Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Table of Contents

General Information

All solvents and chemicals (including the starting materials in Table 3 and Table 4) were obtained commercially and were used as received. $H_2{}^{18}O$ (97% ^{18}O-enriched) was purchased from Qingdao., Ltd. Tenglong Weibo Technology co., (Qingdao, China) and $CH_3{}^{18}OH$ (98% 18O-enriched) were purchased from Cambridge Isotope Laboratories, Inc. (MA, USA).

NMR spectra were measured using a Bruker ARX 400 or ARX 100 spectrometer at 400 MHz (^1H) and 100 MHz (^{13}C). All spectra were recorded in $CDCl_3$ and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks. Mass spectra were in general recorded on an HP 6890/5973 GC-MS. MS-EI spectra were measured using a Bruker micrOTOFQⅡ.

Experimental Section

Typical procedure for oxidative ring-opening esterification reactions 1

0.5mmol amines, 0.4mmol catalyst, 5mmol (50%) H_2O_2 and 2 mL methanol/ethanol/propanol were added into a 38 mL pressure tubes under an atmosphere. The reaction was carried out with magnetic stirring speed of 450 rpm at 65 °C for 24h. After completion of the reaction, it was cooled to room temperature. 6 mL ethanol was added to dissolve the reaction mixture and the product was detected by GC-MS. The GC-yield was determined by GC-FID using biphenyl as internal standard and the isolated

yields were obtained by flash column chromatography. The catalyst was separated from the reaction mixture by centrifugation and prepared to reused for the next time.

Typical procedure for bromination of benzenepropanoic acid, 2-nitro-, methyl ester 2

0.5mmol 1, 2, 3, 4-tetrahydroquinolines, 1.0 eq AIBN, 1.5 eq NBS and CCl_4 (0.2M) were added into a 38 mL pressure tubes under an atmosphere. The reaction was carried out with magnetic stirring speed of 450 rpm at 80 °C for 4h. Then it was cooled to room temperature and the isolated yield 110.8mg (73%) was obtained by flash column chromatography.

Typical procedure for elimination reaction 3

0.5mmol methyl 2-bromo-3-(2-nitrophenyl)propanoate, 1.0 eq DBU, and THF (0.2M) were added into a 38 mL pressure tubes under an atmosphere. The reaction was carried out with magnetic stirring speed of 450 rpm at 60 °C for 2h. Then it was cooled to room temperature and the isolated yield 98.3 mg (88%) was obtained by flash column chromatography.

Typical procedure for producing 1-hydroxy-3,4-dihydroquinolin-2(1H)-one 4[1]

0.5mmol 1, 2, 3, 4-tetrahydroquinolines, 0.01mmol Na_2WO_4, 1.5mmol (50%) H_2O_2 and 5 mL methanol were added into a 38 mL

pressure tubes under an atmosphere. The reaction was carried out with magnetic stirring speed of 450 rpm at room temperature for 24h. After completion of the reaction, it was cooled to room temperature. 6 mL ethanol was added to dissolve the reaction mixture and the product was detected by GC-MS. The GC-yield was determined by GC-FID using biphenyl as internal standard and the isolated yields were obtained by flash column chromatography.

Typical procedure for intermediates detected by GC-MS and GC 5

The commercial 3,4-dihydroquinolin-2(1H)-one and obtained 1-hydroxy-3,4-dihydroquinolin-2(1H)-one were detected by GC-MS and GC. The reaction mixtures were obtained as typical procedure for oxidative ring-opening esterification reactions 1 at 1h, 3h, 6h, 12h, 15h, 18h and 24h and detected by GC-MS and GC. By contrast we confirm that the intermediate are 3,4-dihydroquinolin-2(1H)-one and obtained 1-hydroxy-3,4-dihydroquinolin-2(1H)-one. Yields of 1-hydroxy-3,4-dihydroquinolin-2(1H)-one at different reaction time were obtained by GC standard curve.

Typical procedure for oxidative ring-opening esterification reactions 6

0.5mmol 1, 2, 3, 4-tetrahydroquinolines, 1.5mmol H_2WO_4, 5 mmol (50%) H_2O_2 and 15mL tert-butanol were added into a 38 mL pressure tubes under an atmosphere. The reaction was carried out with magnetic stirring

speed of 450 rpm at 80 °C for 24h. After completion of the reaction, it was cooled to room temperature. The isolated yields were obtained by flash column chromatography.

Typical procedure for catalyst recovery reactions[2]

After the reaction, the catalyst was separated from the reaction mixture by centrifugation and transfer the catalyst with 10 ml deionized water to a 100 mL round-bottomed flask. Then mixture was treated with 1M triethylamine at 30°C for 2 h with stirring with the molar ratio of triethylamine to tungsten about 1.7:1 and the reaction mixture turned to brown liquid following. In the acidification process, the treated reaction liquid was added dropwise into 20 mL of nitric acid (2M) solution at 90 °C in 1 h with stirring, yellow precipitation was appeared. Then the system was cooled, and then the mixtures were centrifugalized under atmospheric condition. The obtained precipitation dried in vacuum at 50 °C for 5 h and it was then reused for the ring-opening esterification of the N-heterocycles. The catalyst was reused for five times with 1,2,3,4-tetrahydroquinoline as substrate and the GC-yields of the product were obtained in 94%, 91%, 83%, 81%, and 82%, respectivly.

Enlarge scale reaction for ring-opening esterification reactions

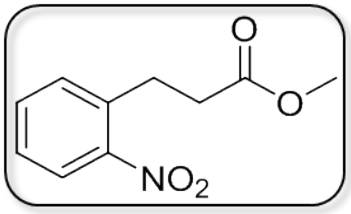
5mmol amines, 0.2mmol catalyst, 5 mL methanol and 25mmol (50%) H_2O_2 (2 equiv to substrate) was added dropwise into a 38 mL pressure tubes under an atmosphere. The reaction was carried out with magnetic

stirring speed of 450 rpm at 65 °C for 24h. Then it was cooled to room temperature and the isolated yields was 0.81g (78%) were obtained by HPLC.

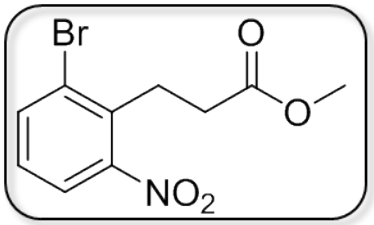
Purification Procedure

The crude products were subjected to silica gel column chromatography (60, 230-400 mesh supplied by Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd). Eluting with~75mL of petroleum ether, followed by 200:1 (Petroleum ether: Ethyl acetate).

NMR peaks and MS-EI of all products

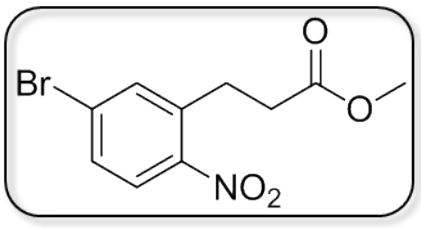


Benzenepropanoic acid, 2-nitro-, methyl ester[3]: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6aa** (97mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.39 (dd, *J* = 14.0, 7.2 Hz, 2H), 3.68 (s, 3H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.79, 135.59, 133.22, 132.18, 127.64, 124.93, 51.76, 34.64, 28.36. HRMS (ESI) calcld for [M + Na^+] 232.0575, found: 232.0580

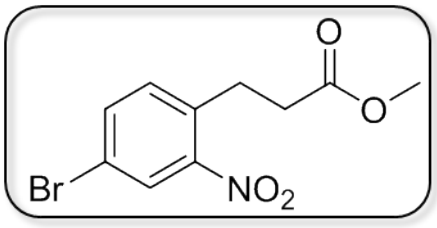


Benzenepropanoic acid, 5-bromo-2-nitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ba** (129mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 22.2, 8.1 Hz, 2H), 7.29 – 7.21 (m, 1H), 3.72 (s, 3H), 3.29 – 3.18 (m, 2H), 2.82 – 2.68

(m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.39, 151.48, 137.23, 128.40, 123.62, 51.90, 32.66, 28.02. HRMS (ESI) calcld for [M + Na^+] 309.9689, found: 309.9685

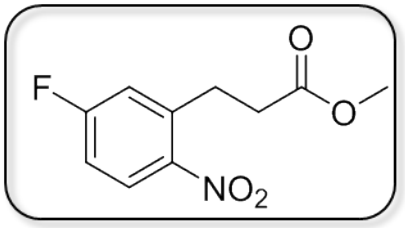


Benzenepropanoic acid, 6-bromo-2-nitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ca** (99mg, 78%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 2.4 Hz, 1H), 8.24 (dd, J = 8.9, 2.4 Hz, 1H), 8.06 (d, J = 8.9 Hz, 1H), 3.70 (s, 3H), 3.30 (t, J = 7.4 Hz, 2H), 2.80 (t, J = 7.4 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 172.04, 137.36, 127.28, 125.96, 122.80, 52.01, 34.02, 27.85.

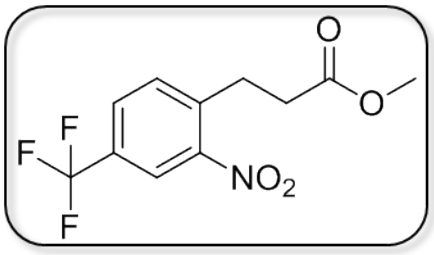


Benzenepropanoic acid, 4-bromo-2-nitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6da** (102mg, 81%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 1.8 Hz, 1H), 7.66 (dd, J = 8.3, 1.8 Hz, 1H), 7.31 (d, J = 8.3 Hz, 1H), 3.67 (s, 3H), 3.18 (t, J = 7.4 Hz, 2H), 2.71 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 172.54, 149.64, 136.20, 134.57, 133.68, 127.84, 120.60, 51.84, 34.32, 27.93.

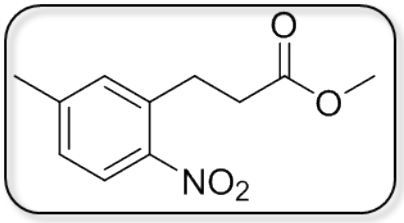


Benzenepropanoic acid, 5-fluoro-2-nitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ea** (72mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.98 (m, 1H), 7.14 – 6.99 (m, 1H), 6.86 – 6.75 (m, 1H), 3.69 (d, J = 3.2 Hz, 3H), 3.25 (td, J = 7.5, 4.1 Hz, 2H), 2.75 (td, J = 7.4, 3.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ172.51, 165.92, 163.37, 139.47, 139.38, 127.98, 127.88, 119.05, 118.82, 114.87, 114.64, 51.85, 34.21, 28.61. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.64.

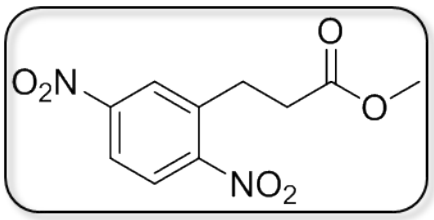


Benzenepropanoic acid, 2-nitro-4-(trifluoromethyl)-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6fa** (121mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 3.68 (s, 3H), 3.30 (t, J = 7.3 Hz, 2H), 2.76 (t, J = 7.4 Hz, 2H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 172.44, 149.21, 139.58, 133.29, 132.44, 130.91, 129.56, 128.81, 122.28, 51.93, 34.19, 28.21. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.90. HRMS (ESI) calcld for [M + Na^+] 300.0443, found: 300.0454

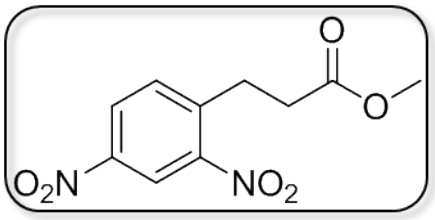


Benzenepropanoic acid, 5-methyl-2-nitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ga** (89mg, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 1H), 7.20 – 7.13 (m, 2H), 3.68 (s, 3H), 3.20 (d, J = 7.7 Hz, 2H), 2.72 (t, J = 7.6 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.91, 144.47, 135.84, 132.79, 128.23, 125.24, 51.73, 34.69, 28.64, 21.39.

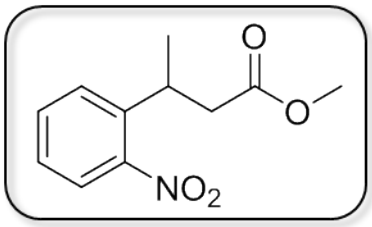


Benzenepropanoic acid, 2,5-dinitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ha** (98mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 2.1 Hz, 1H), 7.52 (dd, J = 8.7, 2.1 Hz, 1H), 3.69 (s, 3H), 3.21 (t, J =

7.5 Hz, 2H), 2.73 (t, J = 7.5 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 172.45, 137.74, 135.17, 130.88, 126.52, 51.87, 34.35, 28.26.

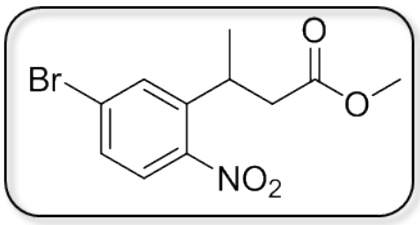


Benzenepropanoic acid, 2,4-dinitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ia** (99mg, 83%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 2.0 Hz, 1H), 7.52 (dd, J = 8.7, 2.1 Hz, 1H), 3.69 (s, 3H), 3.21 (t, J = 7.5 Hz, 2H), 2.73 (t, J = 7.5 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 172.46, 137.74, 135.17, 130.88, 126.52, 51.88, 34.35, 28.26. HRMS (ESI) calcld for [M + Na^+] 277.0442, found: 277.0431

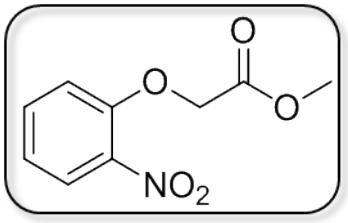


Benzenepropanoic acid, β-methyl-2-nitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ja** (75mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 1H), 7.55 (dd, J = 9.8, 5.5 Hz, 1H), 7.49 – 7.28 (m, 2H), 3.80 (dd, J = 14.4, 7.3 Hz, 1H), 3.60 (s, 3H), 2.82 – 2.49 (m, 2H), 1.37 (d, J = 6.9 Hz, 3H).^{13}C NMR

(101 MHz, $CDCl_3$) δ 171.80, 149.99, 139.61, 132.64, 127.74, 127.16, 124.09, 51.70, 41.97, 30.60, 21.42.

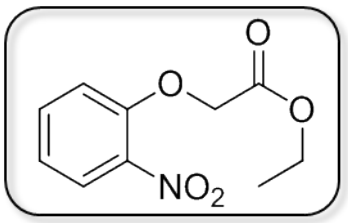


Benzenepropanoic acid, 5-bromo- β-methyl-2-nitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ka** (79mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.6 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.48 (dd, J = 8.6, 2.1 Hz, 1H), 3.61 (s, 3H), 2.72 – 2.56 (m, 2H), 1.79 – 1.63 (m, 1H), 1.37 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.48 (s), 141.98, 131.09, 130.43, 125.78, 51.81, 41.72, 30.58, 21.27. HRMS (ESI) calcld for [M + Na^+] 323.9847, found: 323.9842.

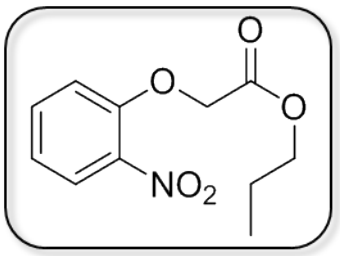


Acetic acid, 2-(2-nitrophenoxy)-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6la** (71mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 8.1, 1.6 Hz, 1H), 7.59 – 7.47 (m, 1H), 7.14 – 7.07 (m, 1H), 6.98 (d, J = 2.0 Hz, 1H), 4.80 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.33, 151.22, 134.08, 125.91,

121.86, 115.20, 66.50, 52.55. HRMS (ESI) calcld for [M + Na^+] 234.0381, found: 234.0373

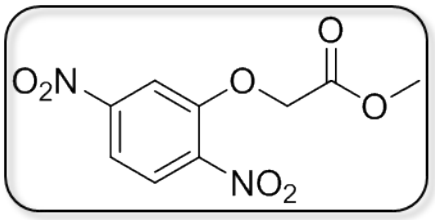


Acetic acid, 2-(2-nitrophenoxy)-, ethyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6lb** (93mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.1, 1.6 Hz, 1H), 7.59 – 7.46 (m, 1H), 7.16 – 7.06 (m, 1H), 7.00 (d, J = 8.4 Hz, 1H), 4.98 – 4.49 (m, 2H), 4.37 – 4.14 (m, 2H), 1.29 (p, J = 5.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.77, 151.32, 134.01, 125.89, 121.75, 115.20, 66.61, 61.76, 14.10.

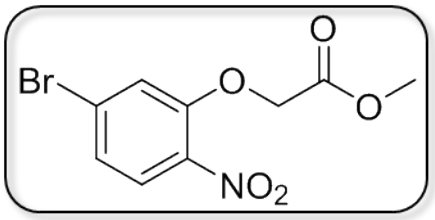


Acetic acid, 2-(2-nitrophenoxy)-, propyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6lc** (78mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.1, 1.5 Hz, 1H), 7.68 – 7.33 (m, 1H), 7.03 (m, J = 20.4, 13.5, 7.4 Hz, 2H), 4.79 (s, 2H), 4.16 (t, J = 6.7 Hz, 2H), 1.67 (dd, J = 14.2, 7.0 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.89, 151.30, 134.00, 125.89, 123.51, 121.71,

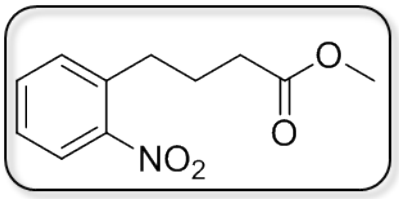
116.44, 115.08, 67.29, 66.51, 21.85, 10.22. HRMS (ESI) calcld for [M + Na^+] 262.0685, found: 262.0686.



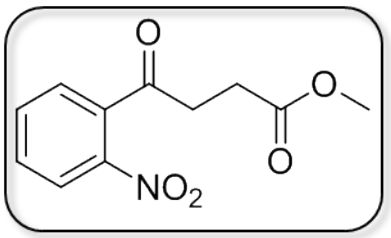
Acetic acid, 2-(2,4-dinitrophenoxy)-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ma** (118mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.85 (s, 1H), 4.92 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.32, 151.33, 150.11, 126.40, 116.70, 110.32, 66.35, 52.87. HRMS (ESI) calcld for [M + Na^+] 279.0222, found: 279.0224.



Acetic acid, 2-(5-bromo-2-nitrophenoxy)-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6na** (75mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 2.8 Hz, 1H), 8.43 (dd, J = 9.3, 2.8 Hz, 1H), 7.11 (d, J = 9.3 Hz, 1H), 4.95 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.01, 155.51, 128.87, 122.09, 114.72, 66.24, 52.89. HRMS (ESI) calcld for [M + Na^+] 311.9474, found:311.9478.

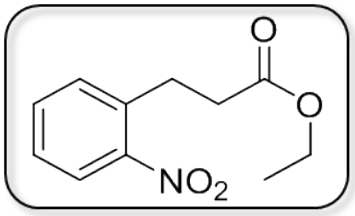


Benzenebutanoic acid, 2-nitro-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6oa** (90mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 1H), 7.53 (t, J = 5.3 Hz, 1H), 7.37 (d, J = 7.6 Hz, 2H), 3.68 (s, 3H), 2.93 (dd, J = 8.7, 6.9 Hz, 2H), 2.41 (t, J = 7.3 Hz, 2H), 2.01 (dt, J = 9.8, 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.51, 136.43, 132.97, 131.96, 127.25, 124.75, 51.60, 33.52, 32.14, 25.77. HRMS (ESI) calcld for [M + Na^+] 246.0738, found: 246.0737.

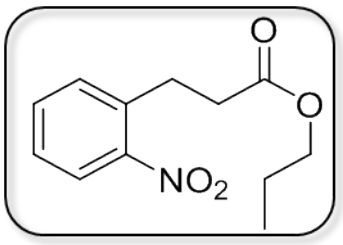


Benzenebutanoic acid, 2-nitro-γ-oxo-, methyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6pa** (102mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.2 Hz, 1H), 7.75 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.7 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 3.73 (s, 3H), 3.14 (t, J = 6.6 Hz, 2H), 2.84 (t, J = 6.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.84, 173.11, 145.55, 137.74, 134.37, 130.60,

127.60, 124.42, 51.99, 37.58, 28.13. HRMS (ESI) calcld for [M + Na^+] 260.0527, found: 260.0529

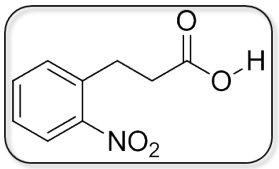


Benzenepropanoic acid, 2-nitro-, ethyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ab** (97mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.1 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.39 (dd, J = 16.6, 7.9 Hz, 2H), 4.03 (t, J = 6.7 Hz, 2H), 3.23 (t, J = 7.5 Hz, 2H), 2.73 (t, J = 7.5 Hz, 2H), 0.90 (d, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.46, 149.27, 135.70, 133.18, 132.18, 127.58, 124.92, 34.82, 28.42, 21.93, 10.35.

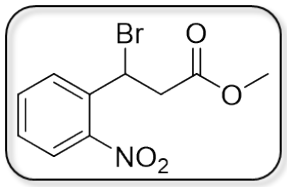


Benzenepropanoic acid, 2-nitro-, propyl ester: The title compound was prepared according to the general procedure and purified by column chromatography to yield the product **6ac** (83mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.53 (dd, *J* = 7.2, 2.8 Hz, 1H), 7.43 – 7.38 (m, 2H), 4.03 (t, *J* = 6.7 Hz, 2H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.77 (dd, *J* = 14.1, 6.5 Hz, 2H), 1.62 (dd, *J* = 14.2, 7.1 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.12, 149.25,

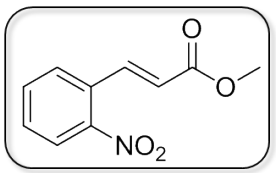
133.20, 132.14, 127.60, 124.96, 66.32, 34.83, 28.41, 21.91, 10.34. HRMS (ESI) calcld for [M + Na^+] 260.0895, found: 260.0893.



3-(2-nitrophenyl)propanoic acid:[5] The title compound was prepared according to the general procedure 6 and purified by column chromatography to yield the product **6ad** (72.3mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.56 (m, *J* = 10.9, 4.1 Hz, 1H), 7.46 – 7.33 (m, 2H), 3.23 (t, *J* = 7.5 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.69, 149.23, 135.26, 133.35, 132.15, 127.79, 125.03, 34.59, 28.06.

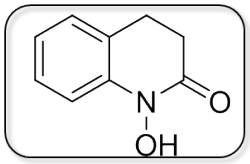


Methyl 2-bromo-3-(2-nitrophenyl)propanoate: The title compound was prepared according to the general procedure 2 and purified by column chromatography to yield the product **8aa** (110.8mg, 73%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (m, J = 17.2, 8.0 Hz, 2H), 7.66 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.7 Hz, 1H), 6.02 (t, J = 7.4 Hz, 1H), 3.70 (s, 3H), 3.32 (d, J = 7.2 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.32, 147.78, 135.24, 133.46, 130.18, 129.37, 124.57, 52.30, 44.73, 40.42



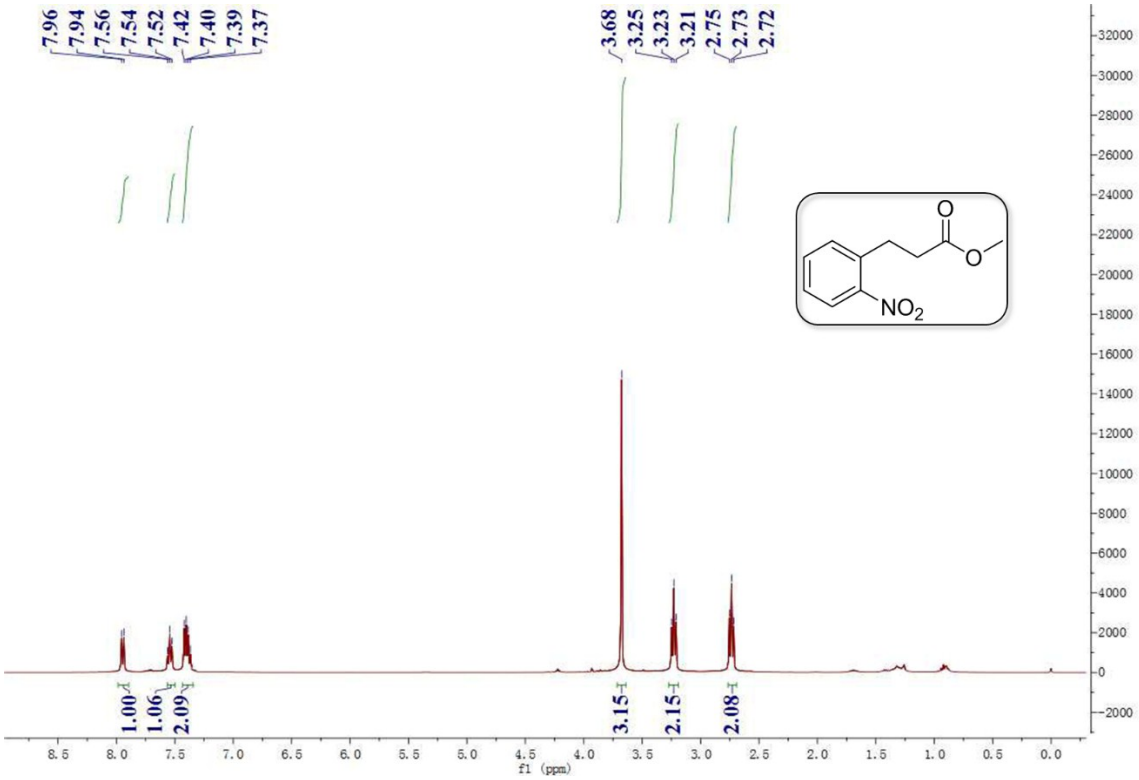
(E)-methyl 3-(2-nitrophenyl)acrylate: The title

compound was prepared according to the general procedure 2 and purified by column chromatography to yield the product **9aa** (98.3mg, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 15.8 Hz, 1H), 8.08 – 7.97 (m, 1H), 7.70 – 7.60 (m, 2H), 7.60 – 7.49 (m, 1H), 6.38 (d, J = 15.8 Hz, 1H), 3.84 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.22, 148.34, 140.18, 133.55, 130.59, 130.33, 129.14, 124.94, 122.89, 52.04.



1-hydroxy-3,4-dihydroquinolin-2(1H)-one: The title compound was prepared according to the general procedure 3 and purified by column chromatography to yield the product **5a** (90.4mg, 81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.41 – 7.25 (m, 2H), 7.18 – 7.11 (m, 1H), 7.05 (td, J = 7.4, 1.1 Hz, 1H), 2.94 (t, J = 7.6 Hz, 2H), 2.84 – 2.64 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 165.10, 137.06, 127.73, 127.37, 123.77, 123.45, 112.98, 29.90, 24.51.

NMR spectra of all products



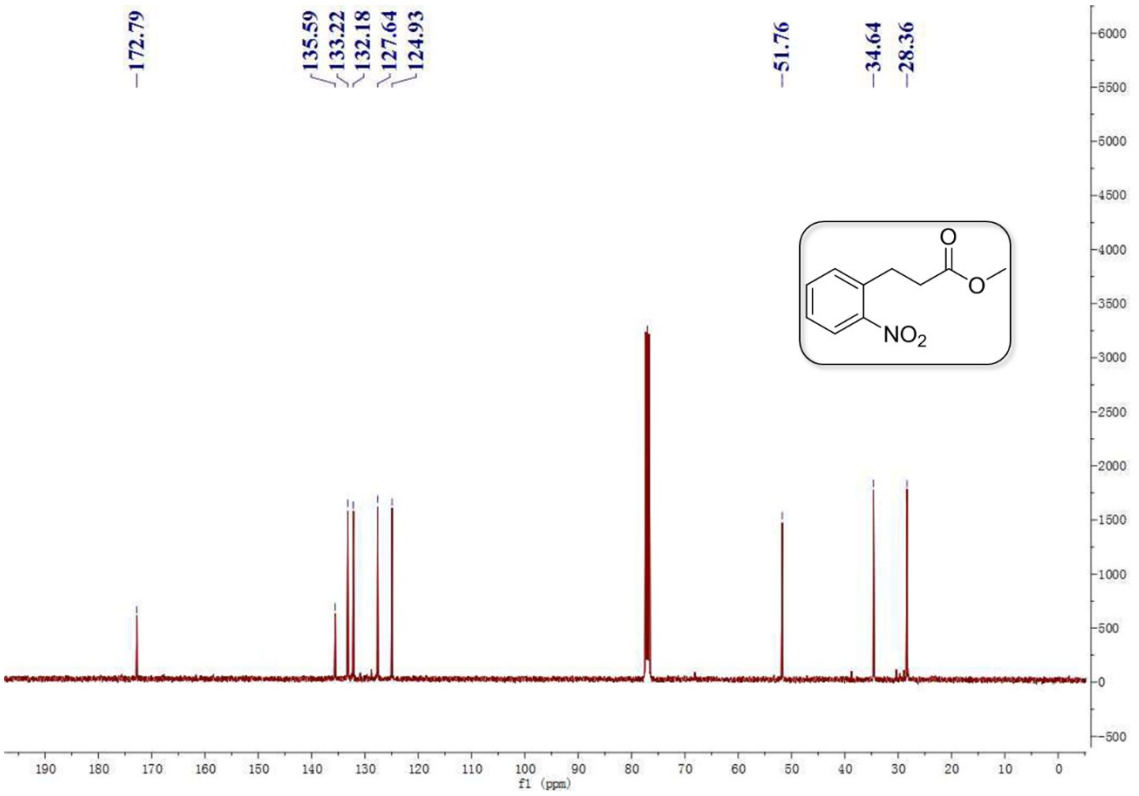


Figure S1. ^{1}H and ^{13}C NMR spectra of **6aa**

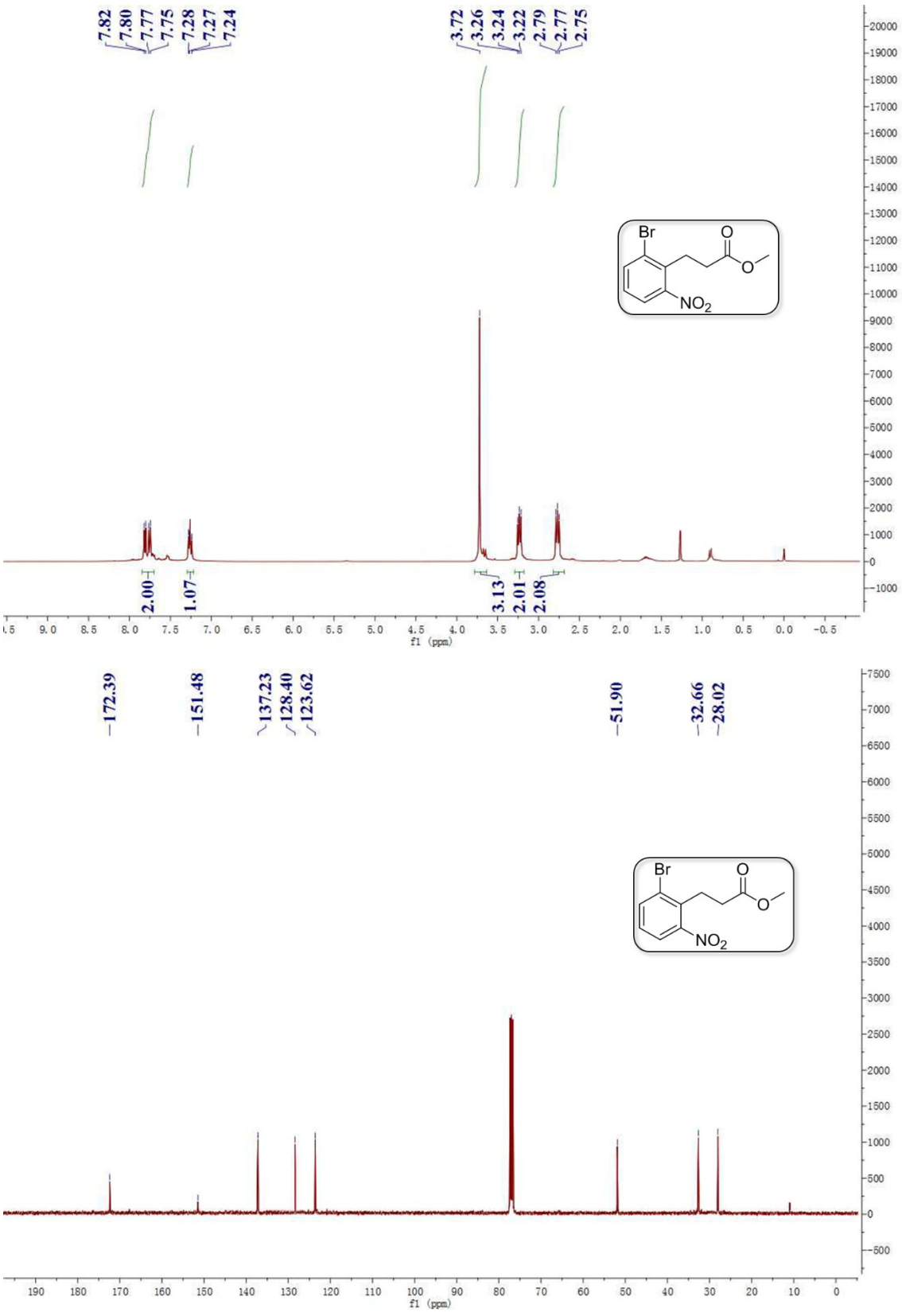


Figure S2. ^{1}H and ^{13}C NMR spectra of **6ba**

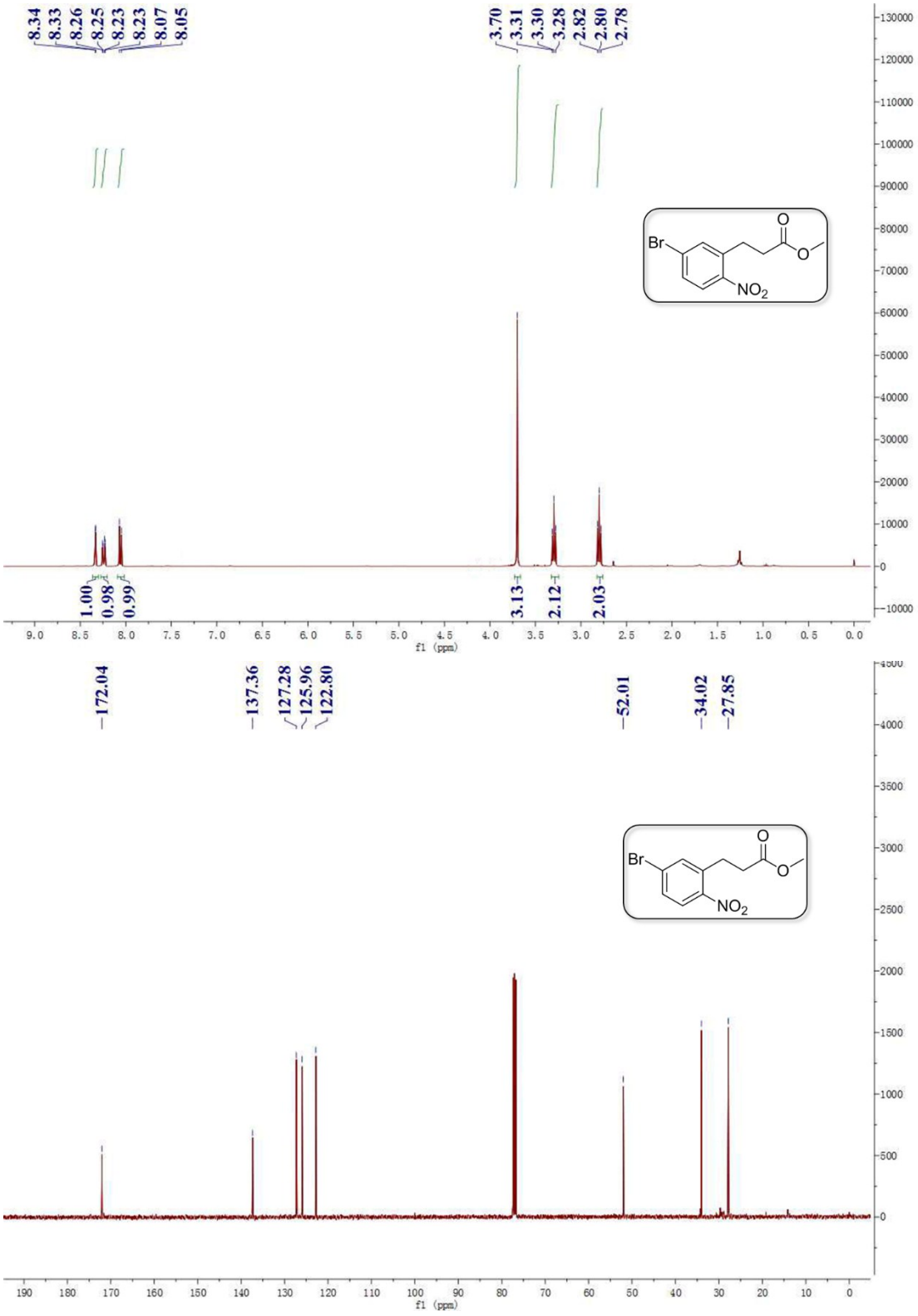


Figure S3. ^{1}H and ^{13}C NMR spectra of **6ca**

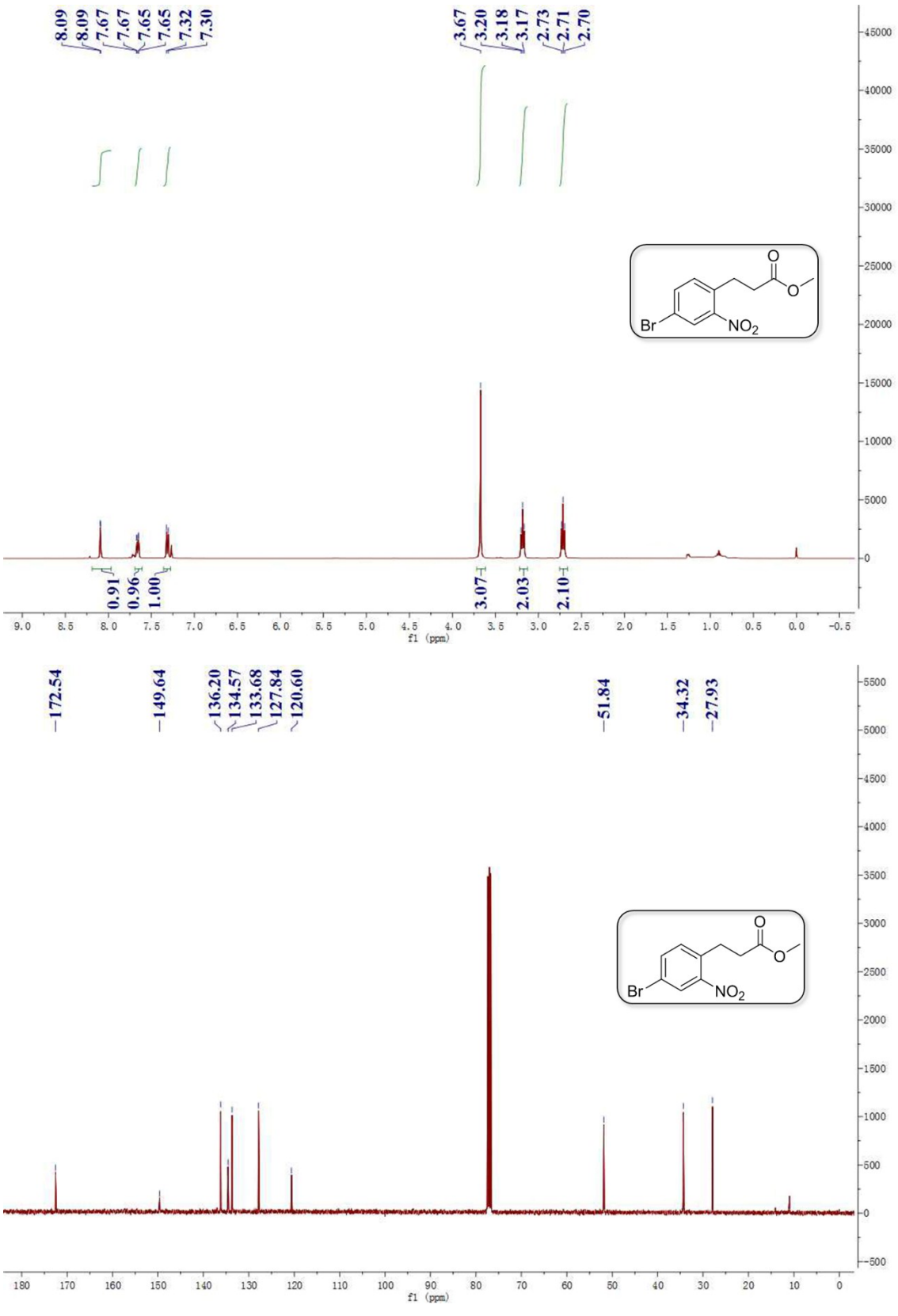
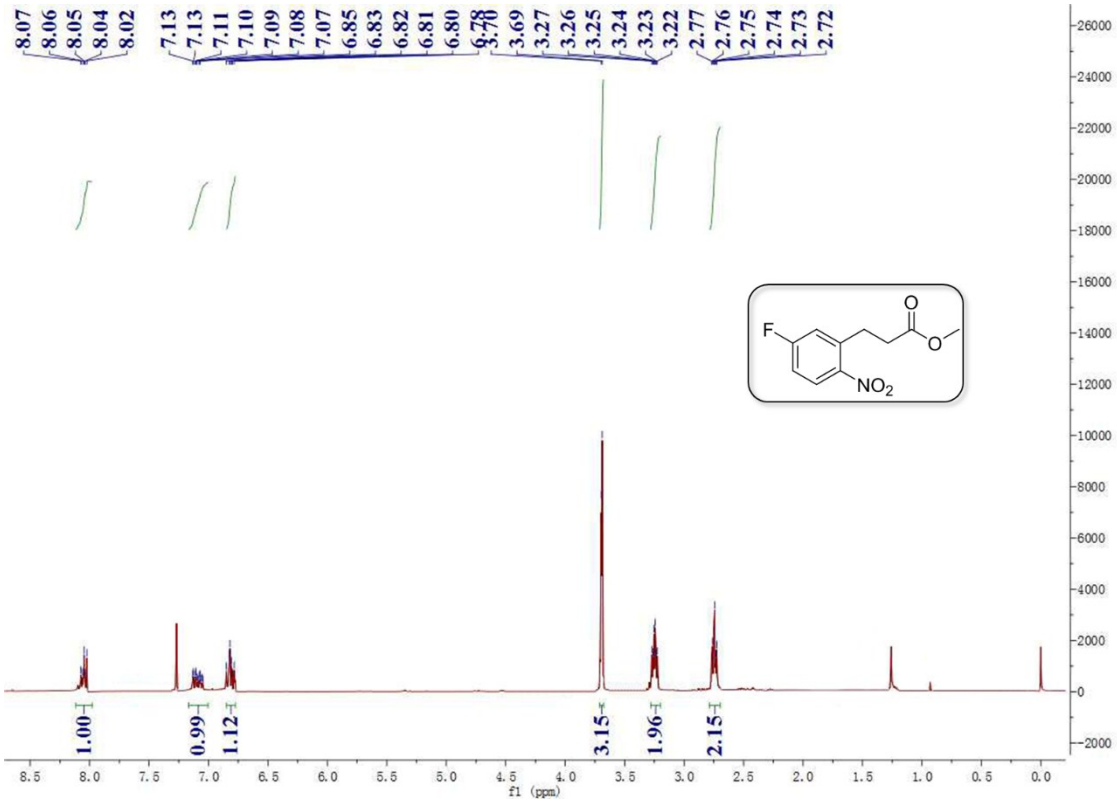
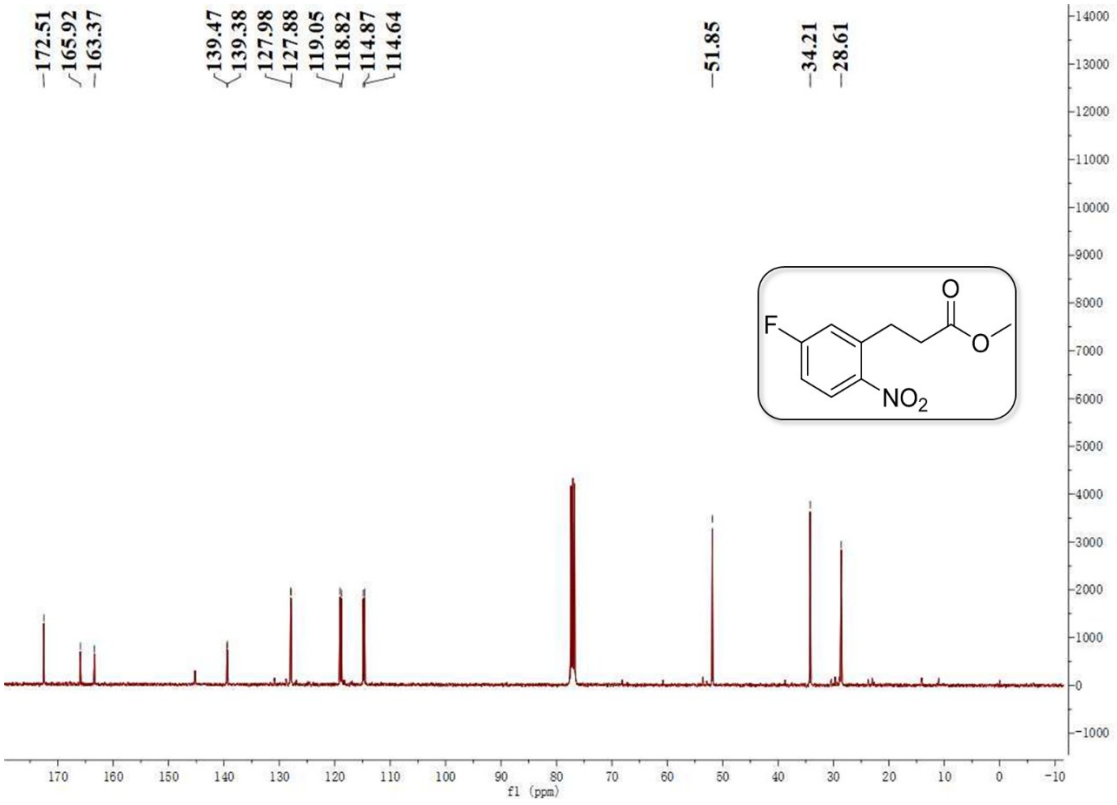


Figure S4. ^{1}H and ^{13}C NMR spectra of **6da**


8.07
8.06
8.05
8.04
8.02
7.13
7.13
7.11
7.10
7.09
7.08
7.07
6.85
6.83
6.82
6.81
6.80
3.69
3.27
3.26
3.25
3.24
3.23
3.22
2.77
2.76
2.75
2.74
2.73
2.72
1.00
0.99
1.12
3.15
1.96
2.15
f1 (ppm)
F
O
O
NO2


172.51
165.92
163.37
139.47
139.38
127.98
127.88
119.05
118.82
114.87
114.64
51.85
34.21
28.61
f1 (ppm)
F
O
O
NO2

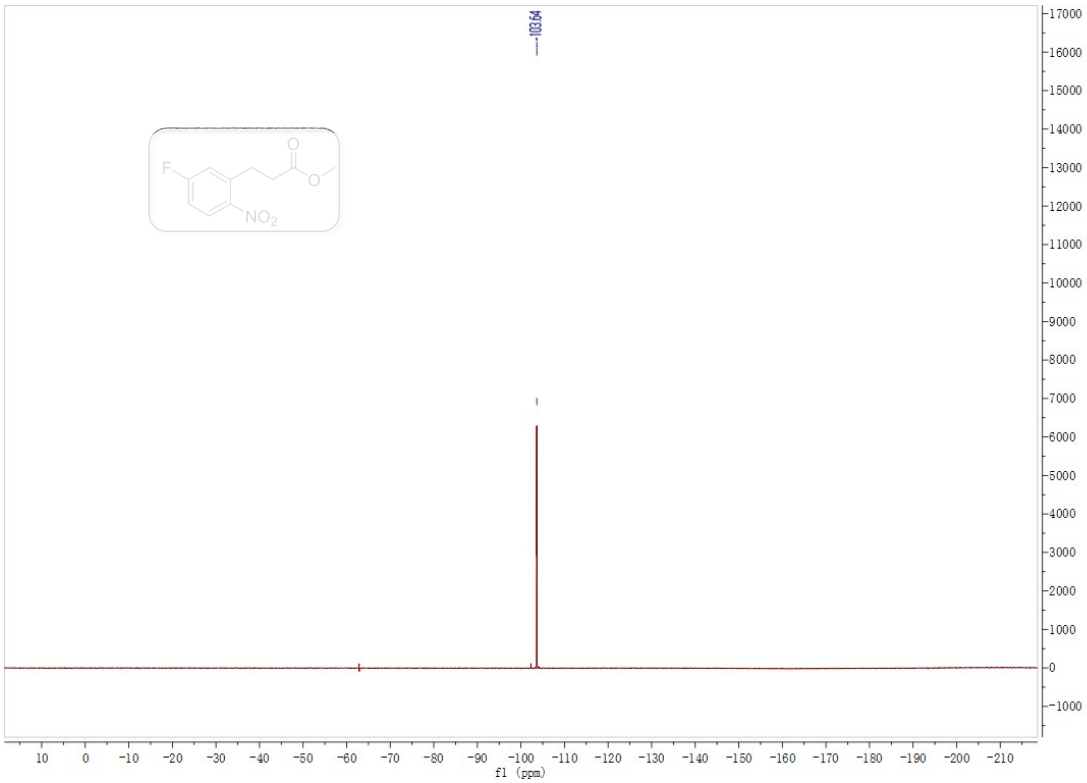
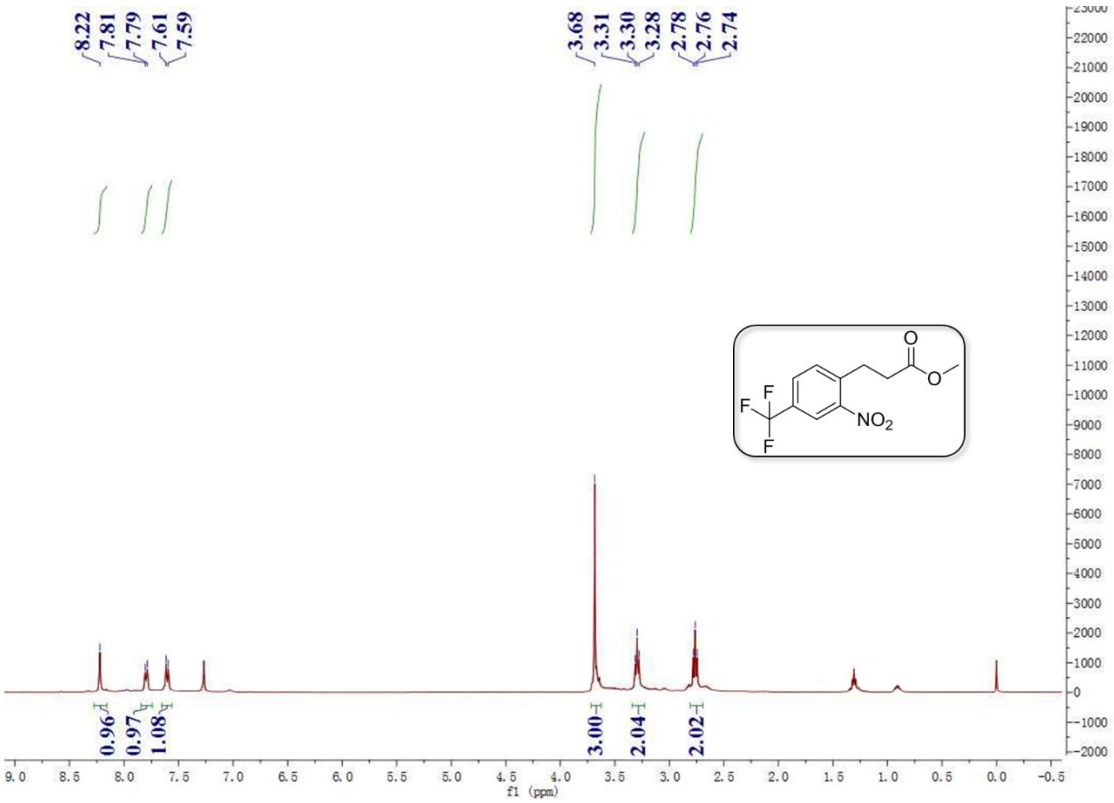
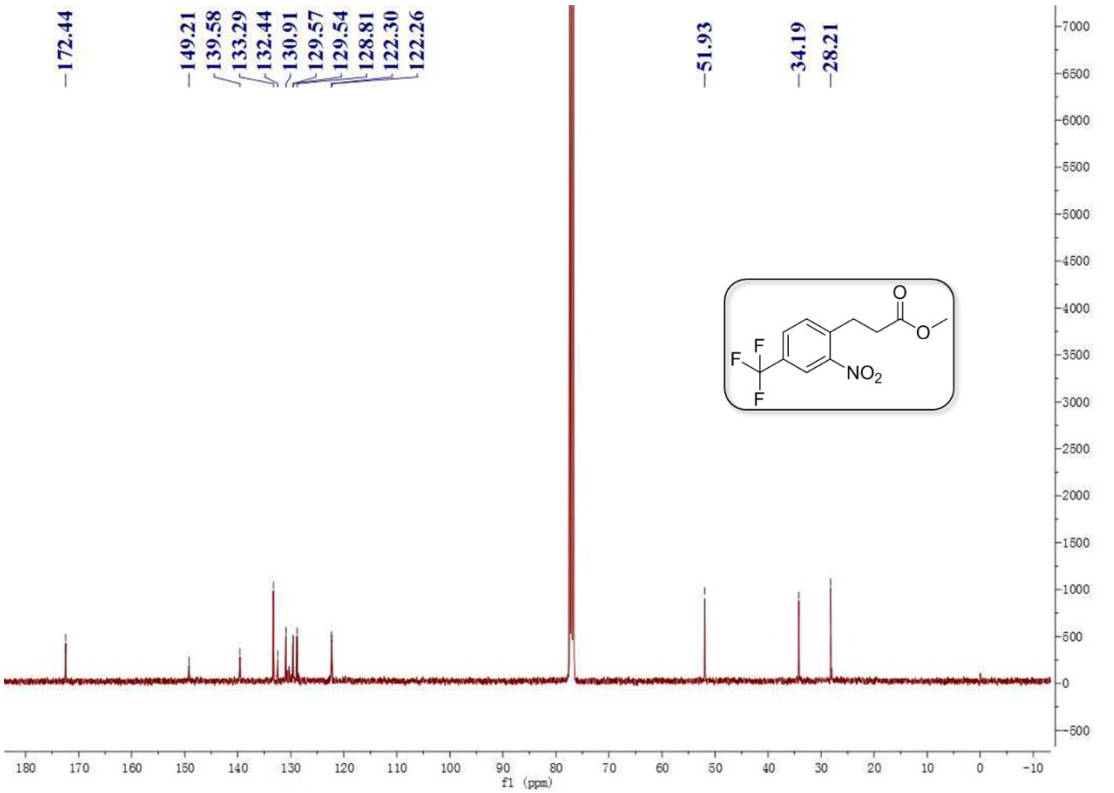


Figure S5. ^{1}H, ^{13}C and ^{19}F NMR spectra of **6ea**


8.22
7.81
7.79
7.61
7.59
3.68
3.31
3.30
3.28
2.78
2.76
2.74
0.96
0.97
1.08
3.00
2.04
2.02
f1 (ppm)


172.44
149.21
139.58
133.29
132.44
130.91
129.57
129.54
128.81
122.30
122.26
51.93
34.19
28.21
f1 (ppm)

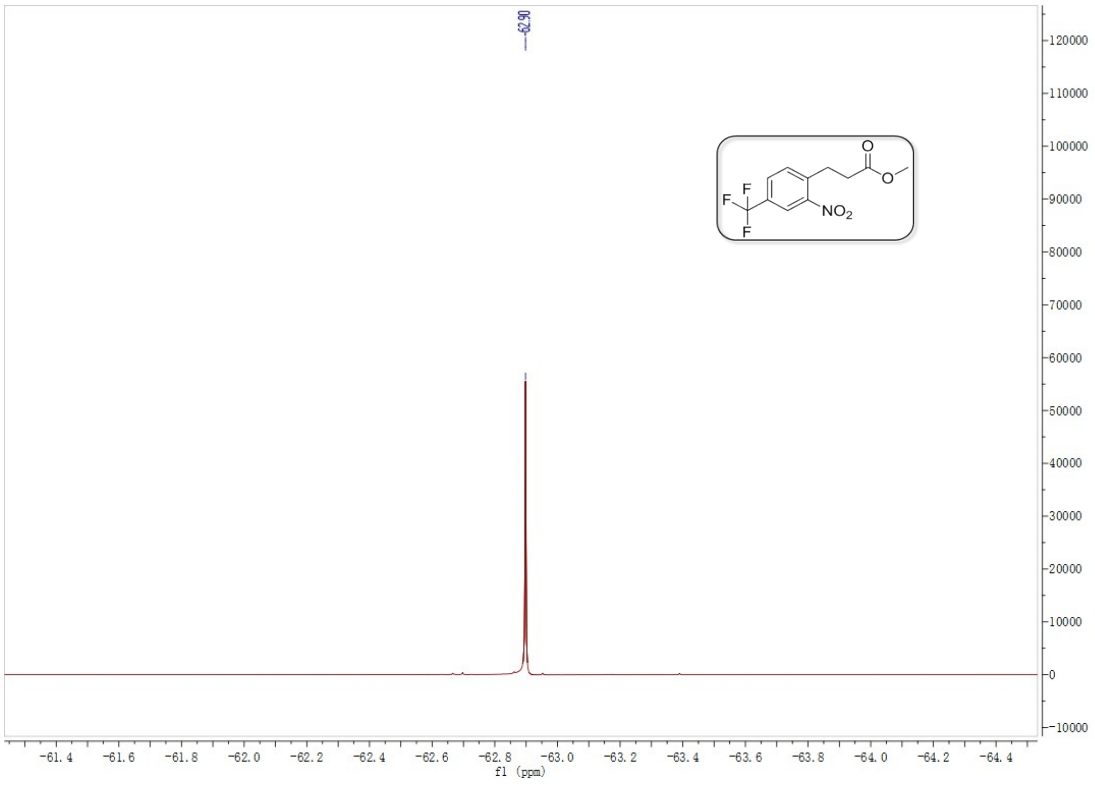


Figure S6. ^{1}H, ^{13}C and ^{19}F NMR spectra of **6fa**

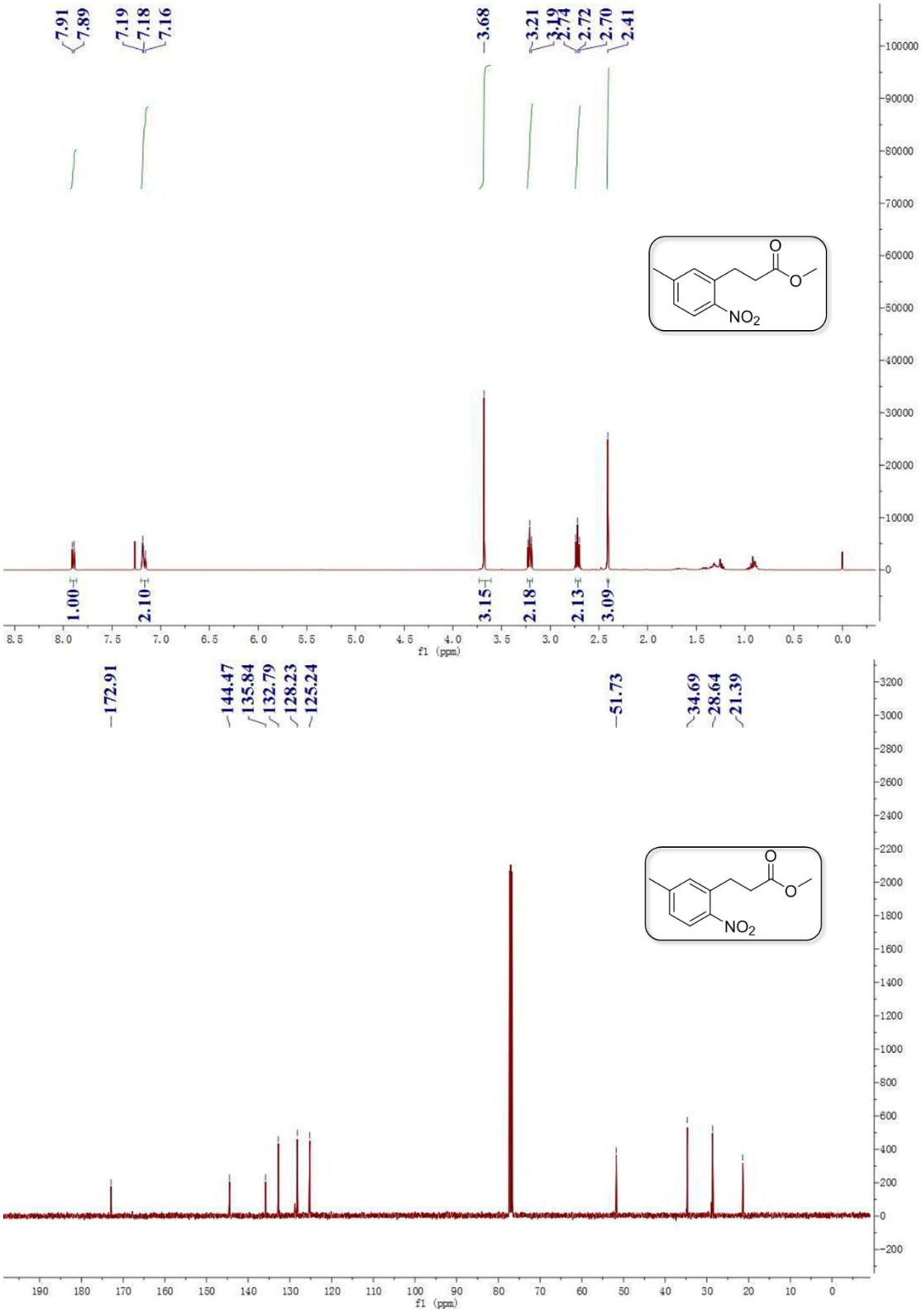


Figure S7. ^{1}H and ^{13}C NMR spectra of **6ga**

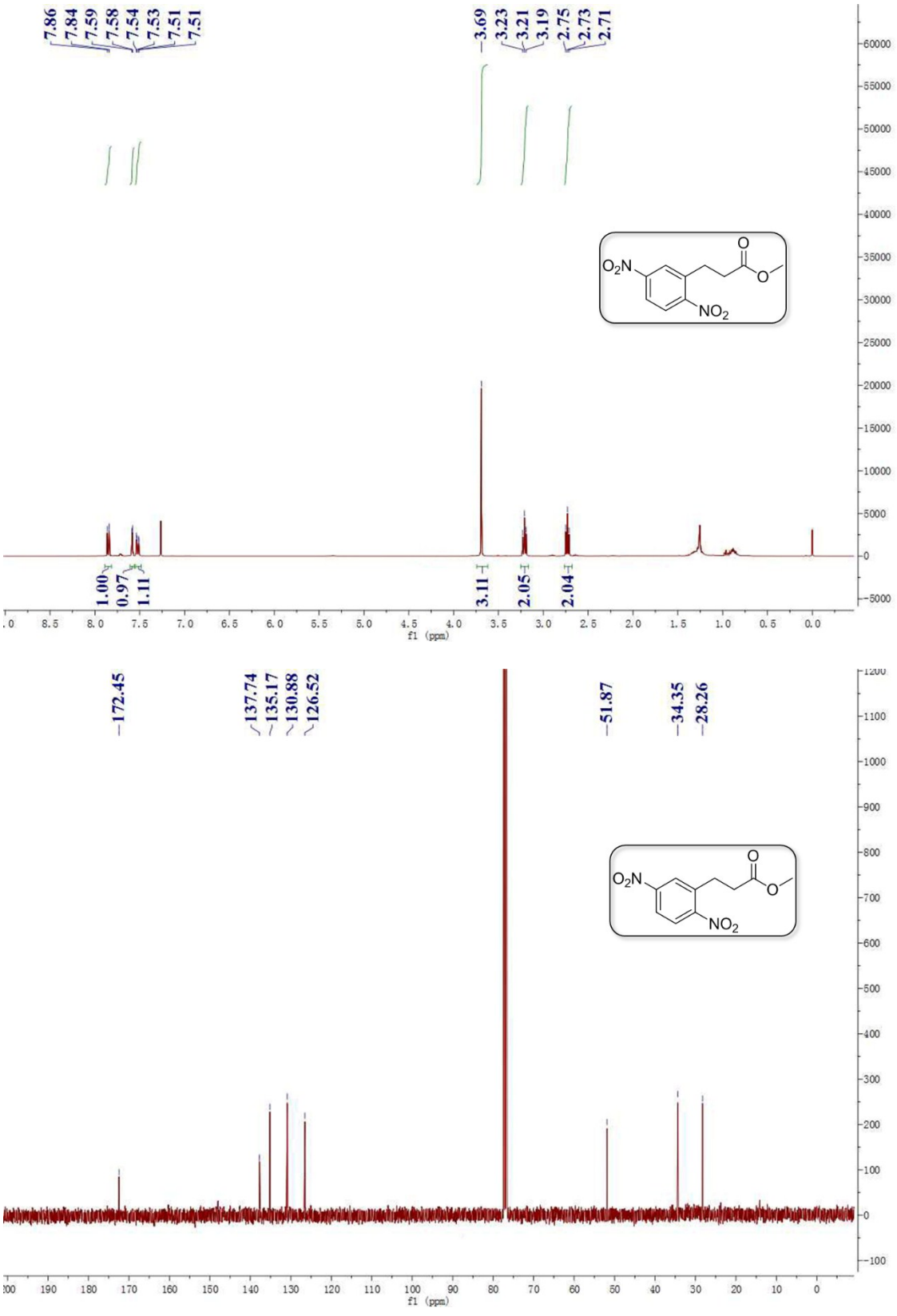


Figure S8. ^{1}H and ^{13}C NMR spectra of **6ha**

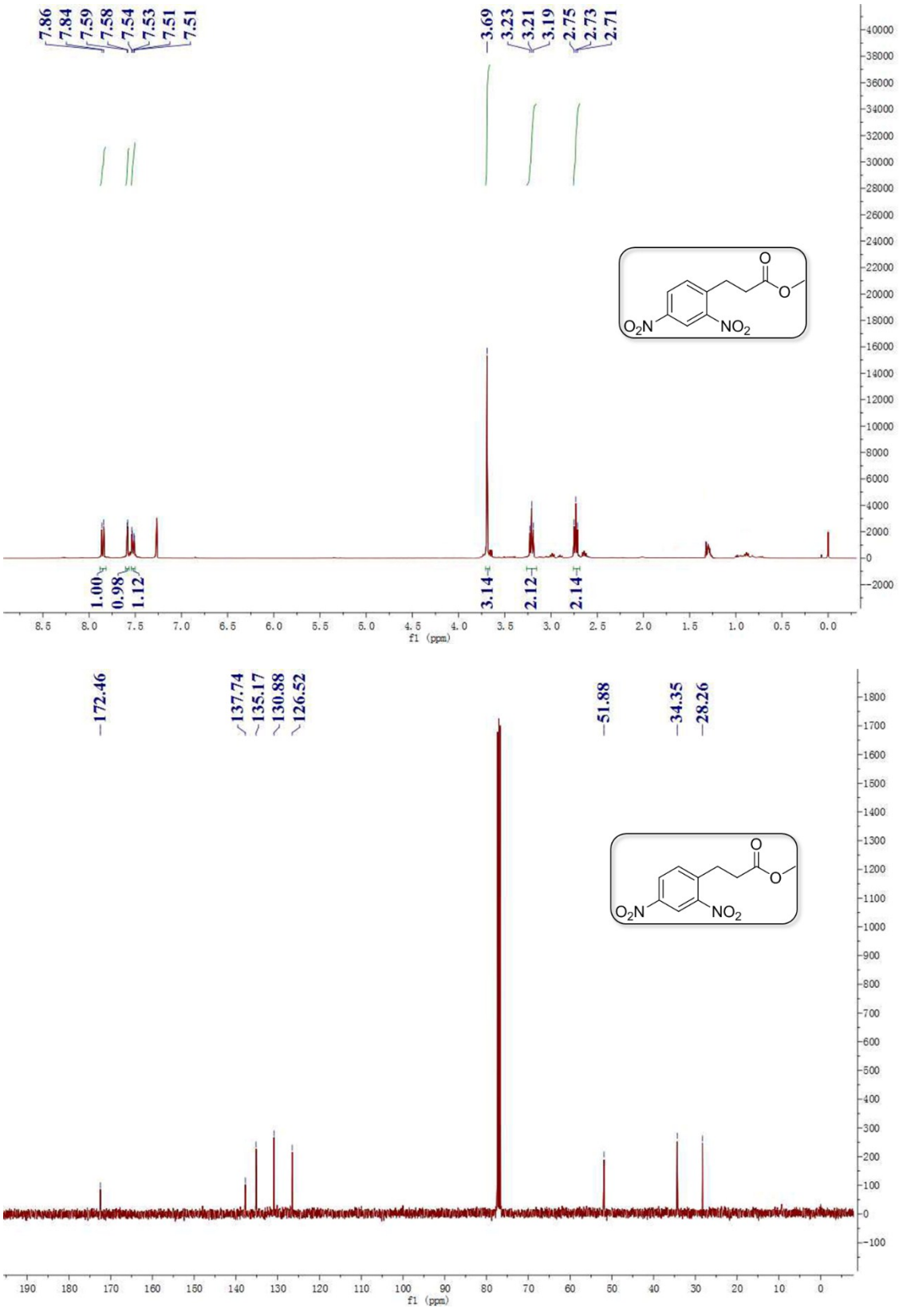


Figure S9. ^{1}H and ^{13}C NMR spectra of **6ia**

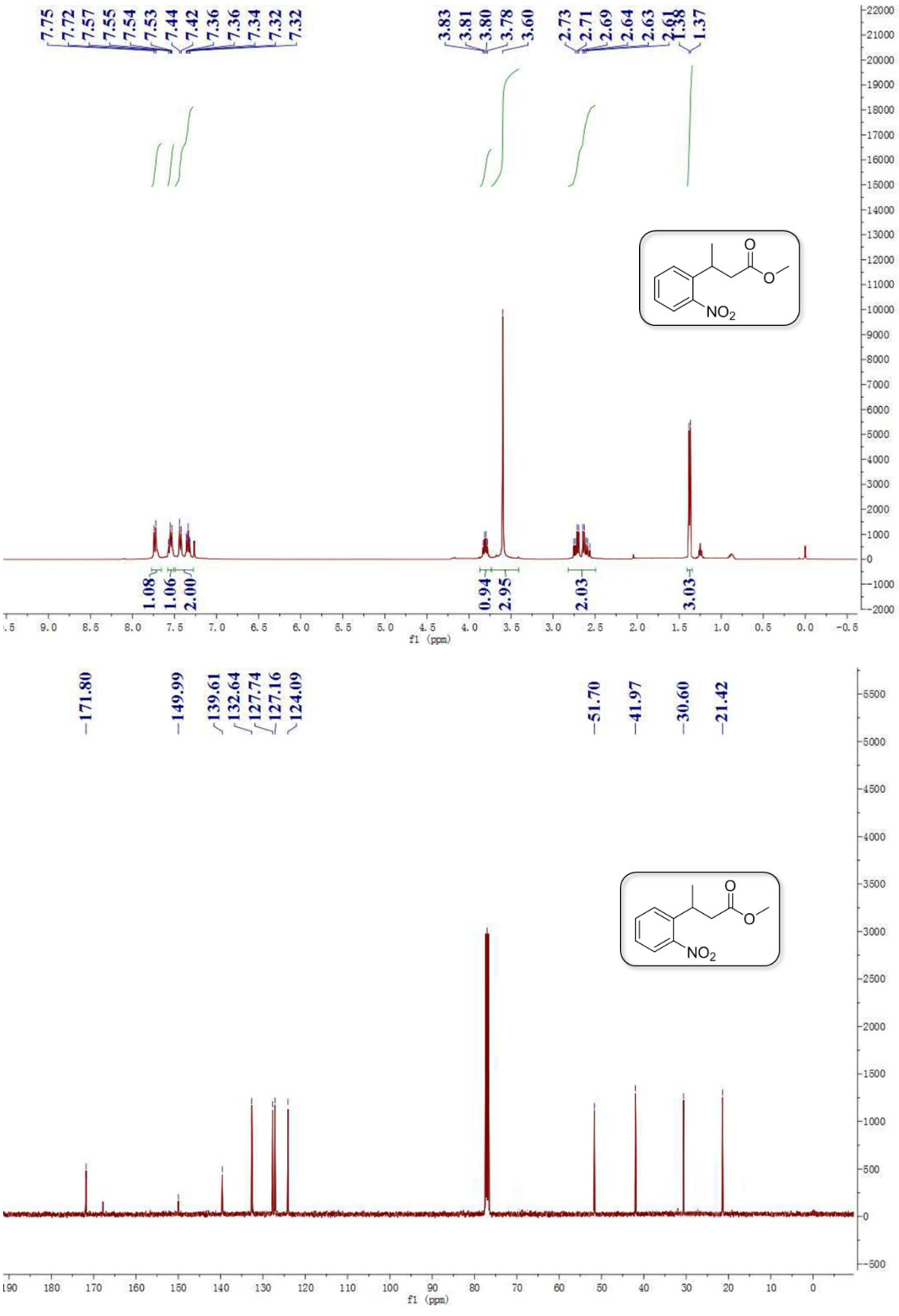


Figure S10. ^{1}H and ^{13}C NMR spectra of **6ja**

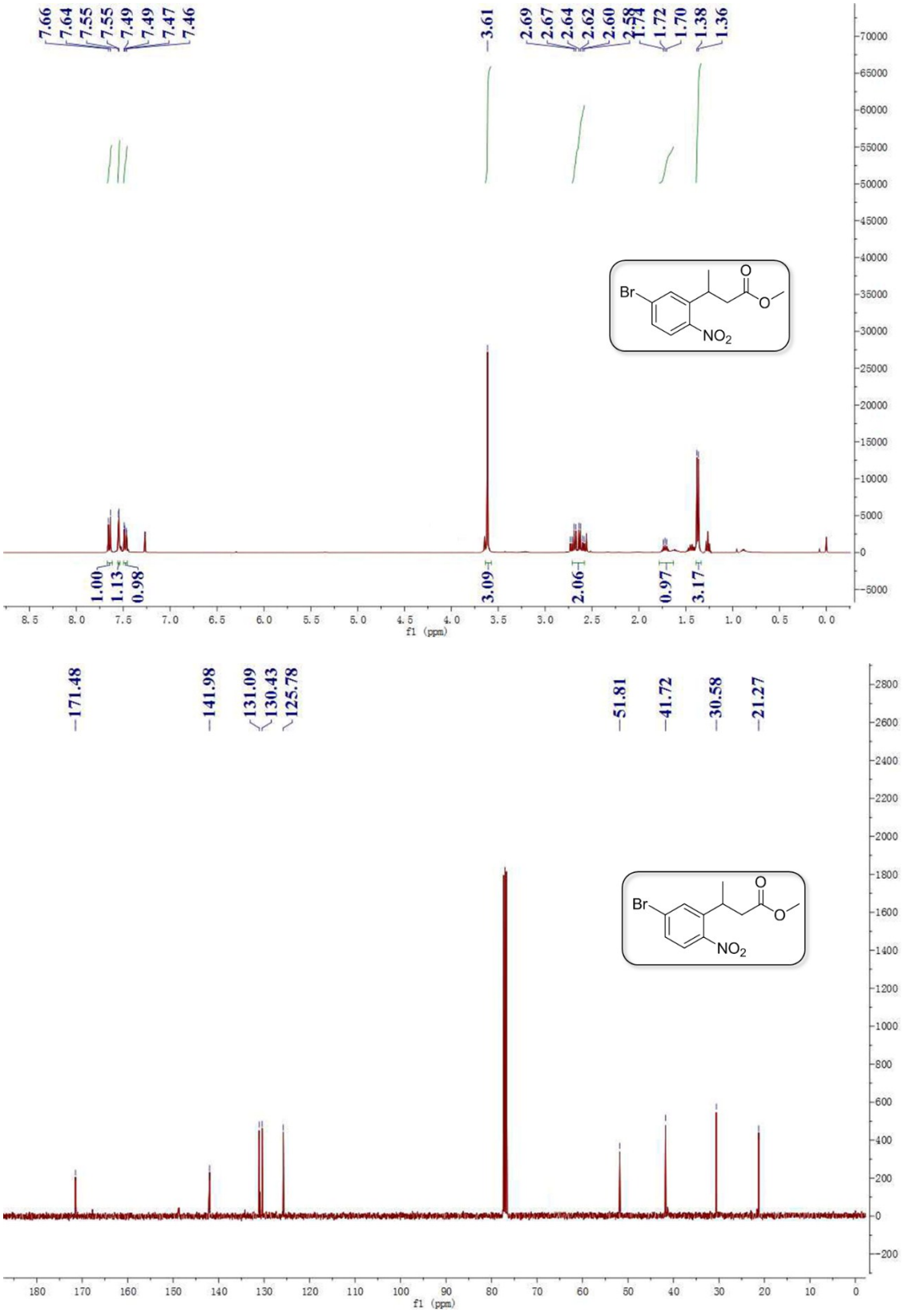


Figure S11. ^{1}H and ^{13}C NMR spectra of **6ka**

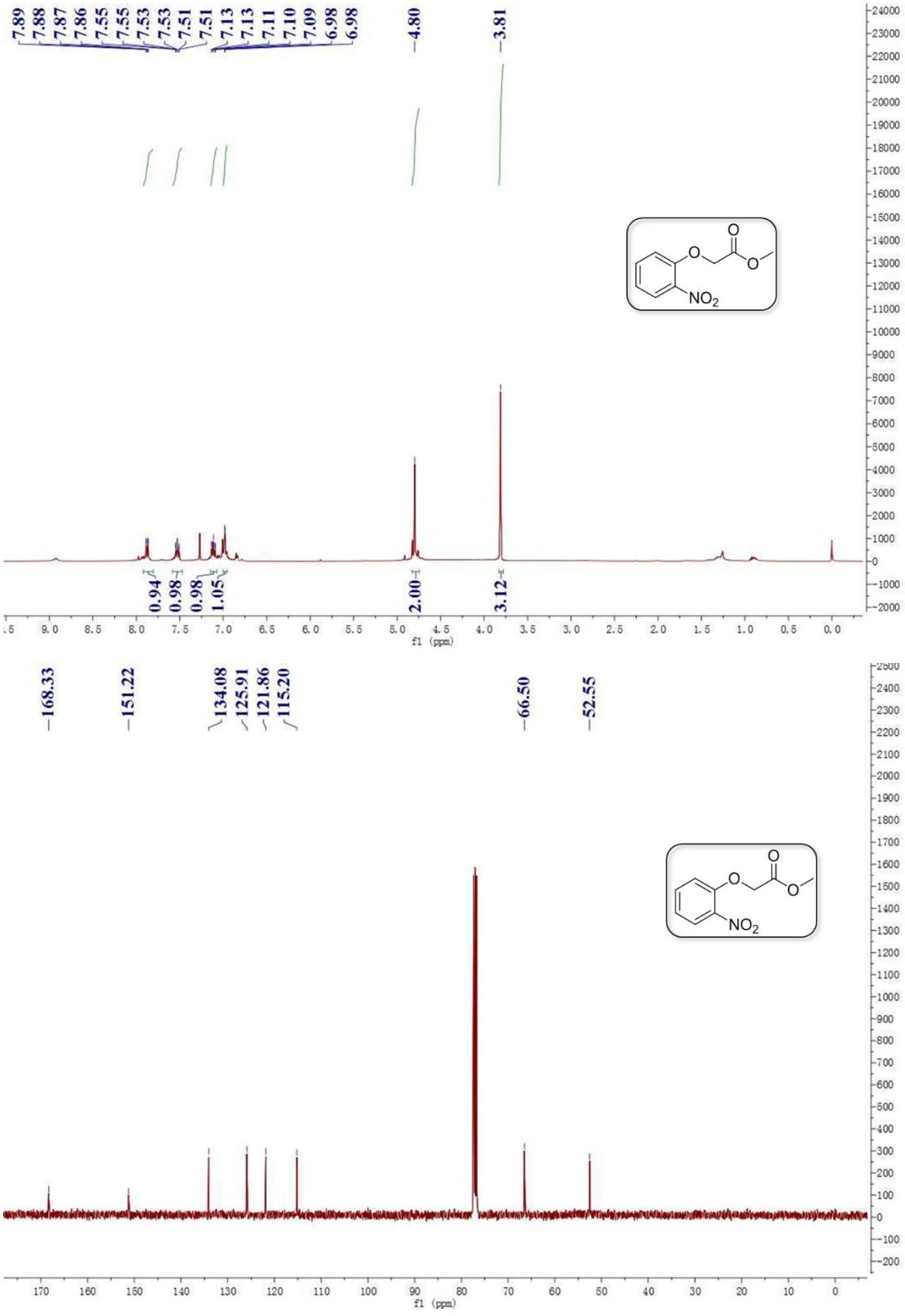


Figure S12. ^{1}H and ^{13}C NMR spectra of **6la**

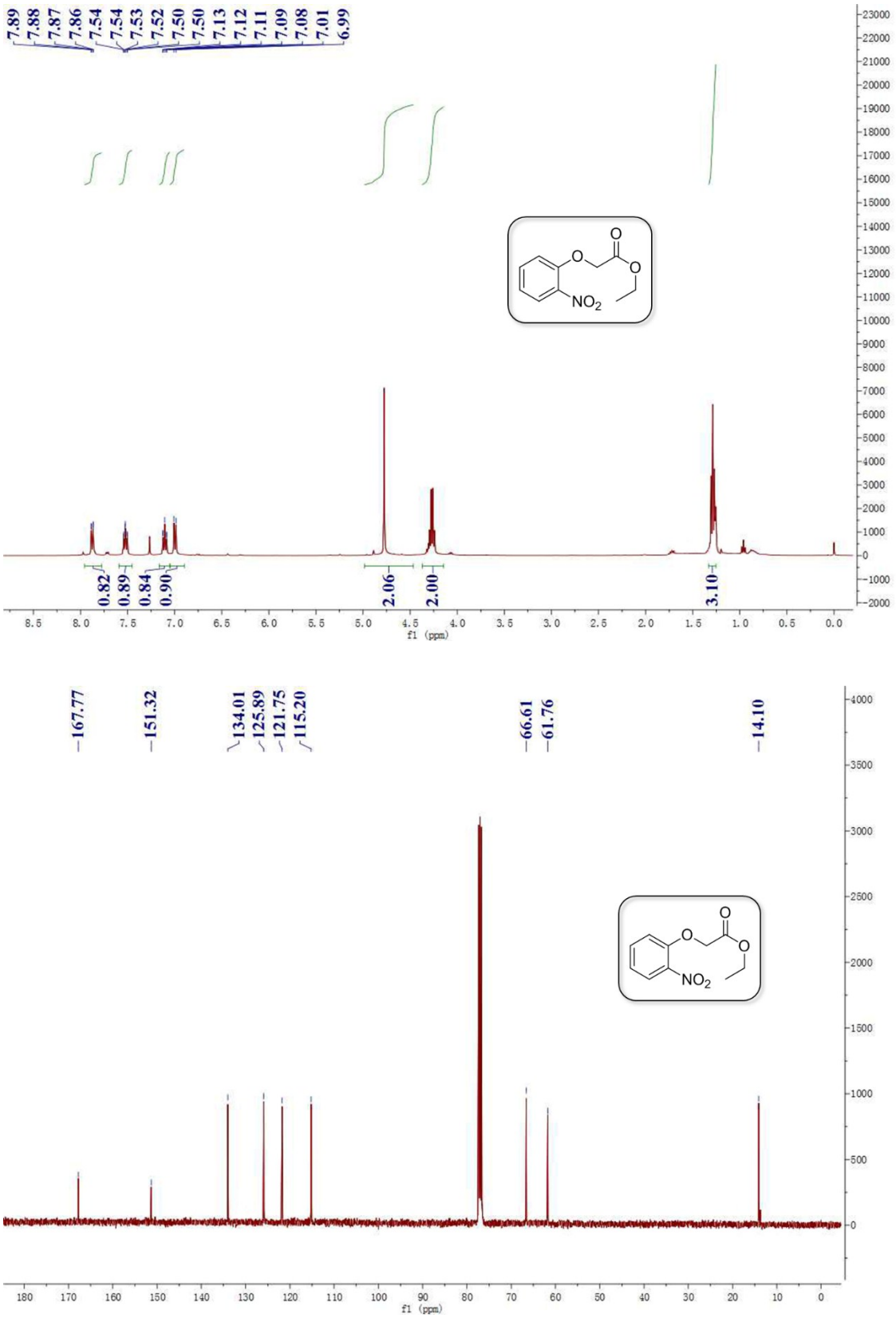


Figure S13. ^{1}H and ^{13}C NMR spectra of **6lb**

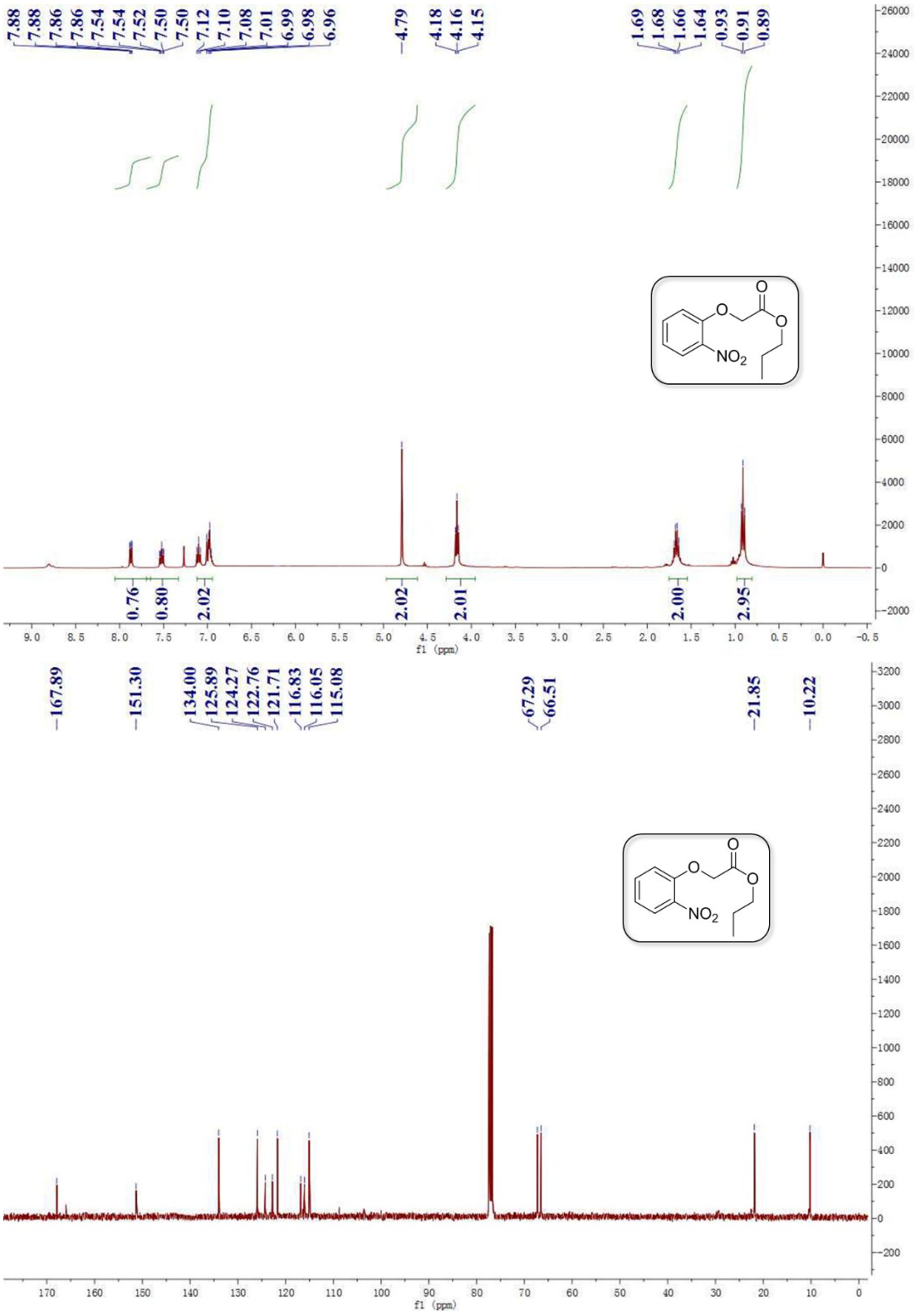


Figure S14. ^{1}H and ^{13}C NMR spectra of **6lc**

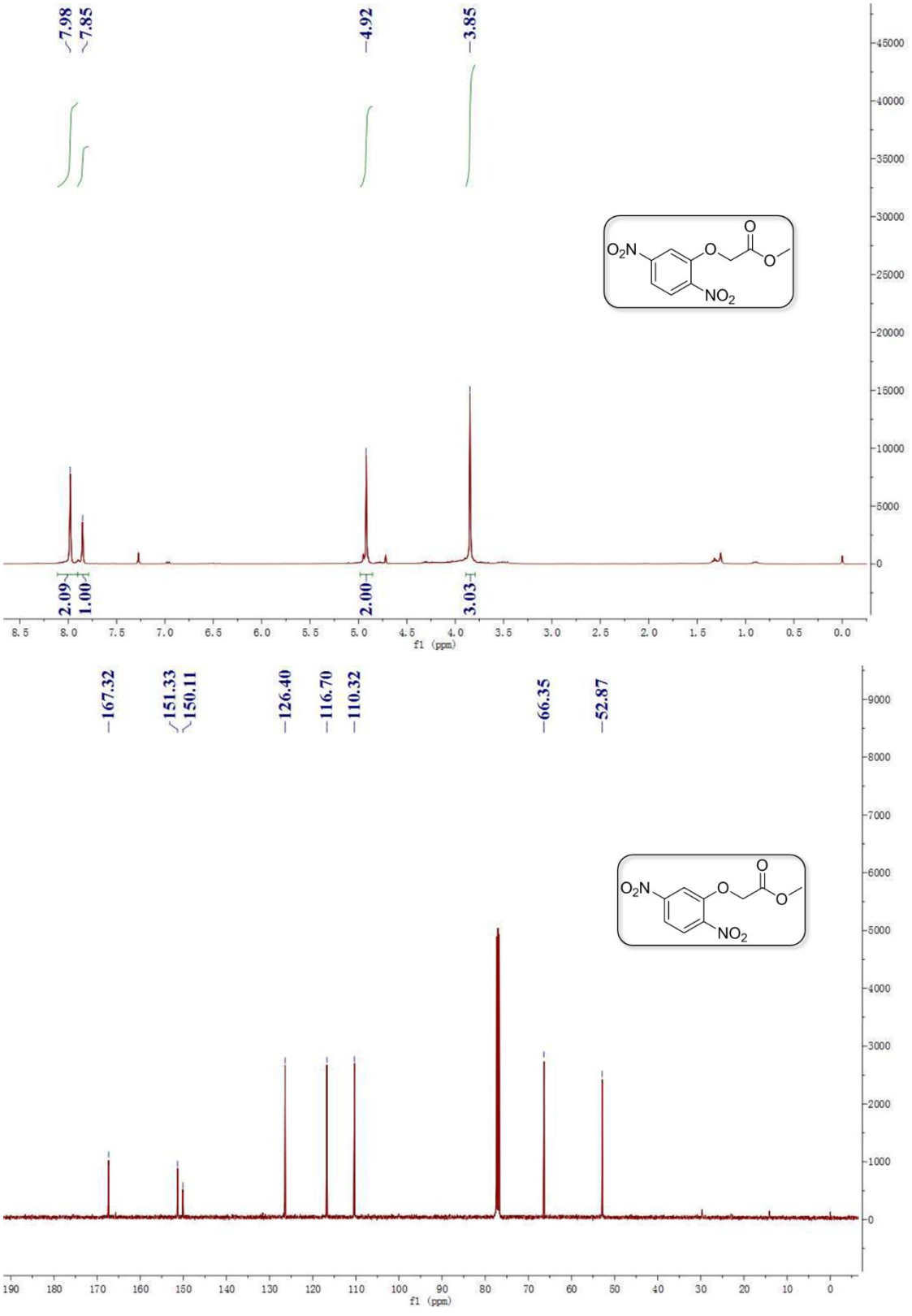


Figure S15. ^{1}H and ^{13}C NMR spectra of **6ma**

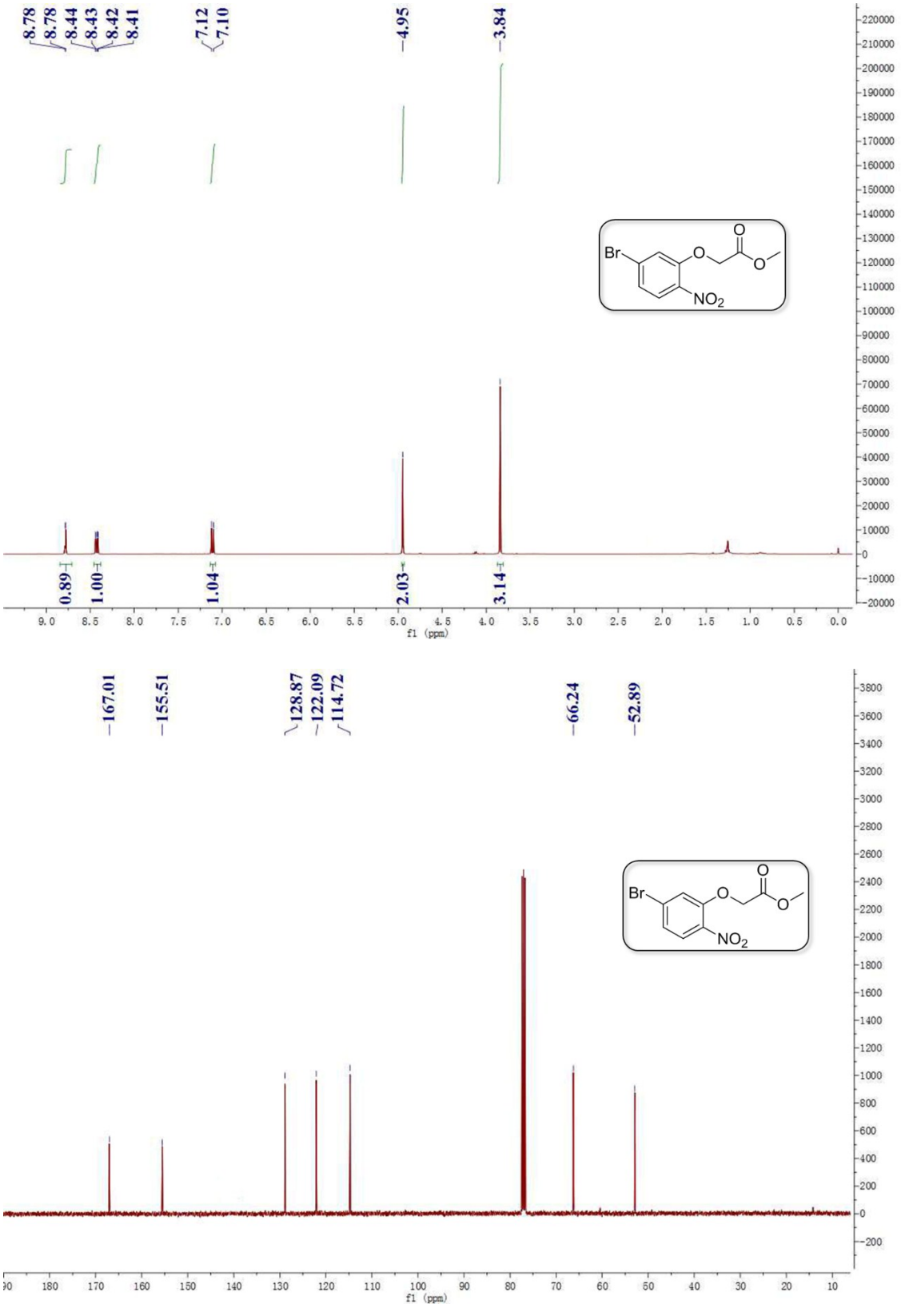


Figure S16. ^{1}H and ^{13}C NMR spectra of **6na**

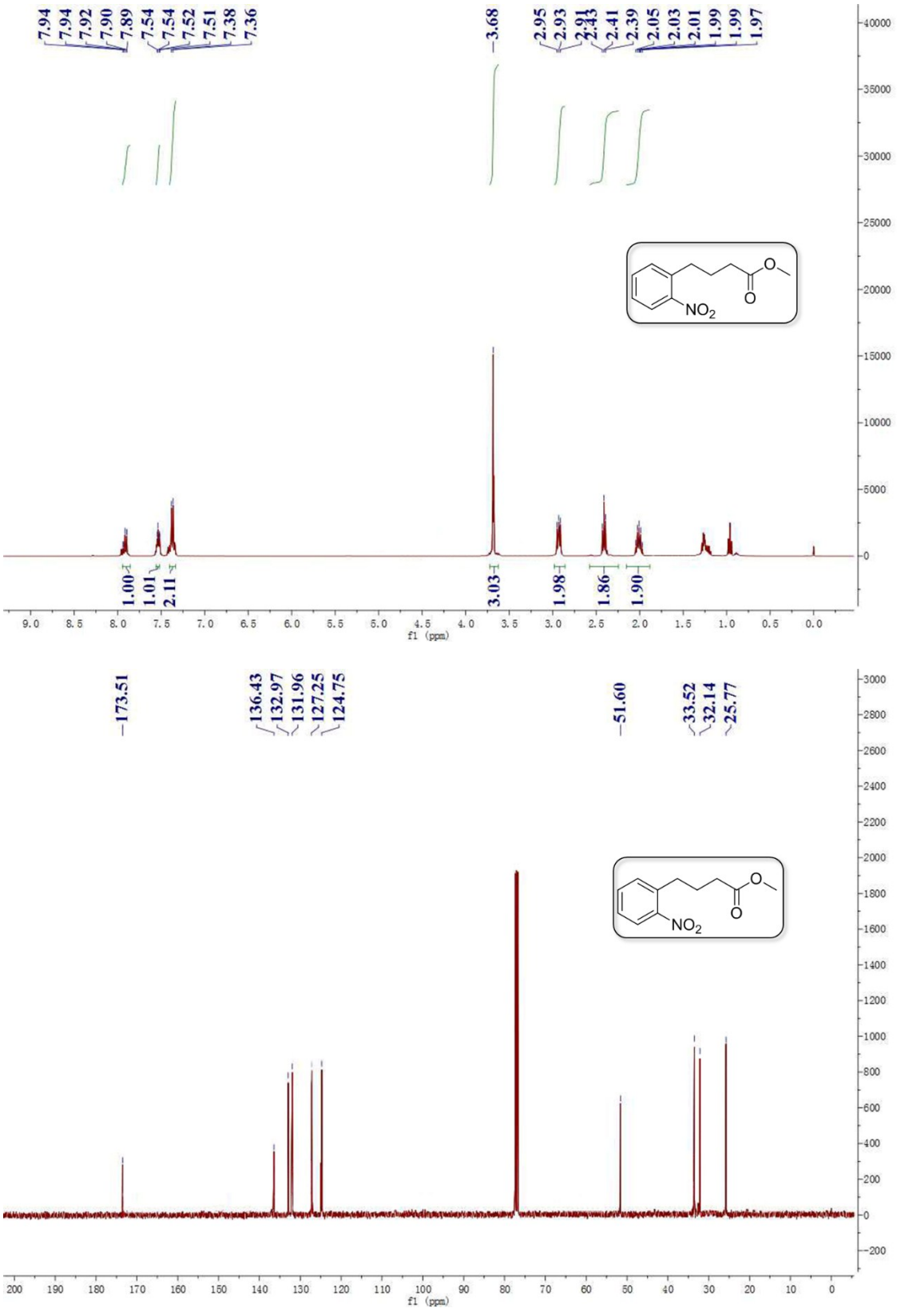


Figure S17. ^{1}H and ^{13}C NMR spectra of **6oa**

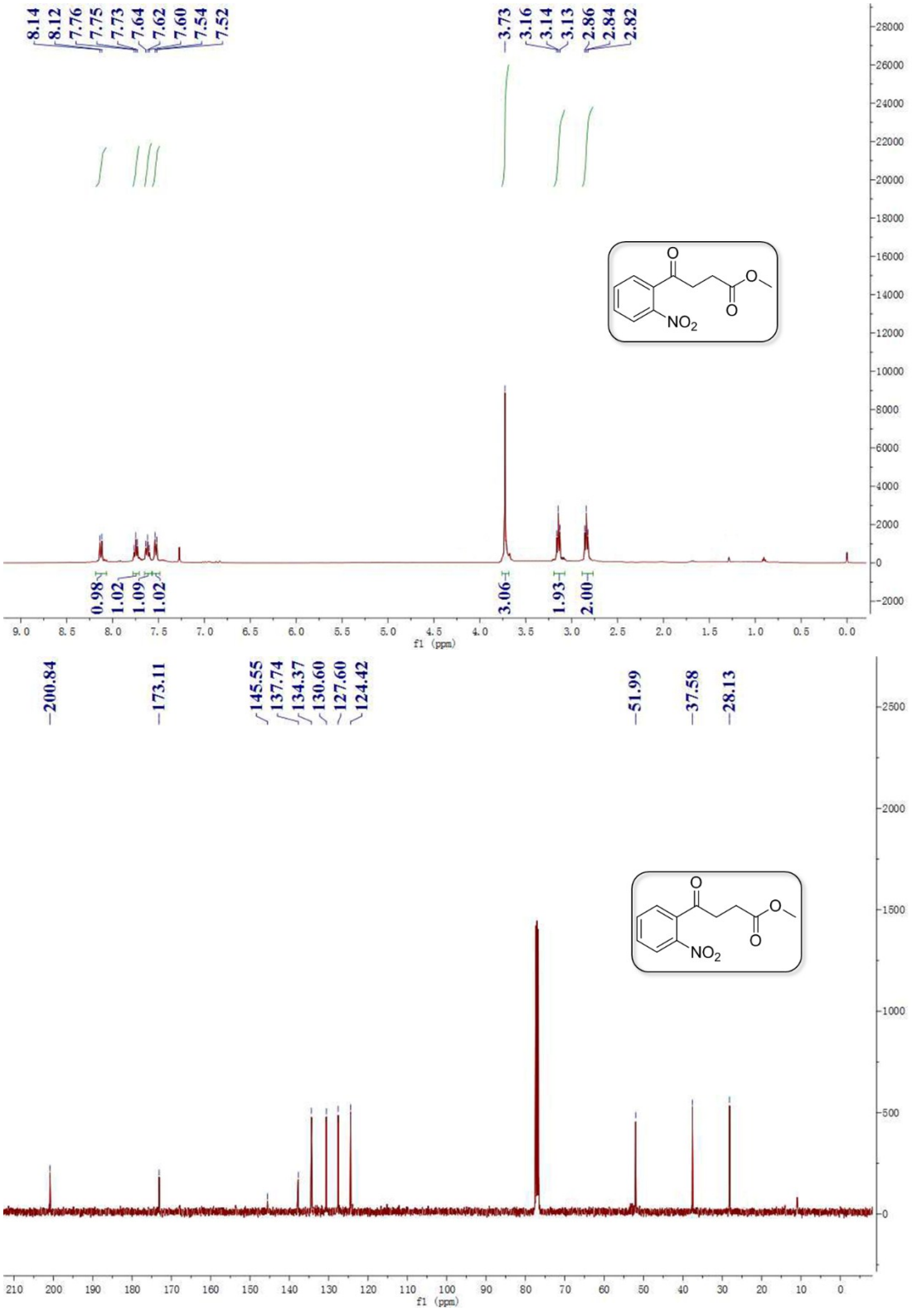


Figure S18. ^{1}H and ^{13}C NMR spectra of **6pa**

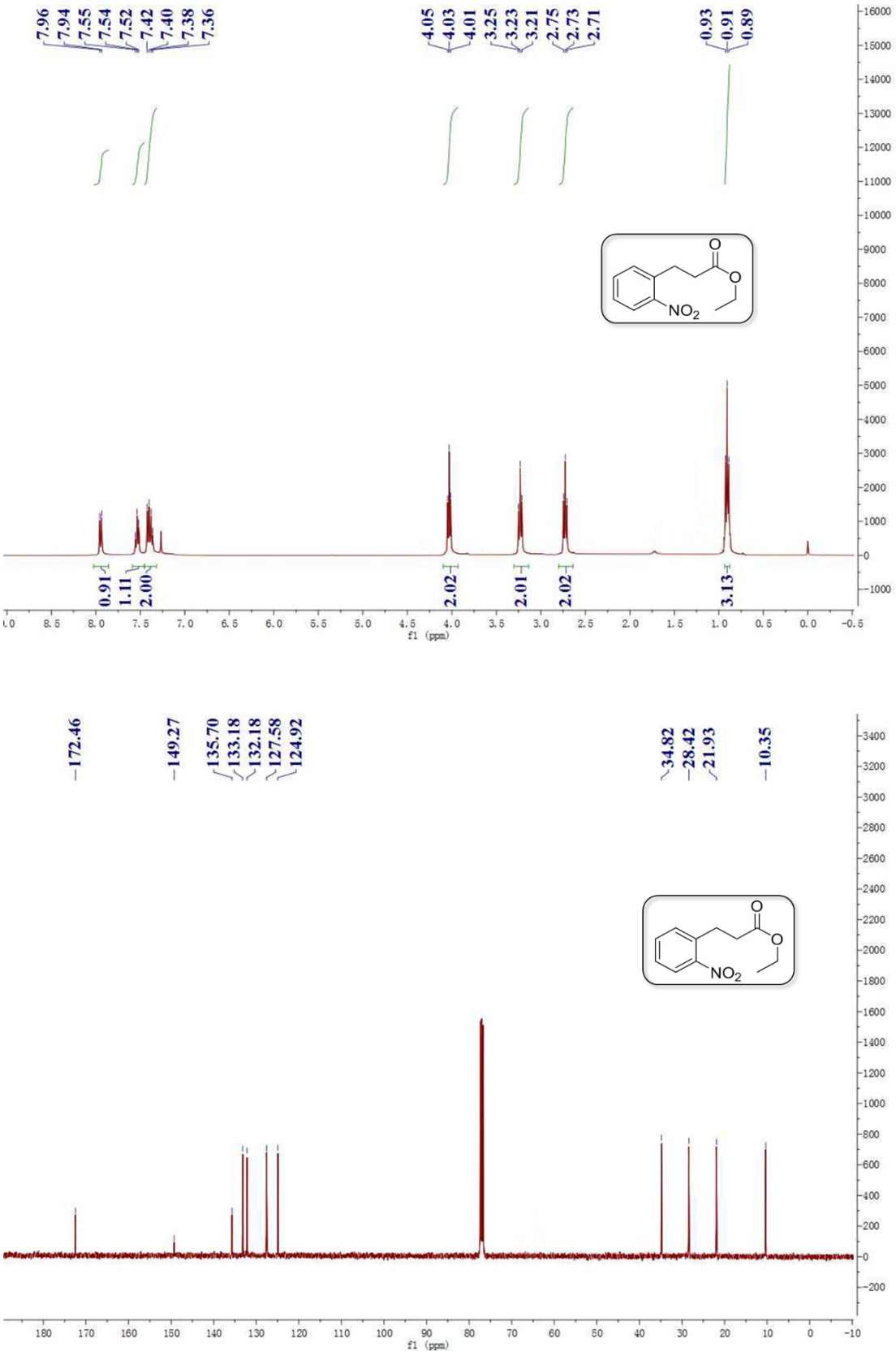


Figure S19. ^{1}H and ^{13}C NMR spectra of **6ab**

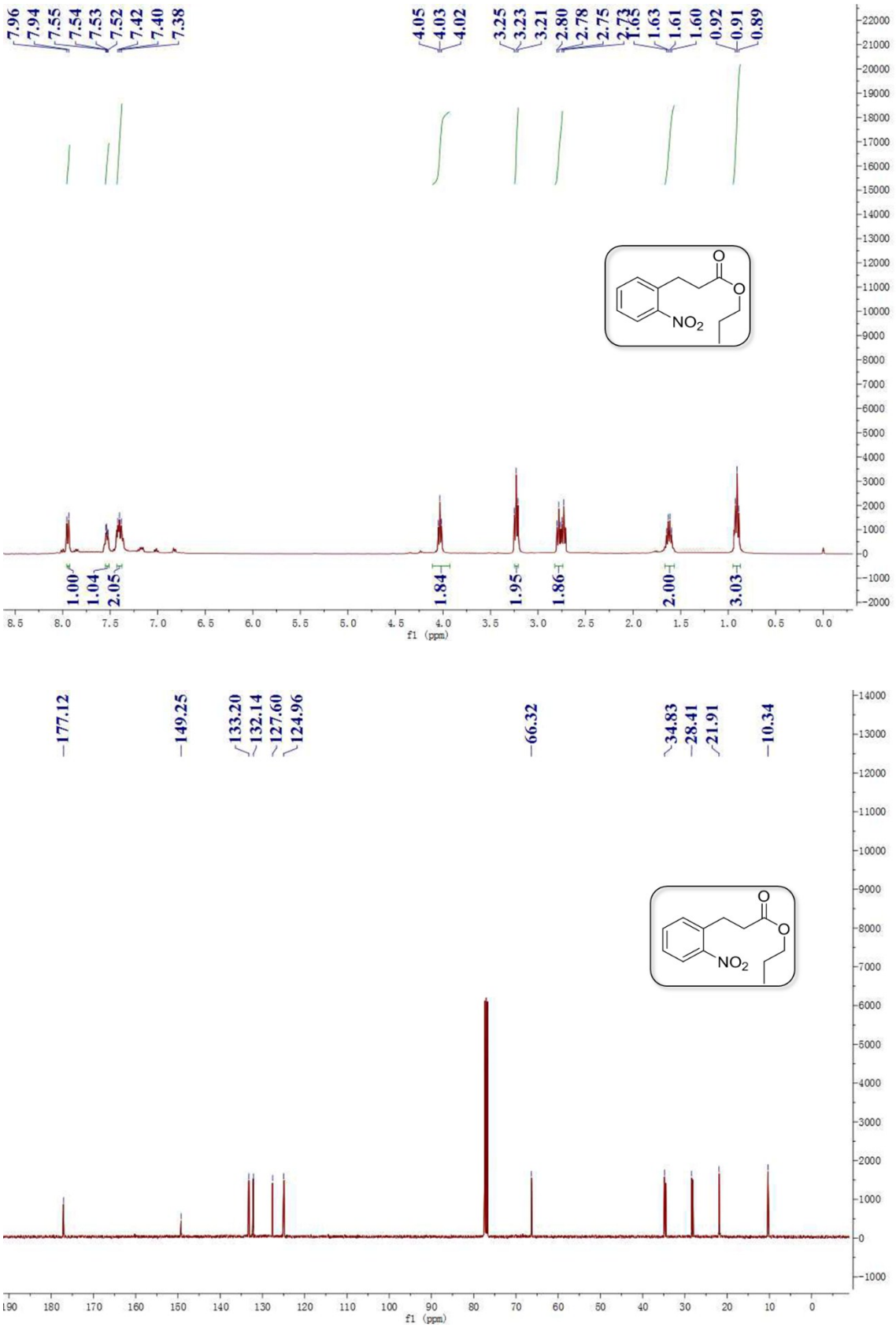


Figure S20. ^{1}H and ^{13}C NMR spectra of **6ac**

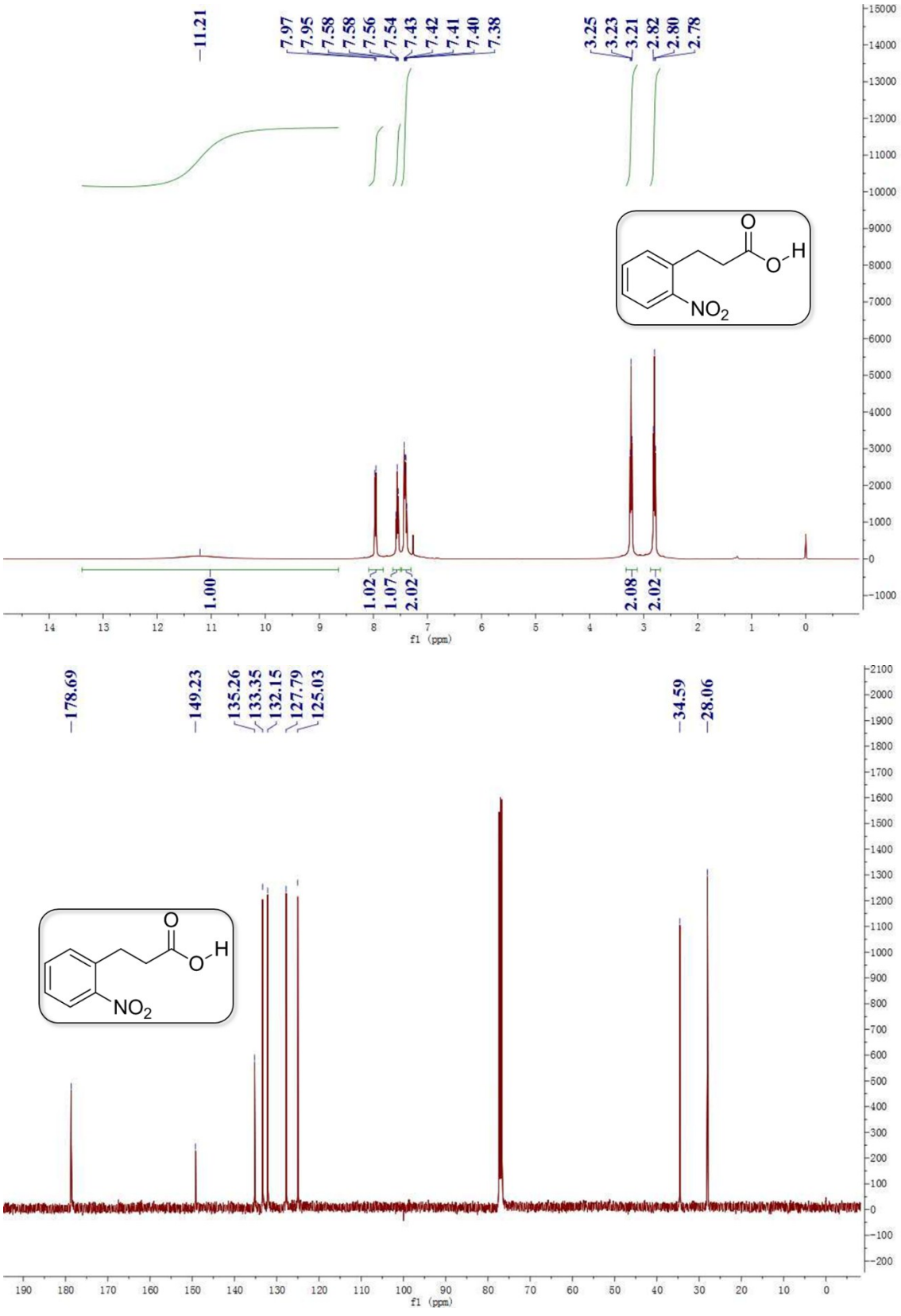


Figure S21. ^{1}H and ^{13}C NMR spectra of **6ad**

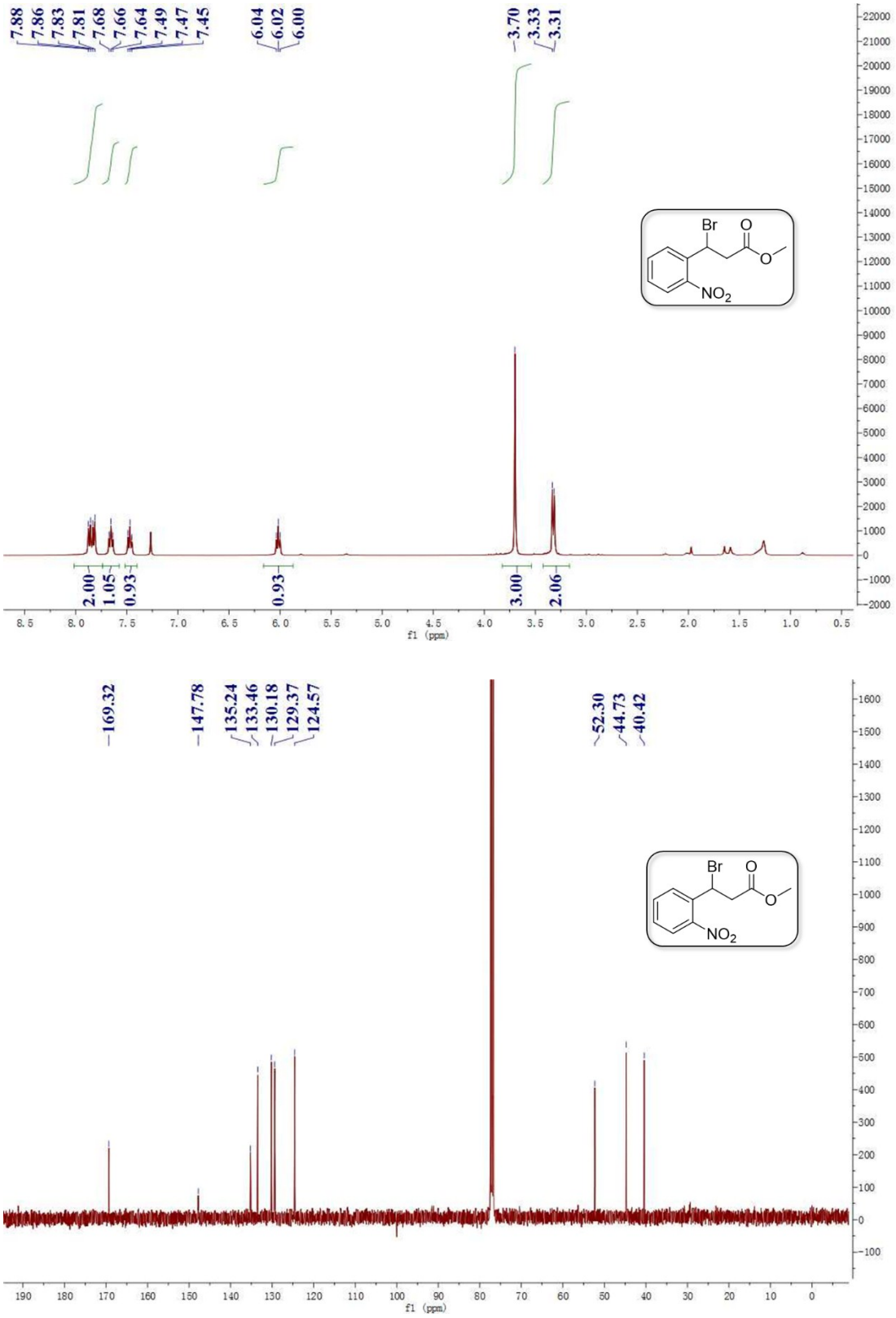


Figure S22. ^{1}H and ^{13}C NMR spectra of **8aa**

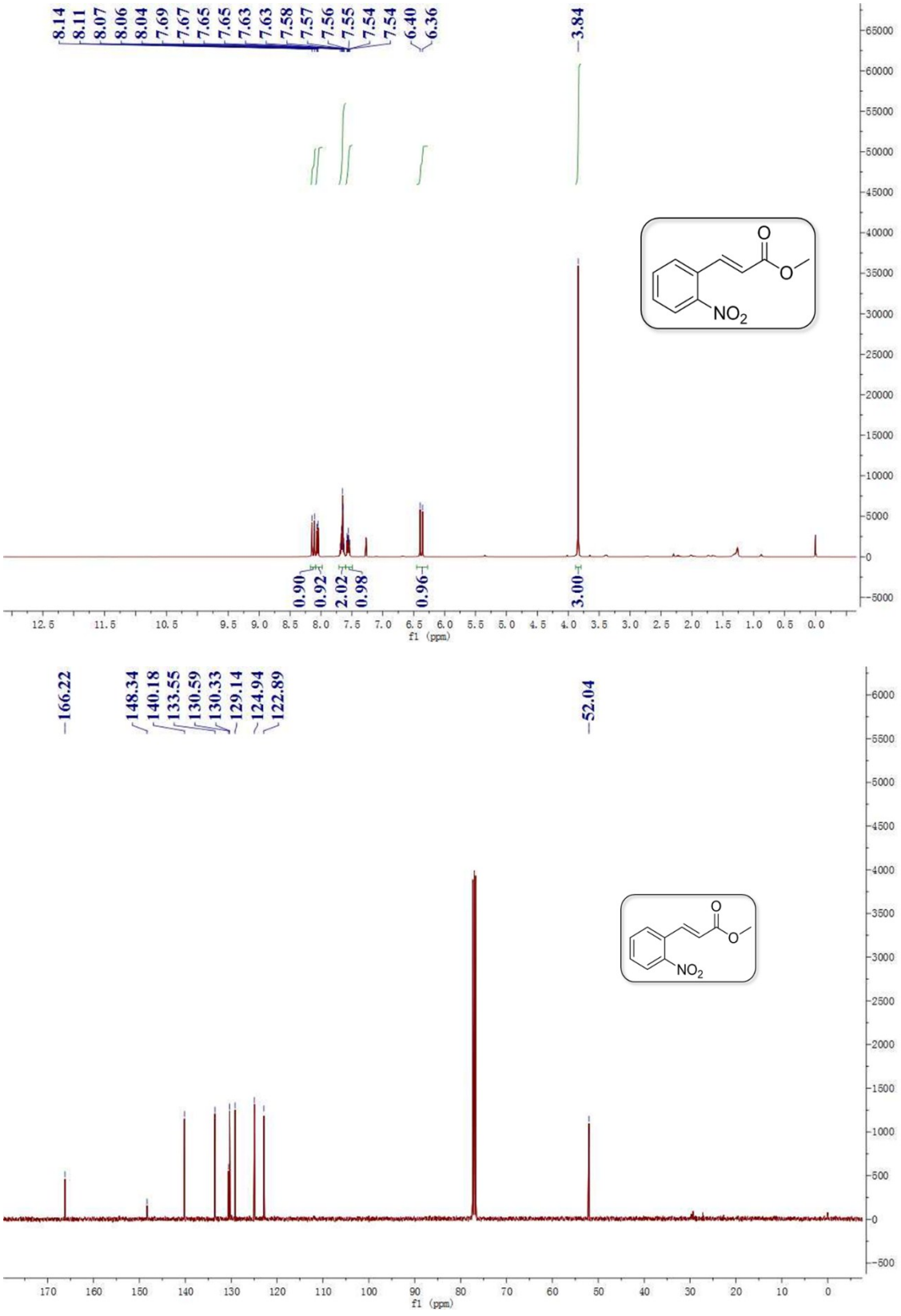


Figure S23. ^{1}H and ^{13}C NMR spectra of **9aa**

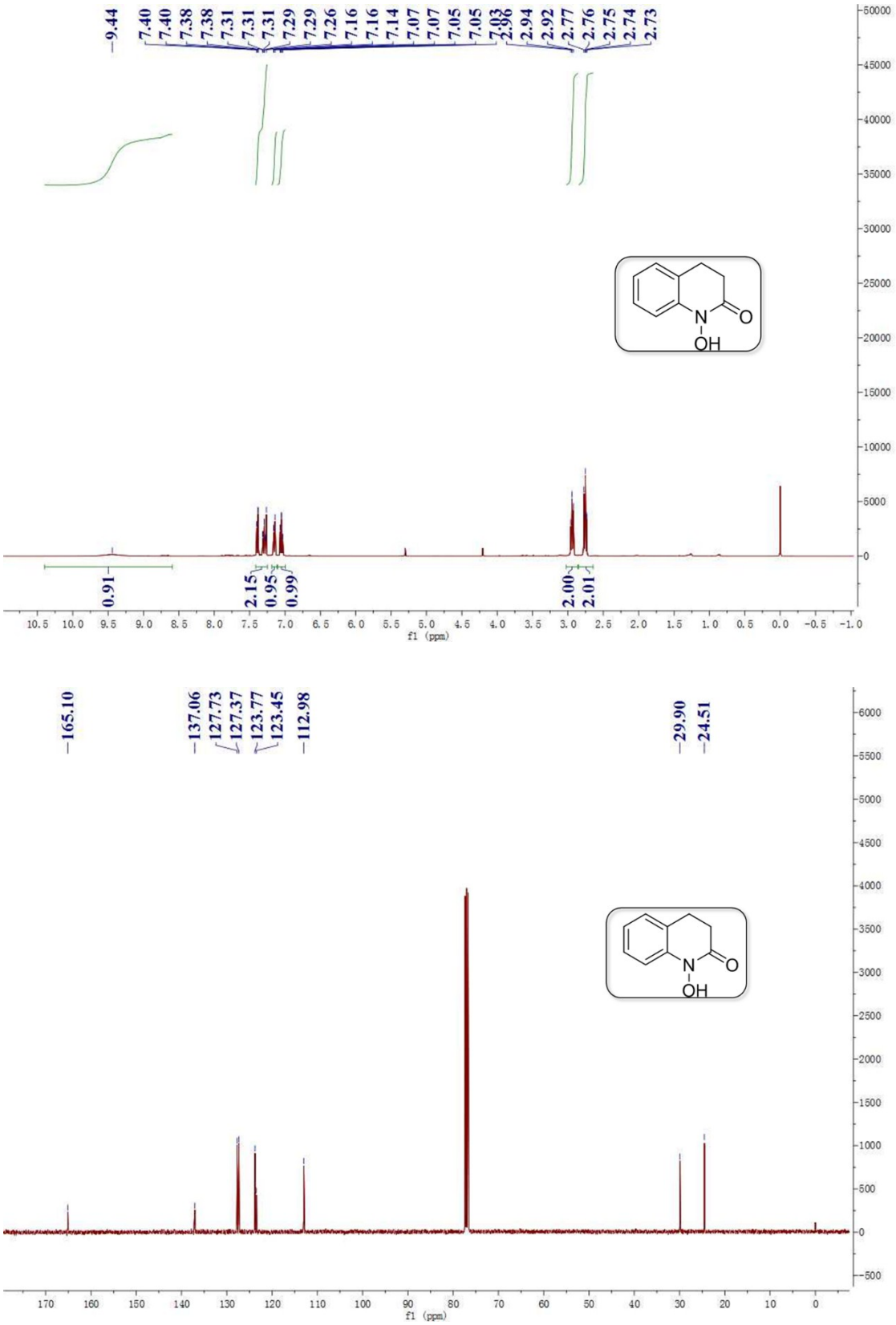


Figure S24. ^{1}H and ^{13}C NMR spectra of **5a**

References

(1) Murahashi, S.; Oda, T.; Sugahara, T.; Masui, Y. *J. Org. Chem.* **1990**, *55*, 1744.

(2) Ye, C.; Jin, P.; Liu, J.; Wen, Y.; Wei, H.; Zheng, X.; Wang, X.; Li, B. *Ind Eng Chem Res* **2013**, *52*, 3600.

(3) Lee, B. S.; Mahajan, S.; Clapham, B.; Janda, K. D. *J. Org. Chem.* **2004**, *69*, 3319.

(4) Since, M.; Terme, T.; Vanelle, P. *Tetrahedron* **2009**, *65*, 6128.

(5) Liu, B.; Hu, L. *Bioorgan Med Chem* **2003**, *11*, 3889.