

## Supplementary Information

# Metal-Mediated Coupling of a Coordinated Isocyanide and Indazoles

**Mikhail A. Kinzhalov,<sup>a</sup> Vadim P. Boyarskiy,<sup>a\*</sup> Konstantin V. Luzyanin,<sup>a,b</sup>**

**Fedor M. Dolgushin,<sup>c</sup> Vadim Yu. Kukushkin<sup>a,d</sup>**

Department of Chemistry, Saint Petersburg State University, Petrodvorec, Universitetskiy pr. 26, 198504 Saint Petersburg, Russian Federation; Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 7ZD, United Kingdom; A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova Street 28, 119991 Moscow, Russian Federation; Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoi Pr. 31, 199004 Saint Petersburg, Russian Federation.

(a) Saint Petersburg State University. E-mail: vadimpb@yahoo.com; (c) University of Liverpool.

(d) A. N. Nesmeyanov Institute of Organoelement Compounds. (e) Institute of Macromolecular Compounds.

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## 1. Experimental

### 1.1. Materials and Instrumentation

Solvents, PdCl<sub>2</sub>, indazole (**2**), 2,4-dimethylaniline and cyclohexyl isocyanide were obtained from commercial sources and used as received, apart from chloroform, which was purified by the conventional distillation over calcium chloride. 5-Methyl-1*H*-indazole (**3**) was prepared by the literature method from 2,4-dimethylaniline.<sup>1</sup> Complex **1** was synthesised by the known procedure.<sup>2</sup> C, H, and N elemental analysis was carried out by the elemental analysis service at the Chemistry Department of Saint Petersburg State University on a Euro EA 3028HT CHNSO analyzer. Mass-spectra were obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source, MeCN was used as the solvent. The instrument was operated both at positive and negative ion modes using *m/z* range of 50–3000. The capillary voltage of the ion source was set at –4500 V (ESI<sup>+</sup>) or 3500 V (ESI<sup>–</sup>) and the capillary exit at ±(70–150) V. The nebulizer gas pressure was 0.4 bar and drying gas flow 4.0 L/min. The most intensive peak in the isotopic pattern is reported. Infrared spectra were recorded on a Shimadzu FTIR 8400S instrument (4000–400 cm<sup>–1</sup>) and on a Bruker Tensor 27 FTIR instrument (400–200 cm<sup>–1</sup>) in KBr pellets. 1D (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, DEPT) NMR spectra were acquired on a Bruker-DPX 300 and Bruker Avance 400 spectrometers, while 2D (<sup>1</sup>H, <sup>1</sup>H-COSY, <sup>1</sup>H, <sup>13</sup>C-HMQC/HSQC, and <sup>1</sup>H, <sup>13</sup>C-HMBC) NMR correlation experiments were recorded on Bruker Avance II+ 500 MHz (UltraShield Magnet) spectrometer, at ambient temperature. Melting points were determined in a capillary on a Büchi Melting Point 530 Apparatus.

### 2.2. Reaction of [PdCl<sub>2</sub>(CNCy)<sub>2</sub>] with the indazoles

A solution of **2** or **3** (0.15 mmol) in CHCl<sub>3</sub> (3 mL) was added to a solution of **1** (60 mg, 0.15 mmol) in CHCl<sub>3</sub> (4 mL) and the reaction mixture was refluxed for 6 h. During this period, the colour of the mixture was gradually turned from pale yellow to bright yellow. After 6 h, the reaction mixture was

evaporated at 20–25 °C, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL), and diluted with Et<sub>2</sub>O (6 mL).

The title products were crystallized slowly at 18–22 °C.

**4**•CH<sub>2</sub>Cl<sub>2</sub> (65 mg, 72%). Anal. Calcd. for C<sub>22</sub>H<sub>30</sub>N<sub>4</sub>Cl<sub>4</sub>Pd: C, 44.13; H, 5.05; N, 9.36. Found: C, 44.35; H, 5.07; N, 9.42. ESI<sup>+</sup>-MS, *m/z*: calcd. for C<sub>21</sub>H<sub>27</sub>N<sub>4</sub>Pd<sup>+</sup> 441.1273, found 441.1267 [M – 2Cl – H]<sup>+</sup>. ESI<sup>–</sup>-MS, *m/z*: calcd. for C<sub>21</sub>H<sub>27</sub>N<sub>4</sub>Cl<sub>2</sub>Pd<sup>–</sup> 511.0653, found 511.0667 [M – H]<sup>–</sup>. IR (KBr, selected bands, cm<sup>–1</sup>): ν(N–H) 3141–3043 (m), ν(C–H) 2936–2855 (m), ν(C≡N) 2237 (s), ν(N–C<sub>carbene</sub>) 1566 (s), ν(Pd–Cl) 320 (s), 296 (s). <sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>, δ, ): 1.17–1.90 (m, 18H, CH<sub>2</sub>), 2.02–2.15 (m, 1H, CH<sub>2</sub>), 2.38–2.47 (m, 1H, CH<sub>2</sub>), 3.73–3.84 (m, 1H, C≡NCH), 4.95–5.10 (m, 1H, NHCH), 5.29 (s, 1H, CH<sub>2</sub>Cl<sub>2</sub>), 7.43 (dd, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 1H, C<sup>5</sup>–H from the indazole ring), 7.69 (dd, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 1H, C<sup>6</sup>–H from the indazole ring), 7.77 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 1H, C<sup>4</sup>–H from the indazole ring), 8.26 (c, 1H, C<sup>3</sup>–H from the indazole ring), 9.20 (d, <sup>3</sup>J<sub>H,H</sub> = 10.2 Hz, 1H, C<sub>carbene</sub>–NH), 9.96 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 1H, C<sup>7</sup>–H from the indazole ring). <sup>13</sup>C{<sup>1</sup>H} NMR (75.47 MHz, CDCl<sub>3</sub>, δ): 21.8 (CH<sub>2</sub>), 21.9 (CH<sub>2</sub>), 24.1 (CH<sub>2</sub>), 24.4 (2C, CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 32.5 (CH<sub>2</sub>), 33.2 (CH<sub>2</sub>), 53.4 (C≡NCH), 55.3 (NHCH), 61.1 (CH<sub>2</sub>Cl<sub>2</sub>), 114.6 (CH, C<sup>7</sup> from the indazole ring), 121.0 (C, C≡N), 122.0 (CH, C<sup>4</sup> from the indazole ring), 125.4 (CH, C<sup>5</sup> from the indazole ring), 127.3 (C, C<sup>9</sup> from the indazole ring), 130.6 (CH, C<sup>6</sup> from the indazole ring), 141.7 (C, C<sup>8</sup> from the indazole ring), 142.8 (CH, C<sup>3</sup> from the indazole ring), 181.5 (C<sub>carbene</sub>). Melting point of complex **4**•CH<sub>2</sub>Cl<sub>2</sub> is 128 °C with decomposition to furnish a dark brown residue.

**5** (66 mg, 83%). Anal. Calcd. for C<sub>22</sub>H<sub>30</sub>N<sub>4</sub>Cl<sub>2</sub>Pd: C, 50.06; H, 5.73; N, 10.61. Found: C, 50.11; H, 5.76; N, 10.58. ESI<sup>+</sup>-MS, *m/z*: calcd. for C<sub>22</sub>H<sub>30</sub>N<sub>4</sub>ClPd<sup>+</sup> 491.1188, found 491.1174 [M – Cl]<sup>+</sup>, calcd. for C<sub>22</sub>H<sub>29</sub>N<sub>4</sub>Pd<sup>+</sup> 455.1422, found 455.1426 [M – 2Cl – H]<sup>+</sup>. ESI<sup>–</sup>-MS, *m/z*: calcd. for C<sub>22</sub>H<sub>29</sub>N<sub>4</sub>Cl<sub>2</sub>Pd<sup>–</sup> 525.0810, found 525.0824 [M – H]<sup>–</sup>. IR (KBr, selected bands, cm<sup>–1</sup>): ν(N–H) 3250–3040 (m), ν(C–H) 2936–2856 (m), ν(C≡N) 2233 (s), ν(N–C<sub>carbene</sub>) 1520 (s), ν(Pd–Cl) 323 (s), 290 (s). <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, δ, ): 1.19–1.83 (m, 18H, CH<sub>2</sub>), 2.06–2.13 (m, 1H, CH<sub>2</sub>), 2.40–2.45 (m, 1H, CH<sub>2</sub>), 2.49 (s, 1H, CH<sub>3</sub>), 3.77–3.82 (m, 1H, C≡NCH), 4.97–5.07 (m,

1H, NHCH), 7.52–7.54 (m, 2H, C<sup>4</sup>-H and C<sup>6</sup>-H from the indazole ring), 8.18 (s, 1H, C<sup>3</sup>-H from the indazole ring), 9.14 (d, <sup>3</sup>J<sub>H,H</sub> = 9.6 Hz, 1H, C<sub>carbene</sub>-NH), 9.82 (d, <sup>3</sup>J<sub>H,H</sub> = 9.2 Hz, 1H, C<sup>7</sup>-H from the indazole ring). <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, CDCl<sub>3</sub>, δ): 21.2 (CH<sub>3</sub>), 21.8 (CH<sub>2</sub>), 21.9 (CH<sub>2</sub>), 24.1 (CH<sub>2</sub>), 24.2 (CH<sub>2</sub>), 24.5 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>), 31.4 (CH<sub>2</sub>), 31.5 (CH<sub>2</sub>), 32.6 (CH<sub>2</sub>), 33.3 (CH<sub>2</sub>), 55.3 (C≡NCH), 61.0 (NHCH), 114.3 (CH, C<sup>7</sup> from the from the indazole ring), 121.4 (CH, C<sup>4</sup> from the from the indazole ring), 127.7 (C, C<sup>9</sup> from the from the indazole ring), 132.3 (CH, C<sup>6</sup> from the from the indazole ring), 135.6 (C, C<sup>5</sup> from the from the indazole ring), 140.2 (C, C<sup>8</sup> from the from the indazole ring), 142.7 (CH, C<sup>3</sup> from the from the indazole ring), 181.3 (C<sub>carbene</sub>), the isocyanide carbon atom was not detected. Complex **5** has no specific melting point. On heating it gradually decomposes starting from 175 °C to furnish a dark brown residue.

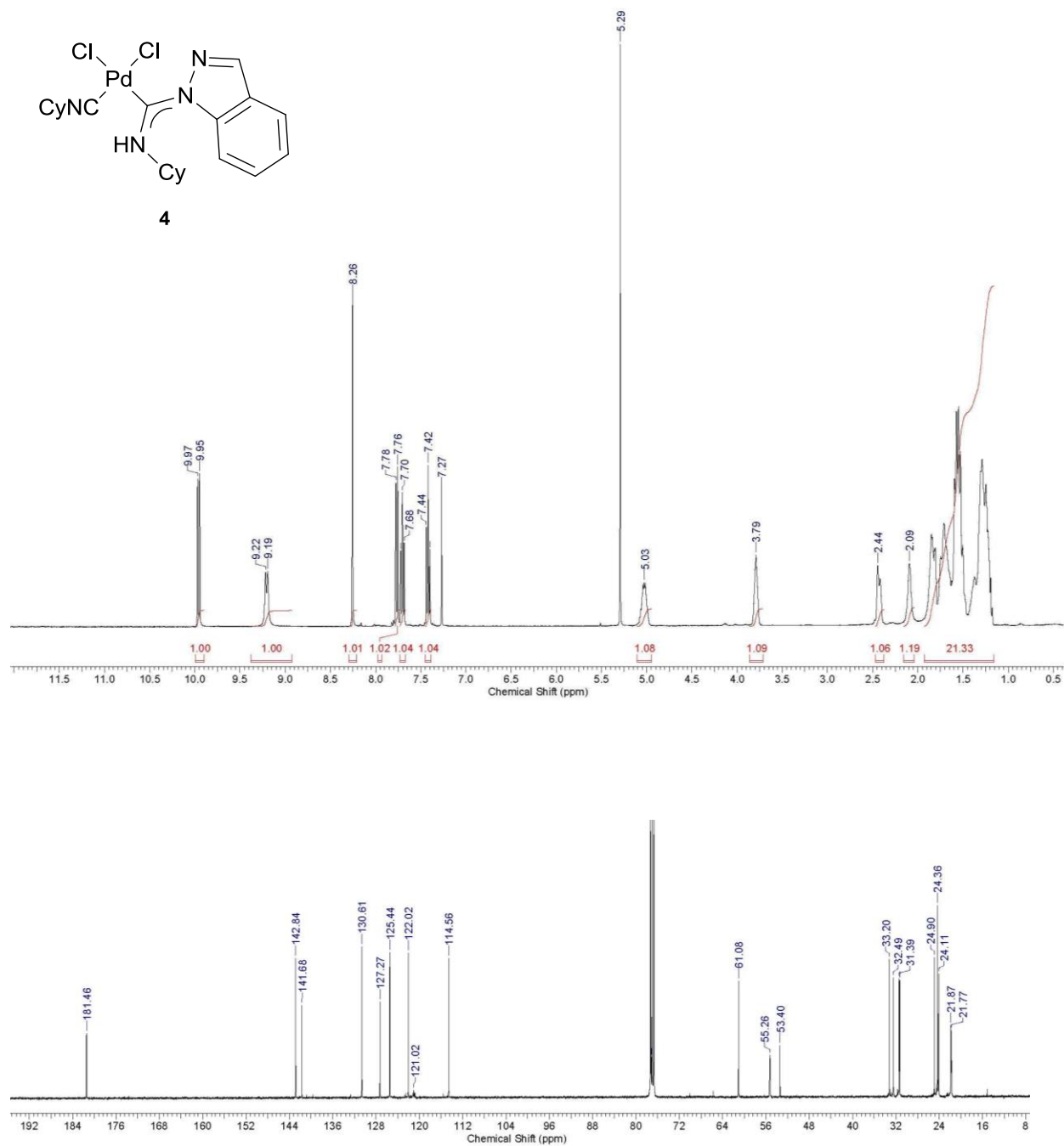
### 1.3. X-Ray diffraction study of 4•CH<sub>2</sub>Cl<sub>2</sub>

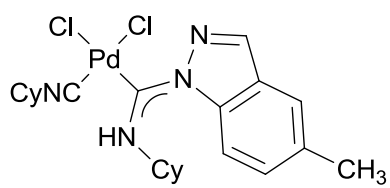
Crystal of 4•CH<sub>2</sub>Cl<sub>2</sub> suitable for X-ray diffraction was obtained upon slow evaporation of a solution of respective compound in CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O mixture under air at room temperature. Single-crystal X-ray diffraction experiment was carried out with a Bruker SMART 1000 CCD diffractometer<sup>3</sup> (graphite monochromated Mo-K<sub>α</sub> radiation, λ = 0.71073 Å, ω-scan technique, T = 120(2) K). A multi-scan absorption correction based on equivalent reflections (SADABS<sup>4</sup>) was applied to the data. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F<sup>2</sup> with the anisotropic thermal parameters for all non-hydrogen atoms using SHELXTL program package.<sup>5</sup> The hydrogen atom of NH group was located from difference Fourier maps and involved in refinement in isotropic approximation. The rest hydrogen atoms were positioned geometrically and included in the structure factors calculations in the riding motion approximation. The crystallographic details are summarized in **Table S1**.

## 2. Crystal data and structure refinement for 4·CH<sub>2</sub>Cl<sub>2</sub>

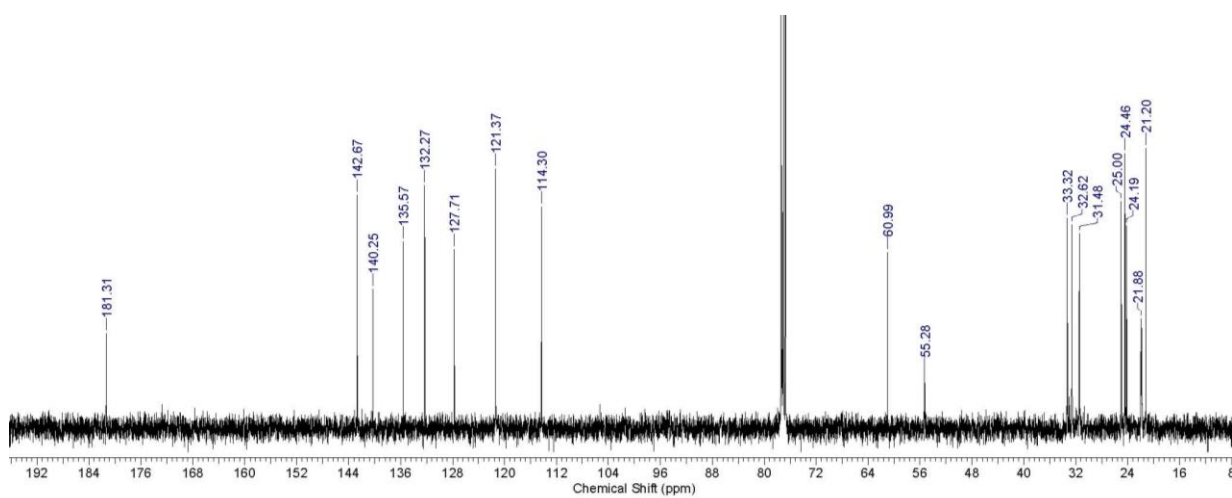
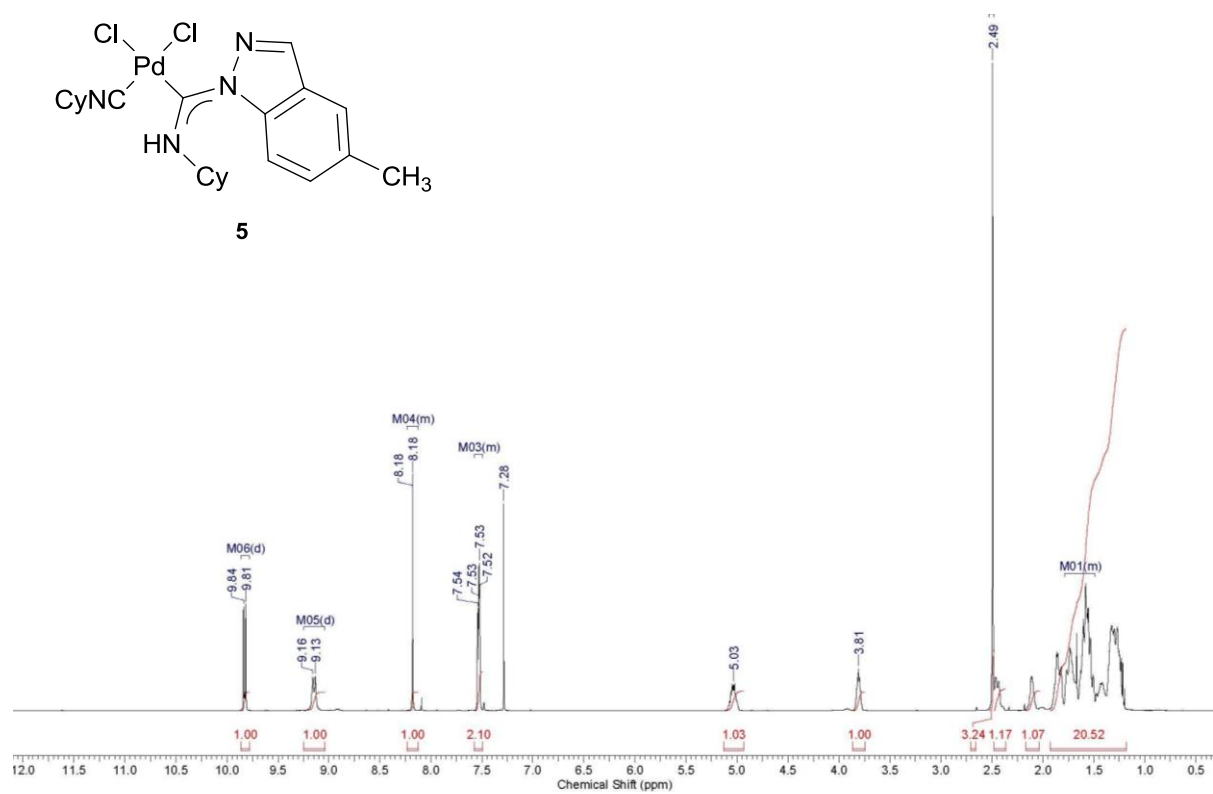
Empirical formula	C <sub>22</sub> H <sub>30</sub> Cl <sub>4</sub> N <sub>4</sub> Pd
Formula weight	598.70
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 21/n
Unit cell dimensions	a = 7.9854(5) Å, α = 90° b = 22.7479(13) Å, β = 105.0570(10)° c = 14.3669(8) Å, γ = 90°
Volume	2520.2(3) Å <sup>3</sup>
Z	4
Density (calculated)	1.578 Mg/m <sup>3</sup>
Absorption coefficient	1.178 mm <sup>-1</sup>
F(000)	1216
Crystal size	0.20 x 0.10 x 0.08 mm <sup>3</sup>
Theta range for data collection	1.72 to 27.00°.
Index ranges	-10 ≤ h ≤ 10, -29 ≤ k ≤ 29, -18 ≤ l ≤ 18
Reflections collected	23681
Independent reflections	5449 [R(int) = 0.0544]
Observed reflections [I > 2σ(I)]	4280
Completeness to theta = 27.00°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.912 and 0.707
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	5449 / 0 / 284
Goodness-of-fit on F <sup>2</sup>	1.073
Final R indices [I > 2σ(I)]	R1 = 0.0391, wR2 = 0.0881
R indices (all data)	R1 = 0.0565, wR2 = 0.0978
Largest diff. peak and hole	0.772 and -0.431 e.Å <sup>-3</sup>

#### 4. $^1\text{H}$ , $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for 4 and 5





5





## 5. References

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