Supplementary Material (ESI) for Chemical Communications


# Achieving conformational control over C–C, C–N and C–O bonds in biaryls, *N*,*N*'-diarylureas and diaryl ethers: advantages of a relay axis.

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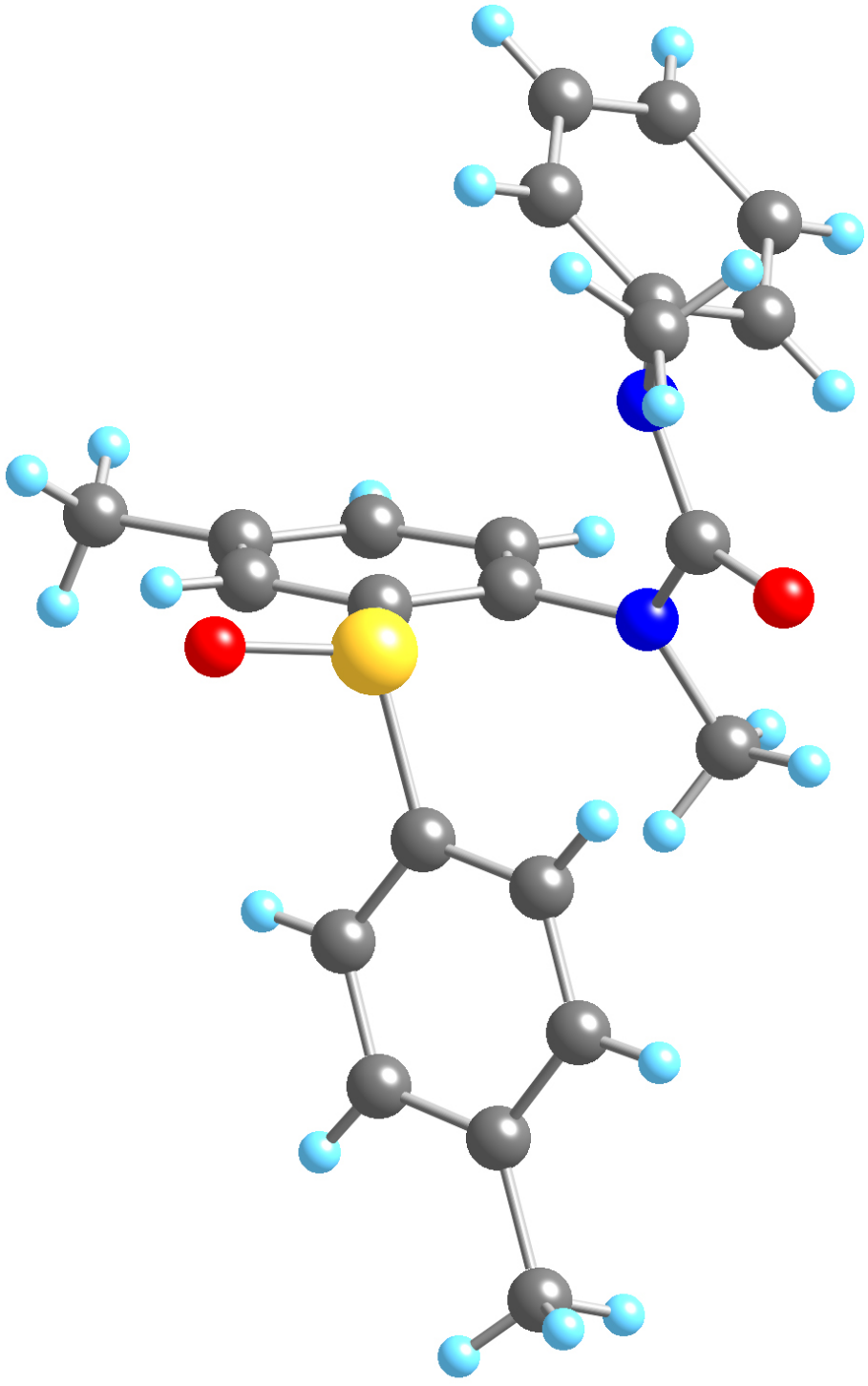
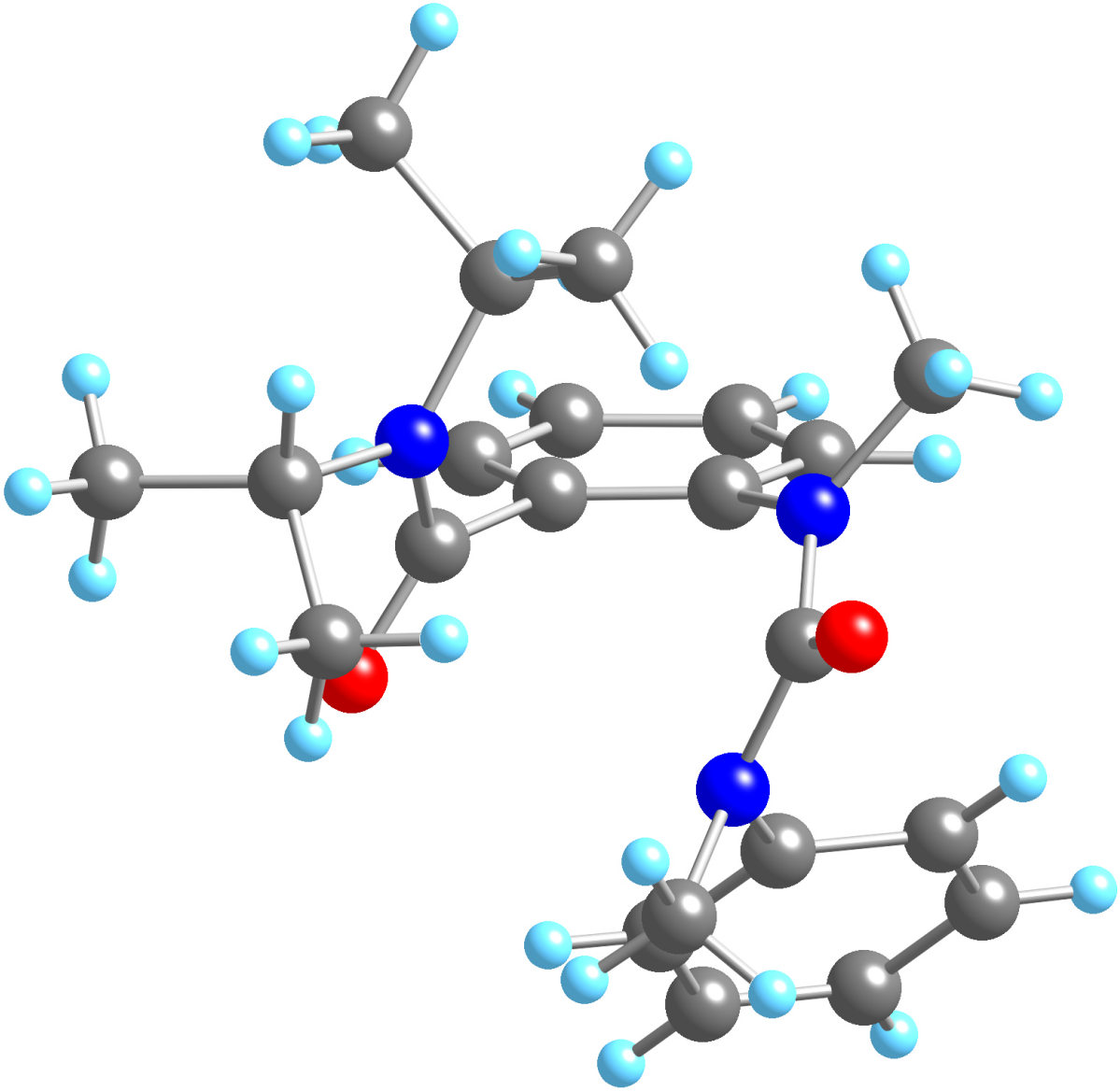
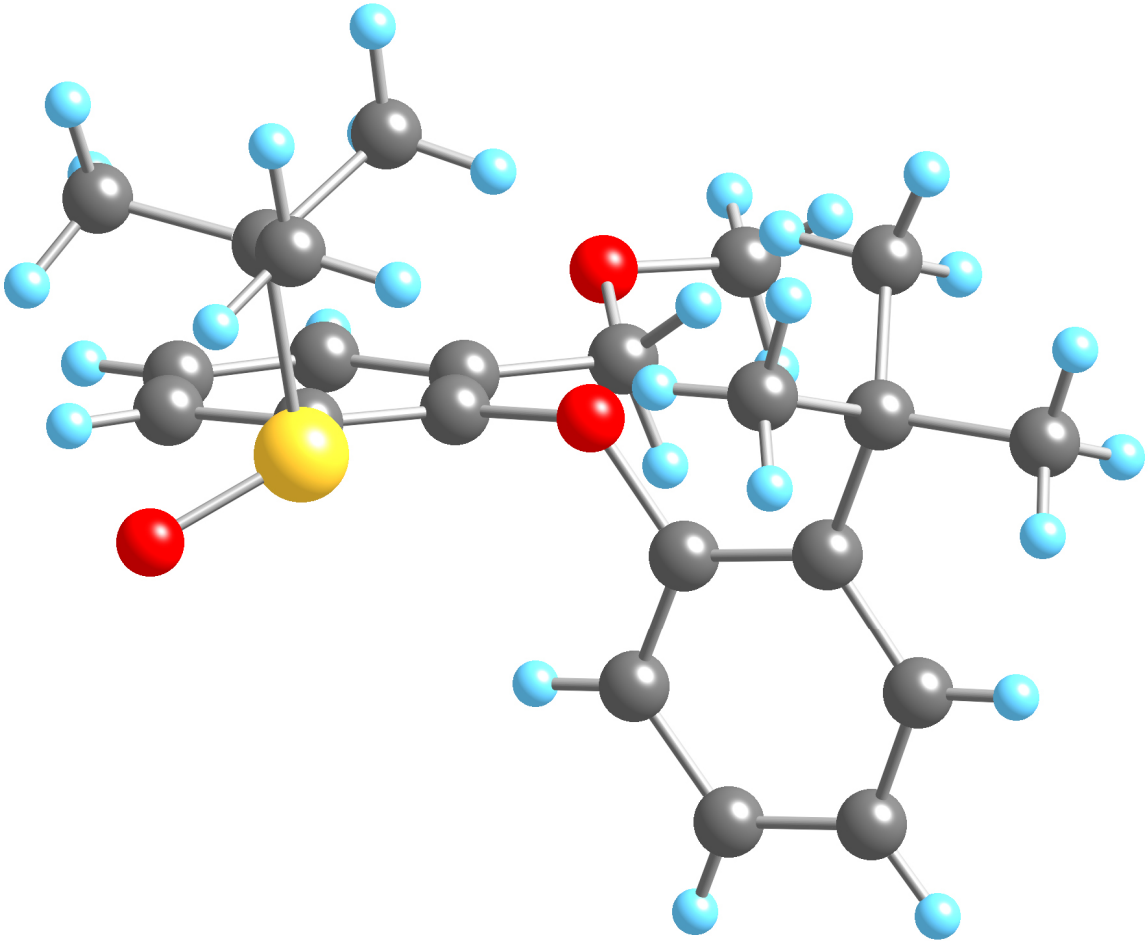
**4x** (R = H, Z = *p*-Tol): $C_{23}H_{24.5}N_2O_{2.25}$; $M = 397.01$; monoclinic, $C2$; $a = 24.932(6)$, $b = 8.345(3)$, $c = 10.856(3)$ Å; $\beta = 108.65(2)°$; $V = 2140.3(10)$ Å$^3$; $T = 100(2)$ K; $Z = 4$; $\mu = 0.173$ mm$^{-1}$; 2700 reflections collected of which 1230 unique; $R_{int} = 0.0425$;



**4z** (R = H): $C_{22}H_{29}N_3O_2$; $M$ = 367.48; orthorhombic, *Fdd*2; $a$ = 25.675(3), $b$ = 39.811(4), $c$ = 7.9886(8) Å; $V$ = 8165.5(15) Å$^3$; $T$ = 100(2) K; $Z$ = 16; $\mu$ = 0.077 mm$^{-1}$; 11773 reflections collected of which 2263 unique; $R_{int}$ = 0.0430;



**5x** (R = $CH_2OMe$, Z = *t*-Bu): $C_{22}H_{30}O_3S$; $M$ = 374.52; monoclinic, $P2(1)/c$; $a$ = 8.3358(11), $b$ = 12.2620(17), $c$ = 20.222(3) Å; $\beta$ = 98.368(2)°; $V$ = 2044.9(5) $Å^3$; $T$ = 100(2) K; $Z$ = 4; $\mu$ = 0.176 $mm^{-1}$; 14180 reflections collected of which 3606 unique; $R_{int}$ = 0.1272;



**10y**: $C_{33}H_{42}N_4O_3$; $M$ = 542.71; orthorhombic, $P2(1)2(1)2(1)$; $a$ = 9.5280(5), $b$ = 15.8200(8), $c$ = 20.1410(10) Å; $V$ = 3035.9(3) Å$^3$; $T$ = 100(2) K; $Z$ = 4; $\mu$ = 0.077 mm$^{-1}$; 26380 reflections collected of which 4121 unique; $R_{int}$ = 0.0374