Supplementary Materials: Metathesis Polymerization Reactions Induced by the Bimetallic Complex $(Ph_4P)_2[W_2(\mu\text{-}Br)_3Br_6]$

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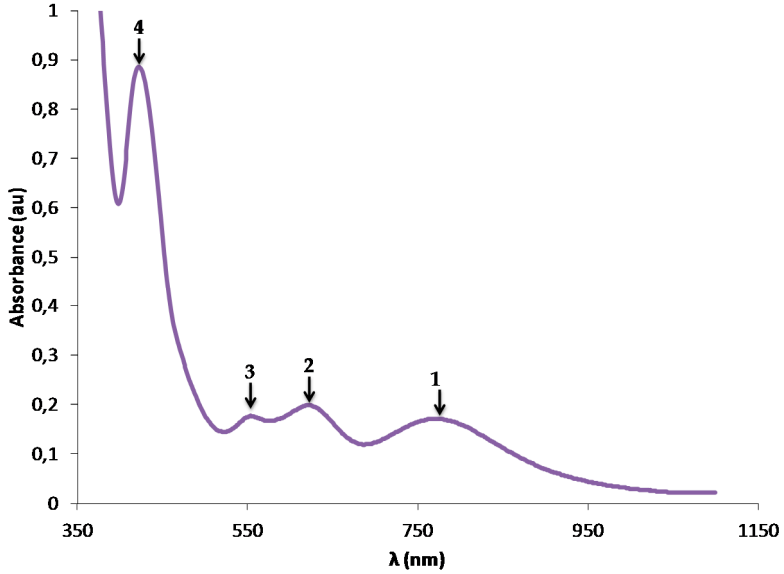


Figure S1. Vis-UV spectrum of $(Ph_4P)_2[W_2(\mu\text{-}Br)_3Br_6]$ (**1**) in MeCN. Concentration: 2.09×10^{-4} M. Peaks 1–4 as defined in Table S1.

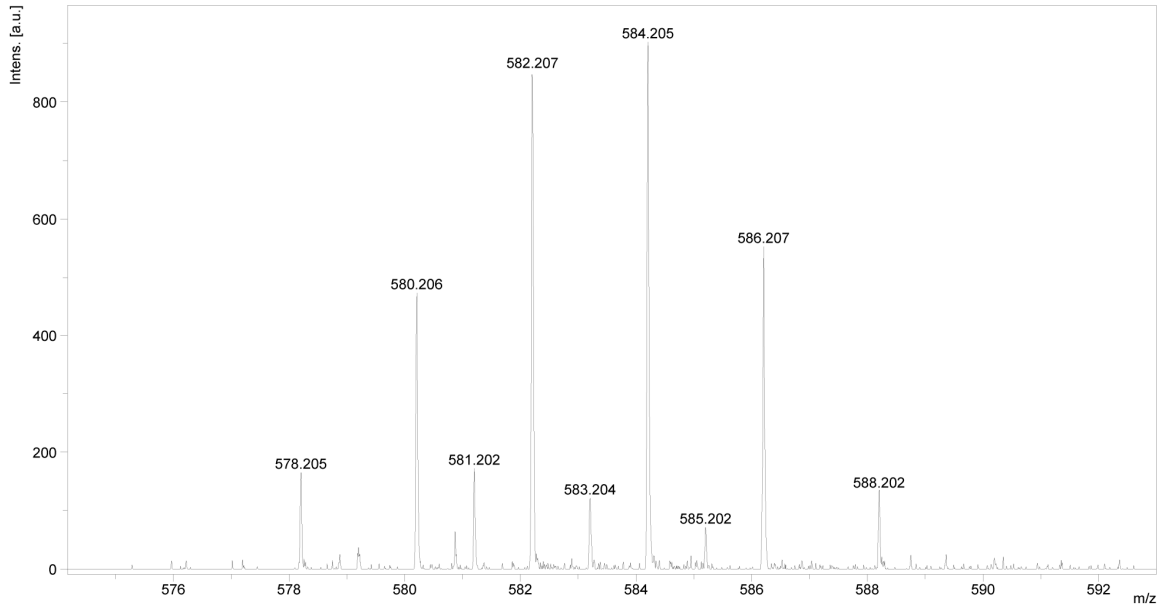


Figure S2. MALDI-TOF mass spectrum of **1** in DCTB (fragment $[WBr_5]^-$).

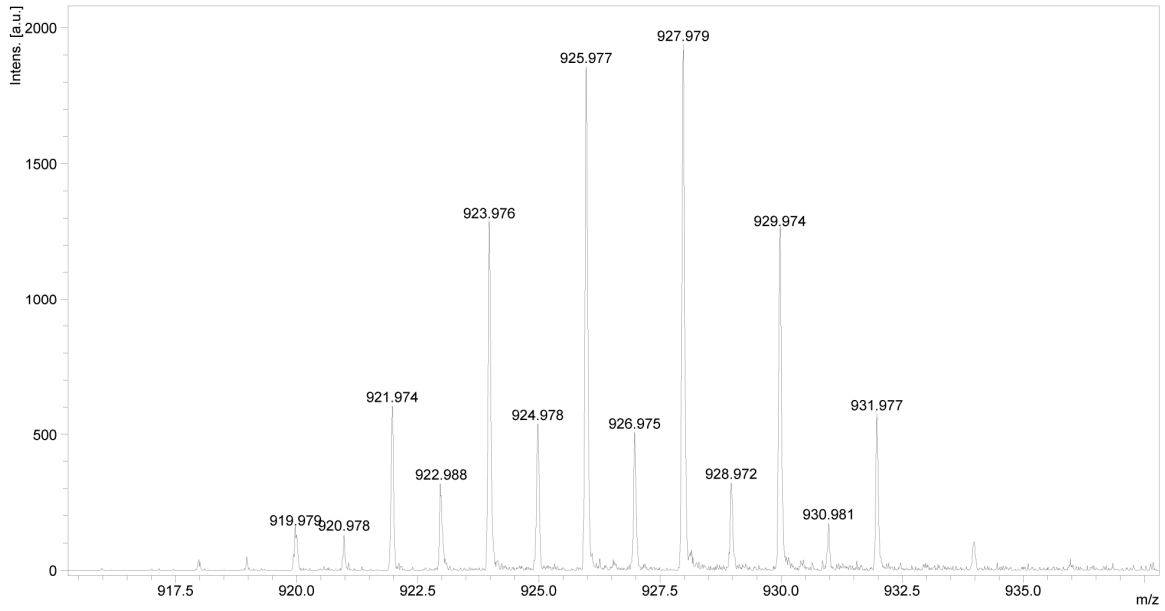


Figure S3. MALDI-TOF mass spectrum of **1** in DCTB (fragment $[W_2Br_7]^-$).

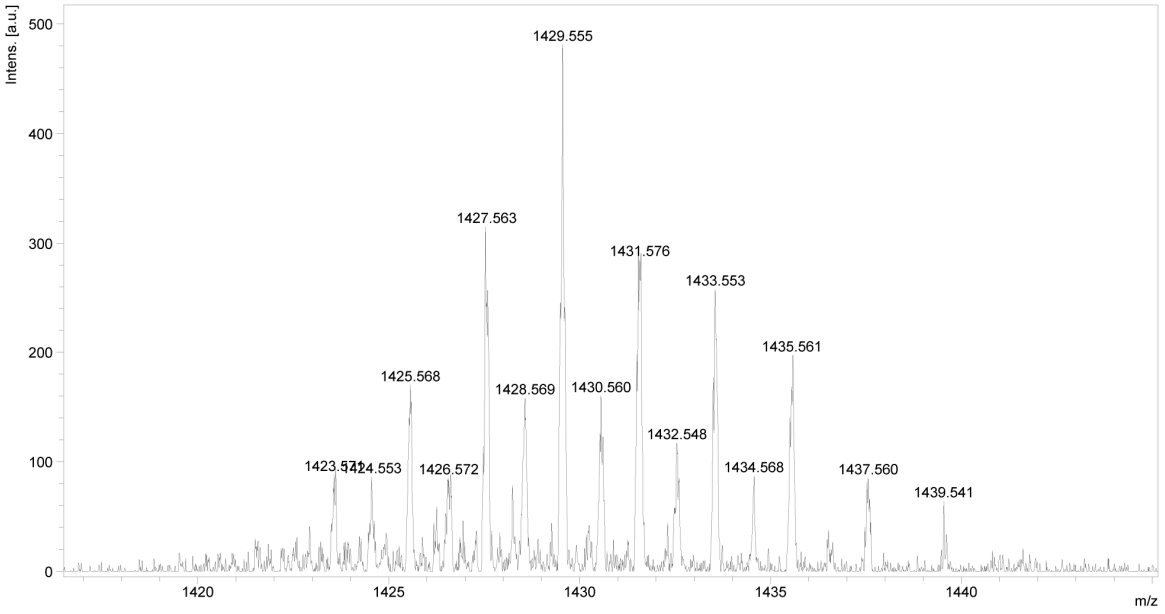


Figure S4. MALDI-TOF mass spectrum of **1** in DCTB (fragment $[Ph_4PW_2Br_9]^-$).

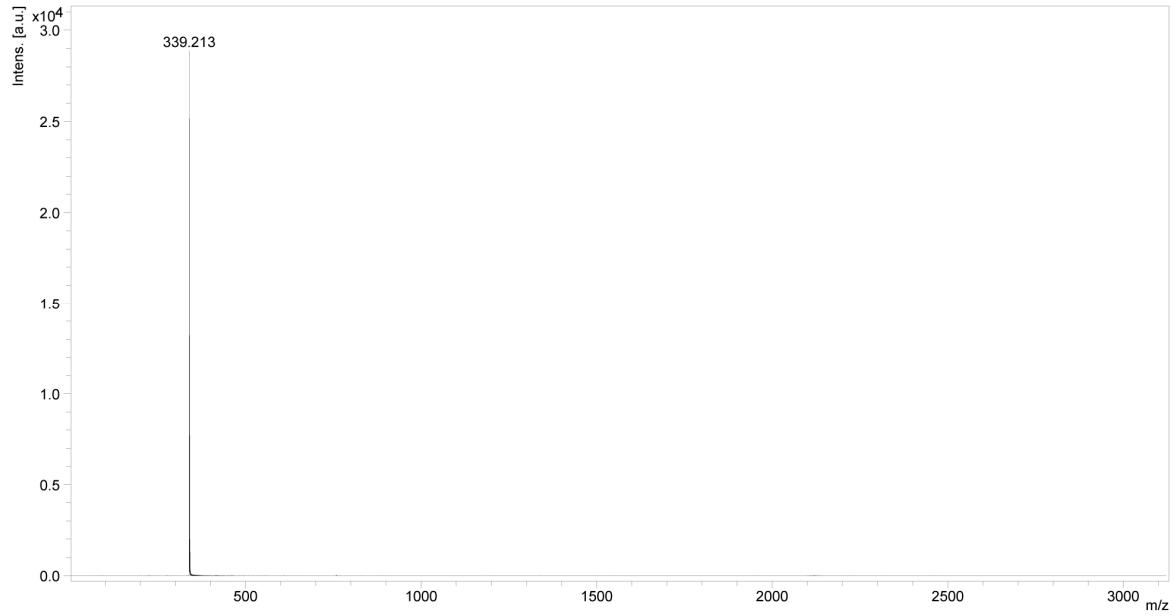


Figure S5. MALDI-TOF mass spectrum of **1** in DCTB (fragment PhP^+).

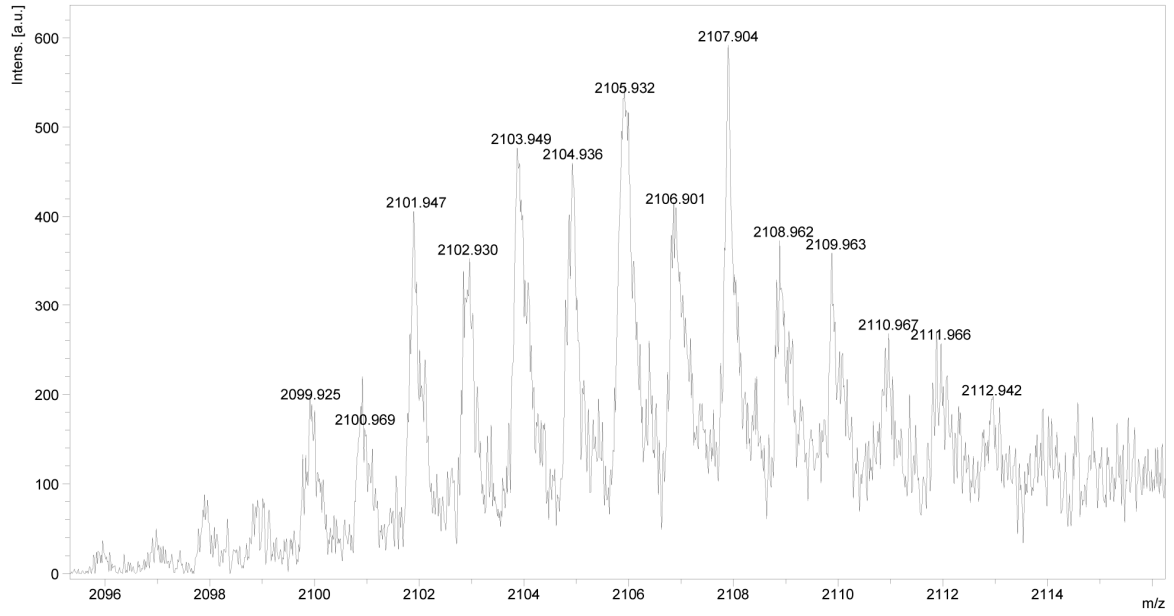


Figure S6. MALDI-TOF mass spectrum of **1** in DCTB (fragment $[(Ph_4P)_3W_2Br_9]^+$).

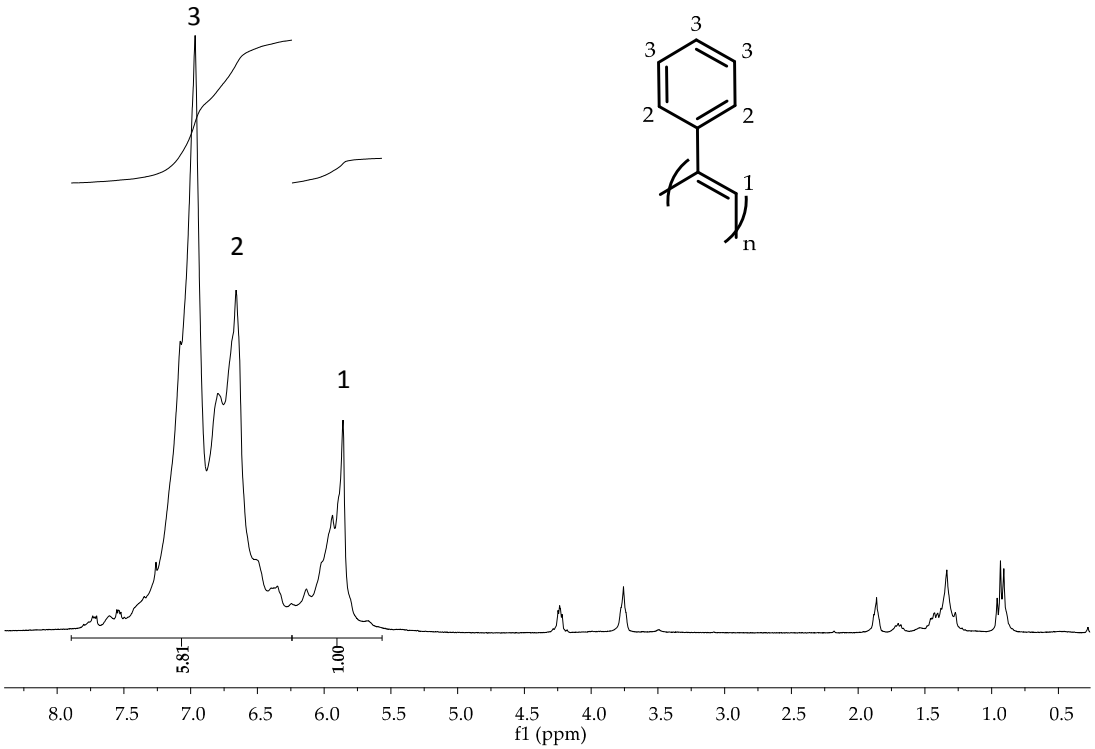


Figure S7. ^{1}H NMR spectrum ($CDCl_3$) of PPA obtained from the reaction of **1**/$AgBF_4$/PA (Table 1, entry 6) in THF.

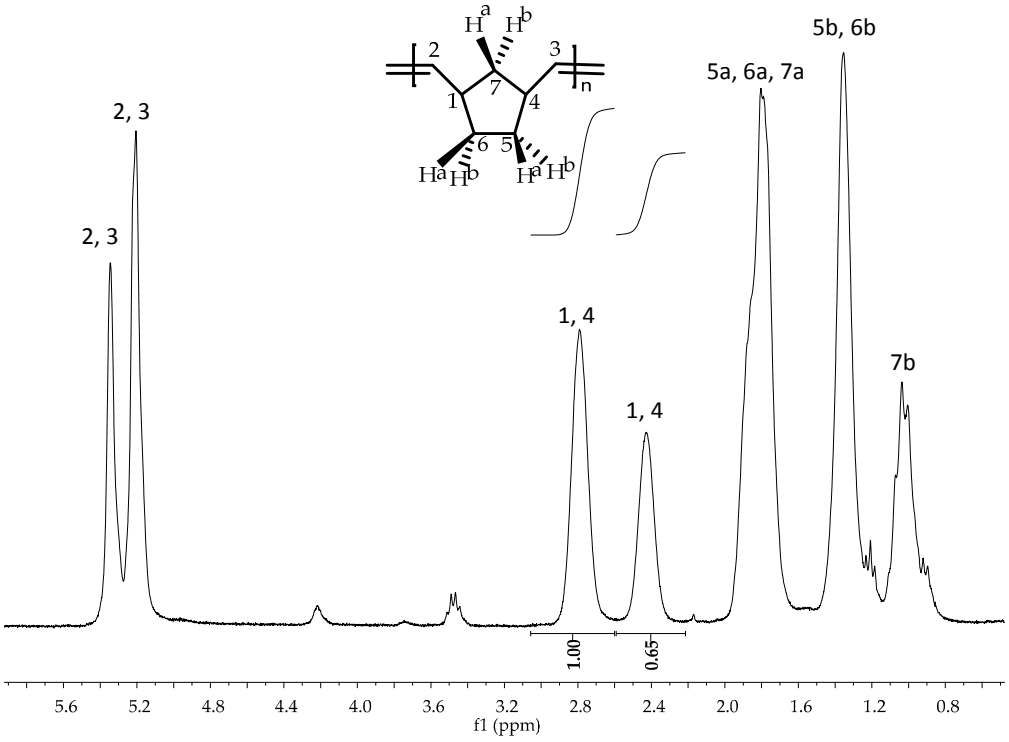


Figure S8. ^{1}H NMR spectrum ($CDCl_3$) of PNBE obtained from the reaction of **1**/$AgBF_4$/NBE (Table 2, entry 3) in CH_2Cl_2.

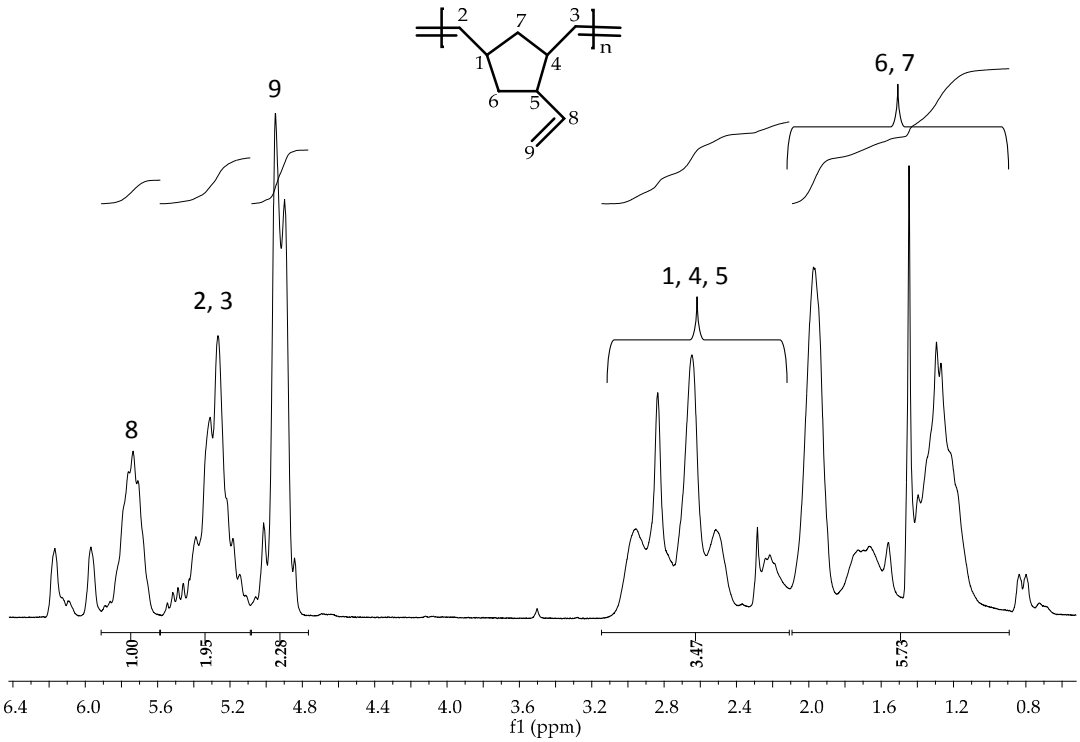


Figure S9. ^{1}H NMR spectrum ($CDCl_3$) of PVNBE obtained from the reaction of **1**/$AgBF_4$/VNBE (Table 3, entry 5) in CH_2Cl_2.

Table S1. UV-Vis spectroscopic data of complex **1** (C = 2.09 × 10^{-4} M). Literature values for ($^{n}Pr_4N)_2[W_2(\mu\text{-}Br)_3Br_6$] are shown in brackets.

Peaks	λ (nm)	A_{max}	ε ($M^{-1}cm^{-1}$)
1	771 (769)	0.171	820 (1100)
2	622 (621)	0.198	950 (1300)
3	554 (549)	0.177	850 (1100)
4	422 (420)	0.885	4200 (5100)

Table S2. Kinetic study of PA polymerization with the catalytic system **1**/$AgBF_4$.

t (h)	Yield (%)	$M_n \times 10^{-3}$	M_w/M_n
2	13	70.5	1.72
4	40	82.4	1.62
6	98	207	1.16
8	79	54.2	1.61
24	59	16.0	2.07

Conditions: molar ratio **1**/$AgBF_4$/PA equal to 1/3/350, 10 mL THF.

Table S3. Kinetic study of NBD polymerization with the catalytic system **1**/$AgBF_4$.

t (min)	Yield (%)
15	12
30	32
45	34
60	69
75	74
90	92

Conditions: molar ratio **1**/$AgBF_4$/NBD equal to 1/4/500, 5 mL CH_2Cl_2.

Table S4. Kinetic study of VNBE polymerization with the catalytic system **1**/$AgBF_4$.

t (h)	Yield (%)
1	5
2	10
3	28
4	54
5	66
6	70
7	87

Conditions: molar ratio **1**/$AgBF_4$/VNBE equal to 1/4/2000, 2 mL CH_2Cl_2.

Table S5. Kinetic study of DCPD polymerization with the catalytic system **1**/$AgBF_4$.

t (h)	Yield (%)
0.5	0
1	5
1.5	11
2	13
2.5	14
3	25
3.5	48
4	51
4.5	52
5	53
5.5	56
6	59
6.5	59
7	61
7.5	62
8	67
10	79
12	81
14	91
16	95

Conditions: molar ratio **1**/$AgBF_4$/DCPD equal to 1/4/250, 5 mL CH_2Cl_2.



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