

Supporting Information

Fire-Resistant Propargyl Ether Networks Derived from Bio-Based Hydroxycinnamic Acids

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Table of Contents

Thermal analysis of thermosets	S2
Microscale combustion calorimetry (MCC) data	S21
Crystallographic data	S28
IR spectra of cured thermosets and monomers	S32
NMR spectra of isolated compounds.....	S34

Thermal Analysis of Thermosets

Figure S1. Differential scanning calorimetry trace for CD (exo = up)

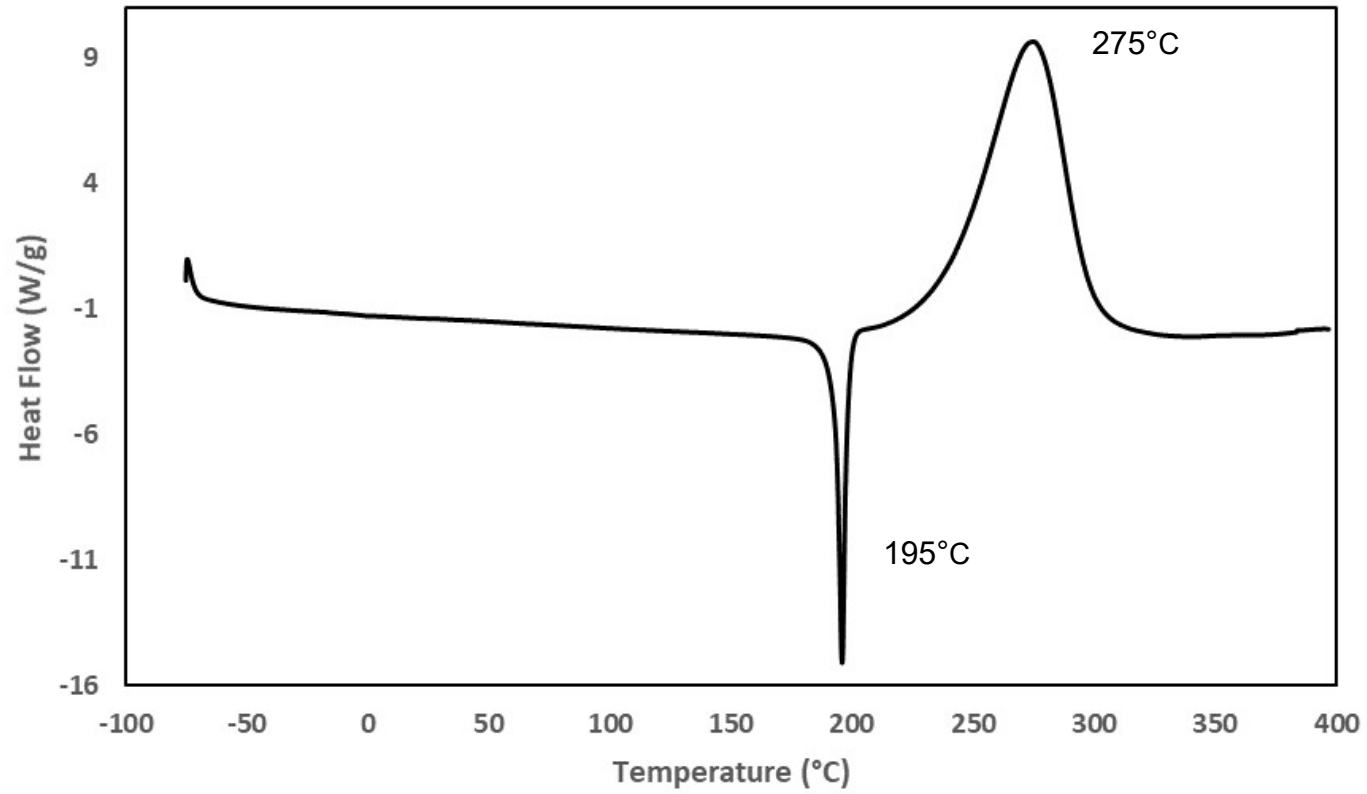


Figure S2. Thermogravimetric analysis of cross-linked CD

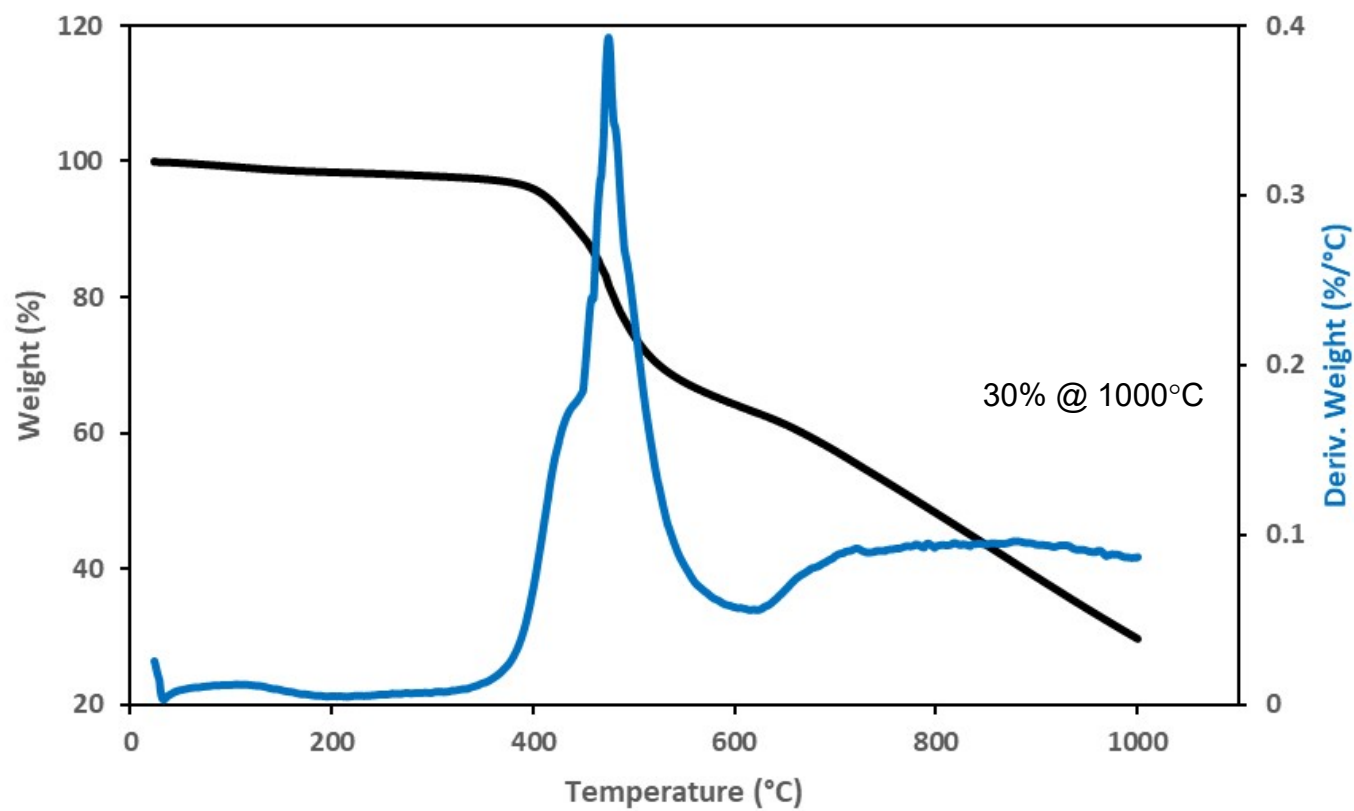


Figure S3. Thermomechanical analysis of cross-linked CD

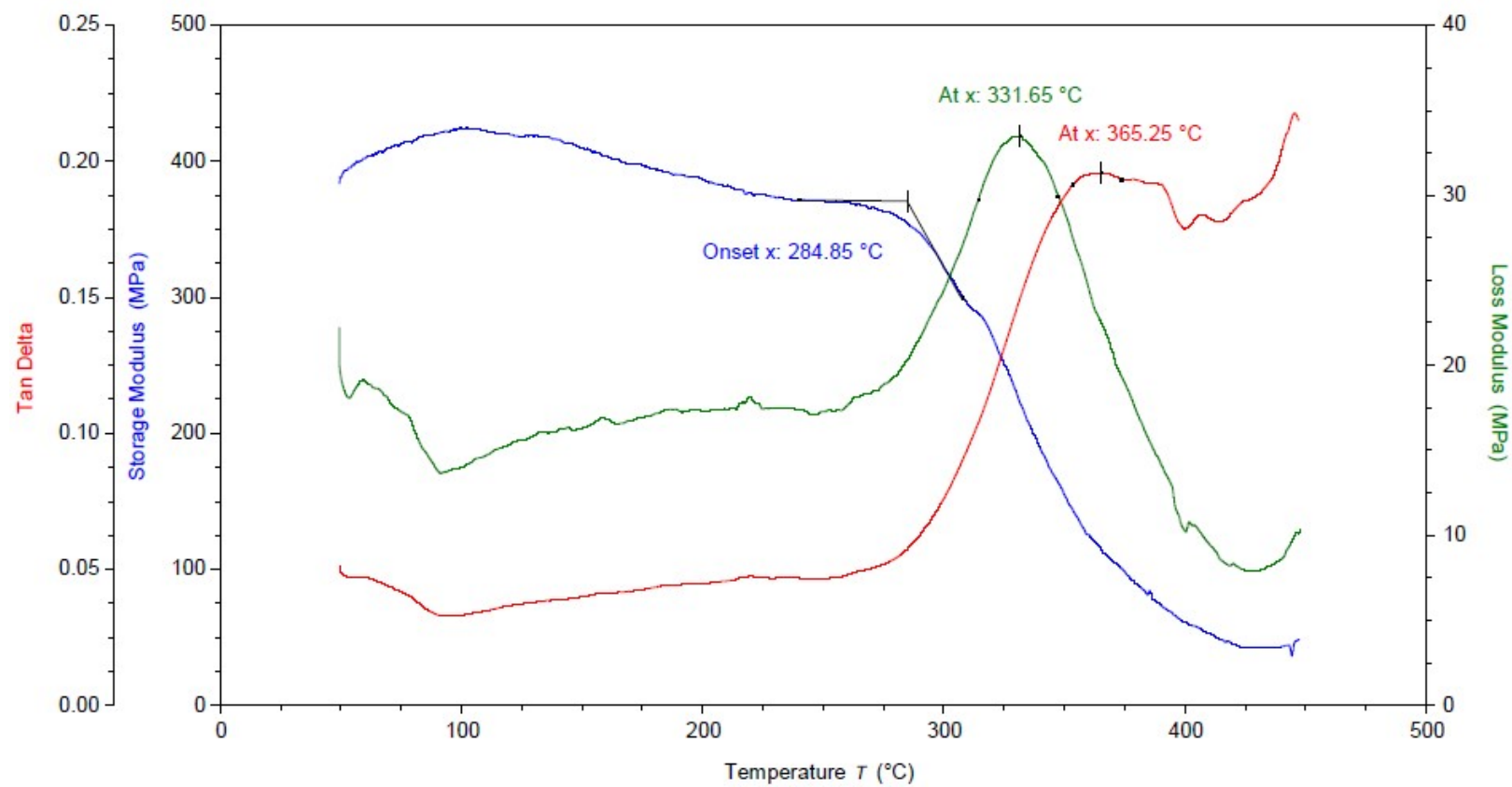


Figure S4. Differential scanning calorimetry trace for FD (exo = up)

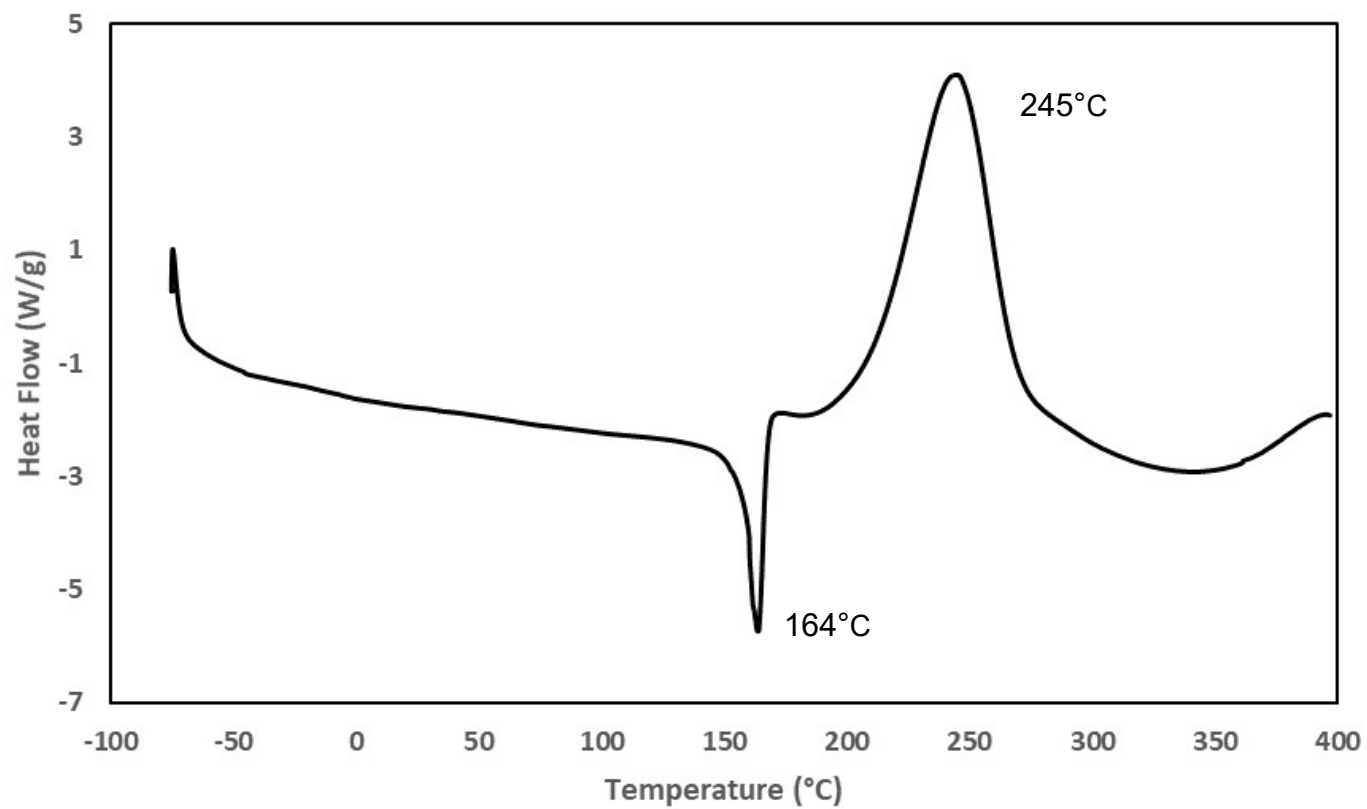


Figure S5. Thermogravimetric analysis of cross-linked FD

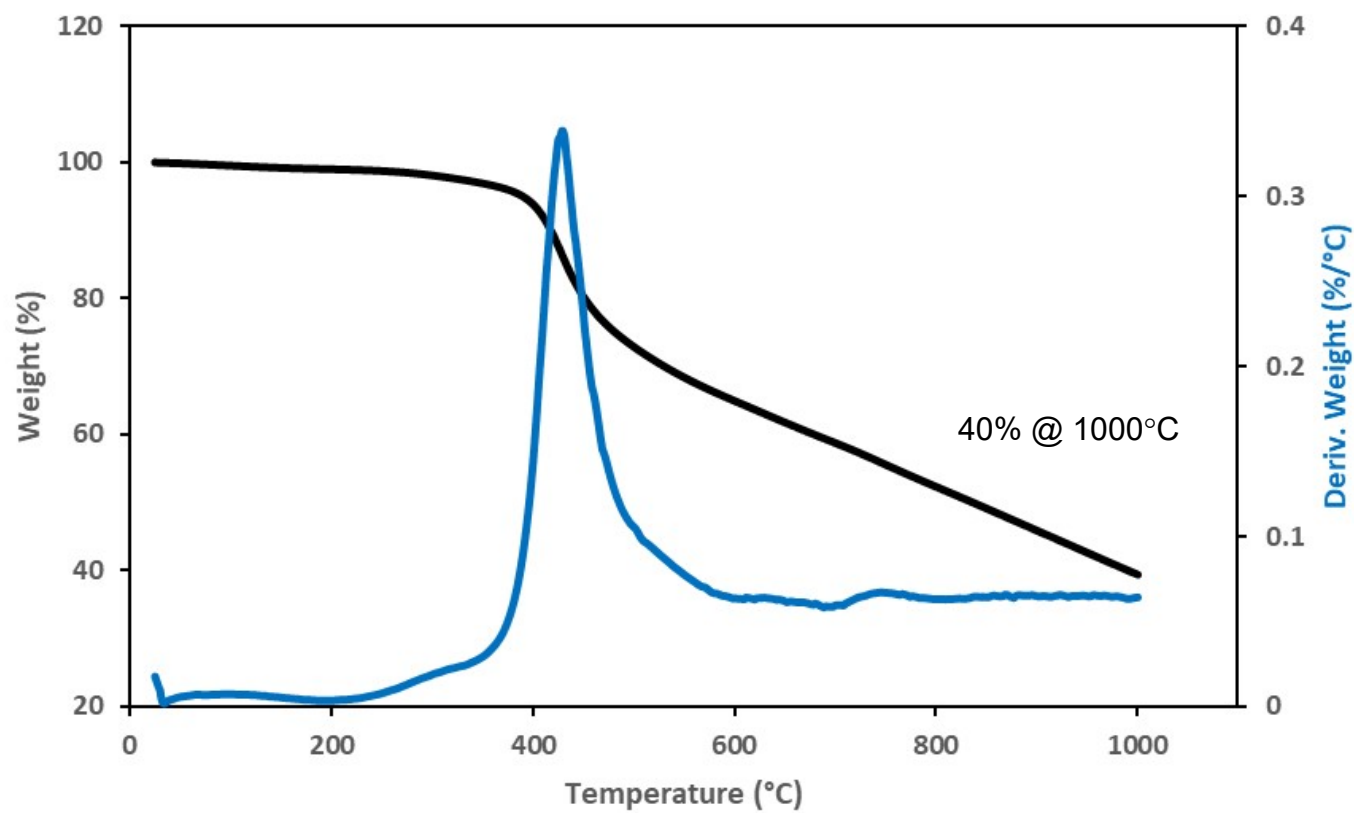


Figure S6. Differential scanning calorimetry trace for SD (exo = up)

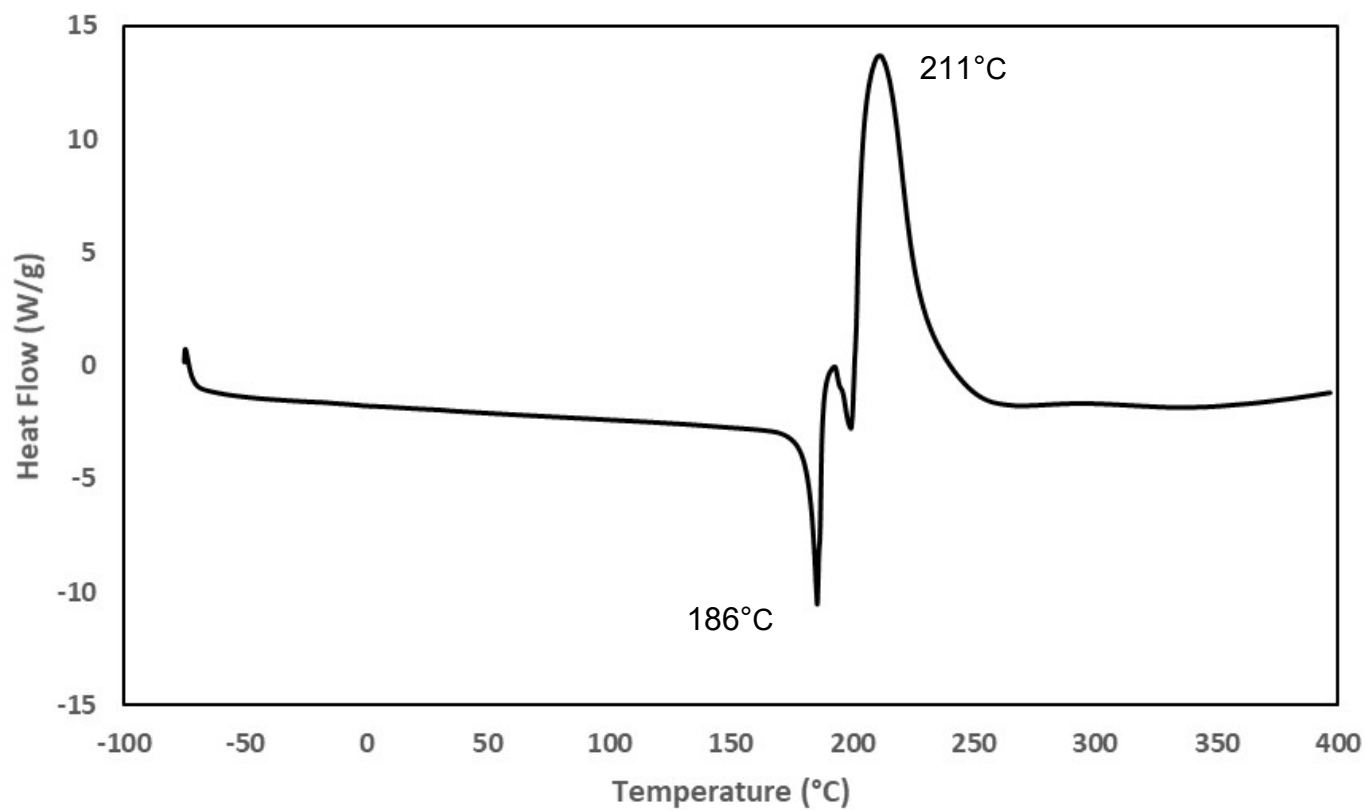


Figure S7. Thermogravimetric analysis of SD

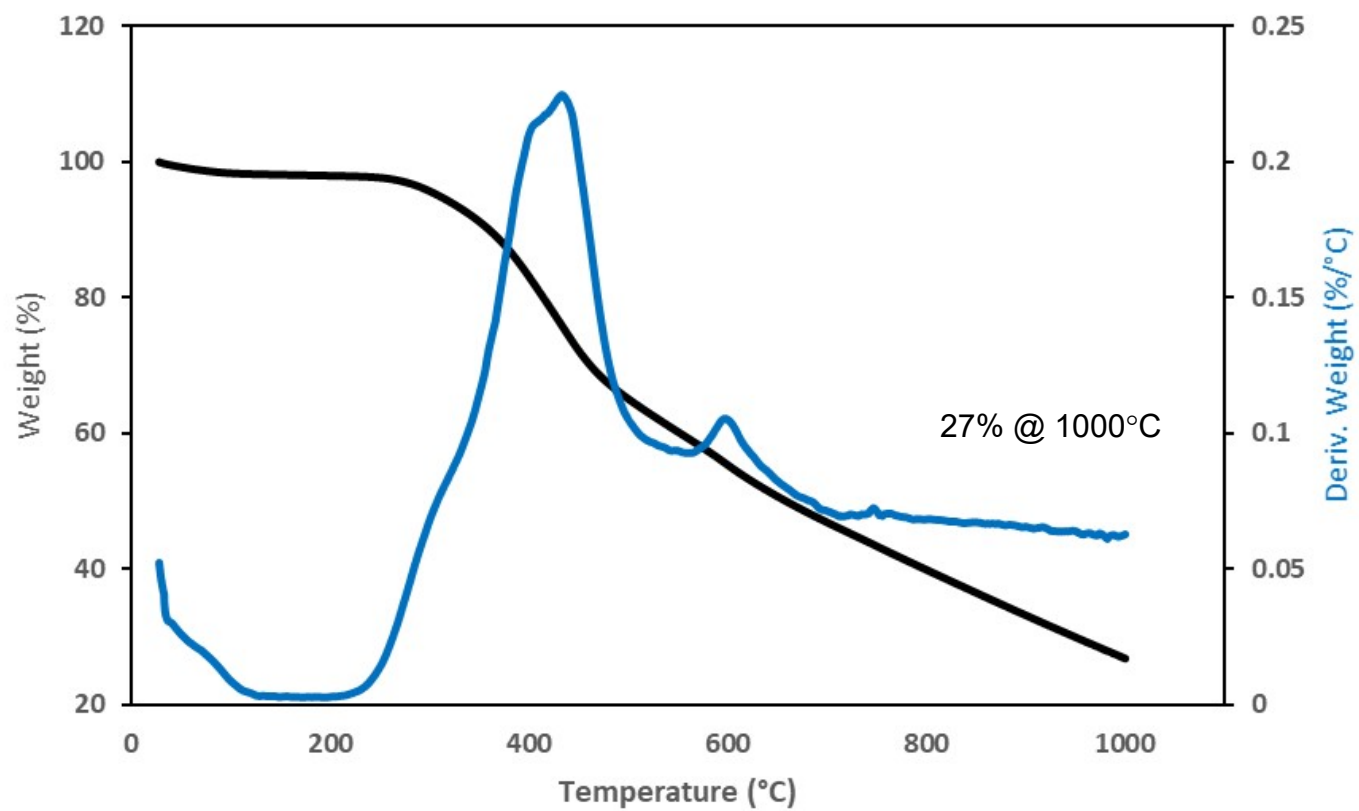


Figure S8. Differential scanning calorimetry trace for the 3:7 PD:CD mixture (exo = up)

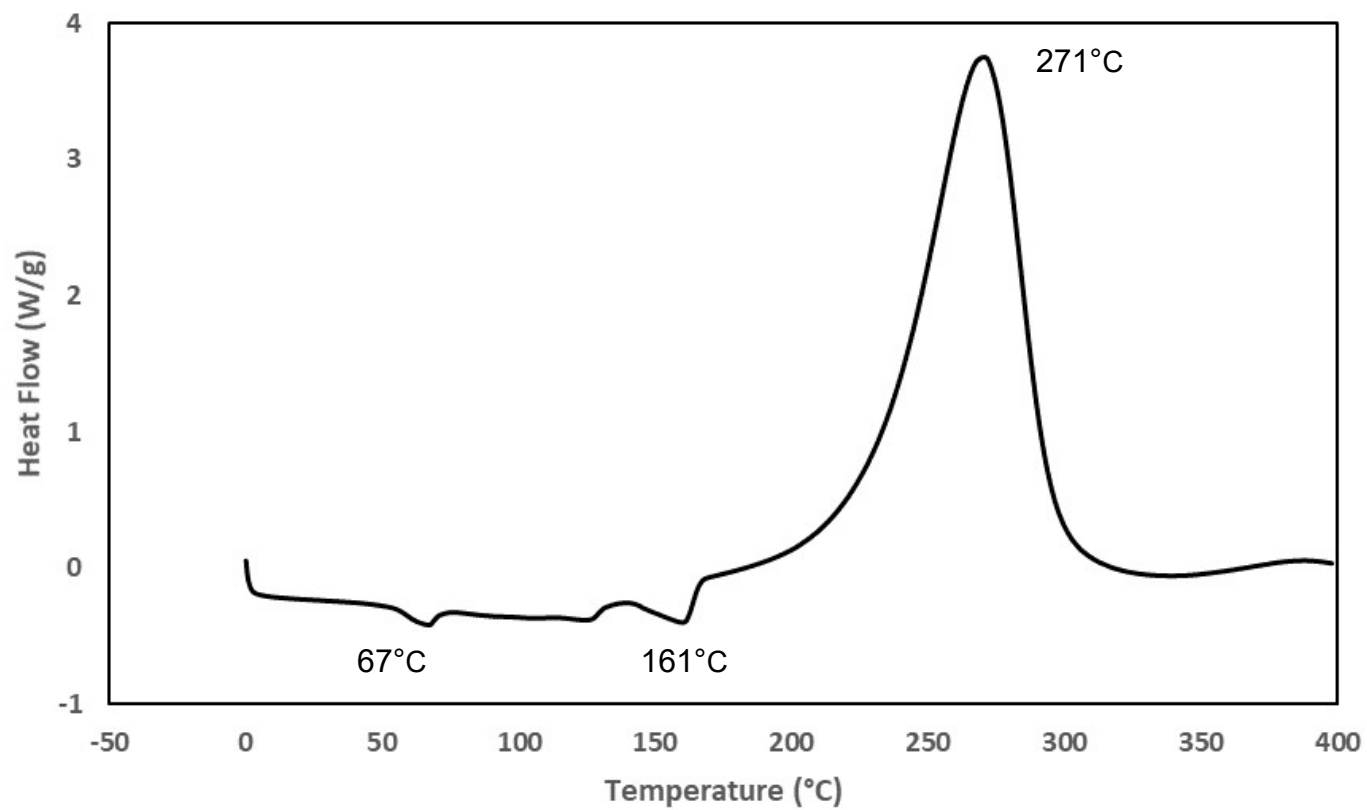


Figure S9. Differential scanning calorimetry trace for the 1:1 PD:CD mixture (exo = up)

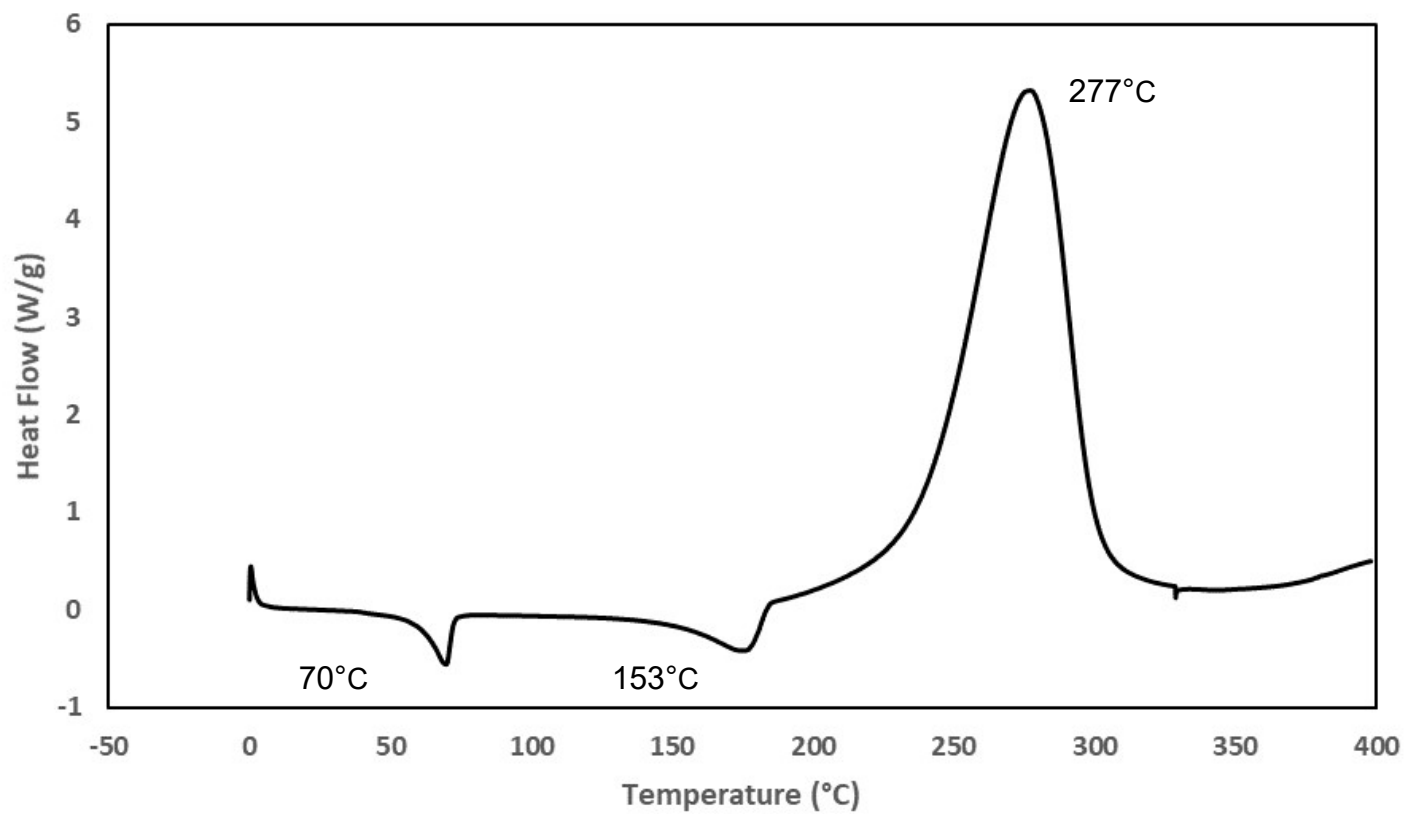


Figure S10. Differential scanning calorimetry trace for the 7:3 PD:CD mixture (exo = up)

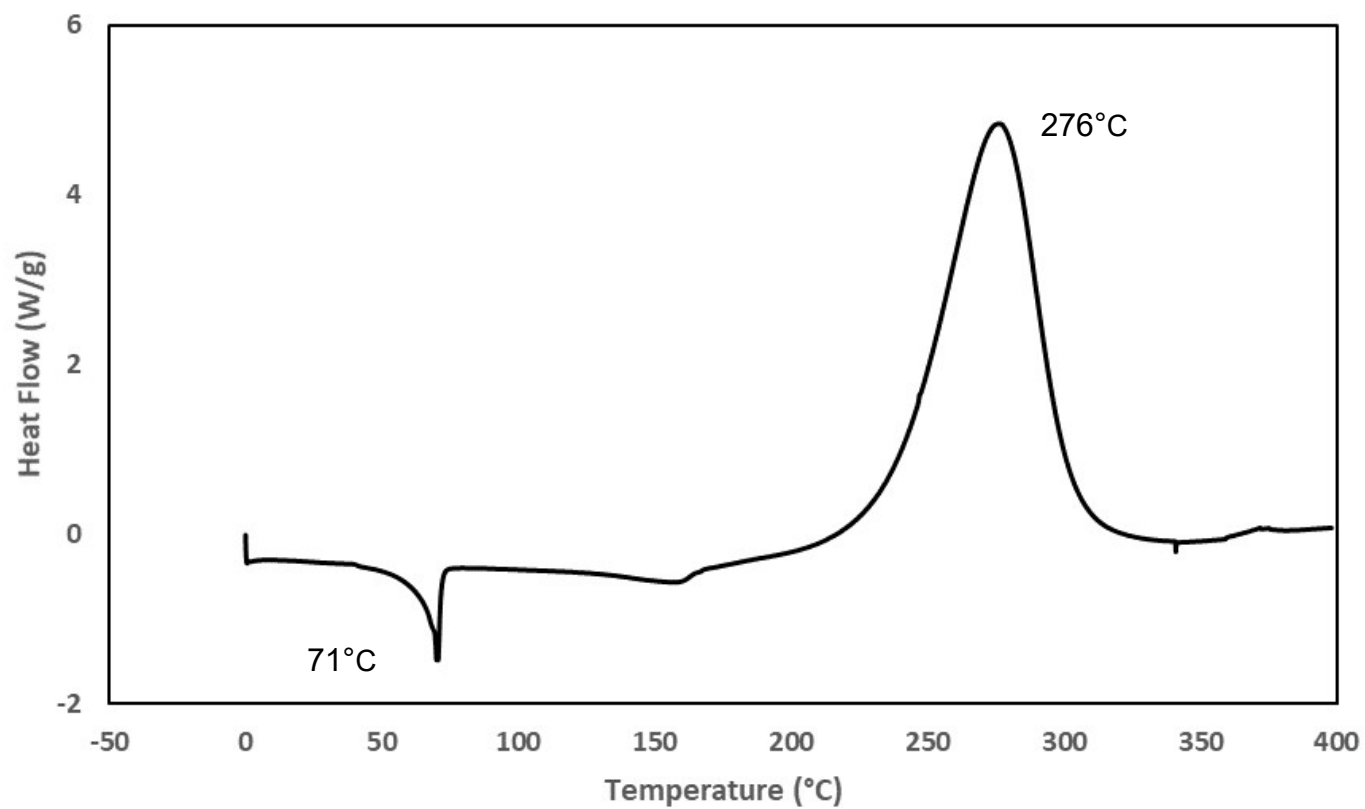


Figure S11. Thermogravimetric analysis of the cross-linked 7:3 PD:CD mixture

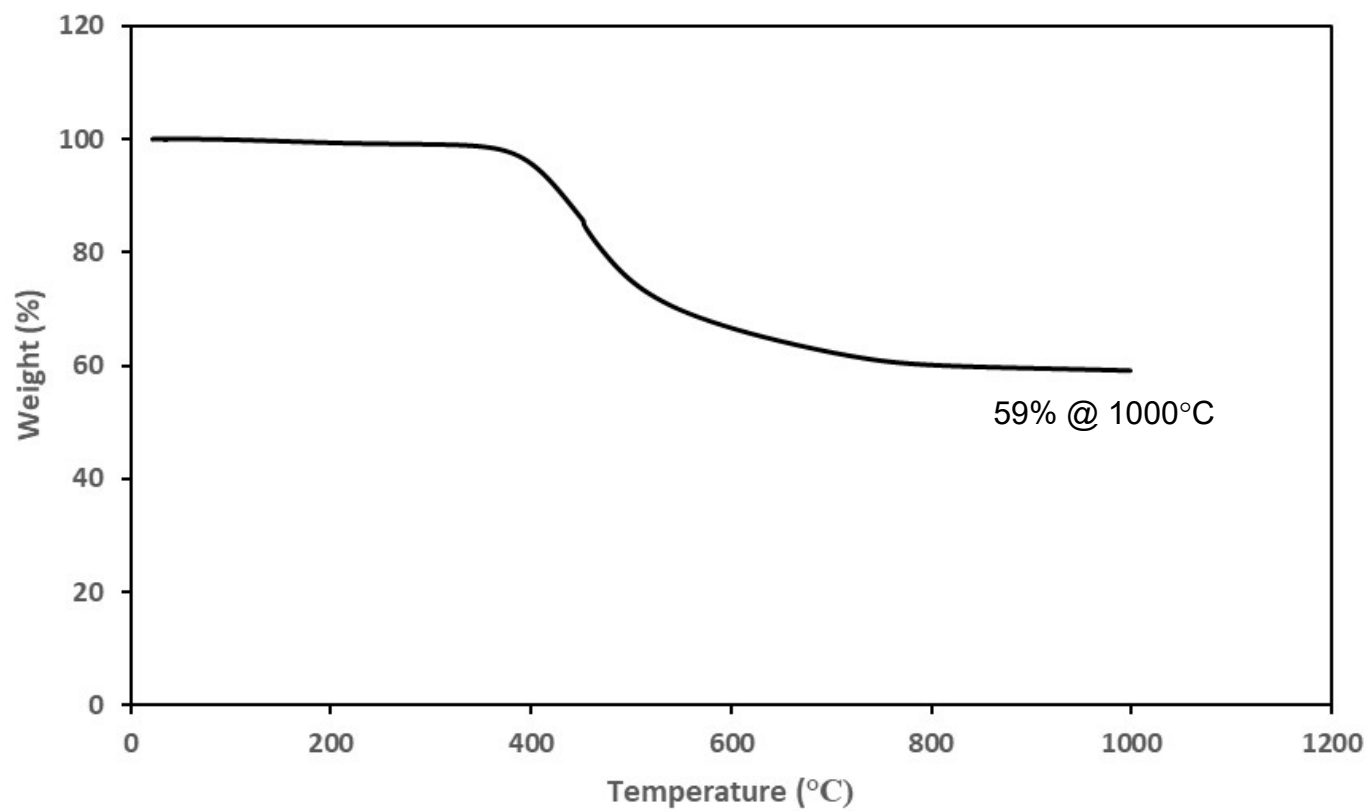


Figure S12. Thermomechanical analysis of a cross-linked 7:3 PD:CD mixture

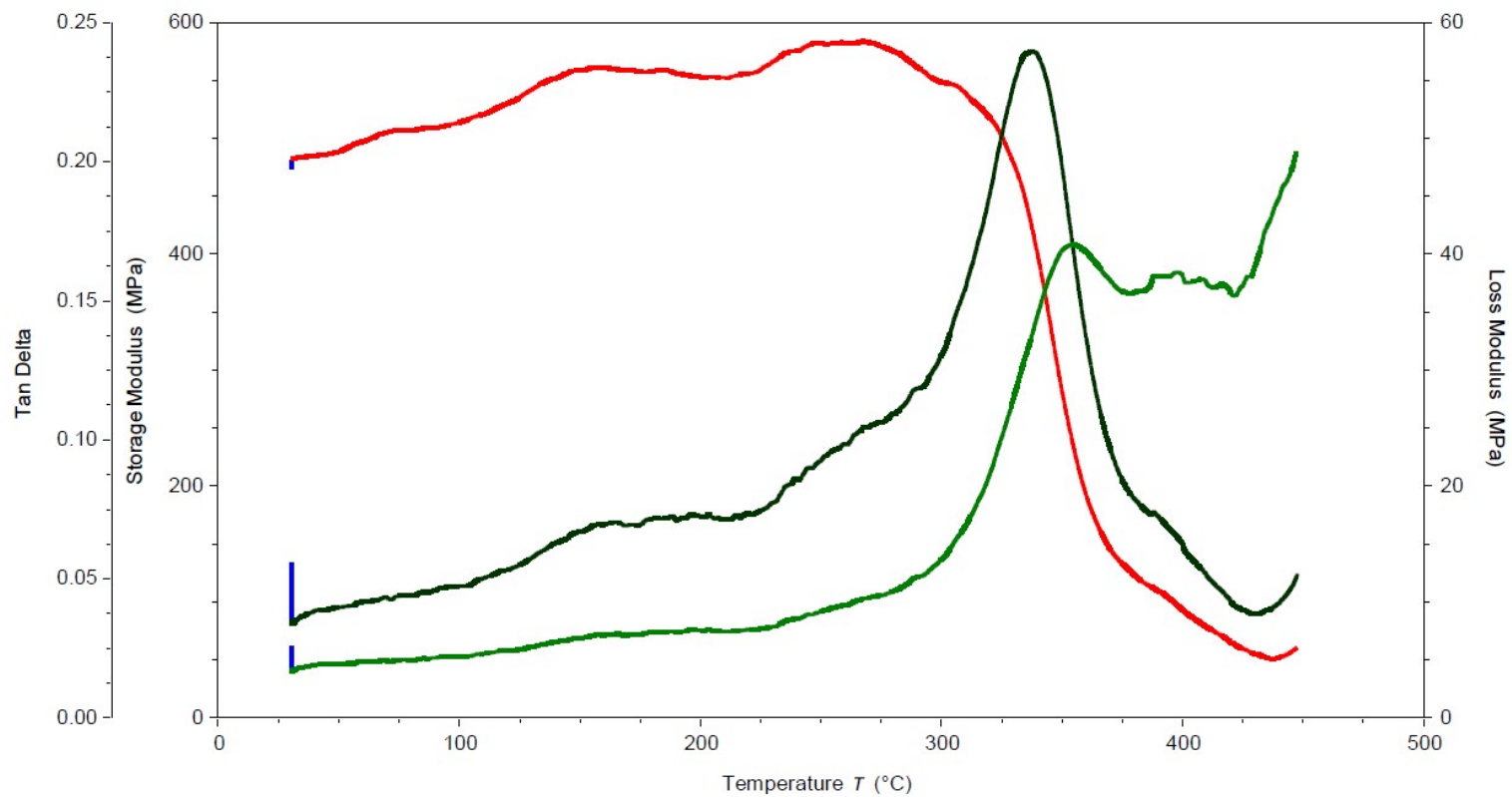


Figure S13. Differential scanning calorimetry trace of a 9:1 PD:CD mixture (exo = up)

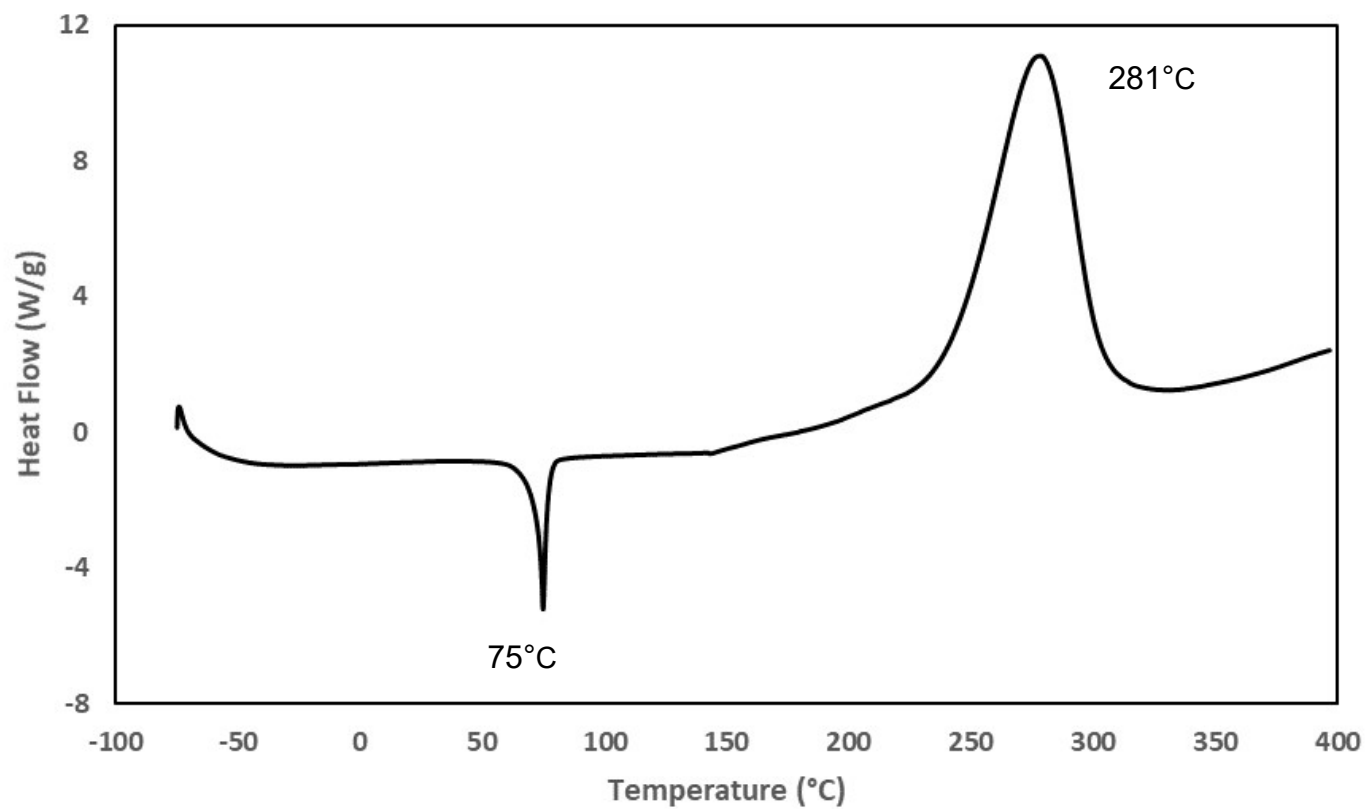


Figure S14. Differential scanning calorimetry trace for TD (exo = up)

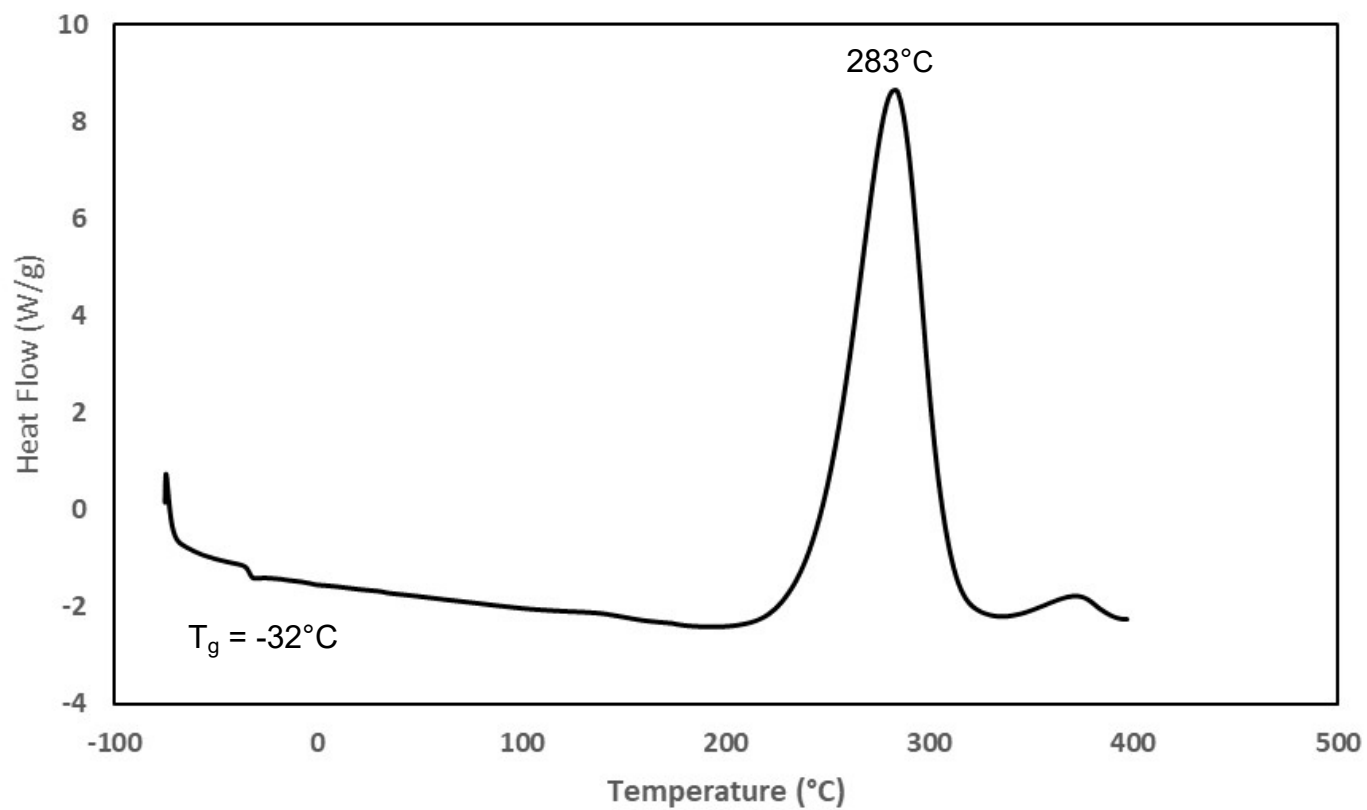


Figure S15. Thermogravimetric analysis of TD

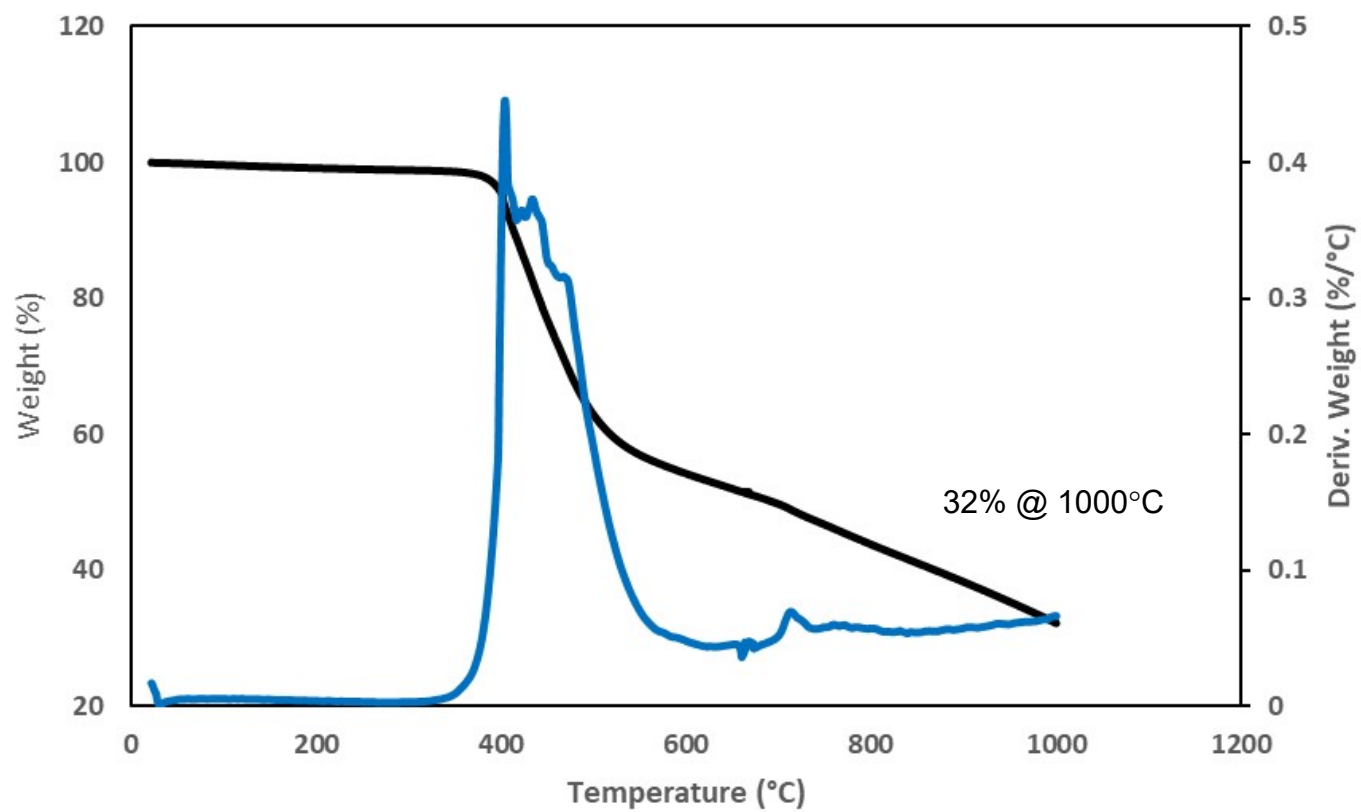


Figure S16. Thermomechanical analysis of TD

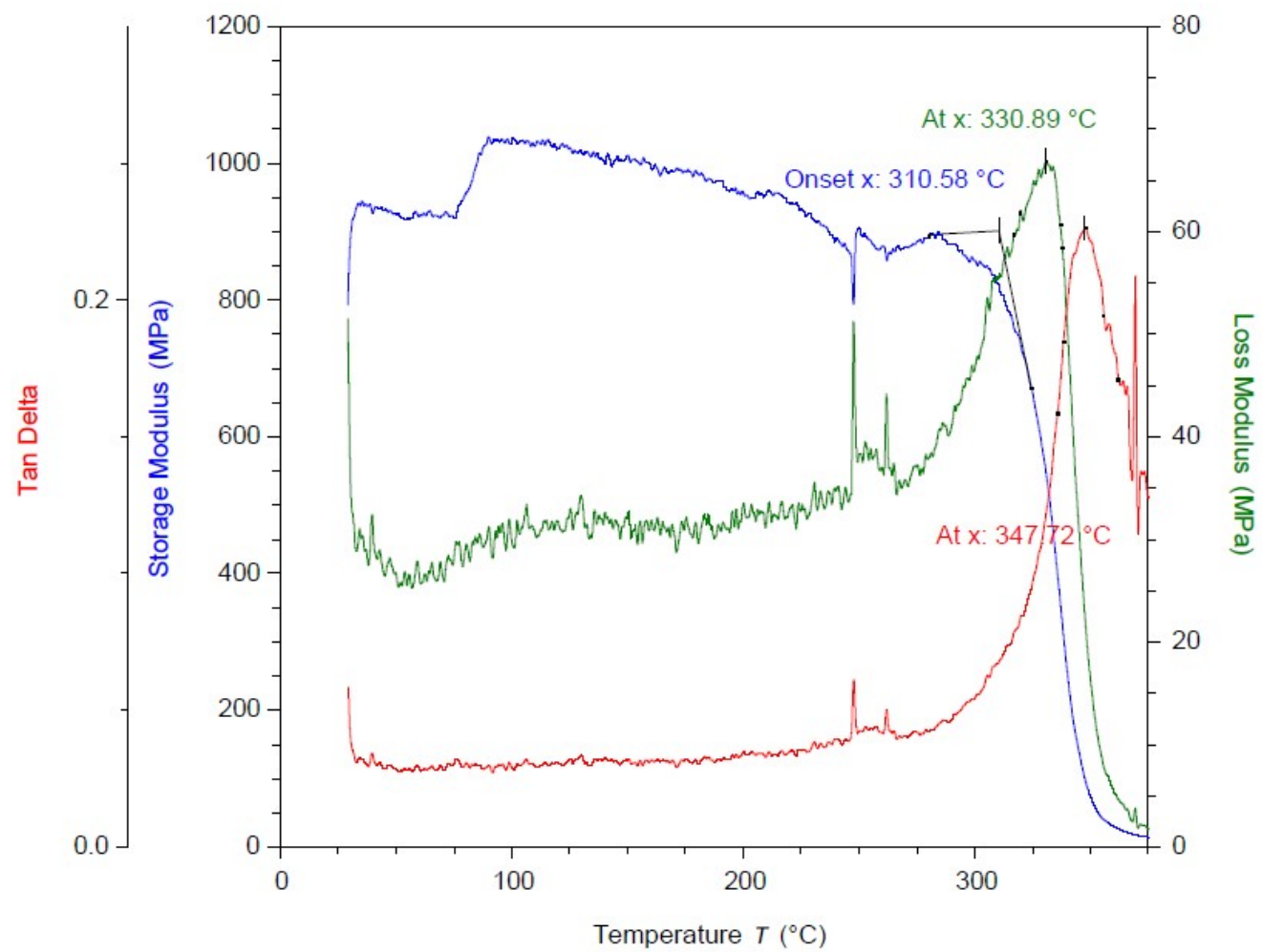


Figure S17. Differential scanning calorimetry trace for the 7:3 TD:CD mixture (exo = up)

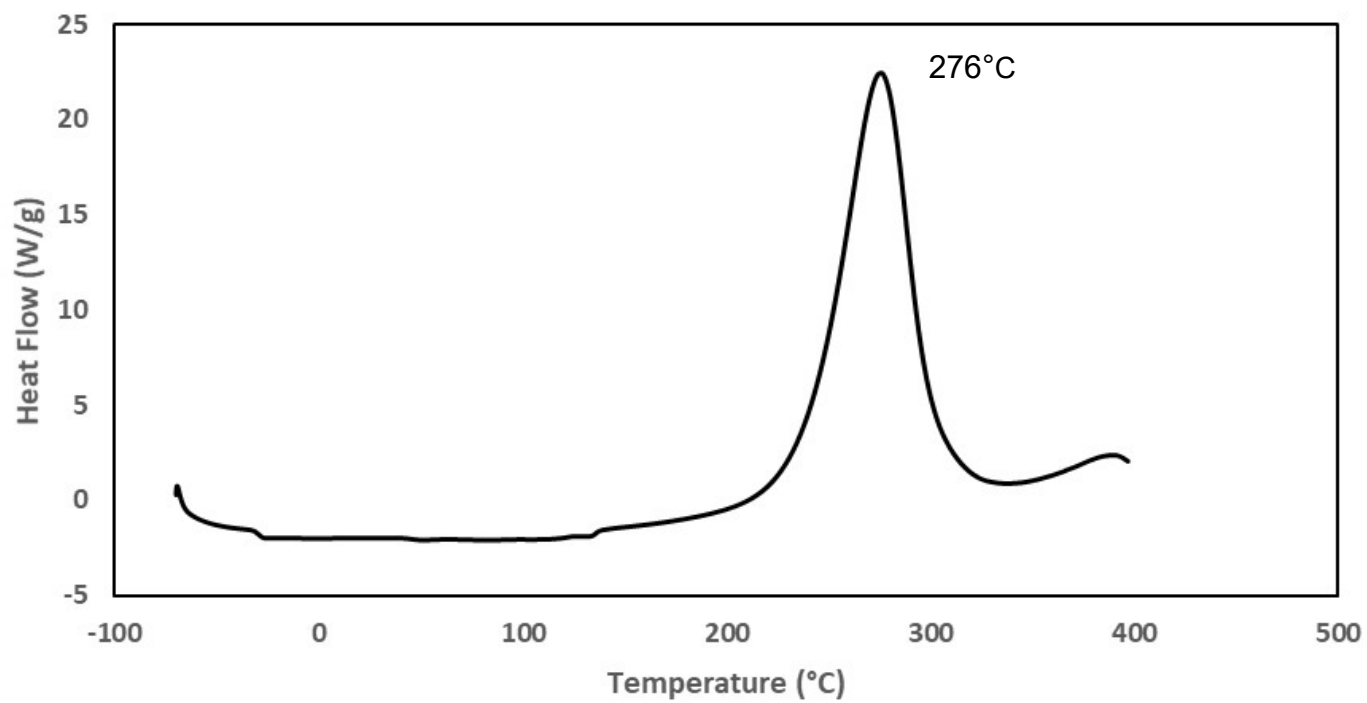


Figure S18. Thermogravimetric analysis of the cross-linked 7:3 TD:CD mixture

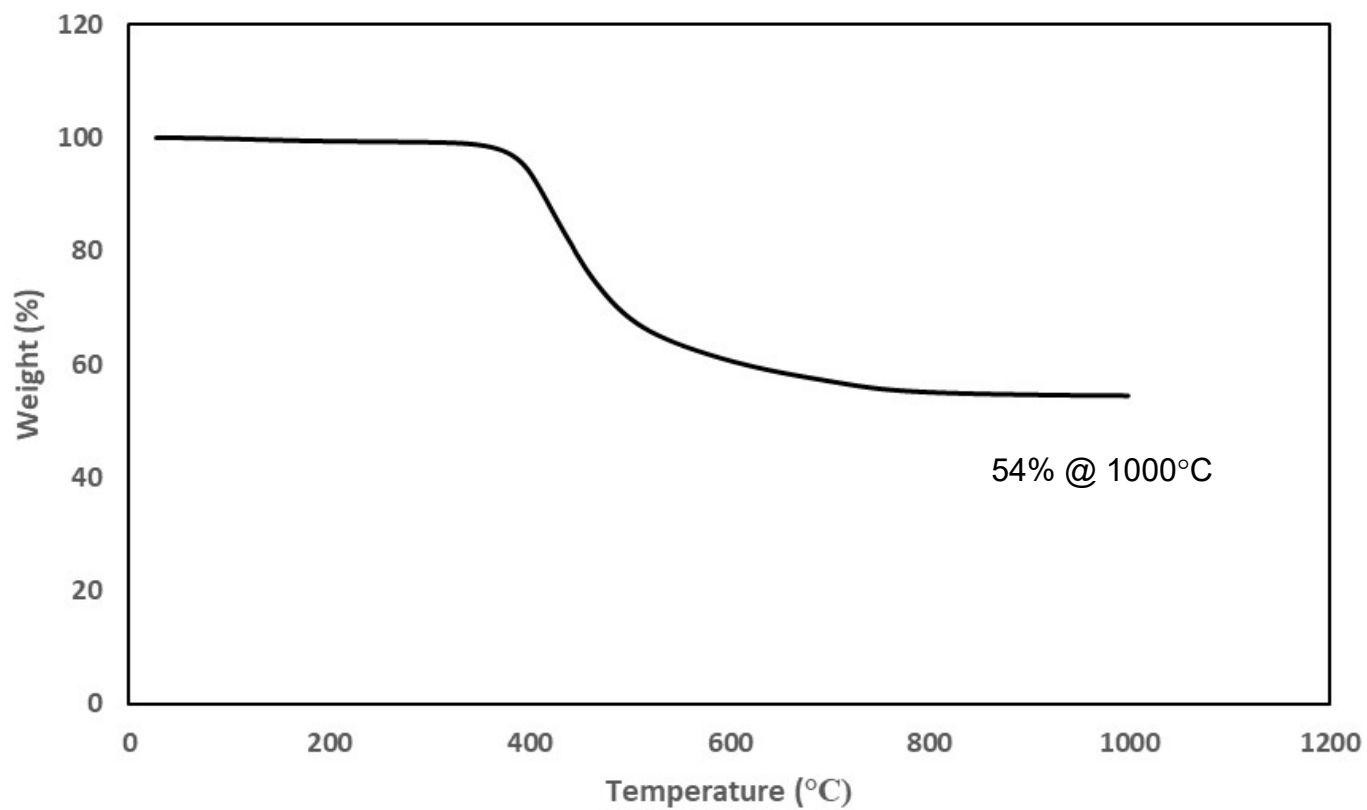
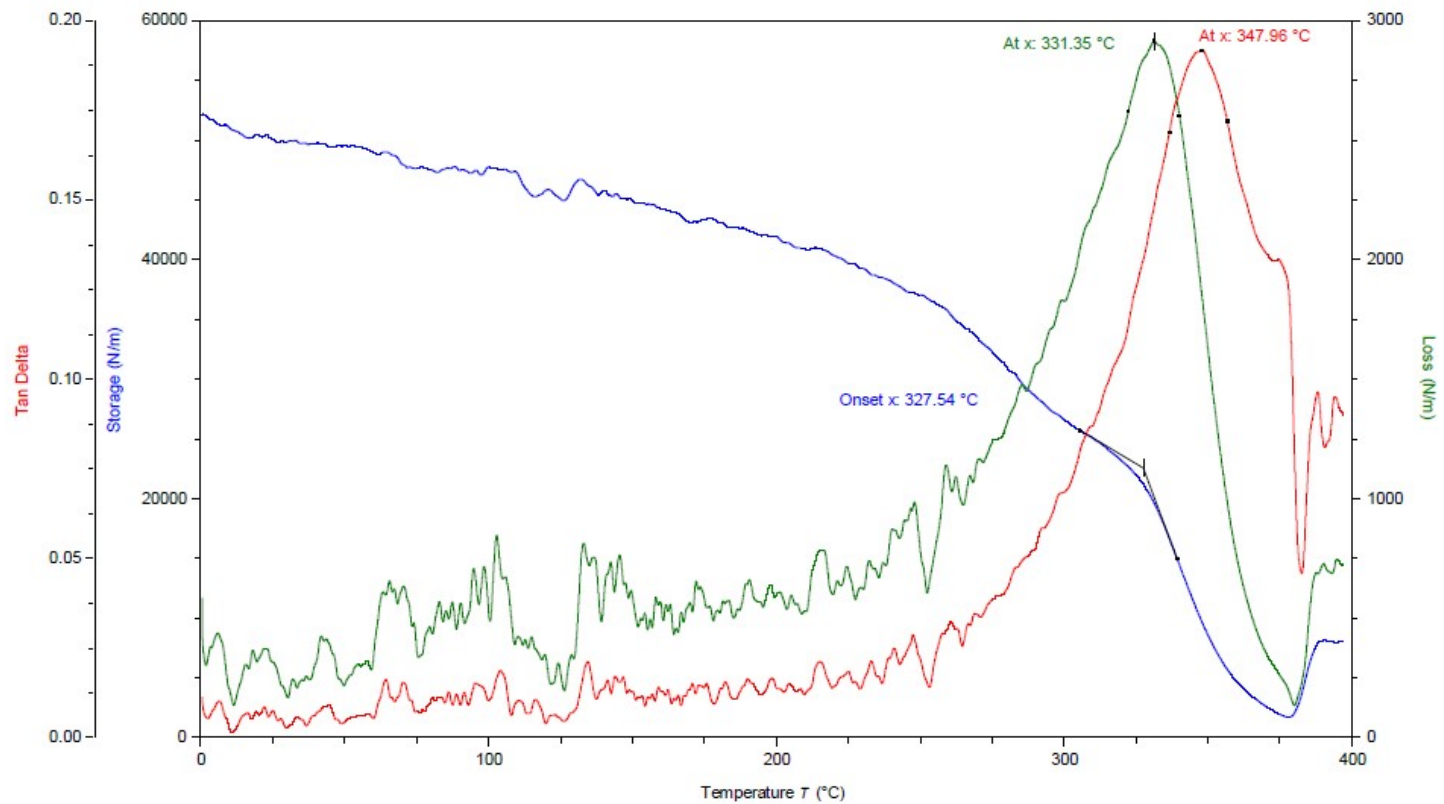


Figure S19. Thermomechanical analysis of the cross-linked 7:3 TD:CD mixture



Microscale Combustion Calorimetry Data

Figure S20. Microscale combustion calorimetry data for cross-linked CD

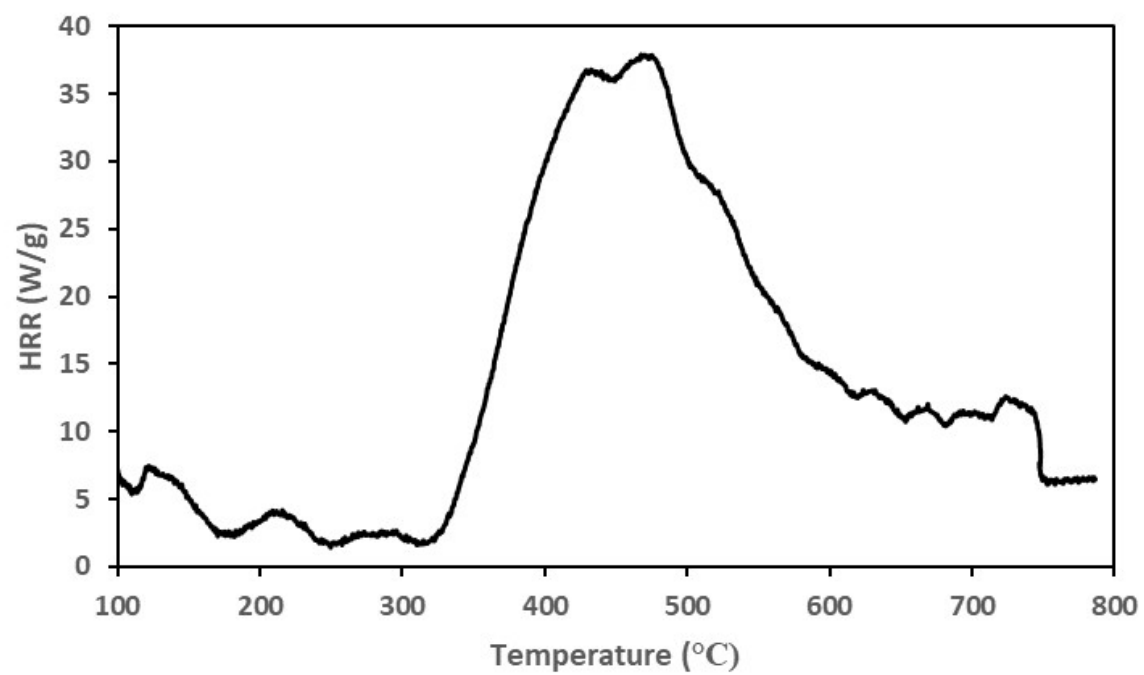


Figure S21. Microscale combustion calorimetry data for cross-linked FD

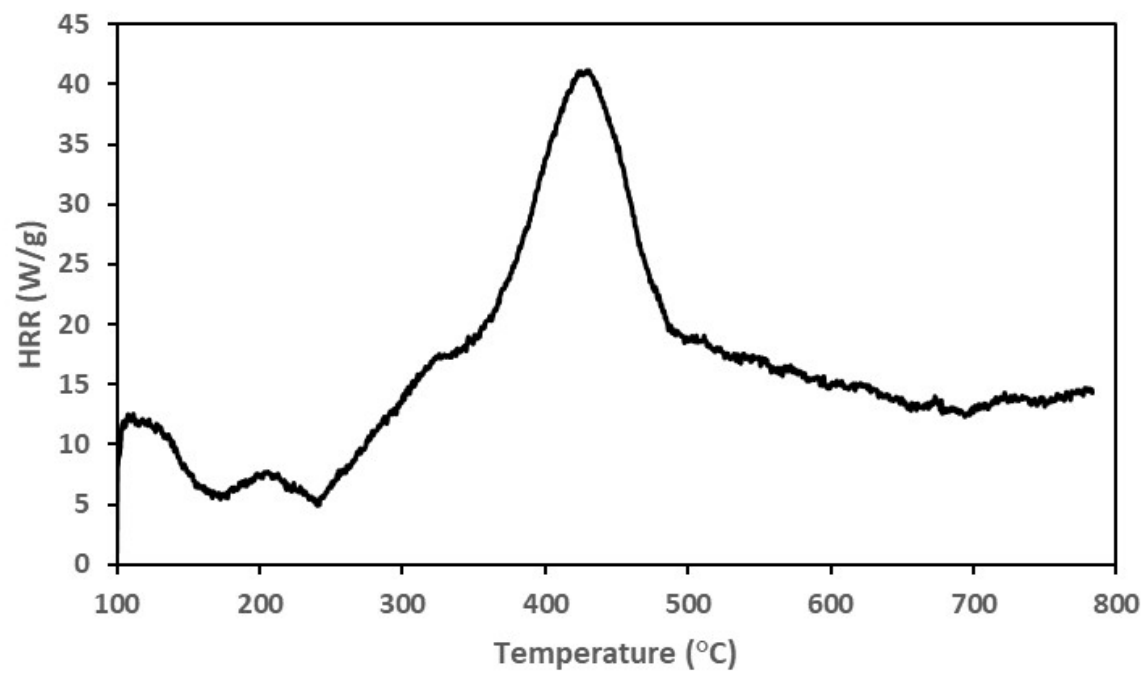


Figure S22. Microscale combustion calorimetry data for cross-linked SD

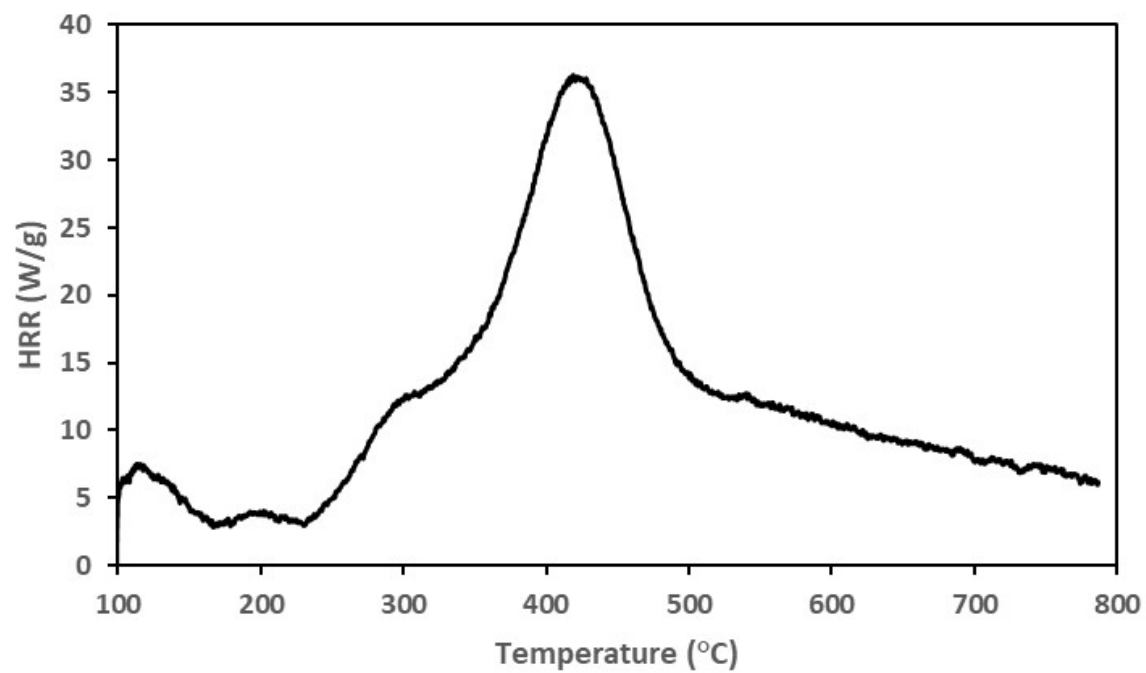


Figure S23. Microscale combustion calorimetry data for the cross-linked 7:3 PD:CD mixture

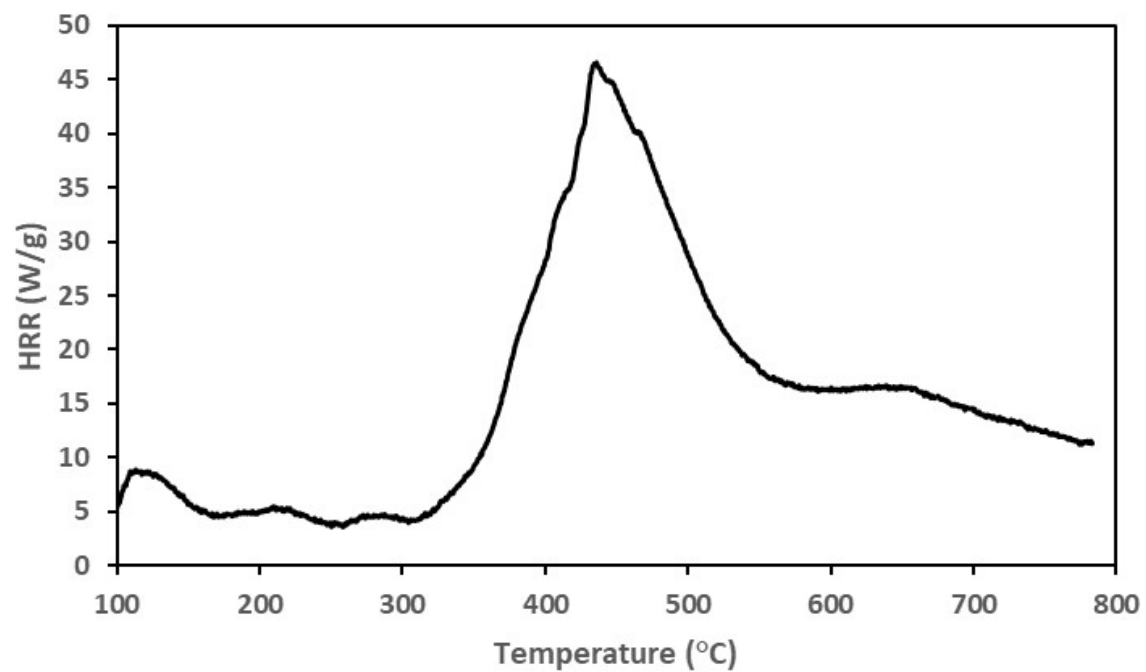


Figure S24. Microscale combustion calorimetry data for the cross-linked 9:1 PD:CD mixture

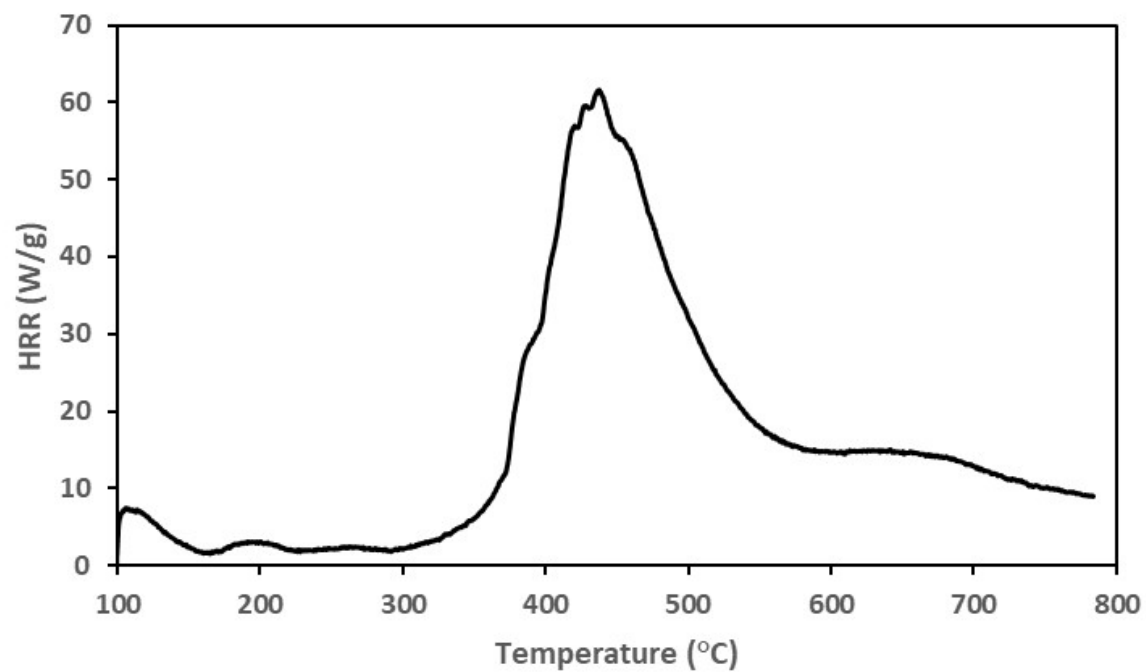


Figure S25. Microscale combustion calorimetry data for cross-linked TD

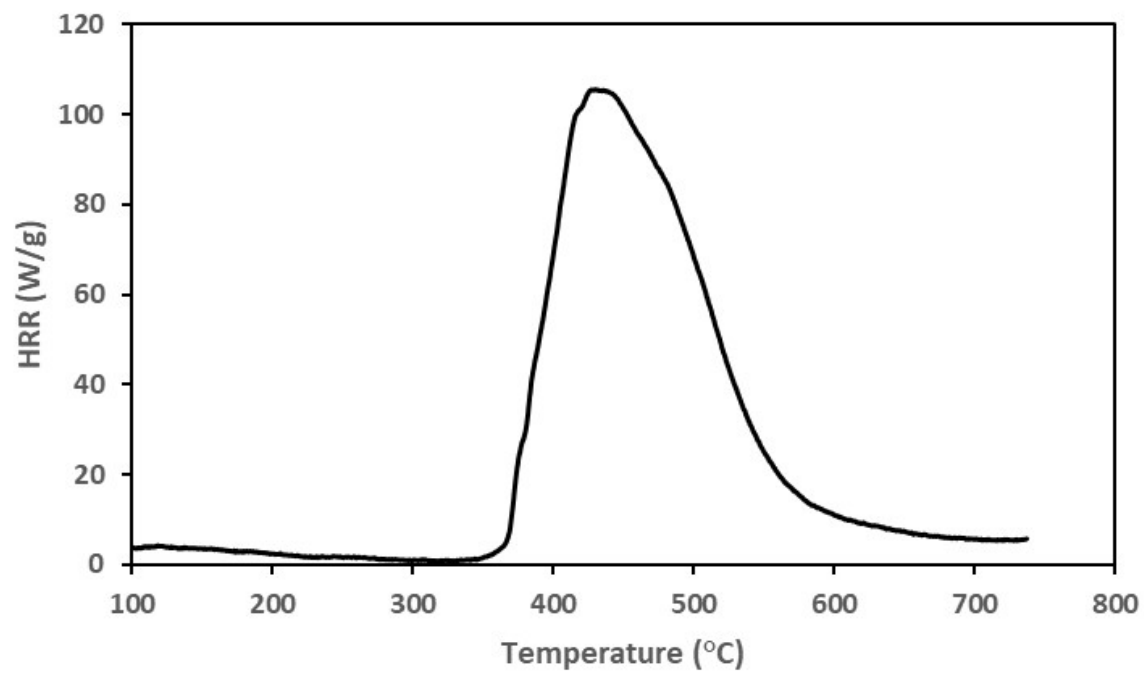
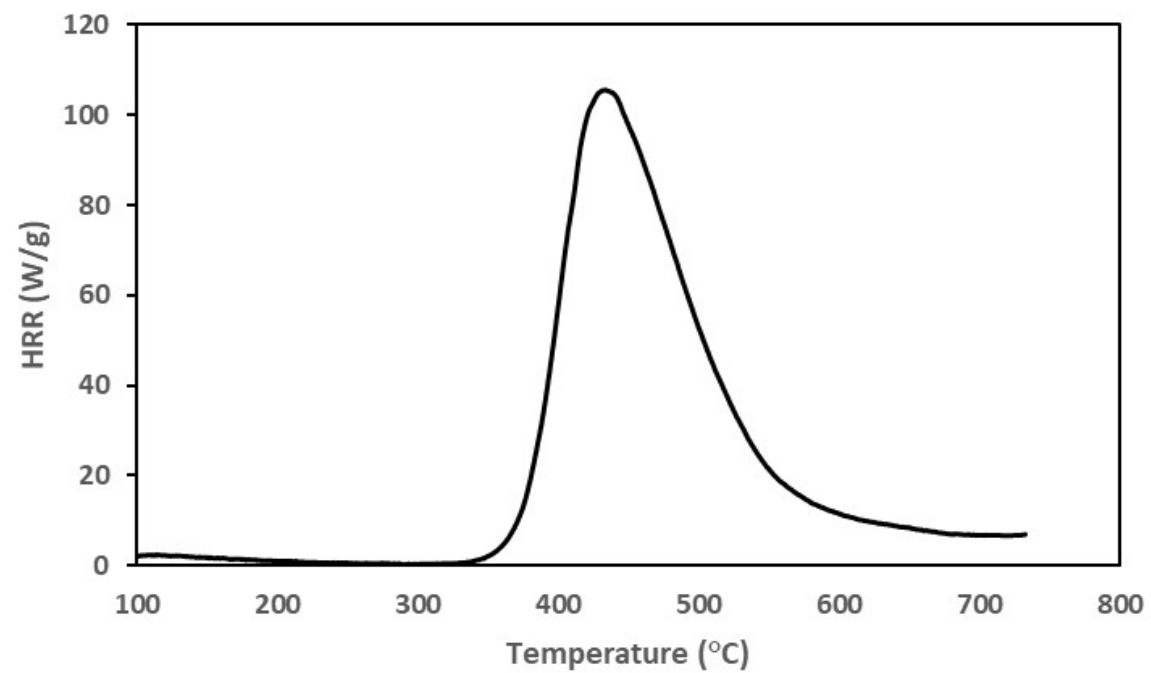


Figure S26. Microscale combustion calorimetry data for the cross-linked 70:30 TD:CD mixture



Crystallographic Data

Table S1. Crystal data and structure refinement for CD

Identification code	CD
Empirical formula	C ₂₀ H ₁₆ O ₂
Formula weight	288.349
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.4595(3)
b/Å	7.9946(3)
c/Å	25.5343(9)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1522.76(10)
Z	4
ρ _{calc} /g/cm ³	1.258
μ/mm ⁻¹	0.635
F(000)	609.9
Crystal size/mm ³	0.169 × 0.108 × 0.037
Radiation	Cu Kα (λ = 1.54178)
2θ range for data collection/°	6.92 to 108.46
Index ranges	-7 ≤ h ≤ 7, -8 ≤ k ≤ 8, -26 ≤ l ≤ 25
Reflections collected	6982
Independent reflections	931 [R _{int} = 0.0438, R _{sigma} = 0.0288]
Data/restraints/parameters	931/0/101
Goodness-of-fit on F ²	1.076
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0415, wR ₂ = 0.0877
Final R indexes [all data]	R ₁ = 0.0467, wR ₂ = 0.0902
Largest diff. peak/hole / e Å ⁻³	0.19/-0.16

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Compound 1
 U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O(001)	4998.8(18)	5702.4(16)	3416.8(5)	26.8(4)
C(002)	4991(3)	4409(2)	3772.2(8)	23.3(6)
C(003)	5804(3)	4459(3)	4261.1(8)	25.3(6)
C(004)	4743(3)	1641(2)	4441.9(8)	24.8(6)
C(005)	4058(3)	2988(2)	3617.3(8)	26.4(6)
C(006)	4577(3)	144(3)	4776.2(8)	28.6(6)
C(007)	6018(3)	7153(2)	3553.3(8)	28.0(6)
C(008)	3954(3)	1636(3)	3949.2(8)	27.1(6)
C(009)	5670(3)	3084(2)	4589.3(8)	26.9(6)
C(00A)	5842(3)	8351(3)	3125.9(9)	32.0(6)
C(00B)	5691(4)	9348(3)	2788.6(10)	43.4(7)

Table S3. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Compound 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(001)	31.9(9)	20.6(8)	28.0(9)	-3.0(7)	-2.2(7)	1.0(7)
C(002)	24.1(13)	19.3(12)	26.6(13)	4.4(10)	4.1(10)	1.5(10)
C(003)	26.1(12)	21.7(13)	28.3(13)	-1.0(10)	1.1(10)	-3.0(9)
C(004)	24.4(12)	20.2(12)	29.9(13)	1.9(10)	5.4(10)	0.1(10)
C(005)	24.5(13)	24.1(13)	30.4(13)	0.6(10)	-2.6(10)	-1.9(10)
C(006)	28.0(13)	24.6(12)	33.1(13)	-1.2(10)	3.8(10)	-3.5(11)
C(007)	34.6(14)	20.7(12)	28.6(13)	-5.5(10)	0.4(10)	-0.9(10)
C(008)	23.1(13)	21.9(12)	36.3(14)	-2.4(10)	0.9(10)	-3.9(10)
C(009)	27.3(13)	29.6(13)	23.8(12)	3.9(11)	1.1(10)	-0.5(10)
C(00A)	39.8(15)	25.4(13)	30.7(13)	-1.5(11)	2.2(11)	-2.7(12)
C(00B)	64.5(19)	31.1(14)	34.6(15)	0.0(13)	2.0(13)	3.1(12)

Table S4. Bond Lengths for Compound 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(001)	C(002)	1.376(2)	C(004)	C(008)	1.389(3)
O(001)	C(007)	1.430(2)	C(004)	C(009)	1.396(3)
C(002)	C(003)	1.388(3)	C(005)	C(008)	1.376(3)
C(002)	C(005)	1.389(3)	C(006)	C(006) ¹	1.325(4)
C(003)	C(009)	1.386(3)	C(007)	C(00A)	1.458(3)
C(004)	C(006)	1.476(3)	C(00A)	C(00B)	1.179(3)

¹1-X,-Y,1-Z**Table S5. Bond Angles for Compound 1.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(007)	O(001)	C(002)	116.81(15)	C(009)	C(004)	C(008)	117.17(19)
C(003)	C(002)	O(001)	124.71(18)	C(008)	C(005)	C(002)	119.67(19)
C(005)	C(002)	O(001)	115.37(17)	C(006) ¹	C(006)	C(004)	126.8(3)
C(005)	C(002)	C(003)	119.91(19)	C(00A)	C(007)	O(001)	107.63(17)
C(009)	C(003)	C(002)	119.28(19)	C(005)	C(008)	C(004)	122.1(2)
C(008)	C(004)	C(006)	119.06(19)	C(004)	C(009)	C(003)	121.86(19)
C(009)	C(004)	C(006)	123.76(19)	C(00B)	C(00A)	C(007)	178.5(2)

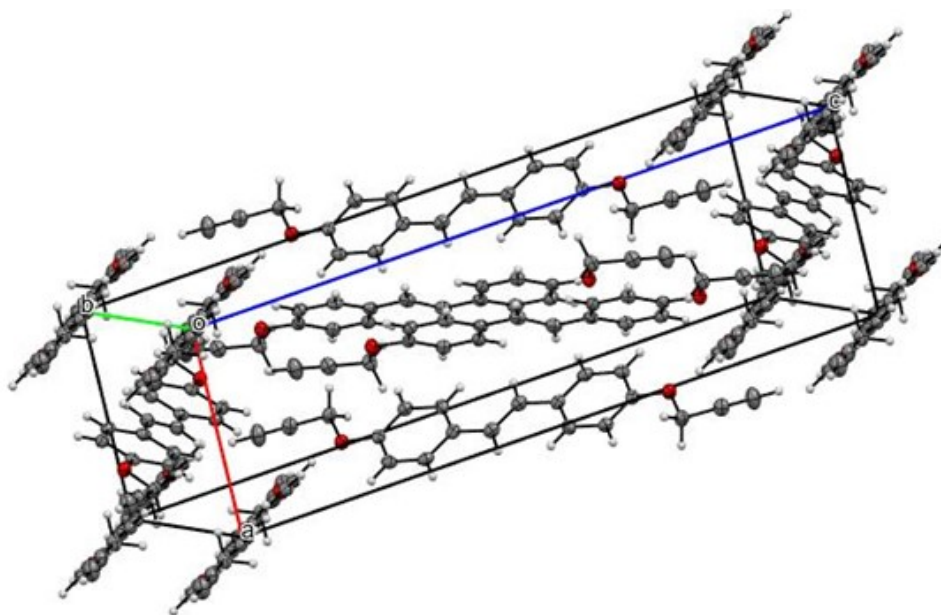
¹1-X,-Y,1-Z**Table S6. Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for Compound 1.**

Atom	x	y	z	U(eq)
H(003)	6444(3)	5426(3)	4369.6(8)	30.4(7)
H(005)	3494(3)	2951(2)	3283.8(8)	31.6(7)
H(006)	3781(3)	-704(3)	4658.1(8)	34.3(7)
H(00a)	5559(3)	7644(2)	3883.0(8)	33.6(7)
H(00b)	7293(3)	6851(2)	3604.3(8)	33.6(7)
H(008)	3322(3)	667(3)	3837.8(8)	32.5(7)

Table S6. Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Compound 1.

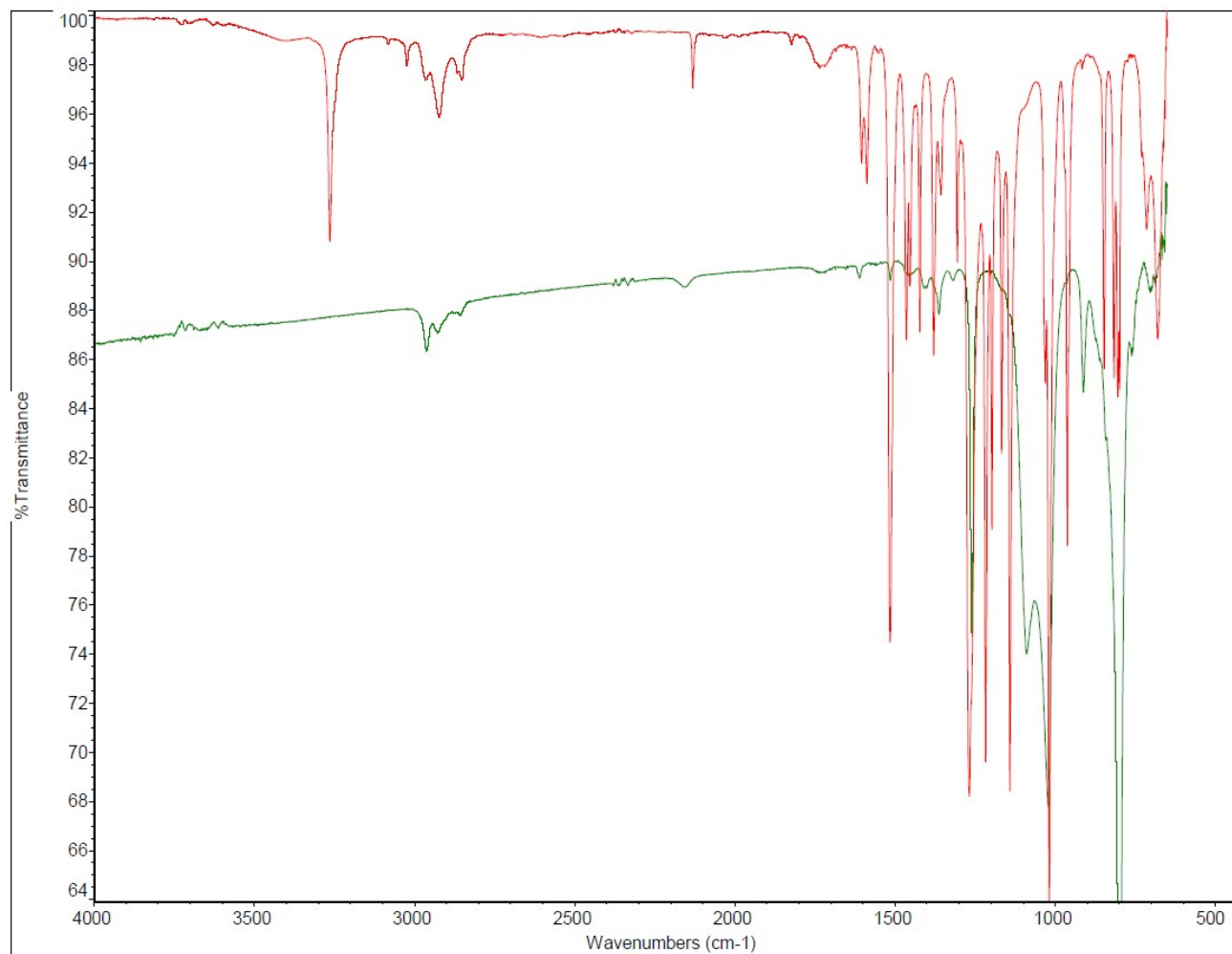
Atom	x	y	z	U(eq)
H(009)	6224(3)	3124(2)	4924.0(8)	32.3(7)
H(00c)	5569(4)	10152(3)	2516.8(10)	52.1(9)

Figure S27. X-ray structure of CD showing staggered π -stacking of aryl rings



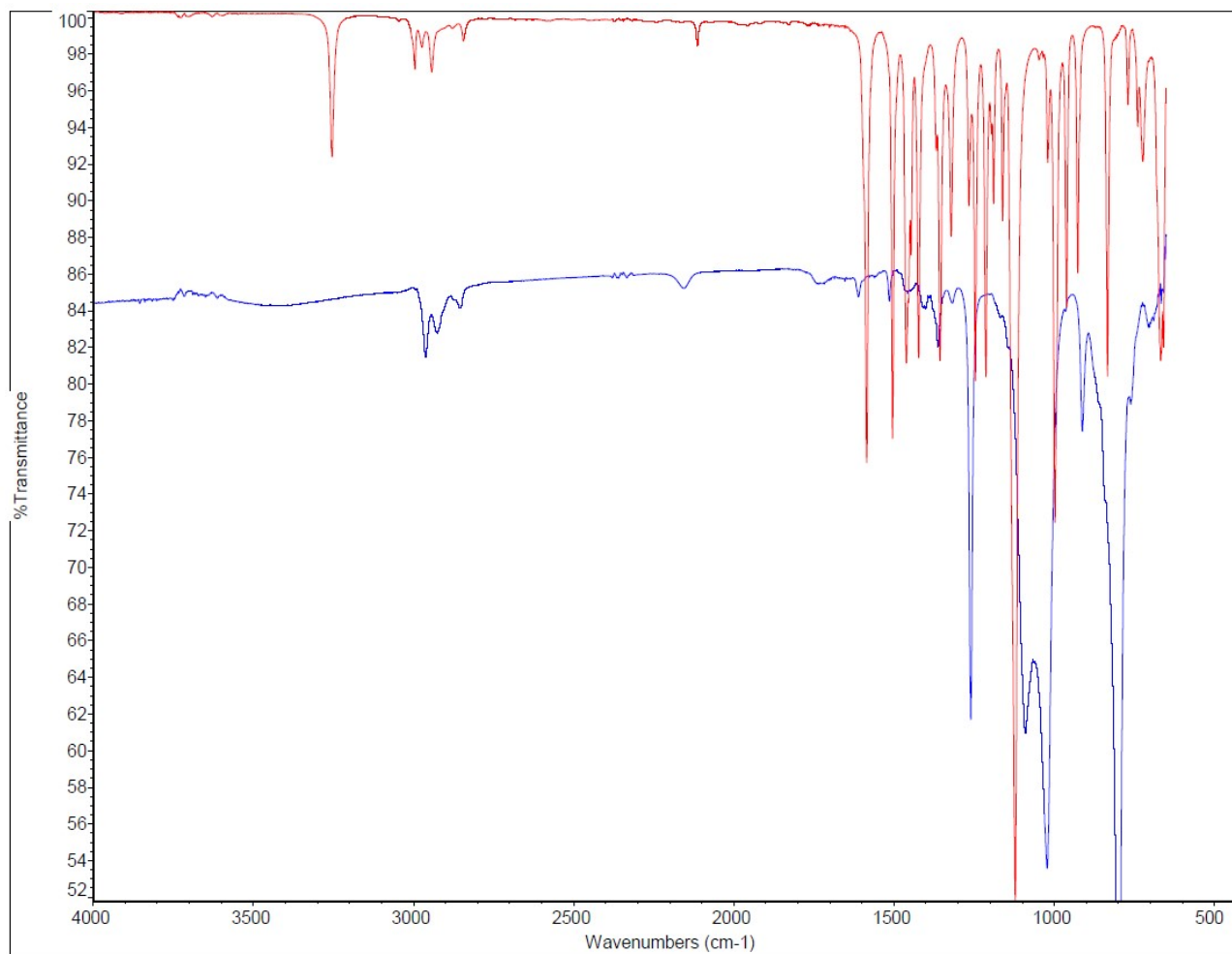
IR Spectra of Cured Thermosets and Monomers

Figure S28.
FTIR
FD (red) and
FD (green)



Stacked
spectra of
cross-linked

Figure S29. Stacked FTIR spectra of SD (red) and cross-linked SD (blue)



NMR Spectra of Isolated Compounds

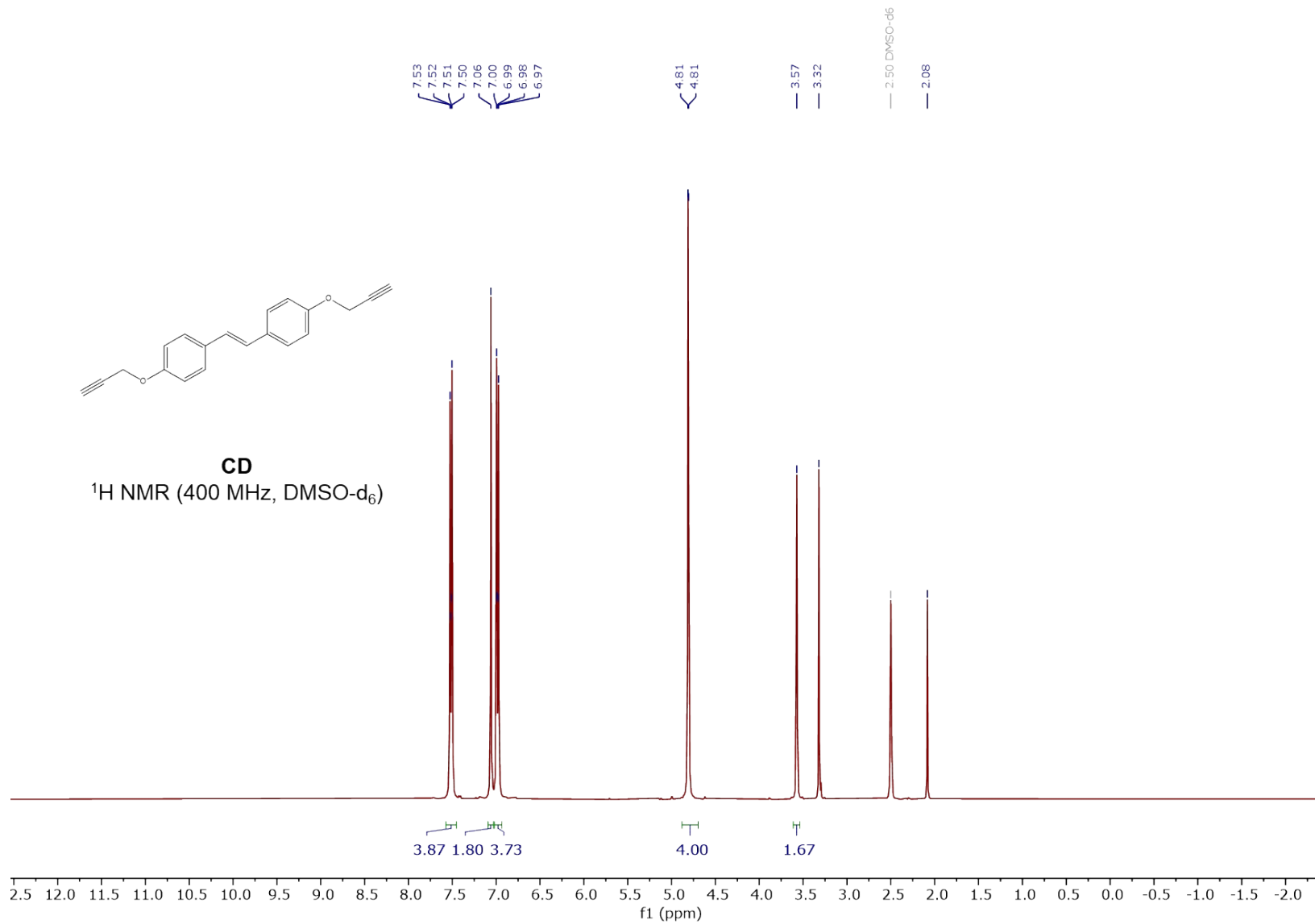


Figure S30. ^1H NMR spectrum of CD

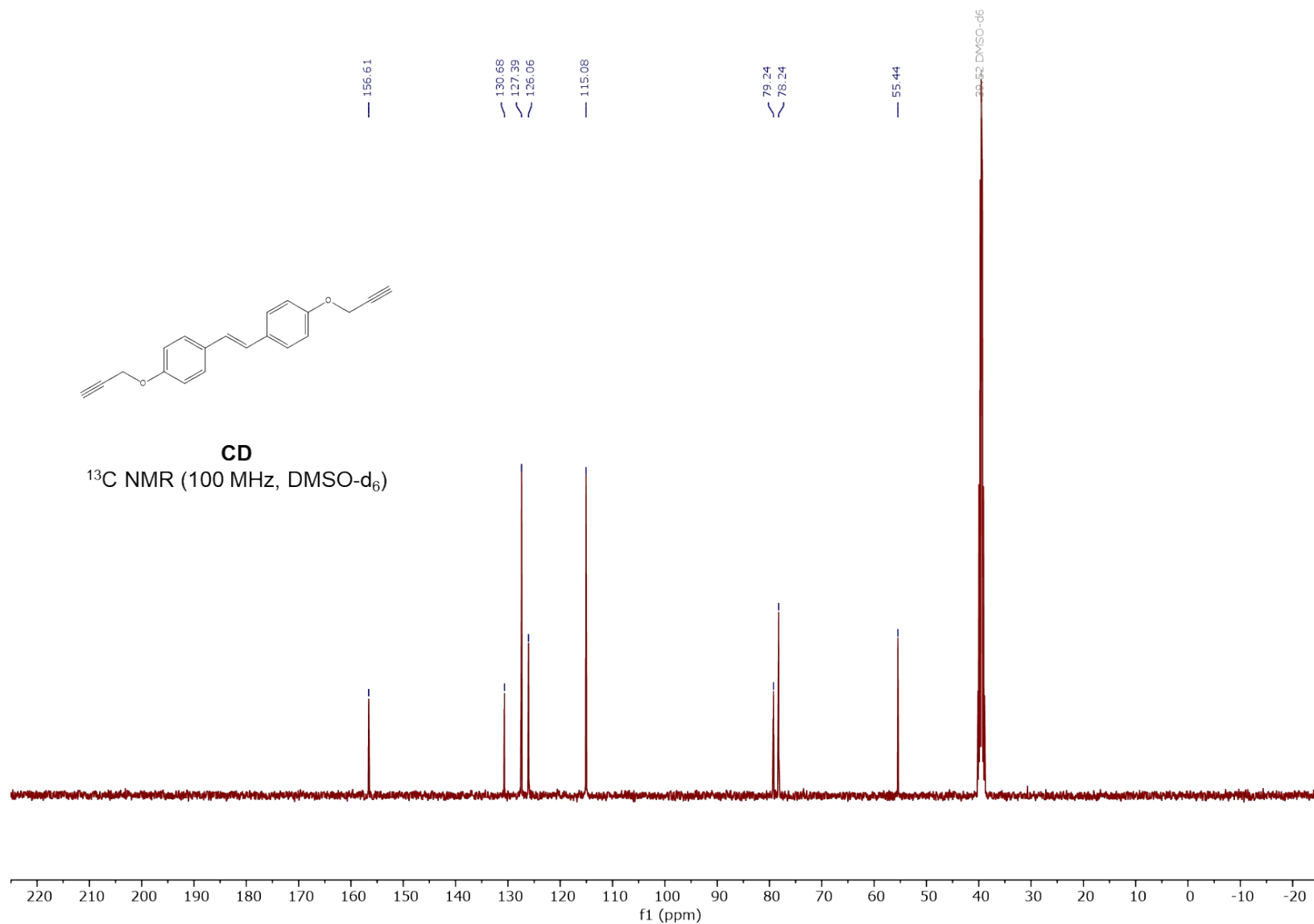


Figure S31. ^{13}C NMR spectrum of CD

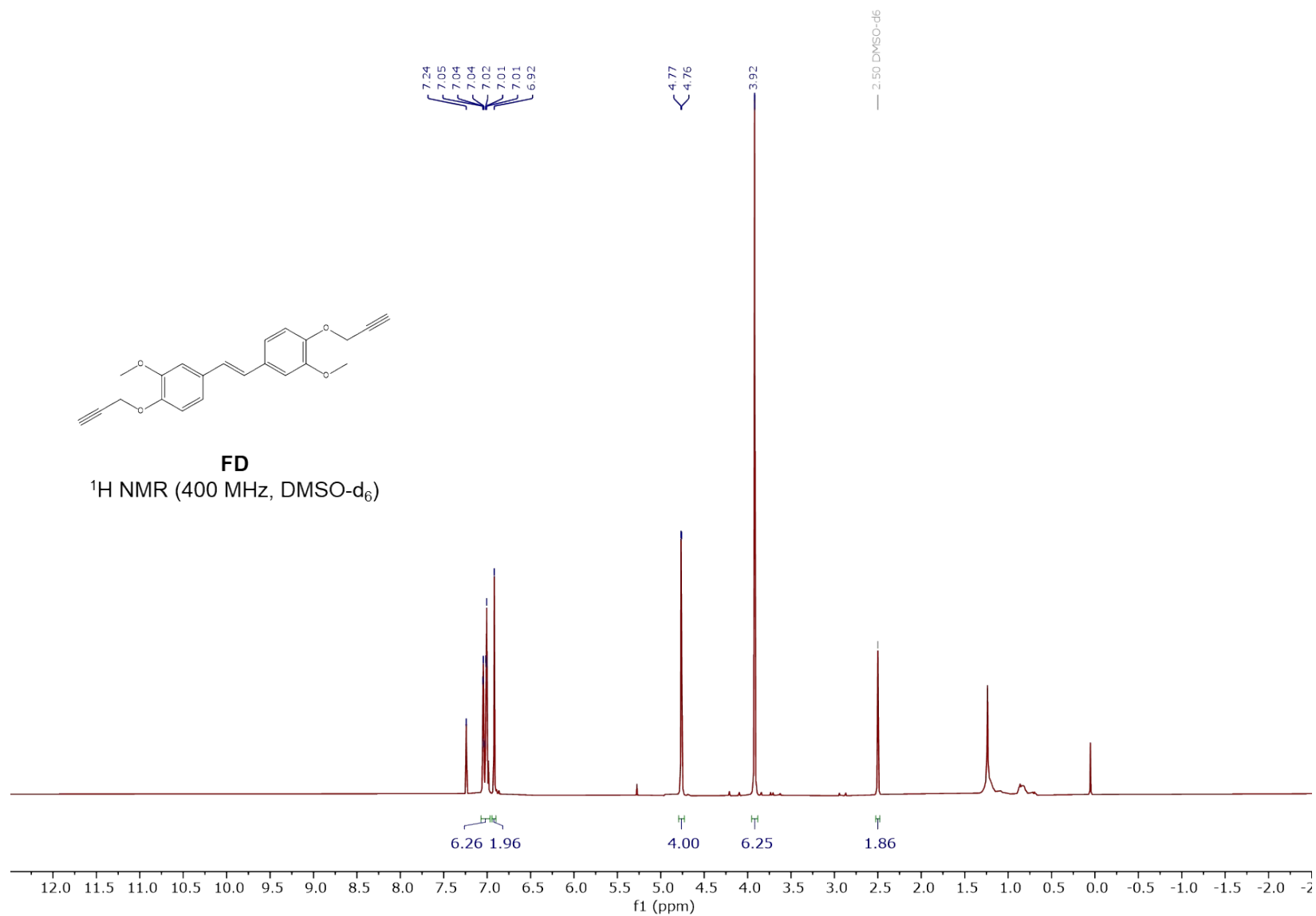
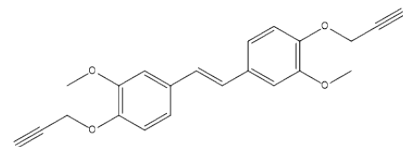


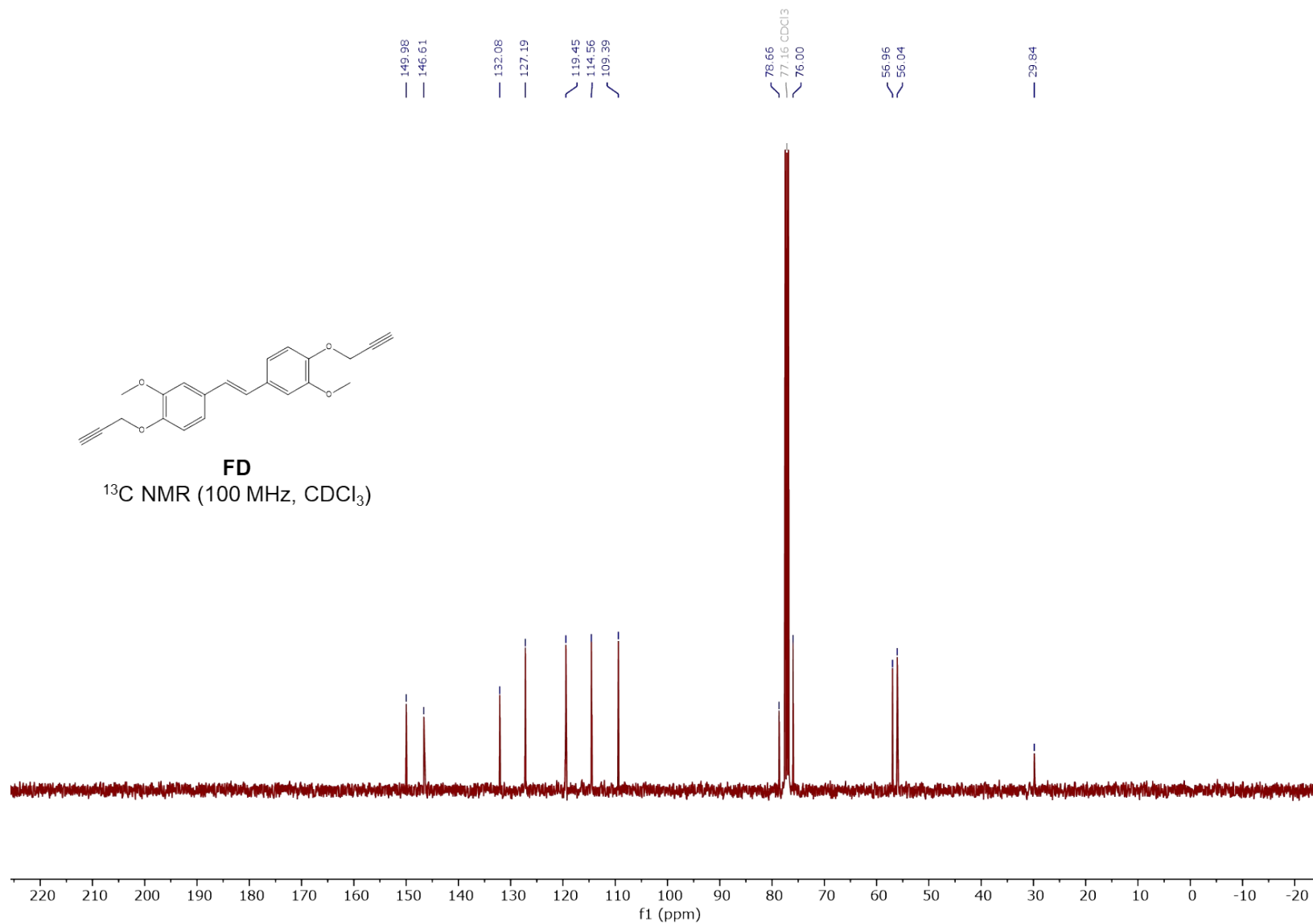
Figure S32. ^1H NMR spectrum of FD

Figure S33. ^{13}C NMR spectrum of FD



FD

^{13}C NMR (100 MHz, CDCl_3)



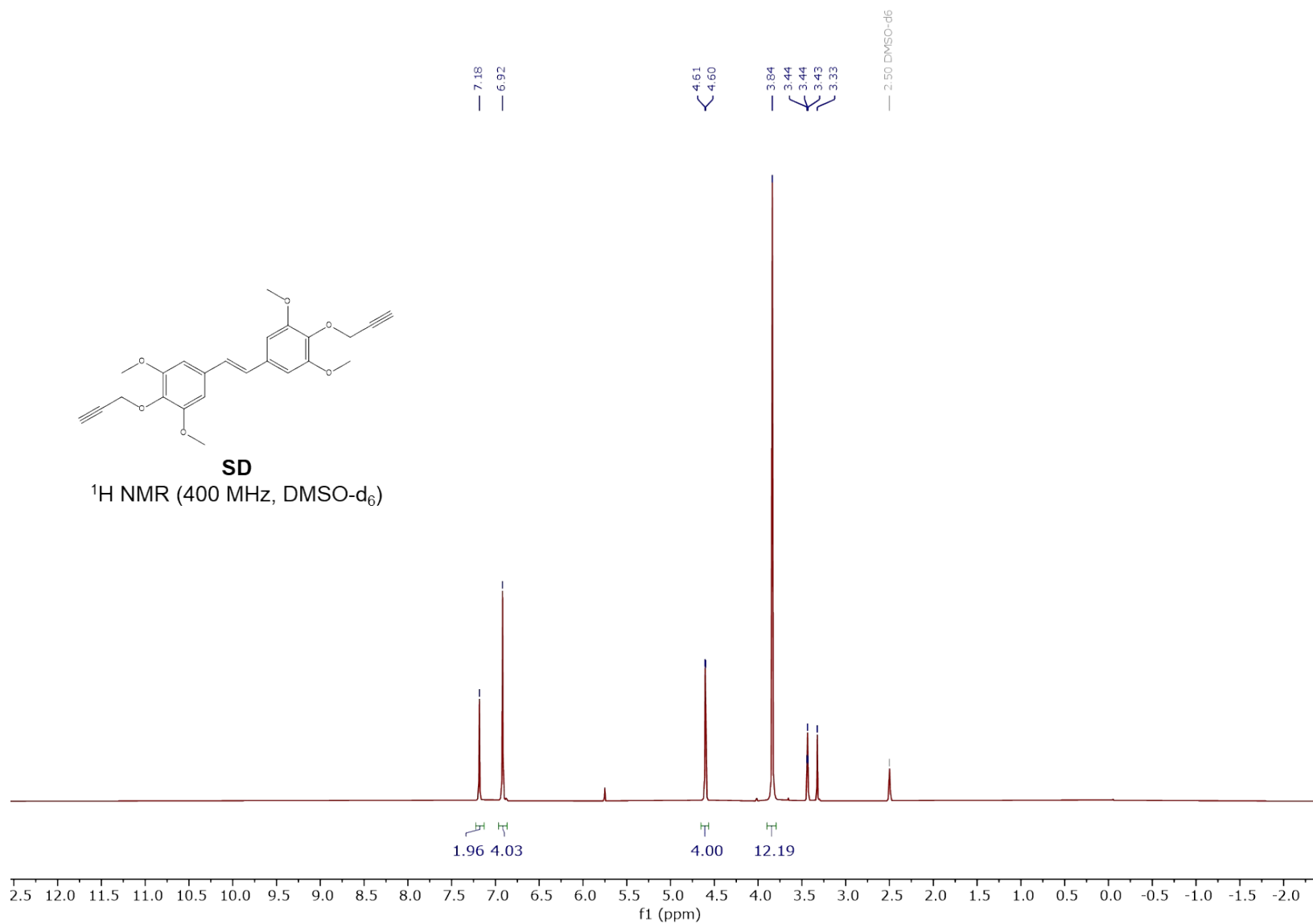


Figure S34. ^1H NMR spectrum of SD

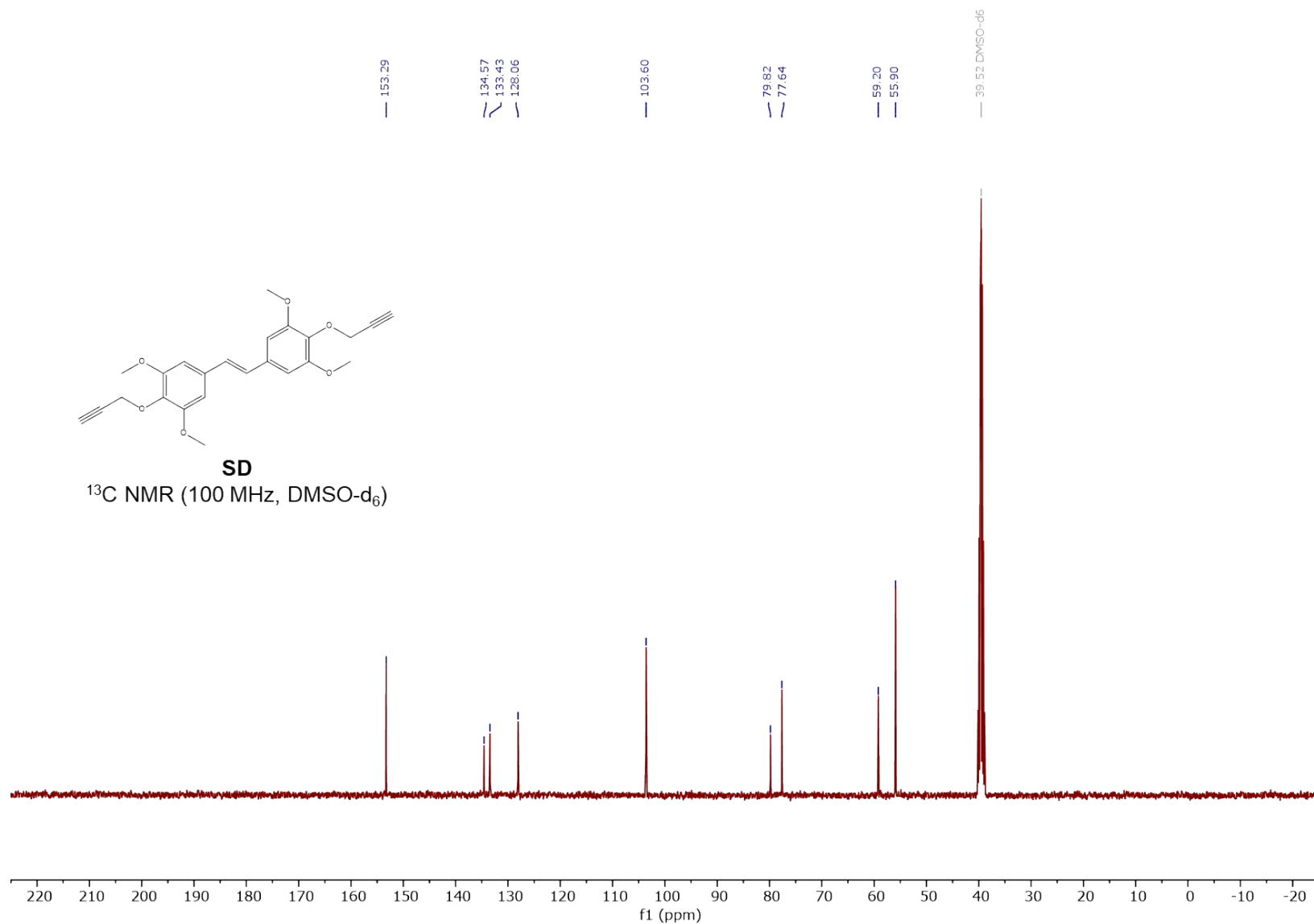


Figure S35. ¹³C NMR spectrum of SD

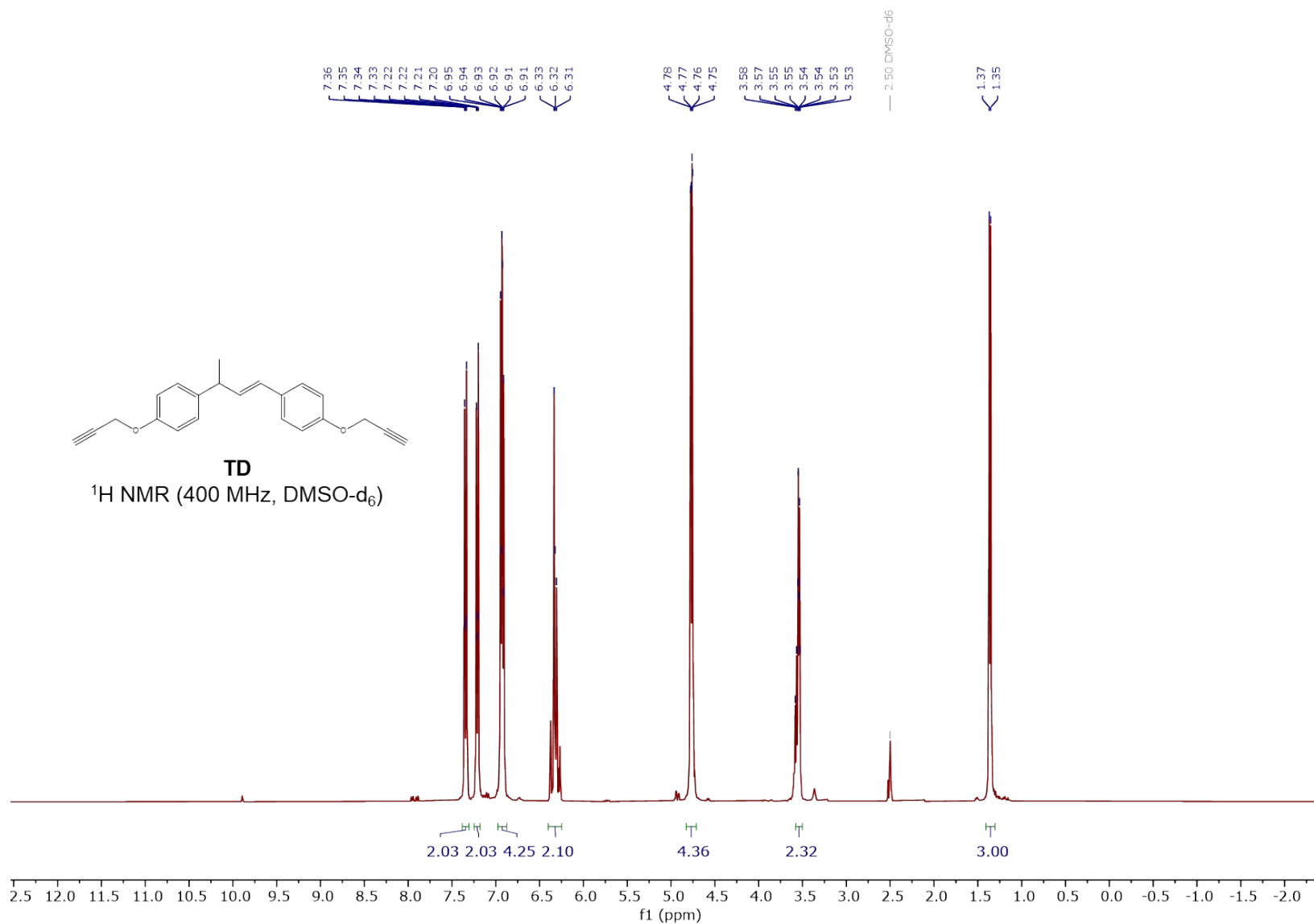


Figure S36. ¹H NMR spectrum of TD

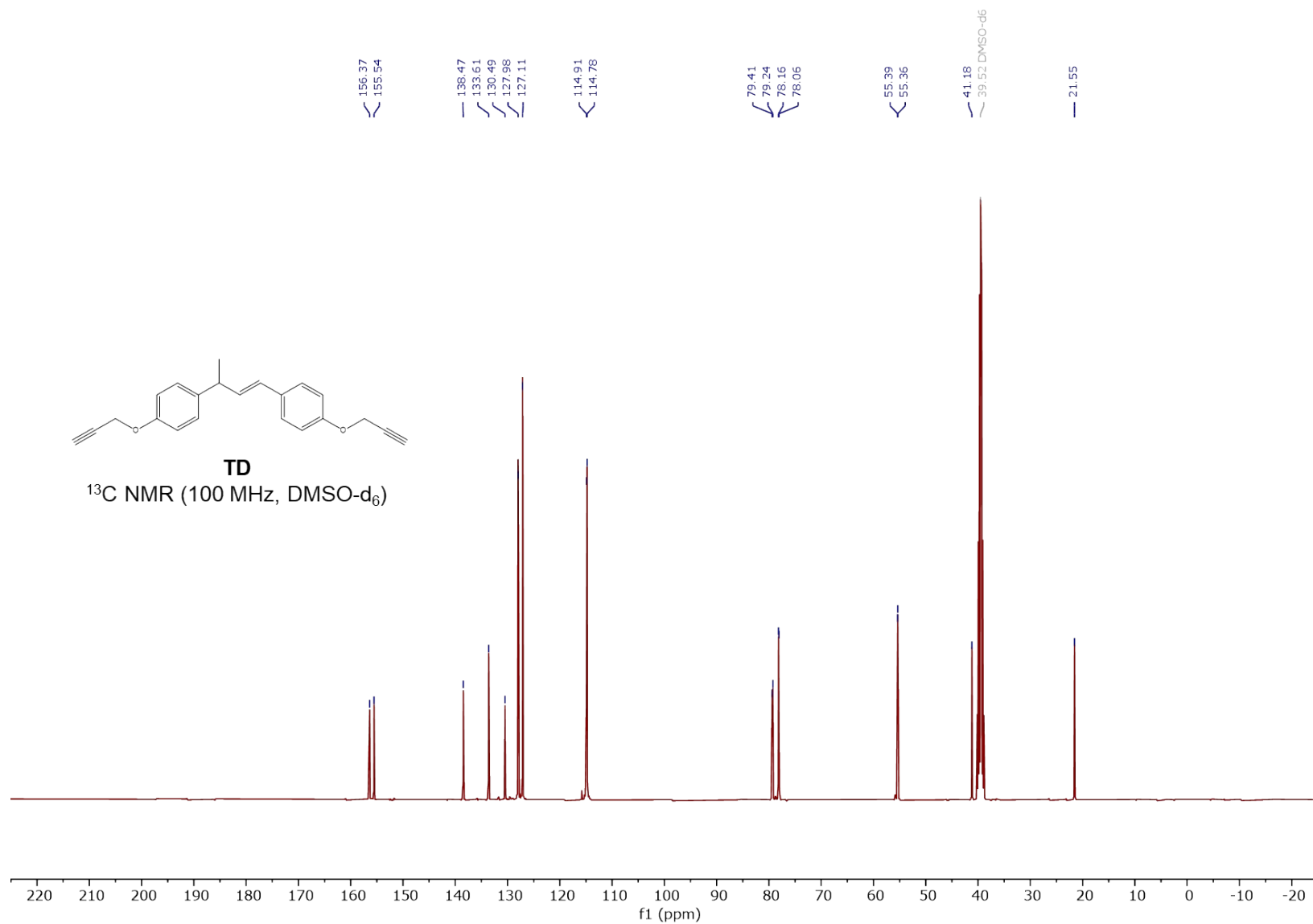


Figure S37. ¹³C NMR spectrum of TD

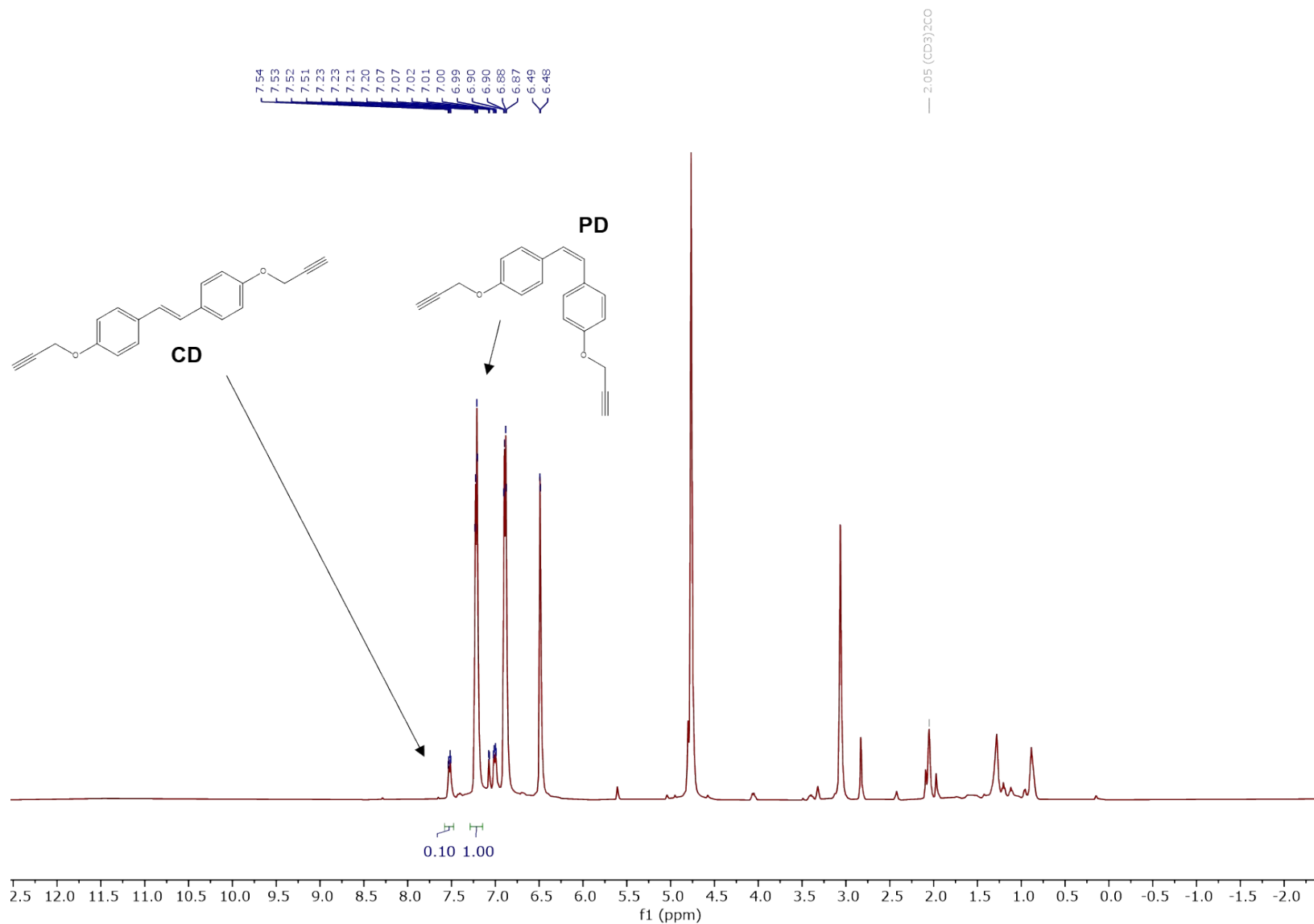


Figure S38. ¹H NMR spectrum of 9:1 PD:CD

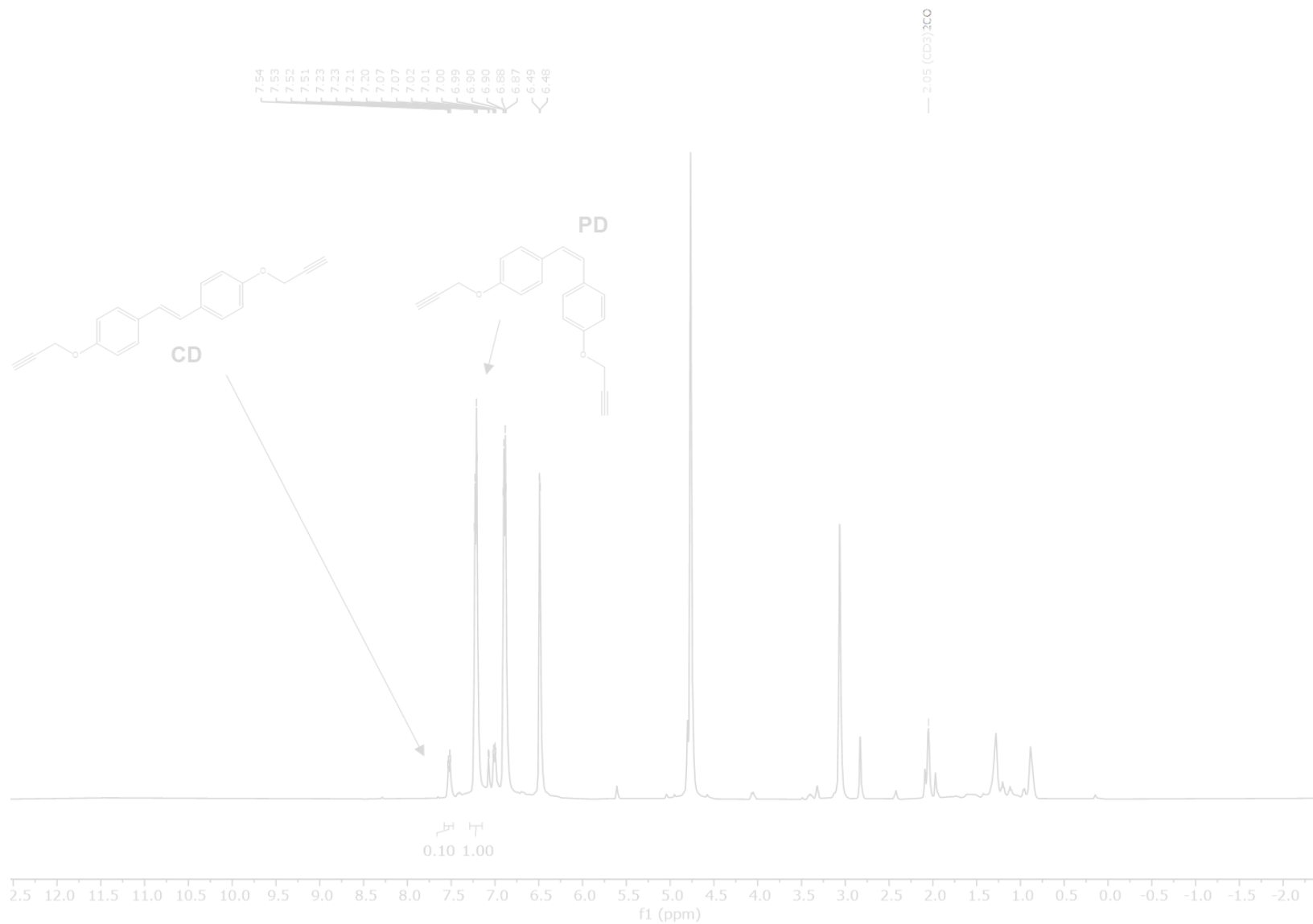


Figure S39. ¹H NMR spectrum of 7:3 PD:CD

