Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Experimental procedures

General. Unless otherwise stated, manipulations were conducted under an inert gas (argon) atmosphere using Schlenk-line techniques. Bis(acetylacetonate)cobalt(II), $Co(acac)_2$ (97%, Sigma Aldrich), benzoyl peroxide (Luperox A70S, 70% in water, Sigma Aldrich), *tert*-butyl peroxide (Luperox DI, 99%, Sigma Aldrich), TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, Apollo Scientific), C_6D_6, CD_2Cl_2 and $CDCl_3$ (99.8% D, Eurisotop) were used as received. Benzoyl peroxide (BPO) was purchased from Sigma-Aldrich and recrystallized from acetone/ethanol at -80°C. After filtration and wash (3 times with cold ethanol), the white solid was dried under vacuum. Vinyl acetate (Sigma-Aldrich) was dried on CaH_2 overnight, distilled under static vacuum and stored under Argon. Reagent grade (99.5%) acetone, ethanol, pentane and diethylether were purchased from Sigma-Aldrich and tetrahydrofuran (≥99.9%) was purchased from Carlo Erba. All solvents were purified by standard methods and distilled under argon prior to use except toluene, which was degassed and stored on 4A molecular sieves (Fluka).

Characterisations. All NMR spectra were recorded on a Bruker Avance III 300 or 400 MHz spectrometer at ambient temperature. ^1H and ^{13}C chemical shifts (δ) are reported in ppm *vs.* $SiMe_4$ and were determined by reference to the residual ^1H solvent peaks. The GC-MS investigation were carried out with a Shimadzu QP2010 Ultra equipped with a Phenomenex ZB-5MSplus column (0.25µm x 0.25mm x 30m). The elemental analyses were carried out by the analytical service of the LCC-Toulouse by using a PerkinElmer 2400 CHNS/O Series II System. The UV-Vis spectra were recorded on a Perkin Elmer Lambda 950 double beam spectrophotometer equipped with tungsten and deuterium sources and a photodiode detector. Cyclic voltammetry (CV) and square-wave voltammetry (SQW) experiments were carried out with an Autolab PGSTAT100 potentiostat (Metrohm) controlled by GPES 4.09 software. Experiments were performed at room temperature in a homemade air-tight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca 1 cm² apparent surface. The working electrode was a platinum microdisk (0.5 mm diameter). The supporting electrolyte [*n*-Bu_4N][PF_6] (Sigma-Aldrich, 99 % electrochemical grade) was dried and degassed under argon. CH_2Cl_2 was freshly purified on an Innovative PURESOLV system equipped with 4Å MS columns prior to use. The solutions used during the electrochemical studies were typically 10^{-3} M in analyte and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). All electrochemical data are referenced versus ferrocenium/ferrocene (FcH^+/FcH) couple by adding ferrocene (10^{-3} M) at the end of the experiments. The measured potential of the FcH^+/FcH couple under the above experimental conditions was 0.386 V *vs.* ECS. The GPC analyses were carried out at 35 °C with a Shimadzu DGU-$20A_{3R}$ equipped with Shim-pack GPC-801 and -805 columns (each having a length of 300 mm and an inner diameter of 8 mm) and a refractive index detector, using THF as mobile phase at a flow rate of 1 mL min^{-1}, and polystyrene standards (PSS) for calibration. The electrospray mass spectrum (ESI-MS) was measured by the ICT service of Paul Sabatier University Toulouse III on a Q-Tof Premier (Waters) instrument using nitrogen

as drying agent and nebulizing gas. The sample for injection was prepared by mixing a polymer solution in a CH_2Cl_2/CH_3CN solvent mixture with addition of NaI.

Bis(acetylacetonato)benzoatocobalt(III). In a round-bottom flask under argon, $[Co(acac)_2]$ (0.5 g, 1.94 mmol) was dissolved in 30 mL of toluene to yield a purple solution. A separately prepared solution of BPO (0.351g, 1.45 mmol) in 2 mL of toluene was then injected into the complex solution, resulting in an instantaneous colour change to dark green. After overnight stirring at room temperature, the solvent was removed by evaporation under reduce pressure. The resulting crude product was washed with diethyl ether (25 mL) and pentane (2x25 mL), then filtered and dried. Yield 0.44 g (60 %). Elemental analysis: calcd for $C_{17}H_{19}CoO_6$ (378.27 g mol^{-1}): C, 53.98; H, 5.06 %. Found: C, 53.22; H, 4.39 %. ^1H NMR (δ/ppm, 400 MHz, C_6D_6): 8.22 (2H, d, CH ortho), 6.94 (1H, tt, CH para), 6.84 (2H, t, CH meta) aromatic protons, 5.28 (2H, s, 2xCH acetonate), 2.04 (6H, s, 2xCH_3 actetonate) and 1.78 (6H, s, 2xCH_3 actetonate).

Bulk polymerisation of vinyl acetate. Compounds $[Co^{III}(acac)_2(O_2CPh)]$ (128.9 mg, 0.34 mmol) and $[Co^{II}(acac)_2]$ (21.85 mg, 0.08 mmol, 0.25 eq.) were placed in a Schlenk tube. Vinyl acetate was then added and the tube was sealed with a rubber septum. The green mixture was stirred and heated at either 30, 40, 50 or 60 °C in the dark. The monomer conversion was monitored gravimetrically by withdrawing aliquots of the reaction mixture at the desired times. The polymer collected was precipitated by addition of pentane, filtered and dried under vacuum to remove the unreacted monomer. The dried polymer samples were then redissolved in THF (3 to 5 mg mL^{-1}) for the GPC analyses.

X-ray structural analysis. A single crystal was mounted under inert perfluoropolyether on the tip of a glass fiber and cooled in the cryostream of a Rigaku Oxford Diffraction GEMINI EOS diffractometer. The structure was solved by the integrated space-group and crystal-structure determination SHELXt software and refined by least-squares procedures on F^2 using SHELXl. All H atoms attached to carbon were introduced in the calculations at idealized positions and treated with the riding model. The drawing of the molecule was realized with the help of ORTEP32. Crystal data and refinement parameters are shown in Table S1. Selected bond distances and angles are given in Table S2.

Computational details. The computational work was carried out using the Gaussian09 suite of programs.[1] The geometry optimisations were performed without any symmetry constraint using BPW91* functional, which is a reparametrized version of B3PW91 with the same parameters previously optimized for B3LYP.[2] This functional was chosen because it has provided the best results in our previous work on the energetics of Co^{III}-R bond cleavage processes.[3] The 6-311G(d,p) basis functions was employed for all light atoms (H, C, N), whereas the Co atom was treated with the SDD basis set augmented by an f polarisation function (α = 2.780).[4] The effect of dispersion forces was considered by using Grimme's D3 empirical method[5] during the optimisation process. The thermal corrections leading to the Gibbs energy (zero-point vibrational energy or ZPVE, PV, and TS) were obtained from the solution of the nuclear equation using the standard ideal gas and harmonic approximations at T = 298.15 K (25 °C) and 333.15 K (60 °C), which also verified the nature of all optimised geometries as local minima or first-order saddle

points. A correction of 1.95 kcal/mol was applied to all G values to change the standard state from the gas phase (1 atm) to solution (1 M).[6]

Characterization data for compound [$Co^{III}(acac)_2(O_2CPh)$]

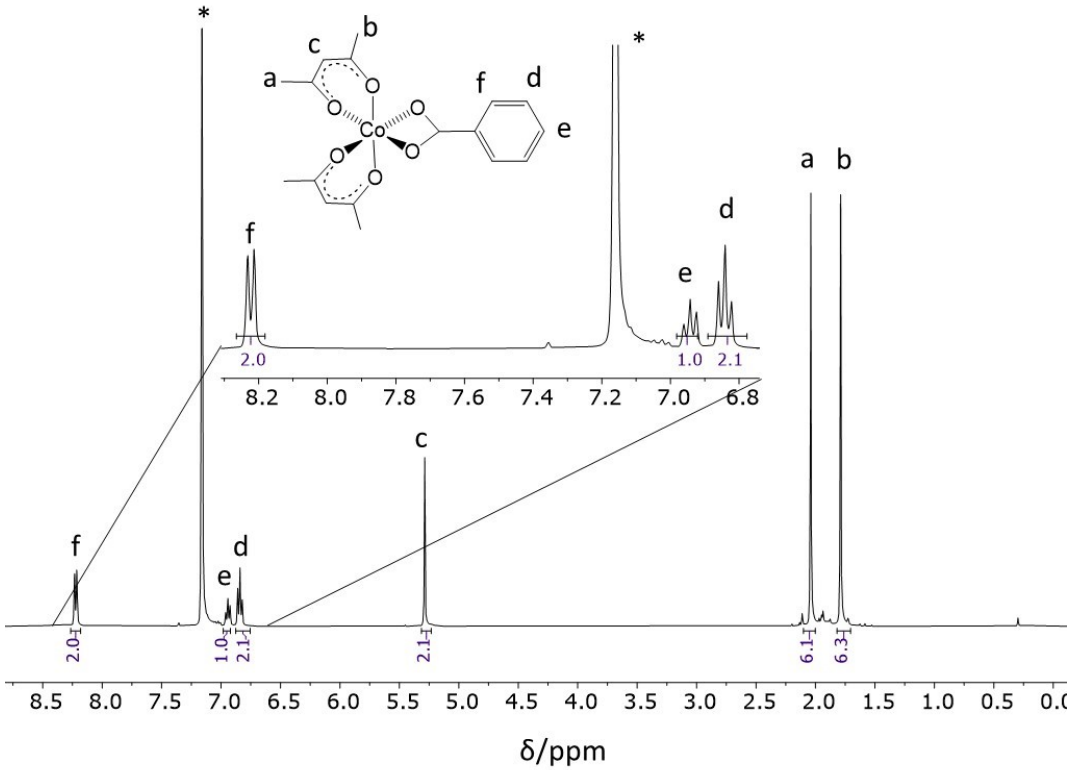


Figure S 1. ^{1}H NMR spectrum of [$Co(acac)_2(O_2CPh)$] in C_6D_6. The starred resonance belongs to the solvent.

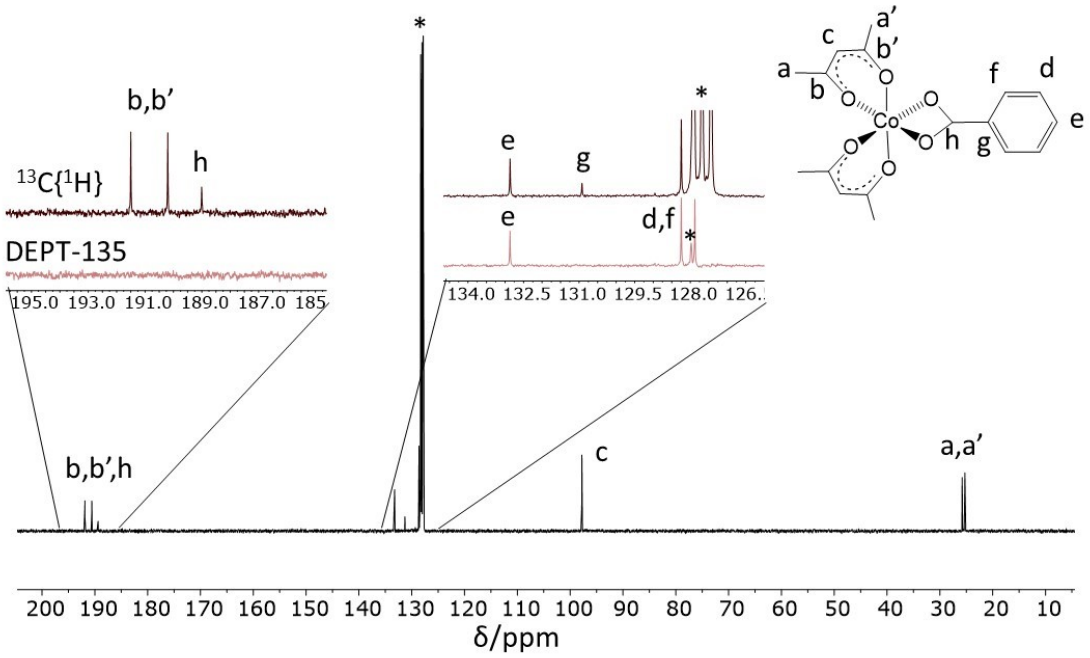


Figure S 2. $^{13}C\{^1H\}$ and DEPT-135 NMR spectra of $[Co(acac)_2(O_2CPh)]$ in C_6D_6. The starred resonances belong to the solvent.

Table S 1. Crystal data and structure refinement parameters for $[Co^{III}(acac)_2(O_2CPh)]$.

CCDC code	**2225026**
Empirical formula	$C_{17}\ H_{19}\ Co\ O_6$
Formula weight	378.25
Temperature. K	130(2)
Wavelength. Å	1.54184
Crystal system	Monoclinic
Space group	C 2/c
Unit cell parameters	
a. Å	10.8167(9)
b. Å	12.0499(11)
c. Å	13.5182(11)
α. °	90.0
β. °	103.533(9)
γ.°	90.0
Volume. $Å^3$	1713.0(3)
Z	4
Density (calc). Mg/m^3	1.467
Abs. coefficient**.** mm^{-1}	8.118
F(000)	784
Crystal size. mm^3	0.220 x 0.100 x 0.030
Diffractometer	Xcalibur. Eos. Gemini ultra
Theta range. °	5.583 à 71.292
Reflections collected	6407
Indpt reflections (R_{int})	1655 (0.1133)
Absorption correction	Multi-scan
Max. / min. transmission	1.0 et 0.4248
Refinement method	Least-squares on F^2
Data /restraints/parameters	1655 / 0 / 114
Goodness-of-fit on F^2	1.827
R1. wR2 [I>2σ(I)]	0.1552. 0.4498
R1. wR2 (all data)	0.2088. 0.5302
$\Delta\rho_{min}/\Delta\rho_{max.}$ e.$Å^{-3}$	1.366 / -2.292

Table S 2. Comparison of selected observed and calculated metric parameters (distances in Å and angles in degrees) for the $[Co^{III}(acac)_2(O_2CPh)]$ structure.

Parameter	X-ray structure	DFT-optimized (singlet)	DFT-optimized (triplet)
Co-O1, Co-O1^i	1.938(10)	1.949, 1.949	1.938, 2.258
Co-O2, Co-O2^i	1.878(11)	1.885, 1.884	1.873, 1.880
Co-O3, Co-O3^i	1.896(11)	1.876, 1.876	1.909, 2.059
O1-C1, O1^i-C1^i	1.286(14)	1.270, 1.270	1.288, 1.246
O2-C21, O2^i-C21^i	1.279(19)	1.268, 1.268	1.274, 1.281
O3-C23, O3^i-C23^i	1.253(18)	1.272, 1.272	1.272, 1.260
C1-C2	1.44(3)	1.492	1.501
C21-C22, C21^i-C22^i	1.35(2)	1.401, 1.401	1.399, 1.393
C22-C23, C22^i-C23^i	1.40(2)	1.397, 1.397	1.399, 1.414
C21-C24, C21^i-C24^i	1.502(18)	1.504, 1.504	1.502, 1.504
C23-C25, C23^i-C25^i	1.52(2)	1.504, 1.504	1.503, 1.508
O1-Co-O1^i	67.2(7)	67.308	62.376
O1-Co-O2, O1^i-Co-O2^i	85.8(4)	87.772, 87.797	87.581, 87.437
O1-Co-O2^i, O1^i-Co-O2	89.6(4)	88.587, 88.513	90.192, 90.236
O1-Co-O3, O1^i-Co-O3^i	167.8(5)	168.433, 168.412	164.042, 170.378
O1-Co-O3^i, O1^i-Co-O3	100.9(5)	101.778, 101.793	101.689, 108.023
O2-Co-O2^i	174.5(6)	175.596	177.337
O2-Co-O3, O2^i-Co-O3^i	97.3(4)	96.037, 96.047	93.298, 92.007
O2-Co-O3^i, O2^i-Co-O3	86.6(4)	87.124, 87.074	89.875, 88.655
O3-Co-O3^i	91.1(7)	89.345	87.900

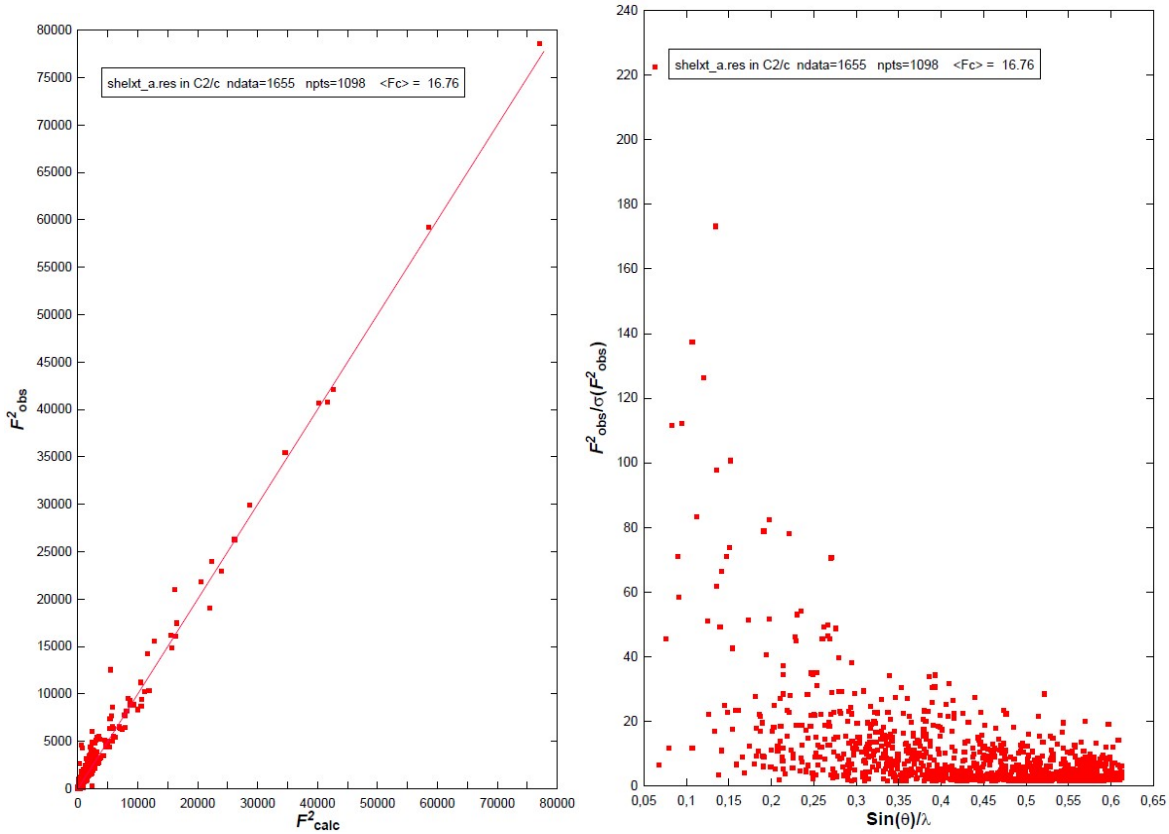


Figure S 3. Plots of F^2_{obs} *vs.* F^2_{calc} (left) and of I/σ *vs.* sin(θ)/λ (right) for the X-ray diffraction study of compound $[Co(acac)_2(O_2CPh)]$.

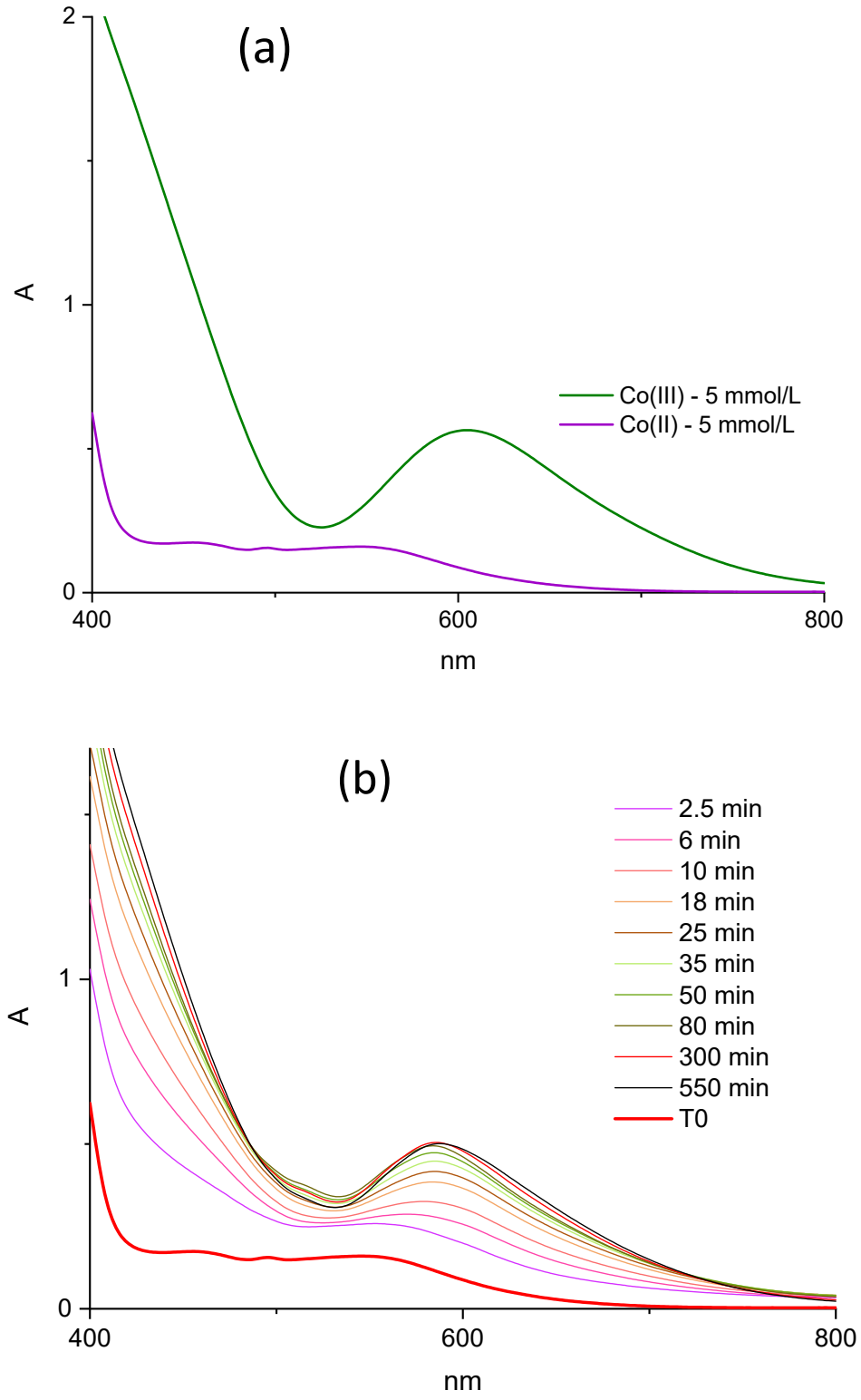


Figure S 4. a) UV/visible spectra of $[Co^{II}(acac)_2]$ and $[Co^{III}(acac)_2(O_2CPh)]$ in toluene solutions ($5 \cdot 10^{-3}$ M). b) UV/visible monitoring of the reaction between $[Co^{II}(acac)_2]$ ($5 \cdot 10^{-3}$ M) and BPO ($3.75 \cdot 10^{-3}$ M) in toluene at room temperature.

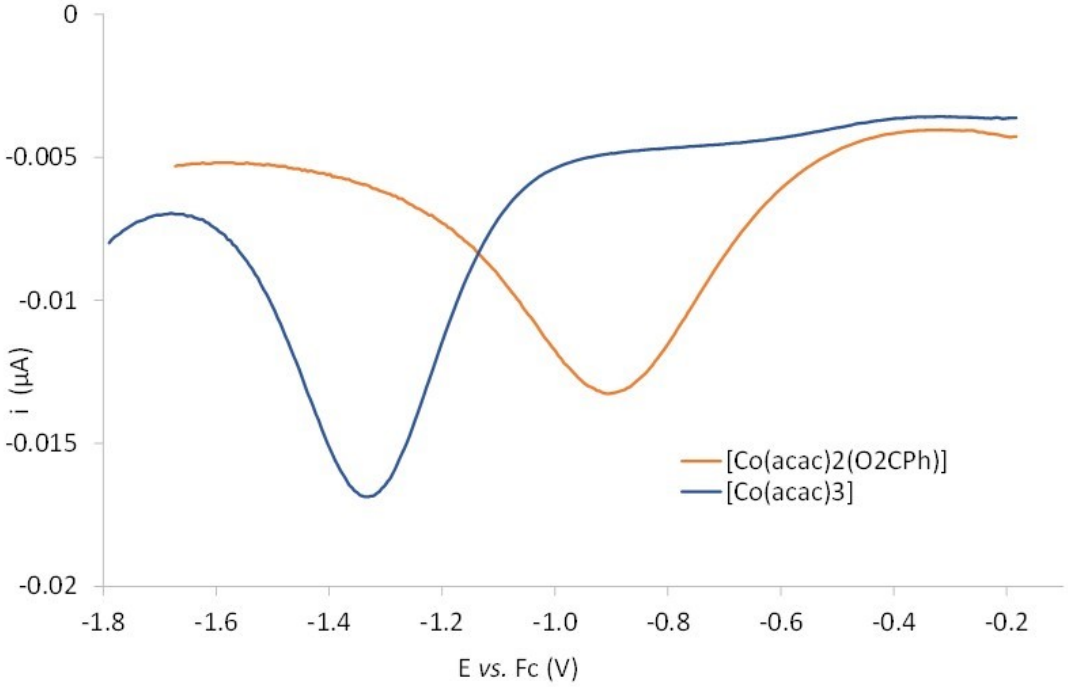


Figure S 5. Square-wave voltammogram of compounds $[Co(acac)_2(O_2CPh)]$ (orange curve) and $[Co(acac)_3]$ (blue curve) in CH_2Cl_2 on a Pt working electrode. [Complex] = 10^{-3} M; supporting electrolyte = nBu$_4$PF$_6$ (0.1 M); v = 100 mV s^{-1}.

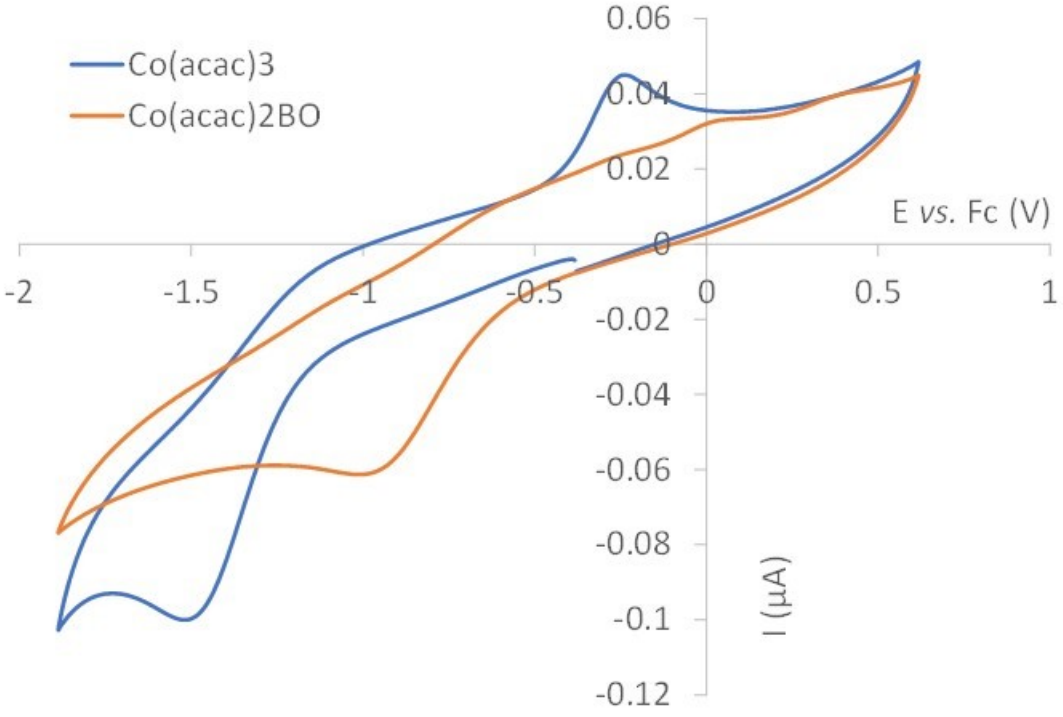


Figure S 6. Cyclic voltammogram of compounds $[Co(acac)_2(O_2CPh)]$ (orange curve) and $[Co(acac)_3]$ (blue curve) in CH_2Cl_2 on a Pt working electrode. [Complex] = 10^{-3} M; supporting electrolyte = nBu$_4$PF$_6$ (0.1 M); v = 200 mV s^{-1}.

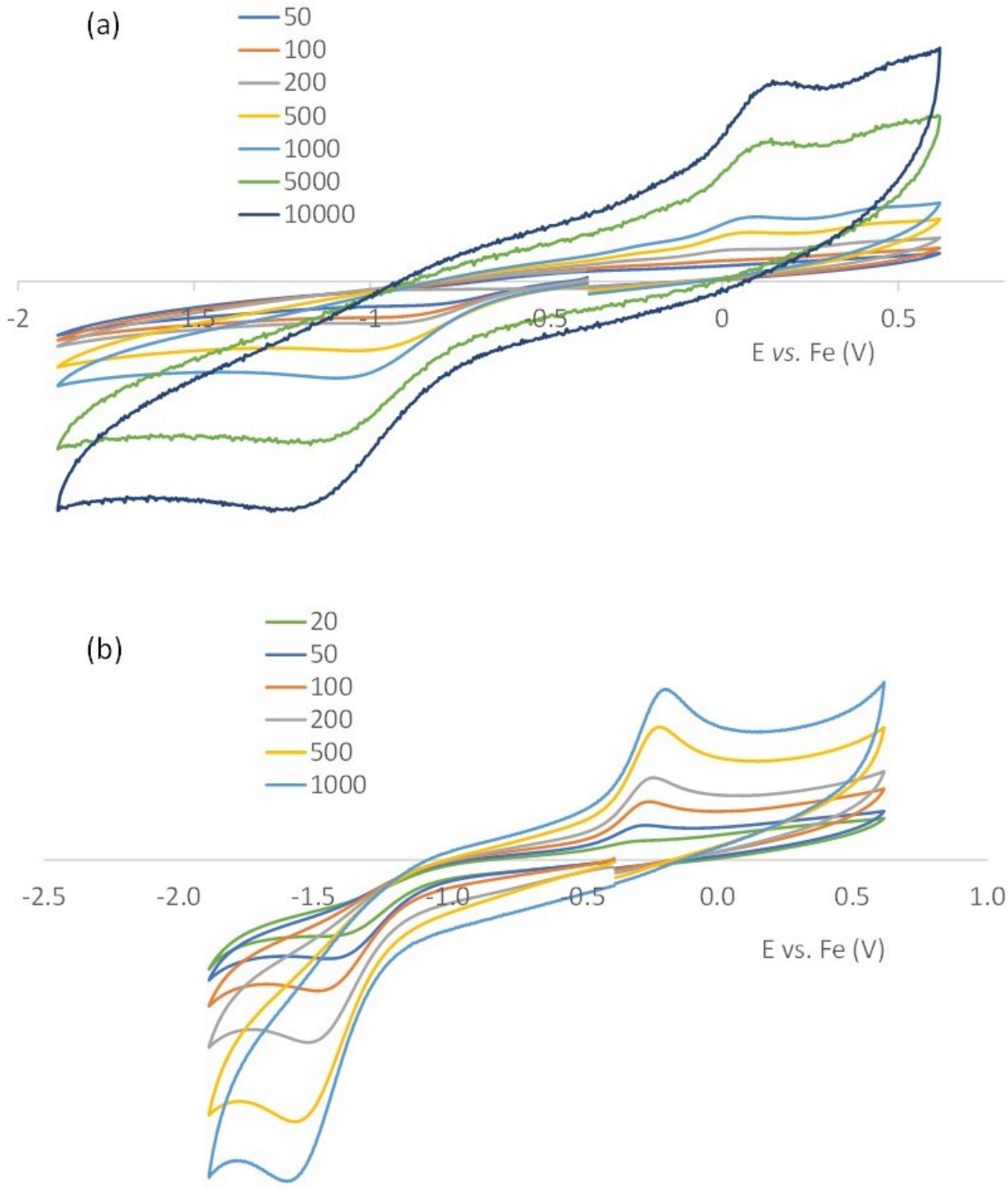


Figure S 7. Cyclic voltammogram of compounds $[Co(acac)_2(O_2CPh)]$ (a) and $[Co(acac)_3]$ (b) in CH_2Cl_2 on a Pt working electrode at various scan rates (values in the legends in mV s^{-1}). [Complex] = 10^{-3} M; supporting electrolyte = nBu$_4$PF$_6$ (0.1 M); v = 200 mV s^{-1}.

Thermal decomposition of $[Co^{III}(acac)_2(O_2CPh)]$

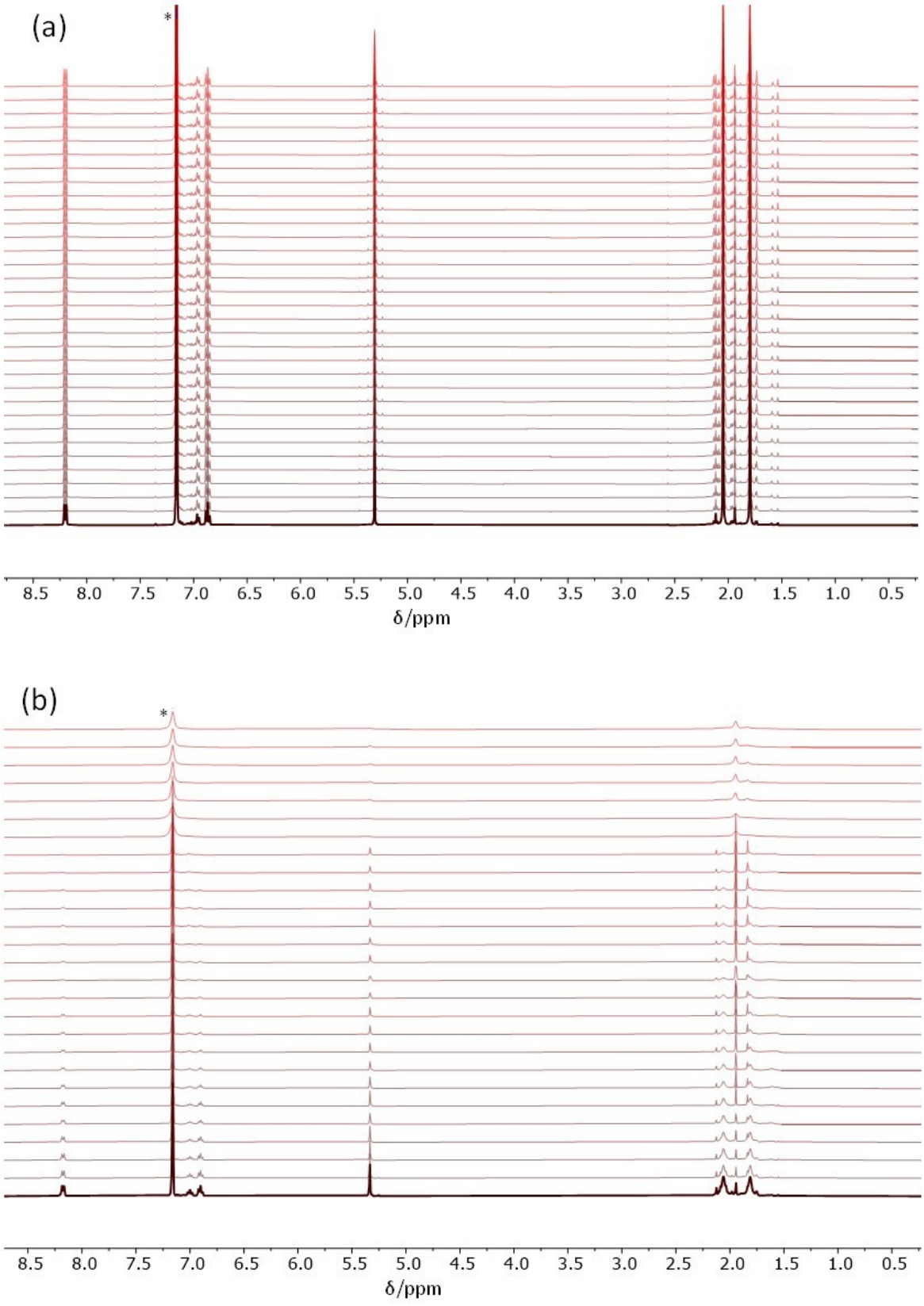


Figure S 8. Time dependence of the acac ^{1}H NMR resonances for $[Co(acac)_2(O_2CPh)]$. (a) At 40°C. (b) At 60°C. Spectra were taken at 30 min intervals, the full monitoring lasting 16 h (a) or 13 h (b). The starred resonance is the residual peak of the C_6D_6 solvent.

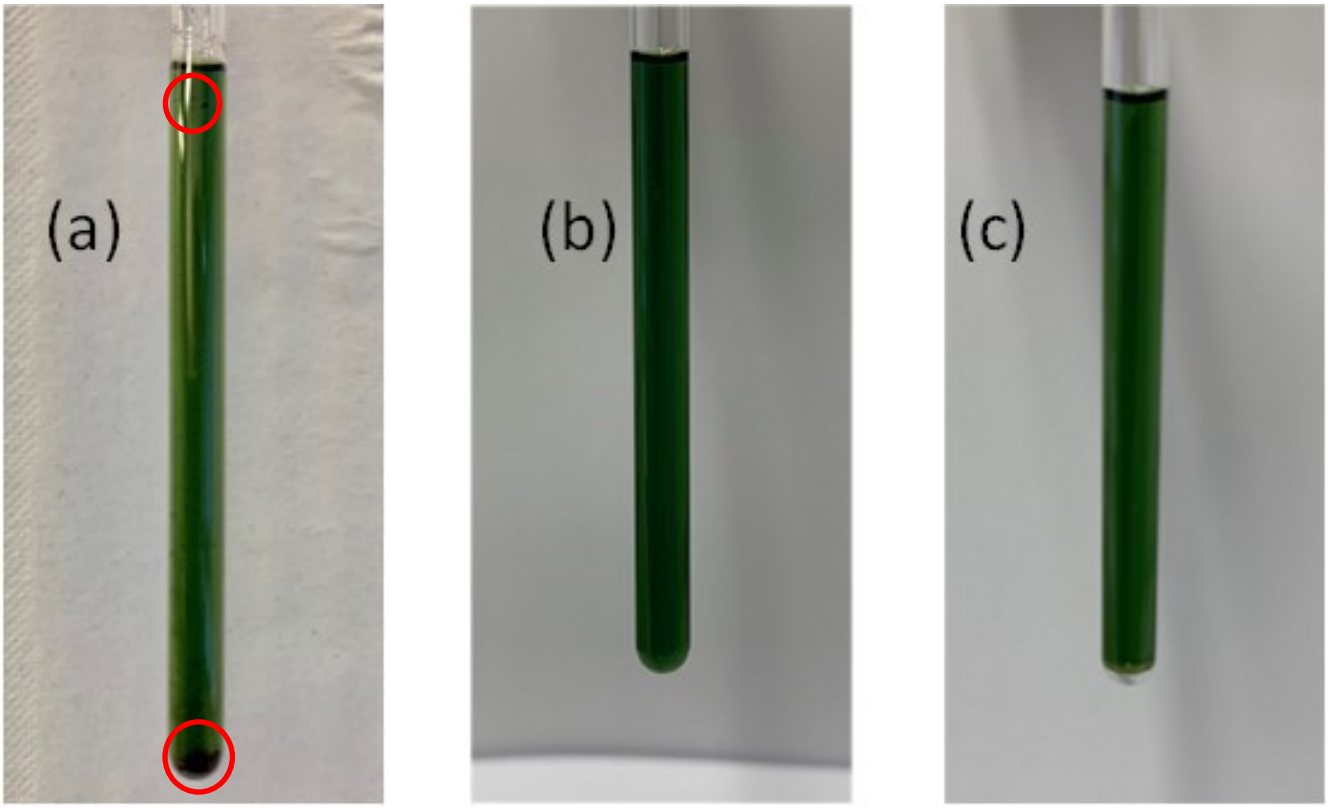


Figure S 9. Photos of $[Co(acac)_2(O_2CPh)]$ solutions in C_6D_6. (a) After 13 h at 60 °C (the red circles highlight deposited pink crystals). (b) After 16 h at 40 °C. (c) After 72 h at room temperature.

Discussion of the GC-MS results of the thermal decomposition of BPO and $[Co^{III}(acac)_2(O_2CPh)]$

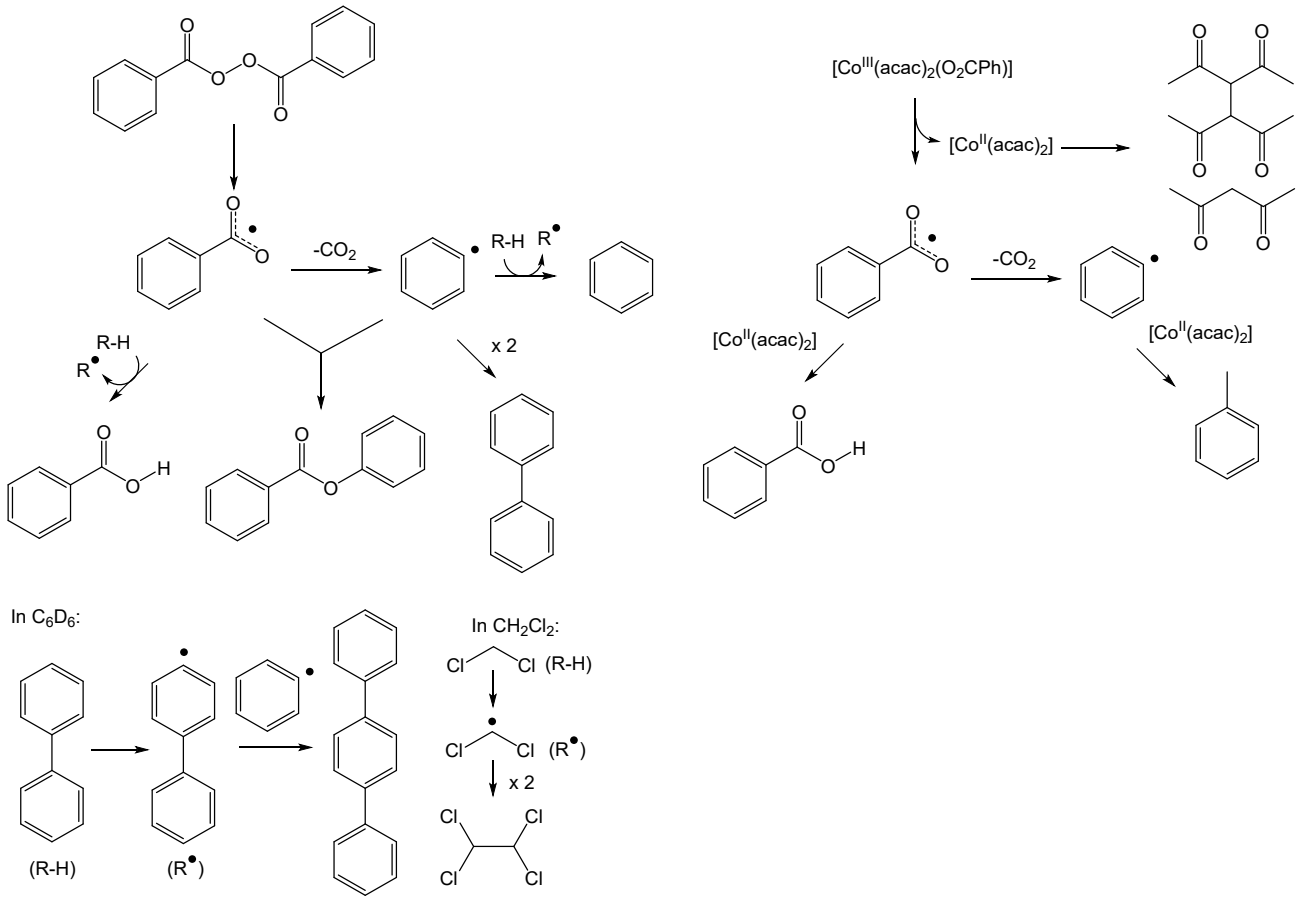
The experiments were conducted by injecting directly a solution of BPO and a solution of the cobalt complex, at room temperature, into the GC/MS instrument, with the injection chamber at 250 °C at the ramp programme set at 50°C (constant for 1 min), then heating 20 °/min until 250 °C (then kept constant for 19 min).

It is useful to first discuss the results of the BPO decomposition. When carried out in C_6D_6 (Figure S9a), the gas chromatogram reveals the formation of PhCOOH, Ph-Ph and PhCOOPh as major peaks. These three compounds are expected from the generation of benzoate ($PhCOO^{\bullet}$) and phenyl ($Ph^{\bullet}$) radicals, the first one by abstraction of an H atom from the medium by $PhCOO^{\bullet}$, the second one by coupling of two $Ph^{\bullet}$ radicals and the last one by coupling of one $PhCOO^{\bullet}$ radical and one $Ph^{\bullet}$ radical (see Scheme S1). Since the solvent (C_6D_6) is not a good source of hydrogen (D) atoms and, at any rate, the m/z of benzoic acid (see Figure S11) fits for PhCOOH and not with PhCOOD, the H atom must be provided by the benzoate or phenyl radicals themselves. Inspection of the lower intensity peaks in the higher retention time region suggests the formation of diphenyl benzene isomers. Higher molecular weight polyaromatics may remain trapped in the column. The mass spectra of a few minor peaks did not match with any of the library compounds.

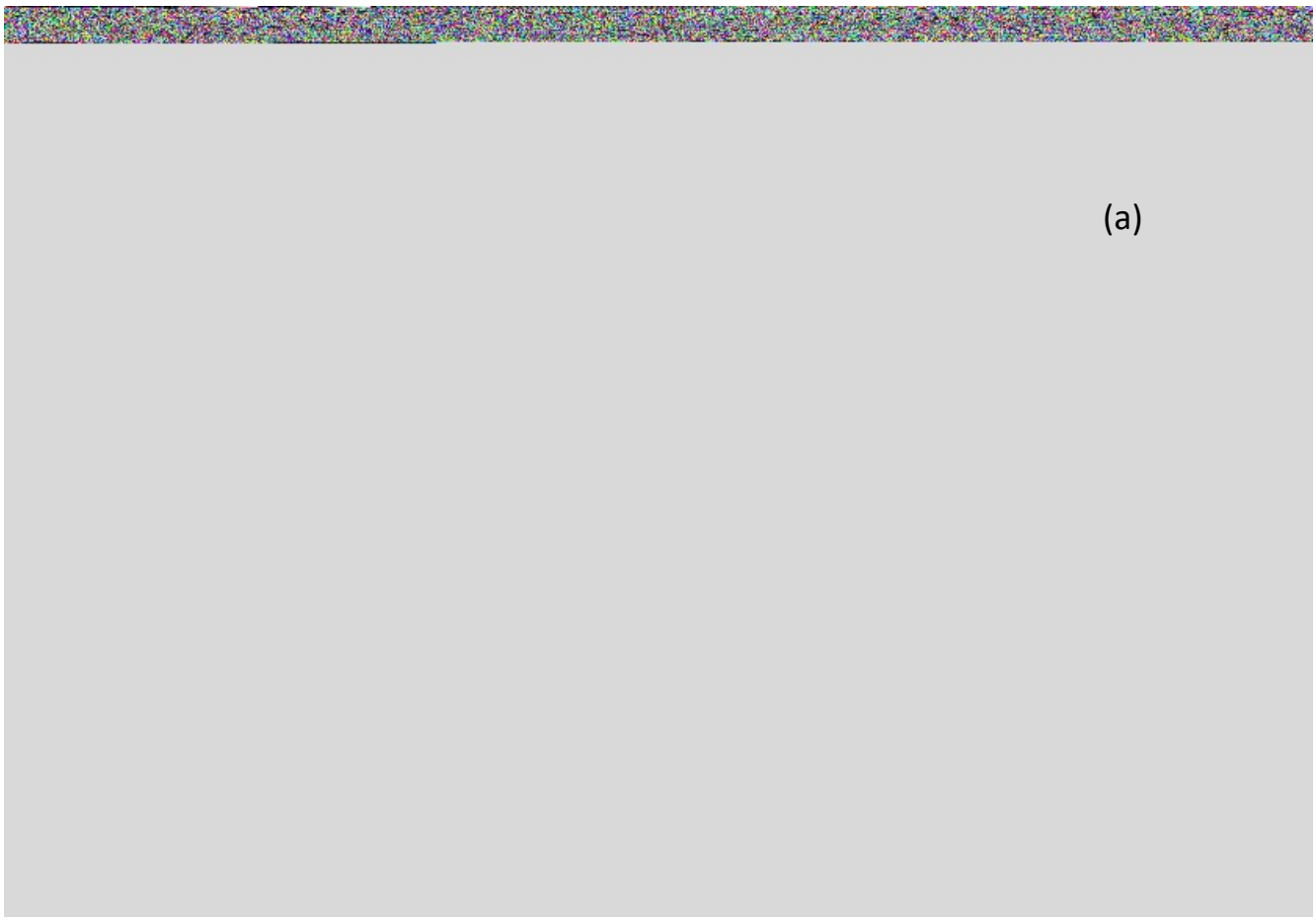
When using dichloromethane as solvent, the same peaks for the BPO decomposition (Figure S10a) are again observed. In addition, peaks matching for benzene and 1,1,2,2-tetrachloroethane are also visible. Their formation can again be rationalized on the basis of the production of phenyl radicals. It is remarkable that, under these conditions, diphenylbenzene isomers by H abstraction from the aryl group are still observed even though CH_2Cl_2 was used in large excess and its C-H bonds are weaker (100.6 kcal mol^{-1})[7] than the aromatic C-H bonds (*e.g.* 113.5 ± 0.5 kcal mol^{-1} for benzene)[8]. This suggests that H abstraction by the benzoate and phenyl radicals mostly occurs after the solvent is fully evaporated, within the radical pair generated by the decomposition of BPO in the gas

phase. However, decomposition must also start to occur prior to full solvent evaporation, otherwise the 1,1,2,2-tetrachloroethane product would not be observed.

The decomposition of the $[Co^{III}(acac)_2(O_2CPh)]$ in C_6D_6 (Figure S9b) reveals again the formation of benzoic acid. In this case, however, the formation of diphenyl and diphenylbenzene isomers is not clearly evident. Conversely, the formation of phenyl radicals is evidenced by the formation of large amounts of toluene. This presumably results from abstraction of a methyl group from an acac ligand within the $\{[Co(acac)_2],Ph^{\bullet}\}$ radical pair. The other major peak in the GC is due to acetylacetone. The corresponding experiment for the dichloromethane solution (Figure S10b) shows the same peaks, and also reveals a peak consistent with the formation of the dimer of acac$^{\bullet}$ radicals. Note that 1,1,2,2-tetrachloroethane is not formed in this experiment. This suggests that the Co^{III} complex is thermally more stable than BPO and its decomposition only occurs after complete solvent evaporation in the GC injection chamber. Note also that benzene is not observed, showing that the phenyl radical abstracts more readily a methyl group than an H atom from the acac ligand within the $\{[Co(acac)_2],Ph^{\bullet}\}$ radical pair.



Scheme S 1. Decomposition mechanism of BPO (left) and $[Co^{III}(acac)_2(O_2CPh)]$ (right) in C_6D_6 and in CH_2Cl_2.



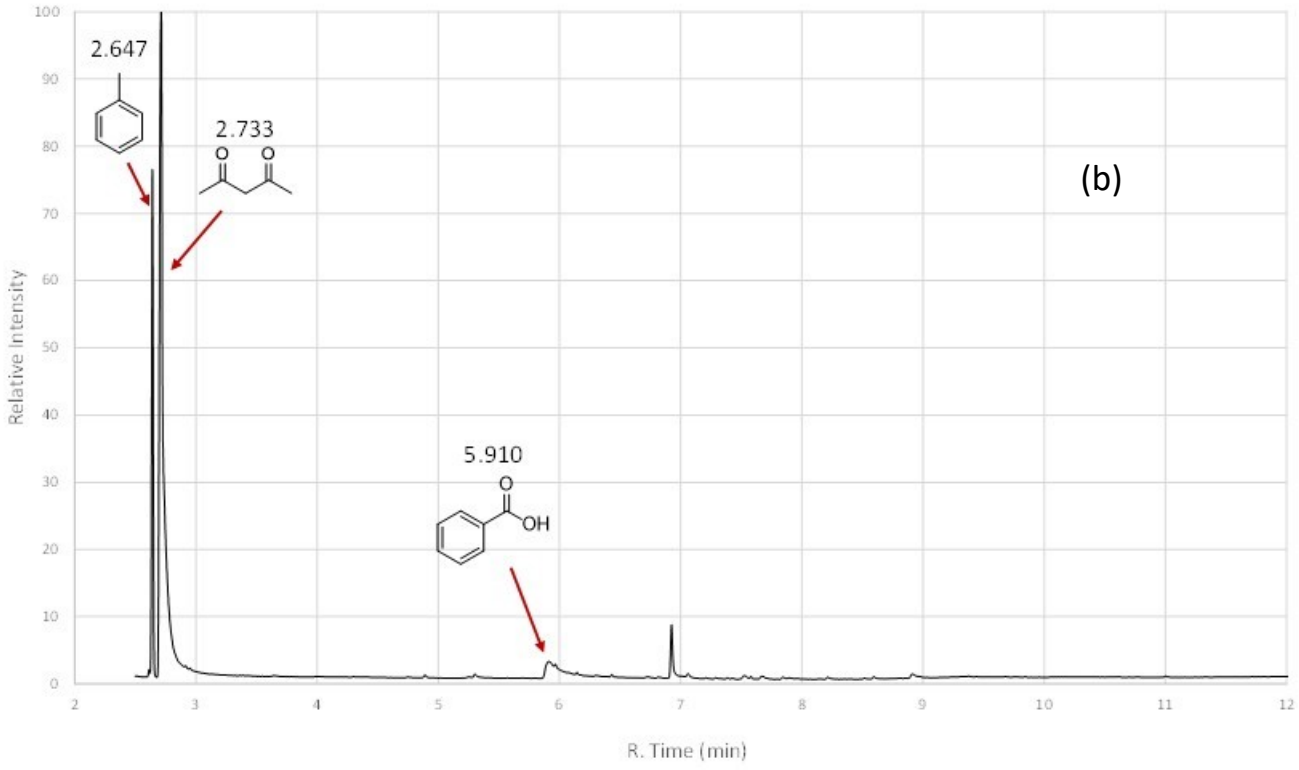


Figure S 10. Comparative GC-MS investigation of the decomposition of (a) BPO and (b) complex $[Co^{III}(acac)_2(O_2CPh)]$ in C_6D_6: GC trace (for the MS characterisation, see Figure S11).

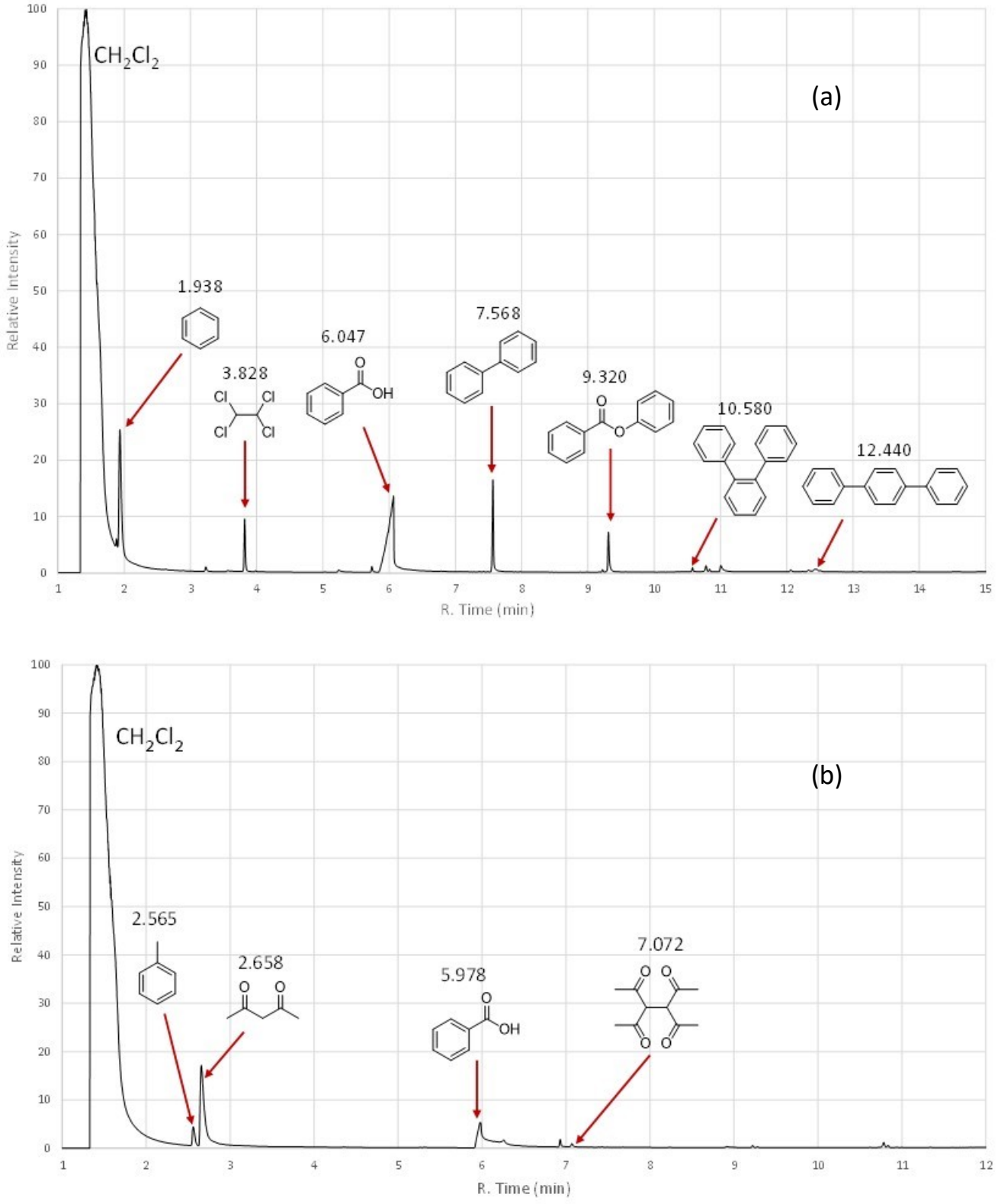


Figure S 11. Comparative GC-MS investigation of the decomposition of (a) BPO and (b) complex $[Co^{III}(acac)_2(O_2CPh)]$ in dichloromethane: GC trace (for the MS characterisation, see Figure S11).

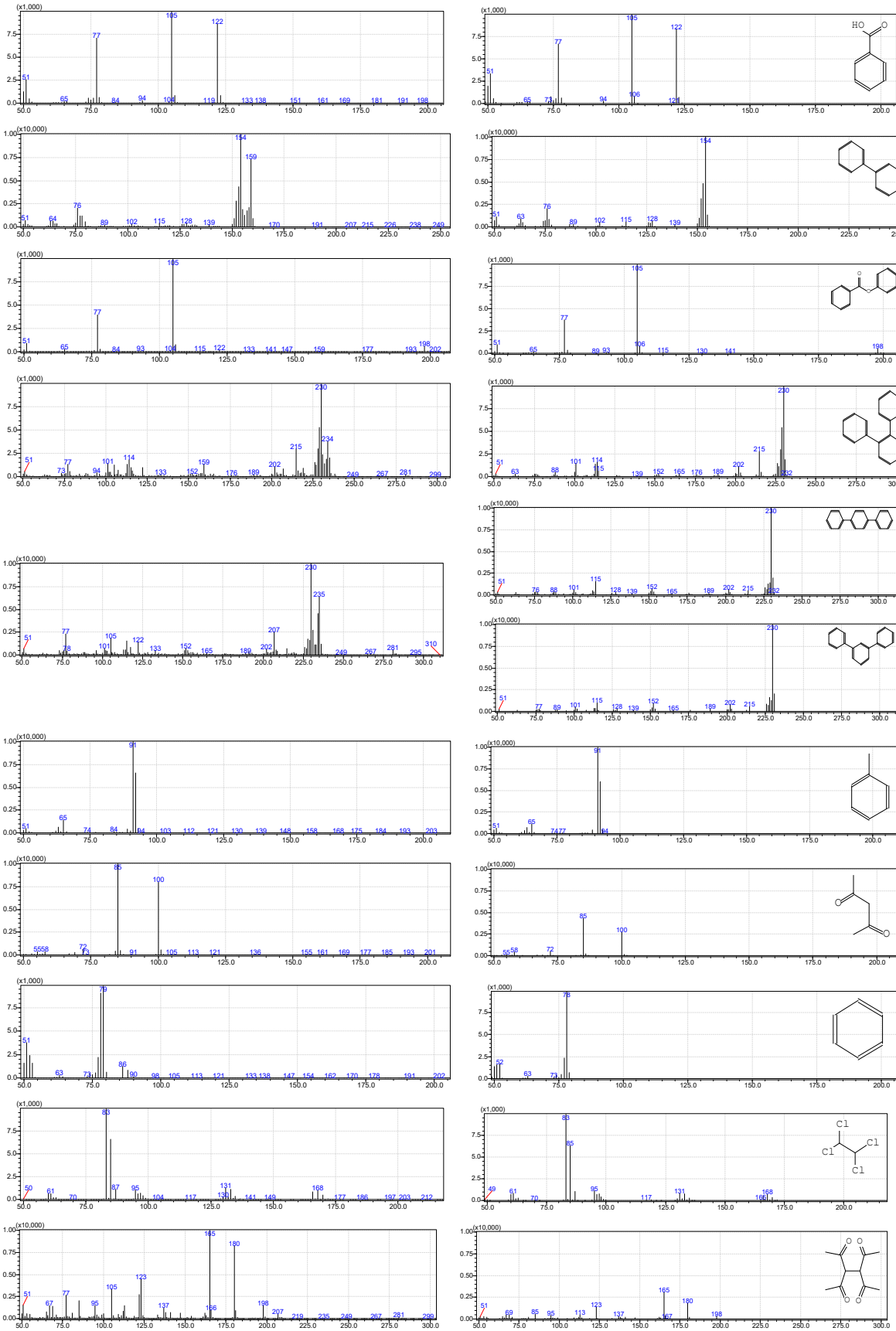


Figure S 12. Comparison of observed (left) and library (right) mass spectra for the compounds indicated in Figure S 10 and Figure S 11.

DFT-Optimized geometries

Table S 3. Energies (in hartrees) and Cartesian coordinates (in Å) of all DFT-optimized geometries.

$[Co^{II}(acac)_2]$

E = -835.887907282
$G_{298.15,1M}$ = -835.709140
$G_{333.15,1M}$ = -835.717073
$<S^2>$ = 3.7592

6	-3.398622000	-1.763206000	1.782945000
6	-2.572237000	-0.878984000	0.888285000
6	-3.214020000	-0.000412000	0.000201000
6	-2.572944000	0.878608000	-0.887893000
6	-3.399985000	1.762480000	-1.782281000
8	-1.310862000	-1.011407000	1.022034000
27	0.000002000	0.000137000	-0.000596000
8	1.311458000	-1.022202000	-1.011469000
6	2.572783000	-0.888151000	-0.878548000
6	3.399674000	-1.782575000	-1.762526000
8	-1.311636000	1.011847000	-1.021855000
8	1.311038000	1.022205000	1.011273000
6	2.572397000	0.888412000	0.878657000
6	3.398932000	1.782800000	1.763011000
6	3.214017000	0.000210000	0.000096000
1	-3.138570000	-1.553402000	2.826197000
1	-4.473302000	-1.628890000	1.642555000
1	-3.133631000	-2.808525000	1.590629000
1	-4.298068000	-0.000739000	0.000299000
1	-3.135429000	2.807914000	-1.590003000
1	-4.474564000	1.627656000	-1.641583000
1	-3.140152000	1.552831000	-2.825619000
1	3.136238000	2.825979000	1.556312000
1	3.136729000	1.587419000	2.808494000
1	4.473593000	1.644794000	1.626092000
1	4.298065000	0.000306000	0.000227000
1	3.137766000	-2.825794000	-1.554997000
1	4.474279000	-1.643761000	-1.625981000
1	3.137030000	-1.588134000	-2.808068000

A. Poly(vinyl acetate) model system

MeCH(OOCMe)•

E = -306.830178726
$G_{298.15,1M}$ = -306.757709
$G_{333.15,1M}$ = -306.762658
$<S^2>$ = 0.7538

6	2.607279000	-0.310789000	0.057466000
6	1.320159000	0.387341000	-0.124903000
8	0.213256000	-0.421188000	-0.048296000
6	-1.024591000	0.162417000	0.009806000
6	-2.089758000	-0.893405000	0.014907000
8	-1.194685000	1.352613000	0.036710000
1	1.152094000	1.449540000	0.011369000
1	3.438289000	0.355641000	-0.191249000
1	2.752483000	-0.654420000	1.096403000
1	2.669660000	-1.199596000	-0.583177000
1	-3.054245000	-0.431697000	0.226224000
1	-2.123785000	-1.379536000	-0.966235000
1	-1.861599000	-1.664712000	0.755688000

$[Co^{III}(acac)_2(\kappa^2$:*C,O*-CH(OOCMe)Me]

E = -1142.76884794
$G_{298.15,1M}$ = -1142.487617
$G_{333.15,1M}$ = -1142.497385

27	0.187561000	0.184321000	-0.022629000
8	-1.145442000	-0.312273000	1.199733000
6	-2.317180000	0.181940000	1.204700000
6	-2.769026000	1.229234000	0.395330000
6	-1.962145000	1.905140000	-0.530850000
8	-0.741689000	1.656217000	-0.766801000
6	-3.250044000	-0.461456000	2.194890000
6	-2.539744000	3.032151000	-1.344401000
1	-3.798928000	1.548191000	0.502779000
1	-2.816588000	-0.388411000	3.197910000
1	-3.335902000	-1.527112000	1.956906000
1	-4.243066000	-0.007176000	2.193594000
1	-2.545867000	2.733533000	-2.398604000
1	-1.890470000	3.909236000	-1.259212000
1	-3.554801000	3.295358000	-1.039202000
8	1.234871000	-1.253741000	0.631333000
6	1.032885000	-2.480131000	0.345959000
6	0.126014000	-2.984692000	-0.585702000
6	-0.678369000	-2.185340000	-1.422731000
8	-0.725313000	-0.927246000	-1.400702000
6	1.909531000	-3.429883000	1.121420000
6	-1.558665000	-2.850746000	-2.452252000
1	0.074051000	-4.060715000	-0.705456000
1	1.728911000	-3.285458000	2.192143000
1	2.959876000	-3.182351000	0.933247000
1	1.732996000	-4.475732000	0.860764000
1	-1.279016000	-2.485824000	-3.446318000
1	-2.596553000	-2.547115000	-2.277785000
1	-1.490295000	-3.941073000	-2.433956000
6	1.018576000	1.381724000	1.230730000
8	2.260173000	1.885752000	0.566679000
6	2.436726000	1.436246000	-0.639602000
8	1.657906000	0.642576000	-1.186314000
6	3.647229000	1.956803000	-1.340704000
1	0.387032000	2.272997000	1.322507000
1	3.812459000	1.394281000	-2.259234000
1	4.516860000	1.889911000	-0.682194000
1	3.489653000	3.013410000	-1.580898000
6	1.405574000	0.822641000	2.568287000
1	1.869278000	1.585493000	3.208170000
1	0.497341000	0.452195000	3.053205000
1	2.086645000	-0.022374000	2.450742000

$[Co^{III}(acac)_2(\kappa^1$:*C*-CH(OOCMe)Me]

E = -1142.76367394
$G_{298.15,1M}$ = -1142.481516
$G_{333.15,1M}$ = -1142.491169

6	-0.048283000	-0.294242000	1.340729000
27	0.472870000	0.072713000	-0.487239000
8	1.679742000	-1.369402000	-0.445583000
6	2.931885000	-1.307979000	-0.227539000
6	3.634997000	-2.636949000	-0.239310000
8	-0.641790000	1.546505000	-0.770610000
6	-1.875860000	1.498882000	-1.071560000
6	-2.592762000	0.329342000	-1.348863000
6	-1.995383000	-0.938617000	-1.378767000
8	-0.772039000	-1.167515000	-1.116699000
6	-2.564876000	2.834618000	-1.103574000
6	-2.810773000	-2.156005000	-1.697970000
8	1.815943000	1.358341000	-0.185846000
6	3.056815000	1.138089000	-0.015683000
6	3.890763000	2.371263000	0.193510000
6	3.653033000	-0.129142000	0.001256000
1	3.701959000	3.075043000	-0.623276000
1	-2.582693000	3.240704000	-0.085425000
1	-1.981356000	3.528386000	-1.716374000
1	4.959312000	2.153082000	0.251575000
1	-3.585937000	2.773883000	-1.487034000

1	3.570399000	2.860227000	1.120491000
1	4.721315000	-0.198749000	0.168515000
1	-3.646051000	0.409450000	-1.591513000
1	3.473739000	-3.117239000	-1.210222000
1	-3.769067000	-1.909918000	-2.161174000
1	4.707036000	-2.547862000	-0.050831000
1	-2.237213000	-2.821758000	-2.348377000
1	3.182825000	-3.285657000	0.518398000
1	-2.989117000	-2.681212000	-0.752175000
1	-0.113506000	-1.385506000	1.351923000
6	0.932771000	0.282008000	2.322710000
8	-1.325862000	0.264335000	1.616216000
6	-2.406573000	-0.549884000	1.686422000
8	-2.374254000	-1.746399000	1.541801000
1	0.639243000	-0.005806000	3.341609000
1	1.936972000	-0.103436000	2.129753000
1	0.952911000	1.372082000	2.254888000
6	-3.635272000	0.258742000	1.994264000
1	-3.806806000	0.974286000	1.185559000
1	-4.492620000	-0.407021000	2.093454000
1	-3.485650000	0.826079000	2.917713000

B. Benzoate system

PhCOO-OOCPh (BPO)

E = -839.728939324
$G_{298.15,1M}$ = -839.563456
$G_{333.15,1M}$ = -839.570803

6	-0.008312000	2.947082000	0.000031000
6	1.381121000	3.115048000	-0.000192000
6	-0.851498000	4.061882000	0.000191000
6	1.916197000	4.397742000	-0.000256000
6	-0.308777000	5.339965000	0.000124000
6	1.074762000	5.508662000	-0.000102000
1	2.032579000	2.247144000	-0.000298000
1	-1.925617000	3.902610000	0.000369000
1	2.994360000	4.530979000	-0.000423000
1	-0.964283000	6.206329000	0.000248000
1	1.499016000	6.509323000	-0.000152000
6	-0.664618000	1.613892000	0.000112000
8	-1.842242000	1.394168000	0.000318000
8	0.308777000	0.642220000	-0.000217000
6	0.008312000	-2.947082000	0.000031000
6	-1.381121000	-3.115048000	-0.000192000
6	0.851498000	-4.061882000	0.000191000
6	-1.916197000	-4.397742000	-0.000256000
6	0.308777000	-5.339965000	0.000124000
6	-1.074762000	-5.508662000	-0.000102000
1	-2.032579000	-2.247144000	-0.000298000
1	1.925617000	-3.902610000	0.000369000
1	-2.994360000	-4.530979000	-0.000423000
1	0.964283000	-6.206329000	0.000248000
1	-1.499016000	-6.509323000	-0.000152000
6	0.664618000	-1.613892000	0.000112000
8	1.842242000	-1.394168000	0.000318000
8	-0.308777000	-0.642220000	-0.000217000

PhCOO•

E = -419.843401538
$G_{298.15,1M}$ = -419.772071
$G_{333.15,1M}$ = -419.776959
$\langle S^2 \rangle$ = 0.7554

6	-0.246432000	0.000205000	0.000426000
6	0.444843000	1.213579000	0.000377000
6	0.444463000	-1.213421000	0.000445000
6	1.833903000	1.210442000	-0.000280000
6	1.833511000	-1.210577000	0.000103000
6	2.526036000	-0.000190000	-0.000421000
1	-0.113586000	2.145944000	0.000507000
1	-0.114092000	-2.145691000	0.001061000
1	2.379413000	2.149731000	-0.000331000
1	2.378781000	-2.150024000	-0.000240000
1	3.612860000	-0.000445000	-0.000792000
6	-1.716235000	0.000366000	0.000281000
8	-2.428849000	-1.039459000	-0.000642000
8	-2.429141000	1.039216000	-0.000081000

[$Co^{III}(acac)_2(\kappa^2\text{-}O_2CPh)$]

E = -1255.80453562
$G_{298.15,1M}$ = -1255.527176
$G_{333.15,1M}$ = -1255.537154

6	1.109063000	3.884937000	1.345508000
6	1.307103000	2.639412000	0.525567000
6	2.341184000	2.577654000	-0.417988000
6	2.546948000	1.484732000	-1.262786000
6	3.629432000	1.527459000	-2.306369000
8	0.470363000	1.718439000	0.767921000
27	0.546169000	-0.000059000	-0.000143000
8	-1.075757000	-0.429600000	0.992959000
6	-1.746287000	-0.000188000	-0.000163000
8	1.877870000	0.402222000	-1.256979000
8	1.877457000	-0.402091000	1.257189000
6	2.546928000	-1.484358000	1.263066000
6	3.629245000	-1.526738000	2.306833000
8	0.471018000	-1.718524000	-0.768274000
6	1.307799000	-2.639366000	-0.525565000
6	1.110169000	-3.885003000	-1.345435000
6	2.341647000	-2.577342000	0.418232000
8	-1.075859000	0.429229000	-0.993353000
1	0.085466000	4.245964000	1.202787000
1	1.815869000	4.675450000	1.085176000
1	1.218295000	3.630426000	2.405071000
1	2.987530000	3.439836000	-0.527820000
1	4.181912000	2.469219000	-2.297846000
1	4.320459000	0.695093000	-2.135939000
1	3.178319000	1.377458000	-3.292740000
1	3.177943000	-1.376765000	3.293122000
1	4.320090000	-0.694214000	2.136436000
1	4.181966000	-2.468358000	2.298471000
1	2.988174000	-3.439366000	0.528232000
1	1.816871000	-4.675463000	-1.084665000
1	0.086512000	-4.246025000	-1.203148000
1	1.219899000	-3.630639000	-2.404984000
6	-3.220474000	-0.000172000	-0.000078000
6	-3.914641000	-0.456729000	1.122676000
6	-3.914763000	0.456420000	-1.122742000
6	-5.304177000	-0.455373000	1.120293000
6	-5.304299000	0.455127000	-1.120181000
6	-5.998528000	-0.000107000	0.000101000
1	-3.350500000	-0.805550000	1.982416000
1	-3.350714000	0.805222000	-1.982551000
1	-5.848815000	-0.808865000	1.991616000
1	-5.849033000	0.808647000	-1.991432000
1	-7.085630000	-0.000080000	0.000170000

C. Acetate system

CH_3COO•

E = -228.260950023
$G_{298.15,1M}$ = -228.238399
$G_{333.15,1M}$ = -228.242361
$\langle S^2 \rangle$ = 0.7552

6	-0.104415000	0.000122000	-0.008250000
8	-0.808190000	-1.040481000	0.001676000
8	-0.808656000	1.040213000	0.001681000
6	1.384564000	0.000250000	-0.002718000
1	1.732330000	-0.008211000	1.035820000
1	1.760740000	-0.894565000	-0.505405000
1	1.760807000	0.902695000	-0.491462000

[$Co^{III}(acac)_2(\kappa^2\text{-}O_2CMe)$] (singlet)

E = -1064.22124745
$G_{298.15,1M}$ = -1063.992669
$G_{333.15,1M}$ = -1064.001746

6	-3.939447000	-0.263819000	-1.121655000
6	-2.642707000	-0.412100000	-0.373556000
6	-2.480441000	-1.454891000	0.547864000
6	-1.336552000	-1.616440000	1.333553000
6	-1.275686000	-2.707450000	2.367306000
8	-1.777293000	0.472204000	-0.651277000
27	-0.009931000	0.450406000	0.002977000
8	0.304019000	2.086694000	-1.008938000
6	-0.086548000	2.739875000	0.008135000
6	-0.175312000	4.229110000	-0.003847000
8	-0.288279000	-0.897524000	1.278475000
8	0.348995000	-0.869308000	-1.281800000
6	1.439346000	-1.522188000	-1.342879000
6	1.445606000	-2.605420000	-2.386525000
8	1.752046000	0.573317000	0.658864000
6	2.669136000	-0.255170000	0.375346000
6	3.953323000	-0.036375000	1.127790000
6	2.571173000	-1.297812000	-0.555419000
8	-0.422612000	2.057933000	1.025605000
1	-4.340194000	0.739660000	-0.945814000
1	-4.680777000	-1.010047000	-0.828612000
1	-3.738356000	-0.349553000	-2.194841000
1	-3.304190000	-2.142902000	0.693523000
1	-2.186211000	-3.309523000	2.395582000
1	-0.416070000	-3.351357000	2.153533000
1	-1.106141000	-2.256045000	3.350422000
1	1.254496000	-2.155462000	-3.366383000
1	0.623846000	-3.300003000	-2.182859000
1	2.389728000	-3.153206000	-2.415894000
1	3.435168000	-1.933417000	-0.706088000
1	4.737765000	-0.735767000	0.831516000
1	4.294786000	0.990172000	0.960324000
1	3.755057000	-0.141615000	2.199754000
1	0.613155000	4.644210000	-0.635160000
1	-1.144074000	4.515863000	-0.427326000
1	-0.106201000	4.617594000	1.013831000

[$Co^{III}(acac)_2(\kappa^2\text{-}O_2CMe)$] (triplet)

E = -1064.20335457
$G_{298.15,1M}$ = -1063.979592
$G_{333.15,1M}$ = -1063.989059
$\langle S^2 \rangle$ = 2.0741

6	-0.991204000	-3.765663000	1.062043000
6	-0.892369000	-2.469538000	0.305773000
6	-1.943078000	-2.048512000	-0.506314000
6	-1.886547000	-0.927948000	-1.366145000
6	-3.016075000	-0.686852000	-2.335165000
8	0.228131000	-1.870689000	0.472321000
27	0.527991000	-0.074031000	0.036101000
8	2.484986000	-0.235347000	1.150512000
6	2.911578000	-0.548493000	0.022058000
6	4.343917000	-0.920048000	-0.232375000
8	-0.932189000	-0.107409000	-1.414728000
8	-0.827935000	0.410057000	1.290335000
6	-1.448813000	1.520170000	1.273200000
6	-2.633482000	1.586098000	2.195083000
8	0.914855000	1.713397000	-0.400204000
6	0.102683000	2.681362000	-0.235092000
6	0.538967000	3.963290000	-0.885768000
6	-1.082750000	2.631316000	0.505569000
8	2.101091000	-0.576124000	-0.978443000
1	-0.149997000	-4.407524000	0.780728000
1	-1.930306000	-4.290205000	0.873710000
1	-0.894483000	-3.556599000	2.132816000
1	-2.819620000	-2.683936000	-0.557182000
1	-3.851002000	-1.378356000	-2.200271000
1	-3.367299000	0.343685000	-2.220186000
1	-2.629630000	-0.783990000	-3.355688000
1	-2.297709000	1.394711000	3.219626000
1	-3.330053000	0.784652000	1.927203000
1	-3.145432000	2.549447000	2.152947000
1	-1.682894000	3.530021000	0.578029000
1	-0.162298000	4.781493000	-0.710629000
1	1.526981000	4.237691000	-0.502016000
1	0.645075000	3.791467000	-1.961979000
1	4.960286000	-0.643447000	0.624108000
1	4.402828000	-2.002171000	-0.389736000
1	4.701304000	-0.430298000	-1.141734000

[$Co^{III}(acac)_2(\kappa^1\text{-}O_2CPh)$] (singlet)

E = -1064.19105282
$G_{298.15,1M}$ = -1063.964011
$G_{333.15,1M}$ = -1063.973193

8	-0.042538000	-0.061811000	1.168741000
27	-0.020799000	0.341808000	-0.612136000
8	1.274535000	-0.857263000	-1.177414000
6	2.467313000	-0.862218000	-0.729608000
6	3.196686000	-2.153329000	-0.927071000
8	-1.341275000	1.648478000	-0.348007000
6	-2.544187000	1.381736000	-0.025652000
6	-3.124680000	0.109936000	-0.087595000
6	-2.469448000	-0.976955000	-0.676726000
8	-1.264329000	-0.960424000	-1.089400000
6	-3.350581000	2.568490000	0.417910000
6	-3.177548000	-2.281808000	-0.892454000
8	1.237136000	1.703697000	-0.357739000
6	2.448789000	1.478227000	-0.027935000
6	3.206061000	2.691161000	0.430293000
6	3.074328000	0.229827000	-0.097477000
1	3.137406000	3.467398000	-0.338761000
1	-2.911590000	2.964742000	1.340199000
1	-3.276259000	3.355691000	-0.339031000
1	4.255788000	2.475319000	0.639244000
1	-4.400364000	2.322450000	0.590336000
1	2.725708000	3.086463000	1.331896000
1	4.096596000	0.133469000	0.247284000
1	-4.151805000	-0.012233000	0.233952000
1	3.055630000	-2.502080000	-1.954168000
1	-4.226972000	-2.246405000	-0.592961000
1	4.261260000	-2.080345000	-0.695356000
1	-3.103364000	-2.561782000	-1.948078000
1	2.715100000	-2.881825000	-0.263697000
1	-2.651406000	-3.051766000	-0.317403000
6	0.158035000	-1.260072000	1.681916000
8	0.462183000	-2.284846000	1.109783000
6	-0.074143000	-1.200036000	3.186373000
1	0.423466000	-0.330145000	3.621838000
1	-1.148184000	-1.097683000	3.372385000
1	0.291132000	-2.122479000	3.640447000

D. Addition of pyridine

Pyridine

E = -248.079453786
$G_{298.15,1M}$ = -248.020303
$G_{333.15,1M}$ = -248.024105

6	0.000000000	0.000000000	-1.382950000
6	0.000000000	1.195270000	-0.671519000
6	0.000000000	1.138803000	0.720482000
7	0.000000000	0.000000000	1.418083000
6	0.000000000	-1.138803000	0.720482000
6	0.000000000	-1.195270000	-0.671519000
1	0.000000000	0.000000000	-2.469938000
1	0.000000000	2.154874000	-1.180727000

1	0.000000000	2.056846000	1.307474000
1	0.000000000	-2.056846000	1.307474000
1	0.000000000	-2.154874000	-1.180727000

***cis*-[Co^{III}(acac)$_2$(O$_2$CMe)(py)]**

E = -1312.34135738
$G_{298.15,1M}$ = -1312.032432
$G_{333.15,1M}$ = -1312.040038

6	2.972122000	-1.510248000	-2.263385000
6	2.331839000	-0.466082000	-1.396932000
6	3.107012000	0.485690000	-0.726900000
6	2.546789000	1.526649000	0.025089000
6	3.427464000	2.616031000	0.574235000
8	1.065837000	-0.552604000	-1.335525000
27	0.066080000	0.260958000	0.030613000
8	1.095259000	-2.759378000	0.447763000
6	1.379590000	-1.933174000	1.303013000
6	2.315976000	-2.272126000	2.454195000
8	1.315730000	1.658638000	0.302954000
8	-0.761256000	1.288816000	-1.348858000
6	-1.537001000	2.271933000	-1.138537000
6	-1.955452000	3.010008000	-2.382046000
8	-0.959828000	1.018763000	1.442031000
6	-1.706142000	2.036533000	1.312913000
6	-2.297824000	2.534767000	2.604300000
6	-2.006387000	2.690098000	0.111312000
8	0.976395000	-0.692951000	1.376522000
1	2.808523000	-2.473595000	-1.765992000
1	4.040969000	-1.342225000	-2.411596000
1	2.462487000	-1.548171000	-3.230982000
1	4.180638000	0.470417000	-0.870380000
1	4.442882000	2.578201000	0.173906000
1	2.977678000	3.588802000	0.353977000
1	3.465348000	2.513287000	1.664806000
1	-2.382135000	2.298126000	-3.096073000
1	-1.065166000	3.443832000	-2.850353000
1	-2.679201000	3.802034000	-2.178371000
1	-2.660463000	3.552904000	0.149346000
1	-2.982302000	3.373157000	2.458951000
1	-2.825385000	1.712569000	3.098787000
1	-1.481869000	2.840908000	3.267728000
1	2.427766000	-3.355052000	2.534856000
1	3.293036000	-1.821549000	2.247222000
1	1.949088000	-1.847868000	3.392529000
6	-3.072541000	-3.175930000	-0.472375000
6	-2.715622000	-2.723505000	0.793115000
6	-1.799614000	-1.689514000	0.901596000
7	-1.258887000	-1.117301000	-0.179267000
6	-1.589500000	-1.544723000	-1.401171000
6	-2.499818000	-2.574239000	-1.586892000
1	-3.782496000	-3.990361000	-0.587943000
1	-3.128446000	-3.169772000	1.691761000
1	-1.460514000	-1.293693000	1.852379000
1	-1.091338000	-1.041542000	-2.221154000
1	-2.743502000	-2.898459000	-2.593359000

***trans*-[Co^{III}(acac)$_2$(O$_2$CMe)(py)]**

E = -1312.33820723
$G_{298.15,1M}$ = -1312.029155
$G_{333.15,1M}$ = -1312.036728

8	1.770200000	0.008035000	0.553720000
27	-0.058139000	0.004361000	0.108643000
8	0.140091000	1.296417000	-1.245613000
6	0.694888000	2.416662000	-1.021757000
6	1.250467000	3.082876000	-2.243886000
8	-0.274829000	-1.313093000	1.462187000
6	0.283903000	-2.452908000	1.378237000
6	0.847665000	-2.999065000	0.220579000
6	0.727973000	-2.394490000	-1.037480000
8	0.171660000	-1.273851000	-1.256174000
6	0.299989000	-3.231598000	2.664936000
6	1.286542000	-3.052654000	-2.263775000
8	-0.294193000	1.308399000	1.470003000
6	0.256653000	2.453528000	1.394168000
6	0.264698000	3.223221000	2.686267000
6	0.816423000	3.011501000	0.241102000
1	-0.742807000	3.223756000	3.114049000
1	0.960383000	-2.717124000	3.372216000
1	-0.704186000	-3.233400000	3.100259000
1	0.611476000	4.251168000	2.561019000
1	0.644873000	-4.259044000	2.530563000
1	0.918952000	2.703350000	3.395217000
1	1.293733000	3.981262000	0.312328000
1	1.328985000	-3.967340000	0.285228000
1	0.520017000	3.035402000	-3.056776000
1	1.608055000	-4.081157000	-2.086211000
1	1.551142000	4.117670000	-2.066259000
1	0.546319000	-3.023239000	-3.068834000
1	2.119103000	2.484554000	-2.545279000
1	2.140636000	-2.441956000	-2.580695000
6	2.789947000	0.026446000	-0.259610000
8	2.778405000	0.092605000	-1.480205000
6	4.097198000	-0.062949000	0.518824000
1	4.120581000	0.697372000	1.304919000
1	4.157055000	-1.041780000	1.006218000
1	4.942557000	0.064212000	-0.159883000
6	-4.699010000	-0.034745000	-0.653646000
6	-4.197374000	-0.032380000	0.644043000
6	-2.822747000	-0.021000000	0.831631000
7	-1.975810000	-0.012216000	-0.203386000
6	-2.444267000	-0.013943000	-1.456174000
6	-3.806490000	-0.025320000	-1.720572000
1	-5.771071000	-0.043606000	-0.830770000
1	-4.857158000	-0.039150000	1.505647000
1	-2.356563000	-0.018331000	1.810831000
1	-1.687550000	-0.005560000	-2.233341000
1	-4.153551000	-0.026496000	-2.748759000

[Co^{II}(acac)$_2$(py)]

E = -1083.99964662
$G_{298.15,1M}$ = -1083.745137
$G_{333.15,1M}$ = -1083.752202
$\langle S^2 \rangle$ = 3.7609

6	1.042421000	1.152947000	1.795124000
7	0.533916000	1.130490000	0.558934000
6	0.613214000	2.226933000	-0.203726000
6	1.212552000	3.396388000	0.245036000
6	1.744640000	3.423418000	1.530625000
6	1.656342000	2.281804000	2.321439000
27	-0.328439000	-0.585822000	-0.253048000
8	-1.723609000	-1.048987000	1.096140000
6	-2.973108000	-0.845710000	1.005172000
6	-3.795550000	-1.380719000	2.150965000
6	-3.617179000	-0.173405000	-0.047943000
6	-2.960512000	0.381631000	-1.157368000
8	-1.708179000	0.341366000	-1.368582000
6	-3.765532000	1.102962000	-2.209469000
8	0.997756000	-1.764750000	0.725502000
6	2.243290000	-1.818810000	0.493871000
6	2.886081000	-1.285764000	-0.636163000
6	2.215611000	-0.707846000	-1.728096000
6	3.007789000	-0.291927000	-2.943493000
8	0.965186000	-0.513765000	-1.802611000
6	3.062996000	-2.544528000	1.533201000
1	-3.633090000	-2.461289000	2.228376000
1	2.898242000	-2.076071000	2.509948000
1	2.702794000	-3.576260000	1.609936000
1	-4.864289000	-1.181218000	2.042229000
1	4.132599000	-2.551023000	1.309668000
1	-3.435446000	-0.935260000	3.084776000
1	-4.694572000	-0.063923000	0.007755000
1	3.961288000	-1.406616000	-0.710038000

1	-3.591901000	0.623192000	-3.178823000
1	4.079311000	-0.482012000	-2.844510000
1	-4.837173000	1.114873000	-1.996804000
1	2.622833000	-0.828070000	-3.817666000
1	-3.401302000	2.133062000	-2.291944000
1	2.843163000	0.776001000	-3.125279000
1	0.175152000	2.130735000	-1.193694000
1	1.259828000	4.265349000	-0.403796000
1	2.221357000	4.322653000	1.911641000
1	2.058078000	2.260943000	3.329619000
1	0.946026000	0.223537000	2.349729000

$[Co^{II}(acac)_2(py)_2]$

E = -1332.11931318
$G_{298.15,1M}$ = -1331.783016
$G_{333.15,1M}$ = -1331.791747
$\langle S^2 \rangle$ = 3.7632

6	-3.156899000	0.371052000	-0.000111000
7	-2.191728000	-0.553589000	-0.000229000
6	-2.533129000	-1.846332000	-0.000317000
6	-3.856681000	-2.267268000	-0.000274000
6	-4.862776000	-1.306335000	-0.000141000
6	-4.505892000	0.038175000	-0.000066000
27	-0.138033000	-0.027110000	-0.000021000
7	1.939395000	0.460664000	0.000212000
6	2.596915000	0.610096000	1.153098000
6	3.952479000	0.911418000	1.199188000
6	4.642524000	1.063521000	0.000109000
6	3.952300000	0.911781000	-1.198927000
6	2.596754000	0.610442000	-1.152746000
8	-0.461703000	1.413030000	-1.435912000
6	-0.698692000	2.640220000	-1.250365000
6	-0.846580000	3.272762000	0.000098000
6	-0.698843000	2.640109000	1.250512000
8	-0.462013000	1.412864000	1.435968000
6	-0.825700000	3.473603000	-2.505667000
6	-0.825866000	3.473378000	2.505883000
8	0.273788000	-1.440258000	1.434749000
6	0.943262000	-2.497547000	1.249896000
6	1.301135000	-3.038068000	-0.000011000
6	0.943747000	-2.497343000	-1.249952000
6	1.370606000	-3.222011000	-2.505925000
8	0.274214000	-1.440092000	-1.434941000
6	1.369454000	-3.222532000	2.505908000
1	-1.597122000	3.033712000	-3.146908000
1	0.118146000	3.422682000	-3.060046000
1	-1.069454000	4.520388000	-2.307191000
1	-1.045621000	4.339111000	0.000126000
1	-1.070186000	4.520055000	2.307525000
1	-1.596831000	3.033075000	3.147383000
1	0.118210000	3.422933000	3.059921000
1	2.026073000	-2.562127000	-3.085948000
1	1.892482000	-4.161791000	-2.308351000
1	0.486901000	-3.416190000	-3.122918000
1	1.874086000	-3.959172000	0.000020000
1	0.485457000	-3.416634000	3.122508000
1	1.891206000	-4.162385000	2.308360000
1	2.024831000	-2.562902000	3.086323000
1	1.990177000	0.477552000	2.045048000
1	4.452876000	1.023890000	2.156158000
1	5.703662000	1.298989000	0.000061000
1	4.452573000	1.024555000	-2.155927000
1	1.989878000	0.478160000	-2.044637000
1	-1.702956000	-2.547479000	-0.000417000
1	-4.088597000	-3.327886000	-0.000343000
1	-5.908936000	-1.601138000	-0.000100000
1	-5.257294000	0.821810000	0.000031000
1	-2.819316000	1.404160000	-0.000059000

e. Addition of Et_3N

Et_3N

E = -292.19231051
$G_{298.15,1M}$ = -292.022317
$G_{333.15,1M}$ = -292.024592

7	0.001155000	-0.406307000	-0.253620000
6	-0.000876000	0.999262000	-0.652297000
1	0.869787000	1.165021000	-1.296023000
1	-0.869523000	1.161505000	-1.299685000
6	-1.197146000	-0.827420000	0.464185000
1	-1.092229000	-1.905037000	0.646126000
1	-1.273111000	-0.357749000	1.466901000
6	1.200251000	-0.823848000	0.464930000
1	1.097490000	-1.901410000	0.648408000
1	1.275189000	-0.352629000	1.466992000
6	-0.005447000	2.034969000	0.477703000
1	0.878063000	1.940062000	1.118807000
1	-0.005984000	3.048875000	0.062300000
1	-0.892112000	1.937153000	1.113977000
6	-2.488415000	-0.586700000	-0.306282000
1	-2.744084000	0.476340000	-0.370059000
1	-2.401143000	-0.980716000	-1.324705000
1	-3.322497000	-1.092959000	0.190970000
6	2.491082000	-0.581742000	-0.305874000
1	2.744919000	0.481650000	-0.370954000
1	3.326103000	-1.085946000	0.191895000
1	2.404353000	-0.977136000	-1.323809000

***cis*-$[Co^{III}(acac)_2(O_2CMe)(NEt_3)]$**

E = -1356.44818543
$G_{298.15,1M}$ = -1356.024248
$G_{333.15,1M}$ = -1356.032754

6	-2.426350000	-2.198343000	-2.319302000
6	-1.260143000	-1.953070000	-1.411502000
6	-0.607143000	-3.023791000	-0.792463000
6	0.466267000	-2.857336000	0.082094000
6	1.161137000	-4.057533000	0.667098000
8	-0.966033000	-0.726638000	-1.264450000
27	0.184221000	-0.062578000	0.052926000
8	-2.976085000	-1.157836000	0.657326000
6	-2.212203000	-0.865882000	1.567135000
6	-2.608460000	-1.066450000	3.024408000
8	0.947910000	-1.745401000	0.466347000
8	1.510985000	0.079172000	-1.311958000
6	2.762093000	0.143930000	-1.093183000
6	3.613095000	-0.022255000	-2.322688000
8	1.356787000	0.596913000	1.407031000
6	2.620333000	0.602212000	1.318359000
6	3.330086000	0.911050000	2.608455000
6	3.358198000	0.367503000	0.149917000
8	-1.021065000	-0.343757000	1.485696000
1	-3.317610000	-1.942606000	-1.734371000
1	-2.491787000	-3.236498000	-2.652066000
1	-2.375737000	-1.527257000	-3.181248000
1	-0.947562000	-4.028439000	-1.010625000
1	0.805603000	-4.996730000	0.238142000
1	2.239597000	-3.962663000	0.506054000
1	0.993050000	-4.067346000	1.749687000
1	3.288667000	0.694007000	-3.084757000
1	3.447426000	-1.025032000	-2.731581000
1	4.677375000	0.115443000	-2.120351000
1	4.439594000	0.399218000	0.206858000
1	4.408194000	1.029538000	2.480497000
1	2.906466000	1.821763000	3.043632000
1	3.134984000	0.096057000	3.314172000
1	-3.626560000	-1.454970000	3.084564000
1	-1.910835000	-1.763601000	3.498992000
1	-2.533791000	-0.116097000	3.562683000

7	-0.578649000	1.851567000	-0.343661000
6	-2.069097000	1.760217000	-0.379735000
1	-2.379226000	1.402125000	0.598567000
1	-2.319757000	0.957613000	-1.071285000
6	-0.040120000	2.386297000	-1.634343000
1	1.048113000	2.358684000	-1.544160000
1	-0.327299000	3.446183000	-1.692298000
6	-0.136787000	2.830507000	0.701178000
1	0.953022000	2.773636000	0.730092000
1	-0.392006000	3.837225000	0.339306000
6	-2.809636000	3.045979000	-0.727065000
1	-3.883964000	2.837849000	-0.692408000
1	-2.611729000	3.854480000	-0.015162000
1	-2.580559000	3.411938000	-1.732833000
6	-0.465725000	1.680194000	-2.908322000
1	-0.144995000	0.640883000	-2.907857000
1	-1.548505000	1.712554000	-3.060037000
1	0.003392000	2.197707000	-3.752992000
6	-0.705628000	2.628013000	2.093564000
1	-0.555571000	1.601698000	2.427925000
1	-0.187552000	3.308071000	2.778705000
1	-1.773375000	2.866111000	2.139232000

***trans*-[$Co^{III}(acac)_2(O_2CMe)(NEt_3)$]**

E = -1356.44884884
$G_{298.15,1M}$ = -1356.022882
$G_{333.15,1M}$ = -1356.031140

8	-1.602388000	0.756751000	0.666333000
27	-0.002293000	-0.075562000	0.098097000
8	-0.904984000	-0.988987000	-1.278129000
6	-1.948732000	-1.683744000	-1.075263000
6	-2.799135000	-1.882750000	-2.292961000
8	0.820575000	0.897660000	1.508257000
6	0.821531000	2.170040000	1.544195000
6	0.541946000	3.010237000	0.463071000
6	0.331861000	2.522954000	-0.833124000
8	0.327919000	1.293254000	-1.152181000
6	1.175740000	2.749966000	2.885042000
6	0.075954000	3.455041000	-1.977982000
8	-0.442113000	-1.416595000	1.370477000
6	-1.512188000	-2.101206000	1.297977000
6	-1.875506000	-2.816904000	2.569190000
6	-2.317360000	-2.226072000	0.162274000
1	-0.993340000	-3.331912000	2.961943000
1	0.372131000	2.507437000	3.589536000
1	2.087592000	2.272211000	3.257327000
1	-2.690702000	-3.530584000	2.432384000
1	1.313573000	3.832794000	2.852531000
1	-2.171466000	-2.067882000	3.312637000
1	-3.222768000	-2.817571000	0.224291000
1	0.544746000	4.081977000	0.620806000
1	-2.170814000	-2.178090000	-3.138580000
1	0.249637000	4.502395000	-1.721790000
1	-3.595513000	-2.614626000	-2.141467000
1	0.693574000	3.168301000	-2.834398000
1	-3.229081000	-0.901866000	-2.529145000
1	-0.972436000	3.305924000	-2.263753000
6	-2.538767000	1.292218000	-0.067293000
8	-2.581102000	1.392122000	-1.284691000
6	-3.666291000	1.816334000	0.814110000
1	-4.112643000	0.982251000	1.364853000
1	-3.265975000	2.520142000	1.550031000
1	-4.422887000	2.303883000	0.196784000
7	1.828341000	-1.005107000	-0.384795000
6	2.882884000	0.046546000	-0.408024000
1	2.550636000	0.802761000	-1.119370000
1	2.868439000	0.522502000	0.572489000
6	1.734462000	-1.702529000	-1.705629000
1	2.633850000	-2.326083000	-1.816223000
1	0.881712000	-2.379585000	-1.626328000
6	2.153579000	-2.074357000	0.610517000
1	2.993696000	-2.661240000	0.210300000
1	1.284602000	-2.734535000	0.634946000
6	4.290936000	-0.426259000	-0.750024000
1	4.962210000	0.438802000	-0.734697000
1	4.676988000	-1.152266000	-0.027520000
1	4.353714000	-0.871075000	-1.748206000
6	1.570709000	-0.820439000	-2.929743000
1	2.456087000	-0.204874000	-3.120505000
1	1.432397000	-1.471827000	-3.799780000
1	0.700637000	-0.172225000	-2.836738000
6	2.480434000	-1.609683000	2.017806000
1	2.597019000	-2.496526000	2.650399000
1	3.420991000	-1.050571000	2.061944000
1	1.681298000	-0.992094000	2.424901000

[$Co^{II}(acac)_2(NEt_3)$]

E = -1128.12030827
$G_{298.15,1M}$ = -1127.746640
$G_{333.15,1M}$ = -1127.757295
$<S^2>$ = 3.7592

27	-0.004402000	-0.000188000	-0.577445000
8	1.396070000	1.414908000	-0.835733000
6	2.625408000	1.243362000	-1.104944000
6	3.423919000	2.509464000	-1.286428000
6	3.265906000	-0.000255000	-1.232578000
6	2.625406000	-1.243827000	-1.104605000
8	1.396108000	-1.415292000	-0.835118000
6	3.423877000	-2.509988000	-1.285835000
8	-1.434821000	1.393632000	-0.940059000
6	-2.692043000	1.238731000	-0.922069000
6	-3.353448000	-0.000008000	-0.857046000
6	-2.692181000	-1.238818000	-0.921909000
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1	-3.210651000	3.159987000	-0.159293000
1	-3.247242000	3.040970000	-1.915258000
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1	1.740928000	0.869816000	1.582752000
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1	1.067774000	-0.885973000	4.032502000
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6	-0.245607000	-2.528891000	1.730121000
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1	-0.001606000	-2.595570000	0.667908000
1	0.665018000	-2.701119000	2.313868000

$[Co^{II}(acac)_2(NEt_3)_2]$

E = -1420.3528749
$G_{298.15,1M}$ = -1419.782643
$G_{333.15,1M}$ = -1419.796031
$\langle S^2 \rangle$ = 3.7597

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6	1.272711000	3.120315000	-0.000348000
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8	0.680749000	1.304050000	1.411795000
6	1.360091000	3.262099000	-2.511653000
6	1.360446000	3.262513000	2.510930000
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1	1.742780000	4.269465000	-2.331466000
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1	2.079397000	2.699221000	3.115532000
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1	-1.742494000	-4.269807000	-2.330855000
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1	-2.079834000	-2.698715000	3.115672000
1	-1.743277000	-4.269359000	2.331071000
1	-0.434774000	-3.324208000	3.094827000
7	-2.127681000	1.106730000	0.000038000
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6	-2.252740000	1.979320000	-1.189217000
1	-3.178619000	2.576796000	-1.113536000
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1	2.926858000	0.599995000	-0.869128000
6	2.252567000	-1.979253000	1.189465000
1	1.423626000	-2.690160000	1.130509000
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1	4.861713000	-1.043737000	-0.885726000
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1	2.156606000	-2.003833000	-3.328543000
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6	-2.217140000	1.259396000	-2.526252000
1	-2.156208000	2.002729000	-3.328874000
1	-1.350561000	0.600160000	-2.593013000
1	-3.122284000	0.666916000	-2.698484000

PVAc characterization data

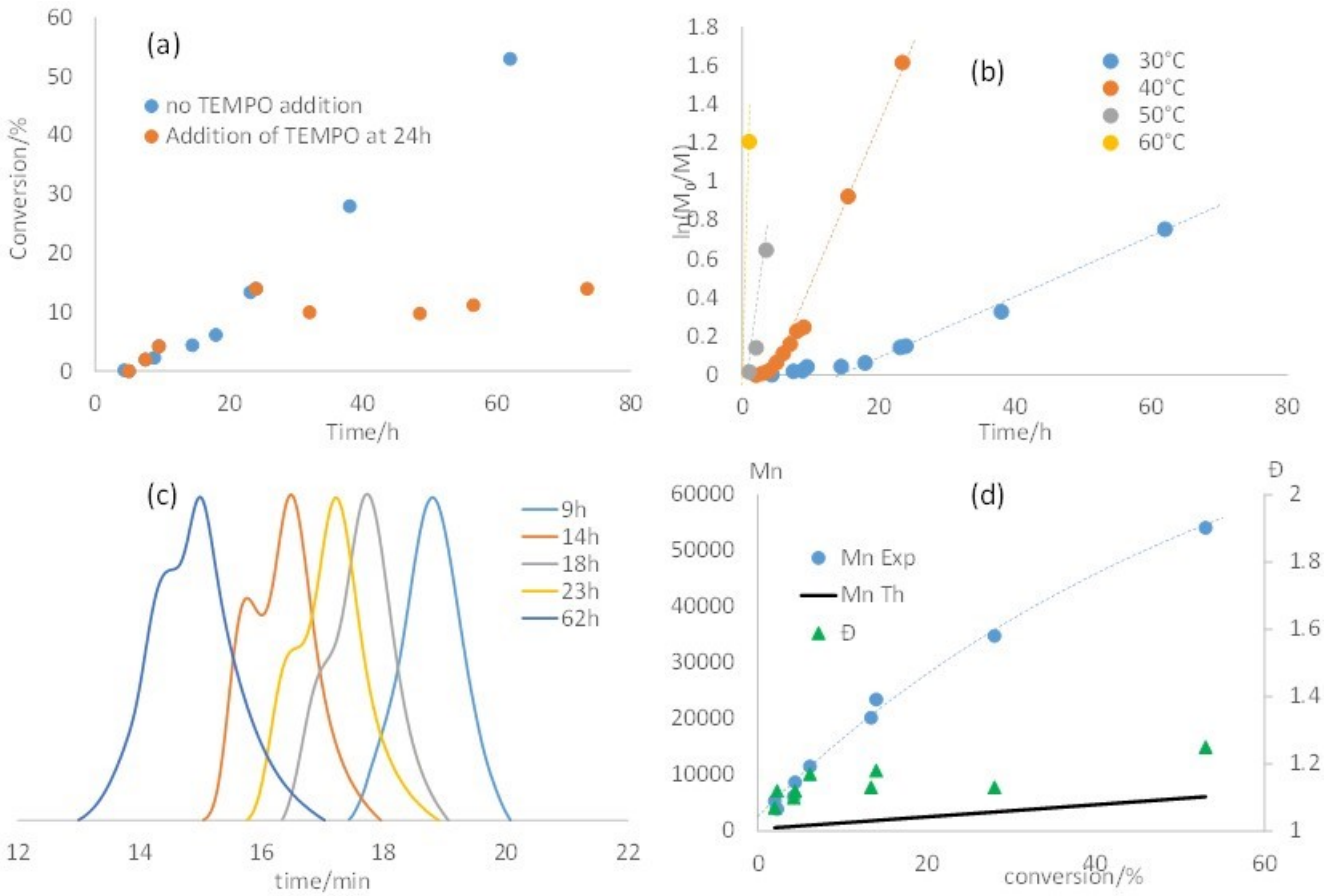


Figure S 13. VAc polymerisation initiated by $[Co^{III}(acac)_2(O_2CPh)]$. Conditions: T = 30°C, bulk, $[VAc]/[Co^{III}]/[Co^{II}]$ = 126/1/0.25. (a) Time-dependent monomer conversion. (b) Monomer conversion first-order kinetics. (c) Evolution of the molar mass distribution (from GPC) with the monomer conversion; note: the shoulder of the low elution time side of the main peak corresponds to terminated chains by coupling with double molar mass, which are generated during the aerial work-up of the polymer and not during the polymerisation process. (d) Evolution of the molar mass (number-average) and dispersity with the monomer conversion.

Discussion on the results of the ESI-MS analysis of the recovered PVAc

The six highest-intensity populations of the ESI-MS spectrum in Figure S13 can be rationalized on the basis of the initiation and polymerisation mechanism shown in Scheme S2. The simulation of the isotopic distribution for each population is given in Figure S14. The polymer chains are initiated by both phenyl and benzoate radicals. The Ph-initiated dormant chains are detected directly ($Co(acac)_2$ ω-end with cationisation by proton addition, population **a**). However, a more abundant population from these chains results from the hydrolytic cleavage (H ω-end, population **b**). The chains with a PhCOO α-end are hydrolysed under the ESI-MS analytical conditions, resulting in OH α-chain ends. Hence, after cationisation by proton addition, chains with both $Co(acac)_2$ (population **d**) and H (population **e**) at the ω-end are detected. The homolytic weakness of the PVAc-$Co(acac)_2$ bond favours radical production during the polymer work up procedure, leading to terminated chains by combination, as also illustrated by the GPC results in Figure S12. Thus, coupling of two PhCOO-initiated chains leads to population **f**; coupling of one PhCOO-initiated chain with one Ph-initiated chain leads to population **c**. Finally, coupling of two Ph-initiated chains should lead to a Ph-VAc_{2n}-Ph population, which is not visible in the ESI-MA spectrum. We presume that this results from the reluctance of these chains to be cationized, presumably because of the more hydrophobic chain ends.

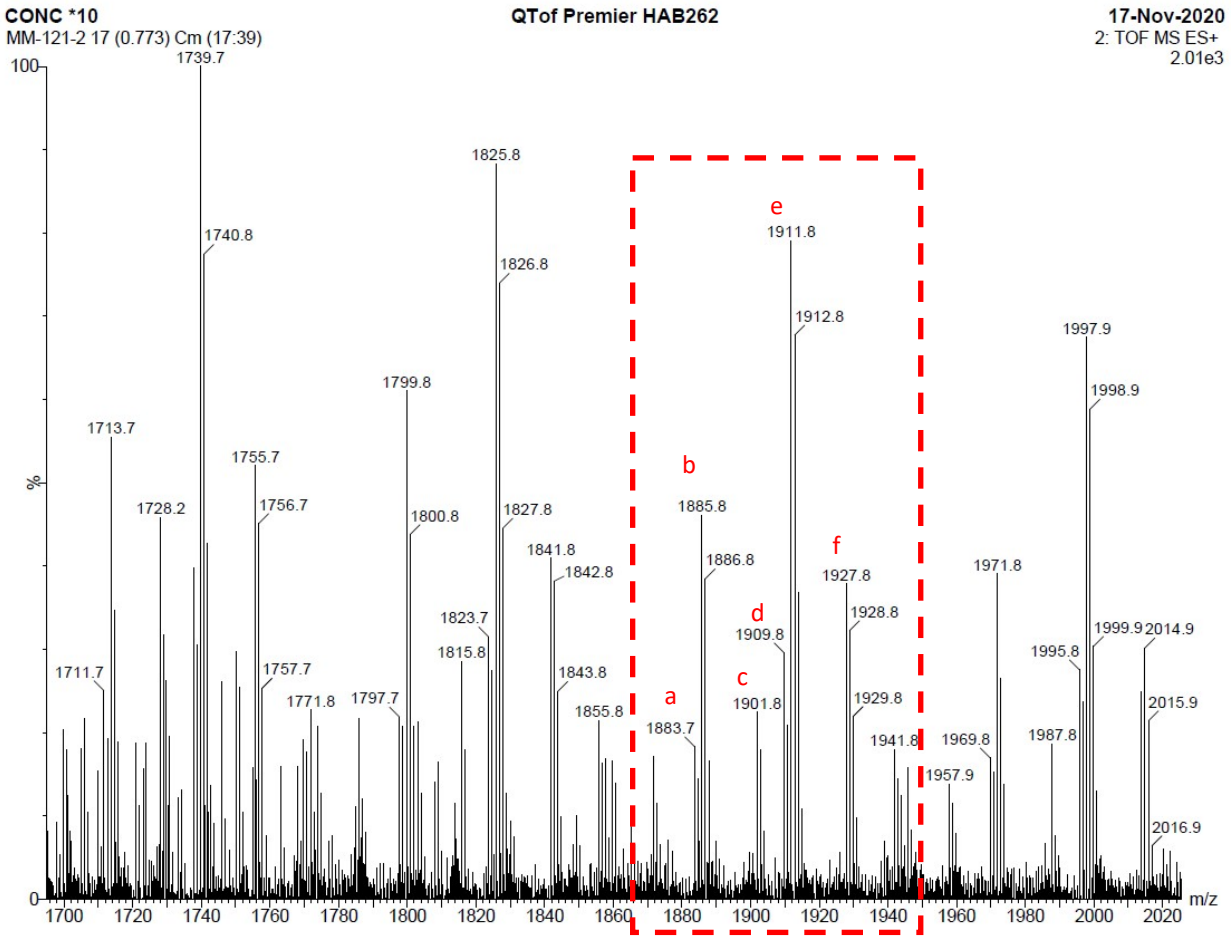
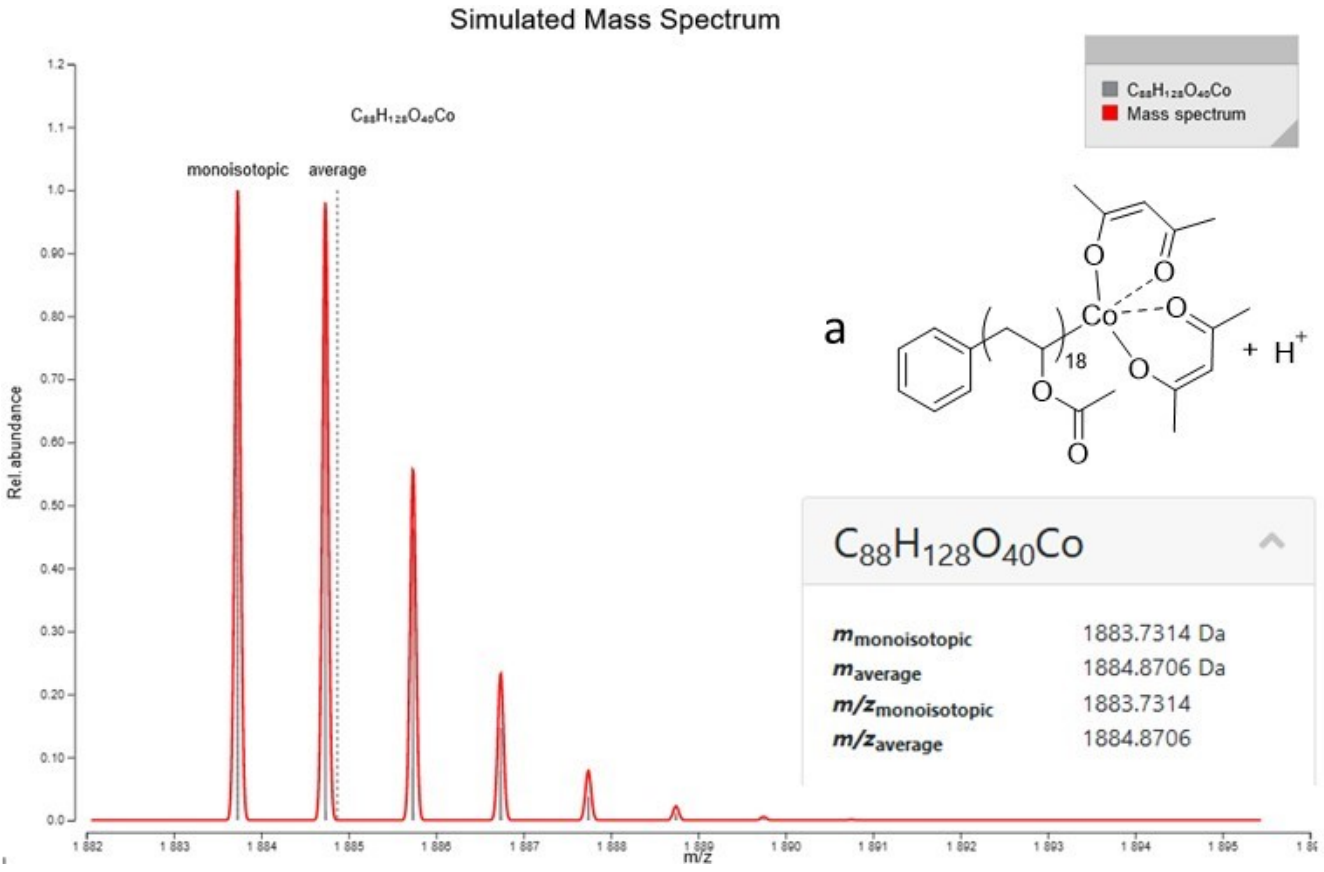


Figure S 14. ESI-MS spectrum (CH_2Cl_2/MeCN solution) of the PVAc generated by [$Co^{III}(acac)_2(O_2CPh)$] initiation.



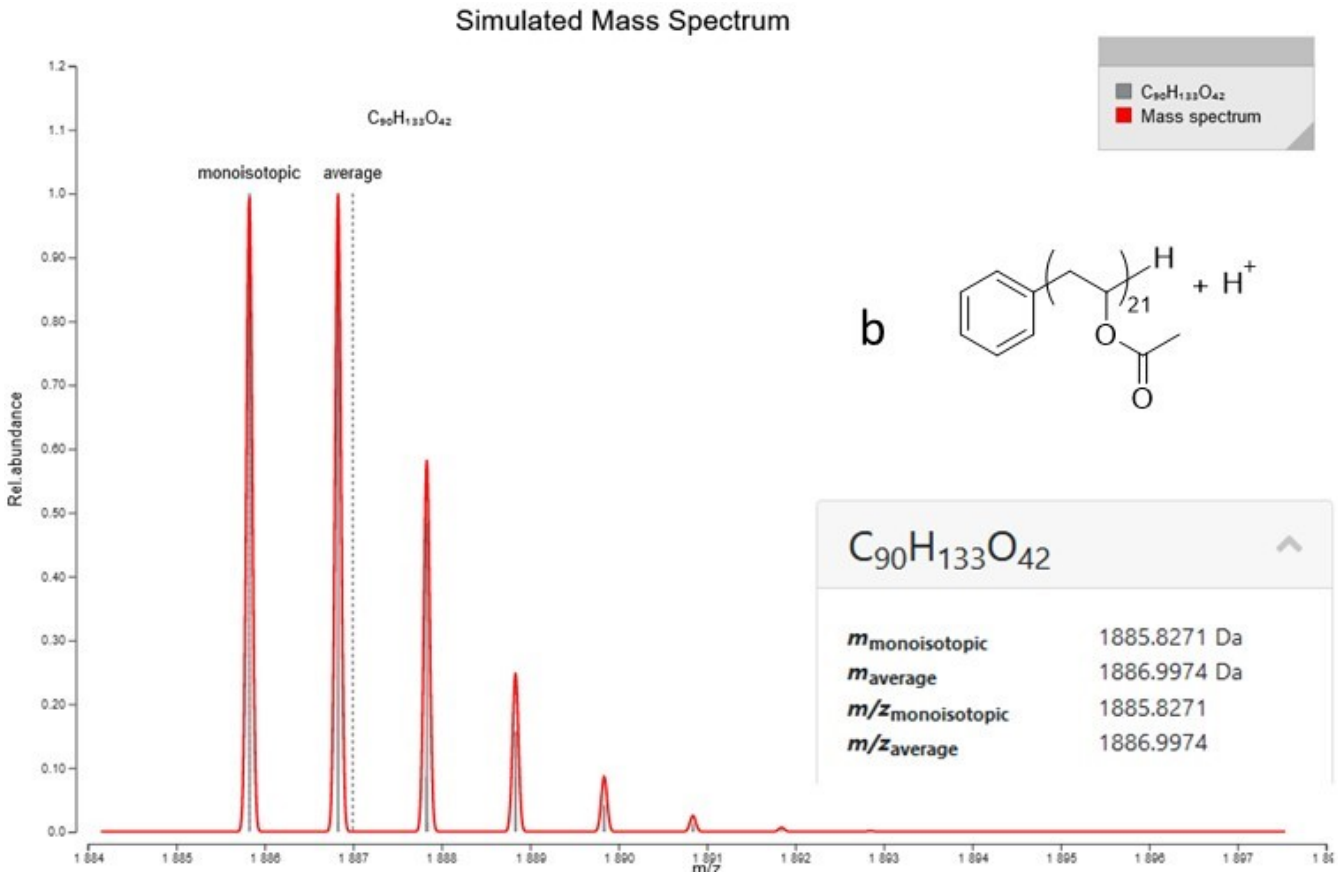
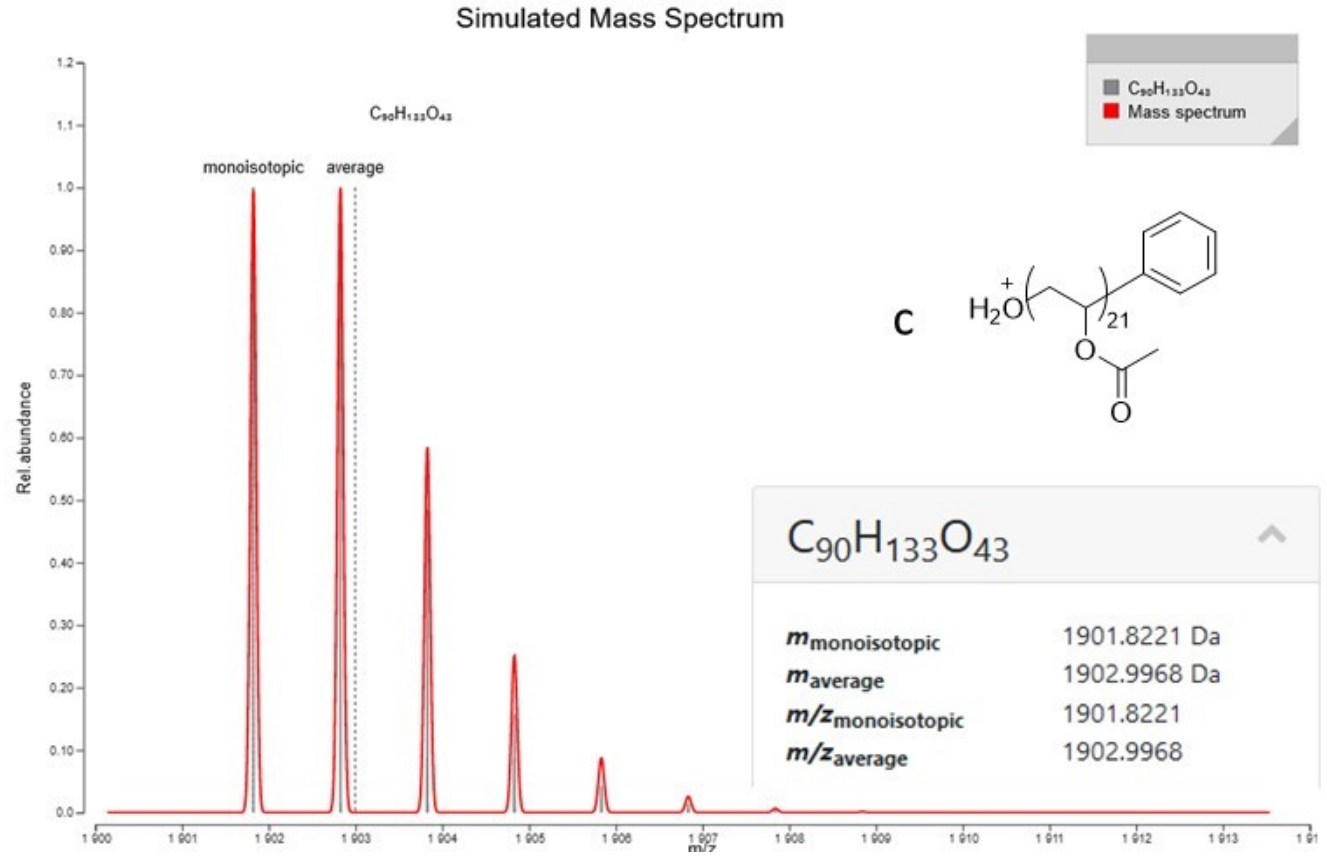


Figure S 15. Simulations of the isotopic envelopes for the six highest-intensity populations (a-f) observed in the ESI-MS spectrum of PVAc shown in Figure S 14.



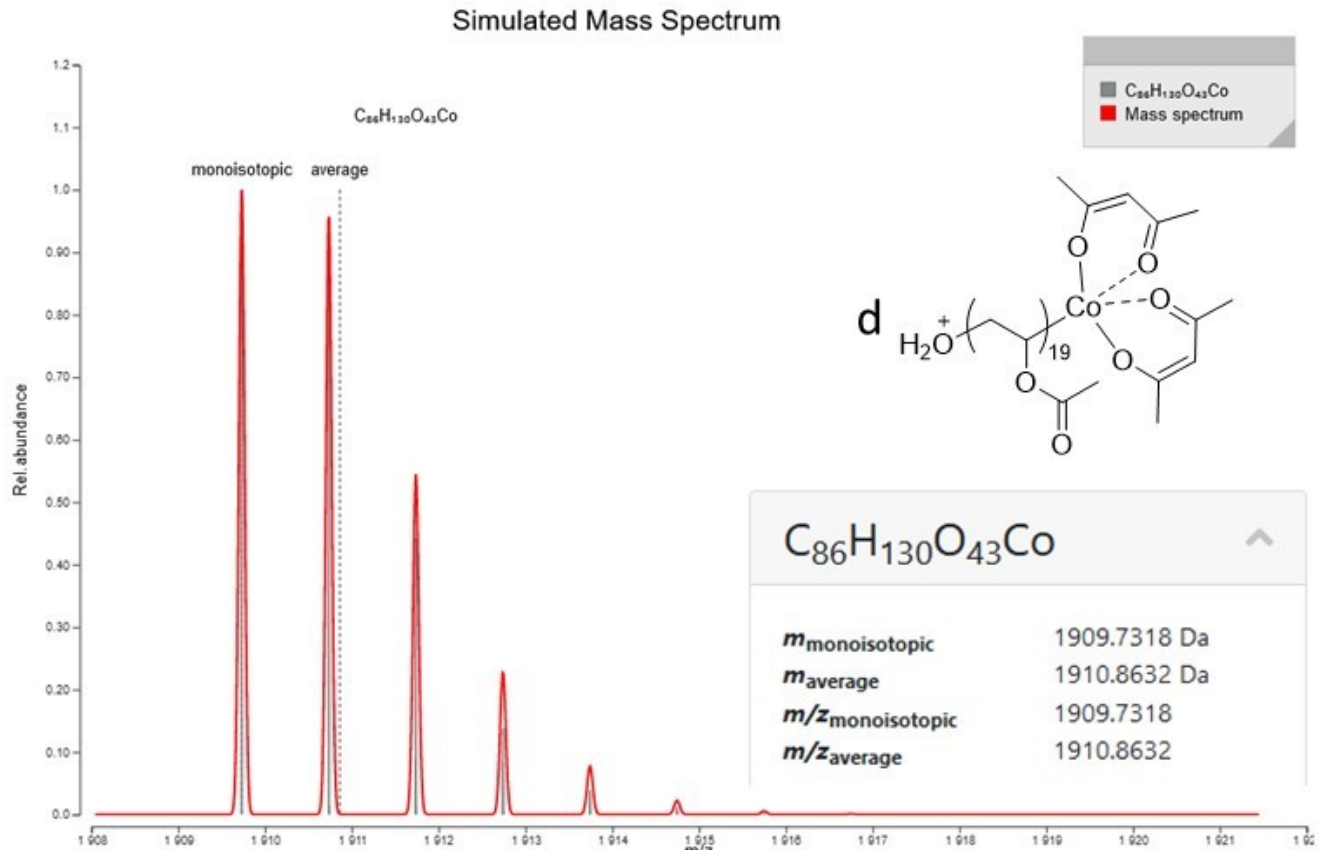
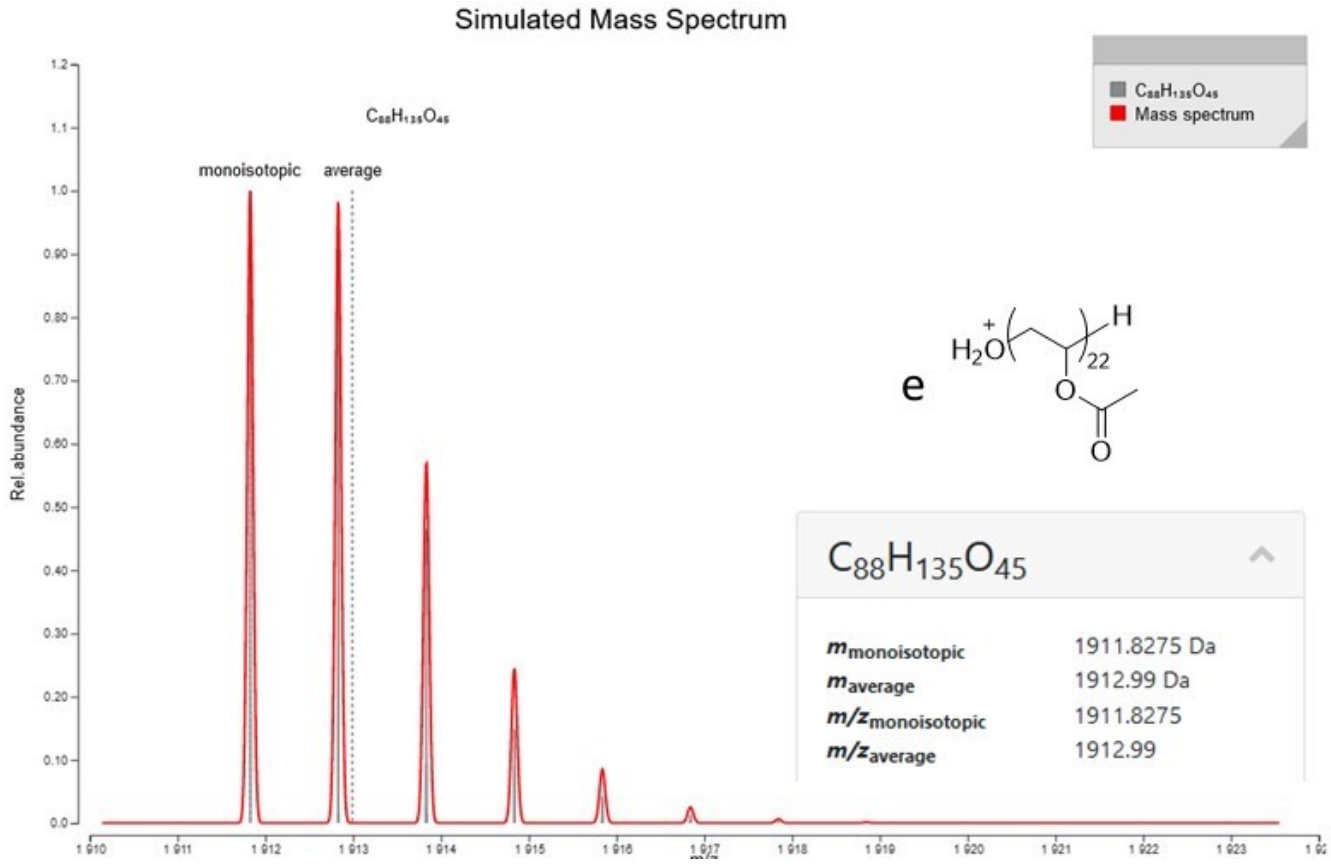


Figure S 15 (continued).



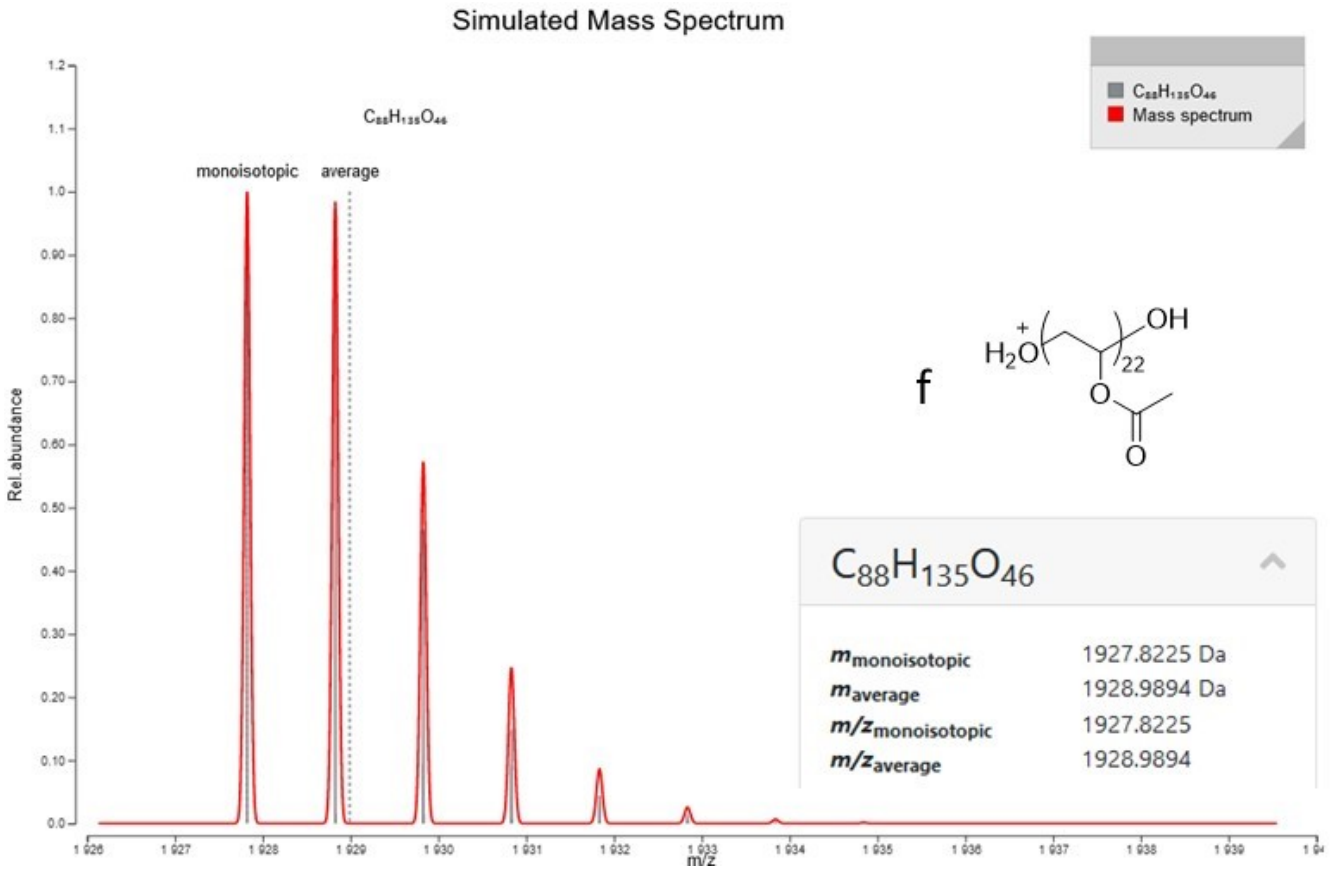


Figure S 15 (continued).

Ligand addition to $[Co^{III}(acac)_2(O_2CPh)]$

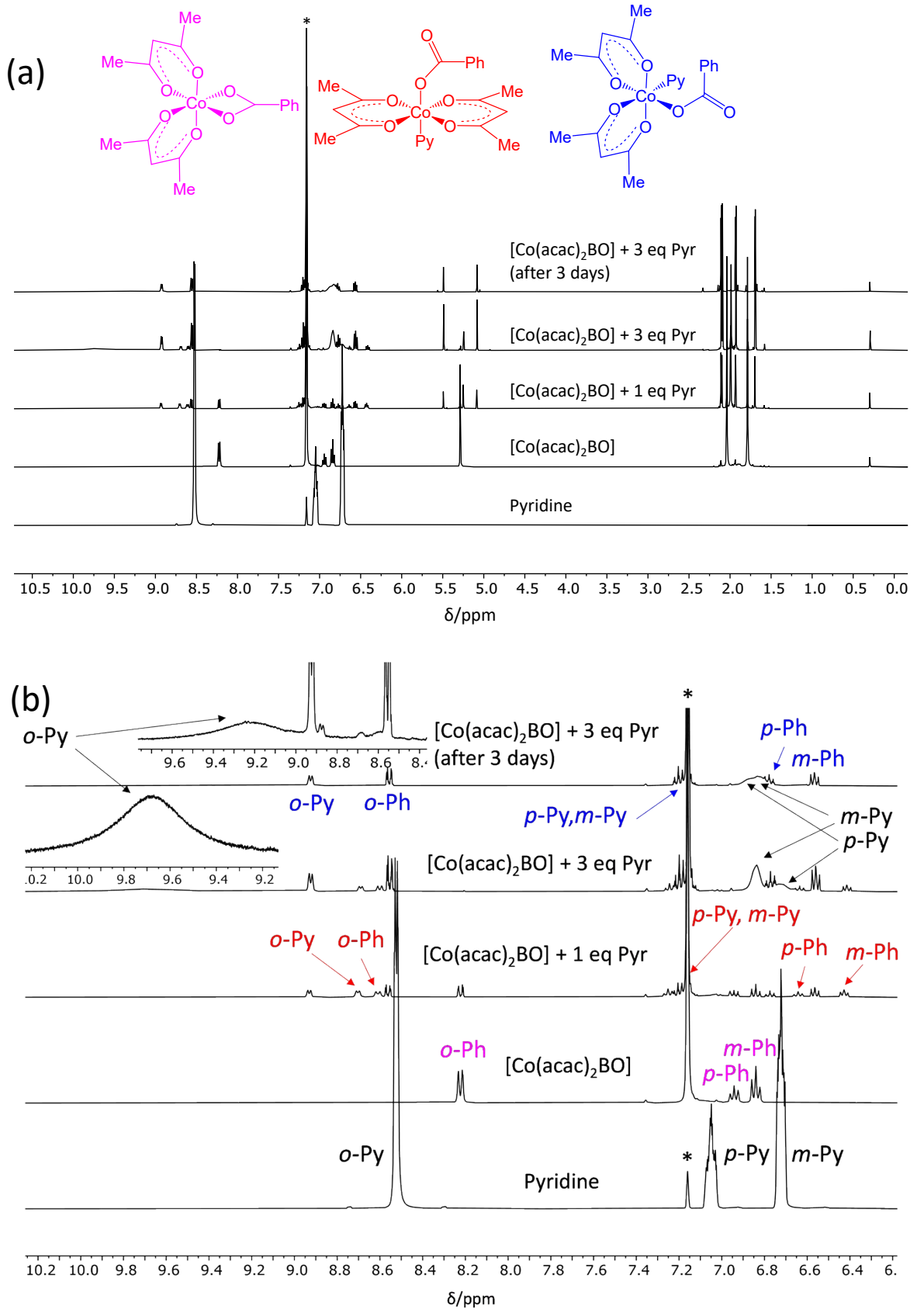


Figure S 16. ^{1}H NMR (400 MHz) investigation of the interaction between $[Co^{III}(acac)_2(O_2CPh)]$ and pyridine. Solvent = C_6D_6. (a) Full spectra. (b) Expansions in the aromatic region. The residual solvent resonance is labelled with an asterisk.

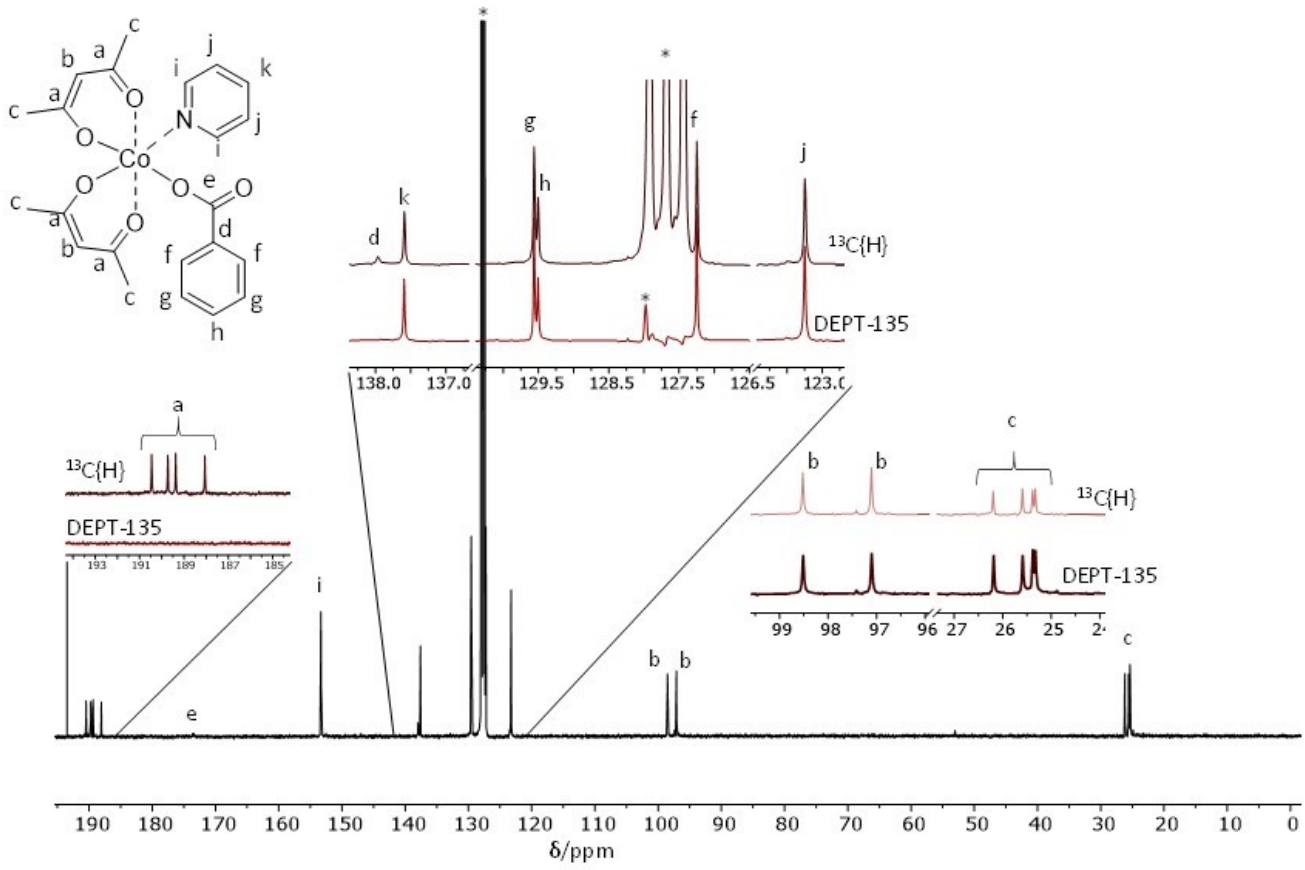


Figure S 17. $^{13}C\{^{1}H\}$ NMR spectrum (with DEPT-135 in selected expanded regions) of the product of the $[Co^{III}(acac)_2(O_2CPh)]$-pyridine reaction, after evaporation to dryness to remove the excess pyridine and redissolution in C_6D_6. The solvent resonances in both spectra are labelled with an asterisk.

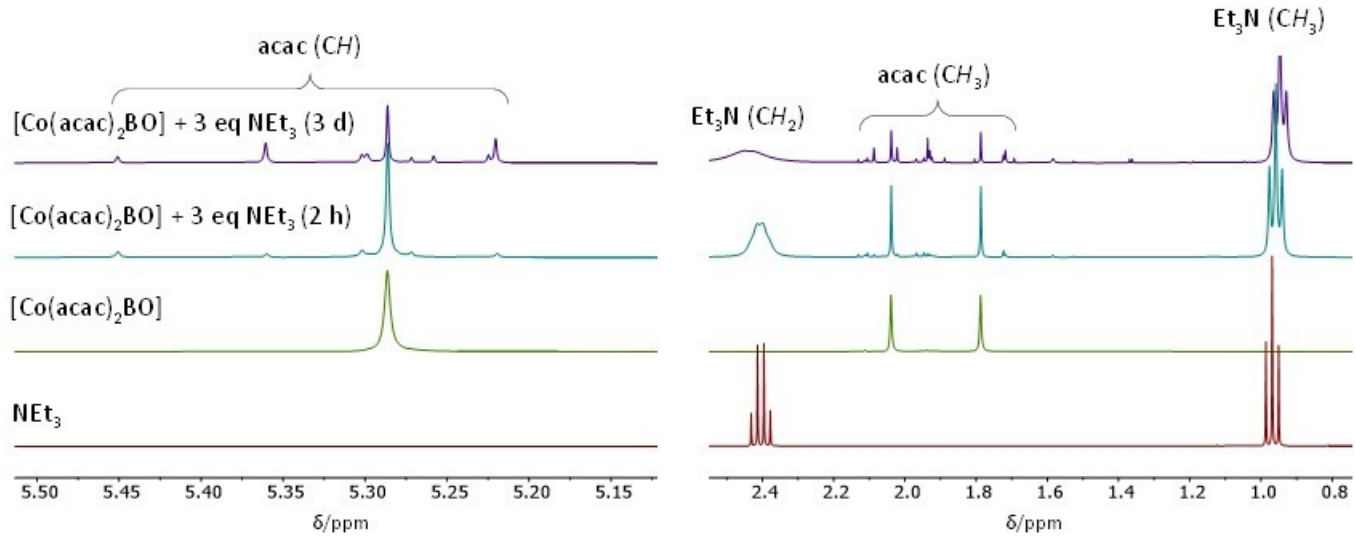


Figure S 18. Expansions of the acac CH and Me regions of the ^{1}H NMR (400 MHz) spectra recorded for the interaction between $[Co^{III}(acac)_2(O_2CPh)]$ and NEt_3. Solvent = C_6D_6.

GPC of PVAc obtained in the presence of pyridine

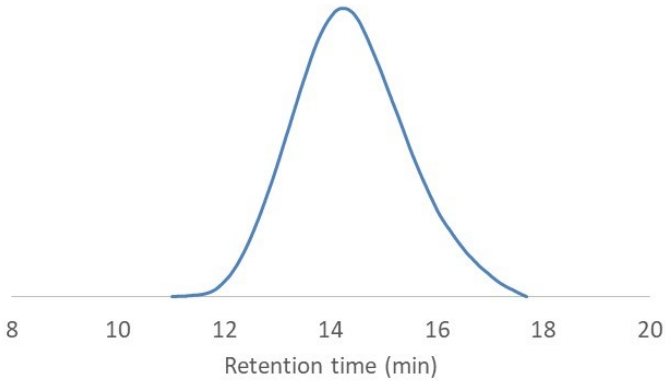


Figure S 19. GPC of the product of the VAc polymerisation at 60 °C initiated by [$Co^{III}(acac)_2(O_2CPh)$] in the presence of pyridine (30 equivalents).

Reaction between BPO and NEt_3

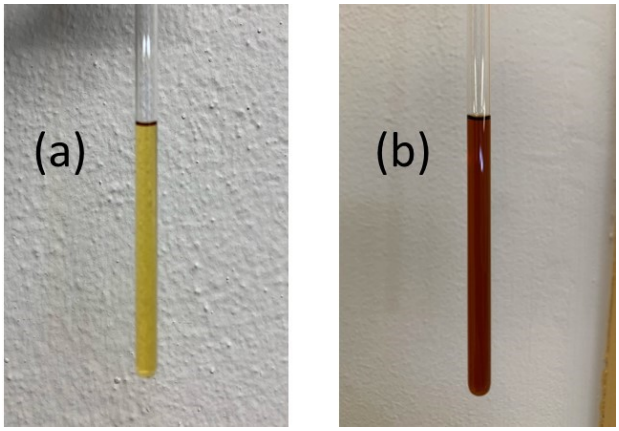


Figure S 20. Photos of the NMR tube containing BPO (5 mg, 0.026 mmol) and NEt_3 (6.2 mg, 0.062 mmol) in C_6D_6. (a) Immediately after mixing. (b) After heating at 40 °C for 2 h.

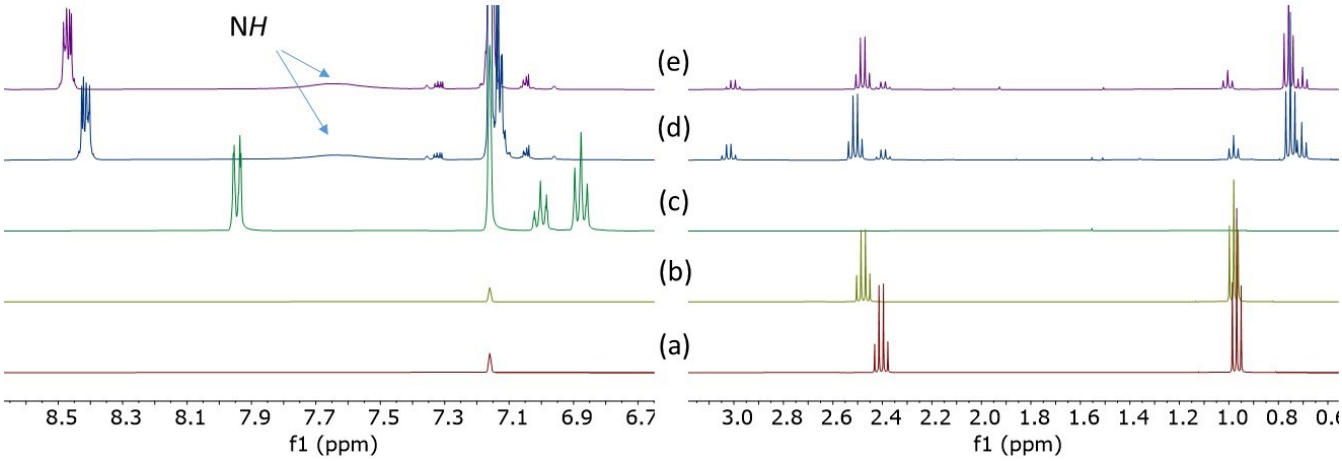


Figure S 21.^{1}H NMR investigation of the reaction between BPO and NEt_3 (conditions given in Figure S 20). (a) Et_3N; (b) Et_2NH; (c) BPO. (d) BPO + NEt_3 after mixing at room temperature (photo in Figure S 20a); (e) As (d), after 2 h at 40 °C (photo in Figure S 20b).

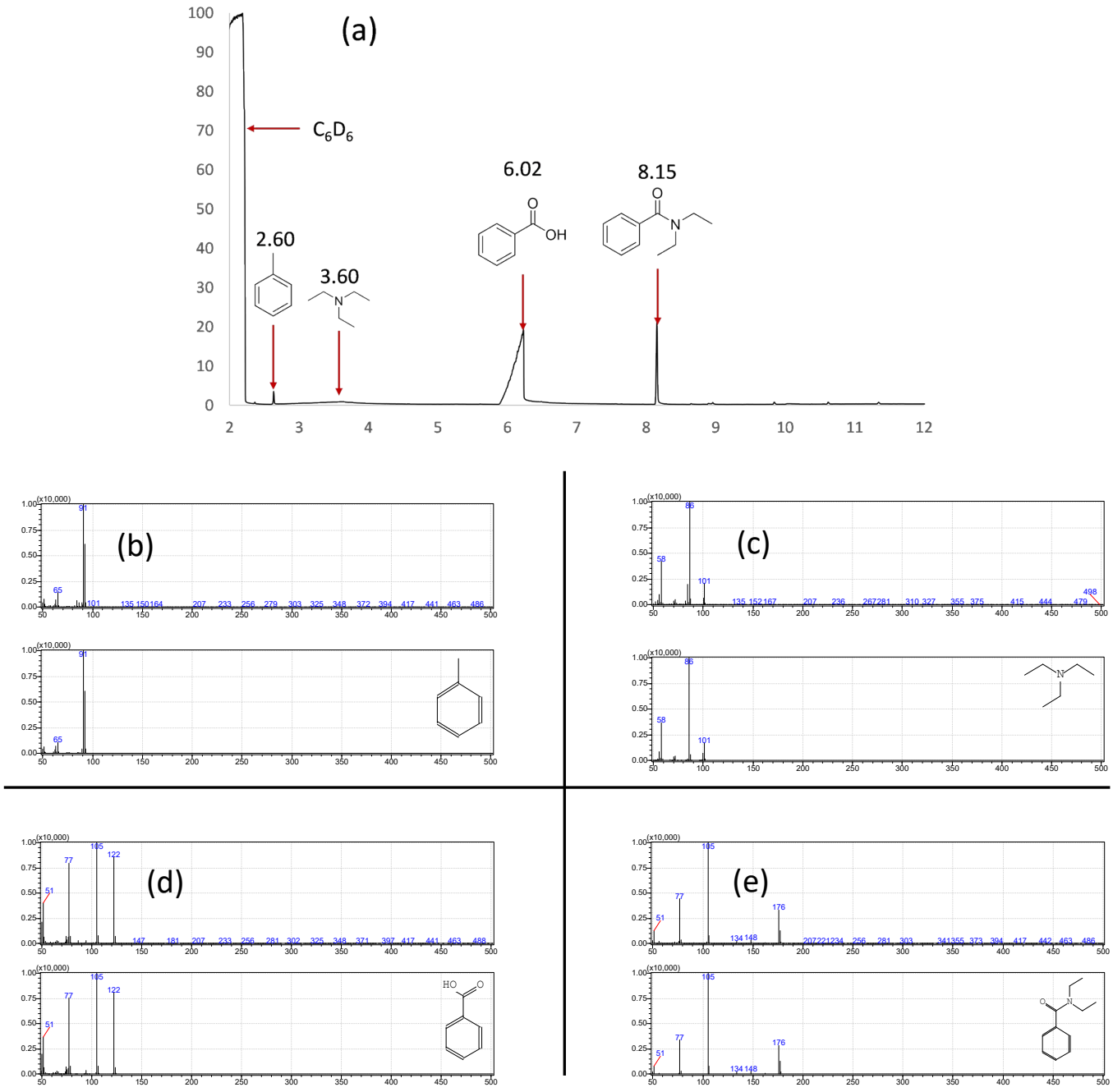


Figure S 22.GG-MS investigation of the reaction between BPO and NEt_3 (conditions given in Figure S 20). (a) GC trace. Experimental (above) and simulated (below) MS of: (b) GC peak at 2.60 min; (c) GC peak at 3.60 min; (d) GC peak at 6.02 min; (e) GC peak at 8.15 min.

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Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, **2009**.

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