Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Simple Synthesis of Highly Functionalized Ketenimines

Mohammad Bayat [a], Hossien Imanieh [a] & Elham Hossieninejad [a]
[a] Department of Chemistry, Imam Khomeini International University, Qazvin, Iran
Published online: 09 Sep 2008.

To cite this article: Mohammad Bayat, Hossien Imanieh & Elham Hossieninejad (2008) Simple Synthesis of Highly Functionalized Ketenimines, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 38:15, 2567-2574, DOI: 10.1080/00397910802219213

To link to this article: http://dx.doi.org/10.1080/00397910802219213

Synthetic Communications®, 38: 2567–2574, 2008

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910802219213

Taylor & Francis
Taylor & Francis Group

Simple Synthesis of Highly Functionalized Ketenimines

Mohammad Bayat, Hossien Imanieh, and Elham Hossieninejad
Department of Chemistry, Imam Khomeini International University, Qazvin, Iran

Abstract: The 1:1 reactive intermediate generated by the addition of alkyl isocyanides to dibenzoylacetylene or dialkyl acetylenedicarboxylates was trapped by fairly strong NH acids such as isatin, phthalimide, 4-nitroimidazole, or 2-benzoylimidazole to yield highly functionalized ketenimines.

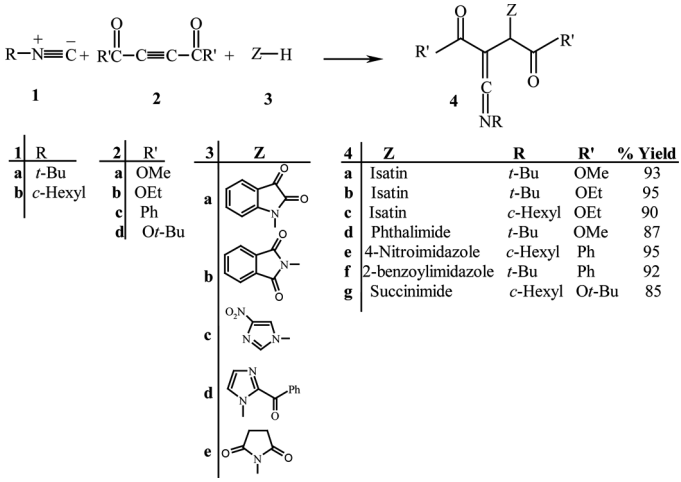
Keywords: Alkyl isocyanides, dibenzoylacetylene, ketenimines, three-component reaction

INTRODUCTION

Development of simple synthetic routes for widely used organic compounds from readily available reagents is one of the major tasks in organic chemistry.[1] A major challenge of modern organic synthesis and drug discovery is the design of highly efficient chemical reaction sequences, which provide a maximum of structural complexity and diversity with just a minimum number of synthetic steps to assemble compounds with interesting properties.[1,2]

Recently, multicomponent reactions (MCRs) have emerged as highly valuable synthetic tools in the context of modern drug discovery. The atom economical and convergent character, the simplicity of a one-pot procedure, the possible structural variations, the accessible complexity of the molecules, as well as the very large number of accessible compounds are among the described advantages of MCRs.[3] Thus, they

Received in the U.K. September 18, 2007
Address correspondence to Mohammad Bayat, Department of Chemistry, Imam Khomeini International University, P.O.Box-288, Qazvin, Iran. E-mail: Bayat_mo@ yahoo.com



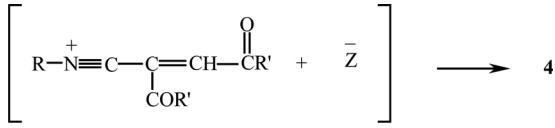
Scheme 1.

are perfectly amenable to automation for combinatorial synthesis.[4] Among the known multicomponent reactions, isocyanide-based MCRs such as the versatile ugi and passerini reactions are especially valuable.[5–7] Many different scaffolds are accessible, each with very many examples.[8,9] Thus, they are prototypic-complexity- and diversity-generating reactions.

ketenimines play a role as discrete but transient intermediates in many interconversions, especially in elimination–addition processes and in the formation of heterocyclic ring systems.[10–13] The spectroscopic properties of ketenimines have been intensively investigated.[14] We report a simple one-pot preparation of stable ketenimines using alkyl isocyanides **1** and dibenzoylacetylene or dialkyl acetylenedicarboxylates **2** in the presence of a NHacid **3** such as isatin, phthalimide, succinimide, 4-nitroimidazole, or 2-benzoylimidazole. This three-component condensation reaction produces highly functionalized ketenimimes **4** in fairly good yield (Scheme 1).

RESULTS AND DISCUSSION

The reaction of alkyl isocyanides **1** with dibenzoylacetylene or dialkyl acetylenedicarboxylates **2** in the presence of NHacids **3** proceeded at room temperature in dry diethyl ether or ethyl acetate and was completed within 24 h. The IR, ^{1}H NMR, and ^{13}C NMR spectra of the crude products clearly indicated the formation of stable ketenimines **4** (Scheme 1).



Scheme 2.

The structures of **4** were deduced from their elemental analyses, mass spectrometric data, and their ^{1}H NMR, ^{13}C NMR and IR spectra. The ^{1}H NMR spectra of **4a** ($CDCl_3$) showed four sharp lines for *tert*-butyl ($\delta = 1.41$ ppm), methoxy ($\delta = 3.63$ and 3.71 ppm), and methine ($\delta = 5.67$ ppm) protons, with the aromatic protons at $\delta = 7.04$–7.59 ppm.

The ^{13}C NMR spectrum of **4a** showd signals for *tert*-butyl ($\delta = 29.68$ ppm), methoxy ($\delta = 52.1$ and 52.3 ppm), and methine ($\delta = 52.11$ ppm) carbons in agreement with proposed structure. Partial assignments of these resonances are given in the methods and marterials section.

The ^{1}H NMR spectra of **4b–i** are similar to that of **4a**, except for the signals of cyclohexyl, ester, and aromatic moieties. The structural assignments of **4b–i** made on the basis of their NMR spectra were supported by their IR spectra. Ketenimines show a strong absorption band at about 2035–2086 cm^{-1} in all compounds.

On the basis of the well-established chemistry of isocynides,[15–16] it is reasonable to assume that compound **4** results from initial addition of alkyl isocyanide to the dibenzoylacetylene or dialkyl acetylenic ester and subsequent protonation of the 1:1 adduct by the NHacid. Then, the positively charged ion is attacked by the nitrogen atom of the anion of the NHacid to form ketenimine **4** (Scheme 2).

In conclusion, the three-component reaction of alkyl isocyanides with electron-deficient acetylenic esters or dibenzoylacetylene in the presence of NHacids provides a simple entry into the synthesis of polyfunctionalized ketenimines of potential synthetic interest. Not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modification.

MATERIALS AND METHODS

Dialkyl acetylenedicarboxylates, *tert*-butyl isocyanide, and other reagents and solvents used in this work were obtained from Fluka (Buchs, Switzerland) and used without further purification. Dibenzoylacetylene, 4-nitroimidazole,[17,18] and 2-benzoylimidazole[19] were prepared according to the published procedures. NMR spectra were recorded with a

Bruker DRX-500 Avance instrument (500.1 MHz for ^{1}H and 125.7 MHz for ^{13}C) with $CDCl_3$ as solvent. Chemical shifts are given in parts per million (δ) relative to internal tetramethylsilane (TMS), and coupling constant (J) are reported in hertz (Hz). Melting points were measured with an electrotherma1 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid Analyzer. These results agreed favorably with the calculated values. Mass spectra were recorded with a Shimadzu QP-GC Mass 1100-EX spectrometer operating at an ionization potential of 70 eV. IR spectra were measured with Bucksience 5000 spectrometer.

Preparation of Dimethyl 2-[(Tert-butylimino)-methylene]-3-(2,3-dioxo-2,3-dihydro-indol-1-yl)-butanedioate (4a): Typical Procedure

To a magnetically stirred solution of 0.147 g of isatin (1 mmol) and 0.142 g of dimethyl acetylendicarboxylate (1 mmol) in 5 mL of ethyl acetate, 0.083 g of *tert*-butyl isocyanide (1 mmol) in 2 mL of ethyl acetate was added dropwise at 0 °C over 20 min. The reaction mixture was then allowed to warm up to room temperature and stand for 24 h. The solvent was removed under reduced pressure, and the residue was purified by silica-gel (Merck silica gel 60, 70–230 mesh) column chromatography using hexane–ethyl acetate (8:2) as eluent. The solvent was removed under reduced pressure to afford the product.

Orange crystals: yield 0.34 g (93%), mp 132–134 °C. IR(KBr) (ν_{max} / cm^{-1}): 2086 (C=C=N), 1740, 1738, and 1680 (C=O). ^{1}H NMR: $\delta = 1.41$ (9H, s, CMe_3), 3.63 and 3.71 (6H, 2 s, 2O*Me*), 5.67 (1H, s, C*H*), 7.05–7.15 (2H, m, arom.), 7.51–7.60 (2H, m, arom.). ^{13}C NMR: $\delta = 30.14$ (CMe_3), 51.84 and 53.27 (2OMe), 52.11 (CH), 59.14 (*C*Me$_3$), 62.81 ($C = C = N$), 111.60, 117.96, 123.80, 125.30, 138.53, 150.14 (arom. carbons), 157.93 ($C = C = N$), 161.60, 167.36, 169.90, and 182.69 (4C = O). MS (EI, 70 eV): m/z (%) = 373 ($M^+ + 1$, 46), 317 (88), 284 (19), 226 (77), 185 (31), 146 (40), 119 (33), 91 (23), 57 (100). Anal. calcd. for $C_{19}H_{20}N_2O_6$ (372.87): C, 61.28; H, 5.41; N, 7.25%. Found: C, 61.4; H, 5.2; N, 7.1%.

Diethyl 2-[(Tert-butylimino)-methylene]-3-(2,3-dioxo-2,3-dihydro-indol-1-yl)-butanedioate (4b)

To a magnetically stirred solution of 0.147 g of isatin (1 mmol) and 0.170 g of diethyl acetylendicarboxylate (1 mmol) in 5 mL of ethyl acetate, 0.083 g of *tert*-butyl isocyanide (1 mmol) in 2 mL of ethyl acetate was added dropwise at 0 °C over 20 min. The reaction mixture was then allowed to warm up to room temperature and stand for 24 h.

Orange crystals: yield 0.38 g (95%), mp 102–104 °C. IR(KBr) (ν_{max} / cm^{-1}): 2079 (C=C=N), 1741, 1738, and 1678 (C=O). ^{1}H NMR: $\delta = 1.11$ (6H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 Me), 1.35 (9H, s, CMe_3), 3.95 and 4.13 (4H, 2q, $^3J_{HH} = 7.1$ Hz, $2OCH_2$), 5.62 (1H, s, CH), 6.98–7.05 (2H, m, arom.), 7.44–7.50 (2H, m, arom.). ^{13}C NMR: $\delta = 13.91$ and 14.30 (2Me), 30.0, (CMe_3), 52.05 (CH), 59.68 (CMe_3), 60.17 and 62.40 ($2OCH_2$), 62.60 ($C = C = N$), 111.59, 117.76, 123.72, 125.10, 138.39, and 150.21 (arom. carbons), 157.74 ($C = C = N$), 162.78, 166.65, 169.17, and 182.60 (4C=O). MS (EI, 70 eV): m/z (%) = 401 ($M^+ + 1$, 77), 345 (85), 298 (37), 254 (72), 198 (52), 171 (81), 146 (48), 119 (44), 57 (100). Anal. Calcd. for $C_{21}H_{24}N_2O_6$ (400.43): C, 62.98; H, 6.04; N, 7.01%. Found: C, 62.5; H, 6.1; N, 6.7%.

Diethyl 2-[(Cyclohexylimino)-methylene]-3-(2,3-dioxo-2,3-dihydro-indol-1-yl)-butanedioate (4c)

To a magnetically stirred solution of 0.147 g of isatin (1 mmol) and 0.170 g of diethyl acetylendicarboxylate (1 mmol) in 5 mL of ethyl acetate, 0.110 g of cyclohexyl isocyanide (1 mmol) in 2 mL of ethyl acetate was added dropwise at 0 °C over 20 min. The reaction mixture was then allowed to warm up to room temperature and stand for 24 h.

Red crystals: yield 0.38 g (90%), mp 126–128 °C. IR(KBr) (ν_{max}/cm^{-1}): 2078 (C=C=N), 1743, 1721, and 1687 (C=O). ^{1}H NMR: $\delta = 1.01$ (3H, t, $^3J_{HH} = 7.2$ Hz, CH_3), 1.22 (3H, t, $^3J_{HH} = 7.2$ Hz, CH_3), 1.09–1.18 (10H, m, $5CH_2$), 4.09 (2H, q, $^3J_{HH} = 7.2$ Hz, OCH_2), 4.18 (2H, q, $^3J_{HH} = 7.2$ Hz, OCH_2), 5.68 (1H, s, CH), 7.03–7.19 (2H, m, arom.), 7.51–7.57 (2H, m, arom.). ^{13}C NMR: $\delta = 13.92$ and 14.32 ($2CH_3$), 23.64, 25.16, 25.41, 32.98, and 33.05 ($5CH_2$), 52.28 (CH), 58.10 (= N-CH), 60.52 and 62.53 ($2OCH_2$), 77.53 ($C = C = N$), 111.66, 117.85, 123.70, 125.21, 138.64, and 150.30 (arom. carbons), 157.96 ($C = C = N$), 162.17, 166.89, 169.40, and 182.81 (4C=O). MS (EI, 70 eV): m/z (%) = 426 (M^+, 6), 298 (100), 280 (25), 251 (52), 198 (16), 170 (33), 148 (43), 119 (39), 98 (35), 55 (31). Anal. calcd. for $C_{23}H_{26}N_2O_6$ (426.46): C, 64.77; H, 6.14; N, 6.56%. Found: C, 64.9; H, 6.2; N, 6.7%.

Dimethyl 2-[(Tert-butylimino)-methylene]-3-(2,3-dioxo-1,3-dihydro-isoindol-2-yl)-butanedioate (4d)

To a magnetically stirred solution of 0.147 g of phthalimide (1 mmol) and 0.142 g of dimethyl acetylendicarboxylate (1 mmol) in 5 mL of ethyl acetate, 0.083 g of *tert*-butyl isocyanide (1 mmol) in 2 mL of ethyl acetate

was added dropwise at 0 °C over 20 min. The reaction mixture was then allowed to warm up to room temperature and stand for 24 h.

Colorless oil: yield 0.32 g (87%). IR(KBr) (ν_{max}/cm^{-1}): 2086 (C=C=N), 1738, and 1678 (C=O). ^{1}H NMR: $\delta =$ 1.49 (9H, s, CMe_3), 3.85 and 3.89 (6H, 2 s, 2OMe), 6.12 (1H, s, CH), 7.75–8.15 (4H, m, arom.). ^{13}C NMR: $\delta = 30.10$, (CMe_3), 51.05 and 53.12 (2OMe), 59.10 (CMe_3), 60.61 ($C = C = N$), 123.71, 128.60, 131.61, 132.10, 134.31 and 134.62 (arom. carbons), 163.90 ($C = C = N$), 167.61, 168.20 and 169.63 (4C=O). MS (EI, 70 eV): m/z (%) = 372 (M^+, 6), 316 (64), 271 (35), 242 (24), 146 (100), 73 (45), 57 (70). Anal. Calcd. for $C_{19}H_{20}N_2O_6$ (372.37): C, 61.28; H, 5.41; N, 7.52%. Found: C, 61.9; H, 5.1; N, 7.2%.

2-[(Cyclohexylimino)-methylene]-3-(4-nitro-1H-imidazol-1-yl)-1,4-diphenyl-1,4-butanedione (4e)

To a magnetically stirred solution of 0.113 g of 4-nitroimidazole (1 mmol) and 0.234 g of dibenzoylacetylene (1 mmol) in 10 mL of dry diethyl ether, 0.110 g of cyclohexyl isocyanide (1 mmol) in 2 mL of dry diethyl ether was added dropwise at 0 °C over 20 min. The reaction mixture was then allowed to warm up to room temperature and stand for 24 h.

Pale yellow powder: yield 0.43 g (95%), mp 146–148 °C. IR(KBr) (ν_{max}/cm^{-1}): 2035 (C=C=N), 1687 (C=O), 1277 and 1594 (NO_2). ^{1}H NMR: $\delta = 1.16$–1.67 (10H, m, $5CH_2$), 3.68 (1H, m, = N-CH), 7.15 (1H, s, CH ofbutanedione), 7.37–7.66 (10H, m, arom.), 7.69 (1H, s, CH of imidazole), 8.05 (1H, s, CH of imidazole). ^{13}C NMR: $\delta = 23.44$, 24.60, 32.83, and 33.04 ($5CH_2$), 59.12 (= NCH), 61.01 (CH ofbutanedione), 68.95 ($C = C = N$), 119.81 (C_5 of imidazole), 127.40, 128.45, 128.67, 129.27, 132.10, and 134.94 (arom. carbons), 133.08 and 138.40 ($2C_{ipso}$ of $2C_6H_5$), 136.27 (C_2 of imidazole), 147.92 (C_4 of imidazole), 155.33 ($C = C = N$), 190.41 and 191.48 (2C=O). MS (EI, 70 eV): m/z (%) = 456 (M^+, 11), 345 (21), 303 (11), 269 (24), 262 (47), 263 (53), 106. (21), 105 (100), 98, (22), 76, (84). Anal. Calcd. for $C_{26}H_{24}N_4O_4$ (456.50): C, 68.41; H, 5.30; N, 12.27%. Found: C, 68.2; H, 5.8; N, 12.1%.

2-[(Tert-butylimino)-methylene]-3-(2-phenyl-methanone-2-H-imidazol-2-yl)-1,4-diphenyl-1,4-butanedione (4f)

To a magnetically stirred solution of 0.172 g of 2-benzoylimidazole (1 mmol) and 0.234 g of dibenzoylacetylene (1 mmol) in 10 mL of dry diethyl ether 0.083 g of *tert*-butyl isocyanide (1 mmol) in 2 mL of dry diethyl ether was added dropwise at 0 °C over 20 min. The reaction

mixture was then allowed to warm up to room temperature and stand for 24 h.

Pale yellow powder: yield 0.44 g (92%), mp 160–163 °C. IR(KBr) (ν_{max}/cm^{-1}): 2080 (C=C=N), 1682 and 1609 (2C=O), 1277 and 1594 (NO_2). ^{1}H NMR: $\delta = 1.07$ (9H, s, CMe_3), 7.34 (1H, s, CH of midazole), 7.37–7.62 (11H, m $3C_6H_5$), 7.56 (1H, s, CH of imidazole), 7.97 (1H, s, CH of butanedione), 8.15 (2H, d, $^3J_{HH} = 7.6$ Hz, $2CH_{ortho}$ of C_6H_5), 8.21 (2H, d, $^3J_{HH} = 7.6$ Hz, $2CH_{ortho}$ of C_6H_5). ^{13}C NMR: $\delta = 29.90$ (CMe_3), 59.78 (CMe_3), 63.54 (CH of butanedione), 70.43 ($C = C = N$), 124.35 (CH of imidazole), 127.37, 127.95, 128.27, 128.68 and 128.95 (arom. carbons), 129.36 (CH of imidazole), 130.89, 131.65, 132.54 and 133.83 (arom. carbons), 134.35, 137.26 and 138.97 ($3C_{ipso}$ of $3C_6H_5$), 142.71 (C_2 of imidazole), 159.84 ($C = C = N$), 184.34, 190.81 and 192.96 (3C=O). MS (EI, 70 eV): m/z (%) = 490 ($M^+ + 1$, 5), 345 (21), 303 (11), 269 (25), 246 (10), 129 (14), 106 (20), 105 (100), 98 (22), 76 (84), 52 (30). Anal. Calcd. for $C_{31}H_{27}N_3O_3$ (489.57): C, 76.05; H, 5.55; N, 8.58%. Found: C, 76.5; H, 5.1; N, 8.2%.

Di-tert-butyl-2-[(cyclohexylimino)-methylene]-3-(2,5-dioxo-pyrrolidin-1-yl)butanedione (4g)

To a magnetically stirred solution of 0.099 g of succinimide (1 mmol) and 0.226 g of di-*tert*-butyl acetylendicarboxylate (1 mmol) in 10 mL of dry diethyl ether, 0.110 g of cyclohexyl isocyanide (1 mmol) in 2 mL of dry diethyl ether was added dropwise at 0 °C over 20 min. The reaction mixture was then allowed to warm up to room temperature and stand for 24 h.

Pale yellow oil: yield 0.36 g (85%). IR(KBr) (ν_{max}/cm^{-1}): 2065 (C=C=N), 1730 and 1687 (C=O). ^{1}H NMR: $\delta =$ 1.35 and 1.64 (18H, 2 s, $2CMe_3$), 1.24–1.48 (10H, m, CH_2), 2.42 (4H, s, $2CH_2$), 3.64 (1H, m, CHN), 6.52 (1H, s, CH).^{13}C NMR: $\delta = 24.71$, 25.12, 25.28, 27.92, 32.34 and 33.09 ($7CH_2$), 27.91 and 28.20 ($2CMe_3$), 52.48 (CH), 60.12 (CHN), 63.34 ($C = C = N$), 81.50 and 82.09 ($2OCMe_3$), 158.19 ($C = C = N$), 167.66, 168.14, 170.85 (3C=O). MS (EI, 70 eV): m/z (%) = 434 (M^+, 2), 336 (8), 292 (25), 142 (38), 98 (100), 82 (54), 56 (46). Anal. Calcd. for $C_{23}H_{34}N_2O_6$ (434.53): C, 63.57; H, 7.88; N, 6.44%. Found: C, 64.4; H, 6.2; N, 6.1%.

REFERENCES

1. Schreiber, S. L. Target-oriented and diversity-oriented organic synthesis in drug discovery. *Science* **2000**, *287*, 1964–1969.
2. Domling, A. Recent advances in isocyanide-based multicomponent chemistry. *Curr. Opin. Chem. Boil.* **2002**, *6*, 297–305.

3. Trost, B. M. Atom-economy-a challenge for organic synthesis: Homogeneous catalysts leads the way. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259–281.
4. Bienayme, H.; Hulme, C.; Oddon, G.; Schmitt, P. Maximizing synthetic efficiency: Multi-component transformations lead the way. *Chem. Eur. J.* **2000**, *6*, 3321–3329.
5. Ugi, I. From isocyanides via four-componenent condensations to antibiotic syntheses. *Angew. Chem., Int. Ed. Eng.* **1982**, *21*, 810–812.
6. Ugi, I.; Lohberger, S.; Karl, R. In *Comprehensive Organic Synthesis*; B. M. Trost, I. Fleming (Eds.); Pergamon: Oxford, 1991, vol. 2, pp. 1083–1106.
7. Domling, A.; Ugi, L. Multicomponent reactions with isocyanides. *Angew. Chem. Int. Ed. Eng.* **2000**, *39*, 3169–3210.
8. Hulme, C.; Ma, L.; Romano, J. J.; Morton, G.; Tang, S. Y.; Cherrier, M. P.; Choi, S.; Salvino, J.; Labaudiniere, R. Novel applications of carbon dioxide/MeOH for the synthesis of hydantoins and cyclic ureas via the Ugi reaction. *Tetrahedron Lett.*, **2000**, *41*, 1889–1893.
9. Ballini, R.; Bosica, G.; Conforti, M. L.; Maggi, R.; Mazzacani, A.; Righi, P.; Sartori, G. Three-component process for the synthesis of 2-amino-2-chromenes in aqueous media. *Tetrahedron Lett.* **2001**, *57*, 1395–1398.
10. Arrieta, A.; Cossio, F. P.; Lecea, B. Competitive mechanism and origins of stereocontrol in the [2 + 2] thermal cycloaddition between imines and keteniminium cations. *J. Org. Chem*. **1999**, *64*, 1831–1842.
11. Aumann, R.; Jasper, B.; Lage, M.; Kerbs, B. Organic syntheses via transition metal complexes: 2-(Acyloxy)-ethenyl-keteneimines by ligand disengagement with isocyanide. *Organometallics* **1994**, *13*, 3502.
12. Getzmann, R.; Moller, M. H.; Rodewald, U.; Frohlich, R.; Grehl, M.; Wurthwein, E. U. Metallated ketenimines: Deprotonation of N-isopropyl-diphenyl-ketenimine and subsequent trapping reaction with electrophiles: A theoretical and experimental study. *Tetrahedron* **1995**, *51*, 3767–3786.
13. Coyl, J. D.; Raply, P. A. Ketenimine: Geometrie und Abhangigkeit der Razemisierungsbarriere von Den Substituenten. *Journal of the Chemical Society, Perkin Transactions 2* **1985**, *1*, 1957–1959.
14. Kosbahn, W.; Runge, W. Electronic spectra and electronic structures of ketenimines and carbodiimides. *Journal of the Chemical Society Perkin Transactions 2* **1981**, *2*, 270–280.
15. Marcaccini, S.; Torroba, T. The use of isocyanides in heterocyclic synthesis. *Org. Prep. Preced. Int.* **1993**, *25*, 141–172.
16. Siddall, T. H.; prohaska, C. A. Geminal proton nonequivalences and related phenomena in some N-substituted amides. *J. Am. Chem. Soc.* **1966**, *88*, 1172–1176.
17. Skattebol, L.; Jones, E. R. H.; Whiting, M. C. *1-Phenyl-1-penten-4-yn-3-ol. Org. Synth.* **1963**, *4*, 792–794.
18. Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. Researches on acetylenic compounds, part I: The preparation of acetylenic ketones by oxidation of acetylenic carbinols. *J. Chem. Soc.* **1946**, 36.
19. Bastiaansen, L. A. M.; Goderoi, E. F. 2-Aroylimidazoles: A simple one-step synthesis. *Synthesis* **1978**, 675–676.