# Electronic Supplementary Information

# Charge Transport and Antiferromagnetic Ordering in Nitroxide Radical Crystals

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**Supplemental Figures**

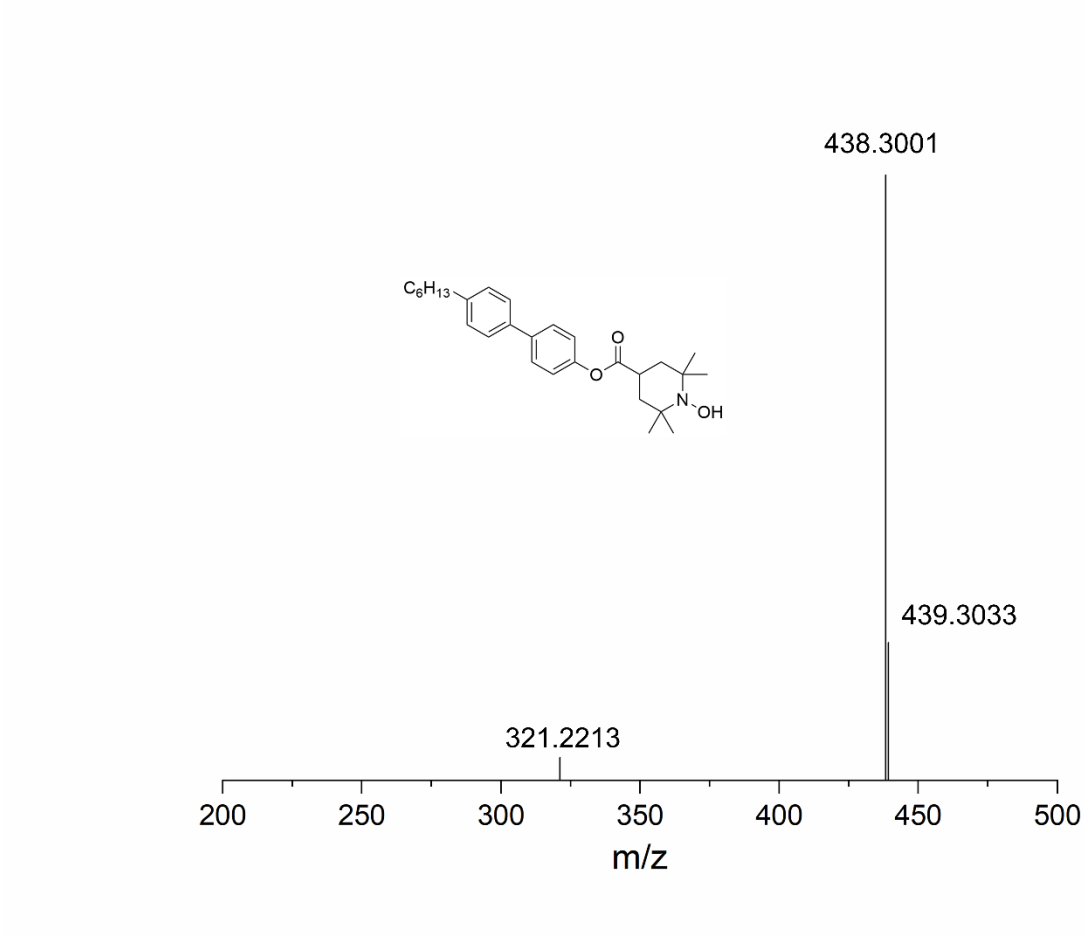


**Figure S1.** Mass spectrum of C6BP-TEMPO obtained using ESI MS operating in positive mode. The radical molecule is reduced to its piperidin-1-ol form during the measurement, and the highest peak belongs to the $[M+H]^+$ species of the closed-shell piperidin-1-ol form. The calculated mass for $C_{28}H_{39}NO_3$ $[M+H]^+$: 438.2963; found 438.3001.

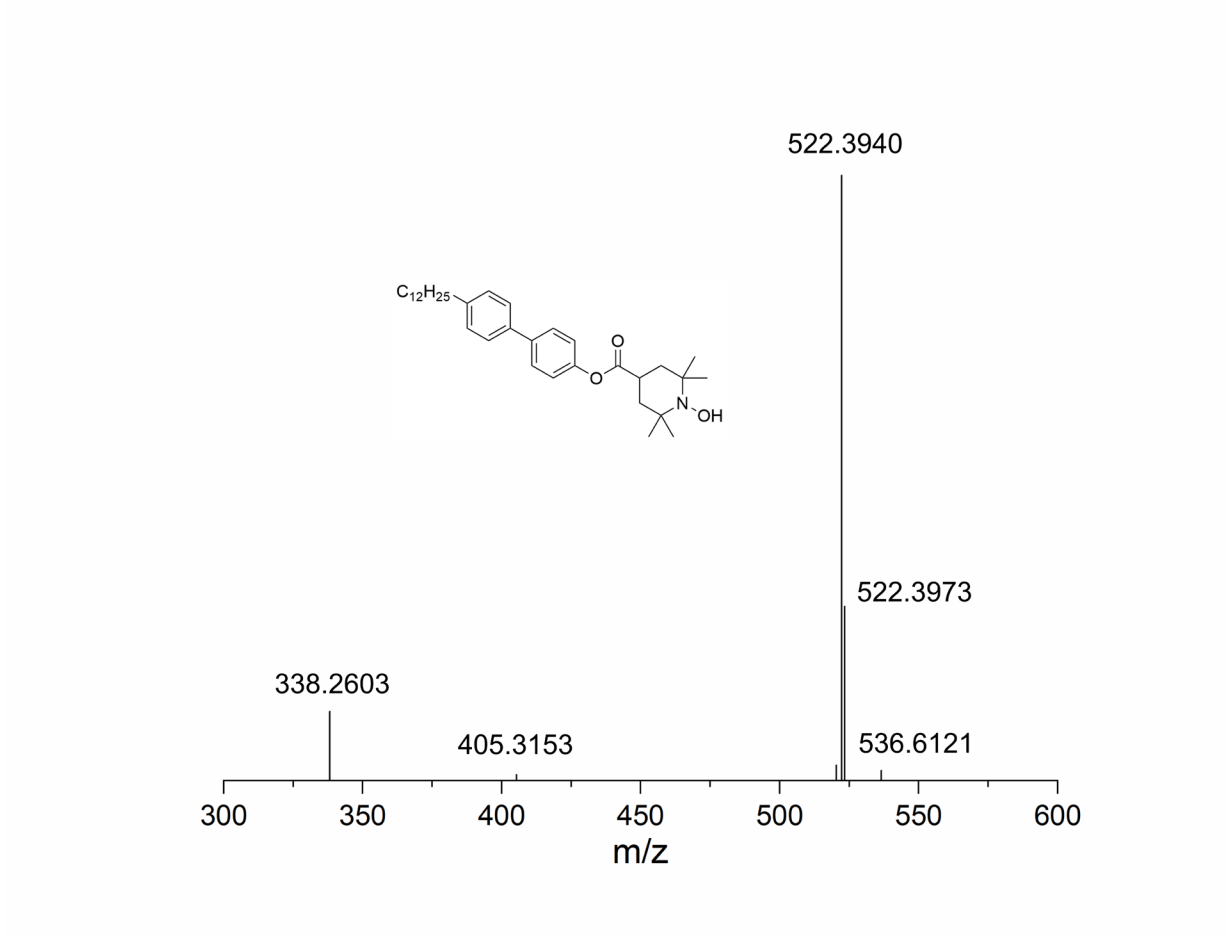


**Figure S2.** Mass spectrum of C12BP-TEMPO obtained using ESI MS operating in positive mode. The radical molecule is reduced to its piperidin-1-ol form in situ during ionization, and the highest peak belongs to the $[M+H]^+$ species of the closed-shell piperidin-1-ol form. The calculated mass for $C_{34}H_{51}NO_3$ $[M+H]^+$: 522.3902; found 522.3940.

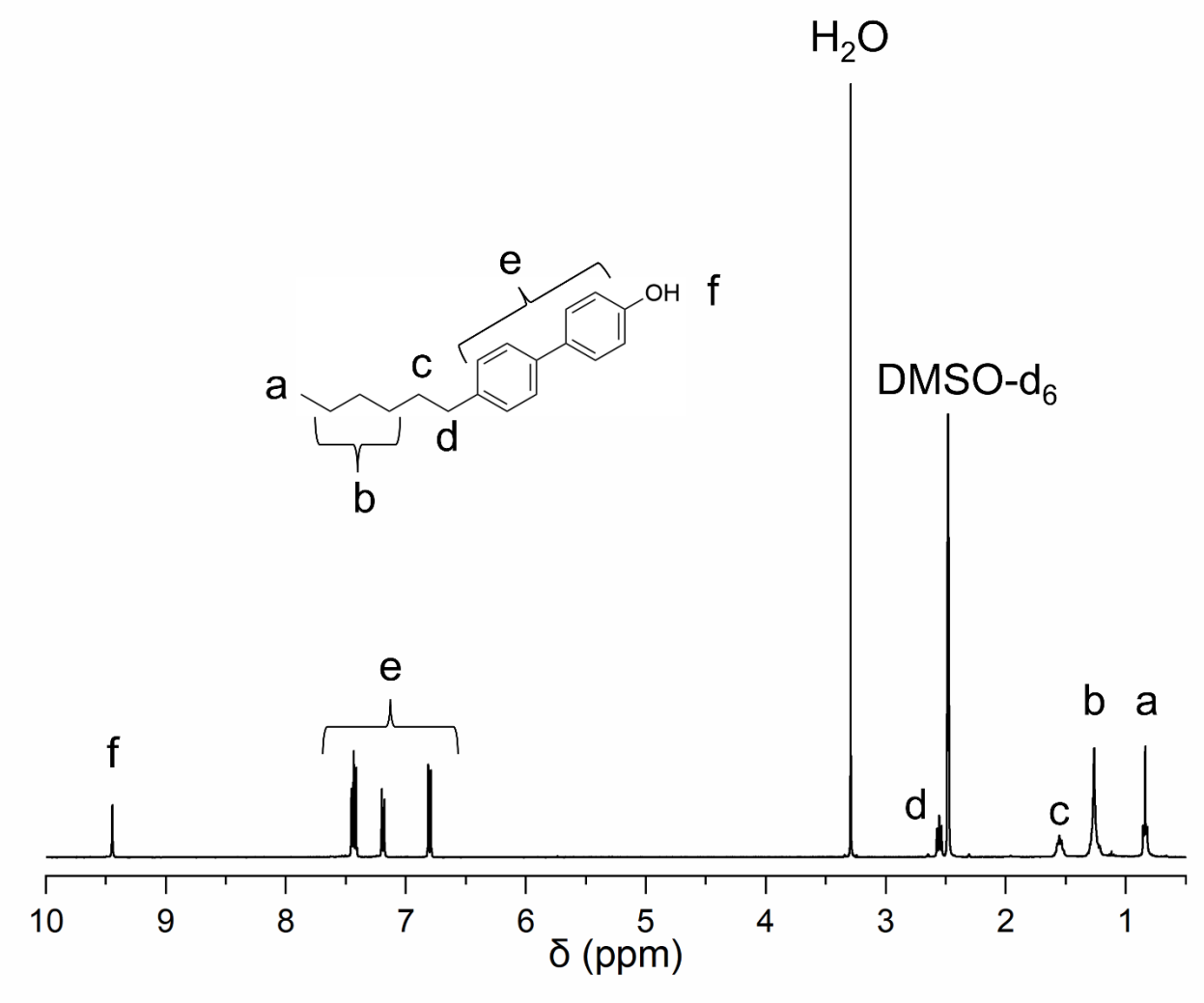


**Figure S3.** The $^{1}$H NMR spectrum of 4'-hexyl-[1,1'-biphenyl]-4-ol (C6BPOH) in deuterated DMSO.

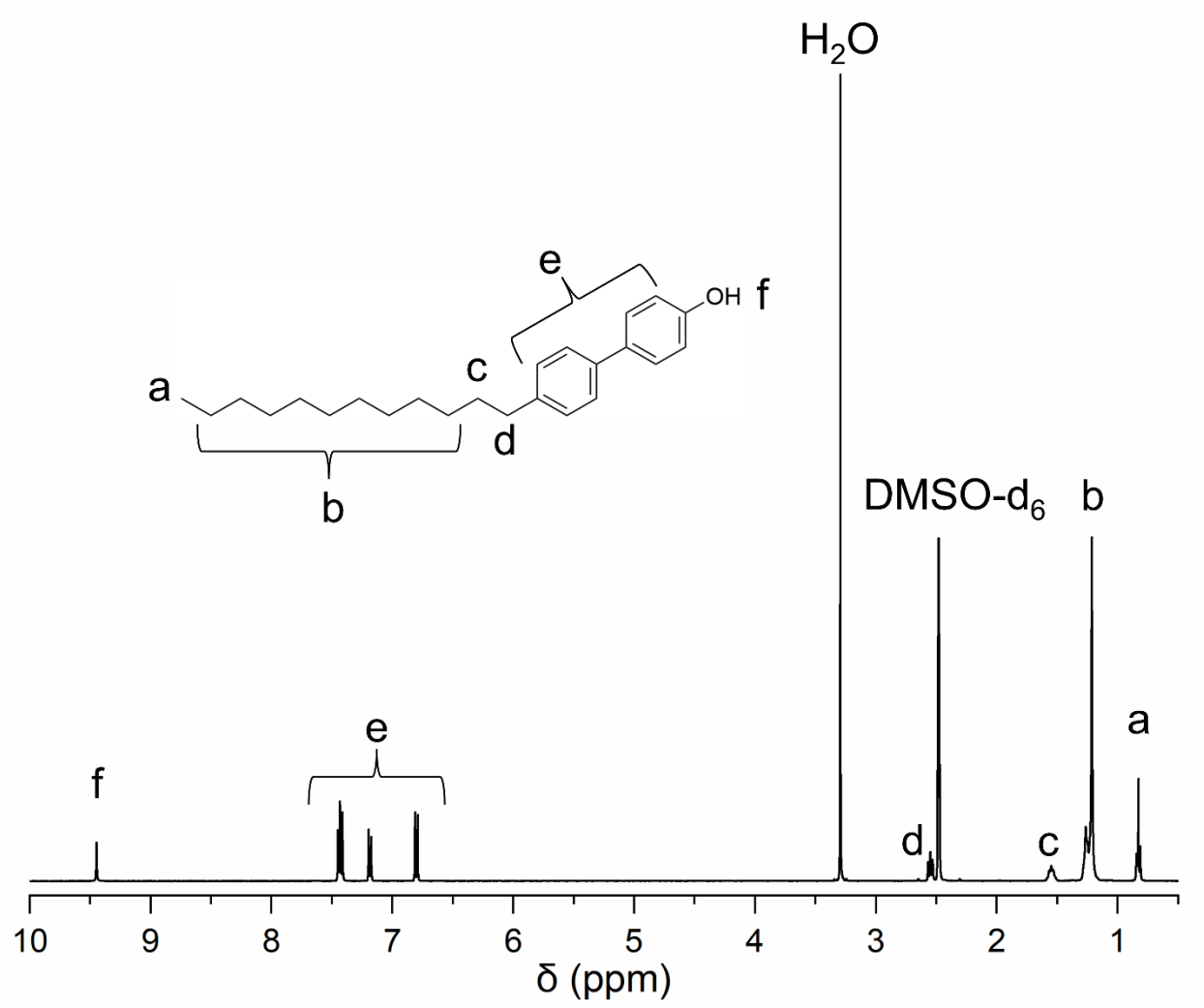


**Figure S4.** $^{1}$H NMR of 4'-dodecyl-[1,1'-biphenyl]-4-ol (C12BPOH) in deuterated DMSO.

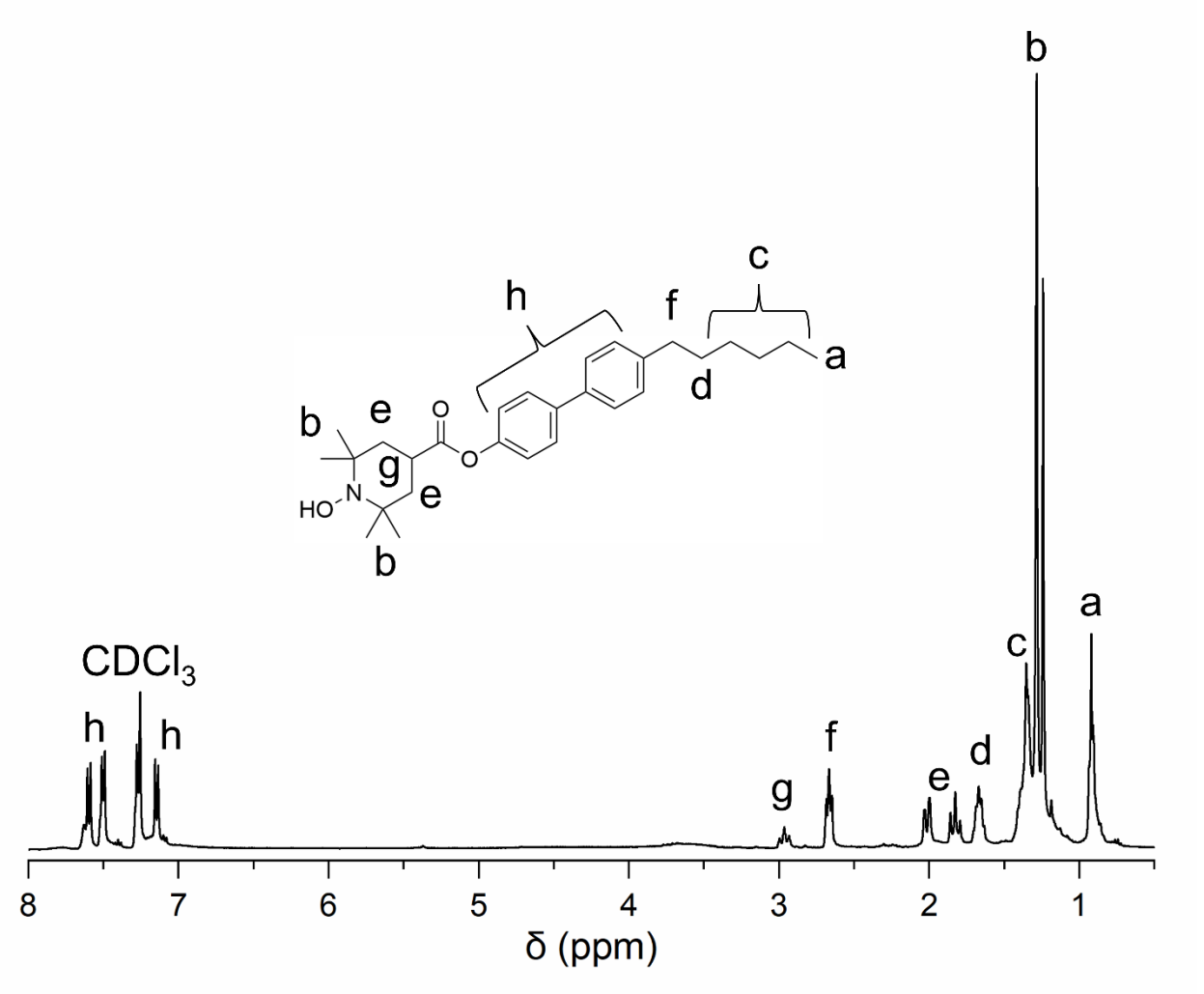


**Figure S5.** The $^{1}H$ NMR spectrum of 4'-hexyl-[1,1'-biphenyl]-4-yl 1-hydroxy-2,2,6,6-tetramethylpiperidine-4-carboxylate (C6BP-TEMPOH) in $CDCl_3$. C6BP-TEMPOH was obtained by quenching the nitroxide radical using L-ascorbic acid.

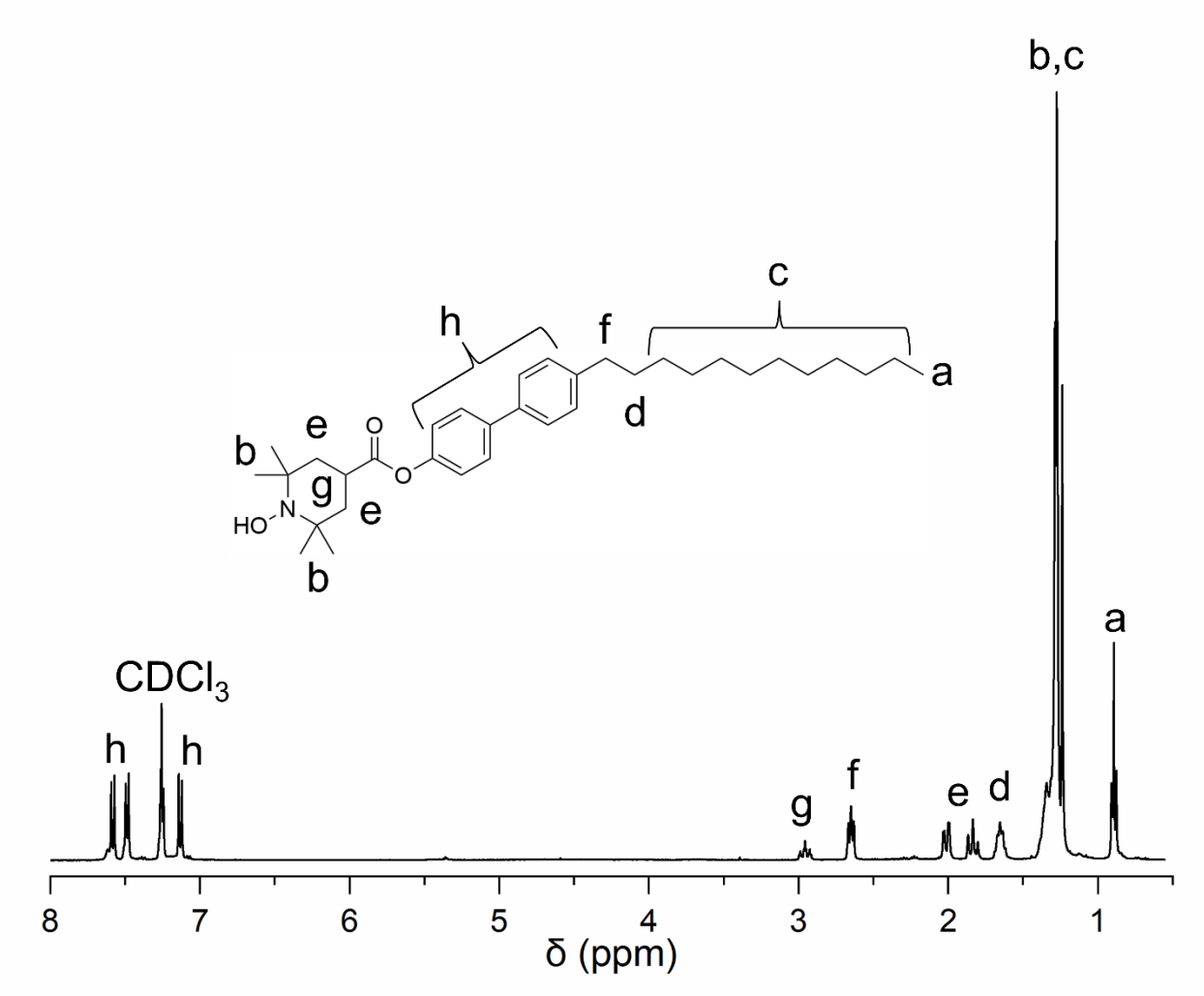


**Figure S6.** $^{1}$H NMR of 4'-dodecyl-[1,1'-biphenyl]-4-yl 1-hydroxy-2,2,6,6-tetramethylpiperidine-4-carboxylate (C12BP-TEMPOH) in $CDCl_3$. C12BP-TEMPOH was obtained by quenching the nitroxide radical using L-ascorbic acid.

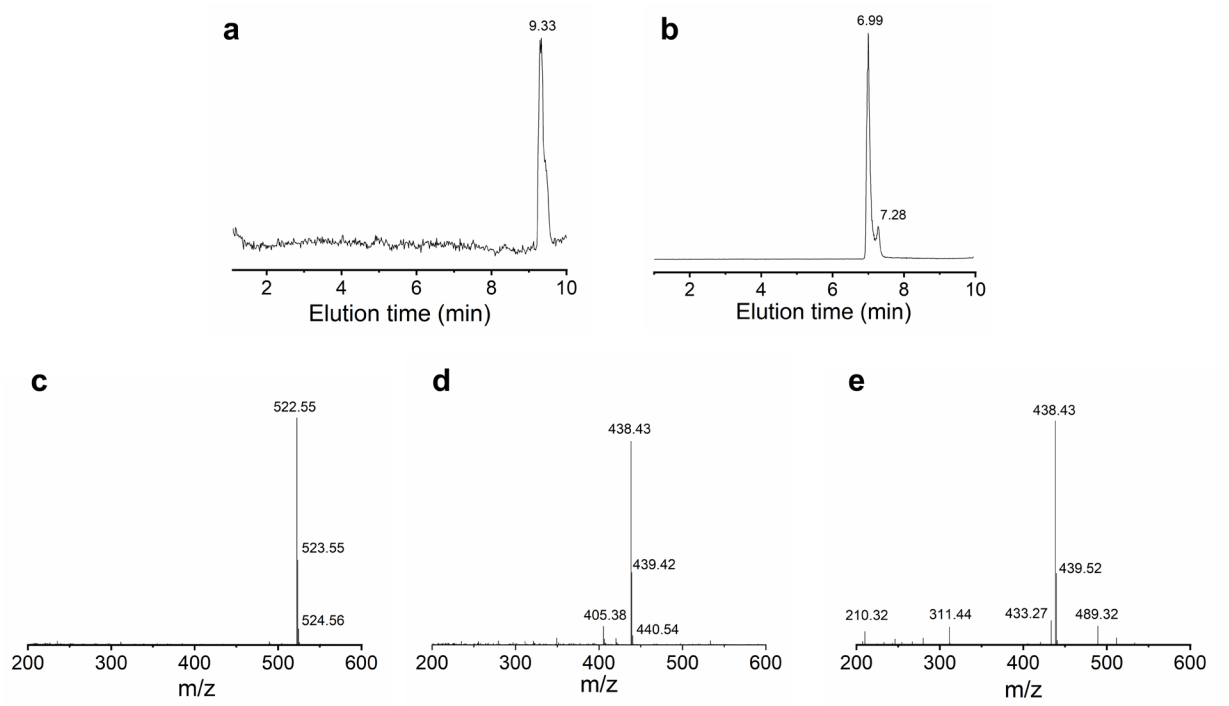


**Figure S7.** UPLC traces of (a) C12BP-TEMPO and (b) C6BP-TEMPO both show a single elution peak, which confirms that no significant impurities exist inside the product after the product is purified on a silica gel column. Mass spectra of (c) C12BP-TEMPO taken at 9.33 min, (d) C6BP-TEMPO taken at 6.99 min, and (e) C6BP-TEMPO taken at 7.28 min. The major peaks in all the mass spectra reveal that the major elution peaks are from the pure products.

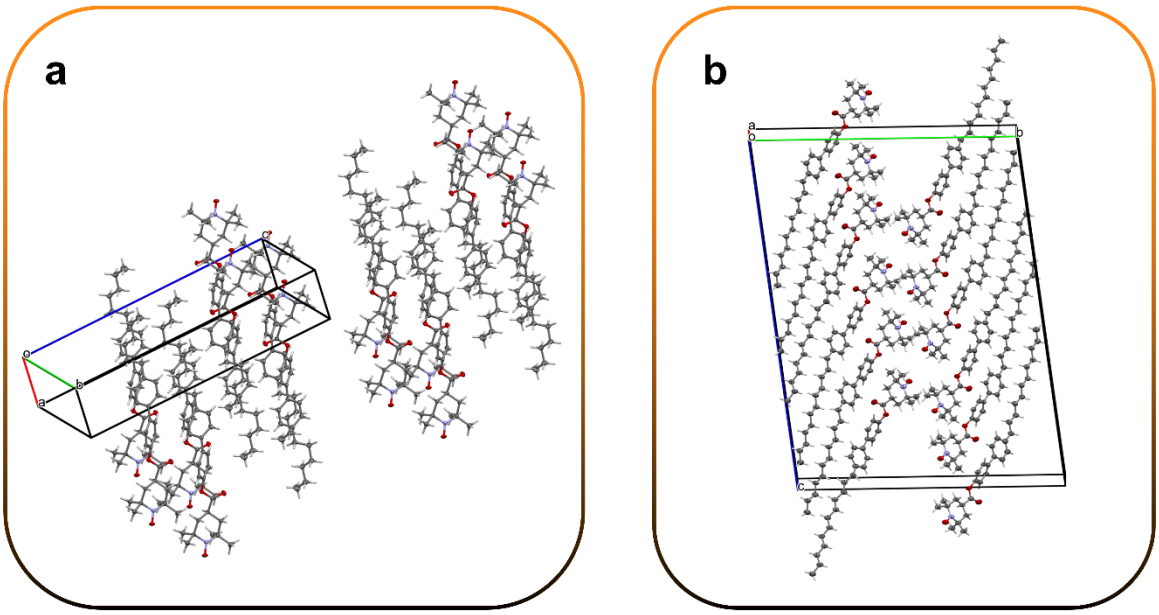


**Figure S8.** The visualized packing of the (a) C6BP-TEMPO and (b) C12BP-TEMPO molecules in the unit cells. C6BP-TEMPO has P -1 space group (triclinic) with lattice parameters a = 5.60 Å, b = 8.08 Å, c = 27.30 Å and α = 83º, β = 88º, γ = 82º. C12BP-TEMPO has P -1 space group (triclinic) with lattice parameters a = 5.63 Å, b = 34.43 Å, c = 47.13 Å and α = 82º, β = 88º, γ = 86º.

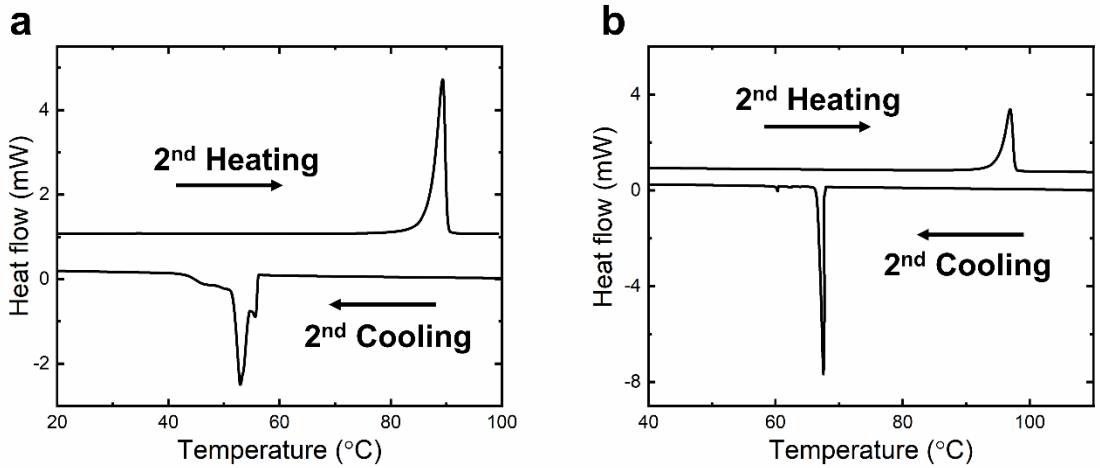


**Figure S9.** DSC traces of (a) C6BP-TEMPO and (b) C12BP-TEMPO. For both molecules, the 2nd heating and 2nd cooling cycle was used. A scan rate of 2 °C $min^{-1}$ was used to collect the data.

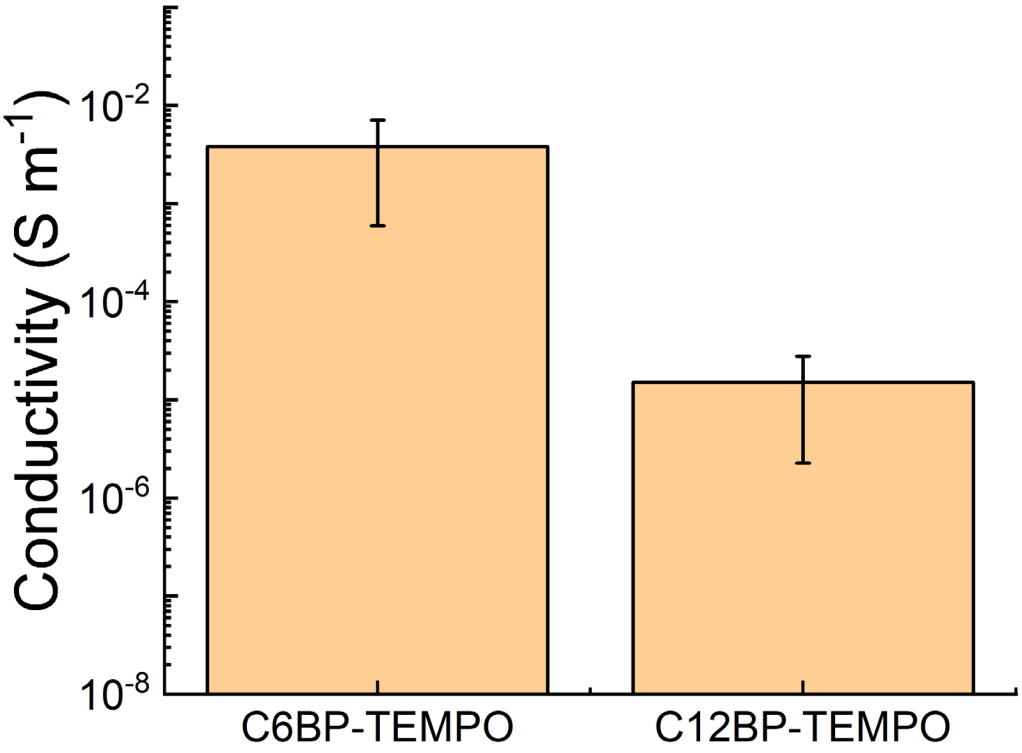


**Figure S10.** Room temperature electrical conductivity values of C6BP-TEMPO and C12BP-TEMPO single crystals. Average electrical conductivity and standard deviation were calculated across three testing samples for both C6BP-TEMPO and C12BP-TEMPO.

**Additional information for single crystal structure analysis**

For all the single crystals in this work, data were collected, reflections were indexed and processed, and the files scaled and corrected for absorption using APEX4 and SADABS.[1-2] The space groups were assigned using XPREP within the SHELXTL suite of programs and solved by dual methods using ShelXT and refined by full matrix least squares against $F^2$ with all reflections using Shelxl2018 using the graphical interface Shelxle.[3-7] If not specified otherwise, the H atoms that were attached to the carbon and nitrogen atoms as well as hydroxyl hydrogens were positioned geometrically and constrained to ride on their parent atoms with bond distances of 0.95 Å for aromatic C-H bonds, and 0.99 and 0.98 Å for C-H bonds in aliphatic $CH_2$ and $CH_3$ moieties, respectively. The H atoms in $CH_3$ moieties were allowed to rotate but not to tip to best fit the experimental electron density. $U_{iso}$(H) values were set to a multiple of $U_{eq}$(C) with 1.5 for $CH_3$, and 1.2 for C-H and $CH_2$ units, respectively.

Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre under deposition numbers CCDC 2189450 (C6BP-TEMPO) and 2189451 (C12BP-TEMPO). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**References**

(1) Bruker (2021). Apex4 v2021.4-0, SAINT V8.40B, Bruker AXS Inc.: Madison (WI), USA.

(2) Krause, L., Herbst-Irmer, R., Sheldrick, G.M. & Stalke, D. (2015). J. Appl. Cryst. 48, 3-10.

(3) SHELXTL suite of programs, Version 6.14, 2000-2003, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin: USA

(4) Sheldrick, G.M. A short history of SHELX. Acta Crystallogr A. 2008, 64(1), 112–122.

(5) Sheldrick, G. M., "SHELXT--Integrated space-group and crystal-structure determination", Acta Crystallogr A. 2015, A71, 3-8.

(6) a) Sheldrick, G.M. University of Göttingen, Germany, 2018. b) Sheldrick, G.M. Crystal structure refinement with SHELXL. Acta Crystallogr Sect C Struct Chem. 2015, 71(1), 3–8.

(7) Hübschle, C.B., Sheldrick, G.M. & Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. J. Appl. Crystallogr. 2011, 44(6), 1281–1284.

**Table S1.** Experimental details in single crystal analysis for C6BP-TEMPO

| | C6BP_TEMPO |
|---|---|
| Chemical formula | $C_{28}H_{38}NO_3$ |
| $M_r$ | 436.59 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 150 |
| $a$, $b$, $c$ (Å) | 5.6017 (3), 8.0854 (5), 27.3009 (18) |
| α, β, γ (°) | 82.667 (3), 87.626 (3), 81.944 (4) |
| $V$ (Å$^3$) | 1213.95 (13) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| μ (mm$^{-1}$) | 0.08 |
| Crystal size (mm) | 0.44 × 0.11 × 0.02 |
| | |
| Data collection | |
| Diffractometer | Bruker AXS D8 Quest<br>diffractometer with PhotonII charge-integrating pixel array detector (CPAD) |
| Absorption correction | Multi-scan<br>*SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48, 3-10. |
| $T_{min}$, $T_{max}$ | 0.571, 0.746 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 25753, 6003, 4887 |
| $R_{int}$ | 0.058 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.667 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.056, 0.148, 1.08 |
| No. of reflections | 6003 |
| No. of parameters | 294 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å$^{-3}$) | 0.37, -0.22 |

**Table S2.** Experimental details in single crystal analysis for C12BP-TEMPO

| | C12BP_TEMPO |
|---|---|
| Chemical formula | $C_{34}H_{50}NO_3$ |
| $M_r$ | 520.75 |
| Crystal system, space group | Triclinic, $P\bar{1}$ |
| Temperature (K) | 150 |
| $a$, $b$, $c$ (Å) | 5.6298 (12), 34.434 (7), 47.132 (8) |
| α, β, γ (°) | 82.237 (6), 88.356 (10), 86.533 (10) |
| $V$ (Å$^3$) | 9035 (3) |
| $Z$ | 12 |
| Radiation type | Cu $K\alpha$ |
| μ (mm$^{-1}$) | 0.55 |
| Crystal size (mm) | 0.31 × 0.28 × 0.05 |
| | |
| Data collection | |
| Diffractometer | Bruker AXS D8 Quest diffractometer with PhotonIII_C14 charge-integrating and photon counting pixel array detector |
| Absorption correction | Multi-scan *SADABS* 2016/2: Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D. (2015). J. Appl. Cryst. 48, 3-10. |
| $T_{min}$, $T_{max}$ | 0.123, 0.320 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 85013, 32201, 16039 |
| $R_{int}$ | 0.109 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.610 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.138, 0.373, 1.03 |
| No. of reflections | 32201 |
| No. of parameters | 2084 |
| H-atom treatment | H-atom parameters constrained |
| | $w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 22.9187P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å$^{-3}$) | 0.41, -0.38 |