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Oxidation of Aliphatic α,β-Unsaturated Aldimines to Amides Specifically by Oxone with $AlCl_3$

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Abstract: α,β-Unsaturated aldimines were specifically oxidized to amides with Oxone in the presence of $AlCl_3$ as a Lewis acid in CH_2Cl_2. No migration of aryl group occurred in the rearrangement reaction.

Keywords: Aldimine; amide; Oxidation; Oxone; rearrangement

α,β-Unsaturated amides are an important kind of building block in organic synthesis.[1] They have been used particularly for preparing natural products.[2] Their amide groups are available for further functionalizations and can activate the double bonds for additions and other reactions. In addition, α,β-unsaturated amides exhibit both biological[3] and insecticide activities.[4] Therefore, the preparation of α,β-unsaturated amides has attracted more attention from chemists and has been achieved via various approaches.[4c,5–10] On reviewing the previous methods, we found that the remaining common problems were either unavailable starting materials or multi step preparations.

Oxone ($2KHSO_5 \bullet KHSO_4 \bullet K_2SO_4$) is a powerful, environmentally friendly oxidant.[11] It has been widely used in organic preparation. It oxidized alcohols to aldehydes and ketones[12] and broke double bonds to give acids.[13] Acetoxylation and etherification of arenes and alkanes were achieved with Oxone in the presence of $Pd(OAc)_2$ used as a

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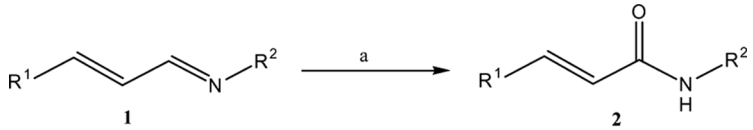


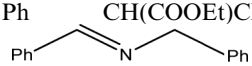
a: Oxone (2 eq.), $NaHCO_3$ (3.5 eq.), $AlCl_3$ (1.2 eq.), CH_2Cl_2, r.t.

Scheme 1. Oxidation of α, β-unsaturated aldimines.

catalyst.[14] An alkyne and an amine were converted to an amide by Oxone.[15] It has been singularly noteworthy that Oxone was particularly favorable for the epoxidation of olefins[11a,16] and for the formation of an oxaziridine intermediate.[17] Our interest in the latter promoted us to carry out this investigation in hope of that an epoxidation might occur on a C−N double bond adjacent to a C=C double bond with Oxone and in turn a complex of the oxygen of an oxazirindine with $AlCl_3$ might form. The resulting complex is expected to undergo a hydride migration to the electron-deficient nitrogen atom as in the Beckmann rearrangement and then a ring opening to give an amide with no migration of aryl group and no change in the α,β-double C=C bonds.

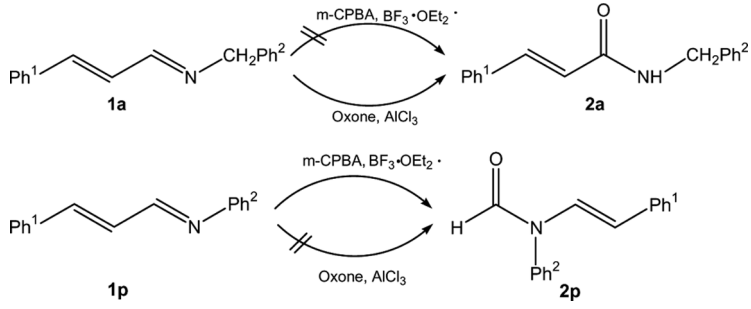
We started with an (*E*)-α, β-unsaturated aldimine **1** (Scheme 1), which was easily prepared by the reaction of an (*E*)-α, β-unsaturated aldehyde with an amine at toluene reflux temperature and by removing water through a water segregator.[18] Treatment of **1** with Oxone in the presence of $AlCl_3$ as a Lewis acid in CH_2Cl_2 at room temperature afforded, after hydrolysis, a single rearranged amide **2** (Scheme 1 and Table 1). Products were characterized by IR, MS, ^1H and ^{13}C NMR. It is particularly worthy pointing out that simple imines without α,β-unsaturated bonds such as **1r** (Table 1) were unfavorable for the reaction. It appears that conjugated double bonds may play a key role in the reaction. In An's work,[19] simple imines were alternatively oxidized to two amides by m-CPBA and $BF_3 \bullet OEt_2$. Their reaction selectivity closely depended on the electron density on the nitrogen atom as well as the difference in the migratory aptitude of groups to an electron-deficient nitrogen atom when the reaction proceeded via an oxaziridine intermediate. Our experiments showed that the two α,β-unsaturated amides employed in An's work[19a] were not obtained under the present conditions (Scheme 2), whereas all substrates employed in the present work were not converted to amides using m-CPBA and $BF_3 \bullet OEt_2$. Furthermore, no migration of the aryl group occurred in the present cases. As such, these two approaches may occur via different mechanisms. The existence of α,β-unsaturated bonds largely disfavored the group migration in an oxaziridine intermediate.

Table 1. Oxidation of α,β-unsaturated aldimines with Oxone and $AlCl_3$ in CH_2Cl_2

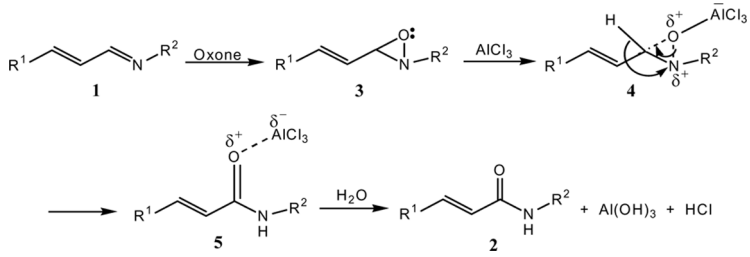
Substrate	R^1	R^2	Yield of **2**(%)[a]	Aldehyde (%)[c]
1a	Ph	CH_2Ph	78	12
1b	Ph	$CH(CH_3)Ph$	75	15
1c	Ph	$C(CH_3)_3$	70	17
1d	Ph	$CH(CH_2)_5$[b]	81	10
1e	(p)-MeO-Ph	CH_2Ph	84	8
1f	(p)-MeO-Ph	$CH(CH_3)Ph$	82	10
1g	(p)-MeO-Ph	$C(CH_3)_3$	78	13
1h	(p)-MeO-Ph	$CH(CH_2)_5$[b]	87	5
1i	(p)-Cl-Ph	CH_2Ph	68	20
1j	(p)-Cl-Ph	$CH(CH_3)Ph$	65	20
1k	(p)-Cl-Ph	$C(CH_3)_3$	60	20
1l	(p)-Cl-Ph	$CH(CH_2)_5$[b]	72	17
1m	(p)-NO_2-Ph	$C(CH_3)_3$	50	21
1n	(p)-NO_2-Ph	$CH(CH_2)_5$[b]	55	23
1o	Ph	$CH_2(CH_2)_{16}CH_3$	66	20
1p	Ph	Ph	0	95
1q	Ph	$CH(COOEt)CH_2Ph$	0	0
1r			0	92

[a]Yields refer to isolated products.
[b]Cyclohexyl.

From Table 1, it can be observed that both substituents of R^1 and R^2 exert significant effects on the reaction. In general, an electron-donating substituent at the *para*-position of a benzene ring in R^1 is favorable for the reaction, whereas an electron-withdrawing group leads to a lower yield of product. R^2 with a large block or an electron-withdrawing character did not favor the reaction. These observations are rationalized by a proposed



Scheme 2. Oxidation of α, β-unsaturated aldimines under different conditions.



Scheme 3. Mechanism for the oxidation of α, β-unsaturated aldimines with Oxone and $AlCl_3$.

mechanism for this reaction depicted in Scheme 3. An aldimine is firstly oxidized by Oxone to an oxazirindine **3**, whose oxygen is active toward $AlCl_3$ and forms its own 1:1 complex **4** as it is produced. So, for every molecule of amine formed in the reaction, one molecule of $AlCl_3$ is used up in complex formation. A stoichiometric amount of $AlCl_3$ is required in this reaction. Complex **4** undergoes an intramolecular hydride migration to the elecron-deficient nitrogen atom and a ring opening to give **5**. At the end of the reaction, addition of water destroys the complex and generates the free amide **2**. Obviously, a bulky or an electron-withdrawing group (R^2) upon the nitrogen atom will slow the formation of oxazirindine by Oxone and inhibit the oxygen of oxazirindine approaching to $AlCl_3$ owing to a steric or an electronic effect. An electron-withdrawing group linked to the nitrogen atom will lead to a decrease in the electron density on the oxygen atom of oxazirindine. Otherwise, the migration of the aryl group linked at β-C of the α,β-double bond will be thermodynamically unfavorable.

The effect of Lewis acids on the reaction was examined using **1a** as a substrate (Table 2). $AlCl_3$ was found to be the most favorable Lewis acid, whereas $ZrCl_4$, $Mg(ClO_4)_2$ and $BF_3 \bullet OEt_2$ did not exert any affect on the reaction.

Table 2. Effect of Lewis acids on the yield of **1a** in CH_2Cl_2

Entry	Lewis acid	Yield of **2a**(%)
1	$AlCl_3$	78
2	$FeCl_3$	55
3	$ZnCl_4$	30
4	$ZrCl_4$	0[a]
5	$Mg(ClO_4)_2$	0[b]
6	$BF_3 \bullet OEt_2$	0

[a]2-Benzyl-3-styryl-1,2-oxaziridine was isolated in 66% yield.
[b]2-Benzyl-3-styryl-1,2-oxaziridine was isolated in 74% yield.

In summary, an approach for preparing α,β-unsaturated amines developed in the present work provides an efficient method for the conversion of aldimines to amides by oxone and $AlCl_3$. No migration of aryl group occurred in the rearrangement reaction.

EXPERIMENTAL

A representative procedure: To a solution containing 0.77 mmol of **1a** in 15 mL of anhydrous CH_2Cl_2, 1.54 mmol of oxone, 2.69 mmol of $NaHCO_3$, and 0.92 mmol of anhydrous $AlCl_3$ were added. The mixture was stirred for 8–12 h at ambient temperature, then quenched with water (20 mL), and extracted with CH_2Cl_2 (3×15 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, concentrated under vacuum, and purified by flash-column chromatography on silica gel (petroleum ether–acetic ether, 5:1). Products were characterized by IR, ^1H and ^{13}C NMR, and MS spectroscopy [IR: Nicolet Nexus 670 FT-IR; NMR: ^1H: 300/400 MHz, ^{13}C: 75/100 MHz, Varian Mercury 300/400 (TMS); MS: HP-5988, EI (70 eV)].

Characterization Data for Products

Compound **2a**[20a]: mp 106–108 °C. IR (KBr): ν_{max} cm^{-1} 3263, 1652, 1615. ^1H NMR(300 MHz, $CDCl_3$): δ 7.67 (d, $J = 15.3$ Hz, 1H, CH=CH), 7.47 (m, 2H, arom), 7.32 (m, 8H, arom), 6.44 (d, $J = 15.3$ Hz, 1H, CH=CH), 6.21 (s, 1H, NH), 4.54 (d, $J = 4.8$ Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8 (1C), 141.3 (1C), 138.2 (1C), 134.7 (1C), 129.6 (2C), 128.7 (2C), 128.6 (1C), 127.9 (2C), 127.8 (1C), 127.5 (2C), 120.4 (1C), 43.8 (1C). MS (EI) m/z (%): 237 (M^+, 42), 160 (5), 131 (93), 106 (57), 103 (76), 91 (45), 77 (100).

Compound **2b**[20b]: ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, $J = 15.6$ Hz, 1H, CH=CH), 7.43 (m, 2H, arom), 7.19 (m, 8H, arom), 6.44 (d, $J = 15.6$ Hz, 1H, CH=CH), 6.29 (s, 1H, NH), 5.25 (q, $J = 7.2$ Hz, 1H, CH), 1.55 (d, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR(100 MHz, $CDCl_3$) δ 165.0 (1C), 143.1 (1C), 141.1 (1C), 134.7 (1C), 129.5 (2C), 128.7 (2C), 128.6 (1C), 127.7 (2C), 127.2 (1C), 126.2 (2C), 120.6 (1C), 48.8 (1C), 21.6 (1C). MS (EI) m/z (%): 251 (M^+, 5), 146 (6), 131 (100), 120 (1), 105 (41), 103 (54), 77 (75).

Compound **2c**[20c]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, $J = 15.3$ Hz, 1H, CH=CH), 7.47 (m, 2H, arom), 7.30 (m, 3H, arom), 6.38 (d, $J = 15.3$ Hz, 1H, CH=CH), 5.79 (s, 1H, NH), 1.42 (s, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2 (1C), 140.0 (1C), 134.8 (1C), 129.3 (2C), 128.6 (1C), 127.5 (2C), 122.0 (1C), 51.4 (1C), 28.7 (3C). MS (EI) m/z (%): 203 (M^+, 14), 188 (8), 146 (39), 131 (100), 103 (48), 77 (43).

Compound **2d**[20d]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $J = 15.6$ Hz, 1H, CH=CH), 7.45 (m, 2H, arom), 7.33 (m, 3H, arom), 6.43 (d, $J = 15.6$ Hz, 1H, CH=CH), 5.94 (s, 1H, NH), 3.90 (m, 1H, CH), 1.97 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 1.24 (m, 2H, CH_2), 1.15 (m, 4H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9 (1C), 140.4 (1C), 134.8 (1C), 129.4 (2C), 128.6 (1C), 127.6 (2C), 121.2 (1C), 48.3 (1C), 33.1 (2C), 25.4 (1C), 24.8 (2C). MS (EI) m/z (%): 229 (M^+, 18), 146 (42), 131 (100), 103 (47), 98 (24), 83 (15), 77 (37).

Compound **2e**[20e]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, $J = 15.3$ Hz, 1H, CH=CH), 7.41 (m, 2H, arom), 7.31 (m, 5H, arom), 6.84 (m, 2H, arom), 6.30 (d, $J = 15.3$ Hz, 1H, CH=CH), 6.15 (s, 1H, NH), 4.53 (s, 2H, CH_2), 3.81 (s, 3H, CH_3). ^{13}C NMR(75 MHz, $CDCl_3$) δ 166.1 (1C), 160.8 (1C), 140.8 (1C), 138.3 (1C), 129.3 (1C), 128.6 (2C), 128.4 (2C), 127.8 (2C), 127.4 (1C), 118.0 (1C), 114.2 (2C), 55.3 (1C), 43.7 (1C). MS-EI m/z (%) 267 (M^+, 36), 161 (100), 134 (52), 106 (31), 91 (87), 77 (39).

Compound **2f**[20f]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, $J = 15.3$ Hz, 1H, CH=CH), 7.28 (m, 7H, arom), 6.83 (t, $J = 7.2$ Hz, 2H, arom), 6.39 (d,$J = 15.3$ Hz, 1H, CH=CH), 6.72 (s, 1H, NH), 5.26 (q, $J = 7.2$ Hz, 1H, CH), 3.79 (s, 3H, CH_3), 1.55 (d, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4 (1C), 160.5 (1C), 143.2 (1C), 140.4 (1C), 129.2 (1C), 128.4 (2C), 127.4 (2C), 127.1 (2C), 126.1 (1C), 118.4 (1C), 114.0 (2C), 55.1 (1C), 48.7 (1C), 21.7 (1C). MS (EI) m/z (%): 281 (M^+, 72), 264 (3), 188 (5), 176 (10), 160 (100), 161 (21), 121 (12), 120 (32), 105 (46), 77 (64).

Compound **2g**[20g]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, $J = 15.9$ Hz, 1H, CH=CH), 7.40 (dd, 2H, $J = 1.5$ Hz, $J = 9$ Hz, arom), 6.85 (dd, 2H, $J = 1.5$ Hz, $J = 9$ Hz, arom), 6.22 (d, $J = 15.9$ Hz, 1H, CH=CH), 5.56 (s, 1H, NH), 3.80 (s, 3H, CH_3), 1.41 (s, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5 (1C), 159.7 (1C), 141.1 (1C), 128.3 (1C), 127.6 (2C), 119.5 (1C), 114.1 (2C), 55.2 (1C), 51.3 (1C), 28.8 (3C). MS (EI) m/z (%): 233 (M^+, 27), 176 (46), 161 (100), 133 (11), 77 (12).

Compound **2h**[20h]: mp 158–160 °C. IR (KBr): ν_{max} cm^{-1} 3275, 3068, 1652, 917. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, $J = 15.3$ Hz, 1H, CH=CH), 7.42 (d, $J = 9$ Hz, 2H, arom), 6.85 (d, $J = 9$ Hz, 2H, arom), 6.27 (d, $J = 15.3$ Hz, 1H, CH=CH), 5.72 (s, 1H, NH), 3.89 (m, 1H, CH), 3.80 (s, 3H, CH_3), 1.97 (m, 2H, CH_2), 1.63 (m, 3H, CH_2), 1.36 (m, 2H, CH_2), 1.15 (m, 3H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2 (1C), 160.6 (1C), 140.2 (1C), 129.1 (1C), 127.5 (2C), 118.7 (1C), 114.1 (2C), 55.2 (1C), 48.2 (1C), 33.2 (2C), 25.4 (1C), 24.8 (2C). MS (EI) m/z (%): 259 (M^+, 2), 176 (12), 161 (100), 133 (23), 98 (17), 83 (15), 77 (34).

Compound **2i**[20i]: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, $J = 15.9$ Hz, 1H, CH=CH), 7.39 (m, 4H, arom), 7.18 (m, 5H, arom), 6.39 (d, $J = 15.9$ Hz, 1H, CH=CH), 6.14 (s, 1H, NH), 4.54 (d, $J = 4.8$ Hz,

Hz, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5 (1C), 140.0 (1C), 138.0 (1C), 135.5 (1C), 133.1 (1C), 129.0 (2C), 128.9 (2C), 128.7 (2C), 127.8 (2C), 127.6 (1C), 120.9 (1C), 43.8 (1C). MS (EI) m/z (%): 271 (M^+, 33), 273 (M + 2, 12), 165 (10), 167 (3), 137 (33), 139 (12), 111 (14), 113 (5), 106 (100), 91 (81), 77 (36).

Compound **2j**[20f]: ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, $J = 15.3$ Hz, 1H, CH=CH), 7.33 (m, 9H, arom), 6.40 (d, $J = 15.3$ Hz, 1H, CH=CH), 6.21 (s, 1H, NH), 5.25 (q, $J = 7.2$ Hz, 1H, CH), 1.54 (d, $J = 7.2$ Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (1C), 142.9 (1C), 139.8 (1C), 135.4 (1C), 133.2 (1C), 128.9 (2C), 128.8 (2C), 128.5 (2C), 127.4 (2C), 126.2 (1C), 121.2 (1C), 48.9 (1C), 21.6 (1C). MS (EI) m/z (%): 285 (M^+, 27), 287 (M + 2, 9), 180 (5), 182 (2), 165 (85), 167 (27), 120 (100), 105 (53), 77 (43).

Compound **2k**[20h]: ^1H NMR (300MHz, $CDCl_3$) δ 7.49 (d, $J = 15.9$ Hz, 1H, CH=CH), 7.38 (dd, 2H, $J = 4.8$ Hz, $J = 8.7$ Hz, arom), 7.27 (dd, 2H, $J = 4.8$ Hz, $J = 8.7$ Hz, arom), 6.32 (d, $J = 15.9$ Hz, 1H, CH=CH), 5.66 (s, 1H, NH), 1.41 (s, 9H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8 (1C), 138.7 (1C), 135.1 (1C), 133.4 (1C), 129.3 (2C), 128.8 (2C), 122.5 (1C), 51.5 (1C), 29.6 (3C). MS (EI) m/z (%): 237 (M^+, 19), 239 (M + 2, 6), 222 (9), 224 (3), 180 (10), 182 (3), 165 (11), 167 (3), 137 (24), 139 (9), 57 (42).

Compound **2l**[20j]: mp 198–200°C. IR (KBr) ν_{max} cm^{-1} 3280, 3077, 1657, 972. ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, $J = 15.3$ Hz, 1H, CH=CH), 7.31 (m, 4H, arom), 6.37 (d, $J = 15.3$ Hz, 1H, CH=CH), 6.78 (s, 1H, NH), 3.89 (m, 1H, CH), 1.10–1.87 (m, 10H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (1C), 139.2 (1C), 135.2 (1C), 133.3 (1C), 128.9 (2C), 128.8 (2C), 122.6 (1C), 48.3 (1C), 33.1 (2C), 25.4 (1C), 24.8 (2C). MS (EI) m/z (%): 263 (M^+, 3), 265 (M + 2, 1), 180 (10), 182 (4), 165 (77), 167 (27), 137 (28), 139 (11), 125 (9), 111 (23), 113 (6), 98 (28), 83 (36).

Compound **2m**[20k]: ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, 2H, $J = 9$ Hz, arom), 7.63 (d, $J = 15.6$ Hz, 1H, CH=CH), 7.59 (d, 2H, $J = 9$ Hz, arom), 6.46 (d, $J = 15.6$ Hz, 1H, CH=CH), 5.62 (s, 1H, NH), 1.42 (s, 9H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1 (1C), 147.4 (1C), 144.0 (1C), 141.3 (1C), 128.2 (2C), 124.2 (C), 122.1 (1C), 48.3 (1C), 28.7 (3C). MS (EI) m/z (%): 248 (M^+, 3), 233 (2), 203 (2), 176 (8), 97 (4), 69 (7), 57 (32).

Compound **2n**[20j]: mp 208–210 °C. IR (KBr): ν_{max} cm^{-1} 3280, 3077, 1657, 1513, 1341, 972, 848. ^1H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, 2H, $J = 8.4$ Hz, arom), 7.64 (d, $J = 15.9$ Hz, 1H, CH=CH), 7.62 (d, 2H, $J = 8.4$ Hz, arom), 6.49 (d, $J = 15.9$ Hz, 1H, CH=CH), 5.62 (s, 1H, NH), 3.91 (m, 1H, CH), 1.98 (m, 2H, CH_2), 1.69 (m, 3H, CH_2), 1.40 (m, 2H, CH_2), 1.20 (m, 3H, CH_2). ^{13}C NMR(75 MHz, $CDCl_3$): δ 163.7

(1C), 147.9 (1C), 141.2 (1C), 137.9 (1C), 128.2 (2C), 125.3 (2C), 122.1 (1C), 48.5 (1C), 33.1 (2C), 25.4 (1C), 24.7 (2C). MS (EI) m/z (%): 274 (M^+, 4), 193 (11), 176 (9), 130 (10), 102 (70), 98 (28), 83 (3).

Compound **2o**: mp 104–106°C. IR (KBr): ν_{max} cm^{-1} 291, 3086, 1654, 970. ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, $J = 15.3$ Hz, 1H, CH=CH), 7.47 (t, $J = 3.6$ Hz, 2H, arom), 7.33 (t, $J = 3.6$ Hz, 3H, arom), 6.39 (d, $J = 15.3$ Hz, 1H, CH=CH), 5.73 (s, 1H, NH), 3.37 (q, $J = 6.3$ Hz, 2H, CH_2), 1.56 (m, 2H, CH_2), 1.29 (m, 30H, CH_2), 0.87 (t, $J = 6.3$ Hz, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.8 (1C), 140.7 (1C), 134.8 (1C), 129.5 (2C), 128.7 (1C), 127.7 (2C), 120.7 (1C), 39.7 (1C), 31.8 (1C), 30.9 (11C), 29.6 (1C), 29.3 (1C), 26.9 (1C), 22.6 (1C), 14.2 (1C). MS (EI) m/z (%): 399 (M^+, 2), 268 (1), 146 (15), 131 (100), 103 (29), 77 (17). HRMS m/z: calcd. for $C_{27}H_{45}NO$: 399.3494; found: 399.3490.

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