Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Thiol-Michael Click Chemistry: Facile Access to a Library of Functional *exo*-7-Oxanorbornenes and their Ring-Opening Metathesis (Co)Polymerization

Meina Liu, Johannes van Hensbergen, Robert P. Burford* and Andrew B. Lowe *

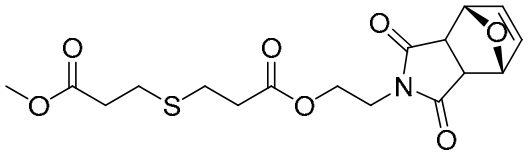
Centre for Advanced Macromolecular Design (CAMD), School of Chemical Engineering,

University of New South Wales, Kensington, Sydney, New South Wales, Australia 2052

Experimental and characterization details

Synthesis of *exo*-7-oxanorbornene monomers

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((3-methoxy-3-oxopropyl)thio)propanoate (**DT1**)*

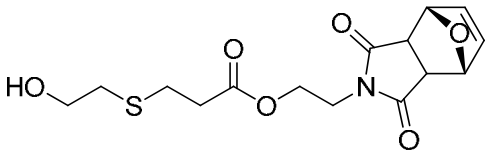


DT1

Using **C** (0.263 g, 1.0 mmol) and methyl-3-mercaptopropionate **T1** (0.11 mL, 1.0 mmol) were reacted for 3 h, **DT1** was isolated as a colorless syrup (0.36 g, 94% yield).

DT1: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.46-2.56 (m, 4H), 2.66-2.73 (m, 4H), 2.82 (s, 2H), 3.62 (s, 3H), 3.66-3.69 (m, 2H), 4.15-4.19 (m, 2H), 5.17 (t, *J* = 0.9 Hz, 2H), 6.46 (t, *J* = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 26.24, 26.45, 34.16, 37.36, 47.16, 51.46, 60.48, 80.55, 136.30, 171.07, 171.84, 175.75. HRMS: calcd. for $C_{17}H_{21}NO_7S$ [M+$Na^{+\cdot}$]: 406.0936, found: 406.0931. IR (neat): υ = 3460, 2954, 2161, 1774, 1731, 1695 cm^{-1}.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((2-hydroxyethyl)thio)propanoate (**DT2**)*



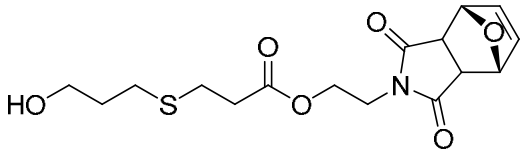
DT2

Using **C** (0.263 g, 1.0 mmol) and 2-mercaptoethanol **T2** (0.06 mL, 1.0 mmol) were reacted for 6 h, **DT2** was isolated as a white solid (0.25 g, 73% yield).

DT2: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.49-2.54 (m, 2H), 2.62-2.73 (m, 4H), 2.83 (s, 2H), 2.92 (s, 1H), 3.67-3.70 (m, 4H), 4.19 (t, *J* = 5.2 Hz, 2H), 5.19 (t, *J* = 1.0 Hz, 2H), 6.46 (t,

J = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 26.25, 34.42, 34.92, 37.60, 47.23, 60.53, 60.63, 80.67, 136.41, 171.50, 176.27. HRMS: calcd. for $C_{15}H_{19}NO_6S$ [M+Na^+]: 364.0831, found: 364.0819. IR (neat): υ = 3490, 3447, 3010, 2962, 1776, 1766, 1698 cm^{-1}. mp: 72-74 ℃.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((3-hydroxypropyl)thio)propanoate (**DT3**)*

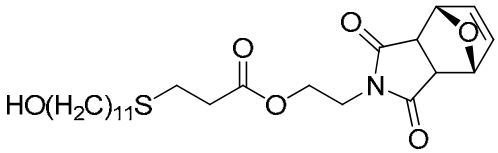


DT3

Using **C** (0.263 g, 1.0 mmol) and 3-mercapto-1-propanol **T3** (0.087 mL, 1.0 mmol) were reacted for 8 h, **DT3** was isolated as a white solid (0.29 g, 82% yield).

DT3: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.71-1.80 (m, 2H), 2.47-2.71 (m, 7H), 2.83 (s, 2H), 3.62-3.70 (m, 4H), 4.18 (t, *J* = 5.3 Hz, 2H), 5.19 (t, *J* = 0.9 Hz, 2H), 6.47 (t, *J* = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 26.33, 28.19, 31.78, 34.29, 37.55, 47.23, 60.54, 60.87, 80.64, 136.32, 171.39, 176.00. HRMS: calcd. for $C_{16}H_{21}NO_6S$ [M+Na^+]: 378.0987, found: 378.0976. IR (neat): υ = 3526, 3448, 3010, 2963, 2950, 2939, 2928, 2864, 1766, 1748, 1732, 1699, 1470, 1449, 1430 cm^{-1}. mp: 64-65 □.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((11-hydroxyundecyl)thio)propanoate (**DT4**)*

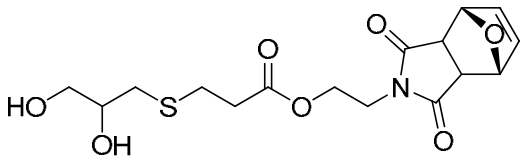


DT4

Using **C** (0.263 g, 1.0 mmol) and 11-mercapto-1-undecanol **T4** (0.204 g, 1.0 mmol) were reacted for 8 h, **DT4** was isolated as a white solid (0.43 g, 92% yield).

DT4: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.20-1.33 (m, 18H), 1.68 (s, 1H), 2.41-2.51 (m, 4H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.81 (s, 2H), 3.55 (t, *J* = 6.7 Hz, 2H), 3.69 (t, *J* = 5.2 Hz, 2H), 4.18 (t, *J* = 4.8 Hz, 2H), 5.19 (t, *J* = 0.9 Hz, 2H), 6.45 (t, *J* = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 25.61, 26.52, 28.72, 29.05, 29.27, 29.34, 29.37, 29.41, 31.86, 32.66, 34.56, 37.66, 47.34, 60.63, 62.78, 80.80, 136.48, 171.54, 175.95. HRMS: calcd. for $C_{24}H_{37}NO_6S$ [M+$Na^{+\cdot}$]: 490.2239, found: 490.2225. IR (neat): υ = 3548, 3010, 2918, 2849, 1704, 1470, 1447 cm^{-1}. mp: 87-88 ^{o}C.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((2,3-dihydroxypropyl)thio)propanoate (**DT5**)*



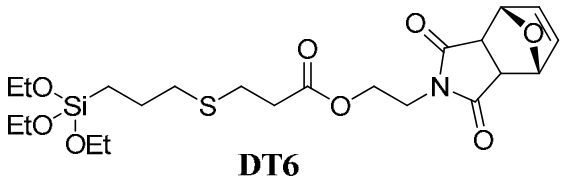
DT5

Using **C** (0.263 g, 1.0 mmol) and 3-mercapto-1,2-propanediol **T5** (0.084 mL, 1.0 mmol) were reacted for 8 h, **DT5** was isolated as a white solid (0.374 g, 95% yield).

DT5: ^{1}H NMR (300 MHz, $MeOD_3$, ppm): δ = 2.53-2.60 (m, 3H), 2.67-2.80 (m, 3H), 2.96 (s, 2H), 3.49-3.61 (m, 2H), 3.72-3.75 (m, 3H), 4.23 (t, *J* = 5.1 Hz, 2H), 4.79 (s, 2H), 5.18 (s, 2H), 6.56 (s, 2H); ^{13}C NMR (75 MHz, MeOD, ppm): δ = 28.26, 35.74, 36.20, 38.65, 48.75, 61.80, 65.94, 72.73, 82.23, 137.65, 173.29, 178.37. HRMS: calcd. for $C_{16}H_{21}NO_7S$ [M+$Na^{+\cdot}$]: 394.0936, found: 394.0926. IR (neat): υ = 3368, 3015, 1774, 1726, 1692, 1435, 1405, 1337, 1303, 1245, 1187 cm^{-1}.

mp: 84-86 □.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((3-(triethoxysilyl)propyl)thio)propanoate (**DT6**)*

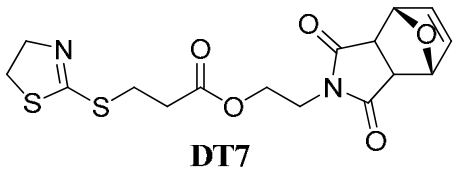


DT6

Using **C** (0.263 g, 1.0 mmol) and 3-mercaptopropyltriethoxysilane **T6** (0.24 mL, 1.0 mmol) were reacted for 3 h, **DT6** was isolated as a colorless oil liquid (0.43 g, 86% yield).

DT6: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.62-0.67 (m, 2H), 1.15 (t, *J* = 7.0 Hz, 9H), 1.56-1.66 (m, 2H), 2.44-2.50 (m, 4H), 2.62-2.68 (m, 2H), 2.81 (s, 2H), 3.66-3.69 (m, 2H), 3.71-3.78 (m, 6H), 4.15-4.19 (m, 2H), 5.17 (t, *J* = 1.0 Hz, 2H), 6.46 (t, *J* = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 9.45, 17.98, 22.78, 26.12, 34.26, 34.59, 37.41, 47.13, 58.02, 60.39, 80.58, 136.23, 171.30, 175.76. HRMS: calcd. for $C_{22}H_{35}NO_8SSi$ [M+$Na^{+\cdot}$]: 524.1750, found: 524.1738. IR (neat): υ = 3469, 3084, 2973, 2926, 1777, 1737, 1699, 1429, 1397 cm^{-1}.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((4,5-dihydrothiazol-2-yl)thio)propanoate (**DT7**)*

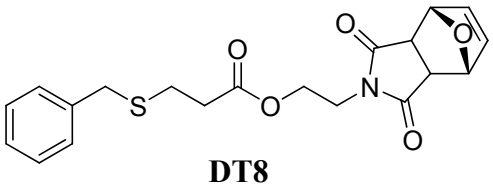


DT7

Using **C** (0.263 g, 1.0 mmol) and 2-thiazoline-2-thiol **T7** (0.119 g, 1.0 mmol) were reacted for 24 h, **DT7** was isolated as a yellow solid (0.21 g, 55% yield).

DT7: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.67 (t, *J* = 6.4 Hz, 2H), 2.83 (s, 2H), 3.20-3.25 (m, 2H), 3.70 (t, *J* = 5.2 Hz, 2H), 3.91 (t, *J* = 6.5 Hz, 2H), 4.12 (t, *J* = 7.8 Hz, 2H), 4.19 (t, *J* = 5.4 Hz, 2H), 5.20 (t, *J* = 0.9 Hz, 2H), 6.46 (t, *J* = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 27.70, 31.37, 37.59, 44.63, 47.49, 57.98, 61.01, 80.91, 136.49, 171.30, 176.06, 197.08. HRMS: calcd. for $C_{16}H_{18}N_2O_5S_2$ [M+$H^{+\cdot}$]: 383.0735, found: 383.0724. IR (neat): υ = 3453, 2947, 1776, 1731, 1693, 1489, 1456 cm^{-1}. mp: 125-126 □.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-(benzylthio)propanoate (**DT8**)*

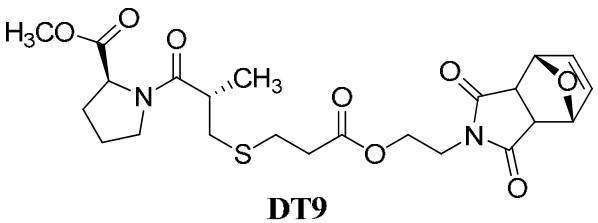


DT8

Using **C** (0.263 g, 1.0 mmol) and benzyl mercaptan **T8** (0.117 mL, 1.0 mmol) were reacted for 1 h, **DT8** was isolated as a white solid (0.35 g, 91% yield).

DT8: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.40-2.46 (m, 2H), 2.53-2.58 (m, 2H), 2.74 (s, 2H), 3.62-3.66 (m, 4H), 4.12-4.16 (m, 2H), 5.13 (t, *J* = 0.9 Hz, 2H), 6.39 (t, *J* = 0.9 Hz, 2H), 7.11-7.22 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 25.76, 33.97, 35.90, 37.43, 47.22, 60.47, 80.61, 126.80, 128.27, 128.62, 136.25, 137.82, 171.25, 175.74. HRMS: calcd. for $C_{20}H_{21}NO_5S$ [$M+H^{+\cdot}$]: 388.1219, found: 388.1203. IR (neat): υ = 3447, 3003, 2959, 2920, 2161, 1772, 1731, 1695, 1604, 1563, 1496, 1435, 1406, 1373, 1352, 1341, 1285, 1272, 1240, 1193 cm^{-1}. mp: 81-82 □.

*Preparation of (2S)-methyl 1-((2R)-3-((3-(2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl)ethoxy)-3-oxopropyl)thio)-2-methylpropanoyl)pyrrolidine-2-carboxylate (**DT9**)*



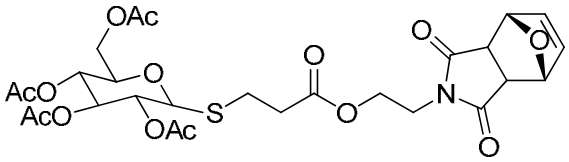
DT9

Using **C** (0.263 g, 1.0 mmol) and captopril methyl ester **T9** (0.231 g, 1.0 mmol) were reacted for 24 h, **DT9** was isolated as a yellow syrup (0.23 g, 47% yield).

DT9: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.14 (d, *J* = 6.5 Hz, 3H), 1.94-2.17 (m, 5H),

2.42-2.50 (m, 2H), 2.59-2.67 (m, 3H), 2.82 (s, 2H), 3.59 (t, J = 7.0 Hz, 2H), 3.64 (s, 3H), 3.66-3.70 (m, 2H), 4.17 (t, J = 5.3 Hz, 2H), 4.46 (dd, J = 4.2 Hz, 3.5 Hz, 1H), 5.18 (t, J = 0.9 Hz, 2H), 6.45 (t, J = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 17.20, 24.77, 27.38, 29.03, 34.54, 35.29, 37.63, 38.80, 46.92, 47.40, 52.01, 58.48, 60.68, 80.82, 136.42, 171.50, 172.72, 173.74, 175.92. IR (neat): υ = 3456, 2960, 2874, 1775, 1737, 1698, 1637, 1429, 1398, 1366, 1332, 1241, 1193 cm^{-1}.

*Preparation of (2S,3S,4S,5R,6R)-6-((3-(2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl)ethoxy)-3-oxopropyl)thio)tetrahydro-2H-pyran-2,3,4,5-tetrayl tetraacetate (**DT10**)*

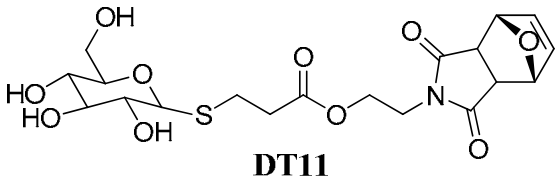


DT10

Using **C** (0.263 g, 1.0 mmol) and 2,3,4,6-tetra-*O*-acetyl-1-thio-*beta*-D-glucopyranoside **T10** (0.364 g, 1.0 mmol) were reacted for 24 h catalyzed by 1 mol % Me_2PPh, **DT10** was isolated as a colorless syrup (0.32 g, 51% yield); the reaction was stirred for 6 h catalyzed by 2 mol % Hexylamine, **DT10** was isolated as a colorless syrup (0.605 g, 96% yield)

DT10: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.93-2.01 (m, 12H), 2.57 (t, J = 7.5 Hz, 2H), 2.70-2.93 (m, 2H), 2.84 (s, 2H), 3.66-3.72 (m, 3H), 4.05-4.20 (m, 4H), 4.51 (d, J = 10.0 Hz, 1H), 4.90-5.04 (m, 2H), 5.15 (d, J = 9.3 Hz, 1H), 5.19 (t, J = 1.0 Hz, 2H), 6.48 (t, J = 1.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 20.20, 20.33, 24.74, 34.89, 37.30, 47.16, 60.51, 61.77, 67.94, 69.37, 73.35, 75.35, 80.57, 83.31, 136.23, 168.98, 169.03, 169.67, 170.23, 170.89, 175.78. HRMS: calcd. for $C_{27}H_{33}NO_{14}S$ [M+$Na^{+\cdot}$]: 650.1519, found:650.1507. IR (neat): υ = 3468, 2958, 1739, 1696, 1430, 1399, 1366, 1336, 1215 cm^{-1}.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-(((2R,3R,4S,5S,6S)-3,4,5,6-tetrahydroxytetrahydro-2H-pyran-2-yl)thio)propanoate (**DT11**)*

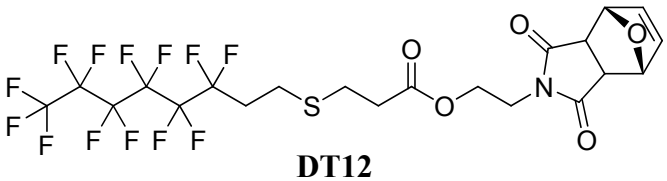


DT11

Using **C** (0.263 g, 1.0 mmol) and 1-thio-*beta*-D-glucose **T11** (0.196 g, 1.0 mmol) were reacted for 48 h catalyzed by 1 mol % Me_2PPh, **DT11** was isolated as a white solid (0.196 g, 43% yield); the reaction was stirred for 8 h catalyzed by 2 mol % Hexylamine, **DT11** was isolated as a colorless syrup (0. 42 g, 92% yield).

DT11: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.71 (t, *J* = 7.4 Hz, 2H), 2.86-3.05 (m, 2H), 3.03 (s, 2H), 3.21-3.41 (m, 7H), 3.68-3.93 (m, 5H), 4.23-4.32 (m, 2H), 4.24 (d, *J* = 9.0 Hz, 1H), 5.23 (t, *J* = 0.9 Hz, 2H), 6.61 (t, *J* = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 25.90, 36.38, 38.58, 48.71, 61.84, 62.92, 71.37, 74.21, 79.45, 81.92, 82.25, 87.16, 137.64, 173.49, 178.41. IR (neat): υ = 3394, 2926, 1772, 1734, 1690, 1432, 1400, 1370, 1335, 1244, 1191 cm^{-1}.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thio)propanoate (**DT12**)*



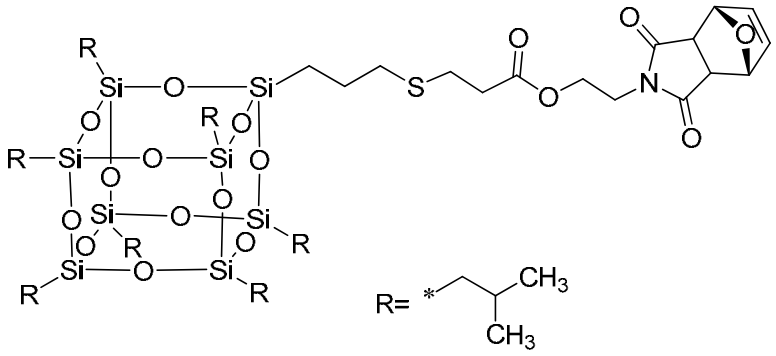
DT12

Using **C** (0.263 g, 1.0 mmol) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanethiol **T12** (0.380 g, 1.0 mmol) were reacted for 1 h, **DT12** was isolated as a white solid (0.61 g, 95% yield).

DT12: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.24-2.41 (m, 2H), 2.50 (t, *J* = 7.2 Hz, 2H),

2.65-2.75 (m, 4H), 2.79 (s, 2H), 3.68 (t, J = 5.2 Hz, 2H), 4.19 (t, J = 5.4 Hz, 2H), 5.17 (t, J = 0.9 Hz, 2H), 6.43 (t, J = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 22.42, 26.56, 31.83, 34.35, 37.63, 47.31, 60.81, 80.79, 110.90-122.78 (m, CF_2, CF_3), 136.38, 171.17, 175.96. ^{19}F {^{1}H} NMR (282 MHz, $CDCl_3$, ppm): δ = -81.15 (ttt, J = 3.0, 2.0, 2.8 Hz, 3F), -114.52 (m, 2F), -122.12 (m, 2F), -123.10 (s, 2F), -123.58 (m, 2F), -126.40 (m, 2F); ^{19}F NMR (282 MHz, $CDCl_3$, ppm): δ = -81.15 (ttt, J = 3.0, 2.0, 2.8 Hz, 3F), -114.52 (m, 2F), -122.11 (m, 2F), -123.10 (s, 2F), -123.59 (m, 2F), -126.40 (m, 2F). HRMS: calcd. for $C_{21}H_{18}NO_5SF_{13}$ [M+$Na^{+\cdot}$]: 666.0596, found: 666.0578. IR (neat): υ = 3066, 3008, 2954, 1775, 1750, 1694, 1435, 1404, 1364, 1347, 1334, 1216, 1181 cm^{-1}. mp: 68-70 □.

Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((3-(3,5,7,9,11,13,15-heptaisobutyl-2,4,6,8,10,12,14,16,17,18,19,20-dodecaoxa-1,3, 5,7,9,11,13,15-octasilapentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]icosan-1-yl)propyl)thio)propanoate ***(DT13)***



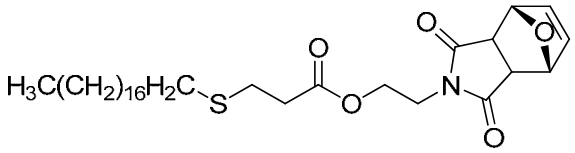
DT13

Using **C** (0.132 g, 0.5 mmol) and PSS-(3-mercapto)propyl-1-heptaisobutyl substituted **T13** (0.446 g, 0.5 mmol) were reacted for 3 h, **DT 13** was isolated as a light yellow syrup (0.52 g, 90% yield).

DT13: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.53 (dd, J_1 = J_2 = 1.5 Hz, 14H), 0.60-0.66 (m, 2H), 0.89 (d, J = 6.6 Hz, 42H), 1.55-1.66 (m, 2H), 1.72-1.86 (m, 7H), 2.43-2.50 (m, 4H), 2.62-2.67 (m, 2H), 2.80 (s, 2H), 3.68 (t, J = 5.6 Hz, 2H), 4.18 (t, J = 5.1 Hz, 2H), 5.18 (t, J = 0.9 Hz, 2H), 6.44 (t, J = 1.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 11.53, 22.38, 22.87, 23.75, 25.61, 26.31, 34.48, 34.75, 37.69, 47.41, 60.64, 80.81, 136.44, 171.49, 175.87.

HRMS: calcd. for $C_{44}H_{83}NO_{17}SSi_8$ [M+$Na^{+\cdot}$]: 1176.3434, found: 1176.3463. IR (neat): υ = 3460, 3003, 2960, 2920, 2160, 1772, 1728, 1695, 1604, 1563, 1496, 1433, 1406, 1373, 1352, 1341, 1285, 1272, 1240 cm^{-1}.

*Preparation of 2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl) ethyl 3-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)thio)propanoate (**DT14**)*

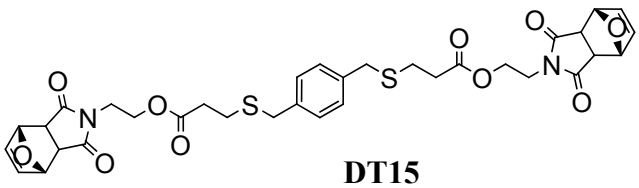


DT14

Using **C** (0.263 g, 1.0 mmol) and 1-octadecanethiol **T14** (0.34 mL, 1.0 mmol) were reacted for 8 h, **DT14** was isolated as a white solid (0.51 g, 93% yield).

DT14: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.81 (t, *J* = 6.8 Hz, 3H), 1.19 (s, 30H), 1.44-1.54 (m, 2H), 2.40-2.50 (m, 4H), 2.63-2.68 (m, 2H), 2.80 (s, 2H), 3.68 (t, *J* = 5.4 Hz, 2H), 4.18 (t, *J* = 5.4 Hz, 2H), 5.18 (t, *J* = 0.9 Hz, 2H), 6.44 (t, *J* = 0.9 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 13.94, 22.49, 26.43, 28.69, 29.04, 29.14, 29.33, 29.40, 29.44, 29.48, 31.72, 31.86, 34.46, 37.56, 47.30, 60.56, 80.70, 136.33, 171.41, 175.78. HRMS: calcd. for $C_{31}H_{51}NO_5S$ [M+$Na^{+\cdot}$]: 572.3386, found: 572.3392. IR (neat): υ = 3468, 2959, 1740, 1695, 1430, 1400, 1366, 1336, 1213 cm^{-1}. mp: 97-98 ℃.

*Preparation of bis(2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2 (3H)-yl)ethyl) 3,3'-((1,4-phenylenebis(methylene))bis(sulfanediyl))dipropanoate (**DT15**)*

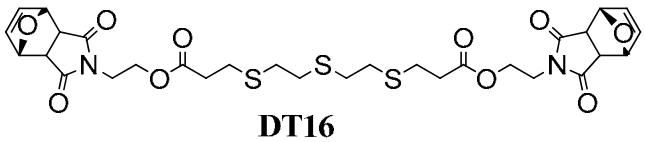


DT15

Using **C** (0.263 g, 1.0 mmol) and 1,4-benzenedimethanethiol **T15** (0.17 g, 1.0 mmol) were reacted for 1 h, **DT15** was isolated as a yellow syrup (0.49 g, 70% yield).

DT15: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.41-2.46 (m, 4H), 2.54-2.59 (m, 4H), 2.78 (s, 4H), 3.61 (s, 4H), 3.66 (t, *J* = 5.4 Hz, 4H), 4.15 (t, *J* = 5.1 Hz, 4H), 5.15 (t, *J* = 1.0 Hz, 4H), 6.43 (t, *J* = 0.9 Hz, 4H), 7.17 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 25.68, 33.88, 35.47, 37.33, 47.17, 60.42, 80.56, 128.82, 136.17, 136.58, 171.20, 175.81. HRMS: calcd. for $C_{34}H_{36}N_2O_{10}S_2$ [M+$Na^{+\cdot}$]: 719.1709, found: 719.1675. IR (neat): υ = 3481, 3006, 2962, 1770, 1735, 1686, 1515 cm^{-1}. mp: 97-98 □.

*Preparation of bis(2-((3aR,7aS)-1,3-dioxo-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindol-2(3H)-yl)ethyl) 3,3'-((thiobis(ethane-2,1-diyl))bis(sulfanediyl))dipropanoate (**DT16)***

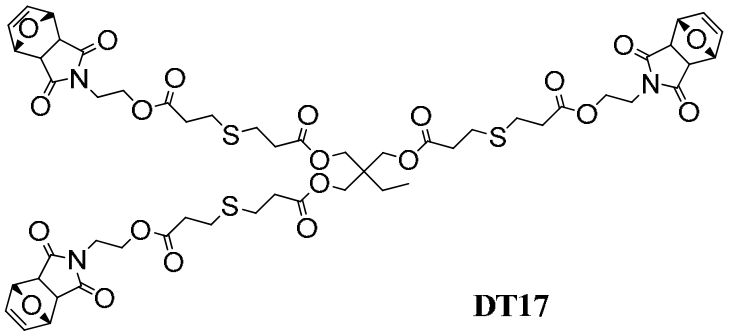


DT16

Using **C** (0.263 g, 1.0 mmol) and 2-mercaptoethylsulfide **T16** (0.13 mL, 1.0 mmol) were reacted for 8 h, **DT16** was isolated as a colorless syrup (0.56 g, 82% yield).

DT16: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.51 (t, *J* = 7.2 Hz, 4H), 2.66-2.75 (m, 12H), 2.85 (s, 4H), 3.69 (t, *J* = 5.3 Hz, 4H), 4.19 (t, *J* = 5.4 Hz, 4H), 5.20 (t, *J* = 0.9 Hz, 4H), 6.49 (t, *J* = 0.9 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 26.18, 31.53, 31.57, 34.23, 37.20, 47.02, 60.32, 80.44, 136.09, 170.90, 175.58. HRMS: calcd. for $C_{30}H_{36}N_2O_{10}S_3$ [M+$Na^{+\cdot}$]: 703.1430, found: 703.1418. IR (neat): υ = 3456, 2926, 1774, 1734, 1693, 1429, 1397, 1367, 1333, 1242, 1191 cm^{-1}.

*Preparation of (**DT17**)*

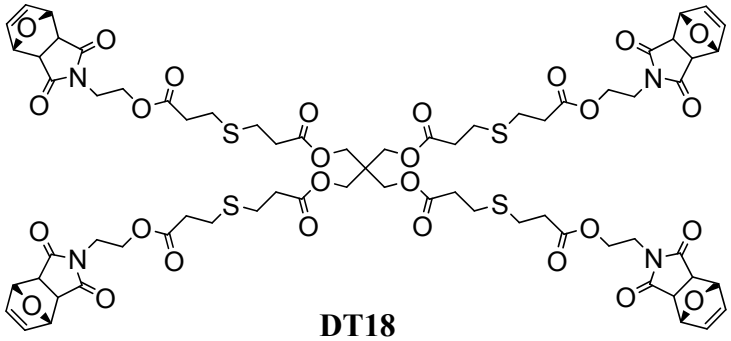


DT17

Using **C** (0.237 g, 0.9 mmol) and trimethylopropane tris(3-mercaptopropionate) **T17** (0.10 mL, 0.3 mmol) were reacted for 6 h, **DT17** was isolated as a colorless syrup (0.19 g, 53% yield).

DT17: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 0.80-0.85 (m, 3H), 1.34-1.46 (m, 2H), 2.47-2.60 (m, 12H), 2.66-2.73 (m, 12H), 2.81 (s, 6H), 3.69 (t, *J* = 5.2 Hz, 6H), 3.98-4.00 (m, 6H), 4.18 (t, *J* = 5.4 Hz, 6H), 5.19 (t, *J* = 1.0 Hz, 6H), 6.46 (t, *J* = 0.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 7.29, 22.78, 26.58, 26.80, 34.43, 37.69, 40.66, 47.42, 60.78, 63.82, 80.85, 136.50, 171.41, 171.92, 176.01. HRMS: calcd. for $C_{54}H_{65}N_3O_{21}S_3$ [M+Na^+]: 1210.3170, found: 1210.3161. IR (neat): υ = 3458, 2965, 2917, 2161, 1774, 1744, 1730, 1695 cm^{-1}.

*Preparation of (**DT18**)*



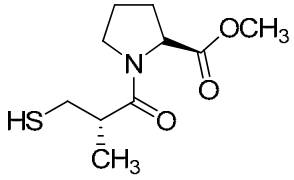
DT18

Using **C** (0.316 g, 1.2mmol) and pentaerythritol tetrakis(3-mercaptopropionate) **T18** (0.11 mL, 0.3 mmol) were reacted for 6 h, **DT18** was isolated as a colorless syrup (0.21g, 45%

yield).

DT18: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 2.47-2.52 (m, 8H), 2.54-2.73 (m, 24H), 2.82 (s, 8H), 3.68 (t, *J* = 5.2 Hz, 8H), 4.10 (s, 8H), 4.18 (t, *J* = 5.2 Hz, 8H), 5.19 (t, *J* = 1.0 Hz, 8H), 6.47 (t, *J* = 0.9 Hz, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ = 19.40, 26.34, 26.57, 34.32, 37.53, 38.05, 41.89, 47.23, 60.66, 61.98, 80.78, 136.41, 171.05, 171.26, 175.86. HRMS: calcd. for $C_{69}H_{80}N_4O_{28}S_4$ [M+H$^{+\cdot}$]: 1542.6514, found: 1542.3207. IR (neat): υ = 3458, 2992, 2161, 1774, 1733, 1727, 1694, 1476 cm^{-1}.

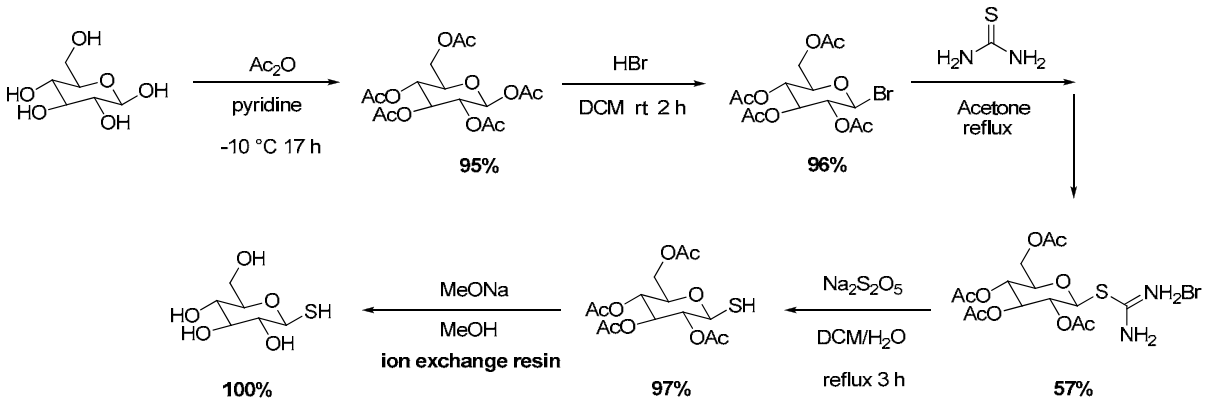
Synthesis of Captopril methyl ester (T9)



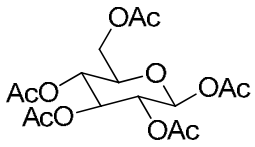
Captopril (5mmol, 1.09 g) was dissolved in methanol (25 mL). Thionyl chloride (1.0 mL, 13.5 mmol) was then added dropwise at 0 °C. The reaction mixture was heated at 60 °C for 4 h. The excess alcohol and thionyl chloride produced hydrogen chloride gas, and was removed in-vacuo to yield the crude ester. The crude product was purified by flash column chromatography on silica gel. The light yellow oil liquid was obtained in 82% yield.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.15 (d, *J* = 6.7 Hz, 3H), 1.48-1.54 (m, 1H), 1.82-2.42 (m, 5H), 2.66-2.90 (m, 2H), 3.58-3.71 (m, 2H), 3.66 (s, 3H), 4.47 (dd, J_1 = 4.5 Hz, J_2 = 4.5 Hz, 1H).

Synthesis of sugar derivatives T10 and T11



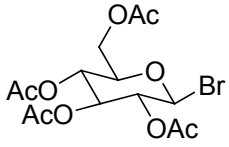
1,2,3,4,6-Penta-*O*-acetyl-α-D-glucopyranose



Freshly acetic anhydride (48 mL, 0.5 mol) was added dropwise to a stirred solution of α-glucose (12.0 g, 68 mmol) in anhydrous pyridine (100 mL) at –10 °C, and the stirring continued at the same temperature for 17 h. After addition of ice into the reaction mixture a powdery white solid precipitated. Filtration of the solid affords 25.1 g of 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranose (95% yield).

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.95, 1.96, 1.98, 2.03 (4 x s, 12H), 2.12 (s, 3H), 4.00-4.08 (m, 2H), 4.18-4.23 (m, 1H), 5.01-5.11 (m, 2H), 5.37-5.44 (m, 1H), 5.46 (d, J = 4.0 Hz, 1H).

2,3,4,6-Tetra-O-acetyl-*α*-D-galactopyranosyl bromide

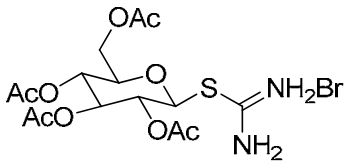


1,2,3,4,6-Pentaacetyl galactose (24.0 g, 62.0 mmol, 1 eq) was dissolved in DCM (120 mL). To

this, hydrogen bromide (33 % in acetic acid, 140 mL) was added. The reaction mixture was stirred under Ar at RT. After 2 hours, TLC (ethyl acetate/petrol 1:1) indicated the formation of product (R_f > 0.5) with complete consumption of the starting material (R_f = 0.5). The reaction mixture was partitioned between DCM (100 mL) and H_2O (100 mL) and the aqueous phase was re-extracted with DCM (2 x 50 mL). The combined organics were washed with sodium hydrogen carbonate until pH 8 was obtained, brine (100 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford 2,3,4,6-tetra-*O*-acetyl-z-D-galactopyranosyl bromide (24.3 g, 96%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.97, 1.99, 2.03, 2.04 (4 x s, 12H), 4.03-4.09 (m, 1H), 4.20-4.29 (m, 2H), 4.75-4.80 (m, 1H), 5.06-5.13 (m, 1H), 5.46-5.52 (m, 1H), 5.54 (d, *J* = 4.4 Hz, 1H).

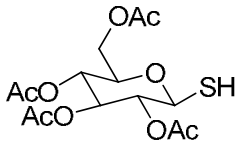
2,3,4,6-Tetra-O-acetyl-*β*-D-galactopyranosyl-1-isothiouronium bromide



2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl bromide (21.0 g, 51 mmol, 1 eq) and thiourea (5.8 g, 76.5 mmol, 1.5 eq) were dissolved in acetone (50 mL) and heated to 60□ under nitrogen. After 2 hours, t.l.c. (ethyl acetate; 100 %) indicated the formation of product (R_f = 0.0) with complete consumption of the starting material (R_f > 0.0). The reaction mixture was concentrated *in vacuo*. Crystallization from acetone/petrol afforded 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-1-isothiouronium bromide (14.2 g, 57 %) as a white solid.

^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ = 1.98, 2.00, 2.02, 2.06 (4 x s, 12H), 4.07-4.23 (m, 3H), 5.08-5.14 (m, 2H), 5.32 (dd, J = 8.9 Hz, 1H), 5.70 (d, J = 10.2 Hz, 1H), 9.06 (s, 2H), 9.25 (s, 2H).

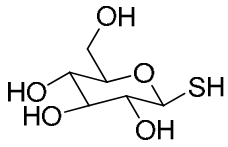
2,3,4,6-Tetra-O-acetyl-1-thio-*β*-D-galactopyranose (T10)



2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-1-isothiouronium bromide (12.3 g, 25.2 mmol, 1 eq) and sodium metabisulfite (4.8 g, 35.3 mmol, 1.4 eq) were added to a stirred solution of DCM (50 mL) and H_2O (50 mL). The mixture was heated to reflux under nitrogen. After 3 hours, t.l.c (ethyl acetate/petrol 1:1) indicated the formation of product (*Rf* = 0.5) with complete consumption of starting material (*Rf* 0.0). The reaction mixture was cooled to RT and the phases separated. The aqueous layer was re-extracted with DCM (2 x 100 mL). The combined organic layers were washed with H_2O (50 mL), brine (50 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford 2,3,4,6-tetra-*O*-acetyl-1-thio-*β*-D-galacto pyranose (8.89 g, 97 %) as a pale yellow oil

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ = 1.94, 1.96, 2.01, 2.03 (4 x s, 12H), 2.25 (d, J = 9.8 Hz, 1H), 3.66 (ddd, J_1 = 9.9 Hz, J_2 = 4.8 Hz, J_3 = 2.1 Hz, 1H), 4.06 (dd, J_1 = 12.5 Hz, J_2 = 2.3 Hz, 1H), 4.19 (dd, J_1 = J_2 = 4.4 Hz, 1H), 4.48 (t, J = 10.0 Hz, 1H), 4.91 (t, J = 10.0 Hz, 1H), 5.04 (t, J = 9.3 Hz, 1H), 5.10-5.16 (m, 1H).

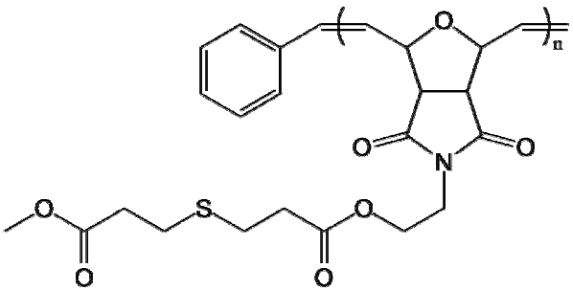
1-Thio-*β*-D-galactose (GalSH) (T11)



To 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranose (1.0 g, 2.7 mmol, 1 eq) was added sodium methoxide [sodium (95 mg, 4.1 mmol, 1.5 eq) dissolved in methanol (10 mL)]. The reaction mixture was stirred at RT. After 30 minutes, t.l.c (ethyl acetate; 100 %) indicated the formation of product (*Rf* = 0.0) with complete consumption of the starting material (*Rf* > 0.0). The reaction mixture was acidified with DOWEX®50WX4-50 Ion exchange resin, filtered and concentrated *in vacuo* to afford 1-thio-β-D-galactose (GalSH) (0.54 g, 100%) as a white solid.

^{1}H NMR (300 MHz, CD_3OD, ppm): δ = 3.10-3.36 (m, 4H), 3.64 (dd, J_1 = 12 Hz, J_2 = 5.1 Hz, 1H), 3.84 (dd, J_1 = 12 Hz, J_2 = 1.8 Hz, 1H), 4.43 (d, J = 9.9 Hz, 1H).

Characterization data for (co)polymers derived from Michael adducts



PT1

PT1: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 2.55-2.69 (m, 4H), 2.74-2.86 (m, 4H), 3.34-3.48 (br, 2H), 3.66-3.73 (br, 2H), 3.74-3.85 (br, 2H), 4.24-4.36 (m, 2H), 4.41-4.66 & 4.92-5.10 (br, 2H), 5.77-5.92 & 6.04-6.21 (br, 2H); IR (neat): υ = 3607, 2954, 2849, 2325, 1779, 1733, 1696, 1602, 1433, 1393, 1331, 1285, 1244 cm^{-1}; M_n (NMR) = 7,100; M_n (THF GPC) = 4,700; PDI = 1.12; c/t ratio = 28.2/71.8; $k_p = 0.092s^{-1}$.

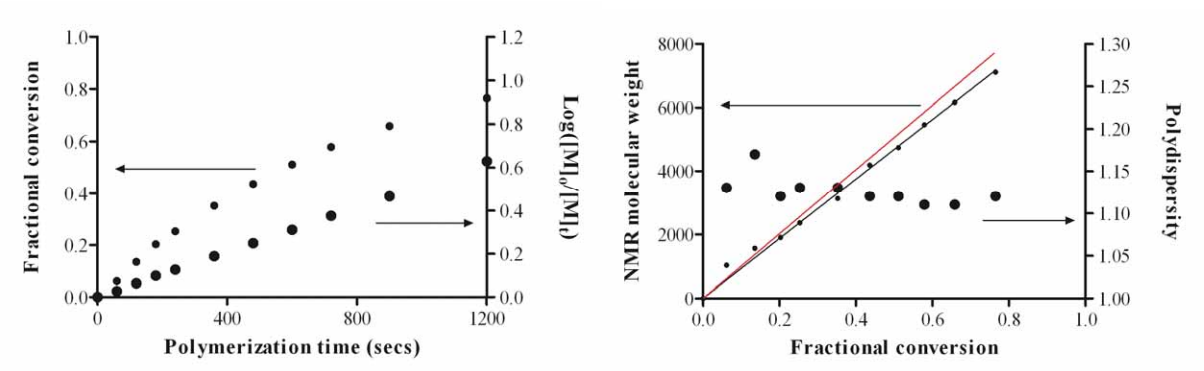
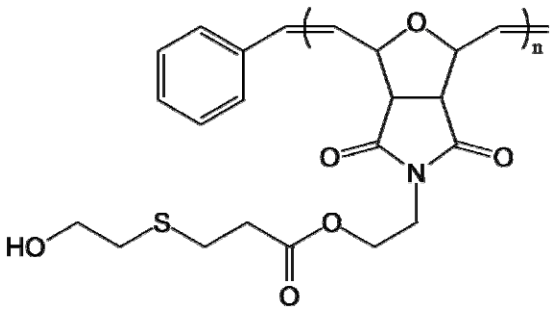


Figure S1: Kinetic and MW vs conversion profiles - homoROMP of **DT1** with **G1** Grubbs catalyst.



PT2

PT2: ^{1}H NMR (300 MHz, $(CD_3)_2SO$, ppm): δ = 2.577 (m, 2H), 2.710 (m, 2H), 3.446 (br, 2H), 3.541 (m, 2H), 3.813 (br, 2H), 4.185 (br, 2H), 4.337-4.816 (br, 2H), 4.892 (br, 1H), 5.677-6.087 (br, 2H); IR (neat): υ = 3466, 3057, 2957, 2875, 1777, 1732, 1698, 1426, 1393, 1331, 1268, 1242 cm^{-1}; M_n (NMR) = 7,4 00; M_n (DMAc GPC) = 22,500; PDI = 1.17; c/t ratio = 71.6/28.4; k_p = 0.1329s^{-1}.

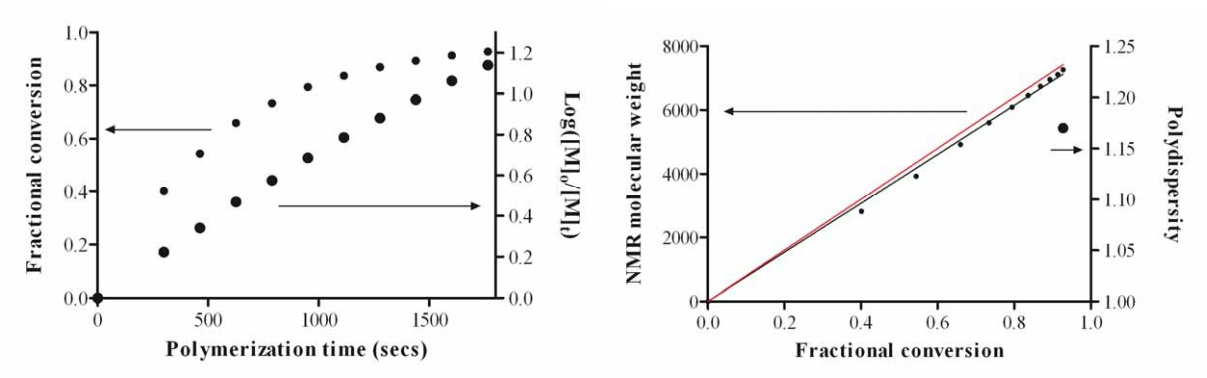
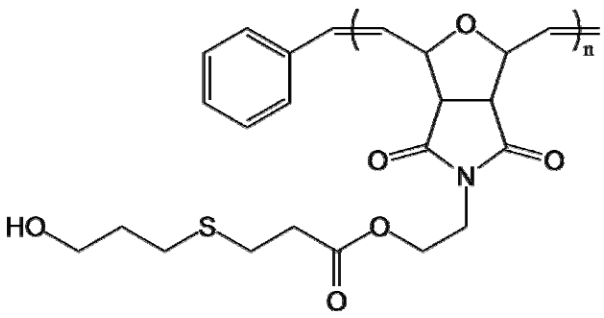


Figure S2: Kinetic and MW vs conversion profiles - homoROMP of **DT2** with **G3** Grubbs catalyst.



PT3

PT3: ^{1}H NMR (300 MHz, $(CD_3)_2SO$, ppm): δ = 1.651 (m, 2H), 2.520 (br, 4H), 2.678 (br, 2H), 3.445 (m, 4H), 3.653 (br, 2H), 4.183 (br, 2H), 4.330-5.027 (br, 2H), 5.670-6.079 (br, 2H); IR (neat): υ = 3464, 2928, 1777, 1737, 1695, 1508, 1454, 1426, 1393, 1330, 1241 cm^{-1}; M_n (NMR) = 9,500; M_n (DMAc GPC) = 21,600; PDI = 1.10 ; c/t ratio = 51.2/48.8; k_p = 0.6448s^{-1}.

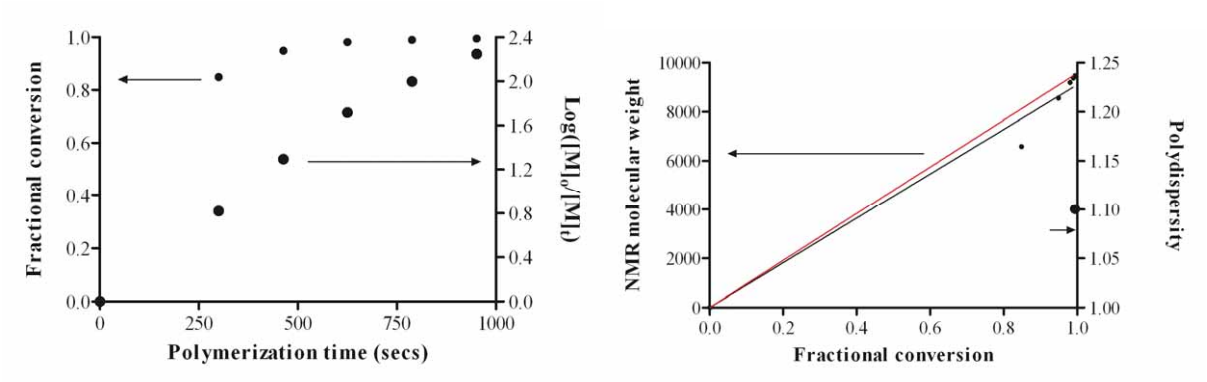
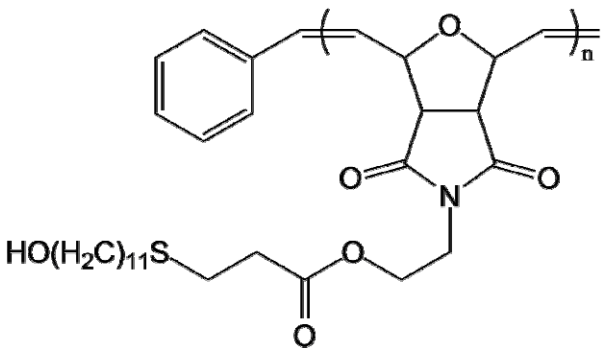


Figure S3: Kinetic and MW vs conversion profiles - homoROMP of **DT3** with **G3** Grubbs catalyst.



PT4

PT4: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.22-1.49 (br, 18H), 1.66-1.77 (br, 1H), 2.50-2.66 (m, 4H), 2.71-2.82 (m, 2H), 3.33-3.48 (br, 2H), 3.56-3.67 (m, 2H), 3.74-3.87 (br, 2H), 4.24-4.37 (m, 2H), 4.47-4.61 & 4.94-5.12 (br, 2H), 5.79-5.93 & 6.07-6.21 (br, 2H); IR (neat): υ = 3465, 2924, 2851, 2161, 1980, 1779, 1700, 1428, 1393, 1367, 1331, 1240 cm^{-1}; M_n (NMR) = 8,800; M_n (THF GPC) = 8,100; PDI = 1.14 ; c/t ratio = 27.0/73.0; k_p = 0.0579s^{-1}.

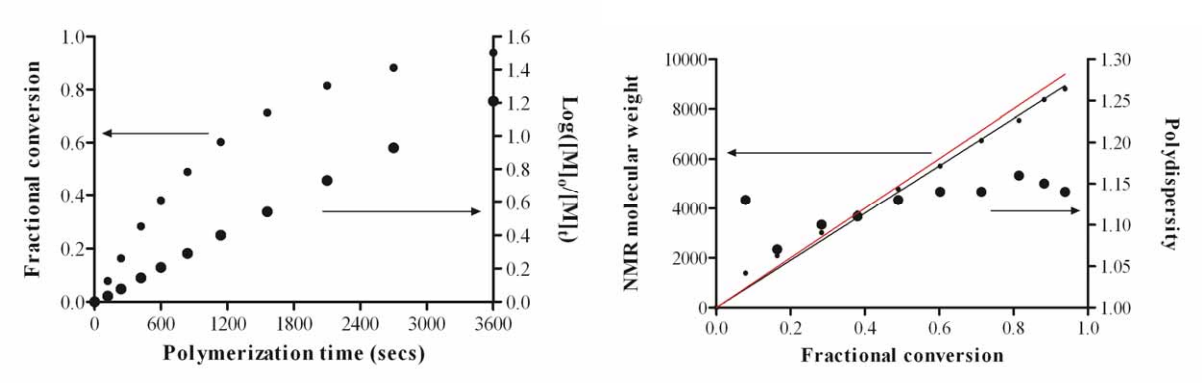
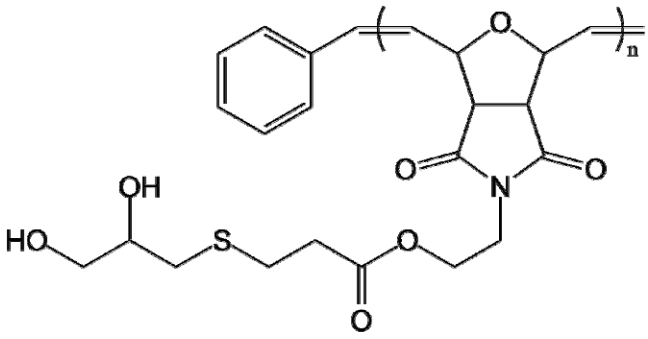
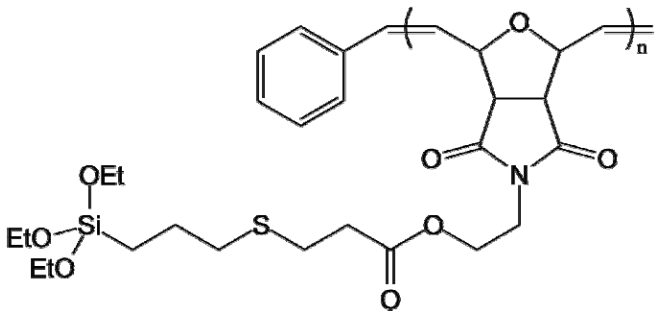


Figure S4: Kinetic and MW vs conversion profiles - homoROMP of **DT4** with **G1** Grubbs.



PT5

PT5: ^{1}H NMR (300 MHz, $(CD_3)_2SO$, ppm): δ = 2.579 (br, 4H), 2.726 (br, 2H), 3.363 (br, 2H), 3.446 (br, 2H), 3.552 (br, 1H), 3.654 (br, 2H), 4.184 (br, 2H), 4.432 (br, 1H), 4.503-4.805 (br, 2H), 4.886 (br, 1H), 5.691-6.075 (br, 2H); IR (neat): υ = 3405, 2922, 1776, 1729, 1695, 1427, 1394, 1368, 1331, 1242, 1185, 1121, 1018 cm^{-1}; M_n (NMR) = 5,800; M_n (DMAc GPC) = 24,000; PDI = 1.16 ; c/t ratio = 51.6/48.4.



PT6

PT6: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.68-0.79 (m, 2H), 1.18-1.29 (m, 8H), 1.63-1.78 (m, 2H), 2.53-2.66 (m, 4H), 2.71-2.82 (m, 2H), 3.35-3.47 (br, 2H), 3.75-3.90 (m, 8H), 4.24-4.36 (m, 2H), 4.46-5.58 & 4.93-5.13 (br, 2H), 5.79-5.94 & 6.08-6.24 (br, 2H); IR (neat): υ = 3446, 2974, 2927, 2883, 1779, 1739, 1700, 1428, 1391, 1366, 1332, 1238, 1188 cm^{-1}; M_n (NMR) = 9,500; M_n (THF GPC) = 8,500; PDI = 1.10 ; c/t ratio = 26.9/73.1; k_p = $0.0681s^{-1}$.

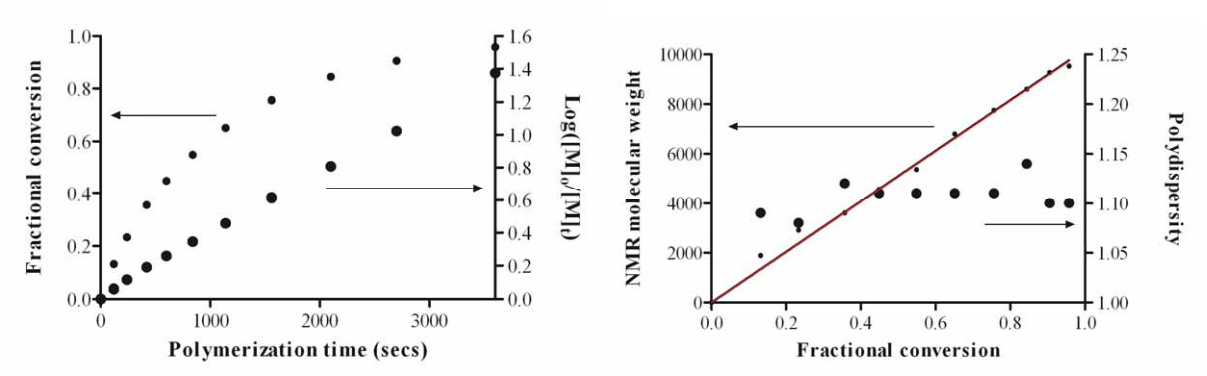
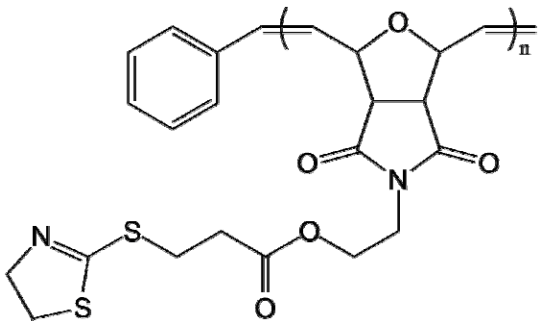


Figure S5: Kinetic and MW vs conversion profiles - homoROMP of **DT6** with **G1** Grubbs catalyst.



PT7

PT7: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 2.71-2.83 (m, 2H), 3.29-3.40 (m, 2H), 3.42-3.54 (m, 2H), 3.75-3.87 (br, 2H), 3.95-4.06 (m, 2H), 4.16-4.26 (m, 2H), 4.26-4.37 (m, 2H), 4.50-4.60 & 4.97-5.10 (br, 2H), 5.81-5.94 & 6.09-6.18 (br, 2H); IR (neat): υ = 3345, 2924, 2324, 2161, 1980, 1779, 1739, 1702, 1491, 1456, 1426, 1393, 1317, 1230, 1184 cm^{-1}; M_n (NMR) = 18,200; M_n (DMAc GPC) = 24,000; PDI = 1.08 ; c/t ratio =55.6/44.4; k_p = 0.7649s^{-1}.

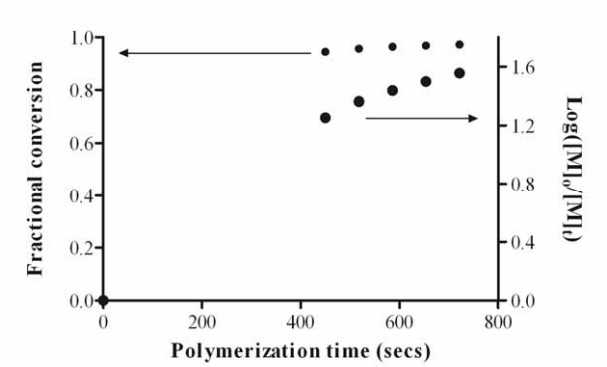
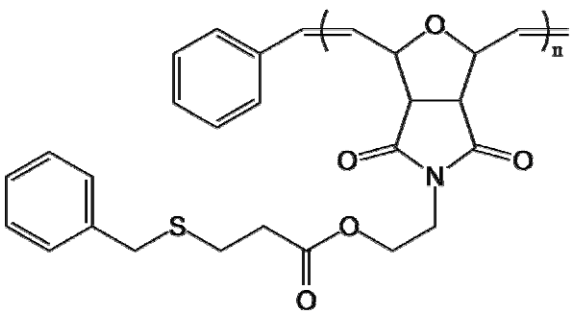


Figure S6: Kinetic profile - homoROMP of **DT7** with **G3** Grubbs.



PT8

PT8: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 2.50-2.61 (m, 2H), 2.63-2.73 (m, 2H), 3.28-3.44 (br, 2H), 3.69-3.85 (br, 2H), 4.21-4.34 (br, 2H), 4.44-4.57 & 4.92-5.09 (br, 2H), 5.78-5.90 & 6.04-6.19 (br, 2H), 7.21-7.53 (m, 5H); IR (neat): υ = 3623, 2956, 2854, 1778, 1737, 1698, 1601, 1495, 1454, 1426, 1393, 1366, 1329, 1236, 1186 cm^{-1}; M_n (NMR) = 11,900; M_n (THF GPC) = 5,100; PDI = 1.31; c/t ratio =28.8/71.2; $k_p = 0.0506s^{-1}$.

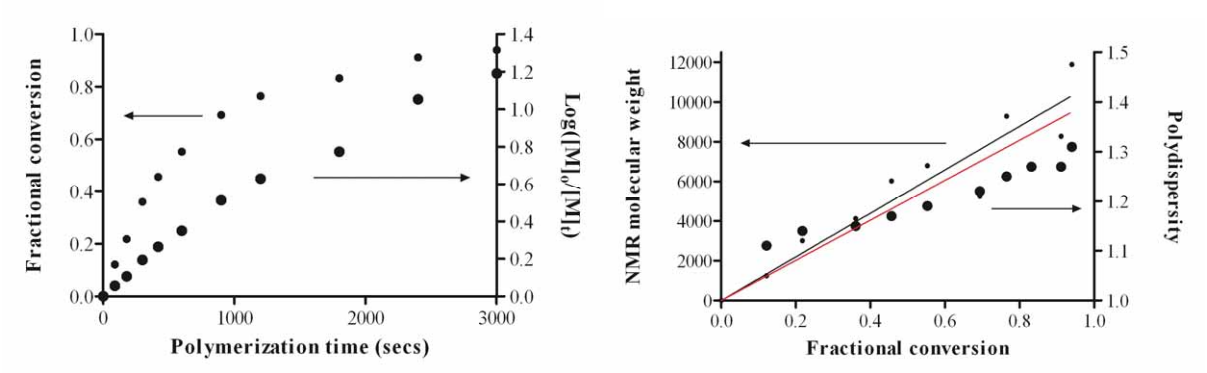
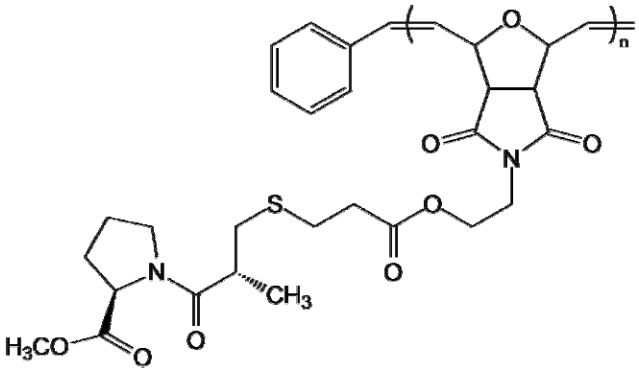


Figure S7: Kinetic and MW vs conversion profiles - homoROMP of **DT8** with **G1** Grubbs catalyst.



PT9

PT9: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.12-1.24 (m, 3H), 1.88-2.35 (m, 5H), 2.50-2.65 (m, 3H), 2.66-2.81 (m, 2H), 2.81-2.95 (m, 2H), 3.37-3.51 (m, 2H), 3.61-3.74 (m, 5H), 3.75-3.86 (br, 2H), 4.22-4.36 (m, 2H), 4.42-4.49 (m, 1H), 4.49-4.59 & 4.93-5.13 (br, 2H), 5.78-5.92 & 6.08-6.17 (br, 2H); IR (neat): υ = 3591, 3467, 2956, 2876, 1778, 1735, 1702, 1636, 1429, 1394, 1366, 1330, 1186, 1121, 1032cm^{-1}; M_n (NMR) = 7,800; M_n (DMAc GPC) = 11,700; PDI = 1.12; c/t ratio =52.9/47.1.2; k_p = 1.5240s^{-1}.

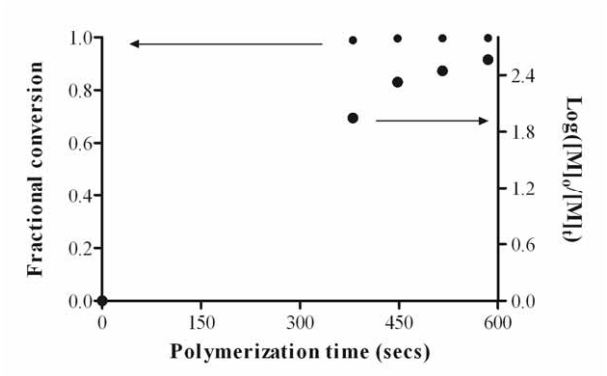
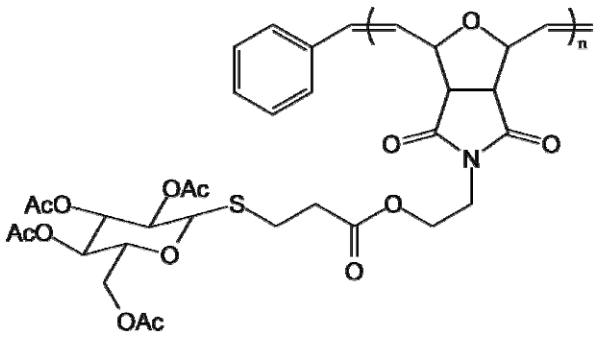


Figure S8: Kinetic profile - homoROMP of **DT9** with **G3** Grubbs.



PT10

PT10: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.88-0.99 (m, 2H), 1.26-1.41 (m, 2H), 1.63-1.72 (br, 2H), 1.96-2.17 (m, 12H), 2.64-2.76 (m, 2H), 2.81-3.06 (m, 2H), 3.34-3.51 (br, 2H), 3.72-3.88 (br, 2H), 4.11-4.38 (m, 4H), 4.40-4.59 & 4.95-5.11 (br, 2H), 4.59-4.69 (m, 1H), 4.94-5.16 (m, 2H), 5.21-5.32 (m, 1H), 5.79-5.95 & 6.06-6.23 (br, 2H); IR (neat): υ = 3464, 2925, 2852, 1778, 1737, 1698, 1465, 1428, 1397, 1331, 1240, 1187 cm^{-1}; M_n (NMR) =

9,300; M_n (THF GPC) = 5,500; PDI = 1.15; c/t ratio =28.4/71.6; $k_p = 0.3621 s^{-1}$.

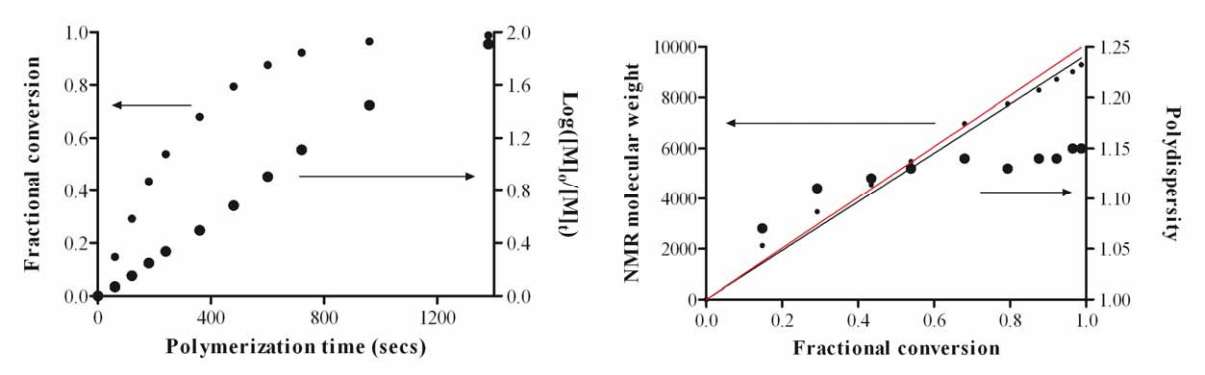
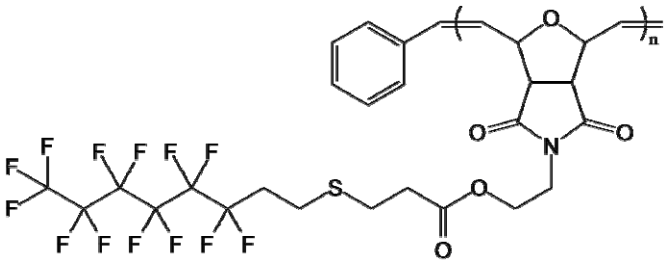


Figure S9: Kinetic and MW vs conversion profiles - homoROMP of **DT10** with **G1** Grubbs.



PT12

PT12: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 1.53-1.63 (br, 4H), 2.35-2.56 (m, 2H), 2.58-2.84 (m, 2H), 2.75-2.89 (m, 4H), 3.33-3.47 (br, 2H), 3.74-3.86 (br, 2H), 4.25-4.37 (br, 2H), 4.47-4.59 & 4.96-5.11 (br, 2H), 5.79-5.92 & 6.08-6.22 (br, 2H); IR (neat): υ = 3628, 2958, 2854, 1781, 1743, 1700, 1623, 1430, 1395, 1366, 1332, 1215, 1204, 1121 cm^{-1}; M_n (NMR) = 9,800; M_n (THF GPC) = 8,000; PDI = 1.12; c/t ratio = 26.0/74.0; $k_p = 0.1432 s^{-1}$.

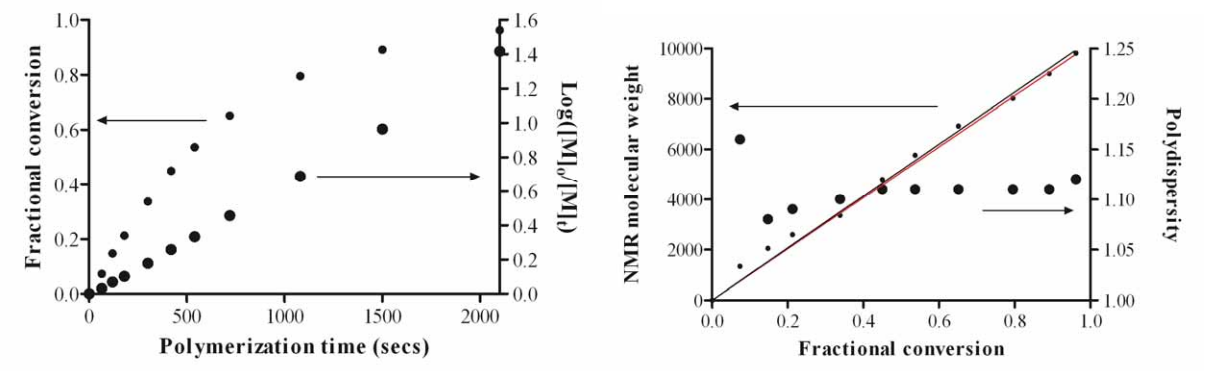
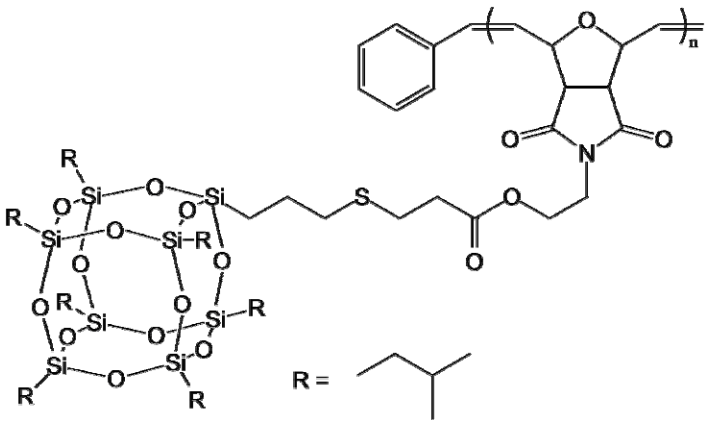


Figure S10: Kinetic and MW vs conversion profiles - homoROMP of **DT12** with **G1** Grubbs.



PT13

PT13: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.664 (m, 2H), 0.752 (m, 2H), 1.016 (br, 42H), 1.718 (m, 2H), 1.911 (m, 7H), 2.575 (m, 4H), 2.765 (br, 2H), 3.393 (br, 2H), 3.795 (br, 2H), 4.303 (br, 2H), 4.391-5.108 (br, 2H), 5.778-6.193 (br, 2H); IR (neat): υ = 2954, 2928, 2870, 1782, 1742, 1711, 1465, 1426, 1395, 1366, 1333, 1228, 1168, 1081, 1035, 920, 837, 740 cm^{-1}; M_n (NMR) = 9,000; M_n (THF GPC) = 8,300; PDI = 1.11; c/t ratio =24.5/75.5; k_p = 0.069s^{-1}.

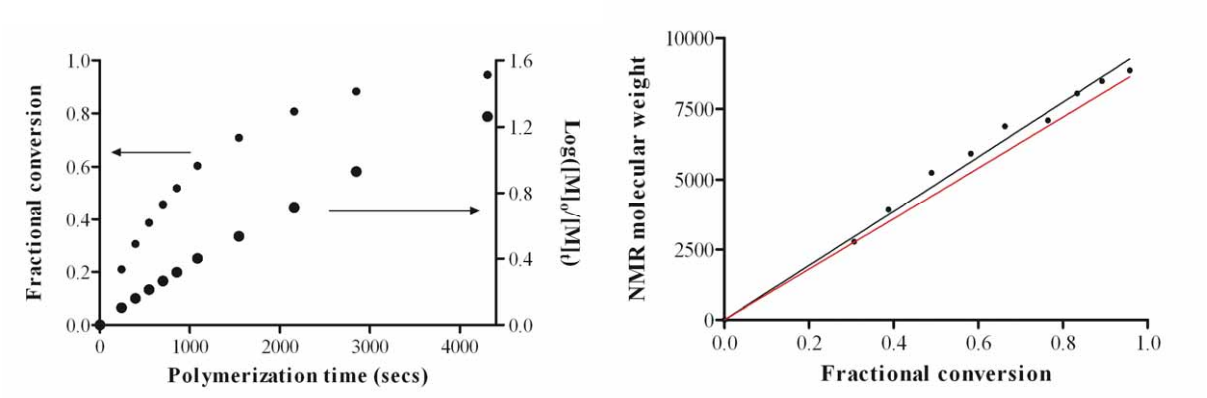
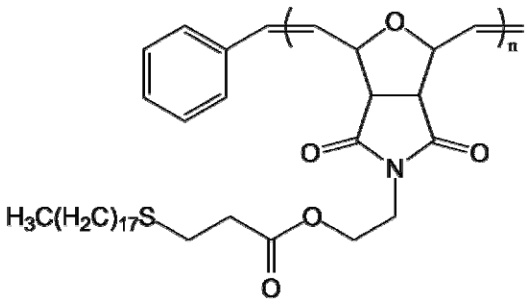


Figure S11: Kinetic and MW vs conversion profiles - homoROMP of **DT13** with **G1** Grubbs.



PT14

PT14: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.929 (m, 3H), 1.311 (br, 32H), 2.580 (m, 4H), 2.774 (m, 2H), 3.403 (br, 2H), 3.798 (br, 2H), 4.295 (br, 2H), 4.405-5.140 (br, 2H), 5.748-6.266 (br, 2H); IR (neat): υ = 2918, 2850, 1779, 1736, 1702, 1467, 1427, 1393, 1367, 1333, 1284, 1238, 1186, 1121, 1027, 970, 915, 846, 822, 764, 720 cm^{-1}; M_n (NMR) = 9,200; M_n (THF GPC) = 10,600; PDI = 1.09; c/t ratio = 26.5/73.5; $k_p = 0.071 s^{-1}$.

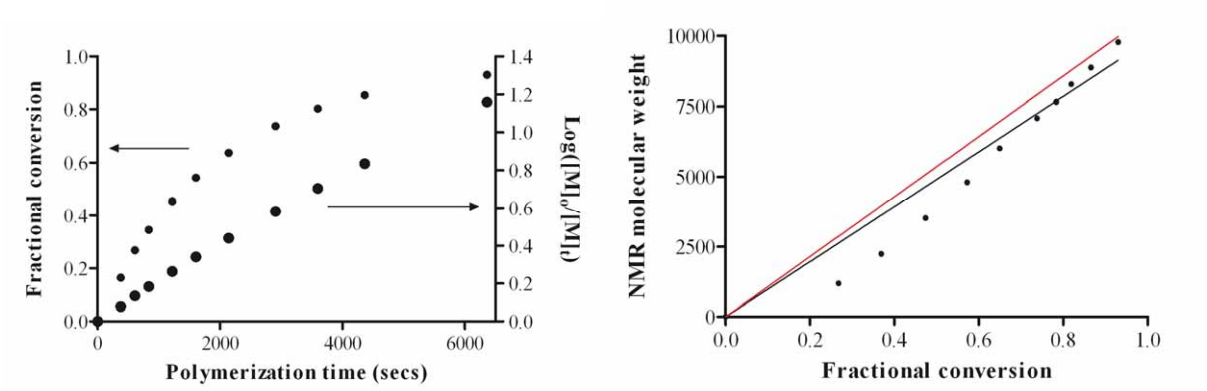
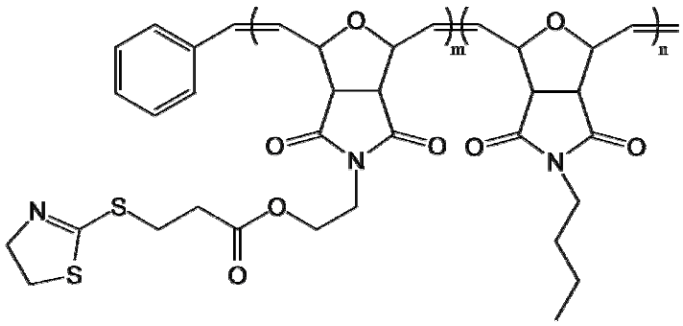
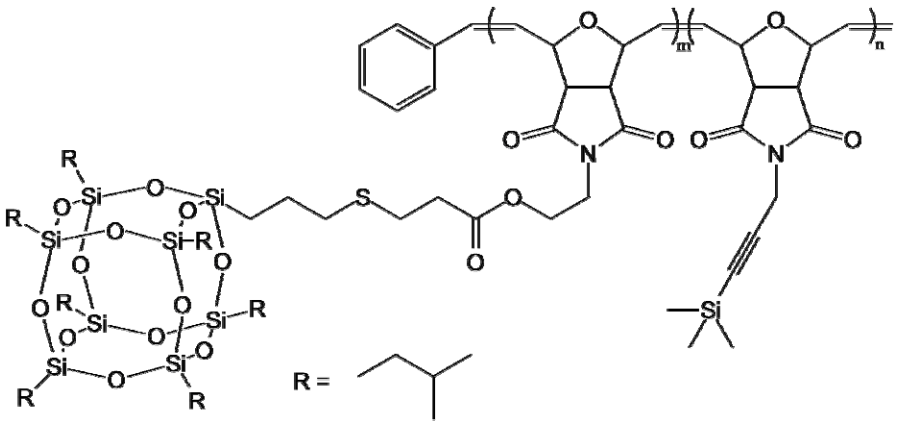


Figure S12: Kinetic and MW vs conversion profiles - homoROMP of **DT14** with **G1** Grubbs catalyst.



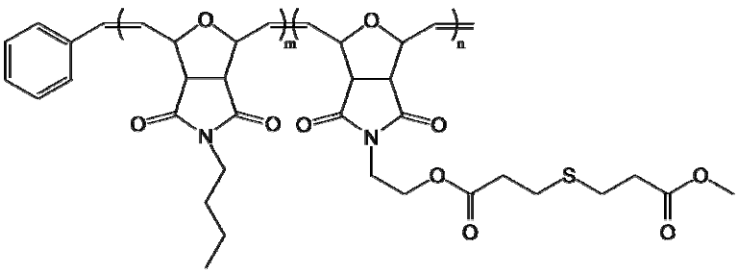
Stat P1

Stat P1: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.89-1.03 (m, 3H), 1.29-1.43 (m, 2H), 1.52-1.66 (m, 2H), 2.69-2.83 (m, 2H), 3.26-3.60 (m, 8H), 3.73-3.88 (br, 2H), 3.94-4.06 (m, 2H), 4.16-4.26 (m, 2H), 4.26-4.37 (m, 2H), 4.43-4.62 & 4.92-5.12 (br, 2H), 5.78-5.95 & 6.05-6.22 (br, 2H); M_n (NMR) = 10,300; M_n (THF GPC) = 6,600; PDI = 1.20; c/t ratio = 30.2/69.8; Molar incorporation of **M1** & **DT7** = 55 : 45.



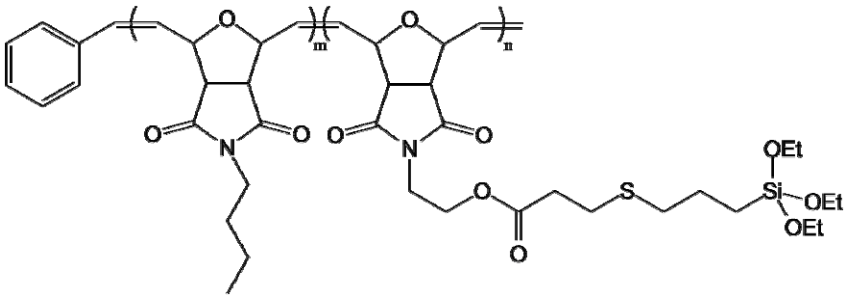
Stat P2

Stat P2: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.206 (br, 7.2H), 0.662 (m, 2.8H), 0.754 (m, 0.4H), 0.993 (m, 8.4H), 1.910 (m, 1.4H), 2.600 (m, 0.8H), 2.766 (m, 0.4H), 3.442 (br, 2H), 3.799 (br, 0.4H), 4.287 (br, 2H), 4.405-5.125 (br, 2H), 5.763-6.228 (br, 2H); IR (neat): υ = 2955, 2927, 2871, 2184, 1783, 1709, 1638, 1465, 1419, 1390, 1333, 1250, 1228, 1171, 1091, 1010, 919, 839, 759, 742 cm^{-}1; M_n (NMR) = 10,700; M_n (THF GPC) = 17,500; PDI = 1.15; c/t ratio =29.8/70.2; Molar incorporation of **M2** & **DT13** (NMR) = 79.8 : 20.2.



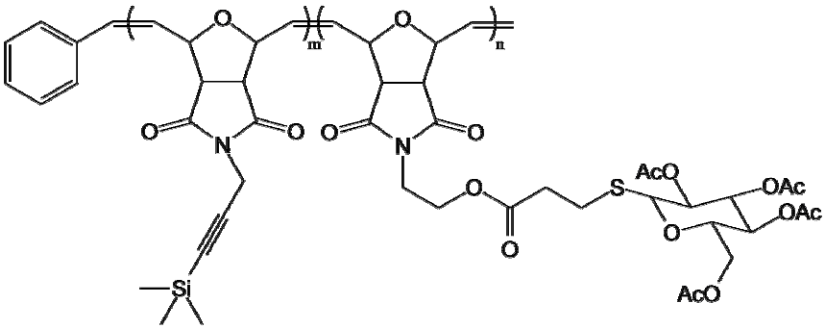
Block P1

Block P1: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.90-1.01 (m, 3H), 1.27-1.42 (m, 2H), 1.51-1.65 (m, 2H), 2.57-2.68 (m, 4H), 3.31-3.57 (m, 6H), 3.67-3.74 (br, 3H), 3.75-3.85 (br, 2H), 4.25-4.36(m, 2H), 4.44-4.58 & 4.93-5.10 (br, 4H), 5.79-5.92 & 6.06-6.20 (br, 4H); M_n (NMR) **M1** block = 10,700; M_n (NMR) **DT1** block = 8,900; M_n (NMR) total = 19,600; M_n (THF GPC) **M1** block = 9,500; M_n (THF GPC) diblock = 17,300; PDI **M1** block = 1.20; PDI diblock = 1.23; c/t ratio diblock = 27.0/73.0; Molar incorporation of **M1** & **DT1** = 67.5 : 32.5.



Block P2

Block P2: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.68-0.79 (m, 2H), 0.89-1.01 (m, 3H), 1.19-1.27 (m, 9H), 1.27-1.43 (m, 2H), 1.50-1.65 (m, 2H), 1.65-1.77 (m, 2H), 2.53-2.65 (m, 4H), 2.71-2.81 (m, 2H), 3.30-3.57 (m, 6H), 3.75-3.88 (m, 8H), 4.24-4.35 (m, 2H), 4.41-4.58 & 4.91-5.11 (br, 4H), 5.78-5.91 & 6.04-6.18 (br, 4H); M_n (NMR) **M1** block = 10,600; M_n (NMR) **DT6** block = 8,100; M_n (NMR) total = 18,700; M_n (THF GPC) **M1** block = 9,400; M_n (THF GPC) diblock = 16,100; PDI **M1** block = 1.20; PDI diblock = 1.25; c/t ratio diblock = 27.7/72.3; Molar incorporation of **M1** & **DT6** = 74.8 : 25.2.



Block P3

Block P3: ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ = 0.15-0.24 (br, 9H), 0.88-0.97 (m, 2H), 1.26-1.40 (m, 2H), 1.97-2.14 (m, 12H), 2.62-2.75 (m, 2H), 2.80-3.05 (m, 2H), 3.35-3.53 (br, 2H), 3.74-3.86 (m, 3H), 4.12-4.37 (m, 2H), 4.44-4.68 & 4.94-5.11 (br, 4H), 4.93-5.14 (m, 2H), 5.21-5.32 (m, 1H), 5.79-5.94 & 6.07-6.21 (br, 4H); M_n (NMR) **M2** block = 7,600; M_n (NMR) **DT10** block = 8,800; M_n (NMR) total = 16,400; M_n (DMAc GPC) **M2** block = 14,900; M_n (DMAc GPC) diblock = 22,600; PDI **M2** block = 1.16; PDI diblock = 1.23 ; c/t ratio diblock = 30.0/70.0; Molar incorporation of **M2** & **DT10** = 66.5 : 33.5.

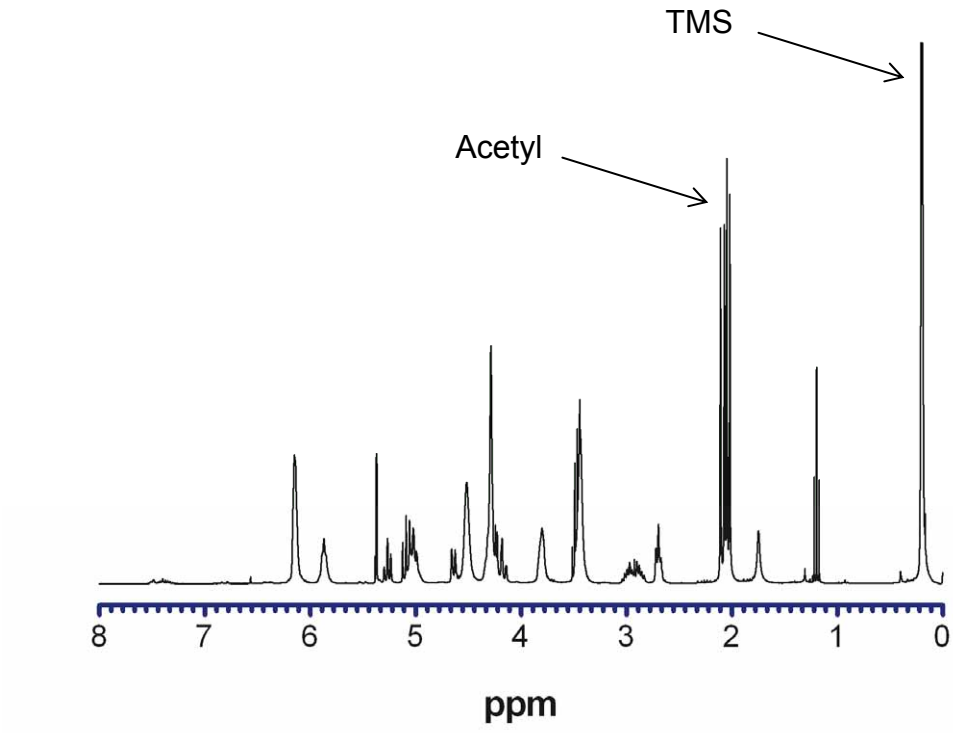


Figure S13: ^{1}H NMR spectrum, recorded in CD_2Cl_2, of block **M2** – **DT10**

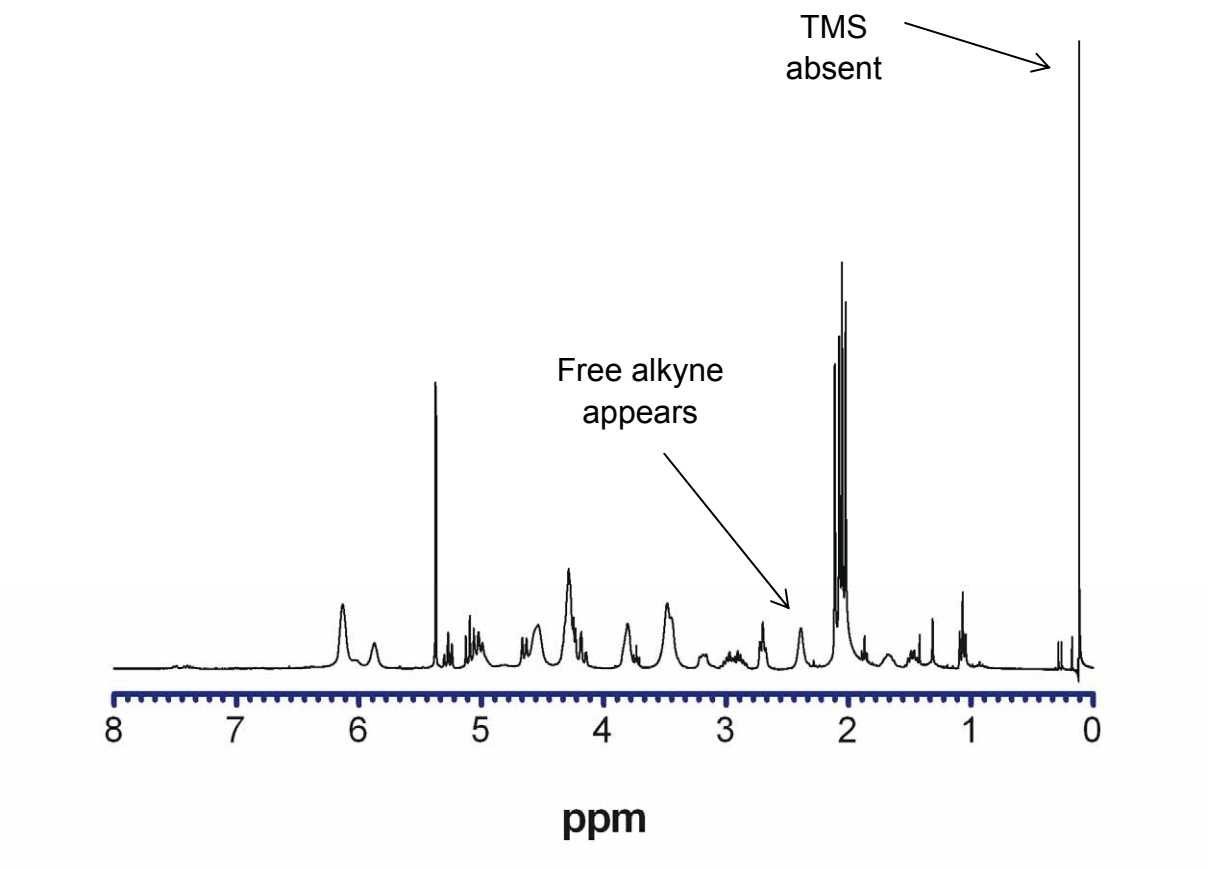


Figure S14: ^{1}H NMR spectrum, recorded in CD_2Cl_2, of block **dep - M2 – DT10**

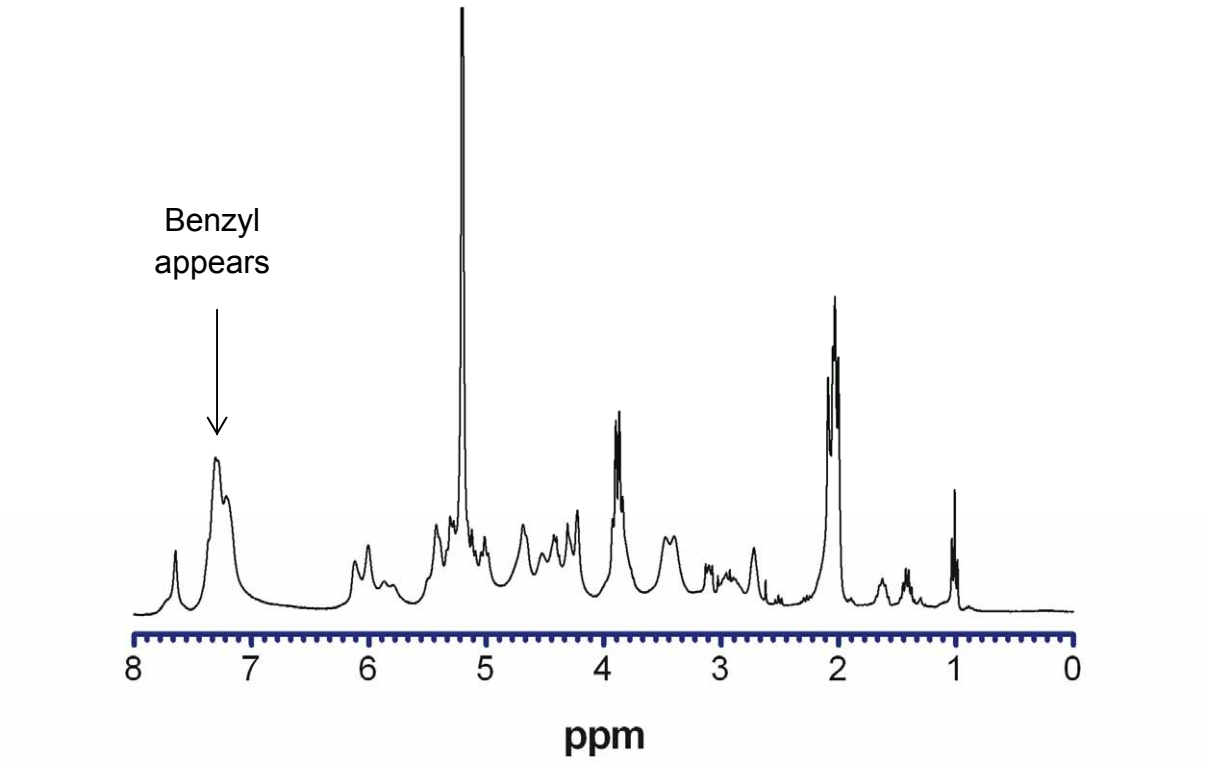


Figure S15: ^{1}H NMR spectrum, recorded in CF_3CD_2OD, of block **CuAAC - M2 – DT10**

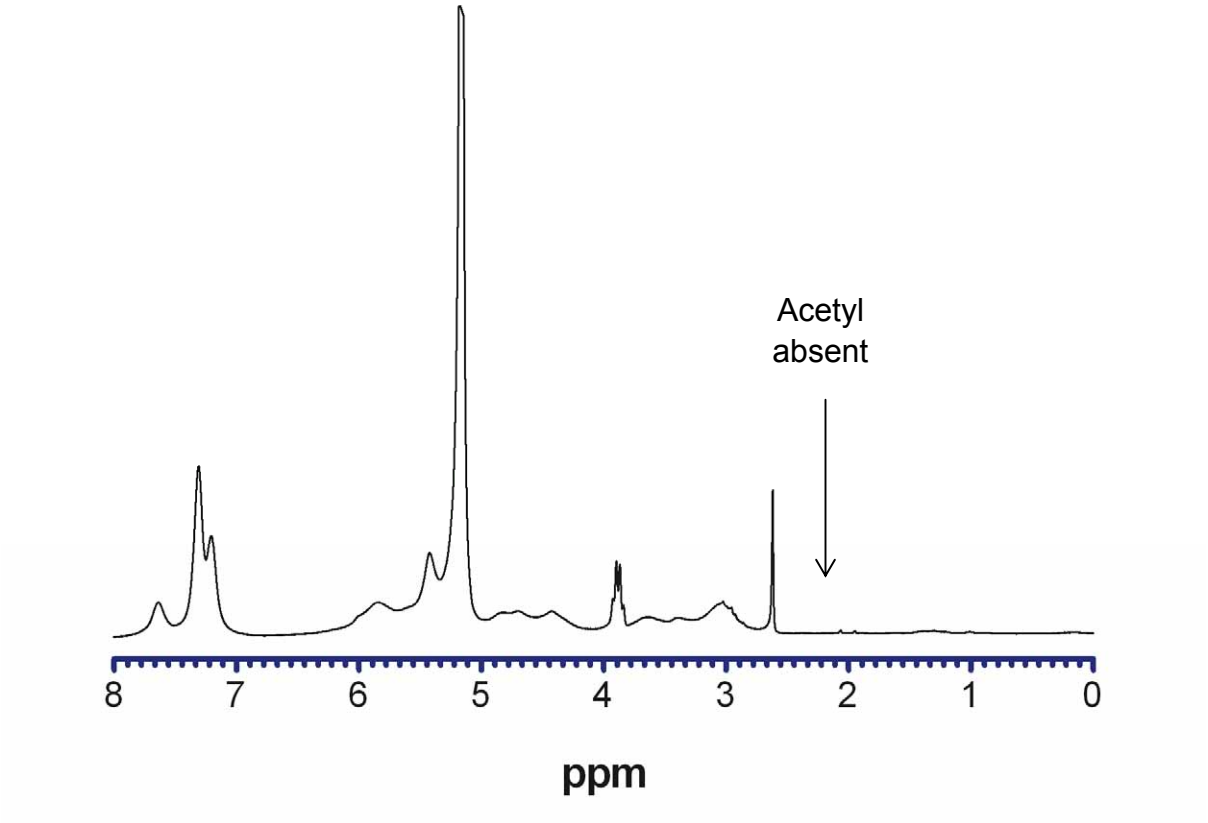


Figure S16: ^{1}H NMR spectrum, recorded in CF_3CD_2OD, of block **CuAAC - M2 – DT11**