Supplementary information

[2+2] Cycloaddition of Phosphaalkenes as Key Step for the Reductive Coupling of Diaryl Ketones to Tetraaryl Olefins

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1. General experimental information

1.1. Synthetic considerations

Unless specified otherwise, all manipulations were carried out using standard Schlenk line or glovebox techniques, in order to exclude air and moisture. Olefins were synthised using standard glove box techniques, while ketone reagents were prepared using standard Schlenk techniques. Glassware was flame-dried, THF and Et_2O were freshly distilled over Na/benzophenone under nitrogen, and ketones were dried under vacuum prior to use. $P(TMS)_3$ is commercially available and was purchased from Strem Chemicals. Commercially available ketones were purchased from Sigma Aldrich, and the synthesis of others are described below. Absolute EtOH, and *n*BuLi (2.5M in hexanes) were used without purification. NMR spectra were recorded on a JEOL (400YH magnet) Resonance 400 MHz spectrometer. Chemical shifts δ are reported in ppm and coupling constants *J* in Hz. ^{1}H NMR and ^{13}C NMR chemical shifts are referenced to the residual protic solvent signal and ^{31}P NMR spectra externally to 85% H_3PO_4(aq). High-resolution mass spectra (HR-MS) were recorded on a Thermo Scientific Orbitrap LTQ XL spectrometer.

1.2. Special note about chromatographic isolation of compounds:

Unless stated otherwise, all final alkene products were purified by column chromatography on an automated low-pressure chromatograph (Biotage PS4). Chromatography was performed on suitably sized, pre-packed silica gel columns (SiliaSep Cartridge from Silicycle Inc.). A minor impurity arose during chromatography giving rise to a signal at $\delta = 0.06$ ppm in the ^{1}H NMR spectra of the otherwise pure compounds. We ascribe this impurity to an organo-ilicon compound originating from the pre-packed column; the characteristic peak at $\delta = 0.06$ ppm was detected by ^{1}H NMR spectroscopy in solvent fractions obtained from a blank chromatographic run after evaporation of solvent.

2. Preparation of LiOEt

Care must be taken when carrying out this procedure as the reaction is exothermic.

*n*BuLi (4.34 mL, 10.85 mmol, 2.5 M in hexanes, 1eq.) was slowly added to a colorless solution of EtOH (0.5g, 10.85 mmol, 1eq.) in 10mL of dry THF. The reaction mixture allowed to stir at room temperature for 24h. The resulting colourless solution was transferred to a 25 mL volumetric flask and made up to the mark with dry THF to give a 0.43 M stock solution.

NB: the solution remains suitably stable for up to 5 days, after which we observed reduced reaction yields and side product formation. Any changes in colour to the solution (e.g. orange-red) indicate decomposition and a fresh solution should be prepared.

3. Preparation of $LiP(TMS)_2$·0.5THF

The title product is highly pyrophoric, and care must be taken when removing residues from the glovebox. Traces and residues were quenched with bleach upon exiting the glovebox.

Freshly prepared LiOEt (4.65 mL, 0.43 M, 1 eq.) was added to a colourless solution of $P(TMS)_3$ (500 mg, 2.00 mmol, 1 eq.) in 15 mL of dry THF at room temperature. The reaction was monitored by ^{31}P NMR spectroscopy using an internal C_6D_6 capillary. Full conversion of starting $P(TMS)_3$ ($\delta = -254$ppm) to desired $LiP(TMS)_2$ ($\delta = -303$ppm in THF) was achieved in 24h. The solvent was removed under reduced pressure to afford $LiP(TMS)_2$·0.5THF as a white solid (according to ^{1}H NMR) The solid was dissolved in dry Et_2O, transferred into a 10mL

volumetric flask and made up to the mark with Et_2O to give a 0.20 M stock solution. The solution was found to be stable for up to 3 days, without visible changes, and solid $LiP(TMS)_2 \cdot 0.5THF$ is stable for upwards of 6 months under inert atmosphere.

^1H NMR (400 MHz, C_6D_6): δ = 3.74 – 3.39 (m, 4H, THF), 1.26 – 1.21 (m, 4H, THF), 0.49 (s, 18H, TMS) ppm.

^{13}C NMR (101 MHz, C_6D_6): δ = 68.8, 24.9, 7.1 ppm.

^{31}P NMR (161 MHz, C_6D_6): δ = -296.6 ppm.

4. Optimization of the reaction of $LiPTMS_2$ with ketones

In a glovebox, a freshly prepared colourless solution of $LiP(TMS)_2$ (1eq) in Et_2O was added to a colourless ethereal solution of ketone (1 eq) at ambient temperature. Aliquots were taken and quenched with a range of bases (see manuscript, Table 1).

5. Isolation of the 1,2-diphosphetane dimer

The reaction was performed according to the procedure described above, using benzophenone as the ketone. The reaction mixture was allowed to stir for 24h at ambient temperature, after which time the volatiles were removed under reduced pressure. The resulting oily residue was taken into pentane, and filtered. Residual benzophenone could be removed by fractional crystallisation (slow evaporation of pentane) to provide the 1,2-diphosphetane as an analytically pure crystalline solid.

^1H NMR (400 MHz, THF-d8): δ = 7.76 – 7.62 (bs, 2H), 7.45 – 7.29 (bs, 2H), 7.23 – 7.12 (bs, 4H), 7.05 (td, *J* = 7, *J* = 1 Hz, 2H), 6.87 – 6.76 (m, 8H), 6.55 – 6.38 (bs, 2H), -0.07 (t, *J* = 2 Hz, 18H) ppm.

^{13}C NMR (101 MHz, THF-d8): δ = 148.6 (dd, *J* = 3, *J* = 3 Hz), 146.4 (dd, *J* = 10, *J* = 10 Hz), 129.3 (dd, *J* = 5, *J* = 5 Hz, 6H), 126.7 (s), 125.4 (s), 125.3 (s), -1.25 (dd, *J* = 9, *J* = 9 Hz, 3H).

^{31}P NMR (161 MHz, THF-d8): δ = -51.02 ppm.

5.1. Stability of the 1,2-diphosphetane dimer.

Crystalline o 1,2-diphosphetane was dissolved in C_6D_6 and the resulting solution was analysed using ^1H NMR and ^{31}P spectroscopy (Figure S1 and S2, respectively). In the spectra taken immediately after dissolution, only the signals corresponding to the 1,2-diphosphetane were observed. In contrast, spectra taken after five days at room temperature show the presence of trace amounts of the monomeric ‘parent’ phosphaalkene as well as the signals corresponding to the 1,2-diphosphetane. No other signal was observed, demonstrating that the 1,2-diphosphetane is in a chemical equilibrium with the phosphaalkene.

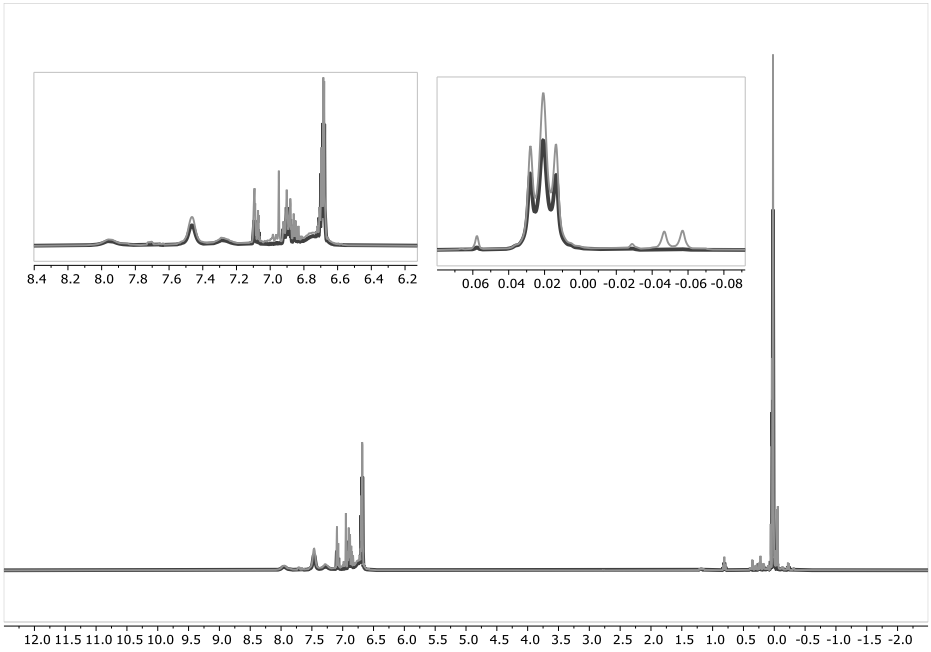


Fig. S1. Comparison of the ^{1}H NMR spectra of **4a** immediately upon dissolving in C_6D_6 (black trace) and after 5 days (grey trace).

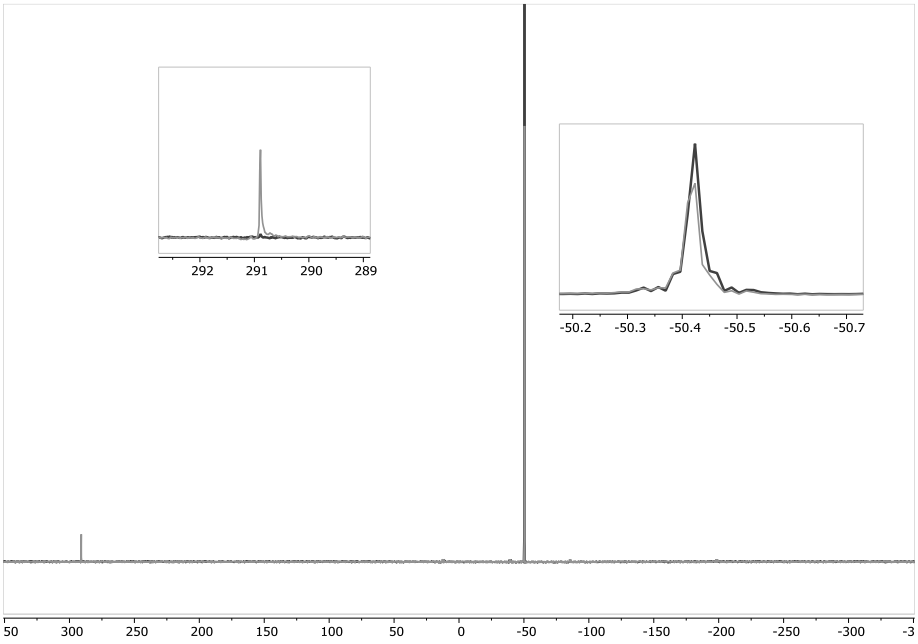
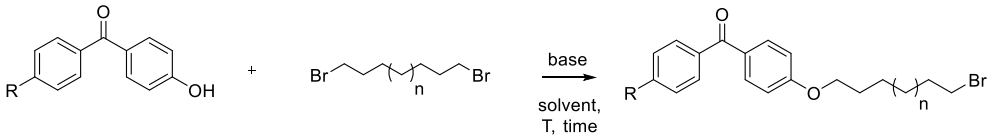


Fig. S2. Comparison of the ^{31}P NMR spectra of **4a** immediately upon dissolving in C_6D_6 (black trace) and after 5 days (grey trace).

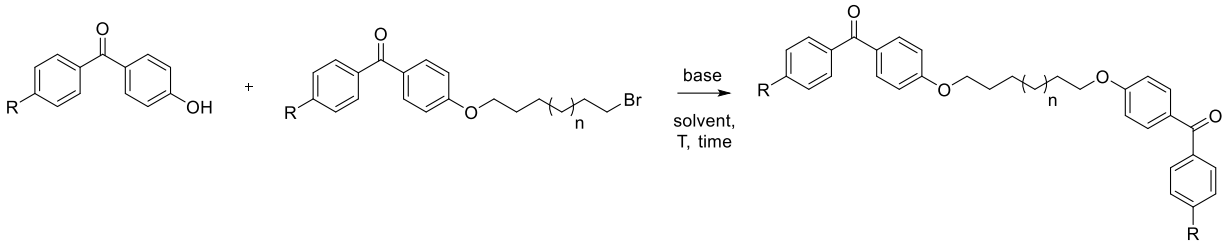
6. Preparation of the ketones

The following section presents general reaction schemes for the preparation of the ketones.

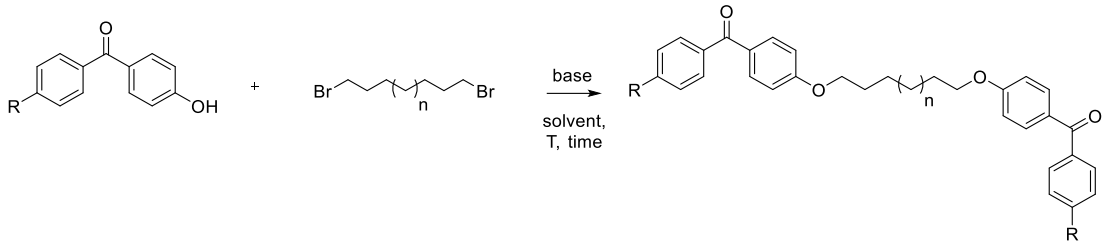
For some entries, reactions stopped at the mono-alkylated product (**Scheme S1**) which can be isolated and subjected to a second alkylation (**Scheme S2**). In other entries, the desired diketones could be accessed directly (**Scheme S3**).



Scheme S1. Synthesis of mono-alkylated ketones.



Scheme S2. Reaction between isolated mono-alkylated ketones and hydroxy-benzophenones yielding the desired diketone products.

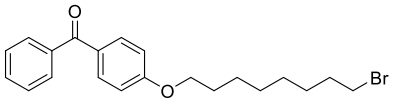


Scheme S3. One-pot direct synthesis of desired diketones.

6.1. General reaction procedures:

A mixture of the three reagents (starting hydroxyl ketone, dibromoalkane, and base) were dissolved in a solvent and stirred in air. Reaction progress was monitored by TLC. Upon completion, water was added, and the aqueous phase was extracted with Et_2O. The collected organic phases were washed with brine, dried over Mg_2SO_4, filtered and the solvent was removed under reduced pressure to afford the crude product. Purification of the ketones was carried out on silica gel column chromatography with 100% DCM as an eluent, unless specified otherwise.

6.1.1. (4-((8-bromooctyl)oxy)phenyl)(phenyl)methanone, **1g**



The reaction was performed according to **Scheme S1** (R = H).

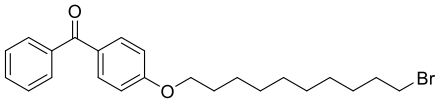
(4-hydroxyphenyl)(phenyl)methanone (2 eq, 2.15 g, 10.9 mmol), 1,8-dibromooctane (1 eq, 1.48 g, 5.43 mmol) and K_2CO_3 (4 eq, 3 g, 22 mmol) were dissolved in 10mL of acetone and stirred under reflux for 24 h. The desired product was obtained as a colourless solid after chromatographic workup. Isolated yield: 1.08 g, 2.72 mmol, 25%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.78 (m, 2H), 7.77 – 7.72 (m, 2H), 7.59 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H), 6.96 – 6.90 (m, 2H), 4.02 (t, $^{3}J_{HH}$ = 6.5 Hz, 2H), 3.40 (t, $^{3}J_{HH}$ = 6.8 Hz, 2H), 1.96 – 1.71 (m, 4H), 1.50 – 1.25 (m, 8H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.7, 162.9, 138.4, 132.7, 131.9, 130.0, 129.8, 128.3, 114.1, 68.3, 34.1, 32.8, 29.2, 29.1, 28.8, 28.7, 28.2 ppm.

HR-MS TOF (+) m/Z = observed 389.1129 $[M + H]^+$, calculated 389.1116 $[C_{21}H_{25}BrO_2 + H]^+$.

6.1.2. (4-((10-bromodecyl)oxy)phenyl)(phenyl)methanone, **1h**



The reaction was performed according to **Scheme S1** (R = H).

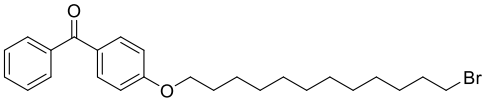
(4-hydroxyphenyl)(phenyl)methanone (1 eq, 1 g, 5.04 mmol), 1,10-dibromodecane (1 eq, 1.2 g, 5.04 mmol) and K_2CO_3 (2 eq, 1.4 g, 10.9 mmol) were dissolved in 10mL of acetone and stirred under reflux for 24h. The desired product was isolated as a colourless solid after filtration and removal of acetone under reduced pressure. Isolated yield: 1 g, 2.4 mmol, 48%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.78 (m, 2H), 7.77 – 7.74 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.43 (m, 2H), 6.95 – 6.92 (m, 2H), 4.02 (t, $^{3}J_{HH}$ = 6.5 Hz, 2H), 3.40 (t, $^{3}J_{HH}$ = 6.9 Hz, 2H), 1.88 – 1.76 (m, 4H), 1.50 – 1.38 (m, 4H), 1.33 – 1.28 (m, 8H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.7, 162.9, 138.4, 132.7, 131.9, 130.0, 129.8, 128.3, 114.1, 68.3, 34.1, 32.9, 29.5, 29.4, 29.4, 29.2, 28.8, 28.78, 28.2 ppm.

HR-MS TOF (+) m/Z = observed 417.1425 $[M + H]^+$, calculated 417.1429 $[C_{23}H_{29}BrO_2 + H]^+$.

6.1.3. (4-((12-bromododecyl)oxy)phenyl)(phenyl)methanone, **1i**



The reaction was performed according to **Scheme S1** (R = H).

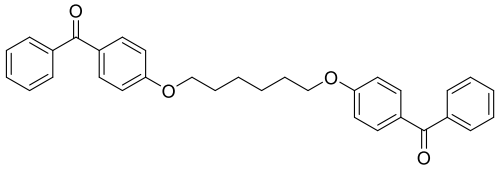
(4-hydroxyphenyl)(phenyl)methanone (1 eq, 1 g, 5.04 mmol), 1,12-dibromododecane (1 eq, 1.2 g, 5.04 mmol) and K_2CO_3 (2 eq, 1.4 g, 10.9 mmol) were dissolved in 10mL of acetone and stirred under reflux for 24h. The desired product was isolated as a colourless solid after filtration and removal of acetone under reduced pressure. Isolated yield: 1.2 g, 2.7 mmol, 53%.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.78 (m, 2H), 7.76 – 7.72 (m, 2H), 7.58 – 7.52 (m, 1H), 7.48 – 7.44 (m, 2H), 6.94 (d, $^{3}J_{HH}$ = 8.9 Hz, 2H), 4.02 (t, $^{3}J_{HH}$ = 6.6 Hz, 2H), 3.40 (t, $^{3}J_{HH}$ = 6.9 Hz, 2H), 1.91 – 1.69 (m, 4H), 1.51 – 1.37 (m, 4H), 1.35-1.25 (m, 12H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ = 195.7, 163.0, 138.4, 132.7, 131.9, 130.0, 129.8, 128.3, 128.3, 114.1, 68.4, 34.2, 32.9, 29.6, 29.6, 29.6, 29.5, 29.48, 29.2, 28.8, 28.2, 26.1 ppm.

HR-MS TOF (+) m/Z = observed 445.1784 $[M + H]^+$, calculated 445.1742 $[C_{25}H_{33}BrO_2 + H]^+$.

6.1.4. ((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone), **6a**



The reaction was performed according to **Scheme S3** (R = H).

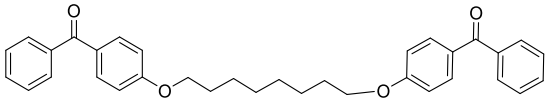
(4-hydroxyphenyl)(phenyl)methanone (2 eq, 250 mg, 1.11 mmol), 1,6-dibromohexane (1 eq, 201 mg, 0.55 mmol) and K_2CO_3 (2 eq, 307 mg, 2.2 mmol) were dissolved in 10mL of DMF and stirred at room temperature for 24h. The desired product was obtained as a colourless solid after chromatographic work-up (R_f = 0.5). Isolated yield: 140 mg, 0.29 mmol, 53%.

^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.86 – 7.80 (m, 4H), 7.77 – 7.72 (m, 4H), 7.57 – 7.54 (m, 2H), 7.50 – 7.43 (m, 4H), 6.96 – 6.92 (m, 4H), 4.05 (t, $^3J_{H\text{-}H}$ = 6.4 Hz, 4H), 1.89 – 1.83 (m, 4H), 1.62 – 1.55 (m, 4H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 195.6, 162.8, 138.4, 132.7, 131.9, 130.1, 129.8, 128.3, 114.1, 68.1, 29.1, 25.9 ppm.

HR-MS TOF (+) m/Z = observed 479.2226 $[M + H]^+$, calculated 479.2222 $[C_{32}H_{30}O_4 + H]^+$.

6.1.5. ((octane-1,8-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone), **6b**



The reaction was performed according to **Scheme S3** (R = H).

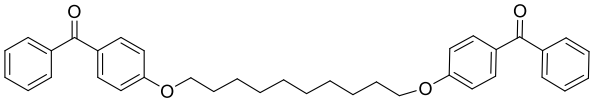
(4-hydroxyphenyl)(phenyl)methanone (2 eq, 472 mg, 2.38 mmol), 1,8-dibromooctane (1 eq, 324 mg, 1.19 mmol) and Cs_2CO_3 (2.1 eq, 815 mg, 2.50 mmol) were dissolved in 10mL of DMF and stirred at 40 °C for 48h. The desired product was isolated as a colourless solid after chromatographic work-up. Isolated yield: 210 mg, 0.41 mmol, 35%.

^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.82 – 7.80 (m, 4H), 7.75 – 7.73 (m, 4H), 7.55 – 7.53 (m, 2H), 7.48 – 7.44 (m, 4H), 6.96 – 6.93 (m, 4H), 4.03 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H), 1.85 – 1.78 (m, 4H), 1.52 – 1.46 (m, 4H), 1.42 – 1.41 (m, 4H) ppm.

^{13}C NMR (101 MHz, 300K) δ = 195.7, 162.9, 138.4, 132.7, 131.9, 130.0, 129.8, 128.3, 114.1, 68.3, 29.4, 29.2, 26.0 ppm.

HR-MS TOF (+) m/Z = observed 507.2530 $[M + H]^+$, calculated 507.2535 $[C_{34}H_{34}O_4 + H]^+$.

6.1.6. ((decane-1,10-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone), **6c**



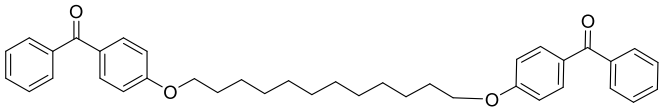
The reaction was performed according to **Scheme S3** (R = H).

(4-hydroxyphenyl)(phenyl)methanone (2 eq, 475 mg, 2.40 mmol), 1,10-dibromooctane (1 eq, 360 mg, 1.20 mmol) and Cs_2CO_3 (2.1 eq, 821 mg, 2.52 mmol) were dissolved in 10mL of DMF and stirred at 40 °C for 48h. The desired product was isolated as a colourless solid after chromatographic work-up. Isolated yield: 560 mg, 1.05 mmol, 87%.

^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 8.08 – 7.77 (m, 4H), 7.76 – 7.71 (m, 4H), 7.59 – 7.50 (m, 2H), 7.49 – 7.41 (m, 4H), 7.03 – 6.86 (m, 4H), 4.03 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H), 1.88 – 1.74 (m, 4H), 1.54 – 1.42 (m, 4H), 1.40 – 1.30 (m, 8H) ppm.

^{13}C NMR (101 MHz, 300K) δ 195.7, 162.9, 138.4, 132.7, 131.9, 130.0, 129.8, 128.3, 114.1, 68.3, 29.6, 29.4, 29.2, 26.1 ppm.
HR-MS TOF (+) m/Z = observed 535.2847 $[M + H]^+$, calculated 535.2848 $[C_{36}H_{38}O_4 + H]^+$.

6.1.7. ((dodecane-1,12-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone), **6d**



The reaction was performed according to **Scheme S3** (R = H).

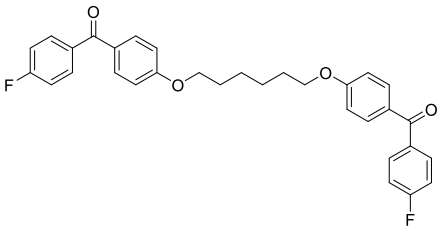
(4-hydroxyphenyl)(phenyl)methanone (2 eq, 472 mg, 2.38 mmol), 1,12-dibromooctane (1 eq, 390 mg, 1.19 mmol) and Cs_2CO_3 (2.1 eq, 815 mg, 2.50 mmol) were dissolved in 10mL of DMF and stirred at 40 °C for 48h. The desired product was isolated as a white solid after chromatographic work-up. Isolated yield: 430 mg, 0.76 mmol, 64%.

^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.82 – 7.79 (m, 4H), 7.75 – 7.73 (m, 4H), 7.57 – 7.53 (m, 4H), 7.50 – 7.44 (m, 4H), 6.95 – 6.92 (m, 4H), 4.02 (t, $^1J_{H\text{-}H}$ = 6.5 Hz, 4H), 1.82 – 1.77 (m, 4H), 1.48 – 1.44 (m, 4H), 1.37 – 1.30 (m, 4H) ppm.

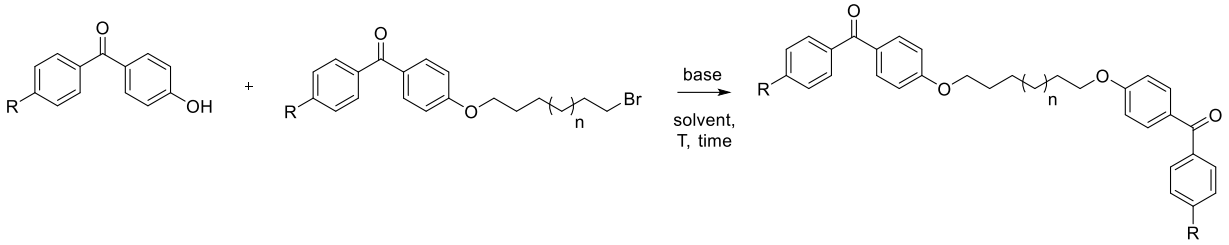
^{13}C NMR (101 MHz, 300K) δ = 195.7, 163.0, 138.4, 132.7, 131.9, 130.0, 129.7, 128.3, 114.1, 68.4, 29.6, 29.6, 29.4, 29.2, 26.1 ppm.

HR-MS TOF (+) m/Z = observed 563.3163 $[M + H]^+$, calculated 563.3161 $[C_{38}H_{42}O_4 + H]^+$.

6.1.8. ((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone), **6e**



The reaction was performed according to



Scheme S2 (R = F).

(4-((6-bromohexyl)oxy)phenyl)(4-fluorophenyl)methanone (1 eq, 500 mg, 1.32 mmol), (4-fluorophenyl)(4-hydroxyphenyl)methanone (1 eq, 285 mg, 1.32 mmol), and Cs_2CO_3 (1.4 eq, 601 mg, 1.85 mmol) were dissolved in 10mL of DMF and stirred at 40 °C for 24h. The desired product was isolated as a white solid after chromatographic work-up. Isolated yield: 430 mg, 0.84 mmol, 63%.

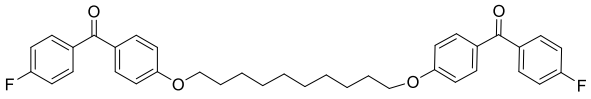
^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.80 – 7.76 (m, 8H), 7.17 – 7.11 (m, 4H), 6.96 – 6.93 (m, 4H), 4.05 (t, $^3J_{H\text{-}H}$ = 6.4 Hz, 4H), 1.89 – 1.85 (m, 4H), 1.57 (m, 8H) ppm.

^{19}F NMR ($CDCl_3$, 376 MHz, 300K) δ = -106.8 ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 194.2, 165.1 (d, *J* = 253.1 Hz), 162.9, 134.5 (d, *J* = 3.0 Hz), 132.5, 132.4 (d, *J* = 9.1 Hz), 129.9, 115.4 (d, *J* = 21.8 Hz), 114.2, 68.2, 29.1, 25.9 ppm.

HR-MS TOF (+) m/Z = observed 515,2030 $[M + H]^+$, calculated 515,2034 $[C_{32}H_{28}F_2O_4 + H]^+$.

6.1.9. ((decane-1,10-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone), **6f**



The reaction was performed according to **Scheme S3** (R = F).

(4-fluorophenyl)(4-hydroxyphenyl)methanone (2 eq, 504 mg, 2.33 mmol), 1,10-dibromodecane (1 eq, 350 mg, 1.17 mmol) and Cs_2CO_3 (2.1 eq, 798 mg, 2.45 mmol) were dissolved in 10mL of DMF and stirred at room temperature for 24h. The desired product was isolated as a colourless solid after chromatographic work-up. Isolated yield: 435 mg, 0.76 mmol, 65%.

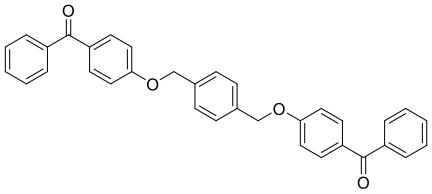
^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.80 – 7.76 (m, 8H), 7.16 – 7.11 (m, 4H), 6.96 – 6.92 (m, 4H), 4.03 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H), 1.84 – 1.77 (m, 4H), 1.49 – 1.47 (m, 4H), 1.45 – 1.34 (m, 8H) ppm.

^{19}F NMR ($CDCl_3$, 376 MHz, 300K) δ = -106.9 ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ 194.2, 165.1 (d, *J* = 253.1 Hz), 163.0, 134.6 (d, *J* = 3.2 Hz), 132.5, 132.4 (d, *J* = 9.0 Hz), 129.9, 115.4 (d, *J* = 21.8 Hz), 114.2, 68.4, 29.6, 29.4, 29.2, 26.1 ppm.

HR-MS TOF (+) m/Z = observed 593.2470 $[M + Na]^+$, calculated 593.2479 $[C_{36}H_{36}F_2O_4 + Na]^+$.

6.1.10 ((1,4-phenylenebis(oxy))bis(4,1-phenylene))bis(phenylmethanone), **6g**



The compound was prepared according to **Scheme S3**:

(4-hydroxyphenyl)(phenyl)methanone (2 eq., 1.5 g, 7.6 mmol) were mixed with 1,4-bis(bromomethyl)benzene (1 eq., 1 g , 3.8 mmol) and potassium carbonate ((4 eq., 2.1 g, 15.2 mmol) in acetone. The suspension was heated to reflux for 24 hours. The final product was isolated as a colourless solid after filtration and removal of the solvent under reduced pressure. The compound has a very low solubility in all common organic solvents. Yield: 1.6 g, 3.2 mmol, 85%.

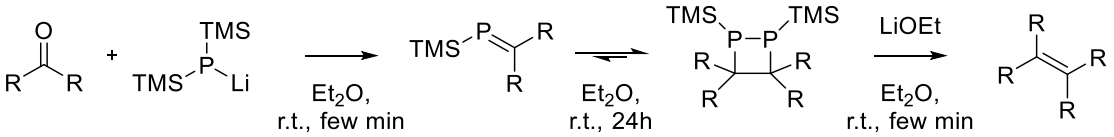
^{1}H NMR (DMSO, 400 MHz, 323K) δ = 7.78 – 7.73 (m, 4H), 7.70 – 7.68 (m, 4H), 7.66 – 7.64 (m, 2H), 7.57 – 7.53 (m, 4H), 7.52 (bs, 4H), 7.22 – 7.12 (m, 4H), 5.25 (s, 4H) ppm.

^{13}C NMR (DMSO, 101 MHz, 323K) δ = δ 194.9, 162.6, 138.4, 136.9, 132.6, 132.6, 130.3, 129.7, 128.9, 128.4, 115.3, 69.9 ppm.

HR-MS TOF (+) m/Z = observed 499.1900 $[M + H]^+$, calculated 499.1909 $[C_{34}H_{26}O_4 + H]^+$.

7. Preparation of the olefins

Scheme S4 presents a general reaction scheme for the preparation of tetrasubstituted olefins.

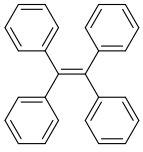


Scheme S4. General reaction procedure for the synthesis of olefins by the cross-coupling of two ketones.

7.1. General reaction procedures:

In a glovebox, a freshly prepared colorless solution of $LiP(TMS)_2$ (1eq) in Et_2O was added to a colourless ethereal solution of ketone (1 eq) at ambient temperature. In the case of cyclic diketones, the stoichiometry was adjusted to 1 eq of ketone and 2 eq of $LiP(TMS)_2$. The reaction was stirred for 24h at ambient temperature to fully convert phosphaalkene intermediates to their corresponding dimers. 1 eq of LiOEt was subsequently added to trigger the formation of the desired tetrasubstituted olefin. The reaction mixture was filtered through a silica plug prior to purification by silica gel column chromatography with gradient from 0% to 5% of EtOAc in Heptane unless specified otherwise (See section 1.2. above).

7.1.1. 1,1,2,2-tetraphenylethene, **5a**

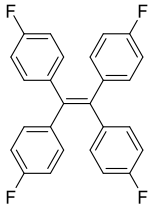


The reaction was carried out using benzophenone (1 eq, 46 mg, 0.25 mmol) and $LiP(TMS)_2$ (1 eq, 0.2M in Et_2O, 0.26 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 36 mg, 0.1 mmol, 85%.

^1H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.11 – 7.01 (m, 20H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 143.8, 141.0, 131.4, 127.7, 126.5.

7.1.2. 1,1,2,2-tetrakis(4-fluorophenyl)ethene, **5b**



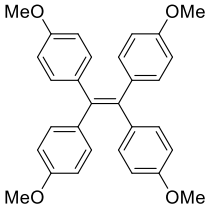
The reaction was carried out using bis(4-fluorophenyl)methanone (1 eq, 57 mg, 0.3 mmol) and $LiP(TMS)_2$ (1 eq, 0.4 M in Et_2O, 0.3 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 31 mg, 0.077 mmol, 59**%**.

^1H NMR ($CDCl_3$, 400 MHz, 300K) δ = 6.97 – 6.91 (m, 8H), 6.84 – 6.78 (m, 8H) ppm.

^{19}F NMR ($CDCl_3$, 376 MHz, 300K) δ = - 114.7 ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 162.82, 160.4, 139.1 (d, *J* = 3.5 Hz), 132.8 (d, *J* = 8.0 Hz), 115.0 (d, *J* = 21.4 Hz) ppm.

7.1.3. 1,1,2,2-tetrakis(4-methoxyphenyl)ethene, **5c**

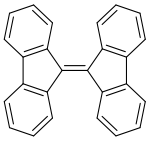


The reaction was carried out using bis(4-methoxyphenyl)methanone (1 eq, 63 mg, 0.3 mmol) and $LiP(TMS)_2$ (1 eq, 0.4 M in Et_2O, 0.3 mmol). The desired product was collected as a colourless solid after chromatographic work-up (0-15% EtOAc gradient in heptane). Isolated yield: 30 mg, 0.066 mmol, 51%.

^1H NMR ($CDCl_3$, 400 MHz, 300K) δ = 6.93 – 6.91 (m, 8H), 6.64 – 6.62 (m, 8H), 3.73 (s, 12H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 157.9, 138.4, 137.0, 132.6, 113.1, 55.2 ppm.

7.1.4. 9,9'-bifluorenylidene, **5d**

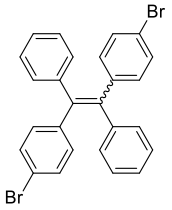


The reaction was carried out using 9H-fluoren-9-one (1 eq, 47 mg, 0.3 mmol) and $LiP(TMS)_2$ (1 eq, 0.4 M in Et_2O, 0.3 mmol). The desired product was collected as a red solid after chromatographic work-up. Isolated yield: 30 mg, 0.09 mmol, 70%.

^1H NMR ($CDCl_3$, 400 MHz, 300K) δ = 8.38 – 8.36 (m, 4H), 7.70 – 7.68 (m, 4H), 7.32 (td, *J* = 7.5, 0.8 Hz, 4H), 7.20 (td, *J* = 7.5, 0.8 Hz, 4H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 141.4, 141.1, 138.3, 129.2, 126.9, 126.8, 120.0 ppm.

7.1.5. (E, Z) 1,2-bis(4-bromophenyl)-1,2-diphenylethene, **5e**

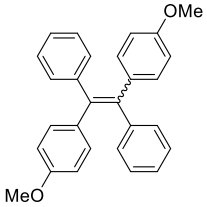


The reaction was carried out using (4-bromophenyl)(phenyl)methanone (1 eq, 68 mg, 0.3 mmol) and $LiP(TMS)_2$ (**1 eq**, 0.4 M in Et_2O, 0.3 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 43 mg, 0.088 mmol, 68%.

^1H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.27 – 7.22 (m, 4H), 7.22 – 7.18 (m, 4H), 7.15 – 7.12 (m, 6H), 7.10 – 7.07 (m, 6H), 7.00 – 6.96 (m, 8H), 6.90 – 6.84 (m, 8H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 143.0, 142.9, 142.5, 142.4, 140.4, 133.0, 133.0, 131.3, 131.3, 131.2, 131.0, 128.1, 127.9, 127.0, 126.9, 120.9, 120.7 ppm.

7.1.6. (E, Z) 1,2-bis(4-methoxyphenyl)-1,2-diphenylethene, **5f**

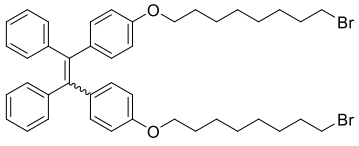


The reaction was carried out using (4-methoxyphenyl)(phenyl)methanone (1 eq, 55 mg, 0.3 mmol) and $LiP(TMS)_2$ (1 eq, 0.4 M in Et_2O, 0.3 mmol). The desired product was collected as a colourless solid after chromatographic work-up (0-10% EtOAc gradient in heptane). Isolated yield: 34 mg, 0.087 mmol, 67**%**.

^1H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.11 – 6.99 (m, 20H), 6.96 – 6.92 (m, 4H), 6.92 – 6.88 (m, 4H), 6.67 – 6.63 (m, 4H), 6.63 – 6.59 (m, 4H), 3.74 (s, 6H), 3.72 (s, 6H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 158.0, 144.4, 144.3, 139.7, 139.7, 136.5, 136.5, 132.6, 132.6, 131.5, 131.5, 127.7, 127.6, 126.3, 113.2, 113.1, 55.2, 55.2 ppm.

7.1.7. (*E-Z*) 1,2-bis(4-((8-bromooctyl)oxy)phenyl)-1,2-diphenylethene, **5g**



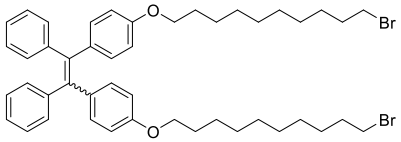
The reaction was carried out using (4-((8-bromooctyl)oxy)phenyl)(phenyl)methanone (1 eq, 93 mg, 0.24 mmol) and $LiP(TMS)_2$ (1 eq, 0.2M in Et_2O, 0.24 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 43 mg, 0.057 mmol, 48%**, 1:1 E:Z** mixture.

^1H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.10 – 6.98 (m, 10H), 6.94 – 6.84 (m, 4H), 6.64 – 6.57 (m, 4H), 3.91 – 3.81 (m, 4H), 3.40 (td, *J* = 6.8, 1.6 Hz, 4H), 1.88 – 1.81 (m, 4H), 1.77 – 1.66 (m, 4H), 1.47 – 1.39 (m, 8H), 1.38 – 1.28 (m, 8H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 157.6, 144.4, 144.4, 139.7, 139.7, 136.4, 136.3, 132.6, 132.6, 131.5, 131.5, 127.7, 127.6, 126.2, 113.7, 113.6, 67.8, 67.8, 34.1, 32.9, 29.4, 29.3, 29.3, 29.3, 28.8, 28.8, 28.2, 26.1, 26.1 ppm.

HR-MS TOF (+) m/Z = observed 851.10650 $[M + Ag]^+$, calculated 851.10545 $[C_{42}H_{50}Br_2O_2 + Ag]^+$.

7.1.8. (*E-Z*) 1,2-bis(4-((10-bromodecyl)oxy)phenyl)-1,2-diphenylethene, **5h**



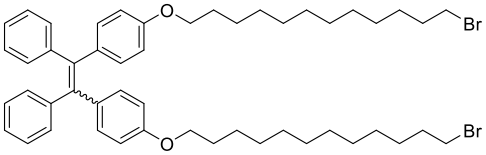
The reaction was carried out using (4-((10-bromodecyl)oxy)phenyl)(phenyl)methanone (**1 eq**, 100 mg, 0.24 mmol) and $LiP(TMS)_2$ (**1 eq**, 0.2M in Et_2O, 0.24 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 56 mg, 0.069 mmol, 58%**, 1:1 E:Z** mixture.

^1H NMR ($CDCl_3$, 400 MHz, 300K): δ = 7.12 – 6.97 (m, 10H), 6.94 – 6.84 (m, 4H), 6.65 – 6.55 (m, 4H), 3.90 – 3.83 (m, 4H), 3.42 (d, *J* = 6.9 Hz, 2H), 3.39 (d, *J* = 6.9 Hz, 2H), 1.88 – 1.80 (m, 4H), 1.72 (dq, *J* = 13.6, 6.7 Hz, 4H), 1.45 – 1.36 (m, 8H), 1.29 (bs, 16H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 157.6, 144.5, 144.4, 139.7, 139.7, 136.3, 136.3, 132.6, 132.6, 131.5, 131.5, 127.7, 127.6, 126.2, 113.7, 113.6, 67.9, 67.8, 34.2, 32.9, 29.5, 29.5, 29.5, 29.4, 29.4, 29.4, 28.8, 28.2, 26.1, 26.1 ppm.

HR-MS TOF (+) m/Z = observed 909.18299 $[M + Ag]^+$, calculated 909.18376 $[C_{46}H_{58}Br_2O_2 + Ag]^+$.

7.1.9. (*E-Z*) 1,2-bis(4-((10-bromodecyl)oxy)phenyl)-1,2-diphenylethene, **5i**



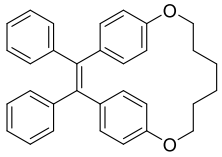
The reaction was carried out using (4-((12-bromododecyl)oxy)phenyl)(phenyl)methanone (**1 eq**, 107 mg, 0.24 mmol) and $LiP(TMS)_2$ (**1 eq**, 0.2M in Et_2O, 0.24 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 57 mg, 0.066 mmol, 55%**, 1:1 E:Z** mixture.

^{1}H NMR (CDCl3, 101 MHz, 300K): δ = 7.09 – 6.96 (m, 10H), 6.93 – 6.87 (m, 4H), 6.64 – 6.58 (m, 4H), 3.92 – 3.80 (m, 4H), 3.40 (d, *J* = 6.9 Hz, 2H), 3.38 (d, *J* = 6.9 Hz, 2H), 2.02 – 1.73 (m, 8H), 1.49 – 1.26 (m, 32H) ppm.

^{13}C NMR (CDCl3, 101 MHz, 300K): δ = 157.5, 144.4, 144.3, 139.6, 136.2, 132.5, 132.5, 131.41, 131.38, 127.6, 127.5, 126.1, 113.6, 113.5, 67.77, 67.75, 34.1, 32.8, 29.5, 29.47, 29.4, 29.37, 29.35, 29.3, 28.7, 28.2, 26.1.

HR-MS TOF (+) m/Z = observed 881.33102 $[M + Na]^+$, calculated 881.33077 $[C_{50}H_{66}Br_2O_2 + Na]^+$.

7.1.10. (Z)-2,3-diphenyl-5,12-dioxa-1,4(1,4)-dibenzenacyclododecaphan-2-ene, **7a**



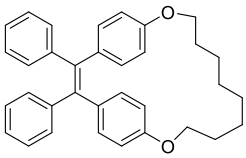
The reaction was carried out using ((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) (1 eq, 61 mg, 0.3 mmol) and $LiP(TMS)_2$ (2 eq, 0.4 M in Et_2O, 0.6mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 12 mg, 0.027 mmol, 21%.

^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.13 – 7.10 (m, 10H), 6.85 – 6.80 (m, 4H), 6.66 – 6.60 (m, 4H), 4.05 (t, $^{3}J_{H\text{-}H}$ = 6.5 Hz, 4H), 1.54 – 1.42 (m, 4H), 1.27 – 1.24 (m, 4H) ppm.

^{13}C NMR (101 MHz, 300K) δ = δ 156.0, 142.4, 141.4, 137.9, 132.4, 131.2, 127.8, 126.6, 116.6, 68.7, 26.6, 23.6 ppm.

HR-MS TOF (+) m/Z = observed 447.2346 $[M + H]^+$, calculated 447.2324 $[C_{32}H_{30}O_2 + H]^+$.

7.1.11. (Z)-2,3-diphenyl-5,14-dioxa-1,4(1,4)-dibenzenacyclotetradecaphan-2-ene, **7b**



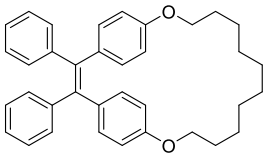
The reaction was carried out using ((octane-1,8-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) (1 eq, 103 mg, 0.20 mmol) and $LiP(TMS)_2$ (2 eq, 0.2M in Et_2O, 0.40 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 46 mg, 0.097 mmol, 47%.

^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.10 (bs, 10H), 6.85 – 6.82 (m, 4H), 6.63 – 6.59 (m, 4H), 4.03 (t, $^{3}J_{H\text{-}H}$ = 6.5 Hz, 4H), 1.63 (p, $^{3}J_{H\text{-}H}$ = 6.7 Hz, 4H), 1.35 – 1.33 (m, 4H), 1.26 – 1.23 (m, 4H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 157.1, 143.1, 140.8, 137.1, 132.5, 131.4, 127.7, 126.5, 114.7, 67.5, 27.9, 27.8, 24.9 ppm.

HR-MS TOF (+) m/Z = observed 475.2631 $[M + H]^+$, calculated 475.2637 $[C_{34}H_{34}O_2 + H]^+$.

7.1.12. (Z)-2,3-diphenyl-5,16-dioxa-1,4(1,4)-dibenzenacyclohexadecaphan-2-ene, **7c**



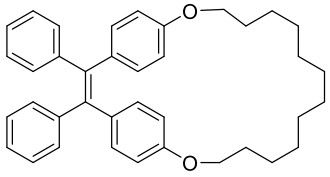
The reaction was carried out using ((decane-1,10-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) (1 eq, 128 mg, 0.24 mmol) and $LiP(TMS)_2$ (2 eq, 0.2M in Et_2O, 0.48 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 65 mg, 0.129 mmol, 54**%**.

^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.08 – 7.04 (m, 10H), 6.89 – 6.85 (m, 4H), 6.66 – 6.61 (m, 4H), 3.98 (t, $^3J_{H\text{-}H}$ = 6.4 Hz, 4H), 1.68 (p, $^3J_{H\text{-}H}$ = 6.6 Hz, 4H), 1.44 – 1.33 (m, 4H), 1.33 – 1.20 (m, 8H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 157.3, 143.7, 140.3, 136.8, 132.6, 131.5, 127.7, 126.4, 114.3, 67.7, 28.4, 28.1, 28.0, 25.1 ppm.

HR-MS TOF (+) m/Z = observed 525.2764 $[M + Na]^+$, calculated 525.2770 $[C_{36}H_{38}O_2 + Na]^+$.

7.1.13. (Z)-2,3-diphenyl-5,18-dioxa-1,4(1,4)-dibenzenacyclooctadecaphan-2-ene, **7d**



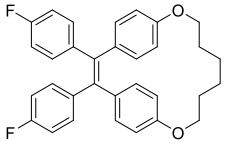
The reaction was carried out using ((dodecane-1,12-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) (1 eq, 135 mg, 0.24 mmol) and $LiP(TMS)_2$ (2 eq, 0.2M in Et_2O, 0.48 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 39 mg, 0.073 mmol, 31%.

^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.09 – 7.02 (m, 10H), 6.91 – 6.87 (m, 4H), 6.64 – 6.60 (m, 4H), 3.93 (t, $^3J_{H\text{-}H}$ = 6.3 Hz, 4H), 1.73 (p, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H), 1.47 – 1.37 (m, 4H), 1.28 (bs, 12H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 157.5, 143.9, 140.1, 136.6, 132.6, 131.5, 127.6, 126.3, 113.9, 67.6, 28.7, 28.4, 28.4, 28.3, 25.6 ppm.

HR-MS TOF (+) m/Z = observed 531.3270 $[M + H]^+$, calculated 531.3263 $[C_{38}H_{42}O_2 + H]^+$.

7.1.14 (Z)-2,3-bis(4-fluorophenyl)-5,12-dioxa-1,4(1,4)-dibenzenacyclododecaphan-2-ene, **7e**



The reaction was carried out using ((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone) (**1 eq**, 124 mg, 0.24 mmol) and $LiP(TMS)_2$ (**2 eq**, 0.2M in Et_2O, 0.48 mmol). First crude product was purified by flash column chromatography and then preparative thin layer chromatography was used to separate compounds **7e** and **8e**.

Compound **7e** was isolated as a colourless solid. Isolated yield: 13 mg, 0.027 mmol, **11%.**

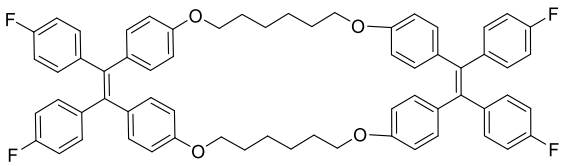
^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.11 – 7.06 (m, 4H), 6.86 – 6.77 (m, 8H), 6.64 – 6.60 (m, 4H), 4.07 – 4.03 (m, 4H), 1.48 – 1.42 (m, 4H), 1.26 – 1.23 (m, 4H) ppm.

^{19}F NMR ($CDCl_3$, 376 MHz, 300K) δ = -115.0 ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 161.6 (d, *J* = 246.7 Hz), 156.2, 140.3, 138.2 (d, *J* = 3.4 Hz), 137.4, 132.8 (d, *J* = 7.9 Hz), 132.3, 116.7, 114.9 (d, *J* = 21.3 Hz), 68.7, 26.56, 23.6 ppm.

HR-MS TOF (+) m/Z = observed 505.1950 $[M + Na]^+$, calculated 505.1955 $[C_{32}H_{28}F_2O_2 + Na]^+$.

7.1.15. (2Z,14Z)-2,3,14,15-tetrakis(4-fluorophenyl)-5,12,17,24-tetraoxa-1,4,13,16(1,4)-tetrabenzenacyclotetracosaphane-2,14-diene, 8e



Compound **8e** was isolated as a side product in the synthesis of **7e** (see preparation details above).

Compound **8e** was isolated as a colourless solid. Isolated yield: 17 mg, 0.0175 mmol, **15%.**

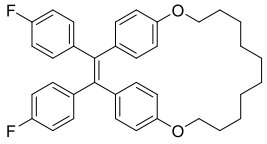
^{1}H NMR ($CDCl_3$, 400 MHz, 300K) δ = 6.96 – 6.93 (m, 4H), 6.90 – 6.88 (m, 4H), 6.80– 6.78 (m, 4H), 6.65 – 6.61 (m, 4H), 3.90 (t, $^3J_{H\text{-}H}$ = 6.5 Hz, 4H), 1.80 – 1.77 (m, 4H), 1.53 – 1.48 (m, 4H) ppm.

^{19}F NMR ($CDCl_3$, 376 MHz, 300K) δ = -115.6 ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 161.4 (d, *J* = 246.2 Hz), 157.7, 140.1 (d, *J* = 3.4 Hz), 135.9, 133.0 (d, *J* = 7.8 Hz), 132.5, 116.7, 114.7 (d, *J* = 21.2 Hz), 113.8, 67.5, 29.2, 25.7 ppm.

HR-MS TOF (+) m/Z = observed 987.40129 $[M + Na]^+$, calculated 987.40069 $[C_{64}H_{56}F_4O_4 + Na]^+$.

7.1.16. (Z)-2,3-bis(4-fluorophenyl)-5,16-dioxa-1,4(1,4)-dibenzenacyclohexadecaphan-2-ene, **7f**



The reaction was carried out using ((decane-1,10-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone) (**1 eq**, 137 mg, 0.24 mmol) and $LiP(TMS)_2$ (**2 eq**, 0.2M in Et_2O, 0.48 mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 70 mg, 0.13 mmol, 54%.

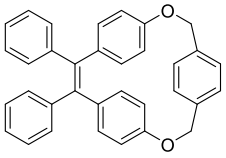
^1H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.03 – 6.98 (m, 4H), 6.86 – 6.76 (m, 8H), 6.64 – 6.60 (m, 4H), 3.98 (t, $^3J_{H-H}$ = 6.5 Hz, 4H), 1.67 (p, $^3J_{H-H}$ = 6.6 Hz, 4H), 1.39 – 1.30 (m, 4H), 1.27 – 1.24 (m, 8H) ppm.

^{19}F NMR ($CDCl_3$, 376 MHz, 300K) δ = -115.5 ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 161.5 (d, *J* = 246.4 Hz), 157.5, 139.5 (d, *J* = 3.4 Hz), 139.3, 136.3, 132.9 (d, *J* = 7.8 Hz), 132.5, 114.8 (d, *J* = 21.3 Hz), 114.4, 67.7, 28.41, 28.0, 28.0, 25.1 ppm.

HR-MS TOF (+) m/Z = observed 561.2577 $[M + Na]^+$, calculated 561.2581 $[C_{36}H_{36}F_2O_2 + Na]^+$.

7.1.17. (Z)-8,9-diphenyl-2,6-dioxa-1,4,7(1,4)-tribenzenacyclononaphan-8-ene, **7g**



The reaction was carried out using (((1,4-phenylenebis(methylene))bis(oxy))bis(4,1-phenylene))bis(phenylmethanone) (1 eq, 64 mg, 0.26 mmol) and $LiP(TMS)_2$ (2 eq, 0.4 M in Et_2O, 0.51mmol). The desired product was collected as a colourless solid after chromatographic work-up. Isolated yield: 15 mg, 0.032 mmol, 25%.

^1H NMR ($CDCl_3$, 400 MHz, 300K) δ = 7.17 (bs, 4H), 7.07 – 7.04 (m, 6H), 7.02 – 7.00 (m, 4H), 6.61 – 6.58 (m, 4H), 6.43 – 6.39 (m, 4H), 5.19 (s, 4H) ppm.

^{13}C NMR ($CDCl_3$, 101 MHz, 300K) δ = 154.7, 142.7, 141.2, 137.2, 136.5, 131.3, 131.1, 129.7, 127.7, 126.5, 117.2, 70.1 ppm.

HR-MS TOF (+) m/Z = observed 489.1822 $[M + H]^+$, calculated 489.1831$[C_{34}H_{26}O_2 + Na]^+$.

7.2. Attempts to characterize by-products of the reaction sequence

The crude reaction mixture after the complete sequence was subjected to GC-MS in an ettempt to characterize by-products of the reaction. In addition to alkene product and traces of ketone starting material, two signals of trace amount were observed. Their mass is consistent with an assignment to EtOTMS and hexamethylcyclotrisiloxane. Further isolation and purification was precluded due to their low concentration and, in case of EtOTMS, the high volatility.

The GC-MS analysis did not exhibit any signals that could be assigned to any phosphorus-containing by-products. Similarly, also NMR monitoring of the reaction of LiOEt with the 1,2-diphotphetane at -40 °C did not allow us to identify any by-products. An observation is

that upon exposure to air, a large amount of precipitate is immediately formed. In general, we assume that upon removal of one TMS group from the 1,2-diphosphetane, highly reactive species are formed which presumable decompose in various pathways, giving rise to multiple species, potentially polymers that may have low solubility (in particular at low temperatures).

8. Crystallographic data

Measurements were performed using graphite-monochromatized Mo K_α radiation at 170 K using a Bruker D8 APEX-II equipped with a CCD camera. The structure was solved by direct methods (SHELXS-2014) and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018). The non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms of the CH_2 / CH groups were refined with common isotropic displacement parameters for the H atoms of the same group, and idealized geometry. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group, and idealized staggered geometry.

Specific for **SO1904/4a**: Single crystals were obtained from concentrated diethyl ether solutions of **4a**. The Olex2 solvent mask function was used to treat solvent accessible voids. Two 491.4 $Å^3$ voids accounting for 82.5 electrons (~1.6 Et2O molecules), and two 550 $Å^3$ voids accounting for 110.5 electrons (~2.1 Et2O molecules) per unit cell were treated. The final output of the solvent mask is appended to the .cif file.

Specific for **SO1905/7a**:
Single crystals were obtained from concentrated pentane/ethyl acetate solutions of **7a**.

Specific for **SO2006/7g**:
Single crystals were obtained from concentrated pentane/ethyl acetate solutions of **7g**. The C10 chain is disordered over two sites, with occupancies of 1/3 and 2/3.

Specific for **SO2008/7f**:
Single crystals were obtained from concentrated pentane/ethyl acetate solutions of **7f**.

Specific for **SO2009/8e**:
Single crystals were obtained from concentrated chloroform solutions of **8e**.

CCDC 2162400-2162404 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Table S1. Selected bond lengths (Å) and angles (°) for **4a**, **7a**, **7f**, **7g**, and **8e**.*Symmetry generated.

Parameter	4a	7a	7f	7g	8e
P1-P2	2.204 (1) 2.200 (1)*	-	-	-	-
P1-C1	1.936 (3) 1.937 (3)*	-	-	-	-
P2-C2	1.972 (3)	-	-	-	-
C1-C2	1.626 (4) 1.629 (4)*	1.357 (3)	1.365 (3)	1.350 (4)	1.351 (5)

C3-C2-C1-C22	-24.2 (3) 23.6	-12.6 (4)	-11.8 (3)	10.7 (4)	10.6 (5)
P2-C2-C1-P1	-27.08 (12) 24.9 (2)*	-	-	-	-

Table S2.Crystal data and structure refinement details.

Compound	**4a**	**7a**	**7f**	**7g**	**8e**
Chemical formula	$3(C_{16}H_{19}PSi)$	$C_{32}H_{30}O_2$	$C_{36}H_{26}F_2O_2$	$C_{34}H_{26}O_2$	$C_{32}H_{28}F_2O_2{\cdot}CHCl_3$
M_r	811.11	446.56	538.65	466.55	601.91
Crystal system, space group	Monoclinic *C2/c*	Monoclinic *P21*	Monoclinic *P21/c*	Monoclinic *P21*	Monoclinic *P21/n*
Temperature (K)	170	170	170	170	170
***a, b, c* (Å)**	26.6644 (13) 42.3661 (13) 9.7021 (3)	9.5099 (4) 9.8152 (4) 13.7004 (5)	10.356 (3) 31.286 (8) 9.517 (2)	9.2899 (2) 10.6993 (2) 13.1402 (3)	13.893 (3) 9.559 (2) 23.430 (6)
β (°)	104.927 (2)	105.846 (1)	108.010 (4)	107.074 (1)	98.908 (13)
***V* (Å^3)**	10590.3 (7)	1230.22 (9)	2932.3 (12)	1248.51 (5)	3074.1 (13)
Z	8	2	4	2	4
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	0.21	0.07	0.08	0.08	0.34
Crystal size (mm)	0.6 × 0.4 × 0.2	0.17 × 0.17 × 0.07	0.57 × 0.30 × 0.11	0.27 × 0.17 × 0.13	0.37 × 0.23 × 0.18
Diffractometer	Bruker D8 APEX-II	Bruker D8 APEX-II	Bruker D8 APEX-II	Bruker D8 APEX-II	Bruker D8 APEX-II
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	0.691, 0.746	0.688, 0.746	0.696, 0.746	0.708, 0.746	0.697, 0.745
No. of measured, independent and observed [I > 2s(I)] reflections	141810 12191 8045	42337 6155 5064	42869 7267 4443	52824 7737 5613	98693 6053 4042
R_{int}	0.102	0.058	0.046	0.066	0.035
(sin θ/λ)$_{max}$ (Å^{-1})	0.650	0.669	0.666	0.719	0.617
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.064, 0.158, 1.04	0.044, 0.102, 1.07	0.067, 0.188, 1.06	0.050, 0.125, 1.05	0.089, 0.296, 1.02
No. of parameters	496	307	406	325	361
No. of restraints	-	1	176	1	-
H-atom treatment	Constrained	Constrained	Constrained	Constrained	Constrained
Δ⟩$_{max}$, Δ⟩$_{min}$ (e Å^{-3})	0.29, –0.27	0.15, –0.21	0.45, -0.53	0.19, -0.24	1.04, -0.98
CCDC No.	2162403	2162400	2162402	2162401	2162404

9. ^{31}P (a) and ^{19}F (b) NMR monitoring of the reaction

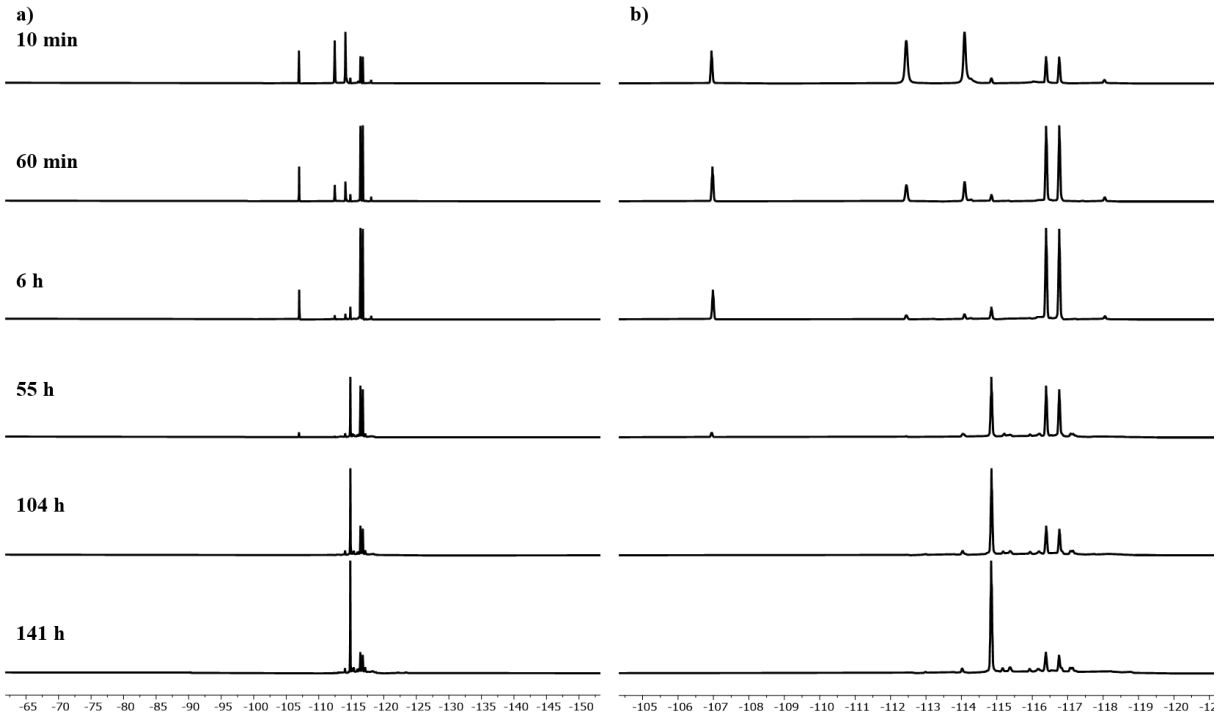


Fig. S3. ^{19}F NMR monitoring of the reaction between 4,4'-difluorobenzophenone and $LiP(TMS)_2$ (**2**). a) Full range spectra; b) zoom into the relevant region between δ = -105 to -120 ppm

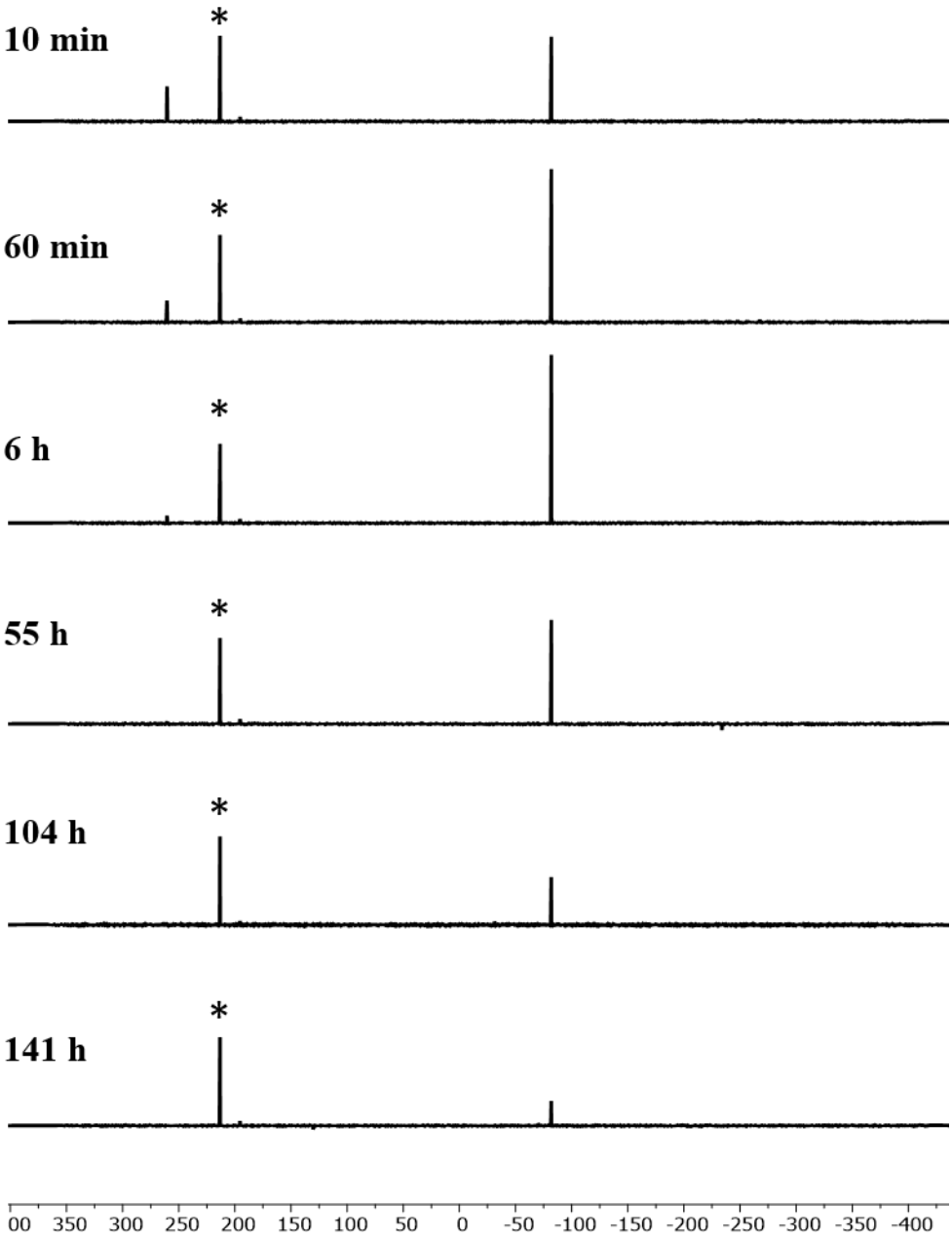


Fig. S4. Full range ^{31}P NMR spectra monitoring of the reaction between 4,4'-difluorobenzophenone and LiP(TMS)2 (2). The signal indicated by * at 244.5 ppm corresponds to (E)-(4-methoxybenzylidene)(2,4,6-tri-tert-butylphenyl)phosphane which is added as a standard for quantification.

10. NMR spectra of isolated compounds

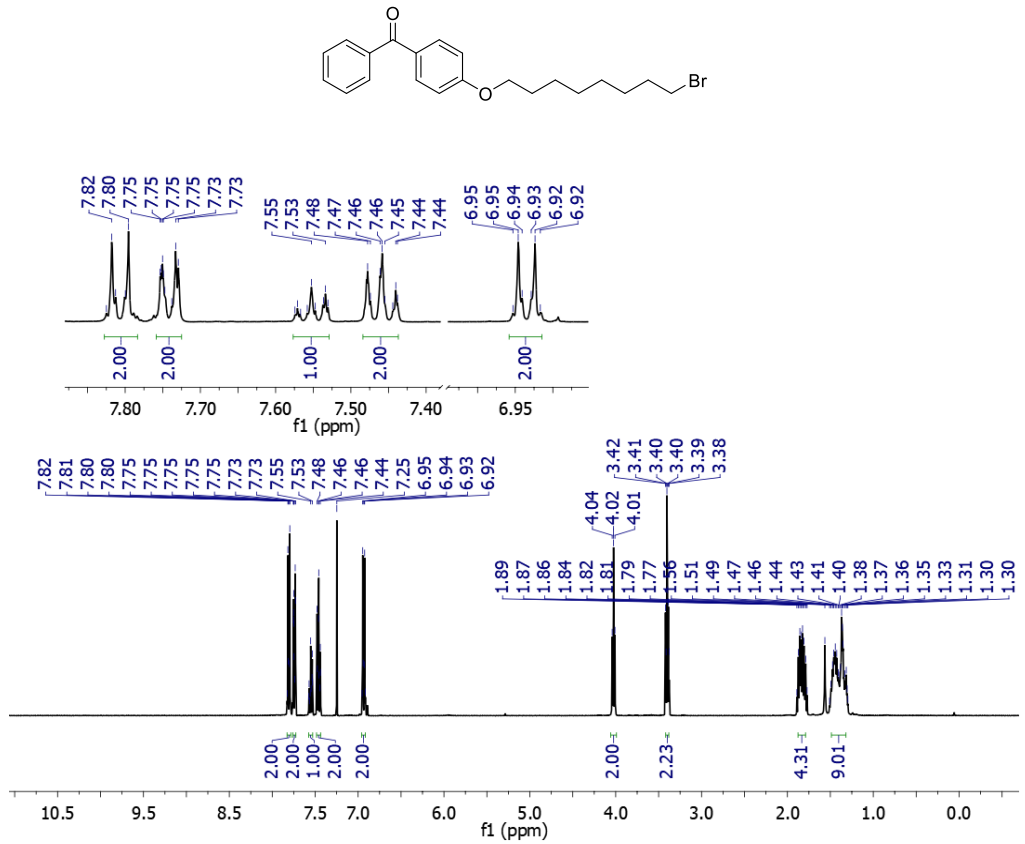


Fig. S5. ^{1}H NMR spectrum of (4-((8-bromooctyl)oxy)phenyl)(phenyl)methanone ($CDCl_3$, 400 MHz, 300K).

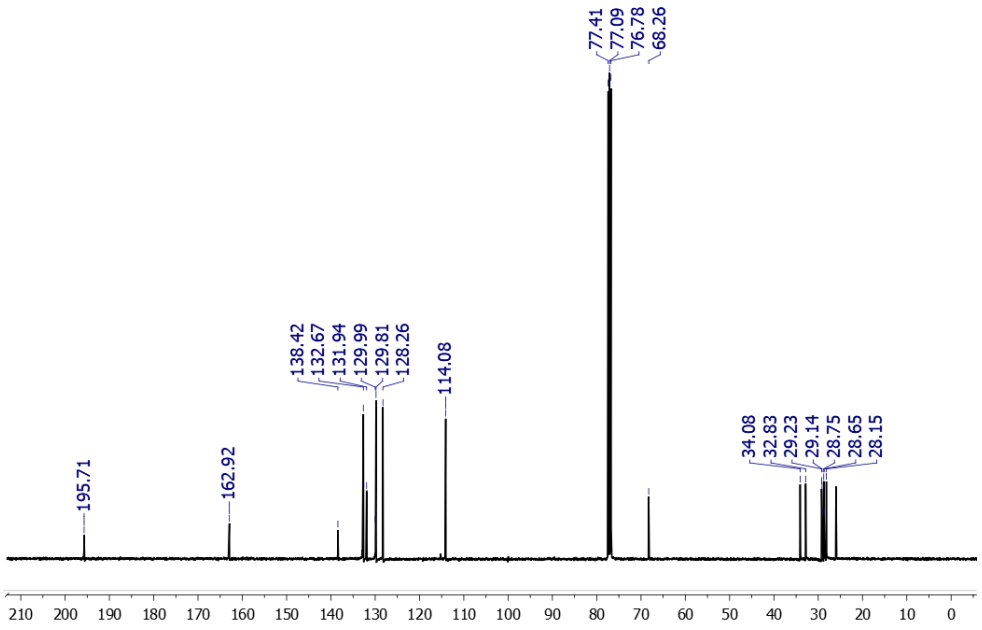


Fig. S6. ^{13}C NMR spectrum of (4-((8-bromooctyl)oxy)phenyl)(phenyl)methanone ($CDCl_3$, 101 MHz, 300K).

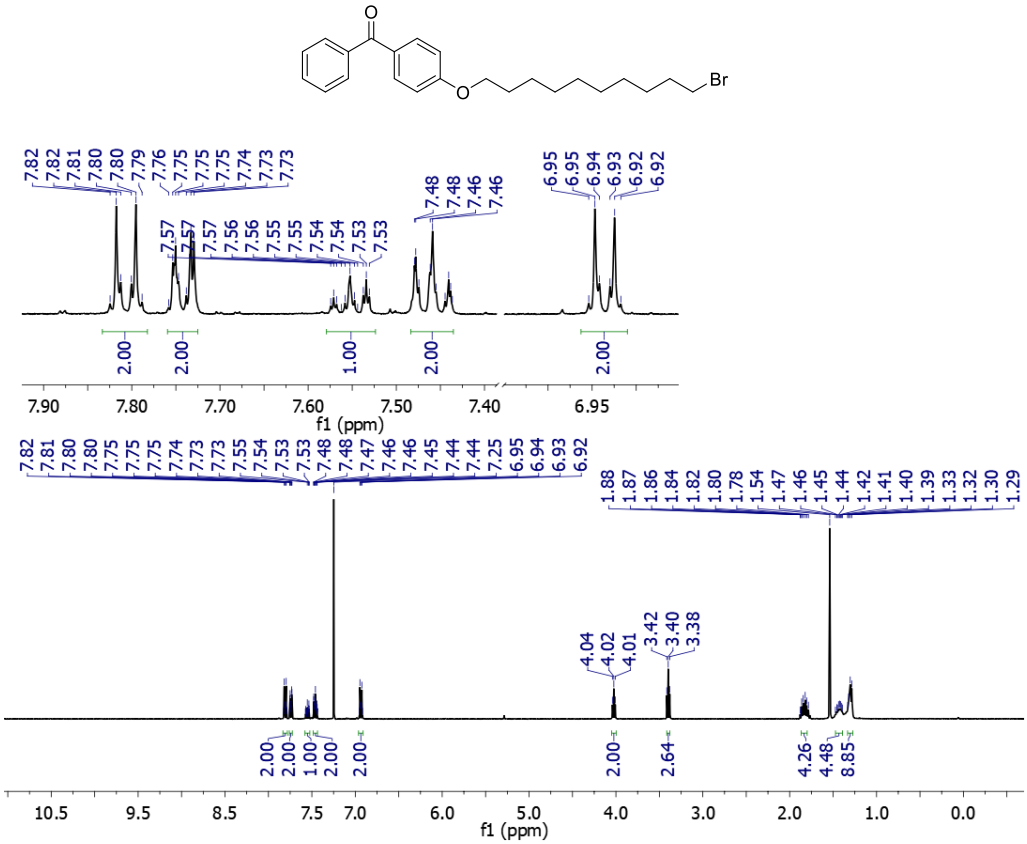


Fig. S7. ^{1}H NMR spectrum of (4-((10-bromodecyl)oxy)phenyl)(phenyl)methanone ($CDCl_3$, 400 MHz, 300K).

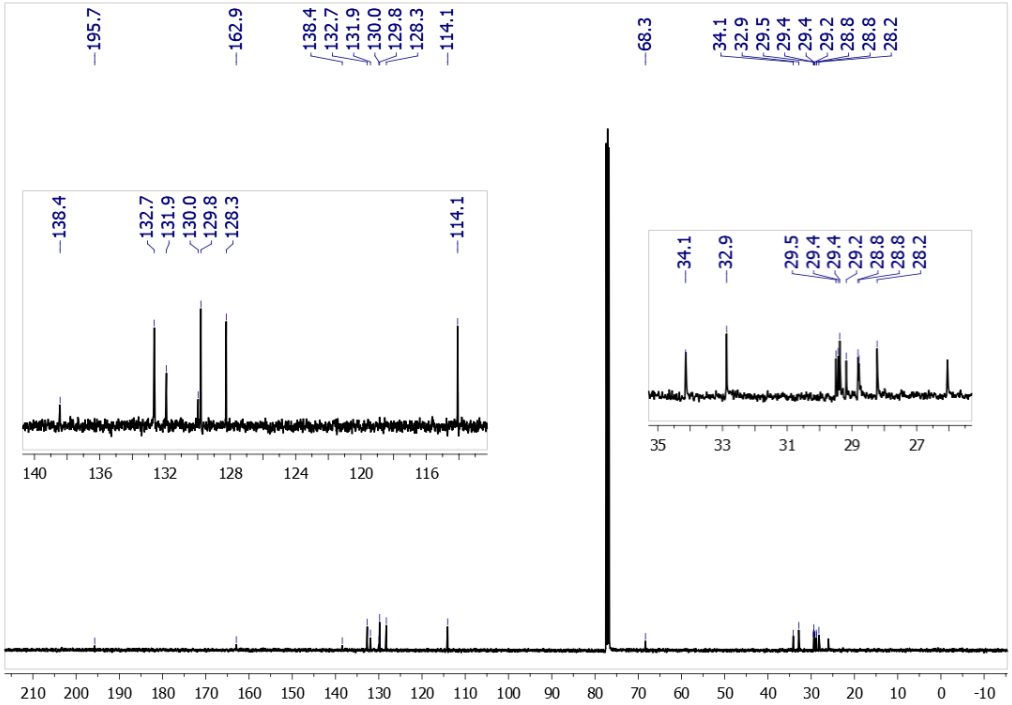


Fig. S8. ^{13}C NMR spectrum of (4-((10-bromodecyl)oxy)phenyl)(phenyl)methanone ($CDCl_3$, 101 MHz, 300K).

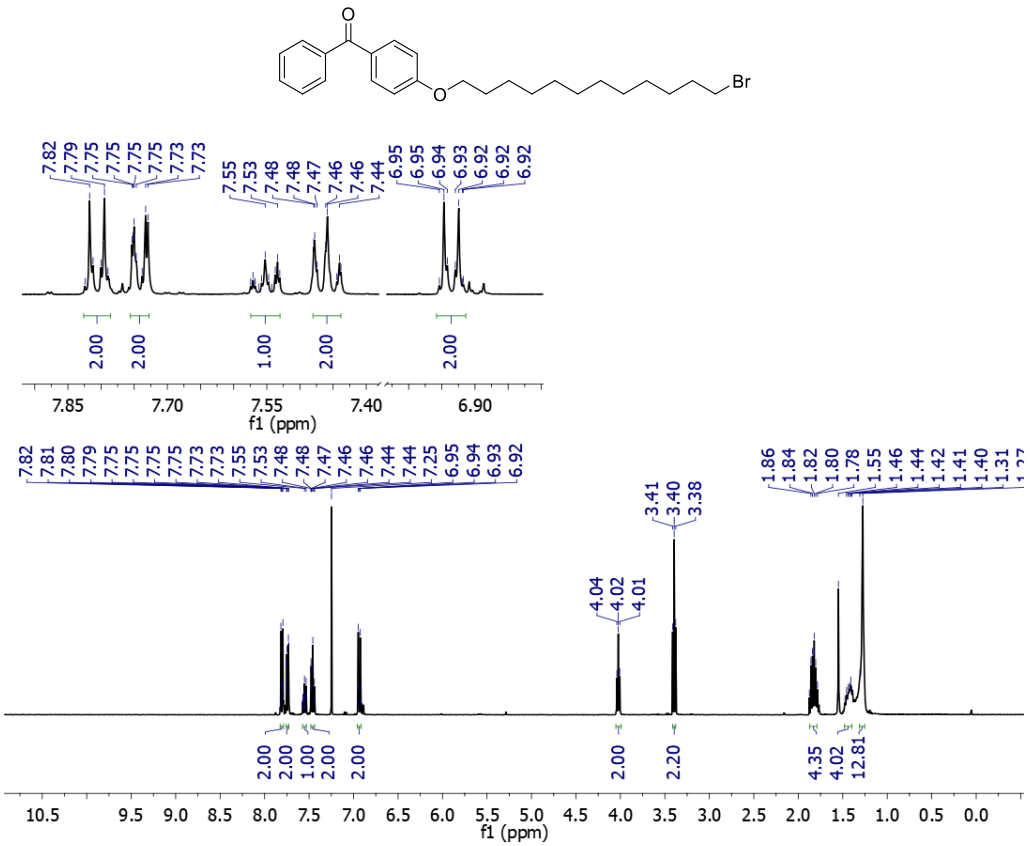


Fig. S9. ^{1}H NMR spectrum of (4-((12-bromododecyl)oxy)phenyl)(phenyl)methanone ($CDCl_3$, 400 MHz, 300K).

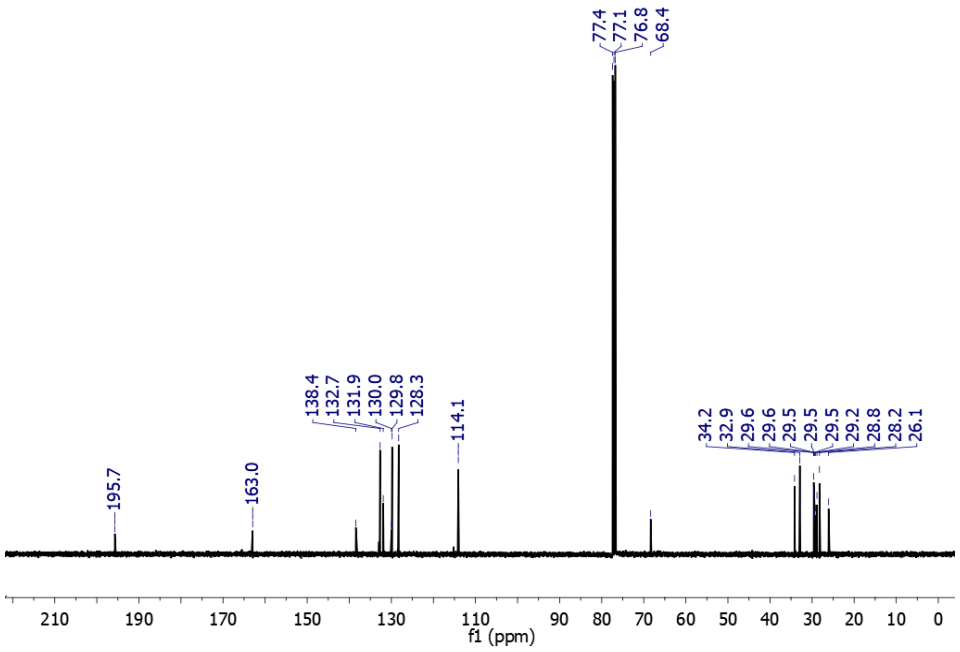


Fig. S10. ^{13}C NMR spectrum of (4-((12-bromododecyl)oxy)phenyl)(phenyl)methanone ($CDCl_3$, 101 MHz, 300K).

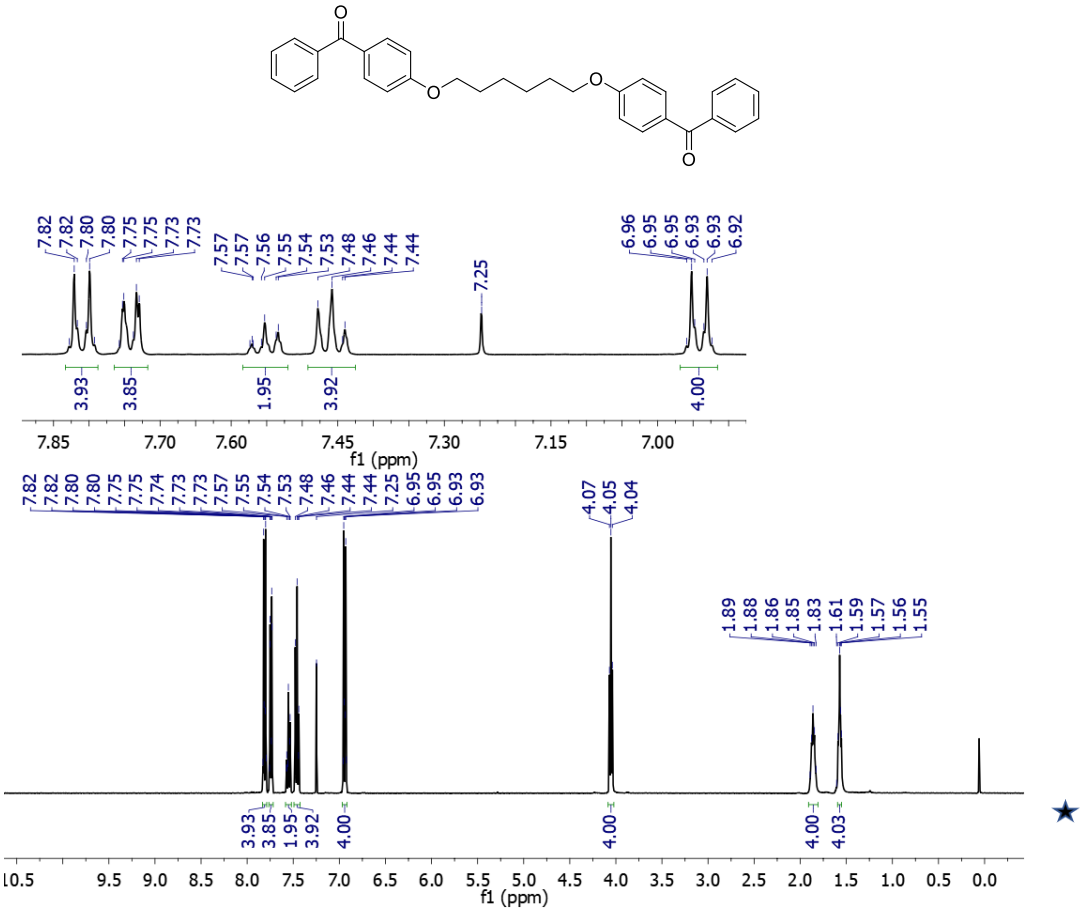


Fig. S11. ^{1}H NMR spectrum of ((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) ($CDCl_3$, 400 MHz, 300K).

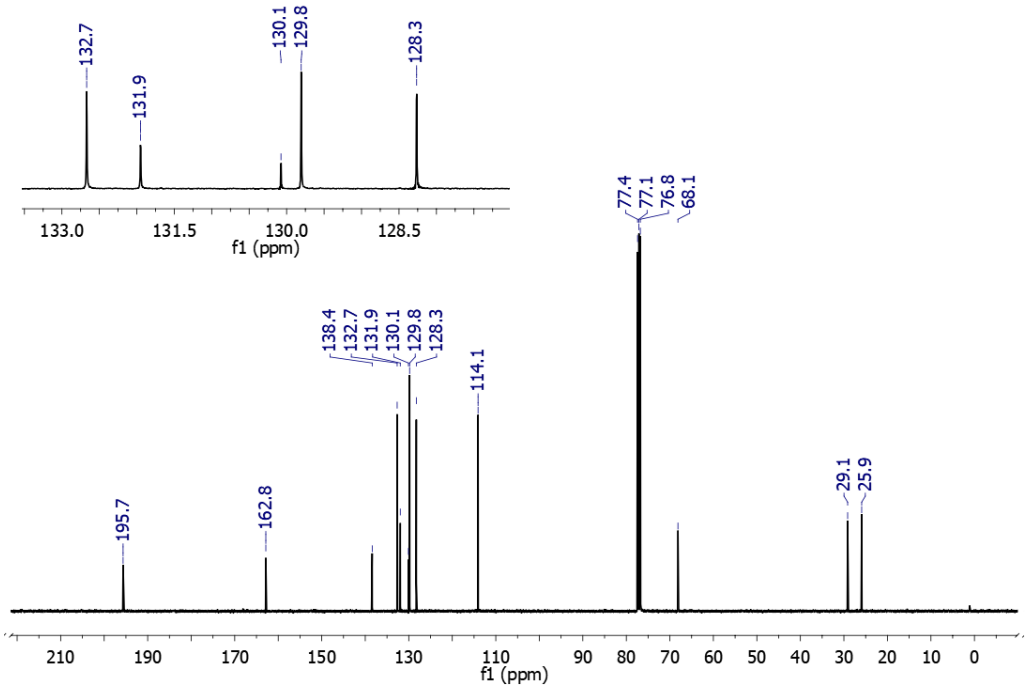


Fig. S12. ^{13}C NMR spectrum of ((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) ($CDCl_3$, 101 MHz, 300K).

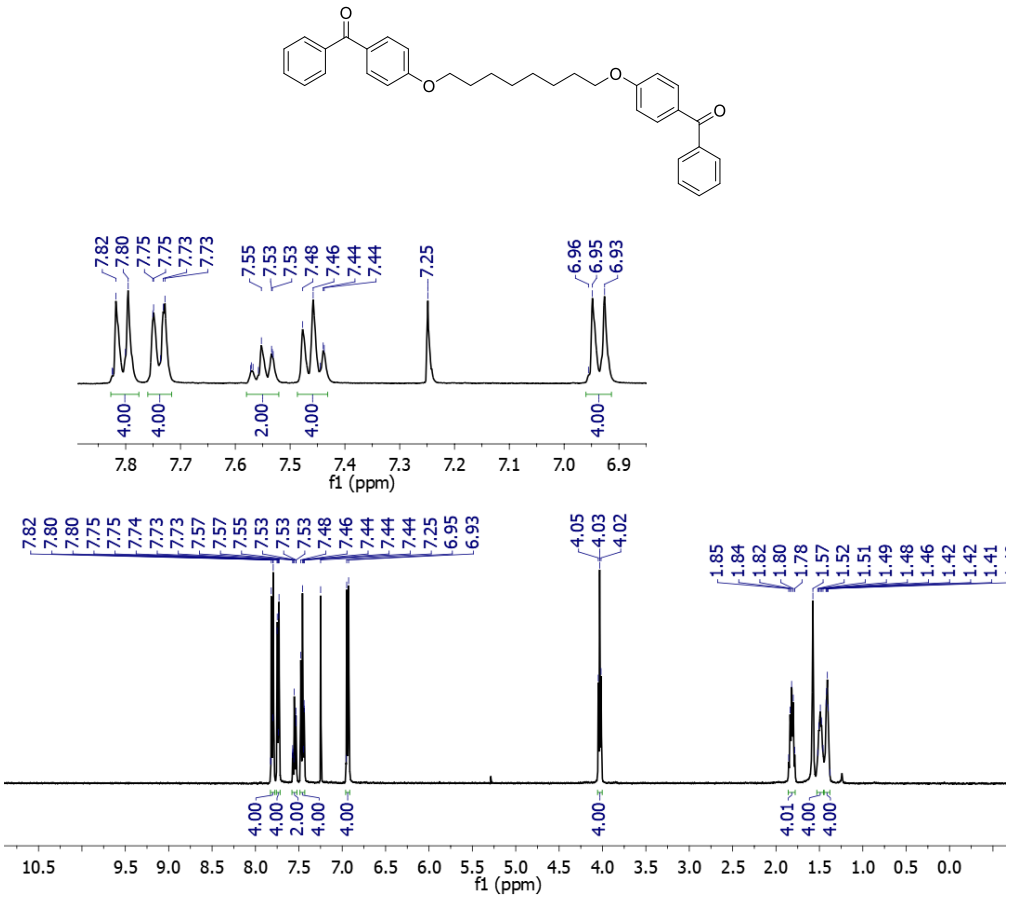


Fig. S13. ^{1}H NMR spectrum of ((octane-1,8-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) ($CDCl_3$, 400 MHz, 300K).

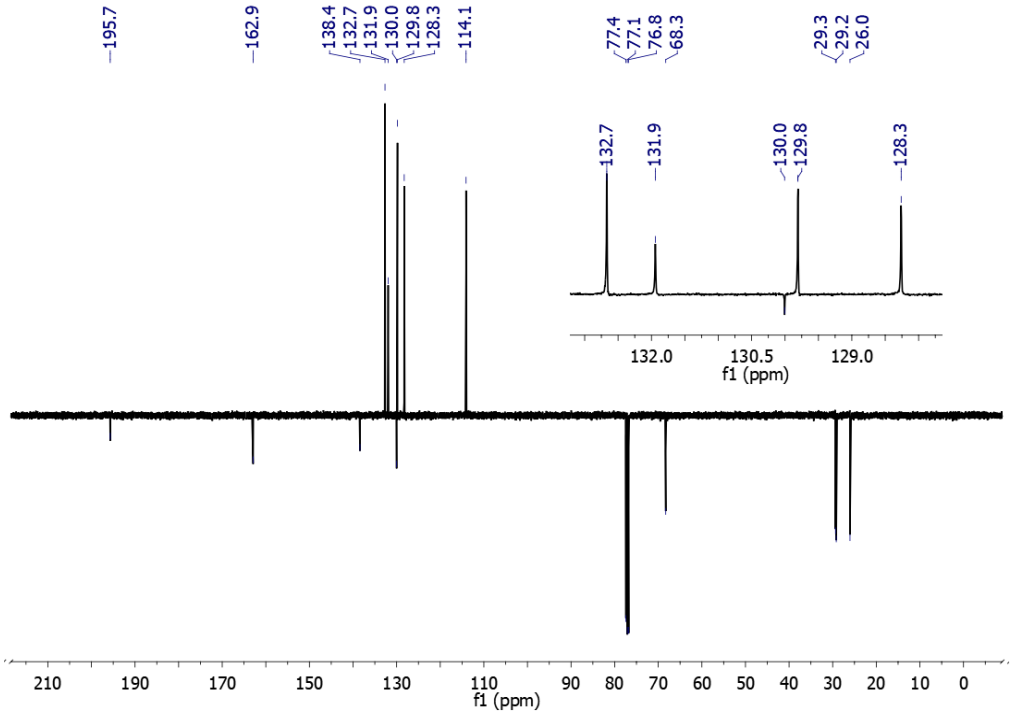


Fig. S14. ^{13}C APT NMR spectrum of ((octane-1,8-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) ($CDCl_3$, 101 MHz, 300K).

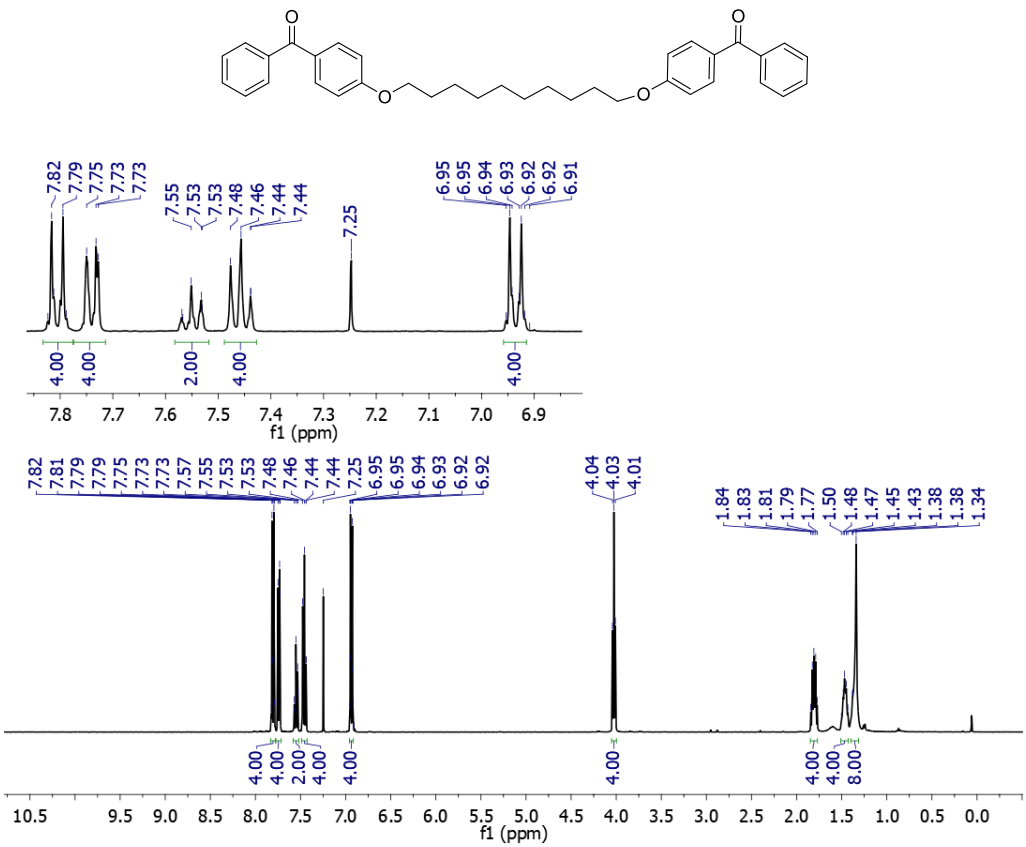


Fig. S1. ^{1}H NMR spectrum of ((decane-1,10-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) ($CDCl_3$, 400 MHz, 300K).

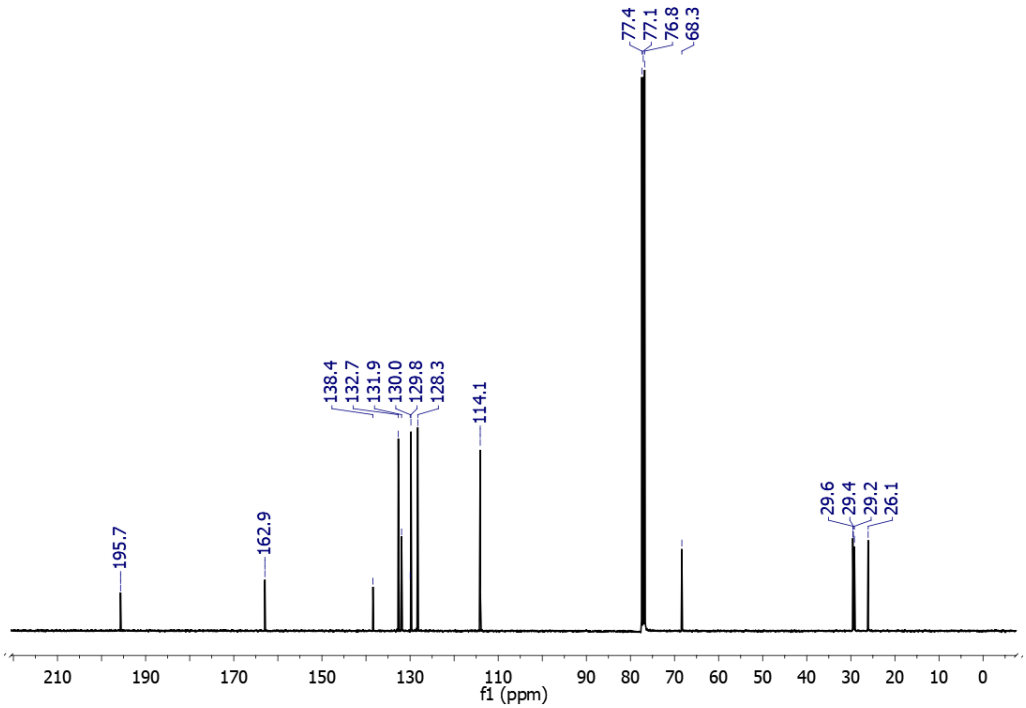


Fig. S16. ^{13}C NMR spectrum of ((decane-1,10-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) ($CDCl_3$, 101 MHz, 300K).

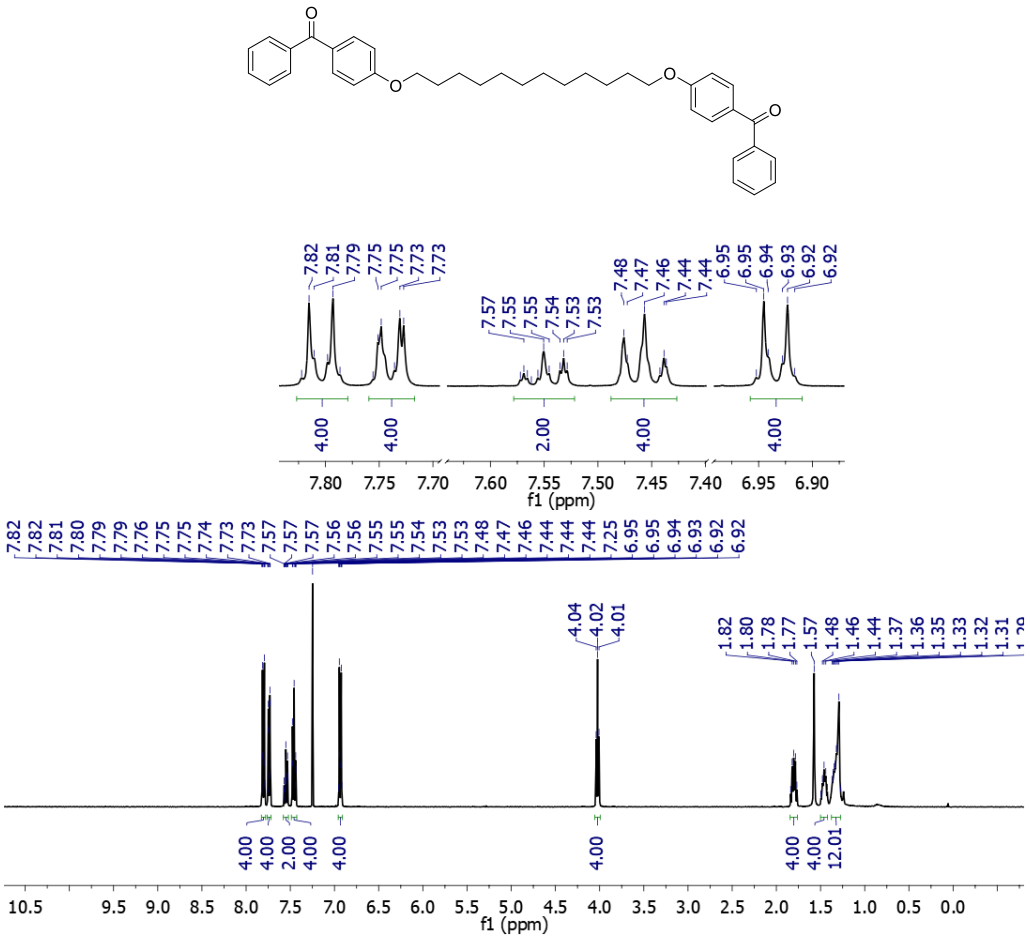


Fig. S17. ^{1}H NMR spectrum of ((dodecane-1,12-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) ($CDCl_3$, 400 MHz, 300K).

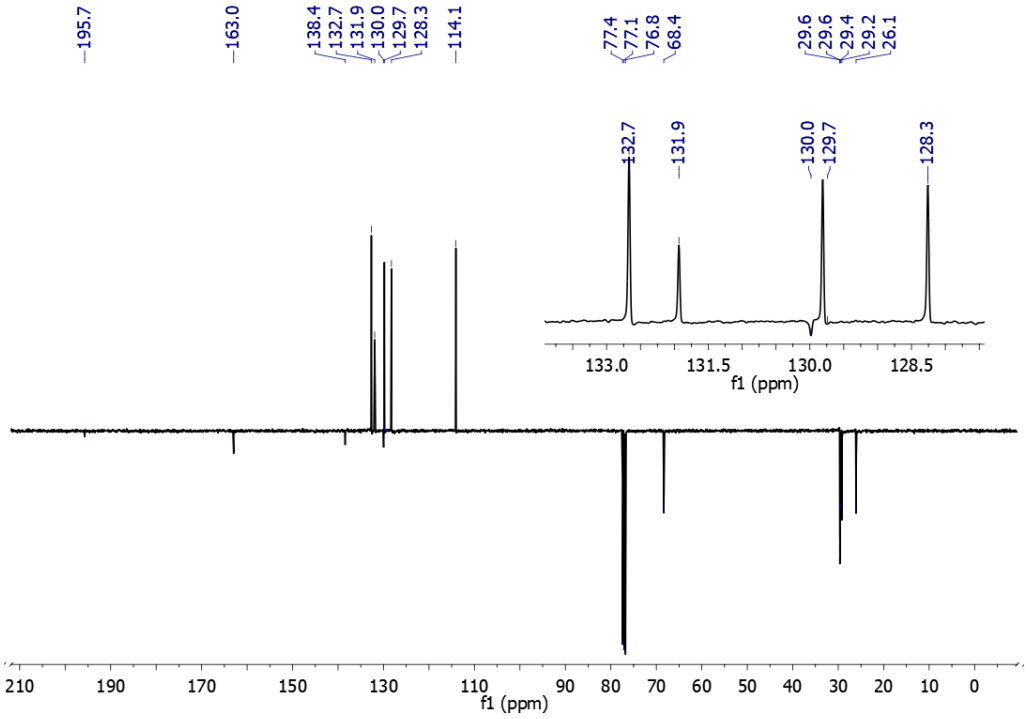


Fig. S18. ^{13}C APT NMR spectrum of ((dodecane-1,12-diylbis(oxy))bis(4,1-phenylene))bis(phenylmethanone) ($CDCl_3$, 101 MHz, 300K).

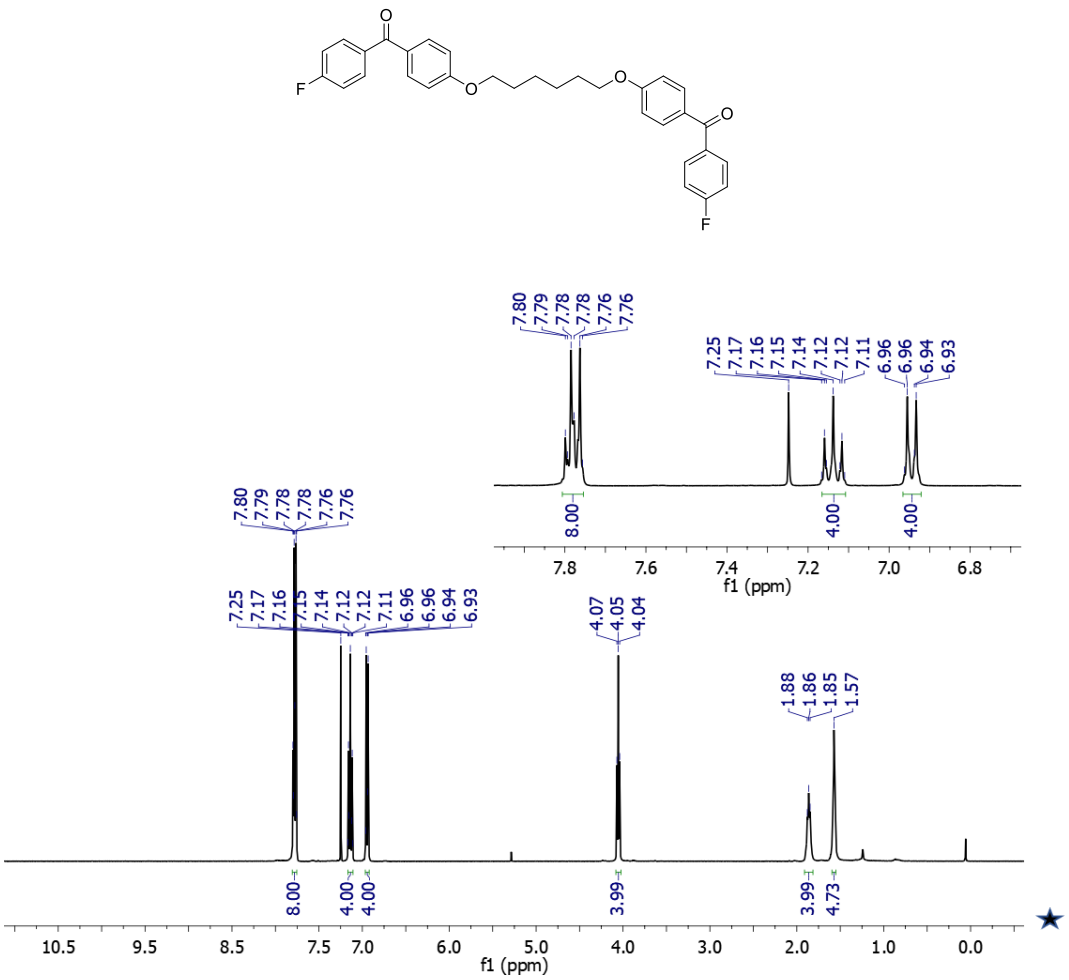


Fig. S192. ^{1}H NMR spectrum of ((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone) ($CDCl_3$, 400 MHz, 300K).

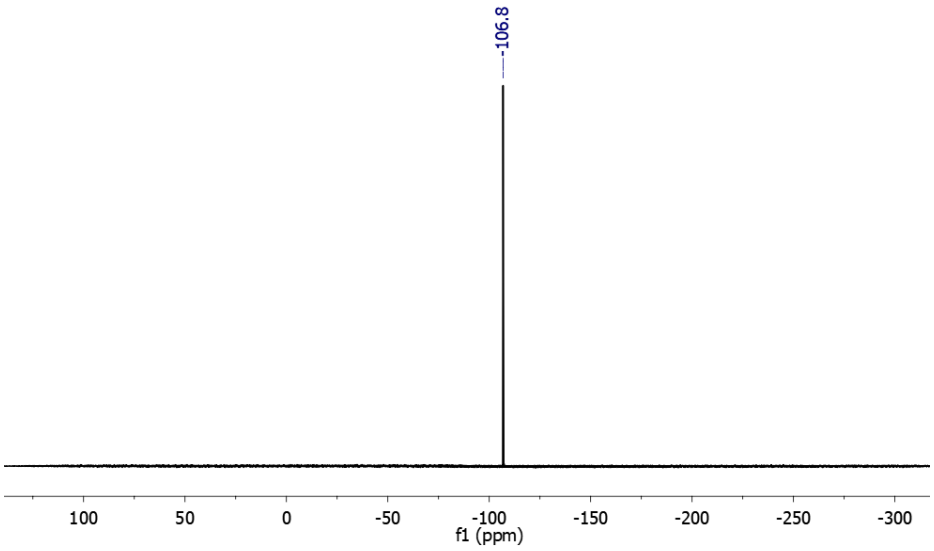


Fig. S20. ^{19}F spectrum NMR of ((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone) ($CDCl_3$, 376 MHz, 300K).

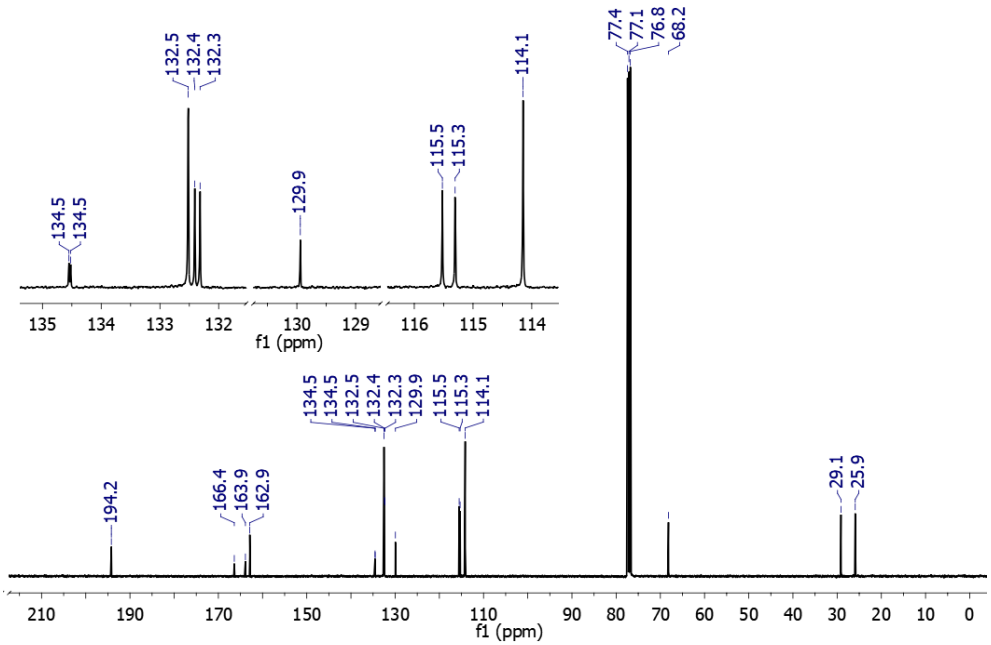


Fig. S21. ^{13}C spectrum NMR of ((hexane-1,6-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone) ($CDCl_3$, 101 MHz, 300K).

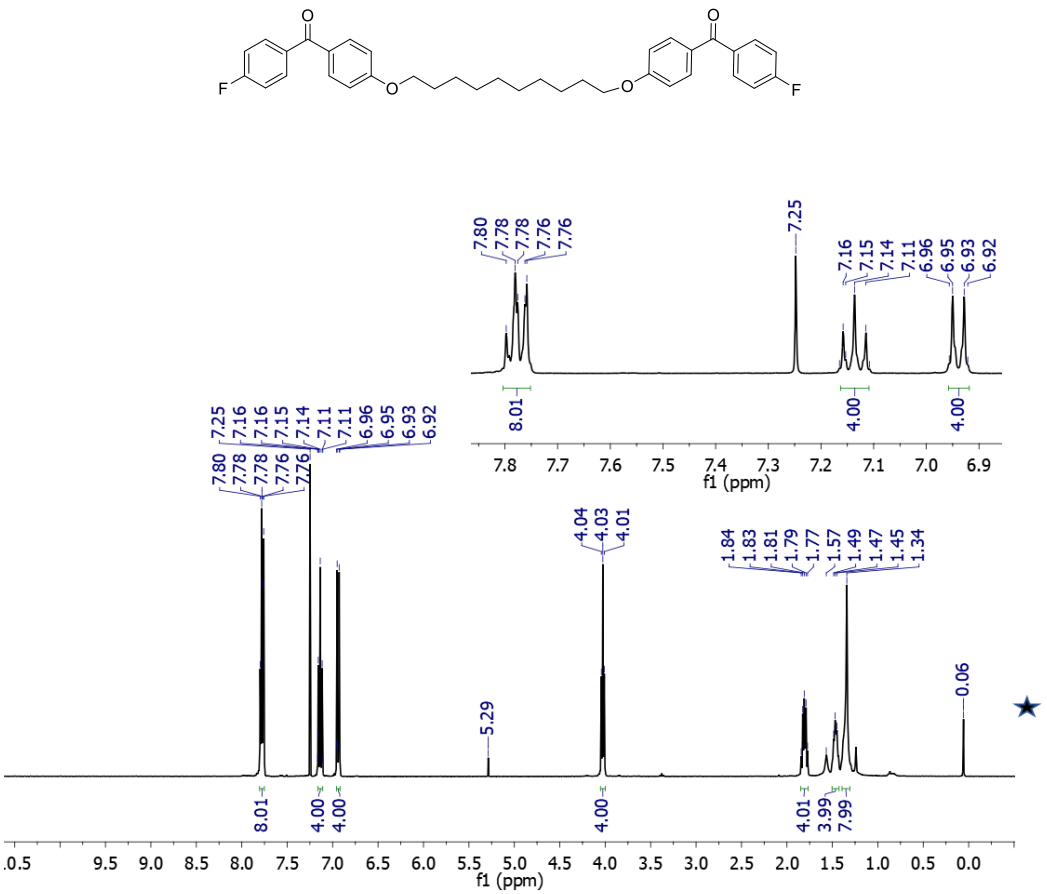


Fig. S22. ^{1}H NMR spectrum of ((decane-1,10-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone) ($CDCl_3$, 400 MHz, 300K).

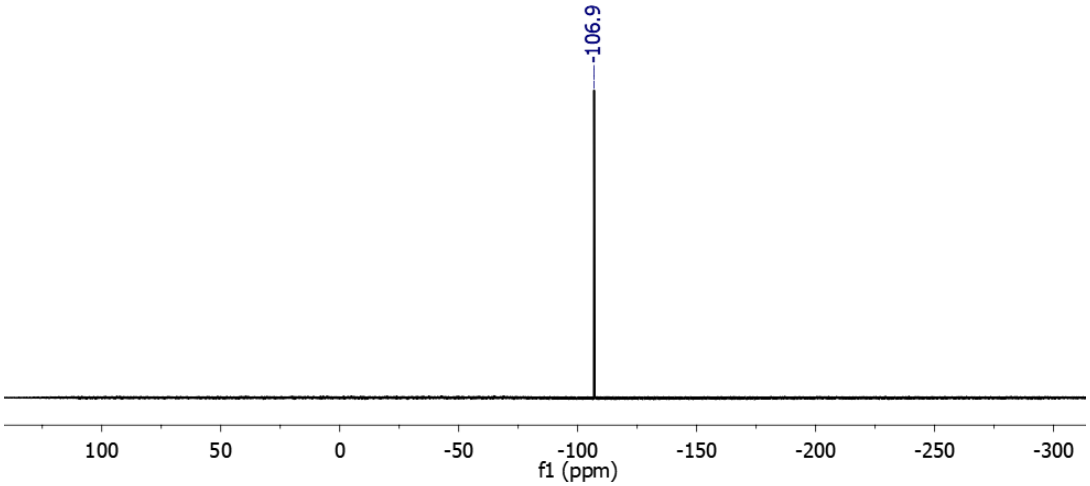


Fig. S23. ^{19}F NMR spectrum of ((decane-1,10-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone) ($CDCl_3$, 376 MHz, 300K).

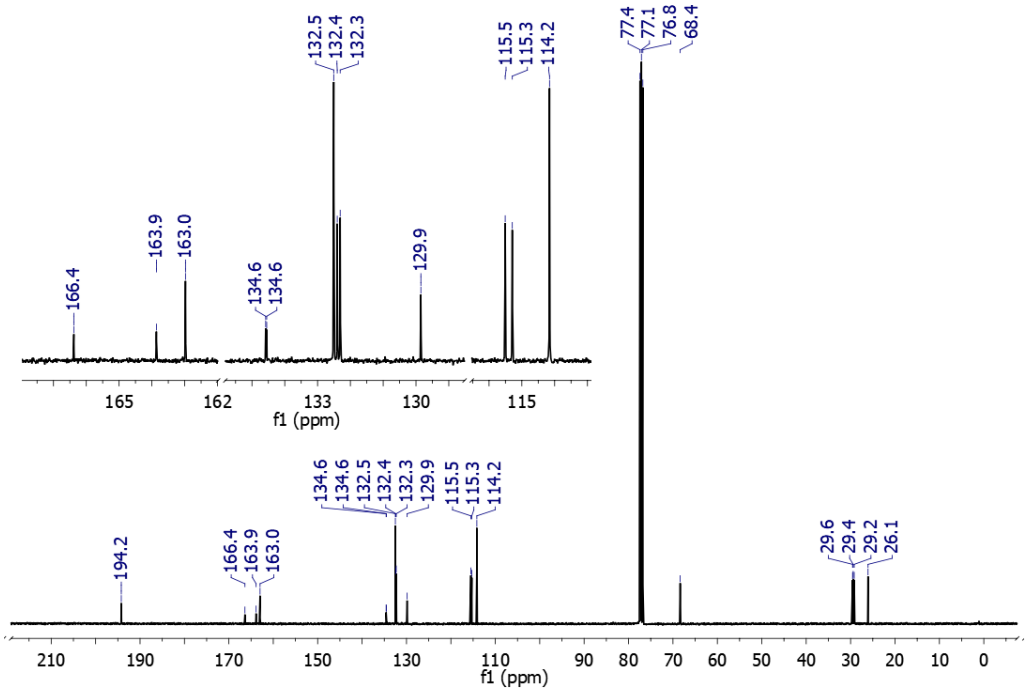


Fig. S24. ^{13}C NMR spectrum of ((decane-1,10-diylbis(oxy))bis(4,1-phenylene))bis((4-fluorophenyl)methanone) ($CDCl_3$, 101 MHz, 300K).

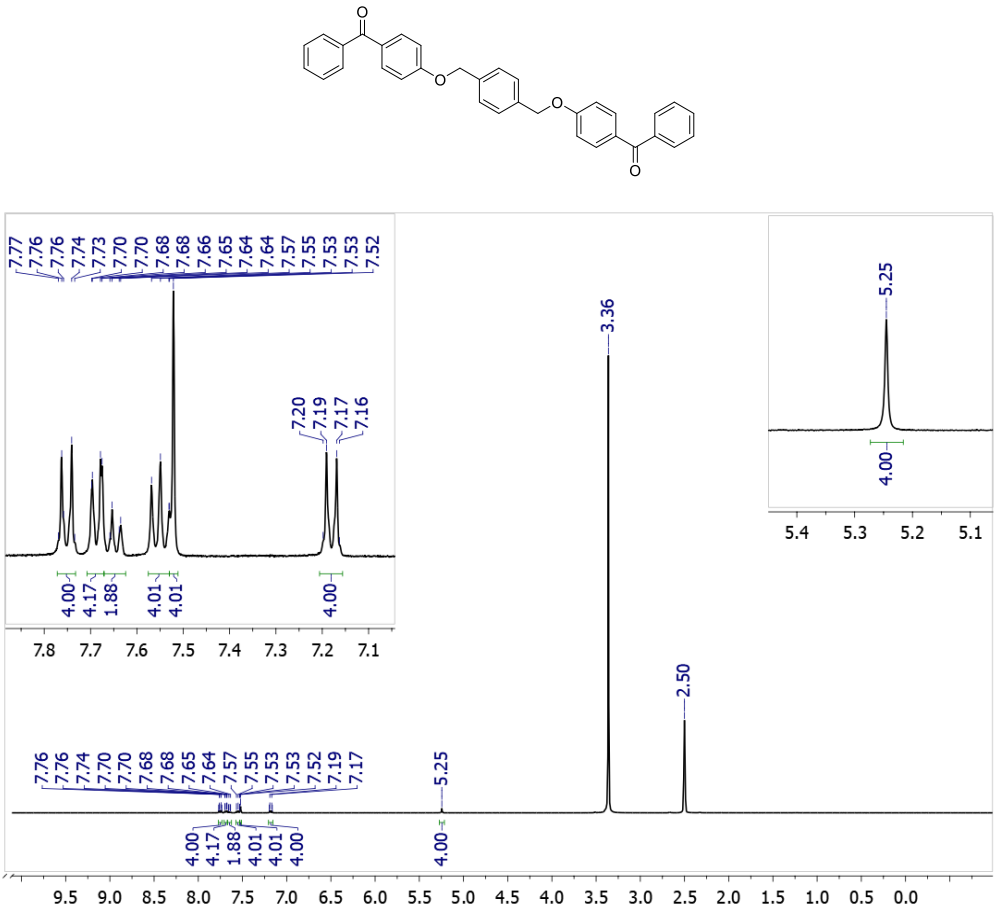


Fig. S25. ^{1}H NMR spectrum of ((1,4-phenylenebis(oxy))bis(4,1-phenylene))bis(phenylmethanone) (DMSO, 400 MHz, 323K). The compound has extremely low solubility.

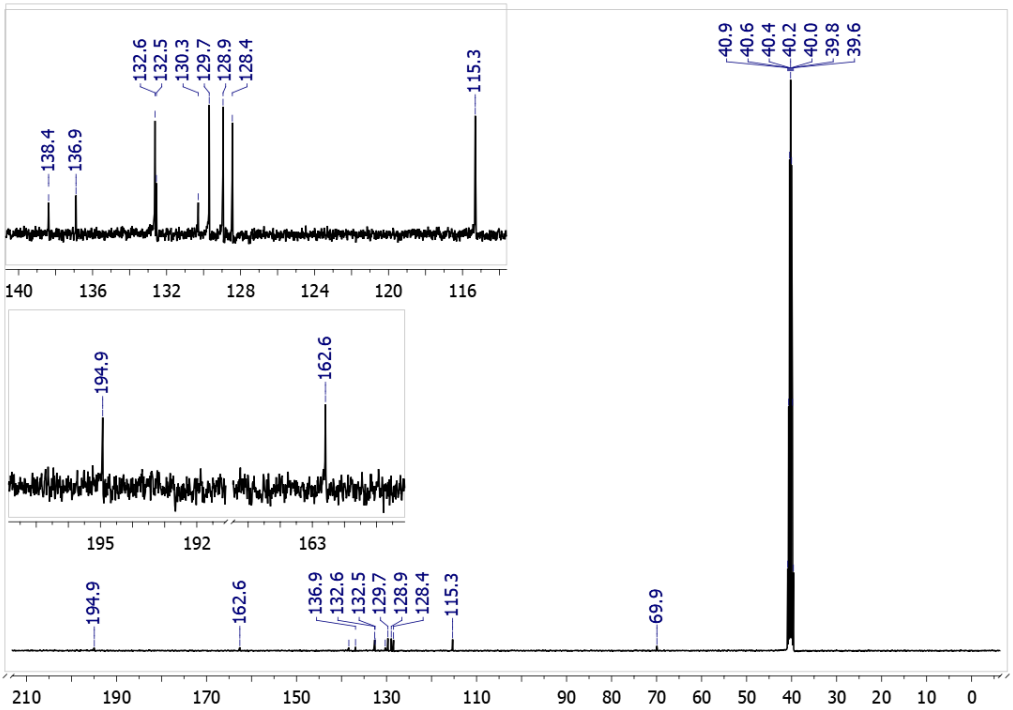


Fig. S26. ^{13}C NMR spectrum of ((1,4-phenylenebis(oxy))bis(4,1-phenylene))bis(phenylmethanone) (DMSO, 101 MHz, 323K). The compound has extremely low solubility.

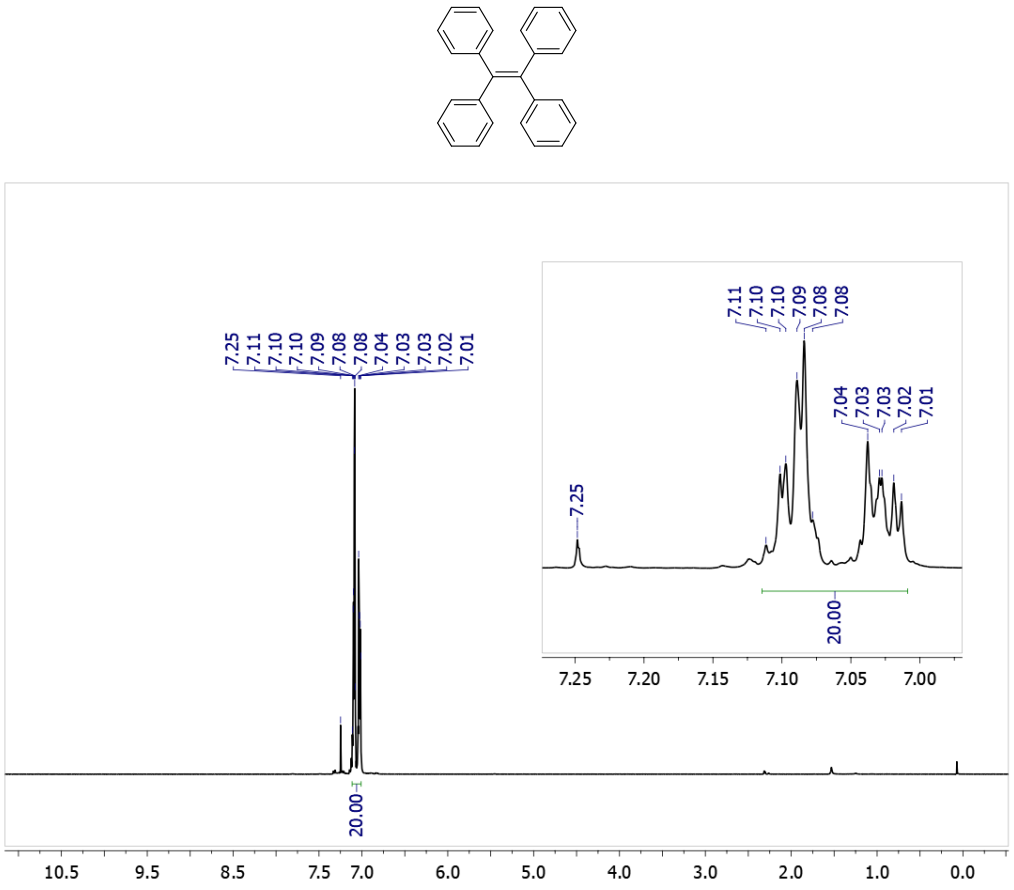


Fig. S27. ^{1}H NMR spectrum of 1,1,2,2-tetraphenylethene ($CDCl_3$, 400 MHz, 300K).

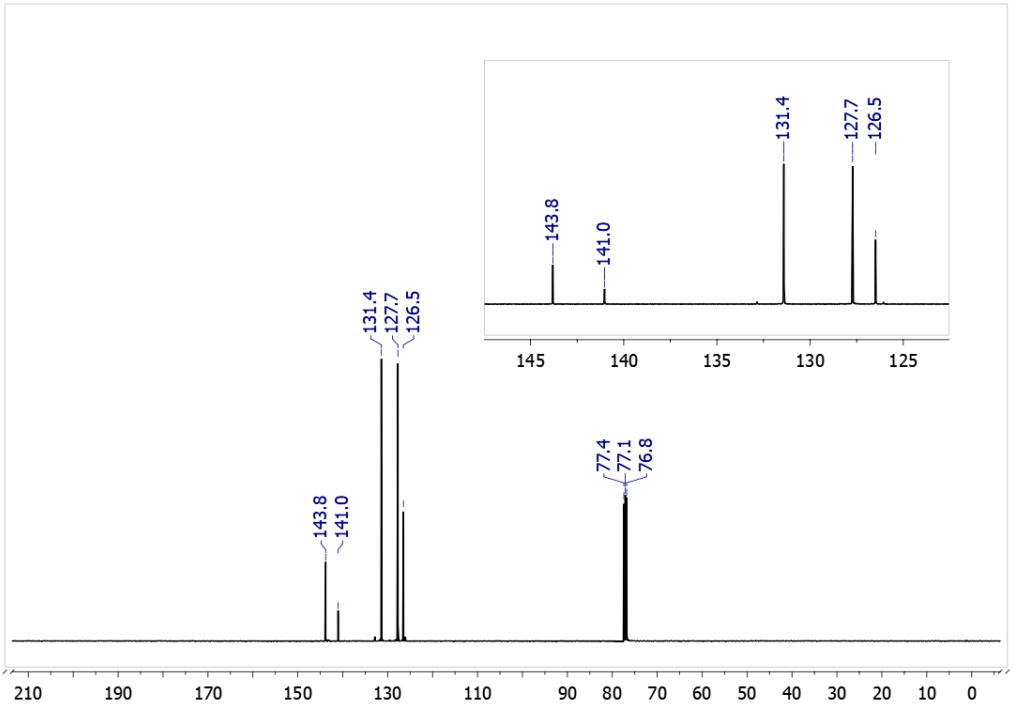


Fig. S28. ^{13}C NMR spectrum of 1,1,2,2-tetraphenylethene ($CDCl_3$, 101 MHz, 300K).

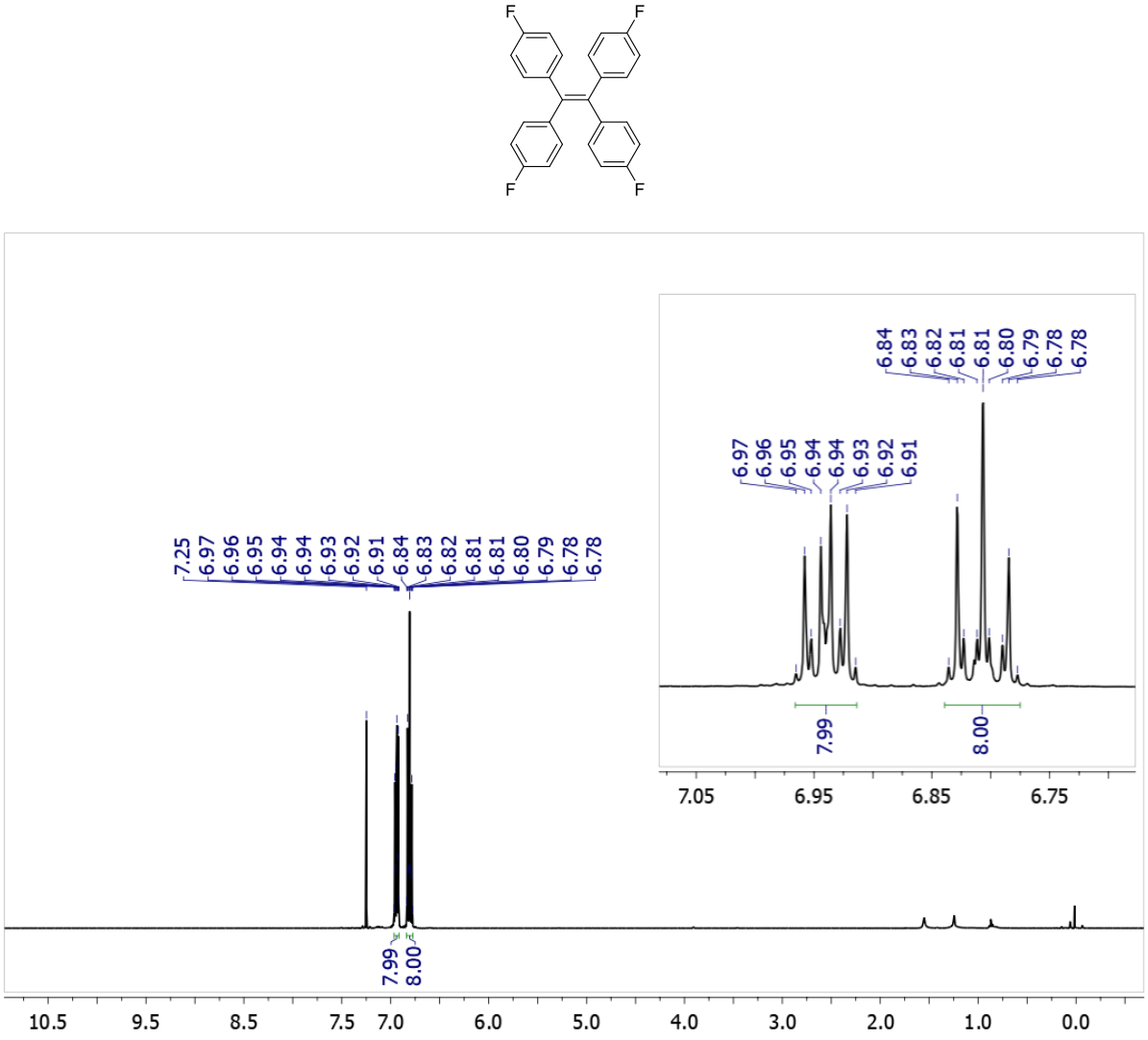


Fig. S29. ^{1}H NMR spectrum of 1,1,2,2-tetrakis(4-fluorophenyl)ethene ($CDCl_3$, 400 MHz, 300K).

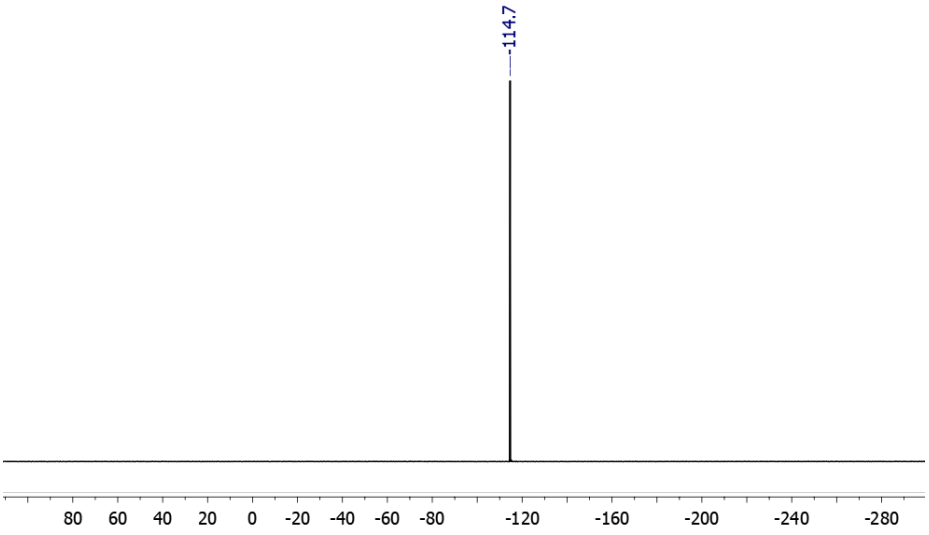


Fig. S30. ^{19}F NMR spectrum of 1,1,2,2-tetrakis(4-fluorophenyl)ethene ($CDCl_3$, 376 MHz, 300K).

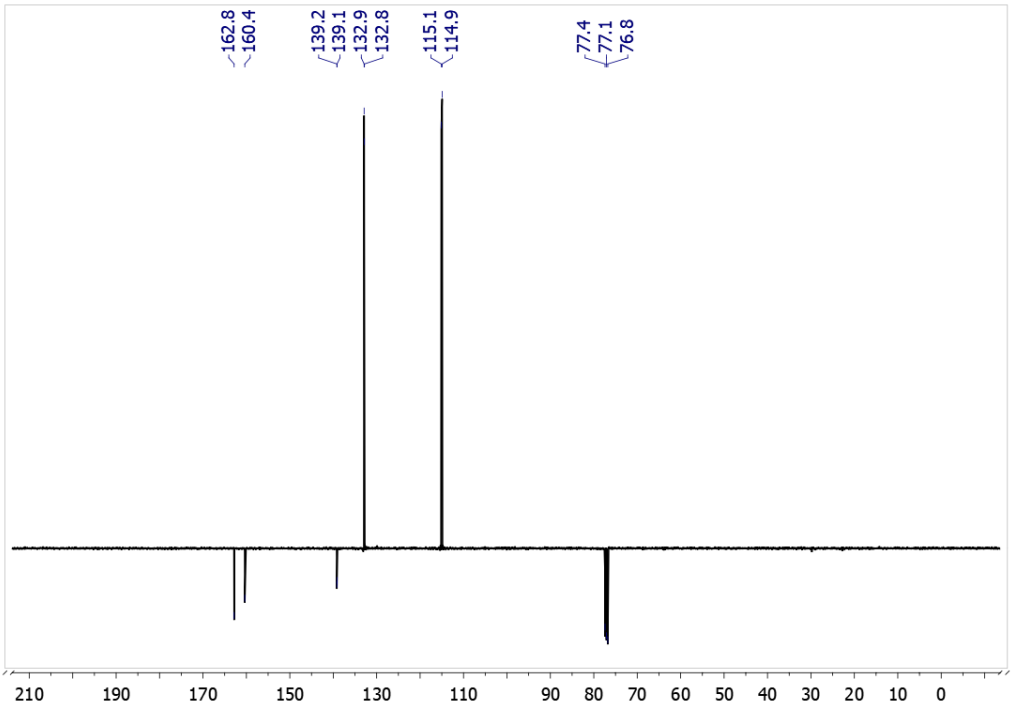


Fig. S31. ^{13}C APT NMR spectrum of 1,1,2,2-tetrakis(4-fluorophenyl)ethene ($CDCl_3$, 101 MHz, 300K).

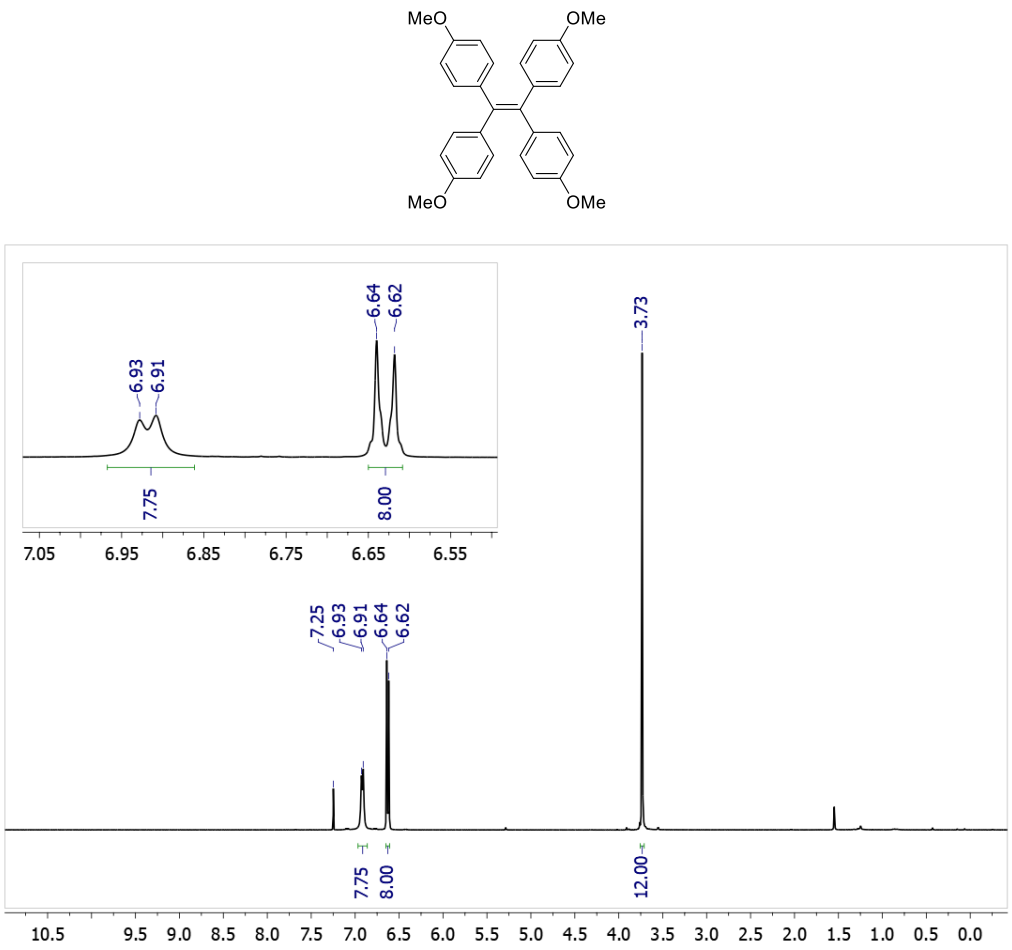


Fig. S32. ^{1}H NMR spectrum of 1,1,2,2-tetrakis(4-methoxyphenyl)ethene ($CDCl_3$, 400 MHz, 300K).

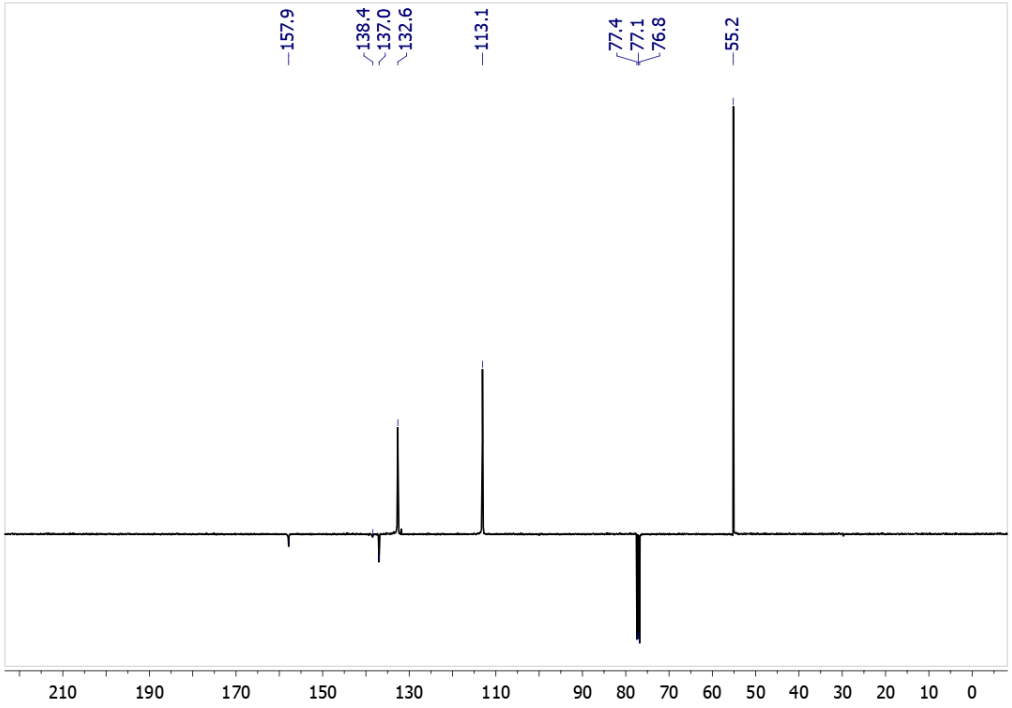


Fig. S33. ^{13}C APT NMR spectrum of 1,1,2,2-tetrakis(4-methoxyphenyl)ethene ($CDCl_3$, 101 MHz, 300K).

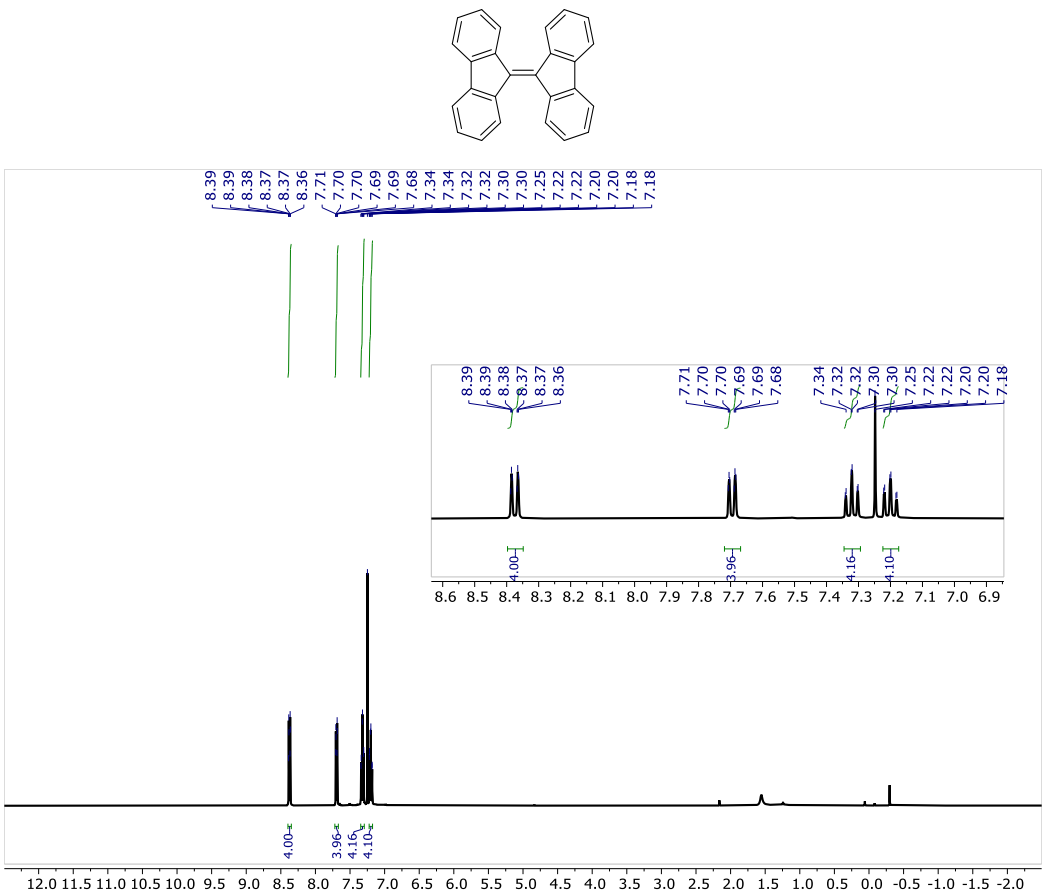


Fig. S34. ^{1}H NMR spectrum of 9,9'-bifluorenylidene ($CDCl_3$, 400 MHz, 300K).

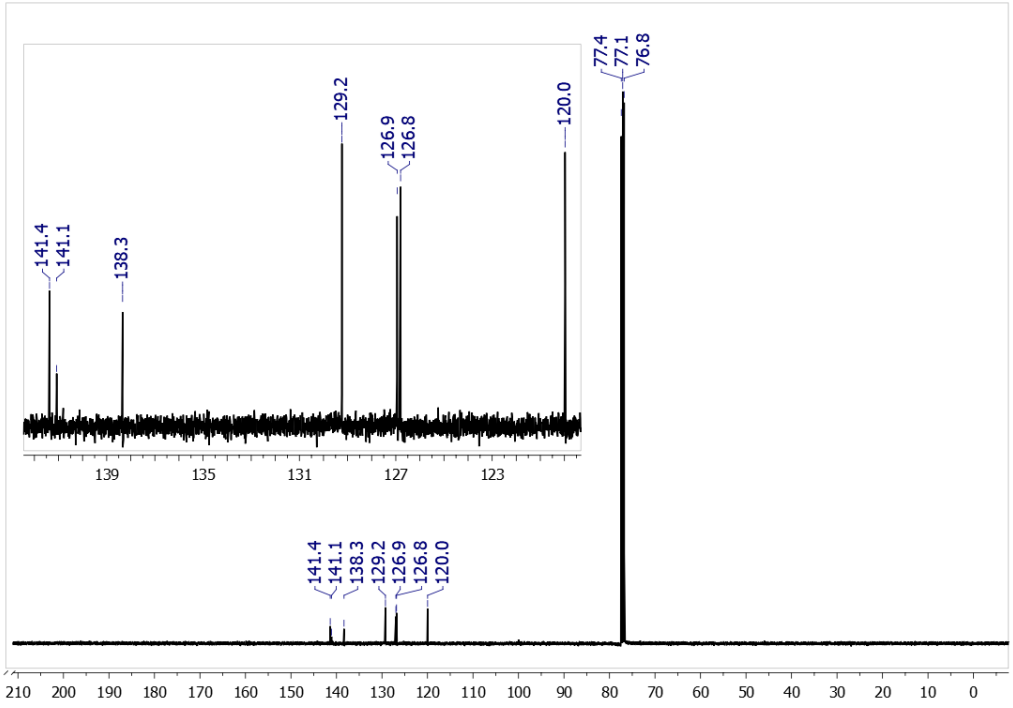


Fig. S35. ^{13}C NMR spectrum of 9,9'-bifluorenylidene ($CDCl_3$, 101 MHz, 300K).

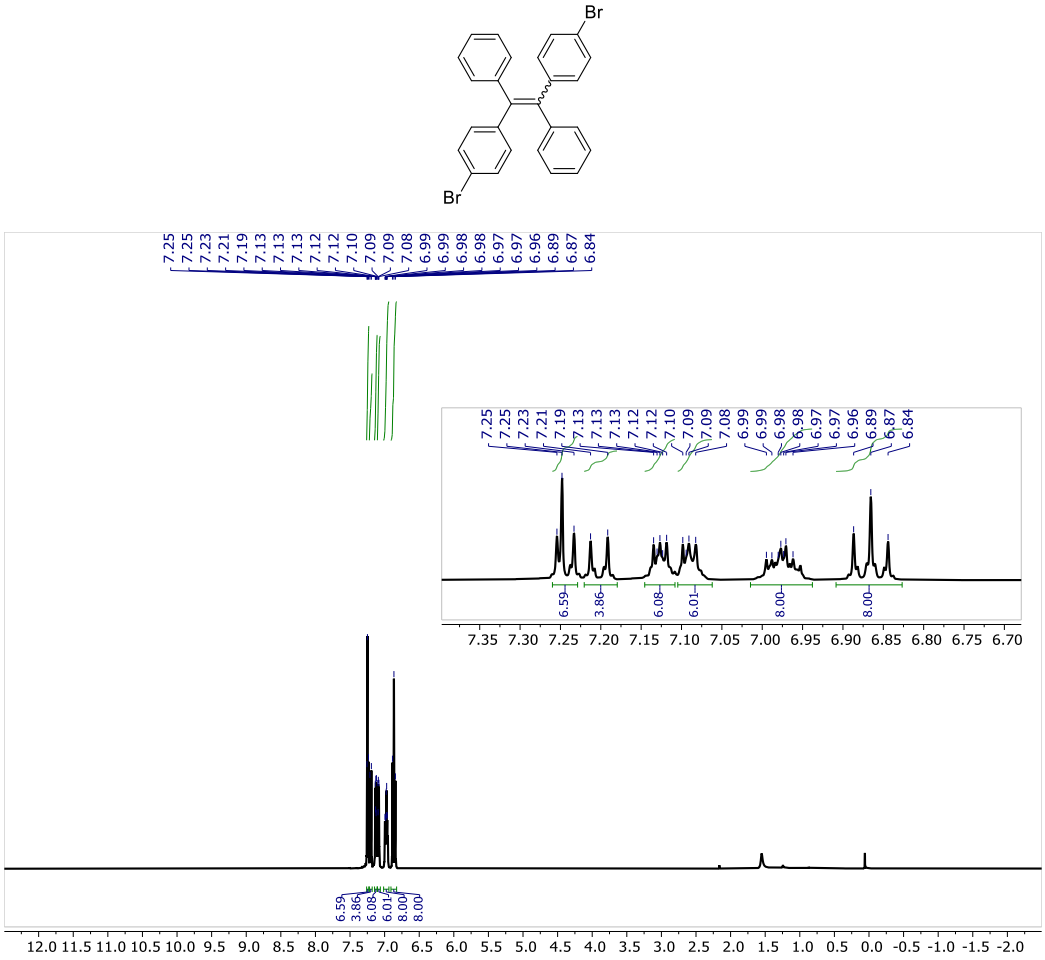


Fig. S36. ^{1}H NMR spectrum of (E - Z) 1,2-bis(4-bromophenyl)-1,2-diphenylethene ($CDCl_3$, 400 MHz, 300K).

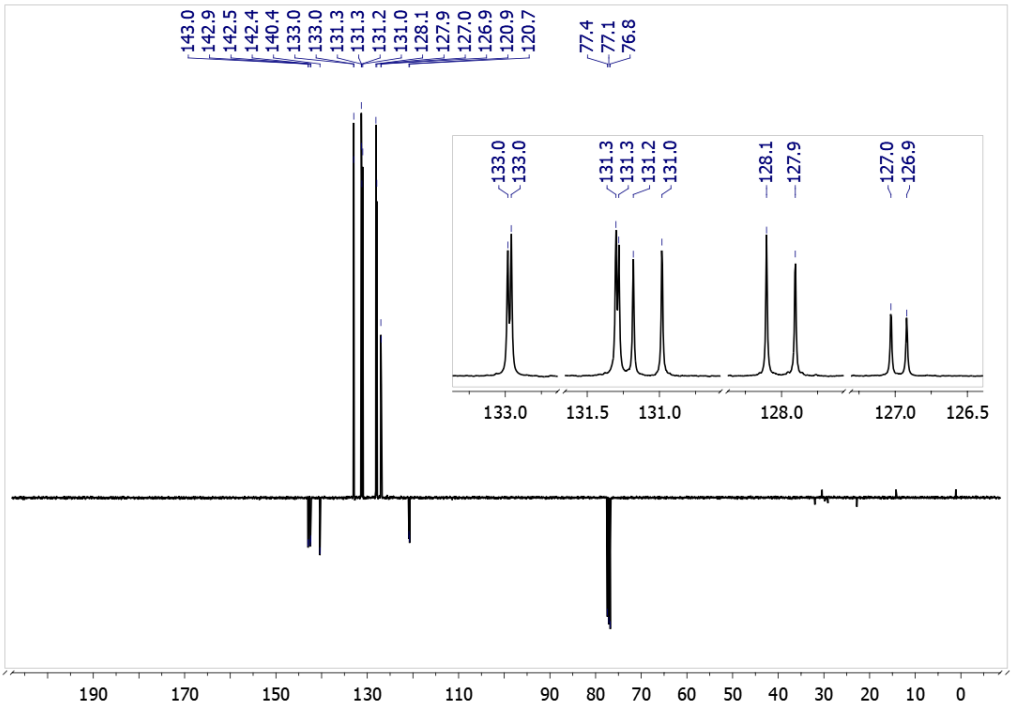


Fig. S37. ^{13}C APT NMR spectrum of (E - Z) 1,2-bis(4-bromophenyl)-1,2-diphenylethene ($CDCl_3$, 101 MHz, 300K).

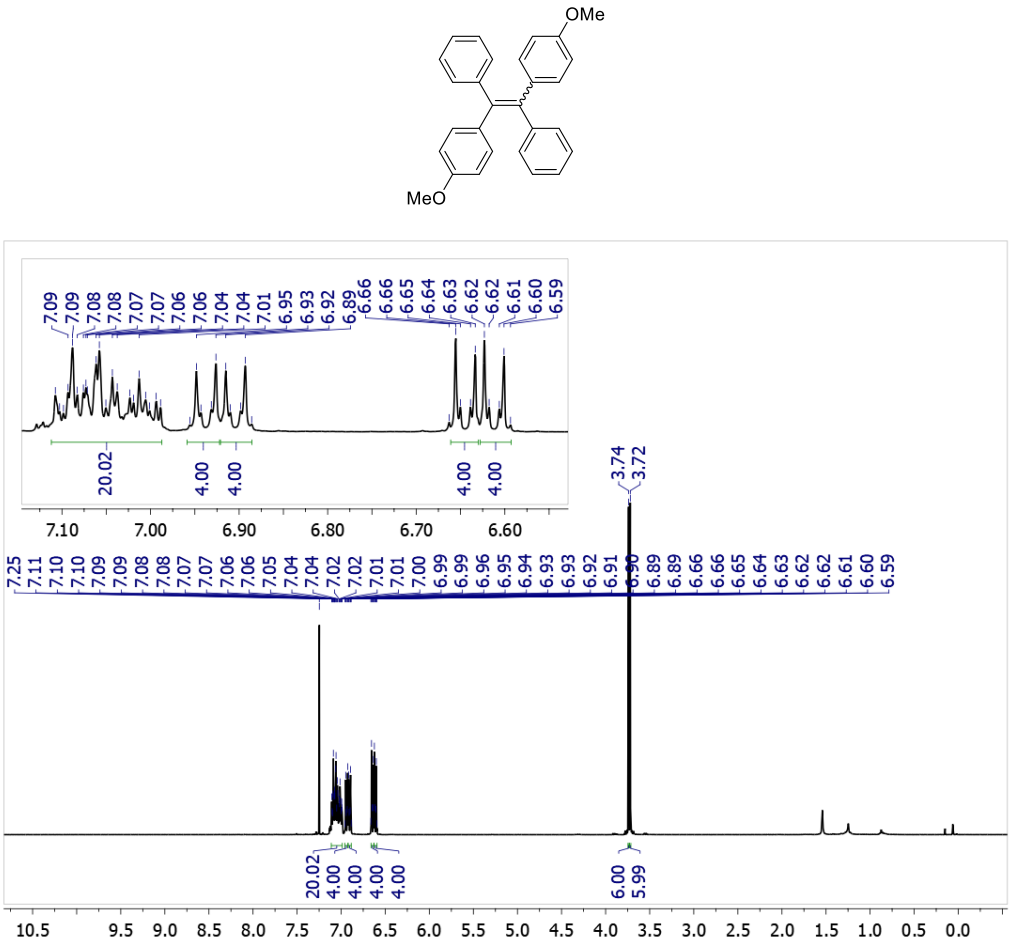


Fig. S 38. ^{1}H NMR spectrum of (E - Z) 1,2-bis(4-methoxyphenyl)-1,2-diphenylethene ($CDCl_3$, 400 MHz, 300K).

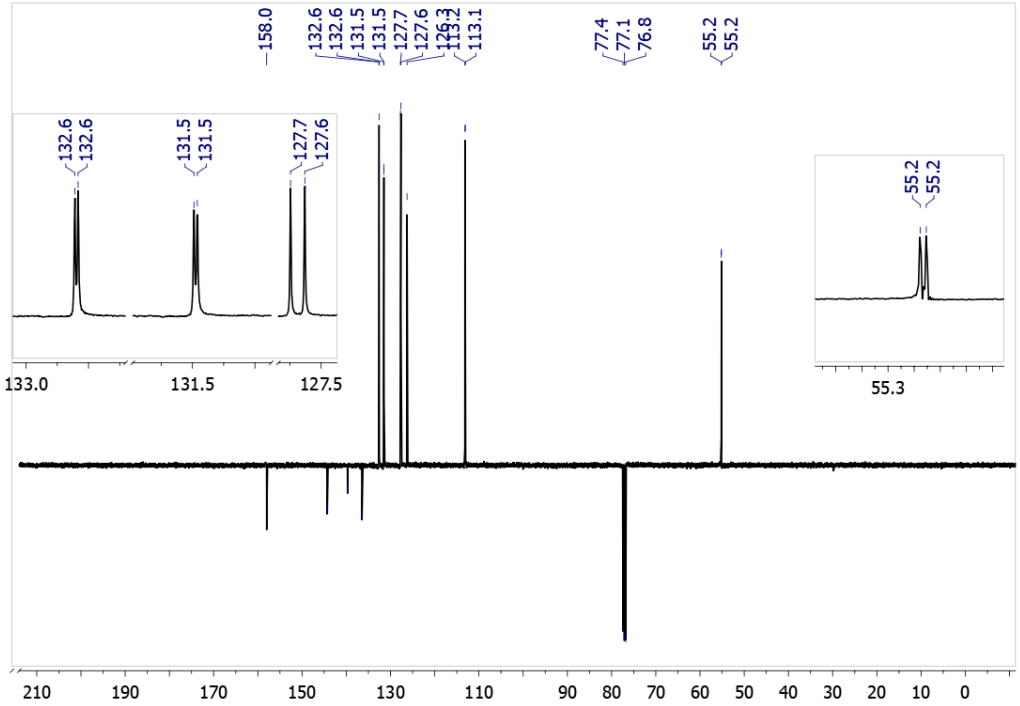


Fig. S39. ^{13}C APT NMR spectrum of (E - Z) 1,2-bis(4-methoxyphenyl)-1,2-diphenylethene ($CDCl_3$, 101 MHz, 300K).

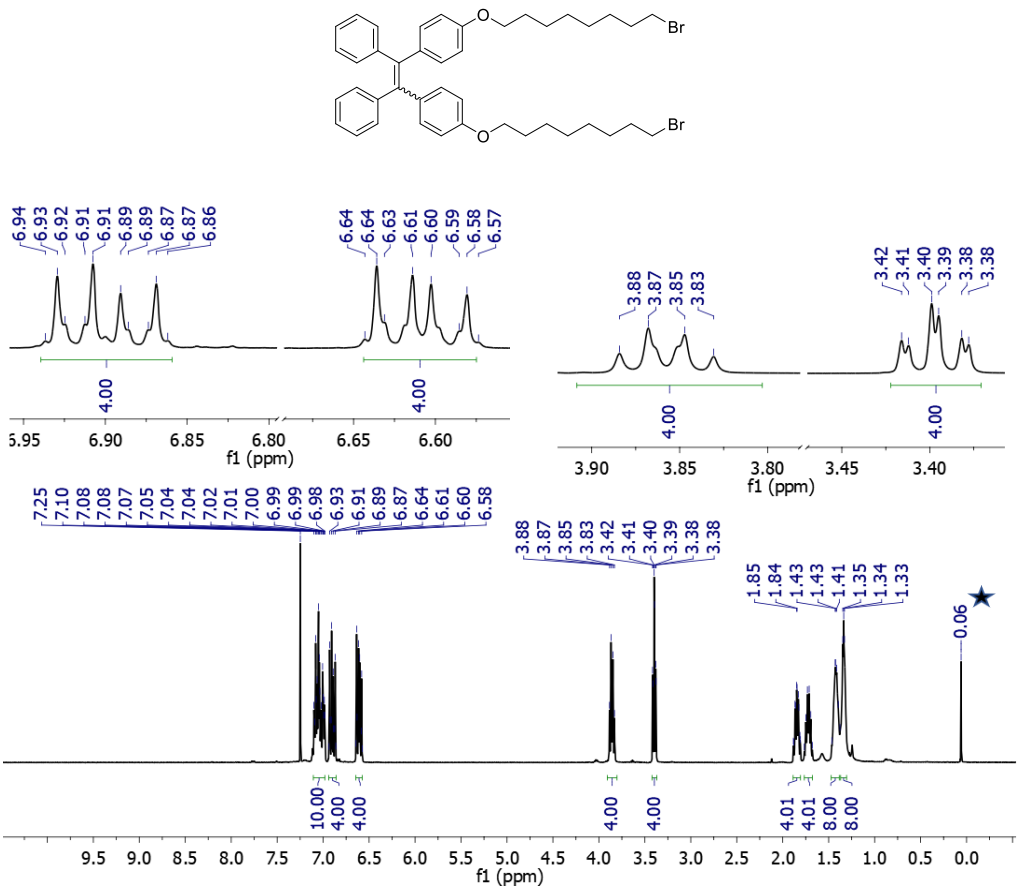


Fig. S 40. ^{1}H NMR spectrum of (E-Z) 1,2-bis(4-((8-bromooctyl)oxy)phenyl)-1,2-diphenylethene ($CDCl_3$, 400 MHz, 300K).

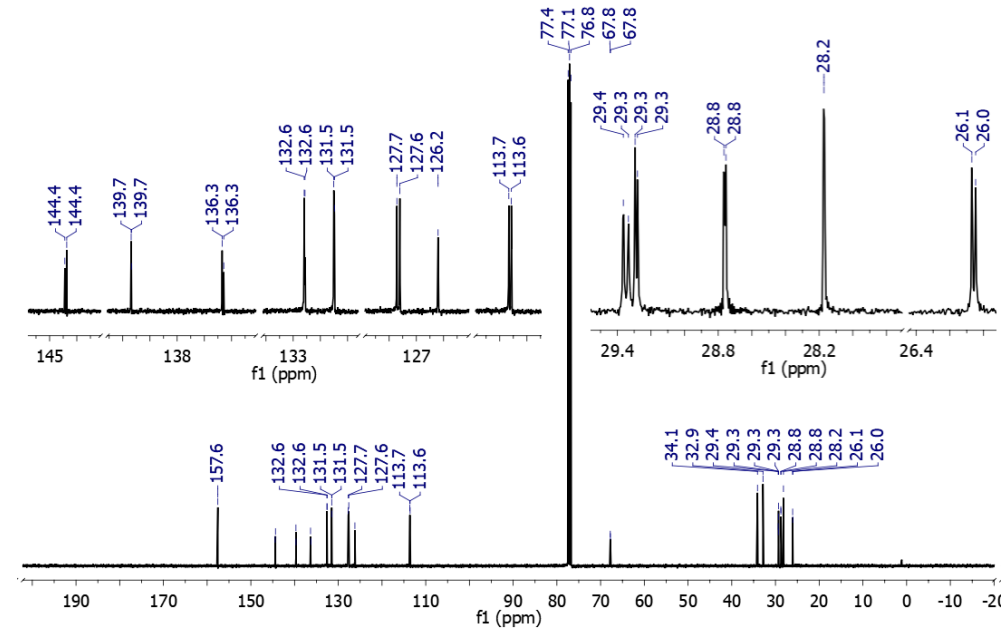


Fig. S41. ^{13}C NMR spectrum of (E-Z) 1,2-bis(4-((8-bromooctyl)oxy)phenyl)-1,2-diphenylethene ($CDCl_3$, 101 MHz, 300K).

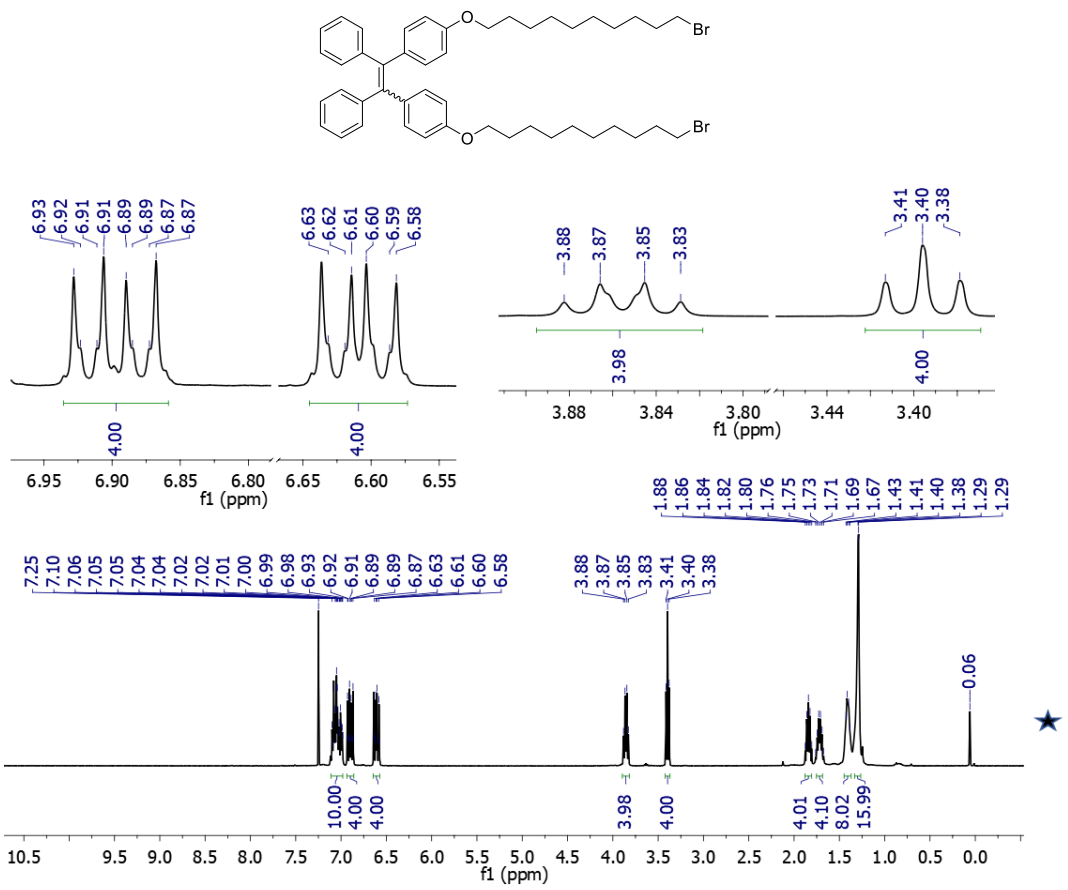


Fig. S42. ^{1}H NMR spectrum of (E-Z) 1,2-bis(4-((10-bromodecyl)oxy)phenyl)-1,2-diphenylethene ($CDCl_3$, 400 MHz, 300K).

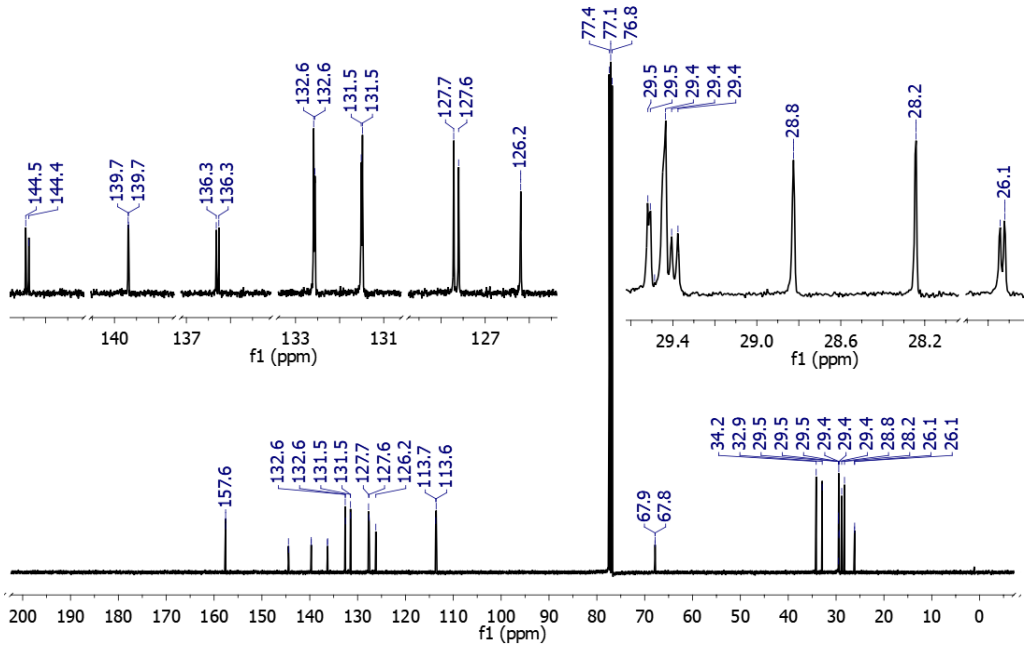


Fig. S43. ^{13}C NMR spectrum of (E-Z) 1,2-bis(4-((10-bromodecyl)oxy)phenyl)-1,2-diphenylethene ($CDCl_3$, 101 MHz, 300K).

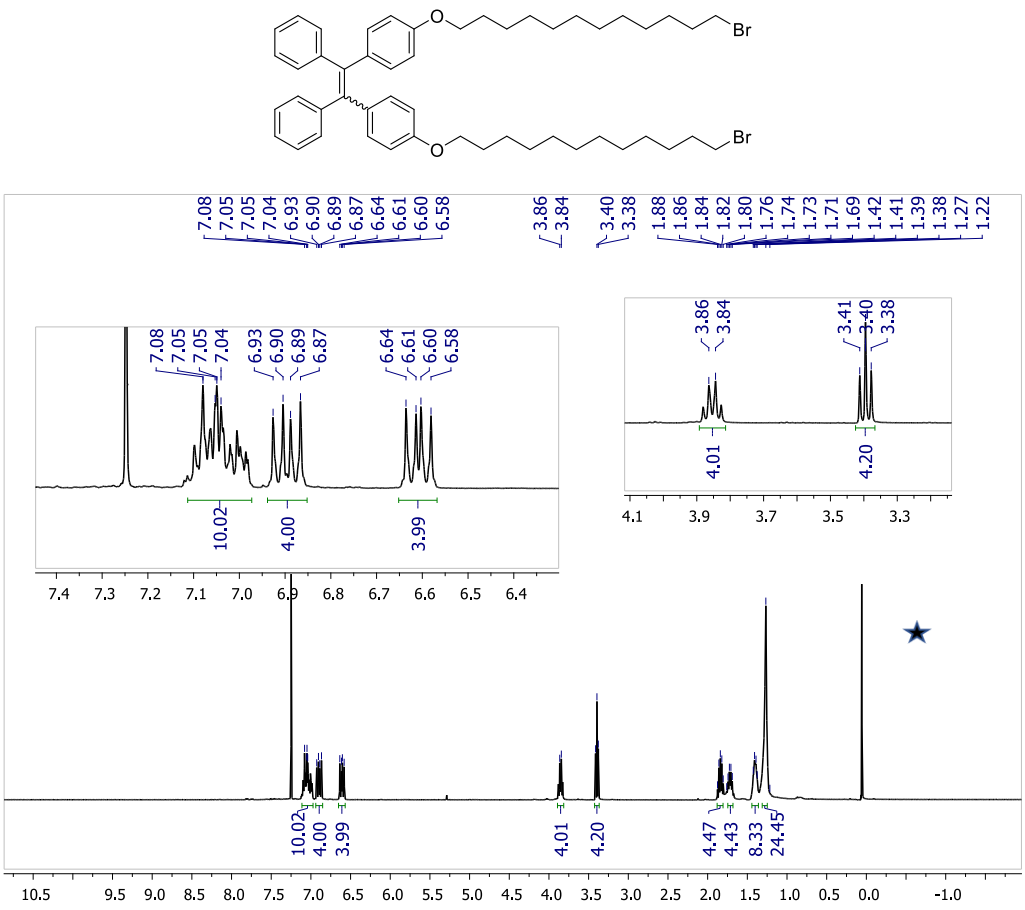


Fig. S 44. ^{1}H NMR spectrum of (E-Z) 1,2-bis(4-((12-bromododecyl)oxy)phenyl)-1,2-diphenylethene ($CDCl_3$, 400 MHz, 300K).

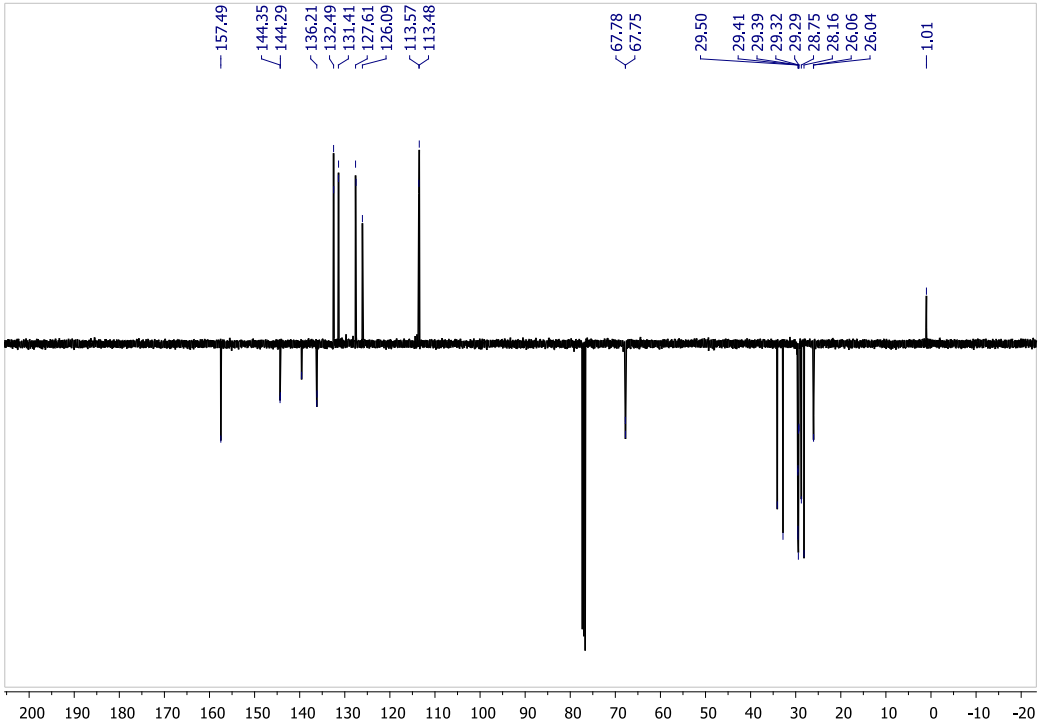


Fig. S45. ^{13}C APT NMR spectrum of (E-Z) 1,2-bis(4-((12-bromododecyl)oxy)phenyl)-1,2-diphenylethene ($CDCl_3$, 100 MHz, 300K).

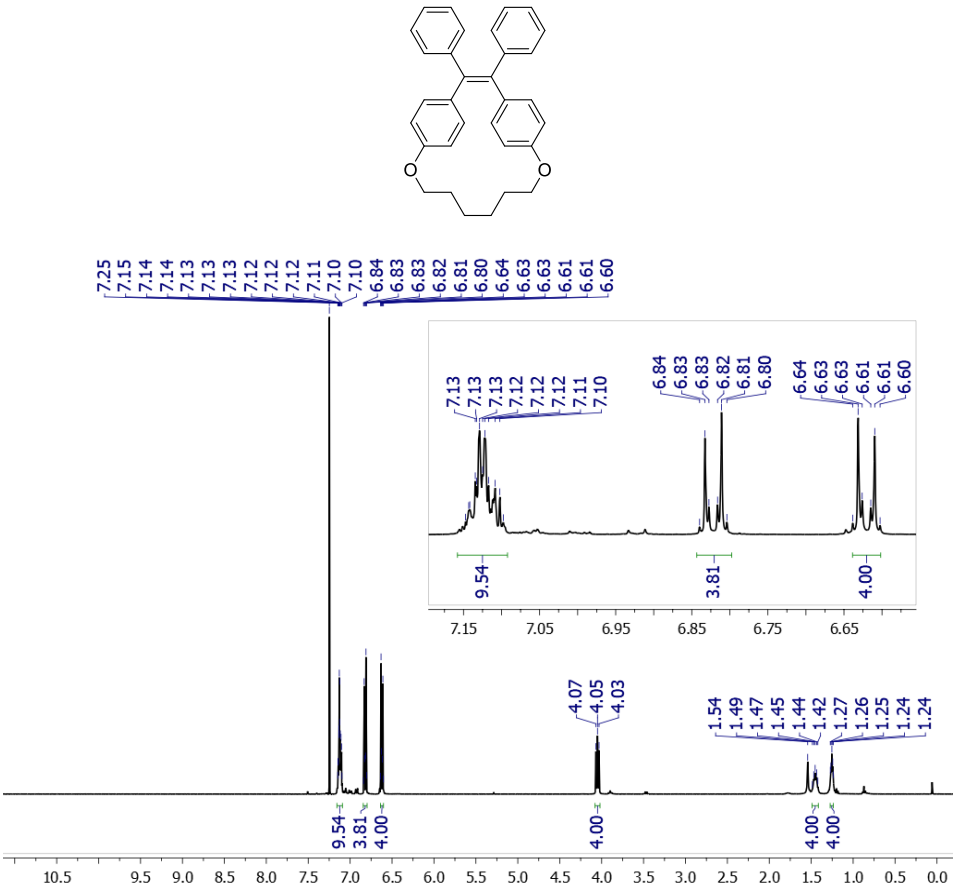


Fig. S46. ^{1}H NMR spectrum of (Z)-2,3-diphenyl-5,12-dioxa-1,4(1,4)-dibenzenacyclododecaphan-2-ene ($CDCl_3$, 400 MHz, 300K).

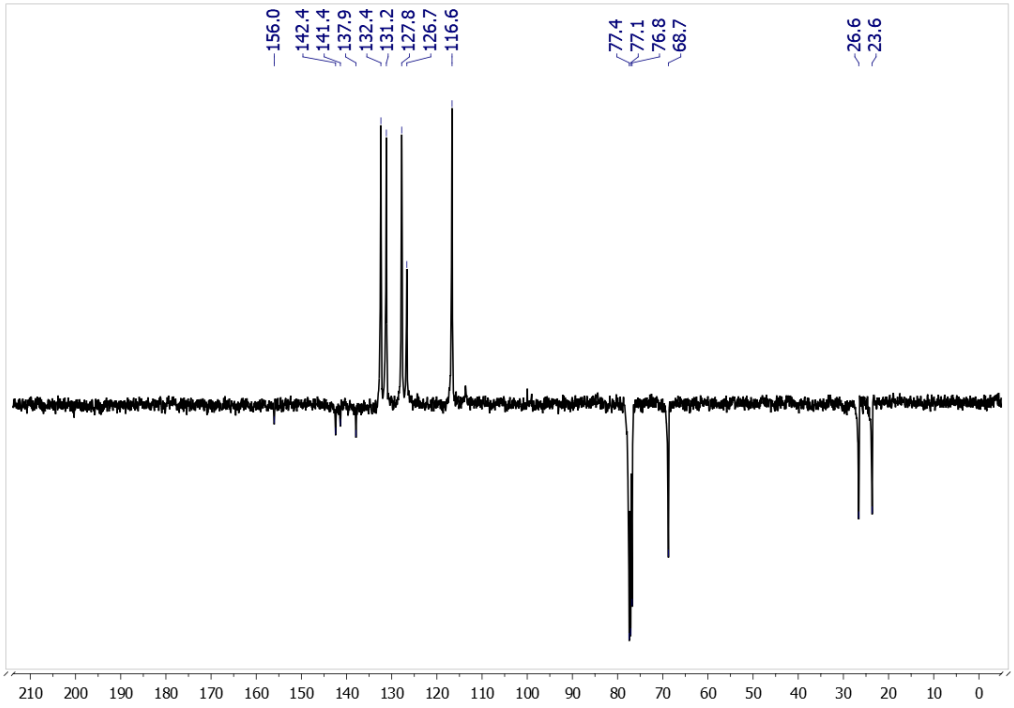


Fig. S47. ^{13}C APT NMR spectrum of (Z)-2,3-diphenyl-5,12-dioxa-1,4(1,4)-dibenzenacyclododecaphan-2-ene ($CDCl_3$, 101 MHz, 300K).

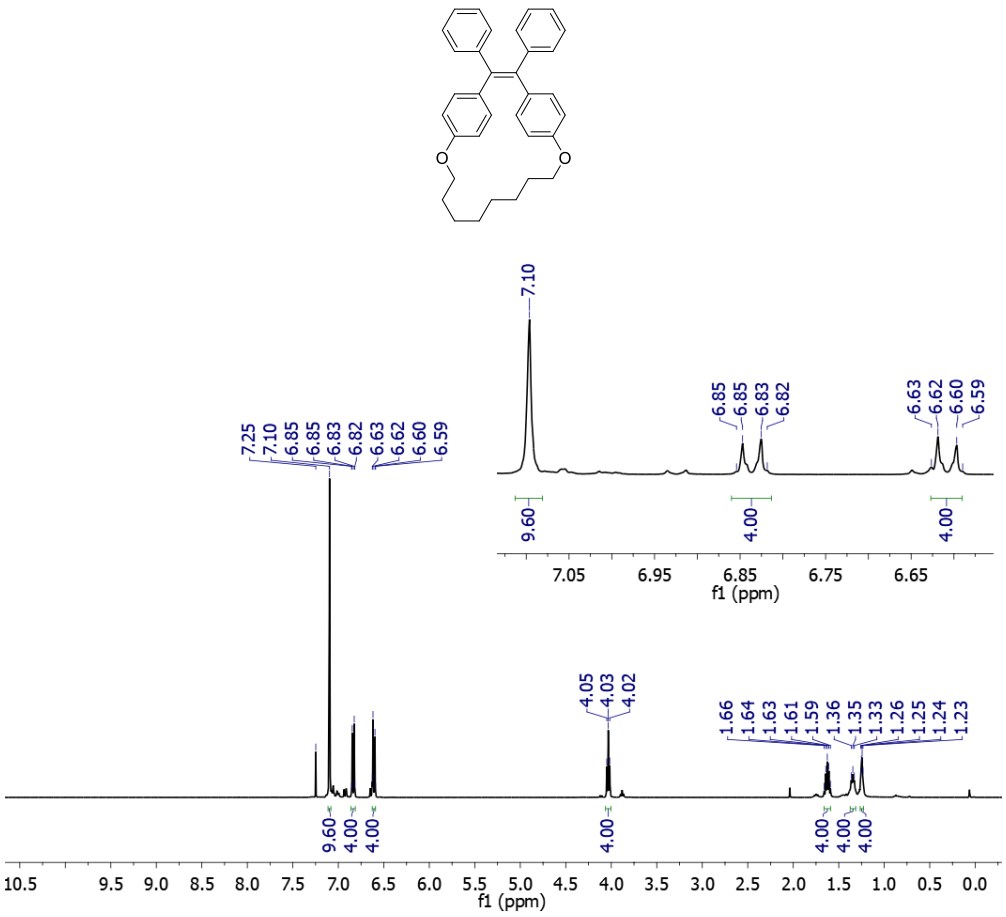


Fig. S48. ^{1}H NMR spectrum of (Z)-2,3-diphenyl-5,14-dioxa-1,4(1,4)-dibenzenacyclotetradecaphan-2-ene ($CDCl_3$, 400 MHz, 300K).

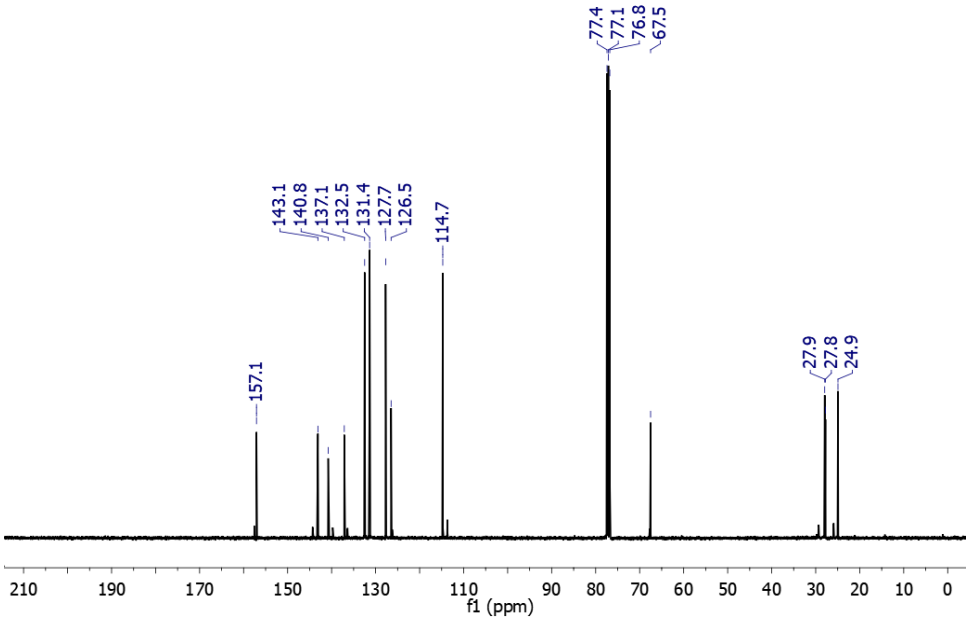


Fig. S49. ^{13}C NMR spectrum of (Z)-2,3-diphenyl-5,14-dioxa-1,4(1,4)-dibenzenacyclotetradecaphan-2-ene ($CDCl_3$, 101 MHz, 300K).

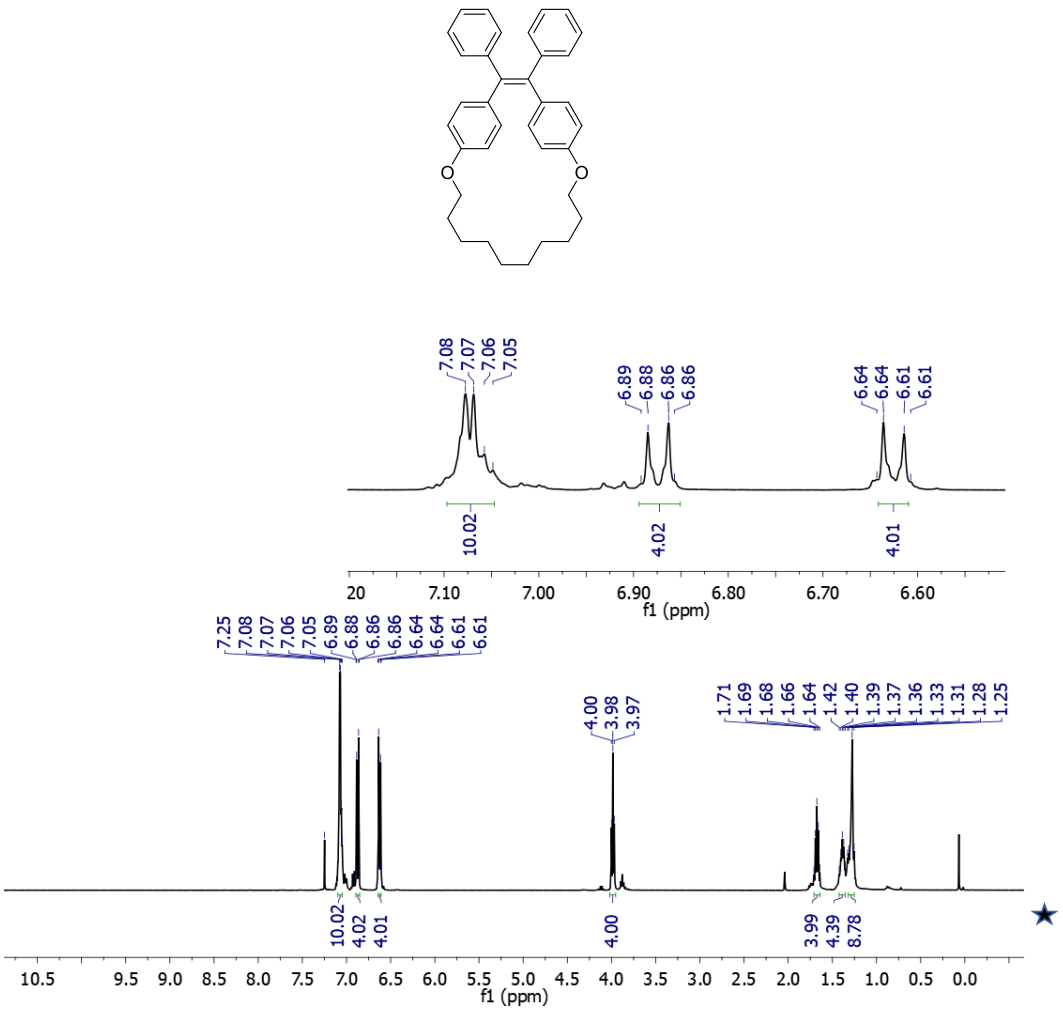


Fig. S50. ^{1}H NMR spectrum of (Z)-2,3-diphenyl-5,16-dioxa-1,4(1,4)-dibenzenacyclohexadecaphan-2-ene ($CDCl_3$, 400 MHz, 300K).

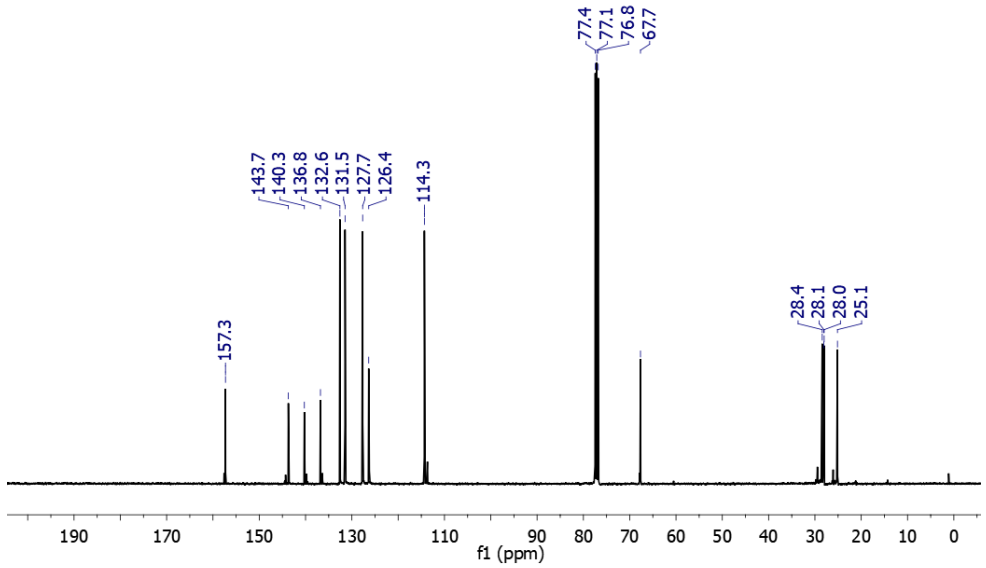


Fig. S51. ^{13}C NMR spectrum of (Z)-2,3-diphenyl-5,16-dioxa-1,4(1,4)-dibenzenacyclohexadecaphan-2-ene ($CDCl_3$, 101 MHz, 300K).

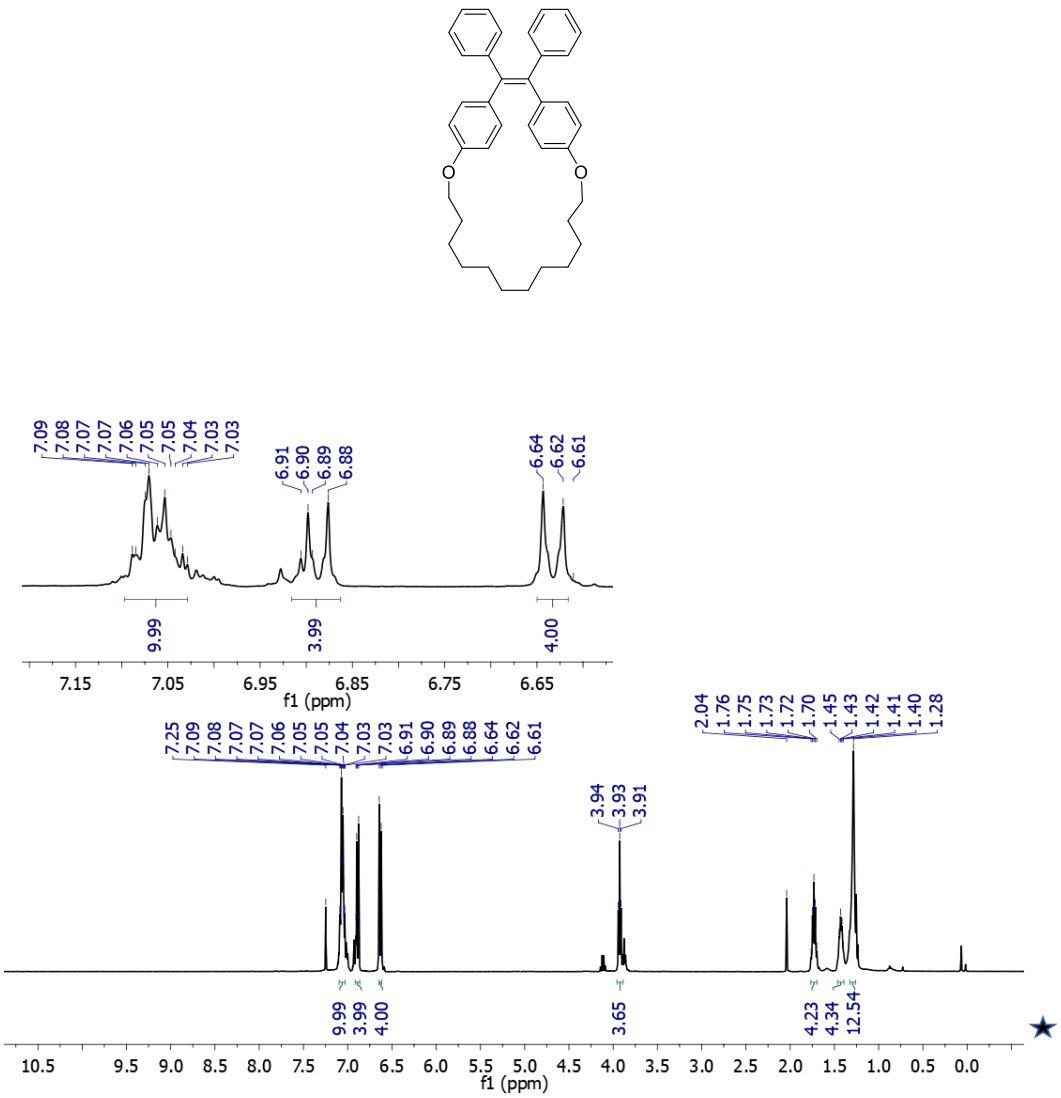


Fig. S52. ^{1}H NMR spectrum of (Z)-2,3-diphenyl-5,18-dioxa-1,4(1,4)-dibenzenacyclooctadecaphan-2-ene ($CDCl_3$, 400 MHz, 300K).

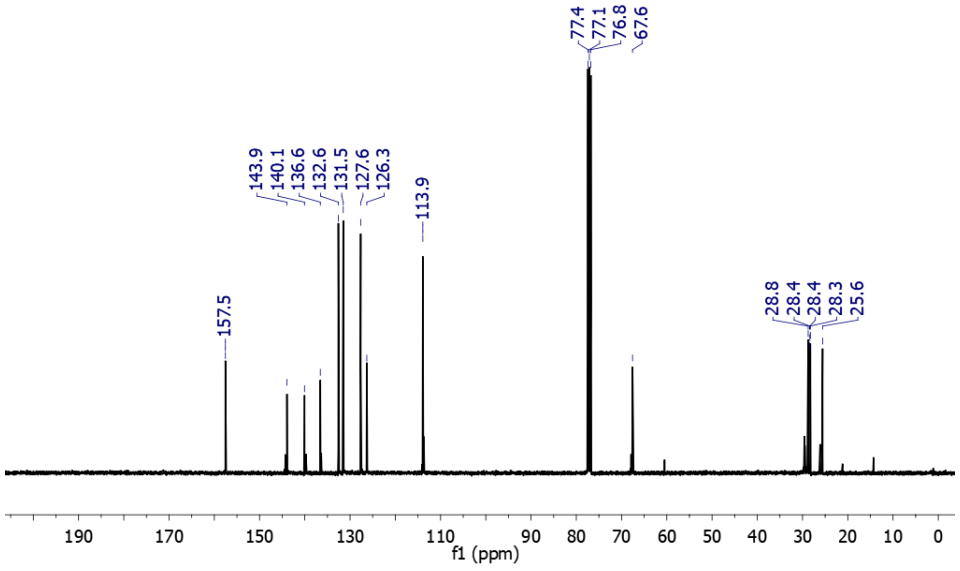


Fig. S53. ^{13}C NMR spectrum of (Z)-2,3-diphenyl-5,18-dioxa-1,4(1,4)-dibenzenacyclooctadecaphan-2-ene ($CDCl_3$, 101 MHz, 300K).

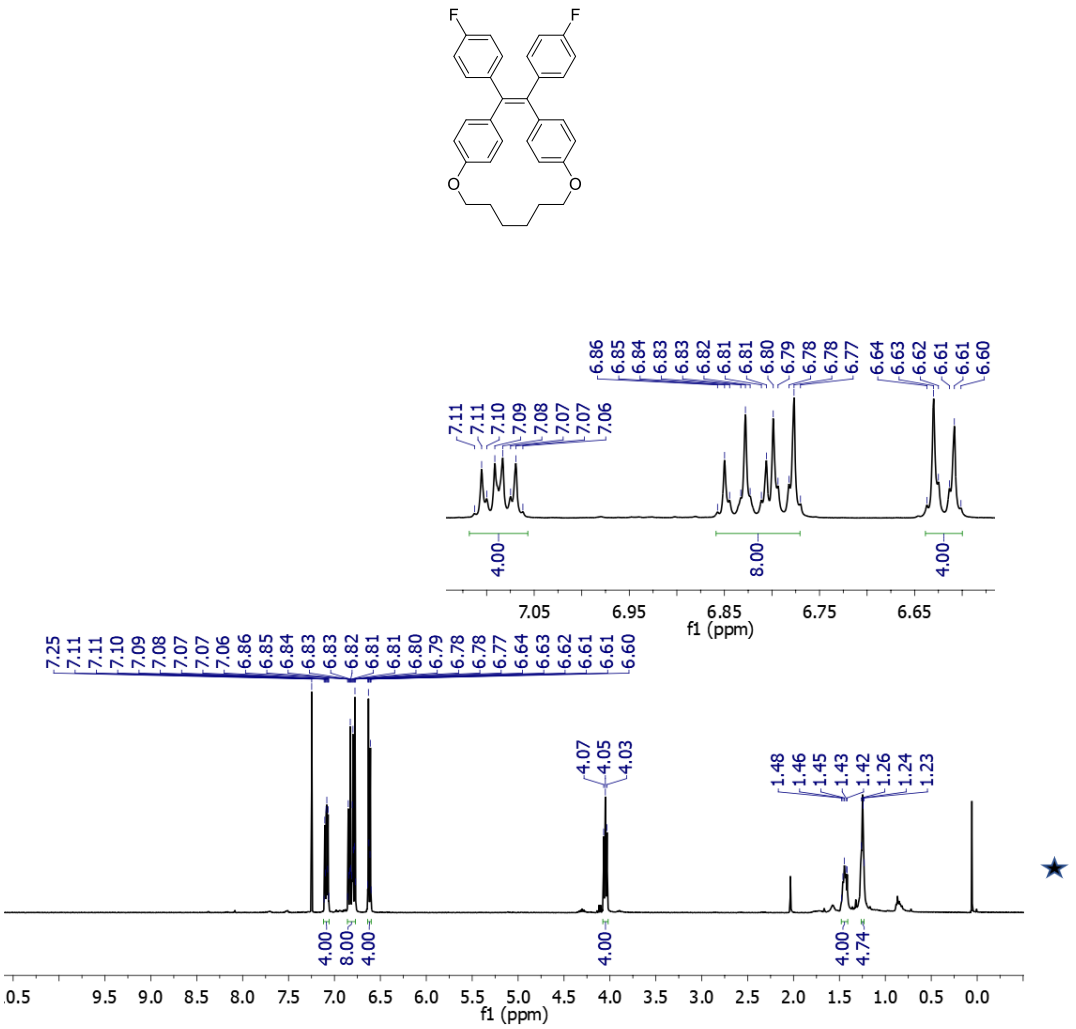


Fig. S54. ^{1}H NMR spectrum of (Z)-2,3-bis(4-fluorophenyl)-5,12-dioxa-1,4(1,4)-dibenzenacyclododecaphan-2-ene ($CDCl_3$, 400 MHz, 300K).

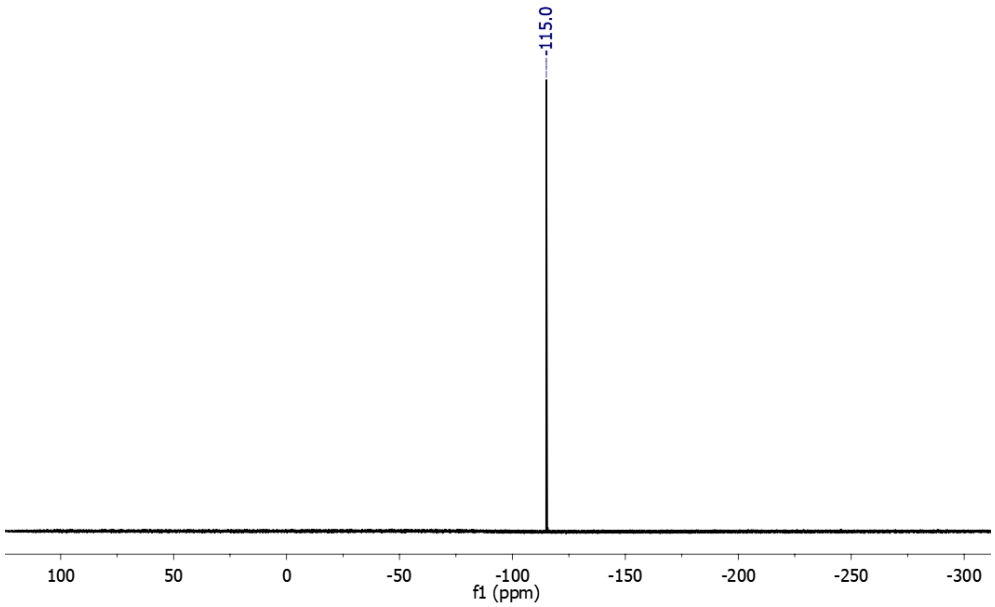


Fig. S55. ^{19}F NMR spectrum of (Z)-2,3-bis(4-fluorophenyl)-5,12-dioxa-1,4(1,4)-dibenzenacyclododecaphan-2-ene ($CDCl_3$, 376 MHz, 300K).

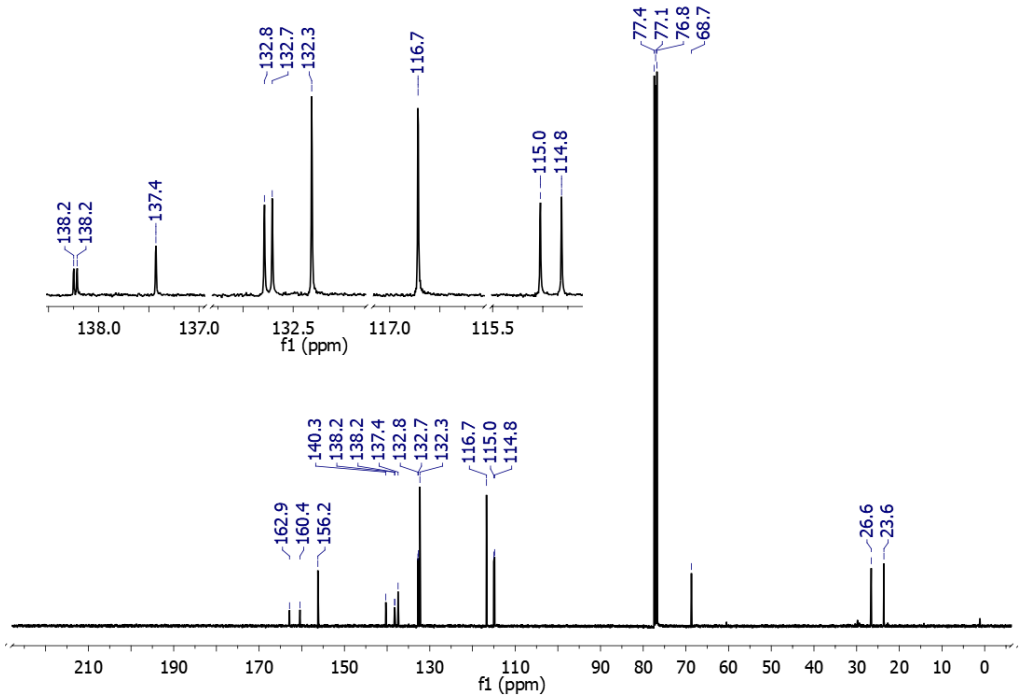


Fig. S56. ^{13}C NMR spectrum of (Z)-2,3-bis(4-fluorophenyl)-5,12-dioxa-1,4(1,4)-dibenzenacyclododecaphan-2-ene ($CDCl_3$, 101 MHz, 300K).

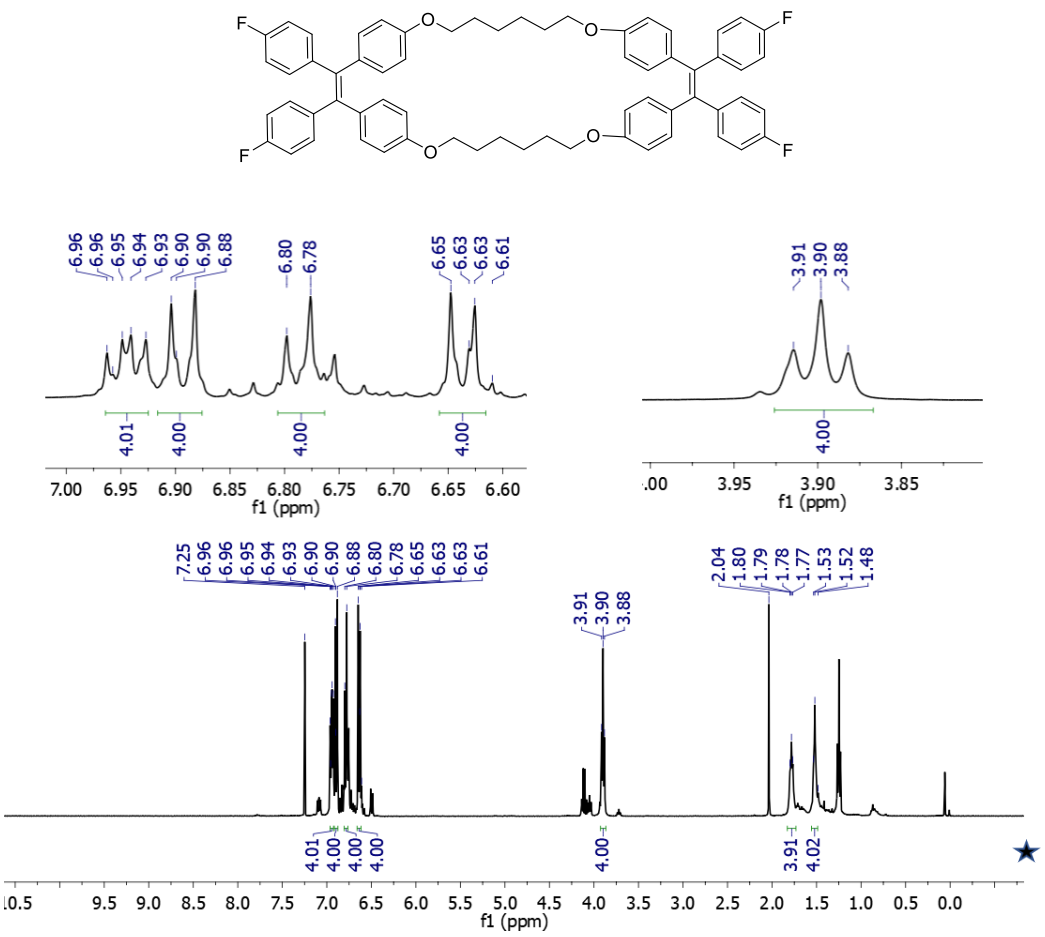


Fig. S57. ^{1}H NMR spectrum of (2Z,14Z)-2,3,14,15-tetrakis(4-fluorophenyl)-5,12,17,24-tetraoxa-1,4,13,16(1,4)-tetrabenzenacyclotetracosaphane-2,14-diene ($CDCl_3$, 400 MHz, 300K).

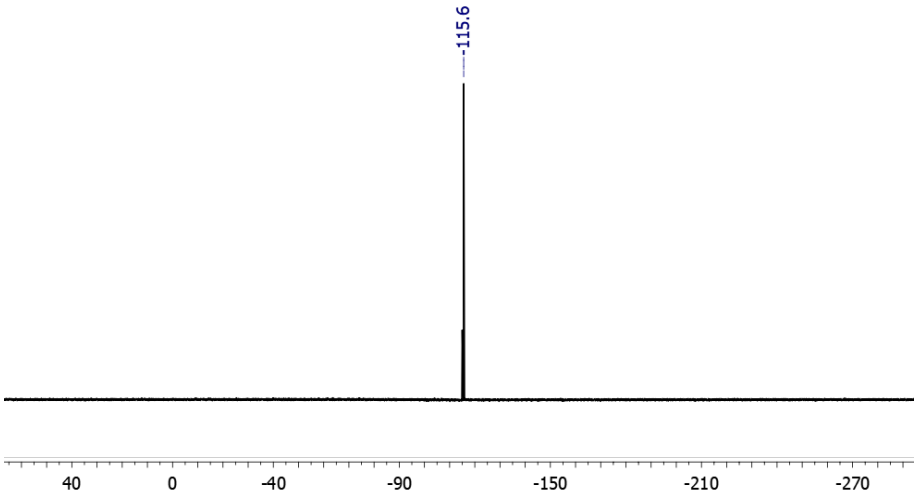


Fig. S58. ^{19}F NMR spectrum of (E)-2,3-bis(4-fluorophenyl)-5,12-dioxa-1,4(1,4)-dibenzenacyclododecaphan-2-ene ($CDCl_3$, 376 MHz, 300K).

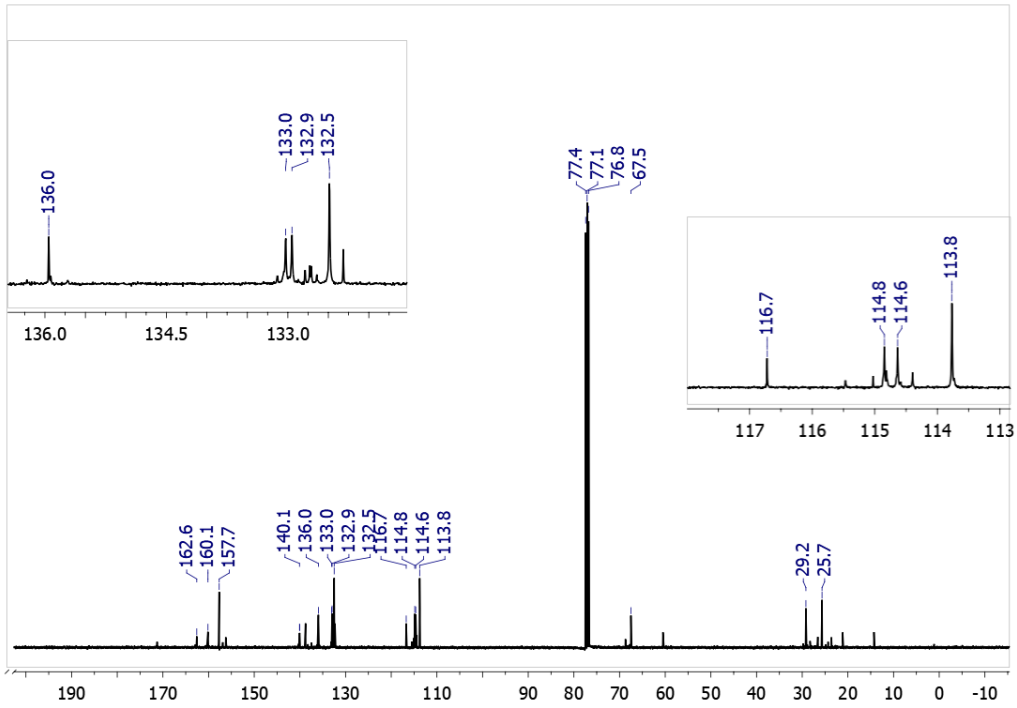


Fig. S59. ^{13}C NMR spectrum of (E)-2,3-bis(4-fluorophenyl)-5,12-dioxa-1,4(1,4)-dibenzenacyclododecaphan-2-ene ($CDCl_3$, 101 MHz, 300K).

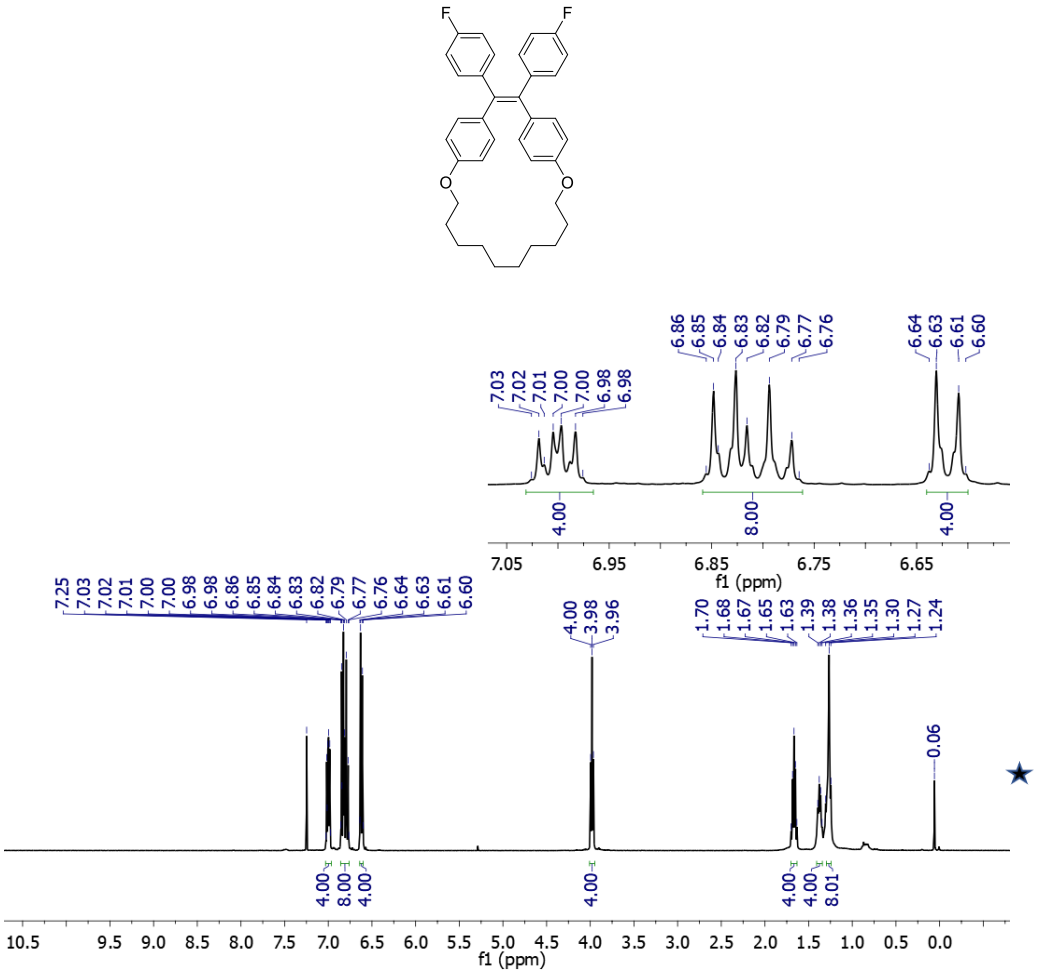


Fig. S60. ^{1}H NMR spectrum of (Z)-2,3-bis(4-fluorophenyl)-5,16-dioxa-1,4(1,4)-dibenzenacyclohexadecaphan-2-ene ($CDCl_3$, 400 MHz, 300K).

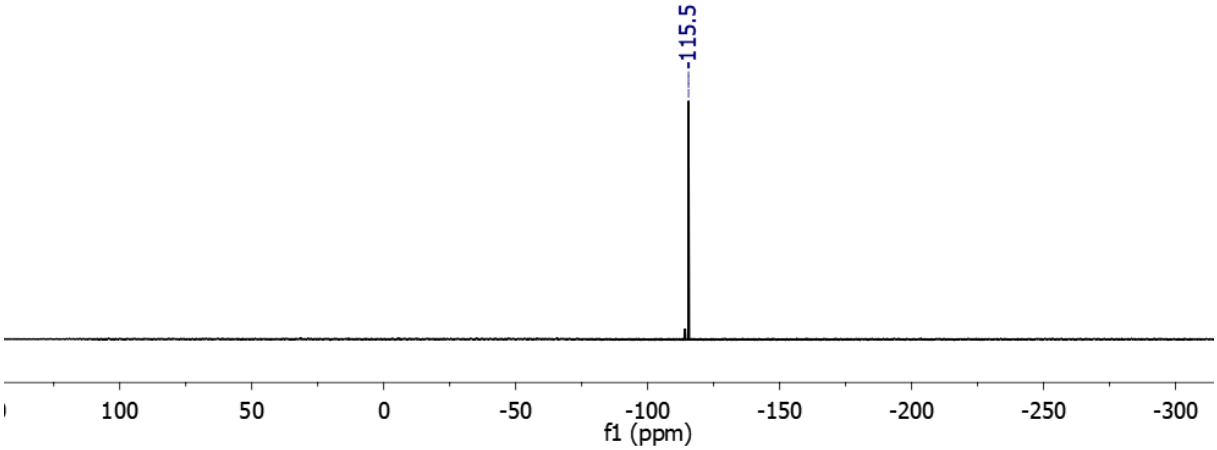


Fig. S61. ^{19}F NMR spectrum of (Z)-2,3-bis(4-fluorophenyl)-5,16-dioxa-1,4(1,4)-dibenzenacyclohexadecaphan-2-ene ($CDCl_3$, 376 MHz, 300K).

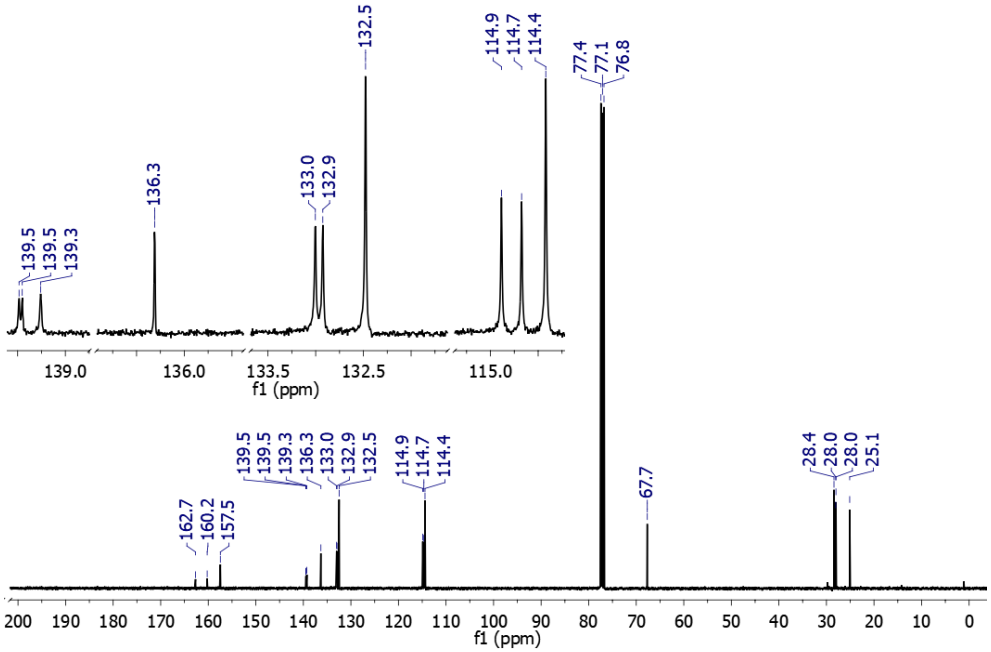


Fig. S62. ^{13}C NMR spectrum of (Z)-2,3-bis(4-fluorophenyl)-5,16-dioxa-1,4(1,4)-dibenzenacyclohexadecaphan-2-ene ($CDCl_3$, 101 MHz, 300K).

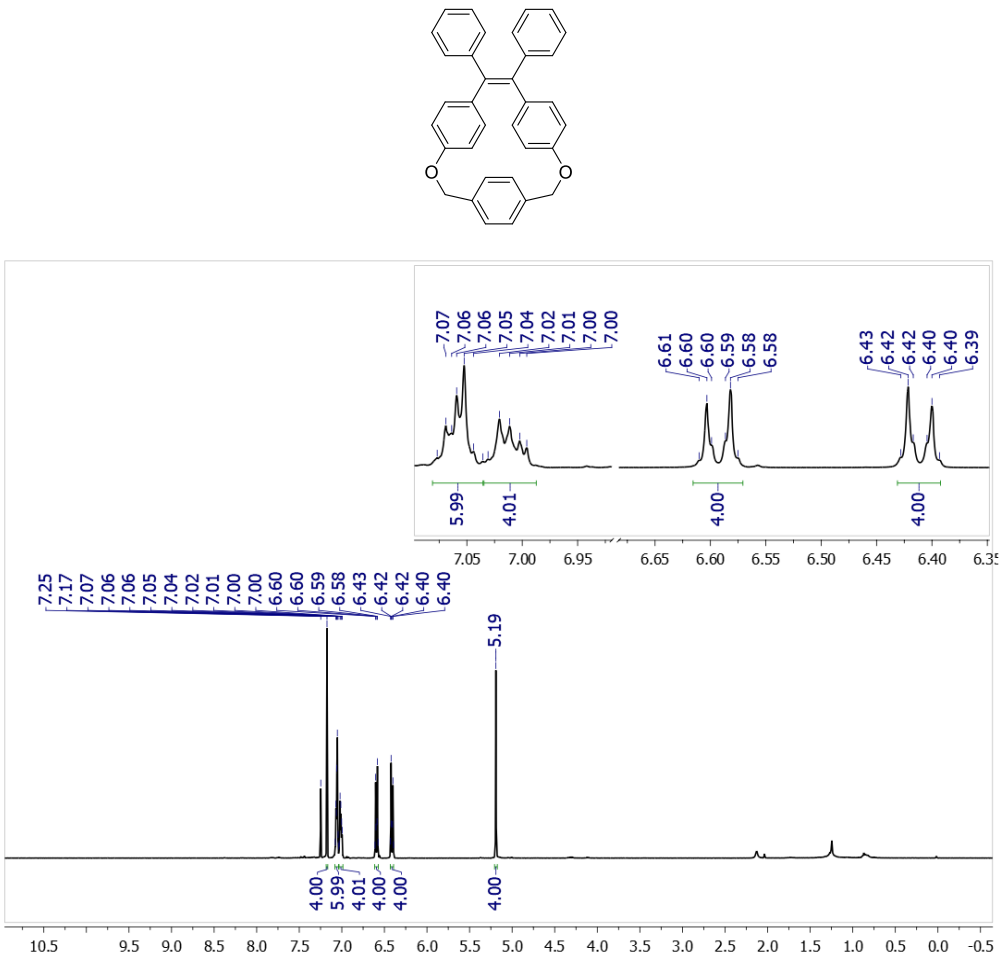


Fig. S63. ^{1}H NMR spectrum of (Z)-8,9-diphenyl-2,6-dioxa-1,4,7(1,4)-tribenzenacyclononaphan-8-ene ($CDCl_3$, 400 MHz, 300K).

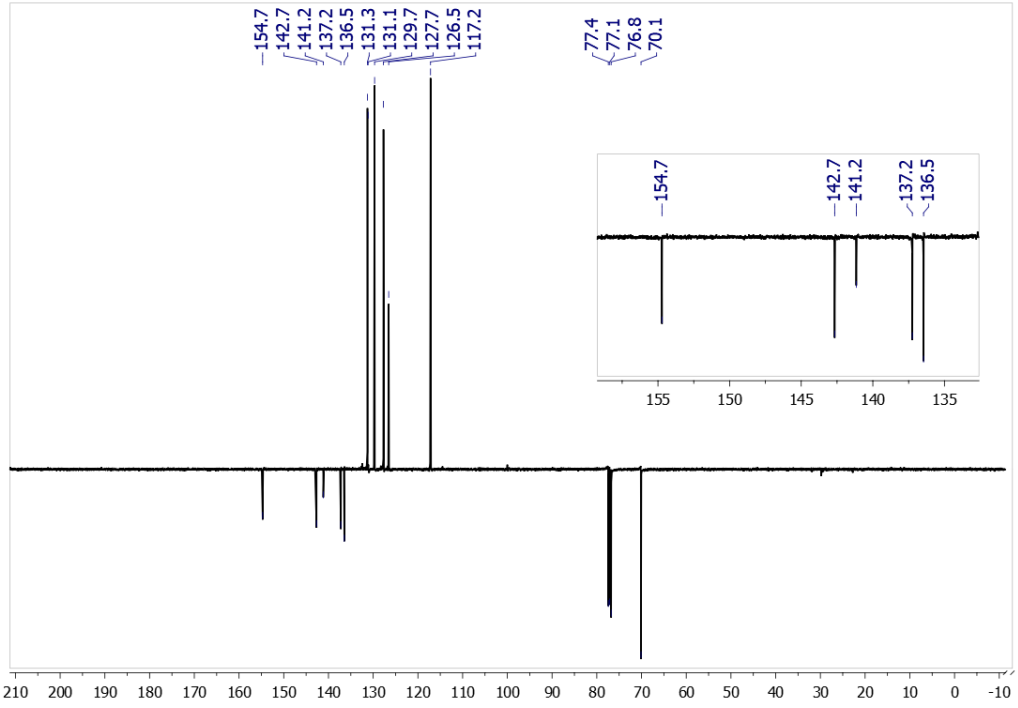


Fig. S64. ^{13}C APT NMR spectrum of (Z)-8,9-diphenyl-2,6-dioxa-1,4,7(1,4)-tribenzenacyclononaphan-8-ene ($CDCl_3$, 101 MHz, 300K).