

## Supporting Information

### **Direct Grafting of Poly(Pentafluorophenyl Acrylate) onto Oxides: Versatile Substrates for Reactive Microcapillary Printing and Self-Sorting Modification**

*Rachelle M. Arnold, Christopher D. McNitt, Vladimir V. Popik, and Jason Locklin*

#### **Experimental**

##### **Materials.**

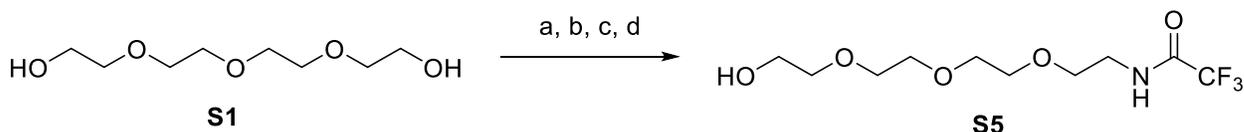
Solvents were purified using an MBraun solvent purification system. Silicon wafers (orientation <100>, native oxide) were purchased from University Wafer. SU-8 2025 photoresist and developer were purchased from MicroChem. PDMS was made using the SYLGARD 184 silicone elastomer kit from Dow Corning. Microfluidic masks were designed on AutoCAD (Autodesk, Inc., San Rafael, CA) and printed on transparencies at 20000 dpi by CAD/Art services, Inc. (Bandon, ORD). Pentafluorophenyl acrylate (PFPA) was synthesized using previously published methods.<sup>1</sup> It was further purified by distillation, and any residual acrylic acid was removed by passing the PFPA through a plug of neutral alumina with DCM. All other chemicals were purchased from Alfa Aesar, Sigma Aldrich, or TCI, and were used as received. Flash chromatography was performed using 40-63  $\mu\text{m}$  silica gel. All NMR spectra were recorded in  $\text{CDCl}_3$  (unless otherwise noted) using 400 MHz instrument.

##### **Polymerization of PFPA.**

4.25 g of PFPA and 25 mL of dry benzene were mixed in a Schlenk flask and degassed with argon for 1 hour at 0 °C. The monomer solution was then transferred with an argon-purged needle to a Schlenk flask containing 0.1 mol % azodiisobutyronitrile (AIBN) that had been evacuated three times and backfilled with nitrogen. The flask was added to an oil bath that was preheated to 70 °C and stirred for 24 hours. Afterwards, most of the benzene was removed and the polymer was precipitated into cold methanol. The polymer was collected, redissolved in benzene, and precipitated again.  $M_n = 267,062$  g/mol,  $M_w = 364,936$  g/mol,  $\bar{D} = 1.366$ .

## Synthesis of DIBO derivative

### Scheme S1. Synthesis of Acetamide-PEG-OH



(a) TosCl, DCM; (b) NaN<sub>3</sub>, acetonitrile; (c) PPH<sub>3</sub>, H<sub>2</sub>O, THF; (d) TFAA

### *p*-Toluenesulfonic Acid 2-(2-(2-(2-Hydroxyethoxy)ethoxy)ethoxy)ethyl ester (S2).<sup>2</sup>

Tetra(ethylene glycol) (20.25 g, 104 mmol) and dry triethylamine (15.83 g, 156 mmol) were added to a solution of *p*-toluenesulfonyl chloride (22.00 g, 115 mmol) in dichloromethane (200 mL) at 0 °C. The reaction was then stirred for 2 hours at 0 °C, and left overnight at room temperature under inert atmosphere. The precipitate was filtered and the reaction mixture was then concentrated in vacuum. The crude mixture was purified by chromatography (hexanes: ethyl acetate 2:8) to provide mono-tosyl tetraethylene glycol (S2, 15.28 g, 42%) as a colorless oil. <sup>1</sup>H-NMR: 7.79-7.81 (d, J = 8Hz, 2H), 7.33-3.35 (d, J = 4Hz, 2H), 4.15-4.18 (t, 2H), 3.59-3.73 (m, 14H), 2.45 (s, 3H). <sup>13</sup>C-NMR: 144.80, 132.83, 129.79, 127.84, 72.43, 70.56, 70.50, 70.31, 70.18, 69.27, 68.54, 61.50, 21.53.

### 2-(2-(2-(2-Azidoethoxy)ethoxy)ethoxy)ethanol (S3).<sup>2</sup>

A solution of S2 (15.285 g, 43.9 mmol) and sodium azide (4.28 g, 65.8 mmol) in acetonitrile (150 mL), was refluxed overnight. After cooling to room temperature, water (100 mL) was added and the mixture was extracted with dichloromethane (300 mL). The organic phase was then dried over MgSO<sub>4</sub> and concentrated in vacuum. The crude mixture was then purified via silica gel chromatography (ethyl acetate) to provide 2-[2-[2-(2-Azidoethoxy)ethoxy]-ethoxy]ethanol (S3, 7.09 g, 74%) as a colorless oil. <sup>1</sup>H-NMR: 3.60-3.74 (m, 14 H), 3.38-3.41 (t, 2H), 2.55-2.58 (t, 1H). <sup>13</sup>C: 72.59, 70.76, 70.72, 70.65, 70.40, 70.11, 61.75, 50.72.

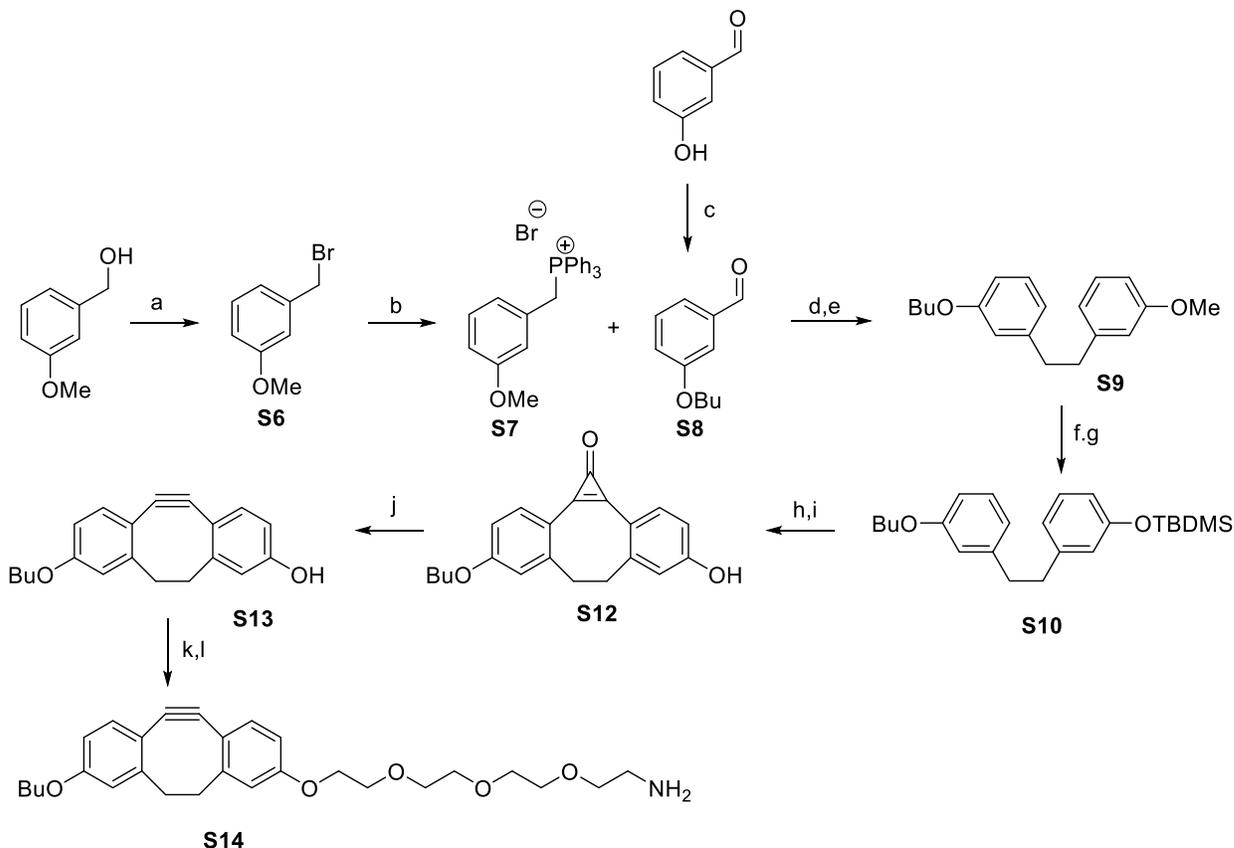
### 2-(2-(2-(2-Aminoethoxy)ethoxy)ethoxy)ethanol (S4).<sup>2</sup>

Triphenylphosphine (9.61 g, 36.7 mmol) was added to a solution of S3 (5.74 g, 26.2 mmol) subsequently dissolved in THF (53 mL). Once a homogenous solution had been obtained, deionized water (0.660 g, 36.7 mmol) was added to a reaction mixture, and the contents were stirred at room temperature overnight. Next, the solution was concentrated in vacuum and purified by chromatography (chloroform: methanol 1:1) to provide 2-[2-[2-(2-aminoethoxy)ethoxy]ethoxy]ethanol (S4, 3.46 g, 68%) as a colorless oil. <sup>1</sup>H-NMR: 3.48-3.73 (m, 14H), 2.85-2.87 (t, 2H). <sup>13</sup>C-NMR: 73.12, 72.97, 70.54, 70.43, 70.23, 70.07, 61.23, 41.45.

**2,2,2-trifluoro-N-(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl)acetamide (S5).**<sup>3</sup>

Trifluoroacetic anhydride (5.26 g, 25.07 mmol) added dropwise to a solution of S4 (3.46 g, 17.91 mmol) and triethylamine (4.53 g, 44.8 mmol) in methanol (35 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The solution was then concentrated in vacuum and purified by chromatography (ethyl acetate) to provide acetamide-PEG-OH (S5, 4.52 g, 87%) as a colorless oil. <sup>1</sup>H-NMR: 8.78 (bs, 1H), 3.55-3.71 (m, 16H). <sup>13</sup>C-NMR: 157.82 (q, J= 37 Hz), 116.26 (q, J= 286 Hz), 72.61, 70.82, 70.49, 70.18, 69.86, 69.66, 61.40, 39.99.

**Scheme S2. Synthesis of DIBO-PEG-Amine**



(a) PBr<sub>3</sub> DCM; (b) PPh<sub>3</sub> acetonitrile; (c) butanol, DIAD, THF, PPh<sub>3</sub>; (d) n-butyllithium, THF; (e) H<sub>2</sub>, Pd/C, ethyl acetate; (f) ethanethiol, NaH, DMF, 120 °C; (g) TBDMSCl, imidazole, DCM; (h) aluminum chloride, tetrachlorocyclopropene, DCM; (i) TBAF, THF; (j) MeOH, 350 nm; (k) S5, ADDP, PBu<sub>3</sub>, THF; (l) K<sub>2</sub>CO<sub>3</sub>, MeOH, H<sub>2</sub>O

**1-(bromomethyl)-3-methoxybenzene (S6).**<sup>4</sup>

Phosphorus tribromide (11.21 g, 41.4 mmol) was added to a solution of 3-methoxybenzyl alcohol (7.78 g, 55.2 mmol) in dichloromethane (200 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 minutes. The reaction was quenched

with saturated sodium bicarbonate (200 mL) and extracted with ether (400 mL). The organic layer was then washed with saturated sodium thiosulfate (200 mL) and brine (200 mL). The organic layer was then dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuum to provide 1-(bromomethyl)-3-methoxybenzene (10.44 g, 94%) as a colorless oil. <sup>1</sup>H-NMR: 7.23-7.27 (t, 1H), 6.97-6.99 (d, J = 7.6 Hz, 1H), 6.93-6.93 (d, J = 2 Hz, 1H), 6.83-6.85 (d, J = 7.6 Hz, 1H), 4.47 (s, 2H), 3.81 (s, 3H).

### ***3-methoxybenzyltriphenylphosphonium bromide (S7).***<sup>5</sup>

Triphenylphosphine (40.9, 148 mmol) was added to a solution of **S6** (10.44g, 51.9 mmol) in acetonitrile (210 mL), the reaction mixture was refluxed for 2 hours, concentrated in vacuum, and diluted with toluene. The precipitate was separated to provide (3-methoxybenzyl)triphenylphosphonium bromide (**S7**, 23.60, 98%) as a white solid. <sup>1</sup>H-NMR: 7.71-7.78 (m, 9H), 7.60-7.65 (m, 6H), 6.99-7.03 (t, 1H), 6.74-6.78 (m, 2H), 6.63-6.65 (m, 1H), 5.36-5.33 (d, J = 12 Hz, 1H), 3.53 (s, 3H).

### ***3-butoxybenzaldehyde (S8).***<sup>6</sup>

Diisopropyl azodicarboxylate (19.87 g, 98 mmol) was added to a solution of 1-butanol (7.28 g, 98 mmol), 3-hydroxybenzaldehyde (12.00 g, 98 mmol), triphenylphosphine (28.8 g, 98 mmol), in THF (200 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 30 minutes. The mixture was concentrated in vacuum, and purified via silica gel chromatography (hexanes: ethyl acetate 10:1) to provide 3-butoxybenzaldehyde (12.11 g, 69%) as a colorless oil. <sup>1</sup>H-NMR: 9.97 (s, 1H), 7.38-7.44 (m, 3H), 4.00-4.04 (t, 2H), 1.76-1.83 (m, 2H), 1.46-1.55 (m, 2H), 0.97-1.01 (t, 3H). <sup>13</sup>C-NMR: 192.36, 159.92, 137.98, 130.16, 123.44, 122.12, 112.98, 68.18, 31.37, 19.40, 14.00.

### ***cis/trans-1-(3-butoxyphenyl)-2-(3-methoxyphenyl)ethane.***

A THF solution of n-butyllithium (22.98 mL, 2.5 M, 60.2 mmol) was added dropwise to a solution of **S7** (24.21 g, 52.3 mmol) in anhydrous THF (450 mL) at -78 °C. The resulting solution was stirred under inert atmosphere for 2 hours, and then **S8** (9.31, 52.3 mmol, 20 mL) was added dropwise. The mixture was then warmed to room temperature and stirred overnight. The reaction mixture was quenched with water (300 mL), extracted with ethyl acetate (3 X 100 mL), and washed with brine (200 mL). The organic layer was then dried over MgSO<sub>4</sub> and concentrated in vacuum. The crude product was purified by chromatography (hexanes: ethyl acetate 10:1) to provide 1-(3-butoxyphenyl)-2-(3-methoxyphenyl)ethane (mixture of *cis*- and *trans*- isomers, 11.98 g, 81%) as a colorless oil. <sup>1</sup>H-NMR: 7.24-7.33 (m, 3H), 7.03-7.17 (m, 6H), 6.78-6.86 (m, 5H), 6.71-6.75 (m, 1.5H), 6.57 (s, 2H), 3.99-4.02 (t, 1.5H), 3.85 (s, 2H), 3.78-3.81 (t, 2H), 3.66 (s, 3H), 1.75-1.82 (m, 1.5 H), 1.64-1.71 (m, 2H), 1.38-1.57 (m, 3.5 H), 0.92-1.01 (m, 5H). <sup>13</sup>C-NMR: 160.07, 159.66, 159.53, 159.12, 138.93, 138.81, 138.77, 138.67, 130.65,

130.41, 129.84, 129.80, 129.39, 129.35, 129.17, 128.96, 121.72, 121.48, 119.46, 119.35, 114.59, 114.12, 113.97, 113.53, 113.46, 112.56, 111.93, 67.87, 67.69, 55.45, 55.26, 31.59, 31.43, 19.50, 19.40, 14.11, 14.03. ESI HRMS: calcd. (M+H<sup>+</sup>): C<sub>19</sub>H<sub>23</sub>O<sub>2</sub> 283.1692, found 283.1685.

***1-(3-butoxyphenyl)-2-(3-methoxyphenyl)ethane (S9).***

A suspension of cis/trans-1-(3-butoxyphenyl)-2-(3-methoxyphenyl)ethene (7.00 g, 24.79 mmol), 10% Pd/C (5.28 g, 2.479 mmol), in ethyl acetate (125 mL) was put on a Parr Shaker at room temperature for 5 hours under H<sub>2</sub> (50 PSI). The reaction mixture was then filtered over celite, concentrated in vacuum, and purified by chromatography (hexanes: ethyl acetate 10:1) to provide 1-(3-butoxyphenyl)-2-(3-methoxyphenyl)ethane (**S9**, 5.63 g, 80%) as a colorless oil. <sup>1</sup>H-NMR: 7.16-7.23 (m, 2H), 6.73-6.80 (m, 6H), 3.91-3.94 (t, 2H), 3.77 (s, 3H), 2.88 (s, 4H), 1.72-1.79 (m, 2H), 1.44-1.56 (m, 2H), 0.96-0.99 (t, 3H). <sup>13</sup>C-NMR: 159.83, 159.42, 143.64, 143.51, 129.49, 129.44, 121.05, 120.85, 115.03, 114.39, 112.08, 111.49, 67.76, 55.33, 38.07, 31.60, 19.49, 14.07. ESI HRMS: calcd. (M+H<sup>+</sup>): C<sub>19</sub>H<sub>25</sub>O<sub>2</sub> 285.1849, found 285.1843.

***1-(3-butoxyphenyl)-2-(3-hydroxyphenyl)ethane.***

Ethaneithiol (12.01 mL, 158 mmol) was added to a solution of **S9** (5.60 g, 19.69 mmol) in DMF (280 mL) at 0 °C, followed by sodium hydride (60% suspension in oil, 5.51g, 138 mmol). The solution was warmed to room temperature, stirred for 30 minutes, and heated at 120 °C for 30 h. After cooling to room temperature, the reaction mixture was diluted with ether (200 mL), quenched with water (100 mL), and acidified by the addition of aqueous 5% HCl (100 mL). The organic layer was washed with water (3 x 100 mL), brine (100 mL), dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuum. The crude mixture was purified by chromatography (hexanes: ethyl acetate 10:1) to provide 1-(3-butoxyphenyl)-2-(3-hydroxyphenyl)ethane (5.01 g, 94%) as a colorless oil. <sup>1</sup>H-NMR: 7.15-7.23 (m, 2H), 6.75-6.80 (m, 4H), 6.68-6.69 (m, 2H), 4.93 (s, 1H), 3.94-3.97 (t, 2H), 2.88 (s, 4H), 1.74-1.81 (m, 2H), 1.46-1.56 (m, 2H), 0.98-1.02 (t, 3H). <sup>13</sup>C-NMR: 159.36, 155.71, 143.95, 143.46, 129.72, 129.47, 121.15, 120.89, 115.57, 115.04, 113.05, 112.10, 67.81, 37.94, 37.83, 31.58, 19.48, 14.08. ESI HRMS: calcd. (M-H<sup>+</sup>): C<sub>18</sub>H<sub>21</sub>O<sub>2</sub> 269.1547, found 269.1549.

***1-(3-butoxyphenyl)-2-(3-(tert-butyldimethylsilyloxyphenyl)ethane (S10).***

Imidazole (1.100g, 16.16 mmol) was added to a solution of 1-(3-butoxyphenyl)-2-(3-hydroxyphenyl)ethane (4.16 g, 15.39 mmol) in dichloromethane (150 mL) at room temperature. Next, TBDMSCl (2.319 g, 15.39 mmol) was added to the reaction mixture, and the reaction was stirred for 2 hours. The reaction mixture was quenched with

saturated ammonium chloride, diluted with ether (400 mL), and layers separated. The organic layer was then washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated in vacuum. The crude mixture was purified by chromatography (hexanes: ethyl acetate 10:1) to provide 1-(3-butoxyphenyl)-2-(3-(tert-butyldimethylsilyloxy)phenyl)ethane (**S10**, 5.56 g, 94%) as a colorless oil. <sup>1</sup>H-NMR: 7.13-7.22 (m, 2H), 6.74-6.82 (m, 4H), 6.68-6.71 (m, 2H), 3.93-3.97 (t, 2H), 2.89 (s, 4H), 1.74-1.81 (m, 2H), 1.49-1.54 (m, 2H), 0.98-1.02 (m, 12H), 0.20 (s, 6H). <sup>13</sup>C-NMR: 159.41, 155.83, 143.55, 143.52, 129.43, 129.35, 121.69, 120.86, 120.47, 117.77, 115.02, 112.04, 67.74, 38.08, 37.86, 31.63, 25.93, 19.50, 18.42, 14.10, -4.19. ESI HRMS: calcd. (M+H<sup>+</sup>): C<sub>24</sub>H<sub>37</sub>O<sub>2</sub>Si 385.2557, found 385.2549.

**4-butoxy-9-((tert-butyldimethylsilyloxy)-6,7-dihydro-1H-dibenzo[a,e]cyclopropa[c][8]annulen-1-one (Photo-DIBO-TBDMS, S11).**

Tetrachlorocyclopropene (1.887 g, 10.40 mmol) was added to a suspension of aluminum chloride (1.401 g, 10.40 mmol) in dichloromethane (300 mL), stirred for 15 min. and cooled to -78 °C. A solution of **S10** (4.00 g, 10.40 mmol) in 10 mL of DCM was added, and the reaction mixture was stirred for 4 h at -78 °C. The reaction mixture was then warmed to room temperature and stirred for an additional hour. The reaction mixture was then diluted with dichloromethane (300 mL), worked up with a 5% HCl solution (200 mL). The organic layer was washed with water, brine, and dried over MgSO<sub>4</sub>. The solution was filtered, concentrated in vacuum, and purified by chromatography to provide Photo-DIBO-TBDMS (**S11**, 2.63 g, 58%) as a white amorphous solid. <sup>1</sup>H-NMR: 7.94-7.91 (d, J= 12 Hz, 1H), 7.89-7.87 (d, J= 8 Hz, 1H), 6.89-6.86 (m, 2H), 6.83-6.81 (m, 2H), 4.05-4.02 (m, 2H), 3.36-3.26 (m, 2H), 2.63-2.57(m, 2H), 1.82-1.75 (m, 2H), 1.55-1.46 (m, 2H), 1.03-0.97 (m, 12H), 0.25 (s, 6H). <sup>13</sup>C-NMR: 162.25, 159.20, 153.96, 148.05, 147.98, 142.76, 142.21, 135.95, 135.76, 121.57, 118.48, 117.20, 116.42, 116.36, 112.38, 68.16, 37.41, 37.17, 31.32, 25.75, 19.37, 18.39, 13.98, -4.13. ESI HRMS: calcd. (M+H<sup>+</sup>): C<sub>27</sub>H<sub>35</sub>O<sub>3</sub>Si 435.2350, found 435.2339.

**4-butoxy-9-hydroxy-6,7-dihydro-1H-dibenzo[a,e]cyclopropa[c]-[8]annulen-1-one (S12, Photo-DIBO-OH).<sup>7</sup>**

Tetrabutylammonium fluoride (7.02 mL, 1.0 M, 7.02 mmol) was added a solution of **S11** (3.05 g, 7.02 mmol) in THF (70 mL), stirred for 30 min, and quenched by saturated ammonium chloride. The reaction mixture was then diluted with dichloromethane (200 mL), and the aqueous layer was extracted 2x with dichloromethane (50 mL). The combined organic layers were washed with brine, and dried over MgSO<sub>4</sub>. The solvent was then concentrated in vacuum and purified by chromatography (dichloromethane: methanol 20:1) to provide Photo-DIBO-OH (**S12**) as a white powder. <sup>1</sup>H-NMR DMSO: 10.42 (s, 1H), 7.75-7.77 (d, J = 8 Hz, 1H), 7.68-7.70 (d, J = 8 Hz, 1H), 7.08 (s, 1H), 6.98-7.01 (m, 1H), 6.89-6.90 (d, J = 4 Hz, 1H), 6.82-6.84 (dd, 8 & 4 Hz, 1H), 4.06-4.09 (t,

2H), 3.34-3.44 (m, 2H), 2.43-2.7 (m, 2H), 1.70-1.75 (m, 2H), 1.41-1.48 (m, 2H), 0.93-0.96 (t, 3H). <sup>13</sup>C-NMR DMSO: 161.36, 161.04, 151.96, 148.13, 147.85, 142.18, 140.78, 135.19, 134.75, 116.94, 116.09, 115.90, 114.48, 113.92, 112.62, 67.57, 36.39, 36.25, 30.60, 18.69, 13.66.

***3-butoxy-9-hydroxy-5,6-didehydro-11,12-dihydrodibenzo[a,e]-[8]annulen-2-yl***  
**(S13, DIBO-OH).**<sup>7</sup>

A solution of Photo-DIBO-OH (**S12**, 0.456 g, 1.423 mmol) in methanol (450 mL) was irradiated for 10 minutes at 350 nm using Rayonet photoreactor. The solution was then concentrated in vacuum, and purified by chromatography (dichloromethane: methanol 40:1) to provide DIBO-OH (**S13**, 0.381 g, 92%) as a white powder (decomp. 74-77 °C). <sup>1</sup>H-NMR: 7.16-7.23 (m, 2H), 6.89 (d, J= 4Hz, 1H), 6.82- 6.83 (d, J= 4 Hz, 1H), 6.76-6.79 (dd, J = 8 & 4 Hz 1H), 6.70-6.73 (dd, J = 8 & 4Hz, 1H), 5.47 (s, 1H), 3.98-4.01 (t, 2H), 3.13-3.22 (m, 2H), 2.41-2.46 (m, 2H), 1.75-1.82 (m, 2H), 1.66-1.56 (m, 2H), 0.98-1.01 (t, 3H). <sup>13</sup>C-NMR: 158.84, 155.39, 155.23, 155.04, 127.06, 126.87, 117.46, 116.95, 116.61, 116.13, 113.31, 112.06, 110.75, 110.37, 68.06, 36.76, 36.66, 31.48, 19.43, 14.04. ESI HRMS: calcd. (M-H<sup>+</sup>): C<sub>20</sub>H<sub>19</sub>O<sub>2</sub> 291.1391, found 291.1376.

***2-((2,2,2-trifluoro-N-(2-(2-(2-(2-(9-butoxy-5,6-didehydro-11,12-dihydrodibenzo[a,e]-[8]annulen-2-yl)oxy)ethoxy)ethoxy)ethyl acetamide*** (DIBO-PEG-Acetamide).

Tributylphosphine (0.305 g, 1.433 mmol, 2 mL THF) was added to a solution of **S14** (0.381, 1.303 mmol), **S5** (0.415 g, 1.433 mmol), and 1,1'-(Azodicarbonyl)dipiperidine (ADDP) (0.395 g, 1.564 mmol) in THF (10 mL) at room temperature. The reaction mixture was stirred overnight, concentrated in vacuum, and purified by chromatography (dichloromethane: methanol 40:1) to afford DIBO-PEG-Acetamide (0.379 g, 52 %) as a yellow oil. <sup>1</sup>H-NMR: 7.59 (s, 1H), 7.18-7.20 (d, J = 8 Hz, 2H), 6.88 (s, 2H), 6.75-6.77 (d, J = 8 Hz, 2H), 4.12-4.14 (m, 2H), 3.95-3.99 (t, 2H), 3.83-3.85 (m, 2H), 3.61-3.74 (m, 10H), 3.51-3.55 (m, 2H), 3.15-3.20 (m, 2H), 2.38-2.47 (m, 2H), 1.74-1.81 (m, 2H), 1.45-1.52 (m, 2H), 0.96-1.00 (t, 3H). <sup>13</sup>C-NMR: 158.88, 158.24, 157.46 (q, J= 37 Hz), 155.02, 126.81, 126.77, 116.91, 116.85, 116.81, 116.11 (q, J= 286 Hz), 116.01, 112.02, 112.01, 110.82, 110.31, 70.92, 70.72, 70.67, 70.39, 69.83, 68.90, 67.93, 67.63, 39.92, 36.79, 36.77, 31.45, 19.39, 13.99. ESI HRMS: calcd. (M+H<sup>+</sup>): C<sub>30</sub>H<sub>37</sub>F<sub>3</sub>NO<sub>6</sub> 564.2567, found 564.2550.

***2-(2-(2-(2-(2-(9-butoxy-5,6-didehydro-11,12-dihydrodibenzo[a,e]-[8]annulen-2-yl)oxy)ethoxy)ethoxy)ethyl amine*** (**S14**, DIBO-PEG-Amine).

A solution of potassium carbonate (0.093 g, 0.672) in water (1.50 mL), was added to a solution of DIBO-PEG-Acetamide (0.379 g, 0.672 mmol) in methanol (3.00 mL) at room temperature. The reaction mixture was stirred overnight, concentrated in vacuum, and the residue was redissolved in dichloromethane/ethyl acetate (1:4). The organic layer

was then washed with water, brine, dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuum, and purified by chromatography (dichloromethane: methanol 10:1 to 10:3) to provide DIBO-PEG-Amine (**S14**, 0.259 g, 82%) as a yellow oil. <sup>1</sup>H-NMR: 7.18-7.20 (d, J = 8 Hz, 2H), 6.87-6.91 (dd, J= 12 Hz & 4 Hz, 2H), 6.74-6.79 (m, 2H), 4.74 (s, 2H), 4.13-4.16 (t, 2H), 3.96-3.99 (t, 2H), 3.84-3.86 (t, 2H), 3.58-3.74 (m, 10H), 3.15-3.20 (m, 2H), 2.96-2.98 (t, 2H), 2.38-2.47 (m, 2H), 1.74-1.81 (m, 2H), 1.55-1.45 (m, 2H), 1.00-0.96 (t, 2H). <sup>13</sup>C-NMR: 158.93, 158.28, 155.11, 155.08, 126.68, 116.99, 116.91, 116.08, 112.25, 112.06, 110.88, 110.36, 70.84, 70.66, 70.62, 70.55, 70.36, 69.84, 68.00, 67.81, 40.92, 36.83, 31.51, 19.44, 14.03. ESI HRMS: calcd. (M+H<sup>+</sup>): C<sub>28</sub>H<sub>38</sub>NO<sub>5</sub> 468.2744, found 468.2727.

### **Spincoating Polymer Films on Silicon Substrates.**

Silicon wafers cut to approximately 1.5 cm x 1.5 cm were sonicated in hexane, IPA, acetone, and deionized water for 15 minutes each. The substrates were dried in a stream of nitrogen and argon plasma cleaned (Harrick Plasma, PDC-32-G, 0.8 mbar, 18 W) for 5 minutes. A 20 mg/mL solution of poly(PFPA) in dry THF was spincoated on the clean substrates at 1000 rpm for 15 s (Chemat Technology Spinocoater KW-4A).

### **Temperature Dependent Annealing Studies.**

Seven different substrates with an initial polymer layer of approximately 160 nm were annealed on a hot plate in a chemical hood at temperatures ranging from 25-150 °C. After 30 minutes, the substrates were removed, sonicated in THF, and dried with nitrogen. Thicknesses were determined using spectroscopic ellipsometry.

### **Time Dependent Annealing Studies.**

A set of eight substrates containing an initial polymer layer of approximately 160 nm were annealed on a hot plate at 110 °C. Individual substrates were removed after different time points (2, 5, 10, 30, 60, 90, 120 min), sonicated in THF, and dried with nitrogen. Thicknesses were determined using spectroscopic ellipsometry.

### **Postpolymerization Aminolysis of Annealed Substrates with 1-Aminomethylpyrene.**

Substrates from the temperature dependent annealing study were placed in a 10 mM solution of 1-aminomethylpyrene (AMP) in dry DMF with an acid scavenger. After four hours, the substrates were removed, rinsed and sonicated in DMF and methanol, and dried with nitrogen.

### **Lithographic Methodology.**

Stamp master molds were created on silicon wafers using a mask aligner (MA6, Karl Suss). Negative photoresist, SU-8 2025, (~ 4 mL) was spincoated onto a clean, dry wafer at 3000 rpm for 30 seconds. The photoresist was then exposed to UV light ( $\lambda = 365$  nm)

through a mask at 20 mW/cm<sup>2</sup>. The wafer was then heat cured and washed with SU-8 developer for 30 min under constant agitation. Wafers were rinsed with isopropanol and dried before a final curing on a hot plate at 70 °C for 10 min. The average thickness of the photo-cured SU-8 photo developer was 29 ± 0.4 μm. The stamps were molded out of PDMS using a 10:1 SYLGARD mixture of the base to curing agent. The mixture was degassed before pouring over the master wafer, followed by 4 hours of curing at 70 °C. Prior to stamp formation, the wafers were coated with trimethylchlorosilane through vapor deposition to ensure the PDMS could be easily removed after curing.

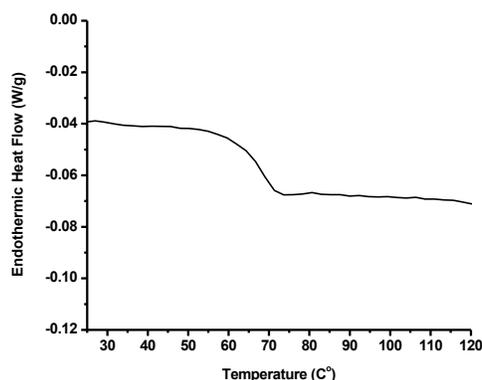
### **Reactive μCaP on Annealed Substrate.**

A PDMS stamp was fabricated according to literature.<sup>8</sup> The microfluidic-based pattern was designed on AutoCAD and was created to fit within a 2 cm<sup>2</sup> area by using channels with a 100 μm width. Prior to use, the stamps rinsed with ethanol and acetone. The pattern was cut in a manner that resulted in channel openings on at least 2 sides of the stamp in order to allow wicking of the DIBO solution through the channels. Once the stamp was placed in contact with the substrate, 1 μL of a 50 mM solution of DIBO in dry DMF was added to one end of the stamp. The printing setup was left for approximately 3 hours until the solvent had evaporated. The stamp was then removed and the substrate was rinsed and sonicated in DMF. For the one-pot, self-sorting postpolymerization modification reaction, a solution consisting of 5 mM fluoresceinamine and 2 mM azido-Texas Red in 1:1 MeOH:DMF with triethylamine as an acid scavenger was used. The patterned substrates were stirred in the solution at 25 °C overnight. Afterwards, the substrate was removed from the solution, rinsed and sonicated in DMF and MeOH, and dried in a stream of nitrogen.

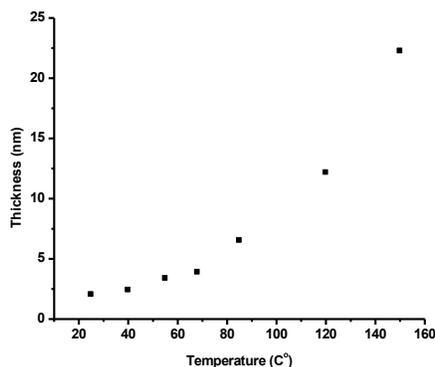
### **Characterization.**

Thickness was determined on a J. A. Woollam M-2000V spectroscopic ellipsometer with a white light source at three angles of incidence (65°, 70°, and 75°) to the silicon wafer normal. A Cauchy model was used to fit the film thickness, with an extinction coefficient of 0 and refractive index of 1.50 for the polymer brush layer. FTIR measurements were taken with a Nicolet Model 6700 with a grazing angle attenuated total reflectance accessory (GATR) at 256 scans with a 4 cm<sup>-1</sup> resolution. Fluorescence microscopy pictures were taken using a Zeiss AX10 Observer inverted microscope with an X-cite Series 120 fluorescent light source and Zeiss filters 38 HE (470/40 nm excitation, 525/50 nm emission) and 43 HE (550/25 nm excitation, 605/70 nm emission), and Chroma Technology UV filter (350 nm excitation, > 430 nm emission). Differential scanning calorimetry (DSC) (Mettler Toledo, DSC823°, 400 W) was used to determine the glass transition temperature (*T<sub>g</sub>*) of poly(PFPA). Samples of approximately 3 mg were placed in standard aluminum DSC pans and loaded at room temperature. A temperature range of 20-250 °C was cycled five times with a ramp of 10 °C/min. The first cycle was used to

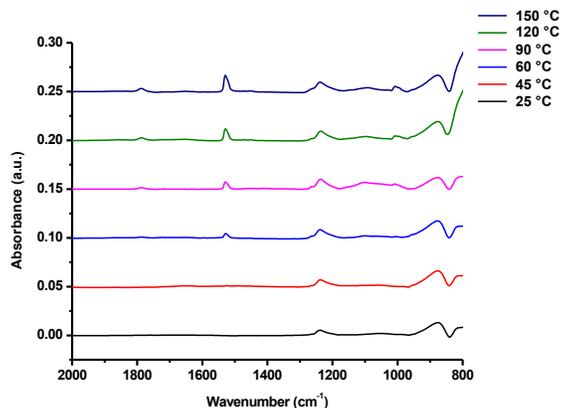
evaporate any remaining solvent or monomer in the polymer. The data collected was analyzed using the STARe software provided by Mettler Toledo. Size-exclusion chromatography (SEC) was conducted on a liquid chromatograph (Shimadzu LC-20AD series) equipped with a RID-10A refractive index detector. Polymer samples were diluted in tetrahydrofuran (THF) mobile phase and passed through three Phenomenex Phenogel (10E3A, 10E4A, and 10E5A) columns at 40 °C under a constant volumetric flow rate (1 mL min<sup>-1</sup>). Molecular weight characteristics of the samples were referenced to polystyrene standards (Agilent technologies EasiCal PS-2). Dynamic light scattering (DLS) of the poly(PFPA) at 2 mg/mL in THF was conducted using a Malvern Instruments Zetasizer Nano ZS instrument (Model ZEN3600) equipped with a 4 mV He-Ne laser operating at  $\lambda = 633$  nm with a measurement angle of 173°. Thickness of the master mold used in soft-lithographic fabrication was determined by profilometry using a Dektak 150 with a 3 mm radius stylus.



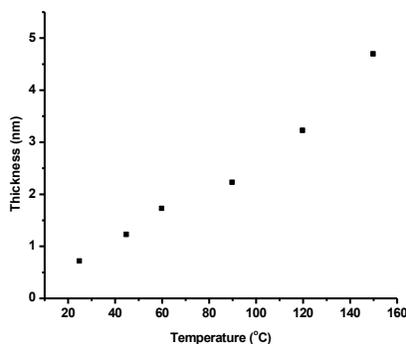
**Figure S1:** DSC scan of poly(PFPA).



**Figure S2:** Thickness vs. temperature of poly(PFPA) in ambient conditions.



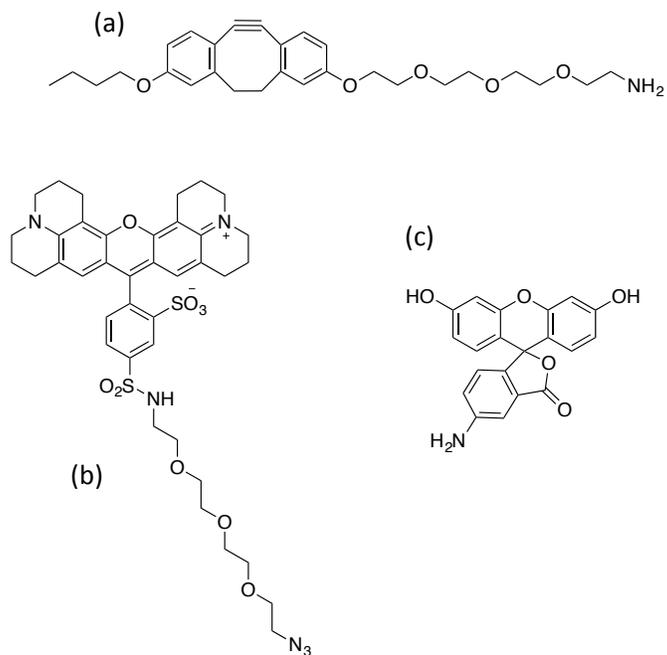
**Figure S3:** FTIR spectra of poly(PFPA) annealed in an inert atmosphere at various temperatures.



**Figure S4:** Thickness vs. temperature of poly(PFPA) annealed in an inert atmosphere.

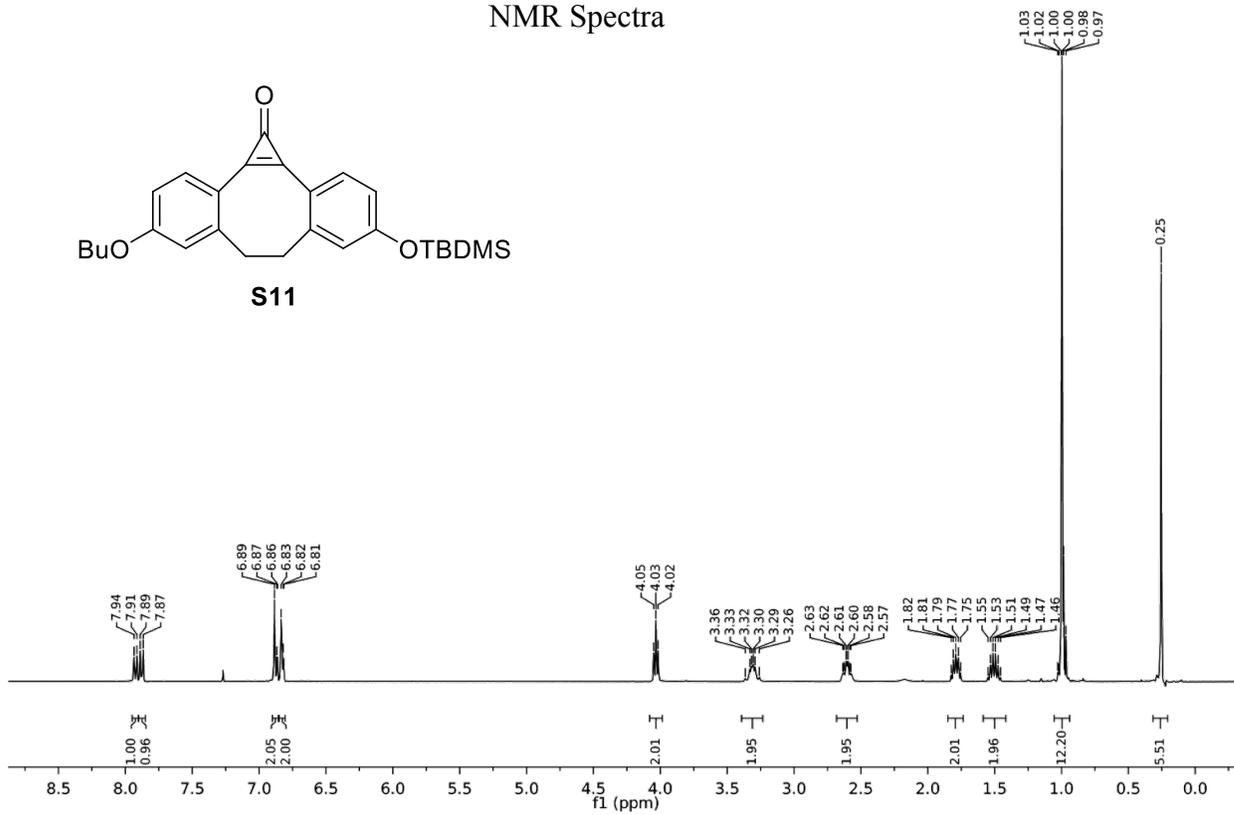
**Table S1** Thicknesses, grafting densities, radius of gyration ( $R_g$ ) and reduced tethering densities ( $\Sigma$ ) of substrates annealed within an inert atmosphere for 30 min

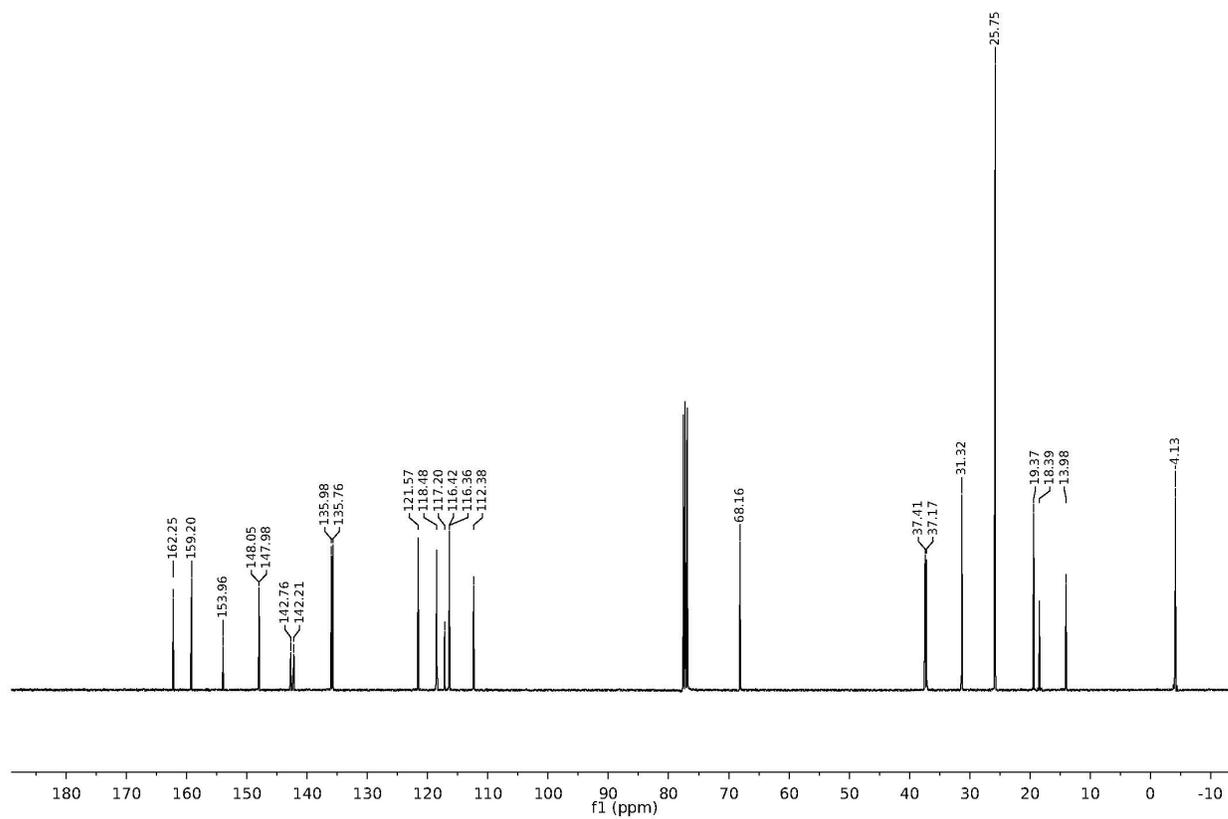
Temperature	Thickness	$\sigma$ (chains/nm <sup>2</sup> )	$R_g$	$\Sigma$
150 °C	4.69 nm	0.0154	16.64 nm	13.4
120 °C	3.22 nm	0.0106	16.64 nm	9.22
90 °C	2.22 nm	0.0073	16.64 nm	6.35
60 °C	1.72 nm	0.0057	16.64 nm	4.96



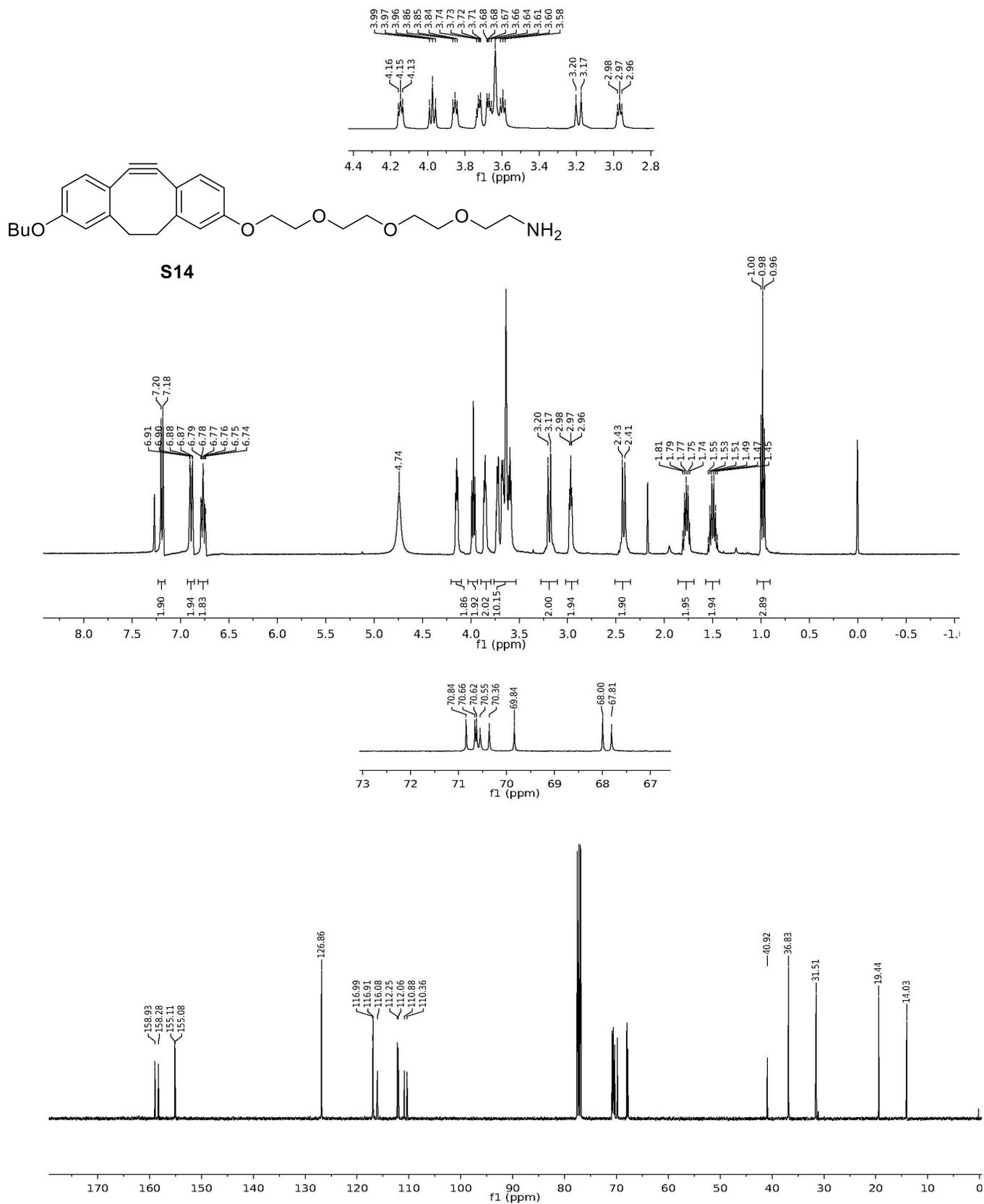
**Figure S5:** Structure of (a) DIBO-amine derivative, (b) azido-Texas Red, and (c) aminofluorescein, isomer 1.

### NMR Spectra









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