Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Towards the Design of Self-Sorting Nanomaterials Through Kinetically Directed Orthogonal Control over Interfacial Surface Chemistry

Praveen N. Gunawardene, Max Weismann, Jack Bowman, Pierangelo Gobbo, Mark S. Workentin

Supporting Information

1.0 General Materials and Methods

Reagents and Solvents. The following materials were used as received. Tetraethylene glycol (99%), p-toluenesulfonyl chloride (≥99%), sodium azide (≥99.5%), triethylamine (≥99%), triphenylmethanethiol (97%), triphenylphosphine (99%), trifluoroacetic acid (99%), triisopropylsilane (98%), gold (III) chloride trihydrate (≥99.9% trace metal basis), sodium borohydride (≥98%), rhodium (II) acetate dimer (99.99% trace metals basis), ethyl diazoacetate (contains ≥13 wt% dichloromethane), bromine (reagent grade), lithium aluminum hydride (95%), potassium *tert*-butoxide (1.0 M in THF), 4-nitrophenyl chloroformate (96%), 3-bromo-1-propanol (97%), 4-azidoanisole solution (0.5 M in *tert*-butyl methyl ether, ≥90%), azidobenzene solution (0.5 M in *tert*-butyl methyl ether), 4-nitroaniline (≥99%), 4-bromopyridine hydrochloride (99%), 2,3,4,5,6-pentafluoroaniline, N-methylhydroxylamine hydrochloride (98%), nitrobenzene (≥99%), zinc dust (<10μm, ≥98%), p-anisaldehyde (98%), benzaldehyde (≥99%), 4-nitrobenzaldehyde (98%), 3-pyridinecarboxaldehyde (98%), 4-nitrobenzonitrile (97%) and dichloromethane-d2 (D 99.5 atom%) were purchased from Sigma-Aldrich (Millipore Sigma). Chloroform-D (D 99.8%) was purchased from Cambridge Isotope Laboratories. Sodium choride, sodium hydroxide pellets, tetrahydrofuran and toluene were purchased from Fischer Scientific. Technical grade ammonium chloride, magnesium sulphate, sodium nitrite, hexanes, dichloromethane, di-ethyl ether, methanol, acetic acid, acetonitrile, pentane and 12 M hydrochloric acid were purchased from Caledon. Ethanol (anhydrous) was purchased from Commercial Alcohols.

Unless otherwise state, all reactions were performed at ambient conditions.

NMR Spectroscopy. ^{1}H and $^{13}C\{^{1}H\}$ spectra were recorded on either a Bruker AvIII HD 400 spectrometer or Varian INOVA 600 spectrometer, as indicated. ^{1}H NMR spectra are reported as δ in units of parts per million (ppm), and referenced against residual protonated chloroform (δ 7.27 ppm, s) or dichloromethane (δ 5.32, t), as indicated. Multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintuplet), m (multiplet) and br (broad signal). Coupling constants are reported as a *J* value in Hertz (Hz) according to the spectrometer frequency.

The number of protons (*n*) for a given resonance is indicated as *n*H, and is based on spectral integration values. $^{13}C\{^{1}H\}$ NMR spectra are reported as δ in units of parts per million (ppm) and referenced against residual protonated chloroform (δ 77.0 ppm, t) or dichloromethane (δ 54.0 ppm, quin), as indicated.

Thermogravimetric Analysis (TGA). TGA was performed using a Mettler Toledo TGA/SDTA 851 instrument from 25°C to 750°C at a heating rate of 10°C/min under a nitrogen flow of 70 mL/min. The sample was prepared by adding a small sample of AuNP-BCN dissolved in dichlormethane onto a pre-weighed alumina crucible, removing the solvent under argon gas flow and drying the sample overnight under high vacuum, which resulted in the formation of a thin AuNP film on the crucible service.

X-Ray Photoelectron Spectroscopy (XPS). The XPS analyses were carried out with a Kratos Axis Ultra spectrometer using a monochromatic Al K(alpha) source (15mA, 14kV). Specimens were mounted on a double side adhesive and the Kratos charge neutralizer system was used on all specimens. Survey scan analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 160 eV. High resolution analyses were carried out with an analysis area of 300 x 700 microns and a pass energy of 20 eV. Spectra have been charge corrected to the main line of the carbon 1s spectrum set to 284.5 eV for graphitic/nanotube type species. Spectra were analyzed using CasaXPS software (version 2.3.14).

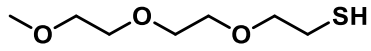
Mass Spectrometry. Electrospray ionization (ESI) mass spectra were obtained in either positive-ion or negative-ion mode using a Bruker microTOF II spectrometer.

Infrared (IR) spectroscopy. Attenuated total reflectance IR (ATR-IR) spectra were recorded using a PerkinElmer Spectrum Two FT-IR spectrometer.

2.0 Experimental Procedures

4-azidoanisole (**azide 2**) and azidobenzene (**azide 3**) were purchased from Sigma Aldrich as a 0.5 M solution in *tert*-butyl methyl ether, which was partitioned between water and ether. The resulting ether phase was dried over magnesium sulphate and the solvent was evaporated under reduced pressure.

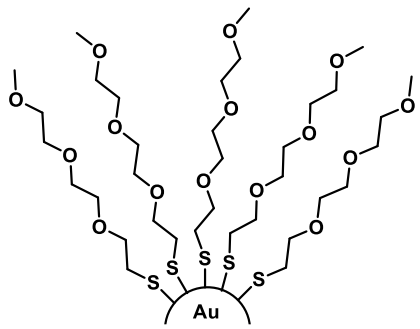
2.1 Synthesis of SH-EG$_3$-Me



* Synthesized according to our previously reported procedure[1].

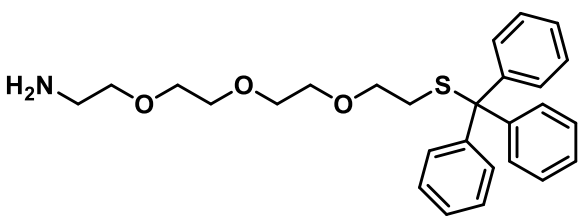
^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm): 3.66 (m, 8H), 3.57 (m, 2H), 3.39 (s, 3H), 2.71 (q, J = 8 Hz, 2H), 1.60 (t, J = 8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ(ppm): 72.8, 17.8, 70.5, 70.3, 70.1, 58.9, 24.2. HRMS (ESI) *m/z* calc. for $C_7H_{16}O_3S$ $(M)^+$: 180.0820, found: 180.0825.

2.2 Synthesis of AuNP-OMe



*Synthesized according to our previously reported procedure[1].

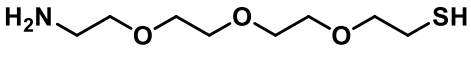
2.3 Synthesis of STrityl-EG$_4$-NH$_2$



*synthesized according to our previously reported procedure.[2] See reference 2 for ^{1}H and ^{13}C{^{1}H} NMR spectra.

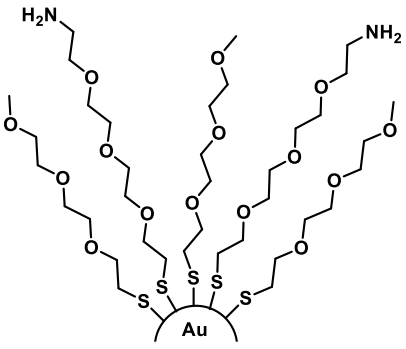
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.43 (m, 6H), 7.18 – 7.30 (m, 9H), 3.55 – 3.63 (m, 6H), 3.49 (t, J = 5.2 Hz, 2H), 3.45 (dd, J = 5.7, 3.9 Hz, 2H), 3.30 (t, J = 6.9 Hz, 2H), 2.93 (t, J = 5.1 Hz, 2H), 2.43 (t, J = 6.9 Hz, 2H), 1.97 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 144.8, 129.6, 127.8, 126.6, 73.0, 70.5, 70.4, 70.2, 70.1, 69.6, 41.6, 31.6. ESI-MS calcd for $C_{27}H_{34}NO_3S^+$ [M+H$^+$] 452.2259, found 452.2240.

2.4 Synthesis of SH-EG$_4$-NH$_2$



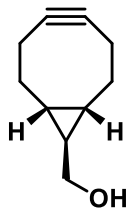
To 4.0 g (8.9 mmol) **STrityl-EG$_4$-NH$_2$** in 100 mL dry dichloromethane was added 2.2 mL (10.6 mmol) triisopropylsilane and then 34 mL (45 mmoL) trifluoroacetic acid. The reaction mixture was stirred for 1 hour while monitoring carefully by TLC, after which the solvent was removed via rotary evaporation. The crude residue was purified by flash column chromatography (3:1 dichlormethane:methanol) to give **SH-EG$_4$-NH$_2$** as a thick white oil in 83% yield (1.55g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.73 (m, 2H), 3.62 (m, 6H), 3.46 (m, 6H), 3.15 (t, J = 8 Hz, 2H), 2.68 (t, J = 8 Hz, 2H), 1.58 (t, J = 4 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): 72.7, 70.2, 70.1, 69.9, 69.7, 66.8, 39.6, 24.0. HRMS (ESI) *m/z* calc. for $C_8H_{19}NO_3S$ $(M)^+$: 209.1086, found: 209.1083.

2.5 Synthesis of AuNP-NH$_2$



To 0.3 g **AuNP-OMe** in 25 mL methanol was added 0.3 g **SH-EG$_4$-NH$_2$** in 5 mL methanol in a round bottom flask. The resulting solution was stirred for 2 hours at room temperature, after which the solvent was removed thoroughly via rotary evaporation to form a black AuNP film in the round bottom flask. The film was washed vigorously by adding 100 mL portions of dichloromethane and swirling the sample for 15 minutes. The dichloromethane was then poured out, and the film was re-dissolved in methanol and methanol was removed under reduced pressure to re-form the AuNP film, which was subsequently washed with two more 100mL portions of dichloromethane in the same way. After the final wash, the sample was dried thoroughly under high vacuum to give AuNP-NH$_2$ in quantitative yield (0.3 g).

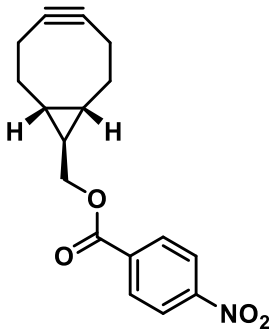
2.6 Synthesis of BCN_{exo}-OH



*Synthesized according to Dommerholt *et al.*[3] See reference 3 for $^{13}C\{^{1}H\}$ NMR

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.56 (d, J = 8 Hz, 2H), 2.42 (d, J = 16 Hz, 2H), 2.30 (t, J = 16 Hz, 2H), 2.17 (d, J = 16 Hz, 2H), 1.42 (m, 3H), 0.69 (m, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): 98.8, 67.1, 33.4, 27.3, 22.6, 21.5. HRMS (ESI) *m/z* calc. for $C_{10}H_{14}O$ $(M)^+$: 150.1045, found: 150.1052.

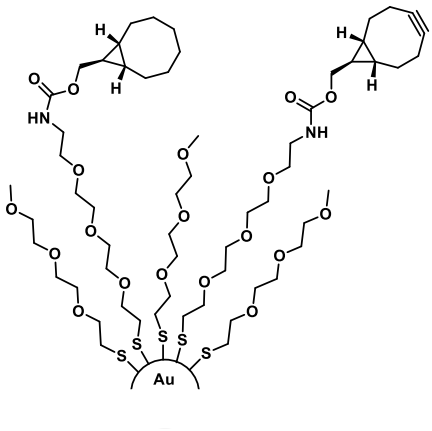
2.7 Synthesis of BCN_{exo}-O-pNP



*Synthesized according to Dommerholt *et al.*[3] See reference 3 for $^{13}C\{^{1}H\}$ NMR

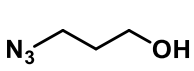
^{1}H NMR ($CDCl_3$, 400MHz): 8.29 (d, J = 8 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 4.23 (d, J = 8 Hz, 2H), 2.46 (m, 2H), 2.32 (m, 2H), 2.20 (m, 2H), 1.44 (m, 2H), 0.86 (m, 3H). ^{13}C NMR ($CDCl_3$, 150MHz): 155.6, 152.4, 145.2, 125.3, 121.7, 98.7, 68.0, 29.1, 21.3, 20.5, 17.2. HRMS (ESI) *m/z* calc. for $C_{17}H_{17}NO_5$ $(M)^+$: 315.1107, found: 315.1223.

2.8 Synthesis of AuNP-BCN



To 350 mg **AuNP-NH_2** in 2 mL methanol, 14 mL dichloromethane and 3.5 mL trimethylamine was added **BCN_{exo}-O- pNP** in 2 mL dichloromethane. The solution was stirred overnight, after which the solvent was removed under reduced pressure and the resulting black film was dried thoroughly under high vacuum. The dried film was washed thoroughly with several 100 mL portions of di ethyl ether to give **AuNP-BCN** as a shiny black solid (370 mg).

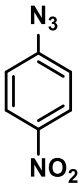
2.9 Synthesis of 1-azido-3-propanol (azide 1)



To 0.65 mL (1.0 g, 7.2 mmol) 3-bromo-1-propanol in 5 mL 1:1 water:ethanol was added 1.4 g (21 mmol) sodium azide. After refluxing the resulting solution at 55°C for 4 hours, the solution was cooled to room temperature and 50 mL water was added. The aqueous phase was extracted with dichloromethane (3 x 10 mL) and the collected organic phases were dried over magnesium sulphate, and concentrated under streaming $Ar_{(g)}$ to give **azido-propanol (azide 1)** as a light yellow oil in 67% yield (0.49 g). *Note:* Due to volatility of azido-propanol, solvent should not be evaporated under reduced pressure. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.74 (t, J = 8 Hz, 2H), 3.44 (t, J = 8 Hz, 2H), 2.03 (s, 1H), 1.82 (quin, J = 4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 59.8, 48.4, 31.4. HRMS (CI) *m/z* calc. for $C_3H_8N_3O$ $(M+1)^+$: 102.0667, found: 102.0672. IR (KBr, cm^{-1}): 3336, 2930, 2882, 2091, 1455, 1344, 1259, 1047.

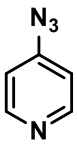
2.10 Synthesis of 1-azido-4-nitrobenzene (azide 4)

Synthesized according to Kwok *et al.*, with minor modifications.[4]



To 40 mL 12 M HCl and 40 mL water was slowly added 2.1 g (15 mmol) 4-nitroaniline, after which 15 mL ethanol was slowly added until the solution became transparent yellow. After cooling the solution to 0°C, 1.6 g (23 mmol) sodium nitrite was added slowly and the solution was stirred for 45 minutes at 0°C. Next, sodium azide (1.5 g, 23 mmol) was added very slowly at room temperature and the resulting solution was stirred for 2 hours, after which 50 mL water and 100 mL ether was added. The organic phase was removed and the aqueous phase was extracted with ether (2 x 50 mL). The collected organic phases were extracted with saturated $NaHCO_3$ (3 x 50 mL) and brine (3 x 50 mL), dried over magnesium sulphate and concentrated via rotary evaporation to give **1-azido-4-nitrobenzene (azide 4)** as a yellow solid in 98% yield (2.4 g). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25 (d, J = 8 Hz, 2H), 7.15 (d, J = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 147.2, 145.0, 125.9, 119.7. HRMS (ESI) *m/z* calc. for $C_6H_4N_4O_2$ $(M)^+$: 164.0334, found: 164.0335. IR (KBr, cm^{-1}): 3113, 3069, 2922, 2403, 2122, 1605, 1590, 1512, 1489, 1444, 1369, 1328, 1287, 1177, 1130, 1118, 1105.

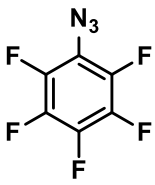
2.11 Synthesis of 4-azidopyridine (azide 5)



Synthesized according to Zhao and Qing, with minor modifications.[5]

To 0.60 g (3.1 mmol) 4-bromopyridine hydrochloride in 6 mL 1:1 water:ethanol (95%) was added 0.060 g (1.5 mmol) sodium hydroxide and 0.50 g (7.7 mmol) sodium azide. After refluxing the resulting solution at 110°C for 4 hours, the solution was cooled to room temperature and 50 mL water and 10 mL dichloromethane was added. The organic phase was removed, and the aqueous phase was extracted with dichloromethane (2 x 10 mL). The collected organic phases were extracted with brine (3 x 30 mL), dried over magnesium sulphate and concentrated under streaming $Ar_{(g)}$ to give **4-azidopyridine (azide 5)** as a light yellow oil in 86% yield (0.42 g). *Note:* Due to volatility of 4-azidopyridine, solvent should not be removed under reduced pressure. ^{1}H NMR ($CDCl_3$, 400 MHz): 8.54 (d, J = 4 Hz, 2H), 6.96 (d, J = 4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ 151.3, 148.9, 114.3. HRMS (ESI) *m/z* calc. for $C_5H_4N_4$ $(M)^+$: 120.0436, found: 120.0439. IR (KBr, cm^{-1}): 3037, 2919, 2850, 2430, 2136, 1614, 1580, 1565, 1493, 1416, 1343, 1298, 1281, 1215, 1137.

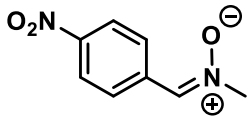
2.12 Synthesis of 1-azido-2,3,4,5,6-pentafluorobenzene (azide 6)



Synthesized according to Li-Mei *et. al.*, with minor modifications.[6]

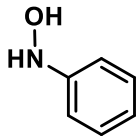
To 2.1 g (10 mmol) 2,3,4,5,6-pentafluoroaniline in 25 mL trifluoroacetic acid was slowly added 0.83 g (12 mmol) sodium nitrite at 0°C. The resulting solution was stirred for 1 hour at 0°C, after which 0.98 g (15 mmol) sodium azide was added portion-wise at 0°C. After stirring the solution for 1 hour at 0°C, 50 mL diethyl-ether was added and the aqueous phase was removed. The organic phase was extracted with water (3 x 50 mL) and $NaHCO_3$ (3 x 50 mL), dried over magnesium sulphate and concentrated via rotary evaporation. The resulting crude residue was purified via flash column chromatography (hexanes) to give **1-azido-2,3,4,5,6-pentafluorobenzene (azide 6)** as a light yellow oil in 89% yield (2.1 g). ^{19}F NMR ($CDCl_3$, 400 MHz): -151.6 (d, 2F), -159.8 (t, 1F), -161.6 (t, 2F). ^{13}C NMR ($CDCl_3$, 400 MHz) : δ 142.2, 139.5, 136.9, 110.0. HRMS (ESI) *m/z* calc. for $C_6F_5N_3$ $(M)^+$: 209.0012, found: 209.0014. IR (KBr, cm^{-1}): 2407, 2120, 1638, 1507, 1462, 1326, 1243, 1103, 1013.

2.13 Synthesis of N-methyl-C-nitrophenyl-nitrone (nitrone 1)



To 0.25 g (3.0 mmol) N-methylhydroxylamine and 0.36 g (9.0 mmol) sodium hydroxide in 10 mL methanol was added 0.70 g (4.5 mmol) nitrobenzaldehyde. After stirring the mixture overnight at room temperature, the solvent was removed via rotary evaporation, the crude solid was suspended in ether, and the resulting insoluble yellow solid was collected by filtration to give **N-methyl-C-nitrophenyl-nitrone (nitrone 1)** in 72% yield (0.39 g). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.38 (d, J = 8 Hz, 2H), 8.23 (d, J = 8 Hz, 2H), *7.53* (s, 1H), 3.90 (s, 3H). ^{13}C NMR (CD_2Cl_2, 400 MHz): δ 148.2, 137.0, 133.2, 128.9, 124.2, 55.7. HRMS (ESI) *m/z* calc. for $C_8H_8N_2O_3$ $(M)^+$: 180.0535, found: 180.0531. IR (KBr, cm^{-1}): 3108, 3082, 3024, 2958.3, 1597, 1956, 1506, 1333, 1184, 1164, 1110.

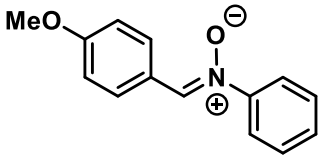
2.14 Synthesis of N-phenyl-hydroxylamine



To 2.0 g (16 mmol, 1.7 mL) nitrobenzene and 0.95 g (18 mmol) ammonium chloride in 25 mL 1:1 water:ethanol was added 2.1g (32 mmol) zinc dust portion-wise over 5 minutes. Note: rate of zinc dust addition was adjusted so as to maintain the elevated temperature at ~60°C. After stirring the resulting suspension for 20 minutes, the grey solid was removed by vacuum filtration, and washed with 50 mL water and 10 mL ether. The organic phase in the filtrate was removed, the aqueous phase was extracted with ether (2 x 10 mL) until the aqueous phase was nearly colorless, and the collected organic phases were dried over magnesium sulphate and concentrated via rotary evaporation to give **N-phenyl-hydroxylamine** in 81% crude yield (1.4 g), which was used without further purification towards the syntheses of Nitrone 2, Nitrone 3, Nitrone 4 and Nitrone 5. Note: Due to the instability of the hydroxylamine, it should be used immediately.

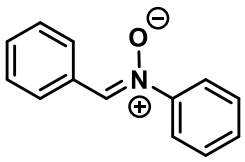
2.15 Synthesis of N-phenyl-C-methoxyphenyl-nitrone (nitrone 2)

To 0.23 g (2.1 mmol) crude **N-phenyl-hydroxylamine** in 5 mL dichloromethane was added 0.34 g (2.5 mmol, 0.30 mL) 4-anisaldehyde and a small amount of magnesium sulphate. The resulting solution was stirred overnight at room temperature, after which the solvent was removed via rotary evaporation. The crude residue was suspended in ether, and the resulting off-white insoluble solid



was collected by vacuum filtration to give **N-phenyl-C-methoxyphenyl-nitrone (nitrone 2)** in 70% overall yield (0.33g). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.41 (d, J = 8 Hz, 2H), *7.88* (s, 1H), 7.76 (d, J = 8 Hz, 2H), 7.48 (m, 3H), 7.00 (d, J = 8 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (CD_2Cl_2, 400 MHz): δ 162.0, 149.6, 134.0, 131.4, 130.0, 129.6, 124.5, 122.1, 114.4, 55.9. HRMS (ESI) *m/z* calc. for $C_{14}H_{13}NO_2$ $(M)^+$: 227.0946, found: 227.0940. IR (KBr, cm^{-1}): 3050, 3013, 2962, 2931, 2839, 1603, 1554, 1506, 1484, 1461, 1399, 1305, 1259, 1193, 1176, 1108, 1064, 1023.

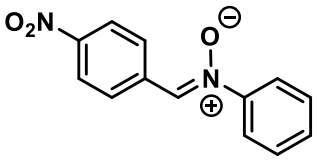
2.16 Synthesis of N-phenyl-C-phenyl-nitrone (nitrone 3)



*synthesized according to our previously reported procedure.[7]

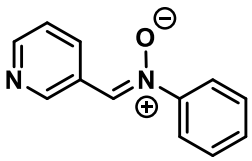
^{1}H NMR (CD_2Cl_2, 400 MHz): 8.41 (m, 2H), *7.95* (s, 1H), 7.78 (m, 2H), 7.49 (m, 6H). ^{13}C NMR (CD_2Cl_2, 400 MHz): δ 149.8, 134.5, 131.6, 131.2, 130.4, 129.6, 129.3, 129.1, 122.2. HRMS (ESI) *m/z* calc. for $C_{13}H_{11}NO$ $(M)^+$: 197.0841, found: 197.0837. IR (KBr, cm^{-1}): 3060, 1593, 1547, 1510, 1484, 1461, 1445, 1396, 1340, 1324, 1298, 1191, 1163, 1067, 1025.

2.17 Synthesis of N-phenyl-C-nitrophenyl-nitrone (nitrone 4)



To 0.21 g (1.9 mmol) crude **N-phenyl-hydroxylamine** in 5 mL dichloromethane was added 0.26 g (2.5 mmol, 0.25 mL) benzaldehyde and a small amount of magnesium sulphate. The resulting solution was stirred overnight at room temperature, after which the solvent was removed via rotary evaporation. The crude residue was suspended in ether, and the resulting white insoluble solid was collected by vacuum filtration to give ***N*-phenyl- *C*-nitrophenyl-nitrone (nitrone 4)** in 64% overall yield (0.29 g). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.56 (d, J = 8 Hz, 2H), 8.30 (d, J = 8 Hz, 2H), *8.10* (s, 1H), 7.80 (m, 2H), 7.54 (m, 3H). ^{13}C NMR (CD_2Cl_2, 400 MHz): δ 149.6, 148.4, 137.0, 132.6, 131.1, 129.9, 129.6, 124.4, 122.2. HRMS (ESI) *m/z* calc. for $C_{13}H_{10}N_2O_3$ $(M)^+$: 242.0691, found: 242.0693. IR (KBr, cm^{-1}): 3104, 3065, 1596, 1544, 1509, 1483, 1459, 1403, 1340, 1319, 1193, 1176, 1157, 1101, 1072.

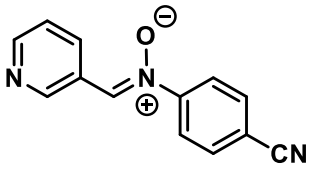
2.18 Synthesis of N-phenyl-C-pyridine-nitrone (nitrone 5)



*synthesized according to our previously reported procedure.[7]

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.19 (s, 1H), 9.07 (d, J = 8 Hz, 1H), 8.65 (d, J = 4 Hz, 1H), 8.05 (s, 1H), 7.95 (d, J = 8 Hz, 2H), 7.83 (d, J = 8 Hz, 2H), 7.43 (m, 1H). ^{13}NMR (CD_2Cl_2, 400 MHz): δ 151.9, 150.9, 135.4, 133.9, 132.8, 127.5, 124.1, 123.1, 118.1, 114.6. HRMS (ESI) *m/z* calc. for $C_{12}H_{10}N_2O$ $(M)^+$: 198.0793, found: 198.0796. IR (ATR, cm^{-1}): 3130, 3065, 3062, 1582, 1555, 1484, 1466, 1403, 1335, 1272, 1203, 1175, 1164, 1072, 1022.

2.19 Synthesis of N-cyanophenyl-C-pyridine-nitrone (nitrone 6)



*synthesized according to our previously reported procedure.[7]

^{1}H NMR (CD_2Cl_2, 400 MHz): δ 9.17 (s, 1H), 9.09 (d, J = 8.0 Hz, 1H), 8.62 (d, J = 8.0 Hz, 1H), 8.00 (s, 1H), 7.79 (m, 2H), 7.50 (m, 3H), 7.41 (m, 1H). ^{13}C NMR (CD_2Cl_2, 400 MHz): δ 151.3, 150.7, 149.4, 135.1, 131.6, 130.8, 129.7, 128.0, 124.0, 122.11, 114.4. HRMS (ESI) *m/z* calc. for $C_{13}H_9N_3O$ $(M)^+$: 223.0746, found: 223.0735. IR (ATR, cm^{-1}): 3104, 3082, 3065, 3054, 2242, 1584, 1498, 1425, 1413, 1338, 1297, 1270, 1209, 1172, 1070, 1026.

3.0 Experimental Spectra and Diagrams

3.1 Experimental Spectra for SH-EG$_3$-Me

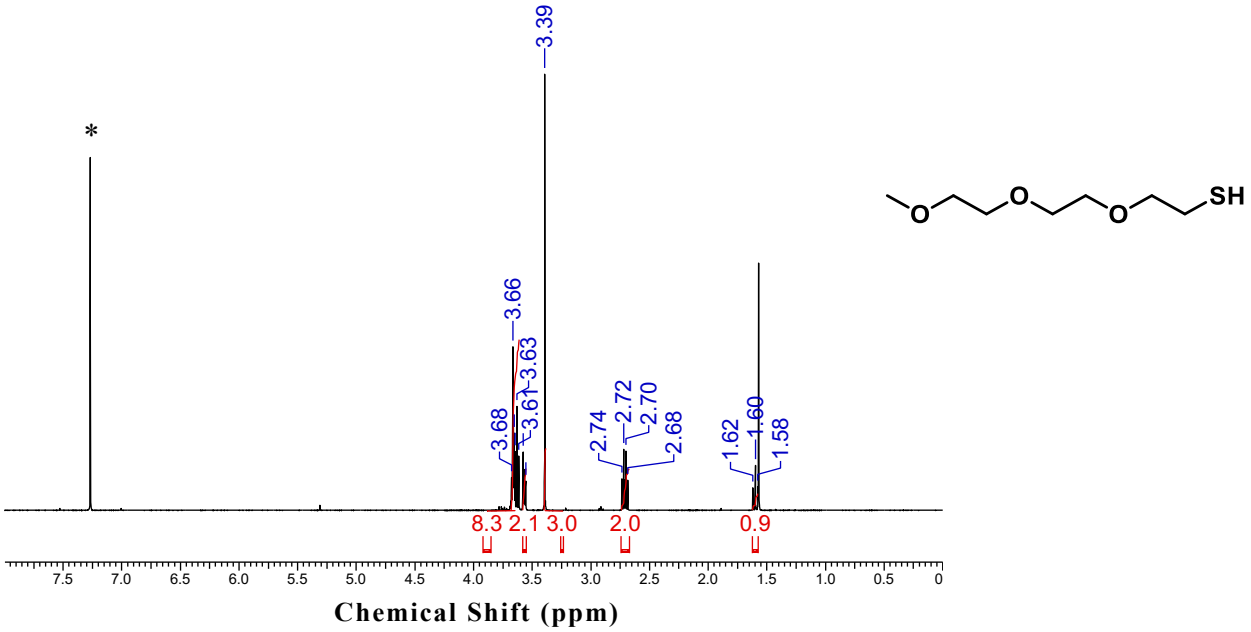


Figure S1. ^{1}H NMR spectrum of **HS-EG$_3$-Me** in $CDCl_3$ at 25°C. * denotes residual protio solvent.

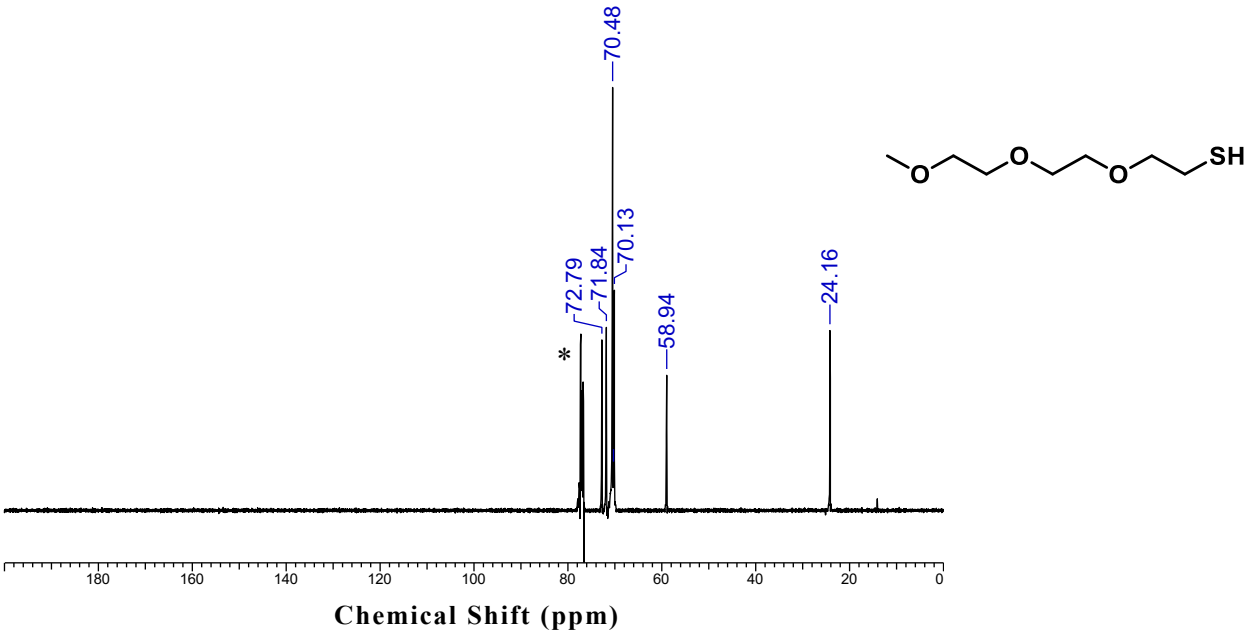


Figure S2. ^{13}C{1H} NMR spectrum of **HS-EG$_3$-Me** in $CDCl_3$ at 25°C. * indicates $CDCl_3$ solvent.

3.2 Experimental Spectra for AuNP-OMe

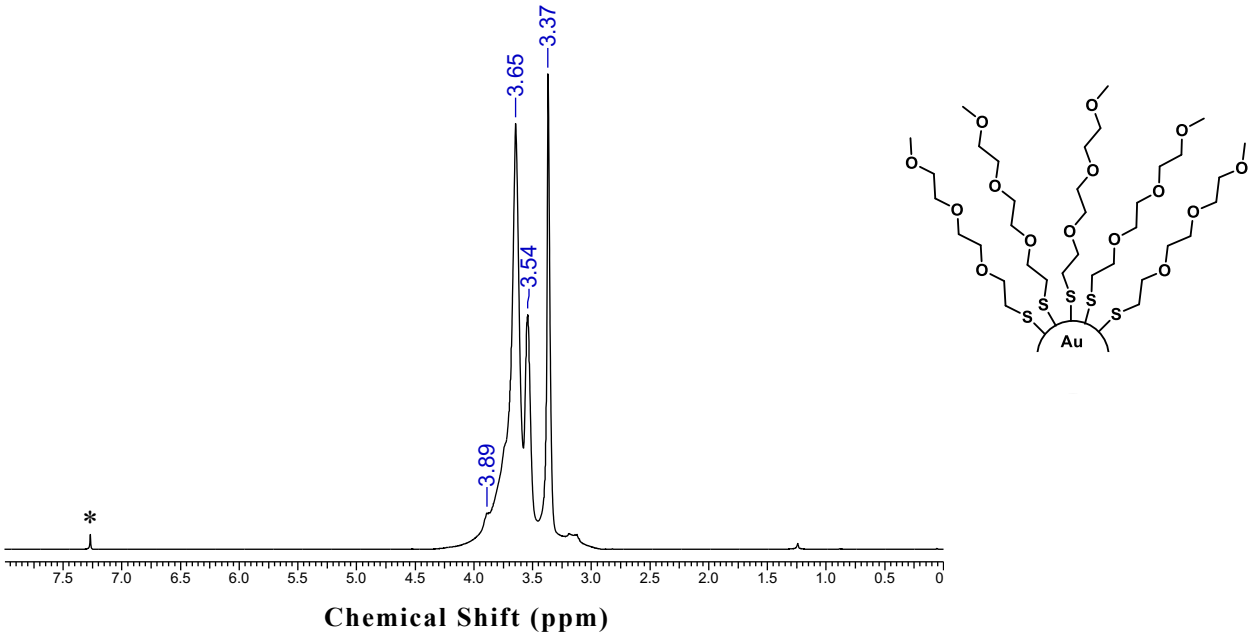


Figure S3. ^{1}H NMR spectrum of **AuNP-OMe** in $CDCl_3$ at 25°C. * denotes residual protio solvent.

3.3 Synthesis of SH-EG$_4$-NH$_2$

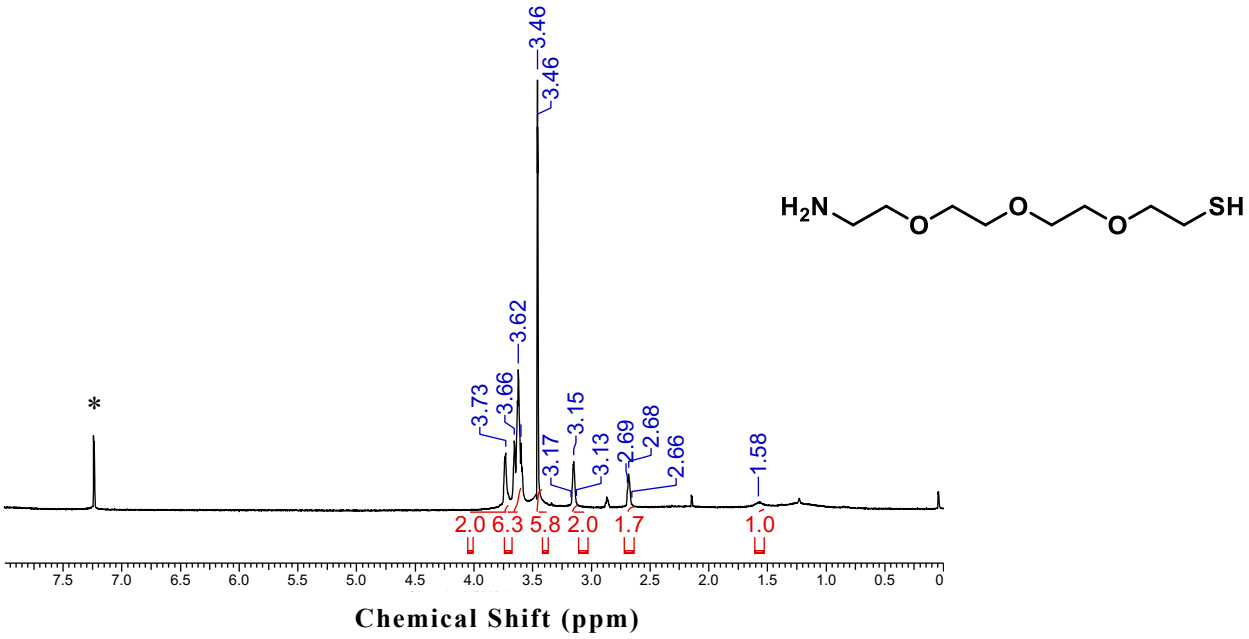


Figure S4. ^{1}H NMR spectrum of **HS-EG$_4$-NH$_2$** in $CDCl_3$ at 25°C. * denotes residual protio solvent.

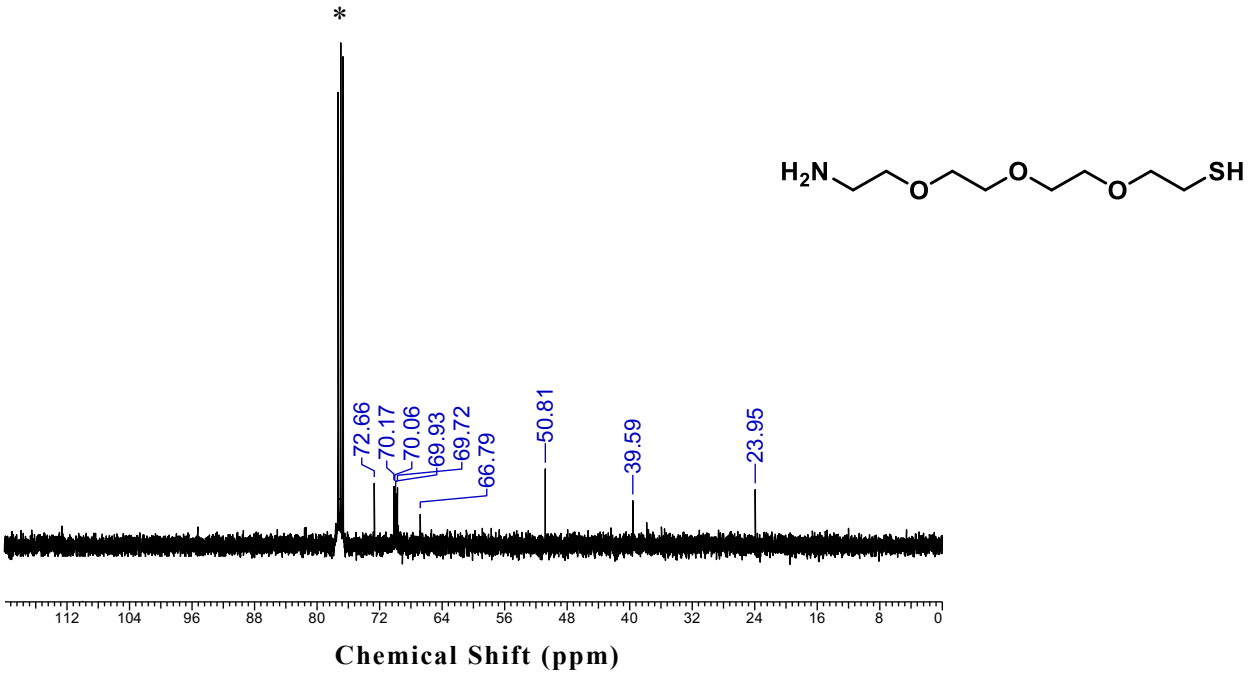


Figure S5. ^{13}C{1H} NMR spectrum of **HS-EG$_4$-NH$_2$** in $CDCl_3$ at 25°C. * indicates $CDCl_3$ solvent.

3.4 Experimental Spectra for AuNP-NH_2

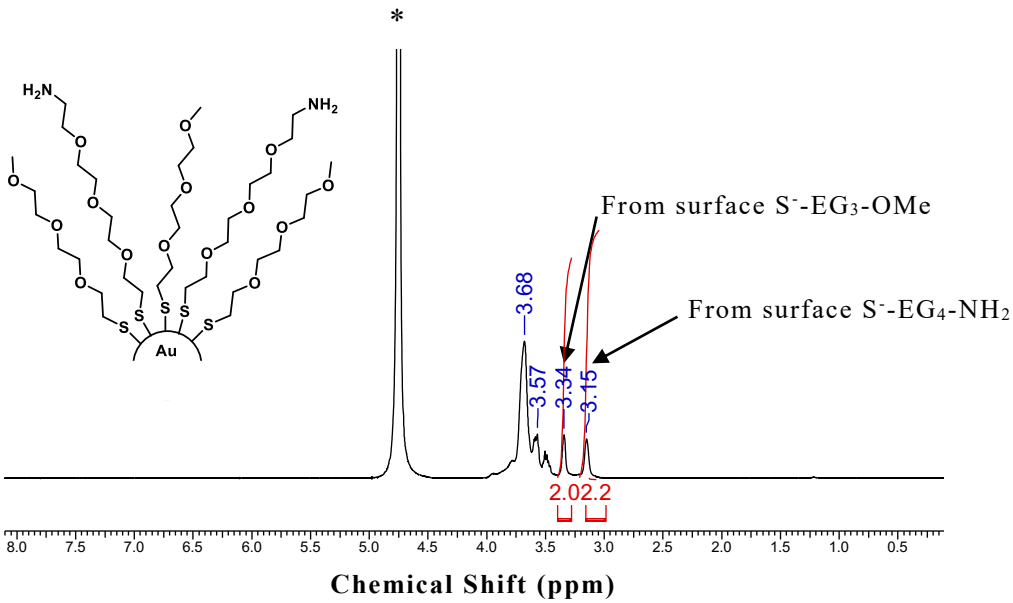


Figure S6. ^{1}H NMR spectrum of **AuNP-NH_2** in D_2O at 25°C. * denotes residual protio solvent.

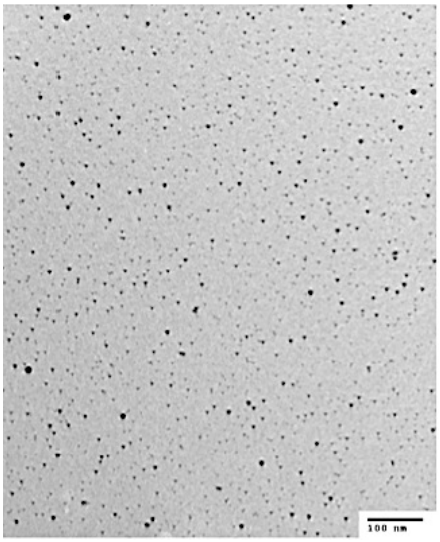


Figure S7. TEM image for **AuNP-NH_2**.

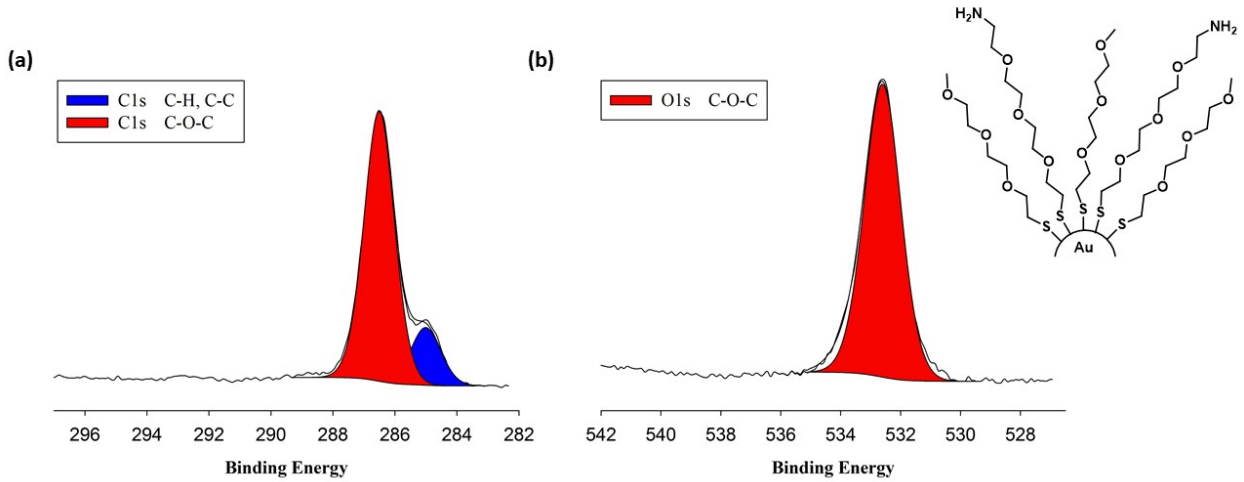


Figure S8. (a) High-resolution carbon 1s XPS spectrum of **AuNP-NH₂** (b) High-resolution oxygen 1s XPS spectrum of **AuNP-NH₂**.

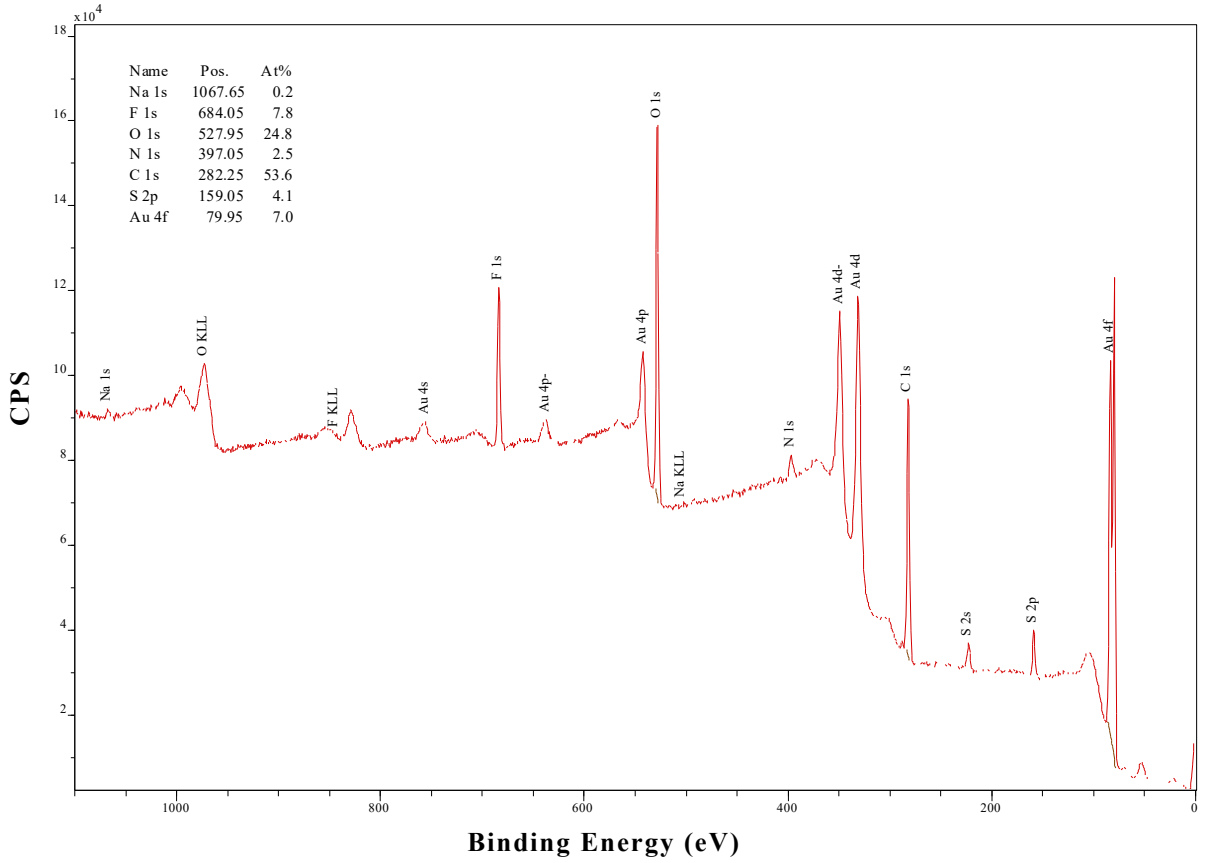


Figure S9. (a) XPS survey scan of **AuNP-NH₂**.

3.5 Experimental Spectra for BCN_{exo}-OH

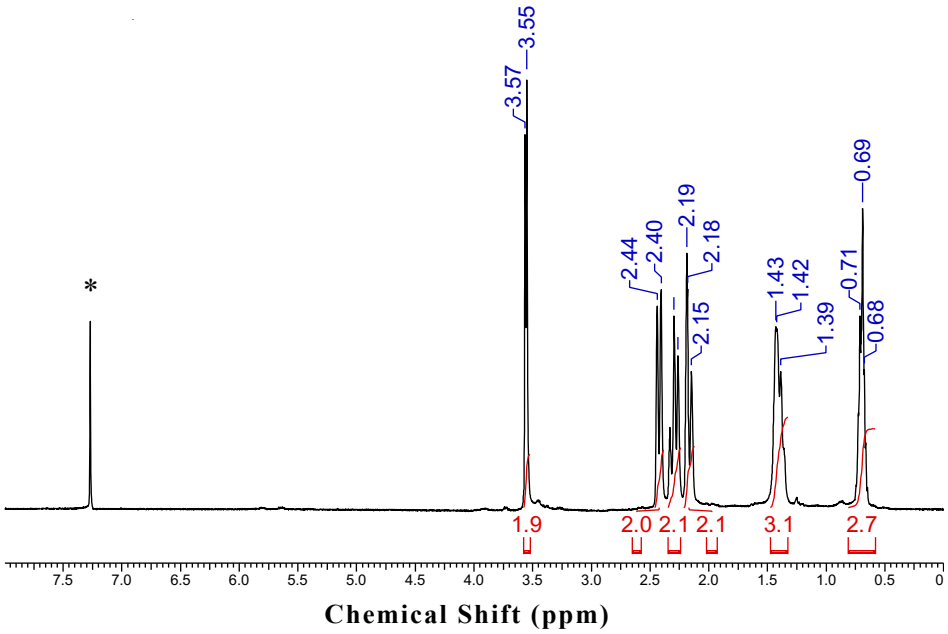


Figure S10. ^{1}H NMR spectrum of **BCN_{exo}-OH** in $CDCl_3$ at 25°C. * denotes residual protio solvent.

3.6 Experimental Spectra for BCN_{exo}-O-pNP

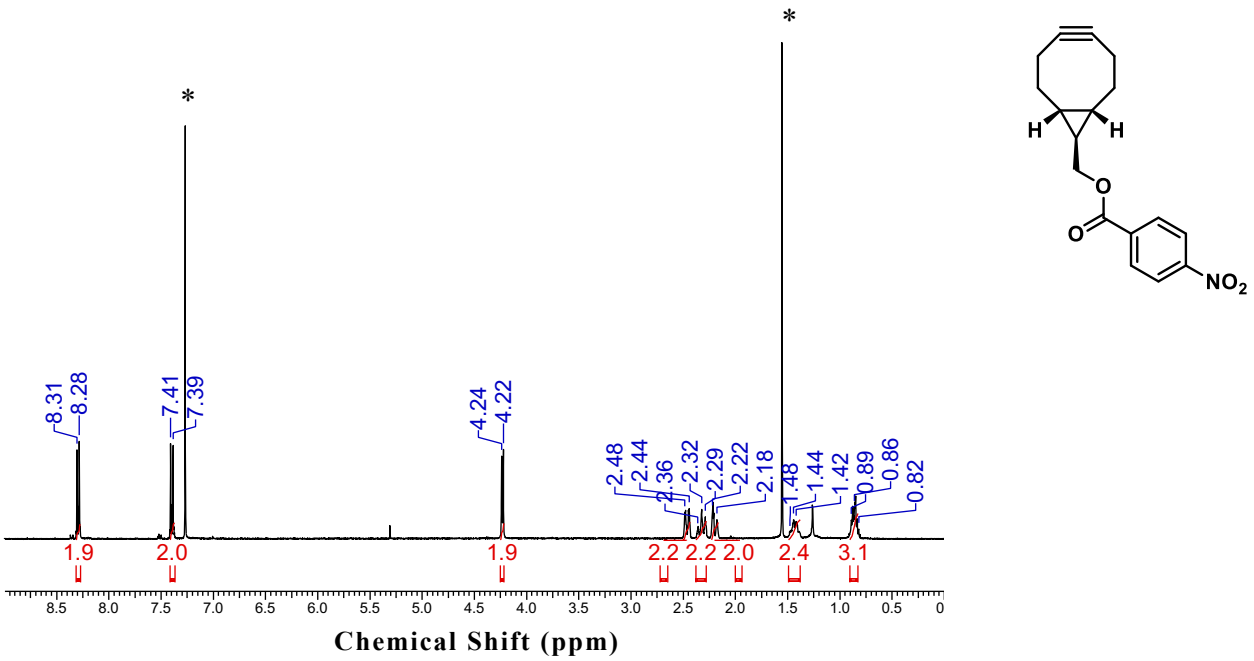


Figure S11. ^{1}H NMR spectrum of **BCN_{exo}-O-pNP** in $CDCl_3$ at 25°C. * denotes residual protio solvent.

3.7 Experimental Spectra for AuNP-BCN

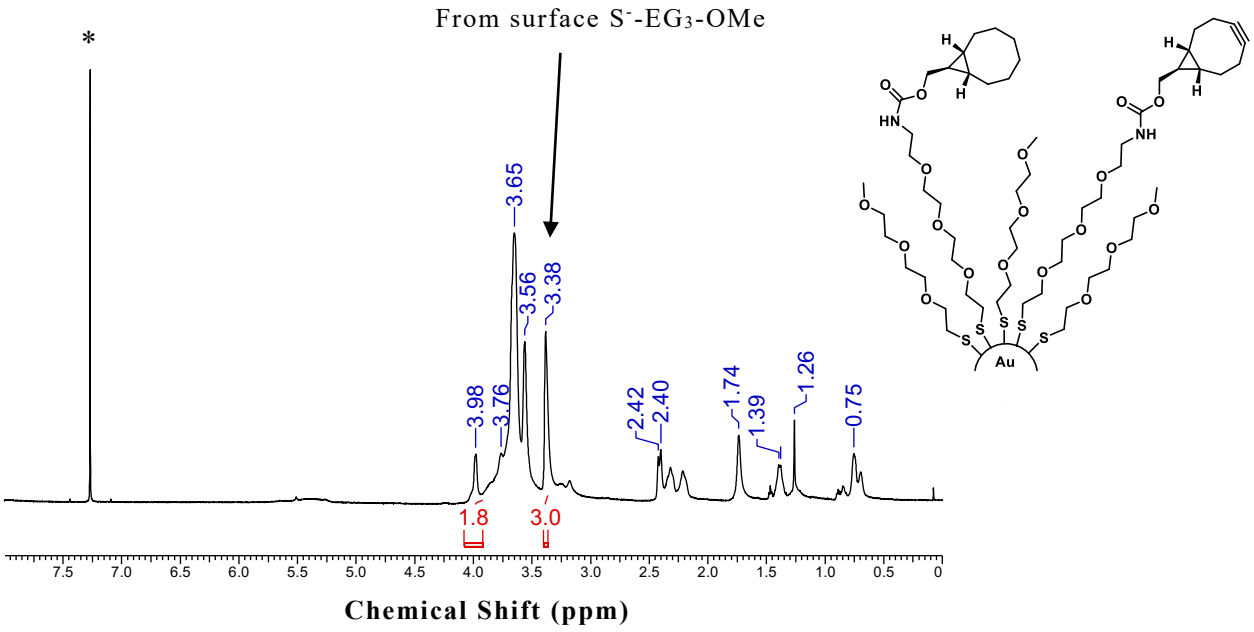


Figure S12. ^{1}H NMR spectrum of **AuNP-BCN** in $CDCl_3$ at 25°C. * denotes residual protio solvent.

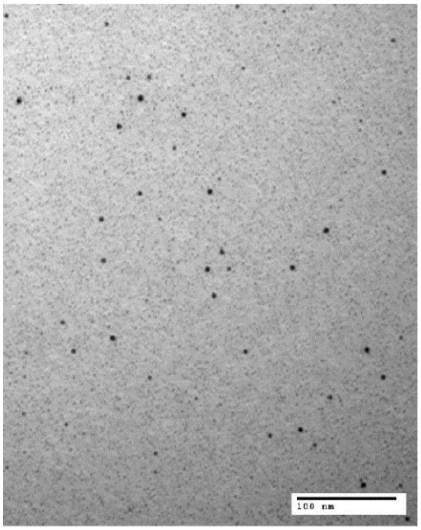


Figure S13. TEM image for **AuNP-BCN**.

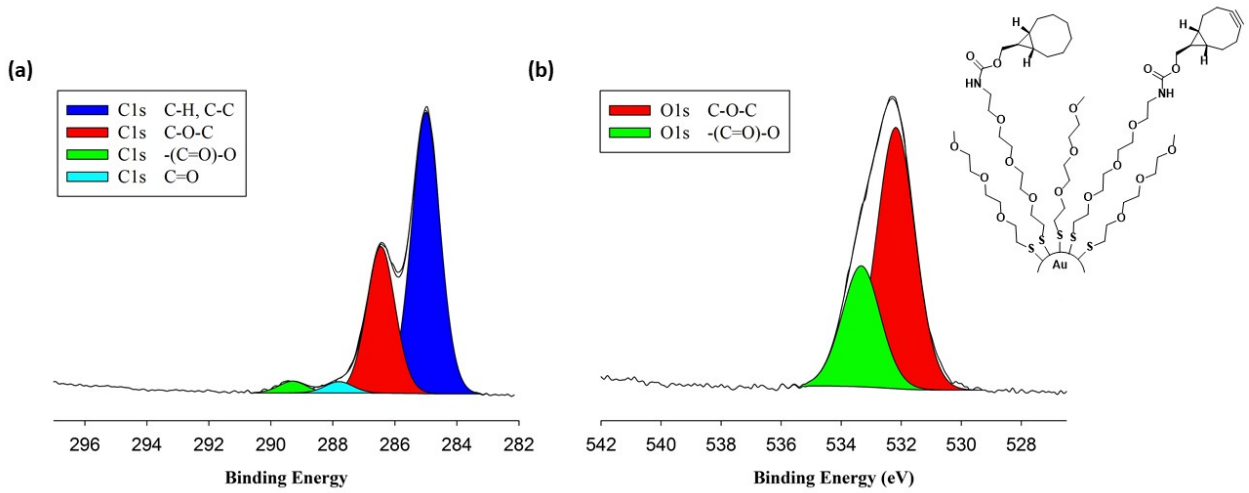


Figure S14. (a) High-resolution carbon 1s XPS spectrum of **AuNP-BCN** (b) High-resolution oxygen 1s XPS spectrum of **AuNP-BCN**.

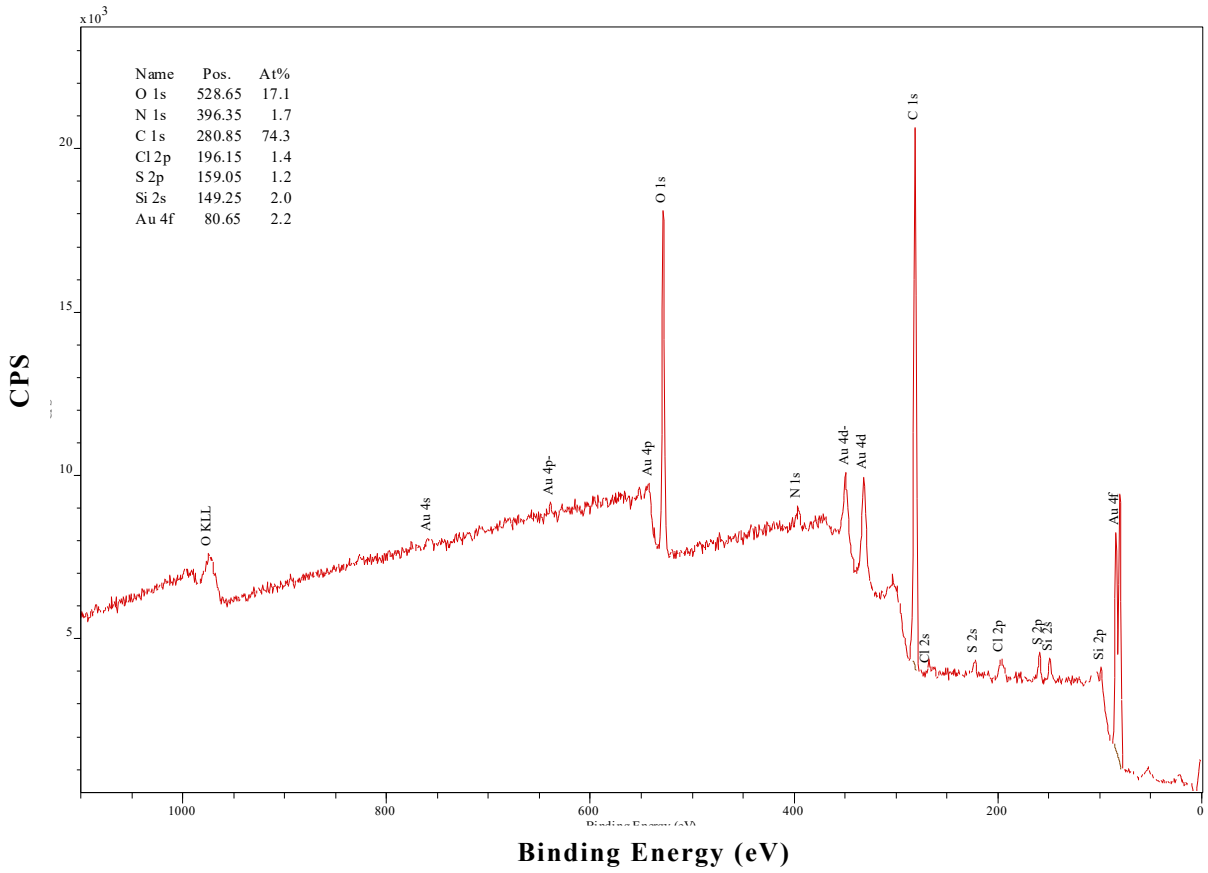


Figure S15. (a) XPS survey scan of **AuNP-BCN**.

3.8 Experimental Spectra for 1-azido-3-propanol (azide 1)

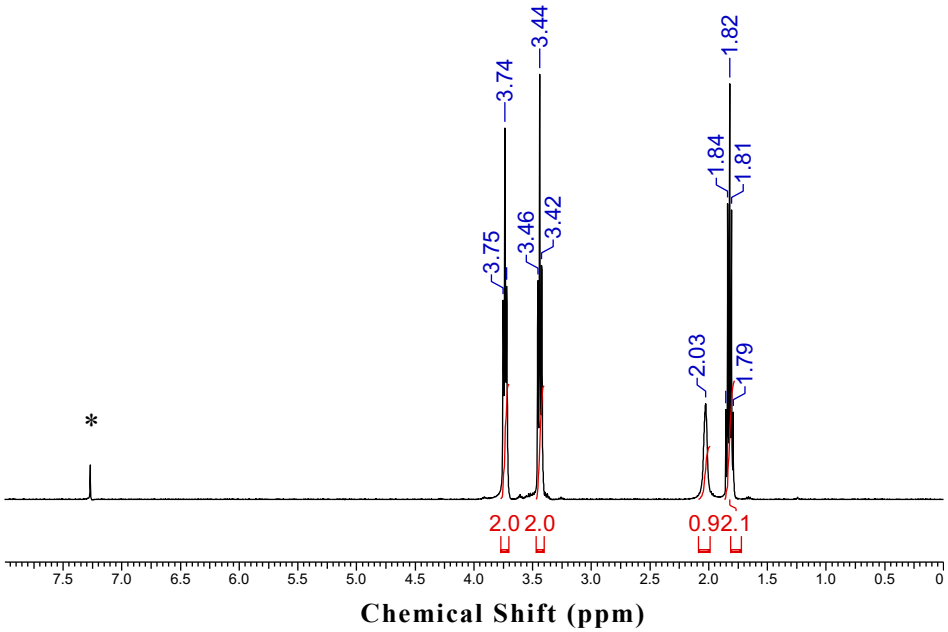


Figure S16. ^{1}H NMR spectrum of **azide 1** in $CDCl_3$ at 25°C. * denotes residual protio solvent.

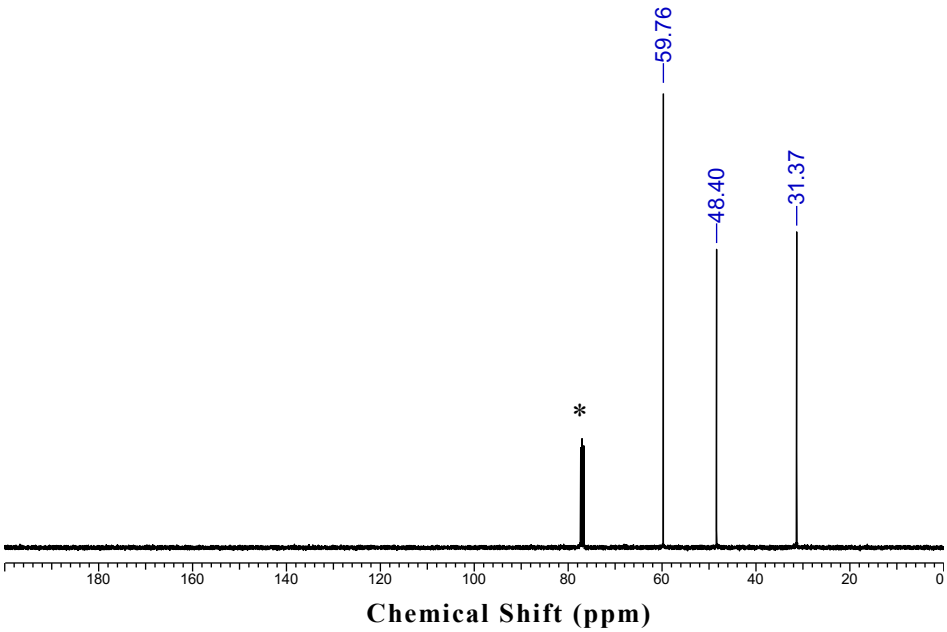


Figure S17. ^{13}C{1H} NMR spectrum of **azide 1** in $CDCl_3$ at 25°C. * indicates $CDCl_3$ solvent.

3.9 Experimental Spectra for 1-azido-4-nitrobenzene (azide 4)

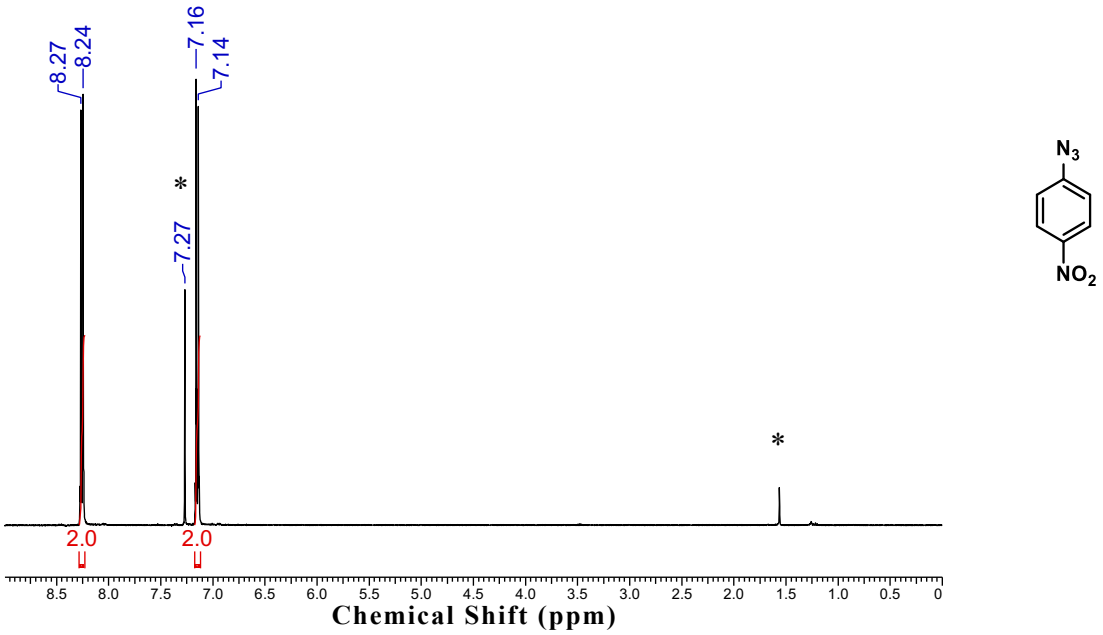


Figure S18. ^{1}H NMR spectrum of **azide 4** in $CDCl_3$ at 25°C. * denotes residual protio solvent.

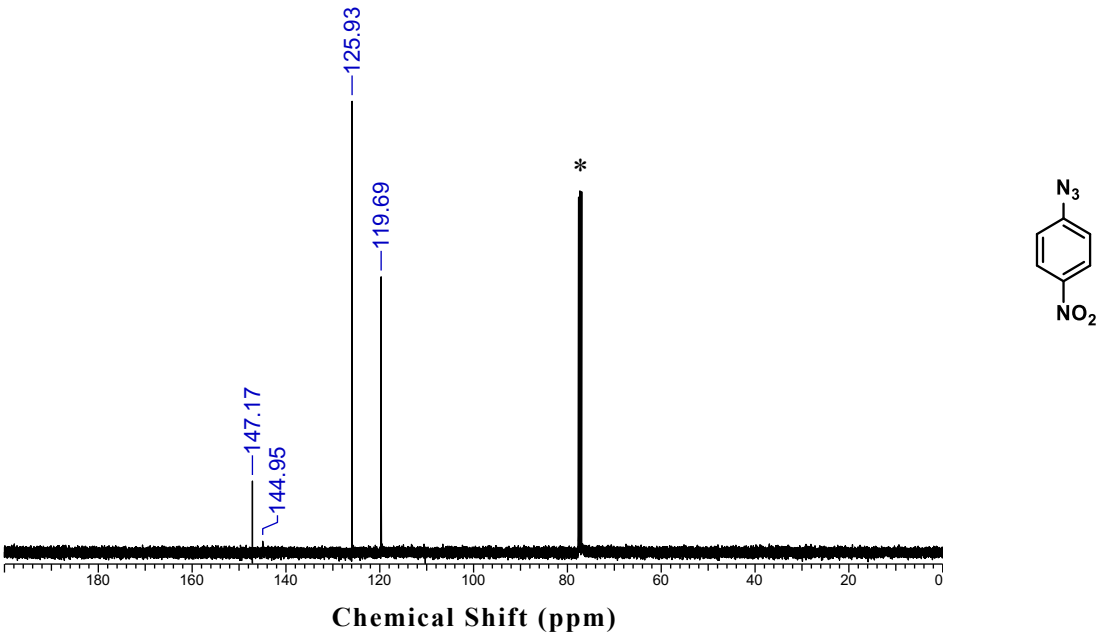


Figure S19. ^{13}C{1H} NMR spectrum of **azide 4** in $CDCl_3$ at 25°C. * indicates $CDCl_3$ solvent.

3.10 Experimental Spectra for 4-azidopyridine (azide 5)

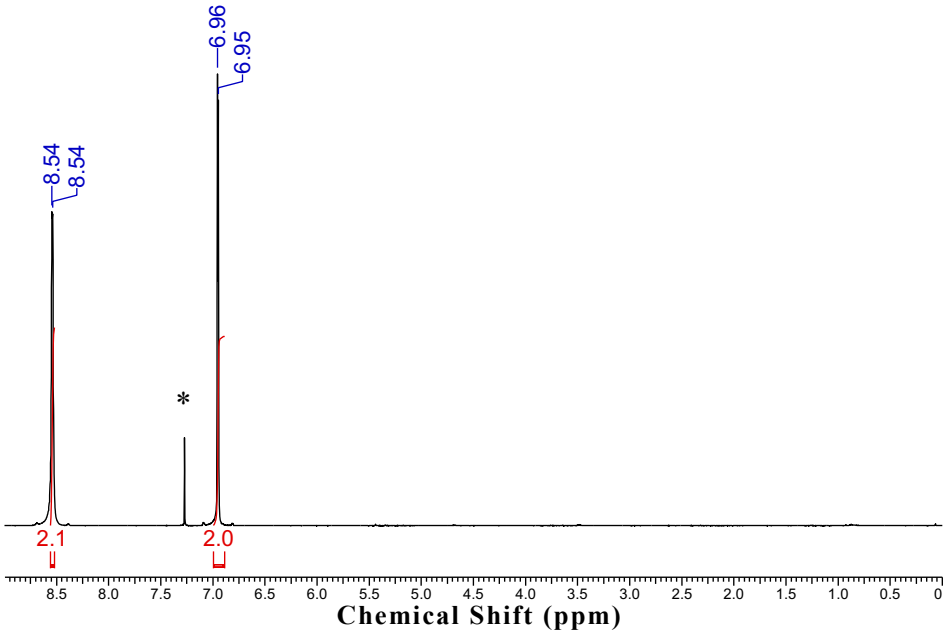


Figure S20. ^{1}H NMR spectrum of **azide 5** in $CDCl_3$ at 25°C. * denotes residual protio solvent.

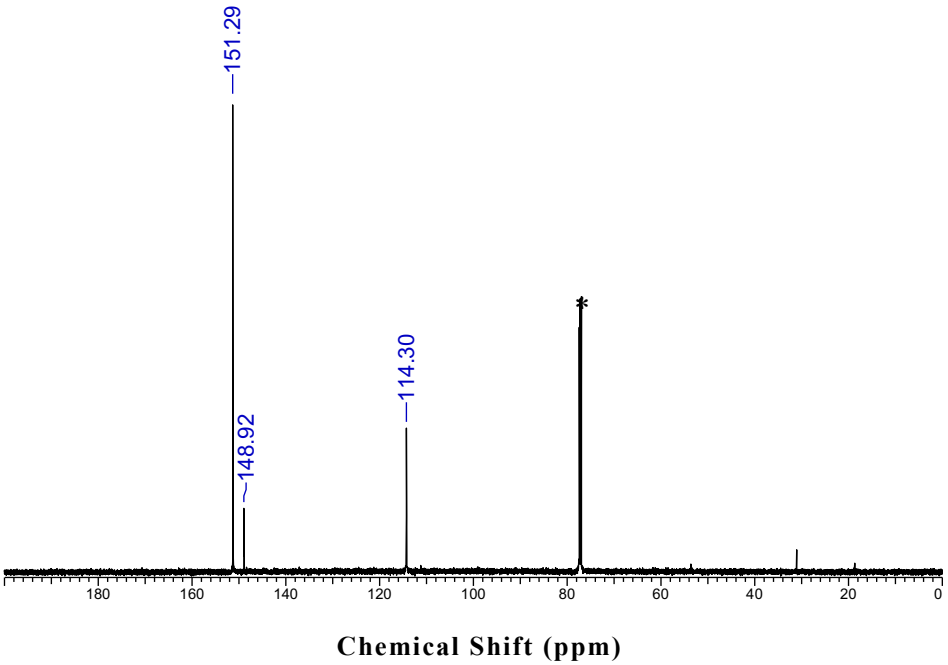


Figure S21. ^{13}C{1H} NMR spectrum of **azide 5** in $CDCl_3$ at 25°C. * indicates $CDCl_3$ solvent.

3.11 Experimental Spectra for 1-azido-2,3,4,5,6-pentafluorobenzene (azide 6)

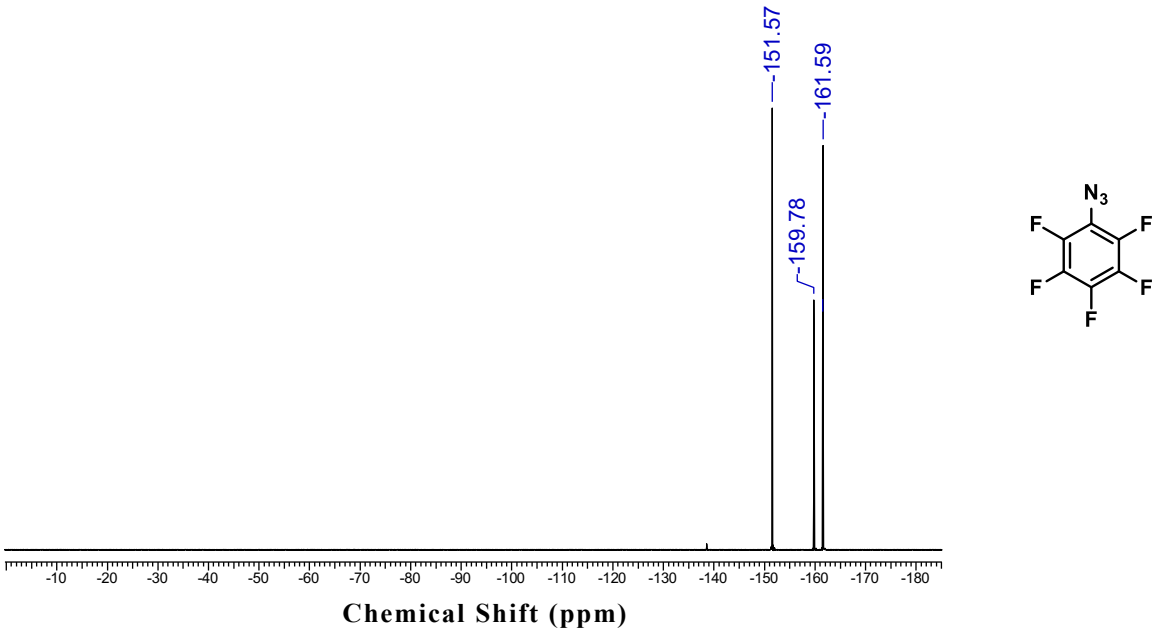


Figure S22. ^{19}F NMR spectrum of **azide 6** in $CDCl_3$ at 25°C.

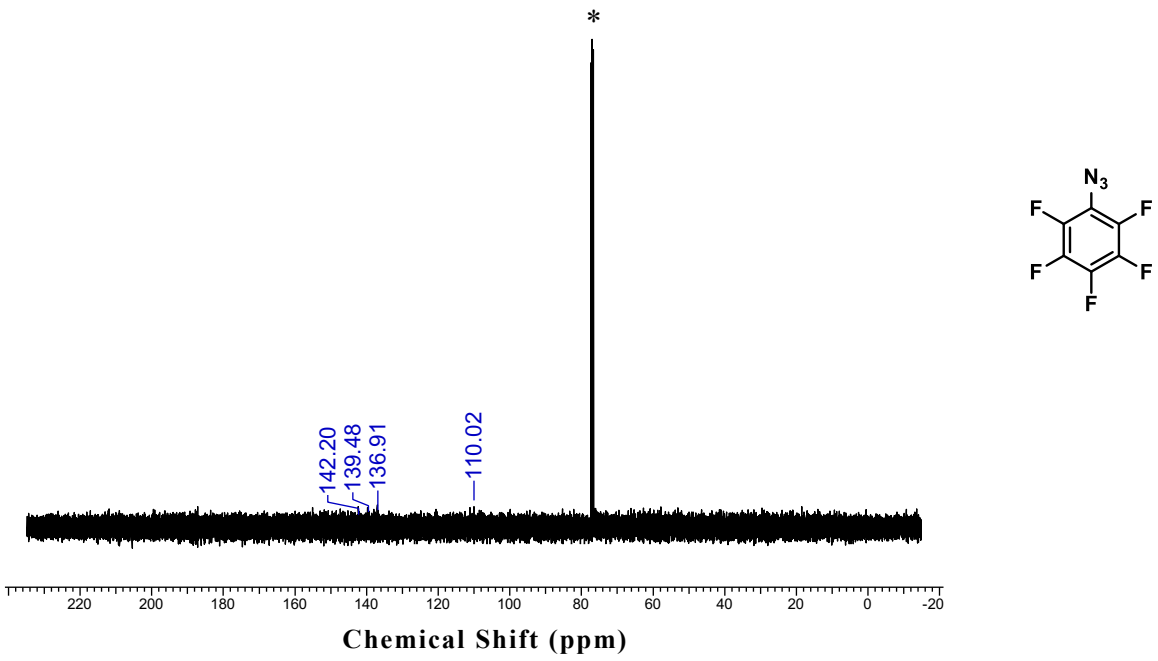


Figure S23. $^{13}C\{1H\}$ NMR spectrum of **azide 6** in $CDCl_3$ at 25°C. * indicates $CDCl_3$ solvent.

3.12 Experimental Spectra for N-methyl-C-nitrophenyl-nitrone (nitrone 1)

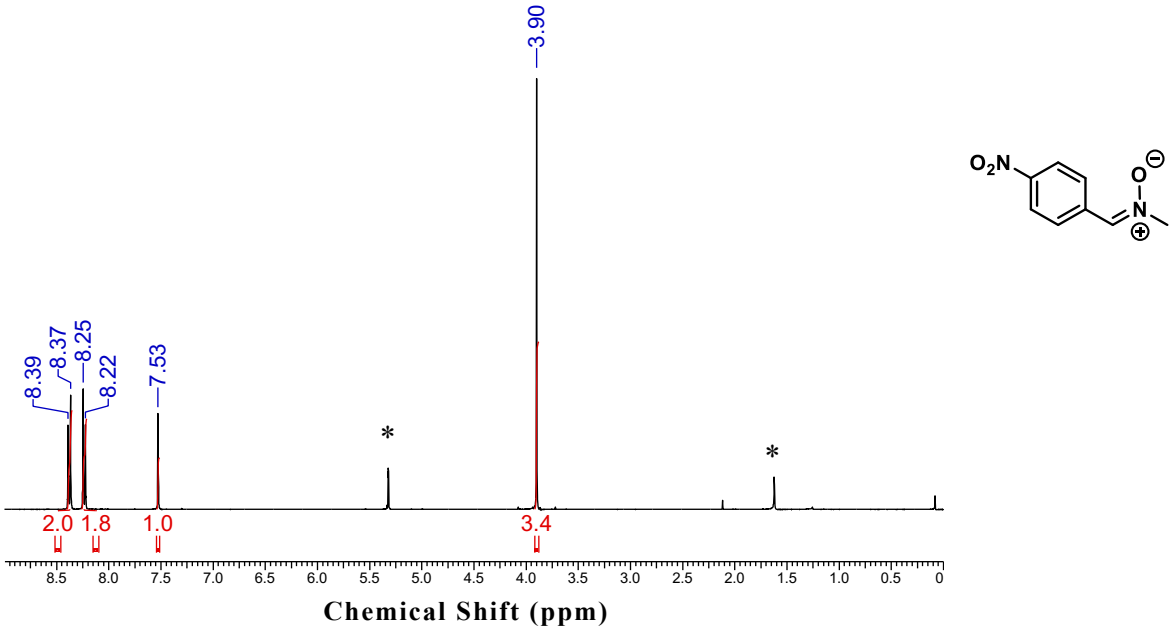


Figure S24. ^{1}H NMR spectrum of **nitrone 1** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

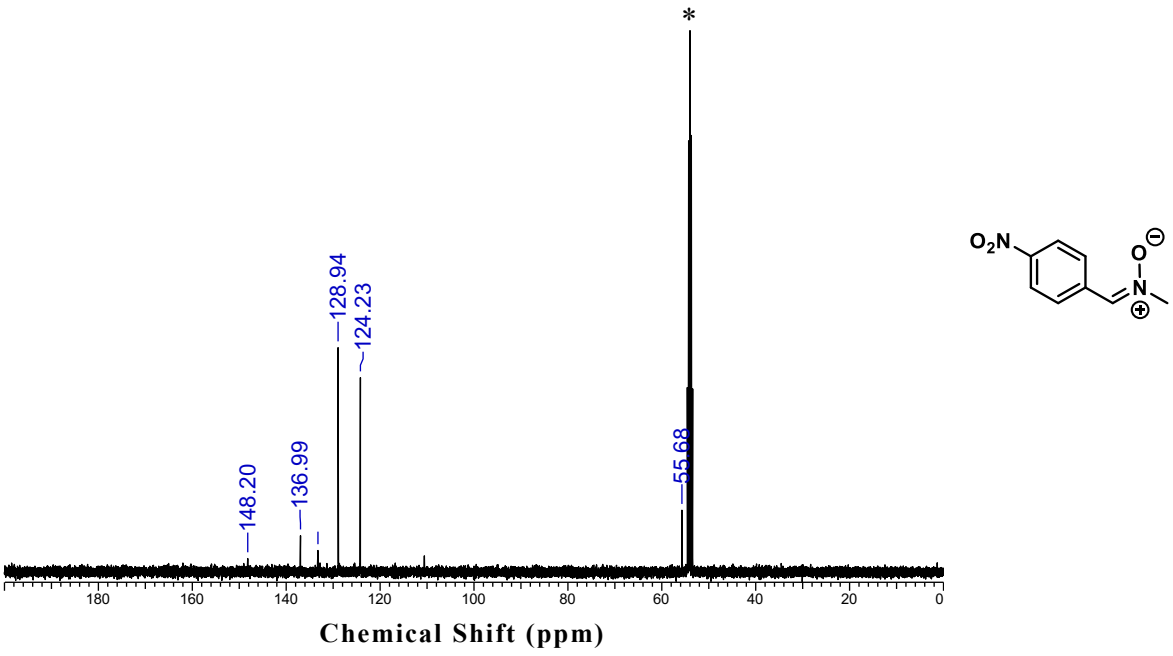


Figure S25. ^{13}C{1H} NMR spectrum of **nitrone 1** in CD_2Cl_2 at 25°C. * indicates CD_2Cl_2 solvent.

3.13 Experimental Spectra for N-phenyl-C-methoxyphenyl-nitrone (nitrone 2)

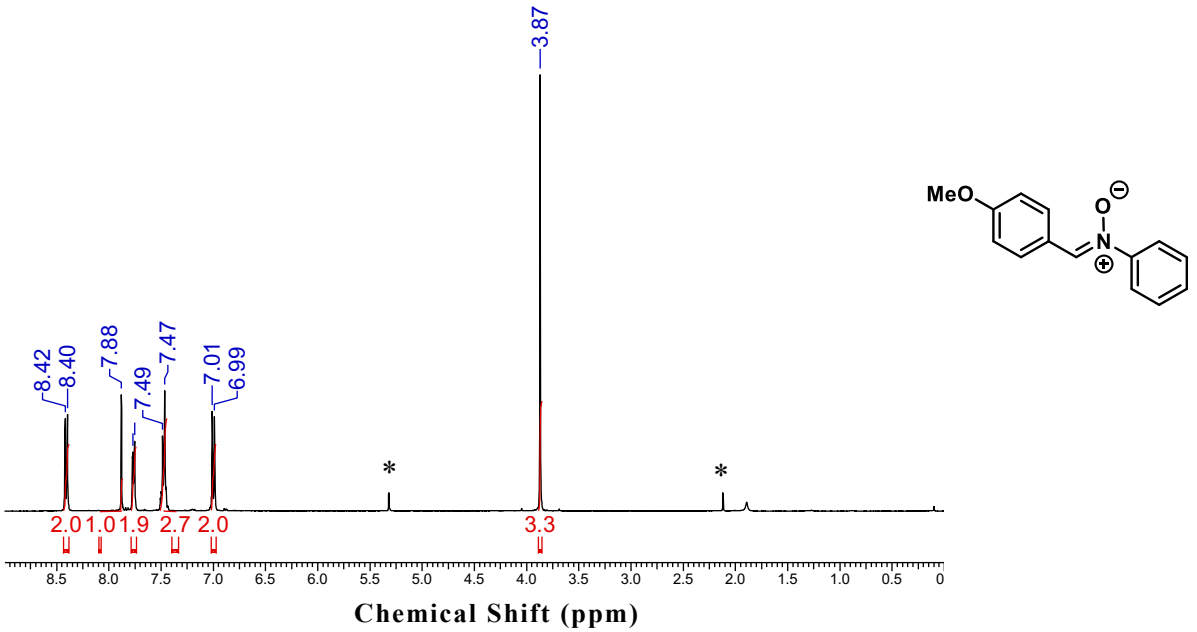


Figure S26. ^{1}H NMR spectrum of **nitrone 2** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

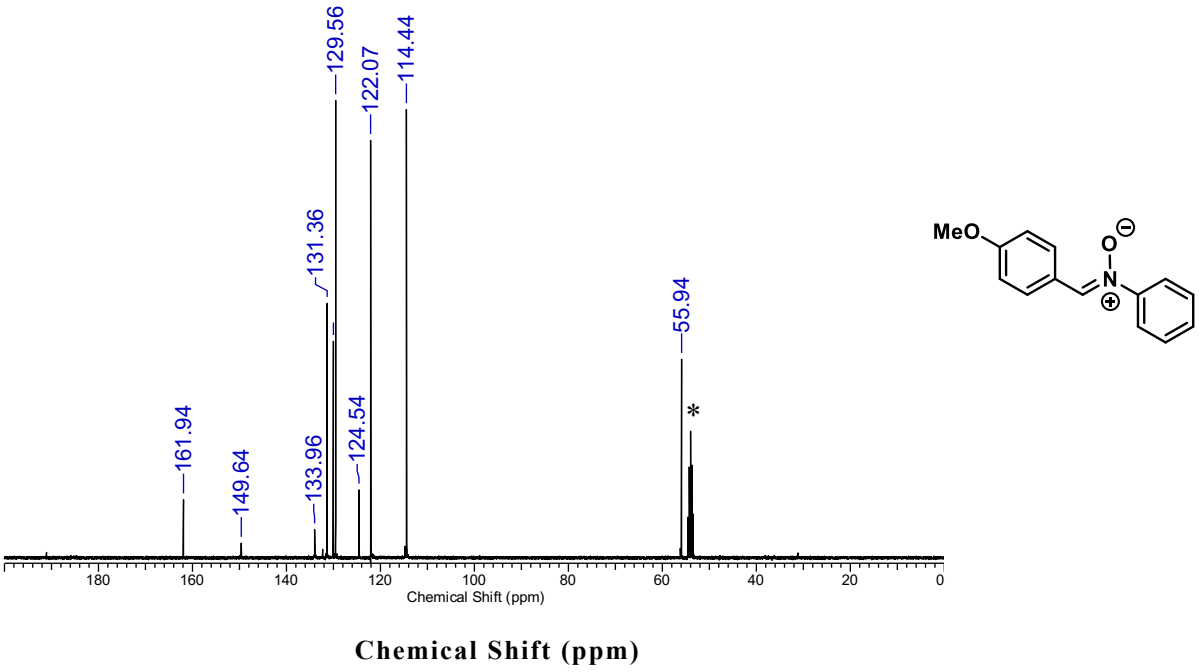


Figure S27. ^{13}C{1H} NMR spectrum of **nitrone 2** in CD_2Cl_2 at 25°C. * indicates CD_2Cl_2 solvent.

3.14 Experimental Spectra for N-phenyl-C-phenyl-nitrone (nitrone 3)

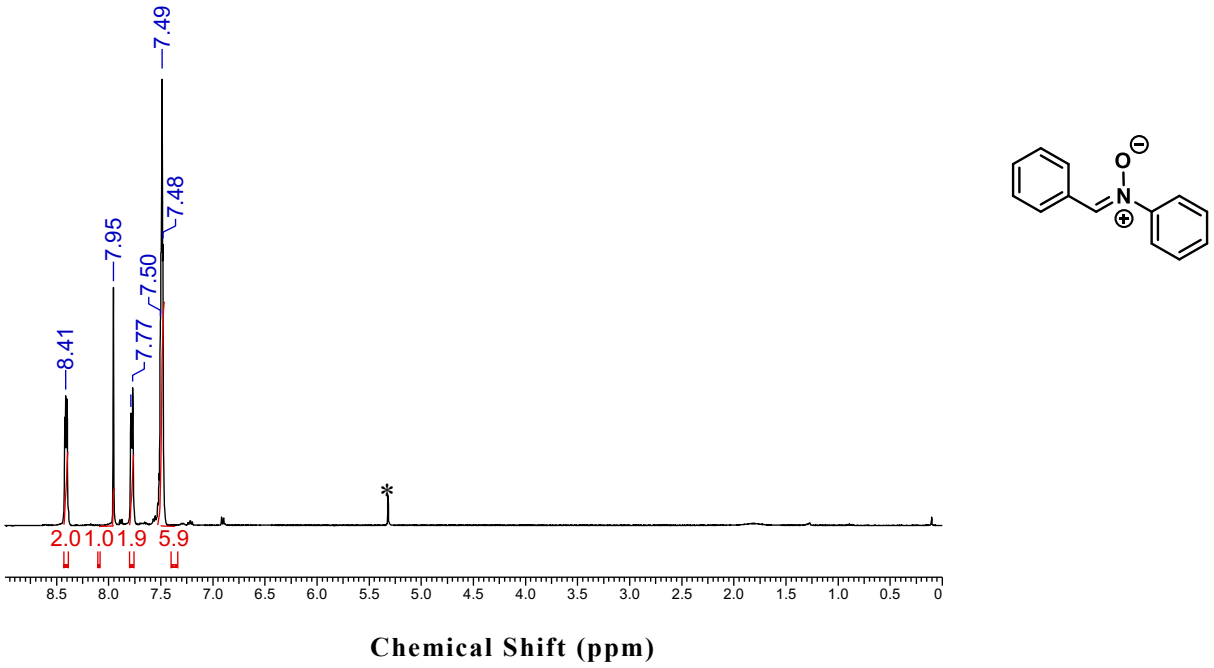


Figure S28. ^{1}H NMR spectrum of **nitrone 3** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

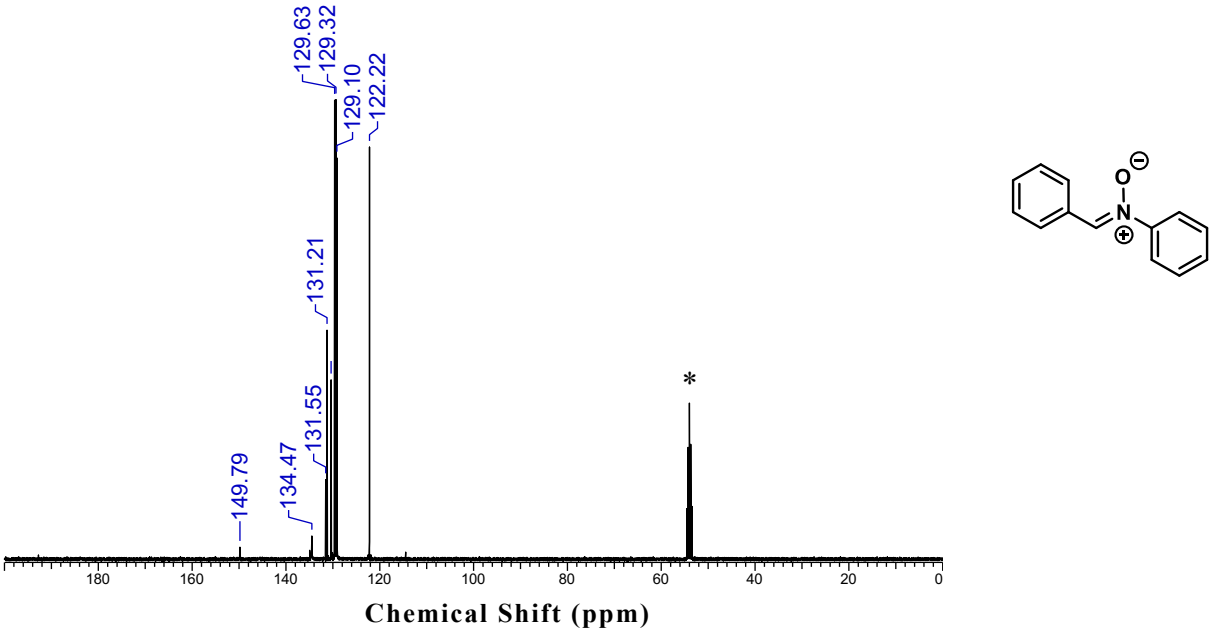


Figure S29. ^{13}C{1H} NMR spectrum of **nitrone 3** in CD_2Cl_2 at 25°C. * indicates CD_2Cl_2 solvent.

3.15 Experimental Spectra for N-phenyl-C-nitrophenyl-nitrone (nitrone 4)

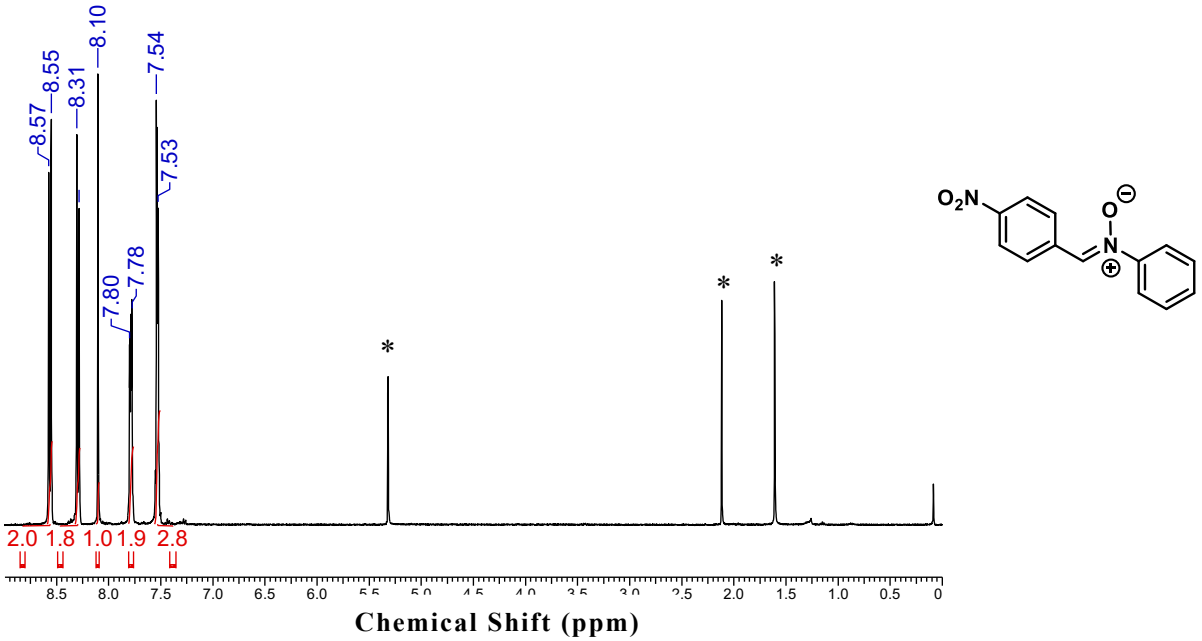


Figure S30. ^{1}H NMR spectrum of **nitrone 4** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

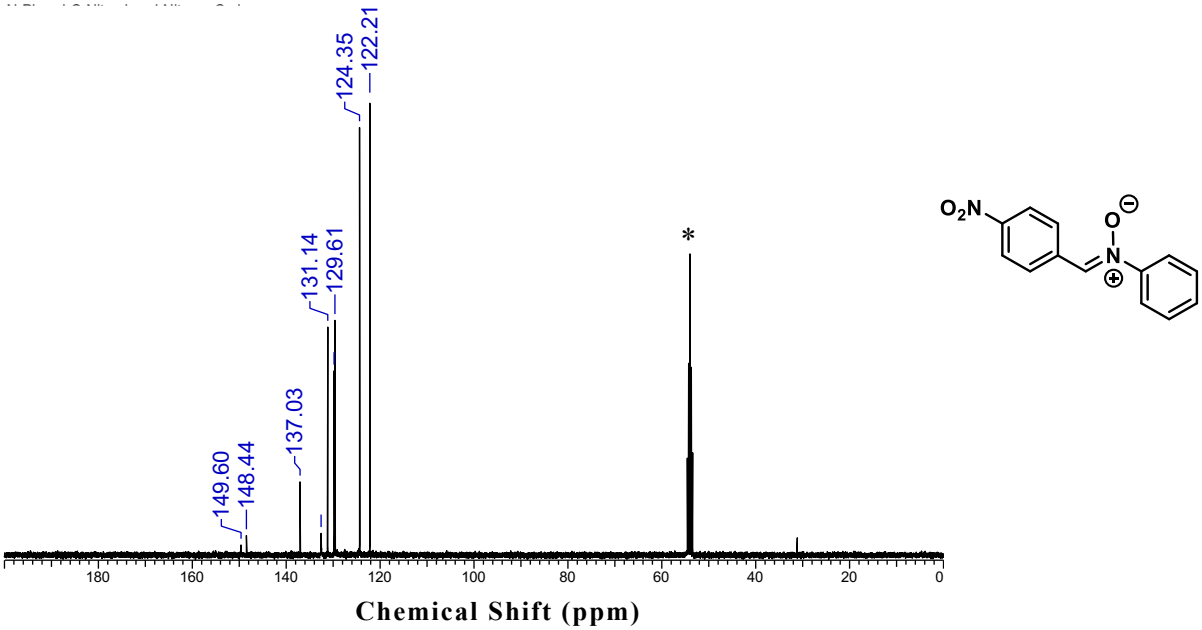
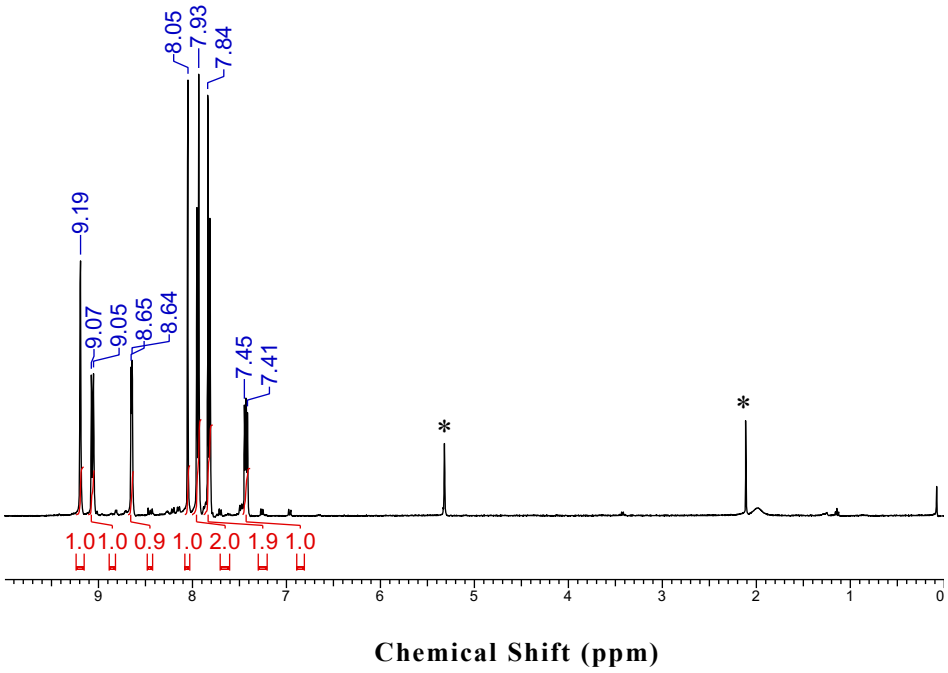


Figure S31. ^{13}C{1H} NMR spectrum of **nitrone 4** in CD_2Cl_2 at 25°C. * indicates CD_2Cl_2 solvent.

3.16 Experimental Spectra for N-phenyl-C-pyridine-nitrone (nitrone 5)



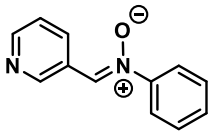
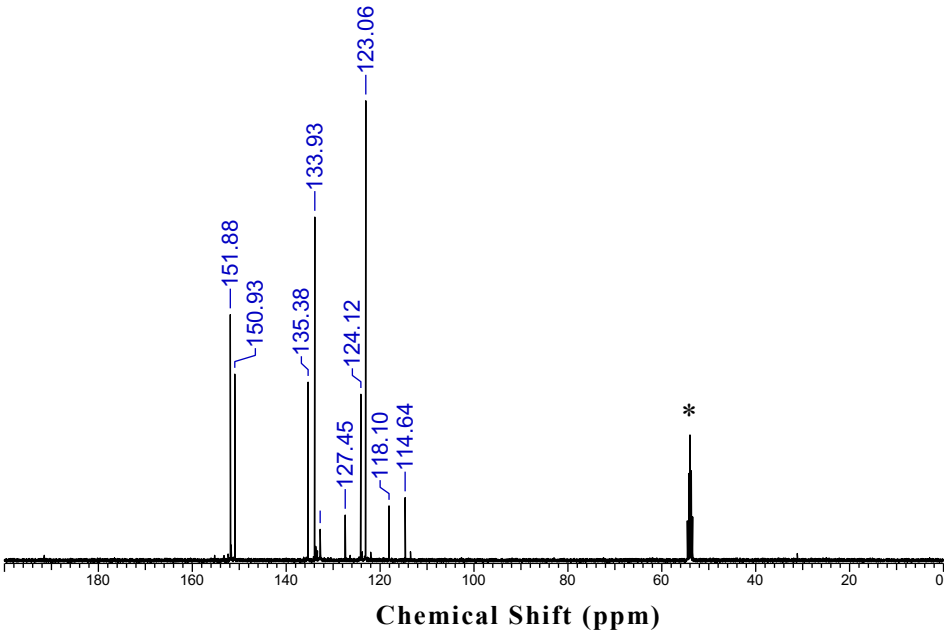


Figure S32. ^{1}H NMR spectrum of **nitrone 5** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.



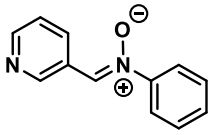


Figure S33. ^{13}C{1H} NMR spectrum of **nitrone 5** in CD_2Cl_2 at 25°C. * indicates CD_2Cl_2 solvent.

3.17 Experimental Spectra for N-cyanophenyl-C-pyridine-nitrone (nitrone 6)

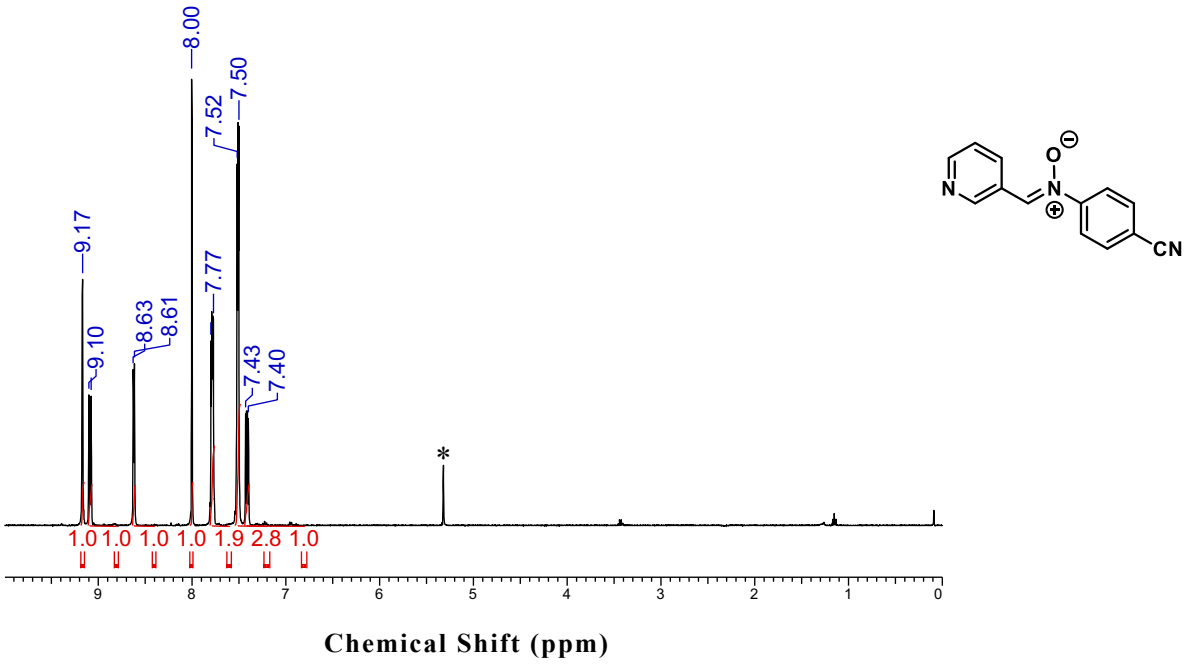


Figure S34. ^{1}H NMR spectrum of **nitrone 6** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

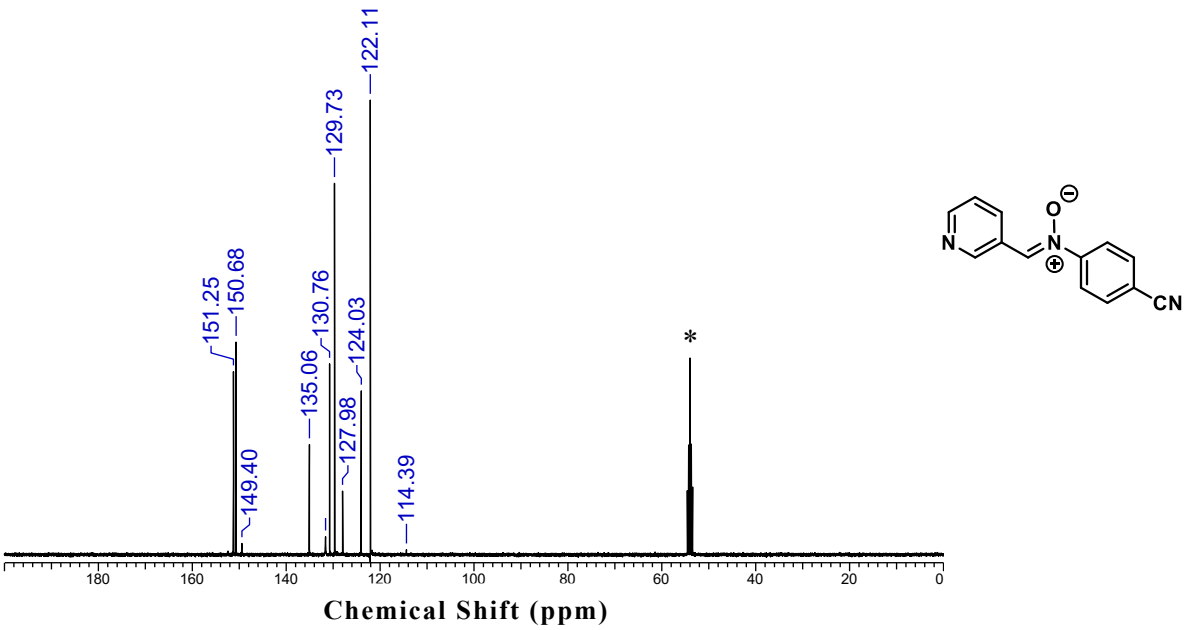


Figure S35. ^{13}C{1H} NMR spectrum of **nitrone 6** in CD_2Cl_2 at 25°C. * indicates CD_2Cl_2 solvent.

4.0 Thermogravimetric Analysis of AuNP-BCN

4.1 General Experimental Details

A crucible containing 1.3 mg of **AuNP-BCN** was heated from 25°C to 750°C under nitrogen for TGA analysis, and the decrease in organic matter was determined with increasing temperature (**Figure S36**).

The derivative of the TGA curve shows two components centered at 233.2°C and 300.0°C resulting from the decomposition of the BCN_{exo}-EG_4-S^- and OMe-EG_3-S^- ligands, respectively, both of which constitutes 64% of the mass of the AuNP sample (**Figure S37**). The area under each normalized curve indicates that BCN_{exo}-EG_4-S^- (MM = 384.492 g/mol) constitutes 28% of the total organic mass (0.23 mg per 1.3 mg AuNP) and OMe-EG_3-S^- constitutes 72% of the total organic mass (0.60 mg per 1.3 mg AuNP). Correcting for the total mass of the AuNP sample, the TGA analysis indicates that there is 0.46 μmol/mg of **AuNP-BCN**.

4.2 Experimental Spectra for TGA Analysis

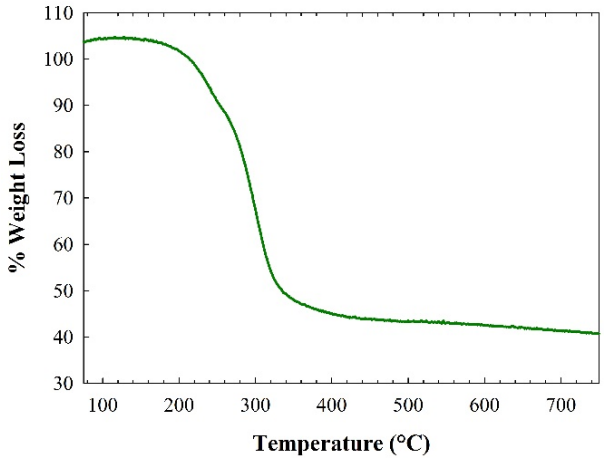


Figure S36. TGA spectrum for **AuNP-BCN**.

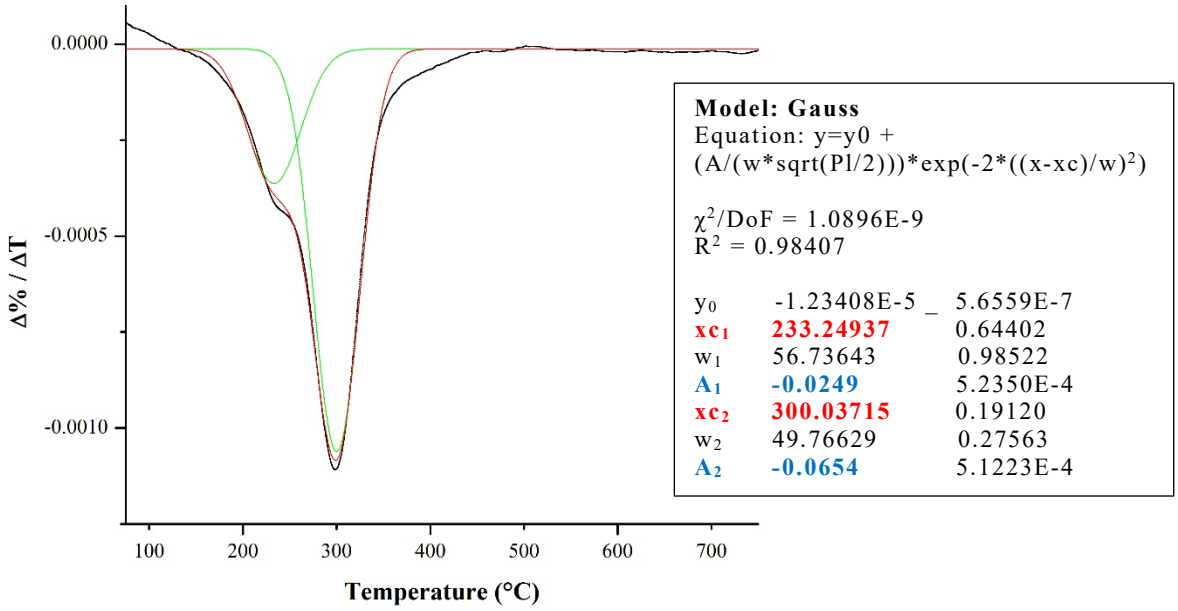


Figure S37. First-derivative of TGA spectrum for **AuNP-BCN**.

5.0 Kinetic Measurements

5.1 General Experimental Details

Estimate rate constants for all azides and nitrones were determined under second order conditions (k_2) in deuterated dichloromethane at 25°C using ^{1}H NMR spectroscopy, by reacting each with both **BCN$_{exo}$-OH** and **AuNP-BCN**.

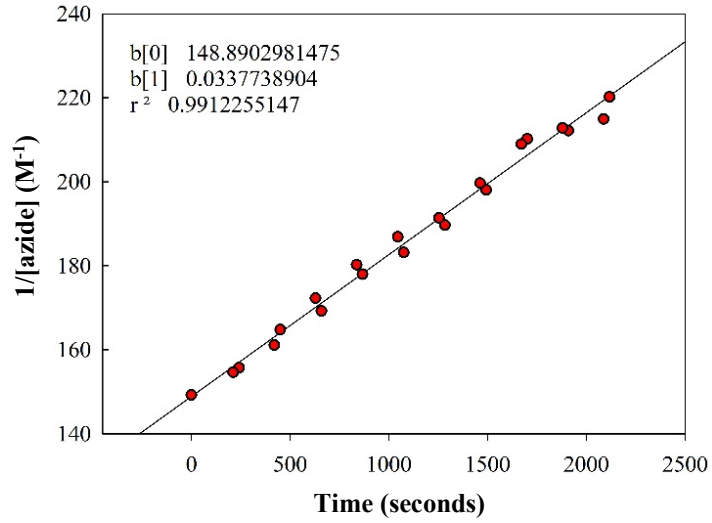
In order to estimate k_2 values for each azide/nitrone with **BCN$_{exo}$-OH**, stock solutions of the azides/nitrones and **BCN$_{exo}$-OH** were first prepared and then equimolar quantities of each were added to an NMR tube. Stock solutions of **BCN$_{exo}$-OH** and each azide/nitrone were prepared by dissolving 100 μmol in 0.5 mL deuterated dichloromethane to give a 0.2 M stock solution of **BCN$_{exo}$-OH** and 0.2 M stock solution of each azide/nitrone. Subsequently, 10 μL (2 μmol) of the azide/nitrone stock solution was added to 0.3 mL deuterated dichloromethane in an NMR tube, and a t_0 (time zero) ^{1}H NMR spectrum was acquired. Next, 10 μL (2 μmol) of the **BCN$_{exo}$-OH** stock solution was added. This solution was shaken vigorously, and ^{1}H NMR spectra were acquired over pre-determined time intervals according to the speed of the reaction.

In order to estimate k_2 values for each azide/nitrone with **AuNP-BCN**, a solution was prepared by dissolving 4 mg (2 μmol) **AuNP-BCN** in 0.3 mL deuterated dichloromethane in an NMR tube. A t_0 (time zero) ^{1}H NMR spectra was taken of this sample. Subsequently, 10 μL (2 μmol) of the azide/nitrone stock solution was added. This solution was shaken vigorously, and ^{1}H NMR spectra were acquired over pre-determined time intervals according to the speed of the reaction.

Upon cycloaddition to **BCN$_{exo}$-OH** and **AuNP-BCN**, the methylene protons alpha to the azide in **azide 1**, and the aromatic protons beta to the azide in **azide 2**, **azide 3**, **azide 4** and **azide 5** produce a ^{1}H NMR signal that decreases over time, and produces a new ^{1}H NMR signal at a higher chemical shift, and so the decrease in the ^{1}H NMR signal from the parent azide was used to obtain a rate of reaction. A rate of reaction for **azide 6** was determined by measuring the reduction in the signal at 4.0 ppm (that appears in the ^{1}H NMR spectrum of both **BCN$_{exo}$-OH** and **AuNP-BCN**), which is not present in the resulting cycloadduct. The hydrogen on the α-carbon on each of the nitrones produces a ^{1}H NMR signal that decreases over time, and produces a new ^{1}H NMR

signal at a higher chemical shift, and so the decrease in the ^{1}H NMR signal from the parent azide was used to obtain a rate of reaction.

5.2 Kinetic Measurements for 1-azido-3-propanol (azide 1)



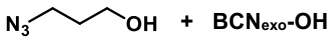
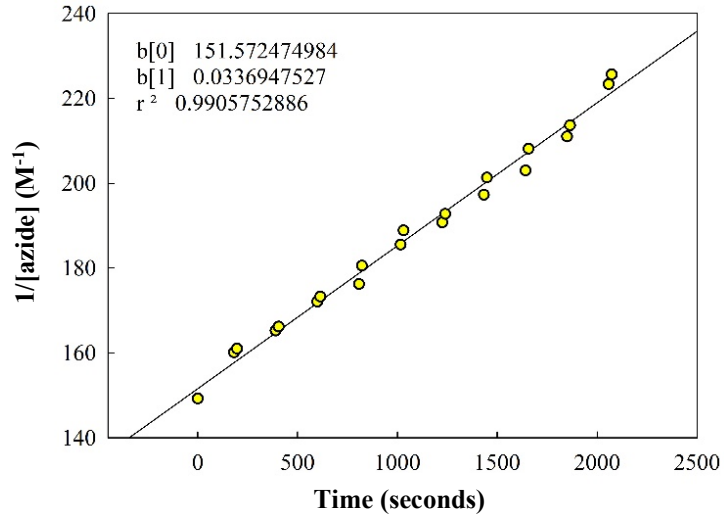


Figure S38. Second order kinetics graph for **azide 1** with **BCN$_{exo}$-OH**.



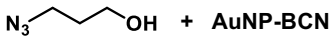


Figure S39. Second order kinetics graph for **azide 1** with **AuNP-BCN**.

5.3 Kinetic Measurements for 4-azidoanisole (azide 2)

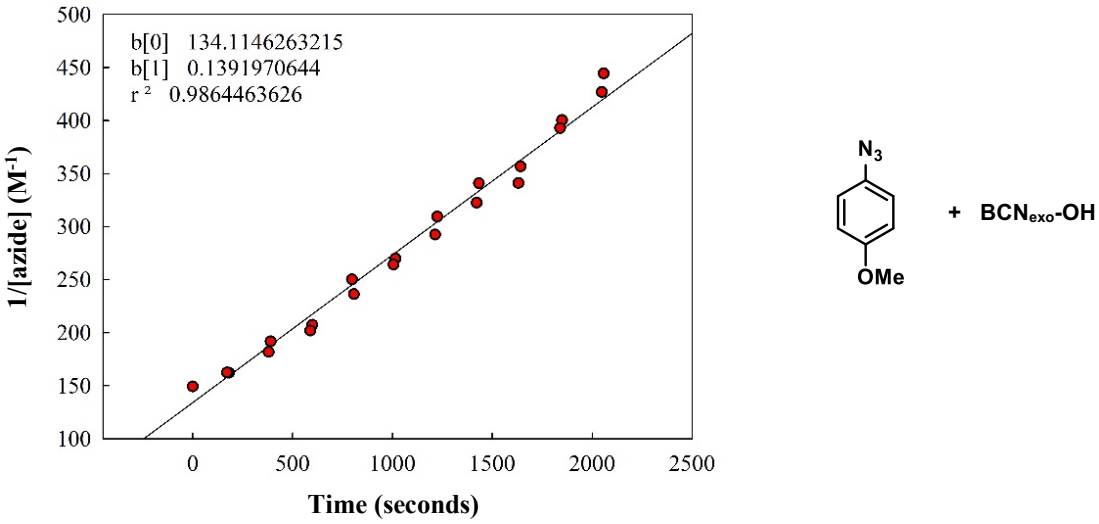


Figure S40. Second order kinetics graph for **azide 2** with **BCN$_{exo}$-OH**.

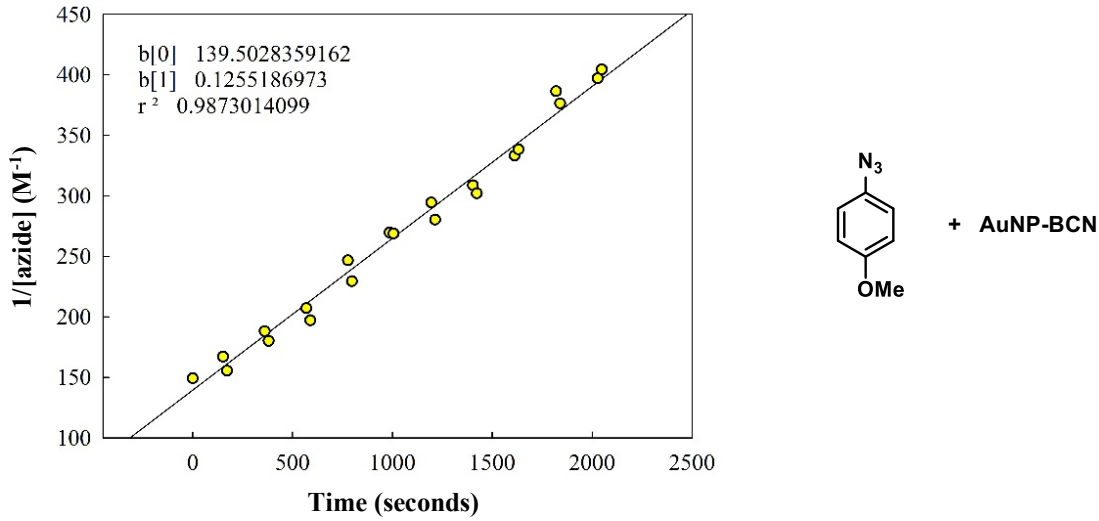
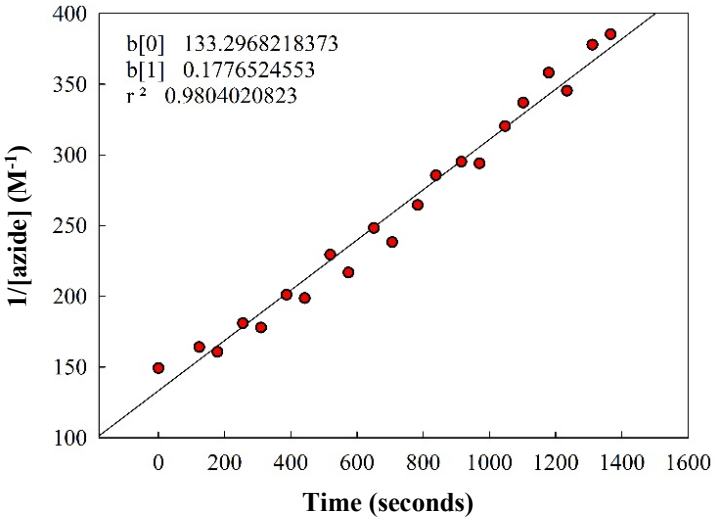


Figure S41. Second order kinetics graph for **azide 2** with **AuNP-BCN**.

5.4 Kinetic Measurements for azidobenzene (azide 3)



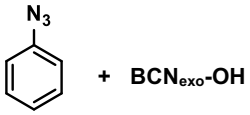
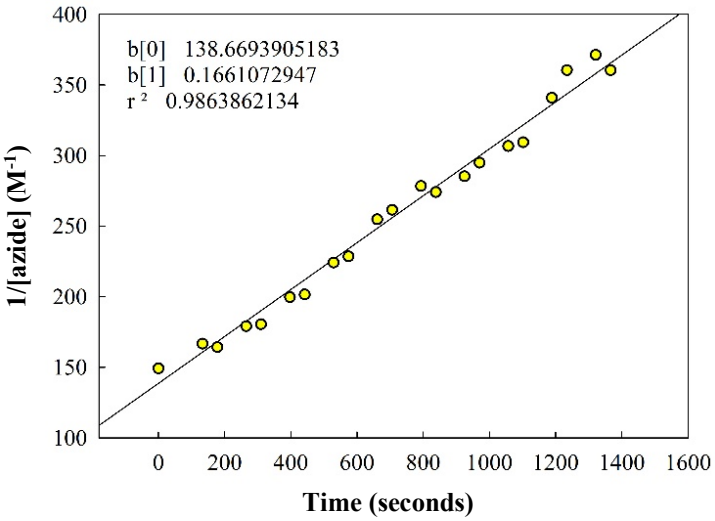


Figure S42. Second order kinetics graph for **azide 3** with **BCN$_{exo}$-OH**.



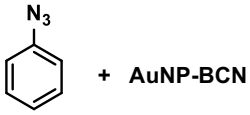


Figure S43. Second order kinetics graph for **azide 3** with **AuNP-BCN**.

5.5 Kinetic Measurements for 1-azido-4-nitrobenzene (azide 4)

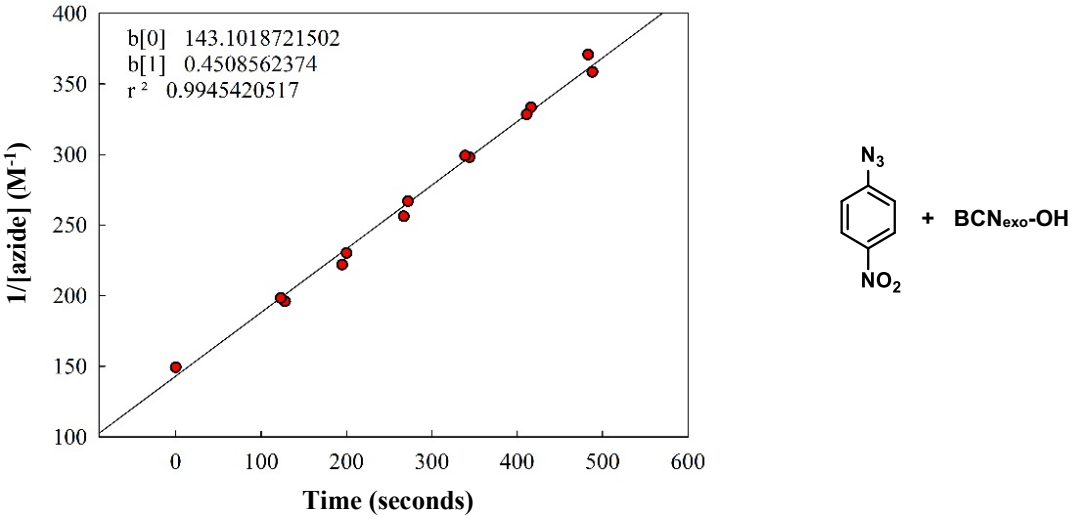


Figure S44. Second order kinetics graph for **azide 4** with **BCN$_{exo}$-OH**.

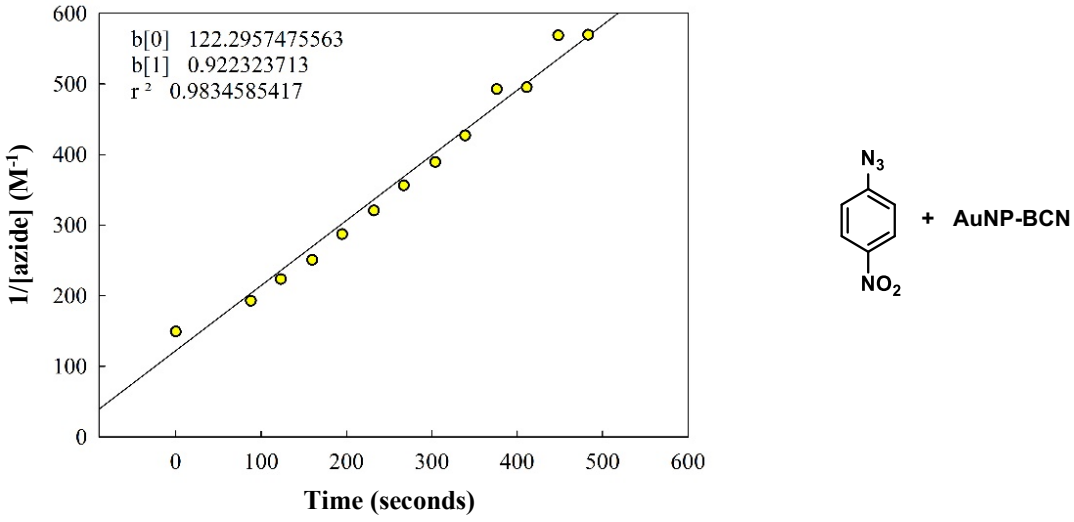


Figure S45. Second order kinetics graph for **azide 4** with **AuNP-BCN**.

5.6 Kinetic Measurements for 4-azidopyridine (azide 5)

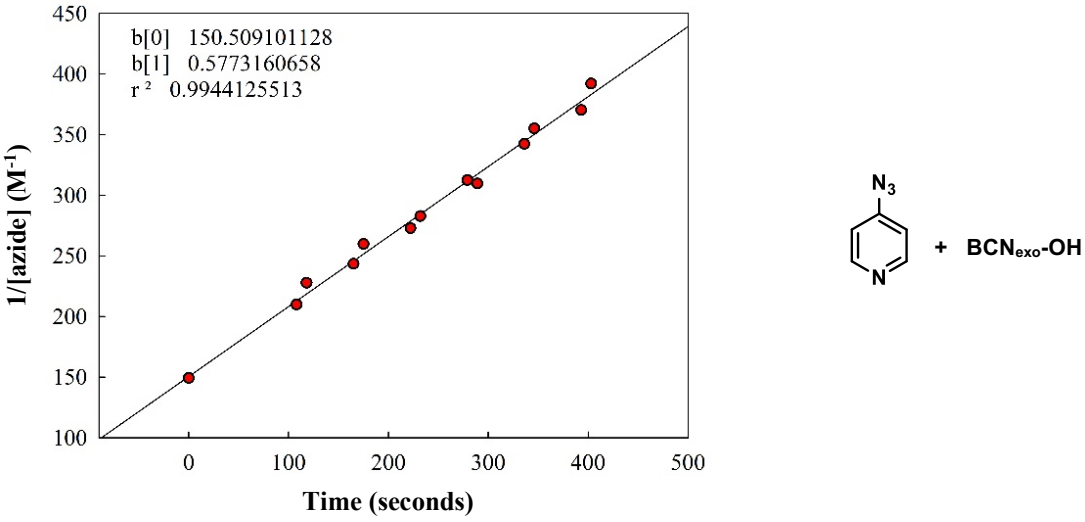


Figure S46. Second order kinetics graph for **azide 5** with **BCN$_{exo}$-OH**.

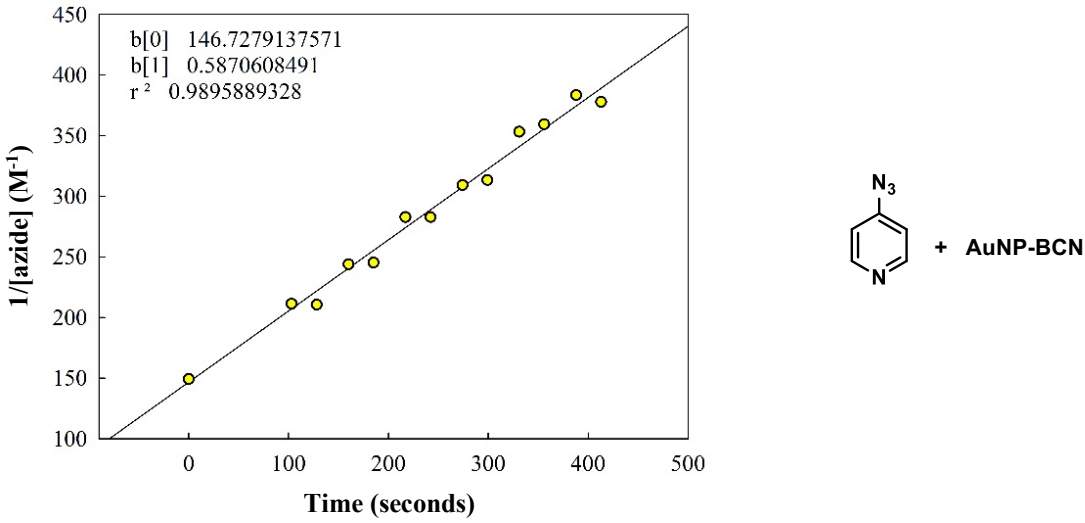
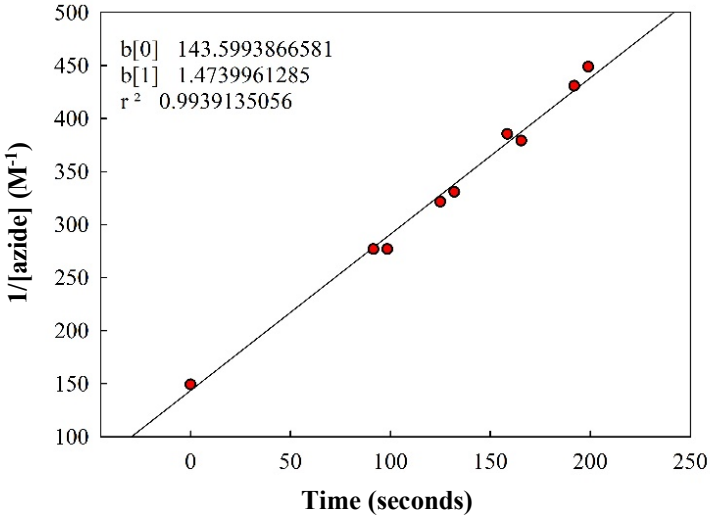
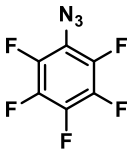


Figure S47. Second order kinetics graph for **azide 5** with **AuNP-BCN**.

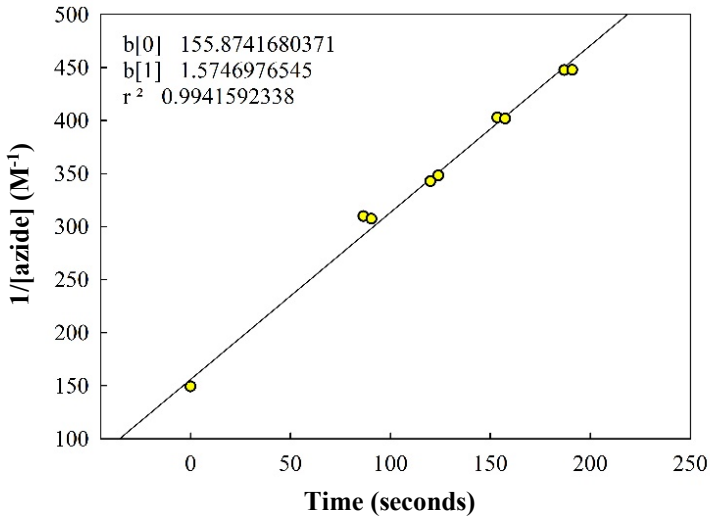
5.7 Kinetic Measurements for 1-azido-2,3,4,5,6-pentafluorobenzene (azide 6)

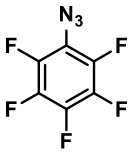




+ BCN_{exo}-OH

Figure S48. Second order kinetics graph for **azide 6** with **BCN_{exo}-OH**.

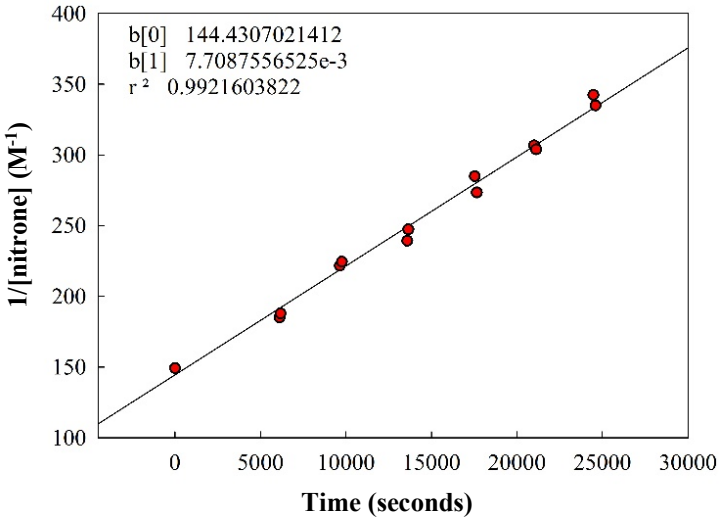




+ AuNP-BCN

Figure S49. Second order kinetics graph for **azide 6** with **AuNP-BCN**.

5.8 Kinetic Measurements for N-methyl-C-nitrophenyl-nitrone (nitrone 1)



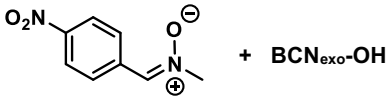
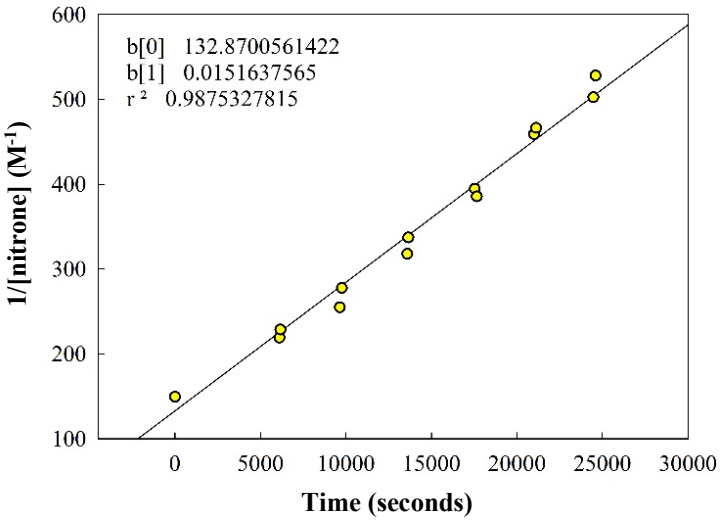


Figure S50. Second order kinetics graph for **nitrone 1** with **BCN$_{exo}$-OH**.



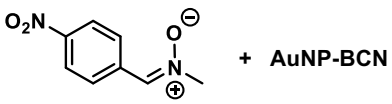
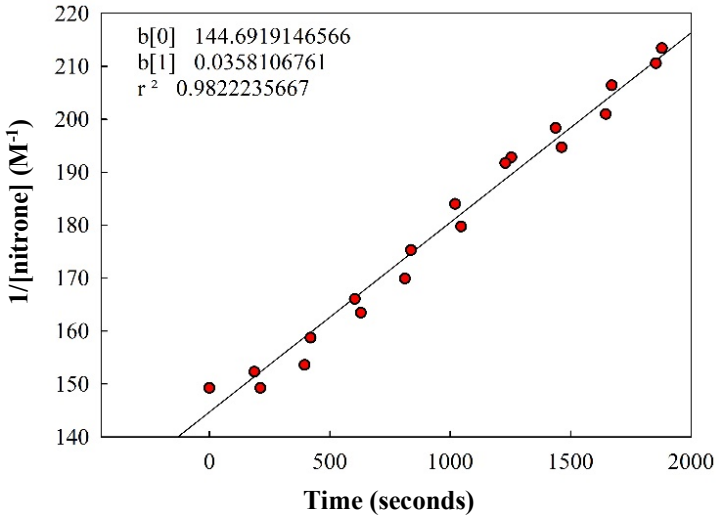


Figure S51. Second order kinetics graph for **nitrone 1** with **AuNP-BCN**.

5.9 Kinetic Measurements for N-phenyl-C-methoxyphenyl-nitrone (nitrone 2)



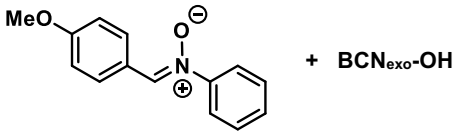
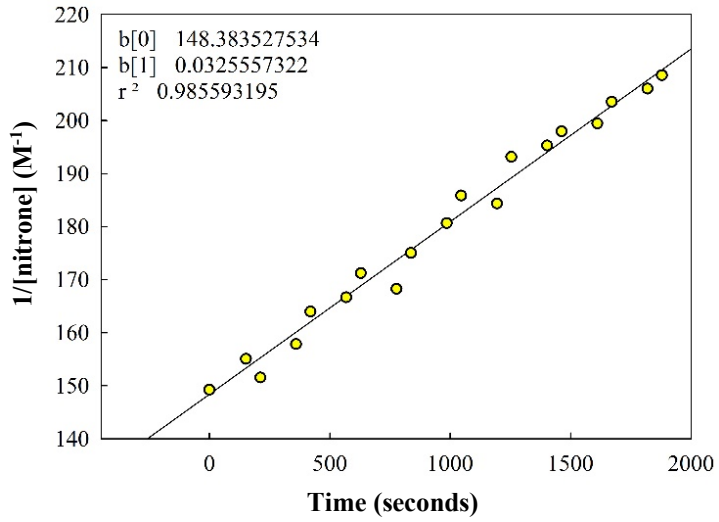


Figure S52. Second order kinetics graph for **nitrone 2** with **BCN$_{exo}$-OH**.



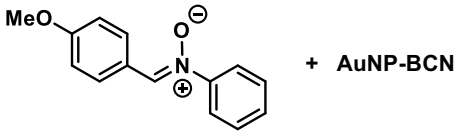


Figure S53. Second order kinetics graph for **nitrone 2** with **AuNP-BCN**.

5.10 Kinetic Measurements for N-phenyl-C-phenyl-nitrone (nitrone 3)

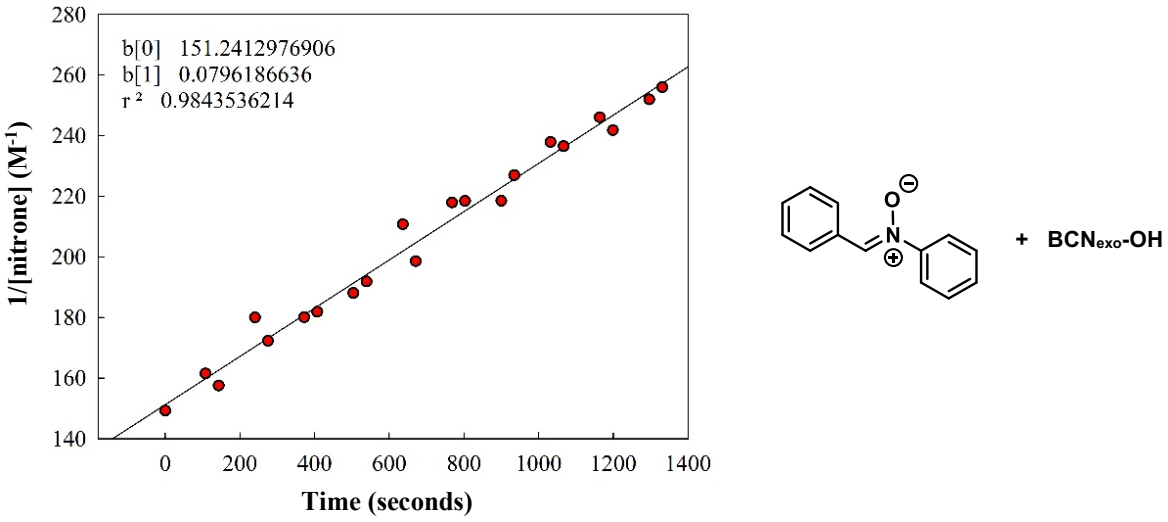


Figure S54. Second order kinetics graph for **nitrone 3** with **BCN$_{exo}$-OH**.

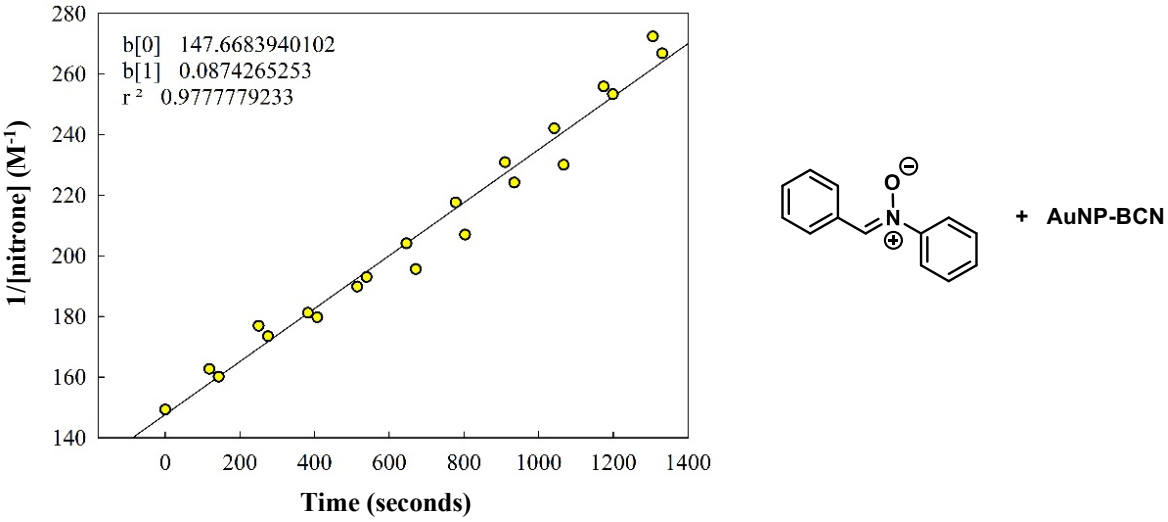


Figure S55. Second order kinetics graph for **nitrone 3** with **AuNP-BCN**.

5.11 Kinetic Measurements for N-phenyl-C-nitrophenyl-nitrone (nitrone 4)

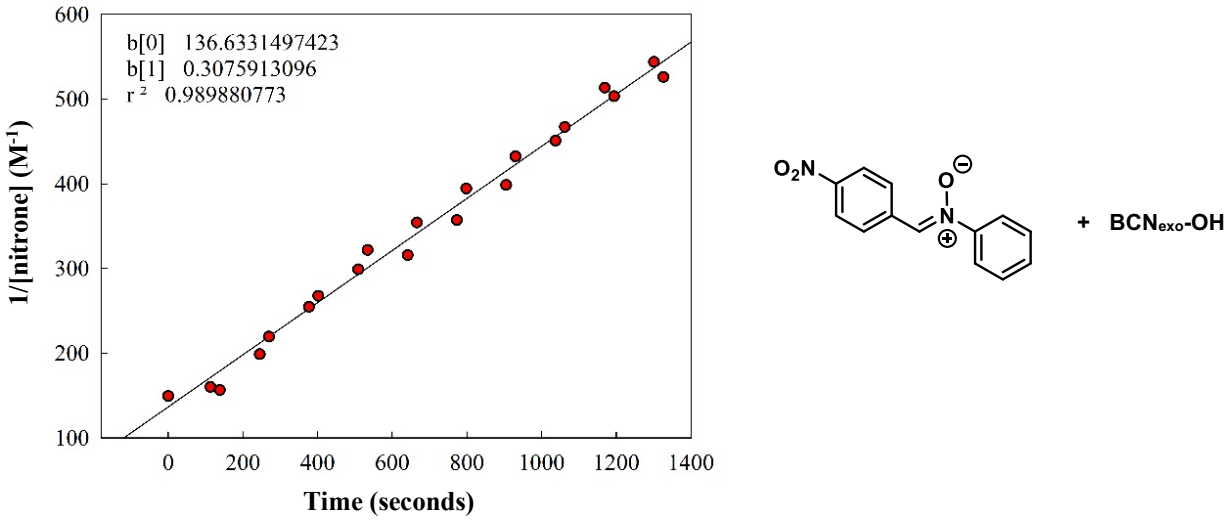


Figure S56. Second order kinetics graph for **nitrone 4** with **BCN$_{exo}$-OH**.

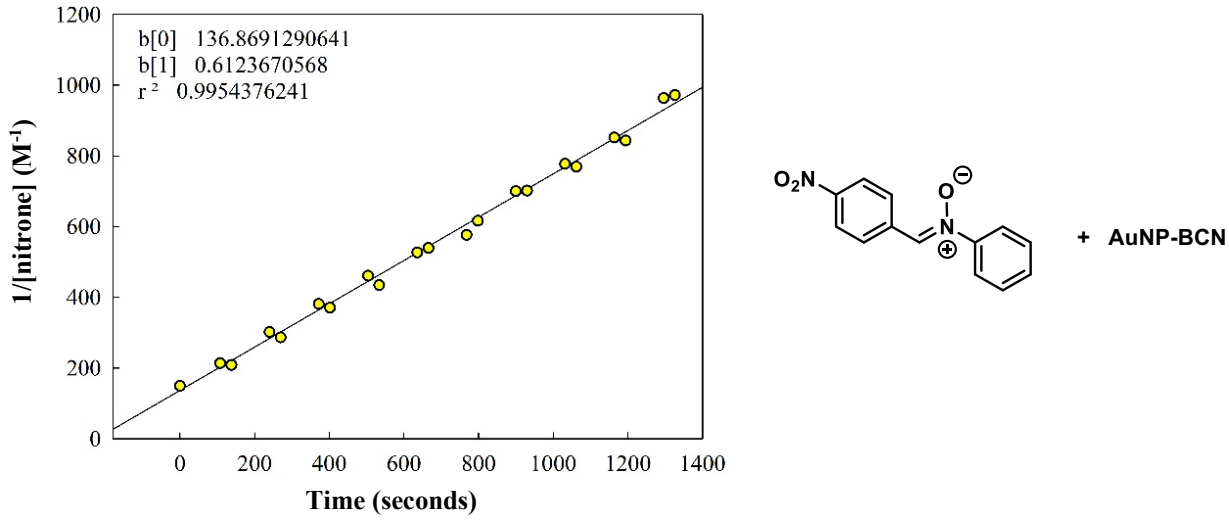
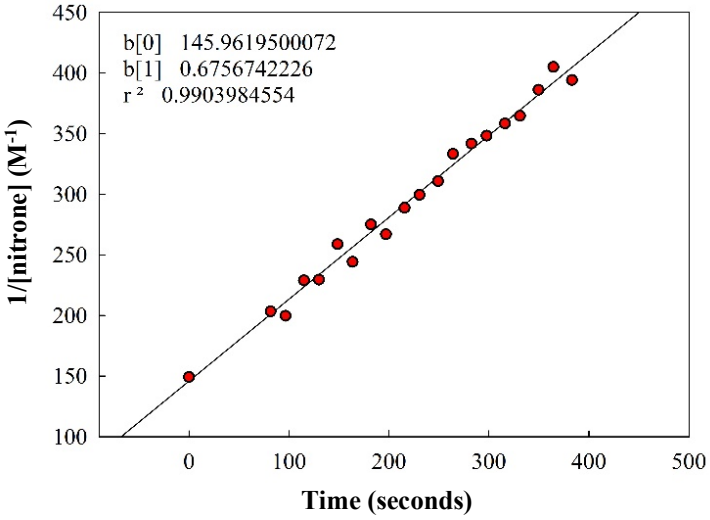
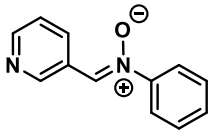


Figure S57. Second order kinetics graph for **nitrone 4** with **AuNP-BCN**.

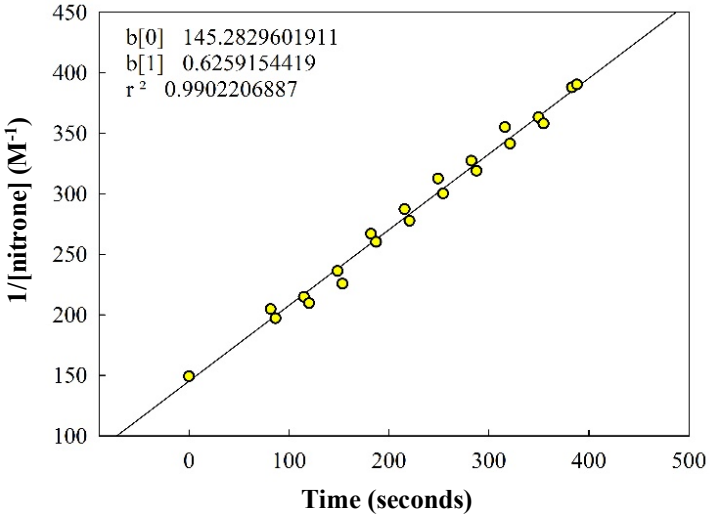
5.12 Kinetic Measurements for N-phenyl-C-pyridine-nitrone (nitrone 5)

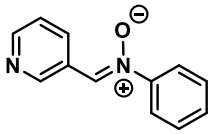




+ BCN_{exo}-OH

Figure S58. Second order kinetics graph for **nitrone 5** with **BCN_{exo}-OH**.





+ AuNP-BCN

Figure S59. Second order kinetics graph for **nitrone 5** with **AuNP-BCN**.

5.13 Kinetic Measurements for N-cyanophenyl-C-pyridine-nitrone (nitrone 6)

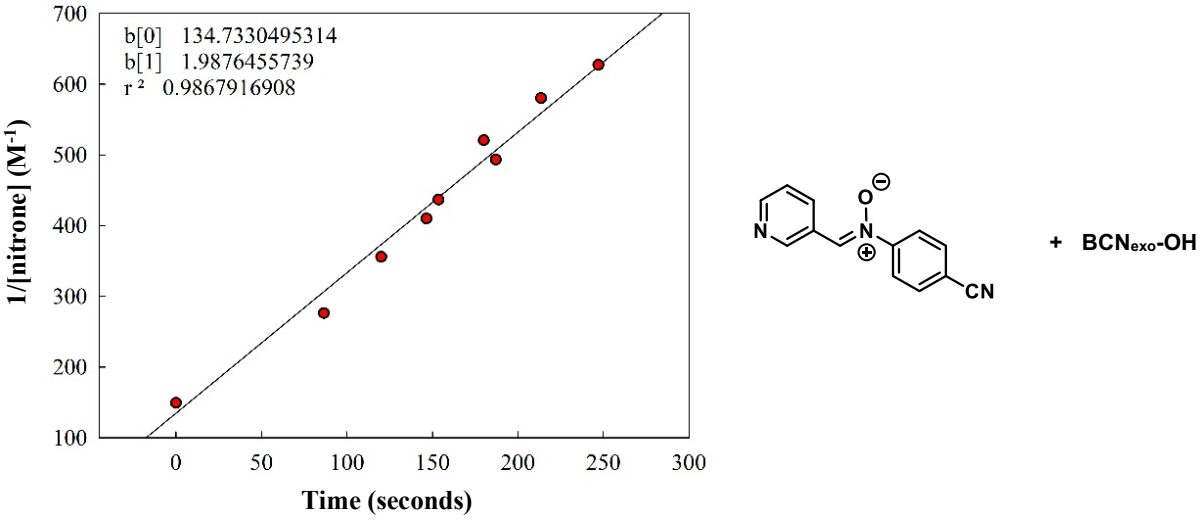


Figure S60. Second order kinetics graph for **nitrone 5** with **BCN$_{exo}$-OH**.

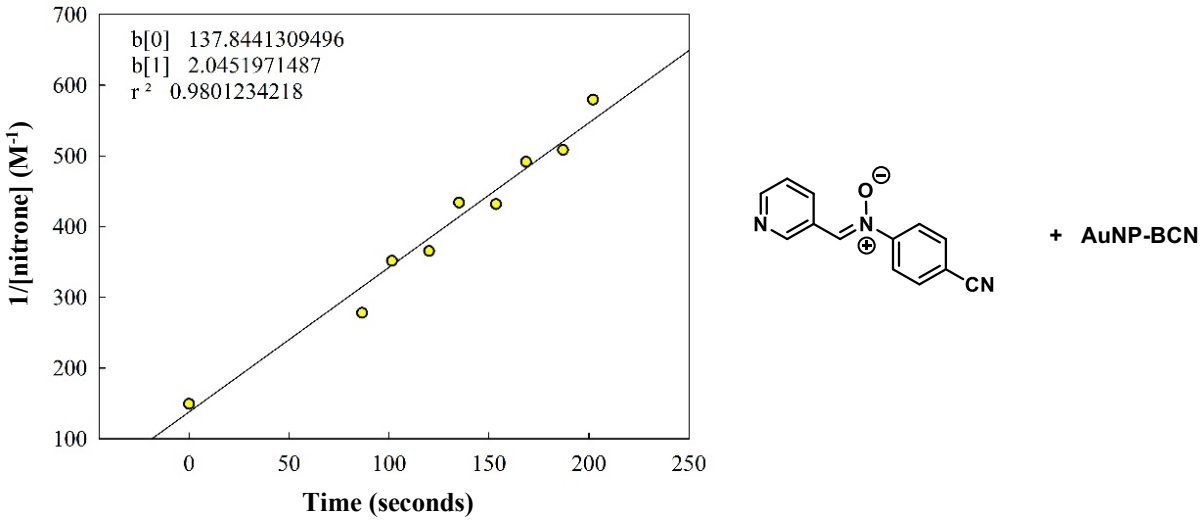


Figure S61. Second order kinetics graph for **nitrone 5** with **AuNP-BCN**.

6.0 Competition Experiments for AuNP-BCN

6.1 General Experimental Details

For the competition experiments between an azide and nitrone, equimolar quantities of one azide, one nitrone and AuNP-BCN were combined in deuterated dichloromethane and monitored by ^{1}H NMR spectroscopy.

First, stock solutions for the azide and nitrone used for each experiment were first prepared as described in **Section 5.1** to generate 0.2 M solutions of each. Then 0.2 mL of azide stock solution was added to 0.2 mL of nitrone stock solution to obtain 1:1 azide:nitrone stock solutions. Subsequently, 20 µL (2 µmol azide and 2 µmol nitrone) of this 1:1 stock solution was added to 0.3 mL deuterated dichloromethane in an NMR tube, and a t_0 (time zero spectrum) ^{1}H NMR spectrum was acquired. Non-coinciding ^{1}H NMR signals were chosen, one produced from a proton environment in the azide, and one produced from a proton environment in the nitrone, and the integrals were determined for these signals to give the $t_{0(azide)}$ and $t_{0(nitrone)}$ integral values.

Next, a solution was prepared by dissolving 4 mg (2 µmol) **AuNP-BCN** in 0.3 deuterated dichloromethane in an NMR tube. Subsequently, 20 µL of the 1:1 azide:nitrone solution was added, the solution was shaken vigorously, and a ^{1}H NMR spectrum was taken after 24 hours to allow the interfacial reaction to go to completion (24 hour spectrum). The integral of non-coinciding signals from the same proton environments chosen before were determined (which decreased as the interfacial reaction had gone to completion), to give the $t_{24(azide)}$ and $t_{24(nitrone)}$ integral values. To determine the % I-SPAAC (i.e. degree of reaction between **AuNP-BCN** and the azide species), the $t_{24(azide)}/t_{0(azide)}$ ratio was determined. To determine the % I-SPANC (i.e. degree of reaction between **AuNP-BCN** and the nitrone species), the $t_{24(nitrone)}/t_{0(nitrone)}$ ratio was determined.

Since **azide 6** does not contain any protons, the reacted percentage of **nitrone 1** in the competition experiment against **azide 6** was determined, and the reacted percentage of **azide 6** was calculated by difference.

6.2 Experimental Spectra for Competition Experiment between azide 1 and nitrone 6

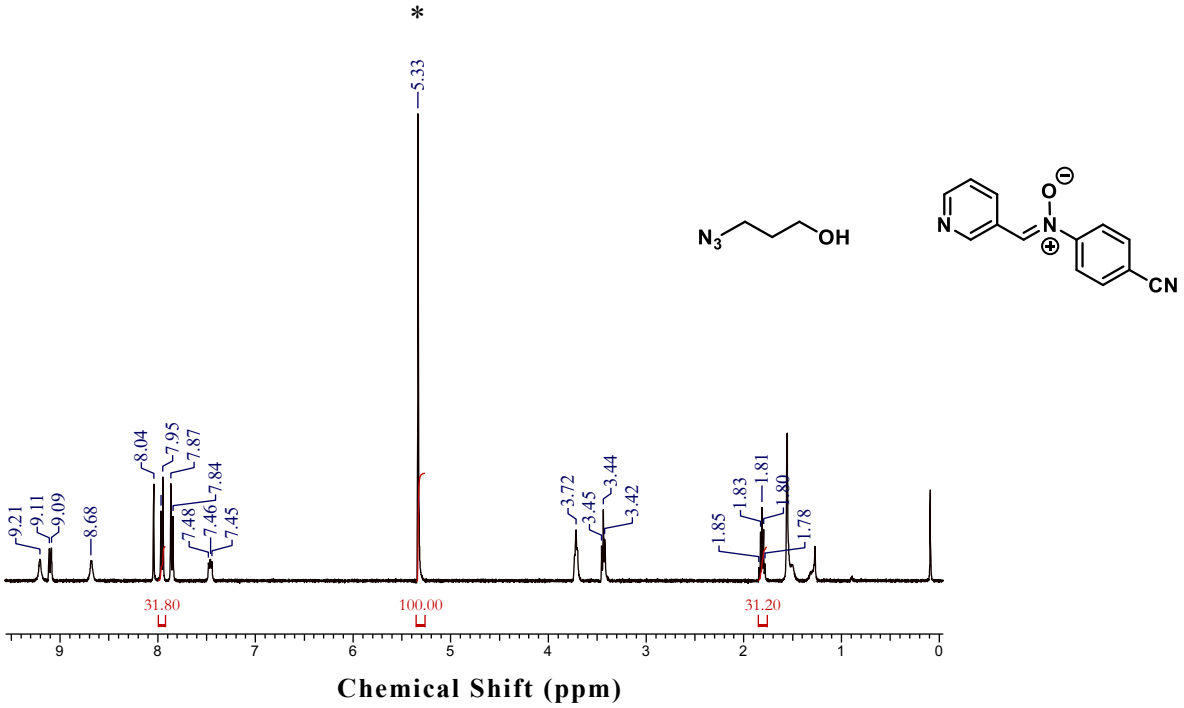


Figure S62. ^{1}H NMR spectrum of equimolar mixture of **azide 1** and **nitrone 6** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

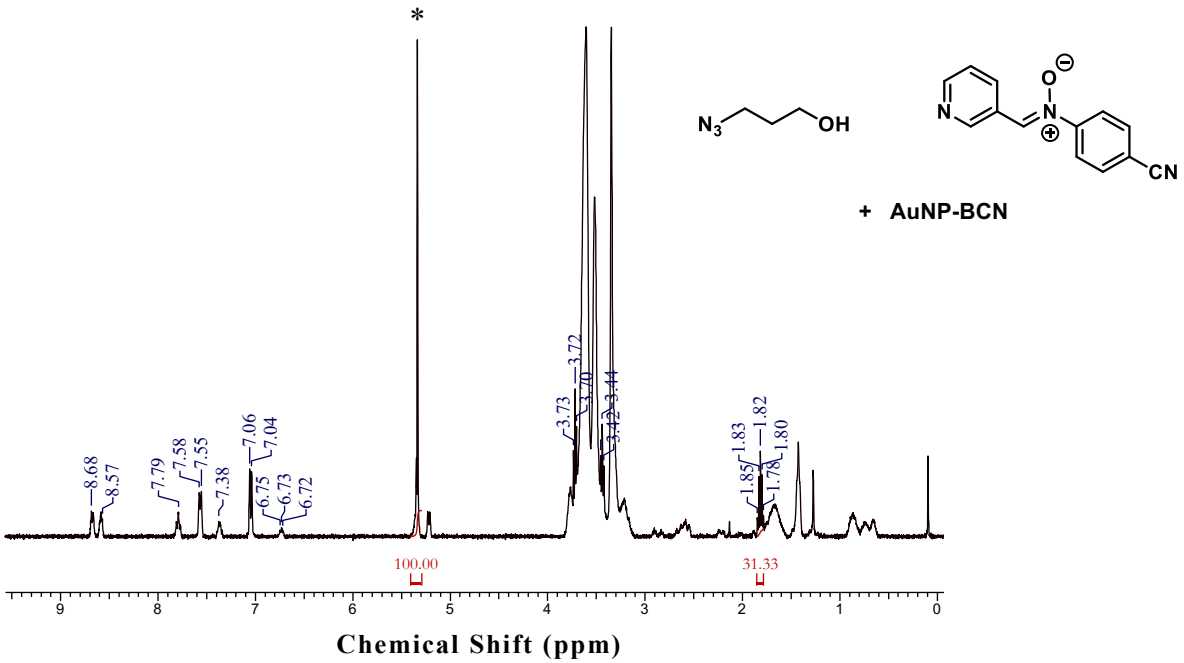


Figure S63. ^{1}H NMR spectrum of equimolar mixture of **azide 1** and **nitrone 6** and interfacial BCN (in **AuNP-BCN)** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

6.3 Experimental Spectra for Competition Experiment between azide 3 and nitrone 4

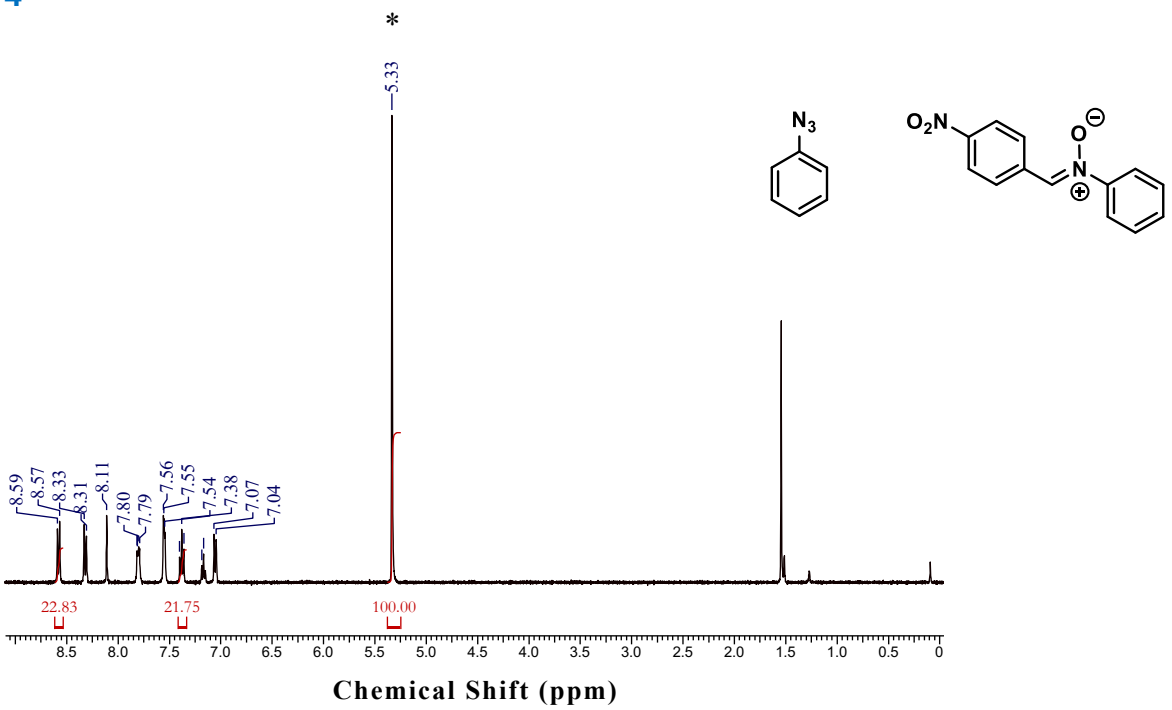


Figure S64. ^{1}H NMR spectrum of equimolar mixture of **azide 3** and **nitrone 4** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

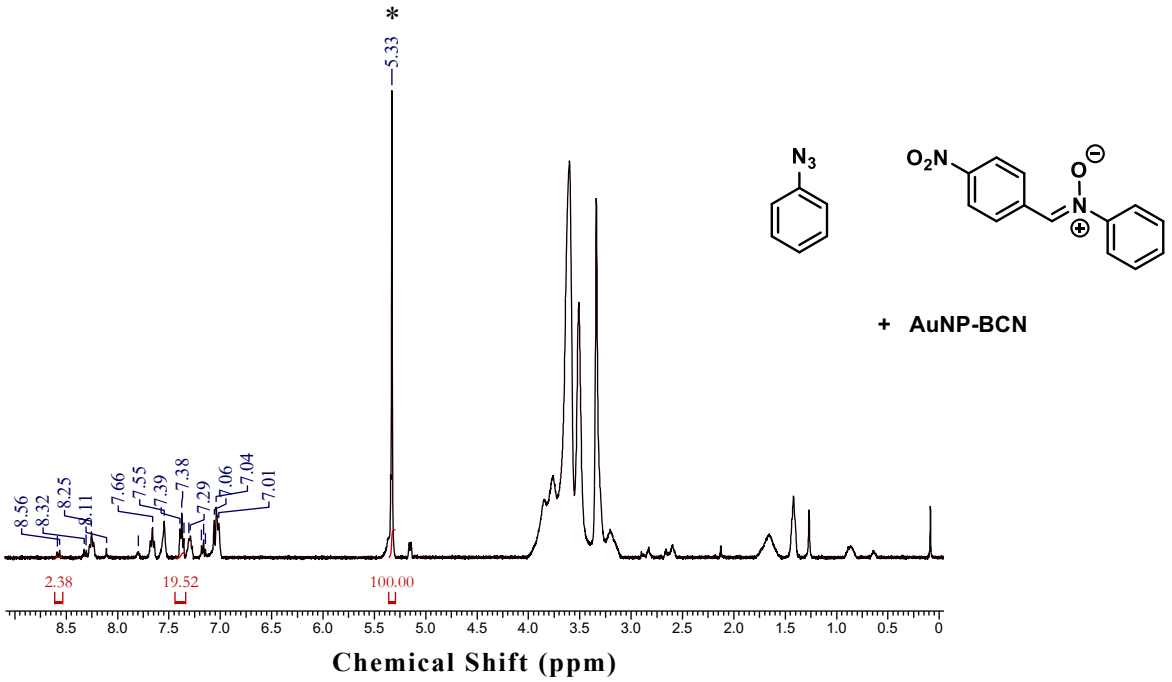


Figure S65. ^{1}H NMR spectrum of equimolar mixture of **azide 3** and **nitrone 4** and interfacial BCN (in **AuNP-BCN)** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

6.4 Experimental Spectra for Competition Experiment between azide 4 and nitrone 4

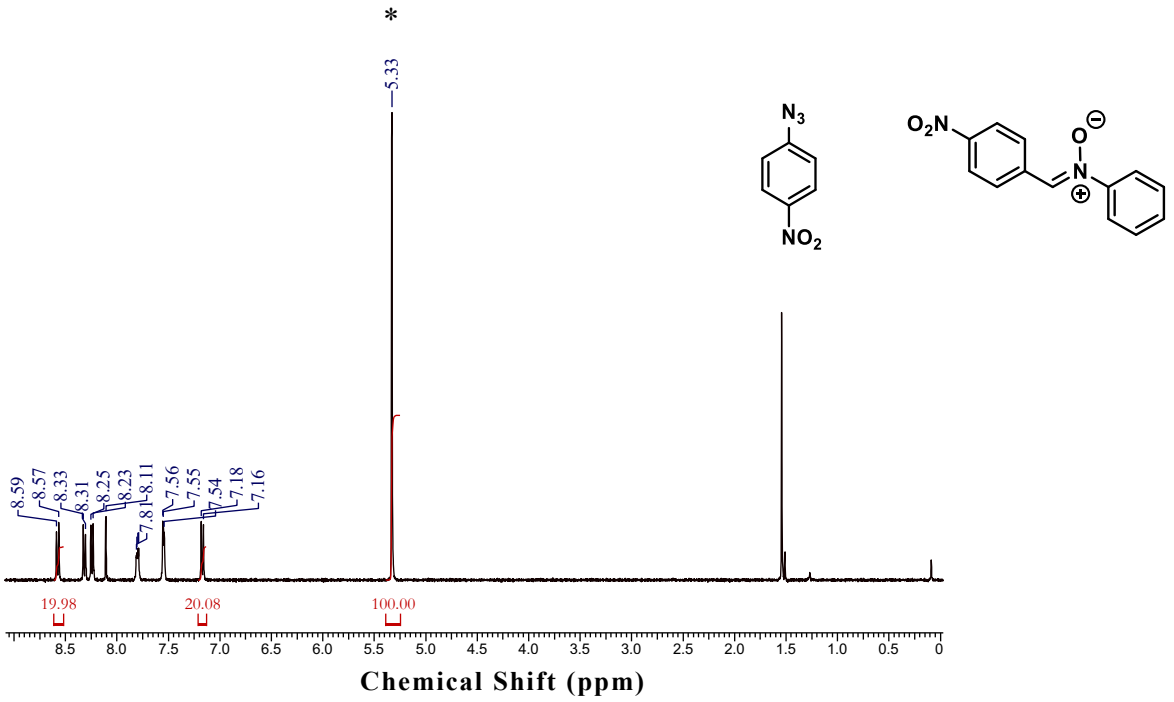


Figure S66. ^{1}H NMR spectrum of equimolar mixture of **azide 4** and **nitrone 4** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

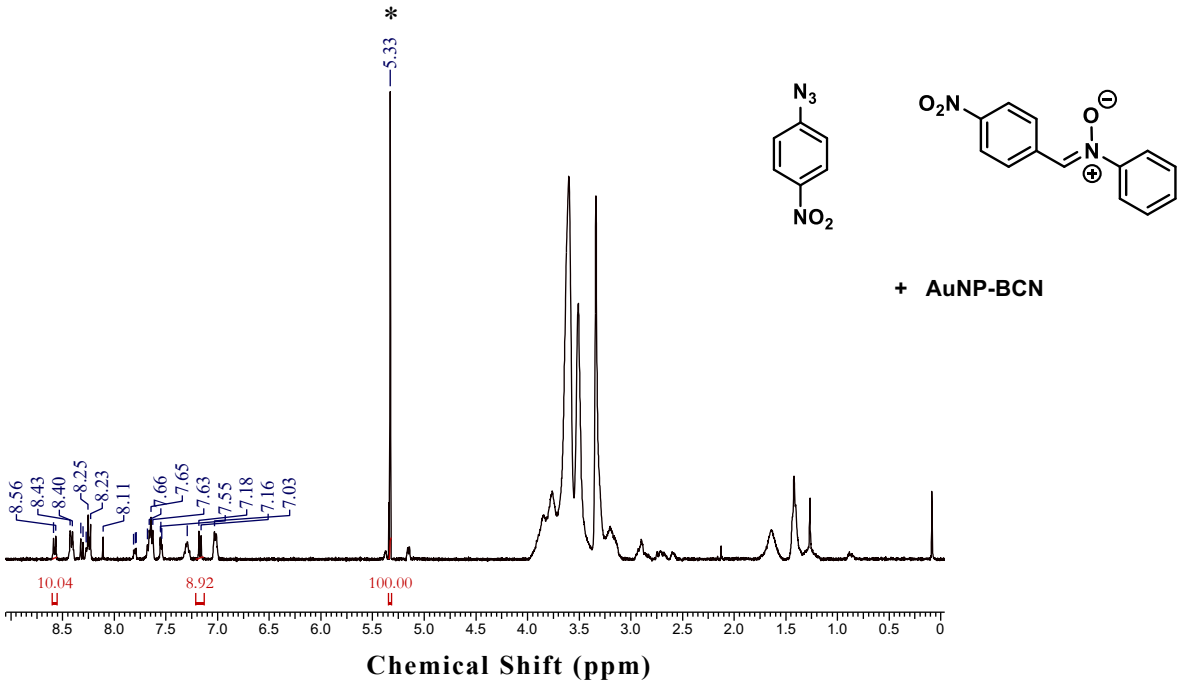


Figure S67. ^{1}H NMR spectrum of equimolar mixture of **azide 4** and **nitrone 4** and interfacial BCN (in **AuNP-BCN)** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

6.5 Experimental Spectra for Competition Experiment between azide 5 and nitrone 2

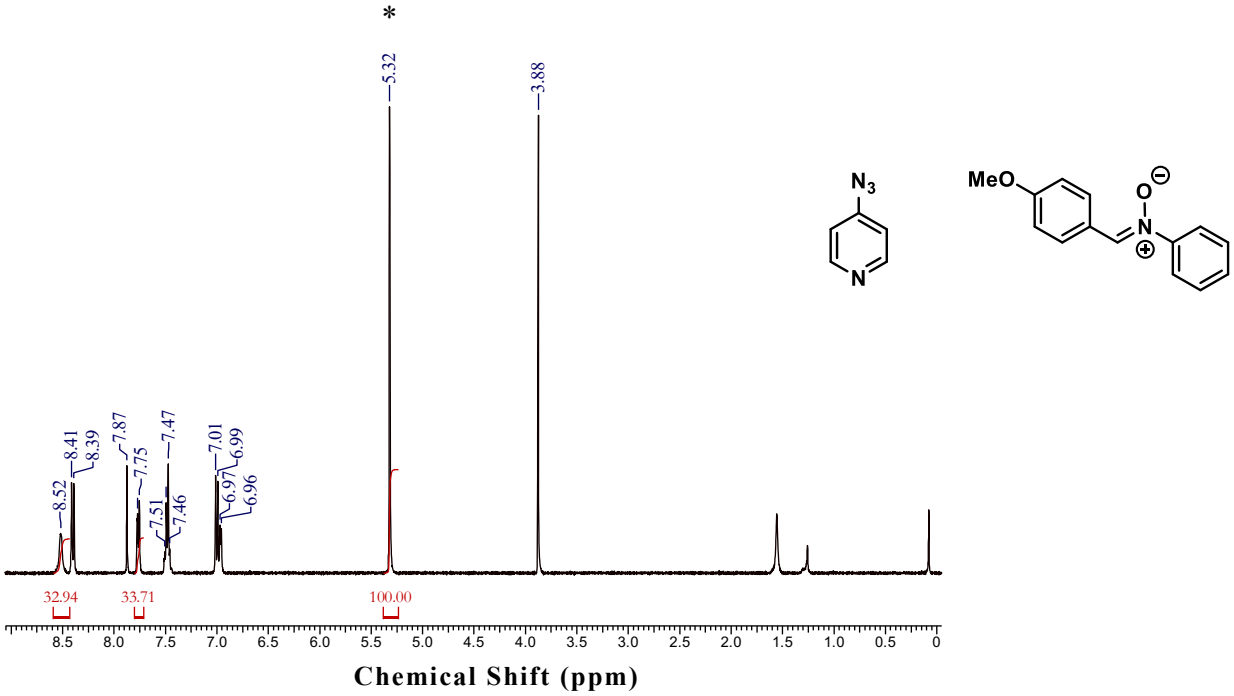


Figure S68. ^{1}H NMR spectrum of equimolar mixture of **azide 5** and **nitrone 2** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

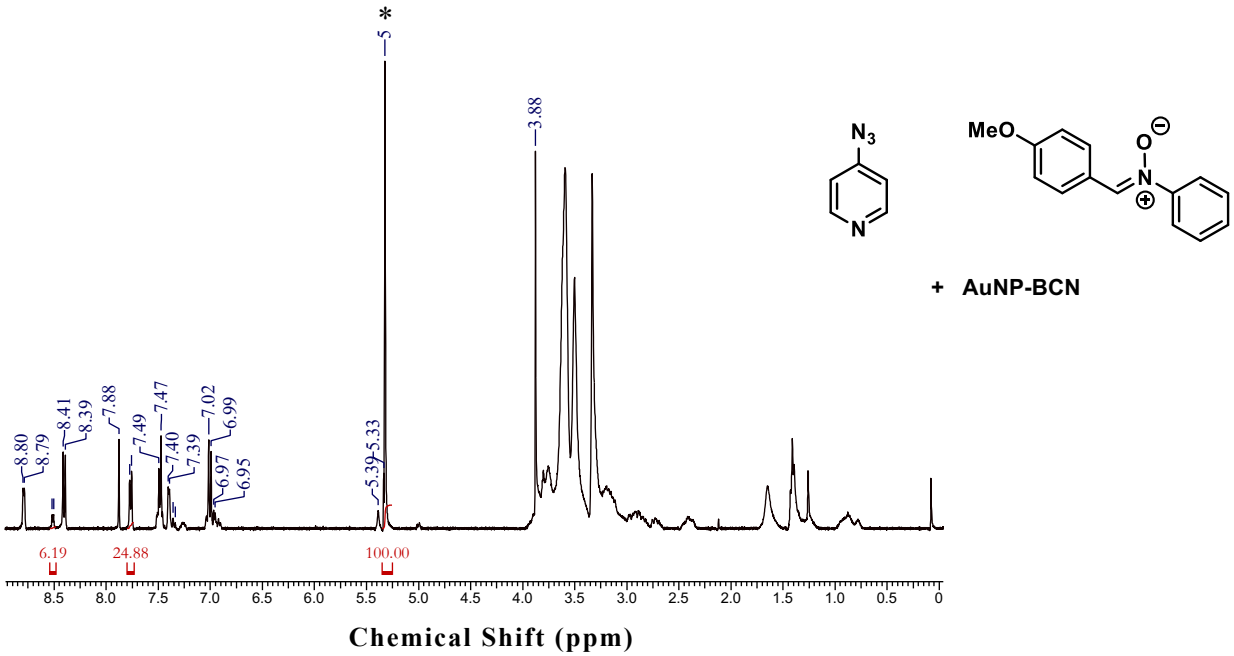


Figure S69. ^{1}H NMR spectrum of equimolar mixture of **azide 5** and **nitrone 2** and interfacial BCN (in **AuNP-BCN)** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

6.6 Experimental Spectra for Competition Experiment between azide 6 and nitrone 1

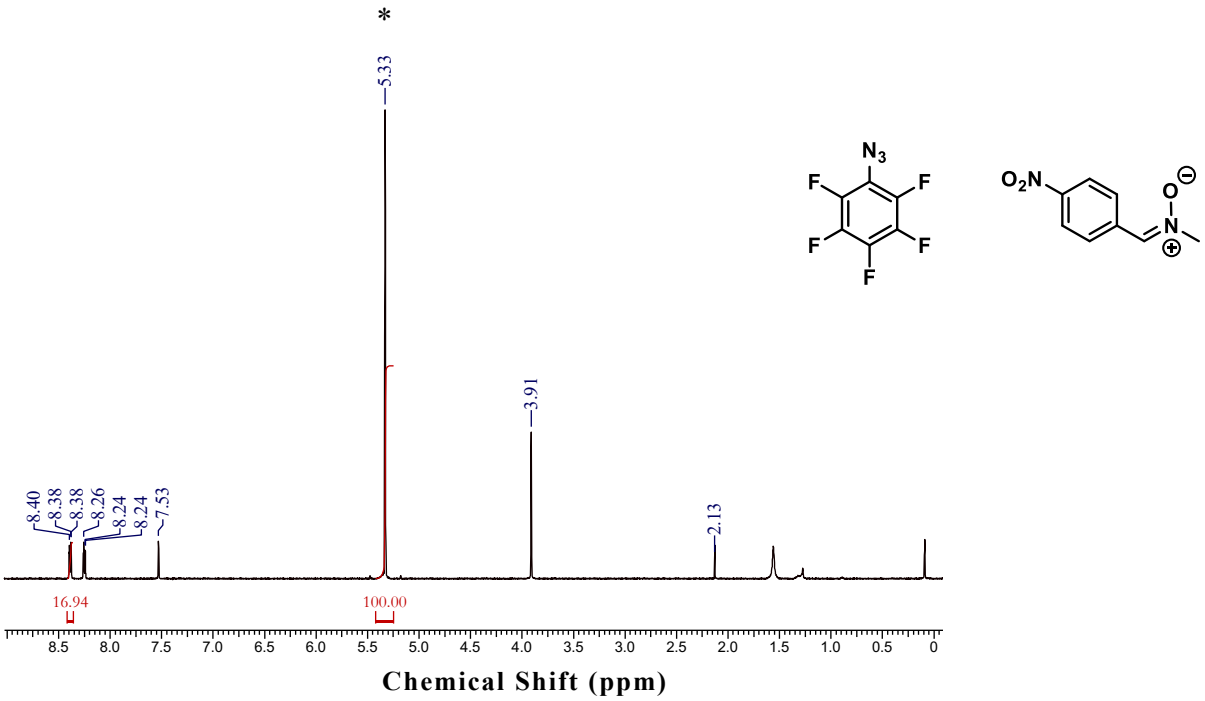


Figure S70. ^{1}H NMR spectrum of equimolar mixture of **azide 6** and **nitrone 1** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

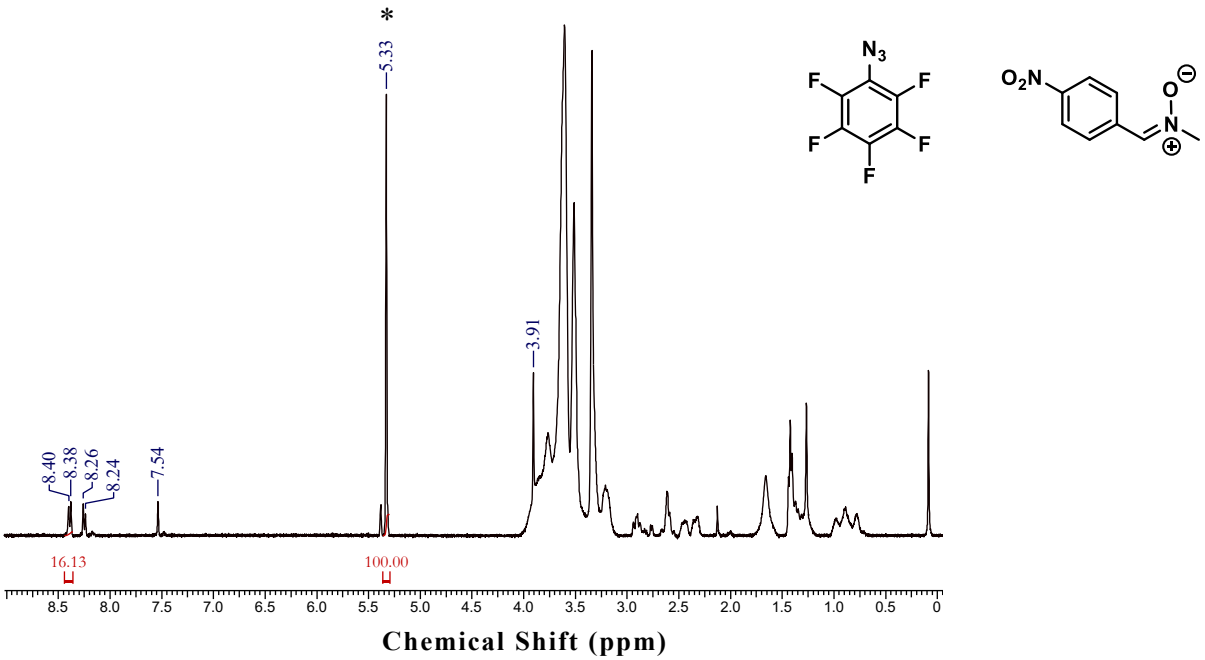


Figure S71. ^{1}H NMR spectrum of equimolar mixture of **azide 6** and **nitrone 1** and interfacial BCN (in **AuNP-BCN)** in CD_2Cl_2 at 25°C. * denotes residual protio solvent.

7.0 References for Supporting Information

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