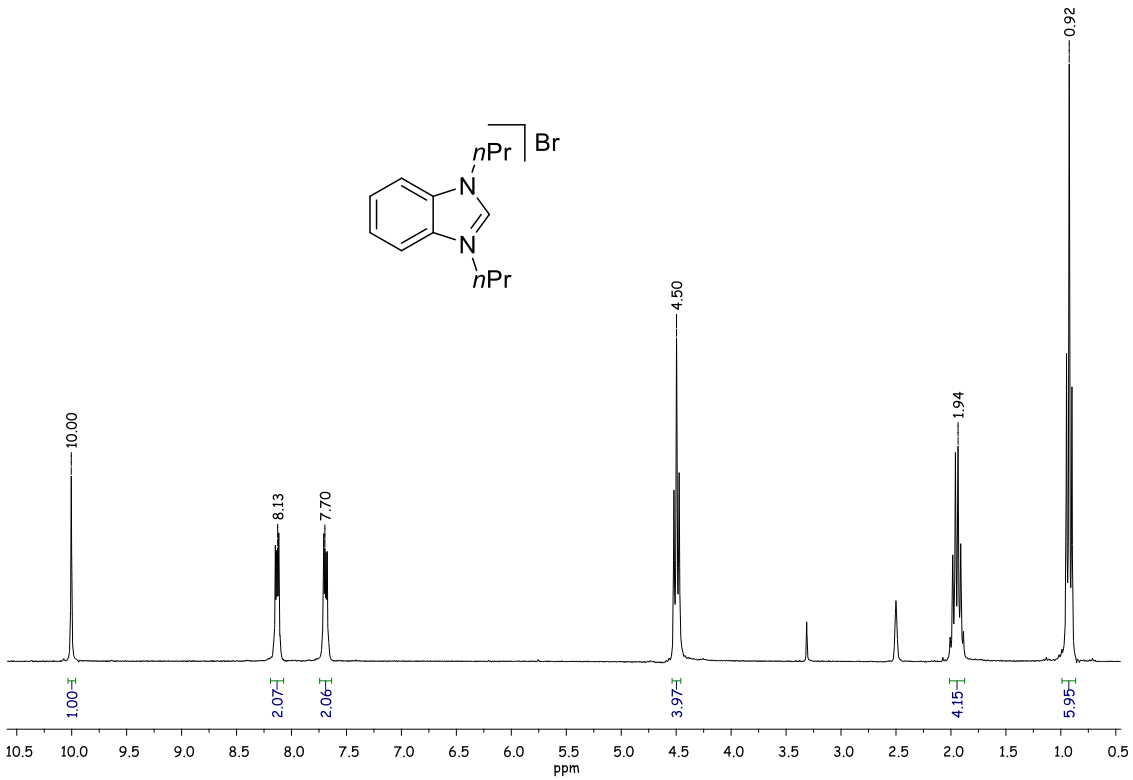
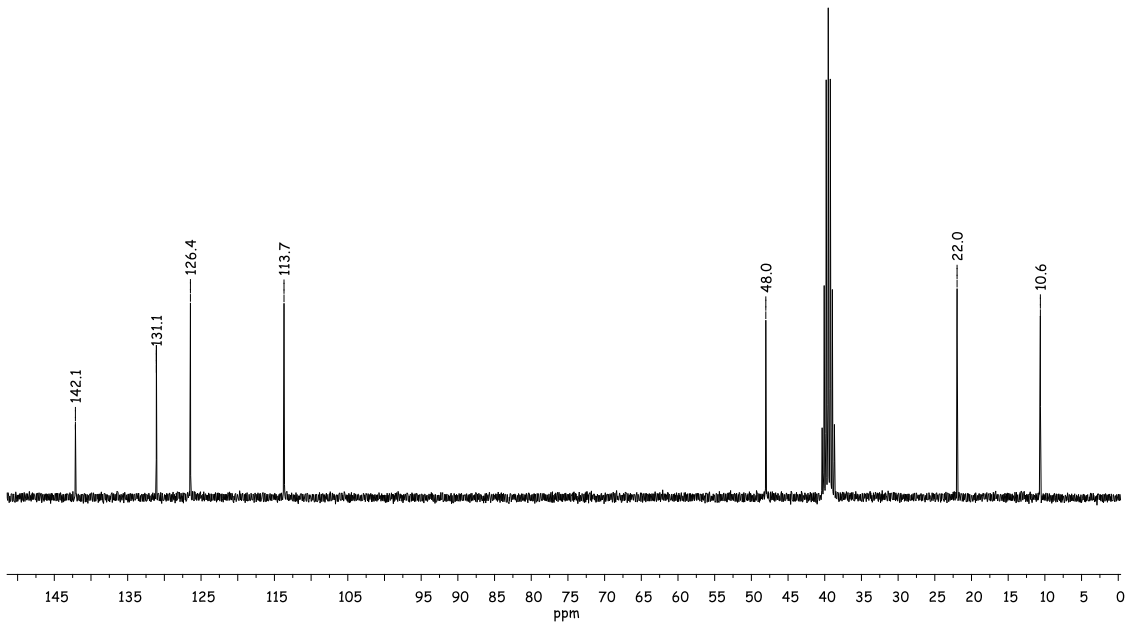
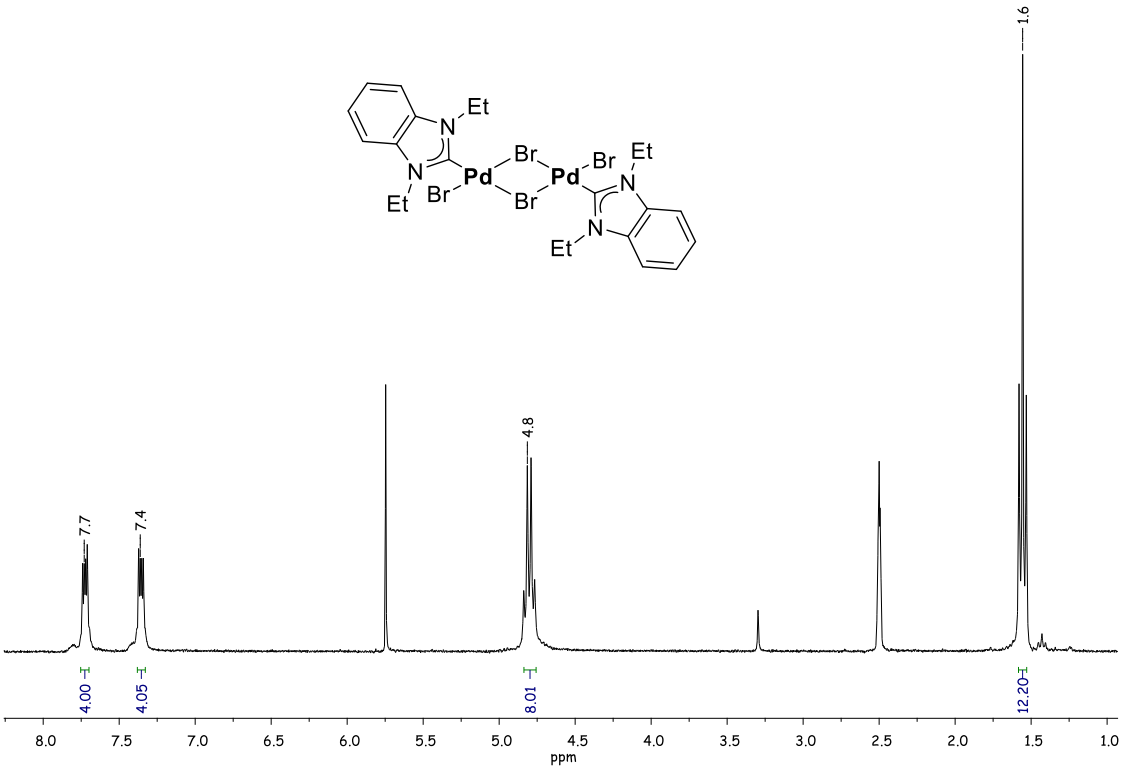
1. Spectroscopic data

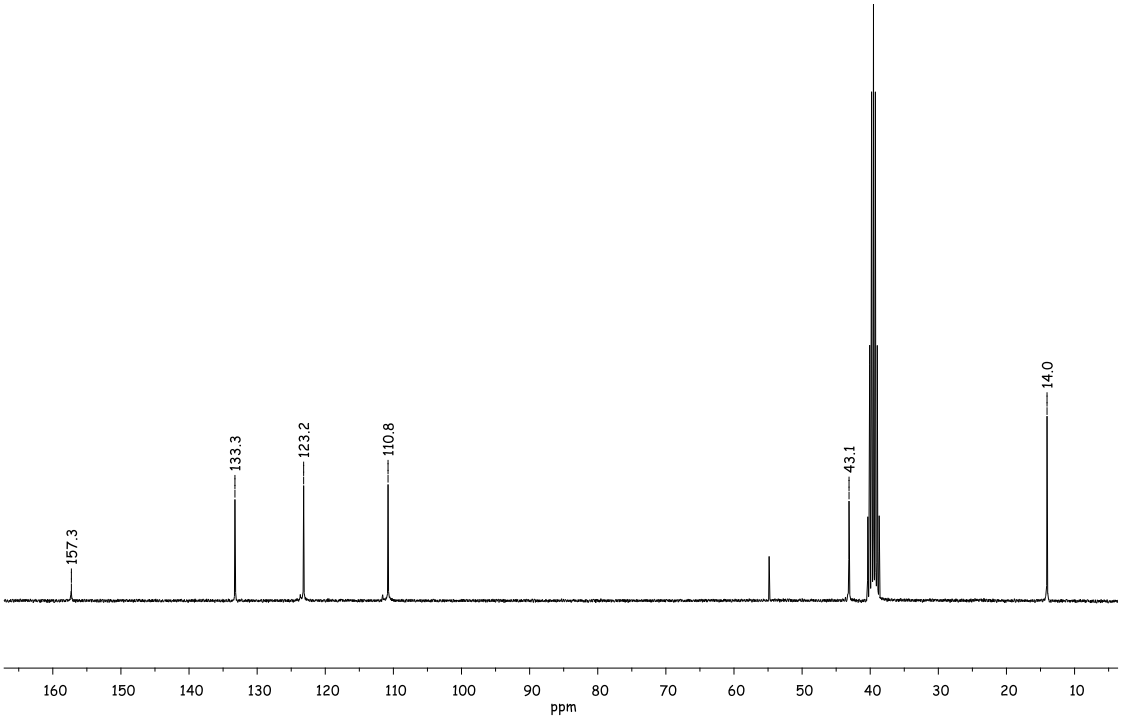
1.1. ^{1}H and ^{13}C NMR spectra of **A-*n*Pr** in dmso-d_6



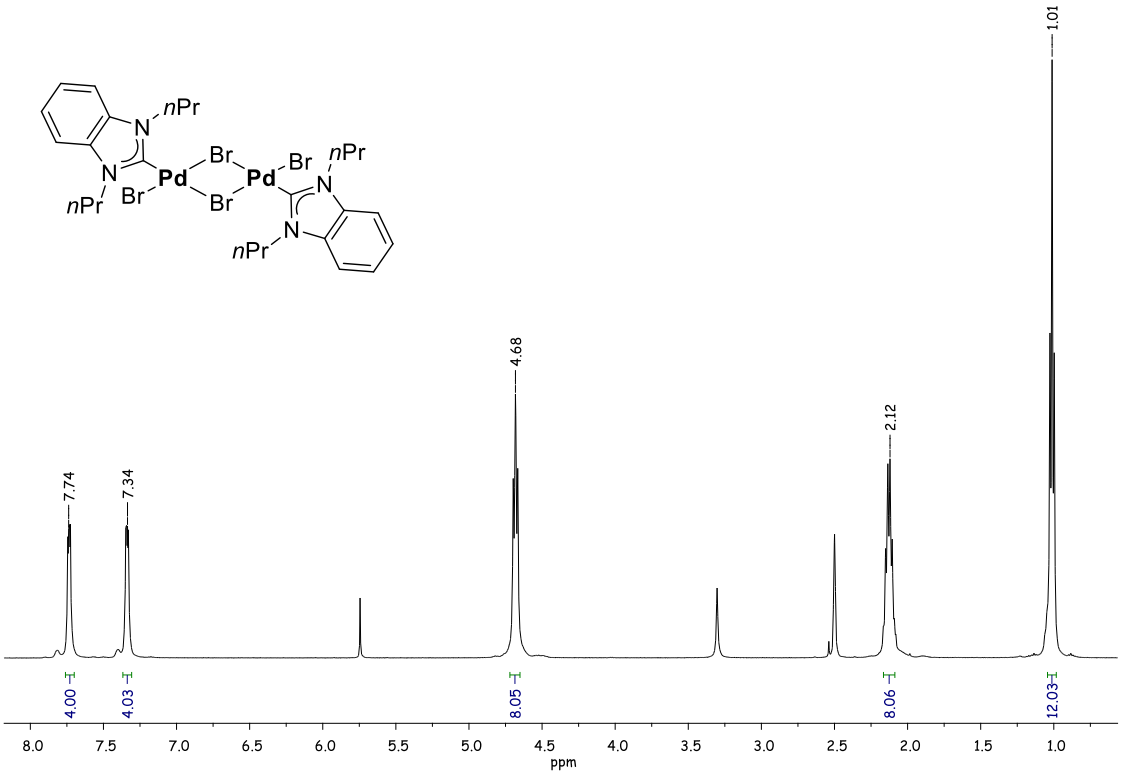


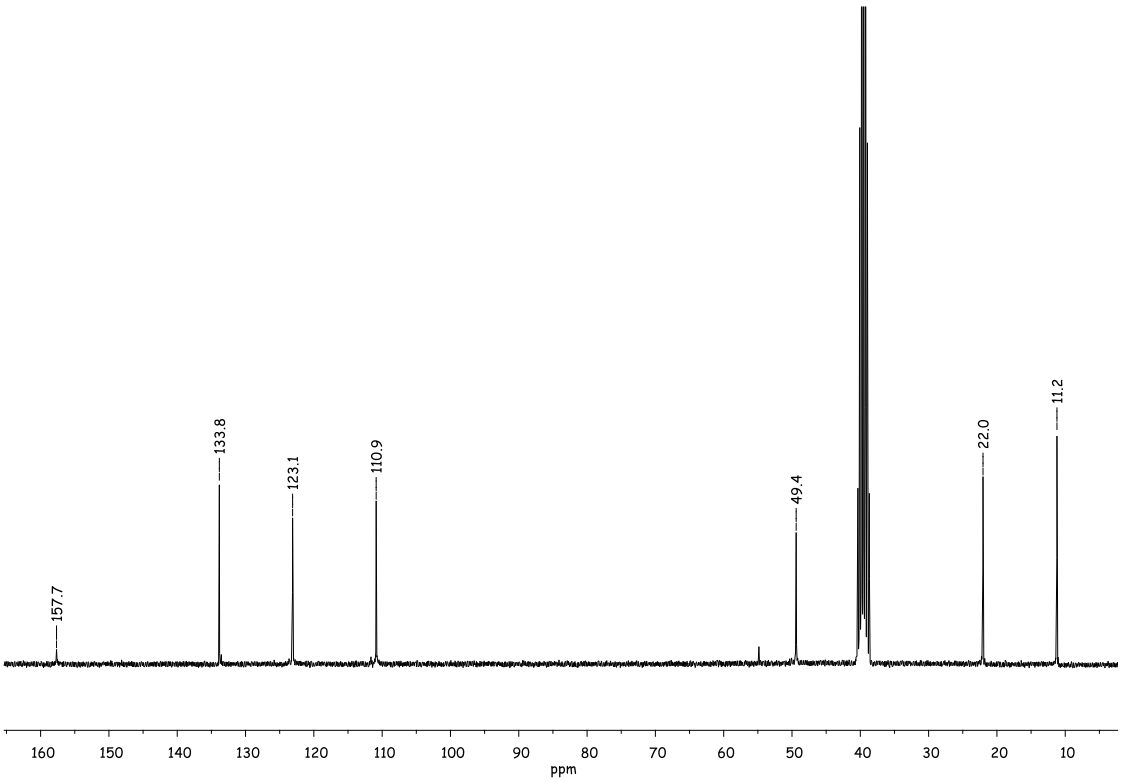
1.2. ^{1}H and ^{13}C NMR spectra of **1-Et** in dmso-d_6

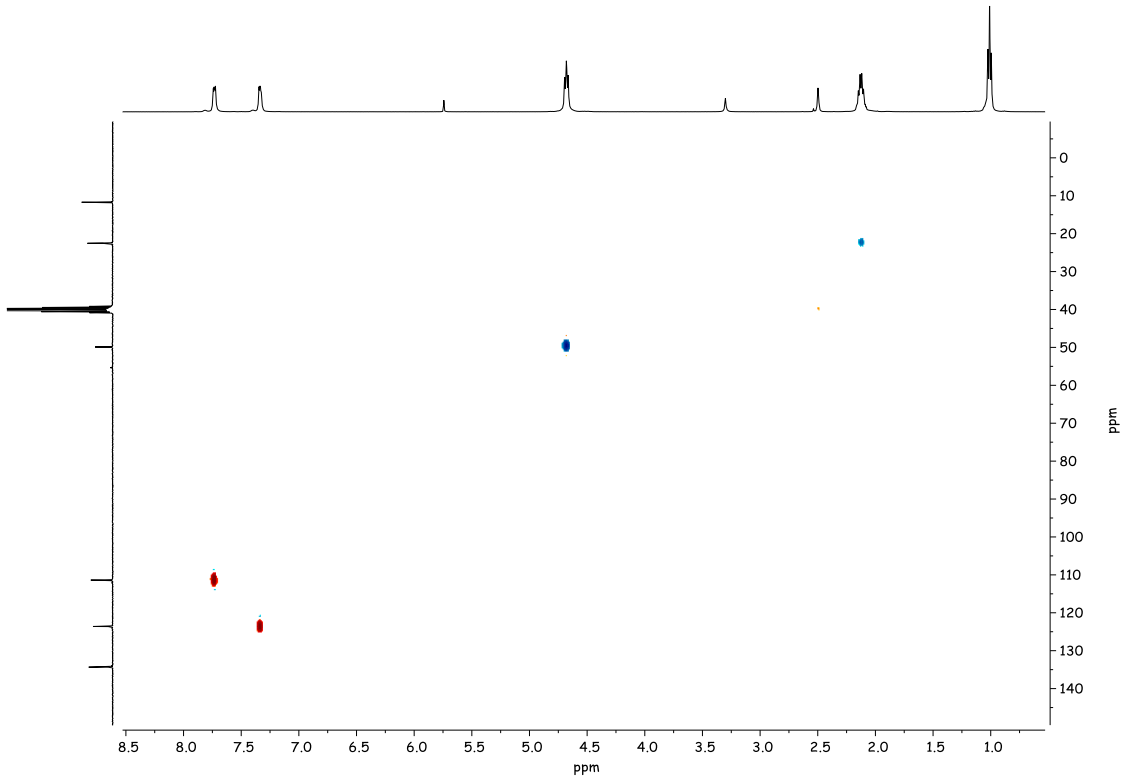




1.3. ^{1}H, ^{13}C and HSQC NMR spectra of **1-*n*Pr** in dmso-d_6



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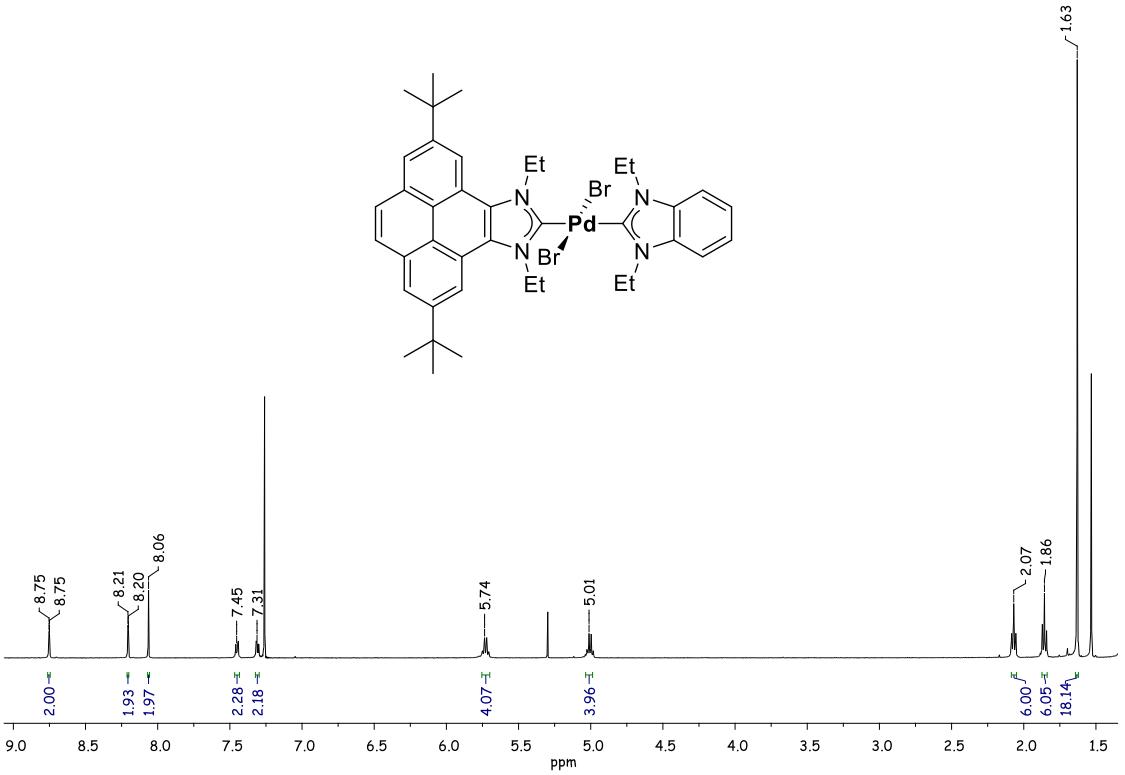
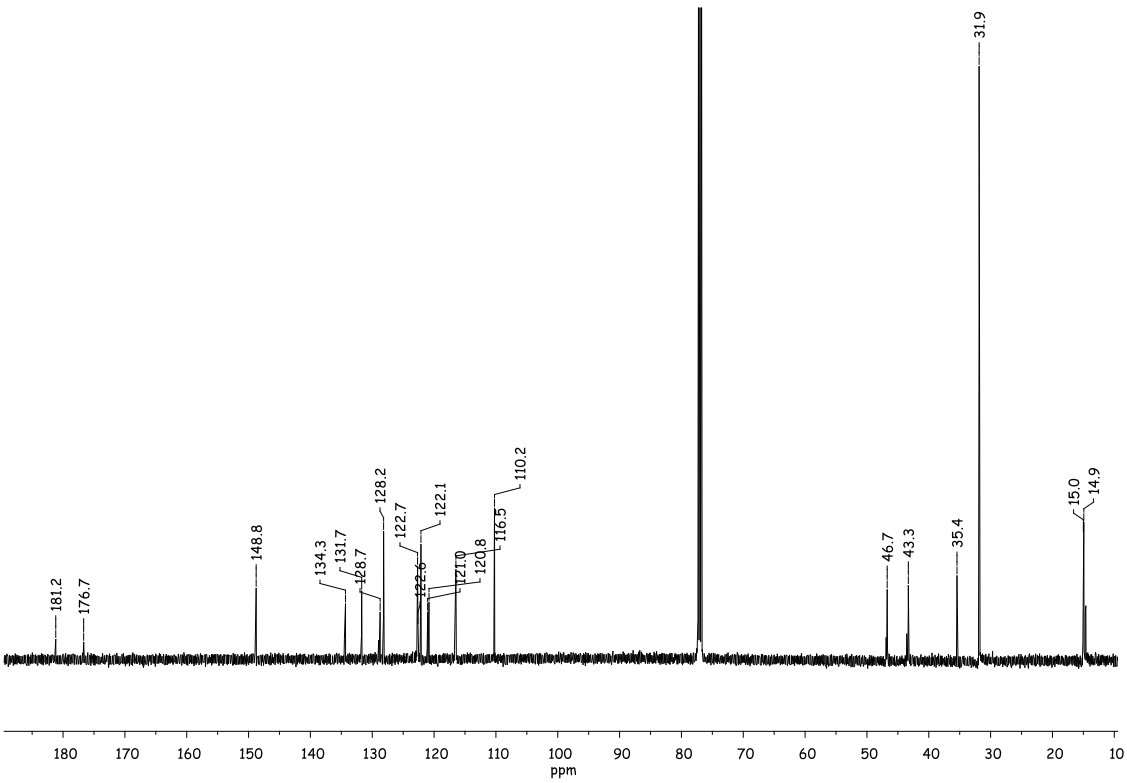
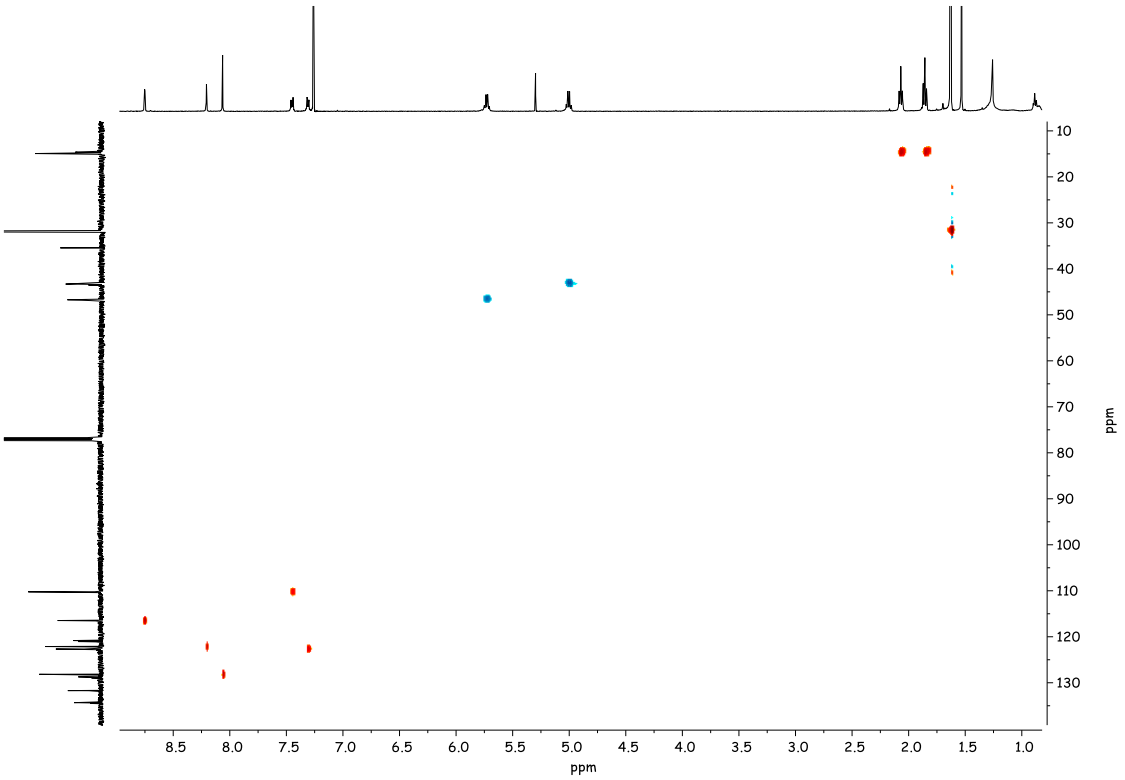
1.4. ^{1}H, ^{13}C and HSQC NMR spectra of **2-Et** in $CDCl_3$



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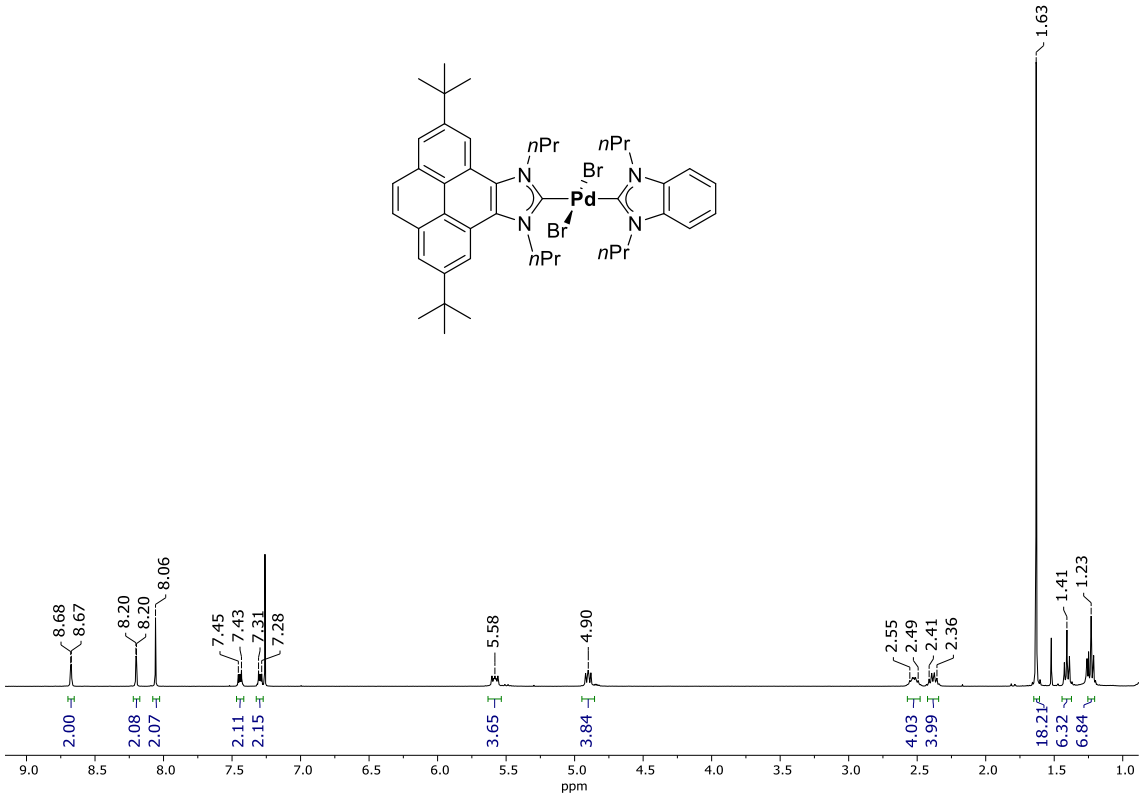
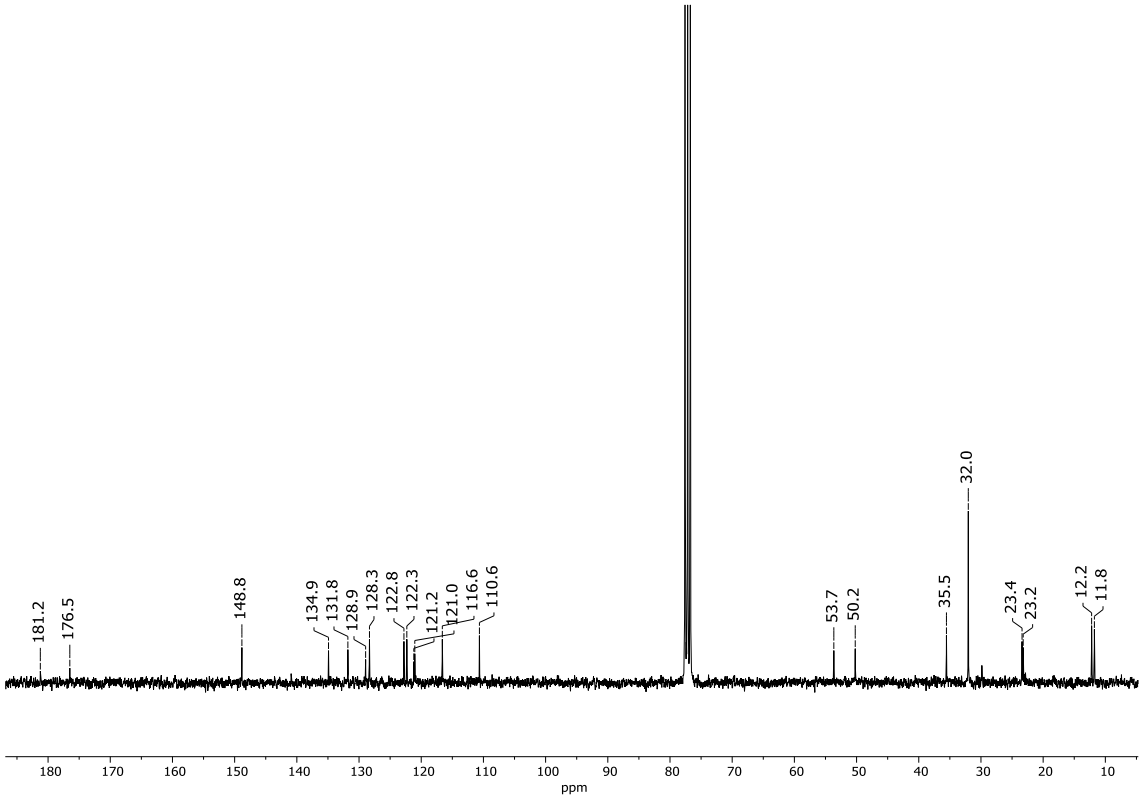
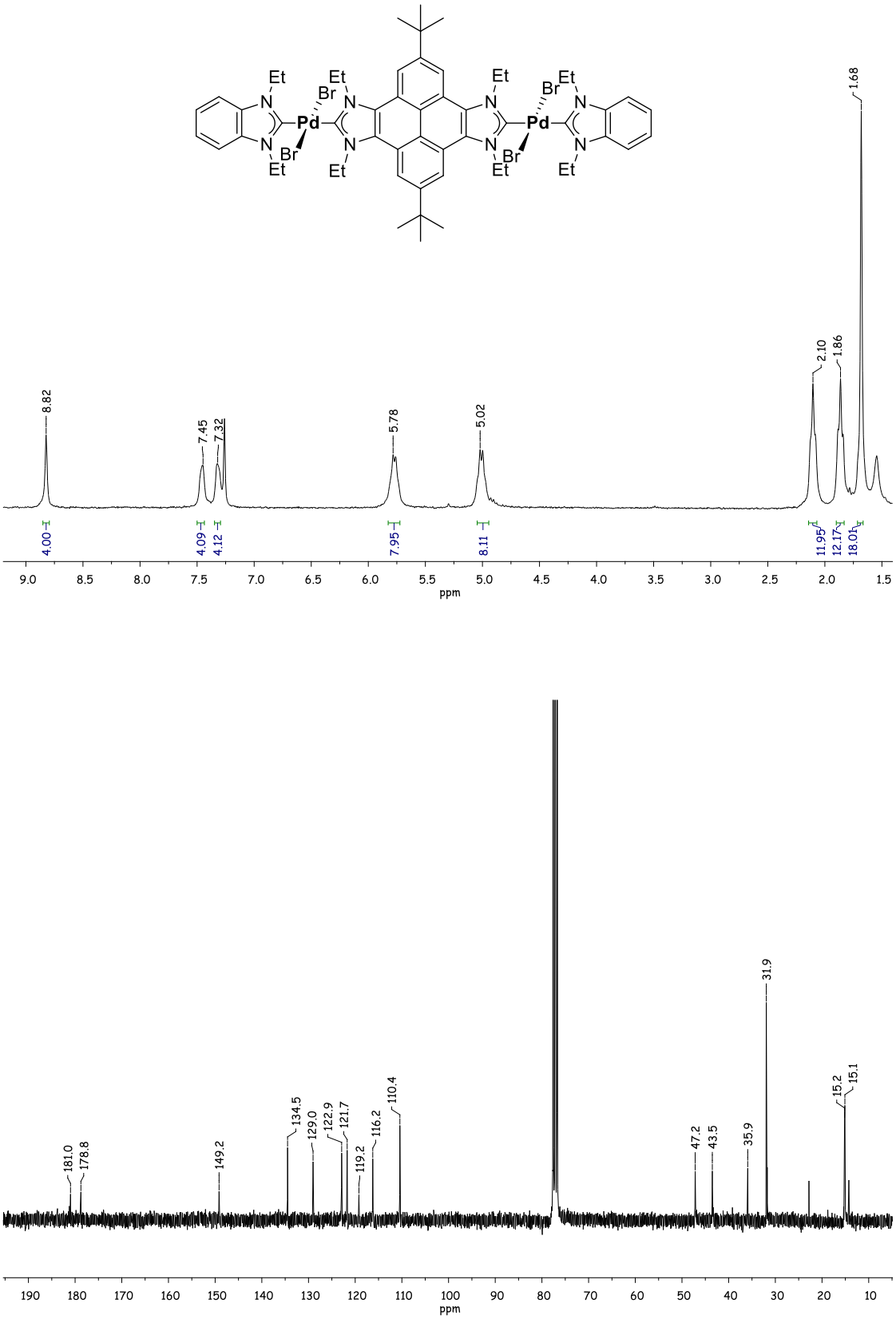
1.5. ^{1}H and ^{13}C NMR spectra of **2-*n*Pr** in $CDCl_3$

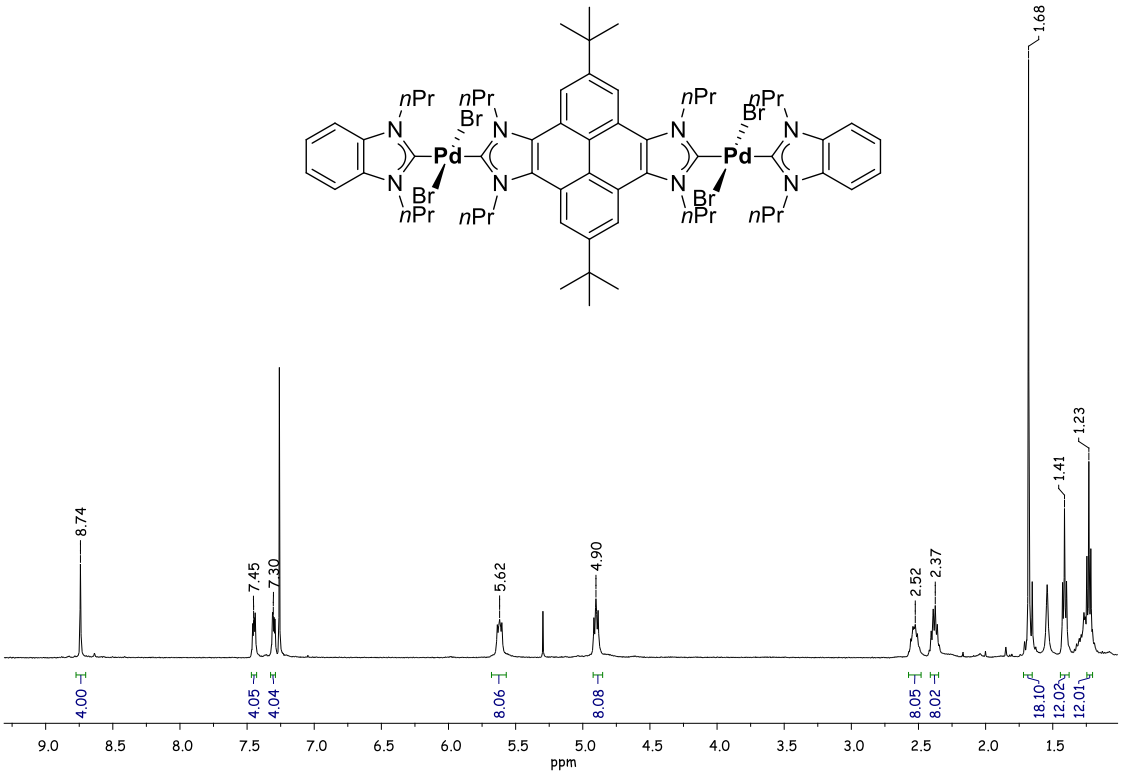


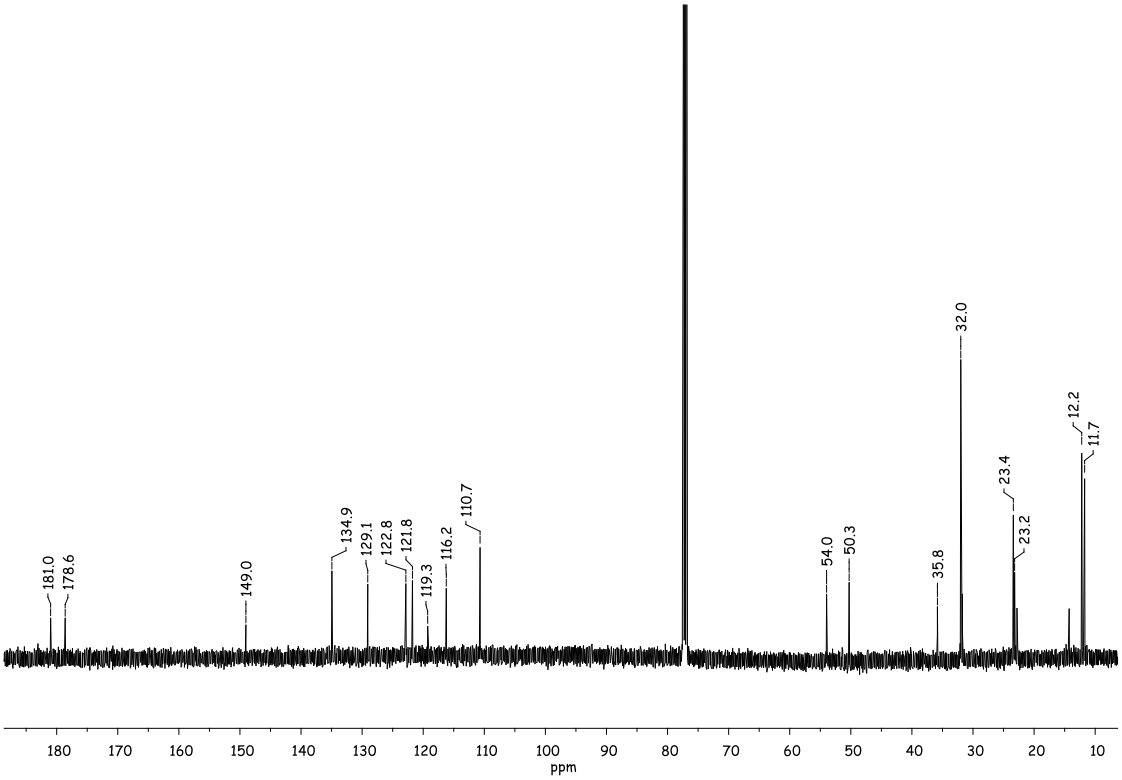


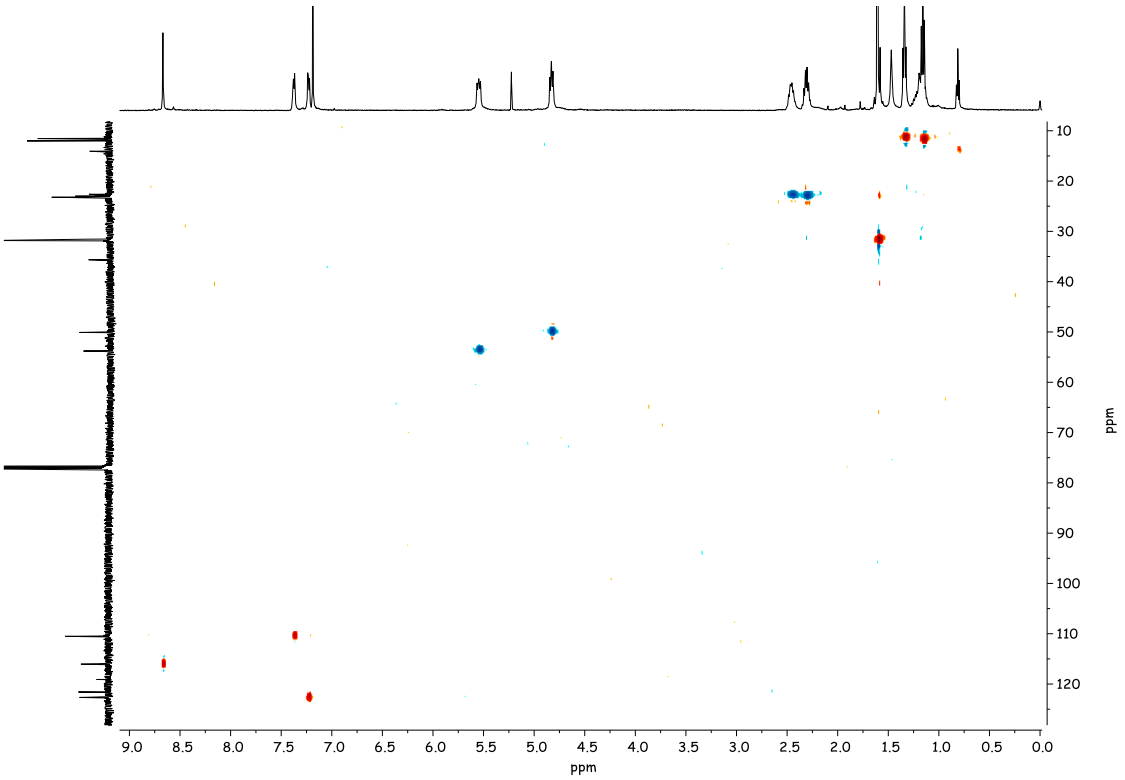
1.6 ^{1}H and ^{13}C NMR spectra of **3-Et** in $CDCl_3$



1.7 ^{1}H, ^{13}C and HSQC NMR spectra of **3-*n*Pr** in $CDCl_3$



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2. X-Ray crystallography

X-Ray Diffraction studies for complexes 1-Et and 3-Et. Crystals suitable for X-Ray studies of complexes **1-Et** and **3-Et** were obtained by slow diffusion of hexane into a concentrated solution of the complexes in chloroform. Diffraction data were collected on an Agilent SuperNova diffractometer equipped with an Atlas CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Single crystals were mounted on a MicroMount® polymer tip (MiteGen) in a random orientation. Absorption corrections based on the multi-scan (complex **1-Et**) and the Gaussian (complex **3-Et**) methods were applied. Using Olex2,[1] the structure of the two complexes was solved using ShelXS and refined with ShelXL[2] refinement package using Least Squares minimisation. Key details of the crystals and structure refinement data are summarized in Supplementary Table S1. Further crystallographic details can be found in the CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The reference number for complexes **1-Et** and **3-Et** were assigned as 1921386 and 1921387, respectively.

Table S1. Summary of crystal data, data collection, and structure refinement details

	1-Et	**3-Et**
Empirical formula	$C_{24}H_{28}Br_4Cl_3N_4Pd_2$	$C_{60}H_{74}Br_4Cl_{12}N_8Pd_2$
Formula weight	1011.32	1865.11
Temperature/K	199.95(10)	293(2)
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1/n$
a/Å	13.6598(4)	12.03665(14)
b/Å	10.8554(4)	7.05702(9)
c/Å	21.6077(7)	45.3772(5)
α/°	90	90.00
β/°	100.661(3)	92.0040(10)
γ/°	90	90.00
Volume/$Å^3$	3148.73(18)	3852.11(8)
Z	4	2
$\rho_{calc}g/cm^3$	2.1332	1.608
μ/mm^{-1}	6.495	10.348
F(000)	1922.2	1852.0
Crystal size/mm^3	0.39 × 0.269 × 0.137	0.335 × 0.087 × 0.057
Radiation	Mo Kα (λ = 0.71073)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.8 to 58.92	7.54 to 141.22

Index ranges	$-17 \leq h \leq 18$, $-15 \leq k \leq 14$, $-29 \leq l \leq 28$	$-14 \leq h \leq 14$, $-8 \leq k \leq 8$, $-52 \leq l \leq 54$
Reflections collected	33293	34923
Independent reflections	4110 [R_{int} = 0.0576, R_{sigma} = 0.0305]	7293 [R_{int} = 0.0441, R_{sigma} = 0.0245]
Data/restraints/parameters	4110/0/169	7293/0/395
Goodness-of-fit on F^2	1.032	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0459, wR_2 = 0.1166	R_1 = 0.0501, wR_2 = 0.1339
Final R indexes [all data]	R_1 = 0.0559, wR_2 = 0.1246	R_1 = 0.0584, wR_2 = 0.1424
Largest diff. peak/hole / e $Å^{-3}$	2.66/-2.87	1.35/-0.99

3. Photophysical studies

3.1 UV-visible spectra of complexes **1**, **2** and **3**

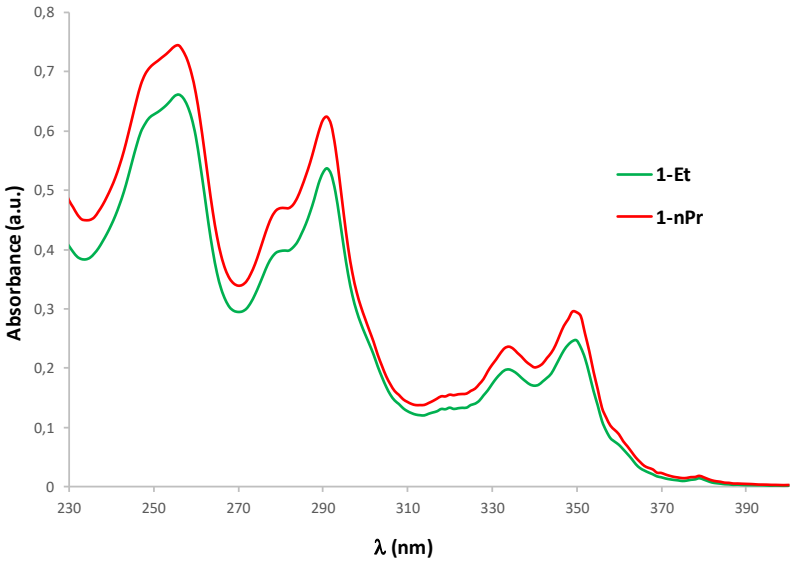

Figure S1. UV-vis spectra of complexes **1**, recorded in dichloromethane at a concentration of 10^{-5} M, under aerobic conditions

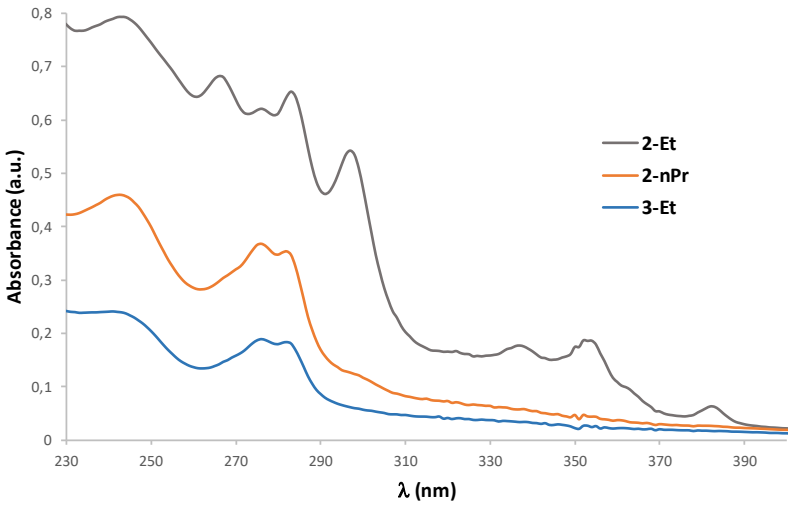

Figure S2. UV-vis spectra of complexes **2** and **3-Et**, recorded in dichloromethane at a concentration of 10^{-5} M, under aerobic conditions

3.2 Emission spectra of complexes **2** and **3-Et**

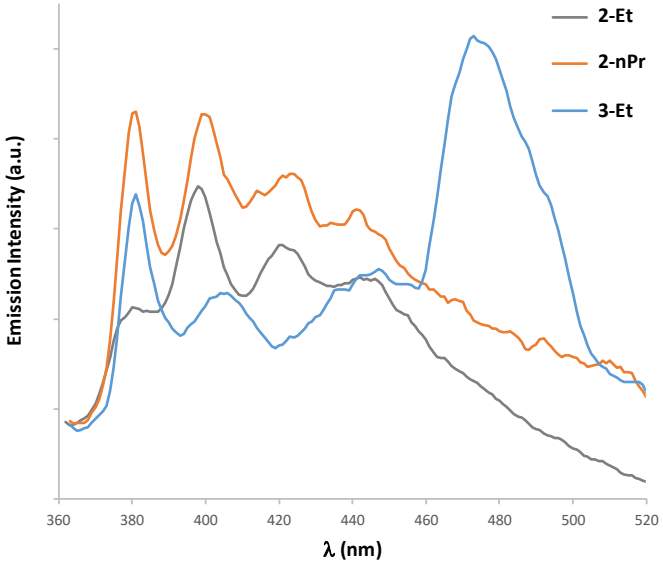

Figure S3. Emission spectra of complexes **2** and **3-Et** in dichloromethane (10^{-5} M under aerobic conditions)

4. References

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009,** *42*, 339-341.
2. Sheldrick, G. M., SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallogr. A* **2015,** *71*, 3-8.