

## Supplementary Information

### Reductive Bergman-Type Cyclizations of Cross-Conjugated Ene-diynes to Fulvene and Fulvalene Anions: The Role of Charge Distribution

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## Complete Citation for Reference 26

Gaussian 98, Revision A.7, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1998.

Table of Intramolecular Distances Between Bond-Forming Carbons in the Dianions

Compound	"bonding" distance (Å)
12	4.153
9	4.202
10	4.215
11	4.271
14	4.312
6	4.322
16	4.323
3	4.349
15	4.350
13	4.361
19	4.390
17	4.395
7	4.395
8	4.428
18	4.463

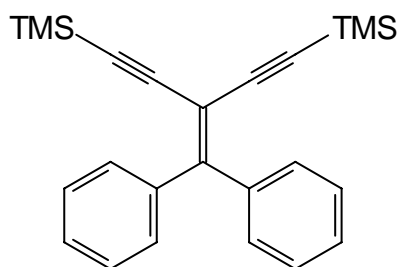
### Preparation of 6, 8, 14-16

10 mmol 9-Trimethylsilyl-9*H*-fluorene/1-Trimethylsilyl-1*H*-indene are dissolved in diethylether and cooled to -20 °C. 10 mmol n-BuLi are added and the temperature is kept at -20 °C. After the addition is completed the solution is allowed to warm to room temperature and stirred for 1 h. The solution is cooled once again to 0 °C and 10 mmol of the ketone dissolved in ether are added dropwise. The cooling bath is removed and the reaction is controlled by TLC. After the reaction is completed it is hydrolysed with aqueous NH<sub>4</sub>Cl and the phases are separated. The water phase is extracted three times with ether, and the combined organic phases are dried and evaporated. The residue is recrystallized in Ethanol or Chloroform/Pentane. Oily compounds are purified by column chromatography (SiO<sub>2</sub>/Pentane:ether 9:1).

## Preparation of 7

4.82 g (15.8 mmol) Benzhydryl-diethyl-phosphonate are dissolved in 100 mL Diethylether. 9.9 mL n-BuLi (1.6 M in Hexane) are added dropwise. After addition the solution is stirred for 1 h. The solution is cooled to -40 °C and 3.52 g (15.8 mmol) 1,5-bis(trimethylsilyl)-penta-1,4-diyne-3-one in 70 mL diethylether are slowly added. The solution is allowed to warm to room temperature and is stirred over night. The mixture is hydrolyzed with  $\text{NH}_4\text{Cl}$  (aq.), extracted with ether, dried over  $\text{MgSO}_4$ , and the solvent is evaporated. The residue is treated with silica and filtered through a short column with pentane to remove the polar compounds. After evaporation of the solvent, the product solidifies upon cooling, and is recrystallized from methanol to give 1.81 g (4.86 mmol) colourless needles in 31 % yield.

1-Trimethylsilanyl-3-trimethylsilanylethynyl-4,4-diphenyl-prop-3-ene-1-yne (7)



$^1\text{H-NMR}$ :  $\delta$ =0.09 ppm(s 18H SiCH<sub>3</sub>), 7.24-7.45(m 10H aromat.).

$^{13}\text{C-NMR}$ :  $\delta$ =0.28 ppm(SiCH<sub>3</sub>), 98.51/103.91(C-3/4/3'/4'), 102.53(C-2), 128.20/131.02(C-6/7/9/10), 129.18(C-8/8'), 140.74(C-5/5'), 159.01(C-1).

IR(KBr):  $\nu$ =3057 cm<sup>-1</sup>(w), 3021(w), 2958(m), 2897(w), 2148(m), 1490(m), 1443(m), 1251(s), 1218(s), 1182(m), 953(s), 934(m), 911(s), 849(s), 764(s), 698(s), 674(s), 622(m).

UV(CH<sub>3</sub>CN):  $\lambda_{\text{max}}$ =192(1.072), 204(0.491), 232(0.267), 244(0.2997), 328(0.328).

MS:  $m/z$ =372(100[M<sup>+</sup>], 357(20), 341(9), 299(14), 283(60), 269(50), 255(12), 239(18), 215(6), 171(10), 159(6), 97(6), 91(15), 73(88).

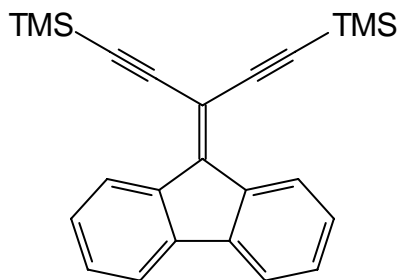
C<sub>24</sub>H<sub>28</sub>Si<sub>2</sub> (372.66)

C calc.: 77.35 %    found: 77.29 %

H calc.: 7.57 %    found: 7.49 %

mp: 126 °C (Methanol)

9-(3-Trimethylsilyl-1-trimethylsilyl-ethynyl-prop-2-ylidene)-9H-fluorene (6)



4.29 g (18 mmol) 9-Trimethylsilyl-9H-fluorene, 11.3 mL n-BuLi (1.6 M), 4 g (18 mmol) 1,5-Bis-trimethylsilyl-penta-1,4-diyne-5-one.

Yield: 5.52 g (14.9 mmol), 83 %.

$^1\text{H-NMR}$ :  $\delta$ =0.35 ppm(s 18H SiCH<sub>3</sub>), 7.22-7.27 (2 dt 4H J<sub>1</sub>=7.4 Hz, J<sub>2</sub>=0.8 Hz, H-2/7), 7.33-7.37(2 dt 4H J<sub>1</sub>=7.4 Hz, J<sub>2</sub>=0.8 Hz, H-3/6), 7.62-7.64(d 2H J=7.4 Hz, H-4/5), 8.65-8.67 (d 2H J=7.8 Hz, H-1/8).

$^{13}\text{C-NMR}$ :  $\delta$ =0.0 ppm(SiCH<sub>3</sub>), 101.17/103.63(C-11/12), 104.83(C-10), 119.73(C-4/5), 126.17(C-1/8), 127.50(C-2/7), 129.99(C-3/6), 137.64(C-1a/8a), 140.50(C-4a/5a), 147.13(C-9).

IR(KBr): $\nu$ =3059 (cm<sup>-1</sup>)(w), 2956(m), 2896(w), 2152(m), 2133(m), 2125(m), 1611(w), 1449(m), 1443(m), 1361(w), 1262(m), 1248(s), 1225(s), 1199(w), 1188(w), 1178(m), 959(s), 917(s), 853(s), 840(s), 778(s), 759(s), 737(m), 717(s), 698(m), 678(m), 668(m), 627(w), 619(w).

UV(CH<sub>3</sub>CN): $\lambda_{\text{max}}$ =192 (nm)(1.493), 230(1.236), 238(1.194), 264(1.119), 272(1.281), 292(0.232), 304(0.237), 324 sh(0.327), 338(0.688), 354(1.357), 374(1.658).

MS: m/z=370 (%) (100)[M<sup>+</sup>], 355(26), 339(19), 198(31), 283(31), 259(15), 238(19), 170(17), 155(9), 111(9), 97(17), 73(27), 71(17), 69(14), 57(16).

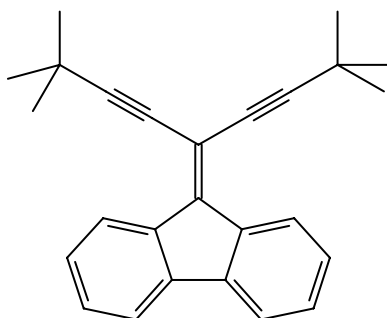
C<sub>24</sub>H<sub>26</sub>Si<sub>2</sub> (370.64)            C calc.: 77.77 %    found: 77.79 %

H calc.: 7.07 %    found: 7.01 %

mp:137 °C (Methanol)



9[1-(3,3-Dimethyl-but-1-ynyl)-4,4-dimethyl-pent-2-ylidene]-9*H*-fluorene (14)



1.03 g (4.33 mmol) 9-Trimethylsilanyl-9*H*-fluorene, 2.7 mL n-BuLi (1.6 M), 822 mg (4.33 mmol) 2,2,8,8-Tetramethyl-nona-3,6-diyne-5-one.

Yield: 1.1 g (3.25 mmol), 75 %.

$^1\text{H-NMR}$ :  $\delta$  = 8.66(d,  $J$ =7.8 Hz, 2 H, H-1/8), 7.65(d,  $J$ =7.4 Hz, 2 H, H-4/5), 7.31-7.35(„dt“,  $J_1$ =7.5 Hz,  $J_2$ =1.2 Hz, 2 H, H-3/6), 7.24-7.28(„dt“,  $J_1$ =7.8 Hz,  $J_2$ =1.2 Hz, 2 H, H-2/7), 1.42(s, 9 H, H-14)

$^{13}\text{C-NMR}$ :  $\delta$  = 142.90(C-9), 139.71(C-4a/5a), 137.79(C-1a/8a), 128.71(C-3/6), 126.92(C-2/7), 124.97(C-1/8), 119.31(C-4/5), 106.98(C-10), 103.09/79.88(C-11/12), 30.69(C-13), 28.77(C-14).

IR(Diamond):  $\nu$  = 3057(w), 2967(s), 2925(m), 2896(m), 2863(m), 2198(m), 1603(w), 1552(w), 1471(m), 1443(s), 1359(w), 1323(m), 1284(s), 1262(m), 1199(m), 1030(w), 929(w), 845(m), 779(s), 722(s), 662(m), 621(w), 574(m).

UV(CH<sub>3</sub>CN):  $\lambda_{\text{max}}$  = 369(4.60), 351(4.52), 336(4.22), 318(3.91), 301(3.91), 273(4.52), 264(4.46), 243(4.53), 231(4.37).

MS:  $m/z$  = 338(100)[M<sup>+</sup>], 323(9), 308(7), 293(16), 277(14), 266(25), 23(252), 239(14), 165(44), 139(11), 132(12), 73(16), 57(9).

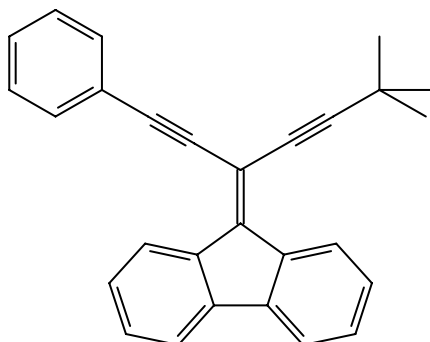
C<sub>26</sub>H<sub>26</sub> (338.48)

C calc.: 92.26 %    found: 91.93 %

H calc.: 7.74 %    found: 7.74 %

mp: 110 °C (CHCl<sub>3</sub>/Pentane)

9-(4,4-Dimethyl-1-phenylethynyl-pent-2-ylidene)-9H-fluorene (15)



500 mg (2.1 mmol) 9-Trimethylsilylanyl-9H-fluorene, 1.3 mL n-BuLi (1.6 M), 440 mg (2.1 mmol) 1-Phenyl-6,6-dimethyl-hepta-1,4-diyne-3-one.

Yield: 460 mg (1.3 mmol), 61 %.

$^1\text{H-NMR}$ :  $\delta$ =8.67-8.71(m, 2 H, H-1/8), 7.61-7.67(m, 4 H, H-4/5/14/18), 7.38-7.44(m, 3 H, H-15/16/17), 7.32-7.37(m, 2 H, H-3/6), 7.26-7.30("dt",  $J_1=7.7$  Hz,  $J_2=1.4$  Hz, 2 H, H-2/7), 1.45(s, 9H, H-22)

$^{13}\text{C-NMR}$ :  $\delta$ = 144.14(C-9), 140.00/139.99(C-4a/5a), 137.68/137.62(C-1a/8a), 131.74(C-17/18), 129.16/129.08(C-3/6), 128.90(C-16), 128.53(C-14/15), 127.36/127.05(C-2/7), 125.30/125.19(C-1/8), 123.04(C-13), 119.46/119.43(C-4/5), 107.66(C-10), 102.15/97.16/89.77/79.10(C-11/12/19/20), 30.71(C-21), 28.86(C-22).  
IR(Diamond):  $\nu$ =3055(w), 3029(w), 2964(m), 2924(w), 2894(w), 2862(W), 2197(m), 1909(w), 1601(w), 1560(m), 1472(m), 1441(m), 1365(m), 1292(m), 1262(m), 1200(m), 1155(m), 1105(m), 1069(w), 1024(w), 938(m), 872(w), 847(m), 780(s), 754(s), 724(s), 689(s), 663(s), 570(m).

UV(CH<sub>3</sub>CN):  $\lambda_{\text{max}}$ =393(4.45), 373(4.52), 274(4.58), 265(4.54), 242(4.59).

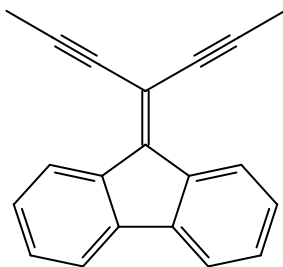
MS:  $m/z$ =358(100)[M<sup>+</sup>], 343(14), 328(48), 326(34), 313(15), 289(10), 265(10), 165(23), 157(10).

C<sub>28</sub>H<sub>22</sub> (358.48)

C calc.: 93.81 %    found: 93.87 %

H calc.: 6.19 %    found: 6.22 %

mp : 107-108 °C (Ethanol)

9-(1-Prop-1-ynyl-but-2-ynylidene)-9H-fluorene (16)

1.19 g (5 mmol) 9-Trimethylsilyl-9H-fluorene, 3.1 mL n-BuLi (1.6 M), 530 mg (5 mmol) Hepta-2,5-diyne-4-one.

Yield: 850 mg (3.4 mmol), 67 %.

$^1\text{H-NMR}$ :  $\delta$ =8.55(d,  $J$ =7.5 Hz, 2 H, H-1/8), 7.63-7.65(dd,  $J_1$ =7.0 Hz,  $J_2$ =0.6 Hz, 2 H, H-4/5), 7.31-7.35("dt",  $J_1$ =7.4 Hz,  $J_2$ =1.1 Hz, 2 H, H-3/6), 7.25-7.29("dt",  $J_1$ =7.4 Hz,  $J_2$ =1.3 Hz, 2 H, H-2/7), 2.24(s, 6H, H-13)

$^{13}\text{C-NMR}$ :  $\delta$ =143.76(C-9), 139.79(C-4a/5a), 137.54(C-1a/8a), 128.95(C-2/7), 127.26(C-3/6), 124.82(C-1/8), 119.34(C-4/5), 102.36(C-10), 95.36/79.98(C-11/12), 5.16(C-13).

IR(Diamond):  $\nu$ =3078(w), 3055(w), 3029(w), 2948(w), 2910(w), 2835(w), 2210(w), 1599(w), 1564(m), 1473(w), 1431(m), 1372(w), 1350(w), 1268(m), 1194(w), 1159(w), 1022(w), 946(w), 828(w), 780(s), 752(w), 727(s), 665(m), 621(w), 571(m).

UV(CH<sub>3</sub>CN):  $\lambda_{\text{max}}$ =365(3.61), 348(3.52), 332(3.21), 316(2.92), 302(2.82), 273(3.51), 264(3.46), 242(3.52).

MS:  $m/z$ =254(100)[M<sup>+</sup>], 253(75), 252(59), 250(36), 239(46), 226(9), 126(15), 125(16), 113(22), 112(12), 100(6), 44(10).

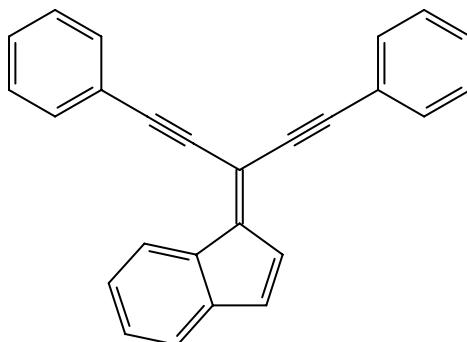
C<sub>20</sub>H<sub>14</sub> (254.33)

C calc.: 94.45 %    found: 94.19 %

H calc.: 5.55 %    found: 5.53 %

mp: 155 °C (CHCl<sub>3</sub>/Pentane)

1-(3-Phenyl-1-phenylethynyl-prop-2-ynylidene)-1*H*-indene (8)



1 g (5.3 mmol) 1-Trimethylsilyl-1*H*-indene, 3.3 mL *n*-BuLi (1.6 M), 1.22 g (5.3 mmol) 1,5-Diphenyl-penta-1,4-diyne-3-one.

Yield: 940 mg (2.9 mmol), 54 %.

$^1\text{H-NMR}$ :  $\delta$ =8.35(dd,  $J_1$ =6.8 Hz,  $J_2$ =1.5 Hz, 1 H, H-1), 7.57-7.66(m, 4 H, H-12/16/20/24), 7.36-7.44(m, 6 H, H-13/14/15/21/22/23), 7.18-7.26(m, 3 H, H-2/3/4), 6.97(d,  $J$ =5.7 Hz, 1 H, H-5), 6.85(d,  $J$ =5.7 Hz, 1 H, H-6).

$^{13}\text{C-NMR}$ :  $\delta$ =151.09(C-8), 143.88/134.47(1a/4a), 133.61(C-6), 131.90/131.85(C-12/16/20/24), 129.23/129.02(C-14/22), 128.80(C-4), 128.62(C-5), 128.58/128.44(13/15/21/23), 126.10(C-2 o. 3), 124.10(C-1), 122.60/122.59 (C-11/19), 121.49(C-2 o. 3), 104.13(C-7), 98.44/95.37(C-9/17), 87.86/87.70(C-10/18).  
IR(Diamond):  $\nu$ =3056(w), 2185(m), 1596(w), 1552(w), 1488(m), 1443(m), 1367(m), 1341(m), 1160(w), 1125(w), 1066(w), 1024(w), 935(w), 912(w), 847(w), 795(m), 750(s), 726(s), 684(s), 587(m), 568(m).

UV(CH<sub>3</sub>CN):  $\lambda_{\text{max}}$ =393(3.52), 303(3.35), 292(3.35), 250(3.47).

MS:  $m/z$ =329(23), 328(100)[M<sup>+</sup>], 327(43), 326(88), 324(36), 300(7), 167(9), 149(31).

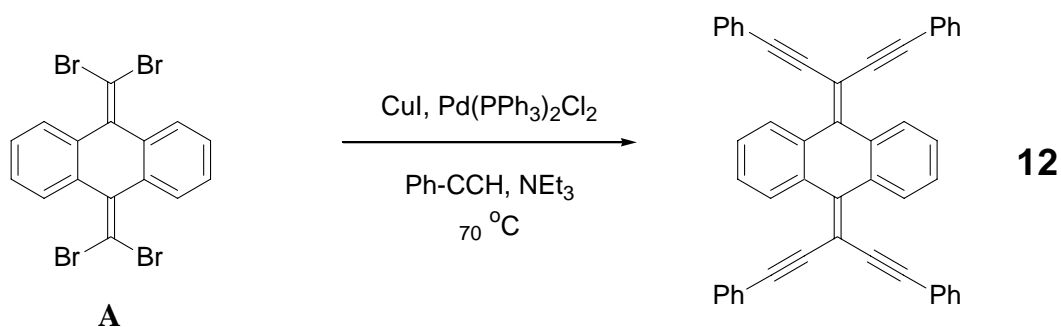
C<sub>26</sub> H<sub>16</sub> (328.41)

C calc.: 95.09 %    found: 94.96 %

H calc.: 4.91 %    found: 4.95 %

mp: 110 °C (CHCl<sub>3</sub>/Pentane)

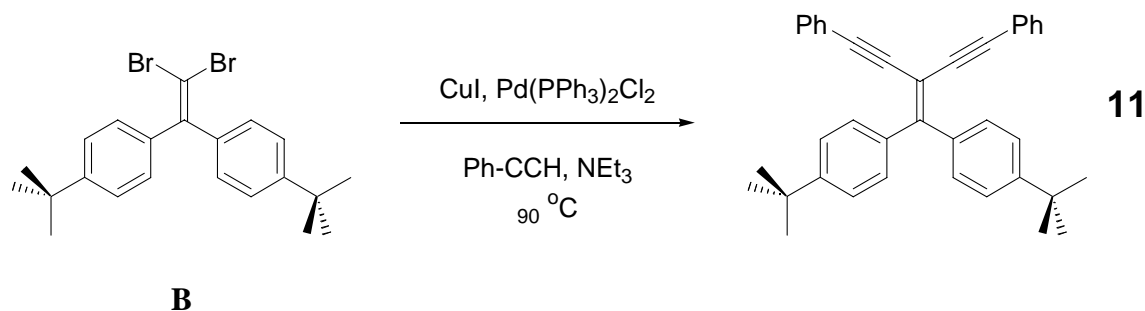
## Preparation and experimental data for 9-12



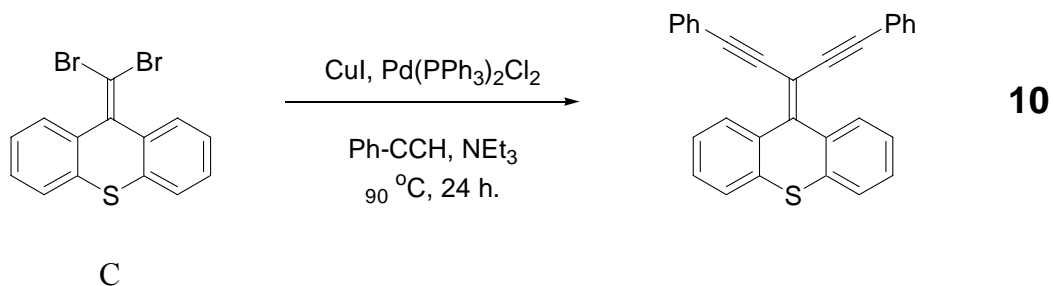
A sample of tetrabromide **A**<sup>1</sup> (561 mg, 1.08 mmol) was added to a stirred suspension of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (57 mg, 0.081 mmol) and CuI (46 mg, 0.24 mmol) in 10 mL of triethylamine in a sealable pressure vessel. The suspension was then purged with nitrogen for 10 min with vigorous stirring. Next, a portion of phenyl acetylene (1.005 g, 9.839 mmol) was added, and the vessel was sealed and heated to 70 °C for 20 h. The reaction mixture was then cooled to room temperature and diluted with 100 mL of dichloromethane. The organic layer was washed with two 50 mL portions of saturated aqueous NH<sub>4</sub>Cl, then with two 50 mL portions of water, dried over MgSO<sub>4</sub>, and evaporated to dryness under reduced pressure to give a dark solid. The solid was adsorbed onto silica gel and chromatographed on a column of silica gel with 5% EtOAc:95% hexanes as eluent to give a solid that was pure by <sup>1</sup>H NMR analysis (lit. NMR<sup>2</sup>). The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/EtOH to give 106 mg (16%) of a red crystal suitable for X-ray analysis (see supporting information). Mp 239 °C (decomposition). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm): 8.48-8.46 (AA' of AA'BB', 4H), 7.55-7.51 (m, 8H), 7.44-7.42 (BB' of AA'BB', 4H), 7.39-7.33 (m, 12H). MS ESI (*m/z*): [M+Na]<sup>+</sup> calcd. for C<sub>48</sub>H<sub>28</sub>Na, 627.2089 Found 627.2094.

<sup>1</sup> Donovan, P.M.; Scott, L.T. *J. Am. Chem. Soc.* **2004**, 126, 3108-3112.

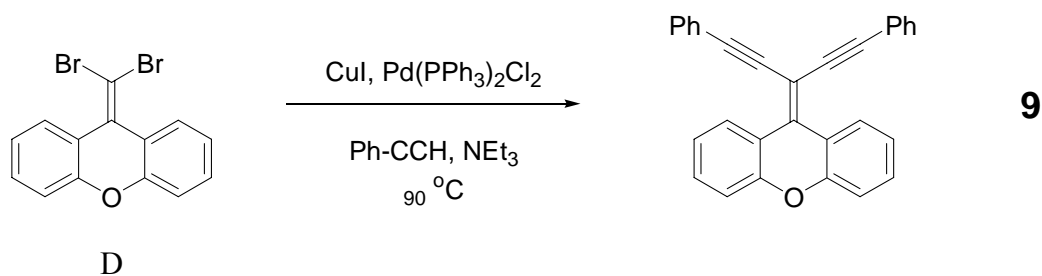
<sup>2</sup> (a) Neidlein, R.; Winter, M. *Synthesis* **1998**, 9, 1362-1366. (b) Hwang, G. T.; Son, H. S.; Ku, J. K.; Kim, B. H. *J. Am. Chem. Soc.* **2003**, 125, 11241-11248.



A sample of dibromide **B** (124 mg, 0.276 mmol) was added to a stirred suspension of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (19 mg, 0.027 mmol) and CuI (17 mg, 0.088 mmol) in 5 mL of triethylamine in a sealable pressure vessel. The suspension was then purged with nitrogen for 10 min with vigorous stirring. Next, a portion of phenyl acetylene (126 mg, 1.24 mmol) was added, and the vessel was sealed and heated to 90 °C for 22 h. The reaction mixture was then cooled to room temperature and diluted with 100 mL of dichloromethane. The organic layer was washed with two 50 mL portions of saturated aqueous NH<sub>4</sub>Cl, then with two 50 mL portions of water, dried over MgSO<sub>4</sub>, and evaporated to dryness under reduced pressure to give a dark solid. The solid was adsorbed onto silica gel and chromatographed on a column of silica gel with 5% EtOAc:95% hexanes as eluent to give a solid that was approximately 95% pure by <sup>1</sup>H NMR analysis. A sample of the pure diyne was obtained as an off white solid by multiple recrystallizations from EtOH (61 mg, 43%). Mp 208 °C. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ (ppm): 7.51 (d, *J* = 8.1 Hz, 4H), 7.39 (d, *J* = 8.4 Hz, 4H), 7.34-7.26 (m, 10H), 1.36 (s, 18H). **MS** ESI (*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>38</sub>H<sub>37</sub>, 493.2895 Found 493.2897.



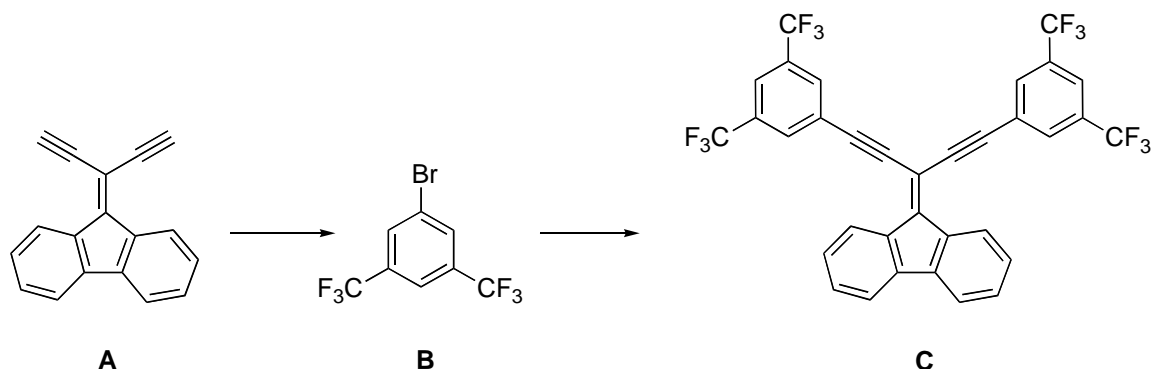
A sample of dibromide **C**<sup>1</sup> (170 mg, 0.462 mmol) was added to a stirred suspension of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (22 mg, 0.032 mmol) and CuI (30 mg, 0.16 mmol) in 5 mL of triethylamine in a sealable pressure vessel. The suspension was then purged with nitrogen for 10 min with vigorous stirring. Next, a portion of phenyl acetylene (297 mg, 2.90 mmol) was added, and the vessel was sealed and heated to 90 °C for 22 h. The reaction mixture was then cooled to room temperature and diluted with 100 mL of dichloromethane. The organic layer was washed with two 50 mL portions of saturated aqueous NH<sub>4</sub>Cl, then with two 50 mL portions of water, dried over MgSO<sub>4</sub>, and evaporated to dryness under reduced pressure to give a dark solid. The solid was adsorbed onto neutral alumina and chromatographed on a column of alumina with 2% EtOAc:98% hexanes as eluent to give a product that was approximately 95% pure by <sup>1</sup>H NMR analysis. A sample of the pure diyne was obtained as a powdery yellow solid by multiple recrystallizations from EtOH (96 mg, 50%). Mp 167 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.24 (dd, *J* = 7.5 and *J* = 1.6, 2H), 7.52 (dd, *J* = 7.5 and *J* = 1.4 Hz, 2H), 7.45-7.41 (m, 4H), 7.38-7.29 (m, 10H). **MS** ESI (*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>30</sub>H<sub>19</sub>S, 411.1207 Found 411.1205.



A sample of dibromide **D** (185 mg, 0.516 mmol) was added to a stirred suspension of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (25 mg, 0.036 mmol) and CuI (28 mg, 0.15 mmol) in 5 mL of triethylamine in a sealable pressure vessel. The suspension was then purged with nitrogen for 10 min with vigorous stirring. Next, a portion of phenyl acetylene (274 mg, 2.68 mmol) was added, and the vessel was sealed and heated to 90 °C for 24 h. The reaction mixture was then cooled to room temperature and diluted with 100 mL of dichloromethane. The organic layer was washed with two 50 mL portions of saturated aqueous NH<sub>4</sub>Cl, then with two 50 mL portions of water, dried over MgSO<sub>4</sub>, and evaporated to dryness under reduced pressure to give a dark solid. The solid was adsorbed onto silica gel and chromatographed on a column of silica gel with 5% EtOAc:95% hexanes as eluent to give a solid that was approximately 95% pure by <sup>1</sup>H NMR analysis. A sample of the pure diyne was obtained as a yellow solid by multiple recrystallizations from EtOH/hexanes (62 mg, 31%). Mp 148 °C. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ (ppm): 8.62 (dd, *J* = 8.0 Hz and *J* = 2.0 Hz, 2H), 7.50-7.54 (m, 4H), 7.47 (td, *J* = 7.1 Hz and *J* = 1.5 Hz, 2H), 7.43-7.31 (m, 6H), 7.28-7.21 (m, 4H). **MS** ESI (*m/z*): [M+H]<sup>+</sup> calcd. for C<sub>30</sub>H<sub>19</sub>O, 395.1436 Found 395.1437.



### Preparation and experimental data for **13**



To a mixture of **A** (0.140 g, 0.619 mmol) and 3,5-bis(trifluoromethyl)bromobenzene (0.365 g, 1.25 mmol) in degassed Et<sub>3</sub>N (25 mL) was added [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (40 mg, 0.057 mmol) and CuI (20 mg, 0.11 mmol). The reaction was stirred at rt for 24 h, the solvent then removed *in vacuo*, and the resulting residue was passed through a short plug (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/hexane 1:1). The solvent was removed to give the crude reaction mixture, which subjected to column chromatography (SiO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>/hexane 1:2, *R<sub>f</sub>* = 0.7) to give **C** (0.144 g, 36%) as a yellow solid. Mp 208 °C (decomposition). IR (CH<sub>2</sub>Cl<sub>2</sub> cast): 1280, 1175, 1133, 1123, 1109, 893. <sup>1</sup>H-NMR (499.8 MHz, CDCl<sub>3</sub>): δ 8.51 (*d*, *J* = 8 Hz, 2 H), 8.05 (*s*, 4 H), 7.90 (*s*, 2 H), 7.66 (*d*, *J* = 8 Hz, 2 H), 7.41 (*t*, *J* = 8 Hz, 2 H), 7.31 (*t*, *J* = 8 Hz, 2 H); <sup>19</sup>F-NMR (470.3 MHz, CDCl<sub>3</sub>): δ -63.5; <sup>13</sup>C-NMR (125.7 MHz, CDCl<sub>3</sub>): δ 148.7, 140.9 (*m*), 136.9 (*m*), 132.4 (*q*, <sup>2</sup>*J*<sub>CF</sub> = 34 Hz), 131.6 (*m*), 130.8, 127.9, 125.6, 124.9, 122.9 (*q*, <sup>1</sup>*J*<sub>CF</sub> = 277 Hz), 122.6 (*m*), 120.1, 98.2, 94.4, 90.0. EI-MS (70 eV): 650.1 (100, *M*<sup>+</sup>). EI-HRMS: 650.0871 (*M*<sup>+</sup>, C<sub>34</sub>H<sub>14</sub>F<sub>12</sub>, calc. 650.0904).

The synthesis of **A** has been reported: Ito, S.; Inabe, H.; Morita, N.; Tajiri, A. *Eur. J. Org. Chem.* **2004**, 1774–1780

## General Crystallographic Experimental Information of **12** (CCDC no. 282741)

Data was collected using a Bruker APEX CCD (charged coupled device) based diffractometer equipped with an LT-2 low temperature apparatus operating at 193 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data was measured using omega scans of 0.3° per frame for 45 seconds, such that a hemisphere was collected. A total of 1305 frames were collected with a maximum resolution of 0.90 Å. Cell parameters were retrieved using SMART<sup>3</sup> software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software<sup>4</sup>, which corrects for Lp and decay. Absorption corrections were applied using SADABS supplied by George Sheldrick. The structures were solved by the direct method using the SHELXS-97<sup>5</sup> program and refined by least squares method on F<sup>2</sup>, SHELXL-97<sup>6</sup>, incorporated in SHELXTL-PC V 6.10<sup>7</sup>.

All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawings are done at 30% ellipsoids.

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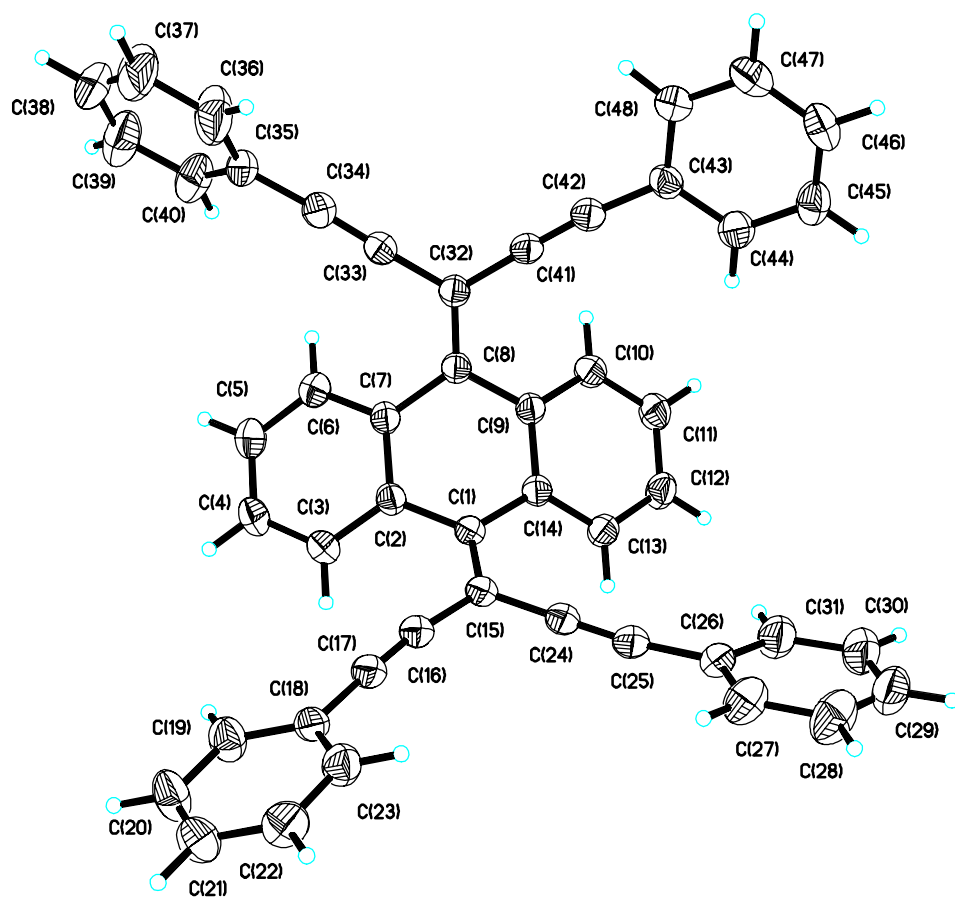
<sup>3</sup> SMART V5.626 (NT) Software for the CCD Detector Systems; Bruker Analytical X-ray Systems, Madison, WI (2001)

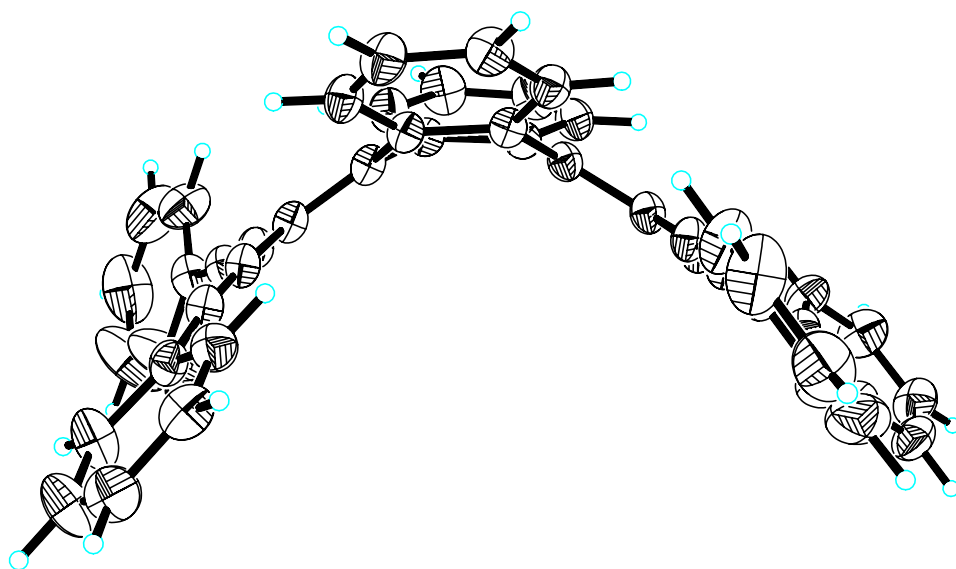
<sup>4</sup> SAINT V 5.01 (NT) Software for the CCD Detector Systems; Bruker Analytical X-ray Systems, Madison, WI (2001)

<sup>5</sup> Sheldrick, G. M. SHELXS-90, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1990

<sup>6</sup> Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, 1997.

<sup>7</sup> SHELXTL 6.0 (PC-Version), Program Library for Structure Solution and Molecular Graphics; Bruker Analytical X-ray Systems, Madison, WI (1998)

ORTEP Drawings of 12



**University of Alberta Department of Chemistry**  
**X-Ray Crystallography Laboratory**

**STRUCTURE REPORT OF 13**

**XCL Code:** RRT0336

**Date:** 10 September 2003

**Compound:** 9-[3-(3,5-Bis(trifluoromethyl)phenyl)-1-(3,5-bis(trifluoromethyl)phenylethynyl)prop-2-ynylidene]-9*H*-fluorene

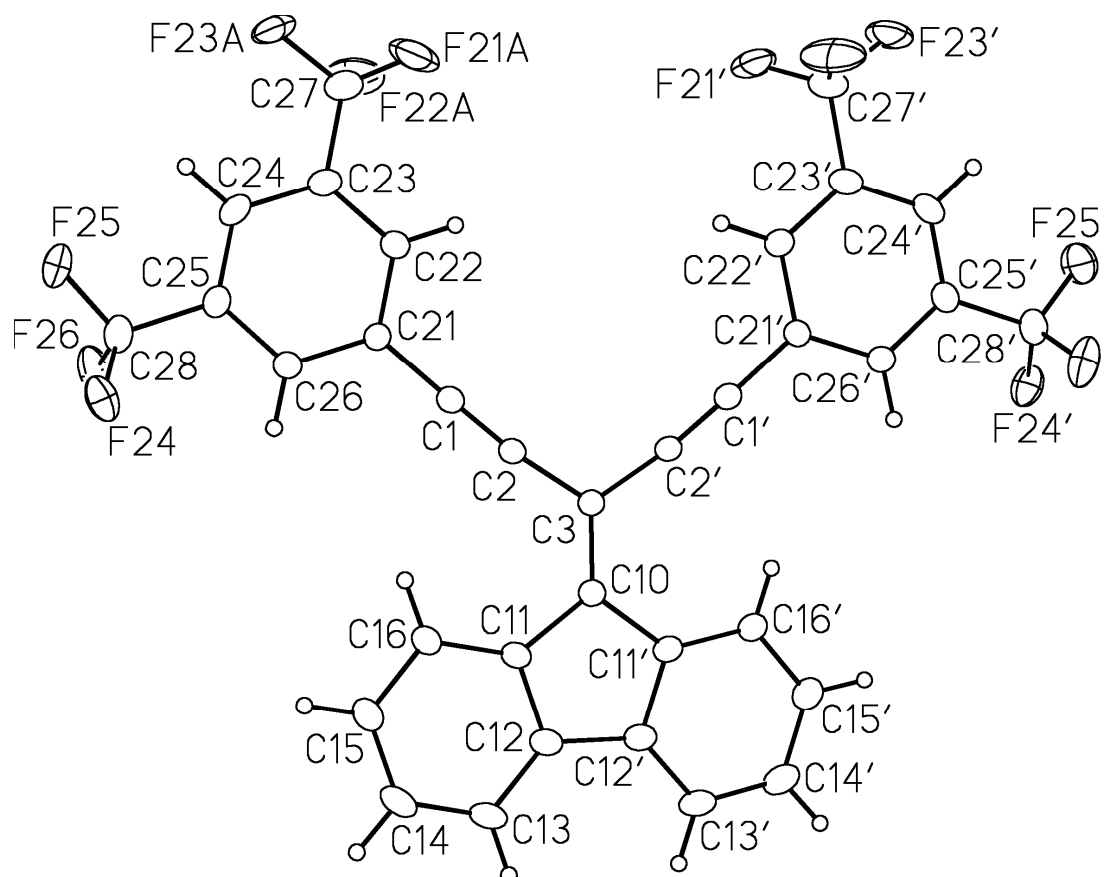
**Formula:** C<sub>34</sub>H<sub>14</sub>F<sub>12</sub>

**Supervisor:** R. R. Tykwinski

**Crystallographer:** R. McDonald

Perspective view of **13**

Perspective view of **13** showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters. Primed atoms are related to unprimed ones via the crystallographic twofold axis (0, *y*, 1/4) upon which C3, C10 and the midpoint of the C12–C12' bond are located.



### Alternate view of **13**

Alternate view of **13** illustrating the very slight twisting about the C3–C10 bond. The angle between the C1–C2–C3–C2'–C1 and fluorene group planes is  $7.62(8)^\circ$  (see Table 6 for least-squares planes calculations).

