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Electronic Supporting Information

Palladium(II) complexes with a phosphino-oxime ligand: Synthesis, structure and applications to the catalytic rearrangement and dehydration of aldoximes

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X-Ray crystal structure determination of compounds 1 and 2.

Crystals of [$PdCl_2${κ^2-(*P,N*)-2-$Ph_2PC_6H_4CH$=NOH}] (**1**) and [Pd{κ^2-(*P,N*)-2-$Ph_2PC_6H_4CH$=NOH}$_2$][Cl]$_2$ (**2**) suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into saturated solutions of the complexes in dichloromethane. The most relevant crystal and refinement data are collected in Table S1. Data collection was performed with an Oxford Diffraction Xcalibur Nova single crystal diffractometer using Cu-Kα radiation (λ = 1.5418 Å) for **1** and Mo-Kα radiation (λ = 0.71073 Å) for **2**. Images were collected at a fixed crystal-to-detector distance of 63 mm for **1** and 45 mm for **2**, using the oscillation method with 1.5º oscillation for **1** and 1º for **2**, and 4.63-52.66 s variable exposure time per image for **1** and 25.4 s for **2**. Data collection strategy was calculated with the program CrysAlis Pro CCD.[1] Data reduction and cell refinement was performed with the program CrysAlis Pro RED.[1] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[1] In both cases the software package WINGX was used for space group determination, structure solution, and refinement.[2]

The structures were solved by direct methods using SIR92 (for **1**)[3] and SIR2004 (for **2**).[4] Isotropic least-squares refinement on F^2 using SHELXL2014 was performed.[5] Compound **2** was refined as a two-component inversion twin (final BASF factor of -0.02). During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were geometrically located and their coordinates were refined riding on their parent atoms. For both **1** and **2** the H1 atom found from the Fourier map and included in a refinement with isotropic parameters. In the crystal of **1**, an independent molecule of the complex was found in the asymmetric unit. In the crystal of **2**, half molecule of the complex was found in the asymmetric unit, being the other half generated by symmetry. In both structures the maximum residual electron density is located near to heavy atoms. The function minimized was $[\Sigma\omega Fo^2 - Fc^2)/\Sigma\omega(Fo^2)]^{1/2}$ where $\omega = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ (a and b values are collected in Table 7) with $\sigma(Fo^2)$ from counting statistics and $P = (\text{Max}\ (Fo^2 + 2Fc^2)/3$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[6] Geometrical calculations were made with PARST.[7] The crystallographic plots were made with ORTEP-3[8] and Mercury.[9]

Table S1 Crystal data and structure refinement for compounds **1** and **2**

	1	**2**
Empirical formula	$C_{19}H_{16}Cl_2NOPPd$	$C_{38}H_{32}Cl_2N_2O_2P_2Pd$
Formula weight	482.60	787.89
Temperature/K	293	124
Wavelength/Å	1.54184	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	F*2dd*
Crystal size/mm	0.11 x 0.11 x 0.08	0.20 x 0.10 x 0.04
a/Å	9.3940(5)	10.2329(6)
b/Å	10.5702(6)	21.508(1)
c/Å	19.7348(8)	31.036(2)
α (º)	90	90
β (º)	90	90
γ (º)	90	90
Z	4	8
Volume/Å^3	1959.6(2)	6830.9(7)
Calculated density/g cm^{-3}	1.636	1.532
μ/mm^{-1}	10.973	0.831
F(000)	960	3200
θ range/º	4.48-69.32	2.95-27.71
Index ranges	$-11 \le h \le 10$	$-12 \le h \le 13$
	$-12 \le k \le 7$	$-26 \le k \le 27$
	$-22 \le l \le 23$	$-40 \le l \le 39$
Completeness to θ_{max}	94.6%	96.2%
No. of reflns. collected	6700	19091
No. of unique reflns.	3006 (R_{int} = 0.0585)	3744 (R_{int} = 0.0308)
No. of parameters/restraints	230/0	218/1
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.068	1.052
Weight function (a, b)	0.0357, 0.6707	0.0222, 9.7014
R_1 $[I > 2\sigma(I)]^a$	0.0407	0.0220
wR_2 $[I > 2\sigma(I)]^a$	0.0920	0.0492
R_1 (all data)	0.0467	0.0243
R_2 (all data)	0.0953	0.0503
Largest diff. peak and hole/e Å^{-3}	0.919 and -0.555	0.431 and -0.343

[a] $R_1 = \sum(|F_o|-|F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

An ORTEP view of the structure of [$PdCl_2${κ^2-(*P,N*)-2-$Ph_2PC_6H_4CH$=NOH}] (**1**), along with selected structural parameters, is shown in Fig. S1.

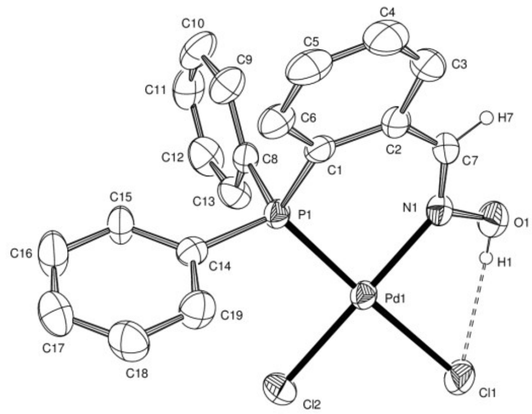

Fig. S1 ORTEP-type view of the structure of complex **1** showing the crystallographic labelling scheme. Hydrogen atoms, except those on C(7) and O(1), have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å): Pd-Cl(1) 2.373(3); Pd-Cl(2) 2.270(2); Pd-P(1) 2.221(2); Pd-N(1) 2.046(8); C(7)-N(1) 1.27(1); N(1)-O(1) 1.39(1). Selected bond angles (˚): Cl(1)-Pd-Cl(2) 90.6(2); Cl(1)-Pd-P(1) 175.6(1); Cl(1)-Pd-N(1) 88.8(2); Cl(2)-Pd-P(1) 92.12(9); Cl(2)-Pd-N(1) 177.3(2); P(1)-Pd-N(1) 88.7(2); C(2)-C(7)-N(1) 125.1(8); C(7)-N(1)-O(1) 113.2(7); C(7)-N(1)-Pd 132.8(6); Pd-N(1)-O(1) 113.9(6).

As expected, a square planar geometry around the metal is observed, with a maximum deviation from the mean $PdCl_2PN$ plane of 0.0474 Å for the palladium atom. The palladium coordination is characterized by metal-centered angles between 88.8(2) and 92.12(9)º, with the two chloride ligands mutually *cis* disposed. The larger Pd-Cl(1) *vs* Pd-Cl(2) bond length found (2.373(3) *vs* 2.270(2) Å) is consistent with the stronger *trans* influence of phosphorus compared to nitrogen. These distances, along with the Pd-P(1) (2.221(2) Å) and Pd-N(1) (2.046(8) Å) ones, are comparable to those described in the literature for related Pd(II) complexes containing more classical imino-phosphine 2-$Ph_2PC_6H_4CH$=NR (R = alkyl or aryl group) ligands.[10] Similarly, the C(7)-N(1) and N(1)-O(1) bond lengths (1.27(1) and 1.39(1) Å) show typical values for an oxime unit coordinated to palladium.[11] On the other hand, the close proximity of the hydroxyl-oxime function to one of the chloride ligands enabled the establishment of an intramolecular hydrogen bond between both groups.[12] The distances and angles of the O(1)-H(1)···Cl(1) contact (O(1)-H(1) = 0.820 Å, H(1)-Cl(1) = 2.351 Å, O(1)-

Cl(1) = 2.961 Å and O(1)-H(1)-Cl(1) = 131.78º) indicate, according with the Jeffrey´s terminology,[13] that the intensity of this H-bond is only moderate (mostly electrostatic).

An ORTEP view of the dication [Pd{κ^2-(*P,N*)-2-$Ph_2PC_6H_4CH$=NOH}$_2$]$^{2+}$ (**2**), where half of the molecule is generated by symmetry due to the presence of crystallographic C_2 axis that contains the palladium atom, is shown in Fig. S2 (selected bond distances and angles are listed in the caption).

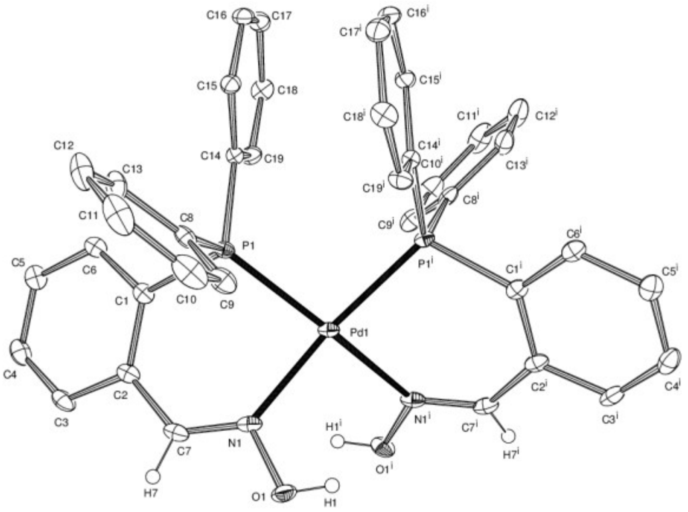

Fig. S2 ORTEP-type view of the structure of complex **2** showing the crystallographic labelling scheme. Atoms labelled with an "i" are related to those indicated by a crystallographic 2-fold symmetry axis. Hydrogen atoms, except those on C(7) and O(1), and chloride anions have been omitted for clarity. Thermal ellipsoids are drawn at 30% probability level. Selected bond lengths (Å): Pd-P(1) 2.256(1); Pd-N(1) 2.112(3); C(7)-N(1) 1.275(4); N(1)-O(1) 1.389(3). Selected bond angles (˚): P(1)-Pd-N(1) 86.20(7); P(1)-Pd-P(1)^i 97.92(4); P(1)-Pd-N(1)^I 164.08(7); N(1)-Pd-N(1)^I 94.0(1); N(1)-Pd-P(1)^I 164.08(7); C(2)-C(7)-N(1) 125.2(3); C(7)-N(1)-O(1) 112.8(3); C(7)-N(1)-Pd 133.5(2); Pd-N(1)-O(1) 113.7(2).

The stereochemistry found, with the two diphenylphosphino and oxime groups mutually *cis* disposed, is consistent with that previously observed in the solid-state structure of the analogous dicationic bis(imino-phosphine)-palladium(II) complex [Pd{κ^2-(*P,N*)-2-$Ph_2PC_6H_4CH$=N^{i}Pr}$_2$][ClO_4]$_2$.[14] The Pd-P(1) (2.256(1) Å) and Pd-N(1) (2.112(3) Å) bond distances in **2**, are also comparable to those found in [Pd{κ^2-(*P,N*)-2-$Ph_2PC_6H_4CH$=N^{i}Pr}$_2$][ClO_4]$_2$ (Pd-P = 2.257(2) and 2.255(2) Å, and Pd-N = 2.116(6) and 2.104(7) Å), for which no C_2 axis was present in the structure. Remarkably, the bond distances and angles for the oxime unit are almost identical to those observed for the neutral complex $[PdCl_2\{\kappa^2\text{-}(P,N)\text{-}2\text{-}Ph_2PC_6H_4CH{=}NOH\}]$ (**1**), reflecting that, once coordinated, the structure of the ligand is non-sensitive to the palladium environment. Also of note is that, in the structure of **2**, the chloride anions establish strong, charge-assisted, hydrogen-bonds with the OH groups of the phosphino-aldoxime ligands (see Fig. S3).

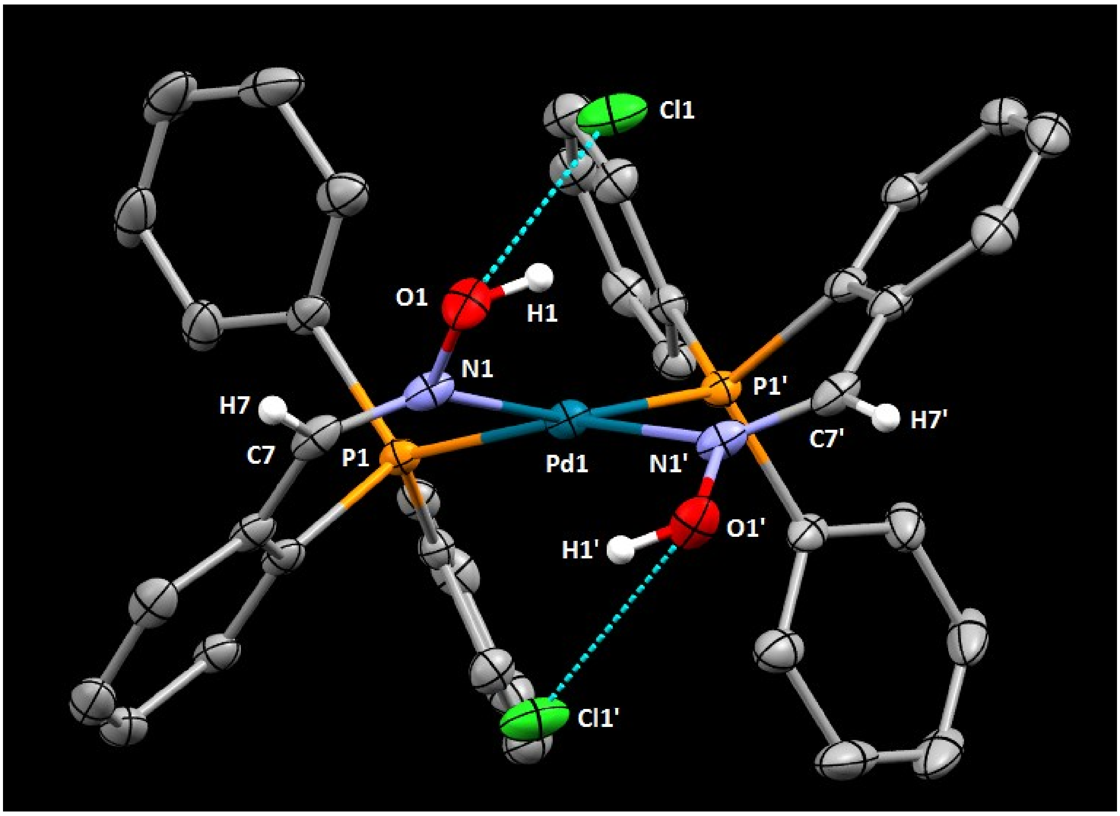

Fig. S3 View of the H-bond interactions present in the structure of complex **2**.

Donor-H	Donor...Acceptor	H...Acceptor	Donor-H......Acceptor
O1-H1	O1...Cl1	H1...Cl1	O1-H1...Cl1
0.820(.002)	2.920(.002)	2.303(.001)	132.52(0.16)

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NMR data for the amides isolated in this work.

Benzamide: ^{1}H NMR (CD_3OD): δ = 7.91-7.87 (m, 2H, CH_{arom}), 7.54 (m, 1H, CH_{arom}), 7.48-7.43 (m, 2H, CH_{arom}) ppm; NH_2 protons not observed. $^{13}C\{^{1}H\}$ NMR (CD_3OD): δ = 171.2 (s, C=O), 133.7 (s, C_{arom}), 131.6 (s, CH_{arom}), 128.1 (s, CH_{arom}), 127.3 (s, CH_{arom}) ppm.

2-Methylbenzamide: ^{1}H NMR ($CDCl_3$): δ = 7.46 (d, 1H, $^{3}J_{HH}$ = 8.1 Hz, CH_{arom}), 7.33 (m, 1H, CH_{arom}), 7.28-7.20 (m, 2H, CH_{arom}), 6.31 (br, 1H, NH), 5.89 (br, 1H, NH), 2.51 (s, 3H, Me) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 172.4 (s, C=O), 136.3 (s, C_{arom}), 135.3 (s, C_{arom}), 131.2 (s, CH_{arom}), 130.3 (s, CH_{arom}), 127.0 (s, CH_{arom}), 125.8 (s, CH_{arom}), 20.0 (s, Me) ppm.

3-Methylbenzamide: ^{1}H NMR (dmso-d_6): δ = 7.99 (br, 1H, NH), 7.70 (m, 2H, CH_{arom}), 7.38 (br, 1H, NH), 7.32 (m, 2H, CH_{arom}), 2.33 (s, 3H, Me) ppm. $^{13}C\{^{1}H\}$ NMR (dmso-d_6): δ = 168.7 (s, C=O), 137.9 (s, C_{arom}), 134.6 (s, C_{arom}), 132.3 (s, CH_{arom}), 128.5 (s, 2C, CH_{arom}), 125.1 (s, CH_{arom}), 21.4 (s, Me) ppm.

4-Methylbenzamide: ^{1}H NMR ($CDCl_3$): δ = 7.73 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, CH_{arom}), 7.26 (d, 2H, $^{3}J_{HH}$ = 7.8 Hz, CH_{arom}), 6.09 (br, 2H, NH), 2.42 (s, 3H, Me) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 170.2 (s, C=O), 142.6 (s, C_{arom}), 130.5 (s, C_{arom}), 129.3 (s, CH_{arom}), 127.4 (s, CH_{arom}), 20.0 (s, Me) ppm.

4-Methoxybenzamide: ^{1}H NMR ($CDCl_3$): δ = 7.79 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz, CH_{arom}), 6.96 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz, CH_{arom}), 5.90 (br, 2H, NH), 3.88 (s, 3H, OMe) ppm. $^{13}C\{^{1}H\}$ NMR (CD_3OD): δ = 174.6 (s, C=O), 166.7 (s, C_{arom}), 133.2 (s, CH_{arom}), 129.5 (s, C_{arom}), 117.3 (s, CH_{arom}), 58.6 (s, OMe) ppm.

4-Methylsulfanylbenzamide: ^{1}H NMR (dmso-d_6): δ = 8.09 (d, 2H, $^{3}J_{HH}$ = 8.1 Hz, CH_{arom}), 7.57 (d, 2H, $^{3}J_{HH}$ = 8.1 Hz, CH_{arom}), 2.78 (s, 3H, SMe) ppm; NH_2 protons not observed. $^{13}C\{^{1}H\}$ NMR (dmso-d_6): δ = 168.2 (s, C=O), 143.3 (s, C_{arom}), 131.0 (s, C_{arom}), 128.8 (s, CH_{arom}), 125.6 (s, CH_{arom}), 14.8 (s, SMe) ppm.

3-Chlorobenzamide: ^{1}H NMR ($CDCl_3$): δ = 7.83 (br, 1H, CH_{arom}), 7.69 (m, 1H, CH_{arom}), 7.54 (m, 1H, CH_{arom}), 7.41 (m, 1H, CH_{arom}), 6.14 (br, 2H, NH) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$):

δ = 168.0 (s, C=O), 135.1 (s, C_{arom}), 134.9 (s, C_{arom}), 132.1 (s, CH_{arom}), 130.0 (s, CH_{arom}), 127.8 (s, CH_{arom}), 125.4 (s, CH_{arom}) ppm.

4-Chlorobenzamide: ^1H NMR (CD_3OD): δ = 7.86 (d, 2H, $^3J_{HH}$ = 8.8 Hz, CH_{arom}), 7.49 (d, 2H, $^3J_{HH}$ = 8.8 Hz, CH_{arom}) ppm; NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 169.7 (s, C=O), 137.6 (s, C_{arom}), 132.3 (s, C_{arom}), 129.0 (s, CH_{arom}), 128.3 (s, CH_{arom}) ppm.

2,6-Dichlorobenzamide: ^1H NMR (CD_3OD): δ = 7.46-7.35 (m, 3H, CH_{arom}) ppm. NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 168.1 (s, C=O), 136.2 (s, C_{arom}), 131.6 (s, C_{arom}), 130.7 (s, CH_{arom}), 127.9 (s, CH_{arom}) ppm.

2-Chloro-6-fluorobenzamide: ^1H NMR (CD_3OD): δ = 7.47-7.40 (m, 1H, CH_{arom}), 7.32 (m, 1H, CH_{arom}), 7.20-7.14 (m, 1H, CH_{arom}) ppm; NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 166.2 (s, C=O), 159.1 (d, $^1J_{CF}$ = 250.5 Hz, C_{arom}), 131.4 (d, $^3J_{CF}$ = 5.7 Hz, C_{arom}), 131.1 (d, $^3J_{CF}$ = 8.9 Hz, CH_{arom}), 125.3 (s, C_{arom}), 125.2 (s, CH_{arom}), 114.1 (d, $^2J_{CF}$ = 22.3 Hz, CH_{arom}) ppm.

Pentafluorobenzamide: $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ = -139.6 (m, 2F), -149.5 (m, 1F), -159.7 (m, 2F) ppm.

2-Nitrobenzamide: ^1H NMR (CD_3OD): δ = 8.08 (m, 1H, CH_{arom}), 7.80-7.62 (m, 3H, CH_{arom}) ppm; NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 170.4 (s, C=O), 146.7 (s, C_{arom}), 133.5 (s, CH_{arom}), 132.5 (s, C_{arom}), 130.5 (s, CH_{arom}), 128.6 (s, CH_{arom}), 124.0 (s, CH_{arom}) ppm.

4-Nitrobenzamide: ^1H NMR (dmso-d_6): δ = 8.28 (m, 3H, CH_{arom} and NH), 8.09 (d, 2H, $^3J_{HH}$ = 9.5 Hz, CH_{arom}), 7.73 (br, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (dmso-d_6): δ = 166.7 (s, C=O), 149.5 (s, C_{arom}), 140.4 (s, C_{arom}), 129.4 (s, CH_{arom}), 123.9 (s, CH_{arom}) ppm.

2-Naphthylcarboxamide: ^1H NMR (dmso-d_6): δ = 8.49 (s, 1H, CH_{arom}), 8.17 (br, 1H, NH), 7.98 (m, 4H, CH_{arom}), 7.60 (m, 2H, CH_{arom}), 7.49 (br, 1H, NH) ppm. $^{13}C\{^1H\}$ NMR (dmso-d_6): δ = 168.5 (s, C=O), 134.7 (s, C_{arom}), 132.6 (s, C_{arom}), 132.0 (s, C_{arom}), 129.3 (s, CH_{arom}), 128.3 (s, 2C, CH_{arom}), 128.1 (s, 2C, CH_{arom}), 127.1 (s, CH_{arom}), 124.9 (s, CH_{arom}) ppm.

Hexanamide: ^{1}H NMR (CD_3OD): δ = 2.21 (t, 2H, $^3J_{HH}$ = 7.2 Hz, CH_2), 1.61 (m, 2H, CH_2), 1.34 (m, 4H, CH_2), 0.96 (t, 3H, $^3J_{HH}$ = 6.9 Hz, Me) ppm; NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 178.3 (s, C=O), 35.2 (s, CH_2), 31.2 (s, CH_2), 25.2 (s, CH_2), 22.1 (s, CH_2), 12.9 (s, Me) ppm.

Heptanamide: ^{1}H NMR ($CDCl_3$): δ = 6.37 (br, 2H, NH), 2.29 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2), 1.64 (m, 2H, CH_2), 1.36 (m, 6H, CH_2), 0.90 (t, 3H, $^3J_{HH}$ = 6.3 Hz, Me) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 177.5 (s, C=O), 35.6 (s, CH_2), 31.5 (s, CH_2), 28.8 (s, CH_2), 25.5 (s, CH_2), 22.6 (s, CH_2), 14.1 (s, Me) ppm.

3-Phenylpropionamide: ^{1}H NMR (CD_3OD): δ = 7.29-7.13 (m, 5H, CH_{arom}), 2.91 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2), 2.50 (t, 2H, $^3J_{HH}$ = 7.5 Hz, CH_2) ppm; NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 176.8 (s, C=O), 140.8 (s, C_{arom}), 128.2 (s, CH_{arom}), 128.0 (s, CH_{arom}), 125.9 (s, CH_{arom}), 37.0 (s, CH_2), 31.4 (s, CH_2) ppm.

Cyclohexylcarboxamide: ^{1}H NMR (CD_3OD): δ = 2.23 (m, 1H, CH), 1.81 (m, 4H, CH_2), 1.78 (m, 1H, CH_2), 1.72-1.49 (m, 5H, CH_2) ppm; NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 180.9 (s, C=O), 44.5 (s, CH), 29.3 (s, CH_2), 25.5 (s, CH_2), 25.4 (s, CH_2) ppm.

(*S*)-Citronellamide: ^{1}H NMR (CD_3OD): δ = 5.12 (m, 1H, =CH), 2.25-1.91 (m, 5H, CH and CH_2), 1.68 (s, 3H, Me), 1.62 (s, 3H, Me), 1.45-1.30 (m, 2H, CH_2), 0.91 (d, 3H, $^3J_{HH}$ = 6.8 Hz, Me) ppm; NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 177.2 (s, C=O), 130.9 (s, =C), 124.2 (s, =CH), 42.9 (s, CH_2), 36.7 (s, CH_2), 30.2 (s, CH), 25.1 (s, Me), 24.6 (s, CH_2), 18.6 (s, Me), 16.5 (s, Me) ppm.

(*E*)-3-Phenylacrylamide: ^{1}H NMR (CD_3OD): δ = 7.58 (d, 1H, $^3J_{HH}$ = 15.9 Hz, =CH), 7.54 (m, 2H, CH_{arom}), 7.36 (m, 3H, CH_{arom}), 6.66 (d, 1H, $^3J_{HH}$ = 15.9 Hz, =CH) ppm; NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 169.7 (s, C=O), 141.5 (s, =CH), 134.9 (s, C_{arom}), 129.7 (s, CH_{arom}), 128.7 (s, CH_{arom}), 127.7 (s, CH_{arom}), 120.1 (s, =CH) ppm.

(*E*)-3-(4-Chlorophenyl)acrylamide: ^{1}H NMR (CD_3OD): δ = 7.57 (d, 2H, $^3J_{HH}$ = 9.0 Hz, CH_{arom}), 7.52 (d, 1H, $^3J_{HH}$ = 15.9 Hz, =CH), 7.42 (d, 2H, $^3J_{HH}$ = 9.0 Hz, CH_{arom}), 6.65 (d, 1H, $^3J_{HH}$ = 15.9 Hz, =CH) ppm; NH_2 protons not observed. $^{13}C\{^1H\}$ NMR (CD_3OD): δ = 169.4 (s, C=O), 139.8 (s, =CH), 135.3 (s, C_{arom}), 133.5 (s, C_{arom}), 129.0 (s, CH_{arom}), 128.8 (s, CH_{arom}), 120.9 (s, =CH) ppm.

NMR data for the nitriles isolated in this work.

Benzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.55 (m, 3H, CH_{arom}), 7.40 (m, 2H, CH_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 132.8 (s, CH_{arom}), 132.0 (s, CH_{arom}), 129.2 (s, CH_{arom}), 118.8 (s, C≡N), 112.3 (s, C_{arom}) ppm.

2-Methylbenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.54 (d, 1H, $^{3}J_{HH}$ = 7.2 Hz, CH_{arom}), 7.44 (dd, (dd, 1H, $^{3}J_{HH}$ = 8.7 and 8.1 Hz, CH_{arom}), 7.25 (m, 2H, CH_{arom}), 2.49 (s, 3H, Me) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 141.8 (s, C_{arom}), 132.7 (s, CH_{arom}), 132.4 (s, CH_{arom}), 130.2 (s, CH_{arom}), 126.2 (s, CH_{arom}), 118.1 (s, C≡N), 112.7 (s, C_{arom}), 20.6 (s, Me) ppm.

3-Methylbenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.45-7.28 (m, 4H, CH_{arom}), 2.37 (s, 3H, Me) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 139.2 (s, C_{arom}), 133.7 (s, CH_{arom}), 132.4 (s, CH_{arom}), 129.2 (s, CH_{arom}), 129.0 (s, CH_{arom}), 119.0 (s, C≡N), 112.1 (s, C_{arom}), 21.1 (s, Me) ppm.

4-Methylbenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.56 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz, CH_{arom}), 7.29 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz, CH_{arom}), 2.44 (s, 3H, Me) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 143.7 (s, C_{arom}), 132.0 (s, CH_{arom}), 129.9 (s, CH_{arom}), 119.2 (s, C≡N), 109.4 (s, C_{arom}), 22.0 (s, Me) ppm.

4-Methoxybenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.60 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz, CH_{arom}), 6.96 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz, CH_{arom}), 3.87 (s, 3H, OMe) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 163.0 (s, C_{arom}), 134.1 (s, CH_{arom}), 119.3 (s, C≡N), 114.9 (s, CH_{arom}), 104.0 (s, C_{arom}), 55.7 (s, OMe) ppm.

4-Methylsulfanylbenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.53 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz, CH_{arom}), 7.25 (d, 2H, $^{3}J_{HH}$ = 8.5 Hz, CH_{arom}), 2.51 (s, 3H, SMe) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 146.1 (s, C_{arom}), 132.2 (s, CH_{arom}), 125.5 (s, CH_{arom}), 119.0 (s, C≡N), 107.6 (s, C_{arom}), 14.7 (s, SMe) ppm.

3-Chlorobenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.66-7.56 (m, 3H, CH_{arom}), 7.46 (m, 1H, CH_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 135.2 (s, C_{arom}), 133.3 (s, CH_{arom}), 131.9 (s, CH_{arom}), 130.5 (s, CH_{arom}), 130.3 (s, CH_{arom}), 117.5 (s, C≡N), 114.0 (s, C_{arom}) ppm.

4-Chlorobenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.62 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz, CH_{arom}), 7.48 (d, 2H, $^{3}J_{HH}$ = 8.4 Hz, CH_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 139.6 (s, C_{arom}), 133.4 (s, CH_{arom}), 129.8 (s, CH_{arom}), 118.1 (s, C≡N), 110.8 (s, C_{arom}) ppm.

2,6-Dichlorobenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.52-7.41 (m, 3H, CH_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 138.4 (s, C_{arom}), 134.0 (s, CH_{arom}), 128.3 (s, CH_{arom}), 114.3 (s, C_{arom} or C≡N), 113.4 (s, C_{arom} or C≡N) ppm.

2-Chloro-6-fluorobenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.55 (m, 1H, CH_{arom}), 7.31 (m, 1H, CH_{arom}), 7.15 (m, 1H, CH_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 159.2 (d, $^{1}J_{CF}$ = 263.2 Hz, C_{arom}), 137.7 (s, C_{arom}), 135.2 (d, $^{3}J_{CF}$ = 9.9 Hz, CH_{arom}), 125.8 (d, $^{4}J_{CF}$ = 3.6 Hz, CH_{arom}), 114.7 (d, $^{2}J_{CF}$ = 18.3 Hz, CH_{arom}), 111.2 (s, C≡N), 103.1 (d, $^{2}J_{CF}$ = 18.2 Hz, C_{arom}) ppm.

Pentafluorobenzonitrile: $^{19}F\{^{1}H\}$ NMR ($CDCl_3$): δ = -131.6 (m, 2F), -142.2 (m, 1F), -158.2 (m, 2F) ppm.

2-Nitrobenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 8.31 (m, 1H, CH_{arom}), 7.94-7.84 (m, 3H, CH_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 148.2 (s, C_{arom}), 135.8 (s, CH_{arom}), 134.7 (s, CH_{arom}), 134.1 (s, CH_{arom}), 125.6 (s, CH_{arom}), 115.2 (s, C≡N), 107.8 (s, C_{arom}) ppm.

4-Nitrobenzonitrile: ^{1}H NMR ($CDCl_3$): δ = 8.37 (d, 2H, $^{3}J_{HH}$ = 8.2 Hz, CH_{arom}), 7.90 (d, 2H, $^{3}J_{HH}$ = 8.2 Hz, CH_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 150.1 (s, C_{arom}), 133.6 (s, CH_{arom}), 124.4 (s, CH_{arom}), 118.4 (s, C_{arom} or C≡N), 116.8 (s, C_{arom} or C≡N) ppm.

2-Naphthylcarbonitrile: ^{1}H NMR ($CDCl_3$): δ = 8.23 (s, 1H, CH_{arom}), 7.98 (m, 3H, CH_{arom}), 7.62 (m, 3H, CH_{arom}) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 134.6 (s, C_{arom}), 134.2 (s, CH_{arom}), 132.2 (s, C_{arom}), 129.2 (s, CH_{arom}), 129.1 (s, CH_{arom}), 128.4 (s, CH_{arom}), 128.1 (s, CH_{arom}), 127.6 (s, CH_{arom}), 126.3 (s, CH_{arom}), 119.3 (s, C≡N), 109.3 (s, C_{arom}) ppm.

Hexanenitrile: ^{1}H NMR ($CDCl_3$): δ = 2.24 (t, 2H, $^3J_{HH}$ = 7.3 Hz, CH_2), 1.57 (m, 2H, CH_2), 1.27 (m, 4H, CH_2), 0.79 (t, 3H, $^3J_{HH}$ = 6.8 Hz, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 119.7 (s, C≡N), 30.6 (s, CH_2), 25.0 (s, CH_2), 21.7 (s, CH_2), 16.9 (s, CH_2), 13.6 (s, Me) ppm.

Heptanenitrile: ^{1}H NMR ($CDCl_3$): δ = 2.32 (t, 2H, $^3J_{HH}$ = 6.5 Hz, CH_2), 1.64 (m, 2H, CH_2), 1.45 (m, 2H, CH_2), 1.30 (m, 4H, CH_2), 0.88 (t, 3H, $^3J_{HH}$ = 6.3 Hz, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 119.8 (s, C≡N), 30.9 (s, CH_2), 28.3 (s, CH_2), 25.3 (s, CH_2), 22.4 (s, CH_2), 17.1 (s, CH_2), 13.9 (s, Me) ppm.

3-Phenylpropionitrile: ^{1}H NMR ($CDCl_3$): δ = 7.41-7.26 (m, 5H, CH_{arom}), 2.96 (t, 2H, $^3J_{HH}$ = 7.9 Hz, CH_2), 2.61 (t, 2H, $^3J_{HH}$ = 7.9 Hz, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 138.2 (s, C_{arom}), 128.9 (s, CH_{arom}), 128.4 (s, CH_{arom}), 127.3 (s, CH_{arom}), 119.3 (s, C≡N), 31.5 (s, CH_2), 19.4 (s, CH_2) ppm.

Cyclohexylcarbonitrile: ^{1}H NMR ($CDCl_3$): δ = 2.56 (br, 1H, CH), 1.76-1.37 (m, 10H, CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 122.8 (s, C≡N), 29.4 (s, CH_2), 27.8 (s, CH_2), 25.2 (s, CH), 24.0 (s, CH_2) ppm.

(*S*)-Citronellylnitrile: ^{1}H NMR ($CDCl_3$): δ = 5.03 (m, 1H, =CH), 2.33-2.16 (m, 2H, CH_2), 1.94 (m, 2H, CH_2), 1.87 (m, 1H, CH), 1.64 (s, 3H, Me), 1.56 (s, 3H, Me), 1.45 (m, 2H, CH_2), 0.94 (d, 3H, $^3J_{HH}$ = 6.9 Hz, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 132.3 (s, =C), 123.7 (s, =CH), 119.2 (s, C≡N), 35.8 (s, CH_2), 30.0 (s, CH), 25.7 (s, CH_2), 25.2 (s, Me), 24.3 (s, CH_2), 19.3 (s, Me), 17.6 (s, Me) ppm.

(*E*)-3-Phenylacrylonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.42 (br, 5H, CH_{arom}), 7.34 (d, 1H, $^3J_{HH}$ = 16.5 Hz, =CH), 5.85 (d, 1H, $^3J_{HH}$ = 16.5 Hz, =CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 150.6 (s, =CH), 133.7 (s, C_{arom}), 131.4 (s, CH_{arom}), 129.2 (s, CH_{arom}), 127.7 (s, CH_{arom}), 118.4 (s, C≡N), 96.4 (s, =CH) ppm.

(*E*)-3-(4-Chlorophenyl)acrylonitrile: ^{1}H NMR ($CDCl_3$): δ = 7.37 (br, 4H, CH_{arom}), 7.33 (d, 1H, $^3J_{HH}$ = 18.9 Hz, =CH), 5.86 (d, 1H, $^3J_{HH}$ = 18.9 Hz, =CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 149.2 (s, =CH), 137.2 (s, C_{arom}), 132.1 (s, C_{arom}), 129.4 (s, CH_{arom}), 128.6 (s, CH_{arom}), 118.2 (s, C≡N), 97.8 (s, =CH) ppm.