Electronic Supplementary Material (ESI) for Chemical Science.

Supplementary Information

Mechanochemical and slow-chemistry radical transformations: A case of diorganozinc compounds and TEMPO

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1. Experimental Details

1.1. General Methods

All reactions were conducted under an inert gas atmosphere (nitrogen or argon) using standard Schlenk techniques. Di-*tert*-butylzinc (MP 28.8 °C; BP 34-35°C (9 Torr))[1] was prepared according the literature procedure.[2] Commercially available (ABCR) 99 % diphenylzinc (MP 102-106 °C;[3,4] BP 280-295 °C[5]) was used. Commercially available 98% TEMPO (Sigma-Aldrich) was further purified (99.9 %) by sublimation under inert gas atmosphere. Solvents were carefully dried and distilled over Na/K alloy prior to use.

1.2. Instrumentation

Single Crystal X-Ray Diffraction (XRD)

The crystals were selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. The X-ray data for complexes $\mathbf{1_2}$ and $\mathbf{3_2}$ were collected at 100(2)K on a SuperNova Agilent diffractometer using using graphite monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). The data were processed with *CrysAlisPro*[6]. The X-ray data for complex **2** were collected on a Nonius Kappa CCD diffractometer.[7] using graphite monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with *DENZO* and *SCALEPACK* (*HKL2000* package)[8]. The structure was solved by direct methods using the SHELXS-97 program and was refined by full matrix least–squares on F^2 using the program SHELXL.[9] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. In comp1 all atomic displacement parameters belonging to disordered residues were restrained to the same value with similarity restraint SIMU and enhanced rigid bond restraints: RIGU, DELU, DANG and DFIX. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Powder X-Ray Diffraction (PXRD)

PXRD patterns were collected on the PANalytical Empyrean diffractometer equipped with 1D X'Celerator detector. Measurements employed Ni-filtered Cu Kα radiation of a copper sealed tube (40 kV, 40 mA). Samples were sealed between two layers of polymer foil in an inert gas atmosphere and measured in a transmission geometry. Diffraction patterns were measured in the 2θ range of 5 – 40 degrees with a step size of 0.008 degree.

Fourier-Transform infrared attenuated total reflectance (FTIR-ATR)

FT-IR spectra were acquired on Bruker TENSOR II FTIR Spectrometer.

Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR spectra were acquired on Varian Inova 500 MHz and Varian Mercury 400 MHz spectrometer. Chemical shifts are expressed in δ (ppm). The following abbreviations are used for NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, br = broad and m = multiplet.

Electron Paramagnetic Resonance Spectroscopy (EPR)

EPR measurements were performed with a Bruker ELEXSYS 500 spectrometer (Jagiellonian University, Cracow, Poland) operating in X-band (9.5 GHz) at modulation frequency 100 kHz, modulation amplitude 0.3 mT and microwave power 0.3–3.0 mW.

2. NMR spectra

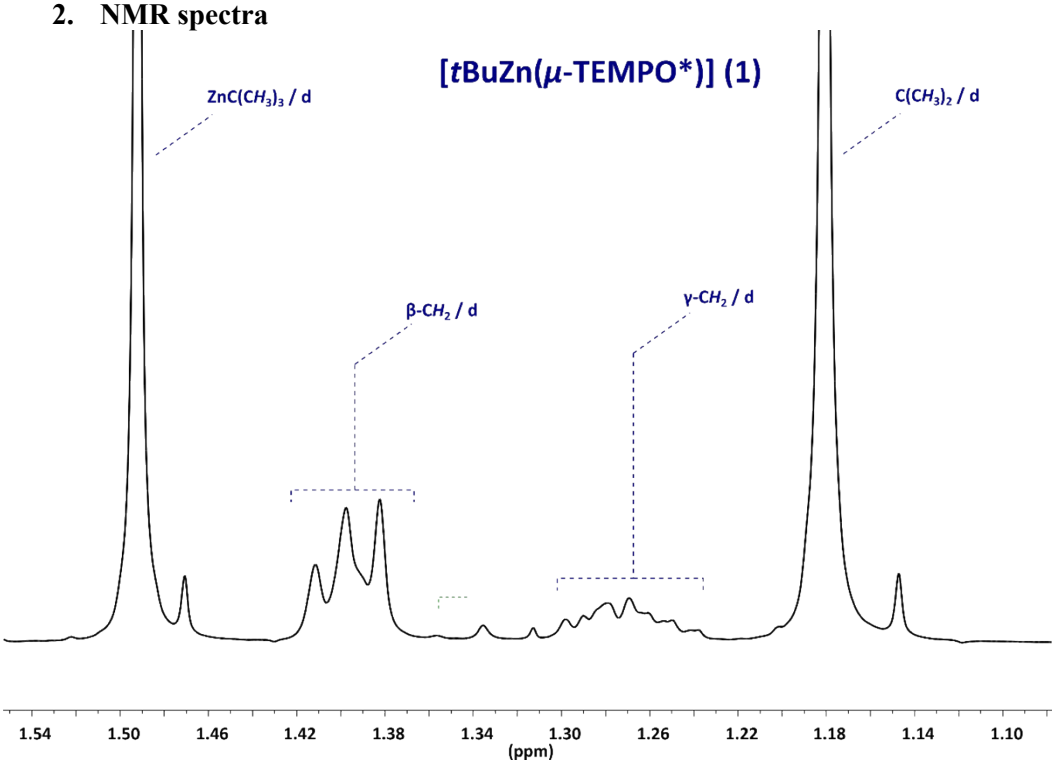

Figure S1. ^{1}H NMR spectrum of **1** in benzene-d$_6$ at 25 °C.

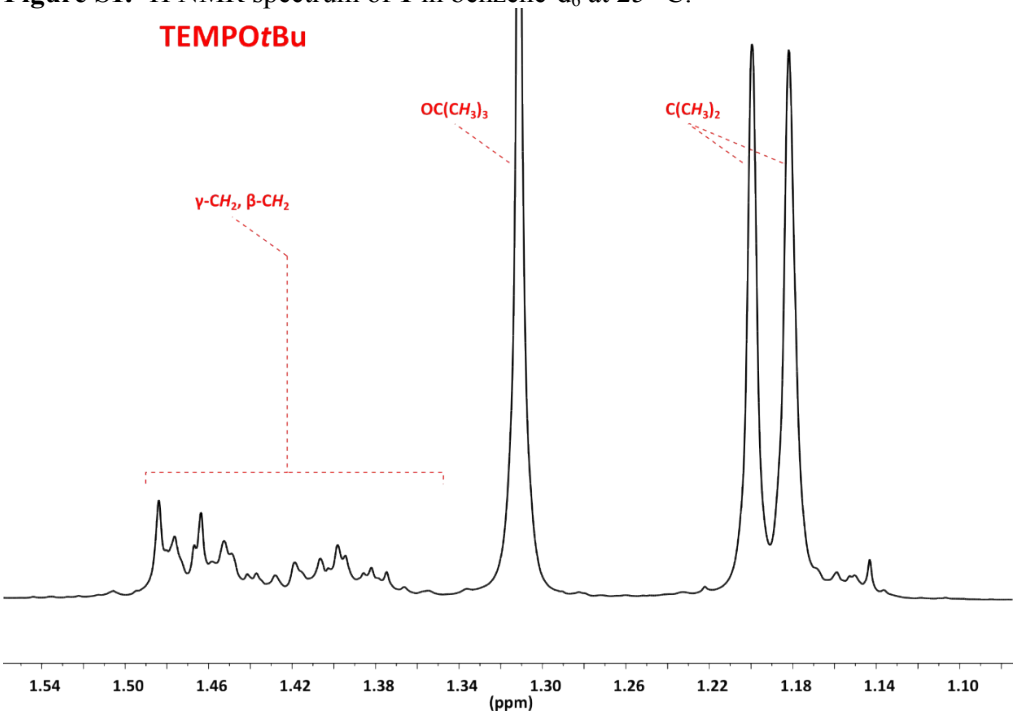

Figure S2. ^{1}H NMR spectrum of TEMPO*t*Bu in benzene-d$_6$, at 25 °C. TEMPO*t*Bu was separated from **1$_2$** by crystallization of **1$_2$** from the crude post-reaction mixture. ^{1}H NMR (benzene-*d$_6$*, 400 MHz, 25 °C, ppm): δ 1.50-1.36 (br. m. 6H; *β*-CH$_2$, *γ*-CH$_2$), 1.31 (s, 9H; OC(C*H*$_3$)$_3$), 1.20 (s, 6H; C(C*H*$_3$)$_2$), 1.18 (s, 6H; C(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (benzene-d$_6$, 400 MHz, 20 °C, ppm): δ 77.41 (O*C*(CH$_3$)$_3$), 59.43 (*C*(CH$_3$)$_2$), 29.7 (OC(*C*H$_3$)$_3$), 41.19 (TEMPO*t*Bu-ring), 35.18 (OC(*C*H$_3$)$_3$), 29.70 (C(*C*H$_3$)$_2$), 20.71 (TEMPO*t*Bu-ring).

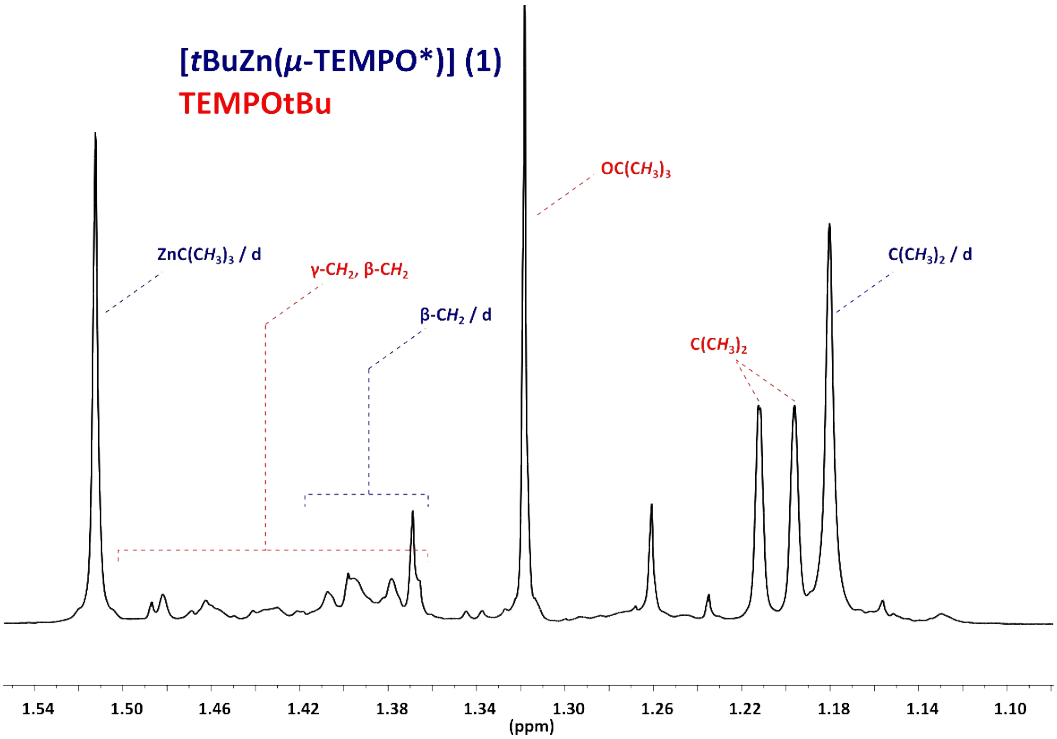

Figure S3. ^{1}H NMR spectrum of the crude products mixture obtained in mechanochemical reaction between *t*Bu$_2$Zn and 2 equiv. of TEMPO, dissolved in benzene-d_6 at 25 °. The proportion of TEMPO*t*Bu to **1** and **1$_2$** was determined by comparing the relative intensities of signals assigned to OC(*C*H$_3$)$_3$ (1.32 ppm, s) of TEMPO*t*Bu and the sharp signal of *t*BuZn(TEMPO) – ZnC(C*H*$_3$)$_3$ (1.17 ppm, s).

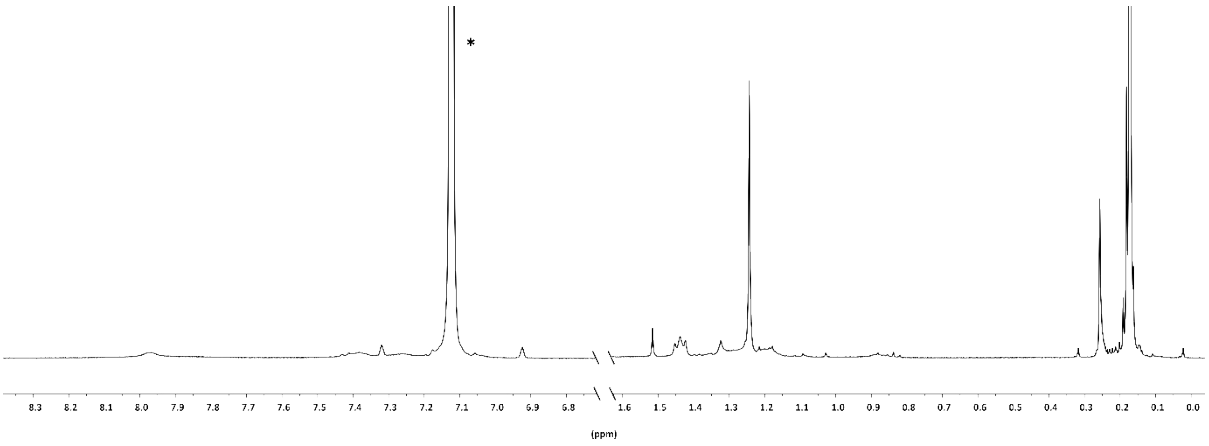

Figure S4. ^{1}H NMR spectrum of **2**•TEMPO in benzene-d_6 at 25 °C. C,H,N analysis (%) calcd for $C_{30}H_{46}N_2O_2Zn_1$: C 67.72, H 8.71, N 5.26; found: C 67.75, H 8.68, N 5.24.

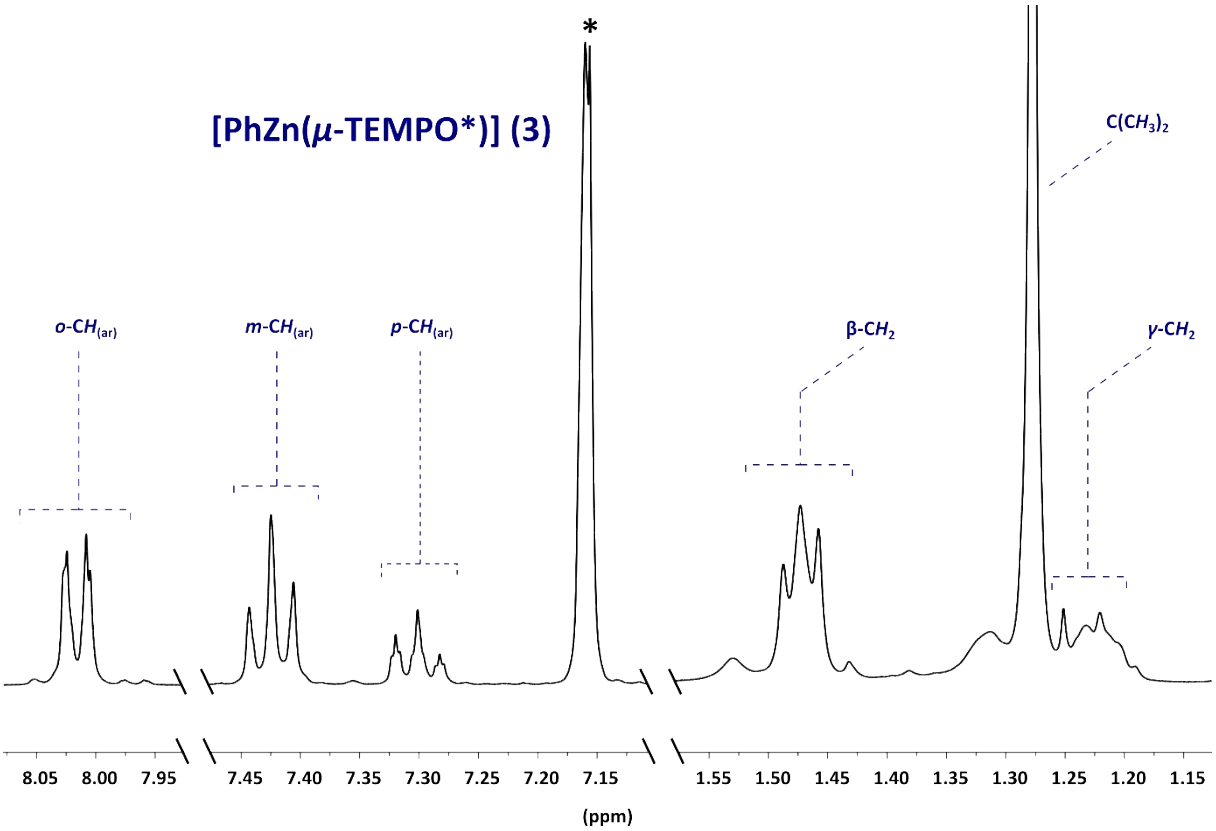

Figure S5. ^{1}H NMR spectrum of **3** in benzene-d_6 at 25 °C.

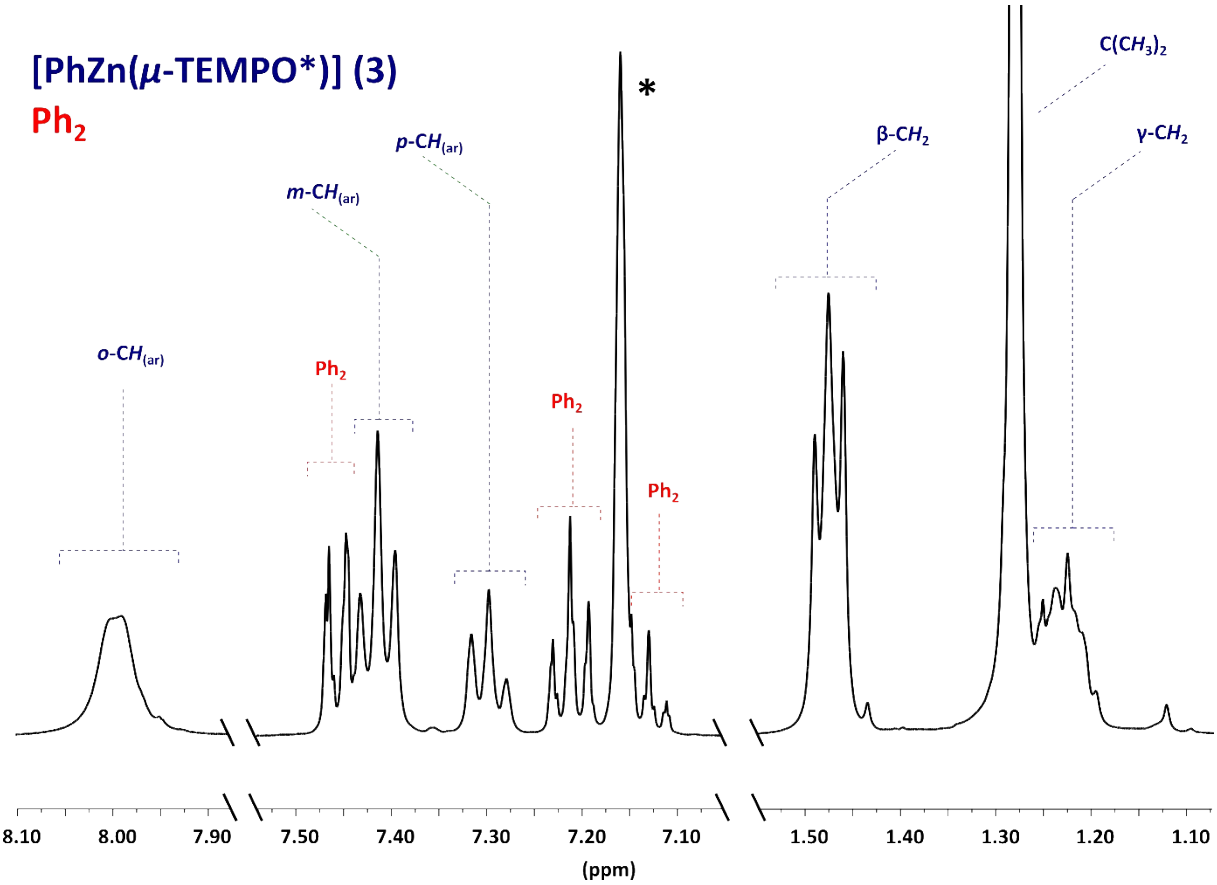

Figure S6. ^{1}H NMR spectrum of post-reaction mixture obtained from Ph_2Zn/TEMPO (1:1) slow chemistry reaction system after 21 days**,** benzene-d_6, 25 °C (* indicates the residual signal of benzene-d_6).

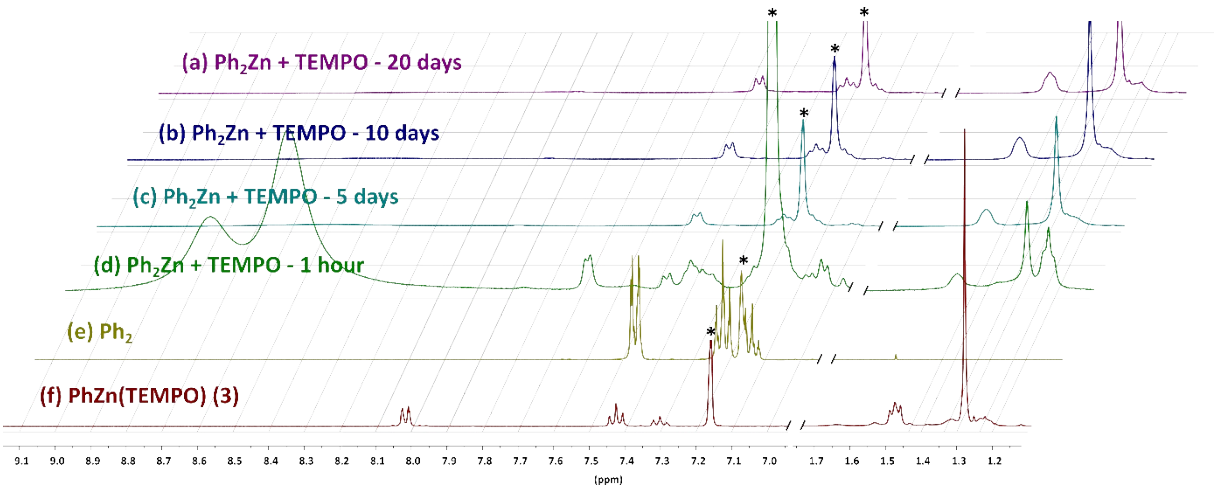

Figure S7. ^{1}H NMR spectra obtained from Ph_2Zn/TEMPO (1:1) solution reaction system as a function of time**,** in benzene-d_6, 25 °C (* indicates the residual signal of benzene-d_6) obtained after: (a) 20 days; (b) 10 days; (c) 5 days; (d) 1 hour; (e) ^{1}H NMR spectrum of Ph_2 (for comparison); (f) ^{1}H NMR spectrum of **3** (for comparison).

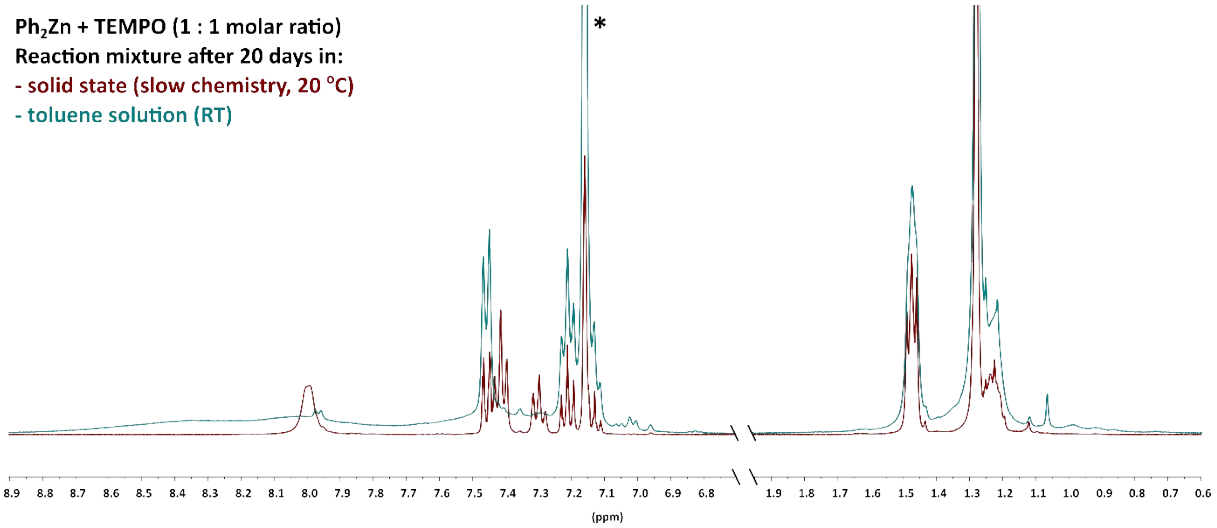

Figure S8. Comparison of ^{1}H NMR spectra obtained from the post-reaction mixtures of Ph_2Zn/TEMPO (1:1) slow chemistry and solution reaction systems, after 20 days, benzene-d_6, 25 °C (* indicates the residual signal of benzene-d_6).

3. PXRD patterns

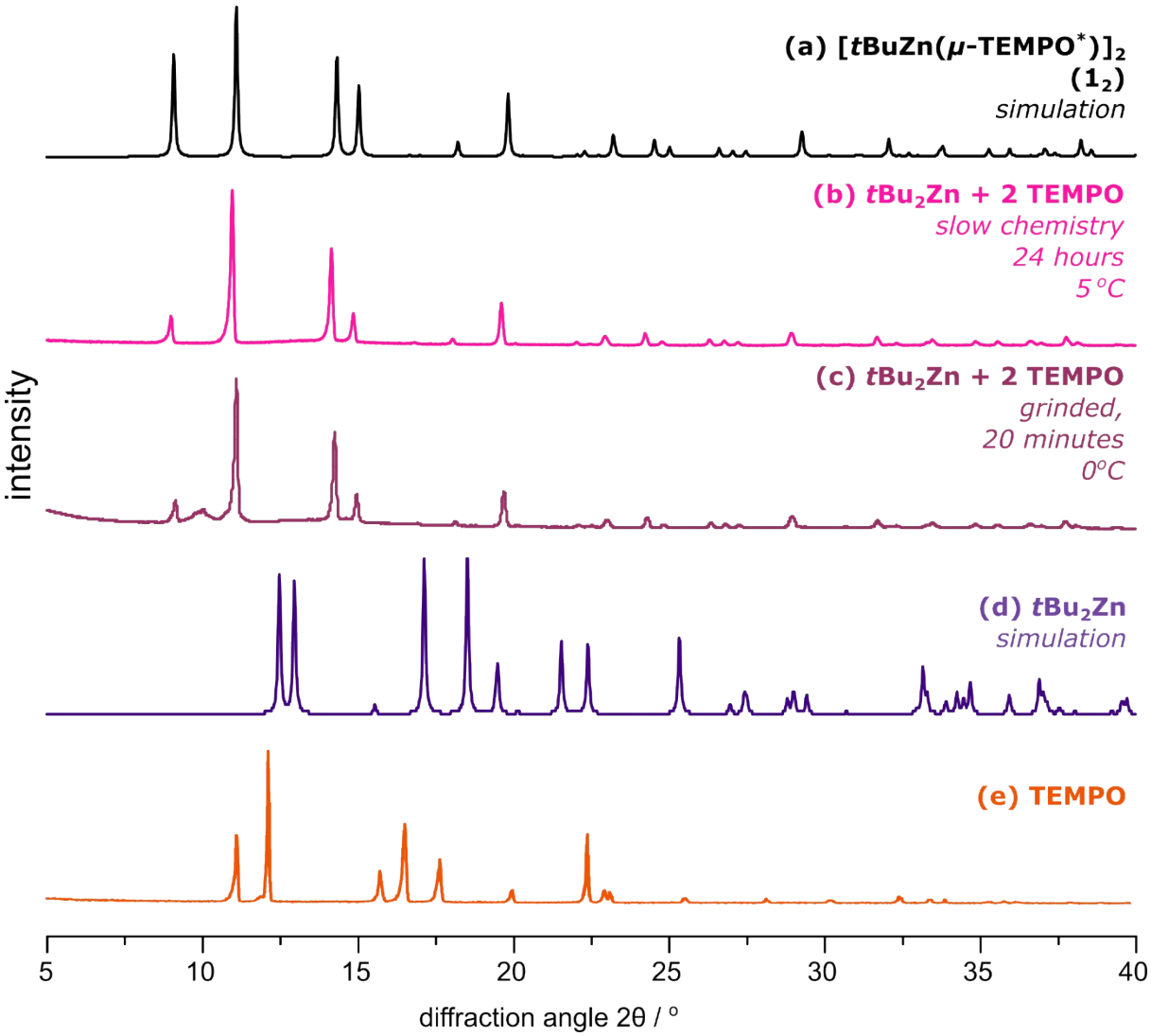

Figure S9. Comparison of the experimental and simulated PXRD patterns for the reactions between tBu$_2$Zn and TEMPO: (a) the simulated PXRD spectrum of **1**$_2$; (b) tBu$_2$Zn and 2 equivalents of TEMPO gently mixed with a needle and stored at 5 °C for 24 hours; (c) tBu$_2$Zn grinded with 2 equivalents of TEMPO with a glass rod for 20 minutes at 0 °C; (d) the simulated PXRD spectrum of tBu$_2$Zn;[2] (e) TEMPO.

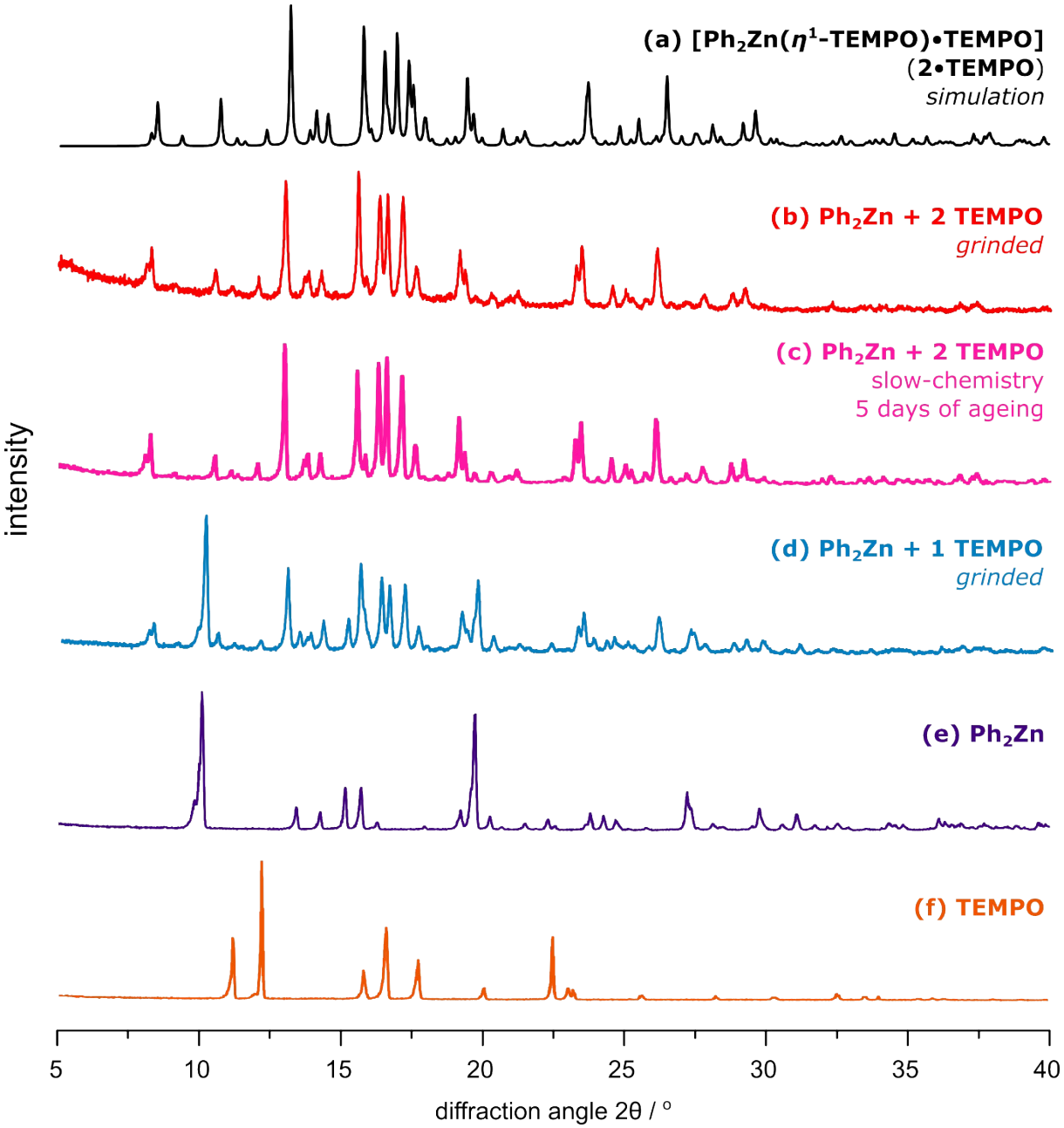

Figure S10. Comparison of the experimental and simulated PXRD patterns for the mechanochemical and slow-chemistry reactions between Ph_2Zn and TEMPO, leading to **2**•TEMPO: (a) the simulated PXRD spectrum of **2**•TEMPO; (b) Ph_2Zn and 2 equivalents of TEMPO grinded in a ball mill for 15 minutes at RT; (c) Ph_2Zn gently mixed with 2 equiv. of TEMPO and stored under inert gas atmosphere at 20 °C for 5 days; (d) Ph_2Zn grinded with 1 equivalent of TEMPO in a ball mill for 15 minutes at RT; (e) Ph_2Zn; (f) TEMPO.

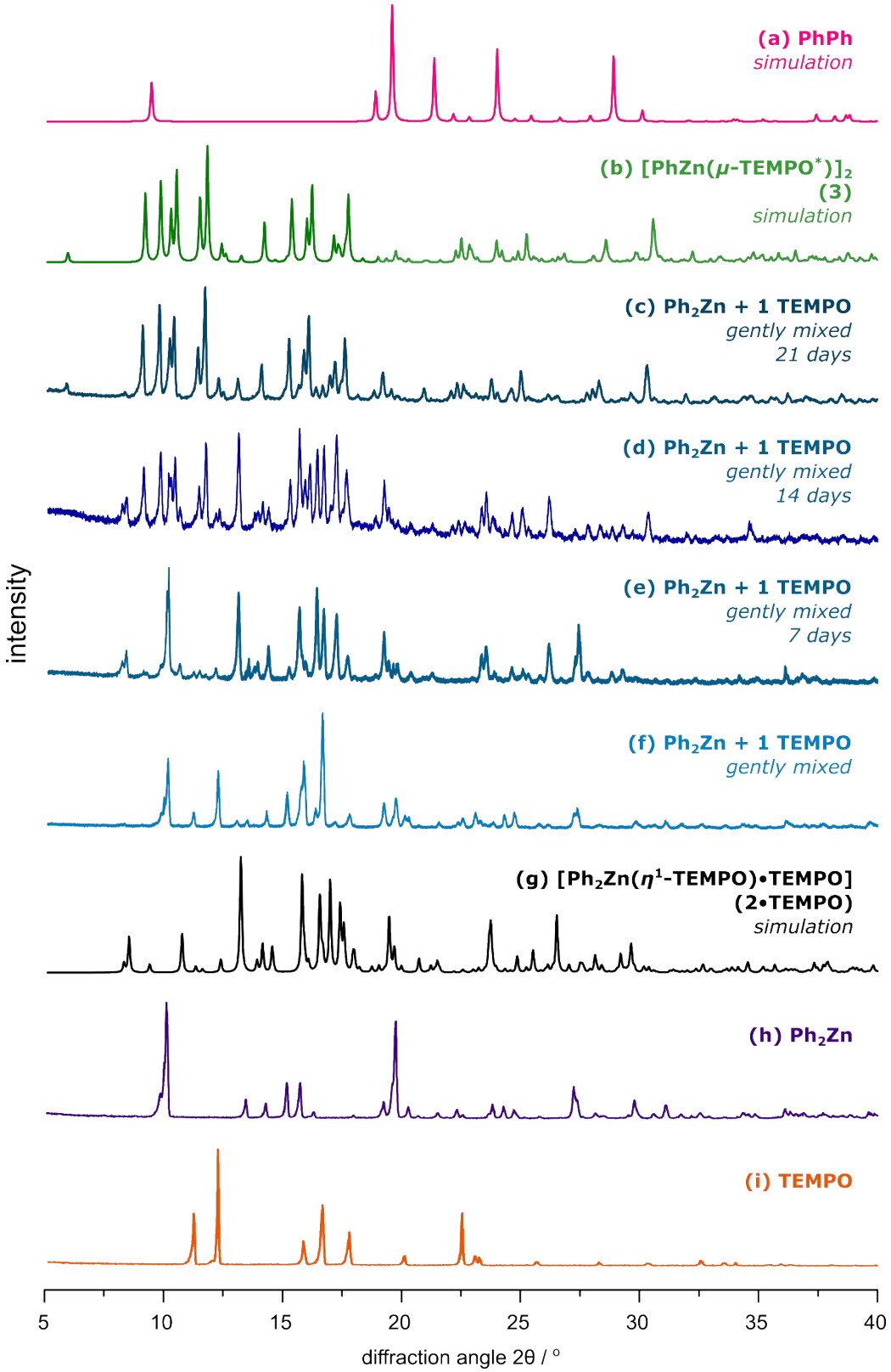

Figure S11. Comparison of the experimental and simulated PXRD patterns for the slow chemistry reactions of TEMPO with Ph_2Zn (substrates initially gently mixed): (a) the simulated PXRD spectrum of PhPh;[10] (b) the simulated PXRD spectrum of $\mathbf{3_2}$; (c) Ph_2Zn gently mixed with 1 equivalent of TEMPO, stored for 21 days at 20 °C; (d) Ph_2Zn gently mixed with 1 equivalent of TEMPO, then stored for 14 days at 20 °C; (e) Ph_2Zn gently mixed with 1 equivalent of TEMPO, then stored for 7 days at 20 °C; (f) Ph_2Zn gently mixed with 1 equivalent of TEMPO; (g) the simulated PXRD spectrum of **2**•TEMPO; (h) Ph_2Zn; (i) TEMPO.

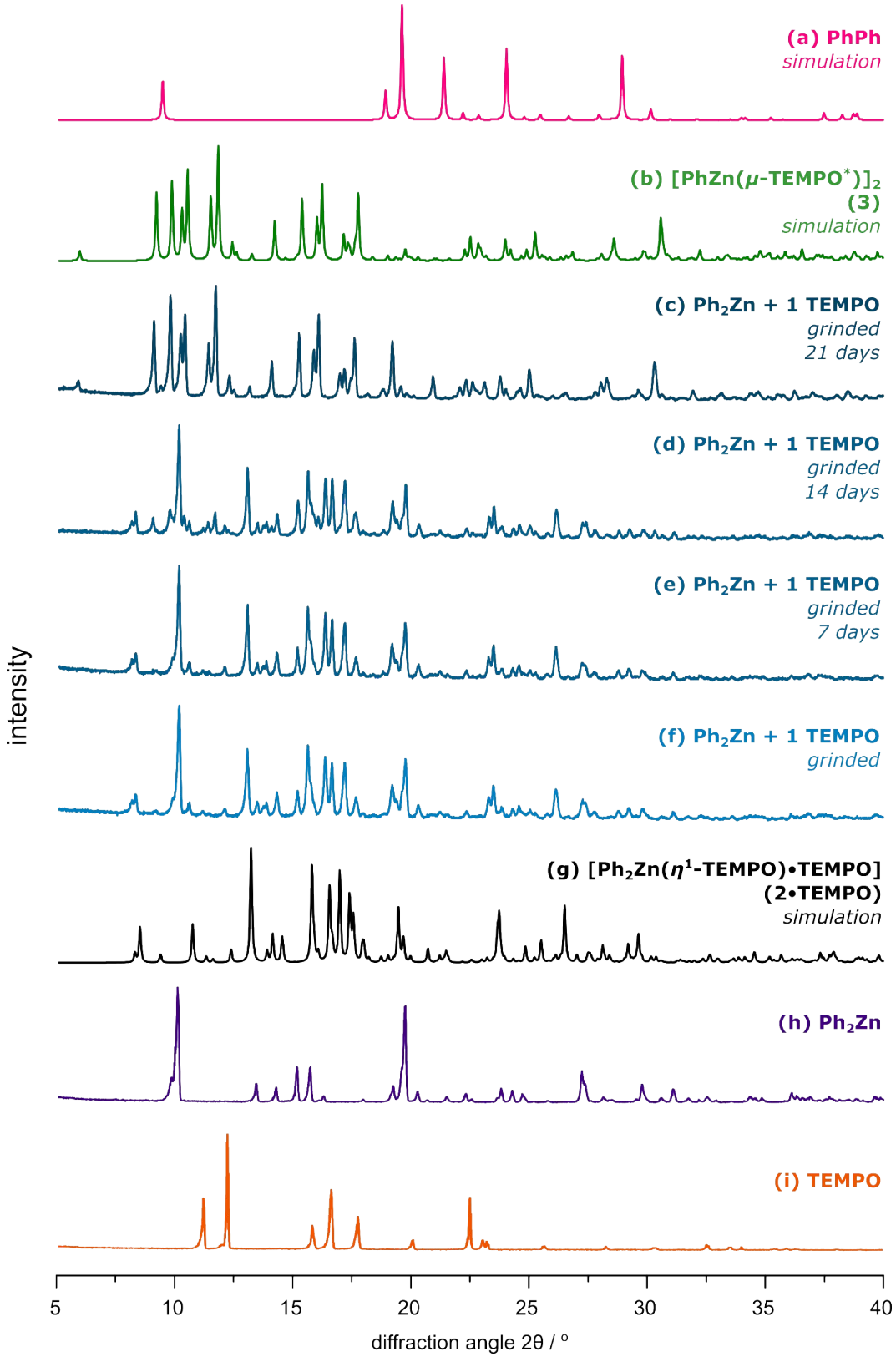

Figure S12. Comparison of the experimental and simulated PXRD patterns for the slow chemistry reactions of TEMPO with Ph_2Zn (substrates initially grinded): (a) the simulated PXRD spectrum of PhPh;[10] (b) the simulated PXRD spectrum of $\mathbf{3_2}$; (c) Ph_2Zn grinded with 1 equivalent of TEMPO, then stored at 20 °C for 21 days; (d) Ph_2Zn grinded with 1 equivalent of TEMPO, then stored at 20 °C for 14 days; (e) Ph_2Zn grinded with 1 equivalent of TEMPO, then stored at 20 °C for 7 days; (f) Ph_2Zn grinded with 1 equivalent of TEMPO; (g) the simulated PXRD spectrum of **2**•TEMPO; (h) Ph_2Zn; (i) TEMPO.

4. EPR spectra

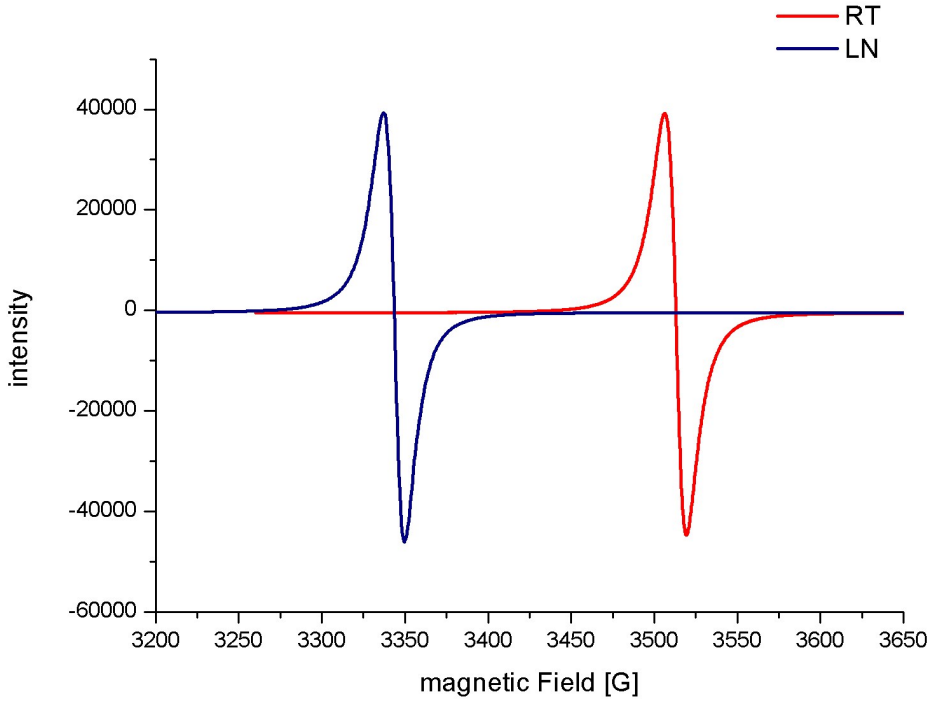

Figure S13. EPR spectrum of **2**•TEMPO at: 25 °C (RT, red line, g = 2.0069); −196 °C (LN, blue line, g = 2.0062).

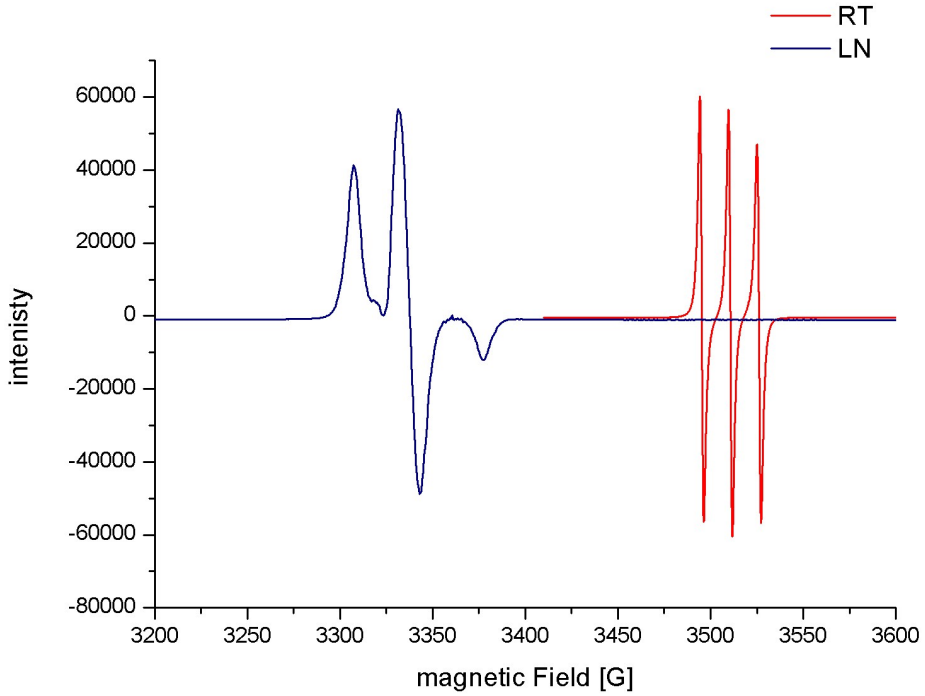

Figure S14. EPR spectrum of toluene solution of **2**•TEMPO at: 25 °C (RT, red line, g = 2.0061, a = 15.45 G); −196 °C (LN, blue line, B = 351.2903 mT).

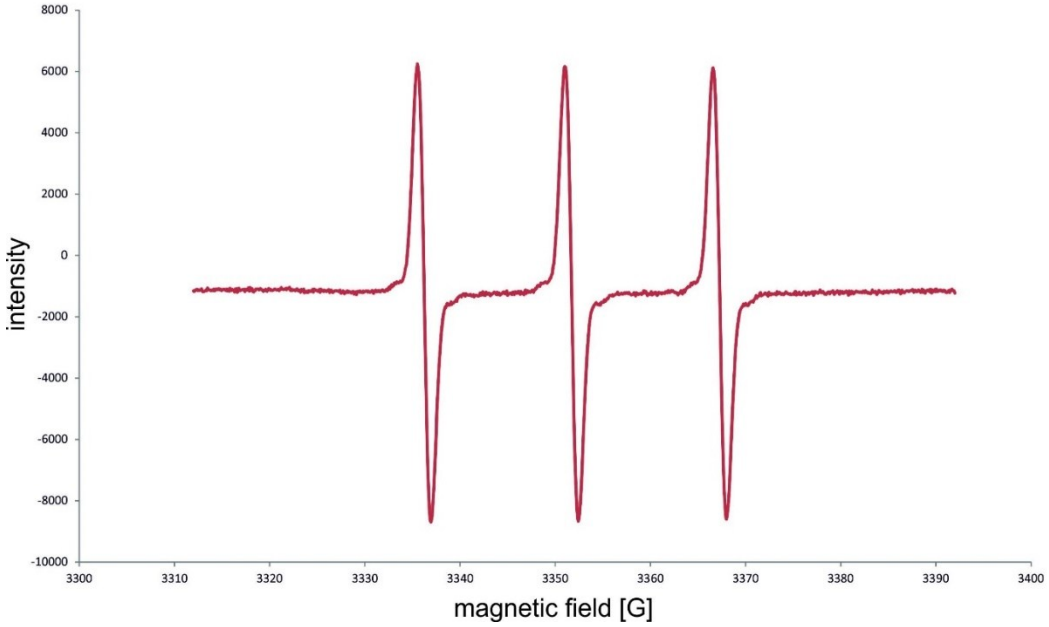

Figure S15. EPR spectrum (0 °C, toluene) obtained from crude product mixture of reaction between Ph_2Zn and TEMPO (1:1) in toluene solution after 21 days in toluene at RT.

5. IR spectra

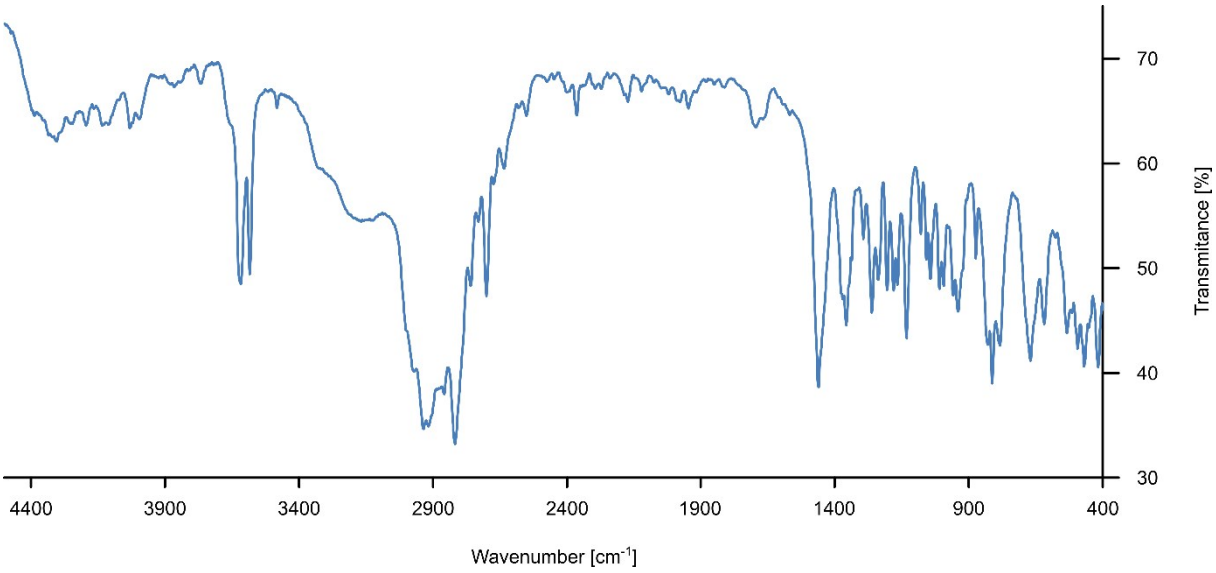

Figure S16. IR spectrum of $\mathbf{1}_2$ at 20 °C.

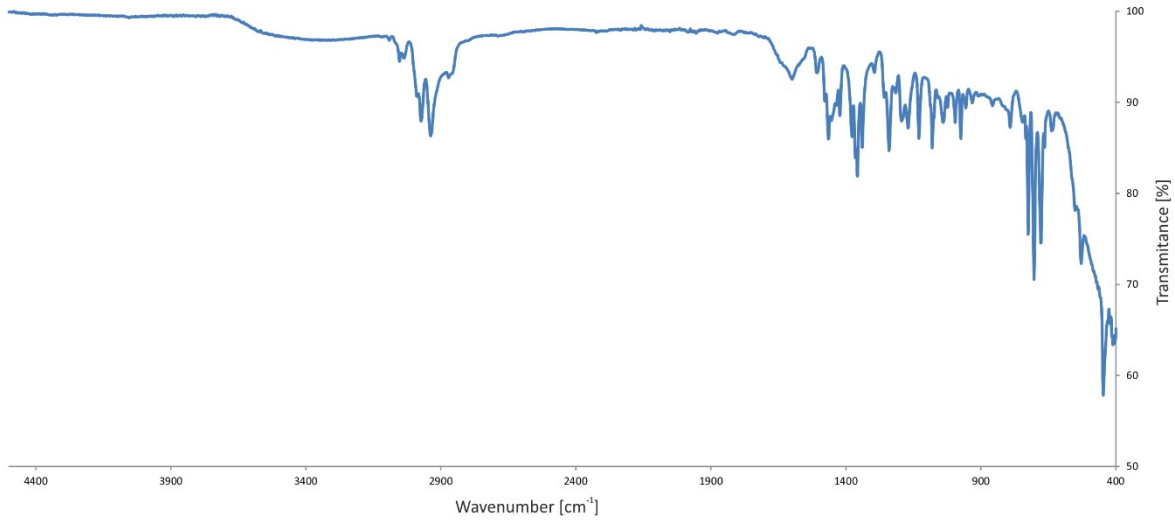

Figure S17. IR spectrum of **2**•TEMPO at 20 °C.

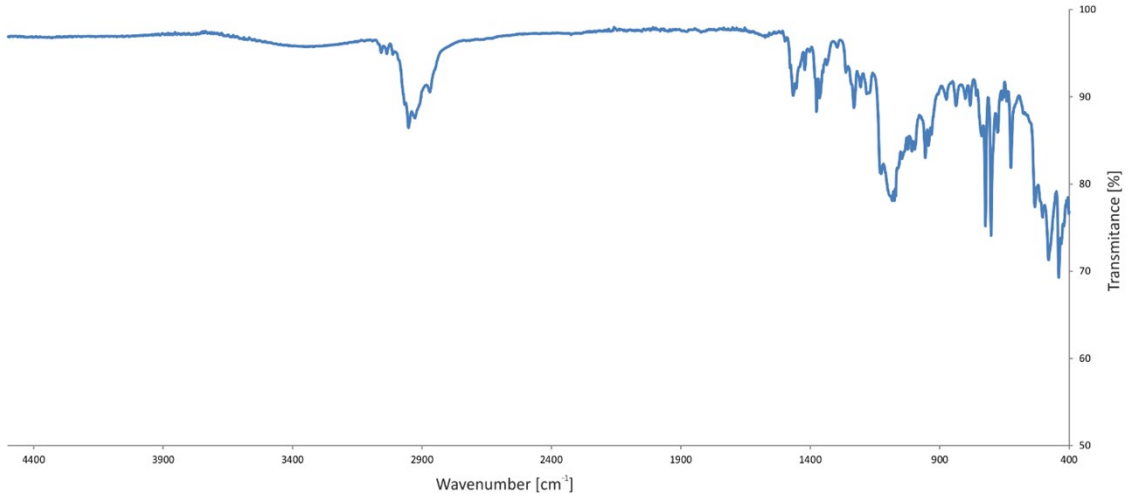

Figure S18. IR spectrum of **3** at 20 °C.

6. DOSY measurements

As already discussed in antecedent works molecular weight can be straightforwardly obtained by combining Stokes-Einstein equation ($D = (kT) / (6\pi\eta r_H)$) and the relationship between molecular weight M and molar radius, which reads $M = (4\pi r_M^3 \rho N_A)/3$, where r_H and r_M are hydrodynamic and molar radii respectively, η is viscosity and ρ is density of the liquid.[1] It has also been shown that these quantities are much alike for small molecules, which is the case in our system, although it has to be noted that such estimation can lead to errors in the range of 10-20%. This is, however, accurate enough for the purposes of assessing the aggregation state of the complexes we deal with. DOSY measurement was performed in dry and oxygen-free toluene-d_8 as we exploited the fact that the physical properties of the diluted solution, namely density and viscosity, deviate only slightly from properties of the pure solvent.

Table S1. Diffusion coefficient of [*t*BuZn(μ-TEMPO*)] (**1**$_2$) and [PhZn(μ-TEMPO*)]$_2$ (**3**); estimated hydrodynamic radii and molecular weights (MW).

Formula	MW_{calcd} / g/mol	$D \cdot 10^{10}$ m^2/s	$D_{average} \cdot 10^{10}$ m^2/s	r / Å	MW_{exp} / g/mol
[*t*BuZn(μ-TEMPO)]	278.77	7.95, 7.37	7.66	4.49	190 ± 28
[PhZn(μ-TEMPO)]	298.76	7.95, 6.69	7.32	5.46	354 ± 35

7. GC-MS analysis of post-reaction mixture of TEMPO and Ph_2Zn

This analysis was conducted to identify the amount of PhPh formed in the reaction between Ph2Zn and TEMPO in toluene solution within 20 days.
In Schlenk flask 0.694 mmol of solid TEMPO (106 mg) and 0.694 mmol (152 mg) of diphenylzinc were dissolved in toluene (8 ml), forming clear yellow solution. The mixture was mixed for over 3 weeks at room temperature. Then 2 ml (of total 8 ml) of the solution were mixed with water solution of KF and extracted with diethyl ether. The organic phase was introduced with 0.0714 mmol of cycloheptanone (8 mg, 1 ml of toluene solution) was added and dried over $MgSO_4$.
The reaction between TEMPO and Ph_2Zn runs according to the equation below:

$$2\ Ph_2Zn + 2\ TEMPO \rightarrow 2\ PhZn(TEMPO) + Ph_2$$

For potential 100 % conversion, 2 ml of the post-reaction mixture should contain $0.694 \cdot 2 / 8 = 0.174$ mmol of PhZn(TEMPO) and $0.174 / 2 = 0.0867$ mmol of Ph_2.
According to the GC-MS results obtained Ph_2 to cycloheptanone ratio is: 22699553 to 53072036, that equals 0.4277, which means that the organic phase contained $0.4277 \cdot 0.0714$ mmol = 0.03054 mmol of Ph_2, that is approximately 35 % of the expected amount.

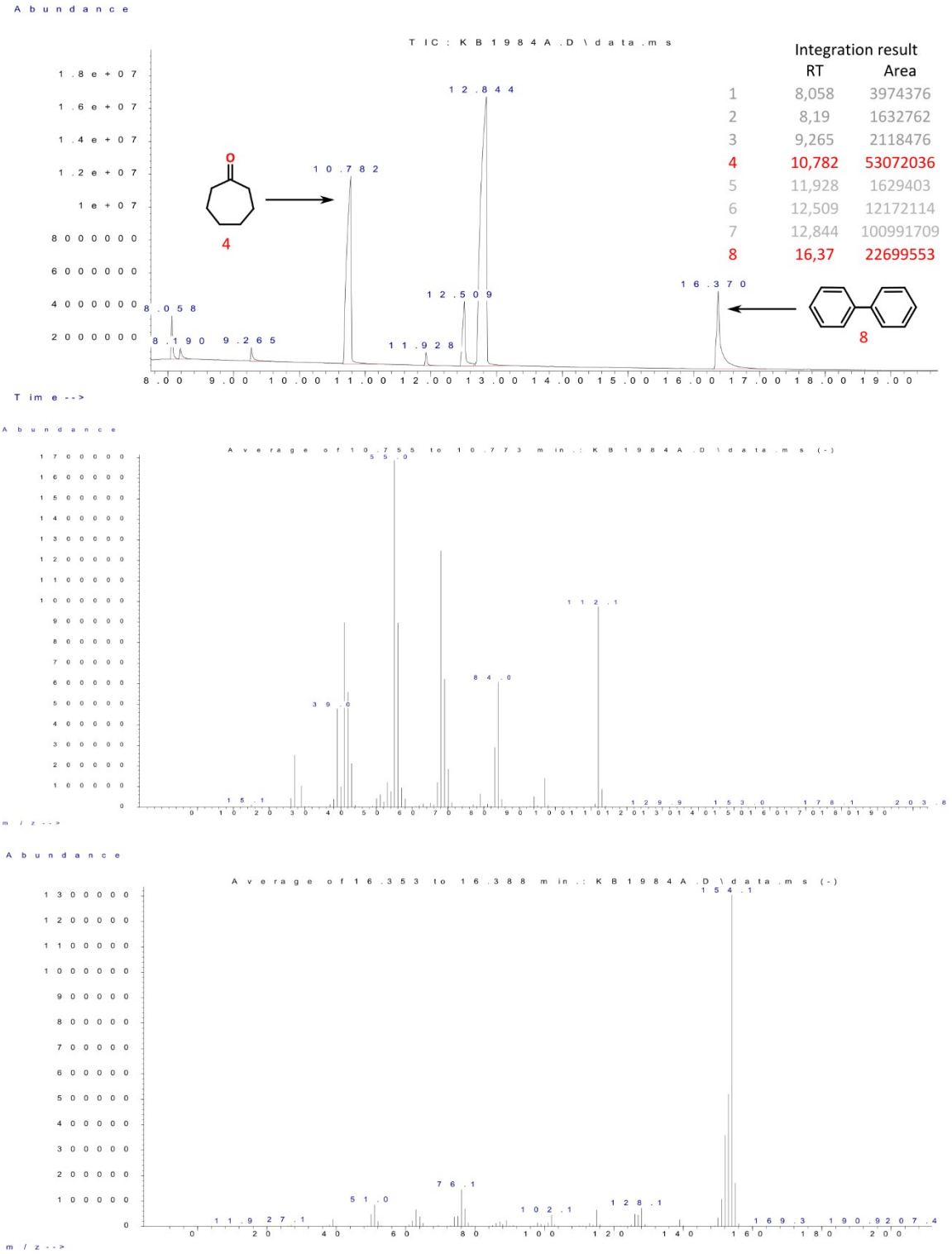

Figure S19. GC-MS results for the solution-method post-reaction (20 days) mixture of TEMPO and Ph_2Zn in toluene, with cycloheptanone as an internal reference.

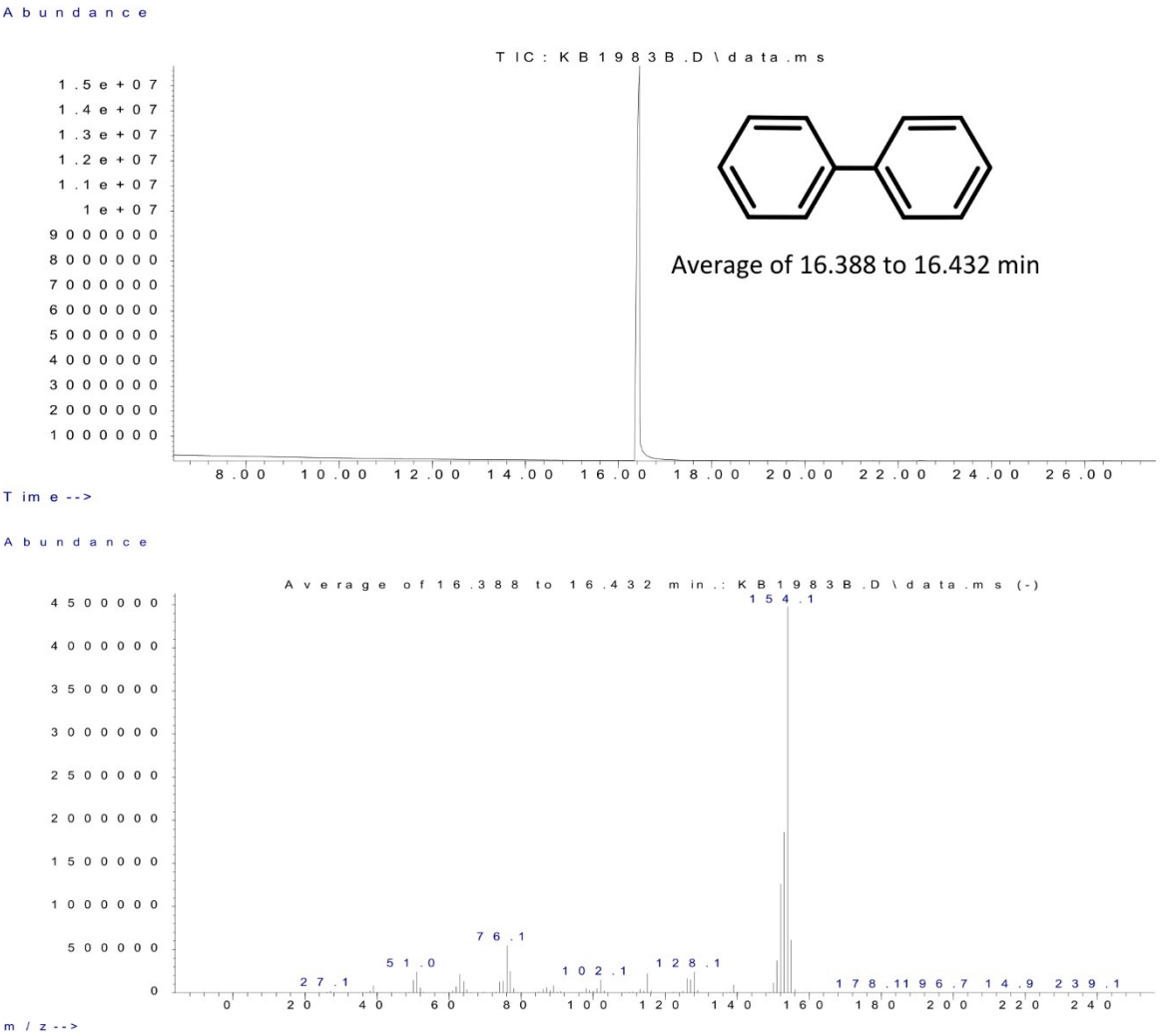

Figure S20. GC-MS reference results for PhPh.

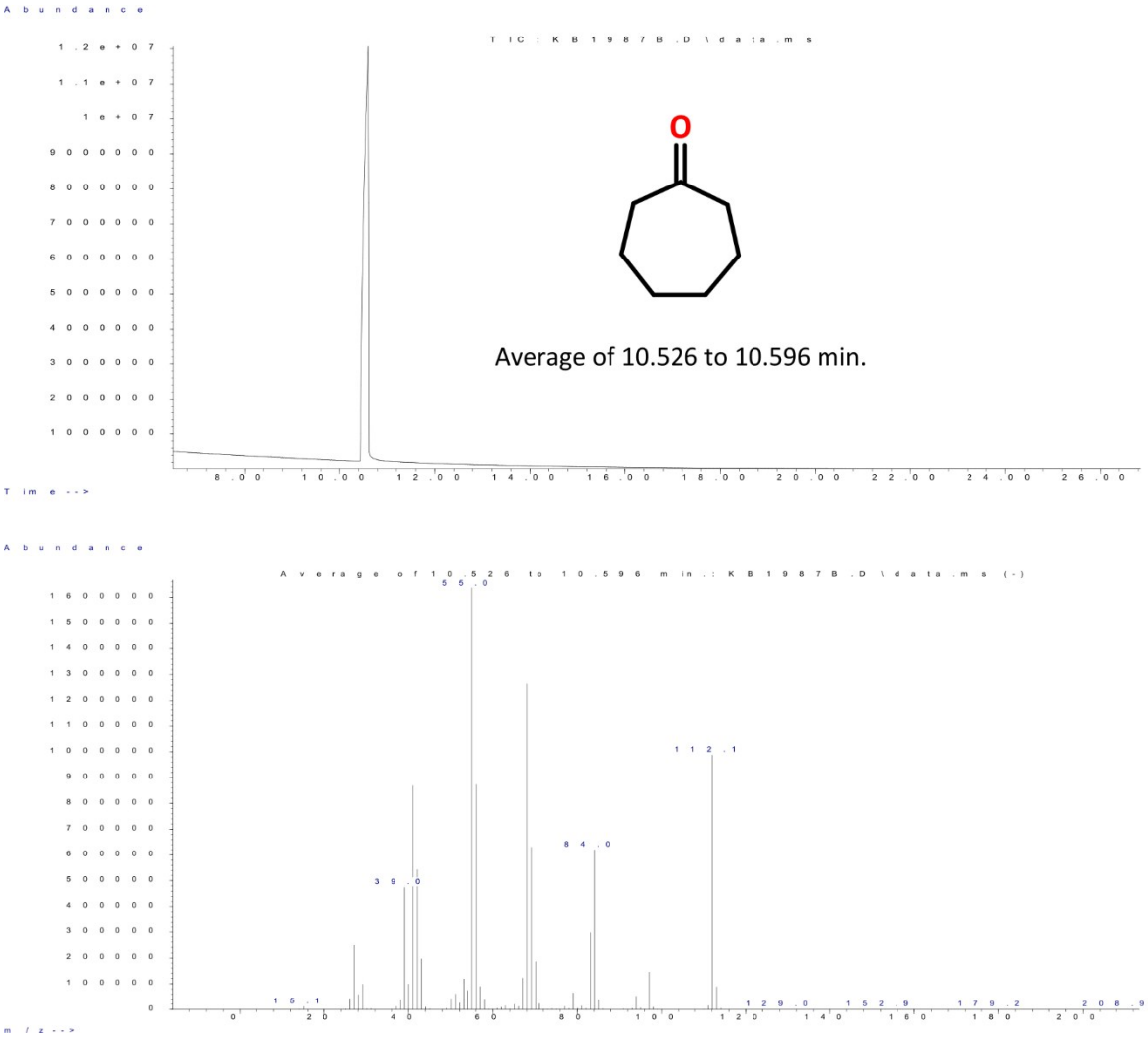

Figure S21. GC-MS reference results for cycloheptanone.

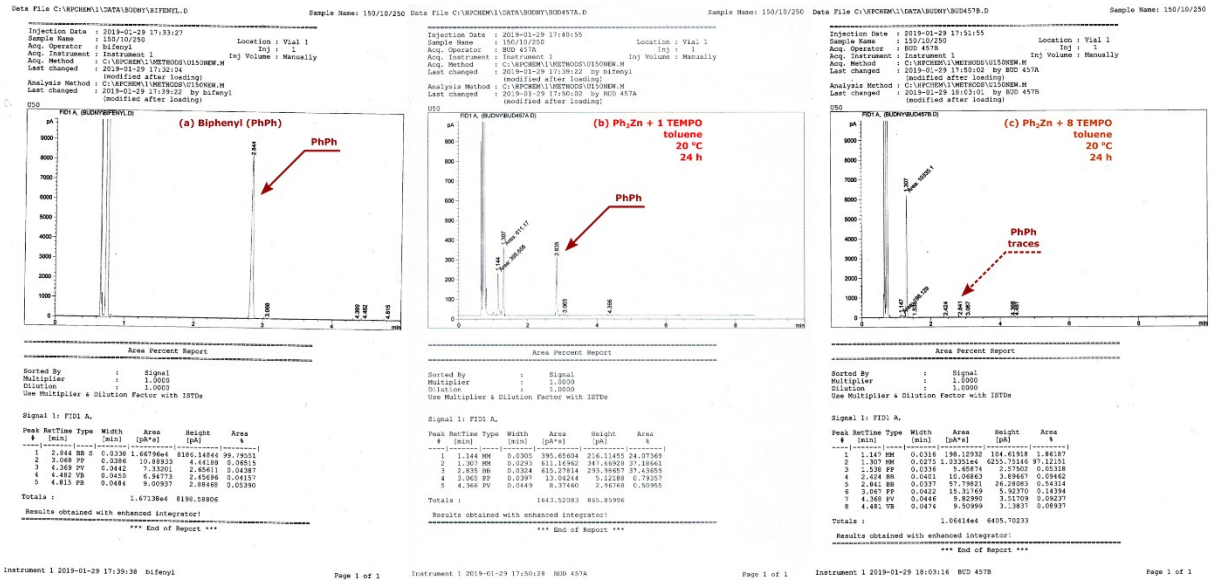

Figure S22. GC result for: (a) PhPh; (b) Ph_2Zn stirred with 1 equiv of TEMPO in toluene for 24 h at 20 °C; (c) Ph_2Zn stirred with 8 equiv of TEMPO in toluene for 24 h at 20 °C.

8. High temperature reactions between Ph_2Zn and TEMPO

8.1. Reaction in the melted phase

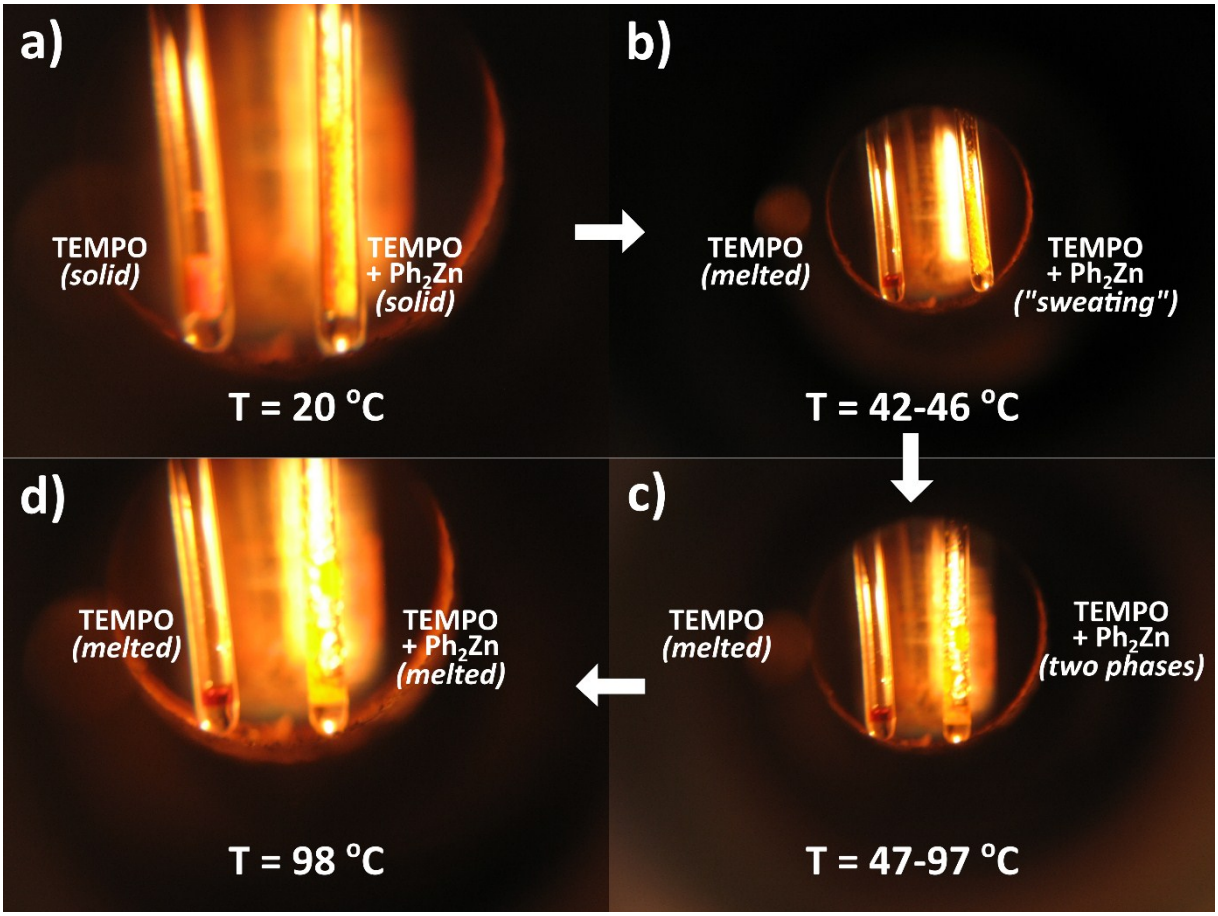

Figure S23. Photographs to compare samples of TEMPO and equimolar TEMPO/Ph_2Zn mixture behaviour at different temperatures: a) T = 20 °C: both samples solid; b) T = 42-46 °C: TEMPO – melted, TEMPO/Ph_2Zn – solid with droplets of orange liquid; c) T = 47-97 °C: TEMPO – melted, TEMPO/Ph_2Zn – two separate phases: white solid, yellow-orange liquid; d) T = 98 °C: TEMPO – melted, TEMPO/Ph_2Zn – homogenous yellow liquid.

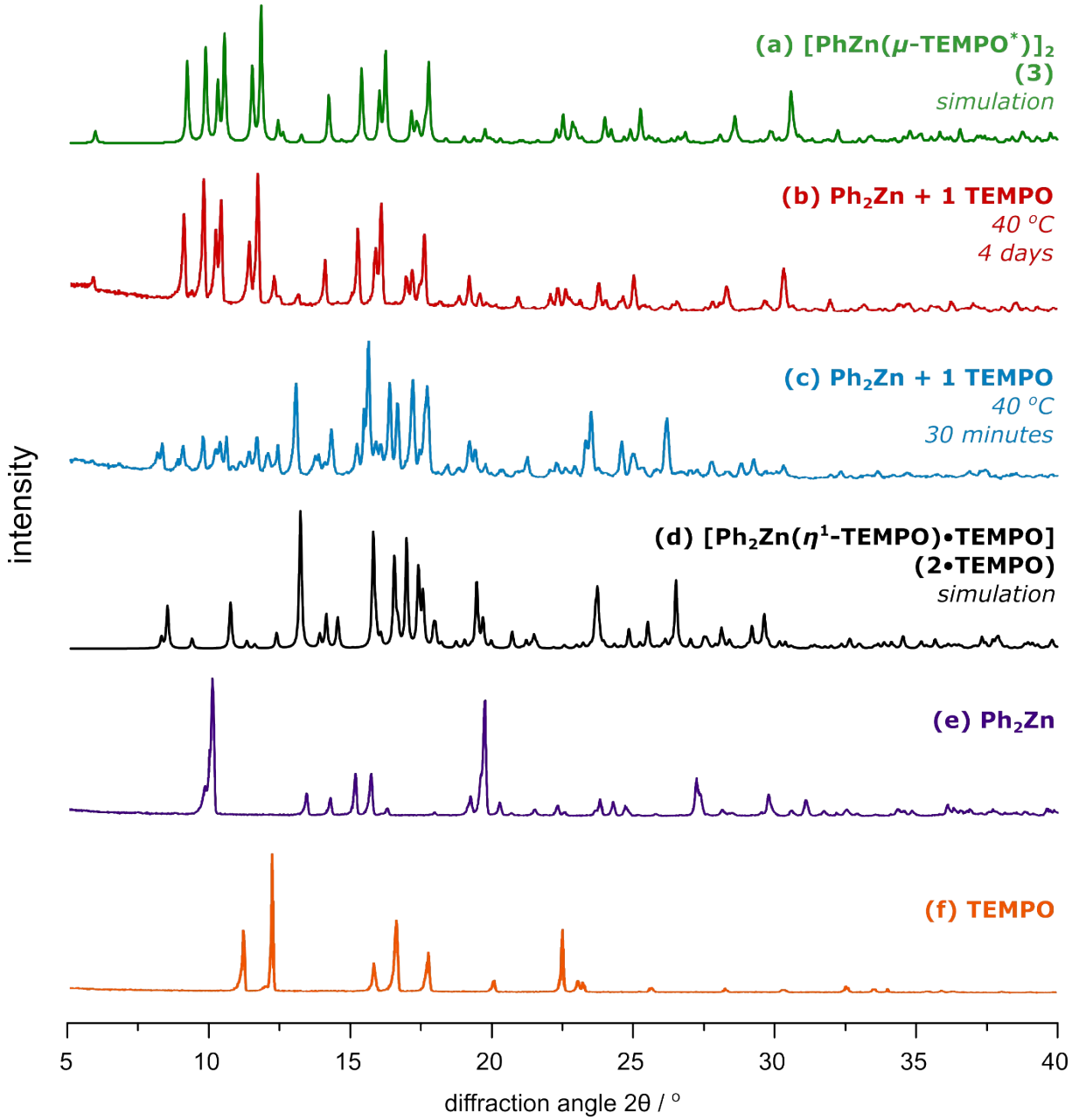

Figure S24. Comparison of the experimental and simulated PXRD patterns for the reactions of TEMPO with Ph_2Zn at 40 °C: (a) the simulated PXRD spectrum of **3**; (b) Ph_2Zn mixed with 1 equivalent of TEMPO, then stored at 40 °C for 4 days; (c) Ph_2Zn mixed with 1 equivalent of TEMPO, then stored at 40 °C for 30 minutes; (d) the simulated PXRD spectrum of **2**•TEMPO; (e) Ph_2Zn; (f) TEMPO.

9. X-ray Crystallographic Data

9.1. Complex $\mathbf{1_2}$ [*t*BuZn(*μ*-TEMPO*)]$_2$

CCDC – 1550886

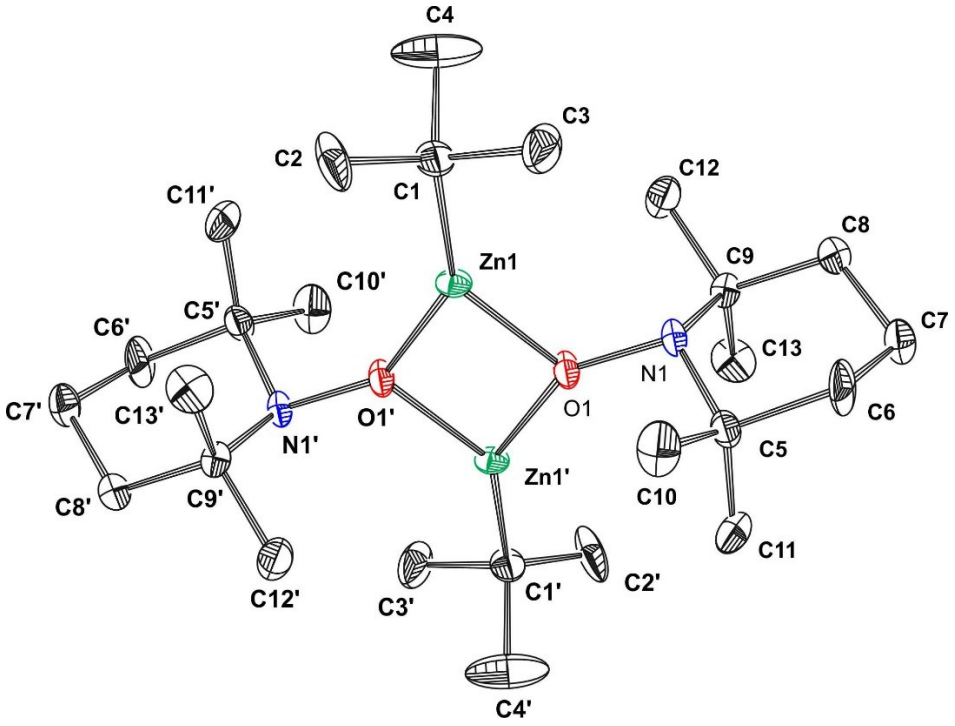

Figure S25. Molecular structure of $\mathbf{1_2}$ with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity. Symmetry codes: (1 -x,-y+1, -z)

Table 2. Crystal data and structure refinement for (**1$_2$**) [*t*BuZn(μ-TEMPO*)]$_2$.

Identification code	**1$_2$**	
Empirical formula	$C_{26}H_{54}N_2O_2Zn_2$	
Formula weight	557.45	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P 42/n	
Unit cell dimensions	a = 12.3523(3) Å	a= 90°.
	b = 12.3523(3) Å	b= 90°.
	c = 19.4557(10) Å	γ = 90°.
Volume	2968.5(2) Å^3	
Z	4	
Density (calculated)	1.247 Mg/m^3	
Absorption coefficient	1.638 mm^{-1}	
F(000)	1200	
Crystal size	0.270 x 0.160 x 0.080 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	SuperNova Agilent	
Theta range for data collection	3.134 to 29.126°.	
Index ranges	-15<=h<=15, -9<=k<=13, -26<=l<=11	
Reflections collected	6809	
Independent reflections	3420 [R(int) = 0.0527]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	multi-scan	
Max. and min. Transmission	0.877 and 0.737	
Refinement method	SHELXL-2016/6	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3420 / 264 / 259	
Goodness-of-fit on F^2	0.998	
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1568	
R indices (all data)	R1 = 0.1062, wR2 = 0.2114	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.012 and -0.987 e. Å^{-3}	

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**1_2**) [*t*BuZn(μ-TEMPO*)]$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2850(4)	5014(10)	-49(3)	33(1)
O(1)	67(3)	5062(3)	618(2)	27(1)
Zn(1)	1239(1)	4996(1)	-43(1)	23(1)
C(2)	3376(12)	5662(18)	-595(8)	71(7)
C(3)	3268(13)	5468(18)	652(6)	69(6)
C(4)	3267(15)	3830(12)	-60(12)	90(9)
C(5)	131(12)	6095(6)	1656(4)	33(2)
C(6)	593(10)	6052(8)	2394(4)	48(3)
C(7)	249(6)	5026(8)	2776(4)	36(2)
C(8)	573(8)	4024(7)	2379(4)	33(2)
C(9)	141(8)	4003(6)	1654(4)	22(2)
C(10)	747(9)	6990(7)	1266(5)	48(3)
C(11)	-1056(8)	6371(9)	1668(4)	47(3)
C(12)	707(8)	3114(7)	1256(4)	39(2)
C(13)	-1093(7)	3728(9)	1672(5)	42(2)
N(1)	447(4)	5058(6)	1334(2)	24(1)
C(2A)	3261(13)	6188(11)	-201(10)	43(5)
C(3A)	3266(13)	4655(15)	632(7)	39(4)
C(4A)	3274(12)	4310(16)	-633(8)	53(6)
C(5A)	-20(30)	6108(19)	1668(12)	40(5)
C(6A)	-510(30)	6080(20)	2398(12)	44(5)
C(7A)	-180(30)	5040(30)	2777(12)	48(6)
C(8A)	-510(30)	4040(20)	2383(12)	40(5)
C(9A)	-110(20)	4017(18)	1649(11)	30(4)
C(10A)	-570(30)	7030(20)	1277(15)	41(6)
C(11A)	1180(20)	6340(30)	1698(16)	44(5)
C(12A)	-750(20)	3140(20)	1280(15)	38(6)
C(13A)	1113(18)	3700(30)	1617(13)	30(5)
N(1A)	-372(15)	5090(17)	1339(8)	24(1)

Table 4. Bond lengths [Å] and angles [°] for (**1₂**) [*t*BuZn(μ-TEMPO*)]$_2$.

C(1)-C(2)	1.481(11)
C(1)-C(3A)	1.488(11)
C(1)-C(4A)	1.525(12)
C(1)-C(4)	1.551(13)
C(1)-C(3)	1.561(11)
C(1)-C(2A)	1.565(13)
C(1)-Zn(1)	1.990(4)
O(1)-N(1)	1.470(5)
O(1)-N(1A)	1.505(17)
O(1)-Zn(1)	1.939(3)
O(1)-Zn(1)#1	1.964(3)
Zn(1)-Zn(1)#1	3.0658(9)
C(5)-N(1)	1.477(9)
C(5)-C(11)	1.506(19)
C(5)-C(10)	1.542(12)
C(5)-C(6)	1.547(11)
C(6)-C(7)	1.529(10)
C(7)-C(8)	1.513(9)
C(8)-C(9)	1.508(9)
C(9)-N(1)	1.493(8)
C(9)-C(12)	1.514(10)
C(9)-C(13)	1.562(12)
C(5A)-N(1A)	1.477(17)
C(5A)-C(11A)	1.51(3)
C(5A)-C(10A)	1.53(2)
C(5A)-C(6A)	1.545(19)
C(6A)-C(7A)	1.536(18)
C(7A)-C(8A)	1.516(18)
C(8A)-C(9A)	1.513(18)
C(9A)-N(1A)	1.491(16)
C(9A)-C(12A)	1.520(18)
C(9A)-C(13A)	1.56(2)
C(3A)-C(1)-C(4A)	112.0(10)
C(2)-C(1)-C(4)	110.7(10)
C(2)-C(1)-C(3)	106.7(10)
C(4)-C(1)-C(3)	103.9(9)
C(3A)-C(1)-C(2A)	109.4(10)
C(4A)-C(1)-C(2A)	106.0(10)
C(2)-C(1)-Zn(1)	116.7(7)
C(3A)-C(1)-Zn(1)	109.7(7)
C(4A)-C(1)-Zn(1)	109.9(7)
C(4)-C(1)-Zn(1)	108.7(9)
C(3)-C(1)-Zn(1)	109.3(7)
C(2A)-C(1)-Zn(1)	109.7(8)
N(1)-O(1)-Zn(1)	113.0(3)
N(1A)-O(1)-Zn(1)	152.7(7)
N(1)-O(1)-Zn(1)#1	143.3(3)
N(1A)-O(1)-Zn(1)#1	103.7(7)
Zn(1)-O(1)-Zn(1)#1	103.52(13)
O(1)-Zn(1)-O(1)#1	76.49(13)
O(1)-Zn(1)-C(1)	138.56(18)
O(1)#1-Zn(1)-C(1)	144.94(17)

O(1)-Zn(1)-Zn(1)#1	38.53(9)
O(1)#1-Zn(1)-Zn(1)#1	37.95(9)
C(1)-Zn(1)-Zn(1)#1	177.02(18)
N(1)-C(5)-C(11)	117.5(9)
N(1)-C(5)-C(10)	106.4(9)
C(11)-C(5)-C(10)	109.0(8)
N(1)-C(5)-C(6)	105.4(8)
C(11)-C(5)-C(6)	110.6(9)
C(10)-C(5)-C(6)	107.4(9)
C(7)-C(6)-C(5)	112.1(7)
C(8)-C(7)-C(6)	110.9(6)
C(9)-C(8)-C(7)	113.4(6)
N(1)-C(9)-C(8)	106.6(6)
N(1)-C(9)-C(12)	107.7(7)
C(8)-C(9)-C(12)	109.1(7)
N(1)-C(9)-C(13)	116.5(7)
C(8)-C(9)-C(13)	109.2(7)
C(12)-C(9)-C(13)	107.7(7)
O(1)-N(1)-C(5)	108.3(6)
O(1)-N(1)-C(9)	108.4(5)
C(5)-N(1)-C(9)	120.9(5)
N(1A)-C(5A)-C(11A)	118(2)
N(1A)-C(5A)-C(10A)	106.7(19)
C(11A)-C(5A)-C(10A)	108.4(19)
N(1A)-C(5A)-C(6A)	105.3(17)
C(11A)-C(5A)-C(6A)	111(2)
C(10A)-C(5A)-C(6A)	107(2)
C(7A)-C(6A)-C(5A)	110.8(18)
C(8A)-C(7A)-C(6A)	111.7(17)
C(9A)-C(8A)-C(7A)	113.5(18)
N(1A)-C(9A)-C(8A)	107.2(16)
N(1A)-C(9A)-C(12A)	109.0(18)
C(8A)-C(9A)-C(12A)	106.5(18)
N(1A)-C(9A)-C(13A)	114.7(18)
C(8A)-C(9A)-C(13A)	111.1(18)
C(12A)-C(9A)-C(13A)	108.1(18)
C(5A)-N(1A)-C(9A)	121.1(14)
C(5A)-N(1A)-O(1)	108.5(15)
C(9A)-N(1A)-O(1)	106.1(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (**1₂**) [*t*BuZn(μ-TEMPO*)]$_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	18(2)	46(3)	34(3)	4(3)	-1(2)	1(4)
O(1)	25(2)	41(2)	16(1)	3(2)	-1(1)	-3(3)
Zn(1)	13(1)	26(1)	31(1)	2(1)	0(1)	0(1)
C(2)	20(8)	158(17)	34(8)	44(11)	-3(7)	-2(10)
C(3)	40(10)	138(17)	29(7)	-15(9)	-7(7)	27(12)
C(4)	25(10)	59(8)	190(30)	-16(9)	-12(10)	12(8)
C(5)	54(7)	25(3)	20(4)	0(3)	-5(5)	8(5)
C(6)	89(8)	38(5)	16(4)	-10(3)	-9(5)	-6(6)
C(7)	47(5)	39(4)	22(3)	0(4)	-4(3)	-4(5)
C(8)	38(5)	36(4)	26(4)	4(3)	0(4)	4(4)
C(9)	17(5)	26(3)	22(4)	-2(3)	1(3)	-9(3)
C(10)	75(8)	27(4)	41(6)	0(4)	5(6)	-14(5)
C(11)	62(6)	47(6)	31(5)	-8(5)	11(5)	15(5)
C(12)	53(6)	33(4)	32(5)	0(4)	12(5)	1(4)
C(13)	24(4)	49(6)	53(6)	8(5)	-3(4)	-17(4)
N(1)	26(2)	31(2)	15(2)	2(2)	-2(2)	-5(4)
C(2A)	26(10)	56(8)	48(10)	34(8)	-4(8)	-14(8)
C(3A)	16(7)	63(8)	39(8)	14(7)	6(6)	2(6)
C(4A)	16(9)	86(13)	56(11)	-7(9)	17(8)	8(8)
C(5A)	60(11)	29(7)	30(8)	1(7)	0(9)	-19(8)
C(6A)	73(14)	33(9)	27(9)	-1(8)	5(11)	-7(13)
C(7A)	79(15)	35(11)	28(9)	0(9)	7(11)	3(14)
C(8A)	62(13)	35(9)	23(9)	7(8)	9(10)	1(12)
C(9A)	41(10)	28(6)	19(8)	2(6)	0(8)	-6(8)
C(10A)	59(14)	31(8)	34(13)	8(10)	14(13)	-13(11)
C(11A)	62(11)	28(10)	43(11)	6(10)	-4(10)	-28(9)
C(12A)	46(14)	30(9)	38(13)	-1(11)	-1(13)	-13(11)
C(13A)	43(10)	28(10)	19(9)	5(9)	-4(9)	-3(8)
N(1A)	26(2)	31(2)	15(2)	2(2)	-2(2)	-5(4)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (**1$_2$**) [*t*BuZn(μ-TEMPO*)]$_2$.

	x	y	z	U(eq)
H(2A)	3103	6406	-580	106
H(2B)	4161	5665	-523	106
H(2C)	3213	5343	-1044	106
H(3A)	2939	5061	1030	104
H(3B)	4058	5394	673	104
H(3C)	3072	6234	691	104
H(4A)	2910	3415	305	135
H(4B)	3103	3502	-506	135
H(4C)	4051	3824	15	135
H(6A)	1393	6082	2373	57
H(6B)	339	6693	2653	57
H(7A)	593	5012	3235	43
H(7B)	-546	5031	2841	43
H(8A)	1373	3980	2363	40
H(8B)	306	3377	2627	40
H(10A)	562	7697	1462	72
H(10B)	1528	6867	1309	72
H(10C)	542	6974	780	72
H(11A)	-1158	7074	1894	70
H(11B)	-1331	6408	1196	70
H(11C)	-1452	5813	1923	70
H(12A)	521	2410	1455	59
H(12B)	475	3136	775	59
H(12C)	1492	3222	1281	59
H(13A)	-1198	3022	1891	63
H(13B)	-1479	4285	1934	63
H(13C)	-1375	3705	1201	63
H(2A1)	2988	6425	-649	65
H(2A2)	3000	6681	157	65
H(2A3)	4055	6194	-207	65
H(3A1)	2976	5127	993	59
H(3A2)	3038	3908	718	59
H(3A3)	4058	4695	634	59
H(4A1)	2983	4571	-1071	79
H(4A2)	4067	4346	-644	79
H(4A3)	3047	3558	-560	79
H(6A1)	-255	6718	2661	53
H(6A2)	-1308	6117	2367	53
H(7A1)	617	5036	2842	57
H(7A2)	-521	5030	3237	57
H(8A1)	-231	3390	2626	48
H(8A2)	-1312	3988	2380	48
H(10D)	-357	7728	1479	62
H(10E)	-349	7013	793	62
H(10F)	-1358	6952	1308	62
H(11D)	1304	7033	1928	67
H(11E)	1546	5761	1956	67

H(11F)	1475	6368	1230	67
H(12D)	-581	2436	1481	57
H(12E)	-1527	3290	1331	57
H(12F)	-560	3142	792	57
H(13D)	1216	2992	1830	45
H(13E)	1348	3676	1137	45
H(13F)	1541	4245	1865	45

9.2. Complex 2•TEMPO [$Ph_2Zn(\eta^1$-TEMPO)•TEMPO]

CCDC – 1550887

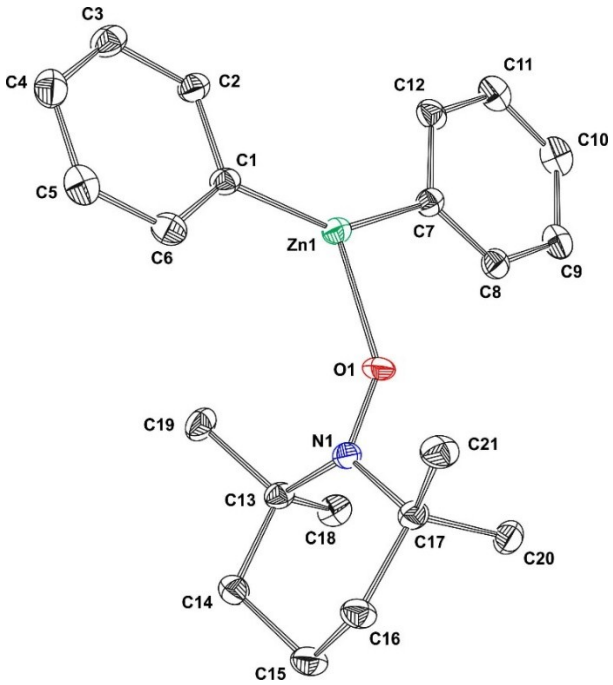

Figure S26. Molecular structure of **2** with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity.

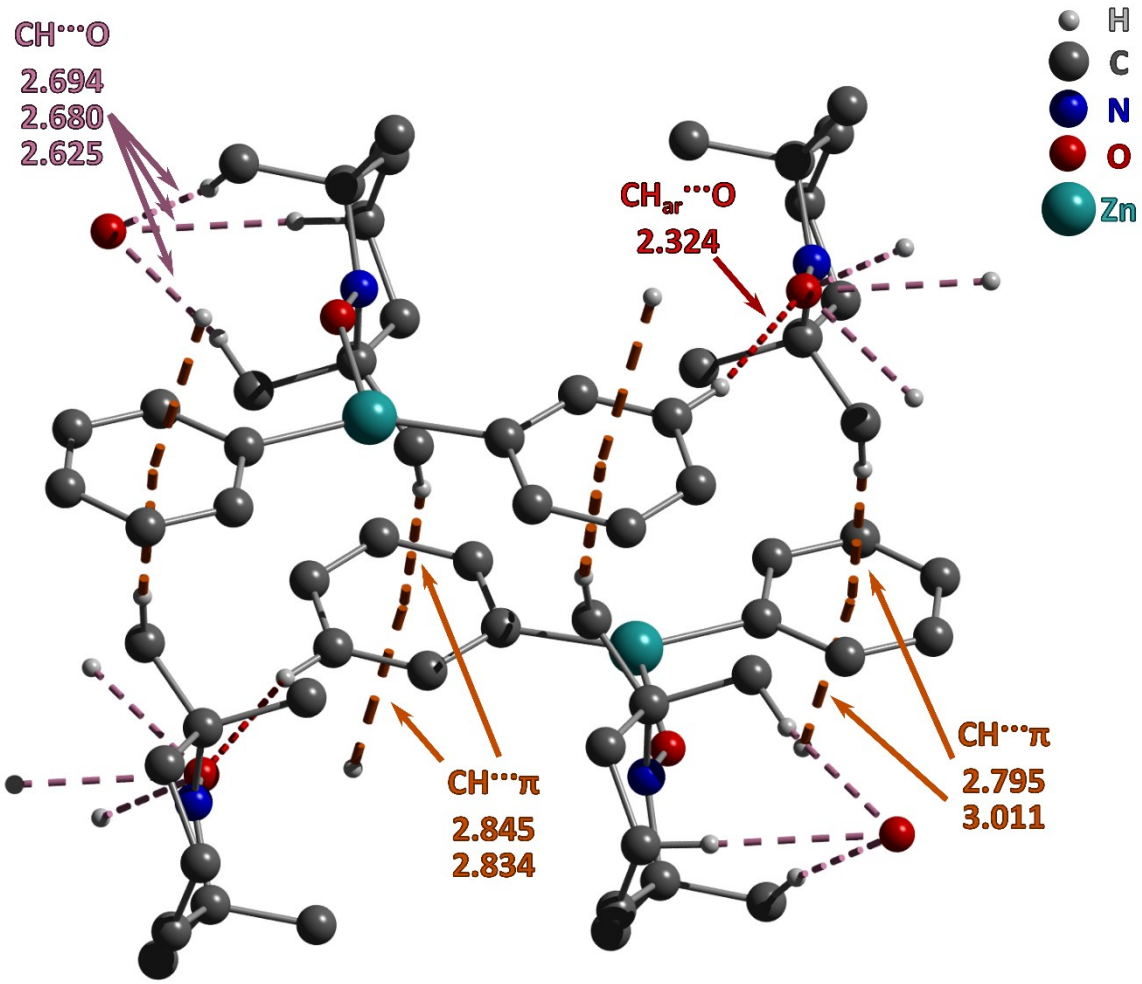

Figure S27. Supramolecular structure of **2**•TEMPO with selected non-covalent (orange: CH-π; pink: CH-O; red: CH_{ar}-O) interactions and their distances (Å). Selected hydrogen atoms have been omitted for clarity.

Table 7. **Crystal data and structure refinement for (**2•TEMPO**) [$Ph_2Zn(\eta^1$-TEMPO)•TEMPO].**

Identification code	**2•TEMPO**	
Empirical formula	$C_{30}H_{46}N_2O_2Zn$	
Formula weight	532.06	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P* 2_1/c	
Unit cell dimensions	a = 10.5250(4) Å	a= 90°.
	b = 22.5030(7) Å	b= 95.8340(10)°.
	c = 12.2960(4) Å	γ = 90°.
Volume	2897.15(17) $Å^3$	
Z	4	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	0.875 mm^{-1}	
F(000)	1144	
Crystal size	0.32 x 0.18 x 0.10 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	Nonius Kappa-CCD	
Theta range for data collection	2.145 to 25.500°.	
Index ranges	-12<=h<=12, -27<=k<=24, -14<=l<=14	
Reflections collected	9392	
Independent reflections	5259 [R(int) = 0.0388]	
Completeness to theta = 25.242°	97.6 %	
Absorption correction	multi-scan	
Max. and min. Transmission	0.916 and 0.828	
Refinement method	SHELXL-2016/4	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5259 / 0 / 324	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0970	
R indices (all data)	R1 = 0.0575, wR2 = 0.1050	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.418 and -0.443 $e.Å^{-3}$	

Table 8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**2**) [$Ph_2Zn(\eta^1$-TEMPO)]. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3821(3)	948(1)	7942(2)	25(1)
C(2)	2994(3)	652(1)	7150(2)	28(1)
C(3)	1729(3)	528(1)	7295(2)	32(1)
C(4)	1239(3)	698(1)	8241(3)	35(1)
C(5)	2015(3)	1000(1)	9049(2)	33(1)
C(6)	3279(3)	1121(1)	8890(2)	29(1)
C(7)	6777(3)	969(1)	6504(2)	26(1)
C(8)	8063(3)	1146(1)	6663(2)	28(1)
C(9)	8888(3)	1093(1)	5856(2)	34(1)
C(10)	8441(3)	860(1)	4846(3)	38(1)
C(11)	7187(3)	679(1)	4651(2)	36(1)
C(12)	6370(3)	730(1)	5467(2)	31(1)
C(13)	7341(3)	969(1)	10480(2)	24(1)
C(14)	7392(3)	1075(1)	11715(2)	29(1)
C(15)	8094(3)	1639(1)	12097(2)	31(1)
C(16)	7414(3)	2170(1)	11531(2)	30(1)
C(17)	7363(3)	2147(1)	10282(2)	26(1)
C(18)	8636(3)	770(1)	10139(2)	31(1)
C(19)	6344(3)	495(1)	10144(2)	33(1)
C(20)	8670(3)	2288(1)	9888(2)	31(1)
C(21)	6364(3)	2583(1)	9776(2)	33(1)
C(22)	2287(3)	2843(1)	7819(2)	29(1)
C(23)	2411(3)	2844(1)	9070(2)	34(1)
C(24)	3118(3)	3387(1)	9570(2)	37(1)
C(25)	2400(3)	3946(1)	9172(2)	34(1)
C(26)	2268(3)	4016(1)	7927(2)	26(1)
C(27)	3558(3)	2698(1)	7365(3)	37(1)
C(28)	1286(3)	2386(1)	7386(3)	37(1)
C(29)	3536(3)	4206(1)	7515(3)	36(1)
C(30)	1254(3)	4484(1)	7579(2)	33(1)
O(1)	6699(2)	1503(1)	8846(2)	32(1)
O(2)	1392(2)	3466(1)	6392(2)	33(1)
ZN1	5577(1)	1059(1)	7609(1)	25(1)
N(1)	6967(2)	1534(1)	9896(2)	24(1)
N(2)	1835(2)	3441(1)	7407(2)	26(1)

Table 9. Bond lengths [Å] and angles [°] for (**2**) [$Ph_2Zn(\eta^1$-TEMPO)].

C(1)-C(6)	1.404(4)
C(1)-C(2)	1.406(4)
C(1)-ZN1	1.948(3)
C(2)-C(3)	1.390(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.374(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.396(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.391(4)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.405(4)
C(7)-C(12)	1.411(4)
C(7)-ZN1	1.958(3)
C(8)-C(9)	1.388(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.386(4)
C(9)-H(9)	0.9500
C(10)-C(11)	1.379(5)
C(10)-H(10)	0.9500
C(11)-C(12)	1.391(4)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-N(1)	1.495(3)
C(13)-C(19)	1.523(4)
C(13)-C(14)	1.532(4)
C(13)-C(18)	1.533(4)
C(14)-C(15)	1.520(4)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.524(4)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.531(4)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-N(1)	1.503(3)
C(17)-C(21)	1.524(4)
C(17)-C(20)	1.538(4)
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-N(2)	1.498(3)

C(22)-C(28)	1.528(4)
C(22)-C(23)	1.531(4)
C(22)-C(27)	1.535(4)
C(23)-C(24)	1.527(4)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.522(4)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-C(26)	1.531(4)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
C(26)-N(2)	1.494(3)
C(26)-C(30)	1.529(4)
C(26)-C(29)	1.536(4)
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
O(1)-N(1)	1.294(3)
O(1)-Zn1	2.0841(18)
O(2)-N(2)	1.288(3)

C(6)-C(1)-C(2)	115.5(3)
C(6)-C(1)-ZN1	127.8(2)
C(2)-C(1)-ZN1	116.6(2)
C(3)-C(2)-C(1)	122.6(3)
C(3)-C(2)-H(2)	118.7
C(1)-C(2)-H(2)	118.7
C(4)-C(3)-C(2)	120.0(3)
C(4)-C(3)-H(3)	120.0
C(2)-C(3)-H(3)	120.0
C(3)-C(4)-C(5)	119.7(3)
C(3)-C(4)-H(4)	120.2
C(5)-C(4)-H(4)	120.2
C(6)-C(5)-C(4)	119.6(3)
C(6)-C(5)-H(5)	120.2
C(4)-C(5)-H(5)	120.2
C(5)-C(6)-C(1)	122.5(3)
C(5)-C(6)-H(6)	118.7
C(1)-C(6)-H(6)	118.7
C(8)-C(7)-C(12)	115.7(3)
C(8)-C(7)-ZN1	123.7(2)
C(12)-C(7)-ZN1	120.6(2)
C(9)-C(8)-C(7)	122.7(3)
C(9)-C(8)-H(8)	118.7
C(7)-C(8)-H(8)	118.7

C(10)-C(9)-C(8)	119.5(3)
C(10)-C(9)-H(9)	120.2
C(8)-C(9)-H(9)	120.2
C(11)-C(10)-C(9)	120.0(3)
C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0
C(10)-C(11)-C(12)	120.1(3)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-C(7)	122.0(3)
C(11)-C(12)-H(12)	119.0
C(7)-C(12)-H(12)	119.0
N(1)-C(13)-C(19)	109.0(2)
N(1)-C(13)-C(14)	109.0(2)
C(19)-C(13)-C(14)	109.4(2)
N(1)-C(13)-C(18)	108.3(2)
C(19)-C(13)-C(18)	109.2(2)
C(14)-C(13)-C(18)	112.0(2)
C(15)-C(14)-C(13)	113.8(2)
C(15)-C(14)-H(14A)	108.8
C(13)-C(14)-H(14A)	108.8
C(15)-C(14)-H(14B)	108.8
C(13)-C(14)-H(14B)	108.8
H(14A)-C(14)-H(14B)	107.7
C(14)-C(15)-C(16)	108.8(2)
C(14)-C(15)-H(15A)	109.9
C(16)-C(15)-H(15A)	109.9
C(14)-C(15)-H(15B)	109.9
C(16)-C(15)-H(15B)	109.9
H(15A)-C(15)-H(15B)	108.3
C(15)-C(16)-C(17)	113.5(2)
C(15)-C(16)-H(16A)	108.9
C(17)-C(16)-H(16A)	108.9
C(15)-C(16)-H(16B)	108.9
C(17)-C(16)-H(16B)	108.9
H(16A)-C(16)-H(16B)	107.7
N(1)-C(17)-C(21)	107.7(2)
N(1)-C(17)-C(16)	109.2(2)
C(21)-C(17)-C(16)	109.9(2)
N(1)-C(17)-C(20)	108.5(2)
C(21)-C(17)-C(20)	109.9(2)
C(16)-C(17)-C(20)	111.6(2)
C(13)-C(18)-H(18A)	109.5
C(13)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(13)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(13)-C(19)-H(19A)	109.5
C(13)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(13)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(17)-C(20)-H(20A)	109.5

C(17)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(17)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(17)-C(21)-H(21A)	109.5
C(17)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(17)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
N(2)-C(22)-C(28)	107.6(2)
N(2)-C(22)-C(23)	109.2(2)
C(28)-C(22)-C(23)	109.7(2)
N(2)-C(22)-C(27)	109.1(2)
C(28)-C(22)-C(27)	109.0(2)
C(23)-C(22)-C(27)	112.2(2)
C(24)-C(23)-C(22)	113.2(2)
C(24)-C(23)-H(23A)	108.9
C(22)-C(23)-H(23A)	108.9
C(24)-C(23)-H(23B)	108.9
C(22)-C(23)-H(23B)	108.9
H(23A)-C(23)-H(23B)	107.8
C(25)-C(24)-C(23)	109.0(2)
C(25)-C(24)-H(24A)	109.9
C(23)-C(24)-H(24A)	109.9
C(25)-C(24)-H(24B)	109.9
C(23)-C(24)-H(24B)	109.9
H(24A)-C(24)-H(24B)	108.3
C(24)-C(25)-C(26)	113.5(2)
C(24)-C(25)-H(25A)	108.9
C(26)-C(25)-H(25A)	108.9
C(24)-C(25)-H(25B)	108.9
C(26)-C(25)-H(25B)	108.9
H(25A)-C(25)-H(25B)	107.7
N(2)-C(26)-C(30)	107.7(2)
N(2)-C(26)-C(25)	109.4(2)
C(30)-C(26)-C(25)	109.9(2)
N(2)-C(26)-C(29)	109.7(2)
C(30)-C(26)-C(29)	108.7(2)
C(25)-C(26)-C(29)	111.4(2)
C(22)-C(27)-H(27A)	109.5
C(22)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(22)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(22)-C(28)-H(28A)	109.5
C(22)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(22)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5

H(29A)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(26)-C(30)-H(30A)	109.5
C(26)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(26)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
N(1)-O(1)-ZN1	143.50(17)
C(1)-ZN1-C(7)	145.61(12)
C(1)-ZN1-O(1)	112.80(10)
C(7)-ZN1-O(1)	101.40(10)
O(1)-N(1)-C(13)	116.9(2)
O(1)-N(1)-C(17)	113.0(2)
C(13)-N(1)-C(17)	125.3(2)
O(2)-N(2)-C(26)	116.1(2)
O(2)-N(2)-C(22)	116.0(2)
C(26)-N(2)-C(22)	124.1(2)

Symmetry transformations used to generate equivalent atoms:

Table 10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (**2**) [$Ph_2Zn(\eta^1$-TEMPO)]. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	24(1)	24(1)	27(1)	4(1)	-2(1)	2(1)
C(2)	29(2)	28(1)	25(1)	-1(1)	-3(1)	-1(1)
C(3)	28(2)	29(2)	37(2)	3(1)	-8(1)	-1(1)
C(4)	25(2)	32(2)	46(2)	8(1)	4(1)	2(1)
C(5)	37(2)	29(2)	32(2)	4(1)	8(1)	10(1)
C(6)	33(2)	26(1)	26(1)	0(1)	-3(1)	3(1)
C(7)	27(2)	22(1)	27(1)	1(1)	0(1)	2(1)
C(8)	32(2)	24(1)	29(1)	4(1)	-1(1)	2(1)
C(9)	30(2)	33(2)	41(2)	10(1)	5(1)	6(1)
C(10)	43(2)	34(2)	38(2)	4(1)	15(1)	9(1)
C(11)	56(2)	27(2)	26(2)	-3(1)	3(1)	2(1)
C(12)	37(2)	24(1)	31(2)	0(1)	1(1)	-1(1)
C(13)	23(1)	22(1)	27(1)	1(1)	-1(1)	0(1)
C(14)	32(2)	28(1)	25(1)	5(1)	0(1)	2(1)
C(15)	39(2)	30(2)	24(1)	-2(1)	-3(1)	2(1)
C(16)	36(2)	25(1)	27(1)	-5(1)	-1(1)	1(1)
C(17)	30(2)	22(1)	26(1)	0(1)	-4(1)	-2(1)
C(18)	31(2)	29(2)	34(2)	-3(1)	3(1)	4(1)
C(19)	32(2)	27(1)	38(2)	3(1)	-5(1)	-3(1)
C(20)	29(2)	29(2)	33(2)	4(1)	-3(1)	-5(1)
C(21)	32(2)	27(1)	38(2)	4(1)	-7(1)	2(1)
C(22)	32(2)	23(1)	31(2)	2(1)	-6(1)	2(1)
C(23)	42(2)	28(2)	31(2)	5(1)	-6(1)	1(1)
C(24)	48(2)	31(2)	30(2)	-2(1)	-10(1)	4(1)
C(25)	41(2)	32(2)	30(2)	-4(1)	-1(1)	2(1)
C(26)	25(2)	21(1)	30(1)	2(1)	-2(1)	3(1)
C(27)	35(2)	32(2)	44(2)	-6(1)	-1(1)	8(1)
C(28)	38(2)	26(2)	42(2)	4(1)	-13(1)	-4(1)
C(29)	29(2)	33(2)	47(2)	-2(1)	2(1)	-3(1)
C(30)	33(2)	27(2)	39(2)	1(1)	-4(1)	6(1)
O(1)	41(1)	32(1)	21(1)	1(1)	-7(1)	-8(1)
O(2)	38(1)	32(1)	25(1)	4(1)	-9(1)	-2(1)
ZN1	25(1)	24(1)	25(1)	-1(1)	-1(1)	-1(1)
N(1)	22(1)	25(1)	24(1)	1(1)	-2(1)	-2(1)
N(2)	27(1)	25(1)	25(1)	2(1)	-2(1)	1(1)

Table 11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for (**2**) [$Ph_2Zn(\eta^1$-TEMPO)].

	x	y	z	U(eq)
H(2)	3314	531	6489	33
H(3)	1202	325	6741	38
H(4)	377	611	8346	42
H(5)	1682	1121	9703	39
H(6)	3795	1328	9444	35
H(8)	8380	1309	7350	34
H(9)	9753	1216	5996	41
H(10)	8998	825	4288	45
H(11)	6881	520	3958	43
H(12)	5511	598	5321	37
H(14A)	6508	1095	11921	34
H(14B)	7817	731	12101	34
H(15A)	8988	1622	11914	38
H(15B)	8105	1680	12899	38
H(16A)	7857	2539	11794	36
H(16B)	6531	2188	11740	36
H(18A)	8603	769	9340	47
H(18B)	8830	369	10418	47
H(18C)	9302	1045	10442	47
H(19A)	5490	653	10219	49
H(19B)	6498	146	10615	49
H(19C)	6403	382	9381	49
H(20A)	9330	2047	10298	46
H(20B)	8866	2710	10009	46
H(20C)	8649	2198	9107	46
H(21A)	6377	2586	8980	49
H(21B)	6556	2982	10065	49
H(21C)	5516	2461	9956	49
H(23A)	1547	2831	9320	41
H(23B)	2871	2481	9341	41
H(24A)	3173	3365	10377	45
H(24B)	3997	3397	9351	45
H(25A)	2853	4297	9505	41
H(25B)	1537	3937	9425	41
H(27A)	3478	2773	6576	56
H(27B)	3772	2279	7504	56
H(27C)	4235	2950	7725	56
H(28A)	452	2499	7609	55
H(28B)	1526	1993	7685	55
H(28C)	1239	2373	6586	55
H(29A)	4223	3946	7833	54
H(29B)	3726	4618	7733	54
H(29C)	3467	4175	6716	54
H(30A)	1245	4561	6794	50
H(30B)	1454	4853	7986	50
H(30C)	414	4339	7736	50

9.3. Complex 3 [PhZn(μ-TEMPO*)]$_2$

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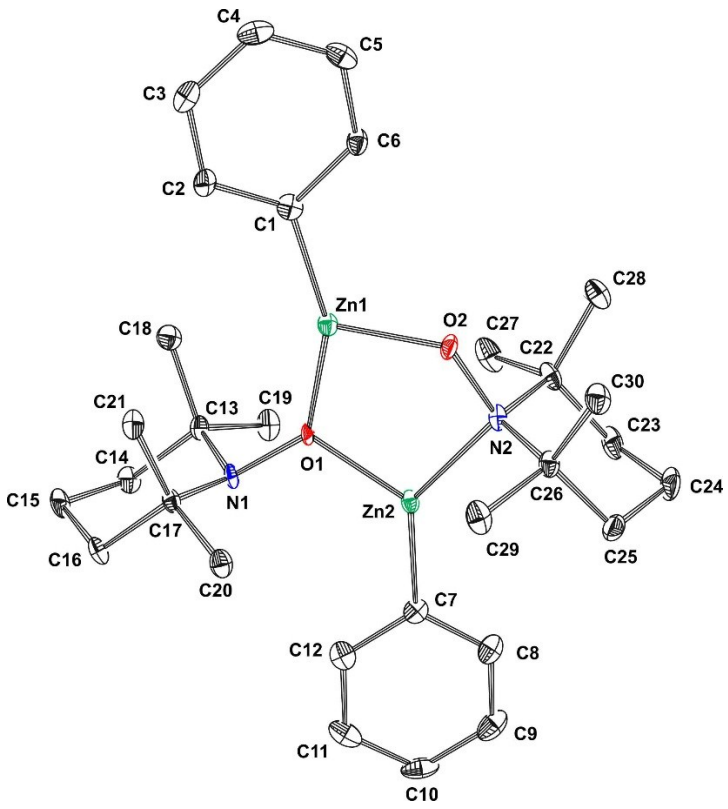

Figure S28. Molecular structure of **3** with thermal ellipsoids set at 40% probability. Hydrogen atoms have been omitted for clarity.

Table 12. Crystal data and structure refinement for (**3**) [PhZn(μ-TEMPO*)]$_2$.

Identification code	**3**	
Empirical formula	$C_{30}H_{46}N_2O_2Zn_2$	
Formula weight	597.43	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 9.4169(3) Å	a= 90°.
	b = 30.0759(6) Å	b= 106.582(3)°.
	c = 10.6586(3) Å	γ = 90°.
Volume	2893.20(14) Å^3	
Z	4	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	1.686 mm^{-1}	
F(000)	1264	
Crystal size	0.340 x 0.240 x 0.080 mm^3	
Crystal color and habit	Colorless Plate	
Diffractometer	SuperNova Agilent	
Theta range for data collection	2.887 to 25.999°.	
Index ranges	-11<=h<=7, -36<=k<=36, -13<=l<=12	
Reflections collected	11913	
Independent reflections	5674 [R(int) = 0.0473]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	multi-scan	
Max. and min. Transmission	0.874 and 0.622	
Refinement method	SHELXL-2016/4	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5674 / 0 / 333	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1196	
R indices (all data)	R1 = 0.0662, wR2 = 0.1282	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.256 and -0.848 e. Å $^{-3}$	

Table 13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (**3**) [PhZn(μ-TEMPO*)]$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5786(5)	1856(1)	1635(4)	16(1)
C(2)	5014(4)	2218(1)	1925(4)	16(1)
C(3)	3909(5)	2430(1)	967(4)	20(1)
C(4)	3535(5)	2279(1)	-306(4)	22(1)
C(5)	4259(5)	1917(1)	-627(4)	21(1)
C(6)	5376(5)	1714(1)	321(4)	17(1)
C(7)	11972(5)	781(1)	5966(4)	17(1)
C(8)	13063(5)	479(1)	5858(4)	21(1)
C(9)	14167(5)	331(2)	6924(5)	28(1)
C(10)	14247(5)	484(2)	8168(4)	27(1)
C(11)	13186(5)	780(1)	8323(4)	26(1)
C(12)	12053(5)	921(1)	7235(4)	21(1)
C(13)	7400(5)	1250(1)	6030(4)	15(1)
C(14)	7518(5)	1316(1)	7480(4)	19(1)
C(15)	7667(5)	1802(1)	7900(4)	20(1)
C(16)	8994(5)	2006(1)	7580(4)	17(1)
C(17)	8949(4)	1963(1)	6134(4)	14(1)
C(18)	5860(5)	1399(1)	5178(4)	20(1)
C(19)	7574(5)	755(1)	5791(4)	22(1)
C(20)	10465(5)	2087(1)	5991(4)	19(1)
C(21)	7807(5)	2288(1)	5289(4)	18(1)
C(22)	9572(5)	582(1)	1881(4)	18(1)
C(23)	10934(5)	280(1)	2225(4)	24(1)
C(24)	12227(5)	460(1)	1795(4)	27(1)
C(25)	12665(5)	914(1)	2420(4)	21(1)
C(26)	11402(5)	1248(1)	2095(4)	16(1)
C(27)	8475(6)	415(1)	2576(4)	28(1)
C(28)	8814(5)	583(1)	408(4)	25(1)
C(29)	11841(5)	1658(1)	2974(4)	22(1)
C(30)	11048(5)	1404(1)	672(4)	22(1)
O(1)	8774(3)	1401(1)	4488(2)	13(1)
O(2)	8842(3)	1340(1)	1893(2)	17(1)
ZN1	7549(1)	1579(1)	2800(1)	14(1)
ZN2	10460(1)	1034(1)	4454(1)	13(1)
N(1)	8710(4)	1482(1)	5818(3)	13(1)
N(2)	10076(4)	1047(1)	2435(3)	14(1)

Table 14. Bond lengths [Å] and angles [°] for (**3**) [PhZn(μ-TEMPO*)]$_2$.

C(1)-C(2)	1.392(5)
C(1)-C(6)	1.409(5)
C(1)-ZN1	1.954(4)
C(2)-C(3)	1.388(6)
C(3)-C(4)	1.378(6)
C(4)-C(5)	1.377(6)
C(5)-C(6)	1.377(6)
C(7)-C(12)	1.398(6)
C(7)-C(8)	1.400(6)
C(7)-ZN2	1.973(4)
C(8)-C(9)	1.378(6)
C(9)-C(10)	1.385(6)
C(10)-C(11)	1.384(6)
C(11)-C(12)	1.399(6)
C(13)-N(1)	1.490(5)
C(13)-C(19)	1.526(5)
C(13)-C(14)	1.530(5)
C(13)-C(18)	1.541(6)
C(14)-C(15)	1.521(6)
C(15)-C(16)	1.516(5)
C(16)-C(17)	1.535(5)
C(17)-N(1)	1.489(4)
C(17)-C(20)	1.524(5)
C(17)-C(21)	1.539(5)
C(22)-C(27)	1.518(6)
C(22)-C(28)	1.528(6)
C(22)-C(23)	1.529(6)
C(22)-N(2)	1.539(5)
C(23)-C(24)	1.519(6)
C(24)-C(25)	1.524(6)
C(25)-C(26)	1.519(6)
C(26)-N(2)	1.522(5)
C(26)-C(30)	1.530(5)
C(26)-C(29)	1.533(5)
O(1)-N(1)	1.457(4)
O(1)-Zn(1)	1.916(3)
O(1)-Zn(2)	1.943(3)
O(2)-N(2)	1.441(4)
O(2)-Zn(1)	1.898(2)
Zn(2)-N(2)	2.078(3)
C(2)-C(1)-C(6)	116.5(4)
C(2)-C(1)-ZN1	126.6(3)
C(6)-C(1)-ZN1	116.4(3)
C(3)-C(2)-C(1)	121.7(4)
C(4)-C(3)-C(2)	120.0(4)
C(5)-C(4)-C(3)	120.0(4)
C(6)-C(5)-C(4)	119.8(4)
C(5)-C(6)-C(1)	122.0(4)
C(12)-C(7)-C(8)	115.9(4)
C(12)-C(7)-ZN2	120.1(3)
C(8)-C(7)-ZN2	123.9(3)
C(9)-C(8)-C(7)	122.8(4)
C(8)-C(9)-C(10)	120.2(4)

C(11)-C(10)-C(9)	119.0(4)
C(10)-C(11)-C(12)	120.2(4)
C(7)-C(12)-C(11)	121.9(4)
N(1)-C(13)-C(19)	107.4(3)
N(1)-C(13)-C(14)	105.5(3)
C(19)-C(13)-C(14)	108.4(3)
N(1)-C(13)-C(18)	117.0(3)
C(19)-C(13)-C(18)	108.2(3)
C(14)-C(13)-C(18)	110.0(3)
C(15)-C(14)-C(13)	113.4(3)
C(16)-C(15)-C(14)	109.5(3)
C(15)-C(16)-C(17)	113.8(3)
N(1)-C(17)-C(20)	107.4(3)
N(1)-C(17)-C(16)	105.4(3)
C(20)-C(17)-C(16)	108.8(3)
N(1)-C(17)-C(21)	116.7(3)
C(20)-C(17)-C(21)	107.8(3)
C(16)-C(17)-C(21)	110.5(3)
C(27)-C(22)-C(28)	108.6(4)
C(27)-C(22)-C(23)	109.1(3)
C(28)-C(22)-C(23)	111.2(3)
C(27)-C(22)-N(2)	107.0(3)
C(28)-C(22)-N(2)	113.3(3)
C(23)-C(22)-N(2)	107.6(3)
C(24)-C(23)-C(22)	113.9(3)
C(23)-C(24)-C(25)	109.1(3)
C(26)-C(25)-C(24)	113.4(4)
C(25)-C(26)-N(2)	109.0(3)
C(25)-C(26)-C(30)	111.3(3)
N(2)-C(26)-C(30)	113.4(3)
C(25)-C(26)-C(29)	109.6(4)
N(2)-C(26)-C(29)	105.7(3)
C(30)-C(26)-C(29)	107.7(3)
N(1)-O(1)-ZN1	133.4(2)
N(1)-O(1)-ZN2	112.0(2)
ZN1-O(1)-ZN2	114.67(11)
N(2)-O(2)-ZN1	125.98(19)
O(2)-ZN1-O(1)	94.08(11)
O(2)-ZN1-C(1)	112.96(14)
O(1)-ZN1-C(1)	152.96(13)
O(1)-ZN2-C(7)	127.37(13)
O(1)-ZN2-N(2)	96.09(11)
C(7)-ZN2-N(2)	136.49(14)
O(1)-N(1)-C(17)	109.7(2)
O(1)-N(1)-C(13)	109.6(3)
C(17)-N(1)-C(13)	120.0(3)
O(2)-N(2)-C(26)	106.5(3)
O(2)-N(2)-C(22)	106.1(3)
C(26)-N(2)-C(22)	117.0(3)
O(2)-N(2)-ZN2	108.03(19)
C(26)-N(2)-ZN2	110.0(2)
C(22)-N(2)-ZN2	108.9(2)

Symmetry transformations used to generate equivalent atoms:

Table 15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (**3**) [PhZn(μ-TEMPO*)]$_2$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	19(2)	15(2)	16(2)	5(2)	8(2)	-4(2)
C(2)	14(2)	17(2)	21(2)	-1(2)	11(2)	-5(2)
C(3)	17(2)	12(2)	33(2)	2(2)	12(2)	-1(2)
C(4)	18(2)	21(2)	24(2)	14(2)	2(2)	-1(2)
C(5)	25(2)	24(2)	14(2)	2(2)	4(2)	-10(2)
C(6)	22(2)	14(2)	17(2)	2(2)	9(2)	5(2)
C(7)	18(2)	14(2)	19(2)	5(2)	8(2)	-2(2)
C(8)	21(2)	21(2)	26(2)	7(2)	15(2)	-1(2)
C(9)	21(2)	32(2)	35(3)	15(2)	15(2)	5(2)
C(10)	17(2)	32(2)	27(2)	16(2)	-3(2)	-5(2)
C(11)	35(3)	20(2)	18(2)	2(2)	3(2)	-12(2)
C(12)	28(3)	13(2)	23(2)	1(2)	9(2)	-3(2)
C(13)	18(2)	13(2)	16(2)	0(2)	9(2)	0(2)
C(14)	24(2)	22(2)	14(2)	5(2)	11(2)	-1(2)
C(15)	31(3)	23(2)	11(2)	0(2)	12(2)	3(2)
C(16)	26(2)	16(2)	12(2)	-4(2)	9(2)	-3(2)
C(17)	21(2)	10(2)	12(2)	-1(1)	6(2)	2(2)
C(18)	20(2)	25(2)	17(2)	1(2)	8(2)	-2(2)
C(19)	31(3)	14(2)	26(2)	2(2)	17(2)	-2(2)
C(20)	23(2)	16(2)	19(2)	-2(2)	11(2)	-2(2)
C(21)	26(2)	13(2)	17(2)	4(2)	11(2)	4(2)
C(22)	30(3)	11(2)	14(2)	-2(2)	8(2)	-1(2)
C(23)	41(3)	13(2)	21(2)	-3(2)	12(2)	6(2)
C(24)	33(3)	25(2)	26(2)	0(2)	14(2)	16(2)
C(25)	17(2)	30(2)	19(2)	3(2)	9(2)	6(2)
C(26)	20(2)	16(2)	14(2)	2(2)	9(2)	2(2)
C(27)	42(3)	19(2)	27(2)	-9(2)	16(2)	-16(2)
C(28)	33(3)	22(2)	19(2)	-7(2)	8(2)	-4(2)
C(29)	30(3)	20(2)	23(2)	-2(2)	17(2)	-9(2)
C(30)	27(3)	23(2)	18(2)	4(2)	12(2)	1(2)
O(1)	14(1)	18(1)	9(1)	-1(1)	8(1)	3(1)
O(2)	19(2)	20(1)	14(1)	3(1)	7(1)	12(1)
ZN1	17(1)	13(1)	13(1)	2(1)	6(1)	2(1)
ZN2	18(1)	11(1)	11(1)	1(1)	7(1)	2(1)
N(1)	18(2)	14(2)	11(2)	-3(1)	10(1)	-1(1)
N(2)	20(2)	11(2)	14(2)	1(1)	10(1)	2(1)

Table 16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (**3**) $[PhZn(\mu\text{-}TEMPO^*)]_2$.

	x	y	z	U(eq)
H(2)	5248	2322	2802	19
H(3)	3411	2680	1188	24
H(4)	2778	2424	-961	26
H(5)	3987	1808	-1500	26
H(6)	5887	1471	82	20
H(8)	13041	373	5014	25
H(9)	14876	122	6806	34
H(10)	15020	387	8903	33
H(11)	13226	887	9171	31
H(12)	11317	1118	7363	25
H(14A)	6624	1190	7659	23
H(14B)	8388	1150	8014	23
H(15A)	6757	1966	7439	24
H(15B)	7795	1823	8853	24
H(16A)	9906	1860	8123	21
H(16B)	9052	2324	7819	21
H(18A)	5649	1698	5437	30
H(18B)	5106	1192	5299	30
H(18C)	5847	1400	4255	30
H(19A)	7312	699	4847	33
H(19B)	6918	584	6175	33
H(19C)	8604	666	6197	33
H(20A)	11197	1866	6444	28
H(20B)	10754	2381	6377	28
H(20C)	10419	2093	5061	28
H(21A)	7698	2231	4361	26
H(21B)	8146	2595	5504	26
H(21C)	6849	2246	5465	26
H(23A)	11261	235	3185	29
H(23B)	10649	-14	1810	29
H(24A)	11941	487	829	32
H(24B)	13078	253	2066	32
H(25A)	13025	878	3382	25
H(25B)	13493	1034	2122	25
H(27A)	8157	114	2274	42
H(27B)	7612	613	2380	42
H(27C)	8950	411	3523	42
H(28A)	8249	307	160	37
H(28B)	9565	605	-64	37
H(28C)	8141	838	182	37
H(29A)	10994	1861	2819	33
H(29B)	12670	1811	2772	33
H(29C)	12140	1566	3894	33
H(30A)	10967	1146	96	33
H(30B)	11843	1599	573	33
H(30C)	10109	1567	436	33

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