Photoredox-catalyzed Giese reaction for the synthesis of γ-nitro alcohols

Ai-Jie He,[a,b] Wen-Jie Jiang,[b,c] Yan-Ping Zhang,[b] Lei Yang,[b] Jian-Qiang Zhao,[b] Zhen-Hua Wang,[b] Wei-Cheng Yuan,*[b] and Yong You*[a,b]

[a]School of Architecture and Civil Engineering, Chengdu University, Chengdu 610106, China.
[b]Institute for Advanced Study, Chengdu University, Chengdu 610106, China.
[c]College of Food and Biological Engineering, Chengdu University, Chengdu 610106, China.

*E-mail: youyong@cdu.edu.cn and yuanwc@cioc.ac.cn

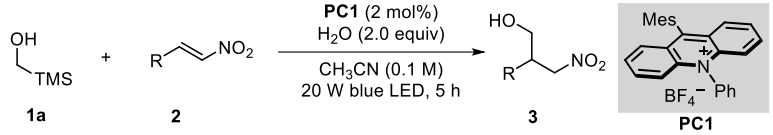
Supporting Information

Contents

1. General information

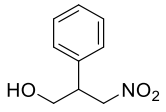
All commercial reagents were purchased and used as received unless mentioned otherwise. All visible-light-induced catalytic reactions were conducted in Schlenk seal tubes (purchased from Syhthware Glass) at room temperature under an argon atmosphere and under irradiation with 20W blue LEDs lamp Kessil PR160L-456 nm. Inert atmosphere techniques were carried out through Schlenk system and Standard Glovebox. Reactions were monitored by thin-layer chromatography (TLC) (purchased from Yantai Xinnuo New Materials Technology Co., LTD). Column chromatography was performed on silica gel (300−400 mesh) using petroleum ether-EtOAc (PE/EA) (v/v). ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded in DMSO-d_6 and $CDCl_3$. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS), with the solvent resonance employed as the internal standard (DMSO-d_6 at 2.50 ppm and $CDCl_3$ at 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (DMSO-d_6 at 39.52 ppm and $CDCl_3$ at 77.16 ppm). HRMS was recorded on the Agilent 6545 LC/Q-TOF mass spectrometer. Melting points were recorded on a OptiMelt MPA 1000. Cyclic voltammograms were collected with a CH Instruments Model 760E Series Electrochemical Analyzer/Workstation containing platinum wire working electrode, platinum wire counter electrode, SCE reference electrode (Sweep rate: 50 mV/s). Electrochemical potentials were obtained with a standard set of conditions to main internal consistency. Fluorescence studies were carried out using Techcomp Fluorescence Spectrophotometer (Model: FL970). The β-nitrostyrene[1-2] were prepared following the procedures reported in literatures.

2. General experimental procedure for the synthesis of compounds 3



To a flame dried reaction tube equipped with a magnetic stir bar was charged with **2** (0.2 mmol, 1.0 equiv), **PC1** (0.004 mmol, 2 mol %), and degassed CH_3CN (2 mL, 0.1 M for **2**) under an argon atmosphere. To this mixture, **1a** (0.4 mmol, 2.0 equiv) and H_2O (0.4 mmol, 2.0 equiv) were added sequentially via syringe. The reaction mixture was then subjected to three cycles of degassing (vacuum/argon) and irradiated at room temperature for 5 hours using a 20 W blue Kessil LED (456 nm) positioned approximately 3 cm away. A high-speed fan was employed to maintain ambient temperature throughout the irradiation period. Upon completion, the solvent was removed under reduced pressure. The crude residue was then purified via flash column chromatography on silica gel to give the products **3**.

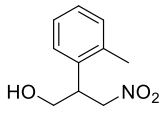
3-nitro-2-phenylpropan-1-ol (3a)



3a

yellow oil; 25.7 mg, 71% yield; eluent: PE/EA = 4/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.2 Hz, 2H), 7.23 (t, *J* = 7.1 Hz, 1H), 7.17 (t, *J* = 5.9 Hz, 2H), 4.81 (dd, *J* = 12.8, 6.8 Hz, 1H), 4.62 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.85 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.76 (dd, *J* = 11.0, 6.8 Hz, 1H), 3.70 – 3.59 (m, 1H), 1.65 (br s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 129.3, 128.2, 127.9, 77.3, 64.4, 46.4.
HRMS (ESI) m/z: Calcd. for $[M-H]^-$ $C_9H_{10}NO_3$ 180.0666; found: 180.0663.

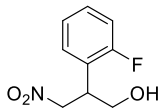
3-nitro-2-(o-tolyl)propan-1-ol (3b)



3b

yellow oil; 19.9 mg, 51% yield; eluent: PE/EA = 4/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 4.2 Hz, 3H), 7.07 (d, *J* = 7.4 Hz, 1H), 4.81 (dd, *J* = 12.9, 7.0 Hz, 1H), 4.62 (dd, *J* = 12.9, 7.8 Hz, 1H), 4.05 – 3.92 (m, 1H), 3.80 (dd, *J* = 11.1, 5.3 Hz, 1H), 3.71 (dd, *J* = 11.1, 7.1 Hz, 1H), 2.34 (s, 3H), 1.65 (br s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 135.2, 131.3, 127.9, 126.7, 125.9, 77.1, 63.9, 41.4, 19.7.
HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{10}H_{13}NNaO_3$ 218.0788; found: 218.0791.

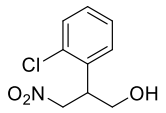
2-(2-fluorophenyl)-3-nitropropan-1-ol (3c)



3c

yellow oil; 20.1 mg, 51% yield; eluent: PE/EA = 5/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.15 (m, 2H), 7.11 – 6.97 (m, 2H), 4.85 (dd, *J* = 12.9, 6.4 Hz, 1H), 4.71 (dd, *J* = 13.0, 7.6 Hz, 1H), 3.99 – 3.78 (m, 3H), 1.67 (br s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0 (d, *J* = 247.4 Hz, 1C), 129.9 (d, *J* = 8.1 Hz, 1C), 129.6 (d, *J* = 4.0 Hz, 1C), 124.8 (d, *J* = 4.0 Hz, 1C), 124.0 (d, *J* = 14.1 Hz, 1C), 116.3 (d, *J* = 22.2 Hz, 1C), 76.0, 63.1, 41.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.0.
HRMS (ESI) m/z: Calcd. for $[M-H]^-$ $C_9H_9FNO_3$ 198.0572; found: 198.0567.

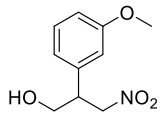
2-(2-chlorophenyl)-3-nitropropan-1-ol (3d)



3d

yellow oil; 25.4 mg, 59% yield; eluent: PE/EA = 5/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.3 Hz, 1H), 7.31 – 7.21 (m, 3H), 4.92 (dd, *J* = 13.0, 7.2 Hz, 1H), 4.79 (dd, *J* = 13.0, 7.2 Hz, 1H), 4.36 – 4.22 (m, 1H), 3.98 (dd, *J* = 11.1, 4.9 Hz, 1H), 3.89 (dd, *J* = 11.2, 6.6 Hz, 1H), 1.72 (br s, 1H).
^{1}H NMR (400 MHz, $CDCl_3$) δ 134.6 134.3, 130.5, 129.3, 128.3, 127.5, 75.8, 62.8, 42.4.
HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_9H_{10}ClNNaO_3$ 238.0241; found: 238.0244.

2-(3-methoxyphenyl)-3-nitropropan-1-ol (3e)



3e

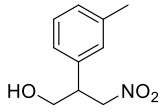
yellow oil; 24.9 mg, 59% yield; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 1H), 6.83 – 6.66 (m, 3H), 4.78 (dd, *J* = 12.9, 6.9 Hz, 1H), 4.60 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.83 (dd, *J* = 11.1, 5.5 Hz, 1H), 3.78 – 3.68 (m, 4H), 3.65-3.55 (m, 1H), 1.72 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 138.7, 130.3, 119.9, 114.1, 113.2, 77.2, 64.3, 55.4, 46.4.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{10}H_{13}NNaO_4$ 234.0737; found: 234.0735.

3-nitro-2-(m-tolyl)propan-1-ol (3f)



3f

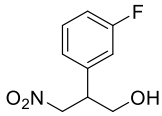
yellow oil; 22.6 mg, 58% yield; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.13 (m, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 4.78 (dd, *J* = 12.7, 6.9 Hz, 1H), 4.60 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.82 (dd, *J* = 11.1, 5.6 Hz, 1H), 3.74 (dd, *J* = 11.0, 6.9 Hz, 1H), 3.67 – 3.53 (m, 1H), 2.27 (s, 3H), 1.70 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 137.0, 129.1, 129.0, 128.6, 124.8, 77.3, 64.4, 46.4, 21.6.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{10}H_{13}NNaO_3$ 218.0788; found: 218.0790.

2-(3-fluorophenyl)-3-nitropropan-1-ol (3g)



3g

yellow oil; 22.2 mg, 56% yield; eluent: PE/EA = 4/1;

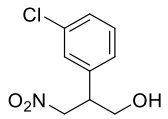
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (q, *J* = 7.3 Hz, 1H), 7.09 – 6.92 (m, 3H), 4.88 (dd, *J* = 13.0, 6.6 Hz, 1H), 4.68 (dd, *J* = 12.9, 8.2 Hz, 1H), 3.93 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.82 (dd, *J* = 11.0, 6.8 Hz, 1H), 3.77 – 3.66 (m, 1H), 1.81 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 248.5 Hz, 1C), 139.7 (d, *J* = 7.1 Hz, 1C), 130.8 (d, *J* = 8.1 Hz, 1C), 123.6 (d, *J* = 3.0 Hz, 1C), 115.2 (d, *J* = 21.2 Hz, 1C), 115.0 (d, *J* = 21.2 Hz, 1C), 77.0, 64.1, 46.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.7.

HRMS (ESI) m/z: Calcd. for $[M-H]^-$ $C_9H_9FNO_3$ 198.0572; found: 198.0569.

2-(3-chlorophenyl)-3-nitropropan-1-ol (3h)



3h

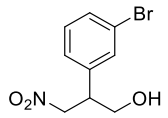
yellow oil; 25.8 mg, 60% yield; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 11.3, 6.4 Hz, 3H), 7.07 (t, *J* = 4.1 Hz, 1H), 4.81 (dd, *J* = 12.9, 6.5 Hz, 1H), 4.60 (dd, *J* = 12.9, 8.2 Hz, 1H), 3.85 (dd, *J* = 11.0, 5.2 Hz, 1H), 3.75 (dd, *J* = 11.1, 6.5 Hz, 1H), 3.61 (dt, *J* = 12.1, 6.6 Hz, 1H), 1.72 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 135.0, 130.48, 128.5, 128.1, 126.1, 76.9, 64.0, 46.0.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_9H_{10}ClNNaO_3$ 238.0241; found: 238.0249.

2-(3-bromophenyl)-3-nitropropan-1-ol (3i)



3i

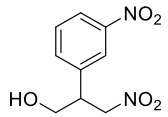
yellow oil; 26.2 mg, 50% yield; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 17.7 Hz, 2H), 7.23 – 7.07 (m, 2H), 4.80 (dd, *J* = 13.0, 6.7 Hz, 1H), 4.60 (dd, *J* = 13.0, 8.2 Hz, 1H), 3.85 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.74 (dd, *J* = 11.0, 6.7 Hz, 1H), 3.60 (dt, *J* = 14.0, 6.7 Hz, 1H), 1.74 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 131.4, 131.0, 130.8, 126.6, 123.2, 76.9, 64.0, 46.0.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_9H_{10}BrNNaO_3$ 281.9736; found: 281.9743.

3-nitro-2-(3-nitrophenyl)propan-1-ol (3j)



3j

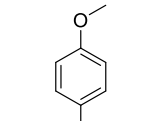
yellow solid; 26.1 mg, 58% yield; m.p. 85.5-85.9 °C; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 – 8.08 (m, 2H), 7.64 (d, *J* = 6.4 Hz, 1H), 7.56 (t, *J* = 8.2 Hz, 1H), 4.96 (dd, *J* = 13.1, 6.2 Hz, 1H), 4.76 (dd, *J* = 13.2, 8.4 Hz, 1H), 4.01 (dd, *J* = 10.7, 4.9 Hz, 1H), 3.95 – 3.80 (m, 2H), 1.81 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 139.6, 134.4, 130.2, 123.3, 122.9, 76.7, 63.7, 45.8.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_9H_{10}N_2NaO_5$ 249.0482; found: 249.0484.

2-(4-methoxyphenyl)-3-nitropropan-1-ol (3k)



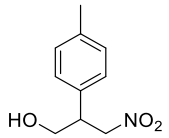
3k

yellow oil; 27.2 mg, 64% yield; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 4.77 (dd, *J* = 12.6, 6.8 Hz, 1H), 4.57 (dd, *J* = 12.6, 8.1 Hz, 1H), 3.81 (dd, *J* = 11.0, 5.6 Hz, 1H), 3.76 – 3.68 (m, 4H),

3.67 – 3.53 (m, 1H), 1.68 (br s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 128.9, 114.6, 77.6, 64.5, 55.4, 45.8.
HRMS (ESI) m/z: Calcd. for $[M+K]^+$ $C_{10}H_{13}KNO_4$ 250.0476; found: 250.0487.

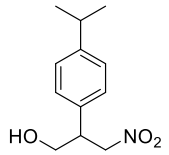
3-nitro-2-(p-tolyl)propan-1-ol (3l)



3l

yellow oil; 23.8 mg, 61% yield; eluent: PE/EA = 4/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.79 (dd, *J* = 12.7, 6.8 Hz, 1H), 4.59 (dd, *J* = 12.7, 8.1 Hz, 1H), 3.83 (dd, *J* = 11.0, 5.5 Hz, 1H), 3.74 (dd, *J* = 11.0, 6.9 Hz, 1H), 3.67 – 3.53 (m, 1H), 2.26 (s, 3H), 1.58 (br s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 133.9, 130.0, 127.7, 77.4, 64.5, 46.1, 21.2.
HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{10}H_{13}NNaO_3$ 218.0788; found: 218.0786.

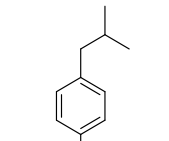
2-(4-isopropylphenyl)-3-nitropropan-1-ol (3m)



3m

yellow solid; 26.6 mg, 60% yield; m.p. 60.0-60.5 °C; eluent: PE/EA = 4/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.04 (m, 4H), 4.79 (dd, *J* = 12.7, 7.0 Hz, 1H), 4.61 (dd, *J* = 12.8, 7.9 Hz, 1H), 3.84 (dd, *J* = 11.1, 5.5 Hz, 1H), 3.75 (dd, *J* = 11.0, 6.8 Hz, 1H), 3.68 – 3.57 (m, 1H), 2.82 (hept, *J* = 6.9 Hz, 1H), 1.58 (br s, 1H), 1.19 – 1.13 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 134.2, 127.8, 127.3, 77.4, 64.5, 46.1, 33.9, 24.0.
HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{12}H_{17}NNaO_3$ 246.1101; found: 246.1098.

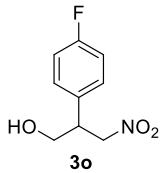
2-(4-isobutylphenyl)-3-nitropropan-1-ol (3n)



3n

yellow oil; 23.1 mg, 49% yield; eluent: PE/EA = 4/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 4H), 4.79 (dd, *J* = 12.7, 6.9 Hz, 1H), 4.60 (dd, *J* = 12.7, 7.9 Hz, 1H), 3.83 (dd, *J* = 11.1, 5.5 Hz, 1H), 3.74 (dd, *J* = 11.1, 6.8 Hz, 1H), 3.66 – 3.56 (m, 1H), 2.37 (d, *J* = 7.2 Hz, 2H), 1.82 – 1.72 (m, 6.8 Hz, 1H), 1.65 (br s, 1H), 0.86 – 0.78 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 134.2, 130.0, 127.5, 77.4, 64.5, 46.1, 45.1, 30.3, 22.5.
HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{13}H_{19}NNaO_3$ 260.1257; found: 260.1255.

2-(4-fluorophenyl)-3-nitropropan-1-ol (3o)



3o

yellow oil; 25.4 mg, 64% yield; eluent: PE/EA = 4/1;

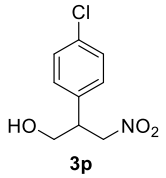
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 2H), 6.97 (t, *J* = 8.6 Hz, 2H), 4.80 (dd, *J* = 12.8, 6.6 Hz, 1H), 4.58 (dd, *J* = 12.8, 8.3 Hz, 1H), 3.83 (dd, *J* = 11.0, 5.4 Hz, 1H), 3.74 (dd, *J* = 11.0, 6.9 Hz, 1H), 3.67 – 3.57 (m, 1H), 1.73 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 248.5 Hz, 1C), 132.9 (d, *J* = 4.0 Hz, 1C), 129.5 (d, *J* = 9.1 Hz, 1C), 116.2 (d, *J* = 22.2 Hz, 1C), 77.4, 64.3, 45.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.9.

HRMS (ESI) m/z: Calcd. for $[M-H]^-$ $C_9H_9FNO_3$ 198.0572; found: 198.0562.

2-(4-chlorophenyl)-3-nitropropan-1-ol (3p)



3p

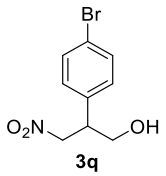
yellow oil; 25.8 mg, 60% yield; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.80 (dd, *J* = 12.9, 6.5 Hz, 1H), 4.58 (dd, *J* = 12.9, 8.3 Hz, 1H), 3.83 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.73 (dd, *J* = 11.0, 6.8 Hz, 1H), 3.65 – 3.56 (m, 1H), 1.75 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 134.1, 129.4, 129.3, 77.1, 64.1, 45.8.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_9H_{10}ClNNaO_3$ 238.0241; found: 238.0247.

2-(4-bromophenyl)-3-nitropropan-1-ol (3q)



3q

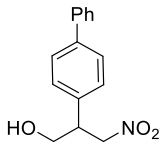
yellow oil; 29.5 mg, 57% yield; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 4.80 (dd, *J* = 12.9, 6.6 Hz, 1H), 4.59 (dd, *J* = 12.9, 8.3 Hz, 1H), 3.84 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.74 (dd, *J* = 10.9, 6.7 Hz, 1H), 3.66 – 3.53 (m, 1H), 1.66 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 132.4, 129.6, 122.2, 77.0, 64.1, 45.9.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_9H_{10}BrNNaO_3$ 281.9736; found: 281.9746.

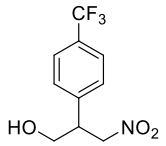
2-([1,1'-biphenyl]-4-yl)-3-nitropropan-1-ol (3r)



3r

yellow solid; 32.3 mg, 63% yield; m.p. 131.1-131.6 °C; eluent: PE/EA = 4/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.45 (m, 4H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 4.83 (dd, *J* = 12.8, 6.7 Hz, 1H), 4.65 (dd, *J* = 12.8, 8.1 Hz, 1H), 3.87 (dd, *J* = 10.9, 5.4 Hz, 1H), 3.78 (dd, *J* = 11.0, 6.8 Hz, 1H), 3.73 – 3.62 (m, 1H), 1.68 (br s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 140.4, 135.9, 128.9, 128.2 127.8, 127.6, 127.1, 77.2, 64.3, 46.0.
HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{15}H_{15}NNaO_3$ 280.0944; found: 280.0946.

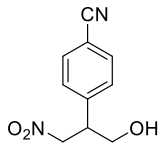
3-nitro-2-(4-(trifluoromethyl)phenyl)propan-1-ol (3s)



3s

yellow oil; 34.2 mg, 69% yield; eluent: PE/EA = 4/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 4.92 (dd, *J* = 13.0, 6.4 Hz, 1H), 4.72 (dd, *J* = 12.9, 8.3 Hz, 1H), 3.95 (dd, *J* = 10.8, 5.1 Hz, 1H), 3.85 (dd, *J* = 11.0, 6.6 Hz, 1H), 3.82 – 3.74 (m, 1H), 1.84 (br s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 130.5 (q, *J* = 32.3 Hz, 1C), 128.4, 126.2 (q, *J* = 4.0 Hz, 1C), 124.0 (q, *J* = 273.7 Hz, 1C), 76.8, 64.0, 46.1.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7.
HRMS (ESI) m/z: Calcd. for $[M-H]^-$ $C_{10}H_9F_3NO_3$ 248.0540; found: 248.0538.

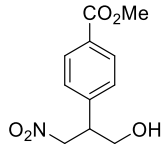
4-(1-hydroxy-3-nitropropan-2-yl)benzonitrile (3t)



3t

yellow oil; 20.5 mg, 50% yield; eluent: PE/EA = 4/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 4.93 (dd, *J* = 13.1, 6.3 Hz, 1H), 4.72 (dd, *J* = 13.1, 8.5 Hz, 1H), 3.96 (dd, *J* = 10.8, 5.0 Hz, 1H), 3.85 (dd, *J* = 10.8, 6.4 Hz, 1H), 3.82 – 3.73 (m, 1H), 1.81 (br s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 132.9, 128.9, 118.5, 112.2, 76.6, 63.7, 46.2.
HRMS (ESI) m/z: Calcd. for $[M-H]^-$ $C_{10}H_9N_2O_3$ 205.0619; found: 205.0616.

methyl 4-(1-hydroxy-3-nitropropan-2-yl)benzoate (3u)



3u

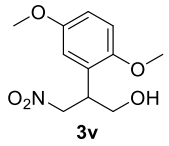
yellow oil; 19.3 mg, 40% yield; eluent: PE/EA = 2/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 4.92 (dd, *J* = 13.0, 6.4 Hz, 1H), 4.71 (dd, *J* = 13.0, 8.2 Hz, 1H), 3.94 (dd, *J* = 10.8, 5.0 Hz, 1H), 3.90 (s, 3H), 3.84 (dd, *J* = 10.7, 6.6 Hz, 1H), 3.81 – 3.73 (m, 1H), 1.91 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 142.4, 130.4, 130.0, 128.0, 64.0, 52.4, 46.3.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{11}H_{13}NNaO_5$ 262.0686; found: 262.0691.

2-(2,5-dimethoxyphenyl)-3-nitropropan-1-ol (3v)



3v

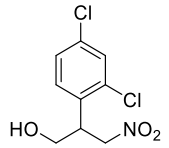
yellow solid; 26.4 mg, 55% yield; m.p. 69.0-69.7 ºC; eluent: PE/EA = 3/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 – 6.63 (m, 3H), 4.79 (dd, *J* = 12.8, 6.8 Hz, 1H), 4.70 (dd, *J* = 12.8, 7.0 Hz, 1H), 3.90 (dt, *J* = 12.3, 6.6 Hz, 1H), 3.83 (d, *J* = 4.4 Hz, 2H), 3.73 (s, 3H), 3.68 (s, 3H), 1.82 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 151.5, 126.2, 115.9, 112.9, 112.1, 76.2, 63.2, 56.1, 55.8, 42.1.

HRMS (ESI) m/z: Calcd. for $[M+H]^+$ $C_{11}H_{16}NO_5$ 242.1023; found: 242.1026.

2-(2,4-dichlorophenyl)-3-nitropropan-1-ol (3w)



3w

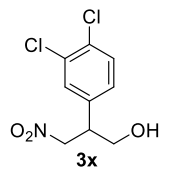
yellow oil; 27.8 mg, 56% yield; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.18 (s, 2H), 4.83 (dd, *J* = 13.0, 7.0 Hz, 1H), 4.69 (dd, *J* = 13.0, 7.4 Hz, 1H), 4.22 – 4.10(m, 1H), 3.89 (dd, *J* = 11.1, 4.7 Hz, 1H), 3.79 (dd, *J* = 11.1, 6.4 Hz, 1H), 1.73 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 134.5, 133.3, 130.3, 129.2, 127.8, 75.6, 62.6, 41.9.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_9H_9Cl_2NNaO_3$ 271.9852; found: 271.9853.

2-(3,4-dichlorophenyl)-3-nitropropan-1-ol (3x)



3x

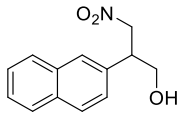
yellow solid; 23.2 mg, 48% yield; m.p. 66.5-67.0 ºC; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.16 (td, *J* = 8.2, 6.0 Hz, 1H), 7.05 (ddd, *J* = 11.1, 8.4, 1.3 Hz, 1H), 5.01 (ddd, *J* = 13.3, 6.5, 2.0 Hz, 1H), 4.87 (dd, *J* = 13.4, 7.7 Hz, 1H), 4.57 – 4.43 (m, 1H), 4.03 – 3.89 (m, 2H), 1.73 (br s, 1H).

13C NMR (101 MHz, CDCl3) δ 137.5, 133.3, 132.4, 131.1, 123.0, 127.3, 76.8, 63.8, 45.4.

HRMS (ESI) m/z: Calcd. for $[M+K]^+$ $C_9H_9Cl_2KNO_3$ 287.9591; found: 287.9593.

2-(naphthalen-2-yl)-3-nitropropan-1-ol (3y)



3y

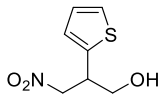
yellow solid; 27.0 mg, 58% yield; m.p. 96.0-96.3 ºC; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.67 (m, 3H), 7.61 (s, 1H), 7.49 – 7.34 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 4.87 (dd, *J* = 12.7, 6.4 Hz, 1H), 4.71 (dd, *J* = 12.7, 7.7 Hz, 1H), 3.90 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.86 – 3.71 (m, 2H), 1.70 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4, 133.5, 133.0, 129.1, 127.9, 127.8, 127.0, 126.7, 126.5, 125.5, 77.2, 64.3, 46.5.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{13}H_{13}NNaO_3$ 254.0788; found: 254.0787.

3-nitro-2-(thiophen-2-yl)propan-1-ol (3z)



3z

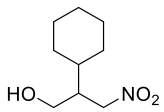
yellow oil; 21.6 mg, 58% yield; eluent: PE/EA = 3/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 5.2 Hz, 1H), 7.06 – 6.91 (m, 2H), 4.87 (dd, *J* = 12.8, 6.8 Hz, 1H), 4.67 (dd, *J* = 12.8, 7.7 Hz, 1H), 4.08 – 4.01 (m, 1H), 3.96 (dd, *J* = 11.1, 4.9 Hz, 1H), 3.87 (dd, *J* = 11.1, 6.3 Hz, 1H), 1.77 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 127.4, 126.0, 125.3, 77.7, 64.4, 41.8.

HRMS (ESI) m/z: Calcd. for $[M-H]^-$ $C_7H_8NO_3S$ 186.0230; found: 186.0227.

2-cyclohexyl-3-nitropropan-1-ol (3aa)



3aa

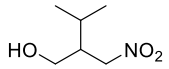
yellow oil; 21.7 mg, 58% yield; eluent: PE/EA = 5/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (dd, *J* = 12.4, 7.5 Hz, 1H), 4.48 (dd, *J* = 12.3, 5.7 Hz, 1H), 3.78 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.75 – 3.67 (m, 1H), 3.66 (dd, *J* = 11.1, 7.0 Hz, 1H), 2.33 – 2.18 (m, 1H), 1.75 (d, *J* = 11.3 Hz, 3H), 1.67 (d, *J* = 10.9 Hz, 3H), 1.51 – 1.41 (m, 1H), 1.22 – 1.18(m, 1H), 1.18 – 1.10(m, 1H), 1.09 – 0.95(m, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 75.7, 61.2, 58.6, 45.4, 37.3, 30.4, 30.1, 26.5, 26.4.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_9H_{17}NNaO_3$ 210.1101; found: 210.1101.

3-methyl-2-(nitromethyl)butan-1-ol (3ab)



3ab

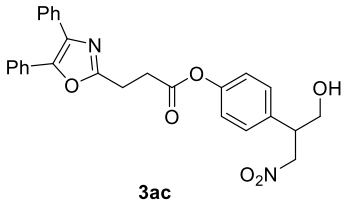
yellow oil; 17.4 mg, 59% yield; eluent: PE/EA = 5/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 (dd, *J* = 12.4, 7.4 Hz, 1H), 4.47 (dd, *J* = 12.4, 5.5 Hz, 1H), 3.79 (dd, *J* = 11.3, 4.5 Hz, 1H), 3.71 – 3.60 (m, 1H), 2.29 – 2.18 (m, 1H), 1.89 – 1.75 (m, 1H), 1.66 (br s, 1H), 1.04 – 0.91(m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 75.7, 61.3, 46.0, 27.3, 19.9, 19.7.

HRMS (ESI) m/z: Calcd. for $[M-H]^-$ $C_6H_{12}NO_3$ 146.0823; found: 146.0820.

4-(1-hydroxy-3-nitropropan-2-yl)phenyl 3-(4,5-dimethyloxazol-2-yl)propanoate (3ac)



3ac

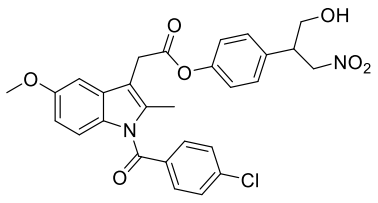
yellow oil; 35.8 mg, 38% yield; eluent: PE/EA = 2/1;

^{1}H NMR (400 MHz, $CDCl_3$) 7.64 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.58 (dd, *J* = 7.8, 1.9 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.37 – 7.33 (m, 4H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 4.85 (dd, *J* = 12.9, 6.7 Hz, 1H), 4.63 (dd, *J* = 12.9, 8.0 Hz, 1H), 3.86 (dd, *J* = 11.1, 5.3 Hz, 1H), 3.76 (dd, *J* = 11.0, 6.8 Hz, 1H), 3.68 (dt, *J* = 13.4, 6.7 Hz, 1H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 1.68 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 161.5, 150.4, 145.8, 135.2, 134.9, 132.4, 129.0, 128.8, 128.73, 128.70, 128.3, 128.0, 126.6, 122.3, 64.2, 45.8, 31.3, 23.6.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{27}H_{24}N_2NaO_6$ 495.1527; found: 495.1530.

4-(1-hydroxy-3-nitropropan-2-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (3ad)



3ad

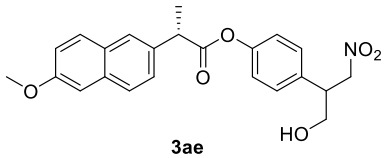
yellow solid; 55.1 mg, 51% yield; m.p. 121.3-121.9 °C; eluent: PE/EA = 2/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.08 – 7.00 (m, 3H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.83 (dd, *J* = 12.9, 6.6 Hz, 1H), 4.63 (dd, *J* = 12.9, 8.2 Hz, 1H), 3.90 (s, 2H), 3.87 – 3.79 (m, 4H), 3.75 (dd, *J* = 10.9, 6.8 Hz, 1H), 3.71 – 3.62 (m, 1H), 2.44 (s, 3H), 1.83 (br s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 168.5, 156.2, 150.4, 139.5, 136.4, 134.9, 133.9, 131.3, 131.0, 130.6, 129.3, 129.0, 122.2, 115.2, 111.93, 111.88, 101.3, 77.1, 64.2, 55.9, 45.8, 30.6, 13.6.6

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{28}H_{25}ClN_2NaO_7$ 559.1242; found: 559.1250.

4-(1-hydroxy-3-nitropropan-2-yl)phenyl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (3ae)



3ae

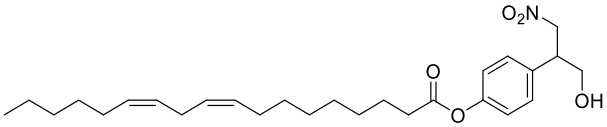
yellow solid; 31.7 mg, 39% yield, >20:1 dr; m.p. 105.2-105.8 °C; eluent: PE/EA = 2/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 8.0 Hz, 3H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.22 – 7.11 (m, 4H), 6.96 (d, *J* = 8.7 Hz, 2H), 4.81 (dd, *J* = 12.9, 6.6 Hz, 1H), 4.60 (ddd, *J* = 12.8, 8.0, 2.4 Hz, 1H), 4.14 – 4.04 (m, 1H), 3.92 (s, 3H), 3.81 (dd, *J* = 11.0, 5.2 Hz, 1H), 3.76 – 3.68 (m, 1H), 3.68 – 3.57 (m, 1H), 1.86 (br s, 1H), 1.69 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 157.9, 150.6, 135.0, 134.7, 134.0, 129.4, 129.1, 128.9, 127.6, 126.3, 126.2, 122.2, 119.3, 105.7, 77.1, 64.2, 55.5, 45.8, 45.6, 18.5.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{23}H_{23}NNaO_6$ 432.1418; found: 432.1421.

4-(1-hydroxy-3-nitropropan-2-yl)phenyl (9*Z*,12*Z*)-octadeca-9,12-dienoate (3af)



3af

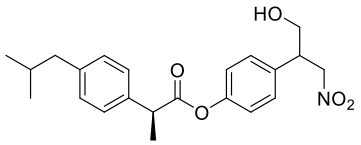
yellow oil; 44.5 mg, 48% yield; eluent: PE/EA = 4/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 5.36 (tt, *J* = 10.9, 5.6 Hz, 4H), 4.85 (dd, *J* = 12.9, 6.5 Hz, 1H), 4.64 (dd, *J* = 12.9, 8.0 Hz, 1H), 3.83 (dd, *J* = 10.9, 5.2 Hz, 1H), 3.72 (ddd, *J* = 22.9, 12.0, 7.2 Hz, 2H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.09 – 2.01 (m, 4H), 1.78 – 1.69 (m, 2H), 1.45 – 1.28 (m, 15H), 0.89 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 134.7, 130.3, 130.1, 128.9, 128.2, 128.0, 122.3, 64.2, 45.8, 34.5, 31.6, 29.7, 29.5, 29.3, 29.21, 29.17, 27.31, 27.29, 25.7, 25.0, 22.7, 14.2.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{27}H_{41}NNaO_5$ 482.2877; found: 482.2882.

4-(1-hydroxy-3-nitropropan-2-yl)phenyl (2*S*)-2-(4-isobutylphenyl)propanoate (3ag)



3ag

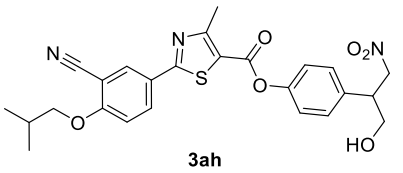
yellow oil; 39.4 mg, 51% yield, >20:1 dr; eluent: PE/EA = 2/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (dd, *J* = 15.8, 8.0 Hz, 4H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.82 (dd, *J* = 12.9, 6.4 Hz, 1H), 4.61 (dd, *J* = 12.7, 8.2 Hz, 1H), 3.94 (q, *J* = 7.1 Hz, 1H), 3.85 – 3.75 (br s, 1H), 3.66 (td, *J* = 15.5, 13.2, 8.9 Hz, 2H), 2.48 (d, *J* = 7.2 Hz, 2H), 2.08 – 1.94 (m, 1H), 1.87 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.60 (d, *J* = 7.1 Hz, 3H), 0.94 – 0.89 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 150.5, 141.1, 137.1, 134.7, 129.7, 128.9, 127.3, 122.1, 77.1, 64.2, 45.8, 45.3, 45.1, 30.3, 22.5, 18.5.

HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{22}H_{27}NNaO_5$ 408.1781; found: 408.1786.

4-(1-hydroxy-3-nitropropan-2-yl)phenyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (3ah)



3ah

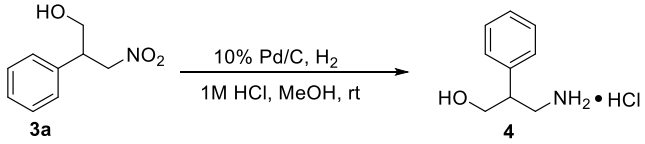
yellow solid; 41.6 mg, 42% yield; m.p. 132.5-133.2 °C; eluent: PE/EA = 1/1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.3 Hz, 1H), 8.11 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 1H), 4.90 (dd, *J* = 12.9, 6.5 Hz, 1H), 4.69 (dd, *J* = 12.9, 8.2 Hz, 1H), 3.94 – 3.88 (m, 3H), 3.81 (dd, *J* = 10.9, 6.8 Hz, 1H), 3.78 – 3.69 (m, 1H), 2.92 – 2.70 (m, 4H), 2.27 – 2.14 (m, 1H), 1.10 – 1.07 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 163.4, 162.8, 160.5, 150.0, 135.3, 132.8, 132.3, 129.1, 125.8, 122.4, 120.4, 115.5, 112.8, 103.1, 75.9, 64.2, 45.9, 28.3, 19.2, 17.8.

HRMS (ESI) m/z: Calcd. for $[M+H]^+$ $C_{25}H_{26}N_3O_6S$ 496.1537; found: 496.1538.

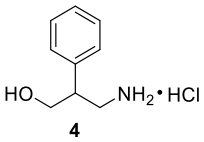
3. General experimental procedure for the synthesis of compound 4



3a **4**

A mixture of compound 3**a** (0.2 mmol, 1.0 equiv), 10 wt% Pd/C (10 mg), and 1 M HCl in methanol (2 mL, 0.1 M) was stirred under a hydrogen atmosphere for 12 hours. The reaction mixture was then filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure to afford compound **4**.

3-amino-2-phenylpropan-1-ol hydrochloride (4)



4

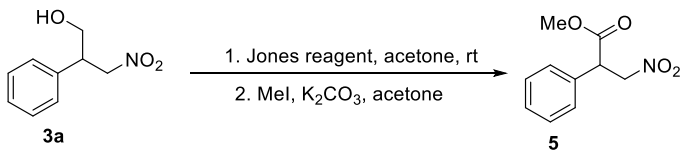
yellow solid; 36.4 mg, 97% yield; m.p. 274.4-275.2 °C;

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.13 (s, 3H), 7.37 – 7.22 (m, 5H), 5.25 – 5.12 (m, 1H), 3.66 – 3.53 (m, 2H), 3.31 – 3.20 (m, 1H), 3.14 – 3.05 (m, 1H), 3.03 – 3.91 (m, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 139.7, 128.5, 128.1, 127.0, 63.5, 45.5, 41.1.

HRMS (ESI) m/z: Calcd. for $[M+H]^+$ $C_9H_{14}NO$ 152.1070; found: 152.1069.

4. General experimental procedure for the synthesis of compound 5

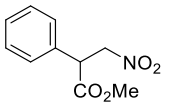


3a **5**

A solution of compound **3a** (0.2 mmol, 1.0 equiv) in acetone (2 mL, 0.1 M) was cooled to 0 °C.

Jones reagent (0.4 mmol, 2.0 equiv) was added dropwise, and the mixture was stirred while warming to room temperature. Reaction progress was monitored by TLC. Upon completion, the reaction was quenched with isopropanol (added dropwise), and the mixture was filtered through a Celite pad to remove chromium salts. The filtrate was concentrated under reduced pressure, and the residue was dissolved in DMF (1 mL). Potassium carbonate (0.2 mmol, 1.0 equiv) and iodomethane (1 mmol, 5.0 equiv) were added sequentially, and the reaction was again monitored by TLC. After completion, the mixture was diluted with ethyl acetate, washed with brine, and the organic phase was concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, eluent: PE:EA = 15:1) to yield compound **5**.

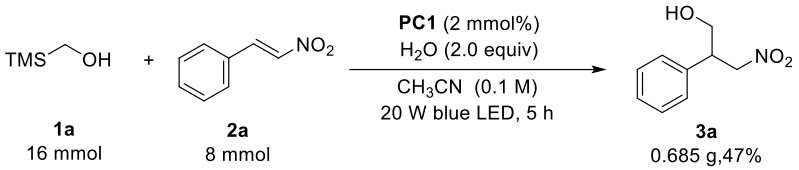
methyl 3-nitro-2-phenylpropanoate (5)



5

yellow oil; 17.3 mg, 41% yield; eluent: PE/EA = 15/1;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 13.1 Hz, 3H), 7.19 – 7.14 (m, 2H), 5.01 (dd, *J* = 14.6, 10.0 Hz, 1H), 4.45 (dd, *J* = 14.7, 5.1 Hz, 1H), 4.35 (dd, *J* = 9.9, 5.1 Hz, 1H), 3.63 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 133.3, 129.5, 128.9, 128.0, 75.9, 53.0, 48.8.
HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{10}H_{11}NNaO_4$ 232.0580; found: 232.0585.

5. Scale-up reaction

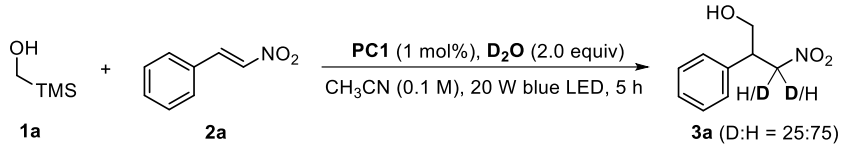


1a 16 mmol | **2a** 8 mmol | **3a** 0.685 g,47%

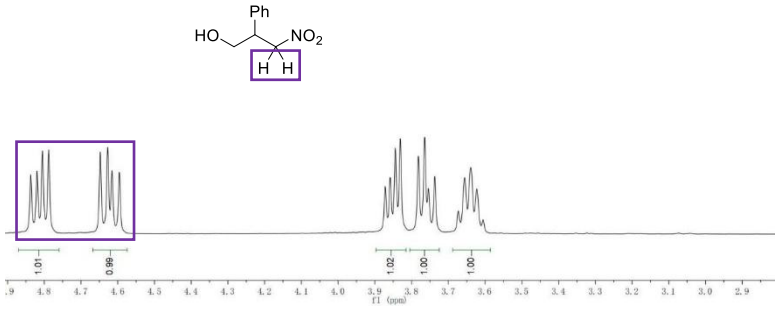
To a flame dried reaction tube equipped with a magnetic stir bar was charged with **2a** (8.0 mmol, 1.0 equiv), **PC1** (0.16 mmol, 2 mol %), and degassed CH_3CN (80 mL, 0.1 M for **2a**) under an argon atmosphere. To this mixture, **1a** (16.0 mmol, 2.0 equiv) and H_2O (16.0 mmol, 2.0 equiv) were added sequentially via syringe. The reaction mixture was then subjected to three cycles of degassing (vacuum/argon) and irradiated at room temperature for 5 hours using a 20 W blue Kessil LED (456 nm) positioned approximately 3 cm away. A high-speed fan was employed to maintain ambient temperature throughout the irradiation period. Upon completion, the solvent was removed under reduced pressure. The crude residue was then purified via flash column chromatography on silica gel to give the products **3**, 0.685 g, 47% yield.

6. Deuterium labelling experiment

To identify the proton source in the proposed mechanism, control experiments were conducted using D_2O in place of H_2O, while keeping all other parameters constant. ^{1}H NMR analysis of the crude product confirmed the incorporation of deuterium, as shown in the spectrum below.



^{1}H NMR of **3a** (H)



^{1}H NMR of Crude **3a** (D)

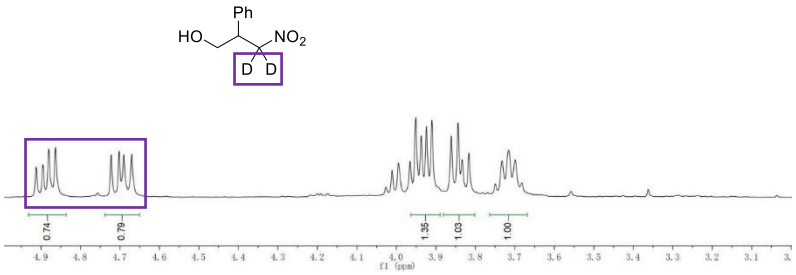
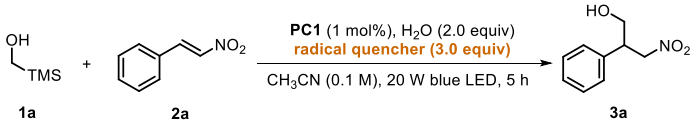


Figure S1. ^{1}H NMR analysis for deuterium labelling experiment

7. Radical trapping experiments

To a flame dried reaction tube equipped with a magnetic stir bar was charged with **2a** (0.2 mmol, 1.0 equiv), **PC1** (0.004 mmol, 2 mol %), a radical quencher (0.6 mmol, 3.0 equiv), and degassed CH_3CN (2 mL, 0.1 M for **2a**) under an argon atmosphere. To this mixture, **1a** (0.4 mmol, 2.0 equiv) and H_2O (0.4 mmol, 2.0 equiv) were added sequentially via syringe. The reaction mixture was then subjected to three cycles of degassing (vacuum/argon) and irradiated at room temperature using a 20 W blue Kessil LED (456 nm) positioned approximately 3 cm away. A high-speed fan was employed to maintain ambient temperature throughout the 5 hours irradiation period. Upon completion, the crude reaction mixture was analyzed by ^{1}H NMR and HRMS. The results (Table S1) indicated significant suppression of **3a** formation. Notably, trace amounts of the 1,1-diphenylethylene adduct **6**, TEMPO adduct **7**, and BHT adduct **8** were detected in the HRMS analysis of the crude mixture (Figure S2). These observations support the generation of a (trimethylsilyl)oxy methyl radical and are consistent with a radical addition pathway.

Table S1 Radical trapping experiments

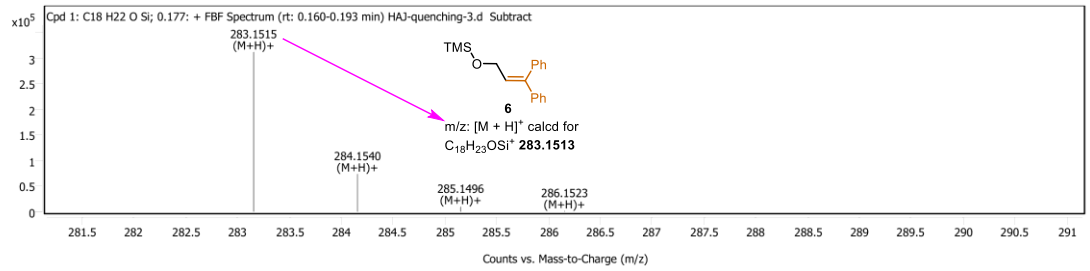


radical quencher	TEMPO	BHT	1,1-Diphenylethylene
Yield	0%	trace	25%

Compound Details

Cpd. 1: C18 H22 O Si

Compound Spectra



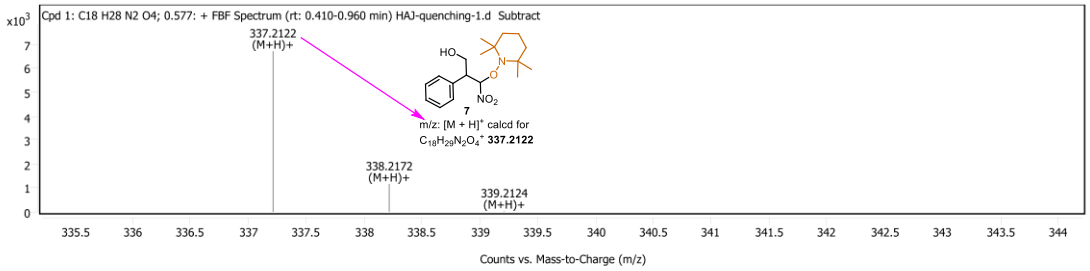
Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
283.1515	283.1513	0.79	312709	100.00	100.00	(M+H)+	1
284.1540	284.1539	0.51	73929	23.64	24.85	(M+H)+	1
285.1496	285.1522	-8.96	10002	3.20	6.41	(M+H)+	1
286.1523	286.1537	-4.76	1821	0.58	0.92	(M+H)+	1

Compound Details

Cpd. 1: C18 H28 N2 O4

Compound Spectra



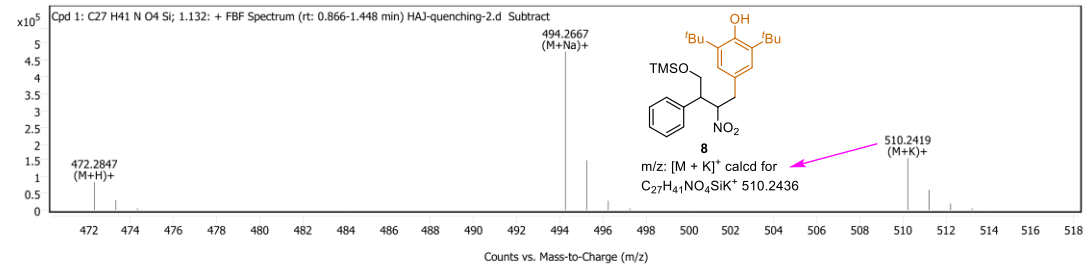
Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
337.2122	337.2122	0.06	6697	100.00	100.00	(M+H)+	1
338.2172	338.2154	5.54	1164	17.37	20.68	(M+H)+	1
339.2124	339.2179	-16.29	32	0.47	2.85	(M+H)+	1

Compound Details

Cpd. 1: C27 H41 N O4 Si

Compound Spectra



Spectrum Peaks

m/z	m/z (Calc)	Diff (ppm)	Abund	Height %	Height % (Calc)	Ion Species	Z
472.2847	472.2878	-6.39	84990	100.00	100.00	(M+H)+	1
473.2880	473.2905	-5.46	30155	35.48	35.28	(M+H)+	1
474.2910	474.2904	1.36	5788	6.81	10.11	(M+H)+	1
494.2667	494.2697	-6.13	476978	100.00	100.00	(M+Na)+	1
495.2694	495.2725	-6.23	149946	31.44	35.27	(M+Na)+	1
496.2709	496.2723	-2.88	28288	5.93	10.11	(M+Na)+	1
497.2723	497.2737	-2.87	5479	1.15	1.94	(M+Na)+	1
510.2419	510.2436	-3.44	157416	100.00	100.00	(M+K)+	1
511.2445	511.2464	-3.85	60616	38.51	35.28	(M+K)+	1
512.2469	512.2444	4.92	20172	12.81	17.33	(M+K)+	1
513.2444	513.2459	-2.95	5398	3.43	4.48	(M+K)+	1

Figure S2. HRMS analysis for radical trapping experiments

8. Stern-Volmer Fluorescence Quenching Experiments

Fluorescence quenching studies were carried out using Techcomp FL970 fluorescence spectrophotometer. Photocatalyst **PC1** (9-Mesityl-10-phenylacridin-10-ium tetrafluoroborate) and different concentrations of added quenchers were prepared in dry CH_3CN in quartz cuvettes. CH_3CN was degassed with a stream of argon gas for 30 min. For the quenching experiments, the

concentration of **PC1** was 5.0 × 10^{-5} M. The solutions were excited at 440 nm in CH_3CN solution and the emission intensity was observed at ~540 nm. Plots were derived according to the Stern–Volmer equation and Ksv was calculated. Stern-Volmer equation: $I_0/I = 1 + Ksv[S]$. Where I_0 is the luminescence intensity of the photocatalyst in the absence of a quencher, I is the intensity of the photocatalyst in the presence of quenchers, [S] is the concentration of added quencher, and Ksv is the Stern– Volmer quenching constant. All emission spectra were recorded after each addition of the quencher. The steady decrease of the emission intensity of the catalyst solution with the gradual increase of the amount of **1a** or **2a** as presented in Figure S1 and Figure S2 supports that reaction mechanism occurring through reductive quenching cycle.

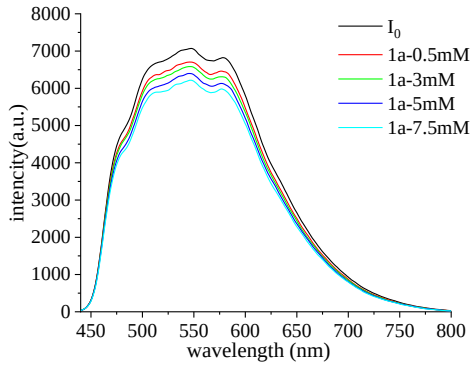


Figure S3. Fluorescence quenching by **1a**

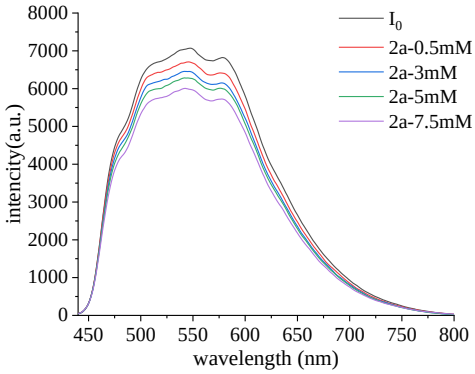


Figure S4. Fluorescence quenching by **2a**

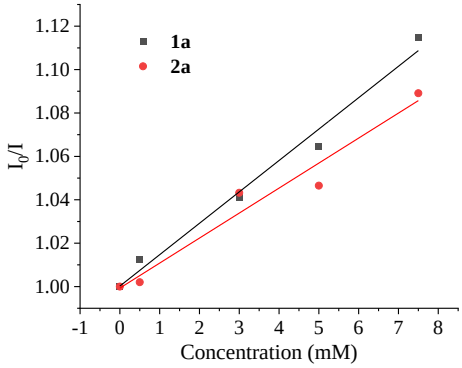


Figure S5. Stern-Volmer plot

9. Electrochemical measurements

Cyclic Voltammetry was performed using a CH Instruments 760E. The redox potentials (vs SCE) were determined using a 5.0 mM solution of the compounds in 0.1 M solution of $^{n}Bu_4NPF_6$ (purged CH_3CN with Ar). Measurements employed a glassy carbon working electrode, saturated calomel reference electrode, and a platinum wire counter electrode. The potential was scanned at a scan rate 50 mV/s. A background of the electrolyte solution was subtracted from the voltammogram. Reduction was measured by scanning potential in the positive direction. The glassy carbon electrode was polished between each scan.

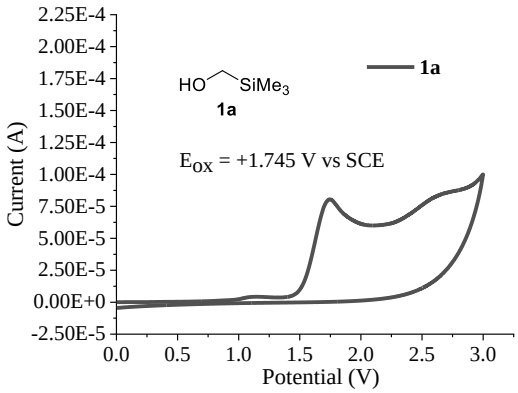


Figure S6. Cyclic voltammogram study for **1a**

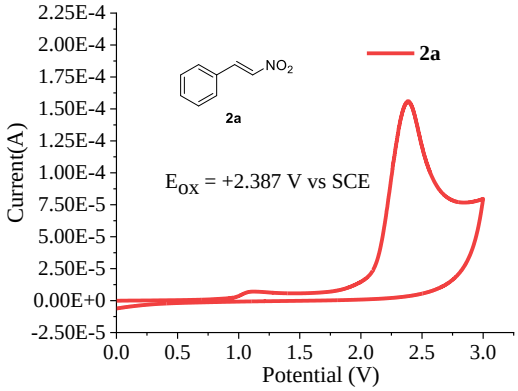


Figure S6. Cyclic voltammogram study for **2a**

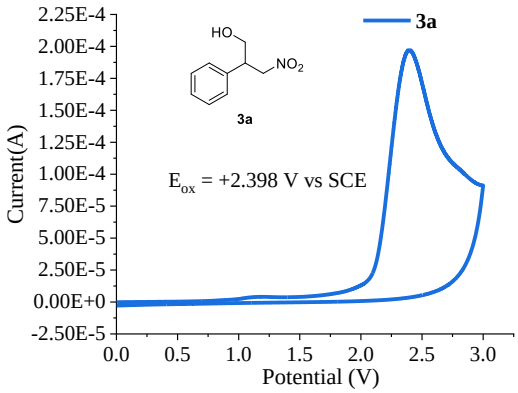
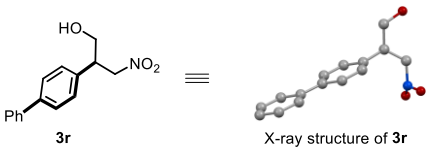


Figure S8. Cyclic voltammogram study for **3a**

10. X-ray crystal structure of 3r

Single crystals of compound **3r** were prepared through dissolving the sample in *n*-pentane/EtOAc at room temperature and crystalizing by slow evaporation of solvent. A suitable crystal was selected for structure determination on an Xcalibur, Eos, Gemini diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[3], the structure was solved with the ShelXS[4]structure solution program using Direct Methods and refined with the ShelXL[5]refinement package using Least Squares minimisation.



ORTEP of **3r** (at 50% level)

Identification code	**3r**
Empirical formula	$C_{15}H_{15}NO_3$
Formula weight	257.28
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.6525(6)
b/Å	5.5652(5)
c/Å	15.5161(11)
α /°	90
β /°	90.246(6)
γ /°	90
Volume/Å^3	660.79(9)
Z	2
ρ_{calc}g/cm^3	1.293
μ /mm^{-1}	0.740
F(000)	272.0
Crystal size/mm^3	0.18 × 0.11 × 0.07
Radiation	Cu K α (λ = 1.54184)
2Θ range for data collection/°	11.406 to 142.186
Index ranges	-9 ⩽ h ⩽ 9, -5 ⩽ k ⩽ 6, -18 ⩽ l ⩽ 18
Reflections collected	6931
Independent reflections	2249 [R_{int} = 0.0349, R_{sigma} = 0.0336]
Data/restraints/parameters	2249/40/184
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2 σ (I)]	R_1 = 0.0578, wR_2 = 0.1659
Final R indexes [all data]	R_1 = 0.0686, wR_2 = 0.1814
Largest diff. peak/hole / e Å^{-3}	0.24/-0.15

11. References

[1] S. P. Midya, S. Mondal, A. S. M. Islam, A. Rashid, S. Mondal, A. Paul and P. Ghosh, *Org. Lett.*, 2022, **24**, 4438-4443.

[2] S. Cai, X. Zhao, X. Wang, Q. Liu, Z. Li and D. Z. Wang, *Angew. Chem. Int. Ed.*, 2012, **51**, 8050-8053.

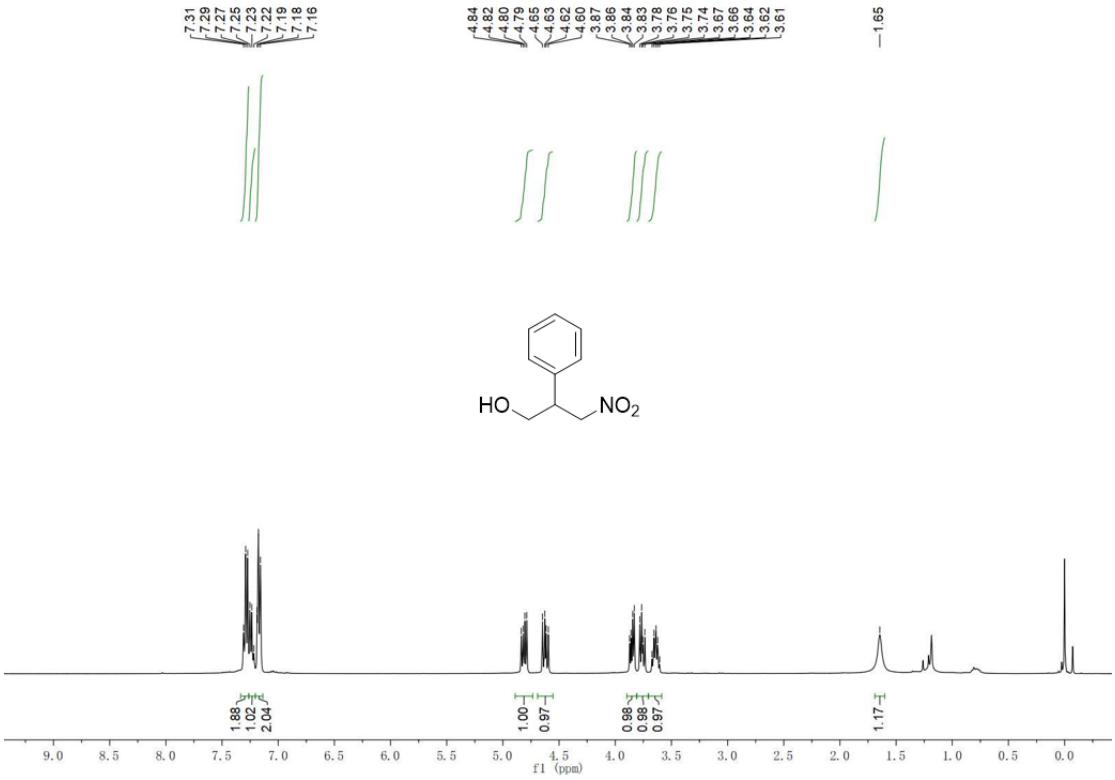
[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

[4] G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112-122.

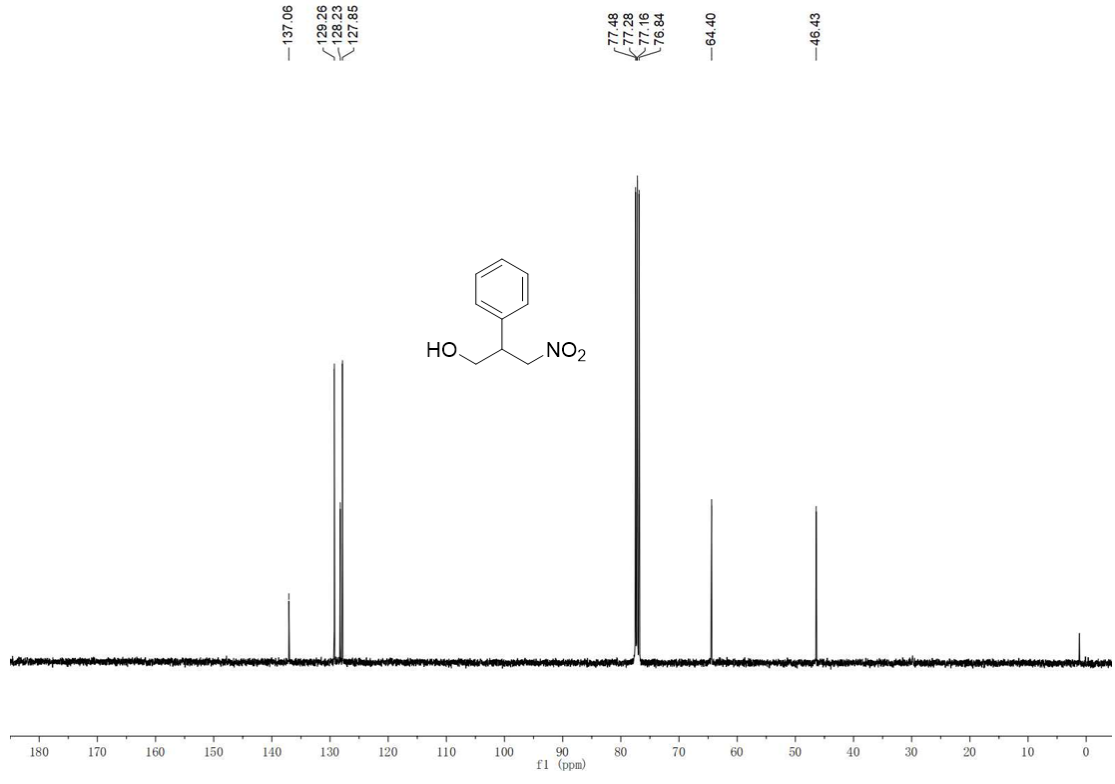
[5] G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

12. ^{1}H, ^{13}C NMR spectra for compounds 3, 4, 5

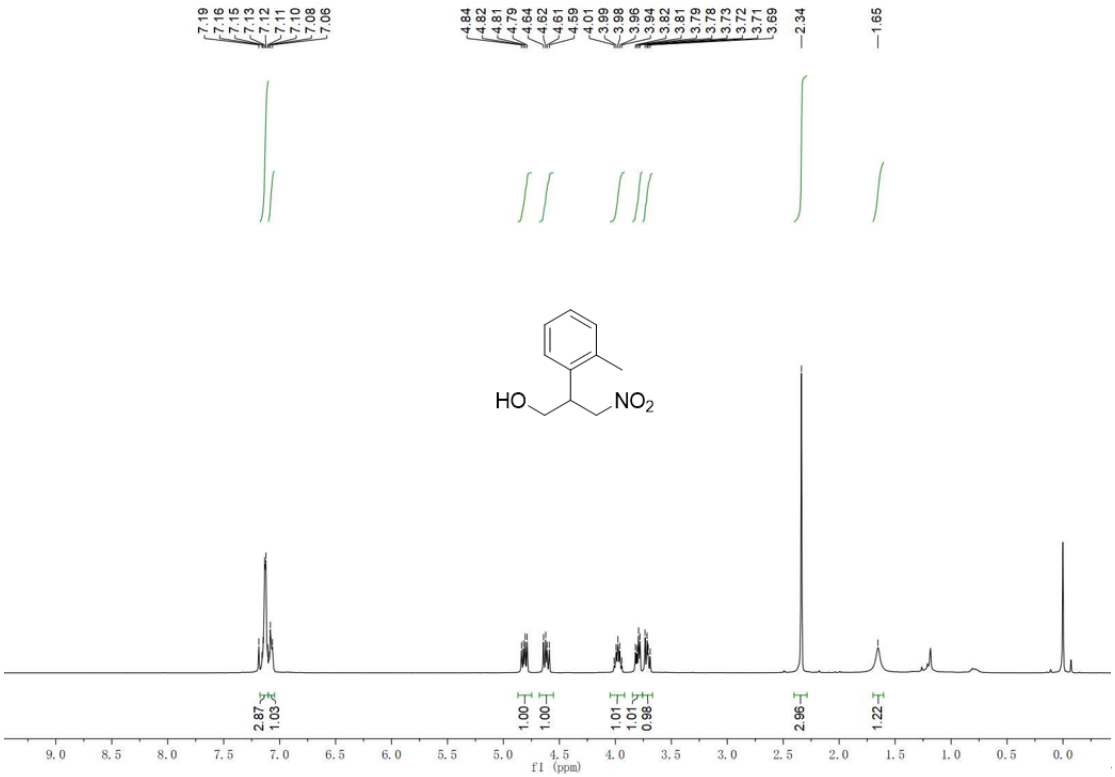
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



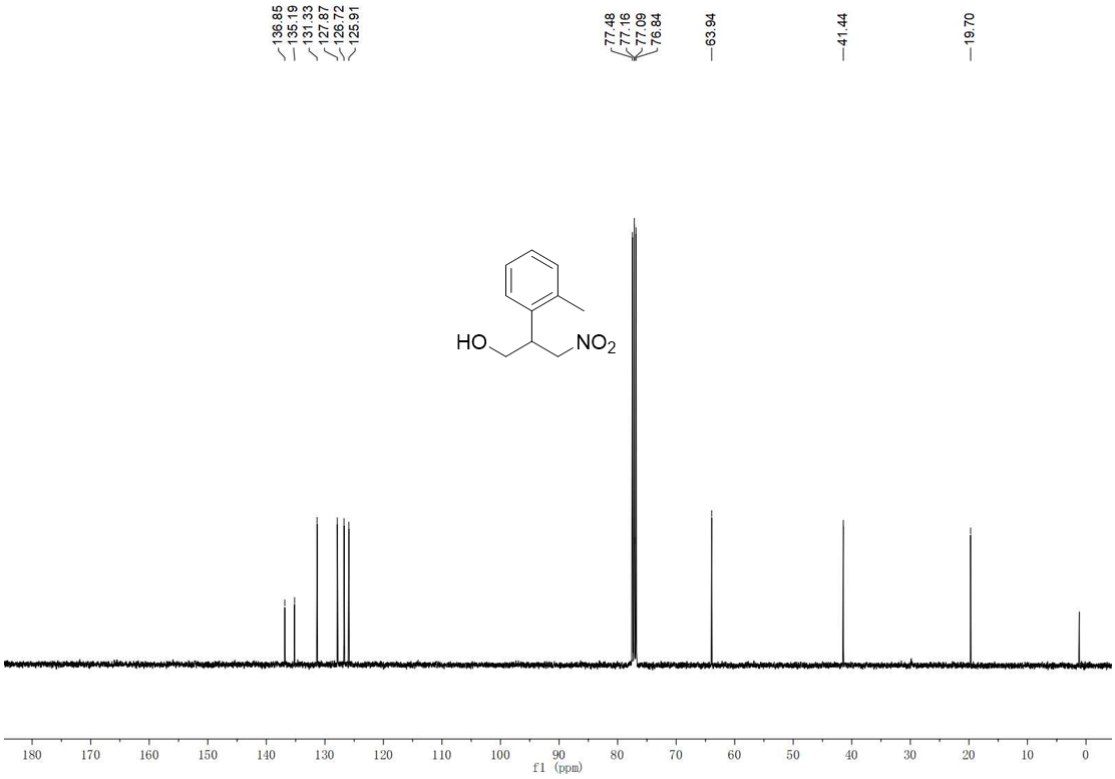
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



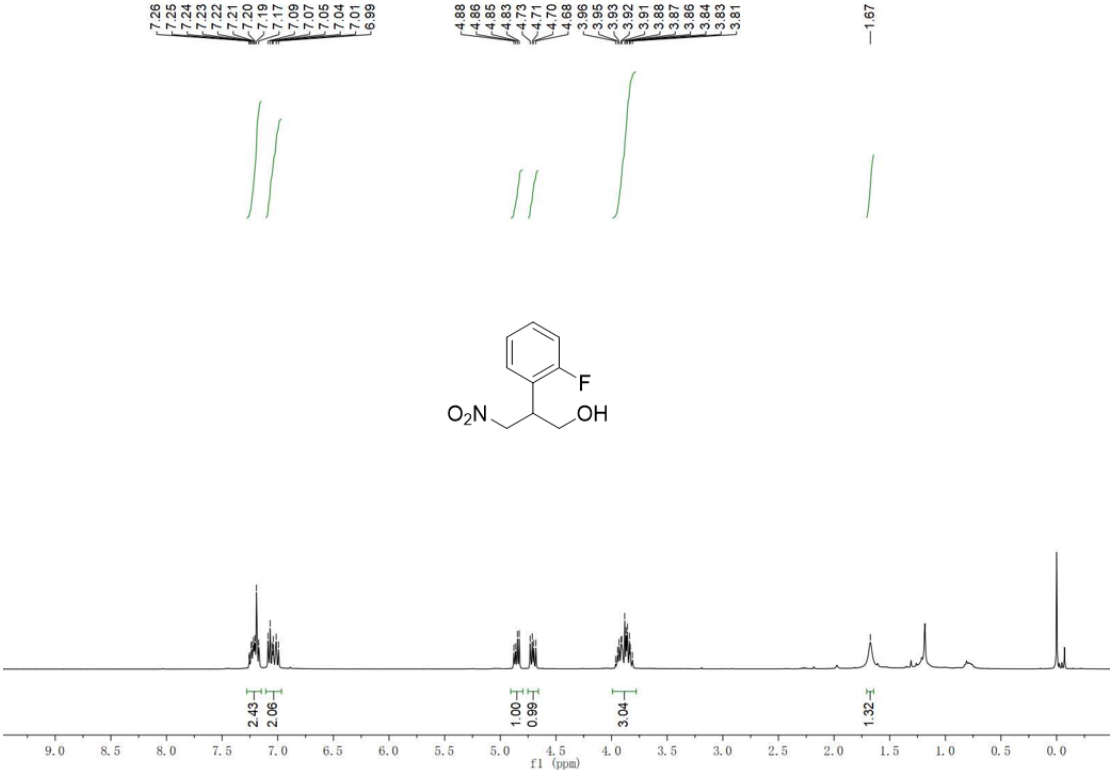
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



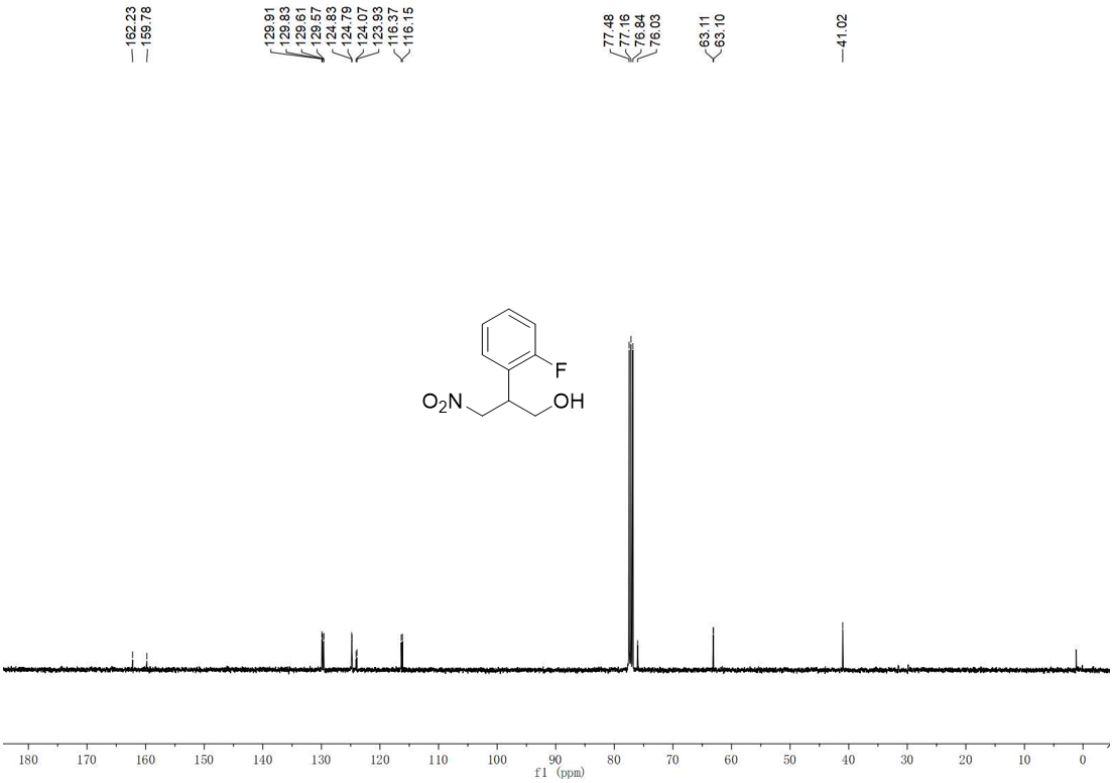
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



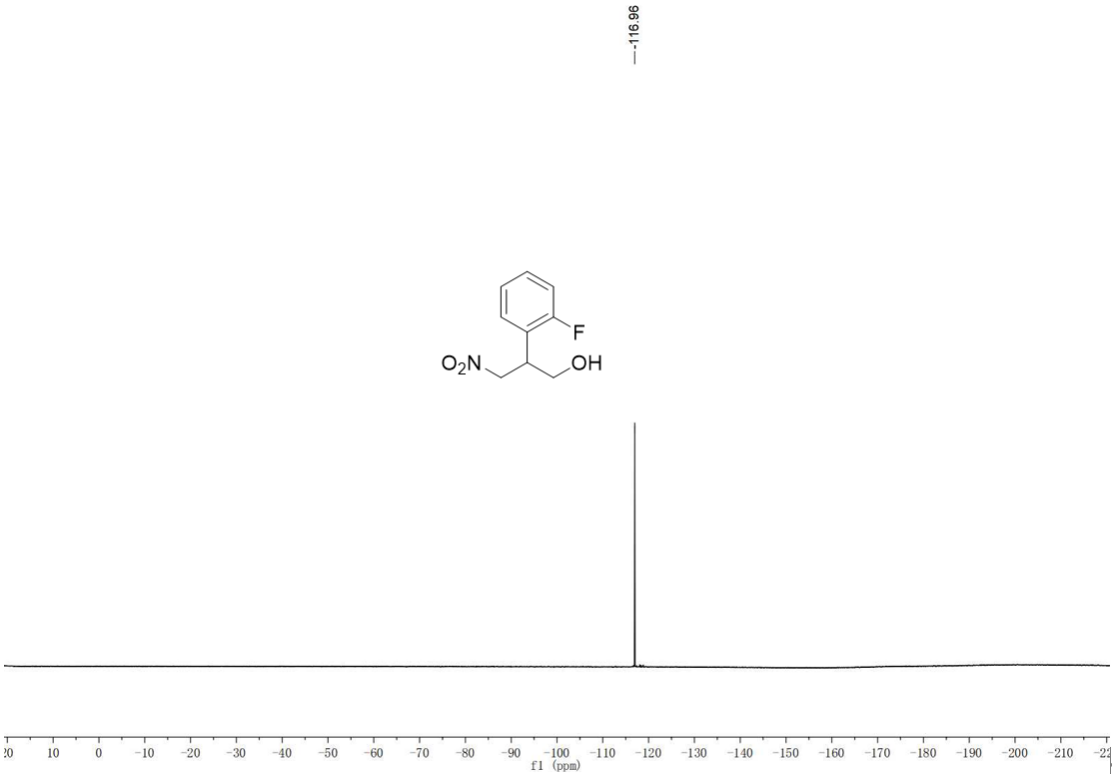
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



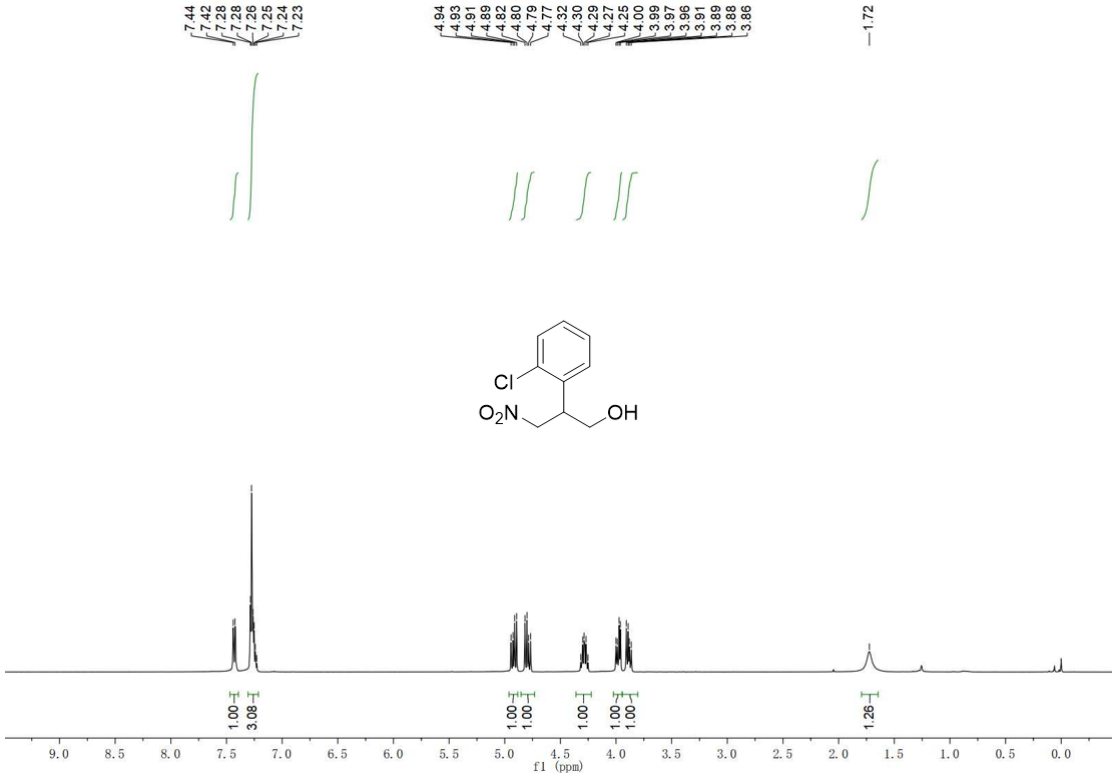
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



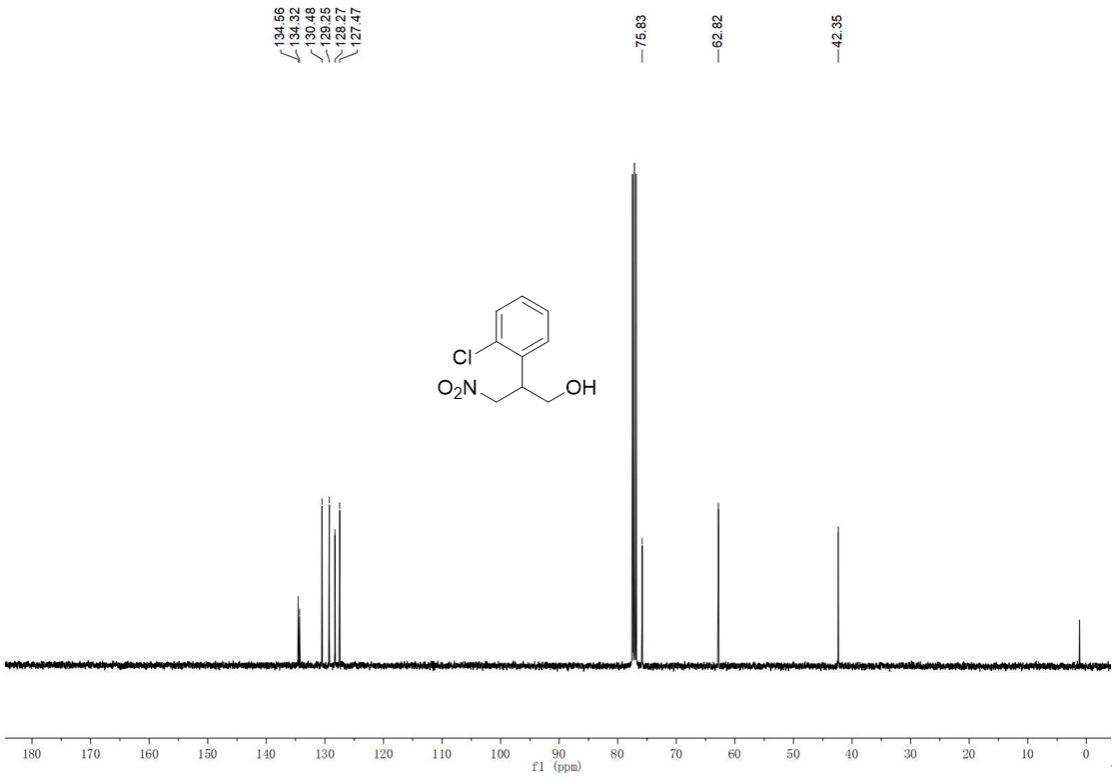
^{19}F NMR (376 MHz, CDCl3) of **3c**



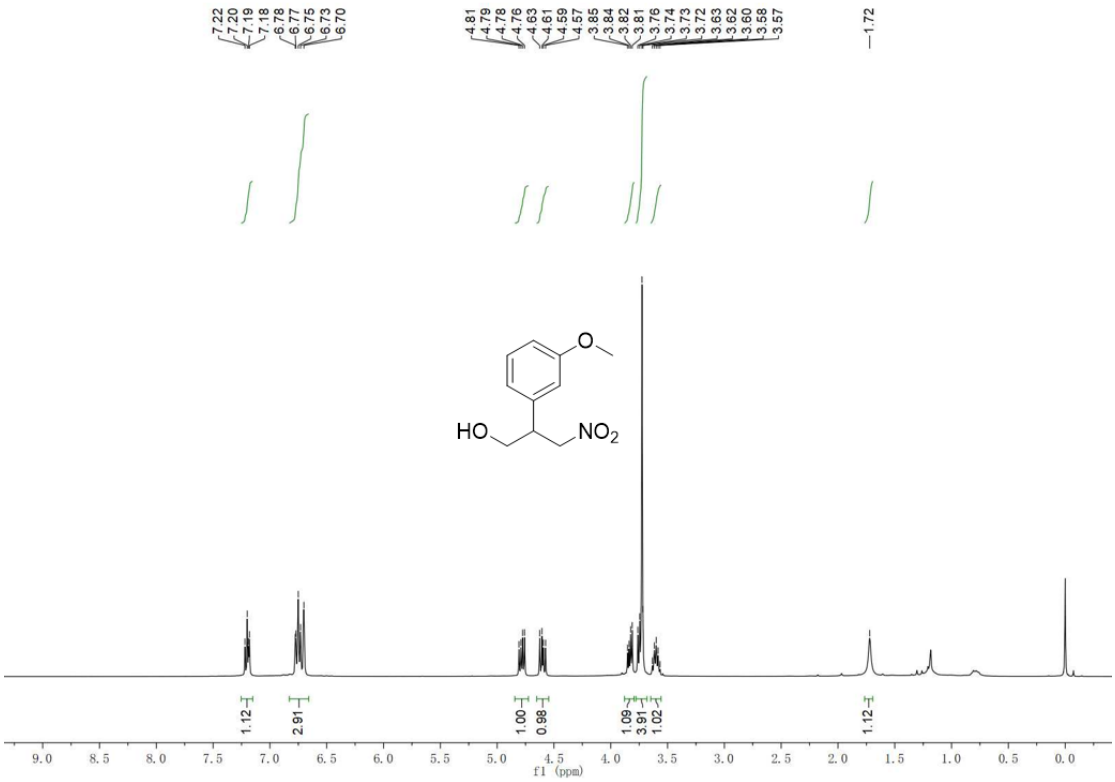
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



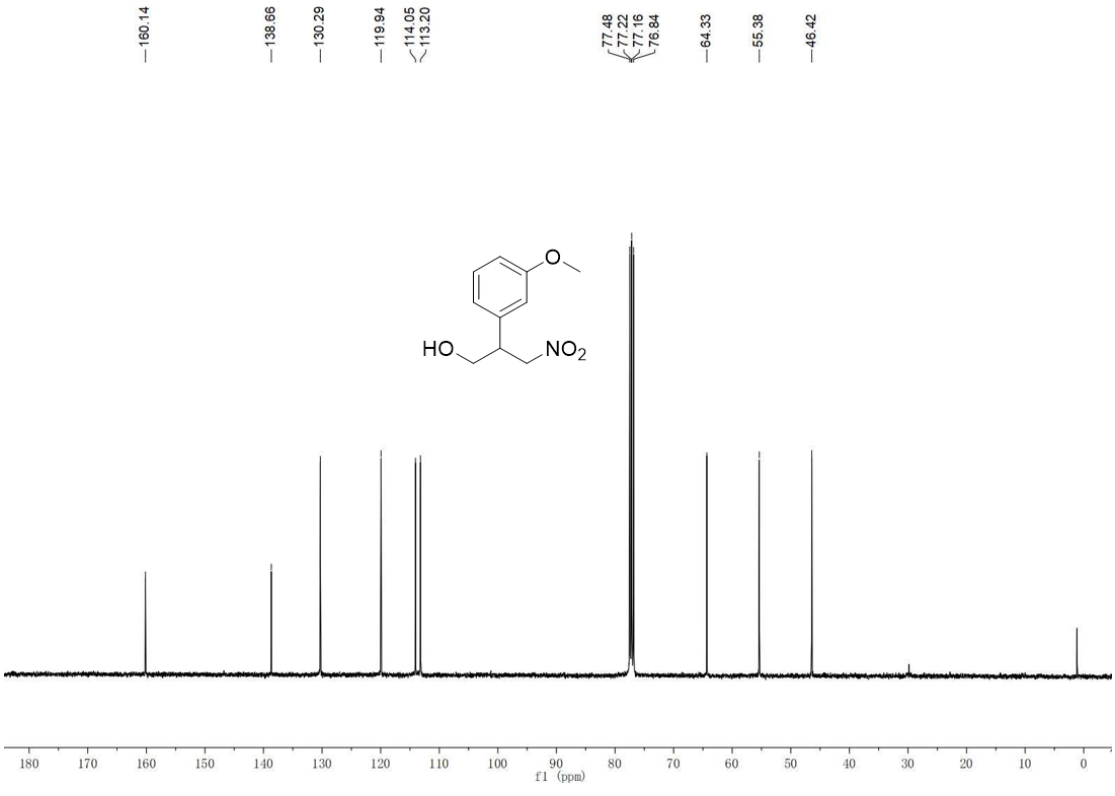
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



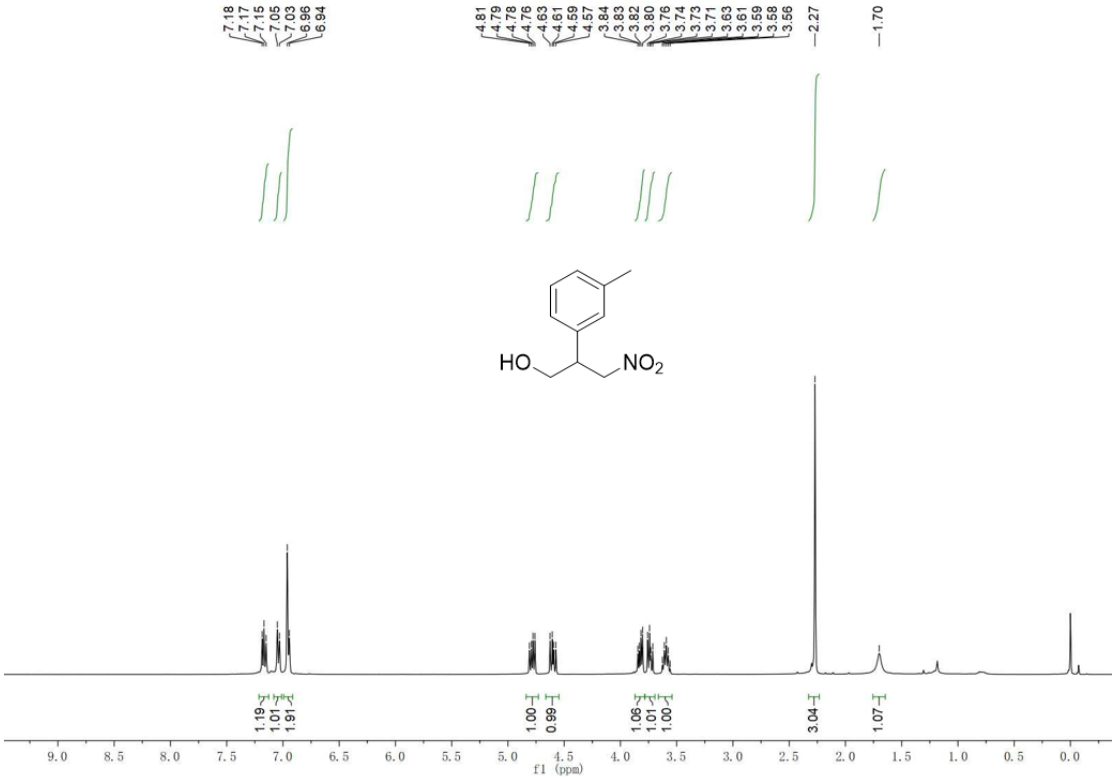
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



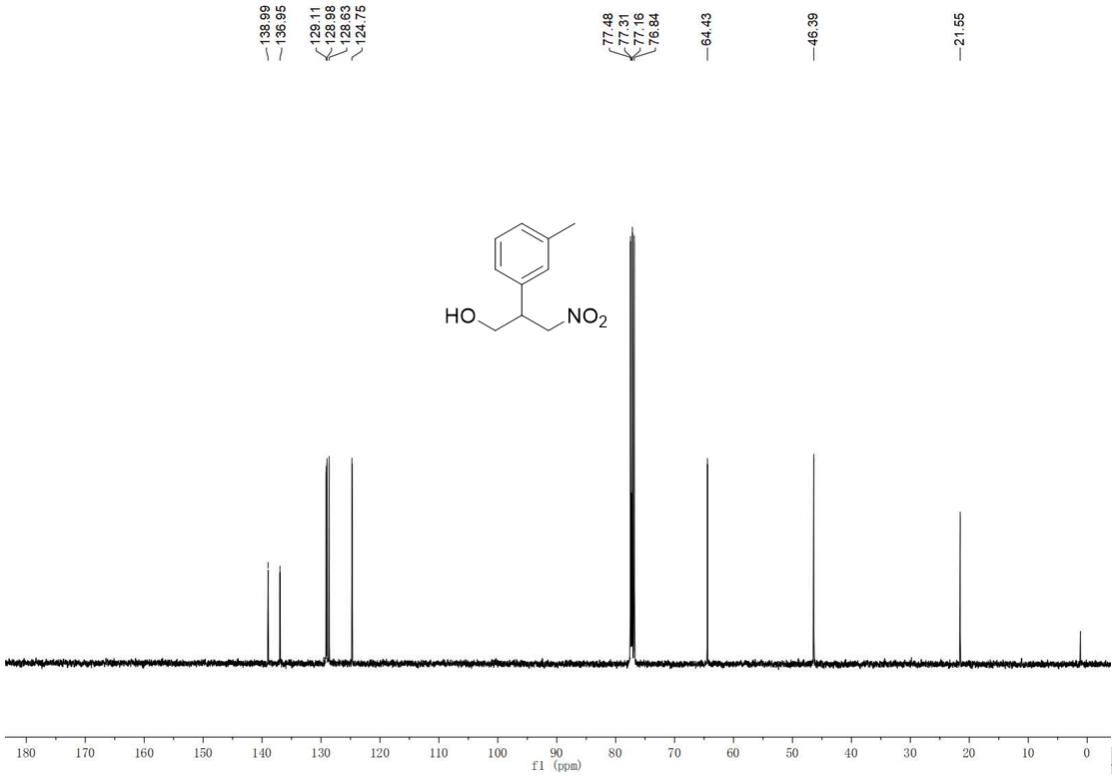
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



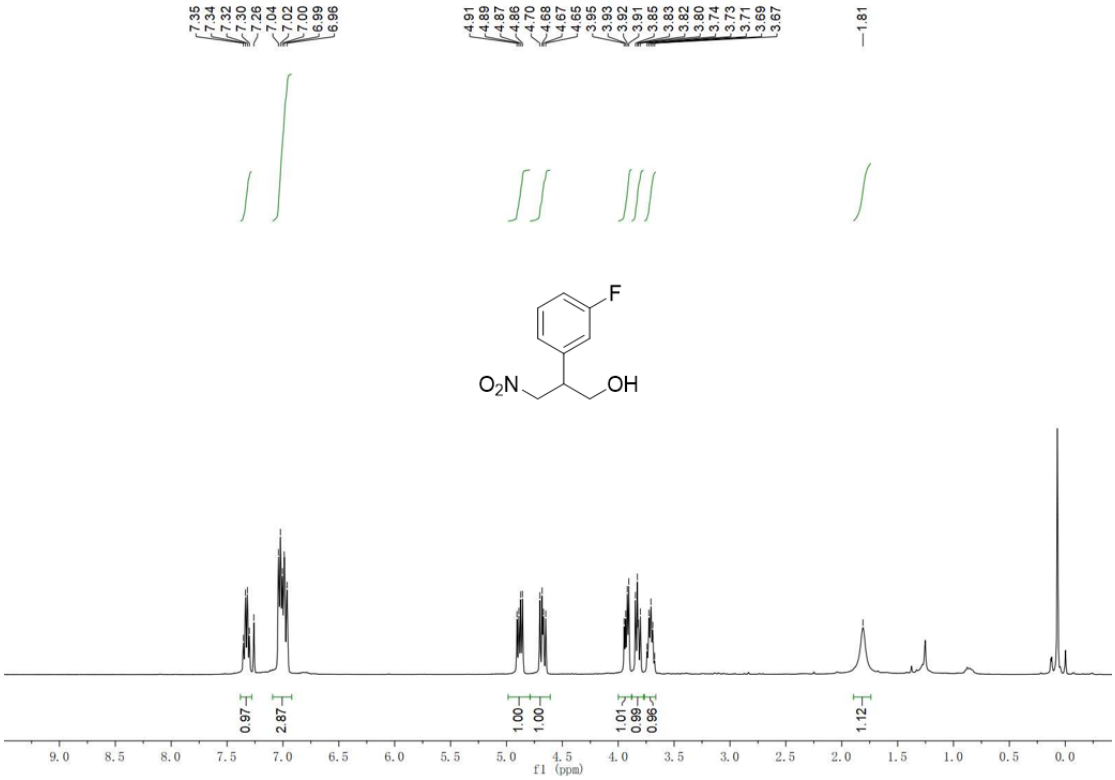
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



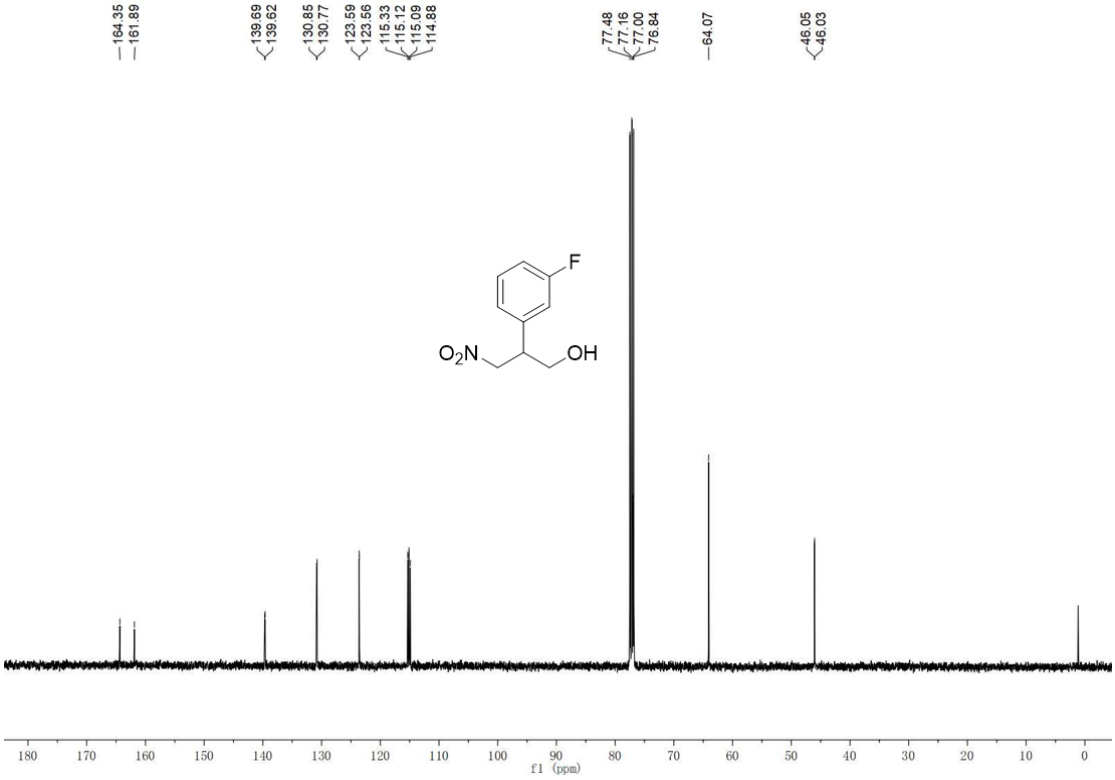
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



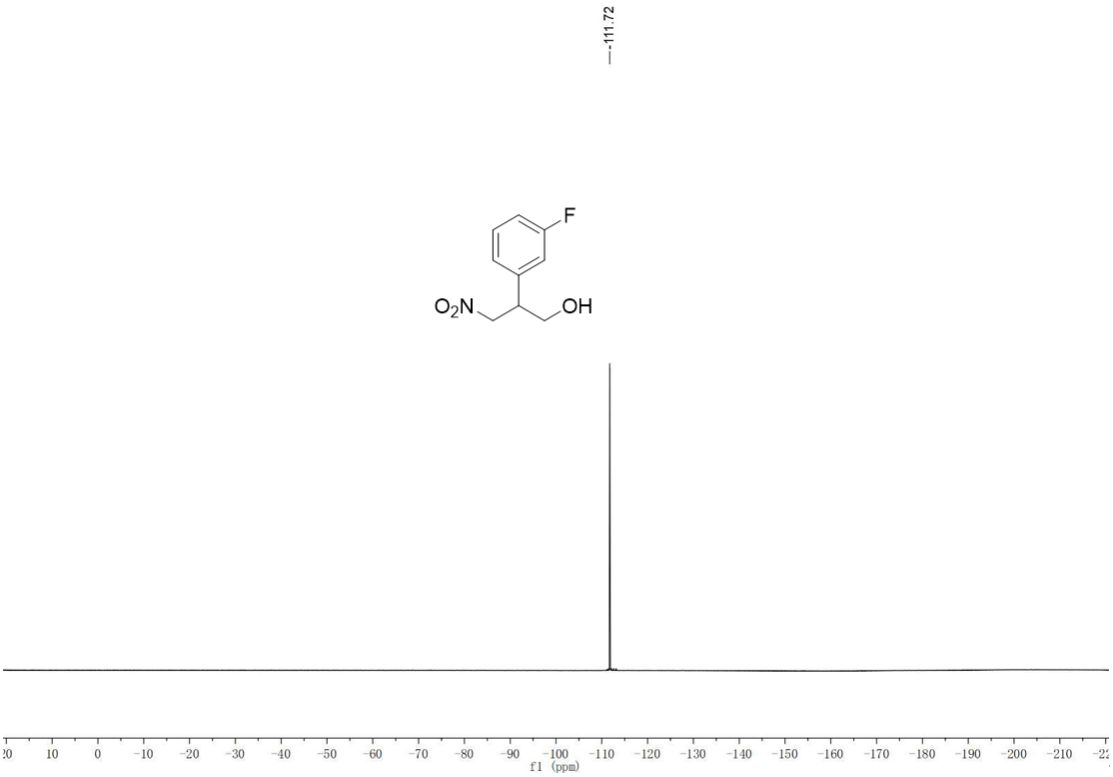
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



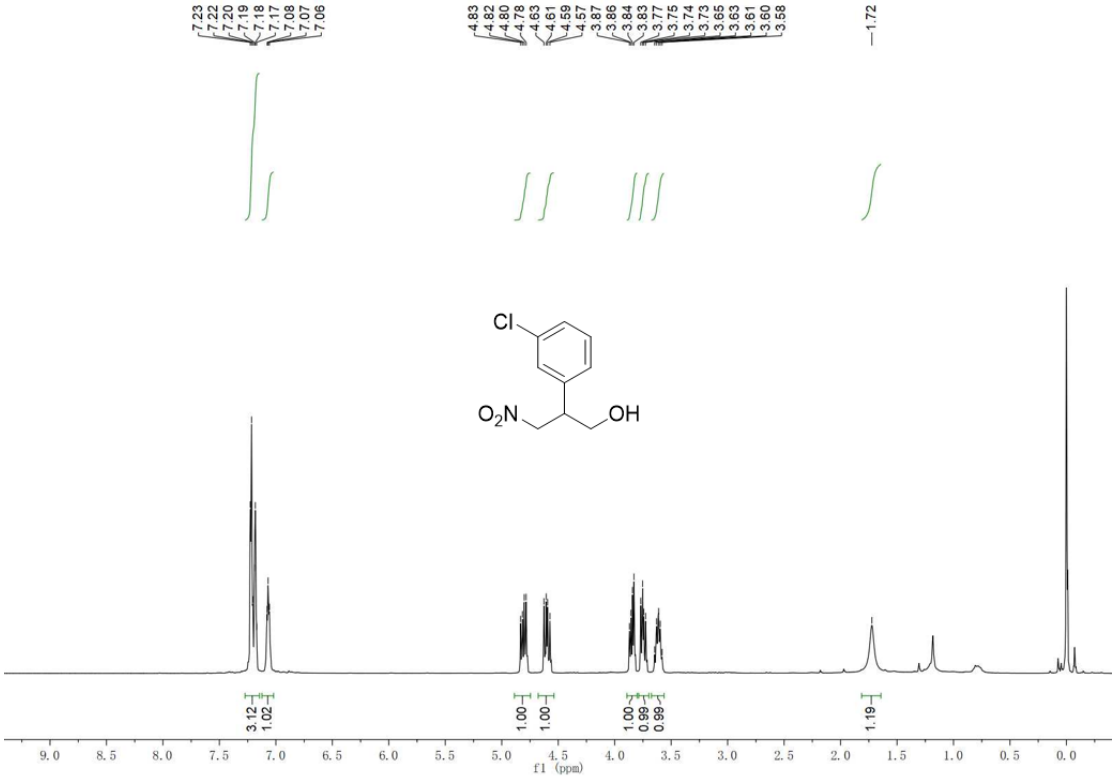
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



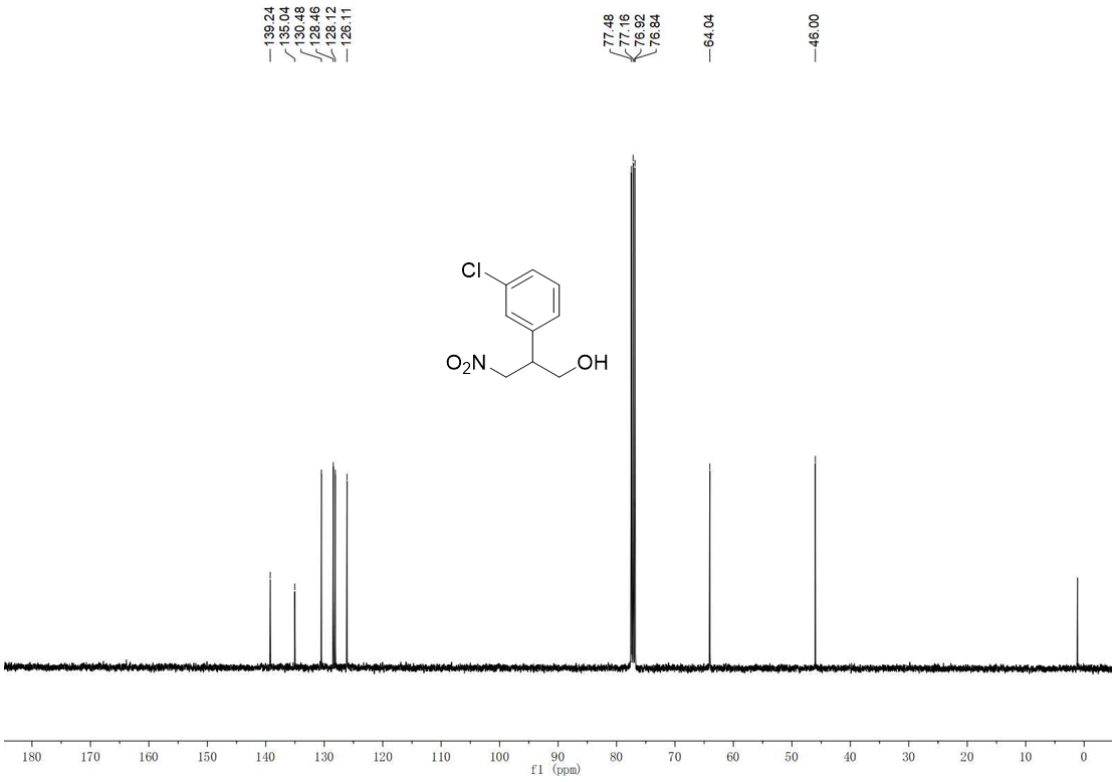
^{19}F NMR (376 MHz, CDCl3) of **3g**



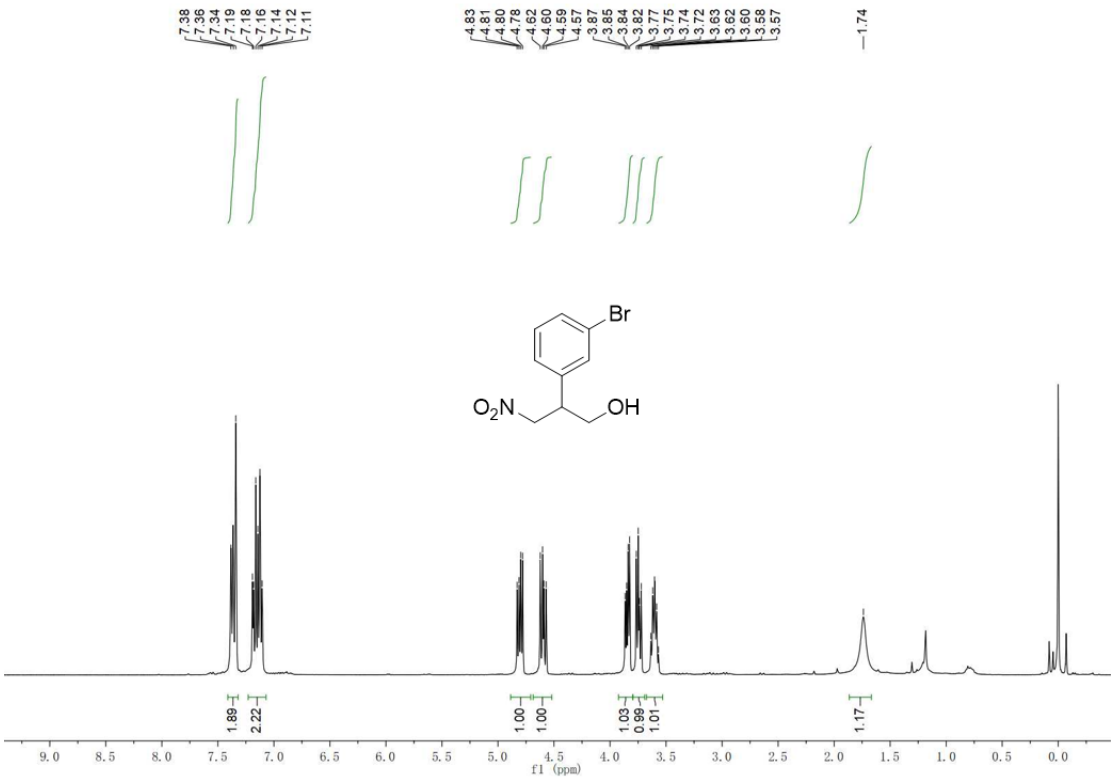
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



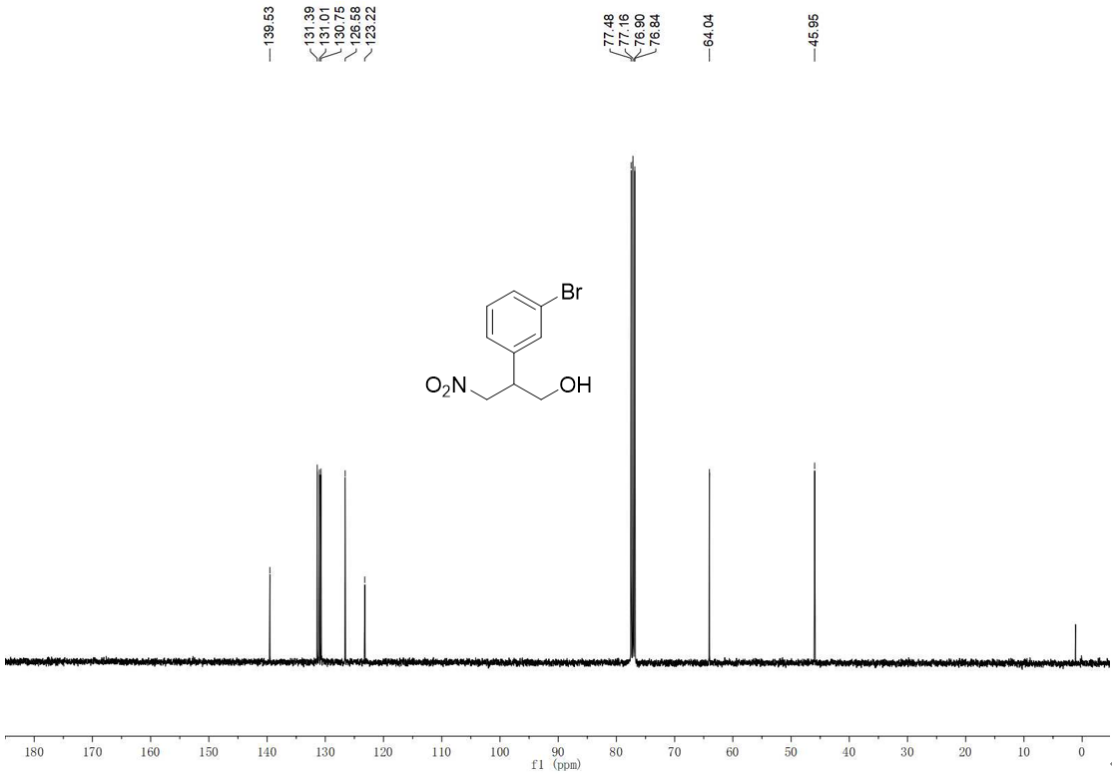
^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



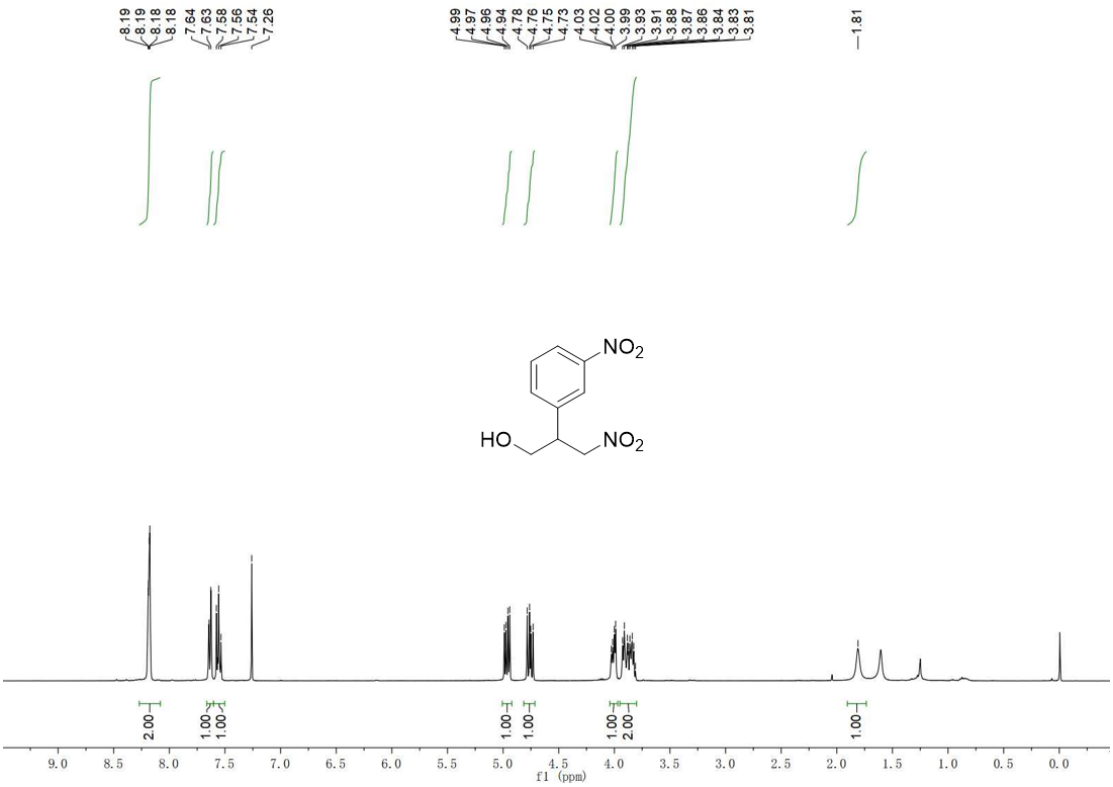
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



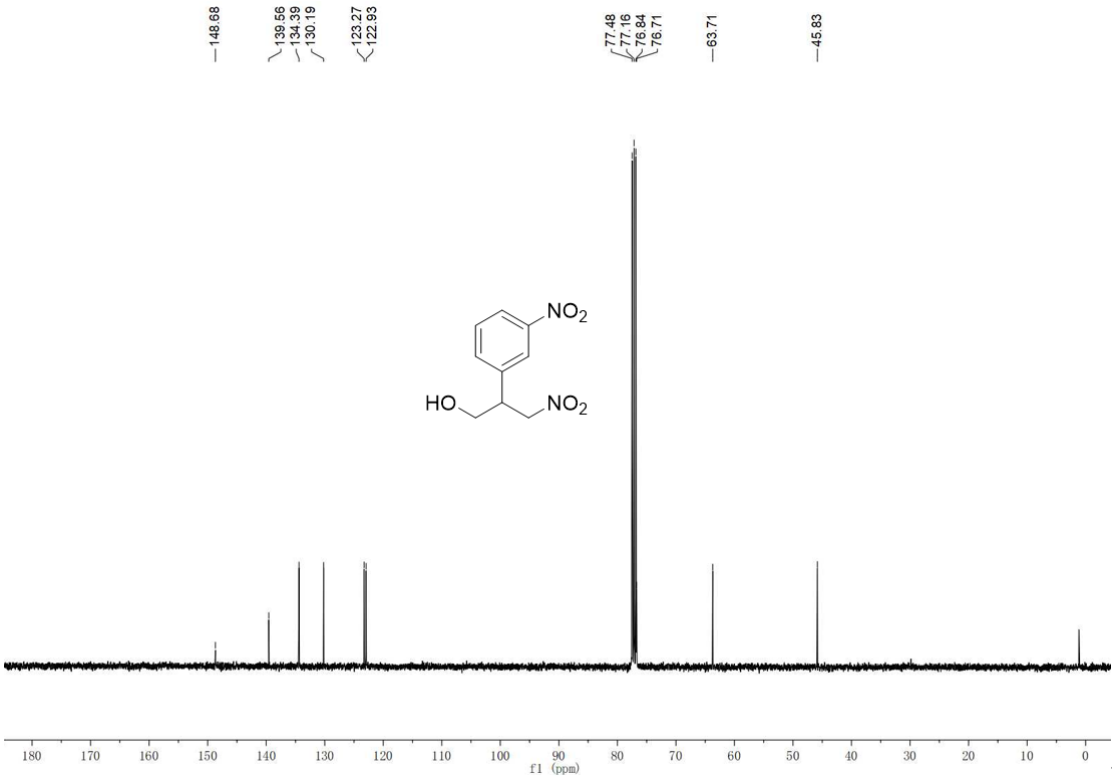
^{13}C NMR (101 MHz, $CDCl_3$) of **3i**



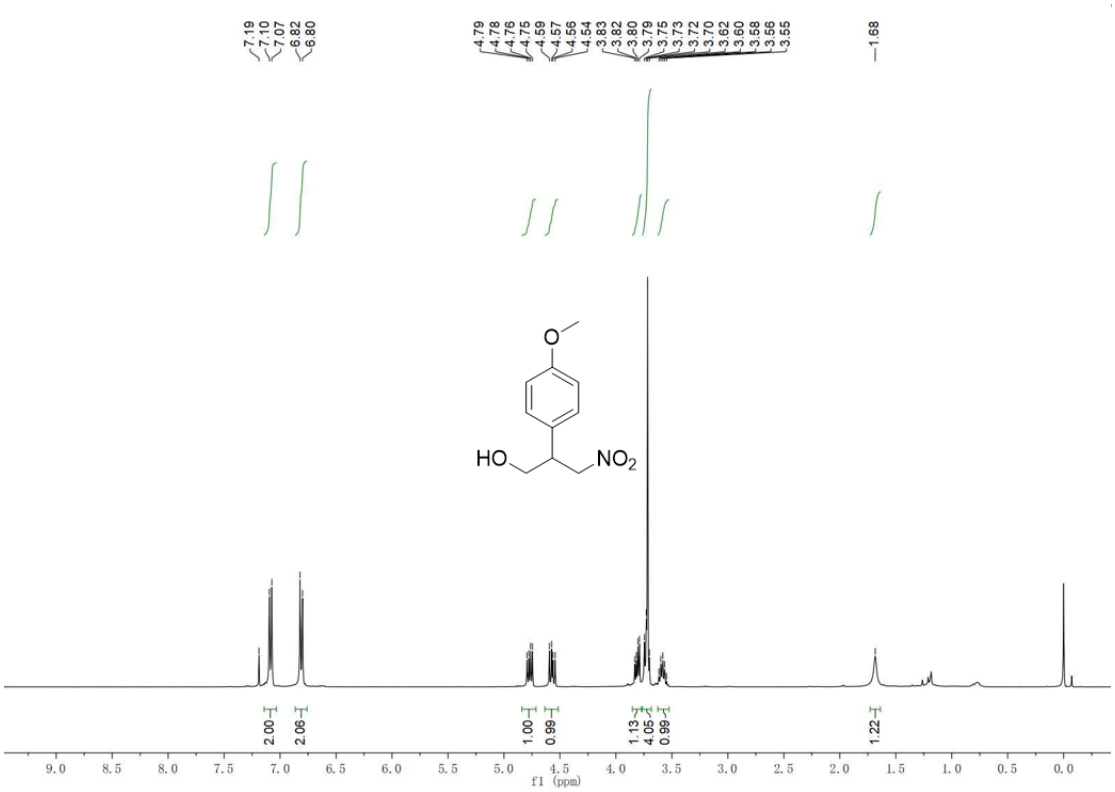
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



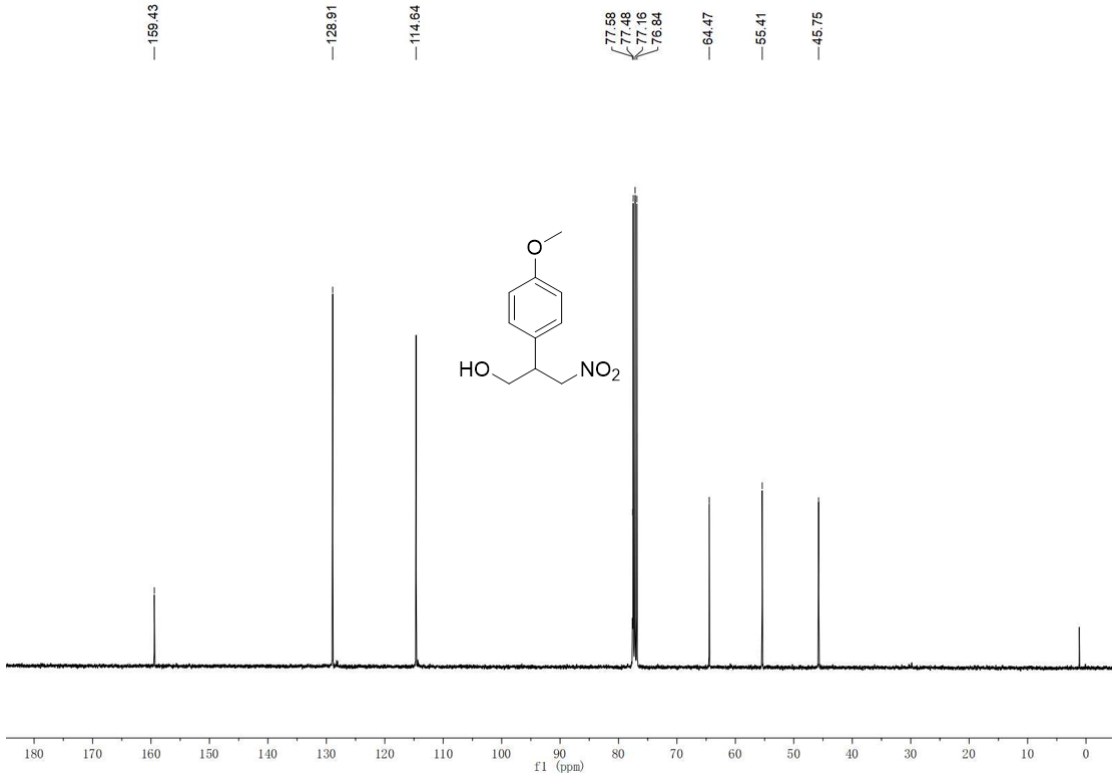
^{13}C NMR (101 MHz, $CDCl_3$) of **3j**



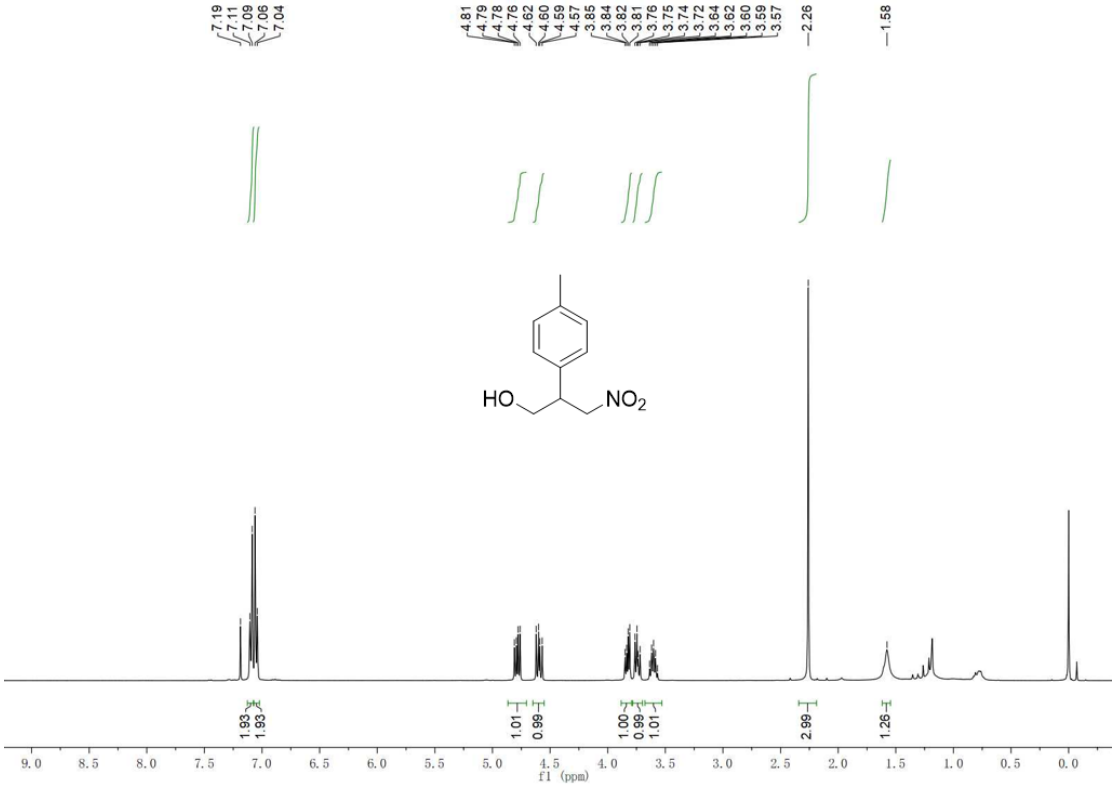
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



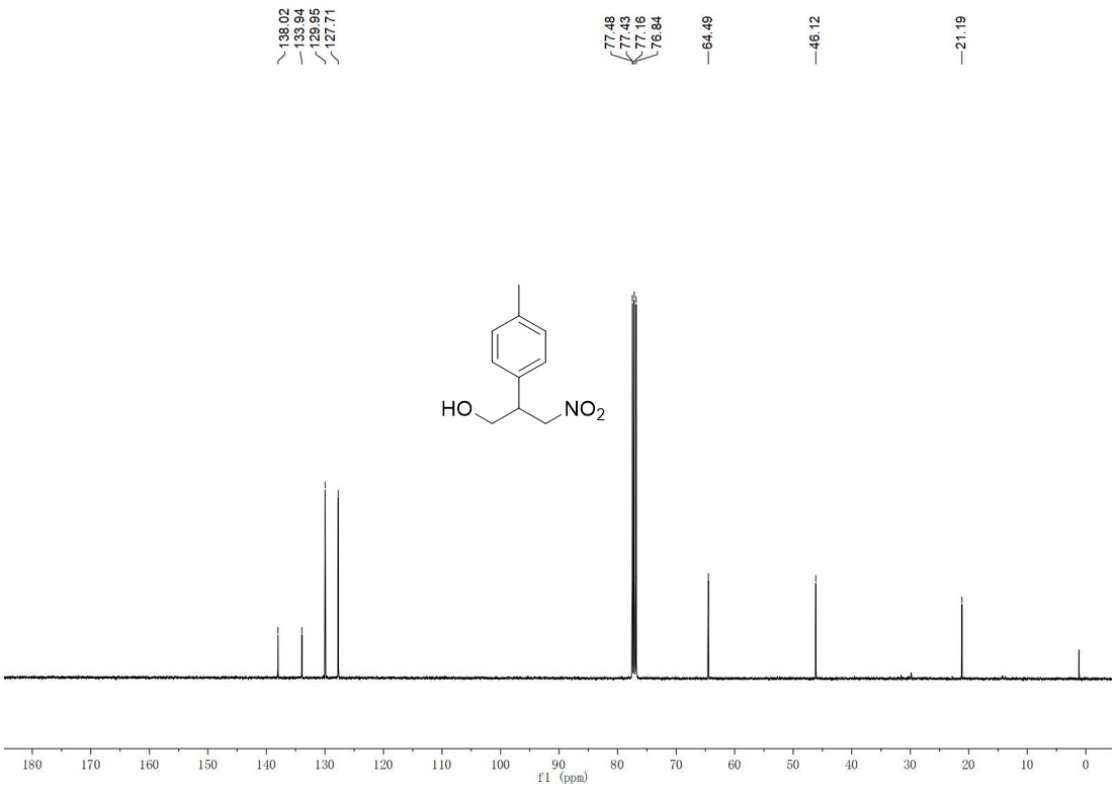
^{13}C NMR (101 MHz, $CDCl_3$) of **3k**



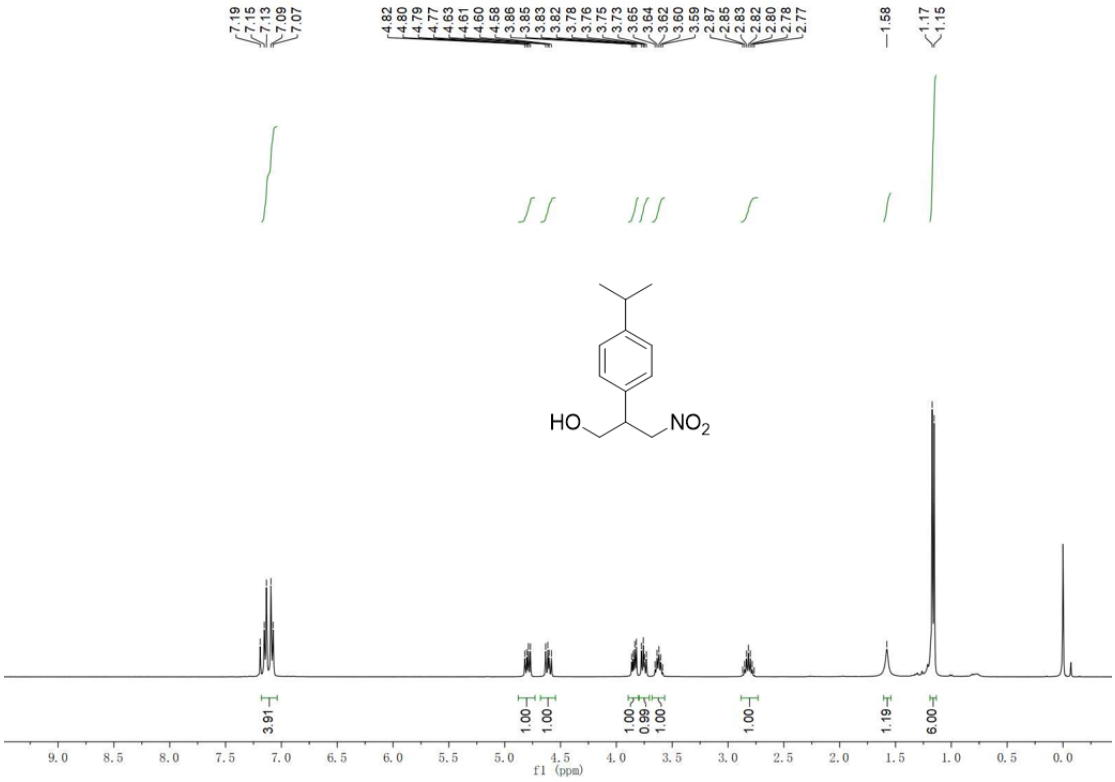
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



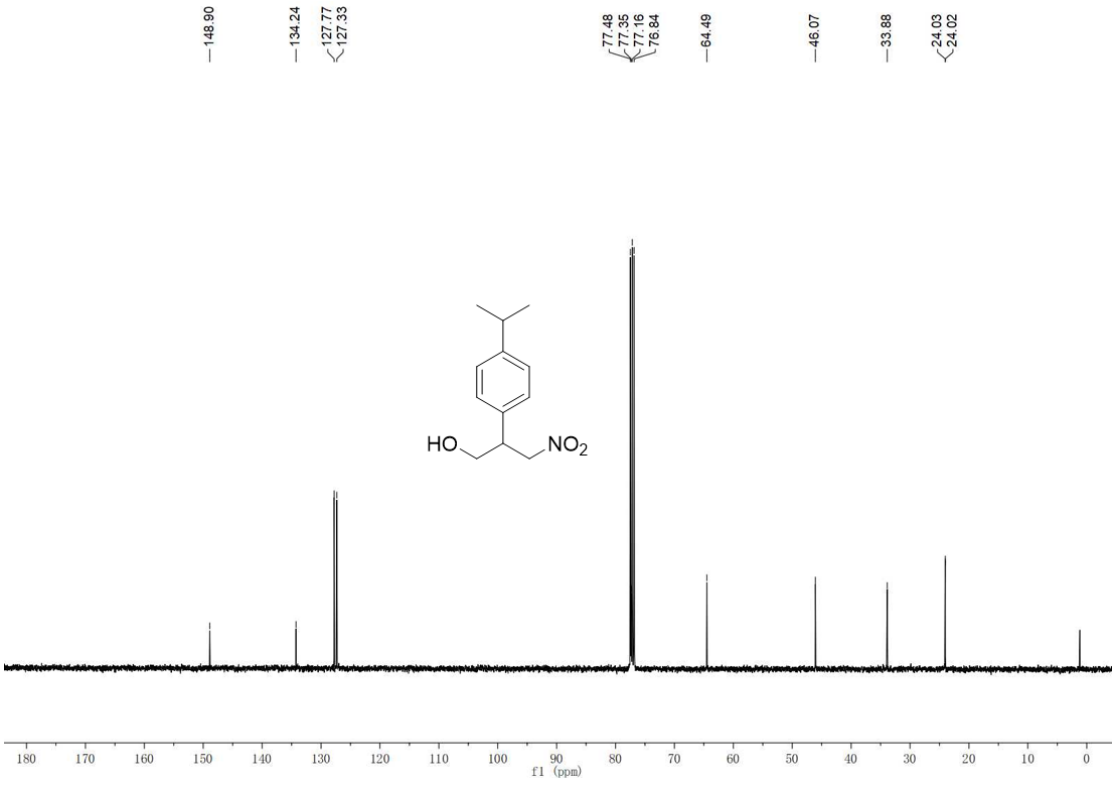
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



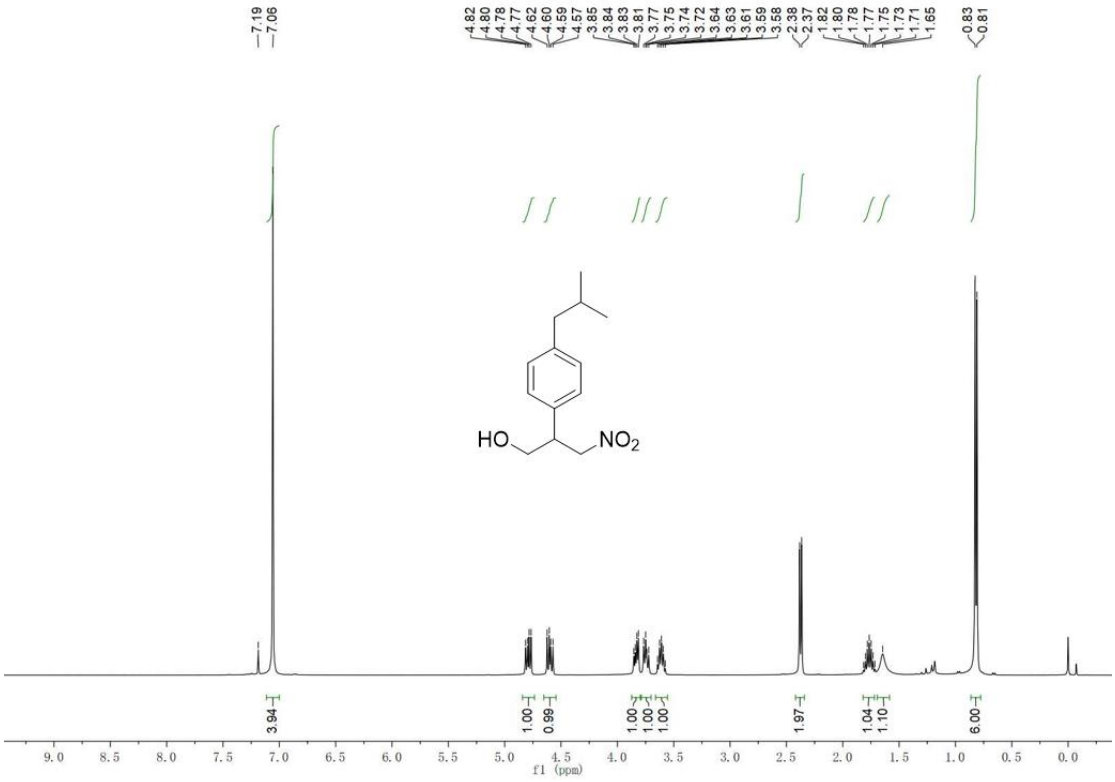
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



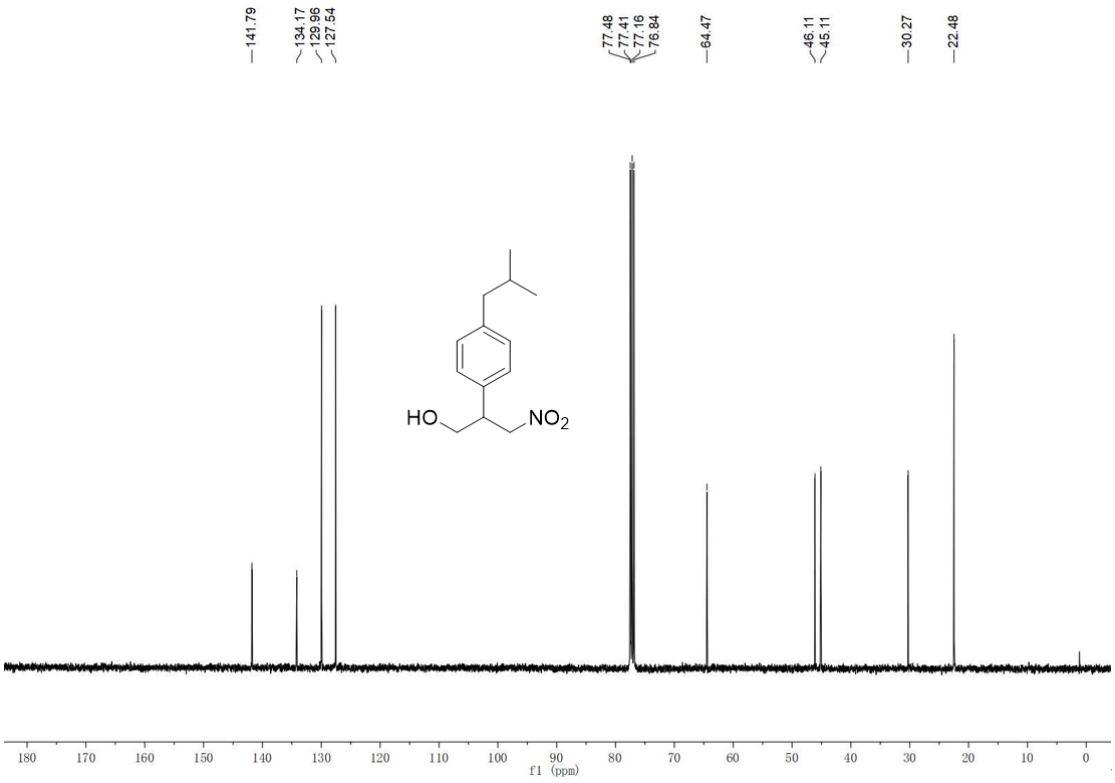
^{13}C NMR (101 MHz, $CDCl_3$) of **3m**



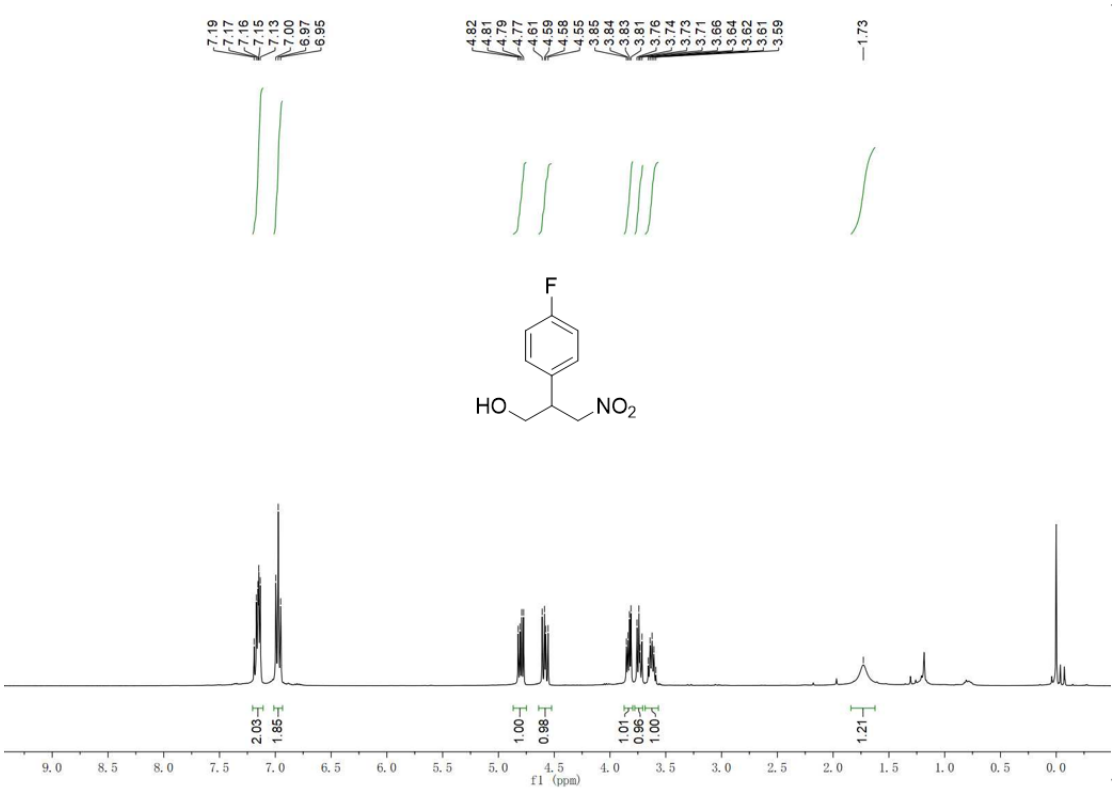
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



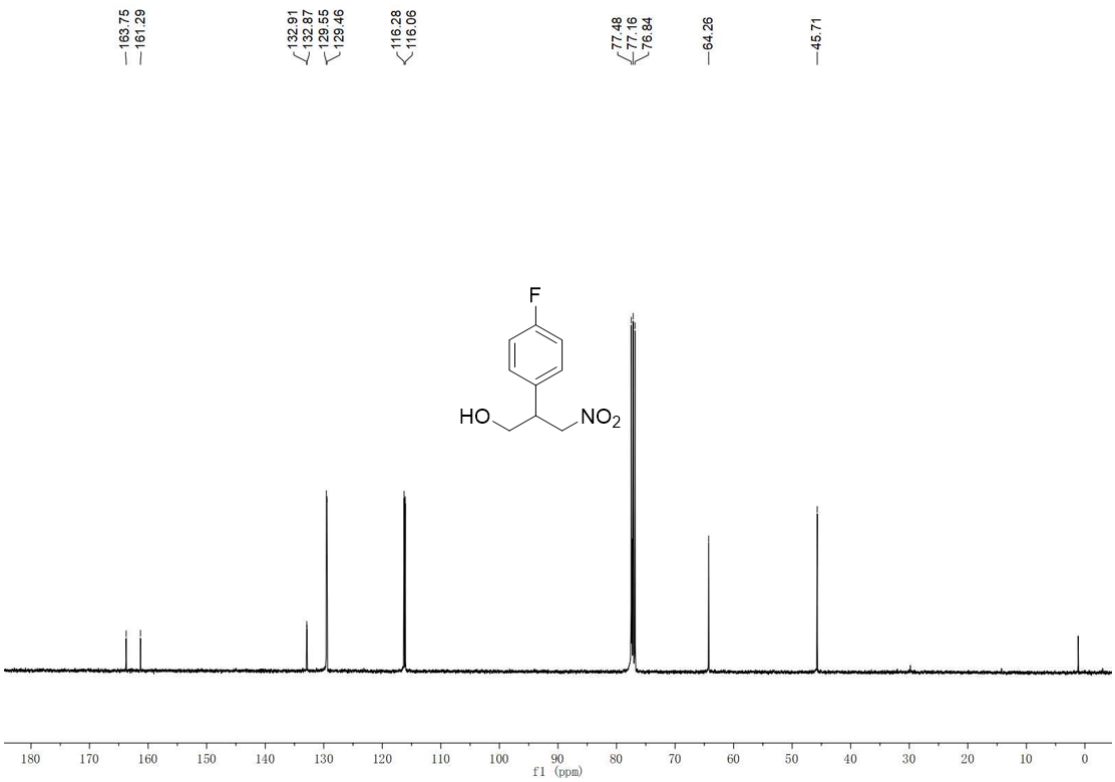
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



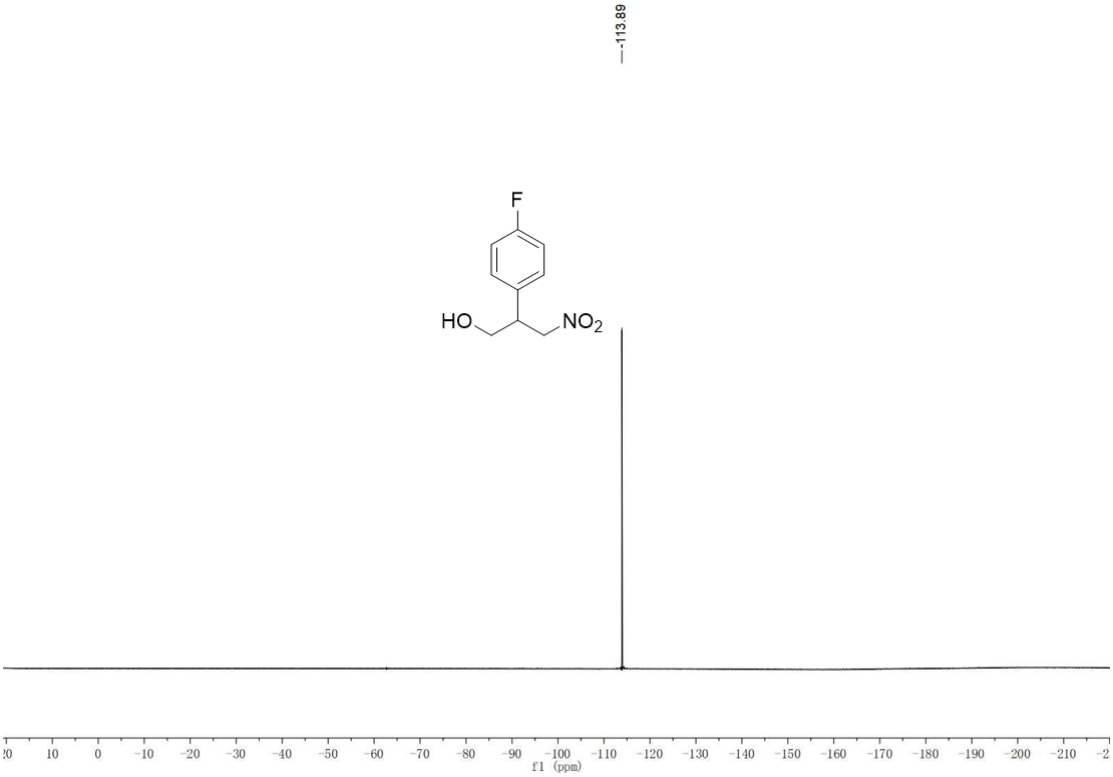
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



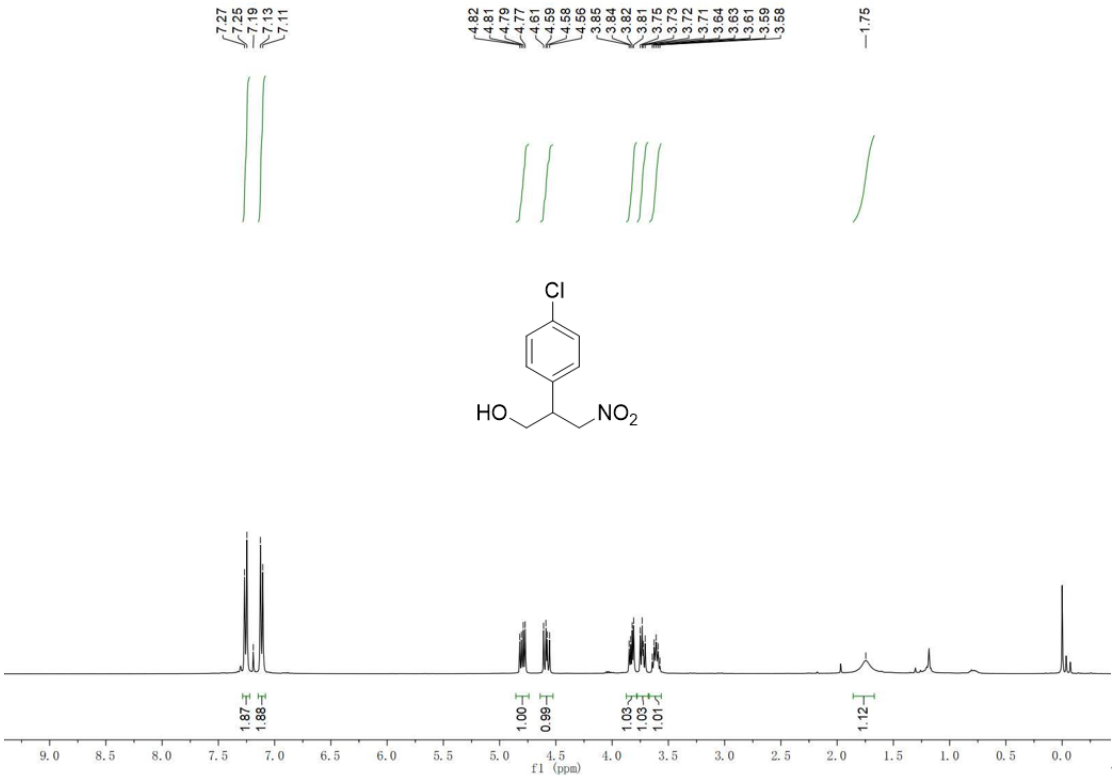
^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



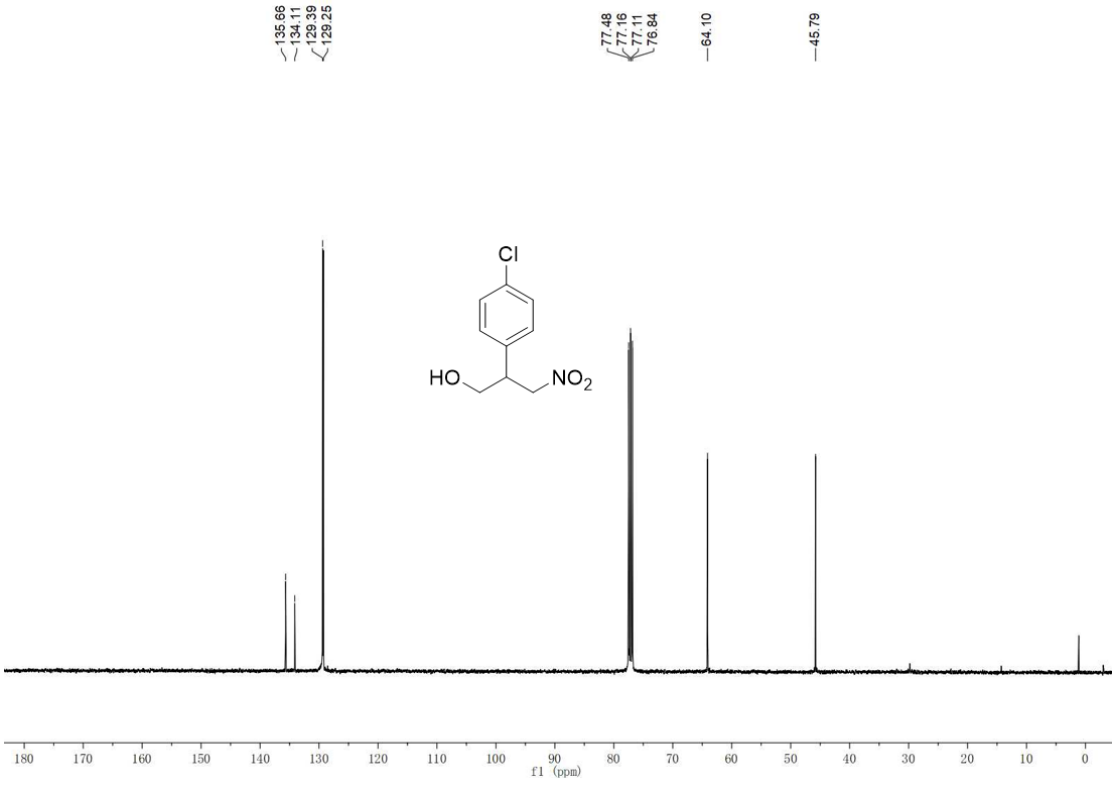
^{19}F NMR (376 MHz, CDCl3) of **3o**



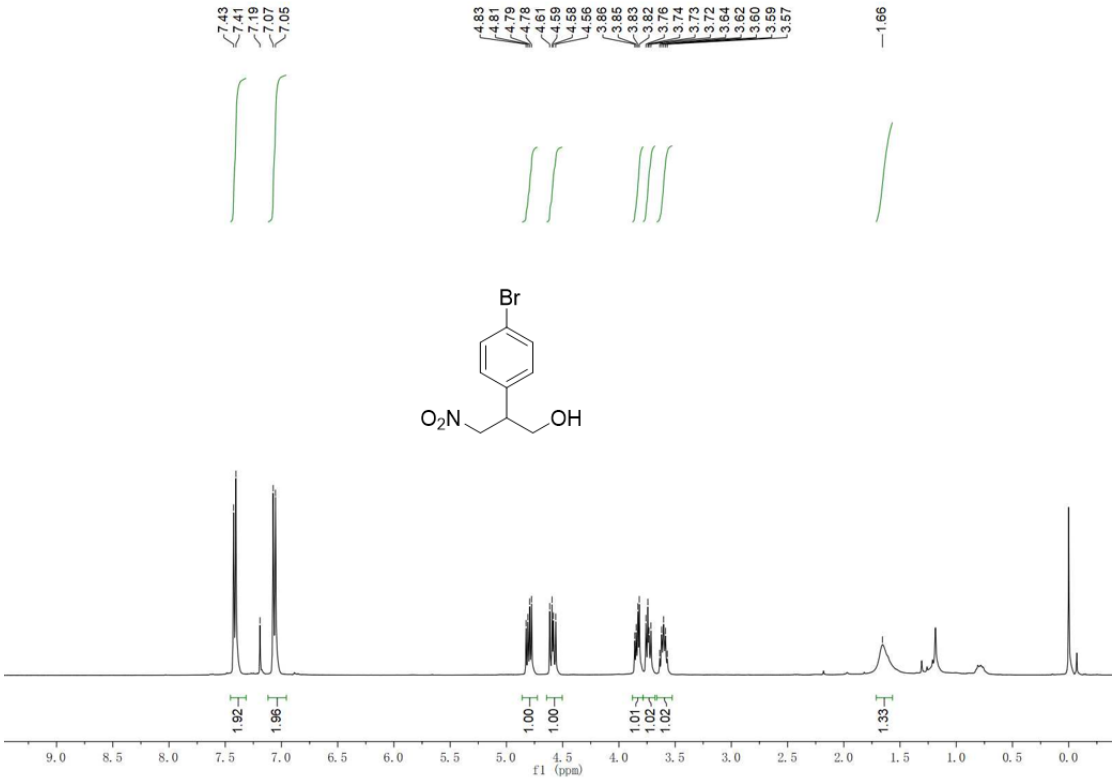
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



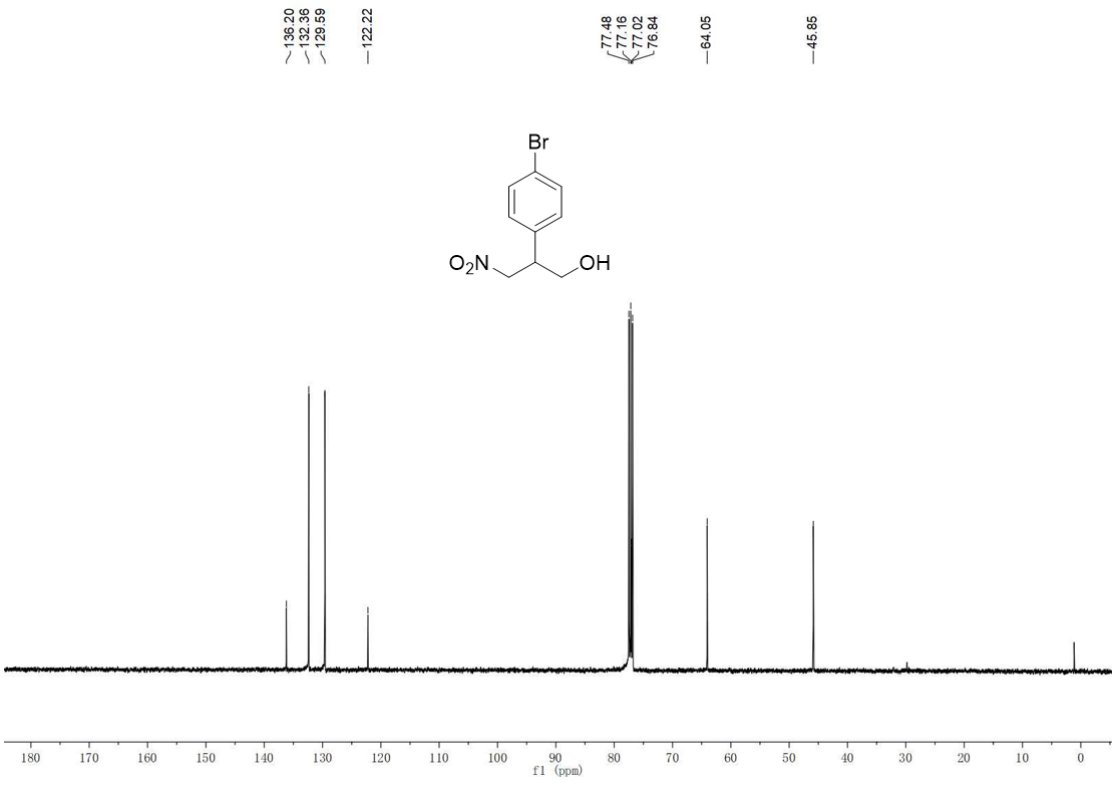
^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



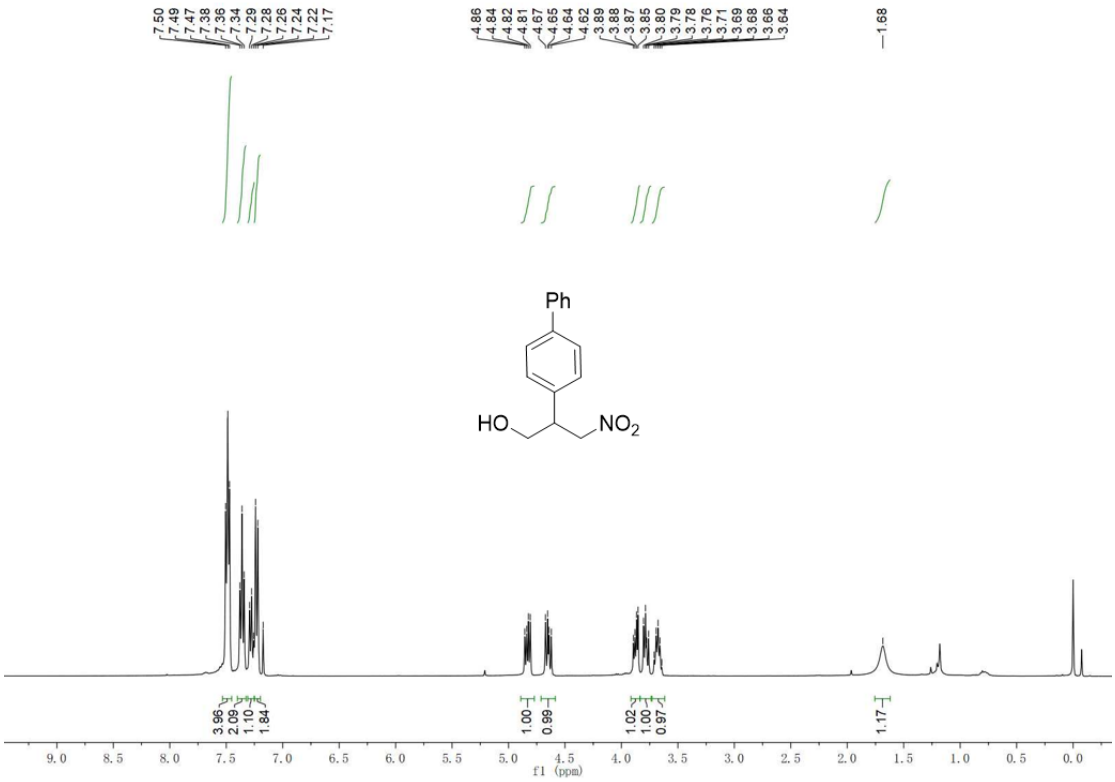
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



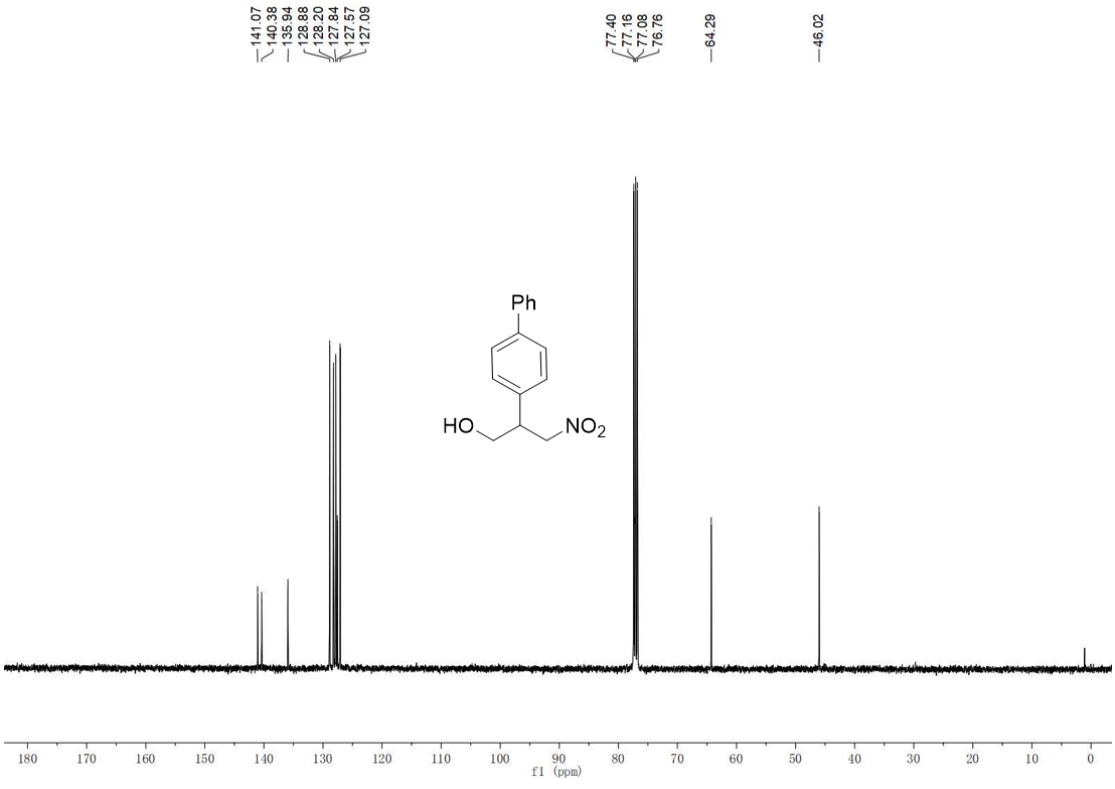
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



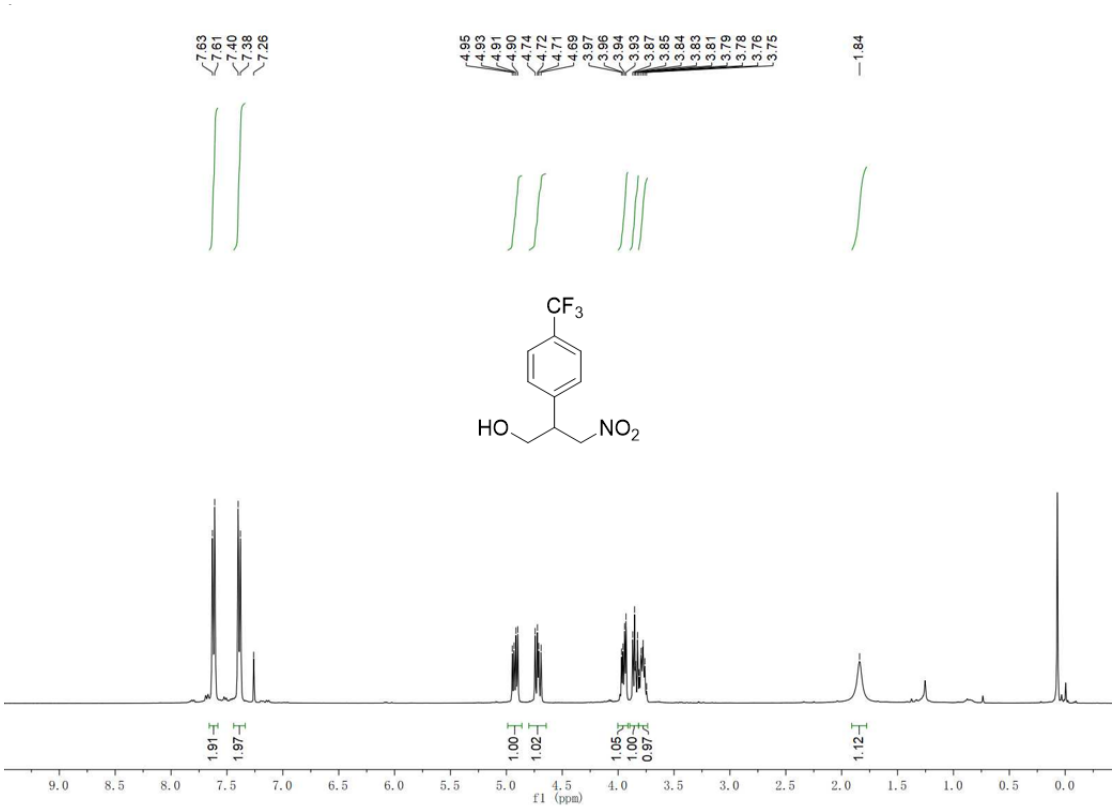
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



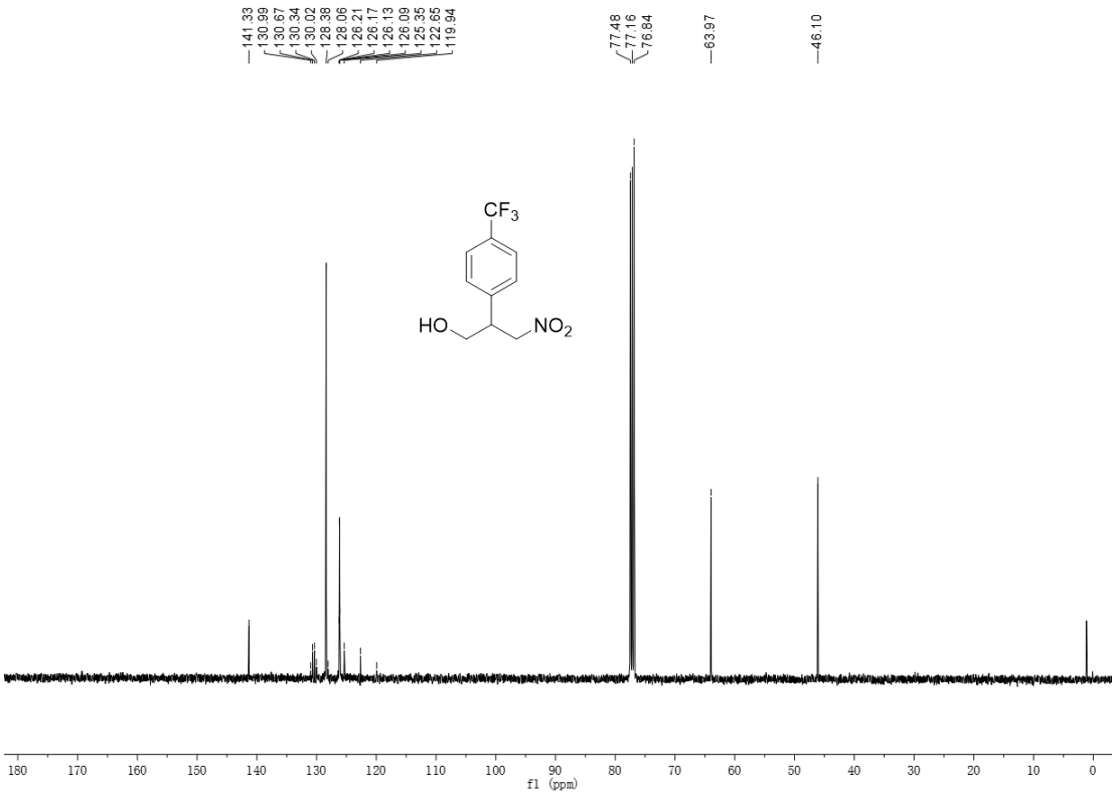
^{13}C NMR (101 MHz, $CDCl_3$) of **3r**



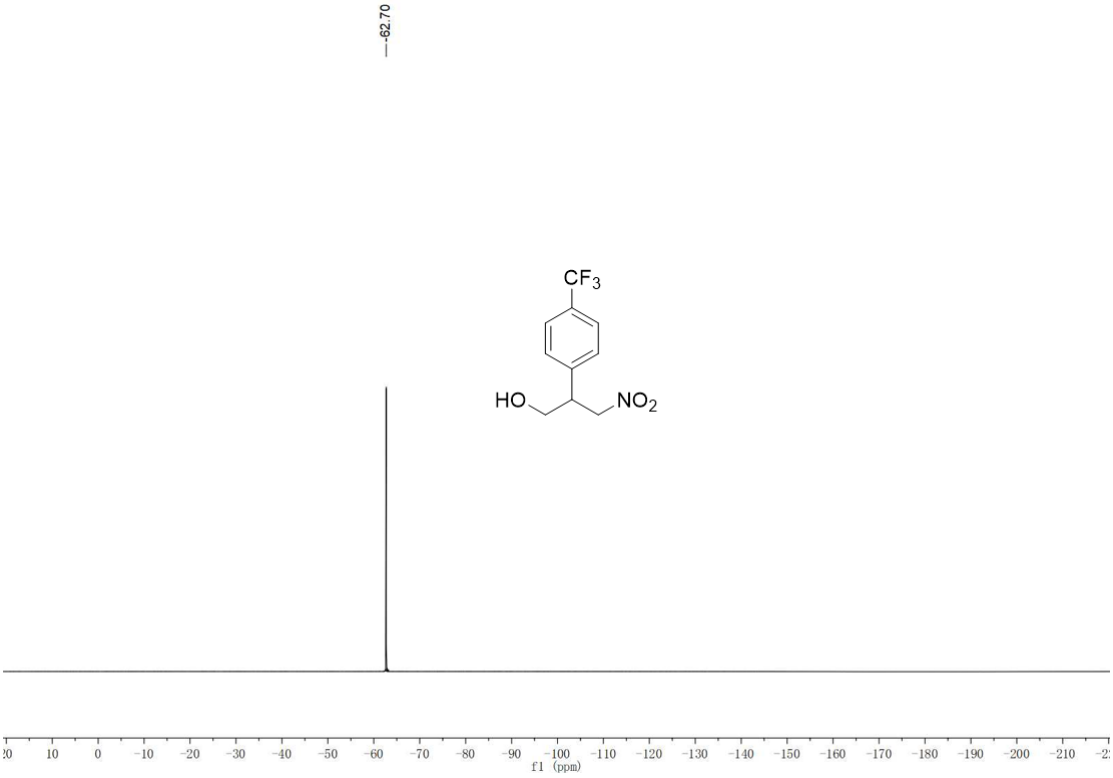
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



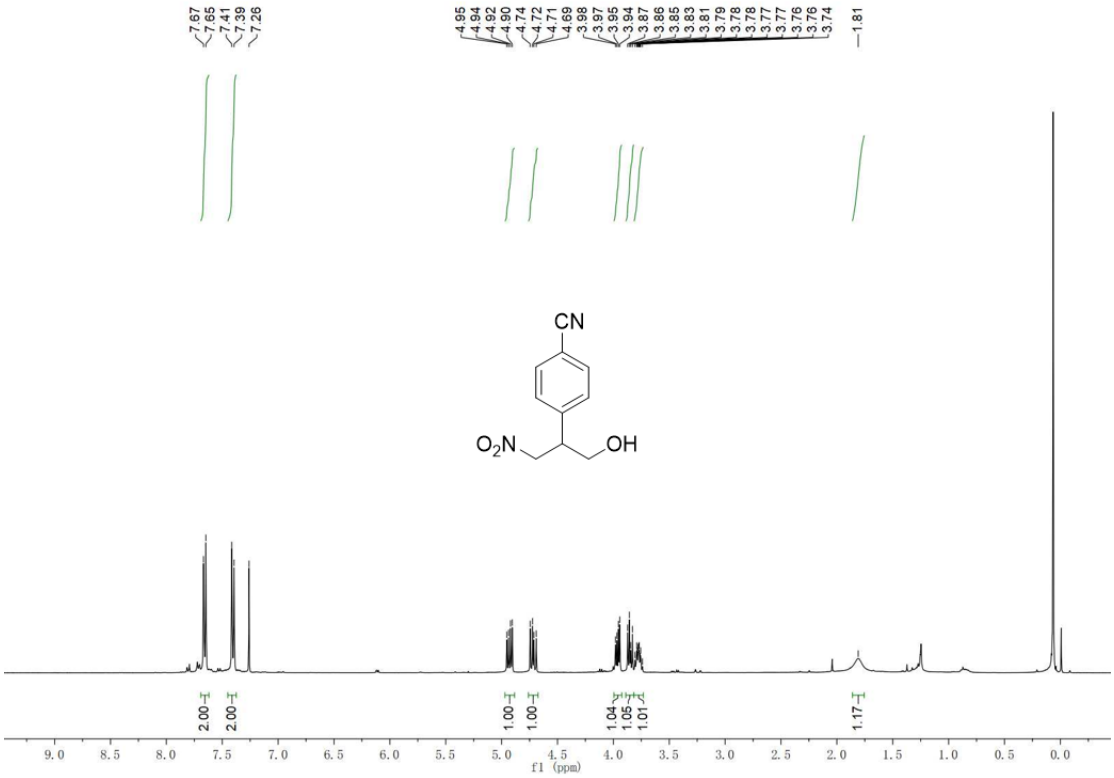
^{13}C NMR (101 MHz, $CDCl_3$) of **3s**



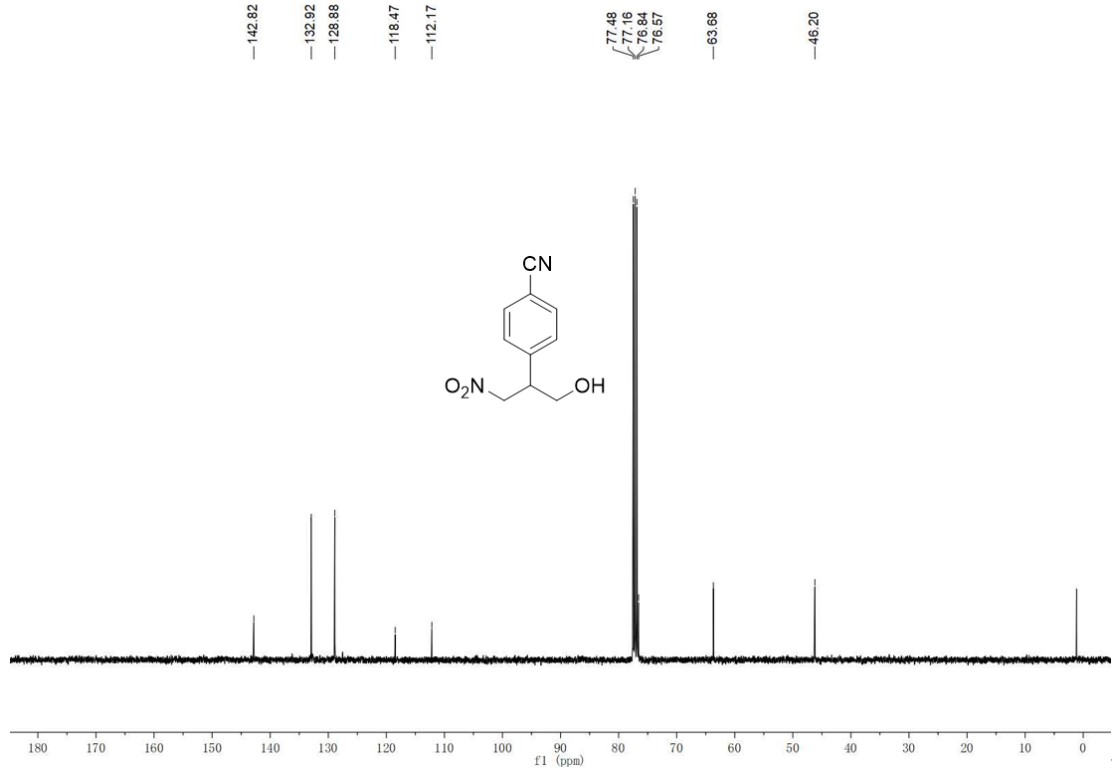
^{19}F NMR (376 MHz, CDCl3) of **3s**



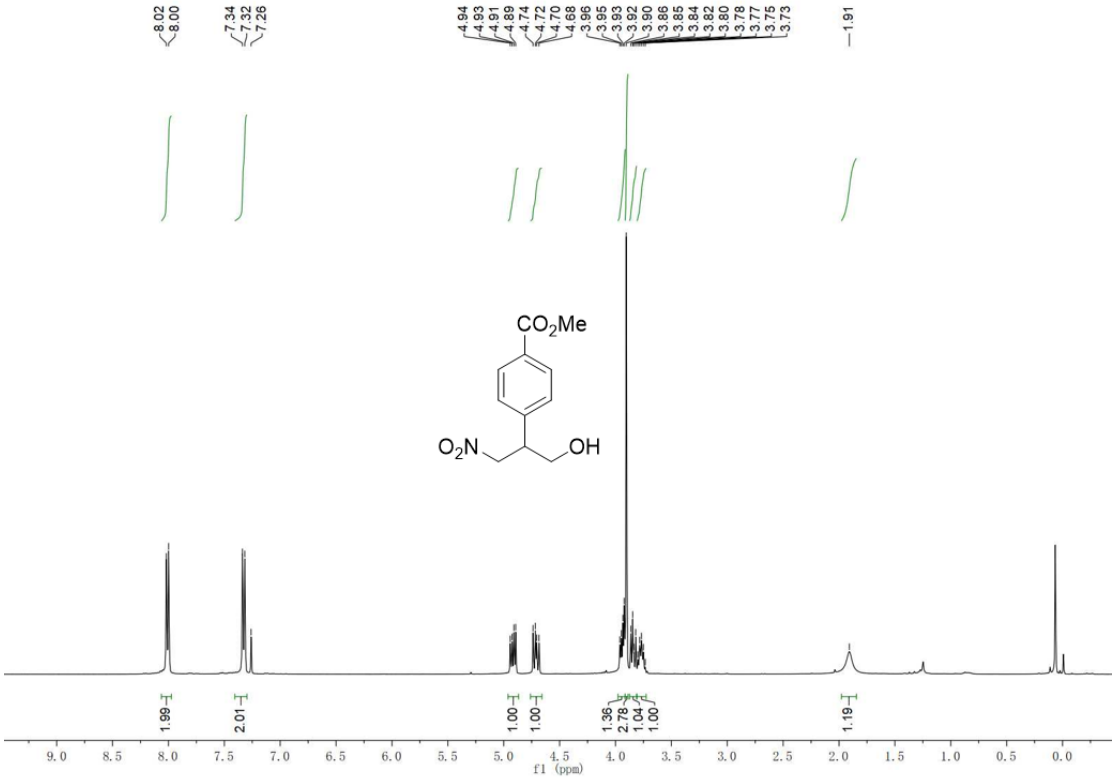
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



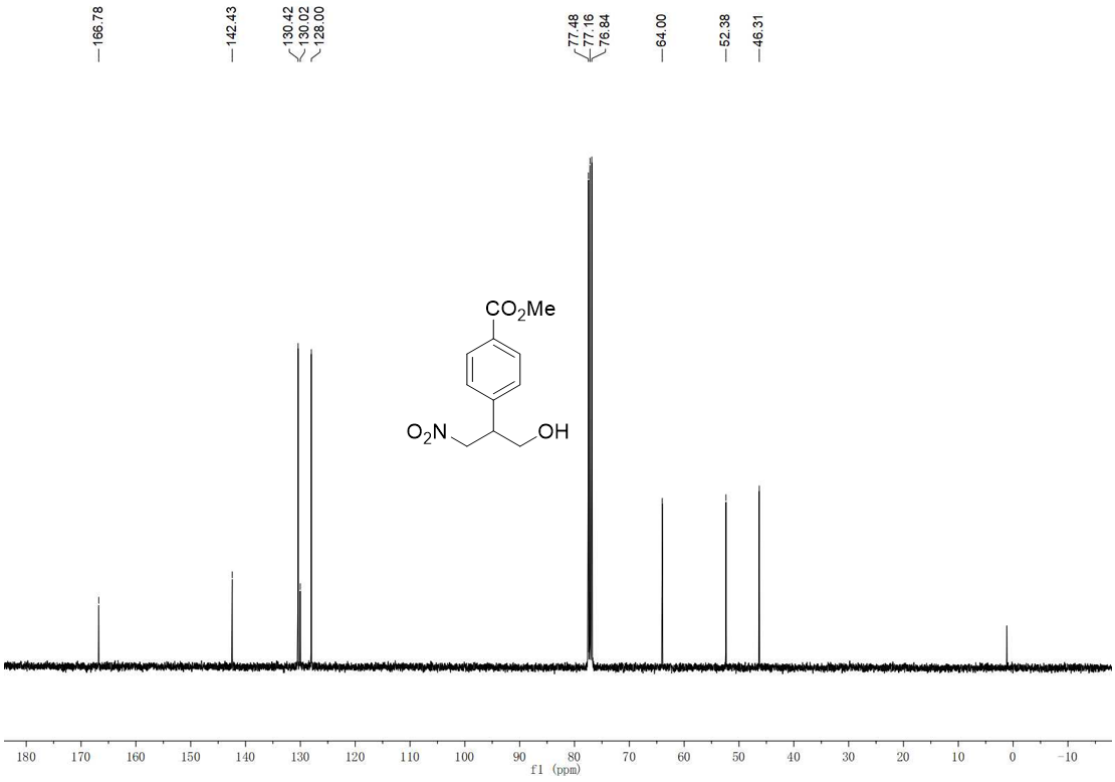
^{13}C NMR (101 MHz, $CDCl_3$) of **3t**



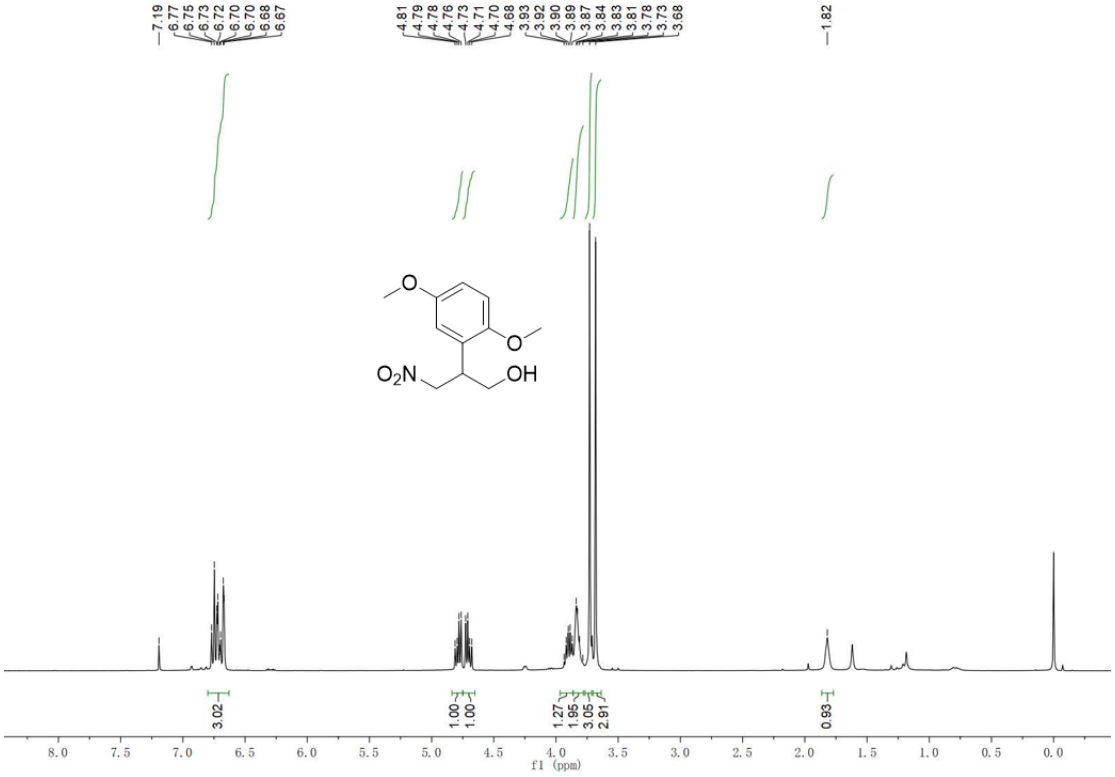
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



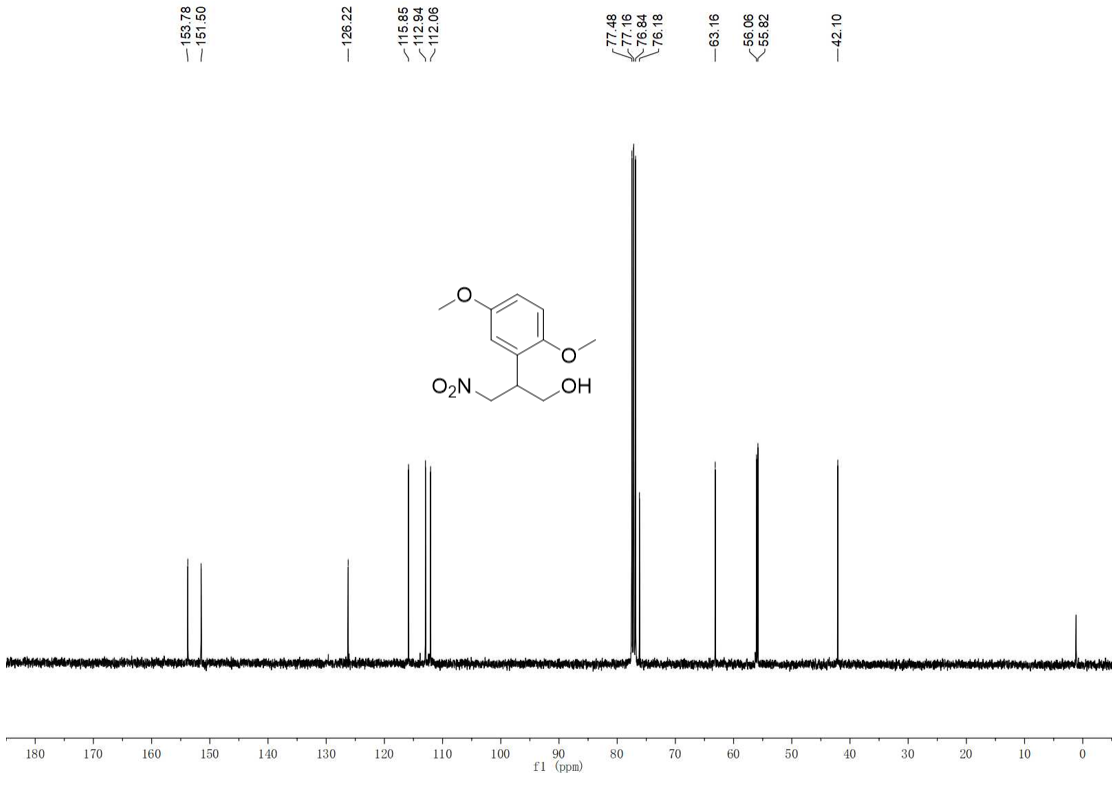
^{13}C NMR (101 MHz, $CDCl_3$) of **3u**



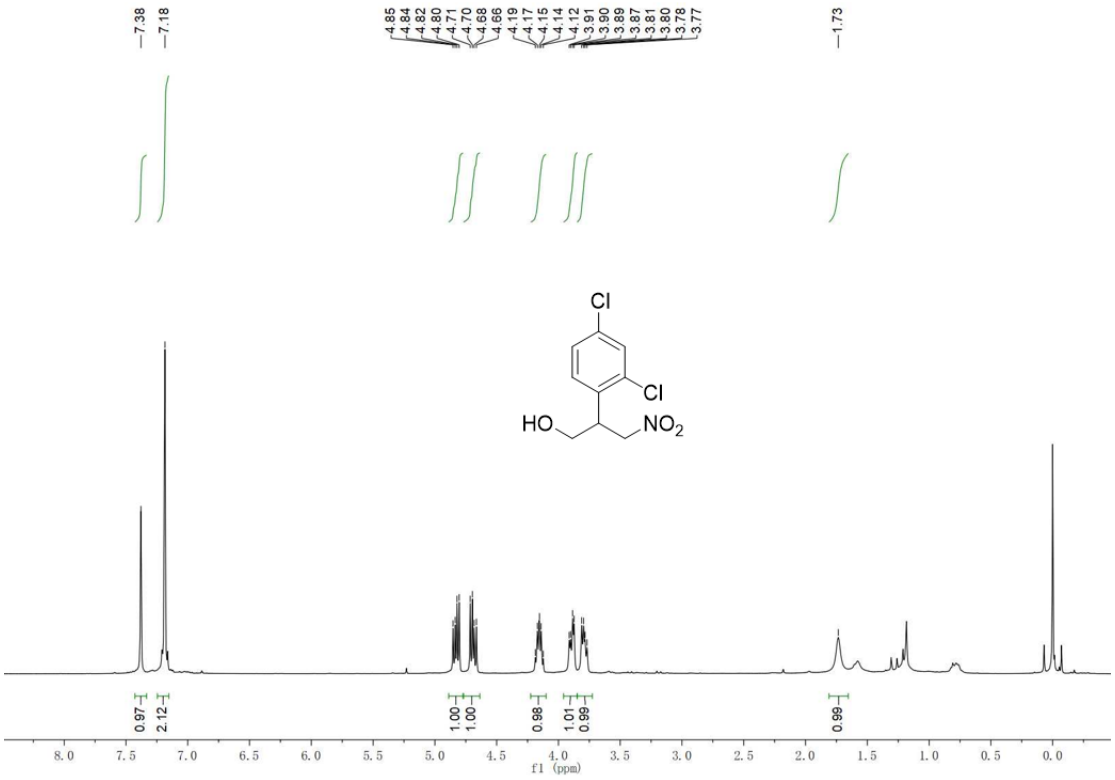
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



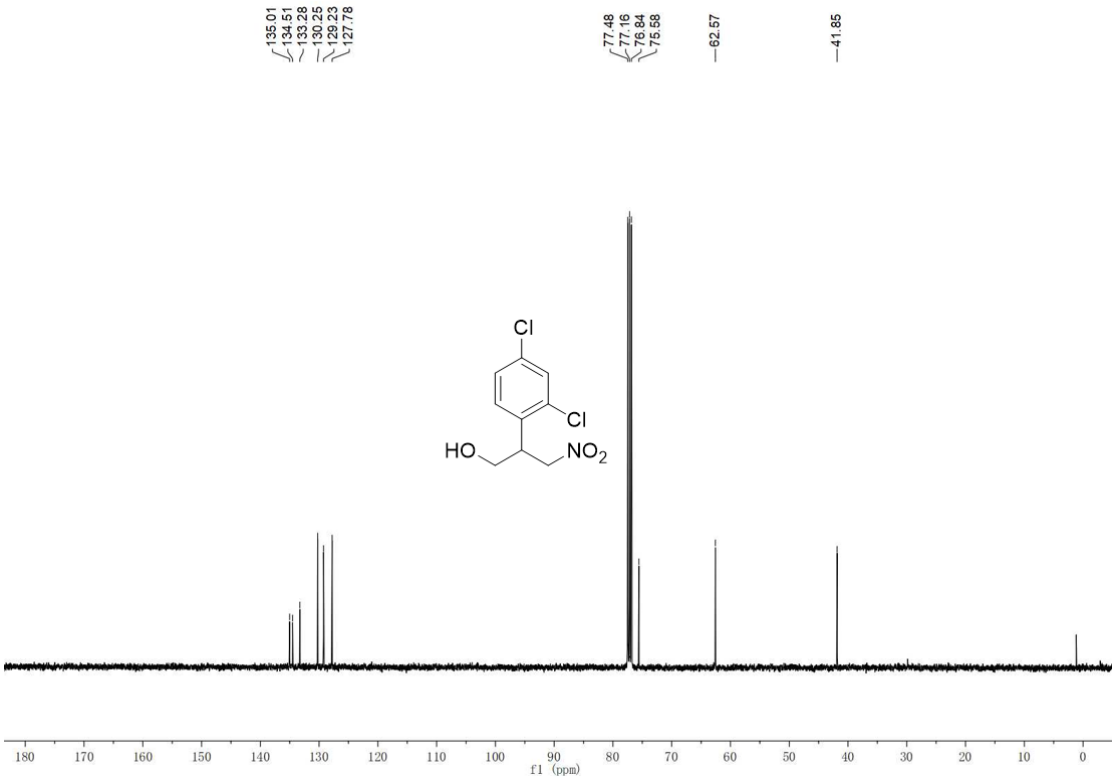
^{13}C NMR (101 MHz, $CDCl_3$) of **3v**



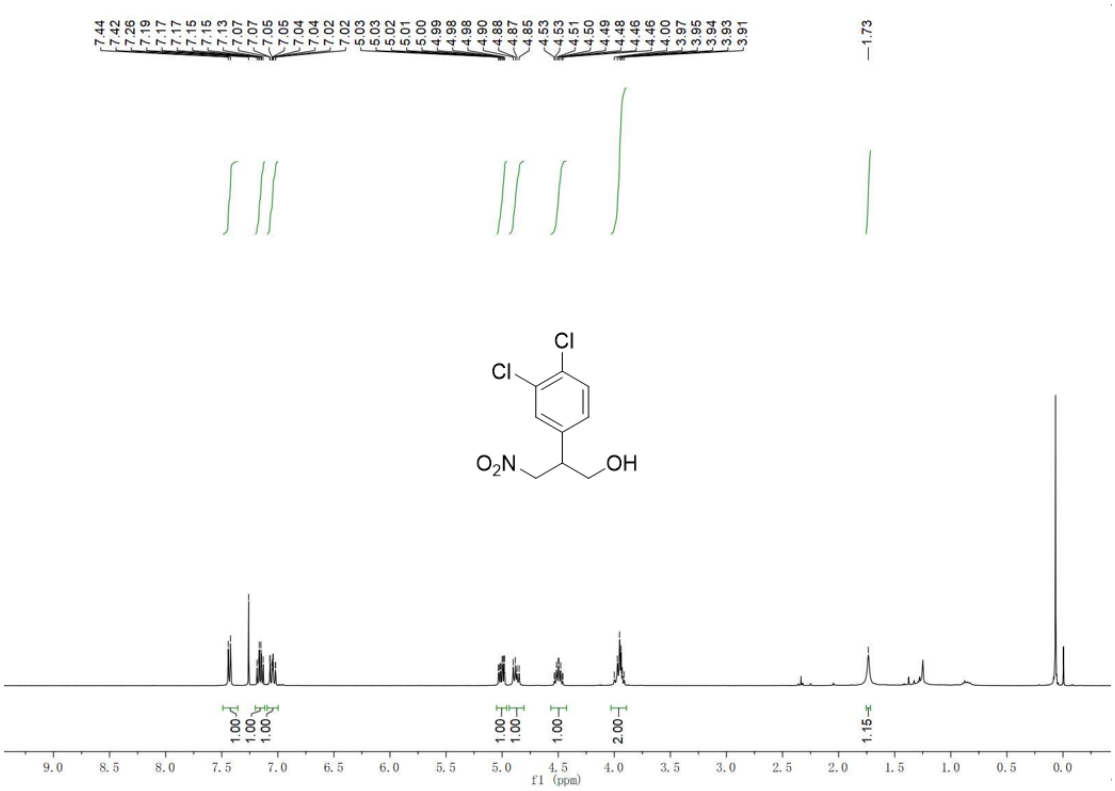
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



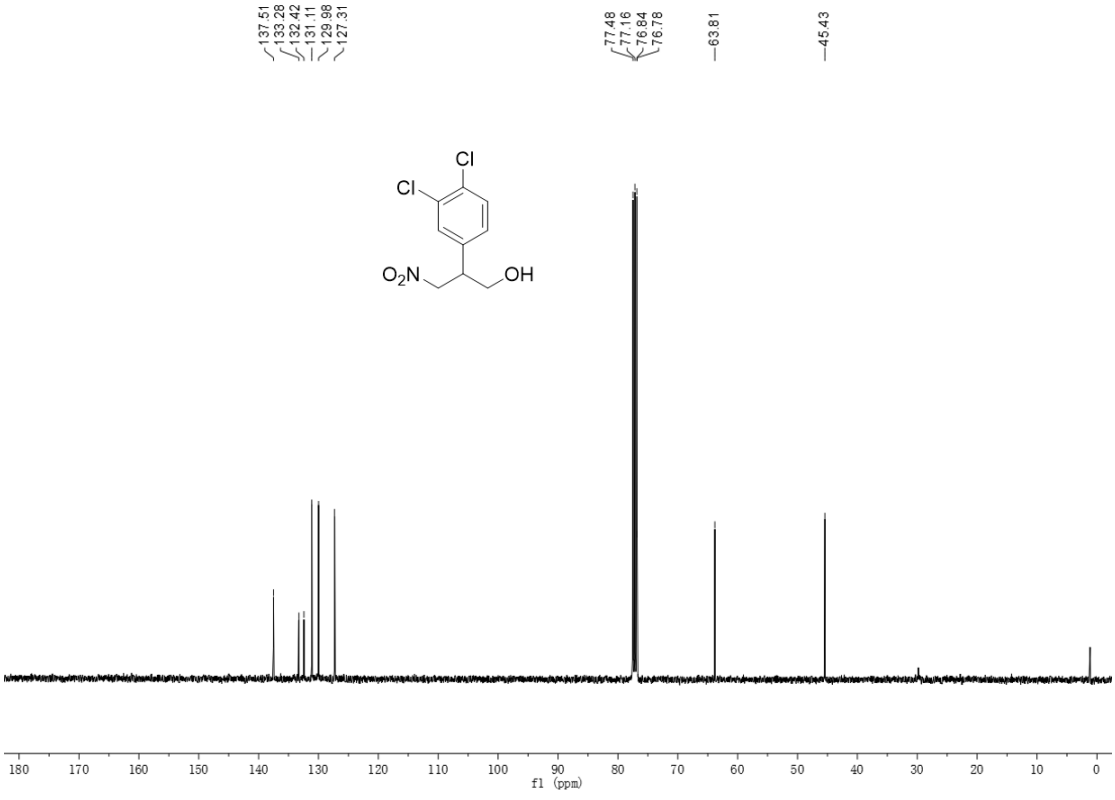
^{13}C NMR (101 MHz, $CDCl_3$) of **3w**



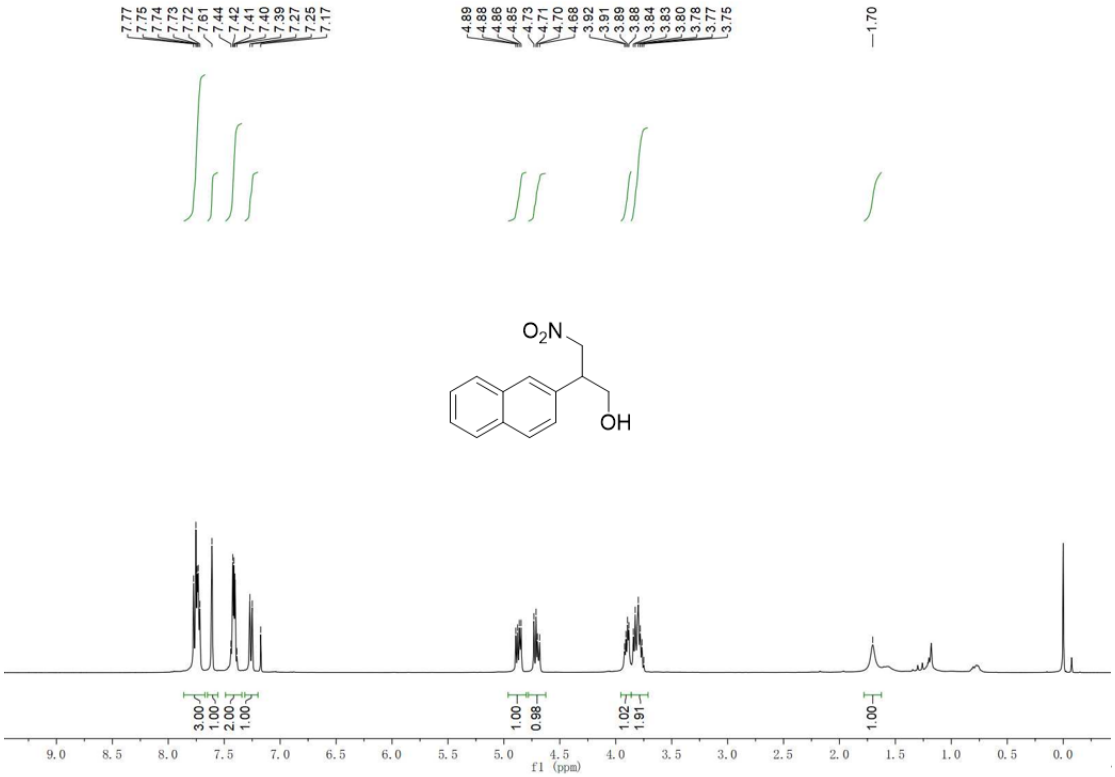
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



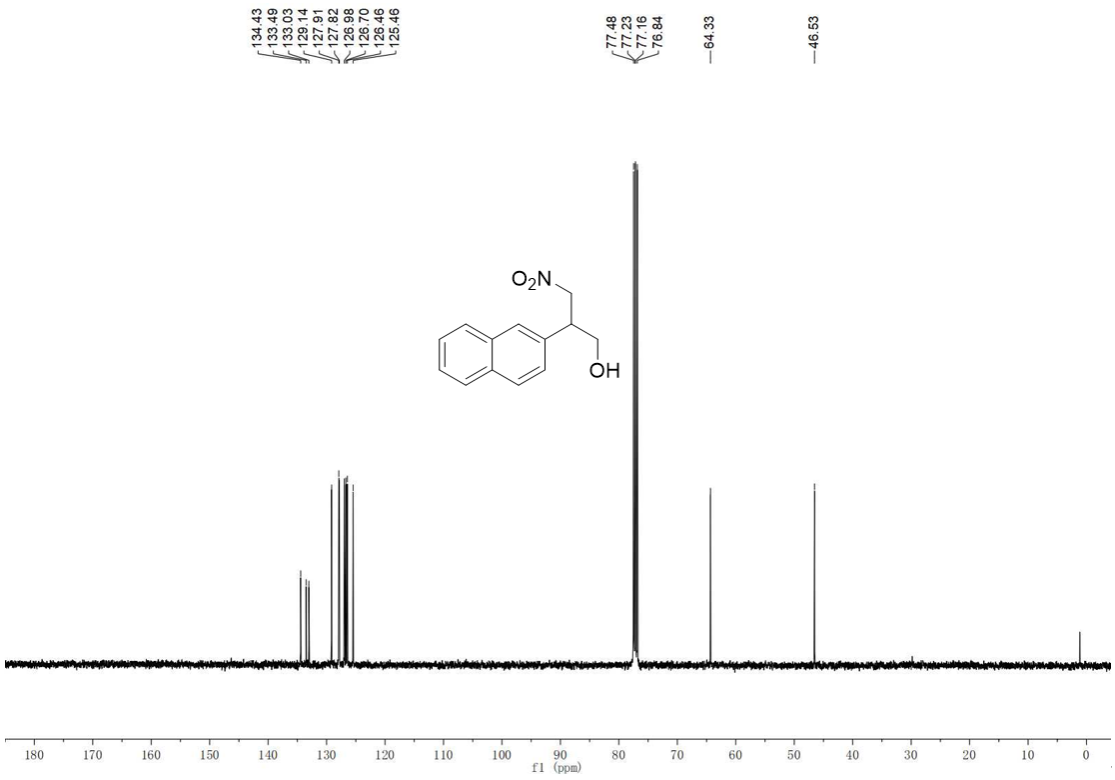
^{13}C NMR (101 MHz, $CDCl_3$) of **3x**



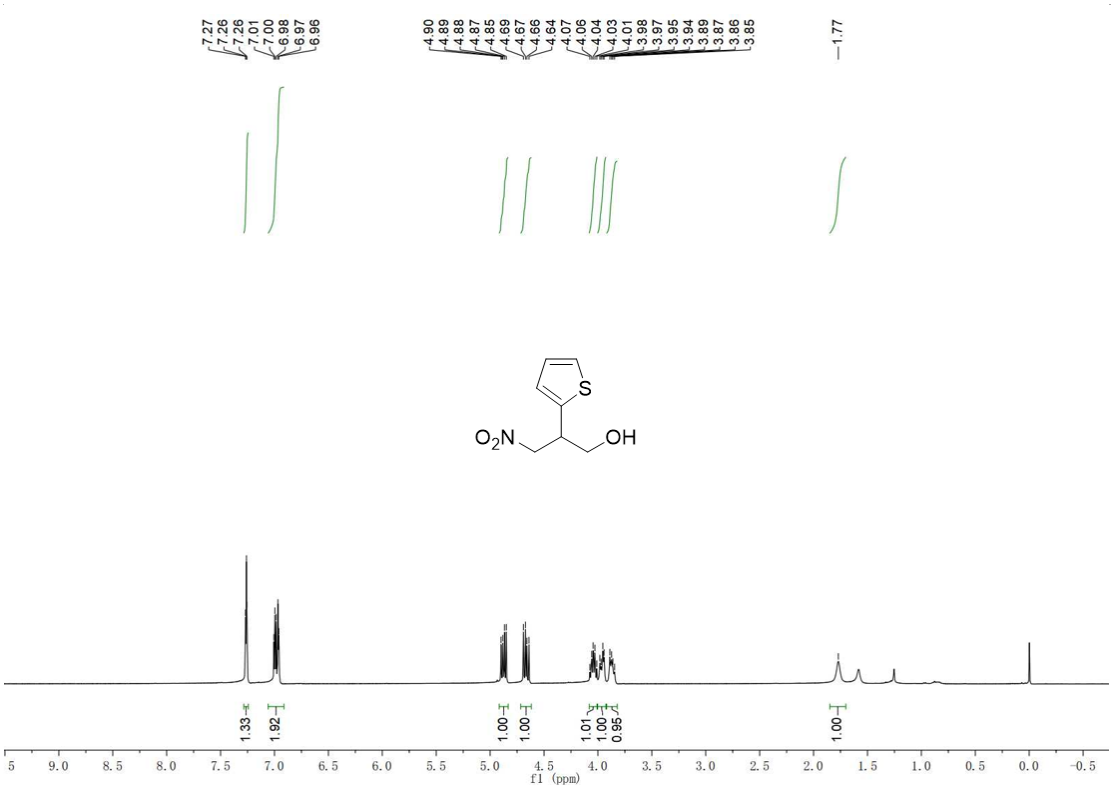
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



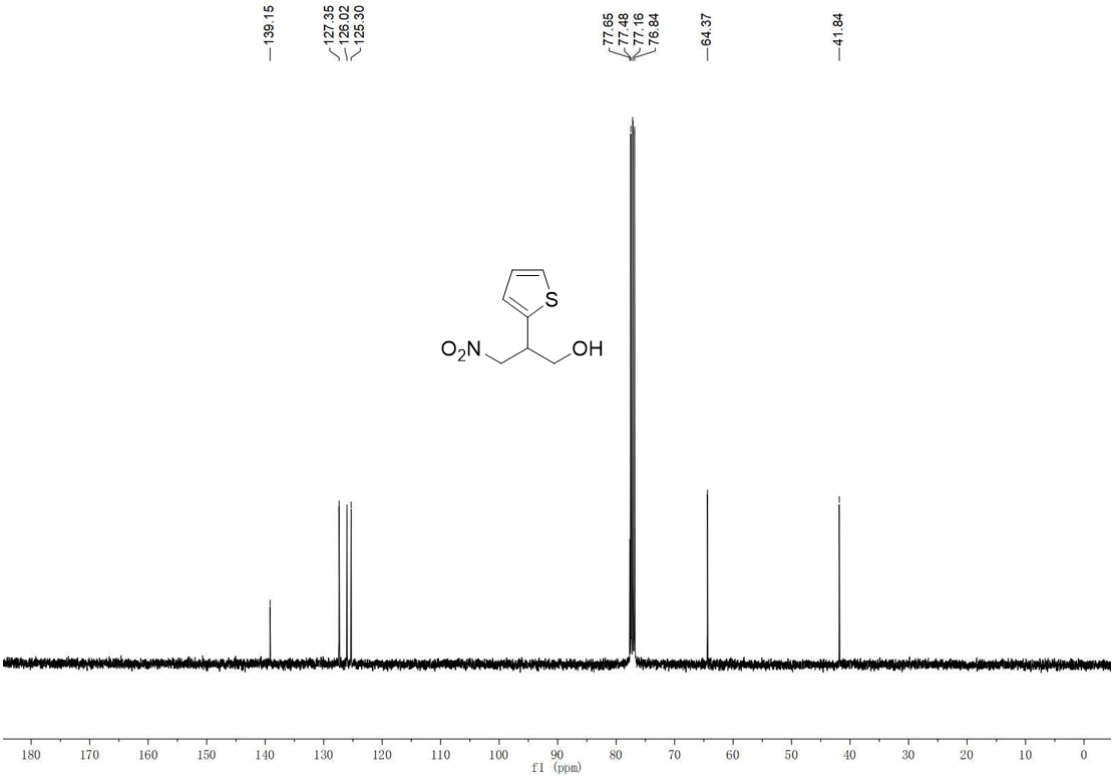
^{13}C NMR (101 MHz, $CDCl_3$) of **3y**



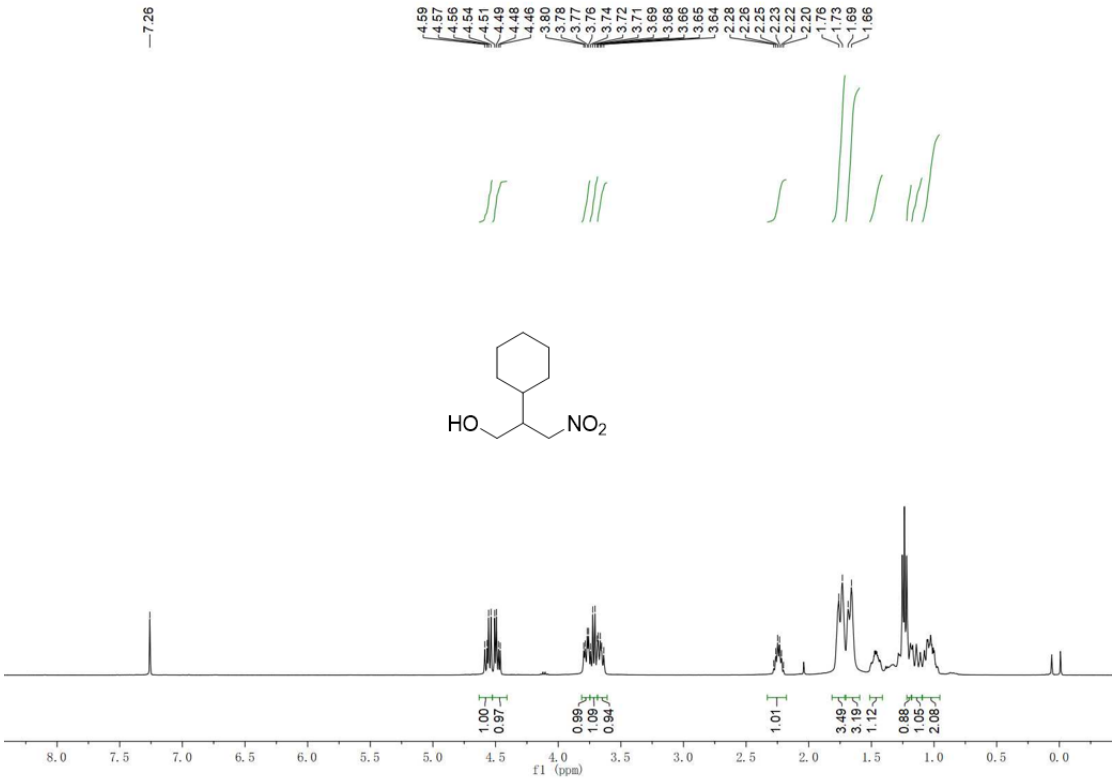
^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



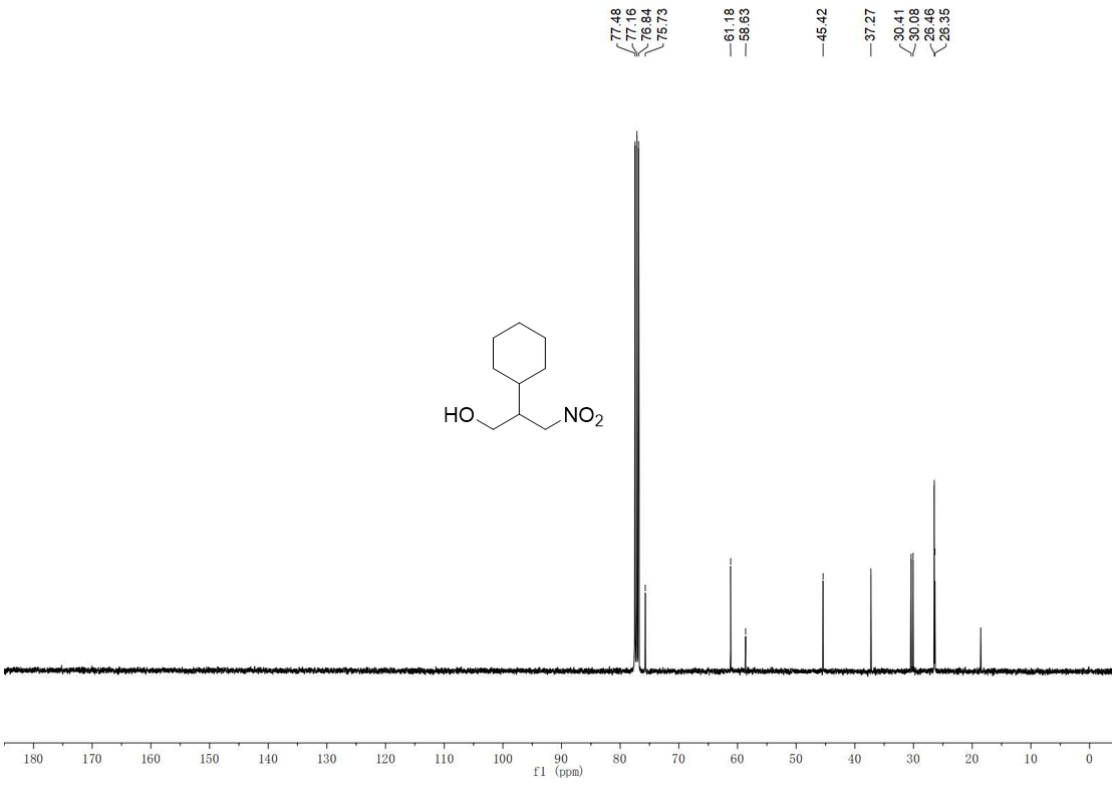
^{13}C NMR (101 MHz, $CDCl_3$) of **3z**



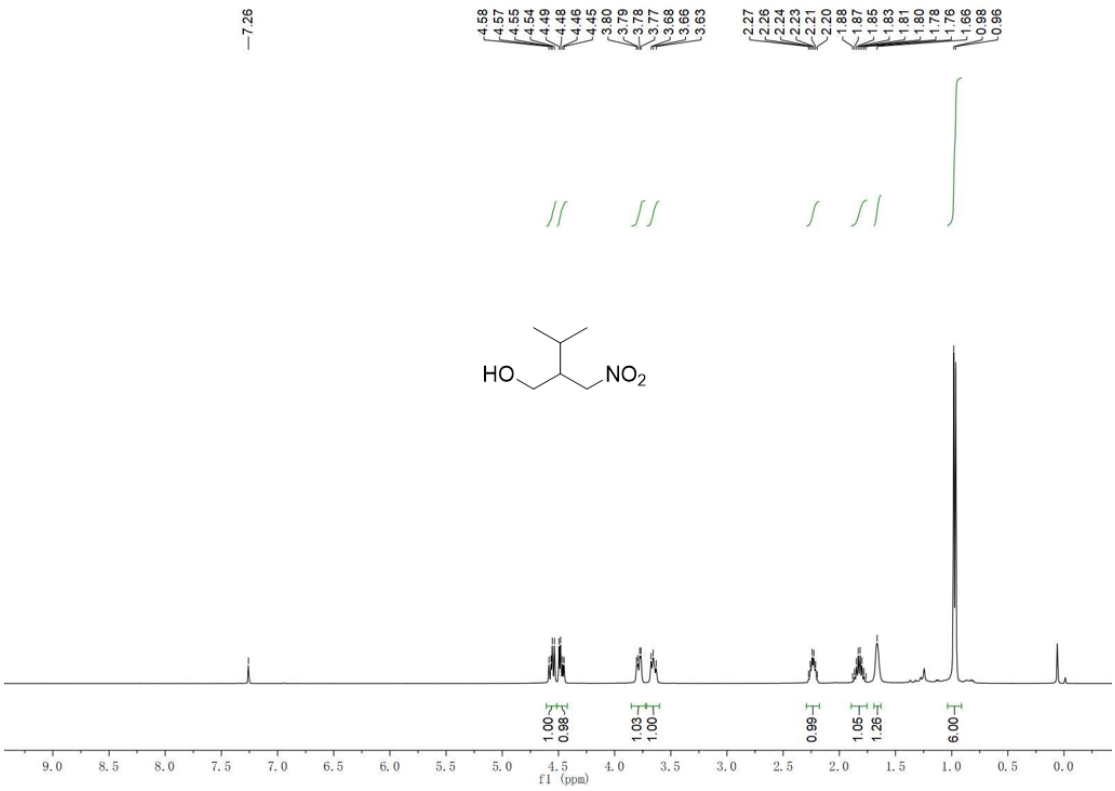
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



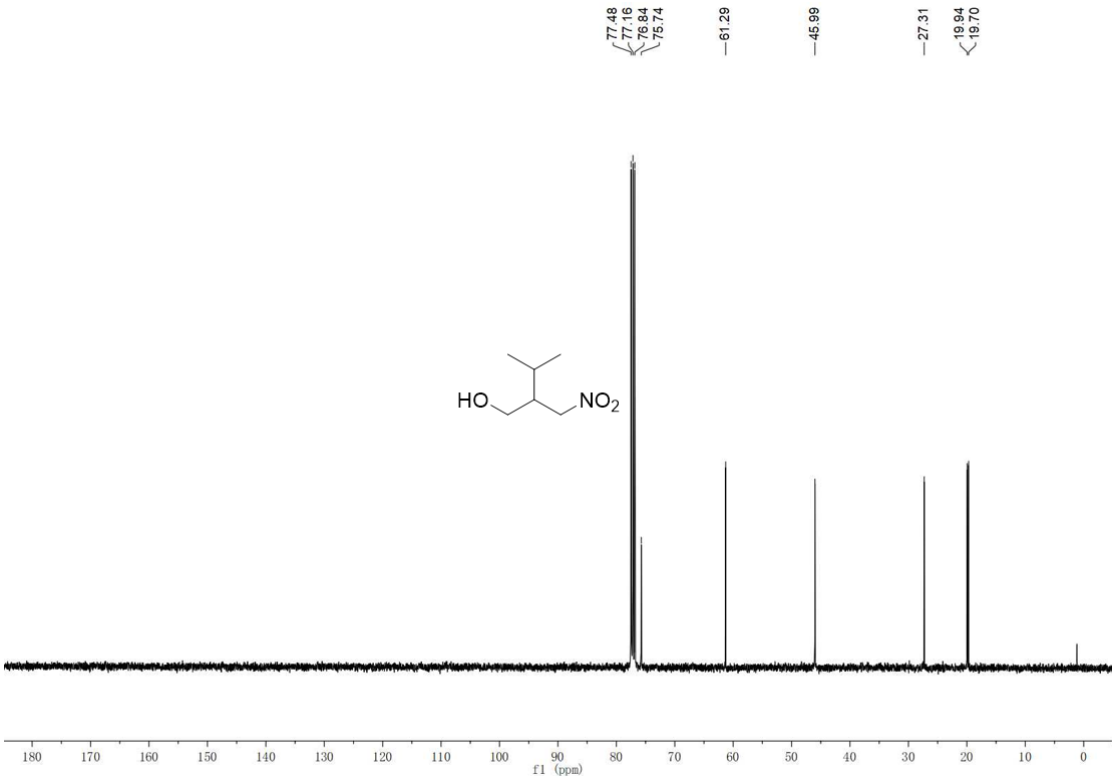
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



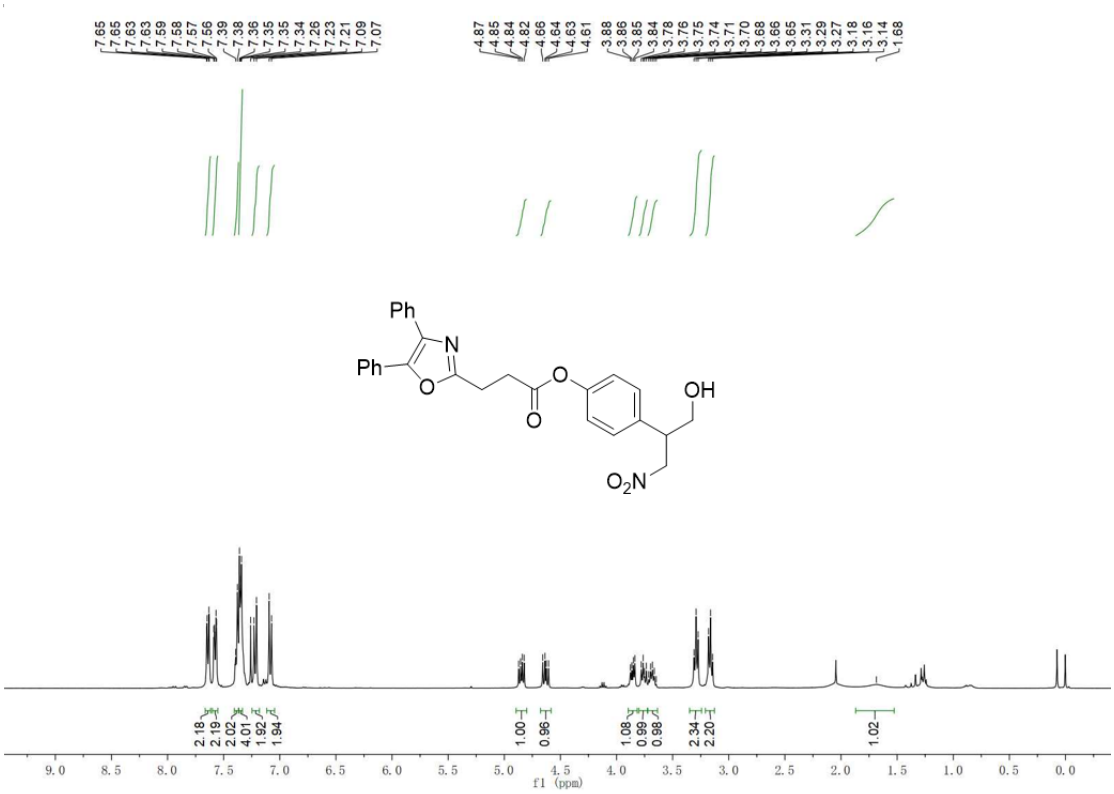
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



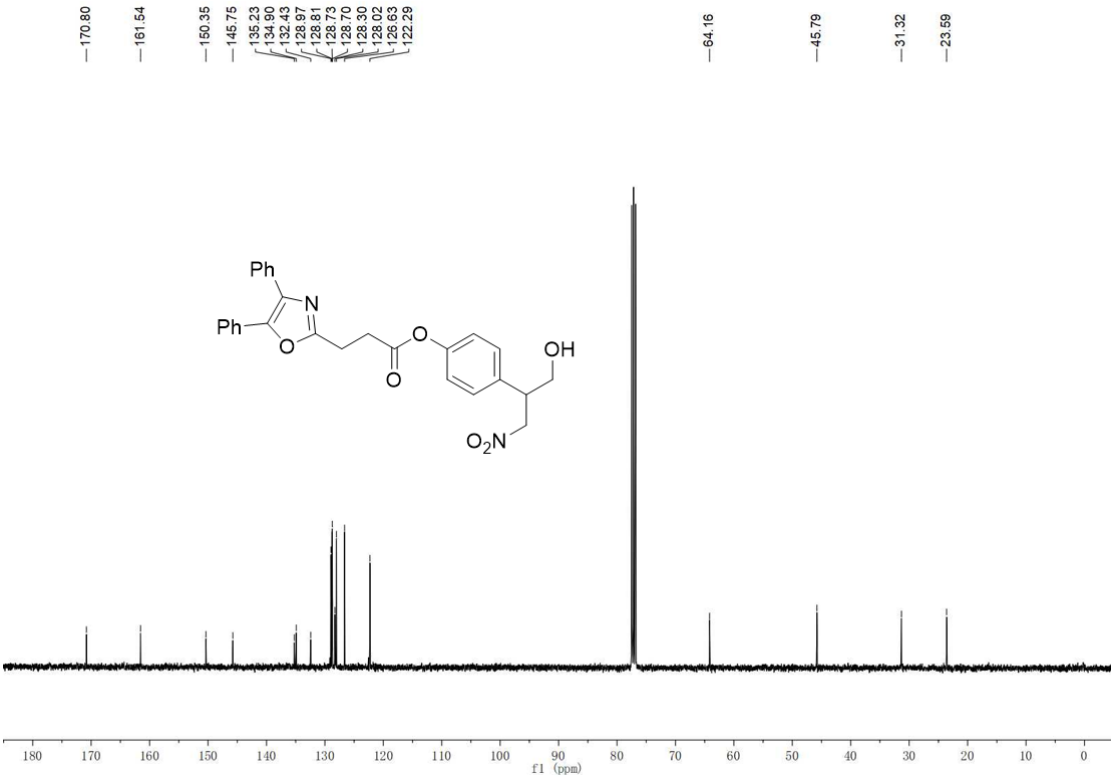
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



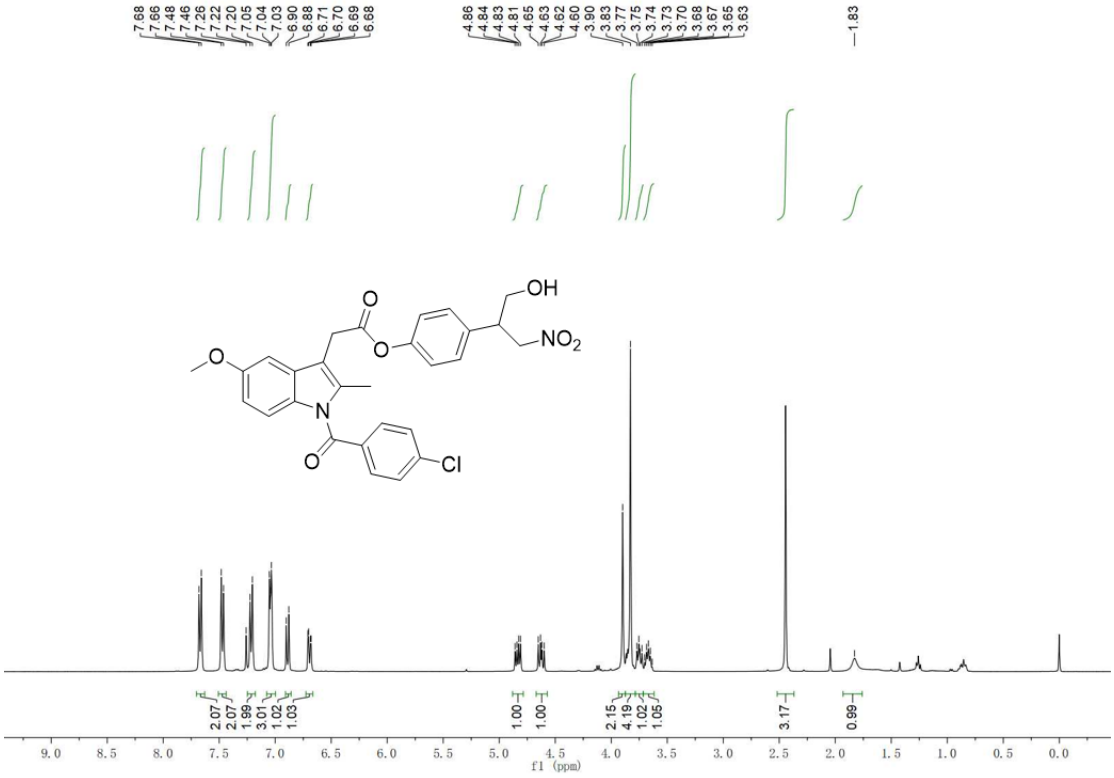
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



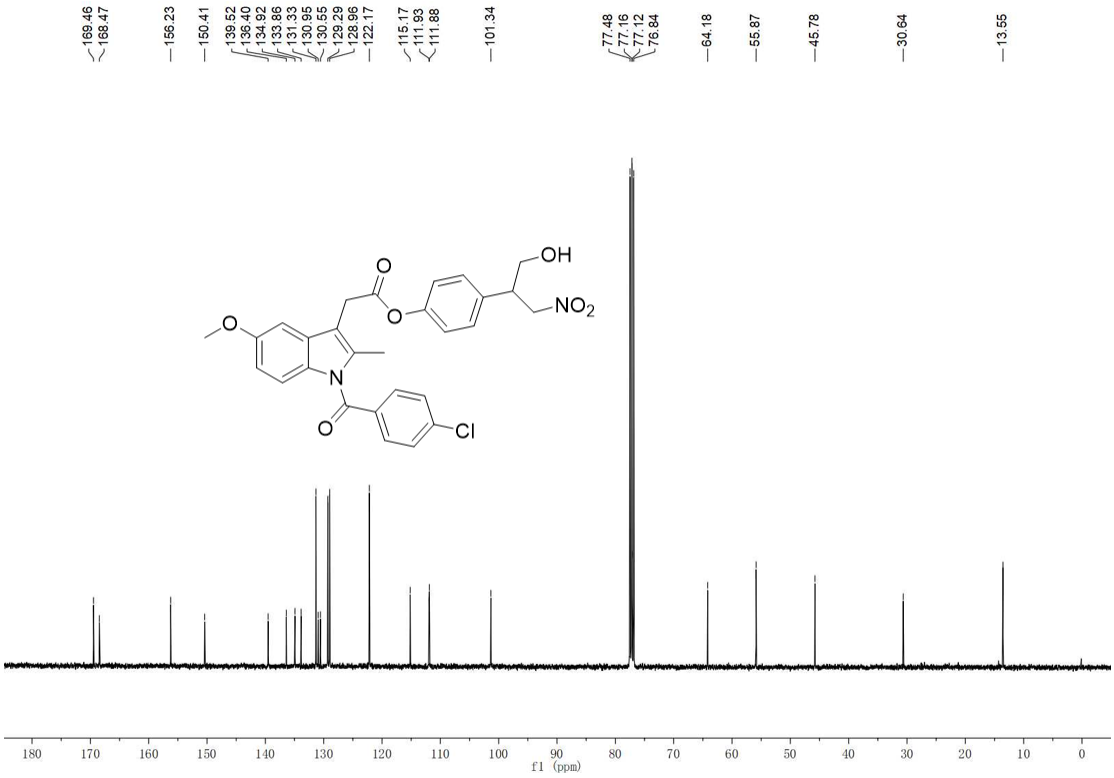
^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**



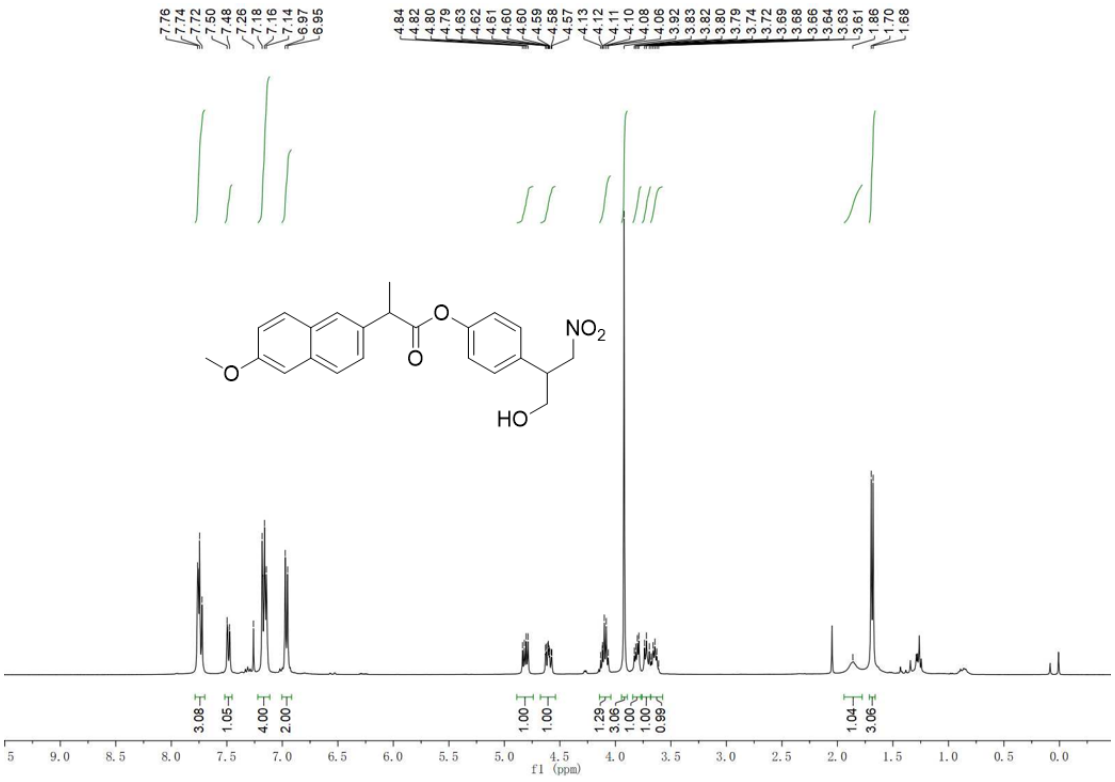
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



^{13}C NMR (101 MHz, $CDCl_3$) of **3ad**

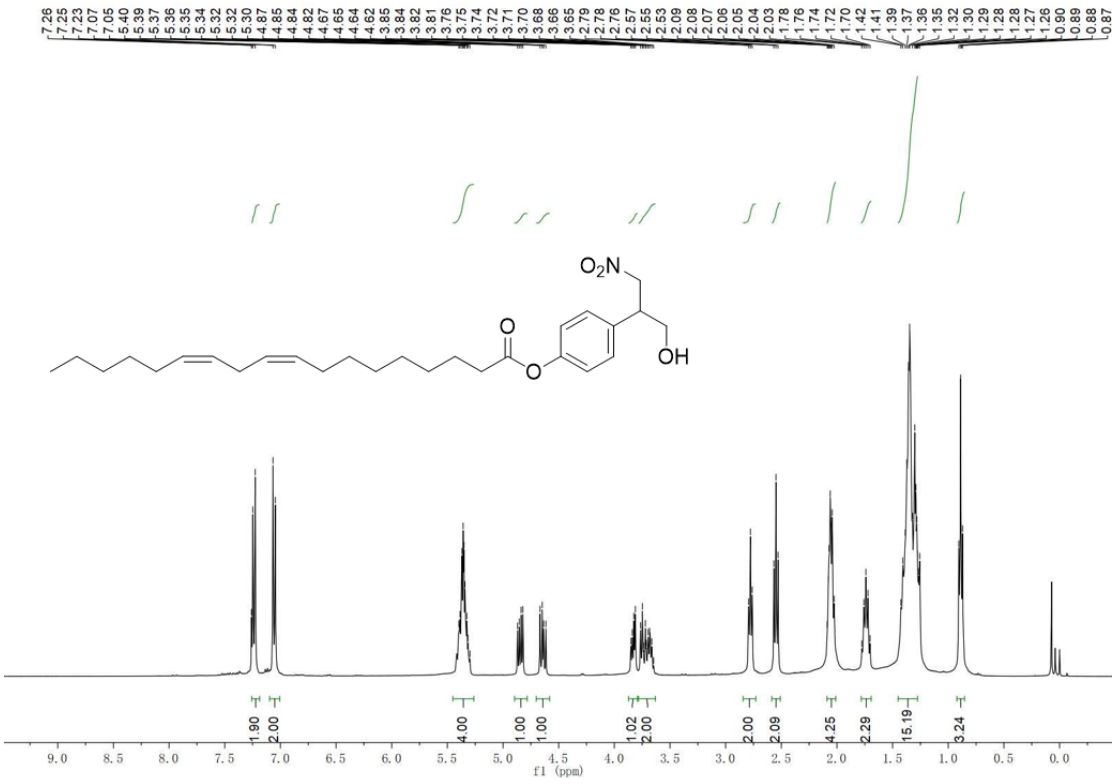


^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**

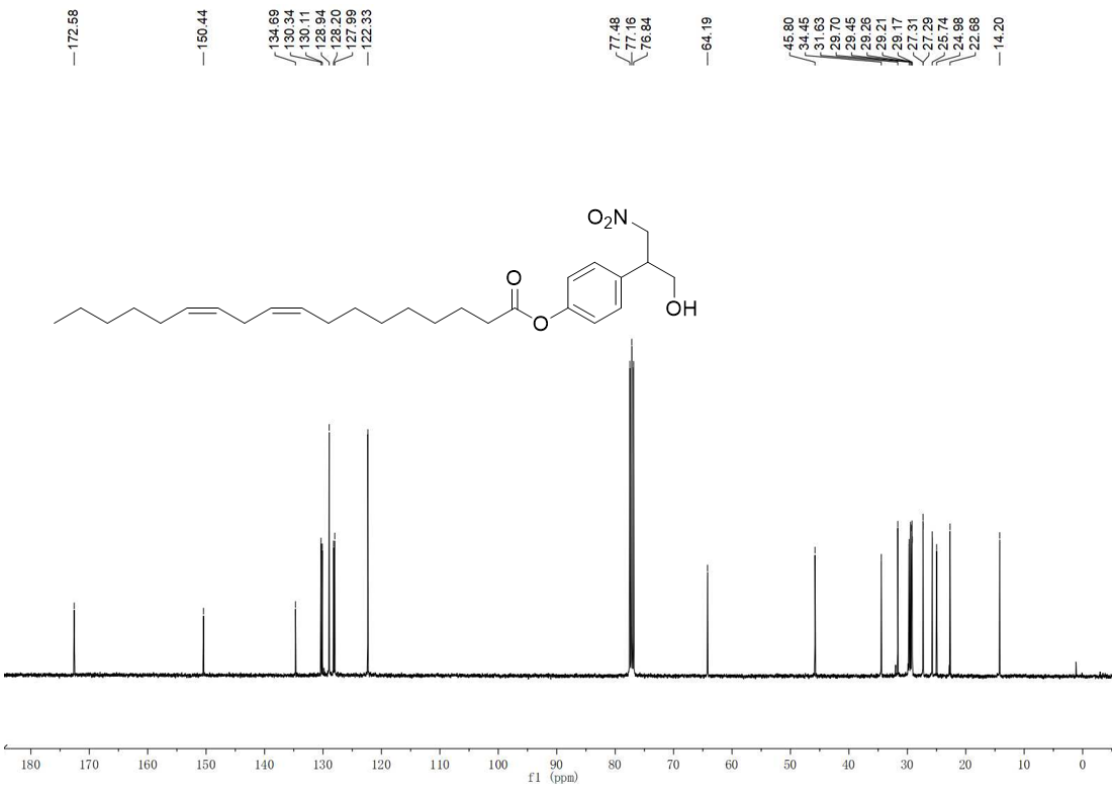


^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**

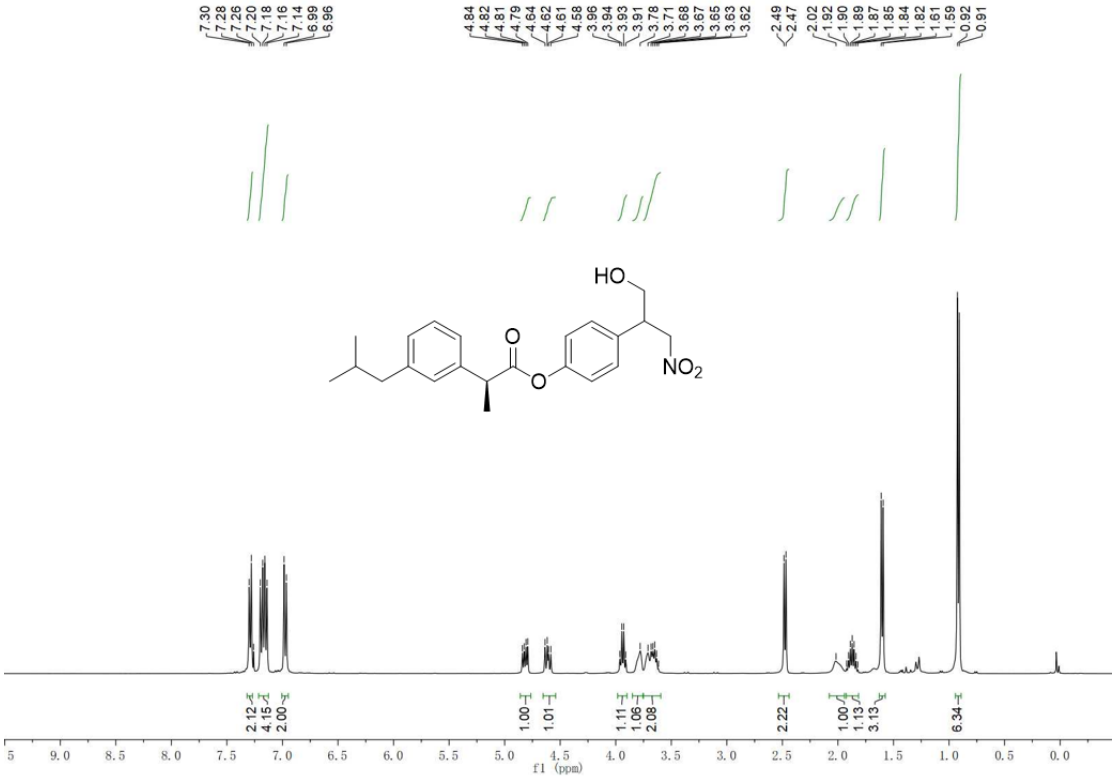
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



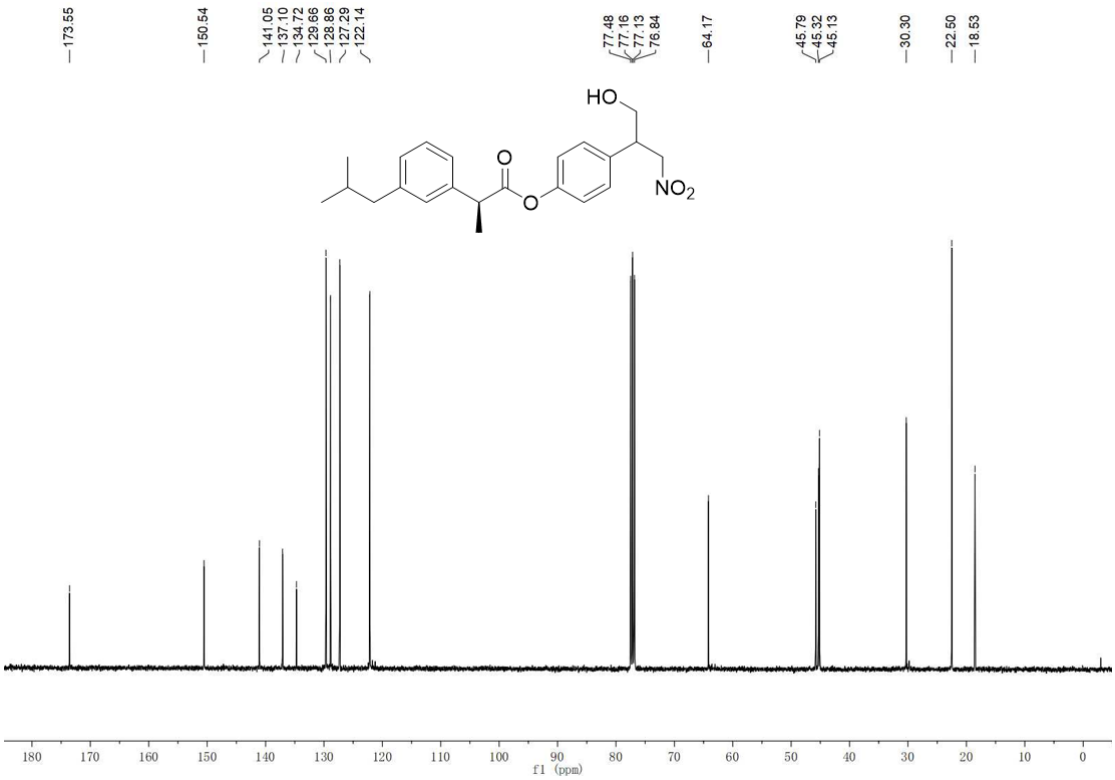
^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



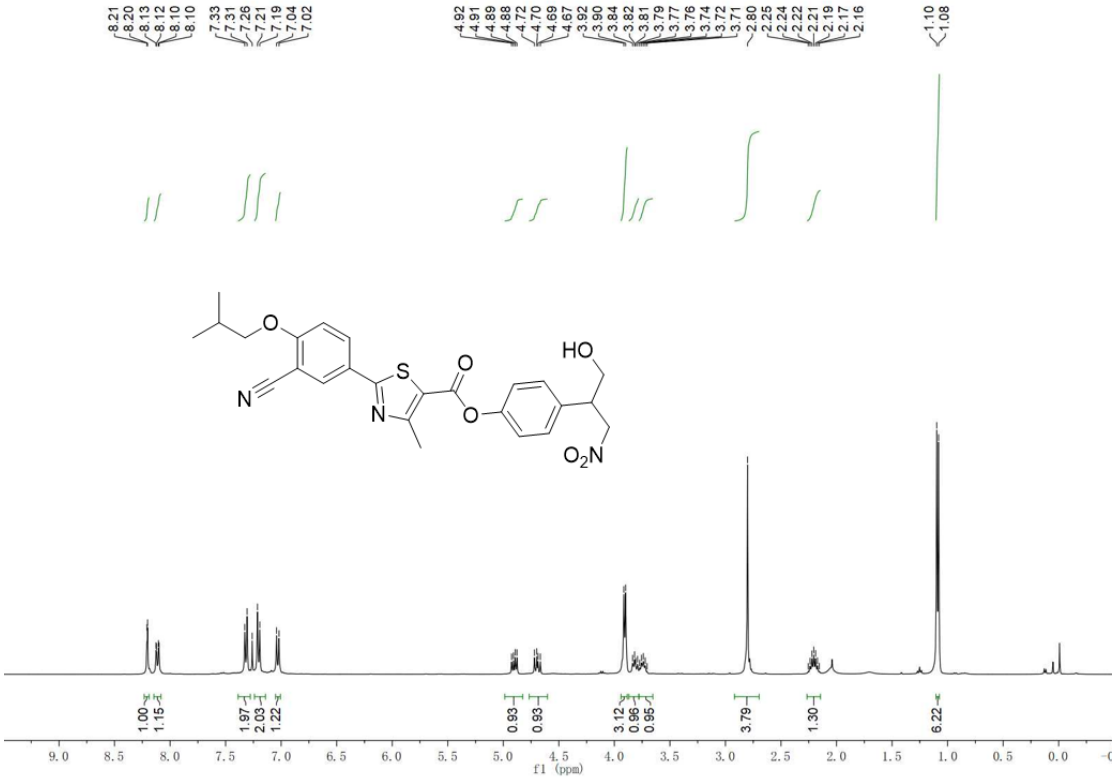
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



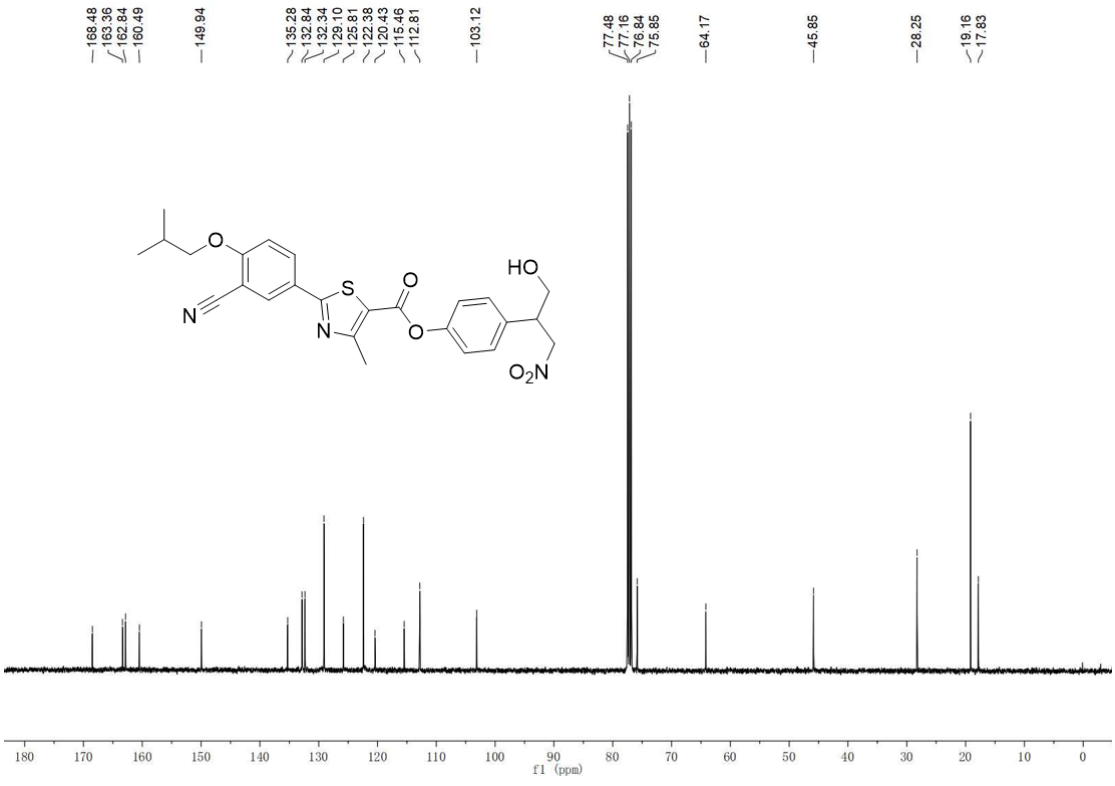
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**



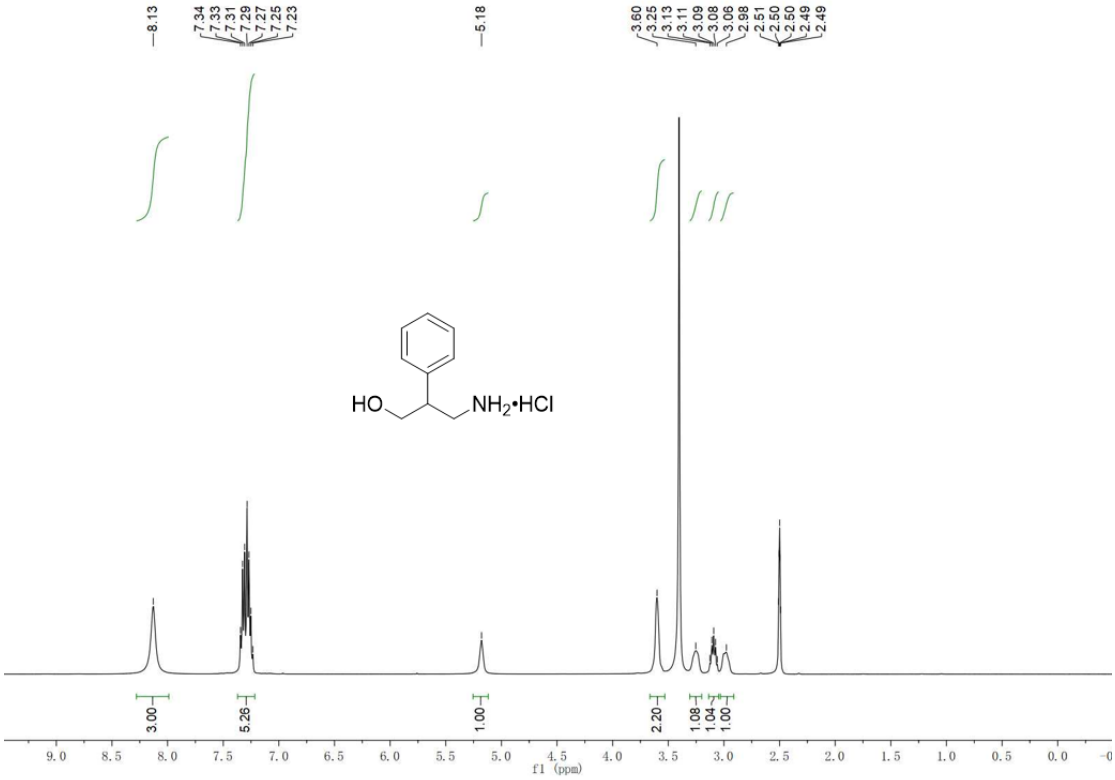
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah**



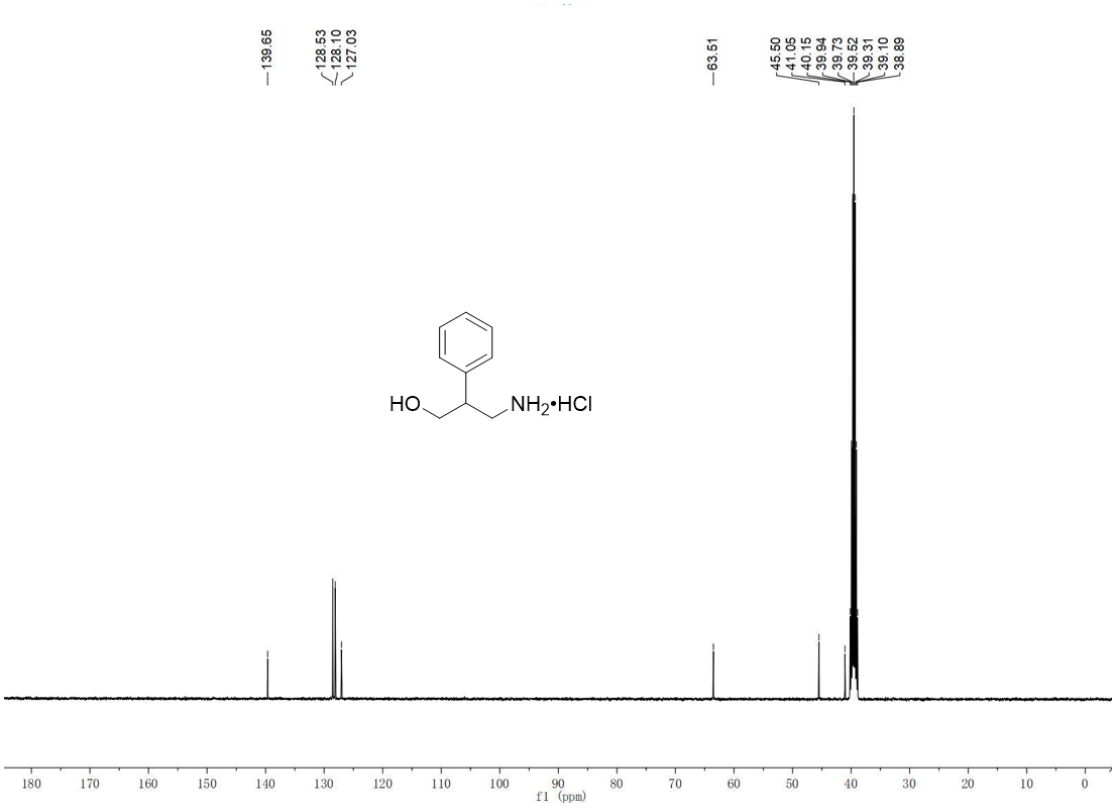
^{13}C NMR (101 MHz, $CDCl_3$) of **3ah**



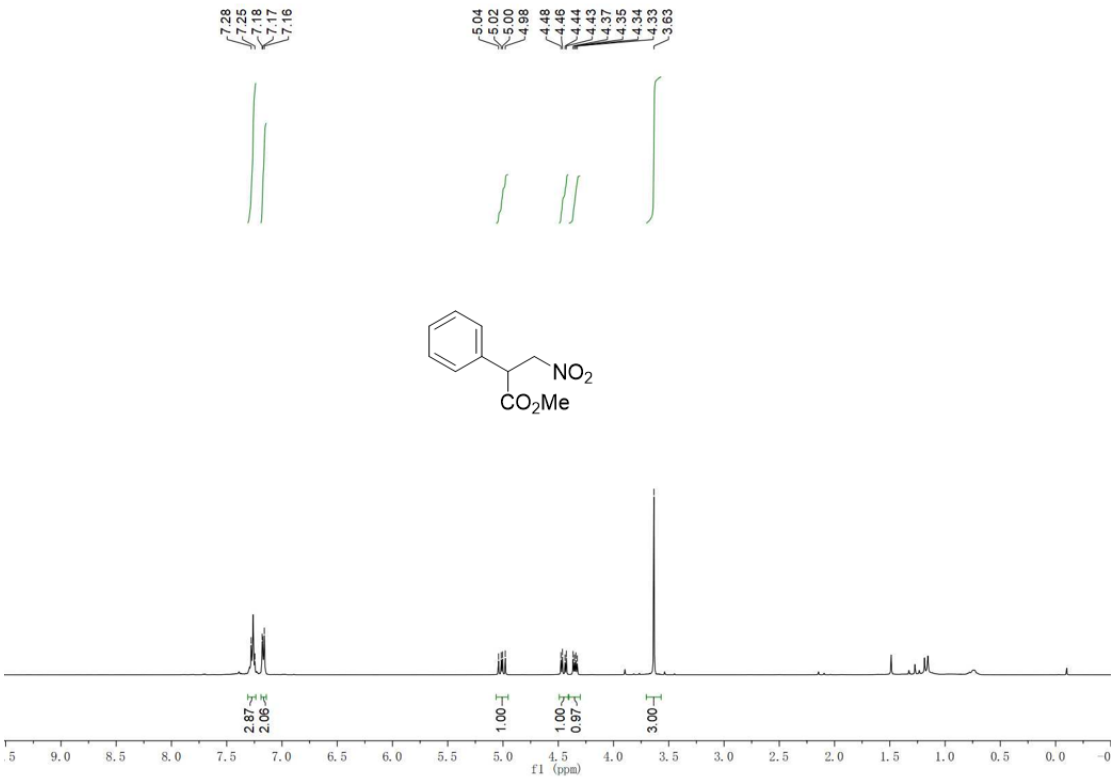
^{1}H NMR (400 MHz, DMSO-d_6) of **4**



^{13}C NMR (101 MHz, DMSO-d_6) of **4**



^{1}H NMR (400 MHz, $CDCl_3$) of **5**



^{13}C NMR (101 MHz, $CDCl_3$) of **5**