Supporting Information

**TFA-Mediated DMSO-Participant Sequential Oxidation/1,3-Dipolar Cycloaddition Cascade of Pyridinium Ylides for Assembly of Indolizines**

**Supporting Information**

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**Experimental Section**

**1. General Methods**

All substrates and reagents were commercial and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm-1. 1H NMR spectra were determined at 25°C on a Varian Mercury 400 or 600 MHz spectrometer. 13C NMR spectra were recorded in CDCl3 or DMSO-*d*6 on 100/150 MHz. Chemical shifts are given in ppm relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on an Apex-Ultra MS equipped with an atmospheric-pressure chemical ionization (APCI) source or electrospray ionization (ESI) source. Melting points were determined using XT-4 apparatus and not corrected. The X-ray crystal-structure determinations were obtained on a Bruker APEX DUO CCD system.

**2.** **General Experimental Details**

Representative procedure for the synthesis of **3a-3q**, and **4a-4f** (**3a** as example).

The mixture of N-phenacylpyridinium iodide **1a** (650.2 mg, 2.0 mmol), TFA (114.0 mg, 1.0 mmol), TMEDA (116.2 mg, 1.0 mmol), and K2S2O8 (1.081 g, 4.0 mmol) was added in DMSO (5 mL), and the resulting mixture was stirred at 130°C for 8 h. After the reaction completed, and then added 100 mL water to the mixture, extracted with CH2Cl2 three times (3 × 100 mL). Dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was puriﬁed by column chromatography on silica gel (petroleum ether/CH2Cl2=1/15) to afford the desired product **3a**.

**3.** **The MS Spectra of intermediates**

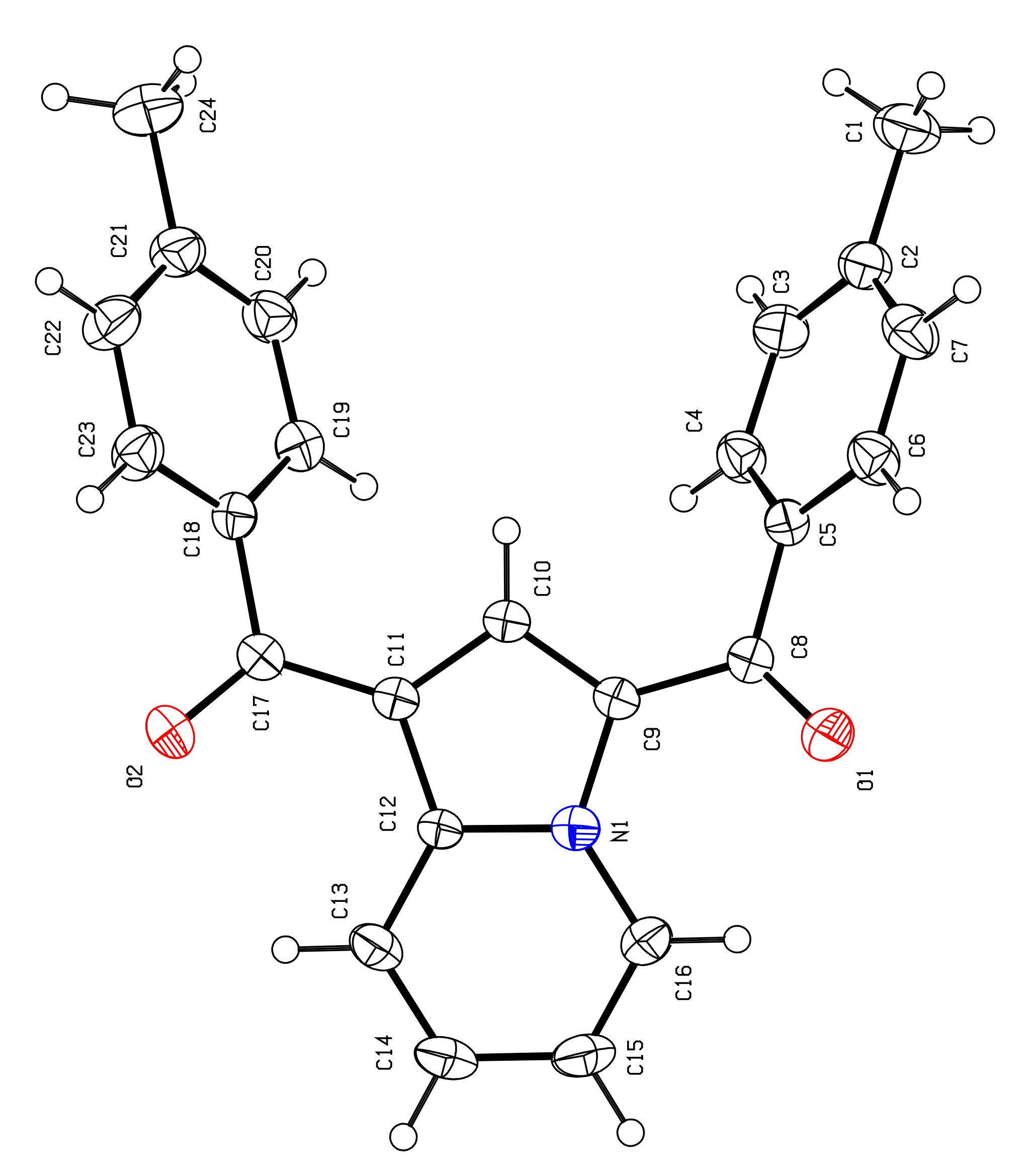
A mixture of N-phenacylpyridinium iodide **1a** (325.2 mg, 1.0 mmol), TFA (57.0 mg, 0.5 mmol), TMEDA (58.1 mg, 0.5 mmol), and K2S2O8 (540.5 mg, 2.0 mmol) was soluted in DMSO (5 mL) at 130 °C for 0.5 h. Then the mixture detected by ITMS (ESI). The following intermediates were detected.







**3. The Crystallographic Data**



**Figure S1**. X-ray structural details of **3b**

**Table S1.** The crystallographic data of **3b** (CCDC: 1848089).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Empirical  formula | C24H19NO2 | | Absorption coefficient | 0.083 mm-1 |
| Formula weight | 353.40 | | F(000) | 372 |
| Temperature | 273(2) K | | Crystal size | 0.22 x 0.20 x 0.18 mm3 |
| Wavelength | 0.71073 Å | | Reflections collected | 45310 |
| Crystal system | Triclinic | | Independent reflections | 7453 [R(int) = 0.0305] |
| Space group | P-1 | | Max. and min. transmission | 0.9920 and 0.9920 |
| Unit cell  dimensions | a = 7.326(2) Å | α = 106.563° | Refinement method Full | Full-matrix least-squares on F2 |
| b = 9.882(3) Å | = 92.469° | Data / restraints / parameters | 5172 / 0 / 246 |
| c = 13.685(4) Å | = 107.893° | Goodness-of-fit on F2 | 1.033 |
| Volume | 894.4(4) Å3 | | Final R indices [I>2sigma(I)] | R1 = 0.0562, wR2 = 0.1168 |
| Z | 2 | | R indices (all data) | R1 = 0.1051, wR2 = 0.2207 |
| Density (calculated) | 1.312 Mg/m3 | | Largest diff. peak and hole | 0.386 and -0.274 e.Å-3 |

**4. Spectroscopic Data**

indolizine-1,3-diylbis(phenylmethanone) (**3a**):

Yield 83% (270.1 mg); yellow solid; m.p. 211–213 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 10.01 (d, *J* = 6.8 Hz, 1H), 8.65 (d, *J* = 8.8 Hz, 1H), 7.85–7.75 (m, 4H), 7.62 (s, 1H), 7.56–7.50 (m, 3H), 7.48–7.44 (m, 4H), 7.17 (t, *J* = 7.6 Hz, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 190.3, 185.5, 140.7, 139.9, 139.7, 131.5, 131.5, 130.4, 129.0, 128.9, 128.9, 128.8, 128.3, 128.3, 122.4, 120.3, 116.3, 113.6; **IR (KBr, cm-1)**:1636, 1608, 1573, 1506, 1444, 1422, 1360, 1344, 1273, 1224, 1145, 1060, 1021, 882, 870, 765, 754, 656; **HRMS (ESI)**: m/z [M+H]+ calcd for C22H16NO2: 326.1176; found: 326.1177.

indolizine-1,3-diylbis(p-tolylmethanone) (**3b**):

Yield 72% (257.9 mg); yellow solid; m.p. 208–210 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.98 (d, *J* = 6.8 Hz, 1H), 8.63 (d, *J* = 9.2 Hz, 1H), 7.74–7.70 (m, 4H), 7.64 (s, 1H), 7.55–7.47 (m, 1H), 7.30–7.25 (m, 4H), 7.17–7.13 (m, 1H), 2.42 (s, 3H), 2.41 (s, 3H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 190.1, 185.4, 142.1, 142.0, 140.7, 137.2, 137.0, 130.1, 129.1, 129.0, 128.9, 128.6, 122.4, 120.3, 116.1, 113.6, 21.5, 21.5; **IR (KBr, cm-1)**: 1617, 1502, 1417, 1345, 1226, 1177, 1154, 1056, 1015, 890, 876, 829, 777, 765, 714, 619, 600; **HRMS (ESI)**: m/z [M+H]+ calcd for C24H20NO2: 354.1489; found: 354.1490.

indolizine-1,3-diylbis((3-methoxyphenyl)methanone) (**3c**):

Yield 82% (316.0 mg); yellow solid; m.p. 121–122 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.96 (d, *J* = 6.8 Hz, 1H), 8.63 (d, *J* = 8.8 Hz, 1H), 7.68 (s, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.39–7.35 (m, 3H), 7.35–7.31 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.10–7.01 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 189.7, 185.0, 159.4, 159.3, 141.0, 140.8, 140.6, 130.3, 129.2, 129.1, 128.9, 128.8, 122.1, 121.2, 120.1, 117.7, 117.6, 116.2, 113.5, 113.4, 55.2, 55.2; **IR (KBr, cm-1)**: 1633, 1578, 1501, 1481, 1432, 1338, 1250, 1209, 1150, 1035, 808, 788, 755, 654; **HRMS (ESI)**: m/z [M+H]+ calcd for C24H20NO4: 386.1387; found: 386.1388.

indolizine-1,3-diylbis((4-methoxyphenyl)methanone) (**3d**):

Yield 65% (250.5 mg); yellow solid; m.p. 179–181 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.93 (d, *J* = 6.8 Hz, 1H), 8.59 (d, *J* = 8.8 Hz, 1H), 7.89–7.74 (m, 4H), 7.63 (s, 1H), 7.53–7.41 (m, 1H), 7.14–7.10 (m, 1H), 6.98–6.95 (m, 4H), 3.87 (s, 3H), 3.86 (s, 3H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 189.1, 184.5, 162.5, 162.4, 140.5, 132.5, 132.2, 131.1, 131.1, 129.4, 128.8, 128.2, 122.3, 120.2, 115.8, 113.6, 113.6, 55.4, 55.3; **IR (KBr, cm-1)**:1629, 1606, 1567, 1509, 1495, 1475, 1421, 1333, 1309, 1228, 1170, 1149, 1058, 1023, 886, 875, 842, 783, 766, 607; **HRMS (ESI)**: m/z [M+H]+ calcd for C24H20NO4: 386.1387; found: 386.1386.

indolizine-1,3-diylbis((3,4-dimethoxyphenyl)methanone) (**3e**):

Yield 76% (338.6 mg); yellow solid; m.p. 208–210 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.92 (d, *J* = 7.2 Hz, 1H), 8.59 (d, *J* = 8.8 Hz, 1H), 7.70 (s, 1H), 7.54–7.51 (m, 1H), 7.49–7.42 (m, 4H), 7.17–7.14 (m, 1H), 6.93–6.89 (m, 2H), 3.96 (s, 6H), 3.95(2) (s, 3H), 3.95(0) (s, 3H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 189.1, 184.4, 152.2, 152.1, 149.0, 148.9, 140.6, 132.6, 132.3, 129.5, 128.8, 128.3, 123.3, 123.2, 122.3, 120.2, 115.9, 113.6, 111.7, 111.7, 110.0, 110.0, 56.0, 56.0, 56.0; **IR (KBr, cm-1)**: 1633, 1598, 1578, 1500, 1426, 1336, 1269, 1219, 1178, 1141, 1098, 1025, 874, 815, 806, 776, 758, 631, 622; **HRMS (ESI)**: m/z [M+H]+ calcd for C26H24NO6: 446.1598; found: 446.1599.

indolizine-1,3-diylbis(benzo[d][1,3]dioxol-5-ylmethanone) (**3f**):

Yield 87% (359.7 mg); yellow solid; m.p. 222–224 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.92 (d, *J* = 6.8 Hz, 1H), 8.60 (d, *J* = 8.8 Hz, 1H), 7.64 (s, 1H), 7.57–7.49 (m, 1H), 7.42–7.39 (m, 2H), 7.36–7.34 (m, 2H), 7.19–7.15 (m, 1H), 6.91–6.89 (m, 2H), 6.08 (s, 2H), 6.07 (s, 2H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 188.8, 184.1, 150.8, 150.7, 147.9, 147.9, 140.7, 134.2, 133.9, 129.5, 128.9, 128.5, 124.8, 124.8, 122.2, 120.3, 116.0, 113.5, 109.2, 109.2, 107.9, 107.8, 101.7, 101.66; **IR (KBr, cm-1)**: 1622, 1591, 1496, 1436, 1348, 1255, 1210, 1161, 1102, 1037, 921, 842, 824, 781, 765, 754, 664; **HRMS (ESI)**: m/z [M+H]+ calcd for C24H16NO6: 414.0972; found: 414.0978.

indolizine-1,3-diylbis((2-chlorophenyl)methanone) (**3g**):

Yield 70% (276.0 mg); yellow solid; m.p. 211–212 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.99 (d, *J* = 6.8 Hz, 1H), 8.65 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 4H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.53 (s, 1H), 7.50-7.45 (m, 4H), 7.22 (t, *J* = 6.6 Hz, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 189.0, 184.2, 141.0, 138.1, 138.1, 138.0, 130.3, 130.2, 129.8, 129.4, 129.2, 128.8, 128.8, 122.3, 120.4, 116.6, 113.5; **IR (KBr, cm-1)**: 1618, 1589, 1510, 1485, 1418, 1357, 1345, 1222, 1157, 1088, 1056, 1013, 879, 838, 779, 758, 702, 688; **HRMS (ESI)**: m/z [M+H]+ calcd for C22H14Cl2NO2: 394.0396; found: 394.0398.

indolizine-1,3-diylbis((4-chlorophenyl)methanone) (**3h**):

Yield 91% (358.8 mg); yellow solid; m.p. 188–190 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.98 (d, *J* = 6.8 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 4H), 7.62–7.58 (m, 1H), 7.53 (s, 1H), 7.48–7.44 (m, 4H), 7.22 (t, *J* = 7.2 Hz, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 189.0, 184.2, 140.9, 138.1, 138.0, 137.9, 137.9, 130.3, 130.2, 129.9, 129.4, 129.2, 128.8, 128.7, 122.2, 120.4, 116.7, 113.4; **IR (KBr, cm-1)**: 1638, 1616, 1589, 1508, 1484, 1441, 1423, 1357, 1342, 1271, 1222, 1177, 1156, 1131, 1086, 1057, 1011, 886, 874, 844, 837, 774, 759, 746, 703; **HRMS (ESI)**: m/z [M+H]+ calcd for C22H14Cl2NO2: 394.0396; found: 394.0398.

indolizine-1,3-diylbis((2,4-dichlorophenyl)methanone) (**3i**):

Yield 92% (424.1 mg); yellow solid; m.p. 153–155 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 10.07 (d, *J* = 7.2 Hz, 1H), 8.67 (d, *J* = 8.8 Hz, 1H), 7.70–7.65 (m, 1H), 7.51–7.46 (m, 2H), 7.37–7.35 (m, 1H), 7.34–7.32 (m, 3H), 7.31–7.27 (m, 1H), 7.05 (s, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 187.6, 182.6, 140.7, 137.9, 137.1, 136.5, 136.3, 132.4, 132.0, 130.8, 130.5, 130.3, 130.2, 130.0, 129.9, 129.6, 127.2, 127.1, 122.9, 120.5, 117.3, 114.5; **IR (KBr, cm-1)**: 1626, 1682, 1511, 1489, 1444, 1421, 1363, 1348, 1219, 1135, 1102, 1077, 1037, 890, 876, 827, 783, 773, 719, 528; **HRMS (ESI)**: m/z [M+H]+ calcd for C22H12Cl4NO2: 461.9617; found: 461.9622.

indolizine-1,3-diylbis((3,4-dichlorophenyl)methanone) (**3j**):

Yield 83% (382.6 mg); yellow solid; m.p. 217–219 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.95 (d, *J* = 7.2 Hz, 1H), 8.63 (d, *J* = 8.8 Hz, 1H), 7.93–7.87 (m, 2H), 7.65–7.60 (m, 3H), 7.58–7.54 (m, 2H), 7.52 (s, 1H), 7.27–7.23 (m, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 187.4, 182.6, 141.0, 139.3, 139.1, 136.3, 136.2, 133.1, 133.1, 130.9, 130.6, 130.6, 129.9, 129.8, 129.2, 127.9, 127.9, 122.0, 120.4, 117.0, 113.2; **IR (KBr, cm-1)**: 1635, 1606, 1502, 1483, 1441, 1422, 1339, 1217, 1166, 1133, 1069, 1027, 923, 781, 761, 717, 520; **HRMS (ESI)**: m/z [M+H]+ calcd for C22H12Cl4NO2: 461.9617; found: 461.9620.

indolizine-1,3-diylbis((3-bromophenyl)methanone) (**3k**):

Yield 81% (391.4 mg); yellow solid; m.p. 179–182 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.98 (d, *J* = 7.2 Hz, 1H), 8.65 (d, *J* = 8.8 Hz, 1H), 7.96–7.93 (m, 2H), 7.72–7.69 (m, 2H), 7.68–7.65 (m, 2H), 7.63–7.59 (m, 1H), 7.56 (s, 1H), 7.39–7.34 (m, 2H), 7.25–7.21 (m, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 188.4, 183.7, 141.6, 141.4, 140.9, 134.6, 134.5, 131.9, 130.4, 130.0, 129.6, 129.2, 127.4, 127.4, 122.7, 122.7, 122.1, 120.4, 116.8, 113.3; **IR (KBr, cm-1)**: 1631, 1615, 1558, 1503, 1482, 1441, 1418, 1337, 1218, 1157, 1055, 877, 765, 728, 682, 649; **HRMS (ESI)**: m/z [M+H]+ calcd for C22H14Br2NO2: 481.9386; found: 481.9391.

indolizine-1,3-diylbis((4-bromophenyl)methanone) (**3l**):

Yield 76% (367.2 mg); yellow solid; m.p. 218–220 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.98 (d, *J* = 7.2 Hz, 1H), 8.65 (d, *J* = 8.4 Hz, 1H), 7.67–7.64 (m, 4H), 7.63–7.62 (m, 3H), 7.61–7.58 (m, 2H), 7.52 (s, 1H), 7.22 (t, *J* = 7.2 Hz, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 189.1, 184.3, 140.9, 138.5, 138.3, 131.8, 131.7, 130.4, 130.4, 129.9, 129.5, 129.2, 126.6, 126.5, 122.2, 120.4, 116.7, 113.4; **IR (KBr, cm-1)**: 1617, 1585, 1505, 1480, 1413, 1357, 1344, 1273, 1221, 1156, 1131, 1066, 1054, 1009, 877, 834, 778, 766, 749, 681, 617, 503, 459; **HRMS (ESI)**: m/z [M+H]+ calcd for C22H14Br2NO2: 481.9386; found: 481.9389.

indolizine-1,3-diylbis(furan-2-ylmethanone) (**3m**):

Yield 82% (250.3 mg); yellow solid; m.p. 186–187 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 10.02 (d, *J* = 6.8 Hz, 1H), 8.88 (s, 1H), 8.73 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 4.2 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.36 (s, 2H), 7.13 (t, *J* = 6.8 Hz, 1H), 6.62 (s, 2H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 175.7, 171.0, 154.1, 153.2, 145.7, 145.5, 141.0, 129.2, 129.0, 128.2, 121.8, 120.4, 117.6, 117.3, 116.3, 112.9, 112.2, 112.1; **IR (KBr, cm-1)**: 1631, 1600, 1566, 1512, 1472, 1441, 1388, 1360, 1279, 1241, 1170, 1062, 1012, 937, 886, 832, 774, 752, 595; **HRMS (ESI)**: m/z [M+H]+ calcd for C18H12NO4: 306.0761; found: 306.0761.

indolizine-1,3-diylbis(thiophen-2-ylmethanone) (**3n**):

Yield 75% (252.9 mg); yellow solid; m.p. 169–170 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.85 (d, *J* = 7.2 Hz, 1H), 8.60 (d, *J* = 8.8 Hz, 1H), 8.24 (s, 1H), 7.81–7.79 (m, 2H), 7.65–7.64 (m, 2H), 7.52–7.46 (m, 1H), 7.20–7.17 (m, 2H), 7.14–7.10 (m, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 180.7, 176.2, 144.7, 143.9, 140.7, 132.1, 132.1, 131.9, 131.8, 128.8, 128.7, 127.8, 127.8, 127.3, 122.1, 120.3, 116.2, 113.5; **IR (KBr, cm-1)**: 1631, 1593, 1511, 1482, 1413, 1357, 1333, 1272, 1234, 1192, 1156, 1058, 1038, 868, 846, 811, 773, 757, 721, 633; **HRMS (ESI)**: m/z [M+H]+ calcd for C18H12NO2S2: 338.0304; found: 338.0301.

indolizine-1,3-diylbis(naphthalen-1-ylmethanone) (**3o**):

Yield 86% (365.9 mg); yellow solid; m.p. 151–152 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 10.22 (d, *J* = 6.8 Hz, 1H), 8.73 (d, *J* = 8.8 Hz, 1H), 8.20–8.14 (m, 2H), 7.83–7.77 (m, 4H), 7.57– 7.52 (m, 3H), 7.46–7.43 (m, 4H), 7.32 (t, *J*=8.0 Hz, 2H), 7.23 (s, 1H), 7.19 (m, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 191.5, 186.5, 140.7, 137.6, 136.9, 133.6, 133.6, 131.4, 130.6, 130.6, 130.5, 130.4, 129.5, 129.4, 128.2, 128.1, 126.9, 126.8, 126.8, 126.5, 126.2, 126.1, 125.5, 125.3, 124.3, 124.2, 123.8, 120.4, 116.6, 115.3; **IR (KBr, cm-1)**: 1638, 1610, 1499, 1452, 1433, 1349, 1281, 1243, 1212, 1154, 1141, 1135, 1051, 894, 832, 823, 810, 789, 769, 643; **HRMS (ESI)**: m/z [M+H]+ calcd for C30H20NO2: 426.1489; found: 426.1487.

indolizine-1,3-diylbis(naphthalen-2-ylmethanone) (**3p**):

Yield 78% (331.9 mg); yellow solid; m.p. 234–235 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 10.09 (d, *J* = 7.2Hz, 1H), 8.73 (d, *J* = 8.8 Hz, 1H), 8.35 (s, 2H), 8.01–7.91 (m, 6H), 7.88 (d, *J* = 6.8 Hz, 2H), 7.80 (s, 1H), 7.66–7.48 (m, 5H), 7.28–7.21 (m, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 190.3, 185.5, 140.8, 137.2, 137.0, 134.8, 132.4, 132.4, 130.5, 130.0, 130.0, 129.1, 129.1, 128.9, 128.3, 128.3, 127.8, 127.7, 126.7, 126.6, 125.4, 125.3, 122.7, 120.4, 116.3, 114.0; **IR (KBr, cm-1)**: 1636, 1606, 1498, 1448, 1422, 1348, 1280, 1248, 1217, 1164, 1149, 1137, 1053, 890, 832, 823, 783, 774, 752, 725, 633, 586, 478; **HRMS (ESI)**: m/z [M+H]+ calcd for C30H20NO2: 426.1489; found: 426.1492.

(6,8-dimethylindolizine-1,3-diyl)bis(phenylmethanone) (**4a**):

Yield 71% (250.9 mg); yellow solid; m.p. 177–178 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.82 (s, 1H), 7.91–7.89 (m, 2H), 7.76–7.73 (m, 2H), 7.57–7.51 (m, 1H), 7.50–7.41 (m, 5H), 7.40 (s, 1H), 7.14 (s, 1H), 2.56 (s, 3H), 2.43 (s, 3H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 190.4, 185.1, 140.2, 139.3, 138.0, 132.4, 132.1, 131.2, 130.9, 130.1, 129.4, 128.9, 128.2, 125.6, 125.01, 121., 116.0, 21.1, 18.3; **IR (KBr, cm-1)**: 1643, 1604, 1573, 1509, 1479, 1439, 1410, 1349, 1247, 1285, 1247, 1175, 1147, 983, 944, 874, 853, 832, 763, 720, 705, 676, 666; **HRMS (ESI)**: m/z [M+H]+ calcd for C24H20NO2: 354.1489; found: 354.1488.

methyl 1,3-dibenzoylindolizine-7-carboxylate (**4c**):

Yield 58% (222.4 mg); yellow solid; m.p. 221–224 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.97 (d, *J* = 7.2 Hz, 1H), 9.25 (s, 1H), 7.88–7.77 (m, 4H), 7.72–7.68 (m, 1H), 7.67 (s, 1H), 7.60–7.53 (m, 2H), 7.51–7.46 (m, 4H), 4.00 (s, 3H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 190.1, 185.8, 165.1, 139.4, 139.2, 139.2, 132.0, 131.9, 130.2, 129.1, 129.0, 129.0, 128.5, 128.4, 128.4, 123.4, 122.4, 116.0, 115.2, 52.7; **IR (KBr, cm-1)**: 1729, 1625, 1610, 1572, 1525, 1500, 1468, 1446, 1411, 1338, 1292, 1225, 1155, 1134, 1049, 967, 908, 881, 721, 673, 665; **HRMS (ESI)**: m/z [M+H]+ calcd for C24H18NO4: 384.1230; found: 384.1233.

1,3-dibenzoylindolizine-7-carbonitrile (**4d**):

Yield 60% (210.2 mg); yellow solid; m.p. 202–204 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 10.00 (d, *J* = 7.2 Hz, 1H), 9.00 (s, 1H), 7.82–7.80 (m, 4H), 7.71 (s, 1H), 7.62–7.57 (m, 2H), 7.53–7.48 (m, 4H), 7.27–7.23 (m, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 190.0, 186.0, 138.9, 138.8, 137.9, 132.4, 132.2, 129.9, 129.1, 129.0, 128.9, 128.6, 128.6, 126.3, 123.8, 117.1, 115.9, 115.8, 110.7; **IR (KBr, cm-1)**: 1622, 1597, 1577, 1512, 1469, 1409, 1351, 1342, 1230, 1168, 1046, 880, 814, 721, 706, 697, 661; **HRMS (ESI)**: m/z [M+H]+ calcd for C23H15N2O2: 351.1128; found: 351.1127.

pyrrolo[2,1-*a*]isoquinoline-1,3-diylbis(phenylmethanone) (**4f**):

Yield 74% (277.8 mg); yellow solid; m.p. 139–142 °C; **1H NMR** (400 MHz, CDCl3): *δ* (ppm) 9.65 (d, *J* = 7.2 Hz, 1H), 8.99 (d, *J* = 8.4 Hz, 1H), 7.94–7.92 (m, 2H), 7.82–7.79 (m, 2H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.55–7.47 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.41 (s, 1H), 7.27 (d, *J* = 7.6 Hz, 1H); **13C NMR** (100 MHz, CDCl3): *δ* (ppm) 192.1, 185.6, 139.6, 139.3, 136.5, 132.5, 131.6, 130.3, 130.2, 129.9, 129.3, 129.0, 128.2, 128.2, 127.6, 126.8, 126.7, 125.7, 124.9, 124.3, 123.0, 117.7, 115.7; **IR (KBr, cm-1)**: 1614, 1573, 1514, 1451, 1419, 1384, 1336, 1268,1207, 963, 872, 802, 713, 652; **HRMS (ESI)**: m/z [M+H]+ calcd for C20H19O2S: 376.1332; found: 376.1335.

**5.** **Appendix: spectral copies of 1HNMR, and 13CNMR**

