One-pot Synthesis of Aromatic Fused 2,3-Dihydroindanone by Tandem Pauson-Khand/Michael/Henry Reaction[†]

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The intermolecular Pauson-Khand reaction between 2-ethynylbenzaldehyde and ethylene promoted by dimethyl sulfide can be utilized to synthesize 2-(2-formylphenyl)cyclopentenone efficiently. This compound and its derivatives undergo a cascade process of Michael addition reaction followed by Henry reaction with nitromethane to construct substituted aromatic fused 2,3-dihydroindanones. Furthermore, direct one-pot synthesis of aromatic fused 2,3-dihydroindanones from 2-ethynylbenzaldehyde is achieved.

Keywords 2-ethynylbenzaldehyde, tandem Pauson-Khand/Michael/Henry reaction, aromatic fused 2,3-dihydroindanone

Introduction

2,3-Dihydroindanones are useful intermediates in organic synthesis. These building blocks exist in many natural products, such as ningalin D, NCS-chrom, pterosins B, fredericamycin A and other kinds of alkaloids.^[1-4] Besides, 2,3-dihydroindanones are crucial components of many HIV-I protease inhibitors and antibacterial agents.^[5-7] Known methods to obtain these compounds refer to Friedel-Crafts acylation or aromatization reaction, which were proven to be less convenient.^[8-10] Recently, some efficient synthetic methods toward 2,3-dihydroindanones have been reported. Shaabani used sodium bromate to oxidize dihydroindenes into dihydroindanones in the presence of catalytic amount of silica/sulfuric acid.^[11] Breit developed a method of hydroacylation of alkenes employing a bifunctional catalyst system.^[12] Ohwada cyclized arylacetoacetates to indene and dihydronaphthalene derivatives in strong acids.^[13]

In our study toward the synthesis of cephalotaxine, we discovered that 2-acetenyl piperonyl aldehyde (1) reacted with ethylene, giving 2-arylcyclopentenone 2 by an intermolecular Pauson-Khand reaction,^[14] and treatment of 2 and nitromethane with piperazine afforded a benzo[4.3.0]bicycle intermediate, which underwent dehydration and aromatization immediately to give the product 3 ultimately (Scheme 1). On this basis, we wish to report the development of an efficient method to construct aromatic fused 2,3-dihydroindanones via a one-

pot multi-component cascade process directly from 2-formyl arylacetylenes.

Experimental

Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Analytical thin-layer chromatography (TLC) was performed on Silicycle silica gel plates with F-254 as an indicator and compounds were visualized by irradiation with UV light. Flash column chromatography was carried out using silica gel H (40 µm). ¹H NMR and ¹³C NMR spectra were recorded on Varian Mercury-vx300 spectrometer (300 MHz for ¹H, 75 MHz for ¹³C) or Varian Mercury-400 spectrometer (400 MHz for ¹H, 101 MHz for 13 C). The spectra were recorded in CDCl₃ or d-DMSO, unless otherwise indicated at room temperature, ¹H NMR and ¹³C NMR chemical shifts are reported in relative to the residual solvent peak $({}^{1}H, {}^{13}C)$ as an internal standard. IR spectra were recorded using Nicolet 380FT-IR instrument and are reported in wavenumbers (cm⁻¹). MS was performed on Agilent 5973N mass instrument (EI). HRMS was performed on Waters Micromass GCT-CA176 (EI).

General procedure for the synthesis of 2-ethynylbenzaldehyde analogues 1a-1h

2-Ethynylbenzaldehyde (1a) 2-Bromobenzaldehyde (5.00 g, 27.02 mmol) was dissolved in THF/TEA (V/V=5/3, 54 mL) under argon atmosphere,

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[†] Dedicated to the Memory of Professor Weishan Zhou.

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Scheme 1 The tandem cyclization of 2-arylcyclopentenone 2 with nitromethane



PdCl₂(PPh₃)₂ (379 mg, 0.54 mmol) and CuI (51 mg, 0.27 mmol) were added and stirred for 5 min at room temperature, trimethylsilylacetylene (2.79 g, 28.35 mmol) was then added and the resulting dark mixture was heated at 80 °C for 5 h and cooled to room temperature. After filtered through a thin pad of Celite, the filtrate was dried under reduced pressure and the residue was dissolved in MeOH (50 mL), anhydrous K₂CO₃ (3.42 g, 27.70 mmol) was added. After stirred at room temperature for 0.5 h, the mixture was poured into saturated NH₄Cl solution (250 mL) and extracted with DCM (100 mL \times 3). The organic phase was combined and dried over anhydrous Na₂SO₄. Purification by silica column chromatography (EA : PE=1 : 50) gave 1a as a light yellow crystal, 2.90 g, 90%. ¹H NMR (400 MHz, CDCl₃) δ : 10.54 (s, 1H), 7.94 (dd, J=7.8, 0.7 Hz, 1H), 7.69 - 7.55 (m, 2H), 7.48 (t, J = 7.5 Hz, 1H), 3.46 (s, 1H).

5-Chloro-2-ethynylbenzaldehyde (1b) Colorless crystal, 82%; ¹H NMR (300 MHz, CDCl₃) δ : 10.47 (s, 1H), 7.94–7.88 (m, 1H), 7.58–7.52 (m, 1H), 7.26 (s, 1H), 3.50 (s, 1H).

5-Fluoro-2-ethynylbenzaldehyde (1c) Colorless crystal, 77%; ¹H NMR (300 MHz, CDCl₃) δ : 10.49 (d, J=3.2 Hz, 1H), 7.59–7.64 (m, 2H), 7.25–7.30 (m, 1H), 3.46 (s, 1H).

5-Methyloxy-2-ethynylbenzaldehyde (1d) Colorless crystal, 82%; ¹H NMR (300 MHz, CDCl₃) δ : 10.49 (s, 1H), 7.53 (d, J=8.6 Hz, 1H), 7.40 (d, J=2.8 Hz, 1H), 7.11 (dd, J=8.5, 2.7 Hz, 1H), 3.87 (s, 3H), 3.37 (s, 1H).

4-Fluoro-2-ethynylbenzaldehyde (1e) Colorless crystal, 62%; ¹H NMR (300 MHz, CDCl₃) δ : 10.46 (s, 1H), 7.97 (dd, J=8.8, 5.9 Hz, 1H), 7.29 (dd, J=8.8, 2.4 Hz, 1H), 7.16-7.21 (m, 1H), 3.52 (s, 1H).

4-Methyl-2-ethynylbenzaldehyde (1f) Colorless crystal, 75%; ¹H NMR (300 MHz, CDCl₃) δ : 10.47 (s, 1H), 7.83 (d, *J*=8.0 Hz, 1H), 7.43 (s, 1H), 7.29 (d, *J*=8.0 Hz, 1H), 3.42 (s, 1H), 2.41 (s, 3H).

3-Ethynylthiophene-2-carbaldehyde (1g) Colorless crystal, 93%. ¹H NMR (300 MHz, CDCl₃) δ : 10.13 (d, *J*=1.5 Hz, 1H), 7.67 (dd, *J*=5.1, 1.5 Hz, 1H), 7.21 (d, *J*=5.1 Hz, 1H), 3.46 (s, 1H).

3-Ethynylisonicotinaldehyde (1h) Colorless crystal, 85%; ¹H NMR (300 MHz, CDCl₃) δ : 10.52 (s, 1H), 8.82 (br, 2H), 7.74 (s, 1H), 3.59 (s, 1H).

General procedure for the one-pot synthesis of aromatic fused 2,3-dihydroindanone 3a-3f

4-Nitro-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-one (3a) Compound 1a (200 mg, 1.54 mmol) and $Co_2(CO)_8$ (631 mg, 1.85 mmol) were stirred in anhydrous xylene (12 mL) under argon atmosphere for 1.5 h to get a dark brown solution which was then transferred into an antoclave, TDMP (264 mg, 2.31 mmol), nitromethane (2 mL) and DMS (4 mL) were added in sequence. After 20 bar ethylene was charged, the antoclave was heated at 130 $^{\circ}$ C for 24 h and cooled to room temperature. The gas was released, the residue was diluted with 50 mL EtOAc and filterd through a thin pad of Celite. The filtrate was concentrated under reduced pressure and then purified by silica column chromatography (EA : PE=1 : 50) to get **3a** as a light yellow crystal, 190 mg, 51%, m.p. 185 °C; ¹H NMR (300 MHz, $CDCl_3$) δ : 9.29 (d, J=8.5 Hz, 1H), 8.99 (s, 1H), 8.09 (d, J=8.2 Hz, 1H), 7.87 (t, J=7.7 Hz, 1H), 7.72 (t, J=7.6 Hz, 1H), 3.75–3.63 (m, 2H), 2.95–2.82 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ : 206.0, 150.5, 134.0, 132.7, 132.3-131.6 (m), 130.0, 128.5, 124.3, 36.6, 26.6. IR (KBr) v: 3383, 3084, 2922, 2850, 1701, 1624, 1593, 1522 cm⁻¹; EI-MS *m/z* (%): 227 (M⁺, 100). HRMS (EI) calcd for C₁₃H₉NO₃: 227.0582; found 227.0582.

7-Chloro-4-nitro-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (3b) Light yellow crystal, 38%, m.p. 215 °C; ¹H NMR (300 MHz, CDCl₃) δ : 9.28 (d, *J*=9.3 Hz, 1H), 8.92 (s, 1H), 8.08 (s, 1H), 7.82 (d, *J*= 9.0 Hz, 1H), 3.71-3.67 (m, 2H), 2.93-2.89 (m, 2H). IR (KBr) *v*: 3081, 1702, 1592, 1525, 1342, 1080, 949, 844 cm⁻¹; EI-MS *m/z* (%): 261.0 (M⁺, 77), 244.0 (100). HRMS (EI) calcd for $C_{13}H_8NClO_3$: 261.0191; found 261.0193.

7-Fluoro-4-nitro-2,3-dihydro-1*H*-cyclopenta[*a*]naphthalen-1-one (3c) Light yellow crystal, 33%, m.p. 193–195 °C; ¹H NMR (300 MHz, CDCl₃) δ : 9.34 (dd, *J*=9.0, 5.7 Hz, 1H), 8.90 (s, 1H), 7.70 (dd, *J*=8.7, 2.4 Hz, 1H), 7.64 (td, *J*=8.4, 2.7 Hz, 1H), 3.67–3.61 (m, 2H), 2.90–2.87 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ : 205.8, 163.0 (d, *J*=187.4 Hz, 1C), 149.5, 144.5, 134.2, 133.2 (d, *J*=75.0 Hz, 1C), 130.9 (d, *J*= 3.9 Hz, 1C), 128.6, 127.0 (d, *J*=6.4 Hz, 1C), 122.8 (d, *J*=18.2 Hz, 1C), 113.4 (d, *J*=1.62 Hz, 1C), 36.5, 26.5; IR (KBr) *v*: 3447, 3088, 1705, 1609, 1532, 1456, 1349, 1160 cm⁻¹; EI-MS *m/z* (%): 245 (M⁺, 74), 170 (100). HRMS (EI) calcd for C₁₃H₈NFO₃: 245.0490; found 245.0488.

7-Methyloxy-4-nitro-2,3-dihydro-1*H*-cyclopenta-[*a*]naphthalen-1-one (3d) Light yellow crystal, 69%, m.p. 226-229 °C; ¹H NMR (300 MHz, DMSO-*d*₆) δ : 9.16 (s, 1H), 9.07 (d, *J*=9.0 Hz, 1H), 7.89 (d, *J*=1.8 Hz, 1H), 7.64 (dd, *J*=9.0, 2.4 Hz, 1H), 3.94 (s, 3H), 3.56-3.52 (m, 2H), 2.84-2.80 (m, 2H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ : 206.7, 159.0, 148.6, 144.4, 133.9, 133.5, 131.1, 126.6, 125.3, 124.9, 109.6, 56.1, 36.8, 26.5; IR (KBr) *v*: 3447, 1701, 1600, 1529, 1464, 1376, 1340, 849 cm⁻¹; EI-MS *m/z* (%): 257 (M⁺, 67), 240 (100). HRMS (EI) calcd for C₁₄H₁₁NO₄: 257.0684; found 257.0688.

8-Fluoro-4-nitro-2,3-dihydro-1*H***-cyclopenta[***a***]naphthalen-1-one (3e) Light yellow crystal, 25%, m.p. 189–190 °C; ¹H NMR (300 MHz, CDCl₃) \delta: 9.00 (s, 1H), 8.98 (dd,** *J***=10.2, 1.8 Hz, 1H), 8.14 (dd,** *J***=9.0, 5.7 Hz, 1H), 7.52 (td,** *J***=8.7, 2.4 Hz, 1H), 3.71–3.67 (m, 2H), 2.92–2.88 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) \delta: 205.6, 166.7 (d,** *J***=191.3 Hz, 1C), 151.5, 143.1, 133.6 (d,** *J***=4.5 Hz, 1C), 133.2 (d,** *J***=9.0 Hz, 1C), 132.7 (d,** *J***=7.7 Hz, 1C), 131.8, 128.8, 119.2 (d,** *J***=19.4 Hz, 1C), 109.1 (d,** *J***=17.5 Hz, 1C), 36.5, 26.7; IR (KBr)** *v***: 1702, 1624, 1600, 1532, 1451, 1419, 1366, 1174 cm⁻¹. EI-MS** *m/z* **(%): 245 (M⁺, 57), 170 (100). HRMS (EI) calcd for C₁₃H₈NFO₃: 245.0492; found 245.0493.**

8-Methyl-4-nitro-2,3-dihydro-1*H***-cyclopenta[***a***]naphthalen-1-one (3f**) Light yellow crystal, 54%, m.p. 180–181 °C. ¹H NMR (300 MHz, CDCl₃) δ : 9.09 (s, 1H), 8.94 (s, 1H), 7.98 (d, *J*=8.4 Hz, 1H), 7.55 (dd, *J*= 8.4, 1.2 Hz, 1H), 3.68–3.64 (m, 2H), 2.89–2.86 (m, 2H), 2.63 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ : 206.1, 150.8, 144.2, 142.7, 133.0, 131.8, 131.7, 130.6, 129.9, 129.7, 123.3, 36.5, 26.6, 22.6; IR (KBr) *v*: 1691, 1624, 1602, 1527, 1422, 1338, 1111 cm⁻¹; EI-MS *m/z* (%): 241 (M⁺, 68), 224 (100). HRMS (EI) calcd for C₁₄H₁₁NO₃: 241.0740; found 241.0739.

Results and Discussion

Initially, analogues of **2a** were prepared though intermolecular Pauson-Khand reaction of 2-ethynylben-

zaldehyde 1a with ethylene (Table 1).^[15-17] Since the intermolecular Pauson-Khand reaction between 2a and ethylene generally gave a low yield, it is crucial to find an appropriate reaction condition, especially an effective promoter. Different promoters were tested and the results were listed in Table 1. The commonly used tertiary amine N-oxides, NMO (N-methylmorpholine, N-oxide), TMANO (trimethylamine, N-oxide) could only afford moderate yields 56%-59% (Entries 1, 2).^[16-18] Mild alkyl methyl sulfide (*n*-BuSMe, PhSMe, $n-C_{10}H_{21}SMe$) also only gave low to moderate yields of 24% - 58% (Entries 3-5), which might be attributed to the bulky phenyl substitute in the cobalt-alkynl complexes hindering the approach of bulk promoters.^[19,20] Thus, a "smaller" promoter DMS (dimethyl sulfide) was used and worked with improved yields (Entries 6, 7), and xylene was also a nice solvent (Entry 8).

 Table 1
 Influence of promoters to the intermolecular Pauson-Khand reaction

	CHO -	co ₂ (CO) ₈ (1.2 e ethylene (30 l promotors solvents, 2	equiv.), bar),	C O O	HO
Entry	Promotor	Solvent	T/°C	<i>t</i> /h	Yield ^a /%
1	TMANO	PhMe/MeOH	[40	6	59
2	NMO	PhMe/DCM	40	8	56
3	<i>n</i> -BuSMe	1,2-DCE	83	24	44
4	PhSMe	1,2-DCE	83	24	24
5	$n-C_{10}H_{21}SMe$	1,2-DCE	120	2	58
6	MeSMe	1,2-DCE	83	8	70
7	MeSMe	1,2-DCE	120	2	71
8	MeSMe	xylene	130	5	71

^a Isolated yields.

Since α,β -unsaturated aldehydes/ketones readily undergo 1,2-addition with nitroalkanes under basic conditions, both the activation of carbonyl group and the controlling of proper pH are crucial to gain the Michael addition reaction product.^[21] Hanessian group has reported that TDMP (trans-2,5-dimethylpiperazine) was an effective base in the Michael addition reaction using nitromethane as an nucleophile.^[22] L-Proline was usually used to activate carbonyl. Based on the above work, we screened conditions for the Michael/Henry cascade reaction (Table 2). Product 3a was isolated in 35% yield when 2a was treated with TDMP (1.0 equiv.), L-proline (2 mol%) and MeNO₂ (2 equiv.) in DCM (Entry 1). The structure of 3a was confirmed by X-ray analysis. For other solvents, **3a** could also be isolated in 8%-87%yield (Entries 2-10). When using chloroform as solvent, 87% yield was obtained (Entry 2). Additional experiments showed that L-proline was not necessary
 Table 2
 Influences of solvent and temperature to the cyclization



Entry	Solvent	<i>T</i> /°C	t/d	Yield ^a /%
1	DCM	r.t.	3	35
2	CHCl ₃	r.t.	9	87
3	EtOH	r.t.	2	34
4	MeOH	r.t.	4	67
5	MeCN	r.t.	6	84
6	DMSO	r.t.	1	30
7	HMPA	r.t.	2	8
8	DMF	r.t.	2	16
9	THF	r.t.	3	31
10	Toluene	r.t.	3	75
$11^{b,c}$	CHCl ₃	r.t.	2	75

^{*a*} Isolated yields; ^{*b*} No *L*-proline was added; ^{*c*} 4 equiv. of TDMP was added.

Scheme 2 The proposed mechanism for the cascade cyclization reaction

and the cyclization reaction rate and yield did not reduce. The cyclization reaction rate increased significantly when 4 equiv. of TDMP was used (Entry 11), but the yield did not improve much, and 1.5 equiv. of TDMP was an optimal dosage. Other catalytic systems, *eg.* rubidium prolinate,^[23] imidazolidine-tetrazole,^[24] salen-Al catalyst^[25] and prolinol derivatives,^[26] *etc.*, proven successful in nitromethane Michael addition were also tested, but none of them gave a positive result. This might be attributed to the conformational differences between open chain enones and cycloenones.

On the basis of the reaction result, we proposed the mechanism for the cascade cyclization reaction (Scheme 2). **IM1** resulted from **2a** and CH₃NO₂ through Michael addition reaction using TDPM as the base; **IM1** then underwent the intramolecualr Henry reaction, giving **IM2** also using TDMP as the base; **3a** was generated through auto dehydration and aromatization from **IM2**.

Efforts were made to achieve a one-pot multi-components cascade synthesis of aromatic fused 2,3-dihydroindanone directly from 2-formylarylacetylene considering that both the Pauson-Khand reaction and later cyclization were conducted under mild and almost neutral conditions. **1a** was used to screen the reaction conditions (Table 3). The desired product **3a** could be obtained in 30% yield when using *n*-BuSM as Pason-Khand reaction promoter and 1,2-DCE as solvent (Entry 1). Reaction conditions were further optimized to improve the yield (Entries 2–6). When reaction was carried out in xylene at 130 °C using 35 equiv. DMS, a moderate yield could be achieved (Entry 6).

The scope of this cascade cyclization reaction was examined for a series of substituted 2-formylarylacetylenes 1a-1h (Table 4).^[26] Remarkably, electron rich



CHO 1a		Co ₂ (CO) ₈ (1.2 equiv. ethylene (30 bar), RSMe (3.5 equiv.), TDMP (1.5 equiv.))	NO ₂		
		MeNO ₂ , solvents, D, 24 h	- //	o 3a		
Entry	R	Solvent	T/°℃	Yield ^a /%		
1	<i>n</i> -Bu	1,2-DCE	83	30		
2	<i>n</i> -Bu	xylene	130	41		
3	$n-C_{10}H_{21}$	1,2-DCE	83	45		
4	Me	1,2-DCE	83	25		
5^b	Me	toluene	110	43		
6 ^b	Mo	vulana	120	51		

Table 3One-pot cyclization of 1a

^{*a*} Isolated yields; ^{*b*} 35 equ. DMS was used considering its low boiling point.

 Table 4
 One-pot Pauson-Khand/Michael/Henry cascade cyclization of substituted 2-formylarylacetylenes^a

	Ar 2 1a - 1h	Co ₂ (CO) ₈ (1.2 equiv.) ethylene (30 bar), DMS (40 equiv.), TDMP (1.5 equiv.) MeNO ₂ /xylene=1:6 (<i>V</i> / <i>V</i>), 130 °C, 24 - 48 h	Ar 2 0 3a - 3h
Ent	ry Product	Ar ring	Yield ^a /%
1	3a	and the second s	51
2	3b		38
3	3c	F 1'2,- 2,5'	33
4	3d	MeO	69
5	3e	F 2 2	25
6	3f	Me 2 5	54
7	3g	2 2 2 S 1 25	_

			Continued
Entry	Product	Ar ring	Yield ^a /%
8	3h	N 2 5	trace

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^{*a*} Isolated yields.

aromatic substrates **3a**, **3d** and **3f** (Entries 1, 4 and 6) gave better results than electron deficient ones **3b**, **3c** and **3e** (Entries 2, 3 and 5). For heterocyclic substrates **3g** and **3h**, the cascade cyclization reaction could not proceed (Entries 7 and 8).

Conclusions

In general we have described a facile, convenient one-pot approach to synthesize the aromatic fused 2,3-dihydroindanones from 2-formylarylacetylenes. Although the reaction only gave a moderate yield, it has advantages of constructing complicated aromatic fused dihydroindanone skeletons in one single step from simple starting materials and tolerating many functional groups. Besides, the nitro group and carbonyl contained in the aromatic fused 2,3-dihydroindanone products make them flexible synthetic intermediates.

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References

- Hamasaki, A.; Zimpleman, J. D.; Hwang, I.; Boger, D. L. J. Am. Chem. Soc. 2005, 127, 10767.
- Xi, Z.; Hwang, G. S.; Goldberg, I. H.; Harris, J. L.; Pennington, W. T.; Fouad, F. S.; Qabaja, G.; Wright, J. M.; Jones, G. B. *Chem. Biol.* 2002, *9*, 925.
- [3] Castillo, U. F.; Wilkins, A. L.; Lauren, D. R.; Smith, B. L.; Alonso-Amelot, M. J. Agric. Food Chem. 2003, 51, 2563.
- [4] Akai, S.; Tsujino, T.; Fukuda, H.; Iio, K.; Takeda, Y.; Kawaguchi, K.; Naka, T.; Higuchi, K.; Akiyama, E.; Fujioka, H.; Kita, Y. *Chem. Eur. J.* **2005**, *11*, 6286.
- [5] Arefalk, A.; Wannberg, J.; Larhed, M.; Hallberg, A. J. Org. Chem. 2006, 71, 1265.
- [6] Ghilsoo, N.; Yang, S. K.; Kyung, C. Bioorg. Med. Chem. Lett. 2010, 20, 2671.
- [7] Brik, A.; Lin, Y. C.; Elder, J.; Wong, C. H. Chem. Biol. 2002, 9, 891.
- [8] Kurouchi, H.; Sugimoto, H.; Otani, Y.; Ohwada, T. J. Am. Chem. Soc. 2010, 132, 807.
- [9] Kangani, C. O.; Day, B. W. Org. Lett. 2008, 10, 2645.
- [10] Yamato, T.; Hideshima, J. C.; Prakash, G. K.; Olah, G. A. J. Org. Chem. 1991, 56, 3955.

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- [11] Shaabani, A.; Soleimani, K.; Bazgir, A. Synth. Commun. 2004, 34, 3303.
- [12] Vautravers, N. R.; Regent, D. D.; Breit, B. Chem. Commun. 2011, 47, 6635.
- [13] Kurouchi, H.; Sugimoto, H.; Otani, Y.; Ohwada, T. J. Am. Chem. Soc. 2010, 132, 807.
- [14] The reviews for Pauson-Khand reaction see: (a) Gibson, S. E.; Mainolfi, N. *Angew. Chem., Int. Ed.* 2005, *44*, 3022; (b) Stevenazzi, A. *Angew. Chem., Int. Ed.* 2003, *42*, 1800; (c) Añorbe, L.; Pérez-Serrano, L.; Domínguez, G.; Pérez-Castells, J. *Chem. Soc. Rev.* 2004, *33*, 32; (d) Shibata, T. *Adv. Synth. Catal.* 2006, *348*, 2328.
- [15] Johannes, G. D.; Alison, R. G.; Craig, J.; William, J. K.; Udo, L. *Tetrahedron* **1996**, *52*, 7391.
- [16] Murray, A.; Hansen, J.; Christensen, B. V. Tetrahedron 2001, 57, 7383.
- [17] Romero, A. V.; Cárdenas, L.; Blasi, E.; Verdaguer, X.; Riera, A.

Org. Lett. 2009, 11, 3104.

- [18] Chung, Y. K.; Lee, B. Y. Organometallics 1993, 12, 220.
- [19] Brown, J. A.; Irvine, S.; Kerr, W. J.; Pearson, C. M. Org. Biomol. Chem. 2005, 3, 2396.
- [20] Pallerla, P. K.; Fox, J. M. Org. Lett. 2005, 7, 3593.
- [21] Szántó, G.; Bombicz, P.; Grún, A.; Kádas, A. Chirality 2008, 20, 1120.
- [22] Hanessian, S.; Pham, V. Org. Lett. 2000, 2, 2975.
- [23] Yamaguchi, M.; Igarashi, Y.; Reddy, R. S.; Shiraishi, T.; Hirama, M. *Tetrahedron* 1997, 53, 11223.
- [24] Prieto, A.; Halland, H.; Jørgensen, K. A. Org. Lett. 2005, 7, 3897.
- [25] Taylor, M. S.; Zalatan, D. N.; Lerchner, A. M.; Jacobsen, E. N. J. Am. Chem. Soc. 2005, 127, 1313.
- [26] Mager, I.; Zeitler, K. Org. Lett. 2010, 12, 1480.
- [27] Ohta, Y.; Kubota, Y.; Watabe, T.; Chiba, H.; Oishi, S.; Fujii, N.; Ohno, H. J. Org. Chem. 2009, 74, 6299.

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