Supplementary Information

Construction of dibenzo-fused seven- to nine-membered carbocycles via Brønsted acid promoted intramolecular Friedel–Crafts type alkenylation

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(Submitted to Chem. Commun.)

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1. Synthesis

1.1. General information

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. Infrared spectra were recorded on a Horiba FT-710 model spectrophotometer. \(^1\)H and \(^13\)C NMR spectral data were recorded at 25 °C unless otherwise noted, on one of the following instruments: Bruker Avance-600, Bruker Avance DPX-400, JEOL JNM-LA 500, or JEOL JNM-AL 300. \(^1\)H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, br = broad, app = apparent), coupling constant (J) in Hertz (Hz), and integration. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS, δ = 0 for \(^1\)H NMR) or CDCl\(_3\) (δ = 77.0, center line, for \(^13\)C NMR). HRMS analysis were performed on Bruker Daltonics microTOF or JEOL JMS-700.

1.2. Synthesis of o-alkynyl(arylalkyl)benzenes 8

1.2.1. Synthesis of 8a (typical synthetic procedure for 8a and 8i-l).

![Scheme S1. Preparation of 1-(3,3-dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8a).](image)

To a mixture of PdCl\(_2\)(PPh\(_3\))\(_2\) (71.0 mg, 101 µmol, 1 mol%), Cul (40.1 mg, 211 µmol, 2 mol%), 2-bromobenzaldehyde (S1a) (1.20 mL, 10.0 mmol), and triethylamine (50 mL) at room temperature was added 3,3-dimethyl-1-butyne (1.60 mL, 13.0 mmol). The mixture was then heated at 75°C for 2 h, cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/50 to give 2-(3,3-dimethylbut-1-yn-1-yl)benzaldehyde (S2a)\(^1\) as a yellow liquid (1.80 g, 9.66 mmol, 97%).

To a solution of S2a (192 mg, 1.0 mmol) in THF (1.0 mL) at 0 °C was added 1.0 M THF solution of benzylmagnesium chloride (1.50 mL, 1.50 mmol). The mixture was stirred for 30 min at 0 °C, quenched with saturated aqueous NH\(_4\)Cl, and then extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried over Na\(_2\)SO\(_4\), and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/16 as an eluent to give 1-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)-3-phenylpropan-1-ol (S3a) as a colorless liquid (213 mg, 730 µmol, 73%): \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 1.31 (s, 9H, Me (t-Bu)), 2.00–2.18 (m, 2H, CH\(_2\)), 2.26 (d, J = 4.5 Hz, 1H, CH\(_3\)).

1H, OH), 2.64–2.79 (m, 1H, CH₂), 2.79–2.94 (m, 1H, CH₂), 5.12 (td, J = 5.0, 7.6 Hz, 1H, CHO), 7.15–7.31 (m, 7H, Ar), 7.36 (dd, J = 1.1, 7.7 Hz, 1H, Ar), 7.44 (d, J = 7.7 Hz, 1H, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 28.1 (C), 30.9 (3CH₃), 32.4 (CH₂), 39.4 (CH₂), 72.0 (CH), 76.9 (C), 103.6 (C), 121.1 (C), 125.2 (CH), 125.7 (CH), 126.8 (CH), 127.9 (CH), 128.3 (2CH), 128.3 (2CH), 132.1 (CH), 142.0 (C), 146.1 (C); HRMS-ESI m/z [M+Na]+ calcd for C₁₂H₁₄NaO: 315.1719, found: 315.1717.

1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8a). To a CH₂Cl₂ solution (3 mL) of 1-(2-(3,3-dimethylbut-1-yn-1-yl)phenyl)-3-phenylpropan-1-ol (S₃a) (112 mg, 0.38 mmol) at 0 °C were added triethylsilane (110 µL, 0.76 mmol) and boron trifluoride etherate (50 µL, 0.35 mmol). The mixture was then stirred at 0 °C for 30 min, quenched with saturated aqueous NaHCO₃, and then extracted with ethyl acetate (2 × 3 mL). The combined organic layers were washed with brine and dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane as an eluent to give 1-(3,3-dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8a) as a colorless liquid (64.4 mg, 0.23 mmol, 61%): ¹H NMR (300 MHz, CDCl₃) δ 1.32 (s, 9H, Me (-t-Bu)), 1.90–2.05 (m, 2H, CH₂), 2.68 (t, J = 7.8 Hz, 2H, CH₂), 2.80 (t, J = 7.8 Hz, 2H, CH₂), 7.10–7.32 (m, 8H, Ar), 7.35 (d, J = 7.3 Hz, 1H, Ar); ¹³C NMR (75.5 MHz, CDCl₃) δ 28.1 (C), 31.1 (3CH₃), 32.1 (CH₂), 34.5 (CH₂), 35.9 (CH₂), 77.7 (C), 102.1 (C), 123.3 (C), 125.6 (CH), 125.7 (CH), 127.5 (CH), 128.3 (2CH), 128.4 (2CH), 128.6 (CH), 132.0 (CH), 142.4 (C), 144.1 (C); HRMS-ESI m/z [M+Na]+ calcd for C₁₂H₁₄Na: 299.1770, found: 299.1771.

1.2.2. 2-(3,3-Dimethylbut-1-yn-1-yl)-4-methoxy-1-(3-phenylpropyl)benzene (8i).

The title compound was synthesized using the same procedure described above. Colorless liquid: ¹H NMR (600 MHz, CDCl₃) δ 1.32 (s, 9H, Me (-t-Bu)), 1.93 (quint, J = 8.3 Hz, 2H, CH₂), 2.66 (t, J = 7.7 Hz, 2H, CH₂), 2.74 (t, J = 7.7 Hz, 2H, CH₂), 3.77 (s, 3H, OMe), 6.75 (dd, J = 2.8, 8.5 Hz, 1H, Ar), 6.89 (d, J = 2.7 Hz, 1H, Ar), 7.05 (d, J = 8.4 Hz, 1H, Ar), 7.16 (d, J = 7.4 Hz, 1H, Ar), 7.19 (d, J = 7.3 Hz, 2H, Ar), 7.26 (s, 1H, Ar), 7.28 (d, J = 7.0 Hz, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃) δ 28.1 (C), 31.1 (3CH₃), 32.4 (CH₂), 33.6 (CH₂), 35.9 (CH₂), 55.3 (CH₃), 77.8 (C), 101.9 (C), 114.3 (CH), 116.3 (CH), 124.0 (C), 125.6 (CH), 128.3 (2CH), 128.4 (2CH), 129.6 (CH), 136.5 (C), 142.5 (C), 157.3 (C); HRMS-ESI m/z [M]+ calcd for C₂₂H₂₆O: 306.1984, found: 306.1985.

1.2.3. 1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-(4-methoxyphenyl)propyl)benzene (8j).

The title compound was synthesized using the same procedure described above. Colorless liquid: ¹H NMR (600 MHz, CDCl₃) δ 1.32 (s, 9H, Me (-t-Bu)), 1.93 (quint, J = 7.7 Hz, 2H, CH₂), 2.62 (t, J = 7.7 Hz, 2H, CH₂), 2.78 (t, J = 7.7 Hz, 2H, CH₂), 3.78 (s, 3H, OMe), 6.82 (d, J = 8.1 Hz, 2H, Ar), 7.06–7.20 (m, 5H, Ar), 7.35 (d, J = 7.7 Hz, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃) δ 28.2 (C), 31.1 (3CH₃), 32.4 (CH₂), 34.5 (CH₂), 35.0 (CH₂), 55.3 (CH₃), 77.7 (C), 102.1 (C), 113.7 (2CH), 123.3 (C), 125.6 (CH), 127.5 (CH), 128.6 (CH), 129.3 (2CH), 132.0 (CH), 134.6 (C), 144.2 (C), 157.7 (C); HRMS-ESI m/z [M]⁺ calcd for C₂₂H₂₆O: 306.1984, found: 306.1984.
1.2.4. 2-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-1-(3-phenylpropyl)benzene (8k).

The title compound was synthesized using the same procedure described above. Colorless liquid: $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.31 (s, 9H, Me (t-Bu)), 1.91–2.01 (m, 2H, CH$_2$), 2.26 (s, 3H, CH$_3$ (p-tol)), 2.67 (t, $J$ = 8.0 Hz, 2H, CH$_2$), 2.76 (t, $J$ = 8.0 Hz, 2H, CH$_2$), 5.18 (m, 2H, CH$_2$), 6.95–7.07 (m, 2H, Ar), 7.13–7.22 (m, 4H, Ar), 7.24–7.29 (m, 2H, Ar); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 20.7 (CH$_3$), 28.1 (C), 31.1 (3CH$_3$), 32.3 (CH$_2$), 34.1 (CH$_2$), 35.9 (CH$_2$), 77.8 (C), 101.7 (C), 123.1 (C), 126.6 (CH), 128.2 (2CH), 128.4 (CH), 128.4 (2CH), 128.5 (CH), 132.5 (CH), 135.0 (C), 141.0 (C), 142.5 (C); HRMS-ESI m/z [M]+ calcd for C$_{22}$H$_{26}$: 290.2035, found: 290.2038.

1.2.5. 1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-(p-tolyl)propyl)benzene (8l).

The title compound was synthesized using the same procedure described above. Colorless liquid: $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.31 (s, 9H, Me (t-Bu)), 1.94 (quint, $J$ = 7.8 Hz, 2H, CH$_2$), 2.30 (s, 3H, CH$_3$ (p-tol)), 2.64 (t, $J$ = 7.8 Hz, 2H, CH$_2$), 2.79 (t, $J$ = 7.8 Hz, 2H, CH$_2$), 7.05–7.11 (m, 5H, Ar), 7.11–7.18 (m, 2H, Ar), 7.35 (d, $J$ = 7.7 Hz, 1H, Ar); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 21.0 (CH$_3$), 28.1 (C), 31.1 (3CH$_3$), 32.3 (CH$_2$), 34.5 (CH$_2$), 35.5 (CH$_2$), 77.7 (C), 102.1 (C), 123.3 (C), 125.6 (CH), 127.5 (CH), 128.3 (2CH), 128.6 (CH), 129.0 (2CH), 131.9 (CH), 135.0 (C), 139.3 (C), 144.2 (C); HRMS-ESI m/z [M]+ calcd for C$_{22}$H$_{26}$: 290.2035, found: 290.2036.

1.2.6. Synthesis of 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-ol (8g) (typical synthetic procedure for 8g and 8b-e).

![Scheme S2. Preparation of 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-ol (8g).](image-url)
CH$_2$), 5.08 (dt, $J = 3.9, 8.9$ Hz, 1H, CH), 7.12 (td, $J = 1.7, 7.7$ Hz, 1H, Ar), 7.15–7.30 (m, 5H, Ar), 7.33 (td, $J = 1.1, 7.7$ Hz, 1H, Ar), 7.50 (dd, $J = 1.0, 8.0$ Hz, 1H, Ar), 7.57 (dd, $J = 1.8, 7.8$ Hz, 1H, Ar).

To a CH$_2$Cl$_2$ solution (110 mL) of 1-(2-bromophenyl)-3-phenylpropan-1-ol (S4a) (3.20 g, 11.0 mmol) at 0 °C were added triethylsilane (3.50 mL, 22.0 mmol) and boron trifluoride etherate (1.72 mL, 12.1 mmol). The mixture was then stirred at room temperature for 17 h, quenched with saturated aqueous NaHCO$_3$, and then extracted with ethyl acetate (2 × 10 mL). The combined organic layers were washed with brine and dried over Na$_2$SO$_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using hexane as an eluent to give 1-bromo-2-(3-phenylpropyl)benzene (S5a) as a colorless liquid (1.69 g, 6.13 mmol, 56%): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.95 (quint, $J = 7.1$ Hz, 2H, CH$_2$), 2.69 (t, $J = 7.5$ Hz, 2H, CH$_2$), 2.77 (t, $J = 7.5$ Hz, 2H, CH$_2$), 7.03 (td, $J = 2.4, 6.7$ Hz, 1H, Ar), 7.13–7.32 (m, 7H, Ar), 7.51 (d, $J = 7.5$ Hz, 1H, Ar).

4-(2-(3-Phenylpropyl)phenyl)but-3-yn-1-ol (8g). A mixture of 1-bromo-2-(3-phenylpropyl)benzene (S5a) (155 mg, 560 µmol), SPhos (13.1 mg, 31.9 µmol, 6 mol%), PdCl$_2$(CH$_3$CN)$_2$ (2.6 mg, 10 µmol, 2 mol%), Cs$_2$CO$_3$ (391 mg, 1.20 mmol), dry CH$_3$CN (5.0 mL), and 3-butyln-1-ol (114 µL, 1.50 mmol) was heated at 60 °C for 7 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with ethyl acetate/hexane = 1/4 as an eluent to give 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-ol (8g) (98.5 mg, 372 µmol, 66%) as a yellow liquid: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.91–2.01 (m, 3H, CH$_2$, OH), 2.63 (t, $J = 7.0$ Hz, 2H, CH$_2$), 2.67 (t, $J = 7.7$ Hz, 2H, CH$_2$), 2.79 (t, $J = 8.1$ Hz, 2H, CH$_2$), 3.74 (t, $J = 6.3$ Hz, 2H, CH$_2$), 7.10 (td, $J = 1.7, 7.5$ Hz, 1H, CH$_2$), 7.14–7.22 (m, 5H, Ar), 7.27 (t, $J = 7.5$ Hz, 2H, Ar), 7.37 (d, $J = 7.7$ Hz, 1H, Ar); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 23.8 (CH$_2$), 32.0 (CH$_2$), 34.2 (CH$_2$), 35.6 (CH$_2$), 61.2 (CH$_2$), 81.0 (C), 89.7 (C), 122.6 (C), 125.7 (2CH), 128.0 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.2 (CH), 142.2 (C), 144.2 (C); HRMS-ESI $m/z$ [M]$^+$ caled for C$_{19}$H$_{20}$O: 264.1514, found: 264.1517.

1.2.7. 1-(3-Methylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8b).

The title compound was synthesized using the same procedure described above. Yellow liquid: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.25 (d, $J = 6.9$ Hz, 6H, Me (i-Pr)), 1.97 (quint, $J = 7.6$ Hz, 2H, CH$_2$), 2.68 (t, $J = 7.7$ Hz, 2H, CH$_2$), 2.75–2.85 (m, 3H, CH, CH$_2$), 7.10 (td, $J = 2.1, 7.3$ Hz, 1H, Ar), 7.14–7.21 (m, 5H, Ar), 7.27 (t, $J = 7.6$ Hz, 2H, Ar), 7.35 (d, $J = 7.6$ Hz, 1H, Ar); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 21.3 (CH), 23.1 (2CH$_3$), 32.1 (CH$_2$), 34.4 (CH$_2$), 35.9 (CH$_2$), 78.4 (C), 99.3 (C), 123.3 (C), 125.6 (CH), 125.7 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.0 (CH), 142.4 (C), 144.1 (C); HRMS-ESI $m/z$ [M]$^+$ caled for C$_{20}$H$_{22}$: 262.1722, found: 262.1726.
1.2.8. 1-(Pent-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8c).

The title compound was synthesized using the same procedure described above. Colorless liquid: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 1.10 (t, \(J = 7.2\) Hz, 3H, Me (n-Pr)), 1.66 (sxt, \(J = 7.2\) Hz, 2H, CH\(_2\) (n-Pr)), 2.01 (quint, \(J = 7.7\) Hz, 2H, CH\(_2\)), 2.42 (t, \(J = 6.9\) Hz, 2H, CH\(_2\) (n-Pr)), 2.72 (t, \(J = 7.7\) Hz, 2H, CH\(_2\)), 2.85 (t, \(J = 7.7\) Hz, 2H, CH\(_2\)), 7.14 (dt, \(J = 1.6, 7.5\) Hz, 1H, Ar), 7.18–7.26 (m, 5H, Ar), 7.31 (dd, \(J = 7.1, 7.3\) Hz, 2H, Ar), 7.41 (d, \(J = 7.5\) Hz, 1H, Ar); \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 13.6 (CH\(_3\)), 21.5 (CH\(_2\)), 22.3 (CH\(_2\)), 32.2 (CH\(_2\)), 34.4 (CH\(_2\)), 35.8 (CH\(_2\)), 79.3 (C), 93.7 (C), 123.4 (C), 125.6 (CH), 125.7 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.2 (CH), 142.4 (C), 144.1 (C); HRMS-ESI m/z [M]\(^+\) calcd for C\(_{20}\)H\(_{22}\): 262.1722, found: 262.1721.

1.2.9. 1-(Phenyleth-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8d).

The title compound was synthesized using the same procedure described above. Yellow liquid: \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 2.05 (quint, \(J = 7.7\) Hz, 2H, CH\(_2\)), 2.72 (d, \(J = 7.7\) Hz, 2H, CH\(_2\)), 2.91 (t, \(J = 7.7\) Hz, 2H, CH\(_2\)), 7.13–7.29 (m, 8H, Ar), 7.30–7.40 (m, 3H, Ar), 7.46 (dd, \(J = 2.0, 6.6\) Hz, 2H, Ar), 7.51 (d, \(J = 7.6\) Hz, 1H, Ar); \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 32.2 (CH\(_2\)), 34.4 (CH\(_2\)), 35.8 (CH\(_2\)), 88.2 (C), 92.9 (C), 122.6 (C), 123.5 (C), 125.7 (CH), 125.8 (CH), 128.1 (CH), 128.3 (2CH), 128.3 (2CH), 128.4 (CH), 128.5 (2CH), 128.8 (CH), 131.5 (2CH), 132.2 (CH), 142.3 (C), 144.4 (C); HRMS-ESI m/z [M]\(^+\) calcd for C\(_{23}\)H\(_{20}\): 296.1565, found: 296.1562.

1.2.10. Trimethyl((2-(3-phenylpropyl)phenyl)ethynyl)silane (8e).

The title compound was synthesized using the same procedure described above. Yellow liquid: \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 0.26 (s, 9H, Me (TMS)), 1.98 (quint, \(J = 7.7\) Hz, 2H, CH\(_2\)), 2.68 (t, \(J = 7.7\) Hz, 2H, CH\(_2\)), 2.83 (t, \(J = 7.7\) Hz, 2H, CH\(_2\)), 7.12 (td, \(J = 1.2, 7.4\) Hz, 1H, Ar), 7.17 (d, \(J = 7.7\) Hz, 2H, Ar), 7.20 (d, \(J = 7.0\) Hz, 2H, Ar), 7.23 (td, \(J = 1.2, 7.5\) Hz, 1H, Ar), 7.28 (t, \(J = 7.6\) Hz, 2H, Ar), 7.43 (dd, \(J = 1.2, 7.7\) Hz, 1H, Ar); \(^13\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 0.0 (3CH\(_3\)), 32.2 (CH\(_2\)), 34.5 (CH\(_2\)), 35.9 (CH\(_2\)), 97.8 (C), 103.9 (C), 122.5 (C), 125.7 (CH), 125.7 (CH), 128.3 (2CH), 128.4 (2CH), 128.6 (CH), 128.7 (CH), 132.5 (CH), 142.4 (C), 144.9 (C); HRMS-ESI m/z [M]\(^+\) calcd for C\(_{20}\)H\(_{24}\)Si: 292.1647, found: 292.1651.

1.2.11. 4-(2-(3-Phenylpropyl)phenyl)but-3-yn-1-amine (8h).

\[
\begin{align*}
\text{Br} & \quad \text{S5a} & & \text{NH}_2 \\
& \quad \text{SPhos (6 mol%)} & \quad \text{PdCl}_2(\text{CH}_3\text{CN})_2 (2 \text{ mol%}) & \quad \text{C}_6\text{H}_5\text{CO}_2 (2 \text{ equiv}) \\
& \quad \text{CH}_3\text{CN, 90 ^\circ C, 23 h} & & \text{NH}_2
\end{align*}
\]

Scheme S3. Preparation of 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (8h).
1-Bromo-2-(3-phenylpropyl)benzene (**S5a**) (50.3 mg, 180 µmol), SPhos (4.1 mg, 10 µmol, 6 mol%), PdCl$_2$(CH$_3$CN)$_2$ (1.0 mg, 3.8 µmol, 2 mol%), Cs$_2$CO$_3$ (144 mg, 440 µmol) and dry CH$_3$CN (1.8 mL) and 3-butylnylamine (50 µL, 550 µmol) were added to a dried shield tube and the mixture was heated with stirring at 90 °C for 23 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with methanol/chloroform = 1/5 as an eluent to give 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (**8h**) (14.5 mg, 55 µmol, 31%) as a yellow liquid: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.63 (app. br s, 2H, CH$_2$), 1.93–2.04 (m, 2H, CH$_2$), 2.54 (t, $J = 6.4$ Hz, 2H, CH$_2$), 2.68 (t, $J = 7.7$ Hz, 2H, CH$_2$), 2.80 (t, $J = 7.2$ Hz, 2H, CH$_2$), 2.89 (app. br s, 2H, NH$_2$), 7.11–7.25 (m, 6H, Ar), 7.28 (t, $J = 7.6$ Hz, 2H, Ar), 7.38 (d, $J = 7.6$ Hz, 1H, Ar); $^{13}$C NMR (75.5 MHz, CDCl$_3$) $\delta$ 24.6 (CH$_2$), 32.1 (CH$_2$), 34.2 (CH$_2$), 35.7 (CH$_2$), 41.3 (CH$_2$), 80.6 (C), 91.2 (C), 122.9 (C), 125.7 (2CH), 127.8 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.3 (CH), 142.3 (C), 144.1 (C); HRMS-ESI $m/z$ [M+H]$^+$ calcd for C$_{19}$H$_{22}$N: 264.1752, found: 264.1741.

1.2.12. **N,N-Dimethyl-4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (8f).**

![Scheme S4](image)

To a mixture of 4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-ol (**8g**) (36.1 mg, 140 µmol), triethylamine (40 µL, 270 µmol) and CH$_2$Cl$_2$ (1.5 mL) at 0 °C was added methanesulfonyl chloride (30 µL, 400 µmol). The mixture was stirred at 0 °C for 2 h, quenched with saturated aqueous NaHCO$_3$, and extracted with CH$_2$Cl$_2$ (2 × 5 mL). The combined organic layers were washed with brine and dried over Na$_2$SO$_4$, and evaporated. To the residue was added 50% aqueous solution of dimethyleamine (1.00 mL, 11 mmol) and ethanol (1 mL). The mixture was stirred at 50 °C for 2.5 h, cooled to room temperature and then extracted with CH$_2$Cl$_2$. The organic layer was washed with brine, dried over Na$_2$SO$_4$, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate as an eluent to give **N,N-dimethyl-4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (8f)** as a yellow liquid (38.9 mg, 130 µmol, 93%): $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.97 (quint, $J = 8.0$ Hz, 2H, CH$_2$), 2.30 (s, 6H, NMe$_2$), 2.55–2.60 (m, 4H, CH$_2$), 2.68 (t, $J = 7.7$ Hz, 2H, CH$_2$), 2.80 (t, $J = 8.0$ Hz, 2H, CH$_2$), 7.10 (td, $J = 1.4$, 7.3 Hz, 1H, Ar), 7.13–7.23 (m, 5H, Ar), 7.28 (t, $J = 7.5$ Hz, 2H, Ar), 7.36 (d, $J = 7.8$ Hz, 1H, Ar); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 18.5 (CH$_2$), 32.1 (CH$_2$), 34.2 (CH$_2$), 35.7 (CH$_2$), 45.2 (2CH$_3$), 58.5 (CH$_2$), 79.9 (C), 91.7 (C), 142.3 (C), 144.1 (C).
123.1 (C), 125.6 (CH), 125.7 (CH), 127.7 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.2 (CH), 142.4 (C), 144.2 (C); HRMS-El m/z [M]+ calcd for C21H25N: 291.1987, found: 291.1983.

1.3. Synthesis of o-alkynyl(arylalkyl)benzenes 7

1.3.1. Synthesis of 7d (typical synthetic procedure for 7c–e and 7g–i).

![Scheme S5. Preparation of 1-(pent-1-yn-1-yl)-2-phenethylbenzene (7d).](image)

To a mixture of 1-bromo-2-iodobenzene (S6a) (1.25 mL, 10.0 mmol), triethylamine (40 mL) and CH3CN (40 mL) were added PdCl2(PPh3)2 (70.2 mg, 100 µmol, 1 mol%) and CuI (38.5 mg, 202 µmol, 2 mol%). The mixture was cooled to 0 °C, to which ethynylbenzene (1.43 mL, 13.0 mmol) was added. The mixture was stirred at room temperature for 22 h, quenched with saturated aqueous NaHCO3, and the mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, dried over Na2SO4, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/50 as an eluent to give 1-bromo-2-(phenylenethynyl)benzene (S7a)2 as a colorless liquid (2.57 g, 9.98 mmol, 100%).

A suspension of S7a (974 mg, 3.78 mmol) and 10% Pd/C (200 mg, 188 µmol) in ethyl acetate (15 mL) was stirred under a balloon of hydrogen for 6 h at room temperature. The reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was evaporated, and the residue was chromatographed on silica gel with hexane as an eluent to give 1-bromo-2-phenethylbenzene (S8a)3 (988 mg, 3.78 mmol, 100%) as a colorless liquid.

1-(Pent-1-yn-1-yl)-2-phenethylbenzene (7d). To a mixture of 1-bromo-2-phenethylbenzene (S8a) (131 mg, 500 µmol), SPhos (12.3 mg, 30.0 µmol, 6 mol%), PdCl2(CH3CN)2 (2.6 mg, 10 µmol, 2 mol%), Cs2CO3 (391 mg, 1.20 mmol) and dry CH3CN (5 mL) were added 1-pentyne (146 µL, 1.5 mmol), and the mixture was stirred at 60 °C for 6.5 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with hexane as an eluent to give 1-(pent-1-yn-1-yl)-2-phenethylbenzene (7d) (93.9 mg, 378 µmol, 76%) as an orange liquid: 1H NMR (300 MHz, CDCl3) δ 1.05 (td, J = 2.3, 7.4 Hz, 3H, Me (n-Pr)), 1.64 (sext, J = 7.1 Hz, 2H, CH2 (n-Pr)), 2.44 (td, J = 2.3, 7.0 Hz, 2H, CH2 (n-Pr)), 2.86–2.96 (m, 2H, CH2), 2.99–3.11 (m, 2H, CH2), 7.07–7.29 (m, 8H, Ar), 7.36–7.45 (m, 1H, Ar); 13C NMR (75.5 MHz, CDCl3) δ 13.6 (CH3), 21.6 (CH2), 22.3 (CH2), 37.0 (2CH2), 79.3 (C), 93.9 (C), 123.4 (C), 125.8 (2CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.7 (CH), 132.2 (CH), 142.1 (C), 143.4 (C); HRMS-El m/z [M]+ calcd for C19H21O: 248.1565, found: 248.1569.

1.3.2. **1-(3,3-Dimethylbut-1-yn-1-yl)-2-phenenylbenzene (7c).**

The title compound was synthesized using the same procedure described above. Colorless liquid: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.35 (s, 9H, Me ($t$-Bu)), 2.91 (d, $J$ = 7.4 Hz, 1H, CH$_2$), 2.93 (d, $J$ = 5.2 Hz, 1H, CH$_2$), 3.04 (d, $J$ = 5.2 Hz, 1H, CH$_2$), 3.06 (d, $J$ = 7.4 Hz, 1H, CH$_2$), 7.10–7.26 (m, 6H, Ar), 7.29 (t, $J$ = 7.5 Hz, 2H, Ar), 7.39 (dd, $J$ = 1.9, 7.5 Hz, 1H, Ar); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 28.2 (C), 31.1 (3CH$_3$), 37.0 (2CH$_2$), 77.6 (C), 102.2 (C), 123.2 (C), 125.8 (2CH), 127.6 (CH), 128.3 (2CH), 128.4 (2CH), 128.9 (CH), 132.2 (CH), 142.1 (C), 143.4 (C); HRMS-ESI $m/z$ [M+Na]$^+$ calcd for C$_{20}$H$_{22}$Na: 285.1614, found: 285.1614.

1.3.3. **Trimethyl[(2-phenenylphenyl)ethynyl]silane (7e).**

The title compound was synthesized using the same procedure described above. Light brown liquid: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 0.08 (s, 9H, TMS), 2.67–2.77 (m, 2H, CH$_2$), 2.78–2.94 (m, 2H, CH$_2$), 6.89–7.10 (m, 8H, Ar), 7.27 (d, $J$ = 7.7 Hz, 1H, Ar); $^{13}$C NMR (75.5 MHz, CDCl$_3$) $\delta$ 15.5 (3CH$_3$), 45.1 (CH$_2$), 45.1 (CH$_2$), 93.7 (C), 98.4 (C), 113.4 (C), 116.1 (2CH), 118.0 (2CH), 118.1 (2CH), 118.3 (CH), 118.5 (CH), 121.5 (CH), 129.0 (C), 130.7 (C); HRMS-ESI $m/z$ [M]$^+$ calcd for C$_{19}$H$_{22}$Si: 278.1491, found: 278.1489.

1.3.4. **1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-methylphenenyl)benzene (7g).**

The title compound was synthesized using the same procedure described above. Yellow solid: mp 34.0–34.5 °C: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 1.34 (s, 9H, CH$_3$ ($t$-Bu)), 2.30 (s, 3H, CH$_3$ ($p$-tol)), 2.80–2.92 (m, 2H, CH$_2$), 2.96–3.09 (m, 2H, CH$_2$), 7.01–7.16 (m, 7H, Ar), 7.33–7.41 (m, 1H, Ar); $^{13}$C NMR (75.5 MHz, CDCl$_3$) $\delta$ 21.0 (CH$_3$), 28.1 (C), 31.1 (3CH$_3$), 36.6 (CH$_2$), 37.1 (CH$_2$), 77.7 (C), 102.0 (C), 123.2 (C), 125.8 (CH), 127.6 (CH), 128.2 (2CH), 128.8 (CH), 129.0 (2CH), 132.1 (CH), 135.1 (C), 139.0 (C), 143.5 (C); HRMS-ESI $m/z$ [M]$^+$ calcd for C$_{21}$H$_{24}$: 276.1878, found: 276.1877.

1.3.5. **1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-trifluoromethylphenenyl)benzene (7h).**

The title compound was synthesized using the same procedure described above. Colorless liquid: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.34 (s, 9H, CH$_3$ ($t$-Bu)), 2.95–3.02 (m, 2H, CH$_2$), 3.02–3.09 (m, 2H, CH$_2$), 7.08 (dd, $J$ = 1.5, 7.2 Hz, 1H, Ar), 7.11–7.20 (m, 2H, Ar), 7.29 (d, $J$ = 8.0 Hz, 2H, Ar), 7.39 (dd, $J$ = 1.9, 7.2 Hz, 1H, Ar), 7.53 (d, $J$ = 8.2 Hz, 2H, Ar); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 28.2 (C), 31.1 (3CH$_3$), 36.5 (CH$_2$), 36.7 (CH$_2$), 77.5 (C), 102.3 (C), 123.3 (C), 124.5 (q, $^1$J = 268.4 Hz, CF$_3$), 125.2 (q, $^3$J = 3.6 Hz, 2CH), 126.0 (CH), 127.6 (CH), 128.2 (q, $^2$J = 32.4 Hz, C), 128.7 (2CH), 128.8 (CH), 132.3 (CH), 142.6 (C), 146.1 (C); HRMS-ESI $m/z$ [M]$^+$ calcd for C$_{21}$H$_{21}$F$_3$: 330.1595, found: 330.1599.

1.3.6. **1-(4-Methylphenenyl)-2-(pent-1-yn-1-yl)benzene (7i).**

The title compound was synthesized using the same procedure described above. Colorless liquid: $^1$H NMR
(300 MHz, CDCl3) δ 1.06 (td, J = 1.6, 7.3 Hz, 3H, Me (n-Pr)), 1.65 (sext, J = 7.2 Hz, 2H, CH2 (n-Pr)), 2.31 (s, 3H, CH3 (p-tol)), 2.44 (td, J = 1.3, 7.0 Hz, 2H, CH2 (n-Pr)), 2.82–2.94 (m, 2H, CH2), 2.97–3.10 (m, 2H, CH2), 7.02–7.17 (m, 7H, Ar), 7.36–7.45 (m, 1H, Ar); 13C NMR (75.5 MHz, CDCl3) δ 13.6 (CH3), 21.0 (CH3), 21.6 (CH2), 22.3 (CH2), 36.6 (CH2), 37.1 (CH2), 79.3 (C), 93.8 (C), 123.4 (C), 125.8 (CH), 127.6 (CH), 128.3 (2CH), 128.7 (CH), 129.0 (2CH), 132.2 (CH), 135.2 (C), 139.0 (C), 143.6 (C); HRMS-EL m/z [M]+ calcd for C20H22: 262.1722, found: 262.1714.

1.3.7. 4-(2-Phenethylphenyl)but-3-yn-1-ol (7f).

To a mixture of 1-bromo-2-phenethylbenzene (S8a) (261 mg, 1.00 mmol), SPhos (27.6 mg, 67.2 µmol, 7 mol%), PdCl2(CH3CN)2 (5.2 mg, 20 µmol, 2 mol%), Cs2CO3 (793 mg, 2.43 mmol) and dry CH3CN (10 mL) were added 3-butyn-1-ol (230 µL, 3.00 mmol), and the mixture was stirred at 60 °C for 6.5 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite.

The filtrate was concentrated in vacuo, and the residue was chromatographed on silica gel with ethyl acetate/hexane = 1/4 as an eluent to give 4-(2-phenethylphenyl)but-3-yn-1-ol (7f) (144 mg, 575 µmol, 58%) as a colorless liquid: 1H NMR (300 MHz, CDCl3) δ 1.93 (app. br s, 1H, OH), 2.72 (t, J = 6.4 Hz, 2H, CH2), 2.86–2.98 (m, 2H, CH2), 2.99–3.11 (m, 2H, CH2), 3.73–3.86 (m, 2H, CH2), 7.08–7.34 (m, 8H, Ar), 7.37–7.45 (m, 1H, Ar); 13C NMR (75.5 MHz, CDCl3) δ 23.9 (CH2), 36.8 (CH2), 37.0 (CH2), 61.2 (CH2), 81.0 (C), 89.9 (C), 122.7 (C), 125.9 (2CH), 128.0 (CH), 128.3 (2CH), 128.4 (2CH), 128.8 (CH), 132.4 (CH), 141.9 (C), 143.6 (C); HRMS-El m/z [M]+ calcd for C16H18O: 250.1358, found: 250.1358.

1.3.8. N,N-Dimethyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7a).

To a mixture of 4-(2-phenethylphenyl)but-3-yn-1-ol (7f) (53.6 mg, 214 µmol), triethylamine (60 µL, 400 µmol) and CH2Cl2 (2.0 mL) was added methanesulfonyl chloride (40.0 µL, 300 µmol) at 0 °C. The mixture was stirred at 0 °C for 2.5 h, quenched with saturated aqueous NaHCO3, and extracted with CH2Cl2 (2 × 5.0
The combined organic layers were washed with brine and dried over Na₂SO₄. Then the solvent was removed under reduced pressure. To the residue were added 50% aqueous solution of dimethylamine (400 µL, 5.0 mmol) and ethanol (1.6 mL), and the mixture was stirred at 50 °C for 2 h. The mixture was extracted with CH₂Cl₂, and the organic layer was washed with brine and dried over Na₂SO₄. Then the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate as an eluent to give N,N-dimethyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7a) as a yellow liquid (41.8 mg, 151 µmol, 71%): 

$^1$H NMR (400 MHz, CDCl₃) δ 2.30 (s, 6H, CH₃(NMe₂)), 2.63 (app. br s, 4H, CH₂(Bn)), 2.88–2.96 (m, 2H, CH₂), 3.01–3.10 (m, 2H, CH₂), 7.09–7.23 (m, 6H, Ar), 7.26–7.32 (m, 2H, Ar), 7.37–7.41 (m, 1H, Ar); $^{13}$C NMR (75.5 MHz, CDCl₃) δ 30.2 (CH₂), 44.9 (CH₂), 45.0 (CH₂), 51.5 (2CH₃), 62.2 (CH₂), 79.3 (C), 88.8 (C), 113.8 (C), 116.1 (2CH), 117.6 (CH), 118.0 (2CH), 118.1 (2CH), 118.4 (CH), 121.2 (CH), 129.1 (C), 130.3 (C); HRMS-El m/z [M]⁺ calecd for C₂₀H₂₃N: 277.1830, found: 277.1825.

1.3.9. N-Methyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7b).

The title compound was synthesized using the same procedure described above. Light brown liquid: $^1$H NMR (500 MHz, CDCl₃) δ 2.46 (s, 3H, CH₃), 2.69 (dd, $J$ = 6.5, 13.2 Hz, 2H, CH₂(Bn)), 2.85 (t, $J$ = 6.5 Hz, 2H, CH₂(Bn)), 2.91 (d, $J$ = 7.1 Hz, 1H, CH₂), 2.93 (d, $J$ = 5.3 Hz, 1H, CH₂), 3.04 (d, $J$ = 5.3 Hz, 1H, CH₂), 3.06 (d, $J$ = 7.1 Hz, 1H, CH₂), 3.10–3.22 (m, 1H, NHCH₃), 7.11–7.16 (m, 2H, Ar), 7.17–7.22 (m, 4H, Ar), 7.26–7.31 (m, 2H, Ar), 7.38–7.43 (m, 1H, Ar); $^{13}$C NMR (125 MHz, CDCl₃) δ 31.6 (CH₂), 43.9 (CH₂), 44.9 (CH₂), 55.5 (CH₂), 79.7 (C), 88.4 (C), 113.7 (C), 116.1 (2CH), 117.7 (CH), 118.1 (2CH), 118.1 (2CH), 118.4 (CH), 121.3 (CH), 129.0 (C), 130.2 (C); HRMS-El m/z [M]⁺ calecd for C₁₉H₂₁N: 263.1674, found: 263.1672.

1.4. Synthesis of o-alkynyl(arylalkyl)benzenes 9

1.4.1. 1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9a) (typical synthetic procedure for 9a–c).

A mixture of (3-iodopropyl)benzene (670 µL, 4.16 mmol), triphenylphosphine (1.13 g, 4.32 mmol) and toluene (1.0 mL) was stirred at 100 °C for 7.5 h and cooled to room temperature. The resulting precipitate
was collected by filtration and washed with dry Et₂O to give the phosphonium salt (1.81 g, 3.56 mmol, 86%) as white needles. To a cold solution of the salt (762 mg, 1.50 mmol) in dry THF (15 mL) at 0 °C was added 1.63 M hexane solution of nBuLi (920 µL, 1.50 mmol). The mixture was stirred at 0 °C for 2 h, cooled to –78 °C, and 2-bromobenzaldehyde (S1a) (173 µL, 1.50 mmol) was added. The resulting mixture was stirred at –78 °C for 2 h and then allowed to warm to room temperature over 30 min. Water was added and the mixture was then extracted with CHCl₃. The organic layer was dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography using hexane as an eluent to give a mixture of E- and Z-alkenes S9a as a yellow liquid (352 mg, 1.23 mmol, 82%).

A suspension of the mixture of E- and Z-alkenes S9a (352 mg, 1.23 mmol) and 10% Pd/C (63.8 mg, 60.0 µmol) in ethyl acetate (12 mL) was stirred under a balloon of hydrogen for 20 h at room temperature. The reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with hexane as an eluent to give 1-bromo-2-(4-phenylbutyl)benzene (S10a) (230 mg, 795 µmol, 65%) as a colorless liquid.

**1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9a).** To a mixture of 1-bromo-2-(4-phenylbutyl)benzene (S10a) (86.7 mg, 300 µmol), SPhos (7.4 mg, 18 µmol, 6 mol%), PdCl₂(CH₃CN)₂ (1.6 mg, 6.2 µmol, 2 mol%), Cs₂CO₃ (235 mg, 720 mmol) and dry CH₂CN (3.0 mL) were added 3,3-dimethyl-1-butyne (110 µL, 900 µmol), and the mixture was stirred at 60 °C for 6 h. After being cooled to room temperature, the reaction mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with hexane as an eluent to give 1-(3,3-dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9a) (82 mg, 282 µmol, 94%) as a colorless liquid: ¹H NMR (300 MHz, CDCl₃) δ 1.31 (s, 9H, Me (t-Bu)), 1.62–1.74 (m, 4H, CH₂), 2.58–2.69 (m, 2H, CH₂), 2.72–2.83 (m, 2H, CH₂), 7.05–7.20 (m, 6H, Ar), 7.21–7.30 (m, 2H, Ar), 7.34 (d, J = 7.4 Hz, 1H, Ar); ¹³C NMR (75.5 MHz, CDCl₃) δ 28.1 (C), 30.2 (CH₂), 31.1 (3CH₃), 31.5 (CH₂), 34.7 (CH₂), 35.9 (CH₂), 77.8 (C), 102.0 (C), 123.2 (C), 125.5 (CH), 125.6 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 131.9 (CH), 142.6 (C), 144.3 (C); HRMS-El m/z [M⁺] calcd for C₂₂H₂₆: 290.2035, found: 290.2028.

**1.4.2. 1-(Pent-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9b).**

Yellow liquid: ¹H NMR (300 MHz, CDCl₃) δ 1.05 (td, J = 3.7, 7.2 Hz, 3H, Me (n-Pr)), 1.61 (sext, J = 3.7 Hz, 2H, CH₂ (n-Pr)), 1.66–1.75 (m, 4H, CH₂), 2.40 (td, J = 3.5, 6.9 Hz, 2H, CH₂ (n-Pr)), 2.55–2.71 (m, 2H, CH₂), 2.73–2.90 (m, 2H, CH₂), 7.12–7.28 (m, 8H, Ar), 7.34–7.41 (m, 1H, Ar); ¹³C NMR (75.5 MHz, CDCl₃) δ 13.6 (CH₃), 21.5 (CH₂), 22.3 (CH₂), 30.2 (CH₂), 31.3 (CH₂), 34.5 (CH₂), 35.8 (CH₂), 79.4 (C), 93.6 (C), 123.4 (C), 125.5 (CH), 125.6 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.1 (CH), 142.7 (C), 144.3 (C); HRMS-El m/z [M⁺] calcd for C₂₁H₂₄: 276.1878, found: 276.1880.

**1.4.3. 1-(Hept-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9c).**
The title compound was synthesized using the same procedure described above. Colorless liquid: \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 0.94 (dt, \( J = 1.0, 7.4 \text{ Hz}, \text{3H}, \text{Me} \)), 1.36–1.42 (m, 2H, CH\(_2\)), 1.45–1.51 (m, 2H, CH\(_2\)), 1.60–1.66 (m, 2H, CH\(_2\)), 1.71–1.74 (m, 4H, 2CH\(_2\)), 2.44 (t, \( J = 7.0 \text{ Hz}, \text{2H}, \text{Me} \)), 2.67 (t, \( J = 6.6 \text{ Hz}, \text{2H}, \text{CH} \)), 2.82 (t, \( J = 6.9 \text{ Hz}, \text{2H}, \text{CH} \)), 7.11–7.13 (m, 1H, Ar), 7.15–7.22 (m, 5H, Ar), 7.27 (t, \( J = 8.3 \text{ Hz}, \text{2H}, \text{Ar} \)), 7.39 (d, \( J = 8.0 \text{ Hz}, \text{1H}, \text{Ar} \)); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 14.0 (CH\(_3\)), 19.5 (CH\(_3\)), 22.2 (CH\(_2\)), 28.5 (CH\(_2\)), 30.2 (CH\(_2\)), 31.1 (CH\(_2\)), 31.3 (CH\(_2\)), 34.5 (CH\(_2\)), 35.8 (CH\(_2\)), 79.3 (C), 93.9 (C), 123.4 (C), 125.5 (CH), 125.6 (CH), 127.5 (CH), 128.2 (2CH), 128.4 (2CH), 128.6 (CH), 132.1 (CH), 142.7 (C), 144.3 (C); HRMS-ESI \( m/z \) [M+Na]\(^+\) calced for C\(_{23}H_{28}Na\): 327.2083, found: 327.2092.

1.4.4. 2-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-1-(4-phenylbutyl)benzene (9d).

The title compound was synthesized using the same procedure described above. Yellow liquid: \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.30 (s, 9H, Me (t-Bu)), 1.62–1.72 (m, 4H, CH\(_2\)), 2.25 (s, 3H, Me (p-tol)), 2.63 (t, \( J = 6.9 \text{ Hz}, \text{2H}, \text{CH} \)), 2.73 (t, \( J = 6.9 \text{ Hz}, \text{2H}, \text{CH} \)), 6.96 (dd, \( J = 1.4, 7.7 \text{ Hz}, \text{1H}, \text{Ar} \)), 7.02 (d, \( J = 7.7 \text{ Hz}, \text{1H}, \text{Ar} \)), 7.12–7.20 (m, 4H, Ar), 7.25 (t, \( J = 8.3 \text{ Hz}, \text{2H}, \text{Ar} \)); \(^{13}C\) NMR (75.5 MHz, CDCl\(_3\)) \( \delta \) 20.7 (CH\(_3\)), 28.1 (C), 30.4 (CH\(_2\)), 31.1 (3CH\(_3\)), 31.5 (CH\(_2\)), 34.2 (CH\(_2\)), 35.9 (CH\(_2\)), 77.9 (C), 101.6 (C), 123.0 (C), 125.6 (CH), 128.2 (2CH), 128.3 (CH), 128.4 (2CH), 128.5 (CH), 132.4 (CH), 135.0 (C), 141.3 (C), 142.7 (C); HRMS-ESI \( m/z \) [M+Na]\(^+\) calced for C\(_{22}H_{28}\): 304.2191, found: 304.2188.

1.4.5. 4-Methyl-2-(pent-1-yn-1-yl)-1-(4-phenylbutyl)benzene (9e).

The title compound was synthesized using the same procedure described above. Yellow liquid: \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.03 (t, \( J = 7.4 \text{ Hz}, \text{3H}, \text{CH} \)), 1.55–1.70 (m, 6H, CH\(_2\)), 2.25 (s, 3H, Me (p-tol)), 2.38 (t, \( J = 6.9 \text{ Hz}, \text{2H}, \text{CH} \)), 2.62 (br t, \( J = 5.8 \text{ Hz}, \text{2H}, \text{CH} \)), 2.73 (br t, \( J = 5.8 \text{ Hz}, \text{2H}, \text{CH} \)), 6.96 (br d, \( J = 7.7 \text{ Hz}, \text{1H}, \text{Ar} \)), 7.01 (br d, \( J = 7.7 \text{ Hz}, \text{1H}, \text{Ar} \)), 7.12–7.18 (m, 4H, Ar), 7.23 (d, \( J = 7.4 \text{ Hz}, \text{2H}, \text{Ar} \)); \(^{13}C\) NMR (76 MHz, CDCl\(_3\)) \( \delta \) 13.6 (CH\(_3\)), 20.7 (CH\(_3\)), 21.5 (CH\(_2\)), 22.3 (CH\(_2\)), 30.4 (CH\(_2\)), 31.3 (CH\(_2\)), 34.0 (CH\(_2\)), 35.8 (CH\(_2\)), 79.5 (C), 93.2 (C), 123.1 (C), 125.6 (CH), 128.2 (2CH), 128.4 (3CH), 128.5 (CH), 132.6 (CH), 135.0 (C), 141.3 (C), 142.8 (C); HRMS-ESI \( m/z \) [M+Na]\(^+\) calced for C\(_{22}H_{26}Na\): 313.1927, found: 313.1927.

1.4.6. 1-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-2-(4-phenylbutyl)benzene (9f).

The title compound was synthesized using the same procedure described above. Yellow liquid: \( ^1H \) NMR (500 MHz, CDCl\(_3\)) \( \delta \) 1.22 (s, 9H, Me (t-Bu)), 1.58–1.63 (m, 4H, CH\(_2\)), 2.21 (s, 3H, Me), 2.53–2.61 (m, 2H, CH\(_2\)), 2.61–2.70 (m, 2H, CH\(_2\)), 6.80–6.84 (m, 1H, Ar), 6.85–6.88 (m, 1H, Ar), 7.07–7.11 (m, 3H, Ar), 7.14–7.21 (m, 3H, Ar); \(^{13}C\) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 21.4 (CH\(_3\)), 28.1 (C), 30.3 (CH\(_2\)), 31.1 (3CH\(_3\)), 31.6 (CH\(_2\)), 34.7 (CH\(_2\)), 36.0 (CH\(_2\)), 77.8 (C), 101.2 (C), 120.2 (C), 125.6 (CH), 126.3 (CH), 128.2 (2CH), 128.4 (2CH), 129.5 (CH), 131.8 (CH), 137.3 (C), 142.7 (C), 144.2 (C); HRMS-ESI \( m/z \) [M+Na]\(^+\) calced for C\(_{23}H_{28}\): 327.2083, found: 327.2089.
1.4.7. 4-Methyl-1-(pent-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9g)

The title compound was synthesized using the same procedure described above. Yellow liquid: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.06 (t, $J$ = 7.6 Hz, 3H, CH$_3$), 1.63 (sext, $J$ = 7.6 Hz, 2H, CH$_2$), 1.68–1.72 (m, 4H, CH$_2$), 2.31 (s, 3H, Me), 2.43 (t, $J$ = 7.8 Hz, 2H, CH$_2$), 2.66 (t, $J$ = 7.4 Hz, 2H, CH$_2$), 2.77 (t, $J$ = 7.4 Hz, 2H, CH$_2$), 6.93 (dd, $J$ = 1.4, 7.7 Hz, 1H, Ar), 6.97 (br s, $J$ = 7.7 Hz, 1H, Ar), 7.17–7.20 (m, 3H, Ar), 7.26–7.30 (m, 3H, Ar); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 13.6 (CH$_3$), 21.4 (CH$_3$), 21.5 (CH$_2$), 22.4 (CH$_2$), 30.3 (CH$_2$), 31.4 (CH$_2$), 34.4 (CH$_2$), 35.9 (CH$_2$), 79.4 (C), 92.8 (C), 120.3 (C), 125.6 (CH), 126.4 (CH), 128.2 (2CH), 128.4 (2CH), 129.4 (CH), 132.0 (CH), 137.4 (C), 142.8 (C), 144.2 (C); HRMS-ESI $m/z$ [M+H]$^+$ calc'd for C$_{22}$H$_{27}$: 291.2107, found: 291.2108.

1.5. Synthesis of alkylidenedibenzo[a,d]cycloheptenes, -octenes, and -nonenes

1.5.1. 12-(2,2-Dimethylpropylidene)-5,6,7,12-tetrahydro-dibenzo[a,d]cyclooctene (2a) (Table 1, entry 4).

TfOH (8.8 µL, 100 µmol) was added to a mixture of 1-(3,3-dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8a) (30.0 mg, 109 µmol) in CH$_2$Cl$_2$ (1 mL) at 0 °C. After being stirred at 0 °C for 10 min, the mixture was quenched with saturated aqueous NaHCO$_3$ and extracted with ethyl acetate (3 × 1 mL). The combined organic layers were washed with brine and dried over Na$_2$SO$_4$ and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/8 as an eluent to give 2a as a colorless solid (29.8 mg, 108 µmol, 99%): mp 53.3–53.6 °C; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.96 (s, 9H, CH$_3$ (t-Bu)), 1.36–2.44 (m, 2H, CH$_2$), 2.49–3.49 (m, 4H, CH$_2$), 5.62 (s, 1H, CH (vinyl)), 6.93–7.17 (m, 7H, Ar), 7.23 (d, $J$ = 7.1 Hz, 1H, Ar); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 28.9 (C), 30.6 (3CH$_2$), 34.1 (CH$_2$), 36.0–38.5 (2CH$_2$), 125.7 (CH), 126.2 (CH), 126.6 (CH), 126.7 (CH), 128.4 (CH), 128.7 (CH), 129.6 (CH), 129.9 (CH), 139.3 (CH), 140.0 (C), 140.1 (C), 141.9 (C), 146.4 (2C); HRMS-ESI $m/z$ [M+Na]$^+$ calc'd for C$_{21}$H$_{24}$Na: 299.1770, found: 299.1771.

1.5.2. 5,6,7,12-Tetrahydro-12-(2-methylpropylidene)-dibenzo[a,d]cyclooctene (2b) (Table 2, entry 1).

The title compound was synthesized using the same procedure described above. Yellow liquid: $^1$H NMR (600 MHz, CDCl$_3$, 320K) $\delta$ 0.96 (d, $J$ = 6.8 Hz, 6H, CH$_3$ (i-Pr)), 1.97 (app. br s, 2H, CH$_2$), 2.05–2.15 (m, 1H, CH (i-Pr)), 2.66 (app. br s, 2H, CH$_2$), 2.91 (t, $J$ = 6.5 Hz, 2H, CH$_2$), 5.60 (d, $J$ = 9.7 Hz, 1H, CH (vinyl)), 7.00 (d, $J$ = 7.2 Hz, 1H, Ar), 7.05–7.16 (m, 6H, Ar), 7.33 (d, $J$ = 7.6 Hz, 1H, Ar); $^{13}$C NMR (150 MHz, CDCl$_3$, 320K) $\delta$ 22.8 (2CH$_3$), 28.5 (CH), 29.5 (CH$_2$), 34.7–35.5 (2CH$_2$), 126.1 (CH), 126.2 (CH), 126.8 (CH), 127.1 (CH), 128.3 (CH), 128.4 (CH), 129.1 (CH), 130.5 (CH), 138.5 (CH), 140.2 (C), 140.4 (C), 140.7 (C), 141.0 (C), 143.5 (C); HRMS-ESI $m/z$ [M]$^+$ calc'd for C$_{20}$H$_{22}$: 262.1722, found: 262.1719.

1.5.3. 12-Butylidene-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctene (2c) (Table 2, entry 2).

The title compound was synthesized using the same procedure described above. Colorless liquid: $^1$H NMR
(400 MHz, CDCl₃) δ 0.88 (t, J = 7.3 Hz, 3H, CH₃ (n-Pr)), 1.41 (sext, J = 7.3 Hz, 2H, CH₂ (n-Pr)), 1.84 (quint, J = 7.3 Hz, 2H, CH₂ (n-Pr)), 1.96 (app. br s, 2H, CH₂), 2.66 (app. br s, 2H, CH₂), 2.88 (t, J = 6.4 Hz, 2H, CH₂), 5.81 (t, J = 7.2 Hz, 1H, CH (vinyl)), 7.01 (dd, J = 1.2, 7.5 Hz, 1H, Ar), 7.05–7.18 (m, 6H, Ar), 7.35 (d, J = 7.6 Hz, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃, 323K) δ 13.9 (CH₃), 140.3 (C), 140.5 (C), 140.9 (C), 143.2 (C), 143.8 (C); HRMS-EI m/z [M⁺] calcd for C₂₀H₂₂: 262.1722, found: 262.1721.

1.5.4. 12-Methylene-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctene (2e') (Table 2, entry 4).

The title compound was synthesized using the same procedure described above. Colorless liquid: ¹H NMR (600 MHz, CDCl₃) δ 1.82 (quint, J = 6.3 Hz, 2H, CH₂), 2.62 (t, J = 6.3 Hz, 4H, CH₂), 5.47 (s, 2H, C=CH₂), 7.05 (dd, J = 2.0, 6.7 Hz, 2H, Ar), 7.17–7.23 (m, 4H, Ar), 7.49 (dd, J = 1.4, 7.2 Hz, 2H, Ar); ¹³C NMR (150 MHz, CDCl₃, 323K) δ 31.4 (CH₂), 32.1 (2CH₂), 118.8 (CH₂), 126.2 (2CH), 127.8 (2CH), 128.0 (2CH), 129.8 (2CH), 139.7 (2C), 141.7 (2C), 150.5 (C); HRMS-EI m/z [M⁺] calcd for C₁₇H₁₆: 220.1252, found: 220.1247.

1.5.5. 5-(Butylidene)-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (1d) (Table 2, entry 6).

To a mixture of 1-(pent-1-yn-1-yl)-2-phenethylbenzene (7d) (24.8 mg, 100 µmol) in CH₂Cl₂ (1 mL) at 0℃ was added TfOH (8.8 µL, 100 µmol). The mixture was stirred at 0℃ for 15 min, quenched with saturated aqueous NaHCO₃, and then extracted with ethyl acetate (3 × 1.0 mL). The combined organic layers were washed with brine and dried over Na₂SO₄, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/8 as an eluent to give 5-(butylidene)-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (1d) as a colorless liquid (23.9 mg, 96.2 µmol, 96%): ¹H NMR (600 MHz, CDCl₃) δ 0.88 (t, J = 7.4 Hz, 3H, CH₃ (n-Pr)), 1.43 (app. br s, 2H, CH₂ (n-Pr)), 2.06 (app. br s, 1H, CH₂), 2.11 (app. br s, 1H, CH₂), 2.77 (app. br s, 1H, CH₂), 2.95 (app. br s, 1H, CH₂), 3.31 (app. br s, 1H, CH₂), 3.40 (app. br s, 1H, CH₂), 5.86 (t, J = 7.4Hz, 1H, CH (vinyl)), 7.02–7.05 (m, 1H, Ar), 7.10–7.21 (m, 6H, Ar), 7.26–7.30 (m, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃, 323K) δ 13.8 (CH₃), 23.0 (CH₂), 31.5 (CH₂), 32.1 (CH₂), 33.8 (CH₂), 125.6 (CH), 126.0 (CH), 126.9 (CH), 127.2 (CH), 127.9 (CH), 128.4 (CH), 128.6 (CH), 129.9 (CH), 132.2 (CH), 137.1 (C), 139.3 (C), 140.3 (C), 141.6 (C), 142.3 (C); HRMS-EI m/z [M⁺] calcd for C₁₉H₂₀: 248.1565, found: 248.1566.

1.5.6. 5-(2,2-Dimethylpropylidene)-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (1c) (Table 2, entry 5).

The title compound was synthesized using the same procedure described above. Colorless liquid: ¹H NMR (300 MHz, CDCl₃) δ 0.98 (s, 9H, CH₃ (t-Bu)), 2.72 (dt, J = 4.2, 13.6 Hz, 1H, CH₂), 2.93 (ddt, J = 4.1, 13.4, 17.3 Hz, 1H, CH₂), 3.30 (dt, J = 4.2, 17.3 Hz, 1H, CH₂), 3.52 (td, J = 3.9, 13.3 Hz, 1H, CH₂), 5.78 (s, 1H, CH (vinyl)), 6.93–7.01 (m, 1H, Ar), 7.07–7.28 (m, 7H, Ar); ¹³C NMR (75.5 MHz, CDCl₃) δ 31.0 (3CH₃), 31.6 (CH₂), 33.7
(CH₂), 33.8 (C), 125.3 (CH), 125.9 (CH), 126.7 (CH), 127.1 (CH), 127.3 (CH), 128.2 (CH), 128.3 (CH),
130.3 (CH), 136.2 (C), 138.7 (C), 139.9 (C), 141.5 (CH), 141.8 (C), 142.8 (C); HRMS-ESI m/z [M+Na]⁺

1.5.7. 5-Methylene-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (1e') (Table 2, entry 7).

The title compound was synthesized using the same procedure described above. ¹H NMR and 
¹³C NMR spectra were identical to those in the literature.⁴

1.5.8. 3-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)-N,N-dimethylpropan-1-amine (1a) (Table 2, entry 8).

To a mixture of N,N-dimethyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7a) (13.8 mg, 49.7 µmol) in CH₂Cl₂ (0.5 mL) at 0 °C was added TfOH (21.9 µL, 250 µmol). The mixture was stirred at 0 °C for 10 min, quenched with saturated aqueous NaHCO₃, and extracted with ethyl acetate (3 × 1.0 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and evaporated. The residue was purified by silica gel column chromatography using chloroform/methanol = 1/1 to give 3-(10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)-N,N-dimethylpropan-1-amine (1a) as a colorless liquid (7.7 mg, 27.8 µmol, 56%): ¹H NMR (600 MHz, CDCl₃) δ 2.20 (s, 6H, CH₃ (NMMe)), 2.28–2.46 (m, 4H, CH₂), 2.71–2.86 (m, 1H, CH₂), 2.91–3.07 (m, 1H, CH₂), 3.26–3.38 (m, 1H, CH₂), 3.38–3.51 (m, 1H, CH₂), 5.88 (t, J = 7.2 Hz, 1H, CH (vinyl)), 7.02–7.07 (m, 1H, Ar), 7.13–7.23 (m, 6H, Ar), 7.28–7.32 (m, 1H, Ar). ¹H NMR and ¹³C NMR spectra were identical to those in the literature.⁵

1.5.9. 3-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)-N-methylpropan-1-amine (1b) (Table 2, entry 9).

To a mixture of N-methyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7b) (6.5 mg, 24.7 µmol) in CH₂Cl₂ (0.25 mL) at 0 °C was added TfOH (10.8 µL, 124 µmol). The mixture was then stirred at 0 °C for 10 min, quenched with saturated aqueous NaHCO₃, and then extracted with ethyl acetate (3 × 1.0 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and evaporated. The residue was purified by PTLC using chloroform/methanol = 1/1 as an eluent to give 3-(10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)-N-methylpropan-1-amine (1b) as a colorless liquid (4.4 mg, 16.7 µmol, 68%): IR (neat) 3417 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 2.02–2.16 (m, 1H, NH), 2.34 (q, J = 7.2 Hz, 2H, CH₂), 2.37 (s, 3H, CH₃ (NMMe)), 2.64–2.72 (m, 2H, CH₂), 2.74–2.86 (m, 1H, CH₂), 2.89–3.06 (m, 1H, CH₂), 3.27–3.46 (m, 2H, CH₂), 5.85 (t, J = 7.7 Hz, 1H, CH (vinyl)), 7.02–7.06 (m, 1H, Ar), 7.11–7.21 (m, 6H, Ar), 7.27–7.30 (m, 1H, Ar).

1.5.10. 3-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)propan-1-ol (1f) (Table 2, entry 10).

The title compound was synthesized using the same procedure described above. Colorless solid: mp 81.5–81.8 °C; IR (KBr) 3394 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.30 (app. br s, 1H, OH), 2.36–2.46 (m, 2H, CH₂), 2.67–3.10 (m, 2H, CH₂), 3.20–3.52 (m, 2H, CH₂), 3.69 (app. br s, 2H, CH₂), 5.89 (t, J = 7.5 Hz, 1H, CH (vinyl)), 7.02–7.06 (m, 1H, Ar), 7.12–7.22 (m, 6H, Ar), 7.28–7.30 (m, 1H, Ar); ¹³C NMR (125 MHz, CDCl₃) δ 32.0 (CH₂), 33.1 (CH₂), 33.7 (CH₂), 62.6 (CH₂), 125.8 (CH), 126.0 (CH), 127.2 (CH), 127.4 (CH), 127.5 (CH), 128.1 (CH), 128.3 (CH), 128.5 (CH), 130.0 (CH), 137.0 (C), 139.3 (C), 139.9 (C), 141.1 (C), 145.2 (C); HRMS-ESI m/z [M+Na]⁺ calcd for C₁₈H₁₈ONa: 273.1250, found: 273.1252.

1.5.11. 3-(6,7-Dihydrodibenzo[a,d][8]annulen-12(5H)-ylidene)-N,N-dimethylpropan-1-amine (2f) (Table 2, entry 11).

The title compound was synthesized using the same procedure described above. Yellow liquid: ¹H NMR (600 MHz, CDCl₃, 323K) δ 1.96 (app. br s, 2H, CH₂), 2.02 (q, J = 7.4 Hz, 2H CH₂), 2.15 (s, 6H, CH₃ (NMe₂)), 2.34 (t, J = 7.7 Hz, 2H, CH₂), 2.63 (app. br s, 2H, CH₂), 2.88 (t, J = 6.6 Hz, 2H, CH₂), 5.83 (t, J = 7.2 Hz, 1H, CH (vinyl)), 6.99 (d, J = 7.4 Hz, 1H, Ar), 7.04–7.17 (m, 6H, Ar), 7.35 (d, J = 7.4 Hz, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃, 323 K) δ 27.6 (CH₂), 29.6 (CH₂), 34.6 (CH₂), 34.9 (CH₂), 45.2 (CH₂), 59.2 (CH₂), 126.2 (2CH), 126.9 (CH), 127.2 (CH), 128.2 (CH), 128.2 (CH), 128.8 (CH), 129.1 (CH), 130.6 (CH), 140.1 (C), 140.4 (C), 140.6 (C), 143.4 (C), 144.4 (C); HRMS-ESI m/z [M+H]⁺ calcd for C₂₁H₂₆N: 292.2060, found: 292.2060.

1.5.12. 3-(6,7-Dihydrodibenzo[a,d][8]annulen-12(5H)-ylidene)propan-1-ol (2g) (Table 2, entry 12).

The title compound was synthesized using the same procedure described above. Colorless liquid: ¹H NMR (400 MHz, CDCl₃) δ 1.18–1.25 (m, 1H, OH), 1.84–2.08 (m, 2H, CH₂), 2.15 (q, J = 6.8 Hz, 2H, CH₂), 2.54–2.75 (m, 2H, CH₂), 2.88 (t, J = 6.6 Hz, 2H, CH₂), 3.67 (t, J = 6.6 Hz, 2H, CH₂), 5.87 (t, J = 7.3 Hz, 1H, CH (vinyl)), 7.02 (dd, J = 1.3, 7.5 Hz, 1H, Ar), 7.06–7.19 (m, 6H, Ar), 7.37 (d, J = 7.2 Hz, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃, 322 K) δ 29.5 (CH₂), 33.0 (CH₂), 34.7 (CH₂), 35.1 (CH₂), 62.4 (CH₂), 126.3 (CH), 126.3 (CH), 126.9 (CH), 127.1 (CH), 127.4 (CH), 128.1 (CH), 128.3 (CH), 129.2 (CH), 130.6 (CH), 140.1 (C), 140.4 (C), 143.3 (C), 145.9 (C); HRMS-ESI m/z [M+H]⁺ calcd for C₁₉H₂₁O: 265.1592, found: 265.1588.

1.5.13. 3-(6,7-Dihydrodibenzo[a,d][8]annulen-12(5H)-ylidene)propan-1-amine (2h) (Table 2, entry 13).

The title compound was synthesized using the same procedure described above. Colorless liquid: IR (neat) 3502 cm⁻¹; ¹H NMR (600 MHz, CDCl₃, 322 K) δ 1.87 (app. br s, 2H, CH₂), 2.08 (q, J = 7.1 Hz, 2H, CH₂), 2.54 (app. br s, 2H, CH₂), 2.75 (t, J = 6.4 Hz, 2H, CH₂), 2.82 (app. br s, 2H, CH₂), 5.22 (app. br s, 2H, NH₂), 5.67 (t, J = 7.0 Hz, 1H, CH (vinyl)), 6.91 (d, J = 7.2 Hz, 1H, Ar), 6.93–6.97 (m, 1H, Ar), 6.99–7.08 (m, 5H, Ar), 7.29 (d, J = 7.5 Hz, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃, 322 K) δ 28.2 (CH₂), 29.6 (CH₂), 34.6 (CH₂), 34.9 (CH₂), 40.2
(CH₂), 124.3 (CH), 126.4 (CH), 126.6 (CH), 127.4 (CH), 127.7 (CH), 127.8 (CH), 128.1 (CH), 129.3 (CH), 130.7 (CH), 139.7 (C), 139.8 (C), 140.3 (C), 142.6 (C), 147.8 (C); HRMS m/z [M+H]+ calcd for C₁₀H₉₂N: 264.1747, found: 264.1742.

1.5.14.  

**(E)-12-(2,2-Dimethylpropylidene)-2-methyl-5,6,7,12-tetrahydro dibenzo[a,d]cyclooctene (E-2j)** (Table 3, entry 7).

To a mixture of 1-(3,3-dimethylbut-1-yn-1-yl)-2-(3-(p-tolyl)propyl)benzene (8I) (29.0 mg, 100 µmol) in CH₂Cl₂ (1 mL) at 0 °C was added H₂SO₄ (9.8 µL, 100 µmol). The mixture was then stirred at 0 °C for 20 min, quenched with saturated aqueous NaHCO₃, and then extracted with ethyl acetate (3 × 1 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/8 as an eluent to give **E-2j** as a colorless liquid (24.9 mg, 85.7 µmol, 86%): ¹H NMR (600 MHz, CDCl₃, 322 K) δ 0.96 (s, 9H, CH₃ (t-Bu)), 1.41–2.20 (m, 2H, CH₂), 2.25 (s, 3H, CH₃ (p-tol)), 2.57–3.29 (m, 4H, CH₂), 5.61 (s, 1H, CH (vinyl)), 6.81–6.87 (m, 2H, Ar), 6.96–7.01 (m, 1H, Ar), 7.02–7.07 (m, 3H, Ar), 7.10–7.14 (m, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃, 322 K) δ 20.9 (3CH₃), 29.3 (CH₂), 30.7 (CH₃), 34.2 (C), 36.3 (CH₂), 37.3 (CH₂), 125.7 (CH), 126.8 (CH), 127.3 (CH), 128.9 (CH), 129.2 (CH), 129.6 (CH), 130.0 (CH), 135.6 (C), 137.1 (C), 139.4 (CH), 139.8 (C), 140.2 (C), 142.0 (C), 146.3 (C); HRMS-El m/z [M]+ calcd for C₂₂H₂₆: 290.2035, found: 290.2035.

1.5.15.  

**(Z)-12-(2,2-Dimethylpropylidene)-2-methyl-5,6,7,12-tetrahydro-dibenzo[a,d]cyclooctene (Z-2j)** (Table 3, entry 6).

The title compound was synthesized using the same procedure described above. Colorless solid: mp 49.7–50.2 °C: ¹H NMR (400 MHz, CDCl₃) δ 0.97 (s, 9H, CH₃ (t-Bu)), 1.49–2.22 (m, 2H, CH₂), 2.25 (s, 3H, CH₃ (p-tol)), 2.52–3.35 (m, 4H, CH₂), 5.60 (s, 1H, CH (vinyl)), 6.87 (d, J = 7.4 Hz, 1H, Ar), 6.90 (d, J = 7.5, 1H, Ar), 6.93 (s, 1H, Ar), 6.98 (dd, J = 1.3, 7.3 Hz, 1H, Ar), 7.04 (dd, J = 1.5, 7.2, 7.5 Hz, 1H, Ar), 7.10 (ddd, J = 1.5, 7.2, 7.5 Hz, 1H, Ar), 7.22 (d, J = 7.3 Hz, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃, 341 K) δ 20.7 (3CH₃), 28.8 (CH₂), 30.4 (CH₃), 33.9 (C), 36.5 (CH₂), 36.6 (CH₂), 125.9 (CH), 126.4 (CH), 127.2 (CH), 128.3 (CH), 129.3 (CH), 129.7 (CH), 134.8 (C), 136.8 (C), 139.2 (CH), 139.6 (C), 140.0 (C), 141.5 (C), 146.3 (C); HRMS-El m/z [M]+ calcd for C₂₂H₂₆: 290.2035, found: 290.2031.

1.5.16.  

**(Z)-12-(2,2-Dimethylpropylidene)-2-methoxy-5,6,7,12-tetrahydro dibenzo[a,d]cyclooctene (Z-2i)** (Table 3, entry 2).

The title compound was synthesized using the same procedure described above. Colorless liquid: ¹H NMR (600 MHz, CDCl₃) δ 0.92 (s, 9H, CH₃ (t-Bu)), 1.29–2.38 (m, 2H, CH₂), 2.44–3.22 (m, 4H, CH₂ (Bn)), 3.67 (s, 3H, OMe), 5.52 (s, 1H, CH (vinyl)), 6.54 (dd, J = 2.7, 8.4 Hz, 1H, Ar), 6.63 (d, J = 2.4 Hz, 1H, Ar), 6.86 (d, J = 8.3 Hz, 1H, Ar), 6.92 (dd, J = 1.3, 7.6 Hz, 1H, Ar), 6.98 (td, J = 1.4, 7.4 Hz, 1H, Ar), 7.03 (td, J = 1.3, 7.4 Hz, 1H, Ar), 7.14 (d, J = 7.2 Hz, 1H, Ar); ¹³C NMR (150 MHz, CDCl₃) δ 29.1 (C), 30.4 (3CH₃), 33.9 (CH₂), 36.4 (CH₂), 36.5 (CH₂), 55.0 (CH₃), 111.5 (CH), 114.6 (CH), 125.9 (CH), 126.4 (CH), 128.4 (CH), 129.7
(CH), 130.3 (CH), 132.4 (C), 139.2 (CH), 139.3 (C), 140.1 (C), 142.8 (C), 146.0 (C), 157.4 (C); HRMS-ESI m/z [M]^+ calcd for C_{22}H_{26}O: 306.1984; found: 306.1982.

1.5.17. (E)-12-(2,2-Dimethylpropyldiene)-2-methoxy-5,6,7,12-tetrahydro-dibenzo[a,d]cyclooctene (E-2i) (Table 3, entry 4).

The title compound was synthesized using the same procedure described above. Yellow liquid: ^1H NMR (600 MHz, CDCl$_3$) δ 0.98 (s, 9H, CH$_3$ (t-Bu)), 2.00–2.41 (m, 1H, CH$_2$), 2.41–3.40 (m, 5H, CH$_2$), 3.79 (s, 3H, OMe), 5.65 (s, 1H, CH (vinyl)), 6.62 (dd, J = 2.9, 8.5 Hz, 1H, Ar), 6.82 (s, 1H, Ar), 6.94 (d, J = 8.2 Hz, 1H, Ar), 7.10 (m, 4H, Ar); ^13C NMR (150 MHz, CDCl$_3$, 323 K) δ 29.2 (C), 30.4 (3CH$_3$), 33.9 (CH$_2$), 35.7 (CH$_2$), 37.1 (CH$_2$), 55.1 (CH$_3$), 111.1 (CH), 114.6 (CH), 125.5 (CH), 126.7 (CH), 128.7 (CH), 129.4 (CH), 130.7 (CH), 132.3 (C), 139.3 (C), 139.4 (CH), 140.1 (C), 141.5 (C), 147.3 (C), 157.8 (C); HRMS-ESI m/z [M]^+ calcd for C$_{22}$H$_{26}$O: 306.1984; found: 306.1982.

1.5.18. (E)-5-(2,2-Dimethylpropyldiene)-10,11-dihydro-3-methyl-5H-dibenzo[a,d]cycloheptene (E-1g) (Table 3, entry 9).

The title compound was synthesized using the same procedure described above. Colorless liquid: mp 82.6–83.0 °C; ^1H NMR (400 MHz, CDCl$_3$) δ 0.98 (s, 9H, CH$_3$ (t-Bu)), 2.29 (s, 3H, CH$_3$ (p-tol)), 2.70 (dt, J = 4.4, 13.6 Hz, 1H, CH$_2$), 2.88 (ddd, J = 4.3, 13.2, 17.1 Hz, 1H, CH$_2$), 3.25 (dt, J = 4.4, 17.1 Hz, 1H, CH$_2$), 3.49 (td, J = 4.3, 13.6 Hz, 1H, CH$_2$), 5.77 (s, 1H, CH (vinyl)), 6.86 (d, J = 8.1 Hz, 1H, Ar), 6.91 (dd, J = 1.7, 7.8 Hz, 1H, Ar), 7.04–7.21 (m, 5H, Ar); ^13C NMR (125 MHz, CDCl$_3$) δ 20.8 (CH$_3$), 31.1 (3CH$_3$), 31.7 (CH$_2$), 33.2 (CH$_2$), 33.8 (C), 125.3 (CH), 127.1 (CH), 127.2 (CH), 127.5 (CH), 128.1 (CH), 128.8 (CH), 130.3 (CH), 133.1 (C), 135.3 (C), 138.8 (C), 140.0 (C), 141.2 (CH), 141.9 (C), 142.5 (C); HRMS-ESI m/z [M]^+ calcd for C$_{21}$H$_{24}$: 276.1878; found: 276.1881.

1.5.19. 10,11-Dihydro-5-methylene-3-(trifluoromethyl)-5H-dibenzo[a,d]cycloheptene (1h’) (Table 3, entry 10).

The title compound was synthesized using the same procedure described above. Colorless liquid: ^1H NMR (600 MHz, CDCl$_3$) δ 3.15–3.19 (m, 2H, CH$_2$), 3.19–3.22 (m, 2H, CH$_2$), 5.47 (d, J = 1.2 Hz, 1H, C=CH$_2$), 5.51 (d, J = 1.2 Hz, 1H, C=CH$_2$), 7.14 (d, J = 7.1 Hz, 1H, Ar), 7.19–7.26 (m, 3H, Ar), 7.37 (dd, J = 1.4, 7.4 Hz, 1H, Ar), 7.46 (d, J = 8.5 Hz, 1H, Ar), 7.61 (s, 1H, Ar); ^13C NMR (150 MHz, CDCl$_3$) δ 32.8 (CH$_2$), 33.1 (CH$_2$), 118.7 (CH$_2$), 124.2 (q, J = 272.0 Hz, CF$_3$), 124.3 (q, J = 3.8 Hz, CH), 124.9 (q, J = 4.1 Hz, CH), 126.5 (CH), 128.0 (CH), 128.3 (CH), 128.6 (q, J = 20.9 Hz, C), 129.0 (CH), 129.3 (CH), 137.8 (C), 140.2 (C), 141.8 (C), 142.4 (C), 150.6 (C); HRMS-ESI m/z [M]^+ calcd for C$_{17}$H$_{13}$F$_3$: 274.0969; found: 274.0965.

1.5.20. (E)-5-(2,2-Dimethylpropyldiene)-10,11-dihydro-3-(trifluoromethyl)-5H-dibenzo[a,d]cycloheptene (E-1h) (Table 3, entry 10).

Light yellow liquid: ^1H NMR (500 MHz, CDCl$_3$) δ 0.99 (s, 9H, CH$_3$ (t-Bu)), 2.75 (dt, J = 4.3, 13.8 Hz, 1H,
1.5.21. (E)-5-Butylidene-10,11-dihydro-3-methyl-5H-dibenzo[a,d]cycloheptene (E-1i) (Table 3, entry 14).

The title compound was synthesized using the same procedure described above. Colorless liquid. $^1$H NMR (600 MHz, CDCl$_3$, 324 K) $\delta$ 0.92 (t, $J = 7.5$ Hz, 3H, CH$_3$ (n-Pr)), 1.44–1.51 (m, 2H, CH$_2$ (n-Pr)), 2.12 (app. br s, 2H, CH$_2$ (n-Pr)), 2.33 (s, 3H, CH$_3$), 2.60–3.61 (m, 4H, CH$_2$), 5.87 (t, $J = 7.7$Hz, 1H, CH (vinyl)), 6.92–6.99 (m, 2H, Ar), 7.11–7.23 (m, 5H, Ar); $^{13}$C NMR (150 MHz, CDCl$_3$, 324 K) $\delta$ 13.6 (CH$_3$), 20.6 (CH$_3$), 22.8 (CH$_2$), 31.3 (CH$_2$), 32.1 (CH$_2$), 33.2 (CH$_2$), 125.4 (CH), 127.0 (CH), 127.5 (CH), 127.8 (CH), 128.2 (CH), 128.9 (CH), 129.7 (CH), 131.6 (CH), 133.9 (C), 135.2 (C), 139.2 (C), 140.3 (C), 141.4 (C), 142.5 (C); HRMS-ESI m/z [M]$^+$ calcld for C$_{21}$H$_{21}$F$_3$: 330.1595, found: 330.1598.

1.5.22. (Z)-12-(2,2-Dimethylpropyldiene)-2-methoxy-3-((Z)-1-(5-methoxy-2-(3-phenylpropyl)phenyl)-3,3-dimethylbut-1-en-1-yl)-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctane (10) (Table 3, entry 1).

Colorless liquid. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 0.94 (s, 9H, CH$_3$ (t-Bu)), 0.95 (s, 9H, CH$_3$ (t-Bu)), 1.36–1.49 (m, 1H, CH$_2$), 1.60–1.73 (m, 2H, CH$_2$), 1.97–2.34 (m, 1H, CH$_2$), 2.39–2.42 (m, 2H, CH$_2$), 2.42–2.50 (m, 2H, CH$_2$), 2.52–3.38 (m, 4H, CH$_2$), 3.68 (s, 3H, OMe), 3.83 (s, 3H, OMe), 5.59 (s, 1H, CH (vinyl)), 5.82 (s, 1H, CH (vinyl)), 6.61 (s, 1H, Ar), 6.70–6.75 (m, 1H, Ar), 6.75 (dd, $J = 2.9$, 8.5 Hz, 1H, Ar), 6.93 (s, 1H, Ar), 6.96–7.01 (m, 2H, Ar), 7.04–7.09 (m, 3H, Ar), 7.11 (t, $J = 7.3$ Hz, 1H, Ar), 7.15 (t, $J = 7.3$ Hz, 1H, Ar), 7.18–7.26 (m, 3H, Ar); $^{13}$C NMR (150 MHz, CDCl$_3$, 322 K) $\delta$ 29.1 (2C), 30.6 (3CH$_3$), 30.9 (3CH$_3$), 31.9 (CH$_2$), 32.0 (CH$_2$), 34.1 (CH$_2$), 34.2 (CH$_2$), 36.1 (CH$_2$), 36.4 (CH$_2$), 55.4 (CH$_2$), 55.9 (CH$_2$), 112.5 (CH), 113.1 (CH), 117.9 (CH), 125.5 (CH), 126.1 (CH), 126.6 (CH), 128.2 (C), 128.2 (2CH), 128.4 (2CH), 128.5 (CH), 129.0 (CH), 130.0 (CH), 132.0 (C), 132.0 (CH), 133.1 (C), 139.7 (C), 139.8 (C), 139.8 (C), 140.4 (C), 141.4 (C), 142.6 (C), 143.3 (2CH), 155.0 (C), 156.5 (C); HRMS-ESI m/z [M]$^+$ calcld for C$_{44}$H$_{52}$O$_2$: 612.3967, found: 612.3970.

1.5.23. 13-(2,2-Dimethylpropyldiene)-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3a) (Table 4, entry 1).

To a mixture of 1-(3,3-dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9a) (29.2 mg, 101 µmol) in CH$_2$Cl$_2$ (1 mL) at 0 °C was added TfOH (8.8 µL, 100 µmol). The mixture was stirred at 0 °C for 10 min, quenched with saturated aqueous NaHCO$_3$, and then
extracted with ethyl acetate (3 × 1 mL). The combined organic layers were washed with brine, dried over Na2SO4, and evaporated. The residue was purified by silica gel column chromatography using hexane as an eluent to give 3a as a colorless liquid (12.4 mg, 42.7 µmol, 43%): 1H NMR (600 MHz, CDCl3) δ 0.94 (s, 10H, CH (t-Bu), CH2), 1.34–1.45 (m, 1H, CH2), 1.71–1.81 (m, 2H, CH2), 2.46–2.56 (m, 2H, CH2), 3.11 (dt, J = 5.3, 13.3 Hz, 1H, CH2), 3.37–3.54 (m, 1H, CH2), 5.51 (s, 1H, CH (vinyl)), 7.01–7.15 (m, 6H, Ar), 7.24–7.30 (m, 2H, Ar); 13C NMR (150 MHz, CDCl3) δ 27.5 (CH2), 29.3 (CH2), 30.4 (CH2), 30.6 (CH2), 30.9 (CH2), 34.5 (C), 125.5 (CH), 125.5 (CH), 126.9 (CH), 127.1 (CH), 128.9 (CH), 129.2 (CH), 129.7 (CH), 129.8 (CH), 137.0 (C), 139.7 (C), 141.4 (C), 141.8 (C), 142.2 (CH), 145.8 (C); HRMS EI m/z [M]⁺ calcd for C22H26: 290.2035, found: 290.2031.

1.5.24. 13-Butylidene-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3b) (Table 4, entry 3).

The title compound was synthesized using the same procedure described above. Colorless liquid: 1H NMR (600 MHz, CDCl3) δ 0.88 (t, J = 7.4 Hz, 3H, CH3 (n-Pr)), 1.43 (sext, J = 7.4 Hz, 2H, CH2 (n-Pr)), 1.44–1.86 (m, 4H, CH2), 1.93 (q, J = 6.6 Hz, 2H, CH2 (n-Pr)), 2.10–3.46 (m, 4H, CH2), 5.70 (t, J = 7.3 Hz, 1H, CH (vinyl)), 7.03 (dd, J = 1.8, 6.9 Hz, 1H, Ar), 7.08 (dd, J = 1.9, 7.6 Hz, 1H, Ar), 7.10–7.18 (m, 5H, Ar), 7.33 (dd, J = 1.9, 6.8 Hz, 1H, Ar); 13C NMR (150 MHz, CDCl3) δ 13.9 (CH3), 22.4 (CH2), 28.7 (CH2), 29.2 (CH2), 30.8 (CH2), 31.0 (CH2), 31.7 (CH2), 125.6 (CH), 125.8 (CH), 126.9 (CH), 127.0 (CH), 128.7 (CH), 129.0 (CH), 129.2 (CH), 129.4 (CH), 132.3 (CH), 140.5 (C), 141.0 (C), 141.1 (2C), 144.0 (C); HRMS-ESI m/z [M]+ calcd for C21H24: 276.1878, found: 276.1877.

1.5.25. 13-Hexylidene-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3c) (Table 4, entry 4).

The title compound was synthesized using the same procedure described above. Colorless liquid: 1H NMR (500 MHz, CDCl3) δ 0.85 (t, J = 7.6 Hz, 3H, CH3), 1.22–1.26 (m, 6H, CH2), 1.37–1.44 (m, 2H, CH2), 1.44–1.70 (m, 2H, CH2), 1.95 (ap q, J = 7.7 Hz, 2H, CH2), 2.20–3.20 (m, 4H, CH2), 5.78 (t, J = 7.2 Hz, 1H, CH (vinyl)), 7.03 (dd, J = 1.7, 7.6 Hz, 1H, Ar), 7.07–7.09 (m, 1H, Ar), 7.11–7.18 (m, 5H, Ar), 7.33 (dd, J = 1.7, 7.6 Hz, 1H, Ar); 13C NMR (126 MHz, CDCl3) δ 14.0 (CH3), 22.5 (CH2), 28.7 (CH2), 28.9 (CH2), 29.0 (CH2), 29.2 (CH2), 30.8 (CH2), 31.5 (CH2), 31.7 (CH2), 125.6 (CH), 125.8 (CH), 126.9 (CH), 127.0 (CH), 128.7 (CH), 129.0 (CH), 129.2 (CH), 129.4 (CH), 132.5 (CH), 140.5 (C), 140.8 (C), 141.1 (C), 141.2 (C), 144.0 (C); HRMS-ESI m/z [M]+ calcd for C22H29: 305.2264, found: 305.2271.

1.5.26. (E)- and (Z)-13-(2,2-Dimethylpropylidene)-2-methyl-6,7,8,13-tetrahydro-5H-dibenzo[a,d]-cyclononene (3d) (Table 4, entry 5).

The title compound was obtained as a mixture of (E)- and (Z)-isomers (major:minor = 52:48) by the same procedure described above. Yellow liquid: 1H NMR (500 MHz, CDCl3) (mixture) δ 0.92–0.95 (m, 20H, CH3 (t-Bu), CH2), 1.33–1.43 (m, 2H, CH2), 1.69–1.81 (m, 4H, CH2), 2.26 (s, 3H, CH3 (p-tol)), 2.30 (s, 3H, CH3 (p-tol)), 2.45–2.53 (m, 4H, CH2), 3.02–3.13 (m, 2H, CH2), 3.32–3.49 (m, 2H, CH2), 5.48 (s, 1H, CH (vinyl)), 5.48 (s, 1H, CH (vinyl)), 6.89–6.93 (m, 3H, Ar), 6.96 (d, J = 7.6 Hz, 1H, Ar), 7.02–7.14 (m, 8H, S21
$^{13}$C NMR (150 MHz, CDCl$_3$) (mixture) $\delta$ 21.0 (CH$_3$), 21.1 (CH$_3$), 27.2 (CH$_2$), 27.5 (CH$_2$), 28.6 (CH$_2$), 29.1 (CH$_2$), 30.0 (CH$_2$), 30.2 (CH$_2$), 30.3 (CH$_2$), 30.4 (CH$_2$), 30.7 (CH$_2$), 34.3 (C), 34.3 (C), 125.2 (CH), 125.3 (CH), 126.6 (CH), 126.8 (CH), 127.5 (CH), 127.5 (CH), 128.5 (CH), 128.7 (CH), 129.0 (CH), 129.4 (2CH), 129.5 (CH), 129.7 (CH), 130.2 (CH), 134.5 (C), 134.6 (C), 136.3 (C), 136.8 (C), 136.9 (C), 138.5 (C), 139.7 (C), 140.9 (C), 141.2 (C), 141.7 (C), 141.8 (CH), 141.8 (CH), 145.3 (C), 145.7 (C); HRMS-El m/z [M]$^+$ ccalc for C$_{23}$H$_{28}$: 304.2191, found: 304.2182.

1.5.27. (E)- and (Z)-13-Butyldiene-2-methyl-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3e) (Table 4, entry 6).

The title compound was obtained as a mixture of (E)- and (Z)-isomers (major:minor = 74:26) by the same procedure described above. Colorless liquid: $^1$H NMR (500 MHz, CDCl$_3$) (major) $\delta$ 0.89 (t, 3H, $J$ = 1.7, 7.6 Hz, CH$_3$), 1.40–1.46 (m, 2H, CH$_2$), 1.52–1.57 (m, 4H, CH$_2$), 1.89–1.97 (m, 2H, CH$_2$), 2.26 (s, 3H, CH$_3$), 2.30–3.20 (m, 4H, CH$_2$), 5.69 (t, $J$ = 6.5 Hz, 1H, vinyl), 6.87 (br s, 1H, Ar), 6.96 (dd, $J$ = 1.4, 7.5 Hz, 1H, Ar), 7.01–7.03 (m, 2H, Ar), 7.12–7.17 (m, 2H, Ar), 7.34–7.31 (dd, $J$ = 1.6, 7.4 Hz, 1H, Ar); $^{13}$C NMR (150 MHz, CDCl$_3$) (major) $\delta$ 13.9 (CH$_3$), 21.0 (CH$_3$), 22.4 (CH$_2$), 28.9 (CH$_2$), 29.1 (CH$_2$), 30.9 (CH$_2$), 31.09 (CH$_2$), 31.13 (CH$_2$) 125.6 (CH), 126.8 (CH), 127.7 (CH), 128.9 (CH), 129.2 (CH), 129.3 (CH), 129.4 (CH), 132.1 (CH), 135.1 (C), 137.9 (C), 140.2 (C), 141.1 (C), 141.3 (C), 144.1 (C); HRMS-ESI m/z [M+Na]$^+$ ccalc for C$_{22}$H$_{26}$Na: 313.1927, found: 313.1932.

1.5.28. (E)- and (Z)-13-(2,2-Dimethylpropyldiene)-3-methyl-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3f) (Table 4, entry 7).

The title compound was obtained as a mixture of (E)- and (Z)-isomers (major:minor = 51:49) by the same procedure described above. Colorless liquid: $^1$H NMR (500 MHz, CDCl$_3$) (mixture) $\delta$ 0.89–1.01 (m, 20H, CH$_3$ (t-Bu), CH$_2$), 1.32–1.46 (m, 2H, CH$_2$), 1.69–1.82 (m, 4H, CH$_2$), 2.26 (s, 3H, CH$_3$), 2.28 (s, 3H, CH$_3$), 2.42–2.56 (m, 4H, CH$_2$), 3.02–3.16 (m, 2H, CH$_2$), 3.33–3.52 (m, 2H, CH$_2$), 5.50 (s, 2H, CH (vinyl)), 6.85–6.96 (m, 4H, Ar), 7.01–7.19 (m, 8H, Ar), 7.21–7.26 (m, 2H, Ar); $^{13}$C NMR (125 MHz, CDCl$_3$) (mixture) $\delta$ 21.2 (3CH$_3$), 21.3 (3CH$_3$), 27.5 (CH$_2$), 27.6 (CH$_2$), 29.3 (CH$_2$), 29.3 (CH$_2$), 30.3 (CH$_2$), 30.4 (CH$_2$), 30.7 (CH$_3$), 30.7 (CH$_3$), 31.0 (CH$_2$), 31.0 (CH$_2$), 34.5 (2C), 125.5 (CH), 125.6 (CH), 126.2 (CH), 126.3 (CH), 126.8 (CH), 127.0 (CH), 128.9 (CH), 129.1 (2CH), 129.6 (CH), 129.7 (CH), 129.8 (CH), 129.8 (CH), 130.4 (CH), 136.4 (C), 136.6 (C), 137.0 (C), 137.2 (C), 138.4 (C), 139.6 (C), 139.7 (C), 141.6 (2C), 141.7 (C), 142.1 (CH), 142.2 (CH), 143.1 (C), 146.1 (C); HRMS-ESI m/z [M+H]$^+$ ccalc for C$_{22}$H$_{29}$: 305.2264, found: 305.2261.

1.5.29. (E)- and (Z)-13-Butyldiene-3-methyl-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3g) (Table 4, entry 8).

The title compound was obtained as a mixture of (E)- and (Z)-isomers (major:minor = 51:49) by the same procedure described above. Colorless liquid: $^1$H NMR (500 MHz, CDCl$_3$) (mixture) $\delta$ 0.87 (t, $J$ = 7.3 Hz, 3H, CH$_3$), 0.88 (t, $J$ = 7.3 Hz, 3H, CH$_3$), 1.38–1.46 (m, 4H, CH$_2$), 1.52–1.57 (m, 8H, CH$_2$), 1.89–1.97 (m, 4H, CH$_2$), 2.28 (s, 3H, CH$_3$), 2.29 (s, 3H, CH$_3$), 2.30–3.20 (m, 8H, CH$_2$), 5.68 (t, $J$ = 7.0 Hz, 1H, vinyl), 5.69 (t, $J$ = 7.0 Hz, 1H, vinyl),
6.85 (br s, 1H, Ar), 6.93–6.97 (m, 4H, Ar), 7.01–7.03 (m, 1H, Ar), 7.06 (app d, J = 7.6 Hz, 1H, Ar), 7.10–7.18 (m, 5H, Ar), 7.23 (d, J = 7.6 Hz, 1H, Ar), 7.29–7.31 (m, 1H, Ar); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) (mixture) \(\delta\) 13.90 (CH\(_3\)), 13.92 (CH\(_3\)), 21.0 (CH\(_3\)), 21.1 (CH\(_3\)), 22.4 (2CH\(_2\)), 28.8 (2CH\(_2\)), 29.2 (2CH\(_2\)), 30.9 (CH\(_2\)), 31.1 (CH\(_2\)), 31.3 (2CH\(_2\)), 31.7 (CH\(_2\)), 31.8 (CH\(_2\)), 125.6 (CH), 125.8 (CH), 126.3 (CH), 126.5 (CH), 126.8 (CH), 126.9 (CH), 128.6 (CH), 128.7 (CH), 129.0 (CH), 129.2 (2CH), 129.4 (CH), 129.8 (CH), 130.3 (CH), 132.0 (CH), 132.2 (CH), 136.4 (2C), 137.5 (C), 140.7 (C), 140.93 (C), 140.94 (C), 140.97 (C), 140.99 (C), 141.06 (C), 141.08 (C), 141.2 (C), 144.2 (C); HRMS-ESI m/z [M+H]+ calcd for C\(_{22}\)H\(_{27}\): 291.2107, found: 291.2115.

1.6. Preparation of 5,6,7,8-tetrahydro-13H-dibenzo[a,d][9]annulen-13-one (6)

1.6.1. 5,6,7,8-Tetrahydro-13H-dibenzo[a,d][9]annulen-13-one (6) (eqn (3)).

To a stirred mixture of 13-butylidene-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3b) (95.7 mg, 350 µmol), RuCl\(_3\) (24.2 mg, 92.6 µmol, 26 mol%), CH\(_3\)CN (5.0 mL) and distilled water (3.0 mL) at room temperature was added a mixture of Oxone (903 mg, 1.47 mmol) and NaHCO\(_3\) (378 mg, 4.52 mmol) in portions over a period of 10 min. The mixture was stirred for 2 h, quenched with saturated aqueous NaS\(_2\)O\(_3\), and then extracted with CH\(_2\)Cl\(_2\). The combined organic layers were washed with water and brine, dried over Na\(_2\)SO\(_4\). Then the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate/hexane = 1/8 as an eluent to give 5,6,7,8-tetrahydro-13H-dibenzo[a,d][9]annulen-13-one (6) as a colorless liquid (50.7 mg, 215 µmol, 61%): IR (neat) 1666 cm\(^{-1}\) (lit.\(^6\) 1655 cm\(^{-1}\)), \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 1.73 (app. br s, 4H, CH\(_2\)), 2.68 (app. br s, 4H, CH\(_2\)), 7.19 (d, J = 7.6 Hz, 2H, Ar), 7.30 (d, J = 7.6 Hz, 2H, Ar), 7.39 (td, J = 1.1, 7.6 Hz, 2H, Ar), 7.48 (d, J = 7.6 Hz, 2H, Ar); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 27.0 (2CH\(_2\)), 32.9 (2CH\(_2\)), 126.1 (2CH), 126.6 (2CH), 130.6 (2CH), 130.9 (2CH), 141.1 (2C), 141.4 (2C), 203.4 (C=O); HRMS-ESI m/z [M+Na\(^+\)] calcd for C\(_{17}\)H\(_{16}\)ONa: 259.1093, found: 259.1089.

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2. NMR spectra

3-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)-N,N-dimethylpropan-1-amine (1a).

3-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)-N-methylpropan-1-amine (1b).
5-(2,2-Dimethylpropylidene)-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (1c).
5-(Butylidene)-10,11-dihydro-5H-dibenzo[a,d]cycloheptene (1d).
3-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)propan-1-ol (1f).
(E)-5-(2,2-Dimethylpropylidene)-10,11-dihydro-3-methyl-5H-dibenzo[a,d]cycloheptene (E-1g).
(E)-5-(2,2-Dimethylpropylidene)-10,11-dihydro-3-(trifluoromethyl)-5H-dibenzo[a, d]cycloheptene (E-1h).
10,11-Dihydro-5-methylene-3-(trifluoromethyl)-5H-dibenzo[\textit{a,d}]cycloheptene (1h').
(E)-5-Butylidene-10,11-dihydro-3-methyl-5H-dibenzo[a,d]cycloheptene (E-1i).
12-(2,2-Dimethylpropyldiene)-5,6,7,12-tetrahydro-dibenzo[\(a,d\)]cyclooctene (2a).
5,6,7,12-Tetrahydro-12-(2-methylpropylidene)-dibenzo[a,d]cyclooctene (2b).
12-Butylidene-5,6,7,12-tetrahydrodibenz[a,d]cyclooctene (2c).
12-Methylene-5,6,7,12-tetrahydrodibenzo[\textit{a,d}]cyclooctene (2e').
3-(6,7-Dihydrodibenzo[a,d][8]annulen-12(5H)-ylidene)-N,N-dimethylpropan-1-amine (2f).
3-(6,7-Dihydrodibenzo[\textit{a,d}]\textit{8}annulen-12(5\textit{H})-ylidene)propan-1-ol (2g).
3-(6,7-Dihydropentzeno[α,β][8]annulen-12(5H)-ylidene)propan-1-amine (2h).
(E)-12-(2,2-Dimethylpropylidene)-2-methoxy-5,6,7,12-tetrahydro-dibenzo[a,d]-cyclooctene (E-2i).
(Z)-12-(2,2-Dimethylpropylidene)-2-methoxy-5,6,7,12-tetrahydro-dibenzo[a,d]-cyclooctene (Z-2i).
(E)-12-((2,2-Dimethylpropylidene)-2-methyl-5,6,7,12-tetrahydrodibenzo[a,d]-cyclooctene (E-2)).
(Z)-12-(2,2-Dimethylpropyldiene)-2-methyl-5,6,7,12-tetrahydro-dibenzo[a,d]-cyclooctene (Z-2).
13-(2,2-Dimethylpropylidene)-6,7,8,13-tetrahydro-5H-dibenzo\[a,d\]cyclononene (3a).
13-Butylidene-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3b).
13-Hexylidene-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3c).
(E)- and (Z)-13-(2,2-Dimethylpropyldiene)-2-methyl-6,7,8,13-tetrahydro-5H-dibenzo[a,d]cyclononene (3d).
(E)- and (Z)-13-Butylidene-2-methyl-6,7,8,13-tetrahydro-5H-dibenzo[a,d]-cyclononene (3e).
(E)- and (Z)-13-(2,2-Dimethylpropylidene)-3-methyl-6,7,8,13-tetrahydro-5H-dibenz[a,d]cyclononene (3f).
(E)- and (Z)-13-Butylidene-3-methyl-6,7,8,13-tetrahydro-5H-dibenzo[a,d]-cyclononene (3g).
5,6,7,8-Tetrahydro-13\textit{H}-dibenzo[\textit{a,d}][9]annulen-13-one (6).
$N,N$-Dimethyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7a).
N-Methyl-4-(2-phenethylphenyl)but-3-yn-1-amine (7b).
1-(3,3-Dimethylbut-1-yn-1-yl)-2-phenethylbenzene (7c).
1-(Pent-1-yn-1-yl)-2-phenethylbenzene (7d).
Trimethyl(2-phenethylphenyl)ethynyl)silane (7e).
4-(2-Phenethylphenyl)but-3-yn-1-ol (7f).
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-methylphenethyl)benzene (7g).
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-(trifluoromethyl)phenethyl)benzene (7h).
1-(4-Methylphenethyl)-2-(pent-1-yn-1-yl)benzene (7i).
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8a).
1-(3-Methylbut-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8b).
1-(Pent-1-yn-1-yl)-2-(3-phenylpropyl)benzene (8c).
1-(Phenylethynyl)-2-(3-phenylpropyl)benzene (8d).
Trimethyl(2-(3-phenylpropyl)phenyl)ethyl)silane (8e).
$N,N$-Dimethyl-4-(2-(3-phenylpropyl)phenyl)but-3-yn-1-amine (8f).
4-(2-(3-Phenylpropyl)phenyl)but-3-yn-1-ol (8g).
4-(2-(3-Phenylpropyl)phenyl)but-3-yn-1-amine (8h).
2-(3,3-Dimethylbut-1-yn-1-yl)-4-methoxy-1-(3-phenylpropyl)benzene (8i).
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-(4-methoxyphenyl)propyl)benzene (8j).
2-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-1-(3-phenylpropyl)benzene (8k).
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(3-(p-tolyl)propyl)benzene (8l).
1-(3,3-Dimethylbut-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9a).
1-(Pent-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9b).
1-(Hept-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9c).
2-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-1-(4-phenylbutyl)benzene (9d).
4-Methyl-2-(pent-1-yn-1-yl)-1-(4-phenylbutyl)benzene (9e).
1-(3,3-Dimethylbut-1-yn-1-yl)-4-methyl-2-(4-phenylbutyl)benzene (9f).
4-Methyl-1-(pent-1-yn-1-yl)-2-(4-phenylbutyl)benzene (9g).
(Z)-12-(2,2-Dimethylpropylidene)-2-methoxy-3-((Z)-1-(5-methoxy-2-(3-phenylpropyl)phenyl)-3,3-dimethylbut-1-en-1-yl)-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctane (10).