Supporting Information to

Synthesis, Characterization and Pd (II)-Coordination Chemistry of the Ligand Tris(quinolin-8-yl)phosphite. Application in Catalytic Aerobic Oxidation of Amines

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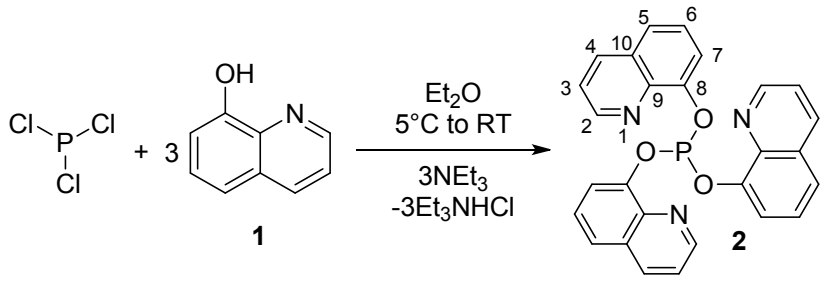
A. General information

All reactions and manipulations were routinely performed under dry nitrogen or argon atmosphere using standard Schlenk techniques. Glassware was flame dried under high vacuum or dried at 120 °C overnight prior to use. Unless otherwise stated, all solvents were degassed and distilled just prior to use from appropriate drying agents. Dichloromethane and CD_2Cl_2 were distilled from calcium hydride (CaH_2). Diethyl ether (Et_2O), THF, THF-d_8 and *n*-hexane were distilled from sodium/benzophenone. DMSO-d_6 and $CDCl_3$ were dried over molecular sieves. 8-Hydroxyquinoline was sublimed under reduced pressure and used fresh. PCl_3 and NEt_3 were distilled just prior to use. The air sensitive phosphite **2** was stored and weighed in a glovebox (*M Braun: 150-GI* or *lab master 130*). [$PdCl_2$(COD)] was prepared using a method described in the literature (COD = 1,5-cyclooctadiene, C_8H_{12}).[1] [$Pd(PPh_3)_2Cl_2$] and $PdCl_2$ were purchased from Aldrich and used as received. [$Pd(P(OPh)_3)_2Cl_2$] was prepared using a method described in the literature.[2] Amines, ^{n}BuLi, 1, 3, 5-trimethoxybenzene and toluene were used as received from the commercial suppliers. Catalytic runs under pressure were conducted in a 96 mL stainless-steel reactor (Parr 5500 Series Compact Reactor) equipped with a small motor for mechanical stirring, a thermostat and a transducer (Parr 4842 controller).

Solution ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on Bruker Avance 300, 400 or 600 MHz spectrometers at Laboratorio Nacional de Resonancia Magnética Nuclear, Instituto Venezolano de Investigaciones Cientificas (IVIC). Peak positions are relative to tetramethylsilane, for ^{1}H and ^{13}C{^{1}H}, and phosphoric acid, for ^{31}P{^{1}H}. The chemical shifts (δ) are measured according to IUPAC,[3] expressed in parts per million (ppm) and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). Coupling constants J are given in Hertz (Hz) as absolute values. The multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets, respectively. The abbreviation br. is given for broadened signals. Quaternary carbon atoms are indicated as C^{quat} and aromatic units as CH^{ar}. All the NMR spectra were recorded at room temperature (25 °C) unless otherwise stated. IR spectra were recorded on a Bruker Alpha Platinum ATR (Regensburg University) and a Nicolet IS10 spectrometer (Universidad Simon Bolivar, Laboratorio de Análisis Instrumental). The absorption bands are described as follows: strong (s), very strong (vs), middle (m), weak (w), or broad (br). HRMS analysis was performed using a Varian HighResMALDI at ETH Zürich DCHAB/LOC MS-Service. LIFDI-MS analysis was performed using a JeolAccuTOF GCX at University of Regensburg/Zentrale Analitik Massenspectromitrie. Low resolution MS analyses (HESI) were performed on a Finnigan LXQ mass spectrometer at IVIC MS-Service. UV-Vis measurements were performed on an Evolution 260 Bio UV-Visible spectrophotometer by Thermo Scientific with a diode array system as detector (Laboratorio de Química Bioinorganica, IVIC). Elemental analyses were carried out in an Elementar Vario Micro Cube instrument, at Regensburg University. X–ray Diffraction studies were performed at T = 100 K on a Bruker SMART Apex II diffractometer equipped with a CCD area detector; MoKα radiation (0.71073 Å) from a fine-focus sealed tube. A summary of crystal data and structure refinement parameters for the ligand $P(Oquin)_3$ (**2**) and its Pd(II) complex [$Pd\{P(Oquin)_3\}Cl_2$] (**3**) is reported in Table S1. The refinement against full matrix (versus F^2) was performed with SHELXL-2016/6 (compound **3**) and SHELXL-97 (compound **2**).[4] All C-H atoms were refined freely. Empirical absorption correction was performed with SADABS (ver. 2.03). All non-hydrogen atoms were refined anisotropically. The H Atoms of the CH_2 group C1S(H1SA,H1SB) in compound 3 were placed in idealized positions and refined using a riding model with appropriate displacement parameters of Uiso(H) = 1.2Ueq(parent). Data for **3** was processed with the OLEX2 Software package.[5]

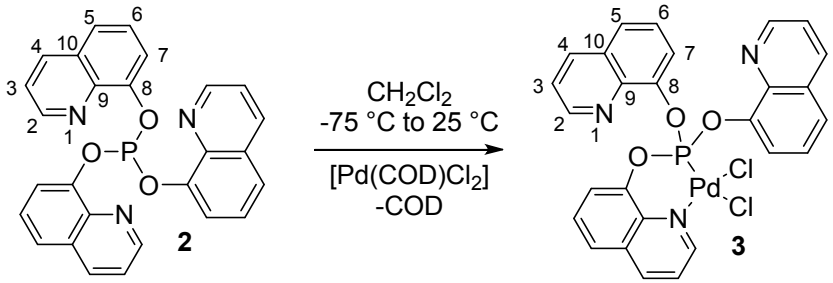
B. Synthesis

Preparation of tris(quinolin-8-yl)phosphite, **2**.



To a solution of 8-hydroxyquinoline (3.28 g, 22.57 mmol) in Et_2O (50 mL) a solution of triethylamine (2.36 g, 23.30 mmol) in Et_2O (50 mL) was added dropwise, while stirring. Then, a solution of phosphorus trichloride (635 µL, ca. 1g, 7.28 mmol) in Et_2O (100 mL) was added dropwise at 5 °C (ice bath) for 1 h. Once this addition was finished, the mixture was left to warm up to room temperature for 3 h. A colorless solid was formed (product **2** plus NEt_3•HCl) and the mother liquors were analyzed by $^{31}P\{^1H\}$ NMR. Typically, PCl_3 reacts within 3-5 h. Depending on the amount of moisture/air present during the reaction a yellow or reddish solution could be formed. The solid was filtered off and washed twice with Et_2O (30 mL) to eliminate unreacted **1**, hydrolyzed product, NEt_3 and the yellow/reddish side product. Then CH_2Cl_2 (50 mL) was added two times to extract the phosphite from the residual ammonium salt. The solvent was removed under reduced pressure to obtain a white powder (2.85 g, 85% yield). ^1H NMR (300.1 MHz, CD_2Cl_2, 25ºC): δ = 8.36 (dd, $^3J_{HH}$ = 4.2 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H2), 8.17 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H4), 7.60-7.49 (m, 3H, H5-7), 7.30 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.2 Hz, 1H, H3). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 25ºC): δ = 150.5 (s, C^{quat}), 148.8 (s, C2), 140.9 (s, C^{quat}), 135.7 (s, C4), 129.6 (s, C^{quat}), 126.8, 122.2 (s, C5 & C6), 121.4 (s, C3), 118.8 (d, $^3J_{PC}$ = 5.5 Hz, C7). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25ºC): δ = 129.0 (s). ^1H NMR (400.1 MHz, THF-d_8, 25ºC): δ = 8.28 (dd, $^3J_{HH}$ = 4.1 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H2), 8.16 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.7 Hz, 1H, H4), 7.56-7.44 (m, 3H, H5-7), 7.26 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.1 Hz, 1H, H3). $^{31}P\{^1H\}$ NMR (162 MHz, THF-d_8, 25ºC): δ = 130.9 (s). HRMS (MALDI): m/z calc. for $C_{27}H_{18}N_3O_3PNa$ 486.0978 $[M+Na]^+$; found 486.0974. Analytically pure samples were only obtained by using ^{n}BuLi (3.05 equiv., 85% yield) instead of NEt_3 as base. Anal. Calcd. for $C_{27}H_{18}N_3O_3P$•$0.5CH_2Cl_2$ C, 65.29; H, 3.79; N, 8.31. Found: C, 65.78; H, 3.95; N, 8.26. ATR IR (ν in cm^{-1}): 3036 w, 3008 w, 1614 w, 1594 w, 1568 w, 1497 m, 1466 m, 1421 w, 1389 w, 1371 w, 1312 m, 1243 s, 1165 w, 1089 s, 1055 s, 1027 w, 962 w, 913 w, 892 s, 844 m, 821 s, 810 s, 788 m, 767 s, 751 s, 711 m, 680 s, 658 m, 632 w, 607 w, 588 w, 573 w, 559 w, 544 m, 532 w, 505 w, 481 w, 465 w, 432 m, 431 m, 415 w.

Preparation of *cis*-dichloro-(*P*,*N*)-tris(quinolin-8-yl)phosphite palladium (II), **3**.



To a solution of $[PdCl_2(COD)]$ (242.0 mg, 0.84 mmol) in CH_2Cl_2 (10 mL) was added a solution of **2** (397.0 mg, 0.85 mmol) in CH_2Cl_2 (10 mL) at -75 °C, and the mixture was stirred for 30 min. Then, the mixture was left to warm up to room temperature and was stirred for additional 3 h. All volatile materials were removed under reduced pressure. The complex was washed twice with dried Et_2O (20 mL) and twice with dried hexane (20 mL). The solid was dried under vacuum to obtain a pale yellow solid (426.0 mg, 79%

yield). ^{1}H NMR (300.2 MHz, $CDCl_3$, 25ºC): δ = 10.26 (d, $^{3}J_{HH}$ = 5.4 Hz, 1H, H2), 8.48 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, H4), 7.79-7.68 (m, 3H, H5-7), 7.62 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 5.4 Hz, 1H, H3). Given the poor solubility of **3** in $CDCl_3$, the ^{13}C resonances are poorly resolved. ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25ºC): δ = 31.8 (s). ^{1}H NMR (600.1 MHz, DMSO-d_6, 25ºC): δ = 10.11 (d, $^{3}J_{HH}$ = 5.1 Hz, 1H, H2), 8.94 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, H4), 8.08 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H, H5), 7.93 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 5.3 Hz, 1H, H3), 7.90-7.85 (m, 2H, H6-7). ^{13}C{^{1}H} NMR (150.9 MHz, DMSO-d_6, 25ºC): δ = 159.1 (s, C2), 142.5 (s, C4), 129.0 (s, C6), 126.2 (s, C5), 123.0 (s, C3), 122.4 (d, $^{3}J_{PC}$ = 5.5 Hz, C7), quaternary carbons (C8-10) are poorly resolved. ^{31}P{^{1}H} NMR (121.5 MHz, DMSO-d_6, 25ºC): δ = 32.3 (s). LRMS (ESI): m/z calc. for $C_{28}H_{21}N_3O_4PPdNa$ 692.96 $[M•MeOH+Na]^{+}$; found 692.96. Analytically pure samples were obtained upon recrystallization in $CHCl_3$. Anal. Calcd. for $C_{27}H_{18}N_3O_3Cl_2PPd•3.5CHCl_3$: C, 34.61; H, 2.05; N, 3.97. Found: C, 34.44; H, 1.99; N, 3.58. IR (KBr disk, ν in cm^{-1}): 1634 m, 1593 w, 1579 w, 1511 m, 1502 w, 1466 m, 1385 m, 1377 m, 1307 m, 1253 m, 1240 w, 1196 m, 1098 m, 923 m, 854 m, 826 m, 760 m, 753 m, 721 m, 603 w, 575 w, 459 w. UV-Vis ($CHCl_3$, λ_{max} in nm): 246, 328.

C. NMR spectra

C.1. ^{1}H NMR of **2** and **3**

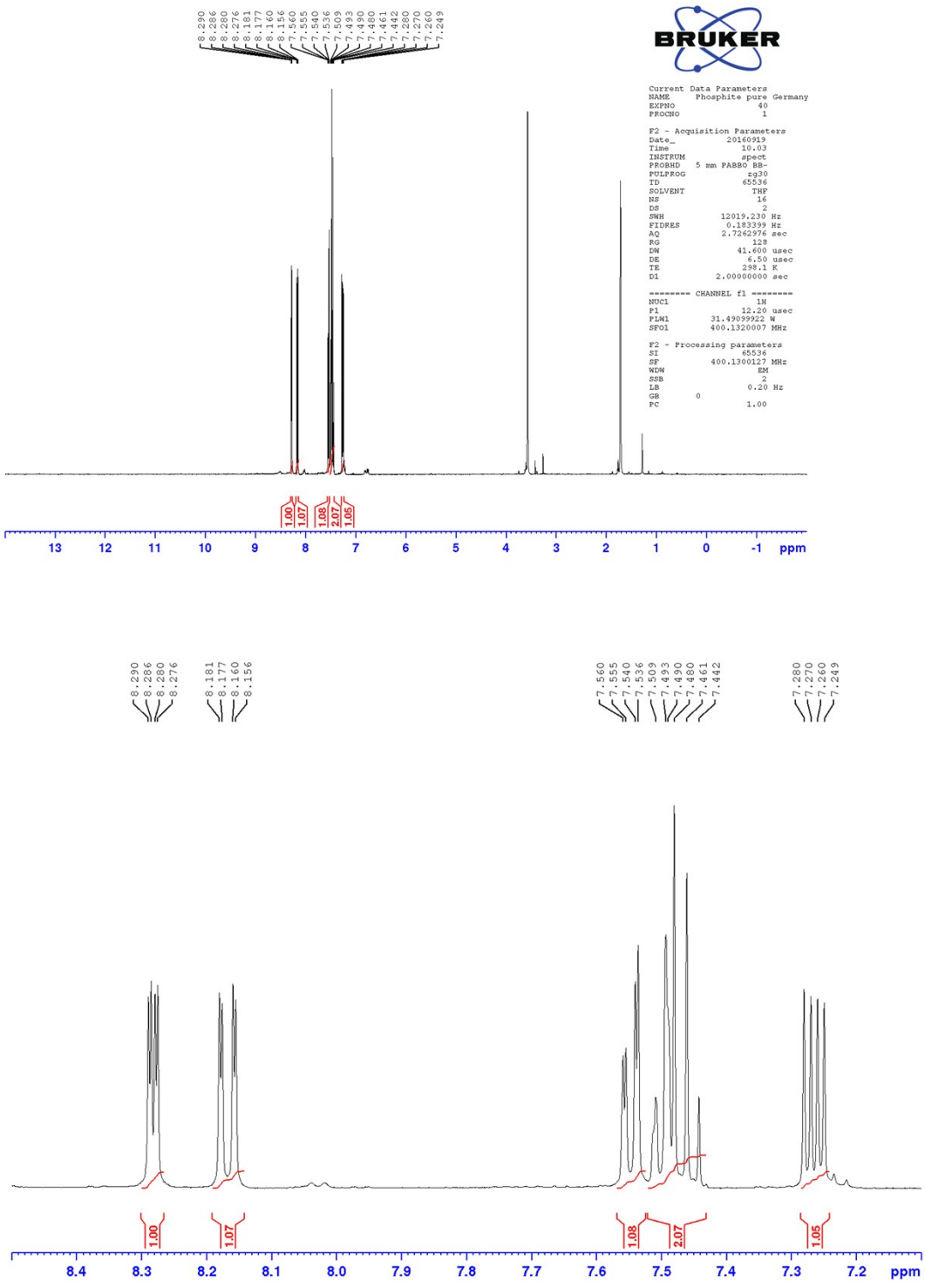


Figure S1. ^{1}H NMR spectrum (400.1 MHz) at 298 K of **2** in THF-d_8.

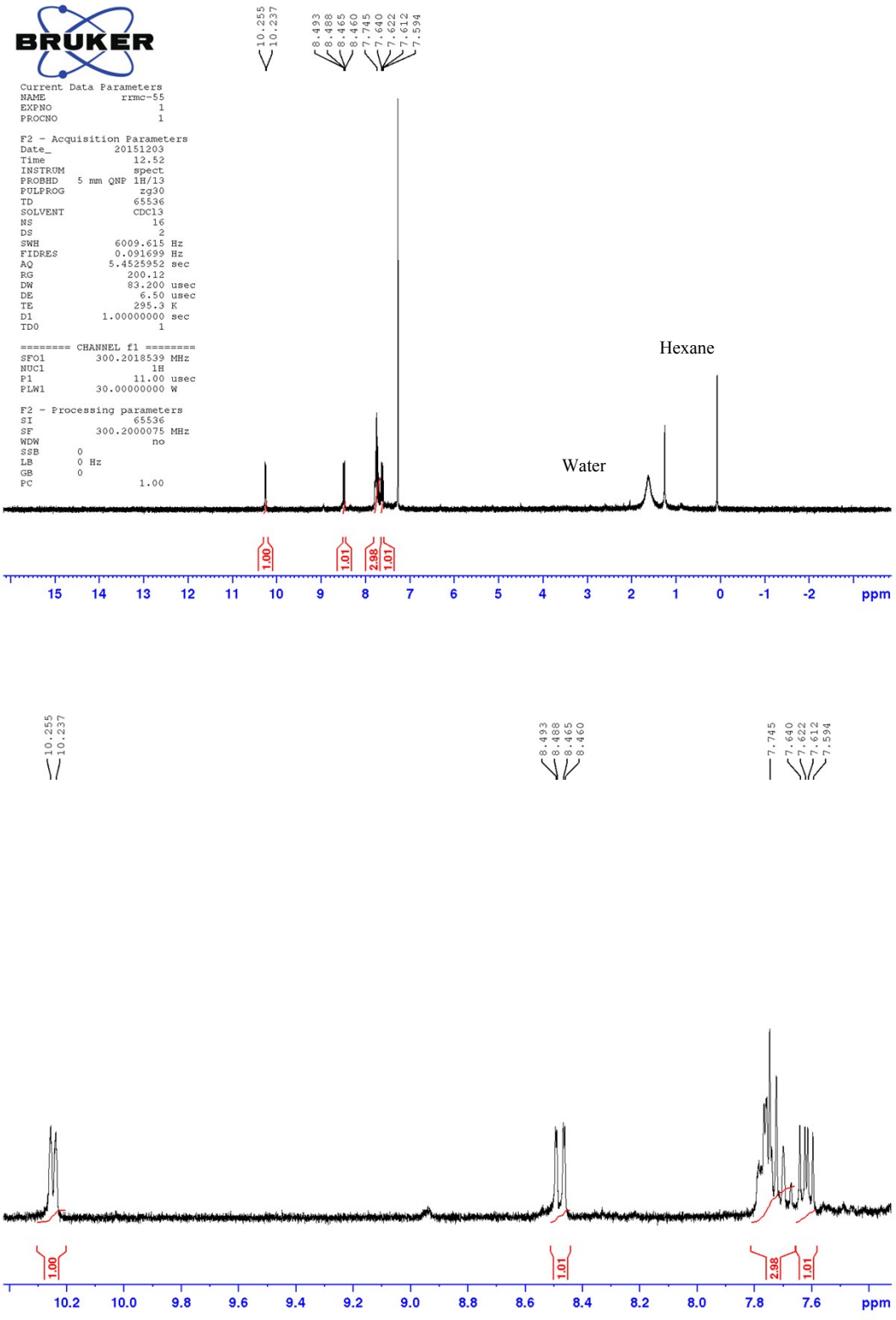


Figure S2. ^{1}H NMR spectrum (300.1 MHz) at 298 K of **3** in $CDCl_3$.

C.2. $^{31}P\{^{1}H\}$ NMR of **2** and **3**

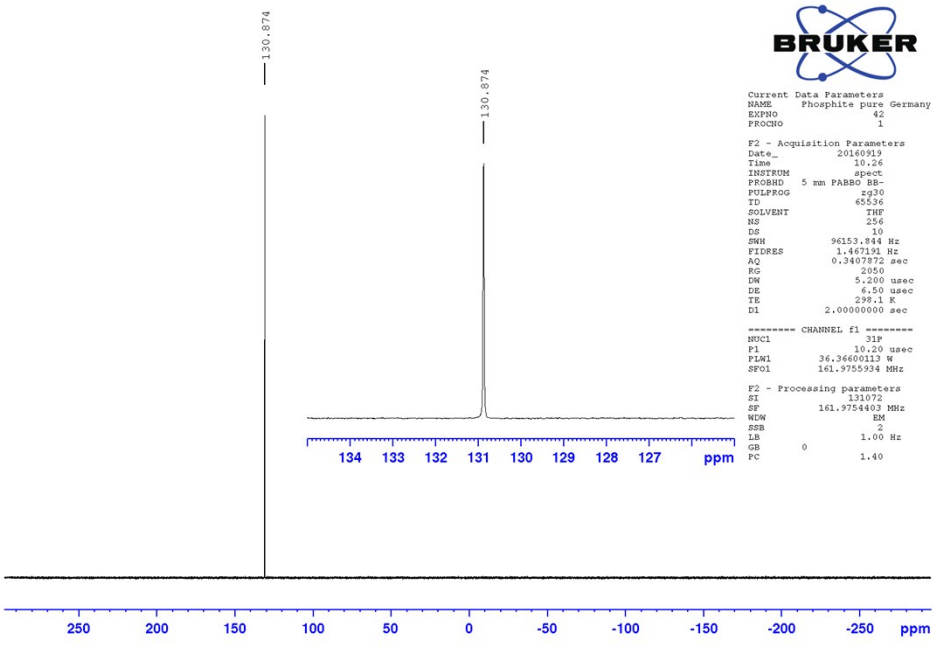


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz) at 298 K of **2** in THF-d_8.

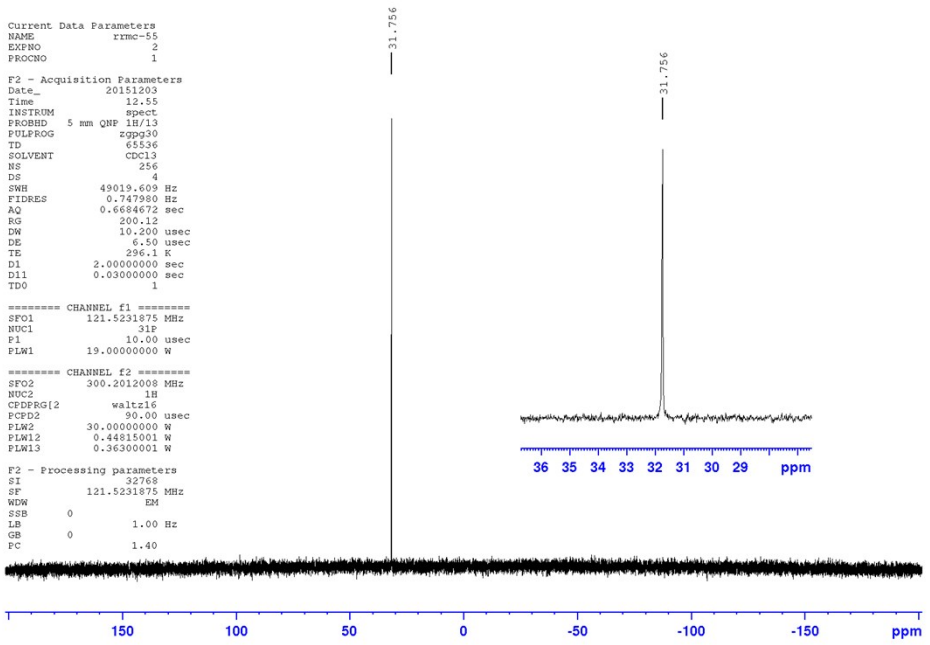


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (121.5 MHz) at 298 K of **3** in $CDCl_3$.

D. IR spectra

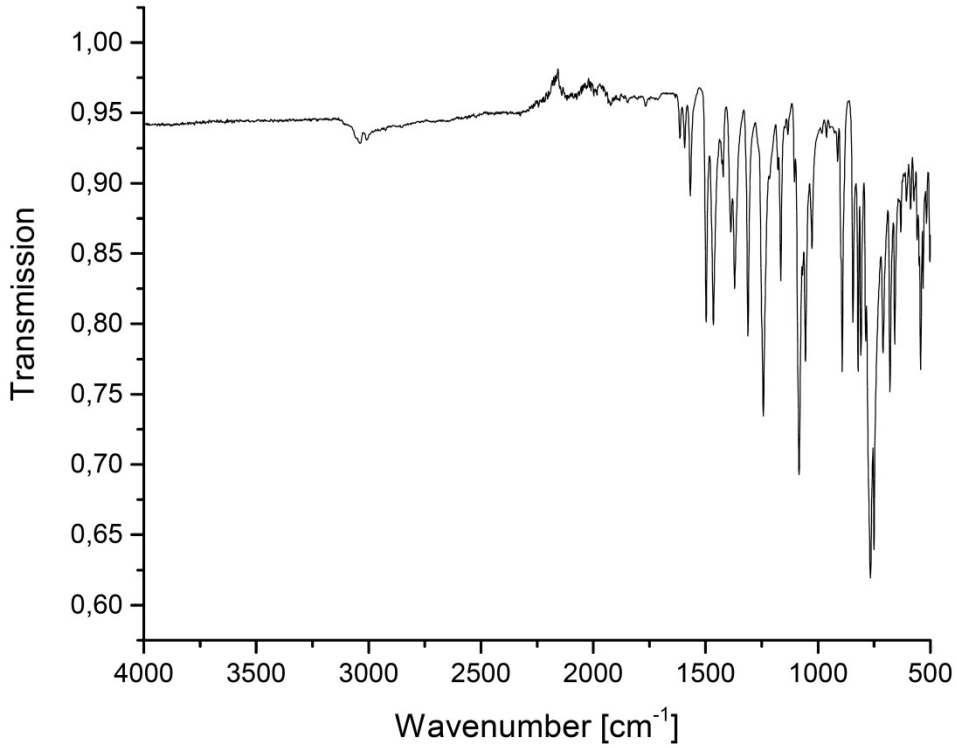


Figure S5. IR (ATR) spectrum of **2**.

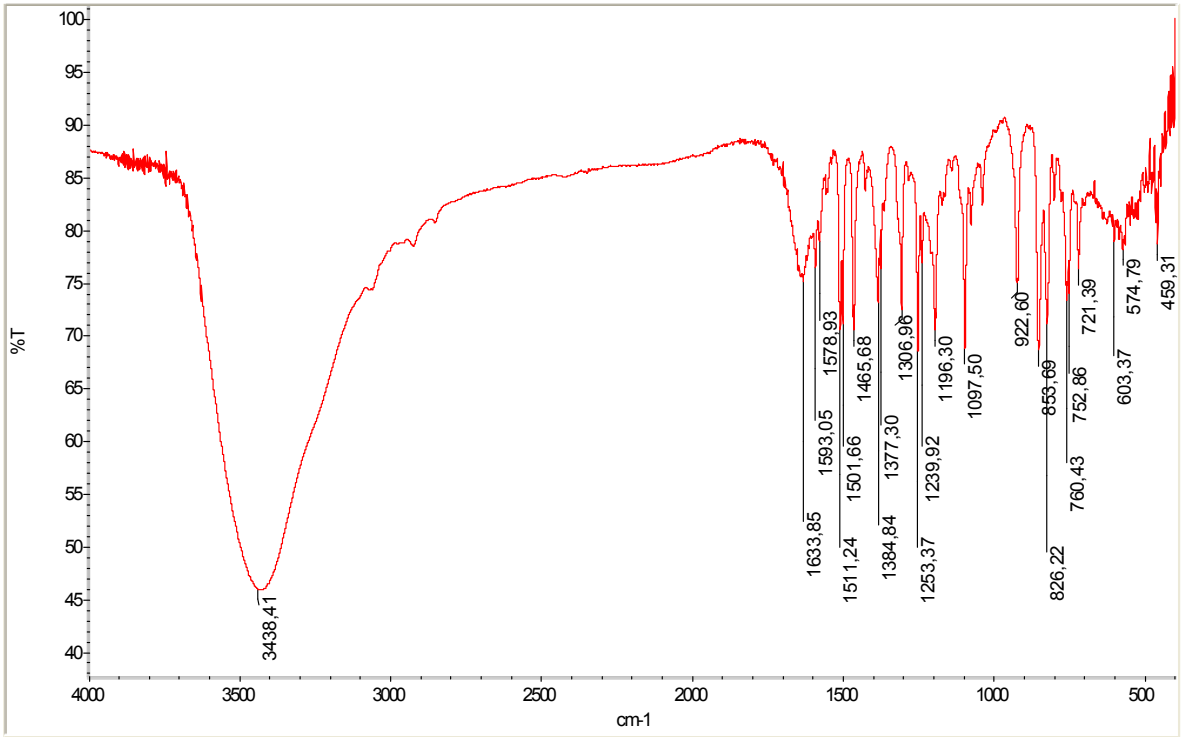


Figure S6. IR (KBr disk) spectrum of **3**.

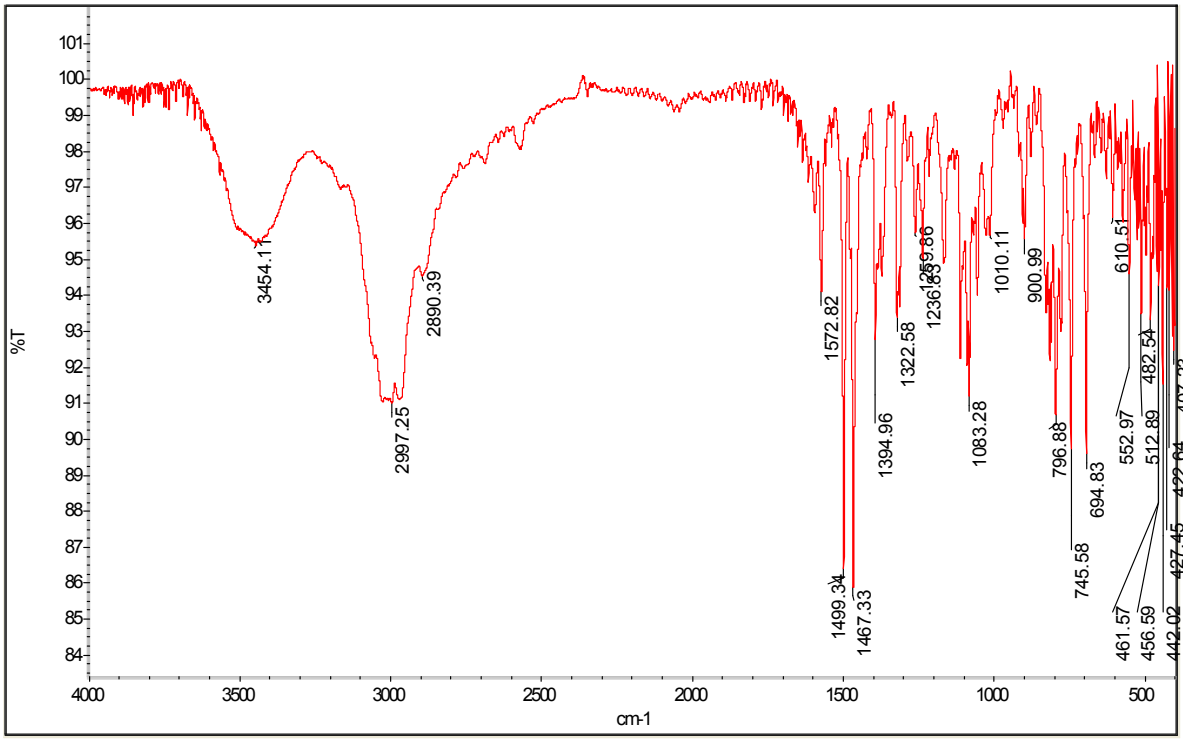


Figure S7. IR (KBr disk) spectrum of **8**/**8'**.

E. High Resolution Mass Spectrum of 2

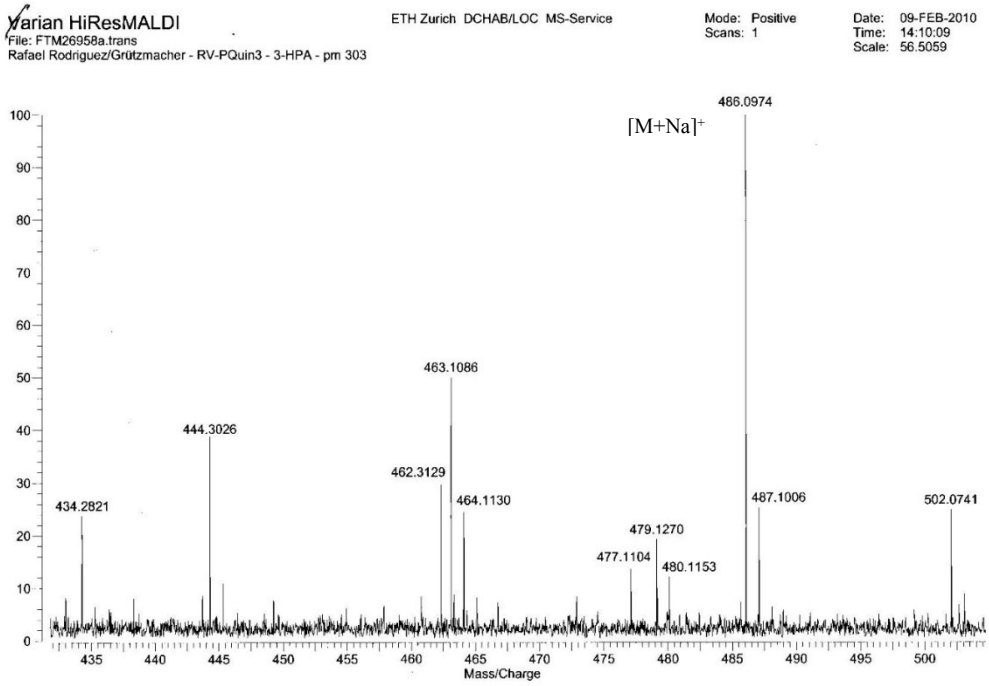


Figure S8. HRMS (MALDI) of **2**: m/z calc. for $C_{27}H_{18}N_3O_3PNa$ 486.0978 $[M+Na]^+$; found 486.0974.

F. UV-Visible spectra

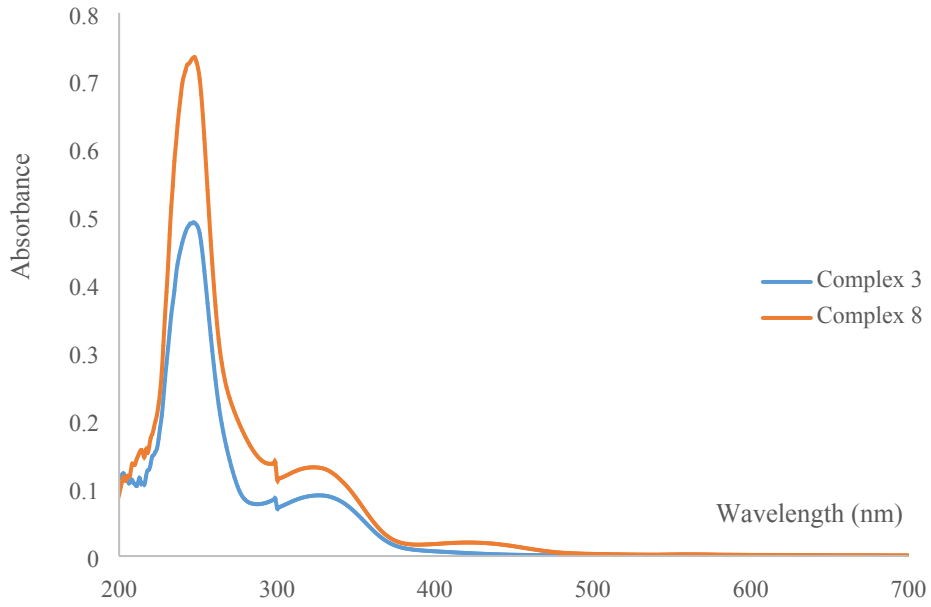
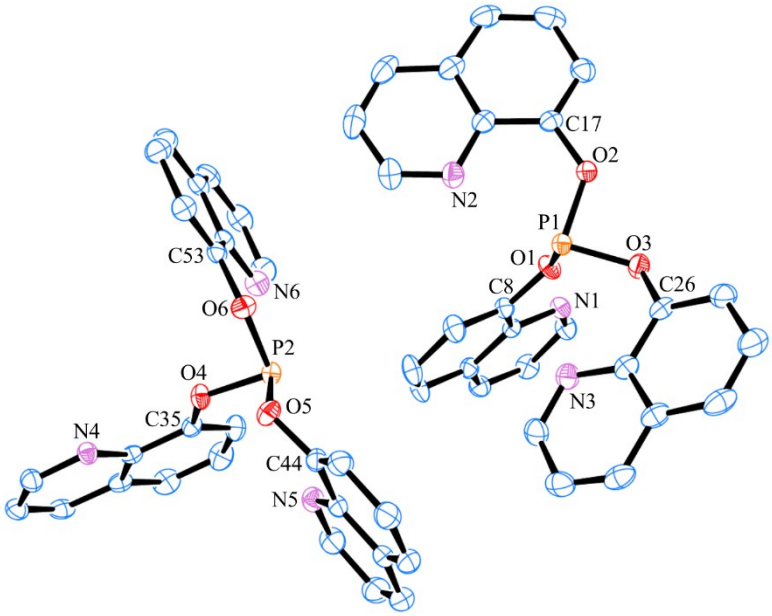


Figure S9. UV-Visible spectra of complexes **3** and **8**/**8'** in $CHCl_3$ (~ 0.1 mmol/L).

G. X-Ray diffraction analyses

a)



b)

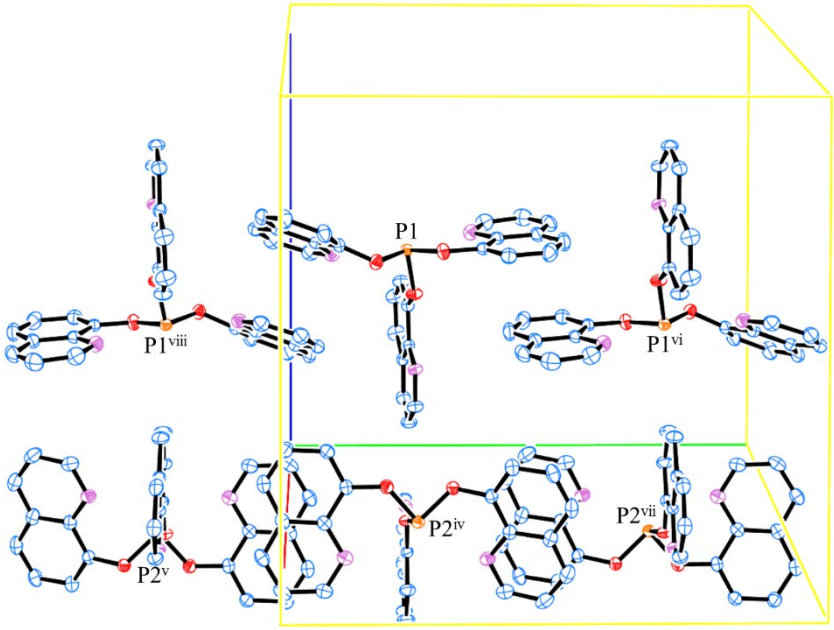


Figure S10. a) ORTEP drawing of the molecular structure of the phosphite ligand tris(quinolin-8-yl)phosphite, $P(Oquin)_3$ **2**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms have been removed for clarity. Two independent molecules per unit cell were found. The values reported for selected bond distances and angles correspond to the average. Selected bond distances [Å] and angles [°]: P1-O1/P2-O4 1.6406 (11), P1-O2/P2-O5 1.6558 (12), P1-O3/P2-O6 1.6526 (12), O1-C8/O4-C35 1.3752 (18), O2-C17/O5-C44 1.3799 (18), O3-C26/O6-C53 1.3767 (19); O1-P1-O2/O4-P2-O5 96.06 (6), O2-P1-O3/O5-P2-O6 88.34 (6), O3-P1-O1/O6-P2-O4 96.23 (6). b) Packing of the molecules in the unit cell: π-stacking between proximal *N*-heterocyclic rings in each one of the independent molecules (view normal to 100). Red: a, green: b, blue: c.

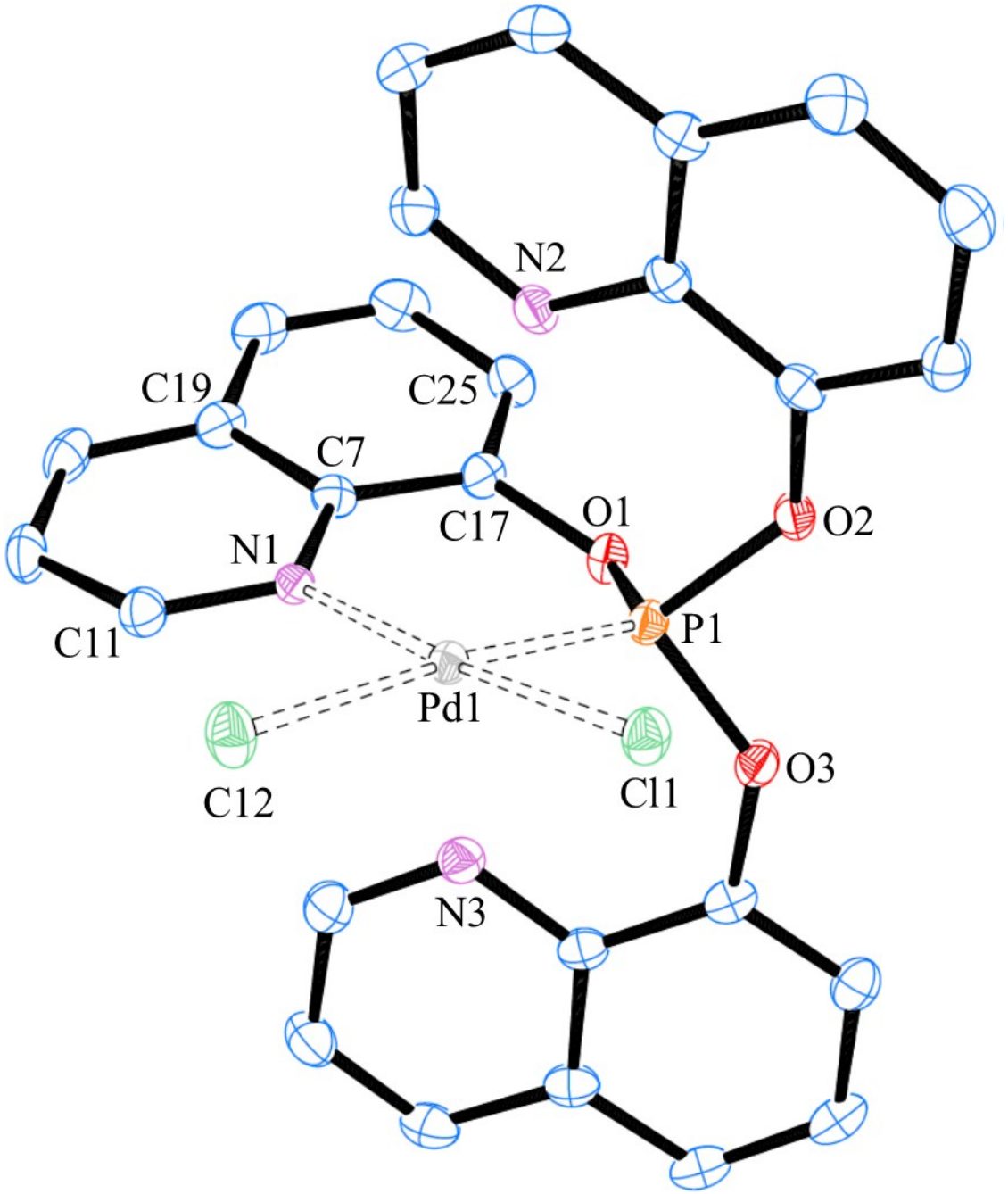


Figure S11. ORTEP drawing of the molecular structure of the complex [Pd{P(Oquin)$_3$}Cl$_2$], **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms and a dichloromethane solvate molecule have been removed for clarity. Selected bond distances [Å] and angles [°]: Pd1—P1 2.1513 (6), Pd1—N1 2.1275 (19), Pd1—Cl1 2.3027 (6), Pd1—Cl2 2.3756 (6), P1—O1 1.5773(16), P1—O2 1.5962(15), P1—O3 1.5846(17); P1—Pd1—N1 91.07(5), Cl1—Pd—Cl2 88.67(2), P1—Pd1—Cl1 85.00(2), N1—Pd1—Cl2 95.43 (5), P1—Pd1—Cl2 172.91(2), N1—Pd—Cl1 174.91(5).

Table S1. Crystal data and structure refinement for **2** and **3**.

	2	**3**
Empirical formula	$C_{27}H_{18}N_3O_3P_1$	$C_{27}H_{18}Cl_2N_3O_3PPd{\cdot}CH_2Cl_2)$
Formula weight	463.42	725.68
CCDC deposition number	1547723	1547722
Temperature	373(2) K	373(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n
Unit cell dimensions	a, b, c / Å = 15.8740(12), 17.2833(13), 16.5573(12) α, β, γ / ° = 90, 104.361(2), 90	a, b, c / Å = 10.7868(11), 23.313(2), 10.9533(11) α, β, γ / ° = 90, 92.511(2), 90
Volume	4400.6(6) $Å^3$	2751.8(5) $Å^3$
Z	7	1
Density	1.399 g/cm^3	1.752 g/cm^3
Absorption coefficient	0.161 mm^{-1}	1.159 mm^{-1}
F(000)	1920	1448
Crystal size		0.36 x 0.32 x 0.16 mm^3
Theta range and data collection	1.59 to 28.38°	2.55 to 28.34°
Index range	-21<=h<=21, -23<=k<=22, -21<=l<=22	-14<=h<=14, -31<=k<=31, -14<=l<=14
Reflections collected	45104	28444
Independent reflections	10994 [R(int) = 0.0704]	6876 [R(int) = 0.0922]
Completeness to theta= 28.38	99.7 %	91.5 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	10994 / 0 / 757	6876 / 0 / 433
Goodness-of-fit F^2	0.917	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.0919	R1 = 0.0352, wR2 = 0.0892
R indices (all data)	R1 = 0.0696, wR2 = 0.0997	R1 = 0.0404, wR2 = 0.0915
Largest diff. Peak and hole	0.564 and -0.290 $e.Å^{-3}$	1.332 and -1.653 $e.Å^{-3}$

H. Catalysis

H.1. General procedure for catalytic oxidative homo-coupling of amines to imines

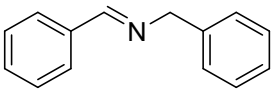
A Glassware flask (5 mL) or Parr Reactor (98 mL) was charged with the catalyst precursor (Table 3, 0.014 mmol, 1 mol%) and the corresponding amine (Table 2-8, 1.4 mmol). If applicable, see Table 4, the corresponding solvent was added (1.4 mL, 1 mol/L). If applicable, an oxidant (Table 6) was added or the autoclave was pressurized at the specified pressure (see Table 7). The reaction mixture was stirred at the specified temperatures and during the time stated (see Table 7). If applicable, the system was cooled to room temperature and the pressure of gas was carefully released. The yield was determined by ^{1}H NMR using 1, 3, 5-trimethoxybenzene as internal standard (121.1 mg, 0.72 mmol). Hexanes were added to the crude of reaction to precipitate the catalyst and the solution was flash chromatographed through silica. The imines **5a-e** were thus obtained upon evaporation of the eluent (hexane and ethyl acetate).

H.2. General procedure for catalytic oxidative cross-coupling of amines to imines

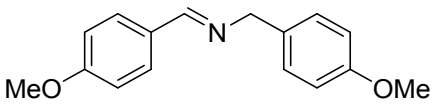
A Parr Reactor (98 mL) was charged with [Pd{P(OQuin)$_3$}Cl$_2$] (0.01 mmol, 1 mol%) , benzylamine (150 mg, 1.4 mmol), and the corresponding aniline (1.4 mmol) or *tert*-butyl amine (307.2 mg, 4.2 mmol). For solid anilines (see Table 9), toluene was added (1.4 mL, 1 mol/L). The Parr reactor was pressurized at 30 psi of air and the reaction mixture was stirred at 60 °C for 6h. The system was cooled to room temperature and the pressure of gas was carefully released. The yield was determined by ^{1}H NMR using 1, 3, 5-

trimethoxybenzene as internal standard (121.1 mg, 0.72 mmol). Hexanes were added to the crude of reaction to precipitate the catalyst and the solution was flash chromatographed through silica. The imines **7a**, **7c**, **7d**, **7f**, **7g** and **7i** were thus obtained upon evaporation of the eluent (hexane and ethyl acetate).

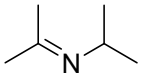
H.3. Spectroscopic data of homo-coupling products



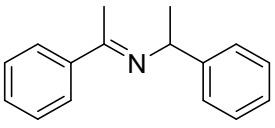
***N*-Benzylidenebenzylamine (5a).** Yellow liquid. Isolated yield: 130.7 mg, 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45 (s, 1H, *H*C=N), 7.91-7.88 (m, 2H, C*H*^{ar}), 7.51-7.49 (m, 3H, C*H*^{ar}), 7.46-7.45 (m, 4H, C*H*^{ar}), 7.39-7.36 (m, 1H, C*H*^{ar}), 4.91 (s, 2H, CH_2). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 161.9 (s, H*C*=N), 139.3 (s, *C*^{quat}), 136.2 (s, *C*^{quat}), 130.1 (s, *C*H^{ar}), 128.5, (s, *C*H^{ar}) 128.4 (s, *C*H^{ar}), 128.2 (s, *C*H^{ar}), 128.0 (s, *C*H^{ar}), 126.9 (s, *C*H^{ar}), 64.9 (s, *C*H_2). MS (ESI): m/z 196.24 [M + 1].



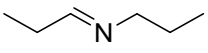
***N*-(4-methoxi)Benzylidene-4-methoxibenzylamine (5b).** Yellow liquid. Isolated yield: 150.7 mg, 82%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (s, 1H, *H*C=N), 8.24 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, C*H*^{ar}), 7.77 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H, C*H*^{ar}), 7.42 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H, C*H*^{ar}), 7.37 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H, C*H*^{ar}), 5.22 (s, 2H, CH_2), 4.27 (s, 3H, OCH_3), 4.25 (s, 3H, OCH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 161.4 (s, *C*^{quat}), 160.7 (s, H*C*=N), 158.3 (s, *C*^{quat}), 131.4 (s, *C*^{quat}), 129.5 (s, *C*H^{ar}), 128.9 (s, *C*H^{ar}), 113.7 (s, *C*H^{ar}), 113.6 (s, *C*H^{ar}), 64.0 (s, *C*H_2), 54.9 (s, O*C*H_3), 54.8 (s, O*C*H_3). **MS** (ESI): m/z 256.16 [M + 1].



***N*-Isoprpylidenepropylamine (5c).** Yellow liquid. Isolated yield: 31.4 mg, 44%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.52 (hept, $^{3}J_{HH}$ = 6.3 Hz, H, C*H*), 1.89 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.01 (d, $^{3}J_{HH}$ = 6.3 Hz, 6H, 2xCH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 163.9 (s, *C*=N), 49.9 (s, *C*H), 29.0 (s, *C*H_3), 23.2 (s, 2x*C*H_3), 17.6 (s, *C*H_3) MS (ESI): m/z 100.3 [M + 1].

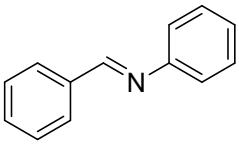


***N*-(Methyl-Benzylidene)Methylbenzylamine (5d).** Yellow liquid. Isolated yield: 90.0 mg, 56%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.22 (m, 10H, C*H*^{ar}), 4.54 (q, $^{3}J_{HH}$ = 6.5 Hz, 1H, C*H*), 1.98 (s, 3H, CH_3), 1.43 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 165.1 (s, *C*=N), 146.6 (s, *C*^{quat}), 145.1 (s, *C*^{quat}), 127.5 (s, *C*H^{ar}), 125.8 (s, *C*H^{ar}), 125.7 (s, *C*H^{ar}), 58.5 (s, *C*H), 29.8 (s, *C*H_3), 23.9 (s, *C*H_3). MS (ESI): m/z 224.4 [M + 1].

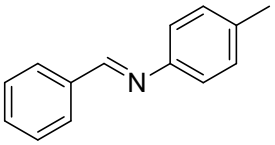


***N*-Propylidenepropylamine (5e).** Yellow liquid. Isolated yield: 31.4 mg, 44%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (tt, $^{3}J_{HH}$ = 4.7 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H, *H*C=N), 3.23 (td, $^{3}J_{HH}$ = 6.9 Hz, $^{4}J_{HH}$ = 1.0 Hz, 2H, N-CH_2), 2.17 (qd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 4.7 Hz, 2H, HC-CH_2), 1.52 (sext, $^{3}J_{HH}$ = 7.2 Hz, 2H, CH_2), 1.00 (t, $^{3}J_{HH}$ = 7.6 Hz, 3H, CH_3), 0.80 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 165.7 (s, *C*=N), 63.1 (s, N-*C*H_2), 28.9 (s, *C*H_2), 23.8 (s, *C*H_2), 11.6 (s, *C*H_3), 10.3 (s, *C*H_3). MS (ESI): m/z 100.1 [M + 1].

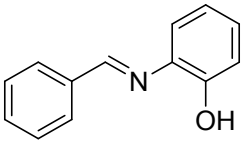
H.4. Spectroscopic data of cross-coupling products



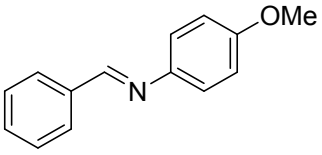
***N*-Benzylideneaniline (7a).** Yellow liquid. Isolated yield: 2.3 mg, 0.8%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (s, 1H, *H*C=N), 7.92-7.89 (m, 2H, C*H*^{ar}), 7.47-7.44 (m, 3H, C*H*^{ar}), 7.42-7.37 (m, 2H, C*H*^{ar}), 7.26-7.20 (m, 3H, C*H*^{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 160.5 (s, *C*=N), 152.1 (s, *C*^{quat}), 136.3 (s, *C*^{quat}), 131.4 (s, *C*H^{ar}), 129.3 (s, *C*H^{ar}), 129.2 (s, *C*H^{ar}), 126.0 (s, *C*H^{ar}), 121.0 (s, *C*H^{ar}).



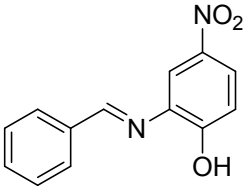
4-methyl-*N*-Benzylideneaniline (7c). Yellow liquid. Isolated yield: 32.4 mg, 10%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (s, 1H, *H*C=N), 7.81-7.78 (m, 2H, C*H*^{ar}), 7.36-7.34 (m, 3H, C*H*^{ar}), 7.11-7.04 (m, 4H, C*H*^{ar}), 2.27 (s, 3H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 159.6 (s, *C*=N), 149.5 (s, *C*^{quat}), 136.5 (s, *C*^{quat}), 135.9 (s, *C*^{quat}), 131.2 (s, *C*H^{ar}), 129.8 (s, *C*H^{ar}), 128.8 (s, *C*H^{ar}), 120.9 (s, *C*H^{ar}), 21.1 (s, *C*H$_3$).



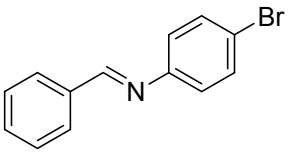
2-hydroxi-*N*-Benzylideneaniline (7d). Yellow liquid. Isolated yield: 34.1 mg, 12%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70 (s, 1H, *H*C=N), 7.95-7.92 (m, 2H, C*H*^{ar}), 7.52-7.50 (m, 3H, C*H*^{ar}), 7.32 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, C*H*^{ar}), 7.23 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, C*H*^{ar}), 7.06 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H, C*H*^{ar}), 6.94 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, C*H*^{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 157.3 (s, *C*=N), 152.4 (s, *C*^{quat}), 136.0 (s, *C*^{quat}), 135.6 (s, *C*^{quat}), 131.7 (s, *C*H^{ar}), 129.0 (s, *C*H^{ar}), 128.9 (s, *C*H^{ar}), 128.8 (s, *C*H^{ar}), 120.2 (s, *C*H^{ar}), 116.0 (s, *C*H^{ar}), 115.1 (s, *C*H^{ar}).



4-methoxi-*N*-Benzylideneaniline (7f). Yellow liquid. Isolated yield: 54.8 mg, 18%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.50 (s, 1H, *H*C=N), 7.97-7.94 (m, 2H, C*H*^{ar}), 7.41-7.49 (m, 3H, C*H*^{ar}), 7.31 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, C*H*^{ar}), 6.99 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, C*H*^{ar}), 4.83 (s, 3H, OCH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 158.2 (s, *C*=N), 144.7 (s, *C*^{quat}), 136.4 (s, *C*^{quat}), 130.9 (s, *C*H^{ar}), 128.6 (s, *C*H^{ar}), 128.5 (s, *C*H^{ar}), 122.2 (s, *C*H^{ar}), 114.3 (s, *C*H^{ar}), 55.3 (s, O*C*H$_3$).



2-hydroxi-5-nitro-*N*-Benzylideneaniline (7g). Yellow liquid. Isolated yield: 97.7 mg, 28%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (s, 1H, *H*C=N), 8.18 (s, 1H, C*H*^{ar}), 8.08 (dd, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = 2.3 Hz, 1H, C*H*^{ar}), 7.91-7.88 (m, 2H, C*H*^{ar}), 7.51-7.46 (m, 3H, C*H*^{ar}), 7.02 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, C*H*^{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 160.6 (s, *C*=N), 132.9 (s, *C*H^{ar}), 129.5 (s, *C*H^{ar}), 129.2 (s, *C*H^{ar}), 124.7 (s, *C*H^{ar}), 115.2 (s, *C*H^{ar}), 112.2 (s, *C*H^{ar}), *C*^{quat} resonances are poorly resolved.



4-bromo-*N*-Benzylideneaniline (7i). Yellow liquid. Isolated yield: 18.7 mg, 4%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (s, 1H, *H*C=N), 7.91-7.88 (m, 2H, C*H*^{ar}), 7.52-7.47 (m, 5H, C*H*^{ar}), 7.09 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H, C*H*^{ar}). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 160.8 (s, *C*=N), 151.1 (s, *C*^{quat}), 136.0 (s, *C*^{quat}), 132.3 (s, *C*H^{ar}), 131.7 (s, *C*H^{ar}), 129.0 (s, *C*H^{ar}), 128.9 (s, *C*H^{ar}), 122.7 (s, *C*H^{ar}), 119.4 (s, *C*^{quat}).

H.5. Reutilization of the catalyst.

From the experiments in neat benzylamine, the catalyst can be recovered almost quantitatively (> 99%) by precipitation with hexanes (5 mL). Upon precipitation, the pale yellow solid was washed with hexane (2 x 5 mL) and dried under vacuum. Yield: 8.8 mg, 99%. ^{1}H NMR (300.2 MHz, $CDCl_3$, 25ºC): δ = 10.26 (d, $^{3}J_{HH}$ =

5.4 Hz, 1H, H2), 8.48 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, H4), 7.79-7.68 (m, 3H, H5-7), 7.62 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 5.4 Hz, 1H, H3). $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$, 25ºC): δ = 31.8 ppm (s). The isolated solid was reused in a next catalytic run as described in H.1. Yield: 95% (determined by ^{1}H NMR using 1, 3, 5-trimethoxybenzene as internal standard) of *N*-benzylidenebenzylamine. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45 (s, 1H, *H*C=N), 7.91-7.88 (m, 2H, C*H*^{ar}), 7.51-7.49 (m, 3H, C*H*^{ar}), 7.46-7.45 (m, 4H, C*H*^{ar}), 7.39-7.36 (m, 1H, C*H*^{ar}), 4.91 (s, 2H, CH_2).

I. General procedure for the kinetic experiments

I.1. *In situ* monitoring of the reaction progress as a function of time

In a round-bottom flask the complex [Pd{P(OQuin)$_3$}Cl$_2$] (0.03 mmol, 1 mol%) and a solution of benzylamine in toluene (5.6 mL from stock solution 0.499 mol/L, 300 mg, 2.8 mmol) were placed. The round flask was connected to a short condenser and the mixture was heated to 80 °C. 1, 3, 5-trimethoxybenzene was used as internal standard (242.2 mg, 1.4 mmol). Samples of 0.4 mL were taken every hour during 5 h and analyzed by ^{1}H NMR. Under these conditions, the amine was cleanly converted into imine and neither benzaldehyde nor benzonitrile were detected as side-products. The progress of reaction, as consumption of benzylamine, was followed on time (Table S2 and Figure S12). The representation of Ln([$BnNH_2$]/[$BnNH_2$]$_o$) vs. time returns a straight line (Figure S13). Here [$BnNH_2$] is the molar concentration of benzylamine at any "t" time and [$BnNH_2$]$_o$ is the initial molar concentration of benzylamine.

Table S2. Progress of reaction, as consumption of benzylamine, on time.

Time (h)	[$BnNH_2$] (mol/L)	Ln([$BnNH_2$]/[$BnNH_2$]$_o$)
0	0.500	0.000
1	0.493	-0.014
2	0.487	-0.027
4	0.467	-0.068
5	0.463	-0.076

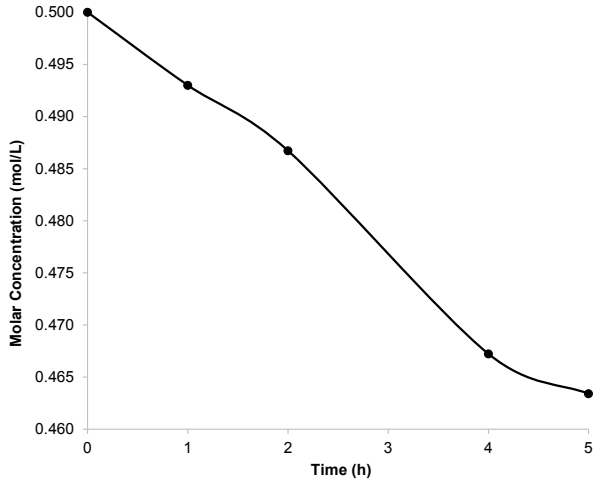


Figure S12. Decreasing benzylamine concentration during the first 5 h of reaction.

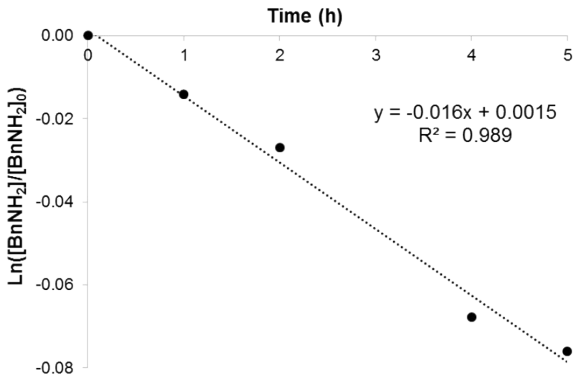


Figure S13. $Ln([BnNH_2]/[BnNH_2]_o)$ vs. time.

I.2. Rate of reaction r as a function of $[BnNH_2]$, [**3**] and $[BnNH_2][\mathbf{3}]$ at constant reaction time, temperature and pressure (2 h, 60 °C, 130 psi air).

a) Rate of reaction r as a function of $[BnNH_2]$ at constant catalyst concentration ([**3**] = 0.015 mol/L), reaction time, temperature and pressure.

A Parr Reactor (98 mL) was charged with the complex $[Pd\{P(OQuin)_3\}Cl_2]$ (9.6mg, 15 μmol, 0.015 mol/L) and an appropriate volume from a stock solution of benzylamine in toluene (5.0 mol/L, final volume: 1.0 mL, Table S3). The Parr reactor was pressurized at 130 psi of air and the reaction mixture was stirred at 60 °C for 2 h. The system was cooled to room temperature and the pressure of gas was carefully released. The yield was determined by ^1H NMR using 1, 3, 5-trimethoxybenzene as internal standard (84.1 mg, 0.5 mmol). The rate of reaction r (mol L^{-1} h^{-1}) was calculated by means of the amount of imine (mmol) formed divided by the total volume (1.0 mL) and the time of reaction (2 h). The representation of log(r) vs. $log([BnNH_2])$ gives a straight line with a slope of 1.07 (Table S3 and Figure S14).

Table S3. Rate of reaction r as a function of amine concentration ($[BnNH_2]$).

Volume from 5.0 mol/L $BnNH_2$ stock solution (mL)	$[BnNH_2]$ (mol L^{-1})	r (mol L^{-1} h^{-1})	$Log([BnNH_2])$	Log(r)
0.10	0.50	0.0039	-0.30	-2.40
0.20	1.00	0.0084	0.000	-2.08
0.30	1.50	0.0125	0.18	-1.90
0.95	4.75	0.0443	0.68	-1.35

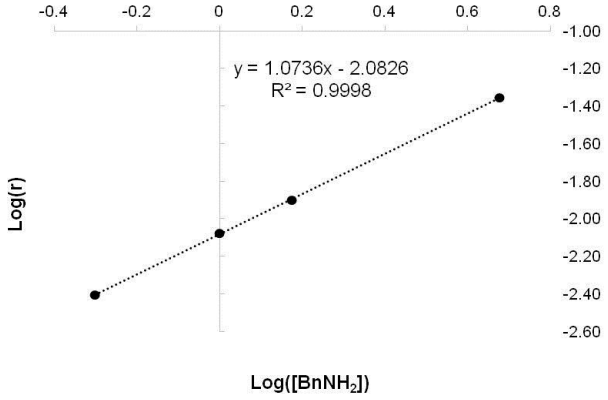


Figure S14. Representation $log([BnNH_2])$ vs. log(r).

b) Rate of reaction r as a function of [**3**] at constant benzylamine concentration ([$BnNH_2$] = 5 mol/L), reaction time, temperature and pressure.

A Parr Reactor (98 mL) was charged with a solution of benzylamine in toluene (0.14 mL from stock solution 10.0 mol/L, final volume: 0.28 mL) and an appropriate amount of the complex [Pd{P(OQuin)$_3$}Cl_2] (0.05, 0.1, 0.15 and 0.2 mol/L, Table S4). The Parr reactor was pressurized at 130 psi of air and the reaction mixture was stirred at 60 °C for 2 h. The system was cooled to room temperature and the pressure of gas was carefully released. The yield was determined by ^{1}H NMR using 1, 3, 5-trimethoxybenzene (11.8 mg, 0.07 mmol) as internal standard. The rate of reaction r (mol L^{-1} h^{-1}) was calculated by means of the amount of imine (mmol) formed divided by the total volume (0.28 mL) and the time of reaction (2 h). The representation of log(r) vs. log([**3**]) gives a straight line with a slope of 1.14 (Table S4 and Figure S15).

Table S4. Rate of reaction r as a function of catalyst concentration ([**3**]).

Mass of complex **3** (mg)	[**3**] (mol L^{-1})	r (mol L^{-1} h^{-1})	Log([**3**])	Log(r)
9.0	0.05	0.154	-1.301	-0.814
18.0	0.10	0.328	-1.000	-0.485
27,0	0.15	0.538	-0.824	-0.270
36.0	0.20	0.740	-0.699	-0.131

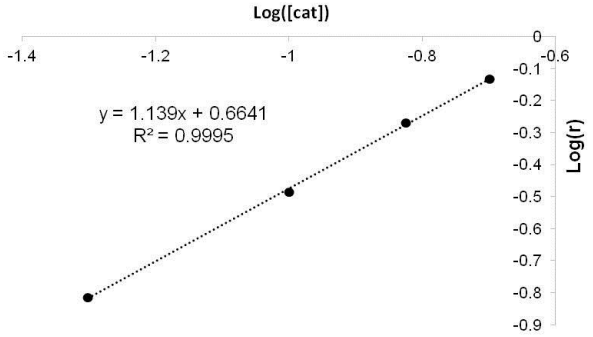


Figure S15. Representation log([**3**]) vs. log(r).

c) Rate of reaction as a function of the product [$BnNH_2$][cat] = P at constant reaction time, temperature and pressure. Determination of the apparent rate constant k_{app}.

A Parr Reactor (98 mL) was charged with a solution of benzylamine in toluene (0.14 mL from stock solution 10.0 mol/L, final volume: 0.28 mL) and an appropriate amount of the complex [Pd{P(OQuin)$_3$}Cl_2] (0.05, 0.1, 0.15 and 0.2 mol/L, Table S5). The Parr reactor was pressurized at 130 psi of air and the reaction mixture was stirred at 60 °C for 2 h. The system was cooled to room temperature and the pressure of gas was carefully released. The yield was determined by ^{1}H NMR using 1, 3, 5-trimethoxybenzene (11.8 mg, 0.07 mmol) as internal standard. The rate of reaction r (mol L^{-1} h^{-1}) was calculated by means of the amount of imine (mmol) formed divided by the total volume (0.28 mL) and the time of reaction (2 h). The representation of log(r) vs. log([P]) gives a straight line with a slope of 0.756 L mol^{-1} h^{-1} (Table S5 and Figure S16).

Table S5. Rate of reaction r as a function of the product [$BnNH_2$][cat] = P.

[**3**] (mol L^{-1})	[$BnNH_2$] (mol L^{-1})	[$BnNH_2$][cat] = P (mol^2 L^{-2})	r (mol L^{-1} h^{-1})
0.05	5.0	0.218	0.154
0.10	5.0	0.467	0.343
0.15	5.0	0.729	0.558
0.20	5.0	1.000	0.740

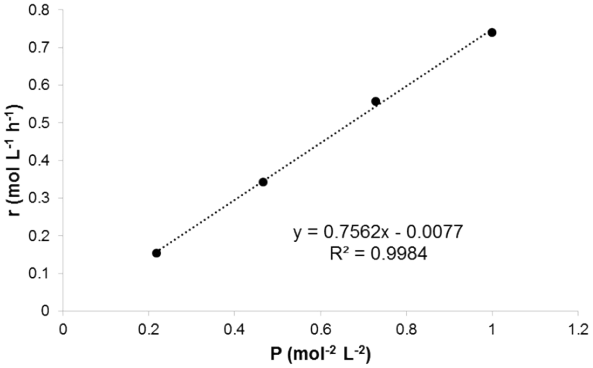


Figure S16. Representation r vs. $[BnNH_2][cat] = P$.

J. *In situ* experiments

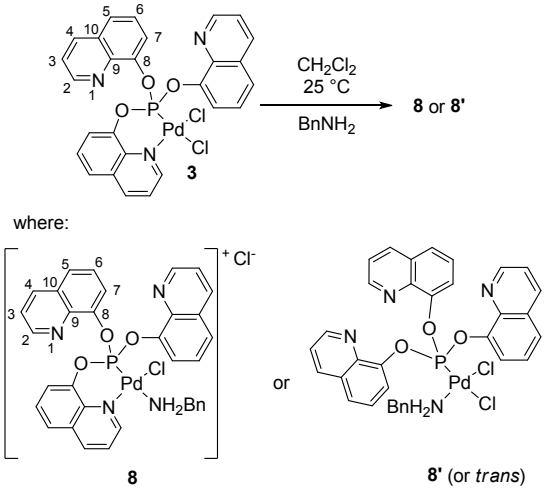
J.1 In neat benzylamine.

Under inert atmosphere, the complex $[Pd\{P(OQuin)_3\}Cl_2]$ (10.0 mg, 16 μmol), benzylamine (ca. 0.4 mL) and a sealed inner tube filled with DMSO-d_6 (ca. 0.1 mL) were placed in a young NMR tube. The mixture was immediately analyzed by ^1H and $^{31}P\{^1H\}$ NMR and then after 0.5 and 1 h. The sample was heated to 60 °C and analyzed twice (1 and 2 h). The tube was pressurized with air (40 psi) and spectra were recorded every hour for two hours. The system was heated to 60 °C and analyzed four times (1, 2, 4 and 16 h). Selected $^{31}P\{^1H\}$ and ^1H NMR spectra are shown in Figure S17 and Figure S18 respectively.

J.2 *In situ* stoichiometric experiment.

Under inert atmosphere, the complex $[Pd\{P(OQuin)_3\}Cl_2]$ (10.0 mg, 16 μmol), benzylamine (4.2 mg, 39 μmol, 2.4 equivalents) and $CDCl_3$ (ca. 0.5 mL). were placed in a young NMR tube. The mixture was immediately analyzed by ^1H and $^{31}P\{^1H\}$ NMR and then after 0.5 and 1 h. The sample was heated to 60 °C and analyzed twice (1 and 2 h). The tube was pressurized with air (40 psi) and spectra were recorded every hour for two hours. The system was heated to 60 °C and analyzed four times (1, 2, 4 and 16 h). Selected $^{31}P\{^1H\}$ and ^1H NMR spectra are shown in Figure S19 and Figure S20 respectively.

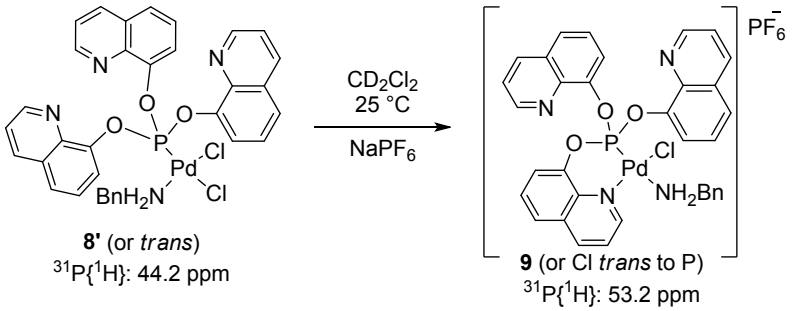
J.3 Isolation of the species observed in the stoichiometric experiments.



To a suspension of **3** (50.0 mg, 0.078 mmol) in CH_2Cl_2 (3 mL) was added a solution of benzylamine (66.9 mg, 0.62 mmol) in CH_2Cl_2 (3 mL) and the mixture was stirred for 1 h. The reaction mixture was filtered-off in order to remove any unreacted **3**. The clear filtrate was concentrated to *ca*. 1 mL and Et_2O (5 mL) was added. A bright yellow solid was formed. The product was washed with Et_2O (3 x 5 mL) and was

carefully dried under vacuum to obtain a yellow solid (53.0 mg, 90% yield). $BnNH_2$ can be readily removed from the Pd coordination sphere by applying vacuum overnight. ^{1}H NMR (600.0 MHz, CD_2Cl_2, 25ºC): δ = 10.02 (t, $^3J_{HH}$ = 4.2 Hz, 1H), 8.78 (br., 2.34H), 8.33-8.19 (m, 5.52H), 7.68-7.23 (m, 32.08H), 7.02-6.97 (m, 1.45H), 6.87-6.82 (m, 1.35H), 3.84 (br., 3.81H, C*H*$_2$). Ratio C*H*^{ar} / C*H*$_2$ = 43.74 / 3.81 = 11.48 / 1 = 22.96 / 2 ~ 23 / 2. ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, 25ºC): δ = 165.9 (s, C^{quat}), 152.3 (s, *C*H^{ar}), 151.5 (s, *C*H^{ar}), 147.2 (s, C^{quat}), 145.9 (s, C^{quat}), 139.5 (s, *C*H^{ar}), 138.5 (s, *C*H^{ar}), 131.5 (s, C^{quat}), 130.4 (s, *C*H^{ar}), 130.3 (s, *C*H^{ar}), 128.7 (s, *C*H^{ar}), 127.5 (s, *C*H^{ar}), 127.0 (s, *C*H^{ar}), 124.8 (s, C^{quat}), 124.1 (s, *C*H^{ar}), 121.8 (s, *C*H^{ar}), 121.6 (s, *C*H^{ar}), 114.6 (s, J_{PC} = 6.4 Hz, *C*H^{ar}), 111.8 (s, *C*H^{ar}), 46.6 (s, *C*H$_2$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25ºC): δ = 44.2 (s). IR (KBr disk, ν in cm^{-1}): 3454 m, 2997 m, 2890 m, 1573 m, 1499 s, 1467 s, 1395 m, 1323 m, 1260 m, 1237 m, 1083 m, 1010 w, 901 w, 797 m, 746 m, 695 m, 611 w, 553 m, 513 m, 483 m. UV-Vis ($CHCl_3$, λ_{max} in nm): 249, 323. Selected ^{1}H NMR and ^{31}P{^{1}H} spectra are shown in Figures S21-S24.

J.4 *In situ* chloride abstraction from **8**/**8'**.



8' (or *trans*)
^{31}P{^{1}H}: 44.2 ppm

9 (or Cl *trans* to P)
^{31}P{^{1}H}: 53.2 ppm

To a solution **8**/**8'** (20.0 mg, 0.027 mmol) in CD_2Cl_2 (0.5 mL) was added $NaPF_6$ (4.7 mg, 0.028 mmol) at room temperature and under inert atmosphere. The reaction takes place within minutes and the precipitate formed (NaCl) was filtered through a millipore filter using a syringe. The clear filtrate was analyzed by ^{1}H and ^{31}P{^{1}H} NMR (^{13}C{^{1}H} resonances are poorly resolved). ^{1}H NMR (300.0 MHz, CD_2Cl_2, 25ºC): δ = 9.72 (m, 1H), 8.79 (br., 2.09H), 8.20 (d, $^3J_{HH}$ = 8.4 Hz, 1.72H), 8.15 (d, $^3J_{HH}$ = 8.0 Hz, 1.72H), 7.52-7.46 (m, 4.18H), 7.36-7.23 (m, 15.63H), 6.92 (d, $^3J_{HH}$ = 7.7 Hz, 3.29H), 6.72 (d, $^3J_{HH}$ = 7.7 Hz, 1.71H), 5.85 (br., 3.45H), 4.03 (br., 3.02H, C*H*$_2$). Ratio C*H*^{ar} / C*H*$_2$ = 34.80 / 3.02 = 11.52 / 1 = 23.04 / 2 ~ 23 / 2. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 25ºC): δ = 53.2 (s, 1P), -143.5 (hept, $^1J_{PF}$ = 711.4 Hz, 1P). Attempts to remove the second Cl^- ligand did not proceed under the specified reaction conditions. Selected ^{1}H NMR and ^{31}P{^{1}H} spectra are shown in Figures S25-S26

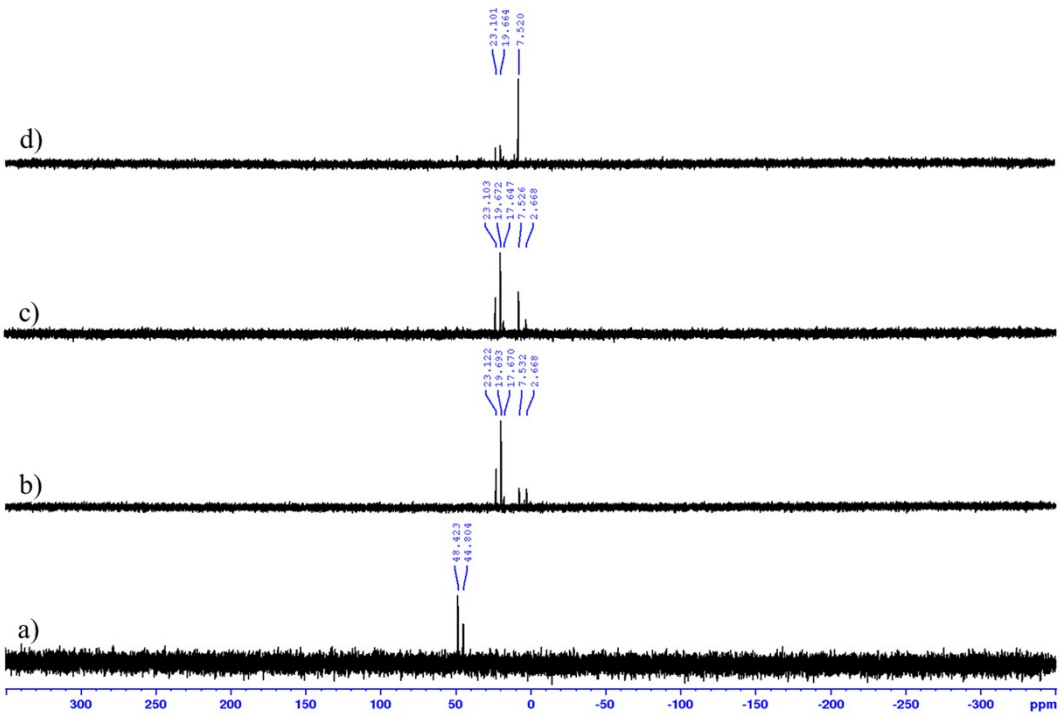


Figure S17. Complex **3** in neat benzylamine: *in situ* NMR monitoring by $^{31}P\{^{1}H\}$ NMR (121.5 MHz). a) Inert atmosphere, room temperature, < 5 minutes after mixing **3** and $BnNH_2$; b) Inert atmosphere, 1 h at 60 °C; c) 40 psi air, 60 °C, < 5 minutes after loading the air pressure; d) 40 psi air, 60 °C, 1 h after loading the air pressure.

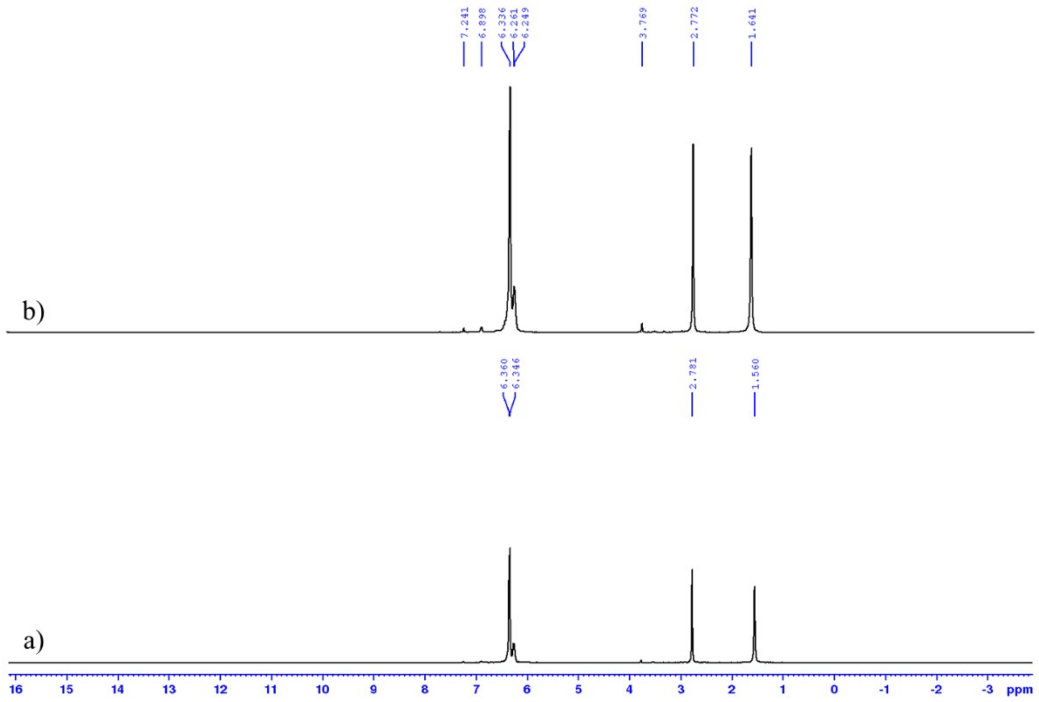


Figure S18. Complex **3** in neat benzylamine: *in situ* NMR monitoring by ^{1}H NMR (300.1 MHz). a) Inert atmosphere, room temperature, < 5 minutes after mixing **3** and $BnNH_2$; b) 40 psi air, 60 °C, 16 h after loading the air pressure.

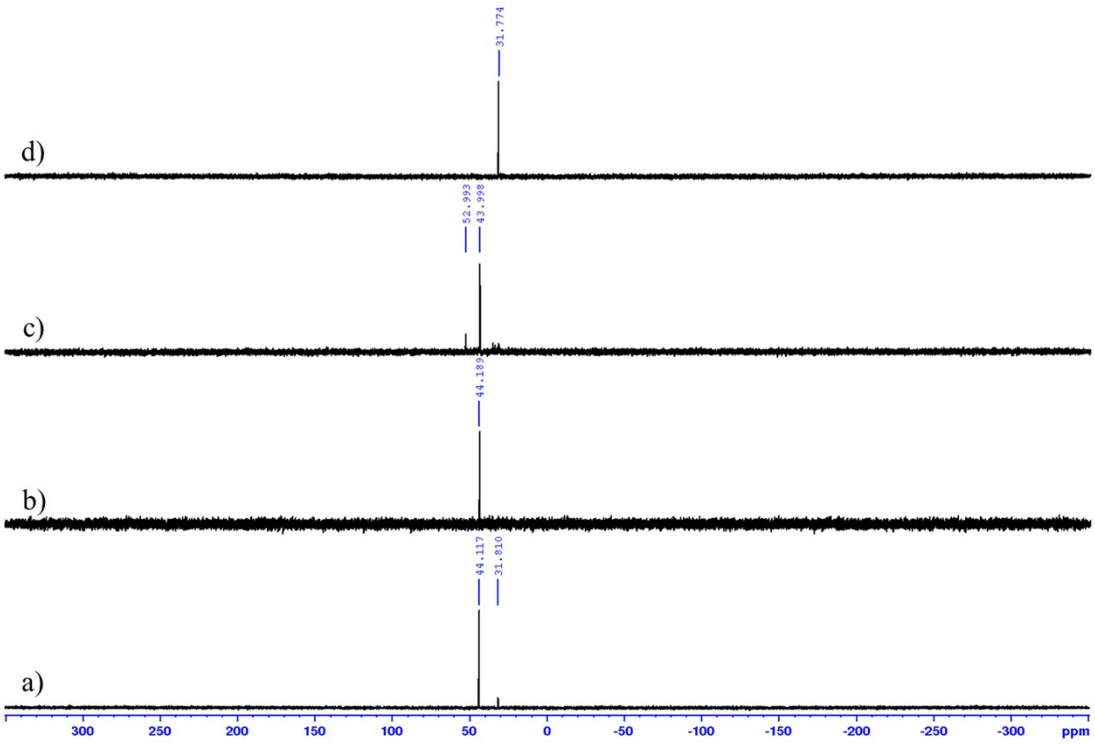


Figure S19. Stoichiometric test **3** + benzylamine: *in situ* NMR monitoring by $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$). a) Inert atmosphere, room temperature, < 5 minutes after mixing **3** and $BnNH_2$; b) Inert atmosphere, 2 h at 60 °C; c) 40 psi air, 60 °C, 4 h after loading the air pressure; d) 40 psi air, 60 °C, 16 h after loading the air pressure.

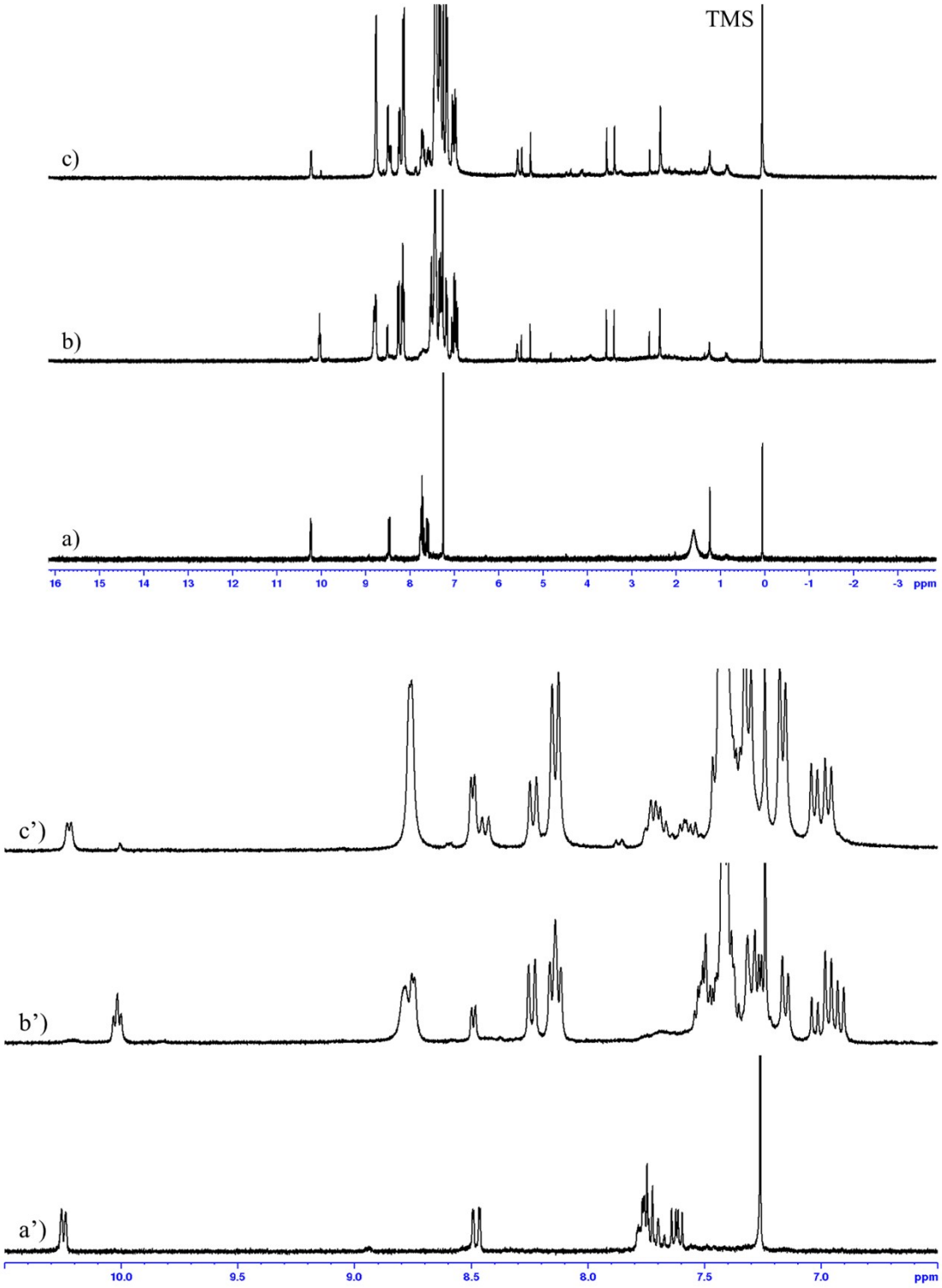


Figure S20. Stoichiometric test **3** + benzylamine: *in situ* NMR monitoring by ^{1}H NMR (300.1 MHz, $CDCl_3$). a) Complex **3** before adding $BnNH_2$; b) Inert atmosphere, 2 h at 60 °C; c) 40 psi air, 60 °C, 16 h after loading the air pressure. a'), b') c'): Zoom (10.5-6.5 ppm) in the aromatic region.

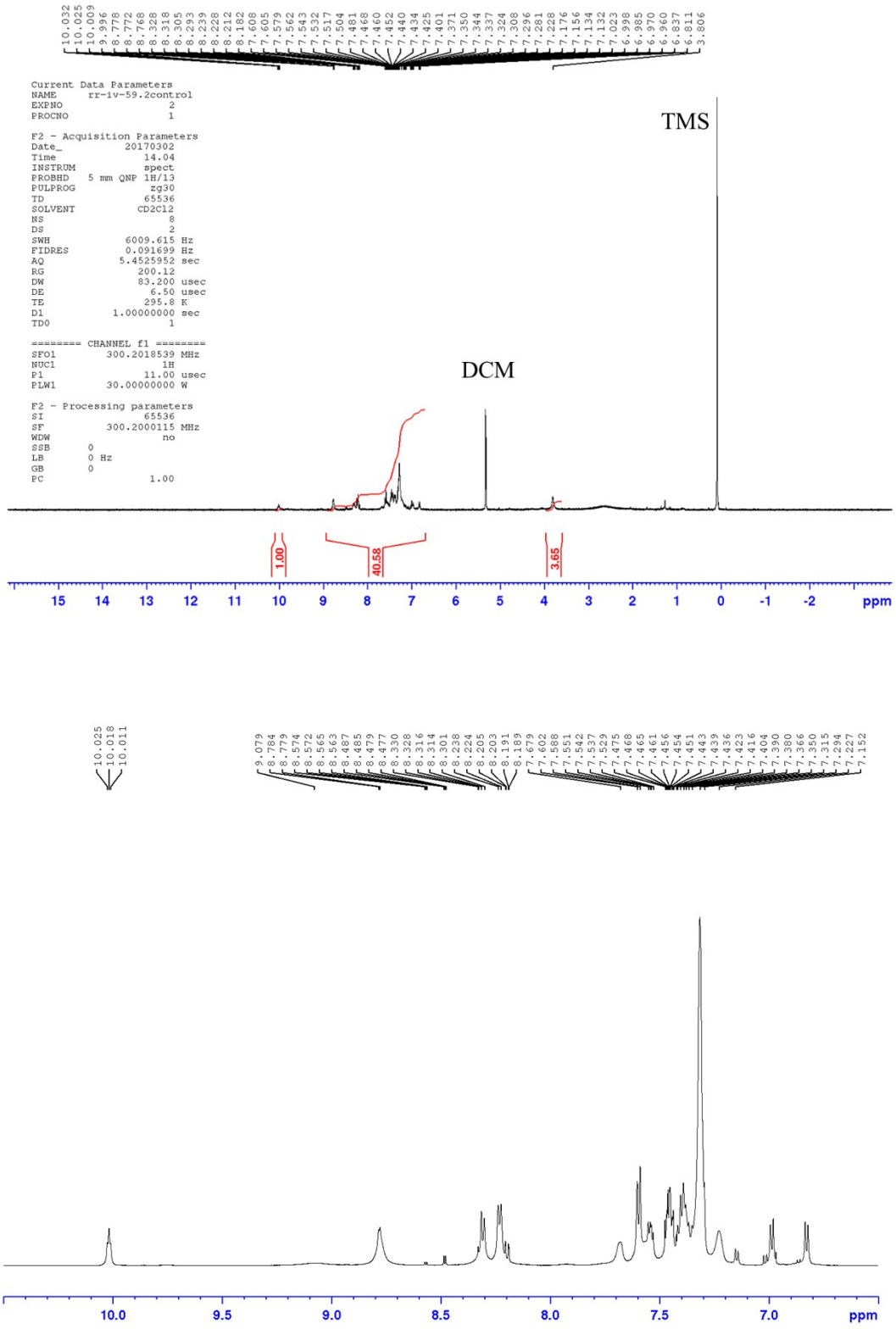


Figure S21. ^{1}H NMR spectrum (300.1 MHz) at 298 K of **8**/**8'** in CD_2Cl_2.

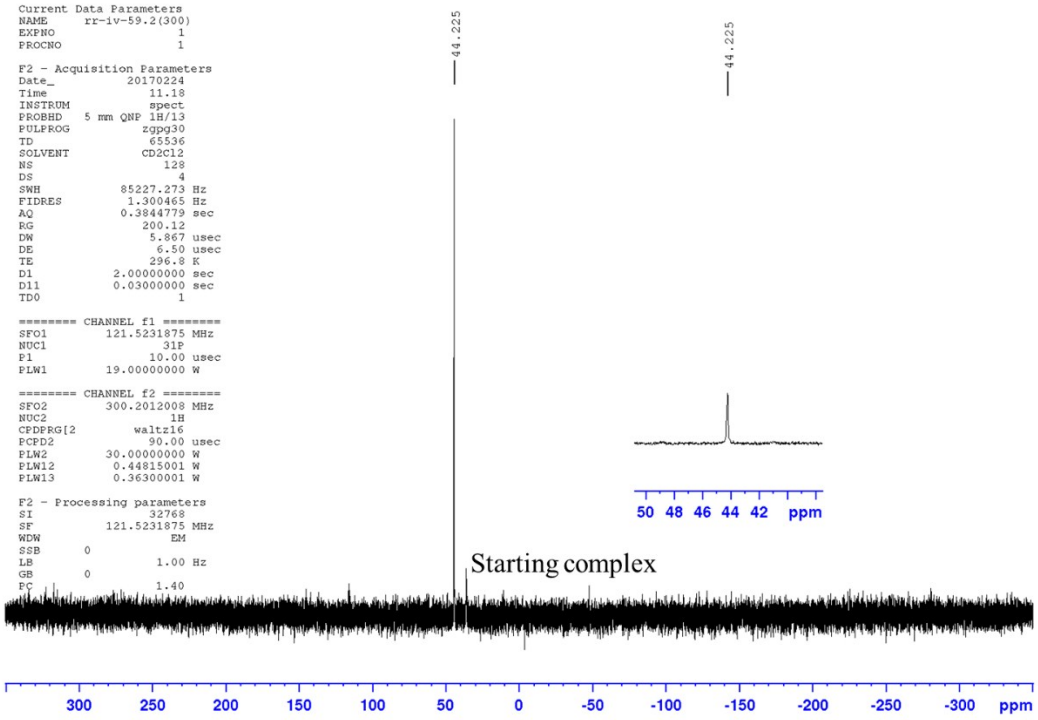


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum (121.5 MHz) at 298 K of **8**/**8'** in CD_2Cl_2.

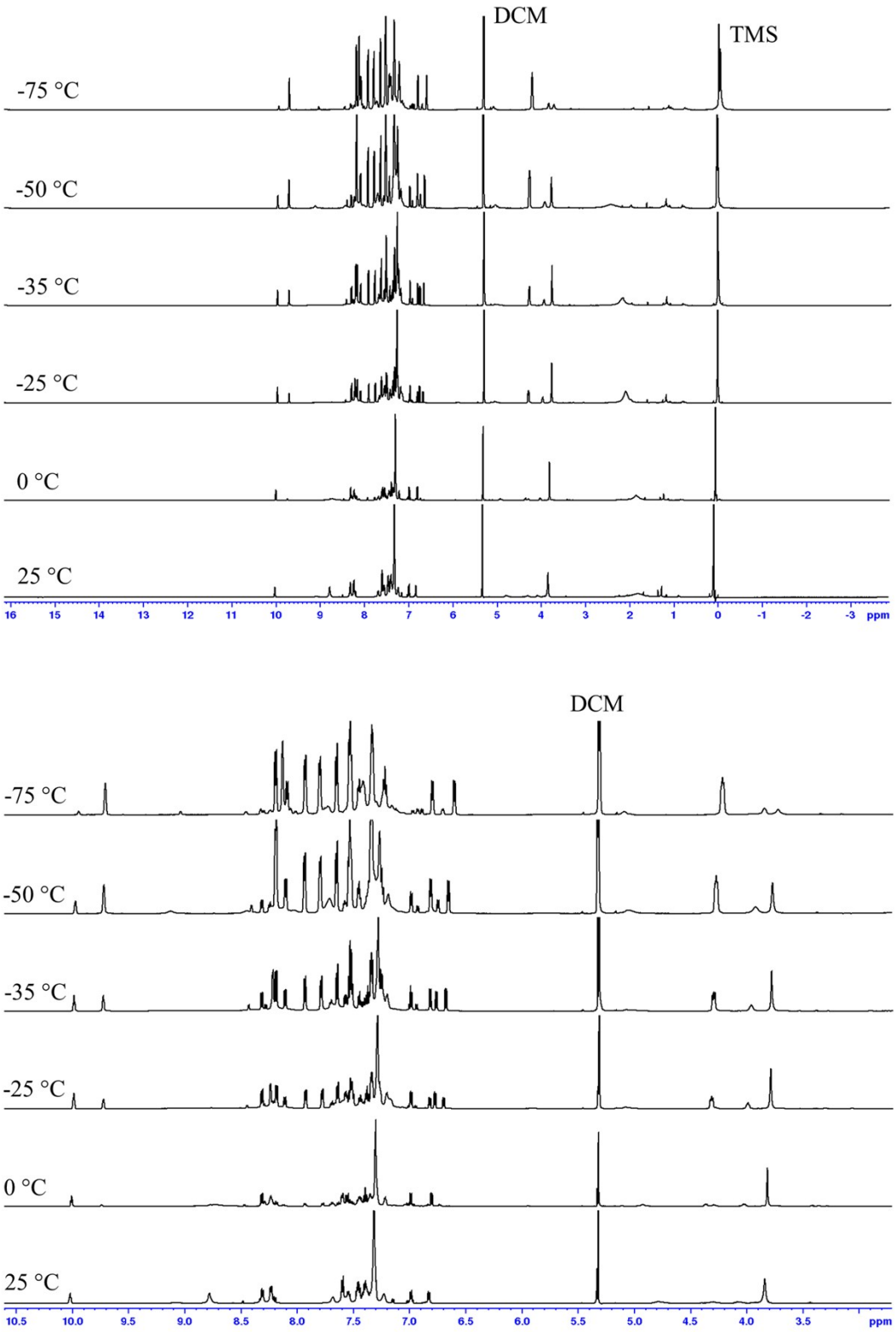


Figure S23. ^{1}H NMR spectra of **8**/**8'** at variable temperature (600.0 MHz, CD_2Cl_2).

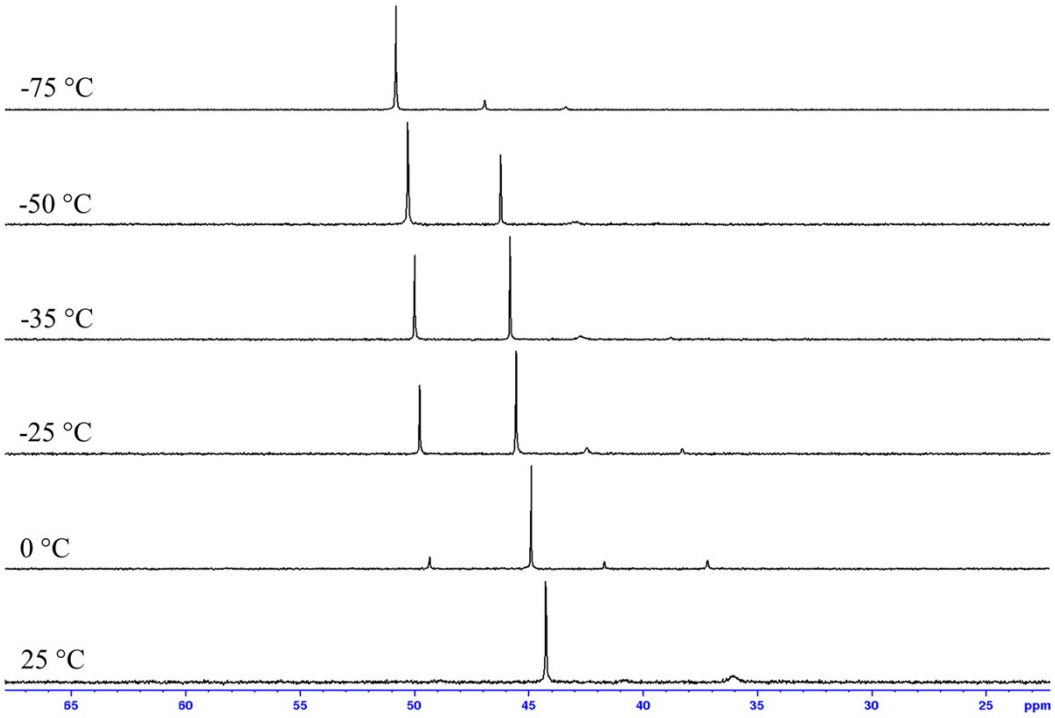


Figure S24. $^{31}P\{^{1}H\}$ NMR spectra of **8**/**8'** at variable temperature (121.5 MHz, CD_2Cl_2).

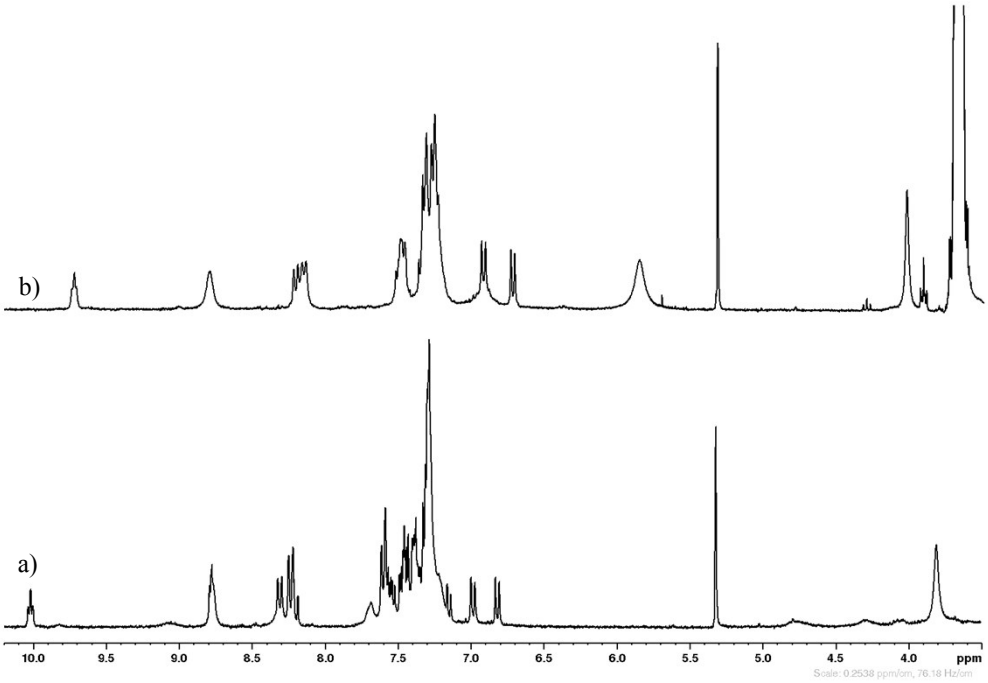


Figure S25. Interaction of complex **8/8'** with $NaPF_6$: *in situ* NMR monitoring by ^1H NMR (300.1 MHz). a) **8/8'** in CD_2Cl_2; b) **8/8'** in CD_2Cl_2 after removal of one Cl^- ligand.

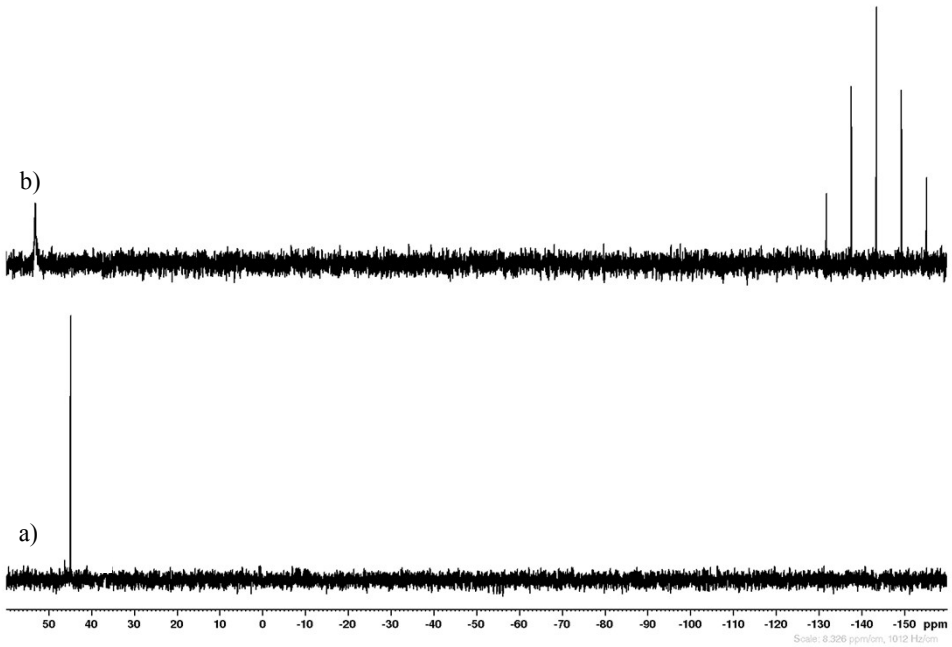


Figure S26. Interaction of complex **8/8'** with $NaPF_6$: *in situ* NMR monitoring by $^{31}P\{^1H\}$ NMR (121.5 MHz). a) **8/8'** in CD_2Cl_2; b) **8/8'** in CD_2Cl_2 after removal of one Cl^- ligand.

K. MS analyses of 8/8’

K.1 LIFDI-MS of **8**/**8’**

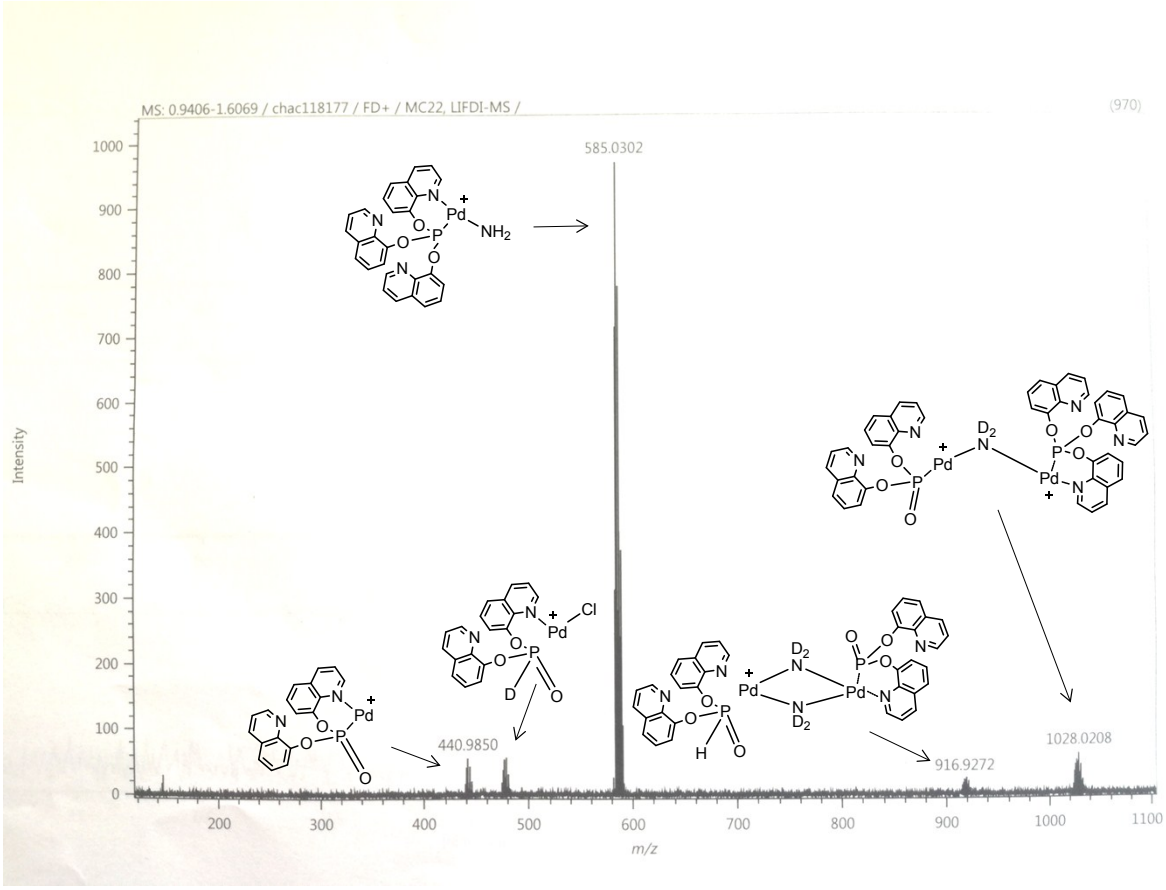


Figure S27. LIFDI-MS of **8**/**8’** in toluene.

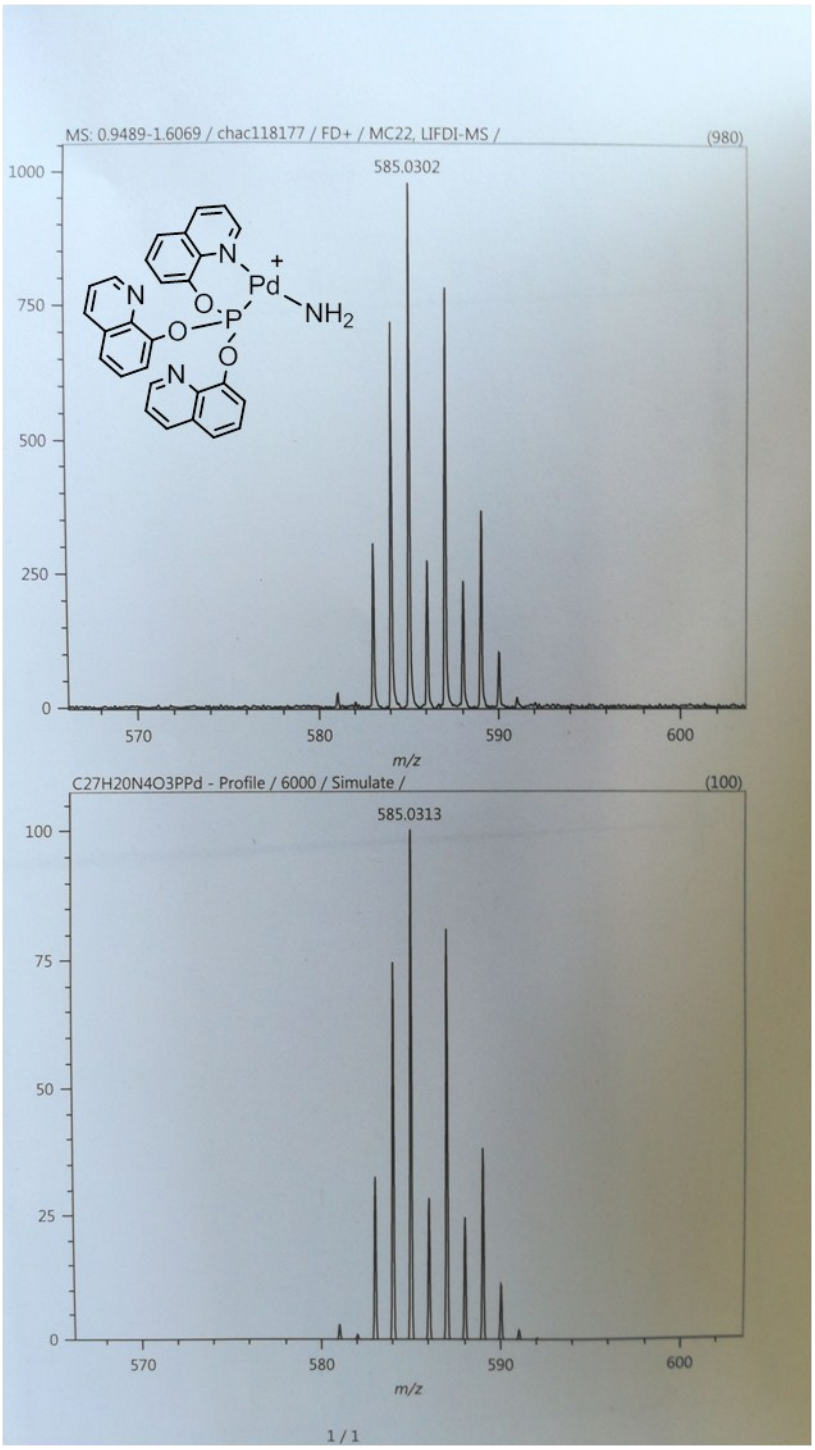


Figure S28. LIFDI-MS of **8**/**8'**: m/z calc. for $C_{27}H_{20}N_4O_3PPd^+$ 585.0313 (bottom); found 585.0302 (top).

K.2 HESI-MS of **8**/**8'**

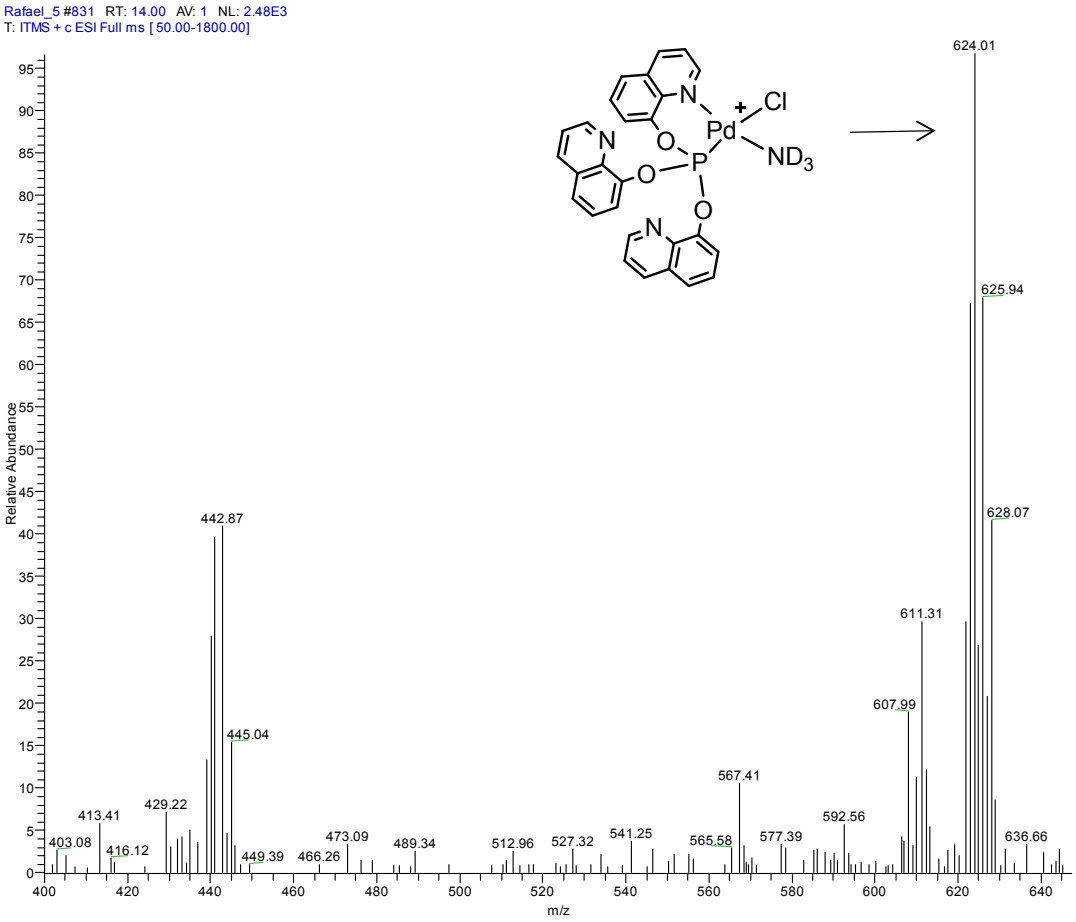


Figure S29. HESI-MS of **8**/**8'** in CH_2Cl_2.

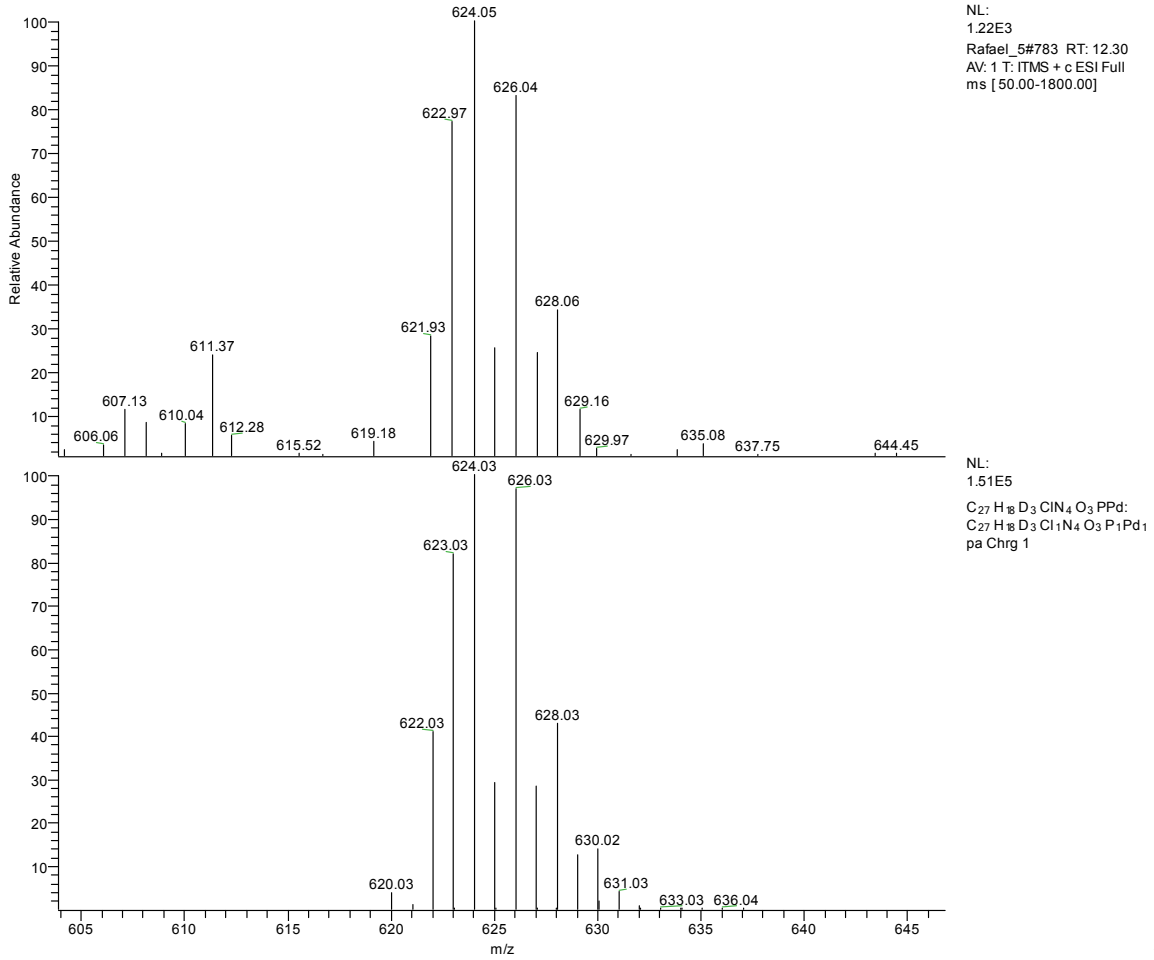


Figure S30. HESI-MS of **8**/**8'**: m/z calc. for $C_{27}H_{18}D_3ClN_4O_3PPd^+$ 623.03 (bottom); found 623.05 (top).

L. NMR spectra of imines (crude of reaction).

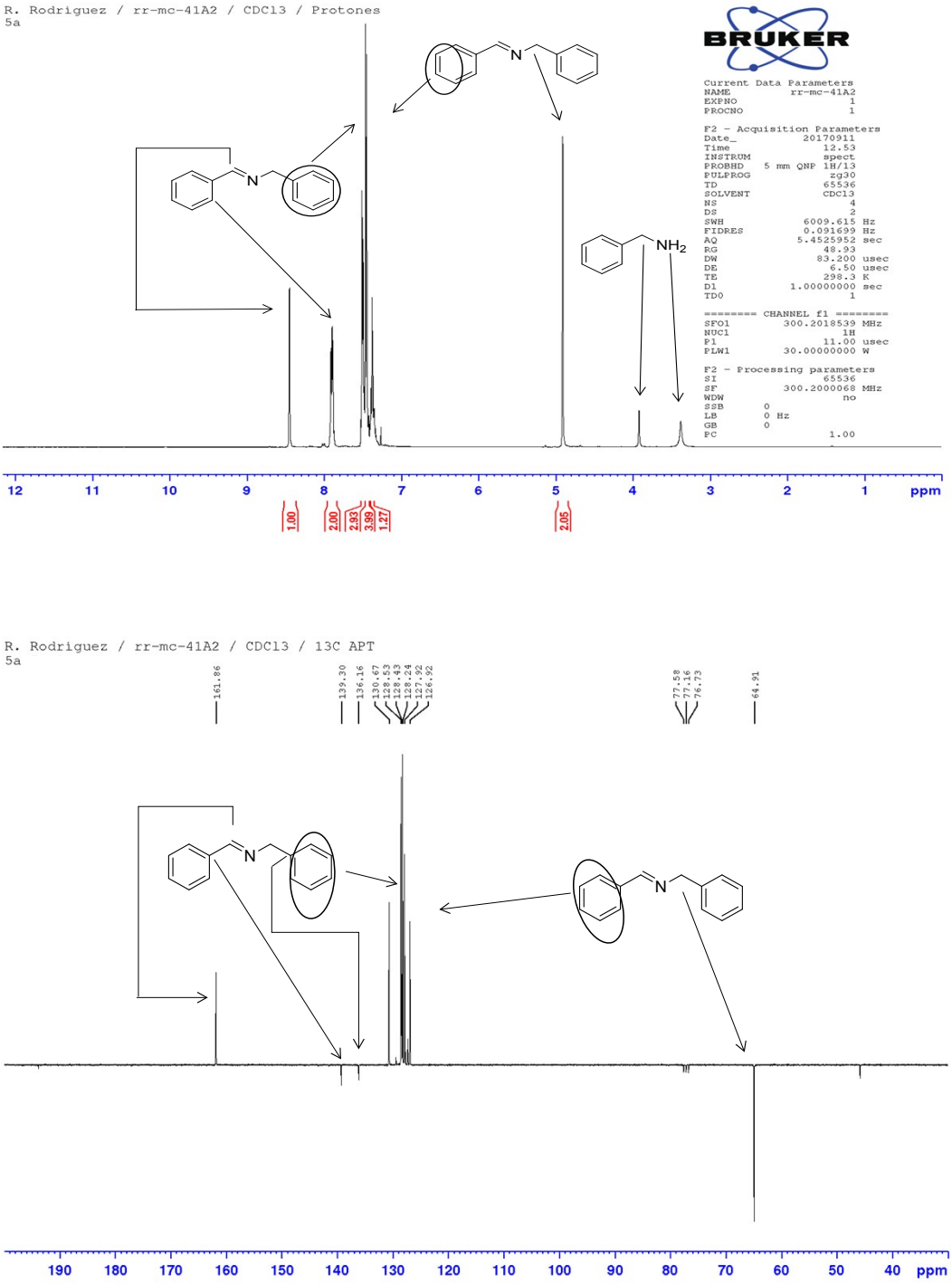


Figure S31. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **5a** crude in $CDCl_3$.

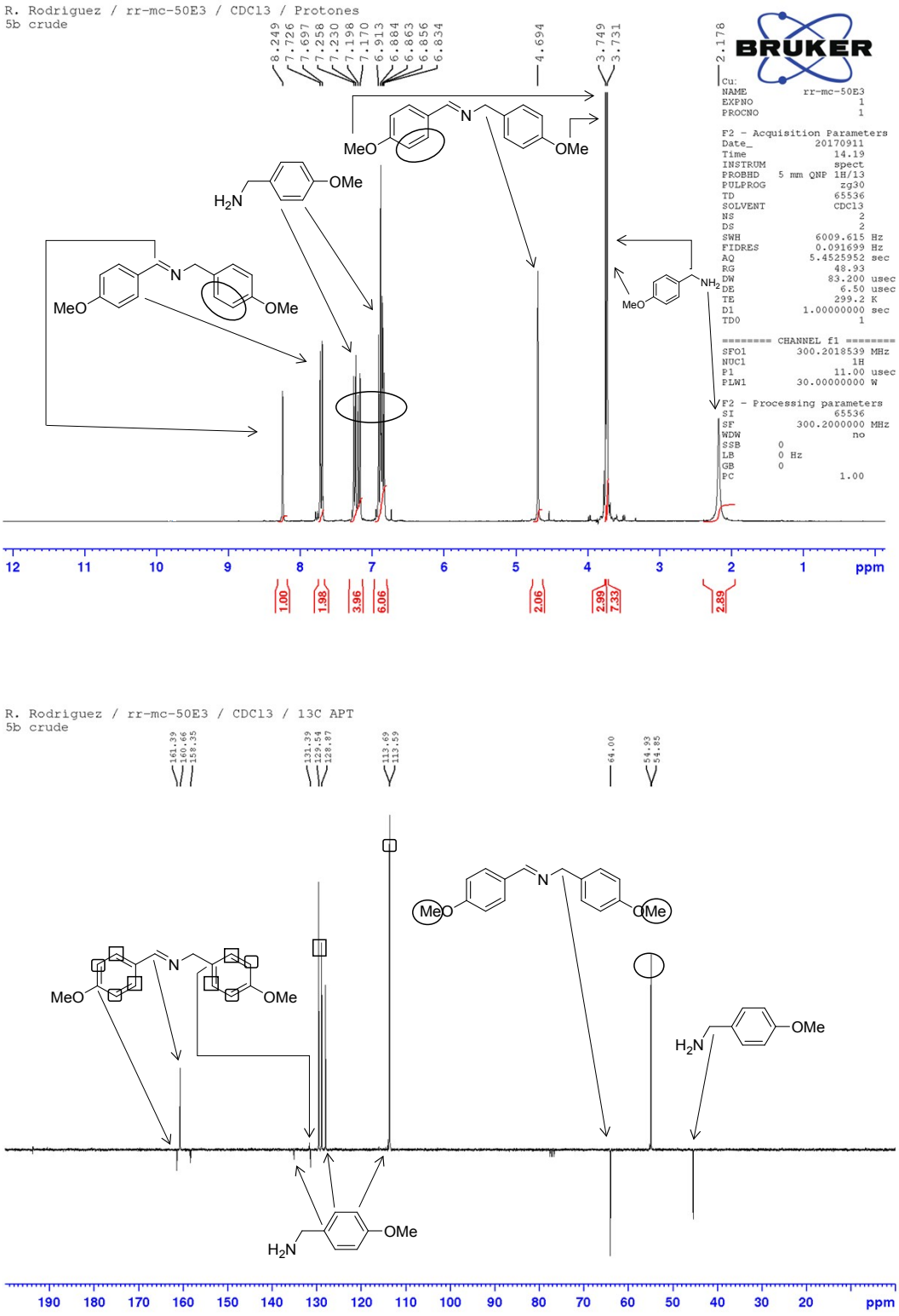


Figure S32. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **5b** crude in $CDCl_3$.

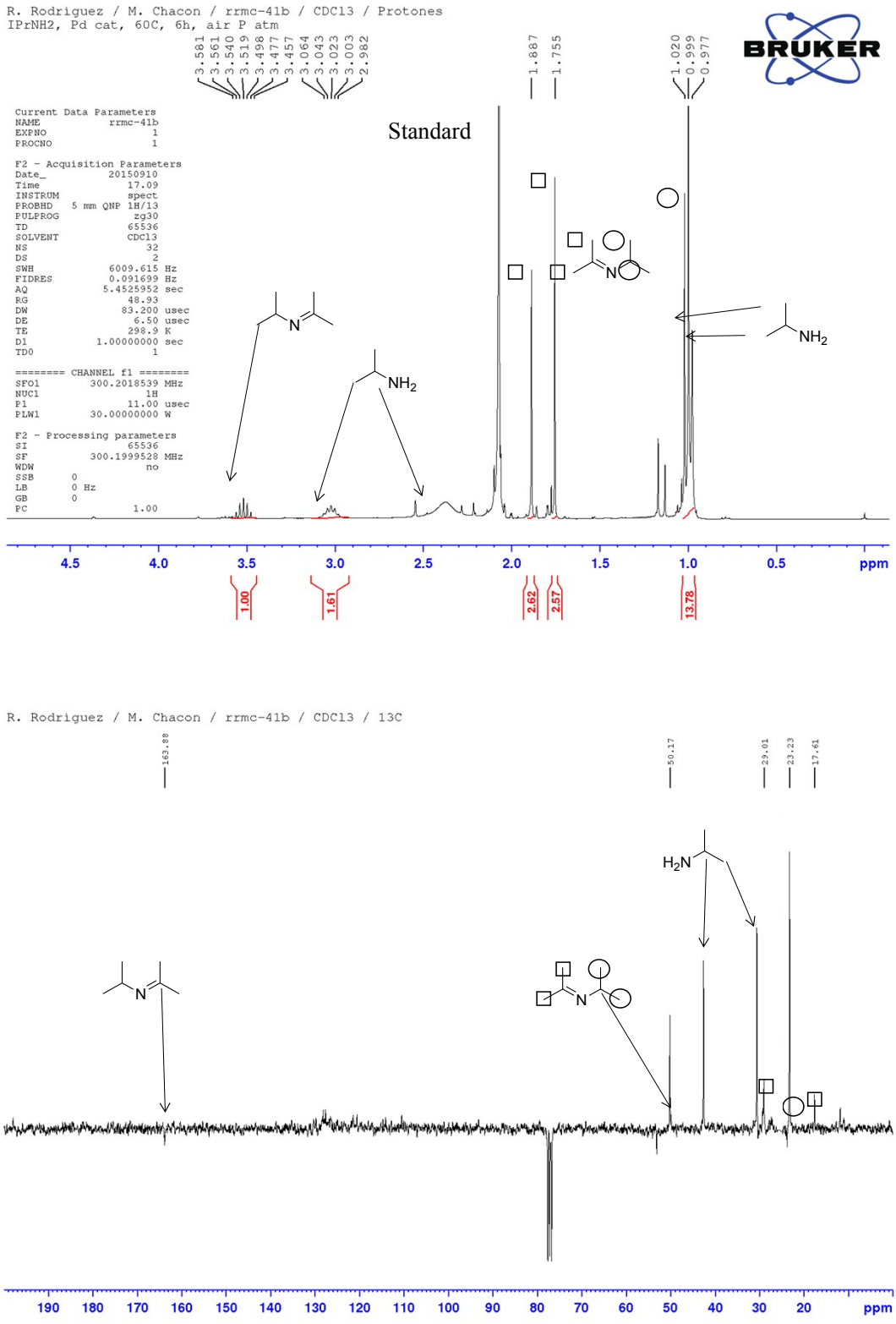


Figure S33. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **5c** crude in $CDCl_3$.

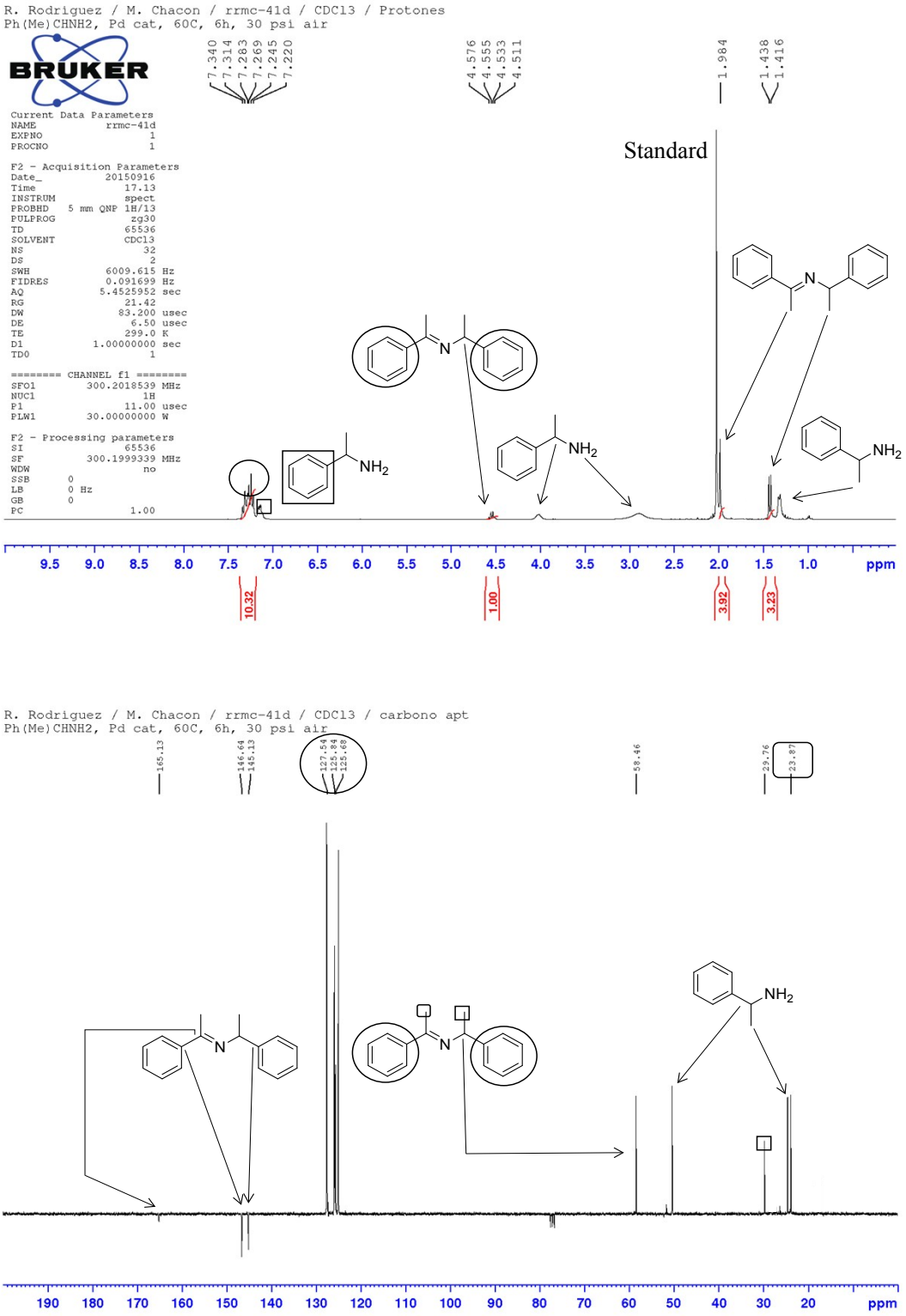


Figure S34. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **5d** crude in $CDCl_3$.

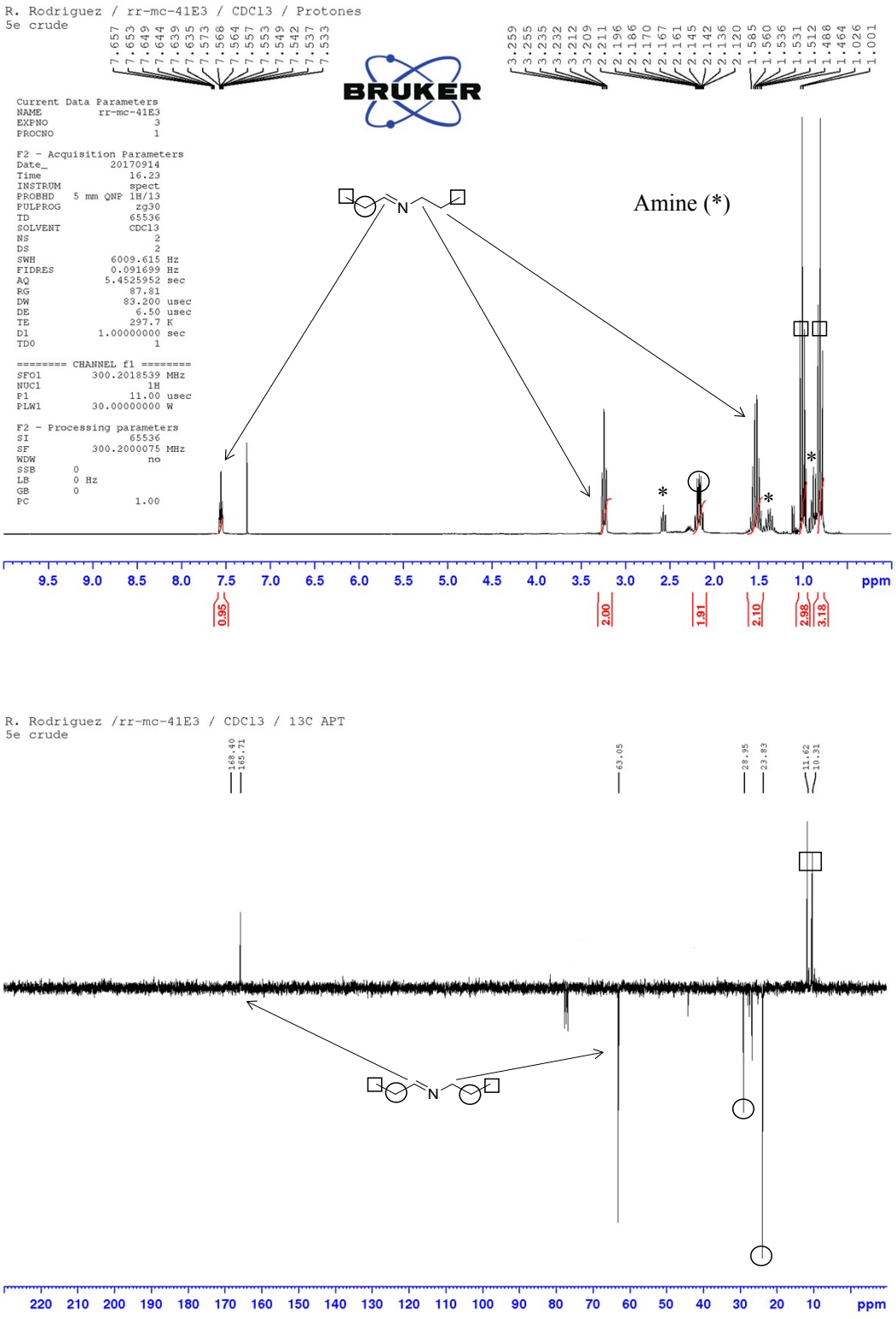


Figure S35. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **5e** crude in $CDCl_3$.

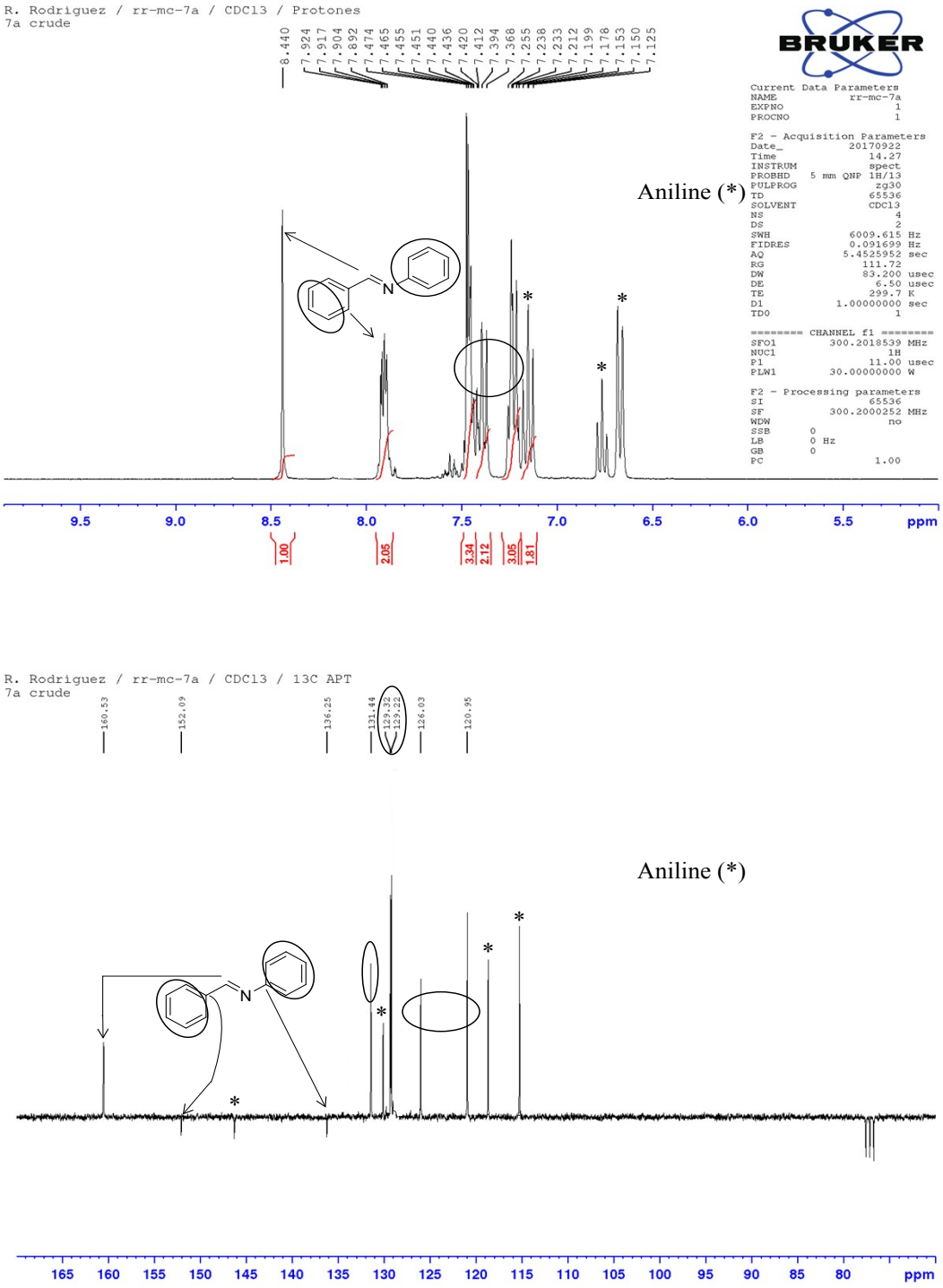


Figure S36. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **7a** crude in $CDCl_3$.

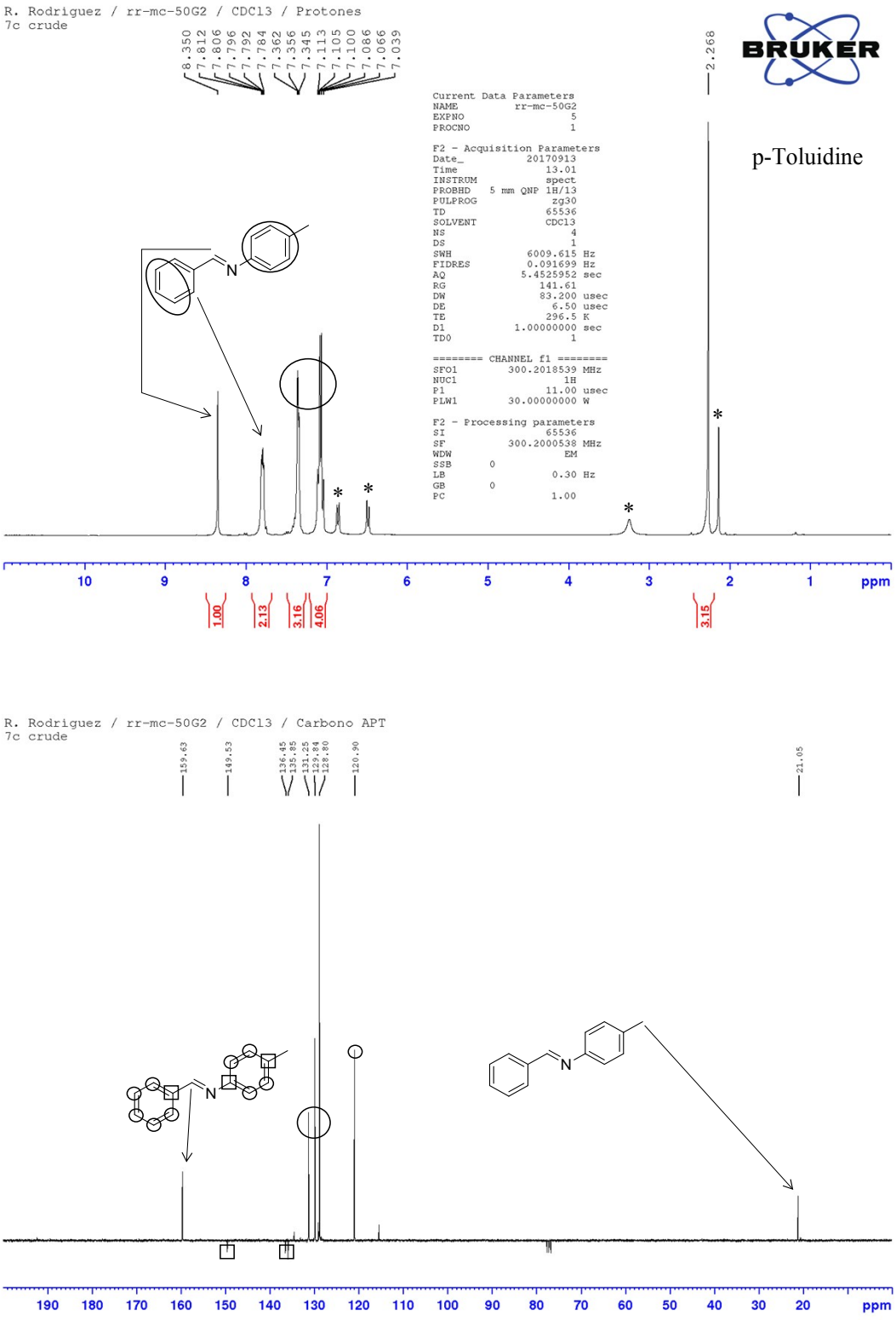


Figure S37. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **7c** crude in $CDCl_3$.

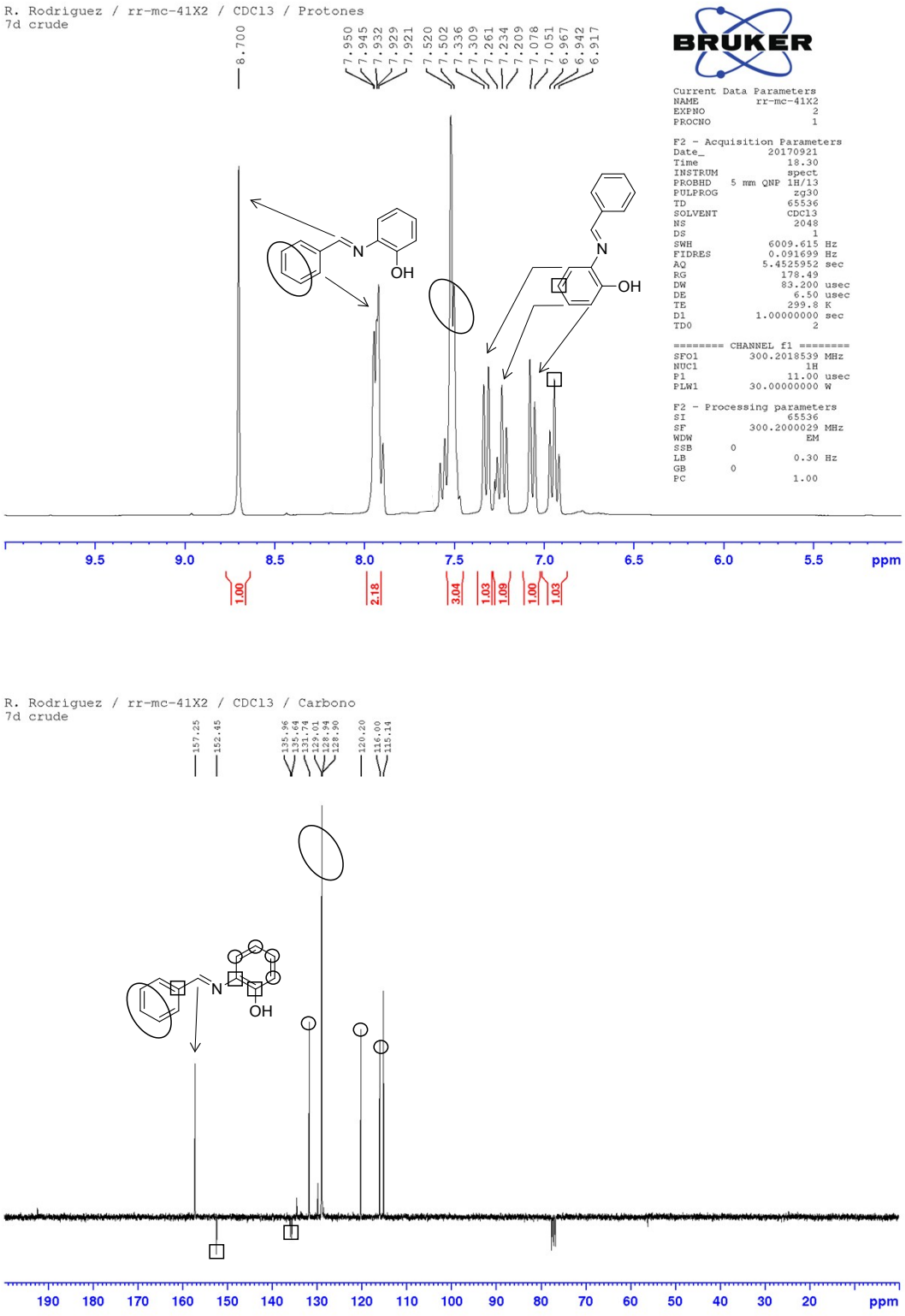


Figure S38. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **7d** crude in $CDCl_3$.

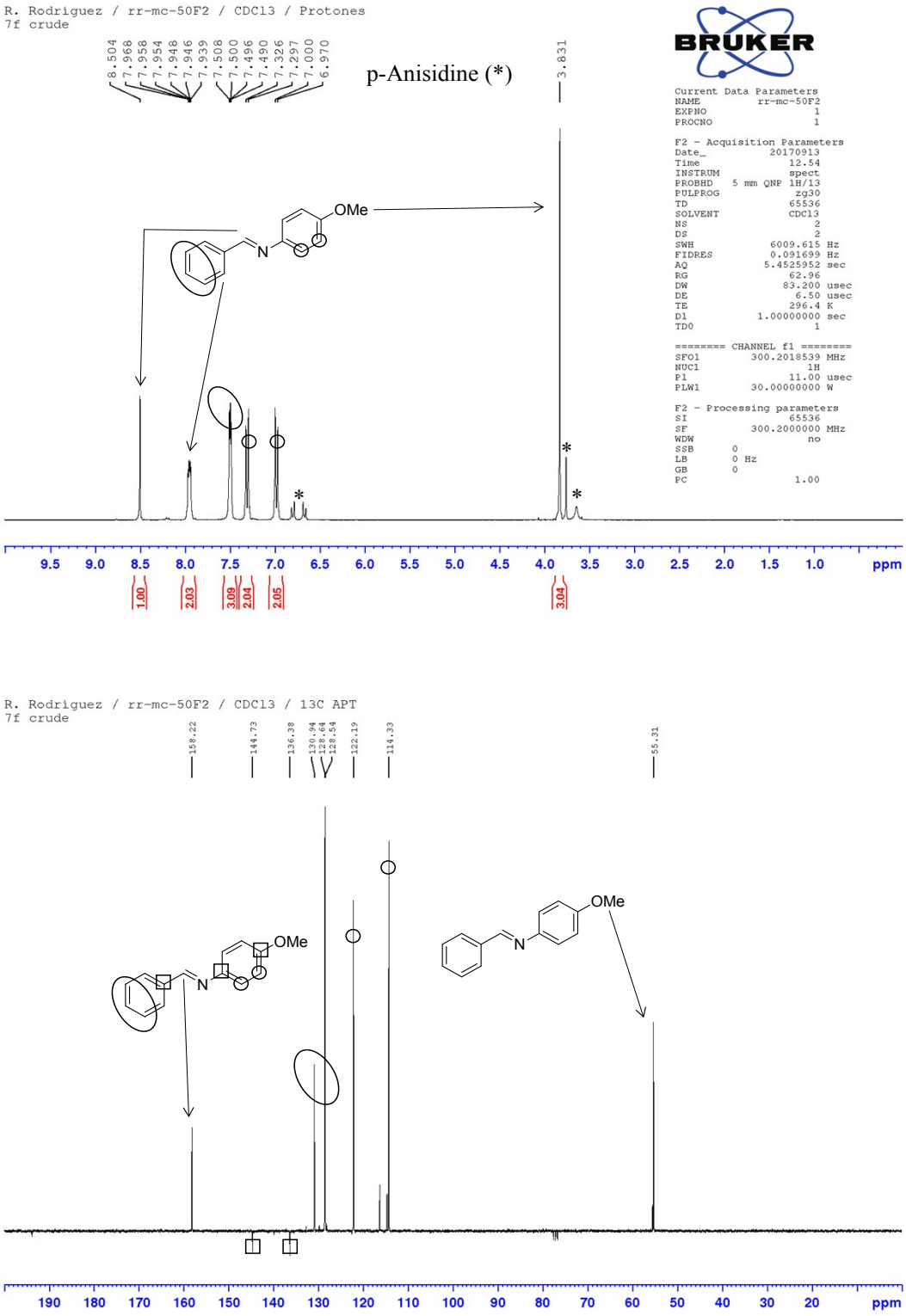


Figure S39. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **7f** crude in $CDCl_3$.

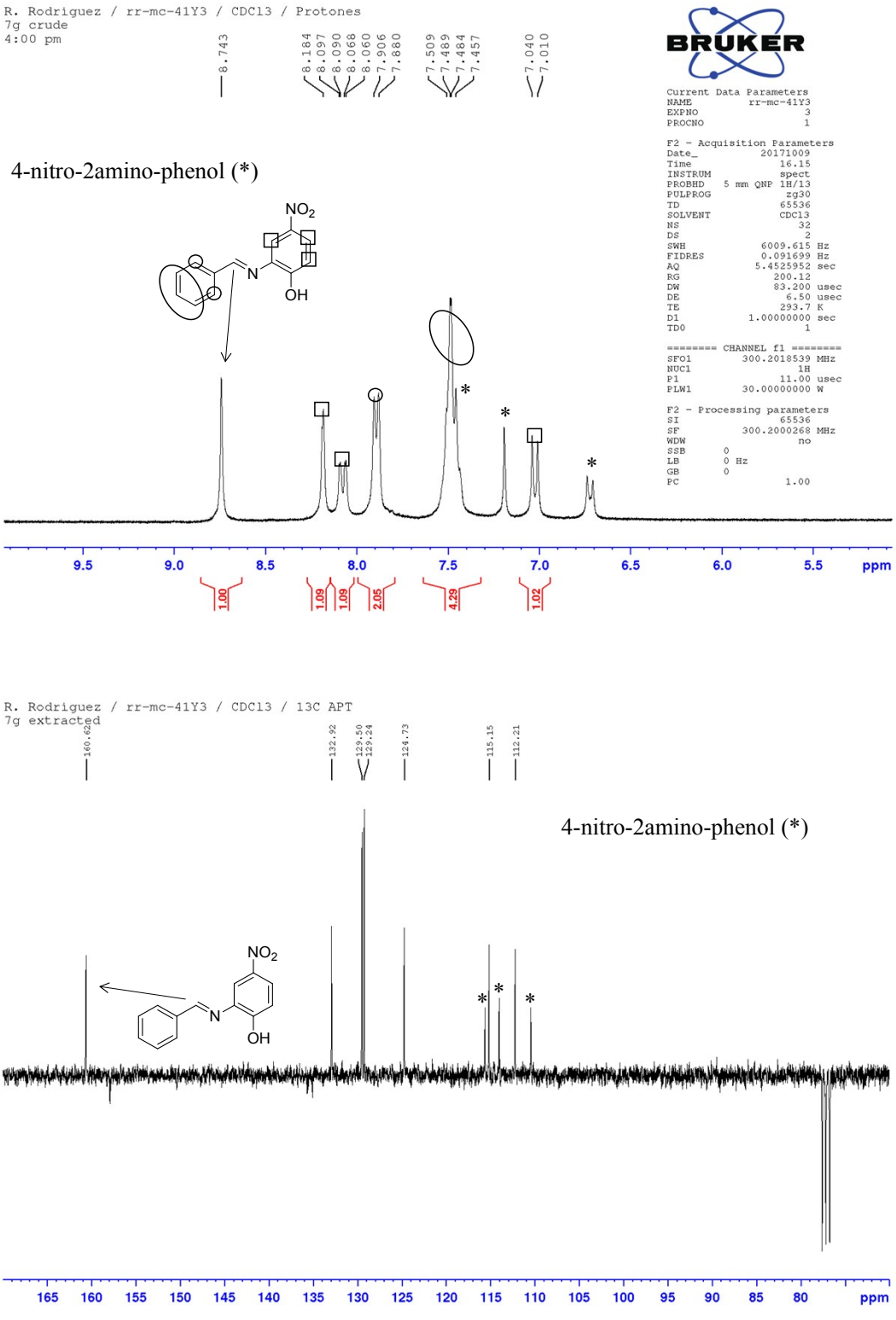


Figure S40. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **7g** crude in $CDCl_3$.

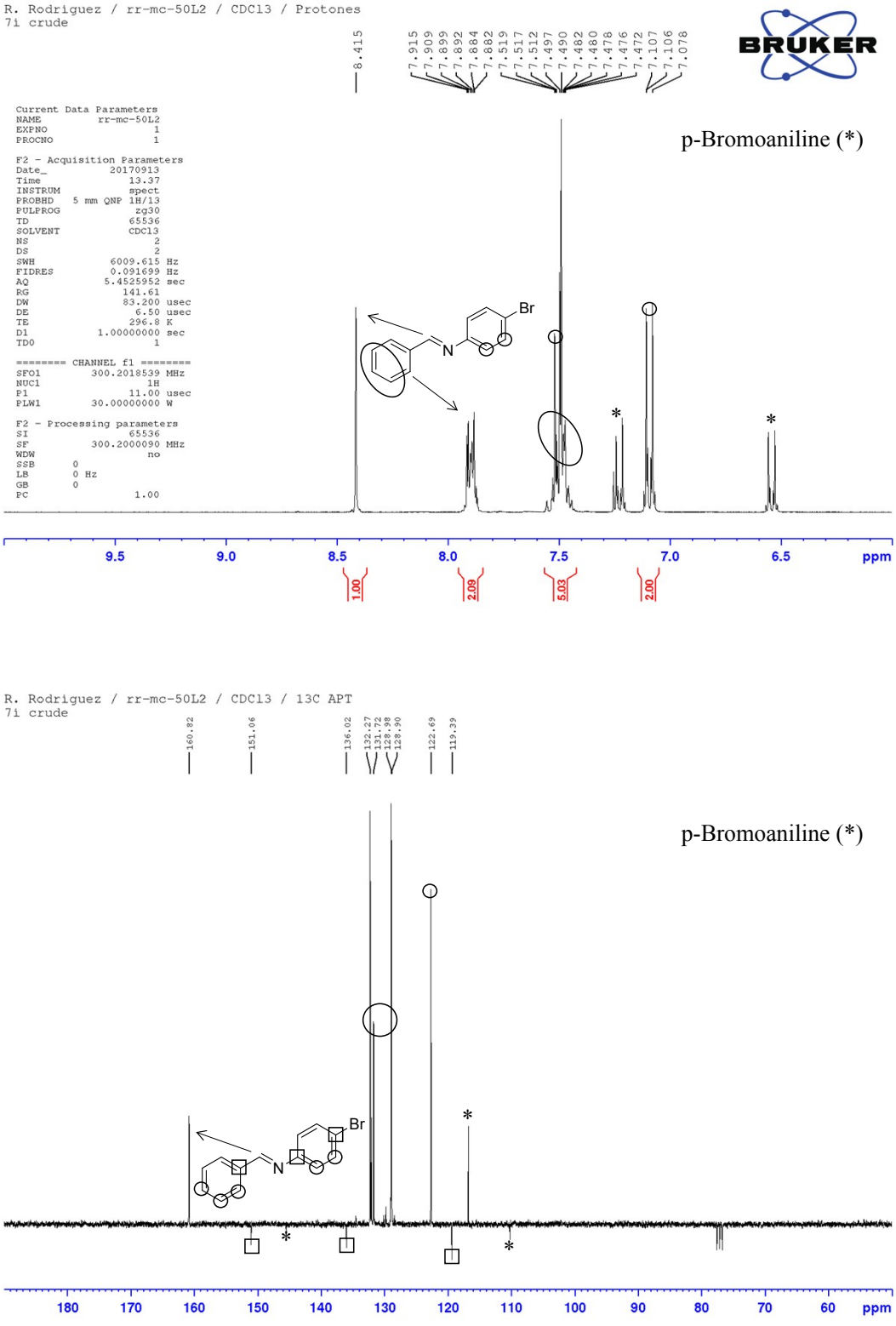


Figure S41. ^{1}H (300 MHz, top) and $^{13}C\{^{1}H\}$-APT (75.5 MHz, bottom) NMR spectra at 298 K of **7i** crude in $CDCl_3$.

M. References

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(3) Harris, R. K.; Becker, E. D.; de Menezes, S. M. C.; Goodfellow, R.; Granger, P. *Pure and Applied Chemistry* **2001**, 73, 1795–1818; *Solid State Nucl. Magn. Reson*. **2002**, 22, 458–483.
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(5) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst*. **2009**, 42, 339-341.