

Supporting Information

Modulation of Lifetimes and Diastereomeric Discrimination in Triplet-Excited Substituted Butan-1,4-diones through Intramolecular Charge-Transfer Quenching

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Experimental Section

General Aspects. UV-vis spectra were run on Cary-1 and Cary-5 spectrophotometers and Infrared spectra were recorded on Perkin-Elmer Infrared Ratio-Recording Spectrometer 1320. NMR spectra were run on Bruker AC 300 instrument with deuterated solvents as the internal standards. Mass spectra were recorded on Finnigan GC/MS 3300 and exact mass on a Kratos Concept/H double focusing mass spectrometer employing perfluoro kerosene as an internal standard. Melting points were taken on Gallenkamp apparatus (England) and are not corrected. The combustion analyses were performed by Canadian Microanalytical Service Ltd., Delta, B.C., Canada.

The solvents were used as received and purified by standard procedures where necessary. The commercial chemicals from Aldrich were used as purchased. Column chromatography was conducted on silica gel (particle size: 60-200 μ ; Mallinckrodt Chemicals, USA). For time-resolved work, spectrograde methanol (ACP Chemicals Inc., Montreal, Canada) and reagent grade acetonitrile (ACP Chemicals Inc., Montreal, Canada) were used without further purification. 4-Methoxypropiophenone (Aldrich) was used as received.

Syntheses. Benzyl *p*-methoxyphenyl ketone was prepared according to the reported procedure from Friedel-Crafts acylation of anisole with phenylacetyl chloride in the presence of AlCl_3 .¹ The other benzyl phenyl ketones and 2,4-dimethoxy acetophenone (**5**) were prepared following the same procedure. For 2,4-dimethoxy phenyl derivatives, 1,3-dimethoxy benzene was employed.

α -(*p*-Tolyl)-*p*-methoxyacetophenone: 63%, viscous oil, which solidified on standing; IR (nujol) cm^{-1} 2900, 1660, 1585, 1495, 1330, 1300; ^1H NMR (CDCl_3 , 300 MHz) δ 2.30 (s, 3H), 3.84 (s, 3H), 4.18 (s, 2H), 6.90 (d, $J = 9\text{Hz}$, 2H), 7.10-7.20 (m, 4H), 7.98 (d, $J = 9\text{Hz}$, 2H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 21.1 (q), 44.9 (t), 55.4 (q), 113.8 (d), 129.2 (d), 129.4

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(d), 129.7 (s), 130.9 (d), 131.9 (s), 136.3 (s), 163.5 (s), 196.4 (s); HRMS m/z calcd for $C_{16}H_{16}O_2$ 240.1146, found 240.1152.

α -(*p*-Trifluorotolyl)-*p*-methoxyacetophenone: 54%, colorless plates, mp 132-134 °C; IR (nujol) cm^{-1} 2900, 1660, 1585, 1445, 1320, 1260; 1H NMR ($CDCl_3$, 300 MHz) δ 3.80 (s, 3H), 4.23 (s, 2H), 6.88 (d, $J = 9$ Hz, 2H), 7.31 (d, $J = 9$ Hz, 2H), 7.51 (d, $J = 9$ Hz, 2H), 7.92 (d, $J = 9$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 44.8 (t), 55.5 (q), 113.9 (d), 125.5 (s), 125.5 (d), 129.3 (s), 129.9 (d), 130.9 (d), 138.9 (s), 163.8 (s), 195.2 (s); HRMS m/z calcd for $C_{16}H_{13}F_3O_2$ 294.0864, found 294.0866.

α -(*p*-methoxyphenyl)-*p*-methoxyacetophenone: 69%, colorless needles, mp 99-100 °C; IR (nujol) cm^{-1} 2900, 1665, 1590, 1495, 1325, 1250; 1H NMR ($CDCl_3$, 300 MHz) δ 3.76 (q, 3H), 3.78 (q, 3H), 4.09 (s, 2H), 6.78 (d, $J = 9$ Hz, 2H), 6.87 (d, $J = 9$ Hz, 2H), 7.10 (d, $J = 9$ Hz, 2H), 7.91 (d, $J = 9$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 44.4 (t), 55.2 (q), 55.5 (q), 113.8 (d), 114.1 (d), 126.9 (s), 129.6 (s), 130.4 (d), 130.9 (d), 158.4 (s), 163.5 (s), 196.6 (s); HRMS m/z calcd for $C_{16}H_{16}O_3$ 256.1095, found 256.1099.

α -Phenyl-2,4-dimethoxyacetophenone: 62%, pale yellow viscous oil; IR (neat) cm^{-1} 1650, 1585, 1495, 1240; 1H NMR ($CDCl_3$, 300 MHz) δ 3.74 (s, 3H), 3.79 (s, 3H), 4.18 (s, 2H), 6.34 (d, $J = 3$ Hz, 1H), 6.42, (dd, $J = 9$ Hz, 1H), 7.10 - 7.25 (m, 5H), 7.71 (d, $J = 9$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 50.0 (t), 55.4 (q), 55.5 (q), 98.3 (d), 105.2 (d), 120.9 (s), 126.4 (d), 128.3 (d), 129.6 (d), 133.1 (d), 135.7 (s), 160.7 (s), 164.5 (s), 197.8 (s); HRMS m/z calcd for $C_{16}H_{16}O_3$ 256.1095, found 256.1104.

α -(*p*-methoxyphenyl)-2,4-dimethoxyacetophenone: 65%, pale yellow viscous oil, IR (neat) cm^{-1} 1665, 1590, 1500, 1250; 1H NMR ($CDCl_3$, 300 MHz) δ 3.69 (s, 3H), 3.75 (s, 3H), 3.80 (s, 3H), 4.13 (s, 2H), 6.36 (d, $J = 2$ Hz, 1H), 6.42 (dd, $J = 9$ Hz, 1H), 6.75 (d, $J = 9$ Hz, 2H), 7.05 (d, $J = 9$ Hz, 2H), 7.71 (d, $J = 9$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 49.1 (t), 55.2 (q), 55.4 (q), 55.5 (q), 98.3 (d), 105.2 (d), 113.8 (d), 120.9 (s), 127.8 (s), 130.6 (d), 133.1 (d), 158.2 (s), 160.6 (s), 164.5 (s), 198.2 (s); HRMS m/z calcd for $C_{17}H_{18}O_4$ 286.1200, found 286.1206.

2,4-Dimethoxypropiophenone: 32%, colorless flakes, mp 69-70 °C; IR (nujol) cm^{-1} 1650, 1590, 1410, 1345, 1325, 1275, 1245; 1H NMR ($CDCl_3$, 300 MHz) δ 1.08 (t, $J = 7$ Hz, 3H), 2.89 (q, $J = 7$ Hz, 2H), 3.78 (s, 3H), 3.81 (s, 3H), 6.39 (d, $J = 2$ Hz, 1H), 6.46 (dd, $J = 8$

Hz, 1H), 7.74 (d, $J = 8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 8.6 (q), 36.8 (t), 55.4 (q), 55.5 (q), 98.4 (d), 105.0 (d), 121.5 (s), 132.6 (s), 146.3 (s), 160.7 (s), 164.2 (s), 201.2 (s); HRMS m/z calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$ 194.0942, found 194.0940.

Preparation of Diketones 1 and 2-CF₃. Both the diastereomers of diketone 1 were prepared following the reported procedure.² A similar procedure was employed for the synthesis of diketones 2-CF₃.

To a solution of the corresponding α -(4-trifluorotolyl)-*p*-methoxyacetophenone (1.47 g, 5 mmol) in dry acetone (30 mL) at reflux was added a finely powdered KMnO_4 in small amounts over a period of 3 h under a nitrogen gas atmosphere. The dark-brown reaction mixture was cooled and acetone removed *in vacuo*. The residue was treated with dil. HCl and hydrogen sulfide was bubbled through the resultant solution. The organic material was extracted with dichloromethane (2 \times 200 mL), washed with water and dried over MgSO_4 . The solvent was removed *in vacuo* and the residue was subjected to silica-gel chromatography (30% ethyl acetate in hexanes) to obtain a mixture of *racemic* and *meso* diastereomers of diketones together with a highly viscous liquid impurity. Slow evaporation of the methanolic solution of the residue led to isolation of 0.13 g (9 %) of a mixture of pure *racemic* and *meso* diastereomers. By repetitive recrystallization from diethyl ether-hexane mixtures, the diastereomers were isolated with < 5% (^1H NMR) contamination of each other.

2-CF₃-*rac*: Colorless powder; IR (nujol) cm^{-1} 1645, 1585, 1315, 1245; ^1H NMR (CDCl_3 , 300 MHz) δ 3.80 (s, 6H), 5.42 (s, 2H), 6.85 (d, $J = 9$ Hz, 4H), 7.13 (d, $J = 8$ Hz, 4H), 7.37 (d, $J = 8$ Hz, 4H), 7.93 (d, $J = 9$ Hz, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 55.5 (q), 57.5 (d), 113.9 (d), 125.7 (d), 128.8 (s), 129.0 (d), 129.9 (s), 131.3 (d), 140.6 (s), 163.7 (s), 196.7 (s); HRMS m/z calcd for $\text{C}_{32}\text{H}_{24}\text{F}_6\text{O}_4$ 586.1577, found 586.1582.

2-CF₃-*meso*: Colorless powder; IR (nujol) cm^{-1} 1645, 1585, 1310, 1255; ^1H NMR (CDCl_3 , 300 MHz) δ 3.79 (s, 6H), 5.75 (s, 2H), 6.81 (d, $J = 9$ Hz, 4H), 7.45 (d, $J = 9$ Hz, 4H), 7.63 (d, $J = 9$ Hz, 4H), 7.84 (d, $J = 9$ Hz, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 55.5 (q), 57.5 (d), 113.9 (d), 125.7 (d), 129.2 (s), 129.3 (d), 130.9 (d), 139.1 (s), 141.1 (s), 163.9 (s), 195.8 (s); HRMS m/z calcd for $\text{C}_{32}\text{H}_{24}\text{F}_6\text{O}_4$ 586.1577, found 586.1581.

General Procedure for the Preparation of Diketones 2-H, -CH₃, -OCH₃, and 3-H, -OCH₃.³ To a magnetically stirred solution of freshly distilled diisopropylamine (10 mmol)

in 10 mL of THF was added, under a nitrogen gas atmosphere, butyllithium (11 mmol, 2.5 mol% in hexanes) at $-78\text{ }^{\circ}\text{C}$. After 15-20 min, aryl benzyl ketone (10 mmol) was added to this solution all at once and allowed to stir for another 30 min. To the resulting lithium enolate in THF was added CuCl_2 (11 mmol) in anhydrous DMF (15 mL). The temperature of the deep green reaction mixture was maintained at $-78\text{ }^{\circ}\text{C}$ for 2h and subsequently allowed to attain room temperature. After stirring for 1h, the reaction mixture was treated with dil. HCl and the organic material was extracted with dichloromethane ($2 \times 200\text{ mL}$). The combined extracts were washed with water, dried over MgSO_4 and the solvent removed *in vacuo*. The crude product mixture was subjected to silica-gel chromatography (20% ethyl acetate in hexanes) to isolate a mixture of *racemic* and *meso* diketones together with a highly inseparable unidentified impurity. The pure diketones were obtained as a mixture of the two diastereomers by repetitive crystallization from diethyl ether and methanol. The *racemic* and *meso* isomers were separated by fractional crystallization from methanol and/or diethyl ether-hexane mixtures.

2-H-*rac*: Colorless microcrystalline powder, mp $136\text{-}137\text{ }^{\circ}\text{C}$; IR (nujol) cm^{-1} 1650, 1580, 1490, 1305, 1250; ^1H NMR (CDCl_3 , 300 MHz) δ 3.78 (s, 6H), 5.32 (s, 2H), 6.82 (d, $J = 9\text{ Hz}$, 4H), 6.90 -7.20 (m, 10H), 7.95 (d, $J = 9\text{ Hz}$, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 55.4 (q), 58.1 (d), 113.6 (d), 127.0 (d), 128.6 (d), 129.0 (d), 129.4 (s), 131.2 (d), 136.9 (s), 163.3 (s), 197.9 (s); HRMS m/z calcd for $\text{C}_{30}\text{H}_{26}\text{O}_4$ 450.1829, found 450.1834.

2-H-*meso*: Colorless powder, mp $258\text{-}260\text{ }^{\circ}\text{C}$; IR (nujol) cm^{-1} 1650, 1590, 1560, 1285, 1250; ^1H NMR (CDCl_3 , 300 MHz) δ 3.77 (s, 6H), 5.71 (s, 2H), 6.78 (d, $J = 9\text{ Hz}$, 4H), 7.00-7.20 (m, 6H), 7.51 (d, $J = 9\text{ Hz}$, 4H), 7.87 (d, $J = 9\text{ Hz}$, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 55.4 (q), 55.6 (d), 113.6 (d), 127.2 (s), 128.7 (d), 128.9 (d), 129.9 (s), 130.8 (d), 137.4 (s), 163.4 (s), 196.9 (s); HRMS m/z calcd for $\text{C}_{30}\text{H}_{26}\text{O}_4$ 450.1829, found 450.1836.

2- CH_3 -*rac*: Colorless plates, mp $196\text{-}198\text{ }^{\circ}\text{C}$; IR (nujol) cm^{-1} 1650, 1580, 1490, 1305, 1250; ^1H NMR (CDCl_3 , 300 MHz) δ 2.18 (s, 6H), 3.78 (s, 6H), 5.27 (s, 2H), 6.81 (d, $J = 9\text{ Hz}$, 4H), 6.89 (s, 8H), 7.95 (d, $J = 9\text{ Hz}$, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 21.0 (q), 55.4 (q), 57.6 (d), 113.6 (d), 128.6 (d), 129.3 (d), 129.5 (s), 131.2 (d), 133.8 (s), 136.5 (s), 163.2 (s), 198.2 (s); HRMS m/z calcd for $\text{C}_{32}\text{H}_{30}\text{O}_4$ 478.2142, found 478.2140.

2- CH_3 -*meso*: colorless crystals, mp $229\text{-}230\text{ }^{\circ}\text{C}$; IR (nujol) cm^{-1} 1645, 1585, 1560, 1495, 1300, 1280, 1255; ^1H NMR (CDCl_3 , 300 MHz) δ 2.16 (s, 6H), 3.76 (s, 6H), 5.66 (s, 2H), 6.78 (d, $J = 7\text{ Hz}$, 4H), 6.97 (d, $J = 7\text{ Hz}$, 4H), 7.37 (d, $J = 7\text{ Hz}$, 4H), 7.87 (d, $J = 7\text{ Hz}$, 4H); ^{13}C NMR (CDCl_3 , 50 MHz) δ 21.0 (q), 55.1 (d), 55.4 (q), 113.6 (d), 128.8 (d), 129.4 (d), 129.9

(s), 130.9 (d), 134.5 (s), 136.7 (s), 163.3 (s), 197.0 (s); HRMS m/z calcd for $C_{32}H_{30}O_4$ 478.2142, found 478.2141.

2-OCH₃-rac: Colorless needles, mp 151-152 °C; IR (nujol) cm^{-1} 1640, 1580, 1495, 1290, 1250; ¹H NMR (CDCl₃, 300 MHz) δ 3.68 (s, 6H), 3.78 (s, 6H), 5.23 (s, 2H), 6.64 (d, J = 9 Hz, 4H), 6.82 (d, J = 9 Hz, 4H), 6.91 (J = 9 Hz, 4H), 7.94 (d, J = 9 Hz, 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 55.1 (q), 55.4 (q), 57.2 (d), 113.6 (d), 114.0 (d), 129.0 (s), 129.5 (s), 129.8 (d), 131.2 (d), 158.5 (s), 163.2 (s), 198.3 (s); HRMS m/z calcd for $C_{32}H_{30}O_6$ 510.2040, found 510.2043.

2-OCH₃-meso: Colorless microcrystalline powder, mp 203-204 °C; IR (nujol) cm^{-1} 1645, 1590, 1490, 1300, 1240; ¹H NMR (CDCl₃, 300 MHz) δ 3.65 (s, 6H), 3.77 (s, 6H), 5.61 (s, 2H), 6.70 (d, J = 9 Hz, 4H), 6.79 (d, J = 9 Hz, 4H), 7.40 (d, J = 9 Hz, 4H), 7.86 (d, J = 9 Hz, 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 54.8 (d), 55.1 (q), 55.4 (q), 113.6 (d), 114.1 (d), 129.5 (2 \times s), 130.0 (d), 130.8 (d), 158.5 (s), 163.3 (s), 197.2 (s); Anal. calcd for $C_{32}H_{30}O_6$ (510.65): C, 75.27; H, 5.93. Found: C, 74.98; H, 5.91.

3-H-rac: Colorless powder, mp 164-165 °C; IR (nujol) cm^{-1} 1640, 1585, 1315, 1265, 1240, 1200; ¹H NMR (CDCl₃, 300 MHz) δ 3.73 (s, 6H), 3.77 (s, 6H), 5.40 (s, 2H), 6.30 (d, J = 2Hz, 2H), 6.43 (dd, J = 9 Hz, 2H), 6.80-6.90 (m, 4H), 6.95-7.05 (m, 6H), 7.88 (d, J = 9 Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 55.2 (q), 55.4 (q), 62.2 (d), 98.4 (d), 105.0 (d), 126.2 (d), 127.7 (d), 127.9 (s), 129.4 (d), 133.6 (d), 137.6 (s), 160.5 (s), 164.2 (s), 198.9 (s); HRMS m/z calcd for $C_{32}H_{30}O_6$ 510.2040, found 510.2046.

3-H-meso: Colorless powder, mp 214-216 °C; IR (nujol) cm^{-1} 1630, 1585, 1480, 1270, 1200; ¹H NMR (CDCl₃, 300 MHz) δ 3.73 (s, 6H), 3.81 (s, 6H), 5.81 (s, 2H), 6.26 (dd, J = 12 Hz, 2H), 6.27 (d, J = 2 Hz, 2H), 7.06 (t, J = 7 Hz, 2H), 7.15 (t, J = 7 Hz, 4H), 7.22 (d, J = 12 Hz, 2H), 7.46 (d, J = 7 Hz, 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 55.4 (2 \times q), 60.1 (d), 98.2 (d), 104.8 (d), 126.6 (d), 127.9 (d), 129.2 (s), 129.7 (d), 132.7 (d), 138.1 (s), 160.0 (s), 163.9 (s), 199.7 (s); HRMS m/z calcd for $C_{32}H_{30}O_6$ 510.2040, found 510.2042.

3-OCH₃-rac: Colorless needles, mp 133-134 °C; IR (nujol) cm^{-1} 1640, 1590, 1480, 1275, 1240; ¹H NMR (CDCl₃, 300 MHz) δ 3.67 (s, 6H), 3.74 (s, 6H), 3.77 (s, 6H), 5.30 (s, 2H), 6.30 (d, J = 2Hz, 2H), 6.43 (dd, J = 9Hz, 2H), 6.58(d, J = 9Hz, 4H), 6.81 (d, J = 9Hz, 4H), 7.85 (d, J = 9Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 55.0 (q), 55.3 (q), 55.4 (q), 61.2 (d),

98.4 (d), 104.9 (d), 113.2 (d), 120.8 (s), 129.7 (s), 130.4 (d), 133.5 (d), 158.0 (s), 160.5 (s), 164.1 (s), 199.0 (s); HRMS m/z calcd for $C_{34}H_{34}O_8$ 570.2244, found 570.2241.

3-OCH₃-meso: Colorless crystals, mp 172-173 °C; IR (nujol) cm^{-1} 1640, 1590, 1490, 1280, 1240; ¹H NMR (CDCl₃, 300 MHz) δ 3.68 (s, 6H), 3.73 (s, 6H), 3.82 (s, 6H), 5.72 (s, 2H), 6.27 (d, J = 9Hz, 2H), 6.29 (s, 2H), 6.69 (d, J = 9Hz, 4H), 7.27 (d, J = 9Hz, 2H), 7.35 (d, J = 9Hz, 4H); ¹³C NMR (CDCl₃, 50 MHz) δ 55.1 (q), 55.3 (q), 55.4 (q), 59.1 (d), 98.2 (d), 104.8 (d), 113.4 (d), 122.0 (s), 130.2 (s), 130.7 (d), 132.7 (d), 158.2 (s), 160.0 (s), 163.8 (s), 199.9 (s); Anal. calcd for $C_{34}H_{34}O_8$ (570.65): C, 71.56; H, 6.01. Found: C, 71.34; H, 6.21.

Preparation of 1,4-bis(4-methoxyphenyl)butan-1,4-dione (6) and 1,4-bis(2,4-dimethoxyphenyl)butan-1,4-dione (7). The diketone **6** was synthesized from the known Friedel-Crafts reaction between anisole and succinyl chloride in the presence of AlCl₃.⁴ The diketone **7** was similarly prepared.

7: 7%, colorless fine needles, mp 128-129 °C, IR (nujol) cm^{-1} 2900, 1630, 1580, 1485, 1410, 1280; ¹H NMR (CDCl₃, 300 MHz) 3.34 (s, 4H), 3.84 (s, 6H), 3.88 (s, 6H), 6.44 (d, J = 2 Hz, 2H), 6.52 (dd, J = 8 Hz, 2H), 7.84 (d, J = 8Hz, 2H); ¹³C NMR (CDCl₃, 50 MHz) δ 38.2 (t), 55.5 (q), 98.3 (d), 105.0 (d), 121.1 (s), 132.8 (d), 160.9 (s), 164.3 (s), 199.1 (s); HRMS m/z calcd for $C_{20}H_{22}O_6$ 358.1414, found 358.1419.

References

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Figure S1. Structures for the lowest energy staggered conformations of **2-H-meso** and **2-H-rac** obtained by MM PI calculations. The distances between the oxygen atoms on the carbonyls and the closest carbon on the β -phenyl rings are indicated in Ångstroms.

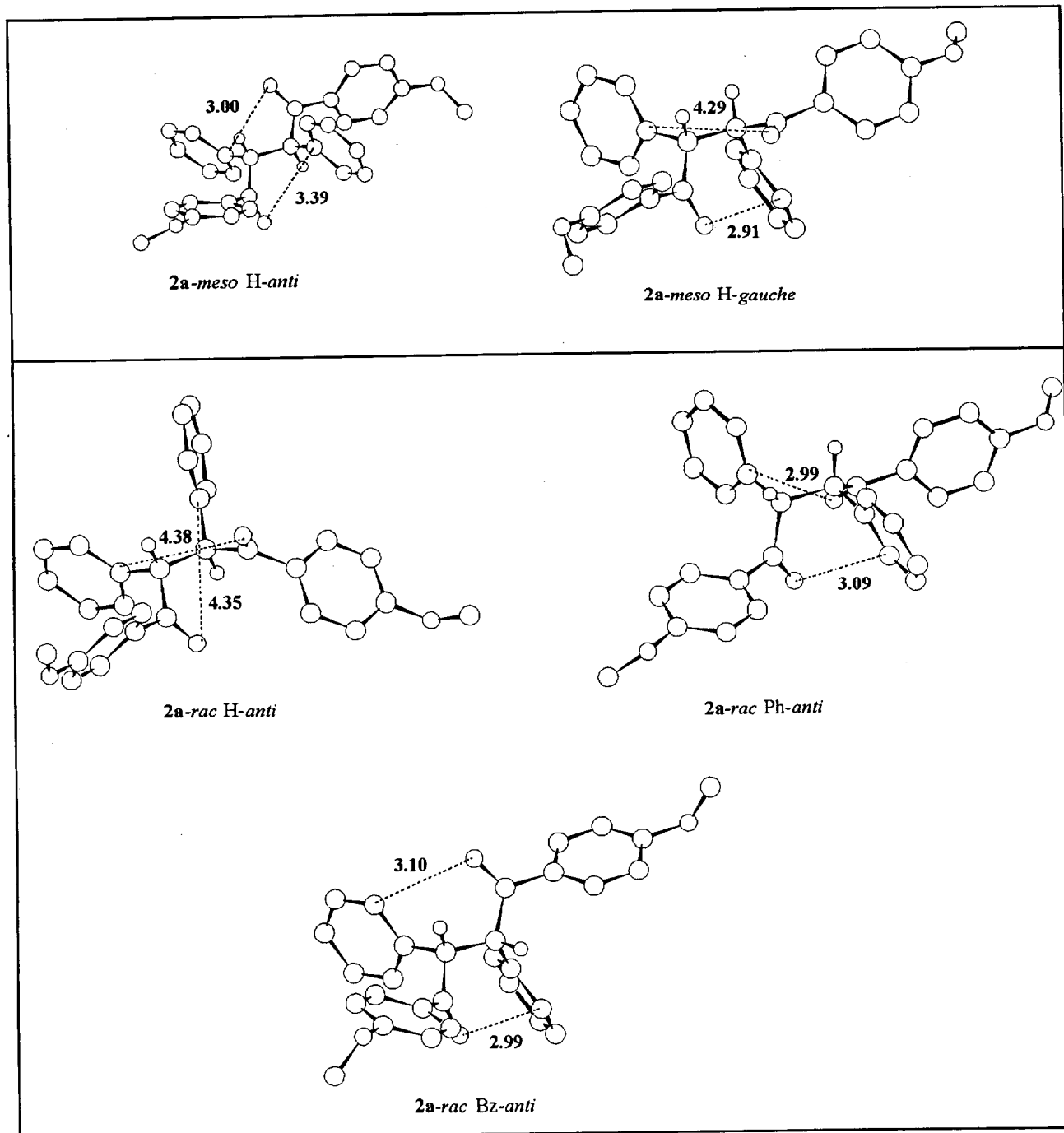


Figure S2. Structures for the lowest energy staggered conformations of **3-H-meso** and **3-H-rac** obtained by MM PI calculations. The distances between the oxygen atoms on the carbonyls and the closest carbon on the β -phenyl rings are indicated in Ångstroms.

