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Electronic Supplementary Information

Facile Synthesis of Substituted 3-Aminofurans Through Tandem Reaction of N-

Sulfonyl-1,2,3-triazoles and Propargyl Alcohols

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1. General information

Unless otherwise noted, all reactions were carried out under an Argon atmosphere underanhydrous conditions and all reagents were purchased from commercial suppliers without further purification. All solvents were distilled from appropriate drying agents prior to use.Reaction progress was monitored by thin layer chromatography (TLC) and components were visualized by observation under UV light at 254nm. Flash column chromatography was performed using silica gel 60 (200-300 mesh).

All ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were given on Bruker AV-III 400 in CDCl₃. Chemical shifts were reported in parts per million (ppm, δ), referenced to the peak oftetramethylsilane,defined at $\delta = 0.00$ (¹HNMR), or the solvent peak of CDCl₃, defined at $\delta = 77.0$ (¹³CNMR). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants were quoted in Hz (*J*). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). Pressed KBr disks for infrared spectra were recorded using a Bruker-VERTEX 70 FT-IR spectrometer. Wavelengths (v) are reported in cm⁻¹. Melting points were recorded using a SGW Melting Point thermometer (X-4).High-resolution mass spectra were obtained using a Thermo Fisher ScientificLTQ FT Ultra.

2. Synthesis

2.1 Preparation and Spectral Data of Propargyl Alcohols



Under an inert gas, to a solution of the appropriate aryl iodide (6.00 mmol) in 10

mL of DMF, 10 mL of TEA, propargylic alcohol (9.00 mmol, 1.5 eq), copper iodide (0.12 mmol, 0.02 eq) and PdCl₂ (PPh₃)₂ (0.06 mmol, 0.01 eq) were added, then the reaction was stirred at room temperature. After completion of the reaction as indicated by TLC, the reaction mixture was filtered through celite and the eluent was concentrated in vacuo and the raw product was purified by column chromatography on silica gel in 81-99% yield as a white solid or a colorless oil.¹

1,3-diphenylprop-2-yn-1-ol (1a)

ŌН ¹H NMR (400 MHz, CDCl₃) δ = 7.61 (d, J = 7.2 Hz, 2H), 7.48-7.46 (m, Ph 2H), 7.40 (t, J =7.2 Hz, 2H), 7.36-7.30 (m, 4H), 5.68 (s, 1H), 2.45 (s, 1H); ¹³CNMR (100 MHz, CDCl₃) δ = 140.6, 131.7, 128.63, 128.57, 128.4, 128.3, 126.7, 122.4, 88.7, 86.6, 65.1.

3-(p-tolyl)prop-2-yn-1-ol (1m)

¹H NMR (400 MHz, CDCl₃) δ = 7.33 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 4.49(d, J = 3.6 Hz, 2H), 2.34 (s, 3H), 2.02-1.98 (m, Me

1H); ¹³CNMR (100 MHz, CDCl₃) δ = 138.6, 131.5, 129.0, 119.4, 86.5, 85.8, 51.6, 21.4.

3-(4-methoxyphenyl)prop-2-yn-1-ol (1n)

¹H NMR (400 MHz, CDCl₃) δ = 7.37 (d, J = 8.0 Hz, 2H), 6.83 (d, J =8.0 Hz, 2H), 4.48 (s, 2H), 3.80 (s, 3H), 2.07 (s, 1H); ¹³CNMR MeO $(100 \text{ MHz}, \text{CDCl}_3) \delta = 159.7, 133.1, 114.6, 113.9, 85.9, 85.6, 55.2, 51.6.$

3-(4-chlorophenyl)prop-2-yn-1-ol (10)

¹H NMR (400 MHz, CDCl₃) δ = 7.35 (d, J = 8.4 Hz, 2H), 7.27 (d, J =8.0 Hz, 2H), 4.49 (s, 2H), 2.28 (s, 1H); ¹³CNMR (100 MHz, $CDCl_3$) $\delta = 134.5, 132.8, 128.6, 120.9, 88.1, 84.5, 51.4.$

3-(4-bromophenyl)prop-2-yn-1-ol (1p)



¹H NMR (400 MHz, CDCl₃) δ = 7.35 (d, J = 7.6 Hz, 2H), 7.19 (d, J =7.6 Hz, 2H), 4.40 (s, 2H), 2.32 (s, 1H); ¹³CNMR (100 MHz,

¹ A. Pharma, S.A. US6479476 B1, 2002.

CDCl₃) δ = 133.0, 131.5, 122.7, 121.4, 88.3, 84.5, 51.4.

3-(3-chlorophenyl)prop-2-yn-1-ol (1q)

 $\begin{bmatrix} CI & T \\ CI & T \\$

3-(2-chlorophenyl)prop-2-yn-1-ol (1r)

 $\begin{bmatrix} c_{1} & & & \\ 0 & & & \\ 0 & & & \\ 1 & & &$

3-(naphthalen-2-yl)prop-2-yn-1-ol (1s)

3-cyclopropylprop-2-yn-1-ol (1v)²

To a solution of cyclopropyl acetylene (5.0 g, 75.8 mmol) in THF (100 mL), at -78 °C, was added n-BuLi (50 mL, 1.5 M in hexanes, 75 mmol) resulting in the formation of a thick white suspension which was warmed to room temperature over 1h. To the suspension was added paraformaldehyde (4.5 g, 152 mmol) and stirring continued at room temperature for 4h. The white suspension was quenched with 1N sodium bisulfate (200 mL) and the biphasic solution separated and the aqueous layer extracted with diethyl ether (2 \times 100 mL). The combined diethyl ether extracts were dried

² I. B. Shredova, G. P. Okonnoshnikova, I. E. Dolgii, D. M. Nefedov, *J. Chem. Soc., Perkin Trans.* 2,1991, **12**, 1875.

(MgSO₄) and concentrated in vacuo and the raw product was purified by column chromatography on silica gelto afforded 3-cyclopropyl-prop-2-yn-1-ol (5.70 g, 78%) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ = 4.21 (s, 2H), 3.22 (s, 1H), 1.29-1.24 (m, 1H), 0.80-0.75 (m, 2H), 0.71-0.68 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 89.0, 73.5, 50.7, 7.9, -0.8.

hept-2-yn-1-ol (1u)³

According to the general procedure described for 1v. ¹H NMR (400 MHz, CDCl₃) δ = 4.18 (s, 2H), 2.15-2.13 (m, 2H), 2.08-1.93 (m, 1H), 1.44-1.31 (m, 4H), 0.86-0.82 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 86.4, 78.2, 51.2, 30.6, 21.8, 18.3, 13.5.

2.2 Preparation and Spectral Data of 1-Sulfonyl-1,2,3-triazoles

$$= R + TsN_3 \xrightarrow{\text{CuTC (10 mol%)}}_{\text{rt, toluene}} \xrightarrow{N^{< N} NTs}_{R}$$

According to the procedure published by Fokin and co-workers:⁴ A 50 mL of round bottom flask with a magnetic stir bar was added copper (I) thiophene-2-carboxylate (CuTC, 0.5 mmol, 0.1 eq in regards to alkyne), toluene (20 mL), and the alkyne (5 mmol, 1.0 eq). The reaction mixture was stirred at room temperature. Subsequently, the sulfonyl azide (5 mmol, 1.0 eq) was added slowly. After completion of the reaction as indicated by TLC, the reaction mixture was filtered through celite and the eluent was concentrated in vacuo and the residue was purified by column chromatography on silica gel (eluted with PE/EA = 8 :1) to give the 1-Sulfonyl-1,2,3-triazoles (1a–k).⁵

³J. G. Miller, A. C. Oehlshlager, J. Org. Chem., 1984, 49, 2332.

⁴ J. Raushel, V. V. Forkin, Org. Lett., 2010, 12, 4952.

⁵ (a) E. J. Yoo, M. Ahlquist, S. H. Kim, I. Bae, V. V. Fokin, K. B. Sharpless, S. Chang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1730. (b) T. Miura, M.Yamauchi, M. Murakami, *Chem. Commun.*, 2009, 1470. (c) B. T. Parr, S. A. Green, H. M. L. Davies, *J. Am. Chem. Soc.*, 2013, **135**, 4716. (d) J. He, Z. Man, Y. Shi, C.-Y. Li, *J. Org. Chem.*, 2015, **80**, 4816.



4-phenyl-1-tosyl-1H-1,2,3-triazole (2a)

¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 8.22$ (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 7.2 Hz, 2H), 7.27-7.17 (m, 5H), 2.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 147.2$, 132.8, 130.3, 128.9, 128.8, 128.7, 128.4, 125.8, 119.0, 21.5.

4-(p-tolyl)-1-tosyl-1H-1,2,3-triazole (2b)

 $\begin{bmatrix} N=N \\ Me \end{bmatrix}^{N=N} H NMR (400 \text{ MHz, CDCl}_3, TMS) \delta = 8.27 (s, 1H), 8.02(d, J=8.4) \\ Hz, 2H), 7.71(d, J = 8.0 \text{ Hz}, 2H), 7.38(d, J = 8.0 \text{ Hz}, 2H), 7.23(d, J) \\ = 8.0 \text{ Hz}, 2H), 2.44 (s, 3H), 2.37(s, 3H); {}^{13}C NMR (100 \text{ MHz}, CDCl}_3) \delta = 147.4, \\ 147.3, 139.1, 133.1, 130.4, 129.6, 128.6, 126.0, 125.9, 118.5, 21.8, 21.3. \end{bmatrix}$

4-(4-propylphenyl)-1-tosyl-1H-1,2,3-triazole (2c)

^{N=N}/_{Hz}, ^{NTS} ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 8.30$ (s, 1H), 8.00(d, J = 8.4Hz, 2H), 7.73(d, J = 8.0 Hz, 2H), 7.35(d, J = 8.0 Hz, 2H), 7.22(d, J = 8.0 Hz, 2H), 2.61-2.57(m, 2H), 2.40 (s, 3H), 1.68-1.59(m, 2H), 0.94-0.91(m, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 147.4$, 147.2, 143.8, 133.0, 130.3, 129.0, 128.5, 126.2, 125.9, 118.5, 37.7, 24.3, 21.7, 13.6; IR (KBr) 3139, 1594, 1495, 1396, 1103, 996, 703, 675, 590 cm⁻¹. HRMS-(DART) (m/z): [M+H]⁺calcd for C₁₈H₂₀N₃O₂S, 342.1276; found 342.1271.

4-(4-methoxyphenyl)-1-tosyl-1H-1,2,3-triazole (2d)

 $\begin{bmatrix} N = N \\ MeO \end{bmatrix}^{N=N} IH NMR (400 MHz, CDCl_3, TMS) \delta = 8.22 (s, 1H), 8.00(d, J = 8.0 Hz, 2H), 7.74(d, J = 8.8 Hz, 2H), 7.36(d, J = 8.0 Hz, 2H), 6.94(d, J = 8.4 Hz, 2H), 3.82 (s, 3H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl_3) \delta = 160.2, 147.22, 147.18, 133.1, 130.3, 128.5, 127.4, 121.4, 117.9, 114.3, 55.2, 21.7.$

4-(4-chlorophenyl)-1-tosyl-1H-1,2,3-triazole (2e)

 $\begin{bmatrix} N=N \\ NTS \end{bmatrix}$ ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 8.32$ (s, 1H), 8.01(d, J = 8.4Hz, 2H), 7.76(d, J = 8.4 Hz, 2H), 7.40-7.37 (m, 4H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 147.5$, 146.3, 134.9, 132.9, 130.5, 129.2, 128.7, 127.4, 127.3, 119.0, 21.8.

4-(4-bromophenyl)-1-tosyl-1H-1,2,3-triazole (2f)

 $\begin{bmatrix} N=N \\ NTS \end{bmatrix}$ ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 8.32$ (s, 1H), 8.02(d, J = 8.4Hz, 2H), 7.70(d, J = 8.4 Hz, 2H), 7.55(d, J = 8.4 Hz, 2H), 7.39(d, J = 8.0 Hz, 2H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 147.5$, 146.3, 132.9, 132.2, 130.5, 128.7, 127.9, 127.5, 123.1, 119.0, 21.8.

4-(4-fluorophenyl)-1-tosyl-1H-1,2,3-triazole (2g)

 $\begin{bmatrix} N^{=N} \\ NTS \\ Hz,2H \end{bmatrix}$ ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 8.29$ (s, 1H), 8.02(d,*J* = 8.4 Hz,2H),7.82-7.78(m, 2H), 7.38(d, *J* = 8.0 Hz, 2H),7.13-7.09 (m, 2H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 163.1$ (d, *J*_{C-F} = 247.4 Hz), 147.4, 146.4, 133.0, 130.4, 128.7.127.9 (d, *J*_{C-F} = 8.3 Hz), 125.1 (d, *J*_{C-F} = 3.3 Hz),118.7, 116.0 (d, *J*_{C-F} = 21.8 Hz), 21.8.

4-(3-chlorophenyl)-1-tosyl-1H-1,2,3-triazole (2h)

 $\begin{bmatrix} N=N \\ NTS \end{bmatrix}$ ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 8.26$ (s, 1H), 7.94(d, J = 8.0Hz, 2H),7.74 (s, 1H), 7.62(d, J = 6.8 Hz, 1H), 7.32-7.25 (m, 4H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 147.5$, 146.0, 135.0, 132.9, 130.6, 130.5, 130.3, 129.1, 128.7, 126.1, 124.1, 119.4, 21.8.

4-(2-chlorophenyl)-1-tosyl-1H-1,2,3-triazole (2i)

 $\begin{bmatrix} CI & N=N \\ NTS \end{bmatrix}$ ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 8.66$ (s, 1H), 8.11(d, J = 7.2 Hz, 1H), 7.95 (d, J = 8.0 Hz, 2H), 7.36(d, J = 7.6 Hz, 1H), 7.31(d, J = 8.4Hz, 2H), 7.27-7.18 (m, 2H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 147.4$, 143.5, 133.0, 131.5, 130.4, 130.3, 130.0, 129.8, 128.7, 127.6, 127.2, 122.4, 21.8.

4-(thiophen-2-yl)-1-tosyl-1H-1,2,3-triazole (2j)

 $\begin{bmatrix} N=N \\ N=N \\ NTs \end{bmatrix}$ ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 8.20$ (s, 1H), 8.02(d, J = 8.4Hz, 2H), 7.44(dd, J = 3.6 Hz, 1.2 Hz, 1H), 7.39(d, J = 8.4 Hz, 2H), 7.34(dd, J = 4.8 Hz, 1.2Hz, 1H), 7.08(dd, J = 4.8 Hz, 3.6Hz, 1H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 147.4$, 142.5, 132.9, 130.8, 130.4, 128.7, 127.8, 126.3, 125.6, 118.1, 21.8.

4-(naphthalen-2-yl)-1-tosyl-1H-1,2,3-triazole (2k)

 $\begin{bmatrix} N = N \\ NTS \end{bmatrix}$ ¹H NMR (400 MHz, CDCl₃, TMS) δ = 8.43 (s, 1H), 8.36 (s, 1H), 8.05(d, *J* = 8.4 Hz, 2H), 7.88-7.82 (m, 4H), 7.51-7.49(m, 2H),7.38 (d,*J* = 8.0 Hz, 2H), 2.43 (s,3H); ¹³C NMR (100 MHz, CDCl₃) δ = 147.4, 147.3, 133.4, 133.3, 133.0, 130.4, 128.8, 128.7, 128.3, 127.8, 126.7, 126.6, 126.1, 125.2, 123.6, 119.2, 21.8.

2.3 General Procedure and Spectral Data of Products



1-Sulfonyl-1,2,3-triazoles (0.50 mmol, 1.0 eq), 2-propyn-1-ol (0.75 mmol, 1.5 eq), Rh₂(OCOtBu)₄ (3.0 mg, 5.0 μ mol, 1 mol%), and toluene (2.5 mL) were added to an oven-dried 10 mL pressure tube equipped with a stirrer bar in the Glove-box. The tube was sealed with a Teflon pressure cap. The mixture was heated at 100 °C for 40 min. After the resulting mixture was cooled, (PPh₃)AuNTf₂ (11.1 mg, 15 μ mol, 3 mol%) was added. The reaction mixture was stirred at 100 °C for 2 h, and it was concentrated under reduced pressure. The resulting residue was purified by flash chromatography (petroleum ether /ethyl acetate 7:1) to give the trisubstituted furans as a white solid or colourless oil.

4-methyl-N-(5-methyl-2-phenylfuran-3-yl)benzenesulfonamide (5a)

Compound **5a** was obtained as a white solid in 82% isolated yield, $R_f = 0.35$ (petroleum ether : ethyl acetate = 5 : 1); mp = 149-150 °C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.66$ (d, J = 8.4 Hz, 2H), 7.38 (d, J = 7.2 Hz, 2H), 7.27-7.17 (m, 5H), 6.23 (s, 1H), 6.02 (s, 1H), 2.35 (s, 3H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 150.8$, 144.7, 143.9, 136.2, 129.6, 129.4, 128.5, 127.4, 127.3, 124.7, 118.3, 107.4, 21.5, 13.8;IR (KBr) 3227, 1494, 1241, 906, 843, 769, 534, 489cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₁₈H₁₈NO₃S, 328.1007; found 328.1001.

4-methyl-N-(5-methyl-2-(p-tolyl)furan-3-yl)benzenesulfonamide (5b)

Compound **5b** was obtained as a white solid in 80% isolated yield, $R_f = 0.44$ (petroleum ether : ethyl acetate = 5 : 1); mp = 124-125°C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.55$ (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H) , 6.93 (d, J = 8.0 Hz, 2H), 6.45 (s, 1H), 5.84 (s, 1H), 2.22 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 150.1$, 145.3, 143.6, 137.1, 136.2, 129.4, 129.0, 127.2, 126.6, 124.6, 117.4, 107.4, 21.3, 21.1, 13.7; IR (KBr) 3226, 2925, 1327, 1161, 1094, 900, 824, 716, 691, 665 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₁₉H₂₀NO₃S, 342.1164; found 342.1157.

4-methyl-N-(5-methyl-2-(4-propylphenyl)furan-3-yl)benzenesulfonamide (5c)

Compound **5c** was obtained as a white solid in 78% isolated yield, $R_f = 0.53$ (petroleum ether : ethyl acetate = 5 : 1); mp = 127-129 °C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.57$ (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.0Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.0 Hz, 2H), 6.32 (s, 1H), 5.89 (s, 1H), 2.44 (t, J = 7.6 Hz, 2H), 2.25 (s, 3H), 2.16 (s, 3H), 1.56-1.47 (m, 2H), 0.83 (t, J = 7.6Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 150.3$, 145.2, 143.7, 142.0, 136.2, 129.4, 128.5, 127.2, 126.9, 124.6, 117.5, 107.4, 37.7, 24.3, 21.4, 13.72, 13.69;IR (KBr) 3215, 2953, 2918, 2858, 1330, 1153, 1093, 824, 697, 662, 530 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₂₁H₂₄NO₃S, 370.1477; found 370.1472.

N-(2-(4-methoxyphenyl)-5-methylfuran-3-yl)-4-methylbenzenesulfonamide (5d)

Compound **5d** was obtained as a white solid in 72% isolated yield, $R_f = 0.30$ (petroleum ether : ethyl acetate = 5 : 1); mp = 122-123°C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.65$ (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H) , 6.77 (d, J = 8.8 Hz, 2H), 6.33 (s, 1H), 5.90 (d, J = 0.8 Hz, 1H), 3.77 (s, 3H), 2.35 (s, 3H), 2.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 158.9$, 149.9, 145.6, 143.7, 136.3, 129.4, 127.3, 126.3, 122.3, 116.6, 113.9, 107.4, 55.2, 21.4, 13.7; IR (KBr) 3251, 1508, 1326, 1300, 1250, 1180, 1162, 690 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₁₉H₂₀NO₄S, 358.1113; found 358.1108.

N-(2-(4-chlorophenyl)-5-methylfuran-3-yl)-4-methylbenzenesulfonamide (5e)

Compound **5e** was obtained as a white solid in 71% isolated yield, $R_f = 0.44$ (petroleum ether : ethyl acetate = 5 : 1); mp = 159-160 °C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.58$ (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4Hz, 2H), 7.14-7.11 (m, 4H) , 6.09 (s, 1H), 5.86 (s, 1H), 2.31 (s, 3H), 2.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 151.1$, 144.7, 144.1, 136.2, 133.1, 129.6, 128.6, 127.9, 127.3, 125.9, 118.4, 108.0, 21.5, 13.8; IR (KBr) 3260, 1556, 1488, 1329, 1161, 1092, 890, 737, 689, 597, 536 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₁₈H₁₇ClNO₃S, 362.0618; found 362.0611.

N-(2-(4-bromophenyl)-5-methylfuran-3-yl)-4-methylbenzenesulfonamide (5f)

Compound **5f** was obtained as a white solid in 75% isolated yield, $R_f = 0.44$ (petroleum ether : ethyl acetate = 5 : 1); mp = 154-155 °C; ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.55$ (d, J = 8.0 Hz, 2H), 7.29-7.23 (m, 4H), 7.07 (d, J = 8.0 Hz, 2H) , 6.56 (s, 1H), 5.80 (s, 1H), 2.27 (s, 3H), 2.15 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 151.0$, 144.8, 144.0, 136.2, 131.4, 129.5, 128.3, 127.2, 126.1, 121.0, 118.4, 108.1, 21.5, 13.7;IR (KBr) 3262, 1485, 1329, 1160, 724, 685, 534 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₁₈H₁₇BrNO₃S, 406.0113; found 406.0107.

N-(2-(4-fluorophenyl)-5-methylfuran-3-yl)-4-methylbenzenesulfonamide (5g)

Compound **5g** was obtained as a white solid in 80% isolated yield, $R_f = 0.41$ (petroleum ether : ethyl acetate = 5 : 1); mp = 146-147 °C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.56$ (d, J = 8.0 Hz, 2H), 7.40-7.36 (m, 2H), 7.08 (d, J = 8.0 Hz, 2H) , 6.83 (t, J = 8.8 Hz,2H), 6.50 (s, 1H),5.77 (d, J = 0.8 Hz,1H), 2.26 (s, 3H), 2.15 (s, 3H);¹³C NMR (100 MHz, CDCl₃) $\delta = 161.9$ (d, $J_{C-F} = 246.1$ Hz), 150.5, 145.1143.9, 136.2, 129.5, 127.3, 126.7 (d, $J_{C-F} = 8.0$ Hz), 125.7 (d, $J_{C-F} = 3.3$ Hz), 117.5, 115.3 (d, $J_{C-F} = 21.6$ Hz), 107.8, 21.4, 13.7;¹⁹F NMR (376 MHz, CDCl₃) δ = -113.5; IR (KBr) 3239, 1505, 1329, 1217, 1161, 1091, 839, 560 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₁₈H₁₇FNO₃S, 346.0913; found 346.0906.

N-(2-(3-chlorophenyl)-5-methylfuran-3-yl)-4-methylbenzenesulfonamide (5h)

Compound **5h** was obtained as a white solid in 70% isolated yield, $R_f = 0.46$ (petroleum ether : ethyl acetate = 5 : 1); mp = 149-150 °C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.56$ (d, J = 8.4 Hz, 2H), 7.29-7.23 (m, 2H), 7.09-7.02 (m, 4H) , 6.50 (s, 1H), 5.91 (d, J = 0.8 Hz, 1H), 2.25 (s, 3H), 2.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 151.3$, 144.0, 143.9, 136.0, 134.3, 131.0, 129.62, 129.58, 127.2, 127.1, 124.4, 122.7, 119.0, 108.2, 21.4, 13.7; IR (KBr) 3243, 1595, 1556, 1406, 1326, 1158, 1091, 893, 573 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₁₈H₁₇ClNO₃S, 362.0618; found 362.0612.

N-(2-(2-chlorophenyl)-5-methylfuran-3-yl)-4-methylbenzenesulfonamide (5i)

Compound **5i** was obtained as a colourless oil in 59% isolated yield, $R_f = 0.48$ (petroleum ether : ethyl acetate = 5 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.43$ (d, J = 8.0 Hz, 2H), 7.29 (dd, J = 8.0, 0.8 Hz, 1H),7.19 (td,J = 7.6, 1.6 Hz,1H) ,7.10 (td, J = 7.6, 0.8 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.92 (dd, J = 7.6, 1.6 Hz, 1H) , 6.38(s, 1H), 6.28(s, 1H),2.289 (s, 3H), 2.285 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 152.3$, 143.4, 141.3, 135.4, 131.3, 130.8, 129.7, 129.4, 129.2, 128.2, 126.9, 126.5, 120.8, 107.0, 21.3, 13.8; IR (KBr) 3279, 1634, 1592, 1472, 1091, 1068, 814, 542 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₁₈H₁₇ClNO₃S, 362.0618; found 362.0612.

4-methyl-N-(5-methyl-2-(thiophen-2-yl)furan-3-yl)benzenesulfonamide (5j)

Compound **5j** was obtained as a white solid in 70% isolated yield, $R_f = 0.35$ (petroleum ether : ethyl acetate = 5 : 1); mp = 161-164 °C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.60$ (d, J = 8.4 Hz, 2H), $\delta = 7.12$ (d, J = 8.4 Hz, 2H), $\delta = 7.09$ (d, J = 4.8 Hz, 1H), $\delta = 6.94$ (d, J = 2.8 Hz, 1H), $\delta = 6.85$ (dd, J = 4.8 Hz, 3.6 Hz, 1H), 6.23 (s, 1H), 5.96 (s, 1H), 2.28 (s, 3H), 2.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 150.8$, 143.8, 140.9, 136.2, 130.8, 129.5, 127.3, 124.4, 123.2, 117.7, 107.0, 21.5, 13.8.;IR (KBr) 3215,1416,1329,1160,1092,981,893,718,691,665 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd forC₁₆H₁₆NO₃S₂, 334.0572; found 334.0565.

4-methyl-N-(5-methyl-2-(naphthalen-2-yl)furan-3-yl)benzenesulfonamide (5k)

Compound **5k** was obtained as a white solid in 75% isolated yield, $R_f = 0.40$ (petroleum ether : ethyl acetate = 5 : 1); mp = 150-151 °C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.67-7.58$ (m, 6H), $\delta = 7.47$ (dd, J = 8.8, 1.6 Hz, 1H), $\delta = 7.38-7.33$ (m, 2H), $\delta = 7.00$ (d, J = 8.0 Hz, 2H), 6.33 (s, 1H), 6.03 (s, 1H), 2.24 (s, 3H), 2.13 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 151.1$, 145.1, 143.9, 136.3, 133.1, 132.4, 129.5, 128.12, 128.08, 127.5, 127.2, 126.8, 126.3, 126.1, 123.3, 122.8, 118.6, 108.0, 21.3, 13.9; IR (KBr) 3280, 1321, 1161, 1093, 892, 822, 756, 694, 667, 567, 470 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₂₂H₂₀NO₃S, 378.1164; found 378.1157.



4-Phenyl-1-tosyl-1,2,3-triazole (0.55 mmol, 1.1 eq), propargyl alcohols (0.50 mmol, 1.0 eq), $Rh_2(OCOtBu)_4$ (3.0 mg, 5.0 µmol, 1 mol%), and toluene (2.5 mL) were added to an oven-dried 10 mL pressure tube equipped with a stirrer bar in the Glove-box. The tube was sealed with a Teflon pressure cap. The mixture was heated at 100 °C for 40 min. After the resulting mixture was cooled, (PPh₃)AuNTf₂ (11.1 mg, 15 µmol, 3 mol%) was added. The reaction mixture was stirred at 100 °C for 4h, and it was concentrated under reduced pressure. The resulting residue was purified by flash chromatography (petroleum ether /ethyl acetate 7:1) to give the tetrasubstituted furans as a white solid or colourless oil.

4-methyl-N-(5-methyl-2,4-diphenylfuran-3-yl)benzenesulfonamide (51)



Compound **51** was obtained as a yellow solid in 88% isolated yield, $R_f = 0.50$ (petroleum ether : ethyl acetate = 5 : 1);mp = 153-154 °C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.82$ (d, J = 7.6 Hz, 2H), 7.26-

7.12 (m, 8H), 6.84-6.83 (m, 2H), 6.75 (d, J = 7.6 Hz, 2H), 6.33 (s, 1H), 2.20 (s, 3H), 2.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 148.1$, 147.3, 143.0, 136.1, 131.0, 129.6, 129.0, 128.7, 128.3, 128.2, 127.5, 127.1, 126.6, 125.3, 122.0, 116.1, 21.4,

12.5; IR (KBr) 3247, 1495, 1428, 1333, 1162, 1093, 808, 763, 706, 666, 569 cm⁻¹; HRMS-(DART) (m/z): $[M+H]^+$ calcd for C₂₄H₂₂NO₃S, 404.1320; found 404.1312.

4-methyl-N-(5-methyl-2-phenyl-4-(p-tolyl)furan-3-yl)benzenesulfonamide (5m)



Compound 5m was obtained as a yellow solid in 86% isolated yield, $R_f = 0.52$ (petroleum ether : ethyl acetate = 5 : 1); mp = 164-165 °C;¹H NMR (400 MHz, CDCl₃, TMS) δ = 7.81 (d, *J* = 7.2 Hz, 2H),

7.25-7.13 (m, 5H), 6.93 (d, J = 7.6 Hz, 2H), 6.76-6.72 (m, 4H), 6.26 (s, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 2.18(s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 148.0, 147.1, 143.0, 136.4, 129.7, 129.0, 128.9, 128.6, 128.2, 128.0, 127.5 127.1, 125.2, 121.9, 116.2, 21.4, 21.2, 12.5; IR (KBr) 3339, 1514, 1160, 963, 766, 692, 663, 565, 546 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd forC₂₅H₂₄NO₃S, 418.1477; found 418.1468.

N-(4-(4-methoxyphenyl)-5-methyl-2-phenylfuran-3-yl)-4-

methylbenzenesulfonamide (5n)

OMe Compound **5n** was obtained as a white solid in 87% isolated yield, $R_f = 0.30$ (petroleum ether : ethyl acetate = 5 : 1); mp = 167-169 TsHN $^{\circ}C_{1}^{1}H$ NMR (400 MHz, CDCl₃, TMS) $\delta = 7.87$ (d, J = 7.6 Hz, 2H), 7.32-7.28 (m, 4H), 7.22 (t, J = 7.2 Hz, 1H), 6.85 (d, J = 8.4 Hz, 4H), 6.73 (d, J = 8.4Hz, 2H), 6.44 (s, 1H), 3.80 (s, 3H), 2.29 (s, 3H), 2.25 (s, 3H); ¹³C NMR (100 MHz, $CDCl_3$) $\delta = 158.5, 147.9, 147.0, 143.0, 136.5, 129.9, 129.7, 129.0, 128.2, 127.4, 127.1, 127.1, 129.0, 128.2, 127.4, 127.1, 129.0, 128.2, 127.4, 127.1, 129.0, 128.2, 129.0, 129.0, 128.2, 129.0, 128.2, 129.0,$ 125.2, 123.3, 121.7, 116.3, 113.7, 55.2, 21.4, 12.5; IR (KBr) 3234, 1510, 1435, 1331, 1245, 1161, 837, 808, 670cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₂₅H₂₄NO₄S, 434.1426; found 434.1418.

N-(4-(4-chlorophenyl)-5-methyl-2-phenylfuran-3-yl)-4-

methylbenzenesulfonamide (50)



Compound 50 was obtained as a pale yellow solid in 92% isolated yield, $R_f = 0.52$ (petroleum ether : ethyl acetate = 5 : 1); mp = 172-173 °C;¹H NMR (400 MHz, CDCl₃, TMS) δ = 7.80 (d, J= 7.6 Hz,

2H), 7.24-7.15 (m, 5H), 7.05 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 6.68 (s, 1H), 2.23 (s, 3H), 2.17 (s, 3H);¹³C NMR (100 MHz, CDCl₃) $\delta =$ S13

148.7, 147.4, 143.4, 136.5,132.7, 130.1, 129.6, 129.4, 129.0, 128.4, 128.3, 127.7, 127.0, 125.3, 121.2, 115.9, 21.4, 12,5;IR (KBr) 3245, 1495, 1325, 1160, 1091, 833, 725, 663, 574, 523cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd forC₂₄H₂₁ClNO₃S, 438.0931; found 438.0922.

N-(4-(4-bromophenyl)-5-methyl-2-phenylfuran-3-yl)-4-

methylbenzenesulfonamide (5p)

Compound **5p** was obtained as a yellow solid in 92% isolated yield, $R_f = 0.50$ (petroleum ether : ethyl acetate = 5 : 1); mp = 172-173 °C;¹H NMR (400 MHz, CDCl₃, TMS) δ = 7.89 (d, *J* = 7.6 Hz, 2H), 7.35-7.26 (m, 7H), 6.87-6.80 (m, 5H), 2.32 (s, 3H), 2.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 148.7, 147.3, 143.4, 136.4, 131.3, 130.5, 130.1 129.4, 129.0, 128.3, 127.7, 126.9, 125.3, 121.2, 120.8, 115.8, 21.5, 12,5;IR (KBr) 3248, 1492, 1329, 1161, 1092, 716, 664, 572cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₂₄H₂₁BrNO₃S, 482.0426; found 482.0417.

N-(4-(3-chlorophenyl)-5-methyl-2-phenylfuran-3-yl)-4-

methylbenzenesulfonamide (5q)



Compound **5q** was obtained as a white solid in 91% isolated yield, $R_f = 0.50$ (petroleum ether : ethyl acetate = 5 : 1); mp = 159-160 °C;¹H NMR (400 MHz, CDCl₃, TMS) δ =7.86-7.84 (m, 2H), 7.29-

7.18 (m, 5H), 7.09-7.07 (m, 2H), 6.83-6.81 (m,3H), 6.71 (s,1H), 6.39 (s, 1H), 2.25 (s, 3H), 2.19 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 148.6, 147.6, 143.5, 136.1,134.2, 133.0, 129.5, 129.4 129.1, 128.7, 128.3, 127.8, 127.1, 126.9, 126.8, 125.3, 120.9, 115.7, 21.5, 12,5; IR (KBr) 3259, 1596, 1494, 1336, 1165, 1093, 666, 571cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₂₄H₂₁ClNO₃S, 438.0931; found 438.0922.

N-(4-(2-chlorophenyl)-5-methyl-2-phenylfuran-3-yl)-4-

methylbenzenesulfonamide (5r)



Compound **5r**was obtained as a pale yellow solid in 75% isolated yield, $R_f = 0.43$ (petroleum ether : ethyl acetate = 5 : 1); mp = 157-158 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ = 7.89-7.87 (m, 2H),

7.29-7.16 (m, 6H), 7.09 (td, J = 7.6 Hz, 1.6 Hz ,1H), 6.95 (td, J = 7.6 Hz, 1.2Hz,1H), 6.78 (d, J = 8.0 Hz, 2H), 6.63 (dd,J = 7.6 Hz, 1.6Hz, 1H), 6.14(s, 1H), 2.20 (s, 3H), 2.10 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 148.6$, 147.9, 143.0, 136.4, 132.9, 132.0, 130.0, 129.41, 129.36, 129.2, 128.6, 128.2, 127.7, 126.8, 126.7, 125.2, 120.0, 116.6, 21.4, 12.6; IR (KBr) 3312, 1329, 1161, 1093, 818, 754, 691, 663, 569 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₂₄H₂₁ClNO₃S, 438.0931; found 438.0922.

4-methyl-N-(5-methyl-4-(naphthalen-1-yl)-2-phenylfuran-3-

yl)benzenesulfonamide (5s)



Compound **5s** was obtained as a white solid in 80% isolated yield, $R_f = 0.43$ (petroleum ether : ethyl acetate = 5 : 1); mp = 152-153 °C;¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 8.01$ (d, J = 7.6 Hz, 2H),

7.74 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.42-7.32 (m, 5H), 7.25-7.17 (m, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 7.2 Hz, 1H), 6.54 (d, J = 8.0 Hz, 2H), 5.95 (s, 1H), 2.09 (s, 3H), 2.07 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 148.4$, 148.1, 142.6, 136.1, 133.6, 131.4, 129.7, 128.9, 128.5, 128.3, 128.1, 127.8, 127.71, 127.66, 126.5, 125.8, 125.34, 125.28, 124.8, 119.9, 117.2, 21.4, 12.8; IR (KBr) 3242, 1329, 1161, 1092, 805, 780, 672, 570 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₂₈H₂₄NO₃S, 454.1477; found 454.1465.

N-(4,5-dimethyl-2-phenylfuran-3-yl)-4-methylbenzenesulfonamide (5t)

Compound **5t** was obtained as a white solid in 80% isolated yield, $R_f = 0.50$ (petroleum ether : ethyl acetate = 5 : 1); mp = 155-157 °C;¹H NMR (400 MHz, CDCl₃, TMS) δ =7.46 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.05 (d, *J* = 6.8 Hz, 3H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.20 (s, 1H), 2.20 (s, 3H), 2.14 (s, 3H), 1.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 146.9, 146.4, 143.5, 136.6, 129.6, 129.2, 128.0, 127.3, 126.9, 124.7, 117.9, 116.3, 21.3, 12.0, 7.5;IR (KBr) 3221, 1598, 1329, 1158, 1092, 813, 769, 685, 544 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₁₉H₂₀NO₃S, 342.1164; found 342.1158.

N-(4-butyl-5-methyl-2-phenylfuran-3-yl)-4-methylbenzenesulfonamide (5u)



Compound **5u** was obtained as a oil in 88% isolated yield, $R_f =$ 0.64 (petroleum ether : ethyl acetate = 5 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) δ = 7.42 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.2 Hz, 2H), 7.02-6.95 (m, 3H), 6.84 (d, J = 8.0 Hz, 2H), 6.63 (s, 1H), 2.12-2.08 (m, 8H), 1.34-1.27 (m, 2H), 1.20-1.11 (m, 2H), 0.79-0.76 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 147.0, 146.4, 143.3, 136.6, 129.6, 129.0, 127.8, 127.1, 126.7, 124.8, 120.9, 117.3, 31.7, 22.4, 22.0, 21.1, 13.7, 12.1; IR (KBr) 3270, 2855, 1599, 1494, 1155, 1093, 813, 763, 566 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺ calcd for C₂₂H₂₆NO₃S, 384.1633; found 384.1625.

N-(4-cyclopropyl-5-methyl-2-phenylfuran-3-yl)-4-methylbenzenesulfonamide (5v)



Compound 5v was obtained as a white solid in 72% isolated yield, $R_f = 0.50$ (petroleum ether : ethyl acetate = 5 : 1); mp = 148-149 °C;¹H NMR (400 MHz, CDCl₃, TMS) δ = 7.62-7.59 (m, 4H), 7.20-

7.12 (m, 3H), 7.07 (d, J = 8.0 Hz, 2H), 6.16 (d, J = 5.2 Hz, 1H), 2.31 (s, 3H), 2.25 (s, 3H), 0.90-0.84 (m, 1H), 0.68-0.64 (m, 2H), 0.39-0.35 (m, 2H); ¹³C NMR (100 MHz, $CDCl_3$ $\delta = 147.9, 146.6, 143.5, 136.9, 129.6, 129.2, 128.0, 127.5, 127.0, 124.8, 121.0, 124.8, 121.0, 124.8, 121.0, 124.8, 121.0, 124.8, 121.0, 124.8, 121.0, 124.8, 1$ 118.6, 21.4, 12.5, 4.8, 3.5; IR (KBr) 3256, 1432, 1329, 1163, 1093, 815, 692, 667, 569, 544cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd for C₂₁H₂₂NO₃S, 368.1320; found 368.1311.

(3,5-diphenyl-1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)(phenyl)methanone (4a)



Compound 4a was obtained as a white solid in 72% isolated yield, R_f = 0.46 (petroleum ether : ethyl acetate = 5 : 1); mp = 188-190 °C; 1 H NMR (400 MHz, CDCl₃, TMS) δ =8.05 (d, J = 7.6 Hz, 2H), 7.52 (t, J

= 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 3.6 Hz, 2H), 7.24-7.20 (m, 4H), 7.15 (t, J = 7.6 Hz, 2H), 7.11-7.06 (m, 4H), 6.97 (d, J = 8.0 Hz, 2H), 6.17 (s, 1H), 6.12 (s, 1H),5.96 (dd, J = 5.6Hz, 1.6Hz,1H),2.31 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ =197.4, 142.7, 138.7, 137.2, 136.4, 136.3, 132.8, 131.3, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 127.9, 127.0, 126.6, 73.4, 71.0, 21.4; IR (KBr) 1695, 1685, 1343, 1162,

1150, 668, 602, 543cm⁻¹; HRMS-(DART) (m/z): $[M+H]^+$ calcd for $C_{30}H_{26}NO_3S$, 480.1633; found 480.1624.

(2-chlorophenyl)(1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)methanone (5i')

Compound **5i**' was obtained as a colourless oil in 23% isolated yield, $R_f = 0.22$ (petroleum ether : ethyl acetate= 5 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.73$ (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.42-7.30 (m, 5H), 5.86 (t, J = 2.4 Hz, 1H), 5.72 (s, 2H), 4.27-4.12 (m, 2H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 198.4$, 143.8, 137.1, 134.7, 131.8, 130.9, 130.2, 129.7, 129.3, 128.6, 127.4, 126.6, 124.5, 74.5, 55.4, 21.4.

(3-cyclopropyl-1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)(phenyl)methanone (5v')



Compound **5v'** was obtained as a white solid in 27% isolated yield, Rf = 0.23 (petroleum ether : ethyl acetate = 5 : 1); ¹H NMR (400 MHz, CDCl₃, TMS) δ = 8.00 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 8.0 Hz,

2H), 7.56 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.60 (t, J = 2.4 Hz, 1H), 5.33 (s, 1H), 4.29-4.18 (m, 2H), 2.40 (s, 3H), 1.00-0.97 (m, 1H), 0.61-0.56 (m, 1H),0.49-0.40 (m, 2H), 0.26-0.19 (m, 1H);¹³C NMR (100 MHz, CDCl₃) $\delta = 197.5$, 143.6, 142.3, 136.1, 134.3, 133.0, 129.6, 128.6, 128.4, 127.4, 118.1, 73.7, 54.3, 21.4, 8.9, 7.6, 5.8.

(5,5-dimethyl-1-tosyl-2,5-dihydro-1H-pyrrol-2-yl)(phenyl)methanone (4ma)

Compound **4ma** was obtained as a white solid in 70% isolated yield, $R_f = 0.46$ (petroleum ether : ethyl acetate = 5 : 1); mp = 148-149 °C; ¹H NMR (400 MHz, CDCl₃, TMS) $\delta = 7.89$ (d, J = 7.2 Hz, 2H), 7.68 (d, J =8.0 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.07 (s, 1H), 5.60 (dd, J = 6.0 Hz, 2.0Hz, 1H),5.52 (dd, J = 6.0 Hz, 2.0Hz, 1H),2.30 (s, 3H), 1.52 (s, 3H), 1.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) $\delta = 195.0$, 143.1, 140.1, 138.7, 135.2, 133.3, 129.2, 128.6, 128.3, 127.7, 120.8, 72.2, 71.5, 28.9, 26.7, 21.4;IR (KBr) 1700, 1597, 1450, 1053, 859, 810, 714, 637, 594 cm⁻¹.

3. Representative synthetic application

N-(5-methyl-2-phenylfuran-3-yl)-N-tosylbenzamide⁶



To a mixture of the corresponding sulfonamide (0.5 mmol), DMAP (0.5 mmol%) and Et_3N (150ul, 1.0mmol) in CH_2Cl_2 (1 ml) was added slowly the benzoyl chloridein CH_2Cl_2 (1ml) at 0°C. The reaction mixture was stirred at room temperature for 2h.the solvent was removed under reduced pressure to give crude product, which was purified by column chromatography onsilica gel to affordN-tosylcarboxylic amideas a white solid in 95%.

N-(5-methyl-2-phenylfuran-3-yl)benzamide⁷ (5a'')



To a 10 mL Schlenk flask equipped with a magnetic stir bar was added N-(5methyl-2-phenylfuran-3-yl)-N-tosylbenzamide (0.2 mmol, 86.4 mg, 1.0 eq), $Ir(ppy)_2(dtb-bpy)PF_6$ (0.004 mmol, 3.4 mg, 2 mol%), Amine (0.4 mmol, 101.3 mg, 2.0 eq) and dry DCM (1.5 mL). The resulting mixture was degassed via 'freezepump-thaw' procedure (3 times). The solution was stirred at a distance of ~5 cm from a 3W white LED at room temperature for 2 days. Upon the completion of reaction monitored by TLC, the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluant: petroleum/ethyl

⁶ M. C. McIntosh, S. M. Weinreb, J. Org. Chem., 1993, 58, 4823.

⁷J. Xuan, B. -J. Li, Z. -J. Feng, G. -D. Sun, H. -H. Ma, Z. -W. Yuan, J. -R. Chen, L.-Q. Lu, W.-J. Xiao, *Chem. Asian J.*, 2013, **8**, 1090.

acetate (8;1) to provide pure product N-(5-methyl-2-phenylfuran-3-yl)benzamide as a white solid in 75% isolated yield, $R_f = 0.50$ (petroleum ether : ethyl acetate = 5 : 1); mp = 147-149 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ = 7.85 (d, *J* = 7.2 Hz, 3H), 7.59-7.53 (m, 3H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 6.69 (s, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ =165.4, 151.0, 140.6, 134.1, 131.9, 130.6, 129.0, 128.8, 127.1, 127.0, 124.5, 120.9, 105.9, 13.8; IR (KBr) 3259, 1653, 1535, 1310, 1134, 803, 759, 711 cm⁻¹; HRMS-(DART) (m/z): [M+H]⁺calcd forC₁₈H₁₆NO₂, 278.1181; found 278.1172.

4.X-ray crystal structures

General procedure for preparation of the crystal(4a): The product (40 mg) was dissolved in ethyl acetate, and then filtered through a pad of filter paper. The filtrate was transferred into several test-tubes by different volumes. Then to these solution were added petroleum ether in dropwise. The samples prepared in this way were allowed to evaporate slowly at room temperature, which would eventually give colorless crystals on the surface of the tubes.

Crystals of 4a,5j,5n were prepared followed the method mentioned above.

Colorless granular-shaped crystals **4a** was obtained from mixed solution (PE:EA =10:1).



CCDC Nr. 1444605

Colorless granular-shaped crystals 5j was obtained from mixed solution (PE: EA = 10:1).





CCDC Nr. 1444603

Colorless granular-shaped crystals **5n** was obtained from mixedsolution(PE:EA= 10:1).





CCDC Nr. 1444604



5.¹H and ¹³C NMR spectra of the products






















































































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