

Supporting Information

Rh(III)-catalyzed annulation of *N*-methoxybenzamides with ynesulfonamides at room temperature: a practical and efficient route to 4-aminoisoquinolone derivatives

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I. General remarks

NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer. The ^1H NMR (400 MHz) chemical shifts were measured relative to CDCl_3 or $\text{DMSO-}d_6$ as the internal reference (CDCl_3 : $\delta = 7.26$ ppm; $\text{DMSO-}d_6$: $\delta = 2.50$ ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using CDCl_3 or $\text{DMSO-}d_6$ as the internal standard (CDCl_3 : $\delta = 77.16$ ppm; $\text{DMSO-}d_6$: $\delta = 39.52$ ppm). High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). X-Ray single-crystal diffraction data were collected on an Oxford Xcalibur E X-ray single crystal diffractometer. Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. *N*-Methoxybenzamide derivatives, ynesulfonamides and CsF-Celite were prepared according to the literature procedures.¹⁻³ MeOH was dried over Mg and distilled prior to use.

II. Optimization of the Rh-catalyzed annulation of *N*-methoxybenzamide **1a** with *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a**

A sealable tube with a magnetic stir bar was charged with $[\text{RhCp}^*\text{Cl}_2]_2$ (7.8 mg, 12.5 μmol , 5 mol%), NaOAc (41 mg, 0.50 mmol, 2.0 equiv), *N*-methoxybenzamide **1a** (37.8 mg, 0.25 mmol), ynesulfonamide **2a** (85.6 mg, 0.30 mmol, 1.2 equiv) and solvent (1.0 mL) under an N_2 atmosphere. The reaction mixture was stirred at room temperature for 16 h. The resulting solution was subsequently diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

III. General procedure for the Rh-catalyzed annulation reaction

A sealable tube with a magnetic stir bar was charged with $[\text{RhCp}^*\text{Cl}_2]_2$ (7.8 mg, 12.5 μmol , 5 mol%), NaOAc (41.0 mg, 0.5 mmol, 2.0 equiv), *N*-methoxybenzamide

derivatives **1** (0.25 mmol), ynesulfonamide **2** (0.30 mmol, 1.2 equiv), and MeOH (1.0 mL) under an N₂ atmosphere. The reaction mixture was stirred at room temperature for 16 h. The resulting solution was subsequently diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

IV. Debenzylation of **3m**

A sealable tube with a magnetic stir bar was charged with 4-methyl-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-*N*-phenylbenzenesulfonamide **3m** (46.6 mg, 0.1 mmol), CsF-Celite (0.2 mmol), and MeCN (1.0 mL) under an N₂ atmosphere. The reaction mixture was stirred at 120 °C for 8 h. The resulting solution was subsequently diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated and the resulting residue was purified by column chromatography on silica gel to provide the desired product **4**.

V. Single crystal X-ray structure of **3m**

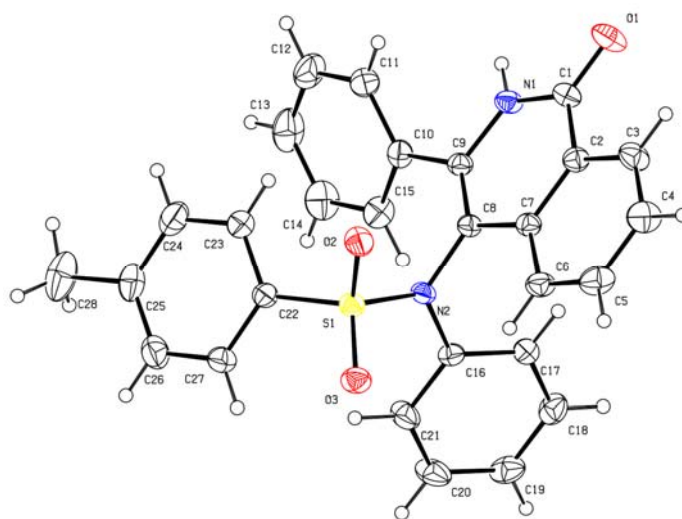
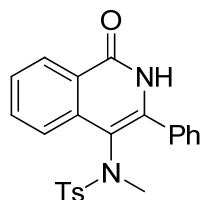


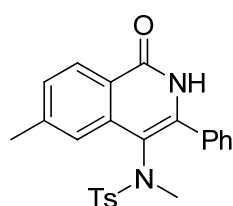
Fig. S1 ORTEP diagram of **3m**. Thermal ellipsoids are shown at the 50% probability level.

VI. Experimental data for the described substances



***N*,4-Dimethyl-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (3a)**

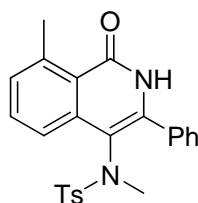
Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3a** as a white solid (86 mg, 86% yield). M.p.: 228-230 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.37 (s, 3H), 3.27 (s, 3H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.37-7.52 (m, 6H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.64-7.68 (m, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 9.70 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 39.3, 117.3, 123.8, 125.8, 127.2, 127.6, 128.2, 128.5, 128.9, 129.4, 129.7, 133.3, 133.8, 136.5, 137.3, 142.1, 143.3, 162.4 ppm. HRMS (ESI): calcd for C₂₃H₂₀N₂NaO₃S [M+Na]⁺ 427.1092, found 427.1096.



***N*,4-Dimethyl-*N*-(6-methyl-1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (3b)**

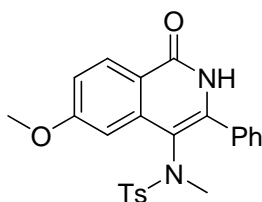
Following the general procedure. *N*-Methoxy-4-methylbenzamide **1b** (41.3 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 12/1, v/v) afforded **3b** as a white solid (81 mg, 78% yield). M.p.: 226-228 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.33 (s, 3H), 2.39 (s, 3H), 3.24 (s, 3H),

7.06-7.10 (m, 3H), 7.28-7.30 (m, 3H), 7.40-7.49 (m, 5H), 8.24 (d, $J = 8.0$ Hz, 1H), 9.18 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 21.6, 22.2, 39.3, 117.0, 123.5, 123.6, 127.7, 128.3, 128.5, 128.8, 129.0, 129.4, 129.7, 133.9, 136.9, 137.0, 142.3, 143.3, 143.9, 162.1$ ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$ 419.1429, found 419.1434.



***N*,4-Dimethyl-*N*-(8-methyl-1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (3c)**

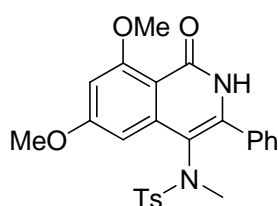
Following the general procedure. *N*-Methoxy-2-methylbenzamide **1c** (41.3 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3c** as a white solid (31 mg, 30% yield). When the reaction was performed at 80 °C for 16 h, the yield was 71%. M.p.: 229-231 °C. ^1H NMR (400 MHz, CDCl_3): $\delta = 2.37$ (s, 3H), 2.72 (s, 3H), 3.22 (s, 3H), 7.03 (d, $J = 8.0$ Hz, 2H), 7.19-7.22 (m, 3H), 7.34-7.38 (m, 2H), 7.41-7.49 (m, 5H), 10.52 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 21.6, 23.6, 39.3, 117.3, 121.7, 124.0, 127.6, 128.68, 128.74, 129.35, 129.37, 130.2, 132.4, 133.7, 136.8, 139.0, 142.2, 142.7, 143.1, 163.8$ ppm. HRMS (ESI): calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 441.1249, found 441.1241.



***N*-(6-Methoxy-1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-*N*,4-dimethylbenzenesulfonamide (3d)**

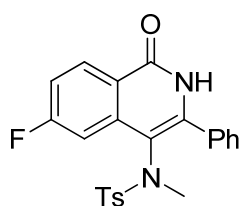
Following the general procedure. *N*,4-Dimethoxybenzamide **1d** (45.3 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol)

were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3d** as a white solid (64 mg, 59% yield). M.p.: 226-228 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.37 (s, 3H), 3.23 (s, 3H), 3.78 (s, 3H), 6.97 (d, *J* = 2.4 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.39-7.50 (m, 5H), 8.27 (d, *J* = 8.8 Hz, 1H), 9.13 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 39.0, 55.5, 104.9, 114.0, 116.9, 117.1, 127.8, 128.5, 129.0, 129.1, 129.5, 129.7, 130.3, 133.9, 136.6, 139.5, 142.9, 143.4, 163.9 ppm. HRMS (ESI): calcd for C₂₄H₂₃N₂O₄S [M+H]⁺ 435.1379, found 435.1378.



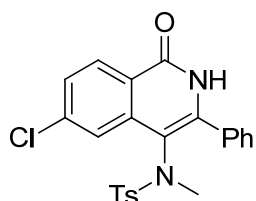
***N*-(6,8-Dimethoxy-1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-*N*,4-dimethylbenzenesulfonamide (**3e**)**

Following the general procedure. *N*,2,4-Trimethoxybenzamide **1e** (55.3 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3e** as a white solid (50 mg, 44% yield). When the reaction was performed at 80 °C for 16 h, the yield was 85%. M.p.: 225-226 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.36 (s, 3H), 3.20 (s, 3H), 3.80 (s, 3H), 3.94 (s, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.33-7.36 (m, 3H), 7.39-7.43 (m, 3H), 7.45 (d, *J* = 8.8 Hz, 1H), 9.59 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 39.3, 56.8, 61.8, 116.7, 119.2, 120.0, 120.6, 127.6, 128.5, 128.9, 129.35, 129.38, 132.4, 133.8, 136.5, 140.0, 143.2, 150.2, 152.0, 160.8 ppm. HRMS (ESI): calcd for C₂₅H₂₄N₂NaO₅S [M+Na]⁺ 487.1304, found 487.1310.



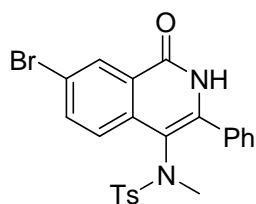
***N*-(6-Fluoro-1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-*N*,4-dimethylbenzenesulfonamide (3f)**

Following the general procedure. 4-Fluoro-*N*-methoxybenzamide **1f** (42.3 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3f** as a white solid (89 mg, 84% yield). M.p.: 221-223 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.38 (s, 3H), 3.22 (s, 3H), 7.06-7.11 (m, 3H), 7.18 (td, *J* = 8.4 Hz, 2.4 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.39-7.50 (m, 5H), 8.30-8.35 (m, 1H), 9.67-9.82 (m, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 39.1, 109.2, 109.5, 115.7, 116.0, 116.8, 116.9, 122.3, 127.6, 128.5, 128.9, 129.5, 129.9, 131.4, 131.5, 133.4, 136.4, 139.9, 140.0, 143.6, 143.8, 161.8, 164.8, 167.4 ppm. HRMS (ESI): calcd for C₂₃H₁₉FN₂NaO₃S [M+Na]⁺ 445.0998, found 445.0995.



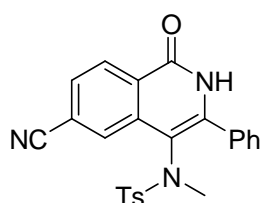
***N*-(6-Chloro-1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-*N*,4-dimethylbenzenesulfonamide (3g)**

Following the general procedure. 4-Chloro-*N*-methoxybenzamide **1g** (46.3 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3g** as a white solid (68 mg, 62% yield). M.p.: 224-226 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.40 (s, 3H), 3.22 (s, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 1.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 7.43-7.52 (m, 5H), 8.27 (d, *J* = 8.4 Hz, 1H), 9.28 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.7, 39.2, 116.4, 123.3, 124.1, 127.6, 127.8, 128.5, 129.1, 129.7, 130.06, 130.08, 133.4, 136.5, 138.4, 140.1, 143.8, 143.9, 161.5 ppm. HRMS (ESI): calcd for C₂₃H₁₉ClN₂NaO₃S [M+Na]⁺ 461.0703, found 461.0705.



***N*-(7-Bromo-1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-*N*,4-dimethylbenzenesulfonamide (**3h**)**

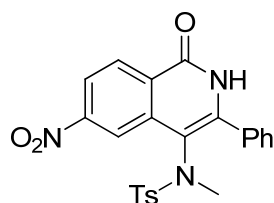
Following the general procedure. 3-Bromo-*N*-methoxybenzamide **1h** (57.3 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3h** as a white solid (75 mg, 62% yield). M.p.: 234-236 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.38 (s, 3H), 3.22 (s, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.38-7.43 (m, 4H), 7.46-7.50 (m, 2H), 7.74 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 9.76 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 39.3, 117.1, 121.3, 125.7, 127.2, 127.6, 128.4, 129.0, 129.5, 129.9, 130.8, 133.4, 136.2, 136.3, 136.5, 142.6, 143.5, 161.2 ppm. HRMS (ESI): calcd for C₂₃H₁₉BrN₂NaO₃S [M+Na]⁺ 505.0197, found 505.0199.



***N*-(6-Cyano-1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-*N*,4-dimethylbenzenesulfonamide (**3i**)**

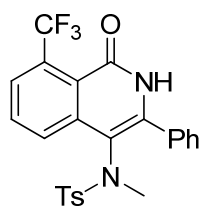
Following the general procedure. 4-Cyano-*N*-methoxybenzamide **1i** (44.0 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. The reaction mixture was stirred at 80 °C for 16 h. Purification via column chromatography on silica gel (DCM/ acetone = 10/1, v/v) afforded **3i** as a white solid (80 mg, 75% yield). M.p.: 236-238 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.38 (s, 3H), 3.17 (s, 3H), 7.23 (m, 4H), 7.33 (s, 1H), 7.42-7.52 (m, 5H), 7.87 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 12.02 (s, 1H) ppm. ¹³C NMR (100

MHz, CDCl₃): δ = 21.7, 39.2, 116.3, 116.8, 117.9, 127.5, 128.1, 128.35, 128.44, 129.0, 129.2, 129.4, 129.9, 130.4, 133.0, 136.3, 137.4, 144.5, 144.7, 161.0 ppm. HRMS (ESI): calcd for C₂₄H₁₉N₃NaO₃S [M+Na]⁺ 452.1045, found 452.1044.



***N*,4-Dimethyl-*N*-(6-nitro-1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (3j)**

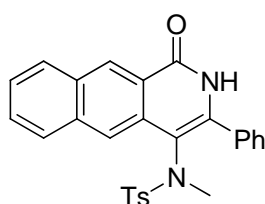
Following the general procedure. *N*-Methoxy-4-nitrobenzamide **1j** (49 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3j** as a pale yellow solid (82 mg, 73% yield). M.p.: 239-241 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.35 (s, 3H), 3.16 (s, 3H), 7.19 (m, 4H), 7.42-7.52 (m, 5H), 8.06 (d, *J* = 2.0 Hz, 1H), 8.24 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 8.47 (d, *J* = 8.8 Hz, 1H), 12.08 (s, 1H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 20.9, 38.6, 115.3, 118.6, 120.3, 127.0, 128.2, 128.8, 129.0, 129.4, 129.6, 129.9, 132.5, 135.7, 137.5, 143.5, 145.9, 150.1, 160.1 ppm. HRMS (ESI): calcd for C₂₃H₁₉N₃NaO₅S [M+Na]⁺ 472.0943, found 472.0938.



***N*,4-Dimethyl-*N*-(1-oxo-3-phenyl-8-(trifluoromethyl)-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (3k)**

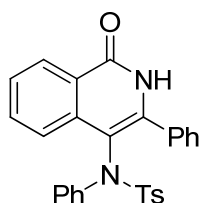
Following the general procedure. *N*-Methoxy-2-(trifluoromethyl)benzamide **1k** (54.8 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3k** as a white solid (66 mg, 53% yield). M.p.:

220-223 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.38 (s, 3H), 3.24 (s, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.36-7.48 (m, 5H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 10.68 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 39.5, 116.7, 122.9, 126.7, 126.8, 127.6, 128.2, 128.4, 129.0, 129.5, 129.8, 130.3, 130.6, 132.2, 132.8, 136.4, 140.5, 143.4, 144.0, 160.1 ppm. HRMS (ESI): calcd for C₂₄H₂₀F₃N₂O₃S [M+H]⁺ 473.1147, found 473.1151.



***N*,4-Dimethyl-*N*-(1-oxo-3-phenyl-1,2-dihydrobenzo[*g*]isoquinolin-4-yl)benzenesulfonamide (3l)**

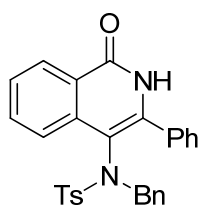
Following the general procedure. *N*-Methoxy-2-naphthamide **1l** (50.3 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2a** (85.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3l** as a white solid (95 mg, 84% yield). M.p.: > 250 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.36 (s, 3H), 3.21 (s, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.37-7.41 (m, 2H), 7.44-7.49 (m, 3H), 7.56 (d, *J* = 9.2 Hz, 1H), 7.68 (td, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 7.77 (td, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 8.18 (d, *J* = 8.8 Hz, 1H), 10.16 (d, *J* = 8.8 Hz, 1H), 12.03 (s, 1H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 21.0, 30.7, 116.2, 118.3, 121.0, 126.3, 126.5, 127.0, 128.2, 128.4, 128.9, 129.2, 129.4, 131.3, 131.5, 132.7, 134.0, 136.0, 139.1, 143.1, 144.6, 161.9 ppm. HRMS (ESI): calcd for C₂₇H₂₂N₂NaO₃S [M+Na]⁺ 477.1249, found 477.1245.



4-Methyl-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-*N*-phenylbenzenesulfonamide

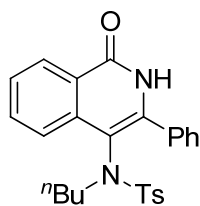
amide (**3m**)

Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and 4-methyl-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide **2b** (99.3 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3m** as a white solid (98 mg, 84% yield). M.p.: 244-246 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.32 (s, 3H), 7.03-7.08 (m, 3H), 7.13-7.16 (m, 4H), 7.21-7.25 (m, 2H), 7.33-7.40 (m, 4H), 7.45-7.57 (m, 3H), 7.65-7.69 (m, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 11.82 (s, 1H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 20.9, 113.3, 119.7, 123.8, 123.9, 125.7, 126.9, 127.2, 127.6, 128.3, 128.7, 129.2, 129.5, 129.6, 132.6, 132.7, 136.2, 137.0, 141.9, 143.8, 144.1, 161.3 ppm. HRMS (ESI): calcd for C₂₈H₂₂N₂NaO₃S [M+Na]⁺ 489.1249, found 489.1256.



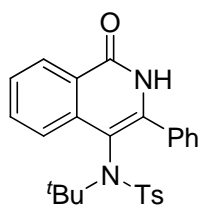
N-Benzyl-4-methyl-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (**3n**)

Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*-benzyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide **2c** (108.3 mg, 0.30 mmol) were used. The reaction was performed at 80 °C for 16 h. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3n** as a white solid (102 mg, 85% yield). M.p.: 201-203 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.45 (s, 3H), 4.43 (d, *J* = 14.0 Hz, 1H), 4.58 (d, *J* = 14.0 Hz, 1H), 6.61 (d, *J* = 7.2 Hz, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 7.04 (t, *J* = 7.2 Hz, 2H), 7.16-7.23 (m, 5H), 7.36-7.55 (m, 6H), 8.33 (d, *J* = 8.4 Hz, 1H), 9.21 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.7, 54.0, 114.0, 124.4, 125.8, 127.1, 128.2, 128.35, 128.44, 128.5, 129.1, 129.3, 129.6, 130.2, 132.9, 133.4, 134.5, 136.7, 137.2, 143.6, 144.0, 161.9 ppm. HRMS (ESI): calcd for C₂₉H₂₄N₂NaO₃S [M+Na]⁺ 503.1405, found 503.1408.



***N*-Butyl-4-methyl-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (3o)**

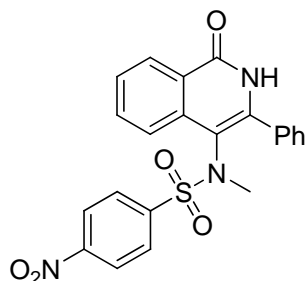
Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*-butyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide **2d** (98.1 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3o** as a white solid (98 mg, 88% yield). M.p.: 208-210 °C. ¹H NMR (400 MHz, CDCl₃): δ = 0.71 (t, *J* = 7.6 Hz, 3H), 0.97-1.10 (m, 2H), 1.15-1.35 (m, 2H), 2.43 (s, 3H), 3.23-3.31 (m, 1H), 3.40-3.48 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.40-7.59 (m, 10H), 8.36 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 9.09 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.7, 20.2, 21.7, 30.4, 51.2, 115.5, 124.5, 125.7, 127.1, 128.1, 128.6, 129.3, 129.5, 129.8, 132.8, 133.6, 137.4, 137.9, 142.6, 143.6, 162.2 ppm. HRMS (ESI): calcd for C₂₆H₂₆N₂NaO₃S [M+Na]⁺ 469.1562, found 469.1560.



***N*-(*tert*-Butyl)-4-methyl-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (3p)**

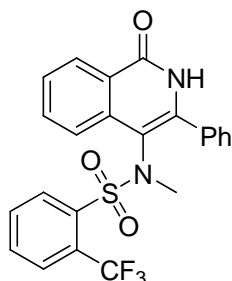
Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*-*tert*-butyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide **2e** (98.1 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3p** as a white solid (79 mg, 71% yield). M.p.: 230-232 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (s, 9H), 2.39 (s, 3H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.22-7.25 (m, 1H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.50-7.56 (m, 5H), 7.94-7.96 (m, 2H), 8.32 (d, *J* = 8.0 Hz, 1H), 9.16 (br, 1H) ppm. ¹³C

NMR (100 MHz, CDCl₃): δ = 21.6, 30.7, 63.9, 117.0, 125.3, 125.6, 126.8, 127.8, 128.8, 129.0, 129.3, 129.9, 130.0, 131.8, 134.8, 138.5, 140.1, 143.2, 143.6, 161.8 ppm. HRMS (ESI): calcd for C₂₆H₂₆N₂NaO₃S [M+Na]⁺ 469.1562, found 469.1562.



***N*-Methyl-4-nitro-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (3q)**

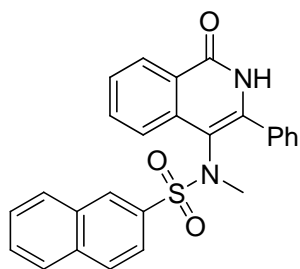
Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide **2f** (94.8 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3q** as a white solid (74 mg, 68% yield). M.p.: 232-234 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.40 (s, 3H), 7.32-7.38 (m, 4H), 7.41-7.49 (m, 3H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.73-7.77 (m, 1H), 8.04 (d, *J* = 8.8 Hz, 2H), 8.41 (d, *J* = 7.6 Hz, 1H), 8.99 (s, 1H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 39.7, 115.2, 122.8, 124.2, 125.4, 126.9, 127.3, 128.1, 128.7, 129.1, 132.7, 133.0, 136.6, 142.9, 144.6, 149.3, 161.2 ppm. HRMS (ESI): calcd for C₂₂H₁₈N₃O₅S [M+H]⁺ 436.0967, found 436.0969.



***N*-Methyl-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-2-(trifluoromethyl)benzenesulfonamide (3r)**

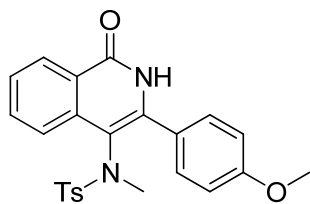
Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol)

and *N*-methyl-*N*-(phenylethynyl)-2-(trifluoromethyl)benzenesulfonamide **2g** (101.7 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3r** as a white solid (97 mg, 85% yield). M.p.: 188-190 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.37 (s, 3H), 7.31-7.41 (m, 6H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.50-7.57 (m, 2H), 7.67-7.70 (m, 2H), 7.73 (s, 1H), 8.32 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 10.01 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 40.0, 116.8, 121.8, 123.3, 124.37, 124.41, 124.5, 124.6, 125.8, 127.4, 128.4, 128.9, 129.1, 129.18, 129.21, 129.3, 129.7, 130.1, 130.5, 131.3, 131.6, 133.3, 133.5, 137.0, 141.0, 142.2, 162.5 ppm. HRMS (ESI): calcd for C₂₃H₁₇F₃N₂NaO₃S [M+Na]⁺ 481.0810, found 481.0812.



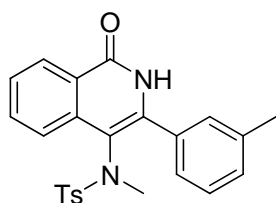
***N*-Methyl-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)naphthalene-2-sulfonamide (**3s**)**

Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*-methyl-*N*-(phenylethynyl)naphthalene-2-sulfonamide **2h** (96.3 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3s** as a white solid (100 mg, 91% yield). M.p.: > 250 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.35 (s, 3H), 7.20-7.28 (m, 4H), 7.37-7.40 (m, 2H), 7.48-7.52 (m, 1H), 7.55-7.67 (m, 5H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 9.58 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 39.7, 117.2, 122.7, 123.8, 127.3, 127.4, 127.8, 128.2, 128.4, 128.8, 128.9, 128.99, 129.02, 129.5, 129.7, 132.0, 133.4, 133.6, 134.8, 136.5, 137.3, 142.0, 162.4 ppm. HRMS (ESI): calcd for C₂₆H₂₁N₂O₃S [M+H]⁺ 441.1273, found 441.1274.



***N*-(3-(4-Methoxyphenyl)-1-oxo-1,2-dihydroisoquinolin-4-yl)-*N*,4-dimethylbenzenesulfonamide (**3t**)**

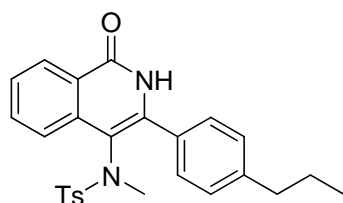
Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*-((4-methoxyphenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide **2i** (94.5 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3t** as a white solid (89 mg, 82% yield). M.p.: 243-245 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.38 (s, 3H), 3.28 (s, 3H), 3.86 (s, 3H), 6.84-6.88 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.24 (s, 1H), 7.32-7.36 (m, 2H), 7.47-7.51 (m, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.63-7.67 (m, 1H), 8.36 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 9.39 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 39.4, 55.5, 114.3, 117.2, 123.6, 125.6, 125.9, 127.1, 127.5, 128.2, 129.3, 129.8, 133.3, 136.9, 137.5, 141.7, 143.1, 160.8, 162.4 ppm. HRMS (ESI): calcd for C₂₄H₂₃N₂O₄S [M+H]⁺ 435.1379, found 435.1380.



***N*,4-Dimethyl-*N*-(1-oxo-3-m-tolyl-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (**3u**)**

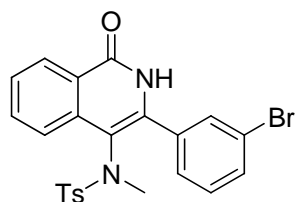
Following the general procedure. *N*-methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-(*m*-tolylethynyl)benzenesulfonamide **2j** (89.7 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/Acetone = 10/1, v/v) afforded **3u** as a white solid (94 mg, 90% yield). M.p.: 218-220 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.30 (s, 3H), 2.37 (s, 3H), 3.27 (s, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.18-7.29 (m, 6H), 7.48-7.52 (m, 1H), 7.63-7.70 (m, 2H), 8.34 (d, *J* = 7.6 Hz, 1H), 9.74 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.5, 21.6, 39.4, 117.3,

123.8, 125.6, 125.7, 127.2, 127.5, 128.2, 128.8, 129.1, 129.3, 130.4, 133.4, 133.6, 136.6, 137.5, 138.7, 142.1, 143.1, 162.5 ppm. HRMS (ESI): calcd for C₂₄H₂₃N₂O₃S [M+H]⁺ 419.1429, found 419.1426.



***N*,4-Dimethyl-*N*-(1-oxo-3-(4-propylphenyl)-1,2-dihydroisoquinolin-4-yl)benzenesulfonamide (3v)**

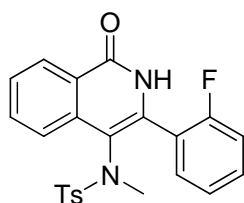
Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*,4-dimethyl-*N*-((4-propylphenyl)ethynyl)benzenesulfonamide **2k** (98.1 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3v** as a white solid (96 mg, 86% yield). M.p.: 228-230 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.02 (t, *J* = 7.2 Hz, 3H), 1.66-1.76 (m, 2H), 2.37 (s, 3H), 2.65 (t, *J* = 8.0 Hz, 2H), 3.27 (s, 3H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.47-7.51 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.64-7.68 (m, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 9.46 (br, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.1, 21.6, 24.5, 38.0, 39.4, 117.2, 123.7, 125.7, 127.1, 127.6, 128.2, 128.3, 128.9, 129.3, 131.1, 133.3, 136.8, 137.5, 142.2, 143.1, 144.6, 162.3 ppm. HRMS (ESI): calcd for C₂₆H₂₇N₂O₃S [M+H]⁺ 447.1742, found 447.1741.



***N*-(3-(3-Bromophenyl)-1-oxo-1,2-dihydroisoquinolin-4-yl)-*N*,4-dimethylbenzenesulfonamide (3w)**

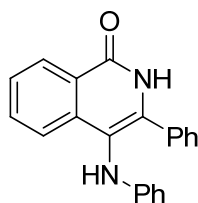
Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*-((3-bromophenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide **2l** (108.9 mg, 0.30

mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3w** as a white solid (80 mg, 67% yield). M.p.: 220-222 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.40 (s, 3H), 3.32 (s, 3H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.24-7.28 (m, 3H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.51-7.57 (m, 3H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.67-7.71 (m, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 10.38 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.7, 39.6, 117.9, 122.8, 123.9, 125.9, 127.29, 127.33, 127.6, 128.3, 129.5, 130.3, 131.7, 132.6, 133.5, 135.4, 136.6, 137.2, 140.4, 143.5, 162.7 ppm. HRMS (ESI): calcd for C₂₃H₂₀BrN₂O₃S [M+H]⁺ 483.0378, found 483.0378.



***N*-(3-(2-Fluorophenyl)-1-oxo-1,2-dihydroisoquinolin-4-yl)-*N*,4-dimethylbenzenesulfonamide (**3x**)**

Following the general procedure. *N*-Methoxybenzamide **1a** (37.8 mg, 0.25 mmol) and *N*-((2-fluorophenyl)ethynyl)-*N*,4-dimethylbenzenesulfonamide **2m** (90.9 mg, 0.30 mmol) were used. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **3x** as a white solid (84 mg, 79% yield). M.p.: 130-132 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.39 (s, 3H), 3.21 (s, 3H), 7.08-7.13 (m, 3H), 7.24-7.28 (m, 3H), 7.43-7.54 (m, 4H), 7.60-7.64 (m, 1H), 8.34 (dd, *J* = 8.0 Hz, 0.8 Hz, 1H), 9.70 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.6, 38.20, 38.24, 116.1, 116.3, 118.9, 121.4, 121.5, 123.8, 124.6, 124.7, 126.1, 127.5, 127.7, 128.3, 129.5, 131.56, 131.58, 131.7, 131.8, 133.2, 136.4, 136.7, 136.8, 143.5, 158.6, 161.0, 162.4 ppm. HRMS (ESI): calcd for C₂₃H₁₉FN₂NaO₃S [M+Na]⁺ 445.0998, found 445.1003.



3-Phenyl-4-(phenylamino)isoquinolin-1(2H)-one (4)

A flame-dried Schlenk tube with a magnetic stirring bar was charged with 4-methyl-*N*-(1-oxo-3-phenyl-1,2-dihydroisoquinolin-4-yl)-*N*-phenylbenzenesulfonamide **3m** (46.6 mg, 0.1 mmol), CsF-Celite (0.2 mmol, 50.4 mg) and MeCN (1 mL) under an N₂ atmosphere. The reaction mixture was stirred at 120 °C for 8 h. Purification via column chromatography on silica gel (DCM/acetone = 10/1, v/v) afforded **4** as a white solid (20 mg, 64% yield). M.p.: 226-228 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 6.46 (d, *J* = 8.0 Hz, 2H), 6.53 (t, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 2H), 7.30 (s, 1H), 7.36-7.37 (m, 3H), 7.49-7.56 (m, 4H), 7.65-7.69 (m, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 11.42 (s, 1H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 112.5, 113.8, 116.6, 123.5, 126.0, 126.5, 127.2, 127.9, 128.8, 128.9, 129.1, 132.5, 133.2, 137.7, 139.5, 148.8, 161.6 ppm. HRMS (ESI): calcd for C₂₁H₁₇N₂O [M+H]⁺ 313.1341, found 313.1339.

VII. References

- 1 B. Li, H. Feng, S. Xu and B. Wang, *Chem. Eur. J.*, 2011, **17**, 12573.
- 2 (a) C.-F. Xu, M. Xu, Y.-X. Jia and C.-Y. Li, *Org. Lett.*, 2011, **13**, 1556; (b) B. Yao, Z. Liang, T. Niu and Y. Zhang, *J. Org. Chem.*, 2009, **74**, 4630
- 3 F. Tamaddon, A. Nasiri and S. Farokhi, *Catal. Commun.*, 2011, **12**, 1477.

VIII. Copies of ^1H and ^{13}C NMR spectra

