Supplemental information

*The effect of orientation of the lateral methyl substituent on the mesophase behavior of 4-alkoxyphenylazo aryl benzoates*

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Table S1. FT-IR absorption spectra of compounds II8a-f and III/2a-f.

| Compound | X        | νCH₃ Asym. | νCH₃ Sym. | νC=O | νC=N | νC-O | νC=O | νNO₂ | νC≡N |
|----------|----------|------------|-----------|------|------|------|------|------|------|
| II8a     | CH₃O     | 2927       | 2857      | 1730 | 1603 | 1469 | 1244 | -    | -    |
| II8b     | CH₃      | 2925       | 2855      | 1738 | 1605 | 1467 | 1246 | -    | -    |
| II8c     | H        | 2925       | 2855      | 1740 | 1602 | 1465 | 1254 | -    | -    |
| II8d     | Br       | 2926       | 2856      | 1740 | 1592 | 1469 | 1255 | -    | -    |
| II8e     | NO₂      | 2925       | 2855      | 1739 | 1602 | 1469 | 1254 | 1526 | -    |
| II8f     | CN       | 2925       | 2855      | 1739 | 1602 | 1466 | 1252 | -    | 2227 |
| III/2a   | CH₃O     | 2928       | 2856      | 1734 | 1603 | 1470 | 1253 | -    | -    |
| III/2b   | CH₃      | 2921       | 2851      | 1737 | 1603 | 1471 | 1250 | -    | -    |
| III/2c   | H        | 2924       | 2853      | 1738 | 1601 | 1469 | 1254 | -    | -    |
| III/2d   | Br       | 2922       | 2853      | 1736 | 1590 | 1467 | 1256 | -    | -    |
| III/2e   | NO₂      | 2929       | 2855      | 1735 | 1608 | 1476 | 1250 | 1524 | -    |
| III/2f   | CN       | 2923       | 2853      | 1739 | 1604 | 1475 | 1250 | -    | 2230 |
Table S2. $^1$H-NMR spectra (in ppm) of compounds II$^8_{a-f}$ and III/1$^2_{a-f}$.

![Diagram of molecule]

| Comp No. | X     | Y     | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 | 11 | 12 |
|----------|-------|-------|----|----|----|----|----|----|----|----|----|----|----|----|
| II$^8_a$ | CH$_3$O| 2-CH$_3$| 0.85 | 1.30 | 1.78 | 3.98 | 6.95 | 7.85 | 7.82 | 7.19 | 2.25 | 8.14 | 6.96 | 3.84 |
| II$^8_b$ | CH$_3$| 2-CH$_3$| 0.93 | 1.37 | 1.84 | 4.06 | 7.00 | 7.92 | 7.81 | 7.27 | 2.34 | 8.14 | 7.03 | 2.48 |
| II$^8_c$ | H     | 2-CH$_3$| 3-CH$_3$| 0.84 | 1.43 | 1.75 | 4.08 | 6.90 | 7.91 | 7.63 | 7.26 | 2.69 | 8.14 | 7.38 |
| II$^8_d$ | Br    | 2-CH$_3$| 0.94 | 1.37 | 1.72 | 4.07 | 7.00 | 7.81 | 7.86 | 7.27 | 2.48 | 8.17 | 7.02 |    |
| II$^8_e$ | NO$_2$| 2-CH$_3$| 0.96 | 1.33 | 1.71 | 3.94 | 6.97 | 7.82 | 7.81 | 7.23 | 2.38 | 8.40 | 8.34 |    |
| II$^8_f$ | CN    | 2-CH$_3$| 0.96 | 1.33 | 1.71 | 3.94 | 6.97 | 7.82 | 7.81 | 7.23 | 2.36 | 8.32 | 7.66 |    |
| III/1$^2_a$ | CH$_3$O| 3-CH$_3$| 0.86 | 1.31 | 1.73 | 4.01 | 6.94 | 7.89 | 7.80 | 7.21 | 2.23 | 8.15 | 7.01 | 3.85 |
| III/1$^2_b$ | CH$_3$| 3-CH$_3$| 0.85 | 1.43 | 1.75 | 4.08 | 7.11 | 7.90 | 7.63 | 7.21 | 2.68 | 8.05 | 7.36 | 2.43 |
| III/1$^2_c$ | H     | 3-CH$_3$| 0.84 | 1.43 | 1.75 | 4.08 | 6.90 | 7.91 | 7.63 | 7.26 | 2.69 | 8.14 | 7.38 | (7.65)* |
| III/1$^2_d$ | Br    | 3-CH$_3$| 0.85 | 1.43 | 1.74 | 4.08 | 7.11 | 7.90 | 7.63 | 7.37 | 2.68 | 8.06 | 7.38 | -   |
| III/1$^2_e$ | NO$_2$| 3-CH$_3$| 0.85 | 1.43 | 1.75 | 4.08 | 7.11 | 7.90 | 7.65 | 7.28 | 2.69 | 8.39 | 7.42 | -   |
| III/1$^2_f$ | CN    | 3-CH$_3$| 0.85 | 1.43 | 1.75 | 4.08 | 7.11 | 7.90 | 7.64 | 7.27 | 2.69 | 8.28 | 7.41 | -   |

*Data for unsubstituted derivative
Table S3. Mass spectra of compounds II8a-f and III12a-f.

| Comp No. | n   | X          | Y   | Molar mass | C₆H₆+1OC₆H₄N₂–C₆H₃(Y)O | OC₆H₆N₂–C₆H₃(Y)O | OC₆H₄N₂ | X–C₆H₄CO | OC₆H₄N₂–C₆H₃(Y)OCOC₆H₄X |
|----------|-----|------------|-----|------------|-------------------------|-------------------|----------|----------|----------------------------|
| II8a     | 8   | CH₃        | 2-CH₃ | 474        | 339                     | 227              | 120      | 135      | 361                        |
| II10b    | 10  | CH₃        | 2-CH₃ | 486        | 367                     | 227              | 120      | 119      | 345                        |
| II10c    | 10  | H          | 2-CH₃ | 472        | 367                     | 227              | 120      | 105      | 331                        |
| II8d     | 8   | Br         | 2-CH₃ | 524        | 339                     | 227              | 120      | 183      | 411                        |
| II8e     | 8   | NO₂        | 2-CH₃ | 489        | 339                     | 227              | 120      | 150      | 376                        |
| II8f     | 8   | CN         | 2-CH₃ | 469        | 339                     | 227              | 120      | 130      | 356                        |
| III12a   | 12  | CH₃        | 3-CH₃ | 530        | 395                     | 227              | 120      | 135      | 361                        |
| III12b   | 12  | CH₃        | 3-CH₃ | 514        | 395                     | 227              | 120      | 119      | 345                        |
| III12c   | 12  | H          | 3-CH₃ | 500        | 395                     | 227              | 120      | 105      | 331                        |
| III12d   | 12  | Br         | 3-CH₃ | 580        | 395                     | 227              | 120      | 183      | 411                        |
| III12e   | 12  | NO₂        | 3-CH₃ | 545        | 395                     | 227              | 120      | 150      | 376                        |
| III12f   | 12  | CN         | 3-CH₃ | 525        | 395                     | 227              | 120      | 130      | 356                        |
Table S4. Elemental analyses calculated (and found) for 4-(4′-alkoxy phenylazo) 2-methyl phenyl 4″-substituted benzoates, IIₜₜₜₜ-⅞ₜₜₜₜ.

| Comp | n | X   | Mol. wt | Elemental analysis Cal. (Found) | % C   | % H   | % N   | % Br |
|------|---|-----|---------|--------------------------------|-------|-------|-------|------|
| II₆ₐ |   | OCH₃ | 446.55  |                                 | 77.62 (77.57) | 6.77 (6.75) | 6.27 (6.33) | -    |
| II₆₉ |   | CH₃  | 430.55  |                                 | 75.32 (75.30) | 7.02 (7.04) | 6.51 (6.53) | -    |
| II₆₅ |   | H    | 416.52  |                                 | 74.97 (74.87) | 6.78 (6.57) | 6.73 (6.50) | -    |
| II₆₈ |   | Br   | 495.42  |                                 | 63.03 (63.05) | 5.49 (5.45) | 5.65 (5.63) | 16.13 (16.16) |
| II₆₆ |   | NO₂  | 461.52  |                                 | 67.66 (67.33) | 5.90 (5.92) | 9.10 (9.80) | -    |
| II₆₇ |   | CN   | 441.53  |                                 | 73.45 (73.42) | 6.16 (6.13) | 9.52 (9.53) | -    |
| II₈₉ | 8 | OCH₃ | 474.60  |                                 | 73.39 (73.61) | 7.22 (7.45) | 5.90 (6.02) | -    |
| II₈₉ |   | CH₃  | 458.60  |                                 | 75.95 (75.89) | 7.47 (7.69) | 6.11 (6.42) | -    |
| II₈₆ |   | H    | 444.58  |                                 | 75.65 (75.93) | 7.26 (7.59) | 6.30 (6.56) | -    |
| II₈₉ |   | Br   | 523.47  |                                 | 64.25 (64.45) | 5.97 (6.14) | 5.35 (5.49) | 15.26 (15.39) |
| II₈₆ |   | NO₂  | 489.57  |                                 | 68.69 (68.94) | 6.38 (6.70) | 8.58 (8.75) | -    |
| II₈₆ |   | CN   | 469.59  |                                 | 74.18 (74.53) | 6.65 (6.86) | 8.95 (8.84) | -    |
| II₁₀₉ | 10 | OCH₃ | 502.66  |                                 | 74.07 (74.23) | 7.62 (7.51) | 5.57 (5.82) | -    |
| II₁₀₉ |   | CH₃  | 486.66  |                                 | 76.51 (76.76) | 7.87 (7.70) | 5.76 (5.48) | -    |
| II₁₀₉ |   | H    | 472.63  |                                 | 76.24 (76.49) | 7.68 (7.95) | 5.93 (6.19) | -    |
| II₁₀₉ |   | Br   | 551.53  |                                 | 65.33 (65.54) | 6.40 (6.23) | 5.08 (5.27) | 14.49 (14.65) |
| II₁₀₉ |   | NO₂  | 517.63  |                                 | 69.61 (69.87) | 6.82 (6.66) | 8.12 (8.39) | -    |
| II₁₀₉ |   | CN   | 497.64  |                                 | 74.82 (74.97) | 7.09 (7.36) | 8.44 (8.71) | -    |
| II₁₂₉ | 12 | OCH₃ | 530.71  |                                 | 74.69 (74.41) | 7.98 (7.69) | 5.28 (5.49) | -    |
| II₁₂₉ |   | CH₃  | 524.71  |                                 | 77.01 (77.27) | 8.22 (8.38) | 5.44 (5.73) | -    |
| II₁₂₉ |   | H    | 500.68  |                                 | 76.77 (76.95) | 8.05 (8.30) | 5.60 (5.86) | -    |
| II₁₂₉ |   | Br   | 579.57  |                                 | 66.32 (66.63) | 6.78 (6.96) | 4.83 (4.98) | 13.79 (13.91) |
| II₁₂₉ |   | NO₂  | 545.68  |                                 | 70.44 (70.59) | 7.20 (7.48) | 7.70 (7.94) | -    |
| II₁₂₉ |   | CN   | 525.69  |                                 | 75.40 (75.77) | 7.48 (7.76) | 7.99 (8.23) | -    |
Table S5. Elemental analyses calculated (and found) for 4-(4’-alkoxy phenylazo) 3-methyl phenyl 4”-substituted benzoates, III_{a-f}.

| Comp. | n | X     | Mol. wt | Elemental analysis Cal. (Found) |
|-------|---|-------|---------|--------------------------------|
|       |   |       |         | % C  | % H  | % N  | % Br |
| III_{6a} | 6 | OCH₃  | 446.55  | 77.62 (77.57) | 6.77 (6.75) | 6.27 (6.33) | -   |
| III_{6b} |   | CH₃   | 430.55  | 75.32 (75.30) | 7.02 (7.04) | 6.51 (6.53) | -   |
| III_{6c} |   | H     | 416.52  | 74.97 (74.75) | 6.78 (6.44) | 6.73 (6.39) | -   |
| III_{6d} |   | Br    | 495.42  | 63.03 (63.05) | 5.49 (5.45) | 5.65 (5.62) | 16.13 (16.16) |
| III_{6e} |   | NO₂   | 461.52  | 67.66 (67.63) | 5.90 (5.92) | 9.10 (9.80) | -   |
| III_{6f} |   | CN    | 441.53  | 73.45 (73.42) | 6.16 (6.13) | 9.52 (9.53) | -   |
| III_{8a} | 8 | OCH₃  | 474.60  | 73.39 (73.55) | 7.22 (7.58) | 5.90 (6.07) | -   |
| III_{8b} |   | CH₃   | 458.60  | 75.95 (75.73) | 7.47 (7.63) | 6.11 (6.35) | -   |
| III_{8c} |   | H     | 444.58  | 75.65 (75.87) | 7.26 (7.55) | 6.30 (6.48) | -   |
| III_{8d} |   | Br    | 523.47  | 64.25 (64.59) | 5.97 (6.04) | 5.35 (5.51) | 15.26 (15.47) |
| III_{8e} |   | NO₂   | 489.57  | 68.69 (68.89) | 6.38 (6.62) | 8.58 (8.81) | -   |
| III_{8f} |   | CN    | 469.59  | 74.18 (74.40) | 6.65 (6.72) | 8.95 (8.79) | -   |
| III_{10a} | 10 | OCH₃  | 502.66  | 74.07 (74.45) | 7.62 (7.34) | 5.57 (5.70) | -   |
| III_{10b} |   | CH₃   | 486.66  | 76.51 (76.69) | 7.87 (7.64) | 5.76 (5.33) | -   |
| III_{10c} |   | H     | 472.63  | 76.24 (76.53) | 7.68 (7.91) | 5.93 (6.01) | -   |
| III_{10d} |   | Br    | 551.53  | 65.33 (65.25) | 6.40 (6.28) | 5.08 (5.30) | 14.49 (14.58) |
| III_{10e} |   | NO₂   | 517.63  | 69.61 (69.93) | 6.82 (6.57) | 8.12 (8.33) | -   |
| III_{10f} |   | CN    | 497.64  | 74.82 (74.95) | 7.09 (7.26) | 8.44 (8.62) | -   |
| III_{12a} | 12 | OCH₃  | 530.71  | 74.69 (74.44) | 7.98 (7.76) | 5.28 (5.45) | -   |
| III_{12b} |   | CH₃   | 524.71  | 77.01 (77.36) | 8.22 (8.08) | 5.44 (5.61) | -   |
| III_{12c} |   | H     | 500.68  | 76.77 (76.83) | 8.05 (8.24) | 5.60 (5.77) | -   |
| III_{12d} |   | Br    | 579.57  | 66.32 (66.54) | 6.78 (6.92) | 4.83 (5.01) | 13.79 (13.98) |
| III_{12e} |   | NO₂   | 545.68  | 70.44 (70.48) | 7.20 (7.52) | 7.70 (7.89) | -   |
| III_{12f} |   | CN    | 525.69  | 75.40 (75.53) | 7.48 (7.61) | 7.99 (8.19) | -   |