Electronic Supplementary Information for

Substituted 6-oxoverdazyl bent-core nematic radicals: synthesis and characterization

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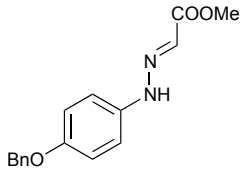
Table of Content:

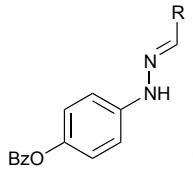
1. Additional synthetic details

Synthesis of methyl glyoxylate 4-benzyloxyphenylhydrazone (4b).



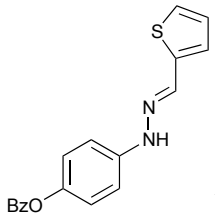
To a suspension of 4-benzyloxyphenylhydrazine hydrochloride[1] (**2**, 2.92 g, 9.69 mmol) in dry THF (10 mL) was added triethylamine (1.3 mL, 9.69 mmol) followed by dropwise addition of a solution of crude, freshly prepared methyl glyoxylate[2] (853 mg, 9.69 mmol) in THF (10 mL) at 0 °C. The mixture was stirred at room temperature overnight, filtered, and the filtrate was washed with 2% HCl (20 mL) and water (2 × 15 mL). After drying of the extracts over Na_2SO_4, the solvents were removed under reduced pressure, and the crude product was purified by flash column chromatography (SiO_2, $CHCl_3$/EtOAc 10:1) to give hydrazone **4b** as a yellow solid (1.37 g, 50%): mp 175-177 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.79 (s, 3H), 5.05 (s, 2H), 6.61 (s_{br}, 1H), 6.95 and 7.13 (2 d_{br}, J = 8.9 Hz, 2H each), 7.30-7.34 (m, 5H), 12.2 (s_{br}, 1H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 51.1 (q), 70.6 (t), 115.2 (d), 115.9 (d), 116.8 (d), 127.5 (d), 127.9 (d), 128.6 (d), 137.0 (s), 137.1 (s, higher int.), 154.9 (s), 164.2 (s); IR (KBr) ν 3265 (NH), 1700 (C=O), 1540, 1505, 1220, 1155 cm^{-1}; ESI-MS (*m*/*z*): 307 (100, $[M+Na]^+$).

Synthesis of hydrazones 5.



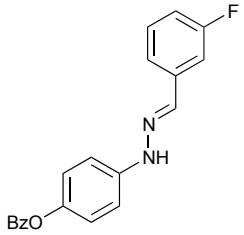
To a suspension of 4-benzoyloxyphenylhydrazine hydrochloride[1] (**3**, 2.65 g, 10.0 mmol) in EtOH (40 mL) the corresponding aldehyde (11.0 mmol) was added dropwise at 0 °C, and the resulting mixture was stirred at room temperature overnight. The mixture was placed in the fridge for 6 hrs, the precipitate was filtered, washed with several portions of cooled ethanol, and air dried to give crude hydrazone, that was used for the next step without further purification. Spectroscopically pure samples were obtained by recrystallization from EtOH.

2-Thienal 4-benzoyloxyphenylhydrazone (5c).



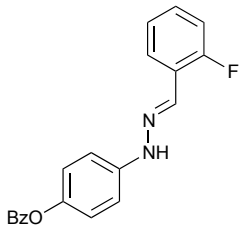
Yellowish crystals (2.48 g, 77%); mp 189-192 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.01 (dd, J = 5.0, 3.6 Hz, 1H), 7.09 (d_{br}, J = 3.6 Hz, 1H), 7.10-7.14 (m, 4H), 7.26 (d_{br}, J = 4.9 Hz, 1H), 7.51 (t_{br}, J = 7.8 Hz, 2H), 7.58 (s_{br}, 1H), 7.61-7.64 (m, 1H), 7.87 (s, 1H), 8.21 (dd_{br}, J_1 = 8.3 Hz, J_2 = 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 113.4 (d), 122.3 (d), 126.0 (d), 126.5 (d), 127.2 (d), 128.5 (d), 129.9 (s), 130.1 (d), 132.5 (d), 133.4 (d), 140.4 (s), 142.4 (s), 144.3 (s), 165.6 (s); IR (KBr) ν 3310 (NH), 1715 (C=O), 1605, 1535, 1515, 1500, 1265, 1195 cm^{-1}; ESI-MS (*m*/*z*): 345 (100, $[M+Na]^+$), 323 (14, $[M+H]^+$).

3-Flurobenzaldehyde 4-benzoyloxyphenylhydrazone (5e).



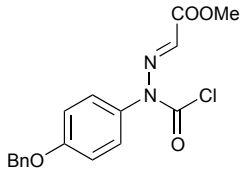
Off-white solid (2.47 g, 74%); mp 191-194 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 6.97-7.02 (m, 1H), 7.15 (s_{br}, 4H), 7.33 (td, J_1 = 7.8 Hz, J_2 = 5.7 Hz, 1H), 7.37 (d_{br}, J = 7.7 Hz, 1 H), 7.40-7.43 (m, 1H), 7.51 (t_{br}, J = 7.8 Hz, 2H), 7.62-7.65 (m, 1H), 7.67 (s, 1H), 8.21 (dd_{br}, J_1 = 8.5 Hz, J_2 = 1.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 112.3 (d, q: $^{2}J_{C\text{-}F}$ = 22.8 Hz), 113.4 (d), 115.3 (d, q: $^{2}J_{C\text{-}F}$ = 21.7 Hz), 122.1 (d, q: $^{4}J_{C\text{-}F}$ = 2.7 Hz), 128.5 (d), 130.0 (d, q: $^{3}J_{C\text{-}F}$ = 8.4 Hz), 130.1 (d), 133.4 (d), 135.9 (d, q: $^{4}J_{C\text{-}F}$ = 3.4 Hz), 137.6 (s, q: $^{3}J_{C\text{-}F}$ = 8.1 Hz), 142.2 (s), 144.5 (s), 163.2 (s, q: $^{1}J_{C\text{-}F}$ = 245.5 Hz), 165.6 (s); $\{^{1}H\}^{19}$F-NMR ($CDCl_3$, 565 MHz) δ –113.2; IR (KBr) ν 3300 (NH), 1715 (C=O), 1590, 1535, 1505, 1280, 1265, 1195, 1130 cm^{-1}; ESI-MS (*m*/*z*): 357 (100, $[M+Na]^+$), 335 (34, $[M+H]^+$).

2-Flurobenzaldehyde 4-benzoyloxyphenylhydrazone (5f).

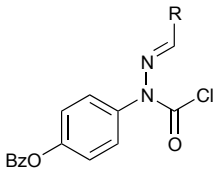


Off-white solid (2.54 g, 76%); mp 202-205 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.03-7.08 (m, 1H), 7.13-7.19 (m, 5H), 7.25-7.29 (m, 1H), 7.51 (t_{br}, J = 7.6 Hz, 2H), 7.63 (t_{br}, J = 7.6 Hz, 1H), 7.79 (s_{br}, 1H, NH), 7.96 (s, 1H), 8.01 (t, J = 7.5 Hz, 1H), 8.21 (d, J = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 113.4 (d), 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 122.4 (d) 123.1 (s, q: $^{2}J_{C\text{-}F}$ = 10.0 Hz), 124.3 (d, q: $^{3}J_{C\text{-}F}$ = 3.4 Hz), 126.2 (d, q: $^{4}J_{C\text{-}F}$ = 3.0 Hz), 128.5 (d), 129.6 (d, q: $^{3}J_{C\text{-}F}$ = 8.2 Hz), 129.8 (s), 130.1 (d), 130.4 (d, q: $^{3}J_{C\text{-}F}$ = 4.9 Hz), 133.4 (d), 142.3 (s), 144.5 (s), 160.5 (s, q: $^{1}J_{C\text{-}F}$ = 245 Hz), 165.6 (s); {^{1}H}^{19}F-NMR ($CDCl_3$, 565 MHz) δ –122.4; IR (KBr) ν 3305 (NH), 1715 (C=O), 1535, 1505, 1280, 1195, 1090 cm^{-1}; ESI-MS (*m/z*): 357 (100, $[M+Na]^+$), 335 (11, $[M+H]^+$).

Synthesis of carbamoyl chlorides 6 and 7.

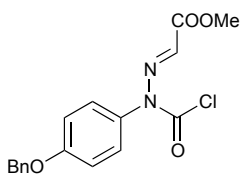


and



To a solution of hydrazone **4** or **5** (8.25 mmol) in dry CH_2Cl_2 (50 mL), pyridine (797 mg, 810 μL, 10.0 mmol) followed by solution of triphosgene (2.45 g, 8.25 mmol) in CH_2Cl_2 (8 mL) were added. The mixture was stirred at room temperature for 2-5 hrs (TLC monitoring) and quenched with 2% HCl (35 mL). The mixture was extracted with CH_2Cl_2 (2 × 30 mL), the organic layer was washed with H_2O (25 mL), extracts were dried ($MgSO_4$), and solvents were removed in *vacuo*. Crude product was flash chromatographed to yield product **6** or **7**, respectively.

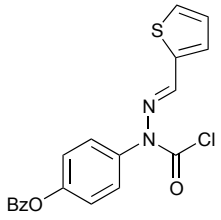
Methyl glyoxylate α-chloroformyl-4-benzyloxyphenyl-hydrazone (6b)



SiO_2 (CH_2Cl_2/AcOEt 40:1); light-orange solid (2.69 g, 94%); mp 154-

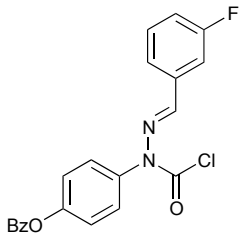
156 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 3.86 (s, 3H), 5.11 (s, 2H), 6.78 (s, 1H), 7.09 and 7.13 (2 d_{br}, J = 8.9 Hz, 2H each), 7.33-7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 52.7 (q), 70.5 (t), 116.9 (d), 127.4 (s), 127.5 (d), 128.3 (d), 128.7 (d), 129.4 (d, broad), 135.8 (d, broad), 136.0 (s), 150.9 (s, broad), 160.3 (s), 162.9 (s); IR (KBr) ν 1755 (C=O), 1725 (C=O), 1605 (C=C), 1505, 1375, 1300, 1245, 1185, 1030, 1015 cm^{-1}; ESI-MS (m/z): 369 (100, $[M+Na]^+$).

2-Thienal α-chloroformyl-4-benzoyloxyphenylhydrazone (7c).



SiO_2 ($CHCl_3$/petroleum ether 3:1); pale yellow crystals (3.14 g, 99%); mp 160-161 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.04 (dd, J = 3.7, 5.0 Hz, 1H), 7.21 (dd, J = 0.9, 3.7 Hz, 1H), 7.35 (d_{br}, J = 8.7 Hz, 2H), 7.43 (dt, J = 0.9, 5.0 Hz, 1H), 7.47 (d_{br}, J = 8.7 Hz, 2H), 7.53-7.56 (m, 2H), 7.64 (s_{br}, 1H), 7.67-7.70 (m, 1H), 8.22 (dd_{br}, J = 1.3, 8.4 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz) δ 123.9 (d), 127.6 (d), 128.7 (d, higher int.), 129.0 (d), 129.4 (s), 130.1 (s), 130.3 (d, higher int.), 131.3 (s), 133.6 (d), 134.0 (d), 138.2 (s), 152.0 (s), 164.7 (s); IR (KBr) ν 1735, 1505, 1285, 1265, 1185, 1200, 1055 cm^{-1}; ESI-MS (m/z): 385 (100, $[M+H]^+$). Anal. Calcd for $C_{19}H_{13}ClN_2O_3S$ (384.0): C 59.30, H 3.40. Found: C 59.41, H 3.38.

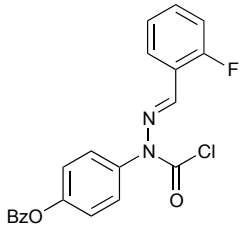
3-Flurobenzaldehyde α-chloroformyl-4-benzoyloxyphenyl-hydrazone (7e).



SiO_2 (CH_2Cl_2); pale yellow crystals (2.68 g, 82%); mp 131-134 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.11 (tdd, J = 1.2, 2.6, 8.3 Hz, 1H), 7.34-7.43 (m, 5H), 7.46-7.49 (m, 3H), 7.56 (t_{br}, J = 7.8 Hz, 2H), 7.67-7.70 (m, 1H), 8.23 (dd_{br}, J = 1.2, 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 113.9 (d, q: $^{2}J_{C\text{-}F}$ = 22.8 Hz), 117.7 (d, q: $^{2}J_{C\text{-}F}$ =

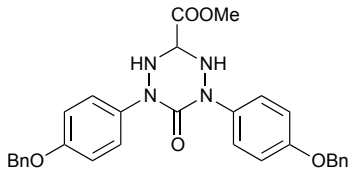
21.6 Hz), 124.0 (d), 124.1 (d, q: $^{4}J_{C\text{-}F}$ = 2.6 Hz), 128.7 (d), 128.9 (s), 130.0 (d, broad), 130.2 (d), 130.3 (d, q: $^{3}J_{C\text{-}F}$ = 8.2 Hz), 133.2 (d, broad), 134.0 (d), 135.5 (s, q: $^{3}J_{C\text{-}F}$ = 7.9 Hz), 144.7 (s, broad), 150.5 (s, broad), 152.1 (s), 163.0 (s, q: $^{1}J_{C\text{-}F}$ = 247.0 Hz), 164.6 (s); {^{1}H}^{19}F-NMR ($CDCl_3$, 565 MHz) δ –112.2; IR (KBr) ν 1720 (C=O), 1505, 1265, 1205 cm^{-1}; ESI-MS (*m*/*z*): 419 (23, [M+Na]$^{+}$), 397 (100, [M+H]$^{+}$). Anal. Calcd for $C_{21}H_{14}ClFN_2O_3$ (396.1): C 63.56, H 3.56. Found: C 63.82, H 3.50.

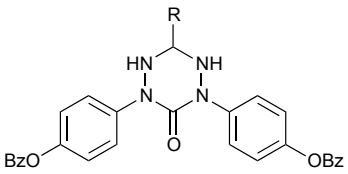
2-Flurobenzaldehyde α-chloroformyl-4-benzoyloxyphenyl-hydrazone (7f).



SiO_2 (CH_2Cl_2/petroleum ether 5:1); pale yellow crystals (3.17 g, 97%); mp 162-164 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.03-7.06 (m, 1H), 7.21 (t_{br}, *J* = 7.6 Hz, 1H), 7.35 (d_{br}, *J* = 8.7 Hz, 2H), 7.37-7.41 (m, 1H), 7.49 (d_{br}, *J* = 8.7 Hz, 2H), 7.55 (t_{br}, *J* = 7.8 Hz, 2H), 7.66-7.69 (m, 1H), 7.73 (s), 8.08 (td, *J* = 1.7, 7.6 Hz, 1H), 8.23 (dd_{br}, *J* = 1.2, 8.3 Hz, 2H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 115.8 (d, q: $^{2}J_{C\text{-}F}$ = 20.9 Hz), 121.2 (s, $^{2}J_{C\text{-}F}$ = 10.0 Hz), 124.0 (d), 124.6 (d, q: $^{3}J_{C\text{-}F}$ = 3.5 Hz), 127.3 (d, q: $^{4}J_{C\text{-}F}$ = 1.8 Hz), 128.7 (d), 129.1 (d), 130.0 (s, broad), 130.1 (d, q: $^{3}J_{C\text{-}F}$ = 1.9 Hz), 130.3 (d), 132.4 (d, q: $^{3}J_{C\text{-}F}$ = 8.5 Hz), 134.0 (d), 152.1 (s), 161.7 (s, q: $^{1}J_{C\text{-}F}$ = 253.1 Hz), 164.5 (s), two C atoms were not found; {^{1}H}^{19}F-NMR ($CDCl_3$, 565 MHz) δ –120.1; IR (KBr) ν 1720 (C=O), 1275, 1205 cm^{-1}; ESI-MS (*m*/*z*): 419 (92, [M+Na]$^{+}$), 397 (100, [M+H]$^{+}$). Anal. Calcd for $C_{21}H_{14}ClFN_2O_3$ (396.1): C 63.56, H 3.56. Found: C 63.55, H 3.53.

Synthesis of tetrazines 8 and 9.

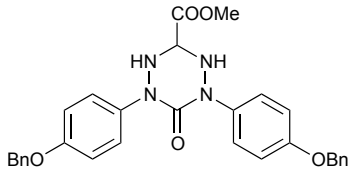




To a solution of freshly prepared carbamoyl chloride **6** or **7** (2.00 mmol) in ethanol (20 mL), appropriate arylhydrazine hydrochloride (**2**, 529 mg, 2.00 mmol or **3**, 605 mg, 2.00 mmol,

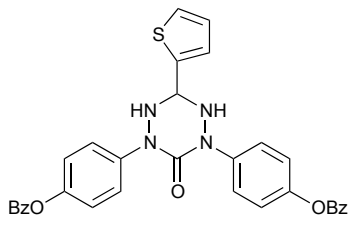
respectively) followed by Et_3N (0.62 mL, 4.2 mmol) were added. The resulting mixture was heated at 60 °C for 6 hrs, and left in the fridge overnight. The precipitate was filtered, washed with several portions of cold EtOH, and dried under high vacuum to afford crude tetrazine **8** or **9**, which was used for the next step without further purification.

1,5-bis(4-Benzoyloxyphenyl)-3-methoxycarbonyl-tetrahydro-1,2,4,5-tetrazin-3(2H)-one (8b).



Off-white solid (535 mg, 51%); mp 201-203 °C (decomp); ^{1}H NMR (DMSO-d_6, 600 MHz) δ 3.70 (s, 3H), 4.91 (t, J = 7.3 Hz, 1H), 5.09 (s, 4H), 6.43 (d, J = 7.3 Hz, 2H), 6.95 (d_{br}, J = 9.1 Hz, 4H), 7.30-7.34 (m, 2H), 7.37-7.46 (m, 12H) ppm; ^{13}C NMR (DMSO-d_6, 151 MHz) δ 52.2 (q), 69.4 (2C), 114.1 (d), 123.6 (d), 127.5 (d), 127.7 (d), 128.4 (d), 136.1 (s), 137.2 (s), 154.8 (s), 155.6 (s), 168.6 (s); IR (KBr) ν 3215 (NH), 1755 (C=O), 1620, 1600, 1505, 1430, 1240 cm^{-1}; EI-MS (*m/z*): 524 (7, $[M]^+$), 91 (100, $[Bn]^+$). Anal. Calcd for $C_{30}H_{28}N_4O_5$ (524.2): C 68.69, H 5.38, N 10.68. Found: C 68.40, H 5.54, N 10.41.

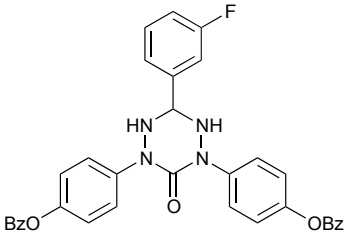
1,5-bis(4-Benzoyloxyphenyl)-3-(thien-2-yl)tetrahydro-1,2,4,5-tetrazin-3(2H)-one (9c).



Off-white solid (992 mg, 86%); mp 197-198 °C (decomp.); ^{1}H NMR (DMSO-d_6, 600 MHz) δ 5.68 (t, J = 8.0 Hz, 1H), 6.63 (d, J = 8.0 Hz, 2H), 7.05 (dd, J = 3.6, 5.0 Hz, 1H), 7.17-7.19 (m, 1H), 7.26 (d_{br}, J = 9.0, 4H), 7.50 (dd, J = 0.9, 5.0 Hz, 1H), 7.62 (t_{br}, J = 7.8 Hz, 4H), 7.68 (d_{br}, J = 9.0, 4H), 7.74-7.78 (m, 2H), 8.15 (dd_{br}, J = 1.2, 8.3 Hz, 4H); ^{13}C NMR (DMSO-d_6, 151 MHz) δ 69.8 (d), 121.8 (d), 122.7 (d), 126.0 (d), 126.5 (d), 127.6 (d), 129.4 (d), 129.5 (d), 130.2 (d), 134.5 (s), 140.9 (s), 141.4

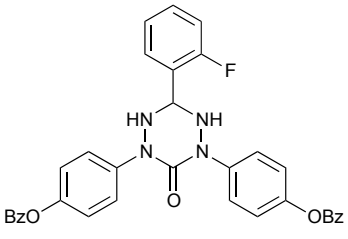
(s), 146.8 (d), 156.8 (s), 165.2 (s); IR (KBr) ν 3245 and 3220 (NH), 1735 (C=O), 1630, 1505, 1395, 1270, 1205, 1080 cm^{-1}; ESI-MS (*m/z*): 599 (11, $[M+Na]^+$), 577 (100, $[M+H]^+$).

1,5-bis(4-Benzoyloxyphenyl)-3-(3-fluorophenyl)tetrahydro-1,2,4,5-tetrazin-3(2H)-one (9e).



Off-white solid (989 mg, 84%); mp 212-213 °C (decomp.); ^{1}H NMR (DMSO-d_6, 600 MHz) δ 5.50 (t, J = 8.9 Hz, 1H), 6.57 (d, J = 8.9 Hz, 2H), 7.16-7.21 (m, 1H), 7.27 (d_{br}, J = 8.8 Hz, 4H), 7.36 (d_{br}, J = 10.2 Hz, 1H), 7.41-7.46 (m, 2H), 7.62 (t_{br}, J = 7.7 Hz, 4H), 7.69 (d_{br}, J = 8.8 Hz, 4H), 7.76 (t_{br}, J = 7.4 Hz, 2H), 8.15 (d_{br}, J = 7.7 Hz, 4H); ^{13}C NMR ($CDCl_3$, 151 MHz) δ 72.1 (d), 113.8 (d, q: $^2J_{C\text{-}F}$ = 22.5 Hz), 115.0 (d, q: $^2J_{C\text{-}F}$ = 20.9 Hz), 121.3 (d), 122.1 (d), 123.1 (d, q: $^4J_{C\text{-}F}$ = 2.5 Hz), 128.9 (d), 129.0 (s), 129.7 (d), 130.4 (d, q: $^3J_{C\text{-}F}$ = 8.2 Hz), 133.9 (d), 140.3 (s, q: $^3J_{C\text{-}F}$ = 7.5 Hz), 140.4 (s), 146.3 (s), 156.7 (s), 162.0 (s, q: $^1J_{C\text{-}F}$ = 243.4 Hz), 164.7 (s); {^{1}H}^{19}F-NMR ($CDCl_3$, 565 MHz) δ −112.8; IR (KBr) ν 3240 (NH), 1740 (C=O), 1625, 1500, 1365, 1270, 1200, 1065 cm^{-1}; ESI-MS (*m/z*): 611 (100, $[M+Na]^+$), 589 (61, $[M+H]^+$).

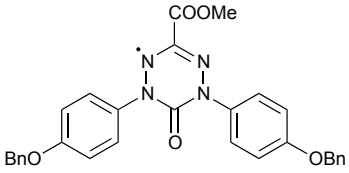
1,5-bis(4-Benzoyloxyphenyl)-3-(2-fluorophenyl)tetrahydro-1,2,4,5-tetrazin-3(2H)-one (9f).

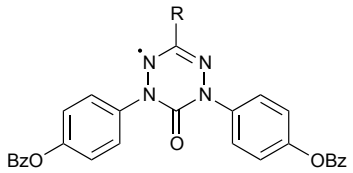


Off-white solid (718 mg, 61%); mp 210-214 °C (decomp.); ^{1}H NMR (DMSO-d_6, 600 MHz) δ 5.64 (t, J = 9.3 Hz, 1H), 6.61 (d, J = 9.3 Hz, 2H), 7.20 (t_{br}, J = 7.6 Hz, 1H), 7.27 (d_{br}, J = 9.0 Hz, 4H), 7.25-7.28 (m 1H), 7.40-7.44 (m, 1H), 7.50-7.54 (m, 1H), 7.62 (t_{br}, J = 7.8 Hz, 4H), 7.67 (d_{br}, J = 9.0 Hz, 4H), 7.74-7.78 (m,

2H), 8.15 (d_{br}, J = 7.2 Hz, 4H); ^{13}C NMR (DMSO-d_6, 151 MHz) δ 68.1 (d), 115.5 (d, q: $^{2}J_{C\text{-}F}$ = 21.6 Hz), 121.4 (d), 121.5 (d), 124.5 (d, q: $^{4}J_{C\text{-}F}$ = 2.6 Hz), 124.9 (s, q: $^{2}J_{C\text{-}F}$ = 13.8 Hz), 128.2 (d, q: $^{3}J_{C\text{-}F}$ = 3.1 Hz), 128.9 (d), 129.0 (d), 129.7 (d), 130.5 (d, q: $^{3}J_{C\text{-}F}$ = 7.4 Hz), 133.9 (s), 140.2 (s), 146.2 (s), 158.2 (s), 159.7 (s, q: $^{1}J_{C\text{-}F}$ = 246.9 Hz), 164.7 (s); {^{1}H}^{19}F-NMR ($CDCl_3$, 565 MHz) δ −117.3; IR (KBr) ν 3280 and 3255 (NH), 1735 (C=O), 1640, 1505, 1390, 1265, 1200, 1065 cm^{-1}; ESI-MS (*m*/*z*): 611 (100, [M+Na]$^+$), 589 (12, [M+H]$^+$).

Synthesis of protected diphenols 10 and 11.

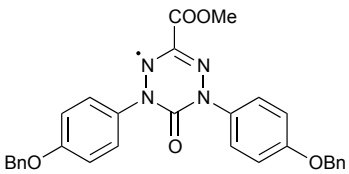




Method A: To a mixture of tetrazine **8** or **9** (5.0 mmol) in CH_2Cl_2 (100 mL), $K_3Fe(CN)_6$ (9.9 g, 30.1 mmol), Na_2CO_3 (0.5 M, 100 mL), and $[Et_4N]^+Br^-$ (210 mg, 20 mol%) were added. The resulting mixture was vigorously stirred for 20h (TLC monitoring), the organic layer was separated, dried (Na_2SO_4), filtered, and the solvent was removed under reduced pressure. Crude product was flash chromatographed (SiO_2, CH_2Cl_2) to furnish radical **10** or **11** as a deeply colored solid.

Method B: To a mixture of tetrazine **8** or **9** (5.0 mmol) in CH_2Cl_2 (100 mL), a mixture of $NaIO_4$ (2.14 g, 10.0 mmol), and $[Et_4N]^+Br^-$ (420 mg, 40 mol%) in H_2O (100 mL) was added. The resulting mixture was vigorously stirred for 48h (TLC monitoring), the organic layer was separated, dried (Na_2SO_4), filtered, and the solvent was removed under reduced pressure. Crude product was flash chromatographed (SiO_2, CH_2Cl_2) to furnish radical **10** or **11**. Analytically pure samples were obtained by additional chromatography purification.

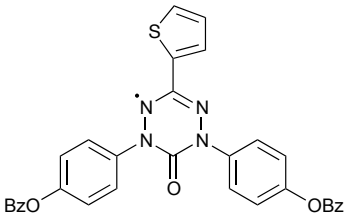
1,5-bis(4-Benzyloxyphenyl)-3-methoxycarbonyl-6-oxoverdazyl (10b).



Wine-red crystals (*Method A*: reaction time 48 h, 1.36 g,

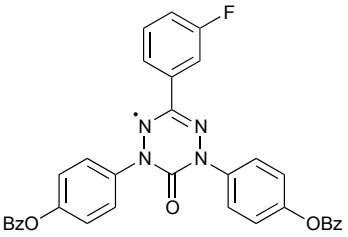
52%; *Method B*: reaction time 18 h, 1.30 g, 50%); mp 178-180 °C; IR (KBr) ν 1735 (C=O), 1700 (C=O), 1600, 1500, 1245, 1165 cm^{-1}; EI-MS (*m/z*): 522 (15, $[M+H]^+$), 521 (11, $[M]^+$], 431 (11, $[M-Bn+H]^+$), 91 (100, $[Bn]^+$). Anal. Calcd for $C_{30}H_{25}N_4O_5$ (521.2): C 69.09, H 4.83, N 10.74. Found: C 69.32, H 5.02, N 10.46.

1,5-bis(4-Benzoyloxyphenyl)-6-oxo-3-(thien-2-yl)verdazyl (11c).



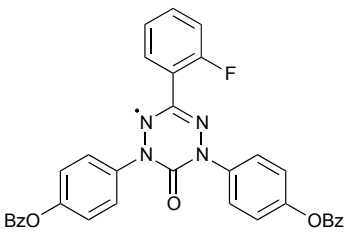
Green solid (*Method A*: 2.06 g, 72%; *Method B*: 1.78 g, 62%); mp 225-227 °C; IR (KBr) ν 1740, 1690, 1505, 1265, 1210, 1060 cm^{-1}; ESI-MS (*m/z*): 596 (100, $[M+Na]^+$), 573 (85, M^+); EI-MS (*m/z*): 573 (7, M+), 105 (100). Anal. Calcd for $C_{32}H_{21}N_4O_5S$ (573.1): C 67.01, H 3.69, N 9.77. Found: C 66.93, H 3.84, N 9.76.

1,5-bis(4-Benzoyloxyphenyl)-3-(3-fluorophenyl)-6-oxoverdazyl (11e).



Pink-red solid (*Method A*: 2.57 g, 88%; *Method B*: 1.37 g, 47%); mp 254-255 °C; IR (KBr) ν 1745, 1695, 1505, 1270, 1205, 1060 cm^{-1}; ESI-MS (*m/z*): 586 (2, [M+H]+), 571 (4, $[M-N]^+$), 557 (11, $[M-CO]^+$), 413 (100). Anal. Calcd for $C_{34}H_{22}FN_4O_5$ (585.2): C 69.74, H 3.79. Found: C 69.82, H 3.61.

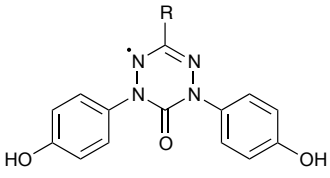
1,5-bis(4-Benzoyloxyphenyl)-3-(2-fluorophenyl)-6-oxoverdazyl (11f).



Pink-red solid (*Method A*: 2.31 g, 79%; *Method B*: 1.26 g, 43%); mp 198-199 °C; IR (KBr) ν 1740, 1700, 1505, 1265, 1210, 1165, 1060 cm^{-1}; EI-

MS (*m*/*z*): 586 (2, M^+), s105 (100). Anal. Calcd for $C_{34}H_{22}FN_4O_5$ (585.2): C 69.74, H 3.79. Found: C 69.70, H 3.96.

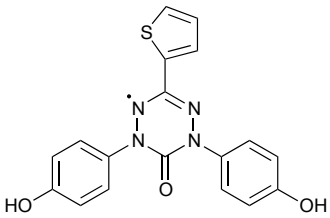
Synthesis of diphenol radicals 12 by hydrolysis of dibenzoates 11.



To a mixture of dibenzoyloxy radical **11** (1.0 mmol) in dry CH_2Cl_2 (30 mL) a solution of KOH (0.1M in methanol, 21 mL, 2.1 mmol) was added dropwise at 0 °C under vigorous stirring. After ca. 30 min (TLC monitoring, CH_2Cl_2/EtOAc 5:1) the mixture was diluted with water (400 mL), EtOAc (200 mL) was added and the layers were separated. The organic layer was washed with H_2O (3 × 60 mL), dried over $MgSO_4$, filtered and the solvents were removed in *vacuo* (cold bath!). Crude product was pre-purified on chromatography column (SiO_2, CH_2Cl_2/EtOAc 7:1) to give solid diphenol verdazyl **12** that was used for the next step as received.

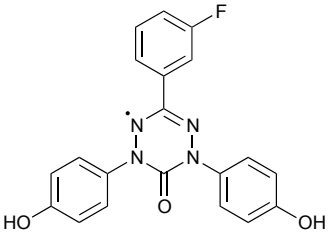
Synthesis of 1,5-bis(4-hydroxyphenyl)-6-oxo-3-phenylverdazyl (**12d**) was reported recently.[1]

1,5-bis(4-hydroxyphenyl)-6-oxo-3-(thien-2-yl)verdazyl (12c).



Deep green crystals (241 mg, 66%); mp 179-181 °C (decomp); IR (KBr) ν 3420 (OH), 1670 (C=O), 1600, 1510, 1450, 1215 cm^{-1}.

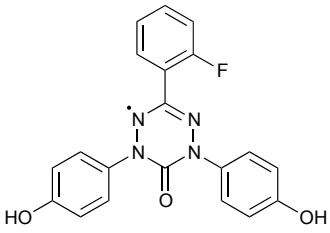
1,5-bis(4-hydroxyphenyl)-3-(3-fluorophenyl)-6-oxoverdazyl (12e).



Dark violet crystals (219 mg, 58%); mp 204-206 °C

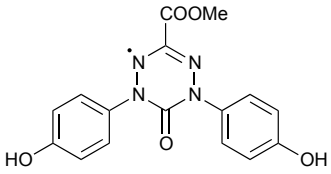
(decomp.); IR (KBr) ν 3550-3425 (OH), 1685 (C=O), 1605, 1510, 1270 cm^{-1}.

1,5-bis(4-hydroxyphenyl)-3-(2-fluorophenyl)-6-oxoverdazyl (12f).



Dark violet solid (155 mg, 41%); mp 187-190 °C (decomp.); IR (KBr) ν 3560-3400 (OH), 1670 (C=O), 1600, 1515, 1460, 1225 cm^{-1}.

Synthesis of 1,5-bis(4-hydroxyphenyl)-3-methoxycarbonyl-6-oxoverdazyl (12b).



To a suspension of 10% Pd/C (250 mg) in EtOH (82 mL) a solution of dibenzyloxy verdazyl **10b** (900 mg, 1.73 mmol) in THF (64 mL) was added, and the resulting mixture was hydrogenated at 50 psi for 48h. The resulting colorless mixture was oxidized with air for ca. 20 min (TLC monitoring, CH_2Cl_2/EtOAc, 10:1) and filtered through Celite, solvents were removed under reduced pressure (cold bath!), and the crude mixture was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc, 7:1) to afford partially purified diphenol radical **12b** (121 mg, 20% yield) as a red-brown solid that was used for the next step without further purification; mp 188-191 °C (decomp); IR (KBr) ν 3420 (OH), 1700, 1600, 1515, 1450, 1225, 1160 cm^{-1}.

2. Multi-component mixtures

Table S1. Thermal properties of pure compounds and binary mixtures in **1[12]a**.[a]

	pure compounds / °C	Binary mixtures in **1[12]a**	
		mol%	Transition temperatures for binary mixtures / °C
1[12]b	Cr 138.6 N 161.4 I[b]	9.9	Cr 134.3 N 160.1 I[b]
1[12]c	Cr 153.4 I	12.9	Cr 135.1 (I_{re} 123.5)[c] N 150.5 I
1[12]d	Cr 156.8 I	8.5	Cr 134.0 (I_{re} 123.1)[c] N 153.2 I
1[12]e	Cr 177.1 (N 169.0) I	8.3	Cr 133.9 (I_{re} 120.6)[c] N 155.8 I
1[12]f	Cr 155.3 I	10.7	Cr 135.1 (I_{re} 124.0)[c] N 144.8 I
1[16]c	Cr 148.5 I	9.5	Cr 135.3 (I_{re} 124.3)[c] N 146.5 I
1[16]d	Cr 159.8 I	10.2	Cr 134.1 (I_{re} 123.5)[c] N 147.2 I

[a] Cr = crystal, N = nematic, I and I_{re} = isotropic; transition temperatures for pure **1[12]a**: Cr 136.9 (I_{re} 121.6) N 152.3 I. [b] Decomposition. [c] Monotropic transition observed on cooling.

Table S2. Thermal properties of multi-component mixtures with **1[12]a**.[a]

	Composition (mole%)	Transition temperatures /°C
1	**1[12]d** (10.0) **1[12]c** (9.6) **1[12]a** (80.3)	Cr 130.9 (I_{re} 123.0)[b] N 149.7 I
2	**1[12]d** (24.9) **1[12]c** (24.2) **1[12]a** (50.9)	Cr 124.8 (I_{re} 103.8)[b] N 138.0 I
3	**1[12]d** (33.5) **1[12]c** (32.6) **1[12]a** (33.9)	Cr 141.7 I[c]
4	**1[12]d** (27.4) **1[12]c** (50.4) **1[12]a** (22.1)	Cr 145.6 I[c]
5	**1[12]d** (24.0) **1[12]c** (26.9) **1[12]e** (24.9) **1[12]a** (24.1)	Cr 155.4 I[c]

[a] Cr = crystal, N = nematic, I and I_{re} = isotropic. [b] Monotropic transition observed on cooling. [c] Non-homogenous.

3. Partial data for TD-DFT calculation for 12 in dioxane dielectric medium

B3LYP/6-31G(2d,p)// CAM-B3LYP/6-31G(2d,p)

12a

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.044-A      2.2840 eV  542.85 nm  f=0.1816
<S**2>=0.795
     84B -> 90B        0.11272
     85B -> 90B       -0.12128
     89B -> 90B        0.97428
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1321.72194688
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  2.087-A      2.7088 eV  457.71 nm  f=0.0440
<S**2>=0.839
     90A -> 95A       -0.11199
     88B -> 90B        0.97839

 Excited State   3:  2.034-A      2.8941 eV  428.41 nm  f=0.0120
<S**2>=0.784
     83B -> 90B       -0.16794
     85B -> 90B        0.94366
     87B -> 90B       -0.19210
     89B -> 90B        0.10860

 Excited State   4:  2.041-A      3.0095 eV  411.97 nm  f=0.0014
<S**2>=0.792
     88A -> 91A       -0.16792
     90A -> 91A        0.94805
     84B -> 90B       -0.14175

 Excited State   5:  2.057-A      3.4322 eV  361.24 nm  f=0.0005
<S**2>=0.808
     85B -> 90B        0.18444
     87B -> 90B        0.96477

 Excited State   6:  2.062-A      3.4814 eV  356.13 nm  f=0.0005
<S**2>=0.813
     90A -> 92A       -0.12072
     86B -> 90B        0.98037

 Excited State   7:  2.055-A      3.6921 eV  335.81 nm  f=0.0069
<S**2>=0.806
     90A -> 91A        0.17612
     90A -> 96A        0.16037
     84B -> 90B        0.93509
     89B -> 90B       -0.12955

 Excited State   8:  3.294-A      3.7550 eV  330.19 nm  f=0.0155
<S**2>=2.462
     86A -> 92A        0.24083
     87A -> 93A        0.23611
     88A -> 95A       -0.17816
```

```
     89A -> 91A       -0.29813
     89A -> 94A        0.30526
     90A -> 94A        0.16504
     90A -> 95A       -0.36970
     86B -> 92B        0.22822
     87B -> 93B       -0.21795
     88B -> 90B       -0.16022
     88B -> 95B       -0.26516
     89B -> 91B        0.37142
     89B -> 94B       -0.29778

 Excited State   9:  3.122-A      3.7600 eV  329.74 nm  f=0.0920
<S**2>=2.187
     86A -> 93A        0.23246
     87A -> 92A        0.23604
     88A -> 91A       -0.14138
     88A -> 94A        0.14429
     89A -> 95A       -0.31735
     90A -> 94A        0.57151
     90A -> 95A        0.11661
     86B -> 93B       -0.22640
     87B -> 92B        0.22571
     88B -> 91B       -0.23857
     88B -> 94B        0.22509
     89B -> 90B        0.11976
     89B -> 91B       -0.10844
     89B -> 95B        0.29844

 Excited State  10:  2.718-A      3.9182 eV  316.43 nm  f=0.0016
<S**2>=1.597
     88A -> 92A        0.13114
     89A -> 93A        0.31386
     90A -> 92A        0.82277
     86B -> 90B        0.12785
     88B -> 92B       -0.24775
     89B -> 93B       -0.30223

 Excited State  11:  2.773-A      3.9438 eV  314.38 nm  f=0.0088
<S**2>=1.672
     88A -> 93A        0.13910
     89A -> 92A        0.34210
     90A -> 93A        0.80628
     87B -> 90B        0.10095
     88B -> 93B        0.25630
     89B -> 92B        0.32981

 Excited State  12:  3.398-A      4.1921 eV  295.76 nm  f=0.0014
<S**2>=2.637
     84A -> 91A       -0.24391
     86A -> 92A       -0.16287
     87A -> 93A       -0.15985
     89A -> 91A       -0.51793
     89A -> 94A       -0.15427
     90A -> 95A        0.23900
     84B -> 91B        0.26432
     86B -> 92B       -0.15354
     87B -> 93B        0.14774
     88B -> 95B        0.10284
```

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     89B -> 91B        0.56550
     89B -> 94B        0.20689

 Excited State  13:  2.852-A      4.4227 eV  280.33 nm  f=0.1503
<S**2>=1.783
     86A -> 93A       -0.33448
     87A -> 92A       -0.34124
     88A -> 94A       -0.12268
     90A -> 91A       -0.13179
     90A -> 94A        0.64757
     84B -> 90B        0.11969
     86B -> 93B        0.33569
     87B -> 92B       -0.34588
     88B -> 91B       -0.11334
     88B -> 94B       -0.11010
```

12b

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.040-A      2.3436 eV  529.03 nm  f=0.1338
<S**2>=0.790
     89A -> 90A       -0.30885
     83B -> 89B        0.13056
     85B -> 89B        0.12079
     88B -> 89B        0.91100
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1212.56319540
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  2.022-A      2.4988 eV  496.18 nm  f=0.0270
<S**2>=0.772
     87A -> 90A       -0.15289
     89A -> 90A        0.90791
     88B -> 89B        0.30043

 Excited State   3:  2.105-A      2.7803 eV  445.93 nm  f=0.0481
<S**2>=0.858
     89A -> 94A        0.12053
     87B -> 89B        0.97307

 Excited State   4:  2.046-A      2.8300 eV  438.10 nm  f=0.0188
<S**2>=0.796
     80B -> 89B       -0.15996
     83B -> 89B       -0.11588
     84B -> 89B        0.47381
     85B -> 89B        0.69794
     86B -> 89B        0.41799
     88B -> 89B       -0.17784

 Excited State   5:  2.071-A      3.5256 eV  351.66 nm  f=0.0005
<S**2>=0.822
     89A -> 93A       -0.13752
     84B -> 89B       -0.19939
     85B -> 89B       -0.38151
     86B -> 89B        0.87934
```

```
 Excited State   6:  2.096-A      3.5844 eV  345.90 nm  f=0.0003
<S**2>=0.848
     89A -> 91A       -0.19252
     84B -> 89B        0.81098
     85B -> 89B       -0.52125

 Excited State   7:  2.835-A      3.6788 eV  337.02 nm  f=0.1627
<S**2>=1.759
     85A -> 91A       -0.11089
     85A -> 93A        0.15385
     86A -> 91A       -0.16239
     87A -> 92A        0.11662
     88A -> 94A        0.26381
     89A -> 92A        0.69564
     89A -> 93A        0.19197
     83B -> 89B        0.16724
     84B -> 91B        0.13521
     85B -> 92B       -0.12766
     86B -> 91B       -0.13666
     87B -> 90B       -0.14811
     87B -> 93B        0.23565
     88B -> 89B       -0.17510
     88B -> 94B       -0.24665

 Excited State   8:  3.341-A      3.7018 eV  334.93 nm  f=0.0077
<S**2>=2.541
     82A -> 90A        0.13368
     85A -> 91A       -0.16319
     86A -> 93A        0.13663
     87A -> 94A        0.12261
     88A -> 90A        0.50447
     88A -> 92A        0.26538
     89A -> 94A        0.24528
     83B -> 89B       -0.14929
     83B -> 90B       -0.13945
     84B -> 91B        0.13397
     86B -> 92B       -0.12128
     87B -> 89B       -0.14934
     87B -> 94B       -0.17915
     88B -> 90B       -0.50288
     88B -> 93B        0.26497

 Excited State   9:  2.268-A      3.7299 eV  332.41 nm  f=0.0003
<S**2>=1.036
     87A -> 92A       -0.12564
     88A -> 94A       -0.16982
     89A -> 90A        0.13750
     89A -> 95A        0.18103
     83B -> 89B        0.87619
     87B -> 93B       -0.12180
     88B -> 94B        0.12338

 Excited State  10:  3.304-A      3.8550 eV  321.62 nm  f=0.0078
<S**2>=2.479
     82A -> 90A        0.12149
     84A -> 90A        0.12007
     85A -> 91A        0.21409
     86A -> 93A       -0.19457
```

```
     87A -> 94A       -0.14823
     88A -> 90A        0.46087
     88A -> 92A       -0.25060
     88A -> 95A        0.12273
     89A -> 91A       -0.19849
     89A -> 94A       -0.33975
     83B -> 90B       -0.15665
     84B -> 91B       -0.17162
     85B -> 91B        0.11111
     86B -> 92B        0.17768
     87B -> 94B        0.21943
     88B -> 90B       -0.33081
     88B -> 93B       -0.26561
     88B -> 95B        0.11856

 Excited State  11:  2.674-A      3.8782 eV  319.70 nm  f=0.0010
<S**2>=1.537
     87A -> 91A        0.12086
     88A -> 91A        0.15991
     88A -> 93A       -0.24884
     89A -> 91A        0.81090
     89A -> 94A       -0.12690
     84B -> 89B        0.16785
     85B -> 89B       -0.11701
     87B -> 91B       -0.23254
     88B -> 91B       -0.14684
     88B -> 92B       -0.20159
     88B -> 93B       -0.13678

 Excited State  12:  2.697-A      3.9064 eV  317.39 nm  f=0.0116
<S**2>=1.568
     87A -> 93A        0.11995
     88A -> 91A       -0.26499
     88A -> 93A       -0.16099
     89A -> 92A       -0.21635
     89A -> 93A        0.79981
     86B -> 89B        0.13905
     87B -> 92B        0.23227
     88B -> 91B        0.25308
     88B -> 92B       -0.17188

 Excited State  13:  2.265-A      4.0961 eV  302.69 nm  f=0.0016
<S**2>=1.033
     84A -> 90A        0.24235
     75B -> 89B        0.10100
     82B -> 89B        0.88819
     85B -> 89B       -0.10856
     85B -> 90B       -0.14216
     88B -> 90B        0.15325

 Excited State  14:  2.056-A      4.1577 eV  298.20 nm  f=0.0287
<S**2>=0.806
     84A -> 90A        0.10599
     88A -> 90A        0.66015
     82B -> 89B       -0.15027
     85B -> 90B        0.10870
     88B -> 90B        0.69337
```

12c

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.014-A      2.1274 eV  582.80 nm  f=0.0906
<S**2>=0.764
     95A -> 96A       -0.23213
     92B -> 95B       -0.10425
     94B -> 95B        0.94870
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1536.51445103
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  2.046-A      2.6361 eV  470.34 nm  f=0.0363
<S**2>=0.796
     92A -> 96A        0.10306
     95A -> 96A        0.65660
     88B -> 95B        0.16836
     89B -> 95B       -0.20970
     90B -> 95B        0.19190
     92B -> 95B        0.59933
     94B -> 95B        0.20695

 Excited State   3:  2.323-A      2.8066 eV  441.76 nm  f=0.0591
<S**2>=1.099
     93A -> 96A        0.18127
     94A -> 96A       -0.18934
     95A ->100A        0.11230
     92B -> 96B       -0.12032
     93B -> 95B        0.90520
     94B -> 96B        0.19612

 Excited State   4:  2.042-A      2.8292 eV  438.23 nm  f=0.0026
<S**2>=0.792
     95A -> 96A        0.56982
     86B -> 95B        0.12668
     88B -> 95B       -0.35130
     89B -> 95B        0.43894
     90B -> 95B       -0.41858
     92B -> 95B       -0.31232
     94B -> 95B        0.14694

 Excited State   5:  2.921-A      3.0149 eV  411.24 nm  f=0.0240
<S**2>=1.884
     93A -> 96A        0.33289
     94A -> 96A       -0.34220
     95A -> 96A        0.17463
     88B -> 95B        0.18914
     89B -> 95B       -0.24482
     90B -> 95B        0.24043
     92B -> 95B       -0.40108
     92B -> 96B       -0.28779
     93B -> 95B       -0.29366
     94B -> 96B        0.42747

 Excited State   6:  2.589-A      3.0534 eV  406.05 nm  f=0.0246
<S**2>=1.425
     93A -> 96A        0.25215
```

```
     94A -> 96A       -0.26709
     95A -> 96A       -0.31584
     88B -> 95B       -0.21336
     89B -> 95B        0.26471
     90B -> 95B       -0.26697
     92B -> 95B        0.58345
     92B -> 96B       -0.21727
     93B -> 95B       -0.17820
     94B -> 96B        0.33164

 Excited State   7:  2.040-A      3.5673 eV  347.56 nm  f=0.0017
<S**2>=0.790
     91B -> 95B        0.99099

 Excited State   8:  2.092-A      3.6030 eV  344.11 nm  f=0.0003
<S**2>=0.844
     95A -> 99A        0.17443
     88B -> 95B       -0.33182
     89B -> 95B        0.47021
     90B -> 95B        0.77619

 Excited State   9:  2.133-A      3.6551 eV  339.21 nm  f=0.0001
<S**2>=0.887
     95A -> 97A       -0.30295
     88B -> 95B        0.73946
     89B -> 95B        0.56570

 Excited State  10:  2.883-A      3.6738 eV  337.48 nm  f=0.1466
<S**2>=1.828
     89A -> 98A        0.11630
     89A -> 99A        0.15164
     90A -> 97A       -0.18157
     92A -> 98A       -0.11903
     93A ->100A       -0.12761
     94A ->100A       -0.25933
     95A -> 98A        0.61561
     95A -> 99A       -0.36334
     88B -> 97B       -0.12697
     88B -> 98B       -0.10043
     89B -> 98B       -0.11516
     90B -> 97B        0.14230
     92B -> 95B       -0.10974
     92B ->100B        0.16157
     93B -> 96B        0.11165
     93B -> 98B        0.16912
     93B -> 99B       -0.18799
     94B -> 95B       -0.12450
     94B ->100B        0.21143

 Excited State  11:  3.266-A      3.7415 eV  331.38 nm  f=0.0298
<S**2>=2.416
     89A -> 97A        0.23808
     90A -> 98A       -0.12275
     90A -> 99A       -0.18407
     92A ->100A       -0.18698
     93A -> 96A       -0.15741
     93A -> 98A       -0.10452
     94A -> 98A       -0.32337
```

```
     94A -> 99A        0.17908
     95A -> 97A        0.10638
     95A ->100A        0.39634
     88B -> 97B       -0.18123
     89B -> 97B       -0.13460
     89B -> 98B        0.10576
     90B -> 98B        0.13243
     90B -> 99B        0.11417
     92B -> 96B        0.13745
     92B -> 98B        0.13184
     92B -> 99B       -0.12058
     93B -> 95B       -0.18186
     93B ->100B        0.27042
     94B -> 96B        0.19981
     94B -> 98B        0.26493
     94B -> 99B       -0.26544

 Excited State  12:  2.592-A      3.8476 eV  322.23 nm  f=0.0005
<S**2>=1.430
     92A -> 97A       -0.11363
     94A -> 97A       -0.10287
     94A -> 99A       -0.21966
     95A -> 97A        0.80845
     88B -> 95B        0.26182
     89B -> 95B        0.19245
     92B -> 99B        0.10366
     93B -> 97B        0.22242
     94B -> 98B        0.12686
     94B -> 99B        0.17364

 Excited State  13:  2.674-A      3.8717 eV  320.23 nm  f=0.0090
<S**2>=1.537
     92A -> 99A       -0.10917
     93A -> 97A       -0.10584
     94A -> 97A       -0.26757
     95A -> 98A        0.42667
     95A -> 99A        0.70264
     89B -> 95B       -0.11652
     90B -> 95B       -0.17133
     92B -> 97B        0.14808
     93B -> 98B        0.17200
     93B -> 99B        0.15944
     94B -> 97B        0.24021
```

12d

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.026-A      2.2533 eV  550.25 nm  f=0.1141
<S**2>=0.776
     94A -> 95A       -0.19497
     89B -> 94B       -0.11494
     91B -> 94B       -0.11057
     93B -> 94B        0.94761
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1215.75523427
 Copying the excited state density for this state as the 1-particle
RhoCI density.
```

```
 Excited State   2:  2.032-A      2.6971 eV  459.70 nm  f=0.0065
<S**2>=0.782
     92A -> 95A        0.10671
     94A -> 95A        0.64399
     88B -> 94B        0.23117
     89B -> 94B       -0.46408
     91B -> 94B        0.49971
     93B -> 94B        0.12226

 Excited State   3:  2.048-A      2.8305 eV  438.03 nm  f=0.0163
<S**2>=0.799
     94A -> 95A        0.58590
     94A -> 98A        0.11810
     85B -> 94B       -0.12231
     88B -> 94B       -0.31742
     89B -> 94B        0.66839
     93B -> 94B        0.20594

 Excited State   4:  2.146-A      2.8444 eV  435.89 nm  f=0.0662
<S**2>=0.901
     94A ->100A        0.12259
     92B -> 94B        0.96306

 Excited State   5:  2.064-A      3.2023 eV  387.17 nm  f=0.0270
<S**2>=0.815
     94A -> 95A       -0.38069
     88B -> 94B       -0.13710
     89B -> 94B        0.31769
     91B -> 94B        0.83526

 Excited State   6:  3.355-A      3.4106 eV  363.53 nm  f=0.0022
<S**2>=2.564
     90A -> 99A        0.25045
     91A -> 95A        0.42587
     93A -> 95A       -0.37588
     90B -> 94B       -0.27428
     90B -> 99B       -0.25032
     91B -> 95B       -0.38194
     91B -> 98B        0.10711
     92B -> 94B        0.13578
     93B -> 95B        0.48863

 Excited State   7:  2.219-A      3.6026 eV  344.15 nm  f=0.0077
<S**2>=0.981
     91A -> 95A        0.13400
     93A -> 95A       -0.17211
     90B -> 94B        0.94281
     93B -> 95B        0.17690

 Excited State   8:  2.106-A      3.6306 eV  341.50 nm  f=0.0005
<S**2>=0.858
     94A -> 97A       -0.22102
     88B -> 94B        0.85845
     89B -> 94B        0.41801

 Excited State   9:  2.168-A      3.6765 eV  337.23 nm  f=0.0000
<S**2>=0.925
     93A -> 97A        0.13800
```

```
     94A -> 96A        0.37840
     87B -> 94B        0.89628

 Excited State  10:  2.912-A      3.6845 eV  336.50 nm  f=0.1424
<S**2>=1.869
     87A -> 96A        0.11026
     88A -> 97A       -0.20481
     89A -> 96A       -0.18094
     92A -> 98A       -0.14915
     93A ->100A        0.28189
     94A -> 97A        0.17742
     94A -> 98A        0.67521
     87B -> 97B       -0.19961
     88B -> 96B        0.18811
     91B ->100B       -0.11870
     92B -> 95B       -0.13043
     92B -> 98B       -0.25416
     93B -> 94B       -0.14593
     93B ->100B       -0.23955

 Excited State  11:  3.228-A      3.7554 eV  330.15 nm  f=0.0212
<S**2>=2.355
     87A -> 97A        0.13196
     88A -> 96A       -0.24881
     89A -> 97A       -0.20304
     91A -> 95A        0.14309
     92A ->100A       -0.18980
     93A -> 97A        0.10226
     93A -> 98A        0.35554
     94A -> 96A        0.12385
     94A ->100A        0.40154
     87B -> 94B       -0.12879
     87B -> 96B       -0.23356
     88B -> 97B        0.21341
     90B -> 94B        0.14176
     91B -> 95B       -0.12592
     91B -> 98B       -0.10652
     92B -> 94B       -0.17742
     92B ->100B       -0.27207
     93B -> 95B       -0.13518
     93B -> 98B       -0.37362

 Excited State  12:  2.552-A      3.8387 eV  322.98 nm  f=0.0002
<S**2>=1.378
     92A -> 96A       -0.10688
     93A -> 97A        0.22825
     93A -> 98A       -0.11100
     94A -> 96A        0.78287
     87B -> 94B       -0.40134
     92B -> 96B       -0.21150
     93B -> 97B       -0.22974

 Excited State  13:  2.630-A      3.8575 eV  321.41 nm  f=0.0101
<S**2>=1.480
     92A -> 97A       -0.12087
     93A -> 96A        0.29113
     94A -> 97A        0.80047
     94A -> 98A       -0.19538
```

```
     88B -> 94B        0.23352
     89B -> 94B        0.11283
     91B -> 96B       -0.10737
     92B -> 97B       -0.22797
     93B -> 96B       -0.27303

 Excited State  14:  3.329-A      4.1371 eV  299.69 nm  f=0.0003
<S**2>=2.521
     86A -> 95A       -0.17456
     88A -> 96A       -0.10436
     90A -> 99A       -0.29561
     91A -> 95A       -0.22621
     91A -> 98A        0.10673
     93A -> 95A       -0.37736
     93A ->101A       -0.14761
     94A -> 99A        0.27314
     94A ->100A        0.16924
     86B -> 95B        0.19115
     90B -> 99B        0.30116
     91B -> 95B        0.19732
     91B -> 98B       -0.12535
     93B -> 95B        0.46443
     93B ->101B       -0.17680

 Excited State  15:  2.403-A      4.1630 eV  297.83 nm  f=0.0471
<S**2>=1.194
     88A -> 97A        0.14901
     89A -> 96A        0.13235
     92A -> 98A        0.17990
     93A ->100A       -0.17701
     94A -> 98A        0.47027
     94A ->101A        0.21398
     86B -> 94B        0.66468
     87B -> 97B        0.16467
     88B -> 96B       -0.15672
     91B -> 94B        0.10711
     92B -> 98B        0.15587
     93B ->100B        0.16829
```

12e

```
 Excitation energies and oscillator strengths:

 Excited State   1:  2.027-A      2.2583 eV  549.03 nm  f=0.1173
<S**2>=0.777
     98A -> 99A        0.22472
     97B -> 98B        0.94086
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1314.99032916
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  2.031-A      2.6609 eV  465.95 nm  f=0.0134
<S**2>=0.781
     96A -> 99A       -0.10842
     98A -> 99A        0.78634
     92B -> 98B       -0.22082
     93B -> 98B        0.22500
```

```
     94B -> 98B       -0.19278
     95B -> 98B       -0.38247
     97B -> 98B       -0.19529

 Excited State   3:  2.077-A      2.8222 eV  439.31 nm  f=0.0323
<S**2>=0.828
     98A -> 99A        0.33378
     89B -> 98B        0.11416
     92B -> 98B        0.43169
     93B -> 98B       -0.48079
     94B -> 98B        0.13677
     95B -> 98B        0.14385
     96B -> 98B        0.58899
     97B -> 98B       -0.14445

 Excited State   4:  2.105-A      2.8250 eV  438.88 nm  f=0.0471
<S**2>=0.857
     98A -> 99A       -0.23698
     92B -> 98B       -0.33807
     93B -> 98B        0.37325
     94B -> 98B       -0.11173
     95B -> 98B       -0.13458
     96B -> 98B        0.76436
     97B -> 98B        0.10036

 Excited State   5:  2.068-A      3.1958 eV  387.96 nm  f=0.0212
<S**2>=0.819
     98A -> 99A        0.30976
     92B -> 98B       -0.21641
     93B -> 98B        0.26475
     95B -> 98B        0.86499

 Excited State   6:  3.243-A      3.3878 eV  365.97 nm  f=0.0017
<S**2>=2.379
     94A -> 99A        0.26654
     94A ->103A        0.14319
     95A -> 99A        0.28771
     95A ->103A       -0.14105
     96A -> 99A       -0.11139
     96A ->103A        0.11015
     97A -> 99A       -0.35299
     94B -> 98B        0.39976
     94B -> 99B       -0.15124
     94B ->103B       -0.17412
     95B -> 99B       -0.34260
     95B ->103B        0.13073
     96B -> 98B        0.12186
     97B -> 99B        0.45746

 Excited State   7:  2.359-A      3.4930 eV  354.95 nm  f=0.0078
<S**2>=1.141
     94A -> 99A       -0.12547
     95A -> 99A       -0.14756
     97A -> 99A        0.21575
     92B -> 98B       -0.10480
     93B -> 98B        0.14045
     94B -> 98B        0.85503
     95B -> 98B       -0.16017
```

```
     95B -> 99B        0.14793
     97B -> 99B       -0.22925

 Excited State   8:  2.090-A      3.6053 eV  343.90 nm  f=0.0003
<S**2>=0.842
     98A ->101A        0.14948
     98A ->102A       -0.12435
     92B -> 98B        0.71144
     93B -> 98B        0.65136

 Excited State   9:  2.126-A      3.6547 eV  339.25 nm  f=0.0001
<S**2>=0.880
     97A ->101A       -0.10127
     98A ->100A       -0.29559
     91B -> 98B        0.93001

 Excited State  10:  2.906-A      3.6810 eV  336.82 nm  f=0.1408
<S**2>=1.862
     92A ->101A        0.17702
     93A ->100A       -0.18926
     96A ->102A        0.10779
     97A ->104A        0.28147
     98A ->101A        0.40776
     98A ->102A        0.56379
     98A ->103A        0.11016
     91B ->101B       -0.18612
     92B ->100B        0.15238
     93B ->100B        0.12117
     96B -> 99B        0.11972
     96B ->102B        0.23003
     97B -> 98B        0.14699
     97B ->104B       -0.24333

 Excited State  11:  3.262-A      3.7538 eV  330.29 nm  f=0.0217
<S**2>=2.410
     92A ->100A        0.24891
     93A ->101A       -0.18670
     93A ->102A        0.12317
     95A -> 99A        0.11035
     96A ->104A        0.16810
     97A ->101A        0.22878
     97A ->102A        0.29091
     98A ->100A        0.11715
     98A ->104A        0.40244
     91B ->100B       -0.23307
     92B ->101B        0.17914
     93B ->101B        0.13245
     95B -> 99B       -0.11663
     96B -> 98B       -0.17252
     96B ->104B        0.27344
     97B -> 99B       -0.14348
     97B ->101B       -0.15610
     97B ->102B       -0.33991
     97B ->103B       -0.12264

 Excited State  12:  2.592-A      3.8487 eV  322.15 nm  f=0.0004
<S**2>=1.429
     96A ->100A        0.10860
```

```
     97A ->101A        0.18823
     97A ->102A       -0.18635
     98A ->100A        0.81225
     91B -> 98B        0.31575
     96B ->100B        0.22246
     97B ->101B       -0.21536
     97B ->102B        0.13344

 Excited State  13:  2.662-A      3.8720 eV  320.21 nm  f=0.0091
<S**2>=1.521
     97A ->100A        0.29803
     98A ->101A        0.67425
     98A ->102A       -0.47934
     92B -> 98B       -0.15908
     93B -> 98B       -0.14280
     96B ->101B        0.21879
     97B ->100B       -0.27967

 Excited State  14:  3.382-A      4.0915 eV  303.03 nm  f=0.0003
<S**2>=2.609
```

12f

```
Excitation energies and oscillator strengths:

 Excited State   1:  2.033-A      2.2961 eV  539.97 nm  f=0.1305
<S**2>=0.783
     98A -> 99A        0.15658
     94B -> 98B        0.12507
     97B -> 98B        0.94990
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1314.98383413
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:  2.029-A      2.7284 eV  454.42 nm  f=0.0023
<S**2>=0.779
     96A -> 99A       -0.11729
     98A -> 99A        0.72134
     98A ->105A        0.10230
     91B -> 98B       -0.11453
     92B -> 98B       -0.28260
     93B -> 98B        0.40126
     95B -> 98B       -0.38354

 Excited State   3:  2.060-A      2.8279 eV  438.42 nm  f=0.0233
<S**2>=0.811
     98A -> 99A       -0.45876
     89B -> 98B       -0.12428
     91B -> 98B       -0.16042
     92B -> 98B       -0.38924
     93B -> 98B        0.54888
     94B -> 98B       -0.30983
     96B -> 98B       -0.33215
     97B -> 98B        0.19722

 Excited State   4:  2.119-A      2.8315 eV  437.87 nm  f=0.0575
<S**2>=0.872
```

```
     98A -> 99A       -0.23438
     98A ->104A       -0.11195
     92B -> 98B       -0.12685
     93B -> 98B        0.16726
     94B -> 98B       -0.10672
     96B -> 98B        0.90499

 Excited State   5:  2.053-A      3.2378 eV  382.93 nm  f=0.0195
<S**2>=0.803
     98A -> 99A        0.33504
     93B -> 98B        0.13894
     94B -> 98B       -0.22433
     95B -> 98B        0.87932

 Excited State   6:  3.178-A      3.5196 eV  352.27 nm  f=0.0021
<S**2>=2.276
     94A -> 99A        0.28271
     94A ->103A        0.11675
     95A -> 99A        0.25777
     95A ->103A       -0.20932
     97A -> 99A        0.31977
     93B -> 98B        0.16652
     94B -> 98B        0.42562
     94B -> 99B       -0.19417
     94B ->101B        0.12377
     94B ->103B       -0.13464
     95B -> 98B        0.10073
     95B -> 99B        0.30509
     95B ->103B       -0.17782
     97B -> 99B       -0.41685

 Excited State   7:  2.421-A      3.5792 eV  346.40 nm  f=0.0043
<S**2>=1.216
     94A -> 99A       -0.14695
     95A -> 99A       -0.15273
     97A -> 99A       -0.19487
     93B -> 98B        0.38513
     94B -> 98B        0.75191
     95B -> 98B        0.17755
     95B -> 99B       -0.16622
     97B -> 99B        0.24178

 Excited State   8:  2.107-A      3.6082 eV  343.62 nm  f=0.0006
<S**2>=0.860
     98A ->102A       -0.18122
     91B -> 98B        0.14184
     92B -> 98B        0.77842
     93B -> 98B        0.50754
     94B -> 98B       -0.18787

 Excited State   9:  2.151-A      3.6659 eV  338.21 nm  f=0.0001
<S**2>=0.906
     98A ->100A        0.34860
     91B -> 98B        0.87961
     92B -> 98B       -0.21755

 Excited State  10:  2.902-A      3.6870 eV  336.27 nm  f=0.1417
<S**2>=1.855
```

```
     91A ->100A        0.10451
     92A ->101A       -0.10348
     92A ->102A        0.13697
     93A ->100A       -0.15438
     96A ->101A        0.11197
     97A ->104A        0.28400
     98A ->101A        0.58042
     98A ->102A        0.33693
     98A ->103A        0.18565
     98A ->105A       -0.11447
     91B ->100B        0.14989
     91B ->102B       -0.10232
     92B ->102B        0.11656
     96B -> 99B       -0.13714
     96B ->101B       -0.18822
     96B ->102B       -0.10687
     96B ->103B       -0.12563
     97B -> 98B        0.15077
     97B ->104B       -0.24832

 Excited State  11:  3.247-A      3.7562 eV  330.08 nm  f=0.0207
<S**2>=2.386
     92A ->100A       -0.22596
     93A ->101A       -0.11649
     93A ->102A        0.18033
     95A -> 99A       -0.11610
     96A ->104A        0.18608
     97A ->101A        0.30482
     97A ->102A        0.15626
     97A ->103A        0.11854
     98A ->100A        0.16675
     98A ->104A        0.39495
     91B -> 98B       -0.12133
     91B ->100B        0.22188
     92B ->101B        0.11584
     92B ->102B       -0.15088
     93B ->102B       -0.11313
     95B -> 99B       -0.12603
     96B -> 98B        0.17178
     96B ->104B       -0.26867
     97B -> 99B       -0.13547
     97B ->101B       -0.30167
     97B ->102B       -0.12855
     97B ->103B       -0.19250

 Excited State  12:  2.575-A      3.8408 eV  322.81 nm  f=0.0020
<S**2>=1.408
     96A ->100A        0.10589
     97A ->100A        0.17984
     97A ->102A       -0.19084
     98A ->100A        0.78352
     98A ->104A       -0.11257
     91B -> 98B       -0.35642
     96B ->100B       -0.21585
     97B ->100B       -0.16463
     97B ->102B        0.18525
```

```
 Excited State  13:  2.654-A      3.8680 eV  320.54 nm  f=0.0108
<S**2>=1.510
     96A ->102A        0.10555
     97A ->100A       -0.21648
     97A ->102A       -0.17549
     98A ->101A       -0.42999
     98A ->102A        0.70421
     92B -> 98B        0.19140
     93B -> 98B        0.12452
     96B ->101B        0.10723
     96B ->102B       -0.19998
     97B ->100B        0.20544
     97B ->102B        0.18553

 Excited State  14:  3.343-A      4.1249 eV  300.57 nm  f=0.0021
<S**2>=2.543
     90A -> 99A       -0.17143
     92A ->100A       -0.12407
     94A -> 99A        0.12476
     94A ->101A       -0.12227
     94A ->103A        0.15491
     95A ->103A       -0.26496
     97A -> 99A       -0.40994
     97A ->105A       -0.14501
     98A ->101A       -0.15234
     98A ->103A        0.17049
     98A ->104A        0.19170
     90B -> 99B        0.18847
     91B ->100B        0.13257
     94B ->101B        0.17904
     94B ->102B        0.10240
     94B ->103B       -0.17352
     95B ->103B       -0.21357
     97B -> 99B        0.44705
     97B ->105B        0.17371

 Excited State  15:  2.560-A      4.1464 eV  299.02 nm  f=0.0454
<S**2>=1.389
     92A ->102A       -0.12089
     93A ->100A        0.12349
     96A ->101A       -0.14441
     96A ->102A       -0.10390
     97A -> 99A       -0.13628
     97A ->104A       -0.17245
     98A -> 99A       -0.11612
     98A ->101A        0.48703
     98A ->102A        0.32555
     98A ->103A       -0.18476
     98A ->105A        0.25365
     90B -> 98B       -0.41831
     91B ->100B       -0.10212
     92B ->102B       -0.13158
     96B ->101B        0.11474
     97B -> 99B        0.10348
     97B ->104B        0.17457
```

4. Archive data for DFT calculations.

CAM-B3LYP/6-31G(2d,p) geometries

12a


```
1\1\GINC-OCTOPUS\SP\UB3LYP TD-FC\6-31G(2d,p)\C15H10F3N4O3(2)\PIOTR\25-
 Dec-2014\0\\#P B3LYP/6-31G(2d,p) TD(NStates=15) SCF=tight Geom(NoAngle
 , noDistance, check) #P guess=check SCRF(solvent=1,4-Dioxane)\\Bis(4-h
 ydroxyphenyl)-3-CF3- oxoverdazyl\\0,2\O,0,-0.0041306748,-0.0194381643,
 2.3653117448\C,0,-0.0041861472,-0.0048079307,1.1595516698\N,0,-1.17031
 20527,0.0658713828,0.4007585621\N,0,-1.187591131,0.0712000601,-0.95249
 66383\C,0,-0.0066618686,0.0278411175,-1.5218224826\N,0,1.1774095653,-0
 .0276235742,-0.9521916081\N,0,1.1630355357,-0.0566221176,0.3992460054\
 C,0,2.4529880317,-0.0436020788,1.0190116323\C,0,2.709508689,-0.7434216
 78,2.1906750718\C,0,3.9826480973,-0.7232195664,2.7360374134\C,0,5.0037
 62805,-0.013442303,2.1155950768\C,0,4.7449594434,0.6789868827,0.937255
 1315\C,0,3.4755418118,0.6637753879,0.3940994624\C,0,-2.459371549,0.046
 942701,1.022772346\C,0,-3.4838141424,-0.6541070067,0.3944721033\C,0,-4
 .7519156481,-0.6738816515,0.9408099547\C,0,-5.0069199861,0.0072180656,
 2.1265029284\C,0,-3.9836657787,0.710455887,2.7509123322\C,0,-2.7122411
 764,0.7353540713,2.2017787293\H,0,3.2677256456,1.1902513679,-0.5278411
 078\H,0,5.5497508236,1.2263783198,0.4625072305\H,0,4.1812180877,-1.270
 5968797,3.6525716349\H,0,1.9209555998,-1.2939546937,2.6803697553\H,0,-
 1.9217876049,1.2804696936,2.6947383535\H,0,-4.1792912417,1.2487302712,
 3.673453809\H,0,-5.5583052686,-1.216299278,0.4630794451\H,0,-3.2792829
 53,-1.1722253376,-0.5329155424\O,0,-6.266472118,-0.0492208876,2.622835
 2821\H,0,-6.3123698671,0.4606646173,3.4374705704\O,0,6.2646922291,0.03
 88663711,2.6087493961\H,0,6.3133465545,-0.4790016455,3.4181814096\C,0,
 0.0118700933,-0.0017588175,-3.0360346208\F,0,-1.1445194782,0.405369504
 9,-3.5425372556\F,0,0.2404937435,-1.2420729775,-3.4769183254\F,0,0.979
 2386504,0.7789630964,-3.5117477998\\Version=EM64L-G09RevD.01\State=2-A
 \HF=-1321.8058808\S2=0.767602\S2-1=0.\S2A=0.750161\RMSD=9.875e-09\PG=C
 01 [X(C15H10F3N4O3)]
```


12b


```
1\1\GINC-OCTOPUS\SP\UB3LYP TD-FC\6-31G(2d,p)\C16H13N4O5(2)\PIOTR\25-De
 c-2014\0\\#P B3LYP/6-31G(2d,p) TD(NStates=15) SCF=tight Geom(NoAngle,
 noDistance, check) #P guess=check SCRF(solvent=1,4-Dioxane)\\1,5-bis(4
 -hydroxyphenyl) 3-COOMe oxoverdazyl in dioxane\\0,2\O,0,-2.0934956221,
 0.0211232236,1.1504821347\C,0,-3.2318618916,0.3984208733,1.2826949067\
 N,0,-3.6808291253,1.6329129042,0.8213306806\N,0,-4.9562864368,2.065894
 3665,0.9489836403\C,0,-5.7704082213,1.2455031803,1.5824256158\N,0,-5.4
 900366498,0.0588270409,2.0843116447\N,0,-4.2176177663,-0.3599691857,1.
 909584589\C,0,-3.9118541089,-1.6222910504,2.5127716493\C,0,-3.01120028
 47,-2.5111557613,1.9405954646\C,0,-2.7715896586,-3.7321376941,2.549963
 6384\C,0,-3.4303728947,-4.0751299579,3.7241703807\C,0,-4.339733687,-3.
 1869466813,4.2884915477\C,0,-4.5774708122,-1.9675950081,3.6854285593\C
 ,0,-2.8199793193,2.5040733731,0.0805060133\C,0,-3.3700457789,3.2379031
 164,-0.9660788873\C,0,-2.587111456,4.1158387536,-1.6896769972\C,0,-1.2
 410528022,4.2670706299,-1.374267948\C,0,-0.6937990677,3.5376775381,-0.
 3258751102\C,0,-1.4785775014,2.6598118565,0.4041991541\H,0,-5.29472105
 79,-1.2768836379,4.1080300945\H,0,-4.8502886139,-3.4673909951,5.201447
 748\H,0,-2.0660509706,-4.4249984069,2.1011354186\H,0,-2.4921032008,-2.
 251460558,1.0310025416\H,0,-1.0447625947,2.0939916072,1.2143055101\H,0
 ,-3.0023389022,4.6917584388,-2.5074628075\H,0,-4.4209832309,3.12310297
 75,-1.1953310247\O,0,-3.2294191437,-5.2559885532,4.3594227654\H,0,-2.5
```

860876468,-5.7762177949,3.8684378694\O,0,-0.516154712,5.1373869266,-2.
1194624064\H,0,0.3918857005,5.1498641338,-1.8017493898\H,0,0.355070930
9,3.6566379855,-0.0710272403\C,0,-7.1920971751,1.6922756127,1.78568332
42\O,0,-7.9692040105,1.1271415382,2.5025691772\O,0,-7.4730442522,2.782
3728887,1.0747494759\C,0,-8.8040913975,3.2678422869,1.2360701604\H,0,-
8.8755334733,4.1515531875,0.6046431541\H,0,-9.5269935051,2.5117077585,
0.9242018639\H,0,-8.9930327596,3.5245803764,2.2800499592\\Version=EM64
L-G09RevD.01\State=2-A\HF=-1212.649321\S2=0.769427\S2-1=0.\S2A=0.75018
\RMSD=9.078e-09\PG=C01 [X(C16H13N4O5)]\\

12c

1\1\GINC-OCTOPUS\SP\UB3LYP TD-FC\6-31G(2d,p)\C18H13N4O3S1(2)\PIOTR\25-
Dec-2014\0\\#P B3LYP/6-31G(2d,p) TD(NStates=15) SCF=tight Geom(NoAngle
, noDistance, check) #P guess=check SCRF(solvent=1,4-Dioxane)\\1,5-Bis
(4-HOphenyl)-3-thienyl oxoverdazyl in dioxane\\0,2\O,0,-2.0945915888,0
.0097732972,1.1535158293\C,0,-3.2365268786,0.3864569873,1.2761472253\N
,0,-3.6869843371,1.6151549021,0.8094897843\N,0,-4.9666685802,2.0413452
614,0.9237180032\C,0,-5.7980910341,1.2244655692,1.5490988843\N,0,-5.50
47545612,0.0380348158,2.058791907\N,0,-4.2231308851,-0.3695110745,1.89
87757885\C,0,-3.9080407375,-1.6219650134,2.5135326702\C,0,-3.037541237
3,-2.5276945036,1.9219078039\C,0,-2.7838741698,-3.7409576806,2.5406032
744\C,0,-3.3986417124,-4.0593213748,3.745479886\C,0,-4.2754431526,-3.1
534111708,4.3322483231\C,0,-4.525704006,-1.9414211549,3.7184229404\C,0
,-2.8227474852,2.487215088,0.0753723827\C,0,-3.3564285005,3.2032245478
,-0.9915503979\C,0,-2.5664440321,4.081260395,-1.7078787563\C,0,-1.2294
590584,4.2496745418,-1.3647019951\C,0,-0.6977994609,3.5366035841,-0.29
7135722\C,0,-1.4898752804,2.659033589,0.4251396909\H,0,-5.2118309689,-
1.2328906486,4.1628679574\H,0,-4.7479851065,-3.4134314732,5.2714064709
\H,0,-2.1020225821,-4.4471390195,2.0761383563\H,0,-2.5517659768,-2.283
9541856,0.9893137512\H,0,-1.0689363425,2.1041437376,1.2496400673\H,0,-
2.969280799,4.6434709357,-2.5412620452\H,0,-4.399698483,3.0727792341,-
1.2460471251\C,0,-7.1809493782,1.6782045738,1.6915453871\C,0,-8.230153
4466,0.9966276986,2.2364349477\S,0,-7.6644015559,3.2439752442,1.142669
3614\C,0,-9.4388461806,1.7397330202,2.213515718\C,0,-9.2811678302,2.96
94404803,1.6515372431\H,0,-8.1255797022,-0.0035614321,2.6331697998\H,0
,-10.3802921309,1.3706474484,2.5981388143\H,0,-10.0274797703,3.7356266
529,1.5060013174\O,0,-3.1832839641,-5.2325067957,4.3909036644\H,0,-2.5
616261784,-5.7644625928,3.8848197664\O,0,-0.4965807323,5.1194857984,-2
.1034000659\H,0,0.4038534186,5.1440339638,-1.7654904813\H,0,0.34434185
83,3.6681428635,-0.0215749073\\Version=EM64L-G09RevD.01\State=2-A\HF=-
1536.5926318\S2=0.772552\S2-1=0.\S2A=0.750232\RMSD=4.558e-09\PG=C01 [X
(C18H13N4O3S1)]\\

12d

1\1\GINC-OCTOPUS\SP\UB3LYP TD-FC\6-31G(2d,p)\C20H15N4O3(2)\PIOTR\25-De
c-2014\0\\#P B3LYP/6-31G(2d,p) TD(NStates=15) SCF=tight Geom(NoAngle,
noDistance, check) #P guess=check SCRF(solvent=1,4-Dioxane)\\1,5-Bix-(
4-hydroxyphenyl)-3 Ph oxoverdazyl, C2 symm in dioxane\\0,2\O,0,0.00060
16016,-0.002398624,2.3718315558\C,0,0.0005215482,-0.0018335773,1.16301
50171\N,0,-1.1593760486,0.0591697884,0.4014002553\N,0,-1.1777235639,0.
0426329097,-0.9522783183\C,0,0.0003423719,-0.0005651089,-1.5535019935\
N,0,1.178487429,-0.0443244096,-0.9524743767\N,0,1.1603184018,-0.062125
1951,0.4011904347\C,0,2.4485826929,-0.045374986,1.0223011101\C,0,2.707
4785348,-0.7559454847,2.1869007779\C,0,3.9786751361,-0.7336466578,2.73
7251526\C,0,4.9970191815,-0.0100558113,2.1288045011\C,0,4.7369236652,0
.6951358957,0.9588861078\C,0,3.4685171443,0.6774801109,0.4118163387\C,
0,0.0002443845,0.0001249406,-3.0358709837\C,0,1.1835131917,-0.21447730
94,-3.7398721875\C,0,1.1812223914,-0.2135109779,-5.1256509605\C,0,0.00

00598615,0.0014192458,-5.8228223657\C,0,-1.1810102286,0.2157020864,-5.
1252951389\C,0,-1.1831175239,0.2153813032,-3.7395158099\C,0,-2.4475585
216,0.0418359289,1.022664674\C,0,-3.4675737744,-0.6804443582,0.4116347
217\C,0,-4.7359077959,-0.6986154552,0.9588554032\C,0,-4.9958488541,0.0
054744336,2.1294714298\C,0,-3.9774246215,0.7284929872,2.7384642706\C,0
,-2.7063006391,0.7513102647,2.1879667951\H,0,3.2579222587,1.2172878552
,-0.5017156295\H,0,5.5389809783,1.255533914,0.4945499301\H,0,4.1778942
661,-1.289827527,3.6484877007\H,0,1.9195299351,-1.3153198431,2.6678938
451\H,0,-2.0994644128,0.3854413548,-3.1889798966\H,0,-2.1071883367,0.3
864619914,-5.6628647955\H,0,-0.0000120334,0.0019225989,-6.9072802389\H
,0,2.1073292785,-0.3837715229,-5.6635016658\H,0,2.0999329682,-0.385048
6429,-3.1896157638\H,0,-1.9182886805,1.3102322115,2.6693817932\H,0,-4.
1765233692,1.2838162555,3.6502496616\H,0,-5.5380262578,-1.2585765219,0
.4940979989\H,0,-3.2570995458,-1.2193920201,-0.5024325963\O,0,-6.25599
22108,-0.0490073597,2.6282484643\H,0,-6.302150464,0.4753543439,3.43352
45684\O,0,6.2572284981,0.0439565272,2.6274660611\H,0,6.3034939133,-0.4
811655548,3.432240399\\Version=EM64L-G09RevD.01\State=2-A\HF=-1215.838
0397\S2=0.771019\S2-1=0.\S2A=0.750206\RMSD=7.133e-09\PG=C01 [X(C20H15N
4O3)]\\

12e

1\1\GINC-OCTOPUS\SP\UB3LYP TD-FC\6-31G(2d,p)\C20H14F1N4O3(2)\PIOTR\25-
Dec-2014\0\\#P B3LYP/6-31G(2d,p) TD(NStates=15) SCF=tight Geom(NoAngle
, noDistance, check) #P guess=check SCRF(solvent=1,4-Dioxane)\\1,5-Bis
(4-hydroxyphenyl)-3-Ph-m-F oxoverdazyl, in dioxane\\0,2\O,0,0.00005934
61,-0.0036159412,2.3688341443\C,0,-0.000375998,-0.0033145072,1.1605763
091\N,0,-1.1613192991,0.058392099,0.3994392686\N,0,-1.1802524095,0.042
8213367,-0.9537248913\C,0,-0.0021926216,-0.0029282107,-1.5535587274\N,
0,1.176363003,-0.0490531267,-0.954733008\N,0,1.1596228439,-0.064630703
4,0.3983920933\C,0,2.4479701447,-0.0494976413,1.0197180316\C,0,2.70677
95052,-0.7679387343,2.1793326977\C,0,3.9775101957,-0.7474035474,2.7305
061863\C,0,4.99495195,-0.0176114589,2.1276282831\C,0,4.7345916119,0.69
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3584,-1.2585090166,0.5073368174\H,0,-3.2609392857,-1.22680089,-0.49313
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12f

1\1\GINC-OCTOPUS\SP\UB3LYP TD-FC\6-31G(2d,p)\C20H14F1N4O3(2)\PIOTR\25-
Dec-2014\0\\#P B3LYP/6-31G(2d,p) TD(NStates=15) SCF=tight Geom(NoAngle
, noDistance, check) #P guess=check SCRF(solvent=1,4-Dioxane)\\1,5(4-h

ydroxyphenyl) Ph-o-F oxoverdazyl, in dioxane\\0,2\O,0,0.0024922051,0.0
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5. References

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