Supporting information for:

Ruthenium(II)-Catalyzed Reductive N-O Bond Cleavage of N-OR (R = H, alkyl, or acyl) Substituted Amides and Sulfonamides

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I. General Information	1
II. Procedures for the Synthesis of Starting Materials	1
III. N-O bond Cleavage of N-OR Substituted Amides and Sulfonamides	5
IV. Gram-scale Reaction	14
V. NMR Spectra	15

I. General Information

[RuCl₂(*p*-cymene)]₂ (98%), Ru(PPh₃)₃Cl₂ (98%), [RhCp*Cl₂]₂ (98%) were purchased from Energy Chemical and used as received. The other commercially available chemicals were used as received. Flash column chromatography was performed using 200–300 mesh silica with the proper solvent system according to thin layer chromatography (TLC) analysis using UV light to visualize the reaction components. NMR spectra were recorded on a Bruker-300 instrument or Bruker-500 instrument. ¹H NMR chemical shifts were referenced to tetramethylsilane (TMS) signal (0 ppm), ¹³C NMR chemical shifts were referenced to the solvent resonance [77.00 ppm, CDCl₃; 40.45, (CD₃)₂SO]. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet. In this report, all the reactions that require heating were using oil bath as the heating source. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer.

II. Procedures for the Synthesis of Starting Materials

General procedure for the synthesis of N-OR substituted amide:

1v and **1ac** were purchased from commercially available resources and used directly. Other *N*-OR substituted amides and sulfonamides were prepared following literature procedures and the analytical data of the known compounds are consistent with those data which have been previously reported. **1w** and **1x** were prepared according to Route B; **1y**, **1z** and **1aa** were prepared

according to Route C; all the others substrates were prepared according to Route A.



Route A¹: A round-bottomed flask was charged with R^1O-NH_2 ·HCl (12 mmol, 1.2 equiv.), K_2CO_3 (20 mmol, 2.0 equiv.), ethyl acetate (EA) (50 mL) and H_2O (25 mL). Then the mixture was added with acyl chloride or sulfonyl chloride (10 mmol) at 0 °C, stirring at room temperature overnight. The reaction was quenched with brine (75 mL), extracted with EA (50 mL x 2). The combined organic layers were dried over anhydrous NaSO₄, filtered, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

Route B: A round-bottomed flask was charged with NH_2OHHC1 (12 mmol, 1.2 equiv.), $NaHCO_3$ (20 mmol, 2.0 equiv.), EA (50 mL) and H_2O (25 mL). Then the mixture was added with acyl chloride (10 mmol) at 0 °C, stirring at room temperature overnight. The reaction was quenched with brine (75 mL), extracted with EA (50 mL x 2). The combined organic layers were dried over anhydrous NaSO₄, filtered, concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

Route C²: For detailed procedures, see reference.

N-Methoxybenzamide (1a).³ ¹H NMR (500 MHz, CDCl₃) δ 9.36 (bs, 1H), 7.75 (d, J = 7.6 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.4 Hz, 2H), 3.86 (s, 3H).

¹ Guimond, N.; Gouliaras, C.; Fagnou, K. J. Am. Chem. Soc. 2010, 132, 6908.

² Guimond, N.; Gorelsky, S.; Fagnou, K. J. Am. Chem. Soc. 2011, 133, 6449.

³ Wrigglesworth, J. W.; Cox, B.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. Org. Lett. 2011, 13, 5326.

N-Methoxy-4-methylbenzamide (1b).³ ¹H NMR (500 MHz, CDCl₃) δ 9.16 (bs, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 3.86 (s, 3H), 2.38 (s, 3H).

N,4-Dimethoxybenzamide (1c).¹ ¹H NMR (500 MHz, CDCl₃) δ 9.10 (bs, 1H), 7.73 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H).

4-Fluoro-*N***-methoxybenzamide (1d).**⁴ ¹H NMR (500 MHz, CDCl₃) δ 9.38 (bs, 1H), 7.80-7.77 (m, 2H), 7.10 (t, *J* = 8.4 Hz, 2H), 3.85 (s, 3H).

4-Fhloro-*N***-methoxybenzamide (1e).**⁴ ¹H NMR (500 MHz, CDCl₃) δ 9.43 (bs, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H).

3-Chloro-N-methoxybenzamide (1f).⁵ ¹H NMR (500 MHz, CDCl₃) δ 9.33 (bs, 1H), 7.75 (t, *J* = 1.8 Hz, 1H), 7.64-7.62 (m, 1H), 7.49 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 3.87 (s, 3H).

N-Methoxy-2-methylbenzamide (1g).⁴ ¹H NMR (500 MHz, d₆-DMSO) δ 11.43 (bs, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.30-7.22 (m, 3H), 3.71 (s, 3H), 2.33 (s, 3H).

2-Ethoxy-N-methoxybenzamide (1h).⁶ ¹H NMR (500 MHz, CDCl₃) δ 10.33 (bs, 1H), 8.20 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.45 (ddd, *J* = 8.4, 7.3, 1.9 Hz, 1H), 7.10-7.07 (m, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 3.89 (s, 3H), 1.54 (t, *J* = 7.0 Hz, 3H).

N-Methoxy-[1,1'-biphenyl]-2-carboxamide (1i).⁷ ¹H NMR (300 MHz, CDCl₃) δ 7.79 (bs, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H), 7.47-7.40 (m, 7H), 3.55 (s, 3H).

2-Hydroxy-*N***-methoxybenzamide (1j).**⁸ ¹H NMR (300 MHz, CDCl₃) δ 11.50 (bs, 1H), 9.20 (bs, 1H), 7.46-7.35 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 3.90 (s, 3H).

N-Methoxy-3,5-dimethylbenzamide (1k).⁶ ¹H NMR (500 MHz, d₆-DMSO) δ 11.63 (s, 1H), 7.35 (s, 2H), 7.17 (s, 1H), 3.69 (s, 3H), 2.30 (s, 6H).

2,6-Dichloro-*N***-methoxybenzamide (11).** ¹H NMR (500 MHz, d₆-DMSO) δ 11.82 (bs, 1H), 7.55-7.47 (m, 3H), 3.74 (s, 3H). ¹³C NMR (125 MHz, d₆-DMSO) δ 159.8, 133.2, 132.0, 131.9, 128.2, 63.2. HRMS (ESI+) calcd for C₈H₇Cl₂NNaO₂⁺ ([M + Na]⁺) 241.9746, found 241.9752.

⁴ Rakshit, S.; Grohmann, C.; Besset, T.; Glorius, F. J. Am. Chem. Soc. 2011, 133, 2350.

⁵ Zhong, H.; Yang, D.; Wang, S.; Huang, J. Chem. Commun. 2012, 48, 3236.

⁶ Wang, G.; Yuan, T. J. Org. Chem. 2010, 75, 476.

⁷ Wang, G.; Yuan, T.; Li, D. Angew. Chem., Int. Ed. 2011, 50, 1380.

⁸ Kozlov, M. V.; Kleymenova, A. A.; Romanova, L. I.; Konduktorov K. A.; Smirnova, O. A.; Prasolov, V. S.; Kochetkov, S. N. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 5936.

N-Methoxy-1-naphthamide (1m).⁴ ¹H NMR (500 MHz, d₆-DMSO) δ 11.69 (bs, 1H), 8.17 (d, *J* = 7.9 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.0-7.99 (m, 1H), 7.62-7.53 (m, 4H), 3.81 (s, 3H).

N-Methoxy-2-naphthamide (1n).⁴ ¹H NMR (500 MHz, CDCl₃) δ 9.36 (bs, 1H), 8.26 (s, 1H),

7.85 (t, *J* = 7.3 Hz, 3H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.54 (dt, *J* = 14.8, 7.1 Hz, 2H), 3.91 (s, 3H).

N-Methoxyisonicotinamide (10).² ¹H NMR (400 MHz, CDCl₃) δ 9.50 (br s, 1H), 8.73 (br s, 4H), 7.63 (br s, 4H), 3.91 (s, 6H).

N-Methoxyfuran-2-carboxamide (1p).⁵ ¹H NMR (500 MHz, CDCl₃) δ 9.02 (bs, 1H), 7.45 (s, 1H), 7.21 (d, *J* = 3.4 Hz, 1H), 6.53-6.52 (m, 1H), 3.89 (s, 3H).

N-Methoxythiophene-2-carboxamide (1q).⁴ ¹H NMR (500 MHz, CDCl₃) δ 9.25 (bs, 1H), 7.71 (s, 1H), 7.54 (d, *J* = 4.8 Hz, 1H), 7.10 (dd, *J* = 4.8, 3.9 Hz, 1H), 3.86 (s, 3H).

N-Methoxy-2-phenylacetamide (1r).⁹ ¹H NMR (500 MHz, CDCl₃) δ 8.82 (bs, 1H), 7.34-7.26 (m, 5H), 3.70 (s, 3H), 3.48 (s, 2H).

N-Methoxy-3-phenylpropanamide (1s).¹⁰ ¹H NMR (400 MHz, CDCl₃) δ 9.79 (bs, 1H), 7.30-7.13 (m, 5H), 3.62 (s, 3H), 2.94 (t, *J* = 7.8 Hz, 2H), 2.40 (t, *J* = 7.6 Hz, 2H).

(**3r**,**5r**,**7r**)-*N*-**Methoxyadamantane-1-carboxamide** (**1t**).¹¹ ¹H NMR (500 MHz, d₆-DMSO) δ 10.74 (bs, 1H), 3.53 (s, 3H), 2.50-2.51 (m, 1H), 1.94 (s, 3H), 1.74 (d, *J* = 2.6 Hz, 5H), 1.68-1.61 (m, 6H).

N-Ethoxybenzamide (1u).³ ¹H NMR (500 MHz, CDCl₃) δ 9.18 (bs, 1H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 4.08 (q, *J* = 6.9 Hz, 2H), 1.31 (t, *J* = 7.0 Hz, 3H). *N*-(Benzyloxy)benzamide (1v).³ ¹H NMR (500 MHz, d₆-DMSO) δ 11.80 (bs, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.49-7.35 (m, 7H), 4.93 (s, 2H).

3-Chloro-*N***-hydroxybenzamide (1x).**⁸ ¹H NMR (300 MHz, d₆-DMSO) δ 11.34 (bs, 1H), 9.17 (bs, 1H), 7.77 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H).

N-Hydroxy-4-methoxybenzamide (1y).⁸ ¹H NMR (300 MHz, d₆-DMSO) δ 11.07 (bs, 1H), 8.90 (bs, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H).

N-Acetoxybenzamide (1z).² ¹H NMR (500 MHz, CDCl₃) δ 9.70 (bs, 1H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 2.27 (s, 3H).

N-(Pivaloyloxy)benzamide (1aa).² ¹H NMR (500 MHz, CDCl₃) δ 9.68 (bs, 1H), 7.80-7.78 (m,

⁹ Willwacher, J.; Rakshit S.; Glorius, F. Org. Biomol. Chem. 2011, 9, 4736.

¹⁰ Miyata, O.; Koizumi, T.; Asai, H.; Iba R.; Naito, T. *Tetrahedron* **2004**, *60*, 3893.

¹¹ Yus, M.; Radivoy, G.; Alonso, F. Synthesis 2001, 914.

2H), 7.53-7.51 (m, 1H), 7.43-7.40 (m, 2H), 1.33 (s, 9H).

N-(Benzoyloxy)benzamide (1ab).² ¹H NMR (300 MHz, d₆-DMSO) δ 12.65 (bs, 1H), 8.10 (d, *J* = 7.3 Hz, 2H), 7.89 (d, *J* = 7.1 Hz, 2H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.70-7.49 (m, 5H).

4-Nitro-*N***-(pivaloyloxy)benzamide (1ac).**² ¹H NMR (500 MHz, CDCl₃) δ 9.72 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 1.36 (s, 9H).

N-Methyl-*N*-(pivaloyloxy)benzamide (1ad). ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 2H), 3.37 (s, 3H), 1.03 (s, 9H). ¹³C NMR (125 MHz, CDCl₃) δ 175.4, 171.4, 133.4, 130.5, 127.8, 127.7, 37.8, 26.8, 26.3. HRMS (ESI+) calcd for C₁₃H₁₇NNaO₃⁺ ([M + Na]⁺) 258.1101, found 258.1122.

N-Methoxybenzenesulfonamide (3a).¹² ¹H NMR (500 MHz, d₆-DMSO) δ 10.55 (bs, 1H), 7.86-7.85 (m, 2H), 7.74-7.71 (m, 1H), 7.66-7.62 (m, 2H), 3.66 (s, 3H).

N-Methoxy-2-methylbenzenesulfonamide (3b).¹³ ¹H NMR (500 MHz, d₆-DMSO) δ 10.54 (bs, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.45-7.42 (m, 2H), 3.62 (s, 3H), 2.60 (s, 3H).

N-Methoxy-4-methylbenzenesulfonamide (3c).¹⁴ ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.07 (bs, 1H), 3.79 (s, 3H), 2.45 (s, 3H)

N-Methoxy-1-phenylmethanesulfonamide (3d).¹⁵ ¹H NMR (500 MHz, d₆-DMSO) δ 10.21 (bs, 1H), 7.41-7.36 (m, 5H), 4.44 (s, 2H), 3.71 (s, 3H).

III. N-O bond cleavage of N-OR substituted amides and sulfonamides:

General procedure for the N-O bond cleavage reaction: To a 10 mL dried Schlenk flask under air, *N*-OR substituted amide or sulfonamide (0.2 mmol), $[RuCl_2(p-cymene)]_2$ (0.0031 g, 0.005 mmol), HCOOH/Et₃N (molar ratio 1/1, 0.5 mL), and H₂O (0.5 mL) were added in sequence. After stirring at 100 °C for 12 hours, the mixture was quenched with saturated NH₄Cl (5 mL), extracted with EA (15 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with PE/EA as the eluent to afford the desired product.

¹² Pu, X.; Li, Q.; Lu, Z.; Yang, X. Eur. J. Org. Chem. 2016, 5937.

¹³ Xu, L.; Shu, H.; Liu, Y.; Zhang, S.; Trudell, M. L. *Tetrahedron* 2006, 62, 7902.

¹⁴ Xie, W.; Yang, J.; Wang, B.; Li, B. J. Org. Chem. 2014, 79, 8278.

¹⁵ Ishiwata, Y.; Suzuki, Y.; and Togo, H. Heterocycles 2010, 82, 339.



Benzamide (2a).¹⁶ Prepared according to the general procedure using 0.0304 g of 1a (0.2 mmol), and 2a was obtained as a white solid (0.0225 g, 92% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.29 (br, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 169.7, 133.5, 132.0, 128.6, 127.4.



4-Methylbenzamide (2b).¹⁷ Prepared according to the general procedure using 0.0332 g of 1b (0.2 mmol), and 2b was obtained as a white solid (0.0249 g, 91% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.07 (br, 2H), 2.40 (s, 3H); ¹³C NMR (125 MHz, d₆-DMSO) δ 167.8, 141.0, 131.5, 128.7, 127.5, 20.9.



4-Methoxybenzamide (2c).¹⁷ Prepared according to the general procedure using 0.0364 g of 1c (0.2 mmol), and 2c was obtained as a white solid (0.0269 g, 89% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 5.85 (bs, 2H), 3.86 (s, 3H); ¹³C NMR (125 MHz, d₆-DMSO) δ 167.5, 161.5, 129.3, 126.4, 113.3, 55.3.



4-Fluorobenzamide (2d).¹⁷ Prepared according to the general procedure using 0.0342 g of 1d (0.2 mmol), and 2d was obtained as a white solid (0.0257 g, 91% yield) after flash column chromatography. ¹H NMR (500 MHz, d₆-DMSO) δ 8.01 (br, 1H), 7.98-7.94 (m, 2H), 7.41 (br,

¹⁶ Ramón, R. S.; Bosson, J.; Díez-González, S.; Marion, N.; Nolan, S. P. J. Org. Chem. 2010, 75, 1197.

¹⁷ Nielsen, D. U.; Taaning, R. H.; Lindhardt, A. T.; Gøgsig, T. M.; Skrydstrup, T. Org. Lett. 2011, 13, 4454.

1H), 7.31-7.26 (m, 2H); ¹³C NMR (125 MHz, d₆-DMSO) δ 166.8, 163.9 (d, *J* = 248.3 Hz), 130.7 (d, *J* = 2.9 Hz), 130.1 (d, *J* = 9.0 Hz), 115.0 (d, *J* = 21.7 Hz).



4-Chlorobenzamide (2e).¹⁷ Prepared according to the general procedure using 0.0368 g of 1e (0.2 mmol), and 2e was obtained as a white solid (0.0268 g, 87% yield) after flash column chromatography. ¹H NMR (500 MHz, d₆-DMSO) δ 8.04 (br, 1H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.45 (br, 1H); ¹³C NMR (125 MHz; d₆-DMSO) δ 166.8, 136.1, 133.1,129.4, 128.2.



3-Chlorobenzamide (**2f**).¹⁸ Prepared according to the general procedure using 0.0344 g of **1f** (0.2 mmol), and **2f** was obtained as a white solid (0.0265 g, 85% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (t, *J* = 1.8 Hz, 1H), 7.68 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.50 (dq, *J* = 8.0, 1.0 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 6.18 (br, 2H); ¹³C NMR (125 MHz; CDCl₃) δ 168.2, 135.2, 134.9, 132.1, 123.0, 127.8, 125.5.



2-Methylbenzamide (**2g**).¹⁸ Prepared according to the general procedure using 0.0334 g of **1g** (0.2 mmol), and **2g** was obtained as a white solid (0.0251 g, 92% yield) after flash column chromatography. ¹H NMR (300 MHz, d₆-DMSO) δ 7.69 (br, 1H), 7.37-7.28 (m, 3H), 7.23-7.18 (m, 2H), 2.37 (s, 3H); ¹³C NMR (125 MHz, d₆-DMSO) δ 171.0, 137.0, 135.1, 130.4, 129.1, 127.0, 125.4, 19.5.



¹⁸ Molander, G. A.; Cavalcanti, L. N. J. Org. Chem. 2011, 76, 7195.

2-Ethoxybenzamide (2h).¹⁹ Prepared according to the general procedure using 0.0393 g of 1h (0.2 mmol), and 2h was obtained as a white solid (0.0318 g, 96% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 8.22 (dd, J = 7.8, 1.8 Hz, 1H), 7.88 (br, 1H), 7.45 (dt, J = 8.4, 1.8 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.49 (br, 1H), 4.20 (q, J = 7.0 Hz, 2H), 1.51 (t, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 167.4, 157.3, 133.3, 132.5, 121.1, 120.9, 112.3, 64.7, 14.8.



[1,1'-Biphenyl]-2-carboxamide (2i).²⁰ Prepared according to the general procedure using 0.0450 g of 1i (0.2 mmol), and 2i was obtained as a white solid (0.0359 g, 92% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.75 (dd, J = 7.7, 1.1 Hz, 1H), 7.49 (dt, J = 7.5, 1.4 Hz, 1H), 7.45-7.34 (m, 7H), 5.92 (br, 1H), 5.31 (br, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.4, 140.2, 139.9, 134.4, 130.5, 130.4, 129.1, 128.8, 128.7, 127.9, 127.6.



2-Hydroxybenzamide (2j).²¹ Prepared according to the general procedure using 0.0300 g of 1j (0.2 mmol), and 2j was obtained as a white solid (0.0216 g, 73% yield) after flash column chromatography. ¹H NMR (500 MHz, d₆-DMSO) δ 13.02 (br, 1H), 8.39 (br, 1H), 7.88 (br, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.40 (dd, *J* = 11.3, 4.1 Hz, 1H), 6.87 (dd, *J* = 14.6, 7.8 Hz, 2H); ¹³C NMR (125 MHz, d₆-DMSO) δ 172.1, 161.1, 134.0, 128.1, 118.3, 117.4, 114.4.



3,5-Dimethylbenzamide (2k).²² Prepared according to the general procedure using 0.0352 g of 1k (0.2 mmol), and 2k was obtained as a white solid (0.0243 g, 83% yield) after flash column

¹⁹ Schade, M. A.; Manolikakes, G.; Knochel, P. Org. Lett. 2010, 12, 3648.

²⁰ Lauwagie, S.; Millet, R.; Pommery, J.; Depreux, P.; Hénichart, J.-P. Heterocycles. 2006, 68, 1149.

²¹ Owston, N. A.; Parker, A. J.; Williams, M. J. Org. Lett. 2007, 9, 3599.

²² Al-Huniti, M. H.; Rivera-Chavez, J.; Colón, K. L.; Stanley, J. L.; Burdette, J. E.; Pearce, C. J.; Oberlies, N. H.;

Croatt, M. P. Org. Lett. 2018, 20, 6046.

chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (s, 2H), 7.15 (s, 1H), 6.24 (br, 2H), 2.35 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 170.1, 138.3, 133.5, 125.1, 125.1, 21.2 .

2,6-Dichlorobenzamide (**21**).²⁰ Prepared according to the general procedure using 0.0439 g of **11** (0.2 mmol), and **21** was obtained as a white solid (0.0263 g, 69% yield) after flash column chromatography. ¹H NMR (500 MHz, d₆-DMSO) δ 8.08 (bs, 1H), 7.81 (bs, 1H), 7.48 (d, *J* = 7.9 Hz, 2H), 7.42-7.38 (m, 1H); ¹³C NMR (125 MHz, d₆-DMSO) δ 165.3, 137.0, 130.7, 130.6, 128.0.



1-Naphthamide (**2m**).²³ Prepared according to the general procedure using 0.0401 g of 1m (0.2 mmol), and **2m** was obtained as a white solid (0.0301 g, 88% yield) after flash column chromatography. ¹H NMR (500 MHz, d₆-DMSO) δ 8.31 (d, *J* = 8.5 Hz, 1H), 8.01-7.96 (m, 3H), 7.65-7.52 (m, 5H); ¹³C NMR (125 MHz, d₆-DMSO) δ 170.6, 134.5, 133.2, 129.7, 129.7, 128.1, 126.6, 126.1, 125.6, 125.1, 124.9.



2-Naphthamide (**2n**).²³ Prepared according to the general procedure using 0.0398 g of **1n** (0.2 mmol), and **2n** was obtained as a white solid (0.0258 g, 76% yield) after flash column chromatography. ¹H NMR (500 MHz, d₆-DMSO) δ 8.52 (s, 1H), 8.15 (br, 1H), 8.03-7.97 (m, 4H), 7.63-7.58 (m, 2H), 7.48 (s, 1H); ¹³C NMR (125 MHz, d₆-DMSO) δ 168.0, 134.2, 132.1, 131.7, 128.8, 127.8, 127.7, 127.6, 127.5, 126.6, 124.4.



Isonicotinamide (20).²⁴ Prepared according to the general procedure using 0.0308 g of 10

²³ Hanada, S.; Motoyama, Y.; Nagashima, H. Eur. J. Org. Chem. 2008, 4097.

²⁴ Abu-Youssef, M. A. M.; Dey, R.; Gohar, Y.; Massoud, A. A.; Öhrström, L.; Langer, V. *Inorg. Chem.* **2007**, *46*, 5893.

(0.2 mmol), and **20** was obtained as a white solid (0.0081 g, 33% yield) after flash column chromatography. ¹H NMR (500 MHz, DMSO- d_6) δ 8.72 (d, J = 6.1 Hz, 2H), 8.25 (br s, 1H), 7.72 (d, J = 6.1 Hz, 2H), 7.73 (br s, 1H); ¹³C NMR (126 MHz, DMSO- d_6) δ 166.3, 150.2, 141.2, 121.4.

Furan-2-carboxamide (2**p**).²² Prepared according to the general procedure using 0.0282 g of **1o** (0.2 mmol), and **2o** was obtained as a white solid (0.0187 g, 84% yield) after flash column chromatography. ¹H NMR (500 MHz, d₆-DMSO) 7.81 (s, 1H), 7.77 (bs, 1H), 7.38 (bs, 1H), 7.10 (d, J = 3.4 Hz, 1H), 6.61-6.60 (m, 1H); ¹³C NMR (125 MHz, d₆-DMSO) δ 159.4, 148.0, 145.0, 113.6, 111.7.

Thiophene-2-carboxamide (2q).²⁰ Prepared according to the general procedure using 0.0313 g of 1p (0.2 mmol), and 2p was obtained as a white solid (0.0251 g, 99% yield) after flash column chromatography. ¹H NMR (500 MHz, d₆-DMSO) δ 7.95 (br, 1H), 7.74 (dd, J = 9.7, 4.2 Hz, 2H), 7.36 (br, 1H), 7.13 (t, J = 4.2 Hz, 1H); ¹³C NMR (125 MHz, d₆-DMSO) δ 162.9, 140.3, 130.9, 128.6, 127.8.

2-Phenylacetamide (2**r**).²⁴ Prepared according to the general procedure using 0.0331 g of 1**q** (0.2 mmol), and 2**q** was obtained as a white solid (0.0225 g, 83% yield) after flash column chromatography. ¹H NMR (500 MHz; CDCl₃) δ 7.37-7.34 (m, 2H), 7.31-7.26 (m, 3H), 5.90 (br, 1H), 5.44 (br, 1H), 3.57 (s, 2H); ¹³C NMR (125 MHz; CDCl₃) δ 173.7, 134.9, 129.4, 129.1, 127.4, 43.3.



3-Phenylpropanamide (2s).²³ Prepared according to the general procedure using 0.0351 g of 1r (0.2 mmol), and 2r was obtained as a white solid (0.0244 g, 84% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.26 (m, 2H), 7.21-7.17 (m, 3H), 5.84 (br,

1H), 5.50 (br, 1H), 2.95 (t, *J* = 7.8 Hz, 3H), 2.52 (t, *J* = 7.8 Hz,3H); ¹³C NMR (125 MHz, CDCl₃) δ 174.8 140.7, 128.6, 128.3, 126.3, 37.5, 31.4.



Adamantane-1-carboxamide (2t).²³ Prepared according to the general procedure using 0.0421 g of 1s (0.2 mmol), and 2s was obtained as a white solid (0.0289 g, 80% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 5.79 (br, 1H), 5.64 (br, 1H), 2.05 (d, *J* = 2.5 Hz, 3H), 1.88 (t, *J* = 4.4 Hz, 6H), 1.73 (q, *J* = 12.3 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 181.0, 40.6, 39.3, 36.5, 28.1.



R = Et, Bn

Prepared according to the general procedure using 0.0330 g of 1u (0.2 mmol), and 2u was obtained as a white solid (0.0221 g, 91% yield) after flash column chromatography. NMR data is consistent with 2a.

Prepared according to the general procedure using 0.0456 g of 1v (0.2 mmol), 2v was obtained as a white solid (0.0214 g, 88% yield) after flash column chromatography. NMR data is consistent with 2a.

Phenylmethanol (2v').²⁵ Colorless oil, 67% yield (0.0154 g, 0.14 mmol). ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.26 (m, 5H), 4.68 (s, 2H), 1.82 (br s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 140.9, 128.6, 127.7, 127.0, 65.4.



R = H, 3-Cl, 4-OMe

Prepared according to the general procedure using 0.0270 g of 1w (0.2 mmol), and the molar ratio of HCOOH/Et₃N is 5/2. The desired product 2w was obtained as a white solid (0.0198 g, 83%)

²⁵ Cano, R.; Yus, M.; Ramón, D. J. Tetrahedron 2011, 67, 8079.

yield) after flash column chromatography. NMR data is consistent with 2a.

Prepared according to the general procedure using 0.0344 g of 1x (0.2 mmol), and the molar ratio of HCOOH/Et₃N is 5/2. The desired product 2x was obtained as a white solid (0.0252 g, 82% yield) after flash column chromatography. NMR data is consistent with 2f.

Prepared according to the general procedure using 0.0332 g of 1y (0.2 mmol), and the molar ratio of HCOOH/Et₃N is 5/2. The desired product 2y was obtained as a white solid (0.0235 g, 78% yield) after flash column chromatography. NMR data is consistent with 2c.



Prepared according to the general procedure using 0.0356 g of 1z (0.2 mmol), and the molar ratio of HCOOH/Et₃N is 5/2. The desired product 2z was obtained as a white solid (0.0155 g, 64% yield) after flash column chromatography. NMR data is consistent with 2a.

Prepared according to the general procedure using 0.0446 g of **1aa** (0.2 mmol), and the molar ratio of HCOOH/Et₃N is 5/2. The desired product **2aa** was obtained as a white solid (0.0191 g, 78% yield) after flash column chromatography. NMR data is consistent with **2a**.

Prepared according to the general procedure using 0.0484 g of **1ab** (0.2 mmol), and the molar ratio of HCOOH/Et₃N is 5/2. The desired product **2ab** was obtained as a white solid (0.0165 g, 68% yield) after flash column chromatography. NMR data is consistent with **2a**.

4-nitrobenzamide (2ac).²⁶ Prepared according to the general procedure using 0.0536 g of 1ac (0.2 mmol), and 2ac was obtained as a yellow solid (0.0224 g, 67% yield) after flash column chromatography. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.36-8.25 (d, *J* = 8.9 Hz, 3H), 8.11 (d, *J* = 8.7 Hz, 2H), 7.74 (br s, 1H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 166.7, 149.5, 140.5, 129.4, 123.9.

²⁶ Li, Y.-T.; Liao, B.-S.; Chen, H.-P.; Liu, S.-T. Synthesis 2011, 16, 2639.



N-Methylbenzamide (**2ad**).²⁷ Prepared according to the general procedure using 0.0351 g of **1ad** (0.2 mmol), and the molar ratio of HCOOH/Et₃N is 5/2. The desired product **2ad** was obtained as a light yellow solid (0.0171 g, 64% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 6.68 (s, 1H), 2.97 (d, *J* = 4.7 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.5, 134.6, 131.3, 128.5, 126.9, 26.8.

Benzoic acid (2ae).²⁸ Prepared according to the general procedure using 0.0436 g of 1ae (0.2 mmol), and 2ae was obtained as a white solid (0.0232 g, 96% yield) after flash column chromatography. ¹H NMR (500 MHz; CDCl₃) δ 10.89 (br, 1H), 8.13 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 172.3, 133.8, 130.2, 129.4, 128.5.

Benzenesulfonamide (4a).²⁹ Prepared according to the general procedure using 0.0373 g of **3a** (0.2 mmol), and **4a** was obtained as a white solid (0.0290 g, 93% yield) after flash column chromatography. ¹H NMR (500 MHz, d₆-DMSO) δ 7.84-7.82 (m, 2H), 7.62-7.55 (m, 3H), 7.36 (bs, 2H); ¹³C NMR (125 MHz, d₆-DMSO) δ 144.2, 131.7, 128.9, 125.6.

2-Methylbenzenesulfonamide (4b).²⁷ Prepared according to the general procedure using 0.0396 g of **3b** (0.2 mmol), and **4b** was obtained as a white solid (0.0311 g, 92% yield) after flash column chromatography. ¹H NMR (300 MHz, d₆-DMSO) δ 7.85 (d, J = 7.7 Hz, 1H), 7.49-7.46 (m, 1H), 7.37-7.35 (m, 4H), 2.59 (s, 3H); ¹³C NMR (125 MHz, d₆-DMSO) δ 142.1, 135.8, 132.1, 131.8,

²⁷ Paul, B.; Panja, D.; Kundu, S. Org. Lett. 2019, 21, 5843.

²⁸ Keshipour, S.; Khezerloo, M. RSC Adv. **2019**, 9, 17129.

²⁹ Tota, A.; John-Campbell, S. S.; Briggs, E. L.; Estévez, G. O.; Afonso, M.; Degennaro, L.; Luisi, R.; Bull, J. A. *Org. Lett.* **2018**, 20, 2599.

127.0, 126.0, 19.8.

4-Methylbenzenesulfonamide (4c).²⁷ Prepared according to the general procedure using 0.0398 g of **3c** (0.2 mmol), and **4c** was obtained as a white solid (0.0337 g, 99% yield) after flash column chromatography. ¹H NMR (300 MHz, d₆-DMSO) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.27 (br, 2H), 2.37 (s, 3H); ¹³C NMR (125 MHz, d₆-DMSO) δ 141.8, 141.4, 129.3, 125.6, 20.9.

Phenylmethanesulfonamide (4d).³⁰ Prepared according to the general procedure using 0.0404 g of 3d (0.2 mmol), and 4d was obtained as a white solid (0.0317 g, 92% yield) after flash column chromatography. ¹H NMR (500 MHz, CDCl₃) δ 7.42-7.38 (m, 5H), 4.76 (br, 2H), 4.29 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 130.8, 129.4, 128.9, 128.9, 61.0.

IV. Gram-scale Reaction

To a 100 mL dried Schlenk flask under air, 1.5340 g (10 mml) of **1a**, 0.1535 g (0.15 mmol) of $[RuCl_2(p-cymene)]_2$, 12.5 mL of HCOOH/Et₃N (molar ratio 1/1) and 12.5 mL of H₂O were added in sequence. After stirring at 100 °C for 12 hours, the mixture was quenched with saturated NH₄Cl (10 mL), extracted with EA (50 mL x 3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel with PE/EA as the eluent to afford 1.1083 g (9.1 mmol, 91% yield) of **2a**.

³⁰ Bahrami, K.; Khodaei, M. M.; Soheilizad, M. J. Org. Chem. 2009, 74, 9287.

V. NMR Spectra



¹H NMR: *N-methoxybenzamide* (1a)



¹H NMR: *N-methoxy-4-methylbenzamide* (1b)



¹H NMR: *N*,4-dimethoxybenzamide (1c)



¹H NMR: 4-fluoro-N-methoxybenzamide (1d)



¹H NMR: 4-chloro-N-methoxybenzamide (1e)



¹H NMR: 3-chloro-N-methoxybenzamide (1f)



¹H NMR: *N-methoxy-2-methylbenzamide* (1g)



¹H NMR: 2-ethoxy-N-methoxybenzamide (1h)



¹H NMR: *N*-methoxy-[1,1'-biphenyl]-2-carboxamide (1i)



¹H NMR: 2-hydroxy-N-methoxybenzamide (1j)



¹H NMR: *N-methoxy-3,5-dimethylbenzamide* (1k)



¹H NMR: 2,6-dichloro-N-methoxybenzamide (11)



¹³C NMR: 2,6-dichloro-N-methoxybenzamide (11)



¹H NMR: *N-methoxy-1-naphthamide* (1m)



¹H NMR: *N-methoxy-2-naphthamide* (1n)



¹H NMR: *N-methoxyfuran-2-carboxamide* (1p)



¹H NMR: *N*-methoxythiophene-2-carboxamide (1q)



¹H NMR: *N-methoxy-2-phenylacetamide* (1r)



¹H NMR: *N-methoxy-3-phenylpropanamide* (1s)



¹H NMR: (3r, 5r, 7r)-N-methoxyadamantane-1-carboxamide (1t)











¹H NMR: *3-chloro-N-hydroxybenzamide* (1x)



¹H NMR: *N-hydroxy-4-methoxybenzamide* (1y)



¹H NMR: *N*-acetoxybenzamide (1z)



¹H NMR: *N*-(*pivaloyloxy*)benzamide (1aa)



¹H NMR: *N*-(benzoyloxy)benzamide (1ab)



¹H NMR: *N-methyl-N-(pivaloyloxy)benzamide* (1ad)



¹³C NMR: N-methyl-N-(pivaloyloxy)benzamide (1ad)



¹H NMR: *N*-methoxybenzenesulfonamide (3a)



¹H NMR: *N*-methoxy-2-methylbenzenesulfonamide (3b)



¹H NMR: *N*-methoxy-4-methylbenzenesulfonamide (3c)



¹H NMR: *N*-methoxy-1-phenylmethanesulfonamide (3d)



¹H NMR: *benzamide* (2a)



¹H NMR: *4-methylbenzamide* (**2b**)



¹³C NMR: *4-methylbenzamide* (**2b**)



¹H NMR: *4-methoxybenzamide* (2c)



¹³C NMR: *4-methoxybenzamide* (2c)



¹H NMR: *4-fluorobenzamide* (**2d**)



¹³C NMR: 4-fluorobenzamide (2d)

- 8.044 - 7.910 - 7.893 - 7.535 - 7.518



¹H NMR: 4-chlorobenzamide (2e)



¹³C NMR: 4-chlorobenzamide (2e)



¹H NMR: 3-chlorobenzamide (2f)







¹H NMR: 2-methylbenzamide (2g)



¹³C NMR: *3-methylbenzamide* (2g)





¹H NMR:2-ethoxybenzamide (2h)



¹³C NMR: 2-ethoxybenzamide (2h)





¹H NMR: [1,1'-biphenyl]-2-carboxamide (2i)







¹H NMR: 2-hydroxybenzamide (2j)



¹³C NMR: 2-hydroxybenzamide (2j)



¹H NMR: 3,5-dimethylbenzamide (2k)



¹³C NMR: *3,5-dimethylbenzamide* (2k)





¹H NMR: 2,6-dichlorobenzamide (21)



¹³C NMR: 2,6-dichlorobenzamide (21)



¹H NMR: *1-naphthamide* (2m)



¹³C NMR: *1-naphthamide* (2m)





¹H NMR: 2-naphthamide (2n)





¹H NMR: *isonicotinamide* (20)



¹³C NMR: *isonicotinamide* (20)



¹H NMR: *furan-2-carboxamide* (**2p**)



¹H NMR: *furan-2-carboxamide* (**2p**)



¹H NMR: thiophene-2-carboxamide (2q)



¹³C NMR: *thiophene-2-carboxamide* (2q)



¹H NMR: 2-phenylacetamide (2r)







¹H NMR: *3-phenylpropanamide* (2s)



¹³C NMR: *3-phenylpropanamide* (2s)





¹H NMR: adamantane-1-carboxamide (2t)



¹³C NMR: adamantane-1-carboxamide (2t)



¹H NMR: 4-nitrobenzamide (2ac)









¹H NMR: *N*-methylbenzamide (2ad)







¹H NMR: *benzoic acid* (2ae)









¹H NMR: *benzenesulfonamide* (4a)



¹H NMR: 2-methylbenzenesulfonamide (4b)



¹³C NMR: 2-methylbenzenesulfonamide (4b)



¹H NMR: 4-methylbenzenesulfonamide (4c)



¹³C NMR: 4-methylbenzenesulfonamide (4c)





¹H NMR: *phenylmethanesulfonamide* (4d)



¹³C NMR: *phenylmethanesulfonamide* (4d)