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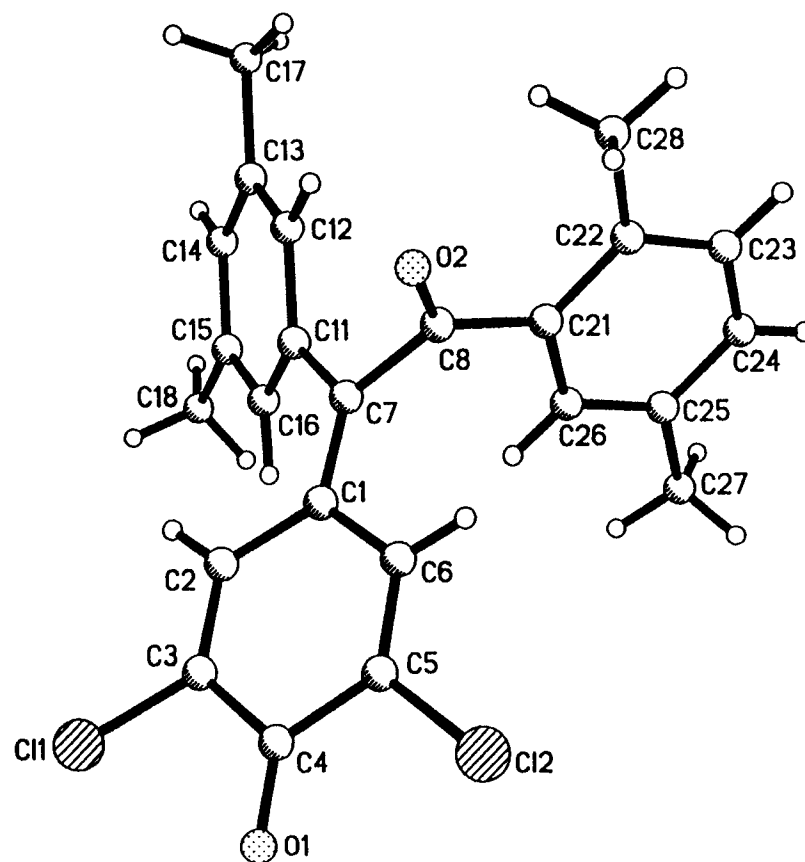


Figure 2. PLUTO perspective of quinone methide **8b** formed as the minor isomer in the photoinduced coupling of *m*-xylyl-*p*-xylylacetylene **XX'** with dichlorobenzoquinone **DB**.

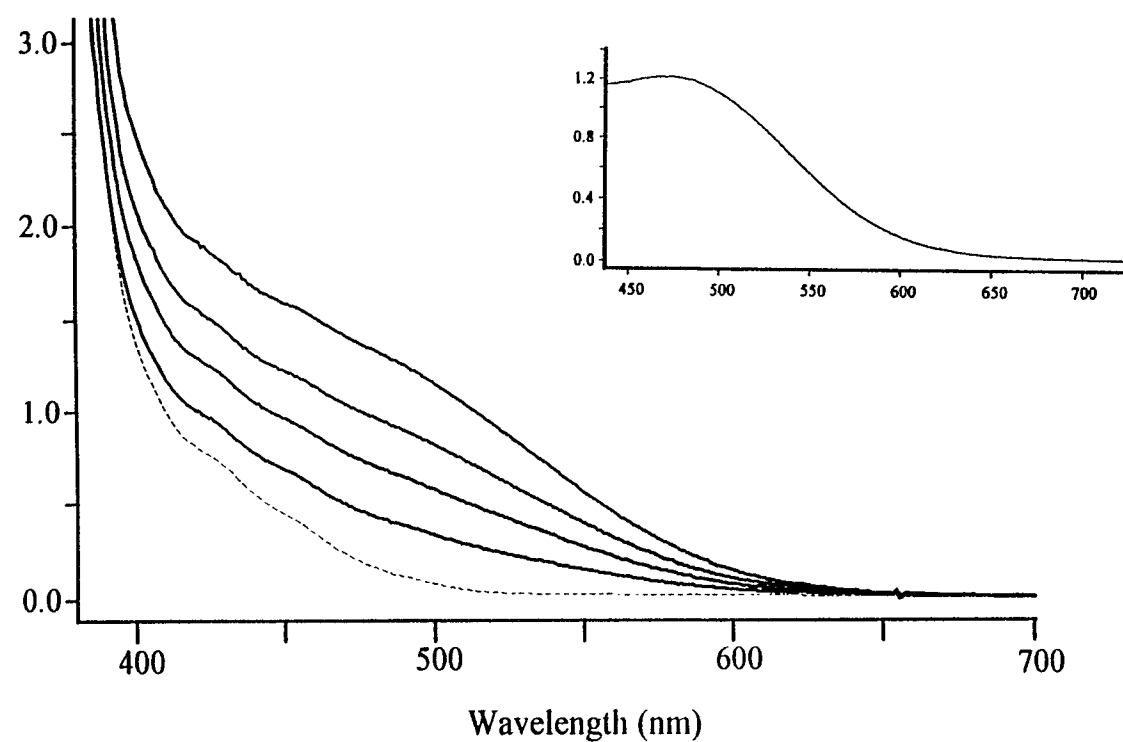


Figure 3. UV-vis spectral changes upon the incremental addition of tolyl(mesityl)acetylene to a dichloromethane solution of 0.03M **DB** and **[TM]** = 0.032, 0.071, 0.11 and 0.17 M (bottom-to-top). Inset: charge-transfer spectrum of **[TM, DB]** by digital subtraction of the **DB** spectrum (dashed line).

Spectroscopic data for the synthesized aryl acetylenes and the quinone methide products.

1,3-Dimethyl-5-(4-methylphenylethynyl)benzene, TX: mp 46 °C; ^1H nmr δ 2.30 (s, 6H), 2.35 (s, 3H), 6.86 (s, 1H), 7.15 (m, 4H), 7.32 (d, $J = 8.1$ Hz, 2H); ^{13}C nmr δ 21.10, 21.48, 88.84, 89.02, 120.33, 123.00, 129.04, 129.20, 129.99, 131.43, 137.81, 138.16; GC-MS m/z 220 (M^+ , 100); Anal. Calcd for $\text{C}_{17}\text{H}_{16}$: C, 92.68; H, 7.32. Found: C, 92.77; H, 7.33. **1,3-Dimethyl-5-(3,5-Dimethylphenylethynyl)benzene, XX:** mp 123 °C; ^1H nmr δ 2.29 (s, 12H), 6.93 (s, 2H), 7.14 (s, 4H); ^{13}C nmr δ 21.08, 88.02, 123.00, 129.22, 130.00, 137.78; GC-MS m/z 234 (M^+ , 100); Anal. Calcd for $\text{C}_{18}\text{H}_{18}$: C, 92.26; H, 7.74. Found: C, 92.33; H, 7.72. **1,3,5-Trimethyl-2-(phenylethynyl)benzene, FM:** mp 35.5 °C (lit.⁵⁹ 36-37 °C); ^1H nmr δ 2.30 (s, 3H), 2.49 (s, 6H), 6.90 (s, 2H), 7.33-7.36 (m, 3H), 7.53 - 7.56 (m, 2H); ^{13}C nmr δ 21.00, 21.30, 87.34, 97.02, 119.93, 124.00, 127.58, 127.91, 128.38, 131.19, 131.41, 137.74, 140.10; GC-MS m/z 220 (M^+ , 99), 205 (100). **1,3,5-Trimethyl-2-(4-methylphenylethynyl)benzene, TM:** mp 86 °C; ^1H nmr δ 2.28 (s, 3H), 2.30 (s, 3H), 2.47 (s, 6H), 6.87 (s, 2H), 6.94 (s, 2H), 7.16 (s, 2H); ^{13}C nmr δ 21.00, 21.11, 21.31, 86.60, 97.41, 127.54, 128.97, 129.82, 137.54, 137.84, 140.04; GC-MS m/z 248 (M^+ , 100); Anal. Calcd for $\text{C}_{18}\text{H}_{18}$: C, 92.26; H, 7.74. Found: C, 92.24; H, 7.75. **1,3,5-Trimethyl-4-(3,5-dimethylphenylethynyl)benzene, XM:** mp 123 °C; ^1H nmr δ 2.28 (s, 3H), 2.30 (s, 6H), 2.47 (s, 6H), 6.87 (s, 2H), 6.94 (s, 1H), 7.16 (s, 2H); ^{13}C nmr δ 21.00, 21.11, 21.31, 86.60, 97.41, 127.54, 128.97, 129.82, 137.54, 137.84, 140.04; GC-MS m/z 248 (M^+ , 100); Anal. Calcd for $\text{C}_{19}\text{H}_{20}$: C, 91.88; H, 8.12. Found: C, 91.90; H, 8.13. **2,3,4-Trimethyl-4-(4-methylphenylethynyl)benzene, TH:** mp 77 °C; ^1H nmr

δ 2.21 (s, 3H), 2.30 (s, 3H), 2.37 (s, 3H), 2.50 (s, 3H), 6.98 (d, $J=7.8$ Hz, 1H), 7.15 (d, $J=7.8$ Hz, 2H), 7.28 (d, $J=7.8$ Hz, 1H), 7.43 (d, $J=7.8$ Hz, 2H); ^{13}C nmr δ 15.76, 18.10, 20.95, 21.50, 88.79, 92.16, 120.75, 120.99, 127.12, 128.98, 131.17, 131.34, 135.24, 136.82, 137.93, 138.12; GC-MS m/z 248 (M^+ , 100); Anal. Calcd for $\text{C}_{18}\text{H}_{18}$: C, 92.26; H, 7.74. Found: C, 92.27; H, 7.78. **2,3,4-Trimethyl-4-(3,5-dimethylphenyl-ethynyl)benzene, XH**: mp 94 °C; ^1H nmr δ 2.17 (s, 3H), 2.26 (s, 3H), 2.29 (s, 6H), 2.48 (s, 3H), 6.92 (s, 1H), 6.95 (d, $J=7.5$ Hz, 1H), 7.15 (s, 2H), 7.26 (d, $J=7.5$ Hz, 1H); ^{13}C nmr δ 15.77, 18.10, 20.89, 21.08, 88.79, 92.36, 120.97, 123.44, 127.12, 129.04, 129.08, 129.79, 135.20, 136.82, 137.77, 138.12; GC-MS m/z 248 (M^+ , 100); Anal. Calcd for $\text{C}_{19}\text{H}_{20}$: C, 91.88; H, 8.12. Found: C, 91.93; H, 8.09. **2,3,4,5,6-Pentamethyl-1-(phenylethynyl)benzene, FP**: mp 129 °C; ^1H nmr δ 2.22 (s, 6H), 2.24 (s, 3H), 2.51 (s, 6H), 7.27-7.38 (m, 3H), 7.53-7.56 (m, 2H); ^{13}C nmr δ 16.55, 16.88, 18.82, 89.18, 96.12, 120.73, 124.23, 127.71, 128.28, 131.22, 132.27, 135.42, 135.45; GC-MS m/z 248 (M^+ , 100); Anal. Calcd for $\text{C}_{19}\text{H}_{20}$: C, 91.88; H, 8.12. Found: C, 91.90; H, 8.11. **3,5-Dimethyl-1-(2,5-dimethylphenylethynyl)benzene, XX'**: mp 74 °C; ^1H nmr δ 2.29 (s, 3H), 2.31 (s, 6H), 2.46 (s, 3H), 6.95 (s, 3H), 7.02 (d, $J=7.8$ Hz, 1H), 7.10 (d, $J=7.8$ Hz, 1H), 7.16 (s, 2H), 7.31 (s, 1H); ^{13}C nmr δ 20.24, 20.75, 21.11, 87.84, 93.30, 122.93, 123.23, 129.01, 129.15, 129.29, 130.02, 132.25, 134.96, 137.00, 137.85; GC-MS m/z 234 (M^+ , 100); Anal. Calcd. for $\text{C}_{18}\text{H}_{18}$: C, 92.26; H, 7.74. Found: C, 92.33; H, 7.77.

1'-(3,5-Dimethylphenyl)-1'-(4-methylbenzoyl)-1-methylene-3,5-dichlorocyclohexa-2,5-dien-4-one, 2a: mp 187 °C; IR ν (KBr) 1651 vs, 1604 cm^{-1} ; ^1H nmr δ 2.35 (s, 6H), 2.41 (s, 3H), 7.08 (s, 2H), 7.31 (m, 3H), 7.51 (s, 1H), 7.72 (d, $J=2.4$ Hz, 1H), 7.83

(br d, $J = 7.2$ Hz, 2H); ^{13}C nmr δ ; 21.14, 21.47, 127.37, 127.52, 129.90, 130.14, 132.87, 133.69, 134.23, 134.34, 134.45, 134.82, 139.01, 139.13, 141.95, 146.34, 158.16, 173.02, 194.35. GC-MS m/z 396 [M^+ ($2\times^{35}\text{Cl}$), 61], 119 (100); Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{Cl}_2\text{O}_2$: C, 69.53; H, 4.57. Found: C, 69.28; H, 4.65. **1'-(4-Methylphenyl)-1'-(3,5-dimethylbenzoyl)-1-methylene-3,5-dichlorocyclohexa-2,5-dien-4-one, 2b:** ^1H nmr 2.34 (6H, s), 2.42 (3H,s), 7.1-7.3 (m, 4H), 7.44 (br s, 2H), 7.68 (d, $J = 2.1$ Hz, 1H), 7.97 (d, $J = 8.1$ Hz, 2H); ^{13}C nmr 21.26, 21.87, 127.11, 127.83, 130.03, 130.25, 130.40, 132.79, 133.06, 133.64, 133.77, 134.29, 134.70, 135.33, 158.39, 195.18; GC-MS m/z 396 [M^+ ($2\times^{35}\text{Cl}$), 33], 133 (98); Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{Cl}_2\text{O}_2$: C, 69.53; H, 4.57. Found: C, 69.67; H, 4.42.

1'-(3,5-Dimethylphenyl)-1'-(3,5-dimethylbenzoyl)-1-methy-lene-3,5-dichlorocyclohexa-2,5-dien-4-one, 3: mp 253 °C; IR ν (KBr) 1668s, 1649 vs, 1609 cm^{-1} ; ^1H nmr δ 2.36 (s, 12H), 7.09 (s, 2H), 7.12 (s, 1H), 7.26 (s, 1H), 7.30 (d, $J = 1.8$ Hz, 1H), 7.54 (s, 2H), 7.71 (d, $J = 1.8$ Hz, 1H); ^{13}C nmr δ 21.19, 21.29, 127.35, 127.54, 127.86, 132.88, 133.08, 133.74, 134.25, 134.47, 134.76, 135.32, 136.81, 139.03, 139.16, 158.49, 173.07, 195.12; GC-MS m/z 410 [M^+ ($2\times^{35}\text{Cl}$), 68], 375 (100), 133 (98); Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{O}_2$: C, 70.08; H, 4.90. Found: C, 69.96; H, 4.95. **1'-(2,3,4-Trimethylphenyl)-1'-(4-methyl-benzoyl)-1-methylene-3,5-dichlorocyclohexa-2,5-dien-4-one, 4a:** mp 194 °C; ^1H nmr δ 2.22 (s, 3H), 2.29 (s, 3H), 2.31 (s, 3H), 2.42 (s, 3H), 7.02 (m, 2H), 7.29 (m, 3H), 7.42 (d, $J = 1.8$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 2H); ^{13}C nmr δ 15.92, 18.36, 20.92, 21.83, 126.83, 127.67, 129.74, 129.82, 129.99, 130.05, 131.16, 133.20, 133.86, 133.95, 134.45, 134.67, 135.19, 137.24, 139.12, 145.91, 158.48, 194.42; GC-MS m/z 410 [M^+ ($2\times^{35}\text{Cl}$), 4], 119 (100); Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{O}_2$: C, 70.08; H, 4.90. Found: C, 69.86;

H, 4.92. Minor isomer **4b** has GC-MS m/z 410 [M^+ ($2x^{35}Cl$), 6], 147 (100). **1'-(2,3,4-Trimethyl-phenyl)-1'-(3,5-dimethylbenzoyl)-1-methylene-3,5-dichlorocyclohexa-2,5-dien-4-one, 5a**: mp 193 °C; 1H nmr δ 2.13 (s, 3H), 2.21 (s, 6H), 2.26 (s, 6H), 6.93-6.96 (m, 3H), 7.15 (s, 1H), 7.34 (s, 1H), 7.41 (s, 2H); ^{13}C nmr δ 15.89, 18.29, 20.86, 21.12, 21.15, 126.76, 127.49, 127.64, 129.60, 130.97, 133.72, 133.88, 134.01, 134.41, 134.54, 134.63, 135.07, 136.32, 136.42, 137.22, 138.80, 139.11, 158.82, 173.17, 195.19; GC-MS m/z 424 [M^+ ($2x^{35}Cl$), 56], 133 (100); Anal. Calcd for $C_{25}H_{22}Cl_2O_2$: C, 70.59; H, 5.21. Found: C, 70.43; H, 5.22. Minor isomer **5b** has GC-MS m/z 424 [M^+ ($2x^{35}Cl$), 41], 147 (100). **1'-(2,4,6-Tri-methylphenyl)-1'-benzoyl-1-methylene-3,5-dichlorocyclohexa-2,5-dien-4-one, 6a**: mp 197 °C; 1H nmr δ 2.21 (s, 6H), 2.31 (s, 3H), 6.94 (s, 2H), 7.19 (d, $J = 2.4$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.58 (d, $J = 2.4$ Hz, 1H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.86 (d, $J = 7.5$ Hz, 2H); ^{13}C nmr δ 21.02, 21.24, 128.84, 129.40, 129.43, 129.67, 131.42, 132.57, 133.65, 133.77, 134.20, 134.47, 134.55, 135.28, 136.65, 136.66, 139.83, 155.07, 173.17, 194.26; GC-MS m/z 396 [M^+ ($2x^{35}Cl$), 6], 105 (100); Anal. Calcd for $C_{23}H_{18}Cl_2O_2$: C, 69.53; H, 4.57. Found: C, 69.36; H, 4.62. Minor isomer **6b**: GC-MS m/z 396 [M^+ ($2x^{35}Cl$), 4], 147 (100). **1'-(2,4,6-Trimethyl-phenyl)-1'-(3,5-dimethylbenzoyl)-1-methylene-3,5-dichlorocyclohexa-2,5-dien-4-one, 7a**: 1H nmr δ 2.21 (s, 6H), 2.30 (s, 3H), 2.33 (s, 6H), 6.94 (s, 2H), 7.18 (d, $J = 1.8$ Hz, 1H), 7.23 (br s, 1H), 7.44 (s, 2H), 7.59 (d, $J = 1.8$ Hz, 1H); ^{13}C nmr δ 21.01, 21.20, 21.24, 127.33, 127.50, 129.39, 131.38, 132.28, 133.75, 133.93, 134.01, 134.49, 134.60, 135.13, 135.87, 135.99, 136.64, 136.76, 138.52, 139.73, 155.89, 173.23, 194.61; GC-MS m/z 424 [M^+ ($2x^{35}Cl$), 13], 133 (100); Anal. Calcd for $C_{25}H_{22}Cl_2O_2$: C, 70.59; H, 5.21. Found: C, 70.50; H, 5.24.

The minor isomer **7b** has GC-MS m/z 424 [M^+ , ($2x^{35}Cl$), 60], 147 (98). **1'-(2,5-Dimethylphenyl)-1'-(3,5-dimethylbenzoyl)-1-methy-lene-3,5-dichlorocyclohexa-2,5-dien-4-one, 8a:** mp 187 °C; 1H nmr δ 2.30 (s, 3H), 2.35 (s, 6H), 2.66 (s, 3H), 7.05 (s, 2H), 7.11 (s, 1H), 7.25 (m, 2H), 7.37 (d, $J = 1.8$ Hz, 1H), 7.41 (s, 1H), 7.68 (d, $J = 1.8$ Hz, 1H); ^{13}C nmr δ 20.87, 21.29, 21.65, 127.37, 127.44, 127.52, 132.69, 133.25, 133.59, 133.68, 133.80, 133.85, 134.33, 134.43, 134.56, 134.66, 134.75, 134.85, 135.90, 138.36, 139.08, 159.46, 173.06, 196.51; GC-MS m/z 410 [M^+ ($2 \times ^{35}Cl$), 6], 133 (100); Anal. Calcd for $C_{24}H_{20}Cl_2O_2$: C, 70.08; H, 4.90. Found: C, 69.95; H, 5.00. **1'-(3,5-Dimethylphenyl)-1'(2,5-dimethylbenzoyl)-1-methylene-3,5-dichlorocyclohexa-2,5-dien-4-one, 8b:** 1H nmr δ 2.31 (s, 3H), 2.33 (s, 3H), 2.36 (s, 6H), 7.03 (s, 2H), 7.17 (m, 1H), 7.27 (m, 1H), 7.29 (d, $J = 2.1$ Hz, 1H), 7.40 (s, 1H), 7.51 (br s, 2H); GC-MS m/z 410 [m^+ ($2 \times ^{35}Cl$), 4], 133 (100); Anal. Calcd. for $C_{24}H_{20}Cl_2O_2$: C, 70.08; H, 4.90. Found: C, 70.14; H, 4.94. **1'-(2,3,4,5-Pentamethylphenyl)-1'-(benzoyl)-1-methylene-3,5-dichlorocyclohexa-2,5-dien-4-one, 9a:** 1H nmr δ 2.15 (s, 6H), 2.21 (s, 6H), 2.26 (s, 3H), 7.20 (d, $J = 2.1$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.59 (t, $J = 7.2$ Hz, 1H), 7.63 (d, $J = 2.1$ Hz, 1H), 7.83 (d, $J = 7.2$ Hz, 2H); ^{13}C nmr δ 16.62, 17.04, 19.24, 128.79, 129.63, 131.79, 132.61, 133.70, 133.99, 134.20, 134.78, 135.16, 136.82, 148.52, 157.25, 194.47; GC-MS m/z 424 [M^+ ($2x^{35}Cl$), 40], 105 (95); Anal. Calcd for $C_{25}H_{22}Cl_2O_2$: C, 70.59; H, 5.21. Found: C, 70.32; H, 5.34.