Syntheses, characterizations and thermal analyses of four novel unsymmetrical β-diketimimates

Siddappa A Patil1, Phillip A Medina1, Joseph W Ziller2 and Bradley D Fahlman1*

Abstract

Four novel unsymmetrical β-diketimimates 2-(2,6-diisopropylphenyl)amino-4-(phenyl)imino-2-pentene (4a), 2-(2,6-diisopropylphenyl)amino-4-(4-methylphenyl)imino-2-pentene (4b), 2-(2,6-diisopropylphenyl)amino-4-(4-methoxyphenyl)imino-2-pentene (4c) and 2-(2,6-diisopropylphenyl)amino-4-(4-chlorophenyl)imino-2-pentene (4d) were synthesized with a 77-84% yield, and were characterized by spectroscopic methods (1H NMR, 13C NMR, IR and mass spectrometry), elemental analysis, and X-ray single-crystal diffraction, respectively. Spectroscopic and X-ray single-crystal diffraction analyses determined the structures of the four β-diketimimates. While thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) showed two distinct endothermic peaks for each β-diketiminate at temperatures of 92.55°C and 221.50°C (4a), 93.51°C and 238.82°C (4b), 109.60°C and 329.22°C (4c), 115.43°C and 243.25°C (4d), respectively, corresponding to their melting and boiling points.

Keywords: Unsymmetrical β-diketiminate, Synthesis, Spectroscopic investigation, X-ray structure, Thermogravimetric analysis

Background

The β-diketiminate class, generally denoted as “nacnac”, or [(ArNC(R))2CH]- (where Ar =aryl and R = Me or another group), occupies a rightful place alongside a narrow list of popular ancillary supports, given its ability to stabilize or generate unique coordination environments and to support reactive organometallic reagents or catalysts (Bourget-Merle et al. 2002; Holland 2008; Mindiola 2006; Cramer and Tolman 2007; Roesky et al. 2004; Piers and Emslie 2002; Rahim et al. 1998). The “nacnac” ligand skeleton is analogous to the “acac” (acetylacetonate) ligand, but the oxygen atoms are exchanged for nitrogen-based moieties such as NR (R = alkyl, silyl, Ar) (Scheme 1). As a result, the substituent at the nitrogen donor atom can allow for steric protection at the metal center unlike “acac” could offer. When small moieties such as H, Me, or the SiMe3 on the nitrogen the substance easily forms dimers and allows higher coordination to the metal center, whereas bulky aryl groups on nitrogen usually lead to the isolation of monomeric species with low coordination numbers at the metal.

The first documented cases of β-diketiminate metal complexes were reported by McGeachin (McGeachin 1968), Parks, and Holm (Parks, and Holm 1968) in 1968. The explosion in popularity of “nacnac” amongst synthetic chemists is driven, in part, by the monoanionic nature of the β-diketiminate group, the chelating nature but also variable mode of hapticity, the ease in preparation, and the versatility to tune both electronic and steric parameters. Till to date the N-aryl substituted “nacnac” ligands [HN(Ar)C(Me)CHC(Me)N(Ar)] (Nagendran and Roesky 2008) and [HN(Ar)C(tBu)CHC(tBu)N(Ar)] (Pfirrmann et al. 2009; Ding et al. 2009) (Ar = 2,6-iPr2C6H3) showed to be the best for stabilization of low coordinate metal sites.

The major breakthrough in this area was achieved in the mid 1990’s, when β-diketiminates were used as spectator ligands, thus offering strong metal-ligand bonds like cyclopentadienyls (Scheme 1). In contrast to the latter, β-diketiminates offer a possibility of subtle tuning of their electronic and steric properties by simple variation of the substituents on nitrogen and adjacent carbon atoms.

The availability of straightforward, multigram syntheses for many classes of β-diketimimates has generated widespread popularity of the ligand for coordination and organometallic chemistry. Prototypical symmetrical β-
diketimines with N-aryl substituents can be synthesized in one step from commercially available anilines and diones through simple condensation reactions (McGeachin 1968; Stender et al. 2001). β-Diketimimates with aliphatic nitrogen substituents can also be prepared by related condensation routes, but often require harsh reagents such as oxonium salts for complete diimine formation (Kuhn et al. 1999). Other variants of the β-diketiminate scaffold have been recently discussed in a comprehensive review (Bourget-Merle et al. 2002). Herein, we demonstrate a synthetic pathway for unsymmetrical β-diketimines and provide detailed characterization by spectroscopic (1H-NMR, 13C-NMR and mass) methods, melting point determination, thermogravimetric analysis (TGA), differential temperature analysis (DTA), and elemental analysis. In addition, the solid state structures of the compounds 4a-d have been analyzed by single crystal X-ray diffraction.

**Results and discussion**

**Synthesis**

The synthetic pathway for unsymmetrical β-diketimimates described in this work is outlined in Scheme 2. As depicted in Scheme 2, the unsymmetrical β-diketimimates 4a-d were synthesized in two steps: (1) condensation of acetylacetone with one equiv. of primary aromatic amine 2,6-diisopropylaniline in methanol, with formic acid as catalyst, afforded the (Z)-4-(2,6-diisopropylphenylamino)pent-3-en-2-one intermediate 3 to give unsymmetrical β-diketimines 4a-d in good yields. In the second step, the one-pot reaction of (Z)-4-(2,6-diisopropylphenylamino)pent-3-en-2-one 3, aromatic amine and para-toluenesulfonic acid failed to give any target product; the reaction of (Z)-4-(2,6-diisopropylphenylamino)pent-3-en-2-one with the para-toluenesulfonic acid took place instead, preventing further reaction with the aromatic amine.

**1H-NMR and 13C-NMR spectra**

The 1H NMR spectra of all the unsymmetrical β-diketimimates show a characteristic downfield shift in the range δ = 12.87-13.14 ppm for the NH proton and high field shift in the range δ = 4.79-4.84 ppm for the methyne proton attributable to the formation of unsymmetrical β-diketimimates from (Z)-4-(2,6-diisopropylphenylamino)pent-3-en-2-one and amines. Two sharp singlets observed at the range 1.69-1.83 and 1.56-1.65 ppm are assigned to the protons of the two methyl groups (CH3C=NAr and CH3CNHAr) of the unsymmetrical β-diketimimates. The resonance due to the four CH3 protons (CH(CH3)2) were observed as a two doublets at the range 1.15-1.19 and 1.09-1.14 ppm while that of CH appeared as a septet at the range 3.12-3.18 ppm.

The 13C NMR is in good agreement with the proposed unsymmetrical β-diketiminate structures as well. The 13C-NMR spectra of unsymmetrical β-diketimimates showed a peak at the range 161.8-164.1 ppm which is assigned to carbon of the C=N group. The methyne carbon appears at the range 95.9-96.6 ppm. Four peaks at the range 24.3-28.7, 20.3-20.6, 21-22.8 and 20.7-21.2 ppm are due to carbons of the six methyl groups (CH3C=NAr, CH3CNHAr and CH(CH3)3) respectively. In addition, their identities have also been confirmed by a molecular ion peak [M+ ] from GC-MS mass spectra.
FT-IR spectra
The FT-IR spectra for the compounds 4a-d are recorded in the solid state using the KBr disc technique at the region from 400 to 4000 cm\(^{-1}\). The (C=N) bands are observed at 1645–1557 (\(\nu\)) cm\(^{-1}\); the position of these bands varies with the molecular structure, though no regularity can be pointed out. The bands at the range 3055–3072 (\(\nu\)) cm\(^{-1}\) is typical of the NH group. Weak to medium absorptions around 3100–3000 cm\(^{-1}\) observed corresponding to the =C–H stretch of aromatic ring.

X-ray crystal structure
Single crystals of unsymmetrical β-diketiminates 4a-d were grown by the slow evaporation method using methanol as the solvent at room temperature. The solid state structures of 4a-d with an atom-numbering scheme are shown in Figures 1, 2, 3 and 4, respectively. The molecular packing diagrams of 4a-d are displaced in Figures 5, 6, 7 and 8, respectively. A crystallographic data and refinement detail of the compounds 4a-d is shown in Table 1, whereas selected bond lengths and bond angles are compiled in Table 2. The analysis of the crystal structures of compounds 4a-d shows that they are coplanar. Compounds 4a-d have two aromatic rings and a central linkage. Compounds 4a-d crystallized in the triclinic space group \(\overline{P} 1\), with two molecules in the unit cell. In these compounds, there is an absence of any lattice held water molecules or organic solvent molecules in the unit cell of the determined structure.

The N=C-C=N-H linkage of the compounds 4a-d is planar; the bond lengths [Table 2] indicate electron delocalization. The C-C bond distances in aromatic rings are in the normal range of 1.37-1.48 Å, which is characteristic of delocalized aromatic rings. The C-C-C bond
angles in aromatic rings are around 120° with the variation being less than 2°, which is characteristic of sp²-hybridized carbons. The molecular packing diagrams of all the four unsymmetrical β-diketiminates 4a-d showed two layers of molecules, which are independently arranged in the unit cell. Molecules forming each layer are not connected through intermolecular hydrogen bonding. In each layer, the molecules are alternatively parallel. The molecular packing diagram also shows the presence of one intra-molecular hydrogen bond. One of the hydrogens, H1 of the NH group, is involved in intra-molecular hydrogen bonding with the N2 of the C=N entity. This hydrogen bonding stabilizes the crystal packing.

Mass spectra and thermal studies
The mass spectra were analyzed by GC-MS. The peaks observed at m/z 334.49, 348.47, 364.36, and 368.92 suggested the molecular formulas C_{23}H_{30}N_{2}, C_{24}H_{32}N_{2}, C_{24}H_{32}N_{2}O, and C_{23}H_{29}ClN_{2} of the compounds 4a-d respectively.

The thermal behavior of the compounds 4a-d have been investigated using thermogravimetric techniques in the temperature range from 25°C to 1000°C at a heating rate of 10°C min⁻¹ under inert nitrogen gas flow. On the temperature difference curves seen in Figure 9, sharp endothermic peaks were observed at temperatures of 92.55, 93.51, 109.60 and 115.43°C, this indicates that the compounds 4a-d melt at 92.55, 93.51, 109.60 and 115.43°C, respectively. Further confirmation of their melting point by glass capillary analysis provided values of 93.0, 94.0, 110.0 and 116.0°C for the compounds 4a-d. The symmetric analogues 2-((phenyl)amino)-4-((phenyl)imino)-2-pentene, 2-((4-methylphenyl)amino)-4-((4-methylphenyl)imino)-2-pentene, 2-((4-methoxyphenyl)amino)-4-((4-methoxyphenyl)imino)-2-pentene and 2-((4-
chlorophenyl)amino)-4-((4-chlorophenyl)imino)-2-pentene melt at 51, 73, 94 and 86°C, respectively (Gong and Ma 2008; Tang et al. 2006). At temperatures of 221.50, 238.82, 329.22 and 243.25°C, additional sharp endothermic peaks occurred corresponding to boiling points of the compounds 4a-d. Onsets of mass loss in the compounds 4a-d occurred at 77.17, 85.29, 91.38 and 93.41°C and terminated at 243.66, 258.89, 329.95 and 260.92°C as observed by the weight loss curve of the TGA data for each compound.

Conclusions
All the four unsymmetrical β-diketiminates (4a-d) were synthesized. The structures were identified by spectroscopic methods (1H NMR, 13C NMR, IR and mass), thermogravimetric analysis (TGA), differential temperature analysis (DTA), elemental analysis, and X-ray diffraction analyses. TGA/DTA analyses of all the four unsymmetrical β-diketiminates 4a-d were studied, showing two distinct endothermic peaks at temperatures of 92.55, 93.51, 109.60, 115.43°C and 221.50, 238.82, 329.22, 243.25°C, corresponding to melting and boiling points, respectively.

Experimental section
General information on reagents and techniques
Reactions were carried out under aerobic conditions. All reagents and solvents are of analytical grade; they were purchased and used without further purification. Acetylacetone, aniline, 4-methylaniline, 4-methoxyaniline, 4-chlororlaniline, formic acid, \textit{para}-toluenesulfoinic acid monohydrate, MgSO$_4$, and sodium carbonate were procured commercially from Sigma-Aldrich chemical company, and were used without further purification. Nuclear magnetic resonance (NMR) spectra were obtained using a 1.0% to 2.5% solution in deuterated benzene (C$_6$D$_6$). 1H and 13C NMR spectra were recorded on a Varian Mercury 500 MHz spectrometer. Proton and carbon chemical shifts are reported in parts-per-million (δ) with respect to tetramethylsilane (TMS) as internal reference (δ = 0.0 ppm). IR spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer employing a KBr disc. Mass spectra were obtained on a GC-MS instrument operating in TOF-MI$^+$ mode. CHN analysis was done by Atlantic Microlab using a CE-1108 Elemental Analyzer, and values were within ±0.4% of the theoretical values. Thermogravimetric analyses (TGA) were made with a Pyris TGA instrument. A heating rate of 10°C/min was used and samples (5–10 mg) were contained in a platinum pan. The sample compartment was purged with dry nitrogen at 50 mL/min during analysis. TA Thermal Advantage software was used for data analysis. Melting points were determined using a Pyris differential scanning calorimeter (DSC). The crystallographic
data for compounds 4a-d were collected on a Bruker SMART APEX II diffractometer. The APEX2 (Version 2010.9–0, 2010) program package was used to determine the unit-cell parameters and for data collection. The raw frame data was processed using SAINT (Version 7.68a, 2009) and SADABS Sheldrick (2008a) to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL (Sheldrick 2008b) program. The structures were solved by direct methods and refined on F2 by full-matrix least-squares techniques. The analytical scattering factors21 for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Center with the deposition numbers 903786, 903787, 903788, and 903789. A copy of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 –033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk].

4-(2,6-diisopropylphenyl)amino-3-penten-2-one (3). 2,6-Diisopropylaniline (1.77 g, 10.0 mmol) was mixed with acetylacetone (1.0 g, 10.0 mmol) in 40 mL of methanol containing a catalytic amount (2 drops) of formic acid. The solution was heated at 85°C for 6–8 h. Removal of volatiles afforded a pale brown oil. This was then stirred with 20 mL 40–60°C petroleum ether at −30°C to precipitate a white solid which was filtered off, washed with 2 x 10 mL cold hexane (−78°C), and dried in vacuo. Yield: 2.30 g (89%). 1H NMR (500 MHz, C6D6) δ (ppm): 12.66 (1H, s, NH), 7.11-7.06 (m, 1H, ArH), 6.97-6.94 (m, 2H, ArH), 5.08 (s, 1H, CH=C(CH3)N), 3.04 (sept, J = 6.8 Hz, 2H, CH(CH3)2), 2.01 (s, 3H, CH3COC), 1.34 (s, 3H, CH3CNHAr), 1.02 (d, J = 6.9 Hz, 6H, CH(CH3)2), 0.96 (d, J = 6.9 Hz, 6H, CH(CH3)2). 13C NMR (100 MHz, C6D6) δ (ppm): 195.69 (C=O), 162.40 (HC(CNHAr), 146.60 (Ar-C), 134.23 (Ar-C), 128.50 (Ar-C), 123.78 (Ar-C), 95.93 (CH), 29.04 (CH3C=O), 28.80 (CH(CH3)2), 24.53 (CH(CH3)2), 22.61 (CH(CH3)2), 18.85 (CH3CNHAr). Mass data (TOF MS EI†): Calcld for C17H25NO [M+] 259.39, found: 259.21. Anal. Calcd for C17H25NO: C, 78.72; H, 9.71; N, 5.40; Found: C, 78.61; H, 9.59; N, 5.36. IR (KBr, cm−1) ν: 3418 (m), 2972 (w), 16015 (s), 1573 (m), 1515 (m), 1467 (w), 1411 (m), 1397 (m), 1344 (m), 1299 (w), 1203 (w), 1137 (m), 1076 (w), 983 (m), 842 (w), 722 (w), 601 (m), 513 (m), 484 (w).

2-(2,6-diisopropylphenyl)amino-4-(phenyl)imino-2-pentene (4a). Aniline (4.55 g, 50.00 mmol), and para-toluene sulfonic acid monohydrate (9.510 g, 50.00 mmol) in 100 mL of toluene were stirred for approximately 3 h at room temperature. To the obtained yellow suspension, 4-(2,6-diisopropylphenyl)amino-3-penten-2-one (12.97 g, 50.00 mmol) was added. A Dean-Stark apparatus was attached and the mixture was heated at reflux for 24 h to remove the water. The reaction mixture was cooled to room temperature and all the volatiles were removed under reduced pressure to give a yellow solid. The solid was treated with diethyl ether (100 mL), water (100 mL) and sodium carbonate (10.60 g, 100 mmol), and the obtained mixture was kept stirred. After complete dissolution, the aqueous phase was separated and extracted with diethyl ether. The combined organic phase was dried over MgSO4 and rotary evaporated to dryness under reduced pressure to afford a brownish yellow solid. Yellow crystals (12.95 g, 77%) were obtained after recrystallization from methanol. 1H NMR (500 MHz, C6D6) δ (ppm): 13.14 (s, 1H, NH), 7.16-7.14 (m, 3H, ArH), 7.10-7.09 (m, 2H, ArH), 6.97-6.94 (m, 2H,
Table 1 Crystal data and the structure refinement of the compounds 4a-d

| Identification code | 4a      | 4b      | 4c      | 4d      |
|---------------------|---------|---------|---------|---------|
| Empirical formula   | C_{23}H_{30}N_{2} | C_{24}H_{32}N_{2} | C_{24}H_{32}N_{2}O | C_{23}H_{28}ClN_{2} |
| Formula weight      | 334.49  | 348.52  | 364.52  | 368.93  |
| Temperature (K)     | 198(2)  | 143(2)  | 88(2)   | 143(2)  |
| Wavelength (Å)      | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system      | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group         | P ⌂ | P ⌂ | P ⌂ | P ⌂ |
| Unit cell dimensions|         |         |         |         |
| a (Å)               | 9.6209(4) | 8.9868(7) | 9.4632(5) | 8.8970(6) |
| b (Å)               | 11.0221(5) | 10.3608(8) | 10.3455(5) | 10.3481(6) |
| c (Å)               | 11.0824(5) | 12.0081(9) | 12.0163(5) | 11.9800(8) |
| α (°)               | 112.2432(5) | 98.8619(9) | 106.1503(5) | 97.8485(9) |
| β (°)               | 97.8486(5) | 106.9857(8) | 107.4448(6) | 98.9102(7) |
| γ (°)               | 102.1196(5) | 106.2382(9) | 107.4484(6) | 92.1628(7) |
| Volume (Å³)         | 1032.76(8) | 1050.44(14) | 1078.59(9) | 1035.36(12) |
| Z                   | 2       | 2       | 2       | 2       |
| Density (calculated) (Mg/m³) | 1.076 | 1.102 | 1.122 | 1.183 |
| Absorption coefficient (mm⁻¹) | 0.062 | 0.064 | 0.068 | 0.193 |
| F(000)              | 364     | 380     | 396     | 396     |
| Crystal size (mm³)  | 0.42 x 0.33 x 0.26 | 0.33 x 0.31 x 0.25 | 0.36 x 0.36 x 0.23 | 0.38 x 0.37 x 0.26 |
| Theta range for data collection (°) | 2.04 to 26.37 | 1.80 to 28.40 | 1.78 to 28.82 | 1.81 to 28.54 |
| Index ranges        | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13 | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 16 | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15 | -12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15 |
| Reflections collected | 11311 | 12098 | 13056 | 12115 |
| Independent reflections | 4202 [R(int) = 0.0142] | 4779 [R(int) = 0.0145] | 5172 [R(int) = 0.0138] | 4753 [R(int) = 0.0172] |
| Refinement method   | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Completeness to theta = 25.50° | 99.7% | 99.6% | 99.6% | 99.6% |
| Max. and min. Transmission | 0.0842 and 0.9742 | 0.0948 and 0.9760 | 0.0946 and 0.9760 | 0.0952 and 0.9295 |
| Data / restraints / parameters | 4202 / 0 / 251 | 4779 / 0 / 277 | 5172 / 0 / 255 | 4753 / 0 / 348 |
| Goodness-of-fit on F² | 1.049 | 1.037 | 1.072 | 1.049 |
| Final R indices [I>2sigma(I)] | R1 = 0.0436, wR2 = 0.1186 | R1 = 0.0438, wR2 = 0.1149 | R1 = 0.0407, wR2 = 0.1089 | R1 = 0.0366, wR2 = 0.0996 |
| R indices (all data) | R1 = 0.0505, wR2 = 0.1248 | R1 = 0.0535, wR2 = 0.1225 | R1 = 0.0452, wR2 = 0.1126 | R1 = 0.0406, wR2 = 0.1031 |
| Largest diff. peak and hole (e.Å⁻³) | 0.264 and −0.197 | 0.264 and −0.201 | 0.328 and −0.325 | 0.328 and −0.225 |

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ArH), 6.88-6.85 (m, 1H, ArH), 4.84 (s, 1H, CH=C(CH₃)N), 3.18 (sept, J = 6.8 Hz, 2H, CH(C₃H₃)₂), 1.82 (s, 3H, CH₃CN=Ar), 1.63 (s, 3H, CH₃CN=Ar), 1.19 (d, J = 7.0 Hz, 6H, CH(CH₃)₃), 1.14 (d, J = 7.0 Hz, 6H, CH(CH₃)₃), 13C NMR (100 MHz, C₆D₆) δ (ppm): 163.1 (NCCH₃), 157.3 (NCCH₃), 144.9 (Ar-C), 142.8 (Ar-C), 141.1 (Ar-C), 129.2 (Ar-C), 125.2 (Ar-C), 123.4 (Ar-C), 123.3 (Ar-C), 122.7 (Ar-C), 96.6 (CH), 28.7 (CH₃CN=Ar), 24.3 (CH(CH₃)₃), 22.7 (CH(CH₃)₃), 21.0 (CH(CH₃)₃), 20.6 (CH₃CN=Ar). Melting point: 93,0°C. Mass data (TOF MS El⁺): Calcd for C₂₃H₃₀N₂ [M⁺] 334.50, found: 334.49. Anal. Calcd for C₂₃H₃₀N₂: C, 82.59; H, 9.04; N, 8.37; Found: C, 82.55; H, 9.01; N, 8.41. IR (KBr, cm⁻¹) ν: 3055 (w), 2960 (w), 2920 (w), 2875 (w), 1925 (w), 1873 (w), 1800 (w), 1740 (w), 1630 (s), 1547 (s), 1489 (w), 1360 (m), 1275 (m), 1260 (m), 1155 (s), 1100 (w), 1030 (w), 800 (s), 798 (s), 750 (s), 699 (m), 595 (w), 501 (w), 425 (m).

2-(2,6-diisopropylphenyl)amino-4-(4-methylphenyl) imino-2-pentene (4b). β-Diketiminate 4b was synthesized by the same procedure as 4a. Yield (14.02 g, 80%).
Table 2 Selected bond lengths and bonds angles of the compounds 4a-d

| Bond length (Å) | 4a | 4b | 4c | 4d |
|----------------|----|----|----|----|
| N(1)-C(2)     | 1.3269(16) | 1.3476(15) | 1.3530(13) | 1.3293(15) |
| N(1)-C(6)     | 1.4151(15) | 1.4220(15) | 1.4222(12) | 1.4148(15) |
| N(2)-C(4)     | 1.3231(15) | 1.2965(14) | 1.3036(13) | 1.3154(14) |
| N(2)-C(12)    | 1.4270(14) | 1.4268(13) | 1.4268(13) | 1.4268(13) |
| C(1)-C(2)     | 1.5065(18) | 1.5015(16) | 1.5039(14) | 1.5059(15) |
| C(2)-C(3)     | 1.4001(17) | 1.3680(16) | 1.3777(14) | 1.3897(16) |
| C(3)-C(4)     | 1.3987(17) | 1.4352(16) | 1.4382(13) | 1.4091(15) |
| C(9)-C(12)    | 1.5093(18) | 1.5093(18) | 1.5093(18) | 1.5093(18) |
| O(1)-C(9)     | 1.3706(12) | 1.3706(12) | 1.3706(12) | 1.3706(12) |
| Cl(1)-C(9)    | 1.4283(15) | 1.4283(15) | 1.4283(15) | 1.4283(15) |

| Bond angles (°) | 4a | 4b | 4c | 4d |
|----------------|----|----|----|----|
| C(2)-N(1)-C(6) | 124.56(11) | 126.93(10) | 127.61(9) | 124.80(10) |
| C(4)-N(2)-C(12) | 123.06(10) | 122.54(10) | 122.54(10) | 122.54(10) |
| N(1)-C(2)-C(3) | 120.69(11) | 120.78(10) | 120.80(9) | 120.80(9) |
| N(1)-C(2)-C(1) | 119.51(11) | 119.58(9) | 119.58(9) | 119.58(9) |
| C(3)-C(2)-C(1) | 117.90(12) | 117.90(12) | 117.90(12) | 117.90(12) |
| C(2)-C(3)-C(4) | 126.12(11) | 126.12(10) | 126.84(9) | 126.84(9) |
| N(2)-C(4)-C(3) | 121.36(12) | 121.22(11) | 121.22(11) | 121.22(11) |
| C(3)-C(4)-C(5) | 117.90(12) | 117.90(12) | 117.90(12) | 117.90(12) |
| C(4)-N(2)-C(13) | 121.25(11) | 121.25(11) | 121.25(11) | 121.25(11) |
| C(9)-O(1)-C(12) | 116.54(9) | 116.54(9) | 116.54(9) | 116.54(9) |

Figure 9 TGA/DTA of unsymmetrical β-diketimines 4a-d.
123.4 (Ar-C), 114.5 (Ar-C), 95.9 (CH), 54.9 (OCH3Ar), 28.7 (CH3C=NAr), 24.2 (CH(CH3)2), 22.8 (CH(CH3)2), 21.2 (CH(CH3)2), 20.3 (CH3CNHAr). Melting point: 110.0°C. Mass data (TOF MS El+): Calcld for C23H32N2O [M+] 364.52, found: 364.36. Anal. Calcld for C24H32N2O: C, 74.88; H, 7.92; Cl, 9.58; N, 7.55. IR (KBr, cm-1) v: 3062 (s), 2960 (m), 1670 (s), 1558 (m), 1530 (w), 1495 (m), 1450 (m), 1417 (s), 1325 (m), 1271 (w), 1239 (m), 1215 (w), 1182 (m), 1120 (m), 1051 (m), 1030 (m), 930 (w), 864 (m), 837 (w), 800 (w), 745 (m), 677 (w), 635 (w).

Competing interests
The authors have no competing interests.

Authors’ contributions
SAP and PAM carried out the syntheses and characterization of the reported compounds. JWZ carried out the X-ray diffraction studies for all compounds reported herein. BDF conceived of the study, participated in its design and coordination, and drafted the manuscript. All authors read and approved the final manuscript.

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Author details
1Department of Chemistry & Science of Advanced Materials Program, Central Michigan University, Mount Pleasant, MI 48859, USA. 2Department of Chemistry, University of California, Irvine, CA 92697, USA.

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