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A Novel and Expeditious Approach to Unusual Spirolactam Building Blocks†

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Abstract: A rapid access to 7-azaspiro[4.5]decan-6-ones **1** involving three regio- and chemoselective reactions starting from tetrabromonorbornyl derivatives is described. The alkaline H_2O_2 cleavage reaction of monosubstituted α-diketones **9** furnished the potential bridged bicyclic lactones **10** in a highly regio- and stereoselective manner. The radical-mediated, intermolecular bridgehead C−C bond formation of the versatile bridged lactones **10** with acrylonitrile followed by LAH reduction of the adduct **13** intriguingly leads to the formation of novel spirolactam building blocks **1**.

The development of synthetic sequences aimed at achieving desired molecular complexity present in multi-stereocentered polycyclic targets employing simple and easily accessible starting materials in a rapid, proficient, and stereoselective manner continues to be a major challenge in contemporary organic synthesis. In this context, we wish to report herein a novel, remarkably efficient, and serendipitously discovered synthesis of functionalized spirocyclic lactams **1** via radical-mediated intermolecular C−C bond formation followed by LAH reduction. There are few methodologies that are known in the literature for the construction of azaspirocyclic ring systems.[1] The azaspirocyclic substructures occur in numerous biologically active alkaloids such as histrionicotoxin,[2] sibirine,[3] nitramine,[3] isonitramine,[3] fasicularin,[4] etc. The lactam ring is present in numerous conformationally constrained peptidomimetics.[5] The spirolactams also function as the crucial building blocks for the synthesis of the 2-azaspiro[5,5]undecane group of alkaloids,[3] and the most important is the very recent synthesis of diazaspiro[4.5]decanes **2** and **3** (Figure 1) as conformationally restricted pseudopeptides by Casamitjana and co-workers.[5]

We have recently reported the development of two synthetically promising methodologies for selective utilization of two sets of halogens (viz. bridgehead vs vinylic)

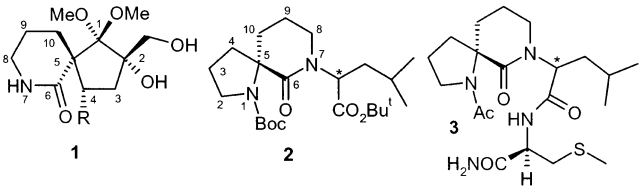
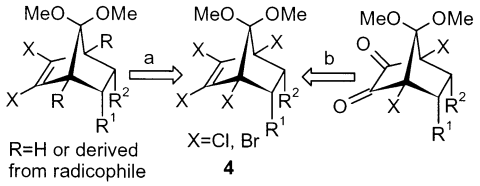


FIGURE 1. Spirolactams **2** and **3** as conformationally restricted pseudopeptides.

SCHEME 1. Selective Utilization of Two Sets of Halogens in Tetrahalonorbornyl Derivatives 4[7,8] [a]



[a] (a) radicophile, Bu_3SnH, PhH, reflux. (b) cat. $RuCl_3 \cdot 3H_2O$, $NaIO_4$, $MeCN-H_2O$ (6:1).

present in tetrahalonorbornenes **4**:[6] (i) for C−C bond formation at the bridgehead in the presence of vinylic halogens[7] and (ii) a new utility of vinylic halogens to obtain synthetically useful α-diketones[8] with the retention of bridgehead halogens, employing both tetrachloro and tetrabromo norbornyl derivatives **4** in high yield (Scheme 1).

In connection with an ongoing project, we became interested in functionalized cyclopentane derivatives **5** possessing an amino-propyl substituent. We envisioned a useful new sequence for stereocontrolled formation of the oxygenated cyclopentane ring systems **5** as diagrammed in retrosynthetic analysis (Scheme 2) via bridgehead C−C bond formation of the bridged bicyclic lactone **7** followed by LAH reduction of the adduct **6** to reveal **5**. However, the LAH reduction of the acrylonitrile addition product **6**, contrary to our expectations, directly provided the spiro amide **1** (Scheme 6).

The bromo bicyclic lactones **10** were easily derived from the H_2O_2/NaOH-mediated cleavage reaction of α-diketones **9** (Scheme 3).[8a] It is interesting to note that the dicarboxylate intermediate **11** resulting from the H_2O_2/NaOH cleavage promotes highly regioselective intramolecular S_N2 reaction at the tertiary bridgehead carbon leading exclusively, after esterification with diazomethane, to **10**. The origin of regioselectivity, in our opinion, is the reactive envelop conformer **11** in which the only unsubstituted methylene carbon prefers the "flap: position while the R group occupies pseudoequatorial position (Scheme 3). In this preferred conformation, the carboxylate group α to the substituent R and the bromide leaving

† Dedicated to Professor G. Mehta on the occasion of his 60th birthday.

(1) (a) For a review, see: Sannigrahi, M. *Tetrahedron* **1999**, *55*, 9007. (b) For a recent example, see: Fenster, M. D. B.; Patrick, B. O.; Dake, G. R. *Org. Lett.* **2001**, *3*, 2109.

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(3) (a) McCloskey, P. J.; Schultz, A. G. *Heterocycles* **1987**, *25*, 437. (b) Quirion, J.-C.; Grierson, D. S.; Royer J.; Husson, H.-P. *Tetrahedron Lett.* **1988**, *29*, 3311. Wanner M. J.; Koomen, G. J. *Tetrahedron Lett.* **1989**, *30*, 2301.

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(5) Fernández, M. M.; Diez, A.; Rubiralta, M.; Montenegro, E.; Casamitjana, N. *J. Org. Chem.* **2002**, *67*, 7587.

(6) For a review on synthetic applications of tetrachloronorbornenes **4** (X = Cl), see: Khan, F. A.; Prabhudas, B.; Dash, J. *J. Prakt. Chem.* **2000**, *342*, 512.

(7) Khan, F. A.; Prabhudas, B. *Tetrahedron Lett.* **1999**, *40*, 9289.

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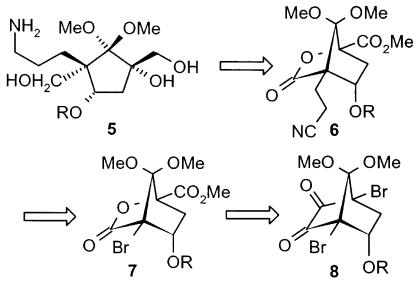
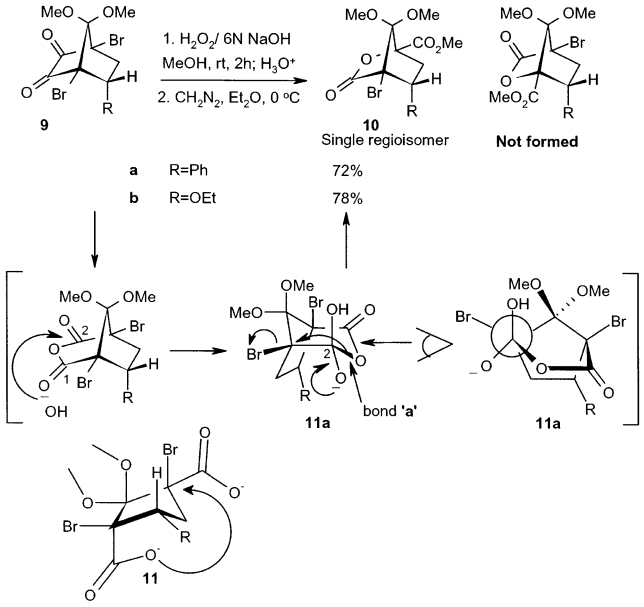
SCHEME 2. Retrosynthetic Analysis Starting from Diketone 8



SCHEME 3. Regioselective Access to Bicyclic Lactones 10

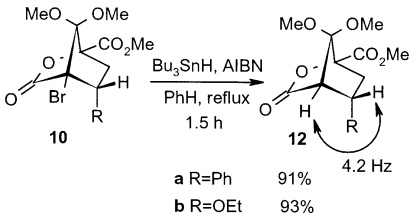


group are suitably disposed for an intramolecular S_N2 reaction. Alternatively, it might be possible that during the hydrolysis of the intermediate anhydride the addition of the hydroxide anion takes place preferentially to the carbonyl (2), furthest from the R-group, as a result of steric reasons, leading to the tetrahedral intermediate **11a**. The intermediate **11a** then collapses such that the bond "a", which is nearly anti-periplanar to the leaving group, migrates to displace the bridgehead bromine to give **10**.[9]

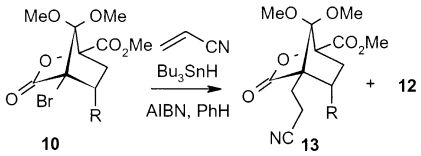
The regiochemistry of **10** was unambiguously proven by hydrodebromination of the bridgehead halide using tributyltinhydride (TBTH/AIBN). The ^{1}H NMR spectrum of the reduced compounds **12** showed clear vicinal coupling between the bridgehead hydrogen and the *exo*-hydrogen (J = 4.2 Hz) attached to the carbon bearing substituent R in both the cases (Scheme 4).

The bicyclic bromolactones **10** proved to be promising substrates for the radical-mediated intermolecular C−C bond formation at the bridgehead.[10] The results are depicted in Scheme 5. A slow addition of a benzene solution of TBTH to a refluxing mixture of **10a** and

SCHEME 4. Reductive Hydrodebromination of Bridged Lactones 10

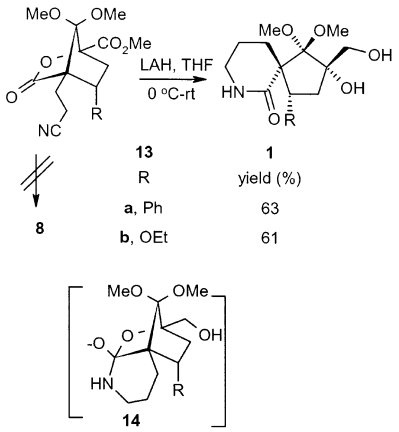


SCHEME 5. Facile C−C Bond Formation of Potential Bridged Lactones 10



R	condition	time (h)	**13**	**12**
a, Ph	reflux	3.5	75%	7%
	hν	4	64%	20%
b, OEt	reflux	4	72%	11%

SCHEME 6. Synthesis of Spirocyclic Lactams 1a,b



13 R	**1** yield (%)
a, Ph	63
b, OEt	61

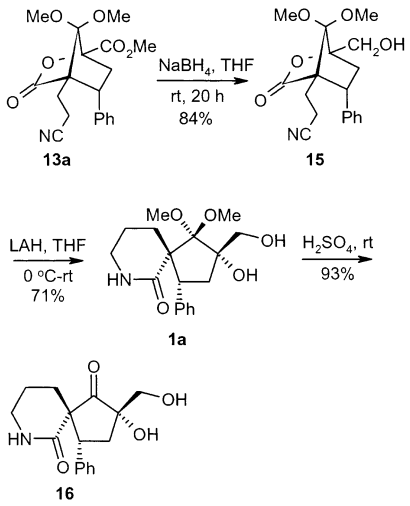
acrylonitrile as the radicophile resulted in the formation of 75% of the bridgehead-functionalized product **13a** along with 7% of the reduced lactone **12a**. By employing photochemical conditions, when a benzene solution of TBTH was added slowly to the solution of **10a** and acrylonitrile in benzene, which was being irradiated with a 200-W bulb, a clean reaction was observed with 64% of **13a** and 20% of the reduced lactone **12a**. The ethoxy derivative **10b** also gave similar results with TBTH/AIBN (Scheme 5).

After successfully accomplishing the synthesis of functionalized lactones **13** in good yield, we wanted to check the feasibility of our plan shown in Scheme 2. The LAH reduction of **13a** was carried out. In contrast to our anticipation, a 7-azaspiro[4.5]decan-6-one **1a** was obtained in 63% yield (Scheme 6), instead of the functionalized cyclopentanoid derivative **8**. The lactam carbonyl group appeared at 174.7 ppm in ^{13}C NMR spectrum. The lactam carbonyl group did not undergo further reduction with LAH in the reaction mixture even when it was refluxed with excess reagent in THF for several hours.

(9) We thank one of the referees for this suggestion.

(10) For the most recent books on radical chemistry, see: *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2001; Vols. 1 and 2.

SCHEME 7. Sodium Borohydride Reduction of Bridgehead Ester



This is probably because of the firm engagement of the lactam carbonyl under the reaction conditions as shown in **14**.

We thought that prereducing the lactone moiety in **13a** chemoselectively to obtain the corresponding lactol and then carrying out the LAH reaction would probably change the reaction course, and we employed $NaBH_4$ for the purpose. However, the reduction of **13a** with $NaBH_4$ in THF at room temperature furnished the alcohol **15** (Scheme 7). This illustrates a new example of $NaBH_4$ reduction of carboxylic esters[11] bearing an α-oxygen substituent. Apparently chelation and/or inductive activation accelerate the reaction. The spiroamide **1a** was realized when the alcohol **15** was treated with LAH. The acidic hydrolysis of the compound **1a** afforded the azaspirocyclic ketone **16**. A single-crystal X-ray analysis was carried out to prove the structure and relative stereochemistry of the aza spirocycle **1a** unequivocally.[12]

In summary, we have developed a valuable new sequence of reactions in which bridgehead C−C bond formation of the bridged bicyclic lactones with acrylonitrile followed by LAH reduction of the resulting adducts provides a short and efficient route to extract entirely novel, unexplored structural motifs, viz. 7-azaspiro[4.5]-decan-6-ones **1** from tetrabromonorbornyl derivatives **4**. The bridged bromolactones **10**, prepared efficiently in two steps from **4**, undergo radical-mediated facile intermolecular C−C bond formation at the bridgehead with acrylonitrile to furnish bridgehead-functionalized adducts **13**. Finally, a chemoselective, LAH-mediated reduction of the lactones **13** furnished the spirolactams **1**, constituting a four-step process starting from tetrabromonorbornyl derivatives **4**, illustrating a good example of selective application of all four bromine atoms originally present in the starting material as useful functional groups.

Experimental Section

General Information. Melting points are uncorrected. IR spectra were recorded as KBr pellets (solids) or thin films (liquids). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ and reported in the δ scale. Tetramethylsilane was used as the internal standard. Column chromatography was performed using silica gel (100−200 mesh), and ethyl acetate−hexane was used as eluant.

Lactone 10a. Yield 72%, colorless solid; mp 149−151 °C; ^{1}H NMR δ 7.36−7.29 (m, 3H), 7.23−7.20 (m, 2H), 3.91 (s, 3H), 3.82 (dd, 1H, J = 10.8, 4.9 Hz), 3.74 (s, 3H), 3.45 (s, 3H), 3.24 (dd, 1H, J = 13.7, 10.8 Hz), 2.45 (dd, 1H, J = 13.7, 5.1 Hz); ^{13}C NMR δ 166.7, 166.1, 135.4, 128.7, 128.6, 128.3, 109.6, 84.9, 70.1, 53.3, 52.0, 51.7, 46.9, 39.3; IR (KBr) 2900, 1790, 1740 cm $^{-1}$. Anal. Calcd for $C_{16}H_{17}BrO_6$: C 49.08, H 4.45. Found: C 49.60, H 4.40.

Lactone 10b. Yield 78%, colorless solid; mp 96−98 °C; ^{1}H NMR δ 4.30 (dd, 1H, J = 8.5, 2.7 Hz), 3.86 (s, 3H), 3.80 (s, 3H), 3.76 (dq, 1H, J = 9.3, 7.0 Hz), 3.62 (s, 3H), 3.65−3.57 (m, 1H), 3.40 (s, 3H), 3.09 (dd, 1H, J = 13.4, 8.5 Hz), 2.02 (dd, 1H, J = 13.4, 8.5 Hz), 1.18 (t, 3H, J = 7.0 Hz); ^{13}C NMR δ 166.8, 165.4, 108.8, 84.9, 78.7, 67.8, 66.8, 53.2, 51.67, 51.65, 40.3, 15.1; IR (KBr) 2850, 1780, 1720. Anal. Calcd for $C_{12}H_{17}BrO_7$: C 40.81, H 4.85. Found: C 40.90, H 4.89.

General Procedure for Bridgehead Reduction. A solution of the bromo lactone **10** (0.5 mmol), Bu_3SnH (0.6 mmol), and AIBN (5 mol %) in benzene (3 mL) was refluxed under an inert atmosphere. After consumption of the starting material (TLC monitoring, 2:1 hexane/EtOAc), benzene was evaporated under reduced pressure. The residue was chromatographed on silica gel using hexane (30 mL) to remove tin impurities, and later on the eluant polarity was increased with ethyl acetate until the product eluted.

Lactone 12a. Yield 94%, colorless solid; mp 120−122 °C; ^{1}H NMR δ 7.33−7.20 (m, 5H), 3.88 (s, 3H), 3.85−3.80 (m, 1H), 3.46 (s, 3H), 3.33 (s, 3H), 3.21 (d, 1H, J = 4.2 Hz), 3.13 (dd, 1H, J = 13.7, 10.5 Hz), 2.33 (dd, 1H, J = 13.7, 5.2 Hz); ^{13}C NMR δ 170.1, 166.8, 138.3, 128.7, 127.5, 127.4, 111.9, 87.0, 55.7, 53.0, 51.5, 51.4, 38.6, 38.5; IR (KBr) 2850, 1790, 1720 cm^{-1}. Anal. Calcd for $C_{16}H_{18}O_6$: C 62.74, H 5.92. Found: C 62.71, H 5.90.

Lactone 12b. Yield 93%, colorless solid; mp 92−94 °C; ^{1}H NMR δ 4.29−4.25 (m, 1H), 3.81 (s, 3H), 3.52 (dq, 1H, J = 8.8, 7.0 Hz), 3.43−3.34 (m, 1H), 3.37 (d, 1H, J = 4.2 Hz), 3.30 (s, 3H), 3.23 (s, 3H), 2.94 (dd, 1H, J = 13.7, 8.5 Hz), 1.91 (dd, 1H, J = 13.7, 2.5 Hz), 1.12 (t, 3H, J = 7.0 Hz); ^{13}C NMR δ 168.7, 166.6, 111.5, 86.8, 72.7, 64.8, 53.6, 53.0, 51.4, 51.3, 39.7, 14.9; IR (KBr) 2900, 1770, 1740 cm^{-1}. Anal. Calcd for $C_{12}H_{18}O_7$: C 52.55, H 6.61. Found: C 52.53, H 6.63.

General Procedure for Intermolecular Bridgehead C−C Bond Formation. To a mixture of bromo lactone **10** (1 mmol), acrylonitrile (10 mmol), and AIBN (0.025 mmol) in benzene (10 mL) at reflux temperature was added a solution of Bu_3SnH (1.5 mmol) and AIBN (0.025 mmol) in benzene (24 mL) over a period of 45 min, and the mixture was refluxed for the specified time (Scheme 5). After consumption of the starting material, as monitored by TLC (1:1 hexane/EtOAc), benzene was removed under reduced pressure. The crude mixture was purified on a silica gel column using hexane (50 mL) to remove tin impurities, and later on the eluant polarity was increased with ethyl acetate until the product eluted.

Photochemical Conditions. A solution of bromo lactone **10a** (193 mg, 0.5 mmol), acrylonitrile (265 mg, 5 mmol), and AIBN (2 mg, 0.012 mmol) in benzene (5 mL) was irradiated at room temperature with a 200-W bulb kept at a distance of 2.5 cm from the reaction flask. A solution of Bu_3SnH (218 mg, 0.75 mmol) and AIBN (2 mg, 0.012 mmol) in benzene (12 mL) was added over a period of 1 h. After the specified time (consumption of starting material as monitored by TLC, 1:1 hexane/EtOAc), benzene was removed under reduced pressure. The crude mixture was purified on a silica gel column using hexane (30 mL) to remove tin impurities, and later on the eluant polarity was increased with ethyl acetate to furnish lactone **12a** (30.6 mg, 20%) and nitrile **13a** (115 mg, 64%).

Nitrile 13a. Yield 75%, colorless solid; mp 102−104 °C; ^{1}H NMR δ 7.35−7.28 (m, 3H), 7.16−7.11 (m, 2H), 3.89 (s, 3H), 3.63 (s, 3H), 3.48 (dd, 1H, J = 10.5, 5.4 Hz), 3.36 (s, 3H), 3.14 (dd, 1H, J = 13.9, 10.5 Hz), 2.81−2.72 (m, 1H), 2.48−2.40 (m, 1H), 2.24 (dd, 1H, J = 13.9, 5.4 Hz), 2.13−2.05 (m, 1H), 1.96−1.88 (m, 1H); ^{13}C NMR δ 171.1, 166.7, 136.6, 128.9, 128.4, 128.3,

(11) Mauger, J.; Robert, A. *J. Chem. Soc., Chem. Commun.* **1986**, 395.

(12) See Supporting Information.

119.8, 112.9, 85.4, 62.7, 53.1, 51.6, 51.5, 45.4, 39.2, 24.3, 12.4; IR (KBr) 2900, 2200, 1770, 1730 cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_6$: C 63.50, H 5.89, N 3.90. Found: C 63.54, H 5.90, N 3.92.

Nitrile 13b. Yield 72%, colorless solid; mp 102−104 °C; ^{1}H NMR δ 4.14 (dd, 1H, J = 8.0, 2.0 Hz), 3.85 (s, 3H), 3.56−3.49 (m, 1H), 3.49 (s, 3H), 3.41 (dq, 1H, J = 8.9, 7.0 Hz), 3.31 (s, 3H), 2.94−2.79 (m, 3H), 2.33−3.28 (m, 2H), 1.90 (dd, 1H, J = 13.4, 2.4 Hz), 1.16 (t, 3H, J = 7.0 Hz); ^{13}C NMR δ 170.3, 166.6, 120.3, 111.4, 85.6, 76.7, 65.2, 61.6, 53.1, 51.6, 51.5, 38.7, 23.1, 15.0, 12.6; IR (KBr) 2900, 1780, 1730 cm^{-1}. Anal. Calcd for $C_{15}H_{21}NO_7$: C 55.04, H 6.47, N 4.28. Found: C 56.01, H 6.49, N 4.30.

$LiAlH_4$ Reduction of Nitriles 13. To a suspension of $LiAlH_4$ (2 mmol) in dry THF (5 mL) cooled in an ice bath was added the nitrile **13** (1 mmol) in THF under argon. The reaction mixture was stirred for 30 min at room temperature until the starting material was consumed, as monitored by TLC (1:6 hexane/EtOAc). The reaction mixture was quenched with EtOAc. Saturated aqueous NH_4Cl solution was added dropwise until a white precipitate was obtained. The reaction mixture was filtered and washed with EtOAc. Concentration of the combined organic filtrate followed by purification of the residue by silica gel column chromatography (elution with 1:5 hexane/EtOAc) afforded the pure spiro lactams **1**.

Spiro Lactam 1a. Yield 63%, colorless crystals (EtOAc); mp 156−158 °C; ^{1}H NMR δ 7.33−7.22 (m, 5H, aromatic), 6.69 (s, 1H, D_2O exchangeable), 6.06 (br s, 1H, D_2O exchangeable), 3.85 (dd, 1H, J = 11.2, 5.8 Hz), 3.69 (dd, 1H, J = 11.2, 7.1 Hz), 3.60 (s, 3H, OMe), 3.59 (s, 3H, OMe), 3.15−3.13 (m, 1H), 2.95 (dd, 1H, J = 12.9, 9.0 Hz), 2.85−2.82 (m, 2H), 2.69 (dd, 1H, J = 14.2, 9.0 Hz), 2.47 (t, 1H, J = 13.5 Hz), 2.10−2.05 (m, 1H), 1.78−1.67 (m, 1H), 1.29−1.24 (m, 1H); ^{13}C NMR δ 174.7, 139.9, 129.2, 128.3, 127.1, 113.0, 82.5, 67.7, 62.8, 52.9, 52.3, 52.2, 44.8, 42.5, 28.6, 19.2; IR (KBr) 3200, 2900, 1590 cm^{-1}. Anal. Calcd for $C_{18}H_{25}NO_5$: C 64.46, H 7.51, N 4.18. Found: C 64.43, H 7.50, N 4.19.

Spiro Lactam 1b. Yield 61%, colorless solid; mp 98−100 °C; ^{1}H NMR δ ^{1}H NMR δ 6.96 (s, 1H, D_2O exchangeable), 6.10 (br s, 1H, D_2O exchangeable), 3.76−3.73 (m, 1H), 3.60−3.59 (m, 2H), 3.51 (s, 3H), 3.50 (s, 3H), 3.37 (dq, 1H, J = 9.3, 7.0 Hz), 3.35−3.31 (m, 2H), 2.79 (m, 2H), 2.08−1.98 (m, 3H), 1.93−1.87 (m, 2H), 1.15 (t, 3H, J = 7.0 Hz); ^{13}C NMR δ 173.4, 111.0, 83.8, 81.8, 67.6, 65.1, 61.6, 52.8, 52.1, 42.9, 42.6, 29.0, 18.9, 15.4; IR (KBr) 3300, 2900, 1610 cm^{-1}. Anal. Calcd for $C_{14}H_{25}NO_6$: C 55.43, H 8.31, N 4.62. Found: C 55.12, H 8.23, N 4.57.

Nitrile 15. A solution of the nitrile **13a** (180 mg, 0.5 mmol) in THF (4 mL) was cooled to 0 °C, and $NaBH_4$ (29 mg, 0.75 mmol) was added to it. The reaction mixture was stirred for 16 h at room temperature until the starting material was fully consumed, as monitored by TLC (1:1 hexane/EtOAc). THF was removed at room temperature under reduced pressure, and the residue was diluted with water. The aqueous layer was extracted with ethyl acetate (3 × 5 mL), and the combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was chromatographed on on silica gel using 2:1 hexane/EtOAc to furnish alcohol **15** (139 mg, 84%) as a colorless solid, mp 130−132 °C; ^{1}H NMR δ 7.27−7.05 (m, 5H), 4.08 (1/2 of ABq, 1H, J = 12.7, 5.5 Hz), 3.93 (1/2 ABq, 1H, J = 12.7, 6.4 Hz), 3.51 (s, 3H), 3.35 (s, 3H), 3.29 (dd, 1H, J = 10.5, 5.4 Hz), 2.75−2.67 (m, 1H), 2.61 (dd, 1H, J = 13.9, 10.5 Hz), 2.42−2.33 (m, 1H), 2.24 (br s, 1H, D_2O exchangeable), 2.10 (dd, 1H, J = 14.2, 5.4 Hz), 2.03−1.95 (m, 1H), 1.86 (dd, 1H, J = 10.7, 5.7 Hz); ^{13}C NMR δ 173.0, 137.4, 128.7, 128.4, 128.0, 120.1, 111.5, 90.5, 61.7, 59.8, 51.9, 51.4, 44.5, 36.7, 24.4, 12.4; IR (KBr) 3300, 2900, 1760 cm^{-1}. Anal. Calcd for $C_{18}H_{21}NO_5$: C 65.24, H 6.39, N 4.23. Found: C 65.17, H 6.35, N 4.25.

Spiro Lactam 16. Yield 93%, colorless solid; mp 120−121 °C; ^{1}H NMR δ 7.42−7.24 (m, 5H), 4.31−4.29 (m, 1H), 3.78 (1/2 ABq, 1H, J = 11.2, 6.2 Hz), 3.67 (1/2 ABq, 1H, J = 10.8, 4.8 Hz), 3.18 (dd, 1H, J = 13.0, 7.0 Hz), 3.14−3.08 (m, 1H), 2.83 (dd, 1H, $J_1 = J_2$ = 13.3 Hz), 2.79−2.70 (m, 1H), 2.61 (dd, 1H, J = 12.8, 7.6 Hz), 2.25−2.17 (m, 1H), 1.80−1.70 (m, 1H), 1.55−1.45 (m, 1H); ^{13}C NMR δ 217.0, 170.2, 138.8, 128.5, 128.1, 127.0, 79.4, 65.2, 59.4, 51.0, 41.4, 39.9, 29.8, 18.9; IR (KBr) 2900, 1750, 1620 cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_4$: C 66.42, H 6.62, N 4.84. Found: C 66.38, H 6.52, N 4.54.

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Supporting Information Available: Preparation of α-diketones **9a**,**b**. X-ray crystal structure and crystallographic data for compound **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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