Base-catalyzed Retro-Claisen Condensation: A Convenient Esterification of Alcohols via C-C Bond Cleavage of Ketones to Afford Acylating Sources

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Supplementary Information

Table of contents

General information

All the obtained products were characterized by melting points (m.p), ^{1}H-NMR, ^{13}C-NMR infrared spectra (IR), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, the solid and new products were further determined by Melting points and mass spectra (MS), respectively. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Bruker Avance 400 MHz NMR spectrometer; Mass spectra were recorded on a Shimadzu GC–MS-QP5050A spectrometer at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter: 0.25 mm, length: 30 m). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a Brucker Vector 22 spectrometer; Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; All the reagents were purchased from commercial sources (J&KChemic, TCI, Fluka, Acros, SCRC), and used without further purification.

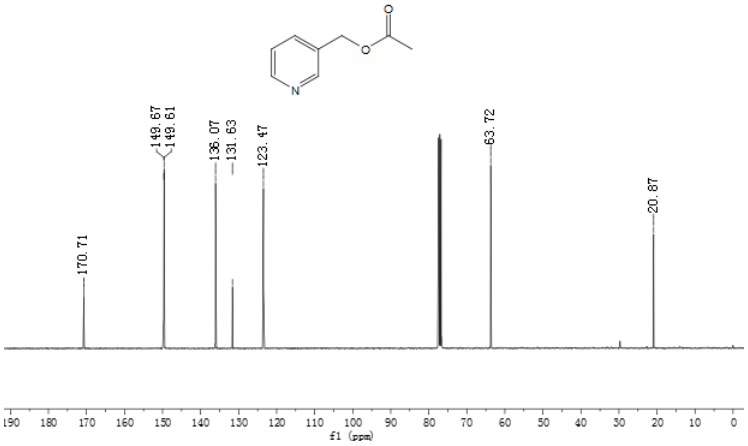
Typical procedure for synthesis of 3-pyridylmethyl acetate (3a).

t-BuONa (0.028 g, 0.3 mmol), 3-(Hydroxymethyl)pyridine **1a** (0.131 g, 1.2 mmol), acetylacetone **2a** (0.1g, 1 mmol) and *t*-amyl alcohol (1 mL) were added successively to a Schlenk tube, it was then closed and the resulting mixture was heated at 120 °C for 18 h in an oil bath. After cooling down to room temperature, the reaction mixture was then filtered and concentrated under vacuum, the obtained crude product was directly purified by preparative TLC on silica, eluting with petroleum ether (60-90°C): ethyl acetate (3:1) to give 3-pyridylmethyl acetate **3a** as a yellow oil (0.110 g, 75%).

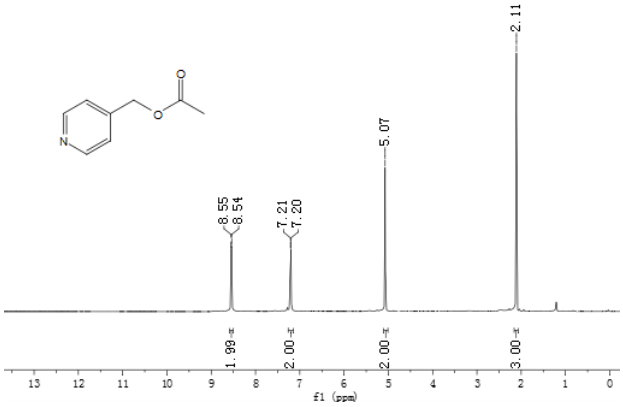
NMR spectra of the obtained compounds

^{1}H-NMR spectrum of 3-Pyridylmethyl acetate (3a)

^{13}C-NMR spectrum of 3-Pyridylmethyl acetate (3a)

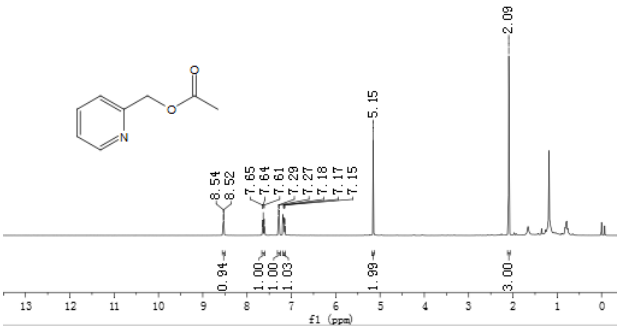


^{1}H-NMR spectrum of 4-Pyridylmethyl acetate (3b)

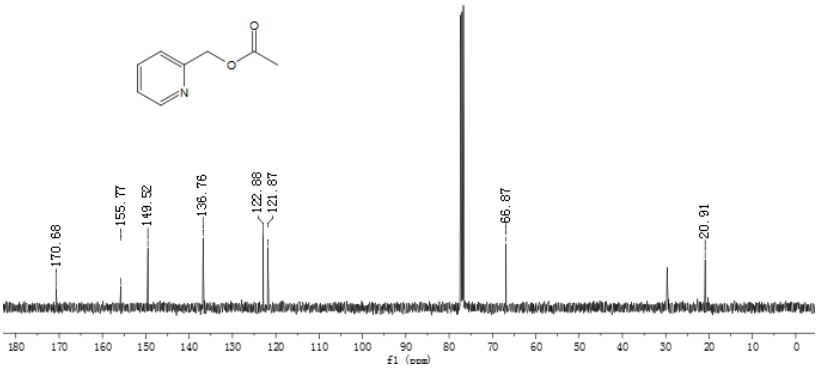


^{13}C-NMR spectrum of 4-Pyridylmethyl acetate (3b)

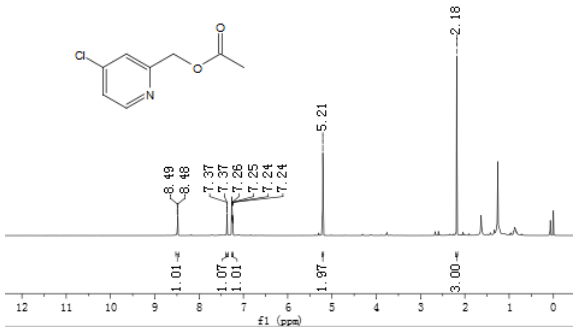
^{1}H-NMR spectrum of 2-Pyridylmethyl acetate (3c)



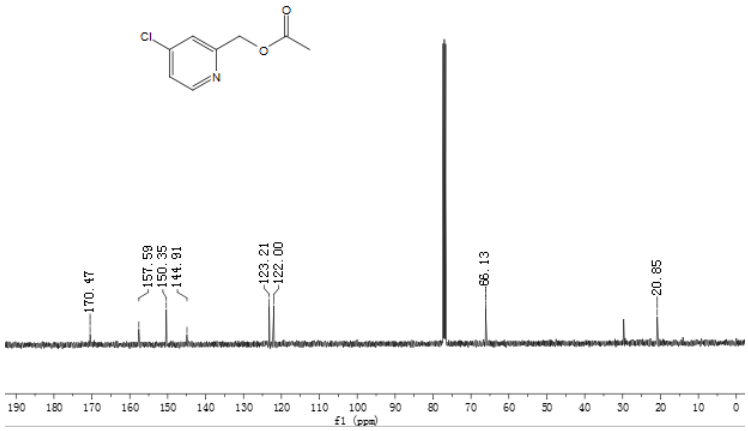
^{13}C-NMR spectrum of 2-Pyridylmethyl acetate (3c)



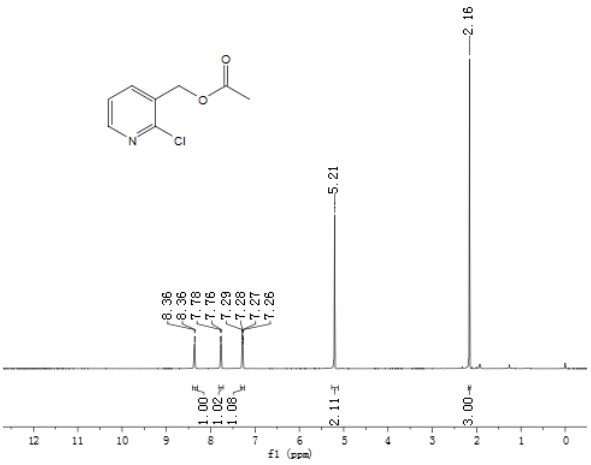
^{1}H-NMR spectrum of (4-chloropyridin-2-yl)methyl acetate (3d)



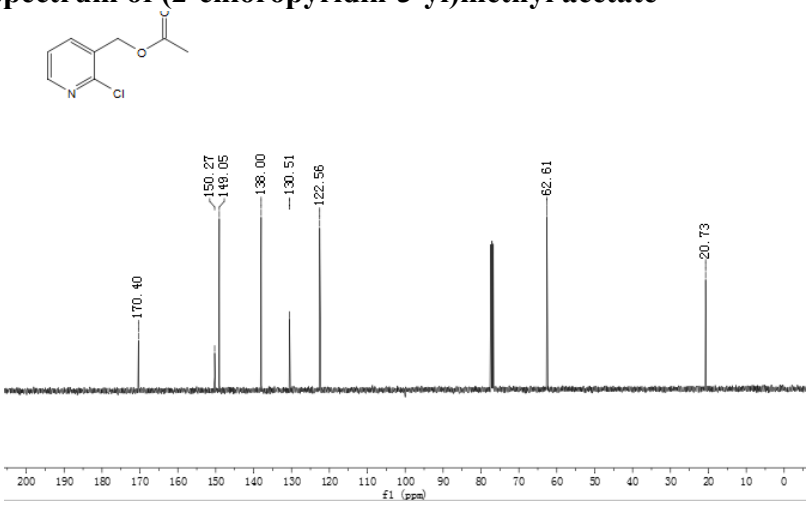
^{13}C-NMR spectrum of (4-chloropyridin-2-yl)methyl acetate (3d)



^{1}H- NMR spectrum of (2-chloropyridin-3-yl)methyl acetate (3e)

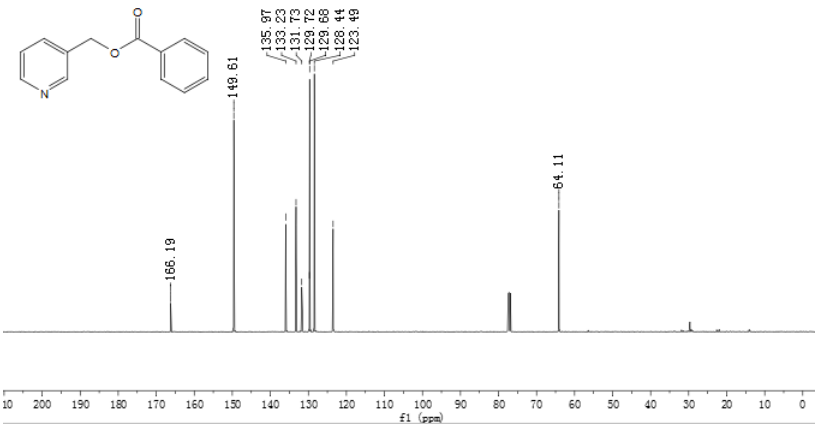


^{13}C-NMR spectrum of (2-chloropyridin-3-yl)methyl acetate

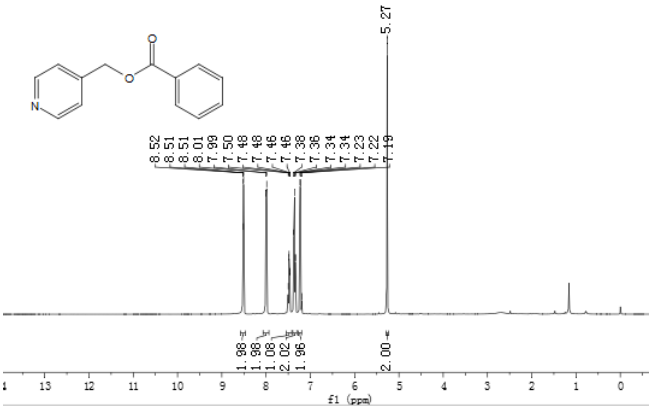


^{1}H- NMR spectrum of 3-Pyridylmethyl benzoate (3f)

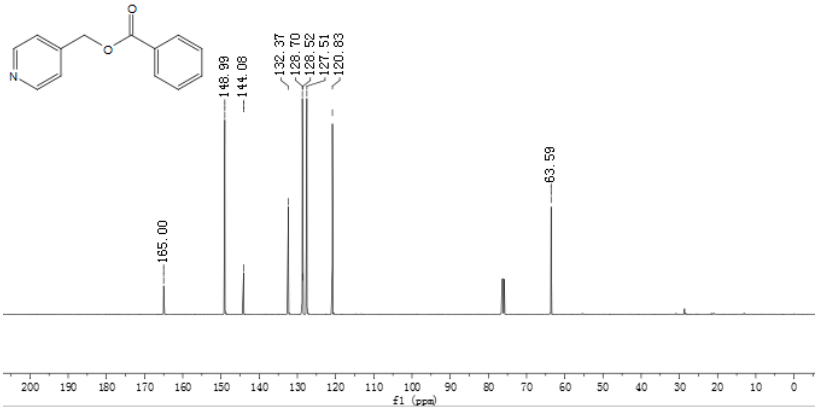
^{13}C-NMR spectrum of 3-Pyridylmethyl benzoate (3f)



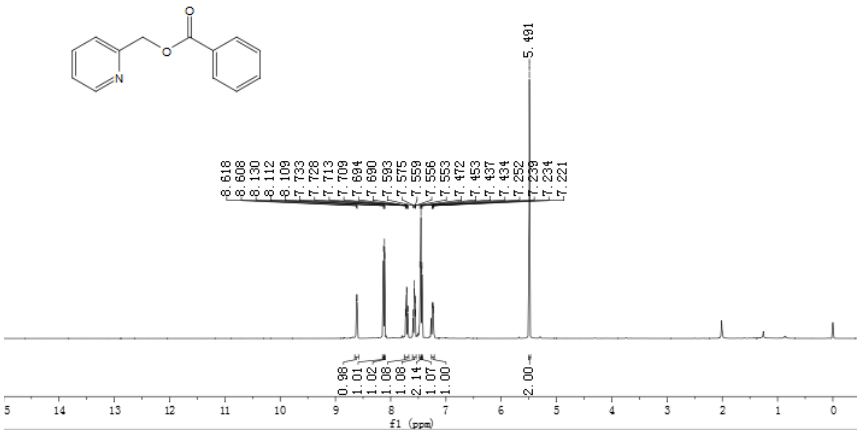
^{1}H-NMR spectrum of 4-Pyridylmethyl benzoate (3g)



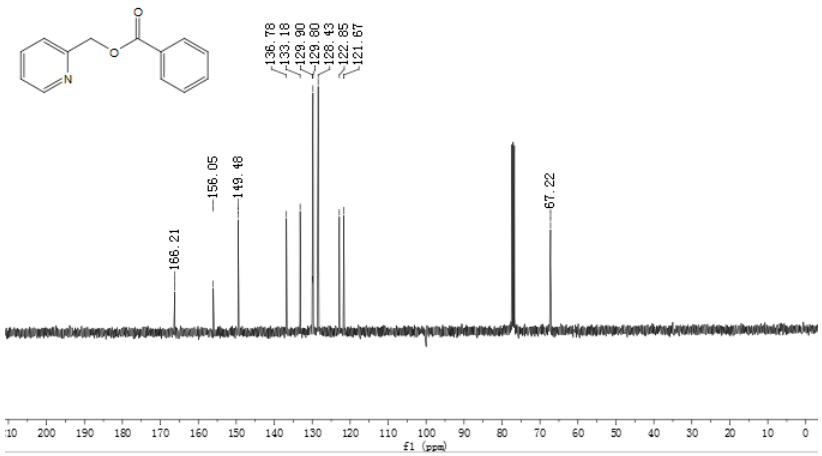
^{13}C-NMR spectrum of 4-Pyridylmethyl benzoate (3g)



^{1}H-NMR spectrum of 2-Pyridylmethyl benzoate (3h)

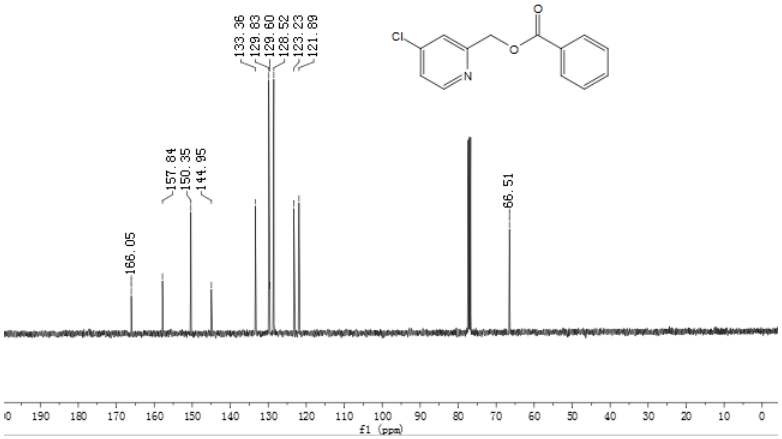


^{13}C-NMR spectrum of 2-Pyridylmethyl benzoate (3h)



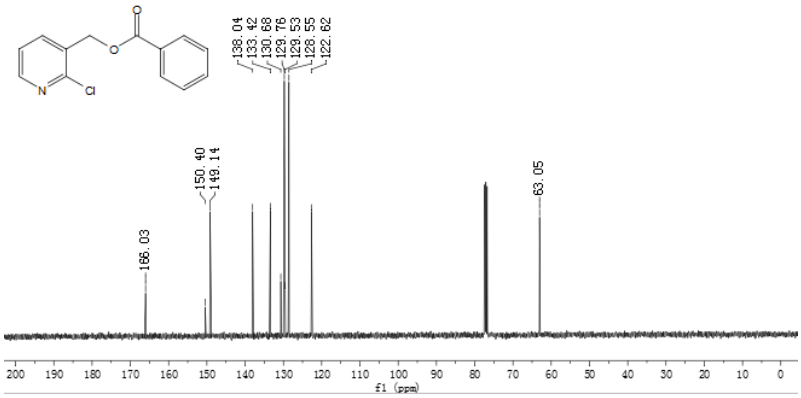
^{1}H-NMR spectrum of (4-chloropyridin-2-yl)methyl benzoate (3i)

^{13}C-NMR spectrum of (4-chloropyridin-2-yl)methyl benzoate (3i)



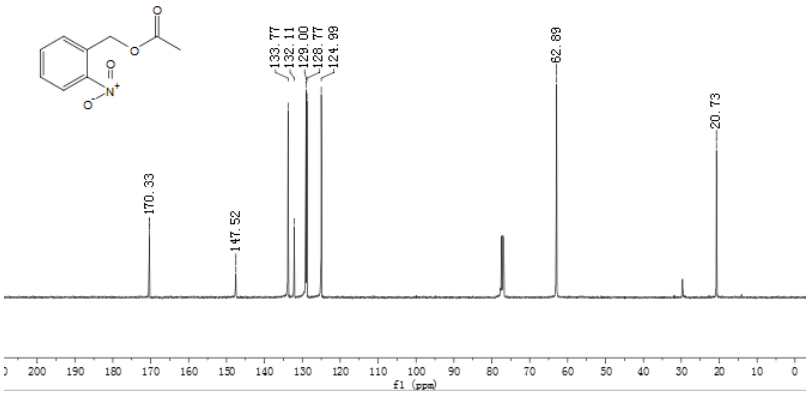
^{1}H-NMR spectrum of (2-chloropyridin-3-yl)methyl benzoate (3j)

^{13}C-NMR spectrum of (2-chloropyridin-3-yl)methyl benzoate (3j)

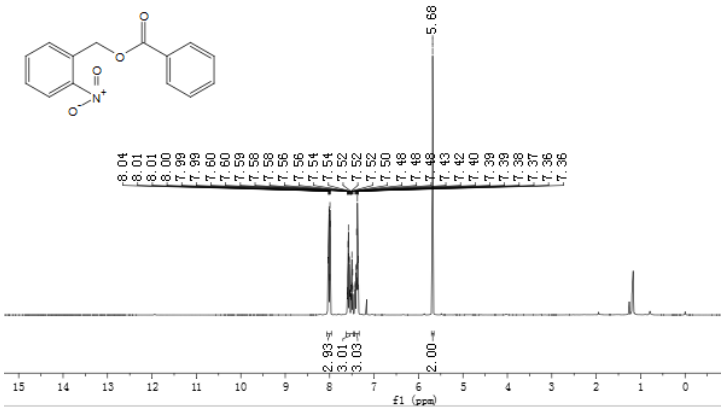


^{1}H- NMR spectrum of 2-nitrobenzyl acetate (3k)

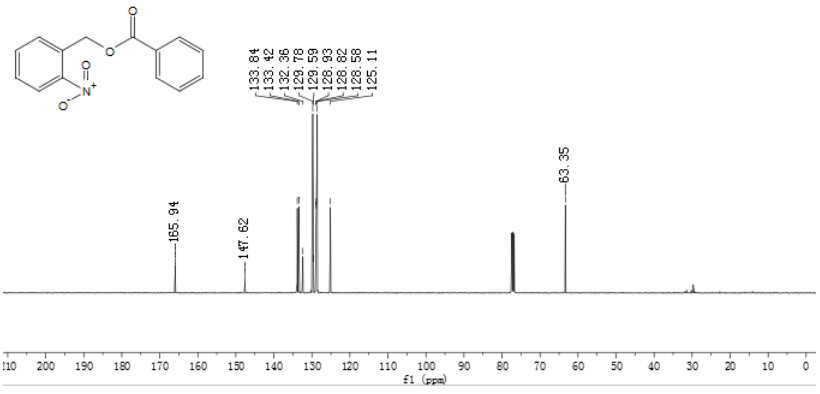
^{13}C-NMR spectrum of 2-nitrobenzyl acetate (3k)



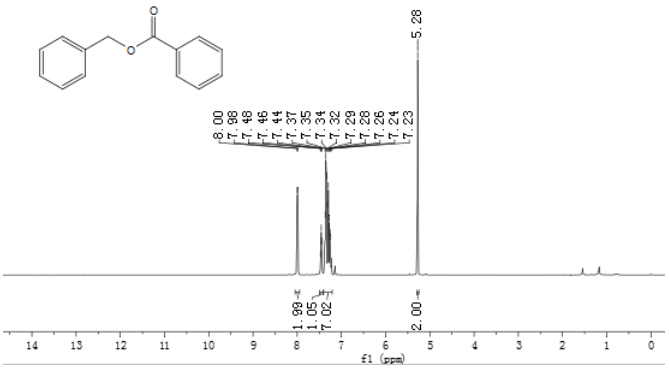
^{1}H-NMR spectrum of 2-nitrobenzyl benzoate (3l).



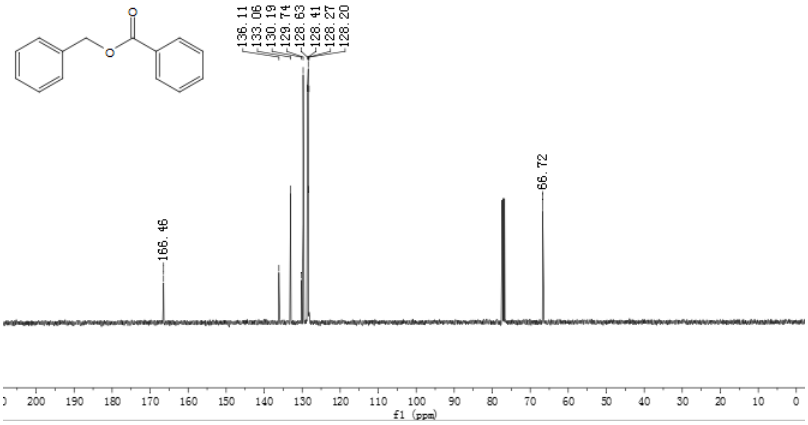
^{13}C-NMR spectrum of 2-nitrobenzyl benzoate (3l)



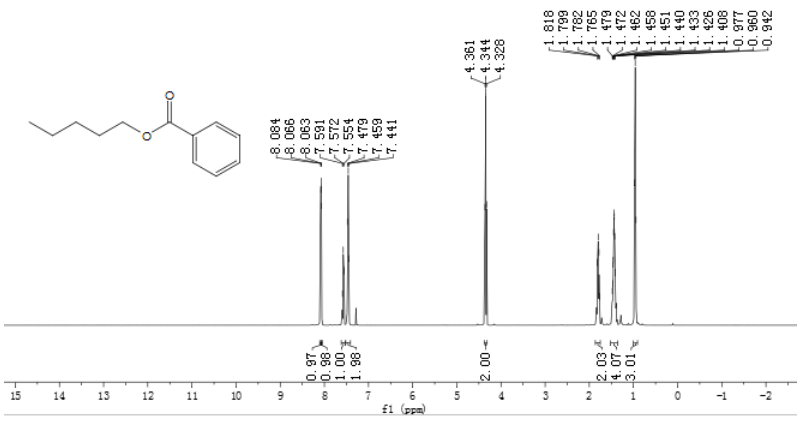
^{1}H- NMR spectrum of benzyl benzoate (3m)



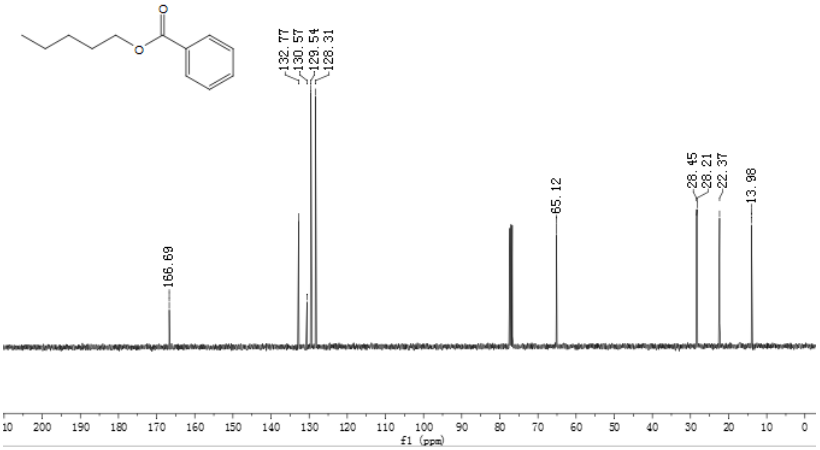
^{13}C-NMR spectrum of benzyl benzoate (3m)



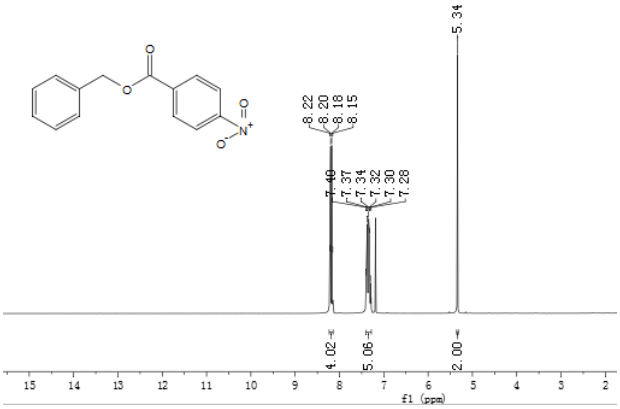
^{1}H- NMR spectrum of pentyl benzoate (3n)



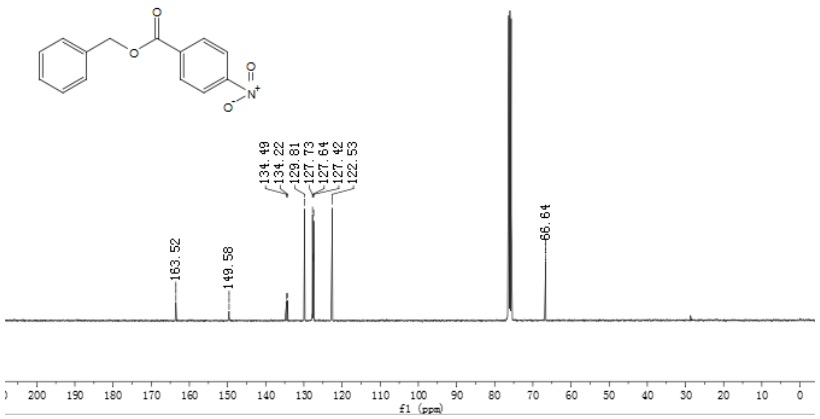
^{13}C-NMR spectrum of pentyl benzoate (3n)



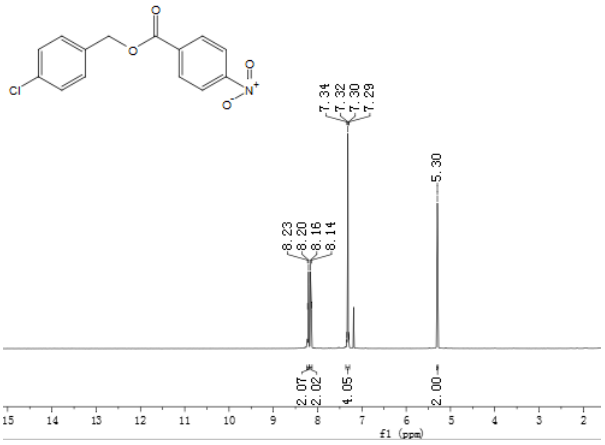
^{1}H-NMR spectrum of benzyl 4-nitrobenzoate (4a)



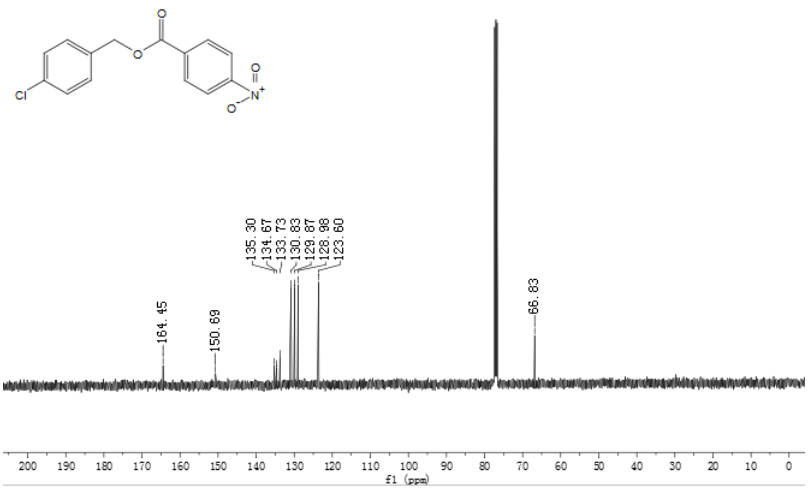
^{13}C-NMR spectrum of benzyl 4-nitrobenzoate (4a)



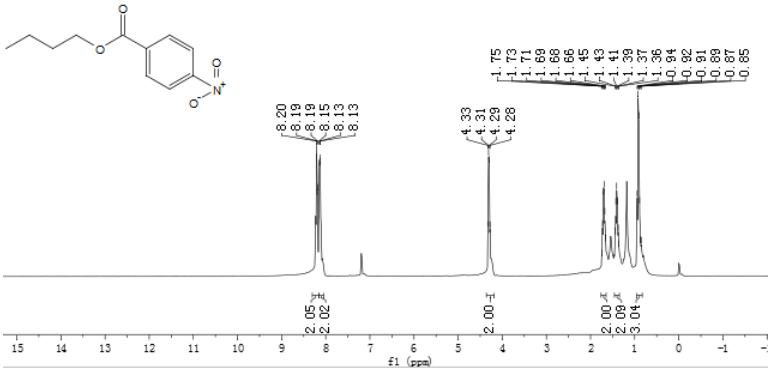
^{1}H-NMR spectrum of 4-chlorobenzyl 4-nitrobenzoate (4b)



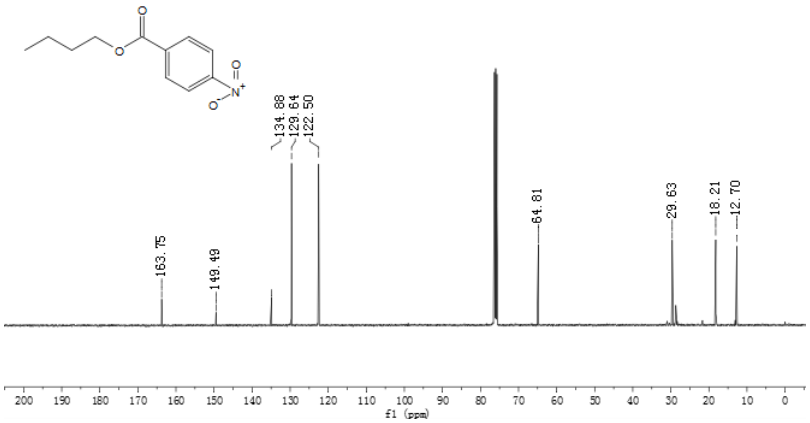
^{13}C-NMR spectrum of 4-chlorobenzyl 4-nitrobenzoate (4b)



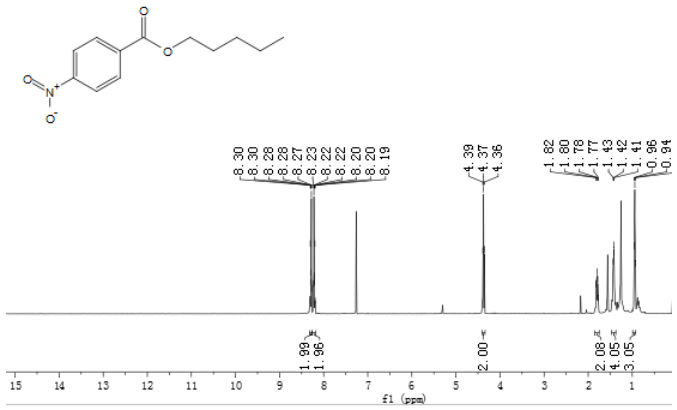
^{1}H-NMR spectrum of butyl-4-nitrobenzoate (4c).



^{13}C-NMR spectrum of butyl-4-nitrobenzoate (4c).

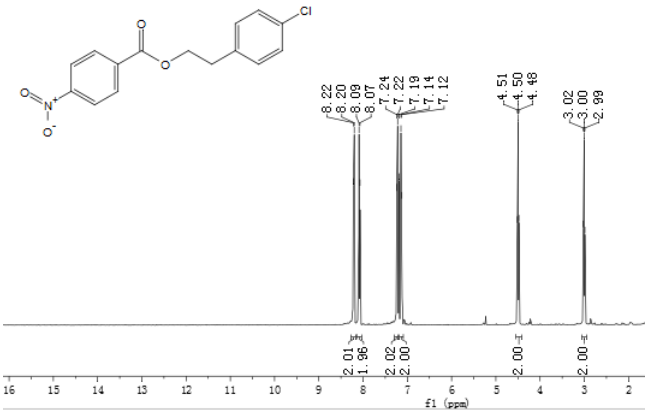


^{1}H-NMR spectrum of pentyl 4-nitrobenzoate (4d)

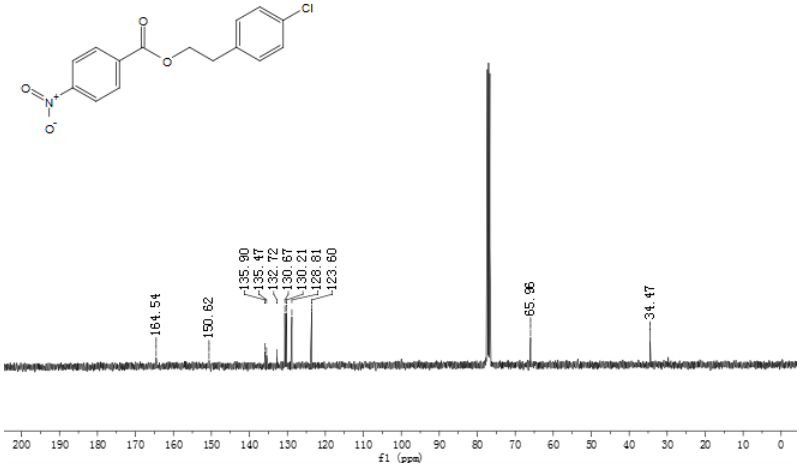


^{13}C-NMR spectrum of pentyl 4-nitrobenzoate (4d)

^{1}H-NMR spectrum of 4-chlorophenethyl 4-nitrobenzoate (4e)

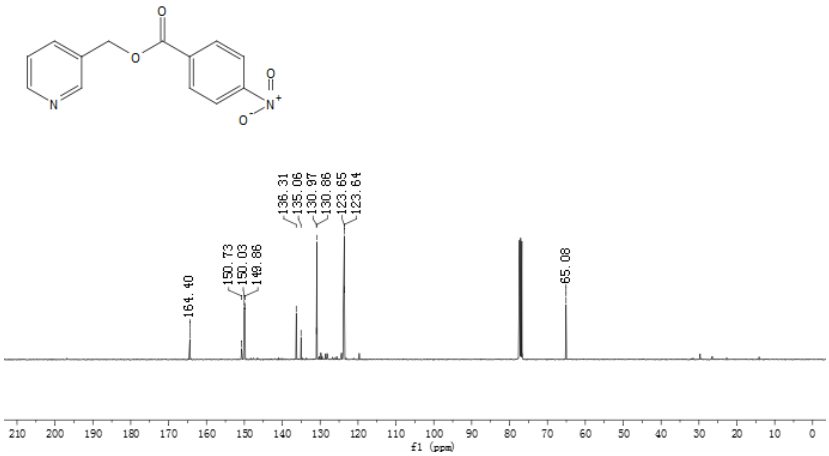


^{13}C-NMR spectrum of 4-chlorophenethyl 4-nitrobenzoate (4e)



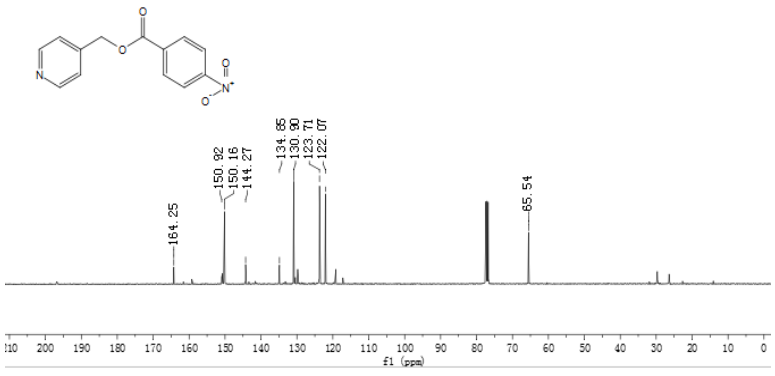
^{1}H-NMR spectrum of 3-Pyridylmethyl-4-nitrobenzoate (4f)

^{13}C-NMR spectrum of 3-Pyridylmethyl-4-nitrobenzoate (4f)

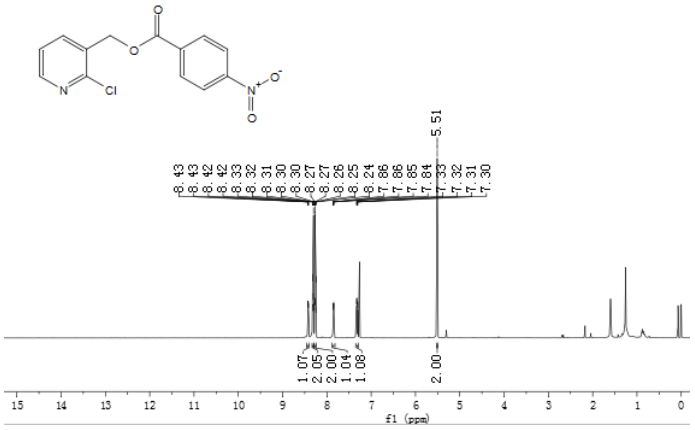


^{1}H-NMR spectrum of 4-Pyridylmethyl-4-nitrobenzoate (4g).

^{13}C-NMR spectrum of 4-Pyridylmethyl-4-nitrobenzoate (4g).



^{1}H-NMR spectrum of (2-chloropyridin-3-yl)methyl 4-nitrobenzoate (4h).



^{13}C-NMR spectrum of (2-chloropyridin-3-yl)methyl 4-nitrobenzoate (4h)