

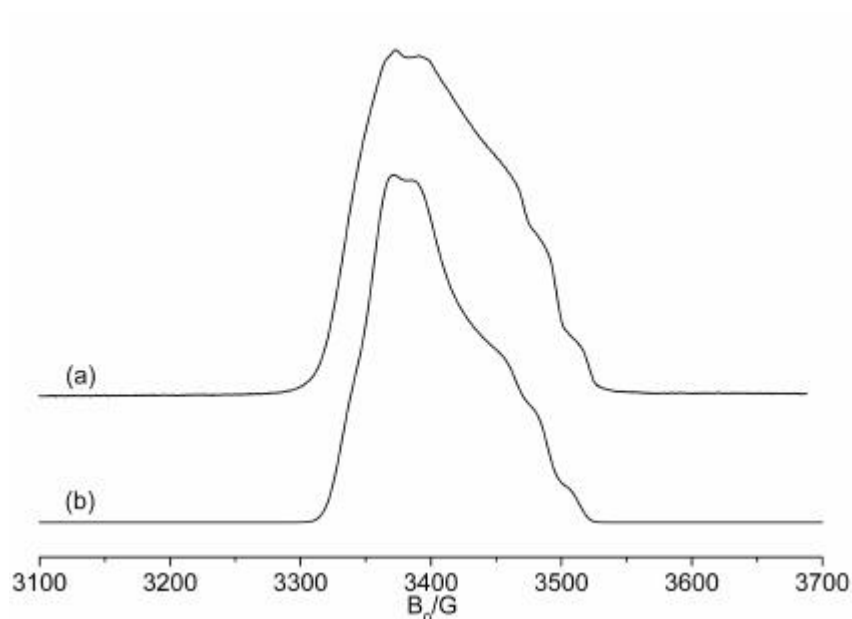
**A cw EPR and ENDOR investigation on a series of Cr(I) carbonyl  
complexes with relevance to alkene oligomerization catalysis:**



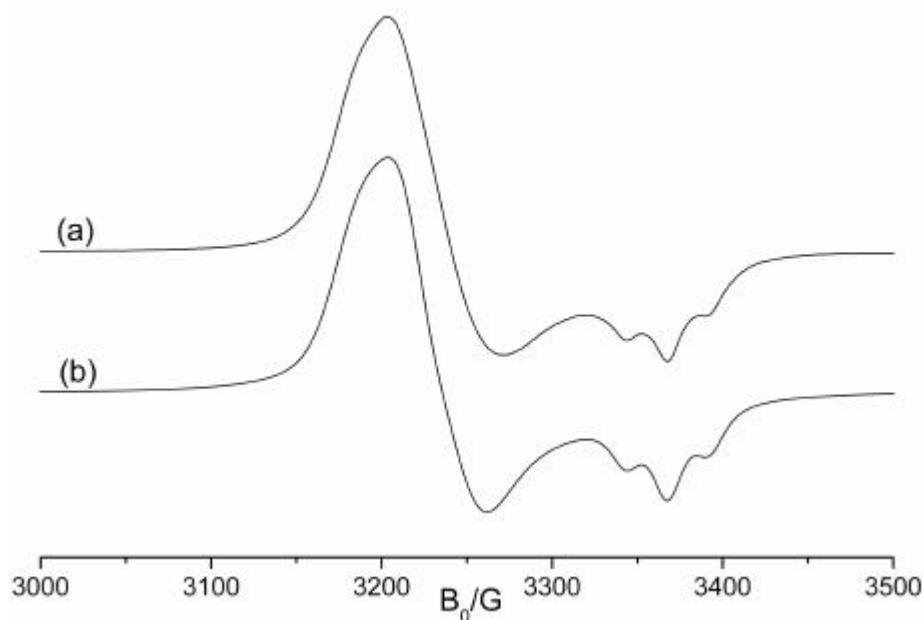
**Electronic Supplementary Information**

**CONTENTS**

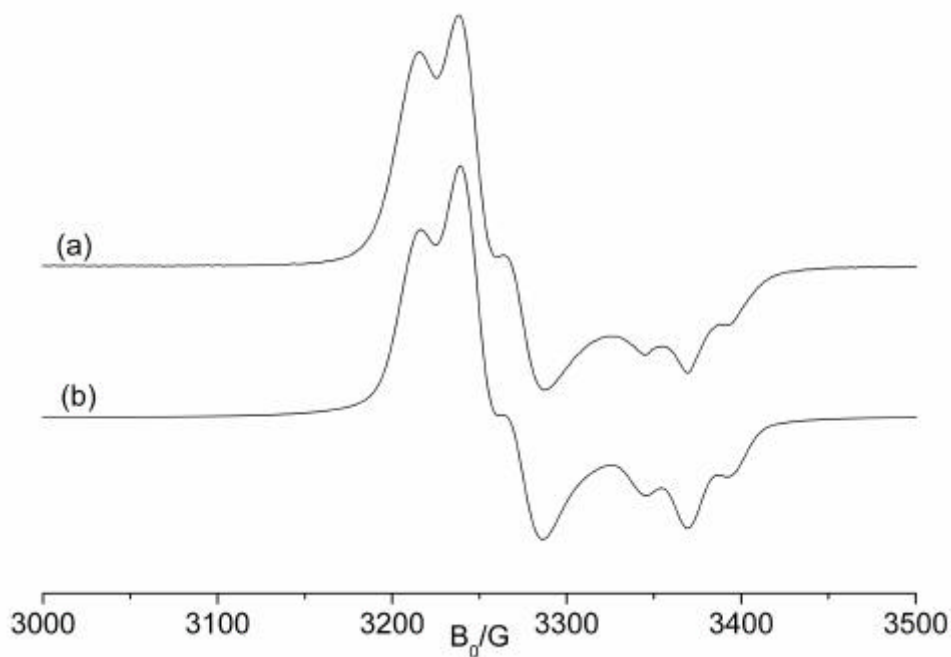
- Figure S1: FSED EPR spectra
- Figure S2a – S2h: Experimental and simulated cw EPR spectra
- Figure S3a – S3f: Additional  $^1\text{H}$  ENDOR data
- Figure S4 : Additional  $^{14}\text{N}$  ENDOR data
- Figure S5: Additional  $^{31}\text{P}$  ENDOR data



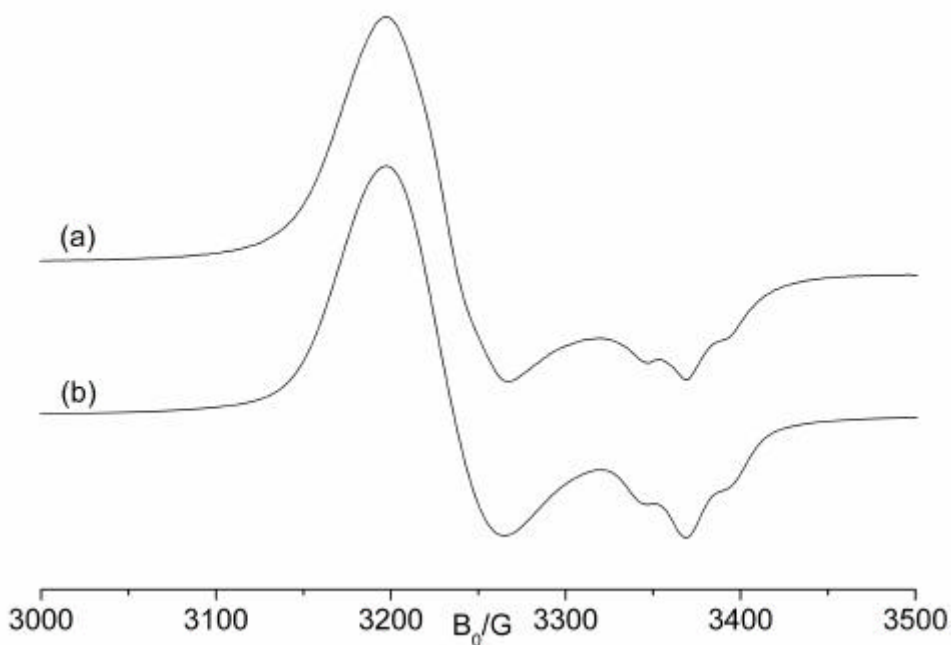
**Figure S1:** Experimental (a) and simulated (b) FSED spectra (130K) of  $[\text{Cr}(\text{CO})_4(\text{dppp})]^+$  (**2b**) recorded in dichloromethane/toluene at a microwave frequency of 9.734 GHz. Spin Hamiltonian parameters:  $g_{\parallel} = 2.062$ ,  $g_{\perp} = 1.987$ ,  $^1A_{\parallel} = 24.9$  G (72.0 MHz),  $^1A_{\perp} = 24.5$  G (68.1 MHz). The FSED spectrum was obtained using a  $\pi/2 - \tau - \pi - \tau$  - echo pulse sequence of  $\pi/2 = 16$  ns  $\pi = 32$  ns,  $\tau = 400$  ns, MW attenuation = 7 dB, Video gain = 2 dB, MW freq = 9.73 GHz, Shot repetition time = 2000 us, Shots per point = 50, Temp = 10K.



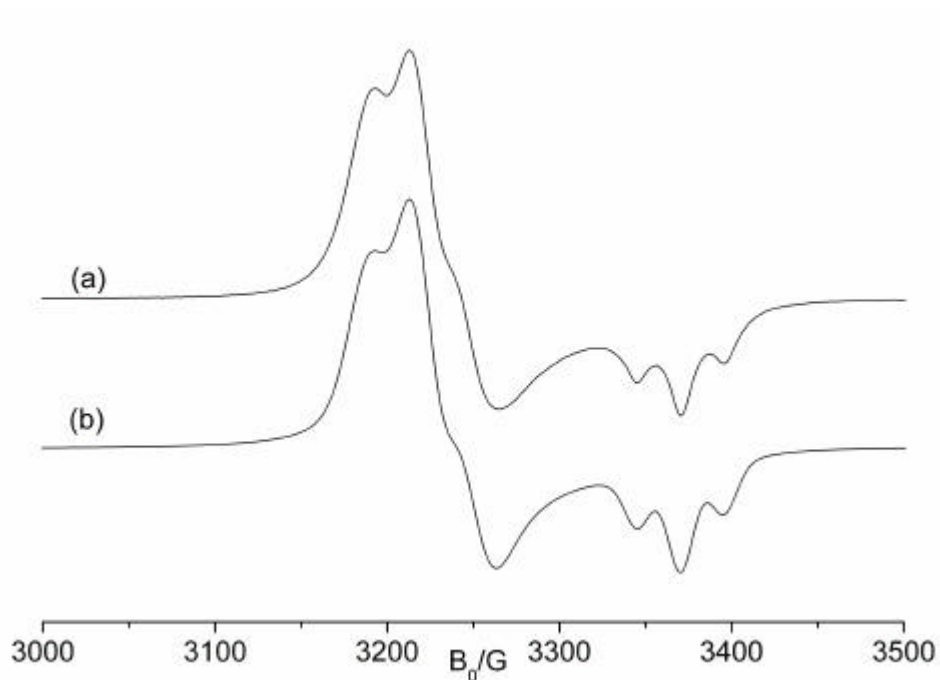
**Figure S2a:** Experimental (a) and simulated (b) cw-EPR spectra (130K) of  $[\text{Cr}(\text{CO})_4(\text{dppe})]^+$  (**2a**) recorded in dichloromethane/toluene at a microwave frequency of 9.381 GHz. For simulation parameters refer to Table 1.



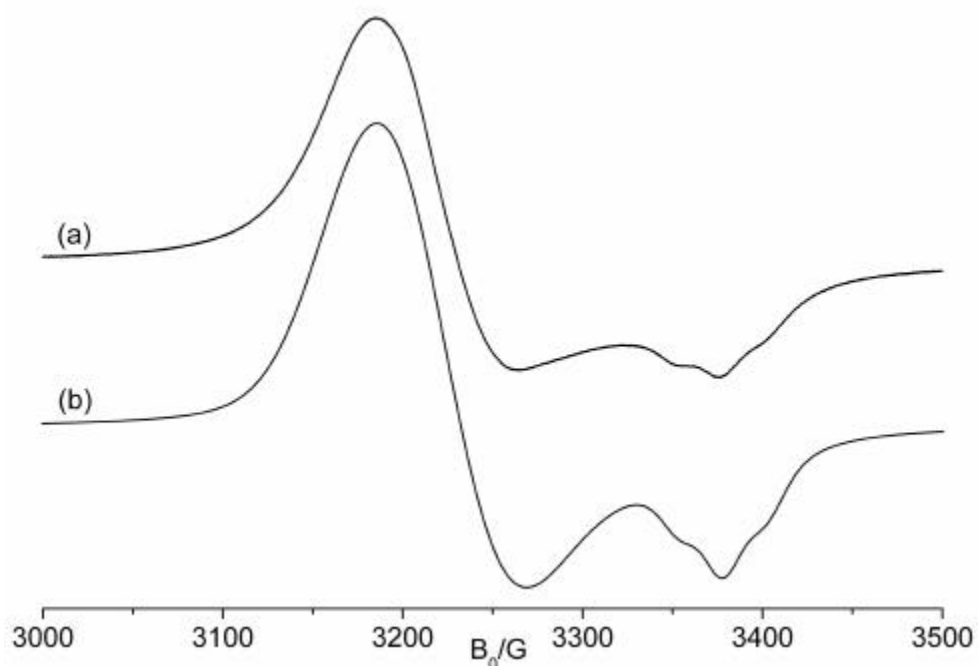
**Figure S2b:** Experimental (a) and simulated (b) cw-EPR spectra (130K) of  $[\text{Cr}(\text{CO})_4(\text{dppp})]^+$  (**2b**) recorded in dichloromethane/toluene at a microwave frequency of 9.371 GHz. For simulation parameters refer to Table 1.



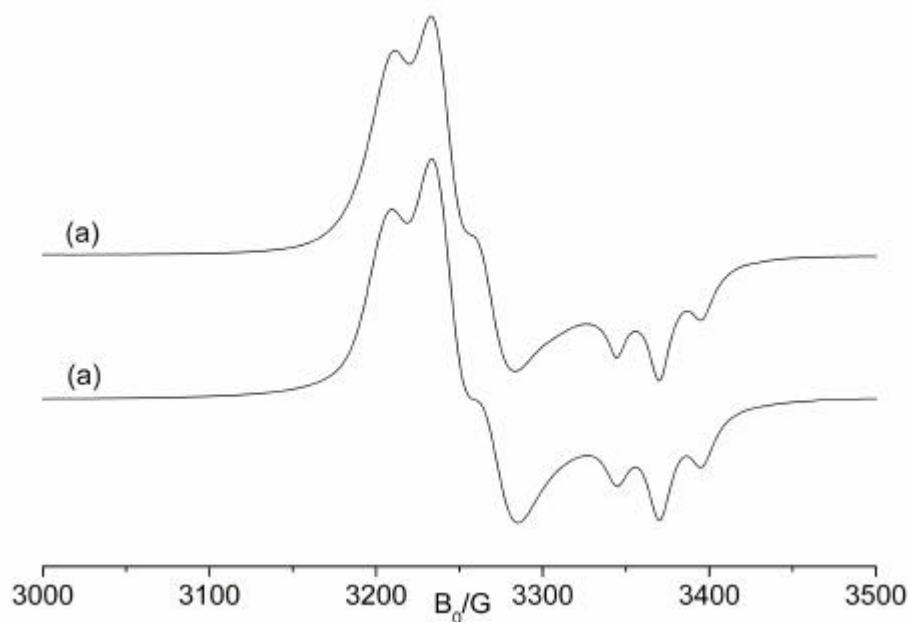
**Figure S2c:** Experimental (a) and simulated (b) cw-EPR spectra (130K) of  $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PBzPPh}_2)]^+$  (**2c**) recorded in dichloromethane/toluene at a microwave frequency of 9.375 GHz. For simulation parameters refer to Table 1.



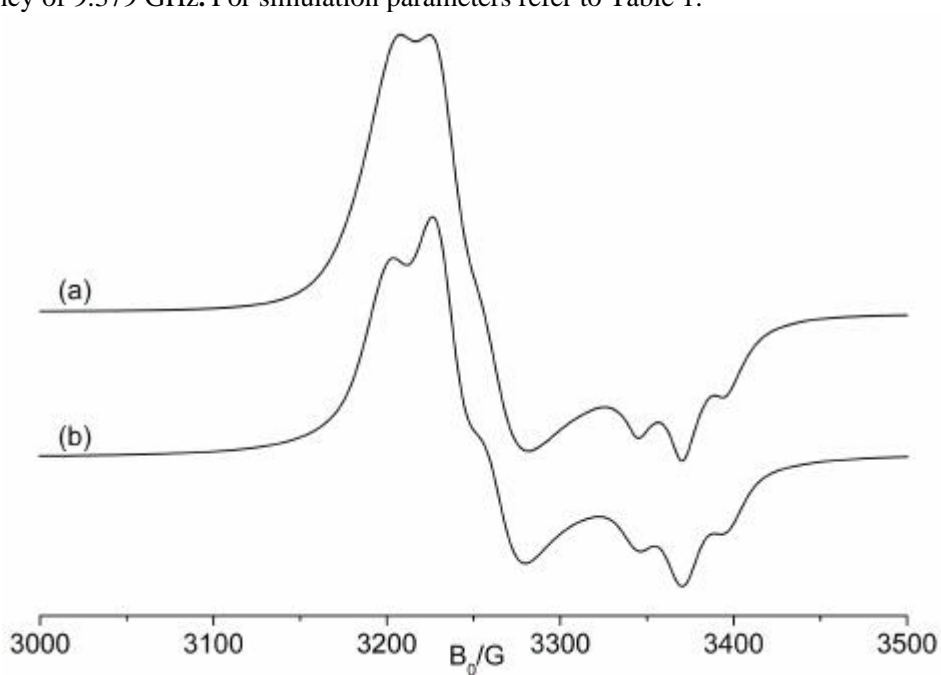
**Figure S2d:** Experimental (a) and simulated (b) cw-EPR spectra (130K) of  $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PN}(\text{Et})\text{PPh}_2)]^+$  (**2d**) recorded in dichloromethane/toluene at a microwave frequency of 9.363 GHz. For simulation parameters refer to Table 1.



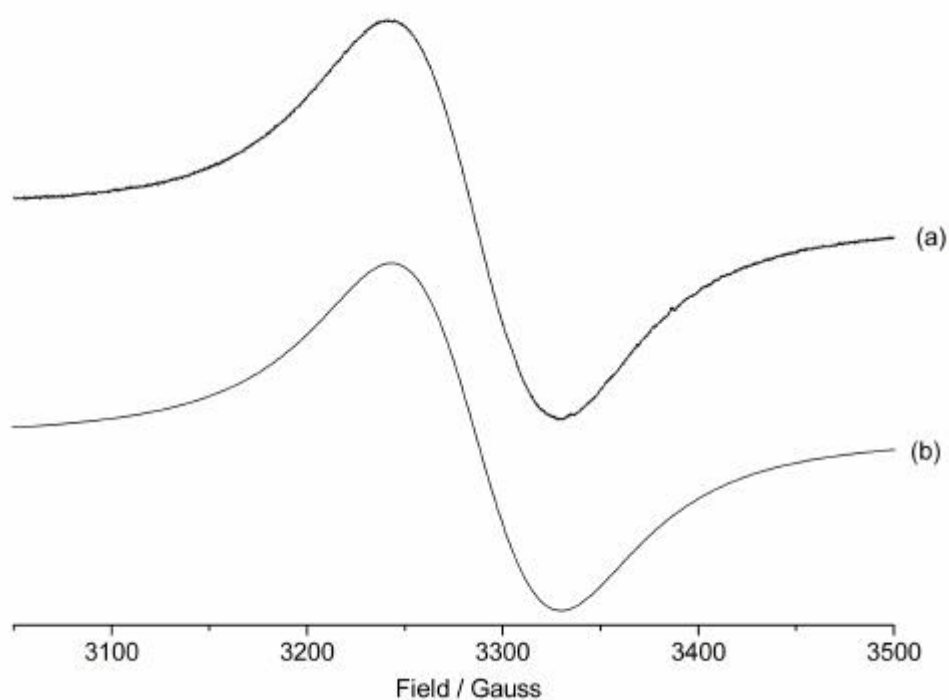
**Figure S2e:** Experimental (a) and simulated (b) cw-EPR spectra (130K) of  $[\text{Cr}(\text{CO})_4(\text{Ar}_2\text{PN}(\text{Me})\text{PAr}_2)]^+$  Ar = 2- $\text{C}_6\text{H}_4(\text{Et})$  (**2e**) recorded in dichloromethane/toluene at a microwave frequency of 9.386 GHz. For simulation parameters refer to Table 1.



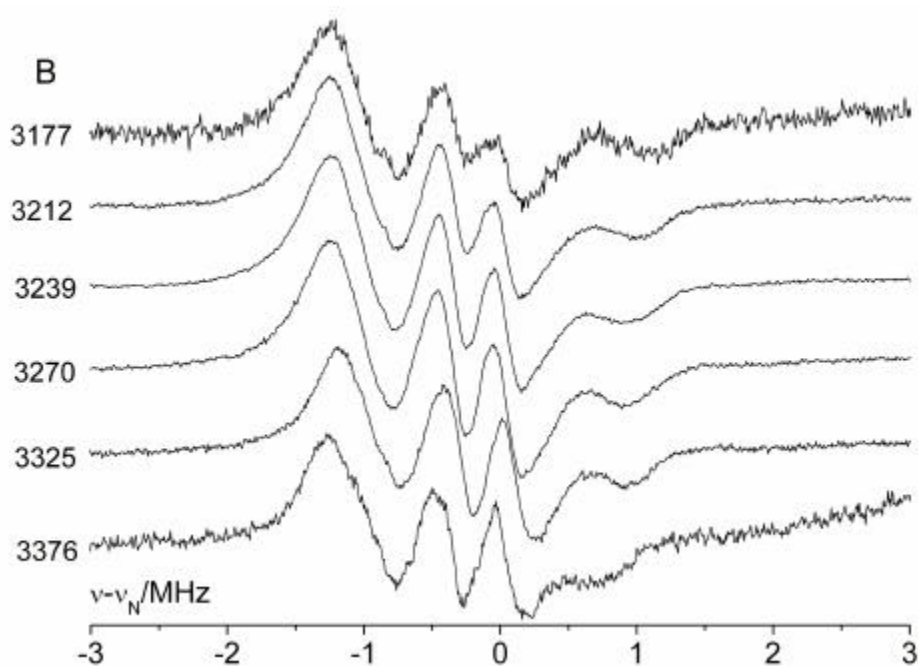
**Figure S2f:** Experimental (a) and simulated (b) cw-EPR spectra (130K) of  $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PN}(i\text{Bu})\text{PPh}_2)]^+$  (**2f**) recorded in dichloromethane/toluene at a microwave frequency of 9.379 GHz. For simulation parameters refer to Table 1.



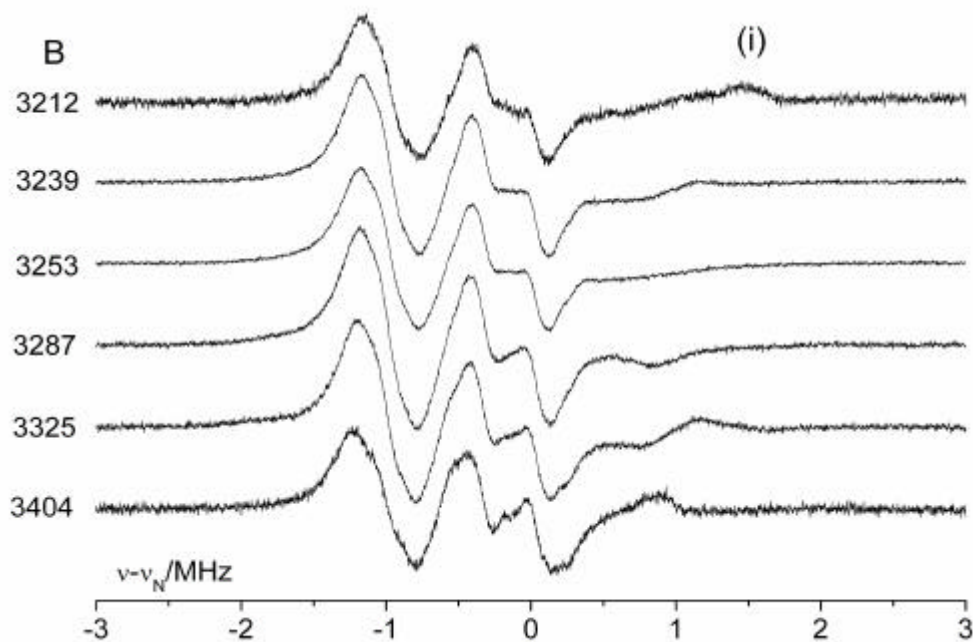
**Figure S2g:** Experimental (a) and simulated (b) cw-EPR spectra (130K) of  $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PN}(i\text{Pr})\text{PPh}_2)]^+$  (**2g**) recorded in dichloromethane/toluene at a microwave frequency of 9.376 GHz. For simulation parameters refer to Table 1.



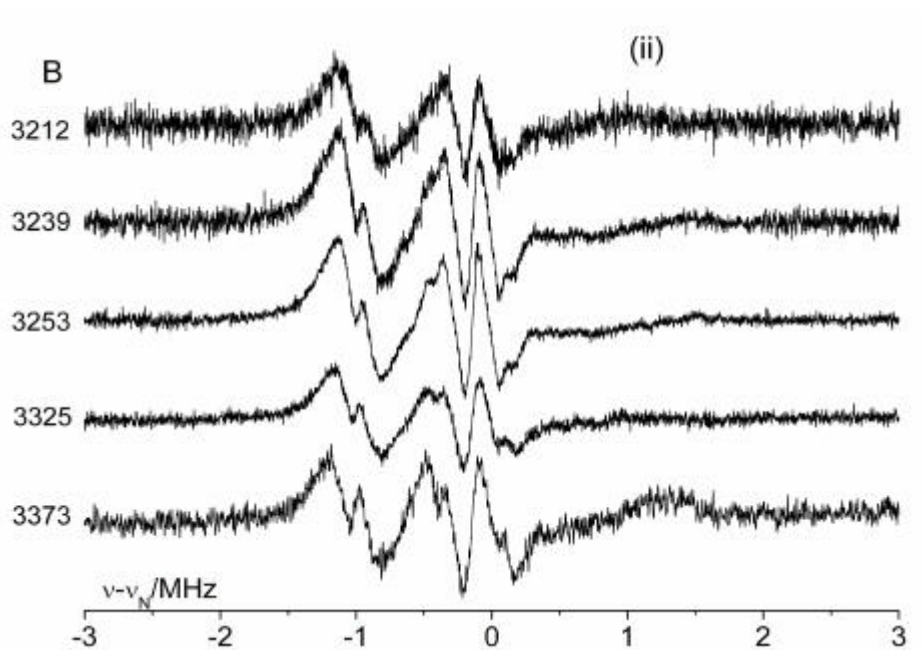
**Figure S2h:** Experimental (a) and simulated (b) cw-EPR spectra (298K) of  $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PN}(\text{dppp})\text{PPh}_2)]^+$  (**2b**) recorded in dichloromethane/toluene at a microwave frequency of 9.384 GHz.  $g_{\text{iso}}$  extracted from simulation = 2.04.



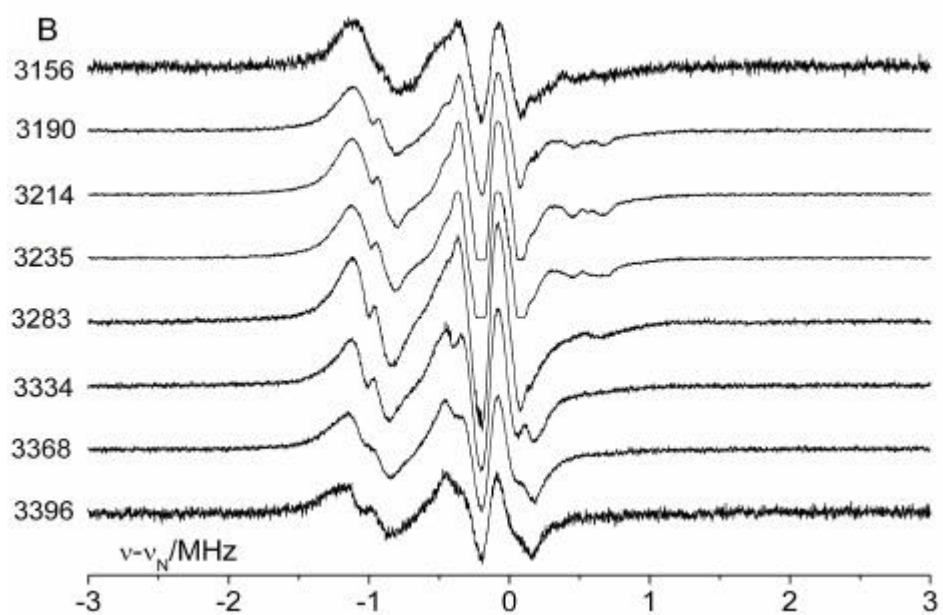
**Figure S3a:** Experimental cw  $^1\text{H}$  ENDOR spectra (10K) of  $[\text{Cr}(\text{CO})_4(\text{dppe})]^+$  (**2a**) recorded in deuterated dichloromethane/toluene at a microwave frequency of 9.493 GHz and a modulation depth of 79 kHz. The angular selective spectra were obtained at the magnetic field positions (B in Gauss) shown in the Figure.



**Figure S3b(i):** Experimental cw  $^1\text{H}$  ENDOR spectra (10K) of  $[\text{Cr}(\text{CO})_4(\text{dppp})]^+$  (**2b**) recorded in deuterated dichloromethane/toluene at a microwave frequency of 9.487 GHz and a modulation depth of 251 kHz. The angular selective spectra were obtained at the magnetic field positions (B in Gauss) shown in the Figure.

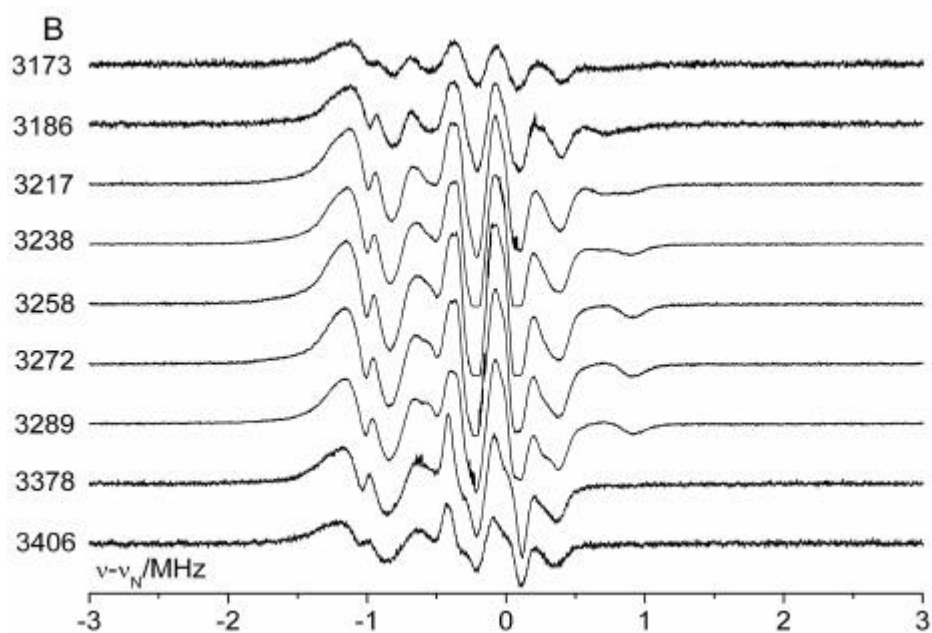


**Figure S3b(ii):** Experimental cw <sup>1</sup>H ENDOR spectra (10K) of [Cr(CO)<sub>4</sub>(dppp)]<sup>+</sup> (2b) recorded in deuterated dichloromethane/toluene at a microwave frequency of 9.493 GHz and a modulation depth of 79 kHz. The angular selective spectra were obtained at the magnetic field positions (B in Gauss) shown in the Figure.

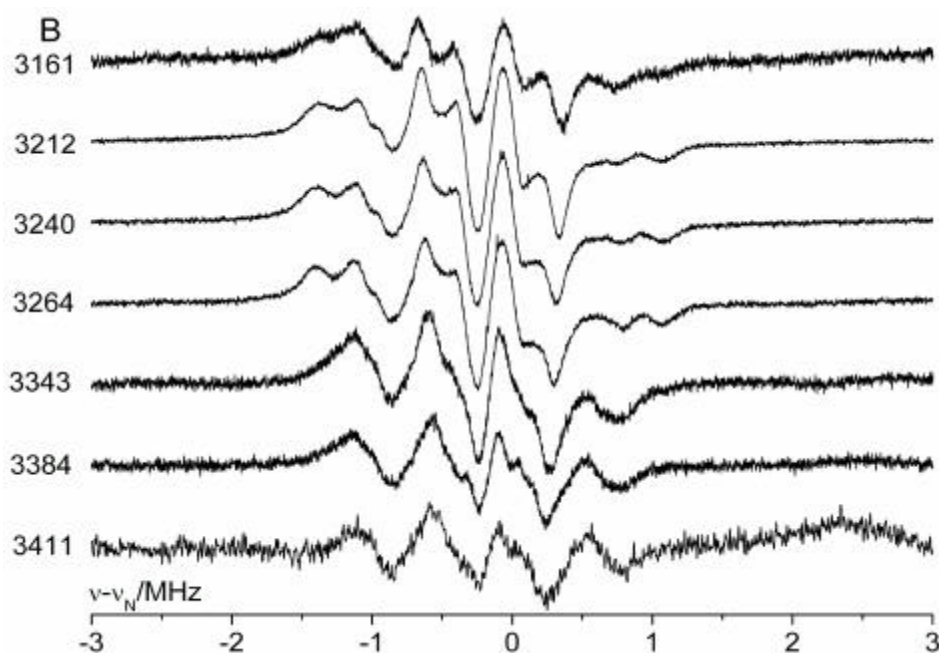


**Figure S3c:** Experimental cw <sup>1</sup>H ENDOR spectra (10K) of [Cr(CO)<sub>4</sub>(Ph<sub>2</sub>PBzPPh<sub>2</sub>)]<sup>+</sup> (2c) recorded in deuterated dichloromethane/toluene at a microwave frequency of 9.485 GHz and a modulation depth of 79 kHz. The angular selective spectra were obtained at the magnetic field positions (B in Gauss) shown in the Figure.

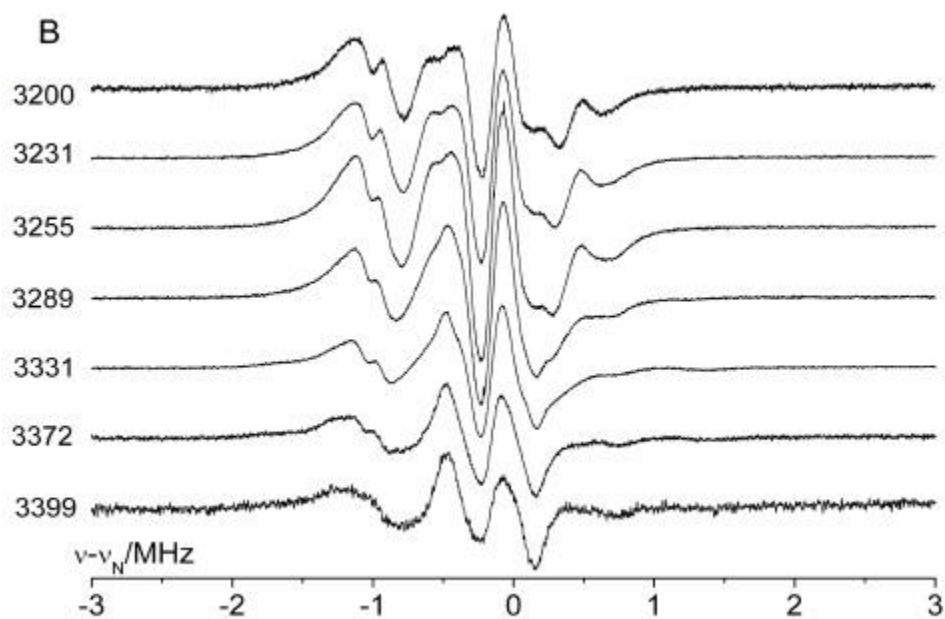




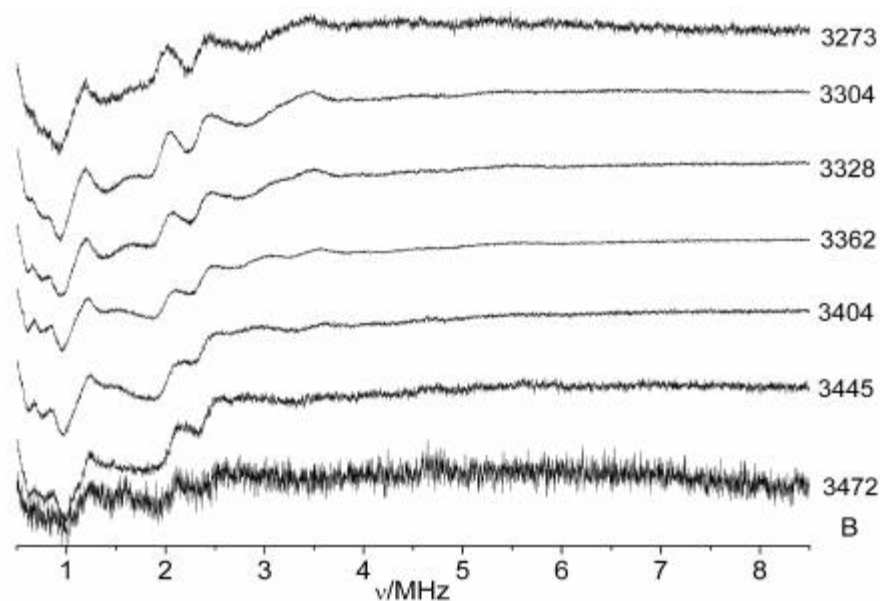
**Figure S3d:** Experimental cw <sup>1</sup>H ENDOR spectra (10K) of  $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PN}(\text{Et})\text{PPh}_2)]^+$  (**2d**) recorded in deuterated dichloromethane/toluene at a microwave frequency of 9.486 GHz and a modulation depth of 79 kHz. The angular selective spectra were obtained at the magnetic field positions (**B** in Gauss) shown in the Figure.



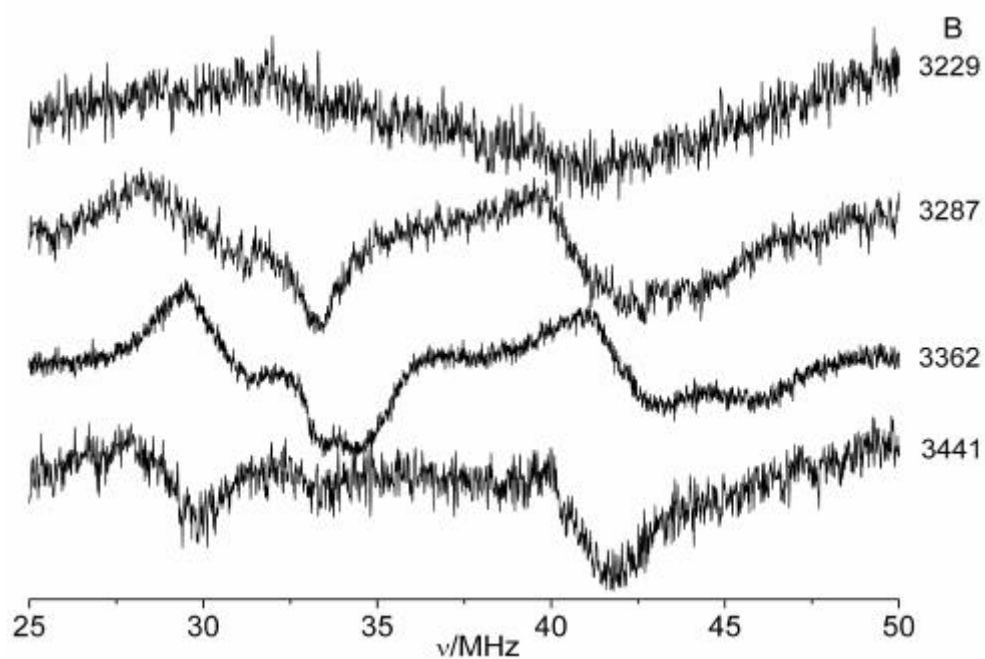
**Figure S3e:** Experimental cw <sup>1</sup>H ENDOR spectra (10K) of  $[\text{Cr}(\text{CO})_4(\text{Ar}_2\text{PN}(\text{Me})\text{PAR}_2)]^+$   $\text{Ar} = 2\text{-C}_6\text{H}_4(\text{Et})$  (**2e**) recorded in deuterated dichloromethane/toluene at a microwave frequency of 9.475 GHz and a modulation depth of 79 kHz. The angular selective spectra were obtained at the magnetic field positions (**B** in Gauss) shown in the Figure.



**Figure S3f:** Experimental cw <sup>1</sup>H ENDOR spectra (10K) of  $[\text{Cr}(\text{CO})_4((\text{Ph}_2\text{PN}(i\text{Bu})\text{PPh}_2))^+ (2f)$  recorded in deuterated dichloromethane/toluene at a microwave frequency of 9.476 GHz and a modulation depth of 79 kHz. The angular selective spectra were obtained at the magnetic field positions (B in Gauss) shown in the Figure.



**Figure S4:** Experimental cw <sup>14</sup>N ENDOR spectra (10K)  $[\text{Cr}(\text{CO})_4((\text{Ph}_2\text{PN}(i\text{Bu})\text{PPh}_2))^+ (2f)$  of recorded in deuterated dichloromethane/toluene at a microwave frequency of 9.475 GHz. The angular selective spectra were obtained at the magnetic field positions (B in Gauss) shown in the Figure.



**Figure S5:** Experimental cw <sup>31</sup>P ENDOR spectra (10K) of  $[\text{Cr}(\text{CO})_4(\text{Ph}_2\text{PBzPPh}_2)]^+$  (**2c**) recorded in deuterated dichloromethane/toluene at a microwave frequency of 9.485 GHz. The angular selective spectra were obtained at the magnetic field positions ( $B$  in Gauss) shown in the Figure.