Synthesis S. Ahmadi, M. Ghanbari Paper

From Furan–Yne Systems to *para*-Benzoquinone Derivatives: Gold-Catalyzed Cyclization and Oxidation, and Further Reduction by Sodium Dithionate

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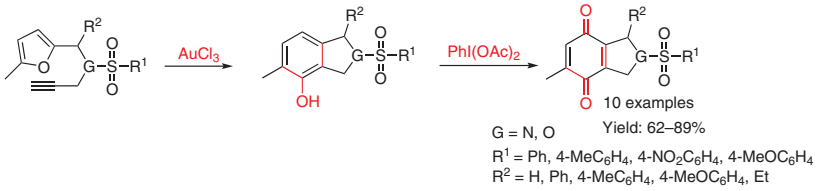

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Abstract A series of furan–yne systems were transformed into the corresponding *para*-benzoquinone derivatives by gold(III) catalyst. The two-step procedure consisted of a phenol synthesis and subsequent oxidation with iodobenzene diacetate. The reactions can be carried out in a one-pot procedure with the same precatalyst. The *para*-benzoquinone could simply be converted into the corresponding hydroquinones by reduction with sodium dithionate. This protocol features high efficiency, mild conditions, and wide substrate scopes.

Key words gold catalyst, furfural, alkyne, benzoquinone, one-pot reaction

para-Benzoquinone is the fundamental structure of quinonoid compounds. They are broadly scattered in the natural world, being found in plants, bacteria, and arthropods and, hence, quinones are ubiquitous in living systems.[1] Quinones play a vital role in biological functions, including electron transfer and oxidative phosphorylation.[2] Their role as electron transfer agents in primary metabolic processes like respiration and photosynthesis is pivotal to human life. *para*-Benzoquinone derivatives such as Streptonigrin (STN),[3] Mitomycin C,[4] and Xylariaquinone A[5] are examples of the most well-known antitumor, anticancer, and antimalarial structures, respectively (Figure 1).

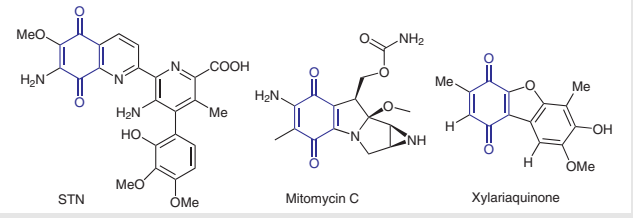
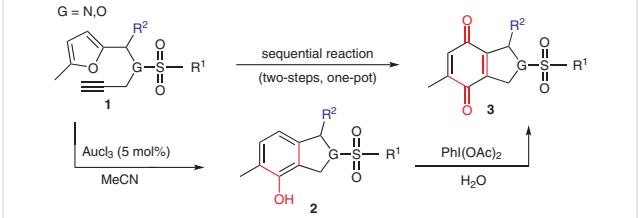


Figure 1 Number of well-known *para*-benzoquinone structures

Since other known *para*-benzoquinone derivatives possess outstanding pharmaceutical applications such as, antibiotics,[6] anticoagulants,[7] antineoplastics,[8] synthetic studies of *para*-benzoquinones skeleton have been actively carried out.

Gold has emerged in the field of organic chemistry as a powerful tool and, due to the high selectivity as well as mild reaction conditions, has become one of the major topics in catalysis research.[9] The extraordinary ability of gold to activate multiple bonds has led to a large number of new approaches for the construction of various heterocyclic structures.[10,11] Most of these reactions are atom-economical and in comparison to classical routes, the reaction conditions are dramatically mild in most cases.[12] In 2000, the Hashmi group published the gold-catalyzed transformation of allenyl ketones to furans by a 5-*endo*-*trig* cyclization.[13] Based on these findings, a large family of gold-catalyzed heterocycle syntheses was developed by different groups. Inspired by the recent reports on gold-catalyzed cyclization reactions,[11,14,15] and as part of our ongoing research program on the development of efficient methods for the preparation of heterocyclic compounds,[16] herein, we report a one-pot reaction that includes gold-catalyzed phenol synthesis and subsequently, gold-assisted oxidation reaction as a promising strategy for synthesis of novel *para*-benzoquinone structures (Scheme 1).



Scheme 1 Gold-catalyzed synthesis of parabenzoquinones **3**

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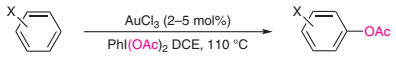
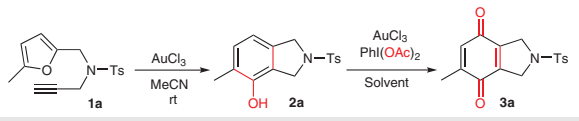
A possible one-pot procedure would be attractive, as purification of the intermediates could be circumvented, which saves time and reduces the waste of production. In 2011, Wang and co-workers reported gold-catalyzed direct acetoxylation of arenes with $PhI(OAc)_2$ (Scheme 2).[17]



Scheme 2 Direct acetoxylation of arenes

Inspired by Wang et al.'s report on gold-catalyzed direct acetoxylation of arenes with iodobenzene diacetate, we considered a one-pot reaction including gold-catalyzed Hashmi phenol synthesis[13] and a subsequent gold-assisted acetoxylation reaction, as a promising strategy towards acetoxylating the phenol systems.

In the Hashmi phenol synthesis reaction, $AuCl_3$ in acetonitrile cleanly transformed **1a** to **2a** within just a few minutes. The reactions proceeded at room temperature, neither air nor water needed to be excluded (Scheme 3).[13] Our initial studies concentrated on the acetoxylation reaction of the products of the phenol synthesis. These screenings were performed with test substrate **2a**, in the presence of $PhI(OAc)_2$ and $AuCl_3$ (5 mol%) in dichloroethane (DCE) at 80 °C for 2 hours under air atmosphere (Table 1, entry 1). During monitoring of the reaction mixture by TLC, we observed that all the substrates of **2a** were turned into the product. After isolation and characterization of the product by spectroscopic analysis, we found that an unexpected product **3a** was obtained (yield 47%). The structure of the product **3a** was confirmed by spectral and analytical data. To achieve suitable conditions for synthesis of **3a** from **2a**, we tested the reaction under various conditions; the results are shown in Table 1. As shown in Table 1, the solvents were found to significantly affect the reaction (entries 1–5). Whereas the reactivity in dichloroethane as well as in chloroform was in moderate yield after 15 hours at room temperature, we were pleased to find that the use of acetonitrile led to 56% of the desired product **3a** after 1 hour at room temperature (entries 2–4).



Scheme 3 Model reaction

It was also observed that the addition of water to acetonitrile led to an increase in the yield of the product **3a** to 87% (Table 1, entry 5). To investigate the effect of gold(III) catalyst, the reaction was performed in the absence of gold catalysts and we observed that the yield of the product dropped conspicuously, indicating tangible role of gold in this reaction (entry 6). An additional experiment including 15 mol% aqueous HCl in the absence of gold catalyst was performed and we observed that no reaction occurred (entry 7). The best conditions for the formation of **3a** from **2a** involved the use of 5-methyl-2-tosylisoindolin-4-ol (**2a**; 1.0 equiv), $PhI(OAc)_2$ (2.0 equiv), and $AuCl_3$ (5 mol%) in MeCN (2 mL) and H_2O (1 mL) at room temperature for 1 hour under an air atmosphere (entry 5).

Table 1 Optimization of Reaction Conditions[a]

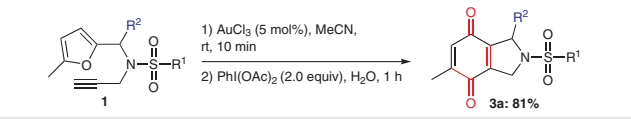
Entry	solvent	Temp (°C)	Reaction time (h)	Yield of **2a** (%)[b]	Yield of **3a** (%)[c]
1	DCE	80	2	–	47
2	DCE	rt	15	–	39
3	$CHCl_3$	rt	15	–	59
4	MeCN	rt	1	–	56
5	**MeCN:H_2O (2:1)**	**rt**	**1**	**–**	**87**
6[d]	MeCN:H_2O (2:1)	rt	1	–	43
7	MeCN:15 mol% aq HCl (2:1)	rt	24	–	0
8[e]	MeCN	rt	1	5	12
9[e,f]	MeCN	rt	1	0	15
10[g]	MeCN:H_2O (2:1)	rt	1	–	81

[a] Reaction conditions: **2a** (1.0 equiv), $PhI(OAc)_2$ (2.0 equiv), $AuCl_3$ (5 mol%), solvent (6 mL) for 1 mmol of **2a** (0.16 M), air.
[b] Isolated yield based on **1a**.
[c] Isolated yield based on **2a**.
[d] The reaction was carried out in the absence of $AuCl_3$.
[e] Reaction conditions: **1a** (1.0 equiv), $PhI(OAc)_2$ (2.0 equiv), $AuCl_3$ (5 mol%), MeCN (2 mL).
[f] $PhI(OAc)_2$: 3.0 equiv.
[g] Sequential one-pot procedure.

With these promising results in hand, we turned our focus to the investigation of a one-pot reaction that started from the corresponding furan–yne system **1a**. For this procedure, 2.0 equivalents of iodobenzene diacetate and 1.0 equivalent of the starting material **1a** were mixed in MeCN, and 5 mol% of $AuCl_3$ was added at room temperature. Unfortunately, after 1 hour, the reaction turned out to be unselective, and only a poor yield of the desired product **3a** besides minor amounts of intermediate phenol **2a** were obtained (Table 1, entry 8), although a complete conversion of the starting material **1a** was monitored.

Besides, an excess amount of iodobenzene diacetate (3.0 equiv) suppressed the formation of the phenol intermediate **2a**, but the yield of the desired product **3a** did not significantly improve (Table 1, entry 9). To circumvent decomposition of the furan–yne substrate **1a**, we changed the protocol to a sequential one-pot procedure (entry 10). With the furan–yne substrate **1a**, a clean and fast formation of phenol **2a** took place within just a few minutes in the presence of $AuCl_3$. After the complete conversion of the starting material was detected by means of thin-layer chromatography, iodobenzene diacetate and water were added. This proce-

dure led to a highly selective formation of 5-methyl-2-tosyl-2,3-dihydro-1*H*-isoindole-4,7-dione (**3a**) in an excellent overall yield of 81% (Scheme 4).



Scheme 4 Cyclization-oxidation sequence for furan–ynes **1**

After optimization of the reaction conditions, to evaluate the general applicability of this sequential one-pot procedure, a series of furan–yne derivatives **1** were converted to the corresponding *para*-benzoquinone derivatives **3**under the same reaction conditions. The results are summarized in Table 2. As can be seen from Table 2, the substrates with additional aromatic substituents **1c–f**, showed no loss of selectivity (Table 2, entries 3–6).

Table 2 Scope of the Reaction[a]

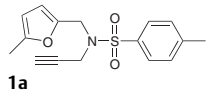
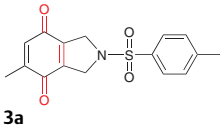
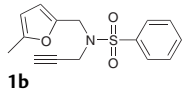
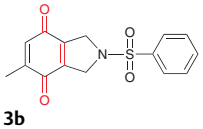
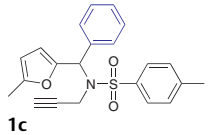
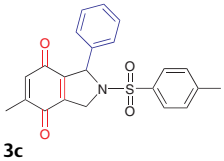
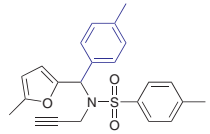
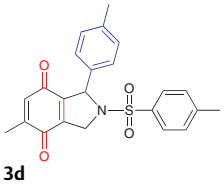
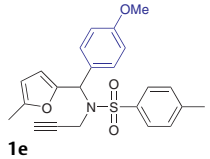
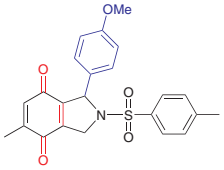
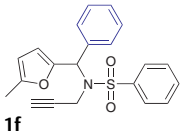
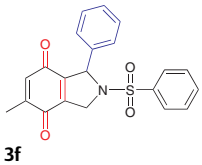
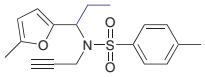
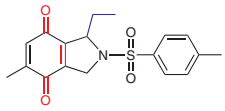
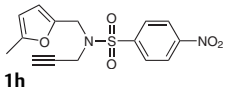
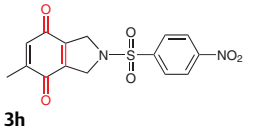
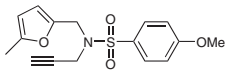
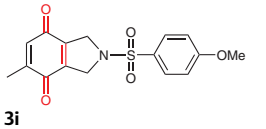
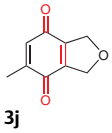
Entry	Compound	Product	Yield (%)
1	 **1a**	 **3a**	81
2	 **1b**	 **3b**	85
3	 **1c**	 **3c**	89
4	 **1d**	 **3d**	80
5	 **1e**	 **3e**	86

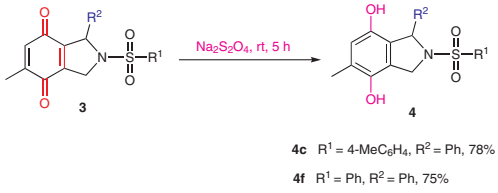
Table 2 (continued)

Entry	Compound	Product	Yield (%)
6[b]	 **1f**	 **3f**	84
7	 **1g**	 **3g**	73
8	 **1h**	 **3h**	79
9	 **1i**	 **3i**	86
10	 **1j**	 **3j**	62

[a] Reaction conditions: **1a** (1.0 equiv), $PhI(OAc)_2$ (2.0 equiv), $AuCl_3$ (5 mol%), MeCN (2 mL) and H_2O (1 mL) (0.16 M), rt, 1 h, air atmosphere.
[b] Product **3f** was obtained at 40 °C.

Despite the additional aromatic moieties, no trace of side product was observed even with 2.0 equivalents of iodobenzene diacetate. The reaction occurred selectively at the electron-rich phenol ring. The substrate **1g** with ethyl substituent could also be converted in good overall efficiency (Table 2, entry 7). Switching the substituent at the phenyl ring of furan–yne **1** to an electron-withdrawing nitro (**1h**) and electron-donating methoxy groups (**1i**) delivered a remarkably overall yield of products (entries 8 and 9). Changing the heteroatom in the starting material **1** from nitrogen to oxygen slightly reduced the yield (entry 10), but the overall yield of this one-pot protocol was still satisfactory. All products were characterized by spectral and analytical data. Unfortunately, all the attempts to obtain single crystals of these products were unsuccessful.

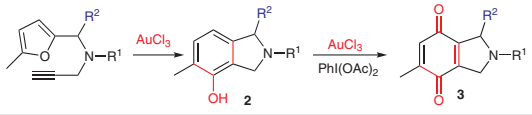
To evaluate the possibility of further derivatization of the *para*-benzoquinone **3**, based on Morey's report,[18] the substrate **3c** (1.0 mmol) and sodium dithionate (20.0 mmol) were grounded together at room temperature. Under this condition, the substrate **3c** was reduced to the corresponding hydroquinone compound **4c** in an excellent



Scheme 5 Reduction of benzoquinone to hydroquinone

yield. Also, the substrate **3f** was converted to hydroquinone **4f** under the same reaction condition (Scheme 5).

Although the mechanism of this reaction has not been established experimentally, however, a possible mechanism for the syntheses of the *para*-benzoquinones **3** according to previous chemistry, is proposed in Scheme 6. The first step of the mechanism involves the formation of phenol derivatives **2** by $AuCl_3$.[14] Then oxidation of phenol **2** in the presence of gold and $PhI(OAc)_2$ leads to the formation of the *para*-benzoquinone derivatives **3**.[19]

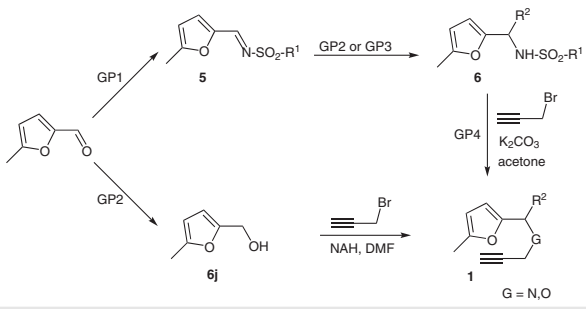


Scheme 6 Proposed mechanistic pathway

In summary, by using the same gold catalyst for two subsequent reaction steps, which consist of a furan–yne cyclization followed by a gold-assisted oxidation, new *para*-benzoquinones are feasible under exceptionally mild reaction conditions and in a one-pot process. Furthermore, the resulting *para*-benzoquinones can be readily transformed into the corresponding hydroquinones through reaction with sodium dithionate. This reaction may serve as a powerful procedure for the synthesis of other quinone systems.

All Chemicals were purchased from a commercial supplier (Aldrich, Merck, Alfa Aesar, and Wako) and were used without further purification. TLC analysis was performed using Silicycle precoated TLC plates (silica gel 60 F_{254}). The products were purified by preparative column chromatography on silica gel (0.063–0.200 mm; Merck). NMR spectra were recorded at rt in $CDCl_3$ on 500, 400, and 300 MHz spectrometers. The chemical shifts for ^1H NMR were recorded in ppm downfield from TMS with $CDCl_3$ (7.26 ppm) as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of $CDCl_3$ (77.16 ppm) as the internal standard. Coupling constants (*J*) are reported in hertz (Hz) and refer to apparent peak multiplications. IR spectra were recorded on a Magna 550 spectrometer. EI-MS (70 eV): HP 5973 GC-MS instrument; in *m*/*z*. Melting points: Electrothermal 9200 apparatus. Elemental analyses were performed with a Thermo Finnigan Flash-1112EA microanalyzer.

The generic route of preparing the substrate **1** is shown in Scheme 7.



Scheme 7 Generic routes of preparing the substrate **1**

Iminosulfones 5; General Procedure 1 (GP1)[20]

Iminosulfones **5** were prepared according to the literature. 5-Methylfurfural (1.0 equiv), sulfonamide (1.5 equiv), and Et_3N (5.0 equiv) were dissolved in CH_2Cl_2 and cooled to 0 °C. Afterwards, $TiCl_4$ (0.5 equiv) in CH_2Cl_2 was added at that temperature, and allowed to warm up to r.t with continuous stirring for 30 min (monitoring by TLC). The mixture was hydrolyzed with sat. aq $NaHCO_3$. The mixture was extracted with CH_2Cl_2 (2 ×) and the combined organic layers were washed with H_2O, dried (Na_2SO_4), and filtered. The solvent was removed under vacuum and the residue was recrystallized.

Aminosulfones 6; General Procedure 2 (GP2)[20]

Aminosulfones **6** were prepared according to the literature. In a Schlenk flask, the substrate **5** (1.0 equiv) was dissolved in MeOH under N_2. Then $NaBH_4$ (1.0 equiv) was added slowly and stirred overnight. After the slow addition of H_2O, the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and filtered. The solvent was removed under vacuum and the residue was washed with Et_2O.

Addition of Grignard Reagents to Iminosulfones 5; General Procedure 3 (GP 3)[14]

In a Schlenk flask, the iminosulfone **5** (1.0 equiv) was dissolved in THF under N_2 and cooled to –47 °C. Afterwards, the Grignard reagent (2.0 equiv) was added dropwise and the reaction mixture was stirred for 6 h at –47 °C, allowing to warm up to rt and then stirred overnight. The reaction was quenched by adding sat. aq NH_4Cl. The mixture was extracted with CH_2Cl_2 and the combined organic phases were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc).

Propargylation of Aminosulfones 6; General Procedure 4 (GP 4)[14]

The aminosulfone **6** was dissolved in acetone, K_2CO_3 (3.0 equiv) and propargyl bromide (3.0 equiv., 80% solution in toluene) were added and the mixture was stirred at rt for 24 h. Then the solvent was removed under vacuum, the residue was partitioned between H_2O and CH_2Cl_2 and the aqueous phase was extracted with CH_2Cl_2 (2 ×). The combined organic phases were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (*n*-hexane/EtOAc).

Gold-Catalyzed Synthesis of *para*-Benzoquinones 3; General Procedure 5 (GP 5)

In a dry Schlenk flask, propargylic aminosulfone **1** (1.0 equiv) was dissolved in anhyd MeCN. The gold catalyst (5 mol%) was added and the reaction mixture was stirred at rt for 10 min. The progress of the

reaction was monitored by TLC and after completion of the first step of the reaction flask was opened and PhI(OAc)$_2$ (2.0 equiv) and H_2O were added to this mixture. The mixture was stirred for 3 h at rt in air. After the completion of the reaction, the solvent was removed under vacuum then the residue extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuum. The product was purified by column chromatography on silica gel (*n*-hexane/EtOAc).

Reduction of *para*-Benzoquinones 3; General Procedure 6 (GP 6)[18]

para-Benzoquinone **3** (1.0 mmol) and sodium dithionite (20.0 mmol) were grounded together with the aid of a pestle and mortar. Drastic color changes were immediately observed. After several hours in an open vessel, the color completely disappeared. The standard workup yielded corresponding hydroquinone **4**.

4-Methyl-*N*-(5-methylfuran-2-ylmethylene)benzenesulfonamide (5a)[20]

According to GP 1, 5-methylfurfural (5.50 g, 50.0 mmol), *p*-toluenesulfonamide (12.84 g, 75.0 mmol), and Et_3N (25.30 g, 250.0 mmol) in CH_2Cl_2 (165 mL) and $TiCl_4$ (4.74 g, 25.0 mmol) in CH_2Cl_2 (16.5 mL) furnished **5a** as a light orange solid after recrystallization; yield: 11.84 g (90%, 45.0 mmol); mp 116–117 °C (Lit.[20] mp 118–119 °C).

IR (KBr): 3088, 2923, 1608, 1554, 1450, 1288, 1151 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69 (s, 1 H), 7.86 (d, *J* = 8.2 Hz, 2 H), 7.82 (d, *J* = 3.2 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 6.29 (d, *J* = 3.2 Hz, 1 H), 2.43 (s, 6 H).

All spectral data are in accordance with previous reports.[20]

***N*-(5-Methylfuran-2-ylmethylene)benzenesulfonamide (5b)**

According to GP 1, 5-methylfurfural (3.85 g, 35.0 mmol), benzenesulfonamide (8.98 g, 52.5 mmol), and Et_3N (17.70 g, 175.0 mmol) in CH_2Cl_2 (115 mL) and $TiCl_4$ (3.31 g, 17.5 mmol) in CH_2Cl_2 (11.5 mL) furnished **5b** as a bright yellow solid after recrystallization; yield: 4.90 g (57%, 20.0 mmol); mp 125–126 °C.

IR (KBr): 3120, 1781, 1604, 1549, 1446, 1322, 1288, 1154 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (s, 1 H), 7.97–7.99 (m, 2 H), 7.59–7.62 (m, 1 H), 7.53 (t, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 3.6 Hz, 1 H), 6.30 (d, *J* = 3.6 Hz, 1 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3, 155.1, 147.6, 138.7, 129.0, 127.8, 111.1, 14.3.

MS (EI, 70 eV): *m*/*z* (%) = 249 [M$^+$, 100], 172 (44), 168 (35), 81 (60), 77 (85).

Anal. Calcd for $C_{12}H_{11}NO_3S$: C, 57.82; H, 4.45; N, 5.62. Found: C, 57.78; H, 4.43; N, 5.60.

4-Methyl-*N*-(5-methylfuran-2-ylmethyl)benzenesulfonamide (6a)[20]

According to GP 2, **5a** (2.08 g, 8.0 mmol) and $NaBH_4$ (0.28 g, 8.0 mmol) in MeOH (12 mL) furnished **6a** as a pure pale white solid; yield: 1.51 g (71%, 5.7 mmol); mp 79–80 °C (Lit.[20] mp 82–83 °C).

IR (KBr): 3256, 2923, 1590, 1570, 1434, 1321, 1219, 1159 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 6.0 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 5.96 (d, *J* = 2.8 Hz, 1 H), 5.77 (s, 1 H), 4.72 (s, 1 H), 4.11 (s, 2 H), 2.42 (s, 3 H), 2.13 (s, 3 H).

All spectral data are in accordance with previous reports.[20]

***N*-(5-Methylfuran-2-ylmethyl)benzenesulfonamide (6b)**

According to GP 2, **5b** (2.50 g, 10.0 mmol) and $NaBH_4$ (0.35 g, 10.0 mmol) in MeOH (12 mL) furnished **6b** as a pure pale white solid; yield: 1.80 g (73%, 7.3 mmol); mp 84–85 °C.

IR (KBr): 3313, 3065, 2922, 1614, 1564, 1441, 1318, 1221, 1156 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 7.2 Hz, 2 H), 7.56 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.2 Hz, 2 H), 5.94 (s, 1 H), 5.75 (s, 1 H), 4.86 (s, 1 H), 4.15 (d, *J* = 6.0 Hz, 2 H), 2.11 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 147.4, 140.0, 132.5, 128.9, 127.0, 109.1, 106.1, 40.2, 13.3.

MS (EI, 70 eV): *m*/*z* (%) = 251 [M$^+$, 100], 174 (80), 156 (55), 141 (40), 110 (35), 95 (65), 77 (75).

Anal. Calcd for $C_{12}H_{13}NO_3S$: C, 57.35; H, 5.21; N, 5.57. Found: C, 57.30; H, 5.28; N, 5.54.

4-Methyl-*N*-[(5-methylfuran-2-yl)(phenyl)methyl]benzenesulfonamide (6c)[14]

According to GP 3, **5a** (1.05 g, 4.0 mmol) and phenylmagnesium bromide (8.0 mL, 8.0 mmol, 1.0 M solution in THF) in THF (15 mL) furnished **6c** as a yellow solid after purification by column chromatography (eluent: PE/EtOAc 4:1); yield: 1.22 g (90%, 3.6 mmol); mp 109–110 °C (Lit.[14] mp 109 °C).

IR (KBr): 3316, 2920, 1599, 1417, 1327, 1157 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.0 Hz, 2 H), 7.20–7.24 (m, 5 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 5.83 (d, *J* = 2.8 Hz, 1 H), 5.74 (d, *J* = 1.6 Hz, 1 H), 5.56 (d, *J* = 7.2 Hz, 1 H), 5.14 (d, *J* = 7.2 Hz, 1 H), 2.38 (s, 3 H), 2.10 (s, 3 H).

All spectral data are in accordance with previous reports.[14]

4-Methyl-*N*-[(5-methylfuran-2-yl)(4-methylphenyl)methyl]benzenesulfonamide (6d)[14]

According to GP 3, **5a** (1.57 g, 6.0 mmol) and *p*-tolylmagnesium bromide (12.0 mL, 12.0 mmol, 1.0 M solution in THF) in THF (20 mL) furnished **6d** as a pale yellow solid after purification by column chromatography (eluent: PE/EtOAc 9:1); yield: 1.95 g (92%, 5.5 mmol); mp 109–110 °C (Lit.[14] mp 111 °C).

IR (KBr): 3287, 2920, 1916, 1599, 1433, 1329, 1157 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.09 (d, *J* = 8.0 Hz, 2 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 5.85 (d, *J* = 2.8 Hz, 2 H), 5.74 (s, 1 H), 5.52 (d, *J* = 7.2 Hz, 1 H), 5.20 (d, *J* = 7.6 Hz, 1 H), 2.38 (s, 3 H), 2.30 (s, 3 H), 2.09 (s, 3 H).

All spectral data are in accordance with previous reports.[14]

***N*-[(4-Methoxyphenyl)(5-methylfuran-2-yl)methyl]-4-methylbenzenesulfonamide (6e)**[21]

According to GP 3, **5a** (1.31 g, 5.0 mmol) and 4-methoxymagnesium bromide (10.0 mL, 10.0 mmol, 1.0 M solution in THF) in THF (20 mL) furnished **6e** as a white solid after purification by column chromatography (eluent: PE/EtOAc 4:1); yield: 1.67 g (89%, 4.5 mmol); mp 98–99 °C (Lit.[21] mp 101–102 °C).

IR (KBr): 3284, 2921, 1612, 1514, 1444, 1324, 1155 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.6 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.11 (d, *J* = 8.4 Hz, 2 H), 6.76 (d, *J* = 8.0 Hz, 2 H), 5.83 (s, 1 H), 5.73 (s, 1 H), 5.50 (d, *J* = 7.2 Hz, 1 H), 5.17 (d, *J* = 7.2 Hz, 1 H), 3.77 (s, 3 H), 2.38 (s, 3 H), 2.09 (s, 3 H).

All spectral data are in accordance with previous reports.[21]

***N*-[(5-Methylfuran-2-yl)(phenyl)methyl]benzenesulfonamide (6f)**

According to GP 3, **5b** (2.00 g, 8.0 mmol) and phenylmagnesium bromide (16.0 mL, 16.0 mmol, 1.0 M solution in THF) in THF (25 mL) furnished **6f** as a bright yellow solid after purification by column chromatography (eluent: PE/EtOAc 4:1); yield: 2.29 g (88%, 7.0 mmol); mp 119–120 °C.

IR (KBr): 3259, 2922, 1562, 1449, 1319, 1161 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.36 (t, *J* = 7.6 Hz, 2 H), 7.20–7.24 (m, 5 H), 5.83 (d, *J* = 2.8 Hz, 1 H), 5.73 (d, *J* = 1.6 Hz, 1 H), 5.59 (d, *J* = 7.6 Hz, 1 H), 5.30 (d, *J* = 7.6 Hz, 1 H), 2.09 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3, 150.1, 140.4, 138.3, 132.2, 128.6, 128.4, 127.9, 127.2, 127.0, 109.3, 106.0, 55.6, 13.3.

MS (EI, 70 eV): *m*/*z* (%) = 327 [M^+, 100], 250 (60), 186 (75), 171 (40), 141 (55), 77 (70).

Anal. Calcd for $C_{18}H_{17}NO_3S$: C, 66.04; H, 5.23; N, 4.28. Found: C, 66.06; H, 5.26; N, 4.27.

4-Methyl-*N*-[1-(5-methylfuran-2-yl)propyl]benzenesulfonamide (6g)[14]

According to GP 3, **5a** (1.31 g, 5.0 mmol) and ethylmagnesium bromide (10.0 mL, 10.0 mmol, 1.0 M solution in THF) in THF (20 mL) furnished **6g** as a white solid after purification by column chromatography (eluent: PE/EtOAc 9:1); yield: 1.20 g (82%, 4.1 mmol); mp 77–78 °C (Lit.[14] mp 77 °C).

IR (KBr): 3256, 3111, 2921, 2855, 1598, 1434, 1321, 1160, 1094, 1042 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (t, *J* = 8.4 Hz, 2 H), 7.20 (t, *J* = 8.0 Hz, 2 H), 5.80 (d, *J* = 6.8 Hz, 1 H), 5.67 (d, *J* = 6.8 Hz, 1 H), 4.76 (t, *J* = 8.4 Hz, 1 H), 4.25 (t, *J* = 8.0 Hz, 1 H), 2.39 (d, *J* = 9.2 Hz, 3 H), 2.05 (d, *J* = 9.2 Hz, 3 H), 1.78 (q, *J* = 8.0 Hz, 2 H), 0.86 (q, *J* = 8.0 Hz, 3 H).

All spectral data are in accordance with previous reports.[14]

***N*-[(5-Methylfuran-2-yl)methyl]-4-nitrobenzenesulfonamide (6h)**[22]

To 5-methylfurfurylamine (2.50 g, 22.5 mmol) and Et_3N (2.28 g, 22.5 mmol) in CH_2Cl_2 (35 mL) at rt was added nosyl chloride (4.98 g, 22.5 mmol) in small portions and then stirred overnight. After the slow addition of H_2O (30 mL), separation of the organic layer, extractions of the aqueous layer with CH_2Cl_2 (2 × 15 mL), the combined organic layers were dried (Na_2SO_4) and filtered. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: PE/EtOAc, 8:2) to afford **6h** as a yellow solid; yield: 5.54 g (83%, 18.7 mmol); mp 93–95 °C.

IR (KBr): 3311, 3059, 2920, 1617, 1562, 1444, 1321, 1220 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 8.2 Hz, 2 H), 7.95 (d, *J* = 8.2 Hz, 2 H), 5.98 (d, *J* = 3.0 Hz, 1 H), 5.86 (d, *J* = 3.0 Hz, 1 H), 4.73 (m, 1 H), 4.16 (d, *J* = 6.0 Hz, 2 H), 2.12 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.2, 150.3, 146.6, 137.7, 129.2, 124.7, 109.2, 106.0, 44.3, 13.3.

MS (EI, 70 eV): *m*/*z* (%) = 296 [M^+, 100], 185 (75), 174 (65), 122(40), 110 (45), 95 (50), 81 (65).

Anal. Calcd for $C_{12}H_{12}N_2O_5S$: C, 48.64; H, 4.08; N, 9.45. Found: C, 48.66; H, 4.09; N, 9.43.

4-Methoxy-*N*-[(5-methylfuran-2-yl)methyl]benzenesulfonamide (6i)[22]

To 5-methylfurfurylamine (2.50 g, 22.5 mmol) and Et_3N (2.28 g, 22.5 mmol) in CH_2Cl_2 (35 mL) at rt was added 4-methoxybenzenesulfonyl chloride (4.65 g, 22.5 mmol) in small portions and then stirred overnight. After the slow addition of H_2O (30 mL), separation of the organic layer, extractions of the aqueous layer with CH_2Cl_2 (2 × 15 mL), the combined organic layers were dried (Na_2SO_4) and filtered. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: PE/EtOAc 8:2) to afford **6i** as a white solid; yield: 5.51 g (87%, 19.6 mmol); mp 76–78 °C.

IR (KBr): 3323, 3055, 2921, 1611, 1560, 1441, 1318, 1222 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 5.97 (s, 1 H), 5.79 (s, 1 H), 4.70 (s, 1 H), 4.13 (d, *J* = 5.0 Hz, 2 H), 3.91 (s, 3 H), 2.15 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.8, 152.3, 147.6, 137.0, 124.8, 115.0, 109.1, 106.2, 53.8, 40.3, 13.3.

MS (EI, 70 eV): *m*/*z* (%) = 281 [M^+, 100], 186 (85), 174 (55), 171(55), 107 (70), 95 (60), 81 (55).

Anal. Calcd for $C_{13}H_{15}NO_4S$: C, 55.50; H, 5.37; N, 4.98. Found: C, 55.48; H, 5.35; N, 4.95.

(5-Methylfuran-2-yl)methanol (6j)[23]

In a flame-dried Schlenk tube under an atmosphere of N_2, 5-methylfurfural (1.25 g, 11.3 mmol) was dissolved in anhyd MeOH (15 mL). $NaBH_4$ (0.85 g, 22.7 mmol) was added, and the mixture was stirred for 16 h at rt. H_2O was added, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and filtered. Evaporation of the solvent afforded **6j** as an orange oil. The crude product was used in the next step without further purification; yield: 1.18 g (94%, 10.6 mmol).

IR (KBr): 3406, 2960, 2940, 2880, 1556, 1442, 1085, 1020 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.14 (d, *J* = 3.0 Hz, 1 H), 5.90 (d, *J* = 3.0 Hz, 1 H), 4.51 (s, 2 H), 2.33 (s, 1 H), 2.26 (s, 3 H).

All spectral data are in accordance with previous reports.[23]

4-Methyl-*N*-[(5-methylfuran-2-yl)methyl]-*N*-(prop-2-yne-1-yl)benzenesulfonamide (1a)[20]

According to GP 4, **6a** (2.60 g, 10.0 mmol), K_2CO_3 (2.70 g, 20.0 mmol), and propargyl bromide (2.38 g, 20.0 mmol, 80% solution in toluene) in acetone (18 mL) furnished **1a** as a pale white solid after purification by column chromatography (eluent: PE/EtOAc 9:1); yield: 2.88 g (95%, 9.5 mmol); mp 69–70 °C (Lit.[20] mp 68–71 °C).

IR (KBr): 3277, 2923, 2118, 1596, 1430, 1159 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 6.16 (s, 1 H), 5.87 (s, 1 H), 4.38 (s, 2 H), 4.02 (s, 2 H), 2.43 (s, 3 H), 2.21 (s, 3 H), 2.06 (s, 1 H).

All spectral data are in accordance with previous reports.[20]

***N*-[(5-Methylfuran-2-yl)methyl]-*N*-(prop-2-yne-1-yl)benzenesulfonamide (1b)**

According to GP 4, **6b** (3.00 g, 12.0 mmol), K_2CO_3 (3.30 g, 24.0 mmol), and propargyl bromide (2.85 g, 24.0 mmol, 80% solution in toluene) in acetone (20 mL) furnished **1b** as a pale-yellow solid after purification by column chromatography (eluent: PE/EtOAc 9:1); yield: 3.29 g (95%, 11.4 mmol); mp 69–70 °C.

IR (KBr): 3288, 3065, 2922, 2120, 1478, 1350, 1163 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 7.0 Hz, 2 H), 7.57 (t, *J* = 7.5 Hz, 1 H), 7.49 (t, *J* = 8.0 Hz, 2 H), 6.15 (s, 1 H), 5.85 (s, 1 H), 4.39 (s, 2 H), 4.03 (s, 2 H), 2.19 (s, 3 H), 2.04 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 146.3, 139.0, 132.7, 128.8, 127.7, 111.1, 106.3, 76.4, 73.8, 42.9, 36.0, 13.5.

MS (EI, 70 eV): *m*/*z* (%) = 289 [M$^+$, 100], 212 (40), 194 (45), 148 (60), 141 (75), 77 (80).

Anal. Calcd for $C_{15}H_{15}NO_3S$: C, 62.27; H, 5.23; N, 4.84. Found: C, 62.30; H, 5.21; N, 4.80.

4-Methyl-*N*-[(5-methylfuran-2-yl)(phenyl)methyl]-*N*-(prop-2-yne-1-yl)benzenesulfonamide (1c)[14]

According to GP 4, **6c** (1.70 g, 5.0 mmol), K_2CO_3 (1.38 g, 10.0 mmol), and propargyl bromide (1.08 g, 10.0 mmol, 80% solution in toluene) in acetone (10 mL) furnished **1c** as a bright yellow oil after purification by column chromatography (eluent: PE/EtOAc 9:1); yield: 1.78 g (94%, 4.7 mmol).

IR (KBr): 3292, 3030, 2923, 2122, 1599, 1449, 1345, 1218, 1160 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.4 Hz, 2 H), 7.32 (m, 6 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 6.30 (s, 1 H), 5.97 (d, *J* = 2.8 Hz, 2 H), 5.84 (s, 1 H), 4.18 (dd, *J* = 18.4, 2 Hz, 1 H), 3.94 (dd, *J* = 18.4, 2 Hz, 1 H), 2.42(s, 3 H), 2.12 (s, 3 H), 1.90 (s, 1 H).

All spectral data are in accordance with previous reports.[14]

4-Methyl-*N*-[(5-methylfuran-2-yl)(4-methylphenyl)methyl]-*N*-(prop-2-yne-1-yl)benzenesulfonamide (1d)[14]

According to GP 4, **6d** (1.42 g, 4.0 mmol), K_2CO_3 (1.65 g, 12.0 mmol), and propargyl bromide (1.08 g, 10.0 mmol, 80% solution in toluene) in acetone (10 mL) furnished **1d** as a white solid after purification by column chromatography (eluent: PE/EtOAc 9:1); yield: 1.41 g (91%, 3.6 mmol); mp 99–100 °C (Lit.[14] mp 101 °C).

IR (KBr): 3296, 2922, 2120, 1597, 1413, 1329, 1157 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 8.0 Hz, 2 H), 6.25 (s, 1 H), 5.97 (d, *J* = 2.8 Hz, 1 H), 5.84 (s, 1 H), 4.18 (dd, *J* = 18.4, 2.4 Hz, 1 H), 3.93 (dd, *J* = 18.4, 2.4 Hz, 1 H), 2.42 (s, 3 H), 2.34 (s, 3 H), 2.12 (s, 3 H), 1.90 (s, 1 H).

All spectral data are in accordance with previous reports.[14]

***N*-[(4-Methoxyphenyl)(5-methylfuran-2-yl)methyl]-4-methyl-*N*-(prop-2-yne-1-yl)benzenesulfonamide (1e)**

According to GP 4, **6e** (1.85 g, 5.0 mmol), K_2CO_3 (2.07 g, 15.0 mmol), and propargyl bromide (1.08 g, 10.0 mmol, 80% solution in toluene) in acetone (10 mL) furnished **1e** as a yellow oil after purification by column chromatography (eluent: PE/EtOAc 9:1); yield: 1.92 g (93%, 4.7 mmol).

IR (KBr): 3288, 2923, 2121, 1609, 1457, 1250, 1160 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.0 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 4 H), 6.84 (d, *J* = 8.4 Hz, 2 H), 6.23 (s, 1 H), 5.97 (d, *J* = 3.2 Hz, 1 H), 5.83 (d, *J* = 3.2 Hz, 1 H), 4.19 (dd, *J* = 18.4, 2.4 Hz, 1 H), 3.97 (dd, *J* = 18.4, 2.4 Hz, 1 H), 3.80 (s, 3 H), 2.42 (s, 3 H), 2.12 (s, 3 H),1.91 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 152.1, 149.2, 143.2, 137.1, 129.6, 129.4, 129.1, 128.6, 127.8, 127.3, 111.4, 106.5, 78.9, 71.7, 55.2, 34.4, 21.5, 13.4.

MS (EI, 70 eV): *m*/*z* (%) = 409 [M$^+$, 90], 328 (75), 318 (45), 254 (80), 208 (75), 155 (55), 91 (100).

Anal. Calcd for $C_{23}H_{23}NO_4S$: C, 67.46; H, 5.66; N, 3.42. Found: C, 67.43; H, 5.64; N, 3.40.

***N*-[(5-Methylfuran-2-yl)(phenyl)methyl]-*N*-(prop-2-yne-1-yl)benzenesulfonamide (1f)**

According to GP 4, **6f** (1.30 g, 4.0 mmol), K_2CO_3 (1.65 g, 12.0 mmol), and propargyl bromide (1.08 g, 10.0 mmol, 80% solution in toluene) in acetone (10 mL) furnished **1f** as a yellow oil after purification by column chromatography (eluent: PE/EtOAc 9:1); yield: 1.24 g (85%, 3.4 mmol).

IR (KBr): 3290, 3063, 2922, 2122, 1605, 1447, 1346, 1219, 1162 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, *J* = 7.2 Hz, 2 H), 7.54 (d, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 8.0 Hz, 2 H), 7.32 (m, 5 H), 6.31 (s, 1 H), 5.96 (d, *J* = 2.8 Hz, 1 H), 5.83 (d, *J* = 2.0 Hz, 2 H), 5.30 (s, 1 H), 4.20 (dd, *J* = 18.4, 2.4 Hz, 1 H), 3.95 (dd, *J* = 18.4, 2.4 Hz, 1 H), 2.11 (s, 3 H), 1.87 (t, *J* = 2.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3, 148.9, 140.1, 136.6, 132.4, 128.4, 128.4, 128.0, 127.9, 127.9, 111.7, 106.1, 78.5, 71.6, 58.8, 34.6, 13.4.

MS (EI, 70 eV): *m*/*z* (%) = 365 [M$^+$, 90], 288 (65), 224 (55), 194 (35), 141 (60), 77 (100).

Anal. Calcd for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24; N, 3.83. Found: C, 68.98; H, 5.22; N, 3.82.

4-Methyl-*N*-[1-(5-methylfuran-2-yl)propyl]-*N*-(prop-2-yne-1-yl)benzenesulfonamide (1g)[14]

According to GP 4, **6g** (1.46 g, 5.0 mmol), K_2CO_3 (2.07 g, 15.0 mmol), and propargyl bromide (1.08 g, 10.0 mmol, 80% solution in toluene) in acetone (10 mL) furnished **1g** as a pale red oil after purification by column chromatography (eluent: PE/EtOAc 9:1); yield: 1.42 g (85%, 4.3 mmol).

IR (KBr): 3275, 2924, 2119, 1597, 1431, 1158, 1115, 1094 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.2 Hz, 2 H), 7.27 (d, *J* = 7.2 Hz, 2 H), 6.00 (s, 1 H), 5.79 (s, 1 H), 4.89 (t, *J* = 7.2 Hz, 1 H), 3.95 (d, *J* = 18.4 Hz, 1 H), 3.76 (d, *J* = 18.4 Hz, 1 H), 2.42 (s, 3 H), 2.04 (s, 3 H), 2.01 (s, 1 H), 1.96–2.02 (q, *J* = 7.2 Hz, 2 H), 1.01 (t, *J* = 7.2 Hz, 3 H).

All spectral data are in accordance with previous reports.[14]

***N*-[(5-Methylfuran-2-yl)methyl]-4-nitro-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1h)**

According to GP 4, **6h** (3.55 g, 12.0 mmol), K_2CO_3 (3.30 g, 24.0 mmol), and propargyl bromide (2.85 g, 24.0 mmol, 80% solution in toluene) in acetone (20 mL) furnished **1h** as a yellow solid after purification by column chromatography (eluent: PE/EtOAc 8:2); yield: 3.64 g (91%, 10.9 mmol); mp 81–83 °C.

IR (KBr): 3293, 2921, 2120, 1595, 1414, 1338, 1156 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, *J* = 8.2 Hz, 2 H), 7.90 (d, *J* = 8.2 Hz, 2 H), 6.15 (s, 1 H), 5.86 (s, 1 H), 4.38 (s, 2 H), 4.02 (d, *J* = 3.0 Hz, 2 H), 2.20 (s, 3 H), 2.06 (t, *J* = 3.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.7, 150.1, 142.9, 137.8, 129.1, 127.8, 112.0, 107.9, 79.6, 71.5, 46.5, 33.5, 13.3.

MS (EI, 70 eV): *m*/*z* (%) = 334 [M$^+$, 100], 295 (70), 239 (65), 212 (40), 194 (35), 122 (75), 116 (60), 95 (80).

Anal. Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.89; H, 4.22; N, 8.38. Found: C, 53.85; H, 4.20; N, 8.37.

4-Methoxy-*N*-[(5-methylfuran-2-yl)methyl]-*N*-(prop-2-yn-1-yl)benzenesulfonamide (1i)

According to GP 4, **6i** (3.37 g, 12.0 mmol), K_2CO_3 (3.30 g, 24.0 mmol), and propargyl bromide (2.85 g, 24.0 mmol, 80% solution in toluene) in acetone (20 mL) furnished **1i** as a white solid after purification by column chromatography (eluent: PE/EtOAc 8:2); yield: 3.60 g (94%, 11.3 mmol); mp 72–74 °C.

IR (KBr): 3285, 2921, 2120, 1611, 1456, 1248, 1161 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 6.9 Hz, 2 H), 7.25 (d, *J* = 6.9 Hz, 2 H), 6.17 (s, 1 H), 5.81 (s, 1 H), 4.35 (s, 2 H), 3.98 (s, 2 H), 3.90 (s, 3 H), 2.19 (s, 3 H), 1.97 (t, *J* = 3.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.0, 152.2, 143.2, 137.7, 125.1, 116.2, 111.5, 106.1, 78.8, 73.5, 52.7, 42.8, 34.5, 13.5.

MS (EI, 70 eV): *m*/*z* (%) = 319 [M^+, 100], 280 (70), 224 (45), 212 (55), 107 (65), 95 (85).

Anal. Calcd for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.37; N, 4.39. Found: C, 60.20; H, 5.38; N, 4.41.

(Methylfuran-2-yl)methanol (1j)[23]

In a three-necked flask under an atmosphere of N_2, alcohol **6j** (5.0 mmol, 1.0 equiv) was dissolved in anhyd DMF (20 mL) and cooled to 0 °C. NaH (2.0 equiv, 60% dispersion in mineral oil) was added slowly. After stirring for 15 min at 0 °C, propargyl bromide (2.0 equiv, 80% in toluene) was added. The mixture was stirred for 16 h at rt. H_2O was added, and the product was extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated. The crude product was purified by column chromatography on silica gel (eluent: PE/EtOAc 9:1) to yield **1j** as a yellow oil; yield: 0.69 g (92%, 4.6 mmol).

IR (KBr): 3295, 2958, 2922, 2129, 1551, 1444, 1221, 1061, 927 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.24 (d, *J* = 3.0 Hz, 1 H), 5.92–5.95 (m, 1 H), 4.49 (s, 2 H), 4.15 (d, *J* = 2.4 Hz, 2 H), 2.46 (t, *J* = 2.4 Hz, 1 H), 2.29 (s, 3 H).

All spectral data are in accordance with previous reports.[23]

5-Methyl-2-tosyl-2,3-dihydro-1*H*-isoindole-4,7-dione (3a)

The reaction was carried out according to GP 5: **1a** (0.15 g, 0.50 mmol, 1.0 equiv), $AuCl_3$ (6 mg, 0.02 mmol, 5 mol%) in anhyd MeCN (4 mL) and $PhI(OAc)_2$ (0.32 g 1.0 mmol, 2.0 equiv) in H_2O (2 mL). Compound **3a** was obtained as a green solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.12 g (81%, 0.40 mmol); R_f = 0.66 (*n*-hexane/EtOAc 8:2); mp 186–187 °C.

IR (KBr): 2924, 1658, 1608, 1457, 1348, 1162 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 10.8 Hz, 2 H), 7.33 (d, *J* = 10.8 Hz, 2 H), 6.50 (d, *J* = 2.4 Hz, 1 H), 4.48 (s, 4 H), 2.41 (s, 3 H), 2.01 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.6, 183.2, 146.4, 144.2, 142.0, 141.8, 133.4, 133.2, 130.0, 127.4, 53.0, 52.9, 21.5, 15.4. DEPT: 133.3, 130.1, 127.5, 53.0, 21.5, 15.4.

MS (EI, 70 eV): *m*/*z* (%) = 317 [M^+, 100], 226 (70), 162 (55), 155 (65), 91 (90).

Anal. Calcd for $C_{16}H_{15}NO_4S$: C, 60.55; H, 4.76; N, 4.41. Found: C, 60.23; H, 4.71; N, 4.35.

5-Methyl-2-(phenylsulfonyl)-2,3-dihydro-1*H*-isoindole-4,7-dione (3b)

The reaction was carried out according to GP 5: **1b** (0.14 g, 0.50 mmol, 1.0 equiv), $AuCl_3$ (6 mg, 0.02 mmol, 5 mol%) in anhyd MeCN (4 mL) and $PhI(OAc)_2$ (0.32 g, 1.0 mmol, 2.0 equiv) in H_2O (2 mL). Compound **3b** was obtained as a pale yellow solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.12 g (85%, 0.42 mmol); R_f = 0.55 (*n*-hexane/EtOAc 8:2); mp 150–151 °C.

IR (KBr): 2924, 1658, 1610, 1445, 1351, 1164 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.5 Hz, 2 H), 7.62 (t, *J* = 7.0 Hz, 1 H), 7.55 (t, *J* = 7.0 Hz, 2 H), 6.51 (s, 1 H), 4.51 (s, 4 H), 2.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.6, 183.2, 146.4, 142.0, 141.8, 136.5, 133.2, 129.5, 127.4, 53.1, 52.9, 15.4.

MS (EI, 70 eV): *m*/*z* (%) = 303 [M^+, 100], 226 (65), 162 (40), 141 (45), 77 (80).

Anal. Calcd for $C_{15}H_{13}NO_4S$: C, 59.40; H, 4.32; N, 4.62. Found: C, 59.51; H, 4.28; N, 4.66.

5-Methyl-1-phenyl-2,3-dihydro-1*H*-isoindole-4,7-dione (3c)

The reaction was carried out according to GP 5: **1c** (0.22 g, 0.60 mmol, 1.0 equiv), $AuCl_3$ (9 mg, 0.03 mmol, 5 mol%) in anhyd MeCN (4 mL) and $PhI(OAc)_2$ (0.38 g, 1.2 mmol, 2.0 equiv) in H_2O (2 mL). Compound **3c** was obtained as a light green solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.20 g (89%, 0.53 mmol); R_f = 0.60 (*n*-hexane/EtOAc 8:2); mp 130–131 °C.

IR (KBr): 3063, 2924, 1663, 1602, 1454, 1342, 1160 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 8.0 Hz, 2 H), 7.26–7.27 (m, 5 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 6.42 (s, 1 H), 5.99 (dd, *J* = 5.6, 2.4 Hz, 1 H), 4.74 (dd, *J* = 17.2, 2.4 Hz, 1 H), 4.61 (dd, *J* = 17.2, 6.0 Hz, 1 H), 2.38 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.3, 182.7, 145.9, 144.0, 143.7, 140.9, 138.0, 135.2, 133.7, 129.6, 128.5, 128.4, 127.5, 127.1, 68.9, 52.7, 21.4, 15.3.

MS (EI, 70 eV): *m*/*z* (%) = 393 [M^+, 100], 316 (75), 302 (50), 238 (45), 161 (60), 91 (80), 77 (75).

Anal. Calcd for $C_{22}H_{19}NO_4S$: C, 67.16; H, 4.87; N, 3.56. Found: C, 67.10; H, 4.84; N, 3.51.

5-Methyl-1-(*p*-tolyl)-2,3-dihydro-1*H*-isoindole-4,7-dione (3d)

The reaction was carried out according to GP 5: **1d** (0.18 g, 0.47 mmol, 1.0 equiv), $AuCl_3$ (6 mg, 0.02 mmol, 5 mol%) in anhyd MeCN (4 mL) and $PhI(OAc)_2$ (0.30 g, 0.94 mmol, 2.0 equiv) in H_2O (2 mL). Compound **3d** was obtained as a yellow solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.15 g (80%, 0.37 mmol); R_f = 0.58 (*n*-hexane/EtOAc 8:2); mp 145–146 °C.

IR (KBr): 2922, 1660, 1601, 1454, 1343, 1161 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 7.5 Hz, 2 H), 7.05 (d, *J* = 7.5 Hz, 2 H), 6.40 (s, 1 H), 5.94 (d, *J* = 5.5 Hz, 1 H), 4.71 (dd, *J* = 17.0, 2.0 Hz, 1 H), 4.60 (dd, *J* = 17.5, 5.5 Hz, 1 H), 2.37 (s, 3 H), 2.30 (s, 3 H), 2.01 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.4, 182.8, 167.7, 145.9, 143.6, 138.3, 135.1, 130.8, 129.5, 129.2, 128.7, 127.4, 127.2, 68.7, 52.6, 21.4, 21.1, 15.3.

MS (EI, 70 eV): *m*/*z* (%) = 407 [M^+, 100], 316 (80), 168 (55), 252 (60), 91 (90).

Anal. Calcd for $C_{23}H_{21}NO_4S$: C, 67.79; H, 5.19; N, 3.44. Found: C, 67.71; H, 5.16; N, 3.40.

1-(4-Methoxyphenyl)-5-methyl-2-tosyl-2,3-dihydro-1*H*-isoindole-4,7-dione (3e)

The reaction was carried out according to GP 5: **1e** (0.28 g, 0.70 mmol, 1.0 equiv), $AuCl_3$ (9 mg, 0.03 mmol, 5 mol%) in anhyd MeCN (4 mL) and $PhI(OAc)_2$ (0.45 g, 1.4 mmol, 2.0 equiv) in H_2O (2 mL). Compound **3e** was obtained as a light green solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.25 g (86%, 0.60 mmol); R_f = 0.55 (*n*-hexane/EtOAc 8:2); mp 122–123 °C.

IR (KBr): 2925, 1661, 1607, 1439, 1343, 1160 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.6 Hz, 2 H), 7.15–7.19 (m, 4 H), 6.78 (d, *J* = 8.0 Hz, 2 H), 6.42 (s, 1 H), 5.96 (s, 1 H), 4.71 (d, *J* = 16.8 Hz, 1 H), 4.59 (dd, *J* = 16.8, 5.6 Hz, 1 H), 3.79 (s, 3 H), 2.38 (s, 3 H), 2.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.4, 182.8, 159.6, 145.9, 144.0, 143.6, 140.6, 135.3, 133.6, 130.1, 129.6, 128.7, 127.1, 113.9, 68.4, 55.2, 52.5, 21.4, 15.3.

MS (EI, 70 eV): *m*/*z* (%) = 423 [M^+, 100], 332 (65), 268 (45), 107 (75), 91 (80).

Anal. Calcd for $C_{23}H_{21}NO_5S$: C, 65.23; H, 5.00; N, 3.31. Found: C, 65.27; H, 5.03; N, 3.28.

5-Methyl-1-phenyl-2-(phenylsulfonyl)-2,3-dihydro-1*H*-isoindole-4,7-dione (3f)

The reaction was carried out according to GP 5: **1f** (0.21 g, 0.60 mmol, 1.0 equiv), $AuCl_3$ (9 mg, 0.03 mmol, 5 mol%) in anhyd MeCN (4 mL) and $PhI(OAc)_2$ (0.38 g, 1.2 mmol, 2.0 equiv) in H_2O (2 mL). Compound **3f** was obtained as a yellow solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.18 g (84%, 0.50 mmol); R_f = 0.60 (*n*-hexane/EtOAc 8:2); mp 107–108 °C.

IR (KBr): 3063, 2924, 1660, 1596, 1448, 1345, 1164, 1098 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 7.6 Hz, 2 H), 7.48 (d, *J* = 7.2 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 3 H), 7.23–7.26 (m, 5 H), 6.42 (s, 1 H), 6.02 (s, 1 H), 4.77 (dd, *J* = 16.8, 2.0 Hz, 1 H), 4.59 (dd, *J* = 16.8, 6.0 Hz, 1 H), 2.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.3, 182.6, 146.0, 144.0, 140.8, 138.3, 137.7, 133.6, 132.7, 131.2, 129.0, 128.6, 127.5, 126.9, 68.9, 52.7, 15.3.

MS (EI, 70 eV): *m*/*z* (%) = 379 [M^+, 100], 302 (65), 238 (50), 141 (45), 77 (95).

Anal. Calcd for $C_{21}H_{17}NO_4S$: C, 66.48; H, 4.52; N, 3.69. Found: C, 66.42; H, 4.50; N, 3.65.

1-Ethyl-5-methyl-2-tosyl-2,3-dihydro-1*H*-isoindole-4,7-dione (3g)

The reaction was carried out according to GP 5: **1g** (0.18 g, 0.55 mmol, 1.0 equiv), $AuCl_3$ (6 mg, 0.02 mmol, 5 mol%) in anhyd MeCN (4 mL) and $PhI(OAc)_2$ (0.35 g, 1.10 mmol, 2.0 equiv) in H_2O (2 mL). Compound **3g** was obtained as a light red oil after column chromatography (eluent: *n*-hexane/EtOAc 9:1); yield: 0.13 g (73%, 0.40 mmol); R_f = 0.52 (*n*-hexane/EtOAc 9:1).

IR (KBr): 2969, 2930, 1659, 1608, 1453, 1348, 1162 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.5 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 6.45 (s, 1 H), 5.02 (s, 1 H), 4.45 (t, *J* = 3.0 Hz, 2 H), 2.40 (s, 3 H), 2.00 (s, 3 H), 1.09 (q, *J* = 7.5 Hz, 2 H), 0.82 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.1, 143.8, 142.0, 138.4, 134.3, 130.5, 130.0, 127.5, 127.3, 67.1, 53.1, 26.9, 21.5, 15.2, 7.9.

MS (EI, 70 eV): *m*/*z* (%) = 345 [M^+, 100], 316 (60), 254 (65), 190 (55), 91 (75).

Anal. Calcd for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06. Found: C, 62.53; H, 5.51; N, 4.03.

5-Methyl-2-[(4-nitrophenyl)sulfonyl]-2,3-dihydro-1*H*-isoindole-4,7-dione (3h)

The reaction was carried out according to GP 5: **1h** (0.17 g, 0.50 mmol, 1.0 equiv), $AuCl_3$ (6 mg, 0.02 mmol, 5 mol%) in anhyd MeCN (4 mL), $PhI(OAc)_2$ (0.32 g, 1.0 mmol, 2.0 equiv), and H_2O (2 mL). Compound **3h** was obtained as a green solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.13 g (79%, 0.39 mmol); R_f = 0.54 (*n*-hexane/EtOAc 8:2); mp 192–194 °C.

IR (KBr): 2967, 2925, 1657, 1611, 1444, 1347, 1161 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 9.1 Hz, 2 H), 7.97 (d, *J* = 9.1 Hz, 2 H), 6.51 (s, 1 H), 4.54 (s, 4 H), 2.02 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.1, 183.3, 151.9, 148.3, 146.3, 143.6, 138.1, 133.6, 129.8, 127.1, 54.1, 53.7, 15.2.

MS (EI, 70 eV): *m*/*z* (%) = 348 [M^+, 100], 226 (70), 185 (85), 162 (50), 122 (75).

Anal. Calcd for $C_{15}H_{12}N_2O_6S$: C, 51.72; H, 3.47; N, 8.04. Found: C, 51.75; H, 3.46; N, 8.04.

2-[(4-Methoxyphenyl)sulfonyl]-5-methyl-2,3-dihydro-1*H*-isoindole-4,7-dione (3i)

The reaction was carried out according to GP 5: **1i** (0.16 g, 0.50 mmol, 1.0 equiv), $AuCl_3$ (6 mg, 0.02 mmol, 5 mol%) in anhyd MeCN (4 mL) and $PhI(OAc)_2$ (0.32 g, 1.0 mmol, 2.0 equiv) in H_2O (2 mL). Compound **3i** was obtained as a yellow solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.14 g (86%, 0.43 mmol); R_f = 0.61 (*n*-hexane/EtOAc 8:2); mp 170–173 °C.

IR (KBr): 2921, 1663, 16010, 1440, 1344, 1158 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 6.9 Hz, 2 H), 7.36 (d, *J* = 6.9 Hz, 2 H), 6.50 (d, *J* = 2.8 Hz, 1 H), 4.46 (s, 4 H), 3.91 (s, 3 H), 2.00 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 183.6, 182.4, 159.7, 146.2, 143.5, 141.4, 133.8, 131.8, 127.2, 117.8, 55.3, 53.3, 52.1, 15.1.

MS (EI, 70 eV): *m*/*z* (%) = 333 [M^+, 100], 226 (75), 171 (50), 162 (55), 107 (80).

Anal. Calcd for $C_{16}H_{15}NO_5S$: C, 57.65; H, 4.54; N, 4.20. Found: C, 57.63; H, 4.53; N, 4.19.

5-Methyl-1,3-dihydroisobenzofuran-4,7-dione (3j)

The reaction was carried out according to GP 5: **1j** (0.075 g, 0.50 mmol, 1.0 equiv), $AuCl_3$ (6 mg, 0.02 mmol, 5 mol%) in anhyd MeCN (4 mL) and $PhI(OAc)_2$ (0.32 g, 1.0 mmol, 2.0 equiv) in H_2O (2 mL). Compound **3j** was obtained as a white solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.05 g (62%, 0.31 mmol); R_f = 0.41 (*n*-hexane/EtOAc 9:1); mp 192–194 °C.

IR (KBr): 2920, 2859, 1661, 1627, 1421, 1233 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 6.56 (s, 1 H), 5.05 (s, 4 H), 2.09 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.4, 186.2, 154.1, 153.2, 139.1, 132.6, 76.1, 75.1, 15.0.

MS (EI, 70 eV): *m*/*z* (%) = 164 [M^+, 100], 150 (75), 120 (60), 106 (50).

Anal. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 65.83; H, 4.90.

5-Methyl-1-phenyl-2-tosylisoindoline-4,7-diol (4c)

The reaction was carried out according to GP 6 with **3c** (0.07 g, 0.20 mmol, 1.0 equiv) and sodium dithionite (0.82 g, 4.0 mmol, 20.0 equiv). Compound **4c** was obtained as a light brown solid after column chromatography (eluent: *n*-hexane/EtOAc 8:2); yield: 0.05 g (78%, 0.15 mmol); R_f = 0.55 (*n*-hexane/EtOAc 8:2); mp 113–114 °C.

IR (KBr): 3438, 2923, 1659, 1495, 1340, 1158, 1095 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.4 Hz, 3 H), 7.25–7.27 (m, 5 H), 7.18 (s, 1 H),7.14 (d, *J* = 8.0 Hz, 2 H), 6.00 (s, 1 H), 5.95 (s, 1 H), 5.30 (s, 1 H), 4.78 (s, 2 H), 2.35 (s, 3 H), 2.14 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.0, 144.1, 142.4, 140.4, 133.7, 129.7, 128.5, 128.1, 127.9, 127.5, 125.6, 123.6, 118.0, 106.9, 68.9, 52.1, 21.4, 15.5.

MS (EI, 70 eV): *m*/*z* (%) = 395 [M^+, 100], 318 (60), 240 (45), 155 (40), 91 (60), 77 (70).

Anal. Calcd for $C_{22}H_{21}NO_4S$: C, 66.82; H, 5.35; N, 3.54. Found: C, 66.87; H, 5.36; N, 3.59.

5-Methyl-1-phenyl-2-(phenylsulfonyl)isoindoline-4,7-diol (4f)

The reaction was carried out according to GP 6 with **3f** (0.09 g, 0.25 mmol, 1.0 equiv), and sodium dithionite (1.03 g, 5.0 mmol, 2.0 equiv). Compound **4f** was obtained as a light brown solid after column chromatography (eluent: *n*-hexane/EtOAc (8:2); yield: 0.06 g (75%, 0.18 mmol); R_f = 0.52 (*n*-hexane/EtOAc 8:2); mp 108–109 °C.

IR (KBr): 3428, 2924, 1658, 1449, 1341, 1161, 1096 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.56 (t, *J* = 7.0 Hz, 2 H), 7.45 (t, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 7.5 Hz, 3 H), 7.23 (s, 5 H), 6.42 (s, 1 H), 5.98 (s, 1 H), 4.83 (d, *J* = 13.5 Hz, 1 H), 4.76 (d, *J* = 11.0 Hz, 1 H), 3.62 (s, 1 H), 2.14 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1, 142.4, 140.1, 138.5, 132.3, 129.5, 128.8, 128.6, 127.9, 127.0, 125.6, 123.5, 118.0, 108.3, 67.8, 52.1, 15.4.

MS (EI, 70 eV): *m*/*z* (%) = 381 [M^+, 100], 304 (85), 240 (60), 141 (45), 77 (90).

Anal. Calcd for $C_{21}H_{19}NO_4S$: C, 66.12; H, 5.02; N, 3.67. Found: C, 66.07; H, 5.00; N, 3.61.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1707371.

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