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Supporting Information

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Fulvenes from Enediynes: Regioselective Electrophilic Domino- as well as Tandem-Cyclizations of Oligoynes and Eneynes

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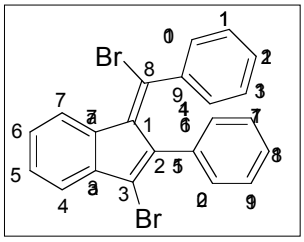
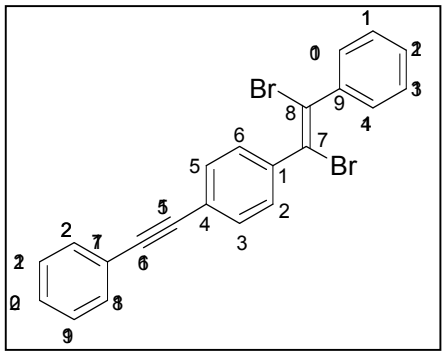
General procedure for brominations: To a solution of the respective alkyne in 25 mL $CHCl_3$ we added dropwisely per mmol of alkyne 2.5 mL of a 0.4 M solution of bromine in $CHCl_3$. The reaction was allowed to stir for 2 h in the dark; the reaction mixture was washed twice with a solution of saturated Na_2SO_3, then twice with water, dried over Na_2SO_4. The solvent was evaporated and the residue was purified by recrystallization (A), through column chromatography (B) or by means of semi-preparative HPLC (C). The Cambridge Crystallographic Data Center (CCDC) numbers are given along with the respective procedures; crystals structures are available free of charge at the CCDC.

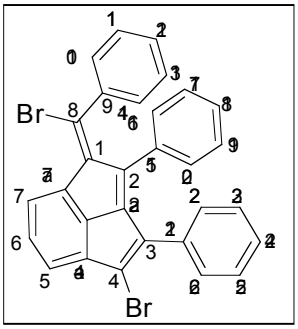


Bromination of 1,2-Bis(phenylethynyl)benzene (4): starting material: **1** (3 mmol, 830 mg). Products: 85% (*E*)-3-Bromo-1-(α-bromo-benzyliden)-2-phenyl-indene **(*E*)-4**, 15% (*Z*)-3-Bromo-1-(α-bromo-benzyliden)-2-phenyl-indene **(*Z*)-4**. **(*E*)-4**: yellow crystals (CCDC 203542); mp = 133 °C. **^{1}H-NMR**: δ = 8.84 (d, 1H, 7-H), 7.52 (m, 3H, 4-H, 5-H, 6-H), 7.14 (m, 2H, Ar-H), 6.99 (m, 8H, Ar-H). **^{13}C-NMR**: δ = 141.10 (q, 1C, C-3a), 140.65 (q, 1C, C-9/C-15), 139.71 (q, 1C, C-9/C-15), 137.95 (q, 1C, C-1), 135.52 (q, 1C, C-7a), 134.82 (q, 1C, C-2), 130.74 (q, 1C, C-8), 130.35 (t, 2C, C-10/C-16, C-14/C-20), 129.51 (t, 2C, C-10/C-16, C-14/C-20), 128.81 (t, 1C, C-5), 128.61 (t, 2C, C-11/C-17, C-13/C-19), 127.08 (t, 2C, C-11/C-17, C-13/C-19), 127.06 (t, 1C, C-12/C-18), 126.95 (t, 1C, C-6), 126.42 (t, 1C, C-12/C-18), 126.25 (q, 1C, C-3), 124.46 (t, 1C, C-7), 120.58 (t, 1C, C-4). **MS** (70 eV) m/z (%): 440 (8), 438 (16), 436 (8) [M^+], 358 (12), 356 (12), 278 (100), 138 (12). **HRMS** Found: 435.9462, Theor.: $C_{22}H_{14}Br_2$ 435.9462. **(*Z*)-4**: yellow solid; mp = 109 °C. **^{1}H-NMR**: δ = 7.46 (m, 10H, 10-H, 14-H, 16-H, 20-H, 11-H, 13-H, 17-H, 19-H, 12-H, 18-H), 7.38 (d, 1H, 4-H), 7.25 (dd, 1H, 5-H), 6.89 (dd, 1H, 6-H), 6.12 (d, 1H, 7-H). **^{13}C-NMR**: δ = 142.29 (q, 1C), 140.68 (q, 1C), 139.95 (q, 1C), 137.93 (q, 1C), 136.11 (q, 1C), 134.79 (q, 1C), 130.30 (t, 2C), 129.61 (t, 1C), 129.04 (t, 2C), 128.63 (q, 1C), 128.57 (t, 2C), 128.46 (q, 1C), 128.19 (t, 2C), 127.88 (t, 1C),

127.79 (t, 1C), 126.66 (t, 1C), 122.99 (t, 1C), 120.16 (t, 1C). **MS** (70 eV) mass peak m/z = 436 [M^+]; ($C_{22}H_{14}Br_2$ 435.99).

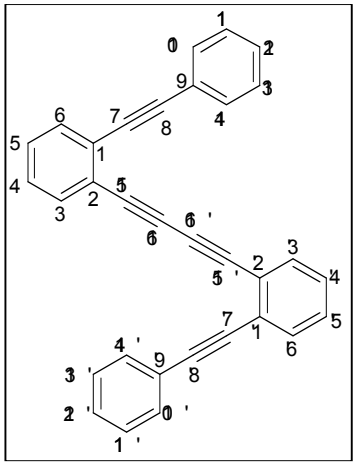


Bromination of 1,4-Bis(phenylethynyl)benzene (8) to 9: Starting material: **8** (3 mmol, 830 mg). Products: 60% (*E*)-1-(1,2-Dibromo-2-phenylvinyl)-4-phenylethynyl-benzene **(*E*)-9**, 40% (*Z*)-1-(1,2-Dibromo-2-phenyl-vinyl)-4-phenyl ethynyl benzene **(*Z*)-9**. **(*E*)-9** could be separated from **(*Z*)-9** by fractionated crystallization; **(*Z*)-9** is not isolable as it is very labile and isomerizes very readily to **(*E*)-9**. As the ^{1}H-NMR shifts are not distinctly different from **(*E*)-9**, only ^{13}C-NMR data are given for this compound (determined from difference spectra to **(*E*)-9**. **(*E*)-9**: colorless crystals (CCDC # 204110); mp 177 °C. **^{1}H-NMR**: d = 7.55 (m, 2H, 3-H, 5-H), 7.51 (m, 6H, 11-H, 13-H, 12-H, 18-H, 22-H, 20-H), 7.41 (m, 2H, 2-H, 6-H), 7.34 (m, 4H, 10-H, 14-H, 19-H, 21-H). **^{13}C-NMR**: □ = 140.62 (q, 1C, C-9), 140.30 (q, 1C, C-1), 131.67 (t, 2C, C-3/C-18, C-5/C-22), 131.52 67 (t, 2C, C-3/C-18, C-5/C-22), 129.25 (t, 2C, C-11/C-19, C-13/21), 129.02 (t, 2C, C-11/C-19, C-13/21), 129.00 (t, 1C, C-12/C-20), 128.49 (t, 1C, C-12/C-20), 128.40 (t, 2C, C-6/C-10, C-2/14), 128.39 (t, 2C, C-6/C-10, C-2/14), 123.93 (q, 1C, C-17), 122.98 (q, 1C, C-4), 118.48 (q, 1C, C-8), 117.34 (q, 1C, C-7), 90.66 (q, 1C, C-16), 88.86 (q, 1C, C-15). **IR** (KBr, Pellet) □ = 3078, 3055, 1954, 1925, 1601, 1572, 1502, 1485, 1441, 1403, 1276, 1244, 1104, 1069, 1019, 914, 856, 835, 826, 758, 751, 732, 694, 671, 613 cm^{-1}. **MS** (70 eV) m/z (%): 440 (16), 438 (32), 436 (16) [M^+], 278 (100), 139 (22). **HRMS** Found: 435.9462, Theor.: $C_{22}H_{14}Br_2$ (435.9462). **^{13}C-NMR (*Z*)-9:** □ = 139.34 (1C, C-9), 139.19 (1C, C-1), 131.60 (2C, C-3/C-18, C-5/C-22), 131.20 (2C, C-3/C-18, C-5/C-22), 129.87 (2C, C-11/C-19, C-13/C-21), 129.76 (2C, C-11/C-19, C-13/C-21), 128.55 (1C, C-12/C-20), 128.39 (1C, C-12/C-20), 128.36 (2C, C-6/C-10, C-2/C-14), 128.19 (2C, C-6/C-10, C-2/C-14), 126.36 (1C, C-17), 124.95 (1C, C-4), 123.33 (1C, C-8), 122.94 (1C, C-7), 90.74 (1C, C-16), 88.79 (1C, C-15).



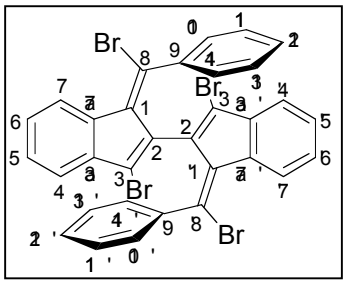
Bromination of 1,2,3-Tris(phenylethynyl)benzene (11) to 12: Starting materials: 1,2,3-Tris(phenylethynyl)benzene **11** (2 mmol, 750 mg). Product: **12** orange-red solid (yield 78%); mp 201 °C. **^{1}H-NMR**: □ = 8.10 (d, 1H, 7-H), 7.43 (t, 1H, 6-H), 7.35 (d, 1H, 5-H), 7.13 (m, 3H-Ar-H), 7.05 (m, 4H, Ar-H), 6.94 (m, 1H, Ar-H), 6.88 (m, 2H, Ar-H),

6.80 (m, 1H, Ar-H), 6.68 (m, 4H, Ar-H). **^{13}C-NMR**: δ = 148.37 (q, 1C, C-7b), 145.70 (q, 1C, C-2a), 142.13 (q, 1C, C-9/C-15/C21), 140.51 (q, 1C, C-9/C-15/C21), 139.85 (q, 1C, C-9/C-15/C21), 136.17 (q, 1C), 135.50 (q, 1C), 134.57 (q, 1C), 133.39 (q, 1C), 131.35 (q, 1C, C-7a), 130.64 (t, 2C), 129.95 (t, 2C), 129.86 (t, 2C), 129.77 (q, 1C, C-4a), 129.35 (t, 1C), 127.77 (t, 2C), 127.72 (t, 1C), 127.62 (t, 1C), 127.58 (t, 2C), 127.28 (q, 1C, C-4), 127.22 (t, 2C), 127.07 (t, 1C, C-6), 123.74 (t, 1C, C-7), 119.58 (t, 1C, C-5). **IR** (KBr, Pellet) ν = 3056, 3015, 2962, 2924, 1740, 1653, 1599, 1582, 1559, 1484, 1457, 1440, 1350, 1261, 1198, 1088, 1044, 1019, 866, 802, 790, 755, 696, 688, 635, 616 cm^{-1}. **MS** (70 eV) m/z (%): 540 (16), 538 (32), 536 (16) [M$^+$], 458 (16), 456 (16), 378 (100), 350 (4), 300 (6), 237 (8), 189 (16), 121 (28). **HRMS** Found: 535.9775, Theor.: $C_{30}H_{18}Br_2$ (535.9775).



2,2'-Bis(phenylethynyl)diphenylbutadiyne (16):

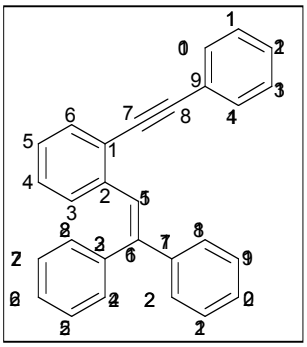
20 mmol $CuAc_2$ (4 g), 70 mL pyridine in methanol/Ether (1:1) were added to 10 mmol 1-(Phenylethynyl)-2-ethynylbenzene (2.0 g) in 10 mL ether; recrystallization from ethanol. Yield: 1.5 g **16** (75%) as light brown crystals (crystal structure CCDC 203543); mp 130 °C. **^{1}H-NMR**: δ = 7.58 (m, 8H, 3,3'-H, 6,6'-H, 10,10'-H, 14,14'-H), 7.32 (m, 10H, 4,4'-H, 5,5'-H, 11,11'-H, 13,13'-H, 12,12'-H). **^{13}C-NMR**: δ = 132.79 (t, 2C, C-3,3'), 131.84 (t, 4C, C-10,10', C-14,14'), 131.69 (t, 2C, C-6,6'), 128.88 (t, 2C, C-4,4'), 128.46 (t, 2C, C-12,12'), 128.27 (t, 4C, C-11,11', C-13,13'), 127.90 (t, 2C, C-5,5'), 127.07 (q, 2C, C-1,1'), 124.47 (q, 2C, C-9,9'), 122.87 (q, 2C, C-2,2'), 94.42 (q, 2C, C-8,8'), 87.71 (q, 2C, C-7,7'), 81.38 (q, 2C, C-16,16'), 77.91 (q, 2C, C-15,15'). **IR** (KBr, Pellet) ν = 3074, 3057, 3022, 2216, 1943, 1910, 1878, 1799, 1684, 1653, 1597, 1567, 1492, 1466, 1441, 1195, 1181, 1155, 1089, 1068, 1024, 940, 911, 758, 747, 688 cm^{-1}. **MS** (70 eV) m/z (%): 402 (100) [M+], 374 (4), 324 (8), 277 (6), 201 (4). **HRMS** Found: 402.1408, Theor.: $C_{32}H_{18}$ (402.1409).



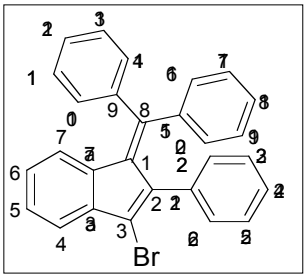
Bromination of 2',2'-Bis(phenylethynyl)-1,4-diphenylbuta-1,3-diin (16) to 17:

Starting materials: **16** (2 mmol, 800 mg). Product: **17** (yield 87%), orange crystals (CCDC 203544); mp 222 °C. **^{1}H-NMR**: δ = 8.24 (m, 2H, 7,7'-H), 7.57 (m, 2H, 4,4'-H), 7.30 (m, 2H, 5,5'-H), 7.22 (m, 6H, 11,11'-H, 13,13'-H, 12,12'-H), 7.01 (m, 2H, 6,6'-H), 6.65 (m, 4H, 10,10'-H, 14,14'-H). **^{13}C-NMR**: δ = 140.80 (q, 2C, C-3a,3a'), 140.42 (q, 2C, C-9,9'), 138.45 (q,

2C, C-1,1'), 135.34 (q, 2C, C-7a,7a'), 133.31 (q, 2C, C-2,2'), 130.28 (q, 2C, C-8,8'), 129.96 (t, 2C, C-Ar), 129.61 (q, 2C, C-3,3'), 128.91 (t, 2C, C-5,5'), 128.37 (t, 2C, C-Ar), 128.14 (t, 2C, C-Ar), 127.09 (t, 2C, C-6,6'), 126.78 (t, 2C, C-Ar), 125.69 (t, 2C, C-Ar), 123.69 (t, 2C, C-7,7'), 120.13 (t, 2C, C-4,4'). **IR** (KBr, Pellet) □ = 3050, 1947, 1082, 1596, 1577, 1486, 1447, 1440, 1347, 1270, 1260, 1230, 1165, 1098, 1076, 1026, 966, 942, 926, 894, 859, 762, 752, 738, 705, 694, 659, 645, 628 cm^{-1}. **MS** (70 eV) m/z (%): 726 (10), 724 (50), 722 (72), 720 (50), 718 (10) [M^+], 355 (40), 278 (24), 178 (16). **HRMS** Found: 717. 8142, Theor.: $C_{32}H_{18}Br_4$ (717.8142).



1-(Phenylethynyl)-2-(2',2'-diphenylvinyl)benzene (18): 10 mmol diphenylmethyl triphenylphosphonium bromide (5.1 g) in 40 mL THF, 10 mmol BuLi, 1.6 M in Hexane (6.3 mL) were added to 10 mmol 2-(Phenylethynyl)benzaldehyde (2.1 g) in 20 mL THF. Yield: 0.6 g **18** (17%) as a colorless solid; mp 86 °C. **^{1}H-NMR**: □ = 7.52 (m, 4H, 6-H, 10-H, 14-H, 15-H), 7.43 (m, 2H, 18-H, 22-H), 7.34 (m, 8H, 11-H, 13-H, 12-H, 19-H, 21-H, 25-H, 27-H, 26-H), 7.23 (m, 3H, 20-H, 24-H, 28-H), 7.12 (m, 1-H, 5-H), 6.79 (m, 1-H, 4-H), 6.86 (m, 1-H, 3-H). **^{13}C-NMR**: □ = 143.82 (q, 1C, C-17/C-23), 143.24 (q, 1C, C-17/C-23), 140.19 (q, 1C, C-16), 139.44 (q, 1C, C-2), 132.18 (t, 1C, C-6), 131.53 (t, 2C, C-10, C-14), 130.58 (t, 2C, C-24, C-28), 129.16 (t, 1C, C-3), 128.43 (t, 2C, C-11, C-13), 128.29 (q, 2C, C-19, C-21), 128.21 (t, 1C, C-12), 128.18 (t, 2C, C-25, C-27), 127.86 (t, 2C, C-18, C-22), 127.61 (t, 1C, C-20/C-26), 127.49 (t, 1C, C-4), 127.41 (t, 1C, C-20/C-26), 126, 49 (t, 1C, C-5), 126.42 (t, 1C, C-15), 123.67 (q, 1C, C-1), 123.33 (q, 1C, C-9), 94.39 (q, 1C, C-8), 88.43 (q, 1C, C-7). **IR** (KBr, Pellet) □ = 3076, 3046, 1958, 1884, 1596, 1570, 1490, 1467, 1441, 1354, 1275, 1177, 1162, 1087, 1074, 1028, 998, 954, 922, 915, 863, 850, 776, 758, 702 cm^{-1}. **MS** (70 eV) m/z (%): 356 (16) [M^+], 280 (24), 202 (100), 178 (5), 168 (24). **HRMS** Found: 356.1565, Theor.: $C_{28}H_{20}$ (356.1565).



Bromination of (E)-1-(Phenylethynyl)-2-(2',2'-diphenylvinyl)benzene (18) to 21:

Starting materials: **18** (1 mmol, 360 mg). Product: **21** (yield 94%), red crystals (CCDC 203545); mp 195 °C. **^{1}H-NMR**: □ = 7.50 (m, 4H, 4-H, Ar-H), 7.42 (m, 2H, Ar-H), 7.30 (m, 1H, 5-H), 7.13 (m, 2H, Ar-H), 6.96 (m, 9H, 6-H, Ar-H), 6.39 (m, 1H, 7-H) . **^{13}C-NMR**: □ = 149.50 (q, 1C, C-8), 142.85 (q, 1C, C-9), 140.86 (q, 1C, C-15/C-21), 140.68 (q, 1C, C-3a), 140.14 (q, 1C, C-15/C-21), 136.57 (q,

1C, C-7a), 136.40 (q, 1C, C-1/C-2), 135.76 (q, 1C, C-1/C-2), 132.06 (t, 2C, C-Ar), 130.80 (t, 2C, C-Ar), 130.36 (t, 2C, C-Ar), 128.98 (t, 1C, C-12/C-18/C-24), 128.63 (t, 2C, C-Ar), 127.99 (t, 1C, C-6), 127.29 (t, 1C, C-5), 127.07 (t, 2C, C-Ar), 126.98 (t, 2C, C-Ar), 126.18 (t, 1C, C-12/C-18/C-24), 126.10 (t, 1C, C-12/C-18/C-24), 125.78 (q, 1C, C-3), 123.12 (t, 1C, C-7), 120.04 (t, 1C, C-4). **IR** (KBr, Pellet) □ = 3075, 3055, 3026, 1952, 1603, 1575, 1551, 1541, 1488, 1481, 1455, 1438, 1345, 1334, 1286, 1269, 1235, 1179, 1154, 1076, 12027, 952, 933, 846, 782, 774, 757, 723, 702, 624, 615 cm^{-1}. **MS** (70 eV) m/z (%): 436 (100), 434 (95) [M+], 355 (40), 278 (24), 178 (16). **HRMS** Found: 434.0670, Theor.: $C_{28}H_{19}Br$ (434.0670).