Electronic Supplementary Information

Rotaxane-branched Radical Dendrimers with TEMPO Termini

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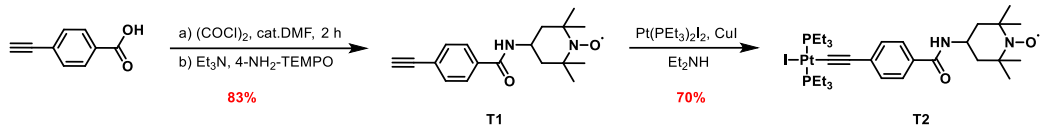
Section A. Materials and General Methods.

All reagents were commercially available and used as supplied without further purification, compounds **G1-c**, **G1-YNE**, **G2-YNE**, and **G3** were prepared according to the published procedures.[S1] Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA).

All solvents were dried according to standard procedures and all of them were degassed under N_2 for 30 minutes before use. All air-sensitive reactions were carried out under inert N_2 atmosphere. ^{1}H NMR and ^{31}P NMR spectra were recorded on Bruker 500 MHz Spectrometer (^{1}H: 500 MHz; ^{31}P: 202 MHz) at 298 K. The ^{1}H chemical shifts are reported relative to residual solvent signals, and ^{31}P $\{^1H\}$ NMR chemical shifts are referenced to an external unlocked sample of 85% H_3PO_4 (δ 0.0). The MALDI MS experiments were carried out on a Bruker UltrafleXtreme MALDI TOF/TOF Mass Spectrometer (Bruker Daltonics, Billerica, MA), equipped with smartbeam-II laser and the matrix is trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB). The HR-ESI mass spectra were performed on an Agilent (Santa Clara, CA, USA) ESI-TOF mass spectrometer (6224). CW X-band EPR spectra for radicals were acquired on Bruker EMX instrument EMXPLUS-10/12. The samples were typically contained in 4.0 mm EPR sample tubes. The liquid sample was encapsulated in 0.9 × 80 mm capillary tube and then placed in a special EPR sample tube. The solid sample was placed directly in the EPR sample tube for testing. For VT EPR experiments, the dewar was added the and the frequency changed from 9.8 (without dewar) to 9.4 GHz. According to the equation $H = h\nu/g\beta$ (H: magnetic field; ν: frequency; h: Planck's constant; g: g-factor; β: Bohr magneton), the EPR signal peaks appeared at 3475-3525 G is correspond to the experiment condition at room temperature in the absence of dewar and 3300-3400 G is correspond to the VT experiment condition with dewar. All the TEM measurements were performed under a Tecnai G2 20 TWIN device and the TEM samples were deposited on copper grids, followed by a slow evaporation in air at room temperature. The r_1 relaxivity constants were determined by Siemens Magnetom Prisma 3T at room temperature. Single crystal X-ray data were measured on a Xcalibur E diffractometer with graphite monochromated Cu-Kα radiation (λ = 1.54184 Å). Data collection and structure refinement details can be found in the CIF files or obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Section B. Synthesis and characterization of the rotaxane-branched radical dendrimers.

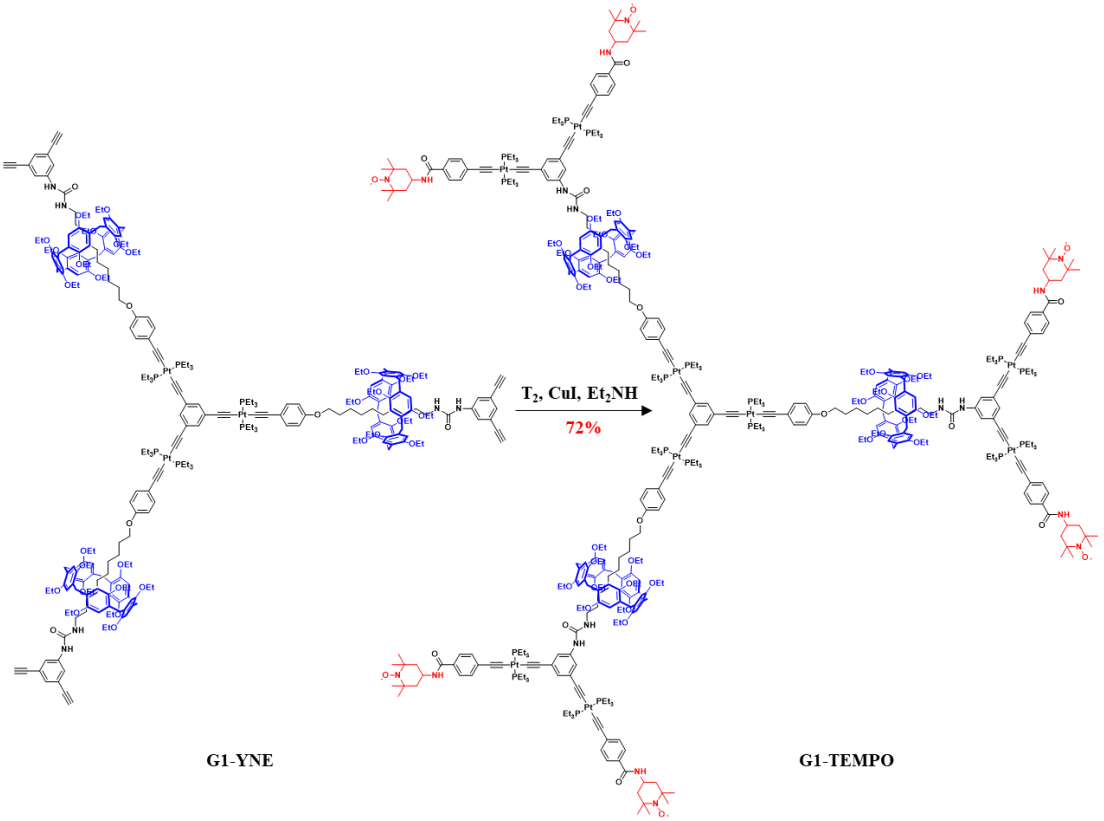
Scheme S1: Synthesis of the radical building block **T2**.



Synthesis of T1: DMF (10 μL) was added to a solution of 4-ethynylbenzoic acid (200 mg, 1.37 mmol) and oxalyl chloride (347 mg, 2.74 mmol) in dry DCM. The mixture was stirred for 2 h at room temperature. The solution was evaporated and the resultant acyl chloride was dried in vacuum at room temperature for 30 min. Then the compound was dissolved in dry DCM and added dropwise to a mixture of 4-NH_2-TEMPO (352 mg, 2.05 mmol) and Et_3N (277 mg, 2.74 mmol) in dry DCM at room temperature. The solution was stirred overnight. The organic layer was washed with water and dried over anhydrous Na_2SO_4, then evaporated under reduced pressure. The crude material was purified by column chromatography on silica gel using PE / EA (1 : 1, v / v) as eluent to afford the orange solid 166 mg with the yield of 83 %. ^{1}H NMR (500 MHz, Acetone-d_6): δ 7.92 (d, J = 5 Hz, 2H), 7.58 (d, J = 5 Hz, 2H), 3.81(s, 1H); HR-ESI-MS: Calcd. For $[C_{18}H_{25}N_2O_2]^+$: 301.1916, Found: 301.1909.

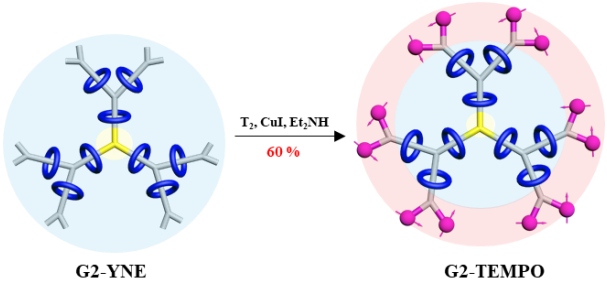
Synthesis of T2: A mixture of compound **T1** (100 mg, 0.33 mmol) and $Pt(PEt_3)_2I_2$ (686 mg, 1.0 mmol) in degassed diethylamine (15 mL) was stirred 2 h at room temperature in the presence of a catalytic amount of CuI. The solution was then evaporated under pressure and the reside was purified by column chromatography on silica gel using PE / EA (1 : 1, v / v) as eluent to afford the pale-yellow solid 200 mg with the yield of 70 %. ^{1}H NMR (500 MHz, Acetone-d_6): δ 7.80 (s, 2H), 7.35 (s, 2H), 2.27(m, 12H), 1.17(m, 18H). ^{31}P NMR (202 MHz, Acetone-d_6): δ 11.54. MALDI-TOF-MS: Calcd. For $[C_{30}H_{52}IN_2O_2P_2Pt]^+$: 856.2, Found: 856.1.

Scheme S2: Synthesis of rotaxane-branched radical dendrimer **G1-TEMPO.**



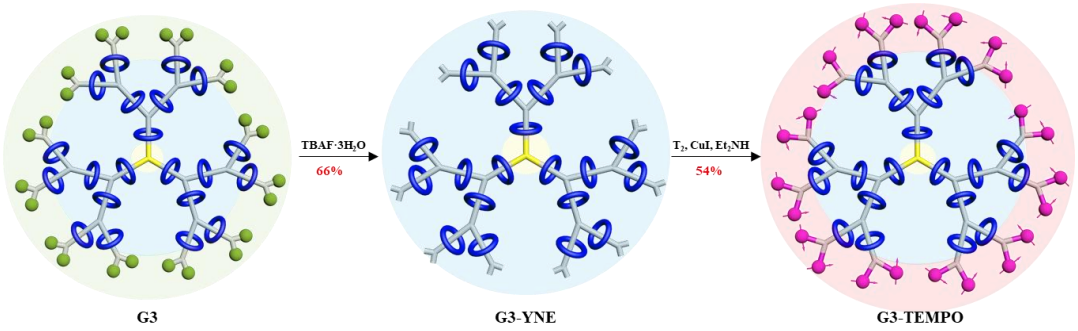
Synthesis of rotaxane-branched radical dendrimer G1-TEMPO: A mixture of compound **G1-YNE**[S1] (64 mg, 0.012 mmol) and **T2** (67 mg, 0.078 mmol) in degassed dichloromethane (10 mL) and diethylamine (5 mL) was stirred at room temperature for 10 min. Then catalytic amount of CuI was added. The solution was stirred overnight and then evaporated under pressure. The reside was first purified by column chromatography on silica gel using DCM / MeOH (1 : 1, v / v) as eluent and then by GPC for further purification to afford the pale-yellow solid 95 mg with the yield of 72 %. ^{31}P NMR (202 MHz, CD_2Cl_2): δ 12.27, 11.89; MALDI-TOF-MS: Calcd. For M_r : = 9806.2 Da; Found: *m/z* =9827.4.

Scheme S3: Synthesis of the rotaxane-branched radical dendrimer **G2-TEMPO.**



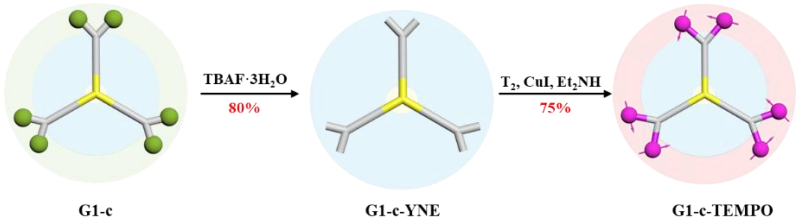
Synthesis of the rotaxane-branched radical dendrimer G2-TEMPO: A mixture of compound **G2-YNE**[S1] (28 mg, 0.0018 mmol) and **T2** (19.8 mg, 0.023 mmol) in degassed dichloromethane (5 mL) and diethylamine (3 mL) was stirred at room temperature for 10 min. Then catalytic amount of CuI was added. The solution was stirred overnight and then evaporated under pressure. The reside was first purified by column chromatography on silica gel using DCM / MeOH (1 : 1, v / v) as eluent and then by GPC for further purification to afford the pale-yellow solid 30 mg with the yield of 60 %. ^{31}P NMR (202 MHz, CD_2Cl_2): δ 12.27, 12.09, 11.90; MALDI-TOF-MS: Calcd. For M_r : = 24745.7 Da; Found: m/z = 24877.2.

Scheme S4: Synthesis of the rotaxane-branched radical dendrimer **G3-TEMPO.**



Synthesis of the rotaxane-branched radical dendrimer G3-TEMPO: A solution of TBAF·3H_2O (21.4 mg, 0.068 mmol) in THF (5 mL) was added dropwise into the solution of **G3**[S1] (58 mg, 0.0014 mmol) in THF (10.0 mL). The reaction mixture was stirred at room temperature for 4 h. The resultant mixture was washed by water, then dried with Na_2SO_4 and concentrated. The residue was first purified by column chromatography on silica gel using DCM / MeOH (10 / 1, v / v) as eluent and then by GPC for further purification to afford the pale-yellow solid **G3-YNE**. The mixture of compound **G3-YNE** and **T2** (32 mg, 0.036 mmol) in degassed dichloromethane (5 mL) and diethylamine (3 mL) was stirred at room temperature for 10 min. Then catalytic amount of CuI was added. The solution was stirred overnight and then evaporated under pressure. The reside was first purified by column chromatography on silica gel using DCM / MeOH (10 : 1, v / v) as eluent and then by GPC for further purification to afford the pale-yellow solid 41 mg with the yield of 54 %. ^{31}P NMR (202 MHz, CD_2Cl_2): δ 12.23, 12.06, 11.87.

Scheme S5: Synthesis of the model radical dendrimer **G1-c-TEMPO.**



Synthesis of the branched radical dendrimer G1-c-TEMPO: A solution of TBAF·3H_2O (163 mg, 0.52 mmol) in THF (5 mL) was added dropwise into the solution of **G1-c**[S1] (160 mg, 0.04 mmol) in THF (35 mL). The reaction mixture was stirred at room temperature for 4 h. The resultant mixture was washed by water, then dried with Na_2SO_4 and concentrated. The residue was first purified by column chromatography on silica gel using DCM / MeOH (10 / 1, v / v) as eluent and then by GPC for further purification to afford the pale-yellow solid **G1-c-YNE**. The mixture of compound **G1-c-YNE** and **T2** (355 mg, 0.42 mmol) in degassed dichloromethane (30 mL) and diethylamine (10 mL) was stirred at room temperature for 10 min. Then catalytic amount of CuI was added. The solution was stirred overnight and then evaporated under pressure. The reside was first purified by column chromatography on silica gel using DCM / MeOH (10 : 1, v / v) as eluent and then by GPC for further purification to afford the pale-yellow solid 185 mg with the yield of 75 %. ^{31}P NMR (202 MHz, CD_2Cl_2): δ 12.20, 11.92.

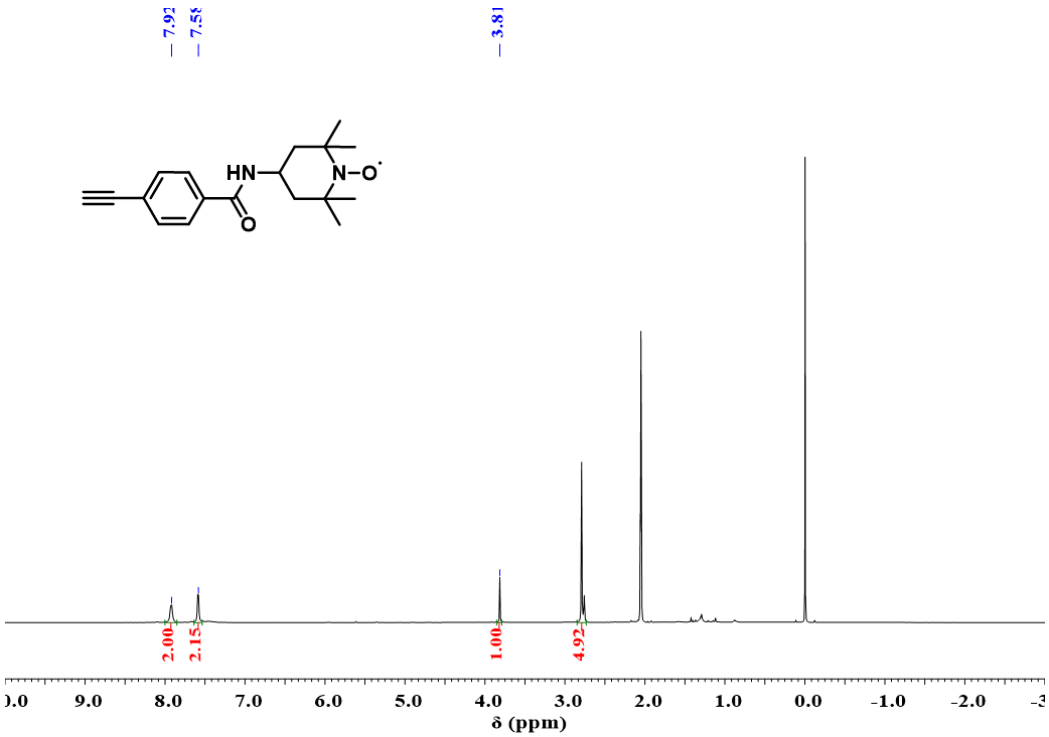


Fig. S1 ^{1}H NMR spectrum (Acetone-d_6, 298 K, 500 MHz) of **T1**.

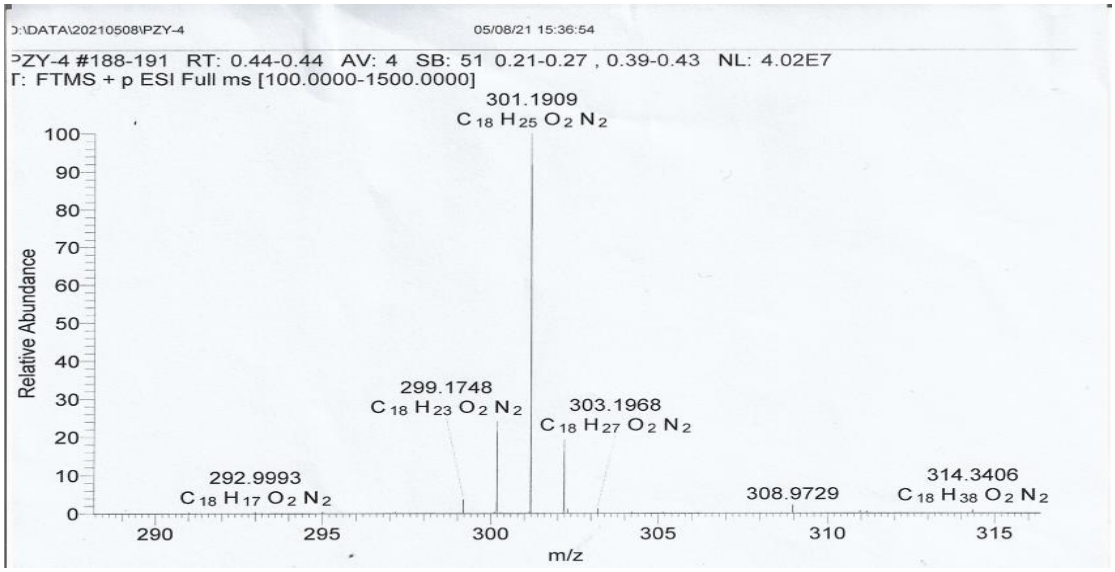


Fig. S2 HR-ESI-MS spectrum of **T1**.

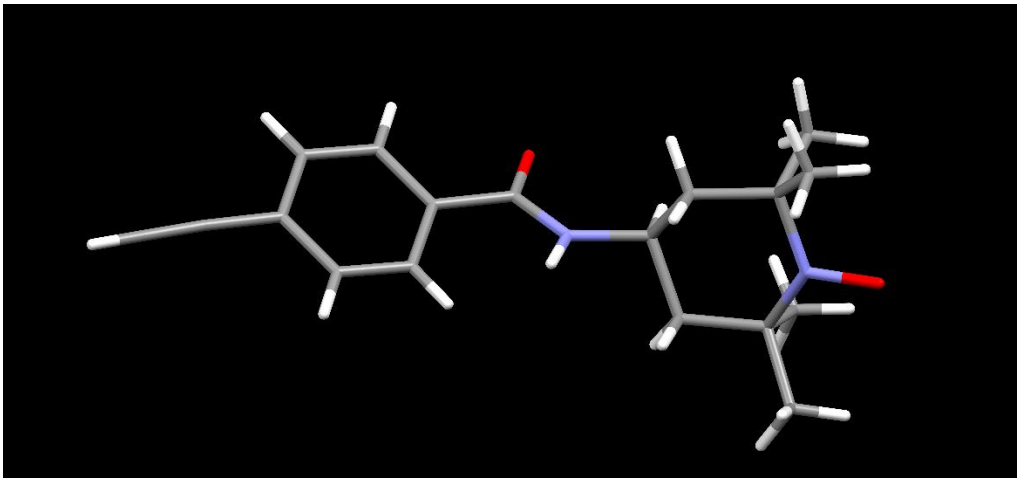


Fig. S3 Stick representation of the X-ray structure of **T1**. Crystallographic data for the structure analyses of the single crystal of **T1** have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as 2108849.

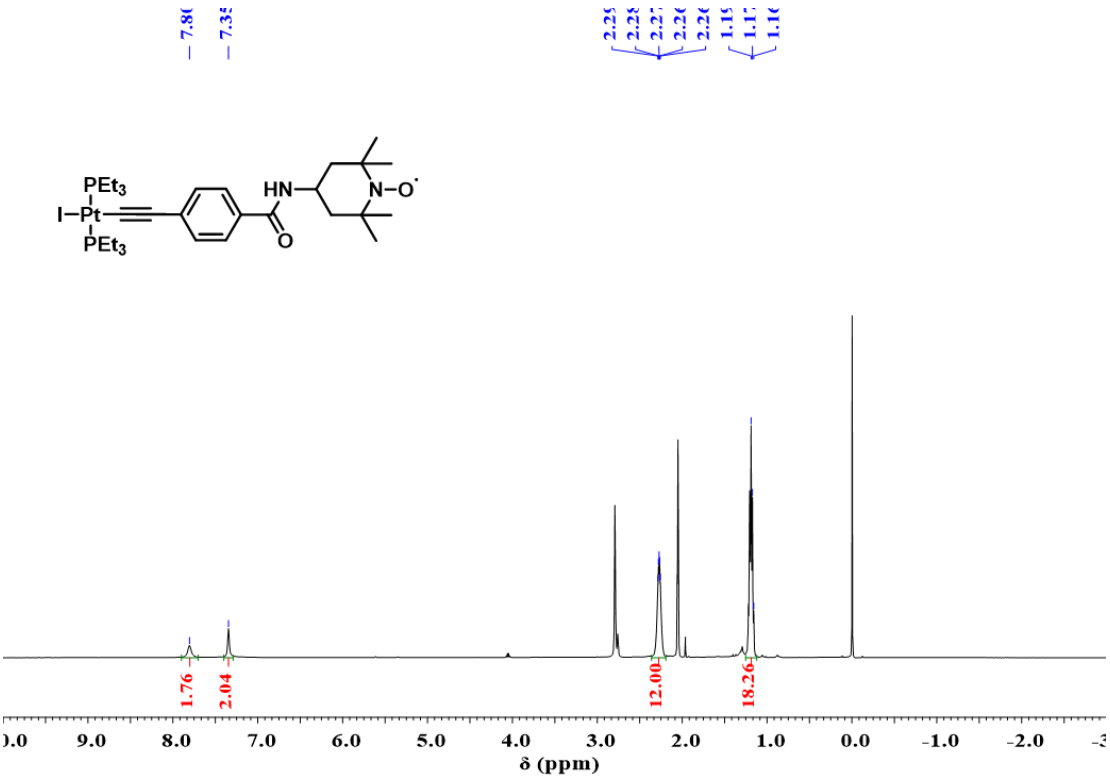


Fig. S4 ^{1}H NMR spectrum (Acetone-d_6, 298 K, 500 MHz) of **T2**.

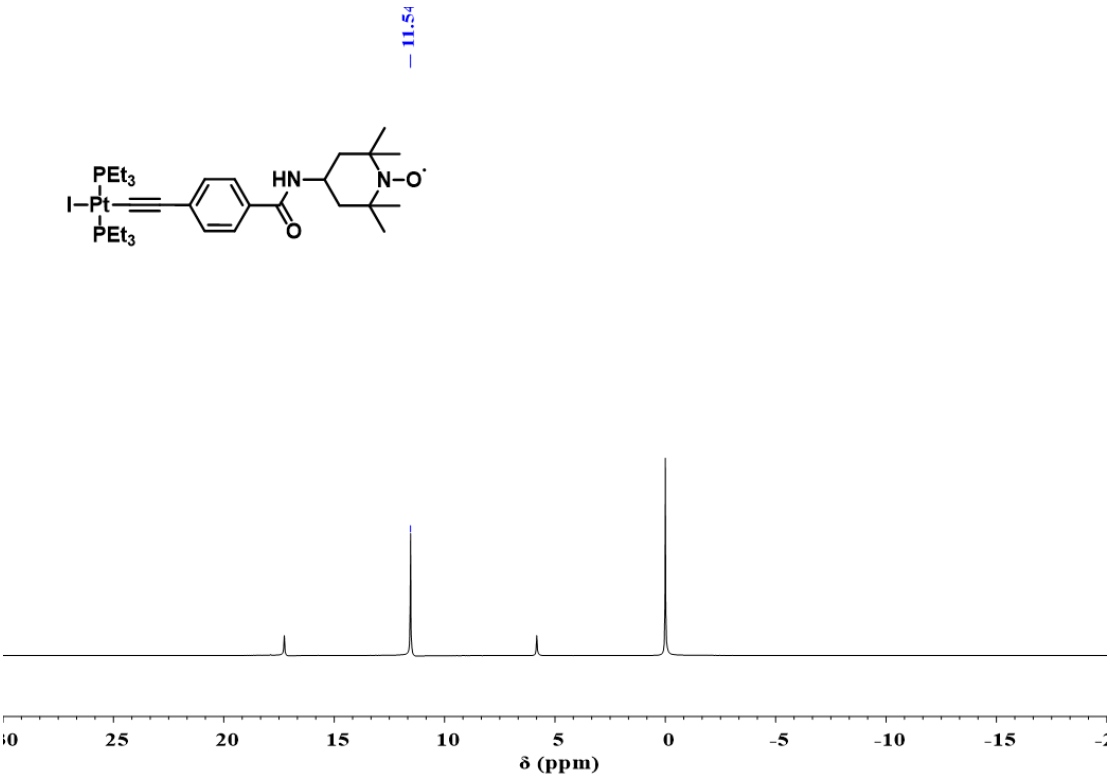


Fig. S5 ^{31}P NMR spectrum (Acetone-d_6, 298 K, 202 MHz) of **T2**.

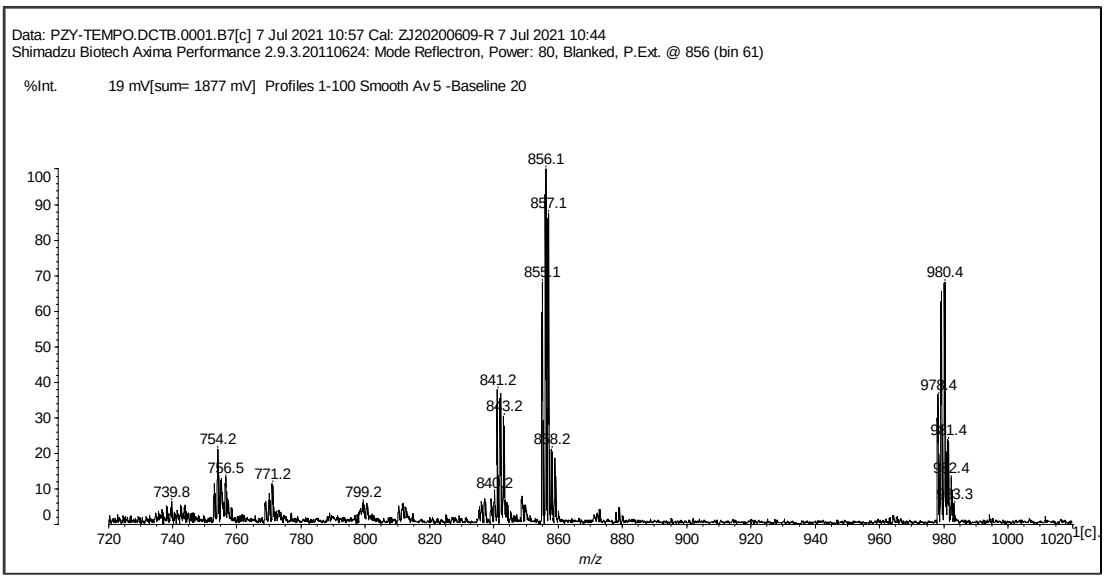


Fig. S6 MALDI-TOF-MS spectrum of **T2**.

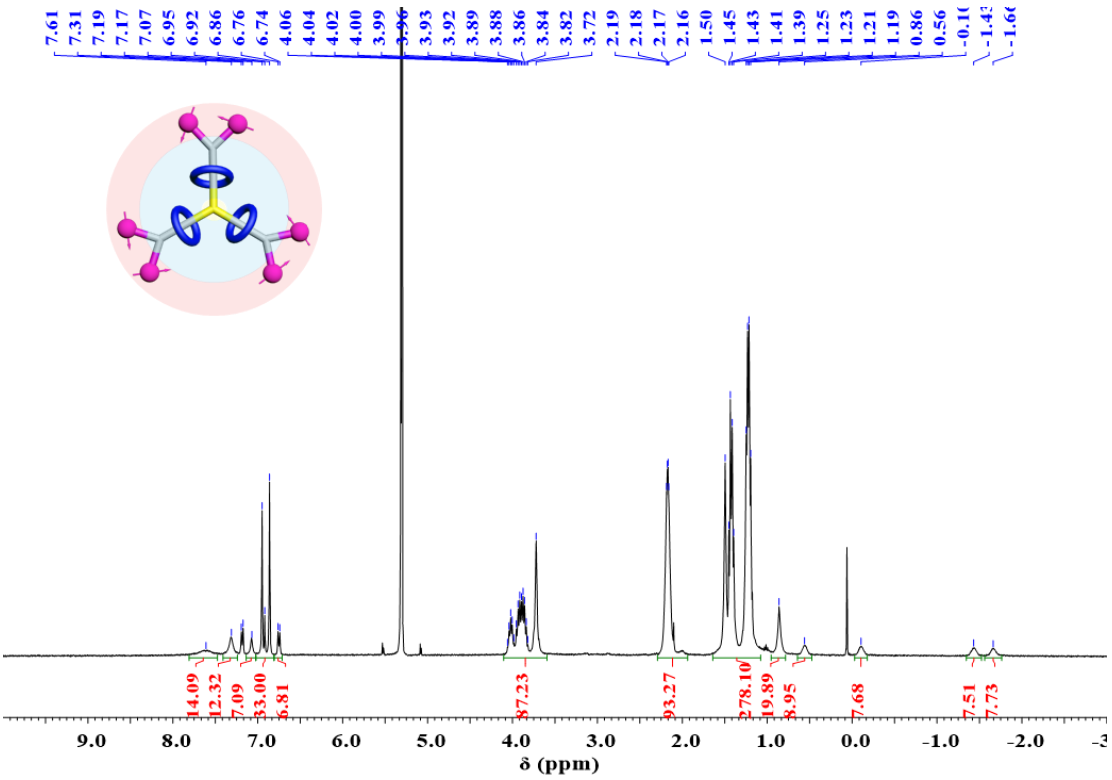


Fig. S7 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 500 MHz) of **G1-TEMPO**.

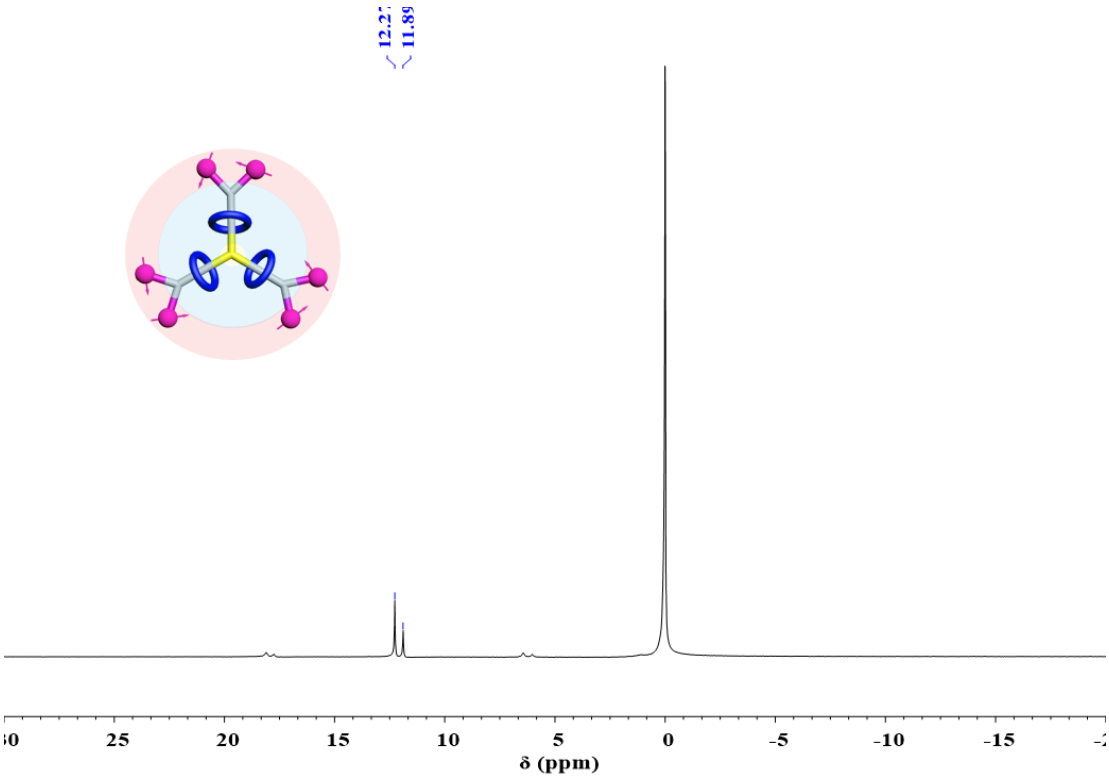


Fig. S8 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 202 MHz) of **G1-TEMPO**.

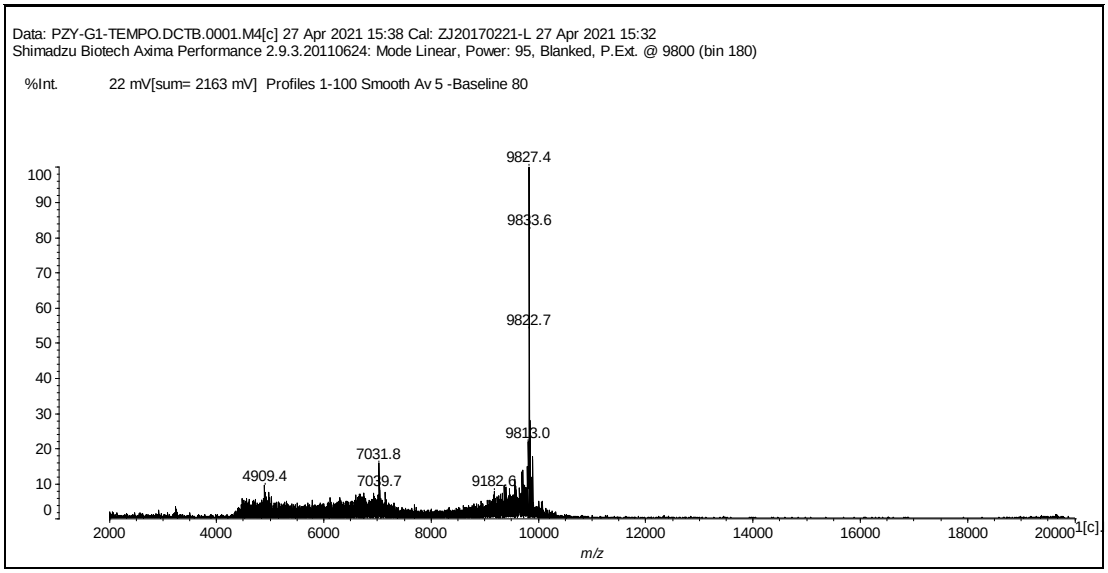


Fig. S9 MALDI-TOF-MS spectrum of **G1-TEMPO**.

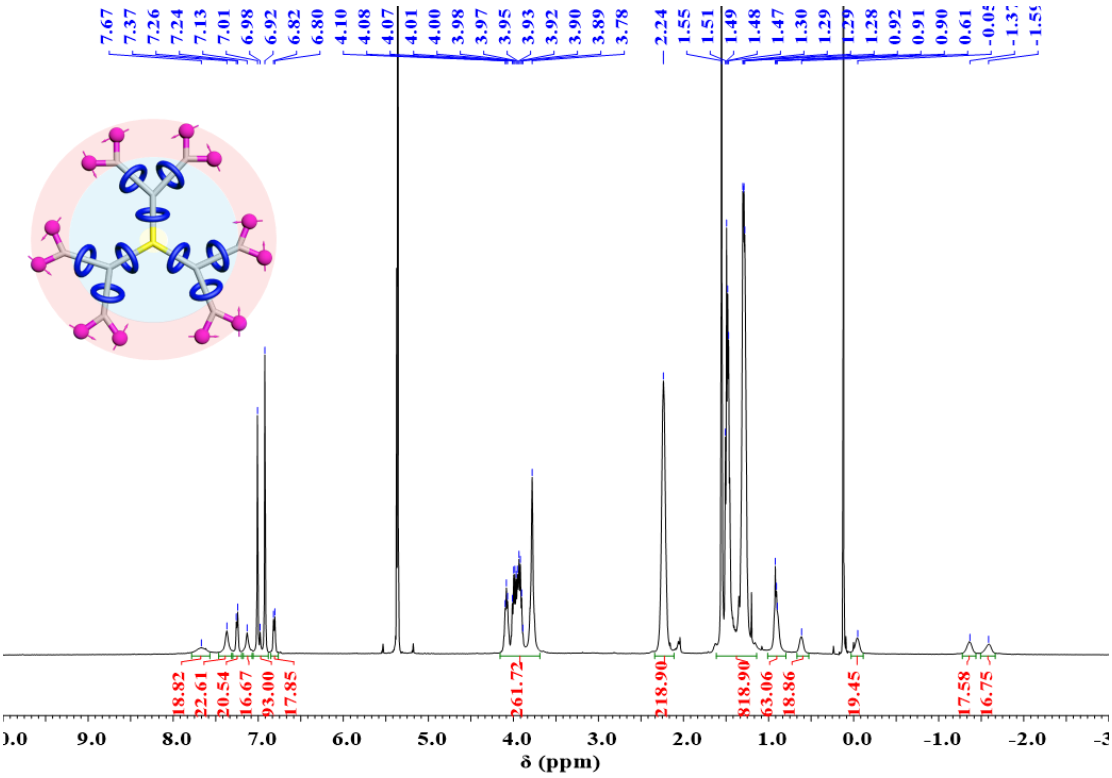


Fig. S10 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 500 MHz) of **G2-TEMPO**.

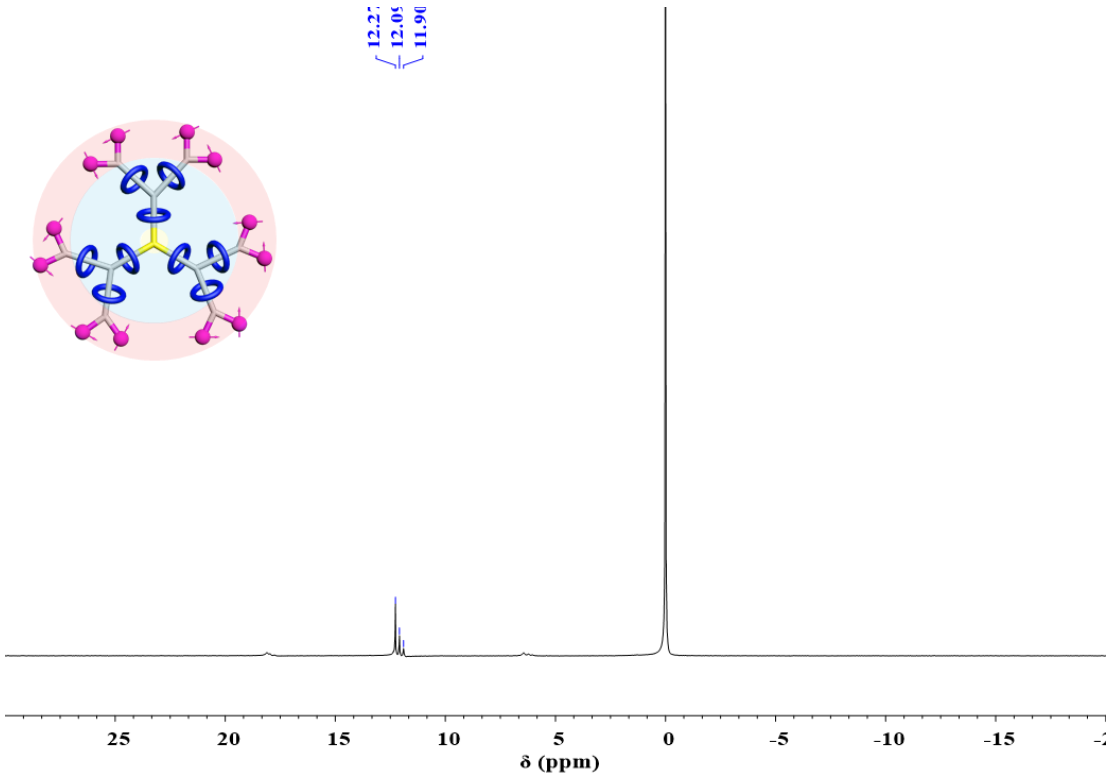


Fig. S11 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 202 MHz) of **G2-TEMPO**.

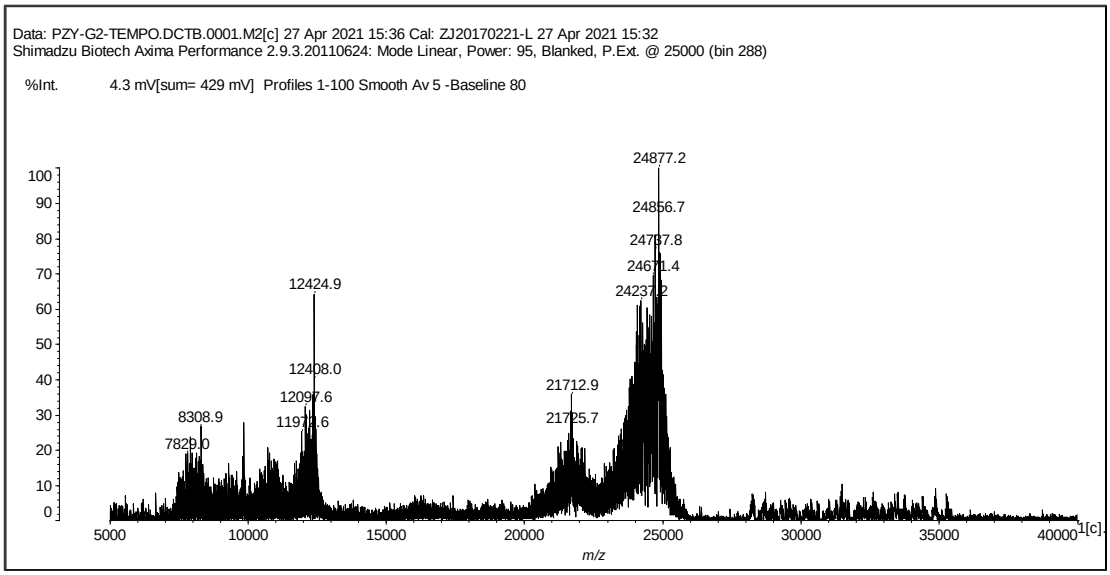


Fig. S12 MALDI-TOF-MS spectrum of **G2-TEMPO**.

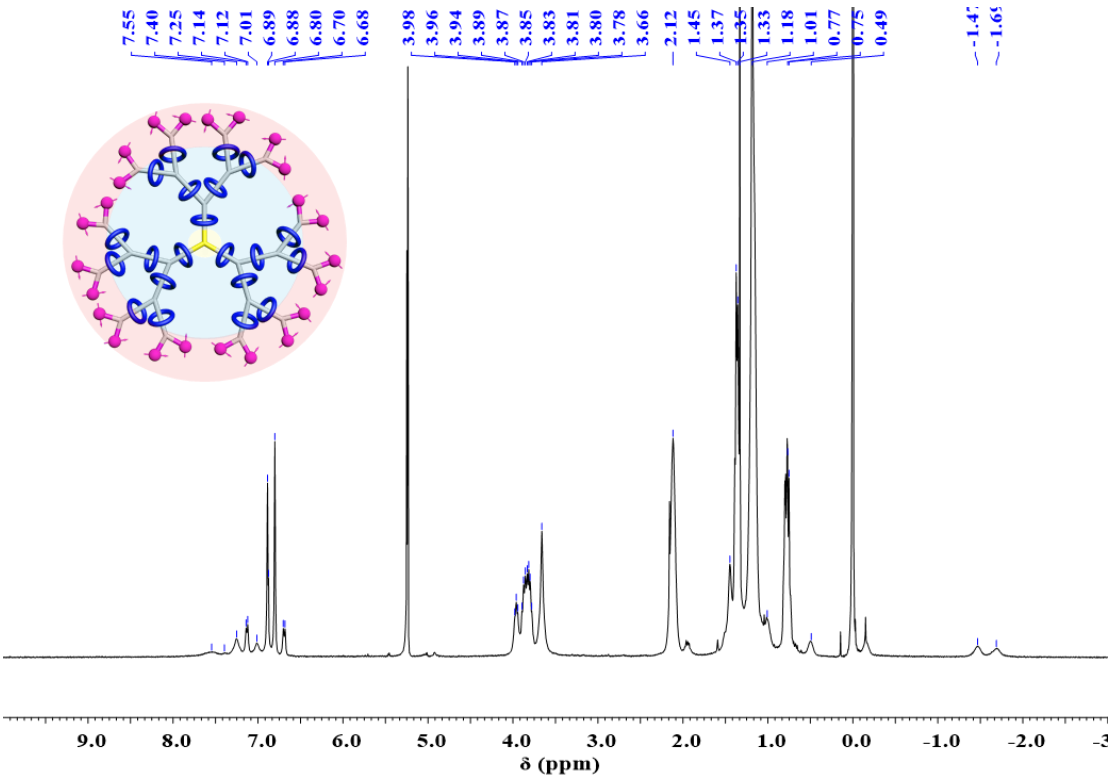


Fig. S13 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 500 MHz) of **G3-TEMPO**.

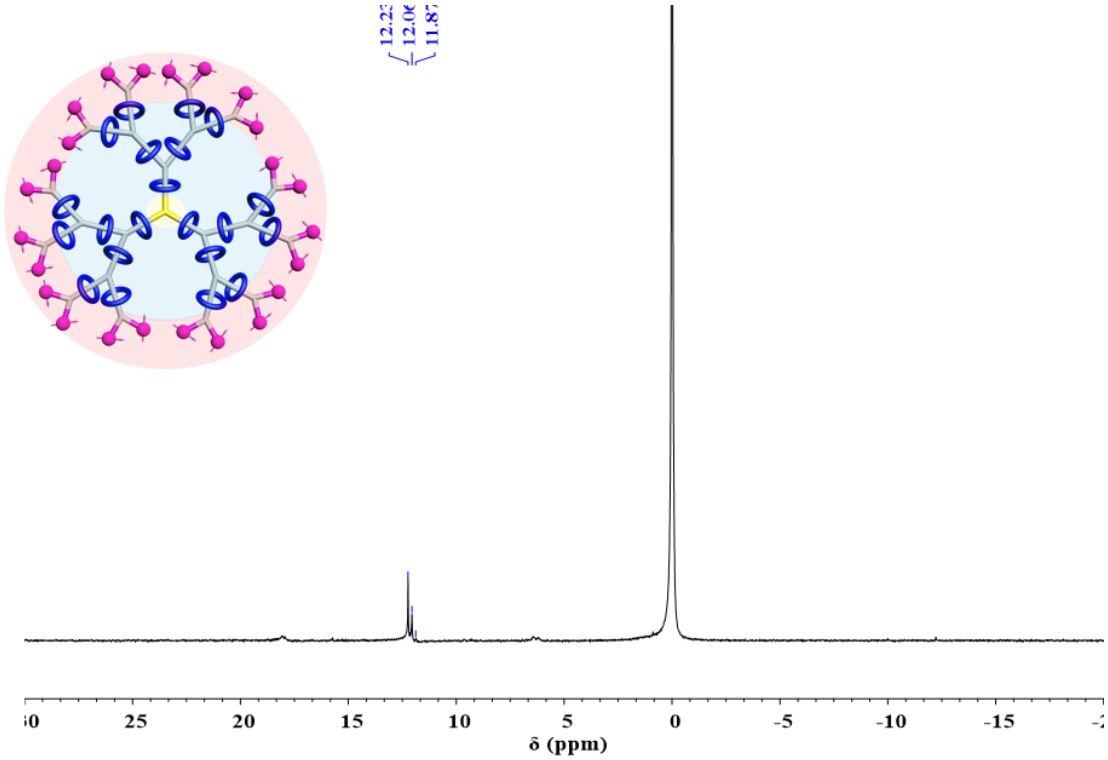


Fig. S14 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 202 MHz) of **G3-TEMPO**.

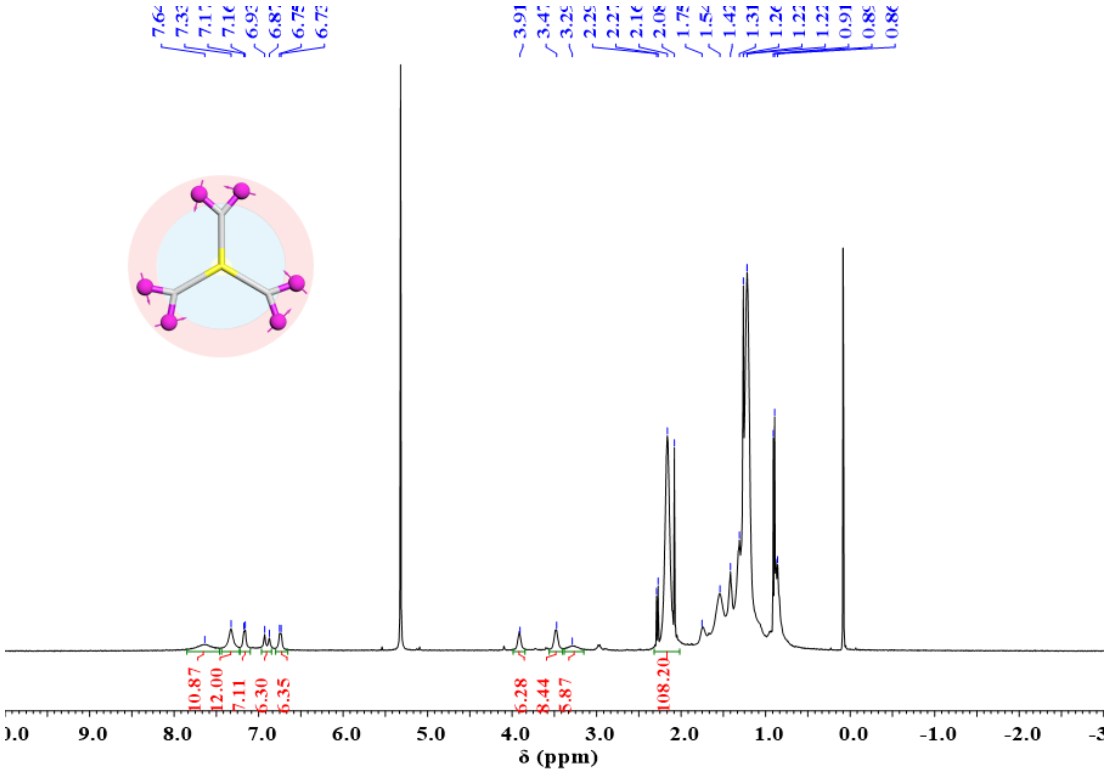


Fig. S15 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 500 MHz) of **G1-c-TEMPO**.

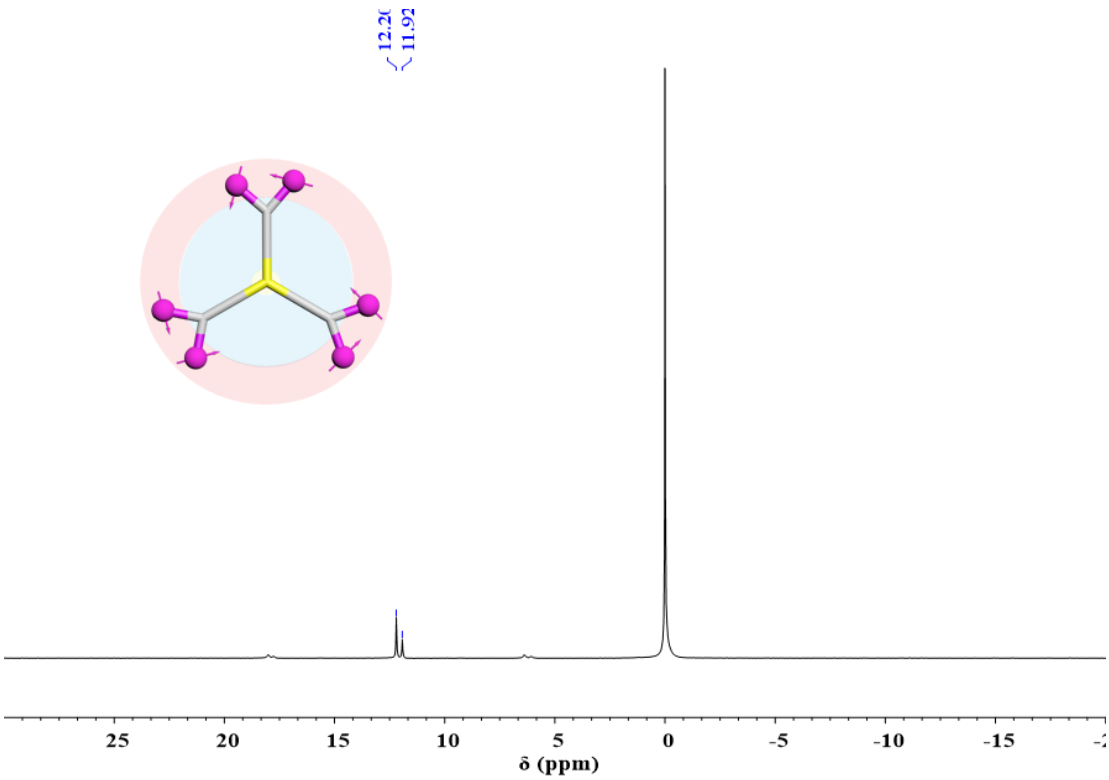


Fig. S16 ^{31}P NMR spectrum (CD_2Cl_2, 298 K, 202 MHz) of **G1-c-TEMPO**.

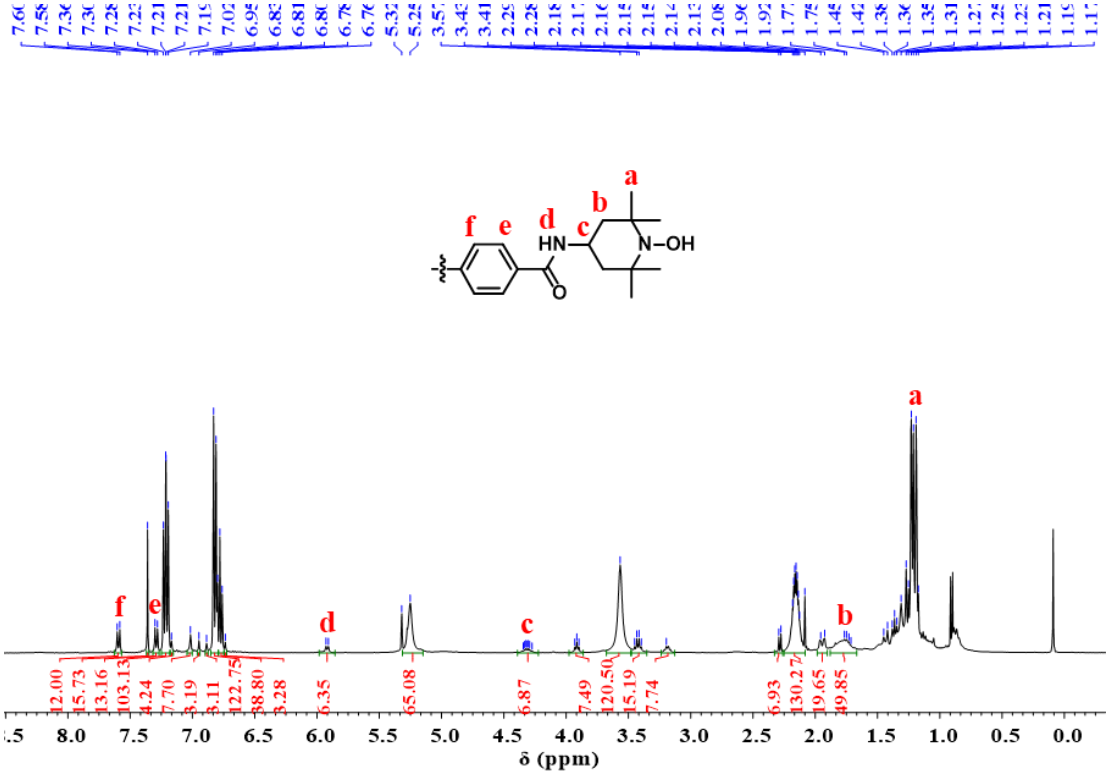


Fig. S17 ^{1}H NMR spectrum (CD_2Cl_2, 298 K, 500 MHz) of **G1-c-TEMPO** in the presence of excess phenylhydrazine.

Section C. EPR data

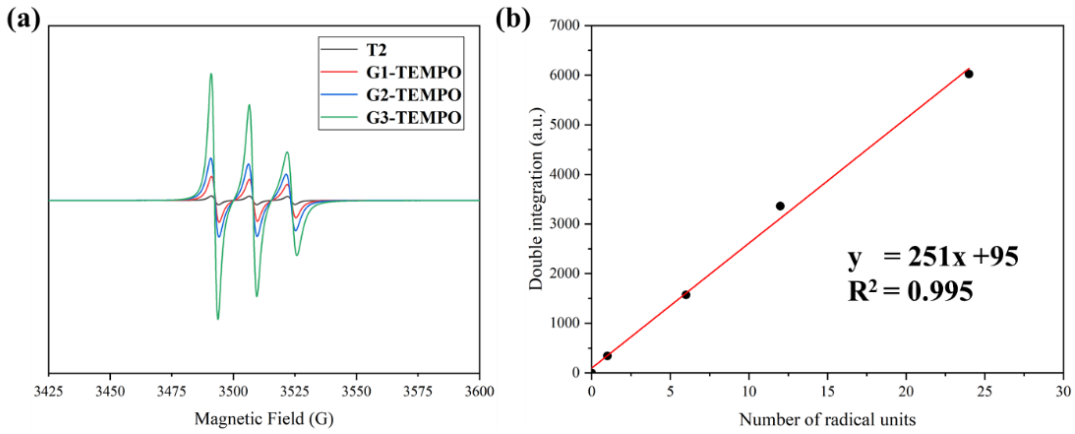


Fig. S18 (a) X-band EPR spectra of **T2**, **G1-TEMPO**, **G2-TEMPO** and **G3-TEMPO** (0.1 mM in THF) obtained under identical conditions; (b) Double integral of the EPR spectra *vs* number of radical units. (All experiments were performed in the same conditions for the evaluation of the numbers of the anchored TEMPO units, especially the EPR's acquisition parameters. EPR spectrum is the first derivative of the absorption spectrum and the EPR intensity of **Gn-TEMPO** can be calculated by double integral which is suitable for quantitative analysis.)

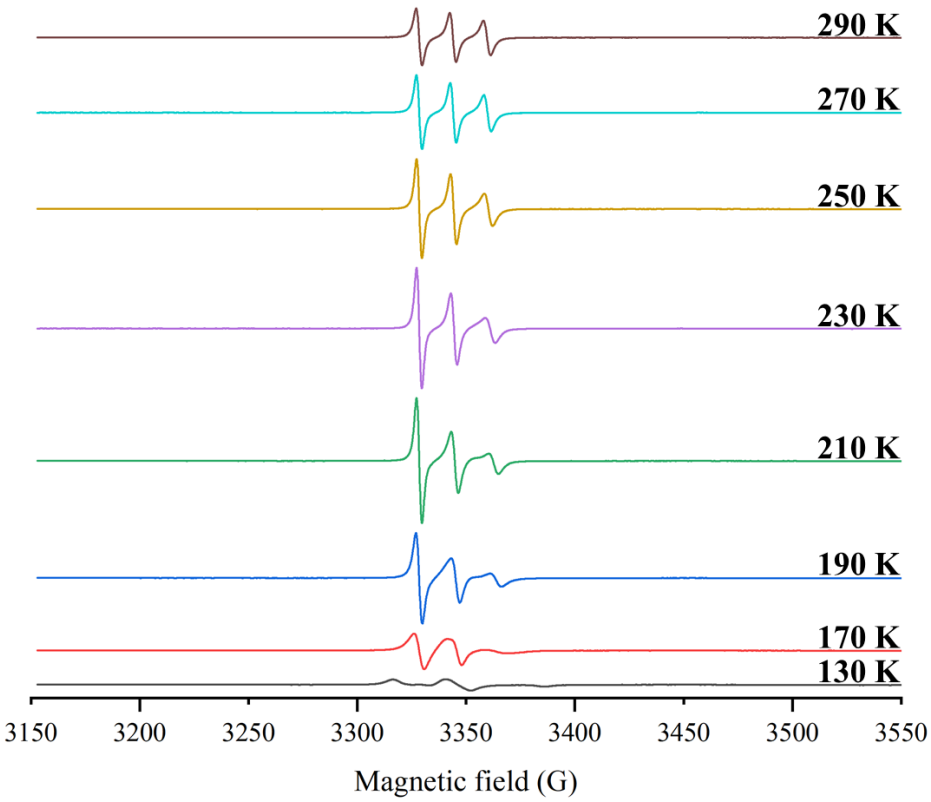


Fig. S19 VT-EPR spectra of **G1-TEMPO** (0.1 mM in THF).

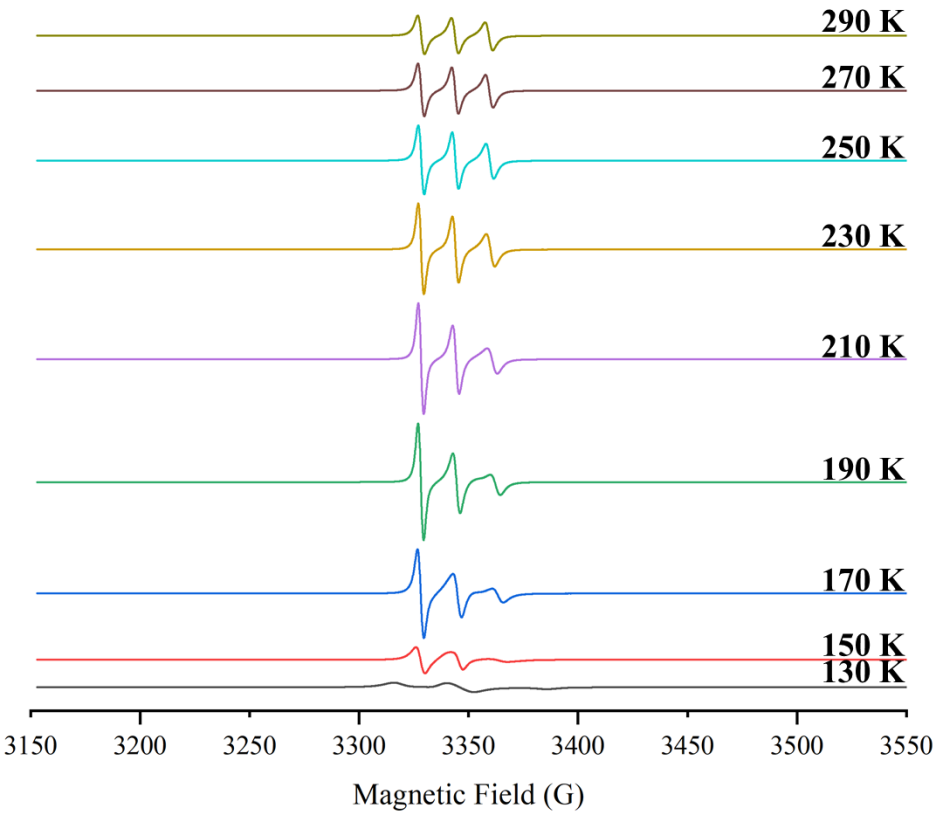


Fig. S20 VT-EPR spectra of **G1-TEMPO** (1 mM in THF).

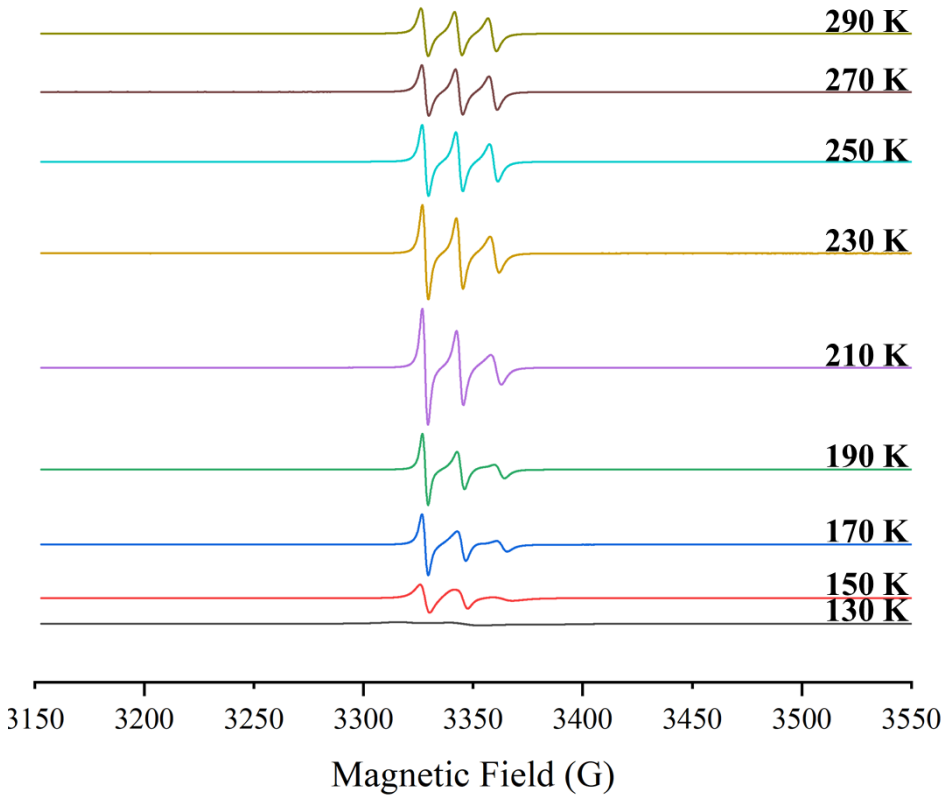


Fig. S21 VT-EPR spectra of **G1-TEMPO** (2 mM in THF).

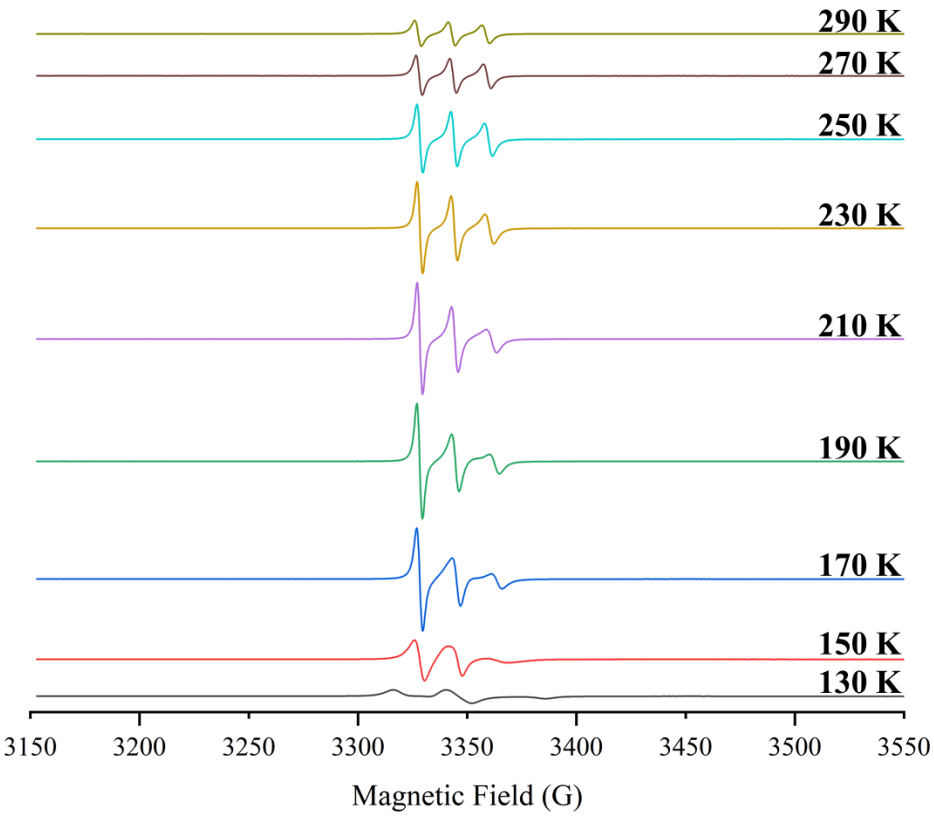


Fig. S22 VT-EPR spectra of **G2-TEMPO** (0.1 mM in THF).

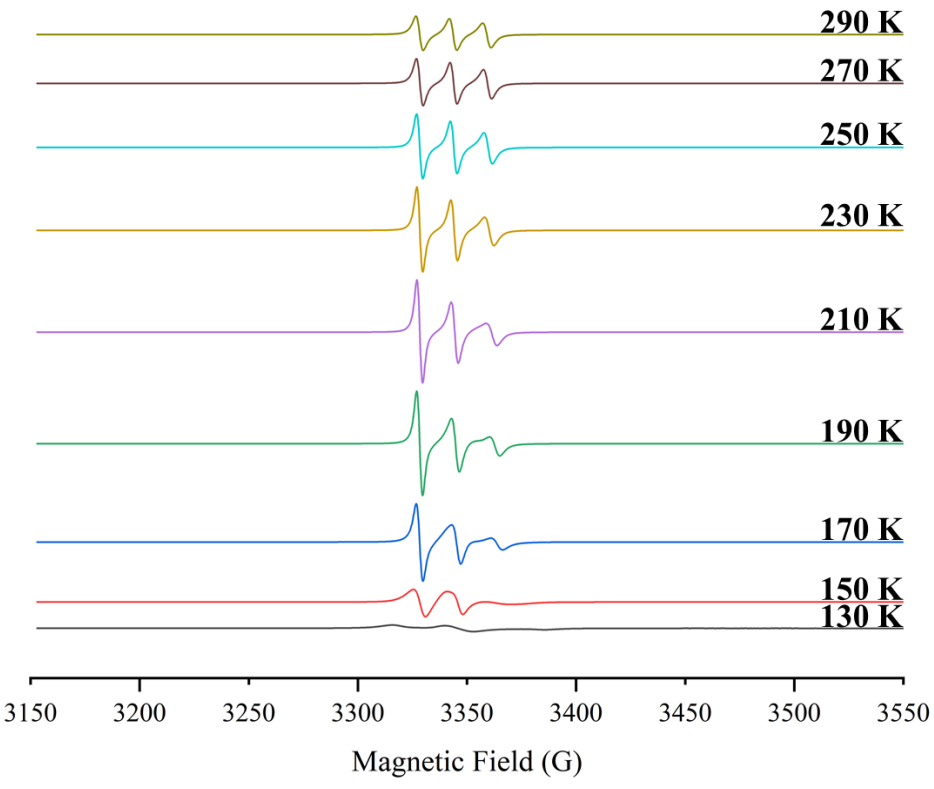


Fig. S23 VT-EPR spectra of **G2-TEMPO** (1 mM in THF).

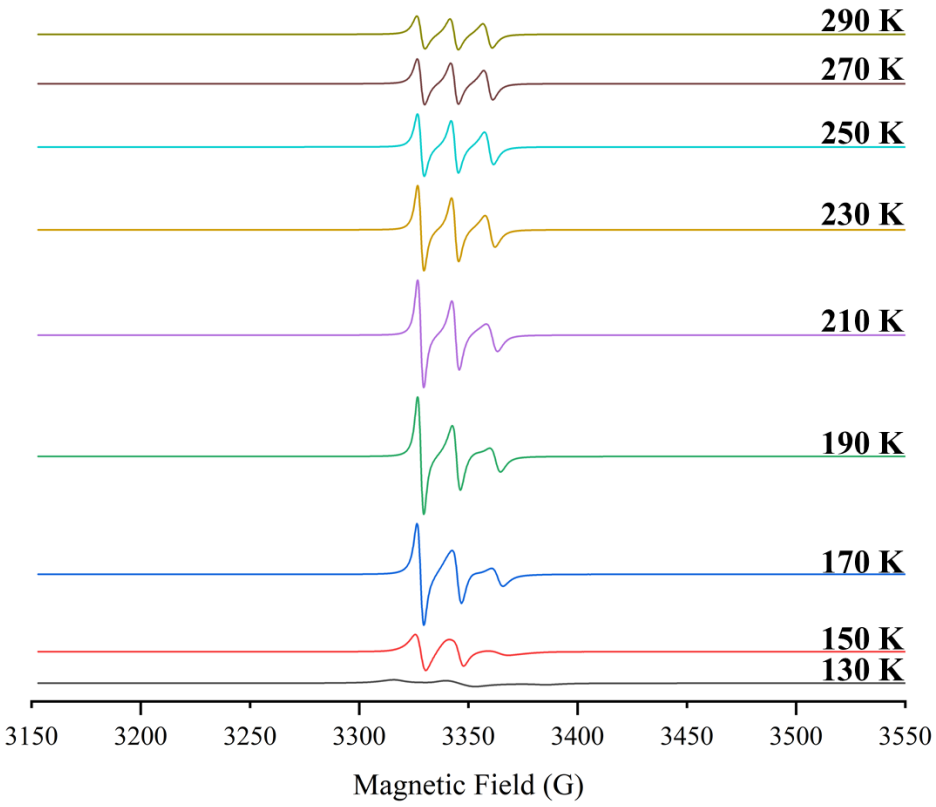


Fig. S24 VT-EPR spectra of **G2-TEMPO** (2 mM in THF).

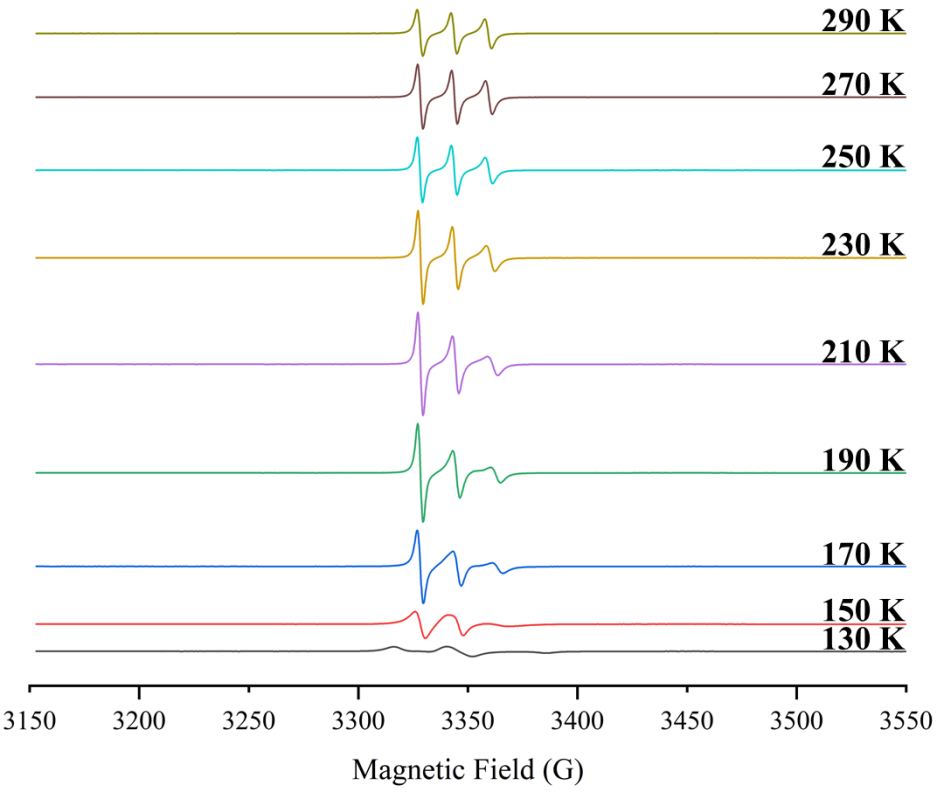


Fig. S25 VT-EPR spectra of **G3-TEMPO** (0.1 mM in THF).

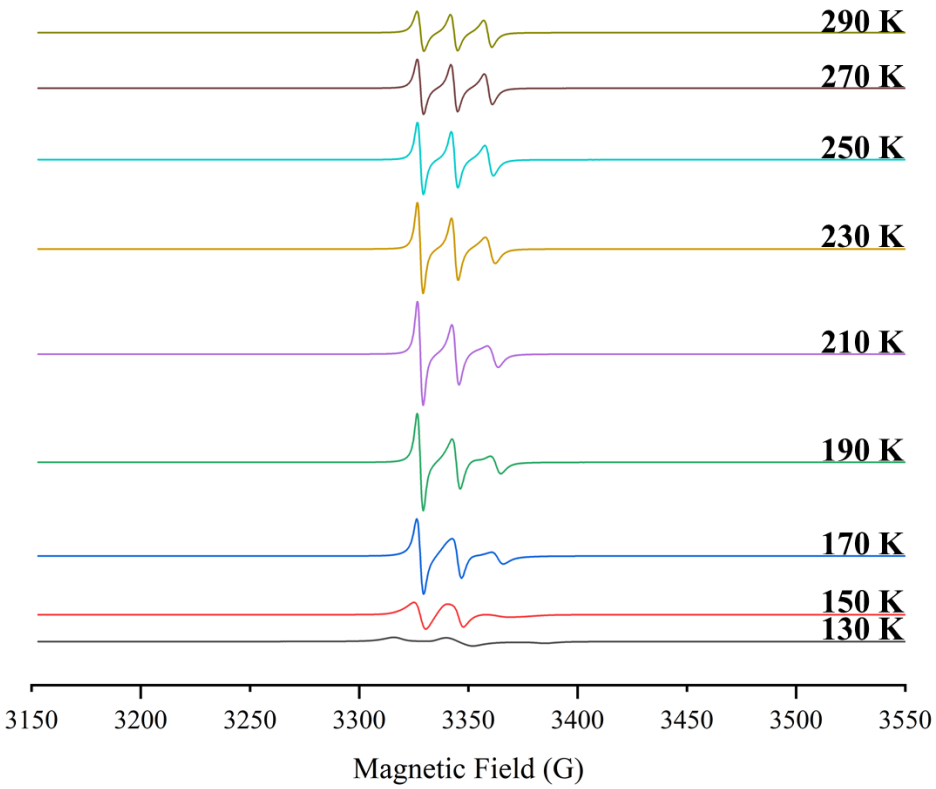


Fig. S26 VT-EPR spectra of **G3-TEMPO** (1 mM in THF).

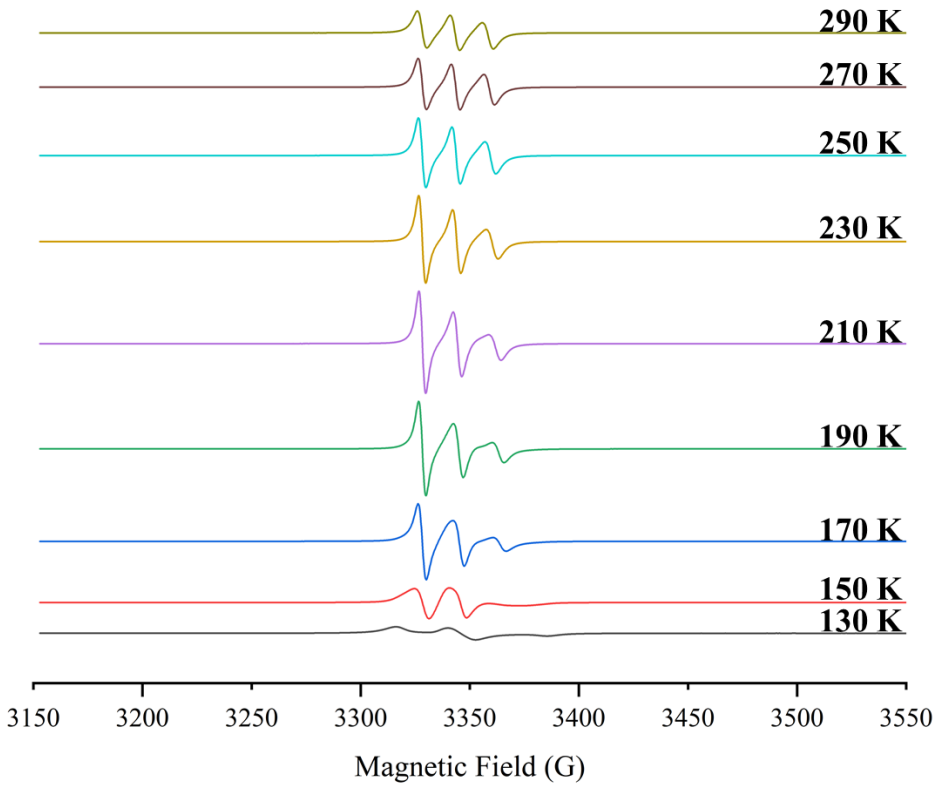


Fig. S27 VT-EPR spectra of **G3-TEMPO** (2 mM in THF).

For all half-field VT-EPR spectra shown below, the broad peak at 1500 G might be attributed to the impurity in the capillary tube or nuclear magnetic tube.

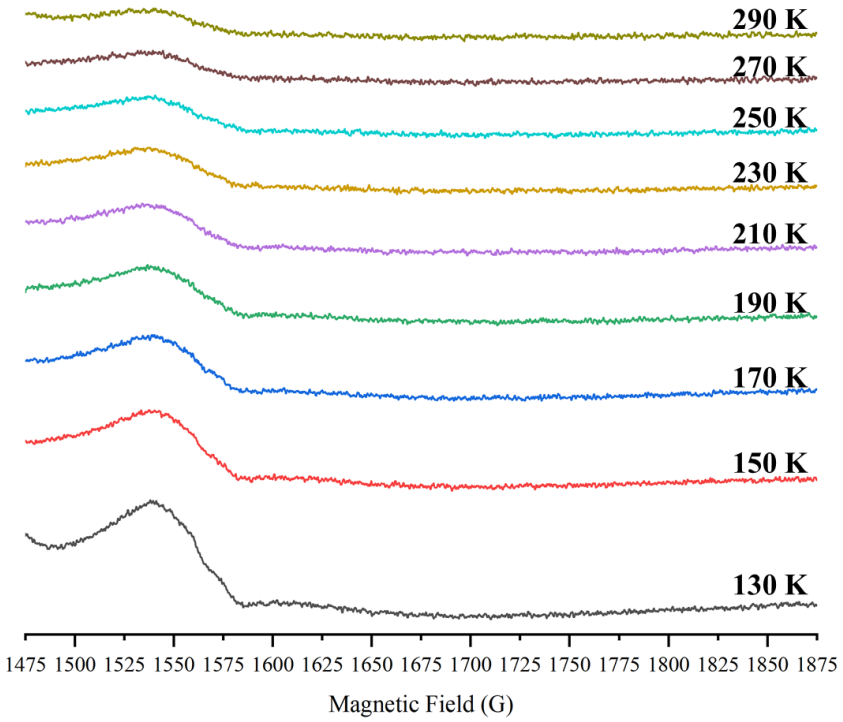


Fig. S28 The half-field VT-EPR spectra of **G1-TEMPO** (0.1 mM in THF).

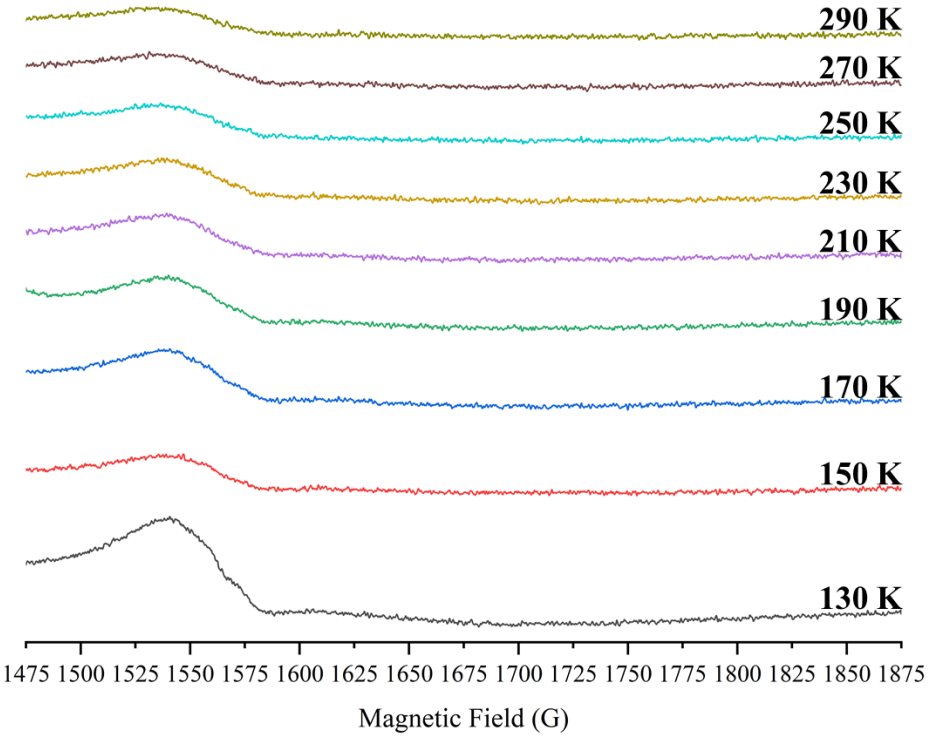


Fig. S29 The half-field VT-EPR spectra of **G1-TEMPO** (1 mM in THF).

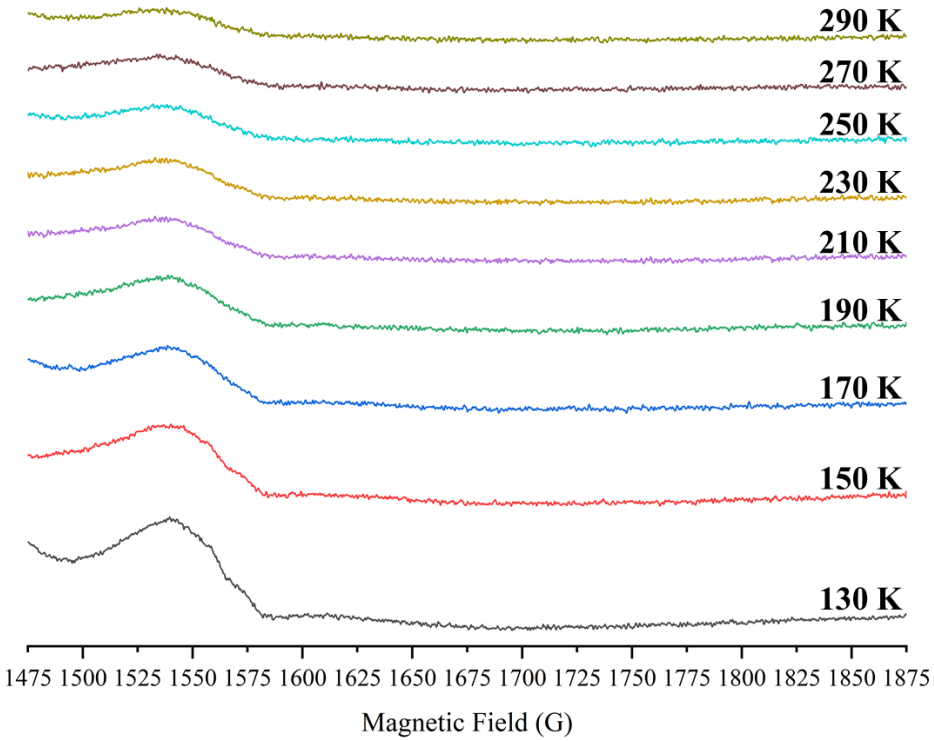


Fig. S30 The half-field VT-EPR spectra of **G1-TEMPO** (2 mM in THF).

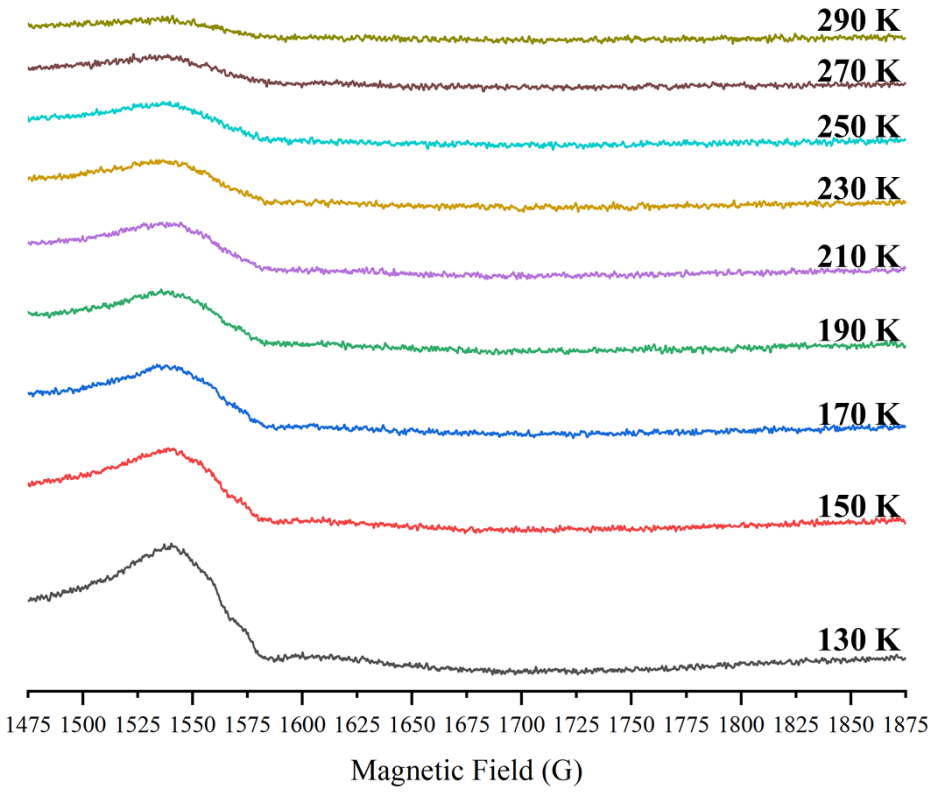


Fig. S31 The half-field VT-EPR spectra of **G2-TEMPO** (0.1 mM in THF).

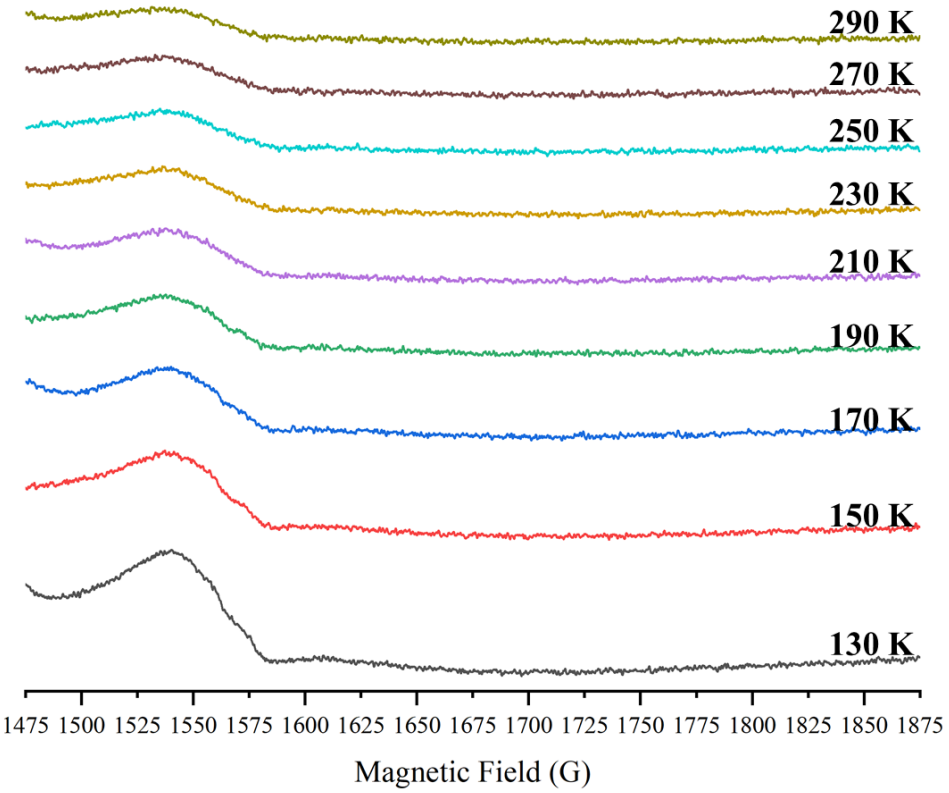


Fig. S32 The half-field VT-EPR spectra of **G2-TEMPO** (1 mM in THF).

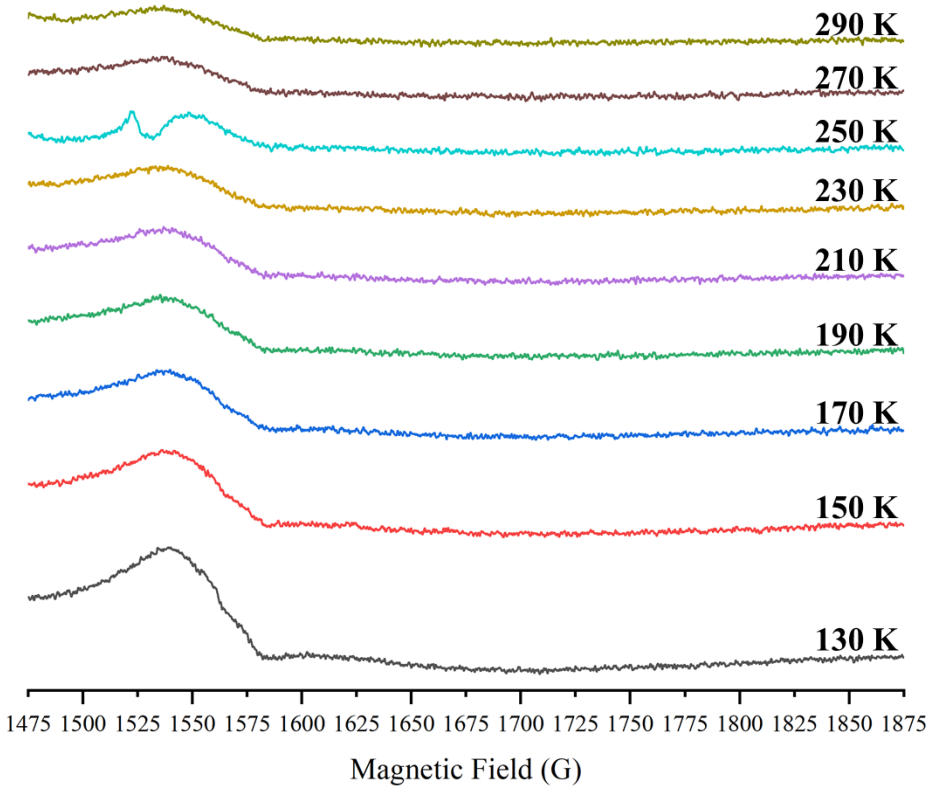


Fig. S33 The half-field VT-EPR spectra of **G2-TEMPO** (2 mM in THF).

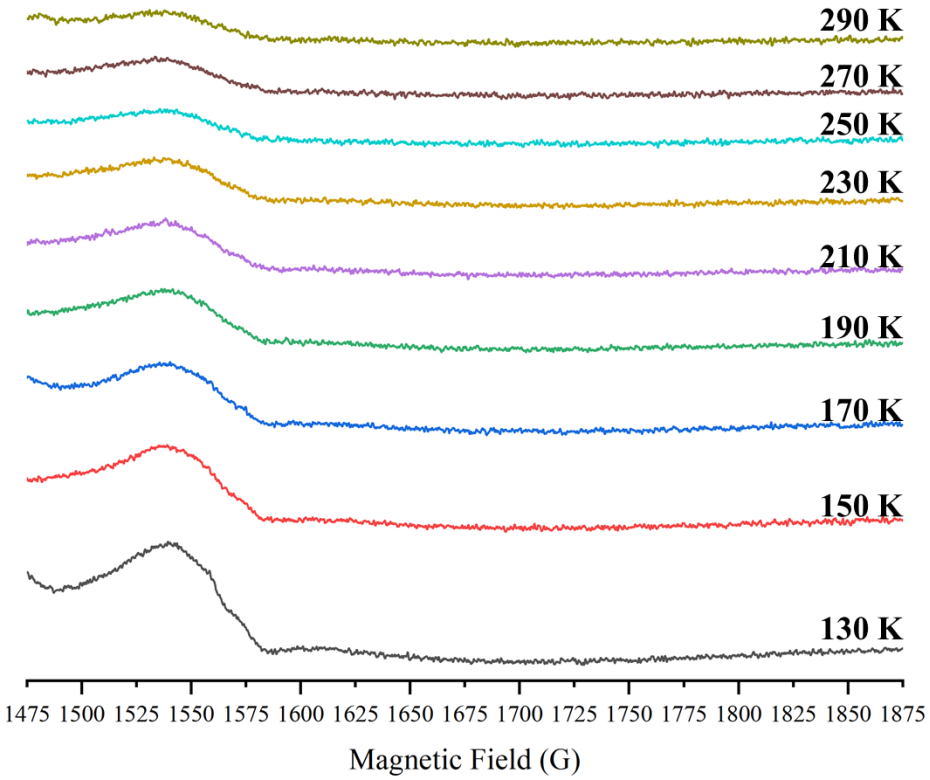


Fig. S34 The half-field VT-EPR spectra of **G3-TEMPO** (0.1 mM in THF).

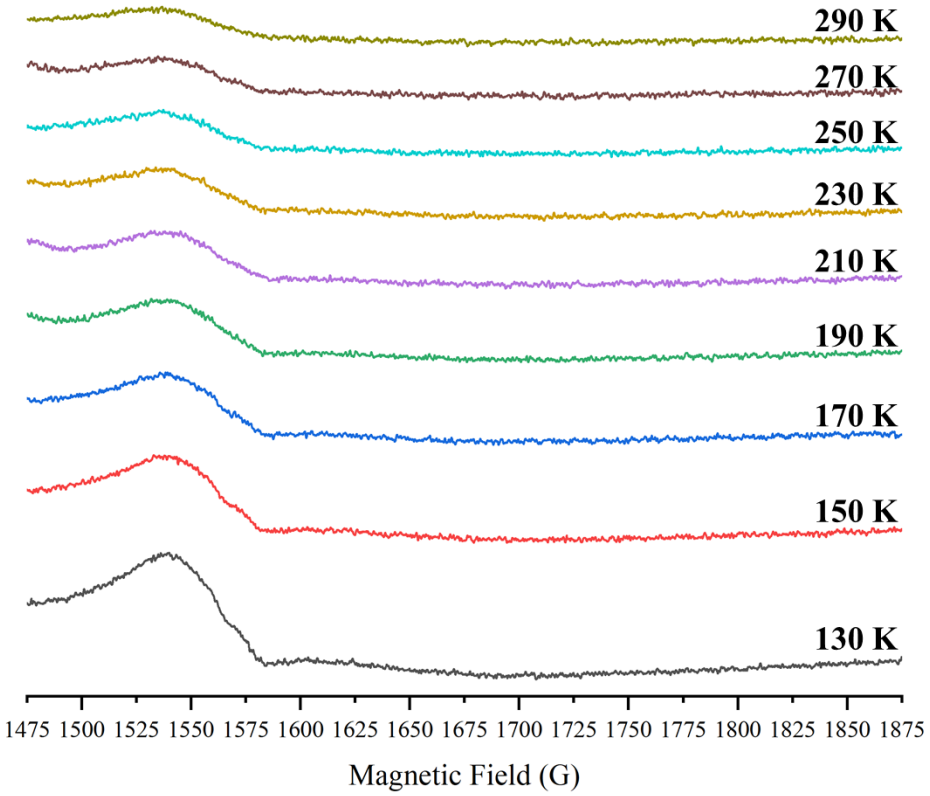


Fig. S35 The half-field VT-EPR spectra of **G3-TEMPO** (1 mM in THF).

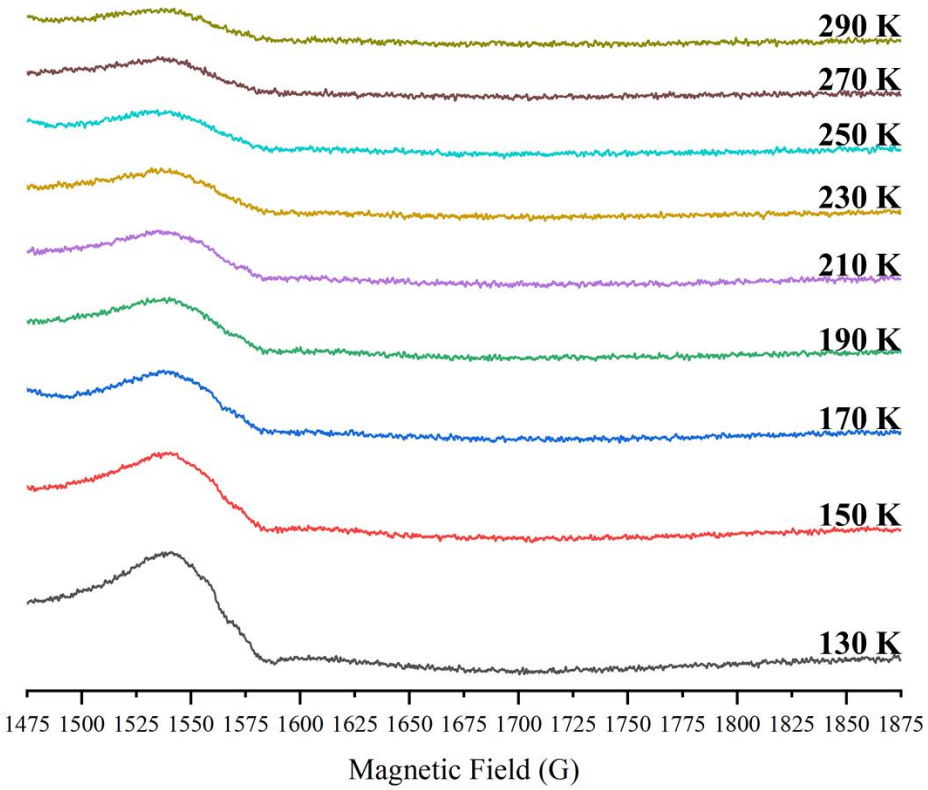


Fig. S36 The half-field VT-EPR spectra of **G3-TEMPO** (2 mM in THF).

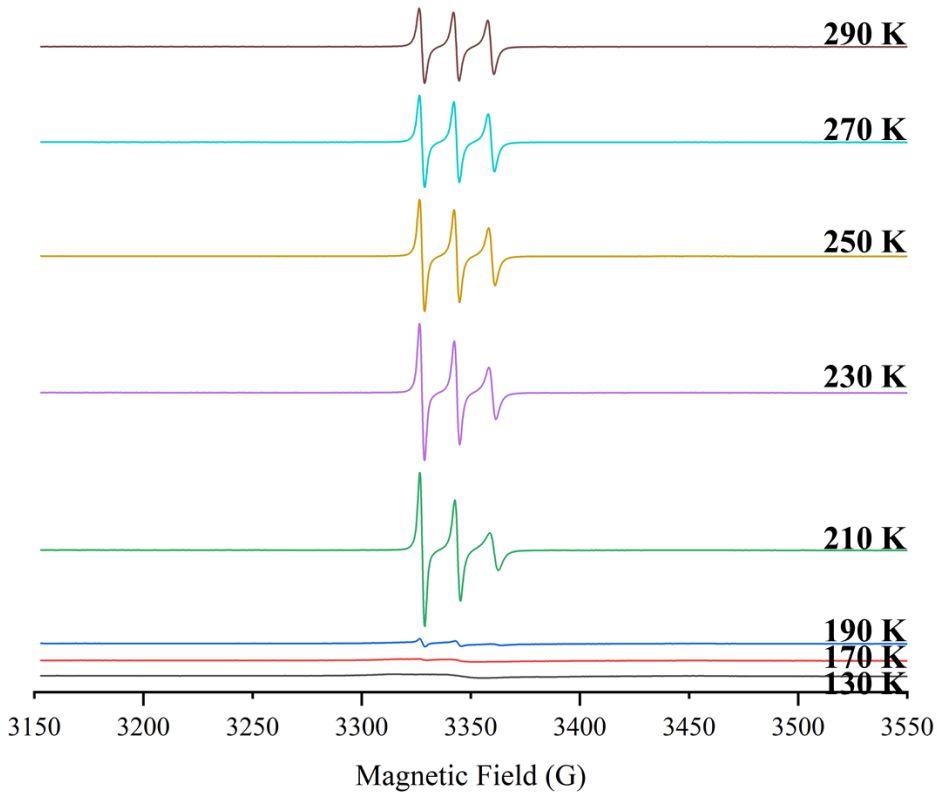


Fig. S37 VT-EPR spectra of **G1-TEMPO** (0.1 mM in DCM).

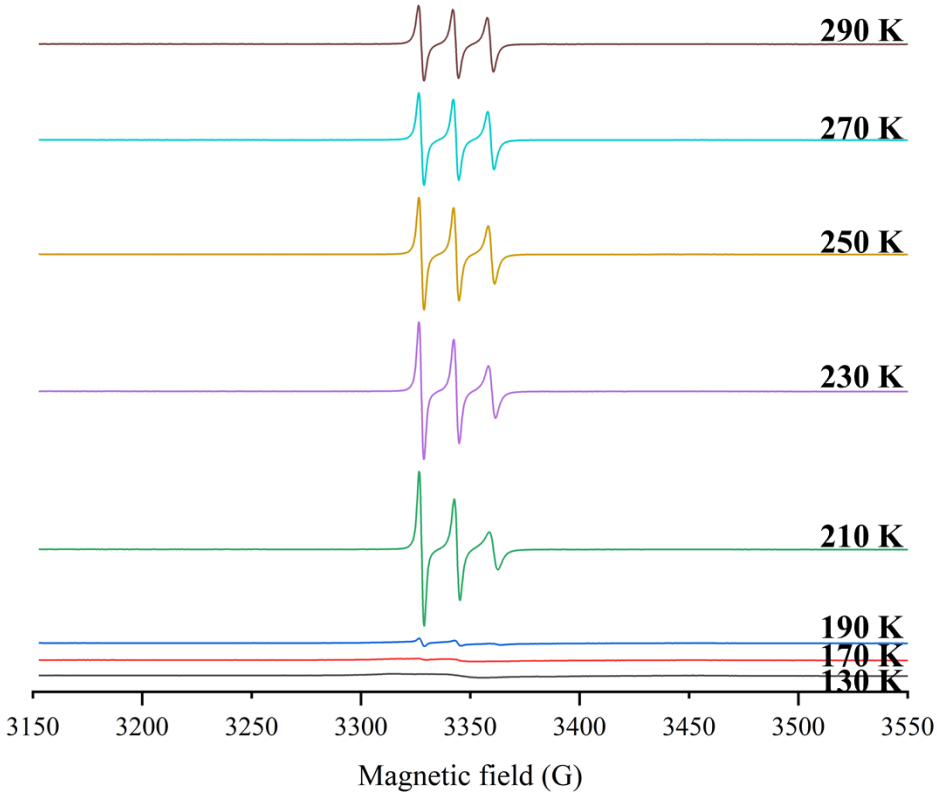


Fig. S38 VT-EPR spectra of **G1-TEMPO** (1 mM in DCM).

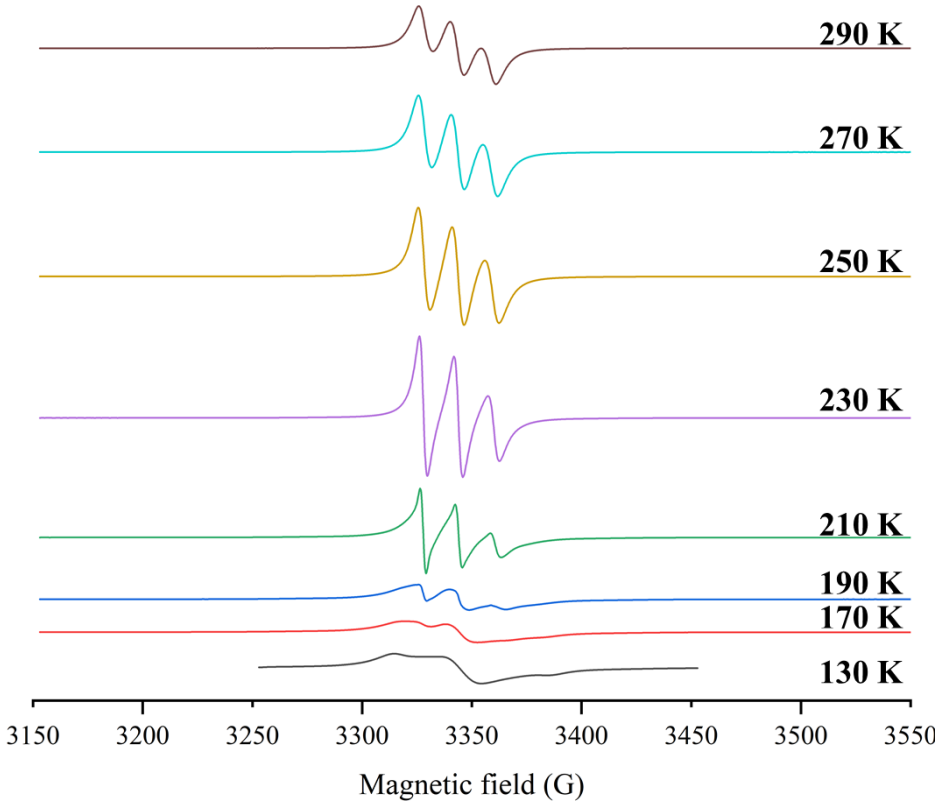


Fig. S39 VT-EPR spectra of **G1-TEMPO** (10 mM in DCM).

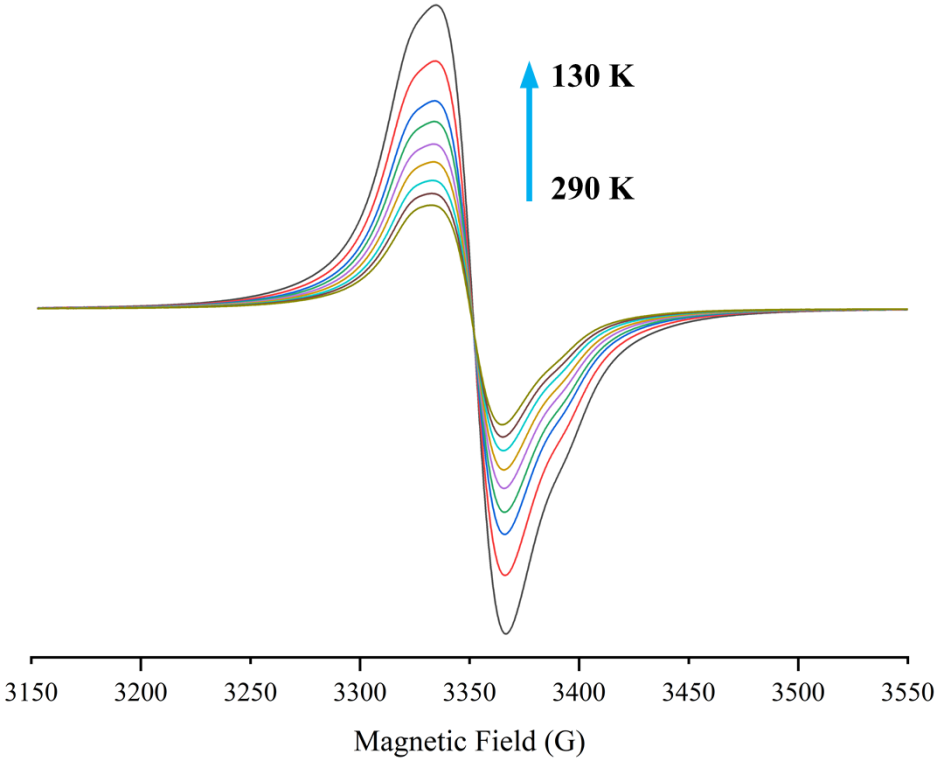


Fig. S40 VT-EPR spectra of **G1-TEMPO** in solid state.

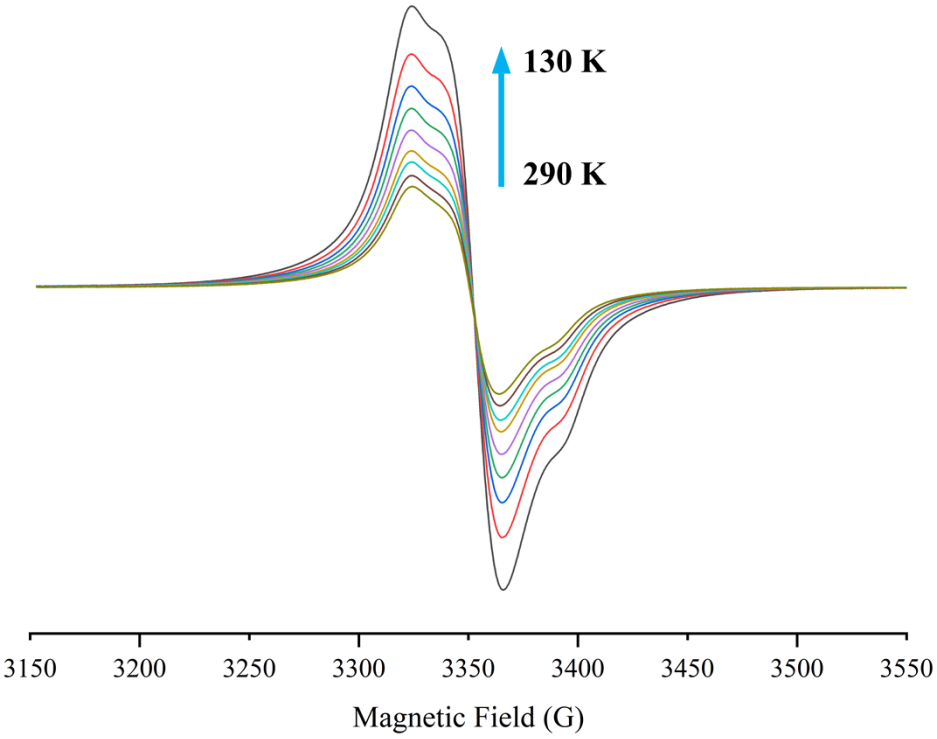


Fig. S41 VT-EPR spectra of **G2-TEMPO** in solid state.

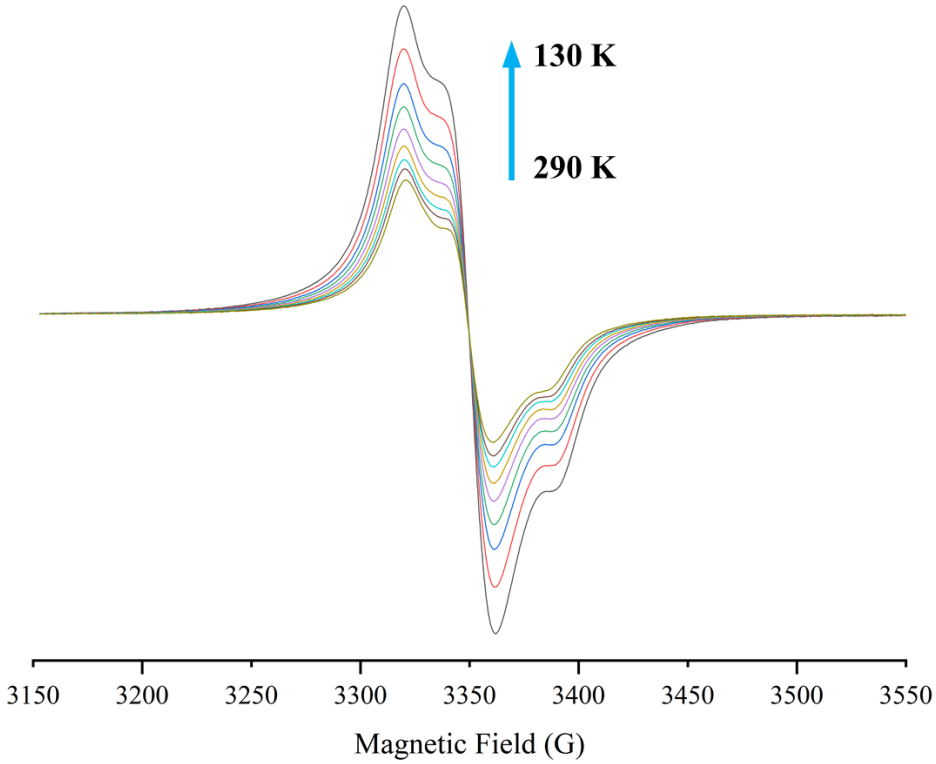


Fig. S42 VT-EPR spectra of **G3-TEMPO** in solid state.

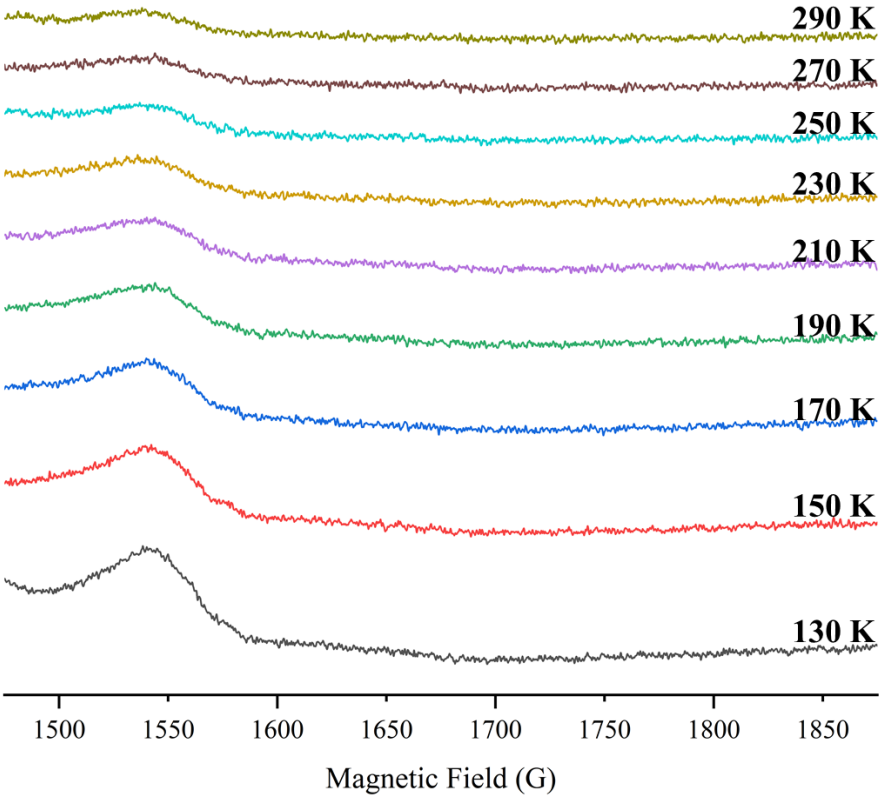


Fig. S43 The half-field VT-EPR spectra of **G1-TEMPO** in solid state.

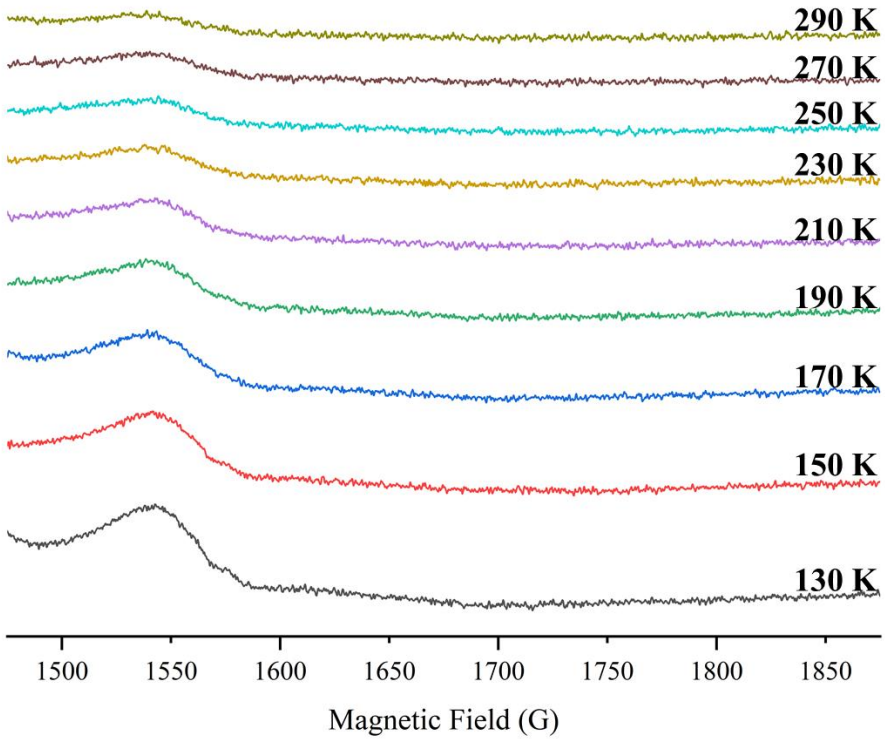


Fig. S44 The half-field VT-EPR spectra of **G2-TEMPO** in solid state.

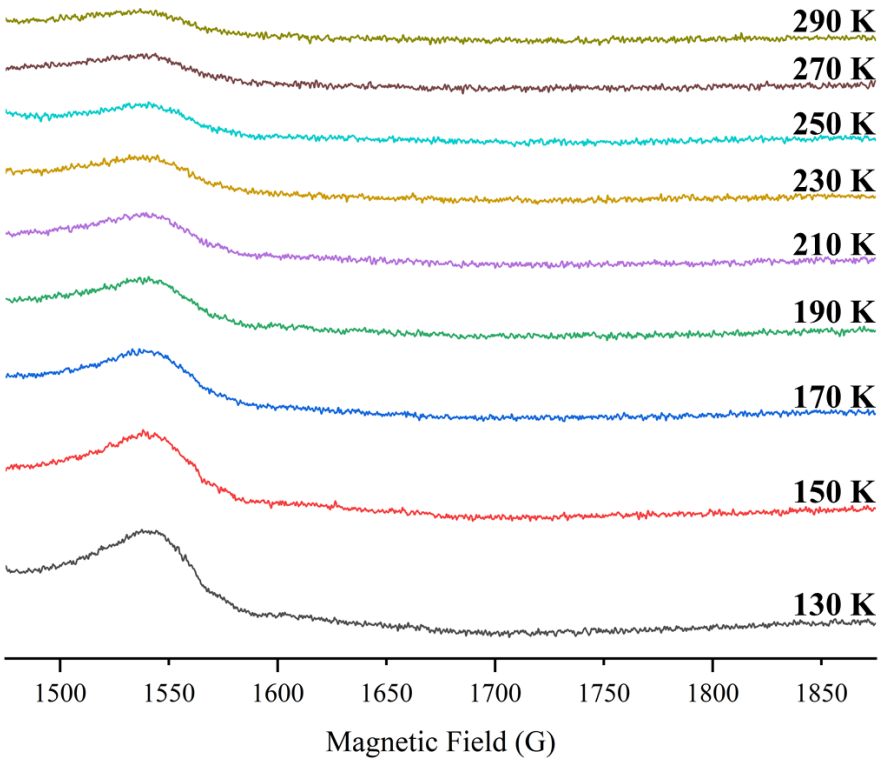


Fig. S45 The half-field VT-EPR spectra of **G3-TEMPO** in solid state.

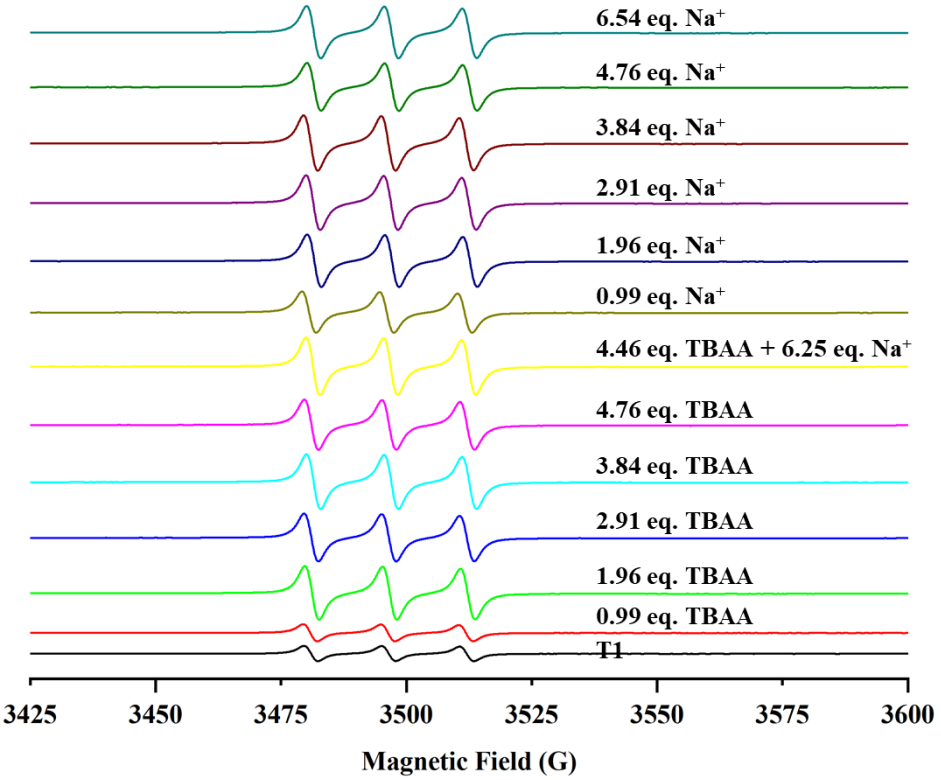


Fig. S46 The EPR spectra of **T1** with the sequential addition of TBAA and Na^+ (0.1 mM in THF).

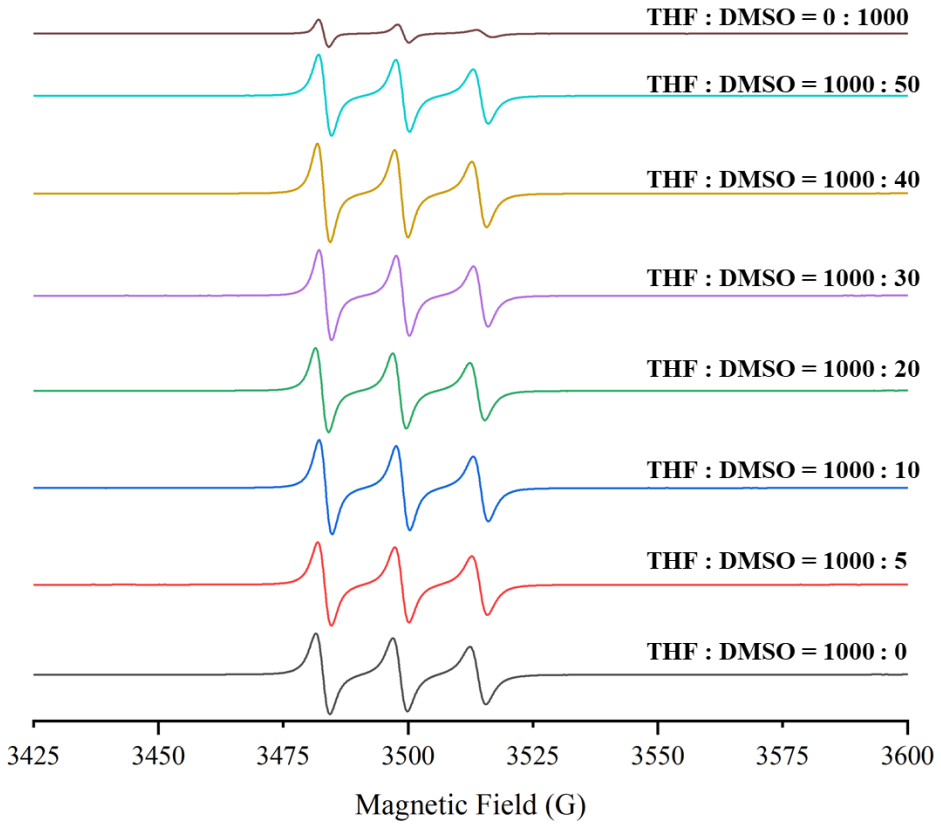


Fig. S47 The EPR spectra of **G1-TEMPO** with the addition of DMSO (0.1 mM in THF).

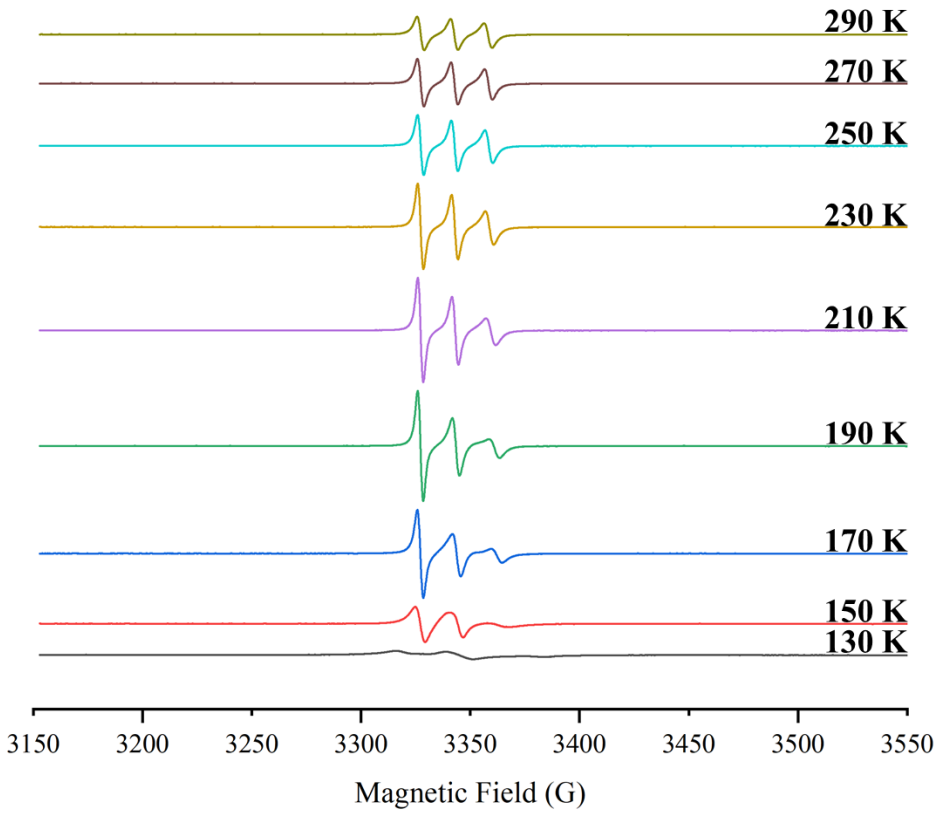


Fig. S48 VT-EPR spectra of **G1-c-TEMPO** (0.1 mM in THF).

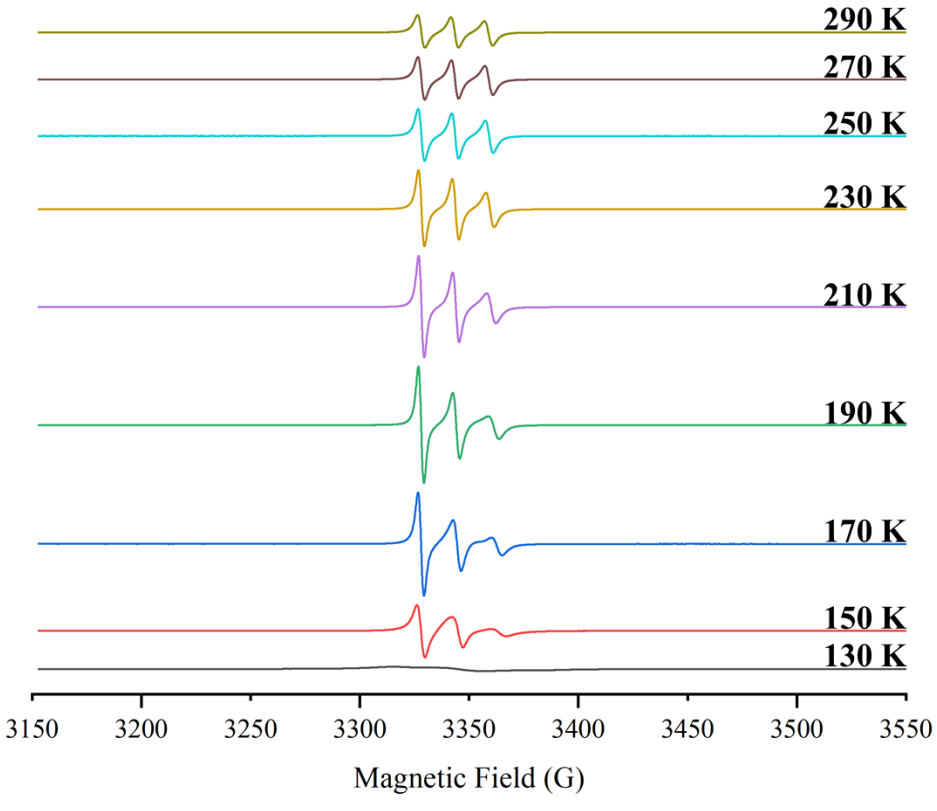


Fig. S49 VT-EPR spectra of **G1-c-TEMPO** (1 mM in THF).

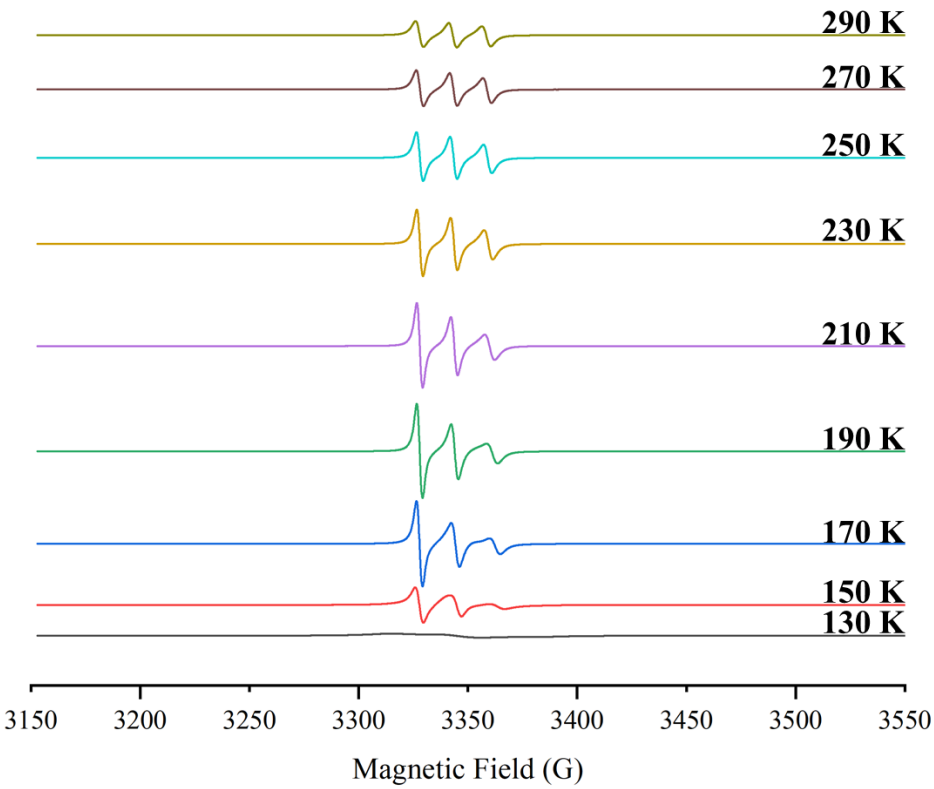


Fig. S50 VT-EPR spectra of **G1-c-TEMPO** (2 mM in THF).

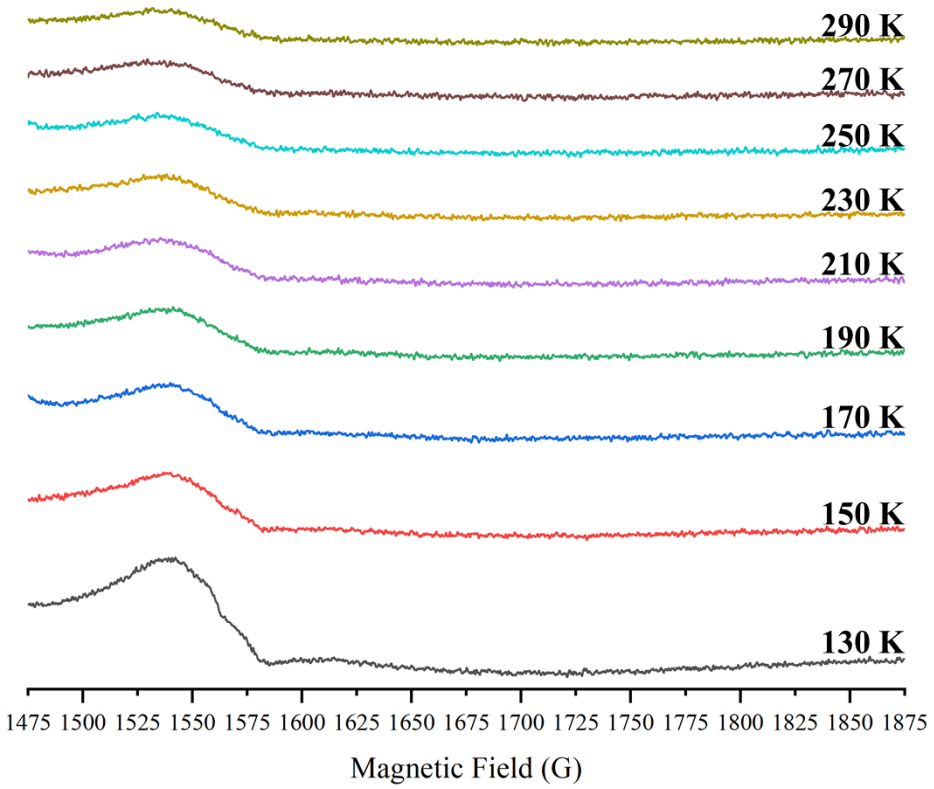


Fig. S51 The half-field VT-EPR spectra of **G1-c-TEMPO** (0.1 mM in THF).

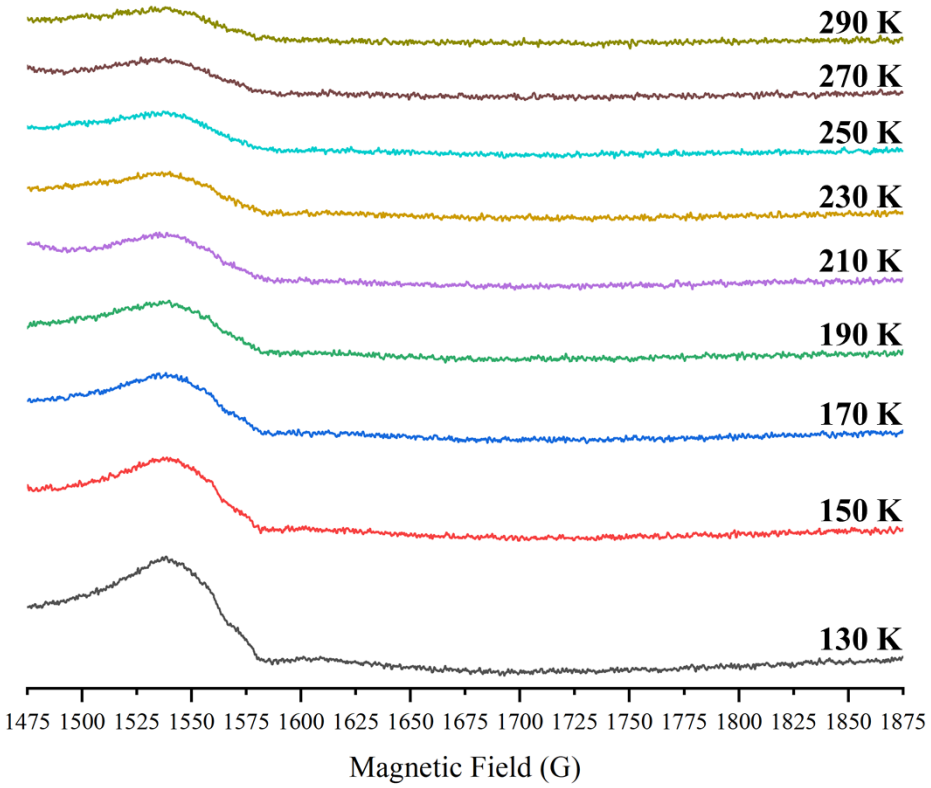


Fig. S52 The half-field VT-EPR spectra of **G1-c-TEMPO** (1 mM in THF).

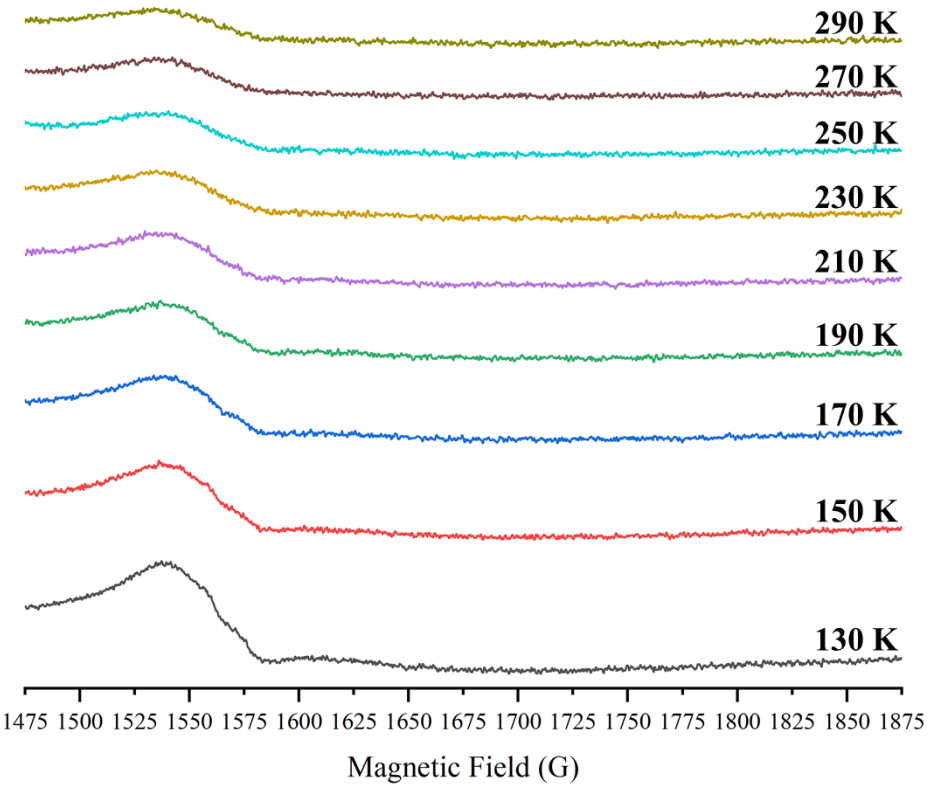


Fig. S53 The half-field VT-EPR spectra of **G1-c-TEMPO** (2 mM in THF).

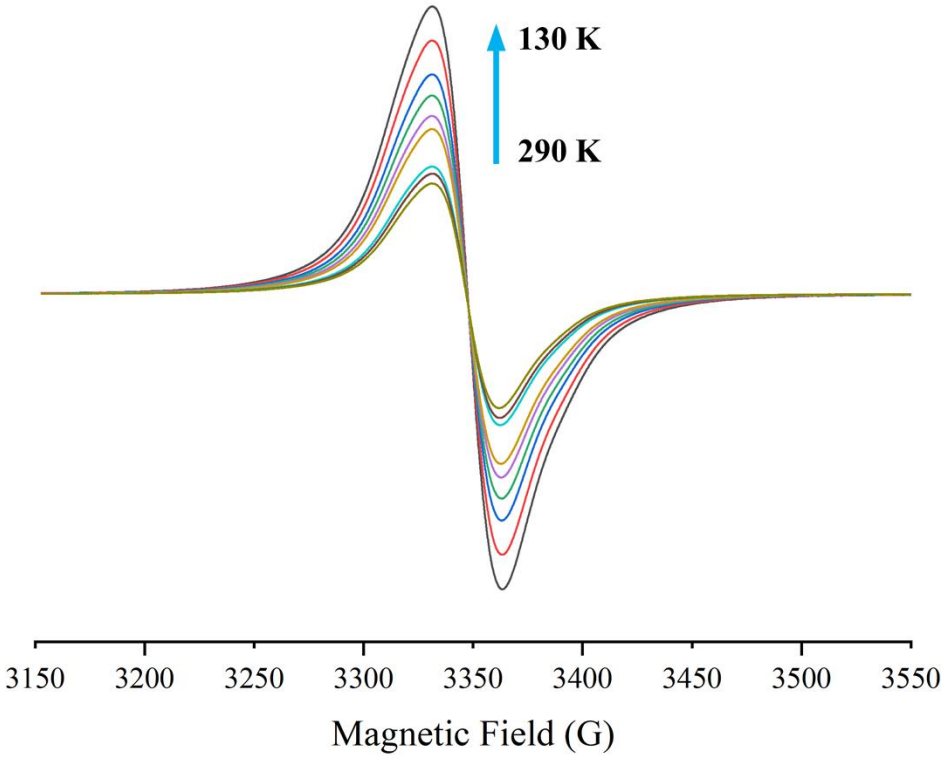


Fig. S54 VT-EPR spectra of **G1-c-TEMPO** in solid state.

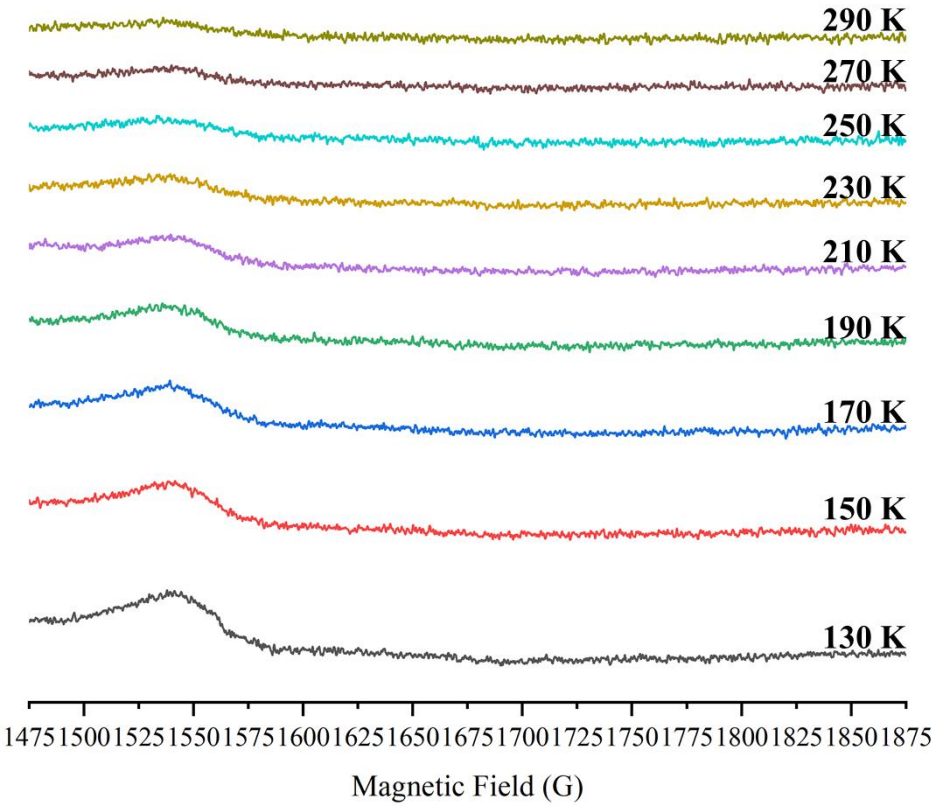


Fig. S55 The half-field VT-EPR spectra of **G1-c-TEMPO** in solid state.

Section D. Preparation and characterization of rotaxane-branched radical dendrimer-based nanoparticles

Preparation of nanoparticle Gn-NPs (n = 1, 2 and 3)[S2]**:** The nanoparticles **Gn-NPs** containing **Gn-TEMPO** (n = 1, 2 and 3) were prepared by film hydration method. Briefly, soya bean lecithin (72 mg), cholesterol (32 mg), PEG_{2000}-DSPE (26 mg) and **Gn-TEMPO** (**G1-TEMPO**: 16.3 mg; **G2-TEMPO**: 20.6 mg; **G3-TEMPO**: 22.8 mg) were dissolved in 10 mL of chloroform dealt with potassium carbonate. The organic solvents were evaporated under reduced pressure by using dried rotary evaporator to form a thin transparent film on the wall of the flask. After being dried under vacuum to eliminate the residual solvent, the film was dissolved with 10 mL MilliQ water, and then evaporated without pressure for 2 h at 55 °C. Finally, the suspensions were passing through a 0.22 μm syringe filter for 10 times and the **Gn-NPs** (n = 1, 2 and 3) were obtained.

Table S1 DLS data of **Gn-TEMPO** and **Gn-NPs** (n = 1, 2 and 3).

	Size (d. nm)
G1-TEMPO	2.4
G2-TEMPO	4.0
G3-TEMPO	5.9
G1-NPs	95.8
G2-NPs	77.7
G3-NPs	100.4

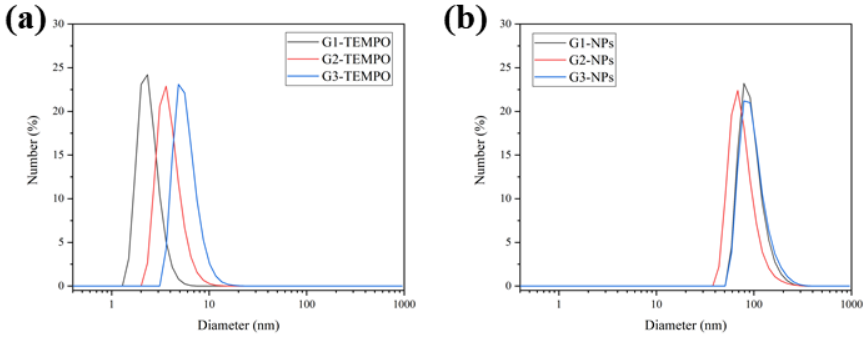


Fig. S56 The DLS spectra of (a) **Gn-TEMPO** (n = 1, 2 and 3) and (b) **Gn-NPs** (n = 1, 2 and 3).

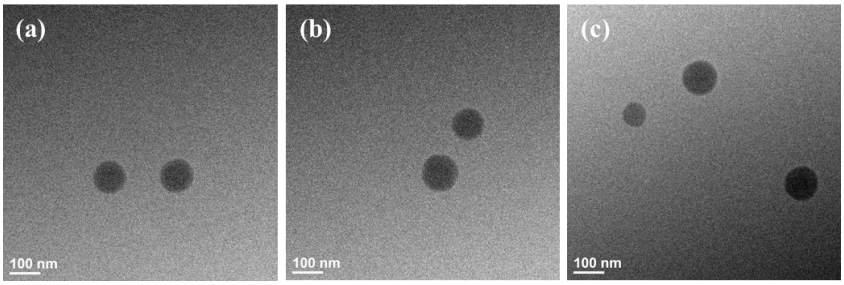


Fig. S57 The TEM images of (a) **G1-NPs,** (b) **G2-NPs** and (c) **G3-NPs**.

Sequence No.: 4
Sample ID: DY-1
Analyst:
Logged In Analyst (Original) : Administrator
Initial Sample Wt:
Dilution:
Wash Time (before sample):

Autosampler Location:
Date Collected: 8/20/2021 12:39:57 AM
Data Type: Reprocessed on 8/20/2021 12:50:10 AM

Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: DY-1

Analyte	Back Pressure	Flow
All	312.0 kPa	0.70 L/min

Replicate Data: DY-1

Repl#	Analyte	Net Intensity	Corrected Intensity	Calib. Conc. Units	Sample Conc. Units	Analysis Time
1	Pt 265.945	1104.3	1054.9	0.718 mg/L	0.718 mg/L	12:40:44 AM
2	Pt 265.945	1140.2	1090.7	0.740 mg/L	0.740 mg/L	12:40:50 AM
3	Pt 265.945	1075.1	1025.6	0.700 mg/L	0.700 mg/L	12:40:57 AM

Mean Data: DY-1

Analyte	Mean Corrected Intensity	Calib. Conc. Units	Calib. Std.Dev.	Sample Conc. Units	Sample Std.Dev.	RSD
Pt 265.945	1057.1	0.719 mg/L	0.0200	0.719 mg/L	0.0200	2.78%

Fig. S58 The actual Pt contents (mg/L) in **G1-NPs** measured by ICP.

Sequence No.: 5
Sample ID: DY-2
Analyst:

Autosampler Location:
Date Collected: 8/20/2021 12:43:26 AM
Data Type: Reprocessed on 8/20/2021 12:50:10 AM

Logged In Analyst (Original) : Administrator
Initial Sample Wt:
Dilution:
Wash Time (before sample):

Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: DY-2

Analyte	Back Pressure	Flow
All	312.0 kPa	0.70 L/min

Replicate Data: DY-2

Repl#	Analyte	Net Intensity	Corrected Intensity	Calib. Conc. Units	Sample Conc. Units	Analysis Time
1	Pt 265.945	3691.7	3642.2	2.303 mg/L	2.303 mg/L	12:44:12 AM
2	Pt 265.945	3663.4	3613.9	2.286 mg/L	2.286 mg/L	12:44:18 AM
3	Pt 265.945	3766.0	3716.5	2.349 mg/L	2.349 mg/L	12:44:23 AM

Mean Data: DY-2

Analyte	Mean Corrected Intensity	Calib. Conc. Units	Calib. Std.Dev.	Sample Conc. Units	Sample Std.Dev.	RSD
Pt 265.945	3657.5	2.313 mg/L	0.0325	2.313 mg/L	0.0325	1.40%

Fig. S59 The actual Pt contents (mg/L) in **G2-NPs** measured by ICP.

Sequence No.: 6
Sample ID: DY-3
Analyst:
Logged In Analyst (Original) : Administrator
Initial Sample Wt:
Dilution:
Wash Time (before sample):

Autosampler Location:
Date Collected: 8/20/2021 12:47:11 AM
Data Type: Reprocessed on 8/20/2021 12:50:10 AM

Initial Sample Vol:
Sample Prep Vol:

Nebulizer Parameters: DY-3

Analyte	Back Pressure	Flow
All	312.0 kPa	0.70 L/min

Replicate Data: DY-3

Repl#	Analyte	Net Intensity	Corrected Intensity	Calib. Conc. Units	Sample Conc. Units	Analysis Time
1	Pt 265.945	1710.6	1661.1	1.089 mg/L	1.089 mg/L	12:47:57 AM
2	Pt 265.945	1722.0	1672.5	1.096 mg/L	1.096 mg/L	12:48:02 AM
3	Pt 265.945	1708.4	1658.9	1.088 mg/L	1.088 mg/L	12:48:07 AM

Mean Data: DY-3

Analyte	Mean Corrected Intensity	Calib. Conc. Units	Calib. Std.Dev.	Sample Conc. Units	Sample Std.Dev.	RSD
Pt 265.945	1664.2	1.091 mg/L	0.0045	1.091 mg/L	0.0045	0.41%

Fig. S60 The actual Pt contents (mg/L) in **G3-NPs** measured by ICP.

Table S2 Double integral of the EPR spectra for **Gn-NPs** (n = 1, 2 and 3).

	G1-NPs	**G2-NPs**	**G3-NPs**
Double Integral	14.2	21.2	14.4

Relaxometric measurements: Longitudinal (r_1) relaxivities were determined per concentration of TEMPO units. Sample at varying concentrations (1 to 20 mM) in water were prepared. The software used for the calculation of T_1 were ImageJ and Mathematica. T_1-weighted MRI images were acquired for each concentration of TEMPO to obtain T_1 maps based on a magnetization saturation experiment and the following parameters: repetition time (TR) = 23, 100, 200, 300, 400, 800, 1200, 1500, 2000 ms, echo time (TE) = 11 ms. The T_1 values were calculated from the mean signal in the region of interest for each repetition time, adjusted to the equation: $S = S_0 \times [1 - \exp(-TR / T_1)]$. The relaxivities r_1 of **Gn-NPs** (n = 1, 2 and 3) was determined from the slopes of linear fits.

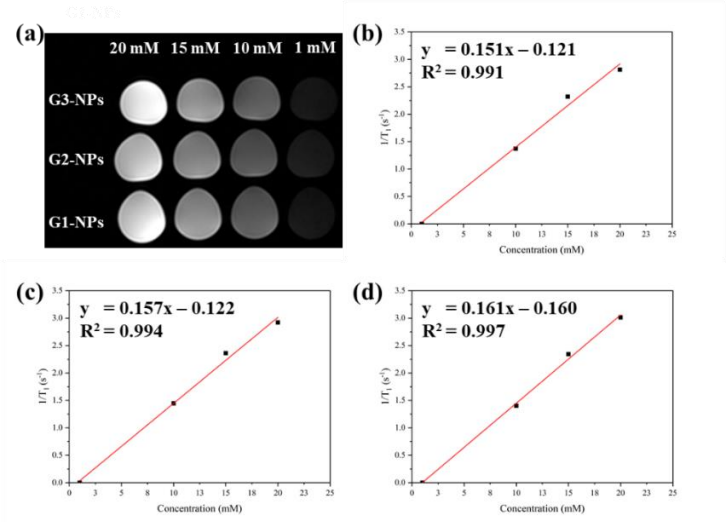


Fig. S61 (a) T_1-weighted MRI images of **Gn-NPs** (n = 1, 2 and 3) at various concentration of TEMPO radicals. The relaxivities r_1 of (b) **G1-NPs**, (c) **G2-NPs** and (d) **G3-NPs** was determined from the slopes of linear fits.

Table S3 Comparison table for the relaxivity of gold-standard GD-DTPA and reported radical dendrimers.

	Per radical ($mM^{-1}s^{-1}$)	**Molecule** ($mM^{-1}s^{-1}$)	**References**
GD-DTPA	--	3.87[a]	*Sci. Rep.,* 2017, **7**, 3799.
G3-TEMPO	0.16[a]	3.86[a]	This work
PAMAM	0.15[c]	5.0[c]	*Magn. Reson. Chem.*, 2002, **48**, 965.
G2-NIT	0.25-0.29[d]	3-3.48[d]	*Magn. Reson. Chem.*, 2003, **41**, 81.
G4	0.42[b]	~ 5[b]	*J. Am. Chem. Soc.*, 2012, **134**, 15724.
G3-Tyr-PROXYL	0.27[b]	12.96[b]	*ACS Appl. Bio. Mater.*, 2020, **3**, 369.

The relaxivities r_1 was determined in room temperature at 3T [a], 7T [b], 1.5T [c] and 0.1 MHz [d].

Section E. References

[S1] X.-Q. Wang, W. Wang, W.-J. Li, L.-J. Chen, R. Yao, G.-Q. Yin, Y.-X. Wang, Y. Zhang, J. Huang, H. Tan, Y. Yu, X. Li, L. Xu and H.-B. Yang, *Nat. Commun.*, 2018, **9**, 3190.

[S2] C. Gao, Q, Cheng, J. Li, J. Chen, Q. Wang, J. Wei, Q. Huang, S. Lee, D. Gu and R. Wang, *Adv. Funct. Mater.*, 2021, **31**. 2102440.