Electronic Supplementary Material (ESI) for RSC Advances.

Utility of a Heterogeneous Palladium Catalyst for the Synthesis of a Molecular Semiconductor *via* Stille, Suzuki, and Direct Heteroarylation Cross-Coupling Reactions

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SUPPORTING INFORMATION

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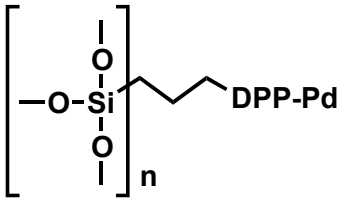
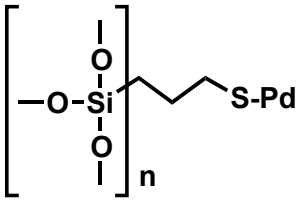
Silia*Cat*® Heterogeneous Catalysts

Table S1: Silia*Cat*® Heterogeneous Catalyst Information.

Heterogeneous Catalyst	 **DPP-Pd**	 **S-Pd**
Loading	0.2 – 0.4 mmol/g	0.4 – 0.6 mmol/g
Pore Size	25 – 70 Å	
Surface Area	300 – 650 m^2/g	
Particle Size Distribution	60 – 250 μm	

Product information available online: http://www.silicycle.com/ca/products/siliacat-heterogeneous-catalysts/siliacat-heterogeneous-catalysts-product-range

Starting Materials Solution ^{1}H NMR Spectra

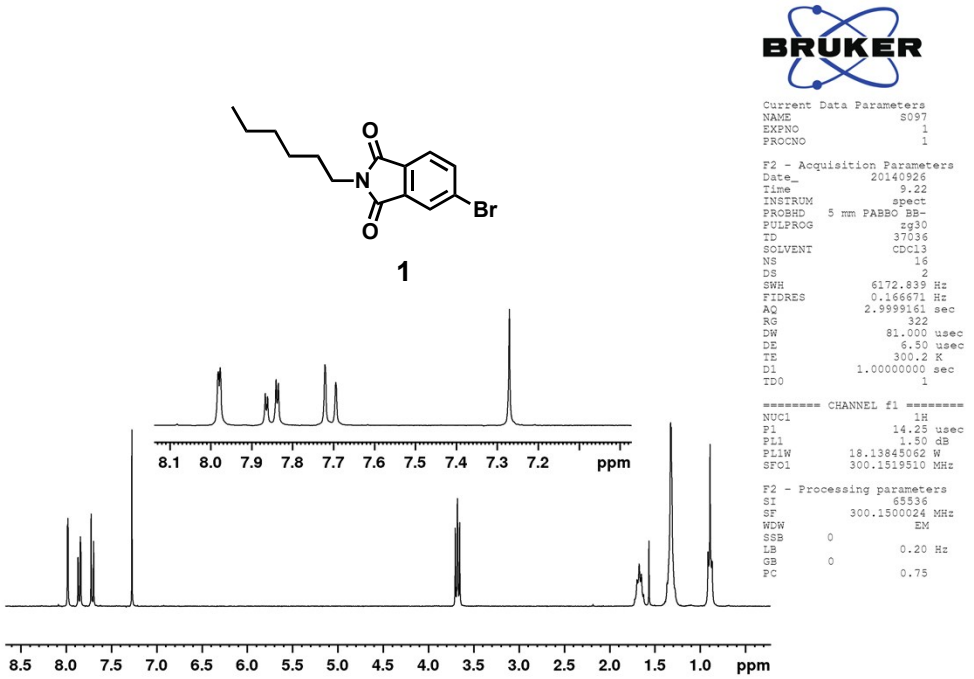


Figure S1: ^{1}H NMR spectra of starting material **1** in $CDCl_3$.

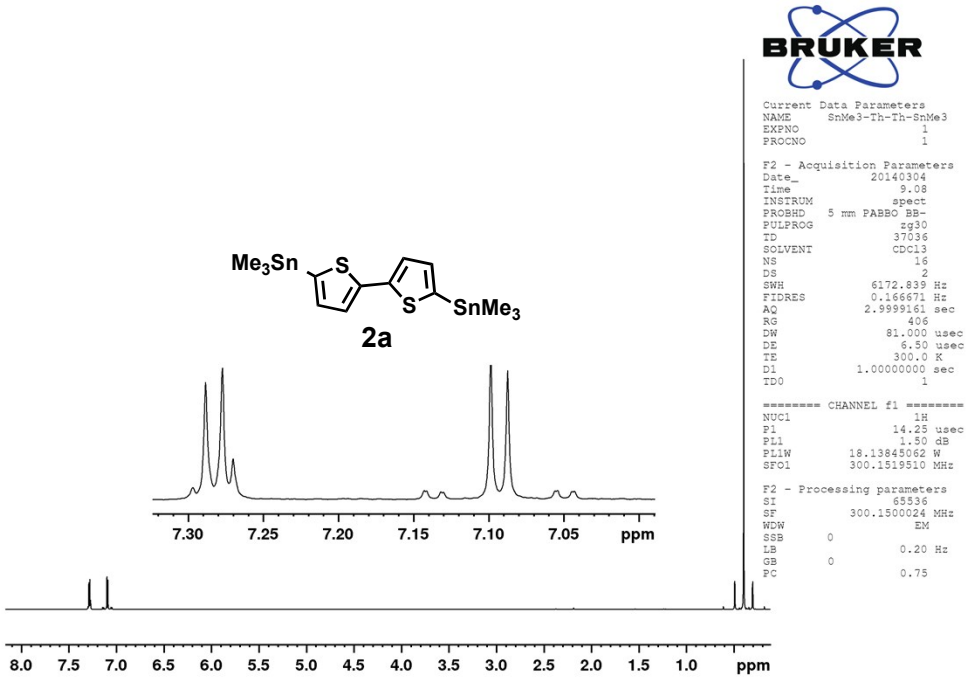


Figure S2: ^{1}H NMR spectra of starting material **2a** in $CDCl_3$.

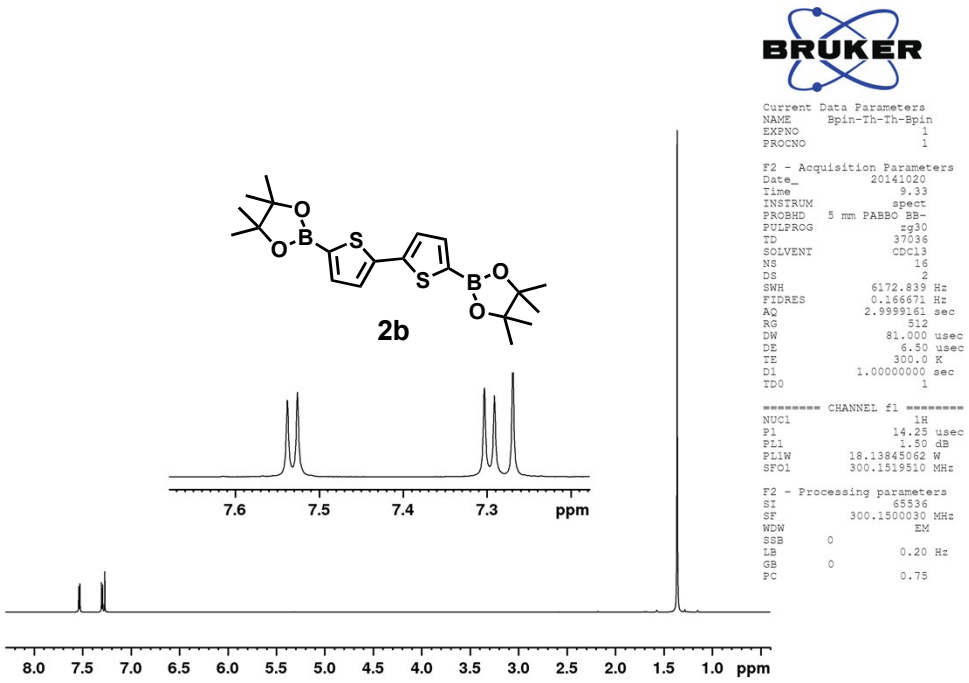


Figure S3: ^{1}H NMR spectra of starting material **2b** in $CDCl_3$.

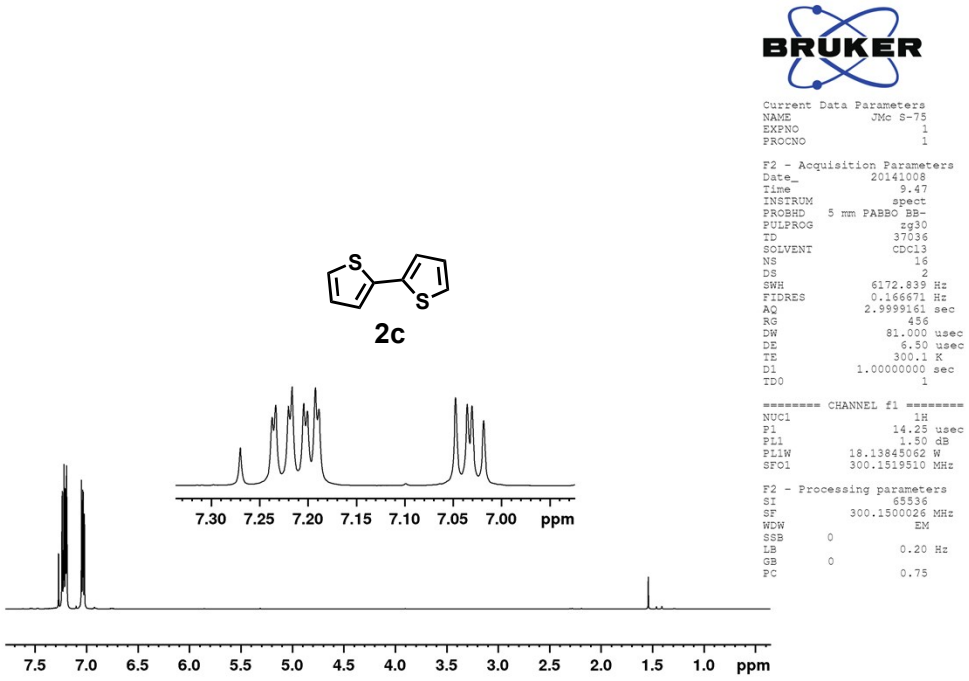


Figure S4: ^{1}H NMR spectra of starting material **2c** in $CDCl_3$.

Product ^{1}H NMR Spectrum

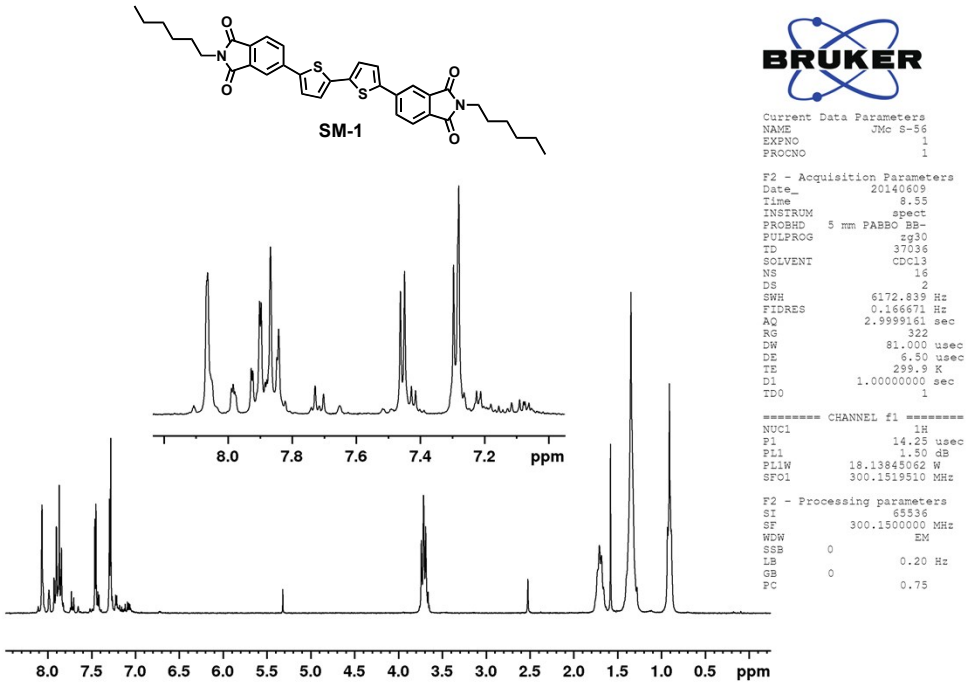


Figure S5: Aromatic region ^{1}H NMR spectra of **SM-1** in $CDCl_3$ with 5.0 mol % catalyst loading under ambient conditions *via* conventional heating methods.

Product 2-D ^{1}H NMR Spectrum

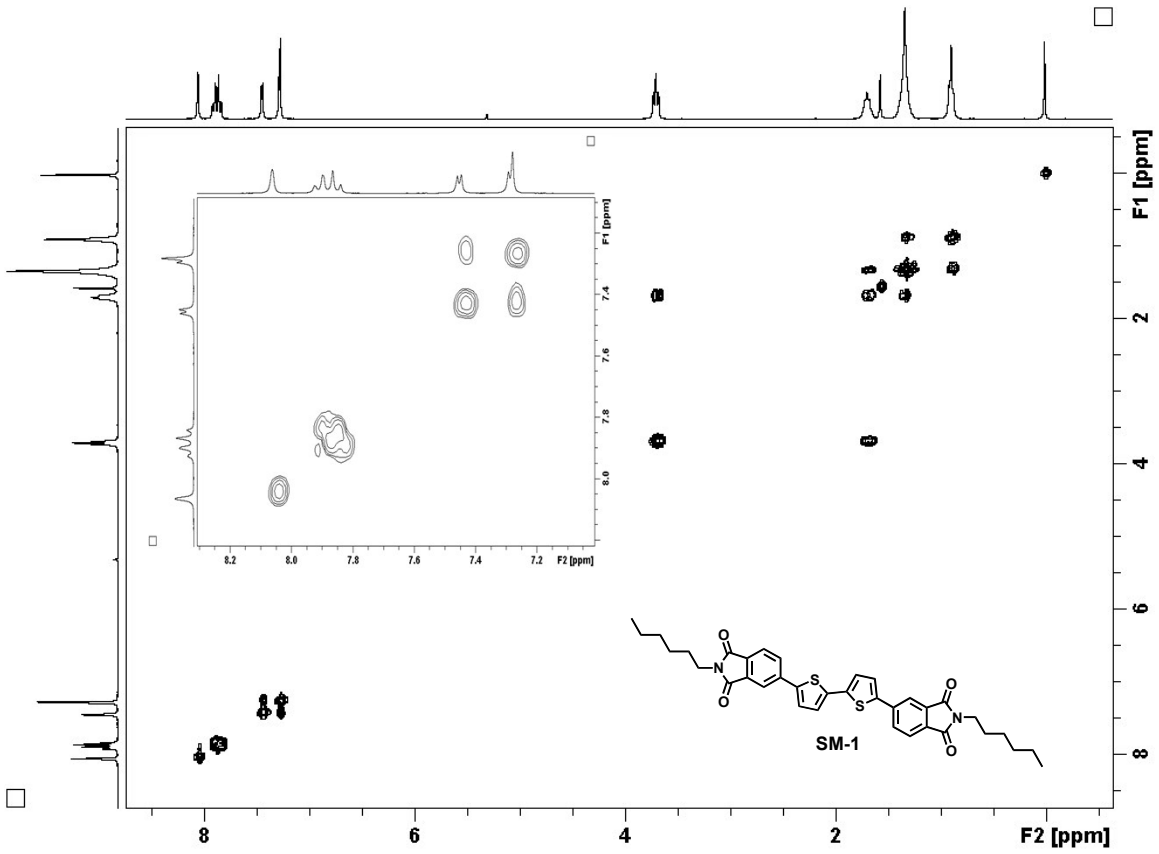


Figure S6: 2-D COSY ^{1}H NMR spectra of the direct heteroarylation product **SM-1** in $CDCl_3$.

ICP-OES Pd Analysis

Table S1: Trace Pd Analysis for the Synthesis of **SM-1** at 5.0 mol % Catalyst Loading *via* Conventional Heating Method.

Catalyst	**Material Yield**		**Pd Content (mg/L)**
$Pd(PPh_3)_4$	0.209 g	82 %	26.25
Silia*Cat*® DPP-Pd	0.251 g	98 %	0.08*

* Detection limit of the instrument.

Samples were prepared from 10 mg of a given material, which was digested with 1.0 mL of 70 wt. % HNO_3 followed by 1.0 mL of 37 wt. % HCl. The contents were allowed to react in air for several hours and then loosely capped and set to stand overnight. Solid particulates were subsequently removed by filtering the solution through a 0.45 μm PTFE filter and sealed in a new vial.

The prepared samples were submitted to Dalhousie University Minerals Engineering Centre (MEC) for trace Pd analysis. The instrument used was a Varian Vista Pro ICP-OES equipped with an OneNeb nebulizer and a glass cyclonic chamber. The prepared samples were diluted 10-fold into 10 % HCl aqueous solution and measurements were taken with the spectral line 340.458 nm, the preferred line for Pd analysis.

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