EurJOC
European Journal of Organic Chemistry

A Journal of
ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201601582

Link to VoR: http://dx.doi.org/10.1002/ejoc.201601582

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10.1002/ejoc.201601582

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FULL PAPER

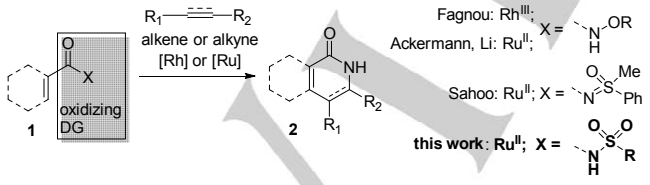
N-Sulfonylcarboxamide as an Oxidizing Directing Group for Ruthenium Catalyzed C-H Activation/Annulation

Elina Petrova,[a] Dace Rasina,[a] Aigars Jirgensons*[a]

Abstract: *N*-Sulfonylcarboxamides can be annulated with alkynes to give isoquinolones under Ru catalysis. *N*-Sulfonylcarboxamide acts as both a directing group for C-H activation and as an internal oxidant. Of all *N*-sulfonylcarboxamides studied, the most efficient was *N*-2,6-difluorophenylsulfonamide which led to the formation of unstable sulfinate that decomposes to 1,3-difluorobenzene under the reaction conditions. The isoquinolone synthesis presented provides an alternative to currently known traceless annulation of hydroxamic acid and sulfoximine derivatives.

Introduction

Functionalization via C-H activation enables atom and step economic synthesis of complex molecules and has motivated considerable progress of method development in recent years.[1] Notably, C-H activation methodology has provided new routes for the construction of variety of heterocycles. For instance, isoquinolone derivatives can be obtained by Pd,[2] Rh,[3] Ru,[4] Co,[5] Ni[6] and Fe[7] catalyzed C(sp^2)-H activation of amides followed by the annulation of the intermediate metallacycle with olefins or alkynes. For the catalytic version of this reaction, the metal has to be recycled in the active oxidation state either by the addition of an external oxidant[2a-d; 3a,b; 4a; 5a-c; 7] or by using directing group which serves as internal oxidant.[3c-k;4b-d; 5d] The latter approach has several benefits - additional reactants are avoided and concomitant cleavage of the directing group is observed. This concept for isoquinolone **2** synthesis was first demonstrated by Fagnou using Rh(III)-catalyzed annulation of hydroxamic acid derivatives **1** (X=OR) (Scheme 1).[3d,e] In these substrates, reduction of N-O bond served as oxidizing step for the catalyst regeneration. Later Ackermann and Li showed that oxidant-free hydroxamic acid annulation with alkenes and alkynes can be achieved with Ru(II) as a catalyst.[4b-d]



Scheme 1. Isoquinolone synthesis by metal catalyzed C-H activation/ annulation using oxidizing directing group

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Recently, Sahoo has introduced phenyl sulfoximine as traceless directing group for synthesis isoquinolone **2** derivatives using cationic Ru(II) complex as a catalyst.[4h-j] This remains the only known example for Ru catalysed annulation were N-S bond cleavage serves as the oxidising step. For other types of Rh[8] and Co[9] catalyzed C-H functionalization reactions *N*-sulfonyl and *N*-sulfinyl ketimines have been used as internal oxidising groups.[10] This implied the potential of *N*-sulfonylcarboxamide as traceless directing group for C-H activation which would be easy to install based on readily available starting materials.

Results and Discussion

We explored the ability of a range of *N*-sulfonylcarboxamides **1.1-1.8** to perform as a directing group[11] and internal oxidant via N-S bond cleavage in Ru catalyzed C-H activation/annulation to form isoquinolones **2** (Table 1).

Table 1. The efficiency of *N*-sulfonyl group as a directing group/internal oxidant for C-H activation/annulation[a]

Entry	Substrate **1**, R	**2a** yield %[b]
1	**1.1**, CH_3	40, 90[c]
2	**1.2**, CF_3	40
3	**1.3**, PhO	55
4	**1.4a**, Benzothiazol-2-yl	30
5	**1.5**, 4-Me-C_6H_4	45
6	**1.6**, 2-F-C_6H_4	52
7	**1.7**, 4-F-C_6H_4	55
8	**1.8a**, 2,6-$F_2C_6H_3$	60

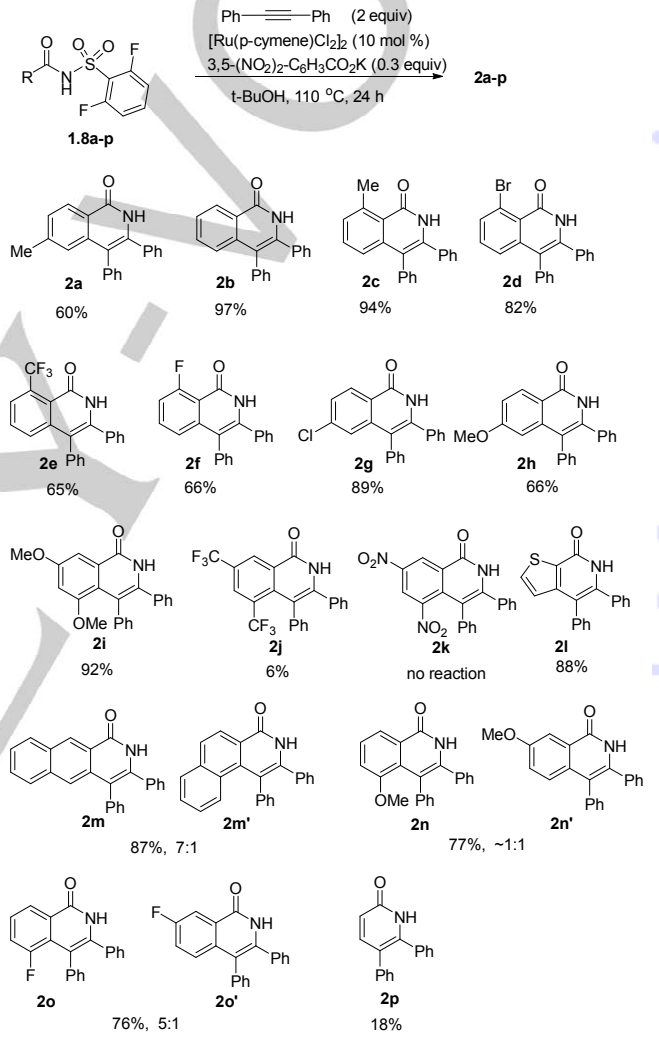
[a] Reaction conditions: *N*-Sulfonylcarboxamide (0.17 mmol), diphenylacetylene (0.34 mmol, 2 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (0.017 mmol, 10 mol%), 3,5-$(NO_2)_2$-C_6H_3COOK (0.051 mmol, 0.3 equiv), *t*-BuOH (4 mL), 110 ºC, 24 h. [b] ^{1}H-NMR yield using 1,3,5-trimethoxybenzene as an internal standard (0.333 equiv).
[c] **1.1** (0.23 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (0.070 mmol, 30 mol%); NaOPiv·H_2O used as base (0.21 mmol, 0.9 equiv), 2 h.

N-Mesyl-*p*-toluamide (**1.1**) gave desired product **2a** in Ru catalyzed reaction with diphenylacetylene under Ackermann conditions using electron deficient carboxylate as a co-catalytic

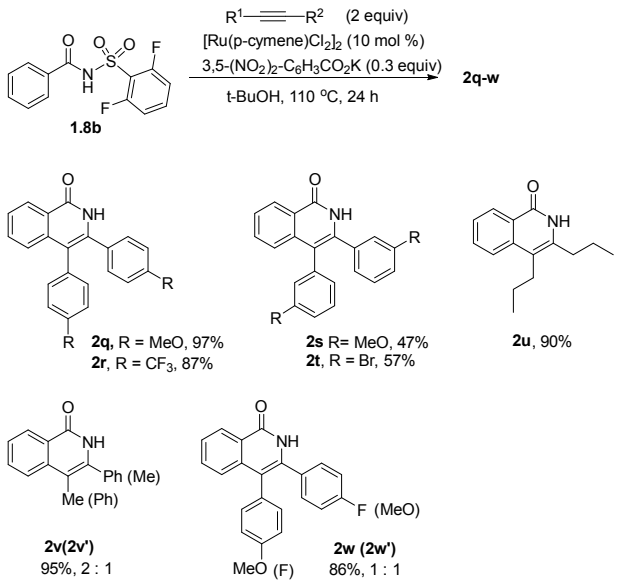
additive.[4e] However, the reaction stopped at ~40% conversion after 3h (Table 1, entry 1). When the catalyst loading was increased to 30 mol%, almost complete conversion and good NMR yield (90%; Table 1, entry 1) of the isoquinolone **2a** was observed. This could indicate that the putative sulfinate by-product of N-S bond cleavage inhibits the reaction due to its strong coordination with Ru catalyst. *N*-Trifluoromethyl-sulfonylcarboxamide **1.2** was explored to generate less coordinating sulfinate, but no increase in yield of the product **2a** was observed (Table 1, entry 2). Improved yield was achieved for *N*-phenyloxysulfonylcarboxamide **1.3** which presumably provides unstable sulfinate by-product (Table 1, entry 3). Benzothiazole-2-sulfonyl carboxamide **1.4a** could also potentially give unstable sulfinate,[12] however, in this case, the yield of the product **2a** was low (table 1, entry 4). The formation of the expected benzothiazole by-product together with *p*-tolunitrile and 2-hydroxybenzothiazole was observed by UPLC/MS (see SI for details). This could be explained by the competitive Smiles rearrangement which takes place in the substrate **1.4a**. *N*-Tosylcarboxamide **1.5** performed poorly (Table 1, entry 5), while the yield improvement was achieved for fluorinated benzenesulfonylcarboxamides **1.6 – 1.8a** (Table 1, entries 6-8). Noteworthy, for 2,6-difluorosulfonyl analogue **1.8a** the formation of 1,3-difluorobenzene was detected by GC/MS and it was the only fluorinated by-product according to ^{19}F-NMR of the reaction mixture (see SI for details). Obviously, this substrate leads to the formation of unstable sulfinate which decomposes to 1,3-difluorobenzene avoiding the presence of strongly coordinating ligand that could deactivate the catalyst.

Further substrate scope studies were performed with substrates containing 2,6-difluorophenylsulfonyl group (Scheme 2). Various substituents at benzenecarboxamides **1.8a** – **1.8i** were tolerated to give isoquinolones **2a-i** in moderate to excellent yields. Substrates **1.8j** and **1.8k** bearing two electron withdrawing groups were unsuitable for C-H activation/ annulation. *N*-Thiophenecarboxamide **1.8l** gave the condensed heterocycle **2l** in good yield. Sulfonylnaphthalene carboxamide **1.8m** could also be annulated to give regioisomeric isoquinolones **2m** and **2m'** in the favor of isomer **2m**. meta-Methoxy substituted substrate **1n** gave the annulation product **2n** and its regioisomer **2n'** in good yield, however practically no selectivity. Considerably improved regioselectivity was observed in the case of the annulation of meta-fluoro substituted substrate **1o** to give preferentially the isoquinolone **2o.** The reaction was also applicable for the synthesis of pyridinone **2p** from *N*-sulfonyl acrylamide **1.8p**, however in low yield. Additionally, several alkynes were explored as substrates for the annulation of *N*-sulfonyl benzenecarboxamide **1.8b** (Scheme 3). Alkynes bearing both electron rich and electron poor aryl groups and alkyl groups gave products **2q-w** in medium to high yields. Annulation of substrate **1.8b** with methylphenylacetylene or alkyne bearing electronically distinct substituents gave mixture of regioisomeric isoquinolones **2v** (**2v'**) and **2w(2w')** with poor selectivity.

According to the mechanism proposed by Ackermann *et al.* [4a] and Li *et al.*,[4c] Ru catalyzed C-H activation/annulation involves directed C-H activation to form 5-membered metallacycle and subsequent carbometallation of alkyne leading to formation of 7-membered metallacycle. We have isolated such an intermediate **3b** in Ru catalyzed annulation of *N*-sulfonyl carboxamide **1.4b** with diphenylacetylene and confirmed its structure by single crystal X-ray diffraction analysis (Scheme 4). The final stages for C-N bond formation from the 7-membered metallacycle **3b** are currently poorly understood. The mechanism for reductive Ru (0) elimination followed by the insertion into N-O bond has been proposed for annulation of the hydroxamic acid derivatives.[4c,e] However, sulfonamides have relatively high reduction potential which makes the pathway involving intermediates **4** and **5** less plausible (Scheme 5).

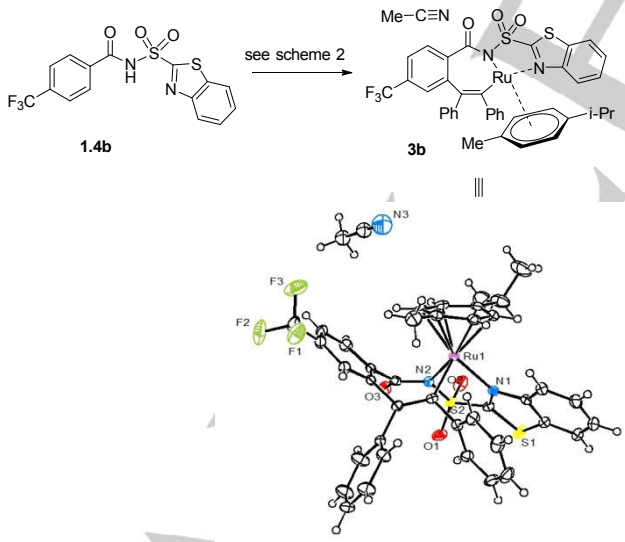


Scheme 2. *N*-2,6-difluorobenzensulfonylcarboxamide scope**.** Reaction conditions: *N*-sulfonylcarboxamide (0.60 mmol), diphenylacetylene (1.20 mmol, 2 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (0.06 mmol, 10 mol%), 3,5-(NO_2)$_2$-C_6H_3COOK (0.18 mmol, 0.3 equiv), *t*-BuOH (10 mL), 110 ºC, 24 h. Isolated yields are given.

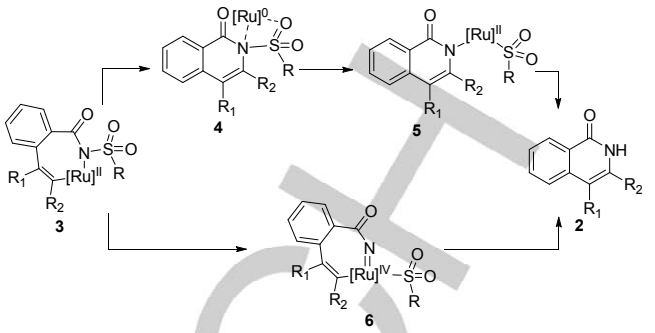


Scheme 3. Alkyne scope. Reaction conditions: *N*-Sulfonyl-carboxamide (0.50 mmol), alkyne (1.0 mmol, 2 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (0.05 mmol, 10 mol%), 3,5-(NO_2)$_2$-C_6H_3COOK (0.15 mmol, 0.3 equiv), *t*-BuOH (7.5 mL), 110 ºC, 24 h. Isolated yields are given.

In analogy to the proposed C-N bond formation for Rh catalyzed annulations,[13,14] an alternative pathway could be proposed which involves Ru (IV) nitrene intermediate **6** formation via an elimination of sulfinate group. Reductive elimination of Ru in intermediate **6** would then lead to isoquinolone **2**.



Scheme 4. Preparation and X-ray structure of ruthenacycle **3b** (CCDC 1531064)



Scheme 5. Possible mechanistic pathways for C-N bond formation in ruthenacycle **3**.

Conclusions

In summary, we have developed an efficient traceless method for the synthesis of isoquinolones by Ru catalyzed annulation of *N*-sulfonylcarboxamide with alkyne. In this reaction, *N*-sulfonylcarboxamide acts as both an internal oxidant and directing group. Catalyst re-oxidation takes place in N-S bond cleavage step. Of all *N*-sulfonylcarboxamides studied, the most efficient was *N*-2,6-difluorophenylsulfonamide which led to the formation of unstable sulfinate and readily decomposed to 1,3-difluorobenzene under the reaction conditions. The isoquinolone synthesis presented provides an alternative to currently known traceless annulation of hydroxamic acid and sulfoximine derivatives.

Experimental Section

General methods: Flash chromatography was carried out using silica gel (230−400 mesh). Thin layer chromatography (TLC) was performed on silica gel and was visualized by UV lamp or staining with $KMnO_4$. NMR spectra were recorded on 300 and 400 MHz spectrometers. Conversion of starting material was detected with UPLC Waters Acquity; detector: PDA; SQ detector with an electrospray ion source (ESI/APCI). Gas chromato-graphic (GC) analysis was performed on Agilent Technologies gas chromatographer with triple-axis detector. Exact molecular masses (HRMS) were determined on a hybrid quadrupole time-of-flight mass spectrometer equipped with an electrospray ion source.

General procedure for synthesis of 6-methyl-3,4-diphenyl-isoquinolin-1(2H)-one (2a). A mixture of *N*-acylsulfonamide **1.8a** (200 mg, 0.64 mmol, 1 eq.), diphenylacetylene (229 mg, 1.28 mmol, 2 eq.), 3,5-dinitrobenzoic acid potassium salt (48.2 mg, 0.19 mmol 0.3 eq.) and [Ru(cymene)Cl_2]$_2$ (39 mg, 0.06 mmol, 10 mol%) in 10 mL of *t*-butanol was stirred at 110ºC in a pressure tube under an atmosphere of argon. After 24 h reaction mixture was cooled to room temperature, diluted with 20 mL of sat. NH_4Cl and extracted with DCM (3 x 20 mL). The combined organic phase was washed with brine (20 mL) and dried over Na_2SO_4. After filtration and evaporation of the solvent *in vacuo*, the crude

product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2a** (120 mg, 60%) as yellowish solid (mp= 275-277 °C).
^{1}H NMR (300 MHz, DMSO-d_6): δ= 11.43 (s, NH), 8.21 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.24 (m, 4H), 7.21 (s, 5H), 7.17 – 7.12 (m, 2H), 6.93 (s, 1H), 2.31 (s, 3H). Analytical data are in accordance with those reported in the literature.[4c]

3,4-Diphenylisoquinolin-1(2H)-one (2b). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8b** (200 mg, 0.67 mmol), diphenylacetylene (240 mg, 1.35 mmol), 3,5-dinitrobenzoic acid potassium salt (51.0 mg, 0.20 mmol) and $[Ru(cymene)Cl_2]_2$ (41.2 mg, 0.07 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2b** (195 mg, 97%) as brownish solid (mp = 250-253 °C). ^{1}H NMR (400 MHz, DMSO-d6): δ=11.54 (s, 1H), 8.32 (dd, J = 8.0, 1.5 Hz, 1H), 7.64 (ddd, J = 8.3, 7.0, 1.5 Hz, 1H), 7.52 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 7.35 – 7.18 (m, 8H), 7.19 – 7.11 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=161.7 (Cq), 138.6 (Cq), 138.1 (Cq), 135.8 (Cq), 134.6 (Cq), 132.5 (CH), 131.7 (CH), 129.8 (CH), 128.23 (CH), 128.18 (CH), 127.7 (CH), 127.0 (CH), 126.8 (CH), 126.3 (CH), 125.0 (Cq), 124.9 (CH), 115.5 (Cq). Analytical data are in accordance with those reported in the literature.[4e]

8-Methyl-3,4-diphenylisoquinolin-1(2H)-one (2c). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8c** (170 mg, 0.55 mmol), diphenylacetylene (195 mg, 1.09 mmol), 3,5-dinitrobenzoic acid potassium salt (41.0 mg, 0.16 mmol) and $[Ru(cymene)Cl_2]_2$ (33.4 mg, 0.05 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2c** (160 mg, 94%) as brownish solid (mp=268-270°C). ^{1}H NMR (300 MHz, DMSO-d_6): δ=11.26 (s, 1H), 7.48 – 7.40 (m, 1H), 7.33 – 7.17 (m, 9H), 7.15 – 7.09 (m, 2H), 6.94 (d, J = 7.9 Hz, 1H), 2.89 (s, 3H). Analytical data are in accordance with those reported in the literature.[4c]

8-Bromo-3,4-diphenylisoquinolin-1(2H)-one (2d). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8d** (185 mg, 0.49 mmol), diphenylacetylene (175 mg, 0.98 mmol), 3,5-dinitrobenzoic acid potassium salt (36.9 mg, 0.15 mmol) and $[Ru(cymene)Cl_2]_2$ (30.1 mg, 0.05 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2d** (151 mg, 82%) as brownish solid (mp = 268-270 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 11.56 (s, 1H), 7.74 (dd, J = 7.7, 0.9 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.35 – 7.18 (m, 4H), 7.18 – 7.10 (m, 2H), 7.09 (dd, J = 8.2, 0.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ= 160.0 (Cq), 141.4 (Cq), 139.7 (Cq), 135.9 (Cq), 134.1 (Cq), 132.9 (CH), 132.6 (CH), 131.8 (CH), 129.7 (CH), 128.4 (two CH overlaps), 127.7 (CH), 127.2 (CH), 125.1 (CH), 122.0 (Cq), 121.9 (Cq), 115.0 (Cq). HRMS (ESI/TOF) calcd. for $C_{21}H_{15}BrNO$ $[M+H]^+$ 376.0337, found 376.0342.

3,4-Diphenyl-8-(trifluoromethyl)isoquinolin-1(2H)-one (2e). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8e** (170 mg, 0.47 mmol), diphenylacetylene (166 mg, 0.93 mmol), 3,5-dinitrobenzoic acid potassium salt (34.9 mg, 0.14 mmol) and $[Ru(cymene)Cl_2]_2$ (28.5 mg, 0.05 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2e** (110 mg, 65%) as brownish solid (mp >260 °C (dec.)). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 7.93 (d, J = 7.5 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.36 – 7.20 (m, 8H), 7.20 – 7.12 (m, 2H).^{13}C NMR (100 MHz, DMSO-d_6):δ=159.0 (Cq), 140.9 (Cq), 140.4 (Cq), 135.7 (Cq), 134.0 (Cq),131.9 (CH), 131.7 (CH), 130.0 (CH), 129.7 (CH), 128.4 (two CH overlaps),128.1 (Cq, J=31.9 Hz),127.7 (CH),127.3 (CH), 125.8 (CH),124.1 (CF_3, J=272.5 Hz), 121.9 (Cq), 114.9 (Cq).^{19}F NMR (376 MHz, DMSO-d_6): δ= -56.14 (s). HRMS (ESI/TOF) calcd. for $C_{22}H_{15}F_3NO$ $[M+H]^+$ 366.1106, found 366.1100.

8-Fluoro-3,4-diphenylisoquinolin-1(2H)-one (2f). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8f** (200 mg, 0.63 mmol), diphenylacetylene (226 mg, 1.27 mmol), 3,5-dinitrobenzoic acid potassium salt (47.6 mg, 0.19 mmol) and $[Ru(cymene)Cl_2]_2$ (38.8 mg, 0.06 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2f** (132 mg, 66%) as brownish solid (mp > 220 °C(dec.)). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 11.53 (s, 1H), 7.59 (td, J = 8.1, 5.1 Hz, 1H), 7.34 – 7.18 (m, 9H), 7.18 – 7.10 (m, 2H), 6.91 (dd, J = 8.2, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ= 161.9 (CF, d, J = 261.5 Hz), 159.1 (Cq, d, J = 3.9 Hz),141.1 (Cq), 139.9 (Cq), 135.8 (Cq), 134.1 (Cq),133.5 (CH, d, J = 10.3 Hz),131.7 (CH), 129.7 (CH), 128.8 (CH, d, J = 4.6 Hz), 128.3 (CH), 127.6 (CH),127.2 (CH), 121.0 (CH, d, J = 4.2 Hz),114.7 (Cq, d, J = 2.6 Hz),113.9 (Cq, d, J = 5.5 Hz), 112.9 (CH, d, J = 21.3 Hz).^{19}F NMR (376 MHz, DMSO-d_6): δ=-111.27 (dd, J = 11.7, 5.3 Hz). HRMS (ESI/TOF) calcd. for $C_{21}H_{15}FNO$ $[M+H]^+$ 316.1138, found 376.1152.

6-Chloro-3,4-diphenylisoquinolin-1(2H)-one (2g). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8 g** (200 mg, 0.60 mmol), diphenylacetylene (215 mg, 1.21 mmol), 3,5-dinitrobenzoic acid potassium salt (45.3 mg, 0.18 mmol) and $[Ru(cymene)Cl_2]_2$ (36.9 mg, 0.06 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2g** (178 mg, 89%) as brownish solid (mp = 267-270 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ=11.71 (s, 1H), 8.31 (dd, J = 8.5, 0.5 Hz, 1H), 7.55 (dd, J = 8.6, 2.1 Hz, 1H), 7.37 – 7.25 (m, 3H), 7.23 (br s, 5H), 7.18 – 7.14 (m, 4H), 7.04 (dd, J = 2.1, 0.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=161.1 (Cq), 140.3 (Cq), 139.7 (Cq), 137.6 (Cq), 135.2 (Cq), 134.2 (Cq), 131.6 (CH), 129.8 (CH), 129.3 (CH), 128.4 (CH), 127.7 (CH), 127.4 (CH), 126.4 (CH), 123.8 (CH), 123.6 (Cq), 114.5 (Cq). Analytical data are in accordance with those reported in the literature.[4c,e]

6-Methoxy-3,4-diphenylisoquinolin-1(2H)-one (2h). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8h** (200 mg, 0.61 mmol), diphenylacetylene (218 mg, 1.22 mmol), 3,5-dinitrobenzoic acid potassium salt (45.9 mg, 0.18 mmol) and $[Ru(cymene)Cl_2]_2$ (37.4 mg, 0.06 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica

gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2h** (132 mg, 66%) as brownish solid (mp > 290 °C (dec.)). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 11.36 (s, 1H), 8.25 (d, J = 9.0 Hz, 1H), 7.35 – 7.23 (m, 3H), 7.22 (s, 5H), 7.14 (ddd, J = 8.8, 4.4, 2.1 Hz, 3H), 6.51 (d, J = 2.5 Hz, 1H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ= 162.3 (Cq), 161.4 (Cq), 140.1 (Cq), 139.2 (Cq), 135.9 (Cq), 134.6 (Cq), 131.7 (CH), 129.8 (CH), 129.1 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.1 (CH), 118.9 (Cq), 115.1 (Cq), 114. 5 (CH), 107.2 (CH), 55.1 (CH_3). Analytical data are in accordance with those reported in the literature.[4c,e]

5,7-Dimethoxy-3,4-diphenylisoquinolin-1(2H)-one (2i). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8i** (200 mg, 0.61 mmol), diphenylacetylene (218 mg, 1.22 mmol), 3,5-dinitrobenzoic acid potassium salt (45.9 mg, 0.18 mmol) and [Ru(cymene)Cl_2]$_2$ (37.4 mg, 0.06 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2i** (185 mg, 93%) as brownish solid (mp >240 °C (dec.)). ^{1}H NMR (400 MHz, DMSO-d_6): δ= 11.46 (s, 1H), 7.40 (d, J = 2.6 Hz, 1H), 7.17 – 6.98 (m, 10H), 6.76 (d, J = 2.6 Hz, 1H), 3.88 (s, 3H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=160.9 (Cq), 158.6 (Cq),157.5 (Cq),139.6 (Cq), 136.2 (Cq), 135.1 (Cq), 130.9 (CH), 130.1 (CH), 127.7 (Cq), 127.6 (CH), 127.4 (CH), 126.4 (CH), 125.4 (CH), 122.4 (Cq), 113.7(Cq), 104.6 (CH), 99.5 (CH), 55.7 (OCH_3), 55.4 (OCH_3). HRMS (ESI/TOF) calcd. for $C_{23}H_{20}NO_3$ $[M+H]^+$ 358.1443, found 358.1440.

3,4-Diphenyl-5,7-bis(trifluoromethyl)isoquinolin-1(2H)-one (2j). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8j** (200 mg, 0.46 mmol), diphenylacetylene (165 mg, 0.92 mmol), 3,5-dinitrobenzoic acid potassium salt (34.7 mg, 0.14 mmol) and [Ru(cymene)Cl_2]$_2$ (28.3 mg, 0.05 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2l** (13 mg, 6%) as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.62 (s, 1H), 8.98 (d, J = 2.1 Hz, 1H), 8.26 (s, 1H), 7.30 – 7.09 (m, 6H), 7.08 – 7.03 (m, 4H). ^{19}F NMR (376 MHz, DMSO-d6): δ= -53.47 (s), -62.84 (s). HRMS (ESI/TOF) calcd. for $C_{23}H_{14}F_6NO$ $[M+H]^+$ 434.0980, found 434.0982.

4,5-Diphenylthieno[2,3-c]pyridin-7(6H)-one (2l). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8l** (120 mg, 0.40 mmol), diphenylacetylene (141 mg, 0.79 mmol), 3,5-dinitrobenzoic acid potassium salt (29.7 mg, 0.12 mmol) and [Ru(cymene)Cl_2]$_2$ (24.2 mg, 0.04 mmol) in 10 mL of *t*-butanol. Crude product was purified by crystallization from i-PrOH to yield **2l** (106 mg, 88%) as white solid (mp = 266-268°C). ^{1}H NMR (400 MHz, DMSO-d_6): δ=11.76 (s, 1H), 8.02 (d, J = 5.3 Hz, 1H), 7.30 – 7.21 (m, 8H), 7.16 – 7.11 (m, 2H), 6.92 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6): δ= 158.1 (Cq), 146.7 (Cq), 139.9 (Cq), 136.3 (Cq), 134.2 (CH), 133.9 (Cq), 130.7 (CH), 130.0 (CH), 128.3 (CH), 128.2 (CH), 128.0 (Cq), 127.8 (CH), 127.0 (CH), 124.5 (CH), 114.7 (Cq). Analytical data are in accordance with those reported in the literature.[4c]

3,4-Diphenylbenzo[g]isoquinolin-1(2H)-one (2m) and 1,2-diphenyl-benzo[f]-isoquinolin-4(3H)-one (2m'). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8m** (200 mg, 0.58 mmol), diphenylacetylene (215 mg, 1.15 mmol), 3,5-dinitrobenzoic acid potassium salt (43.2 mg, 0.17 mmol) and [Ru(cymene)Cl_2]$_2$ (35.3 mg, 0.06 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield **2m** and **2m'** as a mixture (**2m/2m'** 7/1, 175 mg, 87%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ= 11.96 (s, 1H **2m'**), 11.36 (s, 1H **2m**), 9.02 (s, 1H **2m**), 8.38 (d, J = 8.7 Hz, 1H **2m**'), 8.24 – 8.19 (m, 1H **2m**), 8.00 – 7.95 (m, 2H **2m'**), 7.88 – 7.82 (m, 1H **2m**), 7.63 (s, 1H **2m**), 7.60 – 7.53 (m, 2H **2m**), 7.50 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H **2m**'), 7.39 – 7.28 (m, 3H **2m**), 7.29-7.17 (m, 7H **2m** overlaps with 9H **2m**') 7.15 – 7.12 (m, 2H **2m'**), 7.02 (ddd, J = 8.6, 6.8, 1.5 Hz, 1H **2m'**). Analytical data are in accordance with those reported in the literature.[4c]

5-Methoxy-3,4-diphenylisoquinolin-1(2H)-one (2n) and 7-methoxy-3,4-diphenylisoquinolin-1(2H)-one (2n'). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8n** (200 mg, 0.61 mmol), diphenylacetylene (218 mg, 1.22 mmol), 3,5-dinitrobenzoic acid potassium salt (45.9 mg, 0.18 mmol) and [Ru(cymene)Cl_2]$_2$ (37.4 mg, 0.06 mmol) in 10 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (Hex:Acetone 3:1 – 1:1) to yield **2** and **2'** as a mixture (**2/2**' =1/1.2, 153 mg, 77%) as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.08 (br s, 1H-**2n** and 1H-**2n**' overlaps), 8.14 (dd, J = 8.0, 1.3 Hz, 1H-**2n'**), 7.88 (d, J = 2.8 Hz, 1H-**2n**), 7.45 (t, J = 8.0 Hz, 1H-**2n'**), 7.33 – 7.04 (m, 12H-**2n** and 11H-**2n'** overlaps), 3.95 (s, 3H-**2n**), 3.34 (s, 3H-**2n'**). Analytical data are in accordance with those reported in the literature.[4b]

5-Fluoro-3,4-diphenylisoquinolin-1(2H)-one (2o) and 7-fluoro-3,4-diphenylisoquinolin-1(2H)-one (2o'). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8o** (200 mg, 0.63 mmol), diphenylacetylene (226 mg, 1.27 mmol), 3,5-dinitrobenzoic acid potassium salt (47.6 mg, 0.19 mmol) and [Ru(cymene)Cl2]2 (38.9 mg, 0.06 mmol) in 10 mL of t-butanol. Crude product was purified by column chromatography on silica gel (Hex:Acetone 3:1 – 1:1) to yield **2o** and **2o'** as a mixture (**2o/2o'** 1/5, 150 mg, 75 %) as an off-white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ= 9.40 (br s, 1H-2o and 1H-2o' overlaps), 8.30 (dd, J = 8.0, 1.3 Hz, 1H-**2o'**), 8.08 (dd, J = 9.0, 2.7 Hz, 1H-**2o**), 7.45 (td, J = 8.0, 4.5 Hz, 1H-**2o'**), 7.42 – 7.12 (m, 12H-**2o** and 11H-**2o'** overlaps).^{19}F NMR (376 MHz, $CDCl_3$): δ= -107.25 (**2o'**, dd, J = 12.4, 4.3 Hz), -113.41 (**2o**, td, J = 8.5, 5.4 Hz). Analytical data are in accordance with those reported in the literature.[3e]

5,6-Diphenylpyridin-2(1H)-one (2p). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8n** (190 mg, 0.77 mmol), diphenylacetylene (274 mg, 1.54 mmol), 3,5-dinitrobenzoic acid potassium salt (57.7 mg, 0.23 mmol) and [Ru(cymene)Cl_2]$_2$ (47.1 mg, 0.08 mmol) in 10 mL of *t*-butanol. Crude product was purified with Biotage SNAP cartrige (KP-C_{18}-HS), eluent system: CH_3CN/ 0.1% CF_3COOH in H_2O (gradient 20%/80% - 95%/5%). Product

2p (35 mg, 18 %) was isolated as white solid (mp= 266-268 °C). ^{1}H NMR (300 MHz, DMSO-d_6): δ=11.72 (s, 1H), 7.54 (d, J = 9.3 Hz, 1H), 7.36 – 7.11 (m, 8H), 7.02 (dd, J = 7.7, 1.9 Hz, 2H), 6.45 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ=162.3 (Cq), 145.9 (Cq), 143.4 (CH), 138.1 (Cq), 134.8 (Cq), 129.7 (CH), 129.4 (CH), 128.7 (CH), 128.2 (CH), 128.0 (CH), 126.4 (CH), 121.8 (CH), 118.8 (Cq). HRMS (ESI/TOF) calcd. for $C_{17}H_{14}NO$ $[M+H]^+$ 248.1075, found 248.1080.

3,4-Bis(4-methoxyphenyl)isoquinolin-1(2H)-one (2q). Prepared by analogy to compound **2a** from *N*-acyl sulfonamide **1.8b** (150 mg, 0.50 mmol), 1,2-bis(4-methoxy-phenyl)-ethyne (240 mg, 1.01 mmol), 3,5-dinitrobenzoic acid potassium salt (37.9 mg, 0.15 mmol) and $[Ru(cymene)Cl_2]_2$ (30.9 mg, 0.05 mmol) in 7.5 mL of t-butanol. Crude product was purified by column chromatography on silica gel (Hex:EtOAc 3:1-1:1) to yield **2q** (175 mg, 97%) as a brownish solid (mp= 261-264 °C).
^{1}H NMR (400 MHz, DMSO-d_6): δ=11.40 (s, 1H), 8.29 (dd, J = 7.9, 1.1 Hz, 1H), 7.61 (ddd, J = 8.4, 7.1, 1.5 Hz, 1H), 7.48 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.16 (d, J = 8.7 Hz, 3H), 7.05 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H), 3.71 (s, 3H).^{13}C NMR (100 MHz, DMSO-d6): δ=161.8 (Cq), 158.9 (Cq), 158.0 (Cq), 138.6 (Cq), 138.4 (Cq), 132.8 (CH), 132.3 (), 131.1 (CH), 128.0 (Cq), 127.0 (Cq), 126.7 (CH), 125.9 (CH), 124.9 (CH), 124.8 (Cq), 114.7 (Cq), 113.7 (CH), 113.1 (CH), 55.0 (OCH_3), 54.9 (OCH_3). Analytical data are in accordance with those reported in the literature.[4e]

3,4-Bis(4-(trifluoromethyl)phenyl)isoquinolin-1(2H)-one (2r) Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8b** (150 mg, 0.50 mmol), 1,2-bis(4-(trifluoromethyl)phenyl) ethyne (317 mg, 1.01 mmol), 3,5-dinitrobenzoic acid potassium salt (37.9 mg, 0.15 mmol) and $[Ru(cymene)Cl_2]_2$ (30.9 mg, 0.05 mmol) in 7.5 mL of t-butanol. Crude product was purified by crystallization from i-PrOH to yield **2r** (191 mg, 87 %) as a white solid (mp= 266-268 °C).^{1}H NMR (400 MHz, DMSO-d6): δ=11.76 (s, 1H), 8.35 (dd, J = 8.0, 1.0 Hz, 1H), 7.70 – 7.65 (m, 3H), 7.63 (d, J = 8.2 Hz, 2H), 7.57 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H), 7.49 (d, J = 7.9 Hz, 2H), 7.43 (d, J = 7.8 Hz, 2H), 7.11 (d, J = 8.2 Hz, 1H).
^{13}C NMR (100 MHz, DMSO-d6): δ= 161.6 (Cq), 140.0 (Cq), 138.2 (Cq), 137.6 (Cq), 137.3 (Cq), 132.9 (CH), 132.7 (CH), 130.9 (CH), 128.7 (Cq, q, J = 31.8 Hz), 127.8 (Cq, q, J = 31.9 Hz), 127.0 (CH), 126.9 (CH),125.22 (Cq), 125.19 (CH, q, J=3.5 Hz), 124.77 (CH), 124.69 (CH, q, J = 4.0 Hz), 124.2 (Cq, q, J=271.2 Hz), 123.9 (Cq, q, J=272.2 Hz), 114.73 (Cq). ^{19}F NMR (376 MHz, DMSO-d_6): δ= -61.02 (s), -61.22 (s).HRMS (ESI/TOF) calcd. for $C_{23}H_{14}F_6NO$ [M+H]+ 434.0980, found 434.0971.

3,4-Bis(3-methoxyphenyl)isoquinolin-1(2H)-one (2s). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8b** (150 mg, 0.50 mmol), 1,2-bis(3-methoxyphenyl)ethyne (240 mg, 1.01 mmol), 3,5-dinitrobenzoic acid potassium salt (37.9 mg, 0.15 mmol) and $[Ru(cymene)Cl_2]_2$ (30.9 mg, 0.05 mmol) in 7.5 mL of t-butanol. Crude product was purified by column chromatography on silica gel (Hex:Acetone 3:1 – 1:1) to yield **2s** (103 mg, 57%) as a solid oil. (mp= 161-165 °C). ^{1}H NMR (400 MHz, CDCl3): δ= 9.58 (s, 1H), 8.46 (dd, J = 8.0, 1.5 Hz, 1H), 7.59 (ddd, J = 8.4, 7.1, 1.4 Hz, 1H), 7.49 (ddd, J = 8.1, 7.1, 1.2 Hz, 1H), 7.40 (dd, J = 8.2, 0.7 Hz, 1H), 7.25 (t, J =7.7 Hz, 1H, ovewrlaps with $CDCl_3$ signal), 7.18 (t, J = 7.9 Hz, 1H), 6.89 (dt, J = 7.7, 1.2 Hz, 1H), 6.85 (ddd, J = 8.5, 2.7, 0.9 Hz, 1H), 6.83 – 6.77 (m, 3H), 6.74 (dd, J = 2.7, 1.5 Hz, 1H), 3.71 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, CDCl3): δ= 162.8 (Cq), 159.8 (Cq), 159.4 (Cq), 138.7 (Cq), 137.3 (Cq), 136.9 (Cq), 136.4 (Cq), 132.8 (CH), 129.6 (CH), 129.6 (CH), 127.6 (CH), 126.8 (CH), 125.9 (CH), 125.3 (Cq), 124.4 (CH), 121.4 (CH), 117.4 (CH), 117.1 (Cq), 115.4 (CH), 114.3 (CH), 113.2 (CH), 55.4 (OCH_3), 55.3 (OCH_3). HRMS (ESI/TOF) calcd. for $C_{23}H_{20}NO_3$ $[M+H]^+$ 358.1443, found 358.1451.

3,4-Bis(3-bromophenyl)isoquinolin-1(2H)-one (2t). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8b** (150 mg, 0.50 mmol), 1,2-bis(3-bromophenyl)ethyne (339 mg, 1.01 mmol), 3,5-dinitrobenzoic acid potassium salt (37.9 mg, 0.15 mmol) and $[Ru(cymene)Cl_2]_2$ (30.9 mg, 0.05 mmol) in 7.5 mL of *t*-butanol. Crude product was purified by column chromatography on silica gel (Hex:Acetone 3:1 – 1:1) to yield **2t** (142 mg, 62%) as an off-white solid. (mp= 258-262 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ=11.66 (s, 1H), 8.32 (dd, J = 8.0, 1.4 Hz, 1H), 7.68 (ddd, J = 8.4, 7.1, 1.5 Hz, 1H), 7.55 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.42 (t, *J*=1.7 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.26 – 7.17 (m, 3H), 7.13 (d, J = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6): δ= 161.6 (Cq), 138.0 (Cq), 137.5 (Cq), 137.4 (Cq), 136.4 (Cq), 134.2 (CH), 132.8 (CH), 132.6 (CH), 131.3 (CH), 130.9 (CH), 130.4 (CH), 130.2 (CH), 129.8 (CH), 129.0 (CH), 126.9 (CH), 126.6 (CH), 125.1 (Cq), 124.8 (CH), 121.4 (Cq), 120.9 (Cq), 114.5 (Cq). HRMS (ESI/TOF) calcd. for $C_{21}H_{14}Br_2NO$ [M+H]+ 453.9442, found 453.9440

3,4-Dipropylisoquinolin-1(2H)-one (2u). Prepared by analogy to compound 2a from *N*-acylsulfonamide **1.8b** (150 mg, 0.50 mmol), 4-octyne (148 µL, 111 mg, 1.01 mmol), 3,5-dinitrobenzoic acid potassium salt (37.9 mg, 0.15 mmol) and $[Ru(cymene)Cl_2]_2$ (30.9 mg, 0.05 mmol) in 7.5 mL of *t*-butanol. Crude product was purified by crystallization from i-PrOH to yield **2u** (100 mg, 86%) as light yellowish solid (mp > 170 °C(dec.)).
^{1}H NMR (400 MHz, $CDCl_3$): δ=10.86 (br s, 1H), 8.46 (br s, 1H), 7.77 – 7.62 (m, 2H), 7.43 (br s, 1H),2.78 – 2.62 (m, 4H), 1.75 (dq, J = 13.7, 6.7, 6.3 Hz, 2H), 1.60 (dq, J = 14.9, 7.4 Hz, 2H), 1.10 – 1.01 (m, 6H). ^{13}C NMR (100 MHz, CDCl3): δ= 163.8 (Cq), 138.8 (Cq), 137.9 (Cq), 132.4 (CH), 127.8 (CH), 125.5 (CH), 123.3 (Cq), 113.3 (Cq), 33.2 (CH_2), 28.6 (CH_2), 23.9 (CH_2), 22.9 (CH_2), 14.5 (CH_3), 14.1 (CH_3). Analytical data are in accordance with those reported in the literature.

4-Methyl-3-phenylisoquinolin-1(2H)-one (2v) and 3-methyl-4-phenylisoquinolin-1(2H)-one (2v'). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8b** (150 mg, 0.50 mmol), 1-phenyl-1-propyne (126 µL, 117 mg, 1.01 mmol), 3,5-dinitrobenzoic acid potassium salt (37.9 mg, 0.15 mmol) and $[Ru(cymene)Cl_2]_2$ (30.9 mg, 0.05 mmol) in 7.5 mL of t-butanol. Crude product was purified by column chromatography on silica gel (DCM:Hex:EtOAc 1:4:1-1:1:1) to yield a mixture of **2v** and **2v'** (2:1, 113 mg, 95%) as light yellowish solid. ^{1}H NMR (300 MHz,

DMSO-d_6): δ= 11.42 (br s, 1H-**2v**'), 11.22 (br s, 1H-**2v**), 8.28 (d, J = 7.9 Hz, 1H-**2v**), 8.22 (d, J = 7.8 Hz, 1H-**2v**'), 7.84 – 7.75 (m, 2H-**2v**), 7.61 – 7.38 (m, 5H-**2v** and 7H-**2v**' overlaps), 7.27 (d, J = 6.9 Hz, 1H-**2v**), 6.99 (d, J = 8.2 Hz, 1H-**2v**'), 2.12 (s, 3H-**2v**), 2.01 (s, 3H-**2v**'). Analytical data are in accordance with those reported in the literature. [4c]

3-(4-Fluorophenyl)-4-(4-methoxyphenyl)isoquinolin-1(2H)-one (2w) and 4-(4-fluorophenyl)-3-(4-methoxyphenyl)isoquinolin-1(2H)-one (2w'). Prepared by analogy to compound **2a** from *N*-acylsulfonamide **1.8b** (150 mg, 0.50 mmol), 1-fluoro-4-((4-methoxyphenyl)ethynyl)benzene (228 mg, 1.01 mmol), 3,5-dinitrobenzoic acid potassium salt (37.9 mg, 0.15 mmol) and $[Ru(cymene)Cl_2]_2$ (30.9 mg, 0.05 mmol) in 7.5 mL of t-butanol. Crude product was purified by crystallization from i-PrOH to yield a mixture of **2w** and **2w'** (1:1, 150 mg, 86%) as light yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ= 9.18 (s, 1H), 8.95 (s, 1H), 8.47 (dt, J = 7.8, 2.0 Hz, 2H), 7.60 (t, J = 7.6 Hz, 2H), 7.56 – 7.44 (m, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.28 – 7.17 (m, 2H), 7.19 – 6.91 (m, 10H), 6.86 (d, J = 8.7 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 3.79 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ= -111.89 (tt, *J* = 8.6, 5.3 Hz), -114.69 (tt, *J* = 8.6, 5.6 Hz).

Supporting Information (see footnote on the first page of this article): All copies of the ^{1}H NMR and ^{13}C NMR spectra.

Acknowledgements

Financial support from the Latvian Instiute of Organic Synthesis (Project IGP-2015-AJ) is gratefully acknowledged. We thank Dmitrijs Stepanovs (Latvian Institute of Organic Synthesis) for perfoming X-ray analysis. We thank Dr. Liene Grigorjeva for assistance in manuscript preparation.

Keywords: C-H activation • annulation • nitrogen heterocycles • ruthenium

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10.1002/ejoc.201601582

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N-Sulfonylcarboxamides can be annulated with alkynes to give isoquinolones under Ru catalysis. *N*-Sulfonylcarboxamide acts as both a directing group for C-H activation and as an internal oxidant. Of all *N*-sulfonylcarboxamides studied, the most efficient was *N*-2,6-difluorophenylsulfonamide which led to the formation of unstable sulfinate that decomposes to 1,3-difluorobenzene under the reaction conditions.

C-H activation

*Elina Petrova, Dace Rasina, Aigars Jirgensons**

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***N*-Sulfonylcarboxamide as an Oxidizing Directing Group for Ruthenium Catalyzed C-H Activation/Annulation**