Electronic Supplementary Material (ESI) for RSC Advances.

Thiol-yne click reaction: an interesting way to derive thiol-provided catechols

F. Nador, J. Mancebo-Aracil, D. Zanotto, D. Ruiz-Molina and G. Radivoy

Supporting Information

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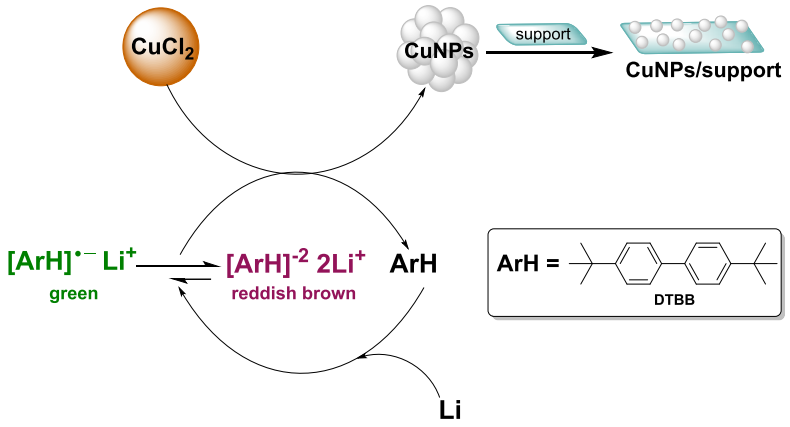
S1. Preparation and Characterization of CuNPs/TiO_2



Scheme S1. Schematic representation of CuNPs/support preparation.

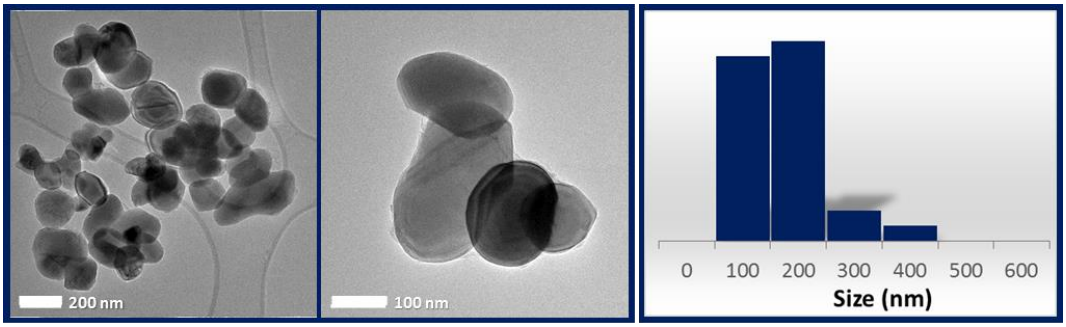


Figure S1. TEM images of TiO_2 support and the corresponding histogram.

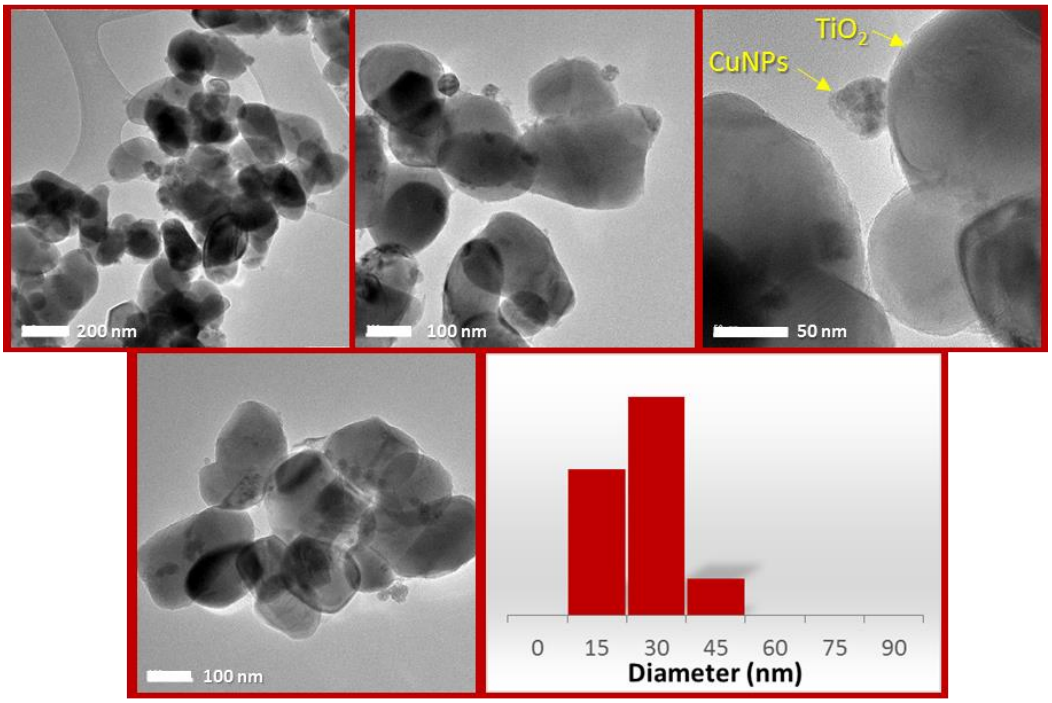


Figure S2. TEM images of CuNPs/TiO_2 and the corresponding histogram for CuNPs.

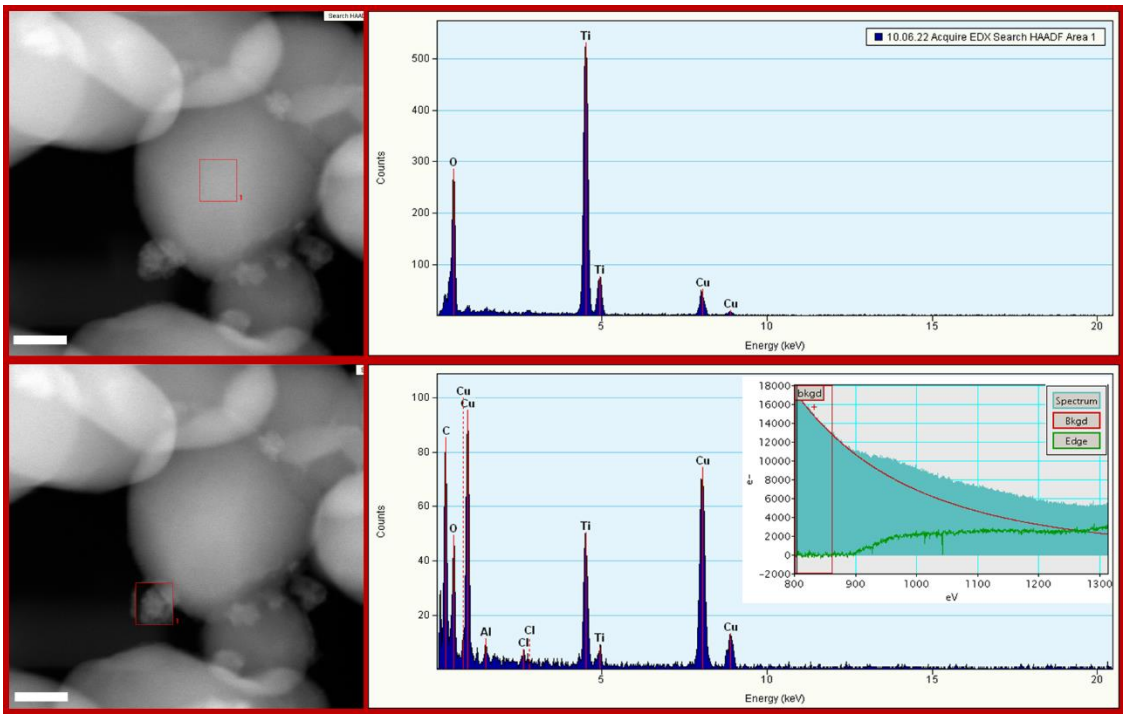


Figure S3. STEM images and EDX analysis on the highlighted area of CuNPs/TiO_2 system. Embedded image corresponds to EEL spectrum of adjacent particle. Scale bars are 50nm.

S2. CNPs structure

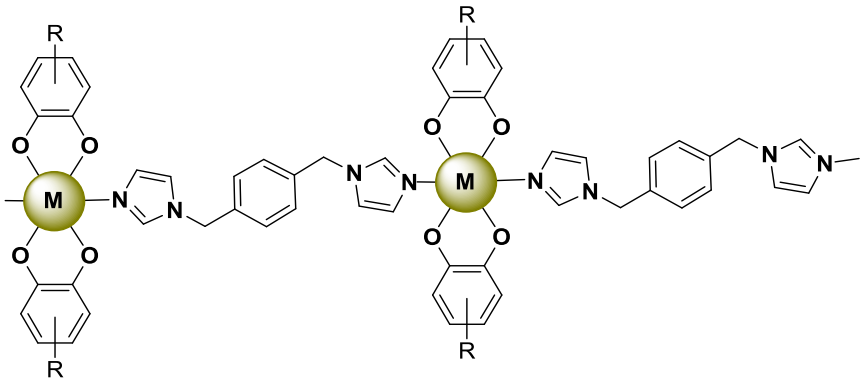


Figure S4. Schematic illustration describing the coordination between catechol derivative ligands and 1,4-bis(imidazole-1-ylmethyl)benzene, with a metal to form a coordination polymer.

S3. NMR characterization

Characterization of Michael adducts (1). These compounds were characterized by comparison of their physical and spectroscopic data with those described in the literature.[1]

- **3-((6-mercaptohexyl)thio)benzene-1,2-diol, 1ª.** Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 6.99 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.91 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.78 (deform dd, *J* = 8.0, 7.8 Hz, 1H), 6.56 (broad s, 1H, OH), 5.44 (broad s, 1H, OH), 2.69 (t, *J* =

7.4 Hz, 2H), 2.48 (deform td, *J* = 7.4, 7.2 Hz, 2H), 1.65-1.46 (m, 4H), 1.42-1.29 (m, 4H), 1.25 (t, *J* = 7.2 Hz, 1H, SH). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 143.9 (C), 143.6 (C), 126.2 (CH), 120.5 (CH), 119.1 (C), 116.1 (CH), 36.1 (CH_2), 33.5 (CH_2), 29.2 (CH_2), 27.7 (CH_2), 27.5 (CH_2), 24.2 (CH_2).

- **3-((4-mercaptobutyl)thio)benzene-1,2-diol, 1b.** Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 6.98 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.90 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.76 (deform dd, *J* = 8.1, 7.7 Hz, 1H), 6.63 (broad s, 1H, OH), 5.82 (broad s, 1H, OH), 2.69 (t, *J* = 6.7 Hz, 2H), 2.47 (deform dt, *J* = 7.8, 7.0 Hz, 2H), 1.74-1.57 (m, 4H), 1.34 (t, *J* = 7.8 Hz, 1H, SH). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 143.9 (C), 143.6 (C), 126.3 (CH), 120.6 (CH), 118.9 (C), 116.2 (CH), 35.6 (CH_2), 32.4 (CH_2), 28.0 (CH_2), 23.8 (CH_2).

- **3-((2-(2-(2-mercaptoethoxy)ethoxy)ethyl)thio)benzene-1,2-diol, 1c.** Orange oil. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 7.61 (broad s, 1H, OH), 7.01 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.75 (deform dd, *J* = 8.0, 7.8 Hz, 1H), 5.59 (broad s, 1H, OH), 3.69-3.62 (m, 6H), 3.57 (t, *J* = 5.8 Hz, 2H), 2.92 (t, *J* = 5.8 Hz, 2H), 2.72 (dt, *J* = 8.1, 6.2 Hz, 2H), 1.66 (t, *J* = 8.1 Hz, 1H, SH). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 145.3 (C), 144.5 (C), 127.3 (CH), 120.5 (CH), 118.3 (C), 116.4 (CH), 72.9 (CH_2), 70.0 (CH_2), 69.8 (CH_2), 68.6 (CH_2), 36.5 (CH_2), 24.2 (CH_2).

- **3-(((*2R**,*3R**)-2,3-dihydroxy-4-mercaptobutyl)thio)benzene-1,2-diol, 1d.** Pale yellow oil. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 6.90 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.75 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.65 (deform dd, *J* = 8.0, 7.8 Hz, 1H), 3.76-3.61 (m, 2H), 3.03 (dd, *J* = 13.5, 5.5 Hz, 1H), 2.91 (dd, *J* = 13.5, 7.6 Hz, 1H), 2.61 (d, *J* = 6.6 Hz, 2H), ArO*H* and CHO*H* n.d. ^{13}C NMR (75 MHz, CD_3OD) *δ*: 146.7 (C), 146.5 (C), 125.7 (CH), 121.8 (C), 120.8 (CH), 116.2 (CH), 75.3 (CH), 71.7 (CH), 38.9 (CH_2), 28.1 (CH_2).

Characterization of Vinyl Sulfides (3)

- **3-((6-((2,3-dihydroxyphenyl)thio)hexyl)thio)acrylamide, 3aa**. The reaction mixture was purified by column chromatography with 8/2 to 4/6 gradient of hexane/ethyl acetate, yielding 40% of a mixture of isomers *Z*:*E*, 83:17. Colourless oil. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 7.57 (d, *J* = 15.0 Hz, $1H_E$), 7.04 (d, *J* = 10.1 Hz, $1H_Z$), 6.84 (dd, *J* = 7.6, 1.8 Hz, $2H_{Z+E}$), 6.73 (dd, *J* = 7.7, 1.8 Hz, $2H_{Z+E}$), 6.67 (deform dd, *J* = 7.7, 7.6 Hz, $2H_{Z+E}$), 5.94 (d, *J* = 10.1 Hz, $1H_Z$), 5.93 (d, *J* = 15.0 Hz, $1H_E$), 2.94-2.69 (m, $8H_{Z+E}$), 1.74-1.53 (m, $8H_{Z+E}$), 1.52-1.36 (m, $8H_{Z+E}$), ArO*H* and CONH_2 n.d; ^{13}C NMR (75 MHz, CD_3OD) *δ*: 171.2 (C), 148.3 (CH), 146.3 (C), 146.2 (C), 124.8 (CH), 122.4 (C), 120.7 (CH), 115.7 (CH), 115.4 (CH), 36.7 (CH_2), 34.7 (CH_2), 31.4 (CH_2), 30.3 (CH_2), 29.1 (CH_2), 28.9 (CH_2). Elemental analysis calcd (%) for $C_{15}H_{21}NO_3S_2$: C 55.02, H 6.46, N 4.28, S 19.58; found: C 55.04, H 6.44, S 19.59.

- **3-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)acrylamide, 3ba**. The reaction mixture was purified by column chromatography with 9/1 to 5/5 gradient of hexane/ethyl acetate, yielding 53% of a mixture of isomers *Z*:*E*, 87:13. Colourless oil. ***Z* and *E* isomers**. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 7.55 (d, *J* = 15.0 Hz, $1H_E$), 7.01 (d, *J* = 10.1 Hz, $1H_Z$), 6.85 (dd, *J* = 7.6, 1.7 Hz, $2H_{Z+E}$), 6.75 (dd, *J* = 7.9, 1.7 Hz, $2H_{Z+E}$), 6.67 (deform dd, *J* = 7.9, 7.6 Hz, $2H_{Z+E}$), 5.96 (d, *J* = 15.0 Hz, $1H_E$), 5.94 (d, *J* = 10.1 Hz,

$1H_Z$), 2.85 (t, *J* = 7.0 Hz, $4H_{Z+E}$), 2.71 (t, *J* = 7.1 Hz, $4H_{Z+E}$), 1.85-1.60 (m, $8H_{Z+E}$), ArO*H* and CONH_2 n.d. ^{13}C NMR (75 MHz, CD_3OD) *δ*: 172.0 ©, 149.0 (CH), 147.2 (C), 147.1 (C), 125.8 (CH), 122.9 (C), 121.6 (CH), 116.7 (CH), 116.4 (CH), 37.1 (CH_2), 35.2 (CH_2), 31.2 (CH_2), 30.0 (CH_2). Elemental analysis calcd (%) for $C_{13}H_{17}NO_3S_2$: C 52.15, H 5.72, N 4.68, S 21.42; found: C 52.18, H 5.71, N 4.71, S 21.40.

- **(*Z*)-3-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy)ethoxy)ethyl)thio)acrylamide, 3ca**. The reaction mixture was purified by washes with hexane/ethyl acetate 5/5 yielding 69% only isomer *Z*. Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 7.57 (broad s, 1H, ArO*H*), 7.01 (d, *J* = 10.0 Hz, 1H), 6.98 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.91 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.73 (deform dd, *J* = 8.0, 7.9 Hz, 1H), 6.25 (broad s, 1H, ArO*H*), 5.81 (d, *J* = 10.0 Hz, 1H), 5.59 (broad s, 2H, CONH_2), 3.77-3.53 (m, 8H), 2.95-2.85 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 168.3 (C), 147.6 (CH), 145.4 (C), 144.6 (C), 127.0 (CH), 120.4 (CH), 118.5 (C), 116.5 (CH), 114.4 (CH), 71.1 (CH_2), 70.1 (CH_2), 70.0 (CH_2), 68.6 (CH_2), 36.2 (CH_2), 35.6 (CH_2). Elemental analysis calcd (%) for $C_{15}H_{21}NO_5S_2$: C 50.12, H 5.89, N 3.90, S 17.84; found: C 50.15, H 5.91, N 3.88, S 17.86.

- **Methyl-3-((6-((2,3-dihydroxyphenyl)thio)hexyl)thio)acrylate, 3ab**. The reaction mixture was purified by column chromatography with 8/2 to 6/4 gradient of hexane/ethyl acetate, yielding 39% of a mixture of isomers *Z*:*E*, 81:19. Yellow oil. ***Z* and *E* isomers** ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 7.69 (d, *J* = 15.2 Hz, $1H_E$), 7.06 (d, *J* = 10.2 Hz, $1H_Z$), 6.97 (dd, *J* = 7.9, 1.6 Hz, $2H_{Z+E}$), 6.90 (dd, *J* = 8.1, 1.6 Hz, $2H_{Z+E}$), 6.76 (deform dd, *J* = 8.1, 7.9 Hz, $2H_{Z+E}$), 5.84 (d, *J* = 10.2 Hz, $1H_Z$), 5.74 (d, *J* = 15.2 Hz, $1H_E$), 3.73 (s, $6H_{Z+E}$), 2.77-2.59 (m, $8H_{Z+E}$), 1.70-1.47 (m, $8H_{Z+E}$), 1.45-1.32 (m, $8H_{Z+E}$). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 167.0 ©, 150.5 (CH), 144.1 (C), 143.7 (C), 126.3 (CH), 120.6 (CH), 119.1 (C), 116.1 (CH), 112.5 (CH), 51.2 (CH_3), 36.2 (CH_2), 35.8 (CH_2), 29.9 (CH_2), 29.3 (CH_2), 27.9 (CH_2), 27.7 (CH_2). Elemental analysis calcd (%) for $C_{16}H_{22}O_4S_2$: C 56.12, H 6.48, S 18.72; found: C 56.16, H 6.52, S 18.83.

- **Methyl-3-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)acrylate, 3bb**. The reaction mixture was purified by column chromatography with 9/1 to 8/2 gradient of hexane/ethyl acetate, yielding 46% of a mixture of isomers *Z*:*E*, 86:14. Pale yellow oil. ***Z* and *E* isomers**. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 7.66 (d, *J* = 15.2 Hz, $1H_E$), 7.02 (d, *J* = 10.1 Hz, $1H_Z$), 6.99 (dd, *J* = 7.8, 1.6 Hz, $2H_{Z+E}$), 6.92 (dd, *J* = 7.9, 1.6 Hz, $2H_{Z+E}$), 6.78 (deform dd, *J* = 7.9, 7.8 Hz, $2H_{Z+E}$), 6.50 (broad s, 2H, ArOH_{Z+E}), 5.86 (d, *J* = 10.1 Hz, $1H_Z$), 5.75 (d, *J* = 15.2 Hz, $1H_E$), 5.42 (broad s, 2H, ArOH_{Z+E}), 3.74 (s, $6H_{Z+E}$), 2.74 (t, *J* = 7.1 Hz, $4H_{Z+E}$), 2.73 (t, *J* = 7.1 Hz, $4H_{Z+E}$), 1.82-1.63 (m, $8H_{Z+E}$). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 167.0 (C), 150.0 (CH), 144.1 (C), 143.8 (C), 126.4 (CH), 120.7 (CH), 118.7 (C), 116.3 (CH), 112.8 (CH), 51.2 (CH_3), 35.8 (CH_2), 35.3 (CH_2), 29.0 (CH_2), 28.2 (CH_2). Elemental analysis calcd (%) for $C_{14}H_{18}O_4S_2$: C 53.48, H 5.77, S 20.39; found: C 53.59, H 5.83, S 20.31.

- **Methyl-3-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy)ethoxy)ethyl)thio)acrylate, 3cb**. The reaction mixture was purified by column chromatography with 7/3 to 5/5

gradient of hexane/ethyl acetate, yielding 36% of a mixture of isomers *Z*:*E*, 80:20. Pale yellow oil. ***Z* and *E* rotamers** are described. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 7.73 (d, *J* = 15.2 Hz, $1H_E$), 7.71 (d, *J* = 15.1 Hz, $1H_E$), 7.56 (broad s, 4H, OH_{Z+E}), 7.19 (d, *J* = 10.1 Hz, $1H_Z$), 7.18 (d, *J* = 10.1 Hz, $1H_Z$), 7.01 (dd, *J* = 7.9, 1.6 Hz, $4H_{Z+E}$), 6.92 (dd, *J* = 8.0, 1.6 Hz, $4H_{Z+E}$), 6.75 (deform dd, *J* = 8.0, 7.9 Hz, $4H_{Z+E}$), 5.85 (d, *J* = 10.2 Hz, $1H_Z$), 5.84 (d, *J* = 10.1 Hz, $1H_Z$), 5.83 (d, *J* = 15.2 Hz, $1H_E$), 5.80 (d, *J* = 15.1 Hz, $1H_E$), 5.59 (broad s, 4H, OH_{Z+E}), 3.76-3.62 (m, $36H_{Z+E}$), 3.56 (t, *J* = 5.8 Hz, $8H_{Z+E}$), 2.96 (t, *J* = 6.4 Hz, $8H_{Z+E}$), 2.91 (t, *J* = 5.8 Hz, $8H_{Z+E}$). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 167.0 (C), 150.7 (CH), 145.3 (C), 144.5 (C), 127.3 (CH), 120.5 (CH), 118.3 (C), 116.4 (CH), 112.7 (CH), 71.1 (CH_2), 70.2 (CH_2), 69.9 (CH_2), 68.6 (CH_2), 51.2 (CH_3), 36.4 (CH_2), 35.3 (CH_2). Elemental analysis calcd (%) for $C_{16}H_{22}O_6S_2$: C 51.32, H 5.92, S 17.12; found: C 51.35, H 5.94, S 17.11.

- **Methyl-3-(((*2R**,*3R**)-4-((2,3-dihydroxyphenyl)thio)-2,3-dihydroxybutyl)thio) acrylate, 3db**. The reaction mixture was purified by column chromatography with 6/4 to 4/6 gradient of hexane/ethyl acetate, yielding 23% of a mixture of isomers *Z*:*E*, 90:10. Yellow oil. ***Z* and *E* isomers**. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 7.81 (d, *J* = 15.2 Hz, $1H_E$), 7.38 (d, *J* = 10.2 Hz, $1H_Z$), 6.91 (dd, *J* = 7.8, 1.6 Hz, $2H_{Z+E}$), 6.76 (dd, *J* = 8.0, 1.6 Hz, $2H_{Z+E}$), 6.65 (deform dd, *J* = 8.0, 7.8 Hz, $2H_{Z+E}$), 5.87 (d, *J* = 15.2 Hz, $1H_E$), 5.86 (d, *J* = 10.2 Hz, $1H_Z$), 3.88 (ddd, J = 8.0, 5.8, 2.5 Hz, $2H_{Z+E}$), 3.72 (s, $6H_{Z+E}$), 3.66 (ddd, *J* = 7.2, 6.0, 2.5 Hz, $2H_{Z+E}$), 3.10-2.89 (m, $8H_{Z+E}$), ArO*H* and CHO*H* n.d. ^{13}C NMR (75 MHz, CD_3OD) *δ*: 168.7 (C), 153.3 (CH), 146.9 (C), 146.5 (C), 125.9 (CH), 121.5 (C), 120.8 (CH), 116.3 (CH), 112.8 (CH), 73.3 (CH), 71.8 (CH), 51.5 (CH_3), 40.0 (CH_2), 38.7 (CH_2). Elemental analysis calcd (%) for $C_{14}H_{18}O_6S_2$: C 48.54, H 5.24, S 18.51; found: C 48.58, H 5.26, S 18.52.

- **3-((4-((2-(pyridine-2-yl)vinyl)thio)butyl)thio)benzene-1,2-diol, 3bc**. The reaction mixture was purified by washes with hexane/ethyl acetate 9/1 yielding 50% of a mixture of isomers *Z*:*E*, 77:23. Yellow oil. ***Z* and *E* isomers**. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 8.54 (d, *J* = 4.7 Hz, $1H_Z$), 8.41 (d, *J* = 5.0 Hz, $1H_E$), 7.82-7.74 (m, $1H_Z$), 7.80-7.71 (m, $1H_E$), 7.53 (d, *J* = 8.0 Hz, $1H_Z$), 7.43 (d, *J* = 15.5 Hz, $1H_E$), 7.40 (d, *J* = 7.9 Hz, $1H_E$), 7.23-7.15 (m, $2H_{Z+E}$), 6.86 (dd, *J* = 7.7, 1.7 Hz, $1H_Z$), 6.84 (dd, *J* = 7.8, 1.6 Hz, $1H_E$), 6.76-6.61 (m, $3H_Z + 2H_E$), 6.53 (d, *J* = 10.9 Hz, $1H_Z$), 6.49 (d, *J* = 15.5 Hz, $1H_E$), 2.95-2.77 (m, $8H_{Z+E}$), 1.93-1.60 (m, $8H_{Z+E}$), ArO*H* n.d. ^{13}C NMR (75 MHz, CD_3OD) *δ*: 157.0 (C), 149.5 (CH), 146.4 (C), 146.3 (C), 137.7 (CH), 135.3 (CH), 125.0 (CH), 124.4 (CH), 124.1 (CH), 122.1 (C), 121.9 (CH), 120.7 (CH), 115.8 (CH), 36.3 (CH_2), 34.3 (CH_2), 30.3 (CH_2), 29.2 (CH_2). Elemental analysis calcd (%) for $C_{17}H_{19}NO_2S_2$: C 61.23, H 5.74, N 4.20, S 19.23; found: C 61.31, H 5.80, N 4.19, S 19.33.

- **3-((2-(2-(2-((2-(pyridine-2-yl)vinyl)thio)ethoxy)ethoxy)ethyl)thio)benzene-1,2-diol, 3cc**. The reaction mixture was purified by column chromatography with 8/2 to 4/6 gradient of hexane/ethyl acetate, yielding 37% of a mixture of isomers *Z*:*E*, 56:44. Pale yellow oil. ***Z* isomer**. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.60 (d, *J* = 4.3 Hz, 1H), 7.61-7.56 (m, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.07-7.01 (m, 1H), 6.95 (dd, *J* = 7.9, 1.7 Hz,

1H), 6.81 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.63 (deform dd, *J* = 8.0, 7.9 Hz, 1H), 6.60 (d, *J* = 10.7 Hz, 1H), 6.42 (d, *J* = 10.7 Hz, 1H), 3.69-3.60 (m, 4H), 3.58-3.52 (m, 4H), 3.01-2.82 (m, 4H), ArO*H* n.d. ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 154.4 (C), 148.4 (CH), 145.3 (C), 144.5 (C), 136.0 (CH), 133.8 (CH), 126.7 (CH), 123.3 (CH), 123.0 (CH), 120.8 (CH), 120.3 (CH), 118.5 (C), 116.3 (CH), 71.0 (CH_2), 69.9 (CH_2), 68.8 (CH_2), 68.6 (CH_2), 38.2 (CH_2), 35.4 (CH_2). ***E* isomer**. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 8.44 (d, *J* = 4.2 Hz, 1H), 7.61-7.56 (m, 1H), 7.37 (d, *J* = 15.3 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.08-6.99 (m, 1H), 6.93 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.64 (deform dd, *J* = 8.0, 7.8 Hz, 1H), 6.45 (d, *J* = 15.3 Hz, 1H), 3.69-3.60 (m, 4H), 3.58-3.52 (m, 4H), 3.01-2.82 (m, 4H), ArO*H* n.d. ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 155.5 (C), 148.7 (CH), 145.6 (C), 144.6 (C), 137.0 (CH), 132.0 (CH), 126.5 (CH), 124.2 (CH), 121.3 (CH), 120.4 (CH), 120.2 (CH), 118.7 (C), 116.2 (CH), 70.1 (CH_2), 70.0 (CH_2), 69.9 (CH_2), 69.4 (CH_2), 35.9 (CH_2), 31.7 (CH_2). Elemental analysis calcd (%) for $C_{19}H_{23}NO_4S_2$: C 57.99, H 5.89, N 3.56, S 16.29; found: C 58.02, H 5.91, N 3.50, S 16.27.

- **3-(((*2R**,*3R**)-2,3-dihydroxy-4-((2-(pyridine-2-yl)vinyl)thio) butyl)thio)benzene-1,2-diol 3dc**. The reaction mixture was purified by column chromatography with 5/5 (hexane/ethyl acetate) to pure AcOEt gradient, yielding 21% of a mixture of isomers *Z*:*E*, 67:33. Pale yellow oil. ***Z* isomer**. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 8.54 (d, *J* = 4.7 Hz, 1H), 7.80-7.68 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.22-7.15 (m, 1H), 6.88 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.76 (d, *J* = 10.9 Hz, 1H), 6.71 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.56-6.50 (m, 2H), 4.02-3.91 (m, 1H), 3.78-3.68 (m, 1H), 3.14-2.91 (m, 4H), ArO*H* and CHO*H* n.d. ^{13}C NMR (75 MHz, CD_3OD) *δ*: 157.9 (C), 150.3 (CH), 147.4 (C), 147.3 (C), 138.5 (CH), 136.5 (CH), 126.8 (CH), 125.3 (CH), 125.0 (CH), 122.8 (CH), 122.3 (C), 121.6 (CH), 117.1 (CH), 73.9 (CH), 72.4 (CH), 41.1 (CH_2), 39.5 (CH_2). ***E* isomer**. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 8.42 (d, *J* = 4.8 Hz, 1H), 7.77-7.64 (m, 1H), 7.43 (d, *J* = 15.6 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.22-7.15 (m, 1H), 6.91 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.75 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.63 (deform dd, J = 7.9, 7.8 Hz, 1H), 6.55 (d, *J* = 15.6 Hz, 1H), 4.02-3.91 (m, 1H), 3.78-3.68 (m, 1H), 3.14-2.91 (m, 4H), ArO*H* and CHO*H* n.d. ^{13}C NMR (75 MHz, CD_3OD) *δ*: 157.1 (C), 150.5 (CH), 147.7 (C), 147.6 (C), 139.4 (CH), 134.7 (CH), 126.7 (CH), 125.8 (CH), 123.4 (CH), 122.9 (CH), 122.4 (C), 121.6 (CH), 117.18 (CH), 72.9 (CH), 72.8 (CH), 39.5 (CH_2), 37.4 (CH_2). Elemental analysis calcd (%) for $C_{17}H_{19}NO_4S_2$: C 55.87, H 5.24, N 3.83, S 17.54; found: C 55.98, H 5.23, N 3.75, S 17.66.

- **(*Z*)-3-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy)ethoxy) ethyl)thio)acrylic acid, 3ce**. The reaction mixture was purified by column chromatography with 6/4 to 4/6 gradient of hexane/ethyl acetate, yielding 14% of only *Z* isomer. Yellow oil. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 7.00 (d, *J* = 9.9 Hz, 1H), 6.90 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.78 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.68 (deform dd, *J* = 7.9, 7.8 Hz, $1H_Z$), 5.84 (d, *J* = 9.9 Hz, $1H_Z$), 3.79-3.56 (m, $8H_Z$), 3.04-2.98 (m, $2H_Z$), 2.94-2.87 (m, $2H_Z$), ArO*H* and COO*H* n.d. ^{13}C NMR (75 MHz, CD_3OD) *δ*: 170.0 (C), 146.9 (C), 146.5 (C), 146.4 (CH), 125.7 (CH), 121.4 (C), 120.8 (CH), 119.4 (CH), 116.4 (CH), 72.2 (CH_2), 71.3 (CH_2), 71.2 (CH_2), 70.7 (CH_2), 35.8 (CH_2), 34.8 (CH_2). Elemental analysis calcd (%) for $C_{15}H_{20}O_6S_2$: C 49.98, H 5.59, S 17.79; found: C 49.97, H 5.57, S 17.81.

- **Dimethyl 2-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)but-2-enedioate, 3bf**. The reaction mixture was purified by column chromatography with 8/2 to 7/3 gradient of hexane/ethyl acetate, yielding 31% of a mixture of isomers *Z*:*E*, 55:45. Pale yellow oil. ***Z* isomer**. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 6.98 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.91 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.78 (deform dd, *J* = 8.0, 7.8 Hz, 1H), 6.52 (broad s, 1H, OH), 6.37 (s, 1H), 5.49 (broad s, 1H, OH), 3.85 (s, 3H), 3.76 (s, 3H), 2.82 (t, *J* = 7.0 Hz, 2H), 2.70 (t, *J* = 6.8 Hz, 2H), 1.73-1.59 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 165.5 (C), 164.8 (C), 148.4 (C), 144.2 (C), 143.9 (C), 126.5 (CH), 120.8 (CH), 119.7 (CH), 118.7 (C), 116.3 (CH), 53.1 (CH_3), 51.7 (CH_3), 35.9 (CH_2), 32.0 (CH_2), 28.4 (CH_2), 28.3 (CH_2). ***E* isomer**. ^{1}H NMR (300 MHz, $CDCl_3$) *δ*: 6.98 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.79 (deform dd, *J* = 8.0, 7.9 Hz, 1H), 6.51 (broad s, 1H, OH), 5.74 (s, 1H), 5.47 (broad s, 1H, OH), 3.88 (s, 3H), 3.72 (s, 3H), 2.85-2.67 (m, 4H), 1.84-1.60 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) *δ*: 165.9 (C), 164.0 (C), 149.8 (C), 144.2 (C), 143.9 (C), 126.5 (CH), 120.9 (CH), 118.5 (C), 116.5 (CH), 113.2 (CH), 53.1 (CH_3), 51.9 (CH_3), 35.7 (CH_2), 31.2 (CH_2), 28.5 (CH_2), 27.0 (CH_2). Elemental analysis calcd (%) for $C_{16}H_{20}O_6S_2$: C 51.60, H 5.41, S 17.22; found: C 51.61, H 5.41, S 17.24.

- **Dimethyl 2-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy) ethoxy)ethyl)thio)but-2-enedioate, 3cf**. The reaction mixture was purified by column chromatography with 6/4 to 4/6 gradient of hexane/ethyl acetate, yielding 63% of a mixture of isomers *Z*:*E*, 39:61. Orange oil. ***Z* isomer**. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 6.86 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.74 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.64 (deform dd, *J* = 7.9, 7.8 Hz, 1H), 6.35 (s, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 3.68-3.52 (m, 8H), 3.04 (t, *J* = 6.1 Hz, 2H), 2.97 (t, *J* = 6.5 Hz, 2H), ArO*H* n.d. ^{13}C NMR (75 MHz, CD_3OD) *δ*: 167.0 (C), 166.0 (C), 150.5 (C), 146.7 (C), 146.6 (C), 125.5 (CH), 121.4 (C), 120.9 (CH), 120.2 (CH), 116.3 (CH), 71.7 (CH_2), 71.3 (CH_2), 71.0 (CH_2), 70.7 (CH_2), 53.5 (CH_3), 52.2 (CH_3), 34.8 (CH_2), 33.2 (CH_2). ***E* isomer**. ^{1}H NMR (300 MHz, CD_3OD) *δ*: 6.86 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.74 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.64 (deform dd, *J* = 7.9, 7.8 Hz, 1H), 5.90 (s, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 3.68-3.52 (m, 8H), 3.04 (t, *J* = 6.1 Hz, 2H), 2.97 (t, *J* = 6.5 Hz, 2H), ArO*H* n.d. ^{13}C NMR (75 MHz, CD_3OD) *δ*: 167.5 (C), 165.6 (C), 151.6 (C), 151.7 (C), 146.4 (C), 125.5 (CH), 121.4 (C), 120.8 (CH), 116.3 (CH), 114.0 (CH), 71.4 (CH_2), 71.1 (CH_2), 70.7 (CH_2), 69.7 (CH_2), 53.6 (CH_3), 52.2 (CH_3), 34.8 (CH_2), 32.5 (CH_2). Elemental analysis calcd (%) for $C_{18}H_{24}O_8S_2$: C 49.99, H 5.59, S 14.83; found: C 50.01, H 5.62, S 14.82.

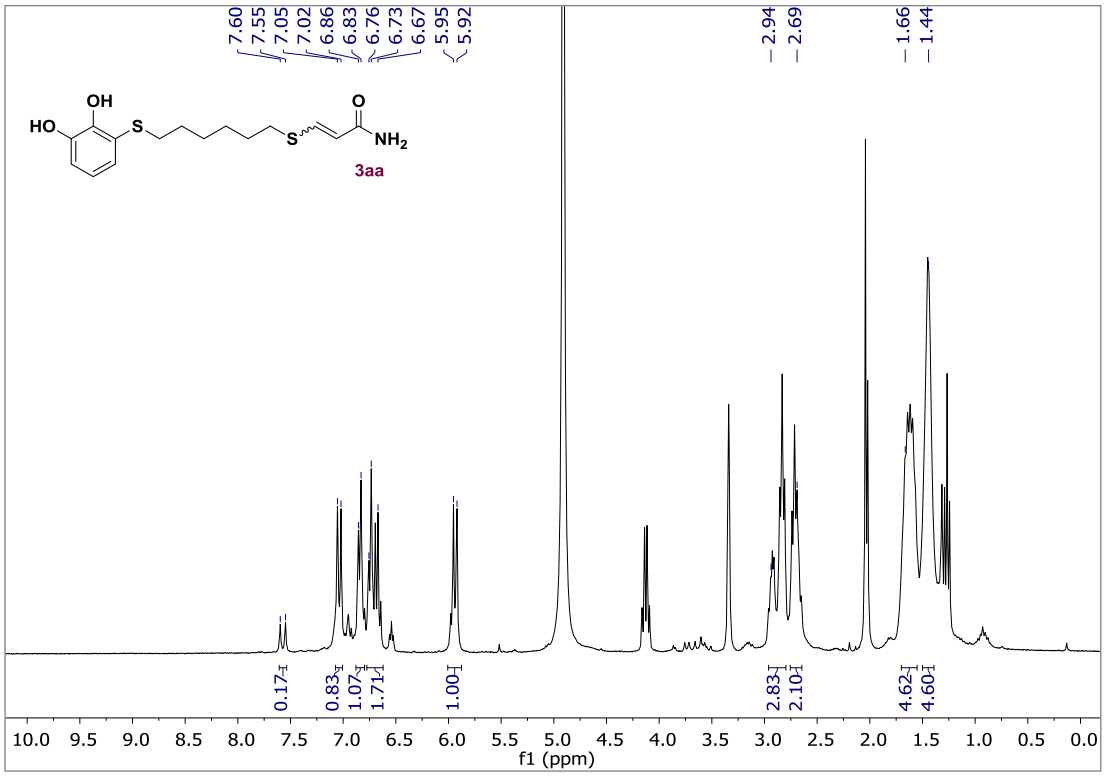


Figure S5. ^{1}H NMR of 3-((6-((2,3-dihydroxyphenyl)thio)hexyl)thio)acrylamide (**3aa**) in CD_3OD.

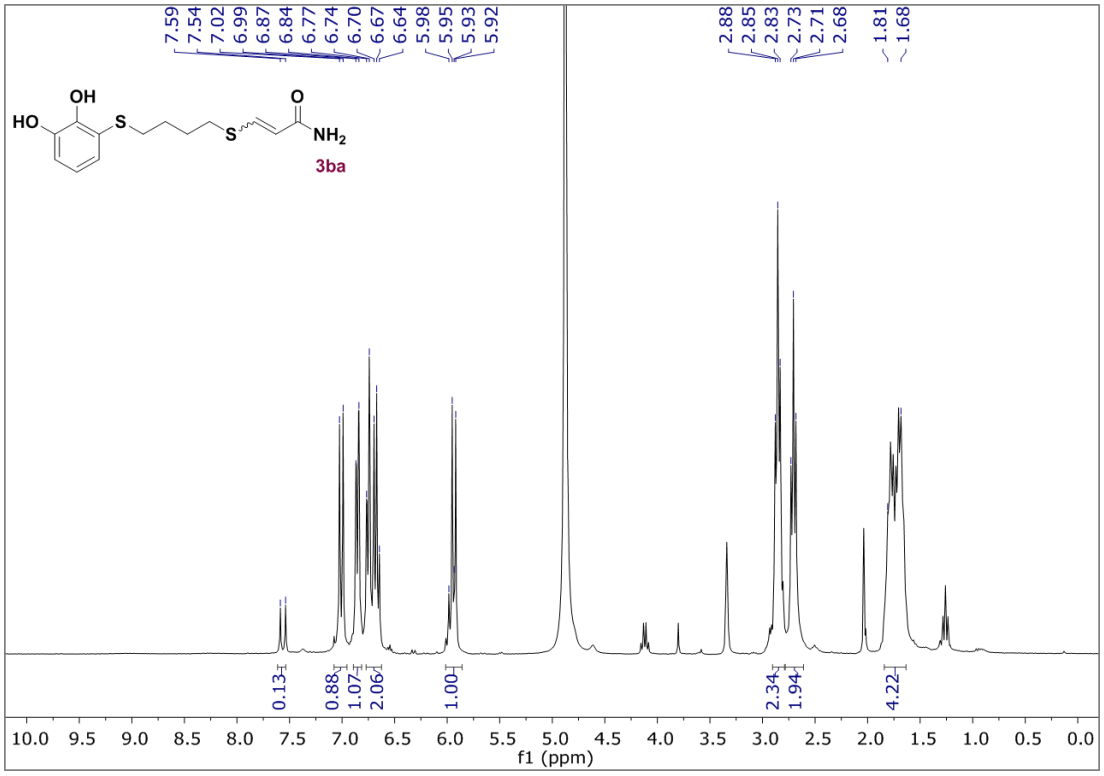


Figure S6. ^{1}H NMR of 3-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)acrylamide (**3ba**) in CD_3OD.

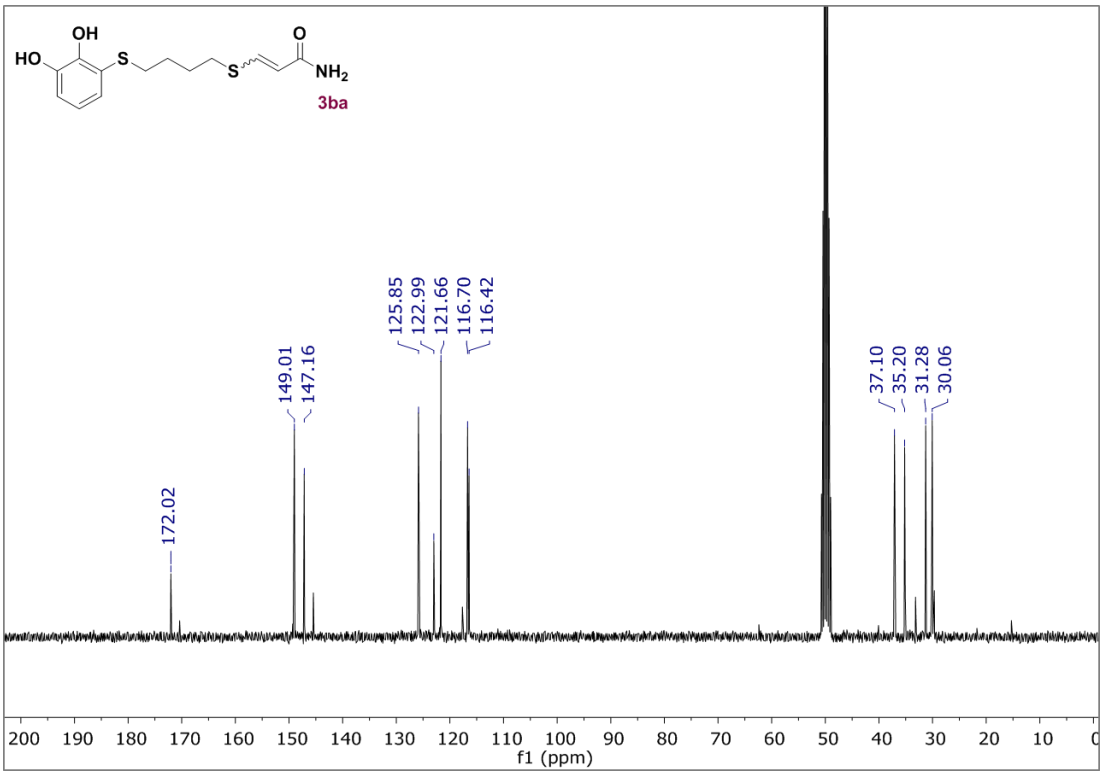


Figure S7. ^{13}C NMR of 3-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)acrylamide (**3ba**) in CD_3OD.

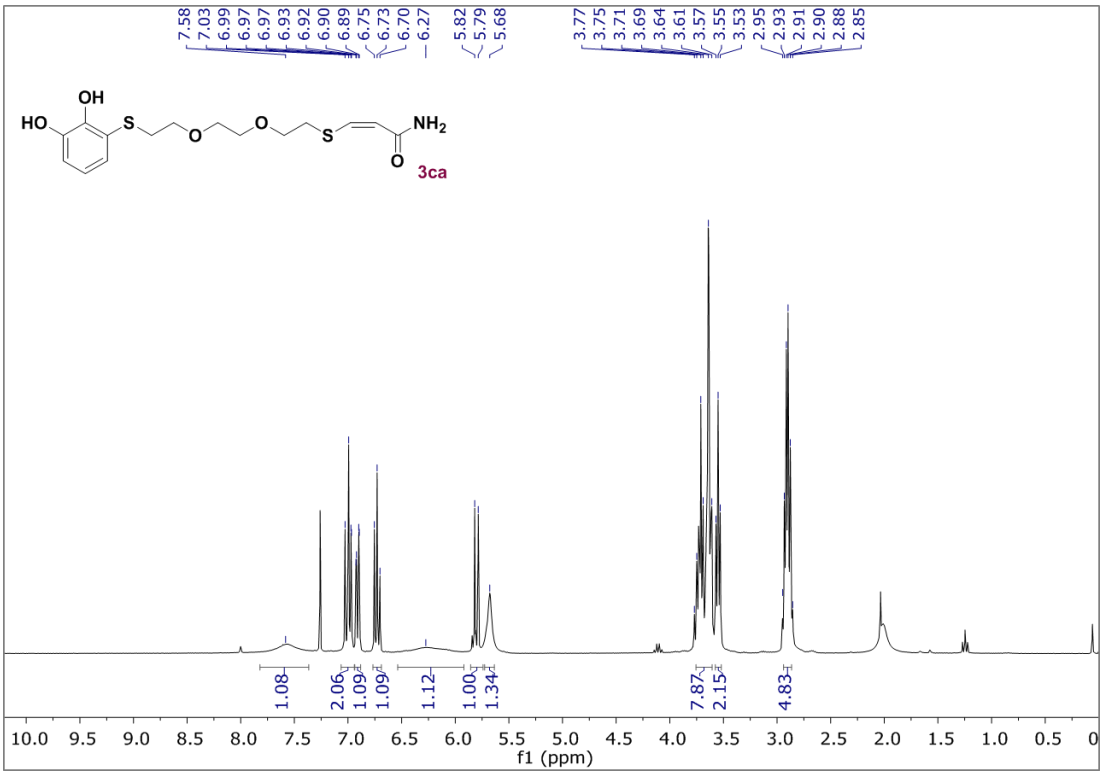


Figure S8. ^{1}H NMR of (*Z*)-3-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy)ethoxy) ethyl)thio) acrylamide (**3ca**) in $CDCl_3$.

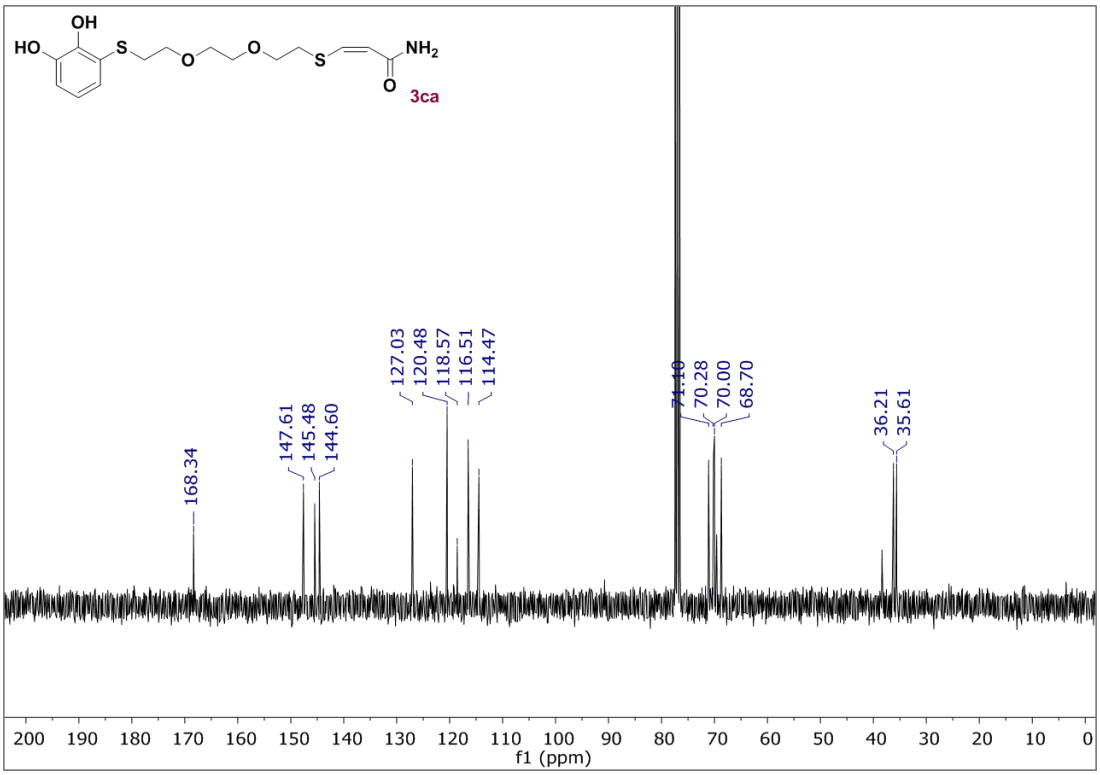


Figure S9. ^{1}H NMR of (*Z*)-3-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy)ethoxy)ethyl)thio) acrylamide (**3ca**) in $CDCl_3$.

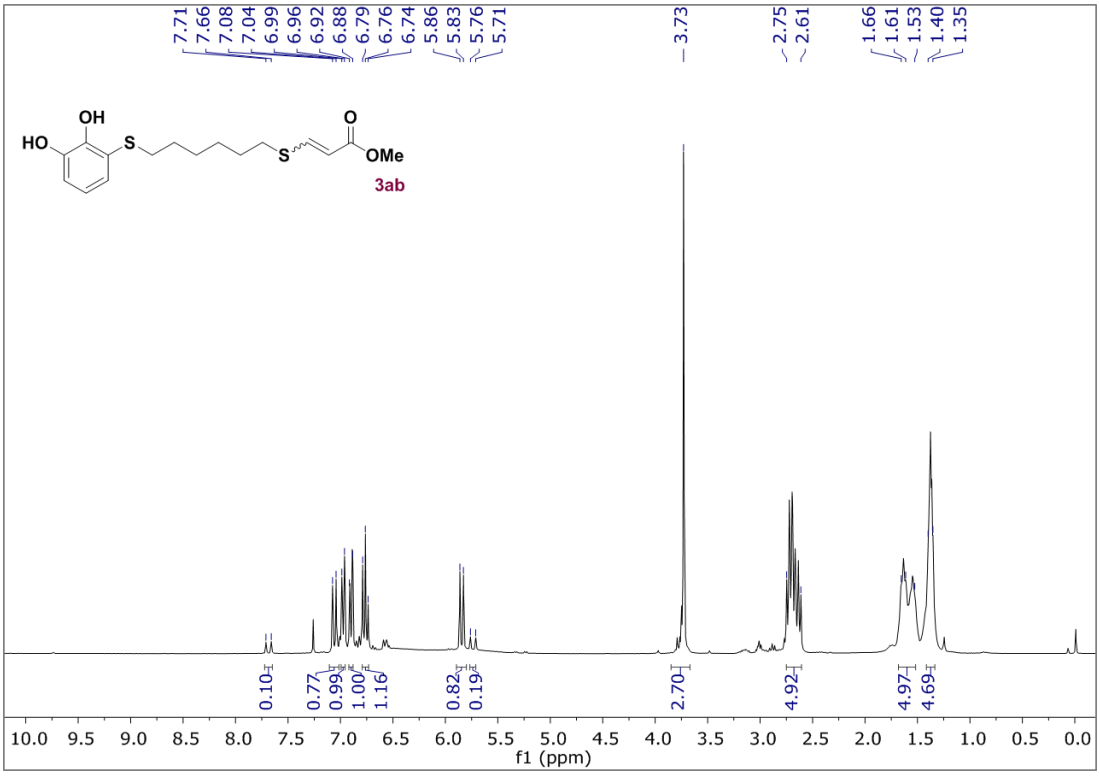


Figure S10. ^{1}H NMR of Methyl-3-((6-((2,3-dihydroxyphenyl)thio)hexyl)thio)acrylate (**3ab**) in $CDCl_3$.

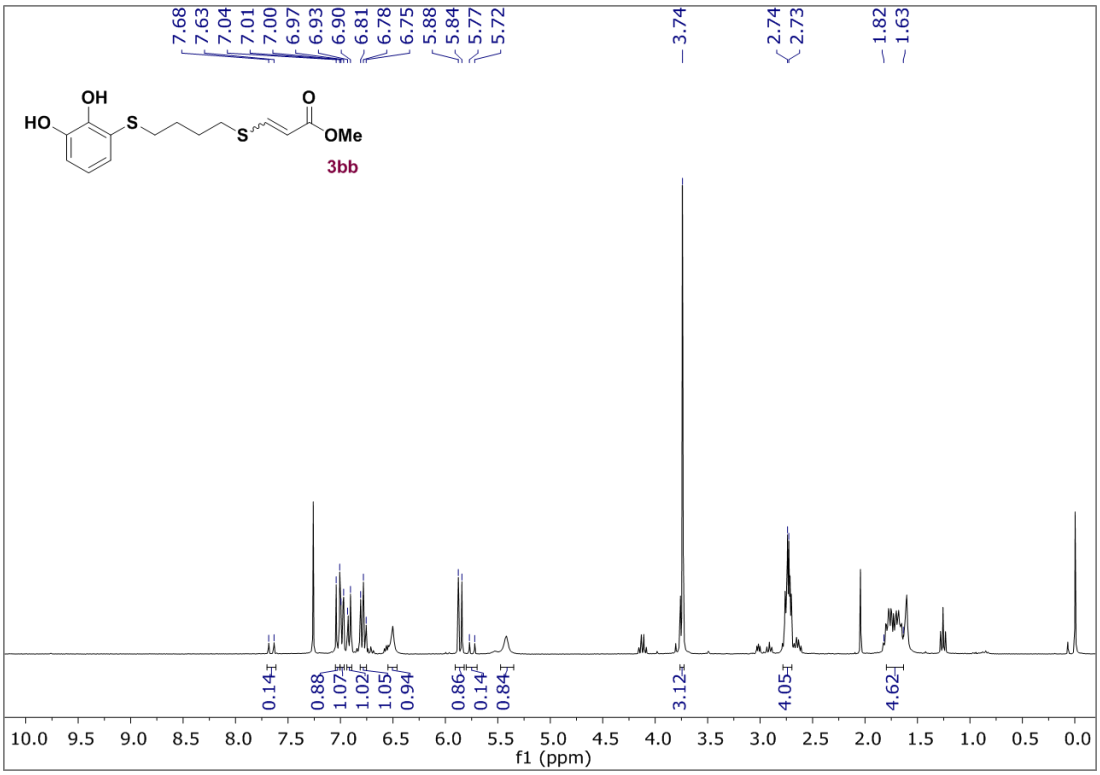


Figure S11. ^{1}H NMR of Methyl-3-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)acrylate (**3bb**) in $CDCl_3$.

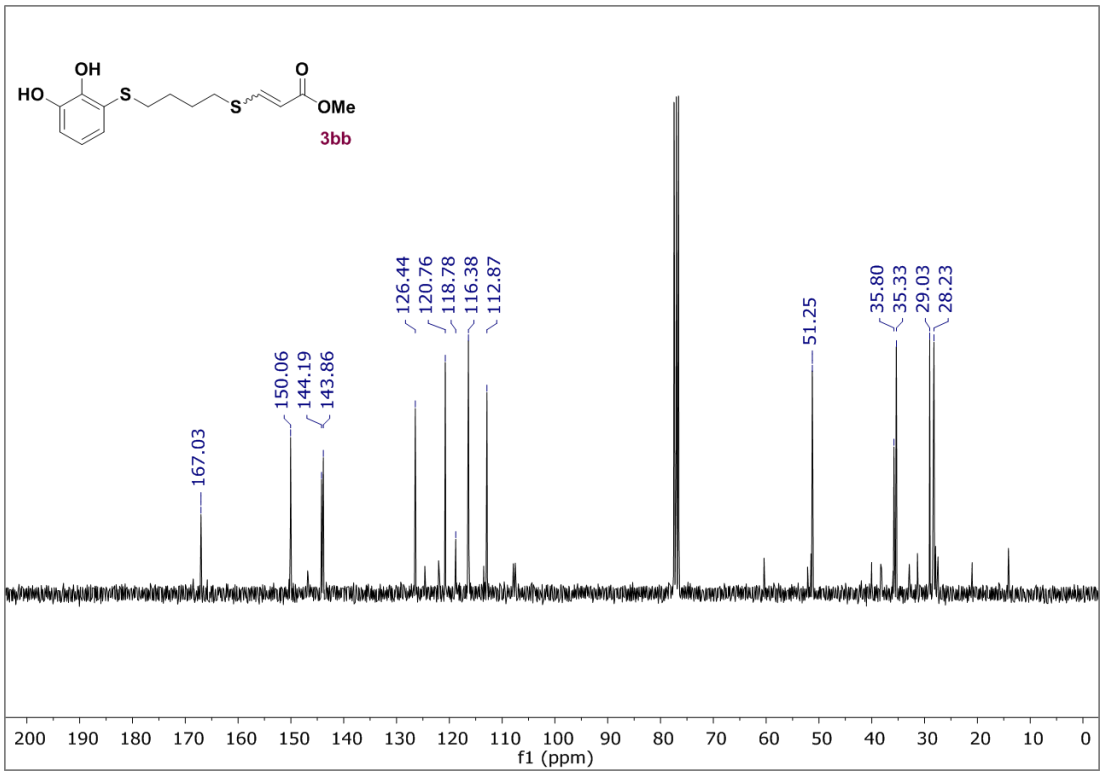


Figure S12. ^{13}C NMR of Methyl-3-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)acrylate (**3bb**) in $CDCl_3$.

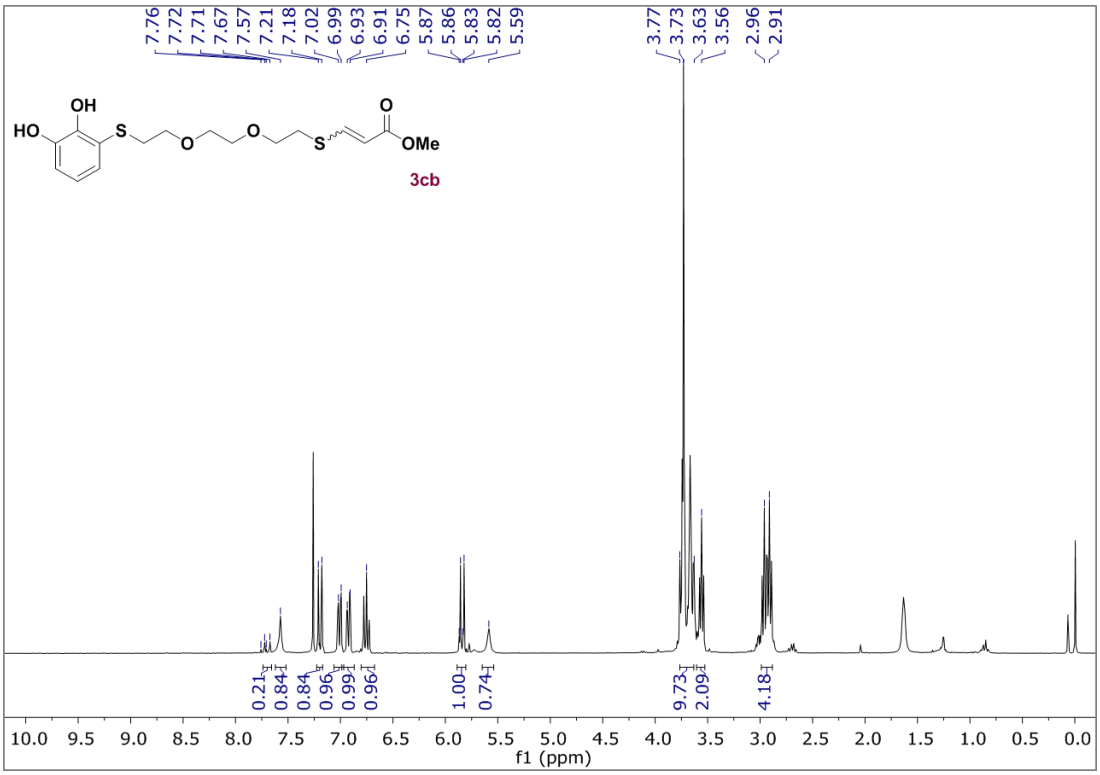


Figure S13. ^{13}C NMR of Methyl-3-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy)ethoxy) ethyl)thio)acrylate (**3cb**) in $CDCl_3$.

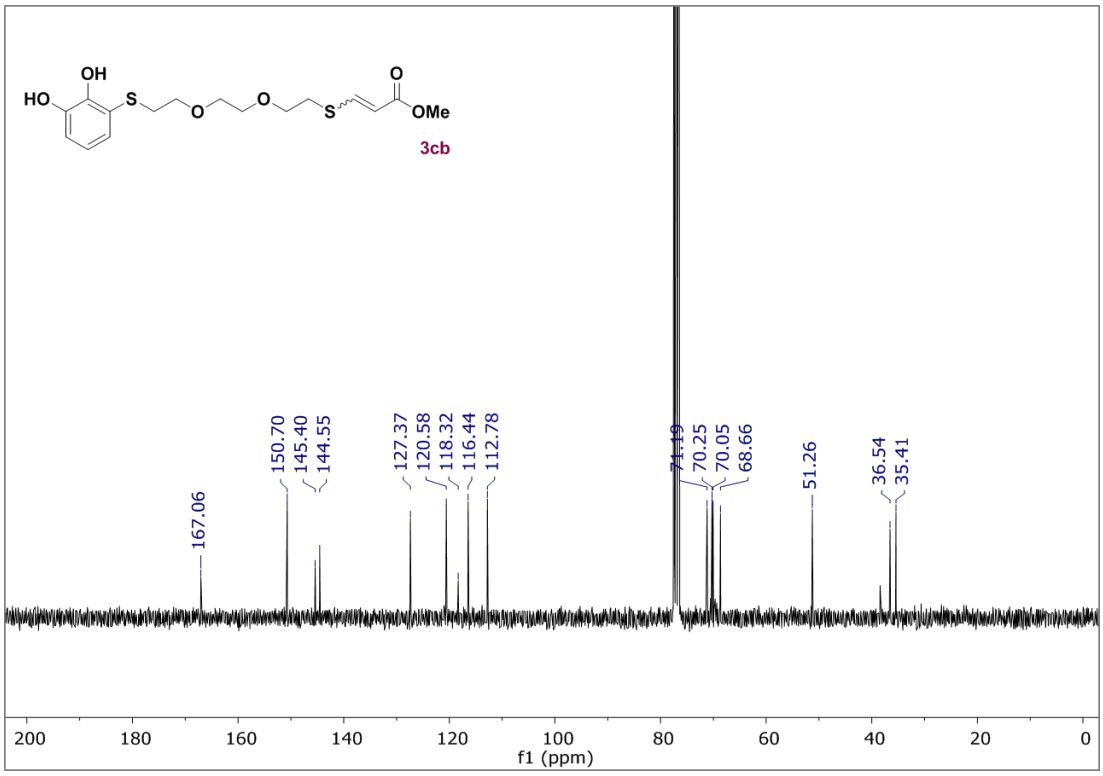


Figure S14. ^{13}C NMR of Methyl-3-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy)ethoxy) ethyl)thio)acrylate (**3cb**) in $CDCl_3$.

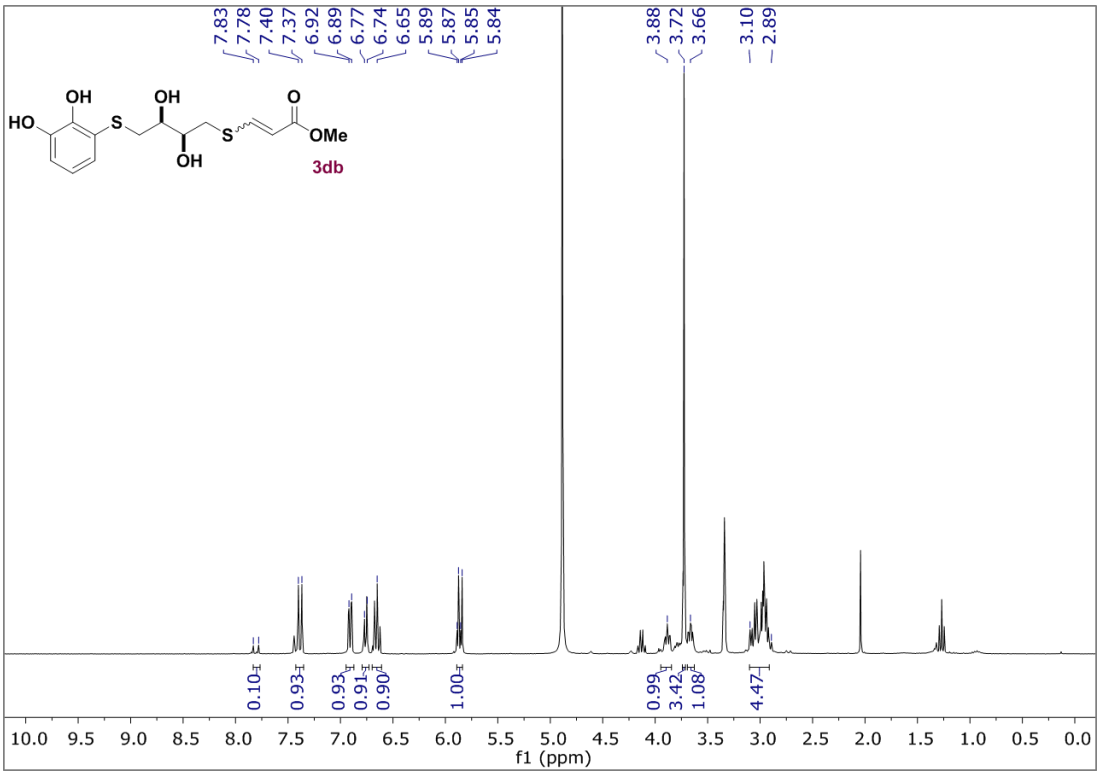


Figure S15. ^{1}H NMR of Methyl-3-(((*2R**,*3R**)-4-((2,3-dihydroxyphenyl)thio)-2,3-dihydroxybutyl)thio)acrylate (**3db**) in CD_3OD.

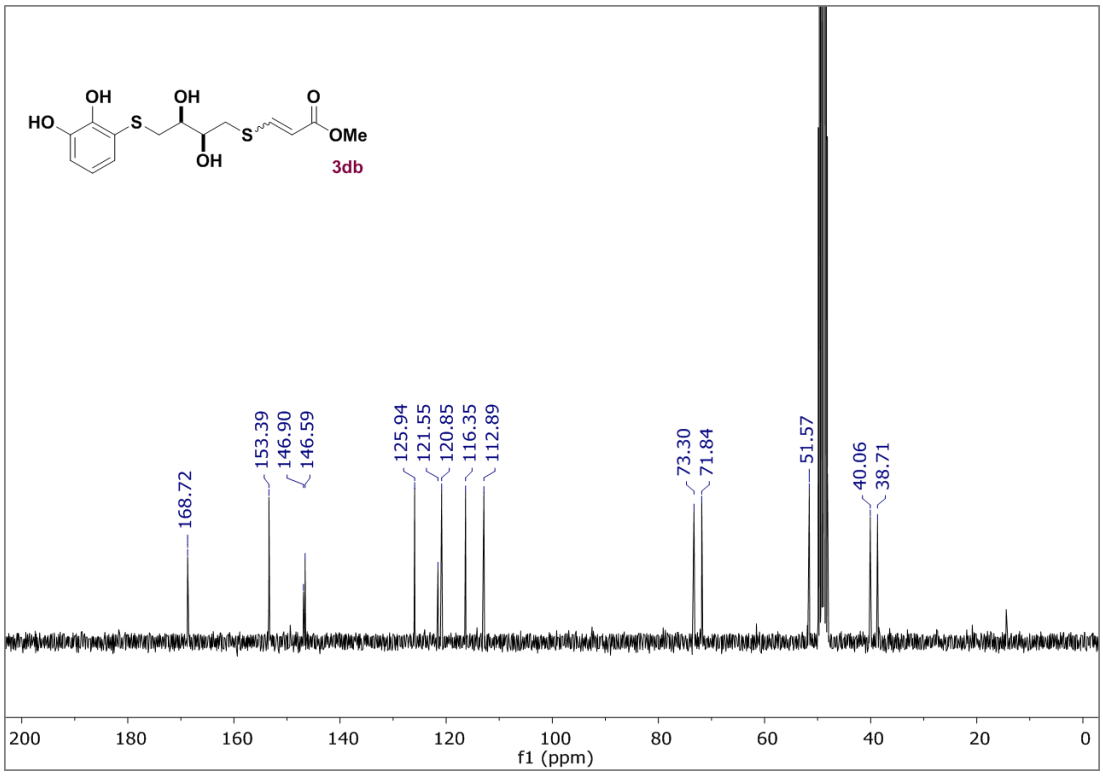


Figure S16. ^{13}C NMR of Methyl-3-(((*2R**,*3R**)-4-((2,3-dihydroxyphenyl)thio)-2,3-dihydroxybutyl)thio)acrylate (**3db**) in CD_3OD.

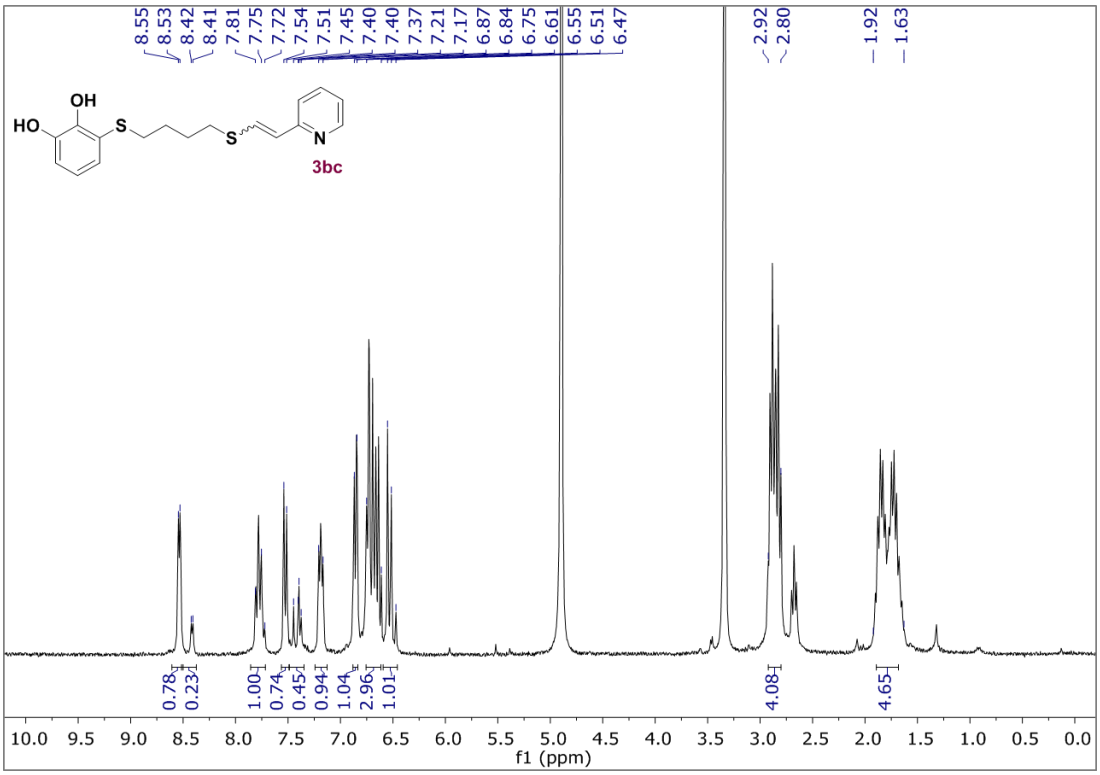


Figure S17. ^{1}H NMR of 3-((4-((2-(15yridine-2-yl)vinyl)thio)butyl)thio)benzene-1,2-diol (**3bc**) in CD_3OD.

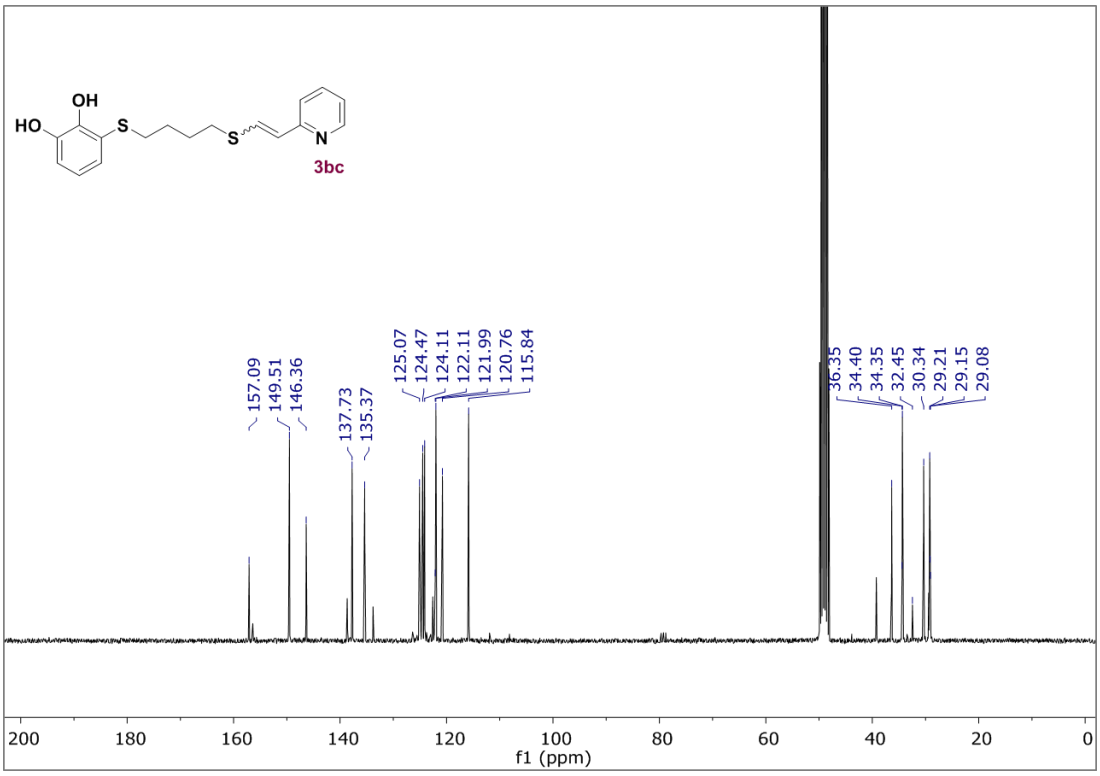


Figure S18. ^{13}C NMR of 3-((4-((2-(pyridine-2-yl)vinyl)thio)butyl)thio)benzene-1,2-diol (**3bc**) in CD_3OD.

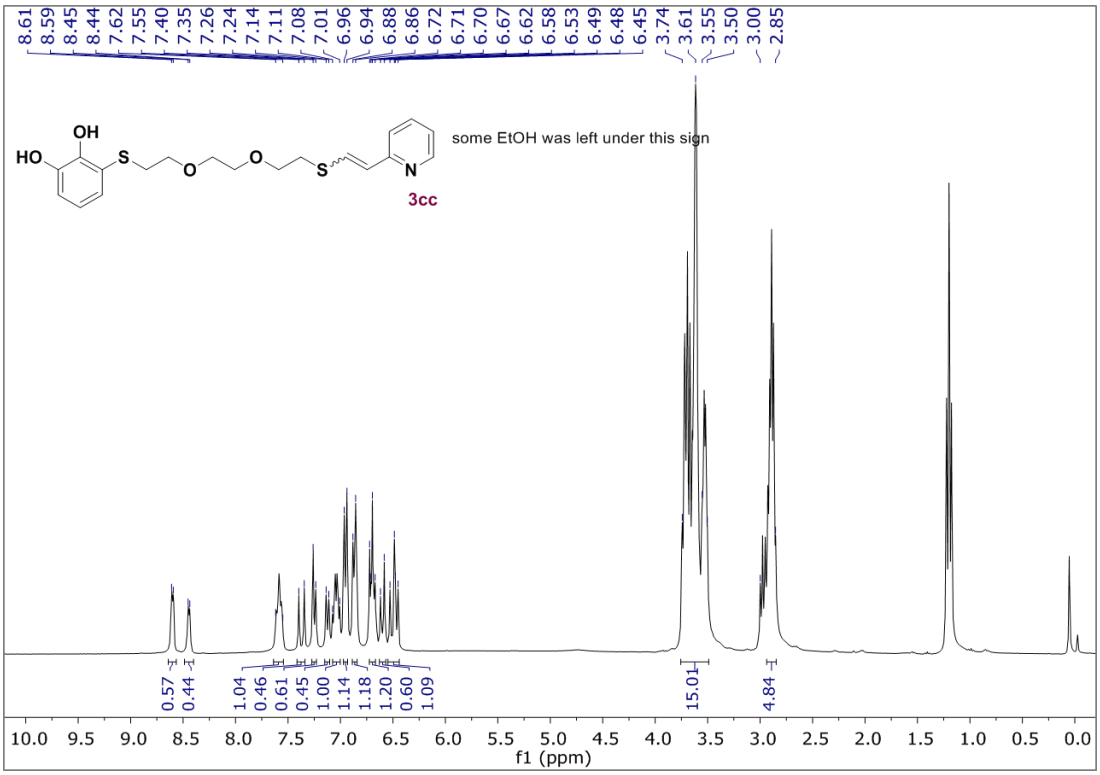


Figure S19. ^{1}H NMR of 3-((2-(2-(2-((2-(pyridine-2-yl)vinyl)thio)ethoxy)ethoxy)ethyl) thio)benzene-1,2-diol (**3cc**) in $CDCl_3$.

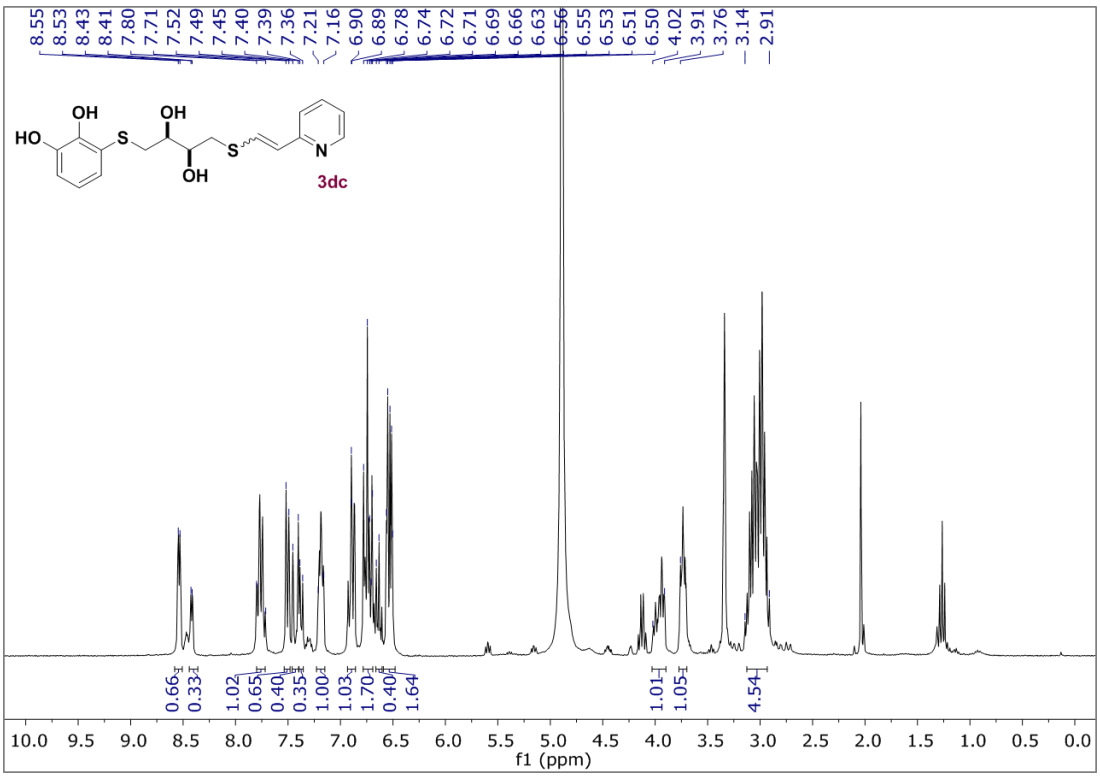


Figure S20. ^{1}H NMR of 3-(((*2R**,*3R**)-2,3-dihydroxy-4-((2-(pyridine-2-yl)vinyl)thio) butyl)thio)benzene-1,2-diol (**3dc**) in CD_3OD.

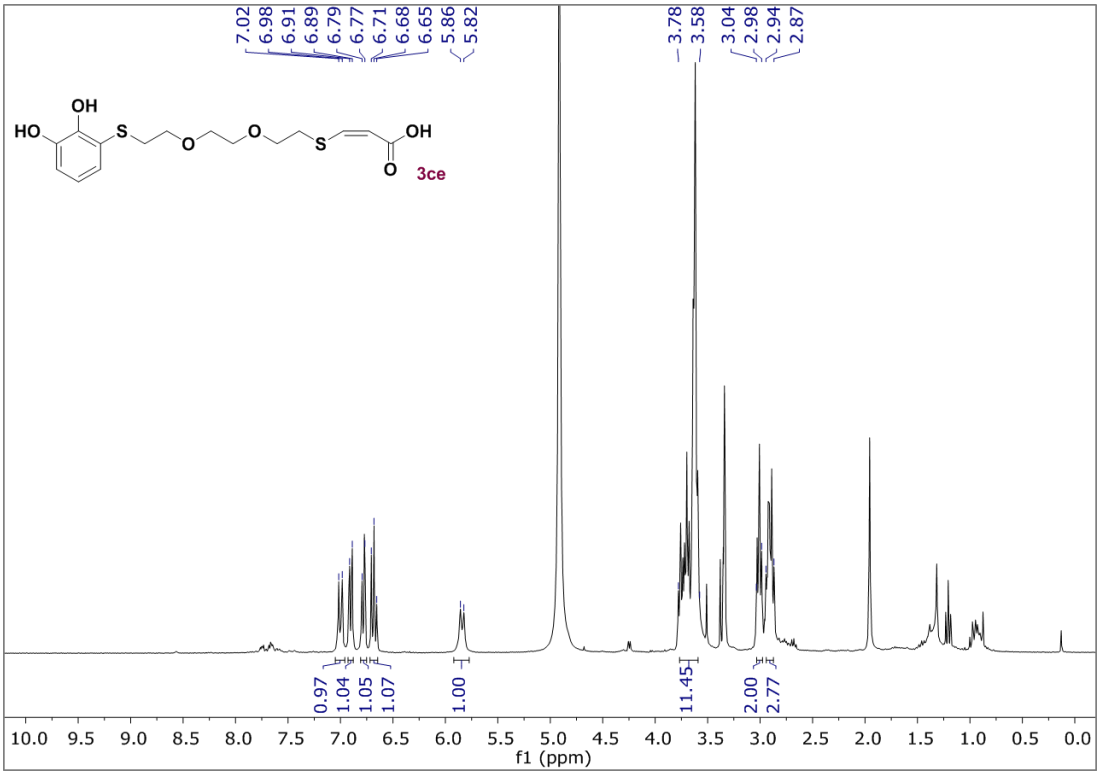


Figure S21. ^{1}H NMR of (*Z*)-3-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy)ethoxy) ethyl)thio)acrylic acid (**3ce**) in CD_3OD.

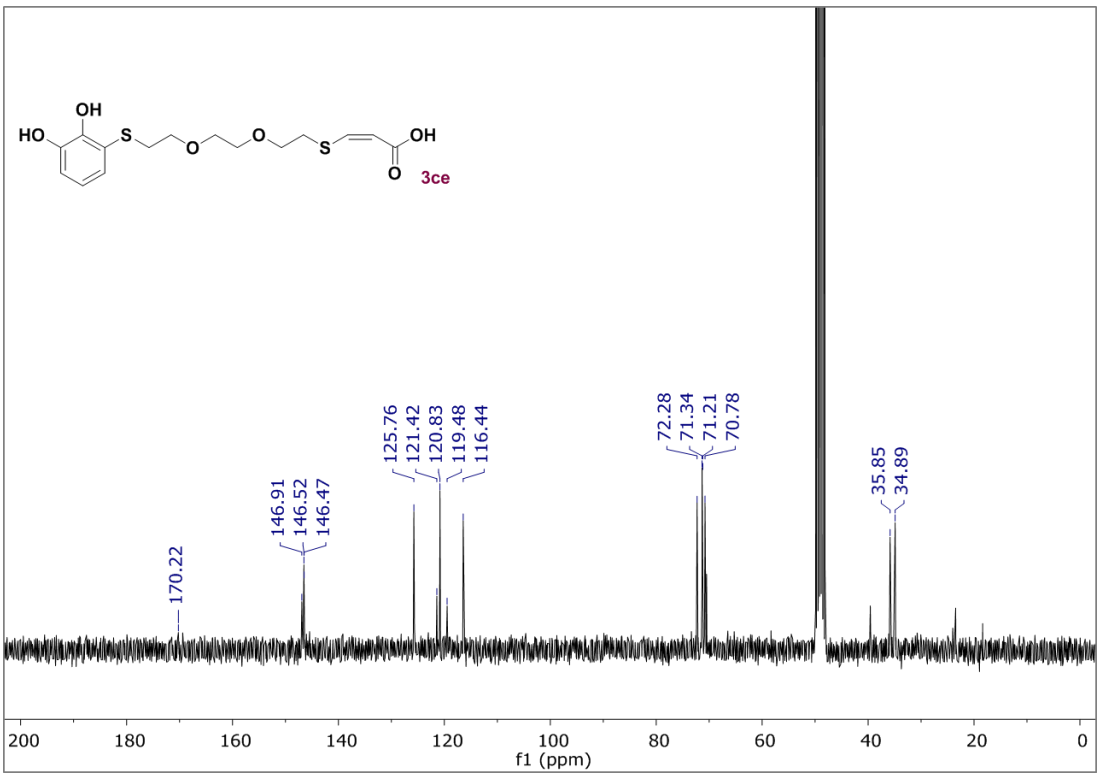


Figure S22. ^{13}C NMR of (*Z*)-3-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy)ethoxy) ethyl)thio)acrylic acid (**3ce**) in CD_3OD.

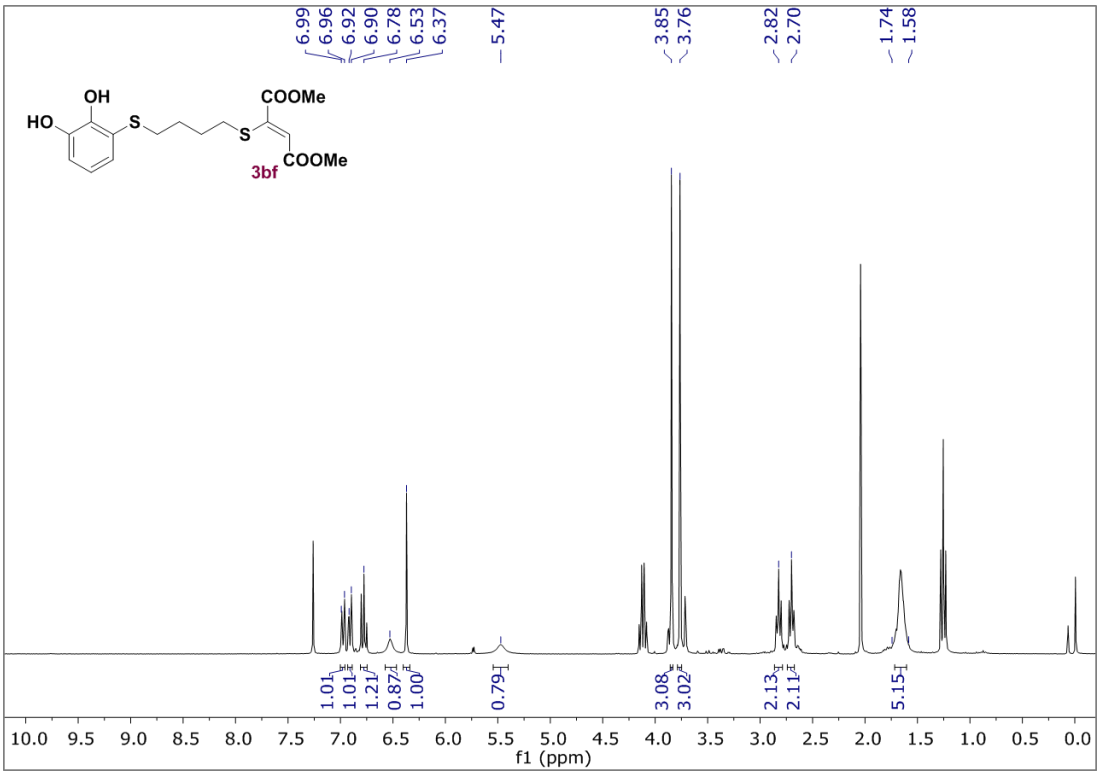


Figure S23. ^{1}H NMR of (*Z*)-dimethyl 2-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)but-2-enedioate (**3bf**) in $CDCl_3$.

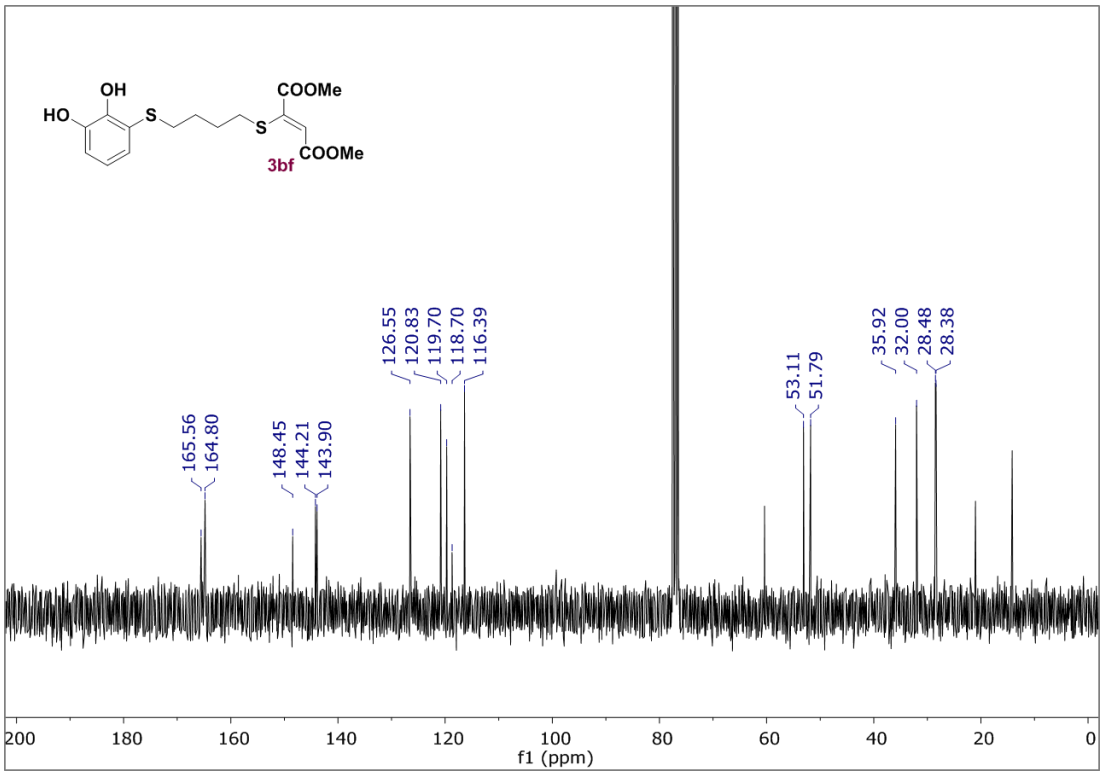


Figure S24. ^{13}C NMR of (*Z*)-dimethyl 2-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)but-2-enedioate (**3bf**) in $CDCl_3$.

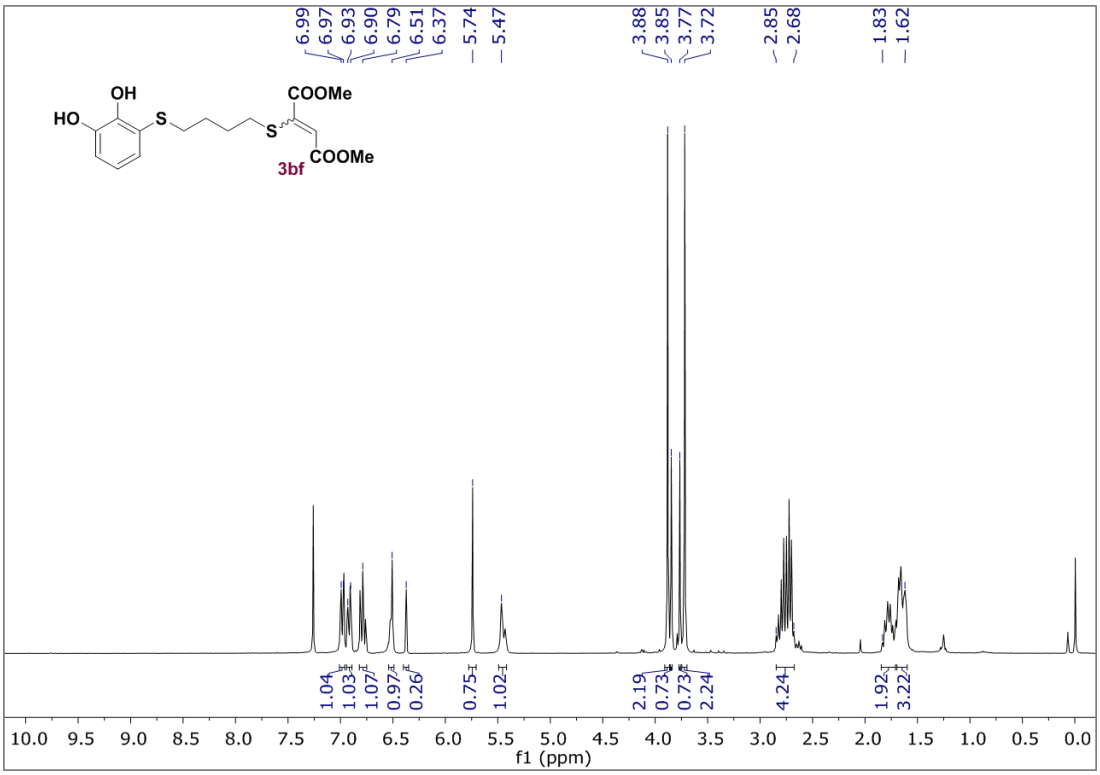


Figure S25. ^{1}H NMR of Dimethyl 2-((4-((2,3-dihydroxyphenyl)thio)butyl)thio)but-2-enedioate (**3bf**) in $CDCl_3$.

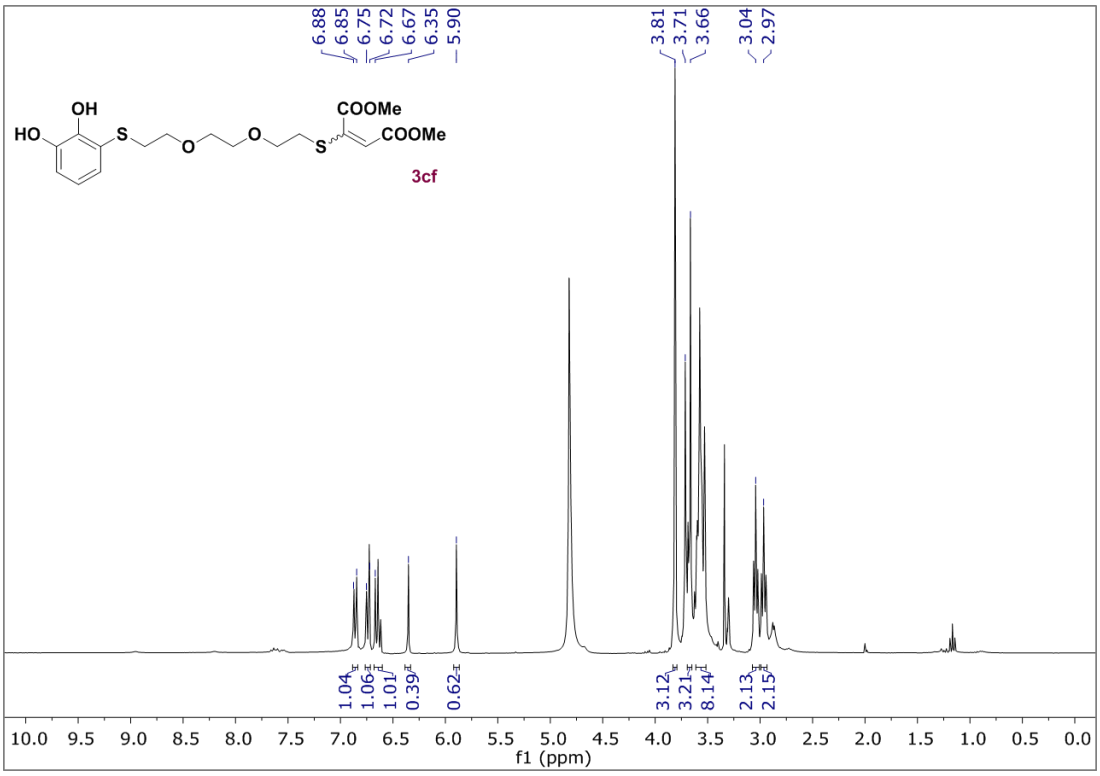


Figure S26. ^{13}H NMR of Dimethyl 2-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy) ethoxy)ethyl)thio)but-2-enedioate (**3cf**) in CD_3OD.

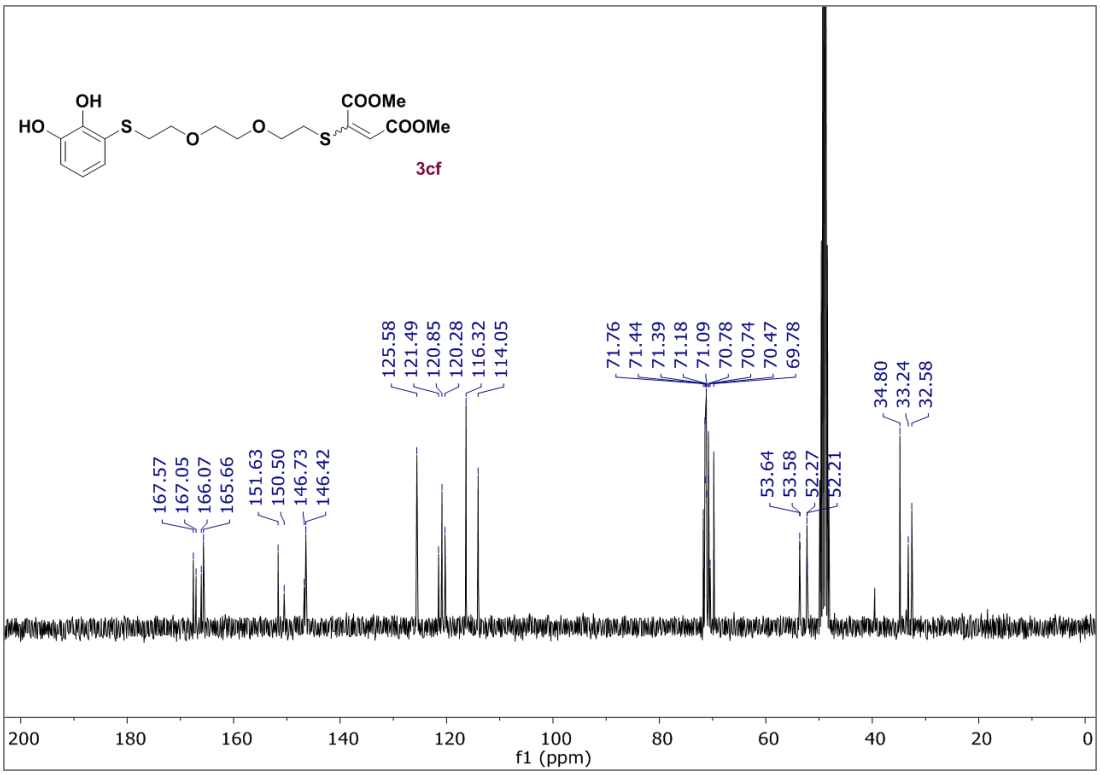


Figure S27. ^{13}H NMR of Dimethyl 2-((2-(2-(2-((2,3-dihydroxyphenyl)thio)ethoxy) ethoxy)ethyl)thio)but-2-enedioate (**3cf**) in CD_3OD.

References

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