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Trialkyl borate assisted amination of fluorinated 1,3-diketones for synthesis of *N,N′*-1,2-phenylen-*bis*(β-aminoenones) and their Ni(II), Cu(II) and Pd(II) complexes

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ABSTRACT

An effecient synthetic method for fluorinated tridentate β-aminoenones and tetradentate *bis*(β-aminoenones) via amination of fluorinated 1,3-diketones with *o*-phenylenediamine in the presence of trialkyl borates was developed. Ni(II), Cu(II) and Pd(II) complexes with tetradentate *bis*(β-aminoenones) were obtained. Their gaschromatographic behaviour and main fragmentation paths in the electron ionization mass spectra were described.

1. Introduction

The modification of known ligand systems, such as 1,3-diketones and their hetero-analogues, provides a considerable contribution to the chemistry of coordination compounds [1]. Introduction of fluorine in 1,3-dicarbonyl compounds or their derivatives substantially changes the electron density distribution that greatly affects their chemical and physical properties [2]. Thus, stability and volatility of diketonate complexes with ions of transition metals usually increase, which has been used for quantitative gaschromatographic determination of many transition and rare earth metals [3] and for obtaining of coats by means of metal organic chemical vapour deposition (MOCVD) [4].

Replacement of an oxygen atom by a NR-group in fluorinated 1,3-dicarbonyl compounds yields enamino-ketones (β-aminoenone, β-aminovinylketone). These chelating agents are of considerable interest for designing tailored coordination compounds due to the possibility to change the steric and electronic envelope of the main chelate site NO.

Generally, the reaction of fluorinated 1,3-diketones with diamine occurs with a comparative ease to afford mono- or *bis*(β-aminoenones) [5,6] depending on reagents ratio. However, when 1,2-diaminoarenes were applied in this reaction, fluorinated 1,5-benzodiazepines or the acidic cleavage products are usually formed [5]. Meanwhile, coordination compounds based on fluorinated tetradentate *bis*(β-aminoenones) with *N,N′*-1,2-arylene bridge can be of significant practical interest, likewise non-aromatic ones. For example, transition metal complexes of *N,N′*-alkylene-*bis*(β-aminoenones) are less volatile, but much more stable and possess improved gaschromatographic (GC) behaviour in comparison with β-aminoenonate [7]. Ni(II), Cu(II) and Pd(II) complexes with fluorinated *N,N′*-ethylene-*bis*(β-aminoenones) were considered as effective organic optical filters [8]. Moreover, complexes of these *bis*(β-aminoenones) are similar to *Salphen* (*N,N′*-1,2-phenylene-*bis*(salicylideneiminato)) complexes that catalytic [9], optic [10] and magnetic [11] properties have been extensively studied.

It was previously found that the reaction of *o*-phenylenediamine (benzene-1,2-diamine) with fluorinated β-alkoxyenones occurred chemoselectively to yield fluorinated tridentate β-aminoenones and tetradentate *bis*(β-aminoenones) with an *N,N′*-1,2-phenylene bridge [12]. Ni(II), Cu(II) and Pd(II) complexes with tetradentate *bis*(β-aminoenones) bearing CF_3 and CH_3 terminal groups were obtained and structurally characterized as well [13].

Despite the fact that the above-mentioned tri- and tetradentate ligands can be obtained starting from fluorinated β-alkoxyenones, availability of various fluorinated 1,3-diketones promotes their usage for the construction of these chelating ligands. Nevertheless, information on such syntheses is scarce. It was shown that 2-polyfluoroacylcycloalkanones react with *o*-phenylenediamine under mild conditions affording tridentate β-aminoenones [14].

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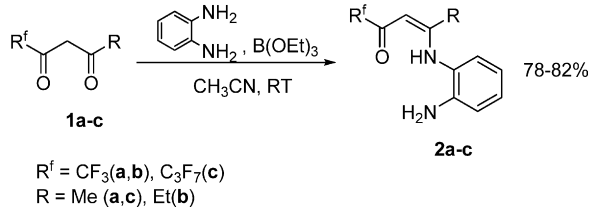


Scheme 1. $B(OEt)_3$ catalyzed synthesis of tridentate β-aminoenones.

There were only two reports [15] where authors declared the formation of *bis*(β-aminoenones) by reaction of fluorinated 1,3-diketones with *o*-phenylenediamine. However, neither elemental analysis nor spectroscopic data were reported for the obtained compounds. Moreover, the melting point (97 °C) of a product from trifluoroacetylacetone [15a] corresponds to tridentate β-aminoenone (96–97 °C) rather than to the claimed *bis*(β-aminoenone) (122–124 °C), both structures being strongly proved [12c].

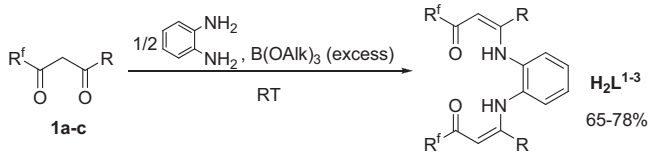
Herein we report on an efficient synthesis of tridentate β-aminoenones and tetradentate *bis*(β-aminoenones) by reaction of fluorinated 1,3-diketones with *o*-phenylenediamine in the presence of trialkyl borate, and on the preparation of Cu(II), Ni(II) and Pd(II) complexes of tetradentate *bis*(β-aminoenones). Gaschromatographic behaviour and electron impact ionization mass spectra of *bis*(β-aminoenones) and their complexes were investigated to estimate their volatility, thermal stability and behaviour under conditions favourable to ionization (high temperature, photoirradiation, etc.).

2. Results and discussion

2.1. Trialkyl borate assisted amination of fluorinated 1,3-diketones

We found that amination of the fluorinated diketones **1a–c** with one equivalent of *o*-phenylenediamine in the presence of one equivalent of triethyl borate gave the tridentate β-aminoenones **2a–c** in good yields (Scheme 1, Table 1; entry 1–3).

The positive effect of $B(OEt)_3$ on the selectivity of this reaction can arise from two main factors. At first, similarly to BF_3, triethylborate is able to form a borate complex with 1,3-diketones, thus activating one of two carbonyl groups of the dicarbonyl moiety. Secondly, water, formed in the course of amination,



R, Rf = Me, CF3 (**1a**, H_2L^1); Et, CF3 (**1b**, H_2L^2); Me, C3F7 (**1c**, H_2L^3)
Alk = Et, Bu

Scheme 2. $B(OAlk)_3$ catalyzed synthesis of tetradentate *bis*(β-aminoenones).

Table 1
Synthesis of β-aminoenones **2a-c** and *bis*(β-aminoenones) H_2L^{1-5}.

Entry	Compounds	R	R^f	Time	Yield (%)[a]
1	2a	Me	CF_3	10 min[b]	78
2	2b	Et	CF_3	15 min[b]	82
3	2c	Me	C_3F_7	10 min[b]	79
4	H_2L^1	Me	CF_3	1 day[c]	76
5	H_2L^2	Et	CF_3	3 days[c]	65
6	H_2L^3	Me	C_3F_7	1day[c]	78
7	H_2L^4	Et	CF_3	2 days[d]	70
8	H_2L^5	Me	C_3F_7	2 days[e]	74

[a] Isolated yields.
[b] $B(OEt)_3$ was used.
[c] $B(OBu)_3$ was used.
[d] From **2b** and β-alkoxyenone **3.**
[e] From **2c** and β-alkoxyenone **3.**

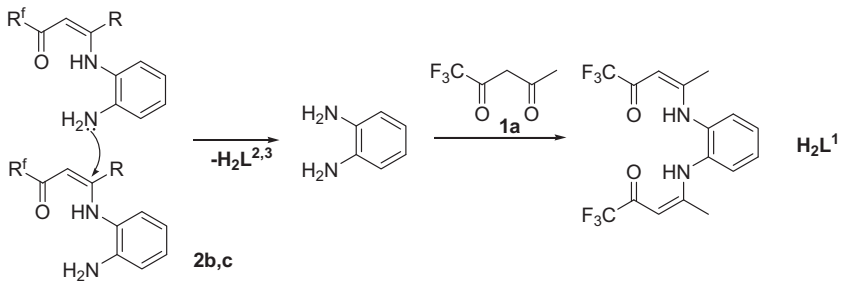
irreversibly reacts with $B(OEt)_3$. Thus, when less than one equivalent of $B(OEt)_3$ was used, the reaction was not completed within 15–20 h (R=Me).

While triethyl borate was used to obtain tetradentate ligands H_2L^{1-3} via the reaction of *o*-phenylenediamine with two equivalents of the fluorinated diketones **1a–c**, only *bis*(β-aminoenones) $H_2L^{1,3}$ were isolated in ~30% yield. Side products of this reaction were determined by means of GC–MS analysis. Thus, the analysis of the hydrolyzed reaction mixture from trifluoroacetylacetone **1a** showed the content of the target compound H_2L^1 ~27%, unreacted diketone **1a** ~25%, tridentate β-aminoenones **2a** ~2% and ~36% of 2-methyl-4-(trifluoromethyl)-3*H*-1,5-benzodiazepine as a result of intramolecular cyclization of **2a**. The use of a large excess of triethyl borate (10 equiv.) increased the yield of $H_2L^{1,3}$ up to ~40%. However, when $B(OEt)_3$ was replaced by a large excess of $B(OBu)_3$, *bis*(β-aminoenones) H_2L^{1-3} were obtained in 65–78% yields (Scheme 2; Table 1, entry 4–6).

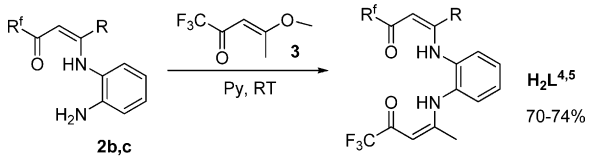
Some unidentified coloured impurities were formed in course of the last reaction. Therefore, the crude *bis*(β-aminoenones) were reacted with an excess of $Cu(CH_3COO)_2$, and the obtained copper complexes were purified by column chromatography. Treatment of the latter with oxalic acid afforded analytically pure *bis*(β-aminoenones) in almost quantitative yields (based on copper complexes).

This approach was not suitable for the preparation of pure unsymmetrical tetradentate ligands by reaction of β-aminoenones **2b,c** with trifluoroacetylacetone **1a**. While the expected *bis*(β-aminoenones) $H_2L^{4,5}$ were formed, minor amounts (10–20%) of the symmetrical compounds $H_2L^{2,3}$ appeared. The presence of ligand H_2L^1 was observed in these cases as well. Probably, this is a result of the competitive intermolecular re-amination of **2b,c** followed by the reaction of trifluoroacetylacetone with the liberated *o*-phenylenediamine (Scheme 3).

Because of non-selective preparation of unsymmetrical *bis*(β-aminoenones) $H_2L^{4,5}$ from diketones, they were obtained by the reaction of β-aminoenones **2b,c** with β-methoxyenone **3** in the



Scheme 3. Plausible mechanism of side-product-formation in course of the unsymmetrical *bis*(β-aminoenones) synthesis.



R^f, R = CF_3, Et (**2b**, $\mathbf{H_2L^4}$); C_3F_7, Me (**2c**, $\mathbf{H_2L^5}$)

Scheme 4. Synthesis of unsymmetrical *bis*(β-aminoenones).

presence of pyridine [12c] (Scheme 4; Table 1, entry 7 and 8) and purified via copper complexes.

The aminoenones **2b,c** and $\mathbf{H_2L^{2-5}}$ were characterized by the elemental analysis, IR and NMR ^{1}H, ^{19}F and ^{13}C spectroscopy. Comparison of compounds **2a** and $\mathbf{H_2L^1}$ with authentic samples [12c] confirmed their structures (Table 1, entries 1 and 4).

The presence of aminoenone fragments was confirmed by signals of olefinic protons at δ_H 5.58–5.72 ppm and NH-protons at δ_H 11.70–12.60 ppm in the ^{1}H NMR spectra. Singlets at δ_C 167.6–173.7 ppm and multiplets (quartets or triplets) at δ_C 177.7–178.8 ppm in the ^{13}C NMR spectra were assigned to the carbon atoms of =C(NHAr) and R^fC=O fragments, respectively. The high-frequency shifts of the N–H groups suggest U-configuration of the aminoenone fragments stabilized by a strong N–H···O intramolecular hydrogen bond [16]. Double-proton broadened singlets at δ_H 3.71–3.80 ppm in the case of **2b,c** were attributed to the NH_2-group. For unsymmetrical *bis*(β-aminoenones) $\mathbf{H_2L^{4,5}}$ double-sets of peaks of NH and olefinic protons together with terminal group signals were observed in the ^{1}H spectra.

2.2. Synthesis of Cu(II), Ni(II) and Pd(II) complexes with tetradentate *bis*(β-aminoenones)

The reaction of tetradentate *bis*(β-aminoenones) $\mathbf{H_2L^{1-5}}$ with Cu(II), Ni(II) and Pd(II) acetates resulted in corresponding complexes. The elemental analysis and IR-spectroscopy data confirm their structure. NMR ^{1}H and ^{19}F spectroscopy was used in case of Ni(II) and Pd(II) complexes. Melting points and IR-spectral data of $\mathbf{NiL^1}$, $\mathbf{CuL^1}$ and $\mathbf{PdL^1}$ corresponded to authentic samples [13].

Noteworthy, the majority of signals of complexes $\mathbf{NiL^{2-5}}$ and $\mathbf{PdL^{2-5}}$ in the NMR ^{1}H and ^{19}F spectra were shifted significantly with respect to signals of free ligands. Thus, signals of the aromatic protons were shifted upfield (Δ for the center of aromatic multiplets was 0.33–0.38 ppm for $\mathbf{NiL^{2-5}}$ and 0.16–0.24 ppm for $\mathbf{PdL^{2-5}}$), while protons of CH_3 and CH_2 groups were shifted downfield (Δ for $\mathbf{NiL^{2-5}}$ and $\mathbf{PdL^{2-5}}$ is 0.34–0.49 ppm and 0.49–0.55 ppm, respectively). The signals of the olefinic protons were slightly shifted downfield (Δ = 0.06–0.17 ppm). In the ^{19}F NMR spectra, the signals of the CF_3 groups of complexes **NiL** and **PdL** were shifted downfield to 3.38–4.51 ppm and 4.27–5.78 ppm, respectively. The values of these shifts are similar to the values of $\mathbf{NiL^1}$ and $\mathbf{PdL^1}$ [13].

The number of absorption bands of the main structural units and their position in the IR spectra were similar for all obtained complexes. Recently we have shown that complexes $\mathbf{NiL^1}$, $\mathbf{CuL^1}$ and $\mathbf{PdL^1}$ have the saddle-shape configuration, which is much different from the *bis*(β-aminoenone) $\mathbf{H_2L^1}$ configuration [13]. Therefore, the same configuration can be attributed for all complexes obtained in this work.

2.3. Gas-chromatography–mass-spectrometry of *bis*(β-aminoenones) and their complexes

It was found that elongation of terminal substituent R and R^f slightly increases the retention time of ligand $\mathbf{H_2L^{1-5}}$ (Table 2, column 5). This is in agreement with general rules of chromatographic retention. The detection limit was 0.02 mg/mL in $CHCl_3$ solution.

Table 2
Relative retention times of *bis*(β-aminoenones) $\mathbf{H_2L^{1-5}}$ and their Cu(II), Ni(II) and Pd(II) complexes.

Entry	Ligand	R/R′	R^f/R^f	Relative retention time[a]			
				$\mathbf{H_2L}$	**NiL**	**CuL**	**PdL**
1	$\mathbf{H_2L^1}$	Me/Me	CF_3/CF_3	0.787	1.172	1.177	1.480
2	$\mathbf{H_2L^2}$	Et/Et	CF_3/CF_3	0.817	1.187	1.183	1.480
3	$\mathbf{H_2L^3}$	Me/Me	C_3F_7/C_3F_7	0.802	1.093	1.091	1.293
4	$\mathbf{H_2L^4}$	Me/Et	CF_3/CF_3	0.801	1.182	1.179	1.482
5	$\mathbf{H_2L^5}$	Me/Me	CF_3/C_3F_7	0.797	1.125	1.122	1.359

[a] Relative to dioctyl phtalate.

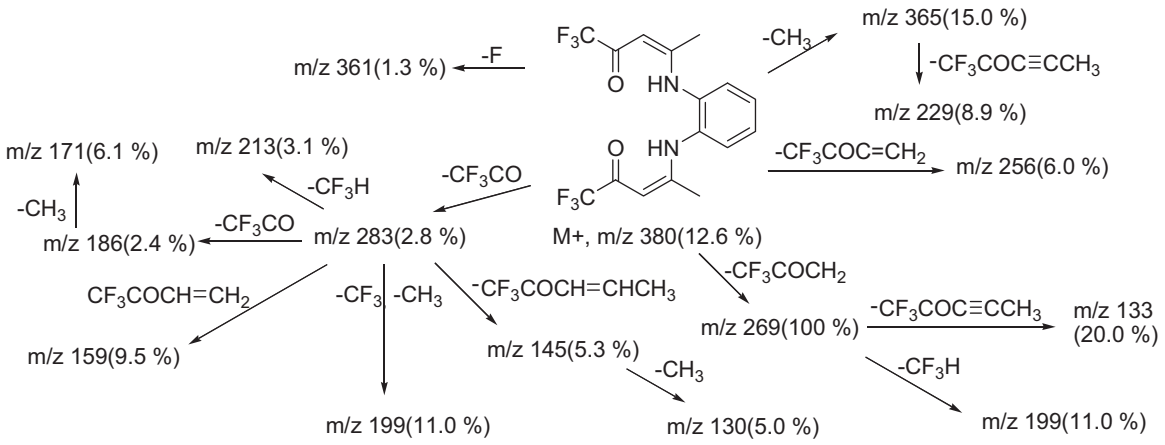
Retention times of **NiL** and **CuL** with equal **L** were similar whereas the times of the corresponding **PdL** complexes were longer (Table 2). In contrast to the free ligands, elongation of R^f in the complexes increases their volatility (Table 2, entries 1, 3 and 5). This is in accordance with the known influence of fluorinated substituents on the complexes volatility. Non-fluorinated R did not affect the retention times of **PdL** but slightly enhanced those for **NiL** and **CuL** (Table 2, entries 1, 2 and 4). All complexes had regular-shaped symmetrical peaks, which were close to the normal distribution. Detection limits of **NiL**, **CuL** and **PdL** in the $CHCl_3$ solution were 0.005 mg/ml, 0.02 mg/ml and 0.05 mg/ml correspondingly. Observed differences of the GC behaviour for these complexes are likely to be due to the different d-shells of the corresponding metals (d^3 for Ni and Cu, and d^4 for Pd).

Low intensive molecular ions for all ligands $\mathbf{H_2L^{1-5}}$ appeared in the mass-spectra. The fragmentation paths of the molecular ions M^+ are similar. In all cases one alkyl group R was eliminated. The peak intensity of these fragments was higher in case of R=C_2H_5. Elimination of CF_3 and C_3F_7, and CF_3CO, and C_3F_7CO groups also afforded low intensity peaks. Peaks with 100% intensity corresponded to fragment ions $[M-R^fCOCH_2]^+$. We did not observe cleavage of the Ar–N bond, whereas in the case of derivatives with an *N*,*N*′-alkylene bridge elimination of $[R^fCOCH_2C(R)NH]$ fragments usually occurs [7d,17]. Additionally, a number of peaks with identical *m*/*z* values 213, 199, 186, 171, 159, 145, 133 were found in the mass-spectra of *bis*(β-aminoenones) $\mathbf{H_2L^{1-5}}$. This is due to the similar fragmentation of ions after elimination of the groups varied depending on *bis*(β-aminoenones).

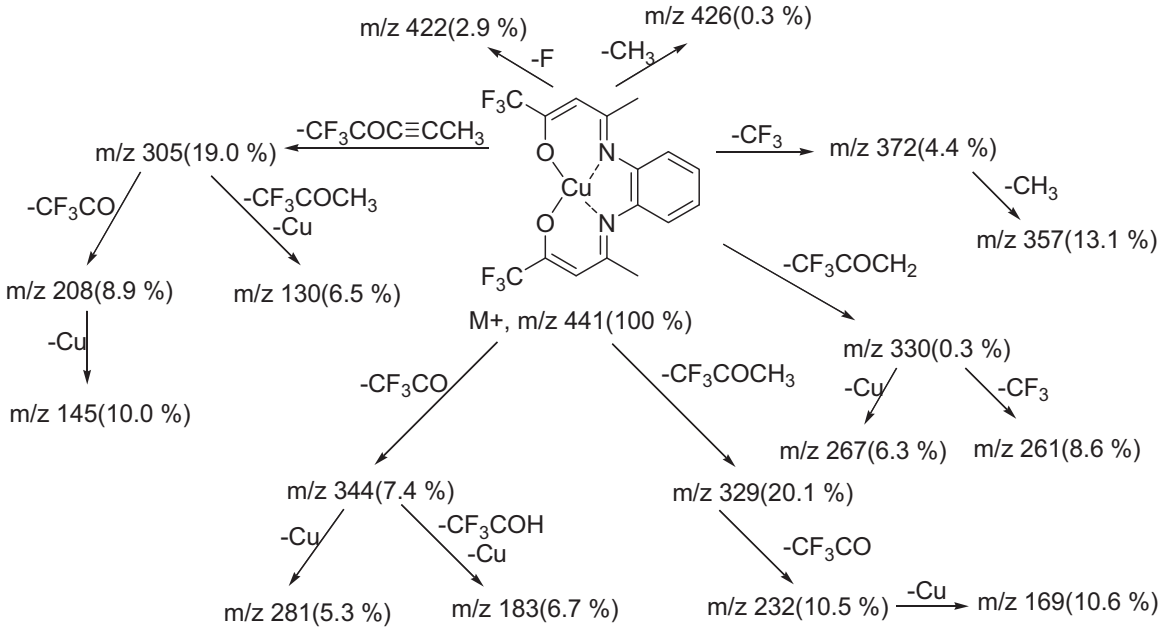
Base peaks of complexes **NiL**, **CuL** and **PdL** in the mass-spectra were molecular ions M^+ with an isotopic pattern identical to isotope distribution of the metal. Mass-spectra showed a wide variety of peaks with highest intensities for **PdL** and lowest intensities for **NiL**. Generally, the elimination of R^fCO-groups is typical for all investigated complexes in the course of their fragmentation. This group can be eliminated either itself or with a metal cation and other fluorinated group, e.g., R^fCOR, R^fCOCCR. In addition, low intensity peak clusters of metal cations (up to 10%) were observed in all spectra. Previously, the presence of cation metal peaks was shown for tetradentate chelate complexes [18]. All that distinguishes the fragmentation of *bis*(β-aminoenones) $\mathbf{H_2L^{1-5}}$ and their Cu(II), Ni(II) and Pd(II) complexes from the fragmentation of their *N*,*N*′-alkylene analogues [7d,15a,17].

Schemes 5 and 6 show a plausible fragmentation paths of *bis*(β-aminoenones) $\mathbf{H_2L^1}$ (as an example of investigated ligands) and $\mathbf{CuL^1}$ (as an example of investigated complexes) respectively. The formed neutral molecules can give various products via transfer proton arrangement.

It is noteworthy that bonds cleavage in ligands $\mathbf{H_2L}$ and their complexes under electron impact ionization occurs mainly by analogous paths. However, while the ligands have main ion peaks



Scheme 5. Plausible fragmentation paths of *bis*(β-aminoenones) $\mathbf{H_2L^1}$.



Scheme 6. Probable fragmentation paths of $\mathbf{CuL^1}$.

$[M-R^fCOCH_2]^+$ in the mass-spectra, peaks of similar fragments are intensive only in the case of copper complexes. The low intensity cluster $[M-R^fCOCH_2]^+$ was fixed for $\mathbf{PdL^1}$ only among other palladium complexes. In the case of complexes **NiL**, analogous fragments were not observed. Nevertheless, there were peaks that can be attributed to fragment ions of a cooperative elimination of R^fCOCH_2 (or R^fCOCH_3) together with other characteristic groups. Therefore, the fragmentation paths of $\mathbf{H_2L}$, **CuL**, and **PdL** hold for nickel complexes.

3. Conclusions

In conclusion, we developed efficient methods for the synthesis of fluorinated tridentate β-aminoenones and tetradentate *bis*(β-aminoenones) via a direct borate assisted reaction of fluorinated 1,3-diketones with *o*-phenylenediamine. Cu(II), Ni(II) and Pd(II) complexes based on tetradentate bis(β-aminoenones) were synthesized. Gas chromatography–mass-spectrometry of bis(β-aminoenones) and their complexes showed a reasonable thermal stability of the investigated compounds and the obvious differences of fragmentation paths under electron impact ionization (at 70 eV) as compared to *N*,*N*′-alkylene analogues.

4. Experimental

4.1. General remarks

Melting points were measured on a *Stuart SMP3* melting points apparatus and are not corrected. The NMR ^1H and ^{19}F spectra were recorded on a *Bruker DRX-400* spectrometer at 400 and 367 MHz respectively in $CDCl_3$ solution. Chemical shifts (δ) are given in ppm relative to Me_4Si (^1H) and C_6F_6 (^{19}F). IR spectra were recorded on a *Spectrum One* FTIR spectrometer with using a diffuse reflectance accessory. GC–MS investigations were carried out on an *Agilent GS 7890A MSD 5975C inert XL* (USA) gas-chromatography–mass spectrometer with a quadrupole mass spectrometric detector at an electron energy of 70 eV, using scanning in the total ion current mode in the *m*/*z* range 30–1000 amu. A fused silica capillary column HP-5MS (30 m; 0.25 mm; 0.25 μm) was used. The initial temperature of column was 100 °C (storage for 3 min); rate 10 °C/min to 300 °C (storage for 30 min). The temperature of the injector was 250 °C. The carrier gas was helium. The split ratio was 1:50, and the gas flow rate through the column was 1.0 mL/min. Course of reactions was monitored by TLC (Silufol UV-254, eluent $CHCl_3$). Methoxyenone **3** was obtained by known method [19].

4.2. General procedure for synthesis of tridentate β-aminoenones 2a–c

o-Phenylenediamine (0.55 g, 5.1 mmol), $B(OEt)_3$ (0.75 g, 5.14 mmol) and 1,3-diketone **1a–c** (5.0 mmol) in CH_3CN (20 mL) were stirred 10–15 min, diluted with water (50 mL) and stirred until solidification of a precipitated oil. The solid was collected, washed with water, dried in the air, dissolved in $CHCl_3$ (3 mL), and passed through silica gel bed (2 cm). Silica gel was washed with $CHCl_3$ (3 × 5 mL). Combined chloroform solutions were evaporated. The residue was recrystallized from hexane–CH_2Cl_2 (3:1) solution. Yields of **2a–c** are collected in the Table 1.

(Z)-4-(2-aminoanilino)-1,1,1-trifluoro-3-penten-2-one (compound **2a**). Pale-yellow crystals: mp 96-97 °C [96-97 °C, ref. [12c].

(*Z*)-4-(2-aminoanilino)-1,1,1-trifluoro-3-hexen-2-one (compound **2b**). Pale-yellow crystals: mp 98–99 °C. IR (DRA): ν 3455, 3358 (NH_2), 3225 (NH...O=), 1629, 1619, 1596, 1500 (O=C–C=C, Ar). ^{1}H NMR spectral data ($CDCl_3$, δ/ppm, J/Hz) δ 1.10 (t, 3H, *J* = 7.5, CH_3), 2.30 (2H, q, *J* = 7.5, CH_2), 3.80 (2H, br.s, NH_2), 5.60 (1H, s, =CH), 6.75–6.81 (2H, m, Ar), 6.99–7.01 (m, 1H, Ar), 7.15–7.19 (m, 1H, Ar), 12.05 (1H, br.s, NH). ^{19}F NMR (376 MHz, $CDCl_3$): δ 84.88 (s). Anal. Calcd for $C_{12}H_{13}N_2F_3O$: C, 55.81; H, 5.07; N, 10.85; F, 22.07. Found: C, 55.58; H, 5.06; N, 10.74; F, 22.20.

(*Z*)-2-(2-aminoanilino)-5,5,6,6,7,7,7-heptafluoro-2-hepten-4-one (compound **2c**). Pale-yellow crystals: mp 80–81 °C. IR (DRA): ν 3469, 3374 (NH_2), 1612, 1585, 1567, 1518, 1500, 1429 (O=C–C=C, Ar). ^{1}H NMR spectral data ($CDCl_3$, δ/ppm, J/Hz) δ 2.02 (s, 3H, CH_3), 3.80 (2H, br. s, NH_2), 5.62 (1H, s, =CH), 6.76–6.82 (2H, m, Ar), 7.00–7.02 (1H, m, Ar), 7.14–7.19 (1H, m, Ar), 12.12 (1H, br. s, NH). ^{19}F NMR (376 MHz, $CDCl_3$): δ 34.93 (s, 2F, $CF_2\mathbf{CF_2}CF_3$), 40.83 (q, 2F, *J* = 8.8 Hz, $\mathbf{CF_2}CF_2CF_3$), 81.16 (t, 3F, *J* = 8.8 Hz, $CF_2CF_2\mathbf{CF_3}$). Anal. Calcd for $C_{13}H_{11}N_2F_7O$: C, 45.36; H, 3.22; N, 8.14; F, 38.63. Found: C, 45.43; H, 2.81; N, 8.22; F, 38.72.

4.3. General procedure for synthesis of symmetrical bis(β-aminoenones) $H_2L^{1–3}$

To a solution of *o*-phenylenediamine (0.162 g, 1.5 mmol) in $B(OBu)_3$ (3.5 g, 15.2 mmol) 1,3-diketone **1a–c** (3.2 mmol) was added and stirred 1–3 days until disappearance of an aminoenone **2** (TLC). Then $CHCl_3$ (10 mL) and water (20 mL) were added and stirred 5 min. Water layer was separated and extracted with $CHCl_3$ (3 × 5 mL). The combined organic solution were evaporated and stirred with suspension of copper acetate (1.5 g) in CH_3CN (20 mL) for 3 h. Then water (50 mL) was added, a precipitation was filtered off, washed with water, dried in the air, and chromatographed (eluent $CHCl_3$). The obtained solution was concentrated to *ca*. 10 mL, and oxalic acid (1.0 g) was added. The suspension was stirred until the green colour disappeared and then passed through a silica gel bed (2 cm). Silica gel was washed with $CHCl_3$ (3 × 5 mL) and combined chloroform solutions were evaporated to afford analytically pure product. Yields of $\mathbf{H_2L^{1–3}}$ are shown in the Table 1.

(*Z*)-1,1,1-Trifluoro-4-(2-{[(*Z*)-4,4,4-trifluoro-1-methyl-3-oxo-1-butenyl]amino}anilino)-3-penten-2-one (compound $\mathbf{H_2L^1}$). Yellow crystals: mp 123–124 °C [122–124 °C, ref. [12c]. EIMS (probe) 70 eV, *m/z* (rel. int.): 380 $[M]^+$ (13), 361 $[M–F]^+$ (1), 365 $[M–CH_3]^+$ (16), 341 $[M–F–HF]^+$ (1), 311 $[M–CF_3]^+$ (4), 283 $[M–CF_3CO]^+$ (3), 269 $[M–CF_3COCH_2]^+$ (100), 256 $[M–CF_3COCHCH_2]^+$ (6), 229 $[C_{10}H_8N_2OF_3]^+$ (9).

(*Z*)-4-(2-{[(*Z*)-1-ethyl-4,4,4-trifluoro-3-oxo-1-butenyl]amino}anilino)-1,1,1-trifluoro-3-hexen-2-one (compound $\mathbf{H_2L^2}$). Yellow crystals: mp 73–74 °C. IR (DRA): ν 3145 (NH...O=), 1600, 1585, 1513 (O=C–C=C, ...Ar), 1489, 1452 (δ CH). ^{1}H NMR spectral data (400 MHz, $CDCl_3$): δ 1.13 (6H, t, *J* = 7.5 Hz, $2CH_3$), 2.32 (4H, q, *J* = 7.5 Hz, $2CH_2$), 5.62 (2H, s, 2 = CH), 7.30–7.33 (2H, m, Ar), 7.41–7.44 (2H, m, Ar), 12.31 (2H, br. s, 2NH). ^{19}F NMR (376 MHz, $CDCl_3$): δ 84.88 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.98 (s, $CH_2\mathbf{CH_3}$), 25.67 (s, $\mathbf{CH_2}CH_3$), 89.80 (q, ^3J = 0.8 Hz, =CH–), 117.25 (q, ^1J = 288.4 Hz, CF_3), 127.80 (s, CH, Ar), 128.72 (s, CH, Ar), 133.22 (s, Ar), 173.58 (s, =C(NHAr)–), 178.03 (q, ^2J = 33.7 Hz, $CF_3\mathbf{C}$=**O**). EIMS (probe) 70 eV, *m/z* (rel. int.): 408 $[M]^+$ (6), 389 $[M–F]^+$ (2), 379 $[M–C_2H_5]^+$ (100), 369 $[M–F–HF]^+$ (1), 339 $[M–CF_3]^+$ (4), 311 $[M–CF_3CO]^+$ (2), 297 $[M–CF_3COCH_2]^+$ (92), 229 $[C_{10}H_8N_2OF_3]^+$ (25). Anal. Calcd for $C_{18}H_{18}N_2F_6O_2$: C, 52.99; H, 4.39; N, 6.87; F, 27.94. Found C, 53.08; H, 4.69; N, 6.79; F, 28.05.

(*Z*)-5,5,6,6,7,7,7-Heptafluoro-2-(2-{[(*Z*)-4,4,5,5,6,6,6-heptafluoro-1-methyl-3-oxo-1-hexenyl]amino}anilino)-2-hepten-4-one (compound $\mathbf{H_2L^3}$). Yellow crystals: mp 85–86 °C. IR (DRA): ν 3123 (NH...O=), 1618, 1604, 1582, 1517 (O=C–C=C, Ar), 1481, 1434 (δ CH). ^{1}H NMR spectral data (400 MHz, $CDCl_3$): δ 2.05 (6H, s, $2CH_3$), 5.64 (2H, s, 2 = CH), 7.31–7.33 (2H, m, Ar), 7.41–7.44 (2H, m, Ar), 12.47 (2H, br. s, 2NH). ^{19}F NMR (376 MHz, $CDCl_3$): δ 34.57 (s, 4F, $2CF_2\mathbf{CF_2}CF_3$), 40.29 (q, 4F, *J* = 8.8 Hz, $2\mathbf{CF_2}CF_2CF_3$), 80.96 (t, 6F, *J* = 8.8 Hz, $2CF_2CF_2\mathbf{CF_3}$). ^{13}C NMR (100 MHz, $CDCl_3$): 19.89 (s, CH_3), 93.34 (t, ^3J = 1.0 Hz, =CH–), 108.71 (tq, ^1J = 265.9, ^2J = 38.3 Hz, $CF_3\mathbf{CF_2}CF_2$), 109.37 (tt, ^1J = 264.9, ^2J = 31.0 Hz, $CF_3CF_2\mathbf{CF_2}$), 117.73 (qt, ^1J = 287.8, ^2J = 34.1 Hz, $\mathbf{CF_3}CF_2CF_2$), 127.59 (s, CH, Ar), 128.74 (s, CH, Ar), 133.12 (s, Ar), 167.64 (s, =C(NHAr)–), 178.73 (t, ^2J = 24.4 Hz, $CF_3\mathbf{C}$=**O**). EIMS (probe) 70 eV, *m/z* (rel. int.): 580 $[M]^+$ (4), 561 $[M–F]^+$ (1), 565 $[M–CH_3]^+$ (12), 541 $[M–F–HF]^+$ (1), 383 $[M–C_3F_7CO]^+$ (4), 369 $[M–C_3F_7COCH_2]^+$ (100), 356 $[M–C_3F_7COCH{=}CH_2]^+$ (6), 329 $[C_{12}H_8N_2OF_7]^+$ (7). Anal. Calcd for $C_{20}H_{14}N_2F_{14}O_2$: C, 41.42; H, 2.43; N, 4.83; F, 45.86. Found C, 41.38; H, 2.44; N, 4.90; F, 45.91.

4.4. General procedure for synthesis of unsymmetrical bis(β-aminoenones) $H_2L^{4,5}$

A solution of β-methoxyenone **3** (0.20 g, 1.2 mmol) and corresponding β-aminoenone **2b,c** (1.0 mmol) in pyridine (2 mL) was stirred for 2 days (TLC control), dried in vacuum and purified via a copper complex as described above. Yields of $\mathbf{H_2L^{4,5}}$ are given in the Table 1.

(*Z*)-1,1,1-Trifluoro-4-(2-{[(*Z*)-4,4,4-trifluoro-1-methyl-3-oxo-1-butenyl]amino}anilino)-3-hexen-2-one (compound $\mathbf{H_2L^4}$). Light-yellow crystals: mp 61–62 °C. IR (DRA): ν 3153 (N–H···O=), 1606, 1586, 1562, 1515 (O=C–C=C, Ar), 1485, 1436 (δ CH). ^{1}H NMR spectral data (400 MHz, $CDCl_3$): δ 1.13 (3H, t, *J* = 7.5 Hz, CH_3), 2.07 (3H, s, CH_3), 2.32 (2H, q, *J* = 7.5 Hz, CH_2), 5.60 and 5.62 (every 1H, two s, 2 = CH), 7.26–7.32 (2H, m, Ar), 7.41–7.43 (2H, m, Ar), 12.31 and 12.33 (every 1H, two br. s, 2NH). ^{19}F NMR (376 MHz, $CDCl_3$): δ 84.79 (s, 3F, CF_3), 84.88 (s, 3F, CF_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.96 (s, $CH_2\mathbf{CH_3}$), 19.95 (s, CH_3), 25.64 (s, $\mathbf{CH_2}CH_3$), 89.84 (q, ^3J = 1.3 Hz, =CH–), 91.95 (q, ^3J = 1.3 Hz, =CH–), 117.21 (q, ^1J = 288.2 Hz, CF_3), 117.28 (q, ^1J = 288.2 Hz, CF_3), 127.41, 127.9, 128.56, 128.74 (four singlets, CH, Ar), 132.93, 133.46 (two singlets, Ar), 167.80 (s, =C(NHAr)–), 173.65 (s, =C(NHAr)–), 177.70 (q, ^2J = 33.7 Hz, $CF_3\mathbf{C}$=**O**), 178.11 (q, ^2J = 33.7 Hz, $CF_3\mathbf{C}$=**O**). EIMS (probe) 70 eV, *m/z* (rel. int.): 394 $[M]^+$ (10), 375 $[M–F]^+$ (2), 379 $[M–CH_3]^+$ (8), 365 $[M–C_2H_5]^+$ (61), 355 $[M–F–HF]^+$ (1), 325 $[M–CF_3]^+$ (4), 297 $[M–CF_3CO]^+$ (2), 283 $[M–CF_3COCH_2]^+$ (100), 270 $[M–CF_3COCH{=}CH_2]^+$ (2), 256 $[C_{12}H_{11}N_2OF_3]^+$ (2), 229 $[C_{10}H_8N_2OF_3]^+$ (16). Anal. Calcd for $C_{17}H_{16}N_2F_6O_2$: C, 51.82; H, 4.09; N, 7.08; F, 28.93. Found C, 51.79; H, 4.04; N, 7.11; F, 28.99.

(*Z*)-5,5,6,6,7,7,7-Heptafluoro-2-(2-{[(*Z*)-4,4,4-trifluoro-1-methyl-3-oxo-1-butenyl]amino}anilino)-2-hepten-4-one (compound $\mathbf{H_2L^5}$). Yellow viscous oil. IR (DRA): ν 3149 (NH...O=), 1614, 1599, 1583, 1519 (O=C–C=C, Ar), 1484, 1436 (δ CH). ^{1}H NMR spectral data (400 MHz, $CDCl_3$): δ 2.05 and 2.07 (every 3H, two s, $2CH_3$), 5.59 and 5.66 (every 1H, two s, 2 = CH), 7.30–7.33 (2H, m, Ar), 7.41–7.43 (2H, m, Ar), 12.35 and 12.47 (every 1H, two br. s, 2NH). ^{19}F NMR (376 MHz, $CDCl_3$): δ 34.61 (s, 2F, $CF_2\mathbf{CF_2}CF_3$), 40.35

(q, 2F, J = 8.8 Hz, **CF_2**CF_2CF_3), 81.02 (t, 3F, J = 8.8 Hz, CF_2CF_2**CF_3**), 84.65 (s, 3F, CF_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.93 (s, CH_3), 19.99 (s, CH_3), 91.90 (q, ^3J = 0.8 Hz, =CH–), 93.47 (t, ^3J = 1.0 Hz, =CH–), 108.75 (tq, ^1J = 265.9, ^2J = 38.3 Hz, CF_3**CF_2**CF_2), 109.44 (tt, ^1J = 264.9, ^2J = 30.7 Hz, CF_3CF_2**CF_2**), 117.77 (qt, ^1J = 287.8, ^2J = 33.7 Hz, **CF_3**CF_2CF_2), 117.27 (q, ^1J = 288.2 Hz, CF_3), 127.54, 127.58, 128.67, 128.77 (four singlets, CH, Ar), 133.07, 133.16 (two singlets, Ar), 167.80 (s, =C(NHAr)–), 167.95 (s, =C(NHAr)–), 177.78 (q, ^2J = 33.7 Hz, CF_3**C=O**), 178.64 (t, ^2J = 24.4 Hz, C_3F_7**C=O**). EIMS (probe) 70 eV, *m/z* (rel. int.): 480 $[M]^+$ (19), 461 $[M-F]^+$ (3), 465 $[M-CH_3]^+$ (30), 441 $[M-F-HF]^+$ (2), 411 $[M-CF_3]^+$ (5), 383 $[M-CF_3CO]^+$ (3), 369 $[M-CF_3COCH_2]^+$ (100), 356 $[M-CF_3COCH{=}CH_2]^+$ (6), 283 $[M-C_3F_7CO]^+$ (4), 269 $[M-C_3F_7COCH_2]^+$ (90), 256 $[M-C_3F_7COCH{=}CH_2]^+$ (6), 229 $[C_{12}H_8N_2OF_7]^+$ (7). Anal. Calcd for $C_{18}H_{12}N_2F_{10}O_2$: C, 45.04; H, 2.94; N, 5.84; F, 39.58. Found C, 45.07; H, 2.69; N, 5.85; F, 39.54.

4.5. General procedure for synthesis of Ni(II) and Cu(II) complexes with H_2L^{1-5}

A solution of *bis*(β-aminoenones) **H_2L^{1-5}** (0.5 mmol) in methanol (5 mL) were added to a solution of $Ni(CH_3COO)_2{\cdot}4H_2O$ (0.124 g, 0.5 mmol) or $Cu(CH_3COO)_2{\cdot}H_2O$ (0.100 g, 0.5 mmol) in methanol (*ca.* 10 mL). The reaction mixture was stirred for 4 h, diluted with water (20 mL). The resulting precipitate was collected, washed with water, dried in the air, and crystallized from an appropriate solvent.

CuL^1. Yield 93%. Deep-green crystals: mp 244–245 °C ($CHCl_3$) [244–246 °C, ref. [13]]. IR (DRA): ν 1608, 1597, 1581, 1514, 1489 (O=C–C=C–N, Ar). EIMS (probe) 70 eV, *m/z* (rel. int.): 441 $[M]^+$ (100), 426 $[M-CH_3]^+$ (0.3), 422 $[M-F]^+$ (3), 402 $[M-F-HF]^+$ (0.1), 372 $[M-CF_3]^+$ (4), 357 $[M-CF_3-CH_3]^+$ (13), 344 $[M-CF_3CO-CH_3]^+$ (8), 329 $[M-CF_3CO-CH_3]^+$ (20), 305 $[M-CF_3COC{\equiv}CCH_3]^+$ (19), 267 $[M-CF_3COCH_2-Cu]^+$ (6), 232 $[M-CF_3CO-CF_3COCH_3]^+$ (11), 232 $[C_{11}H_9N_2Cu]^+$ (11), 208 $[C_9H_9N_2OCu]^+$ (9), 195 $[C_8H_8N_2Cu]^+$ (8), 63 $[Cu]^+$ (10).

CuL^2. Yield 91%. Deep-green crystals: mp 230–231 °C ($CHCl_3$). IR (DRA): ν 1610, 1600, 1587, 1515, 1490 (O=C–C=C–N, Ar). EIMS (probe) 70 eV, *m/z* (rel. int.): 469 $[M]^+$ (100), 450 $[M-F]^+$ (3), 440 $[M-C_2H_5]^+$ (0.6), 400 $[M-CF_3]^+$ (3), 371 $[M-CF_3CO]^+$ (11), 357 $[M-CF_3CO-CH_3]^+$ (8), 343 $[M-CF_3CO-C_2H_5]^+$ (15), 319 $[M-CF_3COC{\equiv}CC_2H_5]^+$ (22), 295 $[M-CF_3COCH_2-Cu]^+$ (7), 260 $[M-CF_3CO-CF_3COCH_3]^+$ (4), 233 $[C_{11}H_9N_2Cu]^+$ (3), 208 $[C_9H_9N_2OCu]^+$ (2), 195 $[C_8H_8N_2Cu]^+$ (2), 63 $[Cu]^+$ (5). Anal. Calcd for $C_{18}H_{16}N_2F_6O_2Cu$: C, 46.1; H, 3.4; N, 5.8; F, 24.3. Found: C, 46.1; H, 3.4; N, 5.8; F, 24.2.

CuL^3. Yield 84%. Deep-green crystals: mp 174–175 °C (hexane). IR (DRA): ν 1609, 1598, 1581, 1504, 1488, 1432 (O=C–C=C–N, Ar). EIMS (probe) 70 eV, *m/z* (rel. int.): 641 $[M]^+$ (100), 626 $[M-CH_3]^+$ (0.1), 622 $[M-F]^+$ (6), 602 $[M-F-HF]^+$ (1), 472 $[M-C_3F_7]^+$ (9), 457 $[M-C_3F_7-CH_3]$ (16), 444 $[M-C_3F_7CO]^+$ (8), 405 $[M-C_3F_7COC{\equiv}CCH_3]^+$ (4), 233 $[C_{11}H_9N_2Cu]^+$ (11), 208 $[C_9H_9N_2OCu]^+$ (6), 195 $[C_8H_8N_2Cu]^+$ (10), 63 $[Cu]^+$ (10). Anal. Calcd for $C_{20}H_{12}N_2F_{14}O_2Cu$: C, 37.5; H, 1.9; N, 4.7; F, 41.5. Found: C, 37.4; H, 1.8; N, 4.4; F, 41.4.

CuL^4. Yield 95%. Deep-green crystals: mp 243–244 °C (CH_2Cl_2–hexane, 1:4). IR (DRA): ν 1613, 1602, 1580, 1513, 1490, 1427 (O=C–C=C–N, Ar). EIMS (probe) 70 eV, *m/z* (rel. int.): 455 $[M]^+$ (100), 453 $[M-CH_3]^+$ (0.3), 436 $[M-F]^+$ (4), 426 $[M-C_2H_5]^+$ (0.6), 416 $[M-F-HF]^+$ (0.1), 386 $[M-CF_3]^+$ (4), 371 $[M-CF_3, -CH_3]^+$ (5), 358 $[M-CF_3CO]^+$ (10), 343 $[M-CF_3CO-CH_3]^+$ (18), 329 $[M-CF_3CO-C_2H_5]^+$ (7), 319 $[M-CF_3COC{\equiv}CCH_3]^+$ (13), 305 $[M-CF_3COC{\equiv}CC_2H_5]^+$ (9), 281 $[M-CF_3COCH_2-Cu]^+$ (7), 246 $[M-CF_3CO-CF_3COCH_3]^+$ (7), 233 $[C_{11}H_9N_2Cu]^+$ (4), 207 $[C_9H_9N_2OCu]^+$ (7), 195 $[C_8H_8N_2Cu]^+$ (5), 63 $[Cu]^+$ (10). Anal. Calcd for $C_{17}H_{14}N_2F_6O_2Cu$: C, 44.9; H, 3.1; N, 6.2; F, 25.1. Found: C, 44.8; H, 3.1; N, 6.1; F, 25.0.

CuL^5. Yield 87%. Deep-green crystals: mp 170–171 °C (hexane). IR (DRA): ν 1610, 1598, 1579, 1500, 1490, 1429 (O=C–C=C–N, Ar). EIMS (probe) 70 eV, *m/z* (rel. int.): 541 $[M]^+$ (100), 526 $[M-CH_3]^+$ (0.2), 522 $[M-F]^+$ (5), 502 $[M-F-HF]^+$ (0.8), 472 $[M-CF_3]^+$ (2), 457 $[M-CF_3-CH_3]^+$ (3), 444 $[M-CF_3CO]^+$ (3), 429 $[M-CF_3CO-CH_3]^+$ (4), 405 $[M-CF_3COC{\equiv}CCH_3]^+$ (6), 367 $[M-C_3F_7]^+$ (7), 372 $[M-C_3F_7CO-Cu]^+$ (5), 367 $[M-CF_3COCH_2-Cu]^+$ (2), 357 $[M-C_3F_7-CH_3]^+$ (19), 344 $[M-C_3F_7CO]^+$ (6), 305 $[M-C_3F_7COC{\equiv}CCH_3]^+$ (11), 233 $[C_{11}H_9N_2Cu]^+$ (7), 208 $[C_9H_9N_2OCu]^+$ (6), 195 $[C_8H_8N_2Cu]^+$ (8), 63 $[Cu]^+$ (8). Anal. Calcd for $C_{18}H_{12}N_2F_{10}O_2Cu$: C, 40.1; H, 2.2; N, 5.2; F, 35.1. Found: C, 40.0; H, 2.4; N, 5.2; F, 35.2.

NiL^1. Yield 90%. IR (DRA): ν 1607, 1597, 1577, 1511, 1489 (O=C–C=C–N, Ar). Dark-red crystals: mp 284–285 °C (CH_3CN) [284–285 °C, Ref. [13]]. EIMS (probe) 70 eV, *m/z* (rel. int.): 436 $[M]^+$ (100), 421 $[M-CH_3]^+$ (2), 417 $[M-F]^+$ (4), 367 $[M-CF_3]^+$ (6), 351 $[M-CF_3H-CH_3]^+$ (3), 339 $[M-CF_3CO]^+$ (15), 300 $[M-CF_3COC{\equiv}CCH_3]^+$ (6), 269 $[C_{13}H_{11}N_2ONi]^+$ (6), 58 $[Ni]^+$ (4).

NiL^2. Yield 94%. Dark-red crystals: mp 212–213 °C (CH_3CN). IR (DRA): ν 1600, 1513, 1489, 1452 (O=C–C=C–N, Ar). ^{1}H NMR spectral data (400 MHz, $CDCl_3$): δ 1.30 (6H, t, J = 7.5 Hz, $2CH_3$), 2.73 (4H, q, J = 7.5 Hz, $2CH_2$), 5.78 (2H, s, 2 = CH), 6.92–6.95 (2H, m, Ar), 7.04–7.06 (2H, m, Ar). ^{19}F (376 MHz, $CDCl_3$): δ 89.36 (s). EIMS (probe) 70 eV, *m/z* (rel. int.): 464 $[M]^+$ (100), 445 $[M-F]^+$ (4), 435 $[M-C_2H_5]^+$ (4), 395 $[M-CF_3]^+$ (4), 367 $[M-CF_3CO]^+$ (11), 58 $[Ni]^+$ (3). Anal. Calcd for $C_{18}H_{16}N_2F_6O_2Ni$: C, 46.6; H, 3.5; N, 6.0; F, 24.6. Found: C, 46.6; H, 3.6; N, 6.1; F, 24.4.

NiL^3. Yield 85%. Dark-red crystals: mp 168–169 °C (hexane). IR (DRA): ν 1596, 1503, 1483, 1429 (O=C–C=C–N, Ar). ^{1}H NMR spectral data (400 MHz, $CDCl_3$): δ 2.40 (6H, s, $2CH_3$), 5.71 (2H, s, 2 = CH), 6.94–6.97 (2H, m, Ar), 7.13–7.15 (2H, m, Ar). ^{19}F (376 MHz, $CDCl_3$): δ 35.01 (s, 4F, $2CF_2$**CF_2**CF_3), 43.84 (q, 4F, J = 8.8 Hz, 2**CF_2**CF_2CF_3), 81.04 (t, 6F, J = 8.8 Hz, $2CF_2CF_2$**CF_3**). EIMS (probe) 70 eV, *m/z* (rel. int.): 636 $[M]^+$ (100), 621 $[M-CH_3]^+$ (1), 617 $[M-F]^+$ (4), 597 $[M-F-HF]^+$ (2), 467 $[M-C_3F_7]^+$ (5), 439 $[M-C_3F_7CO]^+$ (7), 58 $[Ni]^+$ (3). Anal. Calcd for $C_{20}H_{12}N_2F_{14}O_2Ni$: C, 37.8; H, 1.9; N, 4.4; F, 41.8. Found: C, 37.8; H, 1.8; N, 4.5; F, 42.0.

NiL^4. Yield 91%. Dark-red crystals: mp 239–240 °C (CH_2Cl_2–hexane, 1:1). IR (DRA): ν 1602, 1512, 1488, 1429 (O=C–C=C–N, Ar). ^{1}H NMR spectral data (400 MHz, $CDCl_3$): δ 1.30 (t, 3H, J = 7.5 Hz, CH_3), 2.56 (3H, s, CH_3), 2.74 (4H, q, J = 7.5 Hz, CH_2), 5.70 (1H, s, =CH), 5.79 (1H, s, =CH), 6.93–6.96 (2H, m, Ar), 7.12–7.14 (1H, m, Ar), 7.04–7.06 (1H, m, Ar). ^{19}F (376 MHz, $CDCl_3$): δ 89.30 (s, 3F, CF_3), 89.35 (s, 3F, CF_3). EIMS (probe) 70 eV, *m/z* (rel. int.): 450 $[M]^+$ (100), 435 $[M-CH_3]^+$ (3), 431 $[M-F]^+$ (4), 421 $[M-C_2H_5]^+$ (1), 381 $[M-CF_3]^+$ (6), 365 $[M-CF_3H-CH_3]^+$ (2), 353 $[M-CF_3CO]^+$ (14), 314 $[M-CF_3COC{\equiv}CCH_3]^+$ (2), 58 $[Ni]^+$ (4). Anal. Calcd for $C_{17}H_{14}N_2F_6O_2Ni$: C, 45.4; H, 3.1; N, 6.2; F, 25.3. Found: C, 45.3; H, 3.0; N, 6.1; F, 25.1.

NiL^5. Yield 89%. Dark-red crystals: mp 188–189 °C (hexane). IR (DRA): ν 1599, 1504, 1486, 1429 (O=C–C=C–N, Ar). ^{1}H NMR spectral data (400 MHz, $CDCl_3$): δ 2.39 (3H, s, CH_3), 2.41 (3H, s, CH_3), 5.69 (1H, s, =CH), 5.72 (1H, s, =CH), 6.94–6.96 (2H, m, Ar), 7.12–7.15 (2H, m, Ar). ^{19}F (376 MHz, $CDCl_3$): δ 35.05 (s, 2F, **CF_2**CF_2CF_3), 43.73 (q, 2F, J = 8.8 Hz, CF_2**CF_2**CF_3), 81.27 (t, 3F, J = 8.8 Hz, CF_2CF_2**CF_3**), 88.92 (s, 3F, CF_3). EIMS (probe) 70 eV, *m/z* (rel. int.): 536 $[M]^+$ (100), 521 $[M-CH_3]^+$ (1), 517 $[M-F]^+$ (4), 497 $[M-F-HF]^+$ (1), 467 $[M-CF_3]^+$ (1), 451 $[M-CF_3H-CH_3]^+$ (1), 439(2) $[M-CF_3CO]$, 400 $[M-CF_3COC{\equiv}CCH_3]^+$ (1), 367 $[M-C_3F_7]^+$ (7), 339 $[M-C_3F_7CO]^+$ (7), 268 $[C_{13}H_{11}N_2ONi]^+$ (10), 58 $[Ni]^+$ (3). Anal. Calcd for $C_{18}H_{12}N_2F_{10}O_2Ni$: C, 40.3; H 2.3; N, 5.2; F, 35.4. Found: C, 40.4; H, 2.3; N, 5.1; F, 35.5.

4.6. General procedure for synthesis of Pd(II) complexes with H_2L^{1-5}

A cold solution of *bis*(β-aminoenones) **H_2L^{1-5}** (0.22 mmol) in CH_3CN (2 mL) was added slowly to a cold solution of $Pd(CH_3COO)_2$ (0.050 g, 0.22 mmol) in CH_3CN (5 mL), kept for 3 h, and dried in the vacuum. The residue was crystallized from an appropriate solvent.

PdL[1]. Yield 78%. IR (DRA): ν 1598, 1576, 1506, 1486 (O=C–C=C–N, Ar). Yellow-orange crystals: mp 329–331 °C (CH_3CN) [330–331 °C, ref. [13]]. EIMS (probe) 70 eV, *m/z* (rel. int.): 484 $[M]^+$ (100), 469 $[M-CH_3]^+$ (5), 465 $[M-F]^+$ (4), 445 $[M-F-HF]^+$ (0.1), 415 $[M-CF_3]^+$ (4), 413 $[M-CF_3-CH_3]^+$ (2), 387 $[M-CF_3CO]^+$ (6), 281 $[M-CF_3-Pd]^+$ (37), 212 $[C_{13}H_{12}N_2O]^+$ (8), 105 $[Pd]^+$ (9).

PdL[2]. Yield 77%. Yellow-orange crystals: mp 298–299 °C (CH_3CN). IR (DRA): ν 1596, 1509, 1485, 1453 (O=C–C=C–N, Ar). ^1H NMR spectral data (400 MHz, $CDCl_3$): δ 1.40 (6H, t, *J* = 7.5 Hz, $2CH_3$), 2.87 (4H, q, *J* = 7.5 Hz, $2CH_2$), 5.72 (2H, s, 2 = CH), 7.04–7.06 (2H, m, Ar), 7.20–7.25 (2H, m, Ar). ^{19}F (376 MHz, $CDCl_3$): δ 90.65 (s). EIMS (probe) 70 eV, *m/z* (rel. int.): 512 $[M]^+$ (100), 497 $[M-CH_3]^+$ (2), 493 $[M-F]^+$ (4), 483 $[M-C_2H_5]^+$ (8), 473 $[M-F-HF]^+$ (0.1), 443 $[M-CF_3]^+$ (2), 415 $[M-CF_3CO]^+$ (7), 386 $[M-CF_3CO-C_2H_5]^+$ (5), 309 $[M-CF_3-Pd]^+$ (13), 212 $[C_{13}H_{12}N_2O]^+$ (8), 105 $[Pd]^+$ (7). Anal. Calcd for $C_{18}H_{16}N_2F_6O_2Pd$: C, 42.2; H, 3.2; N, 5.5; F, 22.3. Found: C, 42.3; H, 3.1; N, 5.3; F, 22.2.

PdL[3]. Yield 71%. Yellow-orange crystals: mp 178–179 °C (hexane). IR (DRA): ν 1597, 1499, 1483, 1431(O=C–C=C–N, Ar). ^1H NMR spectral data (400 MHz, $CDCl_3$): δ 2.55 (6H, s, $2CH_3$), 5.65 (2H, s, 2 = CH), 7.05–7.08 (2H, m, Ar), 7.32–7.35 (2H, m, Ar). ^{19}F (376 MHz, $CDCl_3$): δ 35.16 (s, 4F, $2CF_2\mathbf{CF_2}CF_3$), 45.23 (q, 4F, ^4J = 8.8, $2\mathbf{CF_2}CF_2CF_3$), 81.19 (t, 6F, *J* = 8.8 Hz, $2CF_2CF_2\mathbf{CF_3}$). EIMS (probe) 70 eV, *m/z* (rel. int.): 684 $[M]^+$ (100), 669 $[M-CH_3]^+$ (4), 665 $[M-F]^+$ (7), 645 $[M-F-HF]^+$ (0.4), 515 $[M-C_3F_7]^+$ (6), 409 $[M-C_3F_7-Pd]^+$ (39), 381 $[M-C_3F_7CO-Pd]^+$ (55), 212 $[C_{13}H_{12}N_2O]^+$ (22), 105 $[Pd]^+$ (8). Anal. Calcd for $C_{20}H_{12}N_2F_{14}O_2Pd$: C, 35.1; H, 1.8; N, 4.1; F, 38.9. Found: C, 35.2; H, 1.7; N, 4.0; F, 38.8.

PdL[4]. Yield 80%. Yellow-orange crystals: mp 289–290 °C (CH_2Cl_2–hexane, 1:1). IR (DRA): ν 1598, 1508, 1485, 1427 (O=C–C=C–N, Ar). ^1H NMR spectral data (400 MHz, $CDCl_3$): δ 1.40 (3H, t, *J* = 7.5 Hz, CH_3), 2.56 (3H, s, CH_3), 2.88 (4H, q, *J* = 7.5 Hz, $2CH_2$), 5.67 (1H, s, =CH), 5.73 (1H, s, =CH), 7.04–7.06 (2H, m, Ar), 7.33–7.35 (2H, m, Ar). ^{19}F (376 MHz, $CDCl_3$): δ 90.61 (s, 3F, CF_3), 90.66 (s, 3F, CF_3). EIMS (probe) 70 eV, *m/z* (rel. int.): 498 $[M]^+$ (100), 483 $[M-CH_3]^+$ (8), 479 $[M-F]^+$ (3), 469 $[M-C_2H_5]^+$ (2), 459 $[M-F-HF]^+$ (0.1), 429 $[M-CF_3]^+$ (3), 427 $[M-CF_3-CH_3]^+$ (2), 401 $[M-CF_3CO]^+$ (8), 373 $[M-CF_3CO-C_2H_5]^+$ (1), 295 $[M-CF_3-Pd]^+$ (23), 212 $[C_{13}H_{12}N_2O]^+$ (3), 105 $[Pd]^+$ (10). Anal. Calcd for $C_{17}H_{14}N_2F_6O_2Pd$: C, 41.0; H, 2.8; N, 5.6; F, 22.9. Found: C, 40.9; H, 2.6; N, 5.8; F, 22.6.

PdL[5]. Yield 72%. Yellow-orange crystals: mp 194–195 °C (hexane). IR (DRA): ν 1595, 1501, 1482, 1426 (O=C–C=C–N, Ar). ^1H NMR spectral data (400 MHz, $CDCl_3$): δ 2.56 (3H, s, CH_3), 2.57 (3H, s, CH_3), 5.65 (1H, s, =CH), 5.66 (1H, s, =CH), 7.05–7.09 (2H, m, Ar), 7.33–7.36 (2H, m, Ar). NMR ^{19}F (376 MHz, $CDCl_3$): δ 35.50 (s, 2F, $CF_2\mathbf{CF_2}CF_3$), 45.39 (q, 2F, *J* = 8.8 Hz, $\mathbf{CF_2}CF_2CF_3$), 81.33 (t, 3F, *J* = 8.8 Hz, $CF_2CF_2\mathbf{CF_3}$), 90.40 (s, 3F, CF_3). EIMS (probe) 70 eV, *m/z* (rel. int.): 584 $[M]^+$ (100), 569 $[M-CH_3]^+$ (5), 565 $[M-F]^+$ (6), 545 $[M-F-HF]^+$ (0.2), 515 $[M-CF_3]^+$ (2), 513 $[M-CF_3-CH_3]^+$ (0.6), 487 $[M-CF_3CO]^+$ (2), 415 $[M\text{-}CF_3COCH{=}CCH_3]^+$ (5), 381 $[M-CF_3-Pd]^+$ (12), 309 $[M-C_3F_7-Pd]^+$ (30), 281 $[M-C_3F_7CO-Pd]^+$ (39), 212 $[C_{13}H_{12}N_2O]^+$ (14), 105 $[Pd]^+$ (9). Anal. Calcd for $C_{18}H_{12}N_2F_{10}O_2Pd$: C, 37.0; H 2.1; N, 4.8; F, 32.5. Found: C, 37.0; H, 2.0; N, 4.6, F, 32.4.

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