Dibenzobarrelene-Derived Pd-NHCs: Efficient Precatalysts for the Suzuki-Miyaura Polycondensations of Dichloroarenes Monomers

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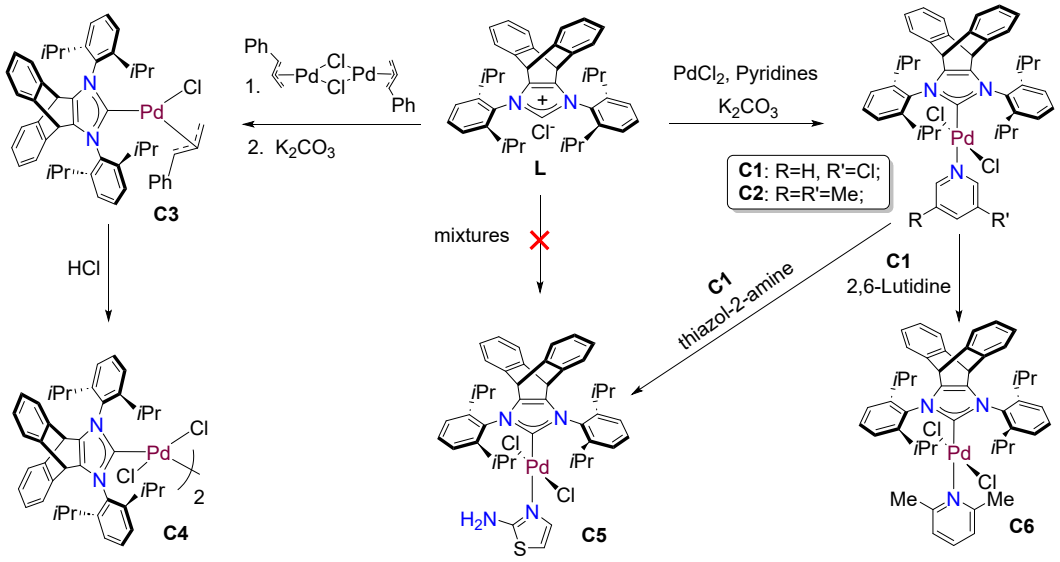
Content of Supporting Information

1. Physical Measurements

NMR spectra were acquired on a Bruker DMX 400 MHz instrument at ambient temperature, using TMS as an internal standard and $CDCl_3$ as the solvent. Single-crystal X-ray diffraction data were collected using the ω-2θ scan mode on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 173 K for compounds **C2**, **C4** and **C5**. Cell parameters were refined globally based on the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects, as well as empirical absorption. Structures were solved by direct methods and refined using full-matrix least squares on F2. Hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed using the SHELXL-97 software package. All non-hydrogen atoms were refined anisotropically, with hydrogen atoms introduced in calculated positions and displacement factors matching those of the host carbon atoms. GPC analyses of the molecular weights and molecular weight distributions (PDI = Mw/Mn) of the polymers were performed on a Waters Breeze 2 GPC chromatograph equipped with a differential refractive-index detector. Tetrahydrofuran (THF) used as the eluent at a flow rate of 1.0 mL/min.

2. Experimental Procedure: General Procedure for the Synthesis of Pd-NHCs

The carbene imidazolium salt of **L** and Pd-NHCs of **C1** were synthesized according to our previous reports.[1]



2.1 Synthesis Procedure of Carbene Palladium Catalyst C2:

Add imidazolium salt **L1** (1 mmol), palladium chloride (1.1 mmol), K_2CO_3 (10 mmol), and 3,5-dimethylpyridine to a 100 mL flask. Stir the mixture at 60°C for 6 hours. After cooling, add dichloromethane (20 mL) to the mixture. Purify the reaction mixture using a short silica gel column with a significant amount of dichloromethane. Distill the filtrate to obtain a yellow solid. Slowly dissolve the yellow solid in a small amount of dichloromethane (approximately 0.5 mL), then add n-hexane to generate a large amount of light yellow powder with a yield of 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 2.0 Hz, 2H), 7.57 (t, J = 7.7 Hz, 2H), 7.42 (d, J = 7.8 Hz, 4H), 7.21 (dd, J = 5.3, 3.2 Hz, 4H), 7.08 (s, 1H), 6.89 (dd, J = 5.4, 3.1 Hz, 4H), 5.15 (s, 2H), 2.88 (p, J = 6.7 Hz, 4H), 2.08 (s, 6H), 1.39 (d, J = 6.5 Hz, 12H), 1.01 (d, J = 6.8 Hz, 12H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 152.89, 148.59, 147.95, 146.05, 144.59, 138.54, 133.06, 132.82, 130.27, 124.87, 124.30, 124.21, 47.33, 28.28, 27.06, 23.97, 18.13. HRMS (ESI) m/z: $[M-Cl]^+$ calcd for $C_{48}H_{53}ClN_3Pd$, 812.2963; found, 812.2960.

2.2 The process of formation of carbene palladium catalyst C3:

To a 100 mL flask was added imidazolium salt **L1** (1 mmol), palladium chloride (1.1 mmol), K_2CO_3 (10 mmol), and Bis[cinnamyl palladium(II) chloride], and the mixture was stirred at 60 °C for 6 h. Then the mixture was cooled and dichloromethane (20 mL) was added. The reaction mixture was washed by short silica. gel column containing a large amount of dichloromethane. The filtrate was distilled to give a yellow solid. The yellow solid was slowly treated with a small amount of dichloromethane until it was completely dissolved (about 0.5 mL), then, hexane was added to produce a yellow powder in 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 7.7 Hz, -1H), 7.33 (d, *J* = 7.7 Hz, -3H), 7.22 (dd, *J* = 5.4, 3.2 Hz, -4H), 7.13 – 7.08 (m, -4H), 6.91 (dd, *J* = 5.5, 3.2 Hz, -4H), 5.11 (s, -1H), 5.02 – 4.87 (m, -1H), 4.21 (d, *J* = 12.6 Hz, -1H), 2.78 (p, *J* = 6.8 Hz, -3H), 1.26 – 1.22 (m, -11H), 1.01 (d, *J* = 6.8 Hz, -13H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.31, 146.81, 146.14, 144.53, 138.08, 134.11, 129.96, 128.18, 127.50, 126.61, 124.99, 124.94, 124.13, 124.01, 123.88, 108.47, 89.94, 48.05, 47.56, 29.74, 28.09, 25.95, 23.44, 14.18.

2.3 Synthesis Procedure of Carbene Palladium Catalyst C4:

Dissolve **C3** (0.5 mmol) in 1,4-dioxane (2 mL) and hydrochloric acid (1 mL) at room temperature for 12 hours. Dilute the mixture with water and filter it. After removing

the solvent from the mixture, dissolve the remaining solid in dichloromethane. Then, add n-hexane to obtain a yellow powder with a yield of 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.3 Hz, 2H), 8.38 (dd, *J* = 5.5, 1.4 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 4H), 7.48 (ddd, *J* = 8.2, 2.4, 1.3 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 8H), 6.99 (dd, *J* = 8.2, 5.6 Hz, 2H), 6.90 (dd, *J* = 5.4, 3.1 Hz, 8H), 5.16 (s, 4H), 2.85 (p, *J* = 6.7 Hz, 8H), 1.38 (d, *J* = 6.5 Hz, 24H), 1.01 (d, *J* = 6.8 Hz, 24H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.36, 150.32, 149.36, 147.91, 145.95, 144.75, 137.22, 132.62, 131.72, 130.41, 124.92, 124.33, 124.26, 124.18, 47.32, 28.29, 27.08, 23.93, 14.12.

2.4 Synthesis Procedure of Carbene Palladium Catalyst C5:

C1 (0.5 mmol) and 2-aminothiazole (0.7 mmol) were added to dichloromethane (1 mL) and reacted at room temperature for 12 hours. The resulting product was then evaporated to dryness, washed with n-hexane 3 times, and filtered to obtain a pale yellow solid with a yield of 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 4H), 7.21 (dd, *J* = 5.4, 3.2 Hz, 4H), 6.89 (dd, *J* = 5.4, 3.1 Hz, 4H), 6.76 (d, *J* = 4.0 Hz, 1H), 6.06 (d, *J* = 4.1 Hz, 1H), 5.56 (s, 1H), 5.29 (s, 1H), 5.16 (s, 2H), 2.82 (p, *J* = 6.7 Hz, 4H), 1.35 (d, *J* = 6.5 Hz, 12H), 1.00 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.00, 152.02, 148.08, 146.02, 144.66, 138.71, 132.79, 130.33, 124.97, 124.36, 124.26, 105.87, 47.38, 28.37, 27.19, 23.90. HRMS (ESI) m/z: $[M\text{-}Cl]^+$ calcd for $C_{44}H_{48}ClN_4PdS$, 805.2323; found, 805.2323.

2.5 Synthesis Procedure of Carbene Palladium Catalyst C6:

Dissolve **C1** (0.5 mmol) and 2,6-dimethylpyridine (0.7 mmol) in dichloromethane (1

mL) and react at room temperature for 12 hours. Then, evaporate the solvent and wash the product with n-hexane 3 times. Filter the mixture to obtain a light yellow solid with a yield of 49%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 2H), 7.43 (d, *J* = 7.8 Hz, 4H), 7.21 (dt, *J* = 7.1, 3.5 Hz, 5H), 6.90 (dd, *J* = 5.4, 3.1 Hz, 4H), 6.71 (d, *J* = 7.7 Hz, 2H), 5.23 (s, 2H), 2.86 (p, *J* = 6.7 Hz, 4H), 2.47 (s, 6H), 1.35 (d, *J* = 6.5 Hz, 12H), 1.01 (d, *J* = 6.8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.77, 155.40, 148.49, 146.10, 144.53, 137.18, 132.98, 130.09, 124.83, 124.41, 123.88, 122.12, 47.59, 28.43, 27.46, 24.77, 23.36.

2.6 General Procedure for Palladium-Catalyzed Suzuki-Miyaura Cross-Coupling Polymerization:

1 mol% N-heterocyclic carbene palladium catalyst was used, with KO^tBu (2 mmol) as the base, and a THF/H_2O (3:1) mixture as the solvent. The reaction between the chloroarene and pinacol boronate ester was carried out at 80°C under nitrogen atmosphere for 12 hours. Post-reaction, the polymer was precipitated and washed using methanol.

3. NMR spectra for the products

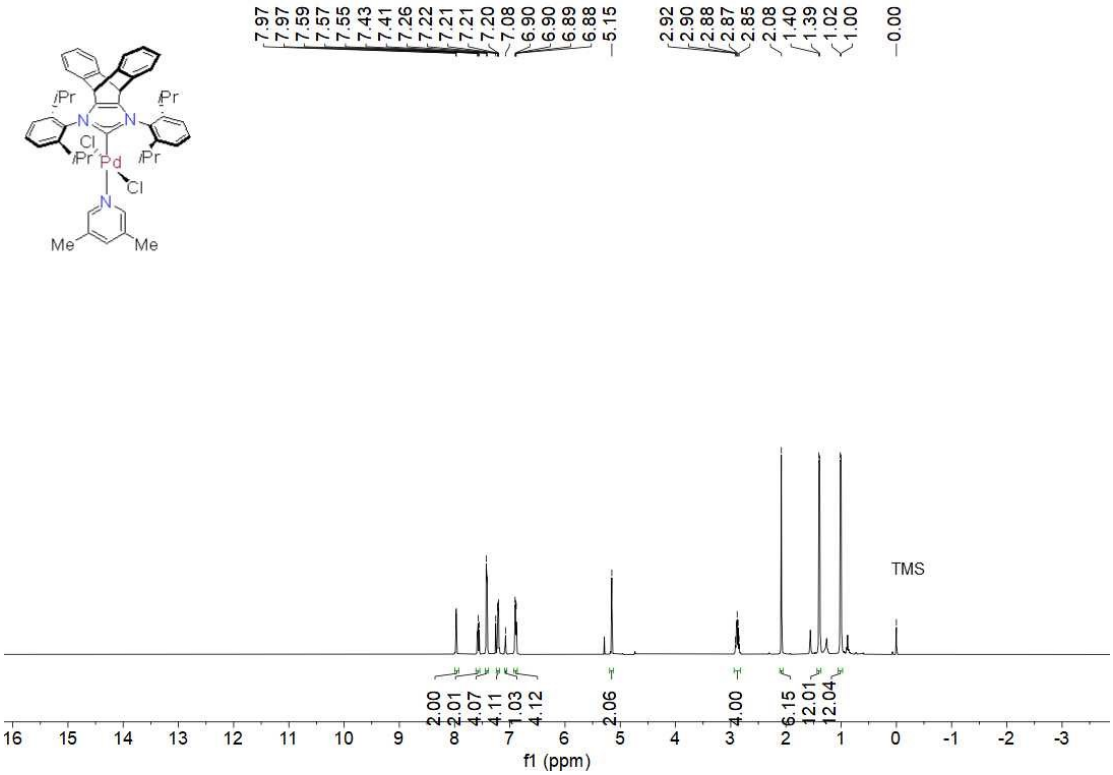


Figure S1. The ^{1}H NMR spectrums of **C2**

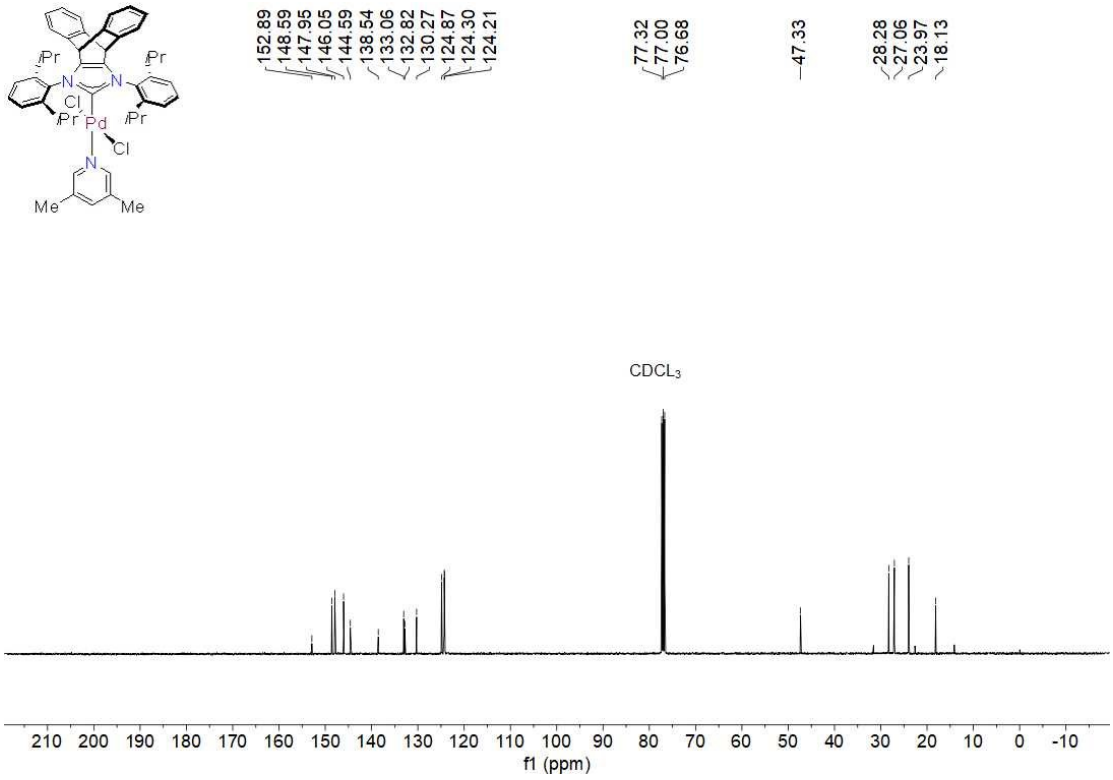


Figure S2. The ^{13}C NMR spectrums of **C2**

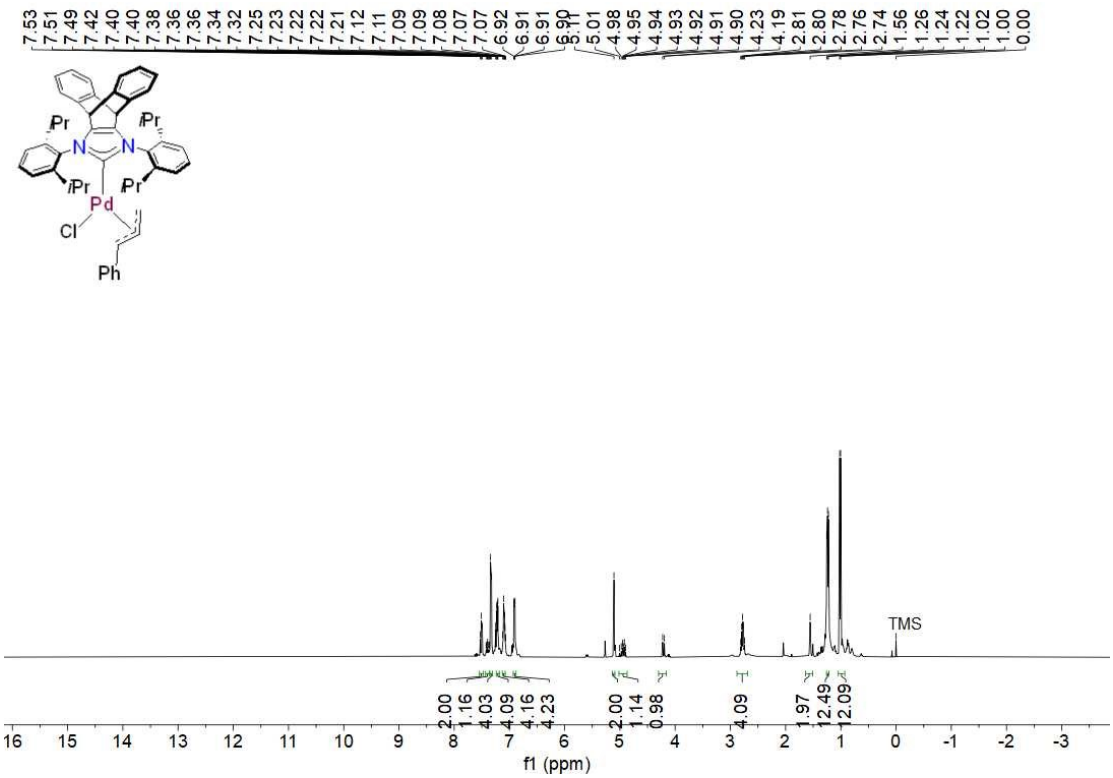


Figure S3. The ^{1}H NMR spectrums of **C3**

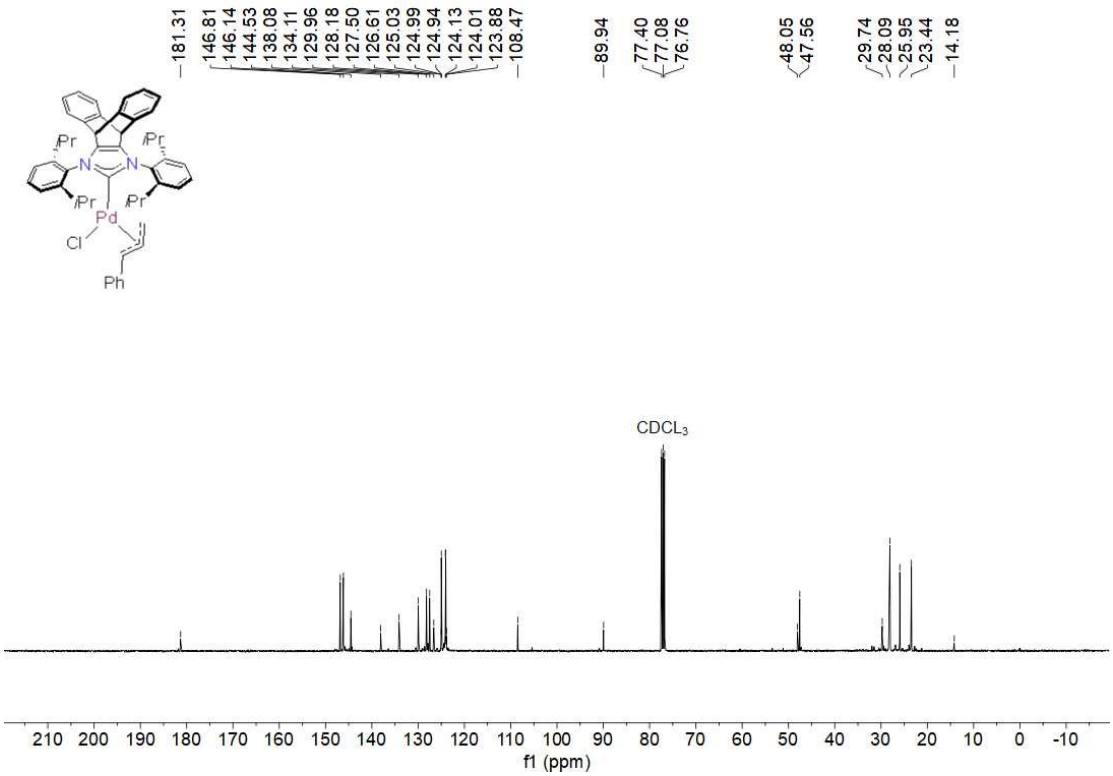


Figure S4. The ^{13}C NMR spectrums of **C3**

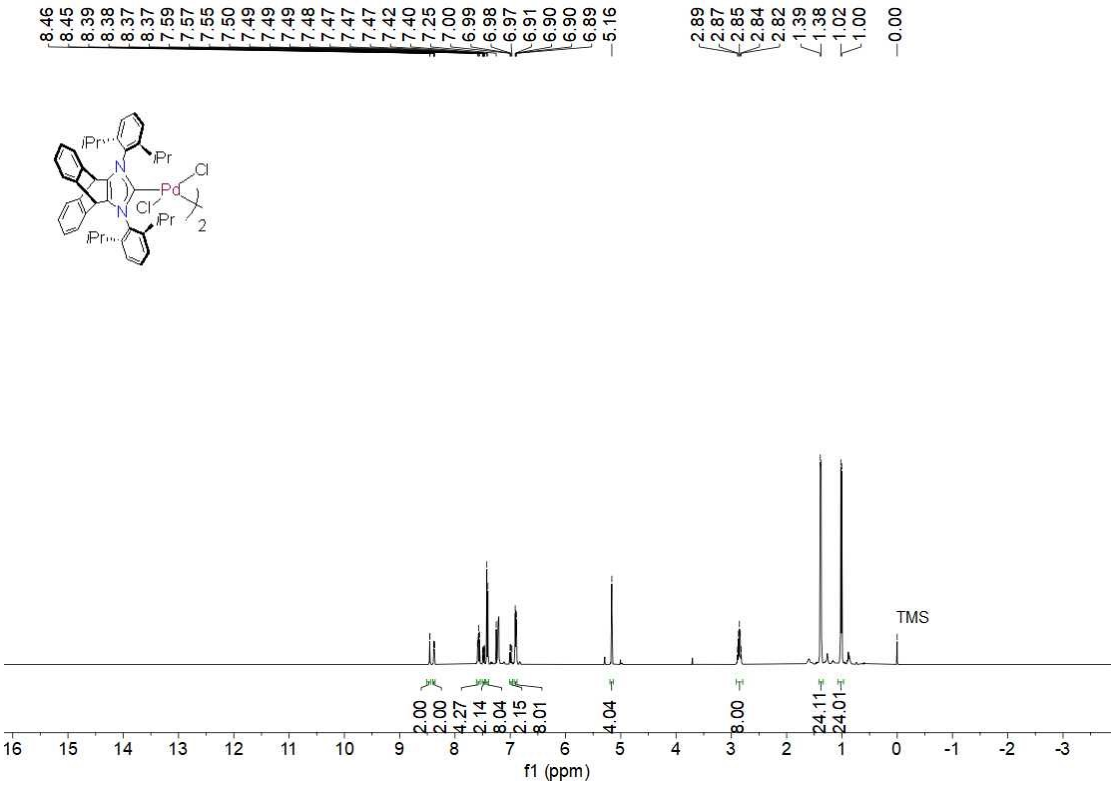


Figure S5. The ^{1}H NMR spectrums of **C4**

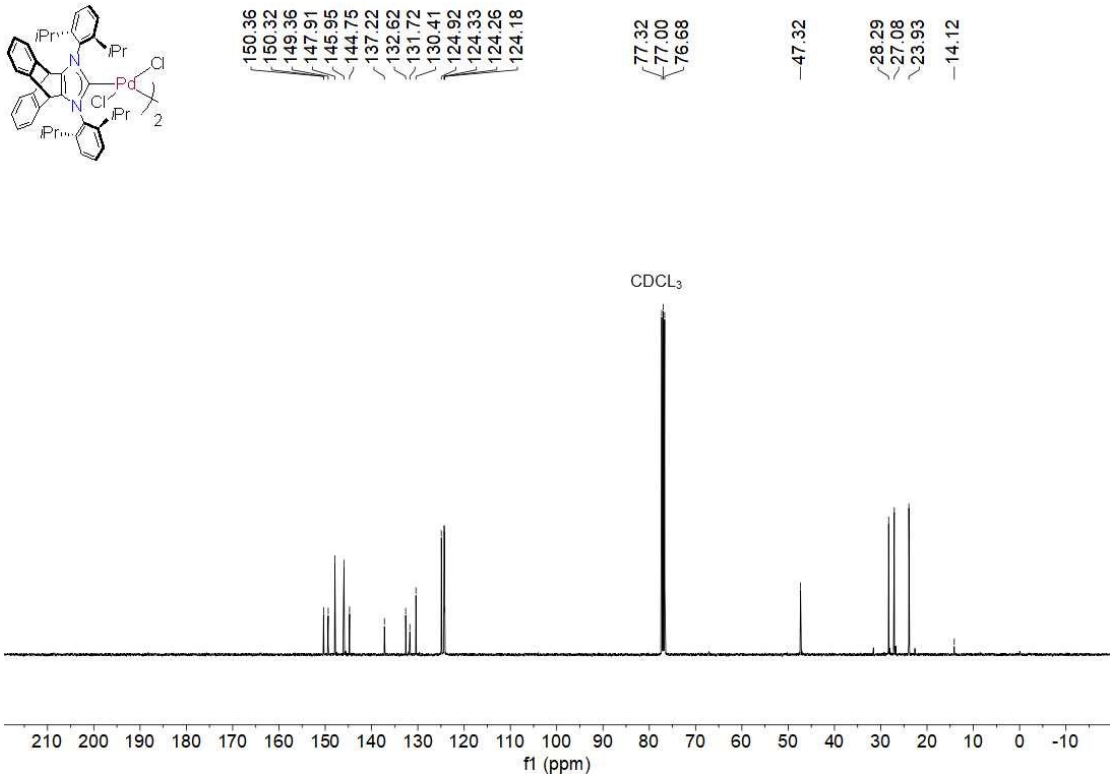


Figure S6. The ^{13}C NMR spectrums of **C4**

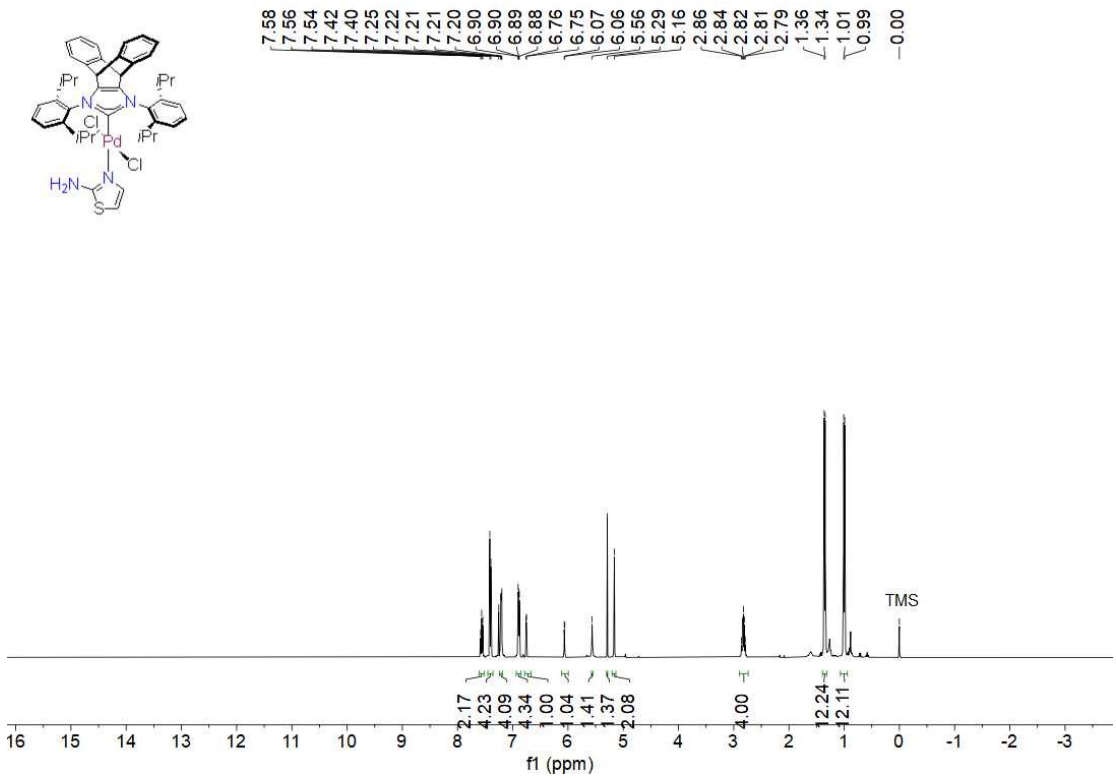


Figure S7. The ^{1}H NMR spectrums of **C5**

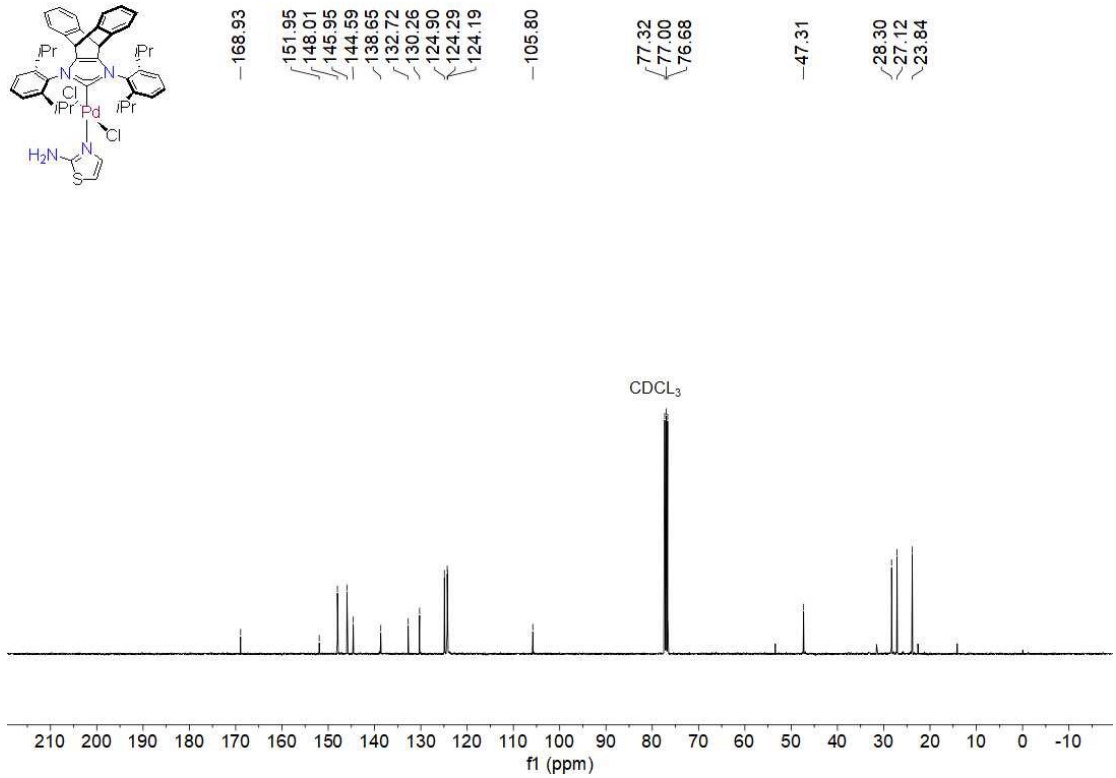


Figure S8. The ^{13}C NMR spectrums of **C5**

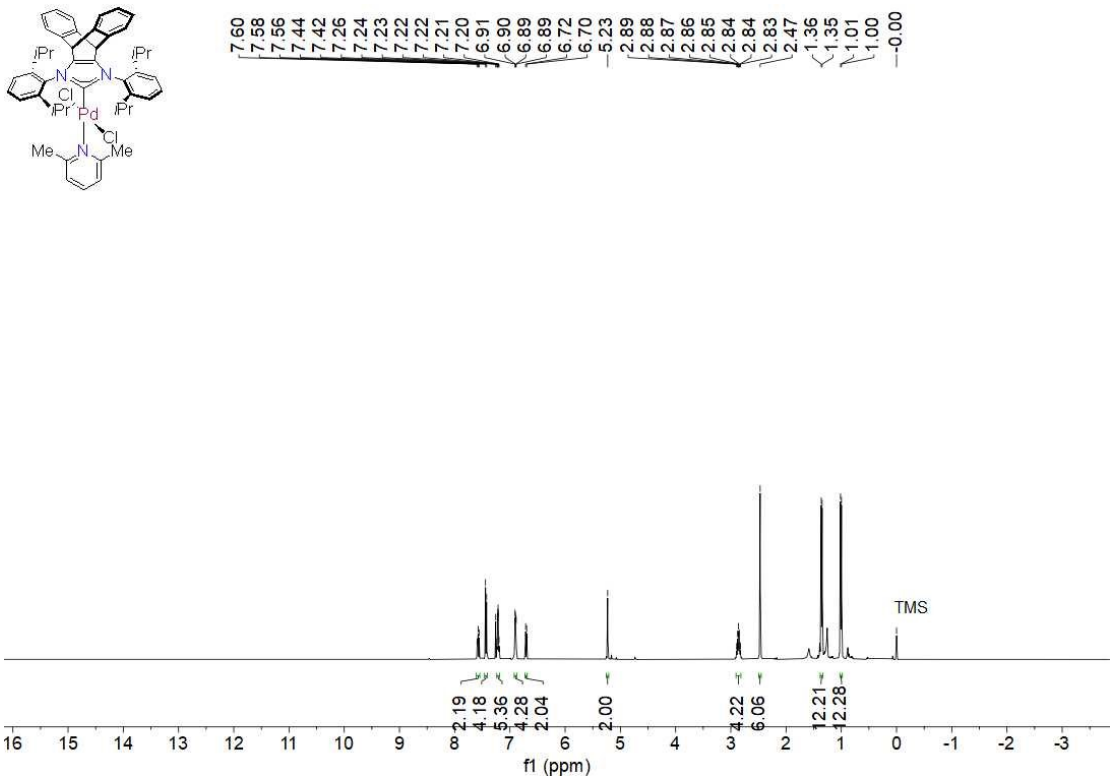


Figure S9. The ^{1}H NMR spectrums of **C6**

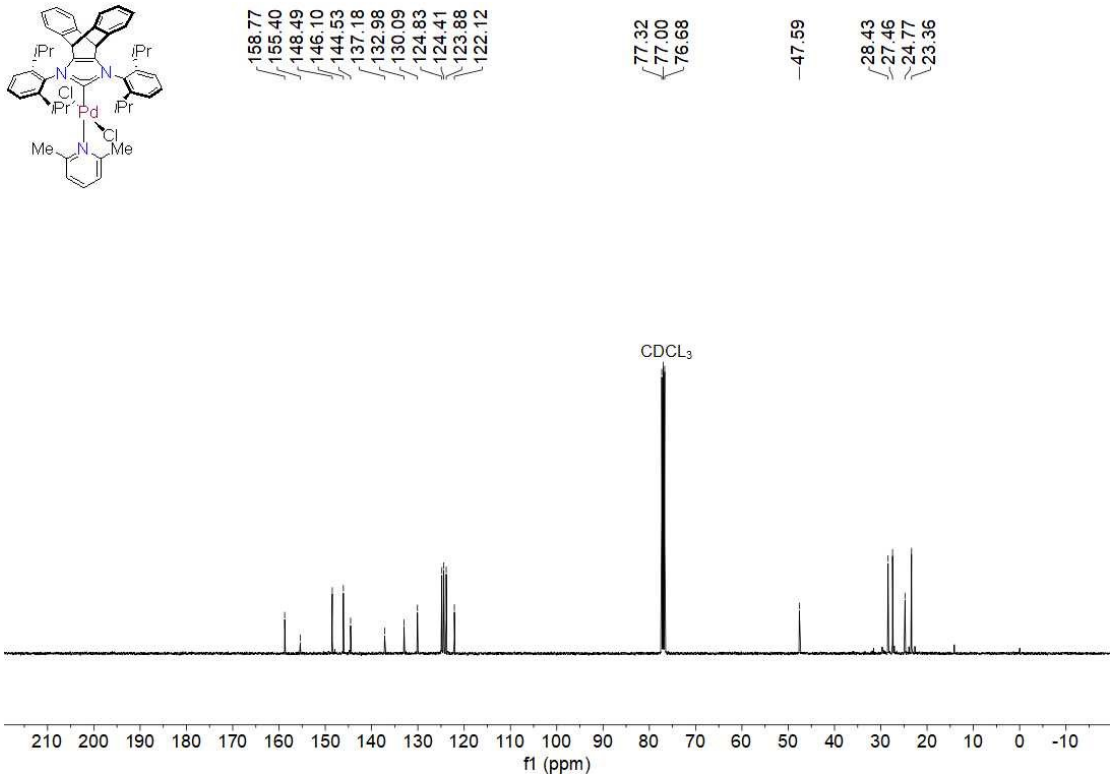


Figure S10. The ^{13}C NMR spectrums of **C6**

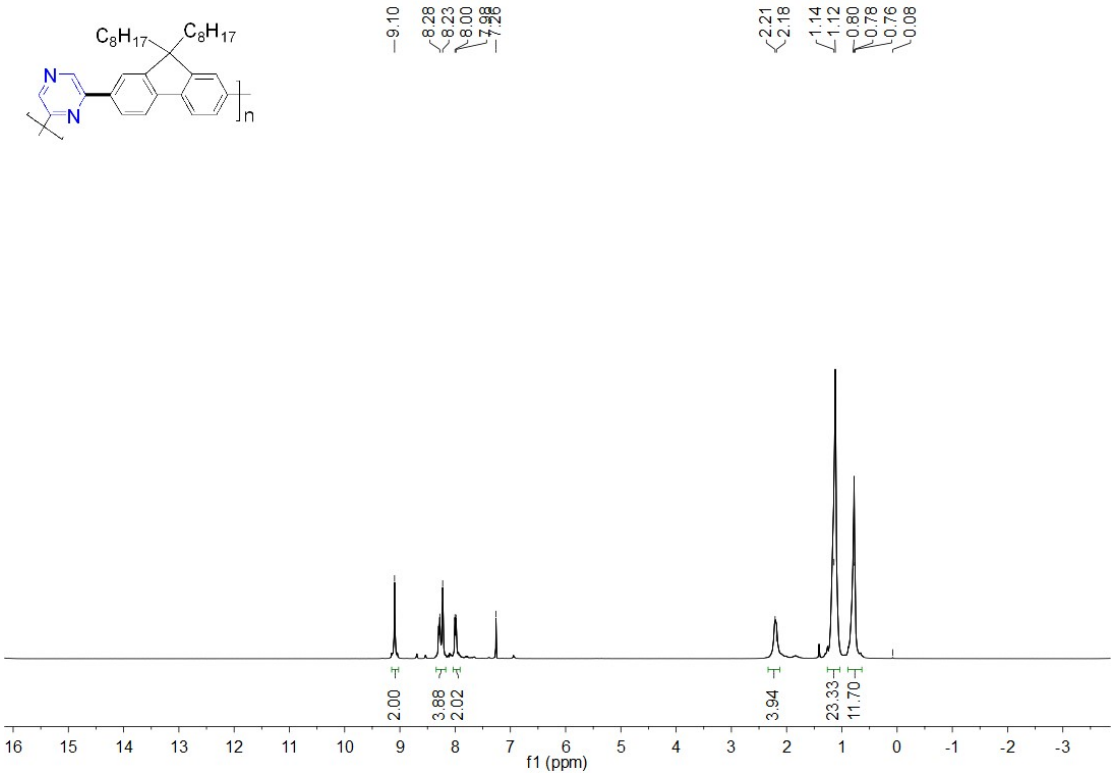


Figure S11. The NMR spectrums of **P1**.

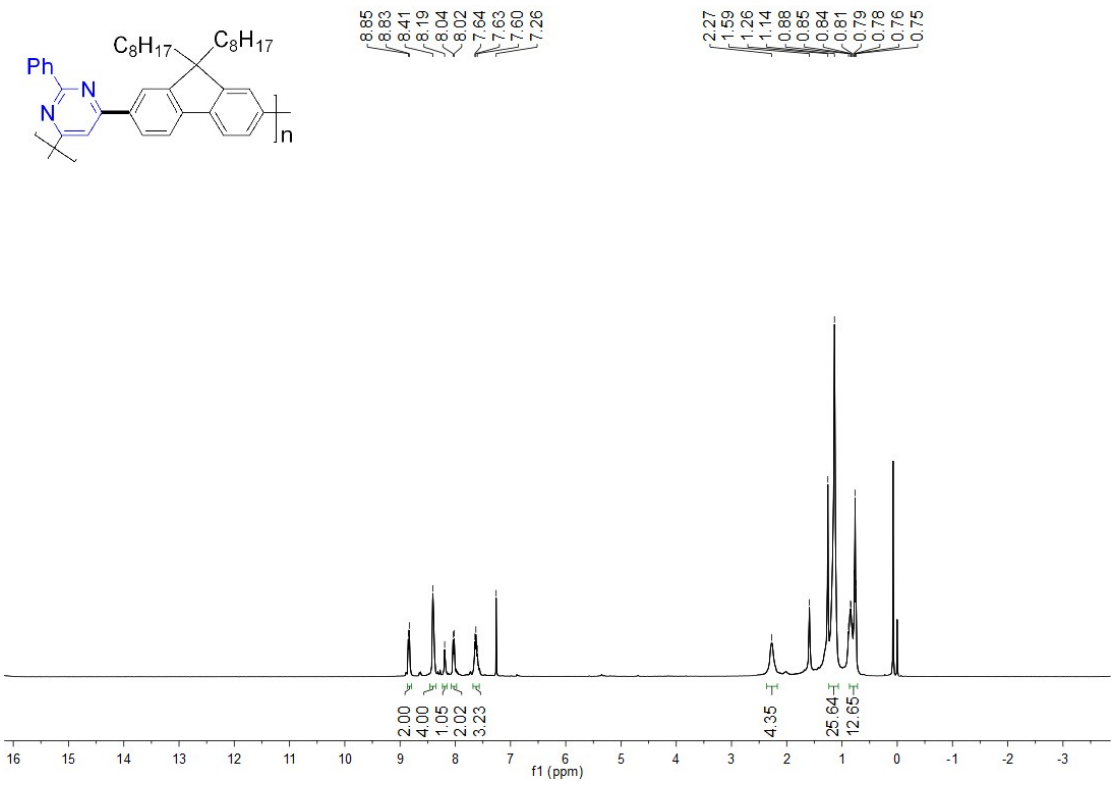


Figure S12. The NMR spectrums of **P2**.

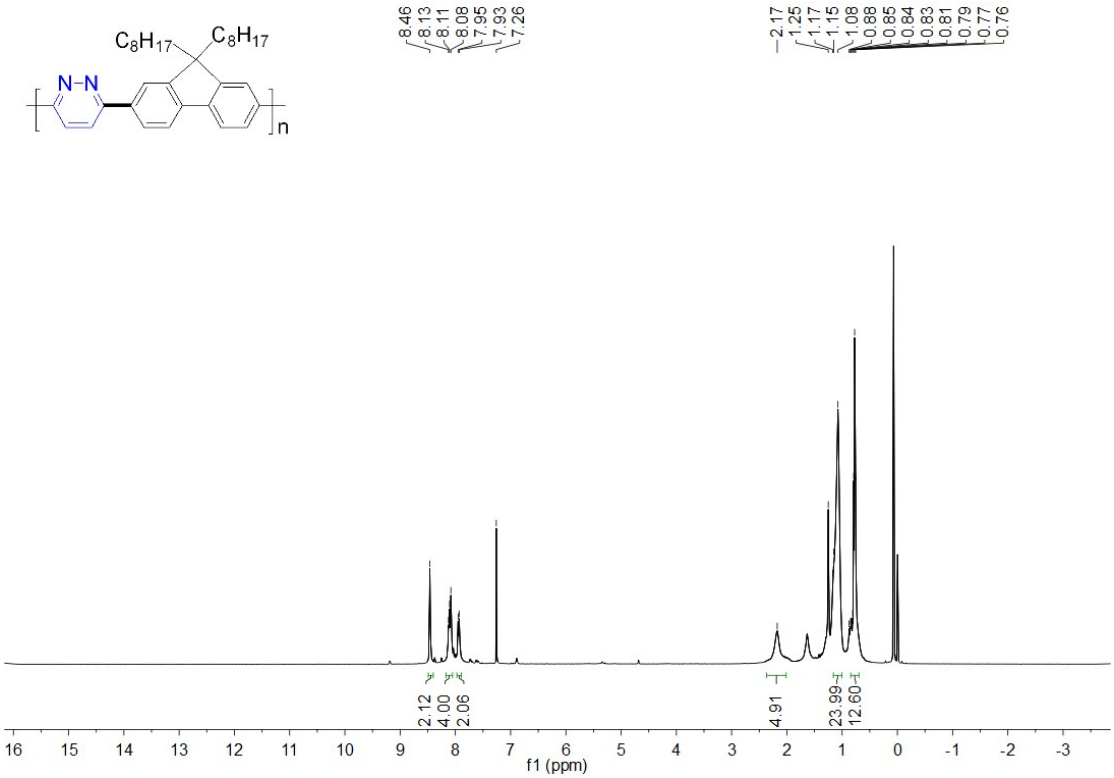


Figure S13. The NMR spectrums of **P3**.

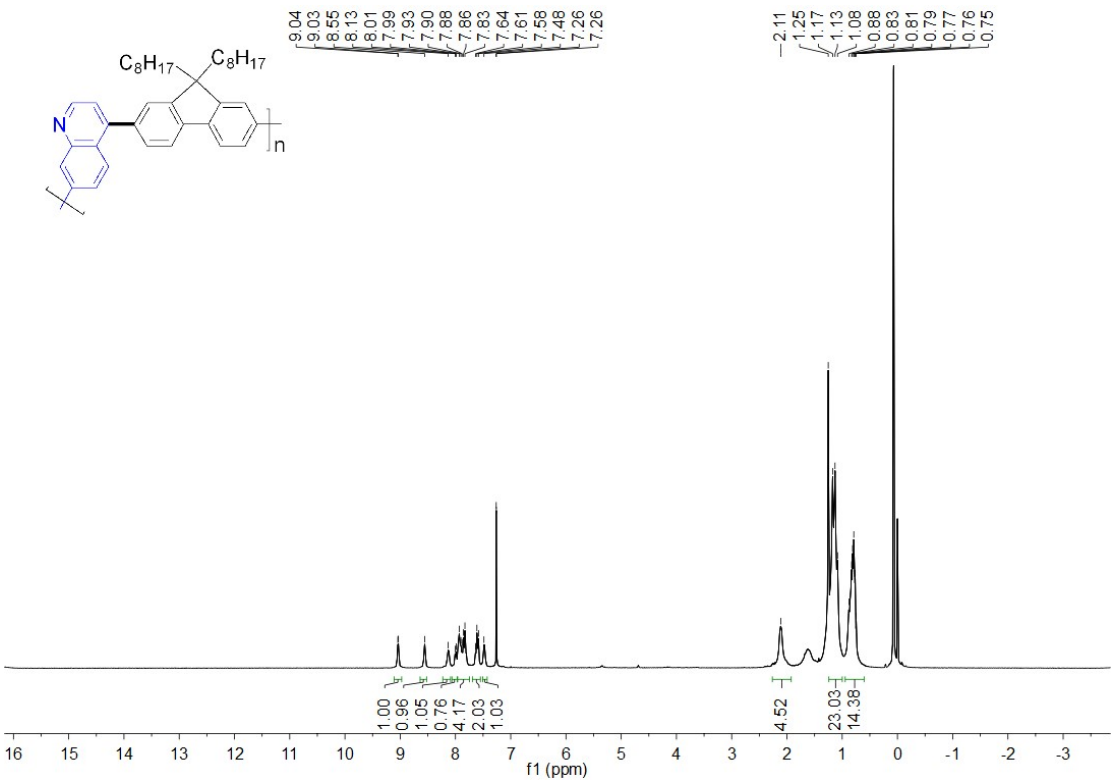


Figure S14. The NMR spectrums of **P4**.

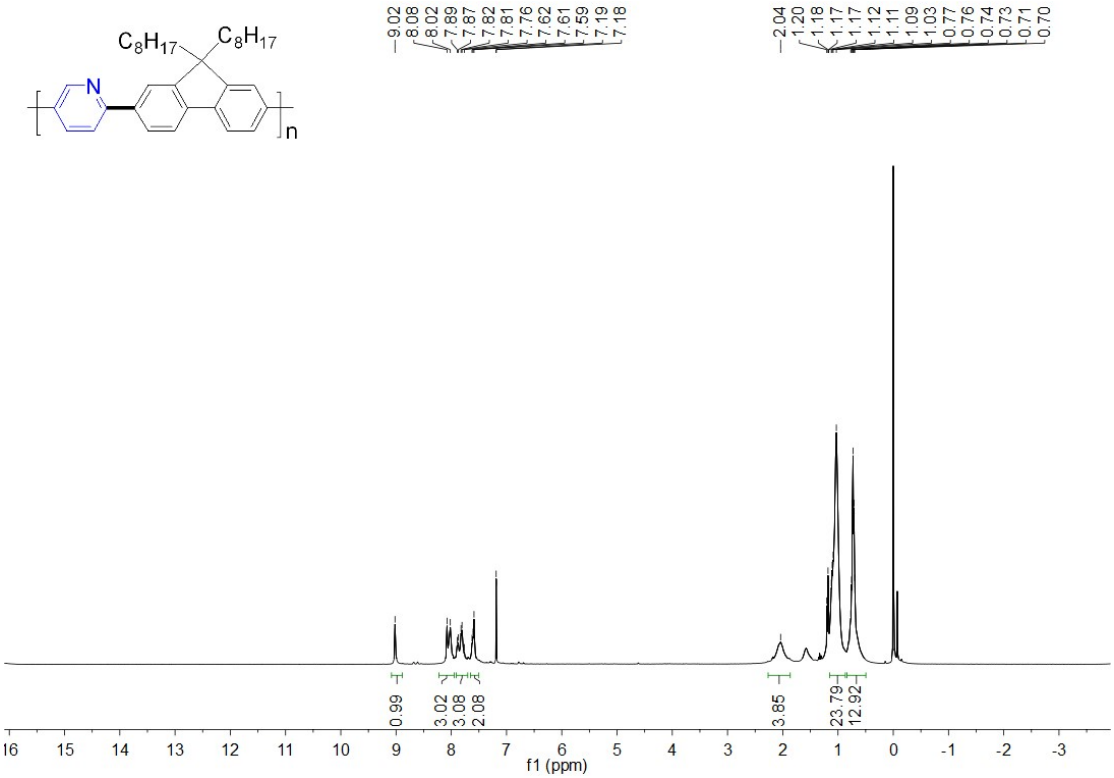


Figure S15. The NMR spectrums of **P5**.

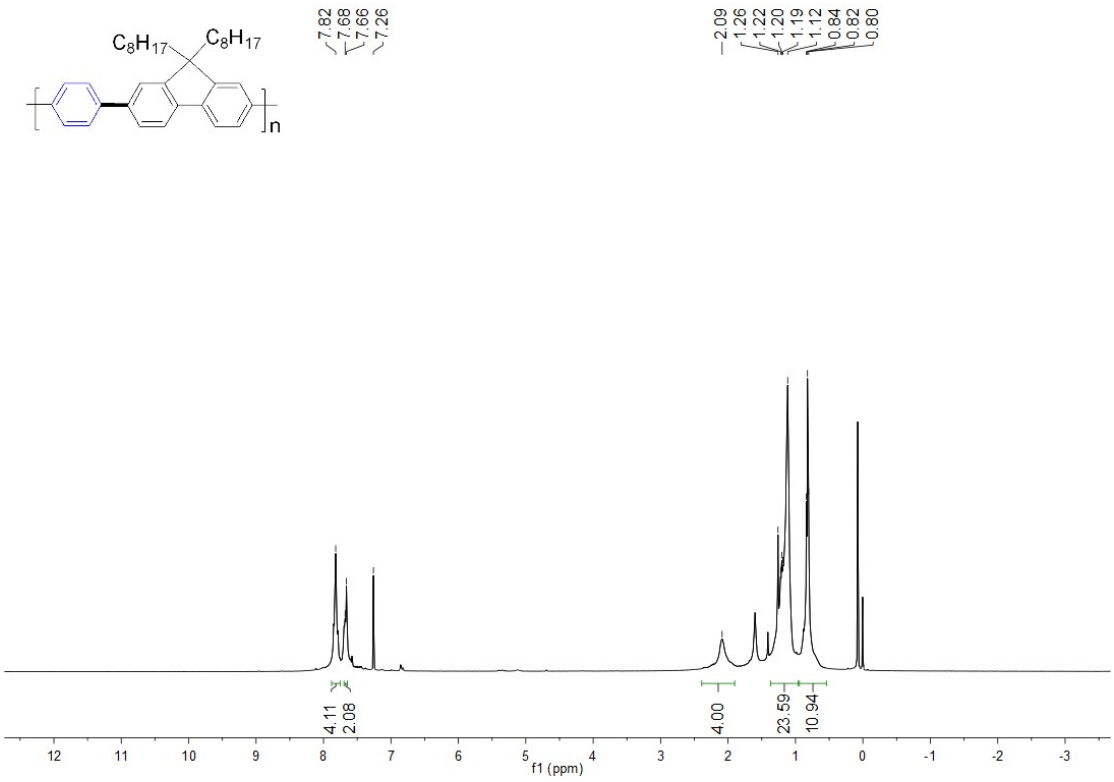


Figure S16. The NMR spectrums of **P6**.

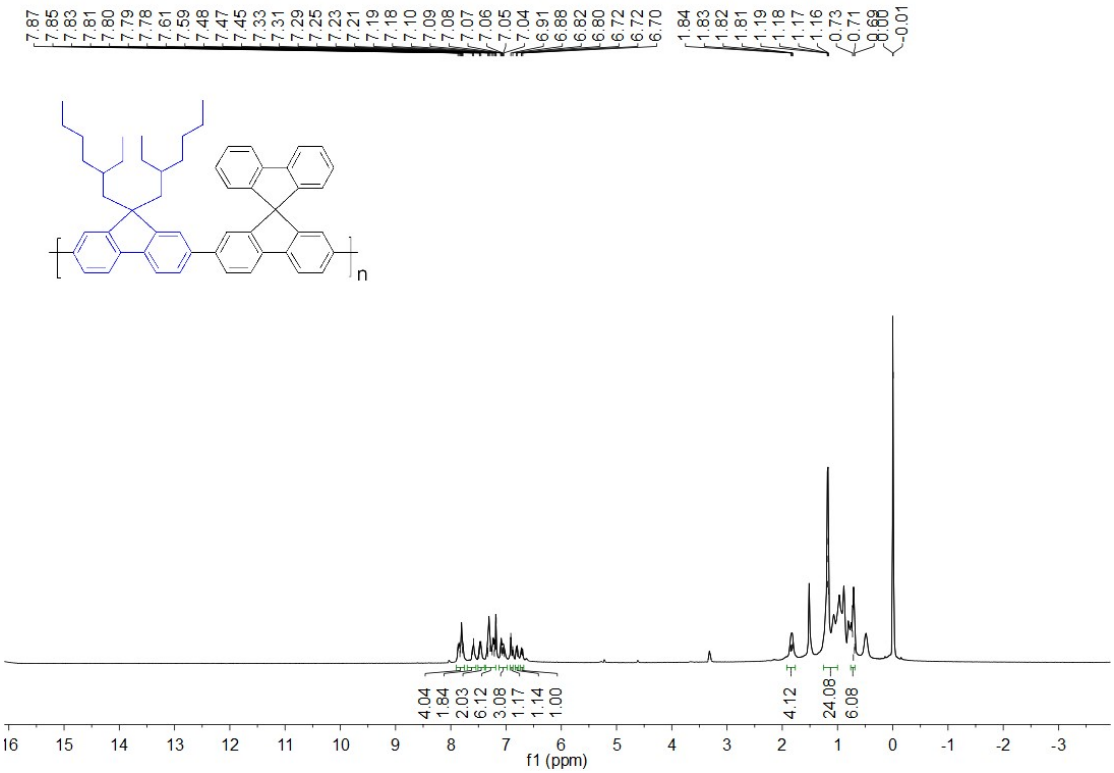


Figure S17. The NMR spectrums of **P7**.

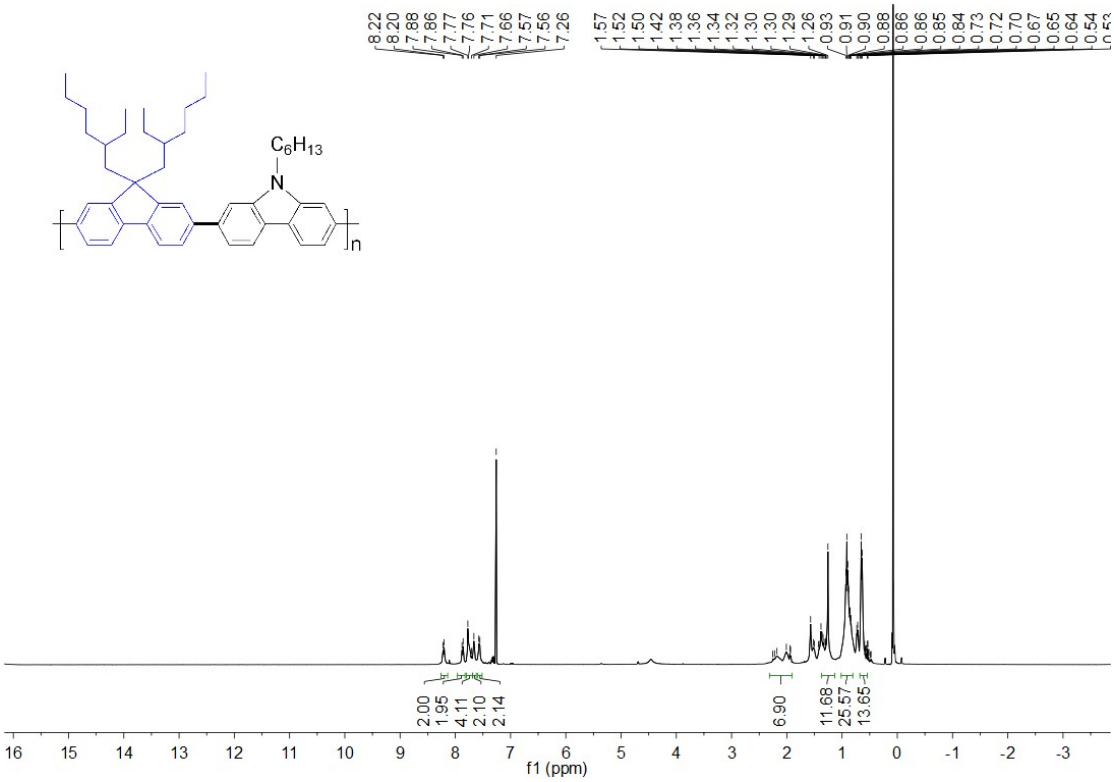


Figure S18. The NMR spectrums of **P8**.

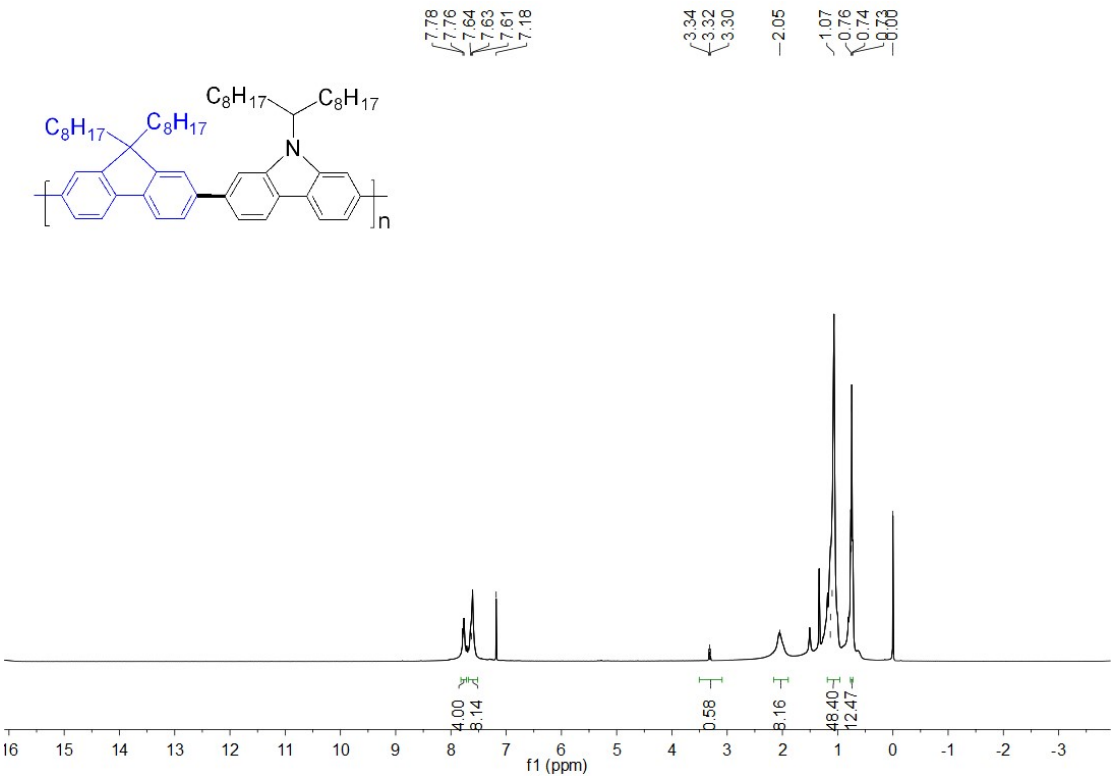


Figure S19. The ^{1}H NMR spectrum of **P9**

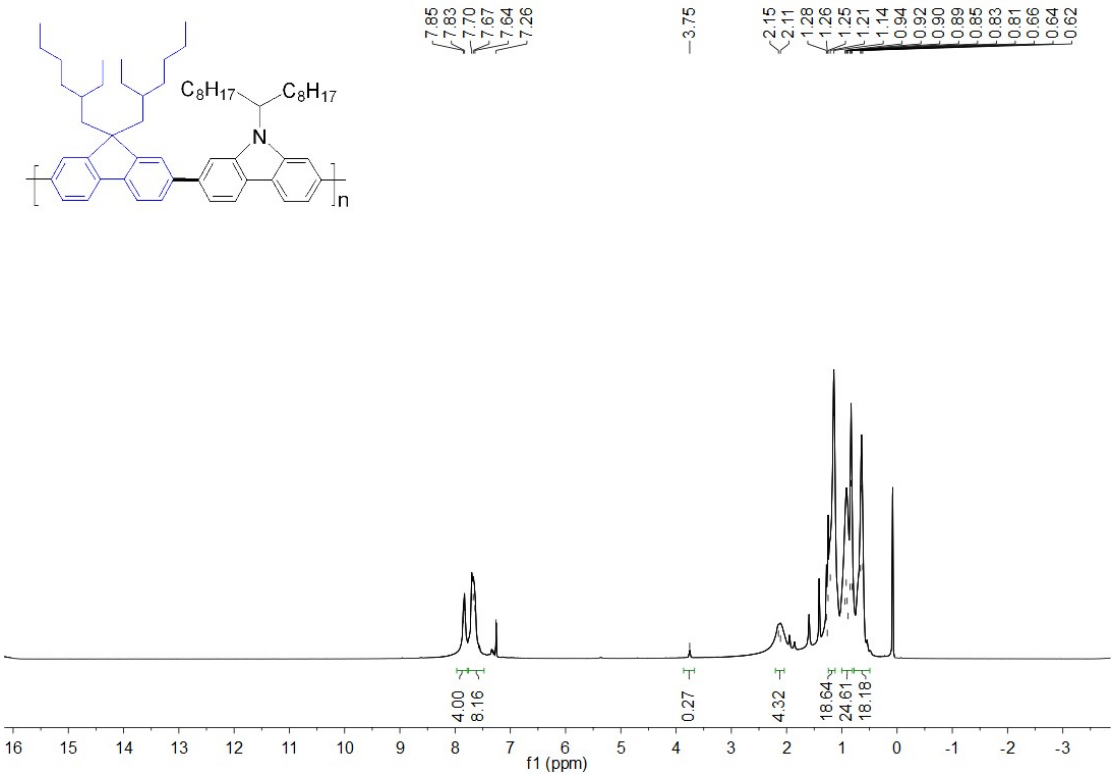


Figure S20. The ^{1}H NMR spectrum of **P10**

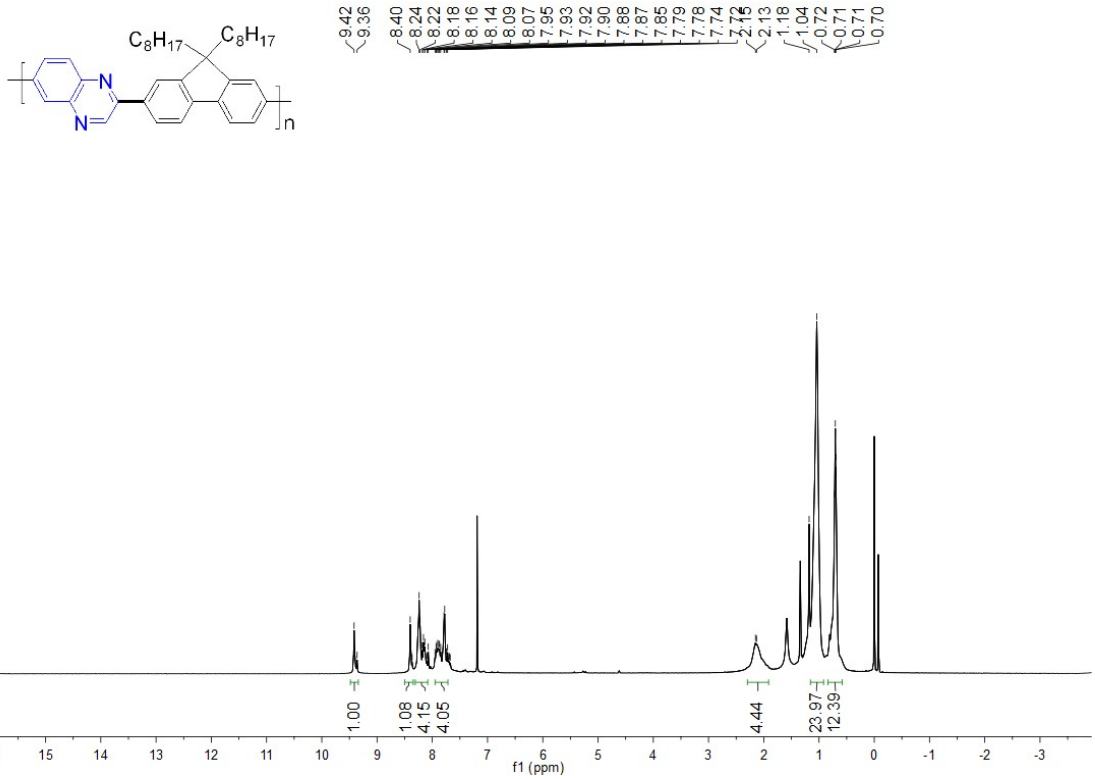


Figure S21. The ^{1}H NMR spectrum of **P11**

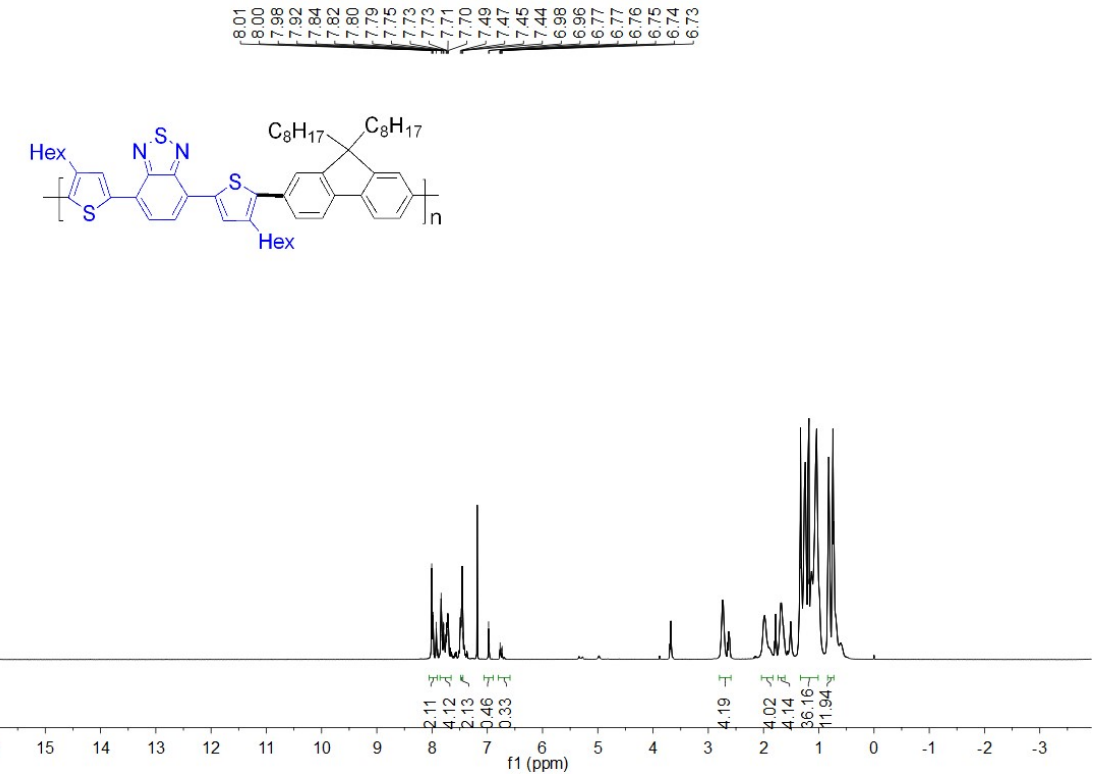


Figure S22. The ^{1}H NMR spectrum of **P12**

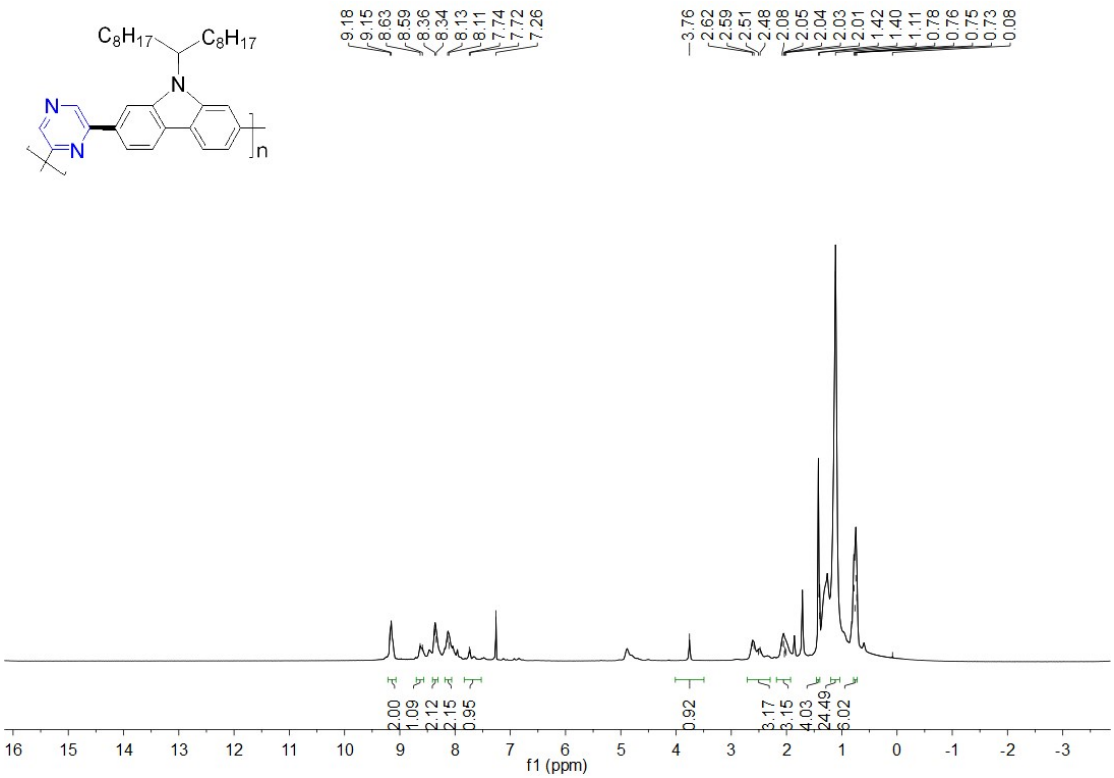


Figure S23. The ^{1}H NMR spectrum of **P13**

4. Single-crystal data for NHC-Pd catalysts

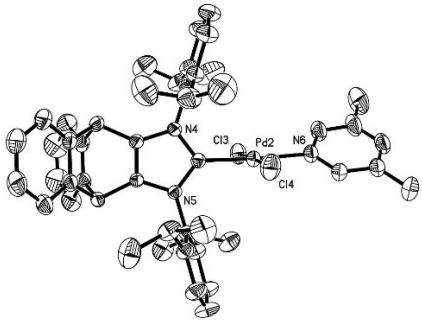


Table S1. Crystal data and structure refinement for C2.

Identification code	**C2**
Empirical formula	$C_{48}H_{53}Cl_2N_3Pd$
Formula weight	849.23
Temperature/K	292.98(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.49350(10)
b/Å	17.71260(10)
c/Å	22.0093(2)
α/°	100.5540(10)
β/°	103.9520(10)
γ/°	96.6100(10)
Volume/Å^3	4581.63(7)
Z	4
ρ_{calc}g/cm^3	1.231
μ/mm^{-1}	4.588
F(000)	1768.0
Crystal size/mm^3	0.15 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.148 to 147.086
Index ranges	-11 ≤ h ≤ 15, -22 ≤ k ≤ 21, -25 ≤ l ≤ 27
Reflections collected	70868
Independent reflections	17881 [R_{int} = 0.0472, R_{sigma} = 0.0373]
Data/restraints/parameters	17881/0/993
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0444, wR_2 = 0.1191
Final R indexes [all data]	R_1 = 0.0540, wR_2 = 0.1250
Largest diff. peak/hole / e Å^{-3}	2.27/-0.79

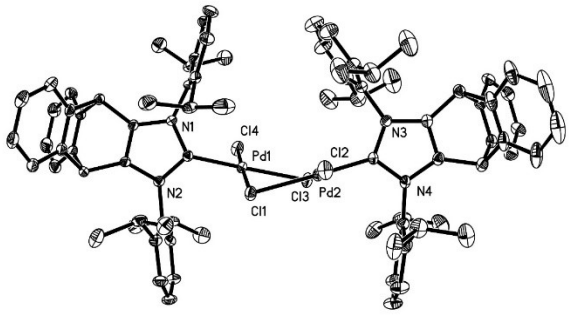


Table S2. Crystal data and structure refinement for C4.

Identification code	**C4**
Empirical formula	$C_{82}H_{88}Cl_4N_4Pd_2$
Formula weight	1484.16
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.9002(4)
b/Å	27.2207(10)
c/Å	20.8068(7)
α/°	90
β/°	90.068(3)
γ/°	90
Volume/Å^3	7306.4(4)
Z	4
ρ_{calc}g/cm^3	1.349
μ/mm^{-1}	5.665
F(000)	3072.0
Crystal size/mm^3	0.15 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.346 to 147.736
Index ranges	$-16 \le h \le 15$, $-33 \le k \le 32$, $-25 \le l \le 24$
Reflections collected	42105
Independent reflections	14193 [R_{int} = 0.1102, R_{sigma} = 0.1261]
Data/restraints/parameters	14193/0/845
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0699, wR_2 = 0.1575
Final R indexes [all data]	R_1 = 0.1117, wR_2 = 0.1778
Largest diff. peak/hole / e Å^{-3}	0.92/-0.95

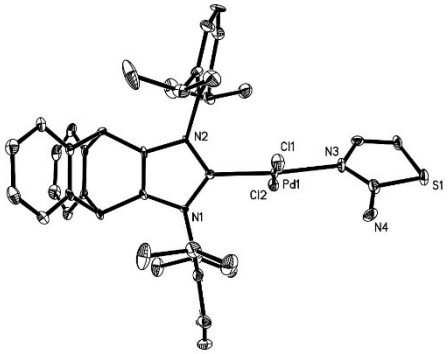


Table S3. Crystal data and structure refinement for C5.

Identification code	**C5**
Empirical formula	$C_{45}H_{50}Cl_4N_4PdS$
Formula weight	927.15
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.0079(2)
b/Å	24.0698(3)
c/Å	13.9399(2)
α/°	90
β/°	101.1780(10)
γ/°	90
Volume/Å^3	4281.75(11)
Z	4
ρ_{calc}g/cm^3	1.438
μ/mm^{-1}	6.530
F(000)	1912.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.346 to 133.156
Index ranges	-12 ≤ h ≤ 15, -28 ≤ k ≤ 28, -16 ≤ l ≤ 16
Reflections collected	32142
Independent reflections	7580 [R_{int} = 0.0571, R_{sigma} = 0.0401]
Data/restraints/parameters	7580/0/512
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0469, wR_2 = 0.1193
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.1227
Largest diff. peak/hole / e Å^{-3}	1.96/-0.97

5. References

1 Y.-M. Guo, Y. Zhang, M.-J. Zhang, T. Li, J.-Y. Wu and F.-S. Liu, Heteroaryl–Heteroaryl Suzuki–Miyaura Cross-Coupling Enabled by Large-but-Flexible Dibenzobarrelene-Derived Pd-NHC Precatalysts, *Organometallics.*, 2023, **42**, 2028-2037.