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A facile approach to α,β-unsaturated lactams by ring-closing metathesis

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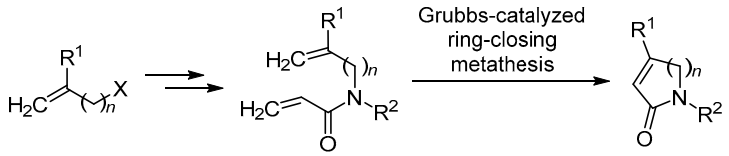


A facile and efficient strategy for the synthesis of α,β-unsaturated lactams through ring-closing metathesis of easily prepared diene amides is being reported here. Reaction conditions were optimized for metathetic cyclization of diene amides to obtain five- to seven-membered unsubstituted and β-substituted α,β-unsaturated lactams in good to excellent yield.

Keywords: α,β-unsaturated lactams, Grubbs catalyst, ring-closing metathesis.

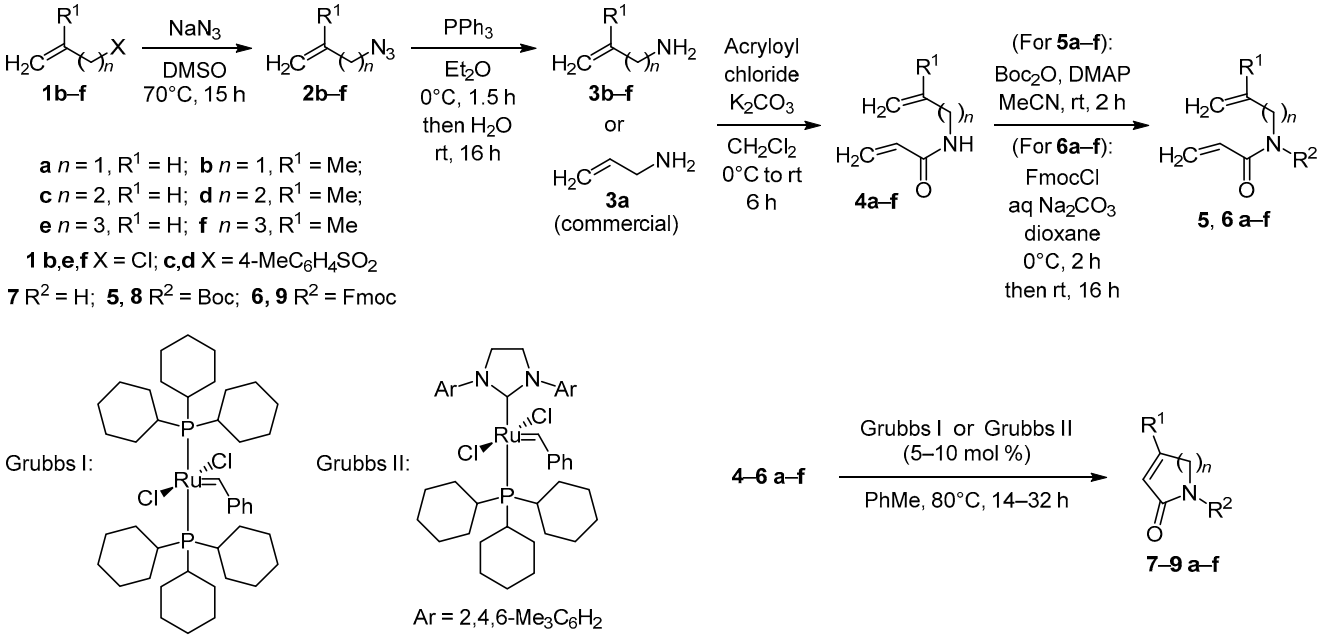
Ring-closing metathesis (RCM) proved itself a powerful technique for crafting variety of heterocycles and carbocycles. It introduces a long range of synthetic applications which is increasing day by day. Lactams are an important class of compounds widely distributed among biologically interesting natural and synthetic compounds.[1] They are also highly versatile intermediates for potential use in organic synthesis.[2] Moreover, α,β-unsaturated lactams are important building blocks of numerous natural compounds which are widely employed to access new molecules by further chemical modifications.[3] Many synthetic efforts for constructing lactams[4] and precisely α,β-unsaturated lactams[5] have been reported including ring-closing metathesis.[6] The versatility of α,β-unsaturated lactams can be further extended by the incorporation of different groups at α- and β-carbon, but reported strategies had certain limitations.[7] Therefore development of general methods from simple and easily available precursors is still the subject of considerable synthetic interests. Subhash and coworkers have reported the preparation 4-methyl-3-pyrrolin-2-one through RCM of a simply prepared diene amide, but not in good yield.[8] We decided to carry out a systematic study to find the optimal conditions and to extend the scope of this methodology for the synthesis of unsubstituted and β-substituted α,β-unsaturated lactams with different size of cycles. Herein, we report a general, convenient, and efficient strategy for the synthesis of well-known pyrrolidinones, pyridinones, and rarely reported azepinones,[9] which is also devoid of the inherent shortcomings.

In this course of study, the key step of ring-closing metathesis of diene amides **4a**–**f** was attempted with Grubbs first and second generation catalysts, benzylidenebis-(tricyclohexylphosphine)dichlororuthenium (Grubbs I) and benzylidene[1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (Grubbs II) (Scheme 1). In an effort to optimize reaction conditions, variations in type and amount of the catalyst, solvent, time, temperature, and additive were evaluated. The influence of substituent at β-carbon and nitrogen of amide on meta cyclization was also studied.

The metathesis precursor diene amides **4a**–**f** were prepared by the condensation of acryloyl chloride with primary amines **3a**–**f** under basic conditions. Required amines **3b**–**f** were obtained by nucleophilic displacement of chlorides **1b**,**e**,**f** or tosylates **1c**,**d** with azide followed by reduction with triphenylphosphine,[8a] whereas allylamine (**3a**) was commercially available. Diene amides **4a**–**f** were further treated with Boc_2O and FmocCl to provide the *N*-protected analogs **5a**–**f** and **6a**–**f**. All of these protected and unprotected diene amides **4**–**6 a**–**f** were subjected to ring-closing metathesis under different conditions (Tables 1, 2) to furnish α,β-unsaturated lactams **7**–**9 a**–**f** (Scheme 1).

After obtaining requisite diene amides **4a**–**f**, we focused on RCM as key step for the preparation of lactams. To explore the feasibility of this approach, the RCM reaction of diene amides **4**–**6 a** were selected as model reactions to examine various conditions for the synthesis of pyrrolidinones **7**–**9 a** (Table 1). The Grubbs I catalyst was found

Scheme 1



very sluggish in the reaction with both free and protected amides **4a** and **5a**, respectively, where only 17–22% conversion was accomplished even after 32 h of heating at 80°C in toluene with 10% of catalyst (Table 1, entries 1–3, 10). Thus, Grubbs I catalyst was not further employed for other molecules. Free diene amide **4a** was not successfully cyclized using the Grubbs II catalyst also, though amount of catalyst was increased up to 10%. (Table 1, entries 4–7). The same trend was followed by all other free amides **4c**–**f** (Table 2, entries 1–4). Yield was increased up to 44% when a few drops of Ti(O-*i*-Pr)$_4$ were added as chelating agent[6b,e,h,8b] to free amides (Table 1, entry 8). RCM cyclization was found further encouraging with Boc-protected diene amide **5a**. In this reaction, 50% conversion was observed with 5% Grubbs II catalyst after 14 h (Table 1, entry 11). To enhance the yield, first we increased reaction

Table 1. Optimization of reaction conditions for the preparation of pyrrolidinones **7**–**9** **a**,**b** by ring-closing metathesis

Entry	Diene amide	R^1	R^2	Grubbs catalyst generation	Catalyst load, mol %	Time, h	Obtained lactam	Yield, %
1	**4a**	H	H	I	5	32	**7a**	–
2	**4a**	H	H	I	7	32	**7a**	Traces
3	**4a**	H	H	I	10	32	**7a**	17
4	**4a**	H	H	II	5	14	**7a**	32
5	**4a**	H	H	II	5	32	**7a**	34
6	**4a**	H	H	II	7	32	**7a**	36
7	**4a**	H	H	II	10	32	**7a**	40
8	**4a**	H	H	II	10	32	**7a**	44*
9	**4b**	Me	H	II	7	32	**7b**	35
10	**5a**	H	Boc	I	10	32	**8a**	22
11	**5a**	H	Boc	II	5	14	**8a**	50
12	**5a**	H	Boc	II	5	32	**8a**	52
13	**5a**	H	Boc	II	7	14	**8a**	83
14	**5a**	H	Boc	II	7	14	**8a**	66**
15	**5b**	Me	Boc	II	5	14	**8b**	51
16	**5b**	Me	Boc	II	7	14	**8b**	85
17	**6a**	H	Fmoc	II	5	14	**9a**	55
18	**6a**	H	Fmoc	II	7	14	**9a**	91
19	**6b**	Me	Fmoc	II	7	14	**9b**	90

* Two drops of Ti(O-*i*-Pr)$_4$ were added.
** Solvent was CH_2Cl_2 (temperature 40°C), whereas all other experiments were carried out in PhMe at 80°C.

Table 2. Experimental conditions for the preparation of α,β-unsaturated lactams **7**–**9 c**–**f** by ring-closing metathesis*

Entry	Diene amide	*n*	R^1	R^2	Grubbs II catalyst load, mol %	Time, h	Obtained lactam	Yield, %
1	**4c**	2	H	H	5	14	**7c**	28
2	**4d**	2	Me	H	5	32	**7d**	29
3	**4e**	3	H	H	5	32	**7e**	20
4	**4f**	3	Me	H	5	32	**7f**	22
5	**5c**	2	H	Boc	5	14	**8c**	50
6	**5c**	2	H	Boc	7	14	**8c**	84
7	**5d**	2	Me	Boc	5	14	**8d**	53
8	**5d**	2	Me	Boc	7	14	**8d**	89
9	**5e**	3	H	Boc	5	14	**8e**	53
10	**5e**	3	H	Boc	7	14	**8e**	88
11	**5f**	3	Me	Boc	5	14	**8f**	55
12	**5f**	3	Me	Boc	7	14	**8f**	87
13	**6c**	2	H	Fmoc	7	14	**9c**	89
14	**6d**	2	Me	Fmoc	7	14	**9d**	93
15	**6e**	3	H	Fmoc	7	14	**9e**	90
16	**6f**	3	Me	Fmoc	7	14	**9f**	92

* Solvent was PhMe at 80°C.

time up to 32 h but no significant change was observed (Table 1, entry 12). The next step was the increase of catalyst amount and fortunately just 2% further addition reasonably improved the yield (83%) of the required lactam **8a** (Table 1, entry 13). Reaction was also attempted in DCM at 40°C but unfortunately decrease in yield was obtained (Table 1, entry 14). Our results are in consistent with previous reports that increase of steric bulk at nitrogen atom of amide group facilitates the RCM cyclization.[9a] Keeping this in mind, we increase the bulk of amide protection by Fmoc group, consequently a further raise (up to 91%) of lactam **9a** yield was achieved (Table 1, entry 18).

Our next target was synthesis of 4-methylpyrrolidinones **7**–**9 b**. In reaction catalyzed by 7% of Grubbs II catalyst the unprotected diene amide **4b** formed only 35% of the required pyrrolidinone **7b** along with unreacted amide **4b** (Table 1, entry 9). The yields were enhanced (85–90%) in the case of protected diene amides **5**–**6 b** using the same catalyst (Table 1, entries 16 and 19). These results infer that substitution at the β-carbon of diene amide does not have any prominent effect, but on the other hand, *N*-substitution has significant influence on the ring-closing metathesis process. Similar conditions were further applied in the synthesis of pyridinones and azepinones **7**–**9 c**–**f** (Table 2). It was observed that unprotected amides **4c**–**f** could not provide good yield of required lactams **7c**–**f** (Table 2, entries 1–4). In the case of Boc-protected amides **5c**–**f** only 50–55% yields of the required products were obtained after 14 h using 5% of Grubbs II catalyst (Table 2, entries 5, 7, 9, 11). However, when catalyst loading was increased to 7%, the reactions were completed in 14 h with good yields (84–89%) (Table 2, entries 6, 8, 10, 12). In the same conditions Fmoc-protected amides **6c**–**f** were successfully cyclized to the required lactams **9c**–**f** in 89–93% yields (Table 2, entries 13–16).

In conclusion, an efficient strategy for the synthesis of five- to seven-membered α,β-unsaturated lactams was developed where metathesis cyclization was successfully employed by using 7% Grubbs II catalyst. Protected diene amides cyclized more efficiently, whereas substitution at β-carbon atom does not have any prominent effect. This ring-closing metathesis strategy offer powerful advantages over traditional approaches that could be attractive for the synthetic as well as medicinal chemistry community.

Experimental

IR spectra were registered on a JASCO A-302 spectrophotometer in $CHCl_3$. ^1H and ^{13}C NMR spectra were registered on a Bruker Avance AM-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$, solvent signal was used as the internal standard. Mass spectra were registered on a double-focusing mass spectrometer Varian MAT 311 A, ionization by electron impact (70 eV). High-resolution mass spectra were registered on a Jeol HX 110 spectrometer, with fast atom bombardment ionization using *m*-nitrobenzyl alcohol matrix. All the reactions were monitored by TLC using precoated (silica gel 60F254) aluminum sheets, visualization by UV light (254 and 365 nm) and by locating agent phosphomolybdic acid. Column chromatography was performed by using Merck silica gel (0.063–0.200 mm). All reagents and solvents used were of analytical grades.

Preparation of diene amides 4a–f (General method). Sodium azide (0.5 g, 8 mmol) was added to the stirred solution of chlorides **1b**,**e**,**f** or tosylates **1c**,**d** (6 mmol) in dry DMSO (8 ml) at room temperature. The reaction mixture was stirred at 70°C for 15 h, then washed well with water (3×10 ml) and extracted with CH_2Cl_2 (2×10 ml).

Combined organic layers were dried over $MgSO_4$, filtered, and concentrated to obtain the crude azides **2b**–**f**. Resulting azides were dissolved in Et_2O (10 ml), PPh_3 (1.6 g, 6 mmol) was added, the reaction mixture was stirred at 0°C for 1.5 h. Then water (1 ml) was added and the reaction mixture was stirred at room temperature overnight. After the completion, the reaction mixture was poured onto crushed ice and extracted with CH_2Cl_2 (3×10 ml). Organic layers were combined and dried over $MgSO_4$, filtered, and concentrated under reduced pressure to obtain amines **3b**–**f**. Solution of amine **3a**–**f** in CH_2Cl_2 (10 ml) was stirred with K_2CO_3 (2.2 g, 16 mmol) at 0°C for 15 min. Acryloyl chloride (0.6 ml, 7 mmol) was added dropwise at 0°C, and the mixture was stirred at room temperature for 6 h. The reaction was monitored by TLC. After completion of the reaction, cold water (10 ml) was added and the mixture was extracted with CH_2Cl_2 (3×10 ml). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude diene amides **4a**–**f** were purified on silica gel column, eluting with EtOAc–petroleum ether with increasing gradient.

***N*-(Prop-2-en-1-yl)prop-2-enamide (4a)**. Yield 62%, colorless oil. IR spectrum, ν, cm^{-1}: 3326, 3069, 2952, 2930, 1699, 1520, 1357. ^1H NMR spectrum, δ, ppm (*J*, Hz): 4.10 (2H, d, *J* = 5.7, NHC$\underline{H}_2$); 5.14–5.22 (2H, m, =CH_2); 5.51 (1H, dd, *J* = 1.7, *J* = 11.2, CH); 5.90 (1H, ddd, *J* = 5.8, *J* = 9.8, *J* = 15.9, CH); 6.11 (1H, dd, *J* = 1.8, *J* = 16.1, CH); 6.44 (1H, dd, *J* = 10.9, *J* = 16.1, CH); 8.60 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 42.1; 117.0; 127.1; 130.9; 134.6; 167.5. Mass spectrum, *m*/*z* (I_{rel}, %): 111 $[M]^+$ (67), 70 (29), 56 (100). Found, *m*/*z*: 111.0719 $[M]^+$. C_6H_9NO. Calculated, *m*/*z*: 111.0684.

***N*-(2-Methylprop-2-en-1-yl)prop-2-enamide (4b)**.[8a] Yield 60%, colorless oil. IR spectrum, ν, cm^{-1}: 3338, 3075, 2973, 2921, 1704, 1516, 1328. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.79 (3H, s, CH_3); 3.66 (2H, s, NHC$\underline{H}_2$); 5.09 (1H, d, *J* = 1.9, CH); 5.25 (1H, d, *J* = 1.9, CH); 5.62 (1H, dd, *J* = 1.7, *J* = 9.6, CH); 6.11 (1H, dd, *J* = 9.6, *J* = 15.9, CH); 6.29 (1H, dd, *J* = 1.7, *J* = 15.9, CH); 8.11 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 21.0; 46.1; 112.3; 125.9; 132.4; 142.8; 168.2. Mass spectrum, *m*/*z* (I_{rel}, %): 125 $[M]^+$ (100), 110 (32), 71 (41), 57 (45), 56 (89). Found, *m*/*z*: 125.0869 $[M]^+$. $C_7H_{11}NO$. Calculated, *m*/*z*: 125.0840.

***N*-(But-3-en-1-yl)prop-2-enamide (4c)**. Yield 61%, colorless oil. IR spectrum, ν, cm^{-1}: 3298, 3075, 2989, 2936, 1701, 1527, 1374. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.29–2.33 (2H, m, CH_2); 3.29 (2H, t, *J* = 6.8, NHC$\underline{H}_2$); 4.96 (1H, dd, *J* = 1.8, *J* = 9.6, CH); 5.05 (1H, dd, *J* = 1.8, *J* = 15.7, CH); 5.64 (1H, dd, *J* = 2.0, *J* = 16.1, CH); 5.86–5.93 (1H, m, CH); 6.11 (1H, dd, *J* = 16.1, *J* = 9.6, CH); 6.49 (1H, dd, *J* = 2.0, *J* = 9.6, CH); 8.31 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 34.2; 41.5; 117.1; 125.9; 132.4; 136.3; 167.2. Mass spectrum, *m*/*z* (I_{rel}, %): 125 $[M]^+$ (78), 117 (100), 99 (74), 69 (35), 56 (63). Found, *m*/*z*: 125.0874 $[M]^+$. $C_7H_{11}NO$. Calculated, *m*/*z*: 125.0840.

***N*-(3-Methylbut-3-en-1-yl)prop-2-enamide (4d)**. Yield 63%, colorless oil. IR spectrum, ν, cm^{-1}: 3352, 3080, 2978, 2932, 1701, 1521, 1366. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.79 (3H, s, CH_3); 2.32 (2H, t, *J* = 6.8, CH_2); 3.37 (2H, t, *J* = 6.8, NHC$\underline{H}_2$); 4.91 (1H, d, *J* = 1.8, CH); 5.15 (1H, d, *J* = 1.8, CH); 5.98 (1H, dd, *J* = 9.3, *J* = 15.9, CH); 6.25 (1H, dd, *J* = 1.6, *J* = 15.9, CH); 6.41 (1H, dd, *J* = 1.6, *J* = 9.3, CH); 8.54 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 21.9; 37.2; 38.5; 112.6; 125.9; 131.2; 142.8; 165.7. Mass spectrum, *m*/*z* (I_{rel}, %): 139 $[M]^+$ (100), 124 (65), 83 (74), 68 (45), 56 (66). Found, *m*/*z*: 139.1021 $[M]^+$. $C_8H_{13}NO$. Calculated, *m*/*z*: 139.0997.

***N*-(Pent-4-en-1-yl)prop-2-enamide (4e)**. Yield 61%, colorless oil. IR spectrum, ν, cm^{-1}: 3267, 3074, 2965, 1704, 1520, 1305. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.96–2.10 (2H, m, CH_2); 2.28 (2H, t, *J* = 6.7, CH_2); 3.26 (2H, t, *J* = 7.0, NHC$\underline{H}_2$); 5.06 (1H, dd, *J* = 1.8, *J* = 9.7, CH); 5.12 (1H, dd, *J* = 1.8, *J* = 15.4, CH); 5.63 (1H, dd, *J* = 1.8, *J* = 15.6, CH); 5.89 (1H, dd, *J* = 9.7, *J* = 15.5, CH); 6.10 (1H, d, *J* = 16.1, CH); 6.52 (1H, dd, *J* = 1.8, *J* = 15.6, CH); 8.30 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 29.8; 32.5; 42.1; 116.6; 125.7; 130.9; 137.8; 169.3. Mass spectrum, *m*/*z* (I_{rel}, %): 139 $[M]^+$ (100), 85 (64), 71 (59), 70 (25), 56 (77). Found, *m*/*z*: 139.1029 $[M]^+$. $C_8H_{13}NO$. Calculated, *m*/*z*: 139.0997.

***N*-(4-Methylpent-4-en-1-yl)prop-2-enamide (4f)**. Yield 62%, colorless oil. IR spectrum, ν, cm^{-1}: 3310, 3045, 2987, 1712, 1525, 1298. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.78 (3H, s, CH_3); 2.29 (2H, t, *J* = 6.4, CH_2); 1.69–1.74 (2H, m, CH_2); 3.23 (2H, t, *J* = 6.8, NHC$\underline{H}_2$); 4.97 (1H, d, *J* = 1.7, CH); 5.21 (1H, d, *J* = 1.7, CH); 5.66 (1H, dd, *J* = 1.7, *J* = 15.2, CH); 6.09 (1H, dd, *J* = 9.6, *J* = 15.2, CH); 6.42 (1H, dd, *J* = 1.7, *J* = 9.6, CH); 7.80 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 22.1; 28.6; 36.8; 41.2; 111.7; 126.9; 132.2; 145.1; 167.8. Mass spectrum, *m*/*z* (I_{rel}, %): 153 $[M]^+$ (100), 138 (64), 97 (88), 82 (51), 56 (61). Found, *m*/*z*: 139.1021 $[M]^+$. $C_9H_{15}NO$. Calculated, *m*/*z*: 153.1154.

Preparation of Boc-protected diene amides 5a–f (General method). A solution of DMAP (13 mg, 0.1 mmol) in dry MeCN (2 ml) was added dropwise to a mixed solution of diene amides **4a**–**f** (1 mmol) and Boc_2O (263 mg, 1.2 mmol) in MeCN (4 ml) at room temperature under inert atmosphere, and the reaction mixture was stirred for 2 h. After completion of the reaction, the mixture was concentrated under reduced pressure and the residue was diluted with water (5 ml) and extracted with CH_2Cl_2 (3×10 ml). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, concentrated at low pressure, and purified on silica gel column using EtOAc–petroleum ether as eluent.

***tert*-Butyl *N*-acryloyl-*N*-(prop-2-en-1-yl)carbamate (5a)**. Yield 81%, colorless oil. IR spectrum, ν, cm^{-1}: 2984, 1731, 1686, 1611, 1422. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.41 (9H, s, $C(CH_3)_3$); 5.01 (2H, m, NCH_2); 5.24 (1H, dd, *J* = 1.6, *J* = 9.4, CH); 5.30 (1H, d, *J* = 1.7, CH); 5.61 (1H, dd, *J* = 1.8, *J* = 9.4, CH); 5.71–5.74 (1H, m, CH); 6.15 (1H, dd, *J* = 9.4, *J* = 16.1, CH); 6.48 (1H, dd, *J* = 1.8, *J* = 16.1, CH). ^{13}C NMR spectrum, δ, ppm: 29.1; 43.9; 81.5; 119.3; 128.2; 132.6; 132.9; 163.3; 176.1. Mass spectrum, *m*/*z* (I_{rel}, %): 211 $[M]^+$ (37), 111 (100), 100 (51), 56 (63). Found, *m*/*z*: 211.1216 $[M]^+$. $C_{11}H_{17}NO_3$. Calculated, *m*/*z*: 211.1208.

***tert*-Butyl *N*-acryloyl-*N*-(2-methylprop-2-en-1-yl)carbamate (5b)**.[8] Yield 83%, colorless oil. IR spectrum, ν, cm^{-1}:

2978, 1737, 1679, 1605, 1427. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.45 (9H, s, $C(CH_3)_3$); 1.80 (3H, s, CH_3); 4.25 (2H, s, NCH_2); 5.22 (1H, d, *J* = 1.9, CH); 5.35 (1H, d, *J* = 1.8, CH); 5.57 (1H, dd, *J* = 1.9, *J* = 9.1, CH); 6.11 (1H, dd, *J* = 1.9, *J* = 15.9, CH); 6.50 (1H, dd, *J* = 9.1, *J* = 15.9, CH). ^{13}C NMR spectrum, δ, ppm: 21.6; 29.2; 49.7; 81.7; 114.1; 126.4; 132.5; 139.2; 153.9; 174.3. Mass spectrum, *m*/*z* (I_{rel}, %): 225 $[M]^+$ (39), 210 (22), 195 (17), 125 (100), 117 (39), 110 (32), 71 (46). Found, *m*/*z*: 225.1406 $[M]^+$. $C_{12}H_{19}NO_3$. Calculated, *m*/*z*: 225.1365.

***tert*-Butyl *N*-acryloyl-*N*-(but-3-en-1-yl)carbamate (5c)**. Yield 80%, colorless oil. IR spectrum, ν, cm^{-1}: 2968, 1732, 1660, 1598, 1412. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.44 (9H, s, $C(CH_3)_3$); 2.35 (2H, m, CH_2); 4.42 (2H, d, *J* = 7.2, NCH_2); 5.11 (1H, dd, *J* = 1.9, *J* = 10.5, CH); 5.19 (1H, dd, *J* = 1.9, *J* = 16.3, CH); 5.62 (1H, dd, *J* = 1.7, *J* = 9.8, CH); 5.79–5.84 (1H, m, CH); 6.13 (1H, dd, *J* = 1.7, *J* = 16.1, CH); 6.45 (1H, dd, *J* = 1.7, *J* = 16.1, CH). ^{13}C NMR spectrum, δ, ppm: 29.2; 34.6; 49.1; 83.4; 117.6; 128.5; 132.3; 137.9; 158.2; 173.5. Mass spectrum, *m*/*z* (I_{rel}, %): 225 $[M]^+$ (100), 211 (19), 125 (78), 117 (69), 99 (53), 56 (64). Found, *m*/*z*: 225.1389 $[M]^+$. $C_{12}H_{19}NO_3$. Calculated, *m*/*z*: 225.1365.

***tert*-Butyl *N*-acryloyl-*N*-(3-methylbut-3-en-1-yl)carbamate (5d)**. Yield 81%, colorless oil. IR spectrum, ν, cm^{-1}: 2978, 1737, 1679, 1605, 1427. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.45 (9H, s, $C(CH_3)_3$); 1.79 (3H, s, CH_3); 2.34 (2H, t, *J* = 6.8, CH_2); 4.59 (2H, t, *J* = 6.8, NCH_2); 5.03 (1H, d, *J* = 1.9, CH); 5.14 (1H, d, *J* = 1.9, CH); 5.64 (1H, dd, *J* = 1.7, *J* = 9.6, CH); 6.16 (1H, dd, *J* = 9.6, *J* = 16.0, CH); 6.41 (1H, dd, *J* = 1.7, *J* = 16.0, CH). ^{13}C NMR spectrum, δ, ppm: 23.1; 29.3; 37.5; 45.2; 83.6; 112.2; 127.8; 132.5; 142.1; 156.3; 172.4. Mass spectrum, *m*/*z* (I_{rel}, %): 239 $[M]^+$ (84), 139 (100), 124 (37), 100 (23), 68 (51). Found, *m*/*z*: 239.1576 $[M]^+$. $C_{13}H_{21}NO_3$. Calculated, *m*/*z*: 239.1521.

***tert*-Butyl *N*-acryloyl-*N*-(pent-4-en-1-yl)carbamate (5e)**. Yield 82%, colorless oil. IR spectrum, ν, cm^{-1}: 2994, 1736, 1683, 1597, 1432. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.46 (9H, s, $C(CH_3)_3$); 1.81 (2H, m, CH_2); 2.37 (2H, m, CH_2); 4.43 (2H, t, *J* = 6.8, NCH_2); 5.03 (1H, dd, *J* = 1.9, *J* = 9.6, CH); 5.12 (1H, dd, *J* = 1.9, *J* = 16.0, CH); 5.62 (1H, dd, *J* = 1.7, *J* = 9.8, CH); 5.87 (1H, dd, *J* = 9.8, *J* = 16.0, CH); 6.11 (1H, dd, *J* = 1.7, *J* = 16.0, CH); 6.48 (1H, dd, *J* = 1.7, *J* = 9.8, CH). ^{13}C NMR spectrum, δ, ppm: 27.5; 28.1; 32.6; 44.7; 84.5; 119.3; 127.4; 132.8; 138.4; 153.7; 172.8. Mass spectrum, *m*/*z* (I_{rel}, %): 239 $[M]^+$ (61), 139 (100), 100 (68), 85 (33), 71 (45). Found, *m*/*z*: 239.1569 $[M]^+$. $C_{13}H_{21}NO_3$. Calculated, *m*/*z*: 239.1521.

***tert*-Butyl *N*-acryloyl-*N*-(4-methylpent-4-en-1-yl)carbamate (5f)**. Yield 80%, colorless oil. IR spectrum, ν, cm^{-1}: 2985, 1734, 1667, 1601, 1413. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.47 (9H, s, $C(CH_3)_3$); 1.65–1.68 (2H, m, CH_2); 1.79 (3H, s, CH_3); 2.23–2.27 (2H, m, CH_2); 4.35 (2H, t, *J* = 7.1, NCH_2); 4.98 (1H, d, *J* = 1.8, CH); 5.21 (1H, d, *J* = 1.8, CH); 5.64 (1H, dd, *J* = 1.9, *J* = 9.6, CH); 6.16 (1H, dd, *J* = 9.6, *J* = 16.0, CH); 6.47 (1H, dd, *J* = 1.9, *J* = 16.0, CH). ^{13}C NMR spectrum, δ, ppm: 22.9; 25.3; 28.7; 37.2; 45.5; 82.4; 111.7; 126.1; 132.4; 145.1; 153.2; 172.5. Mass spectrum, *m*/*z* (I_{rel}, %): 253 $[M]^+$ (63), 153 (100), 138 (44), 101 (21), 97 (76). Found, *m*/*z*: 253.1706 $[M]^+$. $C_{14}H_{23}NO_3$. Calculated, *m*/*z*: 253.1678.

Preparation of Fmoc-protected diene amides 6a–f (General method). Solution of dieneamides **4a**–**f** (1 mmol) in dioxane (2 ml) was stirred with 10% Na_2CO_3 solution (2 ml) and cooled at 0°C. 9-Fluorenylmethyl chloroformate (540 mg, 1.4 mmol) was added slowly and the resulting mixture was stirred at 0°C for 2 h and kept at room temperature overnight. Reaction mixture was diluted with H_2O and extracted with EtOAc (2×7 ml). The organic layer was washed with $NaHCO_3$ solution and acidified with 10% HCl, then extracted with EtOAc (3×7 ml). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified on silica gel column using 5% EtOAc in hexane as eluent.

(9*H*-Fluoren-9-yl)methyl *N*-acryloyl-*N*-(prop-2-en-1-yl)-carbamate (6a). Yield 87%, colorless oil. IR spectrum, ν, cm^{-1}: 2984, 1735, 1667, 1595, 1411. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.37 (1H, t, *J* = 6.4, CH); 4.65 (2H, d, *J* = 6.4, OCH_2); 5.11 (2H, d, *J* = 6.1, NCH_2); 5.24 (1H, dd, *J* = 1.9, *J* = 8.7, CH); 5.29 (1H, dd, *J* = 1.9, *J* = 15.9, CH); 5.61 (1H, dd, *J* = 1.8, *J* = 9.8, CH); 5.88 (1H, dd, *J* = 8.7, *J* = 15.9, CH); 6.12 (1H, dd, *J* = 9.8, *J* = 15.9, CH); 6.41 (1H, dd, *J* = 1.9, *J* = 15.9, CH); 7.28–7.33 (2H, m, H Ar); 7.36–7.41 (2H, m, H Ar); 7.56 (2H, ddd, *J* = 7.2, *J* = 2.1, *J* = 0.7, H Ar); 7.90 (2H, ddd, *J* = 7.1, *J* = 2.6, *J* = 0.7, H Ar). ^{13}C NMR spectrum, δ, ppm: 45.3; 48.1; 69.2; 118.7; 121.5; 125.9; 126.4; 126.9; 131.6; 132.3; 144.1; 153.4; 172.9. Mass spectrum, *m*/*z* (I_{rel}, %): 333 $[M]^+$ (39), 315 (19) 303 (26), 279 (64), 211 (28), 206 (32), 179 (100), 164 (87), 125 (33), 117 (34). Found, *m*/*z*: 333.1387 $[M]^+$. $C_{21}H_{19}NO_3$. Calculated, *m*/*z*: 333.1365.

(9*H*-Fluoren-9-yl)methyl *N*-acryloyl-*N*-(2-methylprop-2-en-1-yl)carbamate (6b). Yield 84%, colorless oil. IR spectrum, ν, cm^{-1}: 2979, 1739, 1678, 1602, 1430. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.83 (3H, s, CH_3); 4.21 (2H, s, CH_2); 4.39 (1H, t, *J* = 6.1, CH); 4.67 (2H, d, *J* = 6.1, CH_2); 5.17 (1H, d, *J* = 1.7, CH); 5.24 (1H, d, *J* = 1.7, CH); 6.09 (1H, dd, *J* = 9.4, *J* = 16.0, CH); 6.37 (1H, dd, *J* = 1.7, *J* = 9.4, CH); 6.44 (1H, dd, *J* = 1.7, *J* = 16.0, CH); 7.25–7.31 (2H, m, H Ar); 7.38–7.45 (2H, m, H Ar); 7.55 (2H, ddd, *J* = 7.4, *J* = 2.2, *J* = 0.8, H Ar); 7.89 (2H, ddd, *J* = 7.2, *J* = 2.6, *J* = 0.8, H Ar). ^{13}C NMR spectrum, δ, ppm: 21.3; 49.6; 68.2; 113.8; 120.6; 125.4; 126.7; 127.1; 132.5; 138.9; 141.7; 142.4; 153.2; 171.9. Mass spectrum, *m*/*z* (I_{rel}, %): 347 $[M]^+$ (45), 329 (26), 206 (39), 125 (76), 179 (87), 164 (100), 110 (19), 71 (23). Found, *m*/*z*: 347.1578 $[M]^+$. $C_{22}H_{21}NO_3$. Calculated, *m*/*z*: 347.1521.

(9*H*-Fluoren-9-yl)methyl *N*-acryloyl-*N*-(but-3-en-1-yl)-carbamate (6c). Yield 89%, yellowish oil. IR spectrum, ν, cm^{-1}: 2992, 1737, 1660, 1598, 1412. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.26–2.29 (2H, m, CH_2); 4.42 (1H, t, *J* = 6.3, CH); 4.79 (2H, d, *J* = 6.3, CH_2); 4.57 (2H, t, *J* = 7.0, CH_2); 5.01 (1H, d, *J* = 1.8, CH); 5.08 (1H, d, *J* = 1.8, CH); 5.83–5.87 (1H, m, CH); 5.79 (1H, dd, *J* = 9.5, *J* = 16.0, CH); 6.18 (1H, dd, *J* = 1.8, *J* = 9.5, CH); 6.44 (1H, dd, *J* = 1.8, *J* = 16.0, CH); 7.27–7.31 (2H, m, H Ar); 7.34–7.39 (2H, m, H Ar); 7.58 (2H, dd, *J* = 7.8, *J* = 2.1, H Ar);

7.79 (2H, dd, *J* = 7.2, *J* = 2.1, H Ar). ^{13}C NMR spectrum, δ, ppm: 31.6; 47.3; 47.8; 68.2; 117.5; 121.2; 124.9; 126.7; 127.1; 132.2; 137.4; 142.2; 143.6; 153.4; 171.7. Mass spectrum, *m*/*z* (I_{rel}, %): 347 $[M]^+$ (22), 329 (17), 179 (42), 167 (55), 164 (28), 152 (65), 125 (100), 99 (31). Found, *m*/*z*: 347.1586 $[M]^+$. $C_{22}H_{21}NO_3$. Calculated, *m*/*z*: 347.1521.

(9*H*-Fluoren-9-yl)methyl *N*-acryloyl-*N*-(3-methylbut-3-en-1-yl)carbamate (6d). Yield 85%, colorless oil. IR spectrum, ν, cm^{-1}: 2987, 1733, 1662, 1589, 1438. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.78 (3H, s, CH_3); 2.39 (2H, t, *J* = 6.8, CH_2); 4.47 (1H, t, *J* = 6.4, CH); 4.54 (2H, t, *J* = 6.8, CH_2); 4.73 (2H, d, *J* = 6.4, CH_2); 4.98–5.02 (1H, m, CH); 5.16 (1H, d, *J* = 1.3, CH); 5.60 (1H, dd, *J* = 9.6, *J* = 15.8, CH); 6.29 (1H, dd, *J* = 1.9, *J* = 9.6, CH); 6.38 (1H, dd, *J* = 1.9, *J* = 15.8, CH); 7.26–7.29 (2H, m, H Ar); 7.37–7.42 (2H, m, H Ar); 7.55 (2H, dd, *J* = 7.2, *J* = 1.9, H Ar); 7.71 (2H, dd, *J* = 7.3, *J* = 2.2, H Ar). ^{13}C NMR spectrum, δ, ppm: 23.1; 37.4; 44.9; 46.8; 68.3; 110.7; 121.2; 124.9; 125.3; 125.2; 126.8; 132.5; 142.8; 143.2; 152.1; 172.3. Mass spectrum, *m*/*z* (I_{rel}, %): 361 $[M]^+$ (58), 343 (14), 330 (43), 206 (19), 179 (33), 166 (100), 164 (45), 139 (84). Found, *m*/*z*: 361.1703 $[M]^+$. $C_{23}H_{23}NO_3$. Calculated, *m*/*z*: 361.1678.

(9*H*-Fluoren-9-yl)methyl *N*-acryloyl-*N*-(pent-4-en-1-yl)carbamate (6e). Yield 87%, colorless oil. IR spectrum, ν, cm^{-1}: 2987, 1733, 1662, 1589, 1438. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.79–1.83 (2H, m, CH_2); 2.19–2.24 (2H, m, CH_2); 4.31 (2H, t, *J* = 6.9, CH_2); 4.44 (1H, t, *J* = 6.5, CH); 4.75 (2H, d, *J* = 6.5, CH); 5.03 (1H, d, *J* = 1.4, CH); 5.08 (1H, d, *J* = 1.4, CH); 5.71 (1H, dd, *J* = 8.9, *J* = 16.1, CH); 5.78–5.86 (1H, m, CH); 6.22 (1H, dd, *J* = 1.7, *J* = 8.9, CH); 6.41 (1H, dd, *J* = 1.7, *J* = 16.1, CH); 7.26–7.31 (2H, m, H Ar); 7.36–7.41 (2H, m, H Ar); 7.59 (2H, ddd, *J* = 7.1, *J* = 2.6, *J* = 0.9, H Ar); 7.86 (2H, ddd, *J* = 7.3, *J* = 2.2, *J* = 0.9, H Ar). ^{13}C NMR spectrum, δ, ppm: 27.8; 32.2; 44.5; 48.3; 68.1; 116.7; 121.4; 125.5; 126.7; 127.1; 132.5; 137.2; 142.9; 143.6; 153.2; 171.9. Mass spectrum, *m*/*z* (I_{rel}, %): 361 $[M]^+$ (44), 343 (19), 206 (27), 166 (95), 164 (100), 139 (77), 85 (53). Found, *m*/*z*: 361.1711 $[M]^+$. $C_{23}H_{23}NO_3$. Calculated, *m*/*z*: 361.1678.

(9*H*-Fluoren-9-yl)methyl *N*-acryloyl-*N*-(4-methylpent-4-en-1-yl)carbamate (6f). Yield 84%, colorless oil. IR spectrum, ν, cm^{-1}: 2993, 1735, 1678, 1607, 1432. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.79 (3H, s, CH_3); 1.65 (2H, m, CH_2); 2.19 (2H, t, *J* = 6.9, CH_2); 4.41 (2H, t, *J* = 7.0, CH_2); 4.48 (1H, t, *J* = 6.6, CH); 4.66 (2H, d, *J* = 6.6, CH_2); 4.97 (1H, d, *J* = 1.8, CH); 5.10 (1H, d, *J* = 1.8, CH); 5.57 (1H, dd, *J* = 9.4, *J* = 15.9, CH); 6.11 (1H, dd, *J* = 1.9, *J* = 9.4, CH); 6.49 (1H, dd, *J* = 1.9, *J* = 15.9, CH); 7.23–7.27 (2H, m, H Ar); 7.33–7.38 (2H, m, H Ar); 7.61 (2H, dd, *J* = 7.1, *J* = 2.3, H Ar); 7.85 (2H, dd, *J* = 7.0, *J* = 2.2, H Ar). ^{13}C NMR spectrum, δ, ppm: 23.4; 25.7; 36.9; 45.2; 48.3; 68.0; 110.4; 120.9; 125.5; 126.4; 126.3; 127.1; 132.6; 141.8; 143.4; 144.2; 151.8; 172.2. Mass spectrum, *m*/*z* (I_{rel}, %): 375 $[M]^+$ (39), 357 (23), 206 (35), 179 (100), 164 (87), 153 (61), 139 (17). Found, *m*/*z*: 375.1869 $[M]^+$. $C_{23}H_{23}NO_3$. Calculated, *m*/*z*: 375.1834.

Ring-closing metathesis reaction of diene amides 4–6 a–f (General method). Method I (Grubbs I catalyst). The Grubbs I catalyst (5–10 mol %) was added to a degassed homogeneous solution of diene amides **4a**, **5a** (1 mmol) in dry PhMe (5 ml) under inert atmosphere, and reaction mixture was heated at 80°C for 32 h. The reaction mixture was concentrated and purified by column chromatography, yielding a small amount of required lactams along with major part of starting diene amides.

Method II (Grubbs II catalyst). Solution of diene amides **4–6 a–f** (1 mmol) in dry PhMe (5 ml) was degassed well, and Grubbs II catalyst (5–10 mol %) was added under inert atmosphere. The resulting mixture was stirred at 80°C for 14 or 32 h. The reaction mixture was concentrated and purified on silica gel column using EtOAc–petroleum ether as eluent.

1,5-Dihydro-2*H*-pyrrol-2-one (7a).[10] Colorless oil. IR spectrum, ν, cm^{-1}: 3437, 2979, 1689, 1450, 1293, 1178. ^{1}H NMR spectrum, δ, ppm: 4.11–4.17 (2H, m, CH_2); 6.14–6.20 (1H, m, CH); 7.11–7.16 (1H, m, CH); 8.01 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 51.64; 114.7; 137.5; 176.2. Mass spectrum, *m*/*z* (I_{rel}, %): 83 $[M]^+$ (100), 61 (45), 57 (39). Found, *m*/*z*: 83.0389 $[M]^+$. C_4H_5NO. Calculated, *m*/*z*: 83.0365.

4-Methyl-1,5-dihydro-2*H*-pyrrol-2-one (7b).[10b,c] Colorless oil. IR spectrum, ν, cm^{-1}: 3448, 2980, 1678, 1447, 1293, 1164. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.05 (3H, s, CH_3); 3.99 (2H, d, *J* = 15.6, NHC$\underline{H}_2$); 5.88 (1H, s, CH); 7.81 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 15.18; 51.67; 104.7; 122.6; 176.4. Mass spectrum, *m*/*z* (I_{rel}, %): 97 $[M]^+$ (100), 82 (35), 58 (24). Found, *m*/*z*: 97.0574 $[M]^+$. C_5H_7NO. Calculated, *m*/*z*: 97.0528.

5,6-Dihydropyridin-2(1*H*)-one (7c).[11] Colorless oil. IR spectrum, ν, cm^{-1}: 3429, 2977, 1686, 1435, 1267, 1089. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.36–2.44 (2H, m, CH_2); 4.13–4.18 (2H, m, CH_2); 6.26 (1H, d, *J* = 9.2, CH); 6.61–6.65 (1H, m, CH); 7.79 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 35.4; 51.4; 105.6; 123.0; 176.8. Mass spectrum, *m*/*z* (I_{rel}, %): 97 $[M]^+$ (100), 74 (65), 61 (45). Found, *m*/*z*: 97.0534 $[M]^+$. C_5H_7NO. Calculated, *m*/*z*: 97.0528.

4-Methyl-5,6-dihydropyridin-2(1*H*)-one (7d). Light-yellow oil. IR spectrum, ν, cm^{-1}: 3416, 2968, 1681, 1465, 1291, 1144. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.05 (3H, s, CH_3); 2.37 (2H, t, *J* = 6.1, CH_2); 3.89 (2H, t, *J* = 6.0, CH_2); 5.88 (1H, s, CH); 7.81 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 15.1; 36.7; 51.7; 102.9; 123.2; 168.9. Mass spectrum, *m*/*z* (I_{rel}, %): 111 $[M]^+$ (100), 96 (72), 74 (49). Found, *m*/*z*: 111.0690 $[M]^+$. C_6H_9NO. Calculated, *m*/*z*: 111.0678.

1,5,6,7-Tetrahydro-2*H*-azepin-2-one (7e).[12] Colorless oil. IR spectrum, ν, cm^{-1}: 3398, 2942, 1669, 1436, 1281, 1155. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.87–2.11 (2H, m, CH_2); 2.47–2.52 (2H, m, CH_2); 3.87–3.91 (2H, m, CH_2); 5.98 (1H, d, *J* = 9.6, CH); 6.4 (1H, m, NH). ^{13}C NMR spectrum, δ, ppm: 29.8; 34.5; 52.6; 106.2; 129.4; 174.1. Mass spectrum, *m*/*z* (I_{rel}, %): 111 $[M]^+$ (100), 95 (21), 74 (32). Found, *m*/*z*: 111.0684 $[M]^+$. C_6H_9NO. Calculated, *m*/*z*: 111.0678.

4-Methyl-1,5,6,7-tetrahydro-2*H*-azepin-2-one (7f). Yellowish oil. IR spectrum, ν, cm^{-1}: 3445, 2976, 1674, 1467,

1288, 1174. ^{1}H NMR spectrum, δ, ppm: 1.75 (3H, s, CH_3); 2.10–2.15 (2H, m, CH_2); 2.39–2.42 (2H, m, CH_2); 3.76–3.81 (2H, m, CH_2); 5.74 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 18.3; 27.6; 31.4; 52.1; 104.9; 123.7; 176.5. Mass spectrum, *m*/*z* (I_{rel}, %): 125 $[M]^+$ (64), 118 (59), 110 (100), 74 (45), 61 (28). Found, *m*/*z*: 125.0871 $[M]^+$. $C_7H_{11}NO$. Calculated, *m*/*z*: 125.0835.

***tert*-Butyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (8a)**.[5e] Colorless oil. IR spectrum, ν, cm^{-1}: 2957, 1740, 1691, 1556, 1482. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.41 (9H, s, $C(CH_3)_3$); 4.29 (2H, d, *J* = 6.6, $NHC\underline{H}_2$); 6.21 (1H, d, *J* = 10.1, CH); 6.43 (1H, dd, *J* = 6.6, *J* = 10.1, CH). ^{13}C NMR spectrum, δ, ppm: 28.2; 53.5; 81.7; 121.6; 146.9; 153.8; 171.3. Mass spectrum, *m*/*z* (I_{rel}, %): 183 $[M]^+$ (43), 111 (62), 83 (100), 73 (35), 58 (86). Found, *m*/*z*: 183.0913 $[M]^+$. $C_9H_{13}NO_3$. Calculated, *m*/*z*: 183.0899.

***tert*-Butyl 4-methyl-2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (8b)**.[8] Colorless oil. IR spectrum, ν, cm^{-1}: 2996, 1738, 1686, 1544, 1423. ^{1}H NMR spectrum, δ, ppm: 1.44 (9H, s, $C(CH_3)_3$); 1.98 (3H, s, CH_3); 4.17 (2H, s, CH_2); 5.93 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 16.1; 27.5; 53.1; 82.4; 122.1; 148.8; 157.2; 169.7. Mass spectrum, *m*/*z* (I_{rel}, %): 197 $[M]^+$ (54), 182 (44), 97 (95), 82 (100), 74 (26). Found, *m*/*z*: 197.1073 $[M]^+$. $C_{10}H_{15}NO_3$. Calculated, *m*/*z*: 197.1046.

***tert*-Butyl 2-oxo-5,6-dihydropyridine-1(2*H*)-carboxylate (8c)**.[13] Colorless oil. IR spectrum, ν, cm^{-1}: 2984, 1738, 1684, 1573, 1461. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.46 (9H, s, $C(CH_3)_3$); 2.27–2.30 (2H, m, CH_2); 3.62 (2H, t, *J* = 6.9, $NHC\underline{H}_2$); 6.11 (1H, d, *J* = 9.4, CH); 6.35–6.39 (1H, m, CH). ^{13}C NMR spectrum, δ, ppm: 24.7; 28.2; 45.5; 81.3; 126.2; 147.0; 153.8; 167.1. Mass spectrum, *m*/*z* (I_{rel}, %): 197 $[M]^+$ (31), 174 (63), 158 (41), 125 (19), 118 (32), 110 (42), 97 (100). Found, *m*/*z*: 197.1061 $[M]^+$. $C_{10}H_{15}NO_3$. Calculated, *m*/*z*: 197.1046.

***tert*-Butyl 4-methyl-2-oxo-5,6-dihydropyridine-1(2*H*)-carboxylate (8d)**. Colorless oil. IR spectrum, ν, cm^{-1}: 2969, 1733, 1677, 1584, 1462. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.41 (9H, s, $C(CH_3)_3$); 1.96 (3H, s, CH_3); 2.26 (2H, t, *J* = 6.8, CH_2); 3.62 (2H, t, *J* = 6.8, $NHC\underline{H}_2$); 6.01 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 20.4; 27.5; 30.2; 42.8; 81.4; 120.1; 150.8; 157.3; 165.7. Mass spectrum, *m*/*z* (I_{rel}, %): 211 $[M]^+$ (42), 175 (37), 142 (56), 128 (21), 110 (100), 99 (43). Found, *m*/*z*: 211.1217 $[M]^+$. $C_{11}H_{17}NO_3$. Calculated, *m*/*z*: 211.1202.

***tert*-Butyl 7-oxo-2,3,4,7-tetrahydro-1*H*-azepine-1-carboxylate (8e)**. Yellowish oil. IR spectrum, ν, cm^{-1}: 2977, 1739, 1683, 1578, 1449. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.43 (9H, s, $C(CH_3)_3$); 1.66 (2H, m, CH_2); 1.97–2.11 (2H, m, CH_2); 4.71 (2H, t, *J* = 6.6, $NHC\underline{H}_2$); 6.25 (1H, d, *J* = 9.5, CH); 6.32–6.37 (1H, m, CH). ^{13}C NMR spectrum, δ, ppm: 27.3; 29.2; 32.4; 47.7; 81.4; 122.8; 142.6; 153.1; 164.3. Mass spectrum, *m*/*z* (I_{rel}, %): 211 $[M]^+$ (58), 125 (41), 117 (34), 111 (100), 99 (65), 74 (39). Found, *m*/*z*: 211.1221 $[M]^+$. $C_{11}H_{17}NO_3$. Calculated, *m*/*z*: 211.1202.

***tert*-Butyl 5-methyl-7-oxo-2,3,4,7-tetrahydro-1*H*-azepine-1-carboxylate (8f)**. Colorless oil. IR spectrum, ν, cm^{-1}: 2983, 1730, 1658, 1582, 1439. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.47 (9H, s, $C(CH_3)_3$); 1.61–1.66 (2H, m, CH_2); 1.91 (3H, s, CH_3); 2.19–2.22 (2H, m, CH_2); 4.71 (2H, t, *J* = 6.9, CH_2); 6.13 (1H, s, CH). ^{13}C NMR spectrum, δ, ppm: 22.9; 27.3; 28.5; 36.2; 49.6; 81.8; 121.0; 148.4; 152.3; 164.1. Mass spectrum, *m*/*z* (I_{rel}, %): 225 $[M]^+$ (84), 212 (66), 174 (43), 142 (51), 125 (100), 110 (37). Found, *m*/*z*: 225.1367 $[M]^+$. $C_{12}H_{19}NO_3$. Calculated, *m*/*z*: 225.1359.

(9*H*-Fluoren-9-yl)methyl 2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (9a). White powder. Mp 54–55°C. IR spectrum, ν, cm^{-1}: 2988, 1736, 1661, 1597, 1442. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.11 (2H, d, *J* = 6.1, CH_2); 4.41 (2H, t, *J* = 6.5, CH_2); 4.71 (2H, d, *J* = 6.5, CH_2); 6.31 (1H, d, *J* = 8.7, CH_2); 6.93–6.98 (1H, m, CH); 7.24–7.30 (4H, m, H Ar); 7.59 (2H, d, *J* = 6.4, *J* = 2.3, H Ar); 7.90 (2H, d, *J* = 6.7, *J* = 2.1, H Ar) . ^{13}C NMR spectrum, δ, ppm: 47.1; 52.3; 66.5; 119.5; 122.1; 123.9; 125.4; 126.2; 129.7; 133.6; 141.5; 149.1; 153.4; 174.8. Mass spectrum, *m*/*z* (I_{rel}, %): 305 $[M]^+$ (45), 179 (100), 123 (84), 83 (66). Found, *m*/*z*: 305.1046 $[M]^+$. $C_{19}H_{15}NO_3$. Calculated, *m*/*z*: 305.1052.

(9*H*-Fluoren-9-yl)methyl 4-methyl-2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylate (9b). White powder. Mp 57–58°C. IR spectrum, ν, cm^{-1}: 2993, 1741, 1670, 1535, 1428. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.76 (3H, s, CH_3); 4.18 (2H, s, CH_2); 4.41 (1H, t, *J* = 6.4, CH); 4.65 (2H, d, *J* = 6.4, CH_2); 6.33 (1H, s, CH); 7.29–7.35 (4H, m, H Ar); 7.57 (2H, dd, *J* = 6.7, *J* = 2.2, H Ar); 7.83 (2H, dd, *J* = 6.6, *J* = 2.5, H Ar). ^{13}C NMR spectrum, δ, ppm: 21.3; 46.8; 51.9; 66.4; 119.2; 122.0; 123.6; 124.9; 126.1; 134.7; 136.8; 141.3; 149.6; 151.1; 170.4. Mass spectrum, *m*/*z* (I_{rel}, %): 319 $[M]^+$ (65), 180 (19), 179 (87), 123 (100), 97 (35), 83 (46). Found, *m*/*z*: 319.1223 $[M]^+$. $C_{20}H_{17}NO_3$. Calculated, *m*/*z*: 319.1202.

(9*H*-Fluoren-9-yl)methyl 2-oxo-5,6-dihydropyridine-1(2*H*)-carboxylate (9c). White powder. Mp 51–53°C. IR spectrum, ν, cm^{-1}: 2975, 1739, 1658, 1546, 1457. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.25–2.28 (2H, m, CH_2); 3.66 (2H, t, *J* = 6.6, CH_2); 4.41 (1H, t, *J* = 6.7, CH); 4.73 (2H, d, *J* = 6.7, CH_2); 6.23 (1H, d, *J* = 8.7, CH); 6.35–6.39 (1H, m, CH); 7.28–7.34 (4H, m, H Ar); 7.56 (2H, dd, *J* = 6.2, *J* = 2.3, H Ar); 7.88 (2H, dd, *J* = 6.6, *J* = 2.5, H Ar). ^{13}C NMR spectrum, δ, ppm: 26.1; 45.9; 47.4; 66.8; 121.8; 123.3; 124.5; 127.4; 128.8; 140.8; 143.7; 147.2; 153.4; 167.8. Mass spectrum, *m*/*z* (I_{rel}, %): 319 $[M]^+$ (45), 179 (64), 164 (100), 97 (53). Found, *m*/*z*: 319.1219 $[M]^+$. $C_{20}H_{17}NO_3$. Calculated, *m*/*z*: 319.1202.

(9*H*-Fluoren-9-yl)methyl 4-methyl-2-oxo-5,6-dihydropyridine-1(2*H*)-carboxylate (9d). White powder. Mp 56–57°C. IR spectrum, ν, cm^{-1}: 2968, 1741, 1673, 1581, 1429. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.78 (3H, s, CH_3); 2.25 (2H, t, *J* = 6.7, CH_2); 3.73 (2H, t, *J* = 6.6, CH_2); 4.42 (1H, t, *J* = 6.1, CH); 4.71 (2H, d, *J* = 6.1, CH_2); 6.19 (1H, s, CH); 7.27–7.34 (4H, m, H Ar); 7.53 (2H, dd, *J* = 6.5, 2.2, H Ar); 7.71 (2H, dd, *J* = 6.4, 1.9, H Ar). ^{13}C NMR spectrum, δ, ppm: 21.4; 46.3; 52.7; 64.8; 103.4; 117.6; 122.0; 123.6; 125.3; 127.2; 128.1; 134.8; 136.4; 142.1; 147.0; 153.4; 173.6. Mass spectrum, *m*/*z* (I_{rel}, %): 333 $[M]^+$ (58), 179 (64), 178 (100), 154 (19), 111 (32), 110 (49), 97 (68). Found, *m*/*z*: 333.1371 $[M]^+$. $C_{21}H_{19}NO_3$. Calculated, *m*/*z*: 333.1359.

(9*H*-Fluoren-9-yl)methyl 7-oxo-2,3,4,7-tetrahydro-1*H*-azepine-1-carboxylate (9e). White powder. Mp 52–53°C. IR spectrum, ν, cm^{-1}: 2994, 1732, 1660, 1593, 1449. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.66–1.69 (2H, m, CH_2); 2.14–2.18 (2H, m, CH_2); 4.75 (2H, t, *J* = 6.1, CH_2); 4.45 (1H, t, *J* = 6.4, CH); 4.75 (2H, d, *J* = 6.4, CH_2); 6.21 (1H, d, *J* = 9.2, CH); 6.33–6.38 (1H, m, CH); 7.26–7.31 (4H, m, H Ar); 7.60 (2H, dd, *J* = 6.7, *J* = 2.2, H Ar); 7.89 (2H, dd, *J* = 6.4, *J* = 2.2, H Ar). ^{13}C NMR spectrum, δ, ppm: 29.2; 34.1; 46.8; 50.0; 67.1; 122.3; 123.9; 125.5; 127.2; 126.4; 129.3; 139.5; 141.8; 142.5; 143.2; 152.4; 168.2. Mass spectrum, *m*/*z* (I_{rel}, %): 333 $[M]^+$ (42), 179 (64), 179 (100), 111 (41), 97 (56). Found, *m*/*z*: 333.1374 $[M]^+$. $C_{21}H_{19}NO_3$. Calculated, *m*/*z*: 333.1359.

(9*H*-Fluoren-9-yl)methyl 4-methyl-7-oxo-2,3,4,7-tetrahydro-1*H*-azepine-1-carboxylate (9f). White powder. Mp 58–59°C. IR spectrum, ν, cm^{-1}: 2989, 1737, 1667, 1573, 1445. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.78 (3H, s, CH_3); 1.69–1.73 (2H, m, CH_2); 2.10–2.14 (2H, m, CH_2); 4.43 (1H, t, *J* = 6.2, CH); 4.72 (2H, d, *J* = 6.2, CH_2); 4.80 (2H, t, *J* = 6.5, CH_2); 6.19 (1H, s, CH); 7.30–7.36 (4H, m, H Ar); 7.60 (2H, dd, *J* = 6.6, *J* = 2.4, H Ar); 7.89 (2H, dd, *J* = 6.5, *J* = 2.2, H Ar). ^{13}C NMR spectrum, δ, ppm: 22.4; 27.8; 40.2; 46.8; 49.3; 68.1; 120.6; 122.0; 125.6; 126.3; 142.1; 143.4; 147.0; 153.4; 166.6. Mass spectrum, *m*/*z* (I_{rel}, %): 347 $[M]^+$ (32), 179 (87), 164 (100), 125 (57), 111 (32), 110 (61). Found, *m*/*z*: 347.1527 $[M]^+$. $C_{22}H_{21}NO_3$. Calculated, *m*/*z*: 347.1515.

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