Supporting Information for

[Ru]-Catalyzed Olefin Metathesis and Ethenolysis for the Synthesis and Recycling of Bio-Based Polycarbonates and Polycyanurates

Dana M. Pinson, Francesca D. Eckstrom, Gregory S. Ostrom, Randall K. McClain, Lawrence C. Baldwin, and Benjamin G. Harvey*

US NAVY, NAWCWD, Research Department, Chemistry Division, China Lake, California 93555

*Corresponding author (email: benjamin.g.harvey.civ@us.navy.mil

Contents

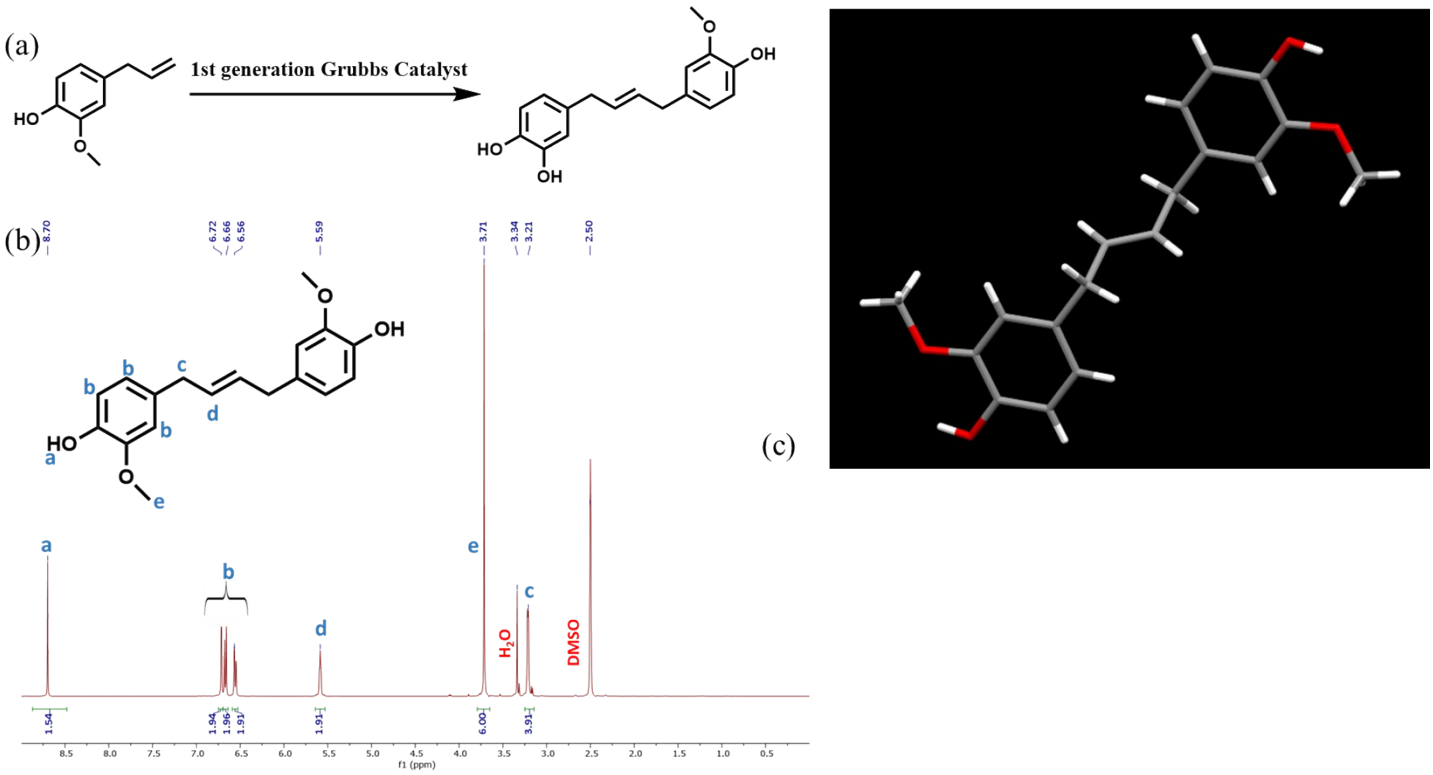

Figure S1. (a) Synthesis of 4,4′-(2-butene-1,4-diyl)bis[2-methoxyphenol] as previously reported. (b) ^{1}H NMR spectrum of of 4,4′-(2-butene-1,4-diyl)bis[2-methoxyphenol]. (c) X-ray crystal structure of 4,4′-(2-butene-1,4-diyl)bis[2-methoxyphenol]

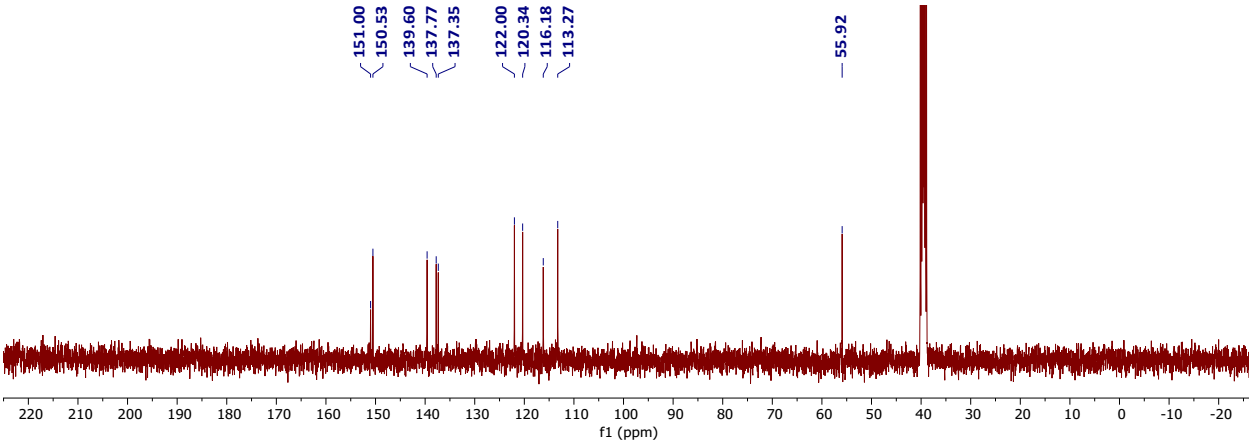

Figure S2. ^{13}C NMR spectrum of bis(4-allyl-2-methoxyphenyl) carbonate (compound **2**)

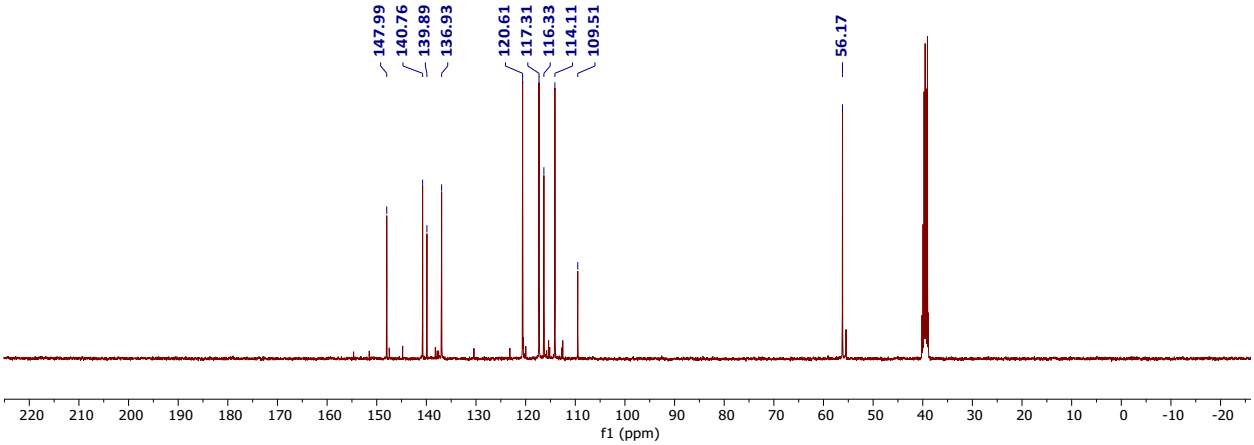

Figure S3. ^{13}C NMR spectrum of 4-Allyl-1-cyanato-2-methoxybenzene (compound **3**)

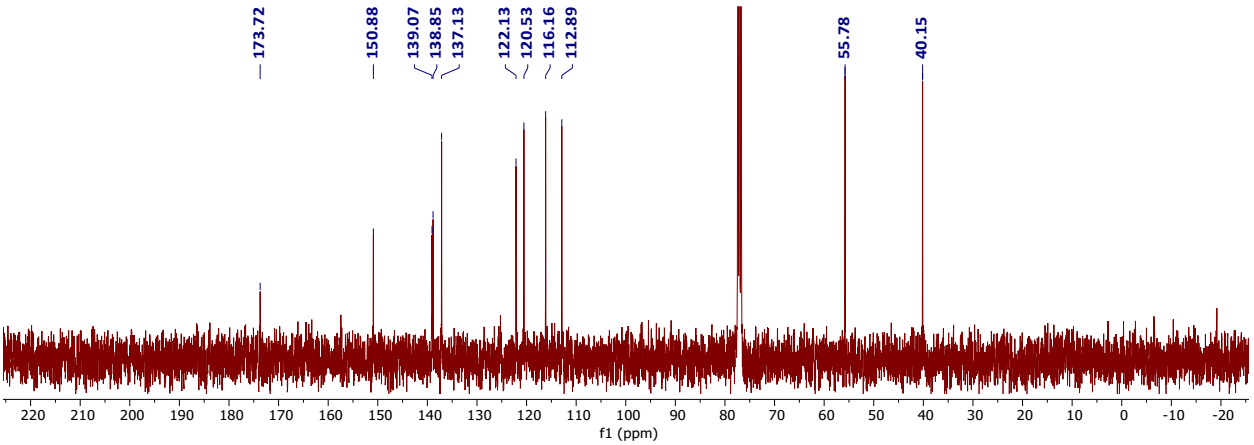

Figure S4. ^{13}C NMR spectrum of 2,4,6-tris(4-allyl-2-methoxyphenoxy)-1,3,5-triazine (compound **4**)

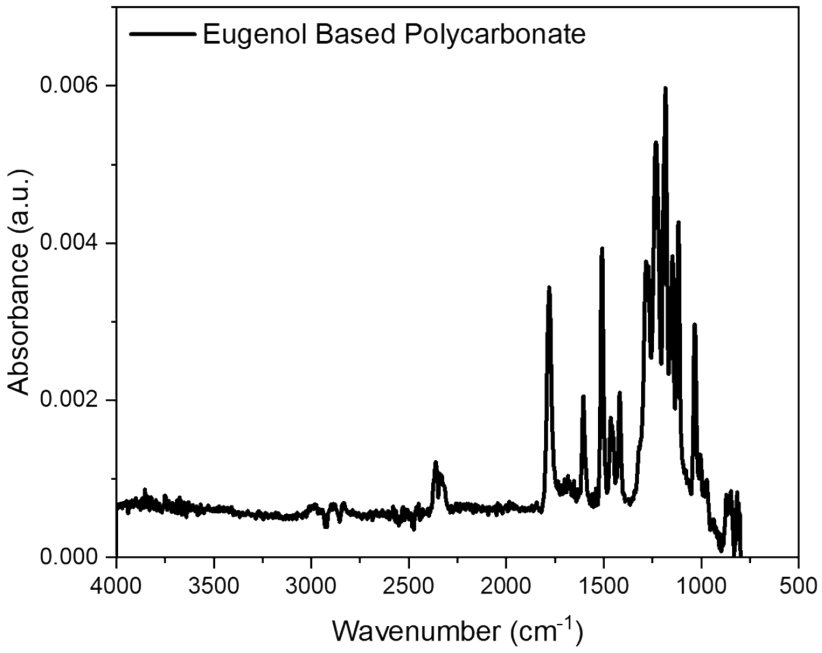

Figure S5. ATR FTIR spectrum of eugenol-based polycarbonate.

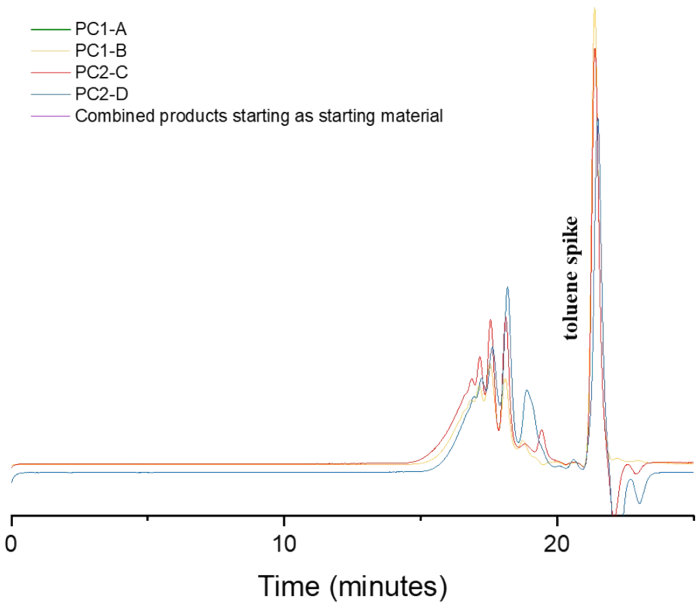

Figure S6. GPC of polycarbonate ethenolysis products from all trials, PC1 refers to starting material and letters refer to line entries in table 2.

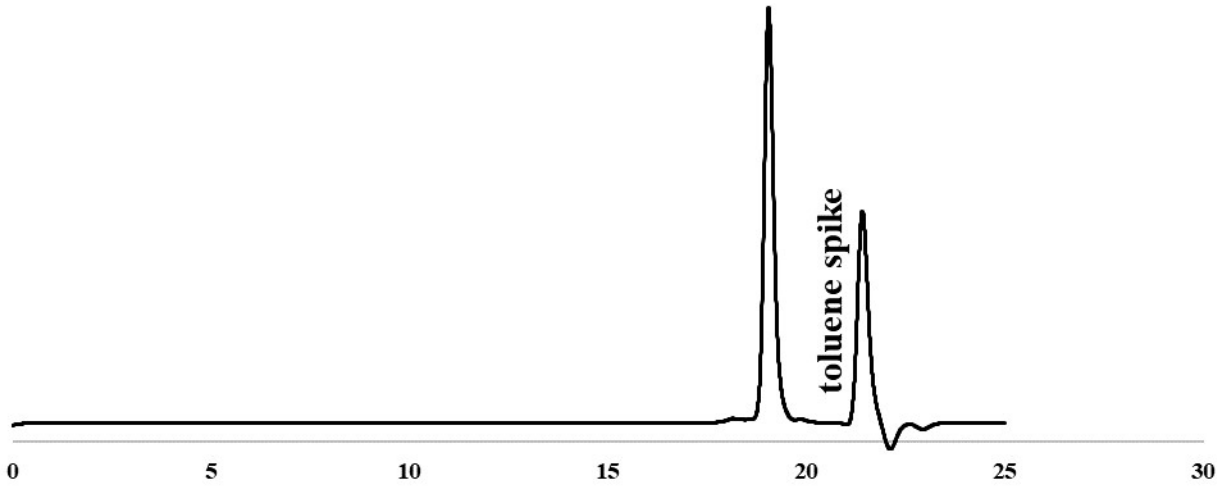

Figure S7. GPC results from the depolymerization of eugenol-based polycarbonate oligomers to yield monomeric material.

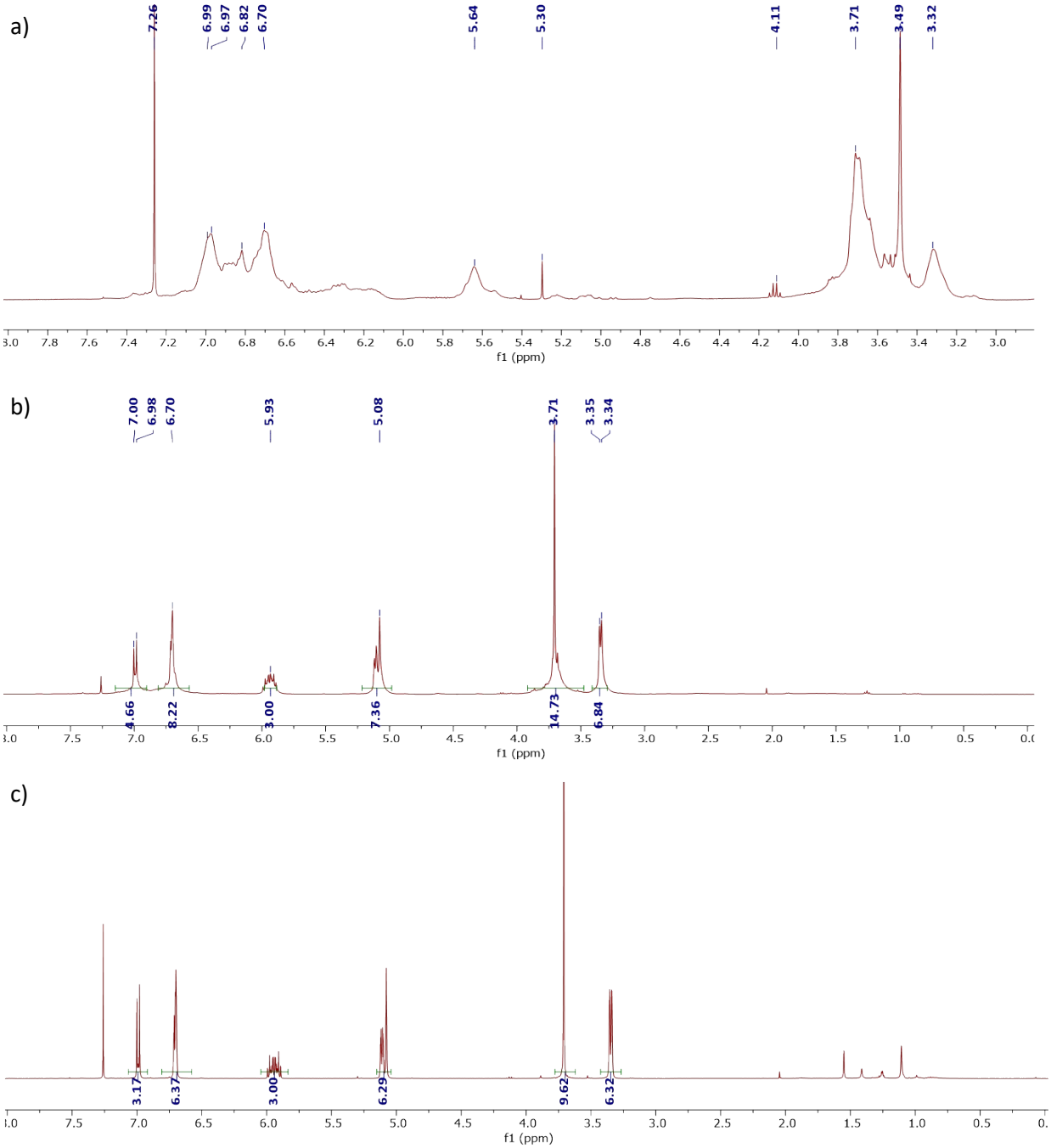

Figure S8. ^{1}H NMR spectra of the 2nd round of re- and de-polymerization for the triazine network. (a) ^{1}H NMR spectrum of the repolymerized network. (b) ^{1}H NMR spectrum of the oligomeric depolymerization product. (c) ^{1}H NMR spectrum of monomer obtained via ethenolysis of oligomers.

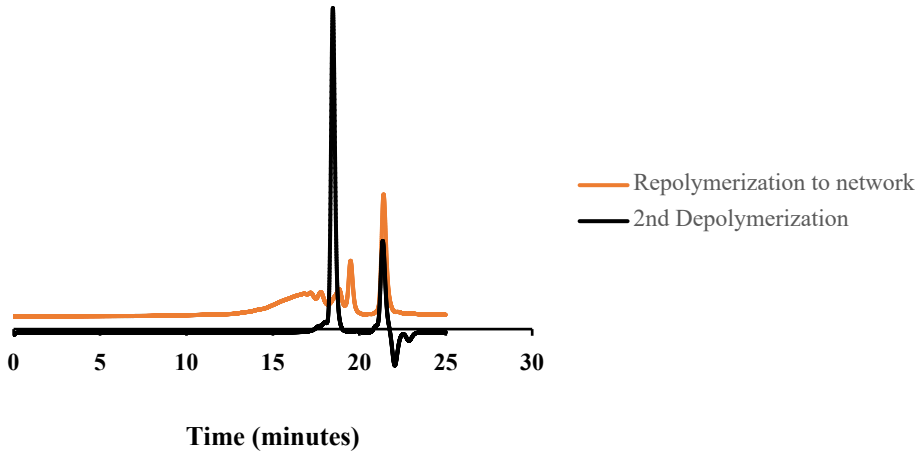

Figure S9. GPC results for a repolymerized triazine network and monomer resulting from full depolymerization.

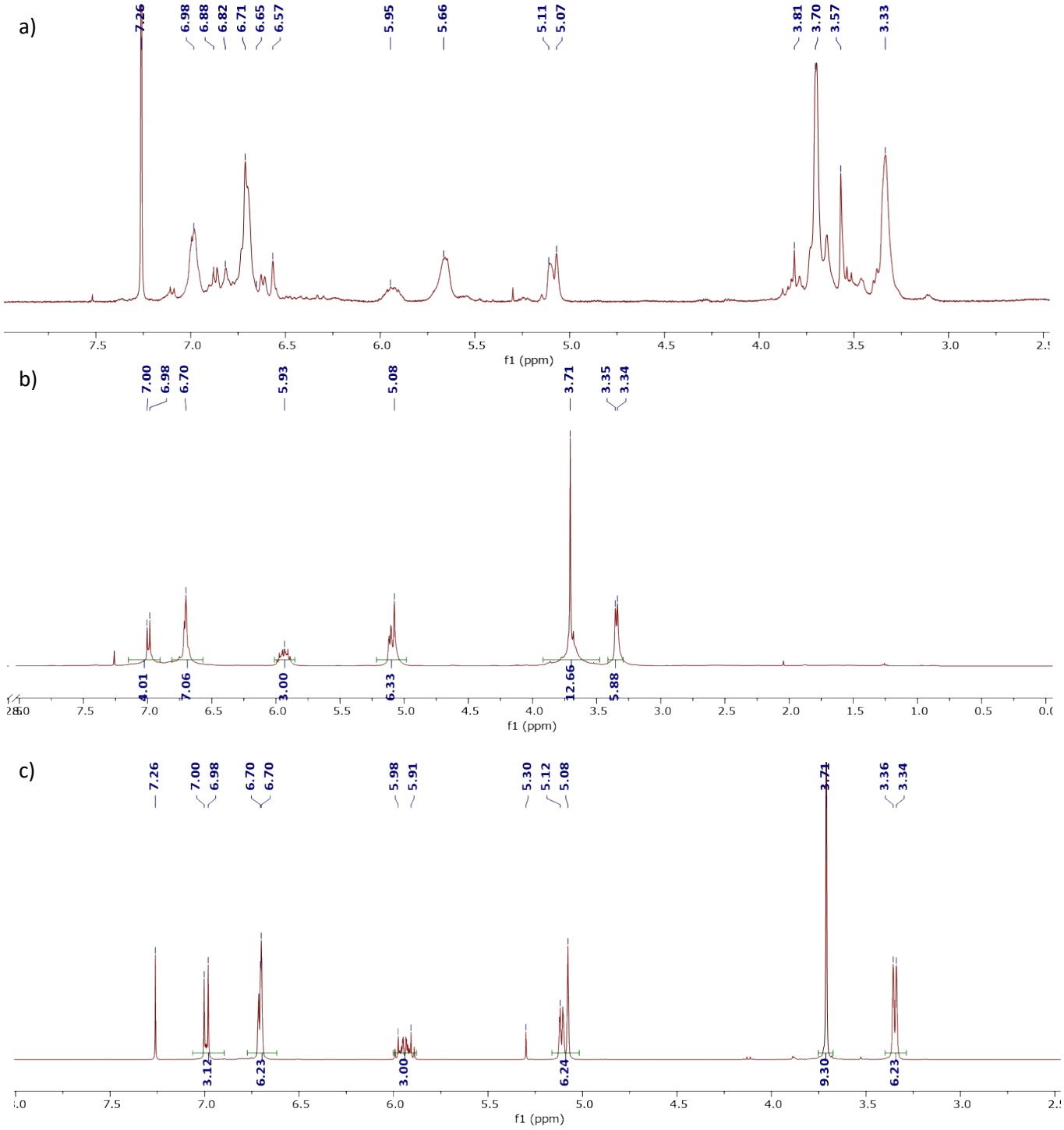

Figure S10. ^{1}H NMR spectrum of the 3rd round of re- and de-polymerization for the triazine network. (a) ^{1}H NMR spectrum of repolymerized triazine. (b) ^{1}H NMR spectrum of oligomers obtained by ethenolyis of the network. (c) ^{1}H NMR spectrum of the monomer obtained via ethnolysis of oligomers.

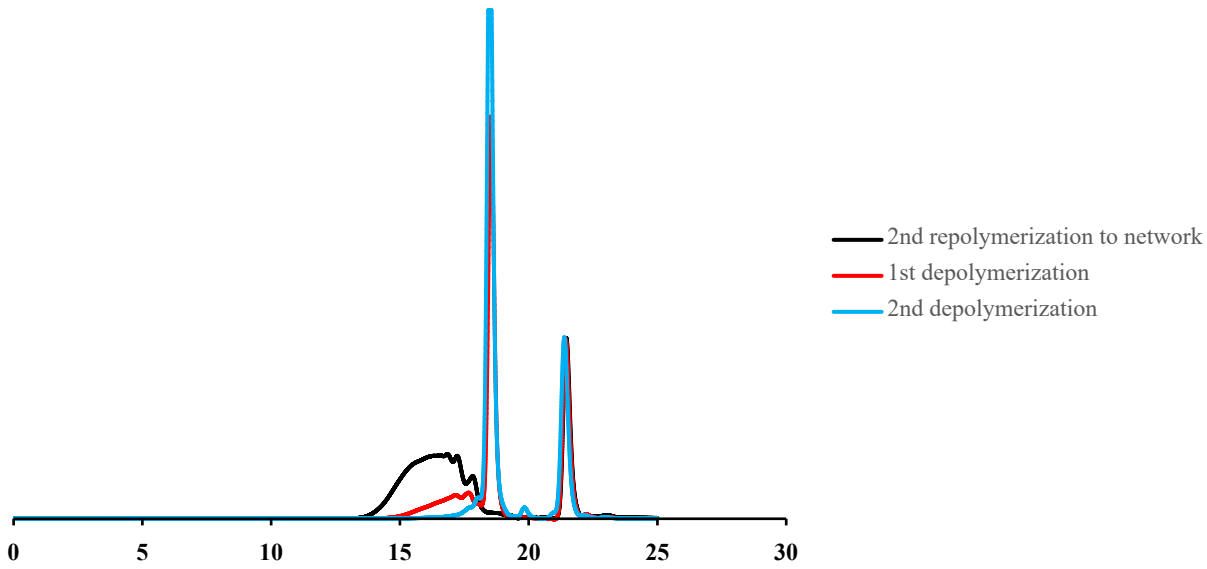

Figure S11. GPC results for the 3rd round of re- and de-polymerization for the triazine network.

X-ray Crystallography Data Collection and Refinement Details:
Crystal Samples were coated with Parabar oil and mounted on a MiTeGen polyimide loop. X-ray intensity data were measured using a Bruker SMART Apex II diffractometer equipped with a PHOTON II detector. Data collection was performed at 100 K or 298 K under the N_2 stream of an Oxford Cryosystems Cryostream with MoKα (graphite monochrometer) or CuKα radiation (IμS source). The frames were integrated and scaling was performed using APEX3 software, including a multi-scan absorption correction.

Structure solutions were obtained with SHELXT using direct methods and refined via least-square refinement against F^2 by SHELXL, as implemented in OLEX2 crystallographic software.[1-3] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed on geometrically calculated positions using the riding model and refined isotropically.

*(E)-4,4'-(But-2-ene-1,4-diyl)bis(2-methoxyphenol) (compound **1**).* This compound crystallized in the space group *Pbca* with half of a molecule in the asymmetric unit. Two reflections (0 2 1, 1 2 2) were omitted from the refinement, as they were likely affected by the beamstop during data collection. The low resolution of this data set (0.95 Å) resulted in one checkCIF A alert. Attempts to isolate single crystals that could yield higher resolution data were unsuccessful.

*Bis(4-allyl-2-methoxyphenyl) carbonate (compound **2**).* This compound crystallized in the space group *C2/c* with half of a molecule in the asymmetric unit. No checkCIF level A or B alerts were found.

*2,4,6-tris(4-allyl-2-methoxyphenoxy)-1,3,5-triazine (compound **4**).* This compound crystallized in the space group $P2_1/n$ with a full molecule in the asymmetric unit. Positive and negative residual density resulted in three checkCIF B alerts. This residual density could not be modelled as any chemically reasonable species and likely results from minor errors in the absorption correction.

Table S1. Crystal data and structure refinement for (E)-4,4'-(But-2-ene-1,4-diyl)bis(2-methoxyphenol) (compound **1**).

CCDC Deposition Number	2360344
Empirical formula	$C_{18}H_{20}O_4$
Formula weight	300.357
Temperature/K	298.00
Crystal system	orthorhombic
Space group	Pbca
a/Å	4.8827(2)
b/Å	10.6999(4)
c/Å	29.5508(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1543.86(10)
Z	4
ρ_{calc}g/cm^3	1.292
μ/mm^{-1}	0.738
F(000)	642.2
Crystal size/mm^3	0.187 × 0.134 × 0.074
Radiation	Cu Kα (λ = 1.54178)

2Θ range for data collection/°	5.98 to 108.44
Index ranges	$-5 \leq h \leq 5$, $-11 \leq k \leq 11$, $-31 \leq l \leq 31$
Reflections collected	27266
Independent reflections	942 [R_{int} = 0.0305, R_{sigma} = 0.0126]
Data/restraints/parameters	942/0/103
Goodness-of-fit on F^2	1.095
Final R indexes [I>=2σ (I)]	R_1 = 0.0307, wR_2 = 0.0805
Final R indexes [all data]	R_1 = 0.0318, wR_2 = 0.0824
Largest diff. peak/hole / e $Å^{-3}$	0.11/-0.10

Table S2. Crystal data and structure refinement for *Bis(4-allyl-2-methoxyphenyl) carbonate (compound **2**)*.

CCDC Deposition Number	2360346
Empirical formula	$C_{21}H_{22}O_5$
Formula weight	354.406
Temperature/K	100.00
Crystal system	monoclinic
Space group	C2/c
a/Å	15.9421(5)
b/Å	8.6790(3)
c/Å	13.2926(4)
α/°	90
β/°	101.624(1)
γ/°	90
Volume/$Å^3$	1801.46(10)
Z	4
$\rho_{calc}g/cm^3$	1.307
μ/mm^{-1}	0.093
F(000)	752.5
Crystal size/mm^3	0.372 × 0.348 × 0.244
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.22 to 50.7
Index ranges	$-19 \leq h \leq 19$, $-10 \leq k \leq 10$, $-16 \leq l \leq 16$
Reflections collected	12445
Independent reflections	1644 [R_{int} = 0.0329, R_{sigma} = 0.0183]
Data/restraints/parameters	1644/0/121
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0287, wR_2 = 0.0721
Final R indexes [all data]	R_1 = 0.0340, wR_2 = 0.0787
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.17

Table S3. Crystal data and structure refinement for 2,4,6-tris(4-allyl-2 methoxyphenoxy)-1,3,5-triazine (compound **4**).

CCDC Deposition Number	2360345
Empirical formula	$C_{33}H_{33}N_3O_6$
Formula weight	567.646
Temperature/K	100.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.0353(5)
b/Å	11.7214(5)
c/Å	20.1820(8)
α/°	90
β/°	107.691(1)
γ/°	90
Volume/Å^3	2937.8(2)
Z	4
ρ_{calc}g/cm^3	1.283
μ/mm^{-1}	0.089
F(000)	1200.8
Crystal size/mm^3	0.524 × 0.247 × 0.072
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.06 to 50.7
Index ranges	$-15 \leq h \leq 15$, $-14 \leq k \leq 14$, $-24 \leq l \leq 24$
Reflections collected	37621
Independent reflections	5374 [R_{int} = 0.0443, R_{sigma} = 0.0276]
Data/restraints/parameters	5374/0/382
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0665, wR_2 = 0.1694
Final R indexes [all data]	R_1 = 0.0828, wR_2 = 0.1828
Largest diff. peak/hole / e Å^{-3}	1.04/-1.00

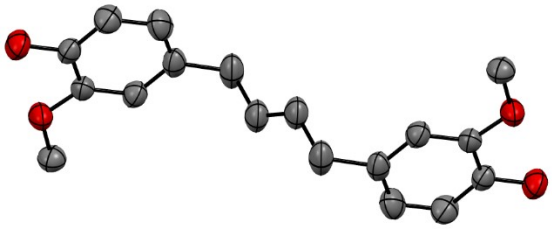

Figure S12. Solid-state structure of compound **1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Grey and red ellipsoids represent C and O atoms, respectively.

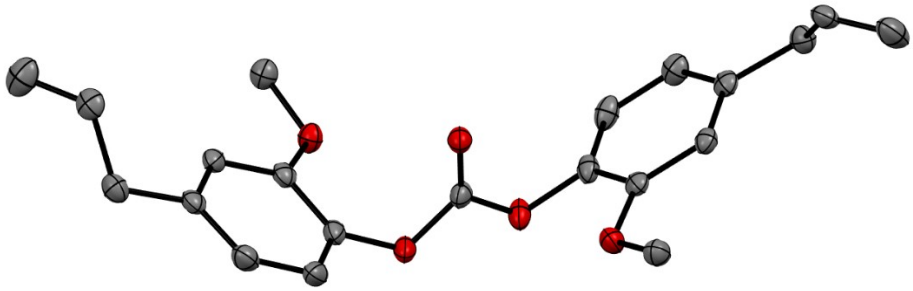

Figure S13. Solid-state structure of compound **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Grey and red ellipsoids represent C and O atoms, respectively.

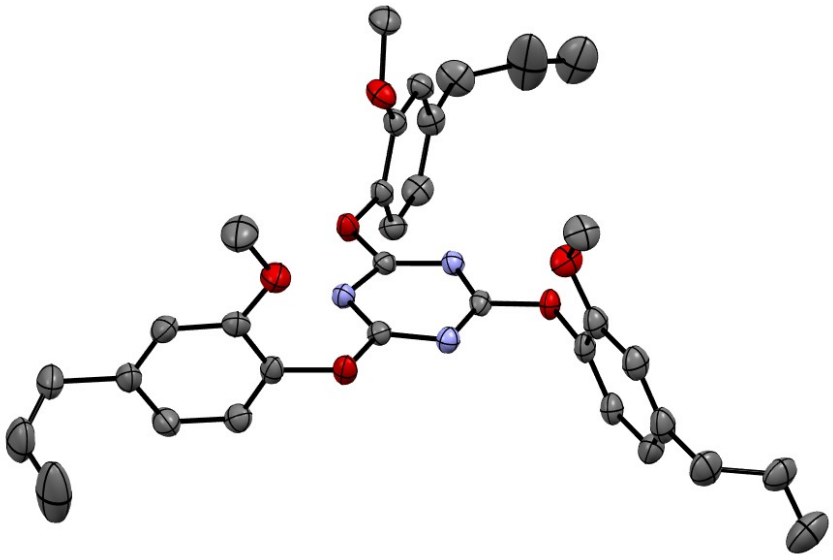

Figure S14. Solid-state structure of compound **4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Grey, blue and red ellipsoids represent C, N and O atoms, respectively.

References

(1) Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. A* **2015**, *71*, 3–8.

(2) Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr. A* **2008**, *64*, 112–122.

(3) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2 : A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42* (2), 339–341.