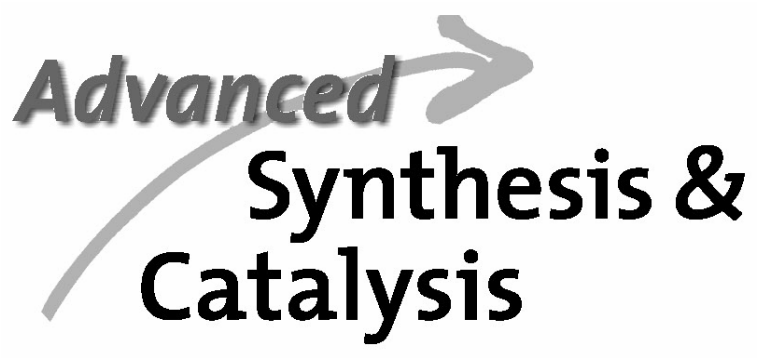

Supporting Information

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Novel and Mild Route to Phthalocyanines and 3-Iminoisoindolin-1-ones via *N*,*N*-diethylhydroxylamine-Promoted Conversion of Phthalonitriles and a Dramatic Solvent-Dependence of the Reaction

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C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ESI mass spectra were obtained on a Bruker *esquire*$_{3000}^{TM}$ (ESI) instrument; samples were dissolved in MeOH. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D NMR experiments, *i.e.* ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F, and 2D NMR correlation experiments, *i.e.* $^{1}H,^{13}C$-HMQC, $^{1}H,^{13}C$-HMBC, $^{1}H,^{15}N$-HMQC and TOCSY spectra were recorded on Bruker Avance DPX 400 (UltraShield^{TM} Magnet) and Varian UNITY 300 spectrometers at ambient temperature. ^{15}N NMR chemical shifts are related to NH_4Cl (0.0 ppm).

6. Anal. Calcd for $C_{32}H_{18}N_8$: C, 74.70; H, 3.53; N, 21.78. Found: C, 74.66; H, 3.47; N, 21.14. **6** was also identified by comparison of its IR spectrum with that of the commercially available **Pc** (Aldrich).

7. Anal. Calcd for $C_{36}H_{26}N_8$: C, 75.77; H, 4.59; N, 19.64. Found: C, 75.53; H, 4.30; N, 19.55. IR spectrum, selected bands, cm^{-1}: 3366 m-w ν(NH), 3082 m-w ν(CH), 1643 m-w ν(C=N), 1502 m-w δ(NH).

8. Anal. Calcd for $C_{32}H_{10}N_8Cl_8$: C, 48.65; H, 1.26; N, 14.18. Found: C, 48.50; H, 1.30; N, 14.07. IR spectrum, selected bands, cm^{-1}: 3309 m-w ν(NH), 3090 m-w ν(CH), 1612 m-w ν(C=N), 1522 ν_{as} and 1338 vs $\nu_s(NO_2)$, 1522 s δ(NH).

18. Anal. Calcd for $C_8H_6N_2O$: C, 65.75; H, 4.14; N, 19.17%. Found: C, 65.60; H, 4.00; N, 18.80%. ESI-MS, *m/z*: 169 $[M + Na]^+$. IR spectrum (selected bands), cm^{-1}: 3263, 3080, 3054, 2968, 2921, 1723, 1699, 1675, 1614, 1539, 1439, 1257, 1219, 1132, 899. ^{1}H NMR spectrum in DMSO-d_6, δ: 7.66–8.02 (m, 4*H*, Ph), 9.59 (s, br, 1*H*, N*H*), 10.35 (s, 1H, N*H*). $^{13}C\{^{1}H\}$ NMR spectrum in DMSO-d_6 (through direct $^{13}C\{^{1}H\}$ observation and $^{1}H,^{13}C$-HMQC, and $^{1}H,^{13}C$-

HMBC experiments), δ: 120.4, 120.8, 122.6, 123.0, 130.8, 131.3, 132.9, 133.4 (Ph), 164.5 and 173.1(HN=C and C=O).

19. Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49%. Found: C, 67.02; H, 4.89; N, 17.21%. ESI-MS, *m/z*: 183 $[M + Na]^+$. IR spectrum (selected bands), cm^{-1}: 3288, 2984, 1726, 1699, 1672, 1617, 1535, 1442, 1219, 1176, 1135, 1053, 904. ^1H NMR spectrum in DMSO-d_6, δ: 2.43 and 2.54 (s, Me, 1H), 7.49–7.87 (m, 3*H*, Ph), 9.81 (s, br, N*H*). $^{13}C\{^1H\}$ NMR spectrum in DMSO-d_6 (through direct $^{13}C\{^1H\}$ observation and $^1H,^{13}C$-HMQC, and $^1H,^{13}C$-HMBC experiments), δ: 20.9 and 21.2 (Me), 121.5, 122.0, 122.4, 132.5, 133.1, 142.2, 143.1 (Ph), 163.3 and 172.3(HN=C and C=O).

20. Anal. Calcd for $C_8H_4N_2Cl_2O$: C, 44.68; H, 1.87; N, 13.03%. Found: C, 44.12; H, 1.80; N, 12.87%. ESI-MS, *m/z*: 215 $[M + H]^+$, 237 $[M + Na]^+$. IR spectrum (selected bands), cm^{-1}: 3287, 3085, 3050, 2919, 1712, 1698, 1673, 1601, 1539, 1458, 1434, 1369, 1242, 1206, 1167, 1127, 904. ^1H NMR spectrum in DMSO-d_6, δ: 7.91 and 8.35 (s, 2*H*, Ph), 9.63 (s, br, 1*H*, N*H*), 10.39 (s, 1H, N*H*). $^{13}C\{^1H\}$ NMR spectrum in DMSO-d_6 (through direct $^{13}C\{^1H\}$ observation and $^1H,^{13}C$-HMQC, and $^1H,^{13}C$-HMBC experiments), δ: 124.0, 124.2, 124.7, 133.5, 133.9, 135.1, 135.2 (Ph), 166.1 and 177.6 (HN=C and C=O).

21. Anal. Calcd for $C_8H_2N_2F_4O$: C, 44.05; H, 0.92; N, 12.84%. Found: C, 43.85; H, 0.87; N, 12.80%. ESI-MS, *m/z*: 219 $[M + H]^+$, 241 $[M + Na]^+$. IR spectrum (selected bands), cm^{-1}: 3290, 2932, 1737, 1723, 1670, 1647, 1607, 1548, 1498, 1490, 1426, 1296, 1193, 1183, 1138, 1086, 922, 897. ^1H NMR spectrum in DMSO-d_6, δ: 9.09 (s, br, 1*H*, N*H*), 10.23 (s, 1H, N*H*). ^{19}F NMR spectrum in DMSO-d_6, δ: - 61.7 (m), - 67.2 (m), - 67.9 (m). $^{13}C\{^1H\}$ NMR spectrum in DMSO-d_6 (through direct $^{13}C\{^1H\}$ observation and $^1H,^{13}C$-HMQC, and $^1H,^{13}C$-HMBC

experiments), δ: 116.5, 118.0, 139.6, 140.7, 140.9, 144.1, 144.3 (Ph), 166.0 and 172.5 (HN=C and C=O).

9. Anal. Calcd for $C_{32}H_{16}N_8Zn$: C, 66.50; H, 2.79; N, 19.39. Found: C, 65.98; H, 2.60; N, 19.02. IR spectrum, selected bands, cm^{-1}: 3002, 2927, 2847, 1616 m-w ν(C=N), 1504, 1470, 1418, 1385, 1339, 1292, 1174, 1119, 1092, 730.

10. Anal. Calcd for $C_{36}H_{24}N_8Zn$: C, 68.20; H, 3.82; N, 17.67. Found: C, 68.12; H, 3.80; N, 17.50. IR spectrum, selected bands, cm^{-1}: 2992, 2925, 2853, 1609 m-w ν(C=N), 1518, 1471, 1423, 1387, 1338, 1297, 1178, 1121, 1092, 732.

11. Anal. Calcd for $C_{32}H_{16}N_8Cd$: C, 61.50; H, 2.58; N, 17.93. Found: C, 61.12; H, 2.46; N, 18.01. IR spectrum, selected bands, cm^{-1}: 2982, 2925, 2854, 1606 m-w ν(C=N), 1515, 1473, 1402, 1392, 1333, 1297, 1176, 1121, 1092, 753.

12. Anal. Calcd for $C_{32}H_{16}N_8Co$: C, 67.26; H, 2.82; N, 19.61. Found: C, 66.92; H, 2.60; N, 19.52. IR spectrum, selected bands, cm^{-1}: 2980, 2925, 2854, 1612 m-w ν(C=N), 1518, 1474, 1420, 1385, 1338, 1297, 1178, 1121, 1094, 739. **12** was also identified by comparison of its IR spectrum with that of the commercially available sample (Aldrich).

13. Anal. Calcd for $C_{36}H_{24}N_8Co$: C, 68.90; H, 3.85; N, 17.86. Found: C, 68.70; H, 3.74; N, 17.63. IR spectrum, selected bands, cm^{-1}: 2992, 2918, 2855, 1614 m ν(C=N), 1512, 1482, 1404, 1389, 1333, 1292, 1182, 1119, 1090, 738.

14. Anal. Calcd for $C_{32}H_{12}N_{12}O_8Co$: C, 51.15; H, 1.61; N, 22.37. Found: C, 51.01; H, 1.55; N, 22.07. IR spectrum, selected bands, cm^{-1}: 2992, 2918, 2855, 1611 m-w ν(C=N), 1512, 1526 ν_{as} and 1332 vs $\nu_s(NO_2)$, 1482, 1396, 1382, 1290, 1187, 1124, 1088, 736.

15. Anal. Calcd for $C_{32}H_{16}N_8Ni$: C, 67.29; H, 2.82; N, 19.62. Found: C, 67.12; H, 2.80; N, 19.44. IR spectrum, selected bands, cm^{-1}: 3098 m-w ν(CH), 1611 m-w ν(C=N). **15** was also identified by comparison of its IR spectrum with that of the commercially available sample (Aldrich).

16. Anal. Calcd for $C_{36}H_{24}N_8Ni$: C, 68.93; H, 3.86; N, 17.86. Found: C, 68.47; H, 3.83; N, 17.78. IR spectrum, selected bands, cm^{-1}: 2992, 2918, 2855, 1609 m ν(C=N), 1512, 1482, 1404, 1389, 1333, 1292, 1182, 1119, 1090, 738.

17. Anal. Calcd for $C_{32}H_{12}N_{12}O_8Ni$: C, 51.16; H, 1.61; N, 22.37. Found: C, 51.12; H, 1.60; N, 21.90. IR spectrum, selected bands, cm^{-1}: 2990, 2917, 2854, 1611 m-w ν(C=N), 1510, 1523 ν_{as} and 1331 vs $\nu_s(NO_2)$, 1482, 1396, 1382, 1290, 1185, 1124, 1088.