In Situ Formation of a Biomimetic Lipid Membrane Triggered by an Aggregation-Enhanced Photoligation Chemistry

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1. General materials.

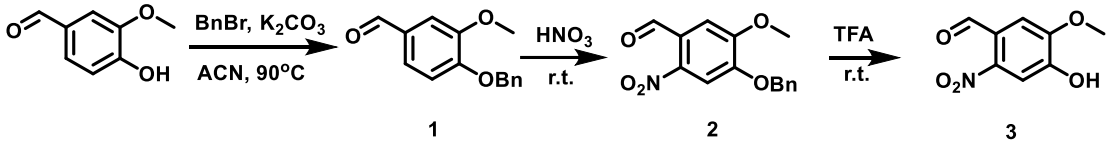
Materials: All synthetic manipulations were performed under an atmosphere of argon gas with magnetic stirring unless otherwise mentioned. Flash chromatography was performed using silica gel (200–300 mesh) as the stationary phase. All reactants and solvents were purchased from commercial suppliers and used without further purification, unless otherwise noted. Dry dichloromethane (DCM) was distilled from calcium hydride; triethylamine (TEA) was redistilled and stored over KOH pellets prior to use. Lysosphingomyelin (Lyso) was purchased from Avanti Polar Lipids and was used without further purification. Glucose oxidase, Horseradish peroxidase (HRP) and Amplex Red were purchased from Life Technologies. Alpha-hemolysin (α-HL), BSA and amino acids were purchased from Sigma Aldrich.

Characterizations: Proton and carbon magnetic resonance spectra (^{1}H, ^{13}C NMR) were recorded on a Bruker Avance 400/600 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from the Me_4Si resonance which was used as the internal standard when recording ^{1}H NMR spectra. The electronic spray

ionization (ESI) mass spectra were obtained on a LCT Premier XE mass spectrometer. Absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrometer. Fluorescence measurements were performed on a Varian Cary Eclipses fluorescence spectrometer equipped with a stirrer and a temperature controller (kept at 25 °C unless otherwise noted). The reversed-phase HPLC was monitored on an Agilent 1200 Series using BetaBasic-18 column. Confocal luminescence imaging was performed with an A1R Nikon confocal microscope with 10× or 40× objective lens. TEM measurements were conducted on a JEM 1400/2100 Transmission Electron Microscopy. Unless otherwise stated, the sample for TEM observations was prepared by placing 5 μL vesicular dispersion on copper grids. SEM measurements were conducted on a S-3400N Scanning Electron Microscope. Small angle XRD measurements were conducted on 2550VB Rotating Anode X-ray Powder Diffractometer. Flow cytometric analysis was conducted on Beckman CytoFLEX Flow Cytometer.

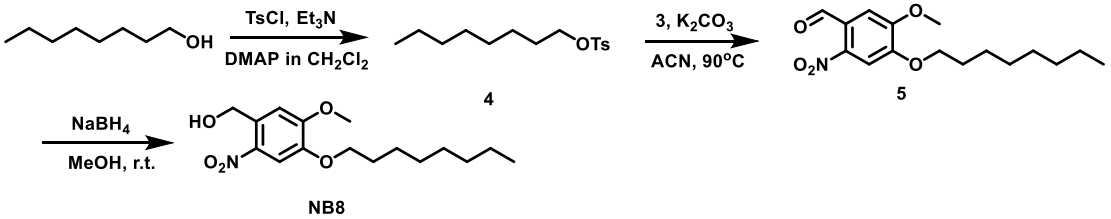
2. Synthesis of compounds.

Synthesis of 3:



Compounds **1**, **2**, **3** was prepared as previously described.[1-3]

Synthesis of NB8:



Compound **4**: To a solution of n-Octanol (3.1 g, 23.8 mmol) and DMAP (10 mg) in DCM (100 mL) was added tosyl chloride (5 g, 26.2 mmol) and triethylamine (7.26 g, 71.4 mmol). The mixture was stirred at room temperature for 12 h. The whole mixture was extracted with DCM and the combined organic layers were dried over Na_2SO_4 and

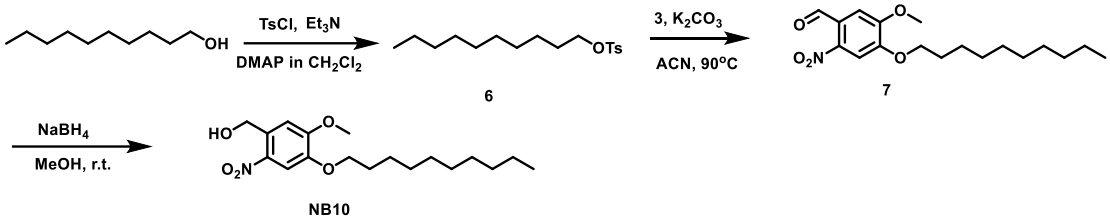
concentrated. The product was purified by silica gel flash column chromatography (DCM/PE=5:1) to afford colorless oil compound **4** (6 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 2H), 7.52 (dd, J = 26.3, 11.9 Hz, 2H), 4.01 (t, J = 6.3 Hz, 2H), 2.42 (s, 3H), 1.69 – 1.45 (m, 2H), 1.37 – 1.02 (m, 10H), 0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.73, 130.22, 127.67, 125.65, 70.92, 31.28, 28.63, 28.35, 28.27, 24.86, 22.18, 21.16, 14.00. MS (ESI): m/z calcd. for $C_{15}H_{24}O_3S$ $[M+Na]^+$: 307.1; found: 307.1.

Compound **5**: To a solution of compound **3** (2.08 g, 10 mmol) in ACN (100 mL) was added K_2CO_3 (2.53 g, 20 mmol) and stirred at room temperature for 15 min. Then compound **4** (1.2 g, 15 mmol) was added and stirred at 90 ºC for 12 h. Then the mixture was cooled to room temperature and K_2CO_3 was filtered. The solvent was removed under vacuum. The product was purified by silica gel flash column chromatography (DCM/MeOH=100:1) to afford yellowish solid compound **5** (3 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.41 (s, 1H), 4.25 – 4.10 (m, 2H), 4.01 (s, 3H), 2.00 – 1.82 (m, 2H), 1.49 (dt, J = 15.1, 6.8 Hz, 2H), 1.41 – 1.20 (m, 8H), 0.89 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.79, 153.43, 152.08, 143.90, 125.20, 109.79, 107.92, 69.99, 56.69, 31.77, 29.24, 29.16, 28.73, 25.82, 22.64, 14.10. MS (ESI): m/z calcd. for $C_{16}H_{23}NO_5$ $[M+Na]^+$: 332.1; found: 332.1.

Compound **NB8**: To a solution of compound **5** (3.0 g, 9.7 mmol) in methanol (100 mL) was added $NaBH_4$ (1.46 g, 38.6 mmol). The mixture was stirred at room temperature for 1 h and acidified with 1 N HCl to pH =6. The volume of the reaction mixture was then reduced to 15 mL under vacuum. The reaction mixture was diluted with brine (100 mL) followed by extraction with DCM (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel flash column chromatography (DCM/MeOH = 100:1) to afford white solid compound **NB8** (2.85 g, 95% yield). ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.65 (s, 1H), 7.38 (s, 1H), 5.57 (t, J = 5.4 Hz, 1H), 4.82 (d, J = 5.4 Hz, 2H), 4.03 (t, J = 6.5 Hz, 2H), 3.91 (s, 3H), 1.89 – 1.62 (m, 2H), 1.40 (dd, J = 13.8, 6.1 Hz, 2H), 1.28 (d, J = 10.4 Hz, 8H), 0.86 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, d_6-DMSO)

δ 154.16, 146.71, 138.80, 134.52, 110.08, 109.15, 69.15, 60.58, 56.51, 31.71, 29.15, 29.13, 28.94, 25.90, 22.56, 14.43. MS (HR-ESI): m/z calcd. for $C_{16}H_{25}NO_5$ $[M+Na]^+$: 334.1630; found: 334.1631.

Synthesis of NB10:

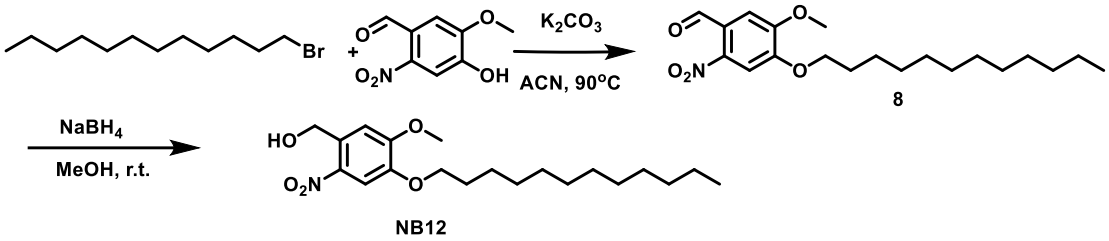


Compound **6** was prepared using a similar method to that described for compound **4** (colorless oil, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.02 (t, J = 6.5 Hz, 2H), 2.45 (s, 3H), 1.71 – 1.52 (m, 2H), 1.43 – 1.10 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.64, 133.22, 129.81, 127.88, 70.73, 31.87, 29.45, 29.39, 29.26, 28.92, 28.80, 25.32, 22.67, 21.63, 14.12. MS (ESI): m/z calcd. for $C_{17}H_{28}O_3S$ $[M+Na]^+$: 335.2; found: 335.2.

Compound **7** was prepared using a similar method to that described for compound **5** (yellowish solid, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.59 (s, 1H), 7.41 (s, 1H), 4.15 (t, J = 6.8 Hz, 2H), 4.01 (s, 3H), 1.99 – 1.82 (m, 2H), 1.56 – 1.43 (m, 2H), 1.42 – 1.13 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.80, 153.44, 152.09, 143.91, 125.20, 109.80, 107.92, 69.99, 56.69, 31.89, 29.52, 29.50, 29.30, 29.28, 28.74, 25.82, 22.68, 14.13. MS(ESI): m/z calcd. for $C_{18}H_{27}NO_5$ $[M+Na]^+$: 360.3; found: 360.3

Compound **NB10** was prepared using a similar method to that described for **NB8** (white solid, 94% yield). ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.65 (s, 1H), 7.38 (s, 1H), 5.57 (t, J = 5.4 Hz, 1H), 4.82 (d, J = 5.4 Hz, 2H), 4.29 – 4.00 (m, 2H), 3.91 (s, 3H), 1.99 – 1.57 (m, 2H), 1.55 – 1.07 (m, 14H), 0.86 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 154.16, 146.71, 138.80, 134.52, 110.08, 109.15, 69.10, 60.58, 56.51, 31.78, 29.46, 29.43, 29.17, 28.94, 25.88, 22.57, 14.43. MS (HR-ESI): m/z calcd. for $C_{18}H_{29}NO_5$ $[M+Na]^+$: 362.1943; found: 362.1942.

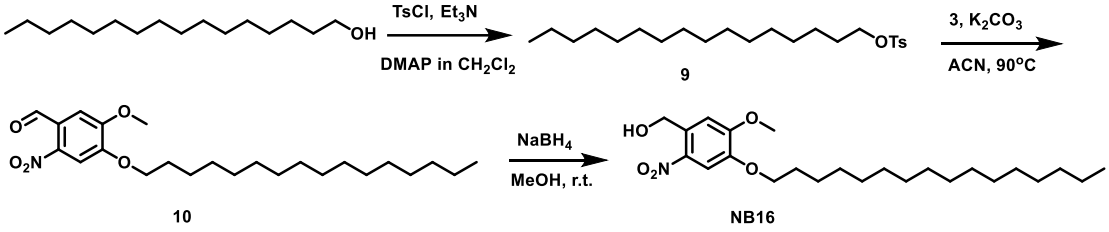
Synthesis of NB12:



Compound **8**: To a solution of 1-Bromododecane (2.98 g, 9.1 mmol) in ACN (100 mL) was added K_2CO_3 (2.53 g, 18.3 mmol) and stirred at room temperature. Then compound **3** (1.2 g, 6 mmol) was added and stirred at 90 °C for 12 h. Then the mixture was cooled to room temperature and K_2CO_3 was filtered. The solvent was removed under vacuum. The product was purified by silica gel flash column chromatography (DCM/MeOH = 100:1) to afford yellowish solid compound **8** (1.75 g, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.59 (s, 1H), 7.41 (s, 1H), 4.15 (t, J = 6.8 Hz, 2H), 4.01 (s, 3H), 1.95 – 1.85 (m, 2H), 1.49 (dt, J = 15.0, 6.8 Hz, 2H), 1.41 – 1.21 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.78, 153.42, 152.08, 143.75, 125.19, 109.71, 107.91, 69.98, 56.68, 31.92, 29.64, 29.57, 29.50, 29.35, 29.28, 28.74, 25.82, 22.69, 14.13. MS (ESI): m/z calcd. for $C_{20}H_{31}NO_5$ $[M+Na]^+$: 388.2; found: 338.2.

Compound **NB12** was prepared using a similar method to that described for **NB8** (white solid, 94% yield). ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.65 (s, 1H), 7.38 (s, 1H), 5.57 (t, J = 5.4 Hz, 1H), 4.82 (d, J = 5.4 Hz, 2H), 4.19 – 3.99 (m, 2H), 3.91 (s, 3H), 1.90 – 1.61 (m, 2H), 1.38 (dd, J = 14.0, 7.0 Hz, 2H), 1.37-1.08 (m, 16H), 0.85 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.16, 146.71, 138.80, 134.52, 110.08, 109.15, 69.14, 60.58, 56.51, 31.77, 29.51, 29.50, 29.46, 29.19, 29.17, 28.93, 25.87, 22.57, 14.42. MS (HR-ESI): m/z calcd. for $C_{20}H_{33}NO_5$ $[M+Na]^+$: 390.2256; found: 390.2255.

Synthesis of NB16:



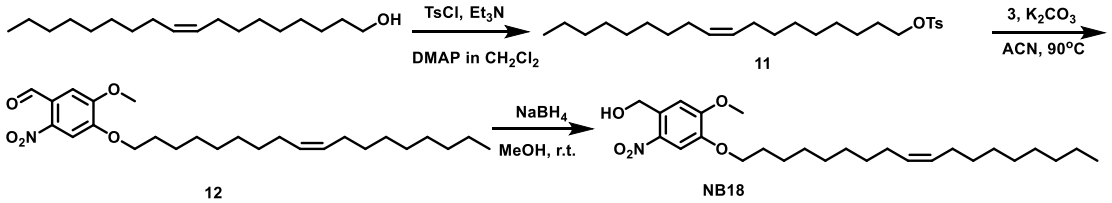
Compound **9** was prepared using a similar method to that described for compound

4 (white solid, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 3.98 (t, J = 6.4 Hz, 2H), 2.44 (s, 3H), 1.63 – 1.48 (m, 2H), 1.46 – 1.01 (m, 26H), 0.87 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.59, 132.71, 129.94, 127.55, 70.63, 31.46, 29.20, 29.18, 29.15, 29.05, 28.96, 28.88, 28.42, 28.29, 24.87, 22.25, 21.26, 14.00. MS (ESI): m/z calcd. for $C_{23}H_{40}O_3S$ $[M+Na]^+$: 419.3; found: 419.3.

Compound **10** was prepared using a similar method to that described for compound **5** (yellowish solid, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 1H), 7.59 (s, 1H), 7.41 (s, 1H), 4.15 (t, J = 6.8 Hz, 2H), 4.01 (s, 3H), 1.95 – 1.85 (m, 2H), 1.54 – 1.44 (m, 2H), 1.36 – 1.24 (m, 24H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.79, 153.43, 152.09, 143.90, 125.20, 109.79, 107.91, 69.99, 56.69, 31.93, 29.71, 29.67, 29.58, 29.51, 29.37, 29.29, 28.74, 25.82, 22.70, 14.14. MS (ESI): m/z calcd. for $C_{24}H_{39}NO_5$ $[M+Na]^+$: 444.3; found: 444.3.

Compound **NB16** was prepared using a similar method to that described for **NB8** (white solid, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.07 (d, J = 58.2 Hz, 1H), 4.95 (s, 2H), 4.07 (t, J = 6.8 Hz, 2H), 3.99 (s, 3H), 1.88 (dd, J = 14.5, 7.3 Hz, 2H), 1.51 – 1.43 (m, 2H), 1.38 – 1.12 (m, 24H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 149.49, 142.83, 135.05, 127.23, 106.46, 104.50, 64.75, 58.22, 51.71, 27.19, 24.96, 24.92, 24.85, 24.79, 24.63, 24.60, 24.13, 21.13, 17.90. MS (HR-ESI): m/z calcd. for $C_{24}H_{41}NO_5$ $[M+Na]^+$: 446.2882; found: 446.2881.

Synthesis of NB18:



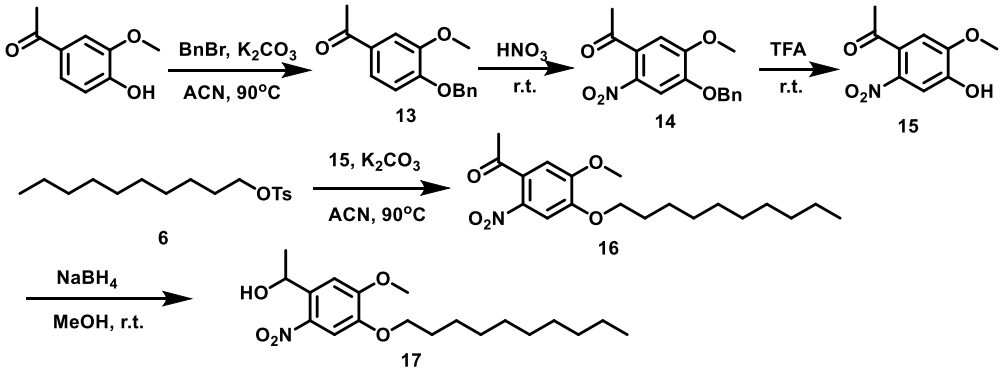
Compound **11** was prepared using a similar method to that described for compound **4** (colorless oil, 90% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 7.77 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 5.48 – 5.17 (m, 2H), 3.99 (t, J = 6.4 Hz, 2H), 2.43 (s, 3H), 2.10 – 1.79 (m, 4H), 1.69 – 1.46 (m, 2H), 1.45 – 1.01 (m, 22H), 0.98 – 0.67 (m, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 146.14, 134.06, 130.94, 130.70, 128.69, 71.96, 32.65,

30.48, 30.41, 30.21, 30.07, 29.99, 29.96, 29.82, 29.51, 29.37, 27.80, 25.96, 23.40, 21.66, 14.42. MS (ESI): m/z calcd. for $C_{25}H_{42}O_3S$ $[M+Na]^+$: 445.3; found: 445.3.

Compound **12** was prepared using a similar method to that described for compound **5** (yellowish oil, 94% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 7.59 (s, 1H), 7.40 (s, 1H), 5.51 – 5.22 (m, 2H), 4.15 (t, J = 6.7 Hz, 2H), 4.01 (s, 3H), 2.20 – 1.78 (m, 6H), 1.59 – 1.44 (m, 2H), 1.44 – 1.16 (m, 20H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.68, 153.39, 152.04, 143.86, 129.98, 129.72, 125.16, 109.74, 107.87, 69.94, 56.64, 31.90, 29.75, 29.72, 29.65, 29.52, 29.39, 29.32, 29.26, 29.19, 28.74, 27.21, 27.17, 25.82, 22.68, 14.11. MS (ESI): m/z calcd. for $C_{26}H_{41}NO_5$ $[M+Na]^+$: 470.3; found: 470.3.

Compound **NB18** was prepared using a similar method to that described for **NB8** (white solid, 94% yield). ^1H NMR (400 MHz, d_6-DMSO) δ 7.64 (s, 1H), 7.38 (s, 1H), 5.58 (t, J = 5.4 Hz, 1H), 5.44 – 5.20 (m, 2H), 4.82 (d, J = 5.3 Hz, 2H), 4.19 – 3.98 (m, 2H), 3.90 (s, 3H), 1.98 (s, 4H), 1.84 – 1.62 (m, 2H), 1.48 – 1.02 (m, 22H), 0.96 – 0.66 (m, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.18, 146.70, 138.58, 134.58, 130.06, 110.04, 109.09, 69.01, 60.59, 56.48, 31.77, 29.58, 29.47, 29.32, 29.19, 29.08, 29.05, 28.95, 27.04, 25.89, 22.57, 14.36. MS (HR-ESI): m/z calcd. for $C_{26}H_{43}NO_5$ $[M+Na]^+$: 472.3039; found: 472.3040.

Synthesis of a control compound 17:



Compound **13**: To a solution of 3-Methoxy-4-hydroxyphenylethanone (10.0 g, 66.0 mmol) in ACN (200 mL) was added BnBr (14.3 g, 92.0 mmol) and K_2CO_3 (11.6 g, 92.0 mmol). The mixture was stirred at 90 °C for 12 h. Then the mixture was cooled to room temperature and K_2CO_3 was filtered. The solvent was removed under vacuum and

colorless oil appeared. The crude product was further purified by recrystallization from ethanol to obtain white solid compound **13** (12.9 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 2.0 Hz, 1H), 7.48 (dd, J = 8.4, 2.0 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.29 (m, 1H), 6.88 (d, J = 8.4 Hz, 1H), 5.20 (s, 2H), 3.92 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.87, 152.40, 149.46, 136.27, 130.68, 128.70, 128.13, 127.22, 123.12, 112.08, 110.48, 70.76, 56.03, 26.22. MS (ESI): m/z: Calcd. For $C_{16}H_{16}O_3$ $[M+H]^+$: 257.1 Found: 257.1.

Compound **14**: Compound **13** (10.0 g, 41 mmol) was added into a concentrated nitric acid (30 mL) at 0 °C. The mixture was stirred at room temperature for 30 min and poured into water. The solid obtained was filtered and dried. The product was further purified by recrystallization from ethanol to obtain yellow solid compound **14** (9.2 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.48 – 7.43 (m, 2H), 7.43 – 7.40 (m, 2H), 7.40 – 7.32 (m, 1H), 6.77 (s, 1H), 5.22 (s, 2H), 3.98 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.14, 154.55, 148.56, 138.28, 135.20, 133.11, 128.86, 128.59, 127.58, 108.82, 108.78, 71.41, 56.69, 30.43. MS (ESI): m/z: Calcd. for $C_{16}H_{15}NO_5$ $[M+H]^+$: 302.1. Found: 302.1.

Compound **15**: Compound **14** (9.0 g, 35 mmol) was dissolved in 100 mL trifluoroacetic acid and the resultant solution was stirred at room temperature for overnight. Trifluoroacetic acid was then evaporated by vacuum and the resulting crude was diluted with ethyl acetate and then basified by aqueous NaOH solution. The pH of the solution was adjusted to 5 by addition of HCl aqueous solution. The whole mixture was extracted with ethyl acetate and the combined organic layers were dried over Na_2SO_4 and concentrated. The product was purified by silica gel flash column chromatography (PE/EA=1:1) to afford yellow solid compound **15** (5.6 g, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 6.80 (s, 1H), 4.01 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.05, 151.02, 146.62, 139.53, 131.92, 110.73, 108.59, 56.76, 30.33. MS (ESI): m/z: Calcd. for $C_9H_9NO_5$ $[M-H]^-$: 210.0. Found: 210.0.

Compound **16**: To a solution of compound **15** (4.2 g, 10 mmol) in ACN (100 mL) was added K_2CO_3 (5.5 g, 20 mmol) and stirred at room temperature for 15 min. Then

compound **6** (9.3 g, 15 mmol) was added and stirred at 90 ºC for 12 h. Then the mixture was cooled to room temperature and K_2CO_3 was filtered. The solvent was removed under vacuum. The product was purified by silica gel flash column chromatography (DCM/MeOH = 100:1) to afford yellowish solid compound **16** (6.0 g, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 6.68 (s, 1H), 4.02 (t, J = 6.7 Hz, 2H), 3.89 (s, 3H), 2.42 (s, 3H), 1.81 (p, J = 6.9 Hz, 2H), 1.44 – 1.35 (m, 2H), 1.34 – 1.13 (m, 12H), 0.85 – 0.76 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.15, 154.25, 149.22, 138.46, 132.52, 108.72, 107.76, 69.74, 56.65, 31.89, 30.39, 29.52, 29.51, 29.30, 28.79, 25.84, 22.68, 14.11. MS (HR-ESI): m/z calcd. for $C_{19}H_{29}NO_5$ $[M+Na]^+$: 374.1940; found: 374.1942.

Compound **17**: To a solution of compound **16** (2.0 g, 9.7 mmol) in methanol (100 mL) was added $NaBH_4$ (0.43 g, 19.4 mmol). The mixture was stirred at room temperature for 1 h and acidified with 1 N HCl to pH = 6. The volume of the reaction mixture was then reduced to 15 mL under vacuum. The reaction mixture was diluted with brine (100 mL) followed by extraction with DCM (3×20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel flash column chromatography (DCM/MeOH = 100:1) to afford white solid compound **17** (1.9 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.21 (s, 1H), 5.47 (q, J = 6.3 Hz, 1H), 3.97 (td, J = 6.9, 1.6 Hz, 2H), 3.90 (s, 3H), 2.23 (s, 1H), 1.83 – 1.74 (m, 2H), 1.48 (d, J = 6.3 Hz, 3H), 1.43 – 1.34 (m, 2H), 1.29 – 1.16 (m, 12H), 0.84 – 0.77 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.07, 147.25, 139.60, 136.57, 108.77, 108.60, 69.50, 65.78, 56.38, 31.90, 29.53, 29.33, 29.31, 28.88, 25.88, 24.24, 22.68, 14.12. MS (HR-ESI): m/z calcd. for $C_{19}H_{31}NO_5$ $[M+Na]^+$: 376.2100; found: 376.2100.

Synthesis of phospholipids Lyso-NB10.

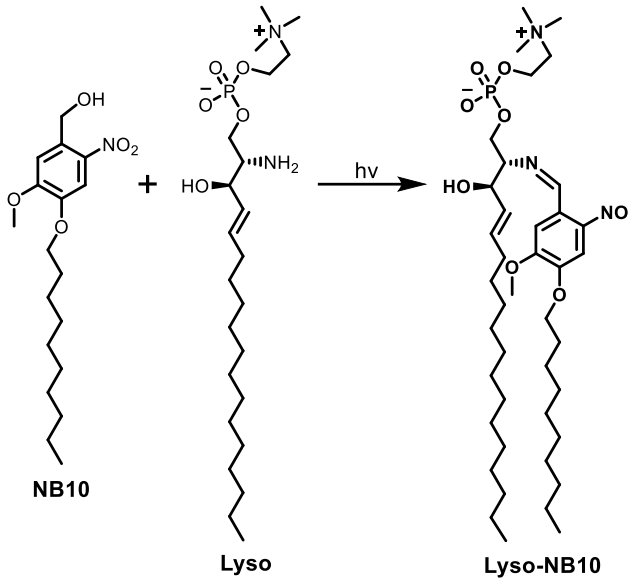


Fig. S1 The synthesis of **Lyso-NB10** from the photoligation of **NB10** and Lyso.

10 mg of **NB10** (1 equiv) and 16.43 mg of lysosphingomyelin (1.2 equiv) were dissolved in 30 mL of ACN-water solution (9/1, v/v). The resulting mixture was magnetically stirred at room temperature and irradiated with a 365 nm light-emitting diode (LED) light source (20 mW cm^{-2}) for 15 min. After 48h stirring at room temperature, the solvent was evaporated and the crude was dissolved in MeOH (5 mL). After filtered using a 0.2 μm syringe-driven filter, the crude solution was purified by HPLC and afforded 15 mg of **Lyso-NB10** as a light yellow solid with a yield of 70% (R_t = 13.5 min, Eclipse XDB-C18 semipreparative column, Eluent: MeOH/H_2O V:V=9:1, 20 min).

^{1}H NMR (600 MHz, *d*$_4$-CD_3OD) δ 7.89 (s, 1H), 6.96 (s, 1H), 6.80 (s, 1H), 5.51 – 5.42 (m, 1H), 5.40 – 5.31 (m, 1H), 5.24 (s, 1H), 4.63 (dt, J = 11.5, 5.9 Hz, 1H), 4.50 (t, J = 8.5 Hz, 1H), 4.31 (ddd, J = 11.2, 5.0, 2.7 Hz, 1H), 4.17 (dd, J = 25.3, 21.6 Hz, 2H), 4.12 – 4.00 (m, 2H), 3.86 (s, 3H), 3.64 (d, J = 6.9 Hz, 1H), 3.56 – 3.52 (m, 2H), 3.15 (s, 9H), 1.87 (dt, J = 14.5, 3.9 Hz, 2H), 1.83 – 1.71 (m, 2H), 1.55 – 1.46 (m, 2H), 1.40 (dd, J = 10.2, 4.9 Hz, 2H), 1.37 – 1.23 (m, 26H), 1.20 – 1.14 (m, 2H), 1.10 – 0.95 (m, 4H), 0.91 (dd, J = 6.9, 1.8 Hz, 6H). ^{13}C NMR (151 MHz, *d*$_4$-CD_3OD) δ 153.24, 149.65, 135.44, 129.45, 128.48, 126.69, 112.99, 110.91, 97.64, 89.81, 71.37, 68.80, 65.99, 62.83, 59.02, 55.21, 53.23, 53.20, 53.18, 31.79, 31.73, 31.69, 29.54, 29.43, 29.40, 29.36,

29.34, 29.25, 29.15, 29.08, 28.93, 28.83, 28.57, 26.71, 25.85, 22.37, 22.35, 13.07, 13.05.

MS (HR-ESI): m/z calcd. for $C_{41}H_{75}N_3O_8$ $[M+H]^+$:768.5292; found:768.5271.

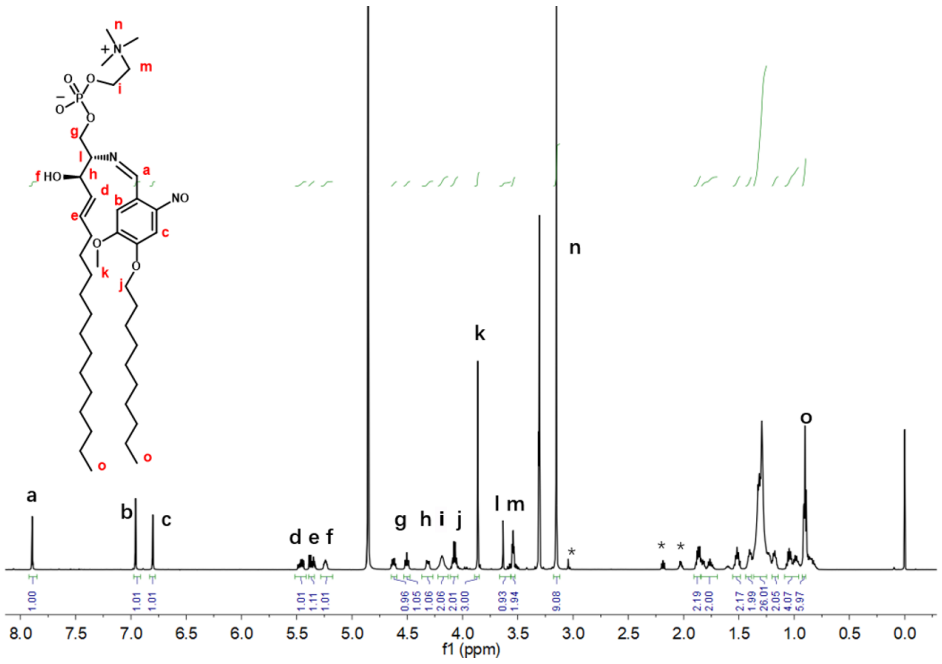


Fig. S2 ^{1}H NMR for the purified **Lyso-NB10** in CD_3OD. * assigned to some impurities.

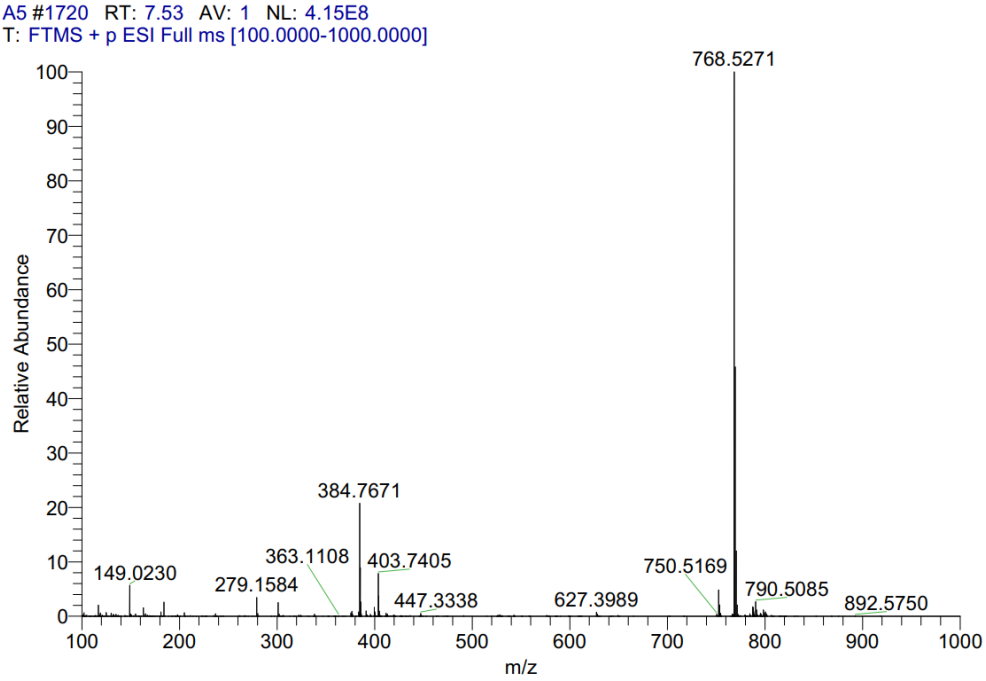


Fig. S3 HRMS for the synthesized **Lyso-NB10**.

3. Photoreaction characterizations.

3.1 UV-vis absorption evolution for NB10 photolysis.

NB10 solution (1×10^{-3} M in CH_3CN/H_2O, V/V=9/1) was irradiated by a LED 365 nm light at 10 mW cm^{-2} in a cuvette with optical path length at 1 mm, and at specific time intervals, the solution was analyzed by UV–vis absorption and HPLC spectra. NMR photolysis analysis was performed by dissolving **NB10** in CD_3CN (1×10^{-3} M), the tracking was similar as that for UV-vis analysis.

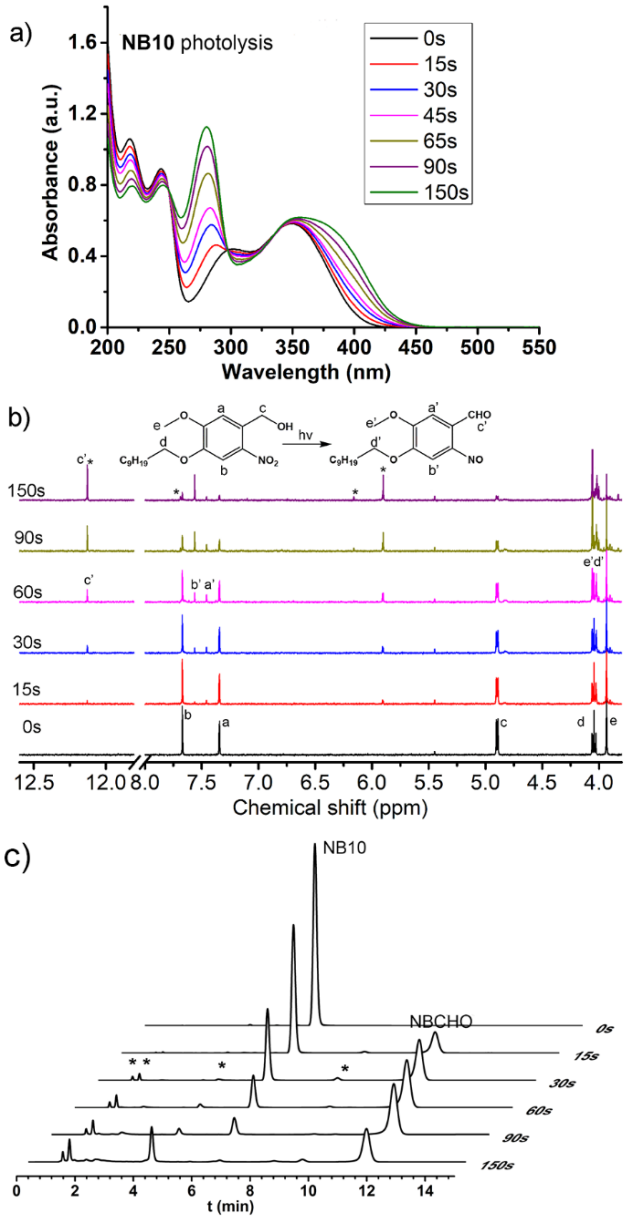


Fig. S4 NB10 photolysis analysis. a) Time-dependent UV-vis spectra for irradiated **NB10** in CH_3CN/H_2O (V/V=9/1) at 1 mM; b) Time-dependent ^1H NMR spectra for irradiated **NB10** in deuterated CH_3CN at 1 mM. c) The corresponding HPLC spectra for **NB10** photolysis. *represents the byproducts from photolysis. A LED 365 nm with intensity of 10 mW cm^{-2} was used for irradiation.

Time-resolved UV-vis absorption, NMR and HPLC spectra confirmed efficient and rapid photolysis and aldehyde generation of **NB10** (**NBCHO**). In the NMR spectra, the signals H_a, H_b, H_c, H_d and H_e assigned to **NB10** decreased in intensity, while a series of new signals $H_{a'}$, $H_{b'}$, $H_{c'}$, $H_{d'}$ and $H_{e'}$ assigned to aldehyde product appeared,[4] which confirmed successful and efficient photolysis and aldehyde generation. In addition, it was found that the yield of **NBCHO** increased first and then decreased with the irradiation time, indicating that **NBCHO** was also photosensitive and excess irradiation would decrease the yield of aldehyde product.

3.2 NB10/Lyso photoligation.

Photoligation in CH_3CN/H_2O (V/V = 9/1): **NB10** (1 mM) and Lyso (1.2 mM) were mixed in 1 mL CH_3CN/ H_2O (V/V = 9/1) and the obtained solution was irradiated by a LED 365 nm light at 10 mW cm^{-2} in a cuvette with optical path length at 1 mm. At specific time intervals, the solution was analyzed by UV–vis absorption spectra.

Photoligation in HEPES (10 mM, pH = 7.2): A **NB10** solution (100 μL, 10 mM in $CHCl_3$) and a lysosphingomyelin (Lyso) solution (120 μL, 10 mM in MeOH) were mixed in a glass tube and dried with N_2 stream to form a transparent film, which was further dried under vacuum overnight. Then, 1 mL HEPES (10 mM, pH = 7.2) was added and the obtained mixture was vortexed to dissolve the film. After curing in a shaker at 37 ℃ (90 rpm/min) for 5 h, the obtained suspension was irradiated by a LED 365 light at 10 mW cm^{-2} in a cuvette with optical path length at 1 mm, and at specific time intervals, the solution was analyzed by UV–vis absorption spectra.

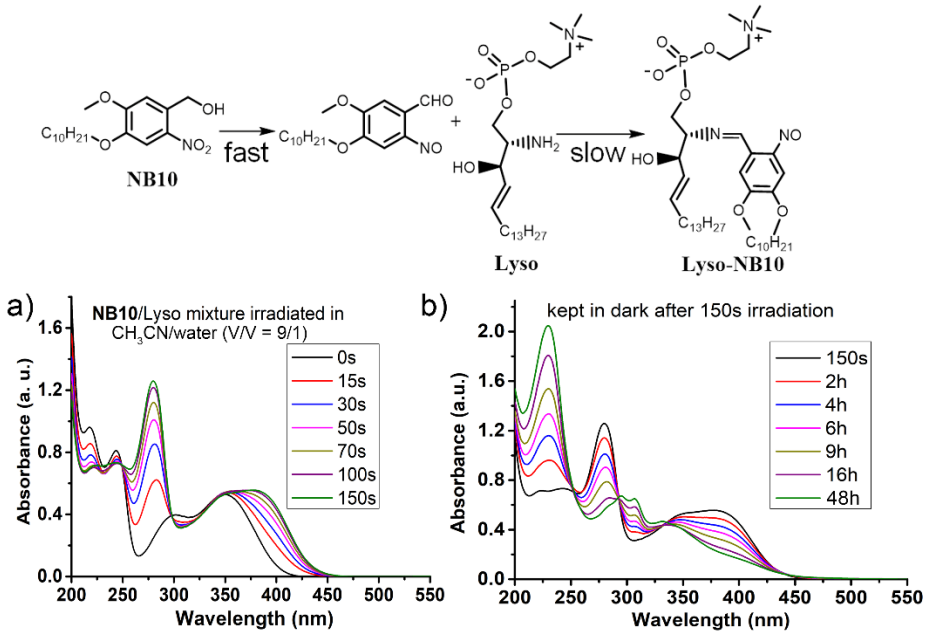


Fig. S5 The **NB10**/Lyso (1/1.2 mM) photoligation in CH_3CN/ H_2O (V/V = 9/1). Time-dependent UV-vis spectra during 0-150 s irradiation (a) and subsequent storage in dark (b).

The dynamic analysis suggested that the photolysis of **NB10** was light dependent. However, the subsequent imine ligation between aldehyde photogenerated from **NB10** and amine of Lyso was quite slow that completed after 48 h.

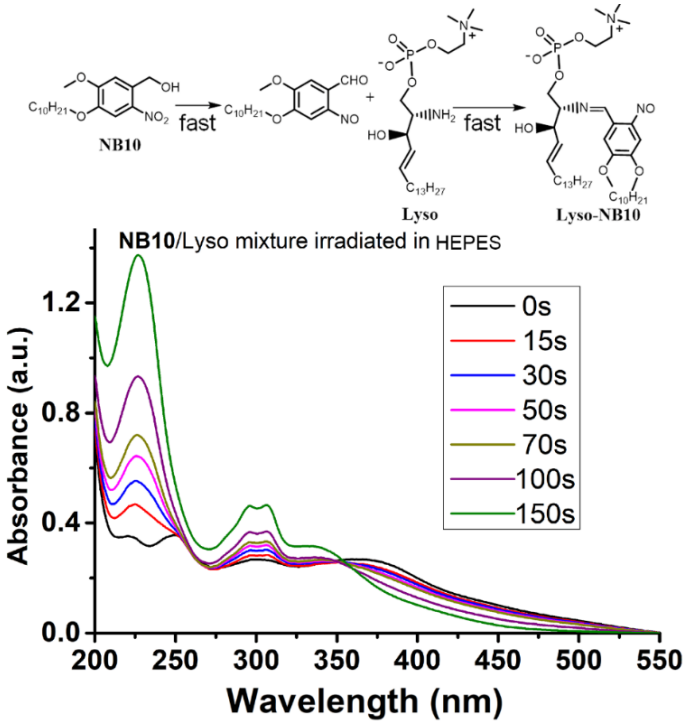


Fig. S6 The **NB10**/Lyso (1/1.2 mM) photoligation in HEPES (10 mM, pH = 7.2).

The dynamic analysis of UV-vis absorption suggested that the imine-ligation process was quite fast. There was no any delay for the ligation after photoirradiation, revealing that the whole photoligation can be controlled by light as demand.

3.3 The exploration of NBCHO stability.

HPLC profiles were performed on a reversed-phase HPLC using a BetaBasic-18 column. A mixture of 85% acetonitrile and 15% water was used as the eluent at a flow rate of 1 mL min^{-1}. The detection wavelength was 320 nm. All the reactants and products were further confirmed by LC-MS.

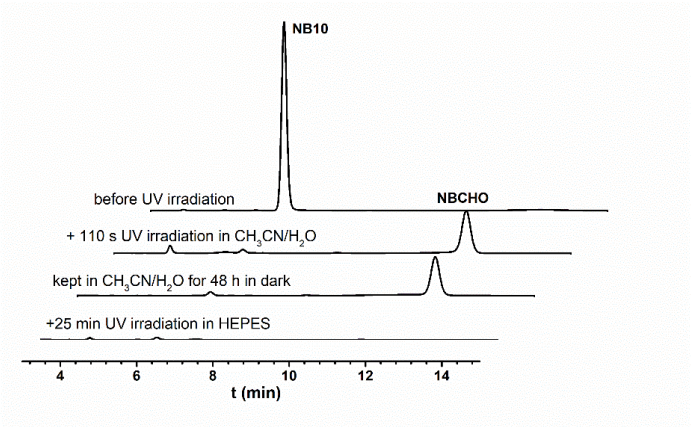


Fig. S7 HPLC tracking for the stability of photogenerated **NBCHO** in CH_3CN/H_2O (V/V = 9/1) and HEPES, respectively. 1 mM of **NB10** was used for analysis.

3.4 HPLC analysis for NB/Lyso photoligation.

The procedure for dynamic HPLC analysis was the same as for UV-vis spectra. Both the photoligation in solution state (CH_3CN/H_2O, 9/1) and aggregation state (HEPES buffer) were explored. HPLC profiles were performed on a reversed-phase HPLC using a BetaBasic-18 column. A mixture of 90% methanol and 10% water was used as the eluent at a flow rate of 1 mL min^{-1}. The detection wavelength was 320 nm. All the reactants and products were further confirmed by LC-MS.

3.5 HPLC analysis for compound 17/Lyso photoligation.

The procedure and detection process were the same as Section 3.4.

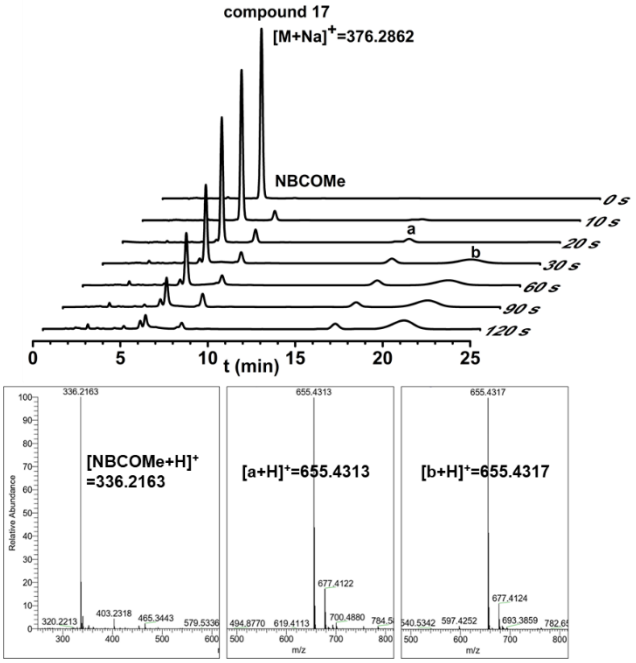


Fig. S8 HPLC and LC-mass analysis of photoligation of the compound **17**/Lyso mixture (1/1.2 mM in HEPES).

There was no ligation product was observed, suggesting that the photogenerated ketone (**NBCOMe**) was inactive to the amine of Lyso. Based on the molecular weight, the peaks a and b should be assigned to the dimerization of nitrosobenzaldehyde.[5]

3.6 Photoligation in buffer at various pH levels or in the presence of amino acids or proteins.

1) In the presence of amine acids and protein: The whole process was similar to above, except the added HEPES buffer was mixed with lysine, glutamate, cysteine and serine (1 mM), and BSA (10 mg/mL), respectively.

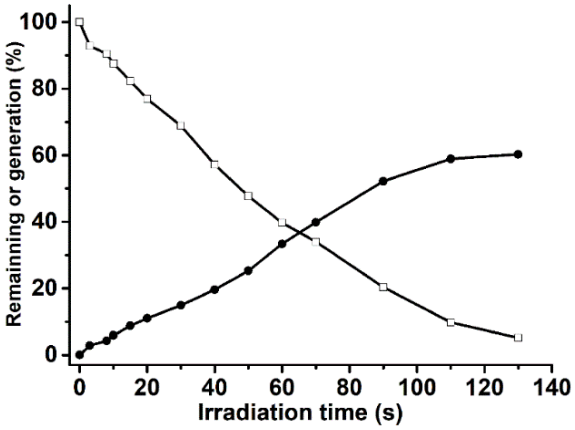


Fig. S9 HPLC quantitative analysis of **NB10** remaining (-□-) and **Lyso-NB10**

generation (-●-) for the photoligation of the **NB10**/Lyso mixture (1/1.2 mM in 10 mM HEPES, pH = 7.2) in the presence of lysine (1mM).

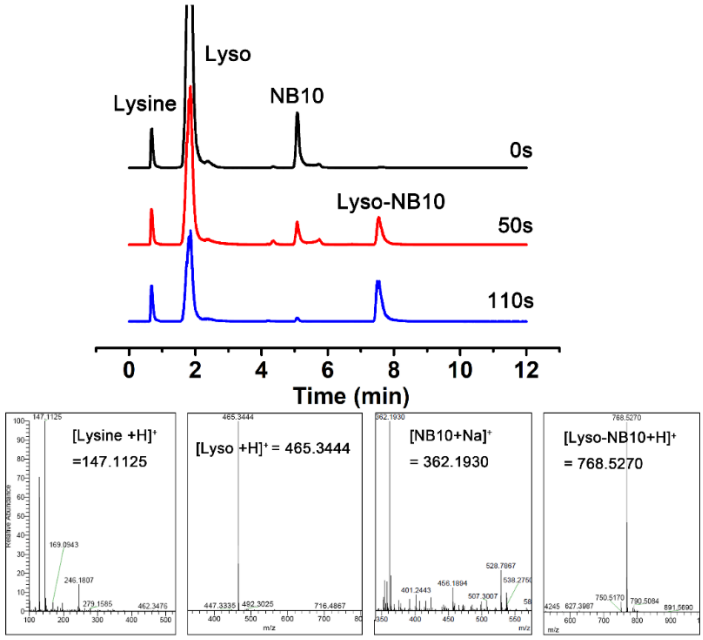


Fig. S10 UPLC-MS analysis of photoligation of the **NB10**/Lyso mixture (1/1.2 mM in HEPES) in presence of lysine (1 mM). Upon irradiation, the preassembly of **NB10**/Lyso facilitated the generation of **Lyso-NB10** without being affected by lysine in solution.

2) At various pH levels: 100 μL of a 10 mM solution of **NB10** in $CHCl_3$ and 120 μL of a 10 mM solution of lysosphingomyelin (Lyso) in MeOH were mixed in a glass tube and dried with N_2 stream to form a transparent film, which was further dried under vacuum overnight. Then, 1 mL of Tris-HCl buffer (50 mM, pH = 5) or HEPES buffer (10 mM, pH = 7.2) or borate buffer solution (50 mM, pH = 10) was added and vortexed to dissolve the film, the obtained mixture was cured in a shaker at 37 ℃ (90 rpm/min) for 5 h. The obtained suspension was then irradiated by a LED 365 nm light at 10 mW cm^{-2} in a cuvette and aliquots of 20 μL solution was taken out and analyzed by HPLC spectra at specific time intervals.

3) The stability of **Lyso-NB10** in different buffer at various pH levels: To the buffer at different pH values was dissolved **Lyso-NB10** (1mM). After 24 h storage in ambient temperature, the remaining of **Lyso-NB10** was analyzed by HPLC spectra. To save the experimental time, a mixture of 95% methanol and 5% water was used as the eluent at a flow rate of 1 mL min^{-1}.

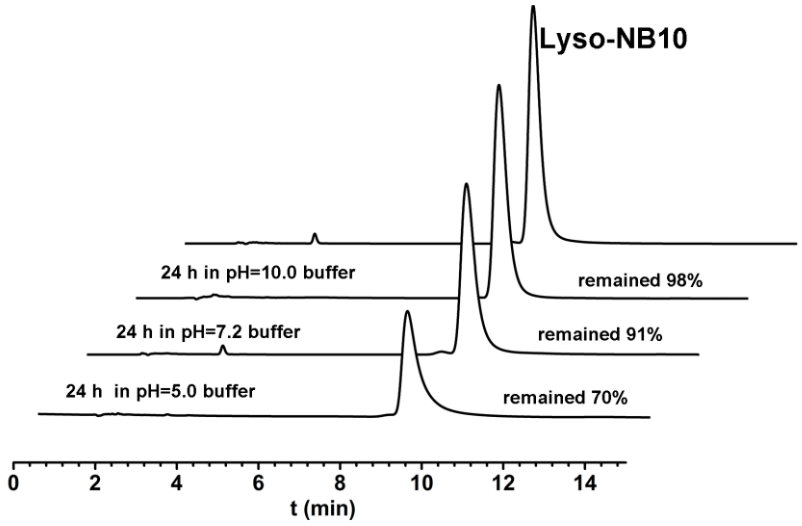


Fig. S11 The stability of **Lyso-NB10** in buffers at different pH values.

In acidic condition, the amount of product reduced ~30% after 24 h storage. However, the reason for the reduction is complicated and cannot be simply attributed to the reversible reaction of imine, since there is no regeneration of **NBCHO** detected by HPLC.

3.7 Photoligation of other NB/Lyso mixtures.

The photoligation process for other **NB/Lyso** mixtures in HEPES was analyzed as that for **NB10**/Lyso mixture.

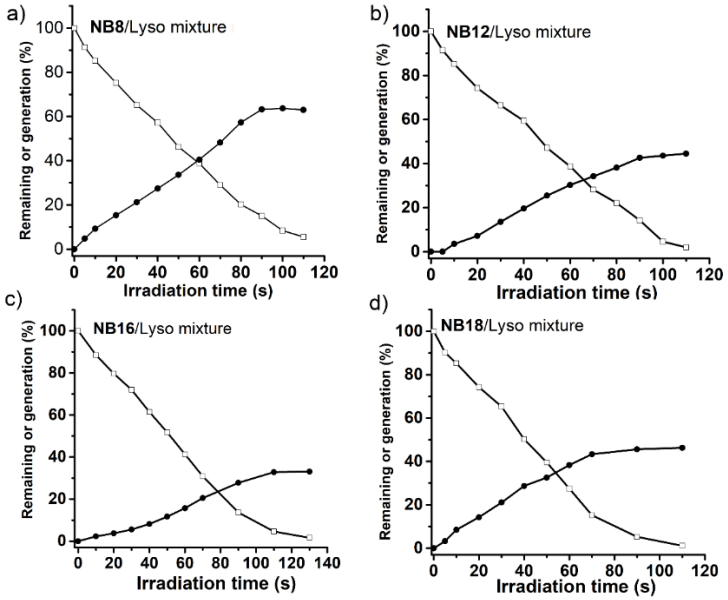


Fig. S12 HPLC quantitative analysis of NBs remaining (-□-) and **Lyso-NB** (-●-) generation for the photoligation. a) **NB8**/Lyso, b) **NB12**/Lyso, c) **NB16**/Lyso, and d) **NB18**/Lyso mixtures (1/1.2 mM in 10 mM HEPES). A LED with an emission wavelength of 365 nm and an intensity of 10 mW cm^{-2} was used for irradiation.

4. Self-assembly analysis.

4.1 NB/Lyso aggregates in HEPES.

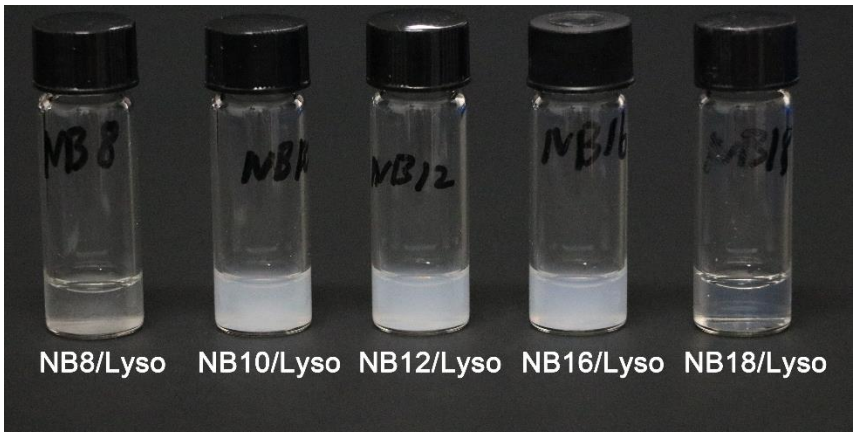


Fig. S13 A photo for NB/Lyso mixtures in HEPES (1/1.2 mM).

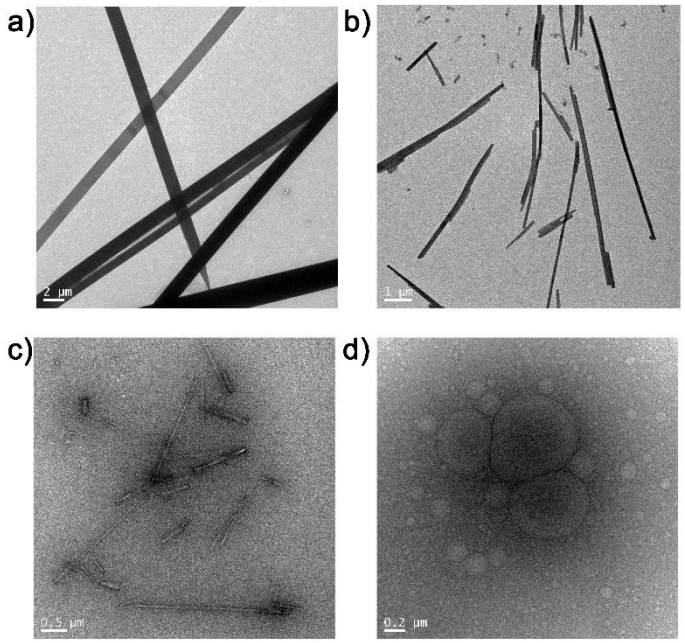


Fig. S14 TEM images of the aggregates of NB/Lyso in HEPES (1/1.2 mM in 10 mM HEPES). a) **NB8**/Lyso mixture, b) **NB12**/Lyso mixture, c) **NB16**/Lyso mixture and d) **NB18**/Lyso mixture, respectively.

4.2 NB10 and Lyso aggregates in HEPES.

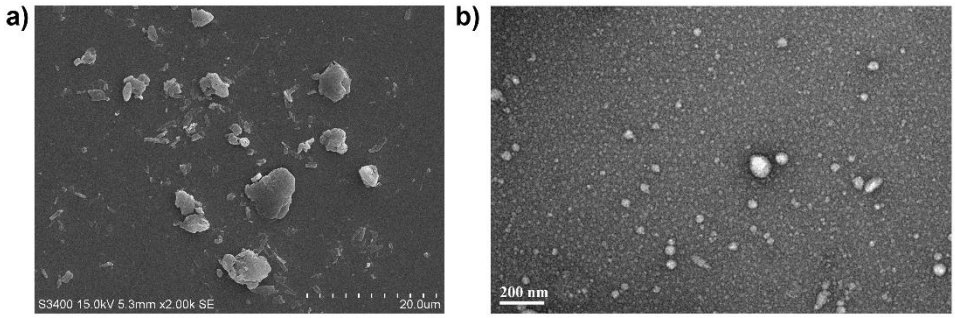


Fig. S15 a) SEM image for **NB10** in HEPES. b) TEM image of Lyso micelles, which were negatively stained by uranyl acetate.

4.3 Photoligation in the presence of CTAB.

The photoligation process in HEPES was analyzed by HPLC spectra as that for **NB10**/Lyso mixture.

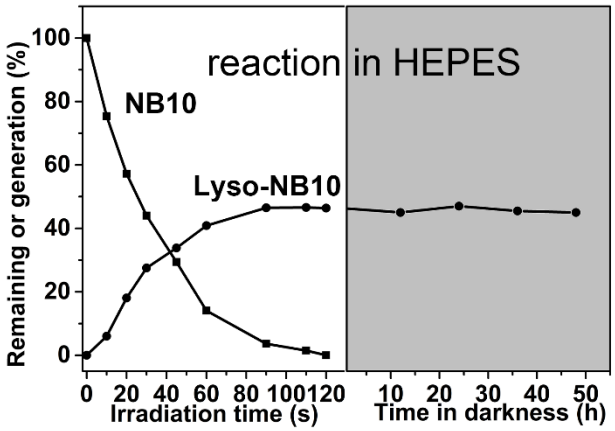


Fig. S16 HPLC quantitative analysis of **NB10** remaining (-■-) and **Lyso-NB10** generation (-●-) for the photoligation of the **NB10**/Lyso mixture (1/1.2 mM in 10 mM HEPES, pH = 7.2) in the presence of CTAB (5 mM).

5. In situ formation of lipid vesicles triggered by irradiation.

5.1 Fluorescent image of the photogenerated vesicles.

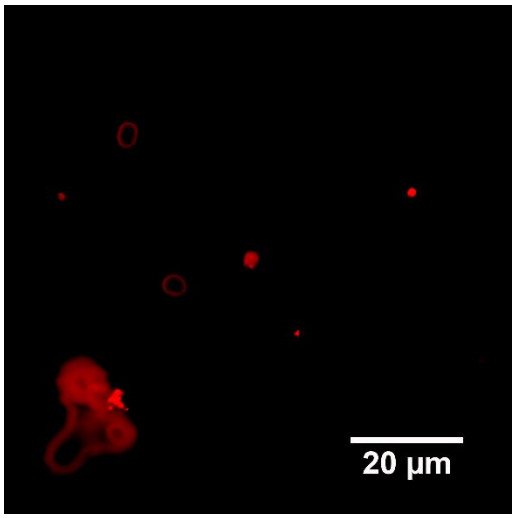


Fig. S17 The fluorescent image of some large synthetic vesicles by addition of Nile Red. 20 μL Nile Red solution in DMSO (1 mM) was added to the photogenerated vesicles.

5.2 Reversible rod-vesicle conversion of NB10/Lyso aggregates in HEPES by heating-cooling recycle.

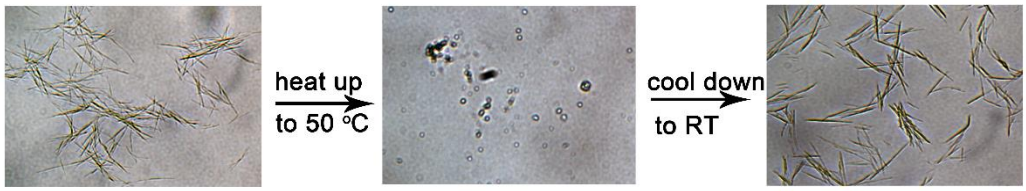


Fig. S18 Thermal reversible self-assembly of the **NB10**/Lyso mixture in HEPES.

5.3 Phototriggered transition.

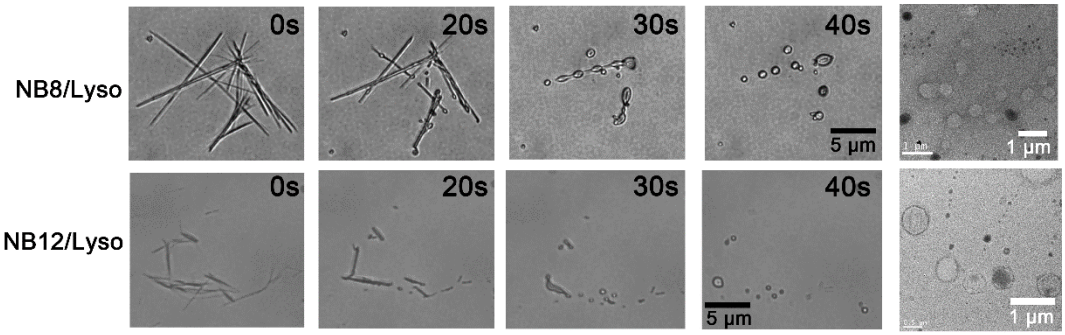


Fig. S19 In situ tracking for the formation of vesicles upon light irradiation. Upper is the **NB8**/Lyso system and down is the **NB12**/Lyso system. The pictures on the far right are TEM images for the photogenerated vesicles.

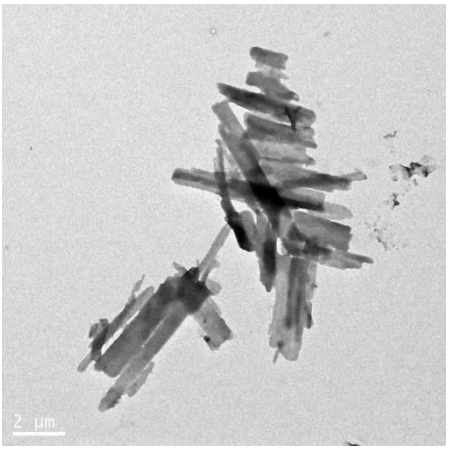


Fig. S20 TEM image for the irradiated **NB16**/Lyso system.

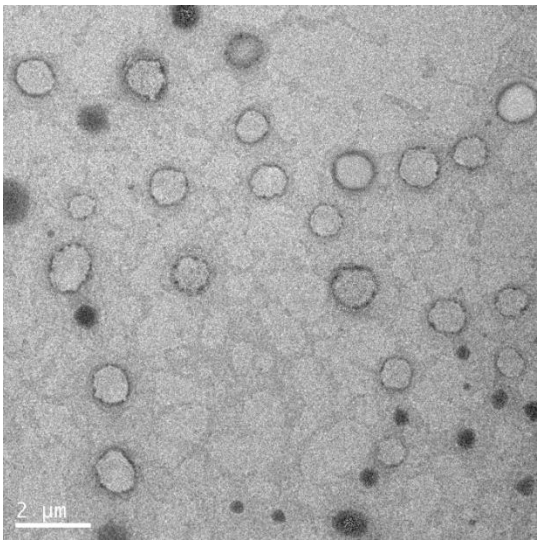


Fig. S21 TEM image for the irradiated **NB18**/Lyso system.

6. In situ encapsulation and release of HPTS dye.

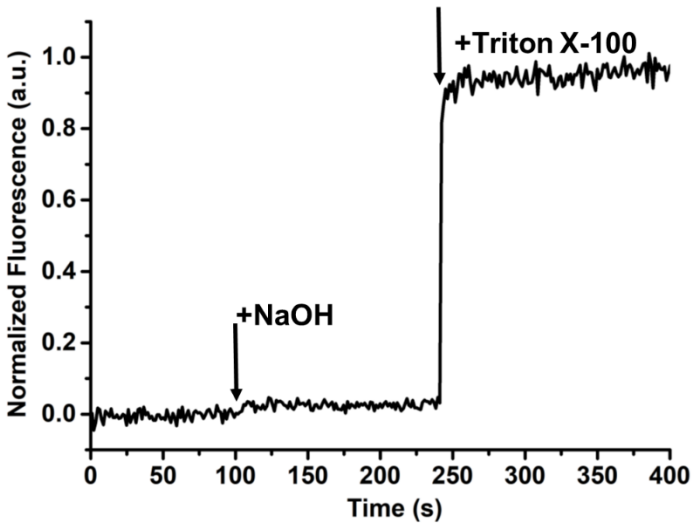


Fig. S22 Illustration of normalized fluorescence change of HPTS enwrapped liposomes after adding base (30 μL, 0.5 M NaOH) and detergent Triton X-100 (60 μL, 5%) successively. The **NB10**/Lyso system was used to prepare HPTS enwrapped liposomes.

HPTS is a pH-sensitive dye and its fluorescence at 510 nm increases with the increase of pH upon 450 nm excitation. The unchanged fluorescence at 510 nm after the addition of base indicated that the photogenerated membrane was stable and formed a barrier for encapsulated HPTS. The subsequent sharp increase in fluorescence following the addition of detergent Triton X-100 indicated membrane disintegration, showing typical characteristics of lipid membranes.

7. In situ enzyme encapsulation and enzymatic cascade reaction.

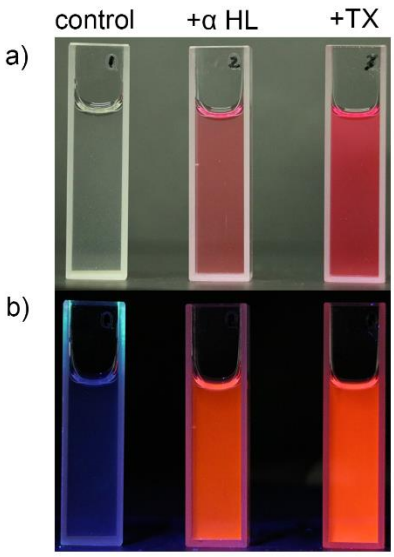
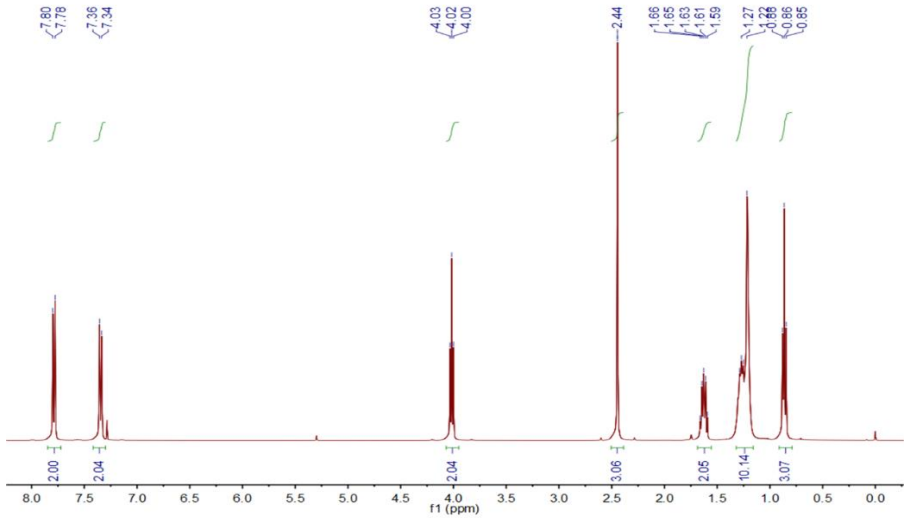
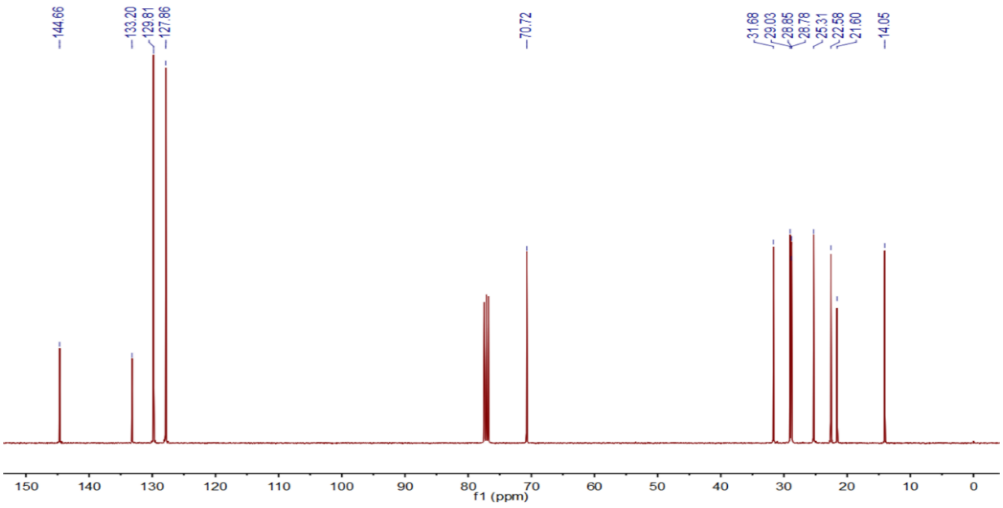


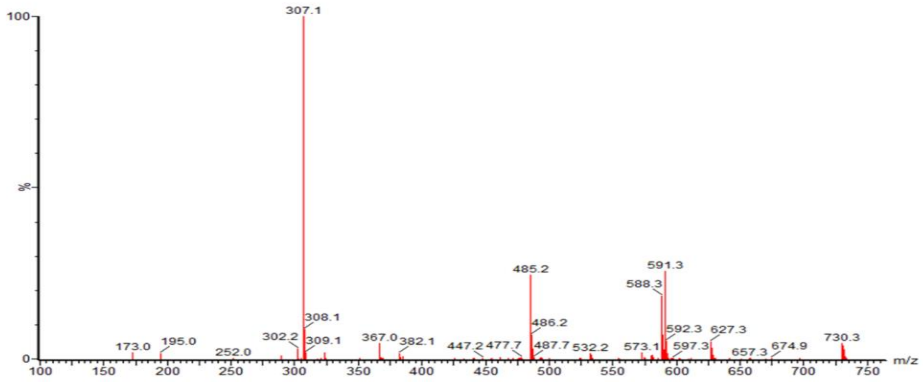
Fig. S23 The photos for the enzymatic cascade reaction after 3 h under different conditions. a) The photos were taken in the bright field. b) The photos were taken in the dark filed with the irradiation of a LED 365 nm light.

8. Appendix: ^{1}H NMR, ^{13}C NMR and Mass spectra for New Compounds:

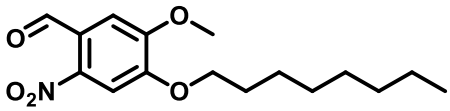
Compound **4** 

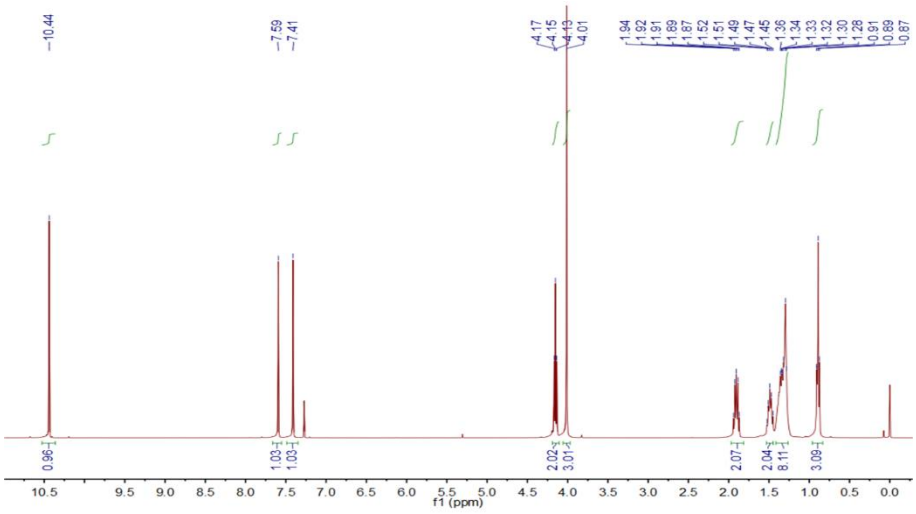


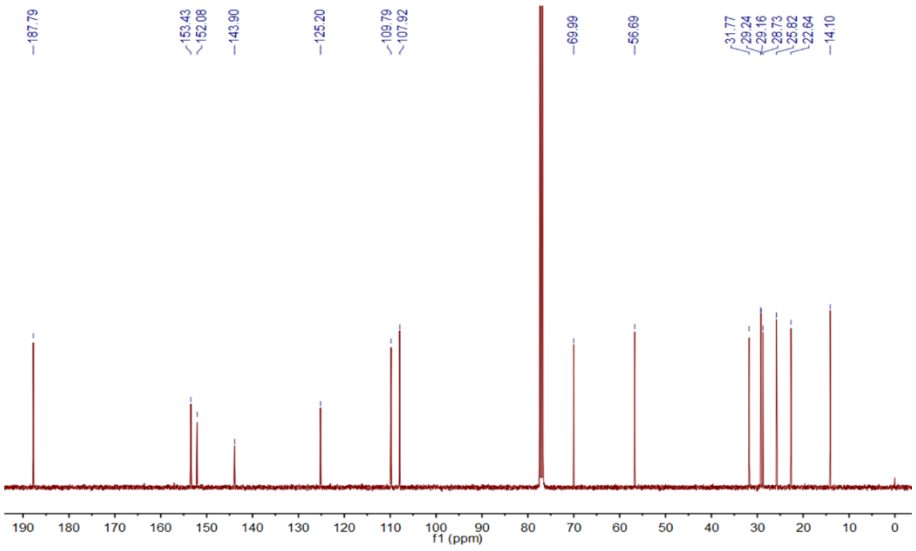


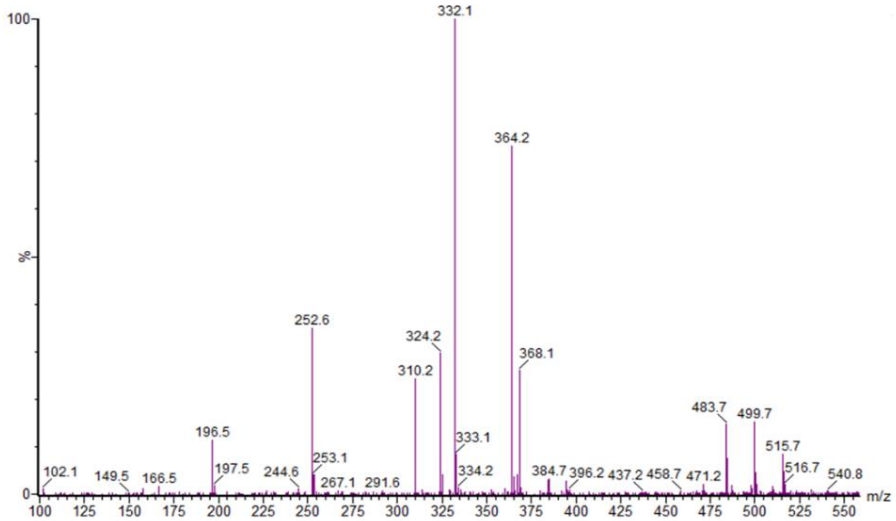


Compound **5**

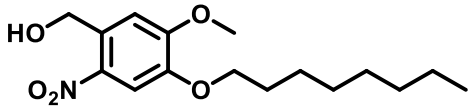


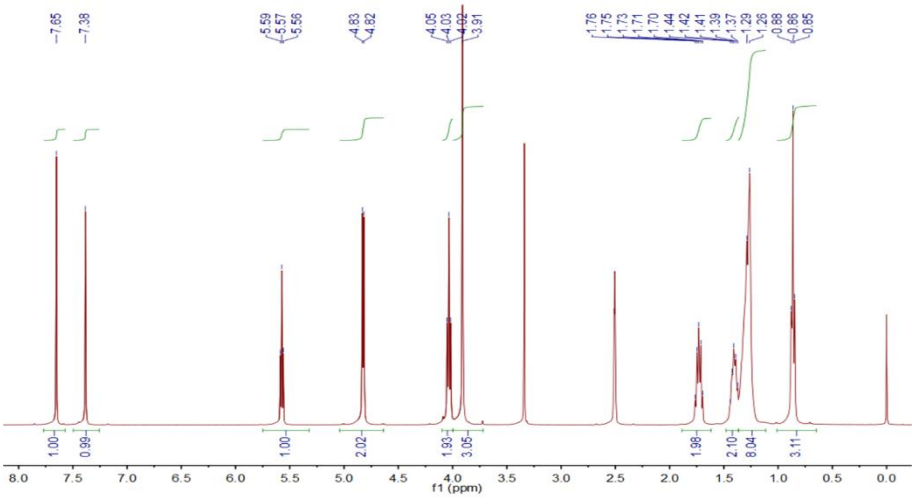

10.44
7.59
7.41
4.17
4.15
4.13
4.01
1.94
1.92
1.91
1.89
1.87
1.52
1.51
1.49
1.47
1.45
1.36
1.34
1.33
1.32
1.30
1.28
0.91
0.89
0.87
0.96
1.03
1.03
2.02
3.01
2.07
2.04
8.11
3.09
f1 (ppm)

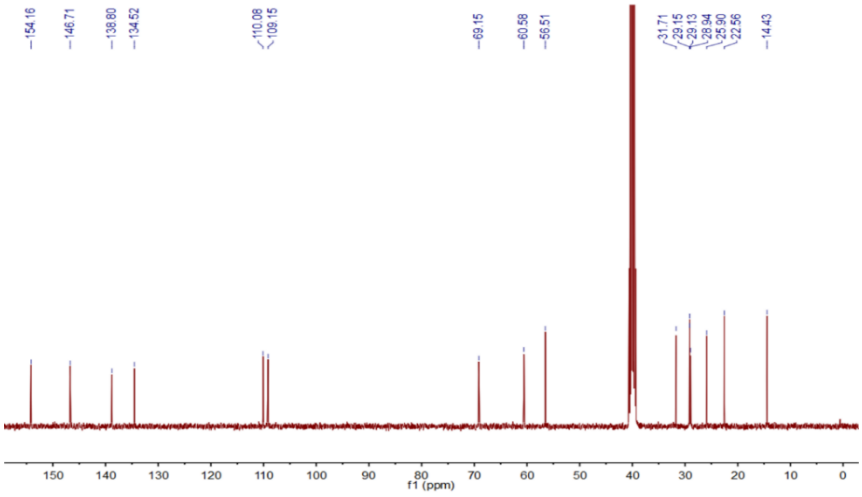

187.79
153.43
152.08
143.90
125.20
109.79
107.92
69.99
56.69
31.77
29.24
29.16
28.73
25.82
22.64
14.10
f1 (ppm)

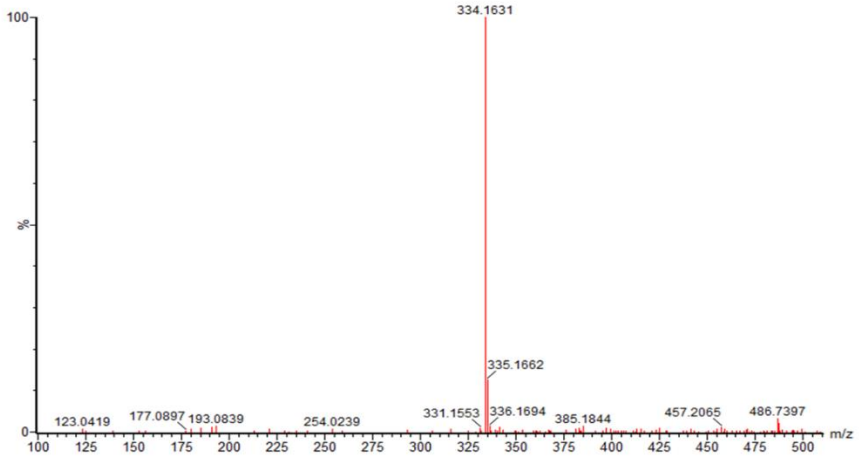

100
%
0
332.1
364.2
252.6
324.2
310.2
368.1
196.5
333.1
253.1
197.5
334.2
102.1
149.5
166.5
244.6
267.1
291.6
384.7
396.2
437.2
458.7
471.2
483.7
499.7
515.7
516.7
540.8
m/z

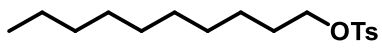
Compound **NB8**

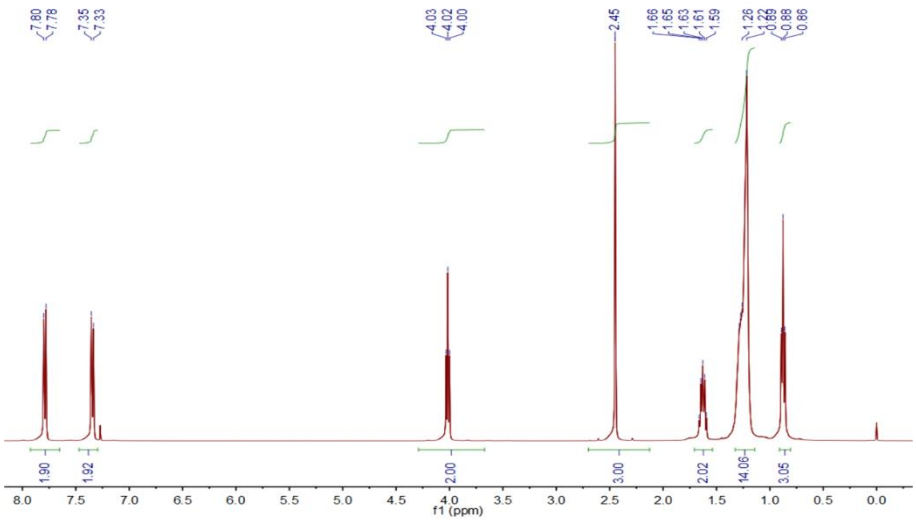


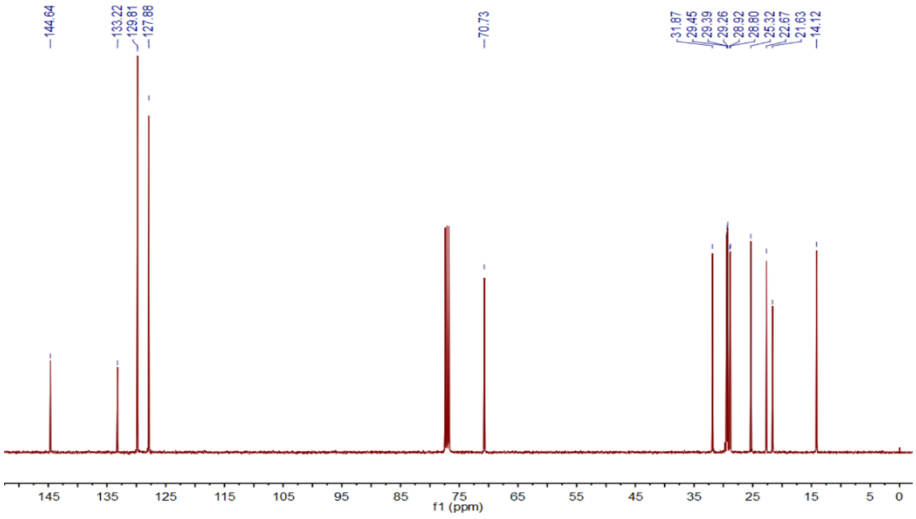


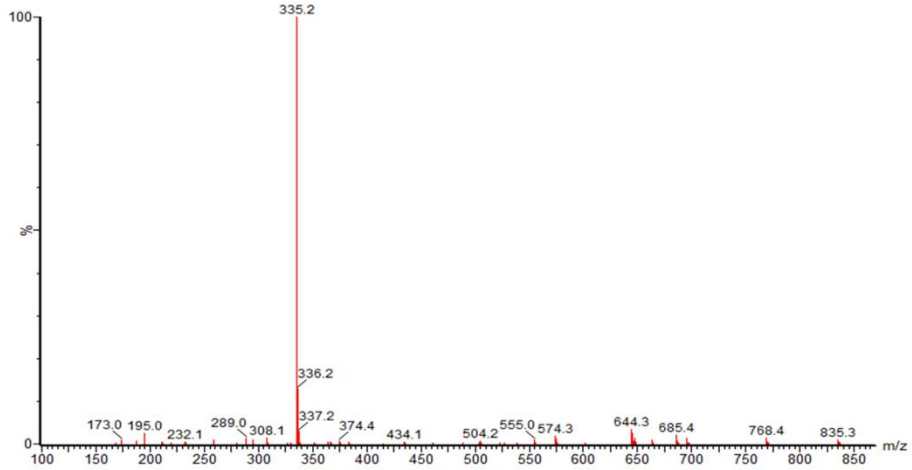




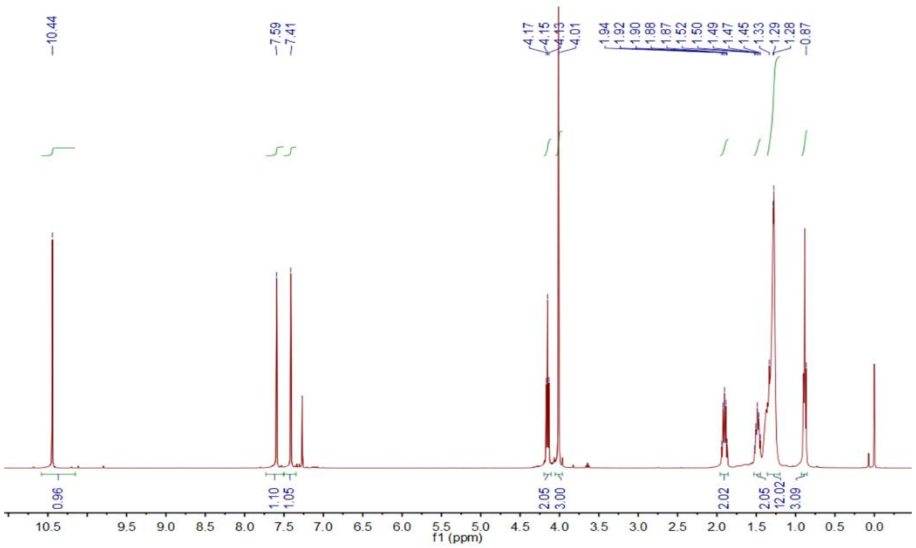
Compound **6** 
OTs

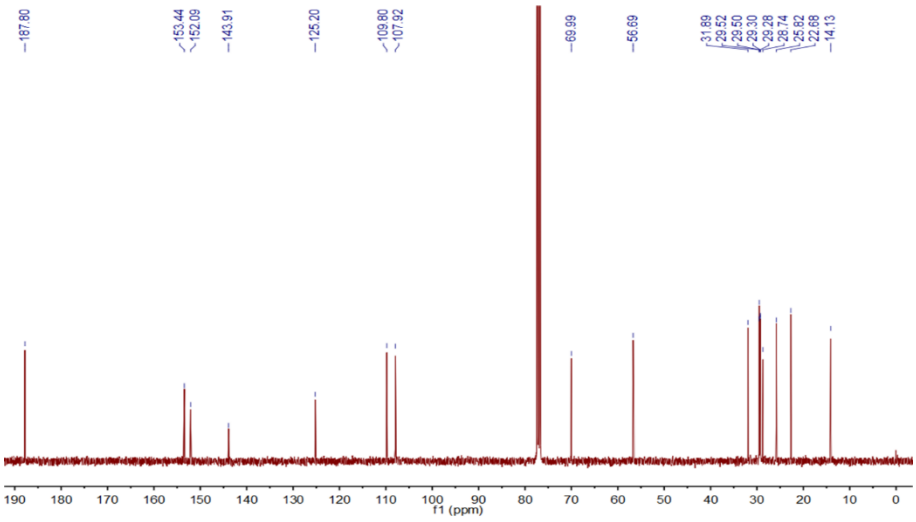

7.80
7.78
7.35
7.33
4.03
4.02
4.00
2.45
1.66
1.65
1.63
1.61
1.59
1.26
0.89
0.88
0.86
1.90
1.92
2.00
3.00
2.02
14.06
3.05
f1 (ppm)

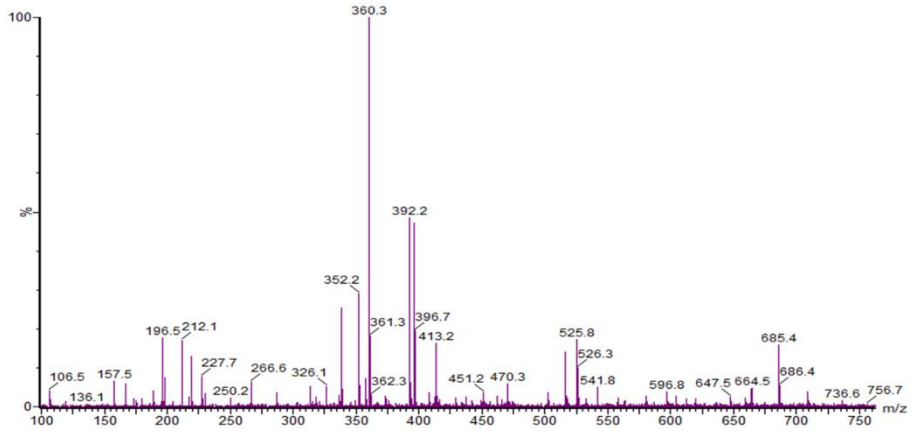

144.64
133.22
129.81
127.88
70.73
31.87
29.45
29.39
29.26
28.92
28.80
25.32
22.67
21.63
14.12
f1 (ppm)


335.2
336.2
337.2
173.0
195.0
232.1
289.0
308.1
374.4
434.1
504.2
555.0
574.3
644.3
685.4
768.4
835.3
%
m/z

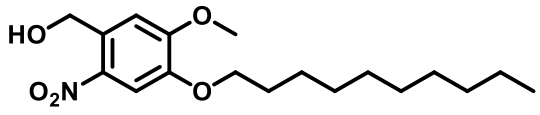
Compound **7**

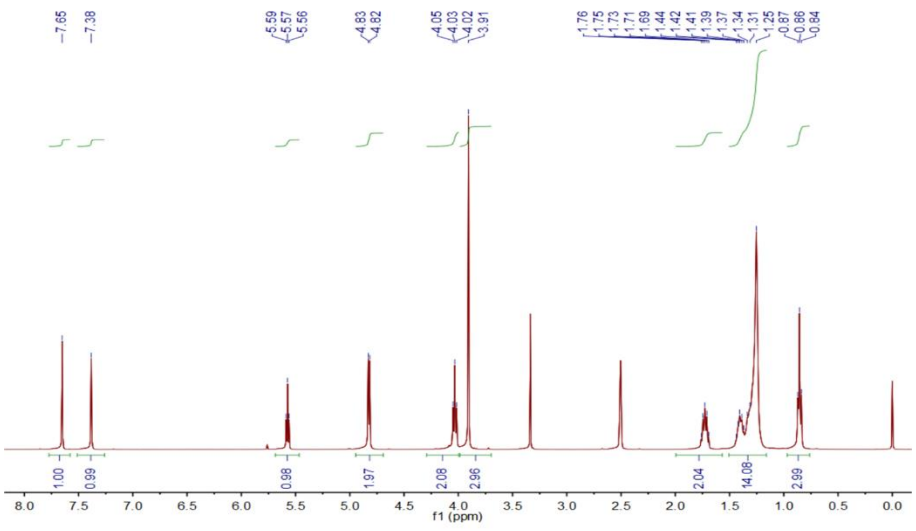

10.44
7.59
7.41
4.17
4.15
4.13
4.01
1.94
1.92
1.90
1.88
1.87
1.52
1.50
1.49
1.47
1.45
1.33
1.29
1.28
0.87
0.96
1.10
1.05
2.05
3.00
2.02
2.05
12.02
3.09
f1 (ppm)

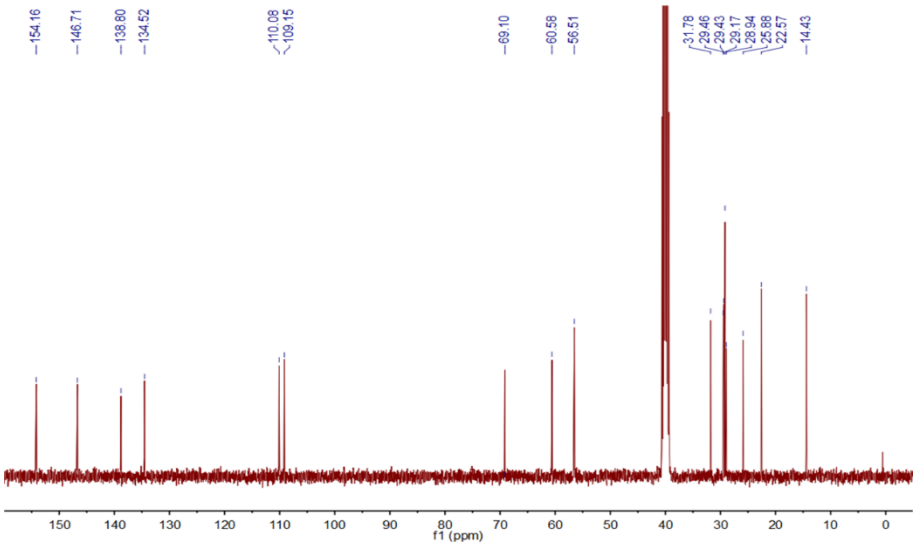

187.80
153.44
152.09
143.91
125.20
109.80
107.92
69.99
56.69
31.89
29.52
29.50
29.30
29.28
28.74
25.82
22.68
14.13
f1 (ppm)

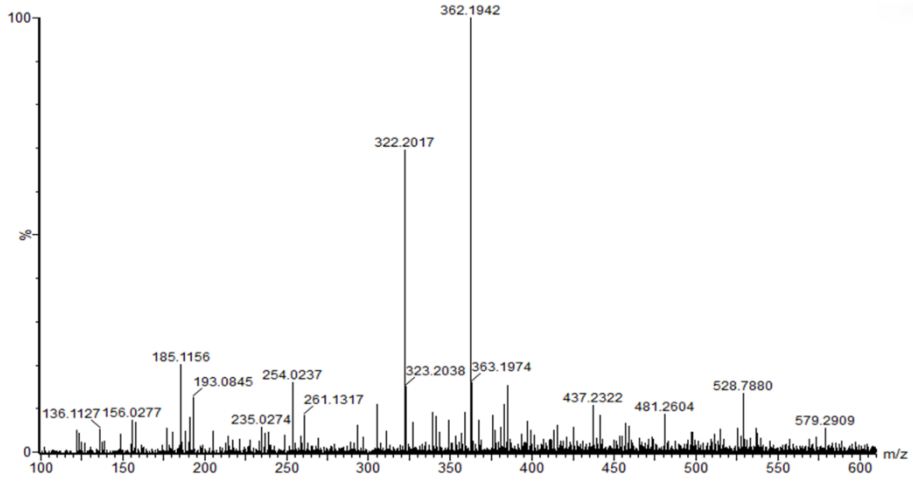

100
%
0
360.3
392.2
352.2
361.3
396.7
413.2
196.5
212.1
227.7
266.6
326.1
106.5
157.5
136.1
250.2
362.3
451.2
470.3
525.8
526.3
541.8
596.8
647.5
664.5
685.4
686.4
736.6
756.7
m/z

Compound **NB10**

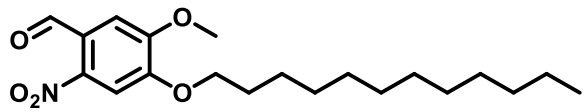


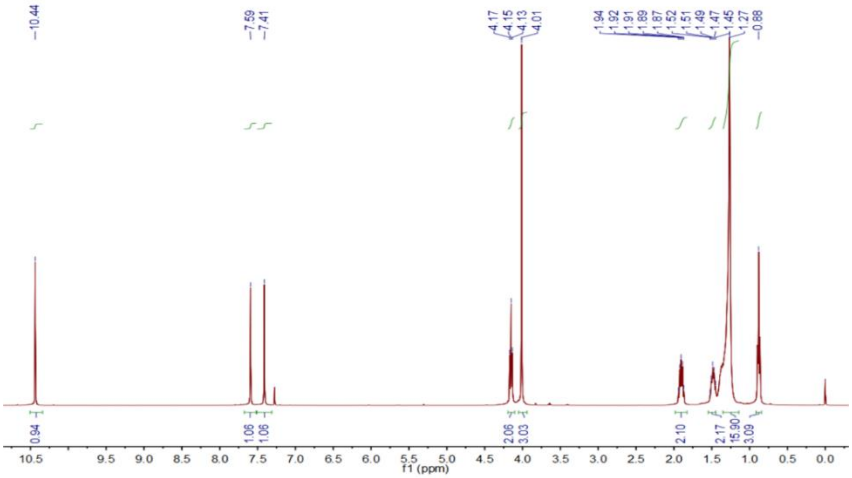


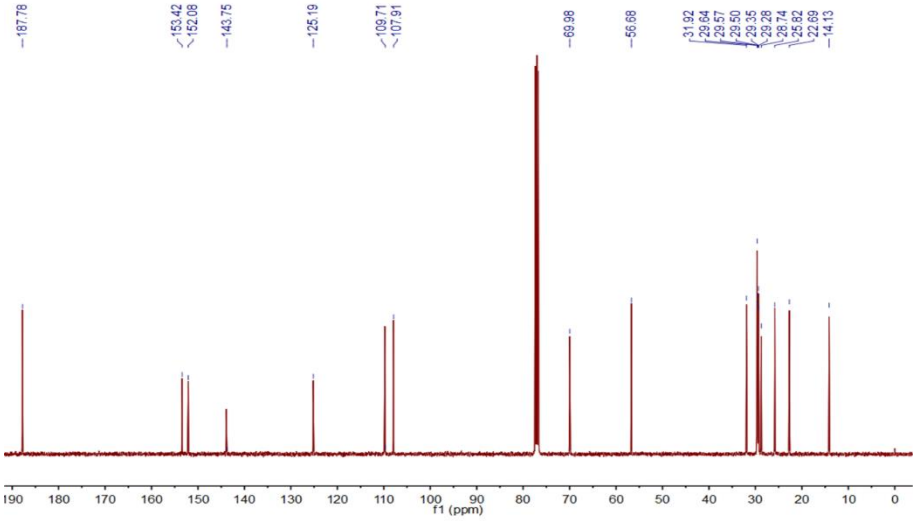


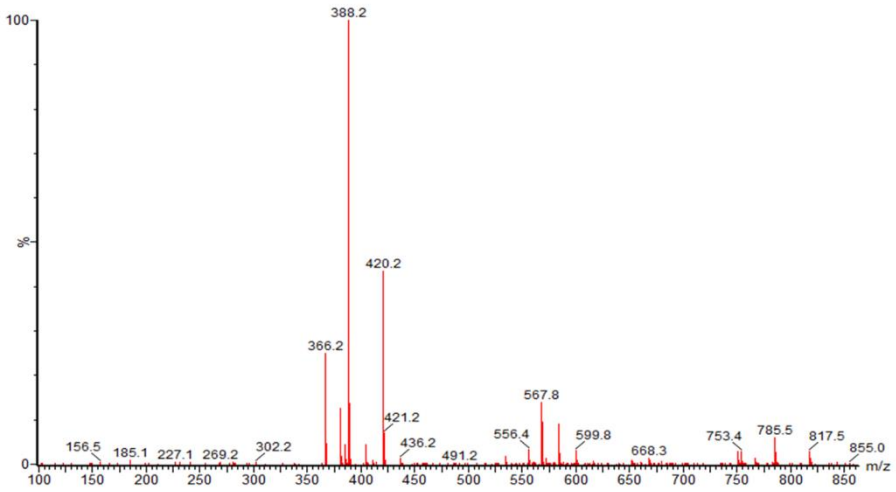


Compound **8**

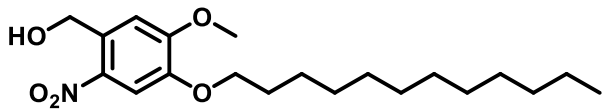


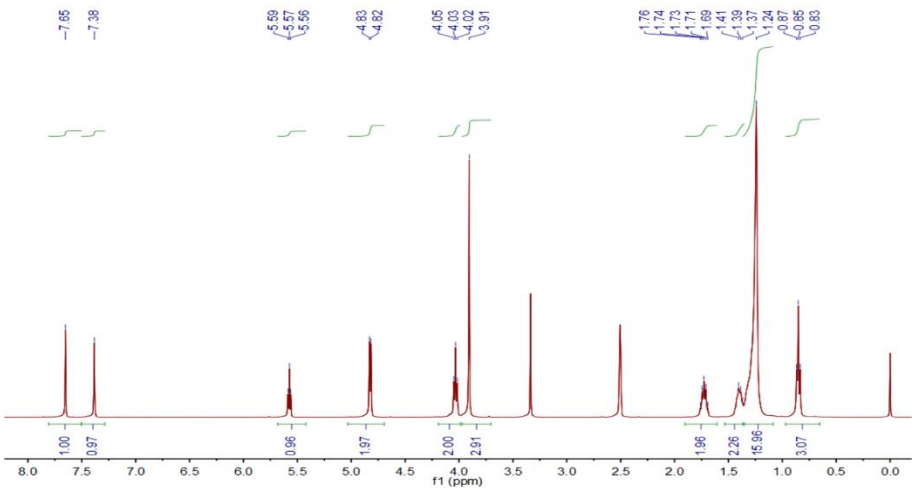

10.44
7.59
7.41
4.17
4.15
4.13
4.01
1.94
1.92
1.91
1.89
1.87
1.52
1.51
1.49
1.47
1.45
1.27
0.88
0.94
1.06
1.06
2.06
3.03
2.10
2.17
15.90
3.09
f1 (ppm)

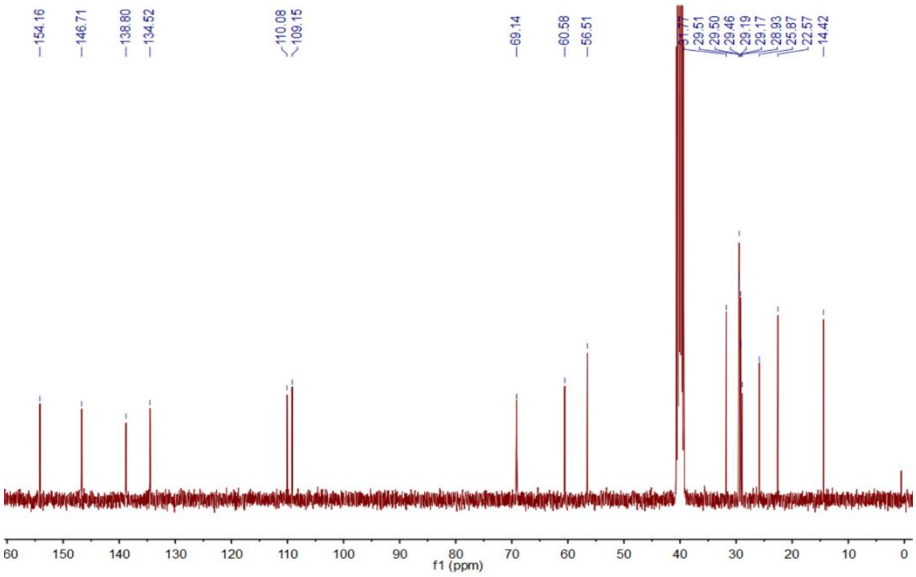

187.78
153.42
152.08
143.75
125.19
109.71
107.91
69.98
56.68
31.92
29.64
29.57
29.50
29.35
29.28
28.74
25.82
22.69
14.13
f1 (ppm)

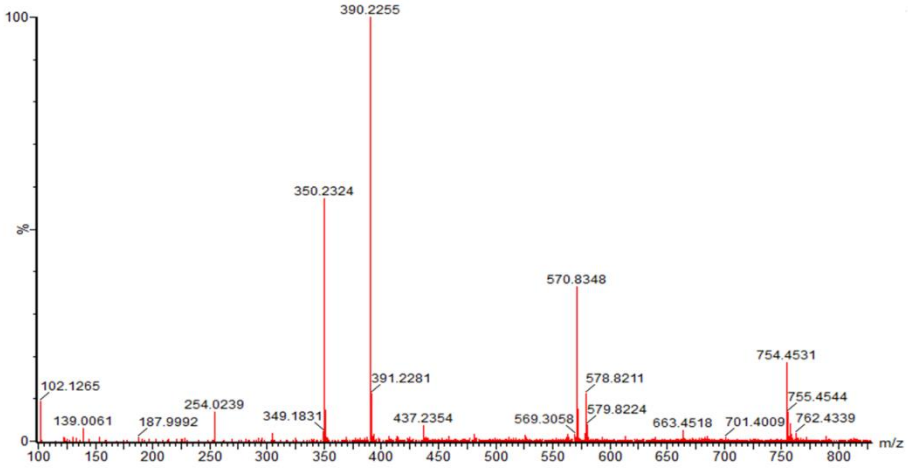

388.2
420.2
366.2
567.8
421.2
436.2
556.4
599.8
753.4
785.5
817.5
855.0
156.5
185.1
227.1
269.2
302.2
491.2
668.3
%
m/z

Compound **NB12**

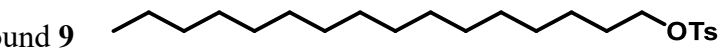


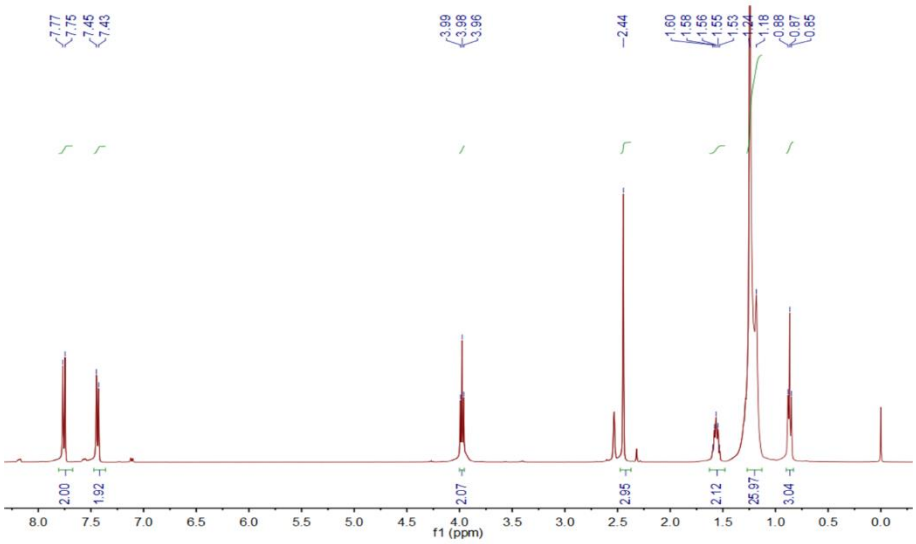


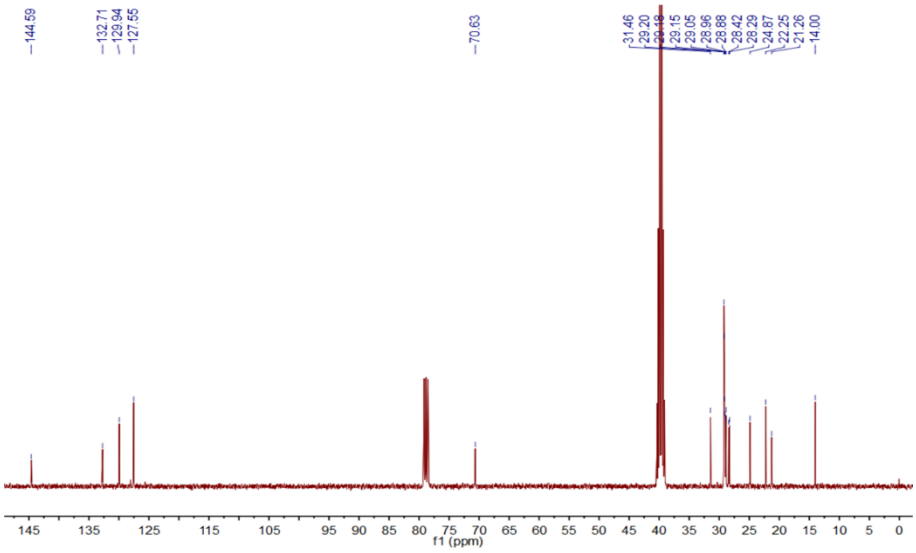


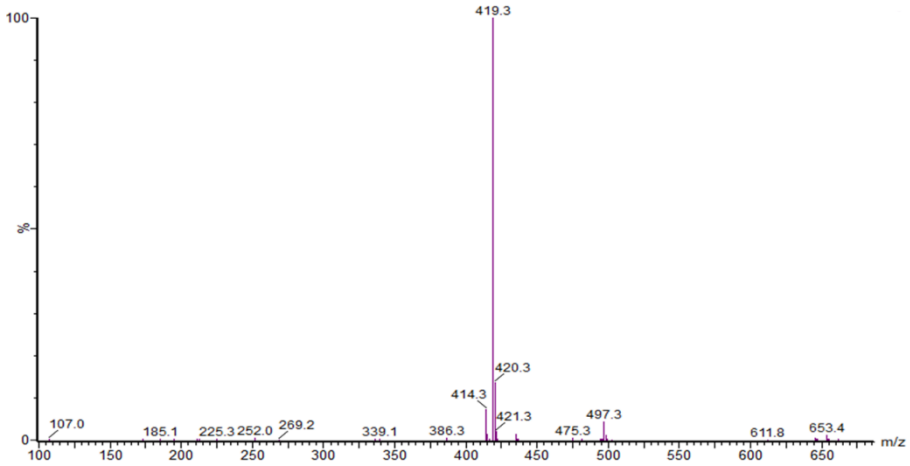


Compound **9**

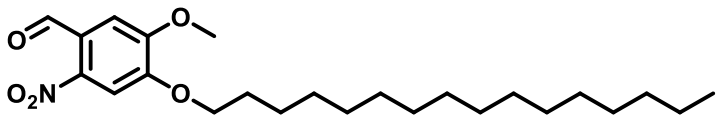

OTs

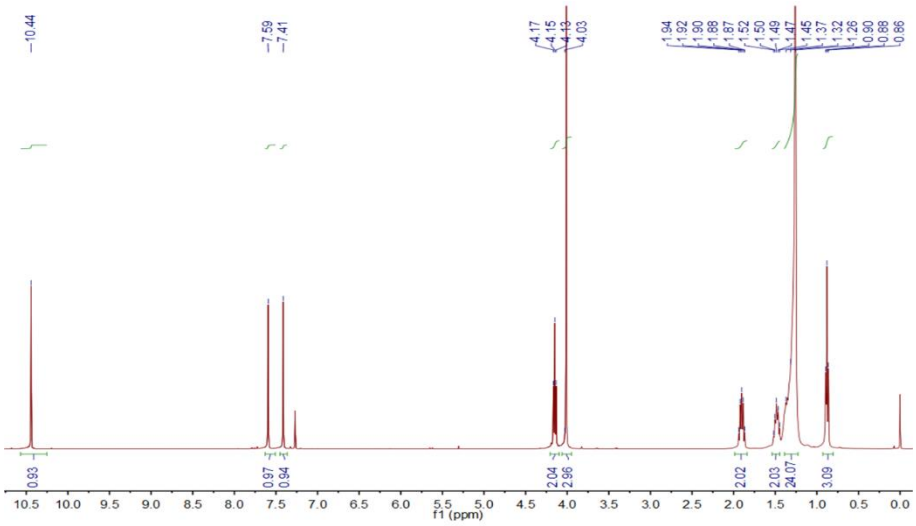

7.77
7.75
7.45
7.43
3.99
3.98
3.96
2.44
1.60
1.58
1.56
1.55
1.53
1.24
1.18
0.88
0.87
0.85
2.00
1.92
2.07
2.95
2.12
26.97
3.04
f1 (ppm)

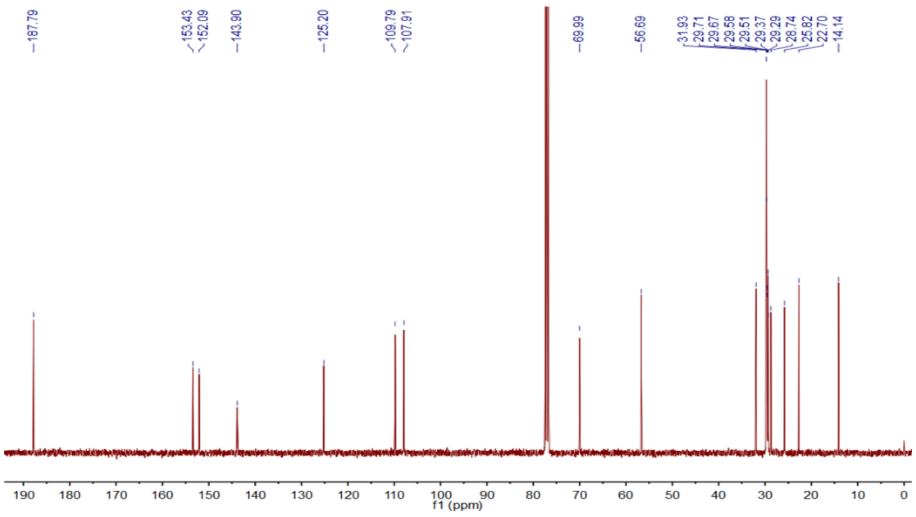

144.59
132.71
129.94
127.55
70.63
31.46
29.20
29.15
29.05
28.96
28.88
28.42
28.29
24.87
22.25
21.26
14.00
f1 (ppm)

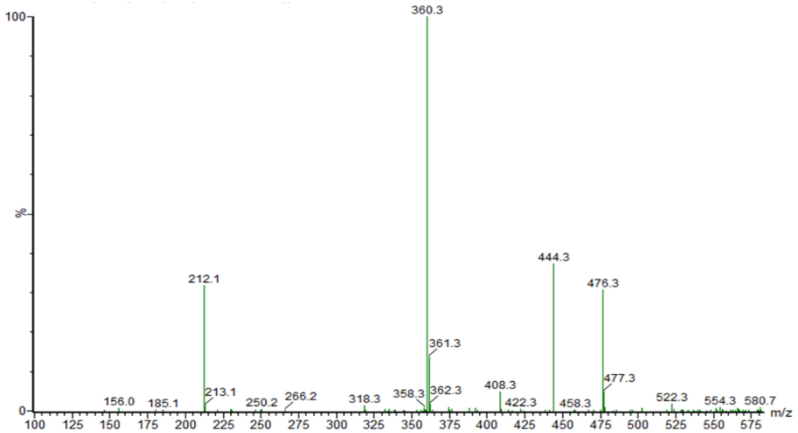

419.3
420.3
414.3
421.3
497.3
107.0
185.1
225.3
252.0
269.2
339.1
386.3
475.3
611.8
653.4
%
m/z

Compound **10**

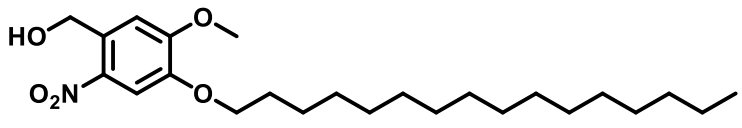


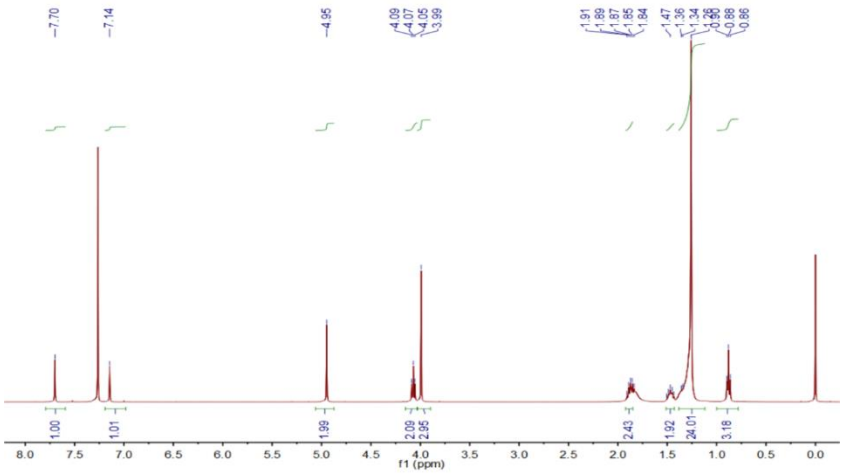

10.44
7.59
7.41
4.17
4.15
4.13
4.03
1.94
1.92
1.90
1.88
1.87
1.52
1.50
1.49
1.47
1.45
1.37
1.32
1.26
0.90
0.88
0.86
0.93
0.97
0.94
2.04
2.96
2.02
2.03
24.07
3.09
f1 (ppm)

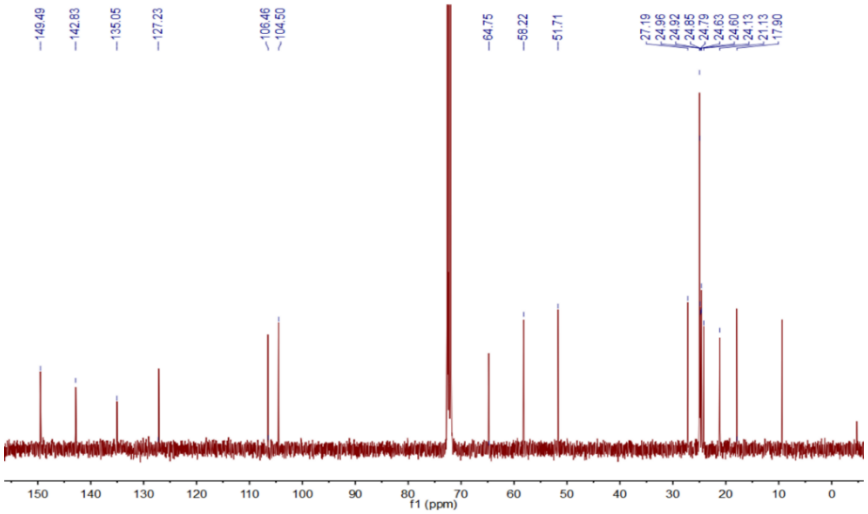

187.79
153.43
152.09
143.90
125.20
109.79
107.91
69.99
56.69
31.93
29.71
29.67
29.58
29.51
29.37
29.29
28.74
25.82
22.70
14.14
f1 (ppm)

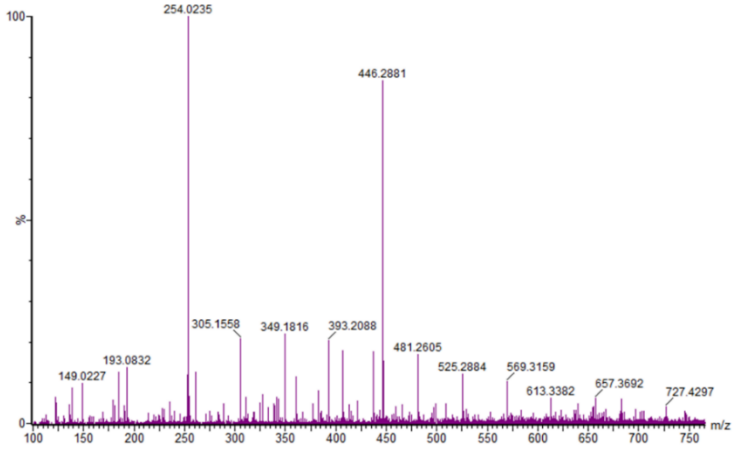

100
%
0
360.3
212.1
444.3
476.3
361.3
477.3
213.1
408.3
362.3
156.0
185.1
250.2
266.2
318.3
358.3
422.3
458.3
522.3
554.3
580.7
m/z

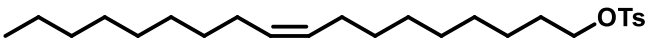
Compound **NB16**

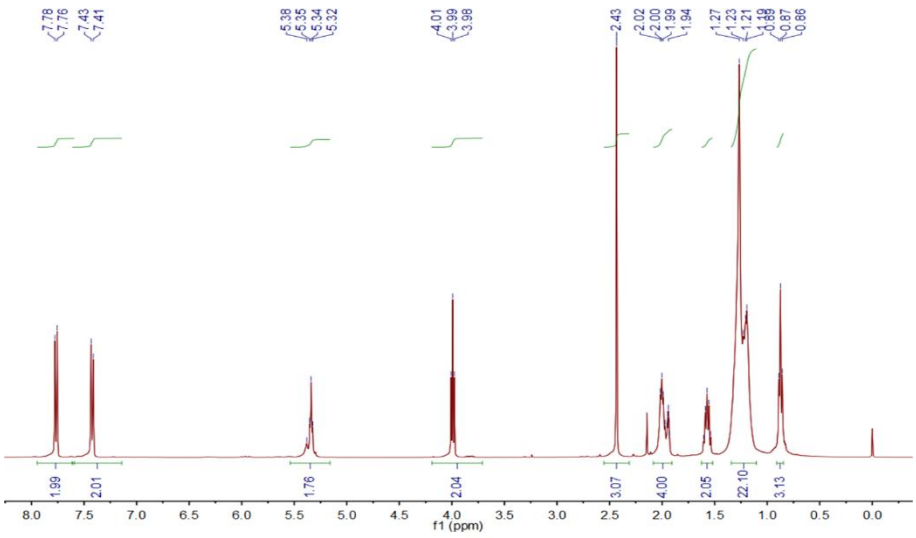


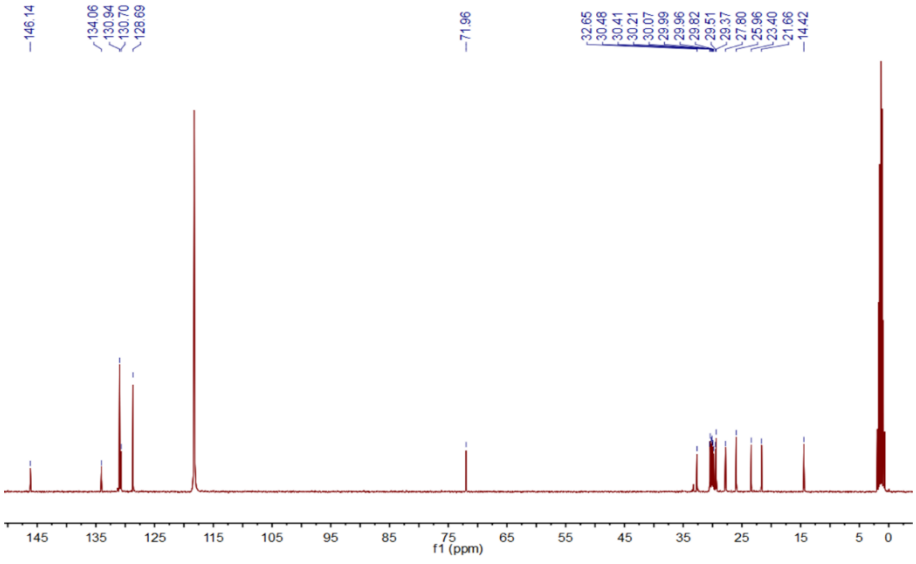


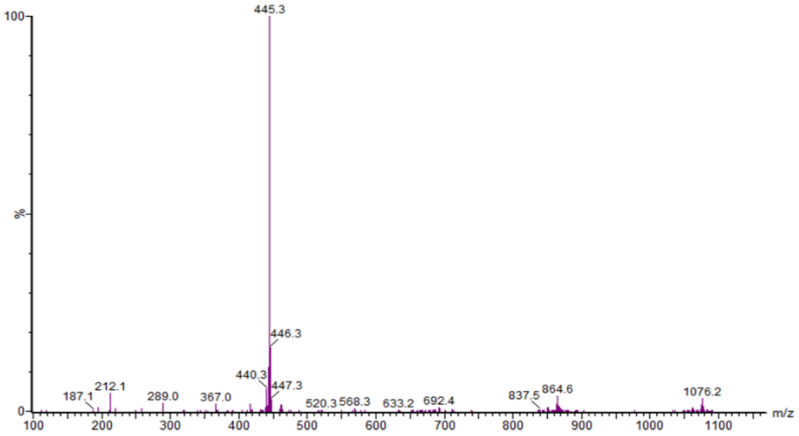




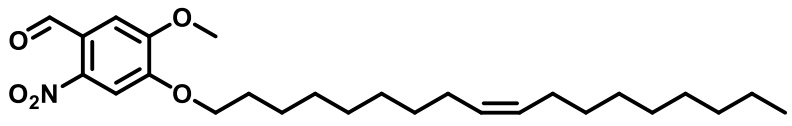
Compound **11** 
OTs

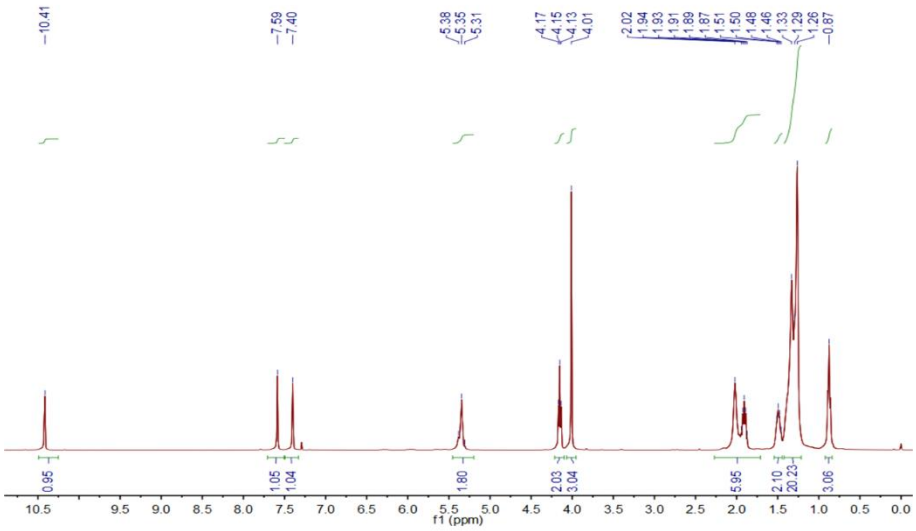

7.78
7.76
7.43
7.41
5.38
5.35
5.34
5.32
4.01
3.99
3.98
2.43
2.02
2.00
1.99
1.94
1.27
1.23
1.21
0.88
0.87
0.86
1.99
2.01
1.76
2.04
3.07
4.00
2.05
22.10
3.13
f1 (ppm)

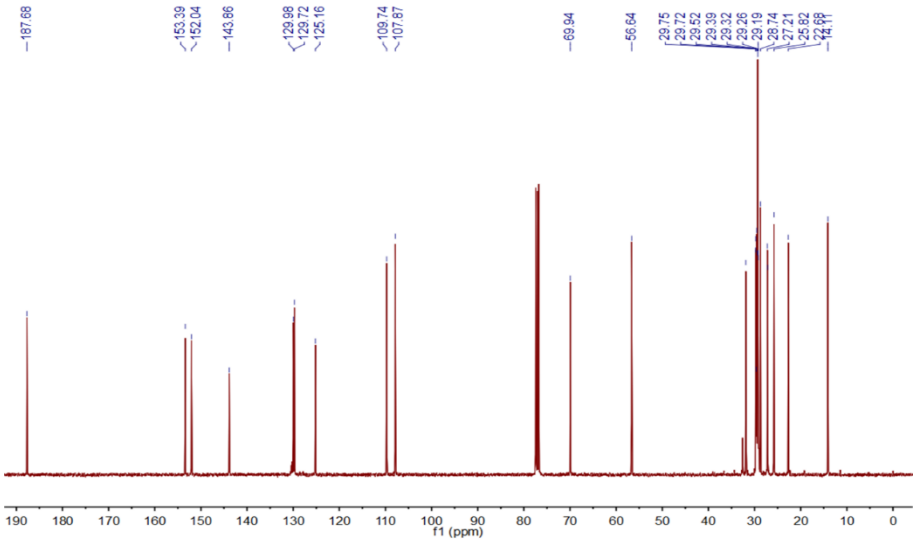

146.14
134.06
130.94
130.70
128.69
71.96
32.65
30.48
30.41
30.21
30.07
29.99
29.96
29.82
29.51
29.37
27.80
25.96
23.40
21.66
14.42
f1 (ppm)

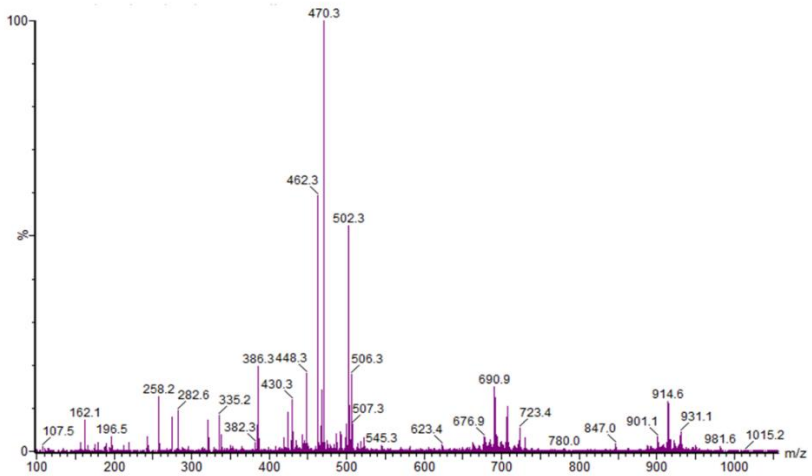

445.3
446.3
440.3
447.3
187.1
212.1
289.0
367.0
520.3
568.3
633.2
692.4
837.5
864.6
1076.2
%
m/z

Compound **12**

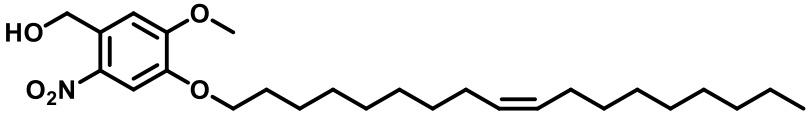


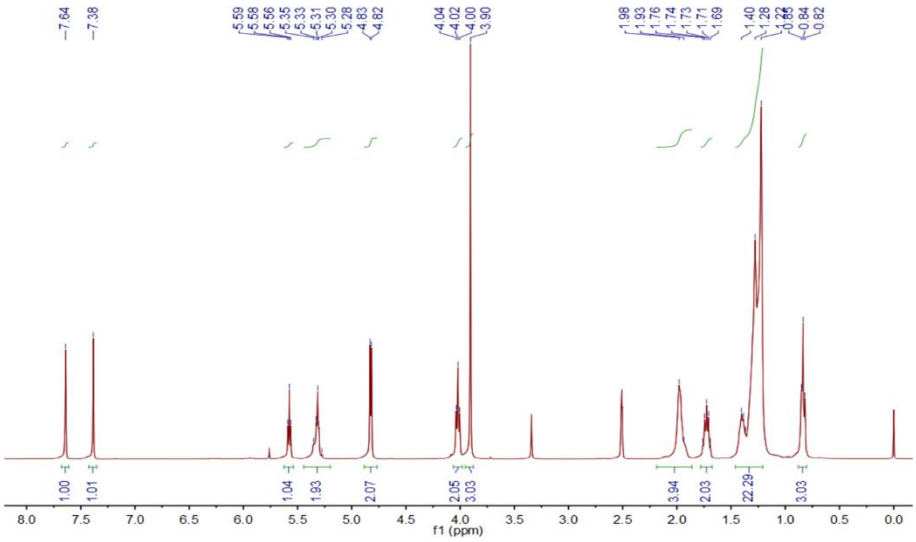

10.41
7.59
7.40
5.38
5.35
5.31
4.17
4.15
4.13
4.01
2.02
1.94
1.93
1.91
1.89
1.87
1.51
1.50
1.48
1.46
1.33
1.29
1.26
0.87
0.95
1.05
1.04
1.80
2.03
3.04
5.95
2.10
20.23
3.06
f1 (ppm)

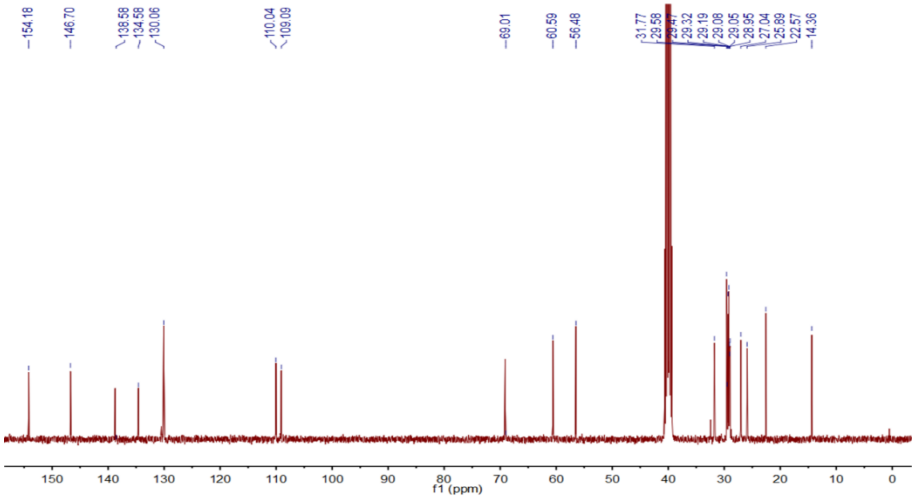

187.68
153.39
152.04
143.86
129.98
129.72
125.16
109.74
107.87
69.94
56.64
29.75
29.72
29.52
29.39
29.32
29.26
29.19
28.74
27.21
25.82
22.68
14.11
f1 (ppm)

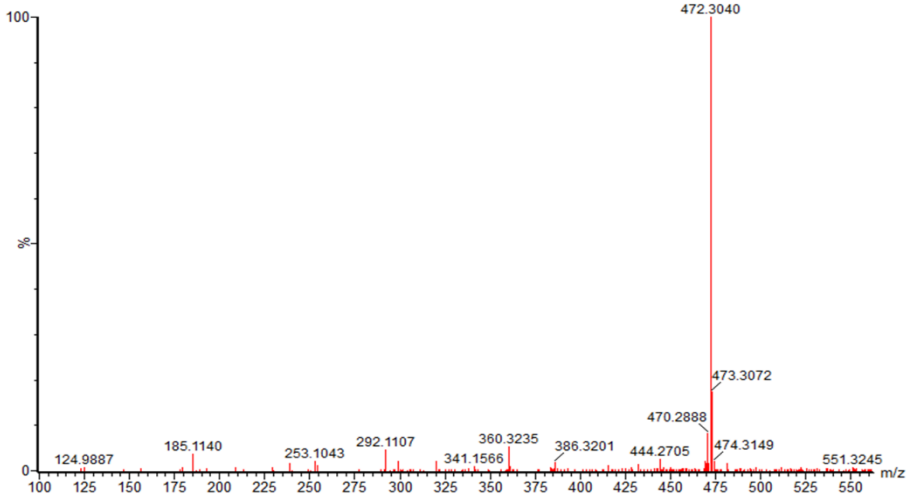

100
%
0
470.3
462.3
502.3
386.3
448.3
506.3
430.3
258.2
282.6
335.2
690.9
914.6
162.1
196.5
382.3
507.3
723.4
931.1
107.5
545.3
623.4
676.9
847.0
901.1
780.0
981.6
1015.2
m/z

Compound **NB18**

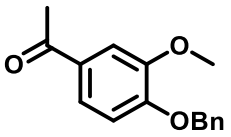


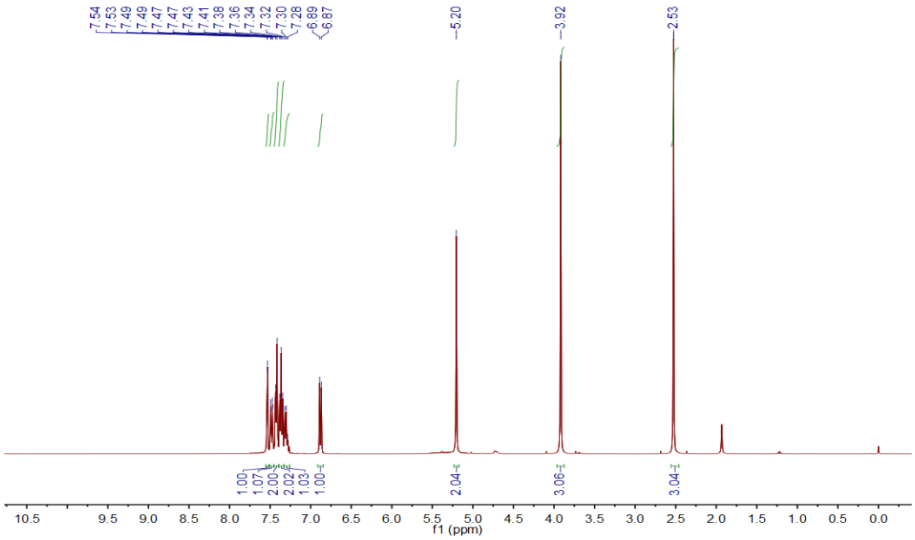


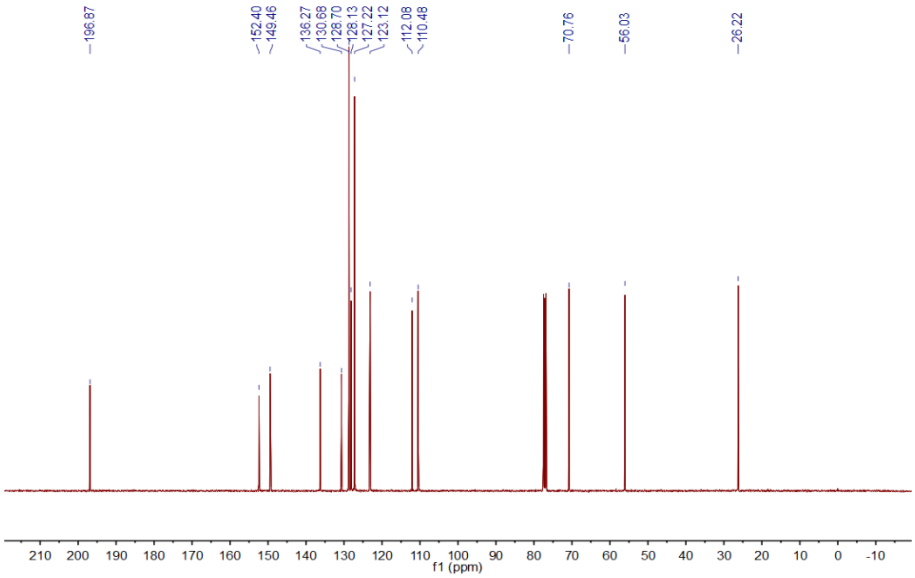


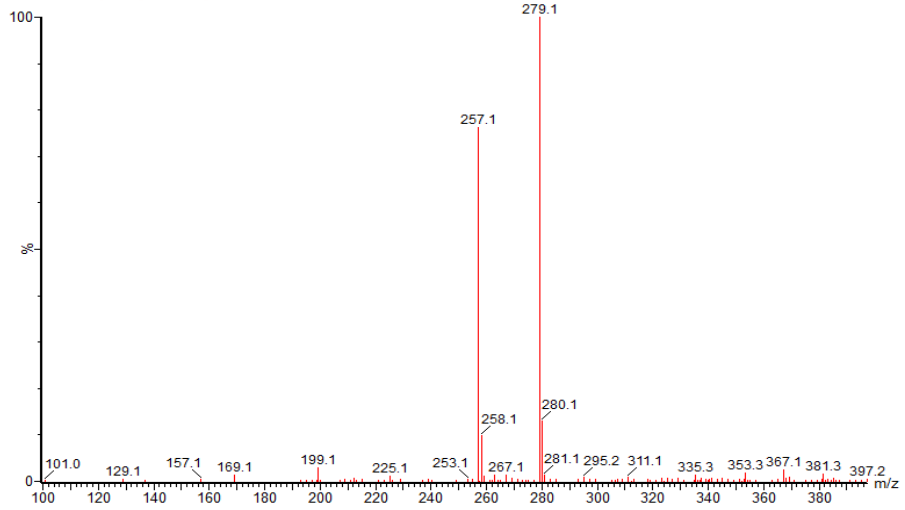


Compound **13**

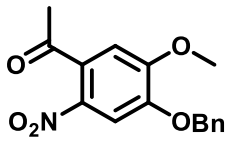

O
O
OBn

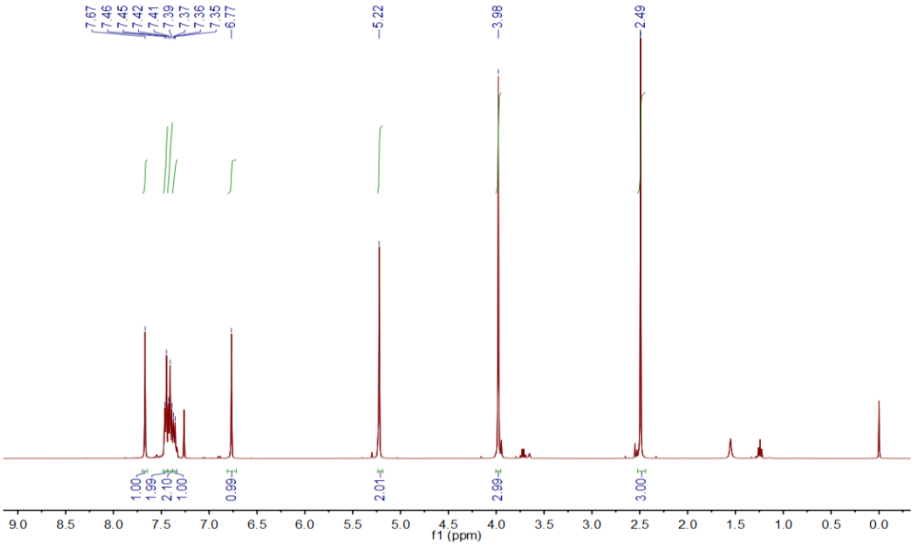

7.54
7.53
7.49
7.49
7.47
7.47
7.43
7.41
7.38
7.36
7.34
7.32
7.30
7.28
6.89
6.87
5.20
3.92
2.53
1.00
1.07
2.00
2.02
1.03
1.00
2.04
3.06
3.04
f1 (ppm)

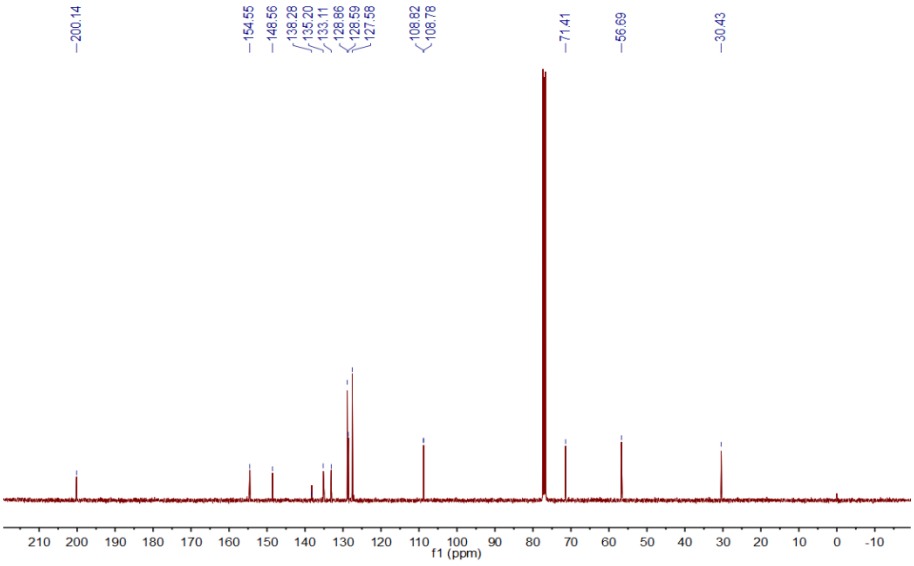

196.87
152.40
149.46
136.27
130.68
128.70
128.13
127.22
123.12
112.08
110.48
70.76
56.03
26.22
f1 (ppm)

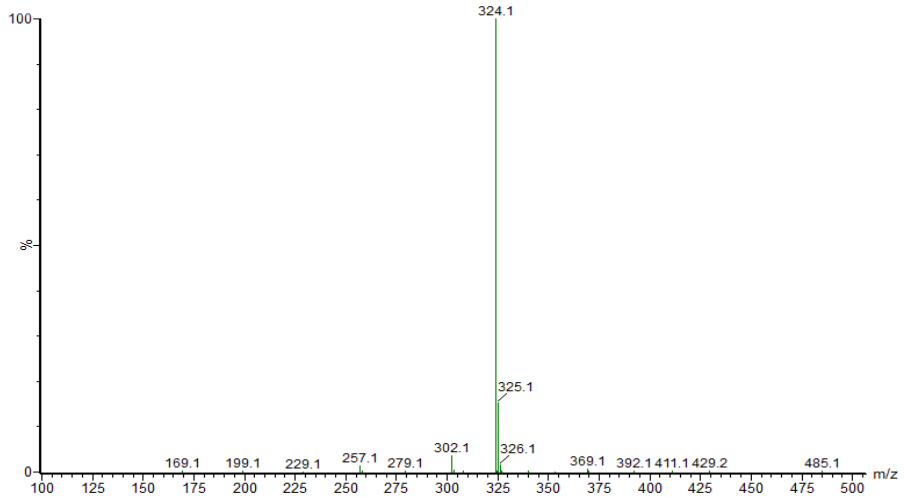

100
%
0
279.1
257.1
280.1
258.1
101.0
129.1
157.1
169.1
199.1
225.1
253.1
267.1
281.1
295.2
311.1
335.3
353.3
367.1
381.3
397.2
m/z

Compound **14**

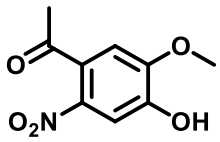

O
O
O2N
OBn

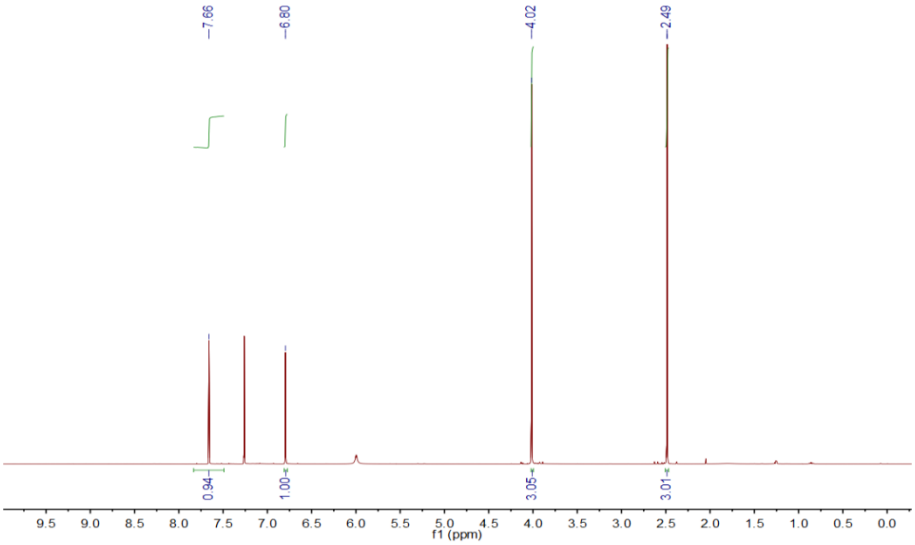

7.67
7.46
7.45
7.42
7.41
7.39
7.37
7.36
7.35
6.77
5.22
3.98
2.49
1.00
1.99
2.10
1.00
0.99
2.01
2.99
3.00
f1 (ppm)

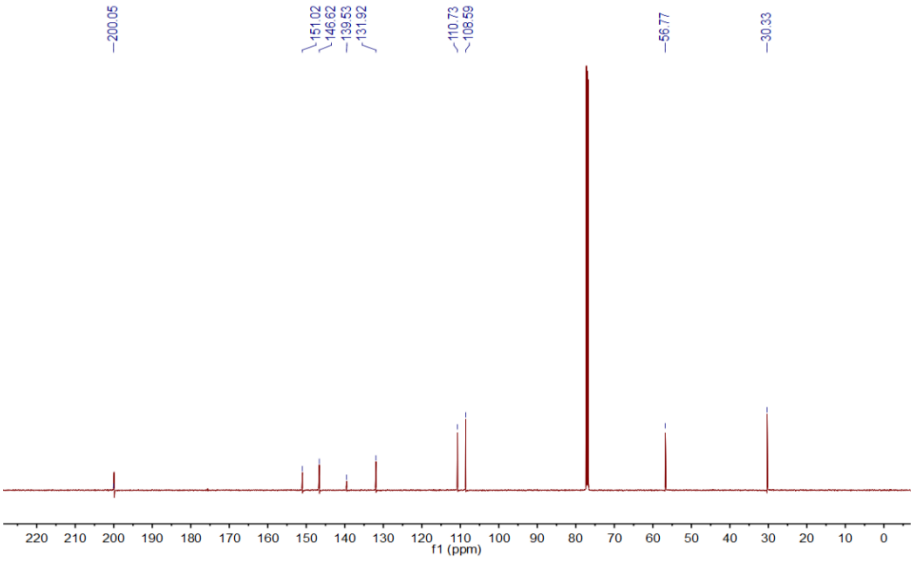

200.14
154.55
148.56
138.28
135.20
133.11
128.86
128.59
127.58
108.82
108.78
71.41
56.69
30.43
f1 (ppm)

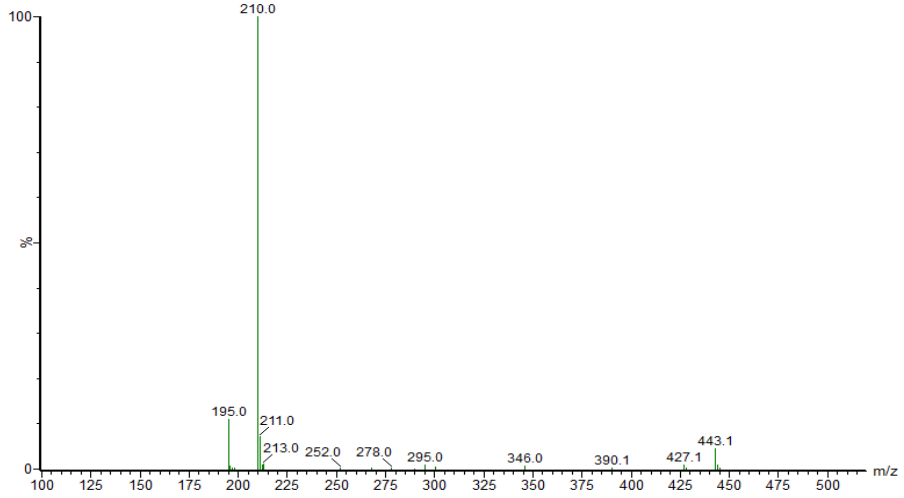

100
%
0
324.1
325.1
326.1
302.1
257.1
279.1
229.1
199.1
169.1
369.1
392.1
411.1
429.2
485.1
m/z

Compound **15**

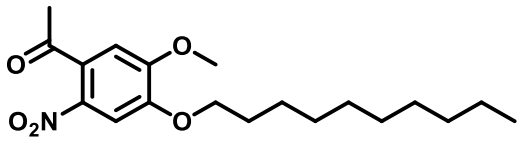

O
O
O2N
OH

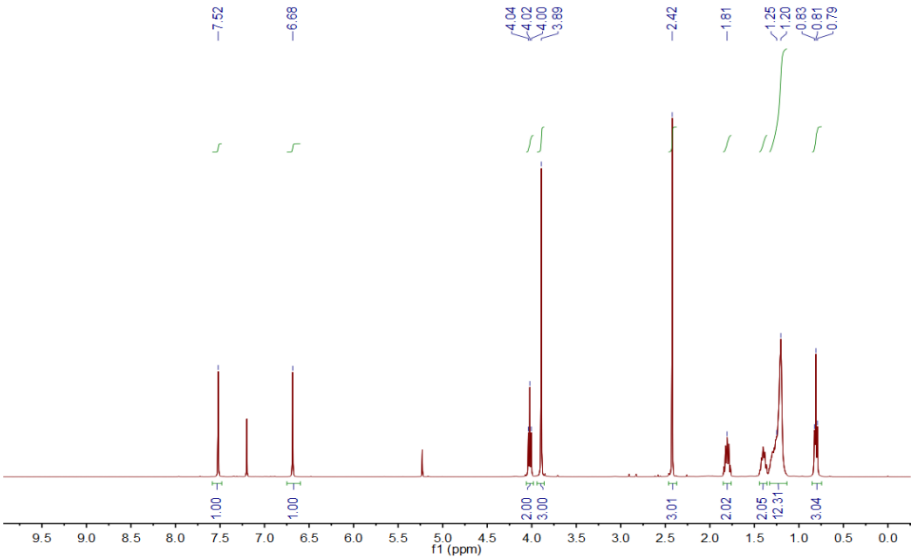

7.66
6.80
4.02
2.49
0.94
1.00
3.05
3.01
f1 (ppm)

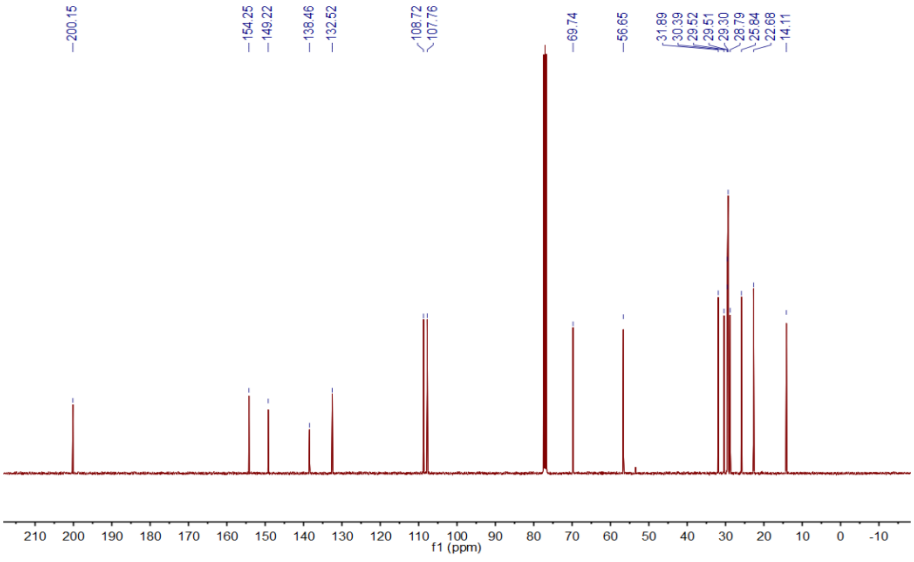

200.05
151.02
146.62
139.53
131.92
110.73
108.59
56.77
30.33
f1 (ppm)


100
%
0
210.0
195.0
211.0
213.0
252.0
278.0
295.0
346.0
390.1
427.1
443.1
m/z

Compound **16**

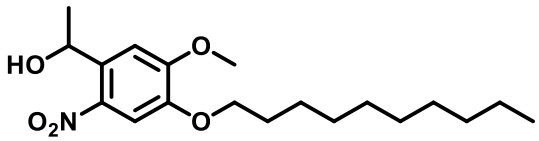

O
O
O2N
O

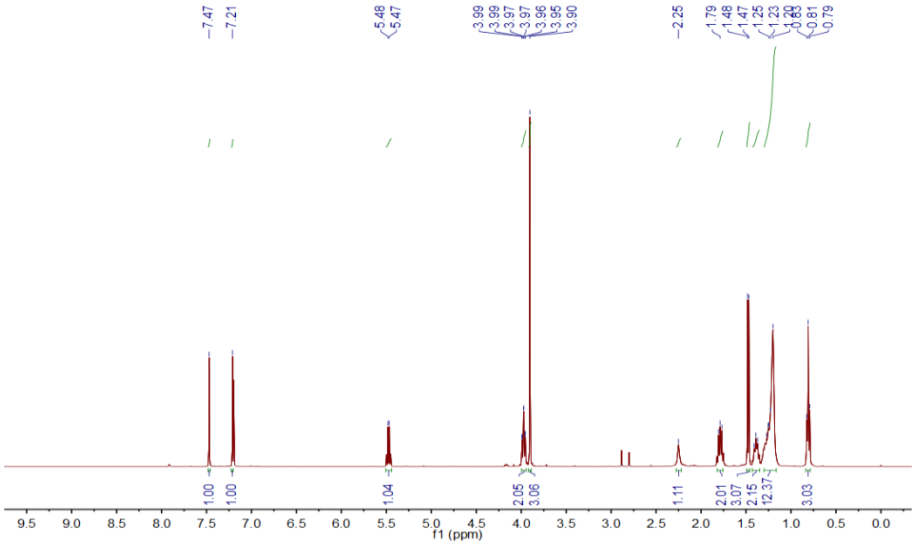

7.52
6.68
4.04
4.02
4.00
3.89
2.42
1.81
1.25
1.20
0.83
0.81
0.79
1.00
1.00
2.00
3.00
3.01
2.02
2.05
12.31
3.04
f1 (ppm)

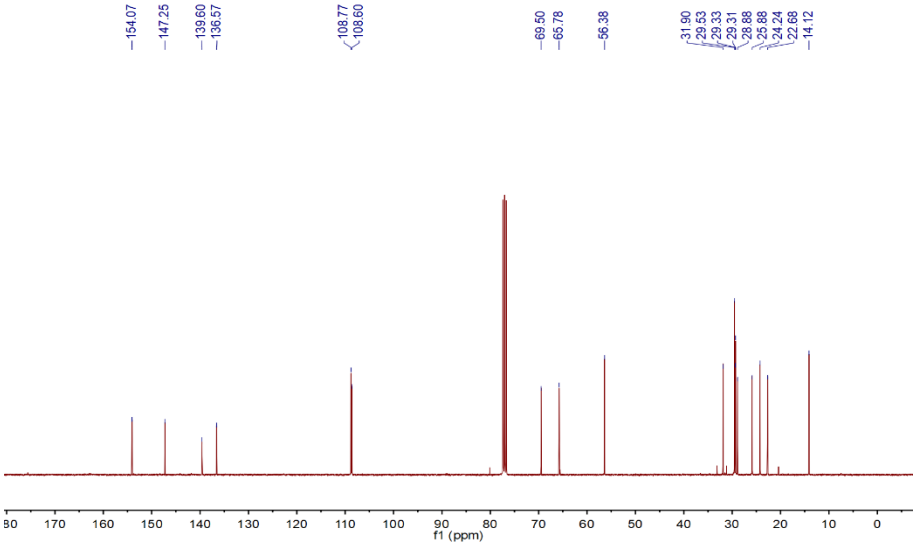

200.15
154.25
149.22
138.46
132.52
108.72
107.76
69.74
56.65
31.89
30.39
29.52
29.51
29.30
28.79
25.84
22.68
14.11
f1 (ppm)

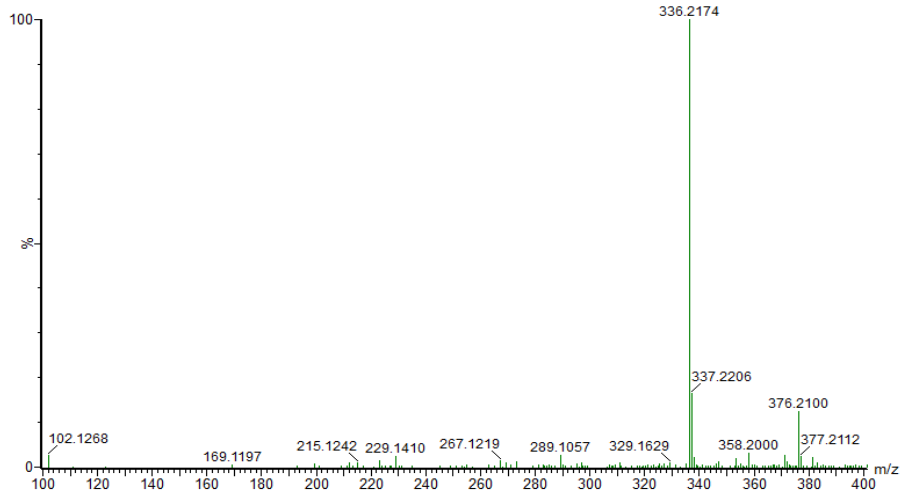

374.1942
352.2121
375.1971
169.1201
199.1298
229.1413
267.1202
324.0842
376.1992
425.2151
485.1121
519.1385
%
m/z

Compound **17**


HO
O
O
O_2N


7.47
7.21
5.48
5.47
3.99
3.97
3.96
3.95
3.90
2.25
1.79
1.48
1.47
1.25
1.23
0.81
0.79
1.00
1.00
1.04
2.05
3.06
1.11
2.01
3.07
2.15
12.37
3.03
f1 (ppm)


154.07
147.25
139.60
136.57
108.77
108.60
69.50
65.78
56.38
31.90
29.53
29.33
29.31
28.88
25.88
24.24
22.68
14.12
f1 (ppm)


336.2174
337.2206
376.2100
377.2112
102.1268
169.1197
215.1242
229.1410
267.1219
289.1057
329.1629
358.2000
%
m/z

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