Supplementary Information (SI) for ChemComm.
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Visible-light-mediated aerobic nitrooxylation for the synthesis of nitrate esters with *t*-BuONO

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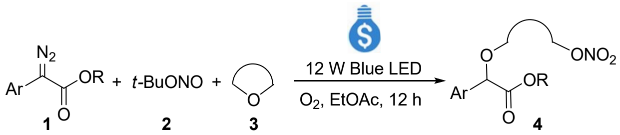
1.General information

All commercially available reagent grade chemicals were purchased from Macklin, MCMEC, Bidepharm and Energy Chemical Company and used as received without further purification unless otherwise stated. The solvents were used as analytical reagent grade. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ on a Bruker Avance III spectrometer with TMS as internal standard (400 MHz ^{1}H, 101 MHz ^{13}C or 500 MHz ^{1}H, 126 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh).

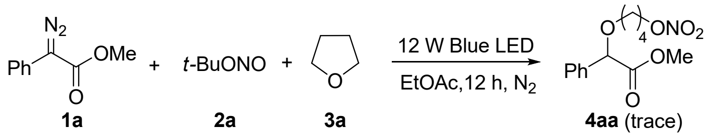
2.General procedure for synthesis of organic nitrate esters



To a mixture of α-diazo ester **1** (0.2 mmol, 1.0 equiv), t-BuONO **2** (0.4 mmol, 47.5 μL), and cyclic ether **3** (Analytical Reagent, 1.5 mL) was added ethyl acetate (Analytical Reagent, 0.5 mL). The reaction mixture was open to molecular oxygen (balloon) and stirred under the irradiation of 12 W blue LEDs at room temperature for 12 h. After completion of the reaction, the reaction mixture was concentrated to remove solvent. The residue was purified by column chromatography (eluent: petroleum ether and ethyl acetate) to afford the product **4**.

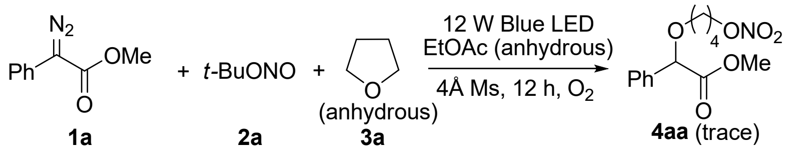
3. Preliminary mechanistic studies

3.1 The model reaction was conducted under N_2.



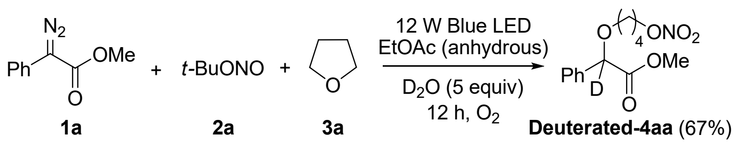
To a mixture of methyl phenyldiazoacetate **1a** (0.2 mmol, 35.2 mg), t-BuONO **2a** (0.4 mmol, 48 μL), and THF **2a** (Analytical Reagent, 1.5 mL) was added ethyl acetate (AR, 0.5 mL). The reaction mixture was stirred under N_2 with the irradiation of 12 W blue LEDs at room temperature for 12 h. After completion of the reaction, the reaction mixture was concentrated to remove solvent. None of desired product **4aa** was detected.

3.2 The model reaction was conducted in anhydrous solvent.

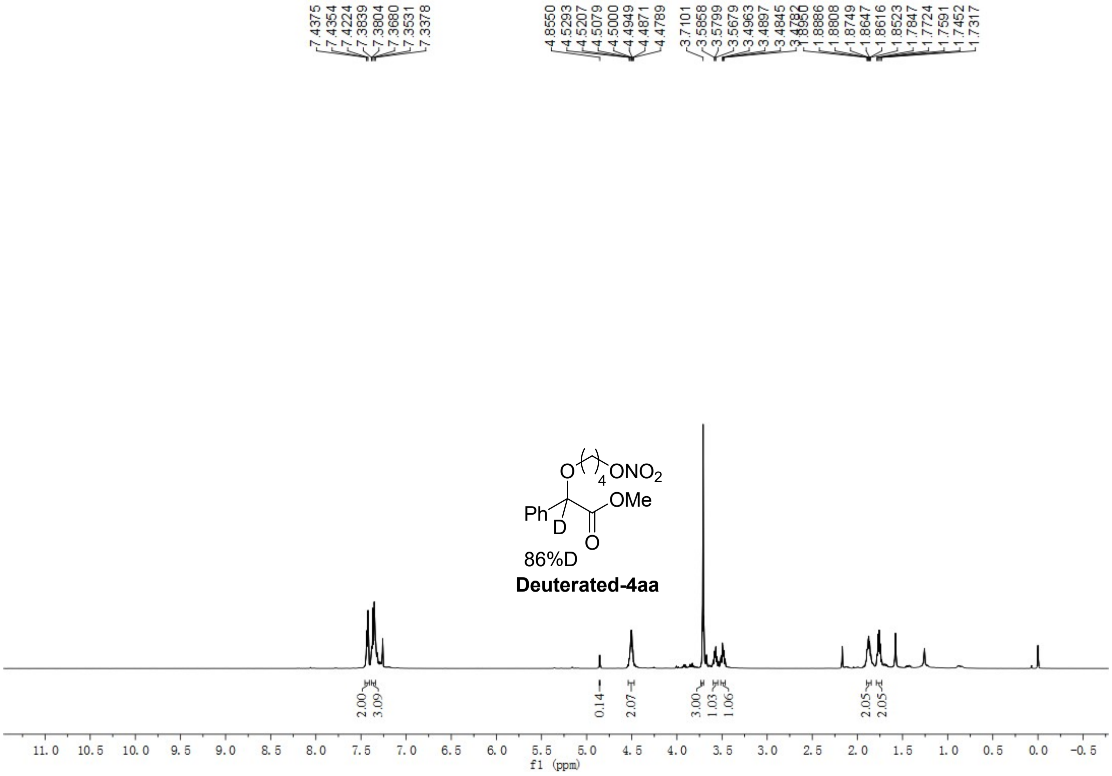


To a mixture of methyl phenyldiazoacetate **1a** (0.2 mmol, 35.2 mg), t-BuONO **2a** (0.4 mmol, 48 μL), 4ÅMS (50 mg) and anhydrous THF **2a** (1.5 mL) was added anhydrous ethyl acetate (0.5 mL). The reaction mixture was stirred under molecular oxygen (balloon) with the irradiation of 12 W blue LEDs at room temperature for 12 h. After completion of the reaction, the reaction mixture was concentrated to remove solvent. The desired product **4aa** was not detected.

3.3The model reaction was conducted in the presence of D_2O.

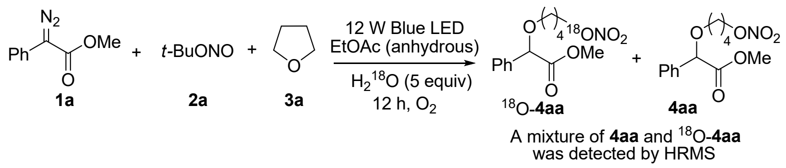


To a mixture of methyl phenyldiazoacetate (0.2 mmol, 35.2 mg), t-BuONO **2a** (0.4 mmol, 48 μL), D_2O (1 mmol, 20 μL) and anhydrous THF **3a** (1.5 mL) was added anhydrous ethyl acetate (0.5 mL). The reaction mixture was stirred under molecular oxygen (balloon) with the irradiation of 12 W blue LEDs at room temperature for 12 h. After completion of the reaction, the solution was concentrated to remove solvent, the product **D-4aa** was obtained in 67% yield (38 mg). The product **D-4aa** was determined by ^{1}H NMR.

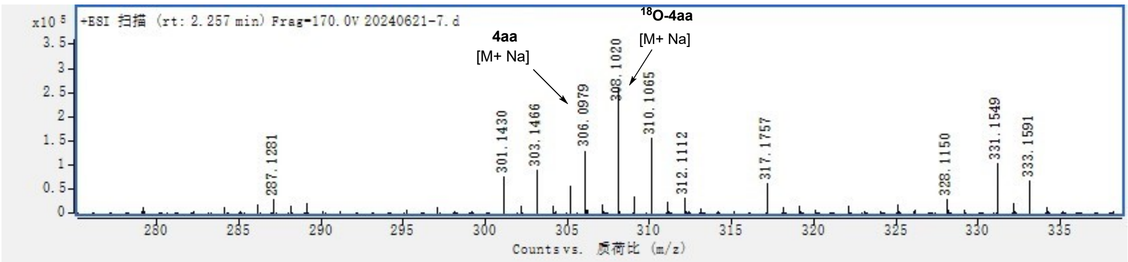


Deuterated-4aa

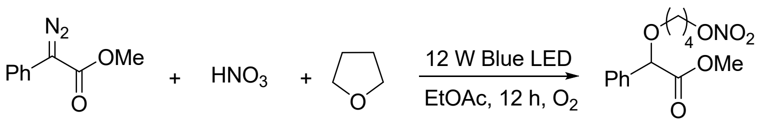
3.4 The model reaction was conducted in the presence of $H_2{}^{18}O$ under O_2.



To a mixture of methyl phenyldiazoacetate **1a** (0.2 mmol, 35.2 mg), t-BuONO **2a** (0.4 mmol, 48 μL), $H_2{}^{18}O$ (1 mmol, 20 μL) and anhydrous THF **3a** (1.5 mL) was added anhydrous ethyl acetate (0.5 mL). The reaction mixture was stirred under molecular oxygen (balloon) with the irradiation of 12 W blue LEDs at room temperature for 12 h. After completion of the reaction, a mixture of **4aa** and ^{18}O-**4aa** was detected by HRMS.



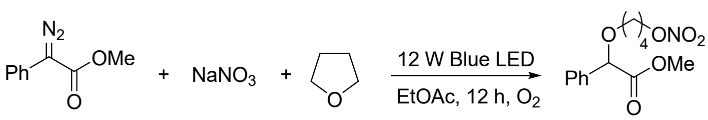
3.5 The reaction of α-diazoester (1a), THF (3a), and HNO_3.



1a **3a** **4aa** (53%)

To a mixture of methyl phenyldiazoacetate (0.2 mmol, 35.2 mg), HNO_3 (0.4 mmol, 28 μL), and THF **3a** (Analytical Reagent, 1.5 mL) was added ethyl acetate (AR, 0.5 mL). The reaction mixture was stirred under molecular oxygen (balloon) with the irradiation of 12 W blue LEDs at room temperature for 12 h. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by column chromatography (eluent: petroleum ether and ethyl acetate 10:1) to afford the product **4aa** in 53% yield (30 mg).

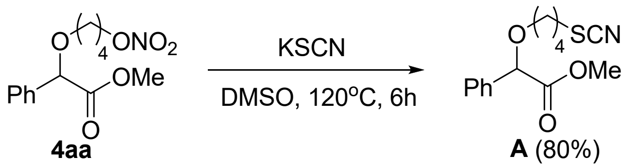
3.6 The reaction of α-diazoester (1a), THF (3a), and $NaNO_3$.



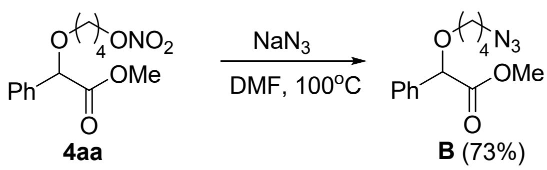
1a **3a** **4aa** (51%)

To a mixture of methyl phenyldiazoacetate (0.2 mmol, 35.2 mg), $NaNO_3$ (0.4 mmol, 34 mg), and THF **3a** (Analytical Reagent, 1.5 mL) was added ethyl acetate (AR, 0.5 mL). The reaction mixture was stirred under molecular oxygen (balloon) with the irradiation of 12 W blue LEDs at room temperature for 12 h. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by column chromatography (eluent: petroleum ether and ethyl acetate 10:1) to afford the product **4aa** in 51% yield (29 mg) .

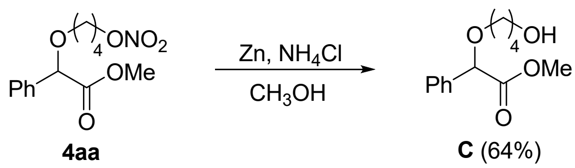
4. Synthetic transformations of product.



Oranic nitrate ester **4aa** (0.1 mmol, 30.5 mg) and KSCN (0.4 mmol, 38.8 mg) were added in a 25 mL reaction tube. Then, DMSO (2 mL) was added to the above mixture. The reaction mixture was stirred at 120°C for 6 h. After completion of the reaction, the reaction mixture was concentrated in vacuum, the desired organic thiocyanate **A** was obtained in 80% yield (22.3 mg).

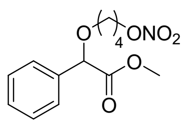


Oranic nitrate ester **4aa** (0.1 mmol, 30.5 mg) and NaN_3 (0.3 mmol, 19.5 mg) were added in a 25 mL reaction tube. Then, DMF (2 mL) was added to the above mixture. The reaction mixture was stirred at 100°C for 6 h. After completion of the reaction, the reaction mixture was concentrated in vacuum, the desired organic thiocyanate **B** was obtained in 73% yield (19.2 mg).

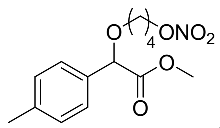


Oranic nitrate ester **4aa** (0.1 mmol, 30.5 mg), NH_4Cl (0.3 mmol, 16 mg) H_2O (1 mmol, 18ul) and Zn (0.35 mmol, 23 mg) were added in a 25 mL reaction tube. Then, CH_3OH (2 mL) was added to the above mixture. The reaction mixture was stirred at 80°C for 4 h. After completion of the reaction, the reaction mixture was concentrated in vacuum, the desired compound **C** was obtained in 64% yield (15.2 mg).

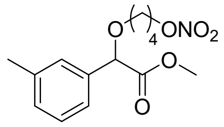
4.Characterization data of products



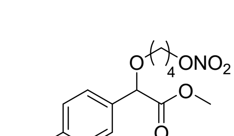
*methyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4aa**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4aa** (42.0mg, 74% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.34-7.39 (m, 3H), 4.86 (s, 1H), 4.49-5.53 (m, 2H), 3.71 (s, 3H), 3.55-3.61 (m, 1H), 3.46-3.51 (m, 1H), 1.85-1.90 (m, 2H), 1.74-1.79 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 171.3, 136.4, 128.8, 128.7, 127.1, 81.1, 73.1, 68.9, 52.3, 25.8, 23.9. ESI HRMS: calculated for $C_{13}H_{17}NO_6Na$ $[M+Na]^+$ 306.0956, found 306.0980.



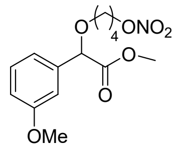
*methyl 2-(4-(nitrooxy)butoxy)-2-(p-tolyl)acetate (**4ba**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4ba** (35.8mg, 60% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.82 (s, 1H), 4.48-4.52 (m, 2H), 3.70 (s, 3H), 3.53-3.60 (m, 1H), 3.44-3.49 (m, 1H), 2.35 (s, 3H), 1.83-1.90 (m, 2H), 1.71-1.78 (m 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 171.4, 138.7, 133.4, 129.4, 127.1, 80.9, 73.1, 68.7, 52.3, 25.8, 23.8, 21.2. ESI HRMS: calculated for $C_{14}H_{19}NO_6Na$ $[M+Na]^+$ 320.1110, found 320.1115.



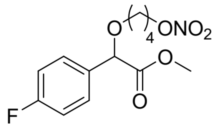
*methyl 2-(4-(nitrooxy)butoxy)-2-(m-tolyl)acetate (**4ca**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4ca** (38.0mg, 64% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.26 (m, 3H), 7.15 (d, J = 7.2 Hz, 1H), 4.81 (s, 1H), 4.49-4.52 (m, 2H), 3.71 (s, 3H), 3.54-3.59 (m, 1H), 3.46-3.50 (m, 1H), 2.36 (s, 3H), 1.85-1.89 (m, 2H), 1.74-1.78 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 171.4, 138.5, 136.3, 129.6, 128.6, 127.8, 124.3, 81.2, 73.1, 68.8, 52.3, 25.8, 23.8, 21.4. ESI HRMS: calculated for $C_{14}H_{19}NO_6Na$ $[M+Na]^+$ 320.1110, found 320.1168.



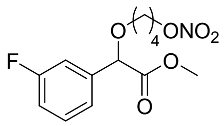
*methyl 2-(4-(tert-butyl)phenyl)-2-(4-(nitrooxy)butoxy)acetate (**4da**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4da** (49.0 mg, 72% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.83 (s, 1H), 4.47-4.53 (m, 2H), 3.71 (s, 3H), 3.54-3.58 (m, 1H), 3.46-3.51 (m, 1H), 1.86-1.89 (m, 2H), 1.74-1.78 (m, 2H), 1.31 (s, 9H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 171.5, 151.8, 133.3, 126.9, 125.7, 80.9, 73.1, 68.8, 52.2, 34.6, 31.3, 31.3, 25.8, 23.8. ESI HRMS: calculated for $C_{17}H_{25}NO_6Na$ $[M+Na]^+$ 362.1580, found 362.1581.



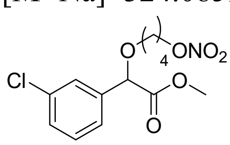
*methyl 2-(3-methoxyphenyl)-2-(4-(nitrooxy)butoxy)acetate (**4ea**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 8:1, v/v) to afford **4ea** (45.0mg, 72% yield), Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-7.30 (m, 1H), 6.98-7.02 (m, 2H), 6.87-6.89 (m, 1H), 4.83 (s, 1H), 4.49-4.53 (m, 2H), 3.81 (s, 3H), 3.71 (s, 3H), 3.54-3.59 (m, 1H), 3.46-3.52 (m, 1H), 1.84-1.90 (m, 3H), 1.74-1.79 (m, 2H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 171.2, 159.8, 137.8, 129.7, 119.5, 114.5, 112.4, 81.0, 73.1, 68.9, 55.3, 52.3, 25.8, 23.9. ESI HRMS: calculated for $C_{14}H_{19}NO_7Na$ $[M+Na]^+$ 336.1059, found 336.1066.



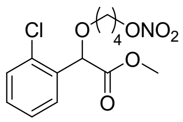
*methyl 2-(4-fluorophenyl)-2-(4-(nitrooxy)butoxy)acetate (**4fa**)*.The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 9:1, v/v) to afford **4fa** (48.5mg, 81% yield), Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.39-7.43 (m, 2H), 7.03-7.07 (m, 2H), 4.84 (s, 1H), 4.49-4.53 (m, 2H), 3.72 (s, 3H), 3.55-3.61 (m, 1H), 3.45-3.51 (m, 1H), 1.84-1.90 (m, 2H), 1.72-1.79 (m, 2H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 171.1, 162.9 (d, J = 246.2 Hz), 132.2 (d, J = 3.2 Hz), 128.9 (d, J = 8.1 Hz), 115.7(d, J = 21.6 Hz), 80.4, 73.0, 68.9, 52.4, 25.8, 23.8. ESI HRMS: calculated for $C_{13}H_{16}FNO_6Na$ $[M+Na]^+$ 324.0859, found 324.0862.



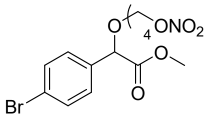
*methyl 2-(3-fluorophenyl)-2-(4-(nitrooxy)butoxy)acetate (**4ga**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 9:1, v/v) to afford **4ga** (53.5 mg, 89% yield), Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.31-7.36 (m, 1H), 7.21 (d, J = 7.7 Hz, 1H), 7.15-7.18 (m, 1H), 7.01-7.06 (m, 1H), 4.86 (s, 1H), 4.49-4.55 (m, 2H), 3.73 (s, 3H), 3.57-3.62 (m, 1H), 3.47-3.53 (m, 1H), 1.86-1.93 (m, 2H), 1.74-1.81 (m, 2H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.8, 162.9 (d, J = 244.9 Hz), 138.8 (d, J = 7.3 Hz), 130.2 (d, J = 8.1 Hz), 122.7 (d, J = 3.0 Hz), 115.7 (d, J = 21.0 Hz), 114.1(d, J = 22.4 Hz), 80.4 (d, J = 1.8 Hz), 73.0, 69.1, 52.4, 25.8, 23.8. ESI HRMS: calculated for $C_{13}H_{16}FNO_6Na$ $[M+Na]^+$ 324.0859, found 324.0860.



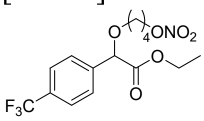
*methyl 2-(3-chlorophenyl)-2-(4-(nitrooxy)butoxy)acetate (**4ha**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4ha** (52.0mg, 82% yield), Yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.43-7.44 (m, 1H), 7.30-7.33 (m, 3H), 4.83 (s, 1H), 4.50-4.53 (m, 2H), 3.73 (s, 3H), 3.56-3.62 (m, 1H), 3.47-3.52 (m, 1H), 1.85-1.91 (m, 2H), 1.75-1.80 (m, 2H); $^{13}C\{1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.7, 138.3, 134.6, 130.0, 128.9, 127.2, 125.2, 80.4, 73.0, 69.1, 52.5, 25.8, 23.8. ESI HRMS: calculated for $C_{13}H_{16}ClNO6Na$ [M+Na]+ 340.0564, found 340.0577.



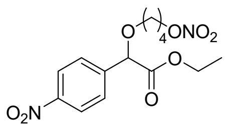
methyl 2-(2-chlorophenyl)-2-(4-(nitrooxy)butoxy)acetate ***(4ia)***. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4ia** (47.0mg, 76% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.49 (m, 1H), 7.39-7.41 (m, 1H), 7.28-7.31 (m, 2H), 5.35 (s, 1H), 4.47-4.51 (m, 2H), 3.73 (s, 3H), 3.62-3.68 (m, 1H), 3.49-3.54 (m, 1H), 1.84-1.90 (m, 2H), 1.73-1.78 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.7, 134.5, 133.8, 130.0, 129.7, 128.7, 127.3, 77.3, 73.0, 69.3, 52.4, 25.8, 23.8. ESI HRMS: calculated for $C_{13}H_{16}ClNO_6Na$ $[M+Na]^+$ 340.0564, found 340.0578.



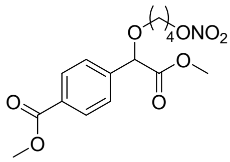
methyl 2-(4-bromophenyl)-2-(4-(nitrooxy)butoxy)acetate ***(4ja)***. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4ja** (49.0mg, 68% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.51 (m, 2H), 7.30-7.33 (m, 2H), 4.81 (s, 1H), 4.49-4.53 (m, 2H), 3.71 (s, 3H), 3.56-3.61 (m, 1H), 3.45-3.50 (m, 1H), 1.86-1.90 (m, 2H), 1.74-1.79 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.8, 135.4, 131.8, 128.7, 122.9, 80.4, 73.0, 69.1, 52.4, 25.8, 23.8. ESI HRMS: calculated for $C_{13}H_{16}BrNO_6Na$ [M+Na]+ 384.0059, found 384.0043.



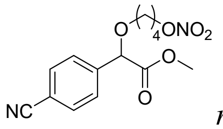
ethyl 2-(4-(nitrooxy)butoxy)-2-(4-(trifluoromethyl)phenyl)acetate ***(4ka)***. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 8:1, v/v) to afford **4ka** (49.0mg, 67% yield), Yellow oil. ^{1}H NMR (500MHz, $CDCl_3$): δ 7.63 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.2 Hz, 2H), 4.89 (s, 1H), 4.51-4.54 (m, 2H), 4.14-4.22 (m, 2H), 3.61-3.66 (m, 1H), 3.49-3.53 (m, 1H), 1.87-1.91 (m, 2H), 1.77-1.81 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (126 MHz, $CDCl_3$): 170.2, 140.4, 130.8 (d, J = 32.3 Hz), 128.9, 127.3, 125.6 (q, J = 3.8 Hz), 123.9 (d, J = 272.6 Hz), 80.6, 73.0, 69.2, 61.6, 25.8, 23.9, 14.1. ESI HRMS: calculated for $C_{15}H_{18}F_3NO_6Na$ $[M+Na]^+$ 388.0984, found 388.1006.



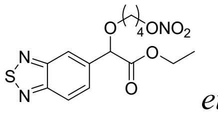
ethyl 2-(4-(nitrooxy)butoxy)-2-(4-nitrophenyl)acetate ***(4la)***. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 8:1, v/v) to afford **4la** (48.0mg, 70% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.7 Hz, 2H), 4.95 (s, 1H), 4.54 (t, J = 6.7 Hz, 2H), 4.16-4.23 (m, 2H), 3.65-3.71 (m, 1H), 3.52-3.57 (m, 1H), 1.88-1.93 (m, 2H), 1.79-1.84 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 169.7, 148.0, 143.5, 127.8, 123.8, 80.2, 73.0, 69.5, 61.8, 25.8, 23.9, 14.1. ESI HRMS: calculated for $C_{14}H_{18}N_2O_8Na$ $[M+Na]^+$ 365.0961, found 365.0982.



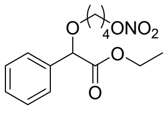
*methyl 4-(2-methoxy-1-(4-(nitrooxy)butoxy)-2-oxoethyl)benzoate (**4ma**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 8:1, v/v) to afford **4ma** (56.5mg, 83% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 4.91 (s, 1H), 4.50-4.53 (m, 2H), 3.92 (s, 3H), 3.72 (s, 3H), 3.60-3.64 (m, 1H), 3.48-3.52 (m, 1H), 1.86-1.91 (m, 2H), 1.75-1.81 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.7, 166.7, 141.2, 130.5, 129.9, 127.0, 80.7, 73.0, 69.2, 52.5, 52.2, 25.8, 23.8. ESI HRMS: calculated for $C_{15}H_{19}NO_8Na$ $[M+Na]^+$ 364.1008, found 364.1009.



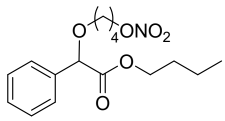
*methyl 2-(4-cyanophenyl)-2-(4-(nitrooxy)butoxy)acetate **(4na)*** The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 8:1, v/v) to afford **4na** (33.2 mg, 54% yield), Yellow oil. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.67 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 4.91 (s, 1H), 4.53 (t, J = 6.5 Hz, 2H), 3.73 (s, 3H), 3.62-3.65 (m, 1H), 3.49-3.54 (m, 1H), 1.86-1.92 (m, 2H), 1.77-1.82 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.3, 141.5, 132.5, 127.6, 118.5, 112.6, 80.4, 72.9, 69.5, 52.7, 25.8, 23.8. ESI HRMS: calculated for $C_{14}H_{16}N_2O_6Na$ $[M+Na]^+$ 331.0906, found 331.0914.



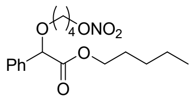
*ethyl 2-(benzo[c][1,2,5]thiadiazol-5-yl)-2-(4-(nitrooxy)butoxy)acetate (**4oa**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 8:1, v/v) to afford **4oa** (52.0 mg, 74% yield), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (s, 1H), 8.01 (d, J = 9.1 Hz, 1H), 7.70-1.72 (m, 1H), 5.02 (s, 1H), 4.52-4.55 (m, 2H), 4.16-4.25 (m, 2H), 3.66-3.71 (m, 1H), 3.55-3.59 (m, 1H), 1.89-1.94 (m, 2H), 1.80-1.84 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (126 MHz, $CDCl_3$): δ 170.0, 154.8, 154.6, 138.3, 128.2, 121.8, 119.9, 80.8, 73.0, 69.3, 61.7, 25.9, 23.9, 14.1. ESI HRMS: calculated for $C_{14}H_{17}N_3O_6SNa$ $[M+Na]^+$ 378.0736, found 378.0773.



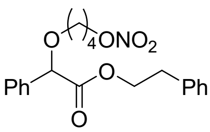
*ethyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4pa**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4pa** (39.5mg, 66% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.45 (m, 2H), 7.33-7.38 (m, 3H), 4.84 (s, 1H), 4.49-4.53 (m, 2H), 4.12-4.22 (m, 2H), 3.56-3.61 (m, 1H), 3.47-3.52 (m, 1H), 1.85-1.90 (m, 2H), 1.73-1.79 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.8, 136.5, 128.7, 128.6, 127.1, 81.2, 73.1, 68.8, 61.3, 25.8, 23.9, 14.1. ESI HRMS: calculated for $C_{14}H_{19}NO_6Na$ $[M+Na]^+$ 320.1110, found 320.1123.



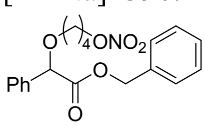
*butyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4qa**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4qa** (34.0mg, 52% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.33-7.38 (m 3H), 4.84 (s, 1H), 4.49- 4.53 (m, 2H), 4.09-4.13 (m, 2H), 3.56-3.62 (m, 1H), 3.47-3.52 (m, 1H), 1.85-1.91 (m, 2H), 1.73-1.79 (m, 2H), 1.54-1.57 (m, 2H), 1.23-1.31 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.9, 136.6, 128.7, 128.6, 127.1, 81.2, 73.1, 68.8, 65.1, 30.5, 25.8, 23.9, 18.9, 13.6. ESI HRMS: calculated for $C_{16}H_{23}NO_6Na$ $[M+Na]^+$ 348.1423, found 348.1434.



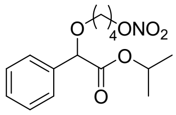
*pentyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4ra**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4ra** (33.0mg, 49% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.45 (m, 2H), 7.33-7.38 (m, 3H), 4.84 (s, 1H), 4.49- 4.53 (m, 2H), 4.10 (t, J = 6.7 Hz, 2H), 3.56-3.62 (m, 1H), 3.48-3.52 (m, 1H), 1.85-1.92 (m, 2H), 1.73-1.80 (m, 2H), 1.55-1.60 (m, 2H), 1.19-1.24 (m, 4H), 0.84 (t, J = 7.1 Hz, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.9, 136.6, 128.7, 128.6, 127.1, 81.2, 73.1, 68.8, 65.3, 28.2, 27.8, 25.8, 23.9, 22.2, 13.9. ESI HRMS: calculated for $C_{17}H_{25}NO_6Na$ $[M+Na]^+$ 362.1580, found 362.1612.



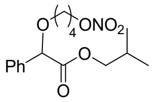
*phenethyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4sa**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 9:1, v/v) to afford **4sa** (54.0mg, 72% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.38 (m, 2H), 7.33-7.35 (m, 3H), 7.21-7.25 (m, 3H), 7.07-7.09 (m, 2H), 4.80 (s, 1H), 4.46-4.50 (m, 2H), 4.31-4.35 (m, 2H), 3.48-3.53 (m, 1H), 3.41-3.46 (m, 1H), 2.85-2.89 (m, 2H), 1.81-1.88 (m, 2H), 1.70-1.75 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.8, 137.5, 136.4, 128.9, 128.7, 128.7, 128.5, 127.1, 126.6, 81.1, 73.1, 68.8, 65.6, 34.9, 25.8, 23.9. ESI HRMS: calculated for $C_{20}H_{23}NO_6Na$ $[M+Na]^+$ 396.1423, found 396.1424.



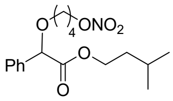
*benzyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4ta**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 9:1, v/v) to afford **4ta** (38.0mg, 53% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.43 (m, 2H), 7.34-7.36 (m, 3H), 7.30-7.31 (m, 3H), 7.21-7.22 (m, 2H), 5.11-5.18 (m, 2H), 4.89 (s, 1H), 4.46-4.49 (m, 2H), 3.55-3.60 (m, 1H), 3.47-3.51 (m, 1H), 1.82-1.87 (m, 2H), 1.73-1.77 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.7, 136.3, 135.4, 128.8, 128.7, 128.5, 128.3, 128.0, 127.2, 81.2, 73.1, 68.9, 66.8, 25.8, 23.9. ESI HRMS: calculated for $C_{19}H_{21}NO_6Na$ $[M+Na]^+$ 382.1267, found 382.1267.



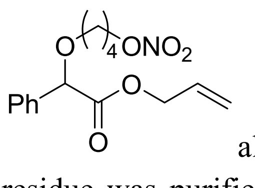
*isopropyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4ua**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4ua** (36.0mg, 58% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.32-7.37 (m, 3H), 5.01-5.06 (m, 1H), 4.80 (s, 1H), 4.49-4.54 (m, 2H), 3.57-3.61 (m, 1H), 3.48-3.52 (m, 1H), 1.86-1.92 (m, 2H), 1.74-1.79 (m, 2H), 1.24 (d, J = 6.3 Hz, 3H), 1.12 (d, J = 6.3 Hz, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.4, 136.6, 128.6, 128.6, 127.0, 81.3, 73.2, 68.8, 68.8, 25.8, 23.9, 21.8, 21.5. ESI HRMS: calculated for $C_{15}H_{21}NO_6Na$ $[M+Na]^+$ 334.1267, found 334.1352.



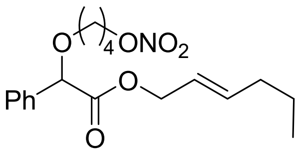
*isobutyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4va**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4va** (47.0mg, 72% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.45 (m, 2H), 7.33-7.38 (m 3H), 4.85 (s, 1H), 4.49- 4.53 (m, 2H), 3.85-3.93 (m, 3H), 3.57-3.62 (m, 1H), 3.47-3.52 (m, 1H), 1.83-1.92 (m, 4H), 1.75-1.80 (m, 2H), 0.83 (d, J = 1.3 Hz, 3H), 0.81 (d, J = 1.3 Hz, 3H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.9, 136.7, 128.7, 128.6, 127.1, 81.2, 73.1, 71.1, 68.8, 27.7, 25.8, 23.9, 18.9. ESI HRMS: calculated for $C_{16}H_{23}NO_6Na$ $[M+Na]^+$ 348.1423, found 348.1437.



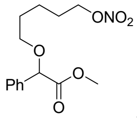
*isopentyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4wa**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4wa** (53.0mg, 78% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42-7.44 (m, 2H), 7.34-7.38 (m, 3H), 4.83 (s, 1H), 4.49-4.53 (m, 2H), 4.09-4.16 (m, 2H), 3.57-3.61 (m, 1H), 3.47-3.51 (m, 1H), 1.86-1.90 (m, 2H), 1.75-1.79 (m, 2H), 1.52-1.57 (m, 1H), 1.45-1.48 (m, 2H), 0.83-0.86 (m, 6H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 170.9, 136.6, 128.7, 128.6, 127.1, 81.2, 73.1, 68.8, 63.9, 37.1, 25.8, 25.0, 23.9, 22.4, 22.3. ESI HRMS: calculated for $C_{17}H_{25}NO_6Na$ $[M+Na]^+$ 362.1580, found 362.1598.



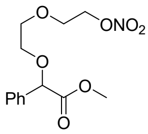
allyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate *(**4xa**)*. The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 9:1, v/v) to afford **4xa** (31 mg, 50% yield), Yellow oil. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.36-7.38 (m, 2H), 7.26-7.31 (m, 3H), 5.73-5.80 (m, 1H), 5.09-5.14 (m, 2H), 4.80 (s, 1H), 4.53-4.55 (m, 2H), 4.42-4.45 (m, 2H), 3.50-3.55 (m, 1H), 3.40-3.45 (m, 1H), 1.79-1.83 (m, 2H), 1.67-1.71 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.5, 136.4, 131.6, 128.8, 128.6, 127.1, 118.5, 81.2, 73.1, 68.9, 65.6, 25.8, 23.9. ESI HRMS: calculated for $C_{15}H_{19}NO_6Na$ $[M+Na]^+$ 332.1110, found 332.1115.



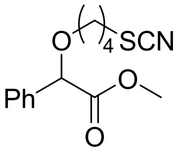
*(E)-hex-2-enyl 2-(4-(nitrooxy)butoxy)-2-phenylacetate (**4ya**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 9:1, v/v) to afford **4ya** (30 mg, 43% yield), Yellow oil. ^{1}H NMR (400MHz, $CDCl_3$): δ 7.35-7.37 (m, 2H), 7.25-7.30 (m, 3H), 5.57-5.63 (m, 1H), 5.38-5.49 (m, 1H), 4.78 (s, 1H), 4.41-4.50 (m, 4H), 3.49-3.54 (m, 1H), 3.40-3.45 (m, 1H), 1.88-1.93 (m, 2H), 1.79-1.83 (m, 2H), 1.67-1.72 (m, 2H), 1.26-1.31 (m, 2H), 0.79 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.6, 136.9, 136.5, 128.7, 128.6, 127.1, 123.3, 81.2, 73.1, 68.8, 65.8, 34.2, 25.8, 23.9, 21.9, 13.5. ESI HRMS: calculated for $C_{18}H_{25}NO_6Na$ $[M+Na]^+$ 374.1580, found 374.1583.



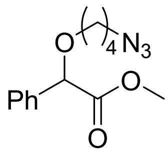
*methyl 2-((5-(nitrooxy)pentyl)oxy)-2-phenylacetate (**4ab**).*The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 10:1, v/v) to afford **4ab** (35.5mg, 60% yield), Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43-7.45 (m, 2H), 7.33-7.39 (m, 3H), 4.86 (s, 1H), 4.44 (t, J = 6.6 Hz, 2H), 3.71 (s, 3H), 3.53-3.57 (m, 1H), 3.42-3.47 (m, 1H), 1.72-1.76 (m, 2H), 1.67-1.71 (m, 2H), 1.50-1.55 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.4, 136.5, 128.7, 128.6, 127.1, 81.2, 73.2, 69.4, 52.3, 29.1, 26.5, 22.4. ESI HRMS: calculated for $C_{14}H_{19}NO_6Na$ $[M+Na]^+$ 320.1110, found 320.1138.

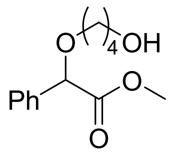


*methyl 2-(2-(2-(nitrooxy)ethoxy)ethoxy)-2-phenylacetate (**4ac**).* The resultant residue was purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc= 6:1, v/v) to afford **4ac** (10.5mg, 18% yield), Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.45 (m, 2H), 7.33-7.39 (m, 3H), 4.97 (s, 1H), 4.61 (t, J = 4.6 Hz, 2H), 3.77-3.83 (m, 2H), 3.70-3.73 (m, 5H), 3.61-3.68 (m, 2H); ^{13}C{1H} NMR (101 MHz, $CDCl_3$): δ 171.2, 136.3, 128.7, 128.6, 127.3, 81.4, 72.2, 70.8, 69.1, 67.3, 52.2. ESI HRMS: calculated for $C_{13}H_{17}NO_7Na$ $[M+Na]^+$ 322.0903, found 322.0935.



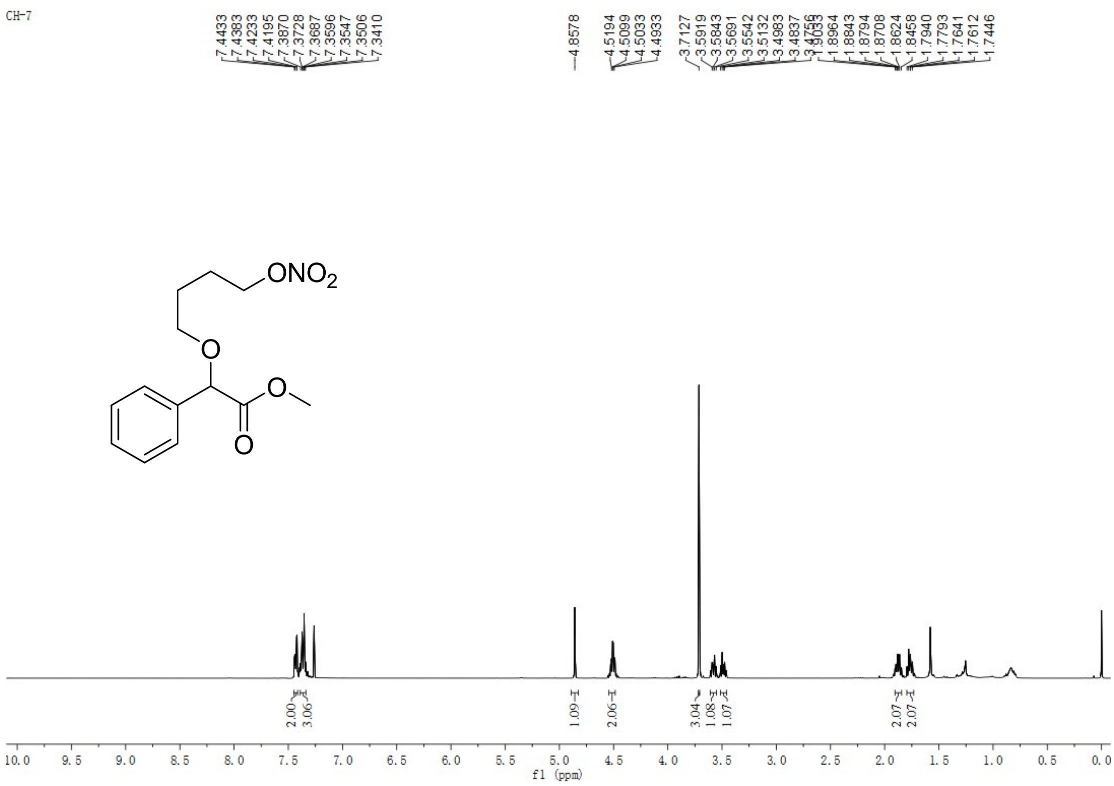
*methyl 2-phenyl-2-(4-thiocyanatobutoxy)acetate (**A**),* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.37 (m, 2H), 7.28 - 7.32 (m, 3H), 4.78 (s, 1H), 3.69 (s, 3H), 3.49 - 3.52 (m, 1H), 3.42 - 3.45 (m, 1H), 2.96 (t, J = 7.2 Hz, 2H), 1.89 - 1.93 (m, 2H), 1.72 - 1.77 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 136.3, 128.8, 128.7, 127.2, 112.3, 81.2, 68.8, 52.3, 33.8, 27.7, 27.0; ESI HRMS: calculated for $C_{14}H_{17}NO_3SNa$ $[M+Na]^+$ 302.0827, found 302.0823.

 *methyl 2-(4-azidobutoxy)-2-phenylacetate (**B**),* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.38 (m, 2H), 7.26 – 7.31 (m, 3H), 4.79 (s, 1H), 3.63 (s, 3H), 3.48 – 3.51 (m, 1H), 3.39 – 3.41 (m, 1H), 3.21-3.23 (m, 2H), 1.62 – 1.66 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 136.5, 128.7, 128.6, 127.2, 81.1, 69.1, 52.2, 51.2, 26.8, 25.7. ESI HRMS: calculated for $C_{13}H_{18}N_3O_3$ $[M+H]^+$ 264.1348, found 264.1343.

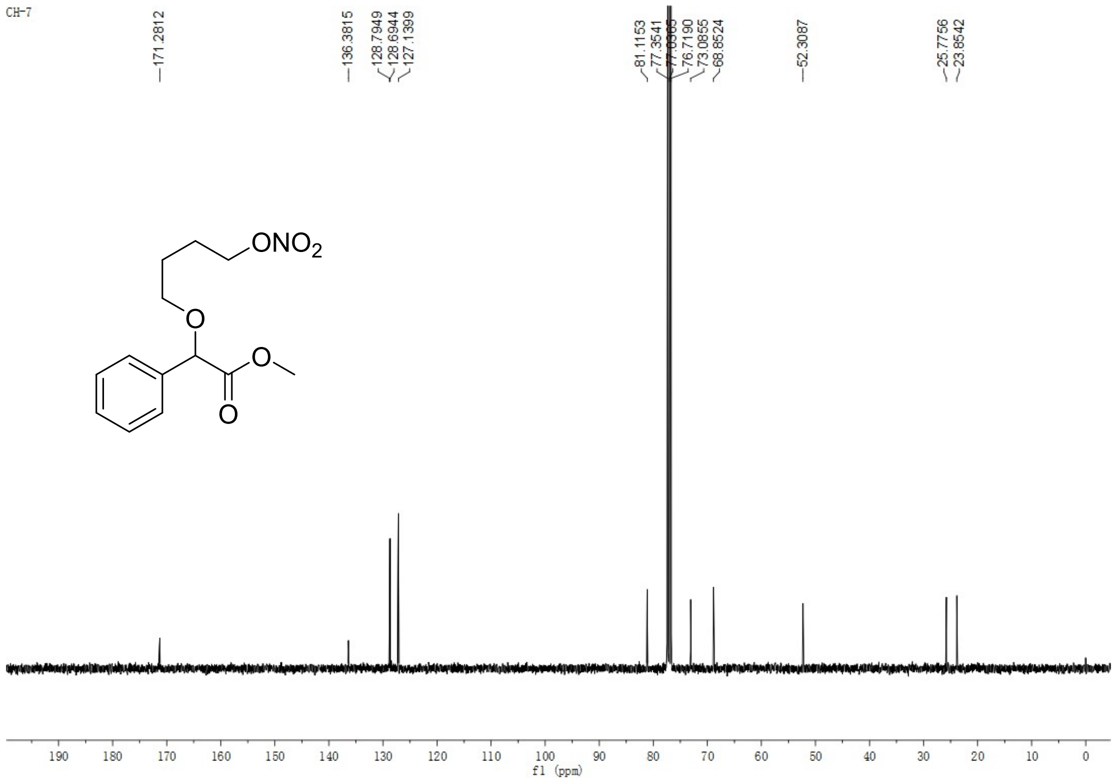
 *methyl 2-(4-hydroxybutoxy)-2-phenylacetate (**C**),* Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.38 (m, 2H), 7.26 – 7.31 (m, 3H), 4.80 (s, 1H), 3.64 (s, 3H), 3.60 (t, J = 6.2 Hz, 2H), 3.48 – 3.52 (m, 1H), 3.39 – 3.44 (m, 1H), 1.90 (brs, 1H), 1.60 – 1.69 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 136.4, 128.7, 128.6, 127.2, 81.2, 69.8, 62.6, 52.3, 29.8, 26.4. ESI HRMS: calculated for $C_{13}H_{19}O_4$ $[M+H]^+$ 239.1283, found 239.1277.

5.Copies of NMR spectra for products

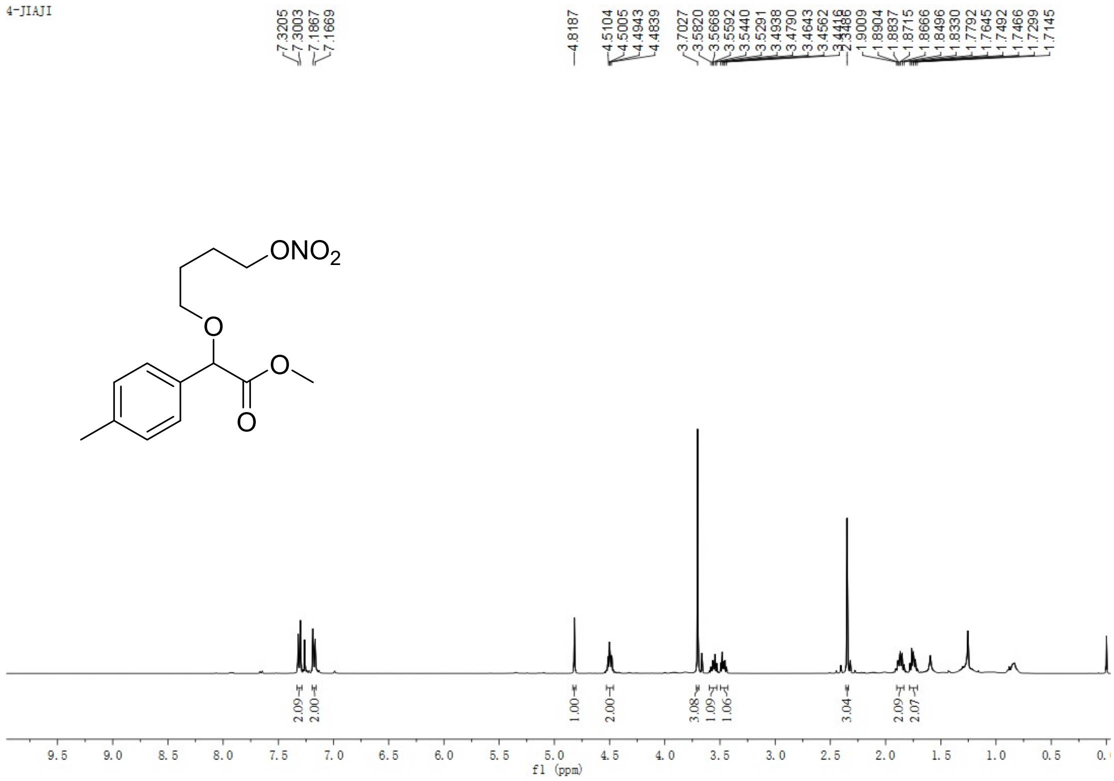
4aa ^{1}H NMR (400 MHz, $CDCl_3$)



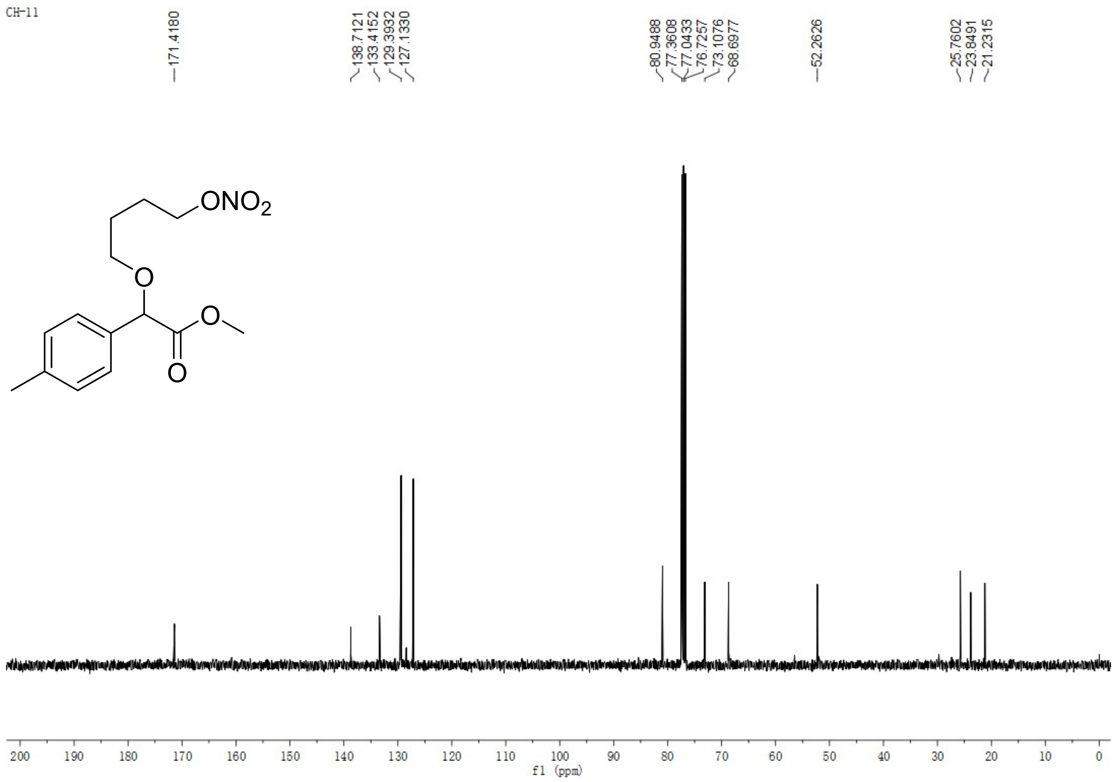
4aa ^{13}C NMR (101 MHz, $CDCl_3$)



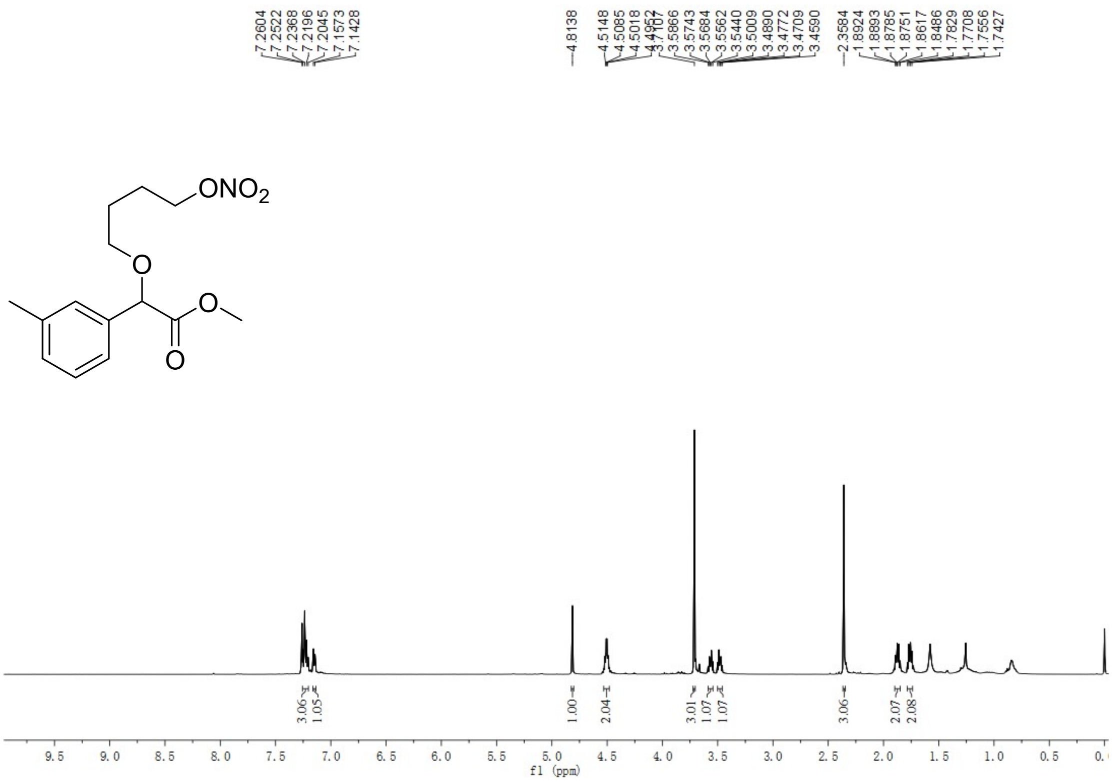
4ba ^{1}H NMR (400 MHz, $CDCl_3$)



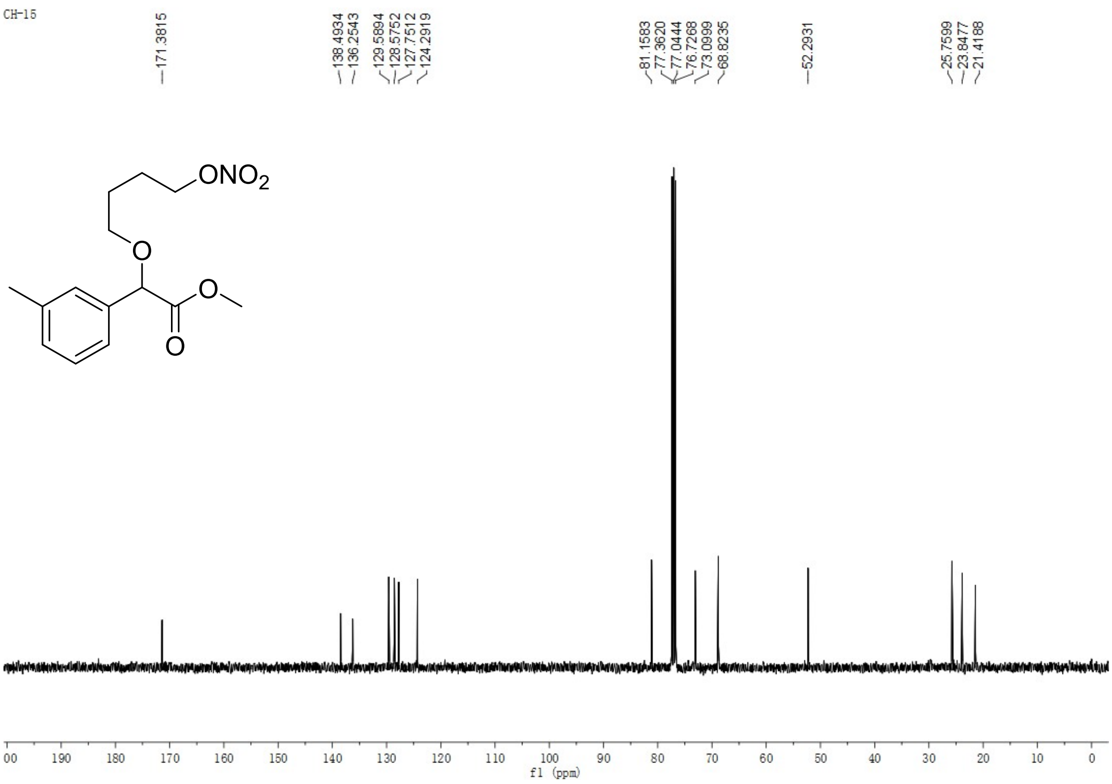
4ba ^{13}C NMR (101 MHz, $CDCl_3$)



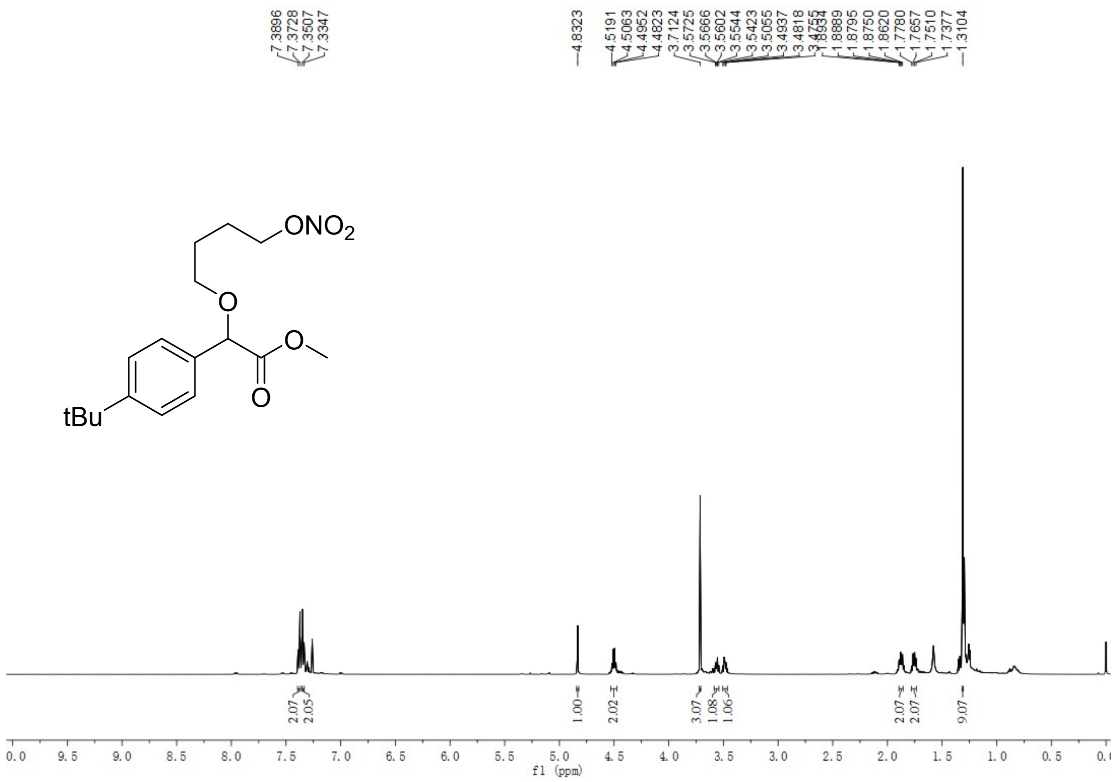
4ca ^{1}H NMR (400 MHz, $CDCl_3$)



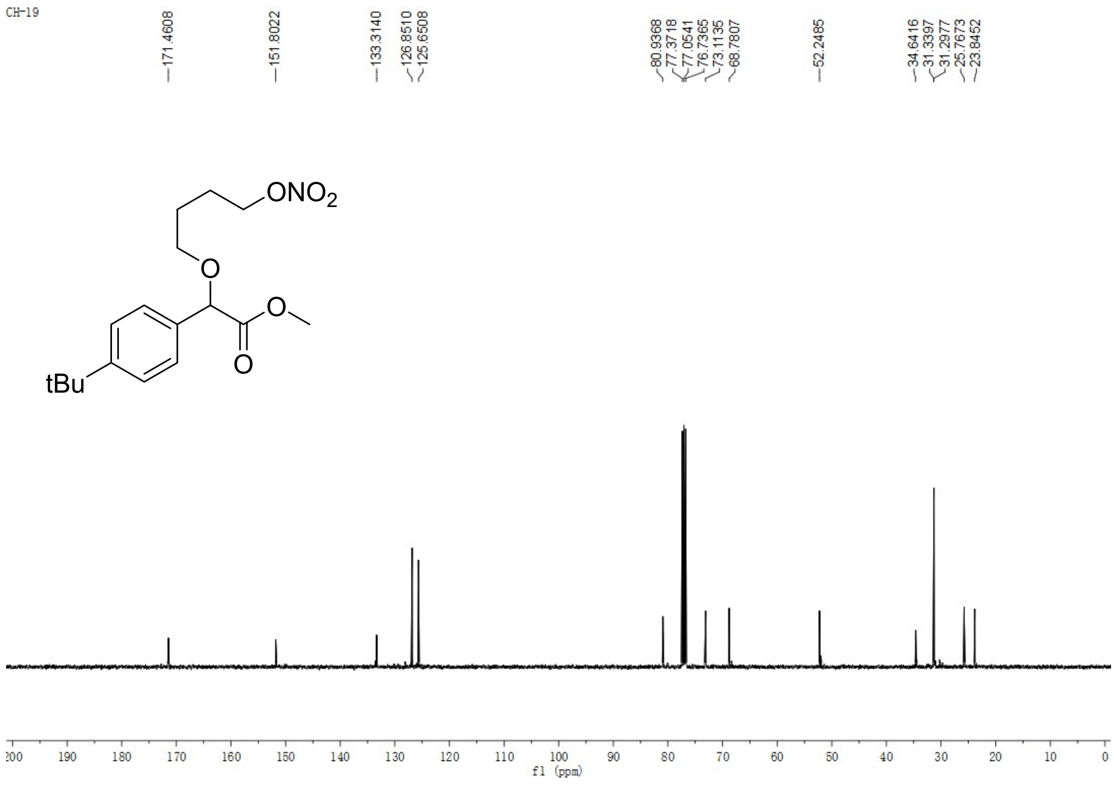
4ca ^{13}C NMR (101 MHz, $CDCl_3$)



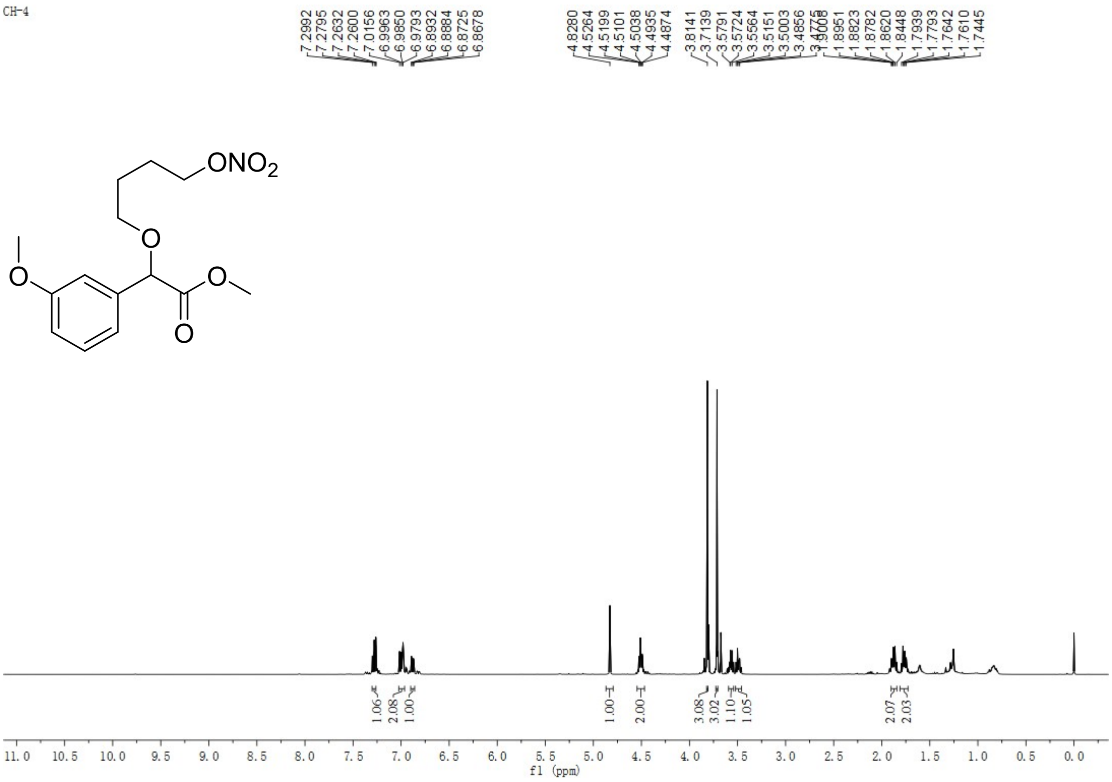
4da ^{1}H NMR (400 MHz, $CDCl_3$)



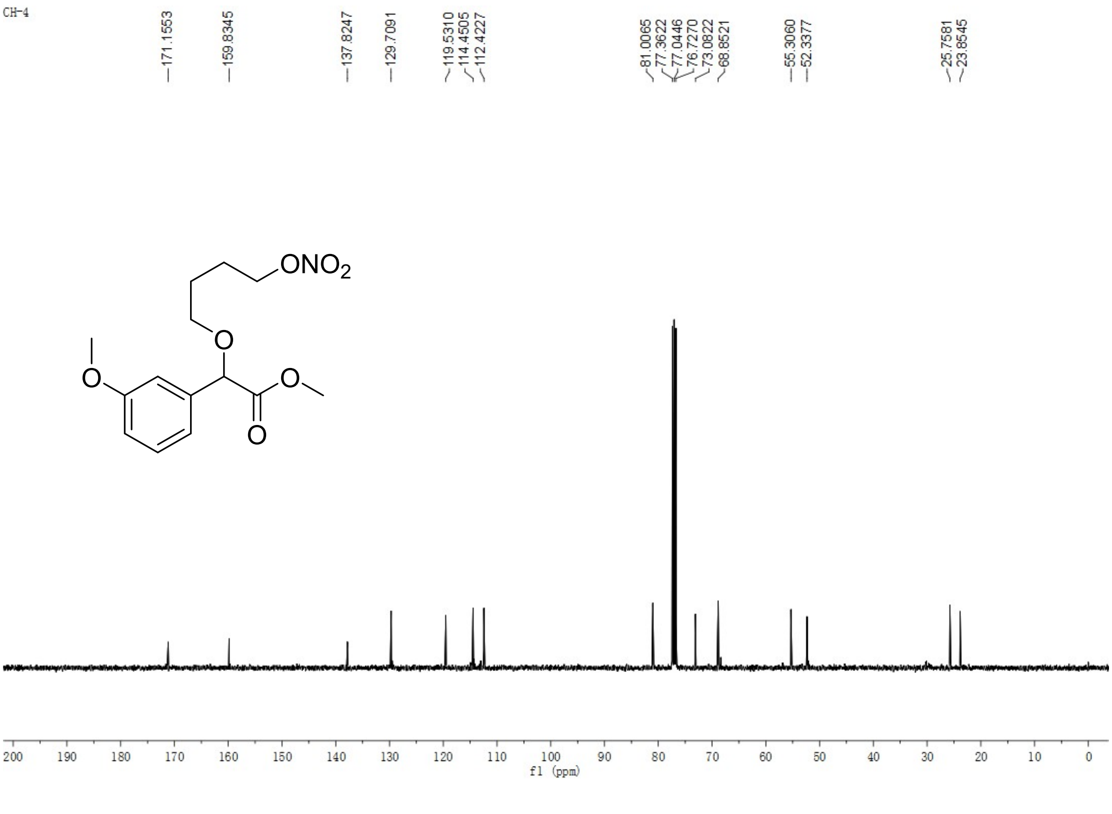
4da ^{13}C NMR (101 MHz, $CDCl_3$)



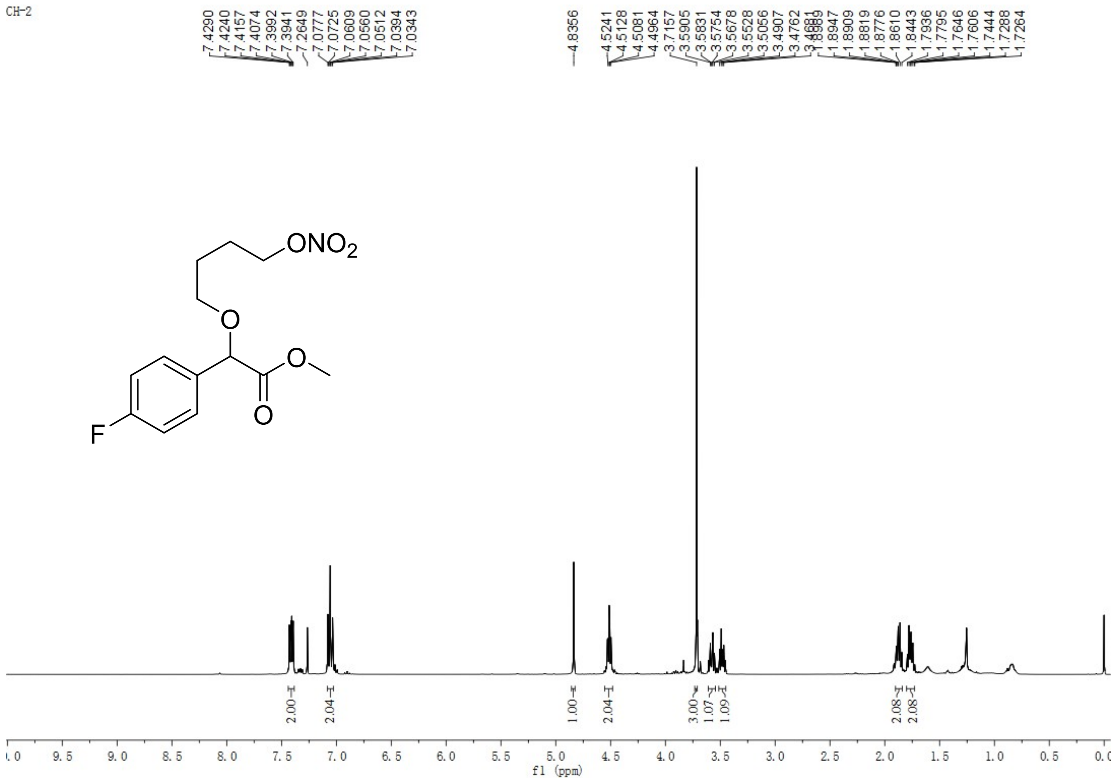
4ea ^{1}H NMR (400 MHz, $CDCl_3$)



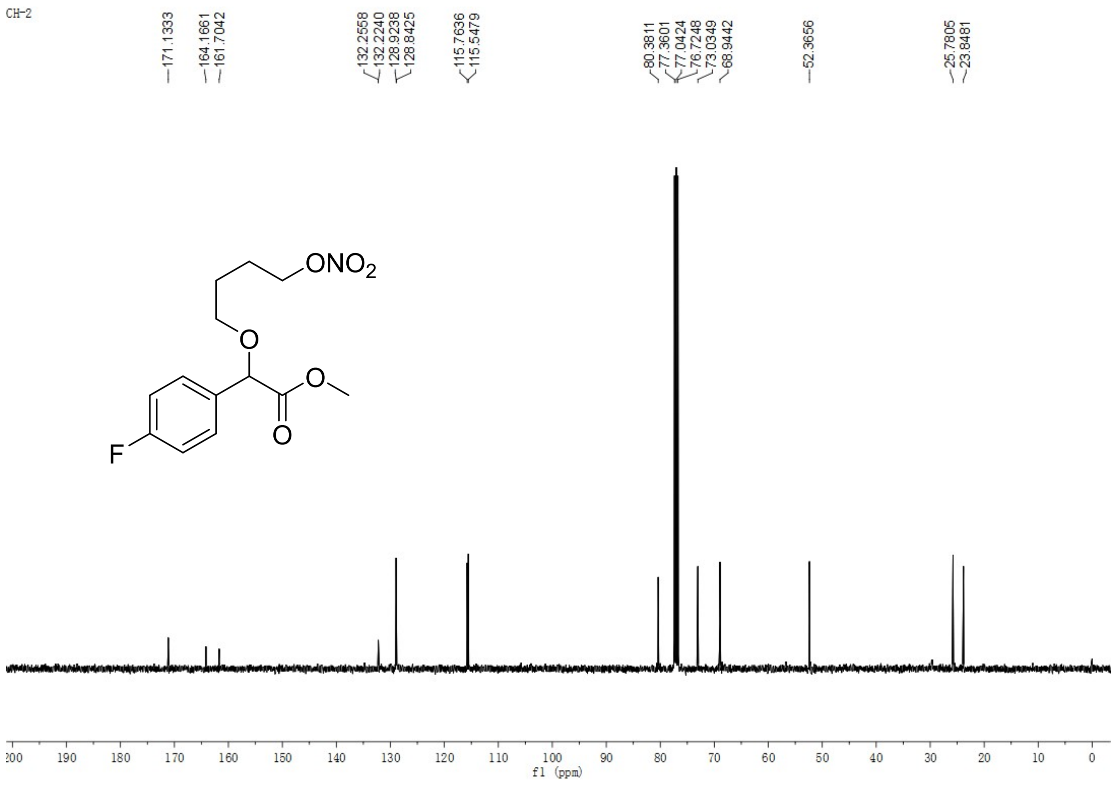
4ea ^{13}C NMR (101 MHz, $CDCl_3$)



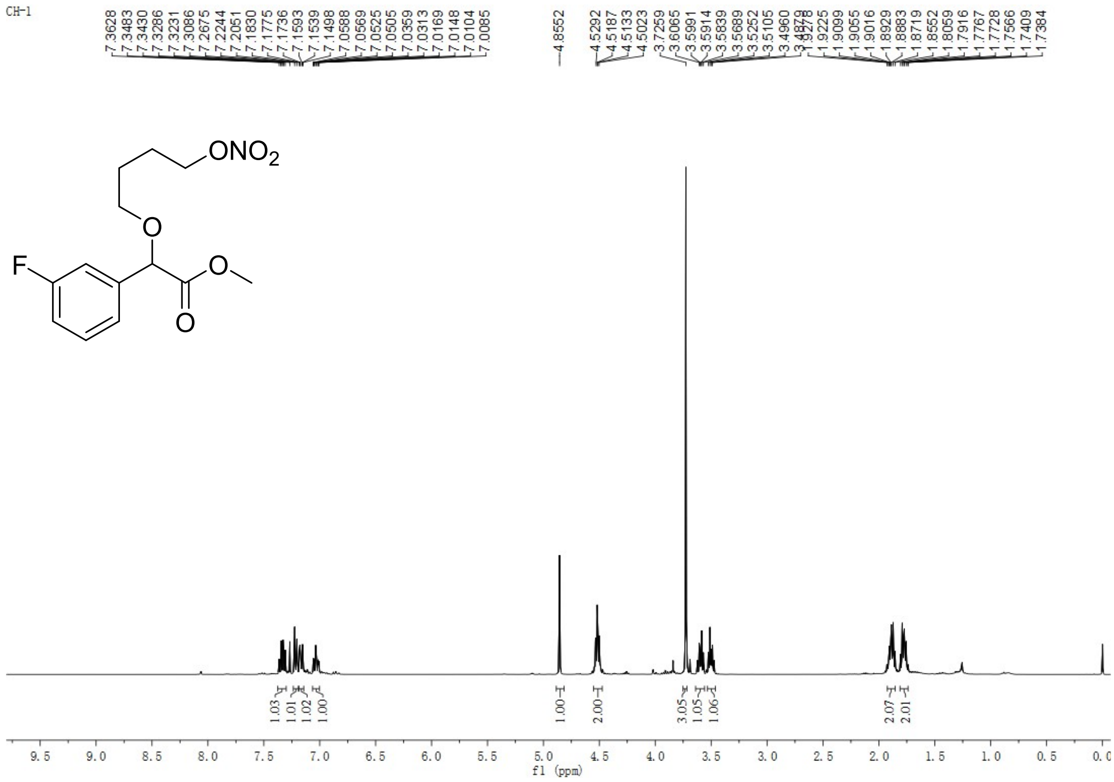
4fa ^{1}H NMR (400 MHz, $CDCl_3$)



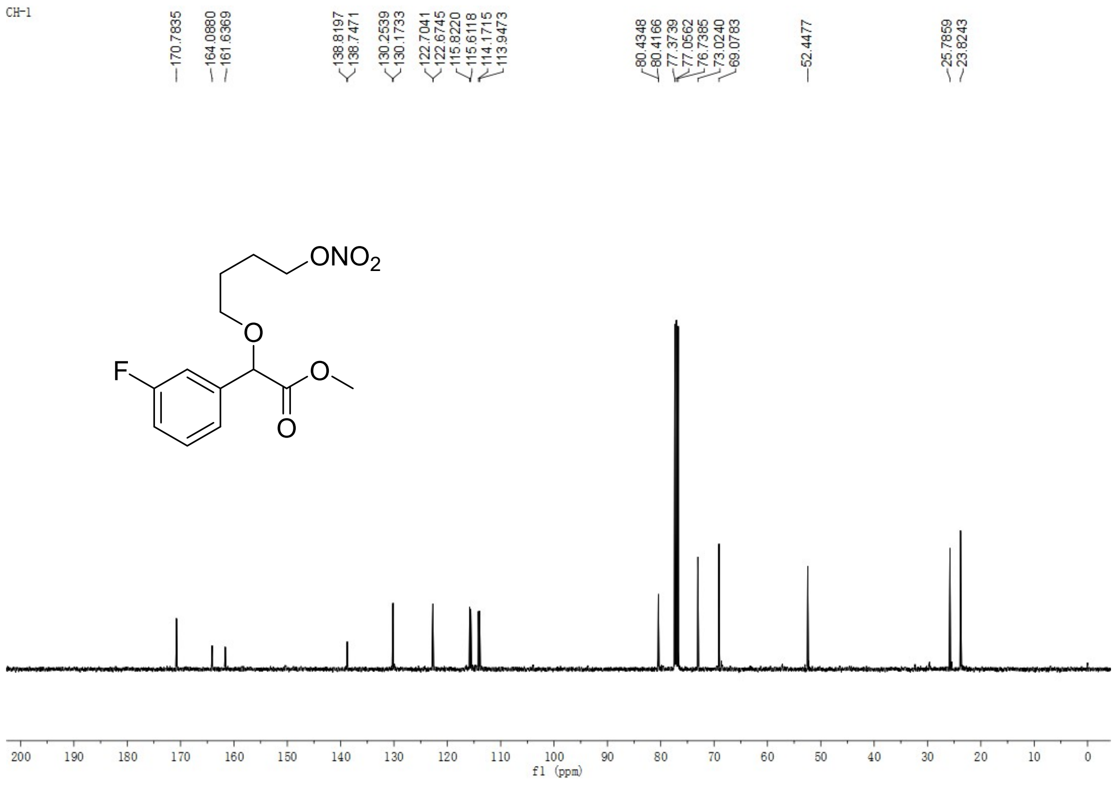
4fa ^{13}C NMR (101 MHz, $CDCl_3$)



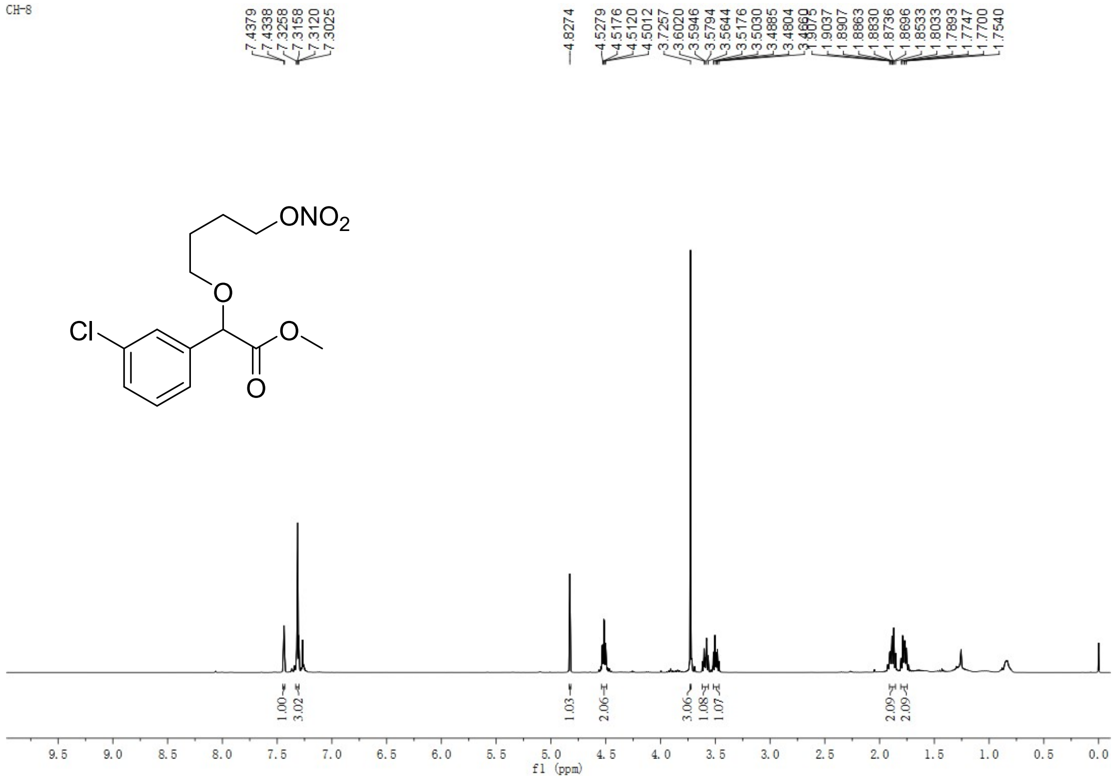
4ga ^{1}H NMR (400 MHz, $CDCl_3$)



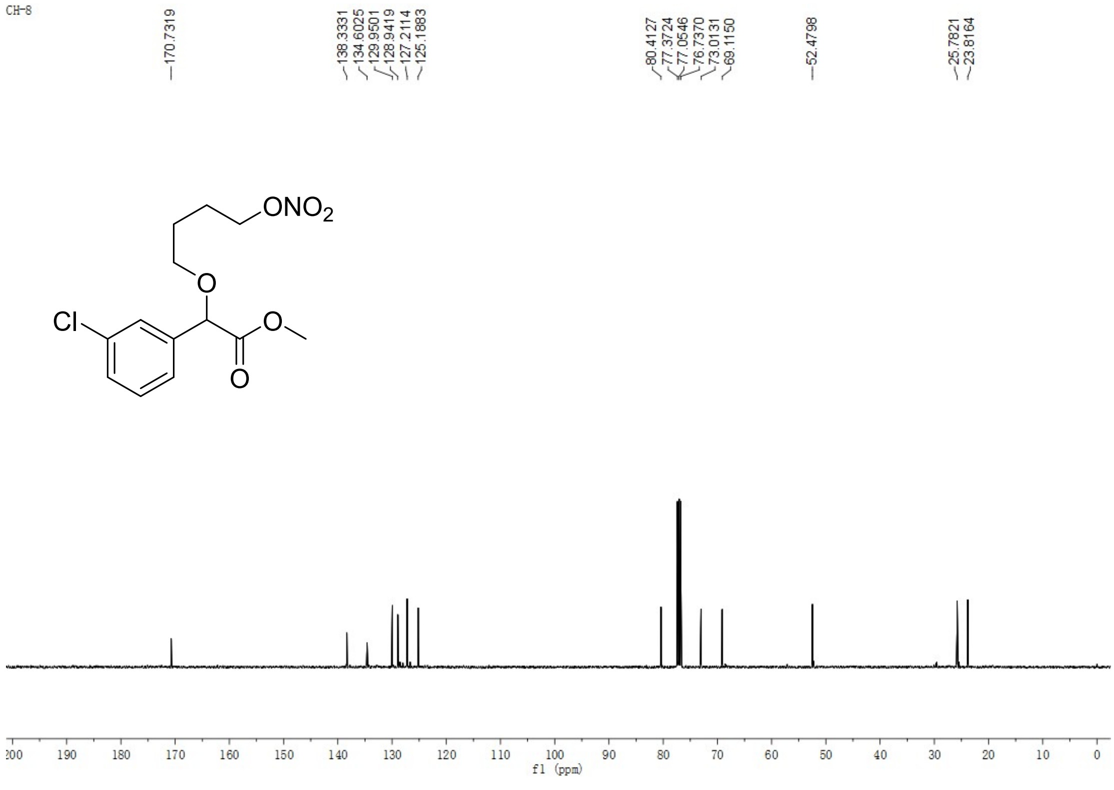
4ga ^{13}C NMR (101 MHz, $CDCl_3$)



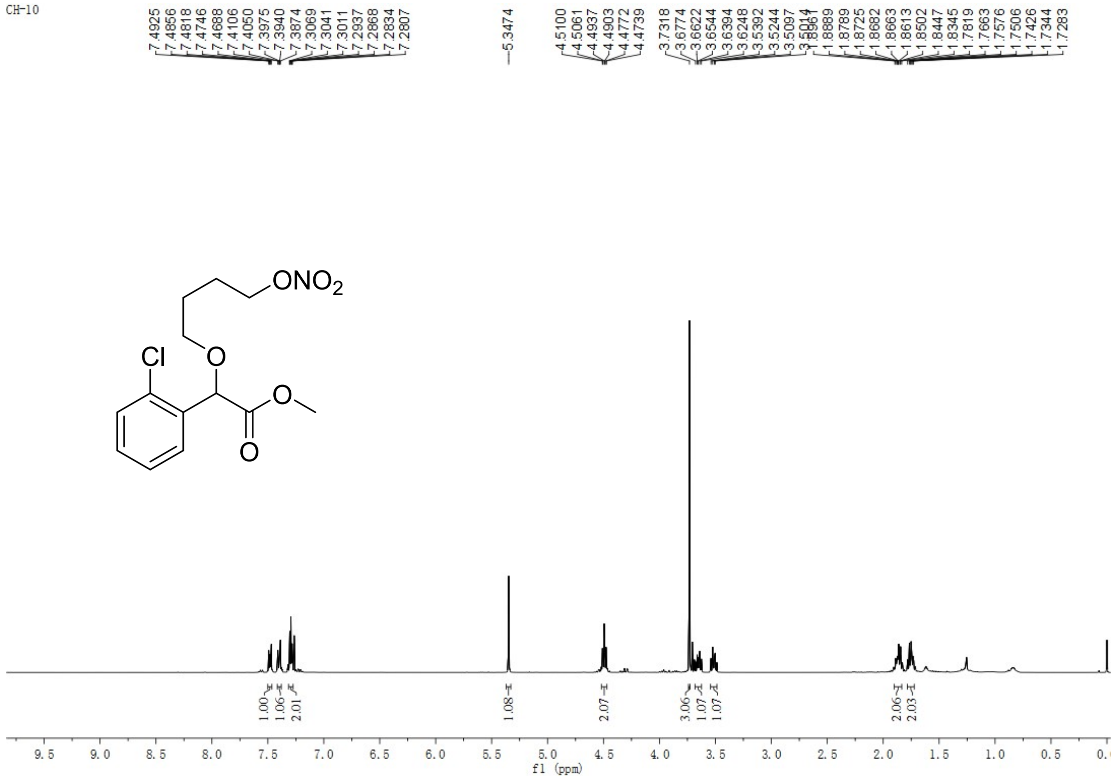
4ha ^{1}H NMR (400 MHz, $CDCl_3$)



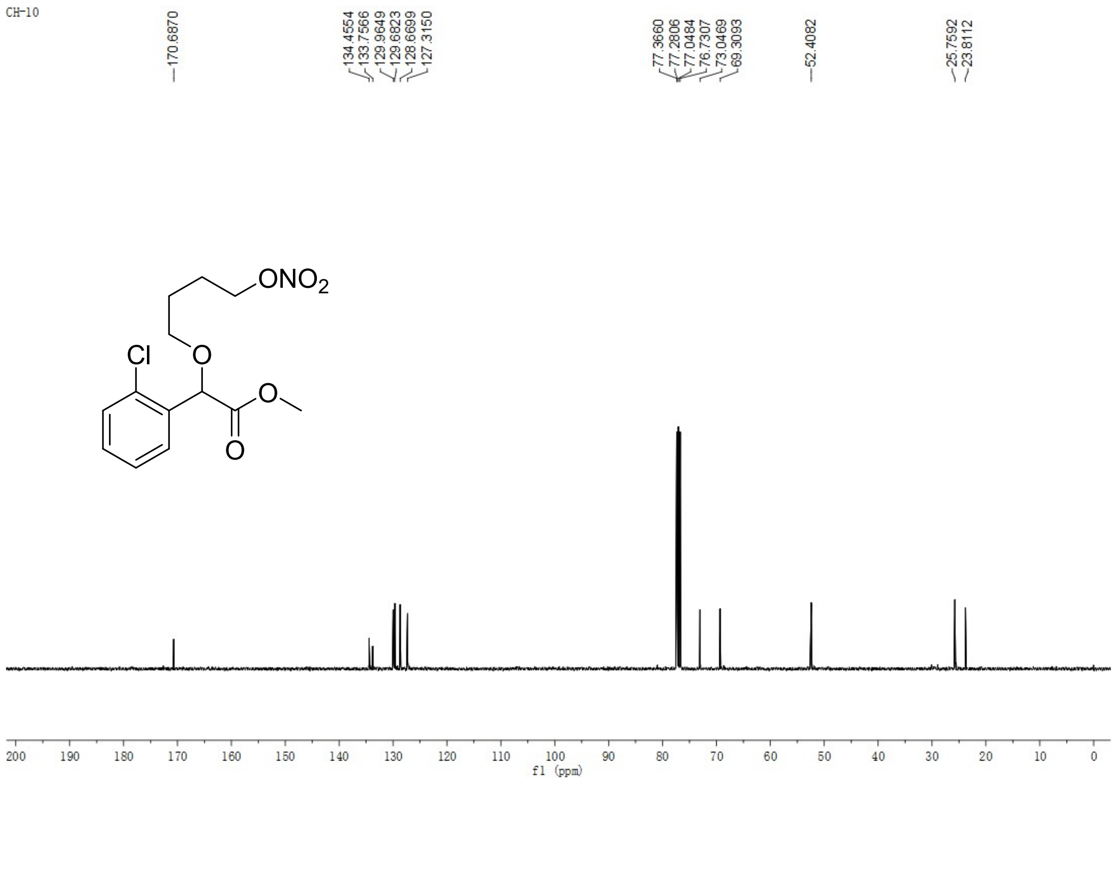
4ha ^{13}C NMR (101 MHz, $CDCl_3$)



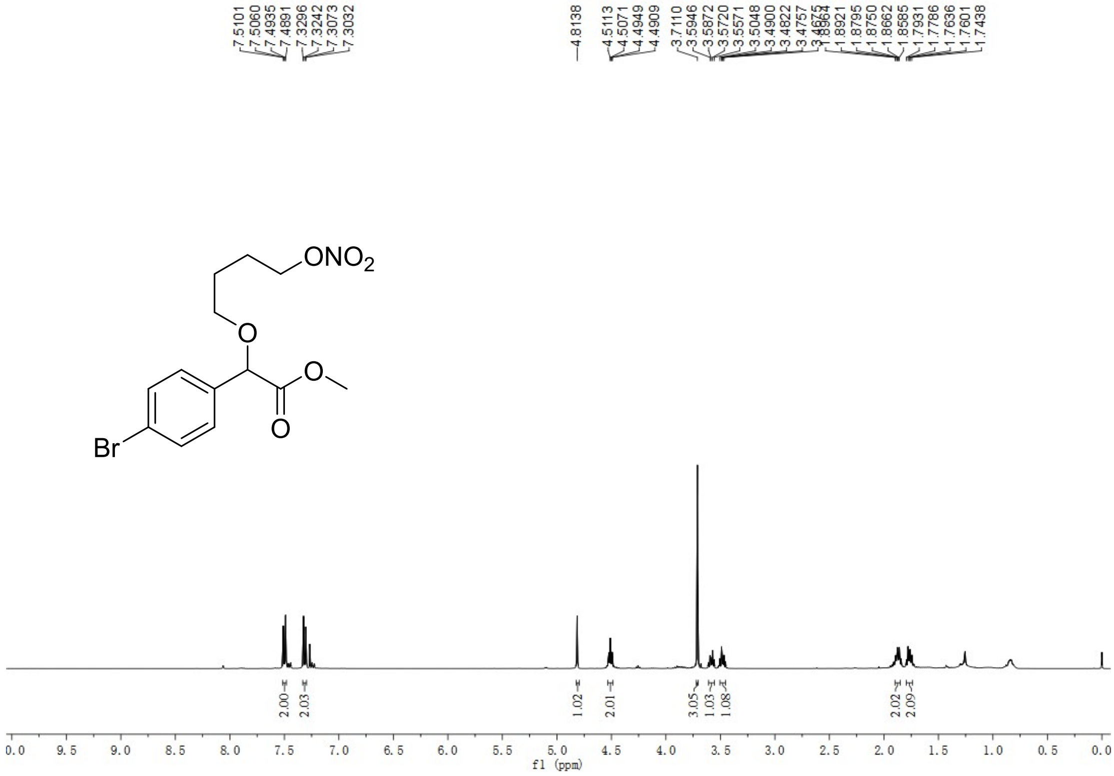
4ia ^{1}H NMR (400 MHz, $CDCl_3$)



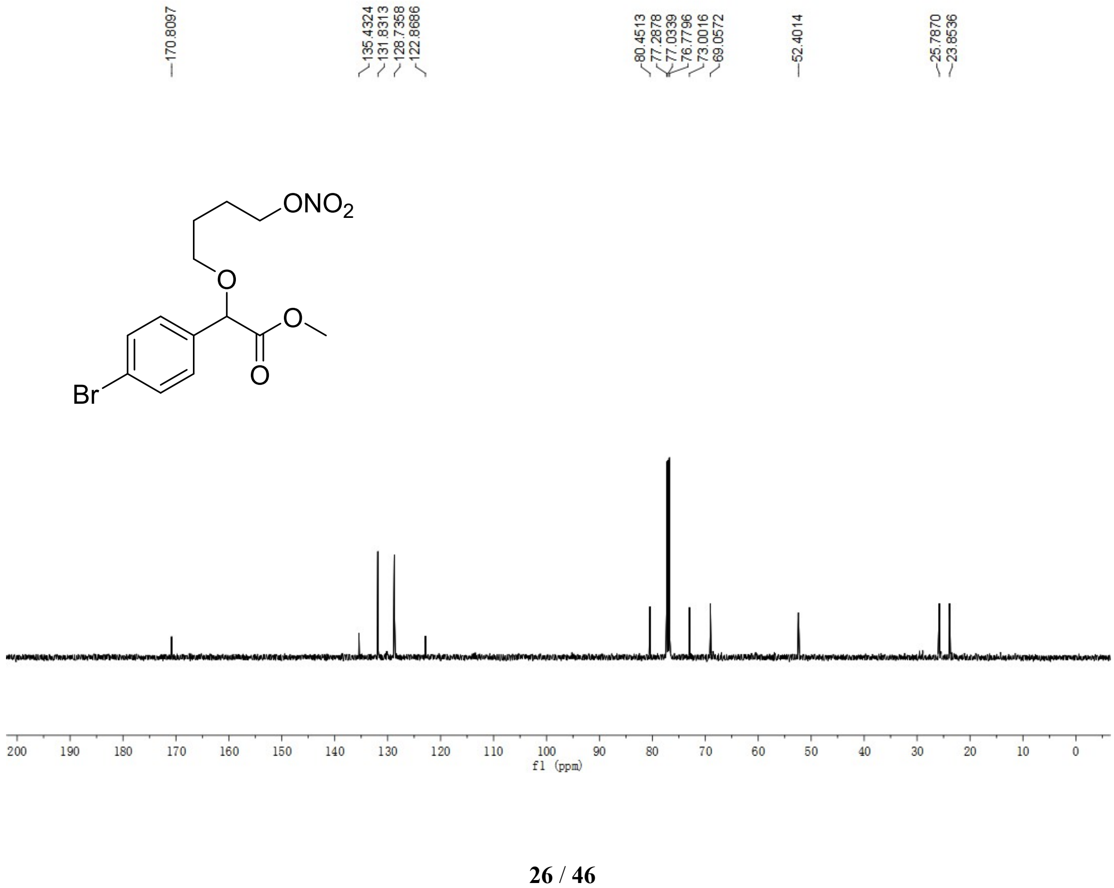
4ia ^{13}C NMR (100 MHz, $CDCl_3$)



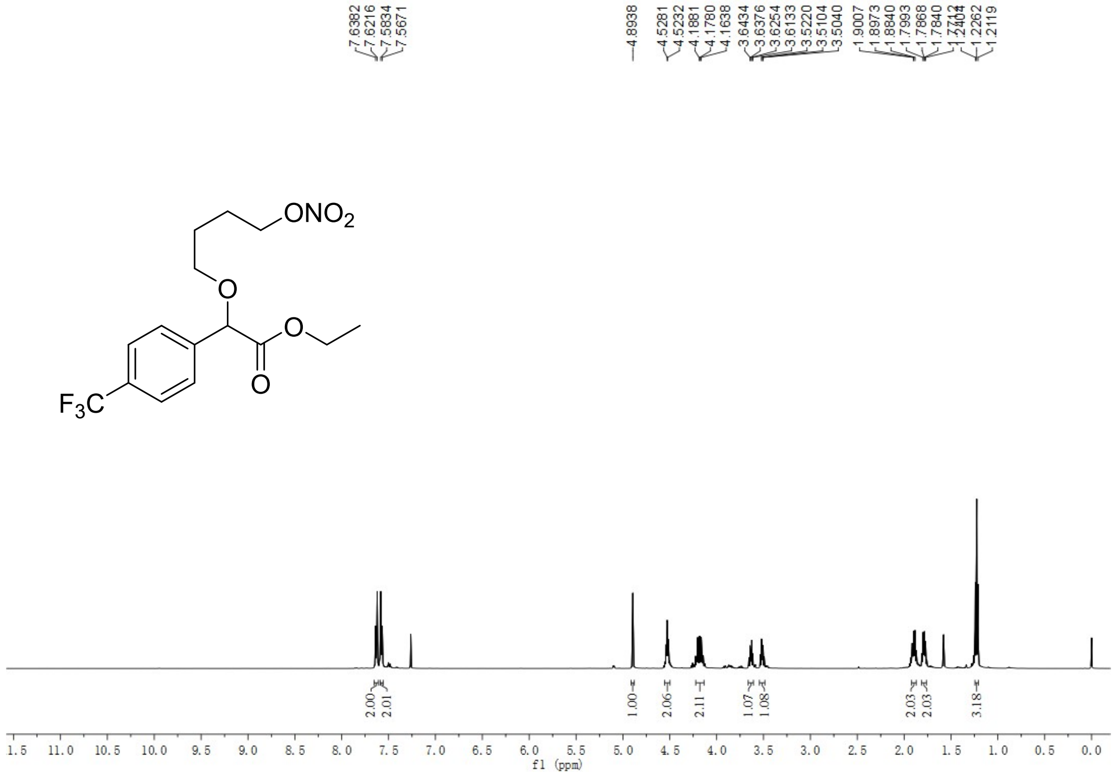
4ja ^{1}H NMR (400 MHz, $CDCl_3$)



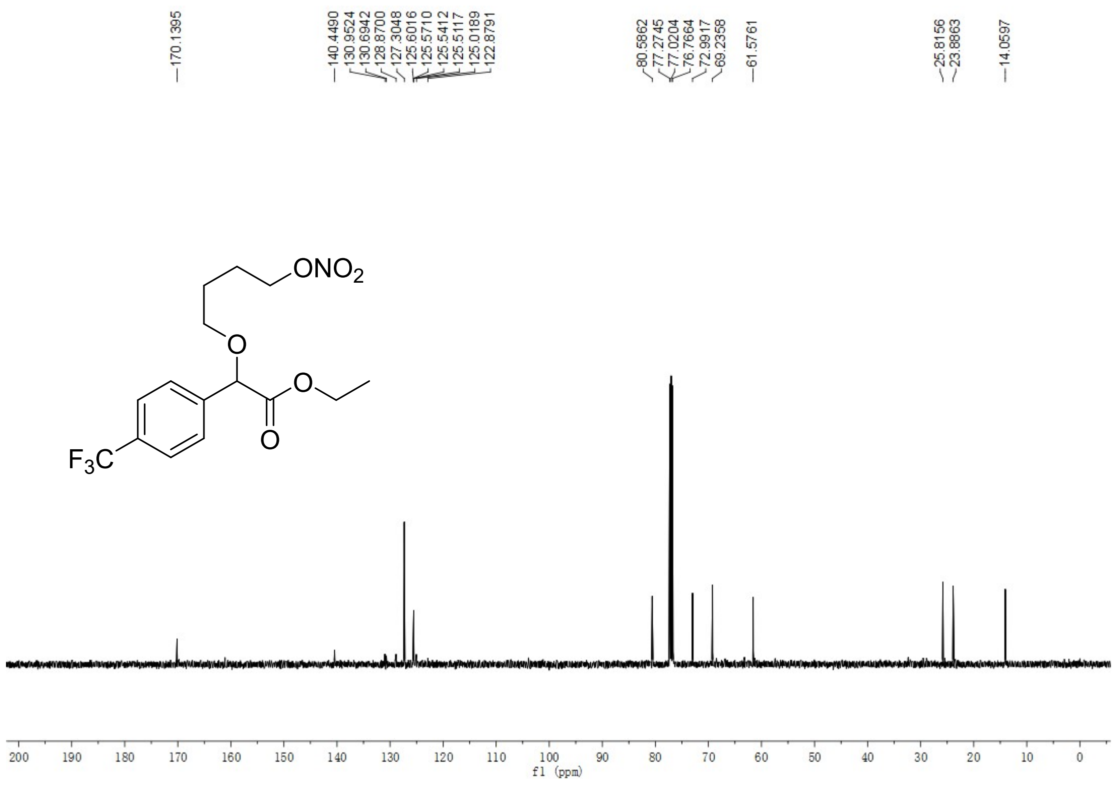
4ja ^{13}C NMR (101 MHz, $CDCl_3$)



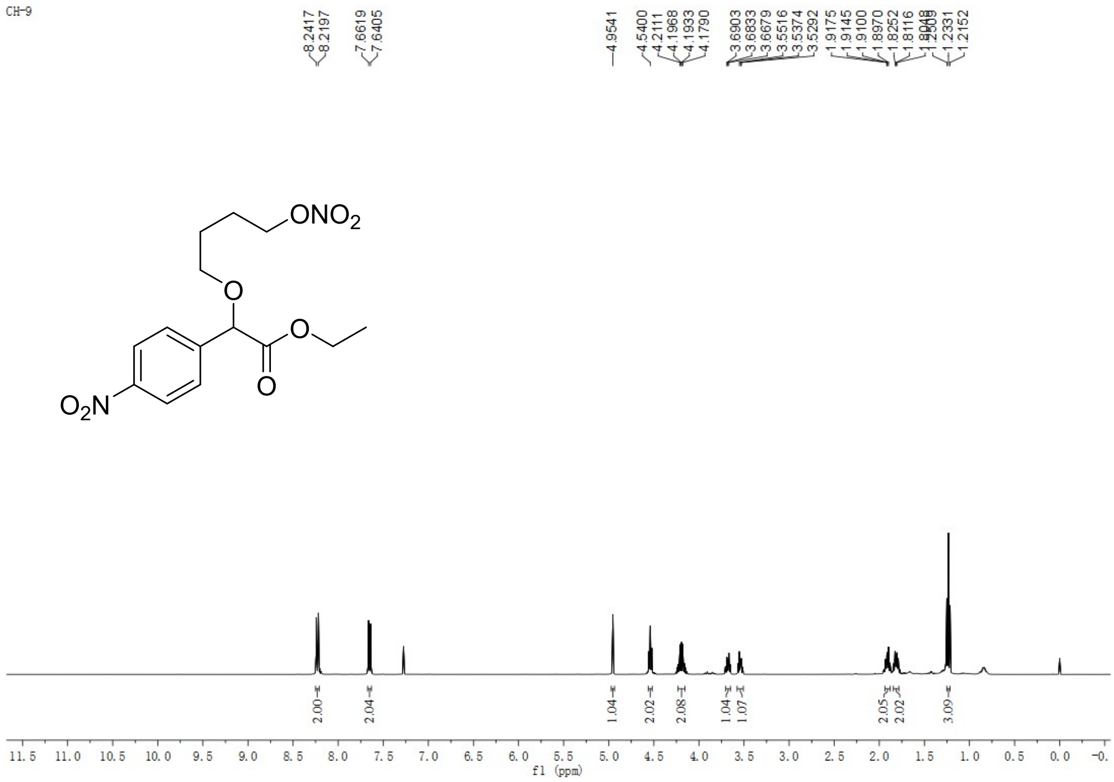
4ka ^{1}H NMR (500 MHz, $CDCl_3$)



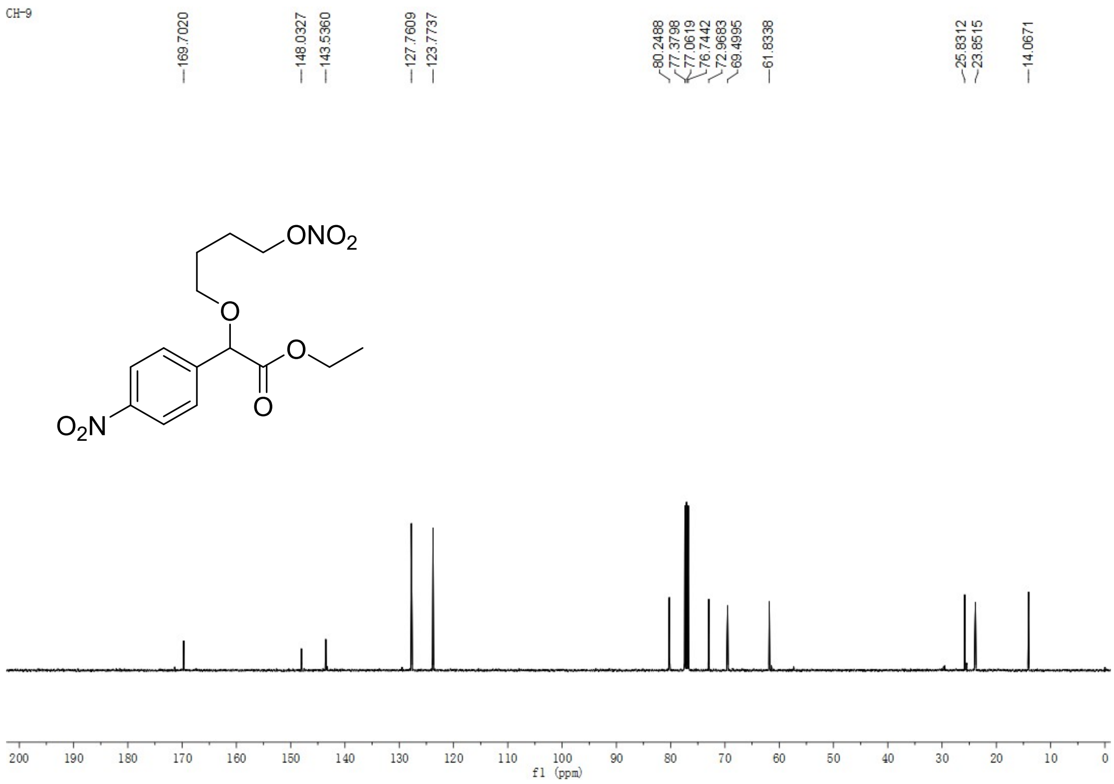
4ka ^{13}C NMR (126 MHz, $CDCl_3$)



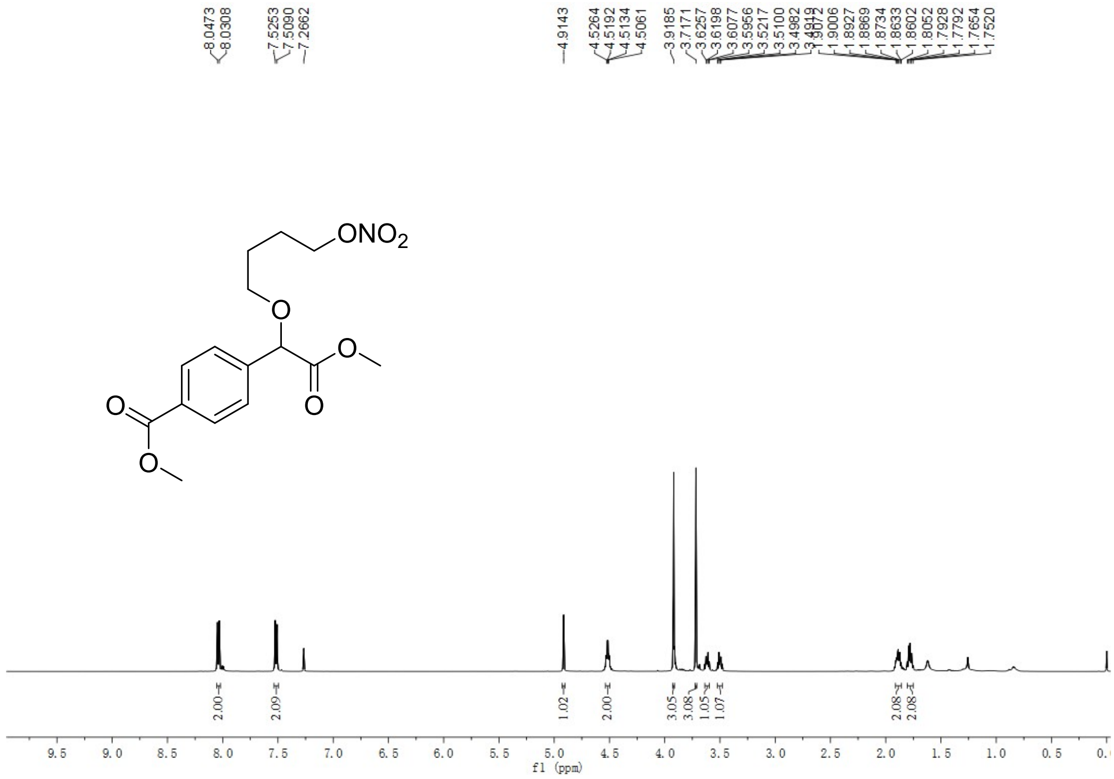
4la ^{1}H NMR (400 MHz, $CDCl_3$)



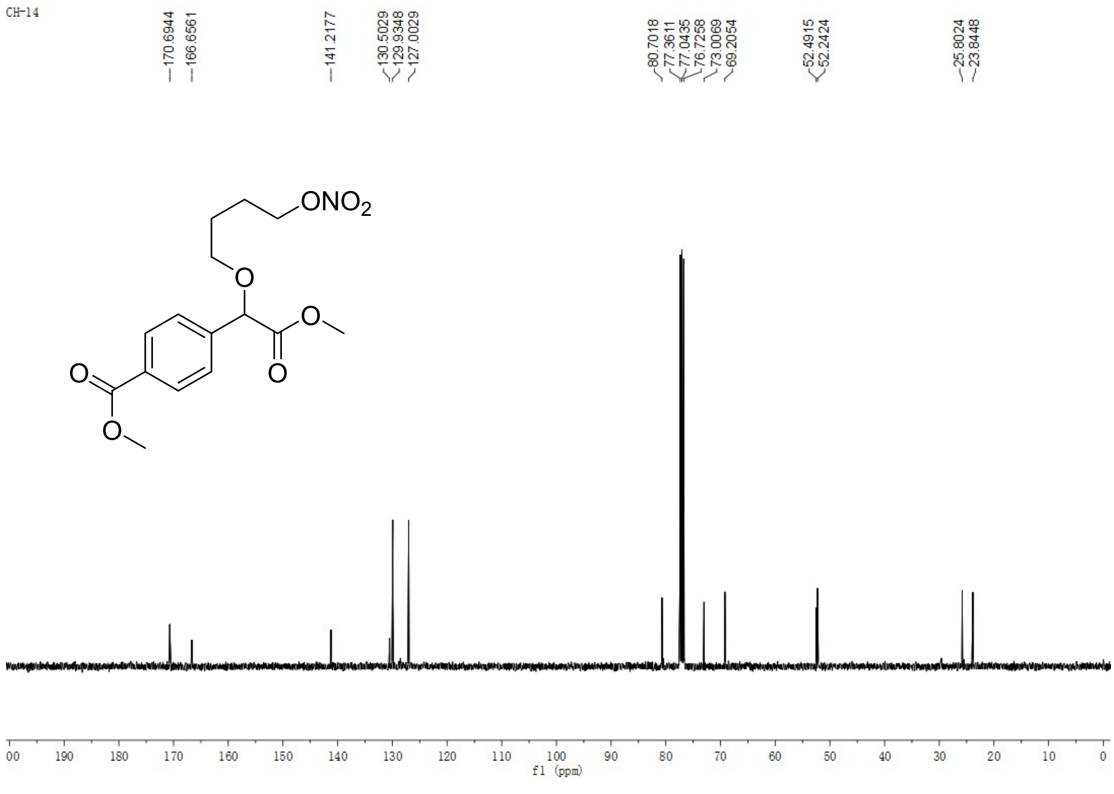
4la ^{13}C NMR (101 MHz, $CDCl_3$)



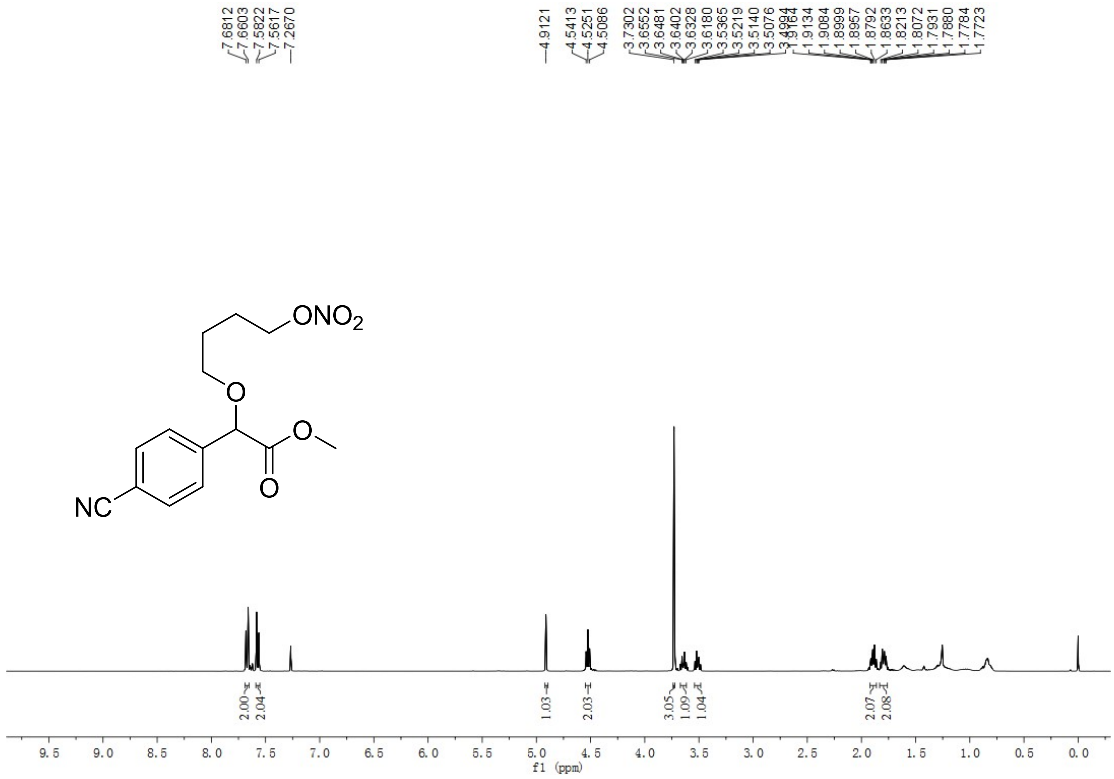
4ma ^{1}H NMR (400 MHz, $CDCl_3$)



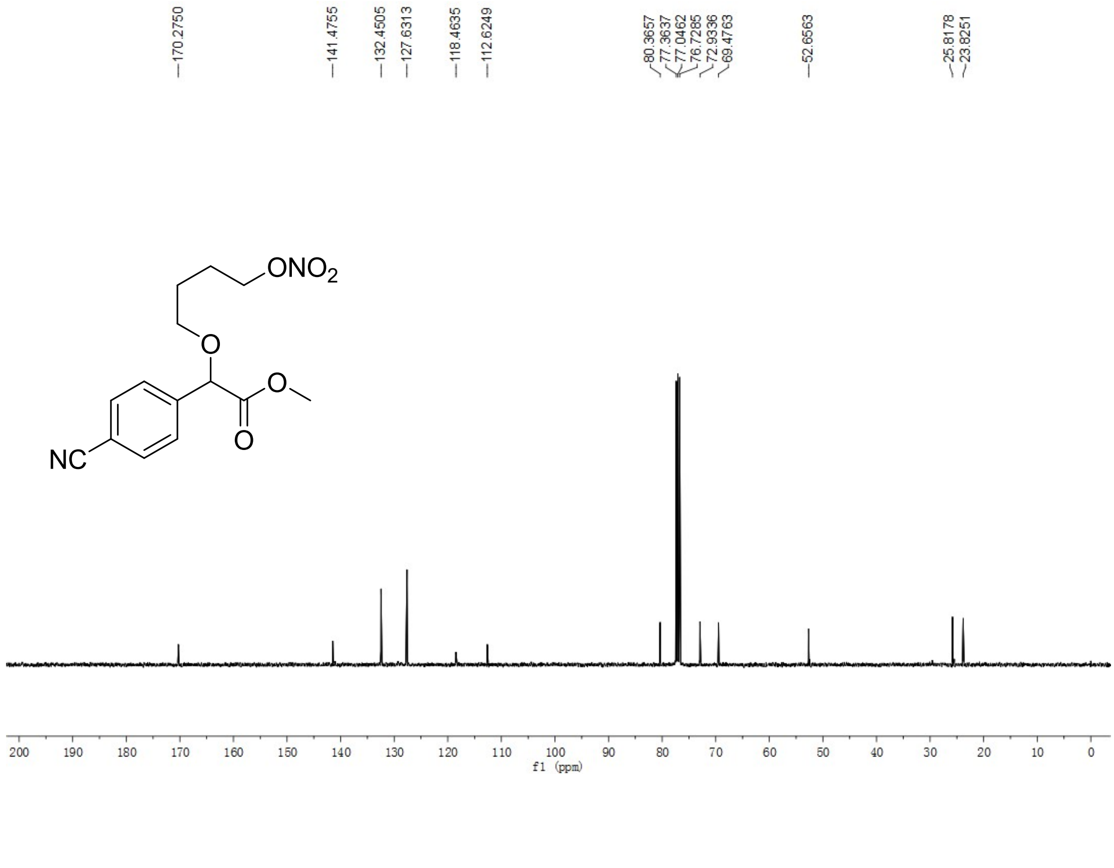
4ma ^{13}C NMR (101 MHz, $CDCl_3$)



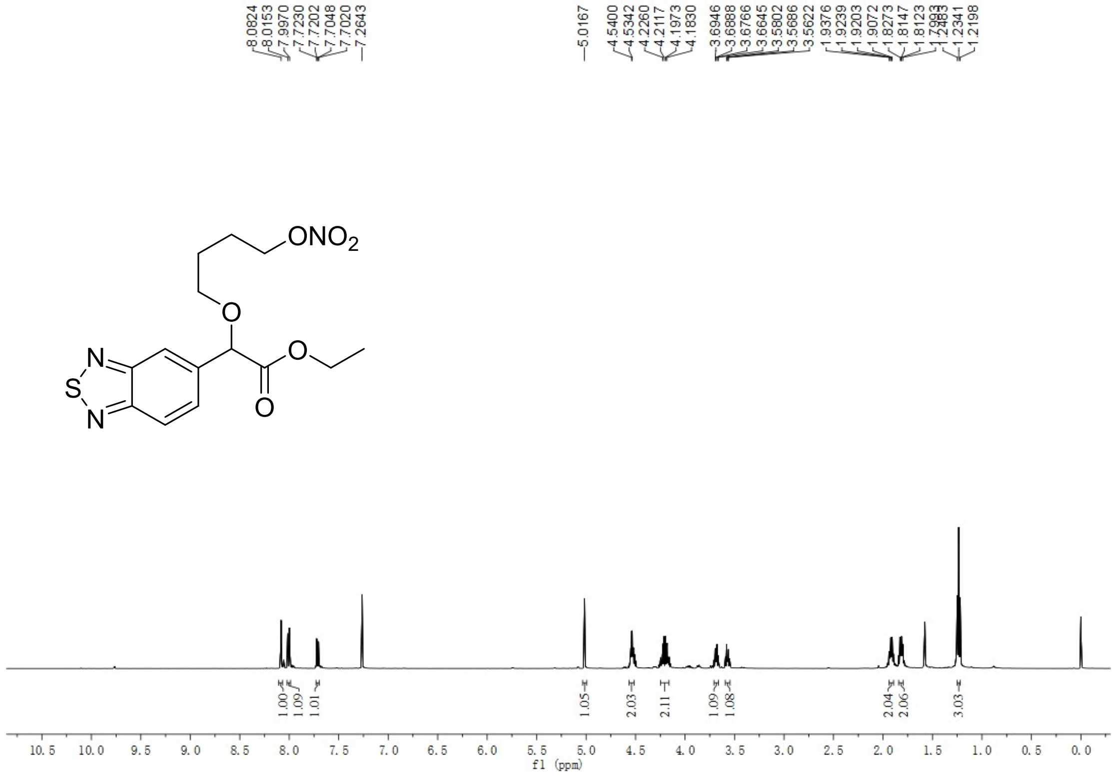
4na ^{1}H NMR (400 MHz, $CDCl_3$)



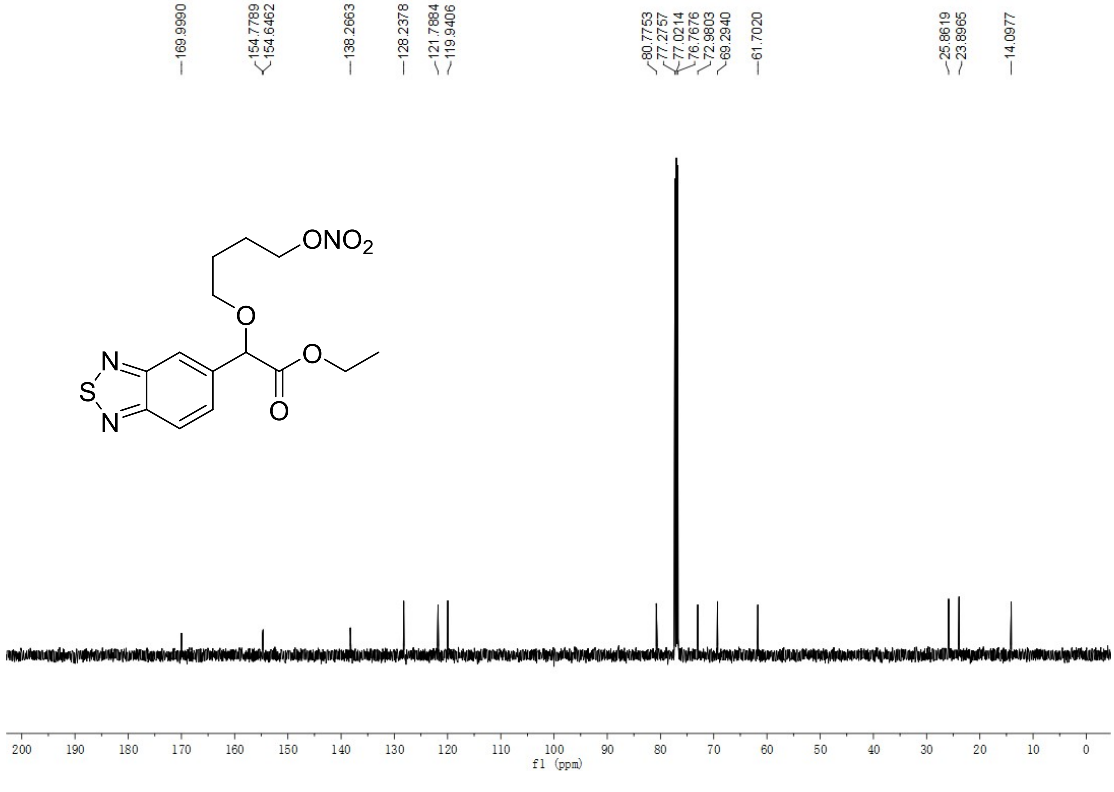
4na ^{13}C NMR (101 MHz, $CDCl_3$)



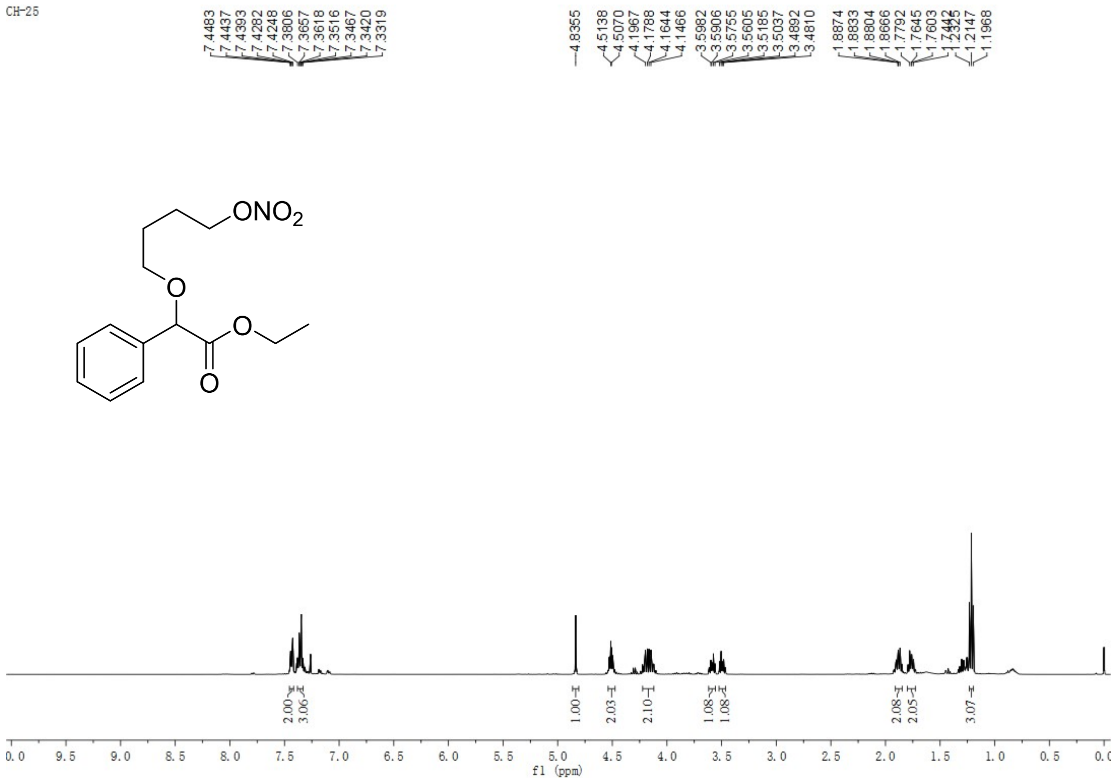
4oa ^{1}H NMR (500 MHz, $CDCl_3$)



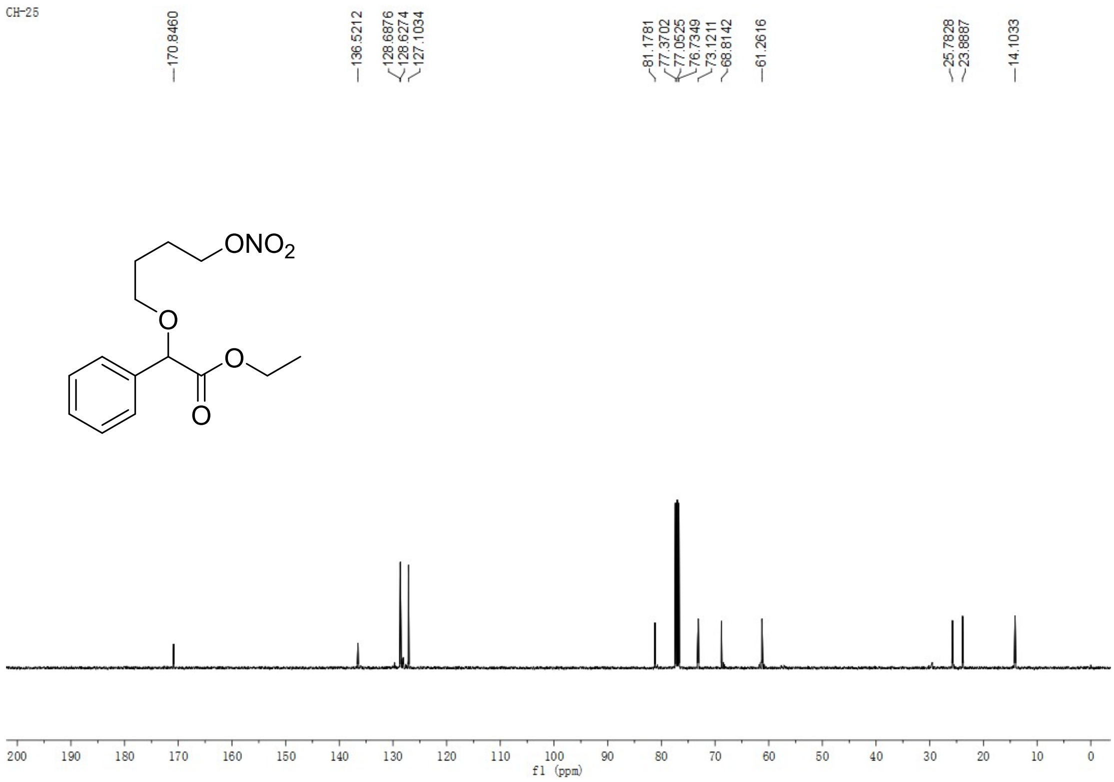
4oa ^{13}C NMR (126 MHz, $CDCl_3$)



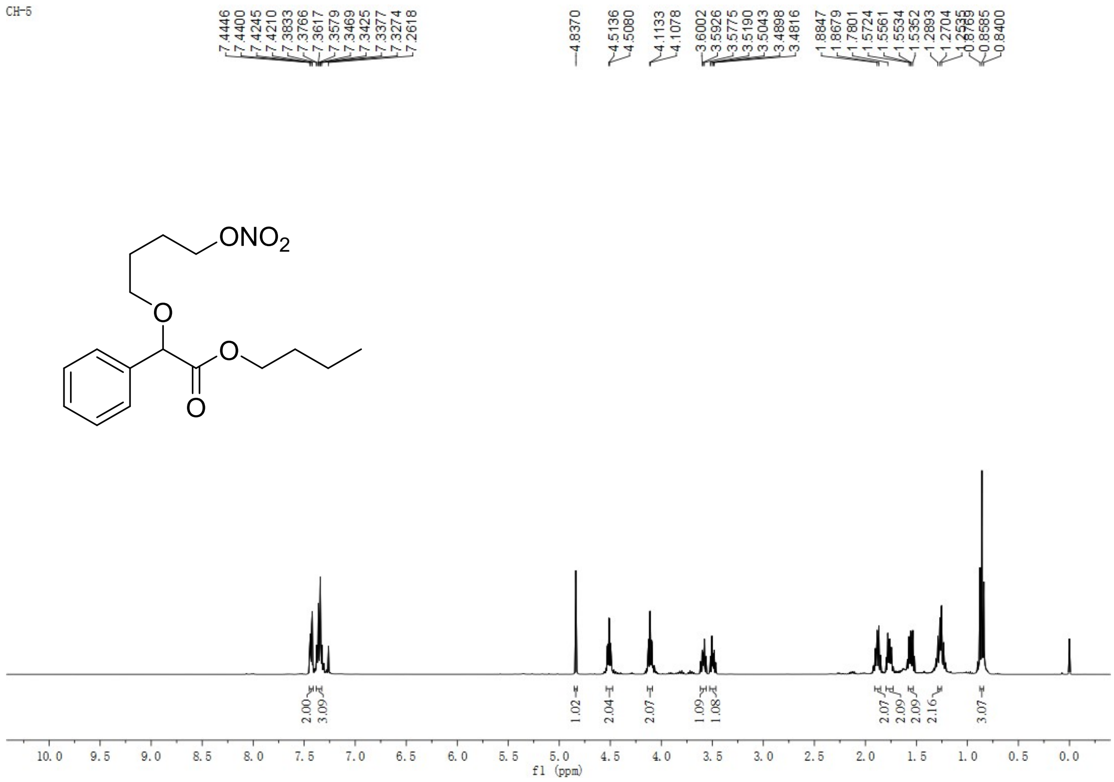
4pa ^{1}H NMR (400 MHz, $CDCl_3$)



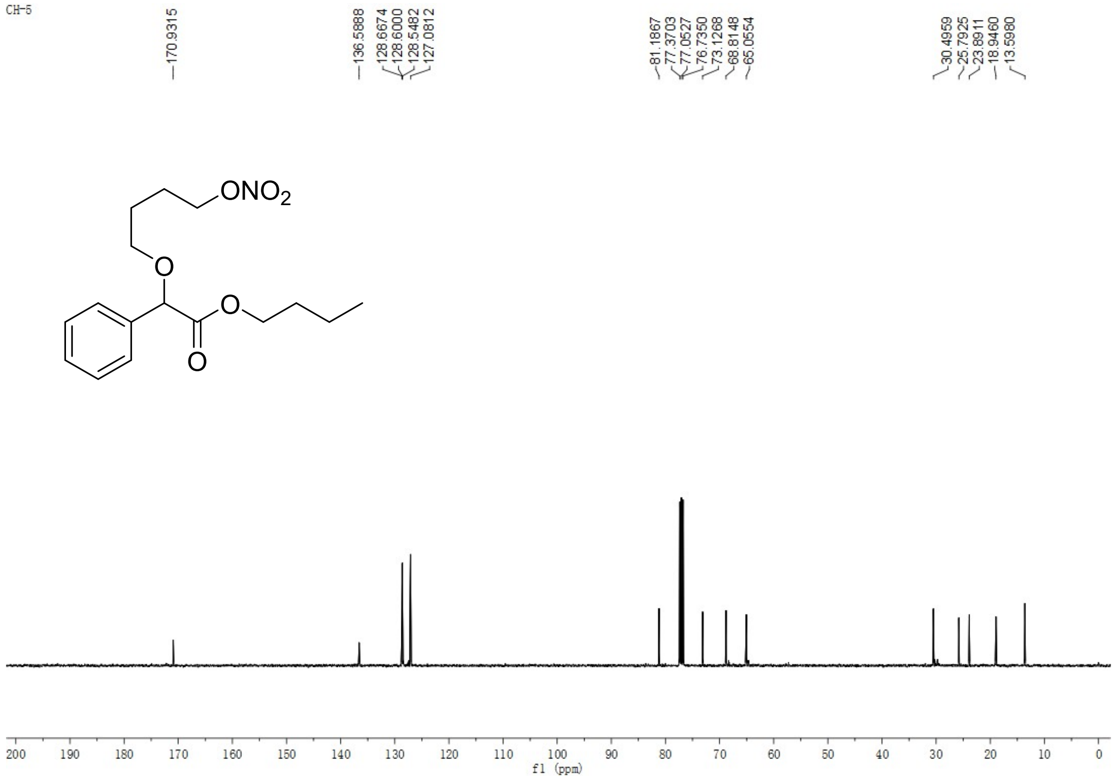
4pa ^{13}C NMR (101 MHz, $CDCl_3$)



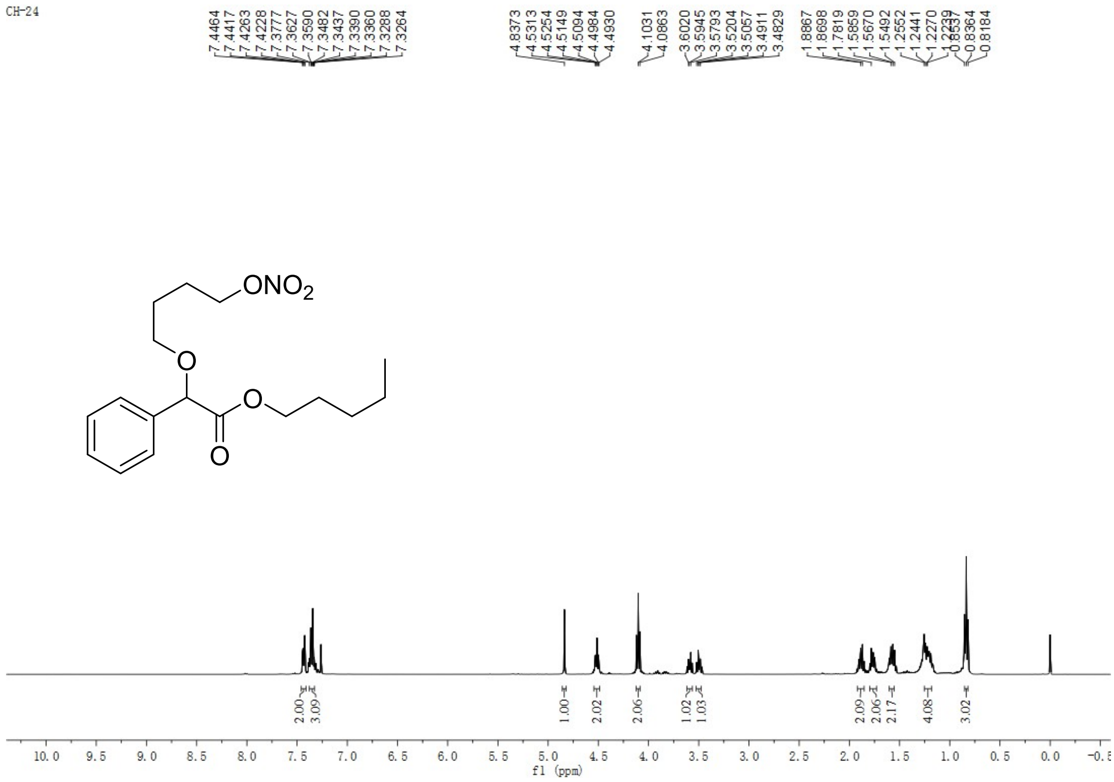
4qa ^{1}H NMR (400 MHz, $CDCl_3$)



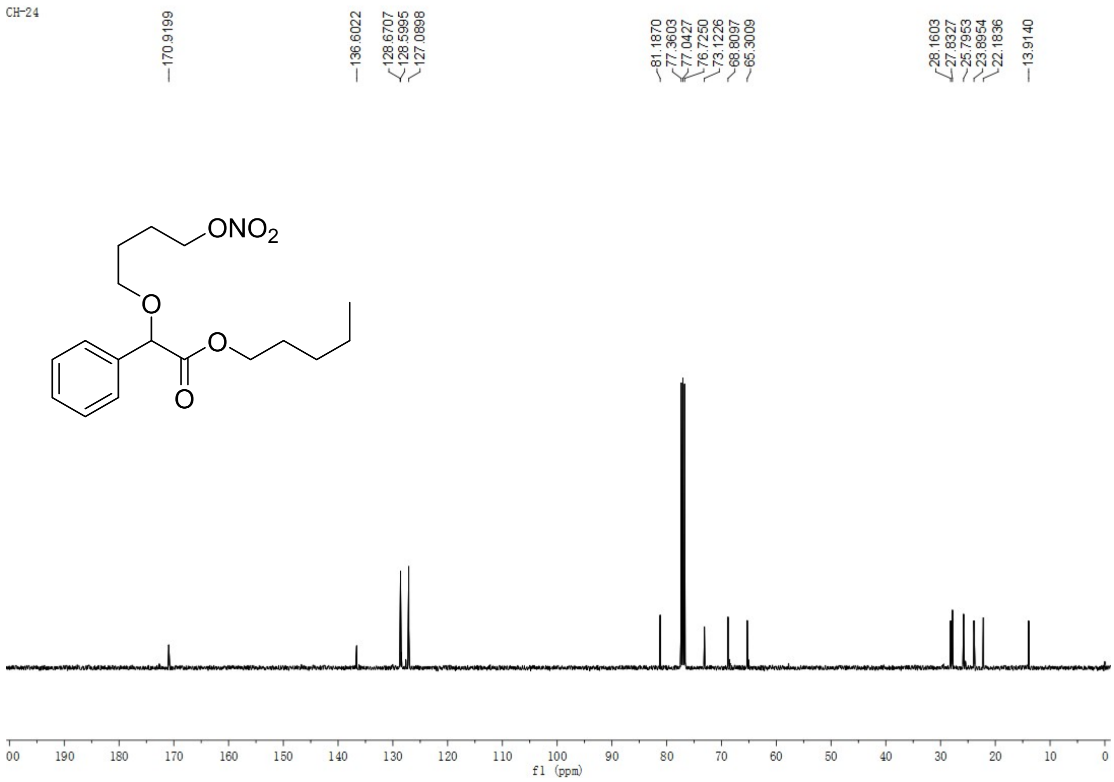
4qa ^{13}C NMR (101 MHz, $CDCl_3$)



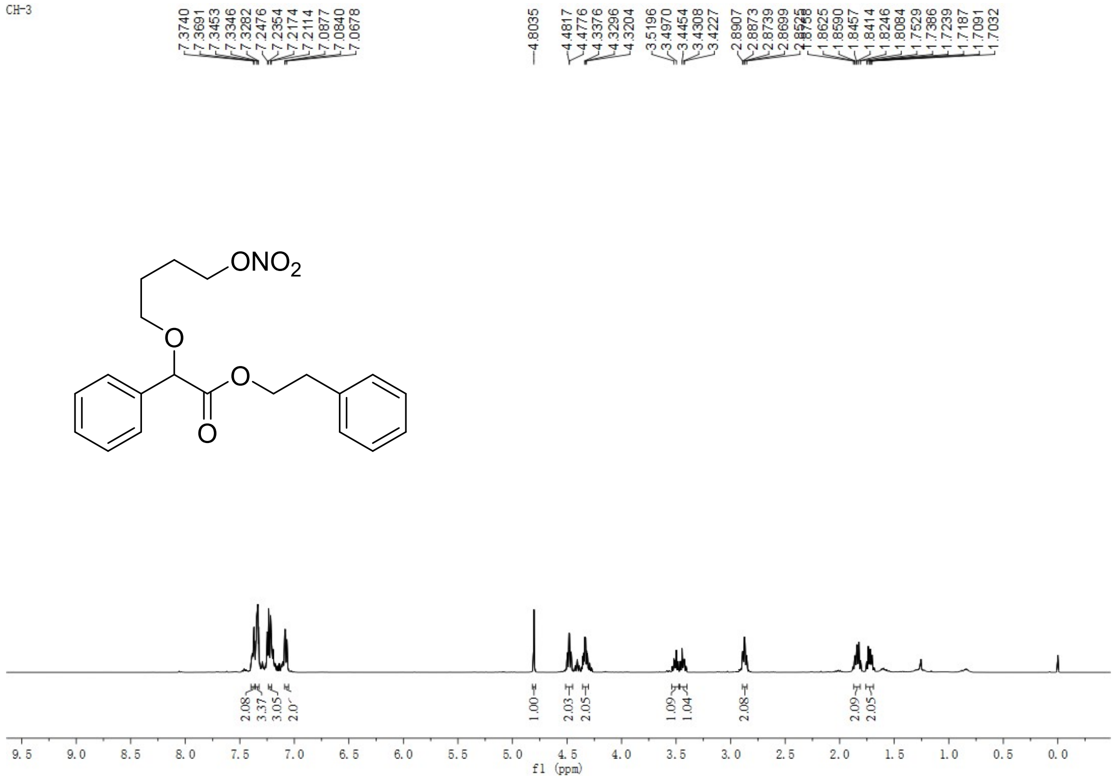
4ra ^{1}H NMR (400 MHz, $CDCl_3$)



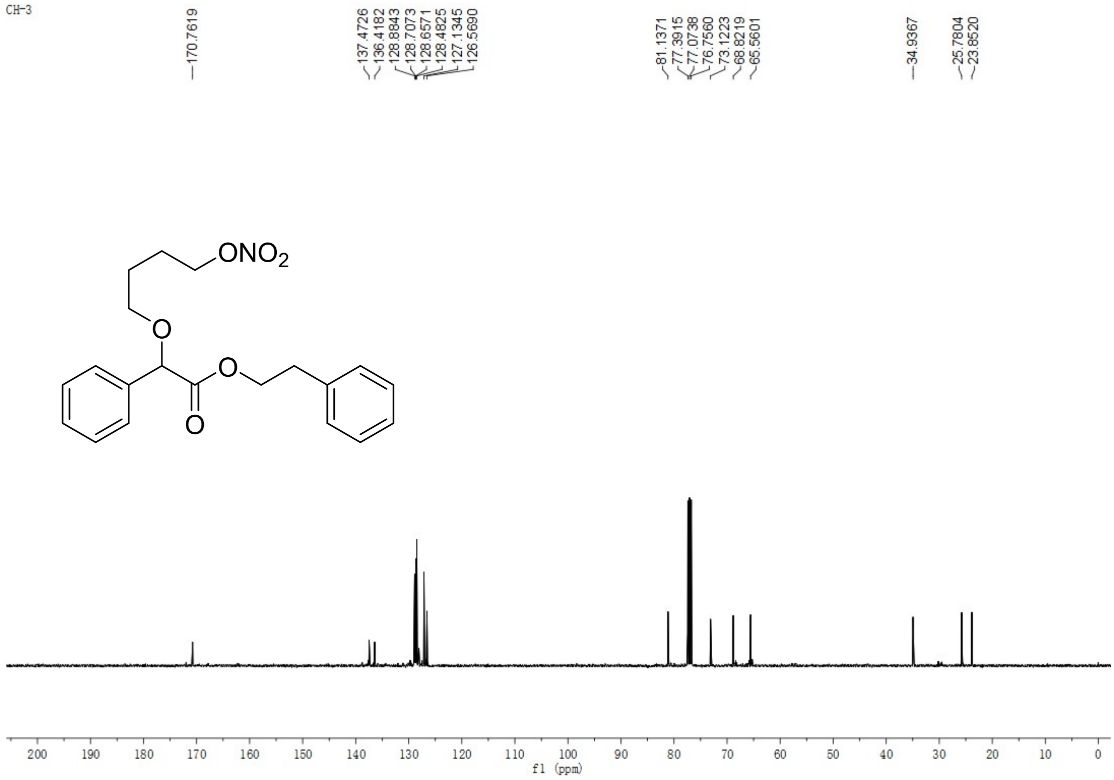
4ra ^{13}C NMR (101 MHz, $CDCl_3$)



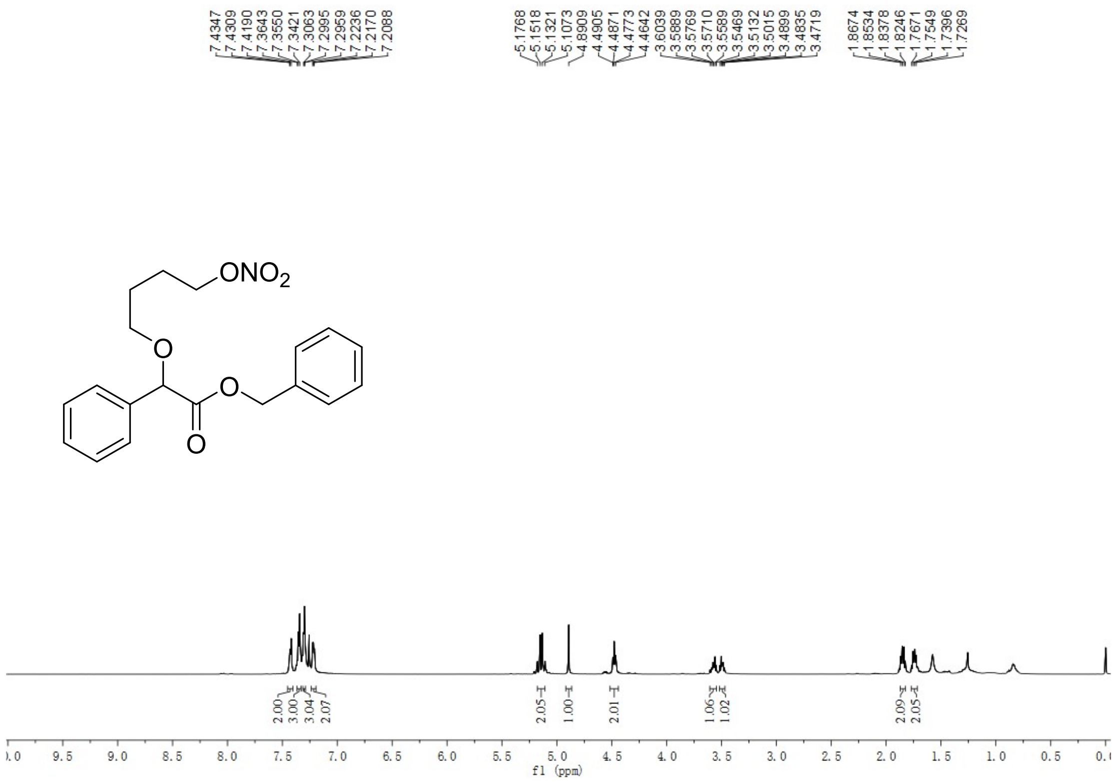
4sa ^{1}H NMR (400 MHz, $CDCl_3$)



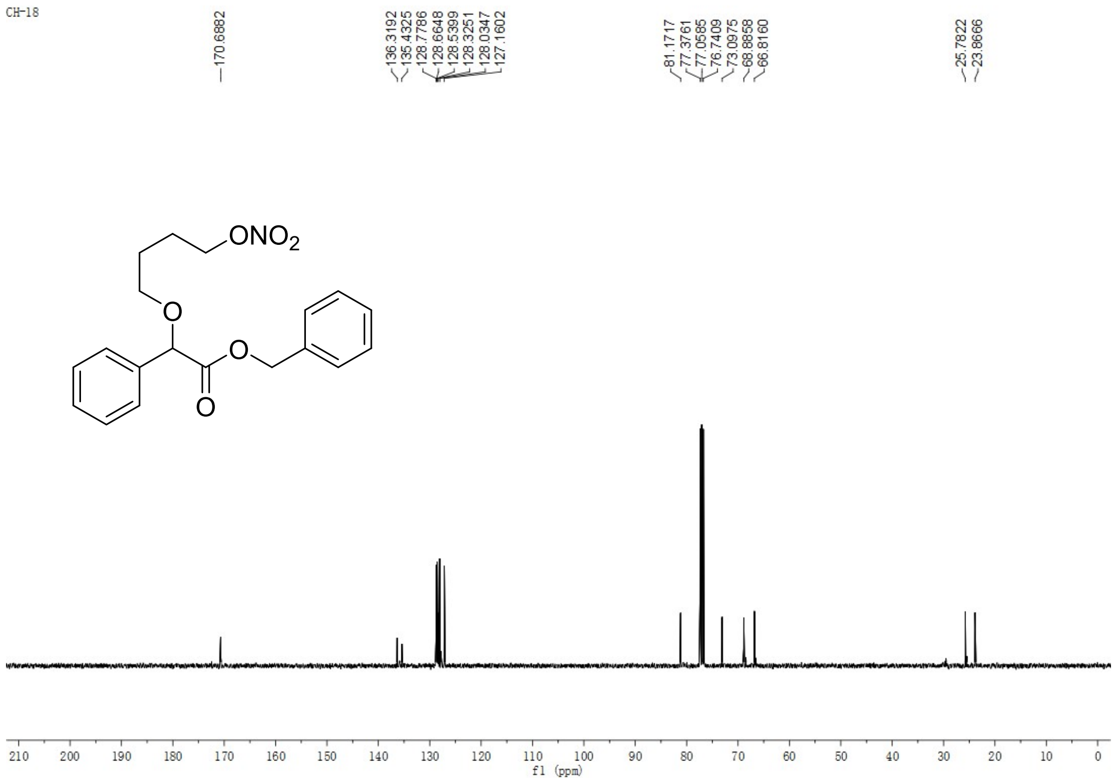
4sa ^{13}C NMR (101 MHz, $CDCl_3$)



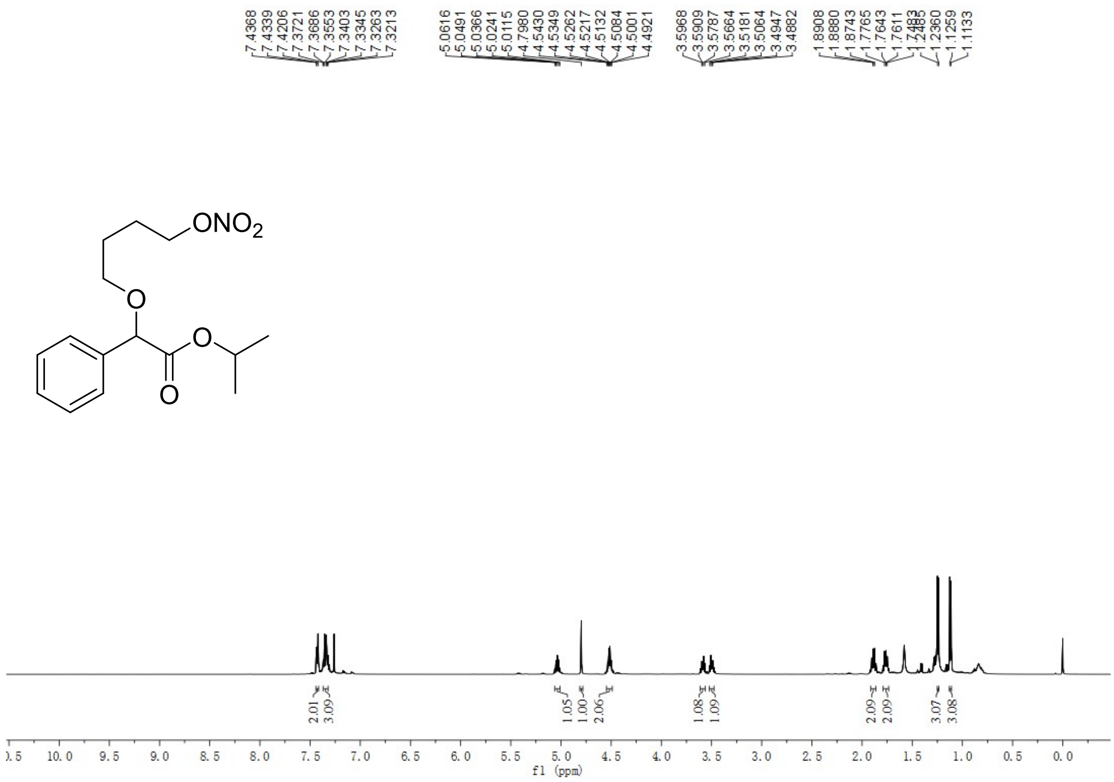
4ta ^{1}H NMR (400 MHz, $CDCl_3$)



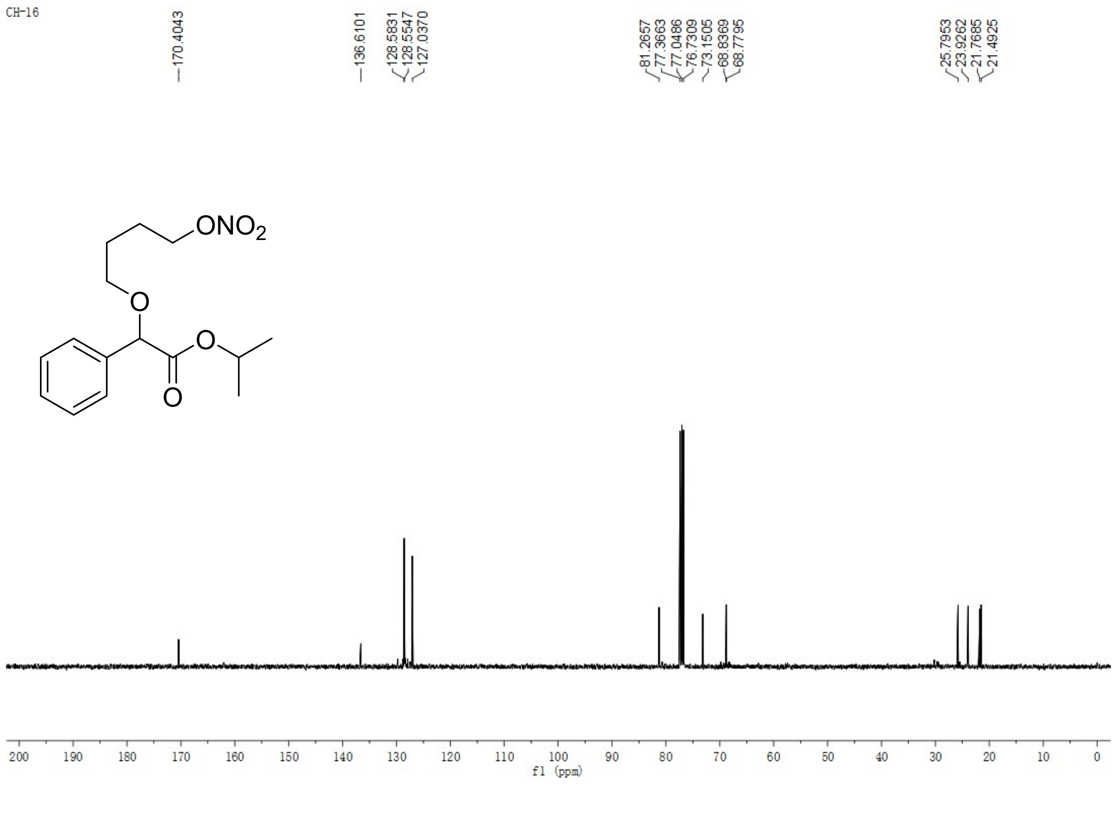
4ta ^{13}C NMR (101 MHz, $CDCl_3$)



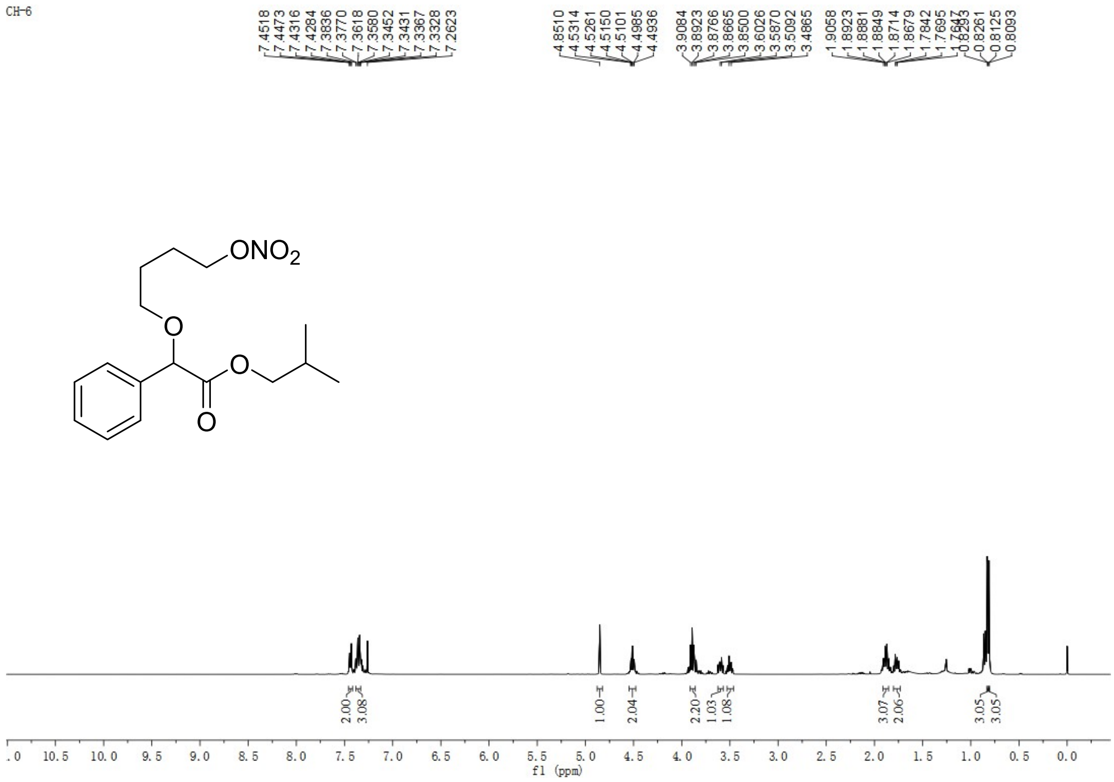
4ua ^{1}H NMR (400 MHz, $CDCl_3$)



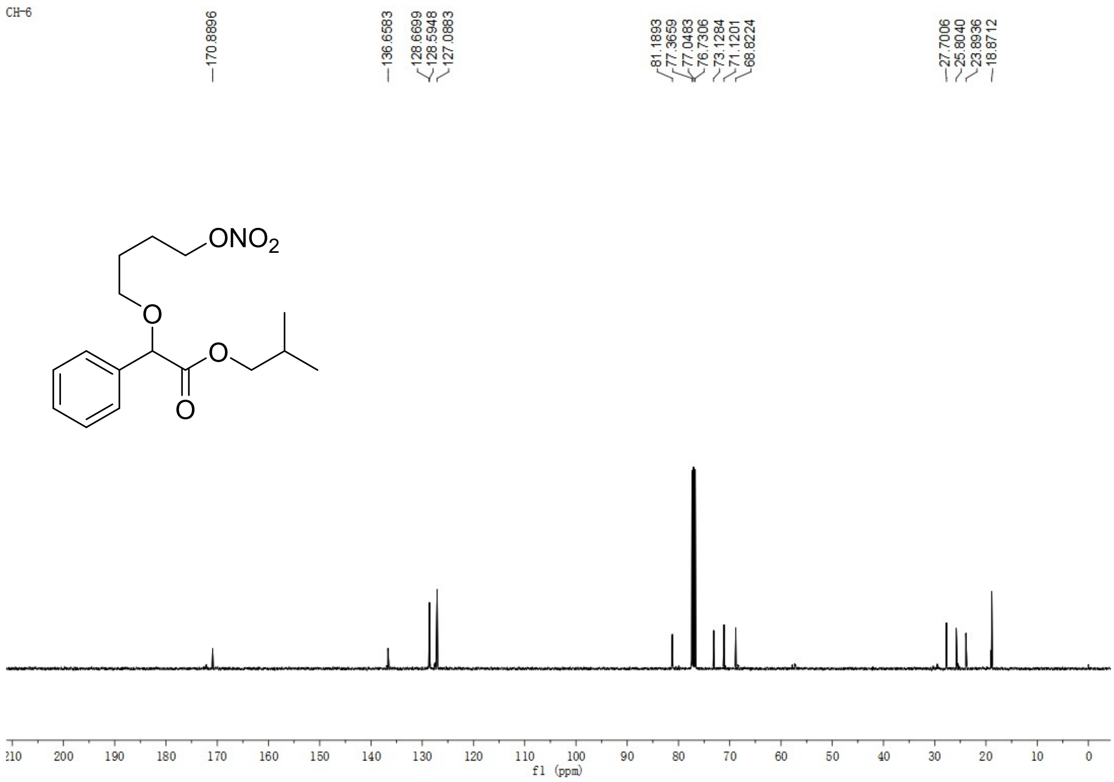
4ua ^{13}C NMR (101 MHz, $CDCl_3$)



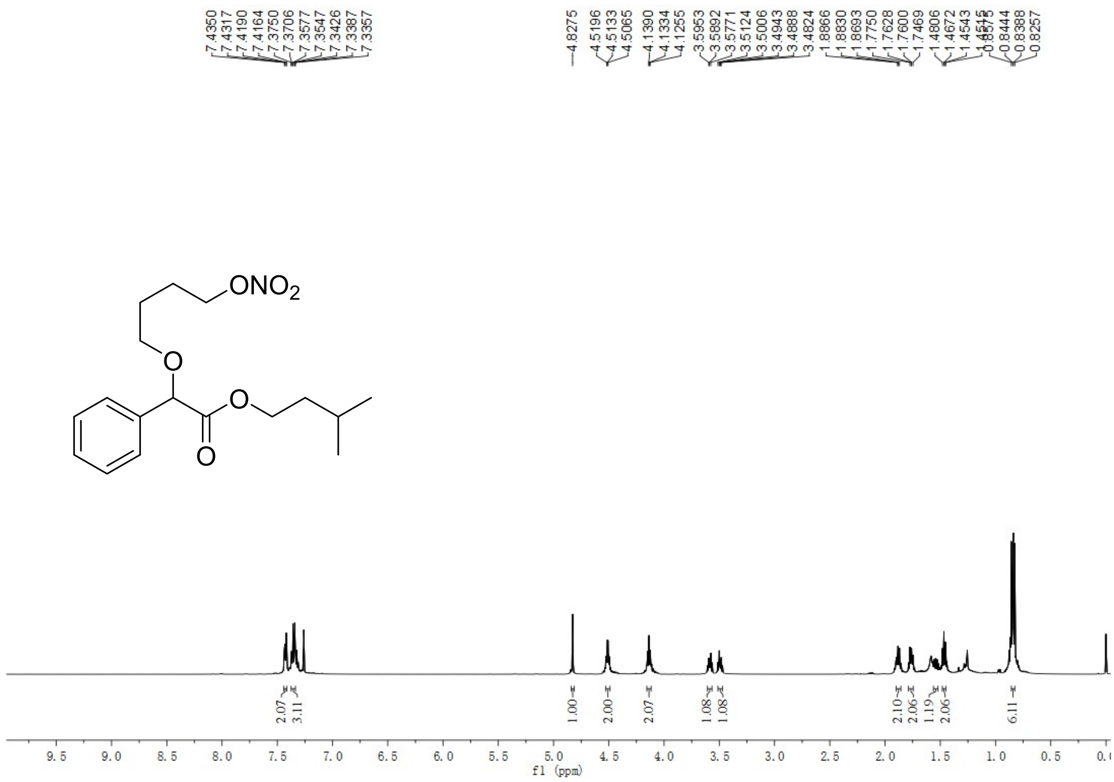
4va ^{1}H NMR (400 MHz, $CDCl_3$)



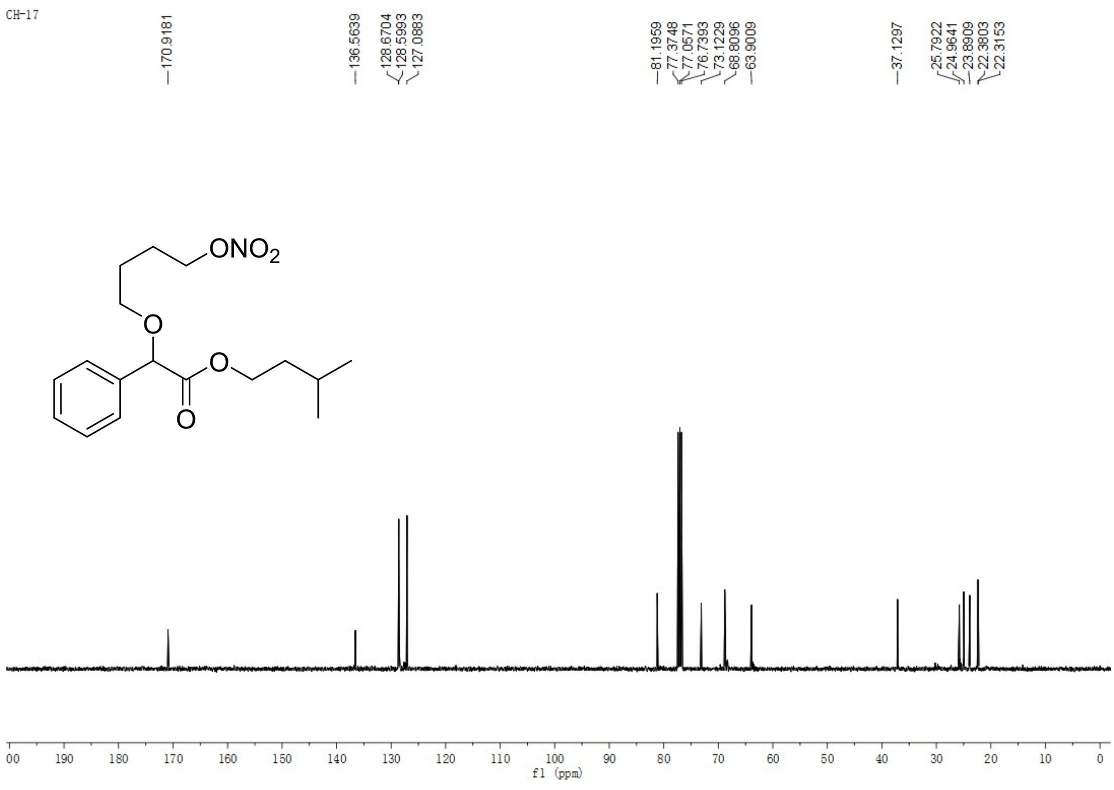
4va ^{13}C NMR (101 MHz, $CDCl_3$)



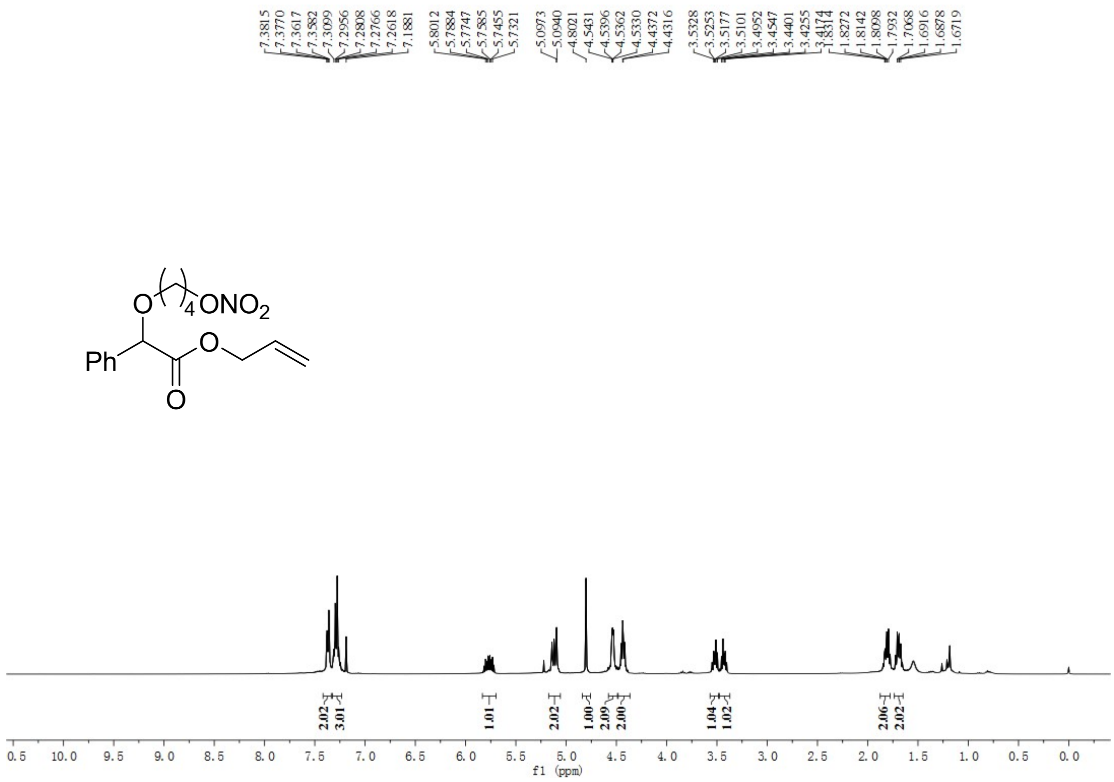
4wa ^{1}H NMR (400 MHz, $CDCl_3$)



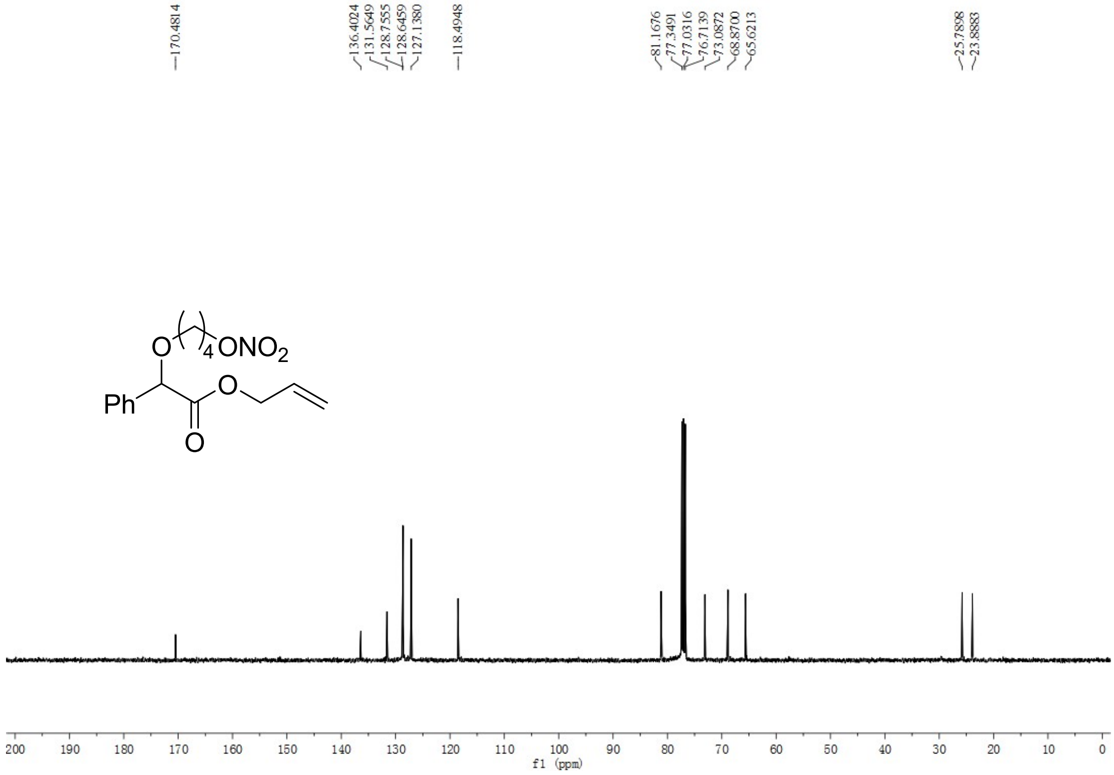
4wa ^{13}C NMR (101 MHz, $CDCl_3$)



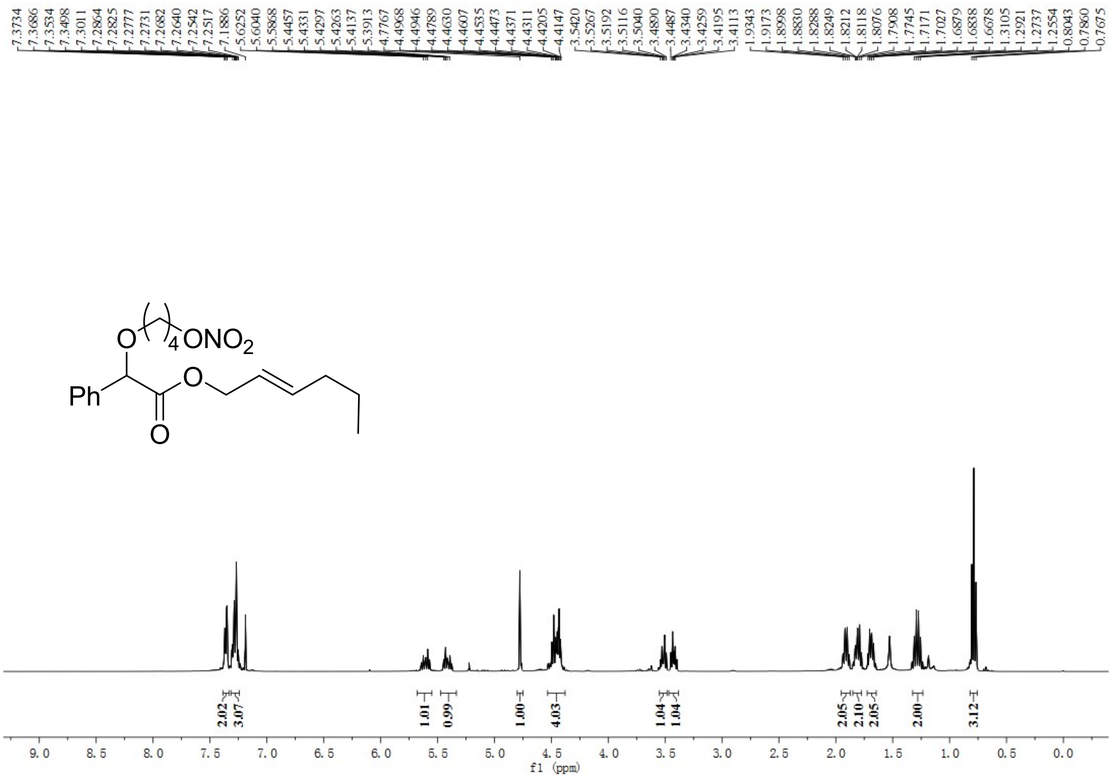
4xa ^{1}H NMR (400 MHz, $CDCl_3$)



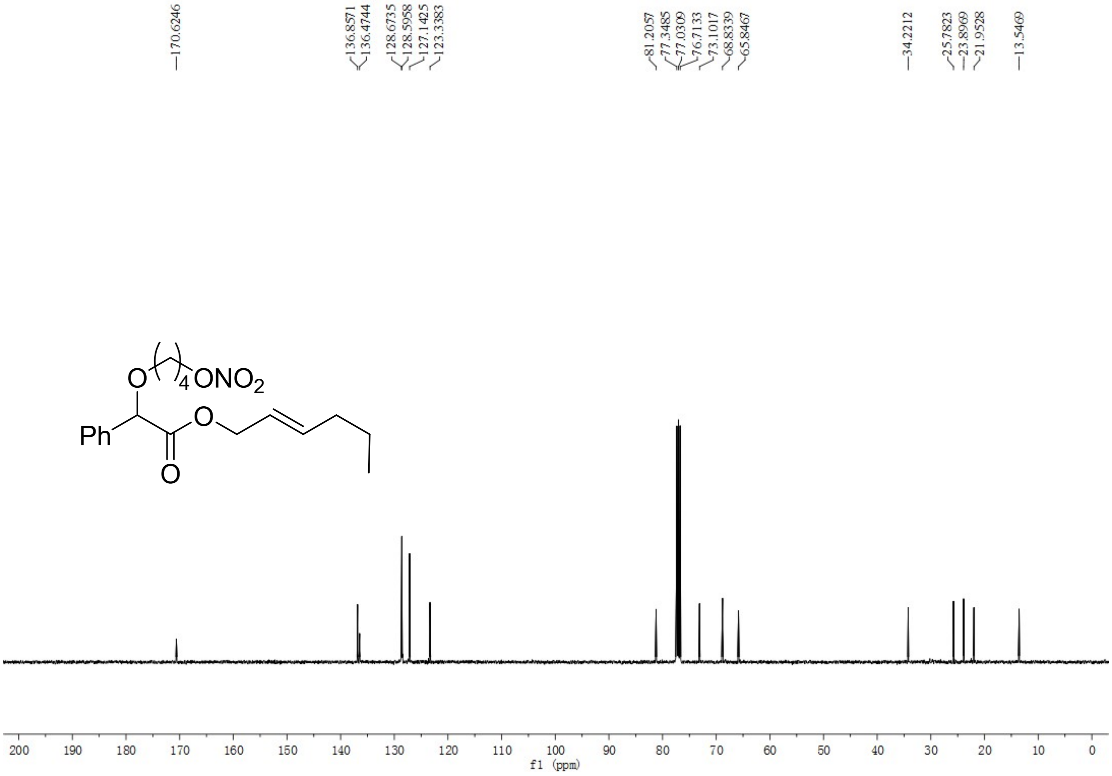
4xa ^{13}C NMR (101 MHz, $CDCl_3$)



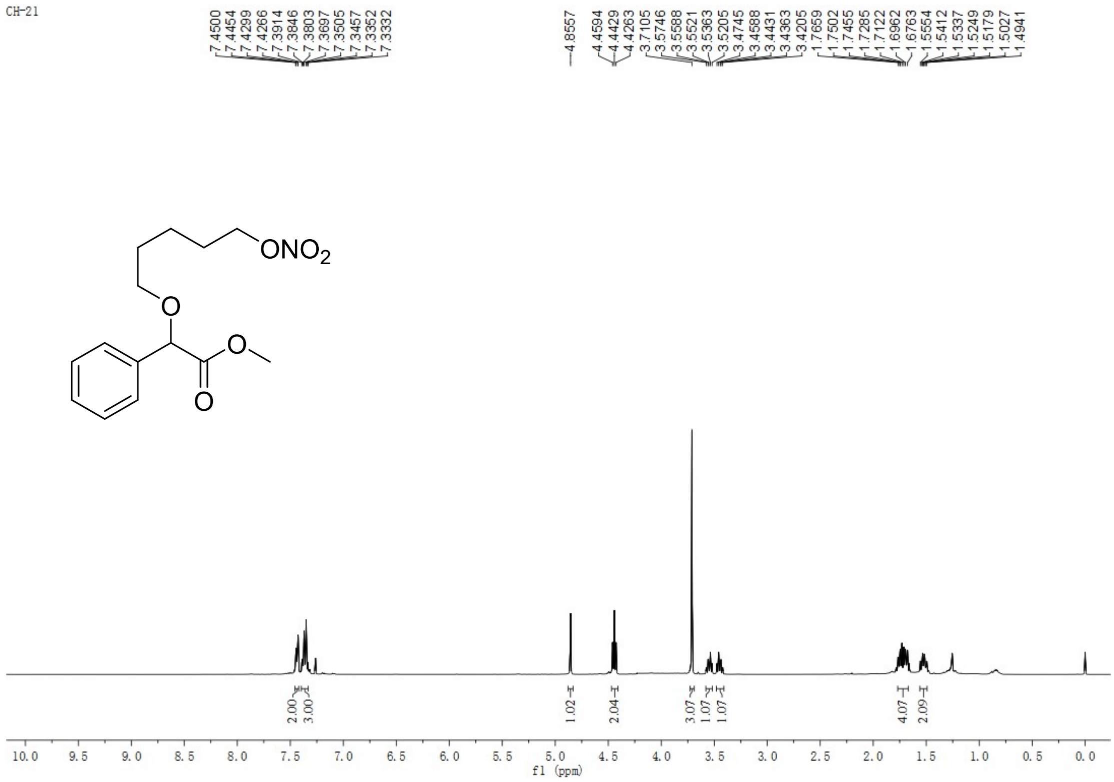
4ya ^{1}H NMR (400 MHz, $CDCl_3$)



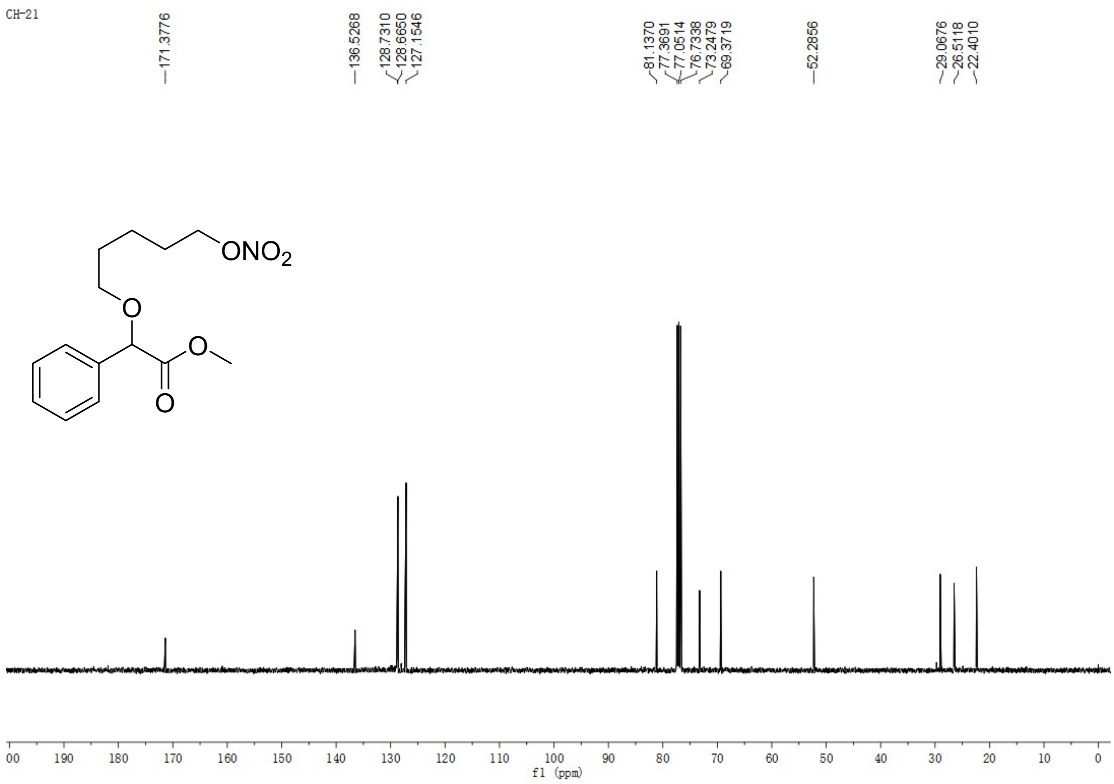
4ya ^{13}C NMR (101 MHz, $CDCl_3$)



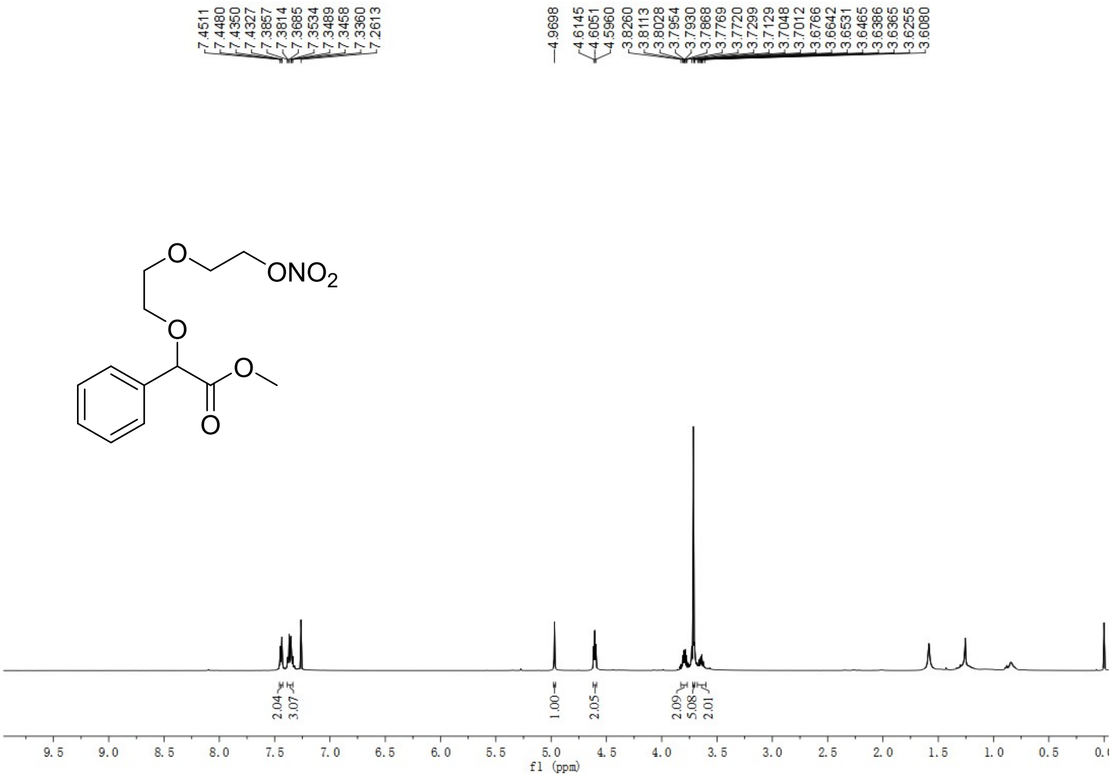
4ab ^{1}H NMR (400 MHz, $CDCl_3$)



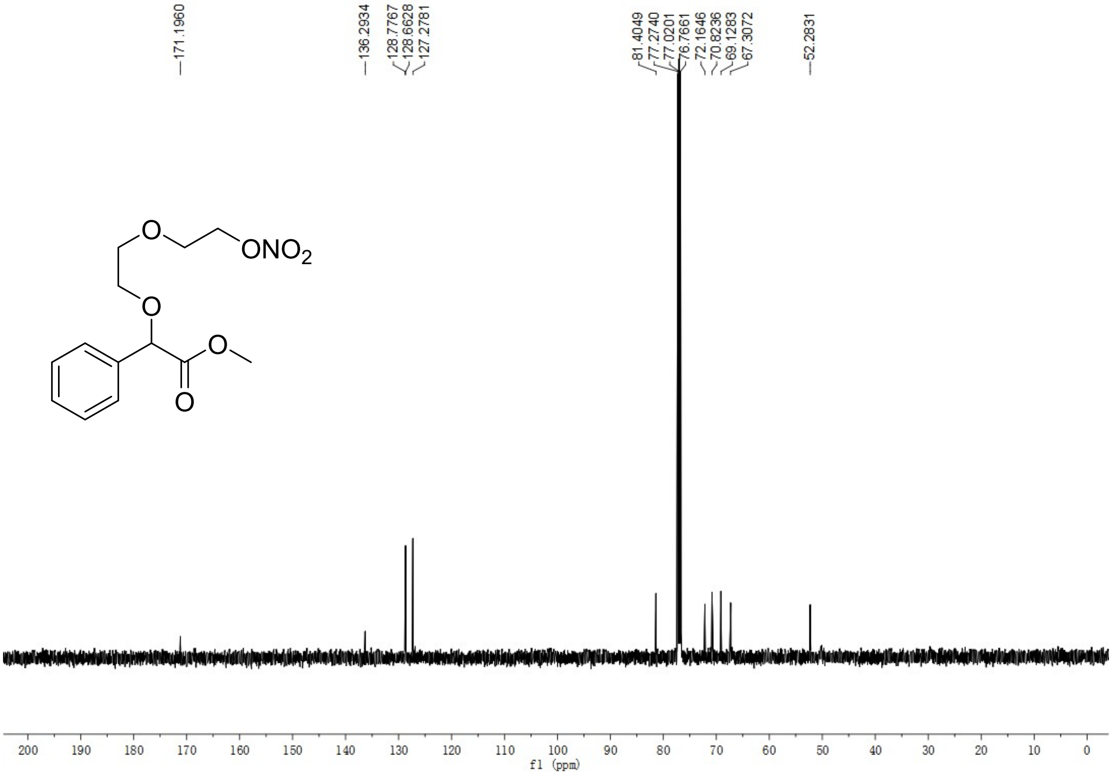
4ab ^{13}C NMR (101 MHz, $CDCl_3$)



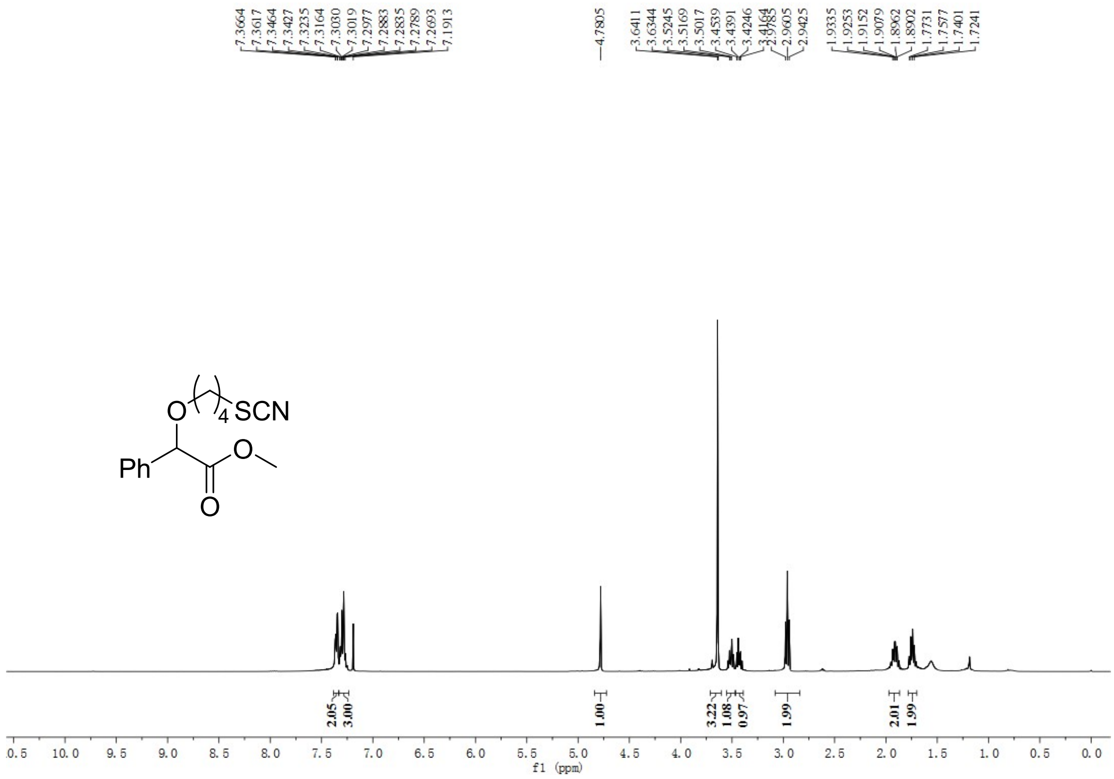
4ac ^{1}H NMR (400 MHz, $CDCl_3$)



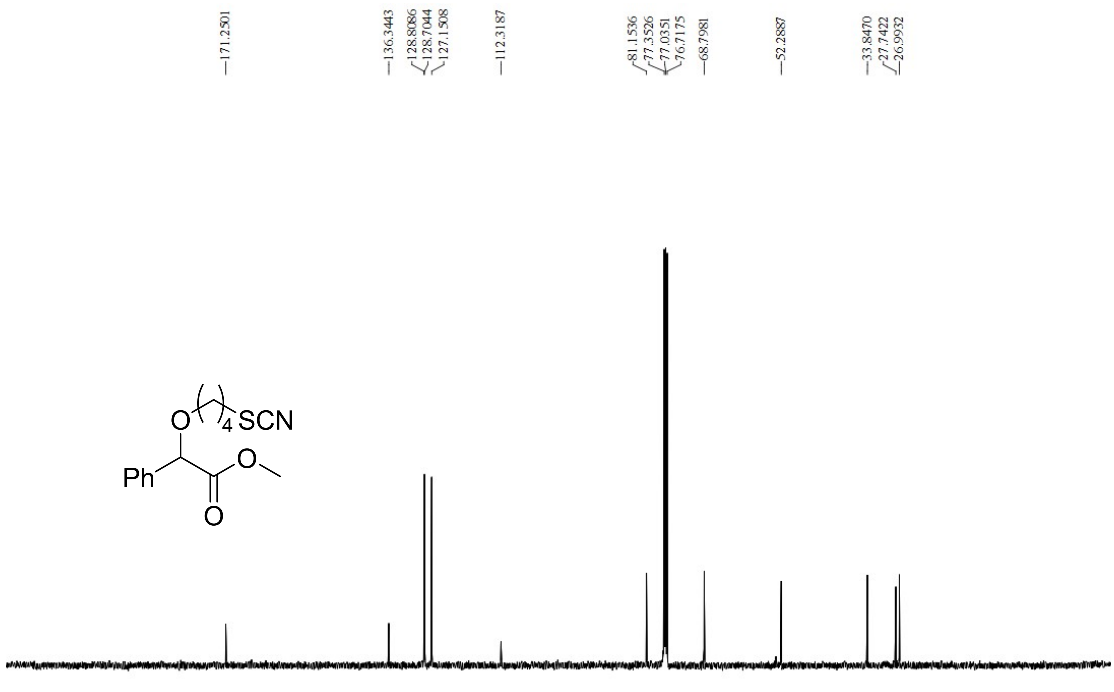
4ac ^{13}C NMR (101 MHz, $CDCl_3$)



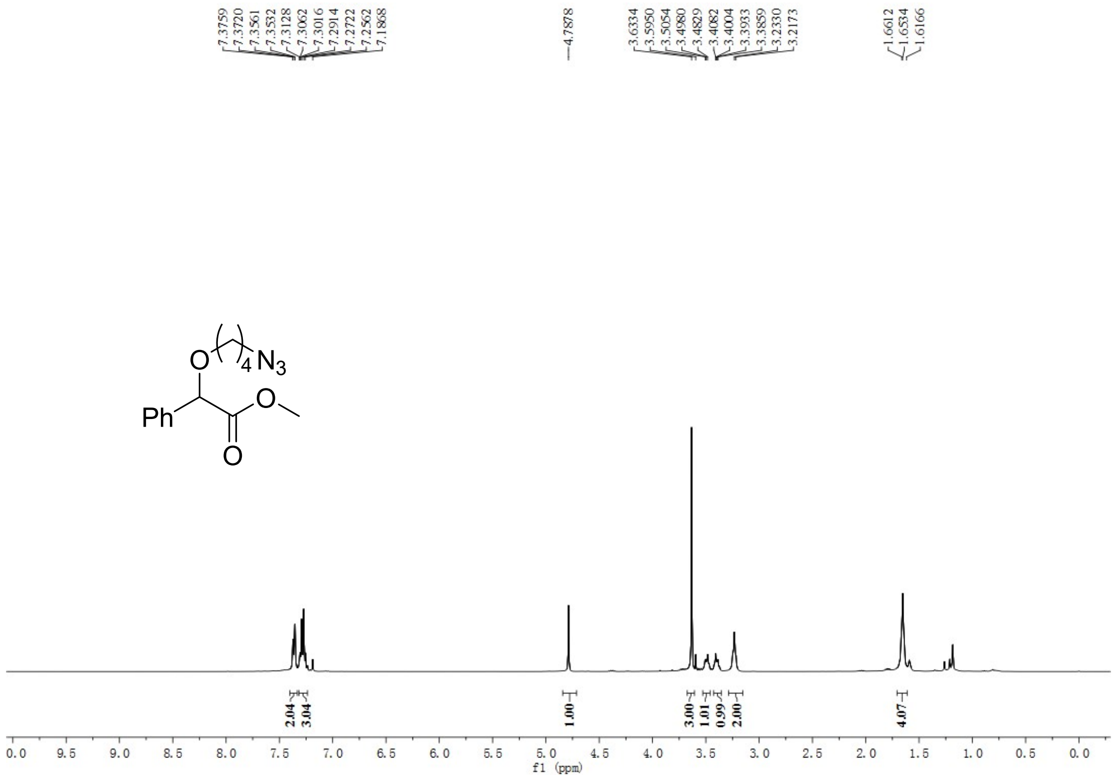
A ^{1}H NMR (400 MHz, $CDCl_3$)



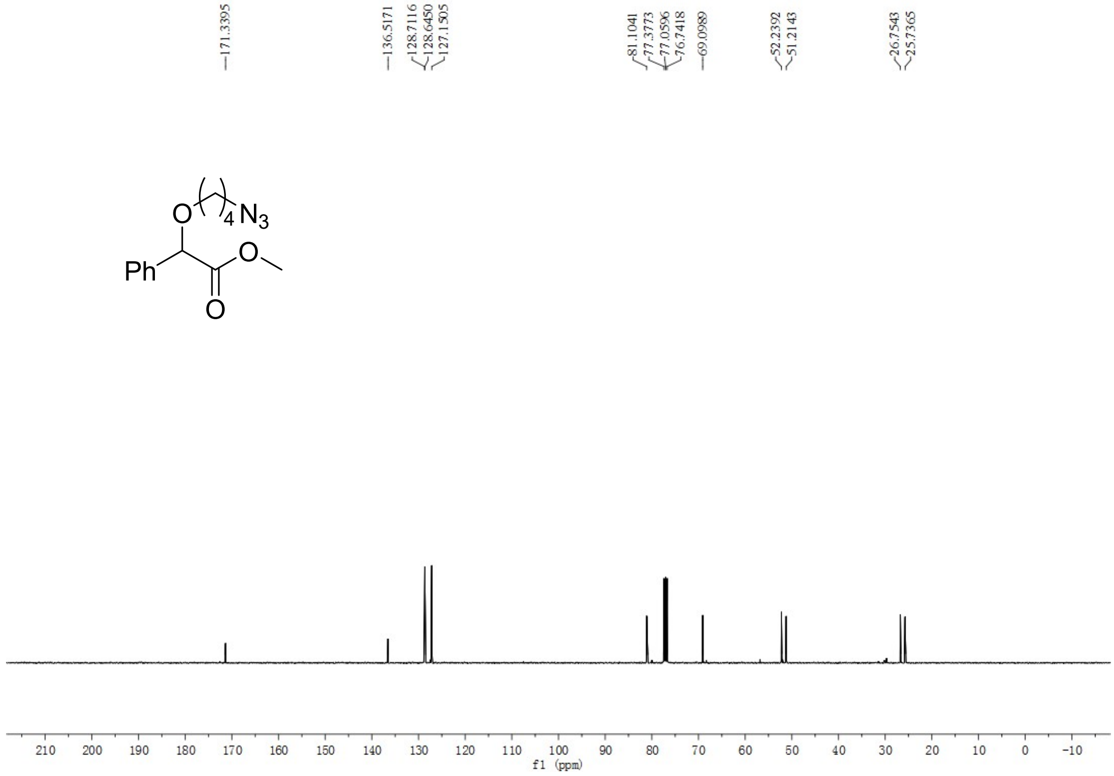
A ^{13}C NMR (101 MHz, $CDCl_3$)



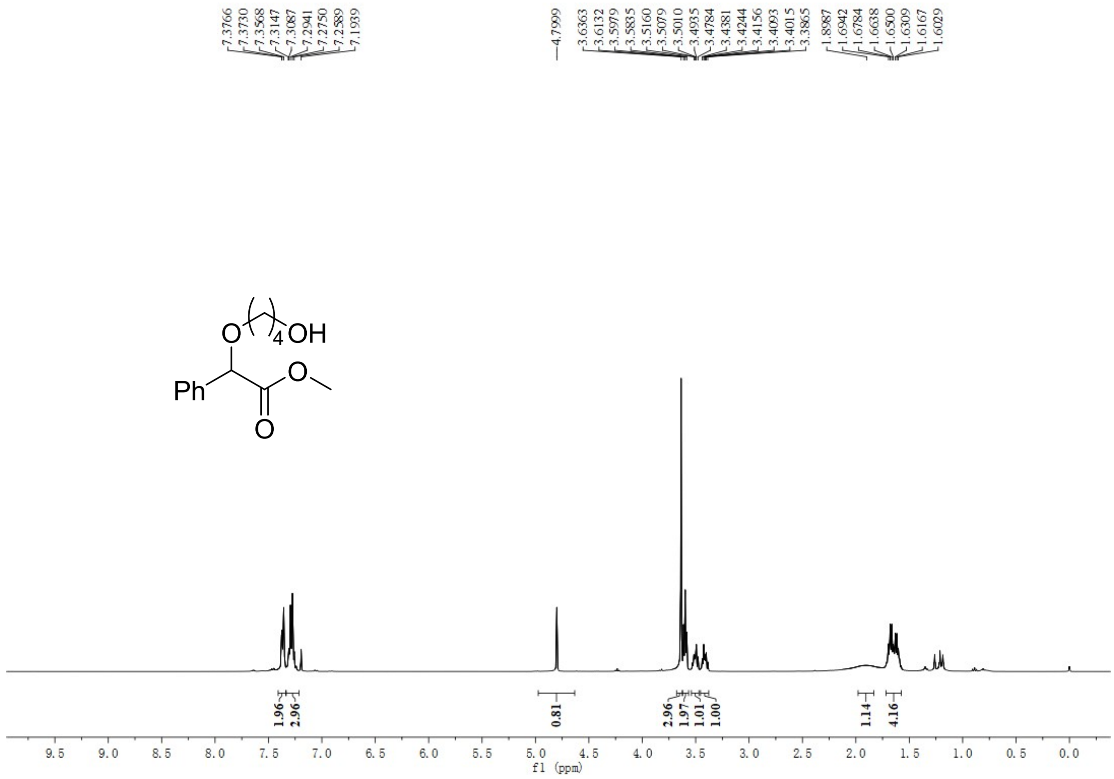
B ^{1}H NMR (400 MHz, $CDCl_3$)



B ^{13}C NMR (101 MHz, $CDCl_3$)



C ^{1}H NMR (400 MHz, $CDCl_3$)



C ^{13}C NMR (101 MHz, $CDCl_3$)