Supporting Information for

# Copper(I)-Catalyzed Olefination of N-Sulfonylhydrazones with Sulfones

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#### 1) General

All reactions were performed under a nitrogen atmosphere in oven-dried reaction flasks. All solvents were freshly distilled and degassed according to the handbook *Purification of Laboratory Chemicals* (4<sup>th</sup> Edition, B. Heinemann, W. L. F. Armarego and D. D. Perrin). The boiling point of petroleum ether (PE) was between 60 and 90 °C. Commercially available reagents were used as received. For chromatography, 200-300 mesh silica gel (Qingdao, China) was used. <sup>1</sup>H NMR spectra were recorded on Bruker ARX 400 (400 MHz); <sup>13</sup>C NMR spectra were recorded on Bruker ARX 400 (101 MHz); The data for NMR spectra were reported as follows: chemical shifts ( $\delta$ ) were reported in ppm, and coupling constants (*J*) are in Hertz (Hz). IR spectra were recorded on Nicolet 5MX-S infrared spectrometer and were reported in terms of frequency of absorption (cm<sup>-1</sup>). Mass spectra were obtained on Agilent 7890A/5975C, HRMS were obtained on Bruker APEX IV FTMS.

### 2) General procedure for preparation of hydrozones

$$\begin{array}{c} O \\ R_1 \\ R_2 \end{array} + TsNHNH_2 \end{array} \xrightarrow{MeOH} \begin{array}{c} NNHTs \\ R_1 \\ \hline R_2 \end{array}$$

The ketone or aldehyde (10 mmol) was added to the methanolic solution (5 mL) of p-toluenesulfonhydrazide (10 mmol). The reaction mixture was heated at 60 °C or at room temperature for 0.5-2 h. Then the mixture was cooled to room temperature. The crystalline product was collected by filtration and washed thoroughly with petroleum ether (20 mL × 3).

$$\begin{array}{c} O \\ R_1 \\ R_2 \end{array} + MeSO_2CI + NH_2NH_2 \cdot H_2O \\ \hline H_2O/MeOH \end{array} \begin{array}{c} NaOH \\ H_2O/MeOH \\ \hline R_1 \\ R_2 \end{array}$$

The MeSO<sub>2</sub>Cl (5 mmol) was added to the aqueous solution (2 mL) of hydrazine hydrate (5 mmol) at 0  $^{\circ}$ C. Then 2M NaOH (5 mmol) aqueous solution was added. After one hour, the methanolic solution (5 mL) of ketone was added to the mixture. The reaction mixture was heated at 40  $^{\circ}$ C for several hours. Then the mixture was cooled to room temperature. The

crystalline product was collected by filtration and washed thoroughly with petroleum ether (20 mL  $\times$  3).

#### 3) General procedure for olefination of hydrozones with sulfones

The hydrazone (0.20 mmol), sulfone (2.0 equiv, 0.40 mmol), LiOtBu (3.0 equiv, 0.6 mmol), CuI (20 mol%, 0.04 mmol) and 0.5 mL dioxane were mixed in an oven-dried reaction flask. The mixture was stirred at 90 °C under nitrogen atmosphere for about 4 hours. Then the crude mixture was cooled to room temperature. Petroleum ether was added to the mixture. The mixture was filtered through *celite*. The solvents were evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel.

Note: with  $Cu(OAc)_2$ ,  $Pd(OAc)_2$ , AgOAc or  $[Rh(cod)Cl]_2$  as the catalyst, only trace or no olefination product was detected; with CuCl, CuBr,  $Cu(MeCN)_4PF_6$  or  $CuBr_2$  as the catalyst, 5-10% olefination product could be observed.

#### 4) Characterization data for the products

## 1-(but-3-en-1-yl)-4-chlorobenzene (3a)<sup>1</sup>



Yield 55%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.80$  (PE); <sup>1</sup>**H NMR** (400 **MHz, CDCl<sub>3</sub>**)  $\delta$  7.25 – 7.22 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 5.82 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.05 – 4.97 (m, 2H), 2.68 (t,

J = 8.0 Hz, 2H), 2.35 (dt, J = 14.2, 7.1 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.2, 137.6, 131.5, 129.8, 128.4, 115.3, 35.4, 34.7.

### 1-bromo-4-(but-3-en-1-yl)benzene (3b)<sup>1</sup>



Yield 64%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.72$  (PE); <sup>1</sup>**H NMR** (400 **MHz, CDCl<sub>3</sub>**)  $\delta$  7.39 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 5.82 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 4.97 (m, 2H), 2.66 (t,

J = 8.0Hz, 2H), 2.34 (dt, J = 14.3, 7.1 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.8, 137.6,

#### 131.3, 130.2, 119.6, 115.3, 35.3, 34.8.

### 1-(but-3-en-1-yl)-3-chlorobenzene (3c)<sup>1</sup>



Yield 67%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.80$  (PE); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.2 –7.12 (m, 3H), 7.06 (d, J = 7.2 Hz, 1H), 5.83 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.11–4.88 (m, 2H), 2.68 (t, J = 12

7.4 Hz, 2H), 2.36 (dt, J = 14.2, 7.1 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.9, 137.5, 134.0, 129.5, 128.6, 126.7, 126.0, 115.3, 35.2, 35.0.

#### 2-methyl-5-(pent-4-en-2-yl)furan (3d)



Yield 65%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.70$  (PE); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.84 (s, 2H), 5.76 (ddt, J = 17.1, 10.1, 7.1 Hz, 1H), 5.06 – 4.99 (m, 2H), 2.87 – 2.78 (m, 1H), 2.49 – 2.42 (m, 1H),

2.25 (s, 3H), 2.23 – 2.18 (m, 1H), 1.20 (d, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 158.3, 150.1, 136.6, 116.2, 105.6, 104.2, 40.0, 32.9, 18.4, 13.5. EI-MS (*m/z*, relative intensity) 150 (M<sup>+</sup>, 10), 136 (2), 109 (100), 91 (8), 81 (5); HRMS (ESI) calcd for: C<sub>10</sub>H<sub>14</sub>O [M]<sup>+</sup> 150.1045, found: 150.1045; **IR (film):** 2964, 2921, 2856, 743, 651 cm<sup>-1</sup>.

tridec-1-ene (3e)<sup>2</sup>



Yield 65%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.95$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl**<sub>3</sub>)  $\delta$  5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.02 – 4.91 (m, 2H), 2.04 (dd, J = 14.3, 6.9 Hz, 2H), 1.37 – 1.26 (m, 18H), 0.88 (t, J = 6.8 Hz,

3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.3, 114.1, 33.9, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.2, 29.0, 22.7, 14.1.

#### buta-1,3-diene-1,1-diyldibenzene (3f)<sup>1</sup>



Yield 58%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.65$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl**<sub>3</sub>)  $\delta$  7.40-7.21 (m, 10H), 6.71 (d, J = 11.0 Hz, 1H), 6.44 (ddd, J = 16.9, 10.5, 10.5 Hz, 1H), 5.39 (d, J = 16.9, 1.2 Hz, 1H), 5.13 (d, J = 10.1,

1.2 Hz, 1H).; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.1, 142.1, 139.7, 135.0, 130.4, 128.5, 128.2, 128.2, 127.6, 127.5, 127.4, 118.6.

### 2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (3g)<sup>3</sup>



Yield 68%; colorless oil; **TLC**  $\mathbf{R_f} = 0.70$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl<sub>3</sub>**)  $\delta$  7.93–7.82 (m, 4H), 7.56–7.48 (m, 3H), 6.03 (d, J = 1.2 Hz, 1H), 5.88 (d, J = 1.6 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  139.0

(q,  $J_F = 30.1$  Hz), 133.3, 133.1, 130.9, 128.5, 128.3, 127.6, 127.0, 126.8, 126.6, 124.7, 123.5 (q,  $J_F = 275.5$  Hz), 120.7 (q,  $J_F = 5.7$  Hz).

#### 1-(3,3,3-trifluoroprop-1-en-2-yl)-4-(vinyloxy)benzene (3h)



Yield 56%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.30$  (PE); <sup>1</sup>**H NMR** (400 **MHz, CDCl<sub>3</sub>**)  $\delta$  7.32 (td, J = 8.3, 1.7 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 6.96 (td, J = 7.5, 0.8 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H),

6.09 (d, J = 1.3 Hz, 1H), 6.06 – 5.94 (m, 1H), 5.66 (d, J = 0.9 Hz, 1H), 5.38 (dm, J = 17.3 Hz, 1H), 5.25 (dm, J = 10.6 Hz, 1H), 4.55 (dt, J = 4.9, 1.5 Hz, 2H).; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.4, 136.1 (q,  $J_F = 31.5$  Hz), 133.0, 130.8, 130.1, 123.3 (q,  $J_F = 5.3$  Hz), 123.1 (q,  $J_F = 282.8$  Hz), 120.5, 117.2, 112.6, 69.1. EI-MS (*m*/*z*, relative intensity) 228 (M<sup>+</sup>, 30), 187 (100), 167 (28), 159 (32), 149 (28), 118 (30), 109 (38), 101 (10), 89 (15), 75 (10); HRMS (ESI) calcd for: C<sub>12</sub>H<sub>11</sub>F<sub>3</sub>O [M]<sup>+</sup> 228.0762, found: 228.0762; IR (film): 2924, 1736, 1246, 1173, 1130, 1046, 752 cm<sup>-1</sup>.

### **4-vinyl-1,1'-biphenyl** (5a)<sup>4</sup>



Yield 50%; white solid; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.60$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl**<sub>3</sub>)  $\delta$  7.60–7.55 (m, 4H), 7.49–7.41 (m, 4H), 7.35–7.32 (m, 1H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.79 (d, J = 17.6 Hz, 1H), 5.27 (d, J =

10.9 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.8, 140.6, 136.6, 136.4, 128.8, 127.3, 127.3, 127.0, 126.7, 113.9.

### **2-vinyl-1,1'-biphenyl** (5b)<sup>5</sup>



Yield 46%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.70$  (PE); <sup>1</sup>**H NMR** (400 MHz, **CDCl**<sub>3</sub>)  $\delta$  7.66–7.63 (m, 1H), 7.4–7.23 (m, 8H), 6.71 (dd, J = 17.5, 11.0 Hz, 1H), 5.70 (dd, J = 17.5, 1.1 Hz, 1H), 5.18 (dd, J = 11.0, 1.1 Hz, 1H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.8, 135.9, 135.7, 130.1, 129.8, 128.0, 127.6, 127.4, 127.0, 125.7, 114.6.

### 2-(prop-1-en-2-yl)naphthalene (5c)<sup>6</sup>



Yield 60%; white solid; **TLC**  $\mathbf{R_f} = 0.60$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl<sub>3</sub>**)  $\delta$  7.84–7.76 (m, 4H), 7.66 (dd, J = 8.6, 1.7 Hz, 1H), 7.47 – 7.41 (m, 2H), 5.53 (s, 1H), 5.19 (s, 1H), 2.26 (s, 1H); <sup>13</sup>C NMR

(**101 MHz, CDCl<sub>3</sub>**) δ 143.0, 138.4, 133.4, 132.8, 128.3, 127.7, 127.6, 126.2, 125.9, 124.3, 123.9, 113.1, 21.9.

### 1,2-dichloro-4-(prop-1-en-2-yl)benzene (5d)<sup>7</sup>



Yield 76%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.85$  (PE); <sup>1</sup>**H NMR** (400 **MHz**, **CDCl**<sub>3</sub>)  $\delta$  7.52 (d, J = 2.1 Hz, 1H), 7.39–7.26 (m, 2H), 5.37 (s, 1H), 5.14 (s, 1H), 2.11 (s, 3H); <sup>13</sup>C **NMR** (101 **MHz**, **CDCl**<sub>3</sub>)  $\delta$  141.3, 141.1, 132.3, 131.2, 130.1, 127.5, 124.8, 114.1, 21.6.

### 1-bromo-4-(prop-1-en-2-yl)benzene (5e)<sup>8</sup>



Yield 65%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}}$ = 0.80(PE); <sup>1</sup>**H NMR** (400 MHz, **CDCl**<sub>3</sub>)  $\delta$  7.45–7.31 (m, 4H), 5.36 (s, 1H), 5.10–5.09 (m, 1H), 2.12 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.2, 140.1, 131.3, 127.2, 121.3,

113.1, 21.7.

### 4-(prop-1-en-2-yl)benzonitrile (5f)<sup>9</sup>



Yield 85%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.40$  (PE:EA = 30:1); <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.62 (d, J = 8.5 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 5.47 (s, 1H), 5.47–5.24 (m, 1H), 2.16 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.7, 141.8, 132.1, 126.1, 119.0, 115.7, 110.9, 21.5.

### ethene-1,1-diyldibenzene (5g)<sup>10</sup>



Yield 70%; colorless oil; **TLC**  $\mathbf{R_f} = 0.45$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl**<sub>3</sub>)  $\delta$  7.34-7.21 (m, 10H), 5.46 (s, 2H); <sup>13</sup>C NMR (101 MHz, **CDCl**<sub>3</sub>)  $\delta$  150.1, 141.5, 128.3, 128.2, 127.7, 114.3.

### 1-chloro-4-(1-phenylvinyl)benzene (5h)<sup>10</sup>



Yield 73%; white solid; **TLC**  $\mathbf{R_f} = 0.85$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl<sub>3</sub>**)  $\delta$  7.34 – 7.22 (m, 9H), 5.45 (d, J = 1.0 Hz, 1H), 5.43 (d, J = 1.0 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.0, 141.0, 140.0,

133.6, 129.6, 128.4, 128.3, 128.2, 128.0, 114.8.

### 4-(1-phenylvinyl)benzonitrile (5i)<sup>10</sup>



Yield 77%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.70$  (PE:EA = 10:1); <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$ 7.62 (d, J = 8.3 Hz, 2H), 7.44 – 7.25 (m, 9H), 5.58 (s, 1H), 5.54 (s, 1H); <sup>13</sup>C **NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$ 148.7,

146.1, 140.2, 132.1, 128.9, 128.5, 128.3, 128.2, 118.9, 116.7, 111.4.

## 1-methoxy-4-(1-phenylvinyl)benzene (5j)<sup>10</sup>



Yield 65%; white solid; **TLC**  $\mathbf{R}_{f} = 0.15$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl**<sub>3</sub>)  $\delta$  7.34 – 7.23 (m, 7H), 6.87 – 6.85 (m, 2H), 5.39 (d, J = 1.1 Hz, 1H), 5.35 (d, J = 1.1 Hz, 1H), 3.81 (s, 3H); <sup>13</sup>C NMR (101

**MHz**, **CDCl**<sub>3</sub>) δ 159.4, 149.5, 141.8, 134.0, 129.4, 128.4, 128.2, 127.7, 113.6, 113.0, 55.3.

### 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) (5k)<sup>11</sup>



Yield 67%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.60$  (PE); <sup>1</sup>**H NMR** (400 **MHz**, **CDCl**<sub>3</sub>)  $\delta$  7.31 – 7.25 (m, 4H), 7.05 – 6.99 (m, 4H), 5.39 (s,

2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.6 (d,  $J_F$  = 247.0 Hz), 148.1, 137.4 (d,  $J_F$  = 3.1 Hz), 129.8 (d,  $J_F$  = 8.0 Hz), 115.1 (d,  $J_F$  = 21.6 Hz), 114.2.

### 4,4'-(ethene-1,1-diyl)bis(chlorobenzene) (51)<sup>12</sup>



Yield 76%; yellow solid; TLC  $\mathbf{R_f} = 0.60$  (PE); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta 7.32 - 7.22$  (m, 8H), 5.44 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta 147.9$ , 139.5, 133.9, 129.5, 128.5, 115.1.

### 4,4'-(ethene-1,1-diyl)bis(methylbenzene) (5m)<sup>10</sup>



128.9, 128.2, 113.0, 21.2.

Yield 57%; colorless oil; **TLC**  $\mathbf{R_f} = 0.50$  (PE); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18 (dd, J = 41.4, 8.0 Hz, 8H), 5.37 (s, 2H), 2.36 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.8, 138.8, 137.5,

## 1-fluoro-4-(1-(4-methoxyphenyl)vinyl)benzene (5n)<sup>13</sup>



Yield 56%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.55$  (PE); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta 7.32 - 7.23$  (m, 4H), 7.04 - 6.98 (m, 2H), 6.88 - 6.84 (m, 2H), 5.37 (d, J = 0.9 Hz, 1H), 5.30 (d, J = 0.9 Hz, 1H),

3.82 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.5 (d,  $J_F$  = 246.6 Hz), 159.4, 148.5, 137.9 (d,  $J_F$  = 3.5 Hz), 133.8, 129.9 (d,  $J_F$  = 8.0 Hz), 129.4, 115.0 (d,  $J_F$  = 21.3 Hz), 113.6, 112.9, 55.3.

#### methyl(3-(1-phenylvinyl)phenyl)sulfane (50)



Yield 72%; colorless oil; **TLC**  $\mathbf{R_f} = 0.30$  (PE); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 (s, 5H), 7.25 – 7.19 (m, 3H), 7.09 (dd, J = 7.3, 1.5 Hz, 1H), 5.47 (d, J = 0.9 Hz, 1H), 5.45 (s, 1H), 2.46 (s,

3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.7, 142.2, 141.1, 138.4, 128.6, 128.2, 128.2, 127.8, 126.4, 125.8, 125.3, 114.7, 15.9; EI-MS (*m*/*z*, relative intensity) 226 (M<sup>+</sup>, 100), 211 (8), 178 (85), 165 (10), 152 (11), 104 (3), 89 (5), 77 (8); HRMS (ESI) calcd for: C<sub>15</sub>H<sub>14</sub>S [M]<sup>+</sup> 226.0816, found: 226.0820; IR (film): 1588, 1563, 1495, 1442, 907, 780, 697 cm<sup>-1</sup>.

#### **3,3'-(ethene-1,1-divl)bis(fluorobenzene)** (5p)<sup>14</sup>



Yield 83%; colorless oil; TLC  $R_f = 0.80$  (PE); <sup>1</sup>H NMR (400) **MHz, CDCl<sub>3</sub>**) δ 7.32 – 7.27 (m, 2H), 7.11 – 7.08 (m, 2H), 7.04 – 7.00 (m, 4H), 5.50 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ162.8

(d,  $J_F = 245.7$  Hz), 148.0, 143.1 (d,  $J_F = 7.4$  Hz), 129.8 (d,  $J_F = 8.2$  Hz), 123.9 (d,  $J_F = 2.8$  Hz), 116.0, 115.1 (d,  $J_F$  = 22.0 Hz), 114.8 (d,  $J_F$  = 21.2 Hz).

### **3,3'-(ethene-1,1-diyl)bis(methylbenzene)** (5q)<sup>15</sup>



128.0, 125.5, 114.1, 21.5.

Yield 52%; colorless oil; TLC  $R_f = 0.75$  (PE); <sup>1</sup>H NMR (400) **MHz**, **CDCl**<sub>3</sub>) δ 7.24–7.12 (m, 8H), 5.42 (s, 2H), 2.34 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ150.3, 141.6, 137.7, 129.0, 128.4,

### 1-fluoro-2-(1-phenylvinyl)benzene (5r)<sup>16</sup>



Yield 78%; colorless oil; TLC  $R_f = 0.65$  (PE); <sup>1</sup>H NMR (400) **MHz, CDCl**<sub>3</sub>)  $\delta$ 7.33 – 7.23 (m, 7H), 7.15 – 7.04 (m, 2H), 5.75 (s, 1H), 5.42 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 160.2 (d,  $J_F$  =

248.6 Hz), 144.2, 140.6, 131.6 (d,  $J_F = 3.6$  Hz), 129.4 (d,  $J_F = 8.3$  Hz), 129.3 (d,  $J_F = 14.1$  Hz), 128.3, 127.8, 126.8, 124.0 (d,  $J_F = 3.6$  Hz), 117.1 (d,  $J_F = 1.8$  Hz), 115.8 (d,  $J_F = 22.4$  Hz).

#### 2,2'-(ethene-1,1-diyl)bis(fluorobenzene) (5s)



Yield 38%; colorless oil; TLC  $\mathbf{R}_{f}$ = 0.40 (PE); <sup>1</sup>H NMR (400 MHz, **CDCl**<sub>3</sub>)  $\delta$ 7.29–7.22 (m, 4H), 7.12 – 7.02 (m, 4H), 5.71 (s, 2H); <sup>13</sup>C **NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  160.0 (d,  $J_F$  = 249.0 Hz), 138.9, 130.6 (d,  $J_F = 3.4$  Hz), 129.3 (d,  $J_F = 8.5$  Hz), 129.0 (d,  $J_F = 13.0$  Hz), 124.0 (d,  $J_F = 3.7$  Hz), 121.2 (t,  $J_F = 3.5$  Hz), 115.8 (d,  $J_F = 22.5$  Hz); EI-MS (*m*/*z*, relative intensity) 216 (M<sup>+</sup>, 100), 201 (45), 196 (44), 188 (3), 183 (10), 120 (15), 101 (15), 94 (10), 75 (18), 74 (8); HRMS (ESI)

calcd for: C<sub>14</sub>H<sub>10</sub>F<sub>2</sub> [M]<sup>+</sup> 216.0751, found: 216.0753; **IR** (film): 1736, 1492, 1452, 1257, 1223, 1096, 920, 830, 762 cm<sup>-1</sup>.

### 9-methylene-9H-fluorene (5t)<sup>17</sup>



Yield 80%; pale yellow solid; TLC  $\mathbf{R}_{f} = 0.45$  (PE); <sup>1</sup>H NMR (400 **MHz, CDCl<sub>3</sub>**)  $\delta$  7.70 (dd, J = 16.7, 7.5 Hz, 4H), 7.33 (dtd, J = 28.7, 7.4, 1.1 Hz, 4H), 6.06 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$ 

143.4, 140.2, 138.1, 128.8, 127.1, 121.0, 119.8, 107.8.

#### ethene-1,1,2-triyltribenzene (7a)<sup>18</sup>



Yield 68%; white solid; TLC  $\mathbf{R}_{f} = 0.45$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl<sub>3</sub>**)  $\delta$  7.35–7.29 (m, 8H), 7.21 (dd, J = 6.8, 2.7 Hz, 2H), 7.16 – 7.10 (m, 3H), 7.04 – 7.02 (m, 2H), 6.97 (s, 1H); <sup>13</sup>C NMR (101 **MHz**, **CDCl**<sub>3</sub>) δ 143.5, 142.6, 140.4, 137.4, 130.5, 129.6, 128.7,

128.3, 128.2, 128.0, 127.7, 127.6, 127.5, 126.8.

### 4,4'-(pent-1-ene-1,1-diyl)bis(fluorobenzene) (7b)<sup>18</sup>



Yield 75%; white solid; TLC  $R_f = 0.55$  (PE); <sup>1</sup>H NMR (400 MHz, **CDCl**<sub>3</sub>)  $\delta$  7.28–7.22 (m, 2H), 7.17–7.11 (m, 5H), 7.03–6.97 (m, 6H), 6.89 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.5 (d,  $J_F =$ 248.3 Hz), 163.3 (d,  $J_F$  = 247.9 Hz), 140.5, 139.4 (d,  $J_F$  = 3.1 Hz), 137.1, 136.0 (d,  $J_F = 3.5$  Hz), 132.1 (d,  $J_F = 8.0$  Hz), 129.5, 129.3 (d,  $J_F = 8.0$  Hz), 128.4, 128.1, 127.0, 115.8 (d,  $J_F = 21.3$  Hz), 115.2 (d,  $J_F = 21.5$  Hz).

### 4,4'-(2-phenylethene-1,1-divl)bis(methoxybenzene) (7c)<sup>18</sup>



Yield 94%; white solid; **TLC**  $R_f = 0.25$  (PE); <sup>1</sup>H NMR (400) **MHz**, **CDCl**<sub>3</sub>) δ 7.27–7.24 (m, 2H), 7.14–7.03 (m, 7H), 6.86– 6.82 (m, 5H), 3.82 (s, 3H), 3.81 (s, 3H); <sup>13</sup>C NMR (101 MHz, **CDCl<sub>3</sub>**)  $\delta$  159.3, 158.9, 141.8, 137.9, 136.5, 132.7, 131.6,

129.4, 128.9, 128.0, 126.4, 126.2, 114.0, 113.6, 55.3, 55.2.

### pent-1-ene-1,1-diyldibenzene (9)<sup>10</sup>



Yield 54%; colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.60$  (PE); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38–7.16 (m, 10H), 6.09 (t, J = 7.5 Hz, 1H), 2.09 (dt, J = 7.4, 7.4 Hz, 2H), 1.46 (tq, J = 7.4, 7.4 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.9, 141.6, 140.4,

130.2, 130.0, 128.1, 128.1, 127.2, 126.8, 126.8, 31.9, 23.2, 13.9.

### (*E*)-(4-chlorostyryl)trimethylsilane (11a)<sup>19</sup>



Yield 67% (E/Z = 9:1); colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.90$  (PE); <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36–7.27 (m, 4H), 6.81 (d, J = 19.1Hz, 1H), 6.45 (d, J = 19.1 Hz, 1H), 0.15 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.2, 136.9, 133.5, 130.5, 128.7, 127.6, -1.3.

## (*E*)-(4-iodostyryl)trimethylsilane (11b)<sup>20</sup>



Yield 70% (E/Z = 9:1); colorless oil; **TLC**  $\mathbf{R}_{\mathbf{f}} = 0.90$  (PE); <sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.64 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 19.1 Hz, 1H), 6.47 (d, J = 19.1 Hz, 1H), 0.15 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.4, 137.9, 137.6,

130.8, 128.1, 93.3, -1.3.

### 5) NMR Spectra





# <sup>1</sup>H NMR Spectrum of 1-bromo-4-(but-3-en-1-yl)benzene (3b)



<sup>13</sup>C NMR Spectrum of 1-bromo-4-(but-3-en-1-yl)benzene (3b)



## <sup>1</sup>H NMR Spectrum of 1-(but-3-en-1-yl)-3-chlorobenzene (3c)





## <sup>1</sup>H NMR Spectrum of tridec-1-ene (3e)



<sup>1</sup>H NMR Spectrum of buta-1,3-diene-1,1-diyldibenzene (3f)



# <sup>13</sup>C NMR Spectrum of buta-1,3-diene-1,1-diyldibenzene (3f)







<sup>13</sup>C NMR Spectrum of 2-(3,3,3-trifluoroprop-1-en-2-yl)naphthalene (3g)



S18



<sup>13</sup>C NMR Spectrum of 1-(3,3,3-trifluoroprop-1-en-2-yl)-4-(vinyloxy)benzene (3h)



## <sup>1</sup>H NMR Spectrum 4-vinyl-1,1'-biphenyl (5a)



# <sup>13</sup>C NMR Spectrum of 4-vinyl-1,1'-biphenyl (5a)



## <sup>1</sup>H NMR Spectrum of 2-vinyl-1,1'-biphenyl (5b)



# <sup>13</sup>C NMR Spectrum of 2-vinyl-1,1'-biphenyl (5b)











<sup>13</sup>C NMR Spectrum of 1,2-dichloro-4-(prop-1-en-2-yl)benzene (5d)



# <sup>1</sup>H NMR Spectrum of 1-bromo-4-(prop-1-en-2-yl)benzene (5e)



# <sup>1</sup>H NMR Spectrum of 4-(prop-1-en-2-yl)benzonitrile (5f)



# <sup>1</sup>H NMR Spectrum of ethene-1,1-diyldibenzene (5g)



# <sup>13</sup>C NMR Spectrum of ethene-1,1-diyldibenzene (5g)



# <sup>1</sup>H NMR Spectrum of 1-chloro-4-(1-phenylvinyl)benzene (5h)



# <sup>13</sup>C NMR Spectrum of 1-chloro-4-(1-phenylvinyl)benzene (5h)



# <sup>1</sup>H NMR Spectrum of 4-(1-phenylvinyl)benzonitrile (5i)





# <sup>1</sup>H NMR Spectrum of 1-methoxy-4-(1-phenylvinyl)benzene (5j)



# <sup>13</sup>C NMR Spectrum of 1-methoxy-4-(1-phenylvinyl)benzene (5j)







<sup>13</sup>C NMR Spectrum of 4,4'-(ethene-1,1-diyl)bis(fluorobenzene) (5k)





4.5

4.0

3.5 3.0

2.5

1.5 1. 0

2.0

0.0

0.5

## <sup>1</sup>H NMR Spectrum of 4,4'-(ethene-1,1-diyl)bis(chlorobenzene) (5l)

<sup>13</sup>C NMR Spectrum of 4,4'-(ethene-1,1-diyl)bis(chlorobenzene) (5l)

7.0 6.5 6.0

10. 0

9.5

9.0 8.5 8.0 7.5





<sup>1</sup>H NMR Spectrum of 4,4'-(ethene-1,1-diyl)bis(methylbenzene) (5m)

S32

90

100 f1 (ppm)

130

120 110

200 190

180 170

160 150 140

70

60

80

50

40 30

20 10

0



# <sup>1</sup>H NMR Spectrum of 1-fluoro-4-(1-(4-methoxyphenyl)vinyl)benzene (5n)

<sup>13</sup>C NMR Spectrum of 1-fluoro-4-(1-(4-methoxyphenyl)vinyl)benzene (5n)



# <sup>1</sup>H NMR Spectrum of methyl(3-(1-phenylvinyl)phenyl)sulfane (50)



# <sup>13</sup>C NMR Spectrum of methyl(3-(1-phenylvinyl)phenyl)sulfane (50)







# <sup>13</sup>C NMR Spectrum of 3,3'-(ethene-1,1-diyl)bis(fluorobenzene) (5p)







<sup>13</sup>C NMR Spectrum of 3,3'-(ethene-1,1-diyl)bis(methylbenzene) (5q)



<sup>1</sup>H NMR Spectrum of 1-fluoro-2-(1-phenylvinyl)benzene (5r)



# <sup>13</sup>C NMR Spectrum of 1-fluoro-2-(1-phenylvinyl)benzene (5r)







# <sup>13</sup>C NMR Spectrum of 2,2'-(ethene-1,1-diyl)bis(fluorobenzene) (5s)



# <sup>1</sup>H NMR Spectrum of 9-methylene-9H-fluorene (5t)



# <sup>13</sup>C NMR Spectrum of 9-methylene-9H-fluorene (5t)



# <sup>1</sup>H NMR Spectrum of ethene-1,1,2-triyltribenzene (7a)















# <sup>1</sup>H NMR Spectrum of 4,4'-(2-phenylethene-1,1-diyl)bis(methoxybenzene) (7c)

ò



110 100 f1 (ppm) 





<sup>1</sup>H NMR Spectrum of (E)-(4-iodostyryl)trimethylsilane (11b)



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