

A New Route to *N*-Aryl 2-Alkenamides, *N*-Allyl *N*-Aryl 2-Alkenamides, and *N*-Aryl α,β -Unsaturated γ -Lactams from *N*-Aryl 3-(Phenylsulfonyl)propanamides

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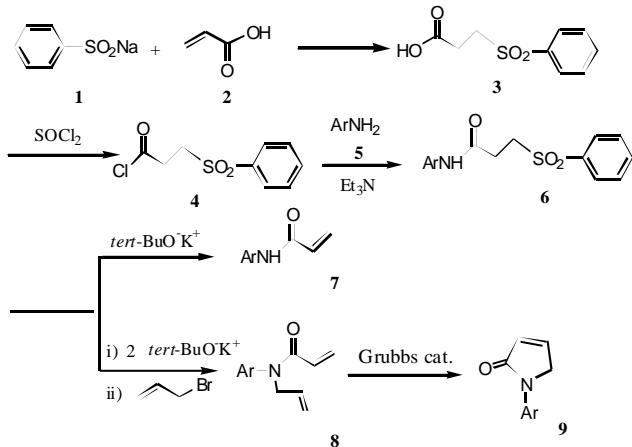
A series of *N*-aryl 2-alkenamides were produced efficiently by treating *N*-aryl 3-(phenylsulfonyl)-propanamides with potassium *tert*-butoxide in THF at 0 °C. Without isolation, it was further treated with an additional equivalent of potassium *tert*-butoxide and allyl bromide to give *N*-allyl *N*-aryl 2-alkenamides in one pot in good yields. Followed by a ring-closing metathesis reaction, these *N*-allyl *N*-aryl 2-alkenamides were respectively converted into corresponding *N*-aryl α,β -unsaturated γ -lactams in moderate yields.

INTRODUCTION

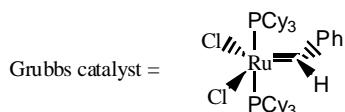
2-Alkenamides or acrylamides, useful monomers for polyacrylamides, have been known to chemists for a long time. In addition, they are widely used as Michaelis acceptors for several nucleophiles such as organolithiums,¹ piperazine,² anion of malonate,³ thiourea,⁴ etc.⁵ It also played as a starting material for producing 1-aza-2-cyano-1,3-butadiene, a key intermediate to give azacyclohexenes,⁶ and also can be converted to a chiral dienophiles for Diels-Alder reaction.⁷ Furthermore, in recent reports *N*-substituted 2-alkenamides having *N*-allyl function, play an important role to certain γ -lactams via radical cyclization⁸ and for α,β -unsaturated γ -lactams by ring-closing metathesis reaction with Grubbs catalyst.⁹ The present industrial preparation for acrylamides, which circumvents the highly unstable and toxic acryloyl chloride as key starting material,¹⁰ adopts the two-step method. This strategy involves the Michael addition and amidation of acrylic ester with 2 equivalents of amine and followed by deamination to give the desired compound at 180–300 °C.¹¹ Other methodologies included the use of hydroxyl group,¹² chloride,¹³ bromide,¹⁴ amine,¹⁵ etc. as leaving group for the preparation of *N*-substituted acrylamides via 1,2-elimination. Their drawbacks include low yield, long reaction time, harsh reaction condition, and the reagent's corrosive, volatile, and toxic nature. Despite the availability of many synthetic methods, there still exists a need to develop more efficient and less toxic procedures than those currently in existence. To the best of our knowledge, all previous reports for *N*-aryl alkenamides have paid no attention to the use of phenylsulfonyl group as leaving group. Herein we wish to

report a new, simple, efficient and less toxic method to prepare *N*-aryl alkenamides by debenzenesulfonation of 3-(phenylsulfonyl)propanamides with one equivalent of potassium *tert*-butoxide (Scheme I). On the other hand *N*-allyl *N*-aryl alkenamides, an important building block for some γ -lactams, prepared merely from a corresponding amine and toxic acryloyl chloride, were disadvantageous.

Scheme I



- a. Ar = C_6H_5 c. Ar = $4\text{-CH}_3\text{OC}_6\text{H}_5$ e. Ar = $4\text{-ClC}_6\text{H}_5$
b. Ar = $4\text{-CH}_3\text{C}_6\text{H}_5$ d. Ar = $4\text{-FC}_6\text{H}_5$ f. Ar = $4\text{-BrC}_6\text{H}_5$



In this reported process, it can be prepared in one pot by treating *N*-aryl 3-(phenylsulfonyl)propanamide with two equivalents of *tert*-butoxide and 1 equivalent of allyl bromide to undergo debenzenesulfonation and followed by allylation. This method led a new route to *N*-allyl *N*-aryl alkenamides and circumvented the use of the toxic and volatile starting material, acryloyl chloride. Furthermore the ring-closure metathesis (RCM) of *N*-allyl *N*-aryl alkenamides with Grubbs catalyst^{16a} was achieved to give a series of *N*-aryl α,β -unsaturated γ -lactams, a key intermediate for mitomycin.¹⁷ Meanwhile the physical data, such as ¹H-NMR, ¹³C-NMR, and EI-MS of some new *N*-aryl α,β -unsaturated γ -lactams are described.

RESULTS AND DISCUSSION

3-(Phenylsulfonyl)propanoic acid (**3**), purchased from Aldrich Co. or prepared from sodium benzenesulfinate (**1**), and acrylic acid (**2**), as general method in 65% yields, was treated with excess thionyl chloride under reflux to give 3-(phenylsulfonyl)propanoyl chloride (**4**). After removing excess thionyl chloride, and without further purification, it was allowed to react with corresponding primary amines in the presence of anhydrous triethylamine to afford *N*-aryl 3-(phenylsulfonyl)propanamides (**5a-f**) in high yields. When compound **5** was reacted with potassium *tert*-butoxide at 0 °C in THF, no cyclization or dimerization, but high yield of elimination products **6** was observed. But the reaction of **5** with potassium *tert*-butoxide was carried out at room temperature in THF, gave a lower yield of **6** together with its dimer. For instance, in the case of compound **5b**, its dimer was given in 10% yields, and showed two singlet methyl signals at δ 2.30 and 2.37; and three doublet doublet olefinic protons at δ 5.54, 6.01, and 6.37 in ¹H-NMR spectrum. By our method running at 0 °C in THF, it gave *N*-phenylacrylamide (**7a**) in 90% yield, *N*-(4-methylphenyl)acrylamide (**7b**) in 95% yield, *N*-(4-methoxyphenyl)acrylamide (**7c**) in 96% yield, *N*-(4-fluorophenyl)acrylamide (**7d**) in 90% yield, *N*-(4-chlorophenyl)acrylamide (**7e**) in 93% yield, and *N*-(4-bromophenyl)acrylamide (**7f**) in 96% yield. Their structures are coincident with the previous reports by comparing with MP, EI-MS and NMR spectra data if available. Furthermore these acrylamides, without isolation or purification, can be extended to the one-pot method for the preparation of *N*-allyl *N*-aryl acrylamides (**8a-f**) in good yields by reacting it with an additional equivalent of potassium *tert*-butoxide and allyl bromide. Their structures were elucidated by spectral data such as NMR, EI-MS, and HRMS. For instance, in the case of

8c, the ¹H-NMR (400 MHz, CDCl₃) spectrum showed a three-proton singlet signal at 3.83 ppm indicating the presence of one methoxyl group; a two-proton doublet triplet at 4.34 ppm corresponding to the methylene of the allyl group in the structure. In addition, a three-one-proton doublet doublet at 5.51 ppm (*J* = 2.0 Hz, and 10.4 Hz), 6.04 ppm (*J* = 10.4 Hz, and 16.8 Hz), and 6.36 ppm (*J* = 2.0, and 16.8 Hz) were indicated, respectively, to the three vinyl protons by *gem-cis*, *cis-trans*, and *gem-trans* coupling. Furthermore the three olefinic protons of the allyl group were shown, respectively, at 5.07 ppm (d, *J* = 1.2 Hz, 1H), 5.11-5.14 ppm (m, 1H), and 5.83-5.93 ppm (m, 1H). The remaining two two-proton aromatic multiplet signals were indicated, respectively, at 6.89-6.92 ppm, and 7.05-7.09 ppm. The EI-MS spectrum showed the molecular ion at *m/z* 217, corresponding to the molecular formula C₁₃H₁₅NO₂. The high-resolution mass of **8c**, C₁₃H₁₅NO₂ found for 217.1103, matched with the calculated one. These results proved the correctness of the structure of **8c**. **8a-f** was a colorless liquid, and difficult to purify by distillation because part of it was polymerized during the process of vacuum distillation. Its purification was subjected to chromatographic silica-gel column using ethyl acetate/n-hexane (1/5) as eluent. Our one-pot method has successfully afforded a new and efficient route to prepare *N*-allyl *N*-aryl acrylamides, and successfully circumvented the use of toxic and volatile starting material, acryloyl chloride. Furthermore cyclization of *N*-allyl *N*-aryl acrylamides (**8a-f**) to *N*-aryl α,β -unsaturated γ -lactams (**9a-f**) was accomplished by olefin ring-closure metathesis in the presence of Grubbs catalyst. As in the general procedure described by Grubbs et al., **8a-f** were cyclized, respectively, to give **9a-f** within 20 hours in 50-65% yields in anhydrous dichloro methane, even prolonging the reaction time to 2-3 days. Recently Furstner, A. et al.,^{16b} using modified Grubbs catalyst to cyclize **8a** in anhydrous toluene at 80 °C to give **9a** in 82% yield was reported. Under the same conditions, in our case using Grubbs catalyst to cyclize **8a** in anhydrous toluene at 80 °C gave **9a** in 55% yields which almost gave the same yield to compare with the reaction running in dried dichloro methane at room temperature. But the decrease of the reaction time from 2 days to 3 hours was observed. The structure of **9a-f** was elucidated by their physical data such as ¹H-NMR, ¹³C-NMR, HETCOR, and HRMS. In the ¹H-NMR spectrum (400 MHz, CDCl₃), a typical pattern was found in this series of compounds. The case of **9d** showed a two-proton triplet at 4.34 ppm (*J* = 2.0 Hz) corresponding to H-5, and two one-proton doublet triplet (*J* = 6.0 Hz, *J* = 2.0 Hz) at 6.19 and 7.10 ppm indicating the presence of olefin protons, H-3 and H-4, respectively. The ¹³C-NMR spectrum (100 MHz, CDCl₃) of **9d** showed one

sp^3 -car bon at 53.42 ppm cor re spond ing to C-5, two olefinic car bons at 129.11 ppm and 142.17 ppm, re spectively, in di cat ing C-3 and C-4, four ar o matic car bon at 115.69 ($J = 21.3$ Hz), 120.70 ($J = 9.1$ Hz), 135.17 ($J = 0$ Hz), and 159.31 ($J = 242.7$ Hz) re spec tively in di cat ing C'-3, C'-2, C'-1, and C'-4, and one car bonyl car bon at 168.98 ppm. Fur ther more be sides the mo lec u lar ion, some char ac ter is tic frag ments such as [$m^+ - 29$], [$m^+ - 55$], and [$m^+ - 82$] in the EI/MS spec tra were com monly found in **9a-f**. The detailed studies about the fragmental be hav iors of *N*-aryl α,β -unsaturated γ -lactam in EI/MS will be re ported else where. The ap pli ca tion of acryl amides to synthe size some other interesting heterocyclic com pounds now is cur rently in prog ress.

EXPERIMENTAL

Melting points (Yanaco mi cro melting-point appara tus) are un cor rected. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spec tra were ob tained on a Varian Gemini-200 or Varian Unity Plus 400 spec trom e ter. Chem i cal shifts are mea sured in parts per mil lion with re spect to TMS. El e men tal anal yses were re corded on a Heraeus CHN-O Rapid an alyzer. Mass spec tra were re corded on Chem/hp/mid dle in stru ment, and HRMS were re corded on JEOL, JMSD-200 or on JEOL, JMS-SX. Sil ica gel (230-400 mesh) for col umn chro ma tog raphy, and precoated sil ica gel plates (60F-254) for TLC were pur chased from E. Merck. UV light (254 nm) was used to de tect spots on TLC plates af ter development.

General procedure for the preparation of *N*-aryl 3-(phenylsulfonyl)propanamide (**6a-f**)

3-(phenylsulfonyl)propanoic acid (**4a-f**) (5 mmol), pre pared from so di um benzenesulfinate and acrylic acid, or pur chased from Aldrich Co., was re acted with ex cess thionyl chlo ride (20 mmol) un der re flux for 12 hr. Then the re ac tion mix ture was con cen trated un der re duced pres sure to re move excess thionyl chloride to afford 3-(phenylsulfonyl)propanoyl chlo ride (**5a-f**). With out fur ther pu ri fi cation, it (**5a-f**) was dis solved in an hy drous di chloro methane (100 mL), and cooled with ice bath. To this cooled so lu tion, it was added dropwise with the cor re spond ing amine (**3a-f**) (5 mmol), and fol lowed with triethylamine (5.5 mmol). The mix ture was stir red at 0 $^\circ\text{C}$ for 2 h, and then it was washed with 2% HCl (10 mL $\times 2$), and with brine (10 mL $\times 2$). Finally the or ganic layer was dried with an hy drous mag ne sium sul fate, and fil tered. The fil trate was con cen trated un der a re duced pres sure to give crude *N*-aryl 3-(phenylsulfonyl)propanamide (**6a-f**) which was pu ri fied by sil ica gel chro mat ographic col umn

(*n*-hexane/ethyl acetate = 1/1). The results obtained are shown as fol lows:

N-Phenyl-3-(phenylsulfonyl)propanamide (**6a**)

Pure (**6a**) (1.37 g, 95%) was ob tained as col or less crys tals; mp 116-117 $^\circ\text{C}$ ($\text{EtOAc} + n\text{-hexane}$); $R_f = 0.56$ ($\text{EtOAc} : n\text{-hexane} = 1 : 1$); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.93 (t, $J = 8.0$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 3.57 (t, $J = 8.0$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 7.08 (t, $J = 7.6$ Hz, 1H, Ar-H), 7.26 (t, $J = 8.0$ Hz, 2H, Ar-H), 7.43 (t, $J = 8.0$ Hz, 2H, Ar-H), 7.56 (t, $J = 7.6$ Hz, 2H, Ar-H), 7.66 (m, 1H, Ar-H), 7.94 (d, $J = 7.6$ Hz, 2H, Ar-H), 8.04 (br s, 1H, NH); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 29.80 (CH_2), 51.89 (CH_2), 119.87, 124.48, 127.96 128.92, 129.47, 134.10, 137.55, 138.63 (Ar-C), 167.01 (C=O); MS (EI, 70 eV), m/z 289 (M^+ , 54.30), 197 (7.26), 148 (2.95), 125 (41.02), 93 (100), 77 (19.07), 55 (34.67). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{S}$: C, 62.26; H, 5.23; N, 4.84. Found: C, 62.20; H, 5.28; N, 4.71.

N-(4-Methylphenyl)-3-(phenylsulfonyl)propanamide (**6b**)

Pure (**6b**) (1.45 g, 96%) was ob tained as col or less crys tals; mp 136-137 $^\circ\text{C}$ ($\text{EtOAc} + \text{hexane}$); $R_f = 0.41$ ($\text{EtOAc} : n\text{-hexane} = 1 : 1$); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 2.29 (s, 3H, CH_3), 2.89 (t, $J = 8.0$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 3.55 (t, $J = 8.0$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 7.07 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.30 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.57 (t, $J = 7.6$ Hz, 2H, Ar-H), 7.66 (t, $J = 7.6$ Hz, 1H, Ar-H), 7.81 (br s, 1H, NH), 7.94 (d, $J = 7.6$ Hz, 2H, Ar-H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 20.82, 29.84, 51.92, 119.99, 127.99, 129.44 134.06, 134.20, 134.92, 138.70, (Ar-C), 166.81 (C=O); MS (EI, 70 eV), m/z 303 (M^+ , 67.34), 197 (1.35), 162 (6.97), 125 (26.80), 107 (100), 106 (20.76), 77 (16.19), 55 (27.12). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$: C, 63.34; H, 5.65; N, 4.62. Found: C, 63.32; H, 5.72; N, 4.53.

N-(4-Methoxyphenyl)-3-(phenylsulfonyl)propanamide (**6c**)

Pure (**6c**) (1.52 g, 95%) was ob tained as col or less crys tals; mp 118-119 $^\circ\text{C}$ ($\text{EtOAc} + \text{hexane}$); $R_f = 0.24$ ($\text{EtOAc} : n\text{-hexane} = 1 : 2$); $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ : 2.85 (t, $J = 7.8$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 3.55 (t, $J = 7.8$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 3.78 (s, 3H, OCH_3), 6.84 (d, $J = 9.1$ Hz, 2H, Ar-H), 7.33 (d, $J = 9.1$ Hz, 2H, Ar-H), 7.42 (br s, 1H, NH), 7.54-7.68 (m, 3H, Ar-H), 7.92-7.96 (m, 2H, Ar-H); $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz) δ : 29.77, 52.00, 55.46, 114.13, 121.85, 128.03, 129.48, 130.58, 134.09, 138.75, 156.62, 166.82 (C=O); MS (EI, 70 eV), m/z 319 (M^+ , 100), 125 (15.74), 123 (98.01), 108 (26.44), 77 (7.13), 55 (23.66). Anal. Calcd for $\text{C}_{16}\text{H}_{17}\text{NO}_4\text{S}$: C, 60.17; H, 5.37; N, 4.39. Found: C, 59.99; H, 5.38; N, 4.30.

N-(4-Fluorophenyl)-3-(phenylsulfonyl)propanamide (**6d**)

Pure (**6d**) (1.49 g, 97%) was ob tained as col or less crys-

tals; mp 117-118 °C (EtOAc + hexane); $R_f = 0.32$ (EtOAc : *n*-hexane = 1 : 1); $^1\text{H-NMR}$ ($\text{DMSO-d}_6 + \text{CDCl}_3$, 200 MHz) δ : 2.94 (t, $J = 7.22$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 3.57 (t, $J = 7.22$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 6.88-6.96 (m, 2H, Ar-H), 7.35-7.42 (m, 2H, Ar-H), 7.51-7.71 (m, 3H, ArH), 7.91-7.95 (m, 2H, Ar-H), 8.33 (br s, 1H, NH); $^{13}\text{C-NMR}$ ($\text{DMSO-d}_6 + \text{CDCl}_3$, 50 MHz) δ : 29.49, 51.87, 115.47 (d, $J_{\text{C-C-F}} = 22.25$ Hz), 121.65 (d, $J_{\text{C-C-C-F}} = 7.80$ Hz), 127.88, 129.48, 133.66 (d, $J_{\text{C-C-C-C-F}} = 2.65$ Hz), 134.17, 138.53, 159.31 (d, $J_{\text{C-F}} = 242.20$ Hz), 167.13 (C=O); MS (EI, 70 eV), m/z 307 (M^+ , 15.69), 125 (63.20), 111 (100), 110 (10.02), 77 (16.42), 55 (32.63). *Anal. Calcd* for $\text{C}_{15}\text{H}_{14}\text{FNO}_3\text{S}$: C, 58.62; H, 4.59; N, 4.56. *Found*: C, 58.96; H, 4.85; N, 4.27.

N-(4-Chlorophenyl)-3-(phenylsulfonyl)propanamide (6e)

Pure (**6e**) (1.59 g, 98%) was obtained as colorless crystals; mp 160-161 °C (EtOAc + *n*-hexane); $R_f = 0.42$ (EtOAc : *n*-hexane = 1 : 1); $^1\text{H-NMR}$ ($\text{DMSO-d}_6 + \text{CDCl}_3$, 200 MHz) δ : 2.78 (t, $J = 7.30$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 3.53 (t, $J = 7.30$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 7.20, 7.92 (each d, $J = 8.0$ Hz, 4H, Ar-H), 7.49-7.70 (m, 5H, ArH), 10.03 (br s, 1H, NH); $^{13}\text{C-NMR}$ ($\text{DMSO-d}_6 + \text{CDCl}_3$, 50 MHz) δ : 29.24, 51.01, 120.34, 127.33, 127.40, 127.95, 128.86, 133.38, 137.08, 138.35, 166.89 (C=O); MS (EI, 70 eV), m/z 325 (M^{+2} , 4.68), 323 (M^+ , 14.32), 197 (10.13), 129 (29.09), 127 (100), 126 (12.53), 125 (90.66), 105 (10.94), 99 (7.21), 77 (28.95), 55 (41.46). *Anal. Calcd* for $\text{C}_{15}\text{H}_{14}\text{ClNO}_3\text{S}$: C, 55.64; H, 4.36; N, 4.33. *Found*: C, 55.86; H, 4.51; N, 4.27.

N-(4-Bromophenyl)-3-(phenylsulfonyl)propanamide (6f)

Pure (**6e**) (1.80 g, 97%) was obtained as colorless crystals; mp 169-170 °C (EtOAc + *n*-hexane); $R_f = 0.33$ (EtOAc : *n*-hexane = 1 : 1); $^1\text{H-NMR}$ ($\text{DMSO-d}_6 + \text{CDCl}_3$, 200 MHz) δ : 2.86 (t, $J = 7.30$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 3.52 (t, $J = 7.3$ Hz, 2H, $\text{SO}_2\text{CH}_2\text{CH}_2$), 7.35, 7.43 (each d, $J = 9.1$ Hz, 4H, Ar-H), 7.52-7.66 (m, 3H, ArH), 7.92 (dd, $J = 1.7$ Hz, 2H, ArH), 9.63 (br s, 1H, NH); $^{13}\text{C-NMR}$ ($\text{DMSO-d}_6 + \text{CDCl}_3$, 50 MHz) δ : 29.44, 51.52, 115.95, 121.05, 127.67, 129.07, 131.30, 133.66, 137.34, 138.53, 167.21 (C=O); MS (EI, 70 eV), m/z 369 (M^{+2} , 37.67), 367 (M^+ , 29.52), 197 (12.77), 173 (91.58), 171 (98.32), 125 (100), 55 (47.33). *Anal. Calcd* for $\text{C}_{15}\text{H}_{14}\text{BrNO}_3\text{S}$: C, 48.92; H, 3.83; N, 3.80. *Found*: C, 49.12; H, 3.51; N, 3.97.

General procedure for the preparation of *N*-aryl acrylamides (7a-f)

Under dry nitrogen, the mixture of *N*-aryl 3-(phenylsulfonyl)propanamides (**6a-f**) (5 mmol) and potassium *tert*-butoxide (0.57 g, 5.05 mmol) was suspended in anhydrous

THF (50 mL) at 0 °C for 1 h. At the end of the reaction, which was monitored by silica gel TLC (*n*-hexane : ethyl acetate = 2 : 1), the mixture was poured into a separating funnel and mixed with EtOAc (100 mL). The solution was washed with brine (10 mL \times 5), then the organic layer was separated, and dried with anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give the desired compound (**7a-f**), which was purified by silica gel chromatographic column (*n*-hexane/ethyl acetate = 2/1). The results obtained are shown as follows:

N-Phenylacrylamide (7a)

Pure (**7a**) (0.66 g, 90%) was obtained as colorless crystals; mp 103-105 °C (EtOAc + *n*-hexane) [lit.^{13b} mp 101-103]; $R_f = 0.42$ (EtOAc : *n*-hexane = 1 : 1.5); $^1\text{H-NMR}$ (CDCl_3 , 400 MHz) δ : 5.72 (dd, $J = 2.0$ Hz; 10.0 Hz, 1H, olefinic H), 6.30 (dd, $J = 10.0$ Hz; 17.0 Hz, 1H, olefinic H), 6.42 (dd, $J = 2.0$ Hz; 17.0 Hz, 1H, olefinic H), 7.11 (t, $J = 7.6$ Hz, 1H, Ar-H), 7.31 (t, $J = 8.4$ Hz, 2H, Ar-H), 7.60 (d, $J = 7.6$ Hz, 1H, Ar-H), 8.00 (br s, 1H, NH); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 120.13 (olefinic), 124.47 (olefinic), 127.59, 128.93, 131.24, 137.79 (Ar-C), 163.82 (C=O); MS (EI, 70 eV), m/z 147 (M^+ , 38.12), 93 (100), 55 (77.04).

N-(4-Methylphenyl)acrylamide (7b)

Pure (**7b**) (0.76 g, 95%) was obtained as colorless crystals; mp 139-140 °C (EtOAc + *n*-hexane) [lit.¹⁸ mp 138-139]; $R_f = 0.66$ (EtOAc : *n*-hexane = 1 : 1.5); $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ : 2.31 (s, 3H, CH_3), 5.72 (dd, $J = 2.0$ Hz; 10.0 Hz, 1H, olefinic H), 6.25 (dd, $J = 10.0$ Hz; 17.0 Hz, 1H, olefinic H), 6.41 (dd, $J = 2.0$ Hz; 17.0 Hz, 1H, olefinic H), 7.12, 7.46 (d, $J = 8.3$ Hz, each 2H, Ar-H), 7.64 (br s, 1H, NH); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 20.90 (CH_3), 120.15 (olefinic), 127.47 (olefinic), 129.52, 131.30, 134.20, 135.20 (Ar-C), 163.82 (C=O); MS (EI, 70 eV), m/z 161 (M^+ , 74.48), 107 (100), 106 (37.99), 55 (77.04).

N-(4-Methoxyphenyl)acrylamide (7c)

Pure (**7c**) (0.85 g, 96%) was obtained as colorless crystals; mp 99-101 °C (EtOAc + *n*-hexane) [lit.¹⁹ mp 95-96]; $R_f = 0.28$ (EtOAc : *n*-hexane = 1 : 1.5); $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ : 3.78 (s, 3H, OCH_3), 5.69 (dd, $J = 2.0$ Hz; 10.0 Hz, 1H, olefinic H), 6.26 (dd, $J = 10.0$ Hz; 17.0 Hz, 1H, olefinic H), 6.40 (dd, $J = 2.0$ Hz; 17.0 Hz, 1H, olefinic H), 6.83, 7.48 (d, $J = 9.0$ Hz, each 2H, Ar-H), 7.91 (br s, 1H, NH); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ : 43.58 (OCH_3), 126.62 (olefinic), 127.47 (olefinic), 127.80, 128.63, 130.65, 138.02 (Ar-C), 165.43 (C=O); MS (EI, 70 eV), m/z 177 (M^+ , 100), 123 (80.28), 122 (27.65), 108 (46.37), 55 (53.01).

N-(4-Fluorophenyl)acrylamide (7d)

Pure (**7d**) (0.743 g, 90%) was obtained as col or less crystals; mp 132–134 °C (EtOAc + *n*-hexane); $R_f = 0.57$ (EtOAc : *n*-hexane = 1 : 2); $^1\text{H-NMR}$ (DMSO-d₆ + CDCl₃, 400 MHz) δ : 5.68 (d, $J = 10.0$ Hz, 1H, olefinic H), 6.33 (d, $J = 16.8$ Hz, 1H, olefinic H), 6.43 (dd, $J = 16.8$ Hz, 10.0 Hz, 1H, olefinic H), 6.98–7.02, 7.67–7.70 (m, each 2H, Ar-H), 9.94 (br s, 1H, NH); $^{13}\text{C-NMR}$ (DMSO-d₆ + CDCl₃, 100 MHz) δ : 114.70 (d, $J_{c-c-F} = 22$ Hz), 120.99 (d, $J_{c-c-c-F} = 7.6$ Hz), 126.11 (olefinic C), 131.37 (olefinic C), 134.85 (d, $J_{c-c-c-c-F} = 2.2$ Hz), 158.20 (d, $J_{c-F} = 240.5$ Hz), 163.19 (C=O); MS (EI, 70 eV), *m/z* 165 (M⁺, 41.99), 112 (4.96), 111 (100), 83 (13.41), 55 (50.29). *Anal.* Calcd for C₉H₈NFO: C, 65.45; H, 4.88; N, 8.48. Found: C, 65.67; H, 4.59; N, 8.76.

N-(4-Chlorophenyl)acrylamide (7e)

Pure (**7e**) (8.42 g, 93%) was obtained as col or less crystals; mp 174–176 °C (EtOAc + *n*-hexane); [lit.²⁰ mp 101–103]; $R_f = 0.73$ (EtOAc : *n*-hexane = 1 : 2); $^1\text{H-NMR}$ (DMSO-d₆ + CDCl₃, 400 MHz) δ : 5.71 (dd, $J = 3.6$ Hz; 8.6 Hz, 1H, olefinic H), 6.39 (m, 2H, olefinic H), 7.23–7.27, 7.67–7.70 (m, each 2H, Ar-H), 9.85 (br s, 1H, NH); $^{13}\text{C-NMR}$ (DMSO-d₆ + CDCl₃, 100 MHz) δ : 120.24, 125.99, 127.26, 127.68, 130.76, 136.88 (Ar-C), 163.00 (C=O); MS (EI, 70 eV), *m/z* 183 (M⁺, 13.36), 181 (M⁺, 42.52), 129 (33.54), 127 (100), 55 (70.31); *Anal.* Calcd for C₉H₈NCIO: C, 59.52; H, 4.44; N, 7.71. Found: C, 59.74; H, 4.68; N, 7.79.

N-(4-Bromophenyl)acrylamide (7f)

Pure (**7f**) (1.08 g, 96%) was obtained as col or less crystals; mp 179–181 °C (EtOAc + *n*-hexane); [lit.¹⁸ mp 178–179]; $R_f = 0.49$ (EtOAc : *n*-hexane = 1 : 2); $^1\text{H-NMR}$ (DMSO-d₆ + CDCl₃, 400 MHz) δ : 5.70 (dd, $J = 3.0$ Hz; 8.6 Hz, 1H, olefinic H), 6.39 (m, 2H, olefinic H), 7.37–7.41 (m, 1H, Ar-H), 7.63 (d, $J = 8.8$ Hz, 1H, Ar-H), 9.89 (br s, 1H, NH); $^{13}\text{C-NMR}$ (DMSO-d₆ + CDCl₃, 100 MHz) δ : 115.29, 120.94, 126.37, 130.96, 131.11, 137.72 (Ar-C), 163.33 (C=O); MS (EI, 70 eV), *m/z* 227 (M⁺, 14.09), 225 (M⁺, 14.05), 173 (34.02), 171 (34.64), 91 (10.54), 55 (100); *Anal.* Calcd for C₉H₈NBrO: C, 47.82; H, 3.57; N, 6.20. Found: C, 47.86; H, 3.51; N, 5.98.

General procedure for one-pot preparation of *N*-Allyl *N*-aryl acrylamide (8a-f)

Under dry nitrogen, the mixture of *N*-aryl 3-(phenylsulfonyl)propanamides (**7a-f**) (5 mmol) and potassium *tert*-butoxide (0.57 g, 5.01 mmol) was suspended in anhydrous THF (100 mL) and stirred at 0 °C for 1 h. Then the mixture was added with an additional *tert*-butoxide (0.57 g, 5.01 mmol), and subsequently followed with allyl bromide (5.01

mmol), and stirred continuously at 0 °C for 1 h. At the end of the reaction, which was monitored by silica gel TLC (hexane/ethyl acetate = 2/1), the mixture was concentrated to remove THF under reduced pressure. The residue was mixed with EtOAc (100 mL), and washed with brine water (10 mL × 5). Then the solution was dried with anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give the desired compound (**8a-f**), which was purified by silica gel chromatographic column (*n*-hexane/ethyl acetate = 2/1).

***N*-Allyl *N*-Phenylacrylamide (8a)^{8b}**

Pure (**8a**) (0.66 g, 70%) was obtained as col or less liquid; $R_f = 0.45$ (EtOAc : *n*-hexane = 1 : 3); $^1\text{H-NMR}$ (CDCl₃, 400 MHz) δ : 4.38 (dt, $J = 6.4$ Hz, 1.2 Hz, 2H, allyl H), 5.09 (dd, $J = 1.2$ Hz; 8.0 Hz, 1H, olefin H), 5.12 (br s, 1H, olefin H), 5.50 (dd, $J = 10.2$ Hz; 1.6 Hz, 1H, olefin H), 5.84–5.93 (m, 1H, olefin H), 6.04 (dd, $J = 10.4$ Hz; 16.6 Hz, 1H, olefin H), 6.37 (dd, $J = 2.4$ Hz; 16.6 Hz, 1H, olefin H), 7.14–7.16 (m, 2H, Ar-H), 7.30–7.42 (m, 3H, Ar-H); $^{13}\text{C-NMR}$ (CDCl₃, 100 MHz) δ : 51.97, 117.44, 127.21, 127.38, 127.76, 128.34, 129.08, 132.59, 141.57, 164.79 (C=O); MS (EI, 70 eV), *m/z* 187 (M⁺, 24.18), 172 (19.51), 159 (12.40), 144 (7.66), 133 (29.07), 132 (50.04), 106 (23.14), 93 (22.18), 77 (35.68), 55 (100); HRMS: Calcd for C₁₂H₁₃NO: 187.0997. Found: 187.1027.

***N*-Allyl *N*-(4-Methylphenyl)acrylamide (8b)**

Pure (**8b**) (0.75 g, 75%) was obtained as col or less liquid; bp 135–145 °C (2.5 mmHg); $R_f = 0.34$ (EtOAc : *n*-hexane = 1 : 3); $^1\text{H-NMR}$ (CDCl₃, 400 MHz) δ : 2.36 (s, 3H, CH₃), 4.36 (dt, $J = 6.0$ Hz, 1.2 Hz, 2H, allyl H), 5.08 (d, $J = 7.6$ Hz, 1H, allyl H), 5.11 (br s, 1H, allyl H), 5.48 (dd, $J_{\text{gem-cis}} = 2.0$ Hz; 10.4 Hz, 1H, vinyl H), 5.83–5.92 (m, 1H, allyl H), 6.05 (dd, $J_{\text{cis-trans}} = 10.4$; 16.8 Hz, 1H, vinyl H), 6.36 (dd, $J_{\text{gem-trans}} = 2.0$ Hz; 16.8 Hz, 1H, vinyl H), 7.04, 7.19 (d, $J = 8.4$ Hz, each 2H, Ar-H); $^{13}\text{C-NMR}$ (CDCl₃, 100 MHz) δ : 20.61 (CH₃), 51.92 (CH₂), 117.34, 126.93, 127.53, 128.37, 129.65, 132.64, 137.23, 138.89, 164.80; MS (EI, 70 eV), *m/z* 201 (M⁺, 27.43), 186 (13.22), 147 (28.38), 146 (35.74), 144 (10.01), 132 (20.70), 120 (24.31), 118 (18.98), 107 (37.34), 91 (39.19), 77 (16.36), 65 (31.14), 55 (100); HRMS: Calcd for C₁₃H₁₅NO: 201.1154. Found: 201.1152.

***N*-Allyl *N*-(4-methoxyphenyl)acrylamide (8c)**

Pure (**8c**) (0.82 g, 76%) was obtained as col or less liquid; bp 165–170 °C (3 mmHg); $R_f = 0.54$ (EtOAc : *n*-hexane = 1 : 3); $^1\text{H-NMR}$ (CDCl₃, 400 MHz) δ : 3.83 (s, 3H, OCH₃), 4.34 (dt, $J = 6.0$ Hz, 1.2 Hz, 2H, allylic H), 5.07 (d, $J = 1.6$

Hz, 1H, allyl H), 5.11-5.14 (m, 1H, allyl H), 5.51 (dd, $J_{\text{gem-cis}} = 2.0$ Hz; 10.4 Hz, 1H, vi nyl H), 5.83-5.93 (m, 1H, allyl H), 6.04 (dd, $J_{\text{cis-trans}} = 10.4$ Hz, 16.8 Hz, 1H, vi nyl H), 6.36 (dd, $J_{\text{gem-trans}} = 2.0$ Hz; 16.8 Hz, 1H, vi nyl H), 7.89-6.92 (m, 2H, Ar-H), 7.05-7.09 (m, 2H, Ar-H); ^{13}C -NMR (CDCl₃, 100 MHz) δ : 52.35 (CH₂), 55.35 (OCH₃), 114.47, 117.80, 127.35, 128.58, 129.24, 132.92, 134.49, 158.84, 165.41 (C=O); MS (EI, 70 eV), m/z 217 (M⁺, 48.23), 163 (32.07), 148 (26.43), 147 (15.77), 134 (35.98), 130 (19.78), 123 (59.82), 120 (11.51), 108 (29.89), 94 (40.08), 77 (31.59), 64 (21.74), 55 (100); HRMS: Calcd for C₁₃H₁₅NO: 217.1103. Found: 217.1103.

N-Allyl N-(4-fluorophenyl)acrylamide (8d)

Pure (**8d**) (0.80 g, 78%) was obtained as col or less liquid; R_f = 0.43 (EtOAc : *n*-hexane = 1 : 3); ^1H -NMR (CDCl₃, 400 MHz) δ : 4.36 (dt, $J = 6.0$ Hz, 1.2 Hz, 2H, allyl H), 5.08 (br s, 1H, allyl H), 5.14 (d, $J = 10.8$ Hz, 1H, allyl H), 5.55 (dd, $J_{\text{gem-cis}} = 2.0$ Hz; 10.0 Hz, 1H, vi nyl H), 5.83-5.92 (m, 1H, allyl H), 6.02 (dd, $J_{\text{cis-trans}} = 10.0$ Hz; 16.8 Hz, 1H, vi nyl H), 6.39 (dd, $J_{\text{gem-trans}} = 2.0$ Hz; 16.8 Hz, 1H, vi nyl H), 7.07-7.17 (m, 4H, Ar-H); ^{13}C -NMR (CDCl₃, 100 MHz) δ : 52.16, 116.12 (d, $J_{\text{c-c-F}} = 8.4$ Hz), 117.92, 127.76, 128.17, 129.75 (d, $J_{\text{c-c-F}} = 22.8$ Hz), 132.54, 137.68, 161.52 (d, $J_{\text{c-F}} = 246.5$ Hz), 164.97; MS (EI, 70 eV), m/z 205 (M⁺, 21.72), 190 (17.87), 177 (11.56), 151 (36.14), 150 (44.70), 148 (11.09), 124 (17.08), 122 (18.68), 111 (25.51), 95 (34.66), 94 (14.18), 55 (100); HRMS: Calcd for C₁₂H₁₂NFO: 205.0903. Found: 205.0903.

N-Allyl N-(4-Chlorophenyl)acrylamide (8e)

Pure (**8e**) (0.80 g, 72%) was obtained as col or less liquid; R_f = 0.49 (EtOAc : *n*-hexane = 1 : 3); ^1H -NMR (CDCl₃, 400 MHz) δ : 4.36 (dt, $J = 6.0$ Hz, 1.2 Hz, 2H, allyl H), 5.08 (d, $J = 1.2$ Hz, 1H, allyl H), 5.14 (d, $J = 10.4$ Hz, 1H, allyl H), 5.56 (dd, $J_{\text{gem-cis}} = 2.0$ Hz, 10.2 Hz, 1H, vi nyl H), 5.82-5.92 (m, 1H, allyl H), 6.03 (dd, $J_{\text{cis-trans}} = 10.2$ Hz, 16.8 Hz, 1H, vi nyl H), 6.39 (dd, $J_{\text{gem-trans}} = 2.0$ Hz, 16.8 Hz, 1H, vi nyl H), 7.09-7.13 (m, 2H, Ar-H); 7.36-7.39 (m, 2H, Ar-H); ^{13}C -NMR (CDCl₃, 100 MHz) δ : 52.21, 118.11, 128.13, 128.27, 129.36, 129.54, 132.58, 133.48, 140.37, 165.01; MS (EI, 70 eV), m/z 223 (M⁺, 4.95), 221 (M⁺, 17.80), 206 (10.33), 178 (5.66), 167 (38.12), 166 (28.05), 140 (20.00), 130 (18.60), 127 (24.45), 111 (16.02), 94 (15.78), 75 (13.48), 55 (100); HRMS: Calcd for C₁₂H₁₂NCl³⁵O: 221.0607. Found: 221.0607.

N-Allyl N-(4-Bromophenyl)acrylamide (8f)

Pure (**8f**) (1.04 g, 78%) was obtained as col or less liquid; R_f = 0.41 (EtOAc : *n*-hexane = 1 : 3); ^1H -NMR (CDCl₃,

400 MHz) δ : 4.32 (dt, $J = 6.0$ Hz, 1.2 Hz; 2H, allyl H), 5.04 (d, $J = 1.2$ Hz, 1H, allyl H), 5.10 (d, $J = 10.4$ Hz, 1H, allyl H), 5.53 (dd, $J_{\text{gem-cis}} = 2.0$ Hz, 10.2 Hz, 1H, vi nyl H), 5.78-5.82 (m, 1H, allyl H), 6.01 (dd, $J_{\text{cis-trans}} = 10.2$ Hz, 16.8 Hz, 1H, vi nyl H), 6.39 (dd, $J_{\text{gem-trans}} = 2.0$ Hz, 16.8 Hz, 1H, vi nyl H), 7.00-7.02 (m, 2H, Ar-H); 7.47-7.50 (m, 2H, Ar-H); ^{13}C -NMR (CDCl₃, 100 MHz) δ : 52.17, 118.13, 121.43, 128.18, 128.25, 129.69, 132.55, 140.87, 164.95; MS (EI, 70 eV), m/z 267 (M⁺, 5.11), 266 (2.38), 265 (M⁺, 5.14), 211 (7.26), 184 (6.56), 171 (6.51), 157 (4.99), 130 (13.53), 94 (9.24), 76 (9.21), 55 (100); HRMS: Calcd for C₁₂H₁₂N Br⁷⁹O: 265.0102. Found: 265.0103.

General procedure for *N*-aryl α,β -unsaturated γ -lactams (**9a-f**)^{16b}

Compound **9a-f** (1 mmol) dissolved in anhydrous toluene (30 mL), was added with Grubbs catalyst (0.05 mmol). The mixture was stirred for 3 h at 80 °C under dry argon. The solvent was removed under vacuum, and the residue was subjected to a silica-gel column (*n*-hexane/MTBE = 1/1) to give **9a-f** in moderate yields.

N-Phenyl α,β -unsaturated γ -lactam (**9a**)

Pure **9a** (0.09 g, 57%) was obtained as col or less crystal, mp 85-86 °C (EtOAc + *n*-hexane) [lit.^{16a} 86 °C]; R_f = 0.53 (EtOAc : *n*-hexane = 1 : 1); IR ν_{max} (CH₂Cl₂) cm⁻¹: 1692.11, 1596.95; ^1H -NMR (400 MHz, CDCl₃) δ : 4.39 (t, $J = 2.0$ Hz, 2H, H-5), 6.22 (dt, $J = 6.0$ Hz, $J = 2.0$ Hz, 1H, H-3), 7.14 (dt, $J = 6.0$ Hz, $J = 2.0$ Hz, 1H, H-4), 7.11 (m, 1H, ArH), 7.35 (m, 2H, ArH), 7.68 (m, 2H, ArH); ^{13}C -NMR (100 MHz, CDCl₃) δ : 53.03 (C-5), 118.65, 123.97, 128.89 (C-3), 138.93, 142.26 (C-4), 169.99 (C=O); MS (EI, 70 eV): m/z 159 (M⁺, 100), 131 (13.16), 130 (60.69), 104 (41.53), 77 (43.44), 51 (12.08); HRMS: Calcd for C₉H₉NO: 159.0684. Found: 159.0684.

N-(4-Methylphenyl) α,β -unsaturated γ -lactam (**9b**)

Pure **9b** (0.11 g, 64%) was obtained as col or less crystal, mp 96-97 °C (EtOAc + *n*-hexane) [lit.^{16a} 95 °C]; R_f = 0.56 (EtOAc : *n*-hexane, 1 : 1); IR ν_{max} (CH₂Cl₂) cm⁻¹: 1694.00, 1598.15; ^1H -NMR (400 MHz, CDCl₃) δ : 2.33 (s, 3H, CH₃), 4.42 (t, $J = 2.0$ Hz, 2H, H-5), 6.26 (dt, $J = 6.0$ Hz, $J = 2.0$ Hz, 1H, H-3), 7.15 (dt, $J = 6.0$ Hz, $J = 2.0$ Hz, 1H, H-4); 7.18, 7.57 (each d, $J = 8.0$ Hz, 2H, ArH); ^{13}C -NMR (100 MHz, CDCl₃) δ : 20.77 (CH₃), 53.38 (C-5), 119.12, 129.24, 129.59 (C-3), 133.91, 136.55, 141.95 (C-5), 170.04 (C=O); MS (EI, 70 eV): m/z 173 (M⁺, 100), 145 (13.97), 144 (64.39), 130 (24.74), 118 (22.53), 91 (28.87), 65 (11.51), HRMS: Calcd for C₁₁H₁₁NO: 173.0841. Found: 173.0841.

N-(4-Methoxyphenyl) α,β -unsaturated γ -lactam (9c)

Pure **9c**(0.10 g, 53%) was obtained as col or less crystal, mp 103-104 °C (EtOAc + *n*-hexane) [lit.^{16a} 103 °C]; R_f = 0.40 (EtOAc : *n*-hexane, 1 : 1); IR ν_{max} (CH₂Cl₂) cm⁻¹: 1681.30, 1609.21; ¹H-NMR (400 MHz, CDCl₃) δ : 3.81 (s, 3H, OCH₃), 4.41 (t, J = 2.0 Hz, 2H, H-5), 6.27 (dt, J = 6.0 Hz, J = 2.0 Hz, 1H, H-3), 6.91-6.94 (m, 2H, ArH), 7.15 (dt, J = 6.0 Hz, J = 2.0 Hz, 1H, H-4), 7.57-7.60 (m, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ : 53.38 (C-5), 55.33 (OCH₃), 114.16, 114.40 120.99, 129.24 (C-3), 141.70 (C-4), 156.37, and 169.81 (C=O); MS (EI, 70 eV): *m/z* 189 (M⁺, 100), 174 (34.59), **160** (18.77), 146 (27.44), **134** (23.34), **107** (7.47), 92 (7.47), 77 (9.47); HRMS: Calcd for C₁₁H₁₁NO₂: 189.0790. Found: 189.0789.

N-(4-Fluorophenyl) α,β -unsaturated γ -lactam (9d)

Pure **9d**(0.11 g, 62%) was obtained as col or less crystal, mp 72-73 °C (EtOAc + *n*-hexane), R_f = 0.47 (EtOAc : *n*-hexane = 1 : 1); IR ν_{max} (CH₂Cl₂) cm⁻¹: 1680.59, 1594.80; ¹H-NMR (400 MHz, CDCl₃) δ : 4.34 (t, J = 2.0 Hz, 2H, H-5), 6.19 (dt, J = 6.0 Hz, J = 2.0 Hz, 1H, H-3), 6.96-7.02 (m, 2H, ArH), 7.10 (dt, J = 6.0 Hz, J = 2.0 Hz, 1H, H-4); 7.55-7.61 (m, 2H, ArH), ¹³C NMR (100 MHz, CDCl₃) δ : 53.42 (C-5), 115.69 (d, J_{c-c-F} = 21.3 Hz), 120.70 (d, J_{c-c-F} = 9.1 Hz), 129.11 (C-3), 135.17 (s, $J_{c-c-c-F}$ = 0 Hz), 142.17 (C-4), 159.31 (d, J_{c-F} = 242.7 Hz), 168.98 (C=O); MS (EI, 70 eV): *m/z* 177 (M⁺, 100), 149 (18.84), **148** (86.95), **122** (36.58), **95** (32.10), 75 (12.47); HRMS: Calcd for C₁₀H₈FNO: 177.0590. Found: 177.0592.

N-(4-Chlorophenyl) α,β -unsaturated γ -lactam (9e)

Pure **9e**(0.11 g, 57%) was obtained as col or less crystal, mp 76-77 °C (EtOAc + *n*-hexane), R_f = 0.53 (EtOAc : *n*-hexane = 1 : 1); IR ν_{max} (CH₂Cl₂) cm⁻¹: 1690.68, 1594.47; ¹H-NMR (400 MHz, CDCl₃) δ : 4.38 (t, J = 2.0 Hz, 2H, H-5), 6.22 (dt, J = 6.0 Hz, J = 2.0 Hz, 1H, H-3), 7.17 (dt, J = 6.0 Hz, J = 2.0 Hz, 1H, H-4); 7.29-7.31 (m, 2H, ArH), and 7.63-7.65 (m, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ : 52.97 (C-5), 119.70 (Ar-C), 126.95 (Ar-C), 128.79 (C-3), 134.12 (Ar-C), 137.51 (Ar-C), 142.41 (C-4), 169.99 (C=O); MS (EI, 70 eV): *m/z* 195 (M⁺, 35.09), 193 (M⁺, 100), 166 (15.52), **164** (42.67), 140 (17.90), **138** (45.11), 130 (41.46), 113 (11.08), **111** (32.99), 75 (15.48); HRMS: Calcd for C₁₀H₈ClNO: 193.0294. Found: 193.0294.

N-(4-Bromophenyl) α,β -unsaturated γ -lactam (9f)

Pure **9f**(0.15 g, 63%) was obtained as col or less crystal, mp 85-86 °C (EtOAc + *n*-hexane), R_f = 0.54 (EtOAc : *n*-hexane = 1 : 1); IR ν_{max} (CH₂Cl₂) cm⁻¹: 1682.77, 1585.45; ¹H-NMR (400 MHz, CDCl₃) δ : 4.40 (t, J = 2.0 Hz, 2H, H-5),

6.25 (dt, J = 6.0 Hz, J = 2.0 Hz, 1H, H-3), 7.19 (dt, J = 6.0 Hz, J = 2.0 Hz, 1H, H-4); 7.44-7.48 (m, 2H, ArH), 7.60-7.63 (m, 2-H, ArH); ¹³C NMR (100 MHz, CDCl₃) δ : 52.94 (C-5), 116.75 (Ar-C), 120.06 (Ar-C), 129.04 (C-3), 131.94 (Ar-C), 138.12 (Ar-C), 142.32 (C-4), 170.02 (C=O); MS (EI, 70 eV): *m/z* 239 (M⁺, 100), 237 (M⁺, 99.52), 210 (35.74), **208** (35.92), 184 (49.99), **182** (48.75), 157 (34.38), **155** (33.24), 130 (64.68), 103 (7.84), 79 (14.63), 76 (20.45), 75 (17.56); HRMS: Calcd for C₁₀H₈BrNO: 236.9798. Found: 236.9800.

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Key Words

N-aryl 3-(phenylsulfonyl)propanamides; *N*-aryl 2-alkenamides; *N*-allyl *N*-aryl 2-alkenamides; *N*-aryl α,β -unsaturated γ -lactams.

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