

Syntheses, X-ray crystal structures and reactivity of fluorenylidene- and dibenzosuberonylidene-allenes: convenient precursors to dispirotetracenes, di-indenotetracenes and 2-phenyl-11*bH*-dibenz[*c,d,h*]azulene

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Electronic Supplementary Information

Synthetic and NMR data for molecules **20b**, **20c**, **21a**, **21b**, **23c** and **24a**.

X-ray crystallographic data (Table SI-1) for molecules **20b**, **21a**, **23c** and **24a** and Figures SI-1, SI-2, SI-3 and SI-4.

1-Bromo-1-trimethylsilyl-2-dibenzo[*a,d*]cycloheptenyldiene-ethene (20b)

To a cooled solution of 5-(4-trimethylsilyl)phenyl-5*H*-dibenzo[*a,d*]cyclohepten-5-ol, **19b**, (560 mg, 1.84 mmol) in acetic acid (15 mL) was added dropwise a solution of hydrobromic acid 2M (47 %, 0.63 g, 3.68 mmol) in water (1.8 mL). Upon stirring for 15 min with cooling, the precipitate was filtered, washed with water and dried. The product was dissolved in ether (10 mL), dried over MgSO₄, filtered and concentrated to give **20b** (0.650 g, 1.77 mmol; 96 %) as a white solid (Found: C, 65.53; H, 5.30. C₂₀H₁₉BrSi requires C, 65.39; H, 5.21); a sample suitable for an X-ray diffraction structural determination was obtained by recrystallisation from diethyl ether; δ_{H} (500 MHz, CDCl₃): 7.42 (dd, *J* 7.6 and 1.1, 2H, H-4, H-6), 7.35 (td, *J* 7.4 and 1.7, 2H, H-3, H-7), 7.29 (td, *J* 7.3 and 1.4, 2H, H-2, H-8), 7.26 (dd, *J* 7.6 and 1.4, 2H, H-1, H-9), 6.76 (s, 2H, H-10, H-11), 0.20 (s, 9H, TMS); δ_{C} (100 MHz,

CDCl₃): 207.9 (C-12), 135.0, 134.9, (suberenyl-C), 131.3 (C-10, C-11), 129.7 (C-2, C-8), 129.2, 129.2, (C-3, C-4, C-6, C-7), 128.1 (C-1, C-9), 113.9 (C-5), 89.8 (C-13), -1.6 (TMS); IR (CDCl₃): 1922 cm⁻¹ (C=C=C).

1-Bromo-1-(α,α,α -trifluoro-*p*-tolyl)-2-dibenzo[*a,d*]cycloheptenyliidene-ethene (20c)

As for **20a**, the alkynol **19c** and HBr gave **20c** (0.99 g, 2.25 mmol; 85%), as a white solid (Found: C, 65.67; H, 3.40; Br, 18.42. C₂₄H₁₄BrF₃ requires C, 65.62; H, 3.21; Br, 18.19); δ_{H} (500 MHz, CDCl₃): 7.65 (d, *J* 8.0, 2H, phenyl *o*-H), 7.58 (d, *J* 8.5, 2H, H-4, H-6), 7.56 (d, *J* 9.0, 2H, phenyl *m*-H), 7.42 (td, *J* 7.5 and 2.5, 2H, suberenyl-H), 7.37 (td, *J* 7.5 and 1.0, 2H, suberenyl-H), 7.37 (d, *J* 7.5, 2H, H-1, H-9), 6.88 (s, 2H, H-10, H-11); δ_{C} (125 MHz, CDCl₃): 206.3 (C-12), 137.4 (phenyl *ipso*-C), 134.7 (C-9a, C-11a), 133.6 (C-4a, C-5a), 131.1 (C-10, C-11), 130.0 (q, ²*J*_{CF} 32.5, phenyl *p*-C), 129.7, 129.1, 129.0, (suberenyl-CH), 128.5 (C-2, C-9), 127.6 (phenyl *o*-C), 125.2 (q, ³*J*_{CF} 3.5, phenyl *m*-C), 123.7 (q, ¹*J*_{CF} 271, CF₃), 118.2 (C-5), 93.5 (C-13); IR (CDCl₃): 1925 cm⁻¹ (C=C=C).

1-Phenyl-2-dibenzo[*a,d*]cycloheptyliidene-ethene (21a)

Method A. To a cooled (0 °C) solution of 1-bromo-1-phenyl-2-dibenzo[*a,d*]cycloheptenyliidene-ethene, **20a**, (1.00 g, 2.69 mmol) in tetrahydrofuran (27 mL), n-BuLi (1.6 M in solution in tetrahydrofuran, 2.31 mL, 3.7 mmol) was added very slowly, at -78 °C. After stirring for 15 min at -78 °C, acetic acid (210 μ L, 3.63 mmol) was added. The mixture was allowed to warm to 0 °C and stirred for 1 h at this temperature. After removal of the solvent, the crude product was dissolved in diethyl ether, filtered through celite and concentrated to give a brown oil. The oil was purified by chromatography on a silica column using pentane / dichloromethane as eluent to give **21a** (29.6 mg, 0.09 mmol, 3 %).

Method B. To a solution of 5-phenylethynyl-5*H*-dibenzo[*a,d*]cycloheptene, **24**, (100 mg, 0.34 mmol) in methanol (5 mL) and *t*-butanol (5 mL), was added potassium *tert*-butoxide (44 mg, 0.39 mmol). After stirring 12 hours at room temperature, the reaction was quenched with water and extracted with diethyl ether several times. The organic layers were washed with brine, dried over MgSO₄, filtered and concentrated to give **21a** (89.4 mg, 0.30 mmol, 90 %) (Found: C, 94.25; H, 5.49. C₂₃H₁₆ requires C, 94.48; H, 5.52); a sample of **21a** suitable for an X-ray crystal structure determination was obtained by recrystallisation from dichloromethane / pentane; δ_{H} (400 MHz, CDCl₃): 7.48-7.43 (m, 4H, suberenyl-H, phenyl *o*-H), 7.46 (t, *J* 7.2, 2H, suberenyl-H), 7.29-7.23 (m, 7H, phenyl *m*-H, *p*-H, suberenyl-H), 6.82 (s, 2H, H-10, H-11), 6.57 (s, 1H, H-13); δ_{C} (100 MHz, CDCl₃): 210.5 (C-12), 136.4 (phenyl *ipso*-C), 134.9, 134.1 (suberenyl-C), 131.5 (C-10, C-11), 129.7, 129.1, 129.0, 129.0, 127.9, (suberenyl-CH, phenyl *m*-C), 127.6 (phenyl *p*-C), 127.0 (phenyl *o*-C), 114.4 (C-5), 95.15 (C-13); IR (CDCl₃): 1938 cm⁻¹ (C=C=C).

Attempted synthesis of 1-trimethylsilyl-2-dibenzo[*a,d*]cycloheptylidene-ethene (**21b**)

As for *Method A* above, 1-bromo-1-trimethylsilyl-2-dibenzo[*a,d*]cycloheptylidene-ethene, **20b**, in THF was treated with *n*-BuLi and then with acetic acid. However, the desired allene, **20b**, was not formed; instead the propargyl-allene, **22b**, was obtained in 58% yield. δ_{H} (400 MHz, CDCl₃): 8.06 (d, *J* 8.0, 2H, suberenyl-H), 7.23 (td, *J* 8.0 and 1.6 Hz, 2H, suberenyl-H), 7.19-7.01 (m, 10H, suberenyl-H), 7.00-6.93 (m, 2H, suberenyl-H), 6.37 (s, 4H, suberenyl-H), 0.138 (s, 9H, TMS), -0.264 (s, 9H, TMS); δ_{C} (100 MHz, CDCl₃): 209.2 (=C=), 136.9, 134.6, 134.4, (suberenyl-C), 131.2, 129.7, 129.3, 129.0, 128.2, 128.0, 127.6, 126.8, 126.7, (suberenyl-CH), 109.3, 107.7, 102.3, 96.7, 54.6, (C≡C, C=•=C), 0.4, 0.2, (TMS); IR (CDCl₃): 2154 cm⁻¹ (-C≡C-), 1911 cm⁻¹ (C=C=C).

1-(α,α,α -Trifluoro-*p*-tolyl)-3-dibenzo[*a,d*]cycloheptenyliidene-ethanone (23c)

When 1-bromo-1-(α,α,α -trifluoro-*p*-tolyl)-3,3-dibenzo[*a,d*]cycloheptenyliidene-allene, **20c**, was left in solution in diethyl ether / pentane at room temperature for several days, the crystalline product of X-ray quality that eventually formed was characterised as 1-(α,α,α -trifluoro-*p*-tolyl)-3,3-dibenzo[*a,d*]cycloheptenyliidene-ethanone, **23c** (Found: C, 76.88; H, 4.36. C₂₄H₁₅F₃O requires C, 76.59; H, 4.02); δ_{H} (400 MHz, CDCl₃): 7.72 (d, *J* 8.0, 2H, phenyl-H), 7.55 (d, *J* 7.2, 1H, suberenyl-H), 7.44 (d, *J* 7.6, 2H, phenyl-H), 7.39-7.31 (m, 2H, suberenyl-H), 7.16 (d, *J* 7.2, 1H, suberenyl-H), 7.13-6.99 (m, 3H, suberenyl-H), 6.96 (d, *J* 11.6, 1H), 6.90 (d, *J* 11.6), 2H, (H-10, H-11), 6.49 (s, 1H, H-12); δ_{C} NMR (100 MHz, CDCl₃): 194.1 (CO), 154.2 (C-5), 140.6 (phenyl ipso-C), 139.4, 136.1, 133.9, 133.7, (suberenyl-C), 133.4 (q, $^2J_{\text{CF}}$ = 32.3 Hz, phenyl *p*-H), 131.4, 131.0, (C-10, C-11), 129.3, 129.3, 129.2, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, (suberenyl-CH, phenyl *o*-H, C-12), 125.0 (q, $^3J_{\text{CF}}$ 3.7, phenyl *m*-H), 123.7 (q, $^1J_{\text{CF}}$ 271, CF₃); δ_{F} (282 MHz, CDCl₃): -63.48.

5-Phenylethynyl-5*H*-dibenzo[*a,d*]cycloheptene (24a)

To 5-phenylethynyl-5*H*-dibenzo[*a,d*]cyclohepten-5-ol, **20a**, (500 mg, 1.62 mmol) in dry dichloromethane (20 mL), and cooled to 0 °C, triethylsilane (310.5 μ L, 1.94 mmol) was added slowly. Boron trifluoride-etherate (246 μ L, 1.94 mmol) was added dropwise and the solution became dark green and then pale wine coloured. After stirring for 1 hour at 0 °C, the reaction was quenched with distilled water (30 mL), and the mixture was extracted with dichloromethane several times. The organic layer was washed with brine, dried over MgSO₄, filtered and concentrated. After trituration with a mixture of pentane / dichloromethane (99:1), 5-phenylethynyl-5*H*-dibenzo[*a,d*]cycloheptene, **24a**, (0.25 g, 0.86 mmol, 53 %) was isolated as a yellow solid, m.p. 102°C-105°C (Found: C, 93.88; H, 5.46. C₂₃H₁₆ requires C, 94.48; H, 5.52); a sample suitable for an X-ray crystal structure determination was obtained

by recrystallisation from dichloromethane / pentane; δ_{H} (400 MHz, CDCl_3): 7.93 (brd s, 2H, H-4, H-6), 7.61 (brd s, 2H, phenyl *o*-H), 7.39 (td, J 7.2 and 1.2, 2H, H-3, H-7), 7.37-7.34 (m, 3H, phenyl *p*-H, *m*-H), 7.32 (dd, J 7.6 and 1.6, 2H, H-1, H-9), 7.28 (td, J 7.2 and 1.2, 2H, H-2, H-8), 7.13 (brd s, 2H, H-10, H-11), 5.27 (s, 1H, H-5); δ_{C} (100 MHz, CDCl_3): 137.7 (C-4a, C-5a), 134.3 (C-9a, C-11a), 131.9 (phenyl *o*-C, *ipso*-C), 131.4 (C-10, C-11), 128.7 (C-3, C-7), 128.5, 128.3, (phenyl *p*-C, *m*-C), 127.9 (C-1, C-9), 126.5 (C-2, C-8), 125.6 (C-4, C-6), 123.5, 88.1, (C-12, C-13), 41.0 (C-5).

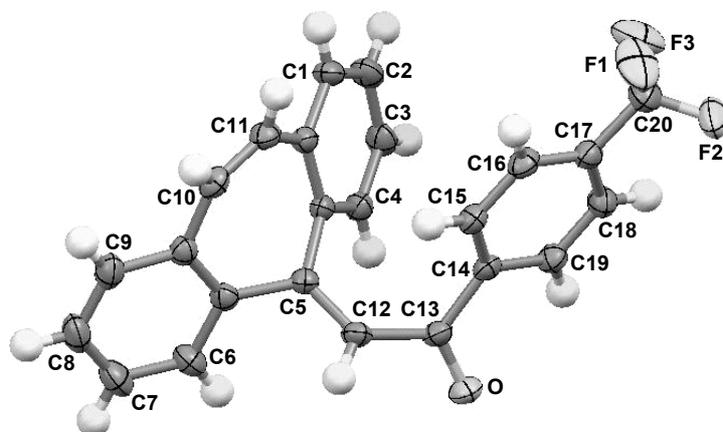


Figure SI-3. X-ray structure of 1-(α,α,α -trifluoro-*p*-tolyl)-3,3-dibenzo[*a,d*]cycloheptenylidene-ethanone, **23c**; thermal ellipsoids are drawn at the 25% probability level.

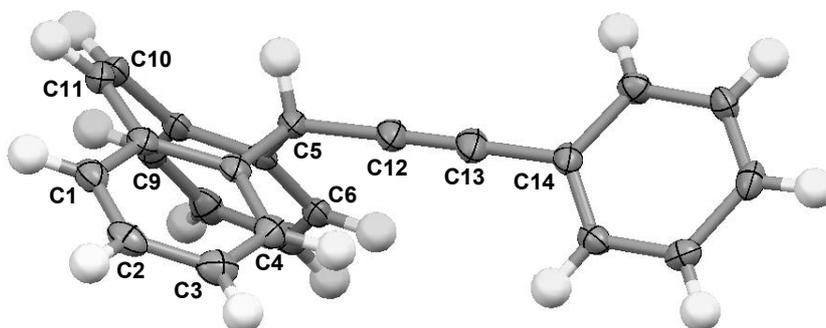


Figure SI-4. View of the X-ray crystal structure of 5-phenylethynyl-5*H*-dibenzo[*a,d*]cycloheptene, **24a**, emphasizing the pseudo-equatorial position of the alkyne; thermal ellipsoids are drawn at the 50% probability level.

Table SI-1. Crystallographic data for **20b**, **21a**, **23c** and **24a**.

| | 20b | 21a | 23c | 24a |
|--|--|---|---|---|
| Formula | C ₂₀ H ₁₉ BrSi | C ₂₃ H ₁₆ | C ₂₄ H ₁₅ OF ₃ | C ₂₃ H ₁₆ |
| <i>M</i> | 367.35 | 292.36 | 376.36 | 292.36 |
| Crystal system | orthorhombic | orthorhombic | monoclinic | monoclinic |
| Space group | <i>Pca</i> 2 ₁ (#29) | <i>P2</i> ₁ 2 ₁ 2 ₁ (#19) | <i>P2</i> ₁ / <i>c</i> (#14) | <i>P2</i> ₁ / <i>n</i> (#14) |
| <i>a</i> [Å] | 16.2272(1) | 6.8227(7) | 10.334(7) | 4.6169(7) |
| <i>b</i> [Å] | 9.46594(8) | 9.1562(10) | 8.900(5) | 19.620(3) |
| <i>c</i> [Å] | 11.59176(7) | 25.406(3) | 20.175(13) | 17.062(2) |
| α [°] | 90 | 90 | 90 | 90 |
| β [°] | 90 | 90 | 100.490(13) | 92.789(3) |
| γ [°] | 90 | 90 | 90 | 90 |
| <i>V</i> [Å ³] | 1780.56(2) | 1587.1(3) | 1825(2) | 1543.7(4) |
| <i>Z</i> | 4 | 4 | 4 | 4 |
| ρ_{calcd} [g.cm ⁻³] | 1.370 | 1.224 | 1.370 | 1.258 |
| <i>T</i> [K] | 100(2) | 100(2) | 100(2) | 100(2) |
| μ mm ⁻¹ | 3.725 | 0.069 | 0.104 | 0.071 |
| <i>F</i> (000) | 752 | 616 | 776 | 616 |
| θ Range [°] | 5.41 to 76.47 ^(a) | 1.60 to 25.00 | 2.00 to 24.00 | 2.08 to 26.00 |
| Index ranges | -20 ≤ <i>h</i> ≤ 20 -9 ≤ <i>k</i> ≤ 11 -14 ≤ <i>l</i> ≤ 14 | -7 ≤ <i>h</i> ≤ 8 -10 ≤ <i>k</i> ≤ 10 -30 ≤ <i>l</i> ≤ 30 | -11 ≤ <i>h</i> ≤ 11 -10 ≤ <i>k</i> ≤ 10 -22 ≤ <i>l</i> ≤ 23 | -5 ≤ <i>h</i> ≤ 5 -24 ≤ <i>k</i> ≤ 24 -21 ≤ <i>l</i> ≤ 20 |
| Reflections measured | 27644 | 14065 | 12850 | 12287 |
| Reflections used | 3619 | 1644 | 2856 | 3032 |
| <i>R</i> _{int} | 0.0536 | 0.0321 | 0.0199 | 0.0258 |
| Data/restraints/parameters | 3619/1/203 | 1644/0/208 | 2856/0/281 | 3032/0/293 |
| Final <i>R</i> values [<i>I</i> > 2σ(<i>I</i>)]: | | | | |
| <i>R</i> 1 | 0.0305 | 0.0288 | 0.0385 | 0.0370 |
| <i>wR</i> 2 | 0.0839 | 0.0658 | 0.1001 | 0.0851 |
| <i>R</i> values (all data): | | | | |
| <i>R</i> 1 | 0.0305 | 0.0321 | | |
| <i>wR</i> 2 | 0.0839 | 0.0674 | 0.0471 | 0.0465 |
| | | | 0.1080 | 0.0915 |
| GOF on <i>F</i> ² | 1.088 | 1.088 | 1.040 | 1.041 |
| Largest diffraction peak and hole (e Å ⁻³) | 0.877 and -0.386 | 0.154 and -0.135 | 0.128 and -0.146 | 0.218 and -0.160 |

(a) Measured with Cu-K α radiation (1.54184 Å)