

# Supporting information

## **Olefin Preparation via Palladium-Catalyzed Oxidative De-Azotative and De-Sulfitative Internal Cross-Coupling of Sulfonylhydrazones**

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## 1. General Experimental details:

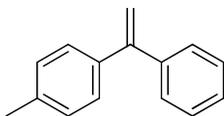
Pd(OAc)<sub>2</sub>; Pd(O<sub>2</sub>CCF<sub>3</sub>)<sub>2</sub>; Pd(COD)Cl<sub>2</sub>; Cl<sub>2</sub>Pd(CH<sub>3</sub>CN)<sub>2</sub>; <sup>t</sup>Bu<sub>2</sub>PMeHBF<sub>4</sub>; DPPB; K<sub>2</sub>CO<sub>3</sub>; *t*-BuOLi, *t*-BuONa; *t*-BuOK; AgOAc; BQ; DCP; Bu<sub>4</sub>NI and Bu<sub>4</sub>NBr were purchased from Aldrich. <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra were measured on a 400Hz spectrometer with TMS as internal standard at room temperature. Chemical shifts (δ) are given in ppm relative to TMS; and the coupling constants (*J*) are given in Hz. unless otherwise stated, all reaction was conducted under air. Column chromatography was performed using silica gel (300-400 mesh). Hyrazone was prepared following by a reported procedure<sup>1</sup>.

## 2. General Procedure for Internal Cross-Coupling reaction of Sulfonylhydrazones:

A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and **7** (0.5 mmol, 0.144 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until HPLC or TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column to obtain the various products.

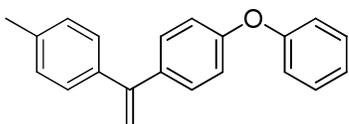
### 3. Experimental procedure and NMR data of synthesized compound :

#### 1-methyl-4-(1-phenylvinyl)benzene (**8**)<sup>2</sup>:



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and **7** (0.5 mmol, 0.144 g) in dimethyl acetamide (1.5mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.5, PE/EA 100:1) to afford **8** (0.079 g, 82%) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 2.42 (s, 3 H), 5.47 (d, *J*=10.54 Hz, 2 H), 7.19 (d, *J*=7.78 Hz, 2 H), 7.29 (d, *J*=8.03 Hz, 2 H), 7.33 - 7.42 (m, 5 H). <sup>13</sup>C NMR (100MHz, CHLOROFORM-d) δ 149.95, 141.73, 138.65, 137.53, 128.88, 128.32, 128.17, 128.14, 127.65, 113.64, 21.19.

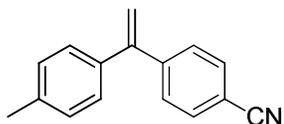
#### 1-methyl-4-(1-(4-phenoxyphenyl)vinyl)benzene (**22**):



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and 4-methyl-N'-(1-(4-phenoxyphenyl) ethylidene)benzenesulfonohydrazide (0.5 mmol, 0.190 g) in dimethyl acetamide (1.5mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture.

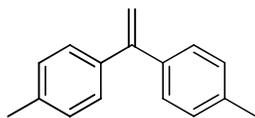
The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.6, PE/EA 100:1) to afford **22** (0.111 g, 78%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 2.29 (s, 3 H), 5.30 (s, 2 H), 6.88 (d, *J*=8.53 Hz, 2 H), 6.94 - 6.99 (m, 2 H), 7.08 (s, 3 H), 7.14 - 7.19 (m, 2 H), 7.20- 7.31 (m, 4 H). <sup>13</sup>C NMR (100 MHz, CHLOROFORM-d): δ 157.11, 157.01, 149.24, 138.68, 137.59, 136.69, 129.79, 129.65, 128.91, 128.19, 123.39, 119.09, 118.33, 113.10, 21.19. HRMS calcd for C<sub>21</sub>H<sub>19</sub>O<sup>+</sup> [M+H]<sup>+</sup>: 287.1430, found: 287.1420. (New compound)

#### 4-(1-(p-tolyl)vinyl)benzonitrile (**23**):



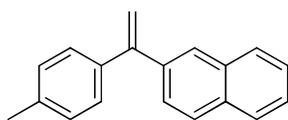
A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and N'-(1-(4-cyanophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (0.5 mmol, 0.156 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.6, PE/EA 100:1) to afford **23** (0.090 g, 82%) as a yellow oil. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 2.31 (s, 3 H), 5.34 - 5.54 (m, 2 H), 7.10 (s, 4 H), 7.37 (d, *J*=7.78 Hz, 2 H), 7.55 (d, *J*=7.78 Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CHLOROFORM-d): δ 147.58, 145.33, 137.17, 136.32, 131.02, 128.13, 127.86, 127.03, 117.89, 115.00, 110.26, 20.16. HRMS calcd for C<sub>16</sub>H<sub>14</sub>N<sup>+</sup> [M+H]<sup>+</sup>: 220.1121, found: 220.1127. (New compound)

#### 4,4'-(ethene-1,1-diyl)bis(methylbenzene) (24)<sup>3</sup>:



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and 4-methyl-N'-(1-(p-tolyl)ethylidene) benzenesulfonohydrazide (0.5 mmol, 0.15 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.5, PE/EA 100:1) to afford **24** (0.088 g, 85%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 2.30 (s, 6 H), 5.31 (s, 2 H), 7.07 (d, *J*=7.78 Hz, 4 H), 7.16 (d, *J*=8.03 Hz, 4 H). <sup>13</sup>C NMR (100 MHz, CHLOROFORM-d): δ 149.77, 138.82, 137.43, 128.82, 128.18, 112.98, 21.17.

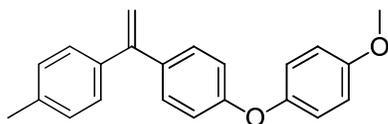
#### 2-(1-(p-tolyl)vinyl)naphthalene (25)<sup>3</sup>:



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and **4-methyl-N'-(1-(naphthalen-2-yl)ethylidene)benzenesulfonohydrazide** (0.5 mmol, 0.169 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to

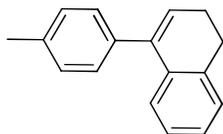
dryness. The residue was purified by a silica column ( $R_f$  0.5, PE/EA 100:1) to afford **25** (0.083 g, 68%) as a yellow oil.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM- $d$ )  $\delta$  ppm 2.31 (s, 3 H), 5.46 (d,  $J=4.27$  Hz, 2 H), 7.09 (d,  $J=8.03$  Hz, 2 H), 7.21 (d,  $J=8.03$  Hz, 2 H), 7.40 (d,  $J=3.01$  Hz, 3 H), 7.71 (s, 4 H).  $^{13}\text{C}$  NMR (100 MHz, CHLOROFORM- $d$ ):  $\delta$  149.91, 139.11, 138.64, 137.63, 133.31, 132.97, 128.95, 128.27, 128.18, 127.64, 127.60, 127.26, 126.51, 126.13, 125.97, 114.19, 21.21.

**1-methoxy-4-(4-(1-(p-tolyl)vinyl)phenoxy)benzene (26):**



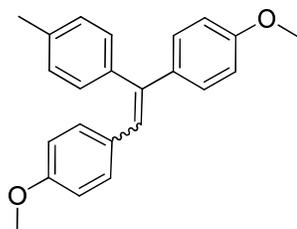
A mixture of  $\text{Pd}(\text{OAc})_2$  (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol),  $\text{K}_2\text{CO}_3$  (0.21 g, 1.5 mmol),  $\text{Bu}_4\text{NI}$  (0.37 g, 1.0 mmol) and **N'-(1-(4-(4-methoxyphenoxy)phenyl)ethylidene)-4-methylbenzenesulfonohydrazide** (0.5 mmol, 0.205 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (1.0 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated to dryness. The residue was purified by a silica column ( $R_f$  0.4, PE/EA 100:1) to afford **26** (0.112g, 71%) as a yellow solid.  $^1\text{H}$  NMR (400 MHz, CHLOROFORM- $d$ )  $\delta$  ppm 2.40 (s, 3 H), 3.84 (s, 3 H), 5.39 (s, 2 H), 6.92 (dd,  $J=8.78$ , 2.26 Hz, 4 H), 7.05 (d,  $J=9.03$  Hz, 2 H), 7.18 (d,  $J=7.78$  Hz, 2 H), 7.24 - 7.34 (m, 4 H).  $^{13}\text{C}$  NMR (100MHz, CHLOROFORM- $d$ ) 158.26, 156.01, 150.00, 149.25, 138.73, 137.53, 135.92, 129.53, 128.87, 128.17, 120.94, 117.05, 114.90, 112.86, 55.68, 21.18. HRMS calcd for  $\text{C}_{22}\text{H}_{21}\text{O}_2^+$   $[\text{M}+\text{H}]^+$ : 317.1536, found: 317.1532. (New compound)

#### 4-(p-tolyl)-1,2-dihydronaphthalene (27)<sup>4</sup>:



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb(43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and N'-(3,4-dihydronaphthalen-1(2H)-ylidene)-4-methylbenzenesulfonylhydrazide (0.5 mmol, 0.157 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.4, PE/EA 100:1) to afford **27** (0.086 g, 78%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 2.31 (s, 5 H), 2.69 - 2.83 (m, 2 H), 5.96 - 6.03 (m, 1 H), 6.92 - 6.96 (m, 1 H), 7.12 (br. s., 5H), 7.17 (d, *J*=7.28 Hz, 2 H). <sup>13</sup>C NMR(100MHz, CHLOROFORM-d) δ138.68, 136.82, 135.80, 135.69, 134.20, 127.88, 127.61, 126.48, 126.19, 125.86, 125.13, 124.42, 27.30, 22.50, 20.16.

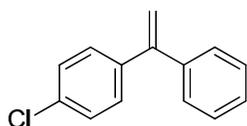
#### 4,4'-(1-(p-tolyl)ethene-1,2-diyl)bis(methoxybenzene) (28):



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and N'-(1,2-bis(4-methoxyphenyl)ethyldiene)-4-methylbenzenesulfonylhydrazide (0.5 mmol, 0.212 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting

material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.6, PE/EA 100:1) to afford **28** (0.115 g, 70%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 2.29 (d, *J*=14.56 Hz, 3 H), 3.68 (d, *J*=1.76 Hz, 3 H), 3.75 (d, *J*=12.55 Hz, 3 H), 6.60 (dd, *J*=8.66, 4.39 Hz, 2 H), 6.70 - 6.82 (m, 3 H), 6.85 - 6.93 (m, 2 H), 6.97 - 7.09 (m, 4 H), 7.11 - 7.18 (m, 2 H). <sup>13</sup>C NMR (100 MHz, CHLOROFORM-d): δ 158.99, 158.80, 158.17, 158.11, 141.18, 140.18, 137.75, 137.00, 136.85, 136.56, 132.98, 131.60, 130.68, 130.60, 130.50, 130.49, 130.27, 129.38, 128.85, 128.60, 127.39, 126.56, 125.83, 114.04, 113.53, 113.39, 99.99, 55.31, 55.16, 29.71, 21.33, 21.11. HRMS calcd for C<sub>23</sub>H<sub>23</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 331.1693, found: 331.1708. (New compound)

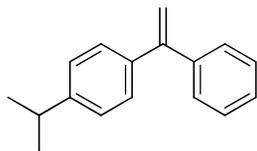
**1-chloro-4-(1-phenylethylidene)benzene (29)<sup>5</sup>:**



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and 4-chloro-N'-(1-phenylethylidene)benzenesulfonohydrazide (0.5 mmol, 0.154 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.5, PE/EA 100:1) to afford **29** (0.082 g, 77%) as a white solid. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 5.36 - 5.43 (m, 2 H), 7.22 (d, *J*=6.02 Hz, 3 H), 7.26 (d, *J*=3.51 Hz, 6 H). <sup>13</sup>C NMR (100MHz, CHLOROFORM-d) δ 147.98, 140.01, 138.94, 132.58, 128.54, 127.33,

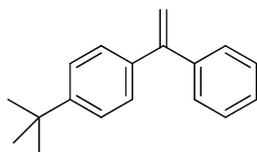
127.25, 127.17, 126.91, 113.66.

**1-isopropyl-4-(1-phenylvinyl)benzene (30)<sup>6</sup>:**



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and 4-isopropyl-N'-(1-phenylethylidene)benzenesulfonohydrazide (0.5 mmol, 0.158 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.5, PE/EA 100:1) to afford **30** (0.089 g, 80%) as a white solid. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.20 (d, *J*=7.03 Hz, 6H), 2.79 - 2.91 (m, 1 H), 5.35 (d, *J*=16.81 Hz, 2 H), 7.08 - 7.14 (m, 2 H), 7.16 - 7.22 (m, 2 H), 7.22 - 7.32 (m, 5 H). <sup>13</sup>C NMR (100MHz, CHLOROFORM-d): δ 148.87, 147.46, 140.69, 137.84, 127.30, 127.12, 127.08, 126.59, 125.18, 112.66, 32.81, 22.95.

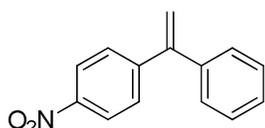
**1-(tert-butyl)-4-(1-phenylvinyl)benzene (31)<sup>7</sup>:**



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and 4-(tert-butyl)-N'-(1-phenylethylidene)benzenesulfonohydrazide (0.5 mmol, 0.165 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The

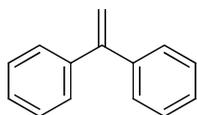
mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.5, PE/EA 100:1) to afford **31** (0.098 g, 83%) as a white solid. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 1.26 (s, 9 H), 5.28 - 5.43 (m, 2 H), 7.26 (br. s., 9 H). <sup>13</sup>C NMR (100MHz, CHLOROFORM-d) δ 149.71, 148.79, 140.67, 137.40, 127.32, 127.07, 126.84, 126.58, 124.02, 112.68, 33.53, 30.33.

**1-nitro-4-(1-phenylvinyl)benzene (32)** <sup>3</sup>:



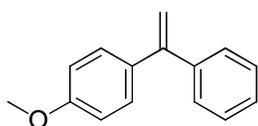
A mixture of Pd (OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and 4-nitro-N'-(1-phenylethylidene) benzenesulfonylhydrazide (0.5 mmol, 0.160 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 16 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.4, PE/EA 100:1) to afford **32** (0.018 g, 16%) as a white solid. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ ppm 5.70 (d, *J*=3.26 Hz, 2 H), 7.26 - 7.33 (m, 2 H), 7.37 - 7.45 (m, 3 H), 7.56 (d, *J*=8.78 Hz, 2 H), 8.24 (d, *J*=8.53 Hz, 2 H). <sup>13</sup>C NMR (100MHz, DMSO-d<sub>6</sub>) δ 147.95, 147.82, 147.35, 140.15, 129.52, 129.10, 128.79, 128.33, 124.14, 118.51.

**Ethene-1,1-diyl dibenzene (33)** <sup>8</sup>:



A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and N'-(1-phenylethylidene) benzenesulfonohydrazide (0.5 mmol, 0.137 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 6 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.5, PE/EA 100:1) to afford **23** (0.071 g, 79%) as a yellow oil. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ ppm 5.48 (s, 2 H), 7.24 - 7.41 (m, 10 H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 149.67, 141.21, 128.84, 128.35, 128.30, 115.15.

**1-methoxy-4-(1-phenylvinyl)benzene (34)** <sup>5</sup>:



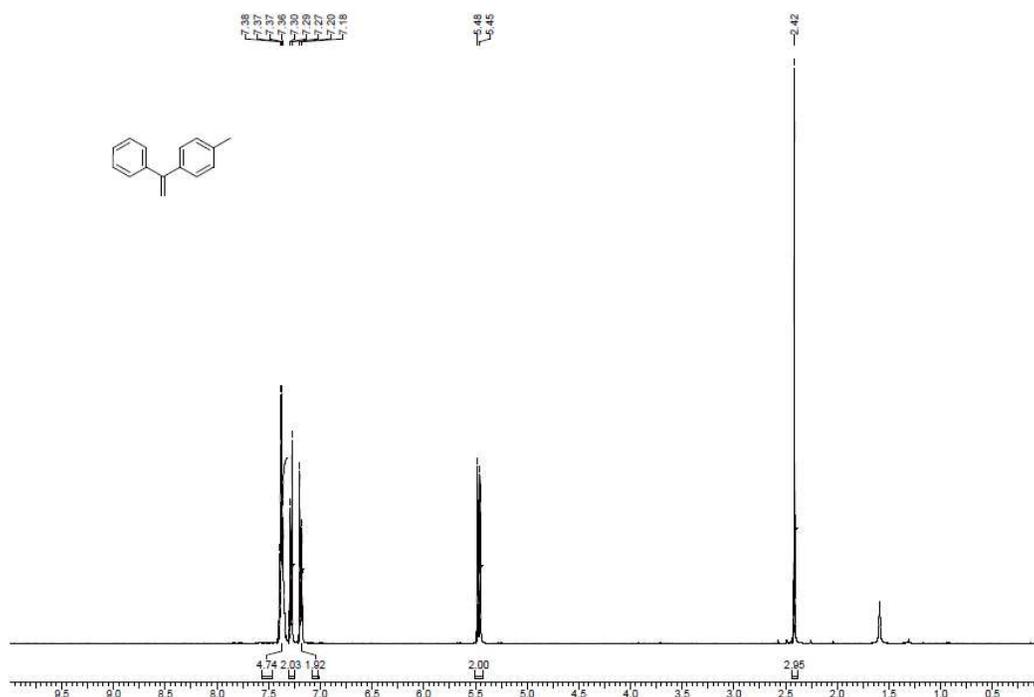
A mixture of Pd(OAc)<sub>2</sub> (11 mg, 0.05 mmol), dppb (43 mg, 0.10 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), Bu<sub>4</sub>NI (0.37 g, 1.0 mmol) and 4-methoxy-N'-(1-phenylethylidene)benzenesulfonohydrazide (0.5 mmol, 0.152 g) in dimethyl acetamide (1.5 mL) was heated to 100 °C in an atmosphere of air. The reaction was stirred at 100 °C for 3 h until TLC analysis indicated consumption of the starting material. The reaction mixture was cooled to 25 °C and water (10 mL) was added to the mixture. The mixture was extracted with ethyl acetate (30 mL) twice and the organic layer was washed with brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by a silica column (R<sub>f</sub> 0.5, PE/EA 100:1) to afford **34** (0.093 g, 89%) as a white solid. <sup>1</sup>H NMR (400 MHz, CHLOROFORM-d) δ ppm 3.76 (s, 3 H), 5.31 (d, *J*=16.31 Hz, 2 H), 6.80 (d, *J*=8.53 Hz, 2 H), 7.17 - 7.23 (m, 2

H), 7.26 (s, 5 H).  $^{13}\text{C}$  NMR (100MHz, CHLOROFORM-d)  $\delta$  159.35, 149.53, 141.84, 134.01, 129.41, 128.34, 128.14, 127.67, 113.54, 112.98, 55.32.

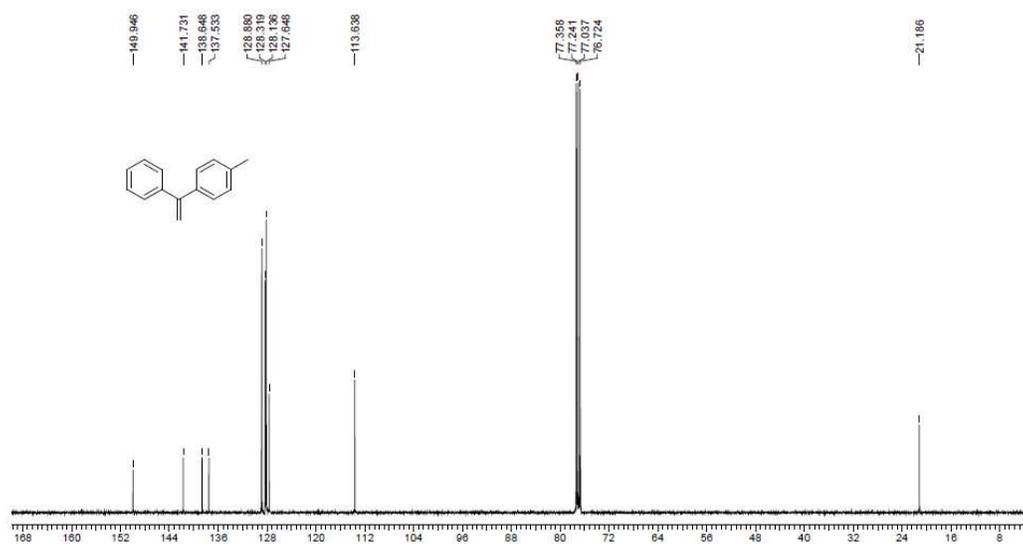
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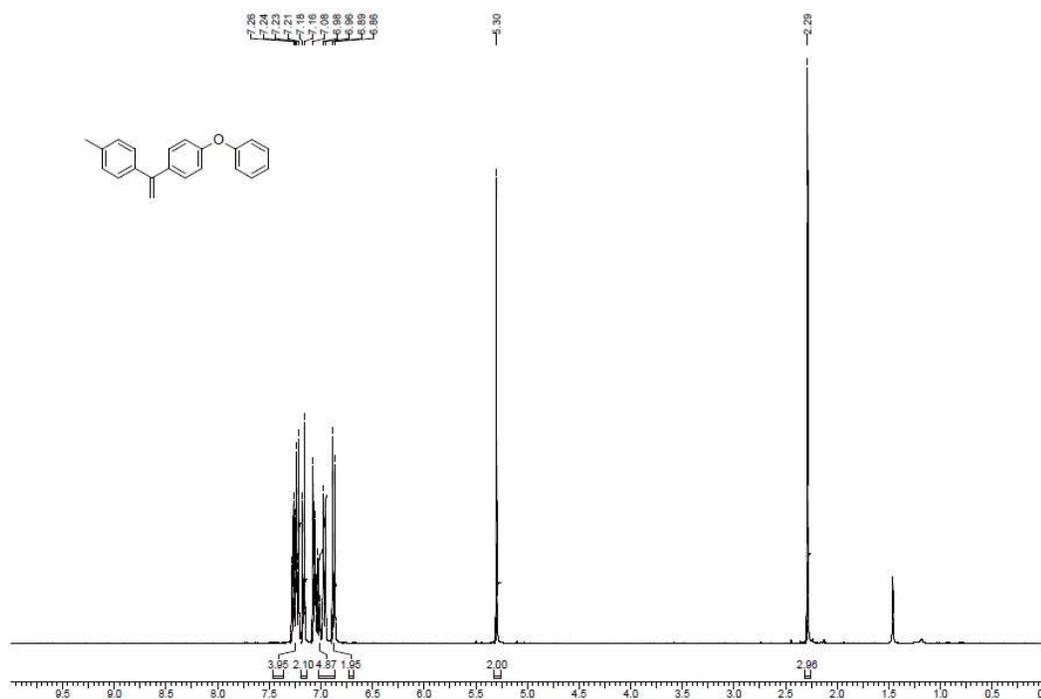
5. Copies of  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR



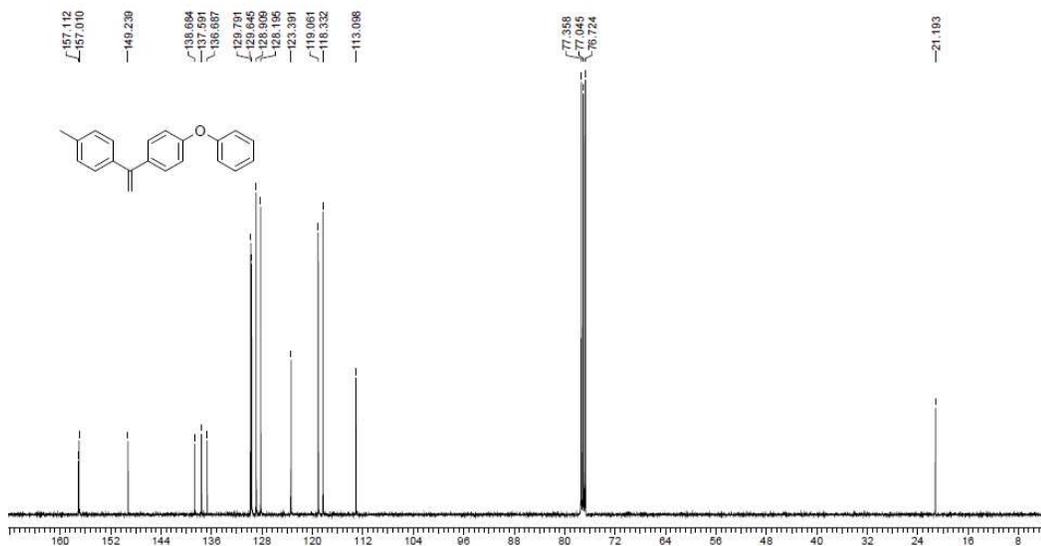
$^1\text{H}$ NMR of 1-methyl-4-(1-phenylvinyl)benzene (8)  
(400 MHz, CHLOROFORM-d)



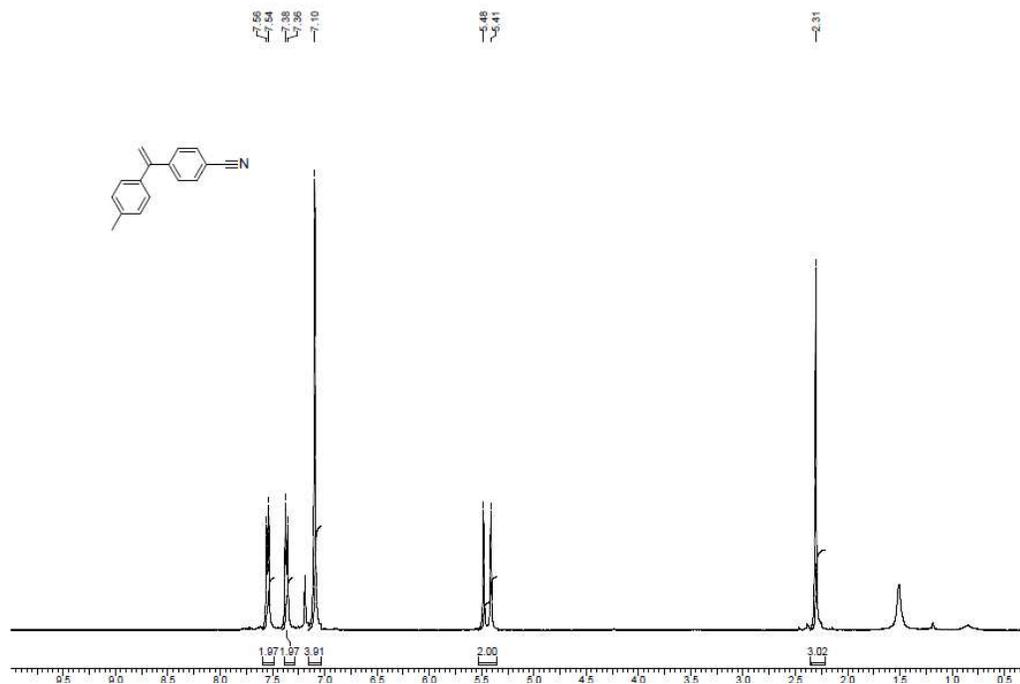
$^{13}\text{C}$ NMR of 1-methyl-4-(1-phenylvinyl)benzene (8)  
(100 MHz, CHLOROFORM-d)



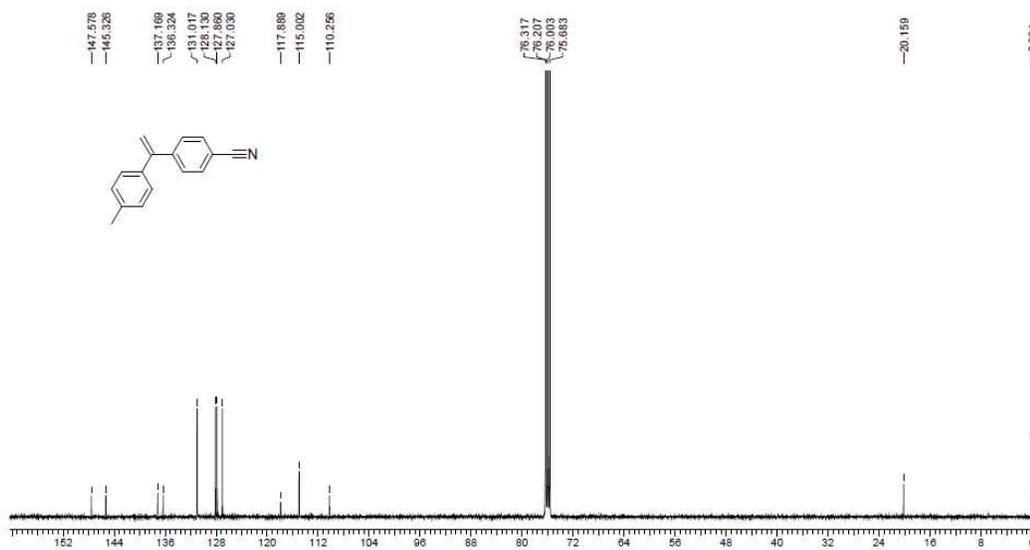
**<sup>1</sup>H NMR of 1-methyl-4-(1-(4-phenoxyphenyl)vinyl)benzene (22)**  
**(400 MHz, CHLOROFORM-d)**



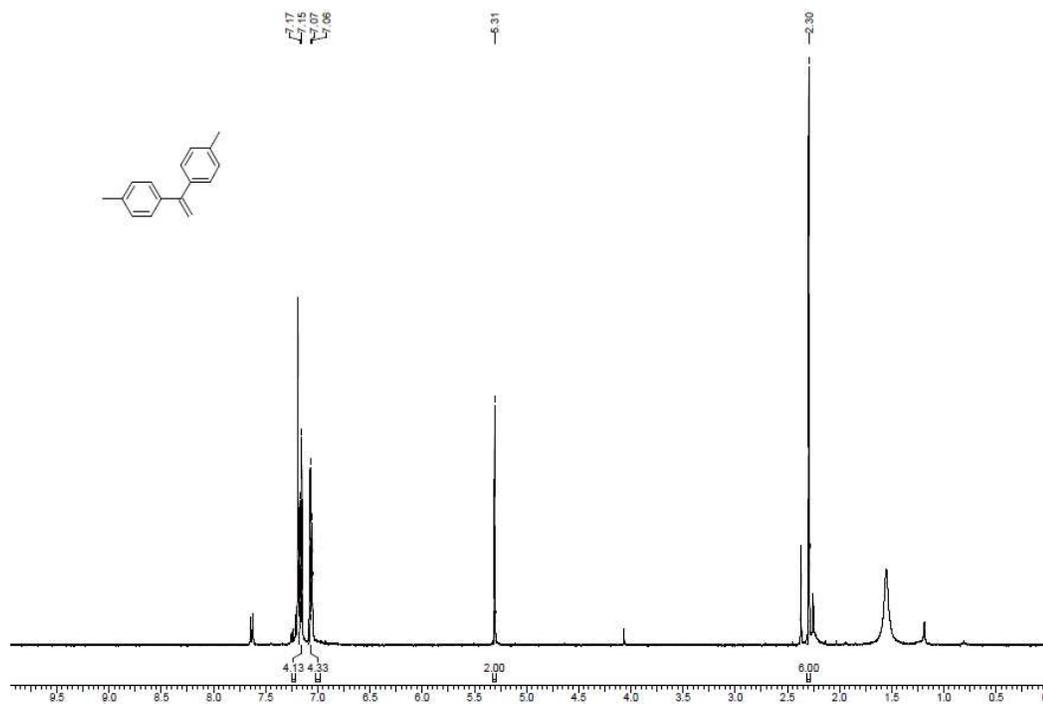
**<sup>13</sup>C NMR of 1-methyl-4-(1-(4-phenoxyphenyl)vinyl)benzene (22)**  
**(100 MHz, CHLOROFORM-d)**



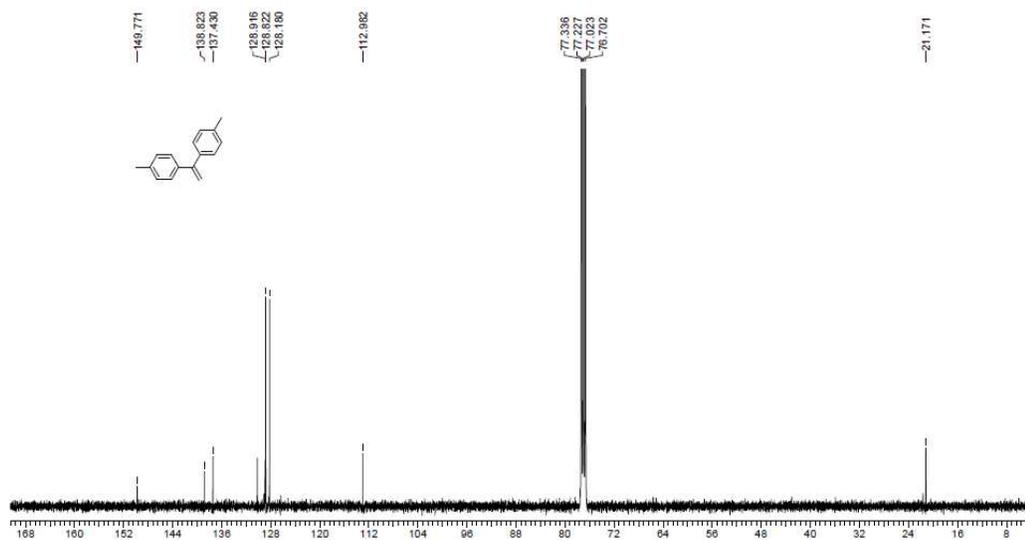
**<sup>1</sup>H NMR of 4-(1-(p-tolyl)vinyl)benzonitrile (23)**  
**(400 MHz, CHLOROFORM-d)**



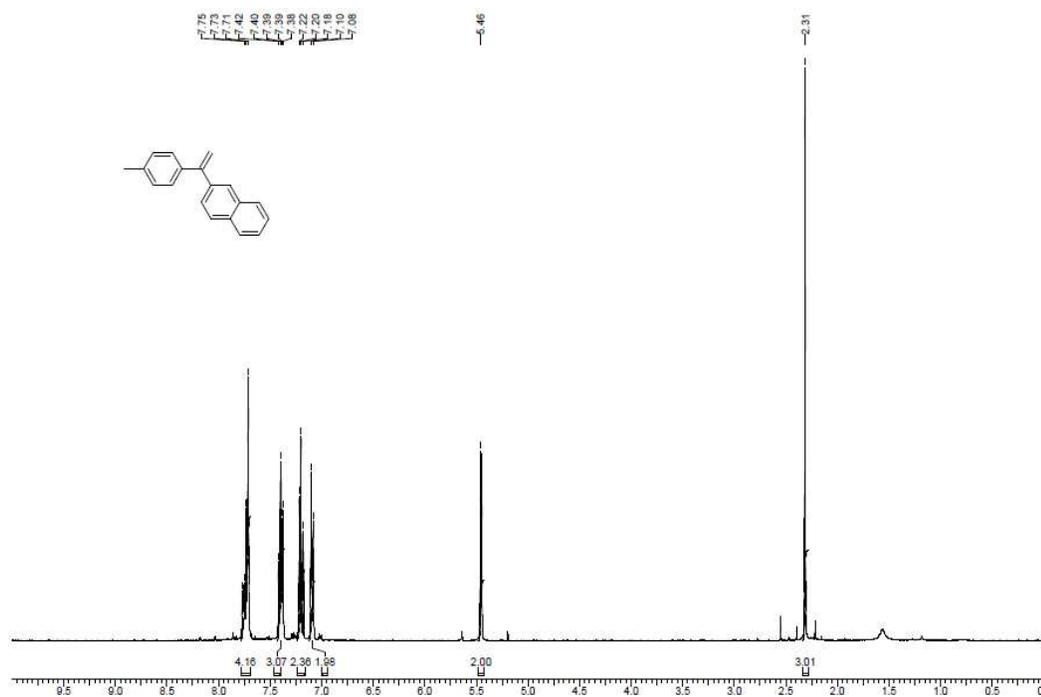
**<sup>13</sup>C NMR of 4-(1-(p-tolyl)vinyl)benzonitrile (23)**  
**(100 MHz, CHLOROFORM-d)**



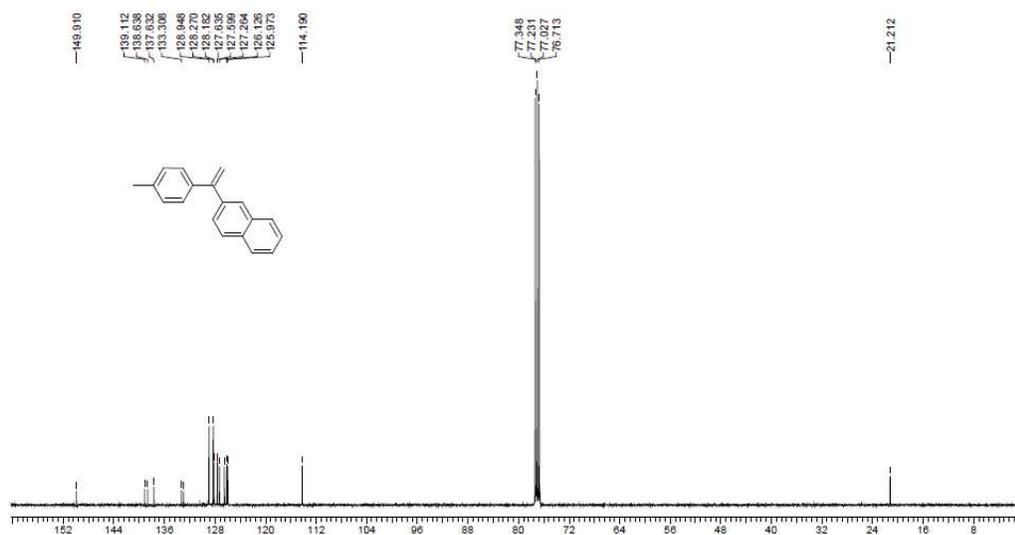
**<sup>1</sup>H NMR of 4,4'-(ethene-1,1-diyl)bis(methylbenzene) (24)**  
(400 MHz, CHLOROFORM-d)



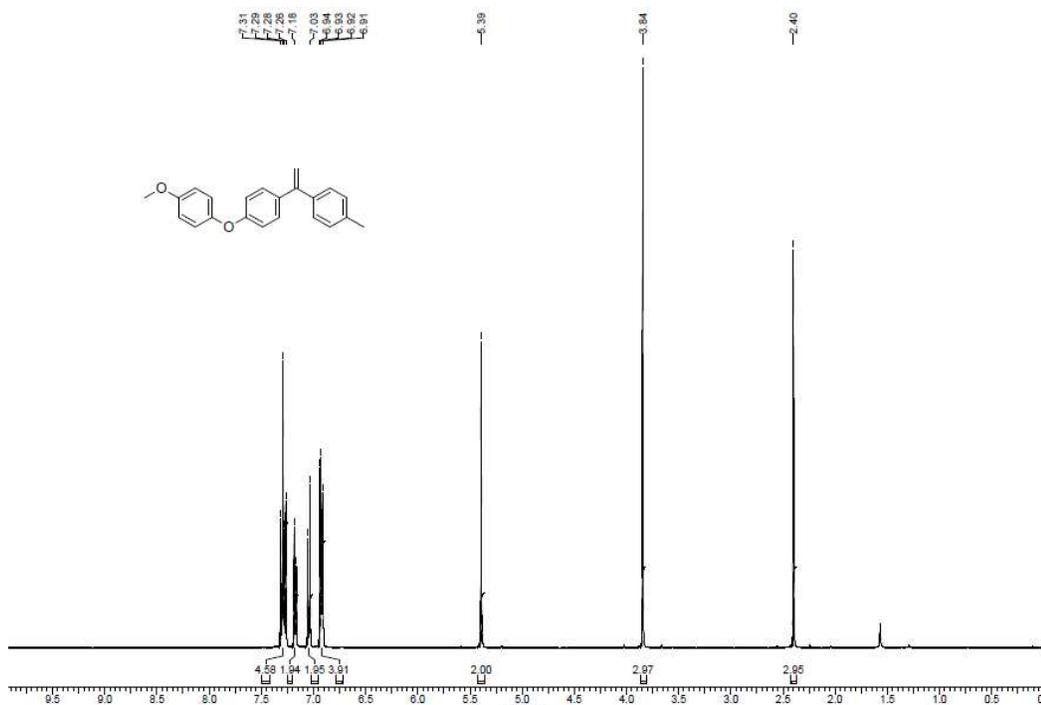
**<sup>13</sup>C NMR of 4,4'-(ethene-1,1-diyl)bis(methylbenzene) (24)**  
(100 MHz, CHLOROFORM-d)



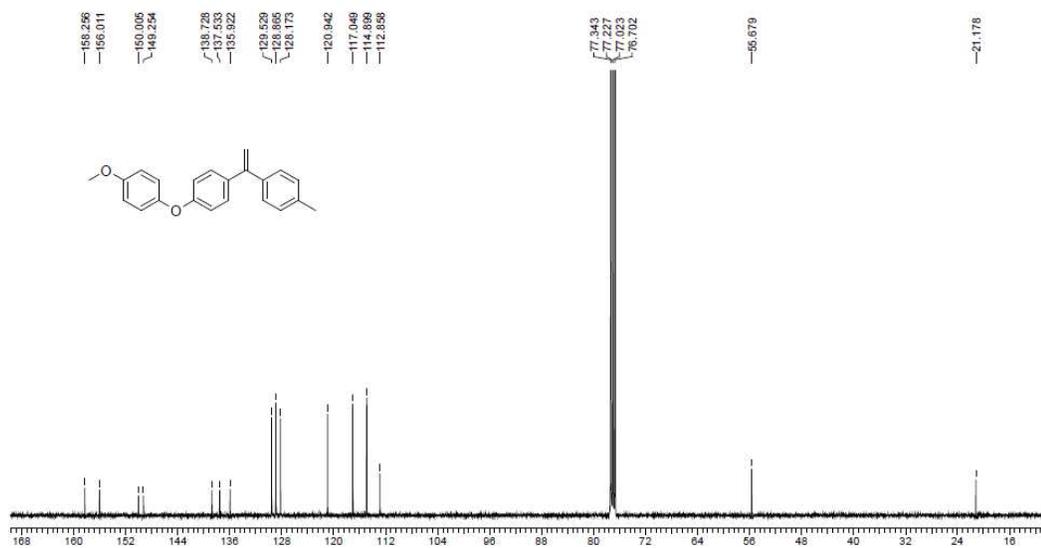
**<sup>1</sup>H NMR of 2-(1-(p-tolyl)vinyl)naphthalene (25)**  
(400 MHz, CHLOROFORM-d)



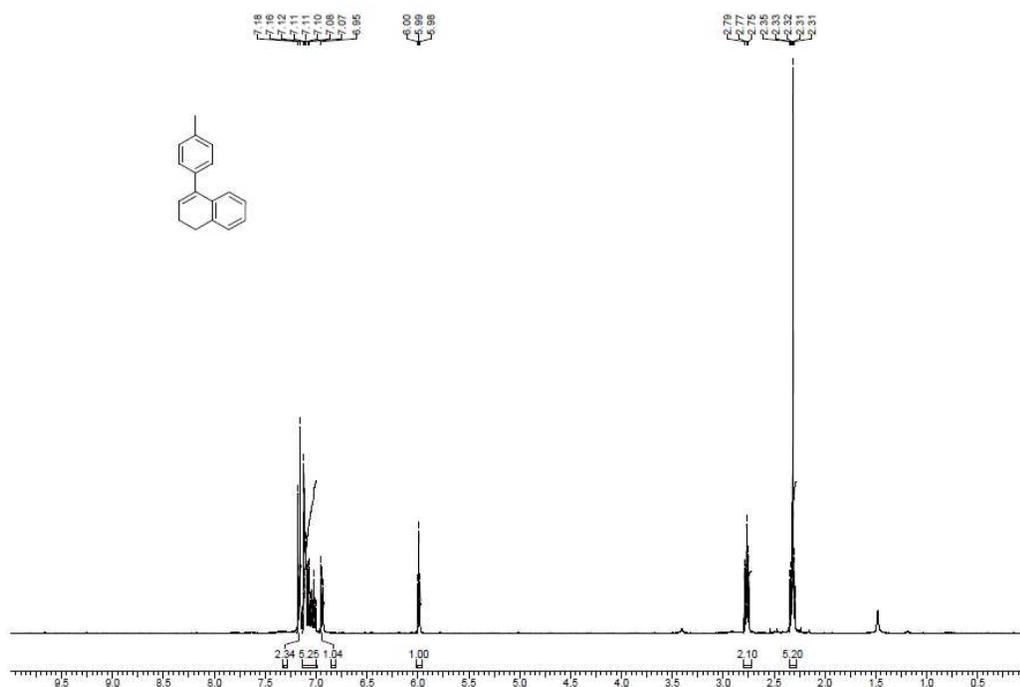
**<sup>13</sup>C NMR of 2-(1-(p-tolyl)vinyl)naphthalene (25)**  
(100 MHz, CHLOROFORM-d)



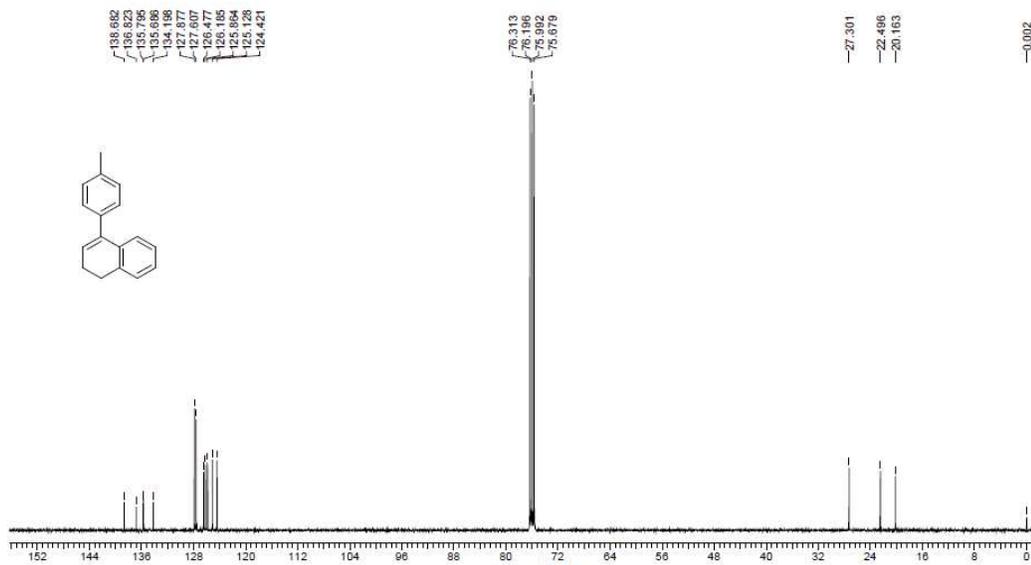
**<sup>1</sup>H NMR of 1-methoxy-4-(4-(1-(p-tolyl)vinyl)phenoxy)benzene (26)**  
**(400 MHz, CHLOROFORM-d)**



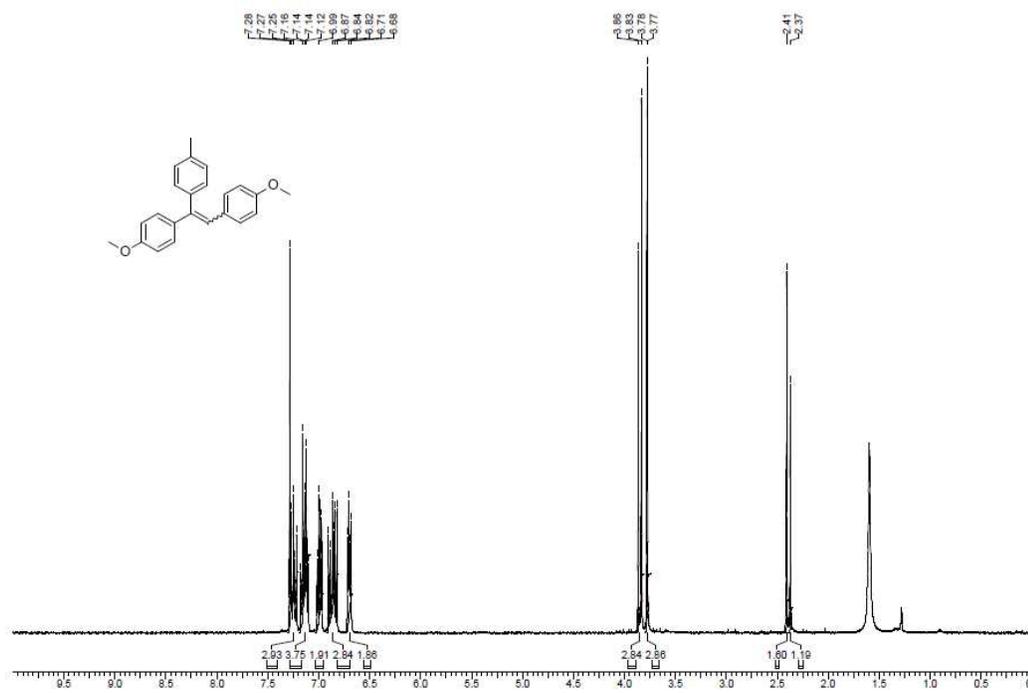
**<sup>13</sup>C NMR of 1-methoxy-4-(4-(1-(p-tolyl)vinyl)phenoxy)benzene (26)**  
**(100 MHz, CHLOROFORM-d)**



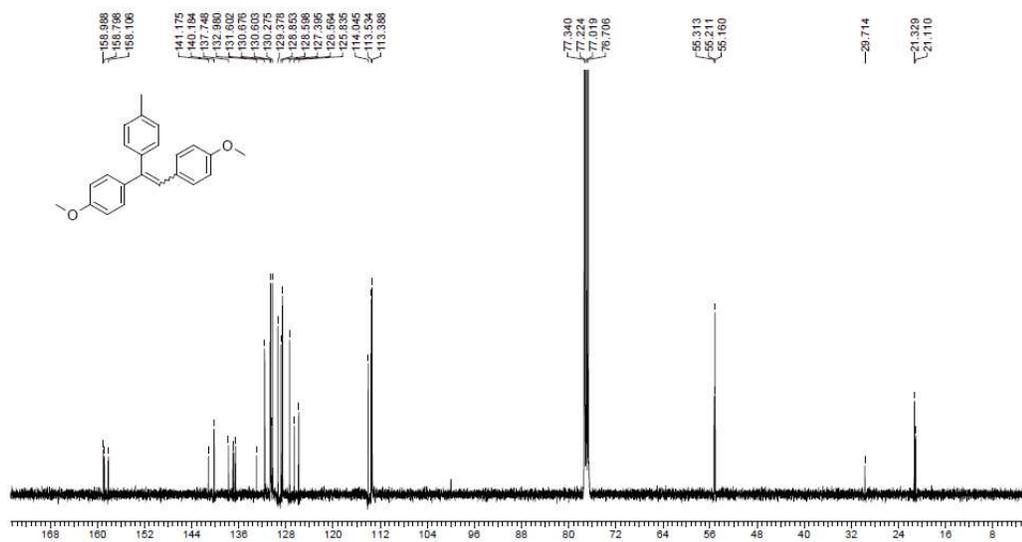
**<sup>1</sup>H NMR of 4-(p-tolyl)-1,2-dihydronaphthalene (27)**  
**(400 MHz, CHLOROFORM-d)**



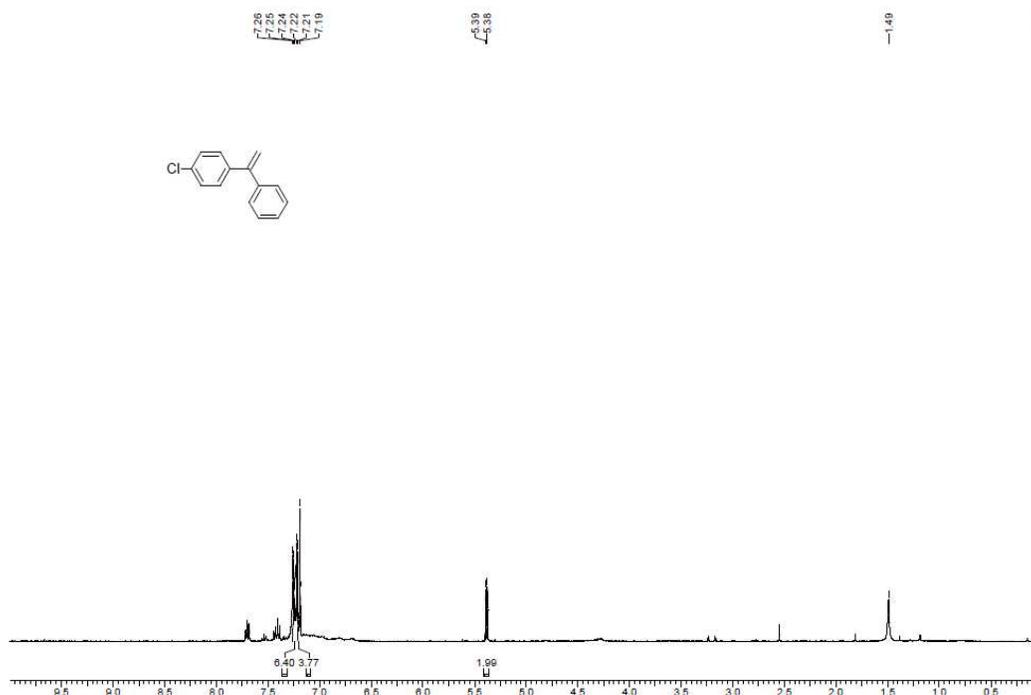
**<sup>13</sup>C NMR of 4-(p-tolyl)-1,2-dihydronaphthalene (27)**  
**(100 MHz, CHLOROFORM-d)**



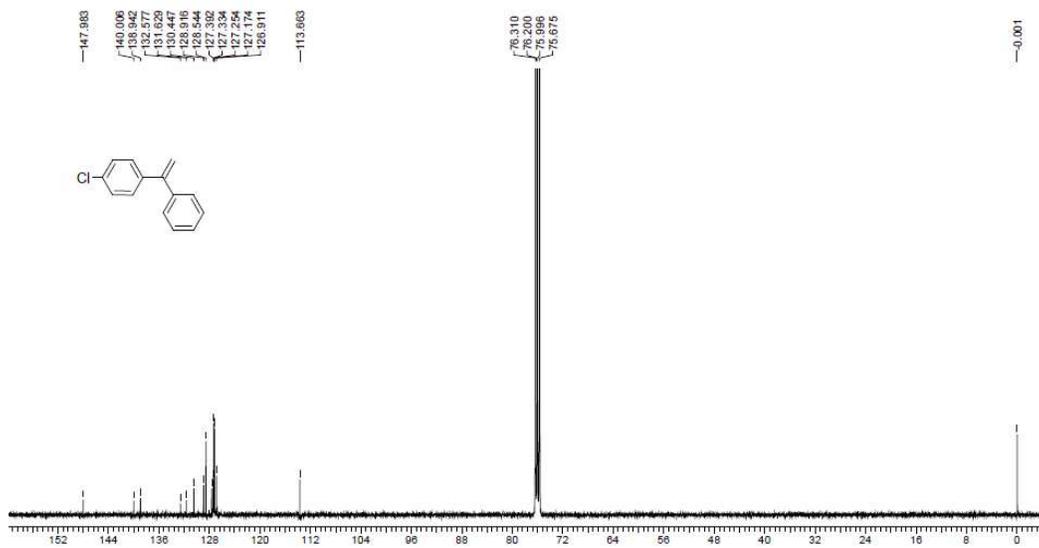
**<sup>1</sup>H NMR of 4,4'-(1-(p-tolyl)ethene-1,2-diyl)bis(methoxybenzene) (28)**  
(400 MHz, CHLOROFORM-d)



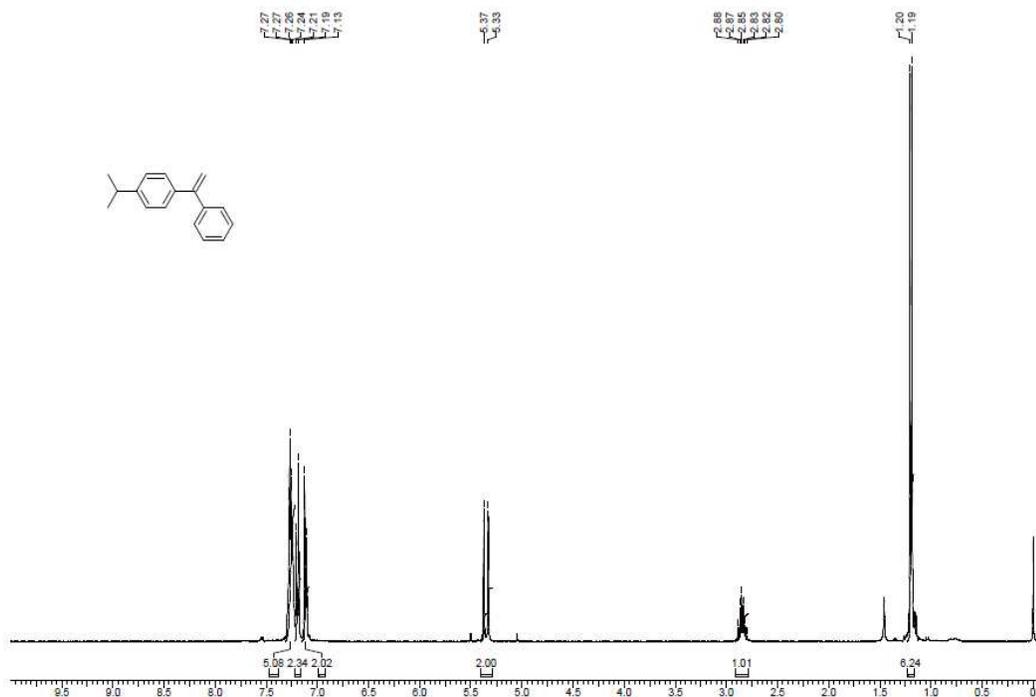
**<sup>13</sup>C NMR of 4,4'-(1-(p-tolyl)ethene-1,2-diyl)bis(methoxybenzene) (28)**  
(100 MHz, CHLOROFORM-d)



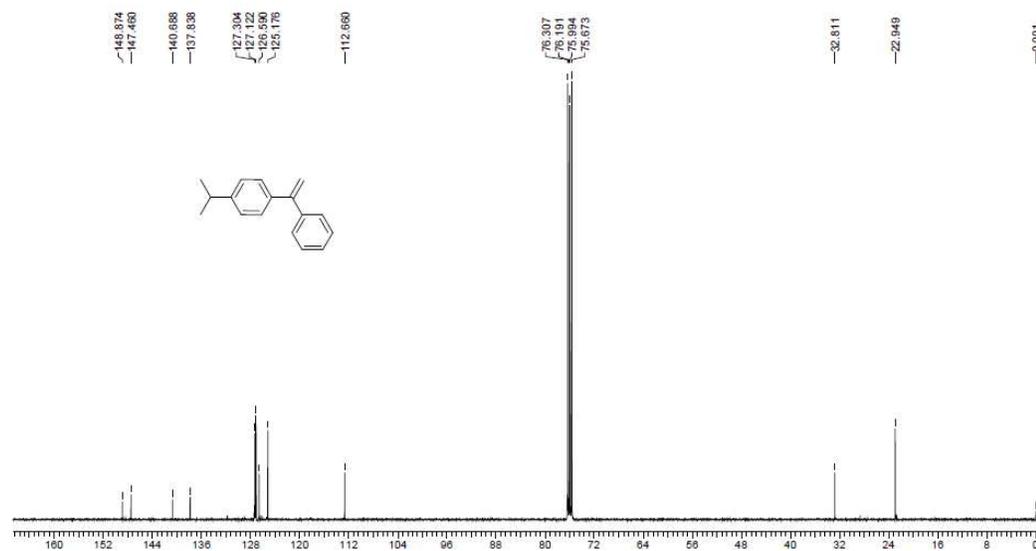
**<sup>1</sup>H NMR of 1-chloro-4-(1-phenylvinyl)benzene (29)**  
(400 MHz, CHLOROFORM-d)



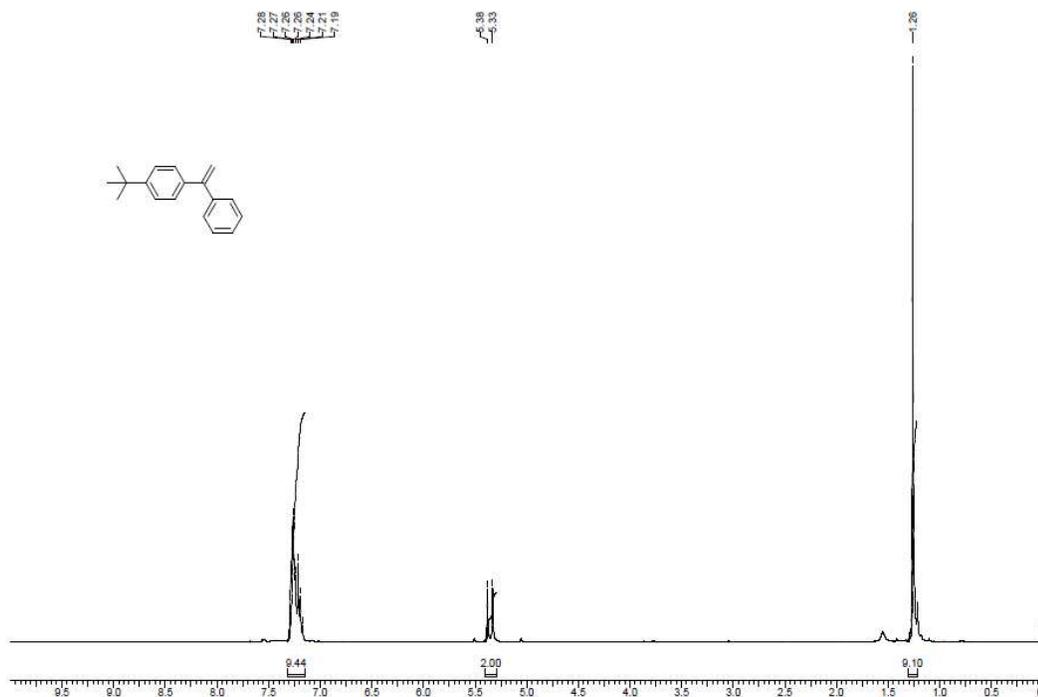
**<sup>13</sup>C NMR of 1-chloro-4-(1-phenylvinyl)benzene (29)**  
(100 MHz, CHLOROFORM-d)



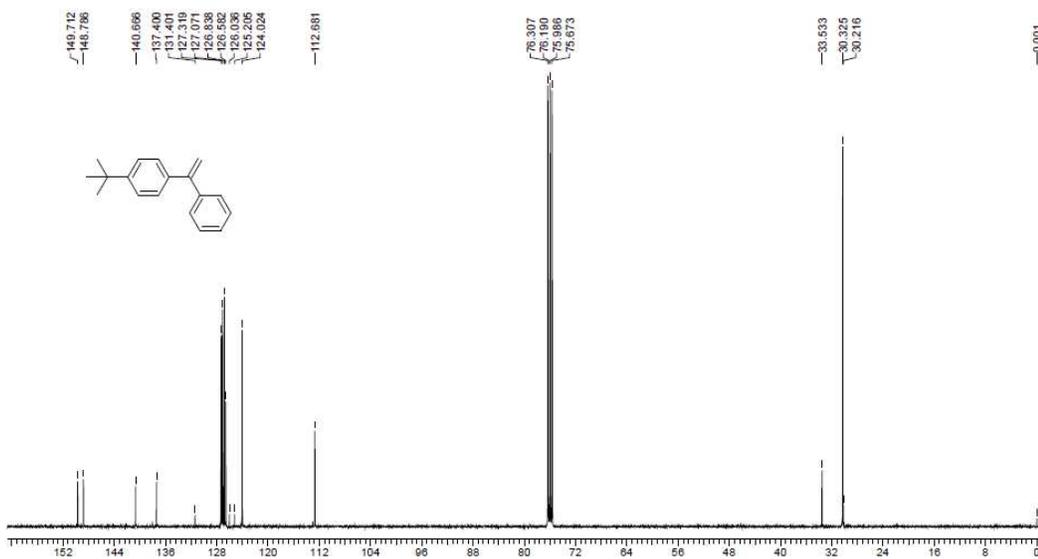
**<sup>1</sup>H NMR of 1-isopropyl-4-(1-phenylvinyl)benzene (30)**  
(400 MHz, CHLOROFORM-d)



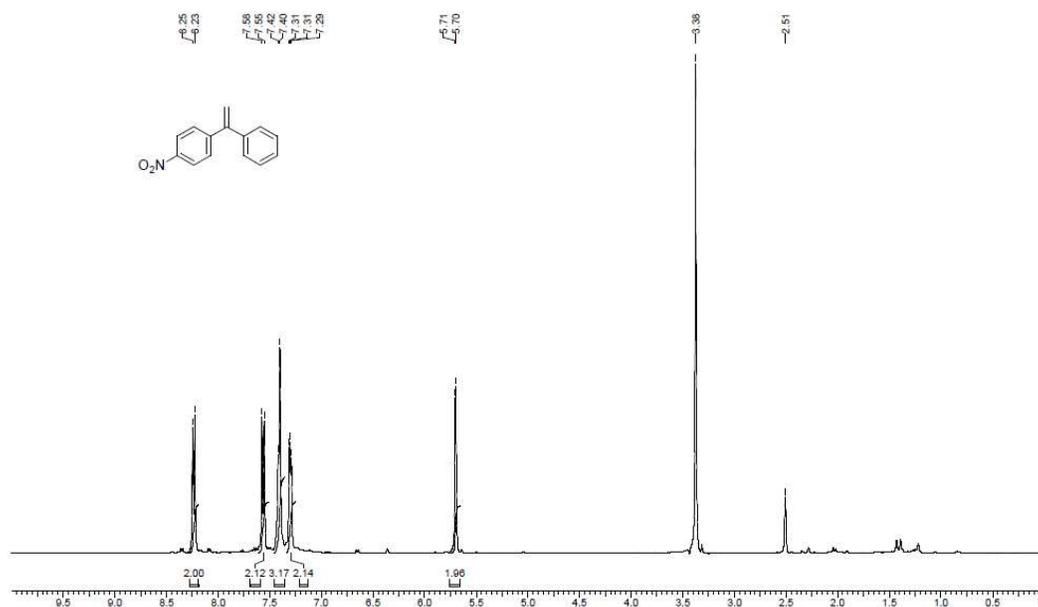
**<sup>13</sup>C NMR of 1-isopropyl-4-(1-phenylvinyl)benzene (30)**  
(100 MHz, CHLOROFORM-d)



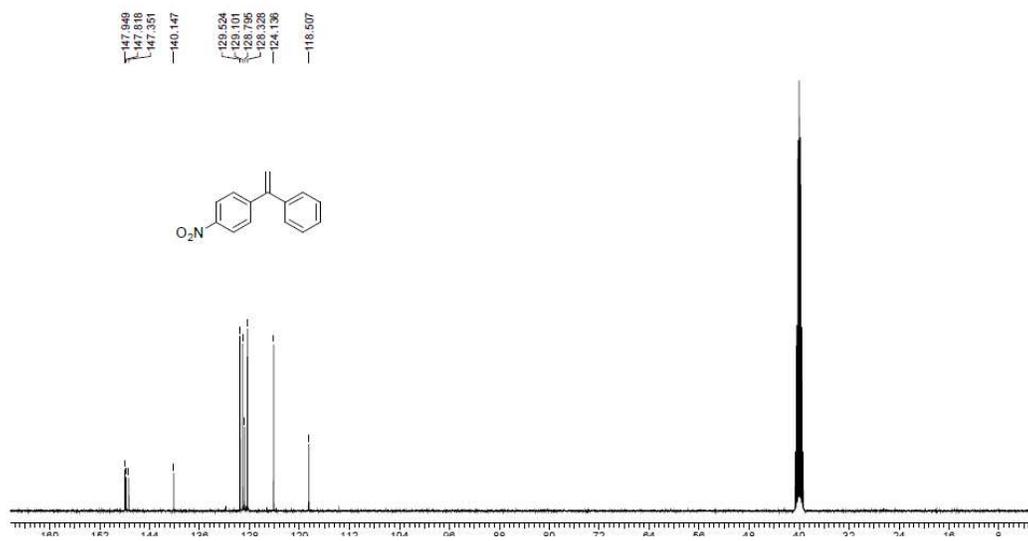
**<sup>1</sup>H NMR of 1-(tert-butyl)-4-(1-phenylvinyl)benzene (31)**  
**(400 MHz, CHLOROFORM-d)**



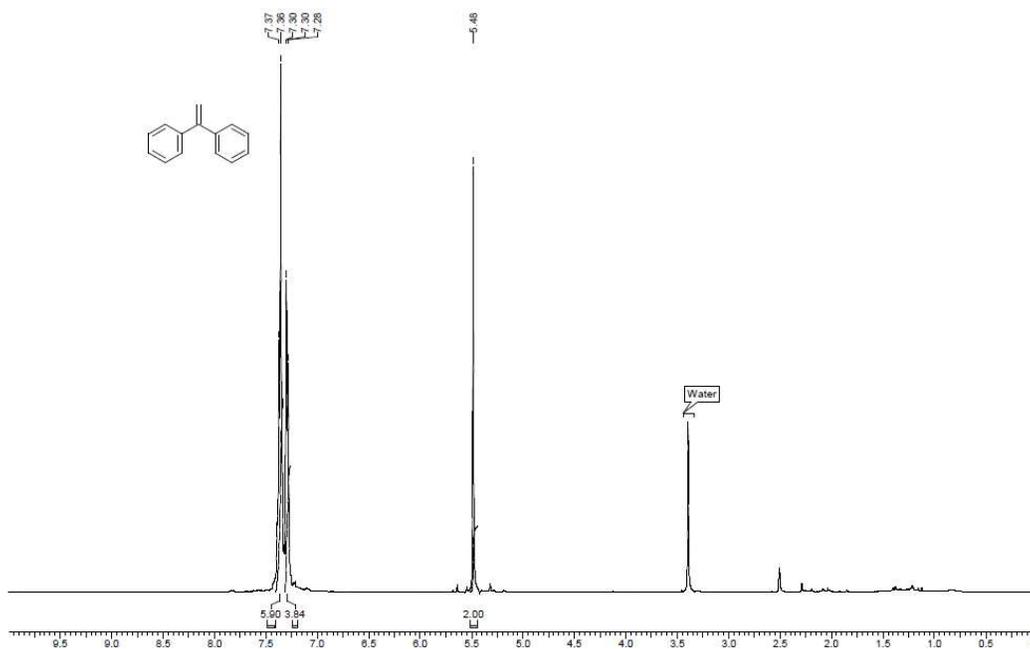
**<sup>13</sup>C NMR of 1-(tert-butyl)-4-(1-phenylvinyl)benzene (31)**  
**(100 MHz, CHLOROFORM-d)**



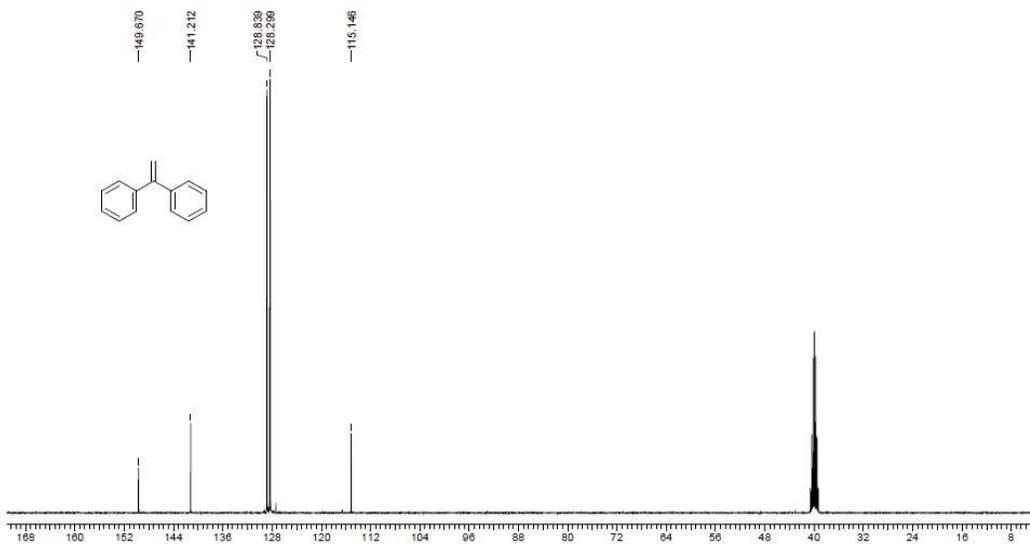
**<sup>1</sup>H NMR of 1-nitro-4-(1-phenylvinyl)benzene (32)**  
**(400 MHz, DMSO-d<sub>6</sub>)**



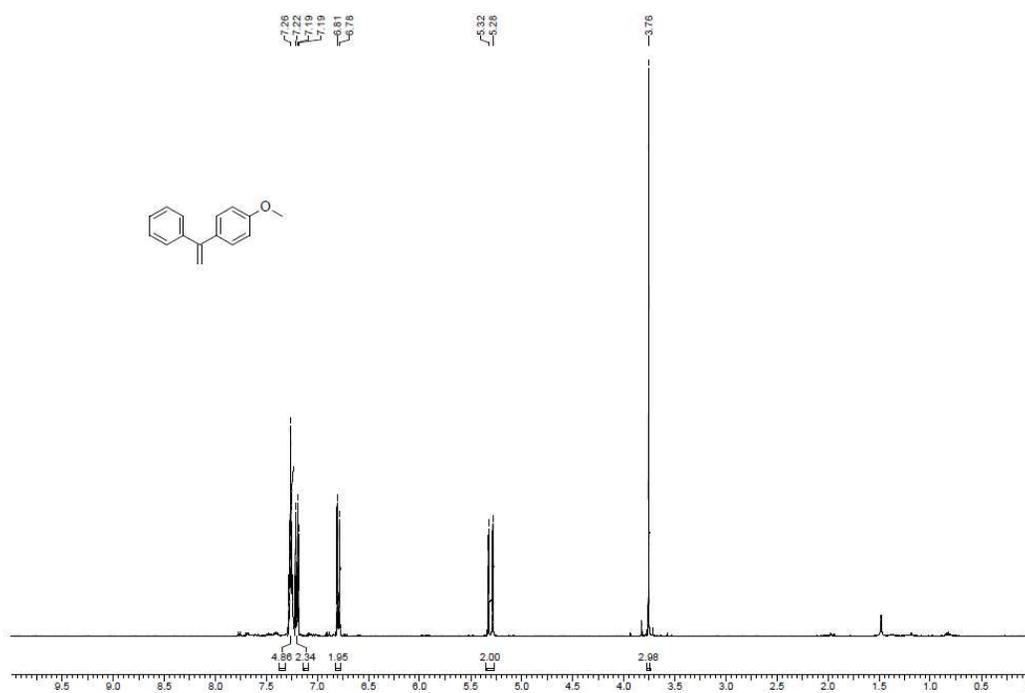
**<sup>13</sup>C NMR of 1-nitro-4-(1-phenylvinyl)benzene (32)**  
**(100 MHz, DMSO-d<sub>6</sub>)**



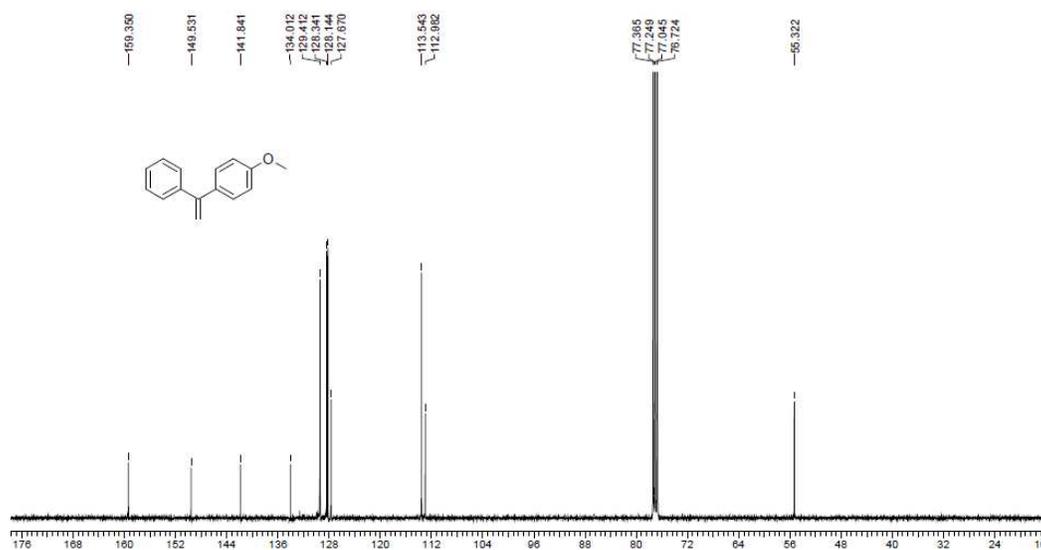
**<sup>1</sup>H NMR of ethene-1,1-diylidibenzene (33) (400 MHz, DMSO-d<sub>6</sub>)**



**<sup>13</sup>C NMR of ethene-1,1-diylidibenzene (33) (100 MHz, DMSO-d<sub>6</sub>)**



**<sup>1</sup>H NMR of 1-methoxy-4-(1-phenylvinyl)benzene (34)**  
**(400 MHz, CHLOROFORM-d)**



**<sup>13</sup>C NMR of 1-methoxy-4-(1-phenylvinyl)benzene (34)**  
**(100 MHz, CHLOROFORM-d)**