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Modular Routes Towards New N,O-Bidentate Ligands Containing an Electronically Delocalised β-Enaminone Chelating Backbone

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Polyketones are synthesised by a transition-metal-catalysed copolymerisation of olefins and carbon monoxide. Nickel complexes with N,O-chelating ligands turned out to be promising catalysts in that field. In this work a series of new N,O ligands with an electronically delocalised β-enaminone backbone were synthesised and fully characterised. The ligand design was inspired by the ligand found in the most efficient nickel catalyst for polyketone synthesis and developed to a highly modular LEGO®-like arsenal of reactions to versatile substituted β-enaminone ligands.

Introduction

The copolymerisation of olefins and carbon monoxide is an area of growing interest[1] and *the* key reaction to polyketones, a class of new polymers with outstanding properties.[2–5] Ketonex® (Shell), Carilon® (BP) or Kadel® (Solvay) are registered trademarks for polyketones and a recent market analysis by Frost & Sullivan predicts a bright future for the polyketone market.[6] Industrially, the copolymerisation reaction is catalysed by palladium complexes[7] with high efficiencies. The major disadvantage is the high cost of the transition metal and the fact, that the catalyst can not be recovered from the polymer. So the search is underway for more efficient and cheaper alternatives. Nickel turned out to be the most promising in that field.[8–12] The most efficient nickel catalyst for the copolymerisation of ethene and carbon monoxide to date is shown in Figure 1. This diamagnetic nickel(II) complex is already structurally characterised[8] and contains a bidentate N,O-chelating ligand which coordinates to the nickel center in a square planar manner forming a six-membered chelate ring. The electron density is delocalised over this ring system. Very little is known to date about the influence of the substituents in the N,O ligand on the catalytic activity of its corresponding nickel complex. Perfluorated alkyl chains (C_3F_7, see Figure 1) lead to very high efficiencies of catalysis up to 11000 g of polyketone per gram Ni whereas alkoxy goups in the same position drops the efficiency to nearly zero.[8]

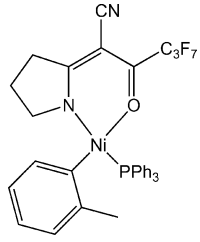

Figure 1. The most efficient nickel complex for the copolymerisation of ethene and CO to date.

We want to get a profound understanding of the factors that determine the efficiency of such nickel complexes as polyketone catalysts. Therefore we have decided to develop a systematic series of N,O-chelating ligands inspired by the ligand found in the most efficient nickel catalyst for polyketone synthesis today. This should then enable us to fine-tune the electron density on the transition metal and therewith control the catalytic behaviour.

Results and Discussion

In order to vary the substitution pattern on a more general N,O ligand we developed modular routes to N,O-bidentate ligands containing an electronically delocalised β-enaminone chelating backbone (see Figure 2). We synthesised and fully characterised a number of new ligand molecules meeting the mentioned criteria. In this work the focus is on variations on the ligand framework, their coordination chemistry will be discussed separately. The substituent R^1 is gradually varied from perfluorated alkyl chains to alkyl chains and substituted aryl residues whereas R^2 is varied from C≡N to H, NO_2 or C(O)OR. The ring size, formed by substituents R^3 and R^4, can be gradually varied from

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five to six- and seven-membered rings. But also open-chain ligands, i.e. R^3 and R^4 being individual substituents such as H, alkyl or substituted aryl, can be synthesised and some representatives are discussed. Furthermore new ligand molecules are presented comprising two β-enaminone chelating backbones and are therefore capable of coordinating two metal sites.

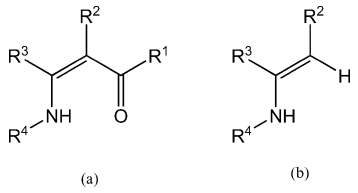
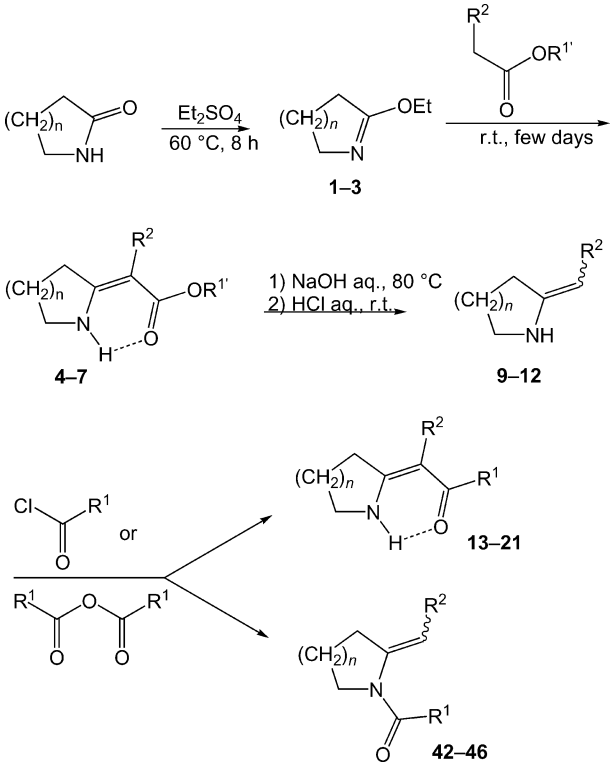


Figure 2. General formula of the ligands (a) and ligand precursors (b) synthesised.

Inspired by ligand **13** which forms the catalytically most efficient nickel complex (see Figure 1), a possible route to ligands with R^3,R^4 = –$(CH_2)_n$– (n = 3,4,5) is shown in Scheme 1 (see Table 1). The first step is the conversion of lactams into *O*-alkylated imines. This is necessary to activate the carbonyl function for the subsequent step and can be accomplished by reaction with dialkyl sulfate[13] or Meerwein salts such as triethyloxonium tetrafluoroborate.[14] The desired products were obtained in 75–90% yield (**1**–**3**). In the next step the substituents R^2 and R^1 are introduced by a Knoevenagel type condensation with appropriate esters such as cyanoacetates (R^2 = CN, **4**–**6**), nitroacetates (R^2 = NO_2, **7**), malonates[15] [R^2 = C(O)OR] or derived acetoacetates such as for example ethyl 4,4,5,5,6,6,6-heptafluoro-3-oxohexanoate, which lead to R^2 = H after decarboxylation. The above-mentioned ester is best prepared from ethyl 4,4,5,5,6,6,6-heptafluorobutyrate and ethyl 2-bromoacetate in a Reformatsky reaction.[16]



Scheme 1. Synthesis of ligands containing R^3, R^4 = –$(CH_2)_n$– with n = 3,4,5.

Table 1. Substitution pattern of ligands and ligand precursors, leading to one N,O-bidentate β-enaminonic coordination site containing R^3, R^4 = –$(CH_2)_n$– with n = 3,4,5 (see Scheme 1).

	R^1	R^2	R^3,R^4
4	OMe	CN	$CH_2CH_2CH_2$
5	OEt	CN	$CH_2CH_2CH_2CH_2$
6	OMe	CN	$CH_2CH_2CH_2CH_2CH_2$
7	OEt	NO_2	$CH_2CH_2CH_2$
8	OEt	–N=CH–Ph	$CH_2CH_2CH_2$
9	_[a]	CN	$CH_2CH_2CH_2$
10	_[a]	CN	$CH_2CH_2CH_2CH_2$
11	_[a]	CN	$CH_2CH_2CH_2CH_2CH_2$
12	_[a]	NO_2	$CH_2CH_2CH_2$
13	*n*-C_3F_7	CN	$CH_2CH_2CH_2$
14	*n*-C_3F_7	CN	$CH_2CH_2CH_2CH_2$
15	*n*-C_3F_7	CN	$CH_2CH_2CH_2CH_2CH_2$
16	*n*-C_3H_7	CN	$CH_2CH_2CH_2$
17	*p*-$O_2NC_6H_4$	CN	$CH_2CH_2CH_2$
18	*p*-ClC_6H_4	CN	$CH_2CH_2CH_2$
19	*p*-$MeOC_6H_4$	CN	$CH_2CH_2CH_2$
20	Naph	CN	$CH_2CH_2CH_2$
21	Mes	CN	$CH_2CH_2CH_2$

[a] Ligand precursor (see Figure 2b).

All compounds prepared by this method comprise at least one oxygen bridged *O*R^1 group owing to the ester used. Compound **7** was already known in the literature,[17] but we improved the synthetic protocol to simplify the work-up and obtained twice the yield reported. In the case of **7** two competing interactions occur: N–H–O hydrogen bonding is possible to the carbonyl group as well as to one nitro oxygen (see Figure 3). Thus, both *E*/*Z* isomers are formed and are observed in the proton NMR spectrum. In contrast, compounds **4**–**6** are formed only as their *Z* isomers since N–H–O hydrogen bonding is only possible to the carbonyl oxygen.

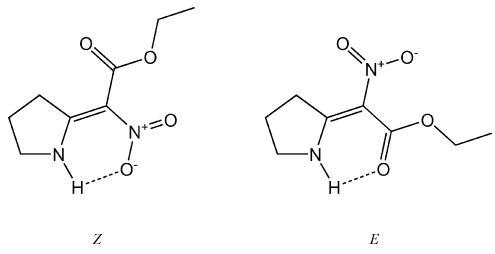


Figure 3. *E*/*Z* Isomerism of ligand **7**.

The nitro function in **7** can be reduced to yield the very air-sensitive amine[17] which can in situ be used for Schiff base condensation. Using benzaldehyde the Schiff base **8** was obtained. This opens a new way to derivatise the β-enaminones in the R^2 position.

Introducing an R^1 residue which is not an alkoxide requires first the C(O)OR^1 ester group to be cleaved under alkaline conditions and then be decarboxylated in acidic medium (**9**–**12**). Here, **9**–**11** are formed as their *E*/*Z* mixture,

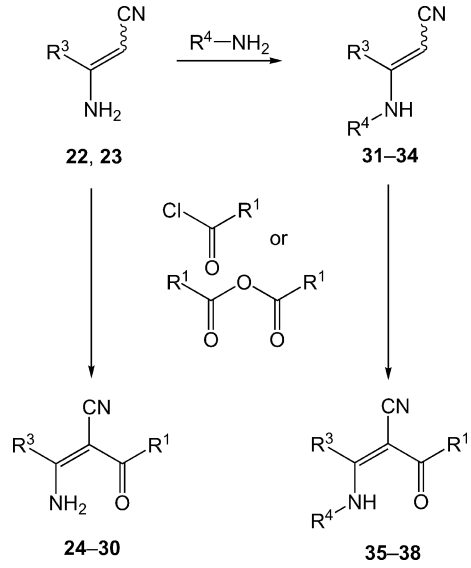
but **12** forms a N–H–O hydrogen bond to one nitro oxygen and therefore results as its *Z* isomer only. The resulting vinylic proton after decarboxylation is relatively acidic due to the electron-withdrawing group in the geminal position. We used this to introduce a non-alkoxide R^1 substituent by reaction with carboxylic acid chlorides or carboxylic acid anhydrides in presence of a base such as triethylamine. The only limitation here is the availability of the acid chloride, so a great variety of substitutions is possible (**13**–**21**). In some cases, *N*-acylation occurs as a side-reaction (**42**–**45**, see Table 2), similar to the reaction of β-enaminonitriles with acid chlorides.[18,19] Cyclohexanecarboxylic acid chloride exclusively leads to the *N*-acylated product (**46**). From these observations arises the assumption that bulky, sterically demanding carboxylic acid chlorides prefer the *N*- vs. *C*-acylation.[19] The *N*-acylation product is easily distinguished from its isomeric *C*-acylation product by the absence of the NH resonance and the characteristic downfield shift of the vinylic proton of more than 2 ppm in the ^{1}H NMR spectrum.[19] Due to the deshielding effect of the N–H–O hydrogen bond in the *C*-acylated product the resonance of the NH proton is shifted more than 6 ppm downfield compared to the NH resonance in non-acylated starting material. The *Z*-configuration of the *C*-acylated product is further supported by the presence and shift of the C=O stretching vibration in the infrared spectrum, which is shifted to lower wave numbers due to the N–H–O hydrogen bonding compared to the stretching frequency of a free carbonyl group.

Table 2. Substitution pattern of *N*-acylated byproducts (see Scheme 1).

	R^1	R^2	R^3,R^4
42	*p*-$O_2NC_6H_4$	CN	$CH_2CH_2CH_2$
43	*p*-$MeOC_6H_4$	CN	$CH_2CH_2CH_2$
44	Naph	CN	$CH_2CH_2CH_2$
45	Mes	CN	$CH_2CH_2CH_2$
46	*c*-C_6H_{11}	CN	$CH_2CH_2CH_2$

All fluorinated compounds have also been characterised by ^{19}F NMR spectroscopy. As expected, the absolute magnitude of the $^3J_{FF}$ coupling constants in the perfluorated alkyl chains is lower than of the $^4J_{FF}$ coupling constants.[20] $^3J_{FF}$ coupling constants were not observed due to their magnitude being in the order of the linewidth.

A different route has to be followed to open-chain ligands with R^3 and R^4 being individual substituents and not forming a closed alkyl chain (see Scheme 2 and Table 3). (*E*/*Z*)-3-Aminobut-2-enenitrile is readily commercially available and can directly be used to react with carboxylic acid chlorides to give the corresponding *C*- and *N*-acylated products (**24**–**26**), respectively.[19] The reaction of acetonitrile with benzonitrile in presence of KO*t*Bu gives (*E*/*Z*)-3-amino-3-phenylacrylonitrile in good yields.[21] The reaction is also successful with *p*-fluorobenzonitrile (**22**) but fails when using pentafluorobenzonitrile. Only starting material is recovered in this case. With terephthalonitrile only one nitrile function reacts to yield 4-(1-amino-2-cyanovinyl)-benzonitrile (**23**). No 3-amino-3-[4-(1-amino-2-cyanovinyl)-phenyl]acrylonitrile was found.



Scheme 2. Synthesis of ligands containing individual substituents R^3 and R^4 (R^2 = CN).

Table 3. Substitution pattern of ligands and ligand precursors, leading to one N,O-bidentate β-enaminonic coordination site containing individual substituents R^3 and R^4, R^2 = CN (see Scheme 2).

	R^1	R^2	R^3	R^4
22	–[a]	CN	*p*-FC_6H_4	H
23	–[a]	CN	*p*-NCC_6H_4	H
24	*n*-C_3F_7	CN	Me	H
25	CF_3	CN	Ph	H
26	CCl_3	CN	Ph	H
27	*n*-C_3F_7	CN	*p*-FC_6H_4	H
28	*n*-C_3F_7	CN	Ph	H
29	*n*-C_7F_{15}	CN	Ph	H
30	CCl_3	CN	Me	H
31	–[a]	CN	Me	$C(O)CCl_3$
32	–[a]	CN	Me	Ph
33	–[a]	CN	Me	*p*-Tol
34	–[a]	CN	Ph	*p*-Tol
35	CCl_3	CN	Me	Ph
36	*n*-C_3F_7	CN	Me	Ph
37	*n*-C_3F_7	CN	Me	*p*-Tol
38	*n*-C_3F_7	CN	Ph	*p*-Tol

[a] Ligand precursor (see Figure 2b).

Like in the case of compounds **9**–**11** the *E*/*Z* ratio of the 3-amino-2-enenitrile does not matter when introducing R^1 (**24**–**30**) by reaction with acyl chlorides or anhydrides, respectively: the newly formed hydrogen bond directs the product into *Z* configuration (see Scheme 2). In the case of **30**, also the *N*-acylated product was observed (**31**). Introduction of an aryl or alkyl residue in position R^4 is accomplished by reaction with primary aryl or alkylamines in aqueous diluted acetic acid. Preparation details date back to the year 1908,[22,23] so we re-investigated the published procedure and characterised the products (**32**–**34**) by mod-

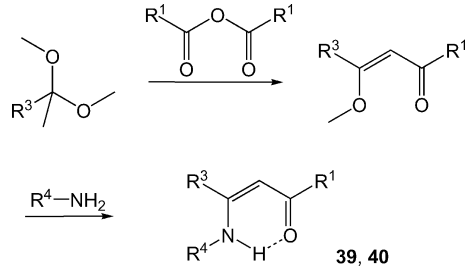
ern techniques such as NMR, IR and MS. The substituent R^1 (**35**–**38**) can then subsequently be introduced as aforesaid.

(*E*/*Z*)-3-Amino-3-phenylacrylonitrile can be converted into 3-oxo-3-phenylpropanenitrile, which has been reported as early as 1890.[24] This reaction is also successful using (*E*/*Z*)-3-amino-3-(4-fluorophenyl)acrylonitrile. These β-cyano ketones can be used in Knoevenagel-type condensations with the designated *O*-alkylated enamine to introduce R^1 and R^2. After the conversion of a β-enaminonitrile comprising an appropriate R^3 residue, the corresponding β-cyano ketone now bears the substituent in the future R^1 position of the target ligand molecule. This opens an alternative route for introducing a desired substituent R^1 besides the reaction of the β-enaminonitrile with acyl chlorides or carboxylic anhydrides, respectively. This might be of importance, e.g. if the acyl chloride or the anhydride, respectively, is not available.

Aromatic and aliphatic nitriles can be converted into imidic acid esters by reaction with dry HCl gas in absolute alcoholic solution and subsequent deprotonation,[25–28] which can then be used in the Knoevenagel condensation. In our experiments, 2,2,2-trifluoroacetamide did neither react with dialkyl sulfate nor with HCl/ethanol to yield ethyl 2,2,2-trifluoroacetimidate. This compound has to be prepared by a different route starting from CF_3CN.[29]

In order to obtain compounds with R^3 = H, we started from alkoxy acrylates such as ethyl (*Z*)-2-cyano-3-ethoxyacrylate, which is reacted with the appropriate primary or secondary amine. The cyano group in the starting material, representing R^2 in the ligand, can be replaced by an ester[30] or nitro function[31,32] with equal success.

Compounds comprising R^2 = H can be obtained in high yields starting from the appropriate dimethoxyethane (see Scheme 3 and Table 4). Reaction with an appropriate carboxylic acid anhydride and subsequently with a primary amine,[33] which introduces R^4, or aqueous ammonia (R^4 = H) yields the target compounds (**39**, **40**). Karpenko et al. prepared compounds of this type via a different route starting from fluorinated β-diketones.[34] β-Enaminones comprising R^2 = H can also be synthesised starting from terminal alkynes and acyl chlorides under modified Sonogashira conditions followed by the reaction with primary amines.[35]



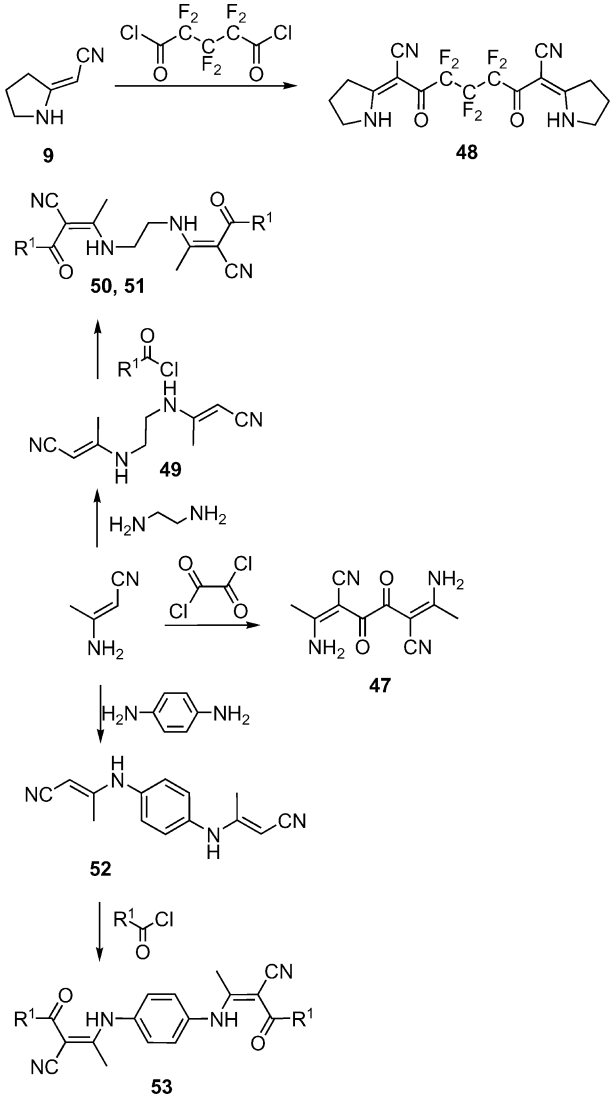
Scheme 3. Synthesis of ligands containing R^2 = H.

Table 4. Substitution pattern of ligands leading to one N,O-bidentate β-enaminonic coordination site containing individual substituents R^3 and R^4, R^2 = H (see Scheme 3).

	R^1	R^2	R^3	R^4
39	n-C_3F_7	H	Me	H
40	n-C_3F_7	H	Ph	H
41	n-C_3F_7	H	H	H

Ligand molecules featuring R^2 = R^3 = H can be prepared from vinyl ethers by reaction with an appropriate acyl chloride, followed by a primary amine,[36] which introduces R^4, or aqueous ammonia (R^4 = H, **41**).

We extended the system to ligands bearing two β-enaminonic coordination sites (see Scheme 4 and Table 5). Generally, this was achieved by linking two single β-enaminone units together at the R^1 and R^4 position, respectively. We synthesised several ligand molecules focusing on perfluorated alkyl chains like in the single coordination site ligands. Diacyl dichlorides can be used to link two β-en-



Scheme 4. Synthesis of ligands bearing two N,O-bidentate β-enaminonic coordination sites.

aminone units via R^1. Benary et al. used 3-amino-3-phenylacrylonitrile in the reaction with oxalyl dichloride in 1923.[37] Similarly, reacting oxalyl dichloride with (*E*/*Z*)-3-aminobut-2-enenitrile yields two directly connected β-enaminone coordination sites (**47**). Analogously, 2,2,3,3,4,4-hexafluoropentanedioyl dichloride reacts with [pyrrolidin-(2*E*/2Z)-ylidene]acetonitrile to yield the corresponding coordination sites linked by a linear $(CF_2)_3$ spacer (**48**).

Table 5. Substitution pattern of ligands and ligand precursors leading to two N,O-bidentate β-enaminonic coordination sites (see Scheme 4).

	R^1	R^2	R^3	R^4
47	link[a]	CN	Me	H
48	$CF_2CF_2CF_2$	CN		$CH_2CH_2CH_2$
49	–[b]	CN	Me	CH_2CH_2
50	*n*-C_3F_7	CN	Me	CH_2CH_2
51	CCl_3	CN	Me	CH_2CH_2
52	–[b]	CN	Me	*p*-Ph
53	*n*-C_3F_7	CN	Me	*p*-Ph

[a] Both carbonyl groups are directly linked together (oxalyl). [b] Ligand precursor (see Scheme 4).

Reaction of (*E*/*Z*)-3-aminobut-2-enenitrile with 1,2-diaminoethane yields a bis(β-amino)-enenitrile linked via R^4 by a $(CH_2)_2$ spacer (**49**).[38] Further reaction with carboxylic acid chlorides such as trichloro acetic acid chloride (**51**) or 2,2,3,3,4,4,4-heptafluorobutyryl chloride (**50**) yields the desired ligand molecules with two β-enaminonic coordination sites. Linking is also possible by the use of a phenylene spacer if *p*-phenylenediamine is used instead of 1,2-diaminoethane. This way a bis-β-amino-ene-nitrile linked via R^4 by a *p*-phenylene spacer is obtained (**52**), which can analogously be reacted with 2,2,3,3,4,4,4-heptafluorobutyryl chloride to yield the corresponding ligand with two β-enaminonic coordination sites (**53**).

Variation of the spacer might be of interest, since the ethylene spacer provides an electronic insulation between the two coordination sites whereas the phenylenediamine linker allows electronic exchange. This is an additional aspect in controlling the electronic structure of coordinated metals bound to a ligand with multiple coordination sites.

Conclusions

We have synthesised a series of new ligand molecules containing one or two N,O-bidentate coordination sites with an electronically delocalised β-enaminone chelating backbone. The ligand design was inspired by a ligand found in a nickel(II) complex which represents the most efficient nickel catalyst for the copolymerisation reaction of ethene and CO to date. We presented versatile and modular routes for the synthesis of such types of ligands rather than focusing on a special pathway yielding only a single compound. We now have a library of ligands. The coordination chemistry of the newly synthesised ligands and their use in nickel-mediated (co)polymerisation reactions is currently ongoing research in our group. Furthermore, naturally occurring β-enaminone ligands, e.g. such as indigo,[39,40] are also interesting as potential ligands for polymerisation catalysts.

Experimental Section

General: All solvents were dried by standard procedures. One-dimensional NMR spectra were recorded at room temperature, proton NMR spectra were recorded on a Bruker Avance DRX 200 spectrometer and ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer. The proton and carbon chemical shifts are given in ppm and referenced to the solvent residual signals[41] [$CDCl_3$: ^1H 7.26 ppm, ^{13}C 77.16 ppm; C_6D_6: ^1H 7.16 ppm, ^{13}C 128.1 ppm. CD_3OD: ^1H 3.31 ppm, ^{13}C 49.0 ppm; $(CD_3)_2CO$: ^1H 2.05 ppm; ^{13}C 29.8/206.3 ppm]. The coupling constants are reported as their absolute value. Ethyl nitroacetate,[42] (*E*)-3-amino-3-phenylacrylonitrile,[21] (*E*)-1-ethoxy-4,4,5,5,6,6,6-heptafluorohex-1-en-3-one[36] and (1,1-dimethoxyethyl)benzene[43] were prepared according to literature procedures. The fluorine chemical shifts are given relative to $CFCl_3$. Infrared spectra were recorded on a FT-IR Bruker IFS 66 spectrometer. EI-MS data were recorded on a Varian MAT 311 A instrument.

Methyl [Cyanopyrrolidin-(2*Z*)-ylidene]acetate (4): 22.6 g (200 mmol) 5-ethoxy-3,4-dihydro-2*H*-pyrrole (**1**) and 69.3 g (700 mmol) methyl cyanoacetate were mixed and kept for several days at room temperature. White crystals formed which were separated and washed with pentane to yield 33 g (85%) of **4**. ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 2.13 (m, 2 H, CH_2–CH_2–CH_2), 2.94 (m, 2 H, CH_2–C–N), 3.71 (m, 2 H, CH_2–N), 3.74 (s, 3 H, CH_3), 8.95 [s (br), 1 H, NH] ppm. IR (KBr disk): $\tilde{\nu}$ = 3318 (s, N–H), 2959 (m, C–H), 2202 (vs, C≡N), 1667 (s, C=O), 1598 (s, C=C) cm^{-1}. MS (EI): *m*/*z* = 166 [M^+], 135 [M^+ – OMe]. $C_8H_{10}N_2O_2$ (166.18): calcd. C 57.82, H 6.07, N 16.86; found C 57.90, H 5.77, N 16.70.

Ethyl [Cyanopiperidin-(2*Z*)-ylidene]acetate (5): The synthesis was carried out according to the literature.[45] ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, ethyl CH_3), 1.79 (m, 4 H, CH_2–CH_2–CH_2–CH_2), 2.69 (m, 2 H, CH_2–C–N), 3.39 (m, 2 H, CH_2–N–C), 4.15 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, ethyl CH_2), 10.12 [s (br), 1 H, NH] ppm. IR (KBr disk): $\tilde{\nu}$ = 3228 (m, N–H), 2956 (s, C–H), 2199 (vs, C≡N), 1666 (s, C=O), 1612 (s, C=C) cm^{-1}. MS (EI): *m*/*z* = 194 [M^+], 149 [M^+ – OEt]. $C_{10}H_{14}N_2O_2$ (194.23): calcd. C 61.84, H 7.27, N 14.42; found C 61.54, H 7.36, N 14.09.

Methyl [Azepan-(2*Z*)-ylidene]cyanoacetate (6): 14.1 g (100 mmol) 7-ethoxy-3,4,5,6-tetrahydro-2*H*-azepine (**3**) and 39.6 g (400 mmol) methyl cyanoacetate were mixed and refluxed for 3 h. After cooling to room temperature, 50 mL of methanol was added, followed by 200 mL of water. A white solid precipitated, was washed with water and dried. Yield 11.5 g (59%). ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 1.6–1.9 (m, 6 H, CH_2–CH_2–CH_2–CH_2–CH_2), 2.82 (m, 2 H, CH_2–C–N), 3.48 (m, 2 H, CH_2–N–C), 3.79 (s, 3 H, CH_3), 10.16 [s (br), 1 H, NH] ppm. IR (KBr disk): $\tilde{\nu}$ = 3268 (s, N–H), 2931 (s, C–H), 2194 (vs, C≡N), 1656 (vs, C=O), 1605 (vs, C=C) cm^{-1}. MS (EI): *m*/*z* = 194 [M^+], 163 [M^+ – OMe]. $C_{10}H_{14}N_2O_2$ (194.23): calcd. C 61.84, H 7.27, N 14.42; found C 61.77, H 7.33, N 14.17.

4,4,5,5,6,6,6-Heptafluoro-3-oxo-2-[pyrrolidin-(2*Z*)-ylidene]hexanenitrile (13): The synthesis was carried out according to the literature.[8] ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 2.25 (qi, $^3J_{HH}$ = 7.8 Hz, 2 H, CH_2–CH_2–CH_2), 3.14 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, CH_2–C–N), 3.92 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, CH_2–N–C), 10.70 [s (br), 1 H, NH] ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp., ppm): δ =

–80.8 (t, $^4J_{FF}$ = 8.9 Hz, 3 F, CF_3), –117.8 (q, $^4J_{FF}$ = 8.9 Hz, 2 F, CO–CF_2), –126.6 (m, 2 F, CF_2–CF_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp., not all C signals were observed): δ = 20.1 (CH_2–C–N), 34.9 (CH_2–CH_2–CH_2), 50.8 (CH_2–N–C), 109.9 (tt, $^1J_{FC}$ = 267, $^2J_{FC}$ = 32 Hz, CF_2–CF_3), 116.1 (CN), 116.5 (t, $^2J_{FC}$ = 33 Hz, CF_3), 118.8 (t, $^2J_{FC}$ = 34 Hz, CO–CF_2), 178.4 (N–C=C), 187.6 (CO) ppm. IR (KBr disk): $\tilde{\nu}$ = 3283 (vs, N–H), 2983 (m, C–H), 2213 (vs, C≡N), 1642 (vs, C=O), 1589 (vs, C=C) cm^{-1}. MS (EI): *m*/*z* = 304 [M^+], 285 [M^+ – F], 135 [$M^+ – C_3F_7$]. $C_{10}H_7F_7N_2O$ (304.17): calcd. C 39.49, H 2.32, N 9.21; found C 39.34, H 2.15, N 9.15.

4,4,5,5,6,6,6-Heptafluoro-3-oxo-2-[piperidin-(2*Z*)-ylidene]hexanenitrile (14): 1.2 g (10 mmol) [piperidine-(2*E*/2*Z*)-ylidene]acetonitrile (**10**) was dissolved in 100 mL of toluene, 1.0 g (10 mmol) triethylamine was added and the solution was cooled to 0 °C. 2.4 g (10 mmol) 2,2,3,3,4,4,4-heptafluorobutyryl chloride was dissolved in 50 mL of toluene and added dropwise to the chilled solution. The mixture was stirred at 0 °C for one hour and subsequently at room temperature overnight. After filtration and treatment with saturated $NaHCO_3$ solution the toluene solution was dried with $MgSO_4$ and the solvent was removed in vacuo. The yellowish solid was recrystallised from diethyl ether yielding 1.9 g (60%) of colourless needles. ^1H NMR (500 MHz, $CDCl_3$, room temp.): δ = 1.91 (m, 4 H, CH_2–CH_2–CH_2–CH_2), 2.84 (m, 2 H, CH_2–C–N), 3.55 (m, 2 H, CH_2–N–C), 12.16 [s (br), 1 H, NH] ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp., ppm): δ = –80.8 (t, $^4J_{FF}$ = 9.2 Hz, 3 F, CF_3), –117.1 (q, $^4J_{FF}$ = 9.2 Hz, 2 F, CO–CF_2), –126.4 (m, 2 F, CF_2–CF_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp., not all C signals were observed): δ = 18.1 (CH_2–CH_2–C–N), 20.6 (CH_2–CH_2–N–C), 28.5 (CH_2–C–N), 42.9 (CH_2–N–C), 80.1 (=C–CN), 115.9 (CN), 174.6 (N–C=C) ppm. IR (KBr disk): $\tilde{\nu}$ = 3139 (m, N–H), 2981 (m, C–H), 2206 (vs, C≡N), 1633 (vs, C=O), 1605 (vs, C=C) cm^{-1}. MS (EI): *m*/*z* = 318 [M^+], 299 [M^+ – F], 149 [$M^+ – C_3F_7$]. $C_{11}H_9F_7N_2O$ (318.19): calcd. C 41.52, H 2.85, N 8.80; found C 41.47, H 2.71, N 8.73.

[2-Azepan-(2*Z*)-ylidene]-4,4,5,5,6,6,6-heptafluoro-3-oxohexanenitrile (15): The synthesis was carried out as for **14**, except that 1.4 g (10 mmol) [azepan-(2*E*/2*Z*)-ylidene]acetonitrile (**11**) was used. Yield 2.3 g (70%) of colourless needles after recrystallisation from diethyl ether. ^1H NMR (500 MHz, $CDCl_3$, room temp.): δ = 1.75 (m, 4 H, CH_2–CH_2–CH_2–C–N), 1.89 (m, 2 H, CH_2–CH_2–N–C), 2.94 (m, 2 H, CH_2–C–N), 3.62 (m, 2 H, CH_2–N–C), 12.09 [s (br), 1 H, NH] ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp., ppm): δ = –80.8 (t, $^4J_{FF}$ = 9.2 Hz, 3 F, CF_3), –116.6 (q, $^4J_{FF}$ = 9.2 Hz, 2 F, CO–CF_2), –126.3 (m, 2 F, CF_2–CF_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp., not all C signals were observed): δ = 23.5 (CH_2–CH_2–C–N), 27.2 (CH_2–CH_2–CH_2–C–N), 30.2 (CH_2–C–N), 32.6 (CH_2–CH_2–N–C), 46.2 (CH_2–N–C), 80.1 (=C–CN), 116.7 (CN), 180.5 (N–C=C) ppm. IR (KBr disk): $\tilde{\nu}$ = 3137 (m, N–H), 2947 (m, C–H), 2209 (vs, C≡N), 1631 (vs, C=O), 1603 (vs, C=C) cm^{-1}. MS (EI): *m*/*z* = 332 [M^+], 313 [M^+ – F], 163 [$M^+ – C_3F_7$]. $C_{12}H_{11}F_7N_2O$ (332.22): calcd. C 43.38, H 3.34, N 8.43; found C 43.38, H 3.44, N 8.26.

2-[1-Aminoeth-(*Z*)-ylidene]-4,4,5,5,6,6,6-heptafluoro-3-oxohexanenitrile (24): 0.86 g (10 mmol) (*E*/*Z*)-3-aminobut-2-enenitrile was dissolved in 100 mL of tetrahydrofuran and 1.1 g (10 mmol) triethylamine was added. The mixture was cooled to 0 °C and a solution of 2.4 g (10 mmol) 2,2,3,3,4,4,4-heptafluorobutyryl chloride in 50 mL of tetrahydrofuran was added dropwise while stirring over a period of 3 h. The yellowish mixture was allowed to thaw overnight and filtered. The solvent was removed in vacuo and the crude product was recrtystallised from CH_2Cl_2 yielding 1.4 g (50%) of **24**. ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 2.46 (s, 3 H, CH_3), 7.65 [s (br), 1 H, NH], 10.82 [s (br), 1 H, NH] ppm. ^{19}F NMR (471 MHz, [D_4]MeOD, room temp.): δ = –82.5 (t, $^4J_{FF}$ = 9.2 Hz, 3 F, CF_3), –118.2 (q, $^4J_{FF}$ = 9.1 Hz, 2 F, CO–CF_2), –127.9 (m, 2 F, CF_2–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3307, 3170 (s, N–H), 2222 (vs, C≡N), 1643 (vs, C=O) cm^{-1}. MS (EI): *m*/*z* = 278 [M^+], 109 [$M^+ – C_3F_7$]. $C_8H_5F_7N_2O$ (278.13): calcd. C 34.55, H 1.81, N 10.07; found C 34.47, H 1.68, N 9.99.

2-[1-Amino-1-phenylmeth-(*Z*)-ylidene]-4,4,4-trifluoro-3-oxobutyronitrile (25): 1.5 g (10 mmol) (*E*)-3-Amino-3-phenylacrylonitrile was dissolved in 20 mL of tetrahydrofuran and 1.0 g (10 mmol) triethylamine was added. This solution was added dropwise to a solution of 3.1 g (15 mmol) trifluoroacetic acid anhydride in 20 mL of tetrahydrofuran. The yellowish solution was heated to reflux for one hour and was left to attain room temperature overnight. The reaction mixture was poured on 100 g of ice and 1 mL of concentrated aqueous HCl (37%) was added. After melting of the ice the organic phase was extracted with dichloromethane (5 × 50 mL), dried with $MgSO_4$ and the solvent was removed in vacuo. The product crystallises after a short time in the refrigerator and was recrystallised from diethyl ether yielding 1.5 g (64%) of **25**. ^1H NMR (500 MHz, $CDCl_3$, room temp.): δ = 6.73 [s (br), 1 H, NH], 7.49–7.59 (m, 2 H, *o*-H), 7.60–7.68 (m, 3 H, *m*,*p*-H), 10.74 [s (br), 1 H, NH] ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp., ppm): δ = –74.6 (s, 3 F, CF_3) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp.): δ = 78.4 (C=C–CN), 116.2 (CN), 116.5 (d, $^1J_{FC}$ = 290 Hz, CF_3), 127.7 (*o*-C), 129.5 (*m*-C), 132.0 (*i*-C), 133.1 (*p*-C), 174.8 (C=C–CN), 179.2 (CO) ppm. IR (KBr disk): $\tilde{\nu}$ = 3307, 3176 (vs, N–H), 2220 (vs, C≡N), 1659 (vs, C=O), 1636 (vs, C=C), 1219, 1175, 1144 (s, C–F) cm^{-1}. MS (EI): *m*/*z* = 240 [M^+], 171 [$M^+ – CF_3$]. $C_{11}H_7F_3N_2O$ (240.18): calcd. C 55.01, H 2.94, N 11.66; found C 54.88, H 2.90, N 11.54

2-[1-Amino-1-(4-fluorophenyl)meth-(*Z*)-ylidene]-4,4,5,5,6,6,6-heptafluoro-3-oxohexanenitrile (27): 1.6 g (10 mmol) (*E*/*Z*)-3-Amino-3-(4-fluorophenyl)acrylonitrile (**22**) was dissolved in 80 mL of tetrahydrofuran and 1.5 g (15 mmol) triethylamine was added. 3.4 g (15 mmol) 2,2,3,3,4,4,4-heptafluorobutyryl chloride was added dropwise via a syringe and the mixture was stirred for three days. Another portion of 1.5 g (6.0 mmol) 2,2,3,3,4,4,4-heptafluorobutyryl chloride and 0.6 g (6.0 mmol) triethylamine was added dropwise and the mixture stirred overnight. After washing with saturated sodium hydrogen carbonate solution and drying over $MgSO_4$ the organic solvents were removed in vacuo yielding 2.2 g (63%) of **27**. ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 6.96 [s (br), 1 H, NH], 7.22 (m, 2 H, *m*-H), 7.62 (m, 2 H, *o*-H), 10.89 [s (br), 1 H, NH] ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp.): δ = 80.1 (C=C–CN), 109.9 (tt, $^1J_{FC}$ = 268, $^2J_{FC}$ = 32 Hz, CF_2–CF_3), 116.1 (CN), 116.8 (d, $^2J_{FC}$ = 22 Hz, *m*-C), 118.8 (t, $^2J_{FC}$ = 33 Hz, CF_3), 129.1 (d, $^4J_{FC}$ = 3.4 Hz, *i*-C), 130.5 (d, $^3J_{FC}$ = 9.2 Hz, *o*-C), 165.4 (d, $^1J_{FC}$ = 256 Hz, *p*-C), 174.1 (C–NH_2), 180.4 (t, $^2J_{FC}$ = 25 Hz, CO) ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp.): δ = –80.7 (t, $^4J_{FF}$ = 9.2 Hz, 3 F, CF_3), –105.0 (tt, $^3J_{HF}$ = 8, $^4J_{HF}$ = 5 Hz, 1 F, *p*-CF), –116.5 (q, $^4J_{FF}$ = 9.3 Hz, 2 F, CO–CF_2), –126.2 (s, 2 F, CF_2–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3304, 3161 (s, N–H), 2221 (vs, C≡N), 1635 (vs, C=O), 1605 (m, C=C), 1189 (vs, C–F) cm^{-1}. MS (FAB): *m*/*z* = 359 [M^+]. $C_{13}H_6F_8N_2O$ (358.19): calcd. C 43.59, H 1.69, N 7.82; found C 43.34, H 1.65, N 7.66.

2-[1-Amino-1-phenylmeth-(*Z*)-ylidene]-4,4,5,5,6,6,6-heptafluoro-3-oxohexanenitrile (28): The synthesis was carried out as for **27**, except that 1.4 g (10 mmol) (*E*)-3-amino-3-phenylacrylonitrile was used. Yield 56%. ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 6.96 [s (br), 1 H, NH], 7.53 (m, 2 H, *o*-H), 7.60 (m, 3 H, *m*,*p*-H),

10.89 [s (br), 1 H, NH] ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp.): δ = 80.1 (C=*C*–CN), 109.9 (t, $^2J_{FC}$ = 32 Hz, *C*F_2–CF_3), 116.2 (CN), 116.5 (t, $^2J_{FC}$ = 34 Hz, CF_3), 118.8 (t, $^2J_{FC}$ = 33 Hz, CO–*C*F_2), 127.8 (*o*-C), 129.4 (*m*-C), 133.0 (*p*-C), 133.1 (*i*-C), 175.2 (C-NH_2), 180.4 (t, $^2J_{FC}$ = 25 Hz, CO) ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp.): δ = –80.7 (t, $^4J_{FF}$ = 9 Hz, 3 F, CF_3), –116.5 (q, $^4J_{FF}$ = 9 Hz, 2 F, CO–CF_2), –126.1 (s, 2 F, C*F*$_2$–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3313, 3184 (s, N–H), 2214 (vs, C≡N), 1657 (vs, C=O), 1632 (s, C=C), 1208 (vs, C–F) cm^{-1}. MS (FAB): *m*/*z* = 340 [M^+], 171 [$M^+ - C_3F_7$], 143 [$M^+ - COC_3F_7$], 77 [Ph^+]. $C_{13}H_7F_7N_2O$ (340.20): calcd. C 45.90, H 2.07, N 8.23; found C 45.92, H 2.17, N 8.20.

2-[1-Amino-1-phenylmeth-(*Z*)-ylidene]-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-pentadecafluoro-3-oxodecanenitrile (29): 1.4 g (10 mmol) (*E*)-3-amino-3-phenylacrylonitrile was dissolved in 100 mL of diethyl ether and 1.0 g (10 mmol) triethylamine was added. The mixture was cooled to –20 °C and 4.3 g (10 mmol) 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoyl chloride was added dropwise while stirring. The solution was allowed to thaw and stir overnight and was washed three times with saturated sodium hydrogen carbonate solution. After drying over Na_2SO_4 the solvent was removed in vacuo and the remaining solid was recrystallised from diethyl ether/pentane to yield 0.9 g (18%) of **29**. ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 6.58 (s, 1 H, NH), 7.54 (m, 5 H, Ph), 10.98 [s (br), 1 H, NH] ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp.): δ = –80.9 (t, $^4J_{FF}$ = 10.1 Hz, 3 F, CF_3), –115.9 (m, 2 F), –121.3 (m, 2 F), –121.9 (m, 2 F), –122.1 (m, 2 F), –122.6 (m, 2 F), –126.0 (m, 2 F) ppm. IR (KBr disk): $\tilde{\nu}$ = 3358 (s, N–H), 2218 (vs, C≡N), 1698 (vs, C=O) cm^{-1}. MS (EI): *m*/*z* = 540 [M^+], 171 [$M^+ - C_7F_{15}$]. $C_{17}H_7F_{15}N_2O$ (540.23): calcd. C 37.80, H 1.31, N 5.19; found C 37.92, H 1.64, N 5.20.

4,4,5,5,6,6,6-Heptafluoro-3-oxo-2-[1-phenylaminoeth-(*Z*)-ylidene]-hexanenitrile (36): 1.9 g (12 mmol) (*E*/*Z*)-3-(phenylamino)but-2-enenitrile (**32**) was dissolved in 100 mL of tetrahydrofuran and 1.2 g (12 mmol) triethylamine was added. A solution of 2.8 g (12 mmol) 2,2,3,3,4,4,4-heptafluorobutyryl chloride (**25**) in tetrahydrofuran was added dropwise. The yellowish solution is stirred overnight. After filtration the solvent was removed in vacuo, the residue dissolved in toluene and extracted three times with saturated sodium hydrogen carbonate solution. After drying over $MgSO_4$ the solvent was removed in vacuo and the remainig solid recrystallised from diethyl ether. Yield 2.1 g (49%). ^1H NMR (500 MHz, $CDCl_3$, room temp.): δ = 2.42 (s, 3 H, CH_3), 7.19 (m, 2 H, *o*-H), 7.45 (m, 3 H, *m,p*-H), 13.33 [s (br), 1 H, NH] ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp., not all C signals were observed): δ = 19.8 (CH_3), 82.3 (C=*C*–CN), 116.0 (CN), 125.6 (*o*-C), 129.4 (*p*-C), 130.2 (*m*-C), 135.5 (*i*-C), 174.2 (*C*=C–CN), 179.5 (CO) ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp.): δ = –80.7 (t, $^4J_{FF}$ = 9.2 Hz, 3 F, CF_3), –116.8 (q, $^4J_{FF}$ = 9.1 Hz, 2 F, CO–CF_2), –126.2 (m, 2 F, C*F*$_2$–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3046 (mw, C–H_{ar}), 2217 (s, C≡N), 1625 (vs, C=O), 1574 (vs, C=C) cm^{-1}. MS (EI): *m*/*z* = 354 [M^+], 185 [$M^+ - C_3F_7$]. $C_{14}H_9F_7N_2O$ (354.23): calcd. C 47.47, H 2.56, N 7.91; found C 47.48, H 2.85, N 8.01.

4,4,5,5,6,6,6-Heptafluoro-3-oxo-2-[1-*p*-tolylaminoeth-(*Z*)-ylidene]-hexanenitrile (37): The synthesis was carried out as for **36** except that 2.1 g (12 mmol) (*E*/*Z*)-3-(*p*-tolylamino)but-2-enenitrile (**34**) was used. Yield 1.6 g (29%). ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 2.39 (s, 3 H, C=C–CH_3), 2.41 (s, 3 H, *p*-CH_3), 7.09 (m, 2 H, *o*-H) 7.27 (m, 2 H, *m*-H), 13.25 [s (br), 1 H, NH] ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp., not all C signals were observed): δ = 19.7 (C=C–*C*H_3), 21.3 (*p*-CH_3), 82.1 (C=*C*–CN), 116.1 (CN), 125.3 (*o*-C), 130.7 (*m*-C), 132.9 (*p*-C), 139.6 (*i*-C), 174.2 (*C*=C–CN), 179.3 (CO) ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp.): δ = –80.7 (t, $^4J_{FF}$ = 9.2 Hz, 3 F, CF_3), –116.8 (q, $^4J_{FF}$ = 9.3 Hz, 2 F, CO–CF_2), –126.2 (m, 2 F, C*F*$_2$–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3157 (m, N–H), 3068, 3043 (m, C–$H_{arom.}$), 2966, 2931 (w, C–H_{ali}), 2219 (vs, C≡N), 1627 (vs, C=O), 1558 (vs, C=C), 1242 (s, C–F) cm^{-1}. MS (EI): *m*/*z* = 368 [M^+], 199 [$M^+ - C_3F_7$]. $C_{15}H_{11}F_7N_2O$ (368.25): calcd. C 48.92, H 3.01, N 7.61; found C 48.86, H 3.28, N 7.46.

4,4,5,5,6,6,6-Heptafluoro-3-oxo-2-[1-phenyl-1-*p*-tolylaminometh-(*Z*)-ylidene]hexanenitrile (38): 2.4 g (10 mmol) (*E*)-3-phenyl-3-(*p*-tolylamino)acrylonitrile (**34**) was dissolved in 100 mL of tetrahydrofuran and 1.0 g (10 mmol) triethylamine was added. 2.3 mL (15 mmol) 2,2,3,3,4,4,4-heptafluorobutyryl chloride were added dropwise with a syringe while stirring. The mixture turns yellowish and a white precipitate forms. After a week of stirring at room temperature the solution was filtered and the solvent was removed in vacuo. The residue was dissolved in toluene and extracted three times with saturated sodium hydrogen carbonate solution. After drying over Na_2SO_4 the solvent was removed in vacuo and the remainig solid recrystallised from diethyl ether. Yield 1.7 g (40%). ^1H NMR (500 MHz, $CDCl_3$, room temp.): δ = 2.26 (s, 3 H, CH_3), 6.72 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, *o*-H_{tol}), 7.00 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, *m*-H_{tol}), 7.35 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, *o*-H_{Ph}), 7.42 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, *m*-H_{Ph}), 7.49 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, *p*-H_{Ph}), 13.38 [s (br), 1 H, NH] ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp.): δ = 21.1 (CH_3), 82.8 (C=*C*–CN), 115.7 (CN), 124.4 (*o*-C_{tol}), 128.8 (*o*-C_{Ph}), 129.2 (*m*-C_{Ph}), 130.1 (*m*-C_{tol}), 130.2 (*p*-C_{tol}), 131.8 (*p*-C_{Ph}), 133.7 (*i*-C_{Ph}), 138.1 (*i*-C_{tol}), 172.4 (*C*=C–CN) ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp.): δ = –80.6 (t, $^4J_{FF}$ = 9.2 Hz, 3 F, CF_3), –116.3 (q, $^4J_{FF}$ = 9.1 Hz, 2 F, CO–CF_2), –126.0 (m, 2 F, C*F*$_2$–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 2963 (m, C–H_{ali}), 2216 (s, C≡N), 1627 (vs, C=O), 1214 (s, C–F) cm^{-1}. MS (EI): *m*/*z* = 430 [M^+], 261 [$M^+ - C_3F_7$]. $C_{20}H_{13}F_7N_2O$ (430.32): calcd. C 55.82, H 3.05, N 6.51; found C 55.95, H 3.22, N 6.58.

(*Z*)-2-Amino-5,5,6,6,7,7,7-heptafluorohept-2-en-4-one (39): 2.1 g (20 mmol) 2,2-dimethoxypropane was dissolved in 5 mL of chloroform and 3.2 g (40 mmol) pyridine was added. The mixture was cooled in an ice bath and a solution of 16.4 g (40 mmol) 2,2,3,3,4,4,4-heptafluorobutyric anhydride in 5 mL of chloroform was added dropwise. After stirring overnight 40 mL of water was added and stirring was continued for further 4 h. The mixture was extracted with 50 mL of dichloromethane and the extract washed with 20 mL of aqueous, diluted hydrochloric acid, 30 mL of 10% sodium carbonate solution and water (2 × 30 mL). After drying over Na_2SO_4 the solvent was removed in vacuo and the dark red oil was dissolved in 40 mL of acetonitrile. 4 mL (55 mmol) concentrated aqueous ammonia solution (25%) was added dropwise with stirring which was continued for further 48 h. The solvent was then removed in vacuo and 50 mL of dichloromethane was added. The solution was washed with water (2 × 30 mL) and dried with Na_2SO_4. The solvent was removed and the residue was recrystallised from pentane yielding 2.0 g (40%) of **39**. ^1H NMR (200 MHz, $CDCl_3$, room temp.): δ = 2.11 (s, 3 H, CH_3), 5.43 (s, 1 H, CH), 5.93 [s (br), 1 H, NH], 10.11 [s (br), 1 H, NH] ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, room temp., not all C signals were observed): δ = 23.1 (CH_3), 90.9 (CH), 168.5 (*C*=CH), 178.4 (CO) ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp.): δ = –81.1 (t, $^4J_{FF}$ = 8.9 Hz, 3 F, CF_3), –121.7 (q, $^4J_{FF}$ = 8.9 Hz, 2 F, CO–CF_2), –127.5 (m, 2 F, CF_2–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3301, 3168 (vs, br, N–H), 1612 (vs, C=O), 1546 (vs, C=C) cm^{-1}. MS (EI): *m*/*z* = 253 [M^+], 84 [$M^+ - C_3F_7$]. $C_7H_6F_7NO$ (253.12): calcd. C 33.22, H 2.39, N 5.53; found C 33.48, H 2.50, N 5.30.

(*Z*)-1-Amino-4,4,5,5,6,6,6-heptafluoro-1-phenylhex-1-en-3-one (40): The synthesis was carried out as for **39**, except that 3.3 g (20 mmol) (1,1-dimethoxyethyl)benzene[43] was used. Yield 4.9 g (78%). ^{1}H NMR (500 MHz, $CDCl_3$, room temp.): δ = 5.84 (s, 1 H, CH), 6.11 [s (br), 1 H, NH], 7.51 (t, $^3J_{HH}$ = 7.8 Hz, 2 H, *m*-H_{Ph}), 7.57 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, *p*-H_{Ph}), 7.61 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, *o*-H_{Ph}), 10.31 [s (br), 1 H, NH] ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, room temp., not all C signals were observed): δ = 89.8 (C=*C*H), 126.5 (*o*-C), 129.5 (*m*-C), 132.2 (*p*-C), 135.5 (*i*-C), 167.3 (*C*=CH), 179.2 (CO) ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp.): δ = –81.0 (t, $^4J_{FF}$ = 8.9 Hz, 3 F, CF_3), –121.5 (q, $^4J_{FF}$ = 8.9 Hz, 2 F, CO–CF_2), –127.3 (m, 2 F, CF_2–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3296, 3155 (s, N–H), 1608 (vs, C=O), 1577 (vs, C=C) cm^{-1}. MS (EI): *m*/*z* = 315 [M$^+$], 146 [M$^+$ – C_3F_7]. $C_{12}H_8F_7NO$ (315.19): calcd. C 45.73, H 2.56, N 4.44; found C 45.64, H 2.55, N 4.34.

(*Z*)-1-Amino-4,4,5,5,6,6,6-heptafluorohex-1-en-3-one (41): 2.7 g (10 mmol) (*E*)-1-ethoxy-4,4,5,5,6,6,6-heptafluorohex-1-en-3-one[36] was dissolved in 10 mL of water and 1.0 mL (13 mmol) concentrated aqueous ammonia solution (25%) was added. Stirring was continued overnight and the mixture was extracted three times with 30 mL of diethyl ether. The collected organic phases were dried with $MgSO_4$ and the solvents were evaporated to yield 1.5 g (63%) of **41** as an oil. ^{1}H NMR (200 MHz, C_6D_6, room temp.): δ = 4.22 [s (br), 1 H, NH], 5.14 [d, $^3J_{HH}$ = 7.2 Hz (*cis*), 1 H, CH–CO], 5.82 [ddd, $^3J_{HH}$ = 7.2 Hz (CH, *cis*), $^3J_{HH}$ = 7.8 Hz (NH, *cis*), $^3J_{HH}$ = 14.8 Hz (NH, *trans*), 1 H, C*H*–NH_2]. 8.90 [s (br), 1 H, NH] ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, room temp.): δ = 89.8 (*C*H–CO), 109.8 (tt, $^1J_{FC}$ = 265, $^2J_{FC}$ = 31 Hz, *C*F_2–CF_3), 117.4 (t, $^2J_{FC}$ = 34 Hz, CF_3), 119.7 (t, $^2J_{FC}$ = 34 Hz, CO–*C*F_2), 155.2 (CH–NH_2), 180.2 (t, $^2J_{FC}$ = 24 Hz, CO) ppm. ^{19}F NMR (471 MHz, C_6D_6, room temp.): δ = –81.1 (t, $^4J_{FF}$ = 8.9 Hz, 3 F, CF_3), –121.3 (q, $^4J_{FF}$ = 8.6 Hz, 2 F, CO–CF_2), –127.3 (s, 2 F, CF_2–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3374, 3222 (m, N–H), 1653 (s, C=O), 1522 (s, C=C), 1229 (vs, C–F) cm^{-1}. MS (EI): *m*/*z* = 239 [M$^+$], 70 [M$^+$ – C_3F_7]. $C_6H_4F_7NO$ (239.09): calcd. C 30.14, H 1.69, N 5.86; found C 30.31, H 1.55, N 5.39.

4,4,5,5,6,6-Hexafluoro-3,7-dioxo-2,8-bis[pyrrolidin-(2*Z*)-ylidene]-nonanedinitrile (48): 1.1 g (10 mmol) [pyrrolidin-(2*E*/2*Z*)-ylidene]-acetonitrile (**9**) was dissolved in 100 mL of toluene and 1.0 g (10 mmol) triethylamine was added. The mixture was cooled to 0 °C. 1.4 g (5 mmol) 2,2,3,3,4,4-hexafluoropentanedioyl dichloride was added dropwise and stirring was continued overnight. The white precipitate was filtered and dried. Water (50 mL) was added, the mixture was stirred for 1 h, filtered and washed with water until the filtrate contais no Cl^-. The white solid was dried. Yield 1.3 g (62%). ^{1}H NMR (200 MHz, [D_6]acetone, room temp.): δ = 2.23 (qi, $^3J_{HH}$ = 7.7 Hz, 4 H, CH_2–CH_2–CH_2), 3.12 (t, $^3J_{HH}$ = 8.0 Hz, 4 H, CH_2–C–N), 3.99 (t, $^3J_{HH}$ = 7.5 Hz, 4 H, CH_2–N–C), 10.80 [s (br), 2 H, NH] ppm. ^{13}C{^{1}H} NMR (126 MHz, [D_6]acetone, room temp., not all C signals were observed): δ = 20.4 (*C*H_2–C–N), 35.9 (CH_2–*C*H_2–CH_2), 52.3 (*C*H_2–N–C), 76.6 (=*C*–CN), 117.1 (CN), 178.9 (*C*=C–CN) ppm. ^{19}F NMR (471 MHz, [D_6]acetone, room temp.): δ = –115.2 (m, 4 F, CO–CF_2), –121.5 (m, 2 F, CF_2–CF_2–CF_2) ppm. IR (KBr disk): $\tilde{\nu}$ = 3258 (vs, N–H), 2211 (vs, C≡N), 1650 (vs, C=O), 1579 (vs, C=C) cm^{-1}. MS (EI): *m*/*z* = 420 [M$^+$], 313 [M$^+$ – $C_6H_7N_2$], 285 [M$^+$ – $C_7H_7N_2O$], 135 [$C_7H_7N_2O$]. $C_{17}H_{14}F_6N_4O_2$ (420.31): calcd. C 48.58, H 3.36, N 13.33; found C 48.30, H 3.55, N 13.09.

2-[1-{2-{(*Z*)-2-Cyano-4,4,5,5,6,6,6-heptafluoro-1-methyl-3-oxohex-1-enylamino}ethylamino}eth-(*Z*)-ylidene]-4,4,5,5,6,6,6-heptafluoro-3-oxohexanenitrile (50): 0.95 g (5.0 mmol) 3-[2-(2-Cyano-1-methylvinylamino)ethylamino]but-2-enenitrile **49** was dissolved in 100 mL of tetrahydrofuran and 1.0 g (10 mmol) triethylamine was added. 2.3 g (10 mmol) 2,2,3,3,4,4,4-heptafluorobutyryl chloride was added dropwise with stirring, and stirring was continued overnight. The solvent was then removed and the solid washed with water until no Cl^- was detected. The residue was dried and dissolved in a minium of acetone. Upon addition of methanol, a white solid precipitated which was collected by filtration and dried. Yield 1.4 g (51%). ^{1}H NMR (200 MHz, [D_6]acetone, room temp.): δ = 2.58 (s, 6 H, CH_3), 4.25 (s, 4 H, CH_2), 11.92 [s (br), 2 H, NH] ppm. ^{13}C{^{1}H} NMR (126 MHz, [D_6]acetone, room temp., CF_x and CO not observed): δ = 19.1 (CH_3), 45.3 (CH_2), 82.1 (C=*C*–CN), 117.2 (CN), 177.3 (*C*=C–CN) ppm. ^{19}F NMR (471 MHz, [D_6]acetone, room temp.): δ = –80.4 (t, $^4J_{FF}$ = 9.4 Hz, 3 F, CF_3), –115.8 (m, 2 F, CO–CF_2), –125.9 (m, 2 F, CF_2–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3094 (w, C–H), 2214 (vs, C≡N), 1630 (vs, C=O), 1587 (vs, C=C), 1228 (vs, C–F) cm^{-1}. MS (EI): *m*/*z* = 582 [M$^+$], 413 [M$^+$ – C_3F_7], 285 [M$^+$ – $C_7H_7N_2O$], 135 [$C_7H_7N_2O$]. $C_{18}H_{12}F_{14}N_4O_2$ (582.30): calcd. C 37.13, H 2.08, N 9.62; found C 37.02, H 2.24, N 9.38.

2-[1-{4-{(*Z*)-2-Cyano-4,4,5,5,6,6,6-heptafluoro-1-methyl-3-oxohex-1-enylamino}phenylamino}eth-(*Z*)-ylidene]-4,4,5,5,6,6,6-heptafluoro-3-oxohexanenitrile (53): 1.2 g (5.0 mmol) 3-[4-(2-Cyano-1-methylvinylamino)phenylamino]but-2-enenitrile **52** and 1.0 g (10 mmol) triethylamine was dissolved in 300 mL of tetrahydrofuran. 2.7 g (11 mmol) 2,2,3,3,4,4,4-heptafluorobutyryl chloride was dissolved in 50 mL of tetrahydrofuran and was added dropwise with stirring during 1 h. Stirring was continued overnight and the precipitate was filtered. The solvent was removed under vacuo and the residue was recrystallised from diethyl ether yielding 2.2 g (70%) of a beige powder. ^{1}H NMR (500 MHz, $CDCl_3$, room temp.): δ = 2.47 (s, 6 H, CH_3), 7.39 (s, 4 H, arom.), 13.38 (s, 2 H, NH) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, room temp.): δ = 19.9 (CH_3), 83.3 (C=*C*–CN), 109.9 (tt, $^1J_{FC}$ = 269, $^2J_{FC}$ = 31 Hz, *C*F_2–CF_3), 115.3 (CN), 116.6 (t, $^2J_{FC}$ = 34 Hz, CF_3), 118.9 (t, $^2J_{FC}$ = 34 Hz, CO–*C*F_2), 127.4 (*o*,*m*-C), 136.1 (*i*-C), 174.1 (*C*=C–CN), 180.1 (t, $^2J_{FC}$ = 25 Hz, CO) ppm. ^{19}F NMR (471 MHz, $CDCl_3$, room temp.): δ = –80.7 (t, $^4J_{FF}$ = 9 Hz, 3 F, CF_3), –116.8 (q, $^4J_{FF}$ = 9 Hz, 2 F, CO–CF_2), –126.1 (s, 2 F, CF_2–CF_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 3426 (w, N–H), 2979 (m, CH), 2216 (vs, C≡N), 1631 (vs, C=O), 1570 (s, C=C), 1236 (vs, C–F) cm^{-1}. MS (EI): *m*/*z* = 630 [M$^+$], 461 [M$^+$ – C_3F_7], 394 [M$^+$ – C(CN)COC_3F_7], 263 [M$^+$ – $CH_3CC(CN)$-COC_3F_7], 200 [C_3F_7CO]. $C_{22}H_{12}F_{14}N_4O_2$ (630.34): calcd. C 41.92, H 1.92, N 8.89; found C 41.86, H 2.22, N 8.74.

Supporting Information (see also the footnote on the first page of this article): Preparation details and full characterisation of compounds **1**–**3**, **7**–**12**, **16**–**23**, **26**, **30**–**35**, **42**–**47**, **49**, **51** and **52**; refs.[44,46–48] refer to material in the Supporting Information.

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