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)° for O1–P1–O2 and 111.54(9)° O3–P2–O4, the angles form by the two nitrogen and phosphorus atom are 104.9(1)° for N1–P1–N2 and 108.0(1)° for O3–P2–O4. Torsion angles between C1 and C4 and between C11 and C14 are respectively 2.4(5)° and 3.1(5)°.

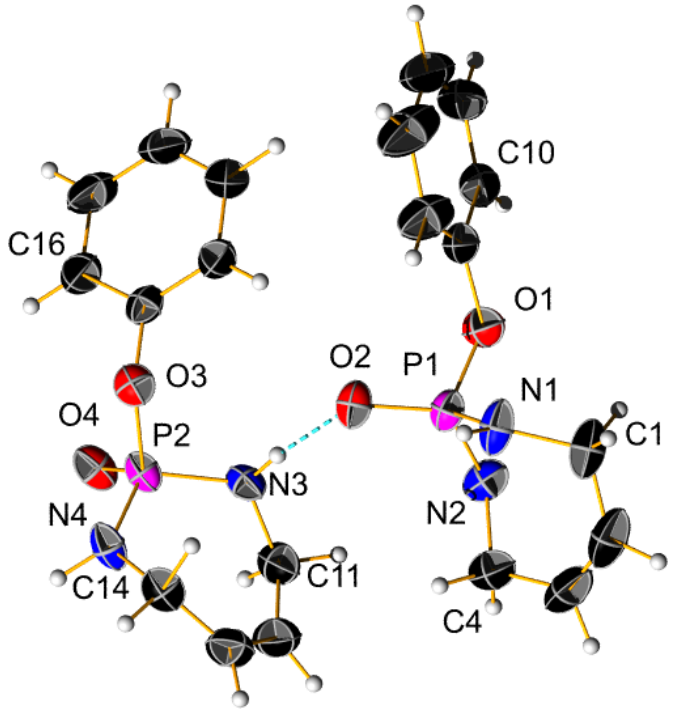

Figure S1: Molecular view of **1**; 50% of probability; H-bonds are represented as blue dash bonds.

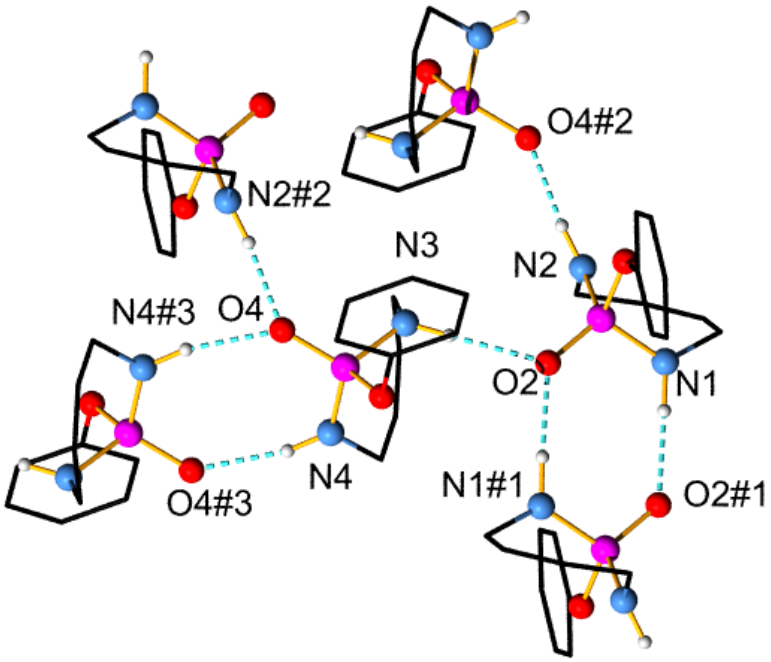

Figure S2: Molecular view of **1**; H-bonds are represented as blue dash bonds; #1: 2-x, -y, 2-z; #2: 1-x, -y, 2-z; #3: 1-x, -y-1, 2-z.

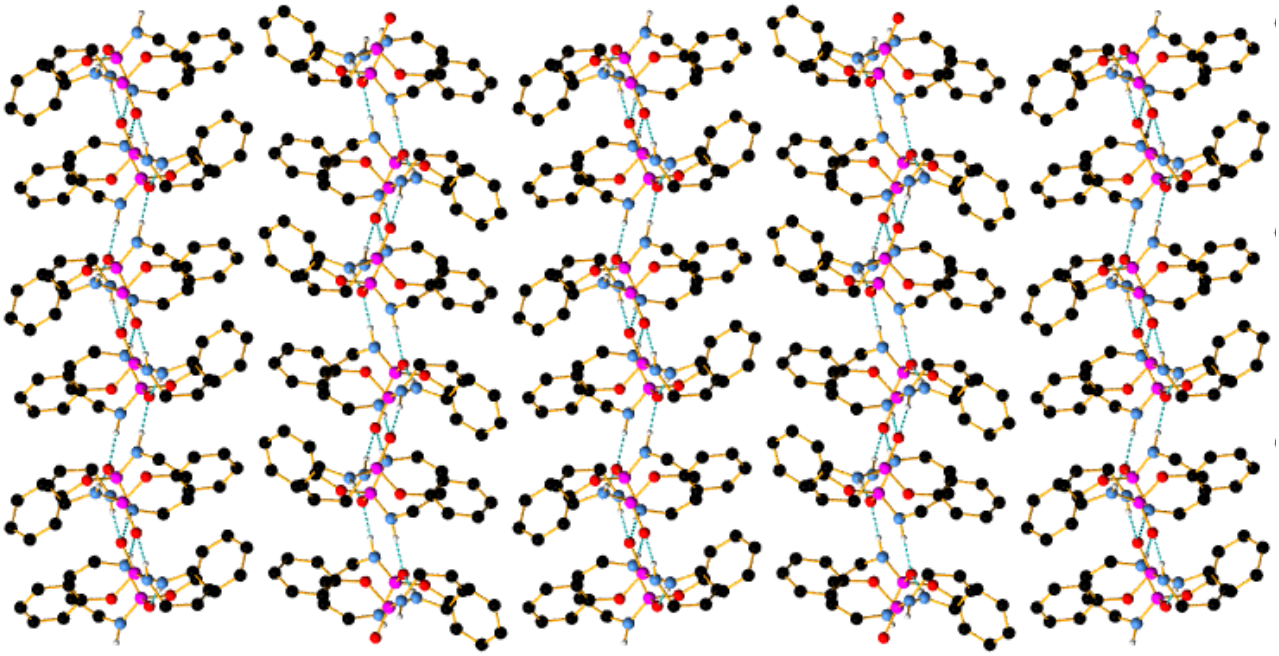

Figure S3: Molecular view of **1** along *a* axis; H-bonds are represented as blue dash bonds.

Table S1. Hydrogen bonds for poph-1 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(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

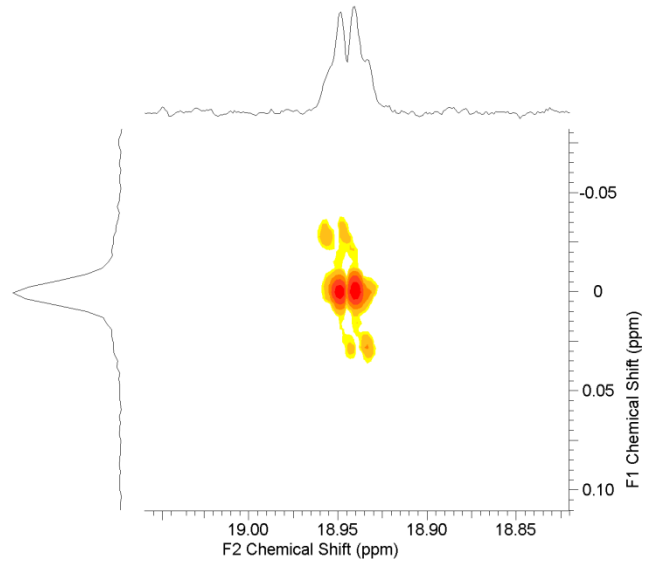

Figure S4: 2D J-resolved ^{1}H NMR spectrum of the new carbene peak resulting from the addition of 1.2 equivalents of **1** to a solution of **G1** and **MNI** shown in Figure 3b.

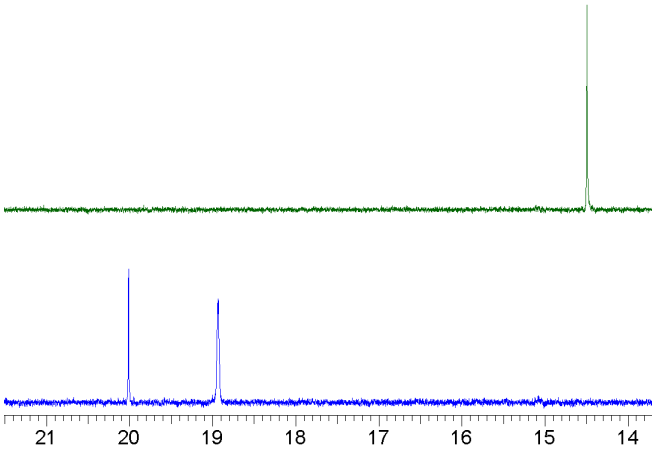

Figure S5: *Bottom*: ^{1}H NMR spectra showing **G1** (20.01 ppm) and **MNI** initiated **G1** catalyst (18.93 ppm, blue). *Top:* After quenching with ethyl vinyl ether only the Fischer carbene signal (14.51 ppm, green) is observed.

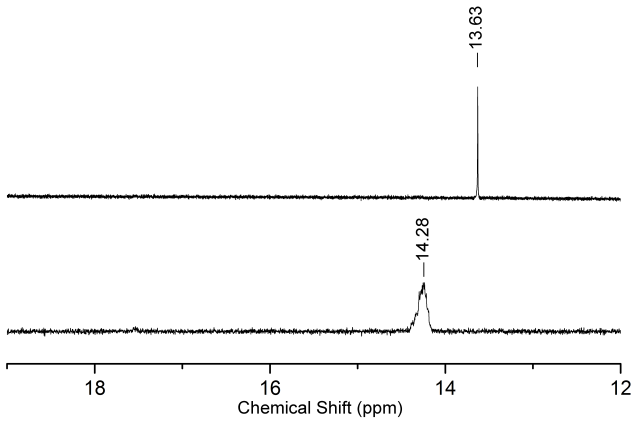

Figure S6: *Bottom*: ^{1}H NMR spectra showing **MNI** initiated **G3** catalyst (14.28ppm). *Top:* After quenching with ethyl vinyl ether only the Fischer carbene signal (13.63 ppm) is observed.

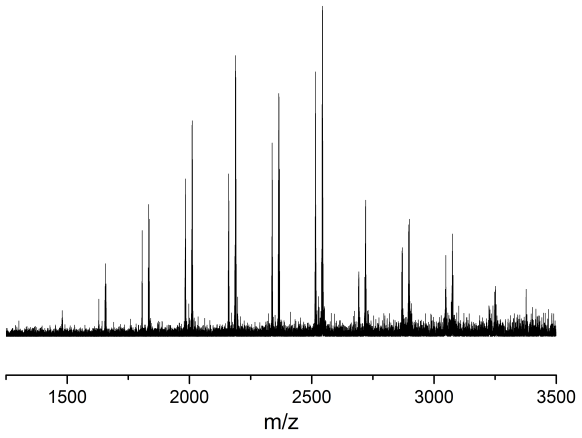

Figure S7: MALDI FT-ICR spectrum of incomplete end functionalized polymer from 2.5 equivalents of **1** with G3 initiated polymer.

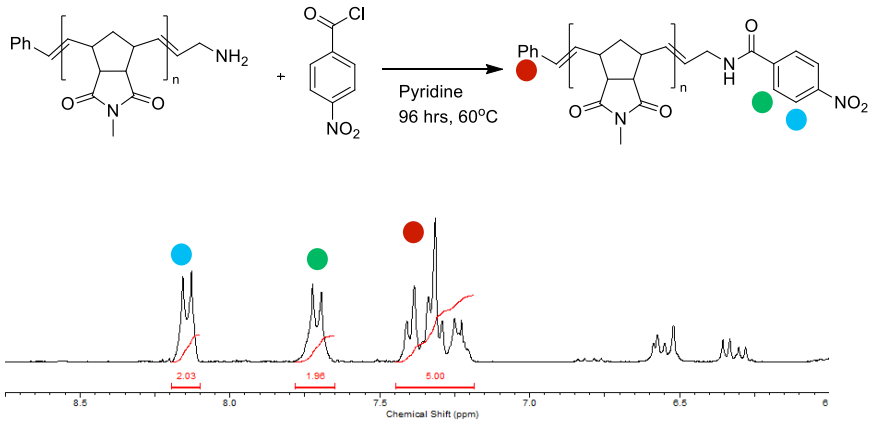

Figure S8: *(top)* Derivatization of the amine end functionalized polymer with p-nitrobenzoylchloride *(bottom)* ^{1}H-NMR of the derivatized polymer showing a degree of functionalization > 95%.