Synthesis of 1,3-dienes via a sequential Suzuki-Miyaura coupling - palladium mediated allene isomerization sequence

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Experimental

A. General Information.

All reagent chemicals were purchased from Sigma-Aldrich Chemical Company Ltd. and Lancaster Chemical Synthesis Ltd. Commercially available reagents were used and without further purification. Palladium reagents were obtained from Sigma-Aldrich Chemical Company Ltd and were handled under argon.

All solvents were directly used commercially except tetrahydrofuran (THF) was distilled from sodium and benzophenone prior to use. Petroleum ether refers to the fractions with a boiling point between 40-60°C. Air-sensitive reactions were carried out using oven-dried glassware under nitrogen atmosphere.

Proton magnetic resonance spectra (¹H NMR) and carbon magnetic resonance spectra (¹³C NMR) were recorded at 400MHz and 100MHz respectively using a Bruker Avance 400MHz spectrometer as solutions in CDCl₃. Coupling constants are measured in hertz (Hz) and chemical shifts are quoted as parts per million (ppm).

Thin layer chromatography (TLC) analysis was carried out on aluminium backed silica plates, and plates were visualized by Ultra Violet light (254nm) or vanillin stain.

Alkynes, 1-ethynylcyclohexanol (17), 1-ethynylcyclopentanol (29), 1-ethynylcycloheptanol (33),¹ 1-ethynylcyclooctanol (35),² 8-ethynyl-1,4-dioxaspiro[4.5]decan-8-ol (37)³, 2-methyl-3-butyn-2-ol (39), 2-phenyl-3-butyn-2-ol (42), 3-methyl-1-pentyn-1-ol (44) and norethisterone (46) were purchased or prepared by literature procedures. All aryl and heteroaryl boronic acids were purchased.

B. General procedure for the preparation of 1,3-dienes.

The boronic acid (3.15 mmol, 3.00 equiv.), the alkyne (1.00 mmol, 1.00 equiv.) were dissolved in 1,4-dioxane (5.0 mL) and 4Å sieves (approx. 400 mg) added. The resultant reaction mixture was then heated to 70 °C under an N₂ or argon atmosphere for 1h. To the

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reaction mixture was then added Pd(PPh\textsubscript{3})\textsubscript{4} (58 mg, 0.05 mmol, 5.0 mol%) in one portion and the resultant yellow solution heated for a further 4h. After this period the reaction mixture was cooled, diluted with Et\textsubscript{2}O (50 mL) and transferred to a separating funnel and washed with NaHCO\textsubscript{3} (50mL). The aqueous layer was then extracted with Et\textsubscript{2}O (50 mL) and the combined organic layers washed with brine (50 mL), dried with MgSO\textsubscript{4}, filtered, and the solvents removed under reduce pressure. The crude residue was then purified by column chromatography (100% petroleum ether unless otherwise stated) to give the following compounds.

\[\text{(E)-2-(cyclohex-1-en-1-yl)ethenyl]benzene (19).}\]

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\text{This compound was prepared in 78\% overall yield according to the general procedure, giving a viscous colourless oil (142mg, R}_f\text{ 0.29); }^1\text{H NMR (400 MHz; CDCl}_3\text{) }\delta\text{ 7.43-7.35 (m, 2H), 7.42-7.32 (m, 2H), 6.80 (d, }J = 16.0 \text{ Hz, 1H), 6.39 (d, }J = 16.0 \text{ Hz, 1H), 5.88 (t, }J = 4.0 \text{ Hz, 1H), 2.30-2.22 (m, 2H), 2.21-2.15 (m, 2H), 1.78-1.69 (m, 2H), 1.60-1.67 (m, 2H) ppm; }^{13}\text{C NMR (100 MHz; CDCl}_3\text{) }\delta\text{ 138.1, 135.9, 132.7, 130.94, 128.8, 128.6, 127.3, 126.9, 126.2, 124.7, 26.2, 24.6, 22.6, 22.6 ppm; IR (neat 3082, 2933, 1641, 1493, 739 cm}^{-1}; \text{HRMS [M+H}^+\text{] calculated for C}_{14}\text{H}_{17} \text{ 185.1325, found 185.1321.}\]

\[1\text{-[(E)-2-(Cyclohex-1-en-1-yl)ethenyl]-3-methylbenzene (20).}\]

\[
\text{This compound was prepared in 99\% overall yield according to the general procedure, to give a viscous colourless oil (198 mg, R}_f\text{ 0.45); }^1\text{H NMR (400 MHz; CDCl}_3\text{) }\delta\text{ 7.15-7.24 (m, 3H), 6.99-6.97 (m, 1H), 6.75 (d, }J = 16.0 \text{ Hz, 1H), 6.39 (d, }J = 16.0 \text{ Hz 1H), 5.87 (t, }J = 4.0 \text{ Hz, 1H), 2.33 (s, 3H), 2.30-2.21 (m, 2H), 2.21-2.13 (m, 2H), 1.78-1.68 (m, 2H), 1.67-1.59 (m, 2H) ppm; }^{13}\text{C NMR (100 MHz; CDCl}_3\text{) }\delta\text{ 138.1, 138.0, 136.0, 132.5, 130.7, 128.5, 127.7, 127.7, 127.7, 126.9, 126.2, 124.7, 26.2, 24.6, 22.6, 22.6 ppm; IR (neat 3082, 2933, 1641, 1493, 739 cm}^{-1}; \text{HRMS [M+H}^+\text{] calculated for C}_{14}\text{H}_{17} \text{ 185.1325, found 185.1321.}\]

127.0, 124.8, 123.4, 26.2, 24.6, 22.6, 22.6, 21.5 ppm; IR (neat): 3045, 2965, 1640, 732 cm\(^{-1}\).

HRMS [M+H\(^+\)] calculated for C\(_{15}\)H\(_{19}\) 199.1418, found 199.1487.

1-[(\(E\))-2-(Cyclohex-1-en-1-yl)ethenyl]-4-methoxybenzene (21).\(^5\)

![1-[(E)-2-(Cyclohex-1-en-1-yl)ethenyl]-4-methoxybenzene](image)

This compound was prepared in 87% overall yield according to the general procedure, giving a colourless oil (186 mg, R\(_f\) 0.52); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \(\delta\) 7.32-7.30 (m, 2H), 6.89-6.85 (m, 2H), 6.65 (d, \(J = 16.4\) Hz, 1H), 6.39 (d, \(J = 16.4\) Hz, 1H), 5.87 (t, \(J = 3.6\) Hz, 1H), 3.80 (s, 3H), 2.30-2.23 (m, 2H), 2.20-2.14 (m, 2H), 1.78-1.68 (m, 2H), 1.67-1.59 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz; CDCl\(_3\)) \(\delta\) 158.8, 135.5, 131.1, 131.0, 129.7, 127.2, 124.1, 114.2, 55.1, 26.2, 24.5, 22.2, 22.1 ppm; IR (neat) 3054, 2986, 1683, 1512, 739 cm\(^{-1}\); HRMS [M+H\(^+\)] calculated for C\(_{15}\)H\(_{18}\)O 215.1436, found 215.1448.

1-[(\(E\))-2-(Cyclohex-1-en-1-yl)ethenyl]-3-methoxybenzene (22).

![1-[(E)-2-(Cyclohex-1-en-1-yl)ethenyl]-3-methoxybenzene](image)

This compound was prepared in 60% overall yield according to the general procedure, giving a viscous colourless oil (129 mg, R\(_f\) 0.54), (ethyl acetate : petroleum ether / 1:10); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \(\delta\) 7.21-7.19 (m, 1H), 6.99 (d, \(J = 16.0\) Hz, 1H), 6.92 (s, 1H), 6.79-6.71 (m, 2H), 6.40 (d, \(J = 16.0\) Hz, 1H), 5.89 (t, \(J = 4.0\) Hz, 1H), 3.81 (s, 3H), 2.30-2.21 (m, 2H), 2.21-2.15 (m, 2H), 1.78-1.68 (m, 2H), 1.67-1.59 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz; CDCl\(_3\)) \(\delta\) 159.9, 139.6, 135.9, 133.0, 131.2, 129.5, 124.6, 119.0, 112.6, 111.4, 55.2, 26.2, 24.6, 22.6, 22.6 ppm; IR (neat) 3010, 2931, 1651, 1157, 771 cm\(^{-1}\); HRMS [M+H\(^+\)] calculated for C\(_{15}\)H\(_{18}\)O 215.1430, found 215.1436.

1-[(\(E\))-2-(Cyclohex-1-en-1-yl)ethenyl]naphthalene (23).

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This compound was prepared in 94% overall yield according to the general procedure, giving a colourless oil (220 mg, \( R_f \) 0.36); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \( \delta \) 8.13-8.11 (m, 1H), 7.82-7.80 (m, 1H), 7.74-7.71 (m, 1H), 7.63-7.61 (m, 1H), 7.53-7.39 (m, 3H), 7.19 (d, \( J = 15.6 \) Hz, 1H), 6.80 (d, \( J = 15.6 \) Hz, 1H), 5.95 (t, \( J = 3.6 \) Hz, 1H), 2.44-2.38 (m, 2H), 2.27-2.18 (m, 2H), 1.82-1.77 (m, 2H), 1.71-1.63 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz; CDCl\(_3\)) \( \delta \) 136.3, 135.8, 135.7, 133.8, 131.4, 131.3, 128.6, 127.3, 125.9, 125.8, 125.7, 123.9, 123.2, 121.6, 26.3, 24.8, 22.7, 22.6 ppm; IR (neat) 3027, 2973, 1655, 732 cm\(^{-1}\); HRMS [M+H\(^+\)] calculated for C\(_{18}\)H\(_{19}\)O\(_2\) 235.1481, found 235.1486.

4-[(\(E\))-2-(Cyclohex-1-en-1-yl)ethenyl]-1,2-dimethoxybenzene (24).

This compound was prepared in 57% overall yield according to the general procedure B, giving a yellow oil (138 mg, \( R_f \) 0.59, ethyl acetate : petroleum ether / 15:85); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \( \delta \) 6.95-6.86 (m, 2H), 6.80-6.78 (d, 1H), 6.62 (d, \( J = 16.4 \) Hz, 1H), 6.36 (d, \( J = 16.0 \) Hz, 1H), 5.87 (t, \( J = 4.4 \) Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 2.30-2.22 (m, 2H), 2.12-2.12 (m, 2H), 1.78-1.68 (m, 2H), 1.67-1.58 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz; CDCl\(_3\)) \( \delta \) 149.1, 148.4, 135.8, 139.7, 130.1, 124.5, 120.9, 119.3, 111.4, 108.6, 56.0, 55.9, 26.2, 24.7, 22.7, 22.6 ppm; IR (neat) 3035, 2973, 1655, 732 cm\(^{-1}\); HRMS [M+H\(^+\)] calculated for C\(_{16}\)H\(_{21}\)O\(_2\) 245.1536, found 245.1534.

5-[(\(E\))-2-(Cyclohex-1-en-1-yl)ethenyl]-1,3-dimethoxybenzene (25).
This compound was prepared in 62% overall yield according to the general procedure B, giving a yellow oil (152 mg, Rf 0.58, ethyl acetate : petroleum ether / 15:85); 

\[ ^1\text{H NMR} (400 MHz; \text{CDCl}_3) \delta 6.72-6.71 \text{ (d, } J = 16.4 \text{ Hz, } 1\text{H}), 6.55 (s, 1\text{H}), 6.54 (s, 1\text{H}), 6.38-6.34 \text{ (d, } J = 16.0 \text{ Hz, } 1\text{H}), 6.32 (m, 1\text{H}), 5.89 (m, 1\text{H}), 3.79 (s, 6\text{H}), 2.30-2.22 \text{ (m, 2H), 2.16-2.12 \text{ (m, 2H), 1.78-1.68 \text{ (m, 2H)}}; \]

\[ ^{13}\text{C NMR} (100 MHz; \text{CDCl}_3) \delta 161.0, 140.2, 135.8, 133.2, 131.3, 128.8, 127.3, 124.7, 124.7, 99.4, 55.4, 26.2, 24.6, 22.6 \text{ ppm; IR (neat) 2931, 2839, 1589, 1280, 1203 \text{ cm}^{-1}; HRMS [M+H$^+$] calculated for C$_{16}$H$_{21}$O$_2$ 245.1536, found 245.1539. \]

1-\[(E)-2-\{(Cyclohex-1-en-1-yl)ethenyl\}-4-methyl(carboxy)benzene (26). \]

![Image](image_url)

This compound was prepared in 70% overall yield according to the general procedure B, giving a yellow oil (170 mg, Rf 0.36, ethyl acetate : petroleum ether / 15:85); 

\[ ^1\text{H NMR} (400 MHz; \text{CDCl}_3) \delta 7.96-7.93 \text{ (m, 2H), 7.45-7.42 (m, 2H), 6.85 (d, } J = 16.0 \text{ Hz, 1H}), 6.43 (d, } J = 16.0 \text{ Hz, 1H}), 5.97-5.95 (m, 1H), 3.88 (s, 3H), 2.30-2.16 \text{ (m, 4H), 1.74-1.70 \text{ (m, 2H)}, 1.66-1.60 \text{ (m, 2H)} ppm; \]

\[ ^{13}\text{C NMR} (100 MHz; \text{CDCl}_3) \delta 167.1, 142.8, 135.8, 135.2, 133.0, 132.9, 130.0, 126.0, 123.7, 52.1, 26.33, 24.5, 22.5, 22.4 \text{ ppm; IR (neat) 2931, 1712, 1604, 1435, 1180, 964 \text{ cm}^{-1}; HRMS [M+H$^+$] calculated for C$_{16}$H$_{18}$O$_2$ 243.1385, found 243.1379. \]

2-\[(E)-2-\{(Cyclohex-1-en-1-yl)ethenyl\}furan (27). \]

![Image](image_url)

This compound was prepared in 66% overall yield according to the general procedure, giving a colorless oil (114 mg, Rf 0.86, ethyl acetate : petroleum ether / 1:10); 

\[ ^1\text{H NMR} (400 MHz; \text{CDCl}_3) \delta 7.31 \text{ (d, } J = 16.0 \text{ Hz, 1H}), 6.78 (d, } J = 16.0 \text{ Hz, 1H}), 6.44-6.42 (m, 1H), 6.20-6.18 \text{ (m, 1H), 6.19-6.17 (m, 1H), 5.88 (t, } J = 3.2 \text{ Hz, 1H}), 2.15-2.12 \text{ (m, 4H), 1.69-1.60 \text{ (m, 2H), 1.59-1.55 \text{ (m, 2H)} ppm; }^{13}\text{C NMR} (100 MHz; \text{CDCl}_3) \delta 153.9, 141.4, 135.5, 131.2, 131.0, \]
113.0, 111.4, 106.9, 26.2, 24.2, 22.6, 22.5 ppm; IR (neat) 2953, 1728, 1635, 1081, 730 cm$^{-1}$; HRMS [M+H$^+$] calculated for C$_{12}$H$_{13}$O 173.0961, found 173.0981.

$[(E)-2-(\text{Cyclopent-1-en-1-yl})\text{ethenyl}]\text{benzene (30).}^4$

This compound was prepared in 61% overall yield according to the general procedure, giving a colourless oil (102 mg, R$_f$ 0.29); $^1$H NMR (400 MHz; CDCl$_3$) δ 7.48-7.46 (m, 2H), 7.36-7.34 (m, 2H), 7.24-7.22 (m, 1H), 6.99 (d, $J$ = 16.0 Hz, 1H), 6.46 (d, $J$ = 16.0 Hz, 1H), 5.89-5.86 (m, 1H), 2.6-2.55 (m, 2H), 2.54-2.49 (m, 2H), 2.05-1.94 (m, 2H) ppm; $^{13}$C NMR (100 MHz; CDCl$_3$) δ 142.9, 137.9, 132.2, 128.8, 128.7, 128.6, 127.2, 126.2, 125.9, 33.1, 31.3, 23.23 ppm; IR (neat) 3054, 2986, 1598, 1420, 738 cm$^{-1}$; HRMS [M+H$^+$] calculated for C$_{13}$H$_{13}$ 169.1012, found 169.1024.

1-[(E)-2-(\text{Cyclopent-1-en-1-yl})\text{ethenyl}]4-\text{methylbenzene (31).}$^4$

This compound was prepared in 61% overall yield according to the general procedure, giving a white solid (122 mg, R$_f$ 0.33); $^1$H NMR (400 MHz; CDCl$_3$) δ 7.30-7.28 (m, 2H), 7.12-7.10 (m, 2H), 6.98 (d, $J$ = 16.0 Hz, 1H), 6.40 (d, $J$ = 16.0 Hz, 1H), 5.81 (t, $J$ = 4.0 Hz, 1H), 2.59-2.50 (m, 2H), 2.49-2.43 (m, 2H), 2.35 (s, 3H), 2.01-1.91 (m, 2H) ppm; $^{13}$C NMR (100 MHz; CDCl$_3$) δ 143.0, 137.0, 135.1, 131.5, 129.8, 129.4, 128.7, 128.4, 126.2, 125.0, 33.1, 31.3, 23.3, 21.3 ppm; IR (neat) 3030, 2986, 1598, 1420, 738 cm$^{-1}$; HRMS [M+H$^+$] calculated for C$_{14}$H$_{16}$ 185.1330, found 185.1319.

1-[(E)-2-(\text{Cyclopent-1-en-1-yl})\text{ethenyl}]4-\text{methoxybenzene (32).}$^4$

$^4$
This compound was prepared in 78% overall yield according to the general procedure, giving a colourless oil (155 mg, Rf 0.73, ethyl acetate : petroleum ether / 1:20); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \(\delta\) 7.38-7.34 (m, 2H), 6.90 (d, \(J = 16.0\) Hz, 1H), 6.87-6.83 (m, 2H), 6.37 (d, \(J = 16.0\) Hz, 1H), 5.79 (t, \(J = 2.0\) Hz, 1H), 3.80 (s, 3H), 2.57-2.50 (m, 2H), 2.49-2.41 (m, 2H), 2.01-1.91 (m, 2H) ppm; \(^13\)C NMR (100 MHz; CDCl\(_3\)) \(\delta\) 159.0, 143.0, 130.9, 130.7, 128.3, 127.5, 123.9, 114.1, 55.4, 33.1, 31.3, 23.3 ppm; IR (neat) 3035, 2947, 1567, 1465, 1172, 732 cm\(^{-1}\); HRMS [M+H\(^+\)] calculated for C\(_{14}\)H\(_{17}\)O 201.1274, found 201.1286.

1-[(\(E\))-2-Phenylethenyl]cycloheptene (34).\(^4\)

\[
\begin{align*}
&\text{This compound was prepared in 80\% overall yield according to the general procedure, giving} \\
&\text{a colorless oil (158 mg, Rf 0.19); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \(\delta\) 7.40-7.38 (m, 2H), 7.16-7.13 (m, 1H), 6.74 (d, \(J = 16.0\) Hz, 1H), 6.43 (d, \(J = 16.0\) Hz, 1H), 6.04 (t, \(J = 6.8\) Hz, 1H), 2.45-2.41 (m, 2H), 2.20-2.18 (m, 2H), 1.80-1.76 (m, 2H), 1.53-1.48 (m, 4H) ppm; \(^13\)C NMR (100 MHz; CDCl\(_3\)) \(\delta\) 143.2, 138.2, 135.6, 133.4, 128.6, 126.9, 126.3, 124.8, 32.4, 28.9, 27.4, 26.9, 26.4 ppm; IR (neat) 3020, 2924, 1618, 1448, 694 cm\(^{-1}\); HRMS [M+H\(^+\)] calculated for C\(_{15}\)H\(_{19}\) 199.1480, found 199.1479. \\
&(1E)-1-[(\(E\))-2-Phenylethenyl] cyclooctene (36).\(^6\)
\end{align*}
\]

\[
\begin{align*}
&\text{This compound was prepared in 75\% overall yield according to the general procedure, giving a} \\
&\text{colorless oil (159 mg, Rf 0.62); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \(\delta\) 7.44-7.42 (m, 2H), 7.31-7.28 (m, 2H), 7.20-7.17 (m, 1H), 6.74 (d, \(J = 16.4\) Hz, 1H), 6.49 (d, \(J = 16.4\) Hz, 1H), 5.85 (t, \(J = 4.2\) Hz, 1H), 2.51-2.48 (m, 2H), 2.27-2.24 (m, 2H), 1.69-1.45 (m, 8H) ppm; \(^13\)C NMR (100 MHz; CDCl\(_3\)) \(\delta\) 139.4, 138.1, 133.9, 132.4, 128.7, 126.9, 126.5, 125.3, 30.6, 28.7, 27.3,
\end{align*}
\]

26.9, 24.5 ppm; IR (neat) 3013, 2916, 1597, 1450, 745 cm⁻¹; HRMS [M+H⁺] calculated for C₁₆H₂₁ 213.1638, found 213.1635.

8-[(E)-2-(3,5-Dimethoxyphenyl)ethenyl]-1,4-dioxaspiro[4.5]dec-7-ene (38).

This compound was prepared in 43% overall yield according to the general procedure, giving a colorless oil (130 mg, R_f 0.18, diethyl ether : hexane / 3:7); ¹H NMR (400 MHz; CDCl₃) δ 6.71 (d, J = 16.0 Hz, 1H), 6.57-6.55 (m, 2H), 6.39 (d, J = 16 Hz, 1H), 6.35-6.31 (m, 1H), 5.78 (t, J = 4.0 Hz, 1H), 3.98 (s, 4H), 3.78 (s, 6H), 2.50-2.47 (m, 2H), 2.44-2.41 (m, 2H), 1.85-1.83 (m, 2H) ppm; ¹³C NMR (100 MHz; CDCl₃) δ 160.9, 139.9, 135.3, 131.8, 127.4, 126.2, 108.1, 104.4, 99.5, 64.6, 55.4, 36.5, 30.9, 23.8 ppm; IR (neat) 3055, 2939, 1589, 1203, 1149, 702 cm⁻¹; HRMS [M+H⁺] calculated for C₁₈H₂₃O₄ 303.1591, found 303.1580.

[(1E)-3-Methylbuta-1,3-dien-1-yl]benzene (40).⁷

This compound was prepared in 85% overall yield according to the general procedure, giving a viscous colorless oil (122 mg, R_f 0.31); ¹H NMR (400 MHz; CDCl₃) δ 7.45-7.43 (m, 2H), 7.37-7.35 (m, 2H), 7.27-7.24 (m, 1H), 6.94 (d, J = 16.0 Hz, 1H), 6.55 (d, J = 16.0 Hz, 1H), 5.15 (s, 1H), 5.15 (s, 1H), 2.01 (s, 3H) ppm; ¹³C NMR (100 MHz; CDCl₃) δ 142.1, 137.5, 131.8, 128.8, 128.7, 127.5, 126.7, 117.4, 22.8 ppm; IR (neat) 3025, 2968, 1645, 1493, 1493, 1265, 739 cm⁻¹; HRMS [M+H⁺] calculated for C₁₁H₁₃ 145.1012, found 145.1021.

1-Methyl-4-[(1E)-3-methylbuta-1,3-dien-1-yl]benzene (41).⁸

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This compound was prepared in 47% overall yield according to the general procedure, giving a white solid (74 mg, Rf 0.39); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \(\delta 7.37-7.34 \text{ (m, 2H), } 7.17-7.14 \text{ (m, 2H), } 6.85 \text{ (d, } J = 16 \text{ Hz, 1H), } 6.52 \text{ (d, } J = 16 \text{ Hz, 1H), } 5.09 \text{ (s, 1H), } 5.04 \text{ (s, 1H), } 2.35 \text{ (s, 3H), } 1.99 \text{ (s, 3H) ppm; } ^{13}\text{C NMR (100 MHz; CDCl}_3\text{}) \delta 142.3, 137.4, 134.7, 130.8, 129.4, 128.7, 126.5, 116.9, 21.3, 18.7 \text{ ppm; IR (neat); 3051, 2986, 1603, 1513, 738 cm}^{-1}; \text{ HRMS [M+H}^+]\text{] calculated for C}_{12}\text{H}_{15} 159.1168, \text{ found 159.1163.}

\[(1E)-3\text{-Phenylbuta-1,3-dien-1-yl]benzene (43).}\]~

This compound was prepared in 74% overall yield according to the general procedure, giving a colorless volatile oil that readily degraded upon standing (152 mg, Rf 0.28); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \(\delta 7.45-7.23 \text{ (m, 10H), } 7.11-7.08 \text{ (m, 1H), } 6.52 \text{ (m, 1H), } 5.46 \text{ (s, 1H), } 5.28 \text{ (s, 1H) ppm; } ^{13}\text{C NMR (100 MHz; CDCl}_3\text{}) \delta 148.2, 140.2, 137.2, 132.0, 130.8, 128.9, 128.6, 128.3, 127.9, 127.8, 126.5, 117.5 \text{ ppm; IR (neat) 3054, 2986, 1642, 1421, 739 cm}^{-1}; \text{ HRMS [M+H}^+]\text{] calculated for C}_{16}\text{H}_{15} 207.1168, \text{ found 207.1165.}

1-Methyl-3-\[(1E,3E)-3\text{-methylpenta-1,3-dien-1-yl]benzene (45).}\]~

This compound was prepared in 55% overall yield according to the general procedure, giving a colorless oil (93 mg, Rf 0.41); \(^1\)H NMR (400 MHz; CDCl\(_3\)) \(\delta 7.28-7.17 \text{ (m, 3H), } 6.98-6.96 \text{ (m, 1H), } 6.79 \text{ (d, } J = 16.0 \text{ Hz, 1H), } 6.38 \text{ (d, } J = 16.0, \text{ 1H), } 5.68 \text{ (q, } J = 6.8 \text{ Hz, 1H), } 2.31 \text{ (s, 3H), } 1.81 \text{ (s, 3H), } 1.78 \text{ (d, 3H) ppm; } ^{13}\text{C NMR (100 MHz; CDCl}_3\text{}) \delta 138.0, 138.0, 133.8,
128.3, 128.0, 127.8, 127.0, 125.0, 123.0, 21.8, 14.0, 12.0 ppm; IR (neat) 3025, 2980, 1640, 1442, 732 cm⁻¹; HRMS [M+H] calculated for C₁₃H₁₇ 173.1325, found 173.1323.

(E)-10,13-Dimethyl-17-(3-methylstyryl)-1,2,6,7,8,9,10,11,12,13,14,15-dodecahydro-3H-cyclopenta[a]phenanthren-3-one (47).

This compound was prepared in 57% overall yield according to the general procedure, to give colorless oil (220 mg, Rf 0.11, ethyl acetate : petroleum ether / 1:10); ¹H NMR (400 MHz; CDCl₃) δ 7.19 (m, 4H), 7.05-7.03 (m, 1H), 6.48 (d, J = 16.0 Hz, 1H), 6.35 (d, J = 16.0 Hz, 1H), 5.69 (s, 1H), 2.40-0.80 (m, 26H) ppm; ¹³C NMR (100 MHz; CDCl₃) δ 199.7, 171.3, 138.3, 137.0, 134.5, 128.6, 128.3, 127.8, 127.1, 124.0, 123.7, 84.0, 53.6, 49.8, 47.1, 38.7, 36.4, 35.7, 32.9, 23.7, 21.5, 20.7, 17.5, 14.2 ppm; IR (neat) 3050, 2955, 1675, 1610, 1450, 732 cm⁻¹; HRMS [M+H⁺] calculated for C₂₈H₃₅O 387.2682, found 387.2677.

C. 1,1'-Buta-1,2-diene-1,3-diyldibenzene (48).⁹

Phenylboronic acid (384 mg, 3.15 mmol), 2-phenylbut-3-yn-2-ol (146 mg, 1.00 mmol) were dissolved in 1,4-dioxane (5.0 mL) and 4Å sieves (approx. 400 mg) added. The resultant reaction mixture was then heated to 70 °C under a N₂ or argon atmosphere for 1h. To the reaction mixture was added Pd(PPh₃)₄ (58 mg, 0.05 mmol, 5.0 mol%) in one portion and the resultant yellow solution heated for a further 4h. After this period the reaction was cooled, diluted with Et₂O (50 mL) and transferred to a separating funnel and washed with NaHCO₃ (50mL). The aqueous layer was then extracted with Et₂O (50 mL) and the combined organic

layers washed with brine (50 mL), dried with MgSO₄, filtered and the solvent removed under reduce pressure. The crude residue was then purified by column chromatography (100% petroleum ether) to give the title compound as a colourless oil (187 mg, 91%) (Rᵣ 0.45, 100% petroleum ether); ^1^H NMR (400 MHz; CDCl₃) δ 7.68-7.61 (m, 2H), 7.51-7.44 (m, 6H), 7.40–7.32 (m, 2H), 6.52 (q, J = 3.2 Hz, 1H), 2.27 (s, 3H) ppm; ^13^C NMR (100 MHz; CDCl₃) δ 207.0, 136.5, 134.7, 128.9, 128.6, 127.2, 127.1, 126.0, 104.7, 96.8, 16.9 ppm; IR (neat) 3082, 3060, 1935, 1686, 1493 cm⁻¹; HRMS [M+H⁺] calculated for C₁₆H₁₄ 207.1174, found 207.1168.