

# **Triply cyclometalated trinuclear iridium(III) and trinuclear palladium(II) complexes with a tri-mesoionic carbene ligand**

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## **Supporting Information**

### **General Procedures.**

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques or in a glove box. Glassware was oven dried at 130 °C. Solvents were distilled by standard procedures prior to use.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on Bruker AVANCE 500 spectrometer or JEOL ECS 400 or JEOL ECP 500 spectrometer. Chemical shifts ( $\delta$ ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz and only given for  $^1\text{H}$ ,  $^1\text{H}$  couplings unless mentioned otherwise. Mass spectra were obtained with Agilent 6210 ESI-TOF. 1,3,5-Tris[4-(2-trimethylsilyl-ethynyl)phenyl]benzene<sup>[1]</sup> and **5**<sup>[2]</sup> were prepared by following the literature procedure.  $\text{PdCl}_2$  and  $[\text{Ir}(\text{Cl})_2\text{Cp}^*]_2$  were purchased from commercial sources and were used as received without further purification.

### **Compound 1.**

1,3,5-Tris[4-(2-trimethylsilyl-ethynyl)phenyl]benzene<sup>[1]</sup> (0.771 g, 1.30 mmol),  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.195 g, 0.781 mmol), sodium ascorbate (0.376 g, 1.90 mmol), ethyl iodide (0.785 g, 5.03 mmol), sodium azide (0.511 g, 7.86 mmol) and  $\text{K}_2\text{CO}_3$  (0.536 g, 3.88 mmol) were suspended in

H<sub>2</sub>O:DMF (10 mL, 8:2, v:v) mixture. To this mixture was added 3 pipette of pyridine. The resulting suspension was stirred at 50 °C for 72 h. The reaction mixture was cooled to ambient temperature and quenched with aqueous Na<sub>2</sub>EDTA/NH<sub>4</sub>OH solution and extracted with dichloromethane. The organic part was dried over MgSO<sub>4</sub>. Removal of the solvent gave a white crude product which was further washed several times with diethyl ether. Yield: 0.512 g (0.865 mmol, 66.5%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.89 (d, <sup>3</sup>J = 8.1 Hz, 6H, H<sub>Ar</sub>), 7.80 (s, 3H, H<sub>Trz</sub>), 7.75 (s, br, 3H, H<sub>Ar</sub>), 7.69–7.67 (m, 6H, H<sub>Ar</sub>), 4.44 (q, <sup>3</sup>J = 7.2 Hz, 6H, N–CH<sub>2</sub>), 1.59 (t, <sup>3</sup>J = 7.2 Hz, 9H, N–CH<sub>2</sub>–CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>): δ = 147.5 (C<sub>Ar</sub>–C<sub>Trz</sub>), 141.9 (C<sub>Trz</sub>–Ar), 140.6 (C<sub>Ar</sub>–C<sub>Ar-central</sub>), 130.1 (C<sub>Ar-central</sub>–C<sub>Ar</sub>), 127.8 (C<sub>Ar</sub>–H), 126.2 (C<sub>Ar</sub>–H), 124.9 (C<sub>Ar-central</sub>–H), 119.3 (C<sub>Trz</sub>–H), 45.5 (N–CH<sub>2</sub>), 15.7 (N–CH<sub>2</sub>–CH<sub>3</sub>) ppm. HRMS (ESI, positive ions): *m/z* = 614.2772 (calcd for [C<sub>36</sub>H<sub>33</sub>N<sub>9</sub>+Na]<sup>+</sup> 614.2757). Anal. Calcd. for **1**: C, 73.07; H, 5.62; N, 21.31. Found: C, 73.06; H, 5.37; N, 20.31.

## Compound 2.

DMF (3 mL) was added to a mixture of trisriazole **1** (0.300 g, 0.507 mmol) and CH<sub>3</sub>I (excess). The resulting solution was heated to 98 °C for 48 h. The reaction mixture was cooled to ambient temperature and to this was added diethyl ether (20 mL). The yellow coloured solid was filtered off and washed with excess amount of diethyl ether. Yield: 0.470 g (0.462 mmol, 91%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 9.31 (s, 3H, H<sub>Trz</sub>), 8.29 (d, <sup>3</sup>J = 8.7 Hz, 6H, H<sub>Ar</sub>), 8.23 (s, 3H, H<sub>Ar</sub>), 7.94 (d, <sup>3</sup>J = 8.7 Hz, 6H, H<sub>Ar</sub>), 4.75 (q, <sup>3</sup>J = 7.4 Hz, 6H, N–CH<sub>2</sub>), 4.38 (s, 9 H, N–CH<sub>3</sub>), 1.64 (t, <sup>3</sup>J = 7.4 Hz, 9H, N–CH<sub>2</sub>–CH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, DMSO-*d*<sub>6</sub>): δ = 142.9 (C<sub>Ar</sub>–C<sub>Ar-central</sub>), 142.5 (C<sub>Trz</sub>–Ar), 141.1 (C<sub>Ar</sub>–N<sub>Trz</sub>), 130.4 (C<sub>Ar</sub>–H), 129.2 (C<sub>Trz</sub>–H), 128.8 (C<sub>Ar</sub>–H), 126.2 (C<sub>Ar</sub>–H), 122.7 (C<sub>Ar-central</sub>–C<sub>Ar</sub>), 49.4 (N–CH<sub>2</sub>), 36.3 (N–CH<sub>3</sub>), 14.7 (N–CH<sub>2</sub>–CH<sub>3</sub>) ppm. HRMS (ESI, positive ions): *m/z* = 890.1777 (calcd for [C<sub>39</sub>H<sub>42</sub>N<sub>9</sub>I<sub>3</sub>–I]<sup>+</sup> 890.1653); 212.1230 (calcd for [C<sub>39</sub>H<sub>42</sub>N<sub>9</sub>I<sub>3</sub>–3I]<sup>3+</sup> 212.1188). Anal. Calcd. for **2**·3H<sub>2</sub>O: C, 43.71; H, 4.52; N, 11.77. Found: C, 44.11; H, 4.47; N, 11.40.

## Compound [3].

To a mixture of trisriazolium salt **2** (0.025 g, 0.025 mmol) and Ag<sub>2</sub>O (0.020 g, 0.086 mmol) was added dichloromethane (20 mL). The resulting mixture was stirred at ambient temperature for 18 h under the exclusion of light. To the reaction mixture was added [Ir(Cl)<sub>2</sub>(Cp\*)]<sub>2</sub> (0.029 g, 0.036 mmol), NaCl (excess) and NaOAc (0.015 g, 0.183 mmol). The reaction mixture was at ambient

temperature for an additional 3 d. The suspension was filtered through a pad of Celite to obtain a clear solution. The solvent was concentrated to 3 mL and addition of an excess diethyl ether gave a yellow precipitate which was filtered and dried in *vacuo*. Yield: 0.036 g (0.021 mmol, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.29–8.17 (m, 3H,  $\text{H}_{\text{Ar}}$ ), 8.02–7.90 (m, 3H,  $\text{H}_{\text{Ar}}$ ), 7.52–7.49 (m, 3H,  $\text{H}_{\text{Ar}}$ ), 7.43–7.27 (m, 3H,  $\text{H}_{\text{Ar}}$ ), 4.57–4.44 (m, 6H,  $\text{N-CH}_2$ ), 4.29 (s, br, 9H,  $\text{N-CH}_3$ ), 1.89–1.86 (s, 10H,  $\text{Cp}^*\text{-CH}_3$ ), 1.79–1.78 (s, 35H,  $\text{Cp}^*\text{-CH}_3$ ), 1.63 (t,  $^3J$  = 7.5 Hz, 6H,  $\text{N-CH}_2\text{-CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 159.6 ( $\text{C}_{\text{Ar}}\text{-Ir}$ ), 156.5 ( $\text{C}_{\text{trz}}\text{-Ar}$ ), 153.1 ( $\text{C}_{\text{trz}}\text{-Ir}$ ), 143.0/142.8/142.5 ( $\text{C}_{\text{Ar}}\text{-C}_{\text{Ar-central}}$ ), 140.9/140.7/140.4 ( $\text{C}_{\text{Ar}}\text{-C}_{\text{trz}}$ ), 136.4 ( $\text{C}_{\text{Ar}}\text{-H}$ ), 136.3 ( $\text{C}_{\text{Ar-central}}\text{-C}_{\text{Ar}}$ ), 125.1 ( $\text{C}_{\text{Ar}}\text{-H}$ ), 121.3/121.1/121.0 ( $\text{C}_{\text{Ar}}\text{-H}$ ), 120.4 ( $\text{C}_{\text{Ar}}\text{-H}$ ), 90.5/89.8 ( $\text{C}_{\text{Cp}^*}$ ), 47.5 ( $\text{N-CH}_2$ ), 37.1 ( $\text{N-CH}_3$ ), 15.7/15.3 ( $\text{N-CH}_2\text{-CH}_3$ ), 10.2/9.7/9.6 ( $\text{Cp}^*\text{-CH}_3$ ) ppm. HRMS (ESI, positive ions):  $m/z$  = 1884.4968 (calcd for  $[\text{C}_{69}\text{H}_{81}\text{N}_9\text{Ir}_3\text{Cl}_3\text{-Cl}]^+$  1884.4863); 823.7659 (calcd for  $[\text{C}_{69}\text{H}_{81}\text{N}_9\text{Ir}_3\text{Cl}_3\text{-2Cl}]^{2+}$  823.7583); 1774.4317 (calcd for  $[\text{C}_{69}\text{H}_{81}\text{N}_9\text{Ir}_3\text{Cl}_2\text{I-Cl}]^+$  1774.4211); 869.7343 (calcd for  $[\text{C}_{69}\text{H}_{81}\text{N}_9\text{Ir}_3\text{Cl}_2\text{I-2Cl}]^{2+}$  869.7266). Satisfactory microanalytical data could not be obtained due to halide scrambling.

#### Compound [4].

To a mixture of tris(triazolium) Iodide salt **2** (0.025 g, 0.025 mmol),  $\text{K}_2\text{CO}_3$  (0.015 g, 0.109 mmol),  $\text{PdCl}_2$  (0.016 g, 0.09 mmol) and KI (excess) was added pyridine (5 mL). The resulting suspension was stirred for 48 h at 84 °C. The pyridine was removed in *vacuo* and the crude mixture was extracted with dichloromethane (15 mL). The solvent was removed and the yellow residue was loaded onto a silica gel column. Elution with a dichloromethane gave compound [4] as a yellow solid. Yield: 0.028 g (0.014 mmol, 56%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.99 (dt,  $^3J$  = 5.0 Hz,  $^4J$  = 1.6 Hz, 6H,  $\text{H}_{\text{Py}}$ ), 8.22–8.20 (m, 6H,  $\text{H}_{\text{Ar}}$ ), 8.18 (s, 3H,  $\text{H}_{\text{Ar}}$ ), 8.08–8.11 (m, 6H,  $\text{H}_{\text{Ar}}$ ), 7.78–7.75 (m, 3H,  $\text{H}_{\text{Py}}$ ), 7.36–7.33 (m, 6H,  $\text{H}_{\text{Py}}$ ), 4.98 (q,  $^3J$  = 7.4 Hz, 6H,  $\text{N-CH}_2$ ), 4.11 (s, 9H,  $\text{N-CH}_3$ ), 1.85 (t,  $^3J$  = 7.4 Hz, 9H,  $\text{N-CH}_2\text{-CH}_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 153.8 ( $\text{C}_{\text{Py}}$ ), 143.1 ( $\text{C}_{\text{trz}}\text{-Ar}$ ), 142.0 ( $\text{C}_{\text{Ar}}\text{-C}_{\text{Ar-central}}$ ), 141.7 ( $\text{C}_{\text{Ar}}\text{-C}_{\text{trz}}$ ), 137.6 ( $\text{C}_{\text{Py}}$ ), 133.1 ( $\text{C}_{\text{trz}}\text{-Pd}$ ), 131.0 ( $\text{C}_{\text{Ar}}\text{-H}$ ), 127.1 ( $\text{C}_{\text{Ar-central}}\text{-C}_{\text{Ar}}$ ), 127.6 ( $\text{C}_{\text{Ar}}\text{-H}$ ), 125.8 ( $\text{C}_{\text{Ar-central}}$ ), 124.3 ( $\text{C}_{\text{Py}}$ ), 51.5 ( $\text{N-CH}_2$ ), 37.8 ( $\text{N-CH}_3$ ), 14.3 ( $\text{N-CH}_2\text{-CH}_3$ ) ppm. Anal. Calcd. for [4]: C, 33.23; H, 2.79; N, 8.61. Found: C, 33.56; H, 2.79; N, 8.38. HRMS (ESI, positive ions):  $m/z$  = 1355.7629 (calcd for  $[[\text{C}_{54}\text{H}_{54}\text{N}_{12}\text{Pd}_3\text{I}_6] - 2\text{Py} - [\text{Pd}(\text{Py})\text{I}_2] + \text{H}]^+$  1355.7676).

### Compound 6.

An oven-dried Schlenk tube was charged with compound **5** (0.100 g, 0.571 mmol) and bromobenzene (0.10 g, 0.637 mmol) under a nitrogen atmosphere, followed by addition of catalyst [**4**] (0.0185 g, 0.0095 mmol), corresponding base (0.136 g, 1.42 mmol) and 10.0 mL toluene (dry and degassed) *via* syringe. The reaction mixture was stirred at 120 °C for 16 h then cooled to ambient temperature. The reaction was quenched with H<sub>2</sub>O (15 mL) and extracted with ethyl acetate. The organic part was dried over MgSO<sub>4</sub> and the solvent was removed. The crude mixture was loaded onto a silica gel column and the elution with hexane:ethyl acetate (100:20, v:v) gave **6**. Yield: 0.101 g (0.402 mmol, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.28–7.18 (m, 6H, H<sub>Ar</sub>), 7.14–7.12 (m, 1H, H<sub>Ar</sub>), 7.04–7.01 (s, 2H, H<sub>Ar</sub>), 5.27 (s, 1H, H<sub>CH-Ar</sub>), 3.73–3.65 (m, 1H, CH<sub>2</sub>), 3.15–3.07 (m, 1H, CH<sub>2</sub>), 3.04 (s, 3H, N–CH<sub>3</sub>), 2.99–2.84 (m, 3H, CH<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.7 (C<sub>C=O</sub>), 140.8 (C<sub>Ar</sub>–CH(CO)), 137.2 (C<sub>Ar</sub>–CH<sub>2</sub>), 133.2 (C<sub>Ar</sub>–CH(CO)), 133.3 (C<sub>Ar</sub>–H), 133.1 (C<sub>Ar</sub>–H), 128.7 (C<sub>Ar</sub>–H), 126.9 (C<sub>Ar</sub>–H), 126.7 (C<sub>Ar</sub>–H), 126.6 (C<sub>Ar</sub>–H), 61.0 (CH–C<sub>Ar</sub>), 46.7 (CH<sub>2</sub>), 35.6 (N–CH<sub>3</sub>), 32.05 (CH<sub>2</sub>) ppm. Anal. Calcd. for **6**: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.87; H, 7.10; N, 5.62. HRMS (ESI, positive ions): *m/z* = 274.1151 (calcd for [[C<sub>17</sub>H<sub>17</sub>NO]+Na]<sup>+</sup> 274.1208).

General procedure transfer hydrogenation Catalysis:

The respective aldehyde/ketones and the corresponding complexes were mixed with KOH (0.0001 mmol, 6 mg) in a Schlenk tube under an inert gas atmosphere, to this mixture was added dry *i*PrOH. The mixtures were heated at 100 °C for the mentioned time and cooled to ambient temperature. The reaction mixture was then filtered through a small pad of silica using *i*PrOH and analysed by either GC-MS chromatography using hexadecane as an internal standard or by NMR spectroscopy using hexamethyl benzene as an internal standard.

General procedure for  $\alpha$ -Arylation of amide:

An oven-dried sealed tube equipped with a stir bar was charged with compound **5** (0.57 mmol) and corresponding bromobenzene (0.637 mmol) under a nitrogen atmosphere, followed by addition of Pd catalyst ([**4**]: 1.67 mol%; **D**: 5 mol%) , corresponding base (1.4 mmol) and 10.0 mL dry toluene *via* syringe. The reaction vessel was sealed and the reaction mixture was stirred at 120 °C for 16 h then allowed to cool to room temperature. The reaction was quenched with H<sub>2</sub>O (15 mL) and extracted with ethyl acetate. The organic part was dried over MgSO<sub>4</sub> and the solvent was removed. The crude mixture was loaded onto a silica gel column and eluted with hexane:ethyl acetate (100:20, v:v).

Suzuki-Miyaura Couplings using 4-bromobenzaldehyde:

4-bromobenzaldehyde (0.092 g, 0.50 mmol), potassium carbonate (0.100 g, 0.72 mmol), and the corresponding boronic acid (1.2 mmol), were suspended in water (ca. 3 mL). The corresponding catalyst (0.5 mol% for complex [**2**], 0.25 mol% of complex [**2**] and 0.166 mol% of catalyst [**7**] or [**9**]) was added to this suspension. The reaction mixture was stirred under air at room temperature for 5 hours. The crude reaction mixture was poured into 30 ml DCM and the DCM part was extracted several times with water. The organic part was dried over sodium sulfate. After filtration the solvent was removed to dryness. Yields were determined via <sup>1</sup>H NMR spectroscopy with the help of the integrals of the aldehyde protons.

### **X-ray Crystallography.**

Single crystals suitable for X-ray diffraction studies were obtained for the complex [4]·2.75CH<sub>2</sub>Cl<sub>2</sub> by the slow diffusion of pentane into a saturated dichloromethane solution of complex [4] at ambient temperature. X-ray diffraction data were collected at  $T = 100$  K with a Bruker D8 Venture diffractometer equipped with a rotation anode using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were collected by the standard ‘phi-omega scan techniques’. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on  $F^2$ .<sup>[3]</sup> Crystallographic details are given in Table S1. The asymmetric unit contains  $\frac{1}{3}$  formula unit of the complex [4] and disorder dichloromethane molecules. The  $\frac{1}{3}$  unit is related to the rest  $\frac{2}{3}$  unit by a crystallographic inversion center. The hydrogen could not be added to the carbon atoms of the disorder dichloromethane molecules.

CCDC 1062049 contain the cif files of complexes [4]·2.75CH<sub>2</sub>Cl<sub>2</sub>. These data can be obtained free of charge from [www.ccdc.cam.ac.uk/data\\_requests/cif](http://www.ccdc.cam.ac.uk/data_requests/cif).

**Table S1.** Selected bond lengths in Å

[4]·2.75CH <sub>2</sub> Cl <sub>2</sub>	
Chemical formula	C <sub>113.76</sub> H <sub>108</sub> Cl <sub>11</sub> I <sub>12</sub> N <sub>24</sub> Pd <sub>6</sub>
<i>M</i> <sub>r</sub>	4361.39
Crystal system	hexagonal
Space group	<i>R</i> -3
<i>a</i> (Å)	35.2807(14)
<i>b</i> (Å)	35.2807(14)
<i>c</i> (Å)	10.4598(4)
$\alpha$ (°)	90.00
$\beta$ (°)	90.00
$\gamma$ (°)	120.00
<i>V</i> (Å <sup>3</sup> )	11275.3(8)
<i>Z</i>	3
Density (g cm <sup>-3</sup> )	1.927
<i>F</i> (000)	6171
Radiation Type	Mo K $\alpha$
$\mu$ (mm <sup>-1</sup> )	3.414
Crystal size	0.26 x 0.15 x 0.07
Meas. Refl.	60558
Indep. Refl.	5059
Obsvd. [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4102
refl.	
<i>R</i> <sub>int</sub>	0.0710
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.0418
w <i>R</i> ( <i>F</i> <sup>2</sup> )	0.1034
<i>S</i>	1.084
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	2.386
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-0.982

**Table S2.** Selected bond lengths in Å

Atoms	[4]·2.75CH <sub>2</sub> Cl <sub>2</sub>
Pd1 – I1	2.5998(7)
Pd1 – I2	2.6138(7)
Pd1 – N4	2.096(6)
Pd1 – C1	1.954(6)
N1 – N2	1.334(7)
N2 – N3	1.324(7)
N1 – C1	1.354(7)
N3 – C2	1.373(7)
C1 – C2	1.387(7)

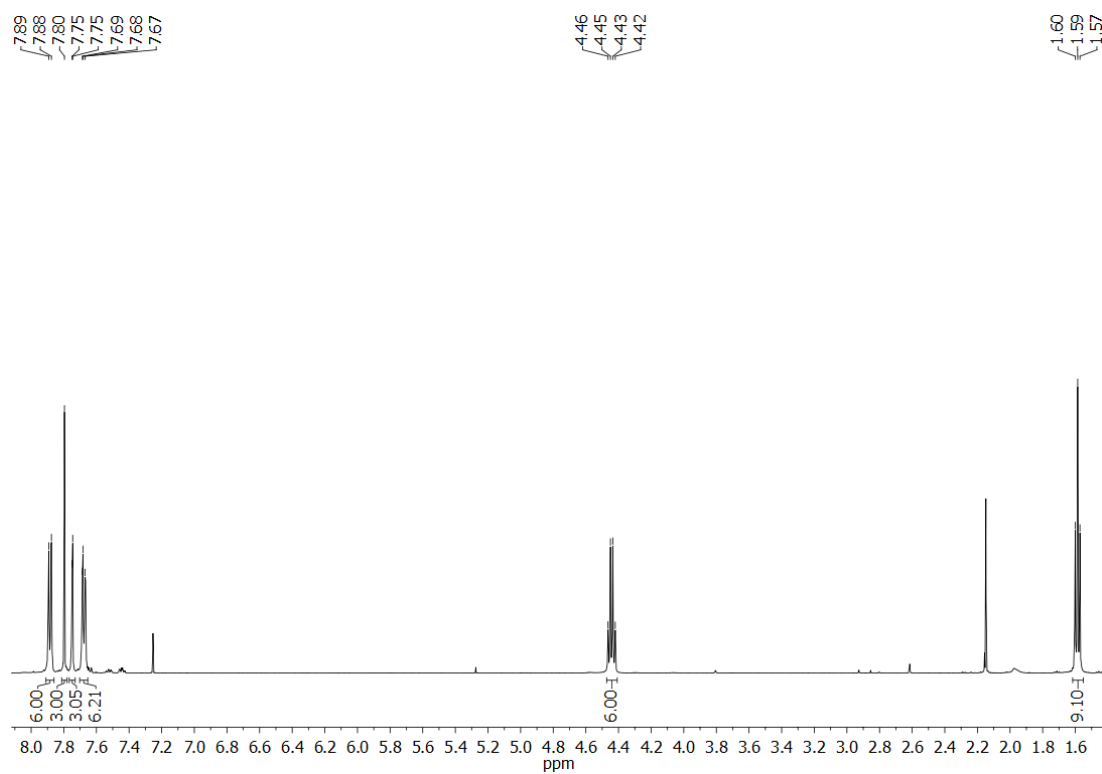
**Table S3.** Selected bond angles in °

Atoms	[4]·2.75CH <sub>2</sub> Cl <sub>2</sub>
I1 – Pd1 – I2	173.92(2)
I1 – Pd1 – N4	92.70(18)
I1 – Pd1 – C1	85.43(18)
C1 – Pd1 – N4	177.4(3)
C2 – C1 – N1	104.1(5)

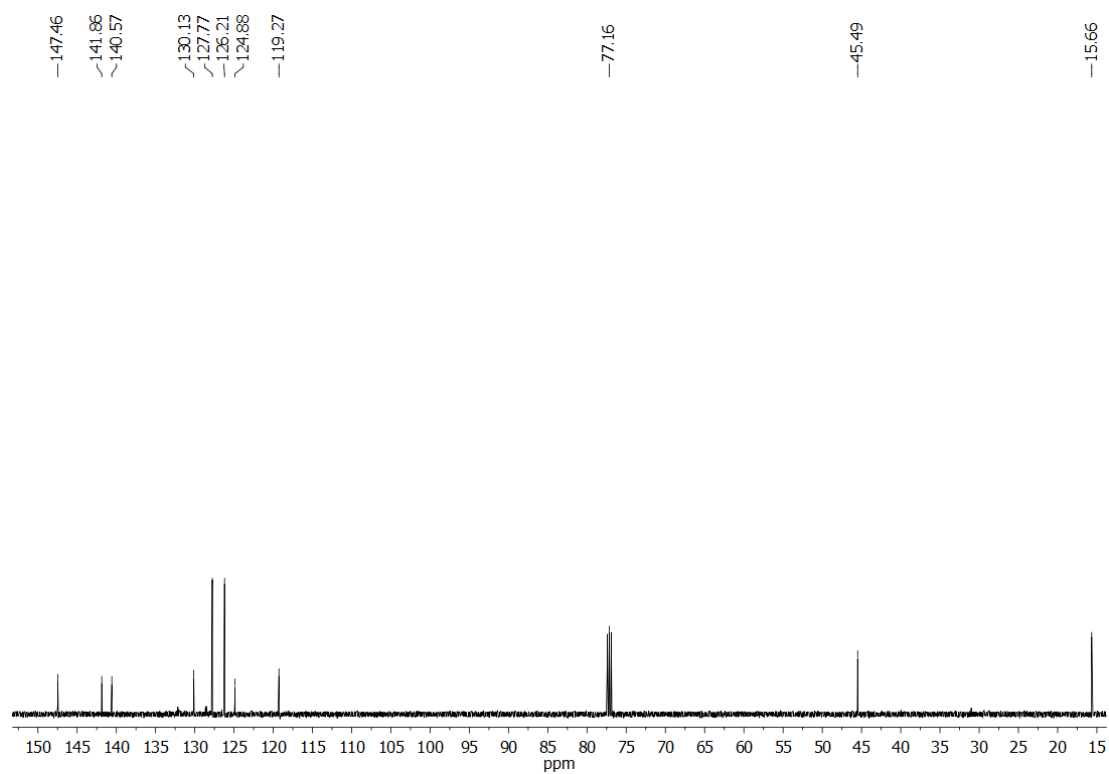
## References

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2. D. Mitchell, L. A. Hay, T. M. Koenig, S. McDaniel, J. S. Nissenb and J. E. Audia, *Tetrahedron: Asymmetry*, 2005, **16**, 3814.
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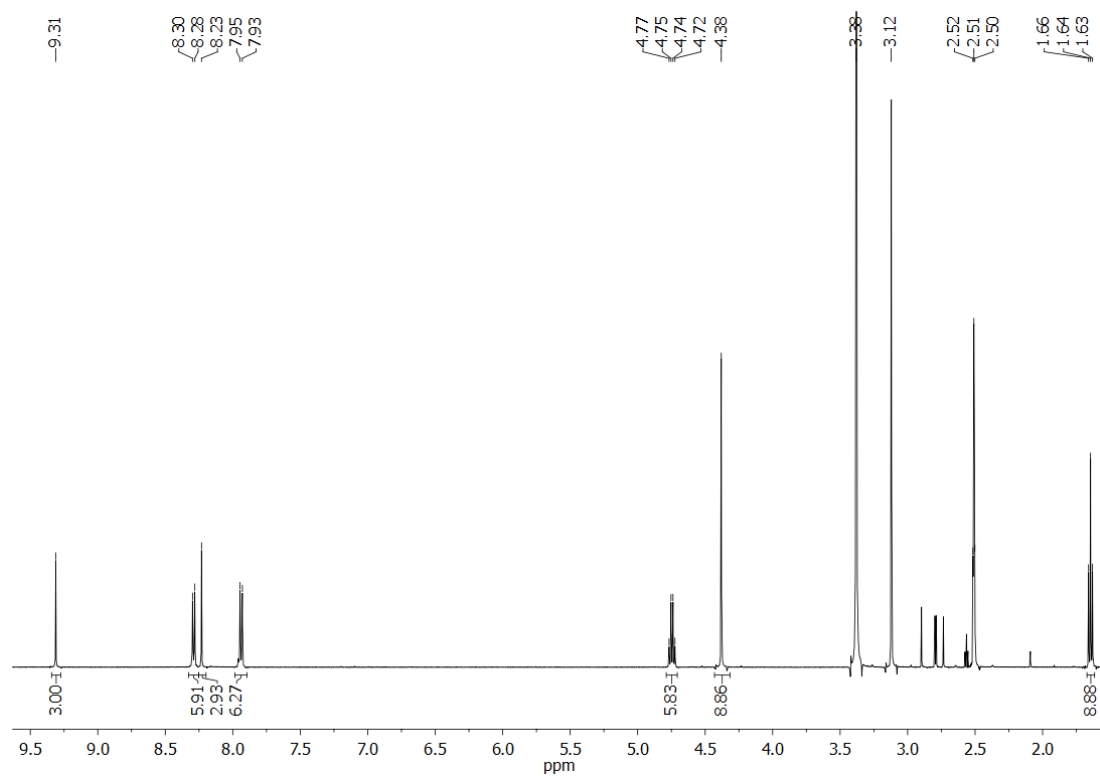




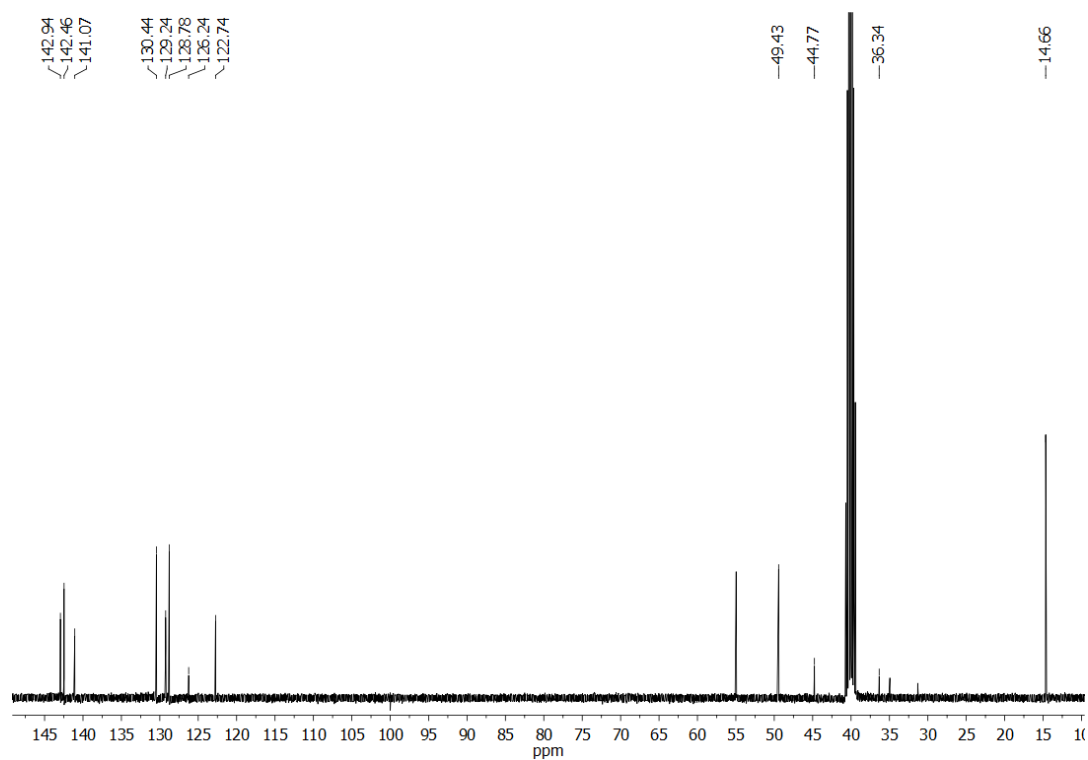
**Figure S1.**  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$ .



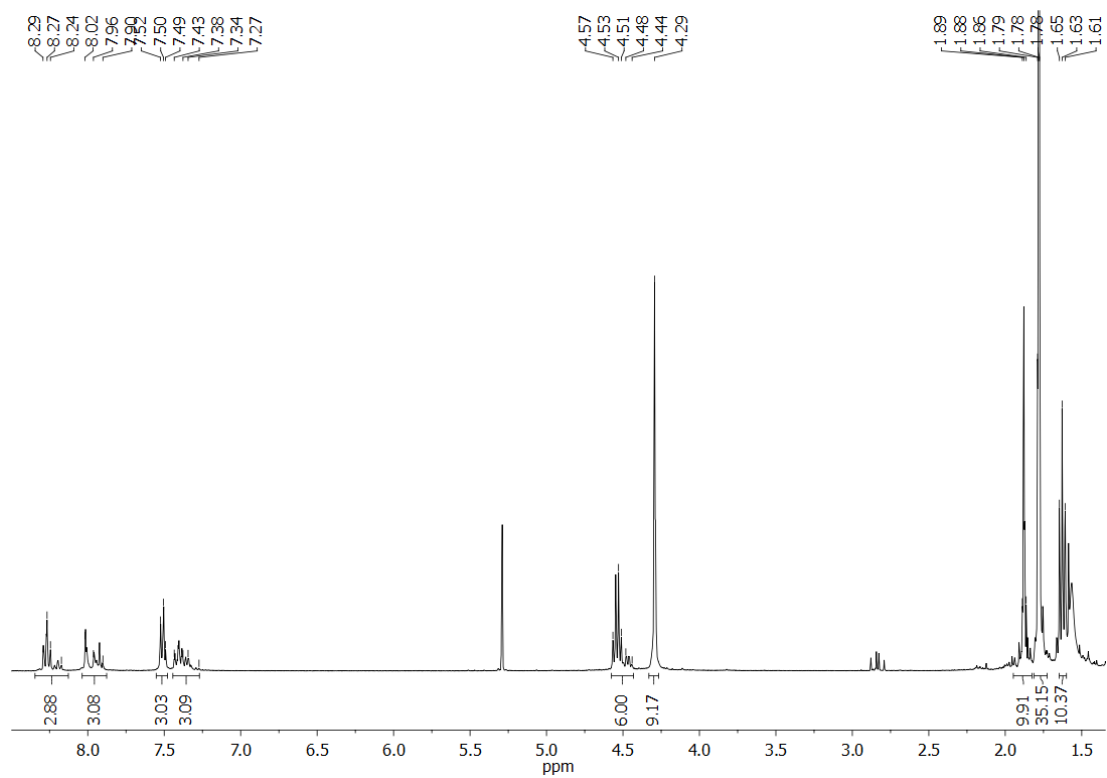
**Figure S2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{CDCl}_3$ .



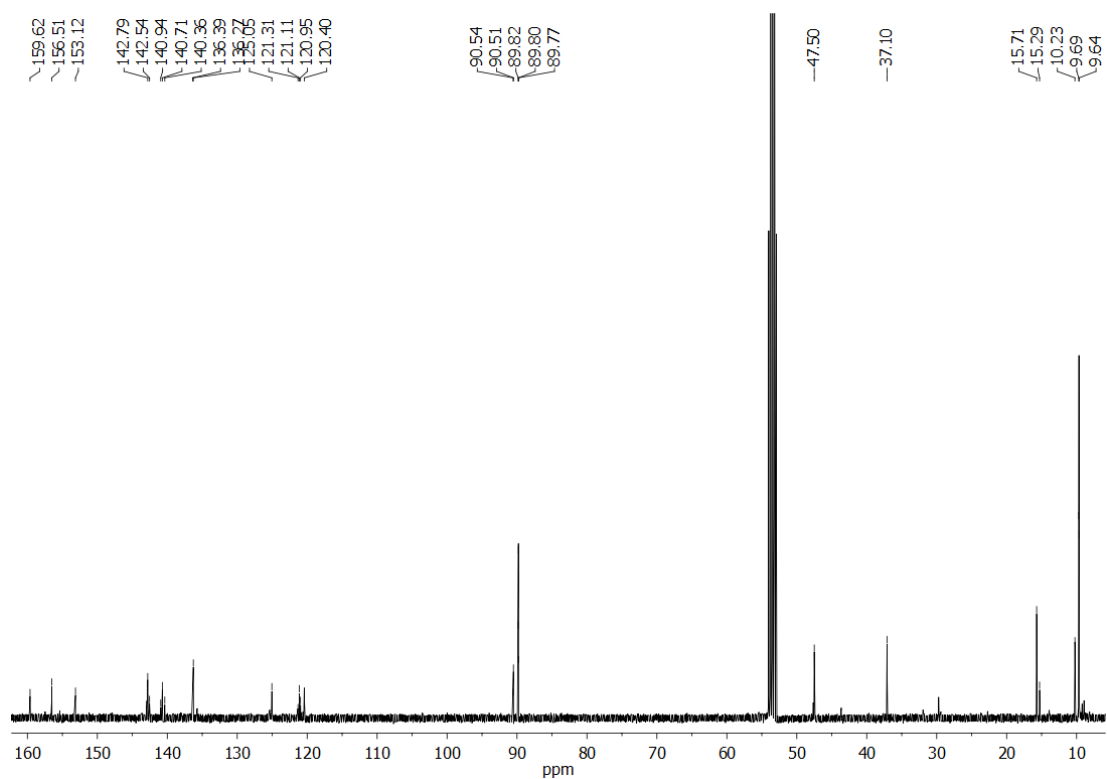
**Figure S3.** <sup>1</sup>H NMR spectrum of **2** in DMSO-*d*<sub>6</sub>.



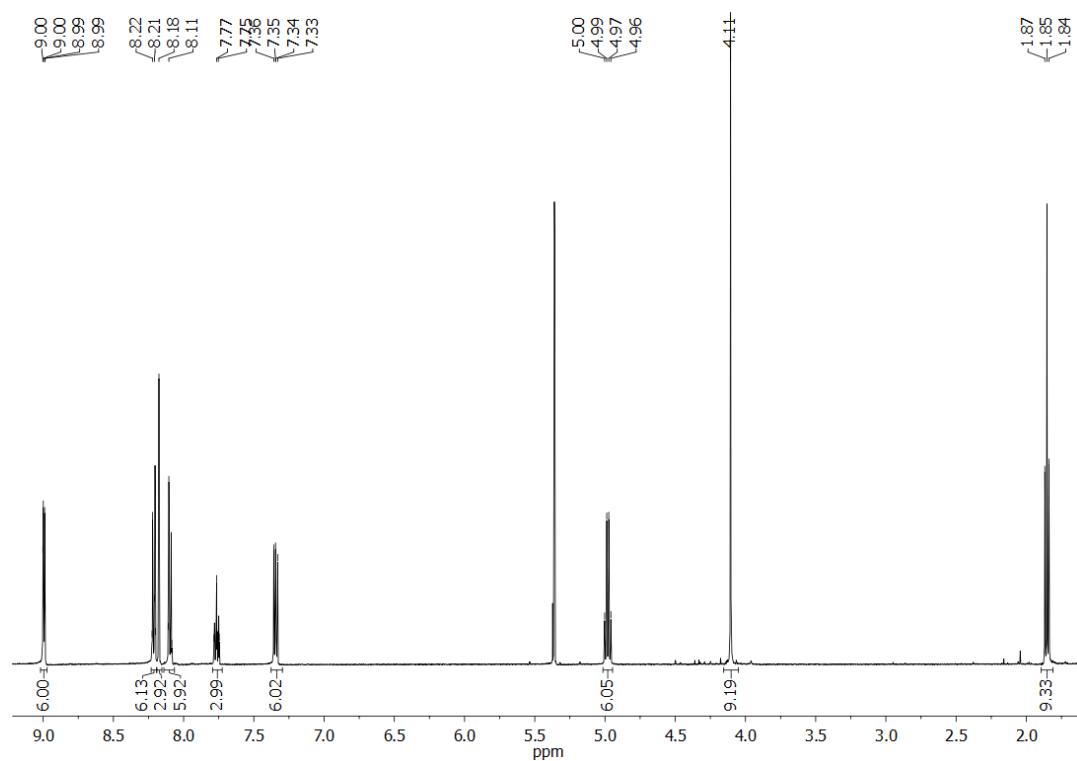
**Figure S4.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **2** in DMSO-*d*<sub>6</sub>.



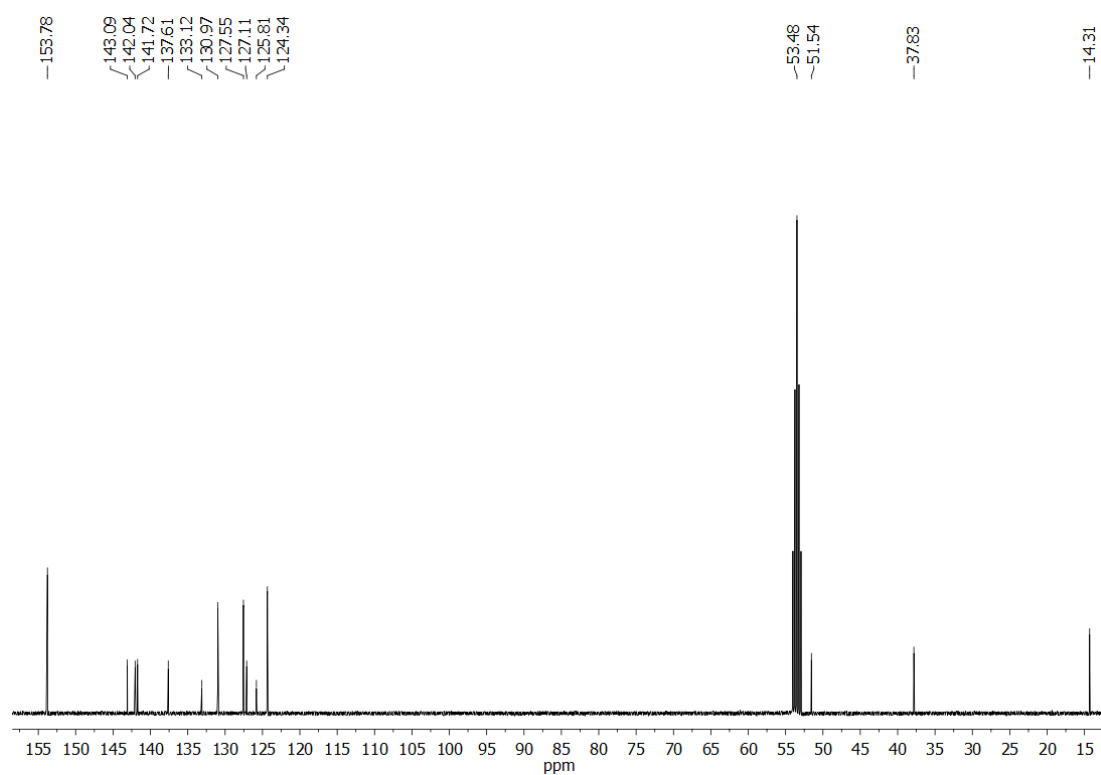
**Figure S5.** <sup>1</sup>H NMR spectrum of [3] in CD<sub>2</sub>Cl<sub>2</sub>.



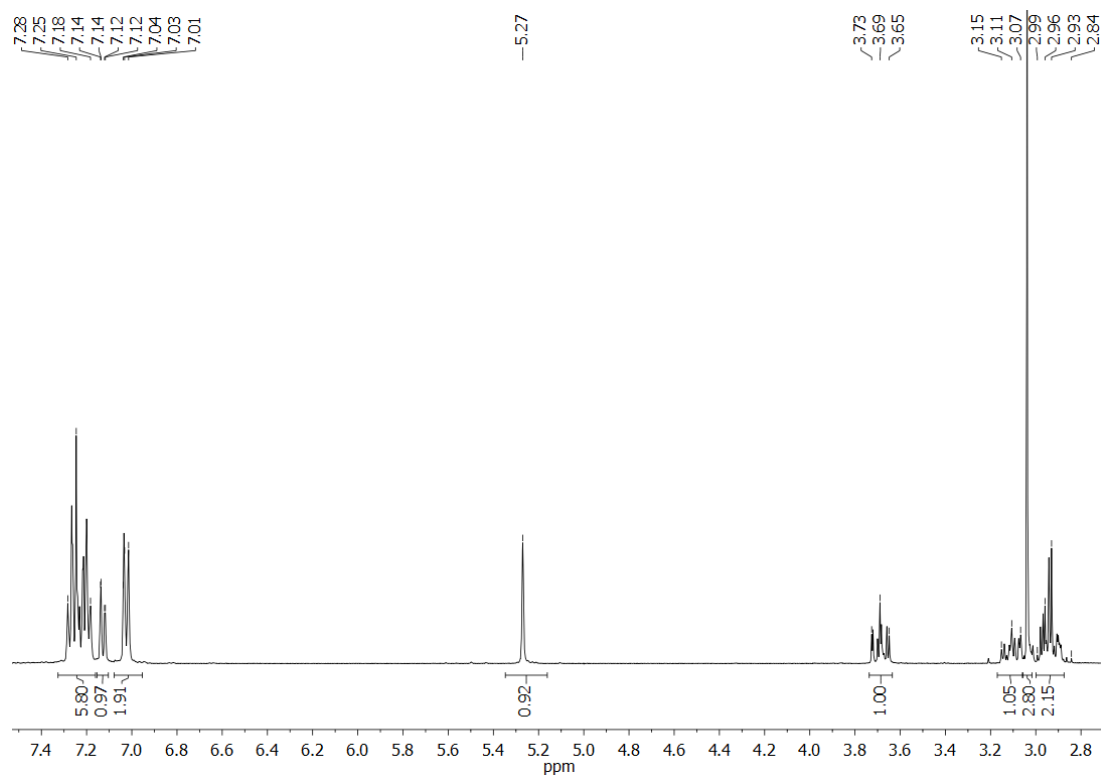
**Figure S6.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [3] in CD<sub>2</sub>Cl<sub>2</sub>.



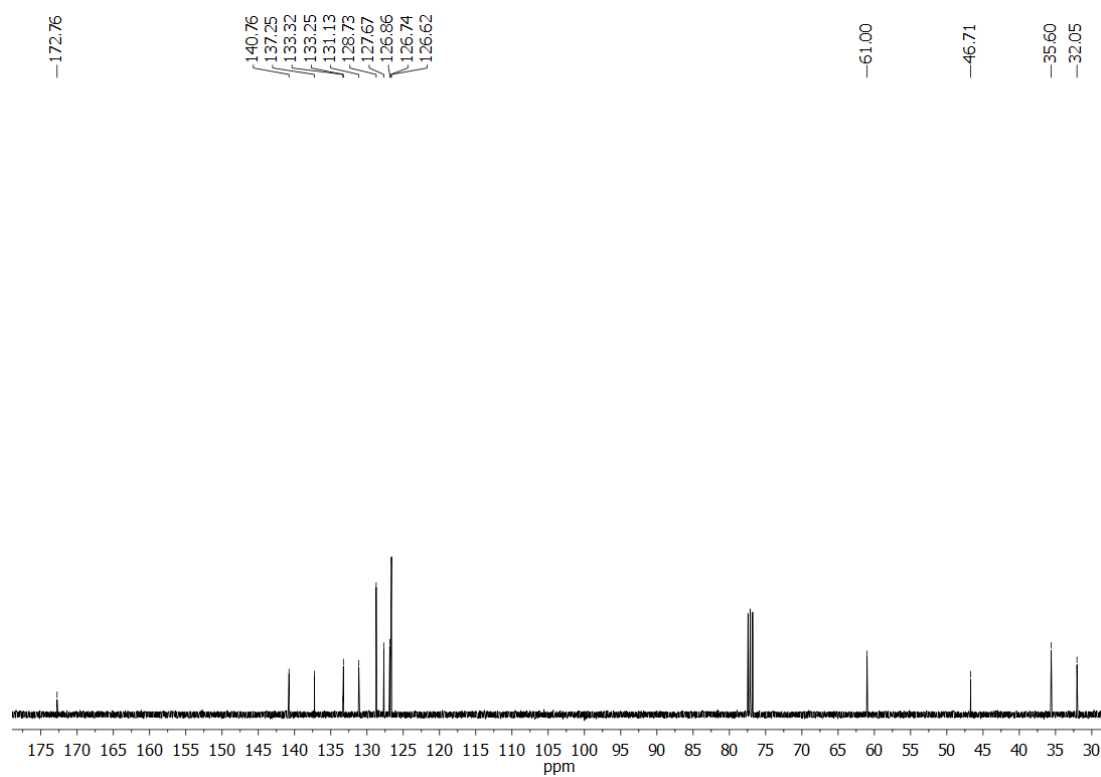
**Figure S7.** <sup>1</sup>H NMR spectrum of [4] in CD<sub>2</sub>Cl<sub>2</sub>.



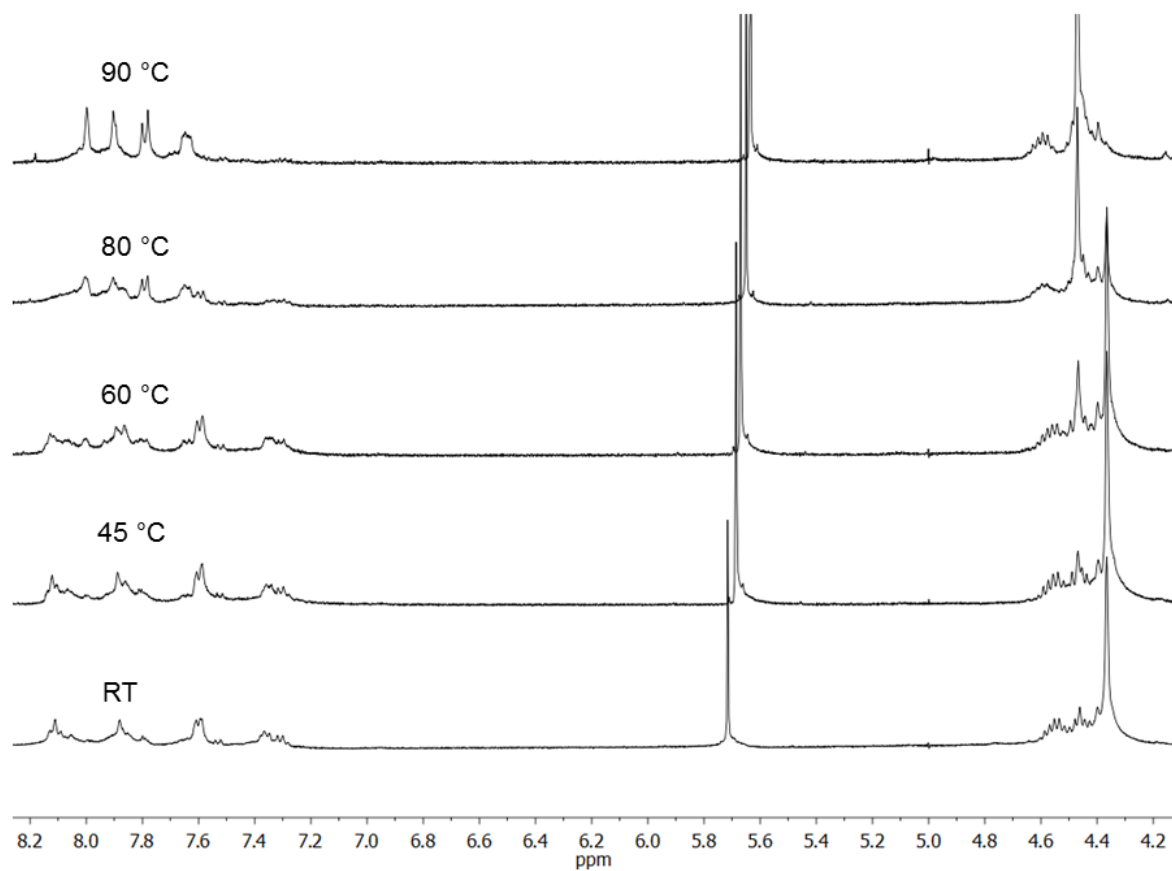
**Figure S8.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of [4] in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S9.** <sup>1</sup>H NMR spectrum of **6** in CDCl<sub>3</sub>.



**Figure S10.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **6** in CDCl<sub>3</sub>.



**Figure S11.**  $^1\text{H}$  NMR spectra of **[3]** in deuterated  $\text{DMSO}$  at various temperatures.