

SUPPORTING INFORMATION FOR

Efficient Amine End Functionalization of Living Ring Opening Metathesis Polymers

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Single crystal X ray diffraction

Compound **1** crystallizes in the monoclinic space group $P2_1/c$, with two molecules per asymmetric unit (Fig. 1 & S1). These two molecules are connected by H-bonds between hydrogen atoms connected to nitrogen of one molecule and oxygen atom connected to the phosphorus atom of the next molecule (Fig. S2 & S3). Angles form by oxygen atoms and phosphorus atom are $111.47(9)^\circ$ for O1–P1–O2 and $111.54(9)^\circ$ O3–P2–O4, the angles form by the two nitrogen and phosphorus atom are $104.9(1)^\circ$ for N1–P1–N2 and $108.0(1)^\circ$ for O3–P2–O4. Torsion angles between C1 and C4 and between C11 and C14 are respectively $2.4(5)^\circ$ and $3.1(5)^\circ$.

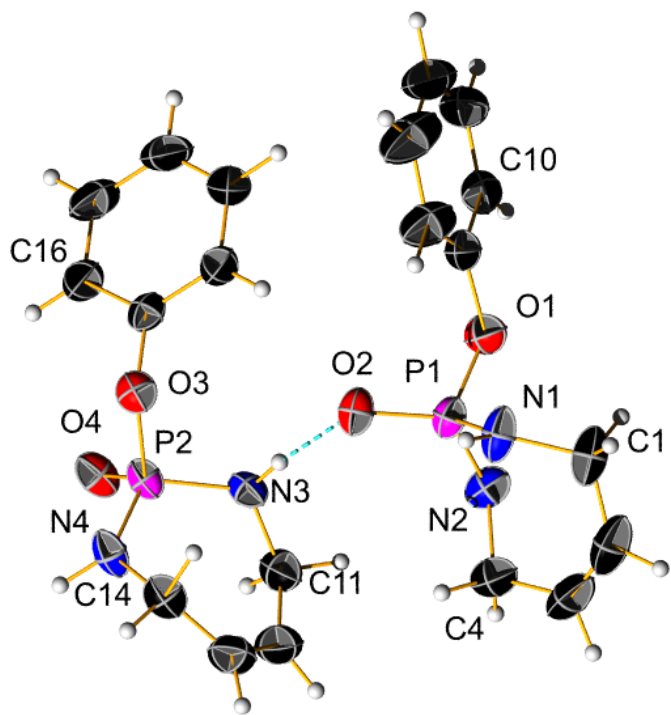


Figure S1: Molecular view of **1**; 50% of probability; H-bonds are represented as blue dash bonds.

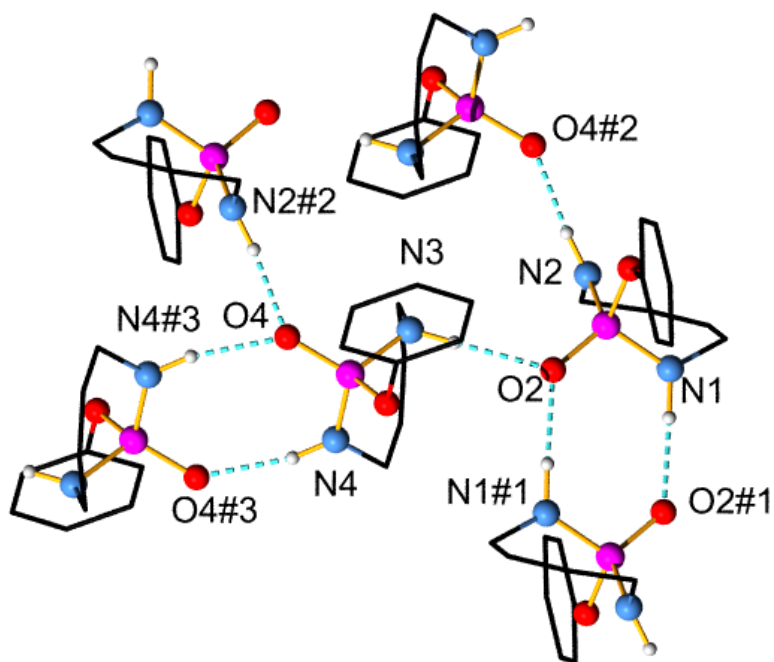


Figure S2: Molecular view of **1**; H-bonds are represented as blue dash bonds; #1: $2-x, -y, 2-z$; #2: $1-x, -y, 2-z$; #3: $1-x, -y-1, 2-z$.

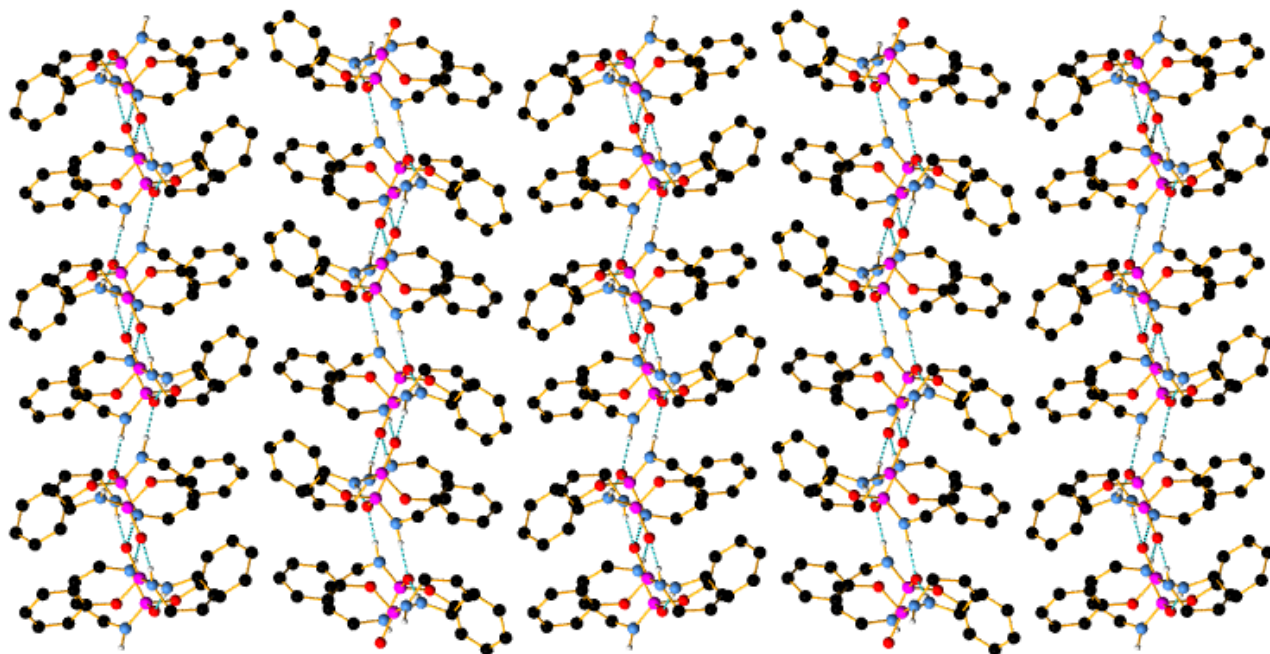


Figure S3: Molecular view of **1** along *a* axis; H-bonds are represented as blue dash bonds.

Table S1. Hydrogen bonds for poph-1 [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(1N)...O(2)#1	0.9683(18)	1.8991(14)	2.860(2)	171.55(13)
N(2)-H(2N)...O(4)#2	0.9283(18)	1.8912(15)	2.814(2)	172.74(13)
N(3)-H(3N)...O(2)	0.9266(17)	2.0364(14)	2.960(2)	174.51(12)
N(4)-H(4N)...O(4)#3	0.9383(17)	1.9629(15)	2.888(2)	168.52(11)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+2, -y, -z+2$ #2 $-x+1, -y, -z+2$ #3 $-x+1, -y-1, -z+2$

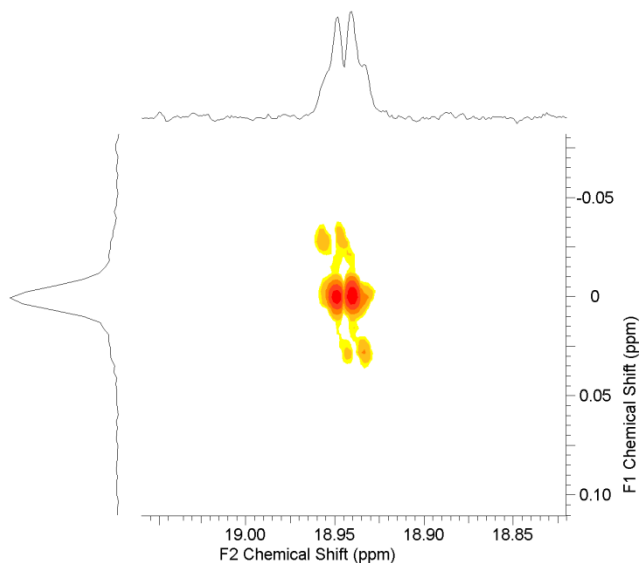


Figure S4: 2D J-resolved ^1H NMR spectrum of the new carbene peak resulting from the addition of 1.2 equivalents of **1** to a solution of **G1** and **MNI** shown in Figure 3b.

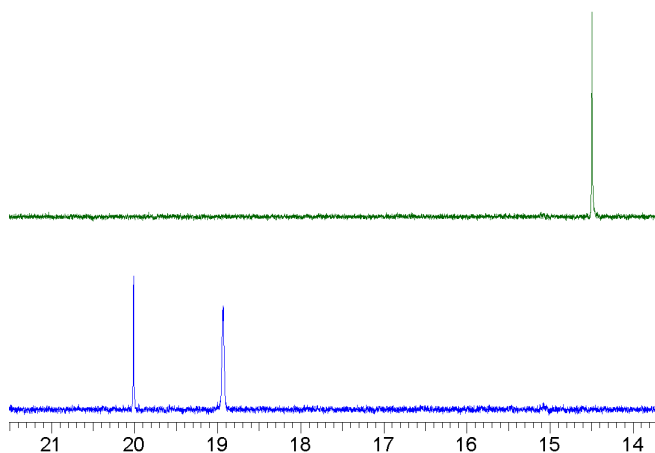


Figure S5: *Bottom:* ^1H NMR spectra showing **G1** (20.01 ppm) and **MNI** initiated **G1** catalyst (18.93 ppm, blue). *Top:* After quenching with ethyl vinyl ether only the Fischer carbene signal (14.51 ppm, green) is observed.

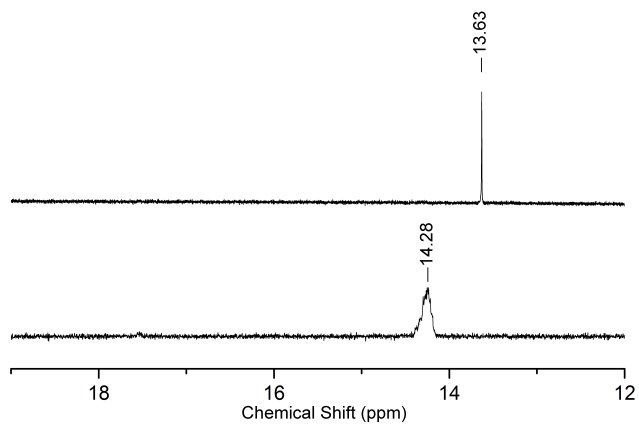


Figure S6: *Bottom*: ¹H NMR spectra showing MNI initiated G3 catalyst (14.28ppm). *Top*: After quenching with ethyl vinyl ether only the Fischer carbene signal (13.63 ppm) is observed.

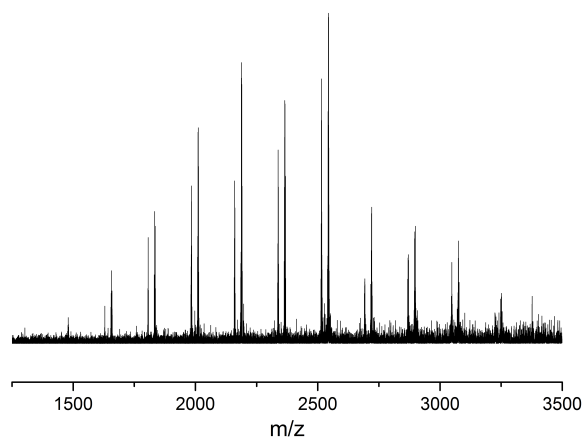


Figure S7: MALDI FT-ICR spectrum of incomplete end functionalized polymer from 2.5 equivalents of **1** with G3 initiated polymer.

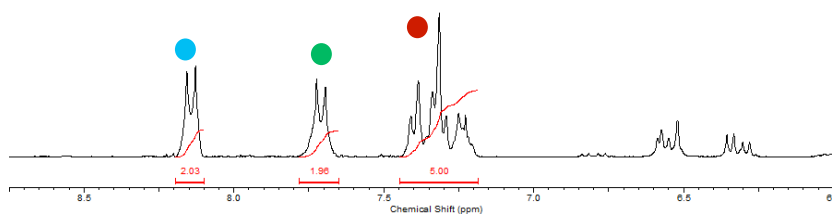
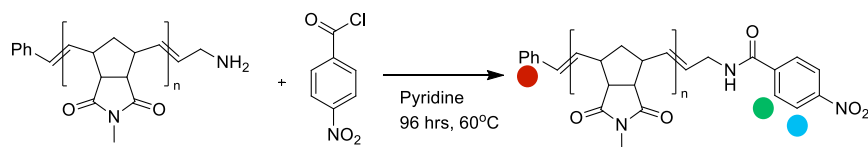


Figure S8: (*top*) Derivatization of the amine end functionalized polymer with p-nitrobenzoylchloride (*bottom*) ¹H-NMR of the derivatized polymer showing a degree of functionalization > 95%.