Electronic Supplementary Material (ESI) for RSC Advances.

A Sensitive and Selective Chemiluminogenic Probe for Palladium

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Supporting Information

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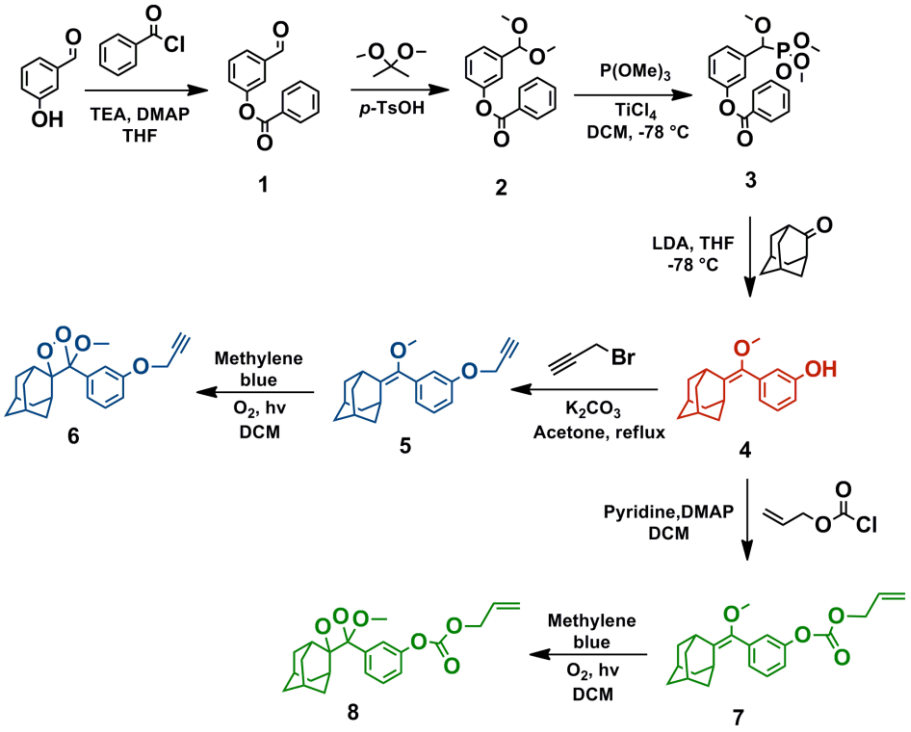
General

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Spectrospin Avance DPX 400 spectrometer using $CDCl_3$ as the solvent. Chemical shifts values are reported in ppm from tetramethylsilane as internal standard. Spin multiplicities are reported as the following: s (singlet), d (doublet), m (multiplet). HRMS data were acquired on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. Chemiluminescence measurements were done on a Varian Eclipse spectrofluorometer. Spectrophotometric grade solvents were used for spectroscopy experiments. Flash column chromatography (FCC) was performed by using glass columns with a flash grade silica gel (Merck Silica Gel 60 (40–63 μm)). Reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates (Merck Silica Gel PF-254), visualized by UV-Vis light. All organic extracts were dehydrated over anhydrous Na_2SO_4 and concentrated by using rotary evaporator before being subjected to FCC. All other chemicals and solvents were supplied from commercial sources and used as received.

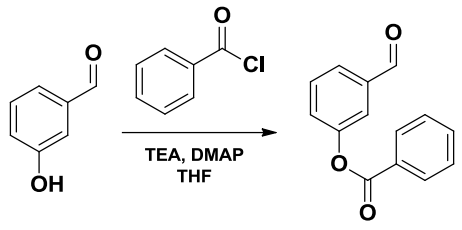
Chemiluminescent Spectroscopic Analysis was performed as follows: Pd(0) was added to vial which contains PPh_3 (1.0 mM) and dioxetane **6** or **8** (200 μM) in DMSO-H_2O (95:5, v/v) solution with Na_2CO_3-$NaHCO_3$ Buffer (50 mM, pH: 9.0). Chemiluminescence was measured for every 2 °C from 60 °C to 80 °C by transferring 1.0 mL solution to the cell and chemiluminescence emission was managed with the addition of NaOH (10 μL) from 10N stock solution. Blank was measured as above in the absence of Pd(0). Stock Solutions were prepared according to the literature.[1,2,3]

Synthesis of the Chemiluminescent Pd(0) Probes:

Pursued synthetic route for the target compounds as follows:



Synthesis of 3-benzyloxybenzaldehyde *(1)*



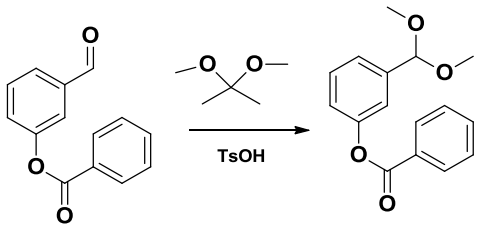
1

3-hydroxy benzaldehyde (1.0 g, 8.19 mmol) was dissolved in dry THF. When reaction mixture was cooled to 0 °C, TEA (1.71 mL, 12.2 mmol) was added and mixed for 20 min. After the addition of catalytic amount of DMAP, benzoyl chloride (1.38 mL, 12.2 mmol) was added dropwise to the reaction mixture and it was left to stir at room temperature. The progress of the reaction was monitored by TLC. When TLC showed no starting material, reaction was concentrated to half of it. The residue was diluted with EtOAc and extracted with brine. Combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc/ Hexane (1:5, v/v) as the eluent. Compound **1** was obtained as white solid (1.41 g, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.04 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 2H), 7.78-7.82 (m, 2H), 7.57-7.69 (m, 2H), 7.51-7.57 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 191.1, 164.8, 151.5, 137.8, 133.9, 130.24, 130.21, 129.0, 128.71, 128.69, 127.9, 127.3, 122.5 ppm.

Synthesis of 3-benzyloxybenzaldehyde dimethyl acetal *(2)*



1 **2**

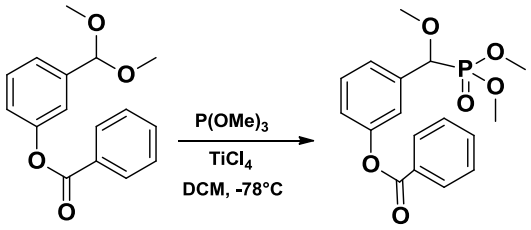
Compound **1** (1.0 g, 4.42 mmol), 2,2-dimethoxy propane (1.2 mL) and catalytic amount of *p*-toluenesulfonic acid was mixed at 78 °C. The progress of the reaction was monitored by TLC. When TLC showed no starting material, reaction was concentrated to half of it. The residue was diluted with EtOAc and extracted with brine. Combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc/ Hexane (1:5, v/v) as the eluent. Compound **2** was obtained as white solid (0.745 g, 62%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.24 (d, *J* = 8.5 Hz, 2H), 7.65 (t, *J*= 7.4 Hz, 1H), 7.39-7.55 (m, 5H), 7.23 (d, *J*= 8.0 Hz, 1H), 5.48 (s, 1H), 3.37 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.1, 151.0, 140.0, 133.6, 130.1, 129.5, 129.3, 128.6, 124.2, 121.7, 120.2, 102.2, 52.5ppm.

MS (TOF- ESI): m/z: Calcd for $C_{16}H_{16}O_4$: 295.09408 $[M+Na]^+$, Found: 295.09078 $[M+ Na]^+$, Δ= 11.18 ppm.

Synthesis of dimethyl 1-methoxy-1-(3-benzyloxyphenyl) methyl phosphonate *(3)*



2 **3**

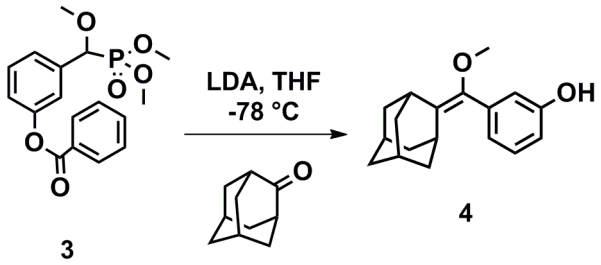
Trimethyl phosphite (0.3 mL, 2.58 mmol) was added to the solution of compound **2** (0.5 g, 1.84 mmol) in DCM at -78 °C under Ar. 15 min later, $TiCl_4$ (0.3 mL, 2.58 mmol) was added dropwise to the reaction mixture at -78 °C. The mixture was stirred for 30 min before allowing it to room temperature and stirred at room temperature for further 1 hour. After the addition of aqueous methanol (2:1), reaction mixture was diluted with DCM and extracted first with saturated solution of $NaHCO_3$ then with brine. Combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc as the eluent. Compound **3** was obtained as white solid (0.583 g, 91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.22 (d, *J*=8.3 Hz, 2H), 7.66-7.68 (m, 1H), 7.52-7.55 (m, 2H), 7.48 (t, *J*= 7.9 Hz, 1H), 7.38 (d, *J*= 7.7 Hz, 1h), 7.34 (s, 1H), 7.24 (d, *J*=8.0 Hz, 1H), 4.60 (d, *J*=15.8 Hz, 1H), 3.74 (dd, *J*=7.1 Hz, 6H), 3.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) *δ* 165.0, 151.19, 151.16, 136.1, 133.6, 130.1, 129.6, 129.5, 128.6, 125.4, 125.3, 121.97, 121.94, 121.19, 121.14, 80.7, 79.0, 59.0, 58.8, 53.98, 53.92, 53.8, 53.7 ppm.

MS (TOF- ESI): m/z: Calcd for $C_{19}H_{17}O_6P$: 373.07657 $[M+ Na]^+$, Found: 373.07657 $[M+ Na]^+$, Δ=12.27 ppm.

Synthesis of 1-(2-adamatylidene)-1-methoxy-1-(3-hydroxyphenyl) methane *(4)*



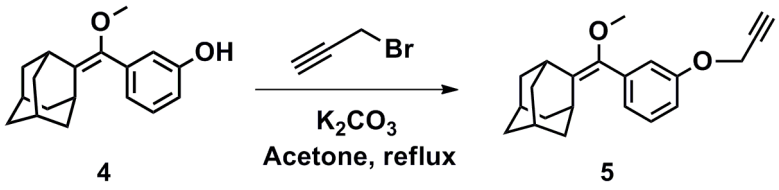
Lithiumdiisopropyl amide (1.8 mL, 3.07 mmol) was added dropwise to the reaction mixture of compound **3** (0.43 g, 1.23 mmol) dissolved in 1 mL dry THF at -78 °C under Ar. After stirring of the reaction mixture for 45 min, 2-adamantanone (0.166 g, 1.11 mmol) dissolved in dry THF was added dropwise to the reaction mixture at -78 °C under Ar. Reaction was left to stir at room temperature overnight. After pouring it into phosphate buffer (0.2M, pH 7), it was extracted with EtOAc. Combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc/ Hexane (1:5, v/v) as the eluent. Compound **4** was obtained as white solid (0.312 g, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.23 (t, *J*= 7.8 Hz, 1H), 6.88-6.91 (m, 2H), 6.80-6.83 (m, 1H), 6.11 (s, br, 1H), 3.36 (s, 3H), 3.27 (s, 1H), 2.68 (s, 1H), 1.80-1.98 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 155.8, 142.8, 136.7, 132.4, 129.1, 121.8, 115.9, 114.6, 57.7, 39.1, 39.0, 37.1, 32.2, 30.3, 28.2.

MS (TOF- ESI): m/z: Calcd for $C_{18}H_{22}O_2$: 271.16926 $[M+H]^+$, Found: 271.16357 $[M+H]^+$, Δ=13.59 ppm.

Synthesis of Compound *(5)*



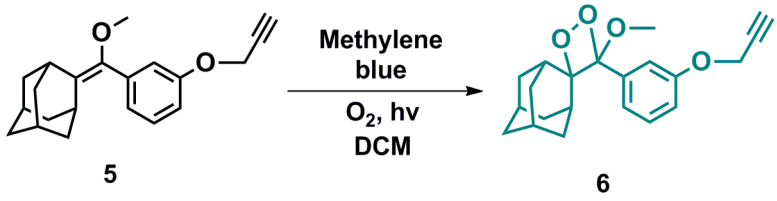
K_2CO_3 (0.107 g, 0.78 mmol) was added to the reaction mixture of compound **4** (0.07 g, 0.26 mmol) and propargyl bromide (45 µL, 0.52 mmol) dissolved in 5 ml acetone. After the addition of catalytic amount of KI, reaction mixture was refluxed at 65 °C. The progress of the reaction was monitored by TLC. When TLC showed no starting material, the reaction was extracted with water (3x100 mL) and combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc / Hexane (1:5, v/v) as the eluent. Compound **5** was obtained as colorless solid (0.075 g, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.29 (td, *J*=8.1, 1.1 Hz, 1H), 6.99-6.97 (m, 2H), 6.94-6.91 (m, 1H), 4.72 (s, 2H), 3.32 (s, 1H), 3.28 (s, 1H), 2.65 (s, 1H), 2.55-2.54 (m, 1H), 2.00-1.81 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 157.3, 143.2, 136.9, 131.7, 128.9, 122.7, 115.6, 114.0, 75.5, 57.7, 55.7, 39.25, 39.07, 37.2, 32.2, 30.2, 28.3.

MS (TOF- ESI): m/z: Calcd for $C_{21}H_{24}O_2$: 309.18491 $[M+H]^+$, Found: 309.18983 $[M+H]^+$, Δ=-1.68 ppm.

Synthesis of Compound *(6)*



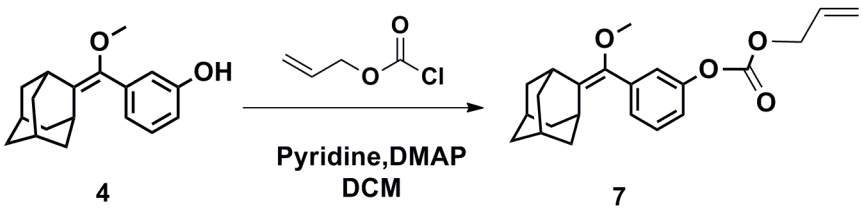
5 6

Compound **5** (0.10 g, 0.32 mmol,) was dissolved in DCM. Methylene blue (5 mg) was added to the reaction mixture which was irradiated while oxygen gas was passing through it. The progress of the reaction was monitored by TLC. When TLC showed no starting material, the mixture was concentrated under vacuo and the residue was subjected to the silica gel flash column chromatography by using DCM as the eluent. Compound **6** was obtained as white solid (0.108 g, 98%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37-7.13 (br, m, 3H), 7.05-7.02 (m, 1H), 4.74 (s, 2H), 3.24 (s, 3H), 3.04 (s, 1H), 2.52 (s, 1H), 2.22 (s, 1H), 1.92-1.01 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 157.5, 136.3, 129.3, 122.8, 121.3, 120.2, 119.1, 116.2, 111.9, 95.4, 75.7, 55.8, 49.9, 36.4, 34.7, 33.1, 32.9, 32.3, 31.6, 31.5, 26.0, 25.9.

Synthesis of Compound (*7*)



4 7

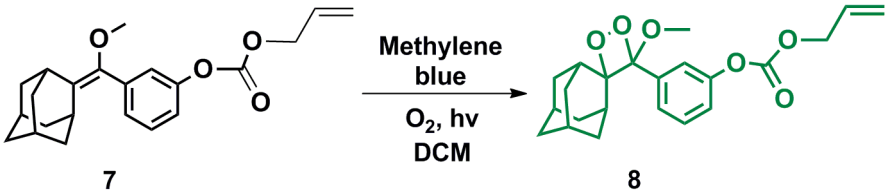
Pyridine (56 µL, 0.7 mmol) was added to the reaction mixture of compound **4** (0.135 g, 0.5 mmol) dissolved in DCM and the reaction mixture was stirred at room temperature for 10 min. After the addition of catalytic amount of DMAP, allyl chloroformate (0.072 g, 0.6 mmol) dissolved in DCM was added dropwise to the reaction mixture while it was kept at 0 °C and left to stir at room temperature overnight. When TLC shows no starting material, the reaction mixture was concentrated under vacuo and crude product was subjected to the flash column chromatography by using EtOAc/Hexane (1:5, v/v) as the eluent. Compound **7** was obtained as colorless solid (0.15 g, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.37 (t, *J*=7.8 Hz, 1H), 7.22 (d, *J*=7.6 Hz, 1H), 7.16 (s, 1H), 7.12 (d, *J*=8.1 Hz, 1H), 6.07-5.99 (m, 1H), 5.45 (d, *J*=14.4 Hz, 1H), 5.34 (d, *J*= 9.2 Hz, 1H), 4.77 (m, 2H), 3.32 (s, 3H), 3.27 (s, 1H), 2.68 (s, 1H), 2.00-1.81 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 153.4, 150.9, 142.5, 137.1, 132.6, 131.1, 128.9, 126.9, 121.7, 119.8, 119.4, 69.1, 57.8, 39.1, 39.0, 37.1, 32.1, 30.2, 26.2.

MS (TOF- ESI): m/z: Calcd for $C_{22}H_{26}O_4$: 355.19039 $[M+H]^+$, Found: 355.19886 $[M+H]^+$, Δ=-1. 52 ppm.

Synthesis of Compound *(8)*



7 8

Compound **7** (0.12 g, 0.34 mmol,) was dissolved in DCM. Methylene blue (5 mg) was added to the reaction mixture which was irradiated while oxygen gas was passing through it. The progress of the reaction was monitored by TLC. When TLC showed no starting material, the mixture was concentrated under vacuo and the residue was subjected to the silica gel flash column chromatography by using DCM as the eluent. Compound **8** was obtained as white solid (0.124 g, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.46 (br, m, 3H), 7.25 (dd, *J*= 9.1, 2.40 Hz, 1H), 6.06-5.96 (m, 1H), 5.47-5.41 (m, 1H), 5.36-5.33 (m, 1H), 4.76 (d, *J*= 5.8 Hz, 2H), 3.23 (s, 3H), 3.04 (s, 1H), 2.15 (s, 1H), 1.82-0.99 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ_C 153.2, 151.1, 136.6, 131.0, 129.3, 127.2, 125.6, 122.3, 122.0, 119.5, 117.5, 95.3, 69.2, 49.9, 36.3, 34.7, 33.1, 32.8, 32.2, 31.7, 31.5, 26.0, 25.8.

Chemiluminescence Spectra

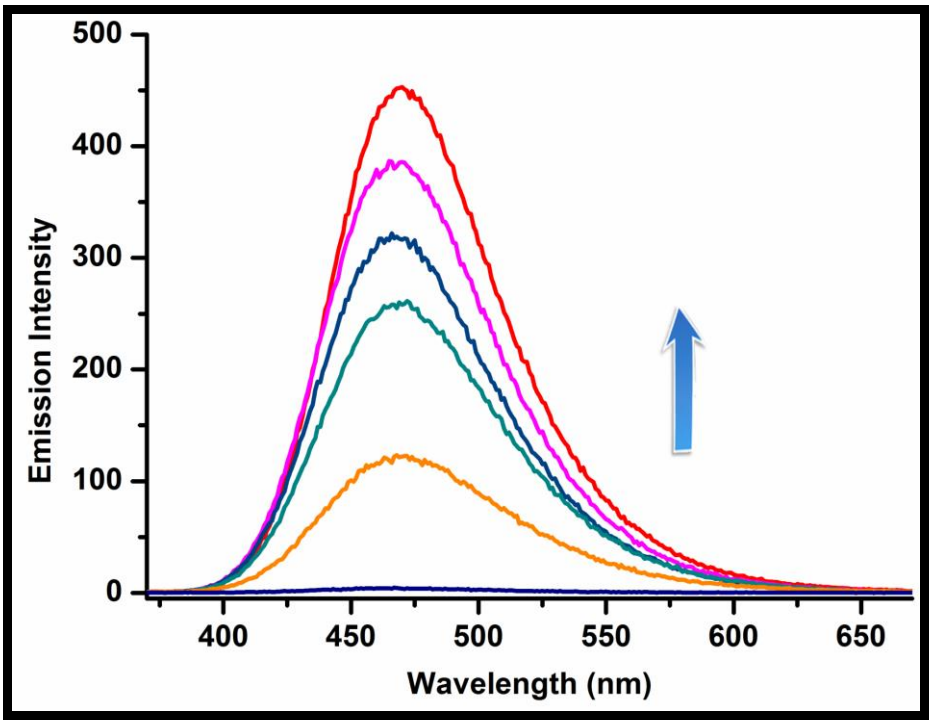


Figure S1. Chemiluminescence Spectra of Dioxetane **6** (200 µM) in the presence of increasing concentrations of $PdCl_2$ (concentrations: 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 mM) in DMSO-H_2O (95:5, v/v) solution with Na_2CO_3-$NaHCO_3$ Buffer (50 mM, pH: 9.0) involving PPh_3 (1.0 mM) at 70°C.

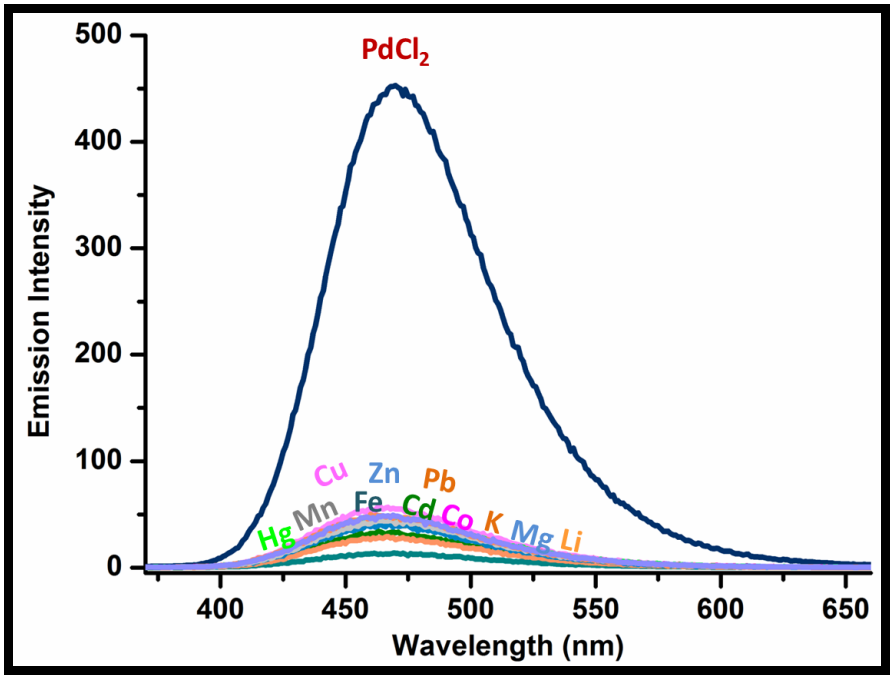


Figure S2. Chemiluminescence Emission Intensity of Dioxetane **6** (200 µM) upon addition of different metal ions in DMSO-H_2O (95:5, v/v) solution with Na_2CO_3-$NaHCO_3$ Buffer (50 mM, pH: 9.0) involving PPh_3 (1.0 mM) at 70°C.

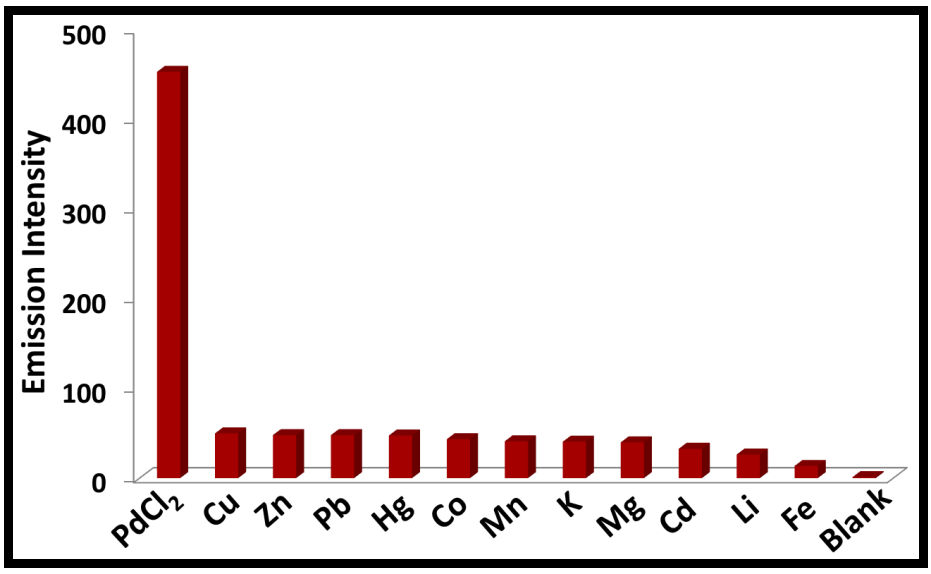


Figure S3. Chemiluminescence Emission Intensity of Dioxetane **6** (200 µM) upon addition of different metal ions in DMSO-H_2O (95:5, v/v) solution with Na_2CO_3-$NaHCO_3$ Buffer (50 mM, pH: 9.0) involving PPh_3 (1.0 mM) at 70°C.

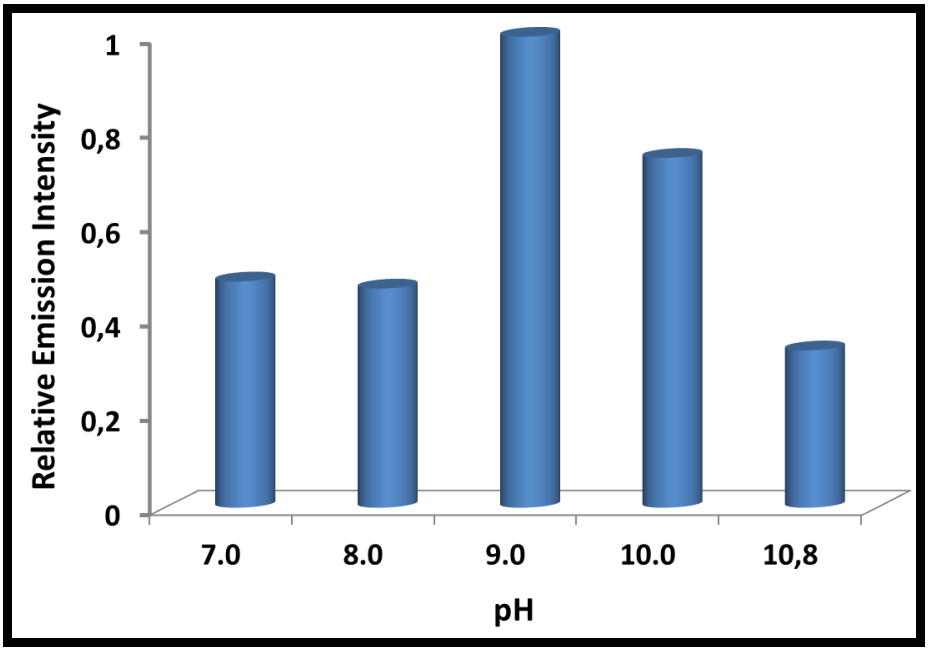


Figure S4. Chemiluminescence Spectra of pH dependent deallylation of Dioxetane **6** (200 µM) in the presence of $PdCl_2$ (0.4 mM), PPh_3 (1.0 mM) in DMSO-H_2O (95:5, v/v) solution with Kpi Buffer (50 mM for pH: 7.0, 8.0) (Na_2CO_3-$NaHCO_3$ Buffer (50mM for pH: 9.0-10.8) involving PPh_3 (1.0 mM) at 70°C

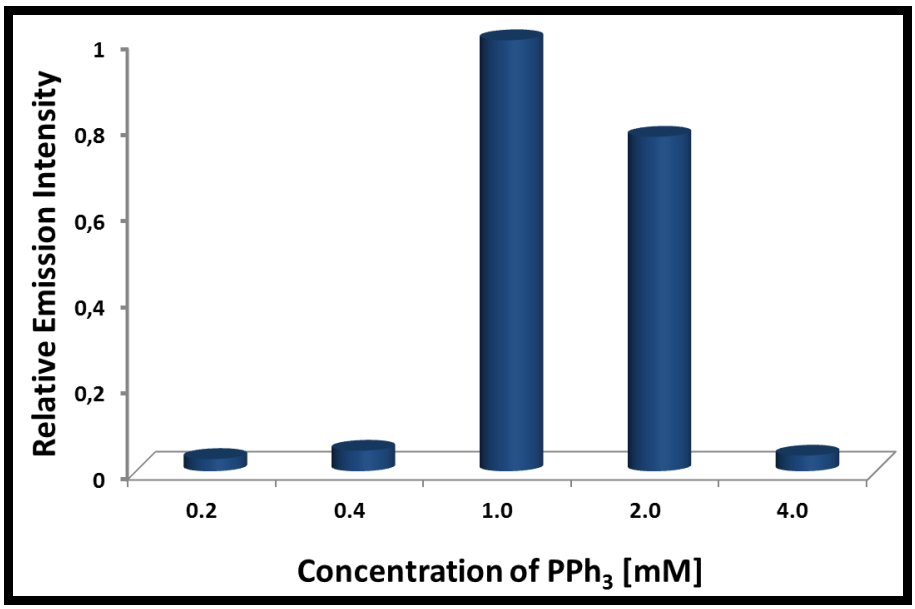


Figure S5. Chemiluminescence Spectra of pH dependent deallylation of Dioxetane **6** (200 µM) in the presence of varying concentrations of PPH_3 in DMSO-H_2O (95:5, v/v) solution with Na_2CO_3-$NaHCO_3$ Buffer (50 mM, pH: 9.0) involving $PdCl_2$ (0.4 mM), at 70°C.

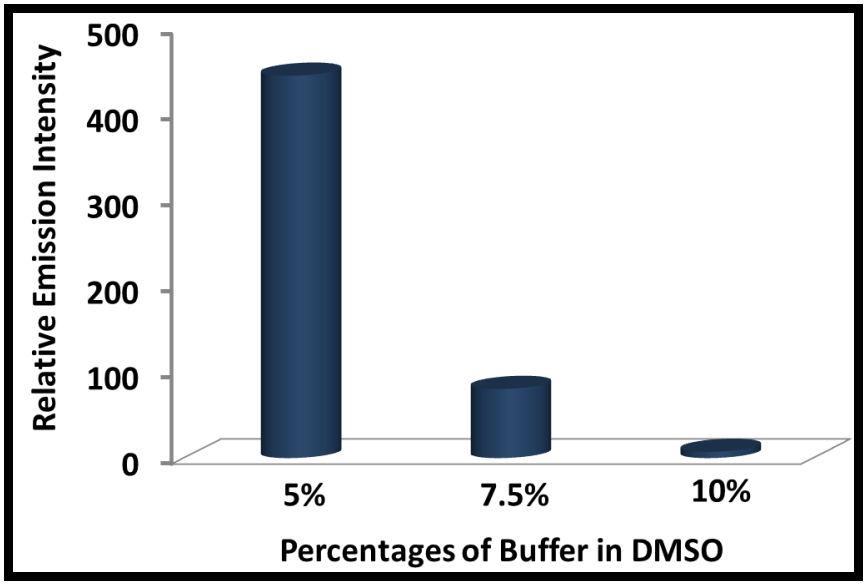


Figure S6. Chemiluminescence Intensity of Dioxetane **6** (200 µM) at diffrent percentages of buffer (Na_2CO_3-$NaHCO_3$ Buffer, 50 mM, pH: 9.0) involving PdCl2 (0.4 mM), PPh_3 (1.0 mM) at 70°C.

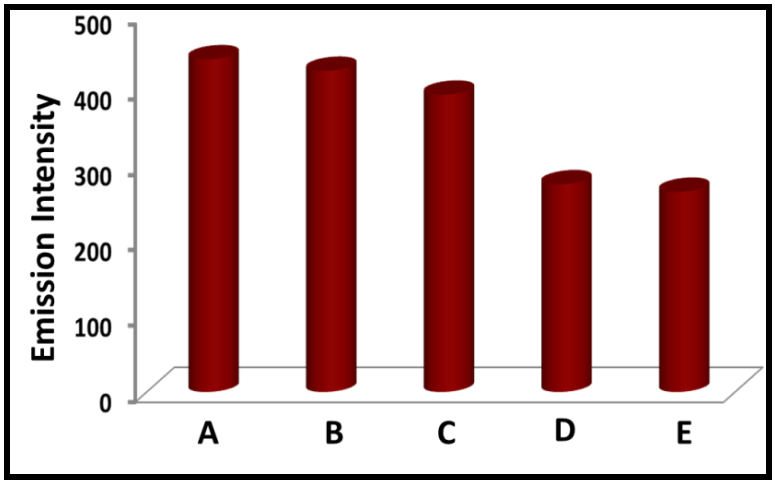


Figure S7. Chemiluminogenic reponse of the probe **6** (200µM) towards various Pd species A= $PdCl_2$, B= Na_2PdCl_4, C= Na_2PdCl_6, D=$Pd(OAc)_2$, E=$Pd(PPh_3)_4$ in Na_2CO_3-$NaHCO_3$ buffer, 50 mM, pH: 9.0) involving $PdCl_2$ (0.4mM), PPh_3 (1.0 mM) at 70°C.

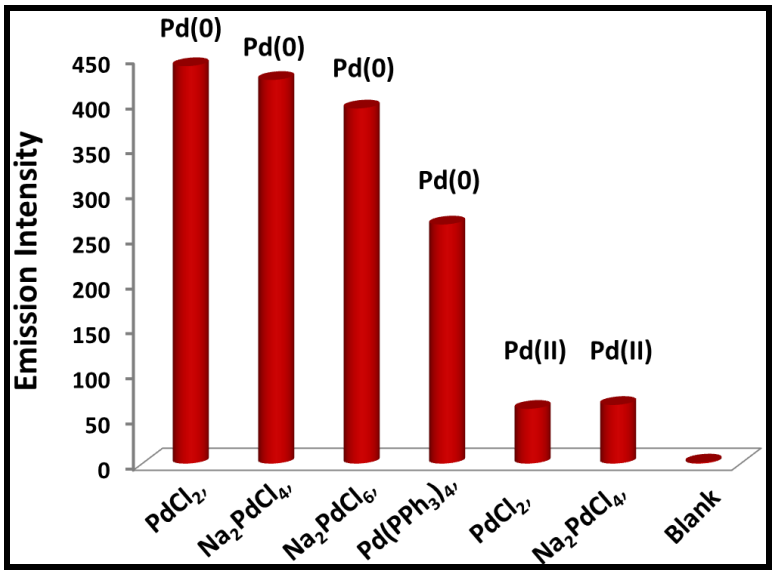


Figure S8. Chemiluminogenic response of the probe **6** (200 μM) towards various Pd species $PdCl_2$, Na_2PdCl_4, Na_2PdCl_6, $Pd(OAc)_2$, $Pd(PPh_3)_4$ with different oxidation states in Na_2CO_3-$NaHCO_3$ buffer, 50 mM, pH: 9.0, each with 1.0 mM PPh_3 and Pd source (0.4 mM) at 70°C. Last two bars before the blank data, correspond to emission signals in response Pd(II) species without any added PPh_3.

Detection Limit Measurements

The detection limit for probe and reference compound was calculated based on chemiluminescence titration. In order to determine the S/N ratio, the chemiluminescence emission intensity of the blanks without Pd was measured 10 times and standard deviation of these blanks was calculated. Chemiluminescence emission intensities of the probe in the presence of Pd ions were plotted as a concentration of Pd in order to determine the slopes. The linear relationship between emission intensity and Pd(0) concentration were determined and detection limits were calculated according to the equation,

$$\text{Detection limit: } 3\sigma/m$$

where σ represents the standard deviation of the blank measurements, m represents the slope between intensity versus sample concentration. Standard Deviation was determined as 0.026268 and the slope of the graph as 885,92 thus in turn, detection limit was calculated according to the equation as 88 μM.

^{1}H-NMR and ^{13}C-NMR Spectra of the Synthesized Compounds

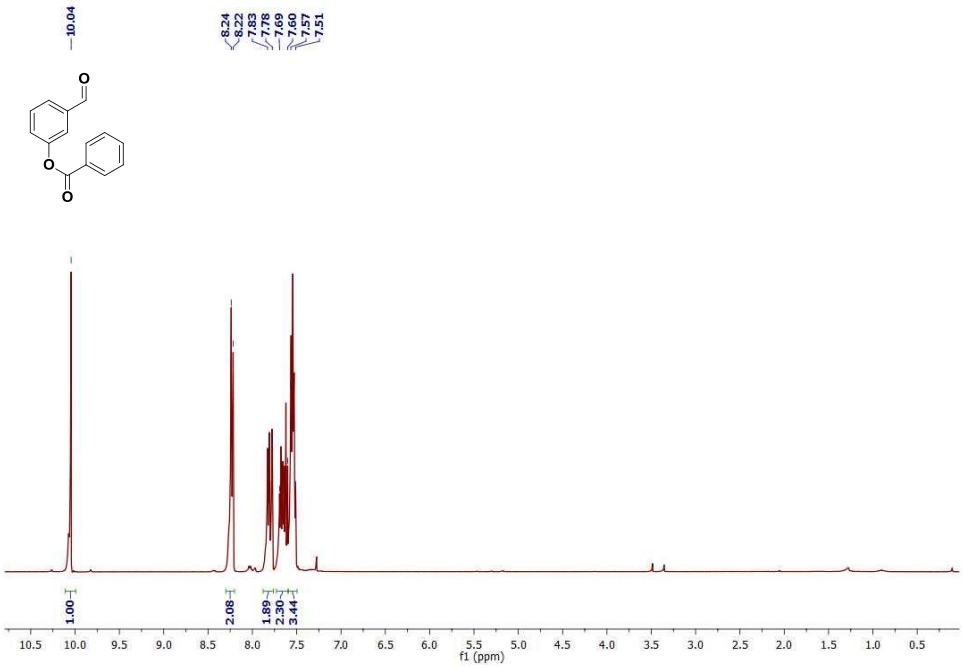


Figure S9. ^{1}H-NMR Spectrum of Compound **1**

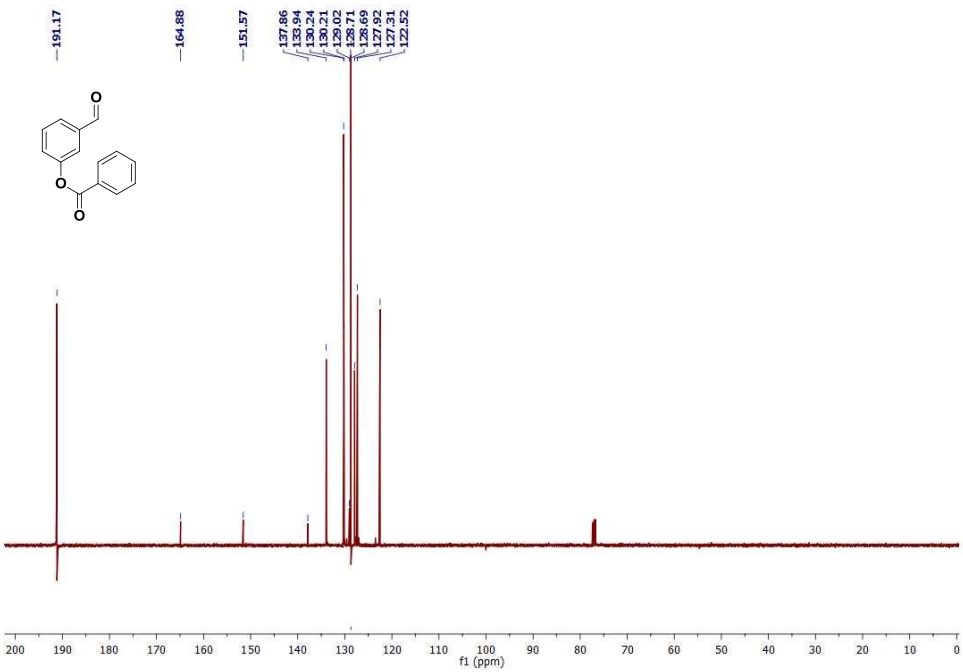


Figure S10. ^{13}C-NMR Spectrum of Compound **1**

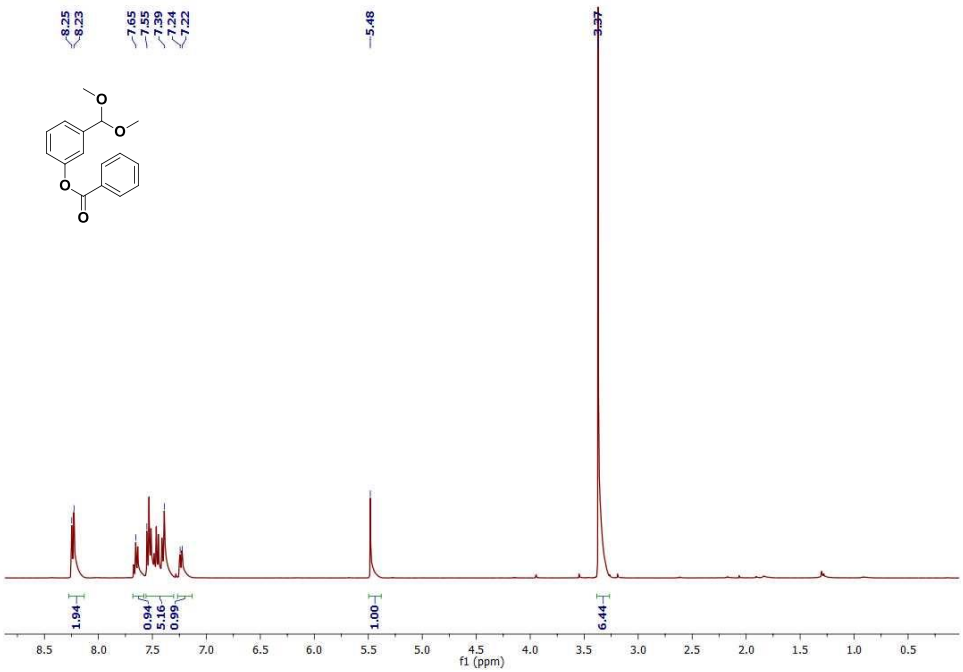


Figure S11. ^{1}H-NMR Spectrum of Compound **2**

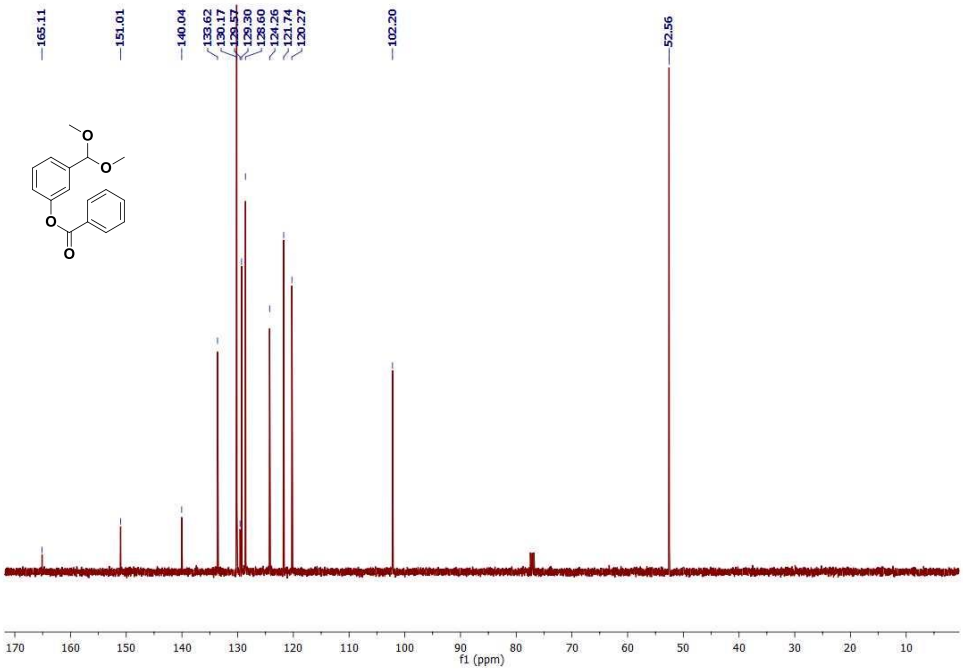


Figure S12. ^{13}C-NMR Spectrum of Compound **2**

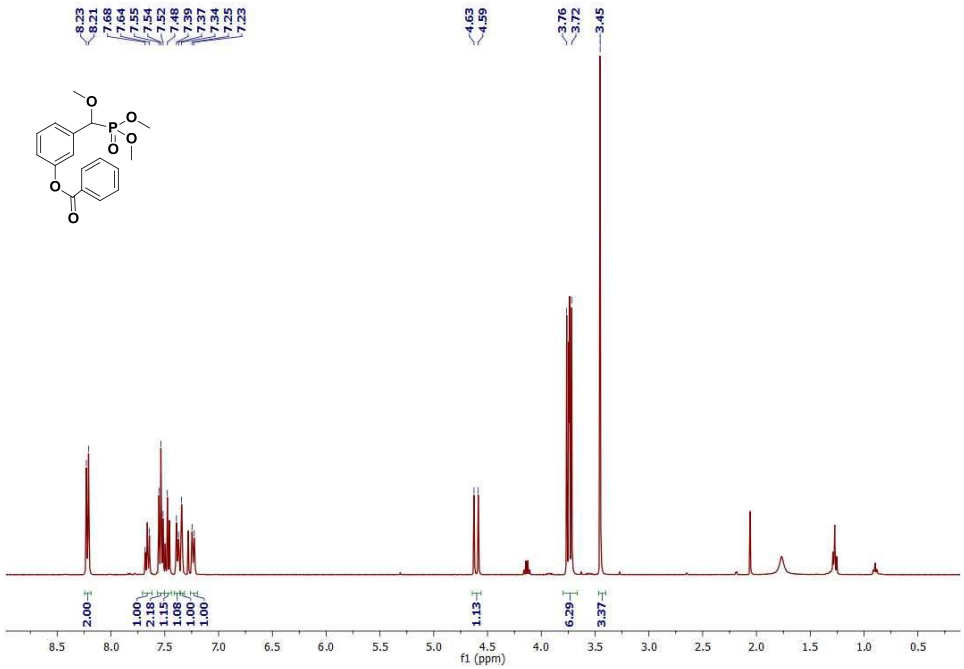


Figure S13. ^{1}H-NMR Spectrum of Compound **3**

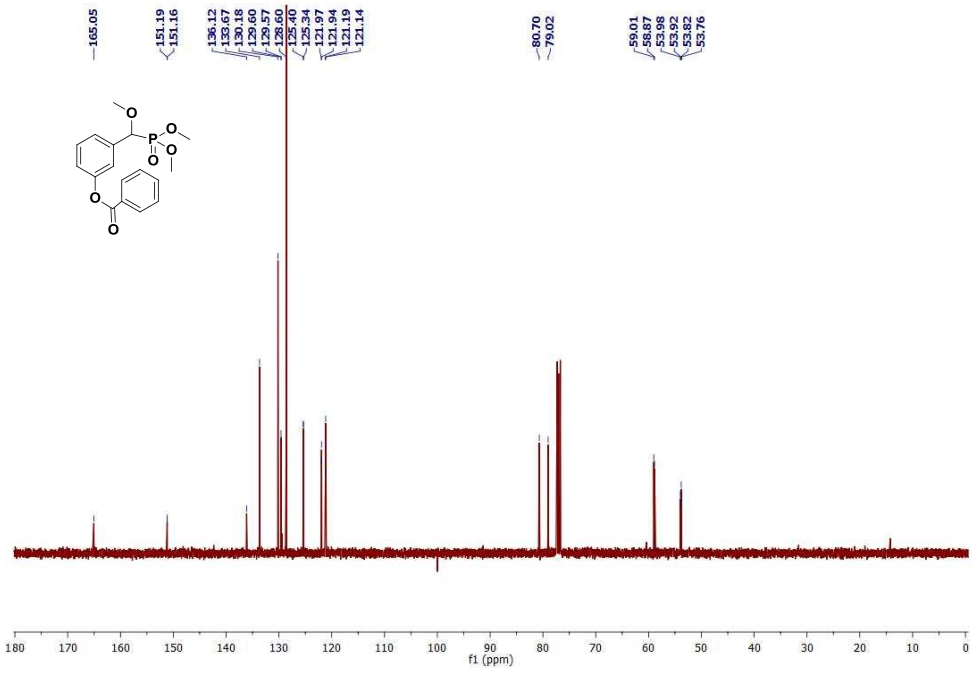


Figure S14. ^{13}C-NMR Spectrum of Compound **3**

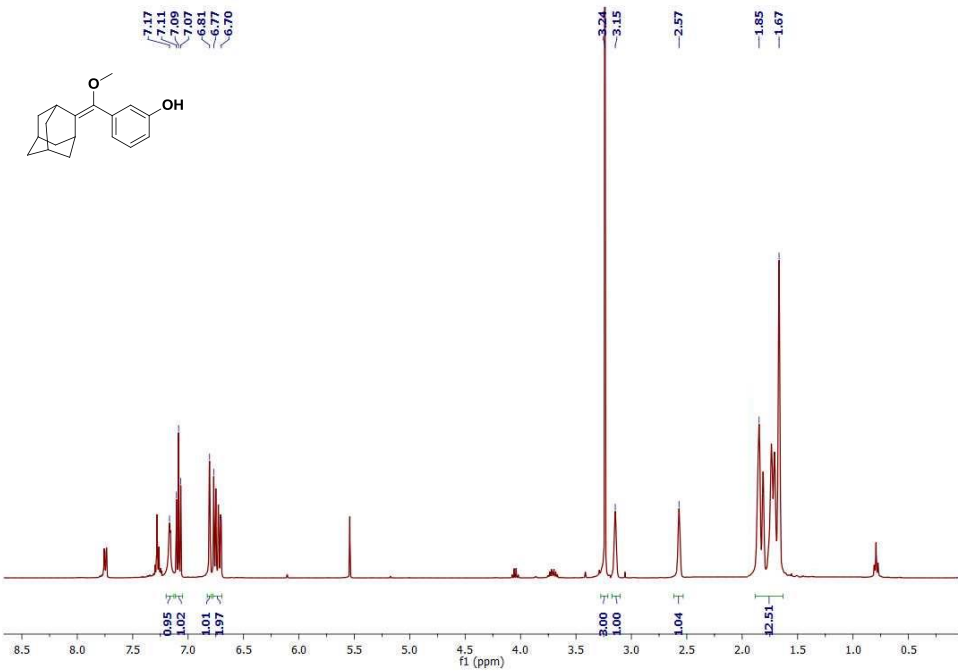


Figure S15. ^{1}H-NMR Spectrum of Compound **4**

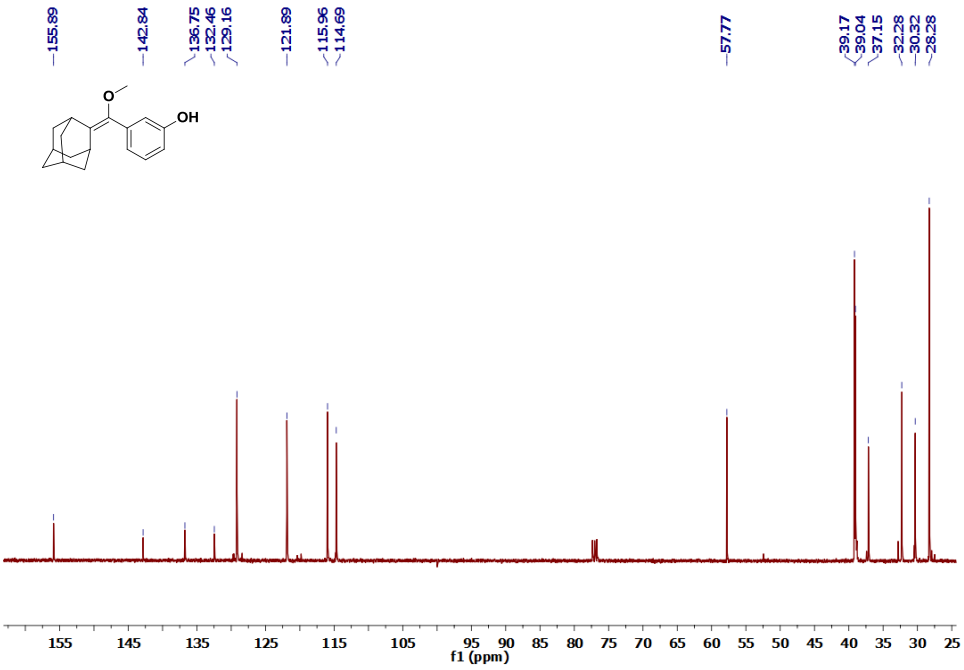


Figure S16. ^{13}C-NMR Spectrum of Compound **4**

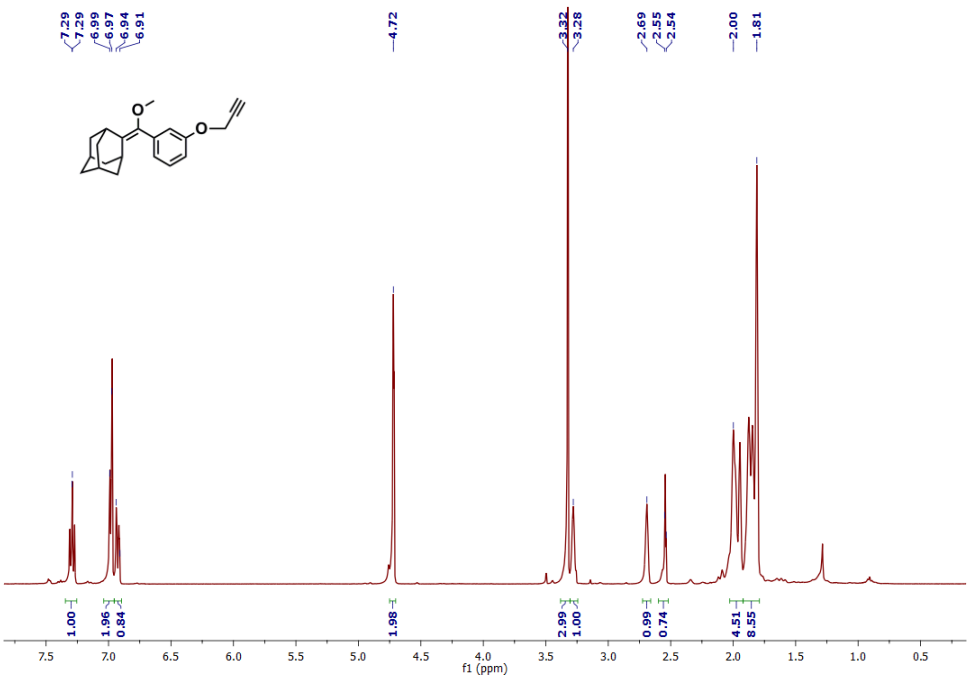


Figure S17. ^{1}H-NMR Spectrum of Compound **5**

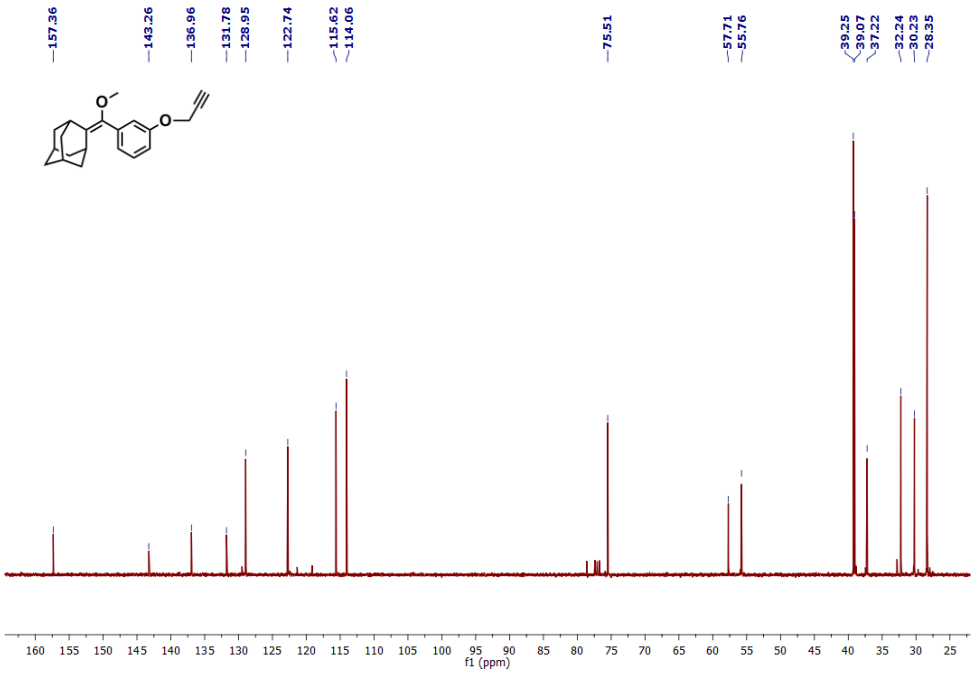


Figure S18. ^{13}C-NMR Spectrum of Compound **5**

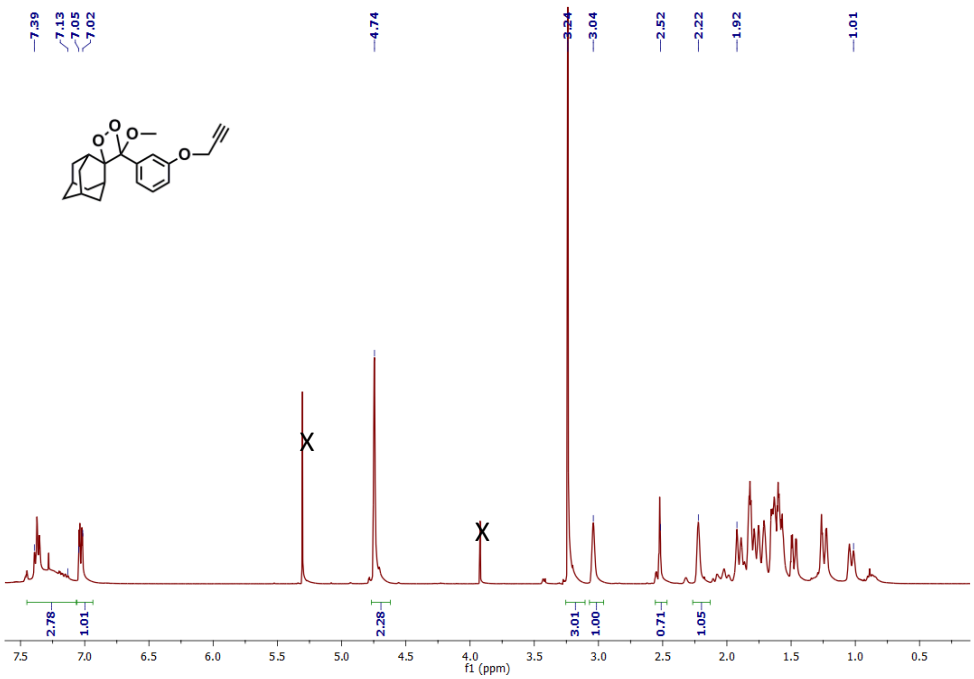


Figure S19. ^{1}H-NMR Spectrum of Compound **6**

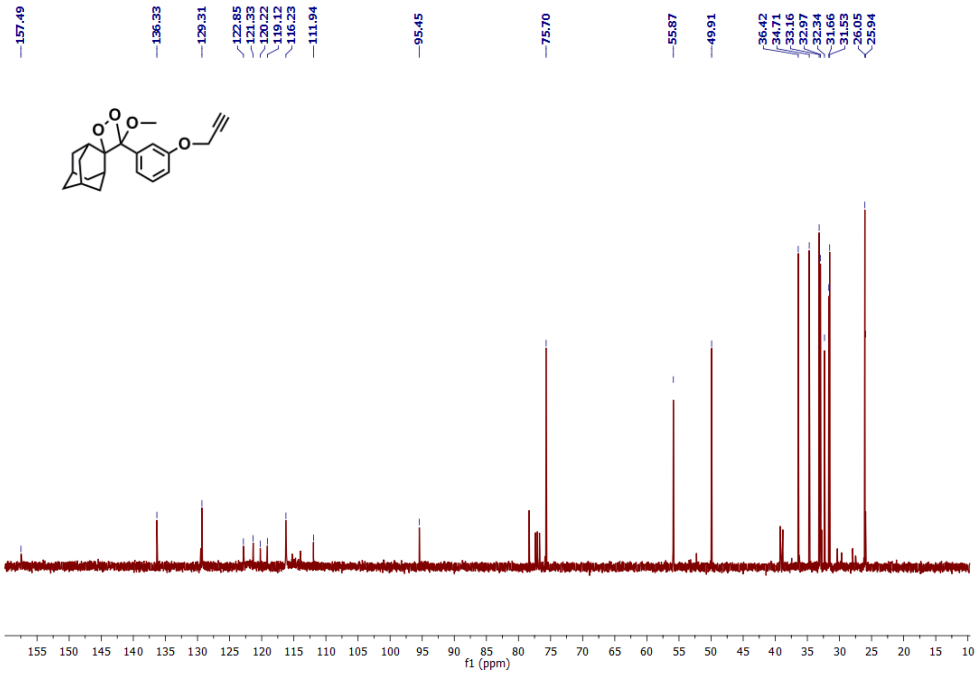


Figure S20. ^{13}C-NMR Spectrum of Compound **6**

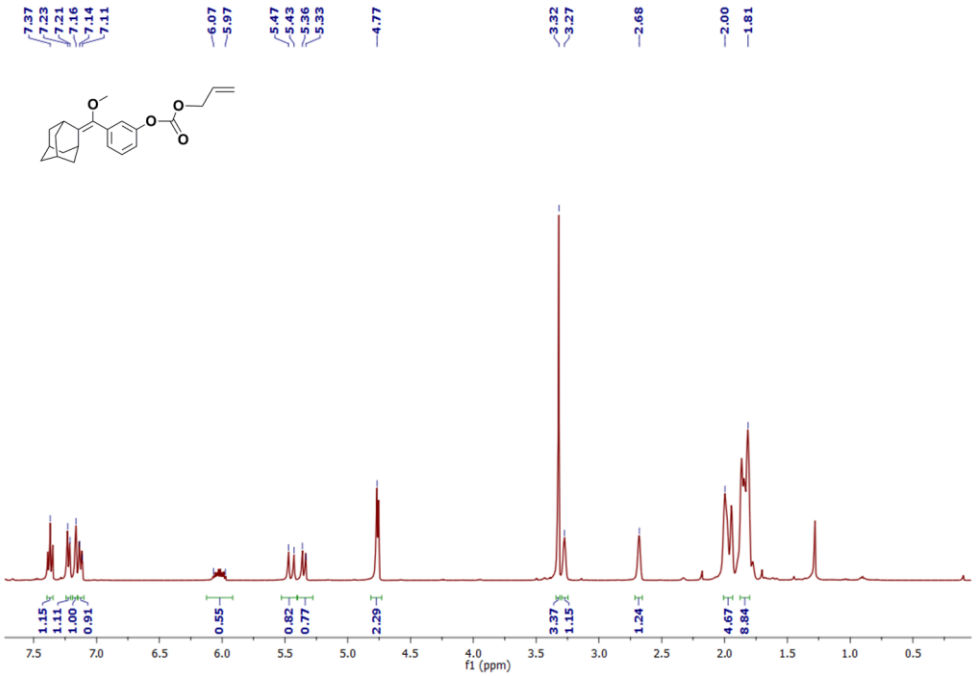


Figure S21. ^{1}H-NMR Spectrum of Compound **7**

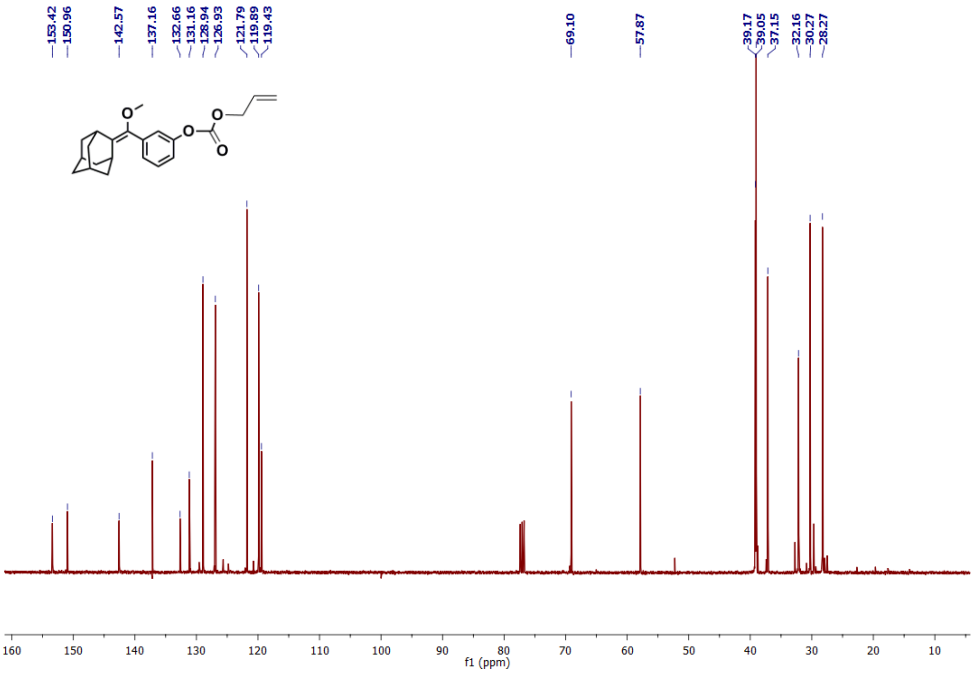


Figure S22. ^{13}C-NMR Spectrum of Compound **7**

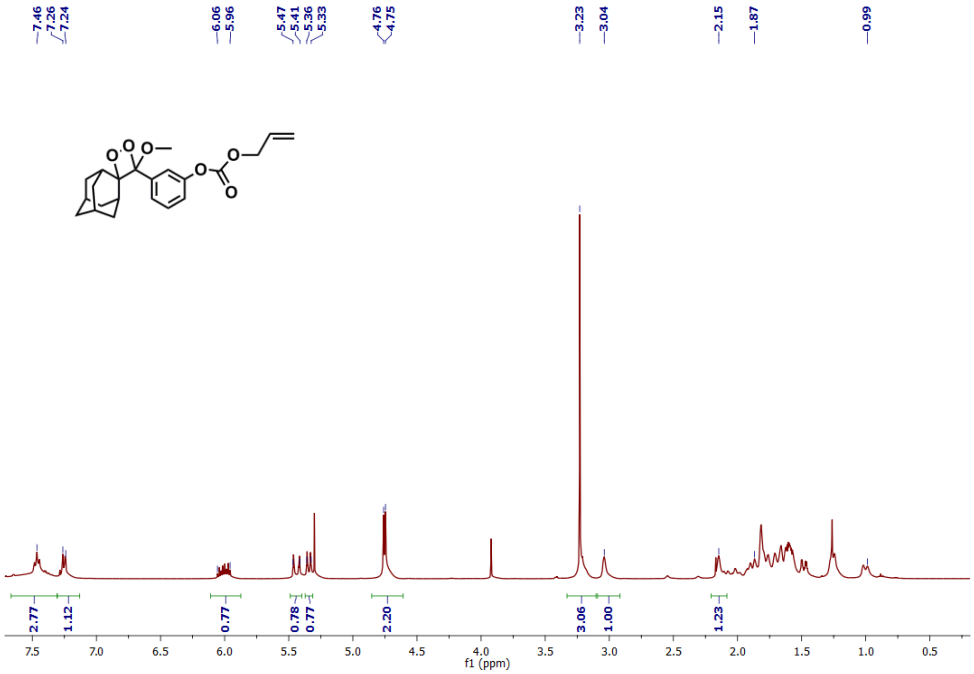


Figure S23. ^{1}H-NMR Spectrum of Compound **8**

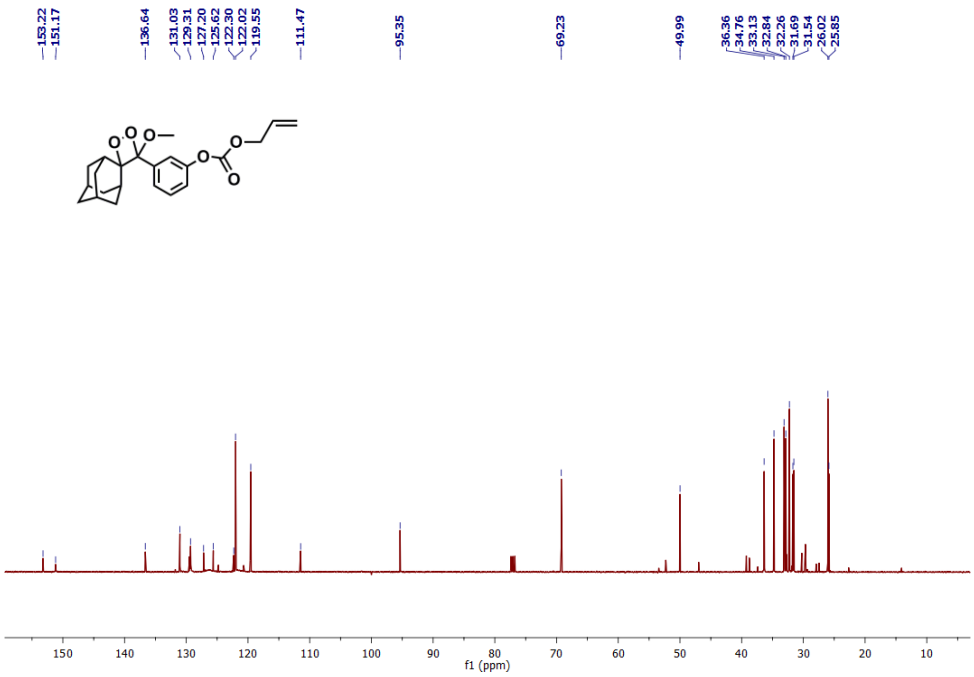


Figure S24. ^{13}C-NMR Spectrum of Compound **8**

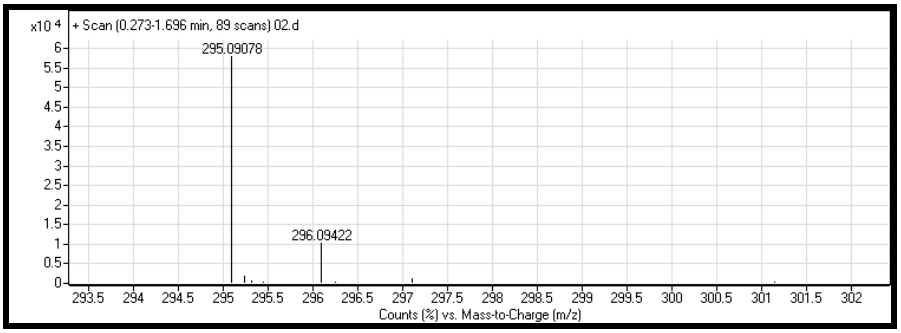


Figure S25. HRMs Spectrum of Compound **2**

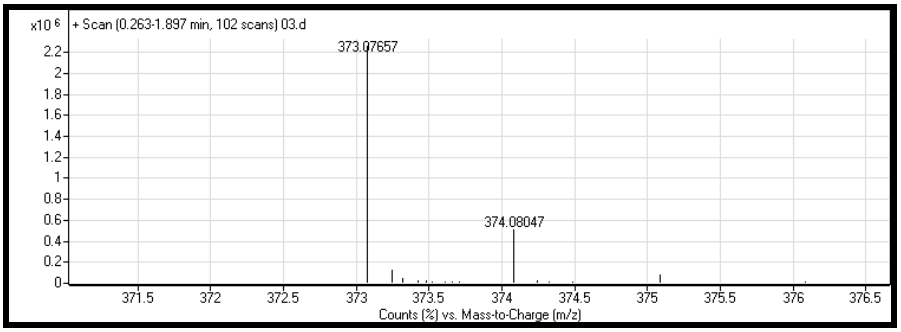


Figure S26. HRMs Spectrum of Compound **3**

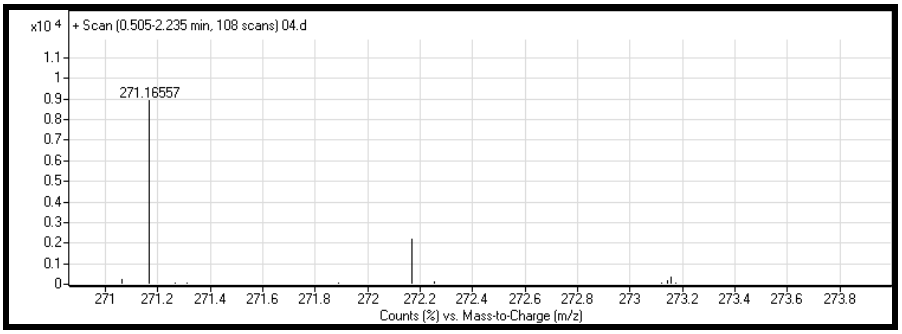


Figure S27. HRMs Spectrum of Compound **4**

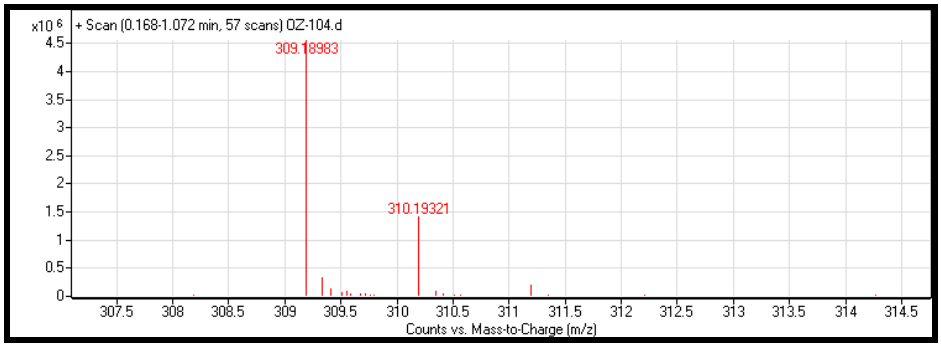


Figure S28. HRMs Spectrum of Compound **5**

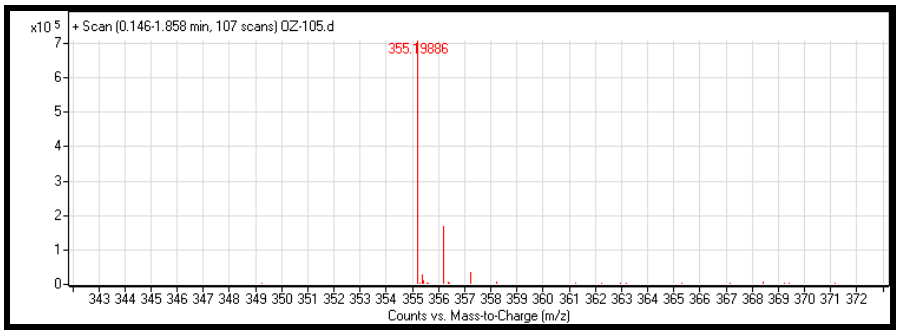


Figure S29. HRMs Spectrum of Compound **7**

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2. B. Liu, H. Wang, T. Wang, Y. Bao, F. Du, J. Tian, Q. Li, R. Bai, *Chem. Commun*., 2012, ***48***, 2867–2869.
3. M. Santra, S.-K. Ko, I. Shin, K. H. Ahn, *Chem. Commun*., 2010, ***46***, 3964–3966.