Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Bisimino-functionalized dibenzo[a,c]acridines as highly conjugated pincer frameworks for palladium(II): synthesis, characterization and catalytic performance in Heck coupling

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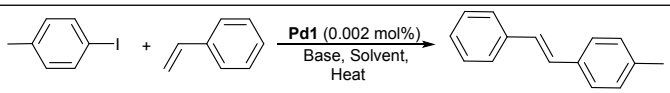
Contents

1. Additional catalytic testing

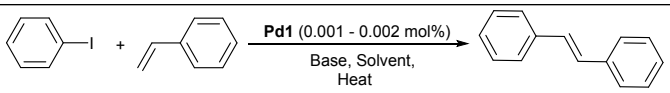
Table S1a. Screening 4-iodotoluene/styrene using **Pd1** as catalyst[a]



Entry	Base	Solvent	Temp. (°C)	Time (h)	Conv. (%)[b]	TON[c]
1	Na_2CO_3	DMF	140	8	96	48000

[a] Reaction conditions: 4 × 10^{-5} mmol **Pd1**, 2.0 mmol 1-iodo-4-methylbenzene, 2.4 mmol styrene, 2.2 mmol base, 4.0 mL solution. [b] Determined by GC. [c] TON: mol product/mol Pd.

Table S1b. Screening 4-iodobenzene/styrene using **Pd1** as catalyst; exploring loading and reaction duration effects

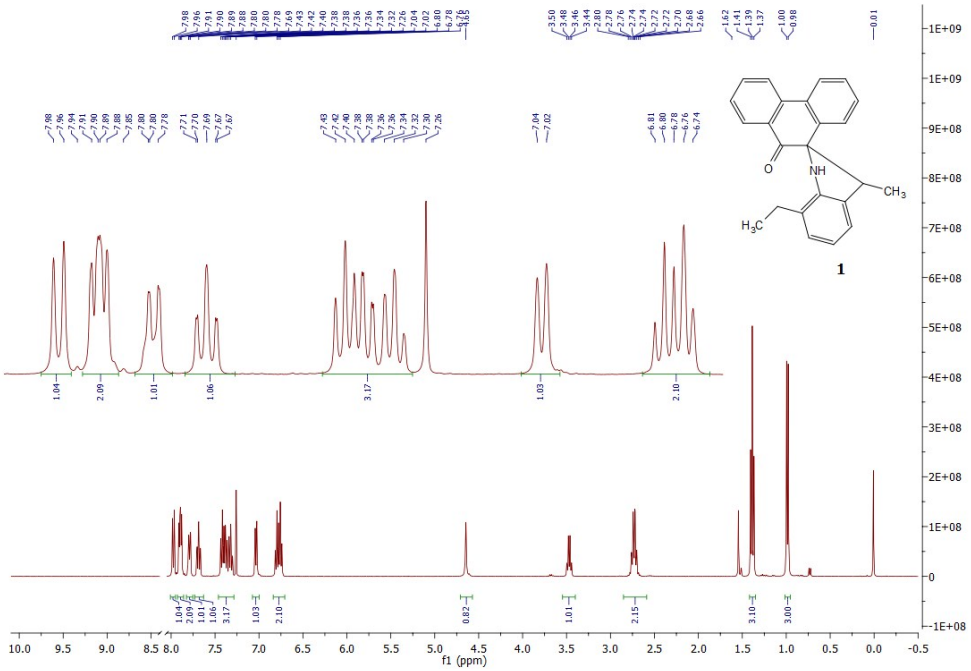


Entry	Base	Solvent	Temp. (°C)	Time (h)	Conv. (%)[b]	TON[c]
2[d]	Na_2CO_3	DMF	140	8	88	88000
3[e]	Na_2CO_3	DMF	140	24	92	46000

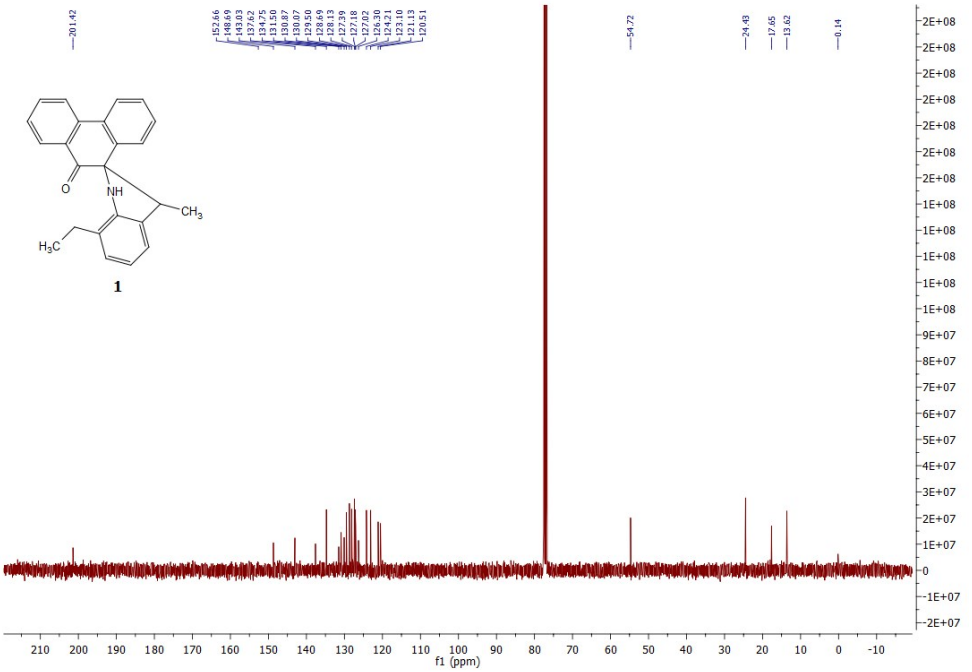
Reaction conditions: [d] 2 × 10^{-5} mmol **Pd1** (0.001 mol%), 2.0 mmol iodobenzene. [e] 4 × 10^{-5} mmol **Pd1** (0.002 mol%), 2.0 mmol iodobenzene.

2. ^{1}H and ^{13}C NMR spectra for all organic and inorganic compounds

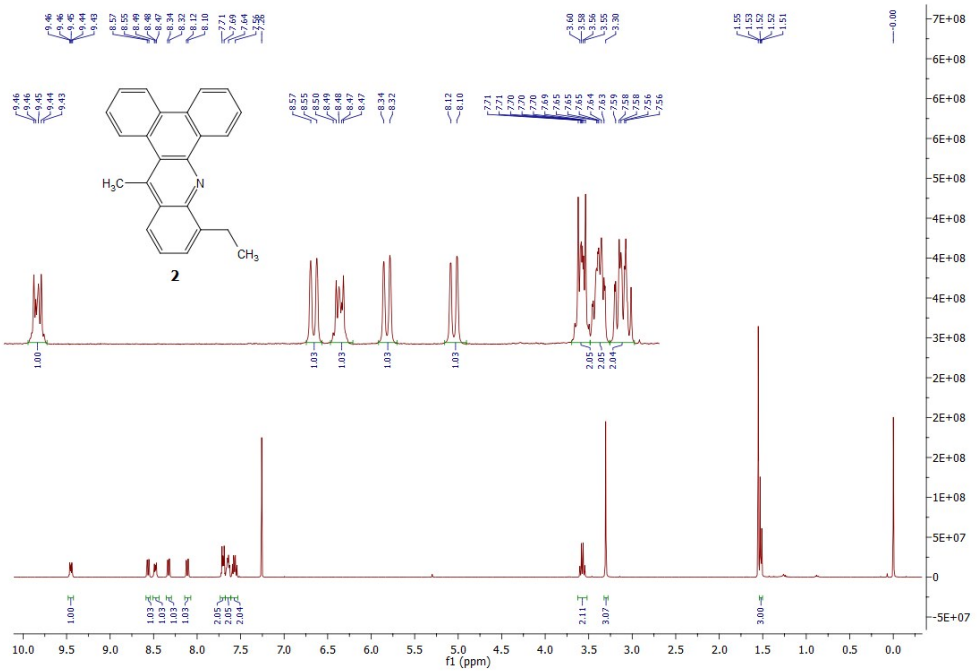
^{1}H NMR spectrum of **1**



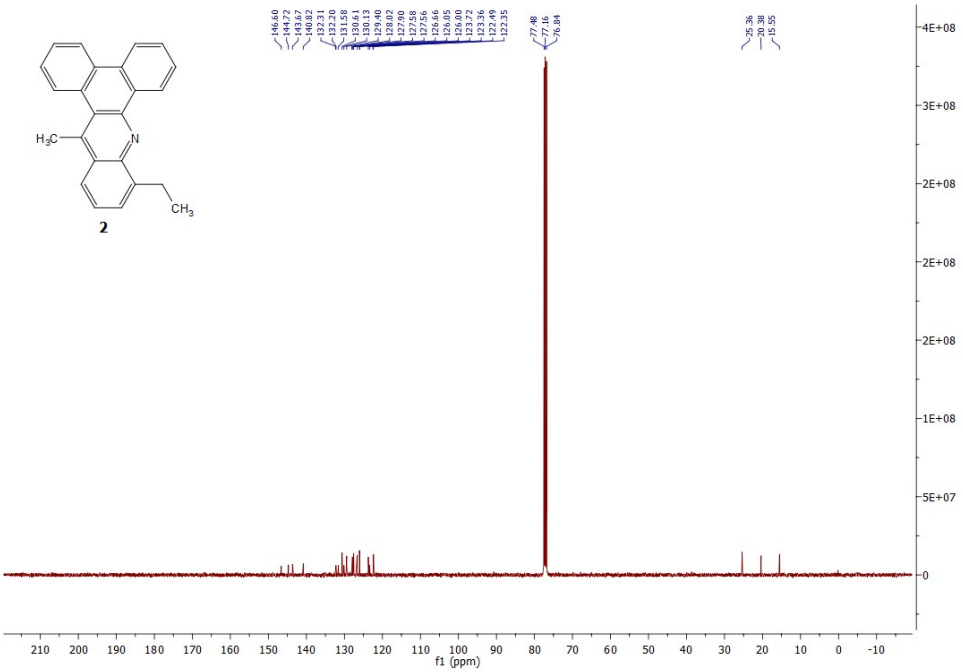
^{13}C NMR spectrum of **1**



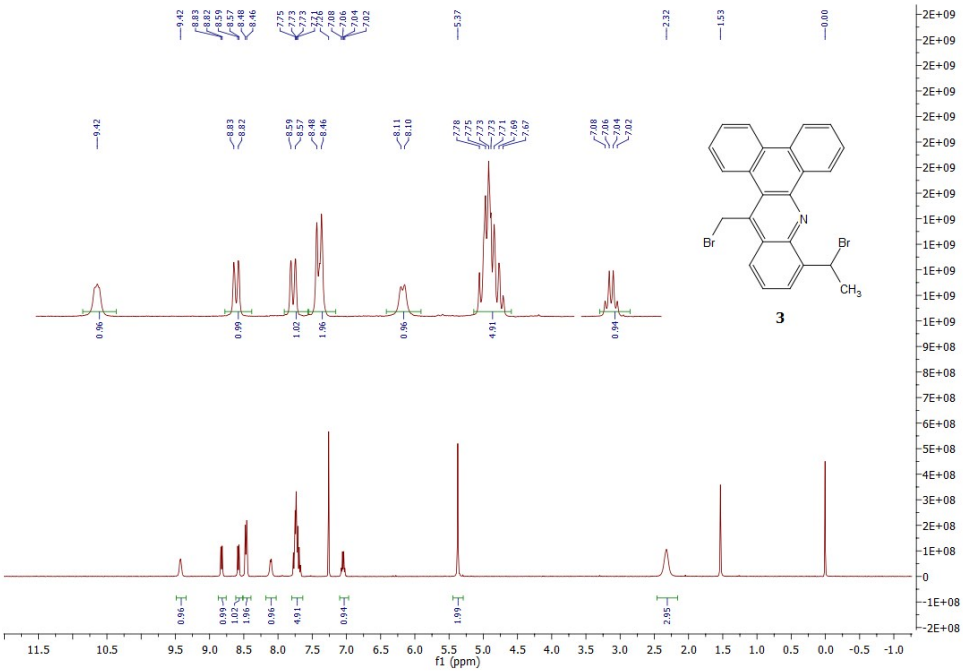
^{1}H NMR spectrum of **2**



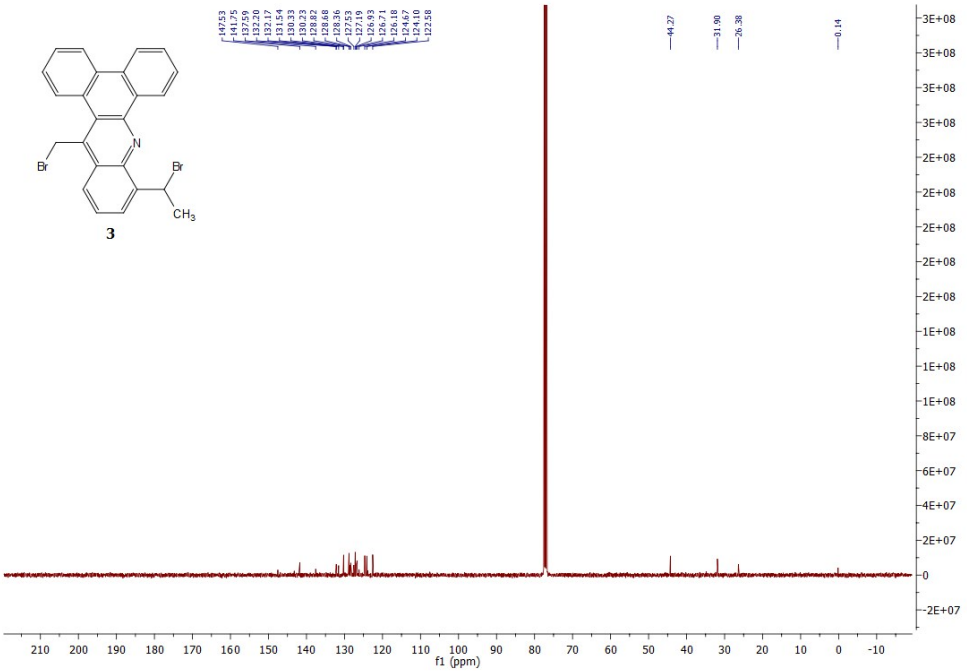
^{13}C NMR spectrum of **2**



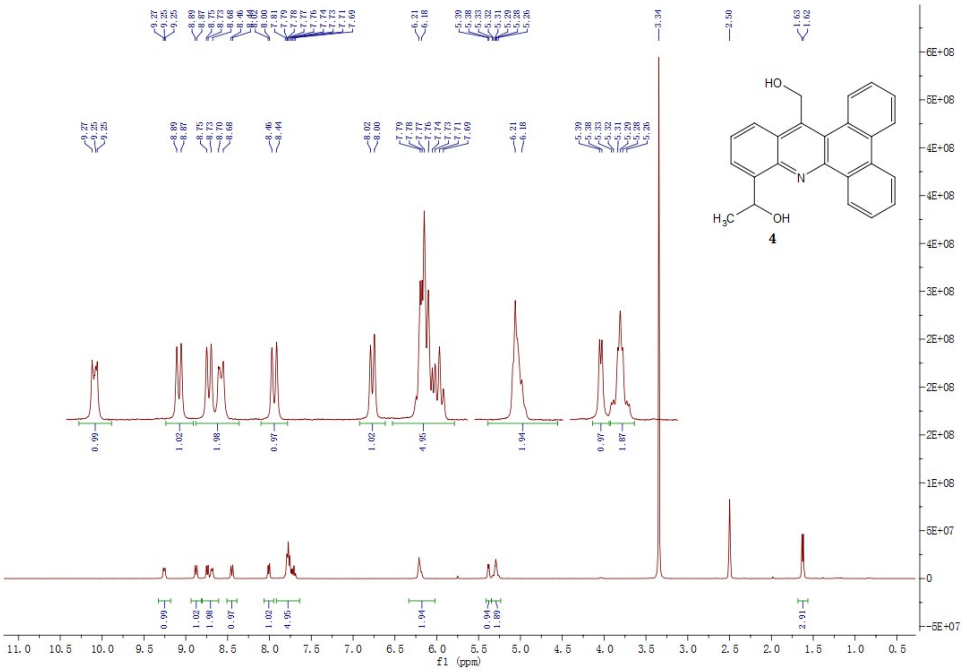
^{1}H NMR spectrum of **3**



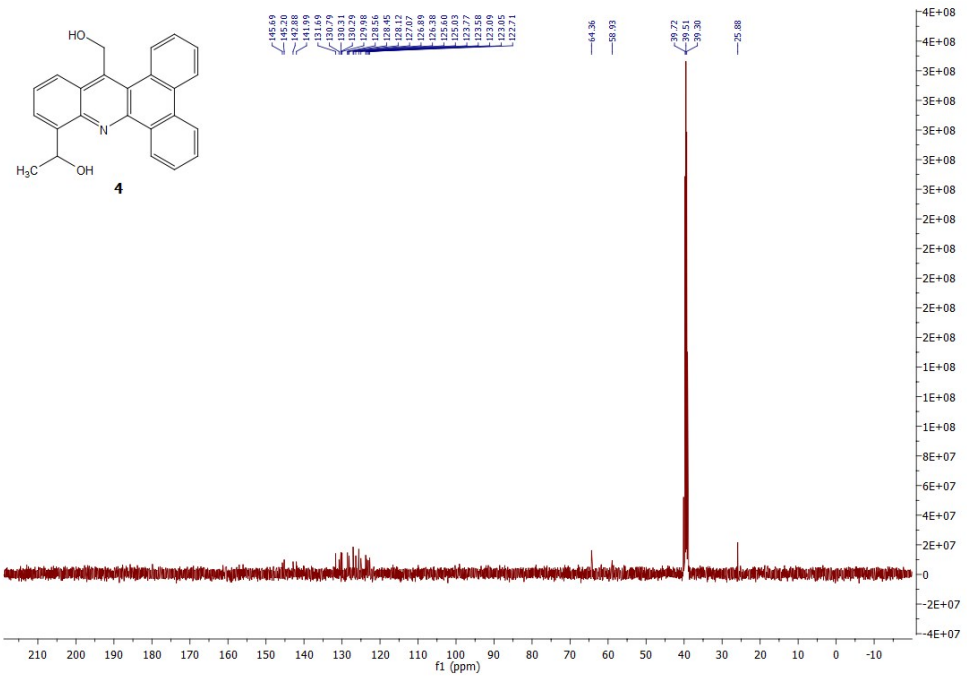
^{13}C NMR spectrum of **3**



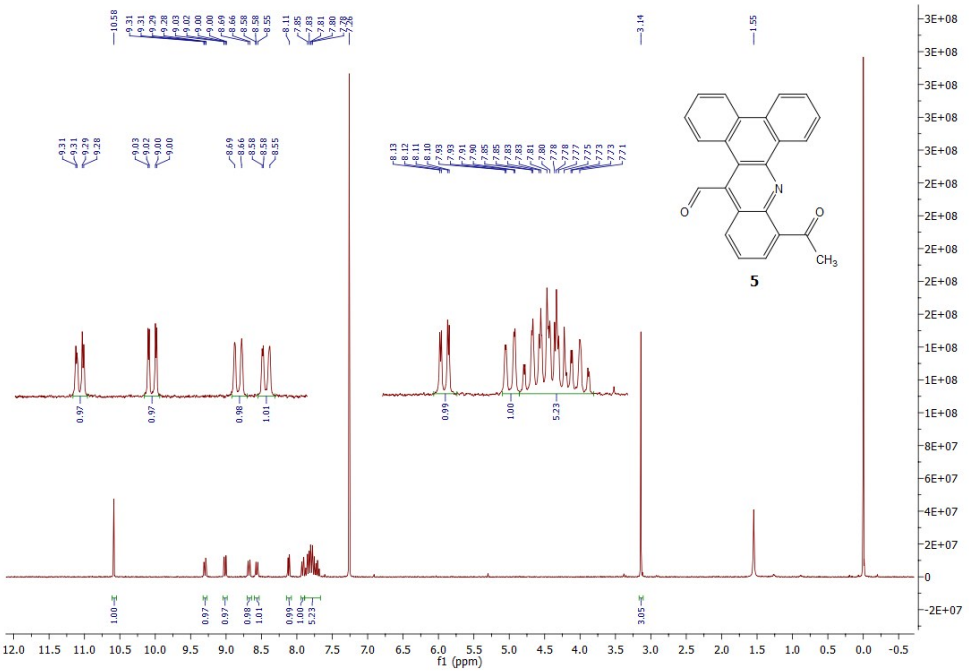
^{1}H NMR spectrum of **4**



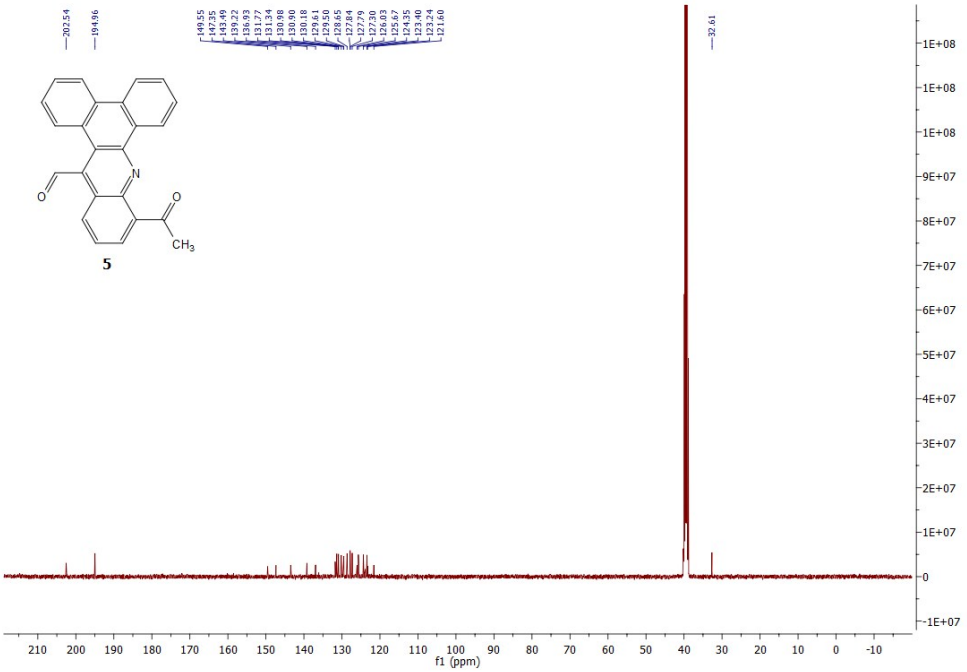
^{13}C NMR spectrum of **4**



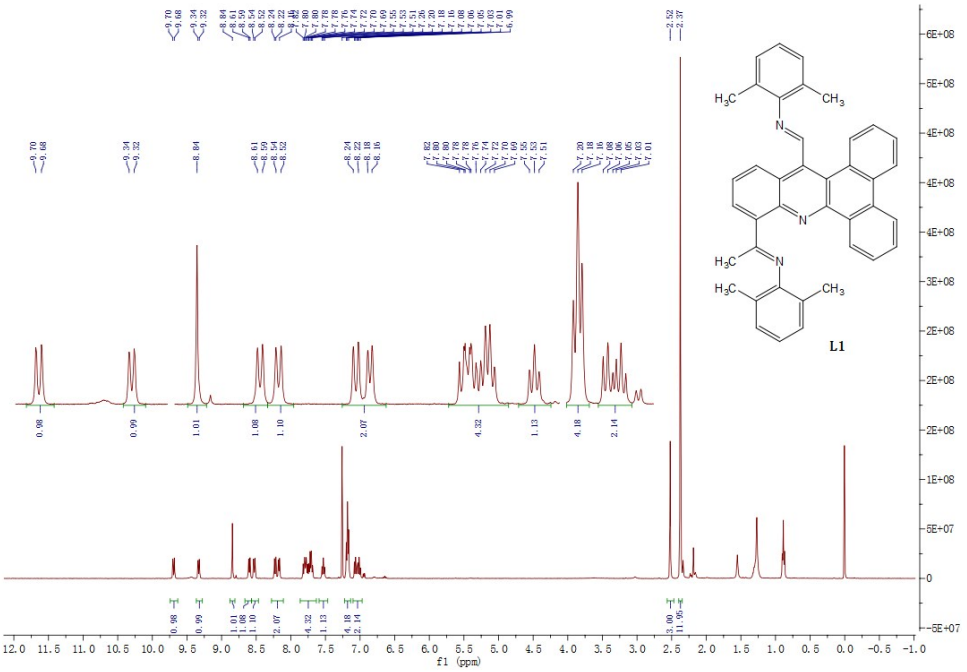
^{1}H NMR spectrum of **5**



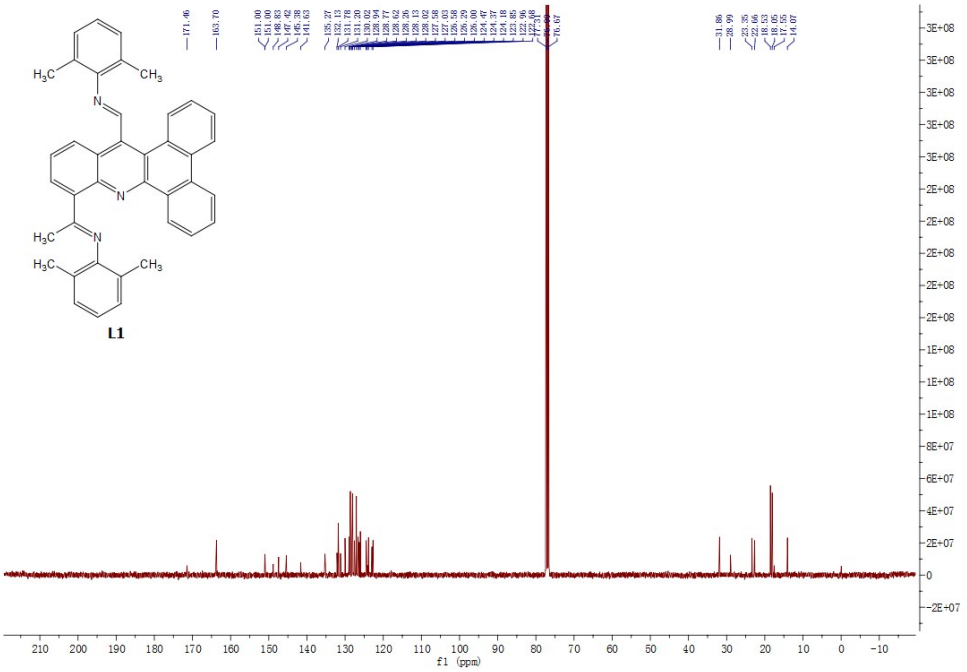
^{13}C NMR spectrum of **5**



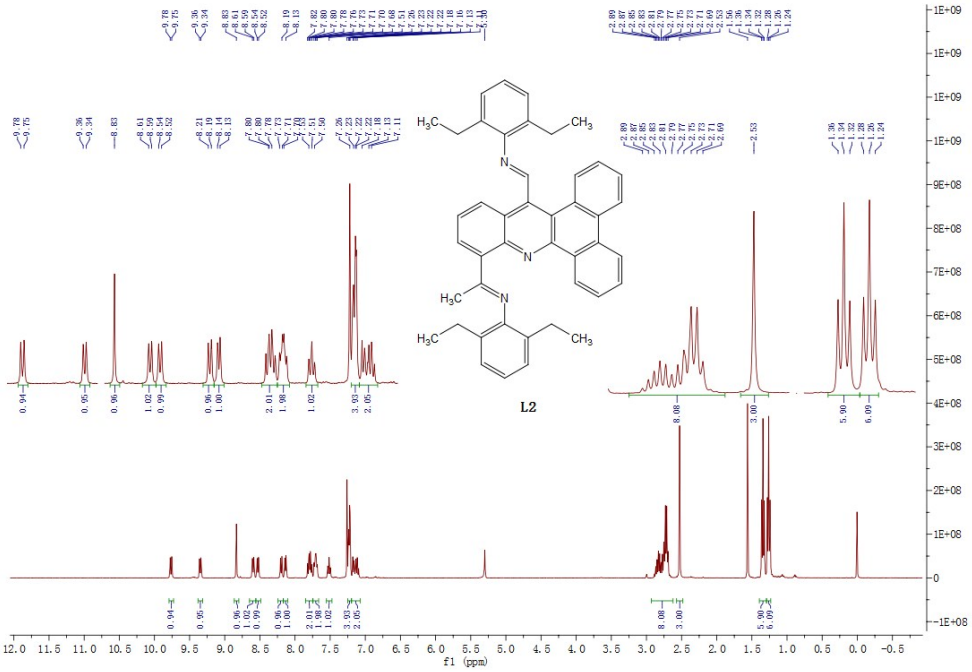
^{1}H NMR spectrum of **L1**



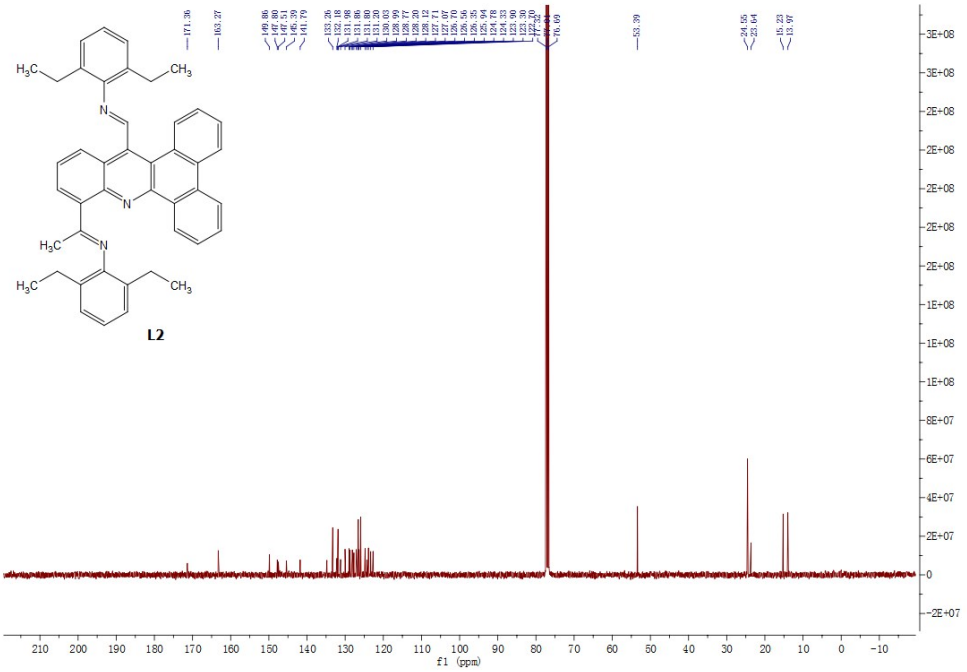
^{13}C NMR spectrum of **L1**



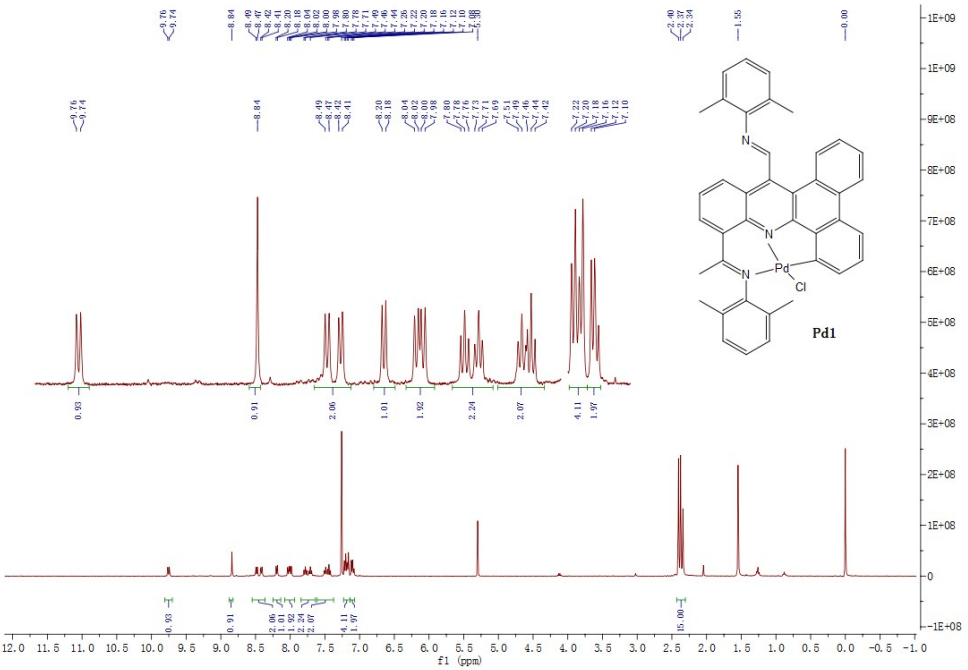
^{1}H NMR spectrum of **L2**



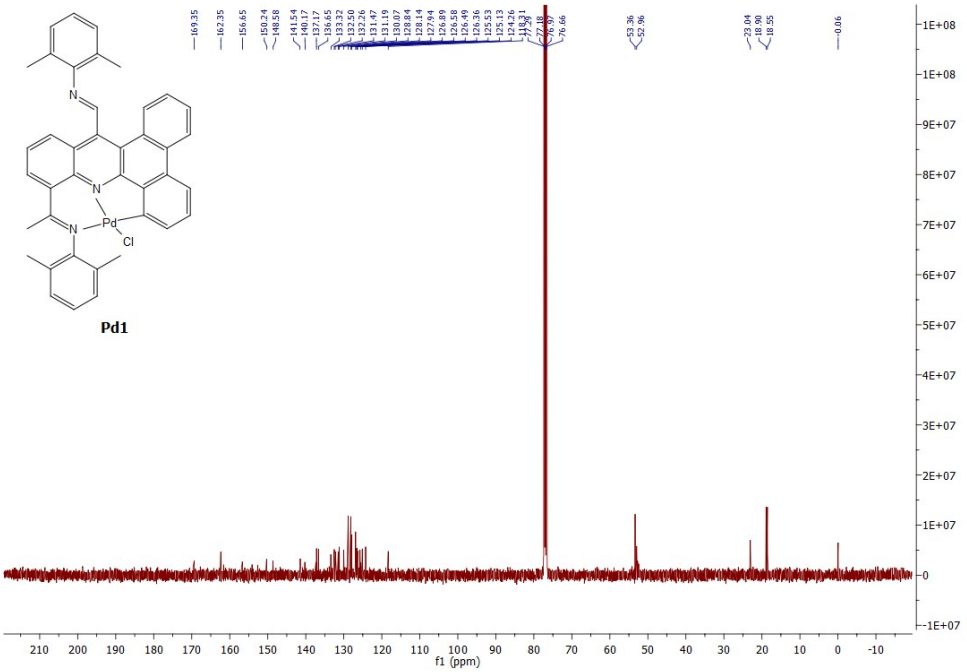
^{13}C NMR spectrum of **L2**



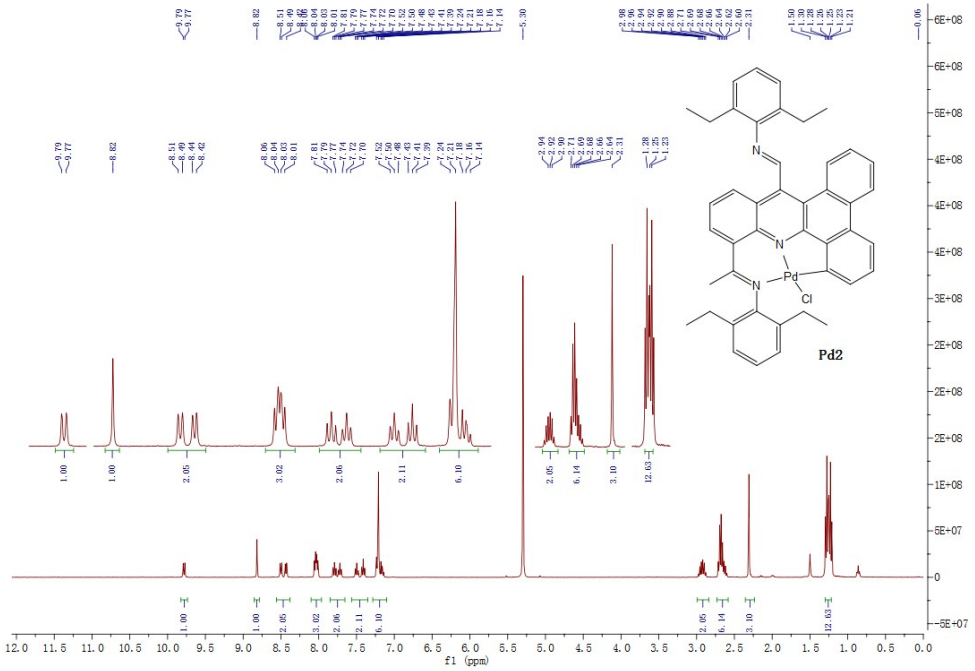
^{1}H NMR spectrum of **Pd1**



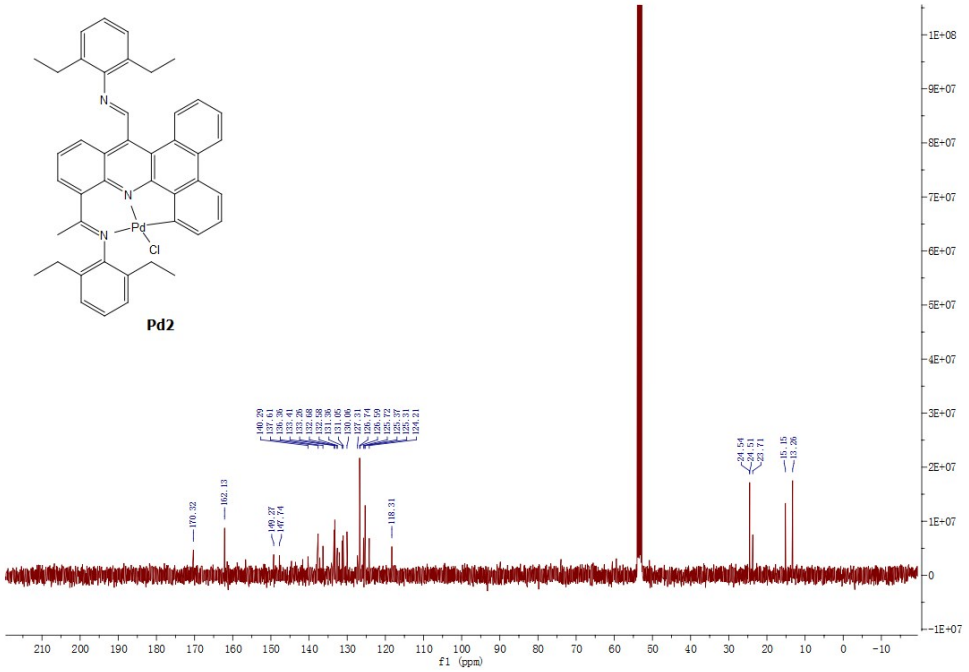
^{13}C NMR spectrum of **Pd1**



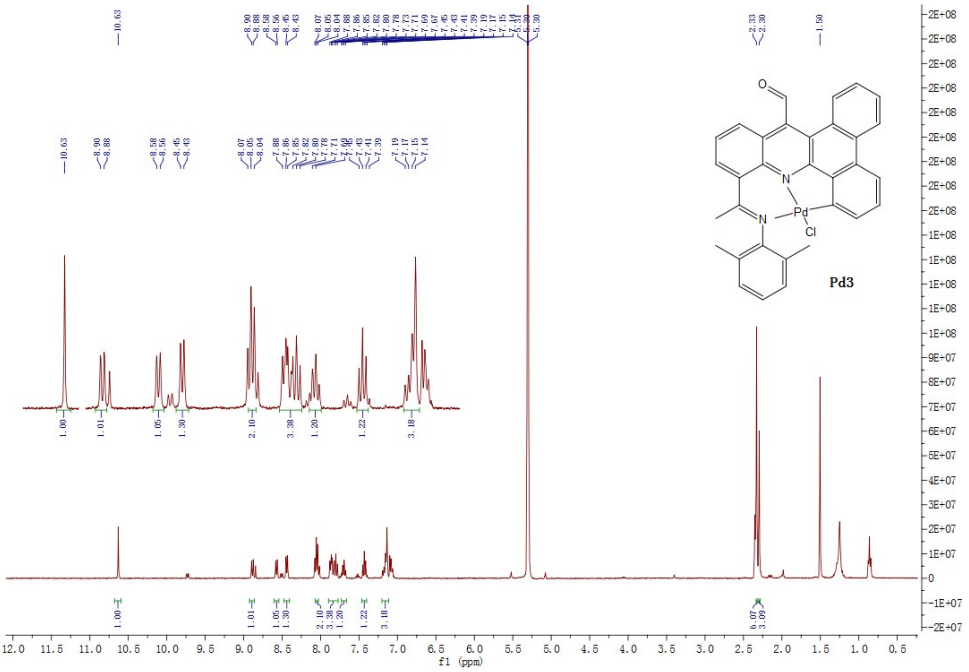
^{1}H NMR spectrum of **Pd2**



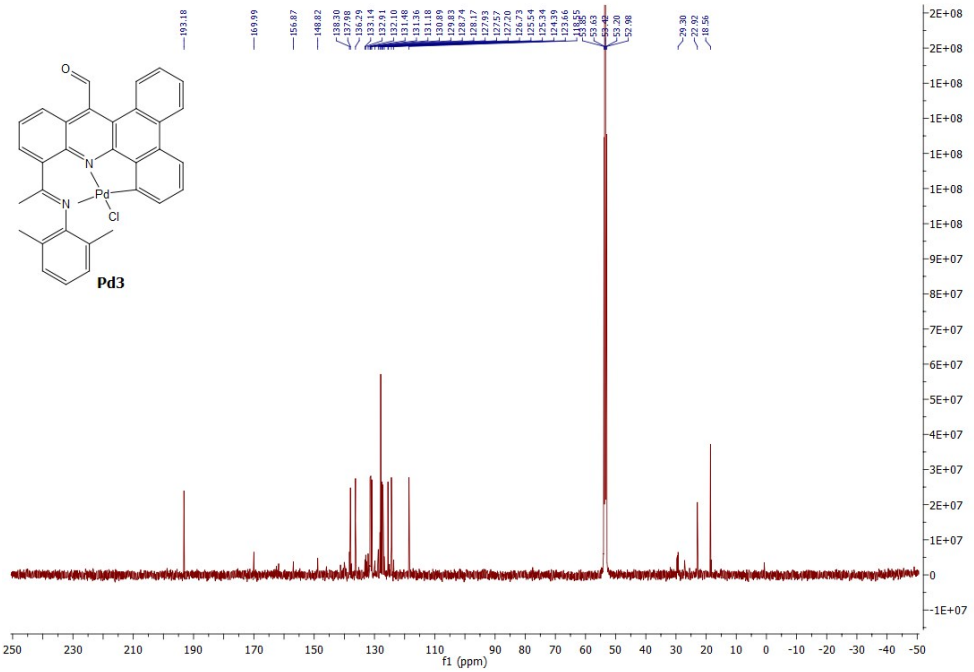
^{13}C NMR spectrum of **Pd2**



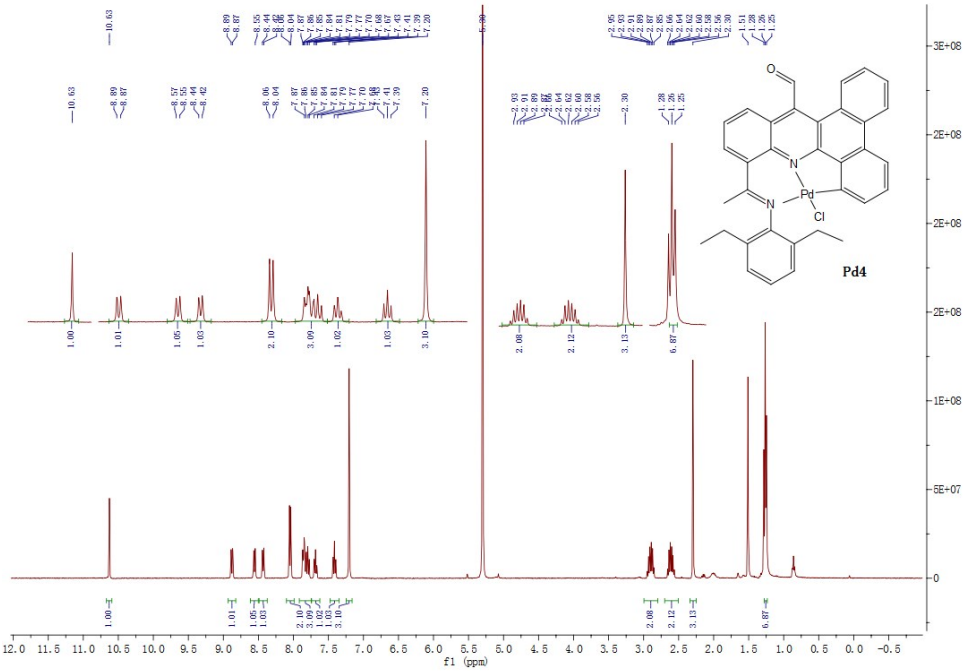
^{1}H NMR spectrum of **Pd3**



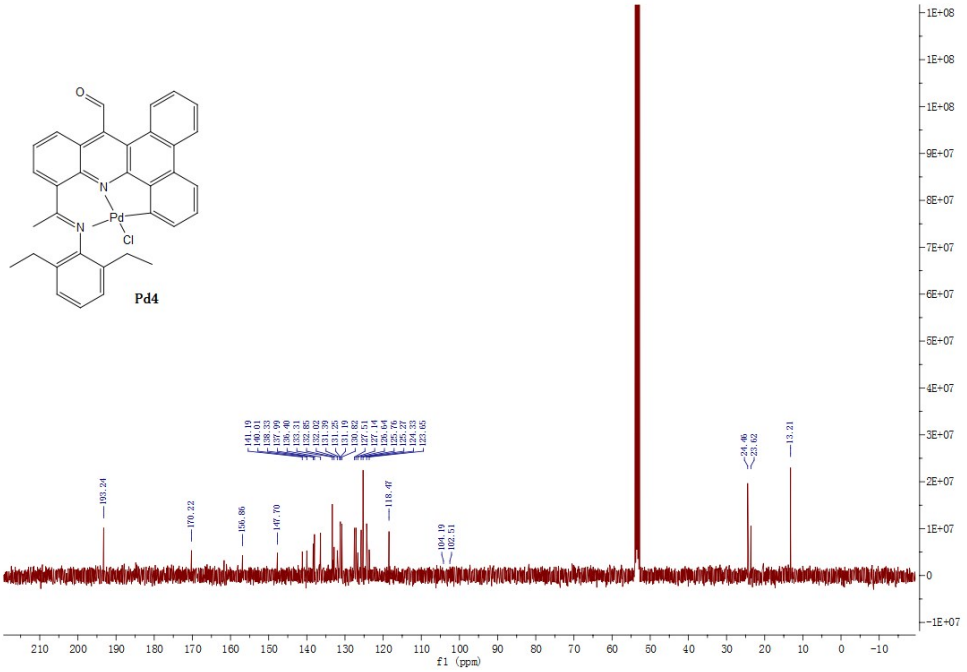
^{13}C NMR spectrum of **Pd3**



^{1}H NMR spectrum of **Pd4**



^{13}C NMR spectrum of **Pd4**



3. Crystal structure description, data and structural refinements for 1 and 2

Suitable crystals for single crystal X-ray diffraction studies of **1** and **2** were grown by layering a dichloromethane solution of **1** and **2** with heptane. ORTEP diagrams of **1** and **2** are shown in Figures S1 and S2; selected bond distances and angles are collected in the corresponding figure caption. The structure of spiro-[7-ethyl-3-methylindoline-2,10-phenanthren-9-one] **1** consists of a six- and five-membered ring systems which are linked by chiral center C13; both enantiomers are present within this centrosymmetric space group. The six-membered ring further contains two linked aryl groups and a ketone unit that are essentially co-planar with each other. By contrast the more strained five-membered ring is completed by a secondary amine and a tertiary carbon which are 1,2-linked by an ethyl-substituted aryl ring. The C14-O1 bond distance of 1.225(3) Å is consistent with a ketonic carbon-oxygen double bond.

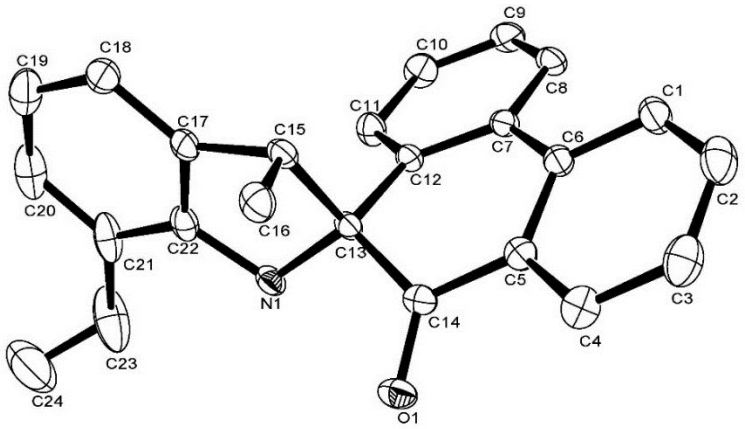


Figure S1. ORTEP diagram of **1** with thermal ellipsoids set at 50% probability level; all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): O(1)-C(14) 1.225(3), N(1)-C(13) 1.462(3), N(1)-C(22) 1.392(3), C(14)-C(13) 1.519(4), C(15)-C(13) 1.585(3), C(12)-C(13) 1.534(3), N(1)-C(13)-C(14) 111.45(19), N(1)-C(13)-C(12) 113.4(2), C(14)-C(13)-C(12) 110.4(2), N(1)-C(13)-C(15) 102.45(19), C(14)-C(13)-C(15) 110.4(2) C(12)-C(13)-C(15) 108.42(19).

The structure of 10-ethyl-14-methyldibenzo[a,c]acridine **2** consists of a slightly twisted dibenzo[a,c]acridine polyaromatic system in which the two fused benzo rings are not perfectly planar (dihedral angle *ca.* 18.0°) with respect to the pyridine ring N1-C14-C13-C15-C17-C22. At the 10- and 15-poistions are located the ethyl and methyl groups, respectively.

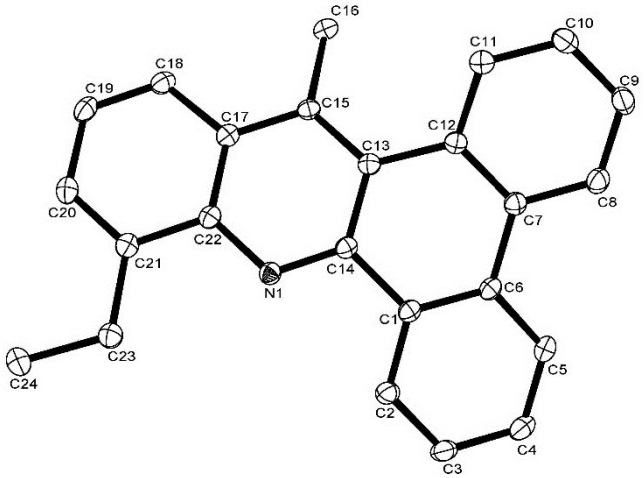


Figure S2. ORTEP diagram of **2** with thermal ellipsoids set at 50% probability level; all hydrogen atoms are omitted for clarity. N(1)-C(14) 1.324(2), N(1)-C(22)1.364(2), C(22)-C(21)1.434(3), C(14)-C(1) 1.479(3), C(1)-C(2) 1.401(3), C(21)-C(23)1.508(3),C(10)-C(11) 1.378(3), N(1)-C(14)-C(1)116.44(17), C(2)-C(1)-C(14)120.05(18), C(22)-C(21)-C(23)118.54(17

Table S1. Crystal data and structure refinements for **1** and **2**

	1	**2**
Empirical formula	$C_{24}H_{21}NO$	$C_{24}H_{19}N$
Formula weight	339.42	321.40
Temperature/K	173(2)	173(2)
Wavelength/ Å	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Pbca$
a/ Å	9.2943(19)	11.335(2)
b/ Å	18.714(4)	7.4991(15)
c/ Å	20.557(4)	37.869(8)
Alpha/°	90.00	90.00
Beta/°	95.79(3)	90.00
Gamma/°	90.00	90.00
Volume/ Å^3	9.2943(19)	3218.9(11)
Z	8	8
D_{calcd}/(g·cm^{-3})	1.268	1.326
μ/mm^{-1}	0.077	0.076
F(000)	1440.0	1360.0
Crystal size/mm	0.375 × 0.261 × 0.083	0.289 × 0.115 × 0.031
θ Range (º)	4.54 to 50	5.6 to 54.96
Limiting indices	$-11 \le h \le 11$, $-21 \le k \le 22$, $-24 \le l \le 24$	$-10 \le h \le 14$, $-9 \le k \le 9$, $-28 \le l \le 48$
No. of rflns collected	19024	11343
No. unique rflns	6173	3672
R(int)	0.0365	0.0472
No. of params	473	228
Completeness to θ	98.6	99.4
Goodness of fit on F^2	1.038	1.172
Final R indices [I >2 Σ (I)]	$R_1 = 0.0700$, $wR_2 = 0.1381$	$R_1 = 0.0693$, $wR_2 = 0.1375$
R indices (all data)	$R_1 = 0.0781$, $wR_2 = 0.1456$	$R_1 = 0.0799$, $wR_2 = 0.1441$
Largest diff. peak, and hole/(e Å^{-3})	0.65/-0.57	0.29/-0.22

4. Perspective views of Pd2 and Pd3

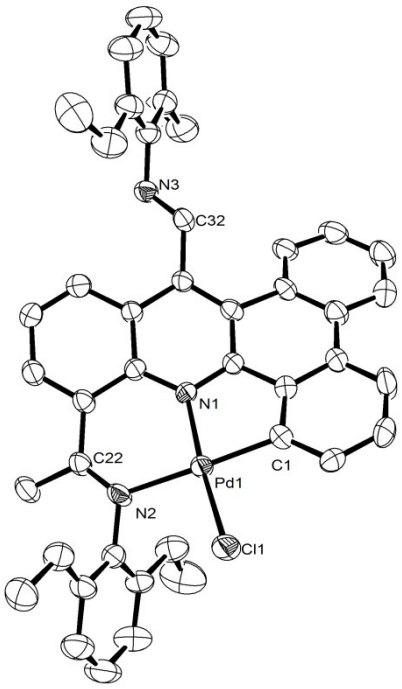


Figure S3. ORTEP diagram of **Pd2** with thermal ellipsoids set at 50% probability level; all hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°) are given in Table 2.

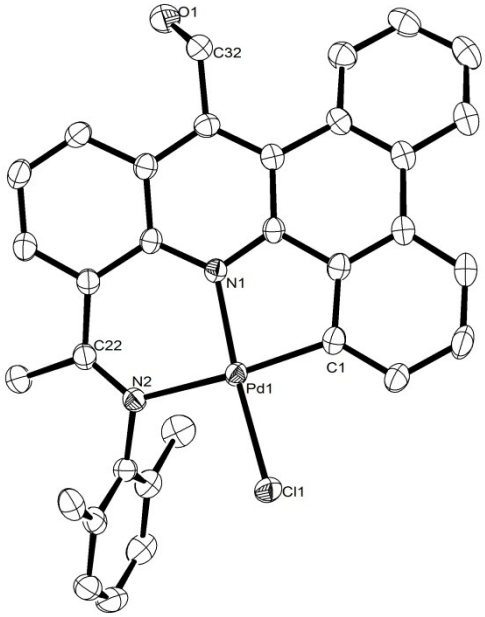


Figure S4. ORTEP diagram of **Pd3** with thermal ellipsoids set at 50% probability level; all hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°) are given in Table 2.