Synthesis of 4-diarylamino-3-iodo-2(5*H*)-furanones via the simultaneous α -iodination and N^β -arylation of An efficient difunctionalizable transfer reagent $\text{PhI}(\text{OAc})_2$

*Fu-Ling Xue, Pai Peng, Jie Shi, Ming-Li Zhong, Zhao-Yang Wang**

School of Chemistry and Environment, South China Normal University; Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, Guangzhou, 510006, P. R. China

*Corresponding Author E-mail: wangzy@scnu.edu.cn, or wangwangzhaoyang@tom.com; fax: 8620-39310187.

SUPPORTING INFORMATION

Full experimental detail

(CHARACTERIZATION DATA and SPECTRA of Compounds 2a-2s are included. For each compound, the former is ^1H NMR, and the latter is ^{13}C NMR, and the last is MS)

EXPERIMENTAL

General

All melting points were determined on an X-5 digital melting points apparatus and were uncorrected. Infrared spectra were recorded on a Bruker Vector 33 FT-IR instrument by liquid film method in the absorption range of 4000-450 cm^{-1} . ^1H and ^{13}C NMR spectra were obtained in CDCl_3 on a Varian DRX-400 MHz spectrometer and tetramethylsilane (TMS) was used as an internal standard. UV absorption peaks were measured by Shimadzu UV-2550 ultraviolet absorption detector with dichloromethane as a solvent. Elemental analysis was performed on a Thermo Flash EA 1112 elemental analyzer. The mass spectra (MS) were recorded on Thermo LCQ DECA XP MAX mass spectrometer.

All reagents and solvents were commercially available and used as received. The intermediates 5-alkoxy-4-arylamino-2(5*H*)-furanones **1** were prepared according to the literature.^[57b]

Typical Procedure

A flame 25-mL round-bottomed flask was charged with 5-alkoxy-4-arylamino-2(5*H*)-furanones **1** (0.2 mmol) in CH_3CN (5 mL), and $\text{PhI}(\text{OAc})_2$ (1.5 eq.) in CH_3CN (5 mL) was added dropwise in 25 min. The mixture was stirred at 60 $^\circ\text{C}$, and the reaction was monitored by TLC. After the completion of the reaction (about 40 h), the reaction was allowed to cool to room temperature. The reaction mixture was diluted with a saturated aqueous solution of NH_4Cl (20 mL) and extracted with ethyl acetate (3×20 mL). Then, the organic layer was dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The purification of the residue by silica gel column chromatography yielded the desired compounds **2** in 57%-91% isolated yields (**Table 2**).

Characterization Data for Compounds 2

3-Iodo-5-methoxy-4-(*N,N*-diphenylamino)-furan-2(5*H*)-one (2a). Yellow solid, yield 86%, m.p. 177.9-179.2 $^\circ\text{C}$; UV-vis (CH_2Cl_2) λ_{max} : 319 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 3.20 (s, 3H), 5.73 (s, 1H), 7.18 (d, J = 8 Hz, 4H), 7.29 (t, J = 8 Hz, 2H), 7.38-7.42 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 55.36, 56.86, 101.65, 126.35, 126.94, 127.10, 127.13, 129.32, 129.42, 142.60, 142.64, 162.47, 169.73; IR (film) ν , cm^{-1} : 3059, 2924, 2851, 1761, 1616, 1585, 1489, 1452, 1377, 1323, 1153, 1119, 951, 750,

698, 515; ESI-MS m/z (%): 408 ($[M+H]^+$, 100), 430 ($[M+Na]^+$, 93); Anal. Calcd for $C_{17}H_{14}INO_3$: C 50.14, H 3.47, N 3.44, Found: C 50.32, H 3.21, N 3.57.

3-Iodo-5-methoxy-4-(*N*-(*p*-tolyl)amino)-furan-2(5*H*)-one (2b). Yellow solid, yield 57%, m.p. 171.8-172.2 °C; UV-vis (CH_2Cl_2) λ_{max} : 323 nm; 1H NMR (400 MHz, $CDCl_3$) δ , ppm: 2.36 (s, 3H), 3.20 (s, 3H), 5.72 (s, 1H), 7.07 (d, J = 8 Hz, 2H), 7.16 (d, J = 8 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 7.27 (t, J = 8 Hz, 1H), 7.35-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ , ppm: 21.10, 54.81, 56.66, 101.55, 126.94, 126.99, 127.05, 129.32, 129.99, 137.23, 140.11, 142.7, 162.45, 169.81; IR (film) ν , cm^{-1} : 3059, 2957, 2924, 2853, 1757, 1616, 1585, 1508, 1491, 1464, 1377, 1325, 1153, 1117, 951, 843, 741, 696, 610; ESI-MS m/z (%): 422 ($[M+H]^+$, 62), 444 ($[M+Na]^+$, 100); Anal. Calcd for $C_{18}H_{16}INO_3$: C 51.32, H 3.83, N 3.33, Found: C 51.21, H 3.69, N 3.48.

3-Iodo-5-methoxy-4-(*N*-(3,4-dimethylphenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2c). Yellowish solid, yield 73%, m.p. 136.4-137.5 °C; UV-vis (CH_2Cl_2) λ_{max} : 322 nm; 1H NMR (400 MHz, $CDCl_3$) δ , ppm: 2.25 (s, 3H), 2.26 (s, 3H), 3.21 (s, 3H), 5.73 (s, 1H), 6.90 (d, J = 8 Hz, 1H), 6.94 (s, 1H), 7.13 (d, J = 8 Hz, 1H), 7.16 (d, J = 8 Hz, 2H), 7.27 (t, J = 8 Hz, 1H), 7.36-7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ , ppm: 19.44, 19.88, 54.17, 56.56, 101.53, 124.49, 126.89, 126.99, 128.16, 129.29, 130.39, 135.91, 137.88, 140.20, 142.74, 162.41, 169.90; IR (film) ν , cm^{-1} : 3059, 2955, 2924, 2853, 1759, 1616, 1585, 1495, 1454, 1375, 1321, 1180, 1146, 1119, 953, 795, 741, 696, 538; ESI-MS m/z (%): 436 ($[M+H]^+$, 100), 458 ($[M+Na]^+$, 63); Anal. Calcd for $C_{19}H_{18}INO_3$: C 52.43, H 4.17, N 3.22, Found: C 52.58, H 4.02, N 3.41.

3-Iodo-5-methoxy-4-(*N*-(4-methoxyphenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2d). Yellowish solid, yield 58%, m.p. 51.9-52.8 °C; UV-vis (CH_2Cl_2) λ_{max} : 320 nm; 1H NMR (400 MHz, $CDCl_3$) δ , ppm: 3.21 (s, 3H), 3.83 (s, 3H), 5.69 (s, 1H), 6.90 (d, J = 8 Hz, 2H), 7.11-7.17 (m, 4H), 7.26 (t, J = 8 Hz, 1H), 7.35-7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ , ppm: 53.69, 55.50, 56.66, 101.49, 114.50, 126.78, 126.87, 128.74, 129.31, 135.54, 142.82, 158.62, 162.51, 169.81; IR (film) ν , cm^{-1} : 3010, 2924, 2853, 1755, 1612, 1585, 1504, 1464, 1377, 1323, 1153, 1115, 1026, 949, 814, 739, 692, 459; ESI-MS m/z (%): 438 ($[M+H]^+$, 100); Anal. Calcd for $C_{18}H_{16}INO_4$: C 49.45, H 3.69, N 3.20, Found: C 49.63, H 3.76, N 3.13.

3-Iodo-5-methoxy-4-(*N*-(4-fluorophenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2e). Yellowish solid, yield 63%, m.p. 157.2-158.8 °C; UV-vis (CH_2Cl_2) λ_{max} : 319 nm; 1H NMR (400 MHz, $CDCl_3$) δ , ppm: 3.21 (s, 3H), 5.69 (s, 1H), 7.07-7.12 (m, 2H), 7.14-7.21 (m, 4H), 7.29 (t, J = 8 Hz, 1H), 7.37-7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ , ppm: 55.31, 56.94, 101.53, 116.35 (d, J = 23 Hz), 126.86, 127.21, 129.04 (d, J = 8 Hz), 129.52, 138.54 (d, J = 3 Hz), 142.63, 161.21 (d, J = 247 Hz), 162.40, 169.57; IR (film) ν , cm^{-1} : 3063, 2953, 2922, 2853, 1757, 1614, 1587, 1501, 1460, 13775, 1323, 1225, 1153, 1119, 947, 802, 741, 675, 482; ESI-MS m/z (%): 426 ($[M+H]^+$, 100); Anal. Calcd for $C_{17}H_{13}FINO_3$: C 48.02, H 3.08, N 3.29, Found: C 48.25, H 3.21, N 3.14.

3-Iodo-5-methoxy-4-(*N*-(4-chlorophenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2f). Yellowish solid, yield 61%, m.p. 39.4-40.3 °C; UV-vis (CH_2Cl_2) λ_{max} : 322 nm; 1H

NMR (400 MHz, CDCl₃) δ , ppm: 3.23 (s, 3H), 5.70 (s, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.30 (t, J = 8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.37-7.42 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ , ppm: 56.86, 57.06, 101.59, 126.96, 127.34, 128.18, 129.54, 129.59, 132.54, 141.00, 142.46, 162.27, 169.47; IR (film) ν , cm⁻¹: 3063, 2957, 2924, 2853, 1763, 1612, 1585, 1489, 1466, 1375, 1323, 1153, 1117, 1090, 1015, 951, 802, 746, 700, 718, 525; ESI-MS m/z (%): 442 ([M+H]⁺, 100); Anal. Calcd for C₁₇H₁₃ClINO₃: C 46.23, H 2.97, N 3.17, Found: C 46.42, H 3.04, N 3.01.

3-Iodo-5-methoxy-4-(*N*-(4-bromophenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2g). Yellowish solid, yield 81%, m.p. 53.0-54.4 °C; UV-vis (CH₂Cl₂) λ_{max} : 323 nm; ¹H NMR (400 MHz, CDCl₃) δ : 3.23 (s, 3H), 5.70 (s, 1H), 7.03 (d, J = 8 Hz, 2H), 7.14 (d, J = 8 Hz, 2H), 7.31 (t, J = 8 Hz, 1H), 7.39-7.43 (m, 2H), 7.51 (d, J = 8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ , ppm: 57.07, 57.11, 101.59, 120.35, 126.98, 127.35, 128.44, 129.60, 132.51, 141.51, 142.40, 162.22, 169.44; IR (film) ν , cm⁻¹: 3067, 2922, 2853, 1759, 1612, 1584, 1483, 1460, 1373, 1323, 1153, 1115, 1072, 949, 851, 756, 704, 619, 530; ESI-MS m/z (%): 486 ([M+H]⁺, 96); Anal. Calcd for C₁₇H₁₃BrINO₃: C 42.00, H 2.70, N 2.88, Found: C 42.21, H 2.59, N 2.96.

3-Iodo-5-methoxy-4-(*N*-(3-chlorophenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2h). Yellowish solid, yield 91%, m.p. 41.5-42.7 °C; UV-vis (CH₂Cl₂) λ_{max} : 321 nm; ¹H NMR (400 MHz, CDCl₃) δ , ppm: 3.23 (s, 3H), 5.70 (s, 1H), 7.04 (d, J = 8.0 Hz, 1H), 7.14 (s, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 1H), 7.30-7.35 (m, 2H), 7.39-7.45 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ , ppm: 57.07, 57.67, 101.62, 124.92, 126.90, 126.99, 127.09, 127.48, 129.66, 130.24, 135.02, 142.28, 143.44, 162.22, 169.37; IR (film) ν , cm⁻¹: 3063, 2922, 2851, 1761, 1614, 1582, 1472, 1373, 1321, 1157, 1119, 1076, 949, 768, 752, 694, 710, 534; ESI-MS m/z (%): 442 ([M+H]⁺, 100), 464 ([M+Na]⁺, 40); Anal. Calcd for C₁₇H₁₃ClINO₃: C 46.23, H 2.97, N 3.17, Found: C 46.39, H 2.84, N 3.05.

5-Benzyloxy-3-iodo-4-(*N,N*-diphenylamino)-furan-2(5*H*)-one (2i). White solid, yield 74%, m.p. 126.9-127.8 °C; UV-vis (CH₂Cl₂) λ_{max} : 325 nm; ¹H NMR (400 MHz, CDCl₃) δ , ppm: 4.27-4.68 (dd, J_1 = 12 Hz, J_2 = 12 Hz, 2H), 5.89 (s, 1H), 6.90 (d, J = 8 Hz, 2H), 7.13 (d, J = 8 Hz, 4H), 7.18-7.23 (m, 3H), 7.27 (t, J = 8 Hz, 2H), 7.33-7.37 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ , ppm: 56.33, 71.64, 98.96, 126.92, 127.01, 128.20, 128.37, 128.45, 129.45, 135.05, 142.80, 162.93, 169.86; IR (film) ν , cm⁻¹: 3059, 2922, 2853, 1759, 1614, 1584, 1489, 1460, 1368, 1325, 1155, 1117, 951, 748, 700, 538; ESI-MS m/z (%): 484 ([M+H]⁺, 100), 506 ([M+Na]⁺, 40); Anal. Calcd for C₂₃H₁₈INO₃: C 57.16, H 3.75, N 2.90, Found: C 57.33, H 3.64, N 2.79.

5-Benzyloxy-3-iodo-4-(*N*-phenyl-*N*-(*p*-tolyl)amino)-furan-2(5*H*)-one (2j). Yellow viscous solid, yield 60%; UV-vis (CH₂Cl₂) λ_{max} : 324 nm; ¹H NMR (400 MHz, CDCl₃) δ , ppm: 2.37 (s, 3H), 4.28-4.68 (dd, J_1 = 12 Hz, J_2 = 12 Hz, 2H), 5.89 (s, 1H), 6.91 (d, J = 8 Hz, 2H), 7.01 (d, J = 8 Hz, 2H), 7.11-7.15 (m, 4H), 7.17-7.23 (m, 2H), 7.25 (t, J = 8 Hz, 2H), 7.33-7.36 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ , ppm: 21.12, 55.33, 71.50, 98.84, 126.80, 126.91, 128.16, 128.32, 128.51 (C-21, C-23), 129.37, 130.02, 135.05,

137.02, 140.30, 142.86, 162.91, 170.01; IR (film) ν , cm^{-1} : 3030, 2922, 2853, 1757, 1612, 1585, 1508, 1489, 1454, 1366, 1325, 1153, 1113, 951, 843, 745, 696, 615; ESI-MS m/z (%): 498 ($[\text{M}+\text{H}]^+$, 82), 520 ($[\text{M}+\text{Na}]^+$, 100); Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{INO}_3$: C 57.96, H 4.05, N 2.82, Found: C 57.76, H 4.25, N 2.75.

5-Benzoyloxy-3-iodo-4-(*N*-(3,4-dimethylphenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2k). Yellowish solid, yield 78%, m.p. 54.5-55.2 °C; UV-vis (CH_2Cl_2) λ_{max} : 326 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 2.19 (s, 3H), 2.27 (s, 3H), 4.28-4.68 (dd, $J_1 = 12$ Hz, $J_2 = 12$ Hz, 2H), 5.88 (s, 1H), 6.86 (d, $J = 8$ Hz, 1H), 6.89 (d, $J = 8$ Hz, 2H), 6.91 (s, 1H), 7.09 (d, $J = 8$ Hz, 1H), 7.12 (d, $J = 8$ Hz, 2H), 7.17-7.21 (m, 2H), 7.25 (t, $J = 8$ Hz, 2H), 7.32-7.37 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 19.45, 19.80, 54.85, 71.43, 98.82, 124.28, 126.75, 127.02, 128.03, 128.12, 128.27, 128.52, 129.31, 130.43, 135.06, 135.69, 137.89, 140.49, 142.80, 162.85, 170.07; IR (film) ν , cm^{-1} : 3059, 2924, 2853, 1759, 1659, 1587, 1530, 1495, 1458, 1366, 1323, 1182, 1148, 1119, 953, 745, 698, 538; ESI-MS m/z (%): 512 ($[\text{M}+\text{H}]^+$, 100), 534 ($[\text{M}+\text{Na}]^+$, 92); Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{INO}_3$: C 58.72, H 4.34, N 2.74, Found: C 58.87, H 4.51, N 2.63.

5-Benzoyloxy-3-iodo-4-(*N*-(4-methoxyphenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2l). Yellowish solid, yield 61%, m.p. 43.6-44.5 °C; UV-vis (CH_2Cl_2) λ_{max} : 324 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 3.82 (s, 3H), 4.28-4.68 (dd, $J_1 = 12.0$ Hz, $J_2 = 12.0$ Hz, 2H), 5.86 (s, 1H), 6.85 (d, $J = 8$ Hz, 1H), 6.93 (d, $J = 8$ Hz, 2H), 7.07 (d, $J = 8$ Hz, 2H), 7.11 (d, $J = 8$ Hz, 12H), 7.19-7.25 (m, 4H), 7.32-7.36 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 54.49, 55.50, 71.49, 98.77, 114.52, 126.70, 126.73, 128.19, 128.34, 128.55, 128.57, 129.36, 132.94, 135.05, 135.71, 158.52, 162.94, 170.02; IR (film) ν , cm^{-1} : 3057, 2924, 2855, 1755, 1611, 1584, 1504, 1460, 1369, 1325, 1250, 1161, 1109, 951, 843, 746, 698, 534; ESI-MS m/z (%): 514 ($[\text{M}+\text{H}]^+$, 48), 536 ($[\text{M}+\text{Na}]^+$, 100); Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{INO}_4$: C 56.15, H 3.93, N 2.73, Found: C 56.31, H 3.81, N 2.89.

5-Benzoyloxy-3-iodo-4-(*N*-(4-fluorophenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2m). Yellowish solid, yield 73%, m.p. 40.3-41.2 °C; UV-vis (CH_2Cl_2) λ_{max} : 323 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 4.30-4.69 (dd, $J_1 = 12.0$ Hz, $J_2 = 12.0$ Hz, 2H), 5.85 (s, 1H), 6.91 (d, $J = 8$ Hz, 2H), 7.00-7.05 (m, 2H), 7.08-7.13 (m, 4H), 7.19-7.25 (m, 3H), 7.28 (t, $J = 8$ Hz, 1H), 7.33-7.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 56.19, 71.63, 98.62, 116.36 (d, $J = 23$ Hz), 126.74, 127.03, 128.32, 128.41, 128.59, 128.85 (d, $J = 9$ Hz), 129.56, 134.83, 138.72 (d, $J = 3$ Hz), 142.78, 161.15 (d, $J = 247$ Hz), 162.87, 169.76; IR (film) ν , cm^{-1} : 3065, 2922, 2855, 1757, 1612, 1585, 1501, 1460, 1368, 1325, 1225, 1155, 1115, 953, 849, 745, 698, 525; ESI-MS m/z (%): 502 ($[\text{M}+\text{H}]^+$, 100), 524 ($[\text{M}+\text{Na}]^+$, 78); Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{FINO}_3$: C 55.11, H 3.42, N 2.79, Found: C 55.33, H 3.31, N 2.95.

5-Benzoyloxy-3-iodo-4-(*N*-(4-chlorophenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2n). Yellow solid, yield 64%, m.p. 49.2-50.3 °C; UV-vis (CH_2Cl_2) λ_{max} : 325 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 4.33-4.70 (dd, $J_1 = 12.0$ Hz, $J_2 = 12.0$ Hz, 2H), 5.85 (s, 1H), 6.90 (d, $J = 4$ Hz, 2H), 7.02 (d, $J = 8$ Hz, 2H), 7.10 (d, $J = 8$ Hz, 2H), 7.20-7.24 (m, 2H), 7.25-7.31 (m, 4H), 7.34-7.39 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 57.69, 71.62, 98.51, 126.89, 127.14, 127.95, 128.35, 128.44, 128.60, 129.57, 129.60,

132.40, 134.71, 141.27, 142.53, 162.77, 169.62; IR (film) ν , cm^{-1} : 3061, 3032, 2924, 2853, 1761, 1611, 1585, 1489, 1456, 1366, 1325, 1155, 1092, 953, 843, 764, 698, 745, 523; ESI-MS m/z (%): 518 ($[\text{M}+\text{H}]^+$, 43), 540 ($[\text{M}+\text{Na}]^+$, 100); Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{ClINO}_3$: C 53.36, H 3.31, N 2.71, Found: C 53.17, H 3.50, N 2.62.

5-Benzoyloxy-3-iodo-4-(*N*-(4-bromophenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2o). Yellow solid, yield 82%, m.p. 50.6-51.7 °C; UV-vis (CH_2Cl_2) λ_{max} : 326 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 4.33-4.70 (dd, $J_1 = 12$ Hz, $J_2 = 12$ Hz, 2H), 5.84 (s, 1H), 6.90 (d, $J = 8$ Hz, 2H), 6.95 (d, $J = 8$ Hz, 2H), 7.10 (d, $J = 8$ Hz, 2H), 7.19-7.25 (m, 2H), 7.26-7.31 (m, 2H), 7.34-7.38 (m, 2H), 7.43 (d, $J = 8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 57.95, 71.61, 98.46, 120.22, 126.91, 127.15, 128.19, 128.36, 128.46, 128.60, 129.60, 132.52, 134.67, 141.78, 142.45, 162.72, 169.59; IR (film) ν , cm^{-1} : 3061, 2924, 2853, 1761, 1611, 1582, 1487, 1460, 1366, 1325, 1153, 1107, 953, 845, 748, 700, 623, 523; ESI-MS m/z (%): 562 ($[\text{M}+\text{H}]^+$, 87), 584 ($[\text{M}+\text{Na}]^+$, 93); Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{BrINO}_3$: C 49.14, H 3.05, N 2.49, Found: C 49.38, H 2.89, N 2.57.

5-Benzoyloxy-3-iodo-4-(*N*-(3-chlorophenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2p). Yellow solid, yield 89%, m.p. 44.7-46.1 °C; UV-vis (CH_2Cl_2) λ_{max} : 326 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 4.31-4.70 (dd, $J_1 = 12$ Hz, $J_2 = 12$ Hz, 2H), 5.85 (s, 1H), 6.91 (d, $J = 8$ Hz, 2H), 6.99 (d, $J = 8$ Hz, 1H), 7.08 (s, 1H), 7.12 (d, $J = 8$ Hz, 2H), 7.19-7.25 (m, 4H), 7.30 (t, $J = 8$ Hz, 2H), 7.35-7.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 58.38, 71.74, 98.69, 124.78, 126.83, 126.91, 126.98, 127.28, 128.35, 128.44, 128.55, 129.66, 130.25, 134.75, 135.09, 142.34, 143.71, 162.69, 169.54; IR (film) ν , cm^{-1} : 3061, 2924, 2853, 1761, 1614, 1584, 1472, 1364, 1323, 1159, 1113, 953, 748, 700, 534; ESI-MS m/z (%): 518 ($[\text{M}+\text{H}]^+$, 100), 540 ($[\text{M}+\text{Na}]^+$, 65); Anal. Calcd for $\text{C}_{23}\text{H}_{17}\text{ClINO}_3$: C 53.36, H 3.31, N 2.71, Found: C 53.54, H 3.11, N 2.94.

5-Ethoxy-3-iodo-4-(*N,N*-diphenylamino)-furan-2(5*H*)-one (2q). Yellow solid, yield 83%, m.p. 125.4-126.3 °C; UV-vis (CH_2Cl_2) λ_{max} : 319 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 0.90 (t, $J = 8$ Hz, 3H), 3.12-3.66 (m, 2H), 5.81 (s, 1H), 7.18 (d, $J = 8$ Hz, 4H), 7.28 (t, $J = 8$ Hz, 2H), 7.36-7.42 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 14.46, 55.40, 66.20, 100.62, 127.03, 127.20, 129.36, 142.72, 162.71, 169.88; IR (film) ν , cm^{-1} : 3059, 2955, 2922, 2853, 1757, 1612, 1584, 1489, 1456, 1368, 1321, 1152, 1113, 951, 750, 696, 523; ESI-MS m/z (%): 422 ($[\text{M}+\text{H}]^+$, 100), 444 ($[\text{M}+\text{Na}]^+$, 72); Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{INO}_3$: C 51.32, H 3.83, N 3.33, Found: C 51.09, H 3.99, N 3.52.

5-Ethoxy-3-iodo-4-(*N*-phenyl-*N*-(*p*-tolyl)amino)-furan-2(5*H*)-one (2r). Brown solid, yield 79%, m.p. 111.3-112.8 °C; UV-vis (CH_2Cl_2) λ_{max} : 319 nm; ^1H NMR (400 MHz, CDCl_3) δ , ppm: 0.91 (t, $J = 8$ Hz, 3H), 2.36 (s, 3H), 3.12-3.66 (m, 2H), 5.79 (s, 1H), 7.07 (d, $J = 8$ Hz, 2H), 7.14-7.20 (m, 4H), 7.24-7.29 (m, 1H), 7.35-7.40 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ , ppm: 14.50, 21.09, 54.41, 66.07, 100.59, 126.89, 127.07, 127.15, 129.29, 129.93, 137.16, 140.18, 142.82, 162.71, 169.98; IR (film) ν , cm^{-1} : 3059, 3032, 2976, 2924, 2855, 1757, 1614, 1585, 1508, 1491, 1454, 1371, 1323, 1153, 1115, 951, 837, 741, 696, 521; ESI-MS m/z (%): 436 ($[\text{M}+\text{H}]^+$, 84), 458 ($[\text{M}+\text{Na}]^+$, 100); Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{INO}_3$: C 52.43, H 4.17, N 3.22, Found: C 52.18, H 4.33, N 3.51.

5-Ethoxy-3-iodo-4-(*N*-(4-methoxyphenyl)-*N*-phenylamino)-furan-2(5*H*)-one (2s). Yellow viscous solid, yield 66%; UV-vis (CH_2Cl_2) λ_{max} : 318 nm; ^1H NMR (400 MHz,

CDCl₃) δ , ppm: 0.93 (t, J = 8 Hz, 3H), 3.13-3.67 (m, 2H), 3.83 (s, 3H), 5.77 (s, 1H), 6.90 (d, J = 8 Hz, 2H), 7.10-7.25 (m, 5H), 7.35-7.40 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ , ppm: 14.54, 53.70, 55.53, 66.07, 100.51, 114.45, 126.83, 126.85, 128.82, 129.28, 135.63, 142.95, 158.59, 162.75, 170.00; IR (film) ν , cm⁻¹: 3061, 2924, 2853, 1753, 1611, 1585, 1504, 1462, 1371, 1321, 1248, 1159, 1111, 1026, 951, 841, 743, 694, 534; ESI-MS m/z (%): 452 ([M+H]⁺, 100), 474 ([M+Na]⁺, 25); Anal. Calcd for C₁₉H₁₈INO₄: C 50.57, H 4.02, N 3.10, Found: C 50.39, H 4.24, N 3.22.

X-ray Structure Determination of Compounds **2a** and **2e**

Two suitable X-ray quality crystals of compound **2a** and **2e** were respectively grown by slow evaporation of petroleum ether/dichloromethane solvent mixture in the temperature variation of 25 °C. Diffraction data of **2a** and **2e** were collected on a Bruker APEX II Smart CCD diffractometer equipped with graphite-monochromated MoK α radiation (λ = 0.71073 Å) using the ω -scan technique. The data were corrected for absorption with the SADABS program. The structures were solved by direct methods using the SHELXS-97 program and all the non-hydrogen atoms were refined anisotropically with the full-matrix leastsquares on F^2 using the SHELX-97 program.^[78] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 962686 and no. 962687. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

Compound 2a

Compound 2a

Compound 2a

dy1 #23-24 RT: 0.28-0.29 AV: 2 NL: 1.78E7
T: + c ESI Full ms [50.00-800.00]

Compound 2b

Compound 2b

Compound 2b

dy16 #19-20 RT: 0.21-0.22 AV: 2 NL: 1.55E7
T: + c ESI Full ms [50.00-700.00]

Compound 2c

Compound 2c

Compound 2c

ZH-DY10 #24-26 RT: 0.25-0.27 AV: 3 NL: 9.08E7
T: + c ESI Full ms [100.00-700.00]

Compound 2d

Compound 2d

Compound 2d

zh-dy2 #34 RT: 0.30 AV: 1 NL: 7.63E7
T: + c ESI Full ms [150.00-600.00]

Compound 2e

Compound 2e

Compound 2e

ZH-DY3 #25-30 RT: 0.24-0.29 AV: 6 NL: 5.92E7
T: + c ESI Full ms [150.00-700.00]

Compound 2f

Compound 2f

Compound 2f

dy4_120806093046 #38-41 RT: 0.42-0.45 AV: 4 NL: 4.23E6
T: + c ESI Full ms [150.00-800.00]

Compound 2g

Compound 2g

Compound 2g

ZH-DY5 #18-26 RT: 0.17-0.24 AV: 9 NL: 8.63E7

T: + c ESI Full ms [200.00-700.00]

Compound 2h

Compound 2h

Compound 2h

ZH-DY8 #30-33 RT: 0.30-0.33 AV: 4 NL: 2.68E7
T: + c ESI Full ms [100.00-700.00]

Compound 2i

Compound 2i

Compound 2i

zh-db1 #37-43 RT: 0.33-0.38 AV: 7 NL: 1.51E7
T: + c ESI Full ms [150.00-600.00]

Compound 2j

Compound 2j

Compound 2j

db16_120830161335 #36-43 RT: 0.44-0.52 AV: 8 NL: 4.13E6
T: + c ESI Full ms [50.00-800.00]

Compound 2k

Compound 2k

Compound 2k

DB10 #26-28 RT: 0.28-0.30 AV: 3 NL: 2.50E7
T: + c ESI Full ms [150.00-800.00]

Compound 21

Compound 2l

Compound 2l

db5 #20-23 RT: 0.21-0.25 AV: 4 NL: 2.45E7
T: + c ESI Full ms [150.00-800.00]

Compound 2m

Compound 2m

Compound 2m

DB2 #35-42 RT: 0.38-0.45 AV: 8 NL: 7.55E6
T: + c ESI Full ms [150.00-800.00]

Compound 2n

Compound 2n

Compound 2n

db4 #24-28 RT: 0.26-0.30 AV: 5 NL: 7.07E6
T: + c ESI Full ms [150.00-800.00]

Compound 2o

Compound 2o

Compound 2o

db3 #29-38 RT: 0.32-0.41 AV: 10 NL: 2.55E6
T: + c ESI Full ms [150.00-800.00]

Compound 2p

Compound 2p

Compound 2p

db8 #30-33 RT: 0.32-0.36 AV: 4 NL: 4.89E6
T: + c ESI Full ms [150.00-800.00]

Compound 2q

Compound 2q

Compound 2q

dy17 #12-15 RT: 0.13-0.17 AV: 4 NL: 6.61E7
T: + c ESI Full ms [50.00-700.00]

Compound 2r

Compound 2r

Compound 2r

dy19 #41-44 RT: 0.41-0.44 AV: 4 NL: 5.13E7
T: + c ESI Full ms [50.00-600.00]

Compound 2s

Compound 2s

Compound 2s

dy18 #24-27 RT: 0.25-0.28 AV: 4 NL: 8.84E7
T: + c ESI Full ms [50.00-700.00]