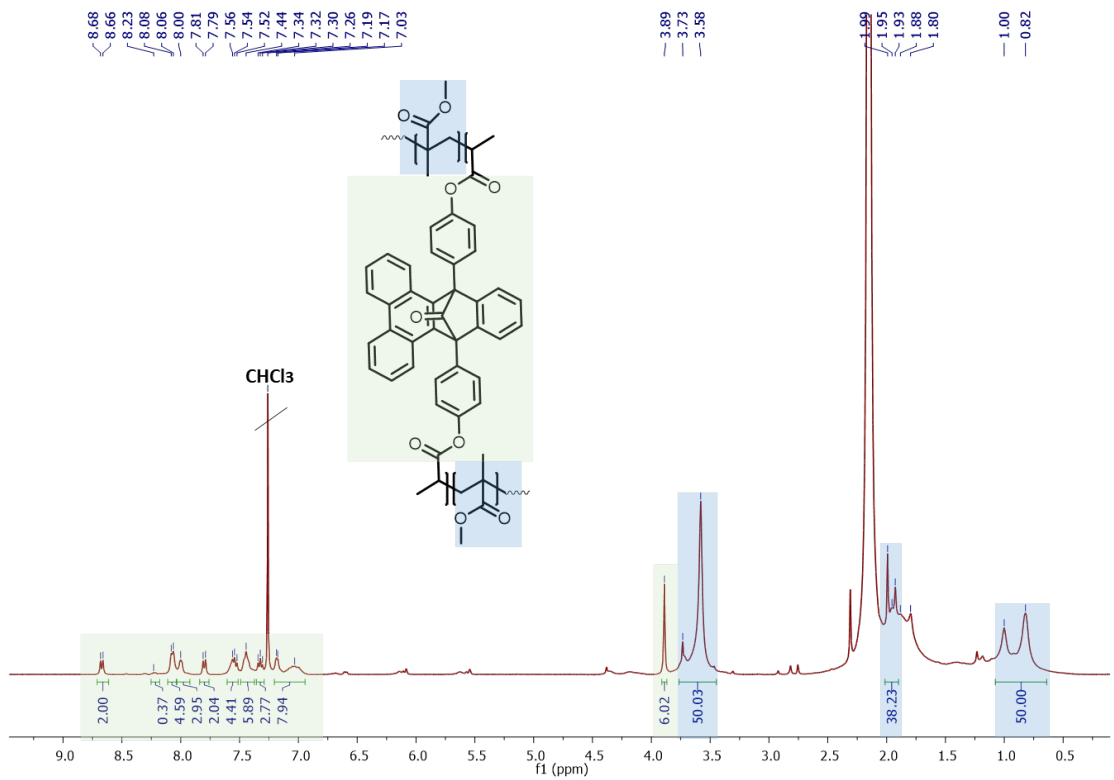



**Fig. S16** [1]H NMR (400 MHz) of active PMMA network in $CDCl_3$.

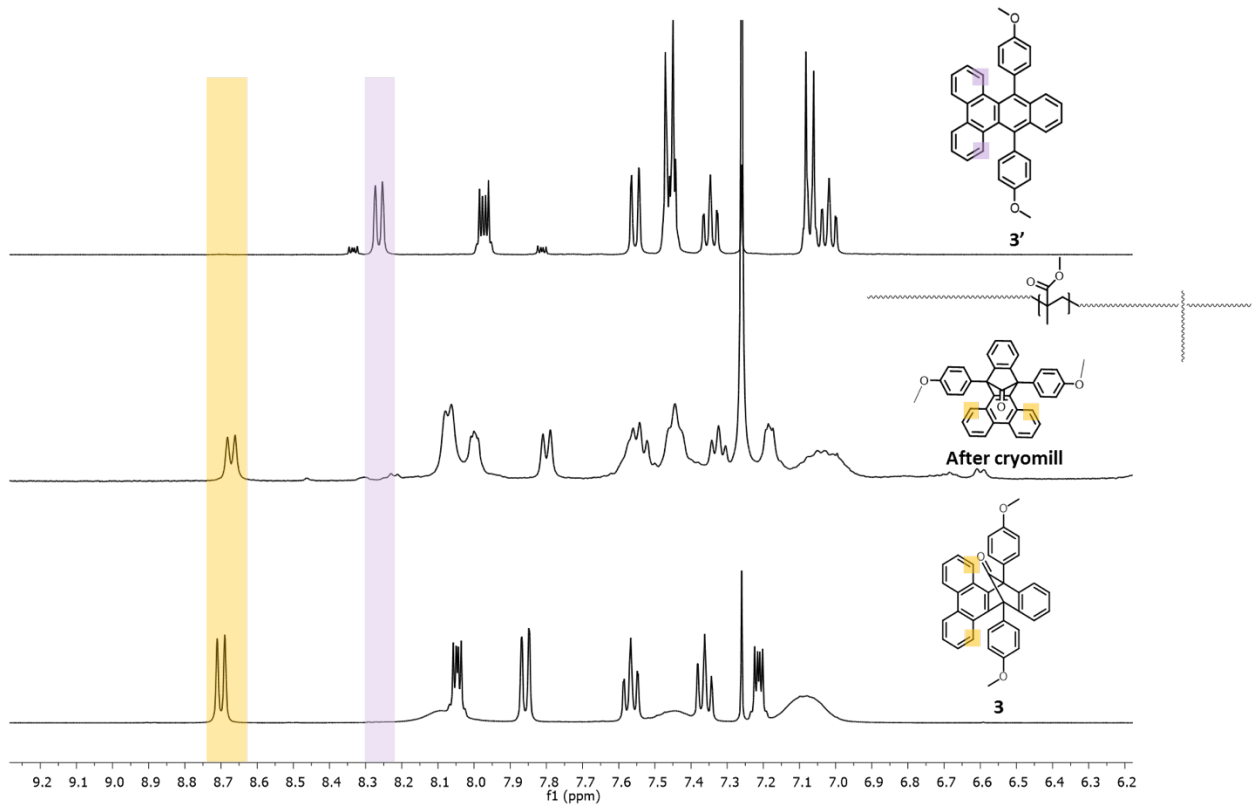
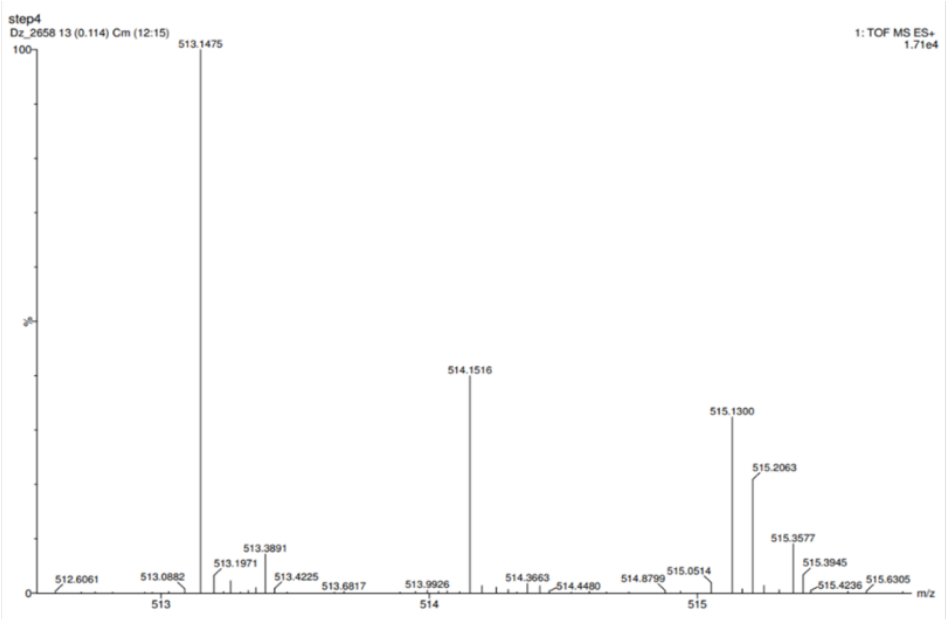



**Fig. S17** [1]H NMR (400 MHz) of control PMMA network (**6**) after cryomilling compared to compounds **3** and **3'.**

## VIII. HR-MS Characterization

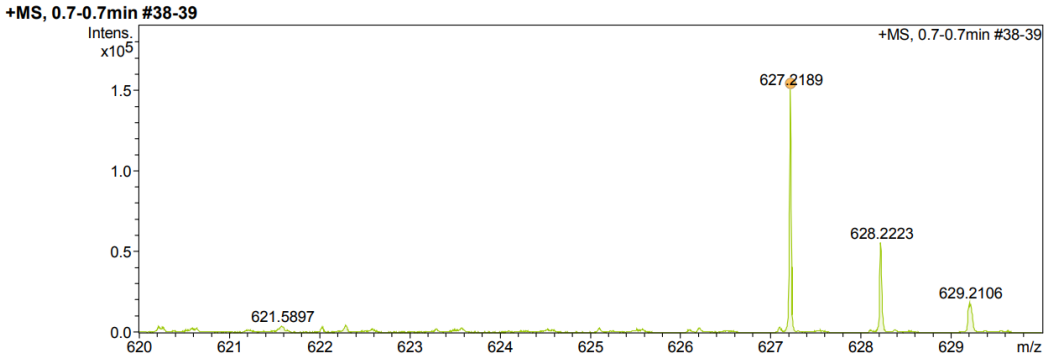



| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|---|---|---|---|---|---|---|---|---|
| 513.1475 | 513.1467 | 0.8 | 1.6 | 24.5 | 401.6 | 1.193 | 30.33 | C35 H22 O3 Na |
| | 513.1491 | -1.6 | -3.1 | 27.5 | 401.5 | 1.065 | 34.49 | C37 H21 O3 |
| | 513.1855 | -38.0 | -74.1 | 26.5 | 401.5 | 1.045 | 35.18 | C38 H25 O2 |

**Fig. S18** High-Resolution Mass spectroscopy of diol CO-mechanophore **4.**

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | APCI | Ion Polarity | Positive | Set Nebulizer | 1.2 Bar |
| Focus | Active | Set Capillary | 3000 V | Set Dry Heater | 120 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 1.5 l/min |
| Scan End | 2000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 5000 nA | Set APCI Heater | 300 °C |

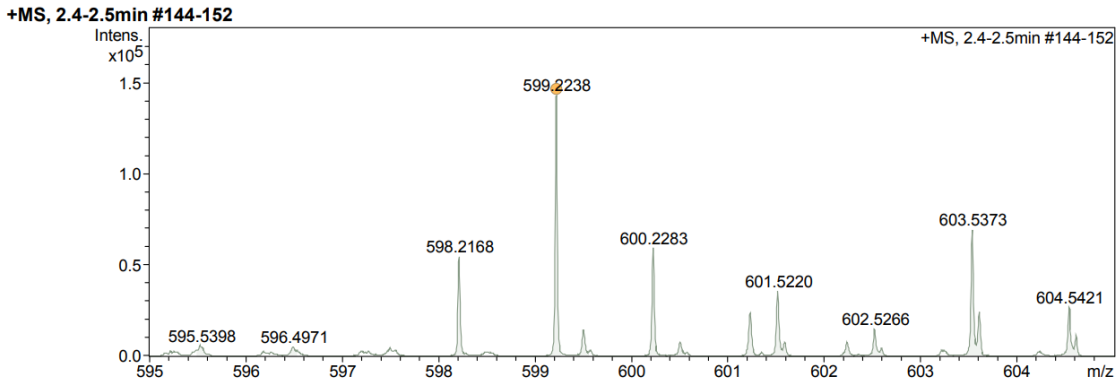



| Meas. m/z | # | Ion Formula | m/z | err [ppm] | mSigma | # mSigma | Score | rdb | e⁻ Conf | N-Rule | \|err\| [mDa] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 627.2189 | 1 | C43H31O5 | 627.2166 | -3.7 | 244.7 | 2 | 100.00 | 28.5 | even | ok | 2.3 |

**Fig. S19** High-Resolution Mass spectroscopy of dimethacrylate CO-mechanophore **5**.

**Acquisition Parameter**

| | | | | | |
|---|---|---|---|---|---|
| Source Type | APCI | Ion Polarity | Positive | Set Nebulizer | 1.2 Bar |
| Focus | Active | Set Capillary | 3000 V | Set Dry Heater | 120 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 1.5 l/min |
| Scan End | 2000 m/z | Set Charging Voltage | 2000 V | Set Divert Valve | Source |
| | | Set Corona | 5000 nA | Set APCI Heater | 300 °C |




| Meas. m/z | # | Ion Formula | m/z | err [ppm] | mSigma | # mSigma | Score | rdb | e⁻ Conf | N-Rule | \|err\| [mDa] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 599.2238 | 1 | C42H31O4 | 599.2217 | -3.5 | 39.3 | 1 | 100.00 | 27.5 | even | ok | 2.1 |

**Fig. S20** High-Resolution Mass spectroscopy of thermal activated dimethacrylate CO-mechanophore **5'.**

## IX. IR Characterization

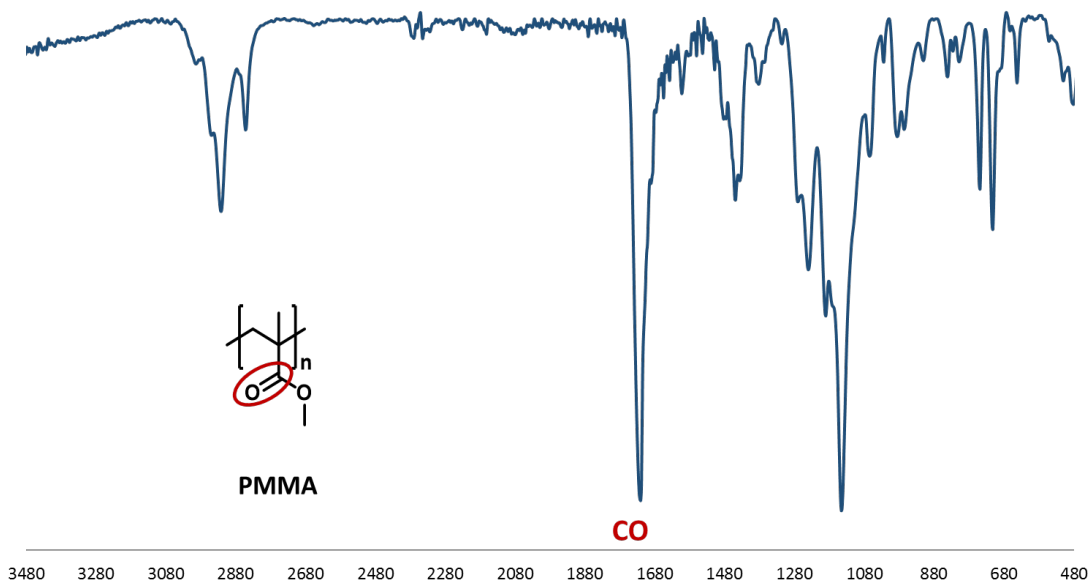



**Fig. S21** IR spectrum of cross-linked PMMA network free of CO-mechanophore molecule.

## X. Raman Characterization

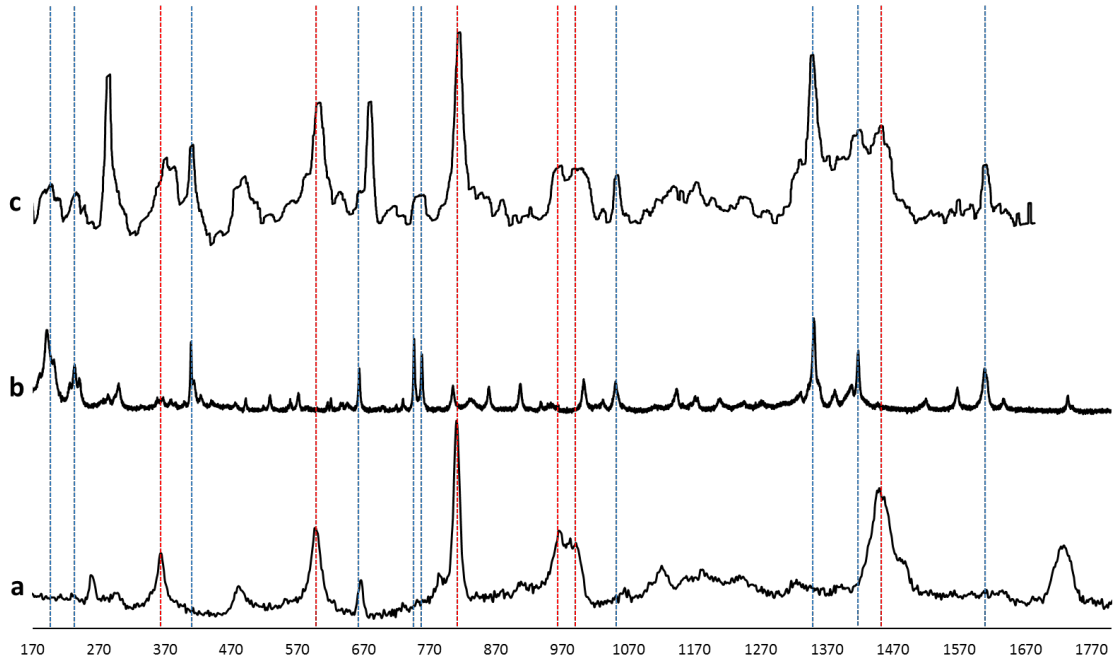



**Fig. S22** Raman spectra of a) pure PMMA b) dimethacrylate CO-mechanophore (5) and c) active network before cryomilling composed of both PMMA peaks (red) and CO-mechanophore peaks (blue).

## XI. UV-Vis Absorption Spectrum

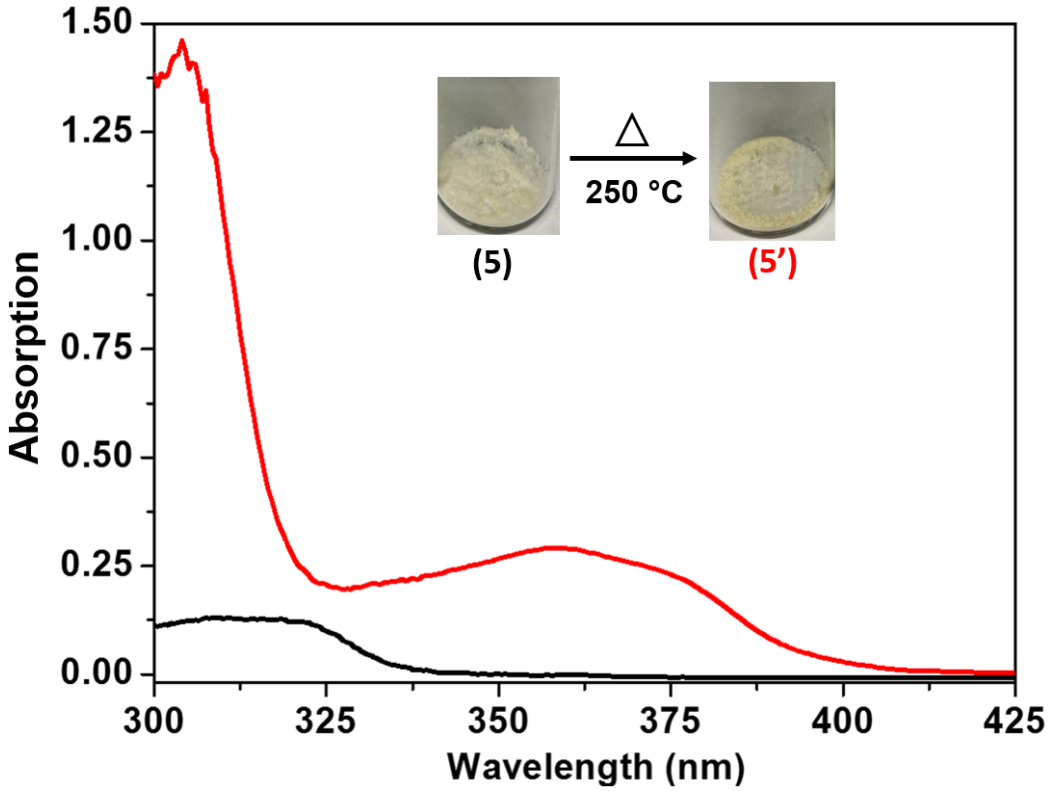



**Fig. S23** UV-Vis absorbance spectra of CO-mechanophore before (5) and after (5') thermal activation.

## XII. Fluorescence Characterization

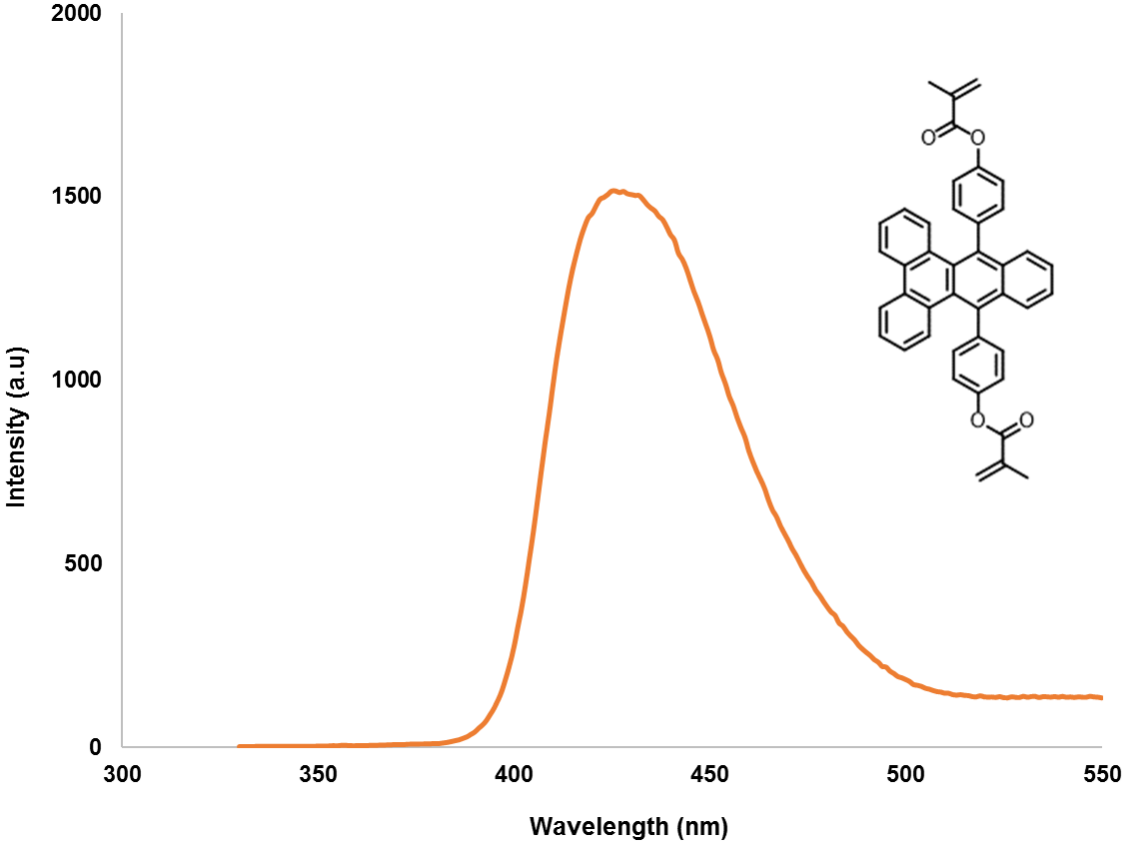



**Fig. S24** Fluorescence emission of CO-mechanophore after thermal activation (5') at 330 nm excitation wavelength.

## XIII. References


1 M. J. E. Resendiz and M. A. Garcia-Garibay, *Org. Lett.*, 2005, **7**, 371–374.

2 D. Chaudhuri, H. Wettach, K. J. Van Schooten, S. Liu, E. Sigmund, S. Höger and J. M. Lupton, *Angew. Chem. Int. Ed.*, 2010, **49**, 7714–7717.

3 S. Mondal and A. J. Bhattacharya, *Curr. Sci.*, 1984, **53**, 676–679.

4 G. Y. Wooi and J. M. White, *Org. Biomol. Chem.*, 2005, **3**, 972.

5 R. P. L'Esperance, D. Van Engen, R. Dayal and R. A. Pascal, *J. Org. Chem.*, 1991, **56**, 688–694.