

## Rhodium-catalyzed C–C coupling reactions involving ring opening of strained molecules

### III \*. Reaction of *N*-allylamides of organic acids

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#### Abstract

The rhodium-catalyzed reaction of diphenyl(methylene)cyclopropane with *N*-allylamides of organic acids involves ring opening followed by regioselective coupling with the internal carbon atom of the allylamide double bond. Formation of an intermediate rhodacycle is postulated.

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#### Introduction

In previous papers [1] we showed that activated olefins or chelating unsaturated acids couple with diphenylmethylenecyclopropanes via  $\text{Rh}^{\text{I}}$ -catalyzed ring opening of the latter. Activated olefins underwent insertion regioselectively, only the terminal carbon atom being involved in carbon–carbon bond formation. In contrast, chelating unsaturated acids underwent non-regioselective reactions, which was rather surprising in view of the high regioselectivity (attack on the terminal carbon atom of the double bond) we had observed [2] in similar reactions of the same acids with alkynes and 1,2- and 1,3-dienes. The absence of regioselectivity was attributed to operation of different mechanisms, true double bond insertion being involved in the latter cases, and metallacycle formation in the case of the cyclopropane ring opening reactions [1].

Extension to other chelating substrates led us to study the behaviour of *N*-allylamides of organic acids, which have been reported to react with rhodium(I) complexes in isomerization reactions [3].

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\* For part II see ref. 1.



Table 1

Reaction of I (1.0 mmol) with *N*-allylamides of organic acids (2.0 mmol) and  $\text{RhCl}(\text{PPh}_3)_3$  (0.02 mmol) in toluene (3.0 ml) at 90°C for 60 h

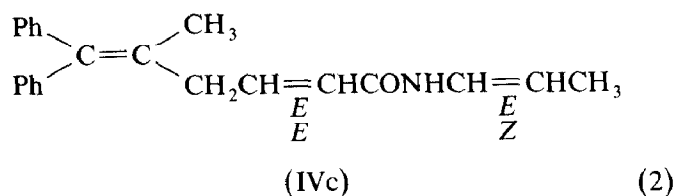
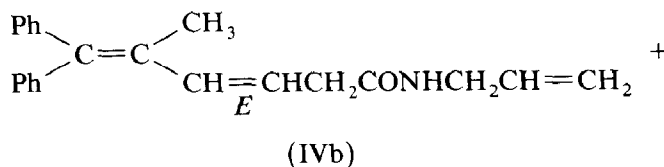
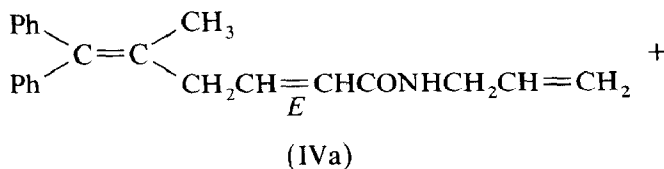
| R in II                                                                   | Conversion <sup>a</sup><br>(%) | Total yield <sup>a</sup><br>III + other<br>stereoisomers<br>(%) | Product yields <sup>a</sup> % |                 |                 |                                  |                 | Isomers and<br>hydrogenated<br>derivatives of<br>I |
|---------------------------------------------------------------------------|--------------------------------|-----------------------------------------------------------------|-------------------------------|-----------------|-----------------|----------------------------------|-----------------|----------------------------------------------------|
|                                                                           |                                |                                                                 | IIIa                          | IIIb            | IIIc            | other IIIa–IIIc<br>stereoisomers |                 |                                                    |
| COCH <sub>3</sub>                                                         | 93                             | 72                                                              |                               | 4               | 56              | 12 <sup>b</sup>                  | 8 <sup>c</sup>  | 3 <sup>d</sup>                                     |
| COCH <sub>3</sub> <sup>e</sup>                                            | 92                             | 53                                                              |                               | 15              | 22              | 16 <sup>b</sup>                  | 12 <sup>c</sup> | 17 <sup>d</sup>                                    |
| COPh                                                                      | 98                             | 73                                                              | 4                             | 10              | 40              | 19 <sup>f</sup>                  | 4 <sup>c</sup>  | 2 <sup>d</sup>                                     |
| COOEt                                                                     | 92                             | 60                                                              | 6                             |                 | 46              | 8 <sup>b</sup>                   | 6 <sup>c</sup>  | 2 <sup>d</sup>                                     |
| COCH=CHCH <sub>3</sub> -( <i>E</i> )                                      | 90                             | 58                                                              |                               |                 | 43              | 15 <sup>g</sup>                  | 7 <sup>c</sup>  | 2 <sup>d</sup>                                     |
| SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> - <i>p</i> -CH <sub>3</sub> | 90                             | 36                                                              | 10 <sup>h</sup>               | 12 <sup>h</sup> | 14 <sup>i</sup> |                                  | 9 <sup>c</sup>  | 3 <sup>d</sup>                                     |

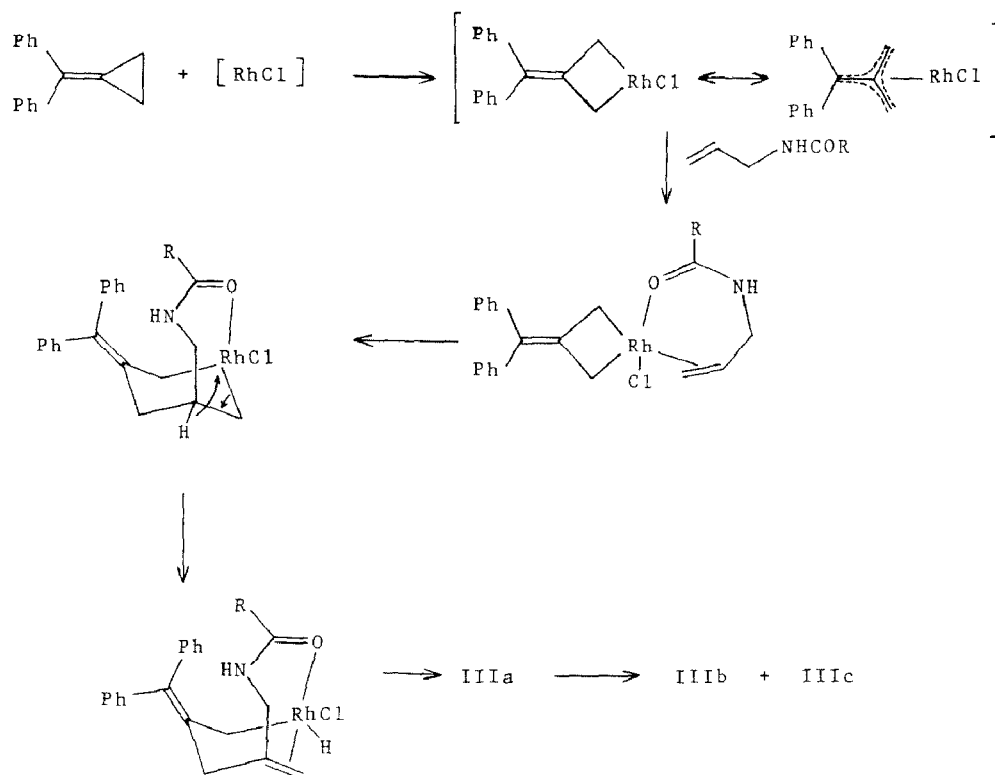
<sup>a</sup> By GLC, based on substrate I. <sup>b</sup> Three IIIa-IIIc stereoisomers. Closely spaced GLC peaks (1/1.5/1.5 ratio areas) which could not be isolated. <sup>c</sup> Three isomers of I [1]. <sup>d</sup> Two hydrogenated derivatives of I [1].

<sup>e</sup> In EtOH at 75°C. <sup>f</sup> Two IIIa-IIIc stereoisomers. Closely spaced GLC peaks (1/1.01) which could not be isolated. <sup>g</sup> Four IIIa-IIIc stereoisomers. Closely spaced GLC peaks (1/1/1.7/1.3) which could not be isolated. <sup>h</sup> Yield based on isolated products. <sup>i</sup> Yield estimated by GLC.

Yields are limited by self-reaction and hydrogenation (hydrogen transfer from the medium, particularly in ethanol) of the cyclopropane moiety, leading to isomers and dimers and to their hydrogenated derivatives [1]. Some (up to 15%) of the amide present in excess is transformed into *E*- and *Z*-enamides [3], along with small amounts of dimers (<10%), the synthesis of which is described in the following paper. *N*-Methyl-*N*-allyl amides do not react with the cyclopropane compound but isomerize to enamides.

It is noteworthy that allyl acrylamide exclusively reacts at the terminal carbon atom of the acrylic site, while the allylic species undergoes some isomerizations (eq. 2, yields: IVa, 26%; IVb, 10%; IVc (*E,E*) 15%; IVc (*E,Z*) 18%), showing that *N*-allylamides are not as reactive as acrylic compounds.





Scheme 1.

Steric effects can reverse the outcome; however, simply adding a terminal methyl group to the acrylic species causes C–C bond formation to occur at the allylic site (eq. 1). A methyl group on the terminal allyl carbon atom also hinders the reaction, as shown with  $PhCONHCH_2CH=CHCH_3$ .

From a mechanistic point of view the reaction can be rationalized in terms of metallacycle formation (Scheme 1, inert ligands are omitted for simplicity). The reason for the preference for the internal position of the double bond is not yet clear. Prior isomerization to enamides can be discarded in view of the fact that both *E*- and *Z*-1-propenyl amides react much more slowly.

We conclude that *N*-allylamides are suitable substrates for the introduction of a three-carbon amine chain into a cyclopropane substrate susceptible to cleavage by rhodium. Regioselective reaction has been achieved, probably via metallacycle formation.

## Experimental

Products were analyzed and quantitatively determined by GLC on a methylsilicone (OV-101 stationary phase) capillary column by use of an internal standard, and were isolated by HPLC, preparative TLC, or flash chromatography. Compounds were identified by comparison with authentic samples or by mass, IR, and NMR spectroscopy. Mass spectra were obtained with a Finnigan 1020 instrument at

70 eV, and IR spectra were recorded on a Perkin–Elmer 298 IR spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with AC100 and CXP200 Bruker spectrometers; chemical shifts are in ppm ( $\delta$ ) from TMS as reference. Melting points were determined with an Electrothermal apparatus, and are uncorrected.

The complex  $\text{RhCl}(\text{PPh}_3)_3$  [5] and the methylenecyclopropane derivatives (I) [6], (diphenyl)methylenecyclopropane [7], 1-methylene-2-phenylcyclopropane [8] and methylenecyclopropane [9] were prepared by published methods.

*N*-Allylacetamide was prepared as described in ref. 3 and *N*-allylamides and carbamates, and allyl-*p*-toluenesulfonamide were prepared by standard methods [10]. The amides and carbamates are colourless liquids except for *p*-toluenesulfonamide, which is a solid, m.p. 67–69°C. Crotylamine was made by the Gabriel synthesis [11] starting from crotyl bromide and potassium phthalimide. All the substrates showed analytical and spectral data consistent with their assigned structures.

*General procedure for the reaction of methylenecyclopropanes with N-allylamine derivatives*

In a Schlenk tube 0.02 g (0.02 mmol) of  $\text{RhCl}(\text{PPh}_3)_3$ , 1.0 mmol of substrate I, and 2.0 mmol of allylamine derivatives II were dissolved in toluene (3.0 ml) under nitrogen (eq. 1). The solution was stirred magnetically at 90°C for 60 h, then allowed to cool to room temperature; 15 ml of  $\text{Et}_2\text{O}$  were then added and the solution was filtered and the solvent distilled off under vacuum. Components were separated from the product mixture ( $\text{R} = \text{COMe}$ ) as described below. Hydrogenation of compounds III gave two diastereoisomers.

Compounds IIIa–IIIc and IVa–IVc were isolated by the following chromatographic procedures (eluent composition in parentheses): IIIb ( $\text{R} = \text{COMe}$ ): preparative TLC on silica gel (n-hexane/ $\text{EtOAc}$  4/6); IIIc ( $\text{R} = \text{COMe}$ ): flash chromatography on silica gel (n-hexane/ $\text{EtOAc}$  9/1); further purified by HPLC on C-18 reverse phase column ( $\text{MeOH}/\text{H}_2\text{O}$  76/24); IIIa, IIIb, IIIc ( $\text{R} = \text{COPh}$ ): flash chromatography on silica gel (n-hexane/ $\text{EtOAc}$  9/1); product IIIc was recrystallized from THF,  $\text{H}_2\text{O}$  solution; IIIa, IIIc ( $\text{R} = \text{COOEt}$  and  $\text{SO}_2\text{C}_6\text{H}_4$ -*p*-Me): flash chromatography on silica gel (n-hexane/ $\text{EtOAc}$  9/1 and 85/15, respectively); IIIc ( $\text{R} = E\text{-COCH=CHMe}$ ): flash chromatography on silica gel (n-hexane/ $\text{EtOAc}$  8/2); IVa–IVc ( $\text{R} = \text{COCH=CH}_2$ ): flash chromatography on silica gel (n-hexane/ $\text{EtOAc}$  6/4); purified by HPLC on C-18 reverse phase column ( $\text{MeOH}/\text{H}_2\text{O}$  73/27).

Melting points, and the  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, mass and IR spectral data for the new compounds III–IV are listed below (NMR spectra were recorded in  $\text{CDCl}_3$  solution unless otherwise indicated).

The *E*-configuration at the trisubstituted double bond has been established for compound IIIc ( $\text{R} = \text{COPh}$ ), and the similar values of the  $\text{CH=CCH}_3$   $^1\text{H}$  NMR coupling constant found for the other IIIb and IIIc compounds make the same configuration seem likely also for these compounds. This point was not investigated further, however.

IIIb ( $\text{R} = \text{COMe}$ ),  $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)=\text{CHNHCOCH}_3$ , oil. MS: ( $m/e$ ): 305 ( $M^+$ ), 246, 231, 191, 165, 138, 96, 91, 73(100), 69. IR film ( $\text{cm}^{-1}$ ): 3330, 2960, 1675, 1530, 1460, 1385, 1290, 815, 780, 720.  $^1\text{H}$  NMR:  $\delta$  1.53, d, 3H,  $\text{H}^a$ ,  $J_{\text{ae}}$  1.2 Hz; 1.68, s, 3H,  $\text{H}^b$ ; 2.06, s, 3H,  $\text{H}^c$ ; 2.84, s, 2H,  $\text{H}^d$ ; 6.62, br d, 1H  $\text{H}^e$ ,  $J_{\text{ef}}$  10.4 Hz; 6.80–7.10, br s, 1H,  $\text{H}^f$ ; 7.10–7.41, m, 10H, 2Ph.

IIIc (R = COMe),  $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3^b)\text{CH}^d=\text{C}(\text{CH}_3^a)\text{CH}_2^f\text{NHCOCH}_3$ , m.p. 109–112°C. MS: ( $m/e$ ): 305 ( $M^+$ ), 247, 246, 233, 231, 215, 191, 165, 96, 91, 73(100). IR (KBr)  $\text{cm}^{-1}$ : 3220, 3050, 2930, 1630, 1550, 1435, 1365, 1285, 1045, 765, 695.  $^1\text{H}$  NMR:  $\delta$  1.38, d, 3H,  $\text{H}^a$ ,  $J_{ad}$  1.3 Hz; 1.85, d, 3H,  $\text{H}^b$ ,  $J_{bd}$  0.5 Hz; 1.90, s, 3H,  $\text{H}^c$ ; 3.67, d, 2H,  $\text{H}^e$ ,  $J_{ef}$  5.7 Hz; 4.9–5.3, br s, 1H,  $\text{H}^f$ ; 5.93, br s, 1H,  $\text{H}^d$ ; 7.01–7.45, m, 10H, 2Ph.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  1.34, d, 3H,  $\text{H}^a$ ,  $J_{ad}$  1.3 Hz; 1.50, s, 3H,  $\text{H}^c$ ; 1.85, d, 3H,  $\text{H}^b$ ,  $J_{bd}$  0.5 Hz; 3.56, d, 2H,  $\text{H}^e$ ,  $J_{ef}$  5.4 Hz; 4.30–4.60, br s, 1H,  $\text{H}^f$ ; 5.87, br s, 1H,  $\text{H}^d$ ; 6.84–7.46, m, 10H, 2Ph. Hydrogenation of IIIc gave two diastereoisomeric products with MS: ( $m/e$ ): 309 ( $M^+$ ), 218, 168, 167(100), 165, 152, 143, 115, 100, 91, 83, 72, 60, 55.

IIIa (R = CPh),  $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3^b)\text{CH}_2^d\text{C}(=\text{CH}_2^a)\text{CH}_2^f\text{NHCOPh}$ , oil. MS: ( $m/e$ ): 367 ( $M^+$ ), 246, 231, 205, 191, 160, 134, 105(100), 77, 71, 57. IR (film)  $\text{cm}^{-1}$ : 3380, 2940, 1645, 1530, 1500, 1455, 780, 715.  $^1\text{H}$  NMR:  $\delta$  1.78, s, 3H,  $\text{H}^b$ ; 2.96, s, 2H,  $\text{H}^d$ ; 3.97, d, 2H,  $\text{H}^e$ ,  $J_{ef}$  5.9 Hz; 5.02, 5.10, 2s, 2H,  $\text{H}^a$ ; 5.90–6.15, br s, 1H,  $\text{H}^f$ ; 7.05–7.84, m, 15H, 3Ph.

IIIb (R = CPh),  $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3^b)\text{CH}_2^d\text{C}(\text{CH}_3^a)=\text{CHNHCOPh}$ , m.p. 107–110°C. MS: ( $m/e$ ): 367 ( $M^+$ ), 246, 246, 231, 205, 160, 134, 105(100), 91, 77. IR (KBr)  $\text{cm}^{-1}$ : 3420, 2940, 1660, 1520, 1495, 1455, 1280, 780, 770, 715.  $^1\text{H}$  NMR:  $\delta$  1.63, d, 3H,  $\text{H}^a$ ,  $J_{ae}$  1.3 Hz; 1.73, s, 3H,  $\text{H}^b$ ; 2.91, s, 2H,  $\text{H}^d$ ; 6.86, br d, 1H,  $\text{H}^e$ ,  $J_{ef}$  10.0 Hz; 6.95–7.86, m, 16 H,  $\text{H}^f$  and 3Ph.

IIIc (R = CPh),  $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3^b)\text{CH}^d=\text{C}(\text{CH}_3^a)\text{CH}_2^f\text{NHCOPh}$ , m.p. 123–125°C. MS: ( $m/e$ ): 367 ( $M^+$ ), 246, 231, 205, 160, 105(100), 91, 77, 57. IR (KBr)  $\text{cm}^{-1}$ : 3310, 3040, 2910, 1630, 1535, 1480, 1410, 1285, 1250, 795, 760, 690.  $^1\text{H}$  NMR:  $\delta$  1.47, d, 3H,  $\text{H}^a$ ,  $J_{ad}$  1.2 Hz; 1.88, s, 3H,  $\text{H}^b$ ; 3.88, d, 2H,  $\text{H}^e$ ,  $J_{ef}$  5.2 Hz; 5.80, br s, 1H,  $\text{H}^f$ ; 6.03, br s, 1H,  $\text{H}^d$ ; 7.05–7.67, m, 15H, 3Ph.  $^{13}\text{C}$  NMR:  $\delta$  16.36, 21.09, 2Me; 47.51,  $\text{CH}_2$ ; 126.14, 126.61, 126.93 (2C), 127.46 (2C), 127.28 (2C), 128.42 (2C), 129.29, 130.02 (2C), 130.23 (2C), 131.31 (16C, =CH); 131.72, 132.45, 134.58, 140.68, 142.71, 143.48 (6qC); 167.30 (CO).

IIIa (R = COOEt),  $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3^b)\text{CH}_2^d\text{C}(=\text{CH}_2^a)\text{CH}_2^f\text{NHCOOCH}_2\text{CH}_3$ , oil. MS: ( $m/e$ ): 335 ( $M^+$ ), 247, 246(100), 231, 217, 204, 191, 167, 115, 91, 56.  $^1\text{H}$  NMR:  $\delta$  1.23, t, 3H,  $\text{H}^c$ ,  $J_{cg}$  7.1 Hz; 1.74, s, 3H,  $\text{H}^b$ ; 2.86, s, 2H,  $\text{H}^d$ ; 3.65, d, 2H,  $\text{H}^e$ ,  $J_{ef}$  6.0 Hz; 4.09, q, 2H,  $\text{H}^g$ ,  $J_{gc}$  7.1 Hz; 4.60, br s, 1H,  $\text{H}^f$ ; 4.94, 5.02, 2s, 2H,  $\text{H}^a$ ; 7.06–7.32, m, 10H, 2Ph.

IIIc (R = COOEt),  $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3^b)\text{CH}^d=\text{C}(\text{CH}_3^a)\text{CH}_2^f\text{NHCOOCH}_2\text{CH}_3$ , oil. MS: ( $m/e$ ): 335 ( $M^+$ ), 246, 233(100), 231, 215, 205, 191, 115, 103, 91. IR (film)  $\text{cm}^{-1}$ : 3370, 3000, 2950, 1720, 1530, 1455, 1260, 780, 715.  $^1\text{H}$  NMR:  $\delta$  1.23, t, 3H,  $\text{H}^c$ ,  $J_{cg}$  7.1 Hz; 1.38, d, 3H,  $\text{H}^a$ ,  $J_{ad}$  1.0 Hz; 1.83, s, 3H,  $\text{H}^b$ ; 3.58, d, 2H,  $\text{H}^e$ ,  $J_{ef}$  6.0 Hz; 4.09, q, 2H,  $\text{H}^g$ ,  $J_{gc}$  7.1 Hz; 4.45, br s, 1H,  $\text{H}^f$ ; 5.92, s, 1H,  $\text{H}^d$ ; 7.06–7.35, m, 10H, 2Ph.

IIIc (R = *E*-COCH=CHMe),  $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3^b)\text{CH}^d=\text{C}(\text{CH}_3^a)\text{CH}_2^f\text{NHCOCH}^g=\text{CHCH}_3$ , oil. MS: ( $m/e$ ): 321 ( $M^+$ ), 263, 247(100), 232, 216, 206, 192, 165, 97, 85, 69. IR (film)  $\text{cm}^{-1}$ : 3310, 2940, 1685, 1640, 1560, 1450, 1235, 980, 780, 715.  $^1\text{H}$  NMR:  $\delta$  1.37, d, 3H,  $\text{H}^a$ ,  $J_{ad}$  1.3 Hz; 1.84, d, 3H,  $\text{H}^b$ ,  $J_{bd}$  0.7 Hz; 1.85, dd, 3H,  $\text{H}^c$ ,  $J_{ch}$  6.8 Hz,  $J_{cg}$  1.6 Hz; 3.73, dd, 2H,  $\text{H}^e$ ,  $J_{ef}$  5.8 Hz,  $J_{ed}$  1.0 Hz; 5.13, br s, 1H,  $\text{H}^f$ ; 5.68, dq, 1H,  $\text{H}^g$ ,  $J_{gh}$  15.2 Hz,  $J_{gc}$  = 1.6 Hz; 5.94, m, 1H,  $\text{H}^d$ ; 6.78, dq, 1H,  $\text{H}^h$ ,  $J_{hg}$  15.2 Hz,  $J_{hc}$  6.8 Hz; 7.01–7.42, m, 10H, 2Ph.

IIIa (R =  $\text{SO}_2\text{C}_6\text{H}_4$ -*p*-Me),  $\text{Ph}_2\text{C}=\text{C}(\text{CH}_3^b)\text{CH}_2^d\text{C}(=\text{CH}_2^a)\text{CH}_2^f\text{NHSO}_2\text{C}_6\text{H}_4\text{CH}_3$ , oil. MS: ( $m/e$ ): 418 ( $M + 1^+$ ), 247, 171, 155, 105, 91, 86, 84(100), 77, 65, 49.  $^1\text{H}$

NMR:  $\delta$  1.66, s, 3H, H<sup>b</sup>; 2.41, s, 3H, H<sup>c</sup>; 2.75, s, 2H, H<sup>d</sup>; 3.42, d, 2H, H<sup>e</sup>,  $J_{ef}$  = 9.8 Hz; 4.40–4.75, br s, 1H, H<sup>f</sup>; 4.91, 5.02, 2s, 2H, H<sup>a</sup>; 6.96–7.76, m, 14H, 2Ph and 4 aromatic H.

IIIc (R = SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-*p*-Me), Ph<sub>2</sub>C=C(CH<sub>3</sub>)CH=C(CH<sub>3</sub>)CH<sub>2</sub>NH<sup>f</sup>SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, oil. MS: ( $m/e$ ): 418 ( $M+1^+$ ), 263, 247, 334, 205, 167, 155, 105, 91(100), 65. IR (film) cm<sup>-1</sup>: 3300, 2950, 1745, 1670, 1610, 1500, 1455, 1340, 1175, 1110, 830, 780, 750, 720, 680. <sup>1</sup>H NMR:  $\delta$  1.33, s, 3H, H<sup>a</sup>; 1.76, s, 3H, H<sup>b</sup>; 2.41, s, 3H, H<sup>c</sup>; 3.34, d, 2H, H<sup>e</sup>,  $J_{ef}$  6.2 Hz; 4.40–4.65, br s, 1H, H<sup>f</sup>; 5.89, br s, 1H, H<sup>d</sup>; 6.97–7.76, m, 14H, 2Ph and 4 aromatic H.

IVa (*E*), Ph<sub>2</sub>C=C(CH<sub>3</sub>)CH<sub>2</sub>CH=CCHCONHCH<sub>2</sub>CH=CHH, oil. MS: ( $m/e$ ): 317 ( $M^+$ ), 233, 218, 217, 205, 203, 181, 171, 165, 155, 150, 141, 128, 123, 115, 105, 99(100), 91, 84, 57, 55. IR (film) cm<sup>-1</sup>: 3295, 3040, 2940, 1680, 1640, 1560, 1455, 1290, 995, 930, 915, 780, 720. <sup>1</sup>H NMR:  $\delta$  1.76, s, 3H, H<sup>a</sup>; 2.95, dd, 2H, H<sup>b</sup>,  $J_{bc}$  6.7 Hz,  $J_{bd}$  1.4 Hz; 3.93, pseudo t, 2H, H<sup>f</sup>,  $J_{fe} = J_{fg} = 5.7$  Hz; 5.12, d, 1H, H<sup>i</sup>,  $J_{ig}$  10.5 Hz; 5.18, d, 1H, H<sup>h</sup>,  $J_{hg}$  17.2 Hz; 5.82, d, 1H, H<sup>d</sup>,  $J_{dc}$  15.0 Hz; 5.84, ddt, 1H, H<sup>g</sup>,  $J_{gh}$  17.2 Hz;  $J_{gi}$  10.5 Hz,  $J_{gf}$  5.7 Hz; 6.08, brt, 1H, H<sup>e</sup>,  $J_{ef}$  5.7 Hz; 6.88, dt, 1H, H<sup>c</sup>,  $J_{cd}$  15.0 Hz,  $J_{cb}$  6.7 Hz; 7.07–7.35, m, 10H, 2Ph.

IVb (*E*), Ph<sub>2</sub>C=C(CH<sub>3</sub>)CH=CHCH<sub>2</sub>CONHCH<sub>2</sub>CH=CHH, oil. MS: ( $m/e$ ): 317 ( $M^+$ ), 233, 218, 203, 191, 155, 115, 99(100), 91, 84, 57. IR (film) cm<sup>-1</sup>: 3310, 2940, 1665, 1650, 1455, 990, 980, 930, 915, 780, 750, 715. <sup>1</sup>H NMR:  $\delta$  1.95, s, 3H, H<sup>a</sup>; 3.01, dd, 2H, H<sup>d</sup>,  $J_{dc}$  7.4 Hz,  $J_{db}$  1.0 Hz; 3.86, pseudo tt, 2H, H<sup>f</sup>,  $J_{fg} = J_{fe} = 5.7$  Hz,  $J_{fi} = J_{fh} = 1.5$  Hz; 5.13, ddt, 1H, H<sup>h</sup>,  $J_{hg}$  10.0 Hz,  $J_{hi} = J_{hf} = 1.5$  Hz; 5.15, ddt, 1H, H<sup>i</sup>,  $J_{ig}$  17.3 Hz,  $J_{ih} = J_{if} = 1.5$  Hz; 5.40–5.70, br s, 1H, H<sup>c</sup>; 5.82, ddt, 1H, H<sup>g</sup>,  $J_{gi}$  17.3 Hz,  $J_{gh}$  10.0 Hz,  $J_{gf}$  5.7 Hz; 5.88, dt, 1H, H<sup>e</sup>,  $J_{cb}$  15.6 Hz,  $J_{cd}$  7.4 Hz; 6.43, dt, 1H, H<sup>b</sup>,  $J_{bc}$  15.6 Hz,  $J_{bd}$  1.0 Hz; 7.05–7.36, m, 10H, 2Ph.

IVc (*E,E*), Ph<sub>2</sub>C=C(CH<sub>3</sub>)CH<sub>2</sub>CH=CHCONHCH=CHCH<sub>3</sub>, oil. MS: ( $m/e$ ): 317 ( $M^+$ ), 260, 233, 218, 203, 191, 155, 115, 99, 91(100), 84, 57. IR (film) cm<sup>-1</sup>: 3350, 1680, 1650, 1270, 1030, 985, 810, 780, 710. <sup>1</sup>H NMR:  $\delta$  1.68, dd, 3H, H<sup>h</sup>,  $J_{hg}$  6.7 Hz,  $J_{hf}$  1.4 Hz; 1.76, s, 3H, H<sup>a</sup>; 2.97, dd, 2H, H<sup>b</sup>,  $J_{bc}$  6.7 Hz,  $J_{bd}$  1.4 Hz; 5.18, dq, 1H, H<sup>g</sup>,  $J_{gf}$  13.8 Hz,  $J_{gh}$  6.7 Hz; 6.72, d, 1H, H<sup>d</sup>,  $J_{dc}$  15.2 Hz; 6.79, m, 1H, H<sup>f</sup>; 6.93, dt, 1H, H<sup>c</sup>,  $J_{cd}$  15.2 Hz,  $J_{cb}$  6.7 Hz; 7.05–7.33, m, 11H, 2Ph and H<sup>e</sup>.

IVc (*E,Z*), Ph<sub>2</sub>C=C(CH<sub>3</sub>)CH<sub>2</sub>CH=CHCONHCH=CHCH<sub>3</sub>, oil. MS: ( $m/e$ ): 317 ( $M^+$ ), 260, 233, 219, 205, 191, 165, 115, 105, 99, 91(100), 55. IR (film) cm<sup>-1</sup>: 3300, 2950, 1670, 1640, 1530, 1275, 990, 815, 775, 715. <sup>1</sup>H NMR:  $\delta$  1.62, d, 3H, H<sup>h</sup>,  $J_{hg}$  7.2 Hz; 1.78, s, 3H, H<sup>a</sup>; 3.00, dd, 2H, H<sup>b</sup>,  $J_{bc}$  6.8 Hz,  $J_{bd}$  1.5 Hz; 4.85, dq, 1H, H<sup>g</sup>,  $J_{gf}$  8.4 Hz,  $J_{gh}$  7.2 Hz; 5.79, d, 1H, H<sup>d</sup>,  $J_{dc}$  15.2 Hz; 6.87, m, 1H, H<sup>f</sup>; 6.98, dt, 1H, H<sup>c</sup>,  $J_{cd}$  15.2 Hz,  $J_{cb}$  6.8 Hz; 7.10–7.33, m, 11H, H<sup>e</sup> and 2Ph.

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