A Highly Sensitive Fluorescent Sensor for Palladium Based on the Allylic Oxidative Insertion Mechanism

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Palladium is a rare transition metal that plays a pivotal role in materials and chemistry. Palladium (Pd)-catalyzed reactions such as the Buchwald−Hartwig, Heck, Sonogashira, and Suzuki−Miyaura reactions are becoming increasingly important because of the power of making difficult covalent bonds.[1] However, even after purification, residual palladium is often found in the final product, which may be a health hazard.[2] While the proposed dietary intake is <1.5 to 15 μg/day per person[3] (10 ppm of Pd in active pharmaceutical ingredients as a threshold),[4] Pd-catalyzed reactions often produce materials contaminated with Pd at a much higher level requiring extensive purifications and analyses.[3,5] Although typical analytical methods for Pd detection require the use of expensive spectrometers (atomic absorption spectroscopy, X-ray fluorescence, plasma emission spectroscopy), a more desirable approach would rely on detection with the naked eye in a high-throughput fashion. Here we report that we have developed a fluorescein-based Pd sensor that relies on fluorescence emission. We found that with a standard fluorometer, less than 1 ppm of Pd can be quantified from a 1-mg sample.

Pd(0) is capable of catalyzing the allylic oxidative insertion to cleave the allylic C−O bond of allylic ethers **A** to form Pd complexes **B** (Figure 1).[6] These complexes then react with various nucleophiles to form compounds **C** and byproducts **D**, which is known as the Tsuji−Trost reaction.[7] Therefore, if **A** is nonfluorescent and **D** is fluorescent, such a system could be used to specifically detect the presence of Pd(0). Moreover, since Pd(II) can be readily reduced to Pd(0), Pd(II) could also be detected by the same principle.

Fluorescein compounds are nonfluorescent when the phenolic hydroxy group is alkylated (**E**) while strongly green fluorescent ($\Phi \approx 0.9$) when the hydroxy group is deprotonated (**F**).[8] This principle has been used for various purposes, primarily in biology for fluorescent imaging.[9] We hypothesized that this same chemical principle could be used for Pd sensing in a scenario where compounds **A** and **D** correspond to **E** and **F**, respectively.

As shown in Scheme 1, allyl ether **2** (corresponding to **A** and **E**) was prepared in two steps from commercially available 2ʹ,7ʹ-dichlorofluorescein (DCF) in multiple gram quantities via the known compound **1**.[10] Compound **2** was converted to compound **3** (corresponding to **D** and **F**) using 0.5 mol % of Pd(PPh₃)₄ in quantitative yield. The same efficient conversion was achieved when Pd(OAc)₂ and PPh₃ were used in lieu of Pd(PPh₃)₄. Compound **3** was 442 times more fluorescent than compound **2** at $\lambda_{em} = 526$ nm (pH 10 borate buffer) and was as fluorescent as fluorescein. Because both of the Pd oxidation states (0 and II) could be present in fine chemicals and pharmaceutical ingredients after Pd-catalyzed cross-couplings, these successful transformations of **2** to **3** and the distinct fluorescent signals were quite encouraging and would allow for fluorescent detection of Pd species. Compound **3** is soluble in both water and organic solvents and might prove to be useful for fluorescein-based sensor development.[11]
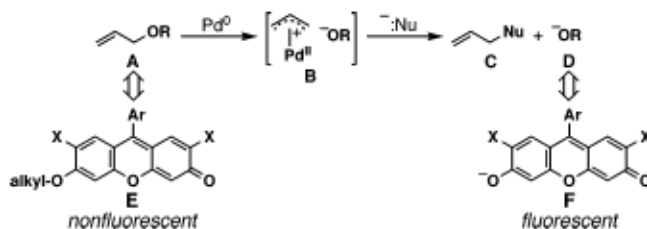

Figure 1. Correlation between palladium-catalyzed allyl ether cleavage and this work: X = H, F, Cl, etc.; Y = CO₂H, etc.

**Scheme 1.** Preparation of Pd Sensor 2 and Pd-Catalyzed Transformation of 2 to 3
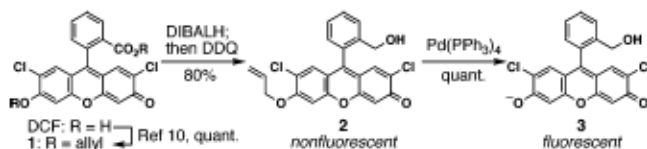
In the next stage, we studied the metal-specificity of this fluorescent sensing system (Figure 2). We found that the conversion of **2** to **3** in pH 10 borate buffer using PPh₃ as a reducing agent and a ligand was particularly efficient with Pd and to a lesser extent with Pt. It is noteworthy that other π-philic metals such as Ag, Ni, Au, Rh, Co, Hg, and Ru did not catalyze the deallylation reaction (**2** to **3**).

We then proceeded to develop a quantitative method to sense Pd. In the pharmaceutical industry, 5 mg samples are routinely used for Pd analyses. Thus, we set out to develop a fluorescent method that allows for the detection of ≤50 ng of Pd (≤10 ppm for a 5 mg sample). The final solutions in each pH 10 borate buffer solution contained Pd(PPh₃)₄ in various quantities and Pd sensor **2** at 10 μM. After 1 h incubation at 24 °C, the fluorescent signal of each sample was measured. As Figure 3a shows, fluorescent signals were linearly correlated ($R^2 = 0.993$) to the Pd concentrations from 3 to 300 nM (0.95 to 95 ng). To verify that this system can detect Pd(II) with the same sensitivity, we compared a Pd(PPh₃)₄ solution with a PdCl₂−PPh₃ solution. As Figure 3b indicates, both samples exhibited nearly the same fluorescence intensity, and PdCl₂ without PPh₃ did not convert **2** to **3** efficiently (almost negligible; data not shown). These results support the generality of the Pd sensor system for both Pd(0) and Pd(II) under reducing conditions.

To determine whether this fluorescent sensor could be applied to Pd analyses in pharmaceutical products, we prepared a sample that contained a commercially available aspirin tablet and PdCl₂ at the 10 ppm level. A solution of this sample containing 1 mg of the drug and 10 ng of PdCl₂ was added to the pH 10 borate buffer solution of Pd sensor **2** and PPh₃. The fluorescent intensity of the resulting solution was then measured (Figure 3c) and compared to a positive control (aspirin-free Pd solution) and a negative control (Pd-free aspirin solution). The signals from the Pd-contaminated aspirin solutions were nearly the same as the positive controls,
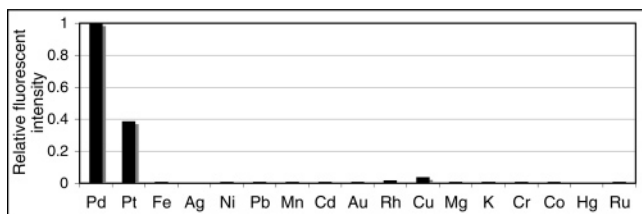
Figure 2. Metal specificity: "Pd" = $PdCl_2$, "Pt" = $PtCl_2$, "Fe" = $FeCl_3$, "Ag" = $AgNO_3$, "Ni" = $NiCl_2$, "Pb" = $Pb(NO_3)_2$, "Mn" = $MnCl_2$, "Cd" = $CdCl_2$, "Au" = $AuCl_3$, "Rh" = $RhCl(PPh_3)_3$, "Cu" = $CuCl_2$, "Mg" = $MgSO_4$, "K" = KCl, "Cr" = $CrCl_3$, "Co" = $CoCl_2$, "Hg" = $HgCl_2$, "Ru" = $RuCl_3$.
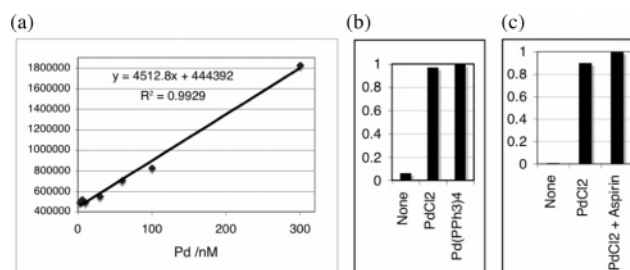
Figure 3. Quantitative fluorescent analysis of Pd: y-axis = relative fluorescent intensity. (a) The linear correlation between Pd quantity and fluorescence. (b) Pd(0) and Pd(II) show nearly the same signals: (left) no Pd reagent; (center) $[PdCl_2]$ = 2.0 μM; (right) $[Pd(PPh_3)_4]$ = 2.0 μM. (c) Proof of concept for Pd detection in drugs: (left) no Pd; (center) $PdCl_2$ (10 ng); (right) $PdCl_2$ (10 ng) + aspirin (1 mg).
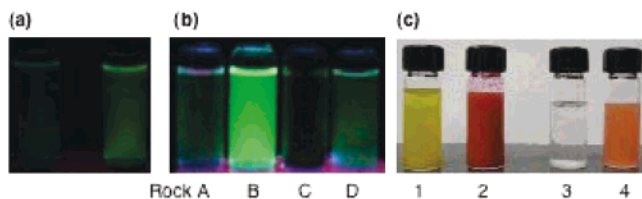
Figure 4. Further applications of **2**. (a) Detection of Pd on the surface of glassware: (left) The solution in a vial not exposed to Pd reagents; (right) the solution in a vial exposed to $Pd_2(dba)_3$ (10 mg) in THF and washed extensively. The photo was taken above a hand-held UV lamp (365 nm). (b) Photo of Pd/Pt detection in rocks: rock A, no metals; rock B, 120 ppm Pd/Pt; rock C, only Au/Ag; rock D, 35 ppm Pd/Pt (Pd/Pt = 3.4:1). The photo was taken above a hand-held UV lamp (365 nm). (c) Naked eye detection of Pd: (vial 1) $PdCl_2$ (1.6 mM), dimethylglyoxime (1% w/v in ethanol) in 0.25 N HCl; (vial 2) $PdCl_2$ (1.6 mM), **2**, $NaBH_4$ in THF; (vial 3) $PdCl_2$ (10 μM), dimethylglyoxime (1% w/v in ethanol) in 0.25 N HCl; (vial 4) $PdCl_2$ (10 μM), **2**, $NaBH_4$ in THF.

supporting the robustness of the Pd sensing method under such heterogeneous conditions.

An additional concern with Pd contamination is the reactors used for Pd-catalyzed reactions. To test whether our method can detect residual Pd in a reactor, a THF solution of $Pd_2(dba)_3$ was stirred in a flask for 1 h at 24 °C. After standard laboratory washing procedure (brushing with detergent, washing with water and acetone), the Pd sensor solution was added to this flask and stirred for 1 h at 24 °C. Presumably because of residual Pd on the glass surface, the solution became more green fluorescent (Figure 4a, right) than a negative control (Figure 4a, left), showing that this Pd sensing method can be used for the quality control of reactors.

Current methods of discovering Pd/Pt-containing rocks (Pd and Pt coexist in most rocks) involve atomic absorption analysis, which miners cannot employ at the mining site. We wanted to determine whether we can detect Pd in rock samples for Pd/Pt detection at mining sites. Rock samples from mining were obtained from

Stillwater Mining. Rock stock solutions (50 μL each) were prepared and mixed with Pd sensor solution for 1 h at 24 °C and the fluorescent intensity of the resulting solutions was measured (see Supporting Information). Rock B contains Pd/Pt (3.4:1, 120 ppm), an economically viable quantity. Rock D contains 30% of Pd/Pt compared to rock B. Rock A contains no transition metals and rock C contains Au/Ag but no Pd/Pt. Only rocks B and D converted **2** to **3** and the fluorescent intensity was relative to the amount of Pd/Pt in the sample. Rock samples A and C exhibited negligible fluorescence demonstrating the viability of our sensor in Pd/Pt detection at mining sites via a simple hand-held UV lamp (Figure 4b).

To demonstrate that Pd can be detected even without a UV lamp, we prepared four $PdCl_2$ solutions (Figure 4c). The Pd sensor was added to vials 2 and 4, and dimethylglyoxime was added to vials 1 and 3. At a lower Pd concentration (vials 3 and 4; $[PdCl_2]$ = 10 μM), only the solution containing our sensor (vial 4) exhibited a color change detectable with the naked eye showing the usefulness of our sensor.

In conclusion, we have developed a highly sensitive and robust fluorescent method to detect small quantities of Pd regardless of its oxidation state. Sensor **2** was readily synthesized and may find other applications such as monitoring the presence of Pd(0) during Pd-catalyzed reactions. Although each sample was incubated for 1 h in this study, Pd quantities can be determined after 5–10 min incubation using a fluorescent plate reader. This user-friendly sensor technology should greatly aid in the detection of Pd in both the pharmaceutical and mining industries by enabling colorimetric analysis of Pd that can be performed even by untrained scientists.

Supporting Information Available: Experimental procedures for Scheme 1, Figures 2, 3, and 4. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information

General Information

All reactions were carried out under a nitrogen atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium-benzophenone, and methylene chloride (CH_2Cl_2) was distilled from calcium hydride. Yields refer to chromatographically and spectroscopically (^1H NMR) homogenous materials, unless otherwise stated.

All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25-mm EMD silica gel plates (60F-254) using UV-light (254 nm), 2.4% phosphomolybdic acid/1.4% phosphoric acid/5% sulfuric acid in water, anisaldehyde in ethanol, or 0.2% ninhydrin in ethanol and heat as developing agents. TSI silica gel (230–400 mesh) was used for flash column chromatography.

NMR spectra were recorded on AM300 (Bruker) instruments and calibrated using a solvent peak or tetramethylsilane as an internal reference. The following abbreviations are used to indicate the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High-resolution mass spectra were obtained by using EBE geometry.

$PdCl_2$, $Pd(PPh_3)_4$ and $Pd_2(dba)_3$ were purchased from Strem and used as received. Aspirin is a product of BAYER Co.

Experimental Section
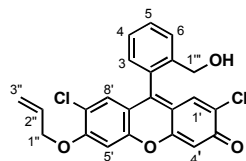
Compound 2. To a solution of compound **1** (4.80 g, 10.0 mmol) in CH$_2$Cl$_2$ (40 mL) was added DIBALH (48 mL, 1.0 M in hexanes, 48.0 mmol) dropwise over 15 min at -78 °C under a nitrogen atmosphere. The mixture was stirred for 5 min at the same temperature and then was warmed to 24 °C. After 2 h, Et$_2$O (90 mL) was added and the reaction mixture was quenched with saturated aqueous NH$_4$Cl (15 mL) at 0 °C. This mixture was warmed to 24 °C again and stirred for 1 h. A second portion of Et$_2$O (180 mL) was added to the mixture followed by DDQ (2.50 g, 11.0 mmol) at 0 °C. After stirring 1 h at 24 °C, the mixture was filtered through Celite® and washed with EtOAc. The filtrate was dried over Na$_2$SO$_4$ and the solvents were evaporated under reduced pressure. Silica gel flash chromatography of the residue (5 → 10 % EtOAc in hexanes) afforded compound **2** as a pink solid (3.43 g, 80%).

Data for **2**: mp = 167–168 °C; R$_f$ = 0.69 (50% EtOAc in hexanes); IR (in CH$_2$Cl$_2$): 3385 (br, OH), 3077, 2923, 2855, 1608, 1486, 1410, 1266, 1191, 1032, 875, 725 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, 293K): δ 7.37–7.40 (m, 2H, Ar), 7.26–7.30 (m, 1H, Ar), 6.89 (s, 1H, Ar), 6.87 (s, 1H, Ar), 6.84 (m, 1H, Ar), 6.83 (s, 1H, Ar), 6.73 (s, 1H, Ar), 6.05 (ddt, J = 17.4, 10.2, 5.1 Hz, 1H, 2″-H), 5.47 (ddt, J = 17.4 , 3.0, 1.5 Hz, 1H, 3″-H$_{trans}$), 5.32 (ddt, J = 10.2, 3.0, 1.5 Hz, 1H, 3″-H$_{cis}$), 5.28 (s, 2H, 1‴-H), 4.63 (ddt, J = 5.1, 1.5, 1.5 Hz, 2H, 1″-H); ^{13}C NMR (75 MHz, CDCl$_3$, 293K): δ 154.6, 152.1, 150.1, 149.5, 143.6, 138.6, 132.1, 129.6, 128.7 (two carbons), 128.6, 123.7, 121.0, 118.2, 118.1, 118.0, 117.2, 115.6, 103.7, 101.5, 83.1, 72.3, 69.8; HRMS (ESI+) calcd for C$_{23}$H$_{17}$Cl$_2$O$_4$ [M+H]$^+$ 427.0504, found 427.0519.
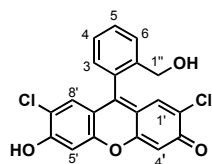
Compound 3. To a solution of compound **2** (855 mg, 2.00 mmol) in THF (20 mL) was added morpholine (192 μL, 2.20 mmol), sodium borohydride (90.8 mg, 2.40 mmol) and Pd(PPh$_3$)$_4$ (11.6 mg, 0.01 mmol) at 24 °C. After 2 h, 3 N HCl (4 mL) was added very slowly to quench the reaction. The mixture was extracted with EtOAc, dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (10% → 60% EtOAc in hexanes) to afford compound **3** as an orange solid (772 mg, 99%).

Data for **3**: mp > 270 °C; R$_f$ = 0.18 (50% EtOAc in hexanes); IR (in CH$_2$Cl$_2$): 3174 (br, OH), 2930, 1634, 1593, 1584, 1521, 1347, 1273, 1043, 839 cm^{-1}; ^{1}H NMR (300 MHz, CD$_3$OD, 293K): δ 7.42–7.47 (m, 2H, Ar), 7.32–7.37 (dd, J = 7.5, 7.5 Hz, 1H, Ar), 6.85 (d, J = 7.5 Hz, 1H, Ar), 6.78 (s,

2H, Ar), 6.74 (s, 2H, Ar), 5.28 (s, 2H, 1″-H). ^{13}C NMR (75 MHz, CD$_3$OD, 293K): δ 155.5, 151.3, 145.5, 140.3, 130.7, 129.9, 124.7, 122.4, 118.2, 117.6, 104.5, 84.8, 73.2 (Although 20 peaks expected, only 13 peaks detected); HRMS (EI+) calcd for C$_{20}$H$_{12}$Cl$_2$O$_4$ [M]$^+$ 386.0113, found 386.0108.

UV-visible spectroscopy. Absorption spectra were acquired on a Pekin Elmer Lambda 19 UV-Visible spectrometer under the control of a Windows-based PC running the manufacturers' supplied software.

Fluorescence spectroscopy. Fluorescence spectra were recorded in a 1 × 1-cm quartz cuvette on a Jobin Yvon FluoroMax-3 spectrometer under the control of a Windows-based PC running FluorEssence software. The samples were excited at 497 nm and the emission intensities were collected at 523 nm. All spectra were corrected for emission intensity using the manufacturer supplied photomultiplier curves.

Preparation of stock solutions. A 10.0 mM solution of compound **2** (42.7 mg, 0.10 mmol) was prepared in DMSO (10 mL) and stored in a refrigerator for use. A 100 mM solution of PPh$_3$ (262.3 mg, 1.00 mmol) was prepared in DMSO (10 mL). A 1.0 mM solution of Pd(PPh$_3$)$_4$ (11.6 mg, 0.010 mmol) was prepared in 95:5 MeOH/DMF (10 mL). A 5.0 mM stock solution of PdCl$_2$ (8.9 mg, 0.05 mmol) was prepared in 75:25 MeOH/brine (10 mL). Further dilution of the 5.0 mM stock solution of PdCl$_2$ with MeOH was done to prepare the 1.0 mM and 100 μM stock solutions.

Aspirin (500 mg) was dissolved in methanol by stirring overnight. After filtration, the solvent was evaporated. The residue was dissolved in 50 mL of borate buffer (pH = 10.0, J.T. Baker) to prepare a 10 mg/mL stock solution. All other metal ion solutions were prepared at 1.0 mM in methanol (or methanol with small amount water).

Preparation of analytic samples for fluorescence detection. To the borate buffer (5 mL, pH = 10.0, J.T. Baker) was added the PPh$_3$ stock solution (5.0 μL, 100 mM). Different amounts of analyte (metal ion solutions or Aspirin solution) were added to obtain different concentrations, and the resulting solutions were agitated. To the mixture was added compound **2** stock solution (5.0 μL, 10.0 mM), and the samples were shaken again and incubated for 1 h before fluorescence measurement.

Fluorescence quantum yield measurements. Quantum yields were determined using fluorescein in 0.1 N NaOH (Φ = 0.95) as a standard. To determine quantum yields relative to fluorescein, stock solutions of compound **2** and **3** were prepared in DMSO (1 mM) and diluted in phosphate buffer (pH = 7.0, J.T.Baker) to OD < 0.09.

Reactors contamination experimental procedure. To two 10 mL round-bottom flasks was added K$_2$CO$_3$ (10 mg) and THF (3 mL). To one of the two flasks was then added Pd$_2$(dba)$_3$ (10 mg). The mixtures in the two flasks were stirred at 24 °C for 1 h, and then all chemicals were removed. The two flasks were washed three times each with acetone and water and one more time with acetone.

To the two washed flasks was added 5 mL of borate buffer (pH = 10.0, J.T. Baker), PPh$_3$ stock solution (5.0 μL, 100 mM) and compound **2** stock solution (5.0 μL, 10.0 mM) at 24 °C. The solutions were stirred at the same temperature for 1 h, then a hand-held UV lamp (366 nm) was used to examine the fluorescence of the two solutions from the two flasks, and photographs were obtained with a digital camera.

Comparison between spot test and current sensor system

Vial 1: To a solution of PdCl$_2$ (1.0 mg) in 0.25 N HCl (2.5 mL) was added dimethylglyoxime solution (1% w/v in EtOH, 1 mL). The resulting solution was agitated and incubated for 1 h.

Vial 2: To a solution of PdCl$_2$ (1.0 mg) in THF (3.5 mL) was added sensor compound (50 mg) and NaBH$_4$ (10 mg). The resulting solution was agitated and incubated for 1 h.

Vial 3: To 0.25 N HCl (2.0 mL) was added dimethylglyoxime solution (1% w/v in EtOH, 1 mL) and a PdCl$_2$ solution (30 μL, 1.0 mM). The resulting solution was agitated and incubated for 1 h.

Vial 4: To sensor compound solution (20 mg) in THF (3.0 mL) was added NaBH$_4$ (5 mg) and a PdCl$_2$ solution (30 μL, 1.0 mM). The resulting solution was agitated and incubated for 1 h.

Vial	1	2	3	4
	Spot test	Pd sensor	Spot test	Pd sensor
[PdCl$_2$]	1.6 mM	1.6 mM	10 μM	10 μM
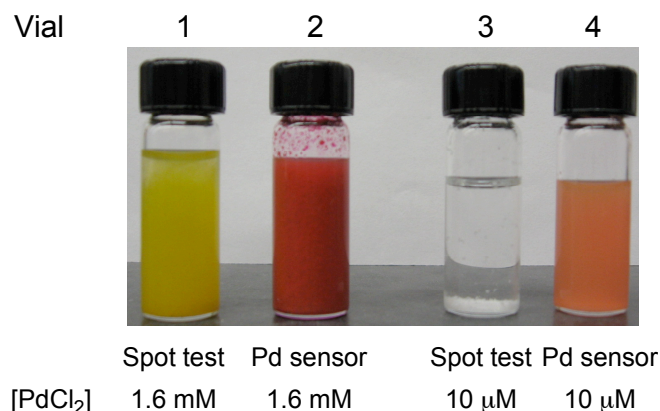
Rock samples preparation procedure

5 g of rock species was fused for 1 h at 650 °C in an oven. After being cooled to room temperature, the melt was boiled in concentrated HCl (75 mL) for 15 min. After being cooled, concentrated HNO_3 (25 mL) was added and soaked overnight. The resulting mixture was boiled for 2 h to evaporate to near dryness. After drying, aqua regia (25 mL) was added and evaporated to a wet salt, this mixture was dissolved and diluted with 100 mL of water, filtered, and the filtrate was kept for use as rock stock solution. 50 μL of the rock stock solution was added to sensor solution ([**2**] = 10 μM and [PPh_3] = 100 μM in pH 10.0 borate buffer (5 mL)) to obtain the rock samples.

Caution: During heating the samples with HCl or HNO_3, the acid vaporizes.
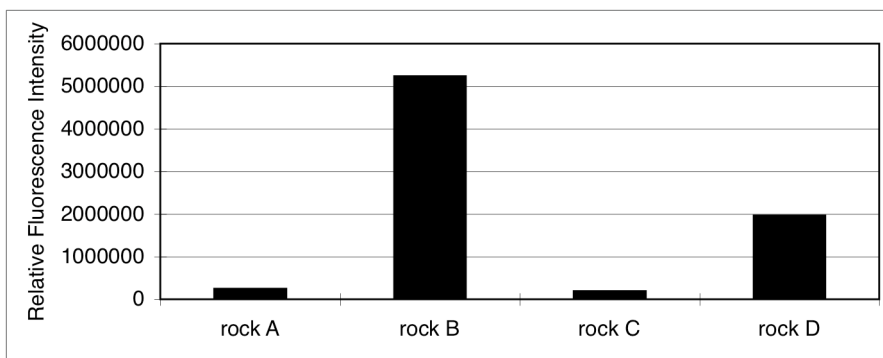
¹H NMR spectrum of compound **2**: CDCl₃, 293K, 300 MHz

Current Data Parameters
NAME   FS2026-1 HNMR
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters
Date_   20070201
Time   0.07
INSTRUM   spect
PROBHD   5 mm DUL 1H-13
PULPROG   zg
TD   65536
SOLVENT   CDCl3
NS   16
DS   2
SWH   6218.905 Hz
FIDRES   0.094893 Hz
AQ   5.2691445 sec
RG   574.7
DW   80.400 usec
DE   6.00 usec
TE   300.0 K
D1   2.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   1H
P1   9.00 usec
PL1   1.00 dB
SFO1   300.3818550 MHz

F2 - Processing parameters
SI   32768
SF   300.3800083 MHz
WDW   EM
SSB   0
LB   0.30 Hz
GB   0
PC   1.00

^{13}C NMR spectrum of compound **2**: CDCl$_3$, 293K, 75 MHz

Current Data Parameters
NAME   FS2026-1 13C
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters
Date_   20070131
Time   23.24
INSTRUM   spect
PROBHD   5 mm DUL 1H-13
PULPROG   zgpg
TD   65536
SOLVENT   CDC13
NS   327
DS   4
SWH   18115.941 Hz
FIDRES   0.276427 Hz
AQ   1.8088436 sec
RG   10321.3
DW   27.600 usec
DE   6.00 usec
TE   300.0 K
D1   10.00000000 sec
d11   0.03000000 sec
DELTA   9.89999962 sec
TD0   1

======== CHANNEL f1 ========
NUC1   13C
P1   9.00 usec
PL1   1.80 dB
SFO1   75.5381641 MHz

======== CHANNEL f2 ========
CPDPRG2   waltz16
NUC2   1H
PCPD2   92.00 usec
PL2   0.00 dB
PL12   20.00 dB
PL13   20.00 dB
SFO2   300.3812015 MHz

F2 - Processing parameters
SI   65536
SF   75.5306127 MHz
WDW   EM
SSB   0
LB   1.00 Hz
GB   0
PC   1.40

S7

Current Data Parameters
NAME   AG5079 after column new
EXPNO   1
PROCNO   1

F2 - Acquisition Parameters
Date_   20070206
Time   18.05
INSTRUM   spect
PROBHD   5 mm DUL 1H-13
PULPROG   zg
TD   65536
SOLVENT   MeOD
NS   16
DS   2
SWH   6218.905 Hz
FIDRES   0.094893 Hz
AQ   5.269445 sec
RG   574.7
DW   80.400 usec
DE   6.00 usec
TE   300.0 K
D1   2.00000000 sec
TD0   1

======== CHANNEL f1 ========
NUC1   1H
P1   9.00 usec
PL1   1.00 dB
SFO1   300.3818550 MHz

F2 - Processing parameters
SI   32768
SF   300.3795306 MHz
WDW   EM
SSB   0
LB   0.30 Hz
GB   0
PC   1.00

Current Data Parameters
NAME   AG5079 13C
EXPNO   2
PROCNO   2

F2 - Acquisition Parameters
Date_   20070206
Time   23.13
INSTRUM   spect
PROBHD   5 mm DUL 1H-13
PULPROG   zgpg
TD   65536
SOLVENT   MeOD
NS   1024
DS   4
SWH   18115.941 Hz
FIDRES   0.276427 Hz
AQ   1.8088436 sec
RG   11585.2
DW   27.600 usec
DE   6.00 usec
TE   300.0 K
D1   10.00000000 sec
d11   0.03000000 sec
DELTA   9.89999962 sec
IDO   1

======== CHANNEL f1 ========
NUC1   13C
P1   9.00 usec
PL1   1.80 dB
SFO1   75.5381641 MHz

======== CHANNEL f2 ========
CPDPRG2   waltz16
NUC2   1H
PCPD2   92.00 usec
PL2   0.00 dB
PL12   20.00 dB
PL13   20.00 dB
SFO2   300.3812015 MHz

F2 - Processing parameters
SI   65536
SF   75.5303779 MHz
WDW   EM
SSB   0
LB   1.00 Hz
GB   0
PC   1.40

73.21
84.81
104.54
117.63
118.24
122.36
124.72
129.94
130.71
140.28
145.54
151.30
155.45