Electronic Supplementary Information

Title:

Direct Synthetic Method for (Nitronyl Nitroxide)-substituted π-Electronic Compounds by Palladium-catalyzed Cross-Coupling Reaction with a Zinc Complex

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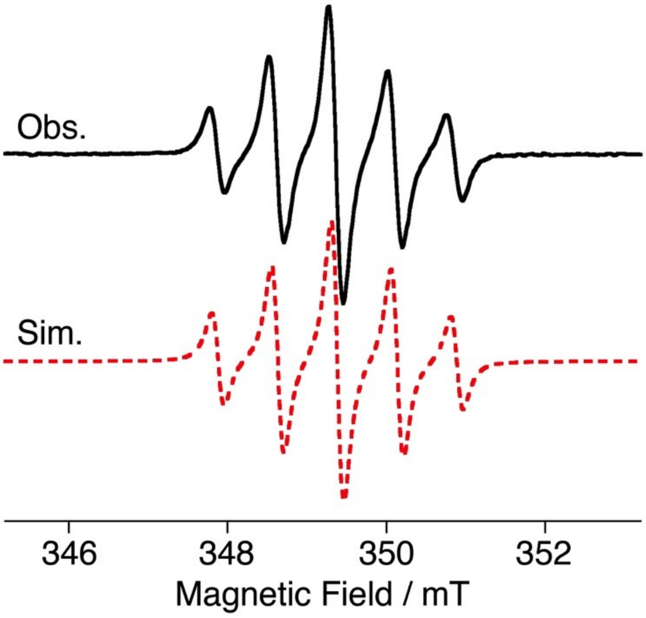

Fig. S1 Observed (solid line) and simulated (red broken line) ESR spectra of **1P**: g = 2.007 (ν_0 = 9.815013 GHz), $|a_N|$ = 0.752 mT in CH_2Cl_2 at room temperature).

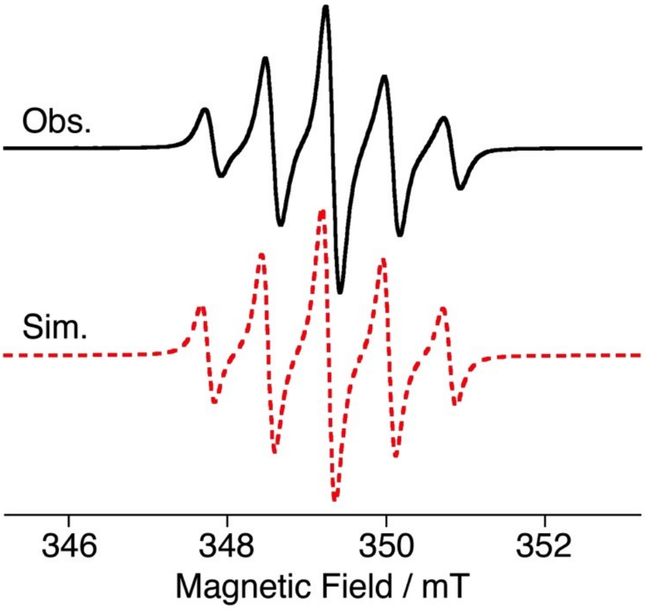

Fig. S2 Observed (solid line) and simulated (red broken line) ESR spectra of **2P**: g = 2.007 (ν_0 = 9.813534 GHz), $|a_N|$ = 0.761 mT in CH_2Cl_2 at room temperature).

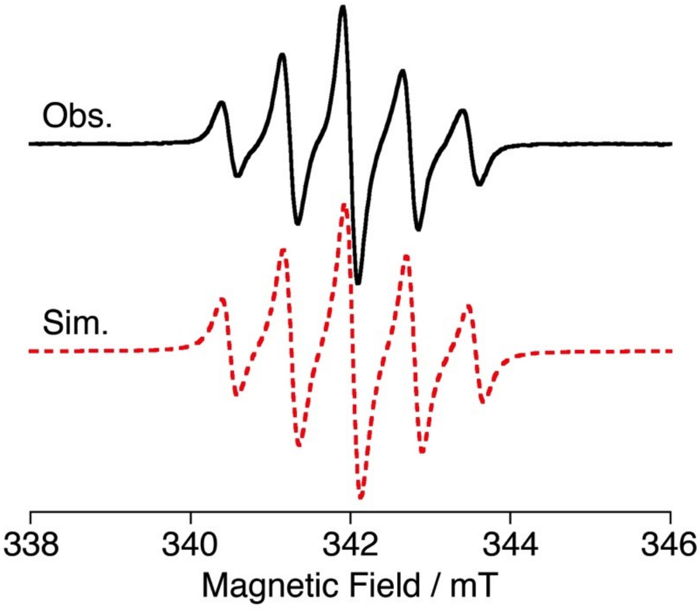

Fig. S3 Observed (solid line) and simulated (red broken line) ESR spectra of **3P**: g = 2.007 (ν_0 = 9.608108 GHz), $|a_\mathrm{N}|$ = 0.769 mT in CH_2Cl_2 at room temperature).

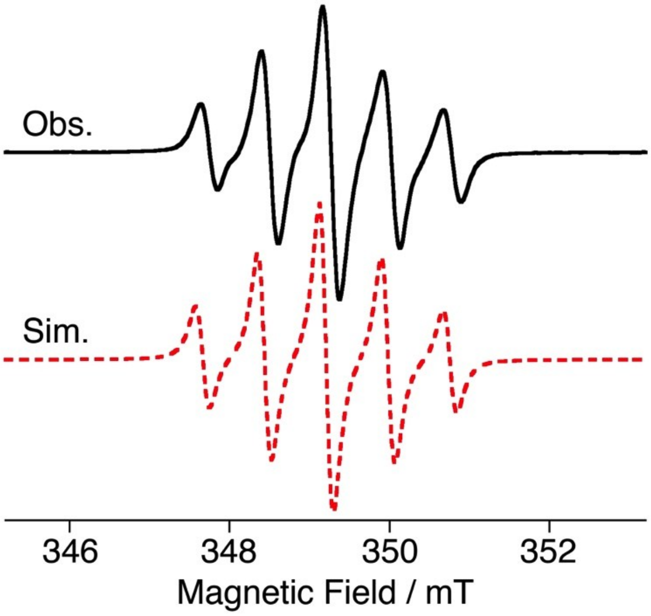

Fig. S4 Observed (solid line) and simulated (red broken line) ESR spectra of **4P**: g = 2.007 (ν_0 = 9.811410 GHz), $|a_\mathrm{N}|$ = 0.773 mT in CH_2Cl_2 at room temperature).

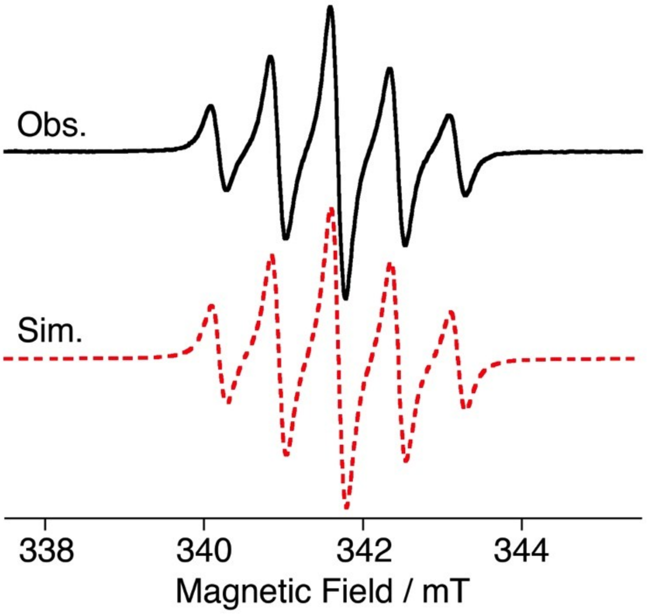

Fig. S5 Observed (solid line) and simulated (red broken line) ESR spectra of **5P**: g = 2.007 (ν_0 = 9.598689 GHz), $|a_\mathrm{N}|$ = 0.752 mT in CH_2Cl_2 at room temperature).

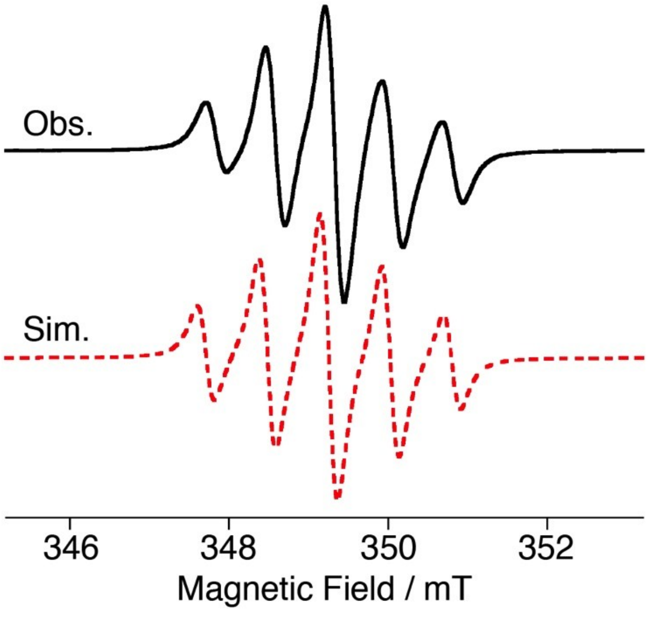

Fig. S6 Observed (solid line) and simulated (red broken line) ESR spectra of **6P**: g = 2.007 (ν_0 = 9.812717 GHz), $|a_\mathrm{N}|$ = 0.773 mT in CH_2Cl_2 at room temperature).

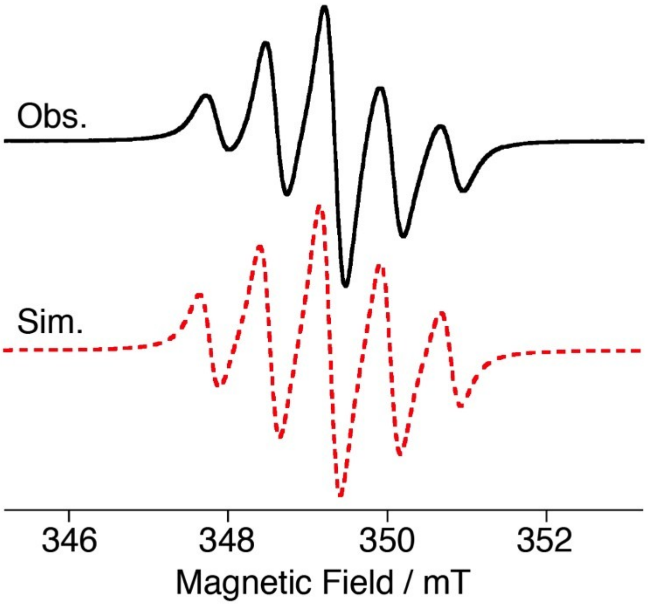

Fig. S7 Observed (solid line) and simulated (red broken line) ESR spectra of **7P**: g = 2.007 (ν_0 = 9.813716 GHz), $|a_N|$ = 0.748 mT in CH_2Cl_2 at room temperature).

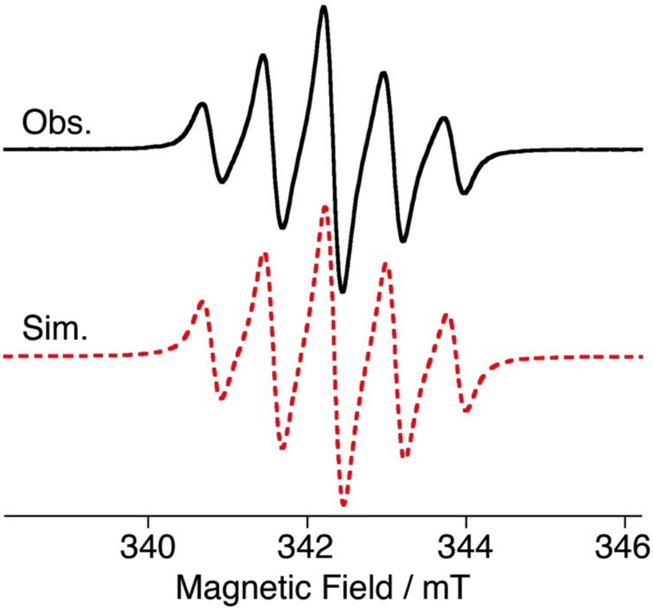

Fig. S8 Observed (solid line) and simulated (red broken line) ESR spectra of **8P**: g = 2.007 (ν_0 = 9.616935 GHz), $|a_N|$ = 0.769 mT in CH_2Cl_2 at room temperature).

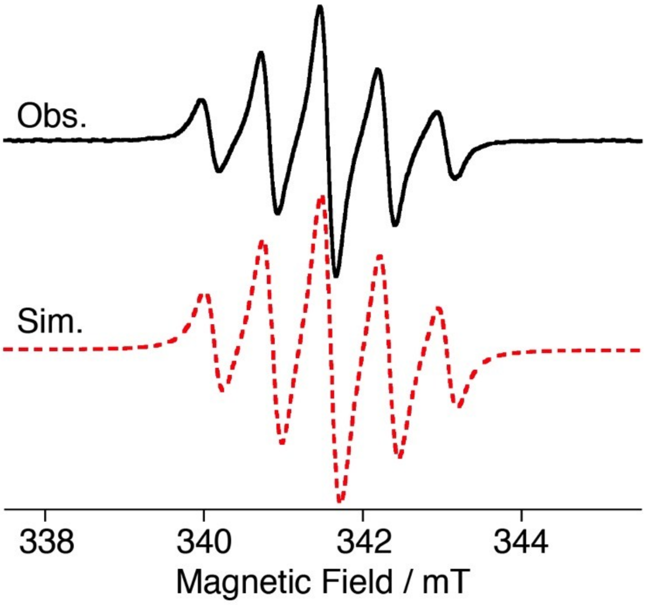

Fig. S9 Observed (solid line) and simulated (red broken line) ESR spectra of **9P**: g = 2.007 (ν_0 = 9.595996 GHz), $|a_N|$ = 0.734 mT in CH_2Cl_2 at room temperature).

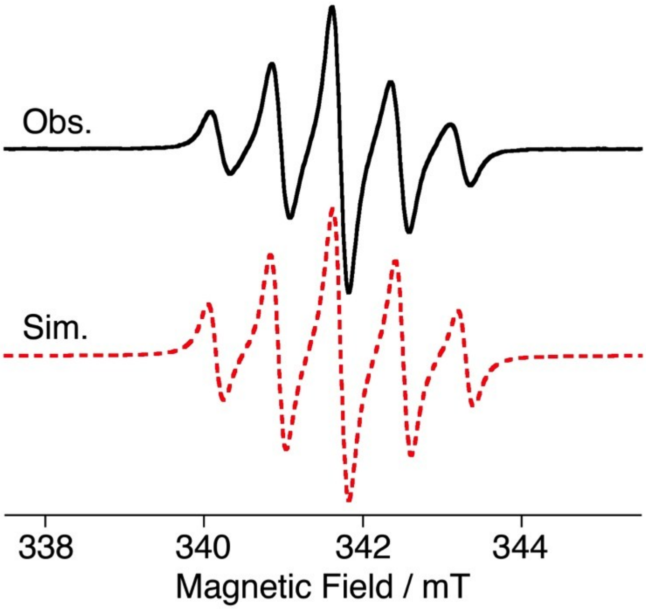

Fig. S10 Observed (solid line) and simulated (red broken line) ESR spectra of **11P**: g = 2.007 (ν_0 = 9.599547 GHz), $|a_N|$ = 0.787 mT in CH_2Cl_2 at room temperature).

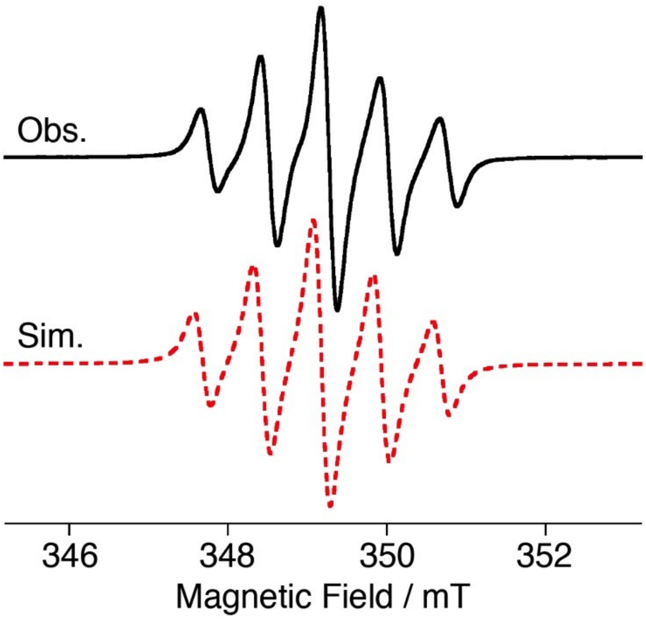

Fig. S11 Observed (solid line) and simulated (red broken line) ESR spectra of **12P**: $g = 2.007$ ($\nu_0 = 9.810618$ GHz), $|a_\mathrm{N}| = 0.752$ mT in CH_2Cl_2 at room temperature).

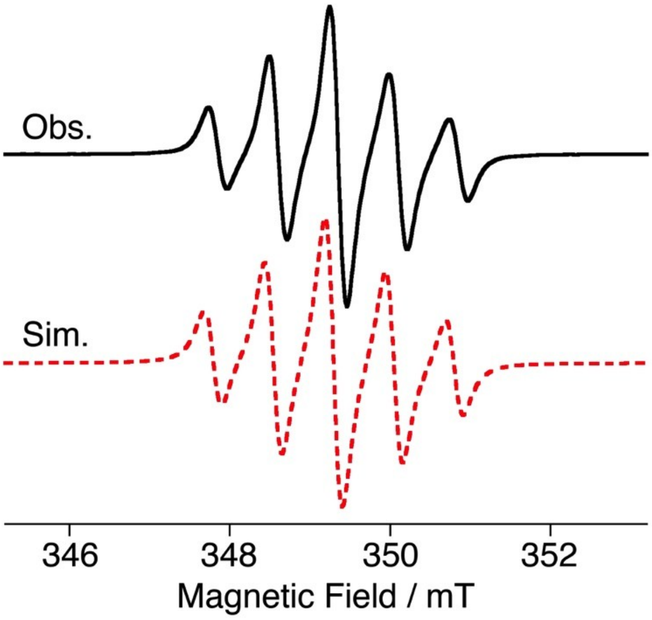

Fig. S12 Observed (solid line) and simulated (red broken line) ESR spectra of **13P**: $g = 2.007$ ($\nu_0 = 9.813807$ GHz), $|a_\mathrm{N}| = 0.752$ mT in CH_2Cl_2 at room temperature).

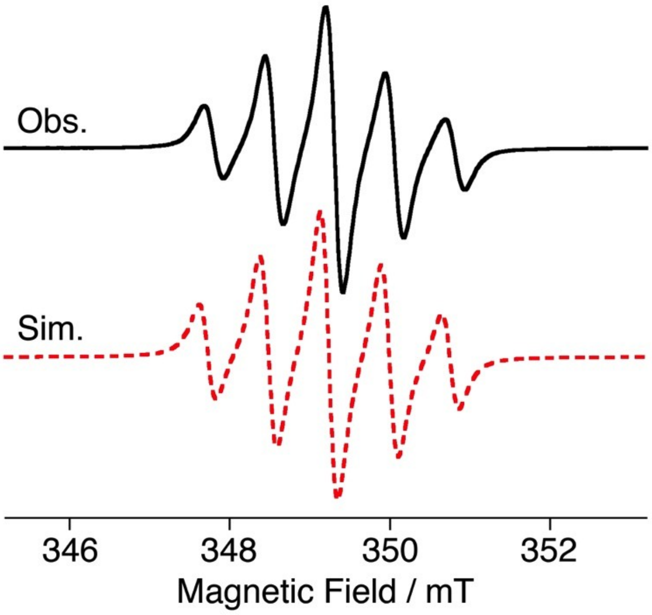

Fig. S13 Observed (solid line) and simulated (red broken line) ESR spectra of **14P**: g = 2.007 (ν_0 = 9.812223 GHz), $|a_N|$ = 0.757 mT in CH_2Cl_2 at room temperature).

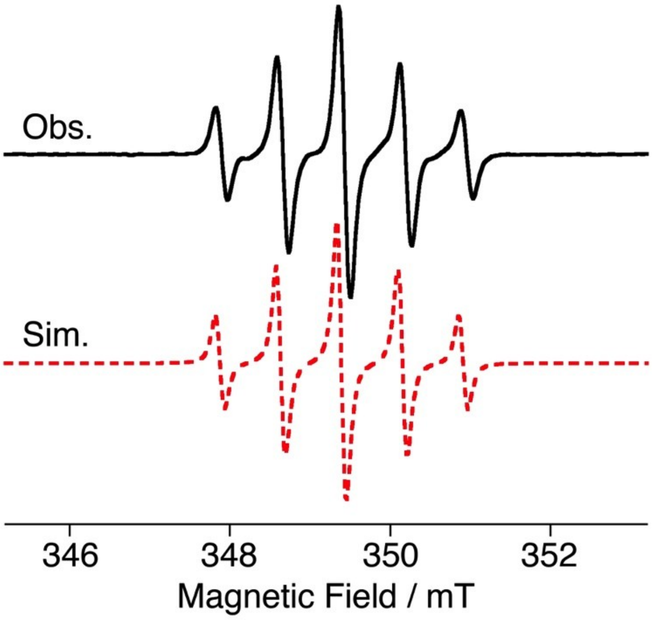

Fig. S14 Observed (solid line) and simulated (red broken line) ESR spectra of **15P**: g = 2.007 (ν_0 = 9.811669 GHz), $|a_N|$ = 0.759 mT in CH_2Cl_2 at room temperature).

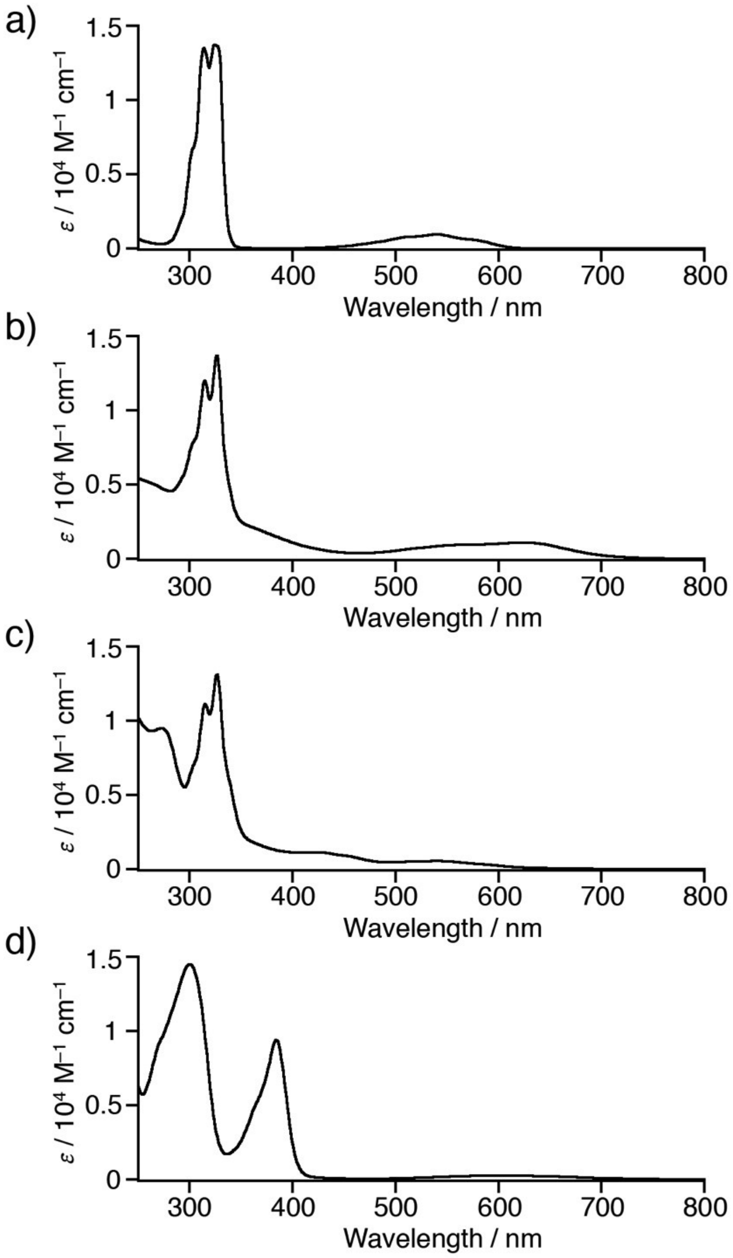

Fig. S15 UV-vis spectra (in THF, 250–800 nm) (a) of **NN-H** as initial state of reaction, (b) after addition of LHMDS, (c) after addition of $ZnCl_2$, and (d) of **1P**.Figure

Table S1. Calculated intermolecular exchange interactions for **15P**$^+$.

Spin state	E / au	$<S^2>$	$J_{\text{intra-calc}}/k_B$ / K [b]
Triplet	–1679.7160710	2.070722	+1031.9
Singlet	–1679.7120841	0.850604	

[a] The calculations were carried out by *Gaussian 09* program with density functional theory at the UB3LYP/6-31G(d,p) level of theory.[S1] The singlet states were calculated using the broken symmetry method using the optimized geometry in the triplet state. [b] Exchange interaction ($J_{\text{intra-calc}}/k_B$) was using an equation, $J_{\text{intra-calc}} = (E^{\text{singlet}} - E^{\text{triplet}})/(<S^2>^{\text{triplet}} - <S^2>^{\text{singlet}})$.[S2]

[S1] *Gaussian 09*, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[S2] K. Yamaguchi, T. Kawakami, Y. Takano, Y. Kitagawa, Y. Yamashita and H. Fujita, *Int. J. Quantum Chem.* **2002**, *90*, 370–385.