

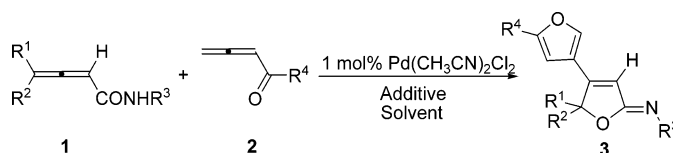
Pd(CH₃CN)₂Cl₂-Catalyzed Oxidative Heterodimerization Reaction of 2,3-Allenamides and 1,2-Allenyl Ketones: An Efficient Synthesis of 4-(Furan-3'-yl)-2(5*H*)-furanimines

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The Pd(II)-catalyzed oxidative heterodimerization reaction of 2,3-allenamides and 1,2-allenyl ketones was studied. It provides an efficient route for the synthesis of the polysubstituted 4-(furan-3'-yl)-2(5*H*)-furanimines, which are not readily available from the known methods. Due to the application of benzoquinone, the loadings of both the palladium catalyst and ketone have been greatly reduced for the oxidative heterodimerization of 2,3-allenamides and 1,2-allenyl ketones in acetic acid.

Introduction

Allenenes are a class of compounds with a 1,2-diene functionality possessing two mutually perpendicular π -orbitals showing unique reactivity and interesting stereoselectivity.^{1–3} Hashmi et al. first reported the homodimerization reaction of 1,2-allenyl ketones.⁴ We also described a Pd(II)-catalyzed one-pot methodology to form bis-butenolides through homodimerization of 2,3-allenoic acids.⁵ Recently, we have focused our attention on the reaction between two different classes of allenenes, i.e., the

cross-coupling cyclization of 2,3-allenoic acids and 1,2-allenyl ketones, in which Pd(II) was regenerated through consuming a large amount of 1,2-allenyl ketones via cyclometalation and the subsequent protonation.⁶ Herein, we wish to report a cross-coupling cyclization reaction between 2,3-allenamides and 1,2-allenyl ketones to form 4-(furan-3'-yl)furanimines, in which Pd(II) was regenerated by the addition of benzoquinone as the oxidant under the acidic conditions.⁷

Results and Discussion

After realizing the heterodimerization of 2,3-allenoic acids and 1,2-allenyl ketones to form polysubstituted 4-(furan-3'-yl)-2(5*H*)-furanones,⁶ we wish to extend this type of oxidative cyclodimerization reaction. We first tried the heterodimerization between 2,3-allenamides and 1,2-allenyl ketones. It is important to note that according to our previous study on the coupling–cyclization reaction of 2,3-allenamides with organic halides there are two cyclization patterns: one is the N-attack to form γ -lactams and the other is the O-attack to form furanimines, which may be determined by the steric effect at the 4-position of 2,3-allenamides and the substituent of the nitrogen atom (Scheme 1).⁸

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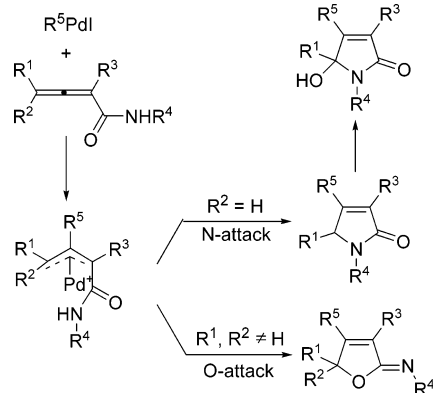
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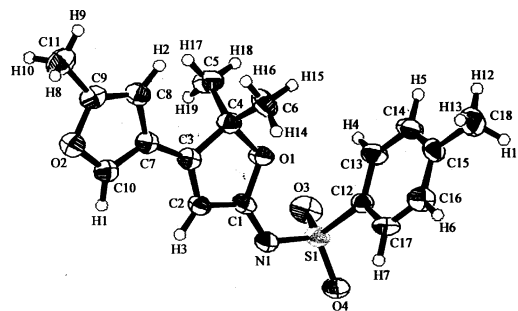
SCHEME 1. Two Pd(0)-Catalyzed Cyclization Patterns of 2,3-Allenamides with Organic Halides

TABLE 1. The Heterocyclizative Dimerization Reaction of 1a and 2

entry	2 (R ⁴)	condition ^a	time/temp (h/°C)	yield of 3 (%)
1	Me (2a)	condition A	3/30	86 (Z-3aa)
2	Me (2a)	condition B	5/30	66 (Z-3aa)
3 ^b	Ph (2b)	condition A	3/30	60 (Z-3ab)
4	Ph (2b)	condition B	5/30	75 (Z-3ab)
5	Bn (2c)	condition B	3/35	63 (Z-3ac)
6	<i>n</i> -Bu (3d)	condition A	1/25	63 (Z-3ad)
7	<i>n</i> -Bu (3d)	condition B	1.5/40	69 (Z-3ad)

^a Condition A: A solution of **1a** (0.25 mmol), **2** (1.25 mmol), and Pd(CH₃CN)₂Cl₂ (5 mol %) was stirred in CH₃CN for the time indicated in the table. Condition B: A solution of **1a** (0.25 mmol), **2** (0.5 mmol), benzoquinone (1.0 equiv), and Pd(CH₃CN)₂Cl₂ (1 mol %) was stirred in CH₃CN for the time indicated in the table. ^b The reaction was carried out in 0.5 mmol scale of **1a**.

Fortunately, when 2,3-allenamide **1a** was used as the substrate to react with 5.0 equiv of 1,2-allenyl ketone **2a** in the presence of 5 mol % of Pd(CH₃CN)₂Cl₂ in CH₃CN, the standard condition for the heterodimerization reaction between 2,3-allenoic acids and 1,2-allenyl ketones,⁶ we obtained heterodimerization product **Z-3aa** in 86% yield as the only product (entry 1, Table 1). It is the O-attack product as determined by the NMR analysis with the comparison to the similar products.⁸ The stereochemistry was established by the X-ray diffraction studies of **Z-3aa** (Figure 1).⁹ Some typical results are listed in Table 1 (entries 1, 3, and 6, Table 1). It should be noted when 1.0 equiv of benzoquinone was introduced to the reaction system, the loading of 1,2-allenyl ketones **2** and the catalyst could be reduced (entries 2, 4, 5, and 7, Table 1).

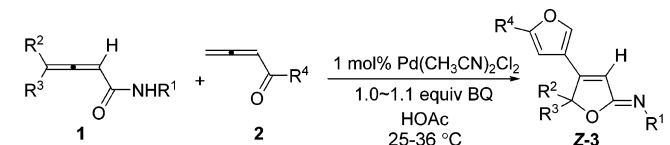
(9) Crystal data for **3aa**: colorless prismatic; crystal dimensions, 0.2 × 0.2 × 0.2 mm³; crystal system, triclinic; lattice type, primitive; space group, P1 (no. 2); Mo Kα (λ = 0.71069 Å), *a* = 7.109(2) Å, *b* = 9.531(2) Å, *c* = 13.161(3) Å, α = 80.08(2)°, β = 83.70(2)°, γ = 85.63(2)°, *V* = 871.5(4) Å³; *T* = 25 °C, *Z* = 2; *D*_{calcd} = 1.316 g/cm³; *F*₀₀₀ = 364.00, μ(Mo Kα) = 2.06 cm⁻¹. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center, CCDC 266567.


FIGURE 1. ORTEP drawing of the product Z-3aa.
TABLE 2. Pd(CH₃CN)₂Cl₂-Catalyzed Oxidative Cyclization–Dimerization Reaction between 2,3-Allenamide 1b and 1,2-Allenyl Ketone 2a^a

entry	2a (equiv)	BQ ^b (equiv)	solvent	time/temp (h/°C)	yield of Z-3ba (%) ^c
1	5		CH ₃ CN	12/19	0
2	5		CH ₃ CN/HOAc = 3:1	6/30	27
3	10		CH ₃ CN/HOAc = 3:1	2/35	50
4	5	1.0	CH ₃ CN/HOAc = 3:1	2/35	82
5	2	1.0	CH ₃ CN/HOAc = 3:1	4/37	84
6 ^d	5	1.0	CH ₃ CN	7.5/36	0
7	2	1.0	DMA/HOAc = 3:1	4.5/36	0
8	2	1.0	HOAc	2/40	84
9 ^e	2	1.0	HOAc	2/36	86
10 ^e	2	1.5	HOAc	2.5/35	86
11 ^e	1.5	1.1	HOAc	2/35	60

^a The reaction was carried out with 0.25 mmol of 2,3-allenamide. ^b BQ = benzoquinone. ^c Isolated yield. ^d 1.0 equiv of HOAc was used. ^e 1 mol % of Pd(CH₃CN)₂Cl₂ was used.

However, to our disappointment, the scope of the reaction is quite limited. When N-benzyl-substituted 2,3-allenamide **1b** was used to react with **2a** in the presence of 5 mol % of Pd(CH₃CN)₂Cl₂ in CH₃CN, no expected product was formed (entry 1, Table 2). It was reported that acids are required to regenerate the catalytically active Pd(II) species via protonation.⁶ Thus, CH₃CN/HOAc = 3/1 was used as the solvent instead of CH₃CN; luckily we obtained the bicyclic product **Z-3ba** in 27% isolated yield (entry 2, Table 2). It is also the O-attack product **Z-3ba** as determined by the NMR analysis with the comparison to similar products.⁸ The yield was improved when 10.0 equiv of **2a** were used since it was reported that compound **2a** may act as the Pd(II)-regenerating reagent (compare entry 2 with entry 3, Table 2).⁶ To reduce the loading of **2a**, 1 equiv of benzoquinone was introduced as the oxidant to regenerate the Pd(II) species.⁷ Fortunately, in the presence of 1.0 equiv of benzoquinone, the yield jumped from 27% to 82% (entry 4, Table 2). The reaction can also afford **Z-3ba** in 84% yield with only 2.0 equiv of **2a** (entry 5, Table 2). No product was formed when only 1.0 equiv of HOAc was used (entry 6, Table 2). DMA is not an effective solvent for the reaction (entry 7, Table 2). The loading of the catalyst, i.e., Pd(CH₃CN)₂Cl₂, also can be reduced to 1

TABLE 3. Pd(CH₃CN)₂Cl₂-Catalyzed Oxidative Cyclization–Dimerization Reaction between 2,3-Allenamides **1** and 1,2-Allenyl Ketones **2**^a


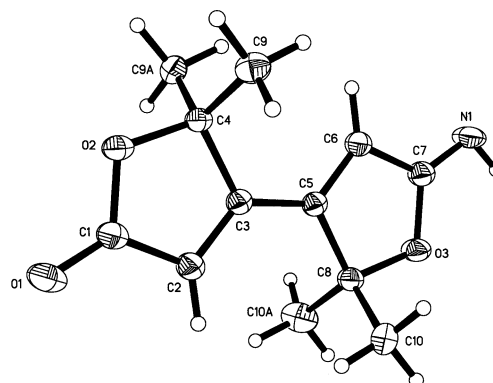
entry	substrate 1			substrate 2	BQ (equiv)	time (h)	yield of 3 (%) ^b
	R ¹	R ²	R ³	R ⁴			
1	Bn	CH ₃	CH ₃ (1b)	CH ₃ (2a)	1.0	2	86 (Z-3ba)
2	Bn	CH ₃	CH ₃ (1b)	Ph (2b)	1.1	2	56 (Z-3bb)
3	Bn	CH ₃	CH ₃ (1b)	Bn (2c)	1.0	10	81 (Z-3bc)
4	Bn	CH ₃	CH ₃ (1b)	<i>n</i> -Bu (2d)	1.1	10	76 (Z-3bd)
5	Bn	CH ₃	CH ₃ (1b)	<i>n</i> -C ₇ H ₁₅ (2e)	1.0	17	64 (Z-3be)
6 ^c	H	CH ₃	CH ₃ (1c)	CH ₃ (2a)	1.1	6	81 (Z-3ca)
7	H	CH ₃	CH ₃ (1c)	Ph (2b)	1.1	11	55 (Z-3cb)
8 ^d	H	CH ₃	CH ₃ (1c)	Bn (2c)	1.1	5	71 (Z-3cc)
9	H	CH ₃	CH ₃ (1c)	<i>n</i> -Bu (2d)	1.0	6.5	76 (Z-3cd)
10	H	CH ₃	CH ₃ (1c)	<i>n</i> -C ₇ H ₁₅ (2e)	1.0	5	59 (Z-3ce)
11	<i>n</i> -Bu	CH ₃	CH ₃ (1d)	CH ₃ (2a)	1.1	4	68 (Z-3da)
12	H	(CH ₂) ₅ (1e)		CH ₃ (2a)	1.1	5.5	80 (Z-3ea)
13	H	(CH ₂) ₅ (1e)		<i>n</i> -Bu (2d)	1.1	6.5	70 (Z-3ed)
14	Bn	CH ₃	Et (1f)	CH ₃ (2a)	1.0	4	69 (Z-3fa)
15	Bn	CH ₃	Et (1f)	<i>n</i> -Bu (2d)	1.0	3	63 (Z-3fd)

^a Condition C: The reaction was carried out with 0.25–0.30 mmol of 2,3-allenamide **1**, 2.0 equiv of 1,2-allenyl ketones **2**, 1.0–1.1 equiv of benzoquinone, and 1 mol % of Pd(CH₃CN)₂Cl₂ in HOAc. ^b Isolated yield. ^c 5.0 equiv of **2a** was used and the reaction was conducted at 50 °C. ^d The reaction was carried out in 0.4 mmol scale of **1c**; HOAc:CH₃CN = 1:1 was used as the solvent.

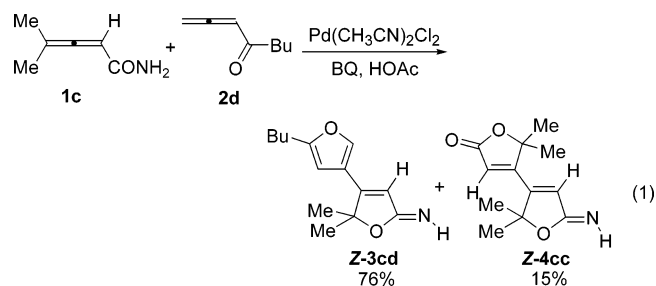
mol % without decreasing the yield (entry 9, Table 2). Increasing the loading of benzoquinone could not improve the yield (entry 10, Table 1), while by reducing the amount of **2a** to 1.5 equiv the yield of **Z-3ba** dropped to 60% (entry 11, Table 2). Acetic acid, together with benzoquinone, may be responsible for the facile regeneration of the catalytically active Pd(II) from the in situ generated Pd(0).

Some typical results of different combinations of 2,3-allenamides with 1,2-allenyl ketones under the standard conditions (2.0 equiv of 1,2-allenyl ketones **2**, 1 mol % of Pd(CH₃CN)₂Cl₂, and 1.0 equiv of benzoquinone in HOAc) are listed in Table 3. The substituent on the nitrogen atom of 2,3-allenamides may be benzyl (entries 1–5, 14, and 15, Table 3), alkyl (entry 11, Table 3), or hydrogen (entries 6–10, 12, and 13, Table 3). The 1,2-allenyl ketones that bear alkyl (entries 1, 4–6, and 9–15, Table 3), aryl (entries 2 and 7, Table 3), and benzyl (entries 3 and 8, Table 3) groups were also successfully cyclodimerized with 2,3-allenamides **1** to afford the corresponding products **3** in moderate to good yields. No expected product was formed by TLC analysis when the mixture of *N*-benzyl 2,3-dodecadienamide or *N*-benzyl 2-methyl-4-phenyl-2,3-butadienamide and 1,2-allenyl ketone **2d** was treated under the standard conditions. In addition, the reaction is sensitive to the steric hindrance of the starting materials since no expected product was observed for the reactions of **1b** with 3-benzyl-3,4-pentadien-2-one and **1c** with 1-(*p*-phenyl)phenyl-1,2-octadien-4-one by TLC analysis.

It is interesting to note when **1c** was reacted with **2d** in the presence of Pd(CH₃CN)₂Cl₂ and benzoquinone in HOAc, besides the expected cross-coupling product **Z-3cd**, the homodimerization monohydrolysis product **Z-4cc** of 2,3-allenamide **1c** was also isolated in 15% yield (eq 1).

**FIGURE 2.** ORTEP representation of the product **Z-4cc**.

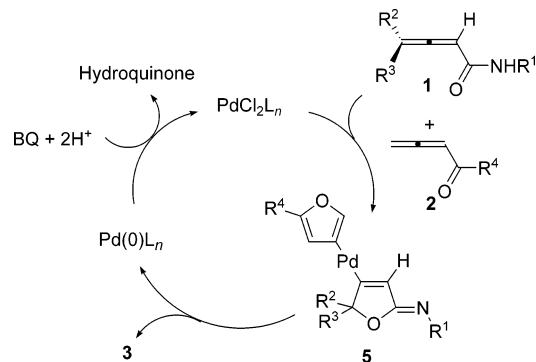
The structure of **Z-4cc** was established by the X-ray diffraction studies (Figure 2).¹⁰



A plausible mechanism for the cross-coupling reaction of 2,3-allenamides with 1,2-allenyl ketones was shown

(10) Crystal data for **4cc**: crystal system, orthorhombic; space group, *Pnma*; wavelength $\lambda = 0.71073$ Å, $a = 16.8651(17)$ Å, $b = 8.9696(10)$ Å, $c = 7.6142(8)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 1151.8(2)$ Å³; $T = 293(2)$ K, $Z = 4$; $D_{\text{calcd}} = 1.276$ g/cm³; $F_{000} = 472$, final R indices [$I > 2\sigma(I)$], $R1 = 0.0579$, $wR = 0.1401$; R indices (all data), $R1 = 0.0688$, $wR = 0.1473$. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center, CCDC 266566.

SCHEME 2. The Plausible Mechanism of the Oxidative Cyclization–Dimerization Reaction of **1** with **2**



in Scheme 2. First Pd(II) species coordinated with **1** and **2**, which was followed by double cyclic oxypalladation to form the intermediate **5**. Subsequent reductive elimination of **5** yielded 4-(furan-3'-yl)furanimines **3** and the Pd(0) species. Then the in situ generated Pd(0) species was reoxidized by benzoquinone in the presence of two protons to the catalytically active Pd(II) species⁷ to complete the catalytic cycle.

Conclusion

In conclusion, we have developed the heterodimerization of 2,3-allenamides with 1,2-allenyl ketones providing an efficient methodology for the synthesis of 4-(furan-3'-yl)furanimines. In this reaction due to the utilization of benzoquinone and HOAc, the catalytically active Pd(II) species was regenerated more efficiently and economically. Due to the presence of the furan ring and the furanimines, especially the C=N bond in these bicyclic compounds, this methodology may be useful in organic synthesis. Further investigation in this area is being intensively carried out in our laboratory.

Experimental Section

Starting Materials. Compounds **1a–e**,¹¹ **1f**,¹² **2a**,¹³ and **2b–e**^{4b} were prepared according to the reported procedure.

General Procedure for Pd(CH₃CN)₂Cl₂-Catalyzed Heterodimerization Reaction of 2,3-Allenamide **1a with 1,2-Allenyl Ketones. Condition A:** A solution of **1a** (0.25 mmol), **2** (1.25 mmol, 5.0 equiv), and Pd(CH₃CN)₂Cl₂ (0.0125 mmol, 5 mol %) in 3 mL of CH₃CN was stirred. After complete consumption of the starting material as monitored by TLC, CH₃CN was evaporated and the residue was directly purified via flash chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford **3**.

Condition B: A solution of **1a** (0.25 mmol), **2** (0.50 mmol, 2.0 equiv), benzoquinone (0.25 mmol), and Pd(CH₃CN)₂Cl₂

(0.0025 mmol, 1 mol %) in 1.5 mL of CH₃CN was stirred. After complete consumption of the starting material as monitored by TLC, CH₃CN was evaporated and the residue was directly purified via flash chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to afford **3**.

5,5-Dimethyl-4-(5'-methylfuran-3'-yl)-N-(4''-methylbenzenesulfonyl)-2(5H)-furanimine (Z-3aa). Condition A: A solution of **1a** (68 mg, 0.257 mmol), **2a** (104 mg, 0.524 mmol), and Pd(CH₃CN)₂Cl₂ (3 mg, 0.0116 mmol) in 3 mL of CH₃CN was stirred at 30 °C for 3 h to afford 76 mg (86%) of Z-3aa.

Condition B: A solution of **1a** (66 mg, 0.249 mmol), **2a** (43 mg, 0.524 mmol), Pd(CH₃CN)₂Cl₂ (0.65 mg, 0.0025 mmol), and benzoquinone (30 mg, 0.278 mmol) in 1.5 mL of CH₃CN was stirred at 31 °C for 5 h to afford 57 mg (66%) of Z-3aa. Solid, mp 108–110 °C (CH₂Cl₂/Et₂O); ¹H NMR (300 MHz, CDCl₃) δ 7.85 (d, *J* = 8.1 Hz, 2 H), 7.60 (s, 1 H), 7.25 (d, *J* = 8.1 Hz, 2 H), 7.03 (br s, 1 H), 6.23 (br s, 1 H), 2.37 (s, 3 H), 2.30 (s, 3 H), 1.59 (s, 6 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 13.2, 21.4, 26.3, 90.1, 104.8, 110.3, 117.4, 126.8, 129.2, 138.8, 141.8, 143.0, 154.8, 164.8, 173.7; EIMS: *m/z* (%) 345 (M⁺, 11.47), 281 (100); IR (KBr) 3122, 1603, 1523, 1155 cm^{−1}; HRMS calcd for C₁₈H₁₉NO₄S [M⁺] 345.1035, found 345.0996.

General Procedure for Pd(CH₃CN)₂Cl₂-Catalyzed Heterodimerization Reaction of 2,3-Allenamides (1b–f**) with 1,2-Allenyl Ketones. Condition C:** A solution of **1** (0.25 mmol), **2** (0.50 mmol), Pd(CH₃CN)₂Cl₂ (0.0025 mmol), and benzoquinone in 1.5 mL of HOAc was stirred. The reaction was monitored by TLC. In some cases the byproduct hydroquinone could not be removed from the products **3** by chromatography on silica gel, thus two different workup procedures were adopted. **Workup A:** After complete consumption of the starting material as monitored by TLC, HOAc was evaporated and the residue was directly purified via flash chromatography on silica gel to afford **3**. **Workup B:** After workup A the crude product, which was contaminated by the in situ formed hydroquinone, was dissolved in CH₂Cl₂ and washed with water to remove the byproduct hydroquinone. Then the organic layer was dried over Na₂SO₄, filtrated, and evaporated to afford the pure products **3**.

5,5-Dimethyl-4-(5'-methylfuran-3'-yl)-N-benzyl-2(5H)-furanimine (Z-3ba). Condition C, workup A: A solution of **1b** (50 mg, 0.249 mmol), **2a** (41 mg, 0.50 mmol), Pd(CH₃CN)₂Cl₂ (0.65 mg, 0.0025 mmol), and benzoquinone (28 mg, 0.259 mmol) in 1.5 mL of HOAc was stirred at 36 °C for 2 h to afford 60 mg (86%) of Z-3ba. ¹H NMR (300 MHz, CDCl₃) δ 7.46 (s, 1 H), 7.38–7.20 (m, 5 H), 6.28 (s, 1 H), 6.18 (s, 1 H), 4.57 (s, 2 H), 2.30 (s, 3 H), 1.60 (s, 6 H); ¹³C NMR (75.4 MHz, CDCl₃) δ 13.2, 26.8, 50.4, 90.1, 105.0, 115.2, 117.9, 126.4, 127.9, 128.2, 139.3, 140.2, 153.9, 155.6, 164.3; EIMS *m/z* (%) 281 (M⁺, 29.30), 176 (100); IR (neat) 2982, 1676, 1631, 1605, 1452, 1141 cm^{−1}; HRMS calcd for C₁₈H₁₉NO₂ [M⁺] 281.1416, found 281.1442.

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Supporting Information Available: Experimental details for all the products not listed in the text and ¹H NMR and ¹³C NMR spectra of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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