Electronic Supplementary Material (ESI) for Dalton Transactions.

-Supporting Information-

Synthesis of Mono-, Di- and Tripalladated 1,3,5-Benzenetristyryl Complexes. CO Insertion to give a Dipalladated Indenone.

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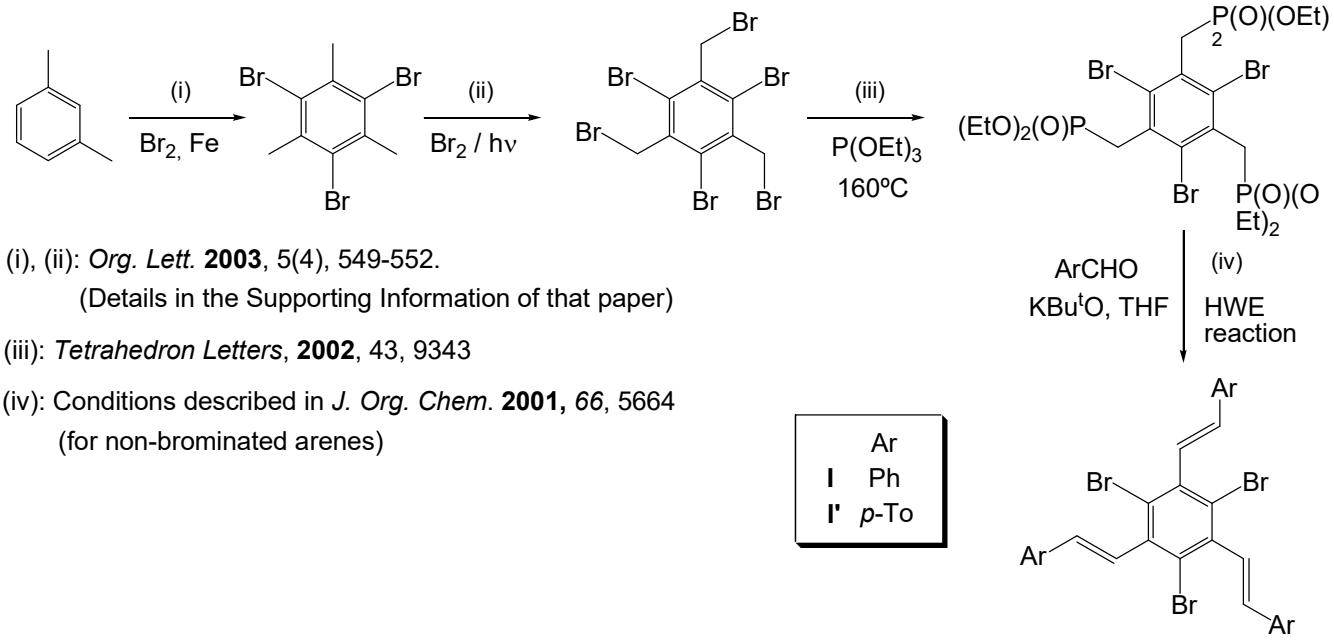
Synthetic route for the arenes *trans*-1,3,5-C_6(*E*-CH=CHAr)$_3$$Br_3$, (Ar = Ph, (I), *p*-Tol (I'))

The starting arenes, *trans*-1,3,5-C_6(*E*-CH=CHAr)$_3$$Br_3$, (Ar = Ph, (**I**), *p*-Tol (**I'**)) were synthesized according to the following procedure:



(i), (ii): *Org. Lett.* **2003**, 5(4), 549-552.
(Details in the Supporting Information of that paper)

(iii): *Tetrahedron Letters*, **2002**, 43, 9343

(iv): Conditions described in *J. Org. Chem*. **2001,** *66*, 5664
(for non-brominated arenes)

	Ar
I	Ph
I'	*p*-To

X-Ray Structure Determinations

Data were recorded at 100 K on an Oxford Diffraction Xcalibur E diffractometer using monochromated Mo Ka radiation. The standard CrysAlisPro software was used. Absorption corrections were based on multi-scans. Structures were refined anisotropically on F^2 using the program SHELX-2018. Hydrogen atoms were included using rigid methyl groups or a riding model.

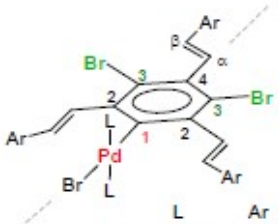
Special features: For **1a'**, a substantial region of residual electron density was tentatively identified as a mixture of chloroform and diethyl ether, but could not be refined adequately, presumably because of disorder. For this reason, a solvent mask was calculated using the platform Olex2, and 174 electrons were found in a volume of 676Å^3 in 1 void per unit cell. This is consistent with the presence of one $CHCl_3$ molecule, and half an ether molecule per asymmetric unit, which would account for 158 electrons per unit cell. However, this assignment of solvent content should be interpreted with caution.

Crystallographic data are summarized in Table S1. Additionally, complete data have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC-2195995 (**1a'**) and -2195996 (**1b**). Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

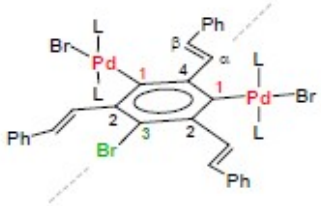
Table S.1. Crystal data and structure refinements for complexes **1a'** and **1b**

	1a'·$CHCl_3$·½$C_4H_{10}O$	**1b**
Empirical formula	$C_{72}H_{63}Br_3Cl_3O_{0.5}P_2Pd$	$C_{46}H_{43}Br_3P_2Pd$
Formula weight	1449.63	1003.87
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Orthorhombic
Space group	P(-1)	$Pna2_1$
Unit cell dimensions	a = 13.4054(5) Å, α = 72.181(5)°	a = 11.3541(3) Å
	b = 14.5302(7) Å, β = 85.818(5)°	b = 40.7113(11) Å
	c = 18.0084(7) Å, γ = 76.627(4)°	c = 8.9369(2) Å
Volume	3248.9(3) $Å^3$	4131.02(18) $Å^3$
Z	2	4
Density (calculated)	1.482 Mg/m^3	1.614 Mg/m^3
Absorption coefficient	2.345 mm^{-1}	3.460 mm^{-1}
F(000)	1460	2000
Crystal size	0.35 x 0.20 x 0.15 mm^3	0.25 x 0.15 x 0.05 mm^3
Theta range for data collection	2.181 to 26.372°	2.333 to 29.127°
Index ranges	-16<=h<=16	-15<=h<=15
	-18<=k<=18,	-55<=k<=55
	-22<=l<=22	-12<=l<=12
Reflections collected	54851	97954
Independent reflections	13267 [R(int) = 0.0414]	11034 [R(int) = 0.0472]
Completeness	99.6 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.94041	1.00000 and 0.76811
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	13267 / 0 / 679	11034 / 1 / 473
Goodness-of-fit on F^2	0.843	0.843
Final R indices [I>2sigma(I)]	R1 = 0.0268, wR2 = 0.0482	R1 = 0.0250, wR2 = 0.0320
R indices (all data)	R1 = 0.0428, wR2 = 0.0491	R1 = 0.0347, wR2 = 0.0326
Absolute structure parameter	-	0.015(2)
Largest diff. peak and hole	0.707 and -0.623 e.$Å^{-3}$	1.080 and -0.613 e.$Å^{-3}$

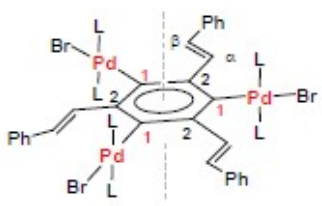
Table S.2. ^{1}H and ^{13}C NMR data for complexes **1-4** and arenes **I,I'**



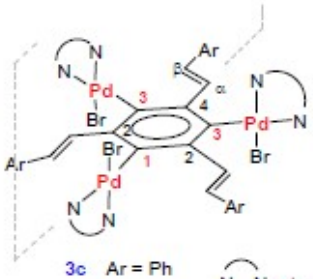
	L	Ar
1a	PPh_3	Ph
1a'	PPh_3	*p*-To
1b	PMe_2Ph	Ph



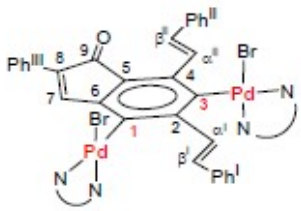
2b
L = PMe_2Ph



3d
L = PMe_3



3c Ar = Ph
3c' Ar = *p*-To
N N = tmeda



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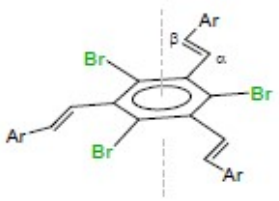
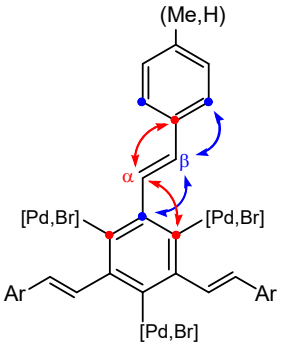


I Ar = Ph
I' Ar = *p*-To

	1a	1a'	1b	2b	3d	3c	3c'	4	I	I'
C-Pd	165.4 (m, 1C, C1)	164.9 (m, 1C, C1)	161.8 (t, $^{2}J_{PC}$ = 2, 1C, C1)	160.7 (m, 2C, C1)	162.8 (m, 3C, C1)	151.7 (1C, C1) 152.1 (2C, C3)	151.1 (1C, C1) 151.6 (2C, C3)	145.0 (C1) 152.3 (C3)		
C-alkenyl	136.1 (t, $^{5}J_{PC}$ = 1, 1C, C4) 140.4 (t, $^{3}J_{PC}$ = 3, 2C, C2)	136.2 (t, $^{5}J_{PC}$ = 1, 1C, C4) 140.4 (t, $^{3}J_{PC}$ = 3, 2C, C2)	135.6 (t, $^{5}J_{PC}$ = 1, 1C, C4) 139.8 (t, $^{3}J_{PC}$ = 2, 2C, C2)	146.0 (m, 1C, C4) 138.2 (m, 2C, C2)	143.6 (m, 3C, C2)	140.52 (1C, C4) 141.4 (2C, C2)	140.4 (1C, C4) 141.3 (2C, C2)	136.5 (C4) 151.4 (C2)	139.6	139.6
C-Br	122.3 (s, 2C, C3)	122.2 (s, 2C, C3)	123.7 (s, 2C, C3)	126.3 (s, 1C, C3)					124.1	124.0
α-CH=	130.6 (s, 1C) 6.77 (1H) 131.2 (t, $^{3}J_{PC}$ = 2, 2C) 7.24 (2H)	129.7 (s, 1C) 6.72 (1H) 130.2 (t, $^{3}J_{PC}$ = 2, 2C) 7.1 (2H)	130.2 (s, 1C) 6.87 (1H) 132.7 (t, $^{4}J_{PC}$ = 1, 2C) 7.46 (2H)	137.4 (s, 1C) 8.26 (1H) 130.5 (m, 2C) 7.81 (2H)	139.3 (m, 3C) 8.59 (3H)	138.9 (1C) 9.23 (1H) 137.7 (2C) 9.25 (2H)	138.0 (1C) 9.20 (1H) 136.6 (2C) 9.16 (2H)	137.6 (I) 9.31 (I) 127.3 (II) 8.59 (II)	128.6 7.00	127.8 6.93
β-CH=	135.1 (s, 1C) 6.47 (1H) 134.3 (s, 2C) 6.59 (2H)	134.9 (s, 1C) 6.42 (1H) 134.2 (s, 2C) 6.54 (2H)	135.5 (s, 1C) 6.54 (1H) 131.8 (t, $^{5}J_{PC}$ = 2, 2C) 8.13 (2H)	129.9 (m, 1C) 8.46 (1H) 134.0 (m, 2C) 8.12 (2H)	125.2 (m, 3C) 8.76 (3H)	125.2 (1C) 9.63 (1H) 128.3 (2C) 8.85 (2H)	124.9 (1C) 9.57 (1H) 128.1 (2C) 8.82 (2H)	130.9 (I) 8.87 (I) 133.4 (II) 9.54 (II)	136.8 6.79	136.7 6.75
i-C Ar	137.2 (s, 1C) 137.5 (s, 2C)	134.4 (s, 1C) 134.7 (s, 2C)	137.1 (1C) 137.4 (2C)	137.6 (s, 1C) 137.8 (s, 2C)	138.4 (3C)	141.2 (1C) 140.49 (2C)	135.1 (1C) 135.4 (2C)	139.2 (I) 138.8 (II))	136.5	133.8
o-CH Ar	126.7 (s, 2C) 7.53 (2H) 127.0 (s, 4C) 7.19 (4H)	126.6 (s, 2C) 127.0 (s, 4C)	126.7 (s, 2C) 7.55 (2H) 126.8 (s, 4C) 7.4 (4H)	126.74 (s, 2C) 126.70 (s, 4C)	126.3 (6C)	126.12 (2C) 126.08 (4C)	126.0 (6C)	127.2 (I) 126.8 (II)	127.0	126.9
m-CH Ar	128.9 (2C) 128.8 (4C)	129.5 (2C) 129.4 (4C)	128.9 (s, 2C) 129.1 (s, 4C)	128.5 (s, 2C) 129.0 (s, 4C)	129.4 (6C)	128.7 (2C) 128.8 (4C)	129.45 (2C) 129.51 (4C)	128.9 (I) 128.6 (II)	129.0	129.6
p-CH Ar *p*-C (To)	128.0 (1C) 127.9 (2C)	137.9 (1C) 137.7 (2C)	128.1 (s, 1C) 128.02 (s, 2C)	127.0 (s, 1C) 127.6 (s, 2C)	127.2 (3C)	125.6 (1C) 125.9 (2C)	138.4 (1C) 137.7 (2C)	126.8 (I) 127.1 (II)	128.6	138.5
Me (To, L)		21.5 (1C) 21.6 (2C)	14.0 (4C) (vt, $^{1}J_{PC}$ + $^{3}J_{PC}$ = 31)	15.8 and 13.3 (4C) (vt, $^{1}J_{PC}$ + $^{3}J_{PC}$ = 30)	15.7 (18C) (vt, $^{1}J_{PC}$ + $^{3}J_{PC}$ = 30)		21.36 (1C) 21.40 (2C)			21.5
o-CH (L)	130.7 (12C) (very broad)	130.3 (12C) (very broad)	130.5 (4C) (vt, $^{2}J_{PC}$ + $^{4}J_{PC}$ = 10)	131.7 (8C) (vt, $^{2}J_{PC}$ + $^{4}J_{PC}$ = 12)	Me tmeda	51.7 (4C) 51.0, 49.2 (2C) 48.55, 48.50 (2C)	51.7, 48.5 (4C) 51.0, 49.1 (2C)			
m-CH (L)	128.0 (12C) (very broad)	127.9 (12C) (very broad)	127.99 (4C) (vt, $^{3}J_{PC}$ + $^{5}J_{PC}$ = 9)	128.4 (8C) (vt, $^{3}J_{PC}$ + $^{5}J_{PC}$ = 10)						
p-CH (L)	not visible	not visible	129.6 (s, 2C)	129.9 (s, 4C)	CH_2 tmeda	63.2, 58.26 (1C) 63.0, 58.32 (2C)	63.1, 58.20 (1C) 63.0, 58.25 (2C)			
i-C (L)	130.9 (6C) (vt, $^{1}J_{PC}$ + $^{3}J_{PC}$ = 46)	131.0 (6C) (vt, $^{1}J_{PC}$ + $^{3}J_{PC}$ = 46)	133.8 (2C) (vt, $^{1}J_{PC}$ + $^{3}J_{PC}$ = 45)	134.7 (4C) (vt, $^{1}J_{PC}$ + $^{3}J_{PC}$ = 44)						

Comments on the NMR data for the arenes I, I' and the complexes 1-4



Alkenyl groups: The alkenyl α and β resonances were assigned with the help of $^{1}H,^{13}C$-HMBC spectra, where there are clear $^{3}J_{CH}$ couplings between the alkenyl α-CH groups and the C-Pd (or C-Br) and aryl *i*-C; and also between the alkenyl β-CH groups and the C2,C4 carbons and aryl *o*-CH groups (in the Figure, the H's have been omitted for clarity).

In the starting arenes, **I** and **I'**, the alkenyl β-^{13}C resonance is higher (ca. 137 ppm) than the α-^{13}C resonance (ca. 128 ppm), similarly to the mononuclear complexes **1a, a'**, while in the trinuclear complexes **3c, 3c'**, **3d**, the resonances are "reversed", the α-^{13}C resonance being higher (ca. 137-139 pm) than the β-^{13}C resonance (ca. 125-128 ppm). In the dinuclear complex **2b**, the alkenyl group located between two [PdBrL_2] moieties also shows the "reversed" resonances, while the two alkenyl groups *ortho* to only one Pd atom show similar resonances to those in **1a**, **1a'**. These oscillations are difficult to explain, as a simplistic interpretation of ^{13}C chemical shifts in terms of the electron density should be avoided.[I] For the ^{1}H resonances, in **I** and **I'** the CH=CH protons resonate at around 7 ppm for the α-H's and 6.8 ppm for the β-H's. In the trinuclear Pd complexes **3c, 3c', 3d**, these ^{1}H's resonate at much higher frequencies, around 9 ppm, and their relative values (α > β or vice versa) varies for the different alkenyl groups as a consequence of the different electronic and isotropic effects of the adjacent groups.

Tmeda ligands: in the two equivalent [PdBr(tmeda)] groups in **3c**, **3c'**, the four Me's are not equivalent, (there should be four Me resonances, each corresponding to two C atoms: 2C:2C:2C:2C pattern). In the third [PdBr(tmeda)] group, the two methyls on each N are equivalent and should give two resonances with a 2C:2C pattern). But some of the resonances are coincident, and thus in the ^{13}C{^{1}H}-NMR spectrum of **3c** only five methyl resonances are observed (one of them corresponding to four C atoms) while for **3c'** only four methyl resonances are observed (two of them corresponding to four C atoms). For the CH_2 groups, there should be (and there are indeed) four resonances, with a 2C:2C:1C:1C pattern.

Fluxionality in the phosphino complexes: In the complexes **1a** and **1a'**, the ^{13}C resonances of the *o*- and *m*-CH groups of the PPh_3 are very broad, and the *p*-CH group is not even observed (the *i*-C's, however, appear as a sharp triplet). In the ^{1}H-NMR spectra of these complexes, a wide and ill-resolved multiplet is observed in the aromatic region, together with other, resolved, resonances. It seems that there is no free rotation within the bulky PPh_3 ligands, as a consequence of the steric hindrance of the neighboring CH=CHAr groups. For the less bulky PMe_2Ph ligands in **1b** and **2b** no such broadening is observed.

[I] Martínez-Viviente, E.; Pregosin, P. S.; Tschoerner, M. ^{13}C-NMR of Pd-Aryl Complexes. Chemical Shifts and Pd-π-Back Bonding. *Magn. Reson. Chem.* **2000**, *38*, 23-28.

^{1}H and APT NMR spectra for the arenes I, I' and the complexes 1-4. Individual reaction schemes.

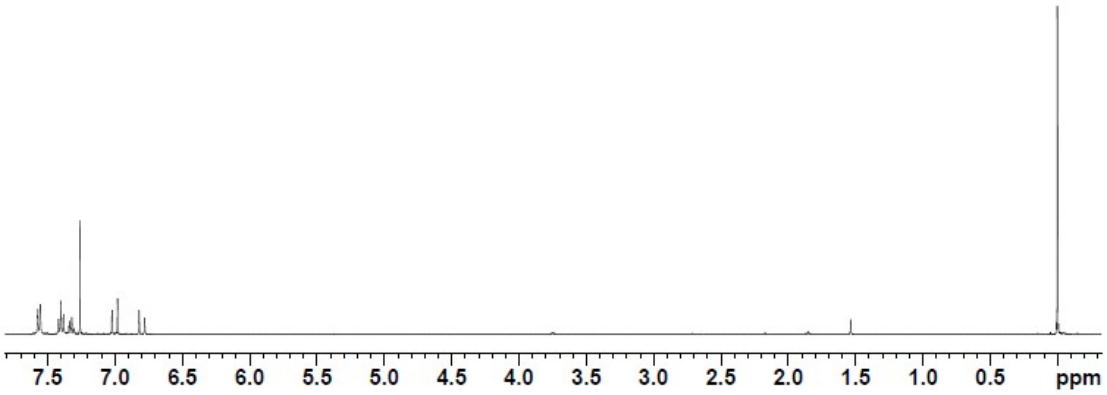


Figure S1. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **I**

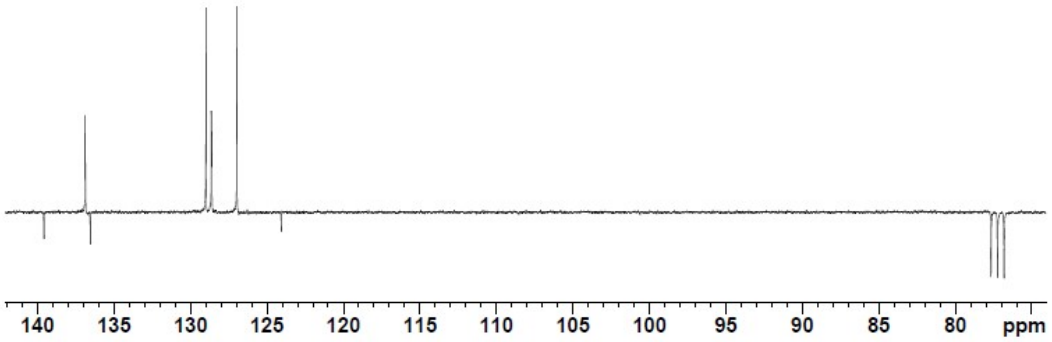


Figure S2. APT spectrum (75.5 MHz, $CDCl_3$) of compound **I**

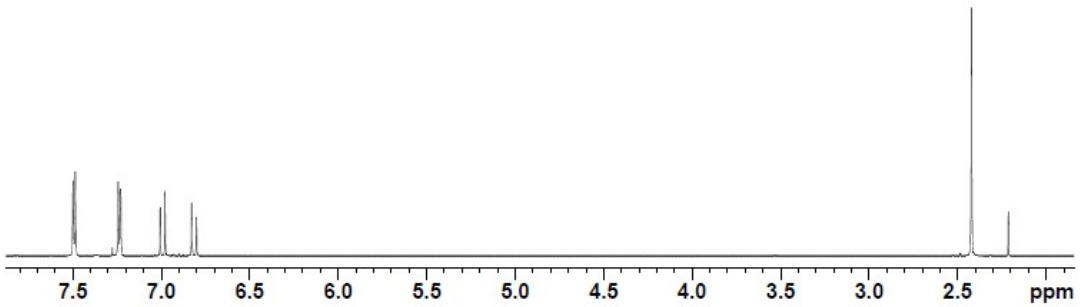


Figure S3. ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of compound **I'**

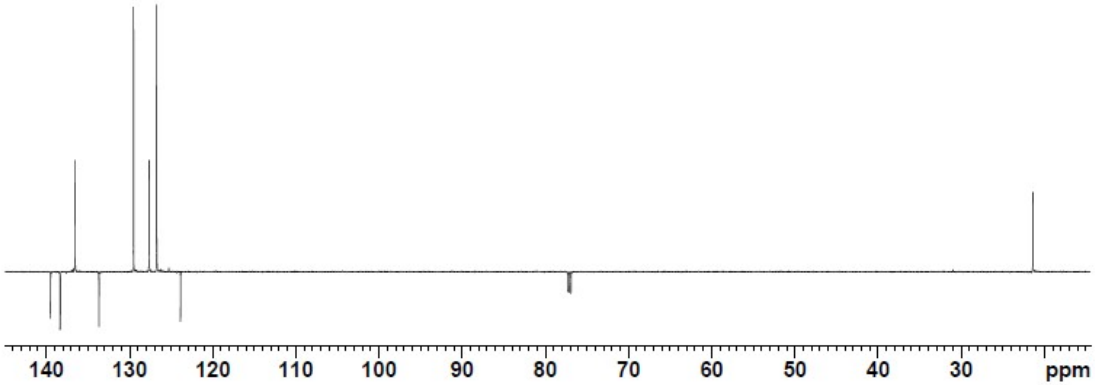
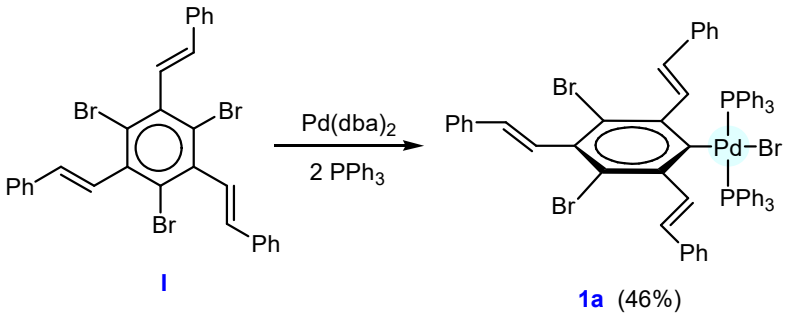


Figure S4. APT spectrum (150.9 MHz, $CDCl_3$) of compound **I'**



I **1a** (46%)

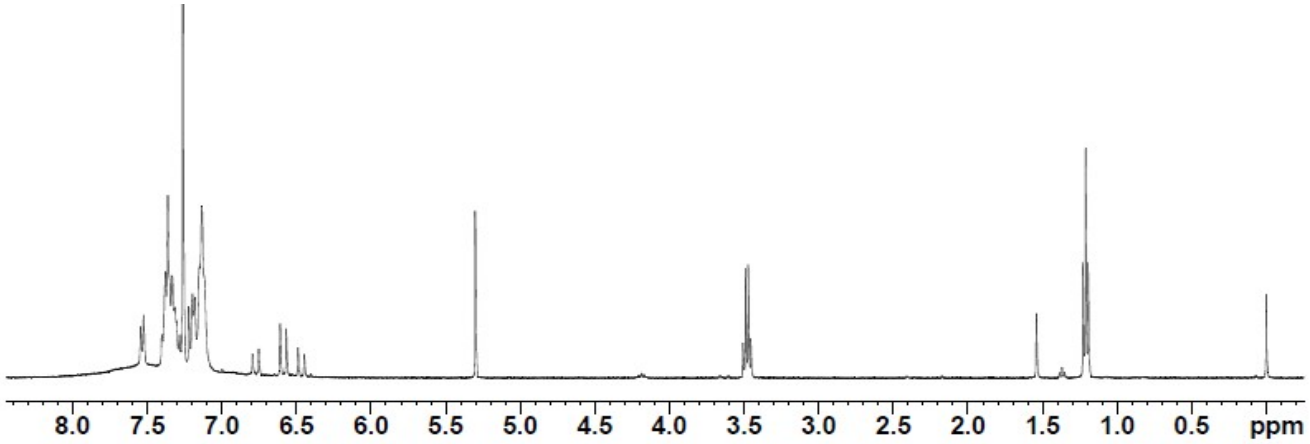


Figure S5. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **1a**

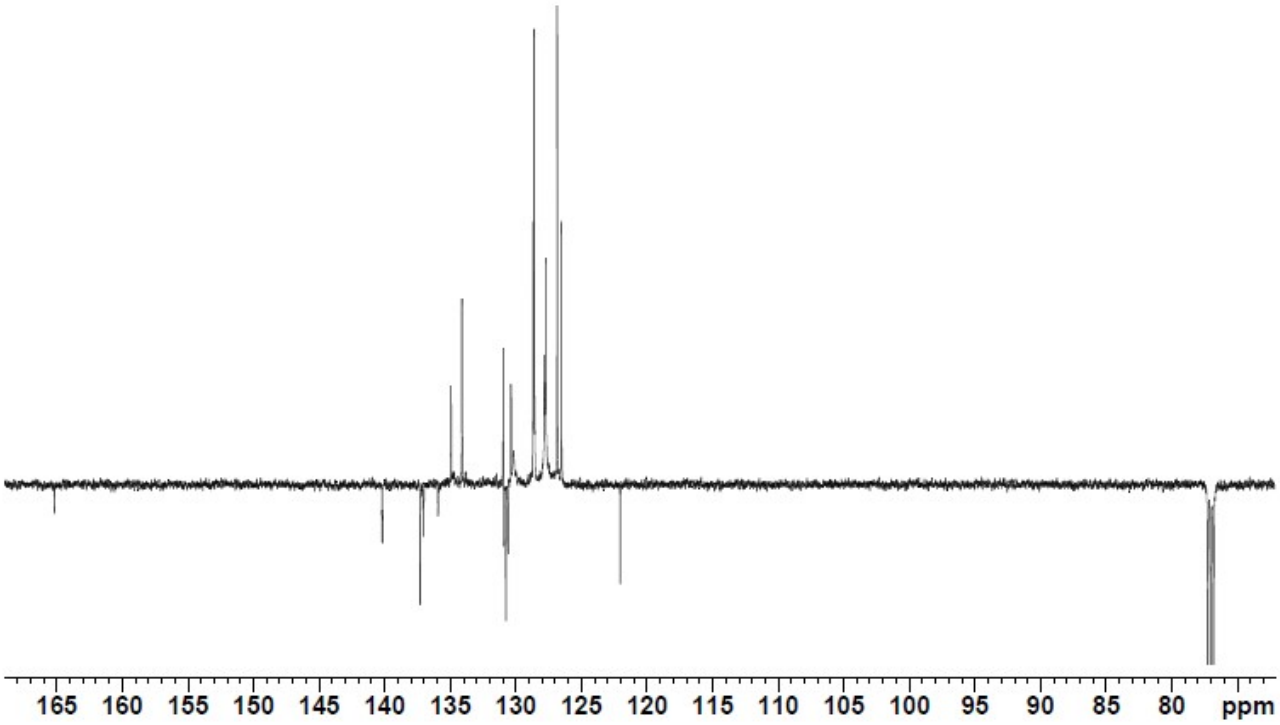
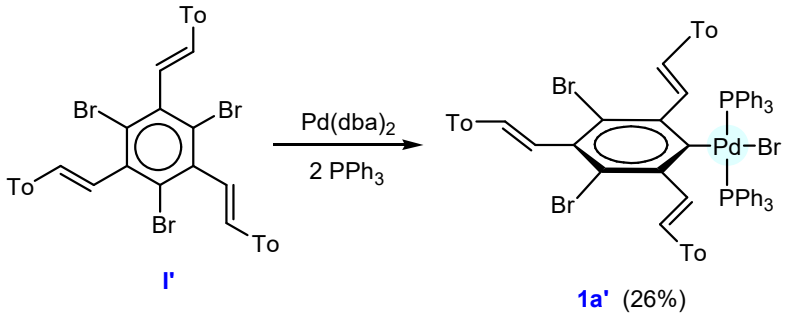


Figure S6. APT spectrum (150.9 MHz, $CDCl_3$) of compound **1a**



I' **1a'** (26%)

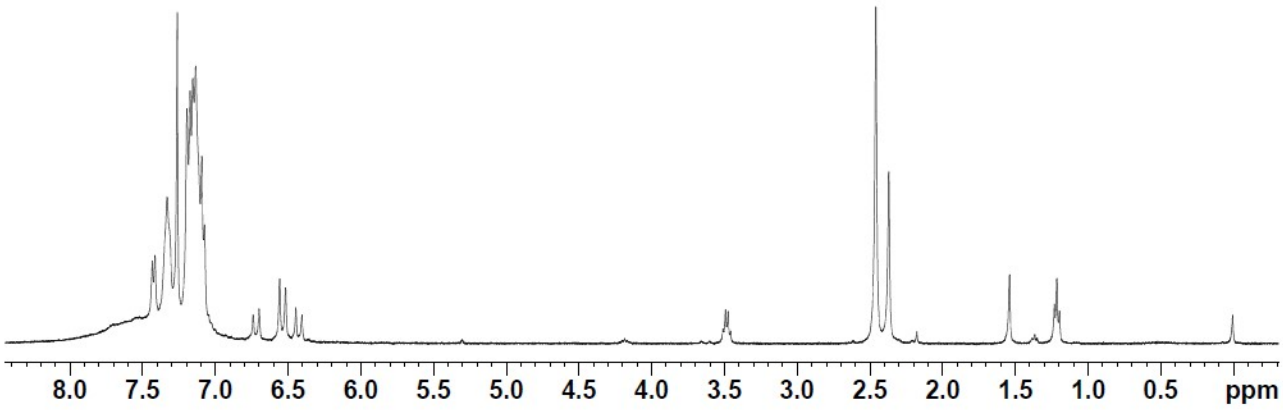


Figure S7. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **1a'**

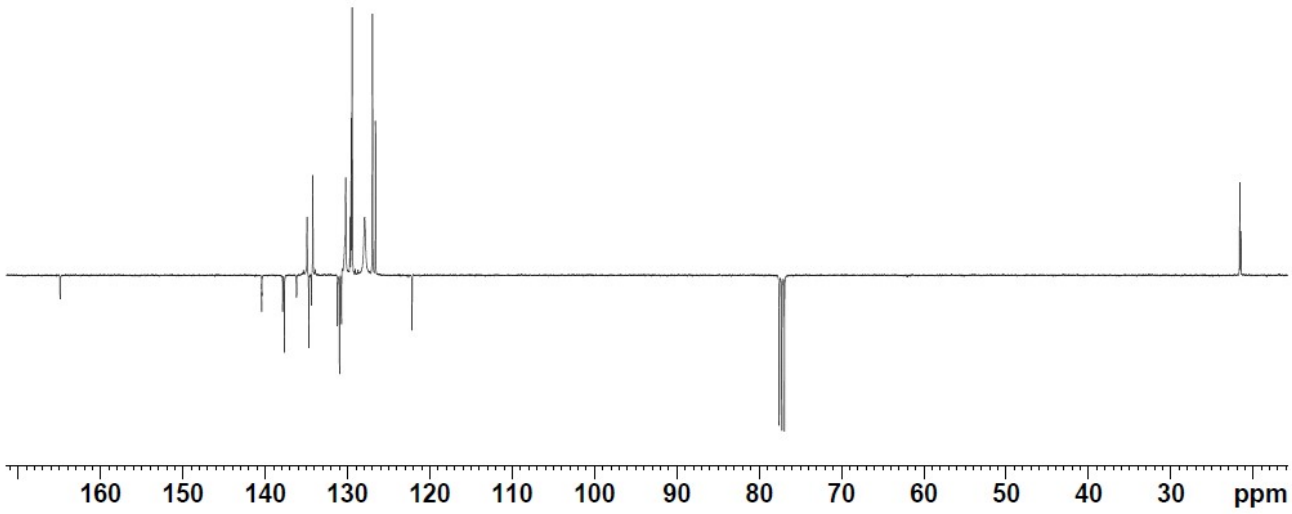
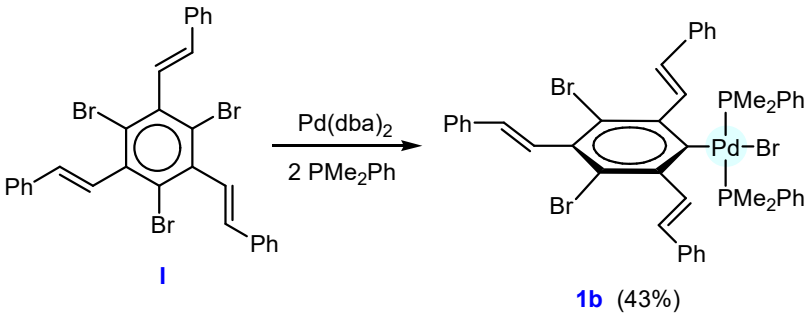


Figure S8. APT spectrum (100.8 MHz, $CDCl_3$) of compound **1a'**



I

1b (43%)

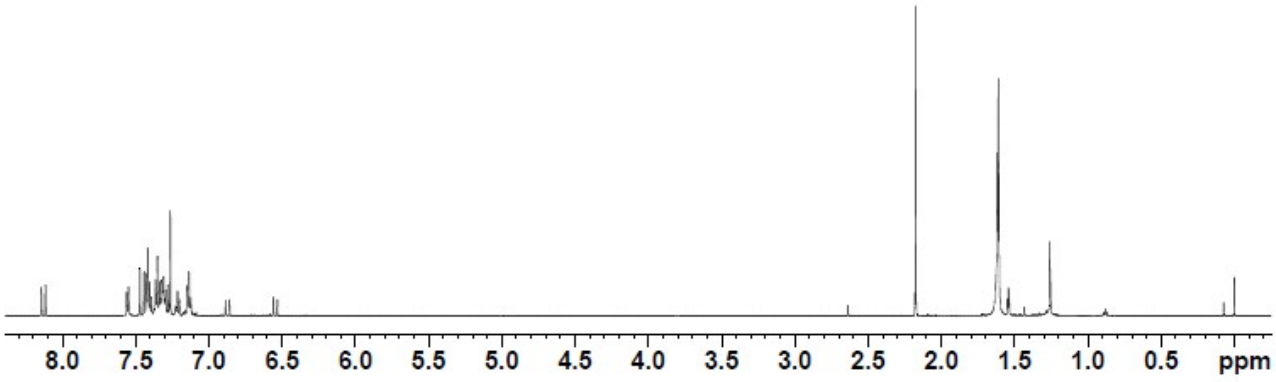


Figure S9. ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of compound **1b**

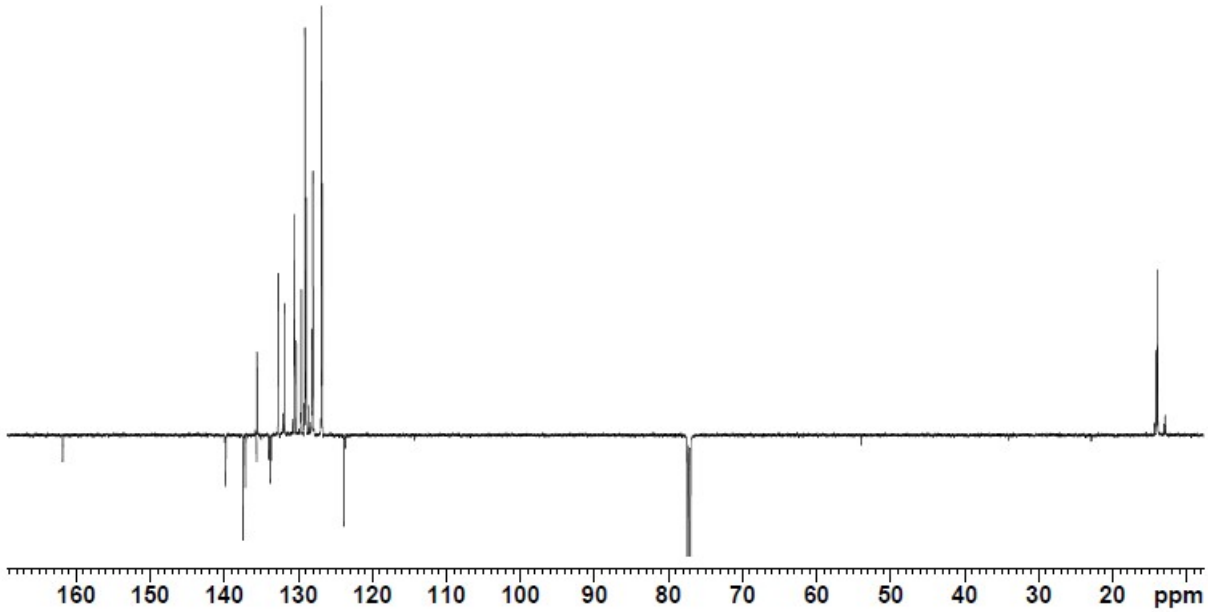
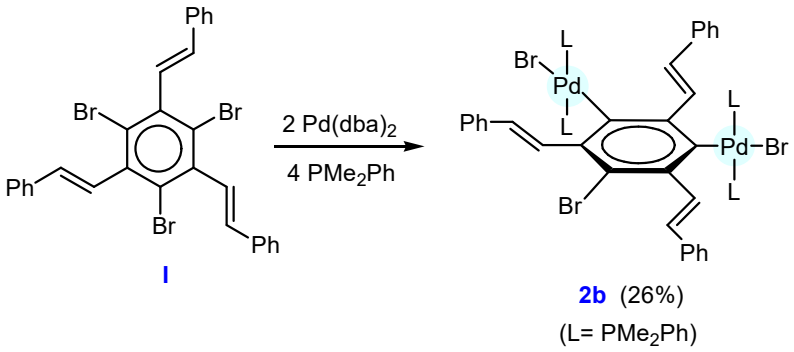


Figure S10. APT spectrum (150.9 MHz, $CDCl_3$) of compound **1b**



I

2b (26%)

(L= PMe_2Ph)

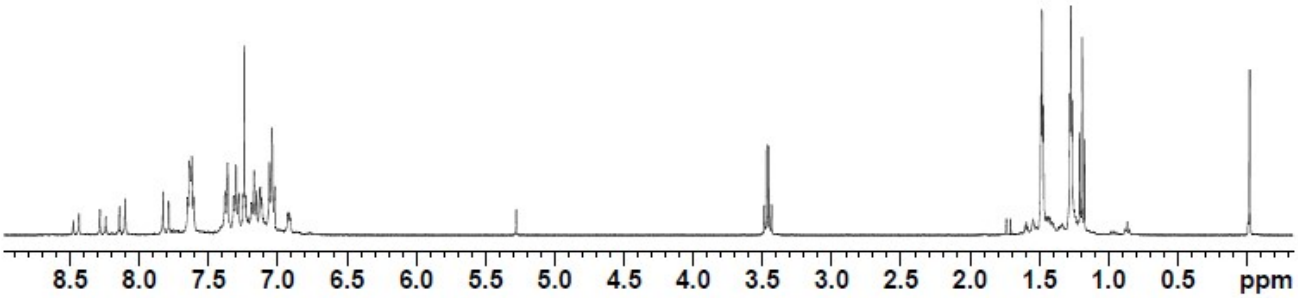


Figure S11. ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **2b**

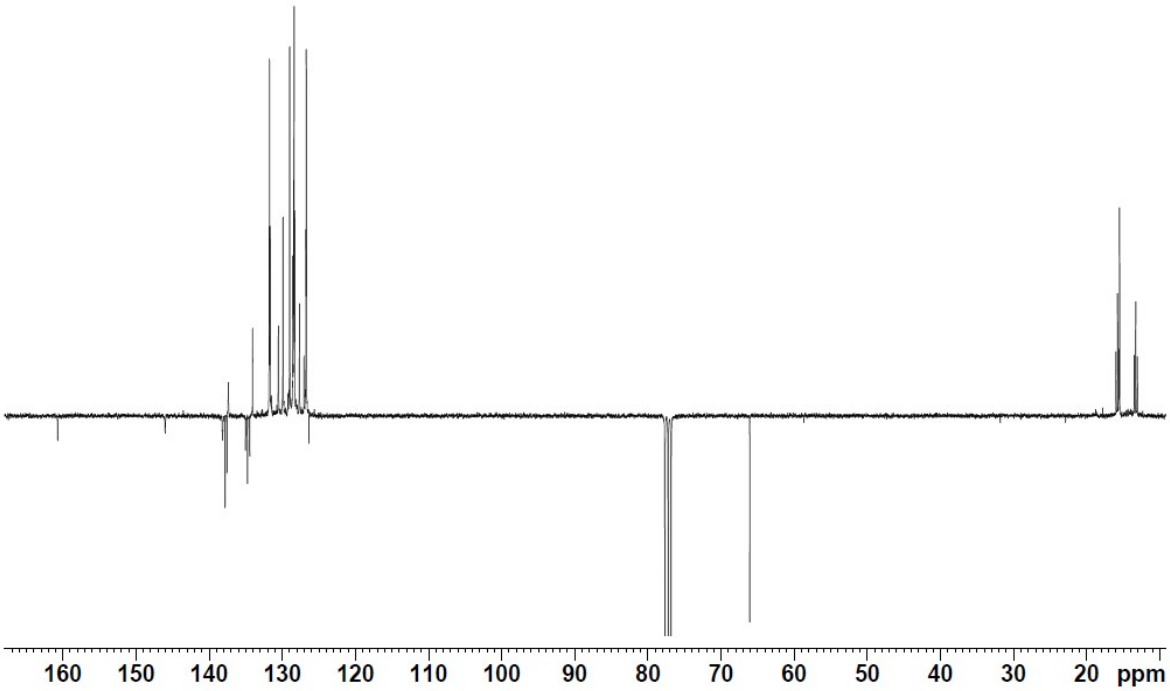
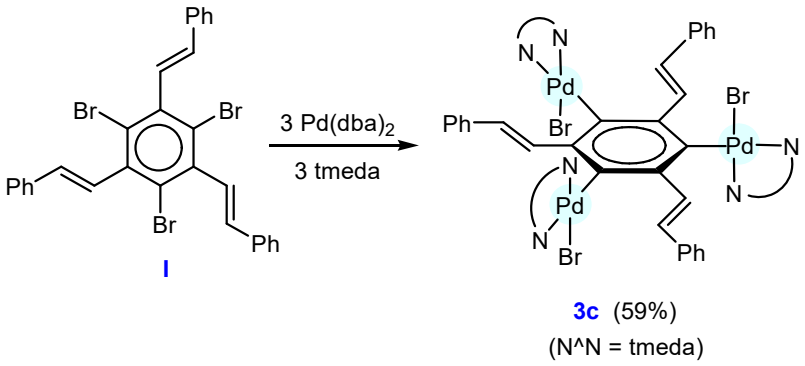


Figure S12. APT spectrum (75.5 MHz, $CDCl_3$) of compound **2b**



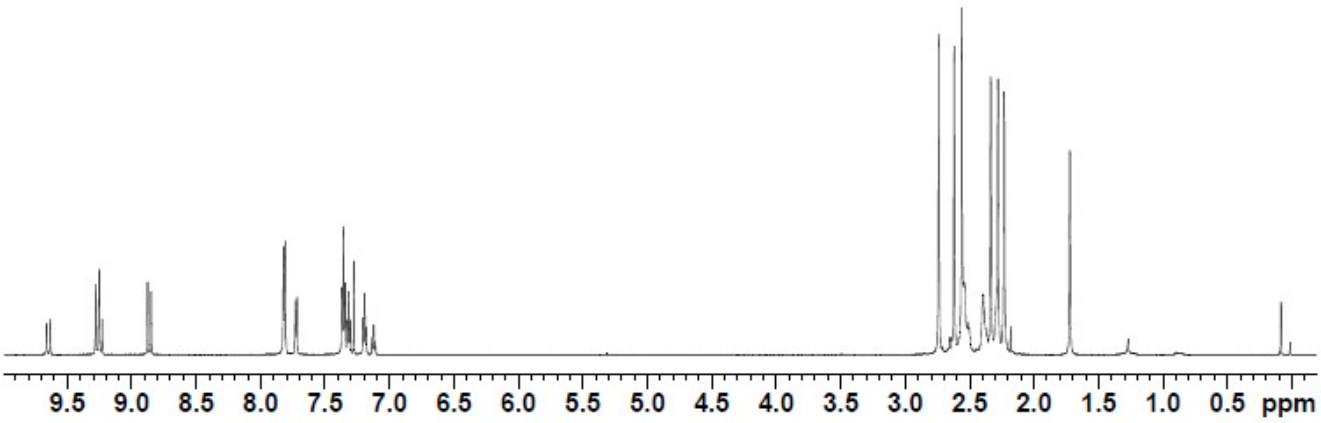


Figure S13. ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of compound **3c**

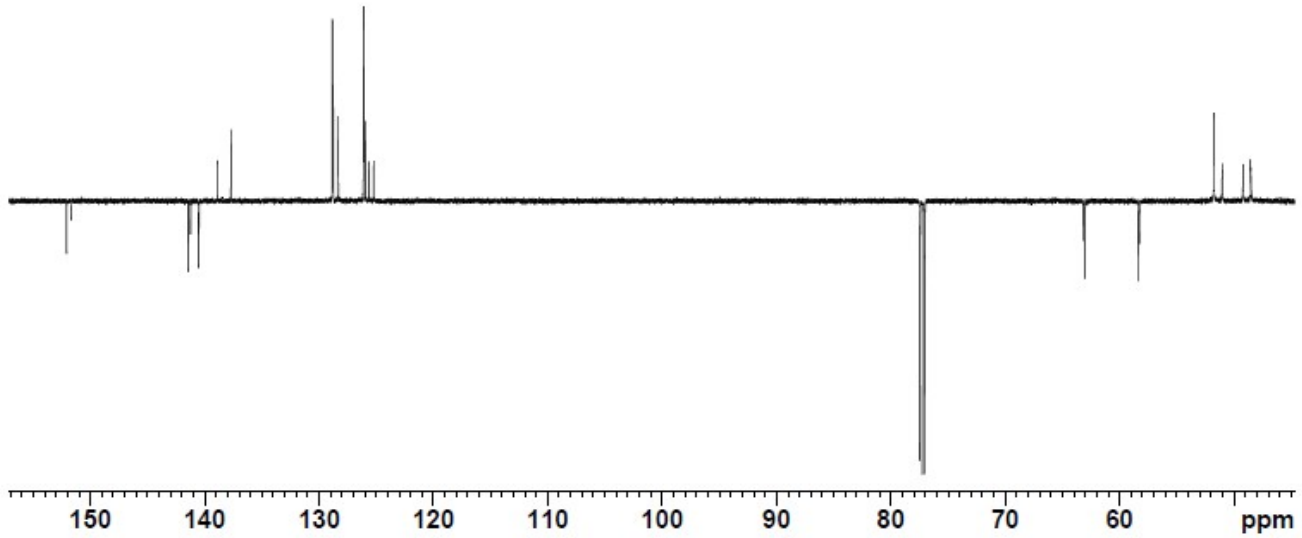
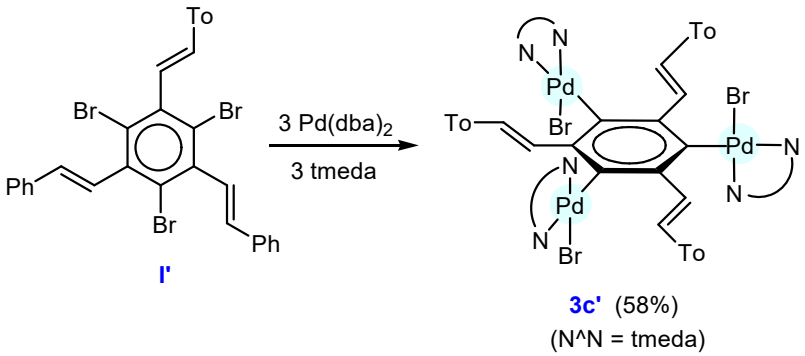


Figure S14. APT spectrum (150.9 MHz, $CDCl_3$) of compound **3c**



I'

3c' (58%)
(N^N = tmeda)

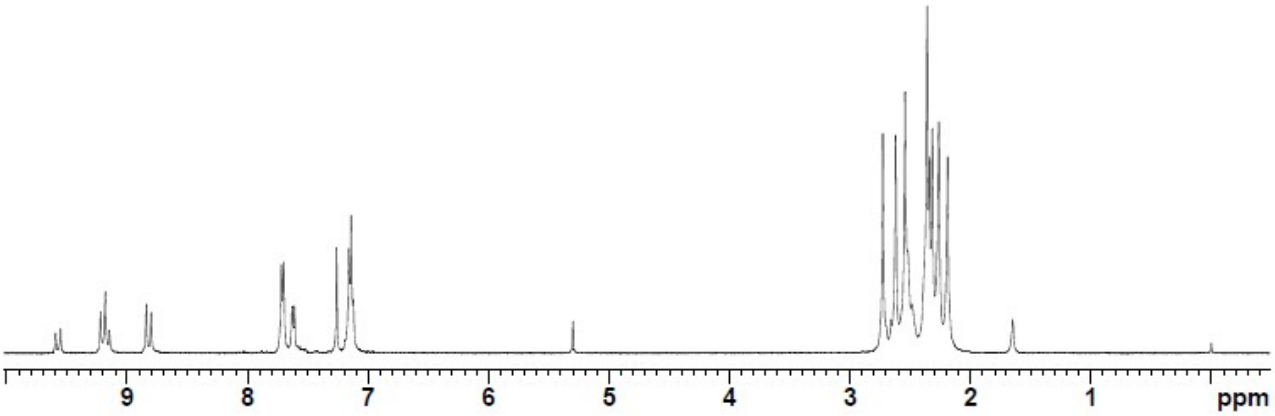


Figure S15 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **3c'**

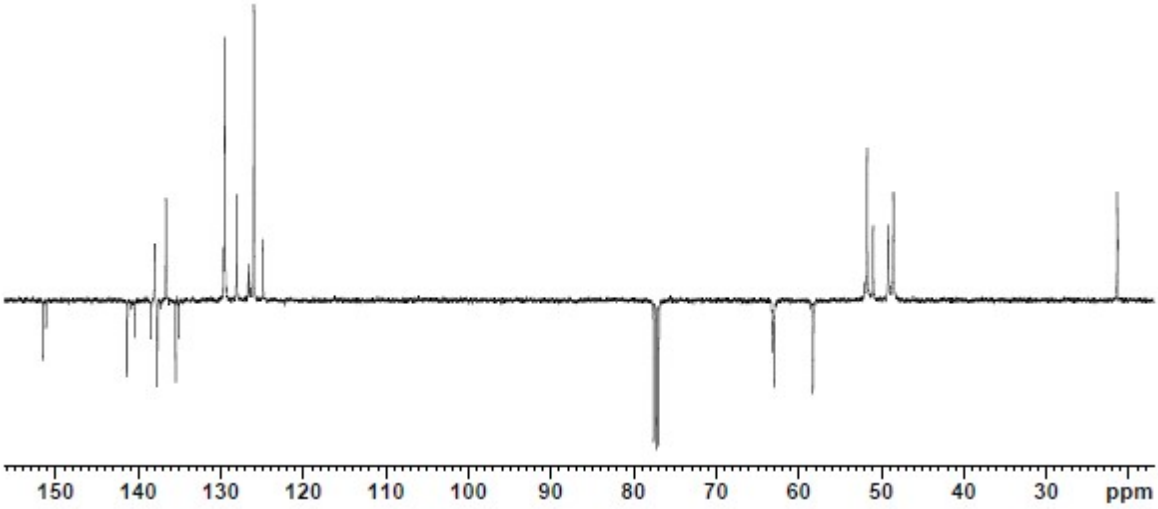
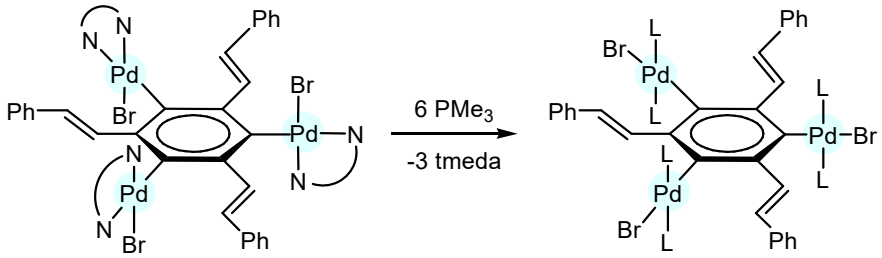


Figure S16. APT spectrum (100.8 MHz, $CDCl_3$) of compound **3c'**



3c'
(N^N = tmeda)

3d
(L = PMe_3)

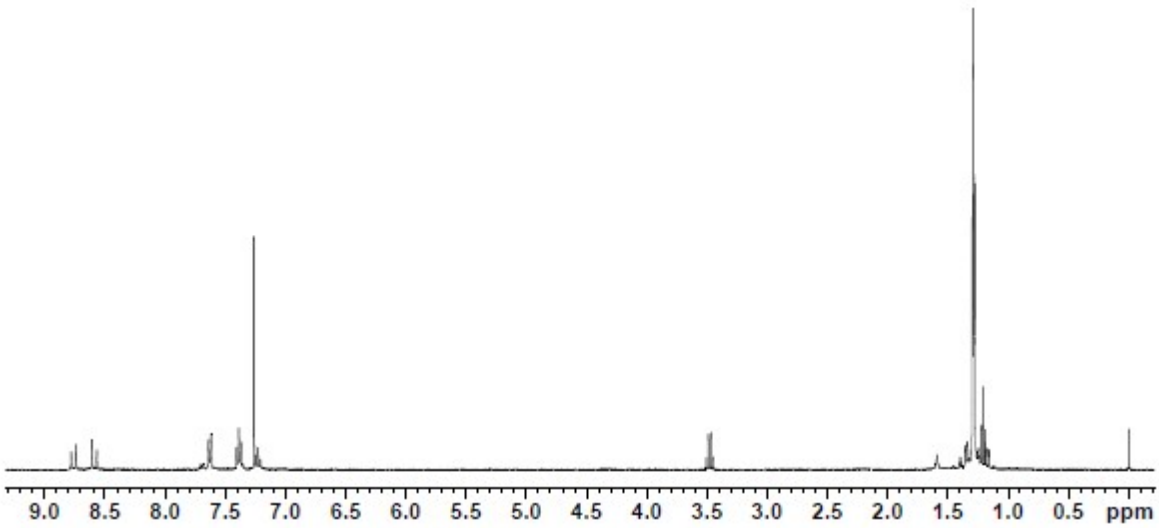


Figure S17 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of compound **3d**

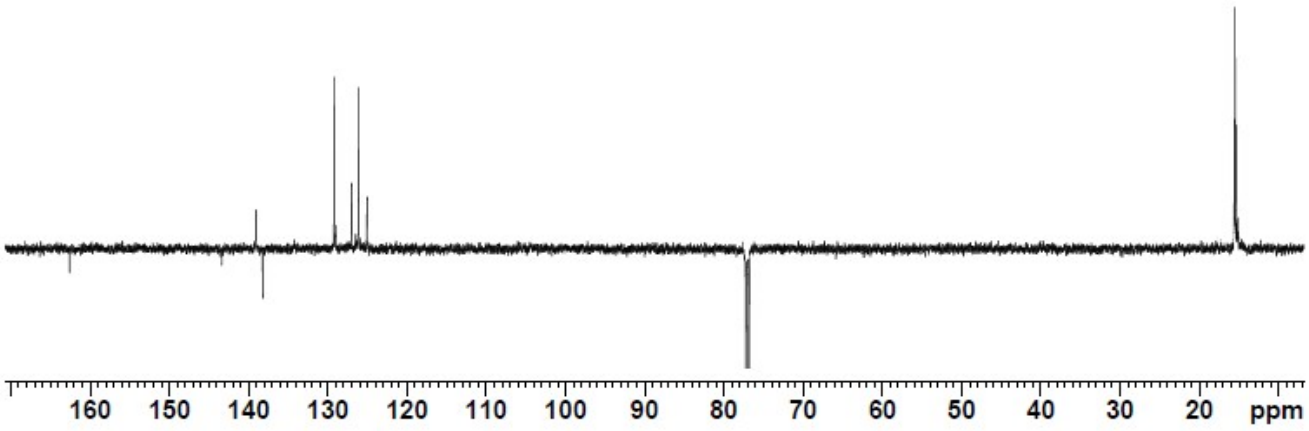
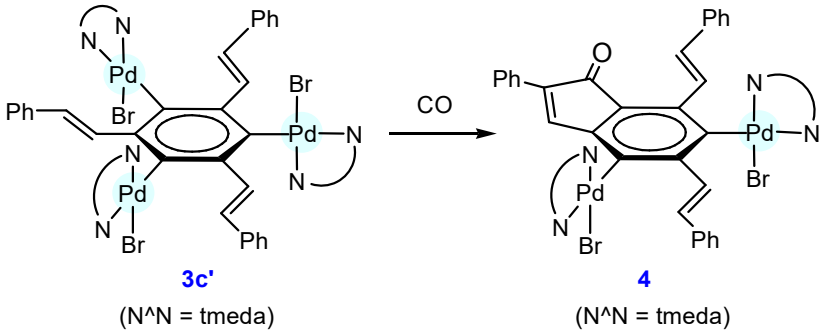


Figure S18. APT spectrum (150.9 MHz, $CDCl_3$) of compound **3d**



3c' (N^N = tmeda) **4** (N^N = tmeda)

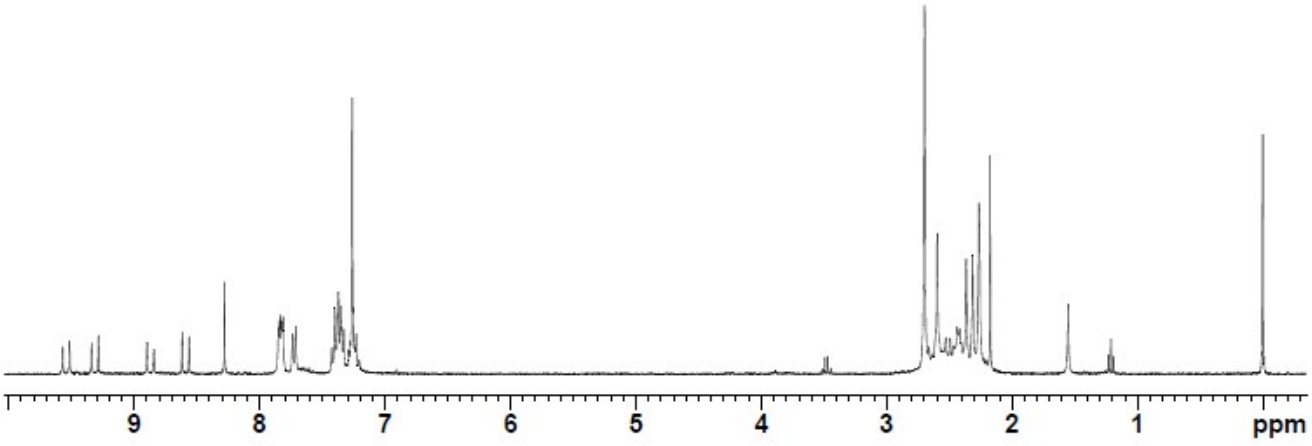


Figure S19 ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of compound **4**

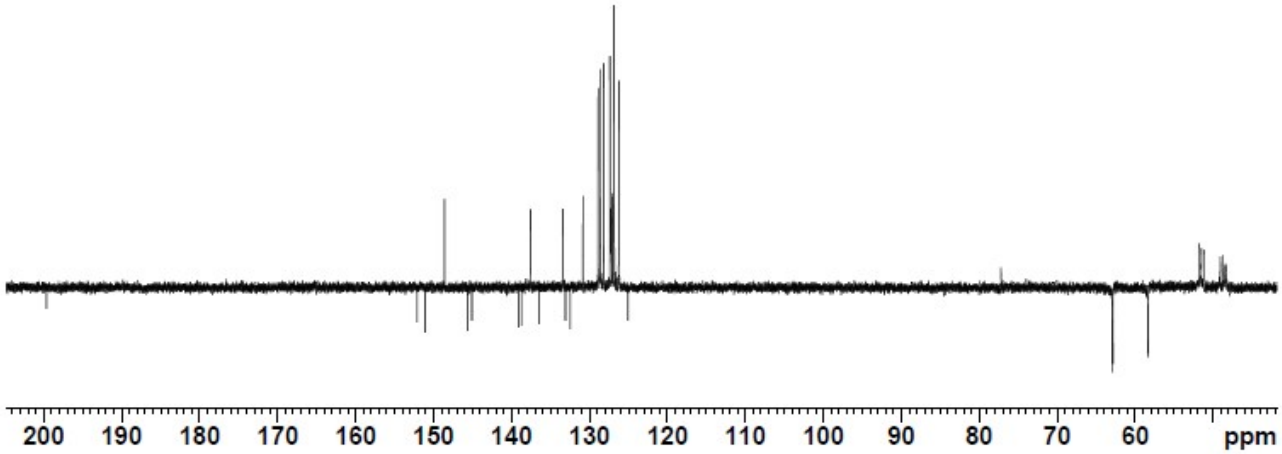


Figure S20. APT spectrum (150.9 MHz, $CDCl_3$) of compound **4**