Monatsh Chem (2013) 144:197–203
DOI 10.1007/s00706-012-0800-y

ORIGINAL PAPER

Diastereoselective three-component Mannich reaction catalyzed by silica-supported ferric hydrogensulfate

Hossein Eshghi · Mohammad Rahimizadeh · Mohsen Hosseini · Aida Javadian-Saraf

Received: 8 November 2011 / Accepted: 23 May 2012 / Published online: 20 June 2012
© Springer-Verlag 2012

Abstract A highly *anti*-diastereoselective three-component Mannich reaction of aromatic amines and aromatic aldehydes with cyclohexanone in the presence of silica-supported ferric hydrogensulfate has been developed. The best selectivity was obtained where there were electron-donating groups on both aldehyde and amine. Selectivity decreases when electron-withdrawing groups are present on the aldehyde; in these cases selectivity is improved if an electron-donating group is present on the amine.

Keywords Three-component · Diastereoselective *anti*-Mannich reaction · Silica-supported ferric hydrogensulfate · Iron heterogeneous catalysis

Introduction

The Mannich reaction is one of the most important methods for construction of carbon–carbon bonds to build β-aminocarbonyl compounds [1–5]. These compounds are useful precursors for synthesis of β-lactams [3, 6, 7], α [8–11] and γ-aminoalcohols [13], α and β-amino acid derivatives [13], peroxy acetylenic alcohols/ethers [4], and medicinally important materials [1].

Several strategies are available for diastereoselective synthesis of β-aminocarbonyl compounds, including organocatalysis [6, 7, 12–21], transition-metal catalysis [8–11, 22–25], Bronsted and Lewis acid catalysis [26–38], phase-transfer catalysis [39–41], HPA catalysis [42, 43], biocatalysis [44], and ionic-liquid catalysis [45, 46]. Organocatalytic asymmetric Mannich reactions are the most important approach to the direct *anti*-enantioselective reaction of aldehydes and ketones [47, 48].

Iron is an important metal in living systems and is a sustainable metal catalyst for performing a wide range of different chemical transformations. Iron salts have often been used in organic synthesis, for example oxidation, reduction, coupling reactions, and cycloaddition, because they are inexpensive, nontoxic, readily available, easily recyclable, and environmentally benign [49, 50].

Therefore, to achieve diastereoselective synthesis of β-aminoketones via a three-component Mannich reaction, we chose ferric hydrogensulfate (FHS) as catalyst. Recently we have successfully used FHS for nucleophilic addition of nucleophiles to aldehydes [51–53]. In this work, we performed nucleophilic addition of enols to aldimines. Herein we report, for the first time, the iron-salt-catalyzed three-component Mannich reaction of aromatic aldehydes and aromatic amines with cyclohexanone to afford Mannich products with high *anti*-diastereoselectivity.

Results and discussion

We selected the three-component Mannich reaction of aniline (1 eq), benzaldehyde (1 eq), and cyclohexanone (1.2 eq) as model reaction to optimize the reaction conditions. When we used FHS (10 mol %) as catalyst in ethanol, moderate diastereoselectivity (*anti*:*syn* = 67:33) was obtained.

Electronic supplementary material The online version of this article (doi:10.1007/s00706-012-0800-y) contains supplementary material, which is available to authorized users.

H. Eshghi (✉) · M. Rahimizadeh · M. Hosseini · A. Javadian-Saraf
Department of Chemistry, School of Sciences, Ferdowsi University of Mashhad, Mashhad 91775-1436, Iran
e-mail: heshghi@um.ac.ir

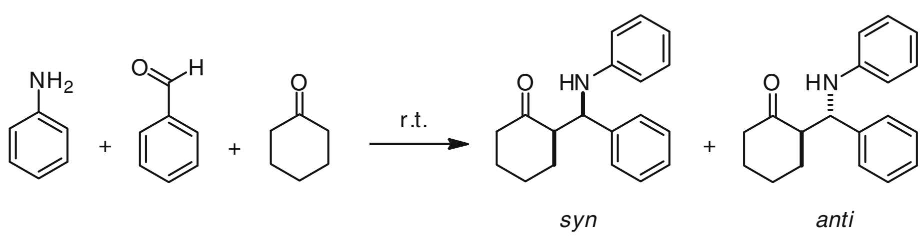
Furthermore reduction of catalyst molar ratio did not change the diastereoselectivity of the reaction significantly (Table 1, entries 2 and 3). Other catalysts, for example $FeCl_2$ and $FeCl_3{\cdot}6H_2O$ (Table 1, entries 10 and 14) also gave moderate diastereoselectivity. With $Mn(HSO_4)_2$ as catalyst the percentage of the *anti* isomer improved to 75 % (Table 1, entry 9). When we used FHS supported on silica (1:9) as catalyst better diastereoselectivity was observed. The best result (>99 % *anti*) was obtained when the molar ratio of catalyst to starting material was approximately 10 mol % (Table 1, entry 6).

As the results in of Table 1 show, silica alone improves the selectivity of the reaction to 84 % *anti* isomer compared with the catalyst free and solid state reactions (Table 1, entries 4, 5, 12). However when FHS is supported on silica using the same conditions the reaction time drops from 2 h to 30 min and diastereoselectivity increases from 84 % to more than 99 %. According to Table 1, when the reaction is carried out under catalyst-free conditions in ethanol, diastereoselectivity decreases to 60:40 ratio (Table 1, entry 4).

We believe diastereoselectivity depends on different factors, for example solvent, silica, and iron salt. When the ratio of ferric hydrogensulfate to silica gel was 9:1, catalytic activity was highest. However, when $NaHSO_4$ was used instead of $Fe(HSO_4)_3$, with the same molar ratio, diastereoselectivity decreased to 72:28. This observation shows that besides the solvent and silica gel, the iron cation has a significant effect on the diastereoselectivity of the reaction.

When the reaction conditions had been optimized for the model reaction, we screened aromatic aldehydes and aromatic amines in reactions with cyclohexanone. As the results in Table 2 show, with benzaldehyde itself the only stereoisomer obtained is *anti*, except with 4-Cl aniline which gives 80 % *anti* isomer (Table 2, entries 1–5). Weak electron-withdrawing or electron donating groups on benzaldehyde, for example 4-chloro and 4-methyl,

Table 1 Catalytic *anti*-diastereoselective three-component Mannich reaction of aniline and benzaldehyde with cyclohexanone



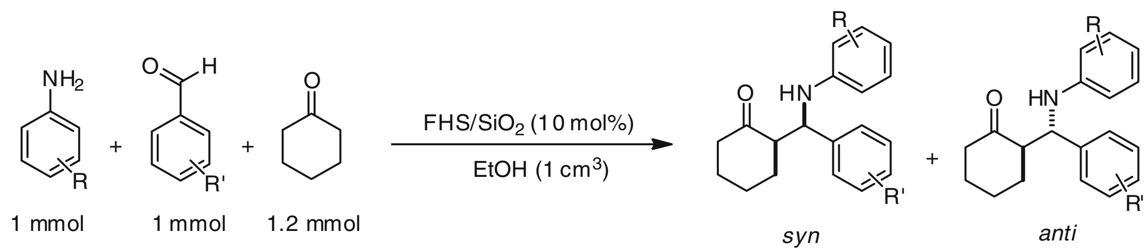
Entry	Cat (mol %)	Solvent	Yield/%[a]	*anti*:*syn*[b]	Time
1	$Fe(HSO_4)_3$ (10 mol %)	EtOH	76	67:33	30 min
2	$Fe(HSO_4)_3$ (5 mol %)	EtOH	72	68:32	30 min
3	$Fe(HSO_4)_3$ (1 mol %)	EtOH	72	68:32	30 min
4	Catalyst-free	EtOH	72	60:40	30 min
5	SiO_2 (0.9 equiv)	EtOH	–	84:16	2 h
6	$Fe(HSO_4)_3/SiO_2$ (10 mol %)[c]	EtOH	72	>99:<1	30 min
7	$Fe(HSO_4)_3/SiO_2$ (5 mol %)	EtOH	72	67:33	30 min
8	$Fe(HSO_4)_3/SiO_2$ (2.5 mol %)	EtOH	77	68:32	2 h
9	$Mn(HSO_4)_2$ (7.5 mol %)	EtOH	87	75:25	30 min
10	$FeCl_2$ (10 mol %)	EtOH	82	67:33	30 min
11	$Fe(HSO_4)_3/SiO_2$ (10 mol %)	CH_3CN	71	71:29	30 min
12	$Fe(HSO_4)_3/SiO_2$ (10 mol %)	Solid state	–	50:50	15 min
13	$Fe(HSO_4)_3$ (10 mol %)	MeOH	–	54:46	30 min
14	$FeCl_3.6H_2O$ (10 mol %)	MeOH	70	67:33	30 min
15	$FeCl_3/SiO_2$ (10 mol %)	EtOH	–	72:28	1 h
16	$NaHSO_4/SiO_2$ (30 mol %)	EtOH	–	74:26	2 h

[a] Isolated yield

[b] Determined by ^{1}H NMR spectroscopy

[c] Ferric hydrogensulfate (10 mmol) and silica for column chromatography (90 mmol, 230 mesh) were mixed

Table 2 Scope of the *anti*-diastereoselective three-component Mannich reaction of aromatic amines and aldehydes with cyclohexanone



Compound	R	R′	Yield/%[a]	*anti*:*syn*[b]	Time	M.p. (lit. m.p.)/°C
1	H	H	72	>99:<1	30 min	117–118 (116–118 [45])
2	2-Me	H	65	>99:<1	24 h	137–138 (not reported [62])
3	3-Me	H	76	>99:<1	1 h	115–116 (123–124 [54])
4	4-Me	H	82	>99:<1	4 h	113–114 (117–118 [45])
5	4-Cl	H	68	80:20	4 h	118–119 (137–138 [55])
6	2-Me	4-Cl	54	>99:<1	24 h	106–107
7	3-Me	4-Cl	77	>99:<1	3 h	127–128 (not reported [37])
8	4-Me	4-Cl	86	>99:<1	4 h	125–126 (119–121 [60])
9	4-Cl	4-Cl	70	>99:<1	3 h	137–138 (98–99 [45])
10	H	4-Me	70	>99:<1	6 h	118–119 (115–118 [56])
11	2-Me	4-Me	60	>99:<1	24 h	114–115
12	3-Me	4-Me	72	>99:<1	4 h	124–125
13	4-Cl	4-Me	68	>99:<1	6 h	138–139 (105.3–105.9 [61])
14	H	4-NO_2	56	64:36	6 h	100–101 (123–125 [58])
15	3-Me	4-NO_2	85	58:42	10 h	161–162 (not reported [63])
16	4-Me	4-NO_2	76	>96:<4	6 h	145–146 (137–138 [45])
17	4-Cl	4-NO_2	76	47:53	8 h	121–122 (169–171 [40])
18	H	3-NO_2	84	58:42	8 h	123–124 (163–165 [40])
19	4-Me	3-NO_2	85	70:30	4 h	136–137
20	4-Cl	3-NO_2	74	48:52	12 h	139–140 (127–128 [45])

[a] Isolated yield

[b] Determined by ^{1}H NMR spectroscopy

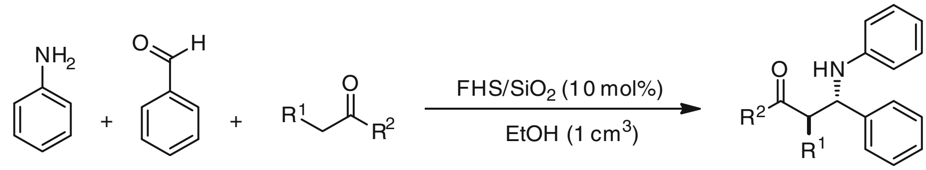
respectively, do not change the diastereoselectivity of the reaction. However, the presence of a strong electron-withdrawing group (EWG), for example NO_2, at the *para* or *meta* positions of the benzaldehyde destroys the diastereoselectivity of the reaction. Interestingly, with these EWGs on the aldehyde, some diastereoselectivity is observed when an electron-donating group (EDG) is present on the aromatic amine (Table 2, compounds **16** and **19**). As expected, the presence of substitution in the *ortho* position of aniline reduces the nucleophilicity of the compound and thus reaction times increase substantially (Table 2, compounds **2**, **6**, and **11**).

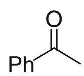
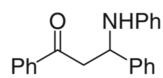
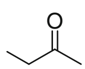
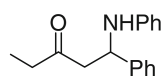
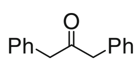
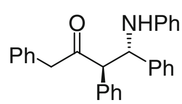
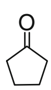
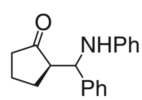
The efficiency of our catalyst was then tested with other ketones as substrates (Table 3). In an initial series of experiments, a representative set of ketones, including both cyclic and acyclic substrates, were reacted with benzaldehyde and aniline in the presence of 10 mol % catalyst. Acyclic ketones required longer reaction times for complete conversion, but regioselectivity was very high. Cyclopentanone behaved similar to cyclohexanone and gave exclusively the *anti* product.

The most plausible mechanism is imine formation between amine and aldehyde followed by nucleophilic addition to the imine of the enol formed by the catalyst. The most probable transition states, which explain the diastereoselectivity of the reaction, are shown in Fig. 1.

We believe the catalyst is mostly involved in the second step of the mechanism. Although it can assist enol formation and nucleophilic addition of enol to aldimine, it mostly controls the diastereoselectivity of the reaction by controlling the stereochemistry of the transition state. As shown in Fig. 1, transition states **A** and **B** are more favorable sterically. These transition states will give the *anti* isomer. Transition states **C** and **D** are highly hindered

Table 3 Regioselective Mannich reactions of some ketones with aniline and benzaldehyde, catalyzed by silica ferric hydrogensulfate



Entry	Ketone	Product	Yield/%[a]	*anti*:*syn*[b]	Time/h	M.p. (lit. m.p.)/°C
1		 **21**	88	–	6	168–169 (168–169 [53])
2		 **22**	85	–	6	88–89 (87–88 [57])
3		 **23**	74	>99:<1	10	169–170 (168–170 [58])
4		 **24**	83	>99:<1	5	165–166 (164–166 [59])

[a] Isolated yield

[b] Determined by ^{1}H NMR spectroscopy

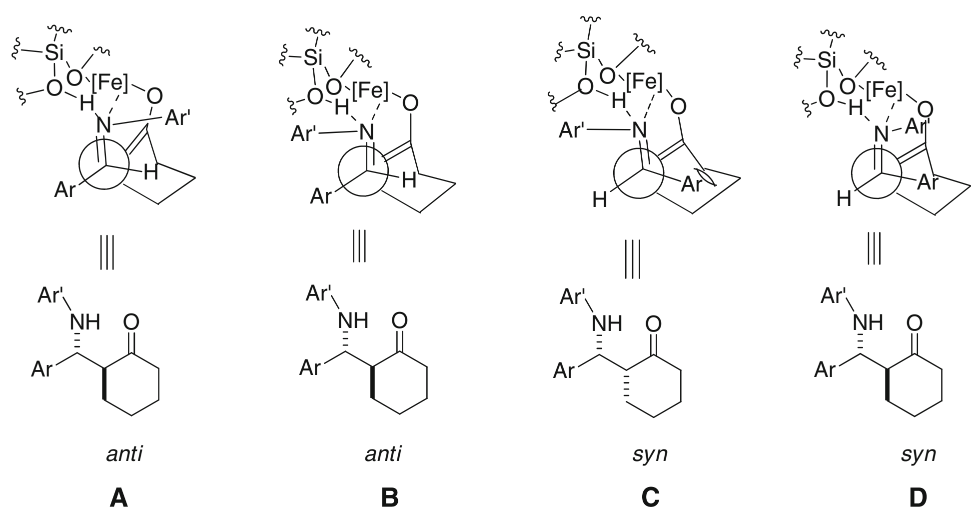


Fig. 1 Probable transition state structures

and so unlikely to be formed in the presence of catalyst. This highly energetic transition state will lead to the *syn* isomer. According to the proposed mechanism the *anti* product is expected from the *cis* imine (Fig. 1, **B**), and, because of the steric effect, the *anti* product is more likely to be formed from the *trans* imine (Fig. 1, **A** and **C**).

Electronic effects of substituents on the aldehyde and amine effect the stability of these transition states. Whereas

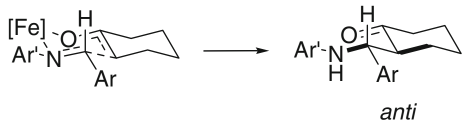


Fig. 2 Electronic effect of the transition state

EWGs on the aldehyde reduce the stability of the transition state and thus destroy the diastereoselectivity of the reaction, EDGs on the amine compensate for the EWGs and increase the diastereoselectivity of the reaction.

We propose that the transition state is chair like and both oxygen and nitrogen coordinate to the iron center (Fig. 2). When the nitro group is located on benzaldehyde the nitrogen of the imine will not coordinate well with the iron center, and thus the steric effect will not determine the diastereoselectivity of the products.

The modified transition state illustrated in Fig. 2 shows that the electronic effect is a major factor affecting the diastereoselectivity of the product. When a methyl group is present at the *para* position of the aniline diastereoselectivity increases. In fact, with imines containing 4-methyl substitution on the aniline ring, the electron density of transition state depicted in Fig. 2 improves and chelation of nitrogen to the iron center will occur more efficiently and diastereoselectivity proceeds toward *anti* (Table 2, compounds **16** and **19**).

In conclusion, we present in this paper a completely diastereoselective three-component Mannich reaction catalyzed by ferric hydrogensulfate supported on silica gel. The advantages of our method are the high yield and excellent selectivity of the reaction, and the inexpensive and heterogeneous catalyst.

Experimental

All solvents and reagents were purchased from Merck and Fluka. The silica for preparation of the supported catalyst was 230 mesh for column chromatography and was purchased from Merck. NMR spectra were recorded on Bruker Aspect 3000 (100 MHz) and Bruker Avance (400 MHz) spectrometers. All chemical shifts are reported as ppm and were referenced to residual solvent signals. IR spectra were recorded on a ThermoNicolet Avatar-370-FTIR spectrometer.

Preparation of silica ferric hydrogensulfate (10 mol %)

Ferric hydrogensulfate (5 mmol) and silica gel 230 mesh for column chromatography (45 mmol) were placed in a mortar and the mixture was ground for 5 min. The mixture was then placed in a 50 cm^3 flask, 25 cm^3 absolute ethanol was added, and the mixture was stirred at room temperature for 10 h. The mixture was then filtered and the residue was dried at 100 °C for 2 h. A white homogeneous powder was obtained which was stored in a desiccator.

Typical procedure for synthesis of β-aminocyclohexanones

To a mixture of aromatic amine (1 mmol), aromatic aldehyde (1 mmol), and cyclohexanone (1.2 mmol) in 1 cm^3 ethanol, 88.7 mg silica ferric hydrogensulfate (10 mol %) was added. The reaction mixture was stirred at room temperature and the progress of the reaction monitored by TLC. After completion of the reaction, 2 cm^3 methanol was added, followed by dropwise addition of water until the product began to precipitate. The mixture was then filtered by suction and the residue was washed with 0.5 cm^3 methanol and 0.5 cm^3 petroleum ether. The crude product was extracted from the precipitate by washing with $CHCl_3$. The solution was dried over Na_2SO_4 then the solvent was removed. The solid product obtained was suitable for spectroscopic application. Further purification was performed by crystallization from aqueous ethanol.

2-[(4-Chlorophenyl)[(2-methylphenyl)amino]methyl]-cyclohexanone (**6**, $C_{20}H_{22}ClNO$)
Yield 54 %; m.p.: 106–107 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.70$-1.90 (m, 3H), 1.90-2.10 (m, 3H), 2.27 (s, 3H), 2.30-2.50 (m, 2H), 2.80-2.90 (m, 1H), 4.67 (d, 1H, $J = 6$ Hz, *anti*), 6.37 (d, 1H, $J = 8$ Hz), 6.65 (t, 1H, $J = 7.5$ Hz), 6.98 (t, 1H, $J = 7.2$ Hz), 7.08 (d, 1H, $J = 5.6$ Hz), 7.34 (AB-q, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.68$, 23.90, 27.92, 31.63, 42.06, 57.50, 57.57, 110.65, 117.29, 126.90, 128.64, 128.69, 128.74, 130.14, 131.60, 140.51, 144.92, 212.95 ppm; IR (KBr): $\bar{\nu} = 3{,}374$ (s, NH), 3,029 (w), 2,945 (s), 1,702 (s, C=O), 1,605 (m), 1,518 (s), 1,449 (m), 1,314 (m), 826 (m), 744 (m) cm^{-1}.

2-[(4-Methylphenyl)[(2-methylphenyl)amino]methyl]-cyclohexanone (**11**, $C_{21}H_{25}NO$)
Yield 60 %, m.p.: 114–115 °C; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.65$-1.85 (m, 2H), 1.86-2.00 (m, 4H), 2.23 (s, 3H), 2.33 (s, 3H), 2.30-2.50 (m, 2H), 2.75-2.85 (m, 1H), 4.65 (d, 1H, $J = 7.2$ Hz, *anti*), 4.60-4.80 (br, NH), 6.41 (d, 1H, $J = 7.6$ Hz), 6.60 (t, 1H, $J = 7.2$ Hz), 6.95 (t, 1H, $J = 7.2$ Hz), 7.05 (d, 1H, $J = 7.2$ Hz), 7.13 (d, 2H, $J = 7.6$ Hz), 7.28 (d, 2H, $J = 8$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.67$, 21.13, 23.42, 27.92, 31.21, 41.68, 57.69, 57.73, 110.65, 116.93, 122.55, 126.85, 127.08, 129.24, 129.99, 136.78, 138.76, 145.16, 213.53 ppm; IR (KBr): $\bar{\nu} = 3{,}402$ (m, NH), 3,382 (m, NH), 3,014 (w), 2,945 (m), 1,701 (s, C=O), 1,604 (m), 1,518 (s), 1,450 (m), 823 (m), 745 (m) cm^{-1}.

2-[(4-Methylphenyl)[(3-methylphenyl)amino]methyl]-cyclohexanone (**12**, $C_{21}H_{25}NO$)

Yield 72 %; m.p.: 124–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.60$-1.82 (m, 2H), 1.82-2.10 (m, 4H), 2.25 (s, 3H), 2.35 (s, 3H), 2.35-2.55 (m, 2H), 2.70-2.80 (m, 1H), 4.65 (d, 1H, $J = 7.2$ Hz, *anti*), 6.39 (d, 1H, $J = 7.6$ Hz), 6.44 (s, 1H), 6.50 (d, 1H, $J = 7.6$ Hz), 7.00 (t, 1H, $J = 7.6$ Hz), 7.16 (d, 2H, $J = 7.6$ Hz), 7.31 (d, 2H, $J = 8$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.13$, 21.48, 23.53, 27.96, 31.20, 41.70, 57.58, 57.62, 110.50, 114.57, 118.44, 127.15, 128.98, 129.21, 130.55, 136.70, 138.77, 147.33, 213.12 ppm; IR (KBr): $\bar{v} = 3{,}359$ (s, NH), 3,051 (w), 2,942 (m), 1,702 (s, C = O), 1,605 (s), 1,533 (m), 1,305 (m), 821 (m), 782 (m) cm^{-1}.

2-[[(4-Methylphenyl)amino](3-nitrophenyl)methyl]-cyclohexanone (**19**, $C_{20}H_{22}N_2O_3$)

Yield 85 %; m.p.: 136–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.50$-1.90 (m, 3H), 1.90-2.20 (m, 3H), 2.21 (s, 3H), 2.30-2.50 (m, 2H), 2.85-2.95 (m, 1H), 4.73 (d, 0.7H, $J = 5.2$ Hz, *anti*), 4.86 (d, 0.3H, $J = 4.4$ Hz, *syn*), 6.48 (d, 2H, $J = 8.4$ Hz), 6.93 (d, 2H, $J = 8$ Hz), 7.49 (t, 1H, $J = 8$ Hz), 7.80 (d, 1H, $J = 7.2$ Hz), 8.09 (d, 1H, $J = 8$ Hz), 8.28 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.38$, 20.40, 24.46, 24.99, 27.21, 27.85, 29.23, 31.98, 42.41, 42.53, 56.37, 57.12, 57.33, 57.91, 113.69, 114.21, 122.23, 122.36, 122.54, 127.31, 127.55, 129.32, 129.38, 129.72, 129.80, 133.72, 134.25, 144.36, 144.66, 148.41, 210.90 (*syn*), 212.03 (*anti*) ppm; IR (KBr): $\bar{v} = 3{,}383$ (s, NH), 2,932 (m), 1,704 (C=O, *syn*), 1.697 (C=O, *anti*), 1,616 (m), 1,518 (s), 1,346 (s), 811 (s), 711 (m) cm^{-1}.

Acknowledgments We are grateful to Ferdowsi University of the Mashhad Research Council for their financial support of this work (grant: 3/16044).

References

1. Arend M, Westermann B, Risch N (1998) Angew Chem Int Ed 37:1044
2. Notz W, Tanaka F, Barbas CF III (2004) Acc Chem Res 37:580
3. Cordova A (2004) Acc Chem Res 37:102
4. Dikusar EA, Kozlov NG, Popova LA, Moiseichuk KL, Yuvchenko AP (2003) Russ J Gen Chem 73:625
5. Kobayashi S, Mori Y, Fossey JS, Salter MM (2011) Chem Rev 111:2626
6. Lou S, Taoka BM, Ting A, Schaus SE (2005) J Am Chem Soc 127:11256
7. Hayashi Y, Tsuboi W, Ashimine I, Urushima T, Shoji M, Sakai K (2003) Angew Chem Int Ed 42:3677
8. Ishitani H, Ueno M, Kobayashi S (1997) J Am Chem Soc 119:7153
9. Kobayashi S, Hamada T, Manabe K (2002) J Am Chem Soc 124:5640
10. Matsunaga S, Kumagai N, Harada S, Shibasaki M (2003) J Am Chem Soc 125:4712
11. Trost BM, Terrell L (2003) J Am Chem Soc 125:338
12. Ibrahem I, Zou W, Engqvist M, Xu Y, Córdova A (2005) Chem Eur J 11:7024
13. Zhang H, Mifsud M, Tanaka F, Barbas CF III (2006) J Am Chem Soc 128:9630
14. Zheng X, Quan Y, Wang Y (2010) Eur J Org Chem 515
15. Zhang H, Chuan Li YZ, Peng Y (2009) Adv Synth Catal 351:2288
16. Ramasartry SSV, Zhang H, Tanaka F, Barbas CF III (2007) J Am Chem Soc 129:288
17. List B (2000) J Am Chem Soc 122:9336
18. List B, Pojarliev P, Biller WT, Martin H (2002) J Am Chem Soc 124:827
19. Notz W, Tanaka F, Watanabe S, Chowdari NS, Turner JM, Thyumanavan R, Barbas CF III (2003) J Org Chem 68:9624
20. Chowdari NS, Suri JT, Barbas CF III (2004) Org Lett 6:2507
21. Cheong PH, Zhang H, Thayumanavan R, Tanaka F, Houk KN, Barbas CF III (2006) Org Lett 8:811
22. Yanagisawa A, Saito H, Harada M, Arai T (2005) Adv Synth Catal 347:1517
23. Qiu R, Yin S, Zhang X, Xia J, Xu X, Luo S (2009) Chem Commun 4759
24. Kureshy RI, Agrawal S, Saravan S, Khan NH, Shah AK, Abdi SHR, Bajaj HC, Suresh E (2010) Tetrahedron Lett 51:489
25. Xia J, Qiu R, Yin S, Zhang X, Luo S, Au C, Xia K, Wong W (2010) J Organomet Chem 695:1487
26. Uraguchi D, Tereda M (2004) J Am Chem Soc 126:5356
27. Blatt AH, Gross N (1964) J Org Chem 29:3306
28. Manabe K, Kobayashi S (1999) Org Lett 1:1965
29. Iimura S, Nobutou D, Manabe K, Kobayashi S (2003) Chem Commun 1644
30. Wu Y, Cai J, Hu Z, Lin G (2004) Tetrahedron Lett 45:8949
31. Akiyama T, Matsuda K, Fuchibe K (2005) Synlett 322
32. Guo Q, Liu H, Quo C, Luo S, Gu Y, Gong L (2007) J Am Chem Soc 129:3790
33. Lu G, Cai C (2010) Catal Commun 11:745
34. Ranu BC, Samanta S, Guchheit SK (2002) Tetrahedron 58:983
35. Loh T, Chen S (2002) Org Lett 4:3647
36. Ollevier T, Nadeau E, Guay-Bégin A (2006) Tetrahedron Lett 47:8351
37. Eftekhari-Sis B, Abdollahifar A, Hashemi MM, Zirak M (2006) Eur J Org Chem 5152
38. Hong D, Yang Y, Wang Y, Liu X (2009) Synlett 1107
39. Ooi T, Kameda M, Fujii T, Maruoka K (2004) Org Lett 6:2397
40. Shen W, Wang L, Tiam H (2008) J Fluorine Chem 129:267
41. Jafari AA, Moradgholi F, Tamaddon F (2009) Eur J Org Chem 1249
42. Azizi N, Torkiyan L, Saidi M (2006) Org Lett 8:2079
43. Das B, Kumar AS, Kanth BR (2009) Synth Commun 39:3111
44. He T, Li K, Wu M, Fang X, Wang N, Wang H, Li C, Lu X (2010) J Mol Catal B Enzyme 67:189
45. Gong K, Fang D, Wang H, Liu Z (2007) Monatsh Chem 138:1195
46. Fang D, Gong K, Zhang D, Liu Z (2009) Monatsh Chem 140:1325
47. Alza E, Rodriguez-Escrich C, Sayalero S, Bastero A, Pericas MA (2009) Chem Eur J 15:10167
48. Martin-Rapun R, Fan X, Sayalero S, Bahramnejad M, Cuevas F, Pericas MA (2011) Chem Eur J 17:8780
49. Plietker B (2008) Iron catalysis in organic chemistry. Wiley-VCH, Weinheim
50. Enthaler S, Junge K, Beller M (2008) Angew Chem Int Ed 47:3317
51. Eshghi H, Bakavoli M, Moradi H (2008) Chin Chem Lett 19:1423
52. Rahimizadeh M, Eshghi H, Bakhtiarpoor Z, Pordel M (2009) J Chem Res 269

53. Eshghi H, Alipour A, Damavandi S (2011) Synth React Inorg Metal-Org Nano-Metal Chem 41:266
54. Kozlov NS, Vorobeva GV (1968) Vestsi Akad Navuk BSSR. Ser Khim Navuk 4:107
55. Kidwai M, Mishra NK, Bansal V, Kumar A, Musomdar S (2009) Tetrahedron Lett 50:1355
56. Sharghi H, Jokar M (2009) Can J Chem 88:14
57. Kumar V, Sharma U, Verma PK, Kumar N, Singh B (2011) Chem Pharm Bull 59:639
58. Nemati F, Fakhaei FS, Amoozadeh A, Hayeniaz YS (2011) Synth Commun 41:3695
59. Yi W-B, Cai C (2006) J Fluorine Chem 127:1515
60. Bigdeli M, Nemati F, Mahdavinia G (2007) Tetrahedron Lett 48:6801
61. Wu H, Chen X-M, Wan Y, Ye L, Xin H-Q, Xu H–H, Yue C-H, Pang L–L, Ma R, Shi D-Q (2009) Tetrahedron Lett 50:1062
62. Xia J, Qiu R, Yin S, Zhang X, Luo S, Au C-T, Xia K, Wong W-Y (2010) J Organomet Chem 695:1487
63. An Y-J, Wang C–C, Liu Z-P, Tao J-C (2012) Helv Chim Acta 95:43