Supporting Information

for

(Z)-Selective Transfer Semihydrogenation of Alkynes Catalyzed by *in situ* Generated Oxidizable Copper Nanoparticles

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1. GENERAL INFORMATION

All chemicals were purchased from Alfa Aesar, Acros Organics, TCI, Fluorochem, Sigma Aldrich, or Strem and used without further purification.

Unless stated otherwise, all reactions were carried out under an argon atmosphere. In case of water-sensitive reactions, the glassware was dried in an oven prior to use. THF and DME were dried with sodium/potassium and distilled under an argon atmosphere. MeOH was dried by the addition of magnesium and sodium and distilled over produced methanolates. EtOH was dried using molecular sieves. Et₃N, MeCN, *I*PrOH were dried with CaH₂ and distilled under argon atmosphere. All chemicals were purchased from Aldrich, Fluorochem or TCI and used without further purification. Merck silica gel (60, 230-400 mesh) was used for column chromatography.

The screening reactions were performed using the Radleys Carousel reactor. GC analyses were performed employing PerkinElmer Clarus 680 chromatograph. Conversions and diastereomeric ratios were determined using GC chromatograms analysis. Durene was used as an internal standard.

¹H NMR, ²H NMR, ¹³C NMR, and ¹⁹F NMR spectra were recorded on Agilent Mercury 400 MHz, Varian 500 MHz, or Varian 600 MHz spectrometer at room temperature. Chemical shifts (δ) were expressed in parts per million (ppm) and referenced to residual CDCl₃ signals. In the ¹H NMR spectra of substrates and products containing aromatic rings, the highest coupling constants were provided and multiplicity was described as a doublet of multiplets (dm) or triplet of multiplets (tm), to be consistent with the cited literature. EI and ESI mass spectra were obtained on AutoSpec Premier spectrometer. IR spectra were recorded on JASCO FT/IR-6200 spectrometer.

2. PROCEDURES

2.1. SUBSTRATES SYNTHESIS

2.1.1. General procedure of aryl-aryl alkynes synthesis from aryl iodides



An oven-dried Schlenk flask was charged with CuI (0.5 mmol, 0.02 equiv.), PPh₃ (0.5 mmol, 0.02 equiv.), Pd(PPh3)₂Cl₂ (0.5 mmol, 0.02 equiv.) and solid aryl iodide (25 mmol, 1 equiv.). The vessel was evacuated and backfilled with argon three times. Subsequently, dry THF (50 ml), phenylacetylene (27.5 mmol, 1.1 equiv.), and dry Et₃N (50 ml) were added and the mixture was stirred. After completion of the reaction, which was indicated by TLC, the mixture was quenched with water and the aqueous phase was extracted three times with AcOEt (3×50 ml). The combined extracts were dried over MgSO₄ and the solvents were evaporated under reduced pressure. The product was purified by column chromatography. Further recrystallization or vacuum distillation was used if needed.

2.1.2. General procedure of aryl-aryl alkynes synthesis from aryl bromides



An oven-dried Schlenk flask was charged with CuI (0.5 mmol, 0.02 equiv.), Pd(PPh3)₄ (1.25 mmol, 0.05 equiv.) and solid aryl bromide (25 mmol, 1 equiv.). The vessel was evacuated and backfilled with argon three times. Subsequently, dry DMF (60 ml), phenylacetylene (50 mmol, 2 equiv.), and dry Et_3N (10 ml) were added and the mixture was stirred at 80 °C. After completion of the reaction, which was indicated by GC or TLC, the mixture was quenched with water and the aqueous phase was extracted three times with AcOEt (3×50 ml). The combined extracts were dried over MgSO₄ and the solvents were evaporated under reduced pressure. The product was purified by column chromatography. Further recrystallization or vacuum distillation was used if needed.

2.1.3. General procedure of aryl-alkyl alkynes synthesis from aryl iodides



An oven-dried Schlenk flask was charged with CuI (0.5 mmol, 0.02 equiv.), PPh₃ (0.5 mmol, 0.02 equiv.), Pd(PPh3)₂Cl₂ (0.5 mmol, 0.02 equiv.) and solid aryl iodide (25 mmol, 1 equiv.). The vessel was evacuated and backfilled with argon three times. Subsequently, dry THF (50 ml), ethynylcyclohexane (27.5 mmol, 1.1 equiv.), and dry Et₃N (50 ml) were added and the mixture was stirred. After completion of the reaction, which was indicated by GC,

the mixture was quenched with water and the aqueous phase was extracted three times with AcOEt (3×50 ml). The combined extracts were dried over MgSO₄ and the solvents were evaporated under reduced pressure. The product was purified by column chromatography. Further vacuum distillation was used.

2.1.4. General procedure of terminal alkynes synthesis from aryl iodides



An oven-dried Schlenk flask was charged with CuI (0.5 mmol, 0.02 equiv.), PPh₃ (0.5 mmol, 0.02 equiv.), Pd(PPh3)₂Cl₂ (0.5 mmol, 0.02 equiv.) and solid aryl iodide (25 mmol, 1 equiv.). The vessel was evacuated and backfilled with argon three times. Subsequently, dry THF (50 ml), trimethylsilylacetylene (27.5 mmol, 1.1 equiv.) and dry Et₃N (50 ml) were added and the mixture was stirred. After completion of the reaction, which was indicated by TLC, the mixture was quenched with water and the aqueous phase was extracted three times with AcOEt (3×50 ml). The combined extracts were dried over MgSO₄ and the solvents were evaporated under reduced pressure. The product was purified by column chromatography followed by vacuum distillation. Subsequently, K₂CO₃ and methanol was added to the flask and the mixture was stirred. After completion of the reaction, which was indicated by TLC, methanol was evaporated and water with Et₂O were added. The aqueous phase was extracted three times with Et₂O. The combined extracts were dried over MgSO₄ and the solvents were evaporated under reduced pressure to obtain a pure product.

2.2. SEMIHYDROGENATION

2.2.1. General procedure of alkyne semihydrogenation in THF-H₂O

$$R^{1} = R^{2} \xrightarrow[]{2 \text{ equiv. } R^{1}} R^{2} \xrightarrow[]{2 \text{ equiv. } NH_{3}BH_{3}} R^{1} \xrightarrow[]{R^{2}} R^{2}$$

A vial was charged with alkyne (0.5 mmol, 1 equiv.), THF (0.5 ml) and $CuCl_2 \cdot 2H_2O$ (0.01 mmol, 0.02 equiv.). Subsequently, ammonia-borane (1 mmol, 2 equiv.), THF (1.5 ml) and water (2 ml) were added to the solution. The mixture was stirred at 60 °C for 2-24 h. After completion of the reaction, which was indicated by GC or TLC, the mixture was quenched

with water and the aqueous phase was extracted with DCM (3×15 ml). The combined extracts were dried over Na₂SO₄ and the solvents were evaporated under reduced pressure to obtain a pure product.

2.2.2. General procedure of alkyne semihydrogenation in AcOEt-H₂O

$$R^{1} = R^{2} \xrightarrow[]{2 \text{ equiv. } R^{2}} R^{2} \xrightarrow[]{2 \text{ equiv. } NH_{3}BH_{3}} R^{1} R^{2}$$

$$H_{2}O + \text{ AcOEt, 60 °C, 2-6 h}$$

A vial was charged with alkyne (0.5 mmol, 1 equiv.), AcOEt (0.5 ml) and CuCl₂·2H₂O (0.01 mmol, 0.02 equiv.). Subsequently, ammonia-borane (1 mmol, 2 equiv.), AcOEt (1.5 ml) and water (2 ml) were added to the solution. The mixture was stirred at 60 °C for 2-24 h. After completion of the reaction, which was indicated by GC or TLC, the mixture was quenched with water and aqueous phase was with DCM (3×15 ml). The combined extracts were dried over Na₂SO₄ and the solvents were evaporated under reduced pressure to obtain pure product.

2.2.3. General procedure of alkyne semihydrogenation in MeOH

$$R^{1} = R^{2} \xrightarrow[H_{2}O]{2 \text{ equiv. } NH_{3}BH_{3}} R^{1} = R^{2} \xrightarrow[H_{2}O]{2 \text{ equiv. } NH_{3}BH_{3}} R^{1} = R^{2}$$

A vial was charged with alkyne (0.5 mmol, 1 equiv.), dry MeOH (0.5 ml), and $CuCl_2 \cdot 2H_2O$ (0.01 mmol, 0.02 equiv.). Subsequently, ammonia-borane (1 mmol, 2 equiv.) and dry MeOH (1.5 ml) were added to the solution. The mixture was stirred at 60 °C for 2-24 h. After completion of the reaction, which was indicated by GC or TLC, the mixture was quenched with water and the aqueous phase was extracted with DCM (3×15 ml). The combined extracts were dried over Na₂SO₄ and the solvents were evaporated under reduced pressure to obtain a pure product.

2.2.4. Recyclability test

Ph Ph Ph
$$2$$
 equiv. H_3BH_3 Ph Ph Ph H_2O + AcOEt, 60 °C, 6 h

A vial was charged with diphenylacetylene (0.5 mmol, 1 equiv.), AcOEt (0.5 ml) and CuCl₂·2H₂O (0.01 mmol, 0.02 equiv.). Subsequently, ammonia-borane (1 mmol, 2 equiv.),

AcOEt (1.5 ml) and water (2 ml) were added to the solution. The mixture was stirred at 60 °C for 6 h and analyzed by GC. Once the black suspension turned into a blue solution, the organic phase was removed and the aqueous one was washed several times with AcOEt. An addition of diphenylacetylene (0.5 mmol, 1 equiv.), AcOEt (0.5 ml), ammonia-borane (1 mmol, 2 equiv.) and AcOEt (1.5 ml) allowed to carry out semihydrogenation of another portion of the substrate using the same catalyst.



2.2.5. Recyclability test after centrifugation of an aqueous phase



A vial was charged with diphenylacetylene (0.5 mmol, 1 equiv.), AcOEt (0.5 ml), and $CuCl_2 \cdot 2H_2O$ (0.01 mmol, 0.02 equiv.). Subsequently, ammonia-borane (1 mmol, 2 equiv.),

AcOEt (1.5 ml) and water (2 ml) were added to the solution. The mixture was stirred at 60 °C for 6 h and analysed by GC. Once the black suspension turned into a blue solution, the organic phase was removed and the aqueous one was washed several times with AcOEt, transferred into an Eppendorf tube, and centrifuged for 20 min (11000 rpm). No precipitate was observed. The aqueous phase was decanted into an empty reaction vessel and followed by the addition of diphenylacetylene (0.5 mmol, 1 equiv.), AcOEt (0.5 ml), ammonia-borane (1 mmol, 2 equiv.) and AcOEt (1.5 ml) to carry out semihydrogenation of another portion of the substrate using the same catalyst.



2.2.6. Reduction of the copper complex

To the aqueous phase containing blue copper complex $Cu[L]_x$ (0.01 mmol, 0.02 equiv.), obtained after semihydrogenation of diphenylactylene and placed in an open reaction tube, ammonia-borane (0.03 mmol, 0.06 equiv.) was added. The mixture was stirred at 60 °C for 10 min until the discoloration of the solution along with metallic copper production. The precipitate dissolving was observed when stirring was prolonged.



2.2.7. Isotope labeling

Ph Ph Ph
$$2$$
 equiv. NH₃BH₃ Ph Ph Ph D₂O + THF, 60 °C, 6 h

An oven-dried and argon-filled vial was charged with alkyne (0.5 mmol, 1 equiv.), THF (0.5 ml), and $CuCl_2 \cdot 2H_2O$ (0.01 mmol, 0.02 equiv.). Subsequently, ammonia-borane (1 mmol, 2 equiv.), THF (1.5 ml) and D₂O (2 ml) were added to the solution. The mixture was stirred at 60 °C for 2-24 h. After completion of the reaction, which was indicated by GC or TLC, the mixture was quenched with water and the aqueous phase was extracted with DCM (3×15 ml). The combined extracts were dried over Na₂SO₄ and the solvents were evaporated under reduced pressure to obtain a pure product.

2.2.8. Tandem Suzuki coupling-semihydrogenation

$$Ph = Br + HQ = Ph \begin{pmatrix} 0.1 \text{ equiv.} \\ Cul \\ 0.2 \text{ equiv.} \\ \hline \\ HO \end{pmatrix} = Ph \begin{pmatrix} 0 \\ Ph \\ \hline \\ 2 \text{ .equiv. } K_3PO_4 \\ EtOH, 100 \ ^\circC, 24 \ h \end{pmatrix} \begin{pmatrix} Ph = Ph \\ Ph \\ \hline \\ EtOH, 90 \ ^\circC \\ 24 \ h \end{pmatrix} = Ph Ph$$

An oven-dried and argon-filled ampula was charged with and **CuI** (0.1 mmol, 0.1 equiv.), 8-hydroxyquinoline (0.2 mmol, 0.2 equiv.), phenylboronic acid (1 mmol, 1 equiv.), and anhydrous K_3PO_4 (2 mmol, 2 equiv.). The vessel was evacuated and backfilled with argon three times. Subsequently, 1-bromo-2-phenylacetylene (1 mmol, 1 equiv.), and dry EtOH (3 ml) were added to the solution. The mixture was stirred at 100 °C for 24 h. After completion of the reaction, the vessel was cooled down to rt and ammonia-borane (3 mmol, 3 equiv.) was added followed by dry EtOH (2 ml). The mixture was stirred at 90 °C for 24 h and quenched with water and the aqueous phase was extracted three times with DCM (3×15 ml). The combined extracts were dried over Na₂SO₄ and the solvents were evaporated under reduced pressure. The product was purified by column chromatography.

2.2.6. Transformation of borate to boric acid

To an aqueous phase containing spent ammonia-borane (0.01 mmol, 0.02 equiv.), obtained after semihydrogenatinon of diphenylactylene, concentrated HCl was added until

the mixture became acidic. The crude was dissolved in DMSO-d $_6$ and analysed using ¹¹B NMR (page S124).

An obtained solid ammonium pentaborate was dissolved in water and concentrated HCl was added until the mixture became acidic. The crude was dissolved in DMSO- d_6 and analysed using ¹¹B NMR (page S125).

3. CRYSTALLOGRAPHIC DATA AND MEASUREMENT DETAILS



The crystal was obtained from the aqueous phase after model semihydrogenation in AcOEt– $\rm H_2O.$

4. GREEN CHEMISTRY METRICS CALCULATIONS

For semihydrogenation of diphenylacetylene carried out in three solvents systems green metrics were provided:



3.1. Atom economy

Atom Economy (AE) is the percentage of the theoretical mass of the desired product to the theoretical mass of all reactants used.

$$AE = \frac{\text{theoretical mass of desired product}}{\text{thoretical mass of reactants}} \cdot 100\%$$

For reaction carried out in MeOH: 180/(178+31+4×32)×100% = 53%

For reaction carried out in THF-H₂O: 180/(178+31+4×18)×100% = 64%

For reaction carried out in AcOEt-H₂O: 180/(178+31+4×18)×100% = 64%

3.2. REACTION MASS EFFICIENCY

Reaction Mass Efficiency (RME) is the percentage of the actual mass of the desired product to the actual mass of all reactants used.

$$RME = \frac{theoretical\ mass\ of\ desired\ product}{actual\ mass\ reactants} \cdot yield$$

For reaction carried out in MeOH: $90/(89+31+64) \times 97\% = 47\%$

For reaction carried out in THF-H₂O: $90/(89+31+36) \times 97\% = 56\%$

For reaction carried out in AcOEt-H₂O: 90/(89+31+36)×96% = 55%

3.3. EFFECTIVE MASS EFFICIENCY

Effective Mass Efficiency (EME) is the percentage of the actual mass of the desired product to the mass of all non-benign reactants used.

$$EME = \frac{\text{theoretical mass of desired product}}{\text{mass of non benign reactants}} \cdot \text{yield}$$

For reaction carried out in MeOH: 90/(89+31)×97%=72%

For reaction carried out in THF-H₂O: 90/(89+31)×97%=72%

For reaction carried out in AcOEt-H₂O: 90/(89+31)×96%=72%

3.4. ENVIRONMENTAL FACTOR

Environmental Factor¹ (E) is ratio of total waste to the actual mass of the products:

$$E = \frac{actual\ mass\ of\ total\ waste}{actual\ mass\ of\ product}$$

$$E = \frac{\sum(mass of reactants) + \sum(mass of solvents) - \sum(products)}{\sum(mass of product)}$$

For reaction carried out in MeOH: (89+31+3168-90*0.97)/(90*0.97) = 37

For reaction carried out in THF-H₂O: (89+31+2000+1767-90*0.97)/(90*0.97) = 44

For reaction carried out in AcOEt-H₂O: (89+31+2000+1800-90*0.96)/(90*0.96) = 44

3.5. ECoScale score

The EcoScale² is used for the evaluation of the effectiveness of chemical synthesis. It ranges from 100-0 points based on parameters referring to price, safety, technical setup, temperature, and workup:

Parameter	MeOH	THF–H₂O	AcOEt-H ₂ O	Lindlar ³ Method
1. Yield	1.5 (97%)	1.5 (97%)	2 (96%)	1.5 (97%)
2. Price of reaction components:				
• Dipehnylacetylene (<10\$)	0	0	0	0
• $CuCl_2 \cdot 2H_2O(<10\$)$	0	0	0	-
• Lindlar Catalyst (<10\$)	-	-	-	0
• Ammonia-borane (>10\$ <50\$)	3	3	3	-
• Hydrogen (<10\$)	-	-	-	0
• Solvent (<10\$)	0	0	0	0
3. Safety:				
Dipehnylacetylene	0	0	0	0
• CuCl ₂ ·2H ₂ O (N)	5	5	5	-
• Lindlar Catalyst (F, N)	-	-	-	10
• Ammonia-borane (F)	5	5	5	-
• Hydrogen (F+)	-	-	-	10
• Quinoline (T, N)	-	-	-	10
• Solvent	10 (T, F)	5 (F)	5 (F)	5 (F)
4. Technical setup:				
Common setup	0	0	0	0
• Inert gass	1	0	0	0
5. Temperature and time:				
• Heating, >1h	3	3	3	-
6. Work-up:				
Liquid-liquid extraction	3	3	3	3
Removal of solvent of low bp	0	0	0	0
Sum of Penalty Points:	31.5	25.5	26	39.5
EcoScale score:	68.5	74.5	74.0	60.5

EcoScale = 100 - penalty points

EcoScale score of the described methodology was compared with Lindlar method³ which was rated as a less eco-friendly approach. In the case of systems based on water, the result is almost excellent (74.5 points). Prices of the components were calculated for the 10 mmol reaction scale.

5. ANALYTICAL AND SPECTRAL DATA

1-methyl-4-(2-phenylethynyl)benzene⁴

White solid. Yield 99%. Prepared using procedure 2.1.1.

¹**H NMR** (500 MHz, CDCl₃) δ (ppm) 7.57 – 7.49 (m, 2H), 7.43 (dm, *J* = 8.2 Hz, 2H), 7.38 – 7.29 (m, 3H), 7.16 (dm, *J* = 7.8 Hz, 2H), 2.37 (s, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ (ppm) 138.4, 131.5, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.5, 88.7, 21.5.



1-methyl-3-(2-phenylethynyl)benzene⁴

Coluorless oil, Yield 86%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.59 – 7.52 (m, 2H), 7.42 – 7.33 (m, 5H), 7.27 (tm, J = 7.5 Hz, 1H), 7.20 – 7.16 (dm, J = 7.8 Hz, 1H), 2.39 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 138.2, 132.3, 131.7, 129.3, 128.8, 128.5, 128.4, 128.3, 123.5, 123.2, 89.7, 89.2, 21.4.



1-*tert*-butyl-4-(2-phenylethynyl)benzene⁵

White solid. Yield 81%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.58 – 7.54 (m, 2H), 7.52 – 7.48 (m, 2H), 7.43 – 7.33 (m, 5H), 1.36 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 151.7, 131.7, 131.5, 128.4, 128.2, 125.5, 123.7, 120.4, 89.7, 88.9, 34.9, 31.3.

1-methoxy-4-(2-phenylethynyl)benzene⁶

White solid. Yield 88%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.55 – 7.50 (m, 2H), 7.48 (dm, J = 8.9 Hz, 2H), 7.38 – 7.28 (m, 3H), 6.88 (dm, J = 8.8 Hz, 2H), 3.83 (s, 3H) ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 159.8, 133.2, 131.6, 128.5, 128.1, 123.8, 115.5, 114.1, 89.5, 88.2, 77.4, 77.2, 76.9, 55.5.



1-fluoro-4-(2-phenylethynyl)benzene⁴

White solid. Yield 78%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.57 – 7.47 (m, 4H), 7.40 – 7.30 (m, 3H), 7.05 (tm, J = 8.7 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 162.65 (d, J_{CF} = 249.4 Hz), 133.63 (d, J_{CF} = 8.5 Hz), 131.71, 128.52, 128.48, 123.24, 119.53 (d, J_{CF} = 3.5 Hz), 115.79 (d, J_{CF} = 22.1 Hz), 89.18, 88.43. ¹⁹F NMR (470 MHz CDCl₃) δ (ppm) -111.03 (tt, J = 8.7, 5.4 Hz).

1-chloro-4-(2-phenylethynyl)benzene⁴

White solid. Yield 99%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) 7.56 – 7.49 (m, 2H), 7.49 – 7.43 (m, 2H), 7.39 – 7.30 (m, 5H)¹³C NMR (126 MHz, CDCl₃) δ (ppm) 134.4, 133.0, 131.7, 128.8, 128.6, 128.5, 123.1, 121.9, 90.5, 88.4.



1-trifluoromethyl-4-(2-phenylethynyl)benzene⁴

White solid. Yield 98%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.66 – 7.58 (m, 4H), 7.58 – 7.51 (m, 2H), 7.41 – 7.33 (m, 3H).¹³C NMR (126 MHz, CDCl₃) δ (ppm) 132.0, 131.9, 130.1 (q, J_{CF} = 32.8 Hz), 129.0, 128.6, 127.3, 125.4 (q, J_{CF} = 3.7 Hz), 124.10 (q, J_{CF} = 272.0 Hz) 122.7, 91.9, 88.1. ¹⁹F NMR (470 MHz CDCl₃) δ (ppm) -62.81 (s).



Methyl 4-(2-phenylethynyl)benzoate⁷

Creamy solid. Yield 64%. Prepared using procedure 2.1.1.

¹**H NMR** (500 MHz, CDCl₃) δ (ppm) 8.02 (dm, *J* = 8.7 Hz, 2H), 7.59 (dm, *J* = 8.7 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.40 – 7.34 (m, 3H), 3.93 (s, 3H).¹³**C NMR** (126 MHz, CDCl₃) δ (ppm) 166.7, 131.9, 131.7, 129.7, 129.6, 128.9, 128.6, 128.2, 122.9, 92.5, 88.8, 52.4.

N-(4-(2-phenylethynyl)phenyl)acetamide⁶

Creamy solid. Yield 99%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.56 – 7.46 (m, 6H), 7.37 – 7.30 (m, 3H), 7.20 (s, 1H), 2.20 (s, 3H).¹³C NMR (126 MHz, CDCl₃) δ (ppm) 168.3, 138.1, 138.0, 132.6, 131.7, 128.5, 128.3, 123.5, 119.5, 119.1, 89.2, 89.2, 24.9.



2-(4-(2-phenylethynyl)phenyl)acetonitrile⁶

White solid. Yield 88%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.59 – 7.52 (m, 4H), 7.41 – 7.31 (m, 5H), 3.79 (s, 2H).¹³C NMR (126 MHz, CDCl₃) δ (ppm) 132.4, 131.8, 130.0, 128.7, 128.5, 128.1, 123.5, 123.1, 117.6, 90.4, 88.6, 23.7.

1-(methylsulfonyl)-4-(2-phenylethynyl)benzene⁸

Tan solid. Yield 40%. Prepared using procedure 2.1.2.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.93 (dm, J = 8.5 Hz, 2H), 7.70 (dm, J = 8.5 Hz, 2H), 7.59 – 7.52 (m, 2H), 7.39 (dd, J = 5.1, 1.9 Hz, 3H), 3.07 (s, 3H).¹³C NMR (126 MHz, CDCl₃) δ (ppm) 139.7, 132.4, 132.0, 129.4, 129.3, 128.7, 127.6, 122.4, 93.6, 87.7, 44.6.



4-(2-phenylethynyl)phenyl methanesulfonate

White solid. Yield 70%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.58 (d, J = 8.8 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.39 – 7.34 (m, 3H), 7.28 (d, J = 8.7 Hz, 2H), 3.16 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 148.9, 133.4, 131.8, 128.8, 128.6, 123.0, 122.9, 122.3, 90.7, 88.0, 37.7. HRMS (EI) m/z Calcd. for C₁₅H₁₂O₃S: 272.0507, Found: 272.0508 MS (EI) m/z 272.0 (M⁺), 193.0 (100%), 165.0, 139.0, 115.0, 81.2, 69.2 EA Calcd. for C₁₅H₁₂O₃S : C: 66.16, H: 4.44, S: 11.77 Found: C: 65.93, H: 4.46, S: 11.53 IR (KBr) cm⁻¹ : 3087, 3036, 3016, 2938, 2220, 1914, 1499, 1366, 1171, 1148, 972, 888, 781, 524 M.p. = 151 °C



5-(2-phenylethynyl)-2,3-dihyrobenzofuran

White solid. Yield 80%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.54 – 7.47 (m, 2H), 7.40 – 7.27 (m, 5H), 6.76 (d, J= 8.3 Hz, 1H), 4.60 (t, J= 8.7 Hz, 2H), 3.22 (t, J= 8.7 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 160.5, 132.3, 131.6, 128.4, 128.4, 128.0, 127.5, 123.9, 115.2, 109.6, 90.0, 87.6, 71.7, 29.6. HRMS (EI) m/z Calcd. for C₁₆H₁₂O: 220.0892, Found: 220.0888 MS (EI) m/z 219.9 (M⁺, 100%), 222.1, 190.9, 164.9, 138.9, 110.0, 82.6, 63.2 EA Calcd. for C₁₆H₁₂O : C: 87.25, H: 5.49 Found: C: 88.78, H: 5.53 IR (KBr) cm⁻¹ : 3046, 2963, 2893, 2849, 2201, 1953, 1877, 1747, 1592, 1495, 1326, 990, 819, 753, 689, 522, 502, 473



5-(2-phenylethynyl)-benzo[1,3]dioxole9

White solid. Yield 100%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.54 – 7.48 (m, 2H), 7.37 – 7.29 (m, 3H), 7.07 (dd, J = 8.0, 1.6 Hz, 1H), 6.98 (d, J = 1.6 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 5.99 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 148.1, 147.6, 131.6, 128.5, 128.2, 126.4, 123.5, 116.7, 111.7, 108.6, 101.5, 89.4, 87.9.



1-methyl-5-(2-phenylethynyl)-1*H*-indole¹⁰

Brown solid. Yield 74%. Prepared using procedure 2.1.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.85 (dd, J = 1.6, 0.7 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.41 (dd, J = 8.5, 1.5 Hz, 1H), 7.38 – 7.27 (m, 4H), 7.08 (d, J = 3.1 Hz, 1H), 6.49 (dd, J = 3.1, 0.9 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 136.4, 131.4, 129.8, 128.3, 128.3, 127.6, 125.2, 124.8, 124.0, 113.8, 109.3, 101.3, 91.2, 87.0, 32.9.



1-(2-phenylethynyl)naphthalene⁵

Pale yellow solid. Yield 88%. Prepared using procedure 2.1.1.

¹**H NMR** (500 MHz, CDCl₃) δ (ppm) 8.47 (ddd, *J* = 8.4, 2.3, 1.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.79 (dt, *J* = 7.1, 1.4 Hz, 1H), 7.67 (dq, *J* = 8.1, 1.4 Hz, 2H), 7.62 (ddt, *J* =

8.2, 6.8, 1.3 Hz, 1H), 7.55 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.48 (dd, J = 8.2, 7.2 Hz, 1H), 7.45 – 7.34 (m, 3H). ¹³**C NMR** (126 MHz, CDCl₃) δ (ppm) 133.4, 133.4, 131.8, 130.5, 128.9, 128.6, 128.5, 126.9, 126.6, 126.4, 125.4, 123.6, 121.1, 94.5, 87.7.

1-(2-cyklohexylethynyl)benzene¹¹

Coluorless oil. Yield 85%. Prepared using procedure 2.1.3.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.43 – 7.36 (m, 2H), 7.30 – 7.22 (m, 3H), 2.59 (tt, J = 9.0, 3.8 Hz, 1H), 1.94 – 1.84 (m, 2H), 1.82 – 1.71 (m, 2H), 1.60 – 1.48 (m, 3H), 1.42 – 1.28 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 131.7, 128.3, 127.5, 124.3, 94.6, 80.7, 32.9, 29.8, 26.1, 25.1.

$$\rightarrow$$

4-*tert*-butylphenylacetylene¹²

Pale-yellow oil. Yield 81%. Prepared using procedure 2.1.4.

¹**H NMR** (500 MHz, CDCl₃) δ (ppm) 7.44 (dm, *J* = 8.5 Hz, 2H), 7.35 (dm, *J* = 8.5 Hz, 2H), 3.03 (s, 1H), 1.32 (s, 9H). ¹³**C NMR** (126 MHz, CDCl₃) δ (ppm) 152.2, 132.0, 125.5, 119.2, 84.0, 76.6, 34.9, 31.3.

1, 4-bis(2-phenylethynyl)benzene¹³

White solid.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.58 – 7.50 (m, 8H), 7.40 – 7.33 (m, 6H) ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 131.8, 131.7, 128.6, 128.5, 123.3, 123.2, 91.4, 89.3.



(*Z*)-2a

(Z)-stilbene¹⁴

Colourless oil. Yield 96%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.31 – 7.18 (m, 10H), 6.63 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 137.4, 130.4, 129.0, 129.0, 128.3, 127.2.



(Z)-4-methylstilbene¹⁴

Colourless oil. Yield 95%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.33 – 7.19 (m, 5H), 7.19 – 7.15 (m, 2H), 7.08 – 7.02 (m, 2H), 6.58 (AB, J= 12.7 Hz, 2H), 2.34 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 137.6, 137.0, 134.4, 130.3, 129.7, 129.0, 129.0, 128.9, 128.3, 127.1, 21.4.

(*Z*)-2c

(Z)-3-methylstilbene¹⁴

Colourless oil. Yield 90%. Prepared using procedure 2.2.1.

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) 7.31 – 7.20 (m, 5H), 7.16 – 7.01 (m, 4H), 6.59 (AB, *J* = 12.6 Hz, 2H), 2.29 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) 137.9, 137.5, 137.3, 130.5, 130.2, 129.7, 129.0, 128.3, 128.2, 128.0, 127.2, 126.0, 21.5.



(*Z*)-4-*tert*-butylstilbene¹⁴

Colourless oil. Yield 92%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.34 – 7.20 (m, 9H), 6.59 (AB, *J* = 12.7 Hz, 2H), 1.33 (s, 9H).
¹³C NMR (101 MHz, CDCl₃) δ (ppm) 150.3, 137.7, 134.3, 130.2, 129.7, 129.0, 128.7, 128.4, 127.1, 125.2, 34.7, 31.4.



(Z)-4-methoxystilbene¹⁴

Colourless oil. Yield 95%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.31 – 7.17 (m, 7H), 6.80 – 6.75 (m, 2H), 6.54 (AB, J = 12.3, 2H), 3.80 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 158.8, 137.7, 130.3, 129.9, 129.8, 128.9, 128.9, 128.4, 127.0, 113.7, 55.3.



(Z)-4-fluorostilbene¹⁴

Colourless oil. Yield 92%. Prepared using procedure 2.2.2.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.29 – 7.19 (m, 7H), 6.96 – 6.89 (m, 2H), 6.62 (A, d, J = 12.2 Hz, 1H), 6.56 (B, d, J = 12.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 162.0 (d, J_{CF} = 246.8 Hz), 137.2, 133.3 (d, J_{CF} = 3.5 Hz), 130.7 (d, J_{CF} = 7.7 Hz), 130.4 (d, J_{CF} = 1.5 Hz), 129.2, 129.0, 128.4, 127.3, 115.3 (d, J_{CF} = 21.4 Hz). ¹⁹F NMR (376 MHz CDCl₃) δ (ppm) -114.66 – -114.78 (m).



(Z)-4-chlorostilbene¹⁴

Colourless oil. Yield 95%. Prepared using procedure 2.2.2.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.28 – 7.15 (m, 9H), 6.63 (A, d, J = 12.2 Hz, 1H), 6.53 (B, d, J = 12.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 137.0, 135.8, 132.9, 131.1, 130.4, 129.1, 128.9, 128.5, 128.5, 127.5.



(Z)-4-trifluoromethylstilbene¹⁴

Colourless oil. Yield 92%. Prepared using procedure 2.2.2.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.49 (dm, J = 7.8 Hz, 2H), 7.36 (dm, J = 7.9 Hz, 2H), 7.31 – 7.20 (m, 5H), 6.75 (A, d, J = 12.2 Hz, 1H), 6.62 (B, d, J = 12.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 141.0 (q, J_{CF} = 1.3 Hz), 136.7, 132.5, 129.3, 129.2 (q, J_{CF} = 32.7 Hz), 129.0, 128.9, 128.6, 127.1, 125.29 (q, J_{CF} = 3.8 Hz), 122.96(q, J_{CF} = 271.7.8 Hz). ¹⁹F NMR (376 MHz CDCl₃) δ (ppm) -62.55. (s).



(Z)-4-methoxycarbonylstilbene¹⁴

Colourless oil. Yield 92%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) (dm, J = 8.2 Hz, 2H), 7.30 (dm, J = 8.1 Hz, 2H), 7.25 – 7.19 (m, 5H), 6.71 (A, d, J = 12.3 Hz, 1H), 6.61 (B, d, J = 12.2 Hz, 1H), 3.90 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 167.1, 142.2, 136.8, 132.4, 129.7, 129.4, 129.0, 128.7, 128.5, 127.7, 52.2.



(Z)-4-acetamidestilbene¹⁵

Creamy solid. Yield 96%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.31 – 7.24 (m, 2H), 7.20 (s, 2H), 7.18 – 7.07 (m, 7H), 6.47 (AB, J = 12.2 Hz, 2H), 2.08 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 168.4, 137.4, 136.9, 133.3, 130.0, 129.7, 129.7, 128.9, 128.4, 127.2, 119.5, 24.8.



(Z)-2-(4-styrylphenyl)acetonitrile

Yellowish oil. Yield 99%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.77 – 7.71 (m, 2H), 7.41 – 7.35 (m, 2H), 7.26 – 7.14 (m, 5H), 6.75 (A, d, *J* = 12.2 Hz, 1H), 6.56 (B, d, *J* = 12.3 Hz, 1H), 3.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 143.2, 138.7, 136.3, 133.6, 129.8, 128.9, 128.7, 128.3, 128.0, 127.4, 44.6. HRMS (EI) *m*/*z* Calcd. for C₁₆H₁₃N: 219.1048, Found: 219.1054 MS (EI) *m*/*z* 219.1 (M⁺), 191.1, 179.1, 152.1, 89.3, 71.5, 57.5, 43.6 EA Calcd. for C₁₆H₁₃N : C: 87.64, H: 5.98, N: 6.39 Found: C: 87.40, H: 6.15, N: 6.19 IR (in CH₂Cl₂) cm⁻¹ : 3665, 3530, 3079, 3053, 3021, 2925, 2251, 1599, 1510, 1492, 1448, 1416, 1183, 1115, 1073, 1021, 924, 819, 775, 899, 512, 464



(Z)-4-methylsufonylstilbene

Creamy wax. Yield 94%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) δ 7.77 – 7.71 (m, 2H), 7.41 – 7.35 (m, 2H), 7.26 – 7.14 (m, 5H), 6.75 (d, J = 12.2 Hz, 1H), 6.56 (d, J = 12.3 Hz, 1H), 3.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 143.2, 138.7, 136.3, 133.6, 129.8, 128.9, 128.7, 128.3, 128.0, 127.4, 44.6.



(Z)-4-styrylphenyl methanesulfonate

Creamy wax. Yield 93%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) δ 7.32 – 7.20 (m, 7H), 7.16 – 7.10 (m, 2H), 6.66 (A, d, J = 12.2 Hz, 1H), 6.55 (B, d, J= 12.2 Hz, 1H), 3.13 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 148.1, 136.8, 136.7, 131.5, 130.6, 128.9, 128.7, 128.5, 127.6, 121.9, 37.5. HRMS (EI) m/z Calcd. for C₁₅H₁₄O₃SNa: 297.0561, Found: 297.0553 MS (ESI) m/z 297.9 ([M+Na]⁺ 100%) EA Calcd. for C₁₅H₁₄O₃S : C: 65.67, H: 5.14, S: 11.69 Found: C: 56.57, H: 5.19, S: 11.74 IR (in CH₂Cl₂) cm⁻¹ : 3901, 3852, 3054, 3023, 2936, 2543, 1598, 1500, 1389, 1200, 1175, 1149, 970, 869, 795, 696, 573, 502



(Z)-2,3-dihydro-5-styrylbenzofuran

Colorless oil. Yield 97%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.32 – 7.17 (m, 5H), 7.13 – 7.08 (m, 1H), 7.08 – 7.00 (m, 1H), 6.66 (dm, J = 8.2 Hz, 1H), 6.54 (A, d, J = 12.2 Hz, 1H), 6.49 (B, d, J = 12.2 Hz, 1H), 4.56 (t, J = 8.7 Hz, 2H), 3.12 (t, J = 8.8 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 159.4, 137.8, 130.3, 129.7, 129.2, 129.0, 128.5, 128.3, 127.0, 127.0, 125.6, 109.1, 71.5, 29.7. HRMS (EI) m/z Calcd. for C₁₆H₁₄O: 222.1045, Found: 222.1046 MS (EI) m/z 222.1 (M⁺, 100%), 178.1, 165.1, 133.2, 115.3, 89.3 EA Calcd. for C₁₆H₁₄O : C: 86.45, H: 6.35 Found: C: 86.15, H: 6.32 IR (film) cm⁻¹ : 3077, 3054, 3008, 2964, 2894, 2855, 1953, 1884, 1609, 1492, 1445, 1236, 1094, 983, 943, 818, 773, 742, 699, 497, 472



(Z)-1-(3,4-methylenedioxyphenyl)-2-phenylethene

Colorless oil. Yield 97%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.31 – 7.17 (m, 5H), 6.78 – 6.68 (m, 3H), 6.53 A, (d, J = 12.2 Hz, 1H), 6.49 (B, d, J = 12.1 Hz, 1H), 5.93 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 147.5, 146.8, 137.4, 131.3, 129.9, 129.4, 128.9, 128.4, 127.2, 123.1, 109.0, 108.3, 101.0.



(Z)-1-methyl-5-styryl-1H-indole

Tan oil. Yield 90%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.55 (q, J = 1.1 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.12 (m, 5H), 7.01 (d, J = 3.1 Hz, 1H), 6.74 (A, dd, J = 12.1, 0.8 Hz, 1H), 6.53 (B, d, J = 12.2 Hz, 1H), 6.40 (d, J = 3.1 Hz, 1H), 3.76 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 138.1, 136.1, 131.6, 129.2, 129.1, 128.6, 128.5, 128.2, 128.1, 126.8, 123.1, 121.6, 109.0, 101.4, 33.0. HRMS (EI) m/z Calcd. for C₁₇H₁₅N: 233.1204, Found: 233.1207 MS (EI) m/z 232.9 (M⁺, 100%), 231.9, 216.9, 189.0, 165.0, 144.1, 108.7, 97.3, 85.4, 71.4, 57.5, 43.6 EA Calcd. for C₁₇H₁₅N : C: 87.52, H: 6.48, N: 6.00 Found: C: 87.32, H: 6.32, N: 5.86 IR (in CH₂Cl₂) cm⁻¹ : 3099, 3053, 3011, 2925, 1950, 1615, 1511, 1490, 1466, 1335, 1245, 1078, 890, 803, 726, 697, 427



(Z)-1-strylnaphthalene

Colorless oil. Yield 97%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.12 – 8.06 (m, 1H), 7.91 – 7.85 (m, 1H), 7.78 (ddd, J = 7.2, 2.6, 1.1 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.38 – 7.32 (m, 2H), 7.09 (s, 5H), 7.06 (A, dd, J = 12.1, 0.7 Hz, 1H), 6.84 (B, d, J = 12.2 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 136.9, 135.4, 133.8, 132.2, 131.7, 129.2, 128.6, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2, 126.1, 125.8, 125.1.



(*Z*)-2r

(Z)-1-(2-cyclohexyl-1-ethenyl)benzene¹⁶

Colorless oil. Yield 93%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.42 – 7.14 (m, 5H), 6.32 (d, *J* = 11.7 Hz, 1H), 5.50 (dd, *J* = 11.7, 10.1 Hz, 1H), 2.59 (ddt, *J* = 14.6, 7.7, 3.9 Hz, 1H), 1.83 – 1.61 (m, 5H), 1.36 – 1.11 (m, 5H).
¹³C NMR (101 MHz, CDCl₃) δ (ppm) 139.2, 138.1, 128.7, 128.3, 126.9, 126.5, 37.0, 33.4, 26.2, 25.8.



(*Z*)-2s

(Z)-1-phenylhex-1-ene¹⁷

Colourless oil. Yield 95%. Prepared using procedure 2.2.1.

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) 7.37 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 6.41 (dt, *J* = 11.6, 1.9 Hz, 1H), 5.68 (dt, *J* = 11.7, 7.3 Hz, 1H), 2.34 (qd, *J* = 7.3, 1.9 Hz, 2H), 1.49 – 1.30 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) 138.0, 133.4, 128.9, 128.8, 128.2, 126.5, 32.3, 28.5, 22.6, 14.1.

(*Z*)-2t

(Z)-dodec-6-ene¹⁴

Colourless oil. Yield 96%. Prepared using procedure 2.2.3.

¹**H NMR** (400 MHz, CDCl₃) δ (ppm) 5.43 – 5.29 (m, 2H), 2.06 – 1.91 (m, 4H), 1.38 – 1.22 (m, 12H), 0.89 (t, J = 6.8 Hz, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ (ppm) 130.1, 31.7, 29.6, 27.3, 22.7, 14.2.



 $\mathbf{Dodec-1-ene}^{17}$

Colourless oil. Yield 84%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.82 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (dq, J = 17.1, 1.7 Hz, 1H), 4.93 (ddt, J = 10.2, 2.3, 1.2 Hz, 1H), 2.09 – 2.00 (m, 2H), 1.41 – 1.19 (m, 16H), 0.88 (t, J = 7.2, 3H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 139.4, 114.2, 34.0, 32.1, 29.8, 29.7, 29.5, 29.3, 29.1, 22.8, 14.3.

(Z)-2v

 $Dec-9-en-1-ol^{18}$

Colourless oil. Yield 87%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (ddt, J = 17.1, 2.2, 1.6 Hz, 1H), 4.93 (ddt, J = 10.2, 2.3, 1.2 Hz, 1H), 3.64 (t, J = 6.6 Hz, 2H), 2.08 – 1.99 (m, 2H), 1.64 – 1.48 (m, 3H), 1.44 – 1.20 (m, 10H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 139.3, 114.3, 63.2, 33.9, 32.9, 29.6, 29.5, 29.2, 29.0, 25.9.



4-*tert*-butylstyrene¹⁹

Yellowish oil. Yield 91%. Prepared using procedure 2.2.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.36 (s, 4H), 6.71 (dd, J = 17.6, 10.9 Hz, 1H), 5.71 (dd, J = 17.6, 1.0 Hz, 1H), 5.20 (dd, J = 10.9, 1.0 Hz, 1H), 1.33 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 151.0, 136.7, 135.0, 126.1, 125.6, 113.1, 34.7, 31.4.

(*Z*)-2x

3-methoxystyrene¹⁸

Yellowish oil. Yield 86%. Prepared using procedure 2.2.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.28 – 7.23 (m, 1H), 7.06 – 6.93 (m, 2H), 6.85 – 6.80 (m, 1H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.75 (dd, *J* = 17.5, 0.9 Hz, 1H), 5.26 (dd, *J* = 10.9, 0.9 Hz, 1H), 3.83 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 160.0, 139.2, 136.9, 129.6, 119.1, 114.3, 113.6, 111.7, 55.4.



1,1-diphenylprop-2-en-1-ol²⁰

Colourless oil. Yield 89%. Prepared using procedure 2.2.1.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.43 – 7.37 (m, 4H), 7.37 – 7.31 (m, 4H), 7.31 – 7.25 (m, 2H), 6.57 – 6.48 (m, 1H), 5.35 (dd, J = 6.6, 1.2 Hz, 1H), 5.32 (s, 1H), 2.30 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ (ppm) 145.9, 143.7, 128.3, 127.4, 127.0, 114.2, 79.5.



(Z, Z)-1,4-distyrylbenzene²¹

Colourless oil. Yield 89%. Prepared using procedure 2.2.1.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.29 – 7.18 (m, 10H), 7.12 (s, 4H), 6.59 (d, J = 12.3 Hz, 2H), 6.54 (d, J = 12.2 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ (ppm) 137.4, 136.2, 130.4, 130.1, 129.0, 128.9, 128.3, 127.3.



d₁-(*Z*)-2a

(Z)-1-deutero-1,2-diphenylethene²¹

Colourless oil. Yield 95%. Incorporation of D: 81%. Prepared using procedure 2.2.5.

¹H NMR (500 MHz, CDCl₃) δ (ppm) 7.35 – 7.18 (m, 10H), 6.64 (s, 1H). ²H NMR (92 MHz, CDCl₃) δ (ppm) 6.65 (s, 1D). ¹³C NMR (126 MHz, CDCl₃) δ 137.4, 137.3, 130.4, 130.3, 129.0, 128.3, 127.2, 127.2. HRMS (EI) m/z Calcd. for C₁₄H₁₁D: 181.1002, Found: 181.0998 MS (EI) m/z 181.1 (M⁺), 180.1 (100%), 179.0, 166.1, 165.1, 152.1, 89.3, 77.4, 51.5

6. NANOPARTICLES CHARACTERIZATION



A-C) TEM images of CuNPs D) Histogram of particle size distribution

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