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Iridium-catalyzed *ortho*-selective carbon–hydrogen amidation of benzamides with sulfonyl azides in ionic liquid†

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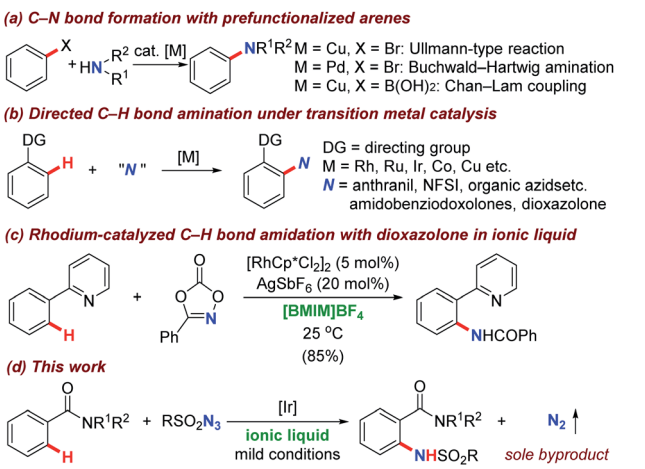
An efficient and convenient iridium(III) catalyzed *ortho*-C–H bond amidation of weakly coordinating benzamides treated with readily available sulfonyl azides as the amino source has been described. In this transformation, ionic liquids represents an ideal reaction medium, giving rise to a broad range of amidation products under mild conditions in the open air. This protocol offers moderate to excellent chemical yields, exclusive regioselectivities, and good functional group tolerance.

Introduction

Molecules containing nitrogen atoms are of great importance in the areas of natural products, materials science, biologically active compounds, and medicines.[1] Among the current available strategies, Ullmann-type coupling reaction,[2] Buchwald–Hartwig amination,[3] and Chan–Lam coupling[4] have been extensively investigated in the last decades towards the desired carbon–nitrogen bond formation and generally exhibited high transformation efficiency (Scheme 1a). However, these methodologies relied heavily on the prefunctionalized haloarenes, which would generate stoichiometric amounts of hydrogen halides and the corresponding salts as byproducts.

Recently, the investigation of synthetic methodologies that accommodate selective functionalization of omnipresent carbon–hydrogen bonds to useful amine/amide functional groups under transition metal catalysis have been recognized as the most straightforward and powerful alternatives.[5] Given the numerous reports concerning this topic, several different transition metals have been introduced to accomplish this target. Meanwhile, different nitrogen sources including anthranils, 1,4,2-dioxazol-5-ones, amidobenziodoxolones, *N*-fluorobenzenesulfonimide (NFSI), organic azides, and nitrosoarenes were successfully employed based on two distinct mechanisms (Scheme 1b).[5–12] Particularly, the Chang group disclosed a significant breakthrough for the direct C(sp^2)–H bond amidation *via* rhodium mediated nitrene insertion pathway deriving from sulfonyl azides in 2012,[6] which represented a green process without the addition of external oxidants and released nitrogen gas as the sole byproduct. Consequently, many groups including Li,[7] Sahoo,[8] Jiao (N.),[9] Ackermann,[10] Glorius,[11] and Kanai[12] *etc.* continuously disclosed directed amidation methodologies and organic azides have been widely used as nitrogen source almost overnight.[13] From then on, research efforts in this area have been devoted to the development of a number of amidation systems based on different combinations of transition metals (rhodium, ruthenium,



Scheme 1 Strategies for the C–N bond formation under transition metal catalysis.

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iridium, cobalt, copper, as well as iron, *et al.*) and organic azides (sulfonyl-, aryl-, benzyl-, and alkyl-azides *etc.*). Notably, almost all of these transformations are conducted in organic solvents, in which the halogenated solvents such as 1,2-dichloroethane (DCE) and 1,2-dichlorobenzene (*o*-DCB) are most commonly choices.[5–13] As far as we know, there are only limited reports focusing on C–N formation in environmental benign solvents.[14]

In the organic reactions, solvent consumption represented a major issue to lead to organic pollution. In order to encounter this problem, much efforts has been devoted to the environmental credentials of the reaction medium itself. As a consequence, a range of reaction mediums with greener character and more sustainable nature have been developed and evaluated over the past years.[15] Ionic liquids, which are salts with room temperature or closed melting points and extremely high enthalpies of vaporization, have shown great potential with extraordinary properties through different cation/anion combinations compared with conventional organic solvents.[15] The cations are normally dependent on the chain length while the counter anions are generally attributed to the enhancement of their water and air stabilities.[16] Moreover, ionic liquids were introduced as reaction medium with great advantages including the lack of vapor pressure, non-volatility, non-flammability, and thermal stability over a wide temperature range. During the last years, ionic liquids have been successfully subjected into the C–H bond functionalization, which opened a new era to make this attractive strategy proceeding in an environmental benign fashion. Very recently, Wang and Wu developed a rhodium(III)-catalyzed C–H bond amidation with dioxazolones as amidating reagent (Scheme 1c).[14b] In this reaction, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) was employed as a green and recyclable reaction media, providing desired amidated product smoothly. This novel strategy, together with the pioneering works concerning sulfonyl azides as amidation precursors[6–13] inspired us to examine the catalytic activity of transition metal for the directing group assisted C–H bond amidation process with organic azides in non-traditional solvent. Based on our previous experience on the transition metal catalyzed C–H bond functionalization,[17] we were hopeful to take advantage of the aforementioned features in our protocol, thereby establishing an environmentally friendly approach that can be applied to a wide range of substrates in the absence of external oxidants to generate nitrogen gas as byproduct (Scheme 1d). We envisioned that ionic liquid could be an effective reaction medium to meet the requirements.

Results and discussion

To examine our hypothesis, we initiated the reaction between *N*-*tert*butylbenzamide (**1a**) and tosyl azide (**2a**) as nitrogen source to identify of the reaction conditions. In this catalytic setup, $[IrCp^*Cl_2]_2$, $AgSbF_6$, and [BMIM]BF_4 were chosen as catalyst, silver salt, and reaction medium rather than organic solvent, respectively. As shown in Table 1, the model substrates underwent C–H amidation as expected, although the corresponding products **3aa**, namely *N*-(*tert*-butyl)-2-[(4-methylphenyl) sulfonamido]benzamide, was generated in low yield (18%) at room temperature (20 °C) (entry 1). However, it was noteworthy that the functionalization indeed occurred exclusively at the *ortho*-position of the starting material **1a**, proving the amidated product **3aa** in a single form with almost unreacted substrate recovery (78%) (isolated after purification by flash column chromatography on silica gel, data not shown in the table). The structure was confirmed unambiguously through NMR (nuclear magnetic resonance) and HR-MS (high resolution mass spectroscopic) analyses. Afterwards, other parameters such as reaction temperature, silver salts, additives, and ionic liquids were systematically investigated. The reaction temperature proven to be an important factor for the system. When the temperature was increased to 30 °C, the yield increased dramatically to 45% after shortened reaction time (entry 2). Silver salts screening indicated that the $AgNTf_2$ was the best (entries 3–6), while $AgBF_4$, which shared the identical anion with reaction medium, only generated a little amount of amidation product (entry 4). It is worth to mention that the amidation happened even when the catalyst loading reduced by half, albeit with slightly lower yield for longer reaction time (entry 7). Then, we attempted with the aid of doubled catalyst loading, but the yield was not substantially enhanced (entry 8). Importantly but not surprisingly, the starting material **1a** remained untouched in the absence of the iridium catalyst (entry 9). In order to investigate the impact of additives on this reaction, we then examined different base and acid. However, the additive exhibited to be detrimental in this transformation, providing decreased or even traces amount of product (entries 10–12). This phenomenon indicated that the aforementioned combination of anion and cation of the ionic liquid (entry 3) was just enough to promote the amidation. Replace the anion of ionic liquid with $[NTf_2]^-$ or $[PF_6]^-$ resulted in an increasing of catalytic performance with [BMIM]PF_6 representing the best result so far. Nevertheless, [BMIM]OTf displayed relative lower reactivity (entries 13–15). All the ionic liquids investigated were bearing neutral or inert anions such as $[BF_4]^-$, $[PF_6]^-$, $[OTf]^-$, and $[NTf_2]^-$. However, the only role of these anions was to provide polarities to the reaction medium by enhancing the catalytic activities and they rarely involved into the catalysis. Additionally, they represented weakly coordinating properties to form hydrogen bonds to stabilize the catalytic system. It seems that the results showed almost an opposite trend with the basicity of them (basicity in decreasing order: $[OTf]^-$ > $[BF_4]^-$ > $[PF_6]^-$ > $[NTf_2]^-$) (entries 2 and 13–15).[18] Remarkably, the result could be further improved when at 40 °C, with **1a** consumed almost completely after 8 h to afford the tosyl amidation product in excellent yield (entry 16). However, the result at higher temperature (*e.g.* 50 °C) changed back into sluggish (entry 17). Therefore, it can be concluded that the optimal reaction conditions are as follows: the catalysis was performed with the aid of 5 mol% of $[IrCp^*Cl_2]_2$ and $AgNTf_2$ with the ratio of 1 : 4 at 40 °C in the open air, in which ionic liquid [BMIM]PF_6 was the optimized reaction medium.

With the amidation conditions established, we were next encouraged to evaluate directing groups with different substituents on the nitrogen atom (Table 2). When the model *t*-butyl group of **1a** was replaced by other alkyl moieties such as methyl

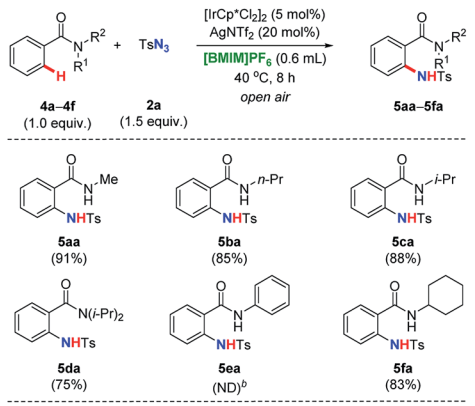
Table 1 Identification of reaction conditions for the iridium-catalyzed amidation between *N*-*tert*butylbenzamide (**1a**) and tosyl azide (**2a**)[a]

Entry	*x* mol%	Silver salt	Additive	Solvent	Temperature (°C)	Time (h)	Yield (%)[b]
1	5	$AgSbF_6$	—	$[BMIM]BF_4$	20	16	18
2	5	$AgSbF_6$	—	$[BMIM]BF_4$	30	8	45
3	5	$AgNTf_2$	—	$[BMIM]BF_4$	30	8	56
4	5	$AgBF_4$	—	$[BMIM]BF_4$	30	8	9
5	5	AgOAc	—	$[BMIM]BF_4$	30	8	38
6	5	AgOTf	—	$[BMIM]BF_4$	30	8	20
7	2.5	$AgNTf_2$[c]	—	$[BMIM]BF_4$	30	24	40
8	10	$AgNTf_2$[d]	—	$[BMIM]BF_4$	30	8	60
9	0	$AgNTf_2$	—	$[BMIM]BF_4$	30	24	ND[e]
10	5	$AgNTf_2$	NaOAc (1.0 equiv.)	$[BMIM]BF_4$	30	8	24
11	5	$AgNTf_2$	Li_2CO_3 (1.0 equiv.)	$[BMIM]BF_4$	30	8	36
12	5	$AgNTf_2$	PivOH (1.0 equiv.)	$[BMIM]BF_4$	30	8	trace
13	5	$AgNTf_2$	—	$[BMIM]NTf_2$	30	8	59
14	5	$AgNTf_2$	—	$[BMIM]PF_6$	30	8	72
15	5	$AgNTf_2$	—	[BMIM]OTf	30	8	34
16	5	$AgNTf_2$	—	$[BMIM]PF_6$	40	8	92
17	5	$AgNTf_2$	—	$[BMIM]PF_6$	50	8	80

[a] Reaction conditions: *N*-*tert*butylbenzamide **1a** (0.40 mmol, 1.0 equiv.), tosyl azide **2a** (0.60 mmol, 1.5 equiv.), indicated amount of catalyst $[IrCp^*Cl_2]_2$, silver salts (4.0 equiv. of catalyst loading), indicated amount of additive in ionic liquid (0.60 mL, 0.67 M) as reaction medium at indicated temperature for indicated reaction time in the open air. [b] Isolated yield after purification by flash column chromatography on silica gel. [c] 10 mol% $AgNTf_2$ was used. [d] 40 mol% $AgNTf_2$ was used. [e] ND = not detected.

(**4a**), *n*-propyl (**4b**), *i*-propyl (**4c**), as well as cyclohexyl (**4f**) groups, the reactivities baring a free N–H unit, although this effect was not especially decreased slightly, resulting in the corresponding products with very good yields (ranging from 83% to 91%). Furthermore, fully substituted benzamide **4d** was less favored compared with **4c** noticeable. Remarkably, substrate **4e** with a phenyl instead of an alkyl group could no longer proceed under the identical reaction conditions, which provided even more available reactive sites in known cases.[19]

Table 2 Variation of directing groups on the benzamides for the iridium-catalyzed amidation with tosyl azide (**2a**) as amino source[a]

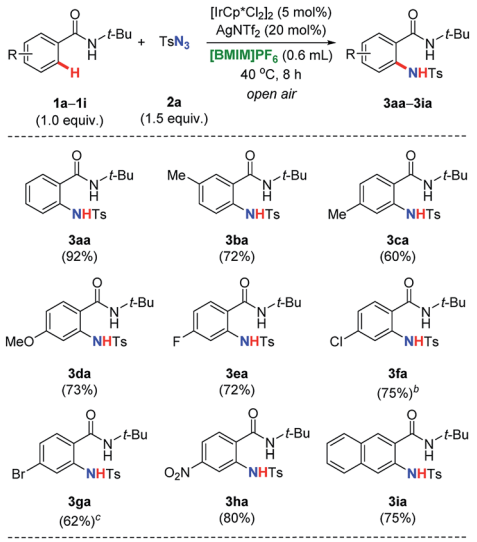


[a] Reaction conditions: *N*-substituted benzamide **4a–4f** (0.40 mmol, 1.0 equiv.), tosyl azide **2a** (0.60 mmol, 1.5 equiv.), $[IrCp^*Cl_2]_2$ (5.0 mol%), $AgNTf_2$ (20 mol%), in $[BMIM]PF_6$ (0.60 mL, 0.67 M) as reaction medium at 40 °C for 8 h in the open air, isolated yield reported after purification by flash column chromatography on silica gel. [b] ND = not detected.

Afterwards, we turned our attention to explore the substrate scope and limitations of various benzamides **1a–1i** with tosyl azide **2a** (Table 3). Starting materials with substituent at the *ortho*-, *meta*-, and *para*-positions of the aromatic ring have been examined, respectively. The desired amidation was proceeded smoothly, leading to the corresponding product in good yields (**1a–1i** → **3aa–3ia**). Importantly, it was observed that **1a** still stood out to be the most effective substrate among its derivatives. The electronic properties of substitution (either electron-donating or -withdrawing group) on the aromatic ring generally played a small role to obtain good yields except for **1f** and **1g**, that the catalysis need to be conducted at elevated temperature (80 °C for the formation of **3fa** and 60 °C for **3ga**, respectively). Interestingly, when naphthalene baring the same directing group at the β-position introduced, a single amidating product was isolated in a 2,3-di-substituted fashion, further indicating the highly regioselectivity of our strategy (**1i** → **3ia**).

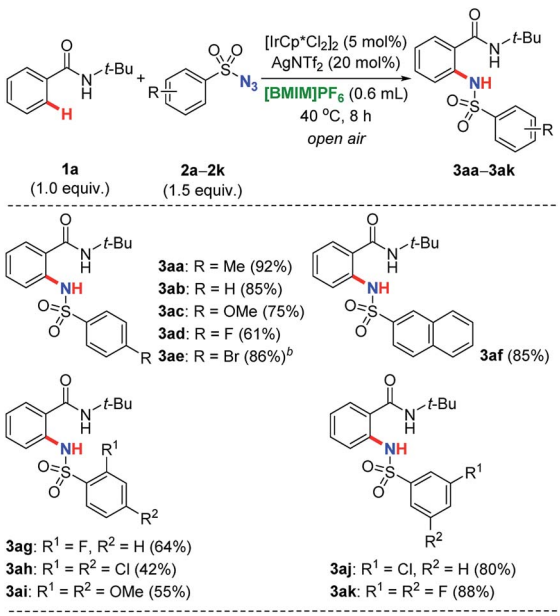
As shown in Table 4, besides **2a**, a variety of other sulfonyl azides **2b–2k** with varied substitution patterns as amidation reagents were investigated. These nitrogen sources

Table 3 Variation of the benzamides substrate for the iridium-catalyzed amidation with tosyl azide (**2a**) as amino source[a]

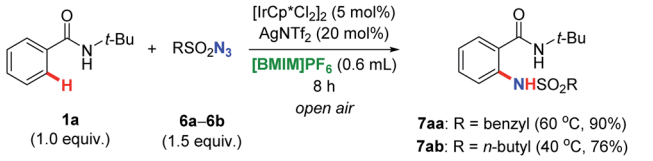


[a] Reaction conditions: *N-tert*butylbenzamides **1a–1i** (0.40 mmol, 1.0 equiv.), tosyl azide **2a** (0.60 mmol, 1.5 equiv.), $[IrCp^*Cl_2]_2$ (5.0 mol%), $AgNTf_2$ (20 mol%), in $[BMIM]PF_6$ (0.60 mL, 0.67 M) as reaction medium at 40 °C for 8 h in the open air, isolated yield reported after purification by flash column chromatography on silica gel. [b] Reaction proceeded at 80 °C. [c] Reaction proceeded at 60 °C.

Table 4 Variation of the sulfonyl azides for the iridium-catalyzed amidation of *N-tert*butylbenzamide (**1a**)[a]



[a] Reaction conditions: *N-tert*butylbenzamide **1a** (0.40 mmol, 1.0 equiv.), sulfonyl azide **2a–2k** (0.60 mmol, 1.5 equiv.), $[IrCp^*Cl_2]_2$ (5.0 mol%), $AgNTf_2$ (20 mol%), in $[BMIM]PF_6$ (0.60 mL, 0.67 M) as reaction medium at 40 °C for 8 h in the open air, isolated yield reported after purification by flash column chromatography on silica gel. [b] Reaction proceeded at 60 °C.

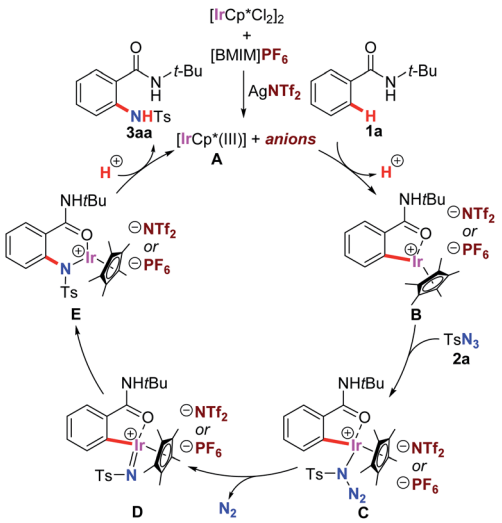


Scheme 2 Benzyl and alkyl azides as nitrogen source for the amidation of benzamide **1a**.

demonstrated to be effective under iridium catalysis, providing *ortho*-selective substituted benzamide derivatives in moderate to excellent yields. Generally, functional groups commonly used in organic synthesis such as methyl (**2a**), hydrogen (**2b**), methoxyl (**2c**), fluoro (**2d**, **2g**), bromo (**2e**) and chloro (**2j**), were well tolerated. This strategy has also been successfully applied for the naphthalene-2-sulfonyl azide (**2f**) to release desired product **3af**. Compared with azides bearing mono-substituent at the aromatic core, disubstituted sulfonyl coupling partners both at 2- and 4-positions have performed reduced reactivities, regardless of the electronic properties (**2h–2i** → **3ah–3ai**). It might be attributed to the effect of steric hindrance, since this phenomenon was not observed for the azide **2k** containing two fluorine atoms both at the *meta* positions (**2k** → **3ak**).

In order to make this methodology more general and applicable, we tried to employ benzyl azide **6a** and alkyl azide **6b** as well under the optimal reaction conditions. Gratifyingly, as illustrated in Scheme 2, the amidation underwent smoothly satisfyingly. These results provided forceful support of our achievements in this transformation.

A plausible mechanism of the amidation was described in Scheme 3 based on our experimental results and previous report.[13c] A cationic iridium(III) species **A** was generated *in situ* by the treatment of $[IrCp^*Cl_2]_2$ with $AgNTf_2$, and it could continuously participated in the C–H bond activation process of **1a** to form a five-membered metallacycle intermediate **B**. Sequential cascade started with coordination of tosyl azide **2a** and followed



Scheme 3 Proposed mechanism of the amidation.

by the dissociation of nitrogen gas provided iridium ion–nitrene complex **D**. This resulting species was active enough to undergo migratory C(Ar)–Ir bond insertion to form **E** with a more stable six-membered ring. Finally, demetalation through the proton exchange with another molecule of starting material **1a** made the successfully product **3aa** delivery and regenerated the reactive **A** to involved in the next catalytic cycle.

Conclusions

To sum up, we have described herein a catalytic transformation for the conversion of C(sp^2)–H bond into C–N bond using organic azides as coupling partners under mild conditions. Benzamides and sulfonyl azides were undertaken for the first time in the greener ionic liquid under iridium catalysis, demonstrated great promise as an attractive alternative to the existing methodologies. The amidation was proceeded exclusively at the *ortho*-position relative to the directing group and generated nitrogen gas as the sole byproduct. This protocol allows the preparation of a range of sulfonyl amine substituted benzamides in moderate to excellent yields with a broad substrate scope. In addition, benzyl and alkyl sulfonyl azides were also tolerated well, demonstrating the reliable and practical features of this strategy. Furthermore, a mechanism was proposed accordingly. The exploration for further application to the synthesis of biologically active molecules, and detailed mechanism investigations are currently underway in our group.

Experimental

General remarks

All reactions were performed in flame-dried glassware with magnetic stirring bar. Liquids and solutions were transferred with syringes. All the benzamide starting materials and sulfonyl azide coupling partners were obtained & used directly or prepared according to the known procedures.[13c,20] Ionic liquids involved were purchased and used as received. Solvents were purified and dried following standard procedures. Technical grade solvents for extraction and chromatography (ethyl acetate, petroleum ether) were distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on silica gel GF_{254} glass plates from Qingdao Haiyang Chemical Co,. Lt. Flash column chromatography was performed on silica gel (300–400 mesh) by Qingdao Haiyang Chemical Co,. Lt using the indicated solvents. Infrared (IR) spectra were recorded on a Bruker (VERTEX 70) FT-IR spectrophotometer by standard KBr-disk method and are reported (br = broad, vw = very weak, w = weak, m = medium, s = strong, vs = very strong) in wavenumbers (cm^{-1}). High resolution mass spectrometry (HRMS) analyses were performed on an Agilent 6460 instrument. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on Bruker Avance III 400 MHz instrument. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: $\delta = 7.26$ ppm for ^1H and $CDCl_3$: $\delta = 77.16$ ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

General procedure for the iridium-catalyzed *ortho*-selective carbon–hydrogen bond amidation of benzamides with sulfonyl azides (GP 1)

A flame-dried Schlenk tube equipped with a magnetic stir bar is successively charged with the benzamides (0.40 mmol, 1.0 equiv.), sulfonyl azides (0.6 mmol, 1.5 equiv.), $[IrCp^*Cl_2]_2$ (0.02 mmol, 5 mol%), and $AgNTf_2$ (0.08 mmol, 20 mol%) in $[BMIM]PF_6$ (0.6 mL, 0.67 mol L^{-1}). The reaction mixture is stirred at the indicated temperature and time. The reaction is monitored by TLC. After completion of the reaction, the reaction mixture is allowed to cool to room temperature and diluted with dichloromethane (2.0 mL). Purification by flash column chromatography on silica gel using mixtures of petroleum ether and ethyl acetate as eluents affords the analytically pure product.

N-(*tert*-Butyl)-2-(4-methylphenylsulfonamido)benzamide (3aa)

Prepared from *N-tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20 : 1) afforded the analytically pure product (127 mg, 92%) as a colorless oil; $R_f = 0.22$ (petroleum ether : ethyl acetate = 20 : 1); IR (KBr): $\tilde{\nu}/cm^{-1} = 3396$ (vs), 2964 (s), 1647 (vs), 1537 (vs), 1455 (m), 1389 (vs), 1232 (m), 1160 (vs), 952 (vs), 873 (s), 851 (w), 742 (s), 664 (vs), 563 (vs), 507 (s), 456 (m); ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 1.41$ (s, 9H), 2.37 (s, 3H), 5.96 (br s, 1H), 7.04 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1H), 7.19 (d, $J = 7.3$ Hz, 2H), 7.21 (dd, $J = 8.4$ Hz, $J = 8.4$ Hz, 2H), 7.64–7.68 (m, 3H), 10.85 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): $\delta = 21.5$, 28.6, 52.2, 121.5, 122.9, 123.5, 126.8, 127.1, 129.6, 132.1, 136.7, 138.5, 143.5, 168.1 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{18}H_{23}N_2O_3S$): calcd m/z 347.1424, found: 347.1421.

N-(*tert*-Butyl)-2-(phenylsulfonamido)benzamide (3ab)

Prepared from *N-tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and benzenesulfonyl azide (**2b**, 110 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether- : ethyl acetate = 8 : 1) afforded the analytically pure product (113 mg, 85%) as a colorless oil; $R_f = 0.5$ (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1} = 3383$ (vs), 3356 (vs), 2968 (s), 1633 (vs), 1535 (vs), 1450 (s), 1338 (vs), 1280 (s), 1163 (vs), 1091 (s), 937 (s), 871 (s), 758 (vs), 686 (s), 584 (vs), 464 (w); ^1H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 1.41$ (s, 9H), 6.00 (br s, 1H), 7.05 (dd, $J = 7.4$ Hz, $J = 7.4$ Hz, 1H), 7.35–7.42 (m, 4H), 7.51 (dd, $J = 7.2$ Hz, $J = 7.2$ Hz, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 7.4$ Hz, 2H), 10.96 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): $\delta = 28.6$, 52.2, 121.1, 123.0, 123.8, 126.9, 127.0, 129.0, 132.2, 132.8, 138.4, 139.5, 168.1 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{17}H_{21}N_2O_3S$): calcd m/z 333.1267, found: 333.1270.

N-(*tert*-Butyl)-2-(4-methoxyphenylsulfonamido)benzamide (3ac)

Prepared from *N-tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and 4-methoxybenzenesulfonyl azide (**2c**, 128 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (108 mg, 75%) as a colorless oil; R_f = 0.41 (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3404 (vs), 2964 (s), 1637 (vs), 1527 (vs), 1460 (m), 1336 (vs), 1261 (vs), 1161 (vs), 1028 (s), 941 (m), 889 (m), 833 (s), 736 (m), 669 (w), 568 (vs), 459 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.43 (s, 9H), 3.83 (s, 3H), 5.99 (br s, 1H), 6.87 (d, J = 7.6 Hz, 2H), 7.05 (dd, J = 7.6 Hz, J = 7.4 Hz, 1H), 7.34–7.39 (m, 2H), 6.67 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 7.6 Hz, 2H), 10.82 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.6, 52.2, 55.6, 114.1, 121.5, 122.9, 123.5, 126.8, 129.2, 131.2, 132.2, 138.7, 162.9, 168.1 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{18}H_{23}N_2O_4S$): calcd m/z 363.1373, found: 363.1379.

N-(*tert*-Butyl)-2-(4-fluorophenylsulfonamido)benzamide (3ad)

Prepared from *N-tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and 4-fluorobenzenesulfonyl azide (**2d**, 120 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (85 mg, 61%) as a colorless oil; R_f = 0.50 (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3367 (vs), 3072 (s), 2972 (vs), 1635 (vs), 1546 (vs), 1494 (s), 1394 (w), 1332 (vs), 1296 (m), 1166 (vs), 1089 (s), 923 (w), 835 (vs), 765 (s), 661 (w), 563 (vs); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.44 (s, 9H), 5.96 (br s, 1H), 7.07–7.14 (m, 3H), 7.35–7.45 (m, 2H), 7.70–7.74 (m, 1H), 7.80–7.86 (m, 2H), 10.82 (d, J = 8.0 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.6, 52.2, 116.1 (d, J = 23 Hz), 121.7, 122.8, 123.8, 126.7, 129.9 (d, J = 9.0 Hz), 132.3, 135.8, 138.5, 164.9 (d, J = 254 Hz), 167.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ = −105.1 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{17}H_{20}FN_2O_3S$): calcd m/z 351.1173, found: 351.1176.

2-(4-Bromophenylsulfonamido)-*N*-*tert*butylbenzamide (3ae)

Prepared from *N-tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and 4-bromobenzenesulfonyl azide (**2e**, 157 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 60 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded the analytically pure product (141 mg, 86%) as a colorless oil; R_f = 0.37 (petroleum ether : ethyl acetate = 8 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3381 (vs), 3087 (m), 2968 (vs), 1637 (vs), 1539 (vs), 1471 (s), 1390 (vs), 1269 (vs), 1166 (vs), 1089 (s), 1010 (s), 939 (m), 817 (s), 748 (vs), 559 (vs), 420 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.45 (s, 9H), 5.99 (br s, 1H), 7.07–7.15 (m, 1H), 7.36–7.43 (m, 2H), 7.53–7.57 (m, 2H), 7.63–7.76 (m, 3H), 11.01 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.6, 52.3, 121.9, 122.9, 124.0, 126.8, 127.6, 128.6, 132.2, 132.3, 138.3, 138.7, 167.9 ppm; HRMS (APCI) exact mass for $[M + Na]^+$ ($C_{17}H_{19}BrN_2NaO_3S$): calcd m/z 433.0192, found: 433.0187.

N-(*tert*-Butyl)-2-(naphthalene-2-sulfonamido)benzamide (3af)

Prepared from *N-tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and naphthalene-2-sulfonyl azide (**2f**, 140 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (130 mg, 85%) as a colorless oil; R_f = 0.53 (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3398 (vs), 2976 (vs), 1930 (w), 1809 (w), 1639 (vs), 1531 (vs), 1369 (vs), 1269 (vs), 1128 (vs), 1070 (vs), 952 (vs), 806 (vs), 707 (vs), 653 (vs), 559 (vs), 472 (vs); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.34 (s, 9H), 5.93 (br s, 1H), 7.02 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.31–7.38 (m, 2H), 7.55–7.63 (m, 2H), 7.72–7.77 (m, 2H), 7.83–7.88 (m, 3H), 8.36 (s, 1H), 11.09 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.6, 52.2, 121.7, 122.3, 123.1, 123.8, 127.0, 127.6, 127.9, 128.6, 128.9, 129.3, 129.4, 132.2, 132.3, 134.9, 136.7, 138.6, 168.2 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{21}H_{23}N_2O_3S$): calcd m/z 383.1424, found: 383.1420.

N-(*tert*-Butyl)-2-(2-fluorophenylsulfonamido)benzamide (3ag)

Prepared from *N-tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and 2-fluorobenzenesulfonyl azide (**2g**, 121 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 3 : 1) afforded the analytically pure product (90 mg, 64%) as a colorless oil; R_f = 0.37 (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3400 (s), 2966 (s), 2852 (m), 1647 (s), 1533 (s), 1473 (s), 1392 (s), 1265 (vs), 1220 (m), 1168 (vs), 1074 (vs), 948 (s), 777 (vs), 698 (m), 584 (vs), 457 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.46 (s, 9H), 5.94 (br s, 1H), 7.03 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.12 (dd, J = 8.8 Hz, J = 8.6 Hz, 1H), 7.23 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.32–7.38 (m, 2H), 7.50–7.55 (m, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.94 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 11.17 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.7, 52.3, 117.1 (d, J = 20 Hz), 120.1, 122.5, 123.2, 124.3 (d, J = 4 Hz), 126.7, 127.7 (d, J = 11 Hz), 130.8, 132.1, 135.1 (d, J = 9 Hz), 138.1, 159.0 (d, J = 262 Hz), 168.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ = −108.5 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{17}H_{20}FN_2O_3S$): calcd m/z 351.1173, found: 351.1177.

N-(*tert*-Butyl)-2-(2,4-dichlorophenylsulfonamido)benzamide (3ah)

Prepared from *N-tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and 2,4-dichlorobenzenesulfonyl azide (**2h**, 151 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded the analytically pure product (67 mg, 42%) as a colorless oil; R_f = 0.62 (petroleum ether : ethyl acetate = 8 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3377 (vs), 3255 (m), 3093 (w), 2974 (m), 1639 (s), 1571 (m), 1454 (m), 1375 (s), 1269 (m), 1164 (vs), 948 (m), 823 (s), 705 (w), 622 (s), 568 (s), 493 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.50 (s, 9H),

6.04 (br s, 1H), 7.04 (dd, $J = 7.4$ Hz, $J = 7.4$ Hz, 1H), 7.31–7.41 (m, 3H), 7.42–7.48 (m, 1H), 7.54–7.59 (m, 1H), 8.06–8.15 (m, 1H), 11.54 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.7, 52.4, 118.6, 121.6, 122.9, 127.0, 127.2, 130.6, 131.6, 132.3, 132.9, 135.5, 137.9, 139.7, 168.0 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{17}H_{19}Cl_2N_2O_3S$): calcd m/z 401.0488, found: 401.0493.

N-(*tert*-Butyl)-2-(2,4-dimethoxyphenylsulfonamido) benzamide (3ai)

Prepared from *N*-*tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and 2,4-dimethoxybenzenesulfonyl azide (**2i**, 146 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) afforded the analytically pure product (86 mg, 55%) as a colorless oil; R_f = 0.50 (petroleum ether : ethyl acetate = 8 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3325 (s), 3012 (w), 2974 (m), 1624 (vs), 1543 (s), 1490 (s), 1340 (m), 1265 (s), 1170 (vs), 1078 (s), 931 (m), 840 (m), 754 (m), 699 (m), 565 (vs), 462 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.53 (s, 9H), 3.88 (s, 3H), 3.92 (s, 3H), 6.03 (br s, 1H), 6.46 (d, $J = 2.0$ Hz, 1H), 6.55 (dd, $J = 8.8$ Hz, $J = 2.1$ Hz, 1H), 6.98 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1H), 7.30–7.40 (m, 1H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.97 (d, $J = 8.8$ Hz, 1H), 11.09 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.8, 52.0, 55.6, 56.1, 99.3, 104.1, 118.6, 119.6, 121.2, 121.9, 126.7, 132.0, 132.6, 139.3, 158.4, 164.9, 167.9 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{19}H_{25}N_2O_5S$): calcd m/z 393.1479, found: 393.1480.

N-(*tert*-Butyl)-2-(3-chlorophenylsulfonamido)benzamide (3aj)

Prepared from *N*-*tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and 3-chlorobenzenesulfonyl azide (**2j**, 130 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (117 mg, 80%) as a colorless oil; R_f = 0.45 (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3390 (vs), 2978 (s), 1637 (vs), 1531 (vs), 1492 (vs), 1460 (m), 1340 (vs), 1267 (vs), 1163 (vs), 1083 (s), 945 (s), 867 (s), 758 (s), 673 (s), 586 (vs), 499 (s); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.40 (s, 9H), 6.02 (br s, 1H), 7.07 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1H), 7.31–7.41 (m, 3H), 7.46 (d, $J = 7.6$ Hz, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.75 (s, 1H), 11.11 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.6, 52.3, 121.7, 122.8, 124.1, 125.2, 126.9, 127.1, 130.3, 132.4, 132.9, 135.1, 138.2, 141.3, 168.0 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{17}H_{20}ClN_2O_3S$): calcd m/z 367.0878, found: 367.0881.

N-(*tert*-Butyl)-2-(3,5-difluorophenylsulfonamido)benzamide (3ak)

Prepared from *N*-*tert*butylbenzamide (**1a**, 70.9 mg, 0.4 mmol, 1.0 equiv.) and 3,5-difluorobenzenesulfonyl azide (**2k**, 132 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (130 mg, 88%) as a colorless oil; R_f = 0.65 (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3408 (vs), 3064 (s), 2978 (s), 1641 (vs), 1541 (vs), 1440 (vs), 1348 (vs), 1294 (vs), 1161 (vs), 987 (vs), 886 (s), 750 (vs), 667 (s), 603 (vs), 540 (w), 497 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.45 (s, 9H), 6.03 (br s, 1H), 6.97 (dd, $J = 8.4$ Hz, $J = 8.4$ Hz, 1H), 7.13 (dd, $J = 7.2$ Hz, $J = 7.2$ Hz, 1H), 7.31–7.35 (m, 2H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.49 (dd, $J = 7.6$ Hz, $J = 7.6$ Hz, 1H), 7.71 (d, $J = 7.4$ Hz, 1H), 11.25 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.6, 52.4, 108.4 (t, J = 25 Hz), 110.8 (d, J = 12 Hz), 110.8 (d, J = 28 Hz), 121.9, 122.8, 124.3, 126.9, 132.5, 138.0, 142.8, 162.6 (dd, J = 253 Hz, J = 11 Hz), 167.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ = −105.6 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{17}H_{19}F_2N_2O_3S$): calcd m/z 369.1079, found: 369.1074.

N-(*tert*-Butyl)-5-methyl-2-(4-methylphenylsulfonamido) benzamide (3ba)

Prepared from *N*-(*tert*-butyl)-3-methylbenzamide (**1b**, 76.5 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether- : ethyl acetate = 8 : 1) afforded the analytically pure product (104 mg, 72%) as a colorless oil; R_f = 0.61 (petroleum ether- : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3377 (vs), 2964 (s), 1637 (vs), 1543 (vs), 1454 (m), 1388 (vs), 1265 (s), 1164 (s), 1093 (vs), 952 (w), 831 (s), 715 (s), 678 (m), 588 (vs), 532 (s), 460 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.41 (s, 9H), 2.31 (s, 3H), 2.38 (s, 3H), 5.88 (br s, 1H), 7.11 (s, 1H), 7.20 (d, $J = 7.8$ Hz, 3H), 7.59 (d, $J = 7.6$ Hz, 1H), 7.64 (d, $J = 7.8$ Hz, 2H), 10.58 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 20.7, 21.5, 28.6, 52.1, 122.2, 123.4, 123.4, 127.1, 129.5, 132.8, 133.4, 135.9, 136.7, 143.3, 168.1 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{19}H_{25}N_2O_3S$): calcd m/z 361.1580, found: 361.1575.

N-(*tert*-Butyl)-4-methyl-2-(4-methylphenylsulfonamido) benzamide (3ca)

Prepared from *N*-(*tert*-butyl)-4-methylbenzamide (**1c**, 76.5 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether- : ethyl acetate = 10 : 1) afforded the analytically pure product (87 mg, 60%) as a colorless oil; R_f = 0.31 (petroleum ether : ethyl acetate = 8 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3396 (vs), 3066 (w), 2964 (m), 1641 (vs), 1533 (vs), 1504 (w), 1386 (vs), 1269 (m), 1220 (m), 1164 (vs), 1089 (s), 962 (w), 813 (vs), 721 (vs), 538 (s), 453 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.42 (s, 9H), 2.35 (s, 3H), 2.39 (s, 3H), 5.86 (br s, 1H), 6.85 (d, $J = 7.8$ Hz, 1H), 7.21 (d, $J = 7.6$ Hz, 3H), 7.52 (s, 1H), 7.69 (d, J = 7.6 Hz, 2H), 10.96 (br s, 0.01H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 21.5, 21.6, 28.7, 52.0, 120.0, 122.0, 124.3, 126.5, 127.1, 129.5, 136.8, 138.7, 143.0, 143.3, 168.1 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{19}H_{25}N_2O_3S$): calcd m/z 361.1580, found: 361.1577.

N-(*tert*-Butyl)-4-methoxy-2-(4-methylphenylsulfonamido) benzamide (3da)

Prepared from *N*-(*tert*-butyl)-4-methoxybenzamide (**1d**, 82.9 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5

equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether-: ethyl acetate = 8 : 1) afforded the analytically pure product (110 mg, 73%) as a colorless oil; R_f = 0.58 (petroleum ether-: ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}$/cm^{-1} = 3398 (vs), 2962 (s), 2869 (w), 1633 (vs), 1535 (s), 1456 (w), 1336 (vs), 1160 (vs), 1269 (vs), 1163 (vs), 972 (s), 804 (s), 707 (vs), 644 (m), 592 (m), 541 (vs); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.41 (s, 9H), 2.37 (s, 3H), 3.80 (s, 3H), 5.79 (br s, 1H), 6.52 (d, J = 8.8 Hz, 1H), 7.19–7.24 (m, 4H), 7.71 (d, J = 7.6 Hz, 2H), 11.35 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 21.5, 28.7, 52.0, 55.5, 105.4, 109.6, 114.5, 127.2, 128.0, 129.6, 136.8, 141.0, 143.5, 162.0, 168.0 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{19}H_{25}N_2O_4S$): calcd m/z 377.1530, found: 377.1532.

N-(*tert*-Butyl)-4-fluoro-2-(4-methylphenylsulfonamido) benzamide (3ea)

Prepared from *N*-(*tert*-butyl)-4-fluorobenzamide (**1e**, 78.1 mg, 0.4 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether-: ethyl acetate = 8 : 1) afforded the analytically pure product (105 mg, 72%) as a colorless oil; R_f = 0.20 (petroleum ether-: ethyl acetate = 8 : 1); IR (KBr): $\tilde{\nu}$/cm^{-1} = 3404 (vs), 3074 (w), 2968 (s), 1916 (w), 1641 (vs), 1497 (vs), 1361 (vs), 1269 (vs), 1155 (vs), 1018 (w), 950 (s), 825 (vs), 729 (vs), 636 (m), 543 (vs), 447 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.46 (s, 9H), 2.42 (s, 3H), 6.01 (br s, 1H), 6.69–6.74 (m, 1H), 7.26 (d, J = 7.6 Hz, 2H), 7.38–7.44 (m, 2H), 7.73 (d, J = 7.2 Hz, 2H), 11.29 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 21.5, 28.6, 52.3, 107.7 (d, J = 26 Hz), 110.2 (d, J = 22 Hz), 118.1 (d, J = 3.0 Hz), 127.0, 128.9 (d, J = 11 Hz), 129.7, 136.4, 141.1 (d, J = 11 Hz), 143.9, 164.3 (d, J = 251 Hz), 167.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$, 298 K): δ = −104.9 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{18}H_{22}FN_2O_3S$): calcd m/z 365.1330, found: 365.1333.

N-(*tert*-Butyl)-4-chloro-2-(4-methylphenylsulfonamido) benzamide (3fa)

Prepared from *N*-(*tert*-butyl)-4-chlorobenzamide (**1f**, 84.7 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 80 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether-: ethyl acetate = 8 : 1) afforded the analytically pure product (114 mg, 75%) as a colorless oil; R_f = 0.51 (petroleum ether-: ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}$/cm^{-1} = 3398 (vs), 3051 (m), 2970 (vs), 1928 (w), 1639 (vs), 1485 (vs), 1334 (vs), 1217 (vs), 1118 (vs), 1018 (w), 933 (vs), 813 (vs), 705 (vs), 626 (m), 538 (vs), 443 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.42 (s, 9H), 2.39 (s, 3H), 5.86 (br s, 1H), 6.98 (d, J = 8.4 Hz, 1H), 7.21–7.25 (m, 3H), 7.70–7.73 (m, 3H), 11.00 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 21.6, 28.6, 52.4, 120.5, 120.9, 123.3, 127.2, 127.8, 129.7, 136.5, 138.2, 140.0, 143.8, 167.4 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{18}H_{22}ClN_2O_3S$): calcd m/z 381.1034, found: 381.1030.

4-Bromo-*N*-(*tert*-butyl)-2-(4-methylphenylsulfonamido) benzamide (3ga)

Prepared from 4-bromo-*N*-*tert*butylbenzamide (**1g**, 102 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 60 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether-: ethyl acetate = 8 : 1) afforded the analytically pure product (105 mg, 62%) as a colorless oil; R_f = 0.64 (petroleum ether-: ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}$/cm^{-1} = 3394 (vs), 3078 (w), 2925 (vs), 1639 (vs), 1566 (m), 1481 (vs), 1336 (vs), 1217 (m), 1164 (vs), 1039 (w), 914 (vs), 738 (vs), 686 (s), 655 (m), 557 (vs), 424 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.44 (s, 9H), 2.42 (s, 3H), 5.90 (br s, 1H), 7.15–7.21 (m, 2H), 7.26 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 7.6 Hz, 2H), 7.89 (s, 1H), 10.98 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 21.6, 28.6, 52.4, 121.0, 123.9, 126.3, 126.4, 127.2, 127.9, 129.7, 136.4, 140.0, 143.9, 167.4 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{18}H_{22}BrN_2O_3S$): calcd m/z 425.0529, found: 425.0536.

N-(*tert*-Butyl)-2-(4-methylphenylsulfonamido)-4-nitrobenzamide (3ha)

Prepared from *N*-(*tert*-butyl)-4-nitrobenzamide (**1h**, 88.9 mg, 0.4 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether-: ethyl acetate = 3 : 1) afforded the analytically pure product (125 mg, 80%) as a colorless oil; R_f = 0.27 (petroleum ether-: ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}$/cm^{-1} = 3413 (s), 3097 (m), 2976 (s), 2856 (w), 1647 (vs), 1533 (vs), 1458 (w), 1352 (vs), 1215 (m), 1161 (vs), 966 (s), 808 (s), 688 (s), 619 (w), 540 (vs), 433 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.48 (s, 9H), 2.41 (s, 3H), 6.21 (br s, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 8.0 Hz, 1H), 7.74–7.80 (m, 3H), 8.45 (s, 1H), 10.93 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 21.6, 28.5, 53.0, 114.7, 117.3, 126.8, 127.2, 128.2, 130.0, 136.0, 139.8, 144.5, 149.5, 166.4 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{18}H_{22}N_3O_5S$): calcd m/z 392.1275, found: 392.1271.

N-(*tert*-Butyl)-3-(4-methylphenylsulfonamido)-2-naphthamide (3ia)

Prepared from *N*-(*tert*-butyl)-2-naphthamide (**1i**, 91 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether-: ethyl acetate = 8 : 1) afforded the analytically pure product (119 mg, 75%) as a colorless oil; R_f = 0.45 (petroleum ether-: ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}$/cm^{-1} = 3390 (vs), 3111 (w), 2962 (m), 1651 (vs), 1597 (m), 1531 (vs), 1446 (m), 1352 (vs), 1222 (w), 1163 (vs), 1089 (m), 923 (s), 709 (s), 653 (w), 572 (vs), 414 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.48 (s, 9H), 2.34 (s, 3H), 6.12 (br s, 1H), 7.15 (d, J = 7.6 Hz, 2H), 7.44 (dd, J = 7.2 Hz, J = 7.2 Hz, 1H), 7.55 (dd, J = 7.2 Hz, J = 7.2 Hz, 1H), 7.67 (d, J = 7.6 Hz, 2H), 7.78 (dd, J = 8.0 Hz, J = 7.6 Hz, 2H), 7.87 (s, 1H), 8.07 (s, 1H), 10.48 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 21.5, 28.7, 52.4, 119.2, 124.1, 126.0, 127.1, 127.5,

127.6, 128.1, 128.4, 129.1, 129.5, 134.1, 134.7, 136.7, 143.4, 168.2 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{22}H_{25}N_2O_3S$): calcd m/z 397.1580, found: 397.1582.

N-Methyl-2-(4-methylphenylsulfonamido)benzamide (5aa)

Prepared from *N*-methylbenzamide (**4a**, 54.1 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (110 mg, 91%) as a colorless oil; $R_f = 0.45$ (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3398 (vs), 2962 (vs), 2856 (m), 1732 (vs), 1649 (vs), 1539 (vs), 1456 (s), 1390 (vs), 1280 (vs), 1157 (vs), 1043 (w), 950 (s), 815 (s), 740 (vs), 565 (vs), 459 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 2.39 (s, 3H), 2.92 (s, 3H), 6.30 (br s, 1H), 7.03–7.10 (m, 1H), 7.23 (d, J = 7.9 Hz, 2H), 7.39 (d, J = 8.1 Hz, J = 8.1 Hz, 2H), 7.65–7.74 (m, 3H), 10.87 (br s, 1H) ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{15}H_{17}N_2O_3S$): calcd m/z 305.0954, found: 305.0955.

2-(4-Methylphenylsulfonamido)-*N*-propylbenzamide (5ba)

Prepared from *N*-propylbenzamide (**4b**, 65.3 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (113 mg, 85%) as a colorless oil; $R_f = 0.33$ (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3392 (vs), 3062 (w), 2966 (m), 1635 (vs), 1537 (s), 1452 (m), 1332 (s), 1211 (m), 1155 (vs), 1089 (vs), 916 (m), 808 (m), 761 (s), 699 (s), 563 (vs), 534 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.94 (t, J = 7.4 Hz, 3H), 1.52–1.61 (m, 2H), 3.35 (s, 3H), 3.28 (q, J = 6.8 Hz, 2H), 6.47 (br s, 1H), 7.03 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.36 (dd, J = 7.8 Hz, J = 7.8 Hz, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 8.0 Hz, 3H), 10.98 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 11.4, 21.5, 22.5, 41.7, 121.2, 121.7, 123.6, 126.9, 127.1, 129.5, 132.3, 136.5, 138.7, 143.6, 168.4 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{17}H_{21}N_2O_3S$): calcd m/z 333.1267, found: 333.1265.

N-Isopropyl-2-(4-methylphenylsulfonamido)benzamide (5ca)

Prepared from *N*-isopropylbenzamide (**4c**, 65.3 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (117 mg, 88%) as a colorless oil; $R_f = 0.69$ (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3384 (vs), 2979 (s), 1633 (vs), 1531 (vs), 1452 (m), 1332 (vs), 1259 (vs), 1213 (m), 1157 (vs), 1089 (vs), 929 (m), 829 (w), 763 (s), 624 (w), 563 (vs), 441 (vw); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.21 (d, J = 6.6 Hz, 6H), 2.35 (s, 3H), 4.07–4.19 (m, 1H), 6.21 (d, J = 7.0 Hz, 1H), 7.03 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.36 (dd, J = 7.8 Hz, J = 7.8 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.62–7.67 (m, 3H), 10.97 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 21.5, 22.4, 42.1, 121.4, 121.9, 123.6, 126.9, 127.1, 129.5, 132.3, 136.6, 138.7, 143.6, 167.6 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{17}H_{21}N_2O_3S$): calcd m/z 333.1267, found: 333.1262.

N,*N*-Diisopropyl-2-(4-methylphenylsulfonamido)benzamide (5da)

Prepared from *N*,*N*-diisopropylbenzamide (**4d**, 82.1 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether- : ethyl acetate = 8 : 1) afforded the analytically pure product (112 mg, 75%) as a colorless oil; R_f = 0.64 (petroleum ether- : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3130 (vs), 2956 (s), 2821 (w), 1608 (vs), 1457 (vs), 1344 (vs), 1259 (w), 1211 (m), 1166 (vs), 1093 (s), 920 (m), 813 (s), 736 (vs), 621 (m), 567 (vs), 493 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.27 (br s, 12H), 2.37 (s, 3H), 3.66 (br s, 2H), 7.04–7.08 (m, 1H), 7.11 (ddd, J = 7.6 Hz, J = 7.6 Hz, J = 1.3 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.27–7.31 (m, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 2H), 8.34 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 20.6, 21.5, 121.9, 123.6, 126.3, 127.1, 127.9, 129.7, 130.1, 135.6, 137.4, 143.8, 169.0 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{20}H_{27}N_2O_3S$): calcd m/z 375.1737, found: 375.1734.

N-Cyclohexyl-2-(4-methylphenylsulfonamido)benzamide (5fa)

Prepared from *N*-cyclohexyl-2-(4-methylphenylsulfonamido) benzamide (**4f**, 81.3 mg, 0.40 mmol, 1.0 equiv.) and tosyl azide (**2a**, 131 μL, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (124 mg, 83%) as a colorless oil; R_f = 0.31 (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3390 (vs), 2933 (vs), 2854 (s), 1631 (vs), 1529 (vs), 1448 (m), 1334 (vs), 1215 (m), 1149 (vs), 1089 (s), 937 (s), 813 (s), 754 (s), 671 (s), 563 (vs), 447 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.17–1.29 (m, 3H), 1.36–1.45 (m, 2H), 1.65–1.69 (m, 1H), 1.75–1.78 (m, 2H), 1.90–1.93 (m, 2H), 2.36 (s, 3H), 3.78–3.87 (m, 1H), 6.19 (d, J = 7.2 Hz, 1H), 7.03 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.36 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.65–7.68 (m, 3H), 10.96 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 21.5, 24.9, 25.4, 32.7, 48.9, 121.3, 121.8, 123.5, 126.8, 127.1, 129.5, 132.3, 136.6, 138.8, 143.5, 167.5 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{20}H_{25}N_2O_3S$): calcd m/z 373.1580, found: 373.1584.

N-(*tert*-Butyl)-2-(phenylmethylsulfonamido)benzamide (7aa)

Prepared from *N*-*tert*butylbenzamide (**1a**, 70.9 mg, 0.40 mmol, 1.0 equiv.) and phenylmethanesulfonyl azide (**6a**, 118 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 60 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) afforded the analytically pure product (125 mg, 90%) as a colorless oil; R_f = 0.45 (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3371 (vs), 2970 (vs), 2920 (s), 1633 (vs), 1537 (vs), 1454 (m), 1334 (vs), 1394 (vs), 1280 (vs), 1159 (vs), 1029 (w), 945 (vs), 746 (vs), 630 (s), 546 (vs), 459 (m); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 1.45 (s, 9H), 4.39 (s, 2H), 6.18 (br s, 1H), 7.09 (ddd, J = 7.6 Hz, J = 7.6 Hz,

J = 0.7 Hz, 1H), 7.24–7.32 (m, 5H), 7.38 (ddd, J = 7.2 Hz, J = 7.2 Hz, J = 1.2 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 10.93 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 28.7, 52.3, 58.4, 119.0, 120.8, 122.8, 127.1, 128.4, 128.8, 128.8, 130.8, 132.6, 139.6, 168.1 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{18}H_{23}N_2O_3S$): calcd m/z 347.1424, found: 347.1420.

N-(*tert*-Butyl)-2-(butylsulfonamido)benzamide (7ab)

Prepared from *N-tert*butylbenzamide (**1a**, 70.9 mg, 0.40 mmol, 1.0 equiv.) and butane-1-sulfonyl azide (**6b**, 98 mg, 0.6 mmol, 1.5 equiv.) according to the **GP 1** at 40 °C for 8 h. Purification by flash column chromatography on silica gel (petroleum ether- : ethyl acetate = 8 : 1) afforded the analytically pure product (95 mg, 76%) as a colorless oil; R_f = 0.46 (petroleum ether : ethyl acetate = 3 : 1); IR (KBr): $\tilde{\nu}/cm^{-1}$ = 3375 (vs), 2964 (vs), 2873 (s), 1635 (vs), 1537 (vs), 1490 (s), 1328 (vs), 1265 (vs), 1145 (vs), 1097 (m), 943 (vs), 887 (s), 763 (vs), 661 (w), 520 (s), 460 (w); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 0.88 (t J = 7.4 Hz, 3H), 1.27–1.43 (m, 2H), 1.49 (s, 9H), 1.73–1.80 (m, 2H), 3.05–3.09 (m, 2H), 6.31 (br s, 1H), 7.10 (dd, J = 7.6 Hz, J = 7.6 Hz, 1H), 7.42 (dd, J = 8.0 Hz, J = 8.0 Hz, 1H), 7.51 (d J = 7.6 Hz, 1H), 7.69 (d J = 8.0 Hz, 1H), 10.74 (br s, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ = 13.6, 21.4, 25.3, 28.7, 51.5, 52.3, 119.5, 121.5, 123.1, 127.4, 132.5, 139.1, 168.3 ppm; HRMS (APCI) exact mass for $[M + H]^+$ ($C_{15}H_{25}N_2O_3S$): calcd m/z 313.1580, found: 313.1584.

Conflicts of interest

There are no conflicts of interest to declare.

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