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Electronic Supplementary Information

Halomethyl-cobalt(*bis*-acetylacetonate) for the controlled synthesis of functional polymers

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General Information

Materials. All manipulations were performed by classical Schlenk techniques under argon. Vinyl acetate (VAc, >99%, Aldrich) was dried over calcium hydride, degassed by several freeze-thawing cycles before distillation under reduced pressure and stored under argon. 1-Vinyl-3-ethylimidazolium bromide (VEtImBr) was synthesized by quaternization of vinyl imidazole by bromoethane according to the procedure reported in [1]. CH_2Cl_2, CH_2Br_2, ethyl acetate and pentane were purchased from Aldrich, dried using 4 Å molecular sieves and degassed by bubbling argon. Milli-Q water was degassed by bubbling argon for 20 min and stored under argon. Tetrahydrofurane and dimethylformamide were purchased from Aldrich and used as received. Bis-(acetylacetonato)cobalt(II) ($Co(acac)_2$) (>98%, Acros) was stored under argon and used as received. 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, 96%, Wako) and azobisisobutyronitrile (AIBN, >98%, Fluka Aldrich) were stored at -20°C and +6°C, respectively, and used as received. *Tris*(trimethylsilyl)silane (TTMSS, >97%, FluoroChem) was dried using 4 Å molecular sieves and degassed by bubbling argon. Sodium azide (99.5%), propargyl benzoate (98%), copper iodide (98%) and triethylamine (99%) were all purchased from Aldrich and used as received. All manipulations were carried out under argon atmosphere. Column chromatography was performed on silica gel (300-400 mesh) under argon atmosphere. Because the complexes **1** and **2** are air sensitive, all their syntheses and handling were carried out under argon atmosphere and by using degassed reagents/solvents.

Characterizations. The molar masses (M_n) and dispersities (Đ) of PVAc were determined by size exclusion chromatography (SEC) in tetrahydrofuran (THF) at 45°C at a flow rate of 1 mL/min with Viscotek 305 TDA liquid chromatograph equipped with 2 PSS SDV analytical linear M 8 mm columns protected by a PL gel 5 µm guard column and calibrated with polystyrene standards.
M_n and Đ of poly(1-vinyl-3-ethylimidazolium bromide) were determined by size exclusion chromatography (SEC) with a SFD S5200 autosampler liquid chromatograph equipped with a SFD refractometer index detector 2000, carried out in tetrahydrofuran (THF) containing 10 mM $LiNTf_2$ (flow rate: 1 mL min^{-1} at 35°C according to a previously reported procedure).[2] PSS SDV analytical linear S 5 µm column (molar mass range: 100-150000 Da) and protected by a PL gel 5 µm guard column, was calibrated with PS standards. Prior to SEC analysis, bromine counter-anion of poly(1-vinyl-3-ethylimidazolium bromide) is exchanged by bis(trifluoromethylsulfonyl)imide according the following procedure. A volume of 2 ml of DMSO was added to each sample and the solutions were stirred for 5 min. After addition of an excess of $LiNTf_2$ (~ 50 mg), each system was left stirring (500 rpm) overnight. The polymer was then precipitated in water, centrifuged at 8000 rpm for 30 min. Water was removed with a pipette and the polymer at the bottom of the vial was washed three times with water and centrifuged (as previously described), in order to remove the residual bromide. The final samples with NTf_2^- counter anion were dried under reduced pressure at 50°C overnight, solubilized in THF/$LiNTf_2$ solution (10 mM) and filtered twice through a nylon membrane filter (size 0.45 µm and 0.20 µm respectively).

The magnetic moment was determined by the Evans method[3, 4] in CD_2Cl_2 using a solution of CH_3NO_2 in CD_2Cl_2 (20:80, v/v) as reference using 250 MHz NMR spectrometer.

Elemental analyses (C,H & N) were realized at Centre Hospitalier Universitaire, Sart-Tilman, Belgium with an analyser Flash EA 1112 Serie, a software Eager 300 from Intersciences and

Balance MX5 from Mettler Toledo. Halogen (Br and Cl) element analyses were performed at CNRS, Institut des Sciences Analytiques, Villeurbanne (France) and at Mirkoanaltisches Labor Pascher, Remagen (Germany), using classical potentiometric and titrimetric methods, respectively.

All NMR experiments were carried out at 298 K. ^{1}H NMR, ^{13}C attached proton test (APT) and heteronuclear single quantum coherence spectroscopy (HSQC) spectra of alkylcobalt(III) were carried out in dried and degassed C_6D_6 or in degassed D_2O with a 400 MHz and a 500 MHz Bruker spectrometer. ^{1}H spectra of reaction mixtures for the determination of the conversions were recorded in $CDCl_3$ (for PVAc) or DMSO-d_6 (for PVEtImBr) with a 250 MHz Bruker spectrometer. After purification, ^{1}H NMR and HSQC spectra of final PVAc were analyzed with a 400 MHz Bruker spectrometer. The chemical shifts (δ) are reported in ppm.

X-ray intensity data were collected on a MAR345 image plate using MoKα radiation (λ= 0.71073 Å, Xenocs Fox3D mirrors) generated by a Rigaku UltraX18 generator. For the pyridinated complex **2**, a crystal (which was submerged into Fomblin YR-1800 after schlenk conditions) was harvested and flash-cooled in a N_2-flow at 150 K. Crystals of the pyridinated complex **1** were transferred to Paratone®-N prior to the measurement at 150K. Diffraction data were integrated by Crysalis[5] and a multi-scan absorption correction was applied. See Table S1 and S3 for crystallographic and refinement details. The structure was solved by direct methods SHELXS97[6] and refined by full-matrix block least squares on F^2 using SHELXL2014.[6] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at calculated positions and refined isotropically with temperature factors fixed at 1.2 $U_{(eq)}$ of the parent atom (1.5 $U_{(eq)}$ for methyl groups). A selected list of bonds and angles for the pyridinated products **1** and **2** can be found in Tables S2 and S4. The crystal of the pyridinated product **2** was refined as a racemic twin with the BASF factor refined to 0.50(3).
Comparing both pyridine adducts of **1** and **2**, by pair-wise fitting of all non-hydrogen atoms, one can conclude that both compounds are isostrucural given the low RMSD of 0.0332.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as deposition No. CCDC-1060544 (**1**) and 1060545 (**2**). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: .44(1223)336033; e-mail : deposit@ccdc.cam.ac.uk).

ESR studies were carried out with a Miniscope MS400 (Magnettech, Berlin, Germany) benchtop spectrometer working at X-band with a modulation amplitude of 200 G, a sweep width of 68 G, a sweep time of 30 s, and a microwave power of 10 mW. The temperature was adjusted at 40°C using a temperature controlled unit TC H03 (Magnettech). All manipulations were performed under argon using a schlenk-type analytical tube (volume: 0.12 mL). The ESR spectra simulations were carried out with the PEST WINSIM program.[7]

Matrix-assisted Laser Desorption/Ionization Time-of-Flight (MALDI-ToF) mass spectra were recorded using a Waters QToF Premier mass spectrometer equipped with a Nd:YAG laser using the 3rd harmonic with a wave length of 355 nm. In the context of this study, a maximum output of ~65 J is delivered to the sample in 2.2 ns pulses at 50 Hz repeating rate. Time-of-flight mass analyses were performed in the reflection mode at a resolution of about 10 000. The matrix, trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB), was prepared as a 40 mg/mL solution in chloroform. The matrix solution (1 µL) was applied to a stainless steel target and air-dried. Polymer samples were dissolved in THF to obtain 1 mg/mL solutions and 20

µL of NaI solution (2 mg/mL in acetonitrile) are added as source of cationization agent. Then, 1 µL aliquots of these solutions were applied onto the target area (already bearing the matric crystals) and then air-dried.

Gas Chromatography-Mass Spectrometry (GC-MS) analysis was performed using a Waters GCT Premier instrument based on a time-of-flight analyzer. The gas chromatograph was equipped with a Restek Rtx-5Sil MS column (30 m length, 0.25 mm ID and 0.25 µm DF). Typical GC conditions were: injector temperature, 250°C; splitless mode; Helium carrier gas flow rate, 1 mL/min; interface temperature: 250°C. The temperature program was as follow: initial temperature, 55°C; 1°C/min ramp; final temperature, 150°C; 5°C/min ramp; final temperature, 250°C (hold 5 min). Electron Ionization (EI) source conditions were: source temperature, 200°C; electron energy, 70 eV; trap current, 200 µa; emission current, 400 µa. All ions were transmitted into the pusher region of the time-of-flight analyzer where they were mass-analyzed with a 1 s integration time. Data were acquired in continuum mode. Sample was diluted 500 000 times in CH_2Cl_2 before injection of 1µL.

Synthesis and characterizations of compound 1 ($BrCH_2$-$Co(acac)_2$)

$Co(acac)_2$ (2.00 g, 7.78 mmol) and the azo initiator V70 (2.4 g, 7.78 mmol) were placed in a round-bottomed flask capped by a three-way stopcock and purged by three vacuum–argon cycles. To the reaction vessel was added an excess of dibromomethane (60 mL) and tris(trimethylsilyl)silane (3.00 mL, 9.72 mmol). The reaction mixture was then stirred at 30°C during 3 days. During this period of time, the original pink-violet suspension gradually became black. The excess pressure caused by nitrogen production during V70 decomposition was regularly released manually. At the end of the reaction, an aliquot is picked out under argon and analyzed by GC-MS (see Figure S1). Dibromomethane was then removed under vacuum to leave a black solid. Degassed dichloromethane (about 50 mL) was added to the product until complete solubilization of the solid and then pentane (500 mL) was added. The flask was then stored at -20°C under argon overnight to precipitate the residual Co(II) salts. The liquid phase was transferred to a round-bottom flask under argon with a cannula. After elimination of the solvents under vacuum at room temperature, the residue was dissolved in a minimum amount of degassed CH_2Cl_2 and purified by elution on a silica column under inert atmosphere. Dichloromethane was first used as the eluent to remove a yellow fraction of residual azo-initiator and its decomposition products. Then a mixture of degassed CH_2Cl_2/EtOAc (85:15) was used as eluent and a red fraction was collected. Compound **1** was then recovered by evaporation to dryness of this red fraction (724 mg, 2.06 mmol, yield = 26.5%). **1** is stored at the dried state under argon atmosphere at -20°C.

^{1}H NMR (D_2O, 298K) : δ/ppm 6.71 (2H), 5.55 (2H), 1.94 (12H) (see Figure 1 in the main manuscript)

^{13}C APT (D_2O, 298K) : δ/ppm 25.4 (4 x CH_3), 33.4 (CH_2), 98.8 (2 x CH), 189.6 (4 x C_{quat}) (see Figure S2 and S3).

Elemental analysis: anal. calcd (found): C 37.63 (37.44), H 4.59 (4.64), Br 22.76 (20.30).

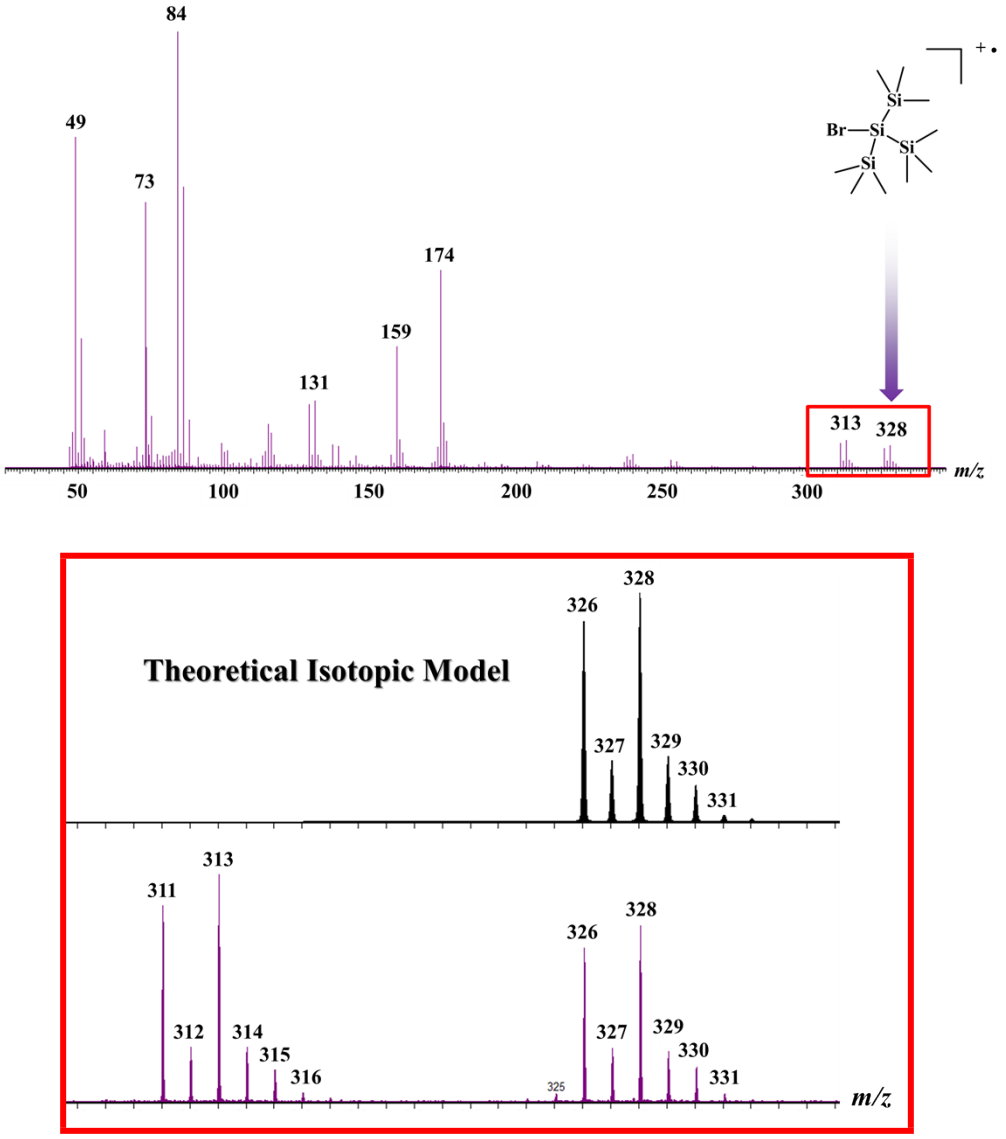


Figure S1. GC-EI mass spectrometry analysis of the crude reaction medium: mass spectrum for retention time 14.6 minutes corresponding to Br-Si(Si(CH_3)$_3$)$_3$ formed during the reaction. EI-HRMS realized on Autospec 6F: $M^{+\cdot}$ Theory (*m/z* 326.0373) Measured (*m/z* 326.0365) (-2.4 ppm error)

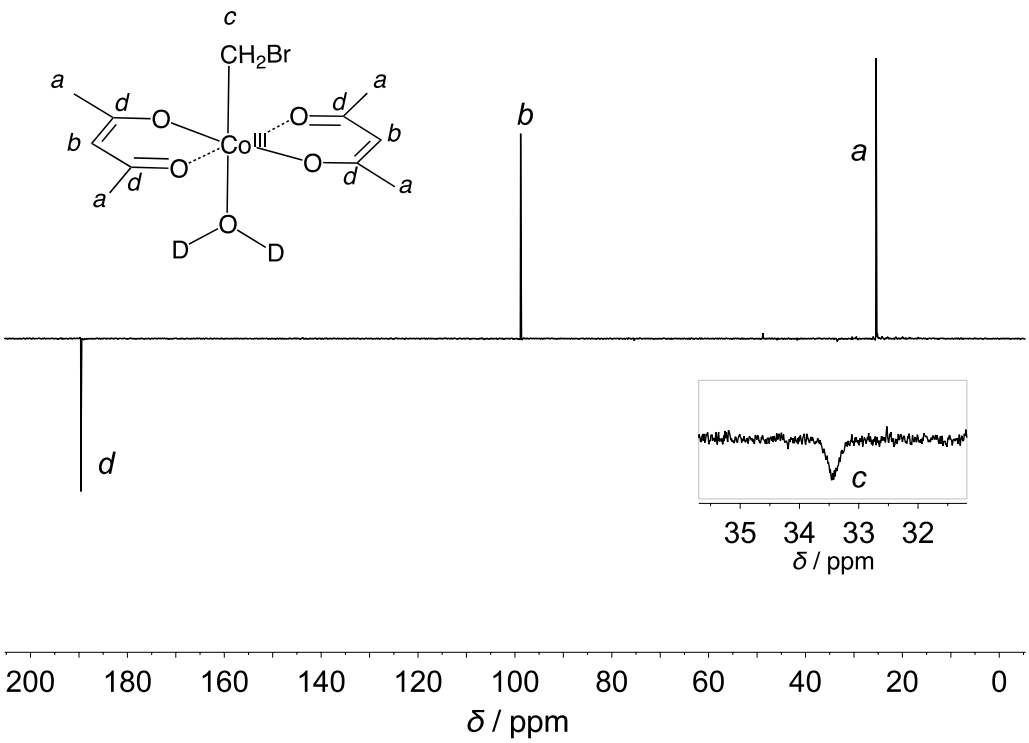


Figure S2. ^{13}C APT analysis of compound **1** in D_2O.

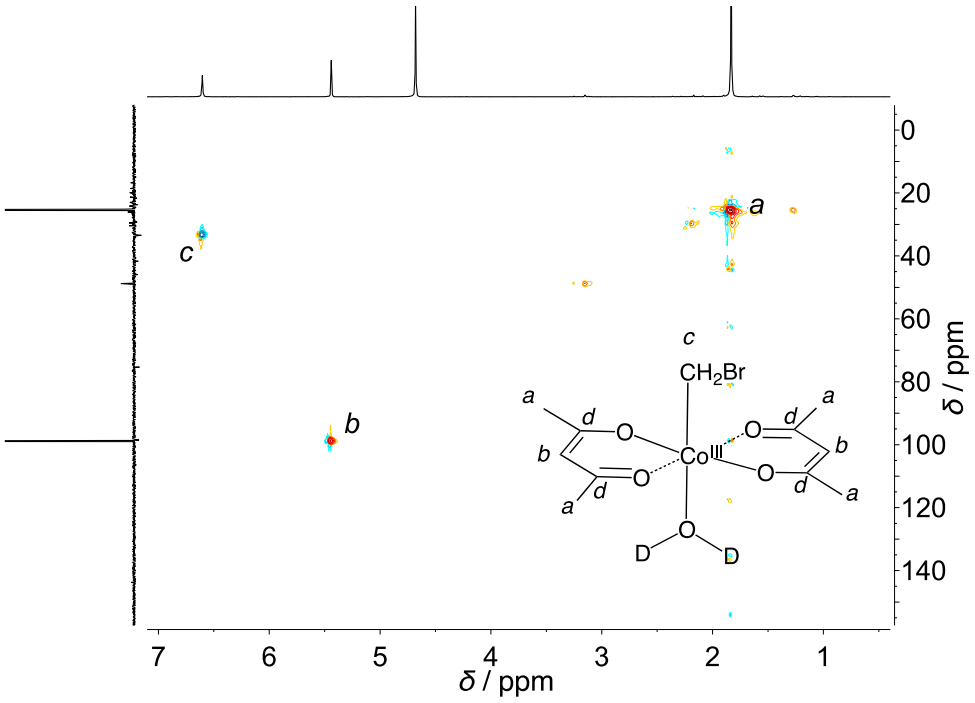
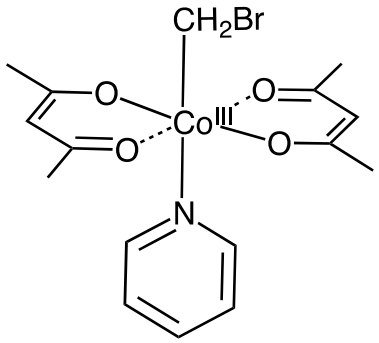


Figure S3. HSQC NMR analysis of compound **1** in D_2O.

Synthesis and characterization of pyridinated compound 1 ($BrCH_2$-$Co(acac)_2(py)$)



Compound **1** (100 mg) was first dried under vacuum and solubilized in a minimum amount of degassed benzene (2 mL), leading to a green solution. Then, degassed pyridine (50 µL, 2 equiv.) was added under stirring overnight, noticed immediately by a change of color from dark green to red. The pyridinated complex was recrystallized by gently adding degassed pentane over the red benzene solution to yield dark red needles after storing the solution at 6°C for 72h. Crystals were recovered by withdrawing the solution with a cannula and by washing them with a fresh fraction of degassed pentane. Finally, crystals were dried under vacuum at room temperature (70 mg, $yield_{recryst.}$= 57%).

Elemental analysis: anal. calcd (found): C 44.67 (45.47), H 4.92 (5.09), N 3.26 (3.94), Br 18.57 (18.50)

Table S1. Crystal data and structure refinement for pyridinated complex **1**.

Empirical formula	C_{16} H_{21} Br Co N O_4
Formula weight	430.18
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*m
Unit cell dimensions	a = 8.2934(10) Å
	b = 13.814(2) Å
	c = 7.8377(11) Å
	β= 92.388(15)°.
Volume	897.1(2) $Å^3$
Z	2
Density (calculated)	1.592 g/cm^3
Absorption coefficient	3.201 mm^{-1}

F(000)	436
Crystal size	0.18 x 0.18 x 0.02 mm^3
Theta range for data collection	2.867 to 25.499°.
Reflections collected	7742
Independent reflections	1667 [$R_{(int)}$ = 0.0459]
Completeness to theta = 25.242°	96.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.86669
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1667 / 2 / 120
Goodness-of-fit on F^2	1.077
Final R indices [I>2sigma(I)]	R_1 = 0.0334, wR_2 = 0.0906
R indices (all data)	R_1 = 0.0346, wR_2 = 0.0914
Absolute structure parameter	0.028(8)
Largest diff. peak and hole	0.628 and -0.332 $e.Å^{-3}$

Table S2. Selected bond lengths [Å] and angles [°] for pyridinated complex **1**.

Co(1)-O(2)#1
Co(1)-O(2)
Co(1)-O(6)
Co(1)-O(6)#1
Co(1)-C(9)
Co(1)-N(11)
C(9)-Br(10)

O(2)#1-Co(1)-O(2)
O(2)#1-Co(1)-O(6)
O(2)-Co(1)-O(6)
O(2)#1-Co(1)-O(6)#1
O(2)-Co(1)-O(6)#1
O(6)-Co(1)-O(6)#1
O(2)#1-Co(1)-C(9)
O(2)-Co(1)-C(9)
O(6)-Co(1)-C(9)
O(6)#1-Co(1)-C(9)
O(2)#1-Co(1)-N(11)
O(2)-Co(1)-N(11)

O(6)-Co(1)-N(11)

O(6)#1-Co(1)-N(11)

C(9)-Co(1)-N(11)

Co(1)-C(9)-Br(10)

NMR in C_6D_6 (500 MHz). When dissolved in C_6D_6, the pyridinated compound **1** is present as a mixture of the pyridinated complex and compound **1**.

*Pyridinated complex **1** (left structure on Figure S4):* ^{1}H NMR (C_6D_6, 298K) δ/ppm 8.41 (2H), 7.26 (1H), 7.16 (1H), 6.67 (1H), 6.43 (2H), 5.25 (1H), 5.19 (1H), 2.13 (3H), 1.81 (3H), 1.75 (3H), 1.71 (3H); ^{13}C APT (C_6D_6, 298K) δ 25.8 (CH_3), 26.4 (CH_3), 27.5 (CH_3), 28.4 (CH_3), 39.2 (CH_2), 97.7 (CH), 98.5 (CH), 123 (CH), 136.6 (2 x CH), 152.8 (2 x CH), 187.1 (C_{quat}), 187.3 (C_{quat}), 187.6 (C_{quat}) 190.2 (C_{quat})

*Complex **1** (right structure on Figure S4):* ^{1}H NMR (C_6D_6, 298K) δ/ppm 7.57 (2H), 4.93 (2H), 1.66 (12H); 47.8; ^{13}C APT (C_6D_6, 298K) δ 26.0 (4 x CH_3), 43.2 (CH_2), 98.6 (2 x CH), 187.7 (4 x C_{quat})

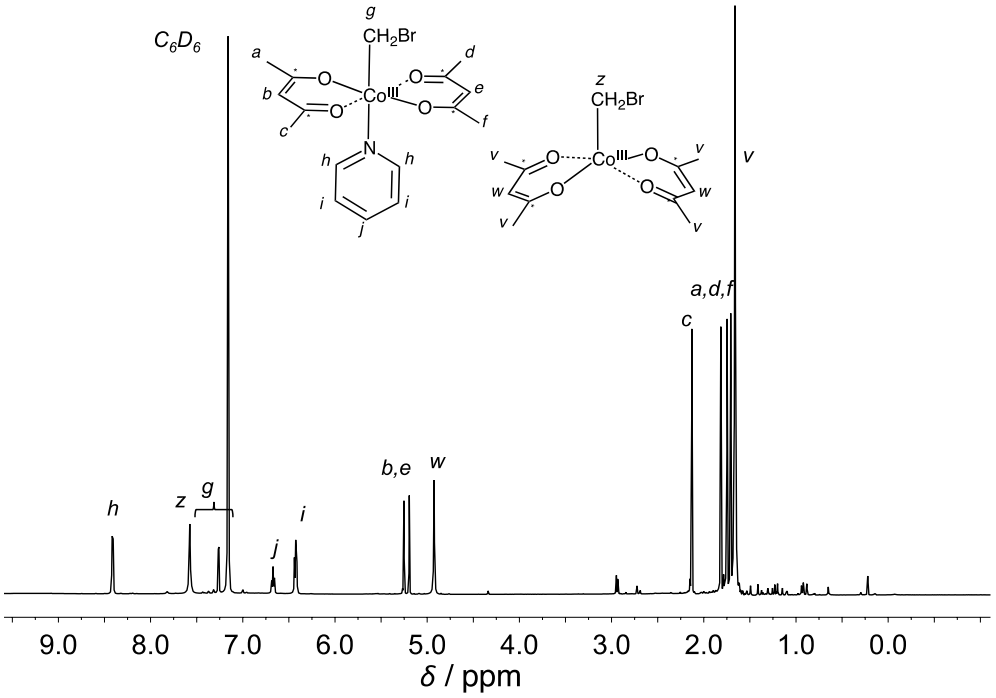


Figure S4. ^{1}H NMR analysis (in C_6D_6) of pyridinated compound **1**.

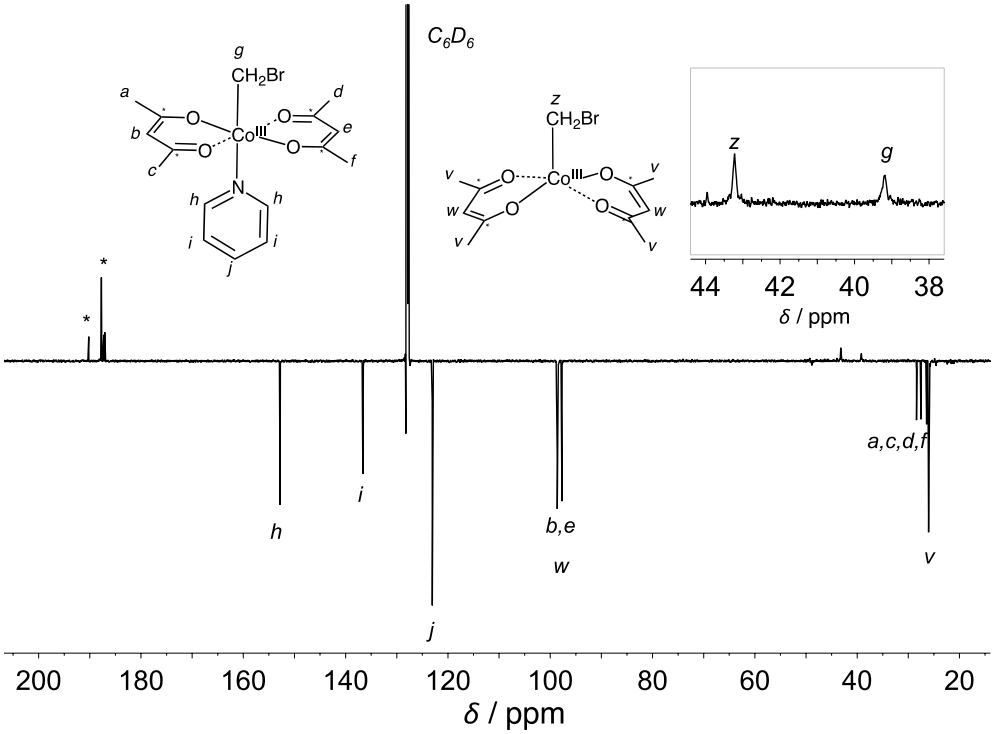


Figure S5. ^{13}C APT (in C_6D_6) analysis of pyridinated compound **1**.

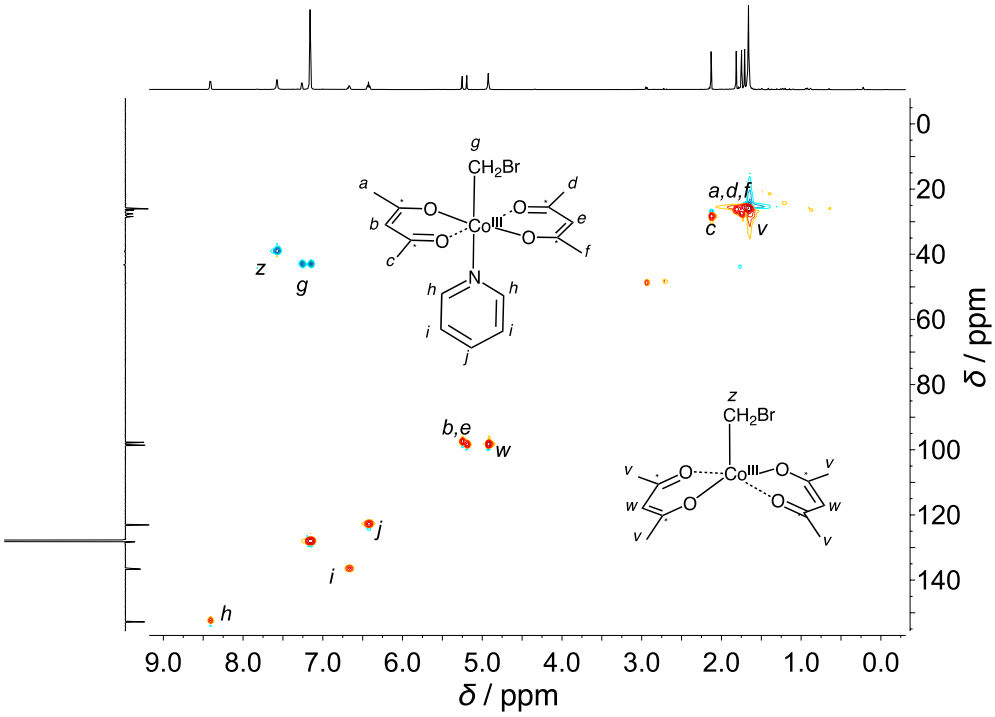


Figure S6. HSQC NMR analysis (in C_6D_6) of pyridinated compound **1**.

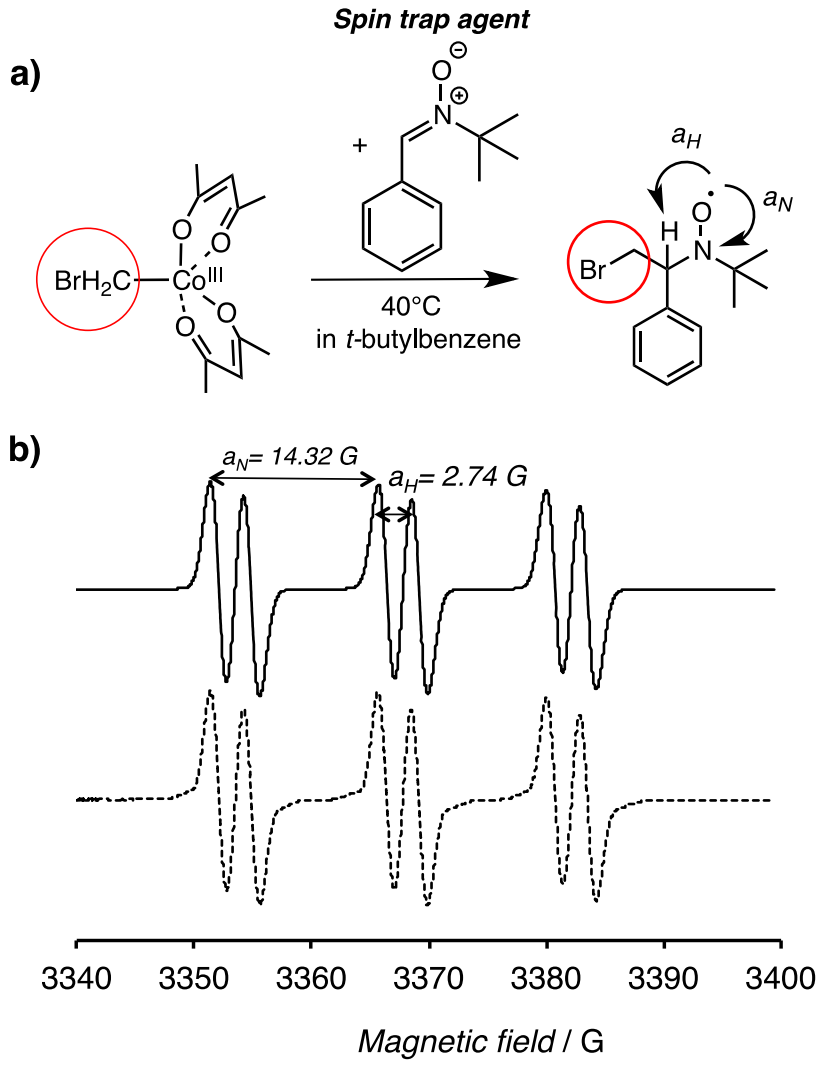


Figure S7. a) Reaction scheme for the spin-trapping experiment between **1** and PBN in *tert*-butylbenzene at 40°C. b) Experimental (dotted line) and simulated (full line) ESR spectra for this experiment (conditions: [PBN]/[**1**]= 12, 25 min).

Synthesis and characterization of compound 2 ($ClCH_2$-$Co(acac)_2$)

$Co(acac)_2$ (2.00 g, 7.78 mmol) and AIBN (1.28 g, 7.78 mmol) were placed in a round-bottomed flask capped by a three-way stopcock and purged by three vacuum–argon cycles. To the reaction vessel was added an excess of dichloromethane (60 mL) and tris(trimethylsilyl)silane (3.00 mL, 9.72 mmol). The reaction mixture was then stirred at 55°C for 2 days. During this period of time, the original pink-violet suspension gradually became black. The excess pressure caused by nitrogen production during AIBN decomposition was regularly released manually. Dichloromethane was then removed under vacuum to leave a black solid. Degassed dichloromethane (about 50 mL) was added to the product until complete solubilization of the solid and then pentane (500 mL) was added. The flask was then stored at -20°C under argon overnight to precipitate the residual Co(II) salts. The liquid phase was transferred to a round-bottom flask under argon with a cannula. After elimination of the solvents under vacuum at room temperature, the residue was dissolved in a minimum amount of degassed CH_2Cl_2 and purified by elution on a silica column under inert atmosphere. Dichloromethane was first used as the eluent to remove a yellow fraction of residual azo-initiator and its decomposition products. Then a mixture of degassed CH_2Cl_2/EtOAc (85:15) was used as eluent and a red fraction was collected. Compound **1** was then recovered by evaporation to dryness of this red fraction (620 mg, 2.02 mmol, yield 26%). **1** is stored at the dried state under argon atmosphere at -20°C.

NMR analysis of **2** in D_2O showed a decrease of the -*CH*- signal intensity (5.5 ppm) on the acac ligand because of its exchange with deuterium of D_2O.[8]

^1H NMR (D_2O, 298K) : δ/ppm 6.91 (2H), 5.79 (1H, acetylacetone), 5.50 (2H), 2.16 (6H, acetylacetone) , 1.89 (12H). (see Figure S8)

^{13}C APT (D_2O, 298K) : δ/ppm 25.3 (4 x CH_3), 25.4 (2 x CH_3, acetylacetone) , 39.2 (CH_2), 98.4 (CH, acetylacetone), 98.8 (2 x CH), 189.6 (4 x C_{quat}), 191.4 (2 x C_{quat}, acetylacetone) (see Figure S9).

Elemental analysis: anal. calcd (found): C 43.09 (42.39), H 5.26 (5.35), Cl 11.56 (11.45).

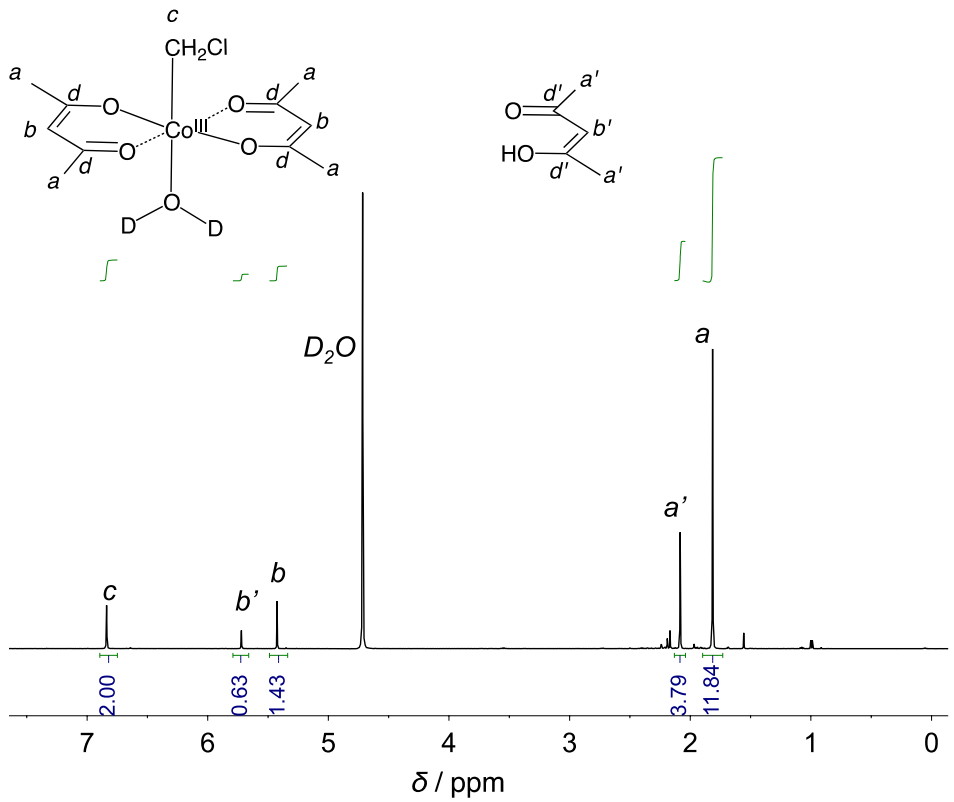


Figure S8. ^{1}H NMR spectrum of compound **2** in D_2O (signals at 1.08, 1.63 and 2.26 ppm are minor traces of unidentified species).

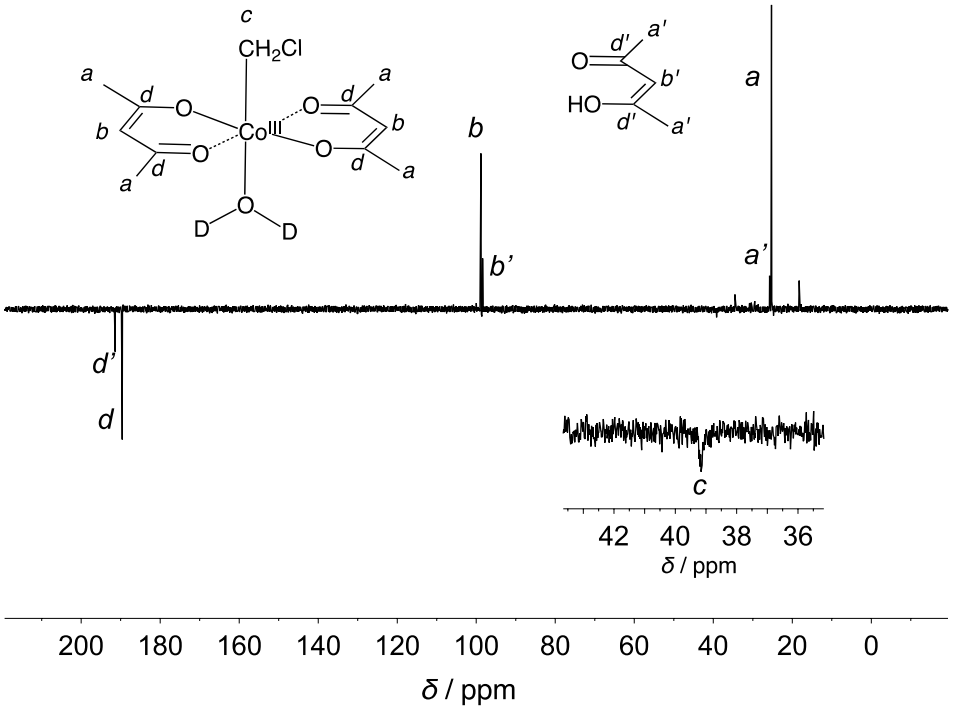


Figure S9. ^{13}C APT spectrum of compound **2** in D_2O (signals at 18.3, 25.8 and 34.5 ppm are traces of unidentified species).

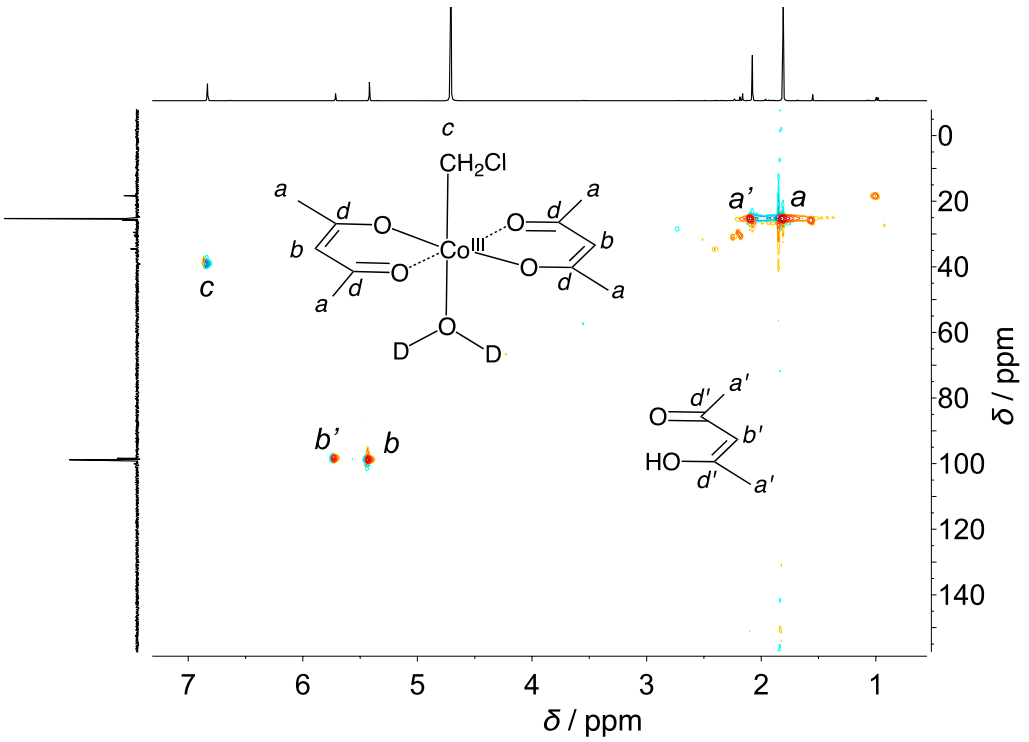
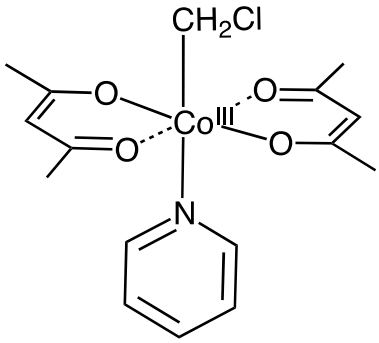


Figure S10. HSQC spectrum of compound **2** in D_2O (signals at 18.3, 25.8 and 34.5 ppm are traces of unidentified species).

Synthesis of pyridinated compound 2 ($ClCH_2$-$Co(acac)_2(py)$)



Compound **2** (93 mg) was first dried under vacuum and solubilized in a minimum amount of degassed benzene (2 mL). Then, degassed pyridine (50 µL, 2 equiv.) was added under stirring overnight, noticed immediately by a change of color from dark green to red. The pyridinated complex was recrystallized by gently adding degassed pentane over the red benzene solution to yield dark red needles after storing the solution at 6°C for 72h. Crystals were recovered by withdrawing the solution with a cannula and by washing the crystals with a fresh fraction of degassed pentane. Finally, crystals were dried under vacuum at room temperature (80 mg, $yield_{recryst.}$ = 68%).

Elemental analysis: anal. calcd (found): C 49.82 (49.71), H 5.49 (5.38), N 3.63 (3.64), Cl 9.19 (9.09).

XRD data : see Figure S11, Table S3 and Table S4.

NMR analyses : see Figures S12, S13 and S14.

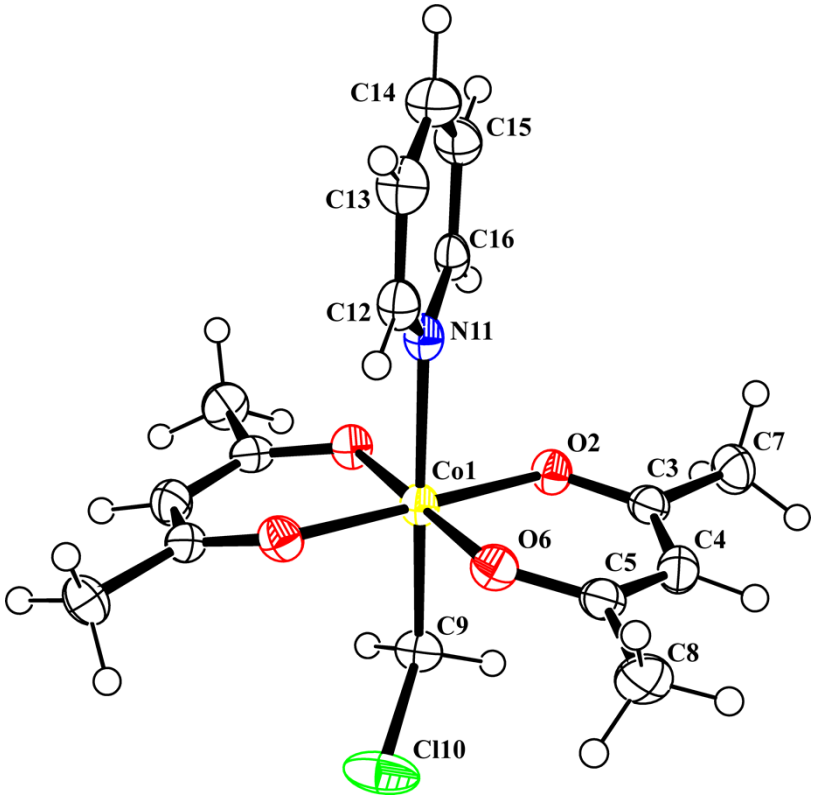


Figure S11. ORTEP representation of $ClCH_2$-Co(acac)$_2$(Py) complex **2** showing displacement ellipsoids drawn at the 50% probability level; selected bond lengths [Å]: Co(1)-O(6) 1.887(4), Co(1)-O(2) 1.889(4), Co(1)-C(9) 1.957(7), Co(1)-N(11) 2.099(7), C(9)-Cl(10) 1.784(7)

Table S3. Crystal data and structure refinement for pyridinated compound **2**.

Empirical formula	$C_{16}\ H_{21}\ Cl\ Co\ N\ O_4$
Formula weight	385.72
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C*m
Unit cell dimensions	a = 8.1891(2) Å
	b = 13.7998(3) Å
	c = 7.73787(19) Å
	β= 91.890(2) °
Volume	873.96(4) $Å^3$
Z	2
Density (calculated)	1.466 g/cm^3
Absorption coefficient	1.152 mm^{-1}
F(000)	400
Crystal size	0.19 x 0.11 x 0.03 mm^3
Theta range for data collection	2.894 to 25.505°.
Reflections collected	3636
Independent reflections	1636 [$R_{(int)}$ = 0.0380]
Completeness to theta = 25.242°	98.6 %
Absorption correction	Semi-empirical from
	equivalents
Max. and min. transmission	1.00000 and 0.88449
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1636 / 2 / 121
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R_1 = 0.0319, wR_2 = 0.0799
R indices (all data)	R_1 = 0.0332, wR_2 = 0.0807
Absolute structure parameter	0.50(3)
Largest diff. peak and hole	0.678 and -0.205 $e.Å^{-3}$

Table S4. Selected bond lengths [Å] and angles [°] for pyridinated compound **2**.

Co(1)-O(6)
Co(1)-O(6)#1
Co(1)-O(2)#1
Co(1)-O(2)
Co(1)-C(9)
Co(1)-N(11)
C(9)-Cl(10)

O(6)-Co(1)-O(6)#1
O(6)-Co(1)-O(2)#1
O(6)#1-Co(1)-O(2)#1
O(6)-Co(1)-O(2)
O(6)#1-Co(1)-O(2)
O(2)#1-Co(1)-O(2)
O(6)-Co(1)-C(9)
O(6)#1-Co(1)-C(9)
O(2)#1-Co(1)-C(9)
O(2)-Co(1)-C(9)
O(6)-Co(1)-N(11)
O(6)#1-Co(1)-N(11)
O(2)#1-Co(1)-N(11)
O(2)-Co(1)-N(11)
C(9)-Co(1)-N(11)
Co(1)-C(9)-Cl(10)

NMR in C_6D_6 (500 MHz). When dissolved in C_6D_6, the pyridinated compound **2** is present as a mixture of the pyridinated complex and compound **2**.

*Pyridinated complex **2** (left structure on Figure S12):* ^{1}H NMR (C_6D_6, 298K) δ/ppm 8.41 (2H), 7.55 (1H), 7.38 (1H), 6.64 (1H), 6.39 (2H), 5.27 (1H), 5.20 (1H), 2.15 (3H), 1.79 (3H), 1.75 (3H), 1.71 (3H); ^{13}C APT (C_6D_6, 298K) δ 25.8 (CH_3), 26.2 (CH_3), 27.5 (CH_3), 28.5 (CH_3), 44.3 (CH_2), 97.5 (CH), 98.6 (CH), 122.9 (CH), 137.7 (CH), 136.5 (CH), 154.8 (CH), 152.9 (CH), 188 (4 x C_{quat})

*Complex **2** (right structure on Figure S12):* ^{1}H NMR (C_6D_6, 298K) δ/ppm 7.81 (2H), 4.92 (2H), 1.64 (12H); 47.8; ^{13}C APT (C_6D_6, 298K) δ 25.8 (4 x CH_3), 47.8 (CH_2), 98.6 (CH_2), 188 (4 x C_{quat})

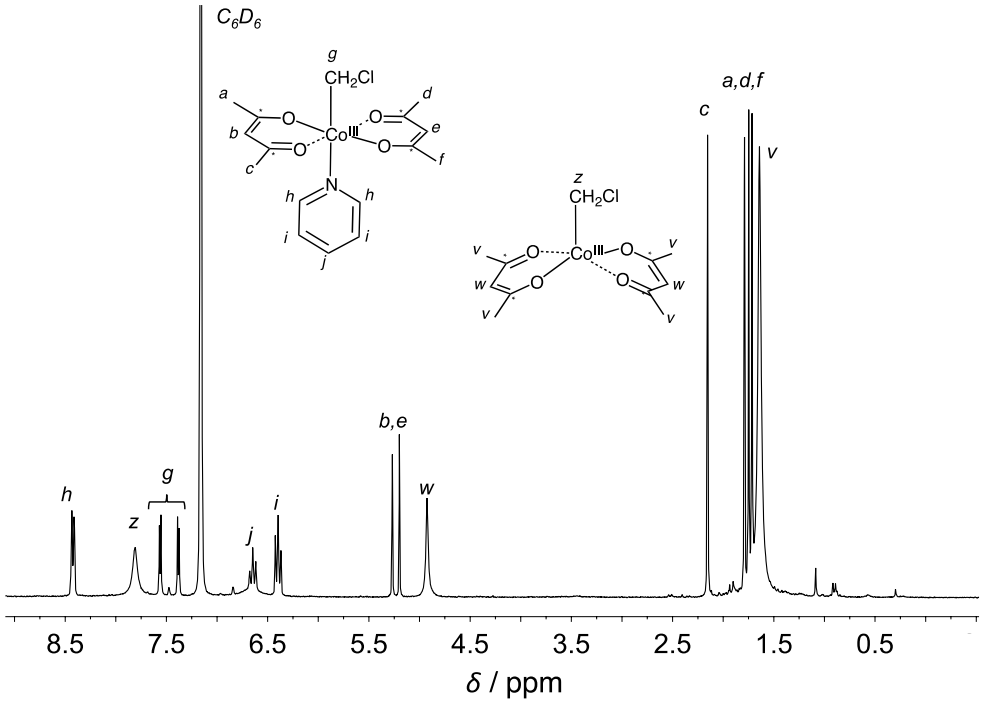


Figure S12. ^{1}H NMR analysis (in C_6D_6) of pyridinated compound **2**.

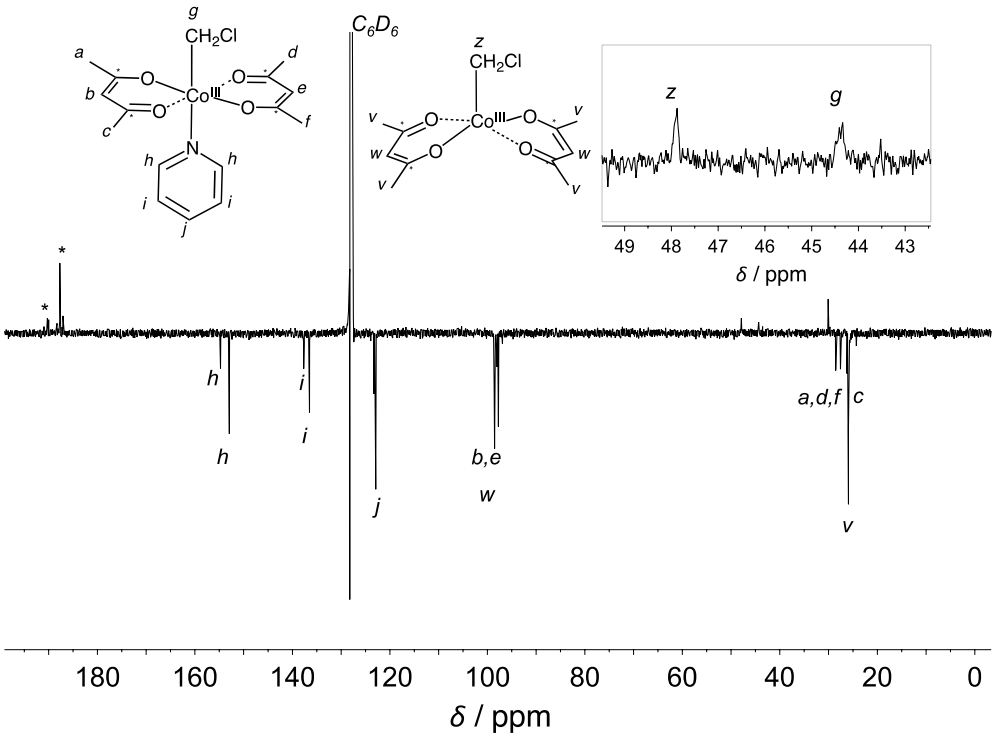


Figure S13. ^{13}C APT analysis (in C_6D_6) of pyridinated compound **2**.

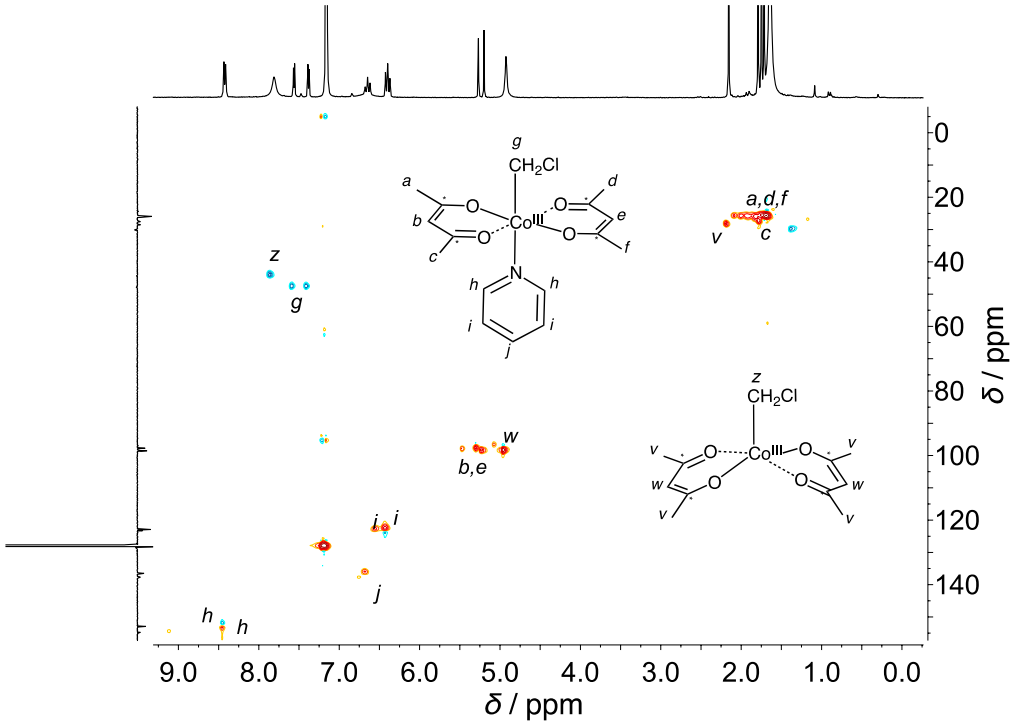


Figure S14. HSQC NMR analysis (in C_6D_6) of pyridinated compound **2**.

Vinyl acetate polymerization, general procedure.

The solution of compound **1** in dichloromethane (1 ml, 0.0562 M; 0.0562 mmol) was introduced under argon in a 30 mL Schlenk tube and evaporated to dryness under reduced pressure at room temperature. Vinyl acetate (VAc; 10 ml; 108.5 mmol) was added under argon. The reaction medium is heated under stirring at 350 rpm at 40°C using an oil bath. Aliquots were regularly picked out the reaction medium with a syringe in order to evaluate the monomer conversion by ^{1}H NMR spectroscopy in $CDCl_3$ and to determine the macromolecular parameters (M_n, Đ) by SEC analysis after quenching the samples by adding and excess of propanethiol. The same protocol is used for the other [VAc]/[**1**] ratios by adapting the amount of monomer added to the reaction medium. Results are summarized in Figure 3 and S15 and in Table S5.

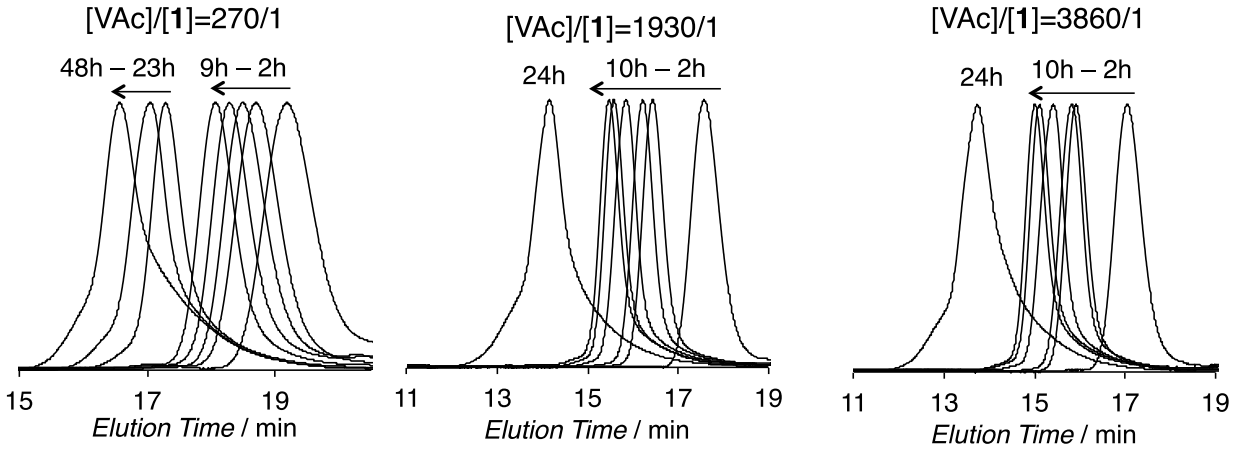


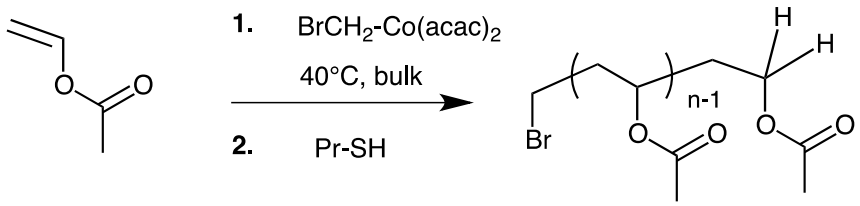
Figure S15. SEC traces of PVAc prepared by **1** in bulk at 40°C using [VAc]/[**1**]=270 (left), [VAc]/[**1**]=1930 (middle) and 3860 (right).

Table S5. Polymerization of vinyl acetate (VAc) initiated by **1** in bulk at 40°C

Entry	[VAc]/[**1**]	time (h)	conv. (%)[a]	$M_{n,SEC}$[b] (g/mol)	Đ[b]
1	270/1	2	11	2200	1.14
		4	17	3500	1.11
		5	19	4100	1.10
		7	23	4900	1.10
		9	26	5800	1.10
		23	42	10000	1.17
		27	45	11100	1.19
		33	48	11900	1.23
		48	57	15000	1.33
2	1930/1	2	5	8900	1.09
		5	12	22000	1.08
		6	14	26200	1.08
		8	19	34300	1.11
		9	22	39800	1.14
		9.5	23	44600	1.11
		24	54	104600	1.52
3	3860/1	2	4	13600	1.09
		5	10	33400	1.08
		6	11	35600	1.10
		8	15	47500	1.15
		9	18	59900	1.10
		9.5	19	61500	1.15
		24	45	127200	1.70

[a]VAc conversion determined by ^{1}H NMR in $CDCl_3$. [b]determined by SEC analysis in THF (PS calibration)

Synthesis of low molar mass PVAc using compound 1 for chain-end analysis.



Scheme S1. Synthesis of PVAc using **1**, followed by deactivation by propanethiol.

The solution of compound **1** in dichloromethane (1 ml, 0.086 M; 0.086 mmol) was introduced under argon in a 30 mL Schlenk tube and evaporated to dryness under reduced pressure at room temperature. Vinyl acetate (VAc; 2.6 ml; 28.2 mmol) was added into the Schlenk under argon with a ratio of [VAc]/[**1**]= 328. The reaction medium is heated under stirring at 350 rpm at 40°C using an oil bath. An aliquot was picked out the reaction medium with a syringe after 3h of reaction to evaluate the monomer conversion by ^{1}H NMR spectroscopy in $CDCl_3$ (~10% conversion). The polymerization was then quenched by the addition of propanethiol and the reaction medium was stirred at room temperature for 24h. After elimination of VAc and propanethiol under vacuum at room temperature, the polymer was dissolved in 5 ml MeOH and purified by dialysis (cut-off = 1000 Da) in MeOH. The molar mass of the polymer determined by SEC using PS as calibration is 2200 g/mol and dispersity is 1.14.

The polymer is analyzed by ^{1}H NMR spectroscopy (Figure S16) and MALDI-ToF analysis (Figure S17).

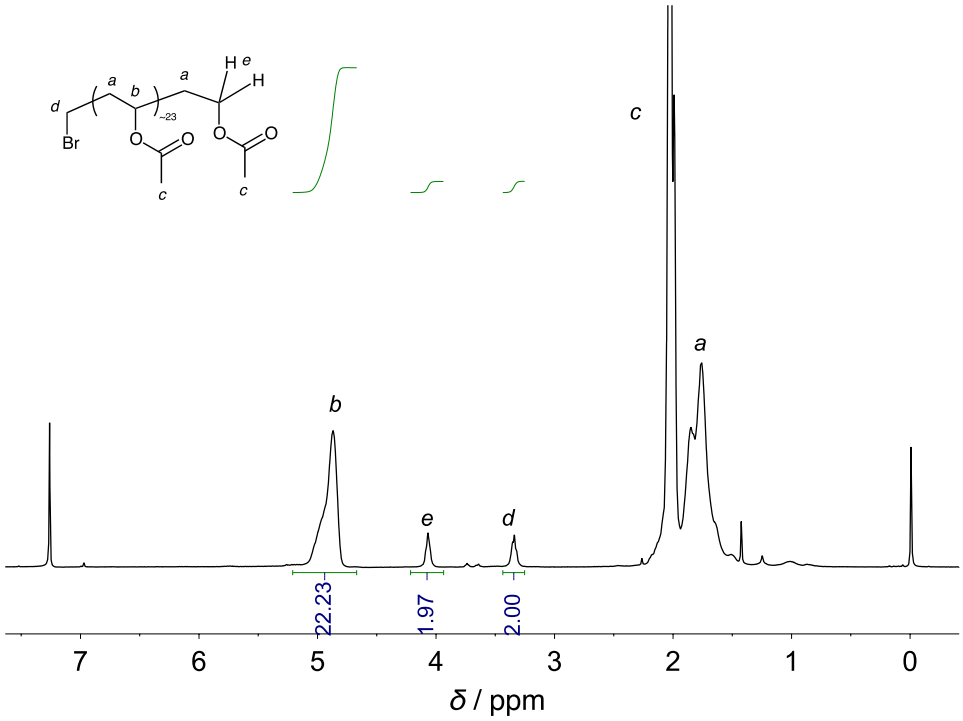


Figure S16. ^{1}H NMR (in $CDCl_3$) analysis of PVAc ($M_{n,SEC}$ = 2200 g/mol, Đ = 1.14) synthesized with compound **1** .

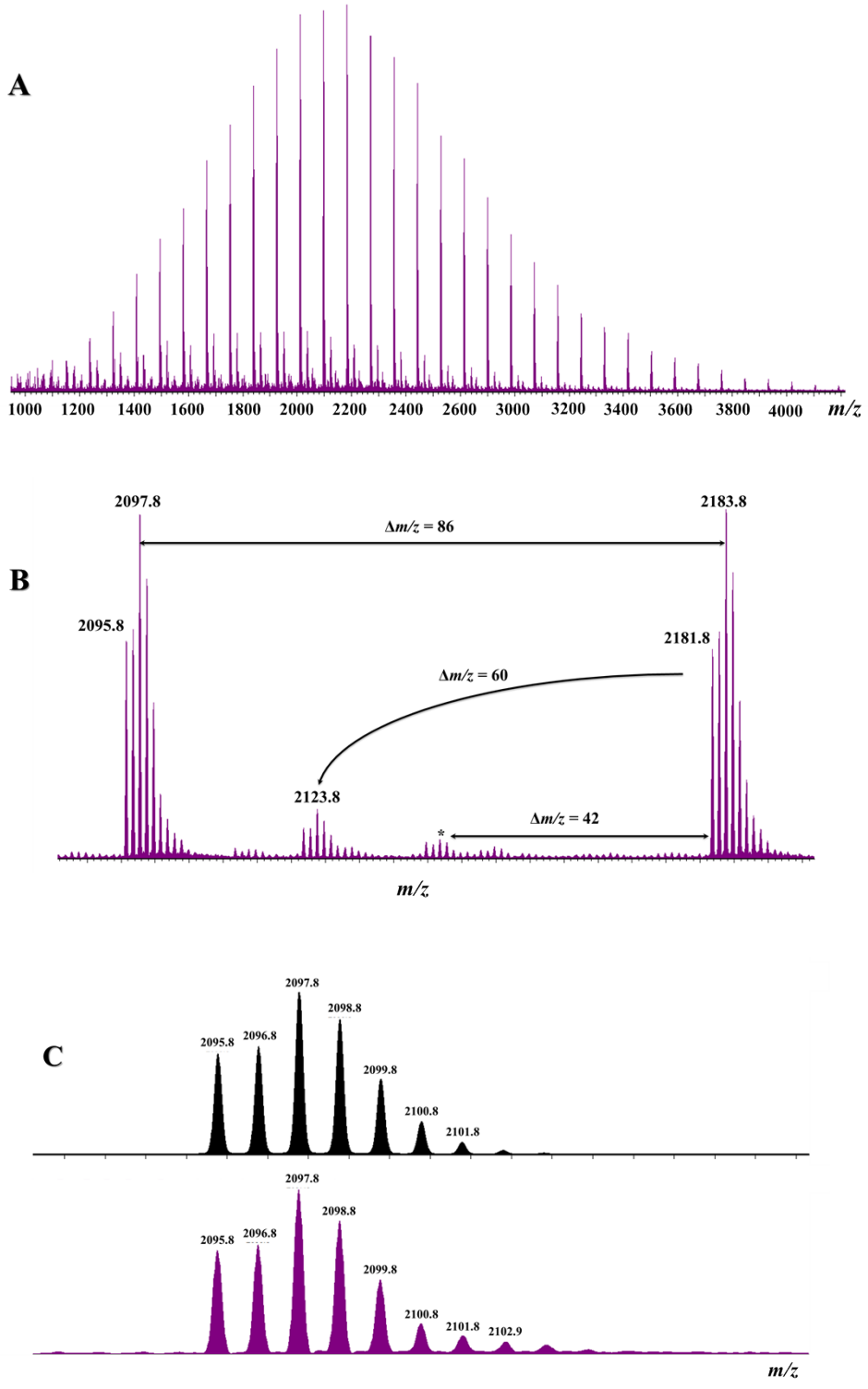


Figure S17. (A) Global MALDI mass spectrum recorded for PVAc synthesized with compound **1**, (B) magnification of the mass spectrum between *m/z* 2090 and *m/z* 2200, and (C) comparison between the theoretical (black) and experimental isotopic distributions (purple) for sodium cationized oligomer with 23 monomer units.

Mass spectrum of PVAc synthesized with compound **1** is reported in Figure S17. The global mass spectrum (Figure S17A), centered around *m/z* 2100, attests the low dispersity of the polymer distribution, in agreement with NMR and SEC data. The magnification between *m/z* 2090 and *m/*z 2200 presented in Figure S17B confirms the high control on the end-groups. Indeed, the only other signals observed between two consecutive oligomer ions are (i) due to K^+ instead Na^+ as cationization agent, (ii) fragmentation induced in the source (peaks at *m/z* 2121 to 2127) involving a McLafferty rearrangement leading to the loss of acetic acid and (iii) the isotopic distribution marked with * is explained by an hydrolysis of one acetate moiety on the polymer chain. Finally, Figure S17C represents the comparison between the experiment data and the theoretical isotopic distribution for oligomer ions constituted by 23 monomer units, Br-CH_2 and H as end-chains and cationized by a sodium. The presence of the bromine atom is easily highlighted by the two first signals characterized by a lower intensity.

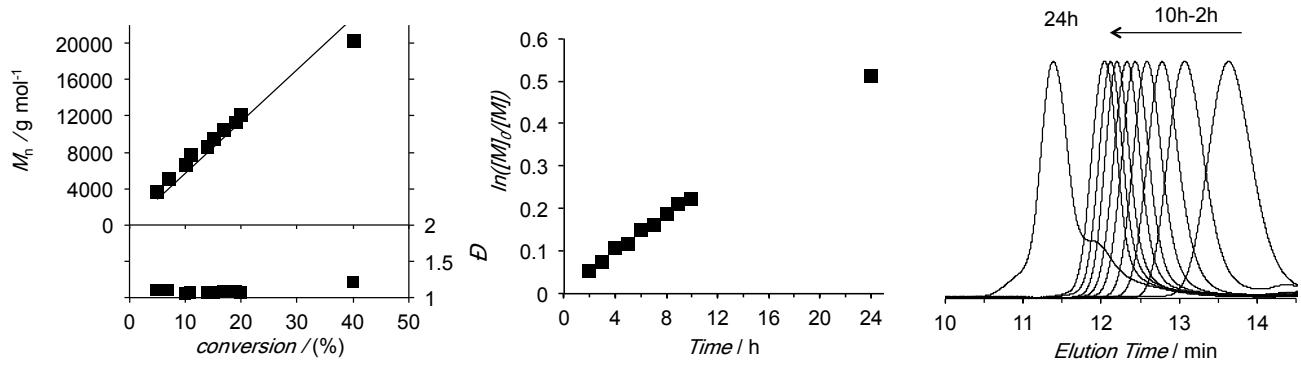
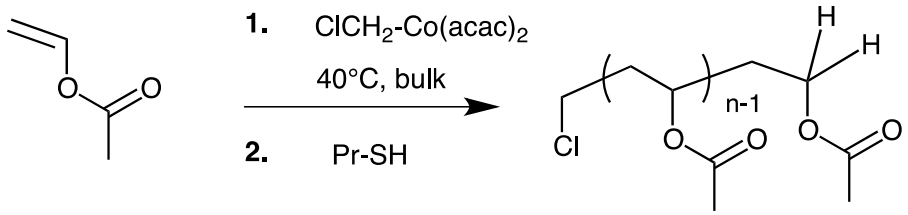


Figure S18. $M_{n\ SEC}$ and Đ evolutions *vs* monomer conversion, ln([M]$_0$/[M]) vs time and SEC traces for the VAc polymerization initiated by **2** in bulk at 40°C with [VAc]/[**2**]=713.

Synthesis of low molar mass PVAc using compound 2 for chain-end analysis.



Scheme S2. Synthesis of PVAc using **2**, followed by deactivation by propanethiol.

The solution of compound **2** in dichloromethane (1 ml, 0.076 M; 0.076 mmol) was introduced under argon in a 30 mL Schlenk tube and evaporated to dryness under reduced pressure at room temperature. Vinyl acetate (VAc; 5 ml; 54.2 mmol) was added and the reaction medium is heated under stirring at 350 rpm at 40°C using an oil bath. An aliquot was picked out the reaction medium with a syringe after 1.5h of reaction to evaluate the monomer conversion by ^{1}H NMR spectroscopy in $CDCl_3$ (4% conversion). The polymerization was then quenched by the addition of propanethiol and the reaction medium was stirred at room temperature for 24h. After elimination of VAc and propanethiol under vacuum at room temperature, the polymer was dissolved in 5 ml MeOH and purified by dialysis (cut-off = 1000 Da) in MeOH. The molar mass of the polymer determined by SEC using PS as calibration is 2400 g/mol and dispersity is 1.09.

The polymer was analyzed by ^{1}H NMR spectroscopy (Figure S19) and MALDI mass spectrometry (Figure S20).

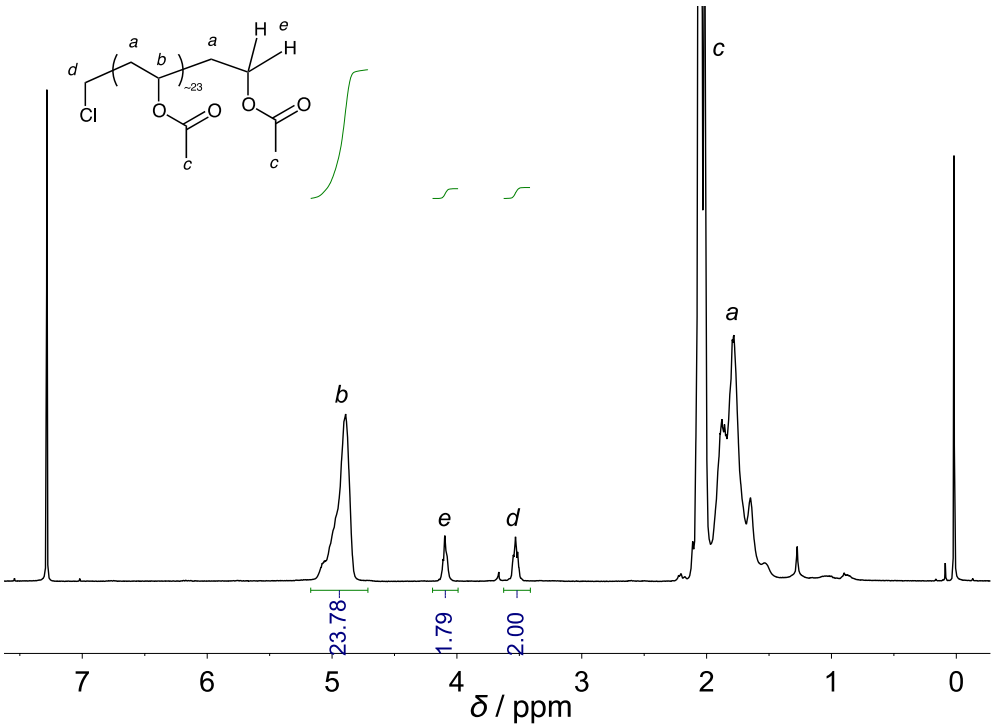


Figure S19. ^{1}H NMR analysis ($CDCl_3$) of PVAc ($M_{n,SEC}$ = 2400 g/mol, Đ = 1.09) synthesized by compound **2**.

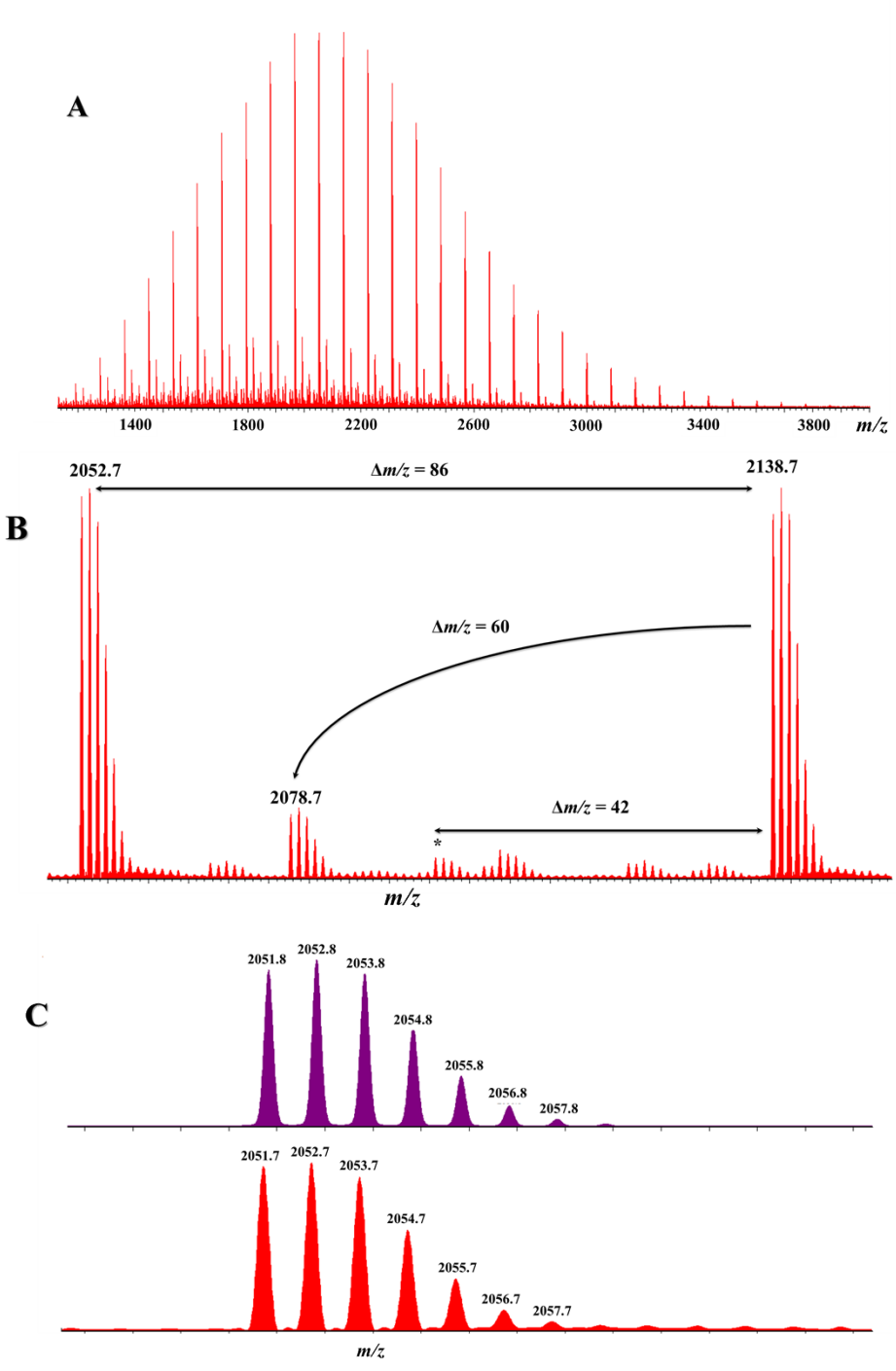
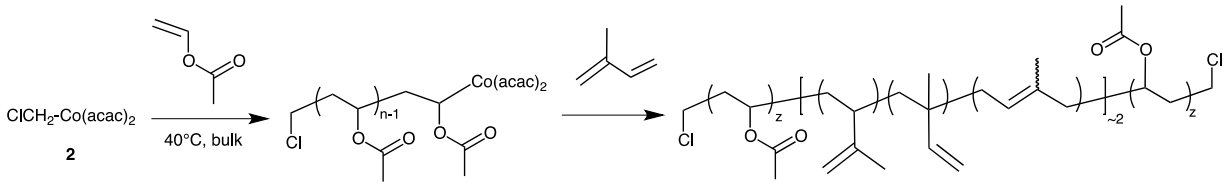


Figure S20. (A) Global MALDI mass spectrum recorded for PVAc synthesized with compound **2**, (B) magnification of the mass spectrum between *m/z* 2048 and *m/z* 2150, and (C) comparison between the theoretical (purple) and experimental isotopic distributions (red) for sodium cationized oligomer with 23 monomer units.

Mass spectrum of PVAc synthesized with compound **2** is reported in Figure S20. The global mass spectrum (Figure S20A), centered around *m/z* 2100, attests the low dispersity of the polymer distribution ($M_{n\ MALDI}$ = 2110 g/mol, Đ = 1.04), in agreement with NMR and SEC data. The magnification between *m/z* 2048 and *m/z* 2150 presented in Figure S20B confirms the high control on the end-groups. Indeed, the only other signals observed between two consecutive oligomer ions are (i) due to K^+ instead Na^+ as cationization agent, (ii) fragmentation induced in the source (peaks at *m/z* 2077 to 2082) involving a McLafferty rearrangement leading to the loss of acetic acid (60 u) and (iii) the isotopic distribution marked with * is explained by an hydrolysis of one acetate moiety on the polymer chain. Finally, Figure S20C represents the comparison between the experiment data and the theoretical isotopic distribution for oligomer ions constituted by 23 monomer units, Cl-CH_2 and H as end-chain and cationized by sodium.

Synthesis of telechelic Cl-PVAc-Cl using compound 2.



Scheme S3. Route to the synthesis of telechelic Cl-PVAc-Cl.

The solution of compound **2** in dichloromethane (1 ml, 0.076 M; 0.076 mmol) was introduced under argon in a 30 mL Schlenk tube and evaporated to dryness under reduced pressure at room temperature. Vinyl acetate (VAc; 5 ml; 54.2 mmol) was added under argon and the reaction medium is heated under stirring at 350 rpm at 40 °C using an oil bath. An aliquot was picked out the reaction medium with a syringe after 1.5h of reaction to evaluate the monomer conversion by ^{1}H NMR spectroscopy in $CDCl_3$ (4% conversion) and to determine the macromolecular parameters of Cl-PVAc ($M_{n,SEC}$ = 2400 g/mol; Đ = 1.09). Excess of isoprene (0.05 mL, 0.50 mmol) was then added and the reaction medium is stirred at room temperature for 24h. After elimination of VAc and isoprene under vacuum at room temperature, the telechelic polymer (Cl-PVAc-Cl) was dissolved in 5ml MeOH and purified by dialysis (cut-off = 1000 Da) in MeOH. The molar mass of the polymer determined by SEC using PS as calibration is 4400 g/mol and dispersity is 1.08.

The polymer was analyzed by MALDI-ToF analysis (Figure S21) and ^{1}H NMR spectroscopy (Figure S22).

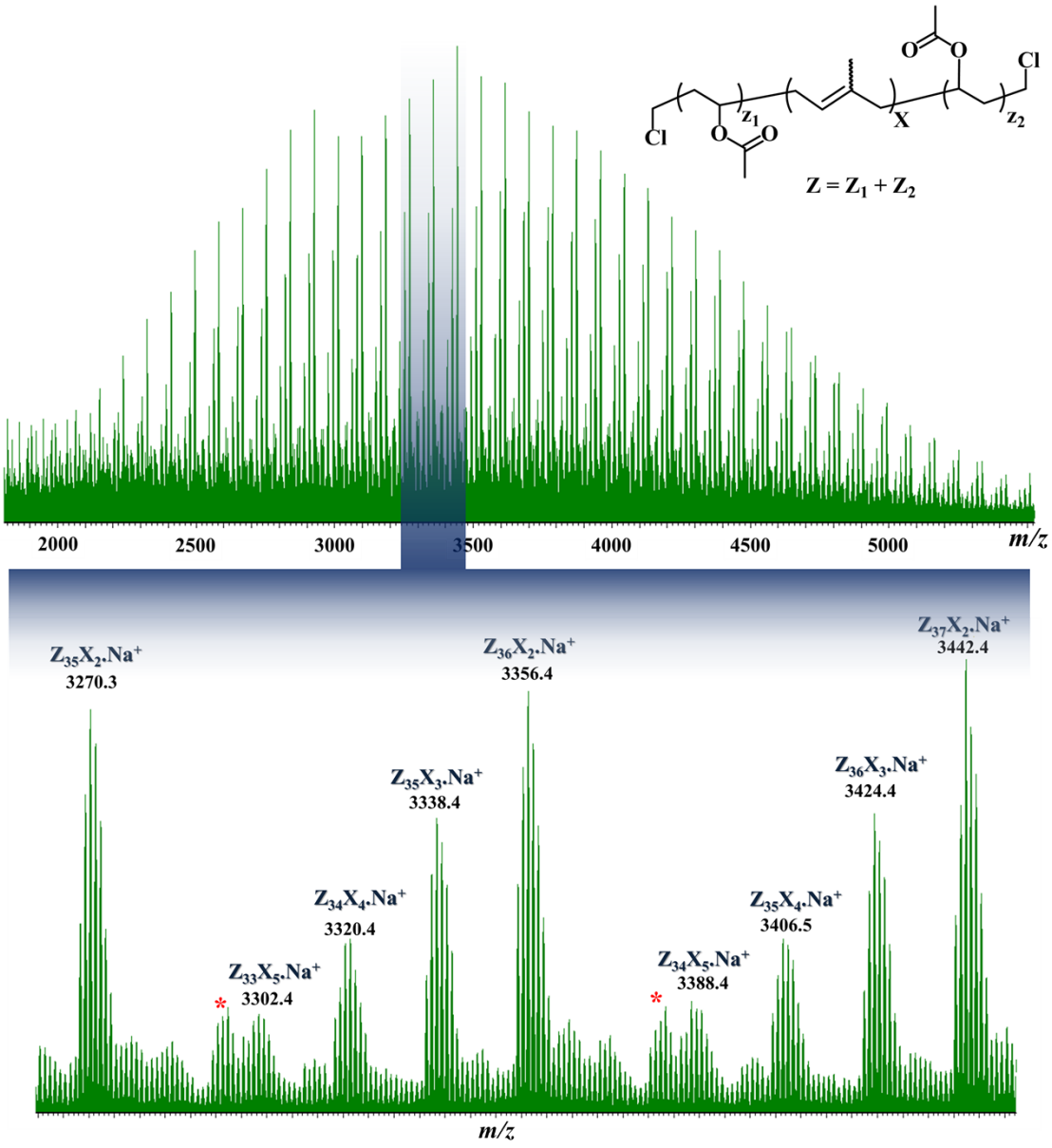


Figure S21. MALDI mass spectrum recorded for Cl-PVAc-Cl: the distribution is centered around *m/z* 3500.Into the enlarged region (*m/z* 3260 – 3450), the mass of the most abundant isotope of each oligomer ions are reported. Moreover, the composition in terms of VAc monomer units (Z) and isoprene units (X) are given. All those polymer ions are characterized by the expected chloromethyl end-groups and cationized with sodium. As expected, based on the reported CMRC mechanism, at least 2 isoprene units are incorporated at the middle of the polymer chain.[9] The * marks correspond to a fragment, loss of 60 mass units.

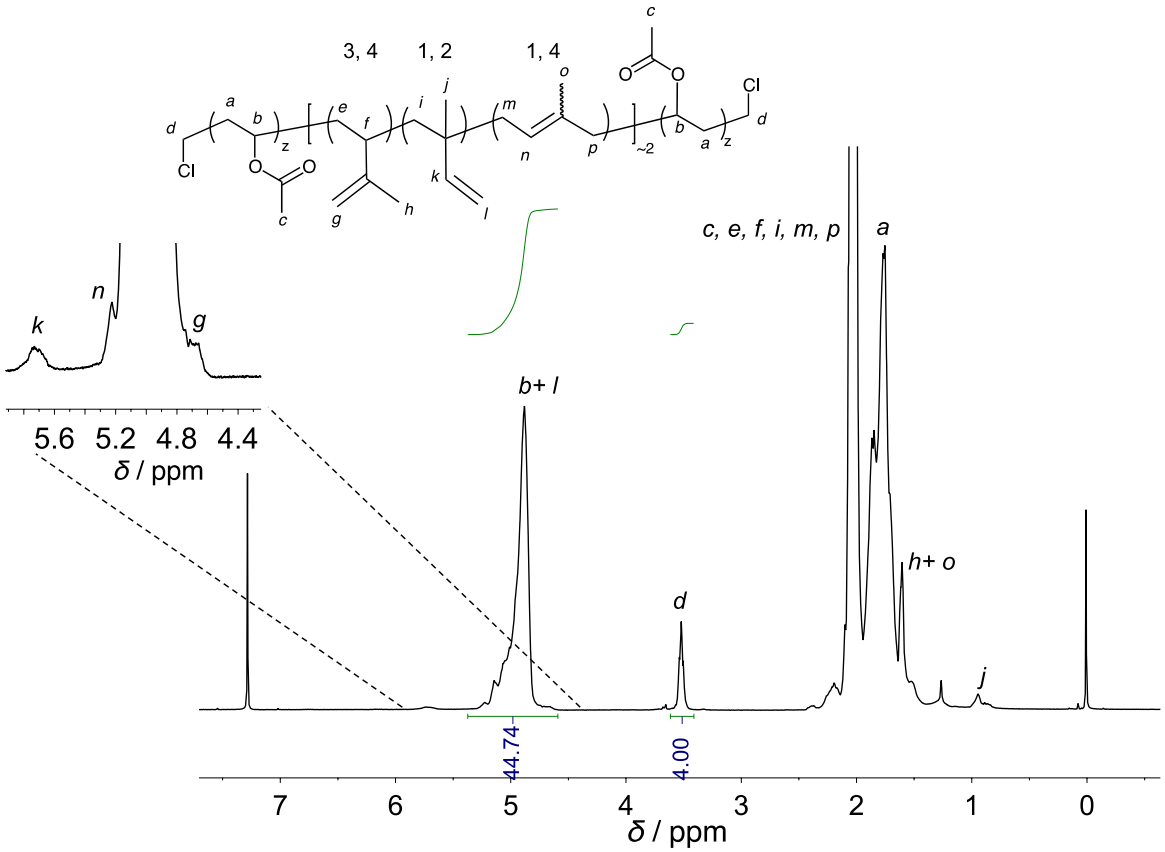


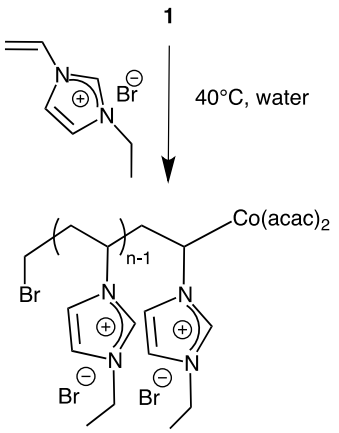
Figure S22. ^{1}H NMR analysis (in $CDCl_3$) of Cl-PVAc-Cl.

Polymerization of 1-vinyl-3-ethylimidazolium bromide initiated by compound 1, general protocol.

[VEtImBr]/[1] = 50. 1-Vinyl-3-ethyl imidazolium bromide (VEtImBr ; 1.53 g, 7.5 mmol) is introduced in a schlenk tube and degassed by three vacuum/argon cycles. Degassed deionized water (6.5 ml) is added to the monomer under argon and the mixture is stirred (500 rpm) until the monomer is completely solubilized. A solution of **1** in CH_2Cl_2 (2.67 mL, 0.056 M, 0.15 mmol) is introduced under argon into a second schlenk tube and CH_2Cl_2 is evaporated under vacuum. Degassed deionized water (1 ml) is then added to solubilize **1** and the solution of the monomer is transferred by cannula into the schlenk containing the solution of **1** under stirring. The polymerization occurs at 40°C under stirring and samples were regularly withdrawn to evaluate the monomer conversion by ^{1}H-NMR in D_2O and the molecular parameters of the polymer by SEC in THF/$LiNTf_2$ after anion-exchange (Br^-/NTf_2^-). Prior to analyses by SEC, TEMPO solubilized in few drops of methanol was added into the vials in order to quench the reaction. The anion exchange procedure is described above in the description of the SEC technique. Results are collected in Figure S23 and S24.

[VEtImBr]/[1] = 100. The same experimental protocol as above is used, by adjusting the amount of **1** added to initiate the polymerization. Results are collected in Figure S23 and S24.

a)



b)

Entry	[VEtImBr]/[**1**]	time (h)	conv. (%)[a]	$M_{n,SEC}$[b] (g/mol)	Đ[b]
1	50/1	0.17	10	3800	1.19
		0.33	31	4700	1.24
		1	59	5600	1.28
		4	87	6400	1.35
2	100/1	0.17	16	4800	1.24
		0.33	33	6100	1.32
		2	60	6500	1.44
		3	67	7800	1.48

Fig. S23. Polymerization of VEtImBr initiated by **1** in water (water:VEtImBr, 5:1 v/w) at 40°C a) reaction scheme and polymer structure, b) polymerization conditions and experimental results. [a]VEtImBr conversion determined by ^{1}H NMR in D_2O. [b]determined after anion exchange (Br^-/NTf_2^-) by SEC analysis in THF + $LiNTf_2$ (PS calibration) following the procedure described in [2,10].

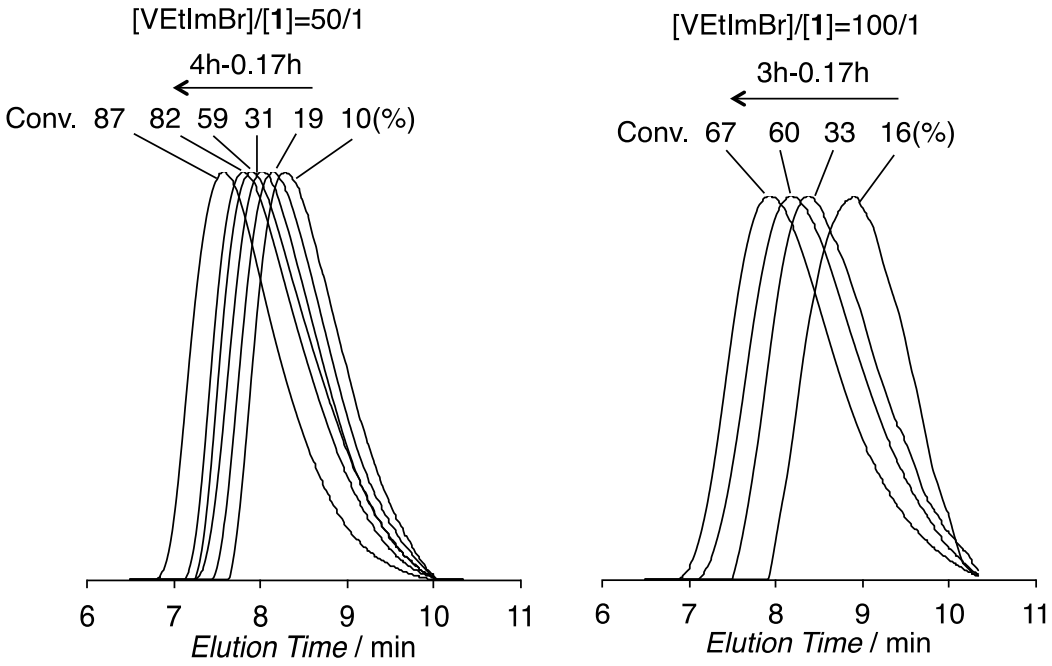
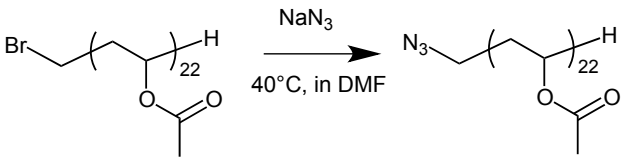


Figure S24. SEC traces for the polymerization of VEtImBr initiated by **1** in water at 40°C using VEtImBr]/[**1**]= 50/1 (left) and [VEtImBr]/[**1**]=100 (right). Conditions: water/VEtImBr, 5:1 (v:w)

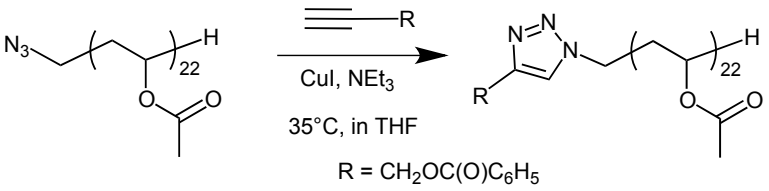
Formation of α-azido poly(vinyl acetate) (N_3-PVAc).



Scheme S4. Synthesis of N_3-PVAc, starting from Br-PVAc

Br-PVAc (200 mg, 9.5 10^{-2} mmol, $M_{n\ SEC}$ = 2100 g/mol, Đ = 1.11) was dissolved in 3ml of DMF in a glass flask, followed by the addition of NaN_3 (8 mg, 0.12 mmol,). The mixture was stirred at 40°C overnight. After elimination of DMF under vacuum, 5 ml of THF was added, and the insoluble salt was removed by centrifugation (10000 rpm at 25°C for 15 min). The copolymer was recovered by filtration of salts and solvent evaporation in vacuum at 60°C and analyzed by MALDI-TOF (Figure S25) and by ^{1}H NMR (Figure S26) in $CDCl_3$.

CuAAc reaction of N_3-PVAc with propargyl benzoate.



Scheme S5. Synthesis of TAz-PVAc, starting from N_3-PVAc

N_3-PVAc (160 mg, 7.6 10^{-2} mmol, 1 eq.) was solubilized in THF (3mL) in a glass flask. Propargyl benzoate (15 µL, 0.1 mmol, 1.3 eq.), CuI (5mg, 2.6 10^{-2} mmol, 0.3 eq.) and NEt_3 (5 µL, 3.6 10^{-2} mmol, 0.5 eq.) were then added to the flask. The mixture was stirred at 35°C overnight. After elimination of THF under vacuum, the solution was filtrated to remove insoluble salts. The polymer was solubilized in 5 ml of MeOH and after a second filtration, the solution was dialyzed in MeOH during 1 day (membrane cut-off: 1000 Da). The copolymer was dried in vacuum at 60°C and analyzed by MALDI-TOF (Figure S25) and by ^{1}H NMR (Figure S26) in $CDCl_3$.

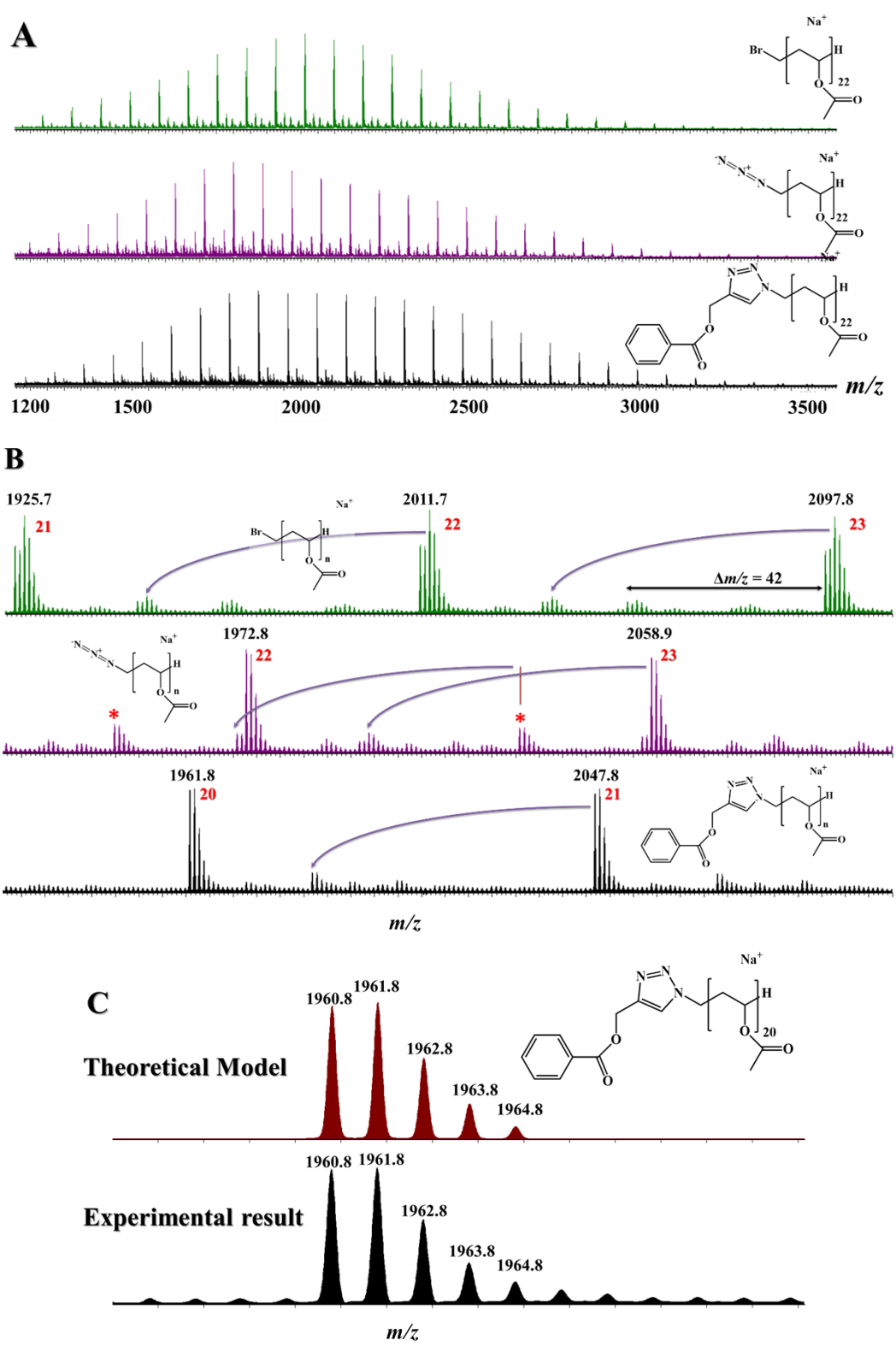


Figure S25. (A) global mass spectrum recorded for Br-PVAc (green), N_3-PVAc (purple) and TAz-PVAc (black), (B) magnification of mass spectra between *m/z* 1920 and *m/z* 2110. Red number indicates the number of monomer units for each oligomer ions, purple arrow corresponds to loss of 60 mass units (u, acetic acid) occurring during the desorption/ionization processes and * is attributed to 28 u loss (N2). The loss of nitrogen is a characteristic fragmentation confirming

the presence of the azide moiety[11] and (C) comparison between the experimental data and theoretical isotopic distribution for TAz-PVAc oligomer ions with 20 monomer units.

By comparing green (Br-PVAc) and purple (N_3-PVAc) spectra, the complete disappearance of polymers ions with bromine confirms the completeness of the reaction, thus the substitution of the halide by azide (Fig. 5 in the main manuscript). Moreover, a signal at 28 u lower (*, Figure S24 purple spectrum) is characteristic of the presence of azide moiety. Based on the MS analysis, the conversion of Br-PVAc to N_3-PVAc can be considered as quantitative. Black mass spectrum (TAz-PVAc) confirms the structure of PVAc bearing the cycloadduct (substituted triazole) at the chain-end. Indeed, as presented in Figure S25C, the perfect matching between the theoretical isotopic model (brown) and the experimental one (black) confirms the efficiency of the click reaction.

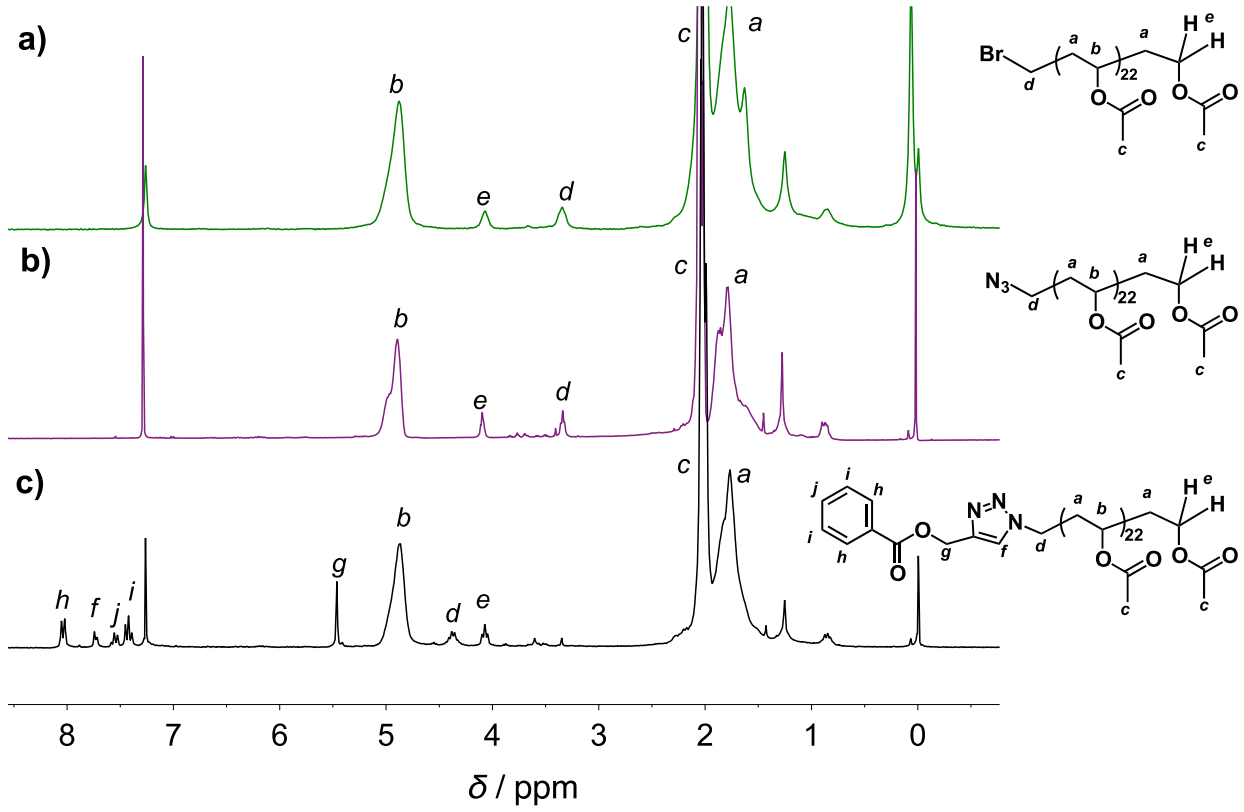


Figure S26. ^{1}H NMR analyses ($CDCl_3$) of (a) Br-PVAc, (b) N_3-PVAc and (c) TAz-PVAc.

Acknowledgments:

The authors thank the ITN Marie-Curie "Renaissance", FRS-FNRS (FRIA and MIS programs) and IAP (P7/05-Functional Supramolecular Systems) for fundings, and G. Cartigny, C. Dannemark, P. de Tullio, C. Damblon and M. Hans for skillful assistance.

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