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Synthesis of Benzofurans *via* Tandem Rhodium-Catalyzed C(sp^3)–H Insertion and Copper-Catalyzed Dehydrogenation

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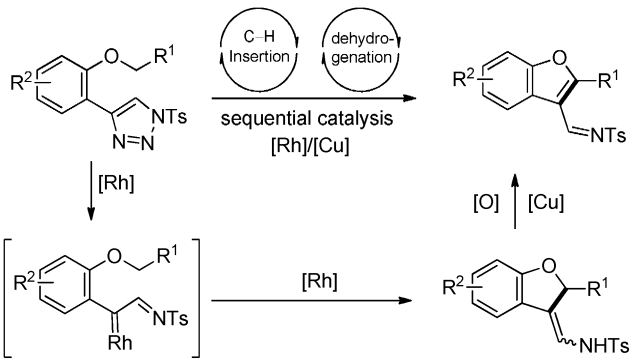
Abstract: A sequentially catalyzed cascade approach for the synthesis of benzofuran derivatives (up to 88% yield) from 1-sulfonyl-1,2,3-triazoles has been developed. The cascade reaction involves sequential rhodium-catalyzed C(sp^3)–H insertion and copper-catalyzed aerobic oxidation. The method was made more convenient towards the synthesis of benzofurans starting from terminal alkynes *via* a one-pot sequential copper-catalyzed alkyne-azide cycloaddition (CuAAC)/C–H insertion/dehydrogenation cascade reaction. Moreover, the utility of the cascade approach was demonstrated in the synthesis of the indole framework.

Keywords: benzofurans; C–H insertion; dehydrogenation; rhodium catalysis

Introduction

Direct and selective functionalization of C–H bond is of great importance in organic synthesis and the transition metal-catalyzed insertion of carbenes into C–H bonds plays a crucial role in this context.[1] Early work in this area focused on the transition metal-catalyzed generation of metal carbenoids from diazo compounds and their insertion into various C–H bonds including C(sp^3)–H bonds.[2] Recently, *N*-sulfonyl-1,2,3-triazoles have emerged as a convenient and stable precursor of rhodium(II) azavinyl carbenes for a variety of synthetically useful transformations[3] such as X–H (X = C, N, O) functionalization,[4] transannulation reactions to generate heterocycles,[5] cyclopropanation,[6] ring expansion,[7] or ylide formation with subsequent rearrangement.[8] However, the insertion of a metal-bound imino carbene intermediate into a C(sp^3)–H bond is quite limited. The Fokin group demonstrated a highly enantioselective insertion of azavinyl carbenes into the C(sp^3)–H bond catalyzed by chiral Rh(II) carboxylates.[4a] Very recently, Wang and Chen reported a one-pot synthesis of 2,3-substituted benzofurans *via* a rhodium-catalyzed intramolecular C–H insertion reaction and subsequent palladium-catalyzed dehydrogenation.[9]

Benzofuran is a privileged structural motif found in a number of natural products, biologically active molecules and pharmaceuticals.[10] Therefore, the development of an efficient and mild approach towards benzofuran derivatives is highly desirable.[11] In this paper we present an efficient approach towards benzofuran derivatives from the transition metal-catalyzed tandem intramolecular C(sp^3)–H insertion of azavinyl carbenes, derived from 1-sulfonyl-1,2,3-triazoles and aerobic oxidation *via* sequential catalysis (Scheme 1).[12]

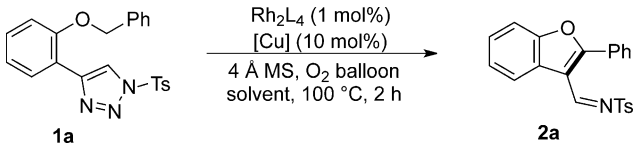


Scheme 1. Construction of benzofuran derivatives from *N*-sulfonyl-1,2,3-triazoles *via* Rh/Cu sequential catalysis.

Results and Discussion

To start with, we chose *N*-Ts-1,2,3-triazole **1a** as model substrate to facilitate the formation of the metal-bound imino carbene and intramolecular C–H insertion. The *N*-Ts-1,2,3-triazole **1a** on treatment with 1 mol% of $Rh_2(TFA)_4$ and 10 mol% of copper(I) thiophene-2-carboxylate (CuTC) in the presence of 4 Å MS in toluene at 100 °C under an O_2 atmosphere, underwent the C–H insertion/dehydrogenation reaction to afford the desired product **2a** in 14% isolated yield (entry 1, Table 1). Inspired by this promising result, several rhodium catalysts with different carboxylates were tested under the same reaction conditions (entries 2–5, Table 1). Among the Rh catalysts tested, $Rh_2(Oct)_4$ displayed an optimal catalytic activity towards C–H insertion and afforded the corresponding product **2a** in 88% yield (entry 5, Table 1). The catalytic combinations of $Rh_2(Oct)_4$ with other copper catalysts such as $CuCl_2$ and $CuBr_2$ were also tested for the pilot reaction, but they were found to be inferior as compared to the $Rh_2(Oct)_4$-CuTC combination (entries 6 and 7, Table 1). As expected, the reaction did not proceed in the absence of $Rh_2(Oct)_4$ (entry 9, Table 1), while only 11% of **2a** could be isolated without CuTC, (entry 8, Table 1). Moreover, the product could be achieved in a moderate yield, when the reaction was carried out under air (entry 10, Table 1). Various solvents were then screened to further optimize the reaction conditions (entries 11–17, Table 1). Among the tested solvents, toluene was the optimal one. Investigations on the effect of substrate concentration revealed that a higher concentration of **1a** (0.15 M, entry 18, Table 1) decreased the yield of the desired product **2a**. It should be noted that an α-amino ketone was the major by-product which was

Table 1. Optimization of the reaction conditions.[a]

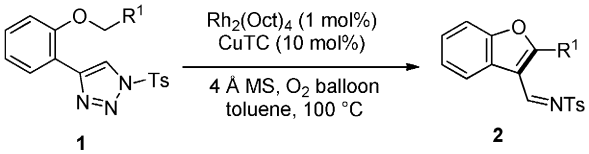


1a 2a

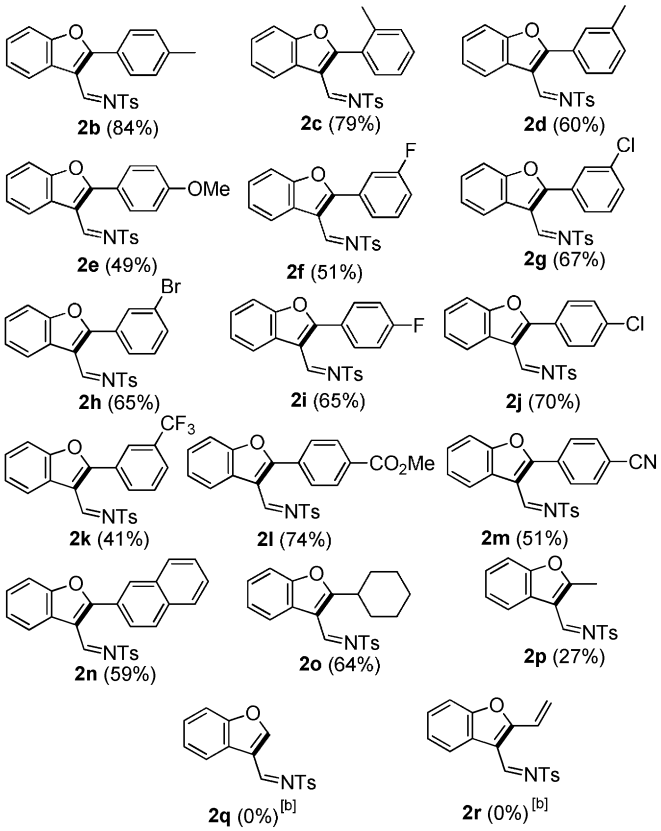
Entry	Rh_2L_4 (1 mol%)	[Cu] (10 mol%)	Solvent	Yield [%][b]
1	$Rh_2(TFA)_4$	CuTC	toluene	14
2	$Rh_2(OAc)_4$	CuTC	toluene	<5
3	$Rh_2(esp)_4$	CuTC	toluene	71
4	$Rh_2(pfb)_4$	CuTC	toluene	N.R.
5	$Rh_2(Oct)_4$	CuTC	toluene	88
6[c]	$Rh_2(Oct)_4$	$CuCl_2$	toluene	67
7[c]	$Rh_2(Oct)_4$	$CuBr_2$	toluene	43
8[c]	$Rh_2(Oct)_4$	–	toluene	11
9[c]	–	CuTC	toluene	N.R.
10[d]	$Rh_2(Oct)_4$	CuTC	toluene	55
11	$Rh_2(Oct)_4$	CuTC	xylene	58
12	$Rh_2(Oct)_4$	CuTC	$PhCF_3$	31
13	$Rh_2(Oct)_4$	CuTC	PhCl	58
14	$Rh_2(Oct)_4$	CuTC	ODCB	59
15[e]	$Rh_2(Oct)_4$	CuTC	$CHCl_3$	43
16[e]	$Rh_2(Oct)_4$	CuTC	DCE	39
17[e]	$Rh_2(Oct)_4$	CuTC	cyclohexane	35
18[f]	$Rh_2(Oct)_4$	CuTC	toluene	61

[a] Triazole **1a** (0.30 mmol, 1.0 equiv.), Rh_2L_n (0.0030 mmol, 0.01 equiv.) and copper catalyst (0.03 mmol, 0.1 equiv.) were combined in solvent (6.0 mL) with under an oxygen balloon at 100 °C for 2 h.
[b] Isolated yields.
[c] 12 h.
[d] Air balloon.
[e] 80 °C.
[f] Concentration of **1a** is 0.15 M.

Table 2. Substrate scope with different R^1 groups.[a]



1 2



[a] Triazole **1** (0.3 mmol, 1.0 equiv.), CuTC (0.03 mmol, 0.1 equiv.), $Rh_2(Oct)_4$ (0.003 mmol, 0.01 equiv.) and 4 Å MS were combined in toluene (6.0 mL) under an oxygen balloon.
[b] Triazoles were consumed, but only a mixture with non-identifiable products could be obtained.

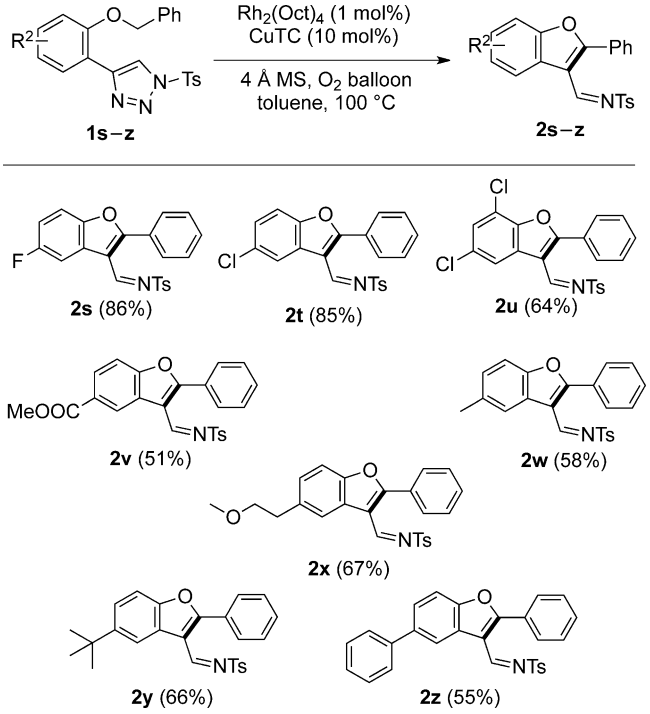
generated from the reaction of **1a** with H_2O[4a] in the absence of 4 Å MS as additive.

With the optimized reaction conditions in hand [1 mol% of $Rh_2(Oct)_4$ and 10 mol% of CuTC as catalysts, 4 Å MS as additive, toluene at 100 °C under an oxygen atmosphere for 2 h], we then investigated the substrate scope of the method (Table 2). We were pleased to see that a wide range of substrates could be tolerated under these reaction conditions to afford the desired benzofuran derivatives in moderate to good yields. Triazoles **1b**, **1c** and **1d** with methyl group on different position of the phenyl ring were converted to the corresponding products **2b**, **2c** and **2d** with 60–84% yields. The intramolecular cascade reaction of the substrate bearing a 4-OMe group on the phenyl moiety went smoothly to afford product **2e** in moderate yield (49%). Likewise, substrates with electron-withdrawing substituents on different positions of the phenyl ring were also converted to the desired products in moderate to good yields (**2f**–**2k**, Table 2). Substrates with sensitive functional groups such as ester and nitrile were also tolerated under the optimal reaction conditions, affording the corresponding products in 74% and 51% yield, respectively (**2l** and **2m**, Table 2). Interestingly, the cascade reaction of the alkyl-substituted substrates also proceed smoothly under these reaction conditions to give the corresponding products **2o** and **2p** in 64% and 27% yield, respectively. However, the desired products **2q** (R^1 = H) and **2r** (R^1 = CH=CH_2) could not be obtained from the corresponding starting triazoles.

In order to demonstrate the generality of this protocol further, reactions of some representative benzyloxytriazole substrates with different substituents (R^2) on the aryl ring were also performed (Table 3). Irrespective of the electronic nature of the substituents on the aryl ring (R^2), all the tested triazoles gave the corresponding benzofuran derivatives with moderate to good yields. It is important to note that substrates with either an ester or an ether group could also be tolerated in our reaction conditions to afford the desired product in moderate yields (**2v** and **2x**, Table 3).

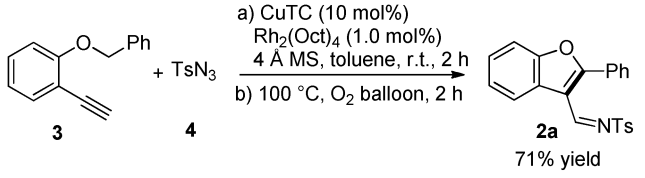
As *N*-sulfonyl-1,2,3-triazoles can be achieved easily from the CuTC-catalyzed azide-alkyne cycloaddition of terminal alkynes with sulfonyl azide, we envisioned that the benzofuran derivatives could be synthesized starting from terminal alkynes in one-pot *via* Cu/Rh/Cu sequential catalysis. For that purpose, we carried out the reaction of terminal alkyne **3** with tosyl azide **4** in the presence of CuTC (10 mol%), $Rh_2(Oct)_4$ (1.0 mol%), 4 Å MS in toluene at room temperature. The terminal alkyne **3** completely was converted to *N*-sulfonyl-1,2,3-triazole **1a** within 2 h. The reaction mixture was then heated to 100 °C and stirred under an oxygen atmosphere for additional 2 h. To our delight, the reaction proceed smoothly to give the desired benzofuran derivative **2a** in 71% yield (Scheme 2), so demonstrating efficiency of the sequential CuAAC/Rh-catalyzed C–H insertion/Cu-catalyzed dehydrogenation cascade reactions.

Table 3. Substrate scope using different R^2 groups.[a]

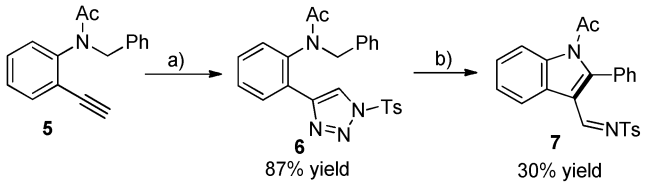


[a] Triazole **1** (0.3 mmol, 1.0 equiv.), CuTC (0.03 mmol, 0.1 equiv.), $Rh_2(Oct)_4$ (0.003 mmol, 0.01 equiv.) and 4 Å MS were combined in toluene (6.0 mL) under an oxygen balloon.

Indole is a ubiquitous heterocyclic motif present in a wide range of natural products and biologically active compounds. In a bid to explore the synthetic utility of our protocol we have demonstrated the synthesis of the 2,3-substituted indole derivative **7** (Scheme 3). The CuTC-catalyzed azide-alkyne cycloaddition (CuAAC) of teminal alkyne **5** and TsN_3 resulted the corresponding triazole **6**, which on treatment with 1 mol% of $Rh_2(Oct)_4$ and 10 mol% of CuTC in the presence of 4 Å MS in toluene at 100 °C under O_2 atmosphere underwent the intramolecular C–H insertion/dehydrogenation cascade reaction to furnish the desired 2,3-substituted indole **7** in 30% yield.



Scheme 2. One-pot synthesis of benzofuran derivative **2a** from terminal alkyne **3** *via* sequential Cu/Rh/Cu catalysis.



a) TsN_3, CuTC, toluene, 2 h, r.t.
b) 1 mol% of $Rh_2(Oct)_4$, 10 mol% of CuTC, 4 Å MS, toluene, 100 °C, O_2, 2 h.

Scheme 3. One-pot synthesis of indole derivative **7** from terminal alkyne **5** *via* sequential Cu/Rh/Cu catalysis.

A plausible mechanism for the Rh-catalyzed C–H insertion/Cu-catalyzed dehydrogenation process is presented in Scheme 4. As reported earlier, an equilibrium is established between the *N*-sulfonyl-1,2,3-triazole **1** and the imino diazo species **I** *via* a reversible ring-chain tautomerization.[13] Imino diazo species **I** then reacts with rhodium(II) with the release of molecular nitrogen to give imino rhodium carbenoid **II** and subsequent intramolecular insertion of the carbenoid into the C(sp^3)–H bond leads to the formation of α-imino dihydrobenzofuran **III**, regenerating the rhodium(II) catalyst. The α-imino dihydrobenzofuran **III** then undergoes imine-enamine tautomerization to the *Z*-selective enamine **IV**, which on CuTC-catalyzed dehydrogenation furnishes the desired product **2**. To support our proposed mechanism, we have isolated the intermediate enamine **IV-2b** from the $Rh_2(Oct)_4$ (1 mol%)-catalyzed reaction of triazole **1b** which on treatment with 10 mol% of CuTC under an oxygen atmosphere in toluene at 100 °C delivered the desired product **2b** in 66% yield.

Conclusions

In conclusion, we have developed a novel cascade approach towards the synthesis of benzofuran derivatives from α-imino rhodium carbenoids generated *in situ* from *N*-sulfonyl-1,2,3-triazoles through a sequential C(sp^3)–H insertion/aerobic oxidation. A one-pot synthesis of benzofuran starting from terminal alkyne has been also realized *via* CuAAC/Rh-catalyzed C–H insertion/Cu-catalyzed dehydrogenation cascade reactions. Furthermore, the reaction protocol has also been explored towards the synthesis of indole derivatives.

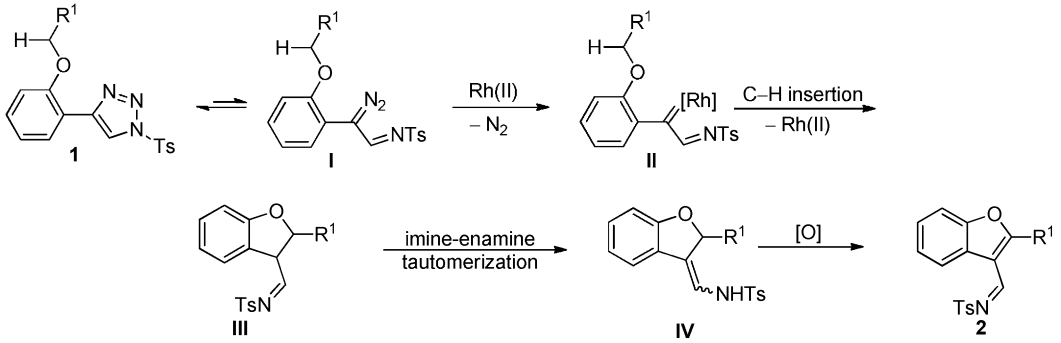
Experimental Section

General Information

All reactions were performed under nitrogen using oven-dried glassware and standard Schlenk techniques. DCM, DCE and $CHCl_3$ were freshly distilled over calcium hydride under nitrogen. Toluene was distilled from sodium under nitrogen and stored under nitrogen. Other solvents were used without further purification. Other substrates were obtained from commercial suppliers and used without further purification. The progress of the reactions was monitored by thin-layer chromatography. Flash column chromatography was carried out using silica gel 300–400 mesh. All other reagents were purchased from TCI, Sigma–Aldrich, Alfa Aesar, Acros, Frontier and Sino compound and used without further purification. Rh(II) acetate (Strem Chemicals), Rh(II) octanoate (Adamas), $Rh_2(esp)_4$ (Aldrich), $Rh_2(TFA)_4$ (Strem Chemicals), and $Rh_2(pfb)_4$ (Aldrich), CuTC (Matrix) were used as received from the commercial sources. $Rh_2(S\text{-}PTTL)_4$,[14] $Rh_2(S\text{-}NTTL)_4$[15] were prepared *via* literature procedures. The ^1H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ using a Bruker AVANCE III spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. Peak multiplicity is indicated as follows: br = broad, s = singlet, d = doublet, t = triplet, m = multiplet. The infrared spectra were recorded on a VERTEX70 infrared spectrometer as KBr pellets with absorption in cm^{-1}. HR-MS were obtained on a Thermo Fisher Scientific LTQ FT Ultra.

Preparation of Triazole Compounds

N-Sulfonyl-1,2,3-triazoles were prepared according to a modified version of the literature procedure.[16] A Schlenk vial was charged with copper(I) thiophene-2-carboxylate (CuTC, 0.011 g, 0.06 mmol, 0.1 equiv. with respect to



Scheme 4. Proposed mechanism for the formation of benzofurans.

alkyne) and toluene (3 mL). Subsequently, the alkyne (0.6 mmol, 1 equiv.) and sulfonyl azide (0.6 mmol, 1 equiv.) were added and the mixture was stirred at room temperature until the reaction was complete (as judged by TLC and LC/MS analysis). The reaction mixture was then diluted with saturated aqueous NH_4Cl solution (5 mL) and extracted into EtOAc (2×5 mL). The combined organics were dried (Na_2SO_4), filtered through celite and concentrated under vacuum. The resulting solid was pulverized in cold cyclohexane and collected by filtration to afford the desired product.

Preparation of Benzofuran and Indole Derivatives

Triazole derivative **1** (0.3 mmol), 4 Å MS (20 mg), CuTC (0.03 mmol, 0.1 equiv.) and $Rh_2(Oct)_4$ (0.003 mmol, 0.01 equiv.) were added to an oven-dried Schlenk tube equipped with a stir bar. The reaction vessel was evacuated and backfilled with O_2 three times before adding freshly distilled toluene (6.0 mL, 0.05 M). The reaction mixture was stirred under an O_2 (balloon) atmosphere at 100 °C (checked by TLC). The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford **2**.

Preparation of Intermediate IV-2b

To a solution of triazole **1b** (0.3 mmol) in toluene at 23 °C was added $Rh_2(Oct)_4$ (0.003 mmol, 0.01 equiv.) under an N_2 atmosphere. The resulting mixture was stirring at 90 °C for 3 h before it was quenched with NH_4Cl (2 mL, saturated aqueous solution). The layers were separated and the aqueous layer was extracted with EtOAc (3×5 mL). The combined organic layers were washed with brine (10 mL), dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford **IV-2b**.

4-Methyl-*N*-[(2-phenylbenzofuran-3-yl)methylene]benzenesulfonamide (2a): white solid; yield: 99 mg (0.264 mmol, 88%); mp 165–167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.39 (s, 1H), 8.32 (d, J = 7.5 Hz, 1H), 7.98 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 9.1 Hz, 2H), 7.62–7.57 (m, 4H), 7.43–7.36 (m, 4H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.48, 163.52, 154.50, 144.28, 135.92, 131.48, 129.78, 129.41, 129.14, 128.27, 127.88, 126.45, 125.19, 124.92, 123.66, 113.22, 111.22, 21.63; IR (KBr plate): ν_{max} = 1594, 1569, 1317, 1306, 1154, 1088, 783, 738, 669, 543 cm^{-1}; HR-MS (MALDI-DHB): m/z = 376.0994, calcd. for $C_{22}H_{18}NO_3S$ $(M+H)^+$: 376.1002.

4-Methyl-*N*-{[2-(*p*-tolyl)benzofuran-3-yl]methylene}benzenesulfonamide (2b): white solid; yield: 98 mg (0.252 mmol, 83%); mp 158–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.36 (s, 1H), 8.29–8.26 (m, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 7.7 Hz, 1H), 7.41–7.32 (m, 6H), 2.48 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.96, 163.68, 154.40, 144.20, 142.25, 136.04, 130.16, 129.76, 129.07, 127.84, 126.27, 125.45, 125.27, 124.84, 123.59, 112.80, 111.15, 21.65; IR (KBr plate): ν_{max} = 3032, 2921, 1581, 1565, 1480, 1452, 1410, 1353, 1318, 1289, 1255, 1198, 1184, 1156, 1198, 1184, 1156, 1110, 1088, 1077, 1017, 916, 848, 818, 794, 777, 749, 670, 645, 610, 551 cm^{-1}; HR-MS (MALDI-DHB): m/z = 390.1149, calcd. for $C_{23}H_{20}NO_3S$ $(M+H)^+$: 390.1158.

4-Methyl-*N*-{[2-(*o*-tolyl)benzofuran-3-yl]methylene}benzenesulfonamide (2c): white solid; yield: 92 mg (0.237 mmol, 79%); mp 117–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (s, 1H), 8.29 (d, J = 7.1 Hz, 1H), 7.90 (d, J = 7.5 Hz, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.37–7.24 (m, 7H), 2.43 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.65, 153.71, 143.22, 137.44, 134.88, 130.59, 130.37, 130.32, 128.72, 126.81, 126.15, 125.28, 125.23, 123.83, 123.43, 122.39, 113.68, 110.25, 20.61, 19.36; IR (KBr plate): ν_{max} = 3059, 2923, 1717, 1699, 1684, 1653, 1585, 1541, 1508, 1448, 1321, 1259, 1202, 1159, 1089, 1075, 1019, 919, 849, 804, 774, 763, 748, 669, 626, 548 cm^{-1}; HR-MS (MALDI-DHB): m/z = 390.1150, calcd. $C_{23}H_{20}NO_3S$ $(M+H)^+$: 390.1158.

4-Methyl-*N*-{[2-(*m*-tolyl)benzofuran-3-yl]methylene}benzenesulfonamide (2d)): white solid; yield: 70 mg (0.18 mmol, 60%); mp 146–149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.34 (s, 1H), 8.29 (d, J = 7.3 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.60–7.54 (m, 3H), 7.47 (t, J = 7.6 Hz, 1H), 7.42–7.32 (m, 5H), 2.48 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.84, 163.64, 154.45, 144.26, 139.34, 135.89, 132.35, 129.79, 129.58, 129.31, 128.18, 127.89, 126.46, 126.38, 125.21, 124.88, 123.65, 113.13, 111.19, 21.66, 21.51; IR (KBr plate): ν_{max} = 2921, 1595, 1578, 1447, 1397, 1359, 1330, 1259, 1213, 1183, 1159, 1111, 1082, 1015, 936, 874, 827, 800, 775, 764, 710, 688, 676, 666, 626, 593, 567, 546 cm^{-1}; HR-MS (MALDI-DHB): m/z = 390.1149, calcd. $C_{23}H_{20}NO_3S$ $(M+H)^+$: 390.1158.

***N*-{[2-(4-Methoxyphenyl)benzofuran-3-yl]methylene}-4-methylbenzenesulfonamide (2e):** white solid; yield: 60 mg (0.147 mmol, 49%); mp 181–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.35 (s, 1H), 8.26 (d, J = 7.2 Hz, 1H), 7.92 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 7.8 Hz, 1H), 7.41–7.30 (m, 4H), 7.09 (d, J = 8.6 Hz, 2H), 3.92 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.89, 163.64, 162.38, 154.27, 144.14, 136.15, 130.79, 129.75, 127.80, 126.12, 125.37, 124.80, 123.49, 120.67, 115.00, 112.20, 111.05, 55.61, 21.65; IR (KBr plate): ν_{max} = 3288, 3059, 2871, 2097, 1623, 1589, 1558, 1507, 1472, 1451, 1434, 1333, 1274, 1252, 1217, 1147, 1082, 1073, 1040, 1018, 802, 750, 731, 698, 671, 610 cm^{-1}; HR-MS (MALDI-DHB): m/z = 406.1098, calcd. $C_{23}H_{20}NO_4S$ $(M+H)^+$: 406.1108.

***N*-{[2-(3-Fluorophenyl)benzofuran-3-yl]methylene}-4-methylbenzenesulfonamide (2f):** white solid; yield: 61 mg (0.153 mmol, 51%); mp 156–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.32 (s, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 8.0 Hz, 2H), 7.59–7.51 (m, 3H), 7.48 (d, J = 9.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.38–7.32 (m, 3H), 7.28 (d, J = 8.5 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.34, 164.32, 164.19, 162.85, 161.71, 154.47, 144.52, 135.53, 131.27, 131.19, 130.18, 130.10, 129.87, 127.97, 126.81, 125.10, 125.02, 124.99, 124.96, 123.75, 118.59, 118.38, 115.92, 115.69, 113.74, 111.31, 21.67; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −110.36; IR (KBr plate): ν_{max} = 2921, 1595, 1572, 1479, 1454, 1359, 1321, 1303, 1292, 1221, 1188, 1155, 1109, 1087, 1016, 944, 884, 826, 777, 748, 706, 671, 628, 566, 545 cm^{-1}; HR-MS (MALDI-DHB): m/z = 394.0899, calcd. $C_{22}H_{17}FNO_3S$ $(M+H)^+$: 394.0908.

***N*-{[2-(3-Chlorophenyl)benzofuran-3-yl]methylene}-4-methylbenzenesulfonamide (2g):** light green solid; yield: 83 mg (0.201 mmol, 67%); mp 145–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.29 (s, 1H), 8.28 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 8.2 Hz, 2H), 7.76 (s, 1H), 7.63 (d, J = 7.2 Hz,

1H), 7.56–7.48 (m, 3H), 7.42 (td, $J=7.9$, 1.2 Hz, 1H), 7.38–7.33 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=164.19$, 162.73, 154.51, 144.52, 135.54, 135.47, 131.41, 130.69, 129.89, 128.75, 127.99, 127.27, 126.83, 125.11, 125.00, 123.74, 113.82, 111.32, 21.69; IR (KBr plate): $\nu_{max}=2921$, 1595, 1580, 1564, 1481, 1454, 1412, 1356, 1319, 1301, 1289, 1200, 1152, 1120, 1076, 1017, 933, 889, 865, 803, 788, 780, 758, 770, 742, 704, 668, 626, 602, 567, 544 cm^{-1}; HR-MS (MALDI-DHB): $m/z=410.0602$, calcd. $C_{22}H_{17}ClNO_3S$ $(M+H)^+$: 410.0612.

***N*-{[2-(3-Bromophenyl)benzofuran-3-yl]methylene}-4-methylbenzenesulfonamide (2h):** white solid; yield: 89 mg (0.195 mmol, 65%); mp 160–163 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.29$ (s, 1H), 8.27 (d, $J=7.5$ Hz, 1H), 7.93 (d, $J=7.9$ Hz, 3H), 7.67 (t, $J=9.2$ Hz, 2H), 7.54 (d, $J=8.1$ Hz, 1H), 7.42 (ddd, $J=10.7$, 9.6, 4.7 Hz, 2H), 7.36 (dd, $J=7.3$, 3.9 Hz, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 164.05, 162.71, 154.50, 144.52, 135.46, 134.32, 131.61, 130.88, 130.10, 129.90, 128.00, 127.72, 126.85, 125.12, 124.98, 123.74, 123.48, 113.83, 111.32, 21.70; IR (KBr plate): $\nu_{max}=2974$, 1598, 1584, 1559, 1541, 1446, 1359, 1329, 1195, 1159, 1080, 1049, 924, 856, 798, 785, 763, 670, 624, 565, 546 cm^{-1}; HR-MS (MALDI-DHB): $m/z=454.0104$, calcd. $C_{22}H_{17}BrNO_3S$ $(M+H)^+$: 454.0107.

***N*-{[2-(4-Fluorophenyl)benzofuran-3-yl]methylene}-4-methylbenzenesulfonamide (2i):** white solid; yield: 77 mg (0.195 mmol, 65%); mp 197–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.32$ (s, 1H), 8.28 (d, $J=7.8$ Hz, 1H), 7.92 (d, $J=8.2$ Hz, 2H), 7.80 (dd, $J=8.7$, 5.2 Hz, 2H), 7.55 (d, $J=$ 8.0 Hz, 1H), 7.41 (td, $J=7.2$, 1.2 Hz, 1H), 7.39–7.33 (m, 3H), 7.29 (t, $J=8.5$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=165.91$, 165.26, 163.38, 163.09, 154.40, 144.39, 135.80, 131.29, 131.20, 129.82, 127.89, 126.55, 125.10, 125.02, 124.55, 124.52, 123.63, 116.94, 116.72, 113.11, 111.21, 21.66; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta=-106.86$; IR (KBr plate): $\nu_{max}=1596$, 1578, 1499, 1481, 1452, 1412, 1351, 1322, 1306, 1233, 1197, 1159, 1092, 1077, 1014, 917, 853, 836, 809, 779, 747, 706, 693, 671, 641, 608, 595, 551, 534 cm^{-1}; HR-MS (MALDI-DHB): $m/z=394.0900$, calcd. $C_{22}H_{17}FNO_3S$ $(M+H)^+$: 394.0908.

***N*-{[2-(4-Chlorophenyl)benzofuran-3-yl]methylene}-4-methylbenzenesulfonamide (2j):** white solid; yield: 86 mg (0.21 mmol, 70%); mp 186–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.32$ (s, 1H), 8.28 (d, $J=7.5$ Hz, 1H), 7.92 (d, $J=8.3$ Hz, 2H), 7.73 (d, $J=8.6$ Hz, 2H), 7.59–7.53 (m, 3H), 7.42 (td, $J=7.4$, 1.4 Hz, 1H), 7.39–7.33 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=164.90$, 162.92, 154.48, 144.42, 137.98, 135.72, 130.22, 129.82, 129.81, 127.91, 126.68, 125.09, 125.06, 123.70, 113.48, 111.25, 21.67; IR (KBr plate): $\nu_{max}=2822$, 1583, 1479, 1450, 1406, 1354, 1324, 1303, 1291, 1196, 1157, 1092, 1075, 1013, 915, 847, 816, 782, 746, 727, 706, 689, 670, 636, 620, 583, 545 cm^{-1}; HR-MS (MALDI-DHB): $m/z=410.0605$, calcd. $C_{22}H_{17}ClNO_3S$ $(M+H)^+$: 410.0612.

Methyl 4-{3-[(tosylimino)methyl]benzofuran-2-yl}benzoate (2k): white solid; yield: 96 mg (0.222 mmol, 74%); mp 227–230 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.38$ (s, 1H), 8.32 (d, $J=7.7$ Hz, 1H), 8.26 (d, $J=8.2$ Hz, 2H), 7.95 (d, $J=$ 8.1 Hz, 2H), 7.89 (d, $J=8.2$ Hz, 2H), 7.59 (d, $J=8.1$ Hz, 1H), 7.46 (t, $J=7.5$ Hz, 1H), 7.41 (d, $J=7.9$ Hz, 1H), 7.38 (d, $J=11.4$, 8.1 Hz, 2H), 4.02 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=166.07$, 164.45, 162.87, 154.64, 144.51, 135.51, 132.40, 132.16, 130.46, 129.85, 128.95, 127.97, 126.93, 125.14, 125.04, 123.82, 114.23, 111.34, 52.59, 21.68; IR (KBr plate): $\nu_{max}=2947$, 1720, 1578, 1565, 1452, 1435, 1411, 1357, 1319, 1279, 1203, 1185, 1158, 1116, 1105, 1088, 1078, 1016, 916, 861, 815, 784, 776, 743, 702, 685, 667, 642, 622, 578, 545 cm^{-1}; HR-MS (MALDI-DHB): $m/z=$ 434.1046, calcd. $C_{24}H_{20}NO_5S$ $(M+H)^+$: 434.1057.

***N*-{[2-(4-Cyanophenyl)benzofuran-3-yl]methylene}-4-methylbenzenesulfonamide (2l):** white solid; yield: 61 mg (0.153 mmol, 51%); mp 219–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.36$ (s, 1H), 8.30 (d, $J=7.6$ Hz, 1H), 7.95–7.85 (m, 6H), 7.58 (d, $J=8.1$ Hz, 1H), 7.46 (t, $J=7.5$ Hz, 1H), 7.42–7.34 (m, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=162.73$, 162.22, 154.73, 144.69, 135.38, 133.04, 132.35, 129.90, 129.40, 127.99, 127.32, 125.36, 124.95, 123.92, 117.86, 114.78, 114.73, 111.43, 21.69; IR (KBr plate): $\nu_{max}=$ 2921, 2859, 1733, 1717, 1699, 1684, 1653, 1594, 1558, 1541, 1507, 1456, 1396, 1324, 1285, 1252, 1196, 1176, 1185, 1149, 1095, 1028, 993, 815, 798, 742, 700, 671, 594, 538 cm^{-1}; HR-MS (MALDI-DHB): $m/z=401.0947$, calcd. $C_{23}H_{17}N_2O_3S$ $(M+H)^+$: 401.0954.

4-Methyl-*N*-({2-[3-(trifluoromethyl)phenyl]benzofuran-3-yl}methylene)benzenesulfonamide (2m): white solid; yield: 55 mg (0.123 mmol, 41%); mp 148–150 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.31$ (s, 1H), 8.31 (dd, $J=7.6$, 0.8 Hz, 1H), 8.07 (s, 1H), 7.95 (d, $J=8.6$ Hz, 1H), 7.92 (d, $J=$ 8.4 Hz, 2H), 7.85 (d, $J=7.9$ Hz, 1H), 7.74 (t, $J=7.8$ Hz, 1H), 7.59 (d, $J=8.1$ Hz, 1H), 7.45 (td, $J=7.3$, 1.4 Hz, 1H), 7.41–7.34 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=163.85$, 162.52, 154.61, 144.58, 135.38, 132.23, 131.92, 130.08, 129.88, 129.14, 128.00, 127.85, 127.82, 126.98, 125.73, 125.69, 125.21, 124.98, 124.86, 123.79, 114.07, 111.37, 21.67; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta=-62.88$; IR (KBr plate): $\nu_{max}=1598$, 1583, 1481, 1454, 1426, 1328, 1304, 1199, 1158, 1122, 1091, 1075, 928, 960, 797, 771, 762, 700, 672, 640, 619, 565, 543 cm^{-1}; HR-MS (MALDI-DHB): $m/z=$ 444.0866, calcd. $C_{23}H_{17}F_3NO_3S$ $(M+H)^+$: 444.0876.

4-Methyl-*N*-{[2-(naphthalen-2-yl)benzofuran-3-yl]methylene}benzenesulfonamide (2n): white solid; yield: 75 mg (0.177 mmol, 59%); mp 170–174 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.44$ (s, 1H), 8.33 (d, $J=7.4$ Hz, 1H), 8.27 (s, 1H), 8.04 (d, $J=8.6$ Hz, 1H), 8.02–7.97 (m, 1H), 7.97–7.91 (m, 3H), 7.87 (dd, $J=10.2$, 1.7 Hz, 1H), 7.67–7.61 (m, 2H), 7.59 (d, $J=8.2$ Hz, 1H), 7.43 (td, $J=7.4$, 1.3 Hz, 1H), 7.40–7.32 (m, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=166.44$, 163.58, 154.59, 144.34, 135.77, 134.37, 132.96, 129.94, 129.83, 129.37, 129.02, 128.30, 127.96, 127.37, 126.52, 125.50, 125.29, 124.97, 124.93, 123.69, 113.43, 111.24, 21.66; IR (KBr plate): $\nu_{max}=2974$, 1595, 1566, 1451, 1362, 1313, 1287, 1187, 1152, 1088, 1071, 953, 916, 877, 858, 818, 760, 749, 705, 669, 648, 620, 606, 551, 470 cm^{-1}; HR-MS (MALDI-DHB): $m/z=426.1150$, calcd. $C_{26}H_{20}NO_3S$ $(M+H)^+$: 426.1158.

***N*-[(2-Cyclohexylbenzofuran-3-yl)methylene]-4-methylbenzenesulfonamide (2o):** white solid; yield: 73 mg (0.192 mmol, 64%); mp 180–183 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=9.28$ (s, 1H), 8.15 (d, $J=7.1$ Hz, 1H), 7.93 (d, $J=8.0$ Hz, 2H), 7.45 (d, $J=7.6$ Hz, 1H), 7.37–7.27 (m, 4H), 3.22 (t, $J=11.8$ Hz, 1H), 2.43 (s, 3H), 2.05–1.74 (m, 7H), 1.52–1.23 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=175.81$, 161.54, 154.32, 144.16, 136.20, 129.73, 127.72, 125.56, 124.57, 124.42, 123.02, 111.86, 110.98, 37.02, 31.41, 25.86, 25.51,

21.66; IR (KBr plate): ν_{max} = 2930, 2854, 1583, 1481, 1451, 1355, 1317, 1286, 1188, 1154, 1088, 1015, 957, 888, 848, 822, 809, 785, 752, 725, 667, 626, 595, 555, 534 cm^{-1}; HR-MS (MALDI-DHB): m/z = 382.1465, calcd. $C_{22}H_{24}NO_3S$ $(M+H)^+$: 382.1471.

4-Methyl-*N*-[(2-methylbenzofuran-3-yl)methylene]benzenesulfonamide (2p): white solid; yield: 26 mg (0.081 mmol, 27%); mp 150–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (s, 1H), 8.12 (d, J = 6.3 Hz, 1H), 7.92 (d, J = 7.8 Hz, 2H), 7.44 (d, J = 7.0 Hz, 1H), 7.37–7.26 (m, 4H), 2.74 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.12, 161.84, 154.41, 144.22, 136.05, 129.75, 127.79, 125.64, 124.65, 124.47, 122.63, 113.76, 110.88, 21.65, 13.36; IR (KBr plate): ν_{max} = 2924, 1597, 1559, 1481, 1453, 1381, 1355, 1315, 1291, 1256, 1196, 1154, 1089, 1025, 945, 847, 815, 804, 788, 757, 671, 646, 609, 571, 551, 537 cm^{-1}; HR-MS (MALDI-DHB): m/z = 314.0841, calcd. $C_{17}H_{16}NO_3S$ $(M+H)^+$: 314.0845.

***N*-[(5-Fluoro-2-phenylbenzofuran-3-yl)methylene]-4-methylbenzenesulfonamide (2s):** light green solid; yield: 102 mg (0.258 mmol, 86%); mp 217–221 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.35 (s, 1H), 7.97–7.90 (m, 3H), 7.80–7.75 (m, 2H), 7.63–7.56 (m, 3H), 7.49 (dd, J = 8.9, 4.0 Hz, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.12 (td, J = 9.0, 2.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 167.68, 163.10, 161.46, 159.06, 150.62, 144.47, 135.67, 131.74, 129.86, 129.50, 129.10, 127.99, 127.91, 126.33, 126.21, 114.33, 114.07, 113.22, 113.18, 112.14, 112.05, 109.72, 109.45, 21.68; ^{19}F NMR (376 MHz, $CDCl_3$): δ = −117.20; IR (KBr plate): ν_{max} = 3067, 2922, 1597, 1568, 1471, 1457, 1445, 1391, 1359, 1319, 1303, 1290, 1266, 1216, 1155, 1136, 1113, 1088, 1064, 955, 874, 814, 781, 770, 742, 681, 663, 632, 613, 593, 554 cm^{-1}; HR-MS (MALDI-DHB): m/z = 394.0900, calcd. $C_{22}H_{17}FNO_3S$ $(M+H)^+$: 394.0908.

***N*-[(5-Chloro-2-phenylbenzofuran-3-yl)methylene]-4-methylbenzenesulfonamide (2t):** white solid; yield: 105 mg (0.255 mmol, 85%); mp >230 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.34 (s, 1H), 8.26 (d, J = 1.8 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.81- 7.75 (m, 2H), 7.63–7.55 (m, 3H), 7.48 (d, J = 8.7 Hz, 1H), 7.39–7.33 (m, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.34, 163.11, 152.81, 144.53, 135.53, 131.82, 130.65, 129.89, 129.75, 129.52, 129.14, 127.96, 127.85, 126.74, 126.55, 126.50, 123.29, 112.65, 112.28, 21.70; IR (KBr plate): ν_{max} = 2974, 1699, 1684, 1653, 1635, 1589, 1561, 1541, 1522, 1507, 1453, 1438, 1359, 1319, 1304, 1289, 1259, 1198, 1153, 1121, 1085, 1054, 929, 859, 812, 778, 698, 679, 655, 627, 611, 551 , cm^{-1}; HR-MS (MALDI-DHB): m/z = 410.0603, calcd. $C_{22}H_{17}ClNO_3S$ $(M+H)^+$: 410.0612.

***N*-[(5,7-Dichloro-2-phenylbenzofuran-3-yl)methylene]-4-methylbenzenesulfonamide (2u):** white solid; yield: 85 mg (0.192 mmol, 64%); mp 199–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (s, 1H), 8.16 (d, J = 1.8 Hz, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.83- 7.78 (m, 2H), 7.66–7.58 (m, 3H), 7.41–7.35 (m, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.47, 162.75, 148.96, 144.73, 135.25, 132.16, 130.92, 129.95, 129.61, 129.26, 128.03, 127.60, 127.36, 126.59, 121.83, 117.45, 112.91, 21.72; IR (KBr plate): ν_{max} = 3032, 2921, 1581, 1565, 1480, 1452, 1410, 1353, 1318, 1289, 1255, 1198, 1184, 1156, 1110, 1088, 1077, 1017, 916, 848, 819, 794, 777, 749, 670, 645, 610, 598, 551 cm^{-1}; HR-MS (MALDI-DHB): m/z = 444.0214, calcd. $C_{22}H_{16}Cl_2NO_3S$ $(M+H)^+$: 444.0222.

Methyl 2-phenyl-3-[(tosylimino)methyl]benzofuran-5-carboxylate (2v): white solid; yield: 66 mg (0.153 mmol, 51%); mp 201–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.37 (s, 1H), 8.95 (d, J = 0.7 Hz, 1H), 8.14 (dd, J = 8.6, 1.4 Hz, 1H), 7.96 (d, J = 8.1 Hz, 2H), 7.80 (dd, J = 7.8, 2.3 Hz, 2H), 7.67–7.57 (m, 4H), 7.37 (d, J = 7.9 Hz, 2H), 3.97 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.33, 166.78, 162.98, 156.82, 144.49, 135.56, 131.84, 129.85, 129.52, 129.18, 128.24, 127.99, 127.80, 127.24, 125.82, 125.35, 113.23, 111.23, 52.35, 21.69; IR (KBr plate): ν_{max} = 3028, 2950, 1726, 1715, 1587, 1574, 1448, 1391, 1321, 1288, 1246, 1184, 1158, 1086, 1064, 985, 926, 865, 812, 768, 744, 681, 647, 624, 612, 584, 550 cm^{-1}; HR-MS (MALDI-DHB): m/z = 434.1046, calcd. $C_{24}H_{20}NO_5S$ $(M+H)^+$: 434.1057.

4-Methyl-*N*-[(5-methyl-2-phenylbenzofuran-3-yl)methylene]benzenesulfonamide (2w): light green solid; yield: 68 mg (0.174 mmol, 58%); mp 187–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (s, 1H), 8.08 (s, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.77 (dd, J = 6.3, 2.8 Hz, 2H), 7.61–7.54 (m, 3H), 7.43 (d, J = 8.4 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.4 Hz, 1H), 2.46 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.76, 163.85, 152.97, 144.26, 135.86, 134.77, 131.39, 129.80, 129.39, 129.12, 128.38, 127.90, 127.67, 125.13, 123.41, 113.03, 110.72, 21.67, 21.52; IR (KBr plate): ν_{max} = 2920, 1653, 1563, 1472, 1444, 1358, 1321, 1303, 1288, 1198, 1153, 1088, 1072, 945, 867, 843, 809, 781, 681, 663, 629, 613, 595, 552 cm^{-1}; HR-MS (MALDI-DHB): m/z = 390.1153, calcd. $C_{23}H_{20}NO_3S$ $(M+H)^+$: 390.1158.

***N*-{[5-(2-Methoxyethyl)-2-phenylbenzofuran-3-yl]methylene}-4-methylbenzenesulfonamide (2x):** white solid; yield: 87 mg (0.201 mmol, 67%); mp 106–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (s, 1H), 8.12 (s, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.80- 7.73 (m, 2H), 7.63–7.56 (m, 3H), 7.47 (d, J = 8.3 Hz, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.30–7.26 (m, 1H), 3.64 (t, J = 6.5 Hz, 2H), 3.36 (s, 3H), 3.00 (t, J = 6.3 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.82, 163.72, 153.39, 144.27, 135.99, 135.86, 131.44, 129.78, 129.40, 129.13, 128.32, 127.90, 127.51, 125.28, 123.37, 113.09, 110.96, 73.78, 58.70, 36.11, 21.66; IR (KBr plate): ν_{max} = 3073, 2937, 2867, 1585, 1471, 1449, 1386, 1353, 1326, 1290, 1197, 1181, 1156, 1107, 1087, 1071, 976, 866, 813, 775, 704, 679, 666, 629, 614, 597, 559, 546 cm^{-1}; HR-MS (MALDI-DHB): m/z = 434.1411, calcd. $C_{25}H_{24}NO_4S$ $(M+H)^+$: 434.1421.

***N*-{[5-(*tert*-Butyl)-2-phenylbenzofuran-3-yl]methylene}-4-methylbenzenesulfonamide (2y):** yellow solid; yield: 85 mg (0.198 mmol, 66%); mp 130–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (s, 1H), 8.31 (s, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.77 (dd, J = 6.5, 3.0 Hz, 2H), 7.60–7.55 (m, 3H), 7.47 (s, 2H), 7.34 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.66, 163.36, 152.78, 148.25, 144.21, 136.14, 131.36, 129.71, 129.39, 129.07, 128.43, 127.79, 124.95, 124.36, 119.73, 113.38, 110.56, 34.98, 31.72, 21.65; IR (KBr plate): ν_{max} = 2957, 2867, 1583, 1570, 1477, 1393, 1320, 1261, 1205, 1184, 1154, 1089, 1065, 1019, 974, 941, 894, 866, 813, 772, 700, 682, 656, 625, 593, 552 cm^{-1}; HR-MS (MALDI-DHB): m/z = 432.1619, calcd. $C_{26}H_{26}NO_3S$ $(M+H)^+$: 432.1628.

***N*-[(2,5-Diphenylbenzofuran-3-yl)methylene]-4-methylbenzenesulfonamide (2z):** white solid; yield: 75 mg (0.165 mmol, 55%); mp 155–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.38 (s, 1H), 8.48 (s, 1H), 7.92 (d, J = 8.2 Hz, 2H), 7.80 (dd, J = 6.5, 3.0 Hz, 2H), 7.66–7.57 (m, 7H), 7.48

(t, $J=7.5$ Hz, 2H), 7.38 (t, $J=7.3$ Hz, 1H), 7.33 (d, $J=8.1$ Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 167.03, 163.56, 154.09, 144.33, 141.05, 138.64, 135.81, 131.57, 129.81, 129.46, 129.16, 128.86, 128.22, 127.89, 127.61, 127.31, 126.07, 125.76, 121.99, 113.32, 111.41, 21.67; IR (KBr plate): $\nu_{max}=$3058, 1652, 1584, 1568, 1541, 1457, 1346, 1327, 1205, 1161, 1153, 1091, 1078, 922, 888, 855, 817, 780, 768, 750, 726, 695, 665, 638, 576, 550 cm^{-1}; HR-MS (MALDI-DHB): $m/z=$ 452.1304, calcd. $C_{28}H_{22}NO_3S$ $(M+H)^+$: 452.1315.

***N*-[(1-Acetyl-2-phenyl-1*H*-indol-3-yl)methylene]-4-methylbenzenesulfonamide (7):** white solid; yield: 37 mg (0.09 mmol, 30%); mp 191–197 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.78$ (s, 1H), 8.43 (d, $J=7.5$ Hz, 1H), 8.24 (s, $J=8.1$ Hz, 1H), 7.85 (d, $J=8.0$ Hz, 2H), 7.65–7.55 (m, 3H), 7.50–7.36 (m, 4H), 7.33–7.27 (m, 2H), 2.41 (s, 3H), 2.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=171.09$, 164.26, 150.00, 144.10, 136.91, 135.98, 130.93, 130.38, 129.71, 129.62, 129.43, 127.77, 126.83, 125.44, 125.31, 122.80, 116.27, 115.43, 27.73, 21.64; HR-MS (MALDI-DHB): $m/z=$417.1259, calcd. $C_{24}H_{21}N_2O_3S$ $(M+H)^+$: 417.1267.

(*Z*)-4-Methyl-*N*-{[2-(*p*-tolyl)benzofuran-3(2*H*)-ylidene]-methyl}benzenesulfonamide (IV-2b): ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.84$ (s, 2H), 7.46–7.40 (m, 3H), 7.31 (d, $J=8.0$ Hz, 2H), 7.19 (d, $J=7.9$ Hz, 2H), 7.14 (t, $J=7.4$ Hz, 1H), 6.97–6.91 (m, 2H), 6.87 (d, $J=10.0$ Hz, 1H), 6.62 (d, $J=8.0$ Hz, 1H), 5.26 (d, $J=10.6$ Hz, 1H), 2.46 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=158.95$, 143.68, 138.43, 132.43, 131.62, 130.21, 129.57, 129.49, 129.34, 127.49, 125.45, 123.65, 121.59, 119.90, 110.62, 87.05, 21.64, 21.38; IR (KBr plate): $\nu_{max}=$2920, 1716, 1699, 1683, 1653, 1636, 1558, 1541, 1521, 1508, 1473, 1457, 1437, 1340, 1319, 1202, 1158, 1086, 911, 812, 743, 697, 672, 606, 555 cm^{-1}; HR-MS (DART positive): $m/z=$392.1309, calcd. $C_{23}H_{22}NO_3S$ $(M+H)^+$: 392.1315.

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