DOI: 10.1002/ejoc.200701038

Intermolecular and Intramolecular Pauson–Khand Reactions of Functionalized Allenes

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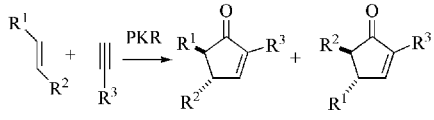
Keywords: Pauson–Khand reactions / Allenes / Cyclizations / Allenamides

Pauson–Khand reactions of functionalized allenes with different alkynes give cyclopentenones with generally high regio- and stereoselectivities. The allenes react through their external double bonds, giving cyclopentenones with exocyclic double bond at their β positions and predominantly with *E* stereochemistry. Some intramolecular reactions with allenynes connected through aromatic rings are described. These give the corresponding heterocycles with moderate to good yields.

Introduction

The scope of the intermolecular Pauson–Khand[1] reaction is still quite limited, as simple alkenes react poorly. The reaction gives good results only with strained olefins such as norbornene, some exocyclic alkenes, and certain allenes.[2] In addition, some vinyl ethers/esters[3] and vinyl sulfoxides[4] are also useful in the intermolecular PKR. Cyclopentenones are structural features present in a large variety of natural products, so an increase in the number of efficient methodologies for intramolecular PKRs would be highly desirable. One strategy that circumvents the scope problem consists of performing an intramolecular PKR with an enyne bearing a traceless tether[5] or directing groups such as pyridylsilyl moieties.[6] These methodologies avoid the formation of regioisomeric mixtures. The intermolecular PKR is regioselective with regard to the alkyne component, the bulkier substituent being situated adjacent to the carbonyl in the final product. It has been demonstrated that both steric and electronic effects may be responsible for this regioselectivity.[7] Unsymmetrical olefins usually give mixtures of regioisomers (Scheme 1).

Allenes are important substrates in various metal-mediated or catalyzed cyclizations.[8] With regard to the PKR, there have been extensive studies in the intramolecular version.[9] On the other hand, intermolecular PKRs have received less attention. The main contributions have come from Cazes' group, who have carried out studies with allenic hydrocarbons.[10]



Scheme 1. Regioselectivity in the intermolecular PKR.

In a preliminary communication of this work, we observed high regio- and stereoselectivities in the reactions between allenamides and alkynes.[11] There we used NMO for promotion and reached yields varying from moderate to good (45–85%). Here we present our complete work on allenes substituted with different heteroatoms and different types of alkynes. We have developed new reaction conditions that have improved on the preliminary results and we include some novel examples of intramolecular reactions with allenynes connected through aromatic rings.

Results and Discussion

The synthesis of starting allenes was effected by classical strategies (Table 1). Starting from functionalized amides, phenols or thiophenols **1**, propargylation under basic or Mitsunobu conditions gave the corresponding propargyl derivatives **2** in good yields. These compounds were converted into the corresponding allenes **3** by treatment with *t*BuOK or NaH. In the synthesis of **3h** some amounts of allene were formed in the propargylation reaction but we were unable to achieve good direct conversions from **1** into **3h** that would improve the two-step process.[12] Some of these allenes contained *o*-ethynyl or vinyl groups to allow competence experiments to be performed or to serve as substrates for intramolecular PKRs. The syntheses of (propa-1,2-diene-1-sulfinyl)benzene (**3k**)[13] and (propa-1,2-diene-1-sulfonyl)benzene (**3l**)[14] were carried out according to litera-

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ture procedures. The syntheses of allenamines were unsuccessful, as we observed extensive decomposition of the products in the reactions with the base.

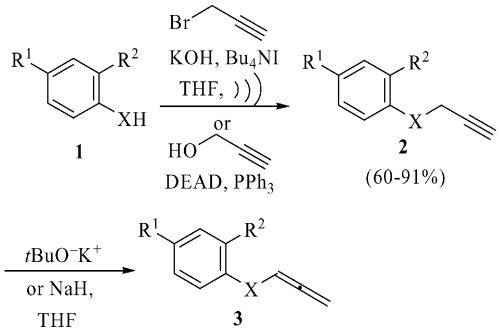
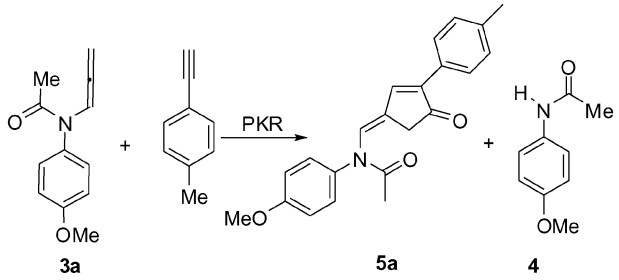


Table 1. Synthesis of starting allenes.

Product	R^1	R^2	X	% Yield[a]
3a	MeO	H	NAc	55
3b	F	H	NAc	69
3c	H	H_2C=CH	NAc	82
3d	MeO	H	NTs	70
3e	MeO	H	NCO_2Et	45
3f	H	HC≡C	NAc	78
3g	H	HC≡C	NTs	86
3h	Cl	H	S	60
3i	Br	H	O	72
3j	H	HC≡C	O	74

[a] Yields of pure product **3** from **1**.

The PKR between compound **3a** and *p*-tolylacetylene was carried out under several sets of conditions, some of them summarized in Table 2. Heat promotion and use of molecular sieves as described by us previously were unsuccessful, due to decomposition of the allenamide (Entries 1 and 2).[15] Under these conditions, the main reaction product was acetanilide **4**. We thus used trimethylamine *N*-oxide (TMANO) and *N*-methylmorpholine *N*-oxide (NMO) as promoters, testing several solvents. With the latter promoter



in CH_3CN (Entry 4) we obtained a 45% yield of the cyclopentenone **5a** and a 7% yield of **4**. Molecular sieves are known for acting as catalysts in the formation of enamines, and it is thus possible that they accelerate the decomposition of our starting materials.[15] To avoid this we washed the zeolites with Et_3N and dried them prior to the PKR. Under these conditions we achieved an 80% yield of **5a**. The only cyclopentenone isolated was assigned as **5a** in view of its NMR spectroscopic data and n.O.e. experiments.[16] Additionally we tried to develop catalytic conditions. Few efficient catalytic intermolecular PKRs have been described to date. In this case we carried out two reactions in the presence of 10% of cobalt under CO (1 atm) at 70 °C (Entries 6, 7). Both reactions gave poor yields of **5a**, reaching 25% when molecular sieves were used (Entry 7).

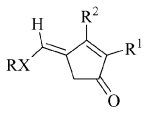
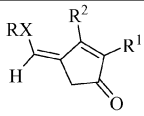
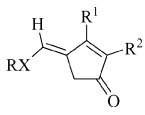
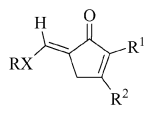
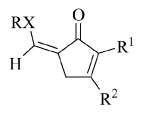
As in most of the examples described previously by Cazes,[10] we only detected the products with the exocyclic double bonds in the β positions. Other products, which we assumed to be the *Z* isomers, could be detected in the crude mixtures but not isolated. The conditions of Entry 4 (Table 1, procedure A) were used with the whole set of functionalized allenes prepared, and the results are shown in Table 3. With substrates **3i**, **3k**, and **3l** the cobalt hexacarbonyl-alkyne complex was preformed and purified in DCM prior to the PKR (procedure B). This procedure was necessary to avoid decomposition of the allene in the presence of cobalt species. The conditions of Entry 5 (procedure C) were developed later, and were used with a selected group of reactions.

In general the reactions were very selective. The allenes reacted through their external double bonds independently of the natures of the substituents, and gave the *E* isomers as the major products. With allenamides **3a**–**3g**, results were similar regardless of the natures of the protecting groups used. In the case of the reaction of trimethyl-pent-1-ynylsilane (Entry 9), a small amount of another isomer was isolated. This compound, **13c**, was the result of the reaction of the alkyne with the other regioselectivity, due to the similar bulkiness of the two constituents. Surprisingly, a small amount of **15c** was also observed in the reaction of protected propargyl alcohol (Entry 11). On the other hand, small amounts of *Z* isomers could be isolated in the reactions of Entries 10, 12 and 13. The reaction of Entry 5 was planned in order to investigate the competition between the allenic PKR vs. the possible reaction with the styrenic double bond. The only reaction product observed in the presence of hex-3-yne was **9a**, showing the preference for

Table 2. PK reaction conditions for allenamide **3a**.

No	Solvent	Metal complex/loading	*T* [°C]	Promoter	% Yield **5a**	**4**
1	toluene	1.5 equiv. $Co_2(CO)_8$	Δ	–	<5	75
2	toluene	1.5 equiv. $Co_2(CO)_8$	room temp.	4-Å MS, 9 equiv. TMANO	10	28
3	CH_3CN	1.5 equiv. $Co_2(CO)_8$	room temp.	9 equiv. TMANO	32	8
4	CH_3CN	1.5 equiv. $Co_2(CO)_8$	room temp.	6 equiv. NMO	45	7
5	CH_3CN	1.5 equiv. $Co_2(CO)_8$	room temp.	4-Å MS (Et_3N), 6 equiv. NMO	80	<5
6	CH_3CN	0.1 equiv. $Co_2(CO)_8$/CO 1 atm	70	–	10	20
7	CH_3CN	0.1 equiv. $Co_2(CO)_8$/CO 1 atm	70	4-Å MS (Et_3N)	25	<5

Table 3. PKRs of functionalized allenes.

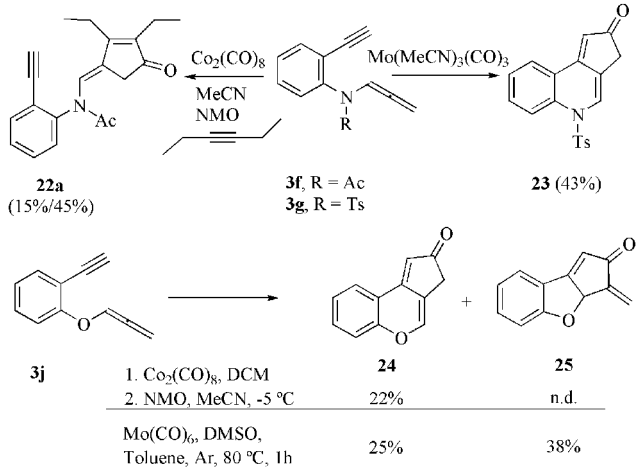
n		RX	R^1	R^2					
1	**3a**	*p*-MeOC$_6$H$_4$N(Ac)–	*p*-MeC$_6$H$_4$	H	**5a** (45%/ 80%)[a]				
2	**3a**	*p*-MeOC$_6$H$_4$N(Ac)–	C$_4$H$_9$	H	**6a** (50%)[b]				
3	**3a**	*p*-MeOC$_6$H$_4$N(Ac)–	Et	Et	**7a** (65%)[b]				
4	**3b**	*p*-FC$_6$H$_4$N(Ac)–	Et	Et	**8a** (61%)[b]				
5	**3c**	*o*-H$_2$C=CHC$_6$H$_4$N(Ac)–	Et	Et	**9a** (58%/ 85%)[a]				
6	**3d**	*p*-MeOC$_6$H$_4$N(Ts)–	Et	Et	**10a** (85%)[b]				
7	**3e**	*p*-MeOC$_6$H$_4$N(CO$_2$Et)–	Et	Et	**11a** (71%)[b]				
8	**3d**	*p*-MeOC$_6$H$_4$N(Ts)–	*p*-MeC$_6$H$_4$	H	**12a** (35%/ 55%)[a]				
9	**3d**	*p*-MeOC$_6$H$_4$N(Ts)–	TMS	C$_3$H$_7$	**13a** (73%)[c]		**13c** (12%)[c]		
10	**3d**	*p*-MeOC$_6$H$_4$N(Ts)–	TMS	TBSOCH$_2$	**14a** (62%/ 70%)[c]	**14b** (9%/ 11%)[c]		**14d** (3%/ -)[b]	**14e** (4%/ -)[b]
11	**3d**	*p*-MeOC$_6$H$_4$N(Ts)–	TBSOCH$_2$-	H	**15a** (37%)[b]		**15c** (7%)[b]		
12	**3h**	*p*-ClC$_6$H$_4$S–	Et	Et	**16a** (25%/ n.r.)[c]	**16b** (4%/ n.r.)[c]			
13	**3i**	*p*-BrC$_6$H$_4$O–	Et	Et	**17a** (29%/ n.r.)[d]	**17b** (20% /n.r.)[d]			
14	**3i**	*p*-BrC$_6$H$_4$O–	Ph	H				**18d** (10%)[e]	**18e** (2%)[e]
15	**3k**	C$_6$H$_4$SO–	Et	Et	**19a** (24%/ 40%)[d]			**19d** (14%/ 20%)[d]	
16	**3k**	C$_6$H$_4$SO–	Ph	H				**20d** (5%/ 15%)[d]	**20e** (5%/ 14%)[d]
17	**3l**	C$_6$H$_4$SO$_2$–	Et	Et	**21a** (19%/ 35%)[d]			**21d** (14%/ 24%)[d]	

[a] Yields of pure products are given as obtained by Procedure A/Procedure C. [b] Yield of pure product obtained by Procedure A. [c] Products **13a** and **13c**, **14a** and **14b**, and **16a** and **16b** were obtained by Procedure A as pure mixtures. Quantities of major products **13a** and **16a** could be obtained pure and characterized; yields for **13c**, **14a**, **14b**, and **16b** are estimated from the ratios in the mixtures. [d] Yields of pure products are given as obtained with Procedure B/Procedure C. [e] Yield of pure product obtained with Procedure B.

the reaction with the allene. Allenes bearing sulfur and oxygen groups reacted with lower yields. Oxygen-containing allene **3i** gave a ca. 1:1 *E*/*Z* mixture of cyclopentenones when reacting with hex-3-yne (Entry 13). However, in the reaction with phenylacetylene (Entry 14) it gave low yields of the products arising from the other regioselectivity with respect to the allene. In the case of the sulfoxide and the sulfone (Entries 15, 16 and 17) the allene reacted partially or only (Entry 16) with this latter regioselectivity.

Traditionally, electron-deficient olefins have been considered bad substrates for PK reactions, although Carretero showed good results in intramolecular PKRs with olefins substituted with EWGs including sulfoxides and sulfones.[17] Our results show that these groups do not prevent the allenic PKR. In addition, no insertion or cyclotrimerization products were detected. The reaction of Entry 17 was described by Cazes previously,[10c] but gave a similar distribution of products and better yields with our Procedure C.

We extended this methodology to some intramolecular examples (Scheme 2). The reaction between allene **3f** and $Co_2(CO)_8$ gave no intramolecular PK products under any conditions. This starting product reacted with hex-3-yne to give **22a** in 15% yield under Procedure A conditions and in 45% yield under Procedure C conditions. Using molybdenum as the metal, under previously described conditions,[18] we detected the intramolecular PKR in the crude mixture of the reaction of **3f**. We decided to switch the protecting group in the allene to tosyl and performed the intramolecular PKR with substrate **3g**. Under these conditions we isolated product **23** in 43% yield. On the other hand, the intramolecular PKR of allene **3j** gave product **24** in 22% yield with $Co_2(CO)_8$. When we applied reaction conditions with $Mo(CO)_6$, a mixture of **24** (25%) and **25** (38%) was obtained. This result follows previous observations by Brum-



Scheme 2. Intramolecular PKRs with allenynes.

mond, who was able to direct the PKR of allenes to either the external or the internal double bond by tuning the reaction conditions.[19]

Conclusions

We have shown that allenes with different functionalities are good substrates for intermolecular Pauson–Khand reactions with symmetric and unsymmetrical alkynes. The reaction conditions have been tuned up and allow excellent yields to be achieved in stoichiometric reactions. Catalytic processes, however, did not give satisfactory results. Under both sets of experimental conditions a positive effect of molecular sieves was observed. The PKRs gave, in general, either single or major products arising from reactions through the external bonds of the allenes. These products present the exocyclic double bonds at the β-positions from the ketones with *E* stereochemistry. As a result of this work, new cyclopentenones with interesting functionalities have been obtained. In addition we have shown some examples of intramolecular PKRs with allenynes connected through aromatic rings that give polycyclic heterocycles.

Experimental Section

Procedure A for Pauson–Khand Intermolecular Reactions: A solution of the alkyne (1.50 mmol) in MeCN (9 mL) and $Co_2(CO)_8$ (1.50 mmol) was stirred for 1 h, and 4-methylmorpholine *N*-oxide (6.00 mmol) was then added at 0 °C. The allene (1.00 mmol) in MeCN (9 mL) was added dropwise, and the mixture was stirred at 0 °C until completion of the reaction (TLC). The reaction was filtered through Celite and was washed with MeCN (20 mL). The solvent was removed under vacuum and the residue was purified by silica gel flash chromatography (hexane/AcOEt, mixtures).

Procedure B for Pauson–Khand Intermolecular Reactions: A solution of the alkyne (1.50 mmol) in DCM (9 mL) and $Co_2(CO)_8$ (1.50 mmol) was stirred for 45 min at room temp. When the complex had been formed (TLC), the solvent was eliminated under vacuum and the residue was purified by flash chromatography (hexane). The complex (1.00 mmol) in MeCN (9 mL) was added at –5 °C to a solution of the allene (1.00 mmol) in MeCN (9 mL) and 4-methylmorpholine *N*-oxide (6.00 mmol), and the mixture was stirred at –5 °C until completion of the reaction (TLC). The reaction mixture was filtered through Celite and was washed with MeCN (20 mL). The solvent was removed under vacuum, and the residue was purified by silica gel flash chromatography (hexane/AcOEt, mixtures).

Procedure C for Pauson–Khand Intermolecular Reactions: A solution of the alkyne (1.50 mmol) in MeCN (9 mL) and $Co_2(CO)_8$ (1.50 mmol) was stirred for 1 h, and powdered molecular sieves (previously washed with Et_3N and dried, 4 g) and 4-methylmorpholine *N*-oxide (6.00 mmol) were then added at 0 °C. The allene (1.00 mmol) in MeCN (9 mL) was added dropwise, and the mixture was stirred at 0 °C until completion of the reaction (TLC). The reaction mixture was filtered through Celite and was washed with MeCN (20 mL). The solvent was removed under vacuum and the residue was purified by silica gel flash chromatography (hexane/AcOEt, mixtures).

General Procedure for the Intramolecular Pauson–Khand Reactions with $Co_2(CO)_8$: A solution of the allenyne (1.00 mmol) in MeCN (9 mL) and $Co_2(CO)_8$ (1.50 mmol) was stirred for 1 h at room temp. 4-Methylmorpholine *N*-oxide (6.00 mmol) was then added at 0 °C, and the mixture was stirred until completion of the reaction (TLC). The reaction was filtered through Celite and was washed with MeCN (20 mL). The solvent was removed under vacuum, and the residue was purified by silica gel flash chromatography (hexane/AcOEt, mixtures).

General Procedure for the Intramolecular Pauson–Khand Reactions with $Mo(CO)_6$: DMSO (0.86 mL, 10.00 mmol) and $Mo(CO)_6$ (317 mg, 1.20 mmol) were added to a solution of the allenyne (1.00 mmol) in toluene (10 mL). The resulting mixture was stirred for 1h at 80 °C. The reaction mixture was filtered through Celite, and the solvent was removed under vacuum. The residue was purified by silica gel flash chromatography (hexane/AcOEt, mixtures).

General Procedure for Intramolecular Pauson–Khand Reactions with $Mo(MeCN)_3(CO)_3$: $Mo(MeCN)_3(CO)_3$ (0.34 mmol) was added at 0 °C to a solution of the allenyne (0.30 mmol) in toluene (15 mL). The resulting mixture was stirred for 1h at room temp. The reaction mixture was filtered through Celite and the solvent was removed under vacuum. The residue was purified by silica gel flash chromatography (hexane/AcOEt, mixtures).

***N*-(4-Methoxyphenyl)-*N*-{(*E*)-[3-(4-methylphenyl)-4-oxocyclopent-2-en-1-ylidene]methyl}acetamide (5a):** Treatment of 1-ethynyl-4-methylbenzene (0.21 g, 1.85 mmol) and *N*-(4-methoxyphenyl)-*N*-(propa-1,2-dienyl)acetamide (0.25 g, 1.23 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **5a** (0.19 g, 45%) as a colorless oil after flash chromatography (hexane/AcOEt, 4:1). After treatment as described in Procedure C, the reaction afforded **5a** (0.34 g, 80%, from 0.25 g, 1.23 mmol of allenamide **3a**). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95 (s, 3 H), 2.20 (s, 2 H), 2.34 (s, 3 H), 3.87 (s, 3 H), 6.98 (d, J = 7.9 Hz, 2 H), 7.16 (d, J = 7.9 Hz, 4 H), 7.64 (d, J = 8.5 Hz, 2 H), 7.71 (s, 1 H), 7.96 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 22.9, 38.8, 55.4, 115.1, 119.6, 125.3, 126.6, 128.7, 129.1, 130.0, 132.1, 138.0, 138.1, 156.0, 160.0, 170.4, 203.5 ppm. n.O.e ($H_{7.96} \rightarrow H_{7.71}$, 6.4%). IR (film): $\tilde{\nu}$ = 1675, 1630 cm^{-1}. $C_{22}H_{21}NO_3$ (347.41): calcd. C 76.06, H 6.09, N 4.03; found C 76.30, H 6.12, N 3.84.

***N*-[(*E*)-(3-Butyl-4-oxocyclopent-2-en-1-ylidene)methyl]-*N*-(4-methoxyphenyl)acetamide (6a):** Treatment of hex-1-yne (0.15 g, 1.85 mmol) and *N*-(4-methoxyphenyl)-*N*-(propa-1,2-dienyl)acetamide (0.25 g, 1.23 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **6a** (0.18 g, 50%) as a colorless oil after flash chromatography (hexane/AcOEt, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (t, J = 7.1 Hz, 3 H), 1.24–146 (m, 4 H), 1.91 (s, 3 H), 2.01 (s, 2 H), 2.15 (t, J = 7.1 Hz, 2 H), 3.84 (s, 3 H), 6.93 (d, J = 8.8 Hz, 2 H), 7.12 (d, J = 8.2 Hz, 2 H), 7.47 (s, 1 H), 7.53 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 22.3, 22.8, 24.2, 29.9, 37.5, 55.4, 115.0, 120.3, 123.7, 129.9, 132.3, 143.0, 156.7, 159.9, 170.3, 205.6 ppm. n.O.e ($H_{7.53} \rightarrow H_{7.47}$, 6.0%). IR (film): $\tilde{\nu}$ = 1680, 1640 cm^{-1}. $C_{19}H_{23}NO_3$ (313.39): calcd. C 72.82, H 7.40, N 4.47; found C 72.99, H 7.25, N 4.28.

***N*-[(*E*)-(2,3-Diethyl-4-oxocyclopent-2-en-1-ylidene)methyl]-*N*-(4-methoxyphenyl)acetamide (7a):** Treatment of hex-3-yne (0.15 g, 1.85 mmol) and *N*-(4-methoxyphenyl)-*N*-(propa-1,2-dienyl)acetamide (0.25 g, 1.23 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **7a** (0.24 g, 65%) as a brown oil after flash chromatography (hexane/AcOEt, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.4 Hz, 3 H), 1.22 (t, J = 7.7 Hz, 3 H), 1.95 (s, 3 H), 2.02 (s, 2 H), 2.21 (q, J = 7.5 Hz, 2 H), 2.60 (q, J = 7.7 Hz, 2H$_2$), 3.87 (s, 3 H), 6.95 (d, J = 8.8 Hz, 2

H), 7.14 (d, J = 8.8 Hz, 2 H), 7.65 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.0, 13.7, 16.2, 19.1, 22.6, 36.8, 55.1, 114.7, 119.5, 121.0, 129.7, 132.4, 140.3, 159.5, 169.9, 170.2, 204.3 ppm. n.O.e ($H_{7.65} \rightarrow H_{2.60}$, 8.2%; $\rightarrow H_{1.22}$, 4.5%). IR (film): $\tilde{\nu}$ = 1670, 1640 cm^{-1}. $C_{19}H_{23}NO_3$ (313.39): calcd. C 72.82, H 7.40, N 4.47; found C 72.54, H 7.67, N 4.40.

***N*-[(*E*)-(2,3-Diethyl-4-oxocyclopent-2-en-1-ylidene)methyl]-*N*-(4-fluorophenyl)acetamide (8a):** Treatment of hex-3-yne (0.16 g, 1.96 mmol) and *N*-(4-fluorophenyl)-*N*-(propa-1,2-dienyl)acetamide (0.25 g, 1.31 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **8a** (0.27 g, 61%) as a yellow oil after flash chromatography (hexane/AcOEt, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.7 Hz, 3 H), 1.19 (t, J = 7.7 Hz, 3 H), 1.92 (s, 3 H), 1.96 (s, 2 H), 2.19 (q, J = 7.5 Hz, 2 H), 2.57 (q, J = 7.7 Hz, 2 H), 7.15–7.22 (m, 4 H), 7.60 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2, 13.9, 16.5, 19.4, 22.9, 37.1, 117.1 (d, J = 22.5 Hz), 120.5, 121.1, 130.7 (d, J = 8.4 Hz), 136.3 (d, J = 3.1 Hz), 141.1, 162.4 (d, J = 249.5 Hz), 169.1, 170.0, 204.2 ppm. n.O.e ($H_{7.60} \rightarrow H_{2.57}$, 7.8%; $\rightarrow H_{1.19}$, 3.6%). IR (film): $\tilde{\nu}$ = 1675, 1640 cm^{-1}. $C_{18}H_{20}FNO_2$ (301.36): calcd. C 71.74, H 6.69, N 4.65; found C 71.40, H 6.39, N 4.70.

***N*-[(*E*)-(2,3-Diethyl-4-oxocyclopent-2-en-1-ylidene)methyl]-*N*-(2-ethenylphenyl)acetamide (9a):** Treatment of hex-3-yne (0.10 g, 1.19 mmol) and *N*-(propa-1,2-dienyl)-*N*-(2-vinylphenyl)acetamide (0.15 g, 0.75 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **9a** (0.13 g, 58%) as a yellow oil after flash chromatography (hexane/AcOEt, 4:1). After treatment as described in Procedure C, the reaction afforded **9a** (0.33 g, 85%) from allenamide **3c** (0.25 g, 1.26 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.4 Hz, 3 H), 1.19 (t, J = 7.7 Hz, 3 H), 1.82 (d, J = 20.9 Hz, 1 H), 1.83 (s, 3 H), 1.93 (d, J = 20.9 Hz, 1 H), 2.16 (q, J = 7.5 Hz, 2 H), 2.57 (q, J = 7.5 Hz, 2 H), 5.36 (d, J = 11.0 Hz, 1 H), 5.80 (d, J = 17.6 Hz, 1 H), 6.58 (dd, J_1 = 17.6, J_2 = 11.0 Hz, 1 H), 7.15 (d, J = 7.1 Hz, 1 H), 7.34 (t, J = 7.1 Hz, 1 H), 7.43 (t, J = 7.4 Hz, 1 H), 7.65 (d, J = 8.2 Hz, 1 H), 7.69 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2, 14.0, 16.4, 19.6, 22.6, 36.5, 118.2, 119.5, 120.4, 126.5, 129.2, 129.5, 129.8, 130.6, 136.3, 137.4, 140.8, 170.1, 204.7 ppm. n.O.e ($H_{7.69} \rightarrow H_{2.57}$, 4.3%; $\rightarrow H_{1.19}$, 2.5%). IR (film): $\tilde{\nu}$ = 1680, 1640 cm^{-1}. $C_{20}H_{23}NO_2$ (309.40): calcd. C 77.64, H 7.49, N 4.53; found C 77.38, H 7.58, N 4.32.

***N*-[(*E*)-(2,3-Diethyl-4-oxocyclopent-2-en-1-ylidene)methyl]-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (10a):** Treatment of hex-3-yne (0.10 g, 1.19 mmol) and *N*-(4-methoxyphenyl)-4-methyl-*N*-(propa-1,2-dienyl)benzenesulfonamide (0.25 g, 0.79 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **10a** (0.29 g, 85%) as a white solid after flash chromatography (hexane/AcOEt, 2:1 to 1:1). M.p. 122–124 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.7 Hz, 3 H), 1.18 (t, J = 7.7 Hz, 3 H), 1.96 (s, 2 H), 2.14 (q, J = 7.7 Hz, 2 H), 2.38 (s, 3 H), 2.53 (q, J = 7.7 Hz, 2 H), 3.75 (s, 3 H), 6.75 (d, J = 9.3 Hz, 2 H), 6.85 (d, J = 8.8 Hz, 2 H), 7.16 (s, 1 H), 7.24 (d, J = 8.2 Hz, 2 H), 7.50 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2, 13.8, 16.3, 19.3, 21.4, 37.0, 55.2, 114.3, 119.1, 122.0, 127.4, 129.2, 129.6, 131.2, 134.6, 140.4, 144.3, 159.8, 169.0, 204.2 ppm. n.O.e ($H_{7.16} \rightarrow H_{2.53}$, 5.8%; $\rightarrow H_{1.18}$, 3.0%). IR (KBr): $\tilde{\nu}$ = 1690, 1630, 1350, 1180 cm^{-1}. $C_{24}H_{27}NO_4S$ (425.54): calcd. C 67.74, H 6.40, N 3.29, S 7.54; found C 67.87, H 6.48, N 3.41, S 7.26.

Ethyl [(*E*)-(2,3-Diethyl-4-oxocyclopent-2-en-1-ylidene)methyl](4-methoxyphenyl)carbamate (11a): Treatment of hex-3-yne (0.10 g, 1.19 mmol) and ethyl *N*-(4-methoxyphenyl)(propa-1,2-dienyl)carbamate (0.15 g, 0.75 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **11a** (0.17 g, 71%) as a yellow oil after flash chromatography (hexane/AcOEt, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.2 Hz, 3 H), 1.19–1.24 (m, 6 H), 2.03 (d, J = 1.1 Hz, 2 H), 2.21 (q, J = 7.7 Hz, 2 H), 2.57 (q, J = 7.7 Hz, 2 H), 3.84 (s, 3 H), 4.23 (q, J = 7.1 Hz, 2 H), 6.88 (d, J = 6.6 Hz, 2 H), 7.10 (d, J = 6.6 Hz, 2 H), 7.34 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.3, 14.0, 14.3, 16.5, 19.5, 37.3, 55.3, 62.9, 114.3, 119.5, 122.8, 129.5, 131.6, 140.3, 154.7, 159.1, 169.8, 204.8 ppm. n.O.e ($H_{7.34} \rightarrow H_{2.57}$, 4.8%; $\rightarrow H_{1.22}$, 2.6%). IR (film): $\tilde{\nu}$ = 1710, 1680, 1650 cm^{-1}. $C_{20}H_{25}NO_4$ (343.42): calcd. C 69.95, H 7.34, N 4.08; found C 70.24, H 7.55, N 3.86.

***N*-(4-Methoxyphenyl)-4-methyl-*N*-{(*E*)-[3-(4-methylphenyl)-4-oxocyclopent-2-en-1-ylidene]methyl}benzenesulfonamide (12a):** Treatment of 1-ethynyl-4-methylbenzene (80 mg, 0.71 mmol) and *N*-(4-methoxyphenyl)-4-methyl-*N*-(propa-1,2-dienyl)benzenesulfonamide (150 mg, 0.48 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **12a** (80 mg, 35%) as a brown oil after flash chromatography (hexane/AcOEt, 4:1). After treatment as described in Procedure C, the reaction afforded **12a** (0.20 g, 55%) from allenamide **3d** (0.25 g, 0.79 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 2 H), 2.35 (s, 3 H), 2.46 (s, 3 H), 3.85 (s, 3 H), 6.84 (d, J = 9.4 Hz, 2 H), 6.93 (d, J = 8.8 Hz, 2 H), 7.17 (d, J = 7.7 Hz, 2 H), 7.31 (d, J = 8.2 Hz, 2 H), 7.34 (s, 1 H), 7.58 (d, J = 8.2 Hz, 2 H), 7.62 (d, J = 8.2 Hz, 2 H), 7.93 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3, 21.7, 38.9, 55.4, 114.6, 118.2, 126.4, 126.6, 127.7, 128.6, 129.2, 129.5, 129.8, 131.6, 134.6, 137.5, 138.1, 144.7, 155.2, 160.3, 203.2 ppm. n.O.e ($H_{7.93} \rightarrow H_{7.34}$, 18.0%). IR (film): $\tilde{\nu}$ = 1680, 1620, 1350, 1160 cm^{-1}. $C_{27}H_{25}NO_4S$ (459.56): calcd. C 70.57, H 5.48, N 3.05; found C 70.33, H 5.65, N 3.30.

(*E*)-*N*-(4-Methoxyphenyl)-4-methyl-*N*-[4-oxo-2-propyl-3-(trimethylsilanyl)cyclopent-2-enylidenemethyl]benzenesulfonamide (13a) and (*E*)-*N*-(4-Methoxyphenyl)-4-methyl-*N*-[4-oxo-3-propyl-2-(trimethylsilanyl)cyclopent-2-enylidenemethyl]benzenesulfonamide (13c): Treatment of trimethyl(pent-1-ynyl)silane (0.22 mL, 1.19 mmol) and *N*-(4-methoxyphenyl)-4-methyl-*N*-(propa-1,2-dienyl)benzenesulfonamide (0.25 g, 0.79 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded **13a** and **13c** (0.33 g, 85%) as a mixture of isomers (4:1). After purification by flash chromatography (hexane/AcOEt, 6:1), pure **13a** (0.28 g, 73%) was obtained as a brown oil.

Data for 13a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.18 (s, 9 H), 1.08 (t, J = 7.4 Hz, 3 H), 1.54–1.67 (m, 2 H), 1.96 (br. s, 2 H), 2.44 (s, 3 H), 2.59–2.64 (m, 2 H), 3.81 (s, 3 H), 6.78–6.82 (m, 2 H), 6.85–6.90 (m, 2 H), 7.29 (d, J = 8.2 Hz, 2 H), 7.30 (s, 1 H), 7.54 (d, J = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –0.4, 14.5, 21.6, 24.3, 30.5, 38.4, 55.4, 114.4, 121.3, 123.3, 127.6, 128.9, 129.7, 131.4, 134.7, 138.1, 144.5, 160.0, 181.0, 209.0 ppm. n.O.e ($H_{2.59} \rightarrow H_{7.30}$, 12.0%; $\rightarrow H_{0.18}$, 5.4%). IR (film): $\tilde{\nu}$ = 1670, 1630, 1360, 1170 cm^{-1}. $C_{26}H_{33}NO_4SSi$ (483.70): calcd. C 64.56, H 6.88, N 2.90, S 6.63; found C 67.31, H 6.65, N 3.08, S 6.49.

Data for 13c: Mixture of isomers **13c** and **13a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.44 (s, 9 H), 0.90 (t, J = 7.4 Hz, 3 H), 1.26–1.36 (m, 2 H), 2.06 (s, 2 H), 2.22–2.27 (m, 2 H), 2.45 (s, 3 H), 3.83 (s, 3 H), 6.79–6.82 (m, 2 H), 6.86–6.94 (m, 2 H), 7.23 (br. s, 1 H), 7.27–7.31 (m, 2 H), 7.50–7.56 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.9, 14.1, 23.4, 27.1, 29.6, 37.5, 55.3, 114.3, 124.9, 125.8, 129.5, 129.6, 130.0, 131.0, 134.6, 152.0, 154.4, 159.7, 166.8, 205.7 ppm.

(*E*)-*N*-[2-(*tert*-Butyldimethylsilanyl)oxymethyl-4-oxo-3-(trimethylsilanyl)cyclopent-2-enylidenemethyl]-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (14a), (*Z*)-*N*-[3-(*tert*-Butyldimethylsilanyl)oxymethyl-4-oxo-2-(trimethylsilanyl)cyclopent-2-enylidenemethyl]-*N*-(4-

methoxyphenyl)-4-methylbenzenesulfonamide (14b), (*E*)-*N*-[4-(*tert*-Butyldimethylsilanyl)oxymethyl-2-oxo-3-(trimethylsilanyl)cyclopent-3-enylidenemethyl]-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (14d), and (*Z*)-*N*-[4-(*tert*-Butyldimethylsilanyl)oxymethyl-2-oxo-3-(trimethylsilanyl)cyclopent-3-enylidenemethyl]-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (14e): Treatment of 3-(*tert*-butyl-dimethyl-silanyloxy)-1-(trimethylsilanyl)propyne (0.29 g, 1.19 mmol) and *N*-(4-methoxyphenyl)-4-methyl-*N*-(propa-1,2-dienyl)benzenesulfonamide (0.25 g, 0.79 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded a mixture of isomers **14a**–**14e** (0.36 g, 78%). After purification by flash chromatography (hexane/AcOEt, 9:1), **14a** and **14b** (0.33 g, 71%) were obtained as a mixture of *Z*,*E* isomers (7:1), while **14d** (14 mg, 3%) and **14e** (18 mg, 4%) were obtained as yellow oils. After treatment as described in Procedure C, the reaction afforded **14a** and **14b** as a mixture of *Z*,*E* isomers (6:1, 0.37 g, 81%) from allenamide **3d** (0.25 g, 0.79 mmol).

Data for (*E*)-*N*-[2-(*tert*-Butyldimethylsilanyl)oxymethyl-4-oxo-3-(trimethylsilanyl)cyclopent-2-enylidenemethyl]-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (14a), (*Z*)-*N*-[3-(*tert*-Butyldimethylsilanyloxy)methyl-4-oxo-2-(trimethylsilanyl)cyclopent-2-enylidenemethyl]-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (14b): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.20 (s, 9 H), 0.22 (s, 6 H), 0.99 (s, 9 H), 2.01 (s, 2 H), 2.43 (s, 3 H), 3.81 (s, 3 H), 4.26 (s, 2 H, isomer **14b**), 4.71 (s, 2 H, isomer **14a**), 6.79 (d, *J* = 9.3 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 7.25 (d, *J* = 8.2 Hz, 2 H), 7.39 (br. s, 1 H, isomer **14b**) 7.52 (d, *J* = 8.2 Hz, 2 H), 7.73 (t, *J* = 1.1 Hz, 1 H, isomer **14a**) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.3, –5.2, –0.2, 0.6, 18.2, 18.3, 21.6, 25.9, 25.9, 37.6, 38.9, 53.7, 55.3, 55.4, 59.2, 114.4, 114.4, 120.0, 124.4, 125.7, 126.7, 127.7, 129.2, 129.4, 129.6, 129.7, 131.3, 131.6, 134.6, 134.8, 138.9, 144.3, 144.5, 148.6, 159.9, 159.9, 172.8, 176.9, 204.4, 209.2 ppm. n.O.e. ($H_{4.71} \rightarrow H_{7.73}$, 9.7%) ppm.

Data for 14d: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 6 H), 0.19 (s, 9 H), 0.79 (s, 9 H), 2.32 (s, 2 H), 2.43 (s, 3 H), 3.82 (s, 3 H), 4.43 (s, 2 H), 6.83 (d, *J* = 9.3 Hz, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 7.58 (d, *J* = 8.2 Hz, 2 H), 7.94 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.7, –0.5, 18.0, 21.6, 25.7, 33.8, 55.2, 62.2, 114.2, 115.3, 127.9, 129.0, 129.7, 131.4, 131.5, 134.7, 138.6, 144.5, 160.1, 179.5, 201.1 ppm. n.O.e. ($H_{2.32} \rightarrow H_{4.43}$, 2.0%; $\rightarrow H_{6.93}$, 5%), ($H_{7.94} \rightarrow H_{7.58}$, 7.0%). IR (film): $\tilde{\nu}$ = 1680, 1620, 1370, 1160 cm^{-1}. $C_{30}H_{43}NO_5SSi_2$ (585.90): calcd. C 61.50, H 7.40, N 2.39, S 5.47; found C 61.19, H 7.77, N 2.53, S 5.11.

Data for 14e: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.02 (s, 9 H), 0.09 (s, 6 H), 0.93 (s, 9 H), 2.42 (s, 3 H), 3.32 (s, 2 H), 3.78 (s, 3 H), 4.54 (s, 2 H), 6.75 (d, *J* = 8.8 Hz, 2 H), 7.02 (s, 1 H), 7.03 (d, *J* = 9.3 Hz, 2 H), 7.24 (d, *J* = 8.2 Hz, 2 H), 7.46 (d, *J* = 8.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.4, –0.8, 18.3, 21.6, 25.7, 36.3, 55.4, 62.3, 113.4, 119.8, 127.9, 129.5, 129.6, 129.7, 133.2, 134.3, 142.0, 144.2, 158.6, 177.7, 195.1 ppm. n.O.e. ($H_{3.32} \rightarrow H_{4.54}$, 1.9%; $\rightarrow H_{7.02}$, 9.4%). IR (film): $\tilde{\nu}$ = 1670, 1620, 1360, 1170 cm^{-1}. $C_{30}H_{43}NO_5SSi_2$ (585.90): calcd. C 61.50, H 7.40, N 2.39, S 5.47; found C 61.37, H 7.66, N 2.01, S 5.19.

(*E*)-*N*-[3-(*tert*-Butyldimethylsilanyl)oxymethyl-4-oxocyclopent-2-enylidenemethyl]-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (15a) and (*E*)-*N*-[2-(*tert*-Butyldimethylsilanyl)oxymethyl-4-oxocyclopent-2-enylidenemethyl]-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (15c): Treatment of *tert*-butyl-(dimethylprop-2-ynyloxy)silane (0.30 g, 2.79 mmol) and *N*-(4-methoxyphenyl)-4-methyl-*N*-(propa-1,2-dienyl)benzenesulfonamide (0.25 g, 0.79 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **15a** (0.15 g, 37%) and **15c** (28 mg, 7%) as colorless oils after flash chromatography (hexane/AcOEt, 4:1).

Data for 15a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 6 H), 0.93 (s, 9 H), 2.03 (d, *J* = 1.1 Hz, 2 H), 2.44 (s, 3 H), 3.82 (s, 3 H), 4.35 (br. s, 2 H), 6.81 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 7.57 (d, *J* = 8.2 Hz, 2 H), 7.65 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.5, 18.3, 21.6, 25.7, 38.2, 55.4, 57.8, 114.5, 118.4, 125.9, 127.6, 128.7, 129.6, 129.7, 131.5, 134.7, 141.9, 144.5, 156.2, 160.2, 203.6 ppm. n.O.e. ($H_{7.65} \rightarrow H_{7.30}$, 15%). IR (film): $\tilde{\nu}$ = 1670, 1620, 1370, 1160 cm^{-1}. $C_{27}H_{35}NO_5SSi$ (513.72): calcd. C 63.13, H 6.87, N 2.73, S 6.24; found C 63.38, H 6.45, N 2.83, S 5.88.

Data for 15c: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.15 (s, 6 H), 0.95 (s, 9 H), 2.05 (s, 2 H), 2.45 (s, 3 H), 3.82 (s, 3 H), 4.69 (s, 2 H), 6.07 (s, 1 H), 6.81 (d, *J* = 7.1 Hz, 2 H), 6.89 (d, *J* = 6.6 Hz, 2 H), 7.22 (s, 1 H), 7.29 (d, *J* = 8.8 Hz, 2 H), 7.54 (d, *J* = 8.2 Hz, 2 H) ppm. n.O.e. ($H_{7.22} \rightarrow H_{7.54}$, 6.9%; $\rightarrow H_{4.69}$, 9.6%). IR (film): $\tilde{\nu}$ = 1670, 1620, 1370, 1160 cm^{-1}. $C_{27}H_{35}NO_5SSi$ (513.72): calcd. C 63.13, H 6.87, N 2.73, S 6.24; found C 62.79, H 6.53, N 2.44, S 6.70.

(4*E*)-4-{[(4-Chlorophenyl)sulfanyl]methylidene}-2,3-diethylcyclopent-2-en-1-one (16a) and (4*Z*)-4-{[(4-Chlorophenyl)sulfanyl]-methylidene}-2,3-diethylcyclopent-2-en-1-one (16b): Treatment of hex-3-yne (0.19 mL, 1.65 mmol) and 1-chloro-4-(propa-1,2-dienylsulfanyl)benzene (0.20 g, 1.11 mmol) as described in Procedure A for Pauson–Khand intermolecular reactions afforded pure **16a** (0.08 g, 25%) as a colorless oil and a mixture (1:1) of **16a** and **16b** (25 mg, 8%) after flash chromatography (hexane/AcOEt, 4:1).

Data for 16a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 7.7 Hz, 3 H), 1.18 (t, *J* = 7.7 Hz, 3 H), 2.30 (q, *J* = 7.7 Hz, 2 H), 2.54 (q, *J* = 7.7 Hz, 2 H), 2.99 (s, 2 H), 6.45 (s, 1 H), 7.34 (s, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.3, 13.8, 16.8, 19.2, 38.4, 118.2, 129.5, 130.9, 133.3, 133.6, 136.8, 144.4, 166.1, 203.4 ppm. n.O.e. ($H_{6.45} \rightarrow H_{7.34}$, 5.1%; $\rightarrow H_{2.54}$, 5.1%; $\rightarrow H_{1.18}$, 2.7%). IR (film): $\tilde{\nu}$ = 1680 cm^{-1}. $C_{16}H_{17}ClOS$ (292.82): calcd. C 65.63, H 5.85, S 10.95; found C 65.87, H 5.59, S 11.27.

Data for 16b: (From the mixture of **16a** and **16b**): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.7 Hz, 3 H), 1.06 (t, *J* = 7.7 Hz, 3 H), 2.30 (q, *J* = 7.7 Hz, 2 H), 2.84 (q, *J* = 7.7 Hz, 2 H), 3.06 (s, 2 H), 6.27 (s, 1 H), 7.32–7.36 (m, 4 H) ppm.

(4*E*)-4-[(4-Bromophenoxy)methylene]-2,3-diethylcyclopent-2-en-1-one (17a) and (4*Z*)-4-[(4-Bromophenoxy)methylene]-2,3-diethylcyclopent-2-en-1-one (17b): Treatment of hex-3-yne (0.12 mL, 1.07 mmol) and 1-bromo-4-(propa-1,2-dienyloxy)benzene (150 mg, 0.71 mmol) as described in Procedure B for Pauson–Khand intermolecular reactions afforded pure **17a** (67 mg, 29%) as a white solid (m.p. 110–112 °C) and **17b** (44 mg, 20%) as a white solid (m.p. 82–84 °C) after flash chromatography (hexane and hexane/AcOEt, 9:1).

Data for 17a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, *J* = 7.7 Hz, 3 H), 1.22 (t, *J* = 7.7 Hz, 3 H), 2.29 (q, *J* = 7.7 Hz, 2 H), 2.54 (q, *J* = 7.7 Hz, 2 H), 3.07 (s, 2 H), 6.77 (s, 1 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 7.46 (d, *J* = 8.8 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4, 14.0, 16.5, 19.7, 36.0, 115.9, 118.4, 121.5, 132.6, 135.3, 142.9, 156.1, 166.0, 203.9 ppm. n.O.e ($H_{6.76} \rightarrow H_{2.54}$, 3.7%; $\rightarrow H_{1.22}$, 2.3%) ppm. IR (KBr): $\tilde{\nu}$ = 2960, 2920, 2860, 1670, 1580 cm^{-1}. $C_{16}H_{17}BrO_2$ (321.21): calcd. C 59.83, H 5.33; found C 59.52, H 5.02.

Data for 17b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, *J* = 7.7 Hz, 3 H), 1.19 (t, *J* = 7.7 Hz, 3 H), 2.30 (q, *J* = 7.7 Hz, 2 H), 2.76 (q,

J = 7.7 Hz, 2 H), 3.01 (s, 2 H), 6.53 (s, 1 H), 6.95 (d, J = 8.8 Hz, 2 H), 7.47 (d, J = 9.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5, 13.6, 16.2, 22.4, 37.6, 115.9, 118.1, 118.9, 132.7, 135.3, 145.3, 156.0, 167.2, 204.4 ppm. n.O.e ($H_{6.53} \rightarrow H_{3.01}$, 4.1%) ppm. IR (KBr): $\tilde{\nu}$ = 2960, 2930, 2870, 1690, 1650, 1580 cm^{-1}. $C_{16}H_{17}BrO_2$ (321.21): calcd. C 59.83, H 5.33; found C 59.52, H 5.62.

(5*E*)-5-[(4-Bromophenoxy)methylidene]-2-phenylcyclopent-2-en-1-one (18d) and (5*Z*)-5-[(4-Bromophenoxy)methylidene]-2-phenylcyclopent-2-en-1-one, (18e): Treatment of ethynylbenzene (0.47 mL, 4.38 mmol) and 1-bromo-4-(propa-1,2-dienyloxy)benzene (0.90 g, 4.25 mmol) as described in Procedure B for Pauson–Khand intermolecular reactions afforded pure **18d** (0.14 g, 10%) and **18e** (28 mg, 2%) as yellow waxes after flash chromatography (hexane and hexane/AcOEt, 2%).

Data for 18d: ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.41 (s, 2 H), 7.26–7.31 (m, 2 H), 7.36–7.45 (m, 3 H), 7.59–7.63 (m, 2 H), 7.70 (s, 1 H), 7.82–7.85 (m, 2 H), 7.98 (t, J = 2.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 28.6, 116.4, 118.4, 119.5, 126.8, 128.3, 128.4, 131.9, 132.9, 143.0, 147.0, 151.9, 155.4, 194.2 ppm. n.O.e ($H_{3.41} \rightarrow H_{7.98}$, 10.0%). IR (film): $\tilde{\nu}$ = 1690, 1640, 1580 cm^{-1}. $C_{18}H_{13}BrO_2$ (341.20): calcd. C 63.36, H 3.84; found C 63.75, H 3.56.

Data for 18e: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.35 (d, J = 2.7 Hz, 2 H), 6.88 (s, 1 H), 7.07 (d, J = 8.8 Hz, 2 H), 7.35–7.44 (m, 4 H), 7.47–7.52 (m, 2 H), 7.65 (t, J = 2.7 Hz, 1 H), 7.82 (d, J = 8.2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.8, 117.2, 117.3, 118.4, 118.9, 127.1, 128.4, 131.9, 132.3, 132.9, 147.2, 149.8, 155.7, 195.0 ppm. n.O.e ($H_{3.34} \rightarrow H_{6.88}$, 4.3%; $\rightarrow H_{7.65}$, 7.0%). IR (film): $\tilde{\nu}$ = 1690, 1640, 1580 cm^{-1}. $C_{18}H_{13}BrO_2$ (341.20): calcd. C 63.36, H 3.84; found C 62.88, H 4.20.

(4*E*)-2,3-Diethyl-4-[(phenylsulfinyl)methylene]cyclopent-2-en-1-one (19a) and (5*E*)-2,3-Diethyl-5-[(phenylsulfinyl)methylene]cyclopent-2-en-1-one (19d): Treatment of hex-3-yne (0.10 mL, 0.90 mmol) and (propa-1,2-diene-1-sulfinyl)benzene (100 mg, 0.60 mmol) as described in Procedure B for Pauson–Khand intermolecular reactions afforded pure **19a** (40 mg, 24%) as a brown solid (m.p. 101–103 °C) and **19d** (23 mg, 14%) as a yellow oil after flash chromatography (hexane and hexane/AcOEt, 1:1). After treatment as described in Procedure C, the reaction afforded **19a** (0.17 g, 40%) and **19d** (83 mg, 20%) from sulfinylallene **3k** (0.25 g, 1.52 mmol).

Data for 19a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99–1.08 (m, 6 H), 2.27–2.34 (m, 2 H), 2.41–2.46 (m, 2 H), 3.21 (d, J = 20.9 Hz, 1 H), 3.43 (d, J = 20.9 Hz, 1 H), 6.39 (s, 1 H), 7.48–7.51 (m, 3 H), 7.60–7.62 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 13.2, 17.0, 19.0, 37.5, 124.0, 127.1, 129.4, 131.0, 143.8, 145.8, 150.0, 164.6, 201.8 ppm. n.O.e ($H_{6.43} \rightarrow H_{2.49}$, 5.7%; $\rightarrow H_{1.10}$, 2.6%). IR (KBr): $\tilde{\nu}$ = 2960, 2920, 2860, 1700, 1600 cm^{-1}. $C_{16}H_{18}O_2S$ (274.38): calcd. C 70.04, H 6.61, S 11.69; found C 70.23, H 6.94, S 11.44.

Data for 19d: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.00 (t, J = 7.7 Hz, 3 H), 1.20 (t, J = 7.7 Hz, 3 H), 2.27 (q, J = 7.7 Hz, 2 H), 2.54 (q, J = 7.7 Hz, 2 H), 3.49 (d, J = 22.0 Hz, 1 H), 3.69 (d, J = 22.0 Hz, 1 H), 6.93 (d, J = 1.6 Hz, 1 H), 7.52–7.54 (m, 3 H), 7.65–7.69 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.9, 13.0, 16.5, 23.7, 32.4, 124.5, 128.2, 129.6, 131.5, 134.3, 140.3, 142.5, 170.8, 194.4 ppm. IR (film): $\tilde{\nu}$ = 2960, 2920, 2880, 1770, 1690, 1610 cm^{-1}. $C_{16}H_{18}O_2S$ (274.38): calcd. C 70.04, H 6.61, S 11.69; found C 69.81, H 6.72, S 11.32.

(5*E*)-2-Phenyl-5-[(phenylsulfinyl)methylene]cyclopent-2-en-1-one (20d) and (5*Z*)-2-Phenyl-5-[(phenylsulfinyl)methylidene]cyclopent-2-en-1-one (20e): Treatment of ethynylbenzene (0.47 mL, 4.38 mmol) and (propa-1,2-diene-1-sulfinyl)benzene (0.65 g, 3.99 mmol) as described in Procedure B for Pauson–Khand intermolecular reactions afforded pure **20d** (50 mg, 5%) as a yellow solid (m.p. 82–84 °C) and **20e** (53 mg, 5%), also as a yellow solid (m.p. 138–140 °C), after flash chromatography (hexane and hexane/AcOEt, 1:1). After treatment as described in Procedure C, the reaction afforded **20d** (68 mg, 15%) and **20e** (62 mg, 14%) from sulfinylallene **3k** (0.25 g, 1.52 mmol).

Data for 20d: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.28 (d, J = 2.2 Hz, 2 H), 7.35–7.44 (m, 6 H), 7.51–7.54 (m, 2 H), 7.66 (t, J = 2.2 Hz, 1 H), 7.68 (br. s, 1 H), 7.78 (d, J = 7.2 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.9, 127.0, 128.2, 128.4, 128.4, 129.4, 130.8, 131.8, 133.1, 135.7, 141.0, 144.7, 149.1, 191.2 ppm. n.O.e ($H_{7.68} \rightarrow H_{3.28}$, 3.7%). IR (KBr): $\tilde{\nu}$ = 1670, 1620, 1590 cm^{-1}. $C_{18}H_{14}O_2S$ (294.37): calcd. C 73.44, H 4.79, S 10.89; found C 73.22, H 5.12, S 10.57.

Data for 20e: ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.38 (s, 2 H), 7.35–7.46 (m, 7 H), 7.58 (d, J = 7.9 Hz, 2 H), 7.83 (d, J = 7.3 Hz, 2 H), 8.00 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 32.4, 126.6, 127.9, 128.3, 128.4, 129.5, 129.7, 129.9, 131.8, 135.7, 137.2, 143.1, 152.5, 193.1 ppm. n.O.e ($H_{3.38} \rightarrow H_{7.35–7.46}$, 3.1%; $\rightarrow H_{8.00}$, 4.5%). IR (KBr): $\tilde{\nu}$ = 1650, 1580 cm^{-1}. $C_{18}H_{14}O_2S$ (294.37): calcd. C 73.44, H 4.79, S 10.89; found C 73.78, H 5.01, S 10.50.

(4*E*)-2,3-Diethyl-4-[(phenylsulfonyl)methylidene]cyclopent-2-en-1-one (21a) and (5*E*)-2,3-Diethyl-5-[(phenylsulfonyl)methylene]cyclopent-2-en-1-one (21d): Treatment of hex-3-yne (0.08 mL, 0.70 mmol) and (propa-1,2-diene-1-sulfonyl)benzene (124 mg, 0.68 mmol) as described in Procedure B for Pauson–Khand intermolecular reactions afforded pure **21a** (37 mg, 19%) and **21d** (27 mg, 14%), as brown waxes after flash chromatography (hexane and hexane/AcOEt, 25%). After treatment as described in Procedure C, the reaction afforded **21a** (0.14 g, 35%) and **21d** (97 mg, 24%) from sulfonylallene **3l** (0.25 g, 1.39 mmol).

Data for 21a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (t, J = 7.7 Hz, 3 H), 1.12 (t, J = 7.7 Hz, 3 H), 2.34 (q, J = 7.7 Hz, 2 H), 2.48 (q, J = 7.7 Hz, 2 H), 3.39 (d, J = 1.6 Hz, 2 H), 6.45 (t, J = 1.6 Hz, 1 H), 7.55–7.69 (m, 3 H), 7.93–7.96 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 13.2, 17.2, 19.1, 37.6, 120.9, 127.4, 129.4, 133.6, 141.3, 149.8, 150.9, 164.0, 202.1 ppm. n.O.e. ($H_{6.45} \rightarrow H_{2.47}$, 5.9%; $\rightarrow H_{1.18}$, 3.0%; $\rightarrow H_{7.95}$, 2.4%), ($H_{3.40} \rightarrow H_{7.95}$, 2.8%). IR (film): $\tilde{\nu}$ = 2980, 2960, 2890, 1710, 1600 cm^{-1}. $C_{16}H_{18}O_3S$ (290.38): calcd. C 66.18, H 6.25, S 11.04; found C 65.95, H 6.02, S 11.32.

Data for 21d: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.7 Hz, 3 H), 1.21 (t, J = 7.7 Hz, 3 H), 2.28 (q, J = 7.7 Hz, 2 H), 2.55 (q, J = 7.7 Hz, 2 H), 3.62 (s, 2 H), 6.94 (s, 1 H), 7.56–7.69 (m, 3 H), 7.94 (d, J = 7.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.8, 12.9, 16.5, 23.8, 33.0, 127.7, 127.8, 129.4, 134.0, 140.2, 142.5, 143.4, 171.8, 194.6 ppm. n.O.e ($H_{3.62} \rightarrow H_{2.56}$, 1.9%; $\rightarrow H_{1.20}$, 2.1%). IR (film): $\tilde{\nu}$ = 2980, 2920, 2880, 1700 cm^{-1}. $C_{16}H_{18}O_3S$ (290.38): calcd. C 66.18, H 6.25, S 11.04; found C 65.98, H 5.96, S 10.69.

***N*-[(*E*)-(2,3-Diethyl-4-oxocyclopent-2-en-1-ylidene)methyl]-*N*-(2-ethynylphenyl)acetamide (22a):** Treatment of hex-3-yne (0.12 g, 1.52 mmol) and *N*-(2-ethynylphenyl)-*N*-propadienylacetamide (0.20 g, 1.01 mmol) as described in Procedure B for Pauson–Khand intermolecular reactions afforded pure **22a** (46 mg, 15%) as a yellow oil after flash chromatography (hexane/AcOEt, 4:1). After treatment as described in Procedure C, the reaction afforded **22a** (0.17 g, 45%) from allenamide **3f** (0.25 g, 1.27 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.97 (t, J = 7.3 Hz, 3 H), 1.21 (t, J = 7.3 Hz, 3 H), 1.84 (d, J = 20.7 Hz, 1 H), 1.95 (s, 3 H), 2.10 (d, J =

20.7 Hz, 1 H), 2.20 (q, J = 7.3 Hz, 2 H), 2.59 (q, J = 7.3 Hz, 2 H), 3.26 (s, 1 H), 7.26–7.29 (m, 1 H), 7.43–7.47 (m, 2 H), 7.61 (s, 1 H), 7.62–7.64 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.3, 14.0, 16.5, 19.5, 22.4, 36.6, 78.8, 83.7, 120.3, 121.0, 123.0, 129.3, 129.5, 130.4, 134.0, 141.0, 142.4, 170.0, 202.3 ppm. n.O.e ($H_{7.61} \rightarrow H_{1.84}$, 0.0%; $\rightarrow H_{2.10}$, 0.0%). IR (KBr): $\tilde{\nu}$ = 1690, 1630 cm^{-1}. $C_{20}H_{21}NO_2$ (307.39): calcd. C 78.15, H 6.89, N 4.56; found C 77.98, H 7.18, N 4.40.

5-[(4-Methylphenyl)sulfonyl]-3,5-dihydro-2*H*-cyclopenta[*c*]quinolin-2-one (23): Treatment of *N*-(2-ethynylphenyl)-4-methyl-*N*-(propa-1,2-dienyl)benzenesulfonamide (100 mg, 0.32 mmol) with $Mo(MeCN)_3(CO)_3$ by the general procedure for intramolecular Pauson–Khand reactions afforded pure **23** (46 mg, 43%) as a yellow solid (dec. 248 °C) after flash chromatography (hexane/AcOEt, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3 H), 3.24 (s, 2 H), 6.16 (s, 1 H), 7.28–7.34 (m, 3 H), 7.48 (t, J = 7.3 Hz, 1 H), 7.71–7.75 (m, 4 H), 8.18 (d, J = 8.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 38.3, 114.2, 119.1, 119.2, 120.6, 121.8, 125.7, 127.3, 127.5, 130.2, 132.0, 134.2, 134.7, 145.8, 160.3, 203.3 ppm. IR (KBr): $\tilde{\nu}$ = 3080, 2940, 1630, 1600, 1580 cm^{-1}. $C_{19}H_{15}NO_3S$ (337.39): calcd. C 67.64, H 4.48, N 4.15, S 9.50; found C 67.29, H 4.75, N 3.88, S 9.78.

3*H*-Cyclopenta[*c*]chromen-2-one (24) and 1-Methylene-1,8a-dihydro-8-oxacyclopenta[*a*]inden-2-one (25): Treatment of 1-ethynyl-2-(propa-1,2-dien-1-yloxy)benzene (156 mg) with $Mo(CO)_6$ by the general procedure for intramolecular Pauson–Khand reactions afforded pure **24** (45 mg, 25%) as a colorless oil and **25** (77 mg, 38%) as a yellow solid (m.p. 79–81 °C) after flash chromatography (hexane/AcOEt, 1:1).

Data for 24: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.16 (s, 2 H), 6.14 (s, 1 H), 7.13 (s, 1 H), 7.32 (t, J = 7.7 Hz, 1 H), 7.56 (t, J = 7.1 Hz, 1 H), 7.72 (d, J = 7.7 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.5, 113.1, 116.9, 118.2, 119.9, 124.9, 126.5, 132.8, 136.8, 152.5, 159.1, 203.2 ppm. IR (film): $\tilde{\nu}$ = 1680, 1650, 1610, 1550 cm^{-1}. $C_{12}H_8O_2$ (184.19): calcd. C 78.25, H 4.38; found C 78.69, H 4.15.

Data for 25: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.73 (d, J = 1.6 Hz, 1 H), 5.93–5.95 (m, 1 H), 6.18 (d, J = 1.6 Hz, 1 H), 6.38 (d, J = 2.7 Hz, 1 H), 7.03–7.11 (m, 2 H), 7.46 (td, J_1 = 1.6, J_2 = 7.2 Hz, 1 H), 7.60 (dd, J_1 = 1.1, J_2 = 7.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 87.1, 112.6, 116.0, 121.4, 122.6, 122.6, 125.2, 134.9, 144.0, 165.5, 173.4, 193.4 ppm. IR (KBr): $\tilde{\nu}$ = 3080, 1690, 1610, 1570 cm^{-1}. $C_{12}H_8O_2$ (184.19): calcd. C 78.25, H 4.38; found C 77.89, H 4.65.

Supporting Information (see also the footnote on the first page of this article): Experimental procedures and data for the synthesis of starting materials.

Acknowledgments

This work was supported by the Spanish Ministerio de Educación y Ciencia (MEC) (grant No. CTQ2006/00601). A. P. and A. G.-G. acknowledge fellowships from the Fundación Universitaria San Pablo-CEU.

[1] Recent reviews on the Pauson–Khand reaction: a) J. Blanco-Urgoiti, L. Anorbe, L. Perez-Serrano, G. Dominguez, J. Perez-Castells, *Chem. Soc. Rev.* **2004**, *33*, 32–42; b) T. Sugihara, M. Yamaguchi, M. Nishizawa, *Chem. Eur. J.* **2001**, *7*, 1589–1595; c) K. M. Brummond, J. L. Kent, *Tetrahedron* **2000**, *56*, 3263–3283.
[2] Review on the intermolecular PKR: S. E. Gibson, N. Mainolfi, *Angew. Chem. Int. Ed.* **2005**, *44*, 3022–3037.
[3] W. J. Kerr, M. McLaughlin, P. L. Pauson, S. M. Robertson, *J. Organomet. Chem.* **2001**, *630*, 104–117.
[4] M. Rodriguez-Rivero, J. C. de la Rosa, J. C. Carretero, *J. Am. Chem. Soc.* **2003**, *125*, 14992–14993.
[5] J. F. Reichwein, S. T. Iacono, B. L. Pagenkopf, *Tetrahedron* **2002**, *58*, 3813–3822.
[6] K. Itami, K. Mitsudo, J. Yos*h*ida, *Angew. Chem. Int. Ed.* **2002**, *41*, 3481–3484.
[7] F. Robert, A. Milet, Y. Gimbert, D. Konya, A. E. Greene, *J. Am. Chem. Soc.* **2001**, *123*, 5396–5400.
[8] a) *Modern Allene Chemistry* (Eds.: N. Krause, A. S. K. Hashmi), Wiley-VCH, Weinheim, **2004**; b) R. Zimmer, C. U. Dinesh, E. Nandanan, F. A. Khan, *Chem. Rev.* **2000**, *100*, 3067–3126; c) J. A. Marshall, *Chem. Rev.* **2000**, *100*, 3163–3186; d) A. Hoffmann-Röder, N. Krause, *Angew. Chem. Int. Ed.* **2002**, *41*, 2933–2935; *Angew. Chem.* **2002**, *114*, 3057–3059; e) A. Hoffmann-Röder, N. Krause, *Angew. Chem. Int. Ed.* **2004**, *43*, 1196–1216; *Angew. Chem.* **2004**, *116*, 1216–1236; f) N. Krause, A. Hoffmann-Röder, *Tetrahedron* **2004**, *60*, 11671–11694; g) S. Ma, *Chem. Rev.* **2005**, *105*, 2829–2871.
[9] Review on the allenic PKR: B. Alcaide, P. Almendros, *Eur. J. Org. Chem.* **2004**, 3377–3383.
[10] a) F. Antras, M. Ahmar, B. Cazes, *Tetrahedron Lett.* **2001**, *42*, 8153–8156; b) F. Antras, M. Ahmar, B. Cazes, *Tetrahedron Lett.* **2001**, *42*, 8157–8160; c) M. Ahmar, O. Chabanis, J. Gauthier, B. Cazes, *Tetrahedron Lett.* **1997**, *38*, 5277–5280; d) M. Ahmar, F. Antras, B. Cazes, *Tetrahedron Lett.* **1995**, *36*, 4417–4420.
[11] L. Añorbe, A. Poblador, G. Domínguez, J. Pérez-Castells, *Tetrahedron Lett.* **2004**, *45*, 4441–4444.
[12] This behavior of tosylamides has been described earlier: L. J. van Boxtel, S. Körbe, M. Noltemeyer, A. de Meijere, *Eur. J. Org. Chem.* **2001**, 2283–2292.
[13] a) P. Hamel, *J. Org. Chem.* **2002**, *67*, 2854–2858; b) S. Ma, H. Ren, Q. Wei, *J. Am. Chem. Soc.* **2003**, *125*, 4817–4830.
[14] A. Padwa, M. Meske, S. S. Murphree, S. H. Watterson, Z. Ni, *J. Am. Chem. Soc.* **1995**, *117*, 7071–7080.
[15] L. Pérez-Serrano, J. Blanco-Urgoiti, L. Casarrubios, G. Domínguez, J. Pérez-Castells, *J. Org. Chem.* **2000**, *65*, 3513–3519, and references therein.
[16] The signal of the CH_2 in the cyclopentenone appears at δ = 38 ppm, which agrees with calculated values for compound **5a**. See experimental for n. O. e. data.
[17] Review on PKRs of electron-deficient alkenes: M. R. Rivero, J. Adrio, J. C. Carretero, *Eur. J. Org. Chem.* **2002**, 2881–2889.
[18] J. Adrio, J. C. Carretero, *J. Am. Chem. Soc.* **2007**, *129*, 778–779.
[19] a) K. M. Brummond, H. Wan, *Tetrahedron Lett.* **1998**, *39*, 931–934; b) J. L. Kent, H. Wan, K. M. Brummond, *Tetrahedron Lett.* **1995**, *36*, 2407–2410; c) K. M. Brummond, H. Wan, J. L. Kent, *J. Org. Chem.* **1998**, *63*, 6535–6545.

Received: November 5, 2007
Published Online: January 15, 2008

