

Regioselective addition reaction of organolanthanide reagents to α, β -unsaturated imines

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Abstract

Organolanthanum reagents [RLaCl₂] generated in situ from LaCl₃ and alkyl lithium or allyl magnesium could undergo a highly regioselective 1,2-addition to *N*-alkyl α, β -unsaturated imines, which provided a new and useful approach to synthesize allyl amines with good yields and high regioselectivity. Furthermore, for *N*-chiral alkyl α, β -unsaturated imine, in the case of *n*-butyl lithium, the diastereoselectivity achieved highly 90%. © 1997 Elsevier Science S.A.

Keywords: Organolanthanide reagent; Regioselective addition; Diastereoselective addition; Alkyl lithium; Allyl magnesium; *N*-alkyl α, β -unsaturated imine; *N*-chiral alkyl α, β -unsaturated imine

1. Introduction

One of the most direct ways to synthesize allyl amines is by the addition of carbon nucleophiles to α, β -unsaturated imines [1]. However, attempted reactions of *N*-alkyl α, β -unsaturated imines which contain hydrogens α - to *N* with usual organometal reagents generally fail to give acceptable yields of allyl amines by simple addition because of the relatively poor electrophilicity of the imine carbon and competing loss of the α -proton, especially following 1,4-addition which produces carbonyl compounds rather than amines [2–6].

The elements of the rare earth series with *f* orbitals exhibit unique electronic and stereochemical properties [7,8]. Although numerous studies have been made on the chemistry of carbon–carbon bond formations between organolanthanide reagents and carbonyl compounds [9–11], the reactions of organolanthanide reagents with *N*-alkyl α, β -unsaturated imines have not been reported so far in the literature. Considering that lanthanides have some special characteristics such as high oxophilicity and tendency to coordinate with nitrogen atom, which benefit to enhance the electrophilicity of the imine carbon and therefore promote 1,2-addition,

we anticipate that organolanthanide reagents may achieve a highly regioselective 1,2-addition to *N*-alkyl α, β -unsaturated imines. Here, we report our results which were expected.

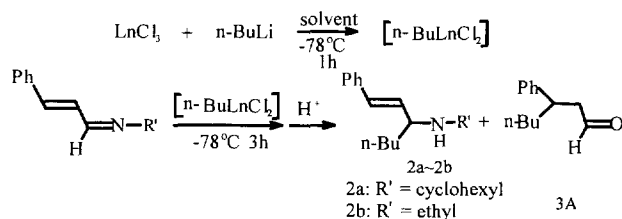
2. Results and discussion

The study was initiated by examining *N*-alkyl cinnamaldimines. Treatment of lanthanide trichloride with an equal equivalent of alkyl lithium or allyl magnesium reagent at -78°C or 0°C afforded an organolanthanide reagent [RLnCl₂], a suspensant slurry, which reacted with *N*-alkyl α, β -unsaturated imines for 3 h under low temperature, producing a mixture of 1,2-addition product (compound **2**) and 1,4-addition product (compound **3**). After quenching the reaction with saturated sodium fluoride water solution, pure **2** and **3** were respectively obtained through column chromatography (Scheme 1).

Effects of lanthanide trichlorides (LnCl₃) on the regioselectivity in the model reaction of *N*-cyclohexyl *trans*-cinnamaldimine with *n*-BuLi are shown in Table 1. The results indicated that lanthanide trichlorides were favorable of 1,2-addition indeed. Furthermore, the regioselectivity highly depended on the kind of rare earth metals. In the case of lanthanum reagent with the largest metal cationic radius, the result was best and the propor-

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Table 1
Effect of lanthanide(III) trichlorides and solvents of butyl lithium



Entry	Solvent of <i>n</i> -BuLi	LnCl ₃	R'	2/3A	Total yield (%) ^a
1	ether	none	cyclohexyl	38/62 (34/66) ^c	61 (61) ^c
2	ether	CeCl ₃ ^b	cyclohexyl	90/10	53
3	ether	GdCl ₃	cyclohexyl	91/9	77
4	ether	DyCl ₃	cyclohexyl	56/44	64
5	ether	YbCl ₃	cyclohexyl	53/47	55
6	ether	LaCl ₃	cyclohexyl	94/6	98
7	hexane	LaCl ₃	cyclohexyl	67/33	80
8	ether	LaCl ₃	ethyl	89/11	75
9	hexane	LaCl ₃	ethyl	72/28	67

^a Isolated yields based on imines.

^b CeCl₃ generated by heating CeCl₃·7H₂O at 130–140°C/1 mmHg for 2h.



^c Figures in parenthesis refer to the yields in the literature [6].

tion of 1,2-addition product achieved highly 94%, moreover, the conversion of the reaction was almost quantitative. Heavy rare earth metal(III) chlorides such as DyCl₃ and YbCl₃ gave lower yields (< 70%) and poor regioselectivity (the ratio of compound **2** and compound **3** is approximately 1:1). It was unexpected that rare earth metal ions have largely different effect on the reactivity and regioselectivity. At present, we have no good explanation for it. The solvents of *n*-butyl lithium also had obvious effect on the reaction. Ether was superior to hexane in promoting 1,2-addition of lanthanide reagents to α,β -unsaturated imines (Table 1).

Several examples of the addition reactions of organolanthanum reagents with *N*-alkyl α,β -unsaturated imines are listed in Table 2. In each case, the adducts were afforded in high yields. For alkyl lithium and allyl magnesium, the results were quite satisfactory: The ratio of compound **2** and compound **3** was over 75:25 and 1,2-addition product predominated. Furthermore, the regioselectivity and diastereoselectivity of alkyl lithium with *N*-chiral alkyl α,β -unsaturated imines have also been examined. Alkyl lithium mainly gave 1,2-addition product (compound **2**), whose ratio of di-

astereoisomers was determined by ¹H NMR. In its ¹H NMR spectrum two resonances appeared at δ 2.65 ppm and 2.50 ppm, which respectively corresponded to hydrogen protons of imine carbons in both of diastereoisomers, thus, providing clear analytic bases for determining the diastereoselectivity of **2**. For *n*-butyl lithium the value of **2** achieved highly 90%, and for methyl lithium

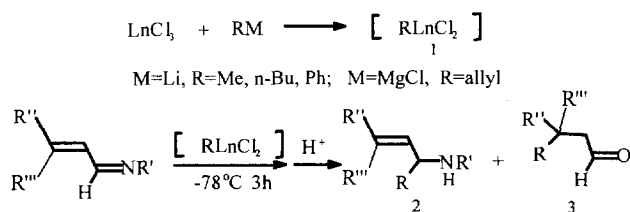
Table 2
Reaction results of organolanthanum reagents with *N*-Alkyl α,β -unsaturated imines

Entry	R	RNH ₂	R'	R''	Product Ratio (2/3)	Total yield (%) ^a
1	<i>n</i> -butyl	cyclohexylamine	ph	H	94/6 2a / 3A	98
2	<i>n</i> -butyl	ethylamine	ph	H	80/20 2b / 3A	75
3	<i>n</i> -butyl	<i>n</i> -propylamine	ph	H	83/17 2c / 3A	81
4	<i>n</i> -butyl	isopropylamine	ph	H	83/17 2d / 3A	84
5	<i>n</i> -butyl		ph	H	90 (95/5) ^b /10 2e / 3A	92
6	Me	cyclohexylamine	ph	H	92/8 2f / 3B	94
7	Me	ethylamine	ph	H	75/25 2g / 3B	73
8	Me	isopropylamine	ph	H	78/22 2h / 3B	81
9	Me		ph	H	93 (72/28) ^b /7 2i / 3B	98
10	allyl	cyclohexylamine	ph	H	75/25 2j / 3C	83
11	allyl	isopropylamine	ph	H	79/21 2k / 3C	71
12	ph	cyclohexylamine	ph	H	40/60 (20/80) ^c 2l / 3D	61 (56) ^f
13	<i>n</i> -butyl	cyclohexylamine	(CH ₃) ₂ C=CHCH ₂ CH ₂	Me	2m	46
14	<i>n</i> -butyl	cyclohexylamine	Me	H	—	—

^a Isolated yields based on imines.

^b *d*e values were determined by ¹H NMR.

^c Figures in parenthesis refer to the yields in the absence of LaCl₃.



Scheme 1.

the diastereoselectivity was modest. In the case of phenyl lithium, 1,4-addition product (**3D**) was major and the ratio of compound **2I** and compound **3D** achieved 40:60, which was contrary to alkyl lithium and allyl magnesium (entry 12 in Table 2). However, when phenyl lithium reacted with *N*-cyclohexyl *trans*-cinnamaldimine in the absence of LaCl_3 , the ratio of compound **2I** and compound **3D** decreased to 20:80, which suggested strongly that lanthanum trichloride could indeed promote 1,2-addition of phenyl lithium to α,β -unsaturated imine despite the fact that 1,4-addition product was still major in the case. In addition, it is worth noting that only 1,2-addition product was obtained in 46% yield and none of 1,4-addition product was tested in the case of *N*-cyclohexyl imine of citral (entry **13** in Table 2). But the result was very complex when butyl lithium reacted with the imine generated from propionaldehyde and cyclohexyl amine (entry **14** in Table 2). During the reaction procedure, addition, reduction-coupling and grabbing hydrogen reactions perhaps took place in the meantime, producing a mixture of various products, which resulted in the fact that no 1,2-addition product could be isolated.

In summary, we found that organolanthanide reagents [RLnCl_2] generated in situ ($\text{R} = \text{alkyl and allyl}$) could undergo a highly regioselective 1,2-addition to *N*-alkyl α,β -unsaturated imines, which afforded a new synthetic approach to allyl amines with good regioselectivity and high yields.

3. Experimental section

NMR spectra were recorded as CDCl_3 solutions on a VXL-300 instrument. The ^1H NMR (300 MHz) chemical shifts were reported as δ values in parts per million (ppm) relative to tetramethyl silane ($\delta_{\text{TMS}} = 0.0$ ppm) as internal standard. Infrared spectra were recorded on a Perkin-Elmer 983 FT-IR spectrometer as liquid forms on potassium bromide plates unless otherwise noted. Mass spectral measurements were performed on a Finnigan 4021 or Finnigan MAT 8430 gas chromatograph-mass spectrometer at 70 eV and mass data were tabulated as m/z . Elemental analyses were determined by Laboratory of Analysis Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China.

Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. *n*-BuLi, MeLi, PhLi and allyl magnesium chloride were prepared according to literatures [12,13]. Column chromatography was performed using standard techniques employing silica gel (300–400 μm). All glassware was flame-dried and cooled under a dry argon atmosphere. All addition reactions were conducted under a positive and dry argon atmosphere in anhydrous solvents in standard Schlenck

flasks. Low temperature baths (-78°C or 0°C) were prepared using a dry ice-acetone slurry or an ice-water mixture.

The preparation of lanthanum (III) chloride [14]: 24.5 g (0.1 mol) lanthanum (III) oxide was dissolved in the HCl-water solution (1000 ml, 6–8 N) at room temperature. The obtained clear solution was concentrated until some solid appeared. Then 64.2 g (1.2 mol) NH_4Cl was added, and the mixture was transferred to a sublimation tube. After the water was removed away in vacuo ($150^\circ\text{C}/10\text{--}1$ mmHg), the temperature was improved to 300°C and at this temperature NH_4Cl was sublimated away completely. Finally, anhydrous lanthanum trichloride was obtained in 85% yield.

General procedure for synthesis of allyl amine: lanthanide trichloride (LnCl_3) (1.0 mmol) was placed in a 25 ml Schenck flask with a stirring bar and dry THF (2 ml) was introduced via syringe. The flask was then stirred at room temperature for 2 h. The resulting white slurry was then cooled to -78°C or 0°C , and the organolithium or organomagnesium (1 mmol) was added dropwise via syringe and continuously stirred for further 4 h at -78°C or 0°C . Then the reaction was quenched with sodium fluoride solution (5 ml) and filtered to remove lanthanide fluoride. The layers were separated and the aqueous layer was extracted with diethyl ether (4×20 ml). The combined organic extracts were washed with brine (2×15 ml), dried over Na_2SO_4 for 2 h and concentrated in vacuo. The residue was chromatographed on silica gel using hexane/EtOAc/ NEt_3 as eluent to give analytically pure products **2** and **3**.

Compound **2a** ^1H NMR (CDCl_3/TMS , 300 MHz) δ (ppm): 7.16–7.40 (m, 5H), 6.42 (d, $J = 15.93$ Hz, 1H), 5.66 (dd, $J = 15.69$ Hz, $J = 8.51$ Hz, 1H), 3.34 (m, 1H), 2.50–2.51 (M, 1H), 0.86–2.01 (m, 20H). EIMS m/z (relative intensity): 272 ($\text{M} + 1^+$, 2.32), 215 (21.15), 214 (100.00), 168 (20.78), 132 (26.76), 117 (15.44), 115 (14.05), 91 (13.16), 55 (7.93). IR (KBr pellet cm^{-1}): 3023 (w), 2926 (s), 2633 (m), 1599 (w), 1493 (m), 1456 (s), 1370 (m), 1251 (w), 1136 (s), 1033 (w), 969 (s), 892 (w), 752 (s), 696 (s). HRMS ($\text{C}_{19}\text{H}_{29}\text{N}$): found: 271.2306; cal: 271.2300.

Compound **2b** ^1H NMR (CDCl_3/TMS , 300 MHz), δ (ppm): 7.14–7.40 (m, 5H), 6.45 (d, $J = 15.88$ Hz, 1H), 6.00 (dd, $J = 15.91$ Hz, $J = 8.51$ Hz, 1H), 3.18 (m, 1H), 2.53–2.61 (m, 2H), 0.86–1.65 (m, 13H). EIMS m/z (relative intensity): 218 ($\text{M} + 1^+$, 1.36), 217 (M^+ , 1.36), 161 (12.24), 160 (82.99), 117 (10.13), 115 (21.16), 114 (100.00), 91 (21.93), 58 (8.73). IR (KBr pellet, cm^{-1}): 3023 (m), 2926 (s), 1590 (m), 1493 (m), 1456 (s), 1360 (m), 1141 (s), 1033 (w), 970 (s), 732 (w), 696 (s). HRMS m/z ($\text{C}_{15}\text{H}_{23}\text{N}$): found: 217.1819; cal. 217.1830.

Compound **2c** ^1H NMR (CDCl_3/TMS , 300 MHz), δ

(ppm): 7.15–7.41 (m, 5H), 6.45 (d, $J = 15.93$ Hz, 1H), 6.01 (dd, $J = 15.82$ Hz, $J = 8.30$ Hz, 1H), 3.16 (m, 1H), 2.47–2.66 (m, 2H), 0.89–1.69 (m, 15H). EIMS m/z (relative intensity): 231 (M^+ , 1.01), 175 (18.50), 174 (100.00), 132 (17.44), 130 (4.41), 117 (7.55), 115 (12.57), 91 (6.91), 43 (4.10). IR (KBr pellet, cm^{-1}): 3023 (s), 2933 (s), 1597 (m), 1490 (m), 1456 (s), 1359 (m), 1143 (m), 1031 (w), 972 (s), 729 (s), 696 (s). HRMS m/z ($\text{C}_{16}\text{H}_{25}\text{N}$): found: 231.1949; cal: 231.1987.

Compound **2d** ^1H NMR (CDCl_3/TMS , 300 MHz), δ (ppm): 7.19–7.40 (m, 5H), 6.42 (d, $J = 15.86$ Hz, 1H), 5.96 (dd, $J = 15.84$, $J = 8.54$ Hz, 1H), 3.23–3.30 (m, 1H), 2.86–2.94 (m, 1H), 0.87–1.56 (m, 16H). EIMS m/z (relative intensity): 232 ($M + 1^+$, 7.29), 231 (M^+ , 1.05), 175 (19.00), 174 (100.00), 129 (10.66), 128 (61.34), 117 (11.82), 115 (14.51), 91 (16.44). IR (KBr pellet, cm^{-1}): 3023 (w), 2936 (s), 2926 (s), 2837 (m), 1596 (w), 1493 (m), 1467 (s), 1360 (w), 1176 (s), 1120 (m), 1073 (m), 970 (s), 732 (s), 696 (s). Elemental analysis ($\text{C}_{16}\text{H}_{25}\text{N}$): found: C, 83.09%, H, 10.95%, N, 5.90%; cal: C, 83.12%, H, 10.82%, N, 6.06%.

Compound **2e** ^1H NMR (CDCl_3/TMS , 300 MHz), δ (ppm): 7.19–7.38 (m, 5H), 6.42 (d, $J = 15.84$ Hz, 1H), 5.96 (dd, $J = 15.87$ Hz, $J = 8.55$ Hz, 1H), 3.22–3.43 (m, 3H), 3.34 (s, 3H), 2.49–2.52 (m, 1H), 1.78–1.80 (m, 1H), 1.26–1.58 (m, 7H), 0.88–1.00 (m, 9H). EIMS m/z (relative intensity): 290 ($M + 1^+$, 11.28), 244 (31.52), 232 (52.06), 174 (16.58), 173 (100.00), 131 (12.75), 117 (67.10), 115 (18.89), 91 (25.70). IR (KBr pellet, cm^{-1}): 3030 (w), 2957 (s), 2928 (s), 2892 (s), 2873 (m), 1600 (w), 1578 (w), 1495 (m), 1460 (m), 1448 (m), 1380 (w), 1362 (w), 1200 (w), 1117 (s), 1030 (w), 969 (s), 748 (s), 692 (s). Elemental analysis ($\text{C}_{19}\text{H}_{31}\text{NO}$): found: C, 78.30, H, 10.97, N, 4.77; cal: C, 78.80, H, 10.73, N, 4.84.

Compound **2f** ^1H NMR (CDCl_3/TMS , 300 MHz), δ (ppm): 7.42–7.13 (m, 5H), 6.42 (d, $J = 15.93$ Hz, 1H), 6.00 (d, $J = 15.66$, $J = 4.26$ Hz, 1H), 3.52 (q, 1H), 2.54 (m, 1H), 2.05–0.85 (m, 14H). IR (KBr pellet cm^{-1}): 3026 (w), 2929 (s), 2638 (m), 1599 (w), 1493 (m), 1456 (m), 1370 (w), 1257 (w), 1136 (m), 1039 (m), 960 (s), 892 (s), 754 (s), 699 (s). Elemental analysis ($\text{C}_{16}\text{H}_{23}\text{N}$): found: C, 83.53%, H, 9.59%, N, 6.40%; cal: C, 83.84%, H, 10.04%, N, 6.11%.

Compound **2g** ^1H NMR (CDCl_3/TMS , 300 MHz), δ (ppm): 7.18–7.38 (m, 5H), 6.46 (d, $J = 15.94$ Hz, 1H), 6.08 (dd, $J = 15.87$ Hz, $J = 7.96$ Hz, 1H), 3.37 (m, 1H), 2.58–2.73 (m, 2H), 1.49 (s, 1H), 1.25 (d, $J = 6.53$ Hz, 3H), 1.12 (t, $J = 7.08$ Hz, 3H). EIMS m/z (relative intensity): 175 (M^+ , 29.12), 160 (100.00), 149 (38.30), 131 (39.75), 115 (37.88), 91 (43.79), 84 (40.51), 42 (30.20). IR (KBr pellet, cm^{-1}): 3023 (m), 2966 (s), 1669 (m), 1598 (m), 1493 (m), 1436 (s), 1372 (m), 1143 (s), 1076 (w), 970 (s), 752 (s), 697 (s). HRMS m/z ($\text{C}_{12}\text{H}_{17}\text{N}$): found: 175.1349; cal: 175.1361.

Compound **2h** ^1H NMR (CDCl_3/TMS , 300 MHz), δ (ppm): 7.21–7.39 (m, 5H), 6.45 (d, $J = 15.78$ Hz, 1H), 6.05 (dd, $J = 15.83$ Hz, $J = 7.97$ Hz, 1H), 3.48 (m, 1H), 2.91 (m, 1H), 1.23 (d, $J = 6.32$ Hz, 3H), 1.07 (d, $J = 2.32$ Hz, 3H), 1.03 (d, $J = 2.26$ Hz, 3H). EIMS m/z (relative intensity): 189 (M^+ , 13.72), 175 (17.16), 174 (100.00), 132 (40.74), 131 (73.51), 115 (33.70), 98 (37.09), 91 (34.09), 42 (17.86). IR (KBr pellet, cm^{-1}): 2962 (s), 1603 (w), 1492 (m), 1431 (m), 1386 (m), 1174 (m), 966 (s), 732 (s), 696 (s). HRMS m/z ($\text{C}_{13}\text{H}_{19}\text{N}$): found: 189.1545; cal: 189.1518.

Compound **2i** ^1H NMR (CDCl_3/TMS , 300 MHz), δ (ppm): 7.16–7.37 (m, 5H), 6.44 (d, $J = 15.9$ Hz, 1H), 6.03 (dd, $J = 15.8$ Hz, $J = 8.08$ Hz, 1H), 3.27–3.49 (m, 3H), 3.33 (s, 3H), 2.51–2.55 (m, 3H), 1.77–1.83 (m, 1H), 1.42 (s, 1H), 1.22 (d, $J = 6.35$ Hz, 1H), 0.91 (d, $J = 4.87$ Hz, 3H), 0.89 (d, $J = 4.87$ Hz, 3H). EIMS m/z (relative intensity): 248 ($M + 1^+$, 17.97), 202 (19.14), 132 (15.27), 131 (100.00), 129 (11.16), 91 (22.20), 45 (10.34), 43 (11.19). IR (KBr pellet, cm^{-1}): 3027 (w), 2959 (s), 2926 (m), 2892 (m), 2874 (s), 2826 (m), 2812 (m), 1600 (w), 1490 (m), 1467 (m), 1447 (m), 1382 (m), 1370 (m), 1115 (s), 967 (s), 746 (s), 692 (s). HRMS m/z ($\text{C}_{16}\text{H}_{25}\text{NO}$): found: 247.1920; cal: 247.1903.

Compound **2j** ^1H NMR (CDCl_3/TMS , 300 MHz), δ (ppm): 7.20–7.41 (m, 5H), 6.47 (d, $J = 15.9$ Hz, 1H), 6.06 (dd, $J = 15.9$ Hz, $J = 8.3$ Hz, 1H), 5.72–5.86 (m, 1H), 5.13 (d, $J = 16.8$ Hz, 1H), 5.09 (d, $J = 9.06$ Hz, 1H), 3.41–3.48 (m, 1H), 2.47–2.54 (m, 1H), 2.29–2.34 (m, 2H), 0.96–2.01 (m, 1H). EIMS m/z (relative intensity): 256 ($M + 1^+$, 1.21), 215 (26.64), 214 (100.00), 133 (7.09), 132 (56.34), 130 (11.04), 115 (34.17), 91 (14.74), 55 (11.00). IR (KBr pellet, cm^{-1}): 3080 (w), 3031 (w), 2928 (s), 2853 (s), 1640 (w), 1491 (m), 1441 (m), 967 (s), 923 (m), 748 (s), 692 (s). HRMS m/z ($\text{C}_{15}\text{H}_{20}\text{N}$): found: 214.1618; cal: 214.1596.

Compound **2k** ^1H NMR (CDCl_3/TMS , 300 MHz), δ (ppm): 7.19–7.40 (m, 5H), 6.47 (d, $J = 16$ Hz, 1H), 6.04 (dd, $J = 16$ Hz, $J = 8$ Hz, 1H), 5.83 (m, 1H), 5.13 (d, $J = 16$ Hz, 1H), 5.09 (d, $J = 8$ Hz, 1H), 3.38 (dd, $J = 15$ Hz, $J = 6.7$ Hz, 1H), 2.89 (m, 1H), 2.31 (dd, $J = 6.9$ Hz, $J = 7.0$ Hz, 2H), 1.43 (s, 1H), 1.07 (d, $J = 6.5$ Hz, 3H), 1.04 (d, $J = 6.2$ Hz, 3H). EIMS m/z (relative intensity): 216 ($M + 1^+$, 0.42), 215 (M^+ , 0.16), 175 (19.12), 174 (100.00), 132 (35.03), 130 (11.50), 117 (6.92), 116 (5.57), 115 (35.37), 91 (9.20). IR (KBr Pellet, cm^{-1}): 3080 (w), 3061 (w), 3026 (m), 2965 (s), 2928 (m), 1640 (m), 1493 (m), 1470 (m), 1447 (m), 1379 (m), 1361 (m), 1171 (m), 1120 (m), 1070 (m), 967 (s), 916 (s), 751 (s), 692 (s). Elemental analysis: found ($\text{C}_{15}\text{H}_{21}\text{N}$): C, 83.31%, H, 9.59%, N, 6.43%; cal: C, 83.72%, H, 9.77%, N, 6.51%.

Compound **2l** ^1H NMR (CDCl_3/TMS , 90 MHz), δ (ppm): 7.0–7.34 (m, 10H), 6.42 (d, $J = 14.4$ Hz, 1H),

6.06 (dd, $J = 14.4$ Hz, $J = 2.7$ Hz, 1H), 4.4 (d, $J = 6.3$ Hz, 1H), 2.34 (m, 1H), 0.64–2.04 (m, 10H). EIMS m/z (relative intensity): 291 (M^+ , 33.91), 290 (15.30), 208 (18.26), 200 (40.88), 194 (20.80), 193 (100.00), 178 (13.57), 115 (44.67). HRMS m/z ($C_{21}H_{25}N$): found: 291.1990; cal: 291.1987.

Compound **2m** 1H NMR (CCl_4/TMS , 90 MHz), 5.10 (m, 1H), 4.83 (d, $J = 9.1$ Hz), 3.85 (m, 1H), 2.41 (m, 1H), 2.07 (s, 9H), 0.82–2.00 (m, 24H). EIMS m/z (relative intensity): 234 (100.00), 215 (21.46), 168 (10.65), 165 (7.56), 81 (7.35), 69 (20.77), 55 (10.40), 43 (6.65). HRMS m/z ($C_{20}H_{37}N$): found: 291.2947; cal: 291.2926.

Compound **3A** 1H NMR (CCl_4/TMS , 90 MHz), 9.52 (s, 1H), 7.31–6.92 (m, 5H), 3.07 (m, 1H), 2.58 (d, $J = 8.1$ Hz, 2H), 0.75–1.80 (m, 9H). EIMS m/z (relative intensity): 190 (M^+ , 45.37), 148 (25.60), 147 (23.16), 133 (100.00), 117 (19.90), 105 (88.93), 104 (23.93), 91 (78.34). HRMS m/z ($C_{13}H_{18}O$): found: 190.1359; cal: 190.1358.

Compound **3B** [15] 1H NMR (CCl_4/TMS , 90 MHz), 9.52 (s, 1H), 7.12 (m, 5H), 2.95 (m, 1H), 2.53 (m, 2H), 1.68 (d, $J = 5.6$ Hz, 3H).

Compound **3C** 1H NMR (CCl_4/TMS , 90 MHz), 9.5 (s, 1H), 7.4–7.0 (m, 5H), 5.8–5.7 (m, 1H), 5.1 (d, $J = 16.9$ Hz, 1H), 5.08 (d, $J = 8.3$ Hz, 1H), 3.0 (m, 1H), 2.3–2.6 (m, 4H). EIMS m/z (relative intensity): 174 (M^+ , 6.37). HRMS m/z ($C_{12}H_{14}O$): found: 174.1043; cal: 174.1045.

Compound **3D** 1H NMR (CCl_4/TMS , 90 MHz), 9.58 (t, $J = 2.97$ Hz, 1H), 6.93–7.53 (m, 10H), 4.46 (t, $J = 6.3$ Hz, 1H), 2.98 (d, $J = 8.1$ Hz, 2H). EIMS m/z (relative intensity): 210 (M^+ , 5.39). HRMS m/z ($C_{12}H_{14}O$): found: 210.1056; cal: 210.1045.

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