Support Information for: Parallel Synthesis of Strongly Fluorescent Polysubstituted

2, 6-dicyanoanilines *via* Microwave-promoted Multicomponent Reaction

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General Experimental Methods. Reactions were carried out in a multi-mode microwave synthesizer. Commercial solvents and reagents were used as received. Column chromatography was carried out on silica gel (10-40 mesh). Infrared spectra were obtained on a FTIR spectrometer. NMR spectra were recorded for ^1H NMR at 500 MHz, for ^{13}C NMR at 125 MHz at 293 K unless otherwise noted. Chemical shifts are reported relative to residue peaks of the solvents either CDCl_3 (7.26 ppm for ^1H and 77.27 ppm for ^{13}C) or $\text{DMSO}-d_6$ (2.50 ppm for ^1H and 40.00 ppm for ^{13}C). Low-resolution MS were obtained using ESI or EI ionization. HRMS were obtained ESI or EI ionization.

General Procedure for Microwave-promoted Parallel synthesis of 2,6-dicyanoanilines in solution. The appropriate aldehydes (10 mmol), ketones (10 mmol), propanedinitrile (25 mmol) and triethylamine (15 mmol) were placed in 5 individual 25 mL glass bottles immersed in a pyrex crystallization dish filled with neutral alumina (500 g, 100-200 mesh). This set-up was placed at the cavity of microwave synthesizer. After irradiation at 300 W for 2 min, the reaction mixture was cooled to room temperature and then dissolved in CH_2Cl_2 . The solution was washed with water, dried over anhydrous Na_2SO_4 and evaporated in vacuum. The crude products were purified by a flash column chromatography on silica gel with ethyl acetate-hexane (1:4, v/v). All the compounds were recrystallized from ethanol.

General Procedure for Microwave-promoted Parallel synthesis of 2,6-dicyanoanilines on PEG support. The appropriate PEG-supported aldehydes (10

mmol), ketones (20 mmol), propanedinitrile (30 mmol) and ammonium acetate (10 mmol) were placed in 5 individual 25 mL glass bottles immersed in a pyrex crystallization dish. This set-up was placed at the cavity of microwave synthesizer. After irradiation at 300 W for 2 min, the reaction mixtures were cooled to room temperature. The polymer-supported products were crystallized from isopropanol (30 mL), washed with diethyl ether and subsequently dried in vacuum. The polymers were treated with 0.1 N NaOMe in anhydrous MeOH (10 mL) at room temperature for 6 h. The detached PEG-OH was precipitated by adding cold diethyl ether (30 mL) and filtered. The filtrates were washed with brine, dried over anhydrous Na₂SO₄ and evaporated in vacuum to afford the corresponding crude products. The pure products were obtained by recrystallization from EtOH.

Characterization Data for Products

2,6-dicyano-4-methyl-3,5-diphenylaniline (4a). A white powder; m.p. 224-226 °C (lit.¹ 229-231 °C); ¹H NMR (CDCl₃) δ 7.49 (m, 6H), 7.30 (m, 4H), 5.13 (bs, 2H), 1.75 (s, 3H) ppm; ¹³C NMR (CDCl₃) δ 150.9, 149.9, 137.9, 129.2, 129.1, 128.6, 125.2, 115.8, 98.2, 17.9 ppm; IR (KBr) ν 3546, 3343, 3236, 2923, 2226, 1637, 1561, 1541, 1431, 1262, 1024, 755, 702 cm⁻¹; MS (ESI) m/z 332.0 ([M+Na]⁺); HRMS (ESI) calcd for C₂₁H₁₅N₃ ([M+Na]⁺), 332.1158; found, 332.1156.

2,6-dicyano-4-methyl-3-(4-methylphenyl)-5-phenylaniline (4b). A white powder; m.p. 216-217 °C; ¹H NMR (CDCl₃) δ 7.49 (m, 3H), 7.30 (m, 4H), 7.19 (d, *J* = 8.05

Hz, 2H), 5.11 (bs, 2H), 2.42 (s, 3H), 1.76 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 151.0, 150.7, 149.9, 139.1, 137.9, 134.9, 129.8, 129.1, 129.1, 128.6, 128.6, 125.3, 116.0, 115.9, 98.2, 98.0, 21.6, 17.9 ppm; IR (KBr) ν 3468, 3358, 3241, 2924, 2222, 1640, 1561, 1437, 1021, 821, 771, 704 cm^{-1} ; MS (ESI) m/z 322.1 ($[\text{M}-\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{17}\text{N}_3$ ($[\text{M}+\text{Na}]^+$), 346.1315; found, 346.1311.

2,6-dicyano-3-(4-fluorophenyl)-4-methyl-5-phenylaniline (4d). A white powder; m.p. 188-190 $^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.53 (m, 2H), 7.49 (m, 1H), 7.45 (m, 2H), 7.37 (m, 4H), 6.61 (bs, 2H), 1.61 (s, 3H) ppm; ^{13}C NMR ($\text{DMSO}-d_6$) δ 162.6 (d, $J_{\text{C-F}} = 244.1$ Hz), 151.3, 150.9, 149.9, 138.3, 134.6 (d, $J_{\text{C-F}} = 3.1$ Hz), 131.3 (d, $J_{\text{C-F}} = 8.3$ Hz), 129.2, 129.1, 128.9, 123.3, 116.2 (d, $J_{\text{C-F}} = 21.4$ Hz), 116.2, 116.1, 97.48, 97.46, 17.9 ppm; IR (KBr) ν 3471, 3360, 3238, 3058, 2223, 1638, 1562, 1512, 1450, 1264, 1226, 1159, 839, 704, 528 cm^{-1} ; MS (ESI) m/z 326.1 ($[\text{M}-\text{H}]^+$); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{14}\text{FN}_3$ (M^+), 327.1166; found, 327.1165.

3-(4-chlorophenyl)-2,6-dicyano-4-methyl-5-phenylaniline (4e). A white powder; m.p. 214-216 $^\circ\text{C}$; ^1H NMR (CDCl_3) δ 7.49 (m, 5H), 7.27 (m, 4H), 5.15 (bs, 2H), 1.74 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 151.1, 150.0, 149.4, 137.7, 136.2, 135.4, 130.1, 129.5, 129.3, 129.1, 128.6, 125.1, 115.67, 115.65, 98.5, 97.9, 17.9 ppm; IR (KBr) ν 3465, 3358, 3242, 3059, 2222, 1639, 1561, 1494, 1438, 1267, 1093, 1016, 831, 774, 706, 526 cm^{-1} ; MS (ESI) m/z 342.6 ($[\text{M}-\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{14}\text{ClN}_3$ ($[\text{M}+\text{Na}]^+$), 366.0768; found, 366.0761.

3-(2-chlorophenyl)-2,6-dicyano-4-methyl-5-phenylaniline (4f). A white powder;

m.p. 223-225 °C; ^1H NMR (CDCl_3) δ 7.51 (m, 4H), 7.42 (m, 2H), 7.28 (m, 3H), 5.15 (bs, 2H), 1.71 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 150.8, 150.0, 147.9, 137.6, 136.7, 132.8, 130.7, 130.3, 130.1, 129.2, 129.1, 129.0, 128.8, 128.6, 127.7, 125.8, 115.7, 115.3, 98.8, 98.0, 17.2 ppm; IR (KBr) ν 3459, 3348, 3240, 3061, 2926, 2225, 1638, 1561, 1435, 1265, 1062, 1027, 760, 707 cm^{-1} ; MS (ESI) m/z 365.9 ($[\text{M}+\text{Na}]^+$); HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{14}\text{ClN}_3$ ($[\text{M}+\text{Na}]^+$), 366.0768; found, 366.0764.

3-(2,6-dichlorophenyl)-2,6-dicyano-4-methyl-5-phenylaniline (4g). A colorless crystals; m.p. 262-264 °C; ^1H NMR (CDCl_3) δ 7.49 (m, 5H), 7.36 (m, 1H), 7.32 (d, J = 6.91 Hz, 2H), 5.17 (bs, 2H), 1.70 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 151.1, 150.2, 145.5, 137.4, 135.5, 134.3, 131.2, 129.3, 129.0, 128.8, 128.7, 125.7, 115.6, 114.8, 99.3, 97.6, 16.6 ppm; IR (KBr) ν 3482, 3380, 3235, 3080, 2931, 2226, 1626, 1561, 1427, 1268, 1190, 1028, 790, 739, 701 cm^{-1} ; MS (ESI) m/z 376.6 ($[\text{M}-\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{13}\text{Cl}_2\text{N}_3$ ($[\text{M}+\text{H}]^+$), 378.0559; found, 378.0566.

2,6-dicyano-3-(3,4,5-trimethoxyphenyl)-4-methyl-5-(4-methylphenyl)aniline (4j). A colorless crystal needle; m.p. 198-200 °C; ^1H NMR (CDCl_3) δ 7.30 (d, J = 8 Hz, 2H), 7.18 (d, J = 8 Hz, 2H), 6.49 (s, 2H), 5.13 (bs, 2H), 3.92 (s, 3H), 3.88 (s, 6H), 2.42 (s, 3H), 1.80 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 153.7, 151.1, 150.6, 149.9, 139.1, 138.6, 134.9, 133.2, 129.8, 128.5, 125.4, 115.9, 115.9, 106.1, 98.2, 97.9, 61.2, 56.5, 25.6, 17.9 ppm; IR (KBr) ν 3396, 3346, 3251, 2940, 2217, 1629, 1585, 1509, 1453, 1308, 1240, 1125, 1006, 819, 618 cm^{-1} ; MS (ESI) m/z 412.2 ($[\text{M}-\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_3$ ($[\text{M}+\text{Na}]^+$), 436.1632; found, 436.1623.

3-(2-chlorophenyl)-2,6-dicyano-4-methyl-5-(4-methylphenyl)aniline (4k). A white powder; m.p. 208-209 °C; ¹H NMR (CDCl₃) δ 7.54 (m, 1H), 7.41 (m, 2H), 7.28 (m, 3H), 7.20 (m, 2H), 5.12 (bs, 2H), 2.42 (s, 3H), 1.72 (s, 3H) ppm; ¹³C NMR (CDCl₃) δ 151.1, 149.9, 147.8, 139.2, 136.8, 134.6, 132.9, 130.7, 130.3, 130.2, 129.8, 128.7, 128.5, 127.7, 126.0, 115.9, 115.3, 98.9, 97.9, 21.6, 17.2 ppm; IR (KBr) ν 3458, 3347, 3238, 2924, 2225, 1637, 1560, 1442, 1261, 1061, 822, 766 cm⁻¹; MS (ESI) m/z 356.2 ([M-H]⁺); HRMS (ESI) calcd for C₂₂H₁₆ClN₃ ([M+Na]⁺), 380.0925; found, 380.0934.

3-(2,6-dichlorophenyl)-2,6-dicyano-4-methyl-5-(4-methylphenyl)aniline (4l). A pale yellow crystal needle; m.p. 257-258 °C; ¹H NMR (CDCl₃) δ 7.48 (d, *J* = 8 Hz, 2H), 7.37 (m, 1H), 7.31 (d, *J* = 8 Hz, 2H), 7.21 (d, *J* = 8 Hz, 2H), 5.14 (bs, 2H), 2.43 (s, 3H), 1.71 (s, 3H) ppm; ¹³C NMR (CDCl₃) δ 151.4, 150.2, 145.4, 139.26, 135.6, 134.4, 134.4, 131.1, 129.7, 128.8, 128.7, 125.9, 115.7, 114.9, 99.4, 97.4, 21.6, 16.7 ppm; IR (KBr) ν 3482, 3379, 3237, 2924, 2226, 1628, 1560, 1427, 1267, 1097, 791 cm⁻¹; MS (ESI) m/z 390.6 ([M-H]⁺); HRMS (EI) calcd for C₂₂H₁₅Cl₂N₃ (M⁺), 391.0637; found, 391.0640.

2,6-dicyano-5-methyl-3-phenylaniline (4m). A green crystal needle; m.p. 188-190 °C; ¹H NMR (CDCl₃) δ 7.49 (m, 5H), 6.71 (s, 1H), 5.25 (bs, 2H), 2.54 (s, 3H) ppm; ¹³C NMR (CDCl₃) δ 152.8, 150.2, 148.0, 137.7, 129.8, 129.1, 128.6, 120.6, 116.3, 115.6, 96.8, 94.2, 21.7 ppm; IR (KBr) ν 3470, 3347, 3240, 2917, 2226, 2212, 1643,

1585, 1288, 859, 752, 697 cm^{-1} ; MS (ESI) m/z 232.0 ($[\text{M}-\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{11}\text{N}_3$ ($[\text{M}+\text{Na}]^+$), 256.0845; found, 256.0843.

2,6-dicyano-3-(furan-2-yl)-5-methylaniline 4n. A green crystal needle; m.p. 213-215 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) δ 7.59 (d, $J = 0.81$ Hz, 1H), 7.38 (d, $J = 3.55$ Hz, 1H), 7.11 (s, 1H), 6.59 (m, 1H), 5.21 (bs, 2H), 2.53 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 153.1, 149.3, 148.0, 144.7, 136.7, 116.7, 116.2, 115.7, 113.0, 112.9, 96.1, 89.0, 21.8 ppm; IR (KBr) ν 3425, 3351, 3250, 2923, 2216, 1652, 1585, 1491, 1302, 1026, 887, 749, 590, 504 cm^{-1} ; MS (ESI) m/z 221.8 ($[\text{M}-\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_9\text{N}_3\text{O}$ ($[\text{M}+\text{Na}]^+$), 246.0639; found, 246.0646.

5-Amino-7-(*p*-tolyl)indan-4,6-dicarbonitrile (4p). An olivine crystal needle; m.p. 181-184 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) δ 7.27 (m, 4H), 5.08 (bs, 2H), 3.10 (t, $J = 7.51$ Hz, 2H), 2.73 (t, $J = 7.35$ Hz, 2H), 2.41 (s, 3H), 2.08 (m, 2H) ppm; ^{13}C NMR (CDCl_3) δ 154.8, 151.6, 146.4, 139.4, 133.9, 133.3, 129.6, 128.6, 116.7, 115.6, 95.6, 93.2, 34.2, 32.2, 24.9, 21.6 ppm; IR (KBr) ν 3407, 3349, 3251, 2962, 2217, 1655, 1572, 1459, 1267, 815, 518 cm^{-1} ; MS (ESI) m/z 295.9 ($[\text{M}+\text{Na}]^+$); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{N}_3$ ($[\text{M}+\text{Na}]^+$), 296.1158; found, 296.1158.

2-Amino-4-phenyl-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (4q). A yellow crystal needle; m.p. 253-254 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) δ 7.47 (m, 3H), 7.21 (d, $J = 6.60$ Hz, 2H), 5.01 (bs, 2H), 2.96 (t, $J = 6.45$ Hz, 2H), 2.29 (t, $J = 6.35$ Hz, 2H), 1.81 (m, 2H), 1.65 (m, 2H) ppm; ^{13}C NMR (CDCl_3) δ 150.5, 149.9, 147.2, 137.3, 129.1, 129.0, 128.4, 126.6, 115.9, 115.7, 96.9, 96.8, 29.8, 27.6, 22.8, 22.1 ppm; IR (KBr) ν

3419, 3352, 3254, 2944, 2217, 1652, 1562, 1458, 1280, 1169, 771, 709, 535 cm^{-1} ; MS (ESI) m/z 272.1 ($[\text{M}-\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{15}\text{N}_3$ ($[\text{M}+\text{Na}]^+$), 296.1158; found, 296.1165.

2-Amino-4-benzo[1,3]dioxol-5-yl-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (4r). A cuticolor powder; m.p. 249-250 $^{\circ}\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 7.02 (d, J = 7.94 Hz, 1H), 6.87 (d, J = 1.27 Hz, 1H), 6.72 (m, 1H), 6.36 (bs, 2H), 6.10 (d, J = 14.31 Hz, 2H), 2.83 (t, J = 6.30 Hz, 2H), 2.21 (m, 2H), 1.72 (m, 2H), 1.58 (m, 2H) ppm; ^{13}C NMR ($\text{DMSO}-d_6$) δ 151.1, 150.2, 147.80, 147.77, 147.1, 131.2, 125.1, 122.5, 116.2, 115.9, 109.3, 109.0, 101.8, 96.3, 96.1, 29.5, 27.2, 22.4, 21.9 ppm; IR (KBr) ν 3454, 3359, 3253, 2929, 2220, 2212, 1648, 1561, 1503, 1457, 1237, 1041, 819 cm^{-1} ; MS (ESI) m/z 340.0 ($[\text{M}+\text{Na}]^+$); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_2$ (M^+), 317.1158; found, 317.1159.

2-Amino-4-(2-chlorophenyl)-5,6,7,8-tetrahydronaphthalene-1,3-dicarbonitrile (4s). A cuticolor crystals; mp 206-208 $^{\circ}\text{C}$; ^1H NMR ($\text{DMSO}-d_6$, 323 K) δ 7.62 (d, J = 7.32 Hz, 1H), 7.49 (m, 2H), 7.31 (d, J = 6.28 Hz, 1H), 6.34 (bs, 2H), 2.87 (m, 2H), 2.07 (m, 2H), 1.72 (m, 2H), 1.60 (m, 2H) ppm; ^{13}C NMR (CDCl_3) δ 149.9, 147.5, 147.4, 136.2, 132.7, 130.6, 130.3, 130.0, 127.6, 126.9, 115.5, 115.3, 97.6, 96.7, 29.8, 26.6, 22.5, 22.0 ppm; IR (KBr) ν 3412, 3344, 3249, 2931, 2860, 2217, 1655, 1562, 1463, 1284, 1170, 1057, 744, 546 cm^{-1} ; MS (ESI) m/z 306.0 ($[\text{M}-\text{H}]^+$); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{14}\text{ClN}_3$ ($[\text{M}+\text{Na}]^+$), 330.0768; found, 330.0768.

3-Amino-1-(2-chlorophenyl)-9,10-dihydrophenanthrene-2,4-dicarbonitrile (4t).

A yellow solid; mp 274-275 °C; ^1H NMR ($\text{DMSO-}d_6$) δ 8.19 (t, $J = 4.85\text{ Hz}$, 1H), 7.67 (d, $J = 3.55\text{ Hz}$, 1H), 7.54 (m, 2H), 7.44 (m, 3H), 7.37 (d, $J = 3.55\text{ Hz}$, 1H), 6.64 (bs, 2H), 2.66 (m, 2H), 2.17 (m, 2H) ppm; ^{13}C NMR ($\text{DMSO-}d_6$) δ 153.1, 146.0, 142.9, 140.5, 136.2, 132.2, 131.3, 131.2, 131.1, 130.8, 130.0, 128.5, 128.3, 127.7, 127.2, 126.6, 117.6, 115.8, 96.4, 93.0, 28.6, 25.5 ppm; IR (KBr) ν 3471, 3366, 3238, 2958, 2215, 1635, 1558, 1434, 1268, 1061, 751 cm^{-1} ; MS (ESI) m/z 354.2 ($[\text{M-H}]^+$); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{14}\text{ClN}_3$ (M^+), 355.0870; found, 355.0870.

2,6-dicyano-3-(4-methyloxycarbonylphenyl)-5-(4-methylphenyl)aniline (7c). A yellow powder; m.p. 221-222 °C; ^1H NMR (CDCl_3) δ 8.11 (d, $J = 8.16\text{ Hz}$, 2H), 7.31 (d, $J = 8.17\text{ Hz}$, 2H), 7.23 (d, $J = 7.80\text{ Hz}$, 2H), 7.11 (d, $J = 7.93\text{ Hz}$, 2H), 5.08 (bs, 2H), 3.88 (s, 3H), 2.35 (s, 3H), 1.67 (s, 3H) ppm; ^{13}C NMR (CDCl_3) δ 166.7, 151.3, 150.0, 149.5, 142.5, 139.3, 134.6, 130.9, 130.4, 129.8, 128.9, 128.5, 125.0, 115.8, 115.6, 98.8, 97.4, 52.6, 21.6, 17.9 ppm; IR (KBr) ν 3424, 3350, 2953, 2224, 1723, 1637, 1560, 1438, 1278, 1116, 1020, 775, 526 cm^{-1} ; MS (EI) m/z 381 (M^+ , 100%); HRMS (EI) calcd for $\text{C}_{24}\text{H}_{19}\text{N}_3\text{O}_2$ (M^+), 381.1472; found, 381.1471.

2,6-dicyano-5-(4-fluorophenyl)-3-(4-methyloxycarbonylphenyl)aniline (7e). A yellow powder; m.p. 265-266 °C; ^1H NMR ($\text{DMSO-}d_6$) δ 8.10 (d, $J = 7.8\text{ Hz}$, 2H), 7.80 (d, $J = 7.8\text{ Hz}$, 2H), 7.72 (m, 2H), 7.39 (m, 2H), 6.95 (bs, 2H), 6.85 (s, 1H), 3.91 (s, 3H) ppm; ^{13}C NMR ($\text{DMSO-}d_6$) δ 166.3, 163.3 (d, $J_{\text{C-F}} = 245.8\text{ Hz}$), 154.5, 149.5, 149.1, 142.4, 134.2 (d, $J_{\text{C-F}} = 2.8\text{ Hz}$), 131.5 (d, $J_{\text{C-F}} = 8.4\text{ Hz}$), 130.8, 129.9, 129.6, 118.9, 116.3, 116.2, 116.2 (d, $J_{\text{C-F}} = 21.6\text{ Hz}$), 95.2, 94.5, 52.9 ppm; IR (KBr) ν 3477,

3364, 2919, 2218, 1723, 1650, 1282, 1105, 833, 708 cm^{-1} ; MS (EI) m/z 371 (M^+ , 100%); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{14}\text{FN}_3\text{O}_2$ (M^+), 371.1065; found, 371.1068.

Methyl 4-(6-amino-5,7-dicyanoindan-4-yl)benzoate (7f). A green needle; m.p. 218-219 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) δ 8.16 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 5.14 (bs, 2H), 3.95 (s, 3H), 3.12 (t, $J = 7.57$ Hz, 2H), 2.70 (t, $J = 7.42$ Hz, 2H), 2.10 (m, 2H) ppm; ^{13}C NMR (CDCl_3) δ 166.6, 155.2, 151.5, 145.0, 141.2, 133.0, 130.9, 130.1, 128.7, 116.1, 115.2, 95.2, 93.2, 52.5, 34.1, 32.0, 24.9 ppm; IR (KBr) ν 3430, 3351, 3247, 2952, 2217, 1720, 1646, 1277, 1108, 735, 500 cm^{-1} ; MS (EI) m/z 317 (M^+ , 100%); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_2$ (M^+), 317.1159; found, 317.1165.

Methyl 4-(3-amino-2,4-dicyano-5,6,7,8-tetrahydronaphthalen-1-yl)benzoate (7g). A yellow needle; m.p. 226-227 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) δ 8.16 (d, $J = 8.2$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 2H), 5.06 (bs, 2H), 3.96 (s, 3H), 2.98 (t, $J = 6.41$ Hz, 2H), 2.26 (t, $J = 6.28$ Hz, 2H), 1.82 (m, 2H), 1.67 (m, 2H) ppm; ^{13}C NMR (CDCl_3) δ 166.7, 149.9, 149.2, 147.6, 141.9, 130.8, 130.3, 128.7, 126.1, 115.6, 115.4, 97.4, 96.3, 52.6, 29.8, 27.5, 22.6, 22.0 ppm; IR (KBr) ν 3426, 3346, 3250, 2940, 2218, 1708, 1650, 1281, 1123, 514 cm^{-1} ; MS (EI) m/z 331 (M^+ , 100%); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{17}\text{N}_3\text{O}_2$ (M^+), 331.1315; found, 331.1323.

Methyl 4-(3-amino-2,4-dicyano-9,10-dihydrophenanthren-1-yl)benzoate (7i). A yellow crystal; m.p. 239-240 $^{\circ}\text{C}$; ^1H NMR ($\text{DMSO}-d_6$) δ 8.16 (m, 1H), 8.10 (d, $J = 8$ Hz, 2H), 7.55 (d, $J = 8$ Hz, 2H), 7.44 (m, 2H), 7.37 (m, 1H), 6.63 (bs, 2H), 3.91 (s, 3H), 2.63 (t, $J = 6.15$ Hz, 2H), 2.26 (t, $J = 6.81$ Hz, 2H) ppm; ^{13}C NMR ($\text{DMSO}-d_6$) δ

166.3, 153.2, 147.8, 143.1, 142.2, 140.5, 131.3, 130.8, 130.5, 129.9, 129.8, 128.5, 127.7, 127.1, 126.1, 117.7, 116.2, 96.0, 92.9, 52.9, 28.7, 26.0 ppm; IR (KBr) ν 3455, 3361, 2955, 2210, 1720, 1629, 1557, 1288, 768, 493 cm^{-1} ; MS (EI) m/z 379 (M^+ , 100%); HRMS (EI) calcd for $C_{24}H_{17}N_3O_2$ (M^+), 379.1315; found, 379.1315.

Optical Spectra Analysis. The UV absorption spectra were recorded with a UV-visible spectrophotometer. Fluorescence spectra were obtained with a spectrofluorophotometer. The concentration of compounds for UV-visible spectra is 5×10^{-5} mol/L and for fluorescence spectra is 10^{-6} mol/L. All spectra were recorded at 20 °C.

The method of choice for the determination of fluorescence quantum yields was to relate the quantum yield of the sample to that of a reference standard. The equation used to relate these quantum yields is given by

$$\Phi_s = [(A_r I_s n_s^2) / (A_s I_r n_r^2)] \Phi_r$$

where the subscript s refers to the sample and the subscript r refers to the reference standard; Φ is quantum yield, A is the absorbance at the excitation wavelength, I is the emission intensity height, and n is the index of refraction (at the sodium D line) of the solvent containing the sample and the reference standard.

The reference standard chosen was 9,10-diphenylanthracene ($\Phi_f = 0.90 \pm 0.02$ in cyclohexane) because its fluorescence emission is in the same range as our samples. The indices of refraction for the solvents used were taken from the Aldrich catalog.

FIGURE 1. UV spectrum for 4p

FIGURE 2. Fluorescence spectrum for 4p

FIGURE 3. UV spectrum for 4u

FIGURE 4. Fluorescence spectrum for 4u

Reaction condition optimization. The synthesis of compound **4m** from **1a** and **2c** as well as propanedinitrile was chosen to establish the optimized reaction conditions. The results are summarized in Tables 1-4.

TABLE 1 Synthesis of Compound 4m using different bases at 300 W for 2 min.

Base	Yield (%)
Ammonium acetate	40
Sodium acetate	No reaction
NEt ₃	53
Piperidine	51

TABLE 2 Synthesis of Compound 4m using different amount of NEt₃ as base at 300 W for 2 min.

Equivalent mol	Yield (%)
0.2	23
0.8	48
1.0	53
1.5	56

TABLE 3 Synthesis of Compound 4m at different irradiation power and time.

Power (W)	Time (min)	Yield (%)
100	5	28
100	10	47
300	2	56

TABLE 4 Synthesis of Compound 4m using different solvents or under solvent-free conditions.

Solvent	Yield (%)
Solvent-free	56
1,4-dioxane	40
DMF	53
DMSO	51
NMP	53
PEG 4000	52

Crystal structure of compound 4c

A colorless needle crystal of $C_{23}H_{17}O_2N_3$ having approximate dimensions of 0.30 x 0.12 x 0.11 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-K α radiation. Indexing was performed from 5 oscillations that were exposed for 300 seconds. The crystal-to-detector distance was 127.40 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

$$\begin{aligned}
 a &= 12.3996(2) \text{ \AA} \\
 b &= 9.3240(1) \text{ \AA} \qquad \beta = 95.5013(4)^\circ \\
 c &= 33.2240(5) \text{ \AA} \\
 V &= 3823.46(9) \text{ \AA}^3
 \end{aligned}$$

For $Z = 8$ and F.W. = 367.41, the calculated density is 1.28 g/cm^3 . The systematic absences of:

$$h0l: h+l \pm 2n$$

$$0k0: k \pm 2n$$

uniquely determine the space group to be:

$$P2_1/n \text{ (\#14)}$$

The data were collected at a temperature of $22 \pm 1^\circ\text{C}$ to a maximum 2θ value of 55.0° . A total of 110 oscillation images were collected. A sweep of data was done using ω scans from 130.0 to 190.0° in 2.0° step, at $\chi=45.0^\circ$ and $\phi = 0.0^\circ$. The exposure rate was $199.8 \text{ [sec./}^\circ]$. A second sweep was performed using ω scans from 0.0 to 160.0° in 2.0° step, at $\chi=45.0^\circ$ and $\phi = 180.0^\circ$. The exposure rate was $199.8 \text{ [sec./}^\circ]$. The crystal-to-detector distance was 127.40 mm . Readout was performed in the 0.100 mm pixel mode.

FIGURE 5. Crystal structure of compound **4c**.

TABLE 5. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
O(1)	C(1)	1.453(5)	O(1)	C(2)	1.314(5)
O(2)	C(2)	1.202(5)	O(3)	C(24)	1.452(5)
O(3)	C(25)	1.318(5)	O(4)	C(25)	1.194(5)
N(1)	C(11)	1.144(5)	N(2)	C(12)	1.347(4)
N(4)	C(14)	1.144(5)	N(5)	C(34)	1.138(5)
N(6)	C(35)	1.359(4)	N(8)	C(37)	1.145(5)
C(2)	C(3)	1.492(5)	C(3)	C(4)	1.389(5)
C(3)	C(8)	1.379(5)	C(4)	C(5)	1.377(5)
C(5)	C(6)	1.386(5)	C(6)	C(7)	1.402(5)
C(6)	C(9)	1.492(5)	C(7)	C(8)	1.383(5)
C(9)	C(10)	1.403(4)	C(9)	C(22)	1.407(5)
C(10)	C(11)	1.435(5)	C(10)	C(12)	1.408(5)
C(12)	C(13)	1.404(5)	C(13)	C(14)	1.438(5)
C(13)	C(15)	1.399(5)	C(15)	C(16)	1.499(5)
C(15)	C(22)	1.407(5)	C(16)	C(17)	1.362(6)
C(16)	C(21)	1.388(6)	C(17)	C(18)	1.401(7)
C(18)	C(19)	1.334(9)	C(19)	C(20)	1.371(9)
C(20)	C(21)	1.395(7)	C(22)	C(23)	1.503(5)
C(25)	C(26)	1.488(5)	C(26)	C(27)	1.373(5)
C(26)	C(31)	1.377(5)	C(27)	C(28)	1.371(5)
C(28)	C(29)	1.384(5)	C(29)	C(30)	1.382(5)
C(29)	C(32)	1.489(5)	C(30)	C(31)	1.382(5)
C(32)	C(33)	1.407(4)	C(32)	C(45)	1.401(5)
C(33)	C(34)	1.439(5)	C(33)	C(35)	1.400(5)
C(35)	C(36)	1.411(5)	C(36)	C(37)	1.433(5)
C(36)	C(38)	1.387(5)	C(38)	C(39)	1.488(5)
C(38)	C(45)	1.403(5)	C(39)	C(40)	1.368(6)
C(39)	C(44)	1.363(5)	C(40)	C(41)	1.378(8)
C(41)	C(42)	1.362(8)	C(42)	C(43)	1.344(9)
C(43)	C(44)	1.396(6)	C(45)	C(46)	1.515(5)

TABLE 6. Bond angles ($^{\circ}$)

atom	atom	atom	angle	atom	atom	atom	angle
C(2)	O(1)	C(1)	115.8(3)	O(1)	C(2)	O(2)	122.6(4)
O(1)	C(2)	C(3)	114.3(3)	O(2)	C(2)	C(3)	123.0(4)
C(25)	O(3)	C(24)	116.0(3)	O(3)	C(25)	O(4)	124.1(4)
O(3)	C(25)	C(26)	112.1(3)	O(4)	C(25)	C(26)	123.9(4)
N(1)	C(11)	C(10)	175.1(4)	N(2)	C(12)	C(10)	121.8(3)
N(2)	C(12)	C(13)	121.8(3)	N(4)	C(14)	C(13)	178.6(4)
N(5)	C(34)	C(33)	178.7(4)	N(6)	C(35)	C(36)	121.9(3)
N(6)	C(35)	C(33)	121.4(3)	N(8)	C(37)	C(36)	176.7(4)
C(2)	C(3)	C(4)	121.9(3)	C(2)	C(3)	C(8)	118.6(3)
C(8)	C(3)	C(4)	119.5(3)	C(3)	C(4)	C(5)	119.4(3)
C(3)	C(8)	C(7)	120.9(3)	C(4)	C(5)	C(6)	122.1(3)
C(5)	C(6)	C(9)	121.3(3)	C(5)	C(6)	C(7)	117.8(3)
C(6)	C(7)	C(8)	120.2(3)	C(9)	C(6)	C(7)	120.8(3)
C(6)	C(9)	C(10)	117.2(3)	C(6)	C(9)	C(22)	122.8(3)
C(9)	C(10)	C(11)	121.4(3)	C(9)	C(10)	C(12)	122.5(3)
C(22)	C(9)	C(10)	120.0(3)	C(9)	C(22)	C(15)	118.2(3)
C(9)	C(22)	C(23)	121.1(3)	C(12)	C(10)	C(11)	116.1(3)
C(10)	C(12)	C(13)	116.4(3)	C(12)	C(13)	C(14)	118.1(3)
C(12)	C(13)	C(15)	122.0(3)	C(15)	C(13)	C(14)	119.8(3)
C(13)	C(15)	C(16)	118.2(3)	C(13)	C(15)	C(22)	120.8(3)
C(15)	C(16)	C(21)	119.7(3)	C(22)	C(15)	C(16)	121.1(3)
C(15)	C(16)	C(17)	121.7(4)	C(15)	C(22)	C(23)	120.6(3)
C(21)	C(16)	C(17)	118.5(4)	C(16)	C(17)	C(18)	120.8(4)
C(16)	C(21)	C(20)	119.8(4)	C(17)	C(18)	C(19)	120.6(5)
C(18)	C(19)	C(20)	120.0(5)	C(19)	C(20)	C(21)	120.3(5)
C(25)	C(26)	C(27)	122.0(3)	C(25)	C(26)	C(31)	118.9(3)
C(31)	C(26)	C(27)	119.0(3)	C(26)	C(27)	C(28)	120.3(3)
C(26)	C(31)	C(30)	120.8(3)	C(27)	C(28)	C(29)	121.3(3)
C(28)	C(29)	C(32)	119.8(3)	C(28)	C(29)	C(30)	118.3(3)
C(29)	C(30)	C(31)	120.2(3)	C(32)	C(29)	C(30)	121.8(3)
C(29)	C(32)	C(33)	117.0(3)	C(29)	C(32)	C(45)	122.8(3)
C(32)	C(33)	C(34)	119.2(3)	C(32)	C(33)	C(35)	122.0(3)
C(45)	C(32)	C(33)	120.2(3)	C(32)	C(45)	C(38)	118.2(3)
C(32)	C(45)	C(46)	120.5(3)	C(35)	C(33)	C(34)	118.8(3)
C(33)	C(35)	C(36)	116.7(3)	C(35)	C(36)	C(37)	117.9(3)
C(35)	C(36)	C(38)	121.8(3)	C(38)	C(36)	C(37)	120.3(3)
C(36)	C(38)	C(39)	118.9(3)	C(36)	C(38)	C(45)	121.0(3)

TABLE 6. Bond angles ($^{\circ}$)-continued

atom	atom	atom	angle	atom	atom	atom	angle
C(45)	C(38)	C(39)	120.0(3)	C(38)	C(39)	C(40)	120.0(3)
C(38)	C(39)	C(44)	121.6(3)	C(38)	C(45)	C(46)	121.2(3)
C(44)	C(39)	C(40)	118.4(4)	C(39)	C(40)	C(41)	120.8(4)
C(39)	C(44)	C(43)	120.7(4)	C(40)	C(41)	C(42)	120.0(5)
C(41)	C(42)	C(43)	120.2(5)	C(42)	C(43)	C(44)	119.8(5)

References

1. Sepiol, J.; Milart, P. *Tetrahedron* **1985**, *41*, 5261-5265.