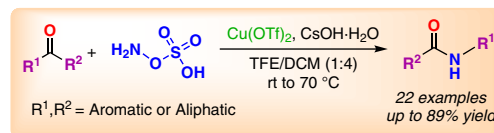


Cu(OTf)₂-Catalyzed Beckmann Rearrangement of Ketones Using Hydroxylamine-O-sulfonic Acid (HOSA)

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- One pot, operationally simple
- Water-soluble by-product
- Open flask
- Secondary amide directly from ketone
- Excellent yields, broad scope
- Wide functional group tolerance

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Abstract The Beckmann rearrangement (BKR) of ketones to secondary amides often requires harsh reaction conditions that limit its practicality and scope. Herein, the Cu(OTf)₂-catalyzed BKR of ketones under mild reaction conditions using hydroxylamine-O-sulfonic acid (HOSA), a commercial water soluble aminating agent, is described. This method is compatible with most functional groups and directly provides the desired amides in good to excellent yields.

Key words hydroxylamine-O-sulfonic acid (HOSA), ketone, Beckmann rearrangement, Cu(OTf)₂, secondary amide

The Beckmann rearrangement (BKR) is a popular method for the formation of amides from ketones and aldehydes via an oxime intermediate.¹ The conversion of an oxime into an amide was done first by the German chemist Ernst Otto Beckmann in 1886.² Notably, the BKR enjoys a prominent industrial role including the manufacture of monomer for polymerization into nylon-6 and nylon-12.³ Also, amides are common components in drugs, natural products, agrochemicals, and functional materials (Figure 1).^{4,5}

The traditional BKR requires harsh conditions such as high reaction temperatures and strongly acidic media, thus restricting the variety of suitable substrates; often, the process requires isolation of the oxime intermediate, which can be labile and involves a cumbersome purification process (Scheme 1a,b).⁶ More recent modifications have addressed these limitations via catalysis with transition metals,⁷ calcium complexes,⁸ organocatalysts,^{9–13} inorganic Lewis acids,¹⁴ and boronic acids.¹⁵ Nevertheless, the need for a mild, inexpensive, and environmentally friendly procedure, especially for the direct conversion from ketones,¹⁶ still persists.

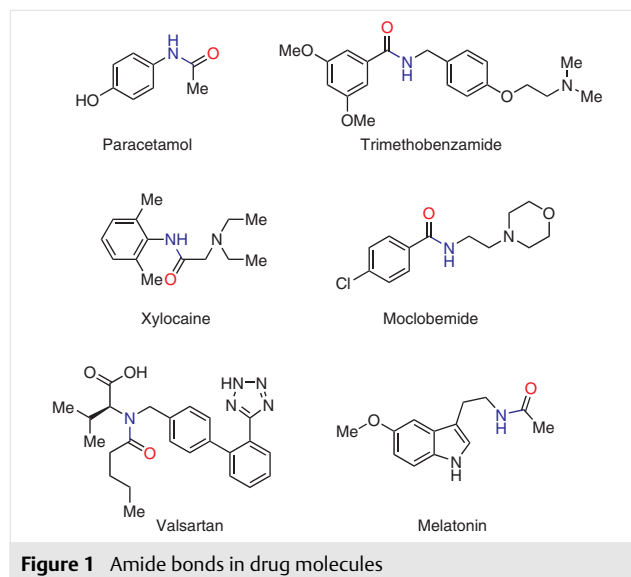
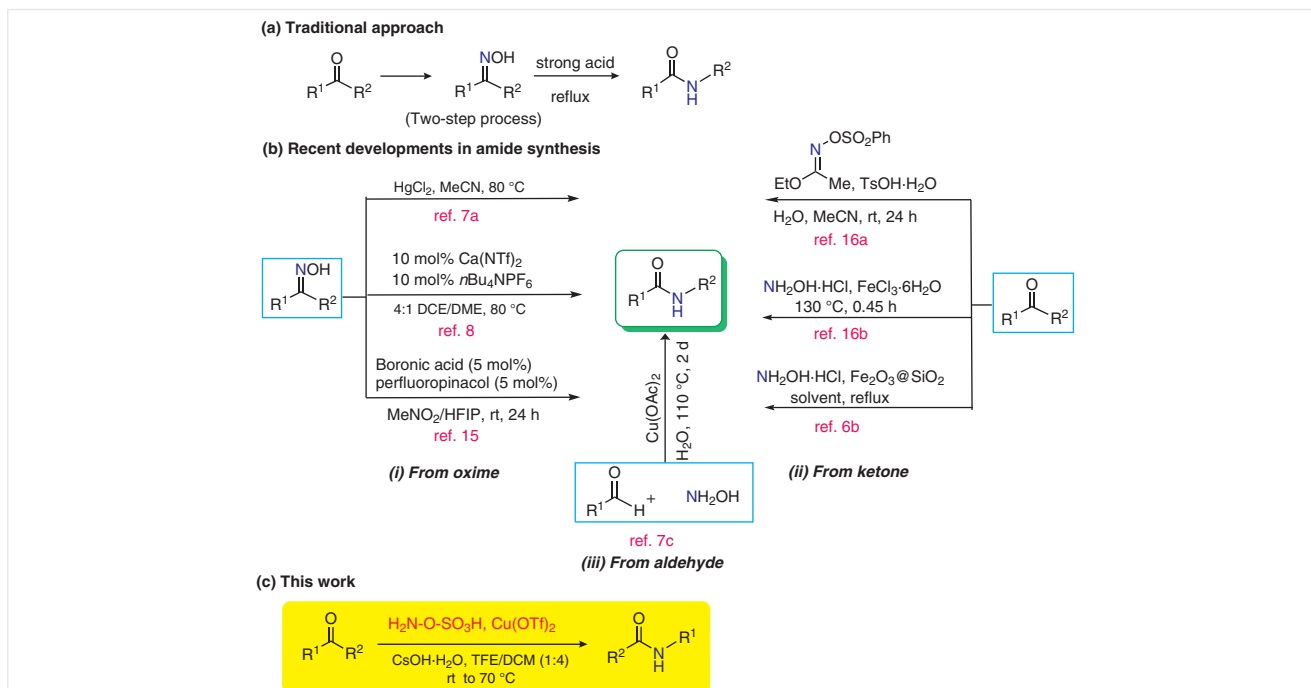


Figure 1 Amide bonds in drug molecules

Hydroxylamine-O-sulfonic acid (HOSA) attracted our attention for the BKR because it is commercial, inexpensive, water soluble, and readily handled.¹⁷ Indeed, it has found sporadic utility in the BKR,¹⁸ but primarily with aliphatic ketones. With aromatic ketones or hindered systems, strong acid and/or high temperatures are still required.¹⁹ Fortunately, we had observed early transition metal salts, especially Cu(OTf)₂, accelerated the condensation and rearrangement of aromatic ketones with HOSA.

To actualize our aim, an introductory study was done using 2-methoxyacetophenone (**1a**) as a representative substrate along with HOSA and Cu(OTf)₂ at room temperature (Table 1). Our investigation to optimize the reaction parameters to obtain amide **2a** from **1a** showed that a base was needed to commence the reaction. With lithium hydroxide (LiOH), 95% of the starting material **1a** was con-



Scheme 1 Beckmann rearrangement of ketones and recent variations

Table 1 Optimization of Reaction Conditions^a

Entry	Base	Solvent	Yield (%)		
			2a	3a	1a ^b
1	LiOH	TFE/CH ₂ Cl ₂ (1:4)	85	10	5
2 ^c	Na ₂ CO ₃	TFE/CH ₂ Cl ₂ (1:4)	10	0	90
3 ^d	Et ₃ N	TFE/CH ₂ Cl ₂ (1:4)	60	40	0
4 ^d	pyridine	TFE/CH ₂ Cl ₂ (1:4)	60	40	0
5 ^d	DMAP	TFE/CH ₂ Cl ₂ (1:4)	40	60	0
6	K ₂ CO ₃	TFE/CH ₂ Cl ₂ (1:4)	NR		100
7^d	CsOH·H₂O	TFE/CH₂Cl₂ (1:4)	88	0	0
8 ^d	CsOH·H ₂ O	HFIP	83	0	0
9 ^d	CsOH·H ₂ O	TFE	84	0	0
10	CsOH·H ₂ O	MeOH	10	90	0
11 ^h	CsOH·H ₂ O	EtOH	0	50	50
12 ⁱ	CsOH·H ₂ O	THF	0	30	70
13	CsOH·H ₂ O	CH ₂ Cl ₂	10	90	0
14	CsOH·H ₂ O	MeCN	NR		100

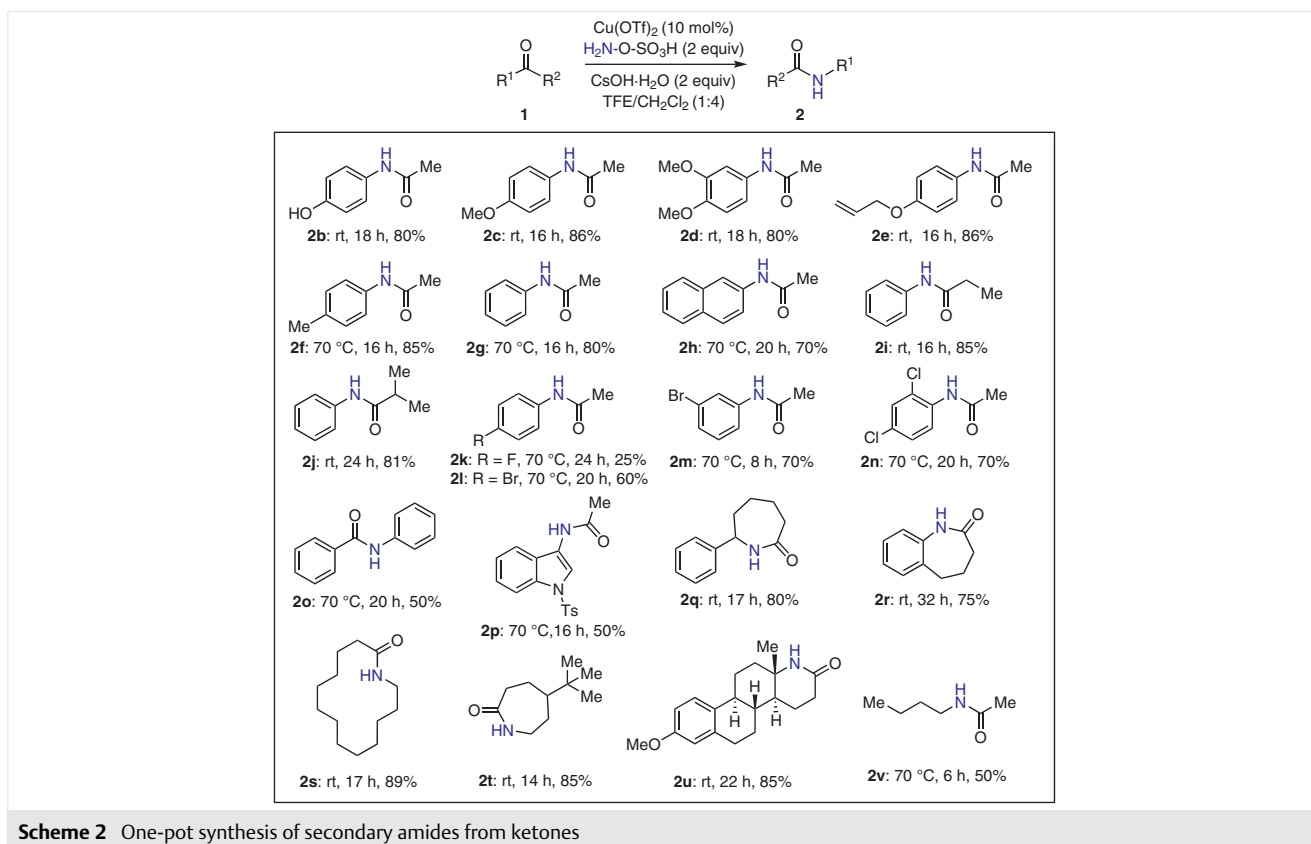
^a Reaction conditions: Cu(OTf)₂ (0.1 equiv), HOSA (2 equiv), CsOH·H₂O (2 equiv), TFE/CH₂Cl₂ (1:4), rt, 14 h. TFE = 2,2,2-trifluoroethanol. NR: No reaction.

^b Recovered **1a**; 0% recovered = 100% consumed.

sumed and the expected amide was obtained in 85% yield along with 10% of oxime **3a** (Table 1, entry 1). The most satisfactory result was achieved with cesium hydroxide monohydrate (CsOH·H₂O) in which the desired amide **2a** was obtained in 88% yield (entry 7) whereas other mild bases were not very effective (entries 2–5) or in the case of K₂CO₃ proved ineffective (entry 6).

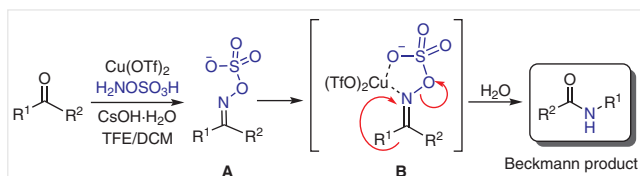
Finally, a variety of solvents were screened including hexafluoroisopropanol (HFIP), 2,2,2-trifluoroethanol (TFE), methanol, ethyl alcohol, tetrahydrofuran (THF), acetonitrile, dichloromethane, and a mixture of TFE/CH₂Cl₂ (1:4) (Table 1). While HFIP and TFE delivered amide **2a** in comparable yields (83% and 84%, respectively; Table 1, entries 8 and 9), a mixture of TFE/CH₂Cl₂ was best for both the yield of amide **2a** (88%, entry 7) and for solubilization of ketones. Only acetonitrile, despite its frequent use in amidation reactions, failed to support the BKR (entry 14).

Having established the optimum reaction conditions, the scope of the methodology was evaluated with a range of representative ketones (Scheme 2). Generally, acetophenones with strong aryl electron-donating groups reacted smoothly at room temperature to deliver the derived *N*-phenylacetamides in very good yields, for example, phenol **2b**, 4-methoxy **2c**, 3,4-dimethoxy **2d**, and 4-allyloxy **2e**. The latter is notable for its chemoselectivity, that is, no allylic²⁰ or CH amination²¹ or aziridination^{17c} under the reaction conditions. In contrast, 4-tolyl **2f**, phenyl **2g**, and naphthyl **2h** required heating for a reasonable reaction rate, although room temperature reactivity was restored in the homologous **2i, j**. The halogenated ketones **2l–n** were well behaved



and provided good yields of amide, except for 4'-fluoroacetophenone which was less reactive, as it delivered the corresponding amide **2k** in 25% yield only at 70 °C in 24 hours. The BKR of benzophenone and 3-acetylindole furnished **2o** and **2p**, respectively, albeit in modest yields. Lactams **2q–t** were readily obtained from the corresponding cyclic ketones in high yields. Following upon well-established migratory priorities, estrone 3-methyl ether and hex-2-one led to **2u** and **2v**, respectively.

We propose the Cu(OTf)_2 has a dual role in catalyzing the BKR (Scheme 3). First, as a mild Lewis acid, it assists in the formation of the transient ketoxime intermediate **A** that could be observed in some cases. Second, by way of the five-membered transition state **B**, the copper catalyzes the migration of the R^1 group to the nitrogen from which the Beckmann product is finally obtained.



In conclusion, we have developed an operationally simple, one-pot BKR route to secondary amides directly from ketones using inexpensive, easily handled HOSA as aminating agent via Cu(II) -catalysis.

Reactions, unless otherwise stated, were carried out with magnetic stirring open to the atmosphere in oven-dried glassware. Reagents were used as received, unless otherwise noted. For TLC precoated plates (Merck silica gel 60, F_{254}) were used and visualized with UV light and/or charring after dipping in PMA or KMnO_4 solution. The compounds were purified by triturating the crude reaction mixture under hexane or by flash column chromatography using silica gel (100–200 mesh) with EtOAc/hexane as eluent. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, in CDCl_3 or $\text{DMSO-}d_6$ as solvent. Chemical shifts δ are reported in parts per million (ppm) relative to residual undeuterated solvent as an internal reference (^1H $\delta = 7.26$ and ^{13}C $\delta = 77.0$ for CDCl_3 , $\delta = 2.50$ and 39.52 for $\text{DMSO-}d_6$, respectively). Standard abbreviations are used to indicate NMR peak multiplicities.

Amides from Ketones; General Procedure

To a stirred solution of Cu(OTf)_2 (0.05 mmol, 10 mol%) in $\text{TFE/CH}_2\text{Cl}_2$ (1:4, 2–3 mL) were added ketone (0.5 mmol, 1.0 equiv), HOSA (2.0 equiv), and $\text{CsOH}\cdot\text{H}_2\text{O}$ (2.0 equiv) at rt. The reaction mixture was maintained at the temperature and for the time indicated in Scheme 2. After completion, the mixture was diluted with CH_2Cl_2 (10 mL) and washed with sat. aq Na_2CO_3 (3 \times 5 mL). The combined organic layers

were washed with brine (5 mL) and dried (anhyd. Na₂SO₄). The crude product obtained after removal of all volatiles in vacuo was purified by SiO₂ (100–200 mesh) chromatography using EtOAc/hexane as eluent.

***N*-(2-Methoxyphenyl)acetamide (2a)**²²

Yield: 73 mg (88%); white solid; mp 72–74 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.35 (dd, *J* = 7.9, 1.7 Hz, 1 H), 7.77 (s, 1 H), 7.03 (td, *J* = 7.8, 1.7 Hz, 1 H), 6.95 (td, *J* = 7.8, 1.5 Hz, 1 H), 6.87 (dd, *J* = 8.1, 1.5 Hz, 1 H), 3.88 (s, 3 H), 2.20 (s, 3 H).

***N*-(4-Hydroxyphenyl)acetamide (2b)**²³

Yield: 60 mg (80%); brown solid; mp 170–171 °C.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.64 (s, 1 H), 9.13 (s, 1 H), 7.33 (d, *J* = 8.9 Hz, 2 H), 6.67 (d, *J* = 8.9 Hz, 2 H), 1.98 (s, 3 H).

***N*-(4-Methoxyphenyl)acetamide (2c)**¹⁵

Yield: 82 mg (86%); white solid; mp 129–130 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.41–7.35 (m, 2 H), 6.87–6.81 (m, 2 H), 3.78 (s, 3 H), 2.14 (s, 3 H).

***N*-(3,4-Dimethoxyphenyl)acetamide (2d)**²⁴

Yield: 78 mg (80%); white solid; mp 126–127.7 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.30 (d, *J* = 2.3 Hz, 1 H), 6.87–6.70 (m, 2 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 2.15 (s, 3 H).

***N*-[4-(Allyloxy)phenyl]acetamide (2e)**²⁵

Yield: 82 mg (86%); white solid; mp 94–95 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.37 (d, *J* = 8.7 Hz, 2 H), 7.14 (s, 1 H), 6.87 (d, *J* = 8.8 Hz, 2 H), 6.04 (ddd, *J* = 21.8, 10.4, 5.2 Hz, 1 H), 5.40 (d, *J* = 17.3 Hz, 1 H), 5.28 (d, *J* = 10.5 Hz, 1 H), 4.51 (d, *J* = 5.1 Hz, 2 H), 2.15 (s, 3 H).

***N*-(*p*-Tolyl)acetamide (2f)**²³

Yield: 63 mg (85%); white solid; mp 151–152 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.37 (d, *J* = 8.3 Hz, 2 H), 7.25 (br s, 1 H), 7.11 (d, *J* = 8.1 Hz, 2 H), 2.31 (s, 3 H), 2.15 (s, 3 H).

***N*-Phenylacetamide (2g)**²⁶

Yield: 54 mg (80%); white solid; mp 114–115 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.49 (d, *J* = 7.7 Hz, 2 H), 7.31 (t, *J* = 7.9 Hz, 2 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 2.17 (s, 3 H).

***N*-(Naphthalen-2-yl)acetamide(2h)**²⁷

Yield: 65 mg (70%); off-white solid; mp 133–135 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.18 (br s, 1 H), 7.80–7.77 (m, 3 H), 7.48–7.37 (m, 4 H), 2.24 (s, 3 H).

***N*-Phenylpropionamide (2i)**¹³

Yield: 63 mg (85%); white solid; mp 107–108 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.52 (d, *J* = 8.0 Hz, 2 H), 7.30 (t, *J* = 8.0 Hz, 2 H), 7.26 (br, 1 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 2.38 (q, *J* = 7.6 Hz, 2 H), 1.24 (t, *J* = 7.6 Hz, 3 H).

***N*-Phenylisobutyramide (2j)**⁹

Yield: 88 mg (81%); white solid; mp 109–111 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.53 (d, *J* = 8.0 Hz, 2 H), 7.31 (t, *J* = 7.8 Hz, 2 H), 7.09 (t, *J* = 7.3 Hz, 1 H), 2.51 (sept, *J* = 6.8 Hz, 1 H), 1.25 (d, *J* = 6.8 Hz, 6 H).

***N*-(4-Fluorophenyl)acetamide (2k)**²⁸

Yield: 19 mg (25%); white solid; mp 153–154.6 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.45 (dd, *J* = 8.8, 4.8 Hz, 2 H), 7.31 (br s, 1 H), 7.00 (t, *J* = 8.6 Hz, 2 H), 2.16 (s, 3 H).

***N*-(4-Bromophenyl)acetamide (2l)**²⁸

Yield: 65 mg (60%); white solid; mp 167–169 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.47–7.36 (m, 4 H), 7.23 (br s, 1 H), 2.17 (s, 3 H).

***N*-(3-Bromophenyl)acetamide (2m)**²⁹

Yield: 75 mg (70%); white solid; mp 81–83 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.81 (s, 1 H), 7.69 (s, 1 H), 7.45 (d, *J* = 7.8 Hz, 1 H), 7.29 (dd, *J* = 16.1, 4.4 Hz, 1 H), 7.20 (t, *J* = 7.9 Hz, 1 H), 2.22 (s, 3 H).

***N*-(2,4-Dichlorophenyl)acetamide (2n)**³⁰

Yield: 38 mg (70%); brown solid; mp 142–144 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.34 (d, *J* = 8.7 Hz, 1 H), 7.55 (s, 1 H), 7.38 (d, *J* = 1.7 Hz, 1 H), 7.28–7.22 (m, 1 H), 2.24 (s, 3 H).

***N*-Phenylbenzamide (2o)**¹³

Yield: 49 mg (50%); white solid; mp 164–165 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.87 (d, *J* = 7.8 Hz, 2 H), 7.80 (s, 1 H), 7.64 (d, *J* = 8.1 Hz, 2 H), 7.56 (t, *J* = 7.0 Hz, 1 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.16 (t, *J* = 7.2 Hz, 1 H).

***N*-(1-Tosyl-1*H*-indol-3-yl)acetamide (2p)**¹⁵

Yield: 82 mg (50%); white solid; mp 193–194 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.20 (s, 1 H), 8.07 (d, *J* = 8.3 Hz, 1 H), 7.76 (d, *J* = 8.4 Hz, 2 H), 7.41–7.32 (m, 2 H), 7.28–7.26 (m, 1 H), 7.25–7.22 (m, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 2.31 (s, 3 H), 2.24 (s, 3 H).

7-Phenylazepan-2-one (2q)³¹

Yield: 76 mg (80%); white solid; mp 134–136 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.41–7.21 (m, 5 H), 6.18 (br s, 1 H), 4.46 (d, *J* = 9.3 Hz, 1 H), 2.66–2.49 (m, 2 H), 2.11–1.83 (m, 4 H), 1.76–1.57 (m, 2 H).

¹³C NMR (101 MHz, CDCl₃): δ = 177.93, 141.92, 129.18, 128.22, 126.24, 58.85, 36.91, 36.79, 29.78, 22.91.

1,3,4,5-Tetrahydro-2*H*-benzo[*b*]azepin-2-one (2r)²⁷

Yield: 61 mg (75%); white solid; mp 137–139 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.56 (br s, 1 H), 7.25–7.20 (m, 2 H), 7.16–7.10 (m, 1 H), 6.96 (d, *J* = 7.6 Hz, 1 H), 2.80 (t, *J* = 7.2 Hz, 2 H), 2.36 (t, *J* = 7.3 Hz, 2 H), 2.27–2.21 (m, 2 H).

Azacyclotetradecan-2-one (2s)³²

Yield: 96 mg (89%); white solid; mp 155–157 °C.

¹H NMR (400 MHz, CDCl₃): δ = 5.57 (br s, 1 H), 3.36–3.26 (m, 2 H), 2.25–2.15 (m, 2 H), 1.76–1.61 (m, 2 H), 1.54–1.44 (m, 2 H), 1.43–1.20 (m, 16 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 173.10, 38.46, 36.27, 28.31, 26.49, 25.79, 25.71, 25.63, 25.41, 25.26, 23.95, 23.70, 23.13.

5-(*tert*-Butyl)azepan-2-one (2t)³³

Yield: 73 mg (85%); semi-solid.

^1H NMR (400 MHz, CD_3OD): δ = 3.33–3.25 (m, 2 H), 2.58–2.48 (m, 1 H), 2.16 (td, J = 13.4, 4.9 Hz, 1 H), 2.07–1.94 (m, 2 H), 1.84 (td, J = 13.9, 5.4 Hz, 1 H), 1.37–1.14 (m, 3 H), 0.90 (s, 9 H).

^{13}C NMR (101 MHz, CD_3OD): δ = 167.50, 48.46, 33.23, 32.60, 28.76, 27.91, 27.64, 26.76.

(4a*S*,4*b*R,10*b*S,12*a*S)-8-Methoxy-12*a*-methyl-3,4,4*a*,4*b*,5,6,10*b*,11,12,12*a*-decahydronaphtho[2,1-*f*]quinolin-2(1*H*)-one (2u)³⁴

Yield: 126 mg (85%); white solid; mp 220–222 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.18 (d, J = 8.6 Hz, 1 H), 6.76–6.46 (m, 3 H), 3.77 (s, 3 H), 2.93–2.79 (m, 2 H), 2.56–2.34 (m, 4 H), 2.15–1.99 (m, 2 H), 1.89–1.81 (m, 1 H), 1.77–1.66 (m, 1 H), 1.58–1.25 (m, 5 H), 1.19 (s, 3 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 171.96, 157.65, 137.57, 131.79, 126.17, 113.52, 111.69, 55.21, 54.49, 46.49, 43.28, 39.85, 39.34, 30.65, 29.88, 26.67, 26.21, 22.19, 19.83.

N-Butylacetamide (2v)³⁵

Yield: 82 mg (50%); clear oil.

^1H NMR (400 MHz, CDCl_3): δ = 5.66 (s, 1 H), 3.26–3.18 (m, 2 H), 1.95 (s, 3 H), 1.52–1.41 (m, 2 H), 1.38–1.28 (m, 2 H), 0.90 (t, J = 7.3 Hz, 3 H).

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0039-1690005>.

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