Organocatalytic Biomimetic Reduction of Conjugated Nitroalkenes

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Abstract: A thiourea-catalyzed biomimetic reduction of conjugated nitroalkenes has been developed. Various aromatic and aliphatic conjugated nitroalkenes can be reduced to give the respective nitroalkanes with good yields under mild conditions. This protocol is not only practical, but may also provide insight into the mechanisms of redox transformations in biological systems.

Key words: biomimetic reduction, Hantzsch ester, hydrogen bonding, nitroalkenes, thiourea

Aliphatic nitroalkanes are valuable building blocks and intermediates in organic synthesis as well as in carbohydrate chemistry.[1] They are very useful tools for carbon–carbon bond formation or carbon skeleton elongation because the high electron-withdrawing power of the nitro group stabilizes α-carbanions and enables their reactions with electrophiles under mild conditions. Moreover, the nitro group itself can be transformed into other functionalities such as, amongst others, carbonyl, amino, oxime, and hydrogen moieties.[2] The preparation and subsequent reduction of conjugated nitroalkenes has been widely accepted as a straightforward route to nitroalkanes, thus, there are quite a number of reducing reagents and reduction methodologies employed in this transformation.[3] Commonly used reductants include borohydride derivatives, metal hydrides, and metal halides. However, the selective reduction of the conjugated double bond is rather difficult because nitro-group reduction often takes place simultaneously.[4] Though sodium borohydride primarily furnishes the corresponding nitroalkanes, these reactions are often accompanied by the formation of polymeric side products through Michael addition of the nitronate intermediate to the starting nitroalkene.[5] Zinc borohydride is reported to be an efficient reagent with which to convert nitroalkenes smoothly into the corresponding nitroalkanes.[6] Metal-catalyzed hydrogenations and transfer hydrogenation are also very effective, however, due to the difficulties in handling or the toxicity of metal ions, new efficient and environmentally friendly methods remain desirable.[7]

In contrast to the chemical conversions described above, biological redox transformations using reduced nicotinamide adenine dinucleotide (NADH) as a coenzyme to reduce unsaturated functionalities, proceeds smoothly under very mild conditions. The ease with which such reactions takes place has been a stimulus for the development of a wide range of NADH models for a variety of reductions.[8] Among these, Hantzsch esters are one of the most widely investigated biomimetic reductants because they are inexpensive, stable and readily available.[9] Recent advances in organocatalysis have shown considerable promise for employing Hantzsch esters as the hydrogen source in asymmetric reductions as well as reductive aminations;[10] however, there is no organocatalytic method for the reduction of conjugated nitroalkenes.[11]

Developments in biological and enzymatic catalysis have shown that isolated enzymes from baker's yeast or Old Yellow Enzyme (OYE), which was termed as nitroalkene reductase, can efficiently catalyze the NADPH-linked reduction of nitro-olefins. The crystal structure of OYE revealed that several amino acid residues around the active site of the enzyme affect catalysis and ligand binding. With a systematic study of the OYE-catalyzed reduction of nitrocyclohexene, a catalytic mechanism was proposed in which the nitrocyclohexene was activated by nitro-oxygen hydrogen bonds to His-191 and Asn-194 (Figure 1, A).[12] A hydride is then transferred to the β-position from the reduced flavin which, ultimately, originated from NADPH. The product is finally formed through proton transfer from the Tyr-196 hydroxyl to the α-position.[12]

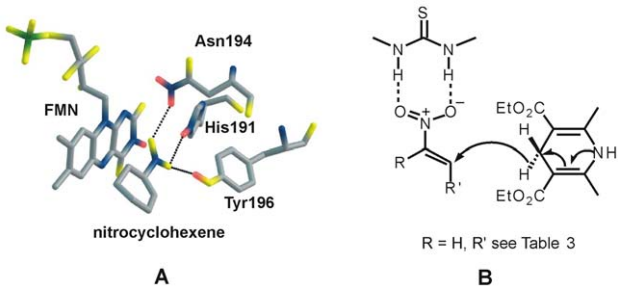

Figure 1 Thiourea-catalyzed biomimetic reduction of nitroalkenes. (A) Key interactions between the enzyme (OYE) and nitrocyclohexene (Protein Databank ID code 1OYB); (B) model of the thiourea-catalyzed biomimetic reduction of conjugated nitroalkenes.

This excellent study inspired us to mimic the procedure in preparative chemistry with an organocatalyst functioning as the 'reductase' and an NADPH analog such as a Hantzsch ester. During our efforts at developing noncovalent organocatalysis mediated through hydrogen bonding,[13] we recently found that thiourea **3** catalyzes the transfer hydrogenation of aldimines with Hantzsch ester **2** as the hydrogen source, at low catalyst loadings

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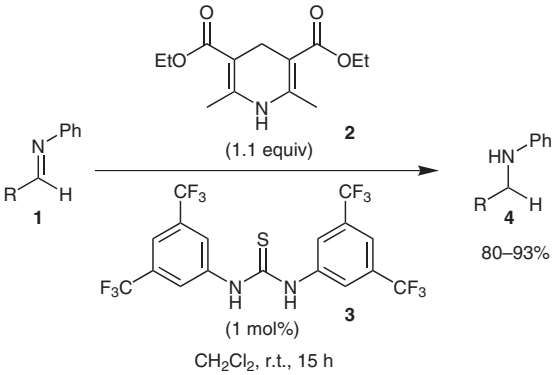
(Scheme 1).[14] We were hopeful that it would be possible to extend this procedure to other electron-deficient α,β-unsaturated conjugated olefins such as nitroalkenes (Figure 1, B). Here we report the first thiourea-catalyzed biomimetic reduction of conjugated nitroalkenes through hydrogen-bonding activation.



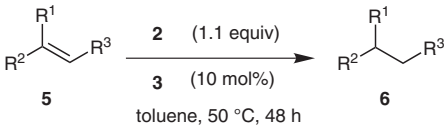
Scheme 1 Thiourea-catalyzed transfer hydrogenation of aldimines.[14]

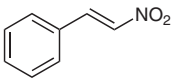
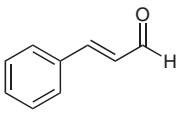
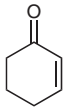
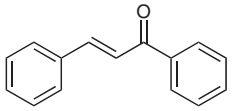
We first examined some representative electron-withdrawing, conjugated olefins such as nitrostyrene (**5a**), cinnamaldehyde (**5b**), 2-cyclohexenone (**5c**) and chalcone (**5d**) with the protocol described in Table 1. Only nitrostyrene could be reduced at 10 mol% loading of **3**; a decrease in the catalyst loading resulted in somewhat reduced yields (Table 1). The rationale behind this effective reduction may be that the nitro group, as the most electron-withdrawing substituent known,[15] forms strong hydrogen-bonding interactions between the nitro group and **3** and is thus very effective in lowering the LUMO energy of the olefin and thus accelerating the reaction.

We then evaluated solvent effects on the reduction of nitrostyrene (Table 2). Reductions in non-polar media such as benzene and toluene, as well as halogenated solvents, proceeded smoothly. Performing the reaction in more polar media led to sluggish reactions and considerably diminished yields. Surprisingly, a moderate yield was also obtained in the protic solvent methanol (entry 9). In order to further clarify this unusual phenomenon, the reaction was repeated in methanol without the addition of catalyst **3**; complete consumption of **5a** was observed and, in addition to the expected nitroalkane, the Michael addition product was also obtained (entry 10).

Using dichloromethane as solvent and **3** (10 mol%) as catalyst, we studied the general applicability of this procedure for reducing various nitroalkenes (Table 3). All aromatic nitroalkenes were smoothly reduced in good yields and varying the substituents had no marked effect on the outcome of this reaction. As expected, the reductions of electron-rich nitrostyrenes took longer and afforded the product in lower yield. Aliphatic nitroalkenes (**5q** and **5r**) were reduced to the corresponding nitroalkane in very good yield. Only the reduction of nitrocyclohexene gave the nitroalkane in poor yield even at 20 mol% load-

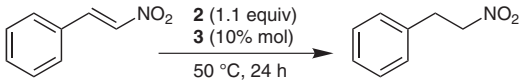
Table 1 Substrate Screening for Thiourea-Catalyzed Reductions



Substrate	Catalyst (mol%)	Product	Yield (%)[a]
 **5a**	–	**6a**	0
5a	**3** (10)	**6a**	87
5a	**3** (5)	**6a**	75
 **5b**	**3** (10)	**6b**	0
 **5c**	**3** (10)	**6c**	0
 **5d**	**3** (10)	**6d**	0

[a] Yield of product after column chromatography.

Table 2 Solvent Effects on the Reduction of Nitrostyrene

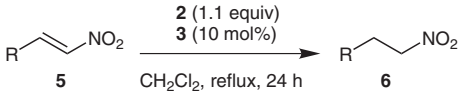


Entry	Solvent	Yield (%)[a]
1	toluene	78
2	benzene	84
3	CH_2Cl_2	88
4	$CHCl_3$	76
5	THF	39
6	1,4-dioxane	30
7	MeCN	39
8	DMF	31
9	MeOH	52
10	MeOH	45[b]

[a] Yield of product after column chromatography.
[b] The reaction was carried out in the absence of catalyst **3**.

ing. Reduction of the nitro group and polymerization of the olefins did not occur in any case.

Table 3 Biomimetic Reduction of Various Nitroalkenes



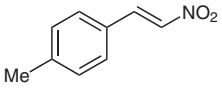
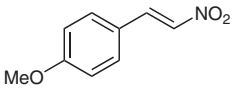
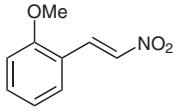
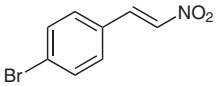
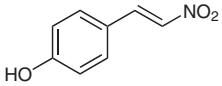
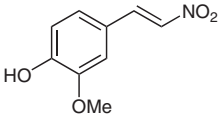
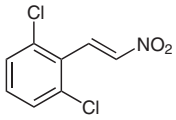
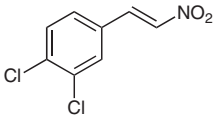
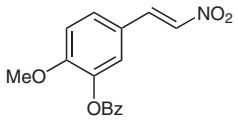
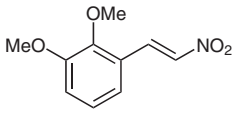
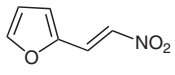
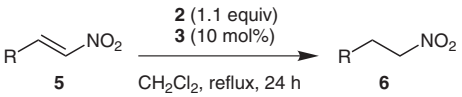
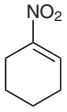
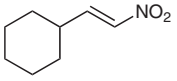
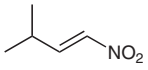
Nitroalkene	Product	Yield (%)[a]
 **5e**	**6e**	80
 **5f**	**6f**	72
 **5g**	**6g**	85
 **5h**	**6h**	79
 **5i**	**6i**	75
 **5j**	**6j**	71
 **5k**	**6k**	82
 **5l**	**6l**	89
 **5m**	**6m**	80
 **5n**	**6n**	71
 **5o**	**6o**	93

Table 3 Biomimetic Reduction of Various Nitroalkenes (continued)



Nitroalkene	Product	Yield (%)[a]
 **5p**	**6p**	37[b] 47[b,c]
 **5q**	**6q**	82
 **5r**	**6r**	87

[a] Yield of product after column chromatography.
[b] A mixture of **5p** and **6p** was isolated; yield was determined by ^{1}H NMR spectroscopy.
[c] 20 mol% of **3** was used.

In summary, we have developed a thiourea-catalyzed biomimetic metal- and acid-free reduction of conjugated nitroalkenes to the respective nitroalkanes utilizing a Hantzsch ester as the hydrogen source. A variety of aromatic and aliphatic conjugated nitroalkenes can be reduced to the respective nitroalkanes with good yields under mild conditions. This protocol is not only practical, but may also provide insights into transformations through hydrogen-bond activation in biological systems. The extension of this protocol to an asymmetric reduction of disubstituted or trisubstituted nitroalkenes, using chiral thiourea derivatives, is under investigation.

Unless otherwise noted, all materials were obtained from commercial suppliers and were used without further purification. Solvents for chromatography were of technical grade and were distilled prior to use. Solvents used in the reactions were reagent grade and were distilled from the indicated drying agents: toluene (P_2O_5), CH_2Cl_2 (P_2O_5), benzene (Na), Et_2O (Na), MeCN (P_2O_5), 1,4-dioxane (Na), DMF (CaH_2), $CHCl_3$ (P_2O_5), THF (Na). For TLC, silica gel coated aluminum plates (Merck, silica gel 60 F_{254}) were used and chromatograms were visualized by irradiation with UV light at 254 nm. Column chromatography was performed using J. T. Baker silica gel (particle size 0.063–0.200 mm). Solvent mixtures are understood as volume/volume. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer at 298 K in 5 mm NMR tubes. The chemical shifts (δ values) were obtained in $CDCl_3$ solutions unless otherwise noted and referenced to residual $CHCl_3$ (^{1}H NMR: δ = 7.25 ppm, ^{13}C NMR: δ = 77.2 ppm). Data are presented as follows: chemical shift, multiplicity, coupling constant in Hertz (Hz), integration. IR spectra were reported in terms of frequency (cm^{-1}) and intensity of absorption (s = strong, m = medium, w = weak). HRMS were recorded on a Thermo Finnigan MAT 95. GC-MS analyses were carried out with a Quadrupole-MS HP MSD 5971 (EI) and HP 5890A gas chromatograph equipped with a J & W Scientific fused silica GC column (30 m × 0.250 mm, 0.25 micron DB-5MS stationary phase: 5% phenyl and 95% methyl silicone) using

He as carrier gas; T-program standard 60–250 °C (15 °C/min heating rate), injector and transfer line 250 °C.

Preparation of Nitro Alcohols; General Procedure

To a solution of the aldehyde (45.4 mmol) and nitromethane (2.5 mL, 46.2 mmol) in EtOH (10 mL) cooled to 0 °C, was added aq NaOH (10 M, 4.54 mL, 45.4 mmol) through a plastic syringe, dropwise, under vigorous stirring (necessary to prevent the formation of a solid mass). After 10 min, the reaction mixture became white and solidified. AcOH (2.6 mL, 45.4 mmol) and subsequently H_2O (20 mL) was added and the aqueous phase was extracted with Et_2O (2 × 500 mL). The combined organic phase was washed with H_2O (5 × 300 mL) until the pH of the washings was about 6. After drying over $MgSO_4$, filtration and concentration in vacuo, the nitro alcohol was obtained and used without further purification.

1-Nitro-2-cyclohexyl-2-ethanol

Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88–1.18 (m, 5 H), 1.28–1.37 (m, 1 H), 1.50–1.56 (m, 2 H), 1.63–1.71 (m, 2 H), 2.65 (br, 1 H, OH), 3.92–3.98 (m, 1 H), 4.25–4.37 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.76, 25.88, 26.09, 27.97, 28.81, 41.45, 72.91, 79.38.

MS: *m*/*z* (%) = 112, 94, 83, 68, 55 (100).

1-Nitro-3-methyl-2-butanol

Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (m, 6 H), 1.72 (m, 1 H), 3.16 (br, 1 H, OH), 4.04 (m, 1 H), 4.32–4.45 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4, 18.3, 31.7, 73.5, 79.4.

MS: *m*/*z* (%) = 91, 90, 86, 73, 69 (100), 62, 55.

Preparation of Aliphatic Nitroalkenes (5q and 5r);[16] Typical Procedure

To a solution of 1-nitro-2-cyclohexyl-2-ethanol (5.06 g, 29.2 mmol) in CH_2Cl_2 (60 mL), cooled to 0 °C, were added successively TFAA (4.34 mL, 30.7 mmol) then, dropwise, Et_3N (8.56 mL, 61.4 mmol). The reaction mixture was allowed to warm to r.t. and stirred for 1 h. CH_2Cl_2 (40 mL) was added and the organic phase was washed successively with H_2O (20 mL), sat. aq NH_4Cl (20 mL) and brine (20 mL) then dried over $MgSO_4$. After filtration and concentration in vacuo, the product was distilled under reduced pressure.

5q

Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06–1.78 (m, 10 H), 2.19 (m, 1 H), 3.09 (m, 1 H), 6.86 (d, *J* = 13.6 Hz, 1 H), 7.15 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.4, 25.6, 31.4, 37.5, 138.3, 147.4.

MS: *m*/*z* (%) = 138, 97, 81, 79, 69, 57, 55 (100).

5r

Yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (d, *J* = 6.79 Hz, 6 H), 2.58 (m, 1 H), 6.94 (m, 1 H), 7.22–7.28 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 28.3, 138.1, 148.5.

MS: *m*/*z* (%) = 100, 67, 57 (100), 53, 51.

Biomimetic Reduction of Nitroalkenes; General Procedure

Nitroalkene (1.0 mmol), thiourea **3** (10 mol%) and Hantzsch ester (**2**; 1.1 equiv) were suspended in anhyd CH_2Cl_2 (5 mL) and the resulting mixture was allowed to reflux for 24 h. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to afford the pure corresponding nitroalkanes. The yields are given in Table 3. ^{1}H NMR data for known compounds were identical to those in the literature: **6a**,[11e] **6f**,[11e] **6e**,[17] **6g**,[11e] **6i**,[18] **6l**,[19] **6m**,[5b] **6o**,[11e] **6p**,[20] and **6q**.[21] The ^{13}C NMR, IR, and MS data are given below. All new compounds or those that have not been well-described in the literature were fully characterized on the basis of IR, ^{1}H NMR, ^{13}C NMR, and HRMS.

6a

Colorless oil.

IR (film): 3031, 1551, 1455, 1379, 1083, 769, 752 cm^{-1}.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.4, 76.3, 127.4, 128.6, 129.2, 135.7.

HRMS: *m*/*z* calcd for $C_8H_9NO_2$: 151.06278; found: 151.06220.

6e

Colorless oil.

IR (film): 3025, 2923, 1905, 1551, 1517, 1433, 1379, 1181, 1115, 811 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3 H), 3.19 (t, *J* = 7.39 Hz, 2 H), 4.49 (t, *J* = 7.39 Hz, 2 H), 7.03 (dd, J_1 = 8.17 Hz, J_2 = 10.31 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 33.1, 76.5, 128.5, 129.6, 132.6, 137.1.

MS: *m*/*z* (%) = 165, 118 (100), 103, 91, 77, 65.

6f

Colorless oil.

IR (film): 3007, 2959, 2937, 2838, 1612, 1551, 1514, 1434, 1379, 1250, 1180, 866, 827 cm^{-1}.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.7, 55.3, 76.6, 114.4, 127.6, 129.6, 158.9.

HRMS: *m*/*z* calcd for $C_8H_{11}NO_3$: 181.07389; found: 181.07319.

6g

Colorless oil.

IR (film): 2941, 2839, 1603, 1589, 1551, 1465, 1380, 1120, 1031, 756 cm^{-1}.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.2, 55.3, 74.7, 110.4, 120.8, 123.9, 128.9, 130.7, 157.5.

HRMS: *m*/*z* calcd for $C_8H_{11}NO_3$: 181.07389; found: 181.07288.

6h

Colorless solid.

IR (KBr): 3029, 2974, 2957, 2911, 1719, 1565, 1488, 1425, 1336, 1295, 1009, 979, 803, 771 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.19 (t, *J* = 7.20 Hz, 2 H), 4.51 (t, *J* = 7.20 Hz, 2 H), 7.01 (d, *J* = 8.43 Hz, 2 H), 7.37 (d, *J* = 8.43 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.75, 75.90, 121.44, 130.31, 132.08, 134.66.

HRMS: *m*/*z* calcd for $C_8H_8BrNO_2$: 228.97384; found: 228.97034.

6i

Colorless oil.

IR (film): 3424, 2984, 1552, 1516, 1445, 1107, 772 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ= 3.13 (t, *J* = 7.41 Hz, 2 H), 4.47 (t, *J* = 7.41 Hz, 2 H), 6.70 (d, *J* = 8.42 Hz, 2 H), 6.94 (d, *J* = 8.42 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.7, 76.6, 116, 130, 155.6.

MS: *m*/*z* (%) = 167, 120 (100), 103, 91, 77, 65, 51.

6j
Colorless oil.

IR (film): 3505, 2941, 1613, 1551, 1517, 1453, 1433, 1033 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.17 (t, *J* = 7.31 Hz, 2 H), 3.80 (s, 3 H), 4.50 (t, *J* = 7.31 Hz, 2 H), 5.52 (br, 1 H, OH), 6.62 (m, 2 H), 6.78 (d, *J* = 7.96 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 33.3, 55.9, 76.7, 111.1, 114.8, 121.3, 127.4, 145.0, 146.7.

HRMS: *m*/*z* calcd for $C_9H_{11}NO_4$: 197.06826; found: 197.06995.

6k
Colorless oil.

IR (film): 3084, 2920, 1437, 1380, 1088, 1025, 779 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.59–3.63 (m, 2 H), 4.47–4.51 (m, 2 H), 7.08–7.13 (t, *J* = 8.04 Hz, 2 H), 7.25–7.27 (d, *J* = 8.04 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.0, 72.0, 128.6, 129.4, 131.4, 135.8.

HRMS: *m*/*z* calcd for $C_8H_7Cl_2NO_2$: 218.98483; found: 218.98395.

6l
Colorless oil.

IR (film): 2977, 2929, 1557, 1279, 865, 772, 566 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.17 (t, *J* = 7.19 Hz, 2 H), 4.52 (t, *J* = 7.19 Hz, 2 H), 6.96 (m, 1 H), 7.22 (m, 1 H), 7.28 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.2, 75.5, 123.0, 128.0, 130.5, 130.8, 135.9.

HRMS: *m*/*z* calcd for $C_8H_7Cl_2NO_2$: 218.98483; found: 218.98395.

6m
Yellow solid.

IR (KBr): 3345, 3038, 2936, 1664, 1590, 1516, 1380, 1349, 1010, 808 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.13 (t, *J* = 7.32 Hz, 2 H), 3.77 (s, 3 H), 4.43 (t, *J* = 7.32 Hz, 2 H), 5.04 (s, 2 H), 6.66 (m, 2 H), 6.75–6.77 (d, *J* = 8.00 Hz, 1 H), 7.17–7.35 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.9, 56.0, 71.2, 76.4, 112.1, 114.6, 121.4, 127.4, 127.9, 128.1, 128.5, 136.7, 148.2, 149.0.

HRMS: *m*/*z* calcd for $C_{16}H_{17}NO_4$: 287.11521; found: 287.11575.

6n
Colorless oil.

IR (film): 2941, 2838, 1588, 1551, 1484, 1278, 1083, 1007, 750 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.22 (t, *J* = 7.45 Hz, 2 H), 3.77 (s, 3 H), 3.79 (s, 3 H), 4.52 (t, *J* = 7.45 Hz, 2 H), 6.68 (m, 1 H), 6.78 (m, 1 H), 6.91 (t, *J* = 7.98 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.7, 55.7, 60.7, 75.2, 110.0, 119.3, 124.3, 129.2, 147.3, 152.7.

HRMS: *m*/*z* calcd for $C_{10}H_{13}NO_4$: 211.08391; found: 211.08459.

6o
Yellow oil.

IR (film): 2921, 1724, 1555, 1507, 1378, 1281, 1145, 741 cm^{-1}.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.0, 73.4, 107.4, 110.1, 143.8, 149.4.

MS: *m*/*z* (%) = 141, 94 (100), 83, 65, 55.

6p
Colorless oil; ratio **6p/5p** = 4:5.

IR (film): 2802, 2669, 1713, 1468, 1431, 1268, 1243, 1223, 1194, 1160 cm^{-1}.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.8, 24.6, 30.8, 84.6.

MS: *m*/*z* (%) = 84, 83, 81, 77, 67, 65, 55 (100).

6q
Colorless oil.

IR (film): 2926, 2854, 1554, 1449, 1385 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.93 (m, 2 H), 1.06–1.18 (m, 4 H), 1.57–1.66 (m, 5 H), 1.84 (q, *J* = 7.11 Hz, 2 H), 4.34 (t, *J* = 7.30 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.9, 26.2, 32.7, 34.6, 34.9, 73.8.

MS: *m*/*z* (%) = 138, 122, 111, 109, 99, 94, 81, 79, 67, 55 (100).

6r
Colorless oil.

IR (film): 2964, 2875, 1785, 1555, 1470, 1382, 1279, 1135 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 6.63 Hz, 6 H), 1.58–1.66 (m, 1 H), 1.85 (q, *J* = 7.27 Hz, 2 H), 4.34 (t, *J* = 7.39 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.0, 25.6, 36.0, 74.3.

MS: *m*/*z* (%) = 71, 69, 67, 62, 59, 55 (100).

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