Supporting Information for

Copper-Catalyzed Highly Efficient Ester Formation from Carboxylic acids /Esters and Formates

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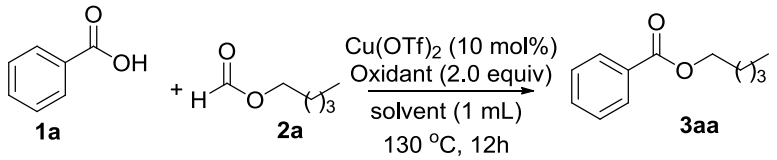
Table of Contents 1

General Information: $Cu(OTf)_2$ was purchased from Accela ChemBio Co., Ltd.. Solvent was dried by molecular sieve 5A. Unless otherwise noted, the other commercial materials were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker ARX400. High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ and referenced to residual $CHCl_3$ at 7.26 ppm, and ^{13}C NMR spectra were referenced to the central peak of $CDCl_3$ at 77.0 ppm. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance.

I. General procedure for screening of reaction conditions: A 50 mL sealed tube (with a Teflon high pressure valve) equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (18.1 mg, 0.05 mmol), followed by benzoic acid (61.1 mg, 0.5 mmol), n-pentyl formate, TBHP, and solvents. After the reaction mixture was stirred at 130 °C for 12 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate and water and then filtered through a small pad of Celite. The filtrate was washed with saturated aqueous $NaHCO_3$ (5 mL) and brine (5 mL, twice). The organic phase was dried (Na_2SO_4) and concentrated in vacuo. The yield was determined by ^1H NMR analysis of crude product using $CHCl_2CHCl_2$ as the internal standard.

Table 1. Survery of Reaction Conditions



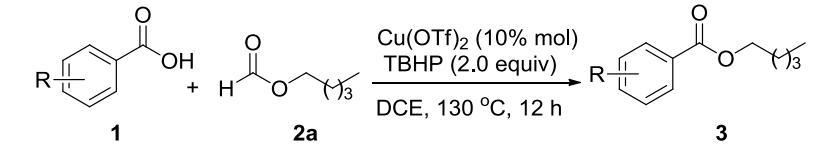
entry	2a	solvent	oxidant	yield %[a]
1	4.0 equiv.	1,4-dioxane	$K_2S_2O_8$	15
2	4.0 equiv.	CH_3CN	$K_2S_2O_8$	NR
3	4.0 equiv.	DMA	$K_2S_2O_8$	NR
4	4.0 equiv.	DMSO	$K_2S_2O_8$	5
5	4.0 equiv.	DCE	$K_2S_2O_8$	27
6	4.0 equiv.	DCE	$(NH_4)_2SO_8$	20
7	4.0 equiv.	DCE	oxone	<3
8	4.0 equiv.	DCE	AcOOH	17
9	4.0 equiv.	DCE	DCP	78
10	4.0 equiv.	DCE	DTBP	91
11	4.0 equiv.	DCE	TBHP	94
12	4.0 equiv.	DCE	TBHP	54[b]
13	4.0 equiv.	DCE	TBHP	<3[c]
14	3.0 equiv.	DCE	TBHP	93(85[d])
15	2.0 equiv.	DCE	TBHP	66
16	1.0 equiv.	DCE	TBHP	49
17	3.0 equiv.	DCE	-----	24
18	3.0 equiv.	DCE	TBHP	<3[e]
19	3.0 equiv.	DCE	TBHP	67[f]

[a] The yields were determined by ^{1}H NMR analysis of crude products using $CHCl_2CHCl_2$ as the internal standard. DBPT = *tert*-Butyl peroxide, TBHP = *tert*-Butyl hydroperoxide, DCP = Dicumyl peroxide, DCE = 1,2-Dichloroethane. Reaction condition: **1a** (0.5 mmol), **2a** (3.0 equiv), $Cu(OTf)_2$ (10% mol), TBHP (2.0 equiv), 130 ℃, 12 h, all of the reactions were run under air. [b] $Cu(OTf)_2$ = 5% mol, [c] $Cu(OTf)_2$ = 1% mol, [d] isolated yield. [e] No $Cu(OTf)_2$. [f] 110 ℃.

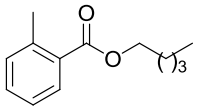
II. General procedure for Cu-catalyzed esterification/transesterification of carboxylic acids/esters： A 50 mL sealed tube (with a Teflon high pressure valve) equipped with a magnetic stir bar was charged with $Cu(OTf)_2$ (18.1 mg, 0.05 mmol) followed by carboxylic acid or benzoates (0.5 mmol), formats (1.5 mmol), THBP (100.2 μL, 1.0 mmol), and DCE (1.0 mL). After the reaction mixture was stirred at 130°C for 12 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate and water and then filtered through a small pad of Celite. The filtrate was washed with saturated aqueous $NaHCO_3$ (5 mL) and brine (5

mL, twice). The organic phase was dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel preparative TLC to give the corresponding product.

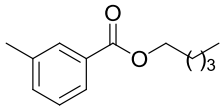
Scheme 1. Copper-Catalyzed Pentylation of Various Aromatic Carboxylic Acids.



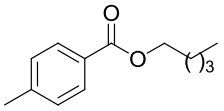
1 **2a** **3**



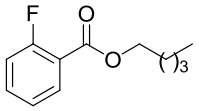
3ba 93%



3ca 85%



3da 88%



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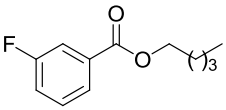

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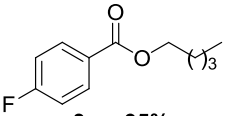
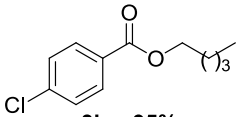


3ga 95%



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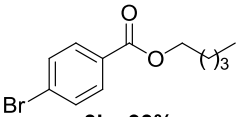

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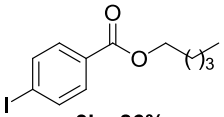

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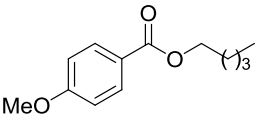

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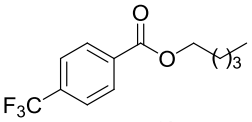
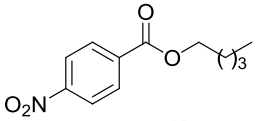


3la 89%



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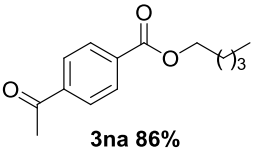

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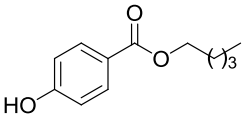

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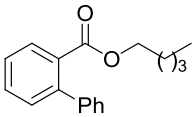

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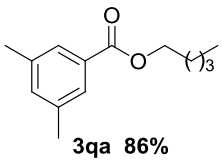

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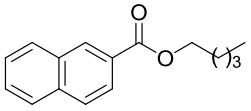

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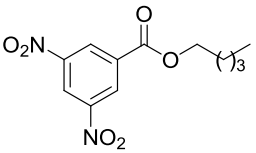

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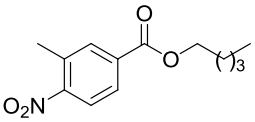

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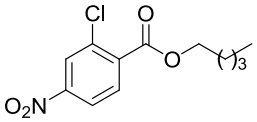

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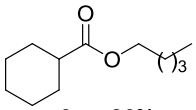

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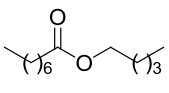

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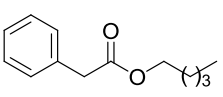

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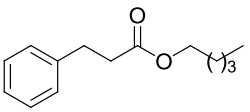

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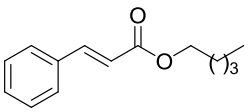
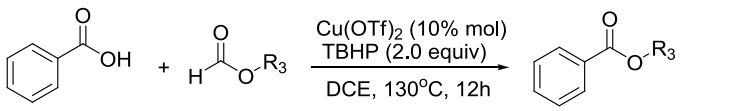


3za 71%

Table 2 Copper-Catalyzed Esterification of Benzoic Acids with Various Formates.



1a **2** **3**

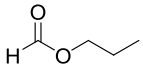
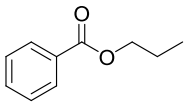
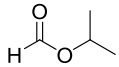
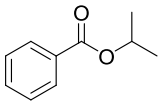
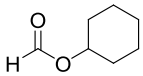
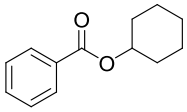
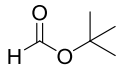
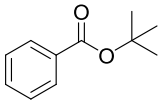
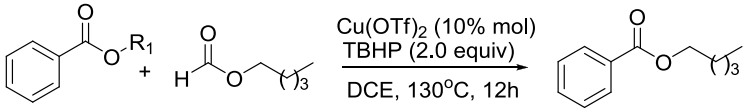
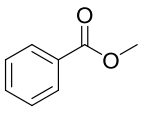
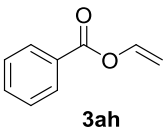
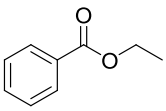
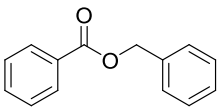
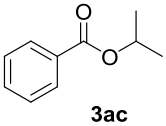
entry	substrate	product	yield
1	 **2b**	 **3ab**	82%
2	 **2c**	 **3ac**	51%[b]
3	 **2d**	 **3ad**	47%
4	 **2e**	 **3ae**	0%

Table 3 Copper-Catalyzed Transesterification of Benzoates with Pentyl Formate.

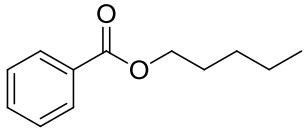


3a **2a** **3aa**

entry	substrate	yield	entry	substrate	yield
1	 **3af**	91%	4	 **3ah**	86%
2	 **3ag**	72%	5	 **3ai**	74%
3	 **3ac**	92%			

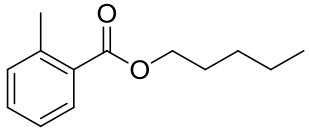
III. Characterization of the synthesized compounds

pentyl benzoate(3aa)



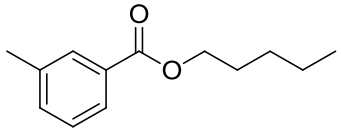
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 7.8 Hz, 2H), 7.55 (m, 1H), 7.44 (m, 2H), 4.32 (t, J = 6.7 Hz, 2H), 1.84-1.69 (m, 2H), 1.49-1.31 (m, 4H), 0.93 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.64, 132.73, 130.52, 129.49, 128.27, 65.08, 28.41, 28.18, 22.34, 13.95. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{16}NaO_2^+$: 215.1043 $(M + Na)^+$, found: 215.1042.

pentyl 2-methylbenzoate(3ba)



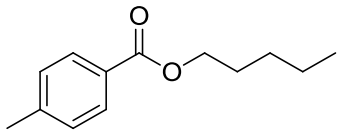
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92-7.90 (m, 1H),7.43-7.36 (m, 1H), 7.29-7.20 (m, 2H), 4.30 (t, J = 6.8 Hz, 2H), 2.60 (s, 3H), 1.81-1.71 (m, 2H), 1.49-1.33 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.77, 139.96, 131,75, 131,60, 130,47, 130.02, 125.63, 64.88, 28.43, 28.26, 22.34, 21.70, 13.96. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{18}NaO_2^+$: 229.1199 $(M + Na)^+$, found: 229.1201.

pentyl 3-methylbenzoate(3ca)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-7.81 (m, 2H), 7.40-7.28 (m, 2H), 4.31 (t, J = 6.8 Hz, 2H), 2.40 (s, 3H), 1.83-1.71 (m, 2H), 1.49-1.30 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.84, 138.05, 133.50, 130.47, 130.04, 128.18, 126.64, 65.04, 28.44, 28.18, 22.35, 21.25, 13.96. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{18}NaO_2^+$: 229.1199 $(M + Na)^+$, found: 229.1196.

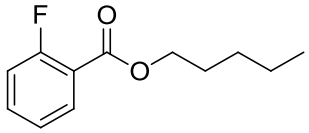
pentyl 4-methylbenzoate(3da)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.30 (t, J = 6.8 Hz, 2H), 2.40 (s, 3H), 1.83-1.70 (m, 2H), 1.49-1.32 (m, 4H), 0.93 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.70, 143.32,

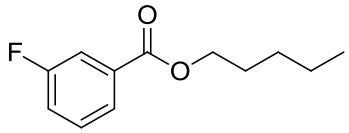
129.52, 128.97, 127.81, 64.88, 28.43, 28.18, 22.33, 21.57, 13.93. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{18}NaO_2^+$: 229.1199 $(M + Na)^+$, found: 229.1199.

pentyl 2-fluorobenzoate(3ea)



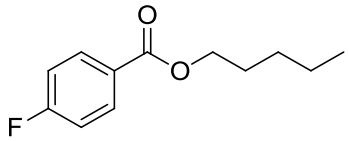
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97-7.87 (m, 1H), 7.55-7.43 (m, 1H), 7.23-7.07 (m, 2H), 4.32 (t, J = 6.8 Hz, 2H), 1.82-1.68 (m, 2H), 1.48-1.31 (m, 4H), 0.92 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.46 (d, $J_{C\text{-}F}$ = 3.6 Hz), 161.89 (d, $J_{C\text{-}F}$ = 258.2 Hz), 134.19 (d, $J_{C\text{-}F}$ = 8.9 Hz), 131.99, 123.81 (d, $J_{C\text{-}F}$ = 3.9 Hz), 119.07 (d, $J_{C\text{-}F}$ = 9.8 Hz), 116.85 (d, $J_{C\text{-}F}$ = 22.3 Hz), 65.39, 28.29, 28.04, 22.59, 13.88. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{15}FNaO_2^+$: 233.0948 $(M + Na)^+$, found: 233.0949.

pentyl 3-fluorobenzoate(3fa)



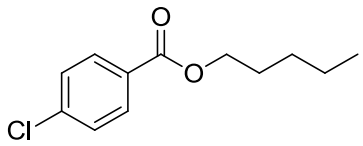
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.79 (m, 1H), 7.76-7.67 (m, 1H), 7.45-7.35 (m, 1H), 7.29-7.19 (m, 1H), 4.31 (t, J = 6.8 Hz, 2H), 1.82-1.70 (m, 2H), 1.48-1.30 (m, 4H), 0.93 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.48 (d, $J_{C\text{-}F}$ = 3.0 Hz), 162.53 (d, $J_{C\text{-}F}$ = 254.3 Hz), 132.71 (d, $J_{C\text{-}F}$ = 7.4 Hz), 129.90 (d, $J_{C\text{-}F}$ = 7.7 Hz), 125.23 (d, $J_{C\text{-}F}$ = 3.1 Hz), 119.79 (d, $J_{C\text{-}F}$ = 21.2 Hz), 116.39 (d, $J_{C\text{-}F}$ = 22.8Hz), 65.47, 28.35, 28.14, 22.31, 13.91. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{15}FNaO_2^+$: 233.0948 $(M + Na)^+$, found: 233.0944.

pentyl 4-fluorobenzoate(3ga)



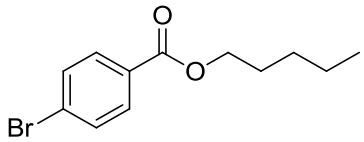
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11-7.99 (m, 2H), 7.16-7.05 (m, 2H), 4.30 (t, J = 6.8 Hz, 2H), 1.81-1.70 (m, 2H), 1.47-1.31 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.67, 165.66 (d, $J_{C\text{-}F}$ = 252.0 Hz), 132.01 (d, $J_{C\text{-}F}$ = 9.2 Hz), 126.77 (d, $J_{C\text{-}F}$ = 3.0 Hz), 115.39 (d, $J_{C\text{-}F}$ = 21.8 Hz), 65.23, 28.39, 28.16, 22.32, 12.93. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{15}FNaO_2^+$: 233.0948 $(M + Na)^+$, found: 233.0942.

pentyl 4-chlorobenzoate(3ha)



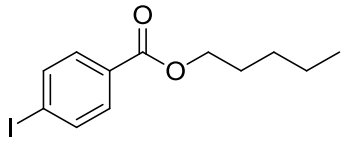
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 4.30 (t, J = 6.7 Hz, 2H), 1.85-1.70 (m, 2H), 1.47-1.32 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.76, 139.20, 130.90, 128.99, 128.63, 65.35, 28.37, 28.15, 22.32, 13.93. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{15}ClNaO_2^+$: 249.0653 $(M + Na)^+$, found: 249.0629.

pentyl 4-bromobenzoate(3ia)



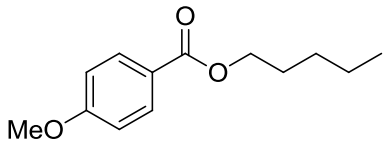
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 4.30 (t, J = 6.7 Hz, 2H), 1.82-1.69 (m, 2H), 1.47-1.29 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.84, 131.60, 131.02, 129.40, 127.82, 65.34, 28.34, 28.12, 22.30, 13.92. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{15}BrNaO_2^+$: 293.0148 $(M + Na)^+$, found: 293.0153.

pentyl 4-iodobenzoate(3ja)



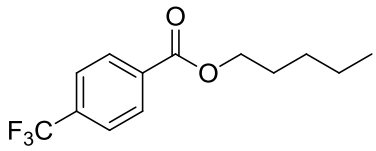
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 4.30 (t, J = 6.7 Hz, 2H), 1.82-1.69 (m, 2H), 1.47-1.28 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.09, 137.64, 130.96, 129.99, 100.47, 65.35, 28.35, 28.13, 22.31, 13.94. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{15}INaO_2^+$: 341.0009 $(M + Na)^+$, found: 341.0009.

pentyl 4-methoxybenzoate(3ka)



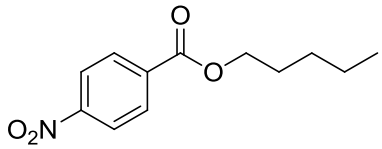
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.9 Hz, 2H), 4.27 (t, J = 6.7 Hz, 2H), 3.84 (s, 3H), 1.81-1.67 (m, 2H), 1.49-1.32 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.39, 163.22, 131.48, 123.00, 113.52, 64.77, 55.35, 28.46, 28.20, 22.34, 13.94. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{18}NaO_3^+$: 245.1148 $(M + Na)^+$, found: 245.1145.

pentyl 4-(trifluoromethyl)benzoate(3la)



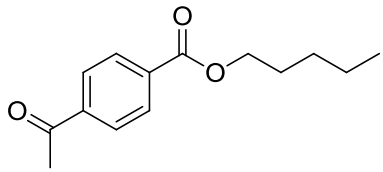
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (d, J = 8.2 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 4.34 (t, J = 6.7 Hz, 2H), 1.81-1.67 (m, 2H), 1.49-1.32 (m, 4H), 0.92 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.44, 134.31 (q, $J_{C\text{-}F}$ = 32.4 Hz), 133.74, 129.92, 125.35 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.65 (q, $J_{C\text{-}F}$ = 271.0 Hz), 65.69, 28.33, 28.14, 22.32, 13.93.

pentyl 4-nitrobenzoate(3ma)



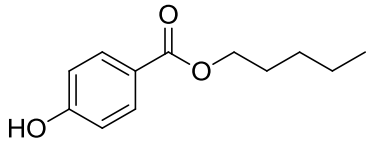
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 4.36 (t, J = 6.8 Hz, 2H), 1.85-1.71 (m, 2H), 1.48-1.32 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.69, 150.46, 135.86, 130.60, 123.45, 66.06, 28.27, 28.08, 22.28, 13.89. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{15}NNaO_4^+$: 260.0893 $(M + Na)^+$, found: 260.0881.

pentyl 4-acetylbenzoate(3na)



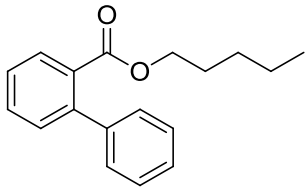
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 4.34 (t, J = 6.7 Hz, 2H), 2.64 (s, 3H), 1.85-1.70 (m, 2H), 1.48-1.33 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.50, 165.77, 140.15, 134.30, 129.75, 128.15, 65.60, 28.35, 28.15, 26.83, 22.32, 13.94. HRMS (ESI-TOF) *m/z*: calcd for $C_{14}H_{18}NaO_3^+$: 257.1148 $(M + Na)^+$, found: 257.1148.

pentyl 4-hydroxybenzoate(3oa)



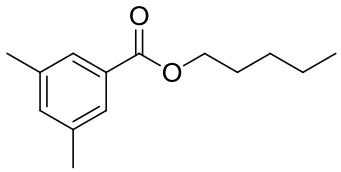
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 6.74 (br, 1H), 4.29 (t, J = 6.6 Hz, 2H), 1.81-1.69 (m, 2H), 1.47-1.29 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.09, 160.32, 131.88, 122.56, 115.25, 65.14, 28.42, 28.18, 22.33, 13.94. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{16}NaO_3^+$: 231.0992 $(M + Na)^+$, found: 231.0986.

pentyl [1,1'-biphenyl]-2-carboxylate(3pa)



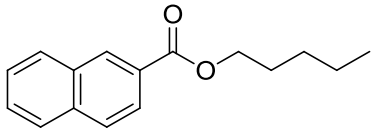
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87-7.79 (m, 1H), 7.67-7.50 (m, 1H), 7.47-7.28 (m, 7H), 4.03 (t, *J* = 6.8 Hz, 2H), 1.42-1.29 (m, 2H), 1.26-1.16 (m, 2H), 1.10-0.99 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.00, 142.31, 141.54, 131.43, 131.00, 130.62, 129.70, 128.35, 128.00, 127.14, 127.10, 65.18, 27.91, 27.86, 22.24, 13.85. HRMS (ESI-TOF) *m/z*: calcd for $C_{18}H_{20}NaO_2^+$: 291.1356 $(M + Na)^+$, found: 291.1367.

pentyl 3,5-dimethylbenzoate(3qa)



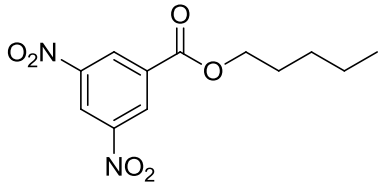
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (s, 2H), 7.18 (s, 1H), 4.30 (t, *J* = 6.7 Hz, 2H), 2.36 (s, 6H), 1.83-1.70 (m, 2H), 1.47-1.34 (m, 4H), 0.94 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.98, 137.90, 134.38, 130.40, 127.20, 64.96, 28.43, 28.16, 22.33, 21.11, 13.93. HRMS (ESI-TOF) *m/z*: calcd for $C_{14}H_{20}NaO_2^+$: 243.1356 $(M + Na)^+$, found: 243.1351.

pentyl 2-naphthoate(3ra)



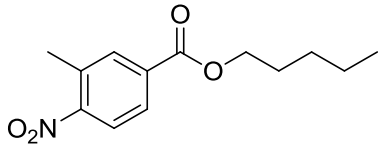
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 8.13-8.02 (m, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.63-7.48 (m, 2H), 4.39 (t, *J* = 6.8 Hz, 2H), 1.89-1.77 (m, 2H), 1.54-1.36 (m, 4H), 0.96 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.78, 135.44, 132.48, 130.88, 129.29, 128.08, 128.03, 127.76, 127.70, 126.52, 125.22, 65.24, 28.46, 28.20, 22.36, 13.96. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{18}NaO_2^+$: 265.1199 $(M + Na)^+$, found: 265.1197.

pentyl 3,5-dinitrobenzoate(3sa)



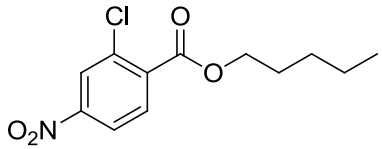
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.26-9.20 (m, 1H), 9.18-9.11 (m, 2H), 4.30 (t, *J* = 6.8 Hz, 2H), 1.90-1.77 (m, 2H), 1.50-1.34 (m, 4H), 0.94 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.53, 148.66, 134.16, 129.37, 122.25, 67.11, 28.22, 27.99, 22.27, 13.89.

pentyl 3-methyl-4-nitrobenzoate(3ta)



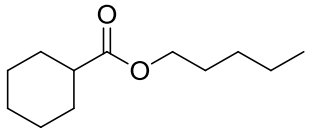
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.97 (s, 2H), 4.34 (t, *J* = 6.8 Hz, 2H), 2.62 (s, 3H), 1.85-1.72 (m, 2H), 1.49-1.30 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.88, 151.79, 134.11, 133.89, 133.38, 127.97, 124.50, 65.94, 28.30, 28.10, 22.30, 20.03, 13.92. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{17}NNaO_4^+$: 274.1050 $(M + Na)^+$, found: 274.1027.

pentyl 2-chloro-4-nitrobenzoate(3ua)



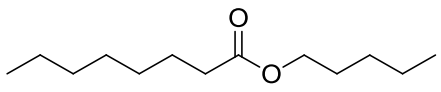
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (d, *J* = 2.4 Hz, 1H), 8.18-8.11 (m, 2H), 7.94 (d, *J* = 8.4 Hz, 1H), 4.38 (t, *J* = 6.8 Hz, 2H), 1.85-1.73 (m, 2H), 1.49-1.31 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.34, 149.34, 136.28, 134.64, 131.89, 125.94, 121.40, 66.60, 28.17, 28.05, 22.24, 13.90. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{14}ClNNaO_4^+$: 294.0504 $(M + Na)^+$, found: 294.0508.

pentyl cyclohexanecarboxylate(3va)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.00 (t, *J* = 6.7 Hz, 2H), 2.30-2.17 (m, 1H), 1.91-1.09 (m, 16H), 0.86 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.02, 64.09, 43.17, 28.95, 28.28, 28.00, 25.70, 25.37, 22.22, 13.83. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{22}NaO_2^+$: 221.1512 $(M + Na)^+$, found: 221.1511.

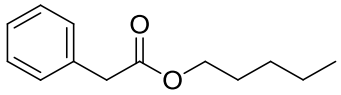
pentyl octanoate(3wa)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.00 (t, *J* = 6.8 Hz, 2H), 2.23 (t, *J* = 7.6 Hz, 2H), 1.67-1.47 (m, 4H), 1.36-1.14 (m, 12H), 0.95-0.71 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.75, 64.20, 34.26, 31.58, 29.02, 28.84, 28.28, 28.01, 24.92,

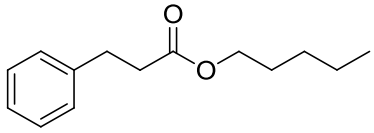
22.49, 22.22, 13.90, 13.80. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{26}NaO_2^+$: 237.1825 $(M + Na)^+$, found: 237.1823.

pentyl 2-phenylacetate(3xa)



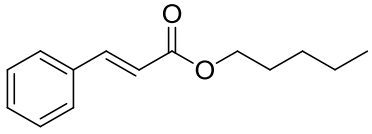
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.24 (m, 5H), 4.11 (t, *J* = 6.8 Hz, 2H), 3.64 (s, 2H), 1.72-1.57 (m, 2H), 1.45-1.25 (m, 4H), 0.91 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.65, 134.18, 128.21, 128.49, 126.98, 64.99, 41.47, 28.23, 27.97, 22.24, 13.91. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{18}NaO_2^+$: 229.1199 $(M + Na)^+$, found: 229.1194.

pentyl 3-phenylpropanoate(3ya)



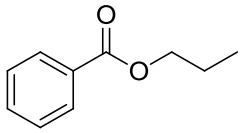
Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.17 (m, 5H), 4.09 (t, *J* = 6.8 Hz, 2H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.65 (t, *J* = 7.7 Hz, 2H), 1.70-1.57 (m, 2H), 1.41-1.25 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.99, 140.56, 128.44, 128.26, 126.20, 64.62, 35.92, 30.99, 28.29, 28.02, 22.29, 13.93. HRMS (ESI-TOF) *m/z*: calcd for $C_{14}H_{20}NaO_2^+$: 243.1356 $(M + Na)^+$, found: 243.1355.

pentyl cinnamate(3za)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 16.0 Hz, 1H), 7.58-7.47 (m, 2H), 7.44-7.36 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.20 (t, *J* = 6.8 Hz, 2H), 1.78-1.67 (m, 2H), 1.45-1.32 (m, 4H), 0.99-0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.99, 140.56, 128.44, 128.26, 126.20, 64.62, 35.92, 30.99, 28.29, 28.02, 22.29, 13.93. HRMS (ESI-TOF) *m/z*: calcd for $C_{14}H_{18}NaO_2^+$: 241.1199 $(M + Na)^+$, found: 241.1200.

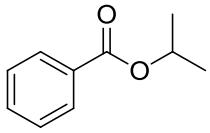
propyl benzoate(3ab)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, *J* = 7.6k Hz, 2H), 7.60-7.48 (m, 1H), 7.48-7.33 (m, 2H), 4.28 (t, *J* = 6.6 Hz, 2H), 1.89-1.67 (m, 2H), 1.03 (t, *J* =

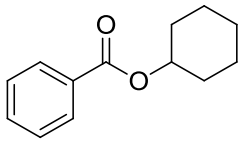
7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.51, 132.65, 130.44, 129.40, 128.18, 66.38, 22.02, 10.39. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_{12}NaO_2^+$: 187.0730 $(M + Na)^+$, found: 187.0732.

isopropyl benzoate(3ac)



Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09-7.97 (m, 2H), 7.59-7.50 (m, 1H), 7.48-7.37 (m, 2H), 5.31-5.19 (m, 1H), 1.37 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.07, 132.64, 130.90, 129.46, 128.21, 68.29, 21.92. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_{12}NaO_2^+$: 187.0730 $(M + Na)^+$, found: 187.0730.

cyclohexyl benzoate(3ad)

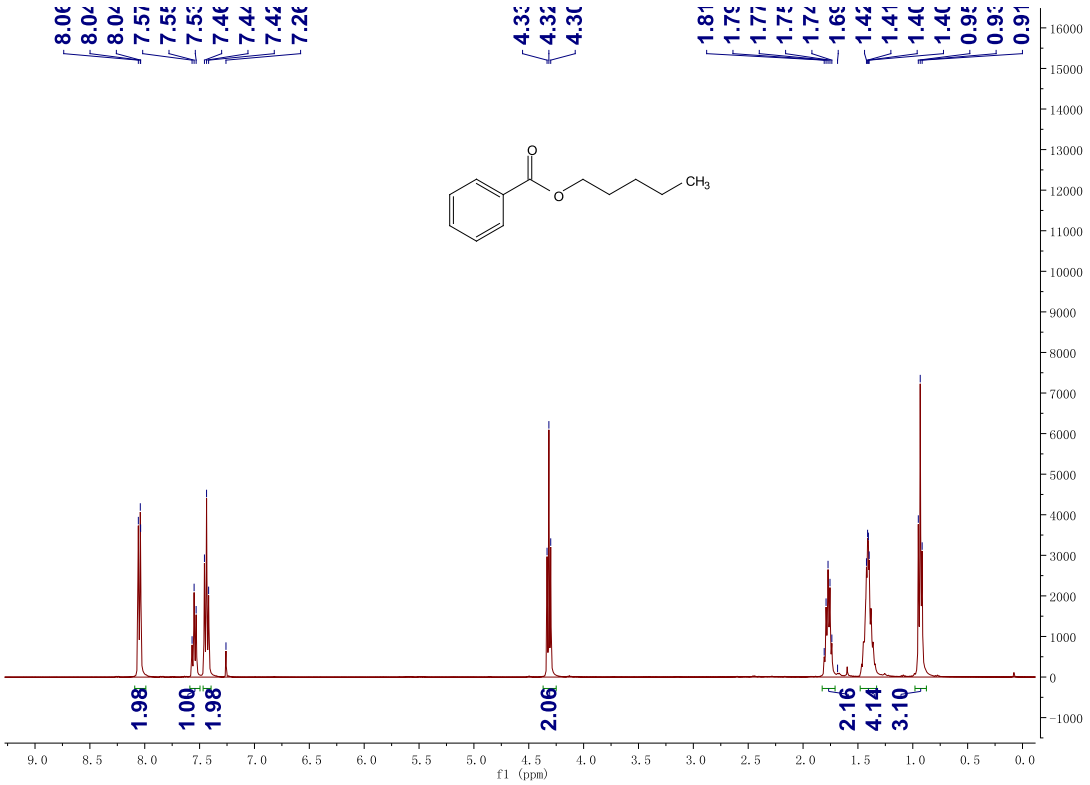


Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09-80.2 (m, 2H), 7.59-7.51 (d, *J* = 7.4 Hz, 1H), 7.47-7.40 (m, 2H), 5.10-4.96 (m, 1H), 2.02-1.89 (m, 2H), 1.95-1.71 (m, 2H), 1.59-1.30 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.98, 132.64, 131.01, 129.51, 128.24, 73.01, 31.64, 25.48, 23.65. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{16}NaO_2^+$: 227.1043 $(M + Na)^+$, found: 227.1042.

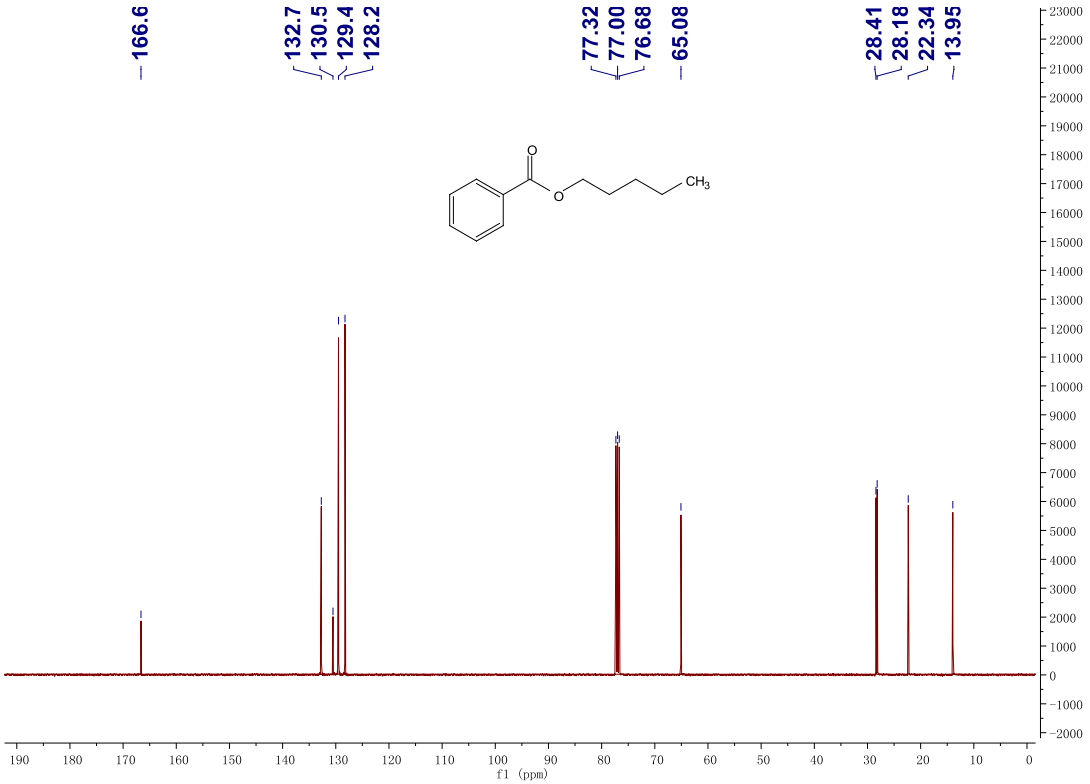
IV. NMR spectra

Compound 3aa

^{1}H NMR

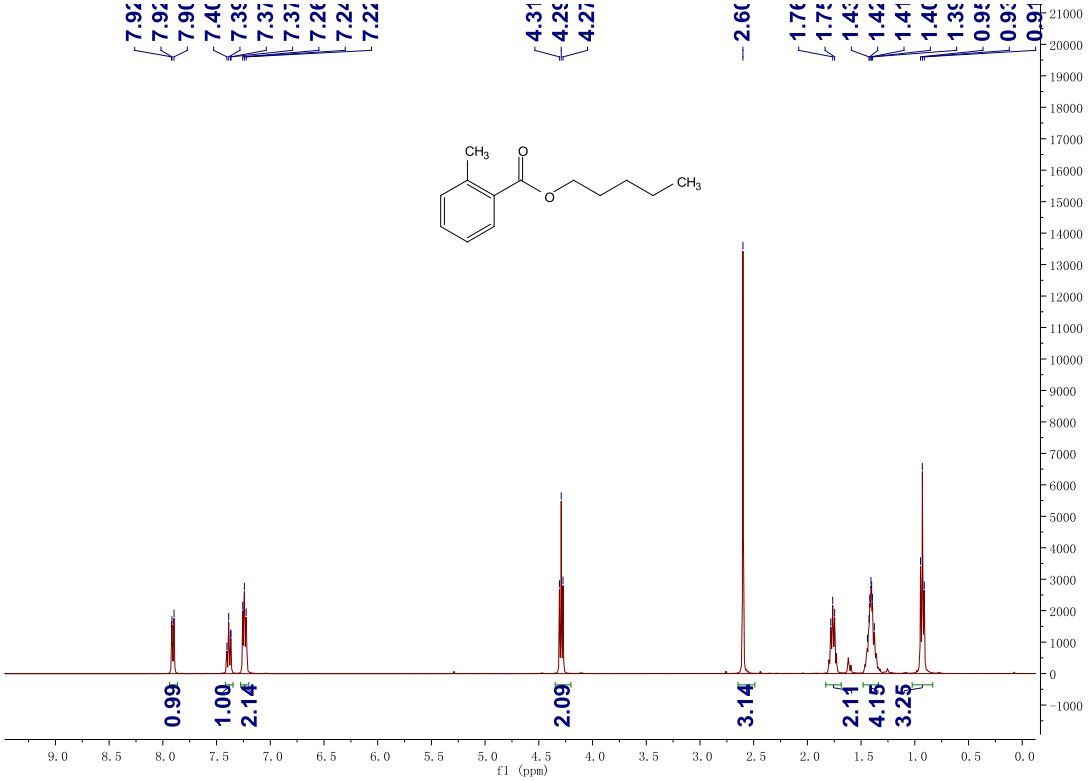


^{13}C NMR

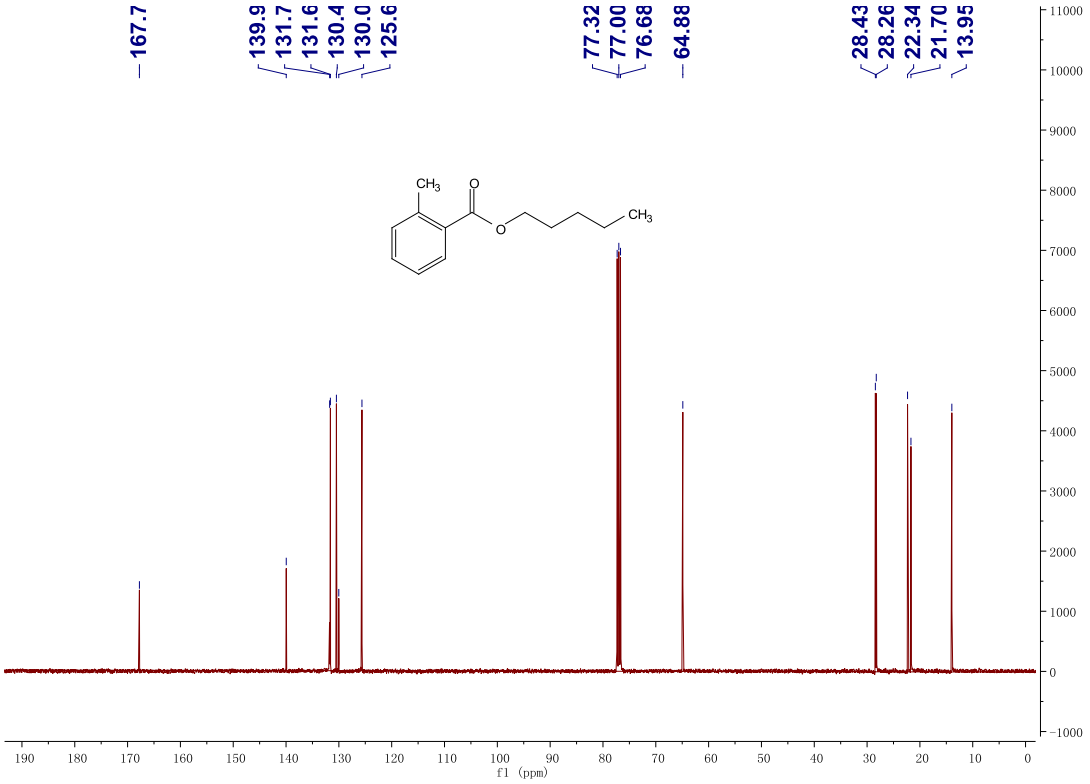


Compound 3ba

^{1}H NMR

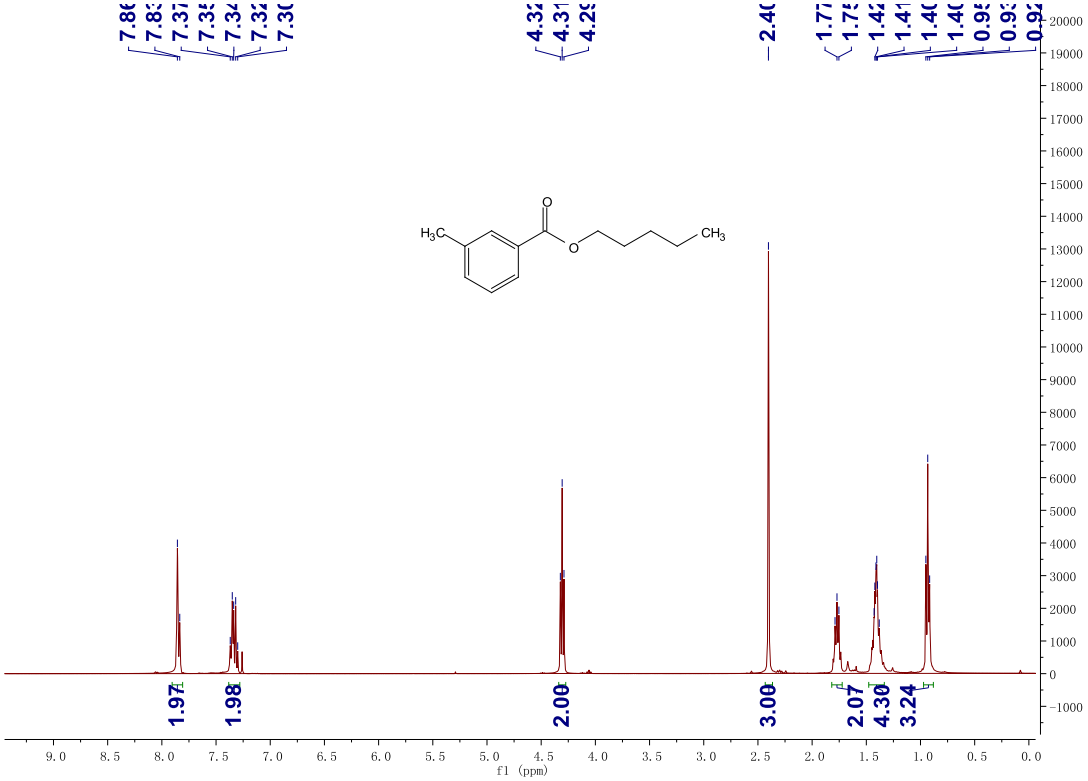


^{13}C NMR

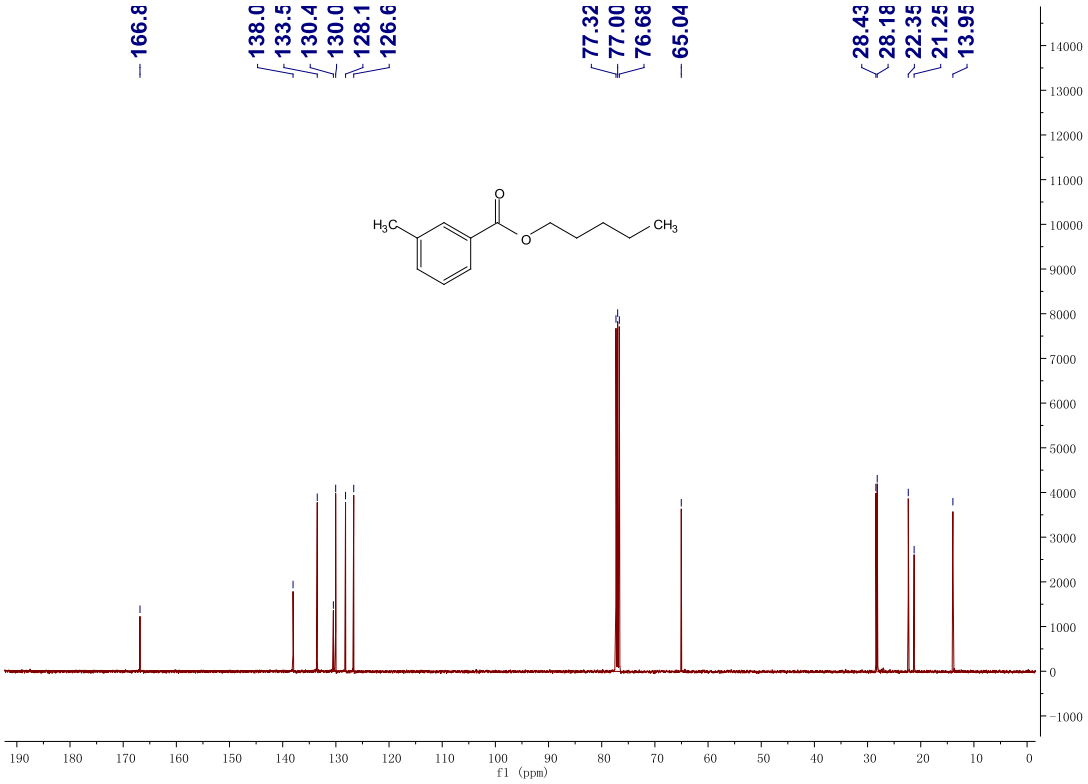


Compound 3ca

^{1}H NMR

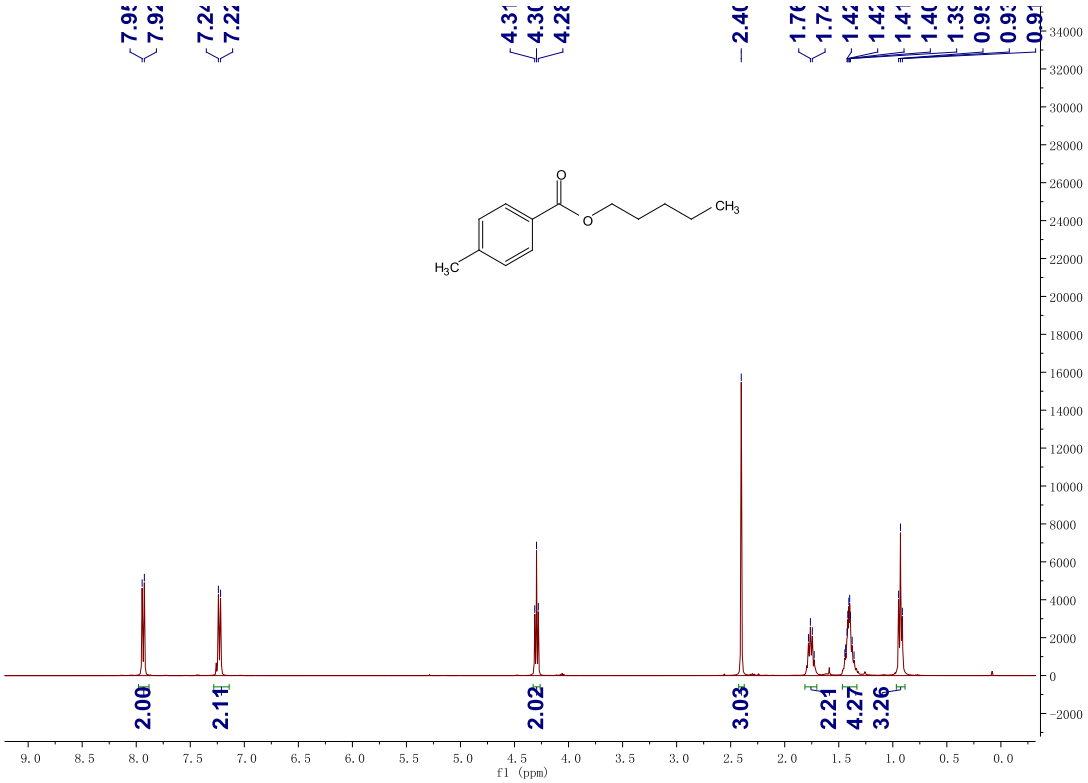


^{13}C NMR

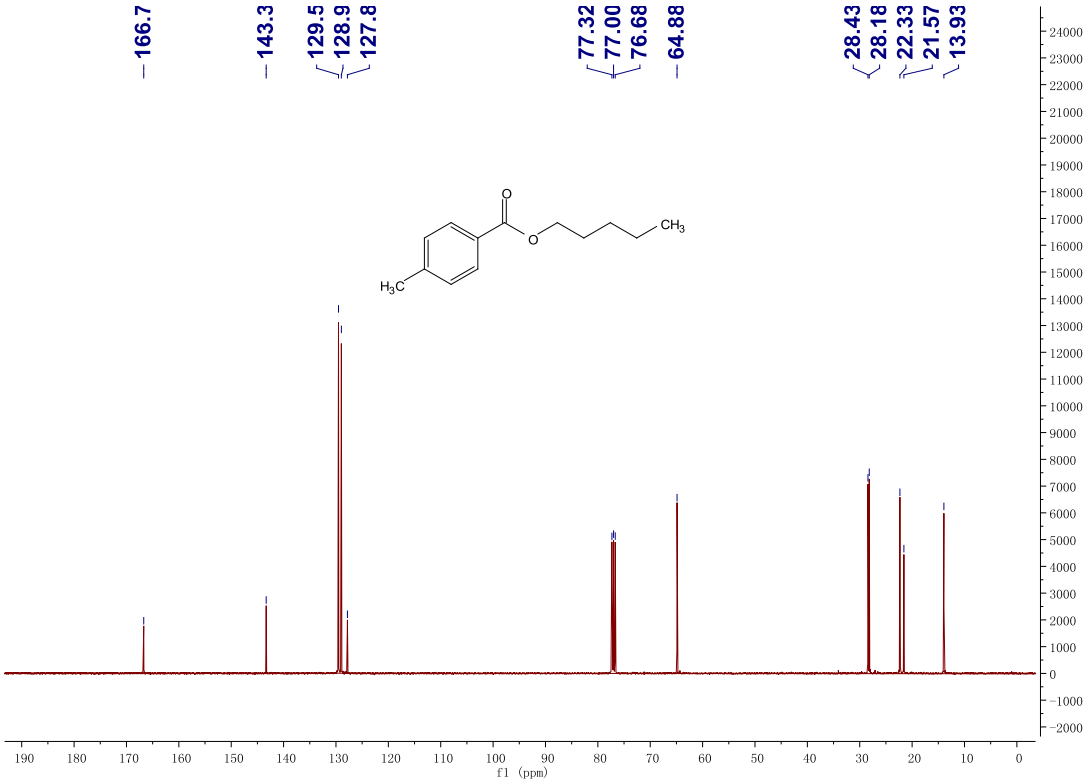


Compound 3da

^{1}H NMR

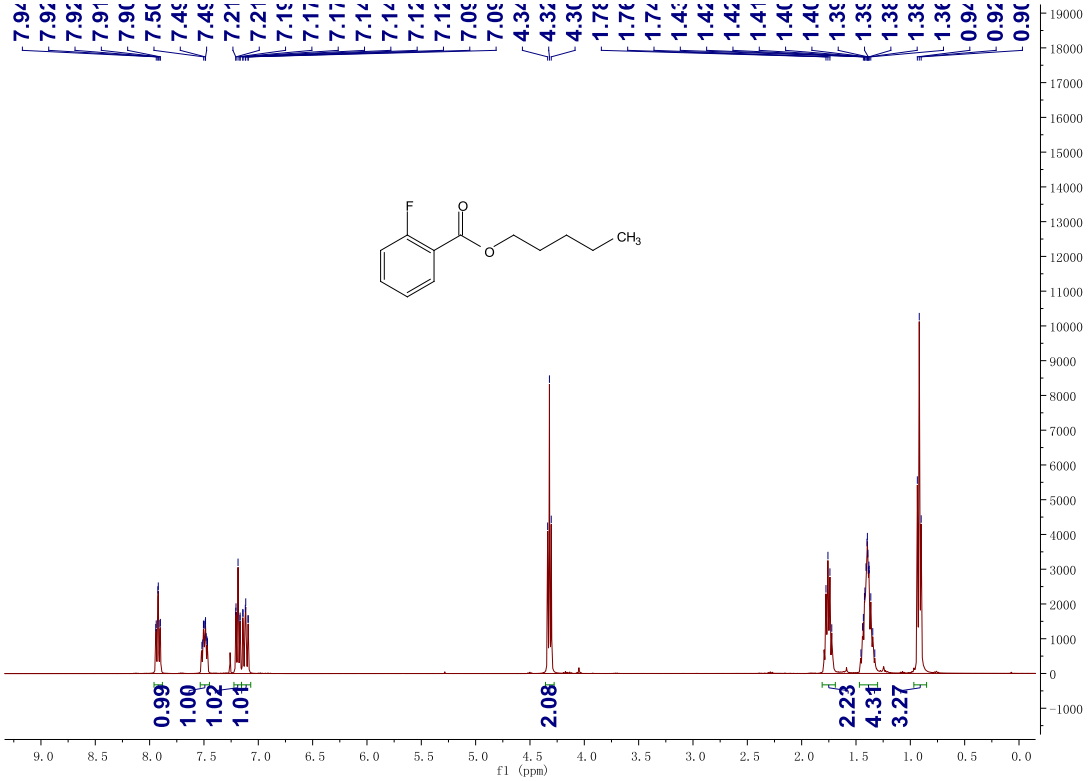


^{13}C NMR

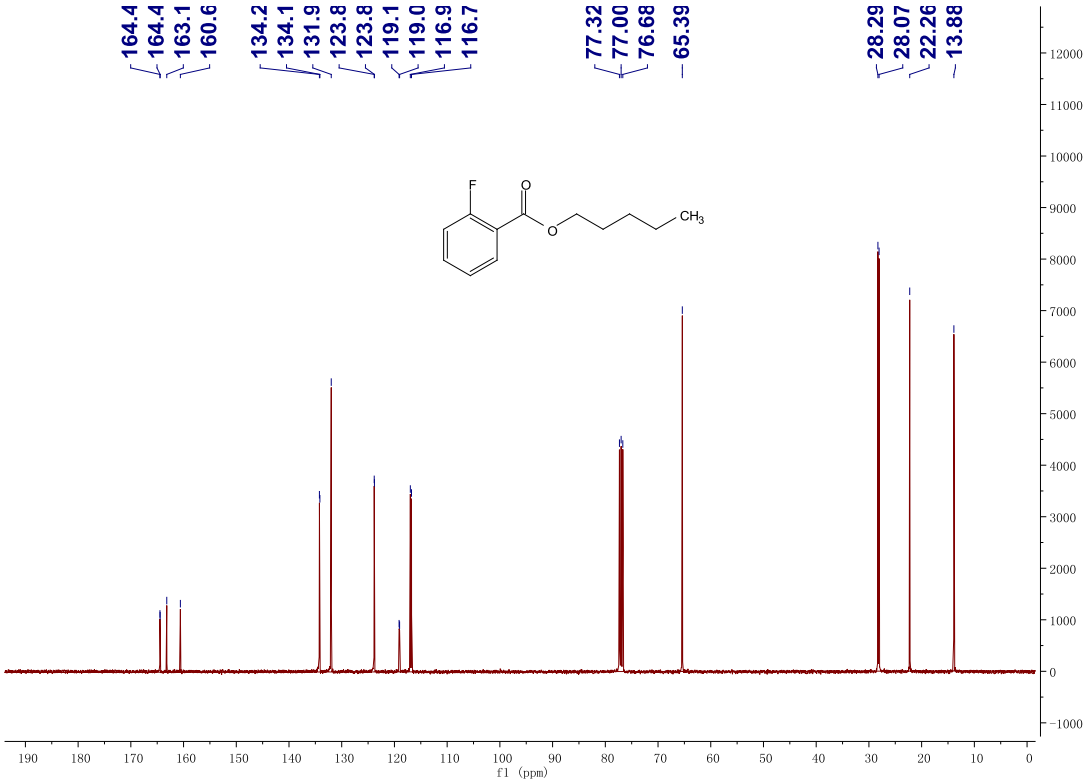


Compound 3ea

^{1}H NMR

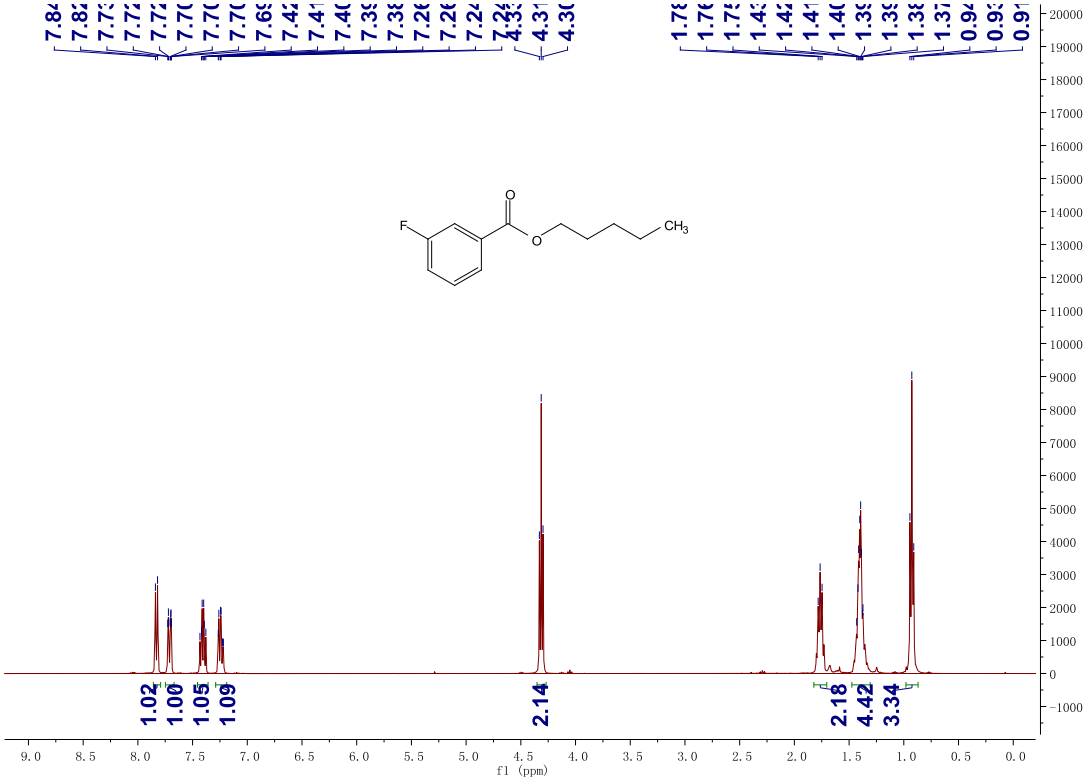


^{13}C NMR

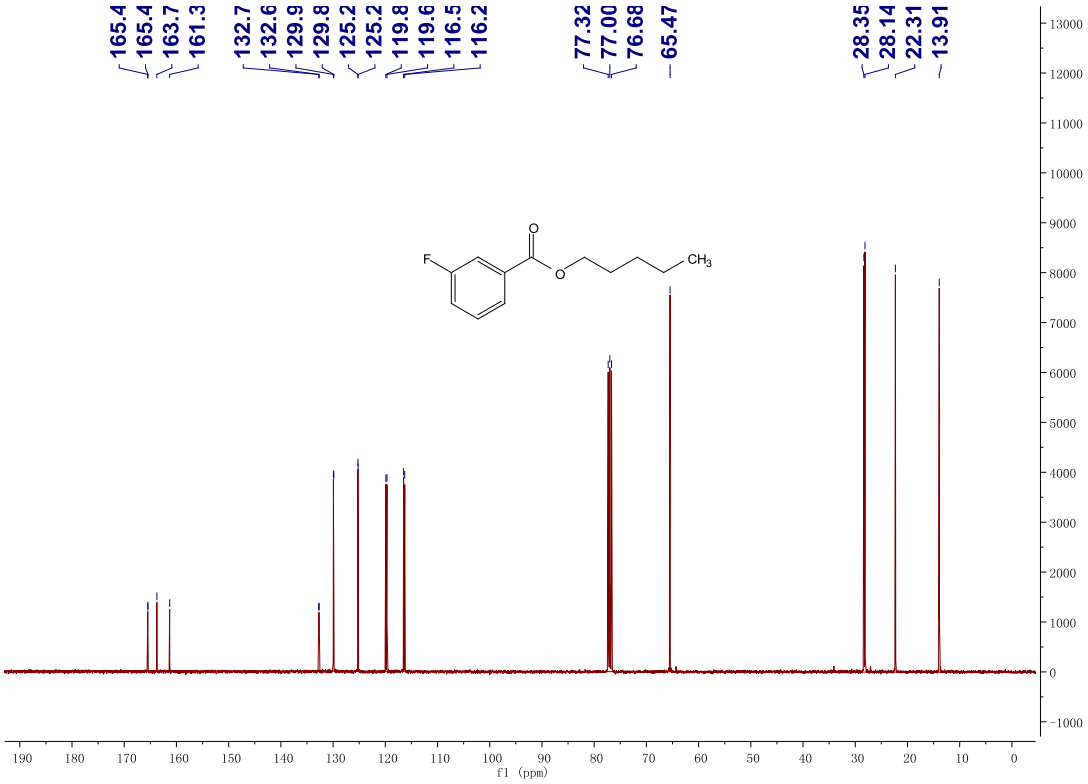


Compound 3fa

^{1}H NMR

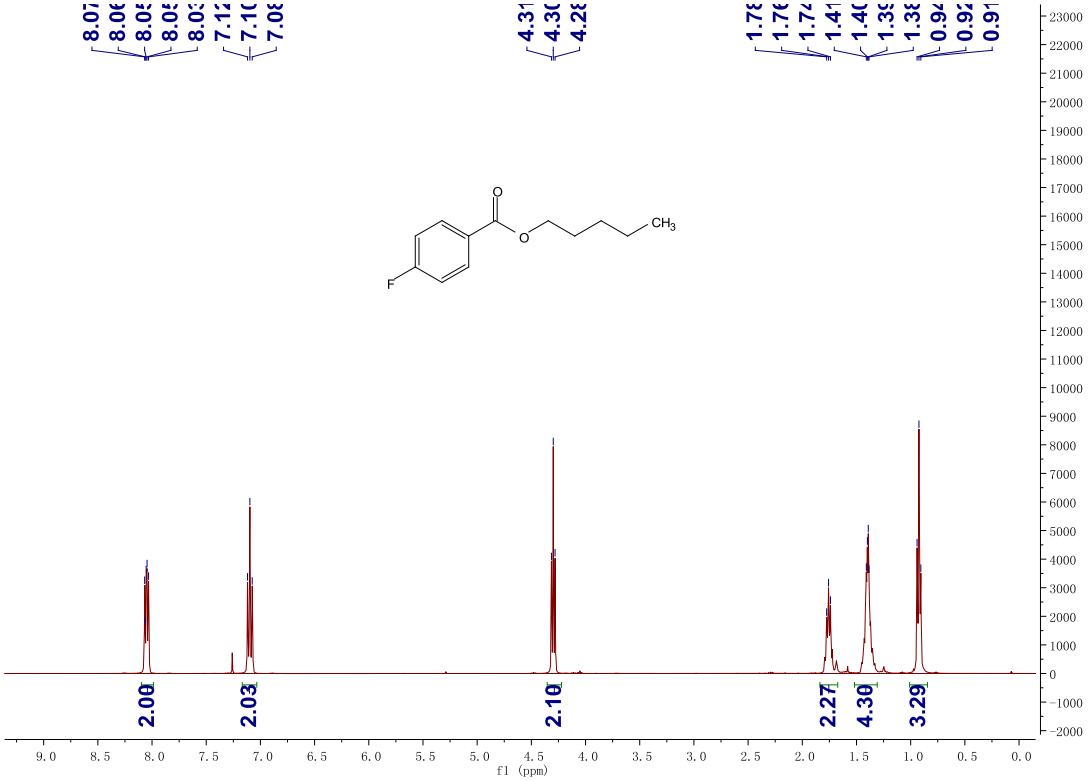


^{13}C NMR

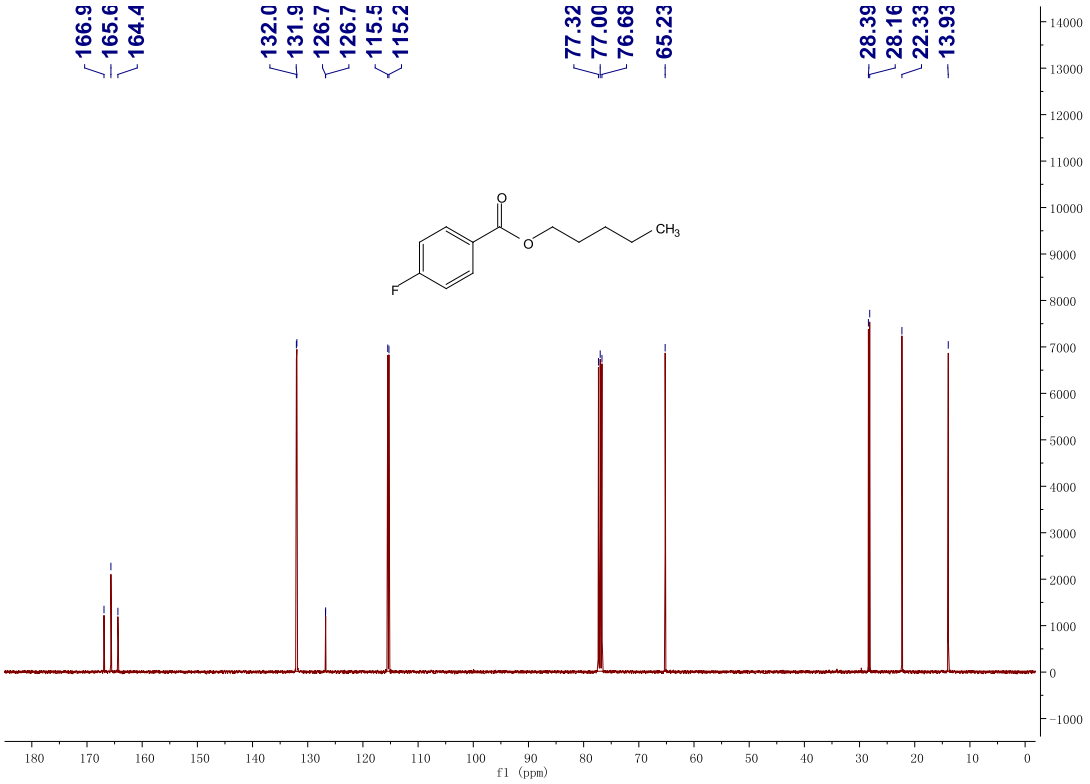


Compound 3ga

^{1}H NMR

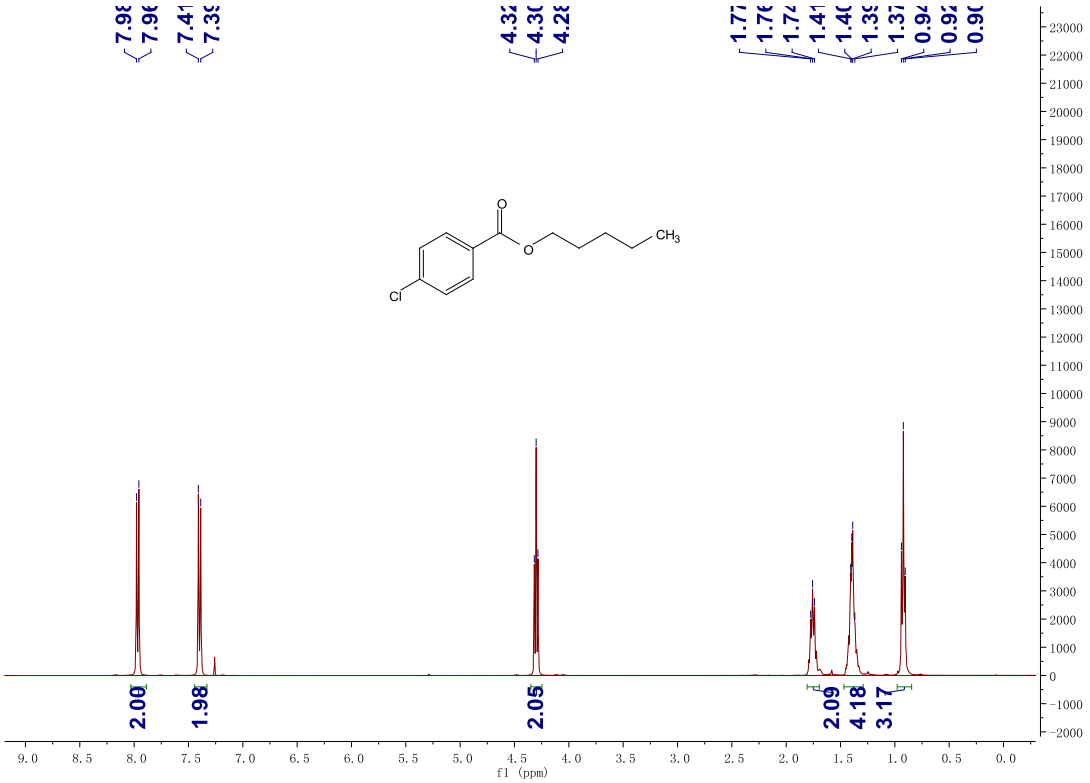


^{13}C NMR

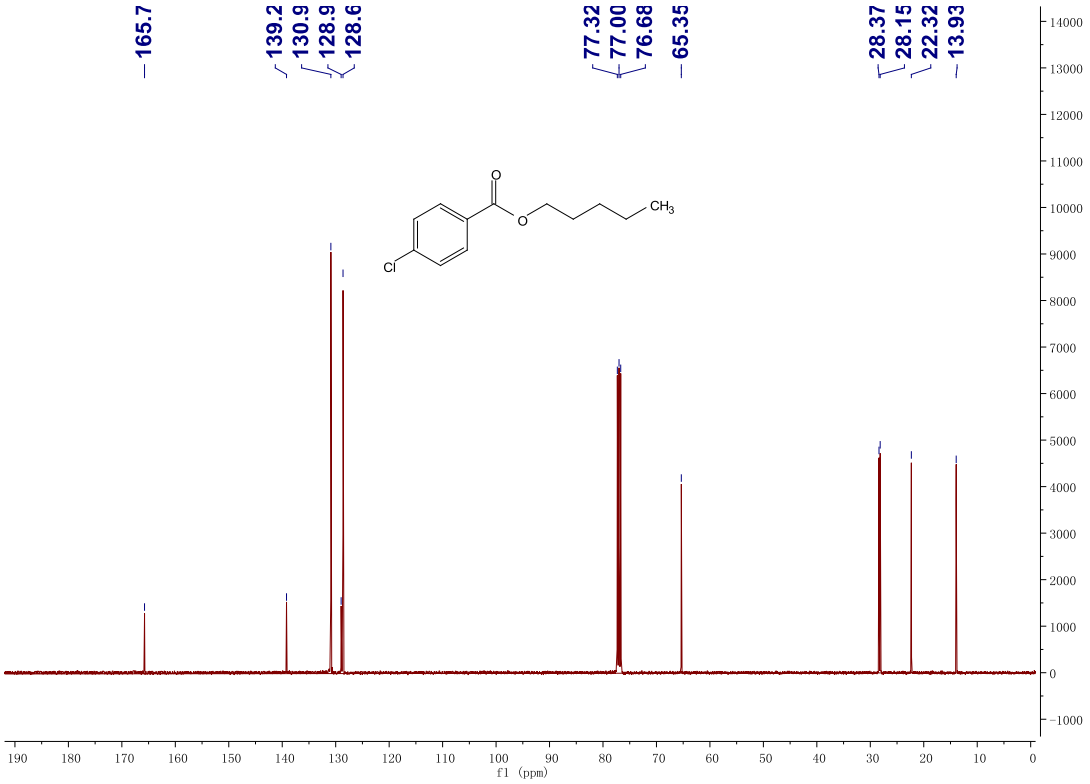


Compound 3ha

^{1}H NMR

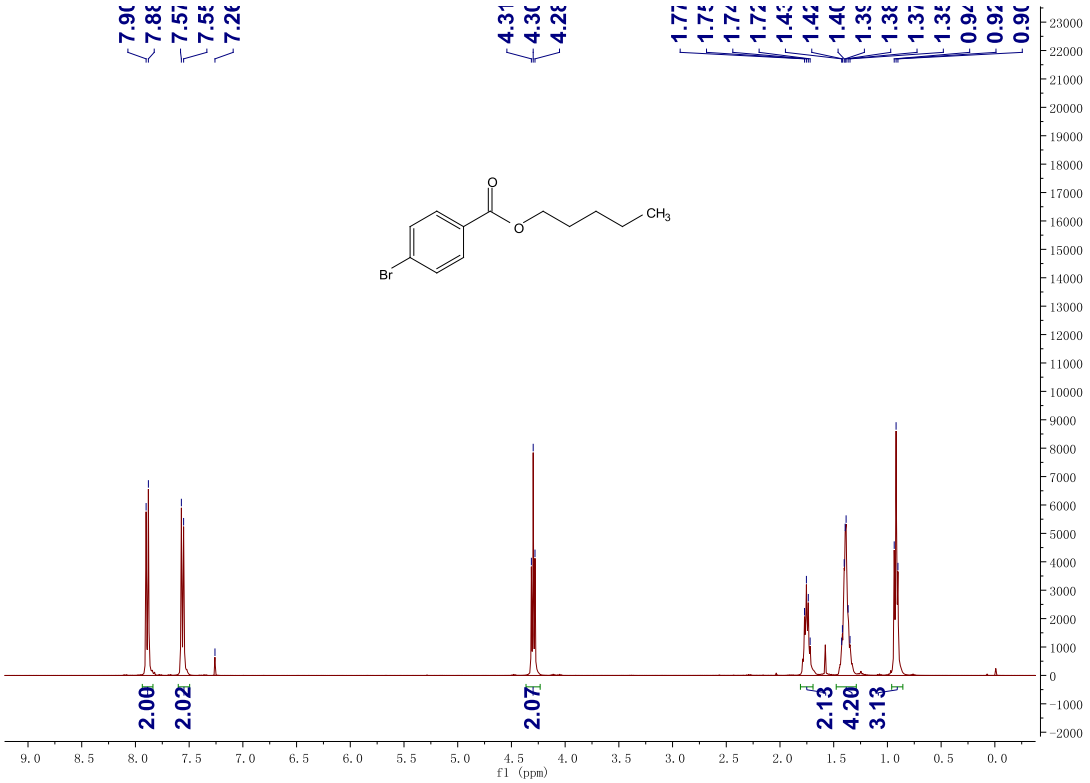


^{13}C NMR

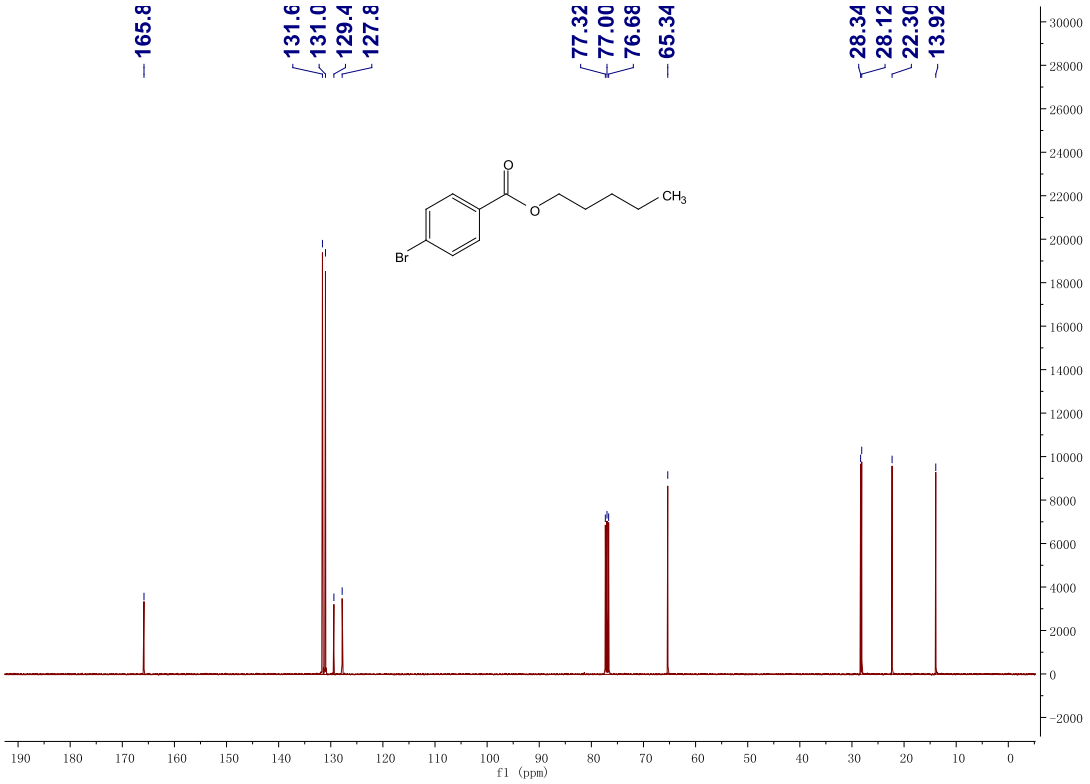


Compound 3ia

^{1}H NMR

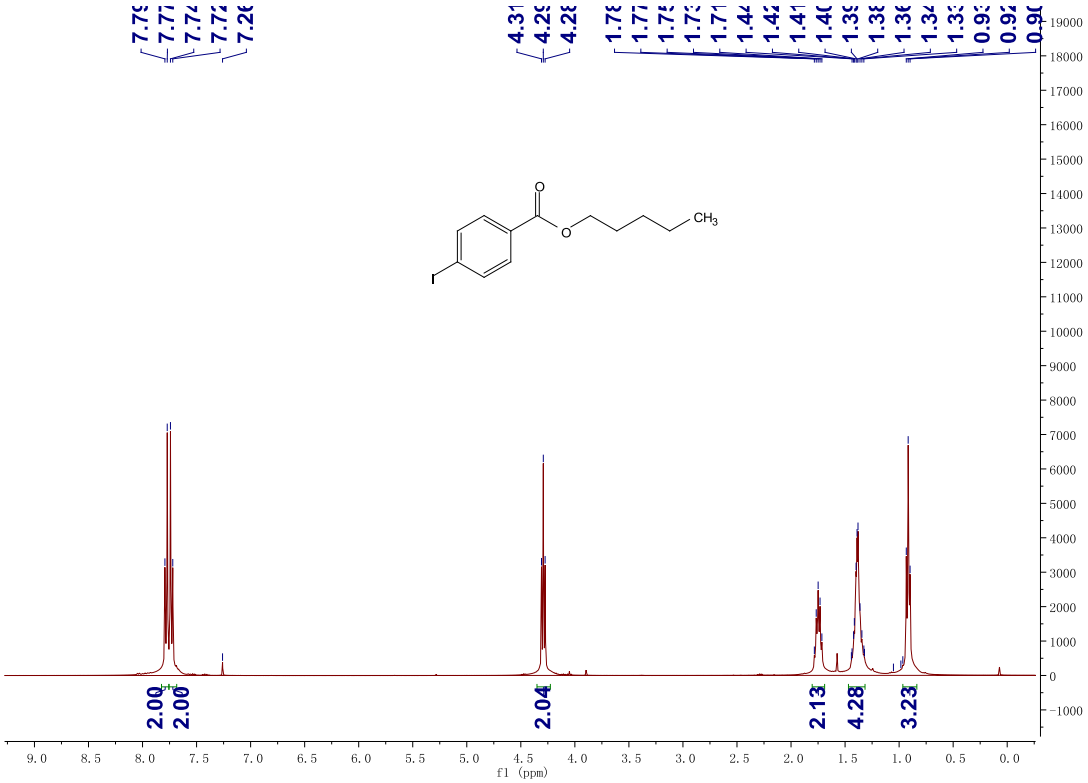


^{13}C NMR

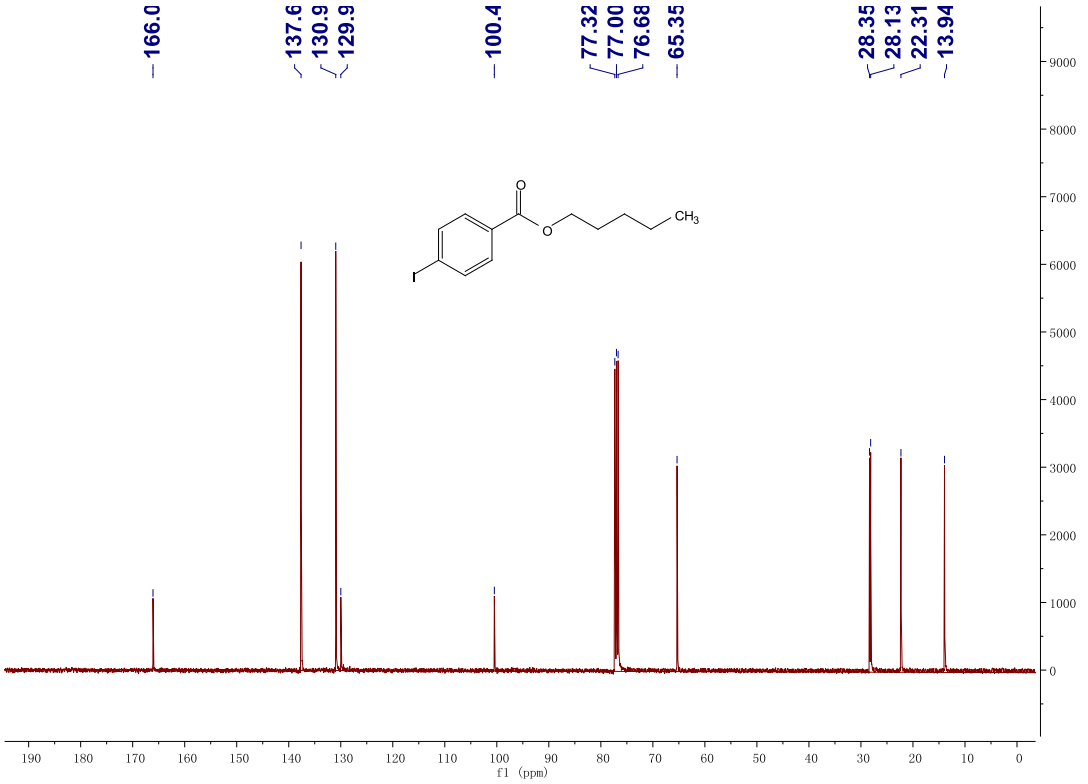


Compound 3ja

^{1}H NMR

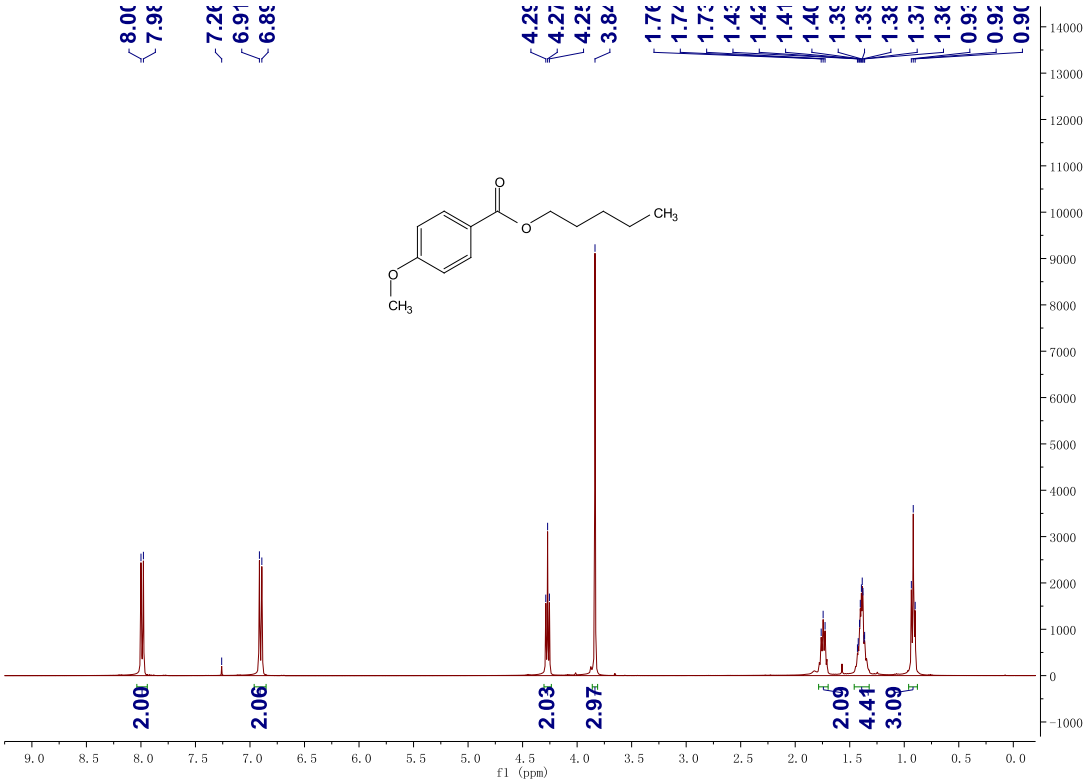


^{13}C NMR

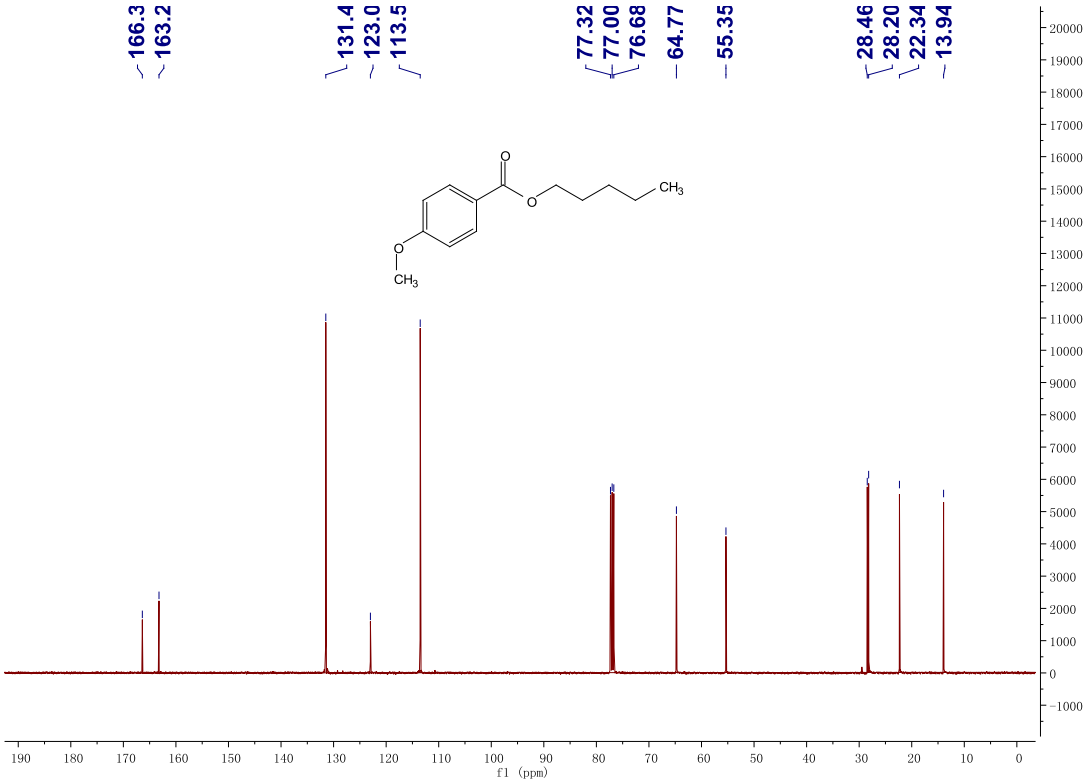


Compound 3ka

^{1}H NMR

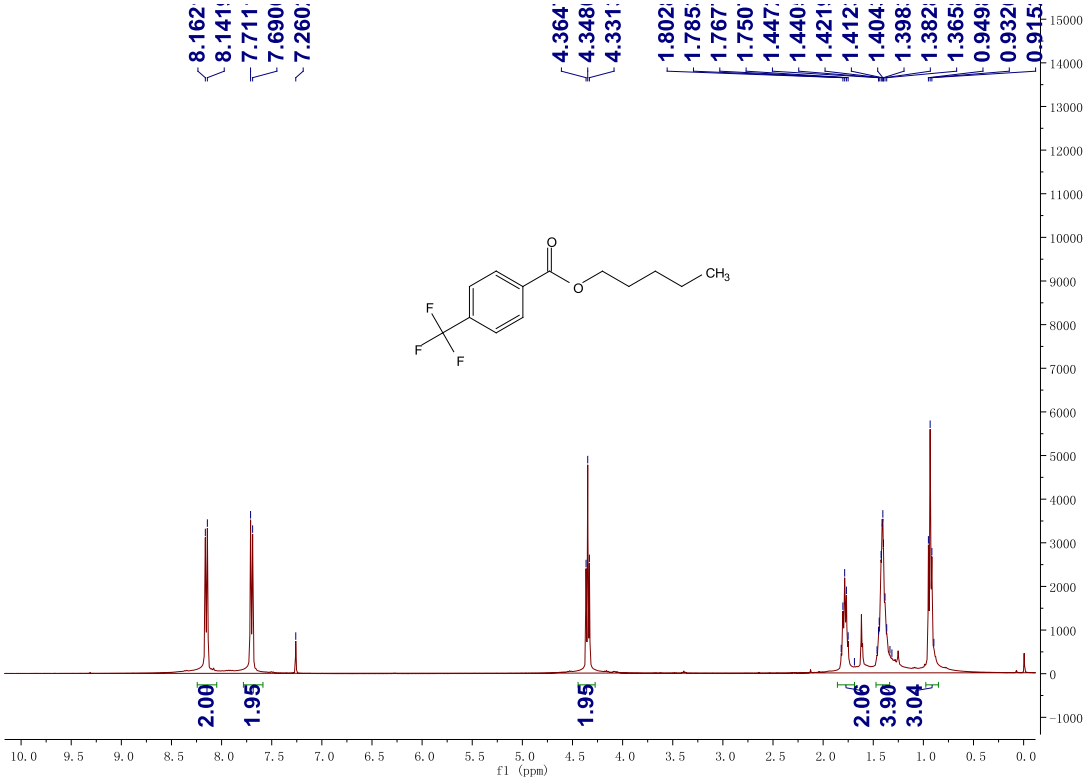


^{13}C NMR

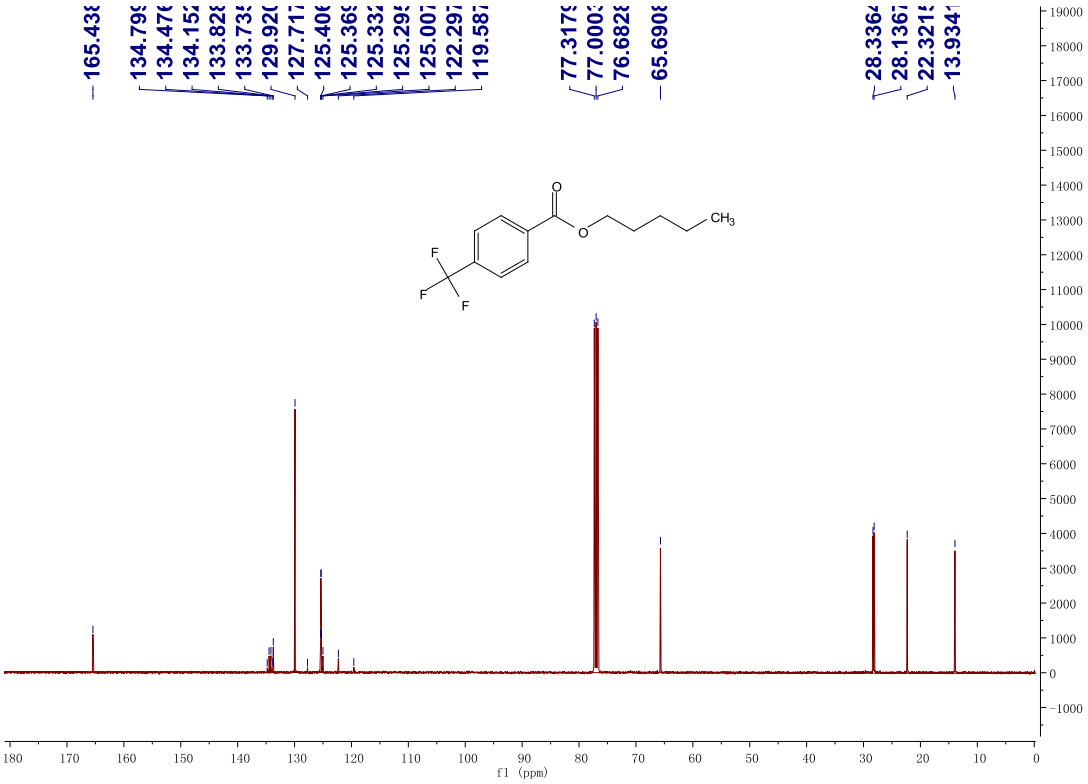


Compound 3la

^{1}H NMR

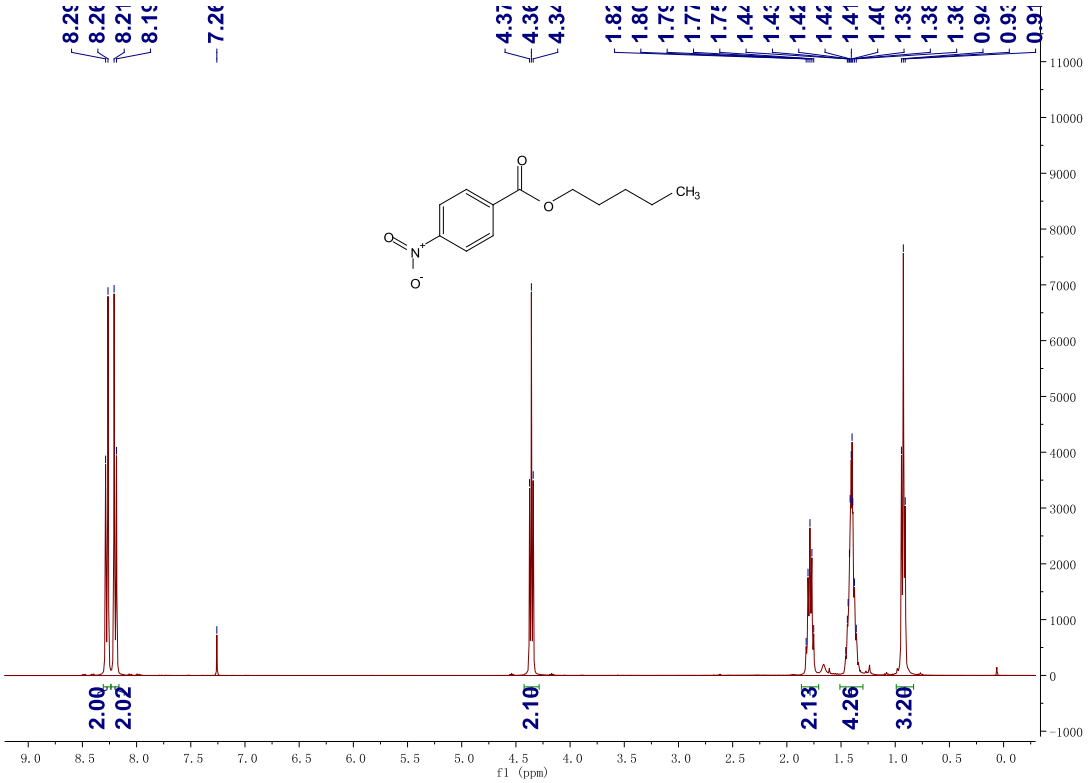


^{13}C NMR

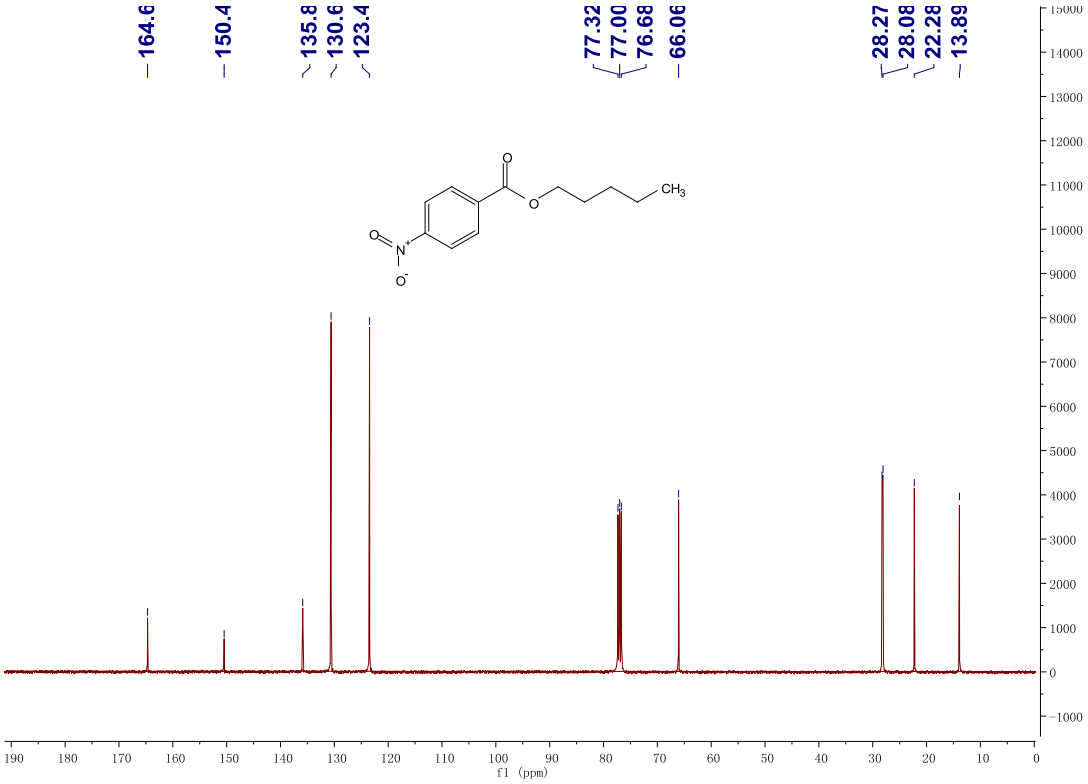


Compound 3ma

^{1}H NMR

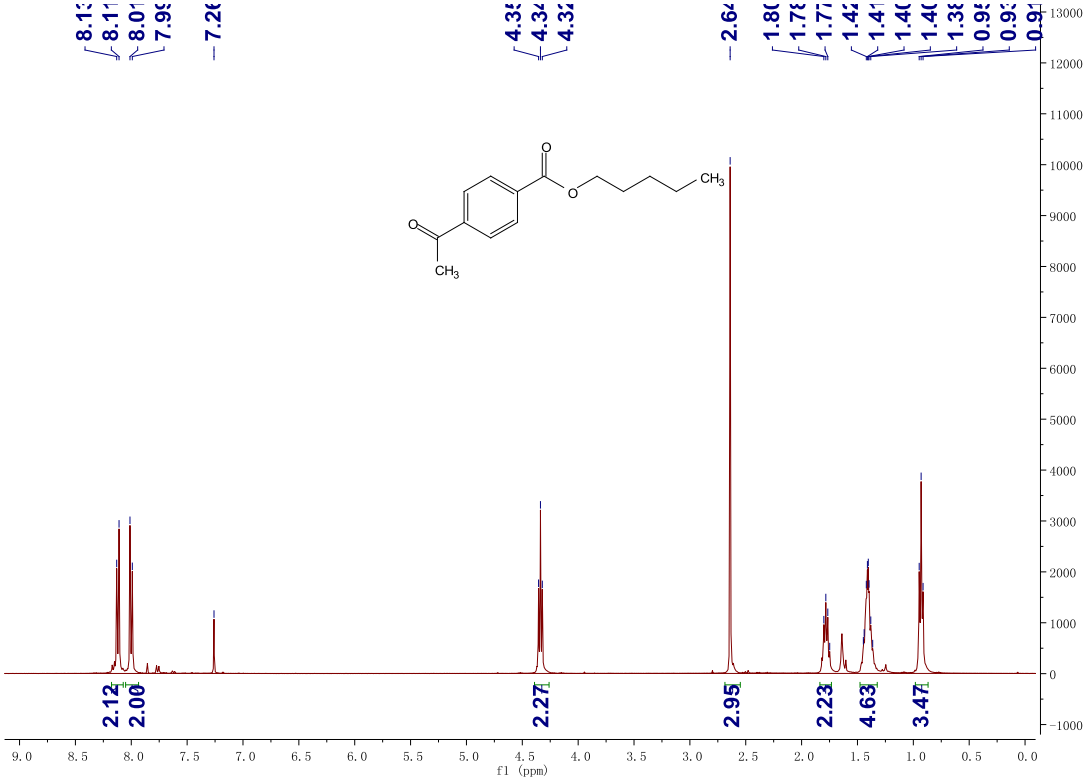


^{13}C NMR

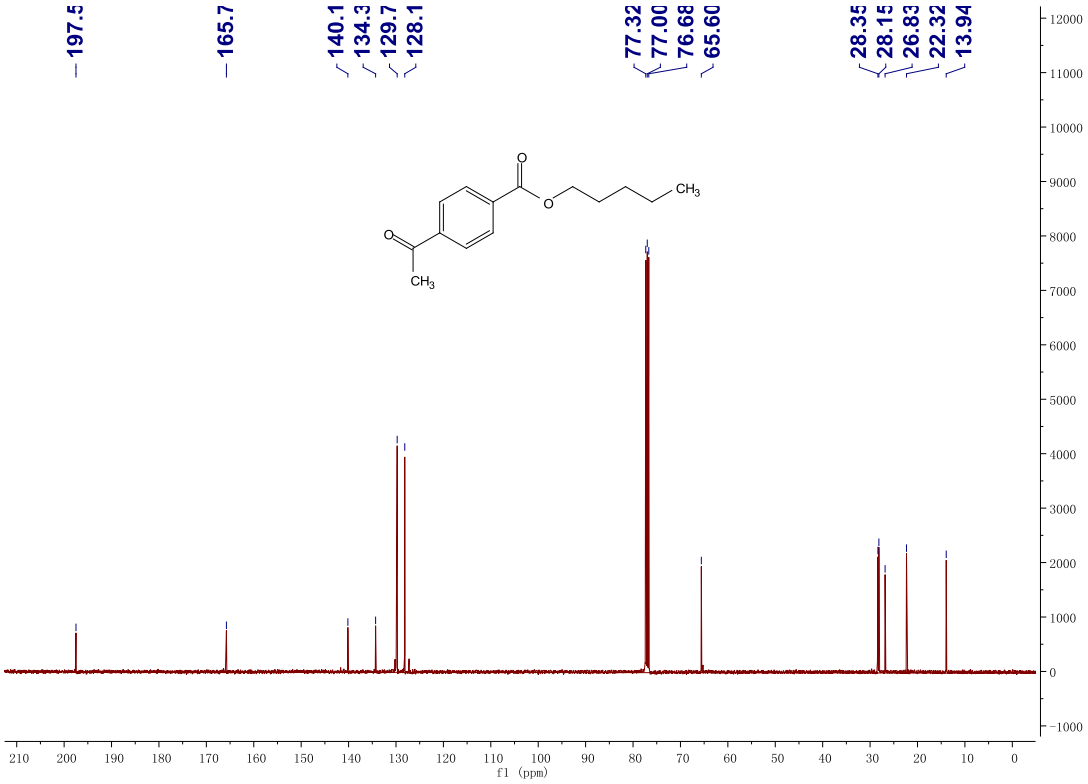


Compound 3na

^{1}H NMR

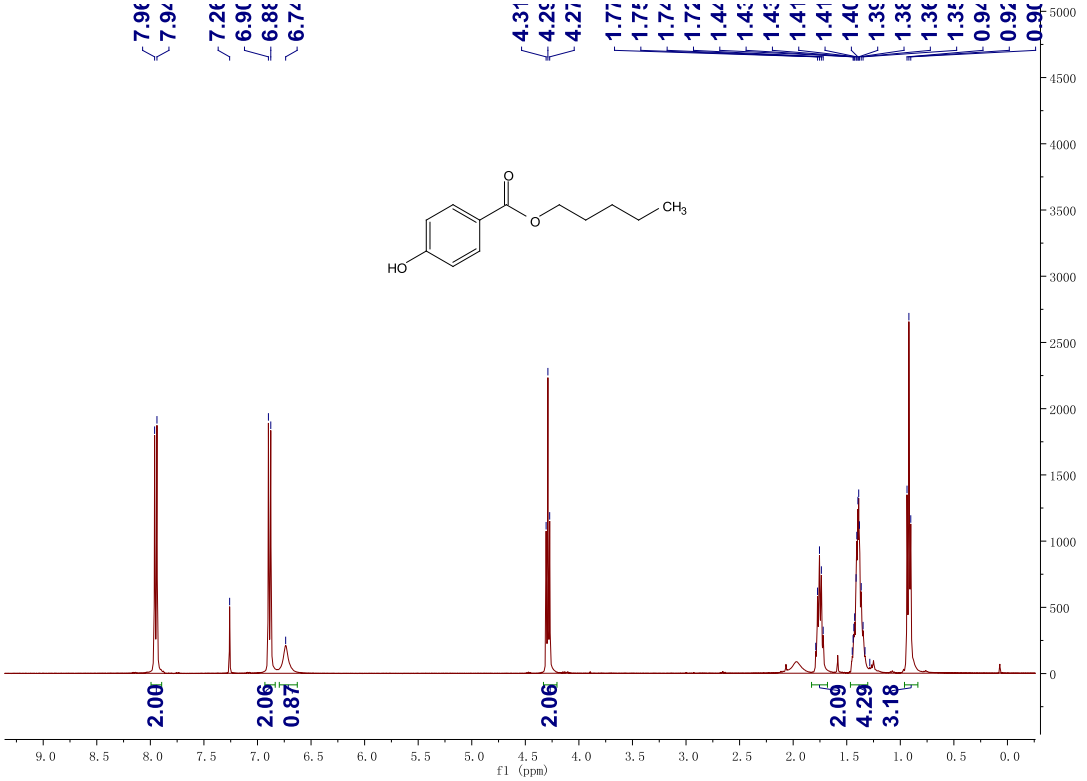


^{13}C NMR

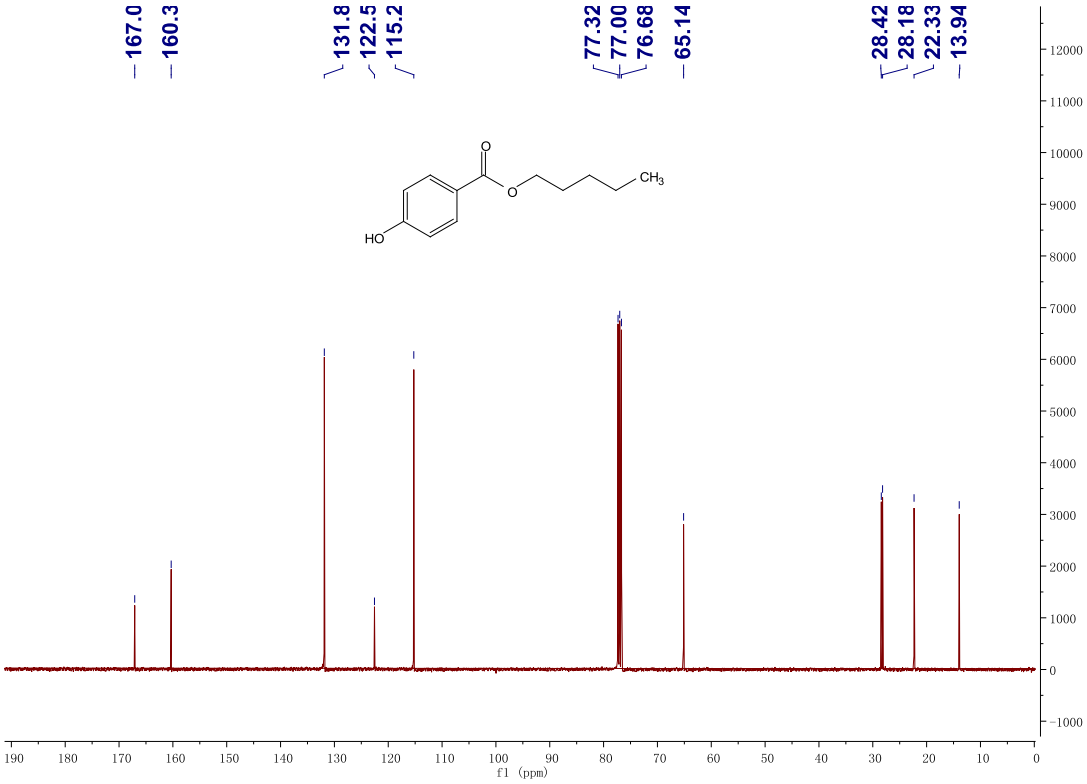


Compound 3oa

^{1}H NMR

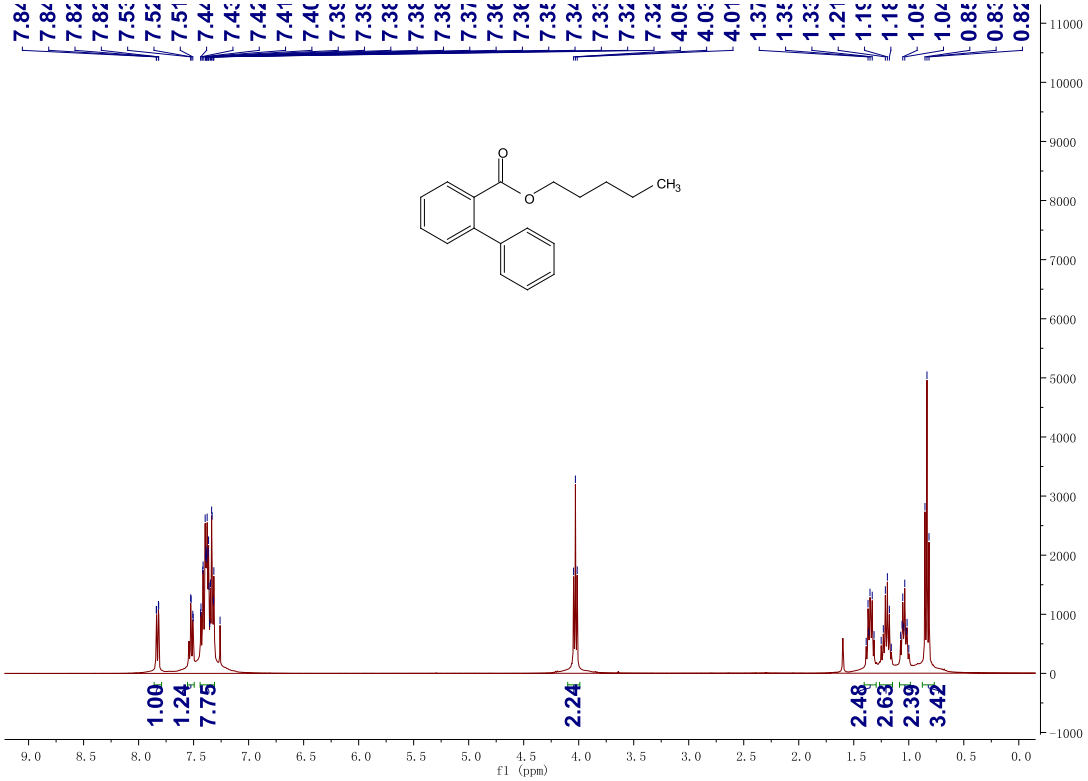


^{13}C NMR

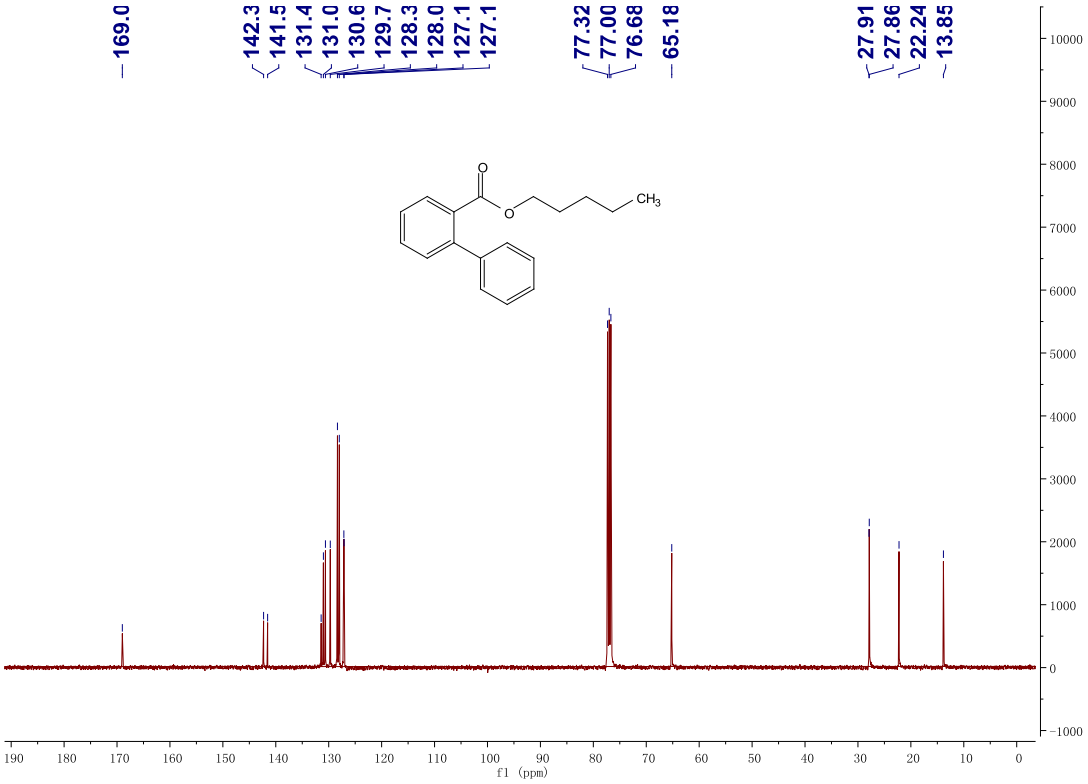


Compound 3pa

^{1}H NMR

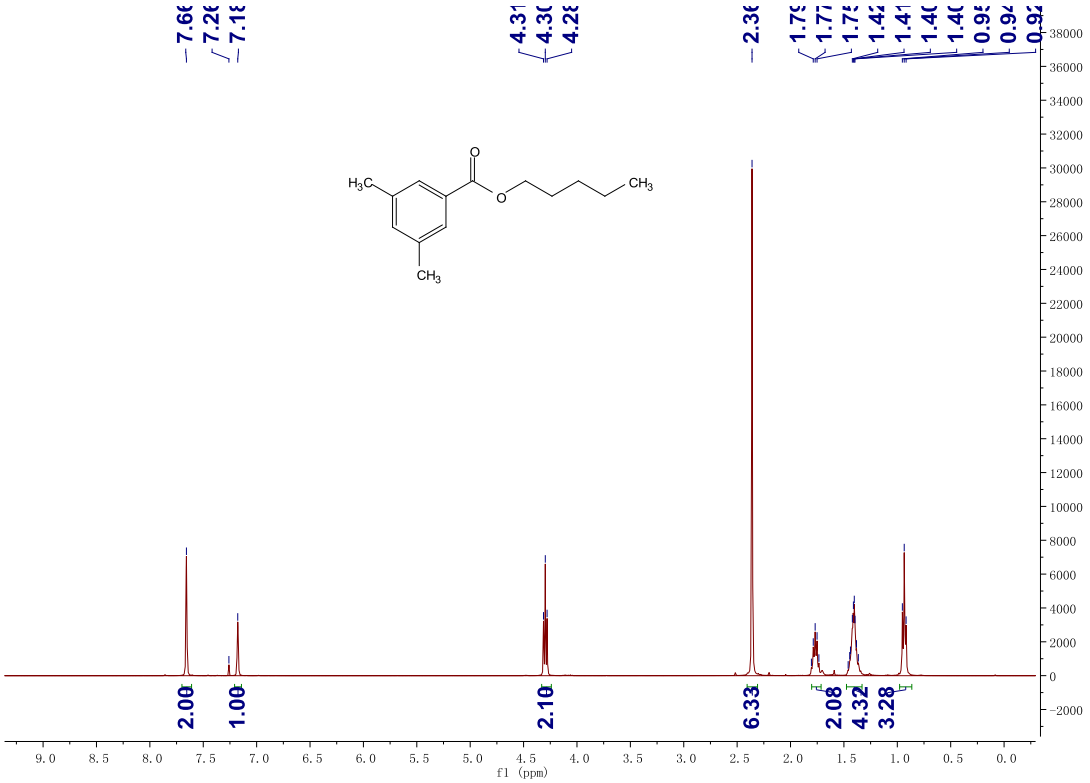


^{13}C NMR

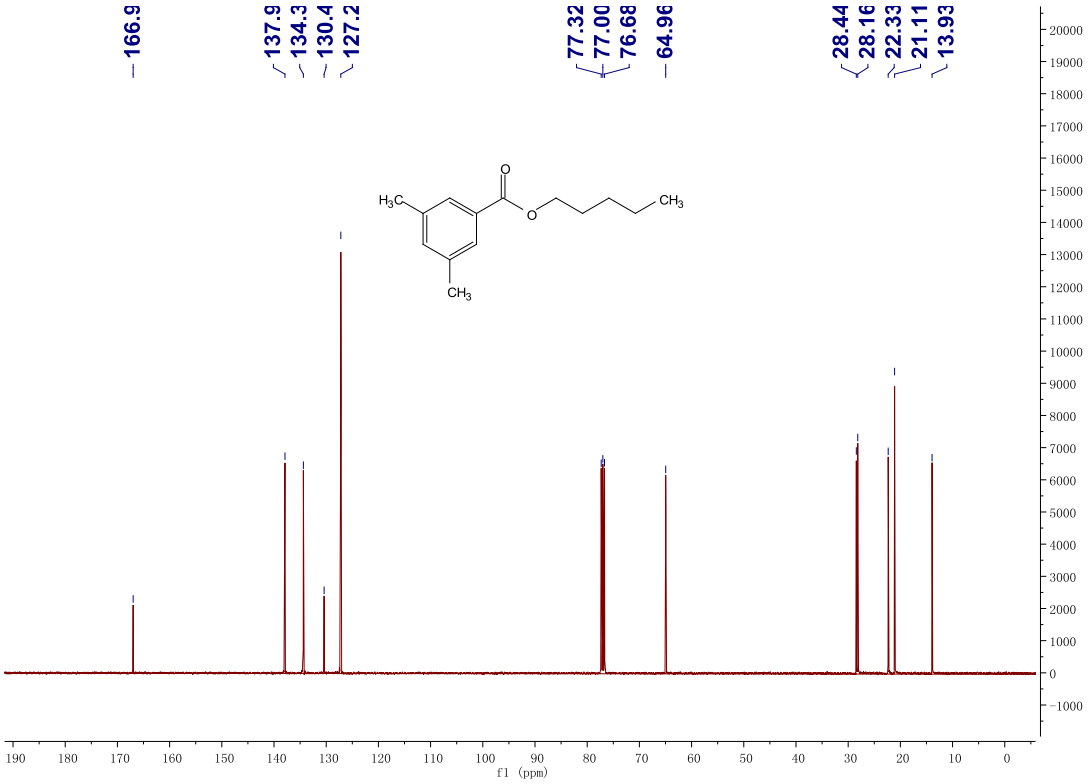


Compound 3qa

^{1}H NMR

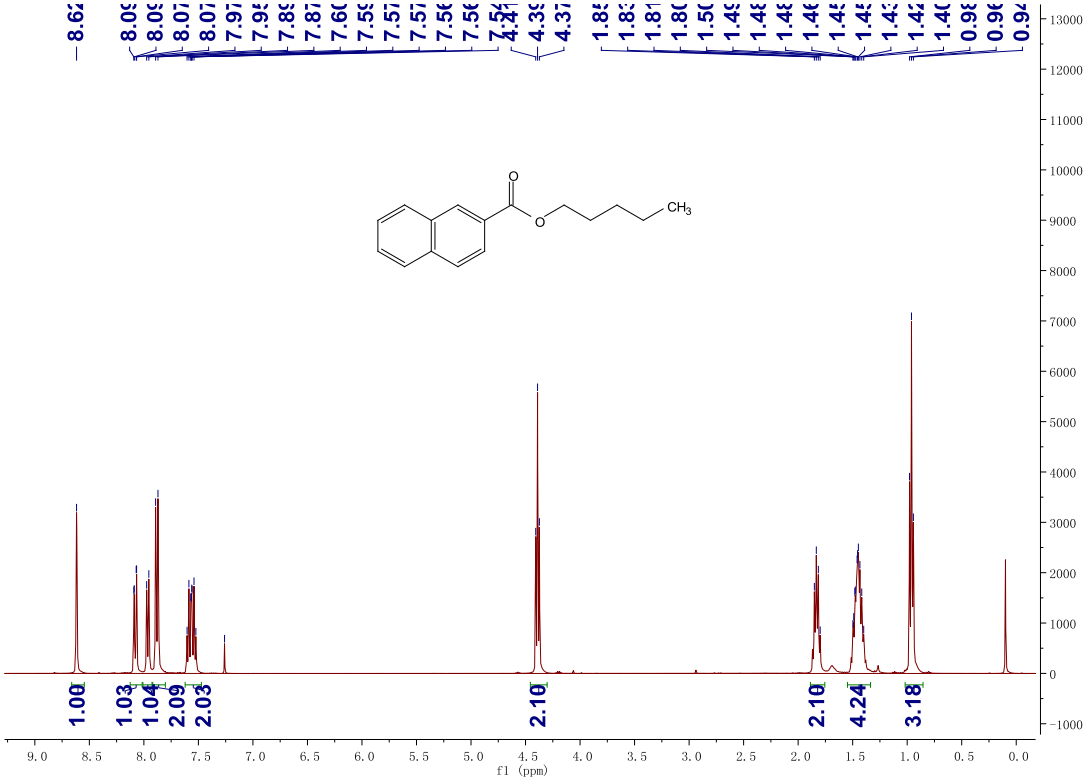


^{13}C NMR

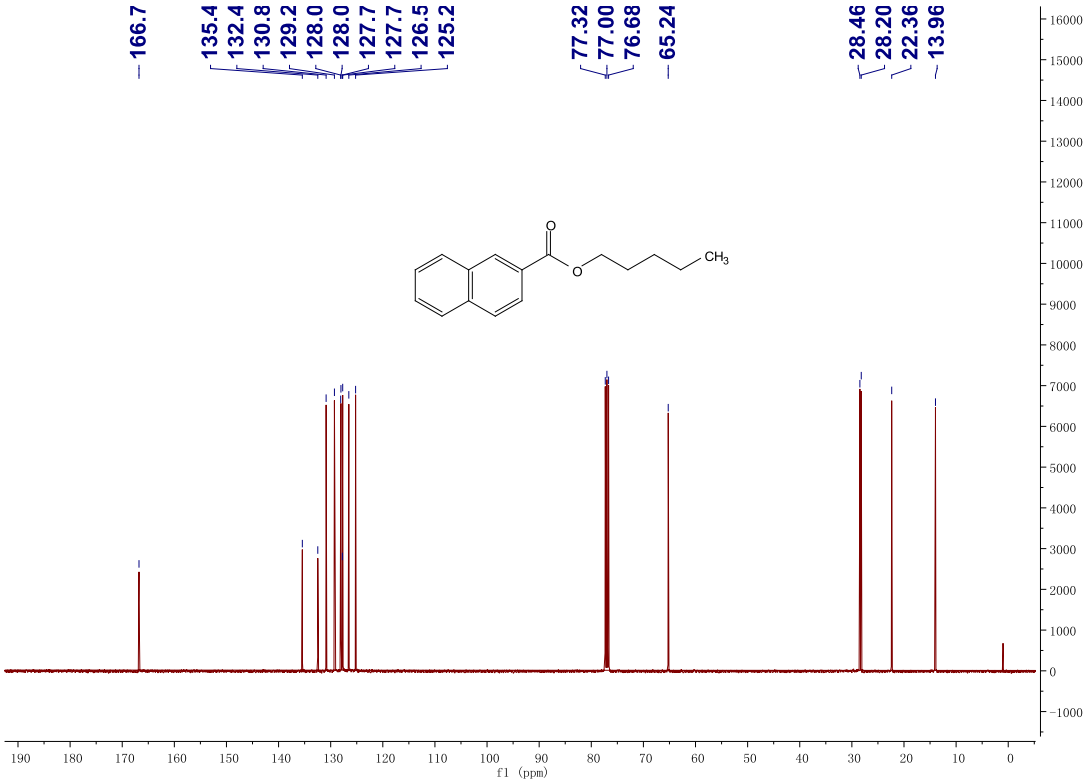


Compound 3ra

^{1}H NMR

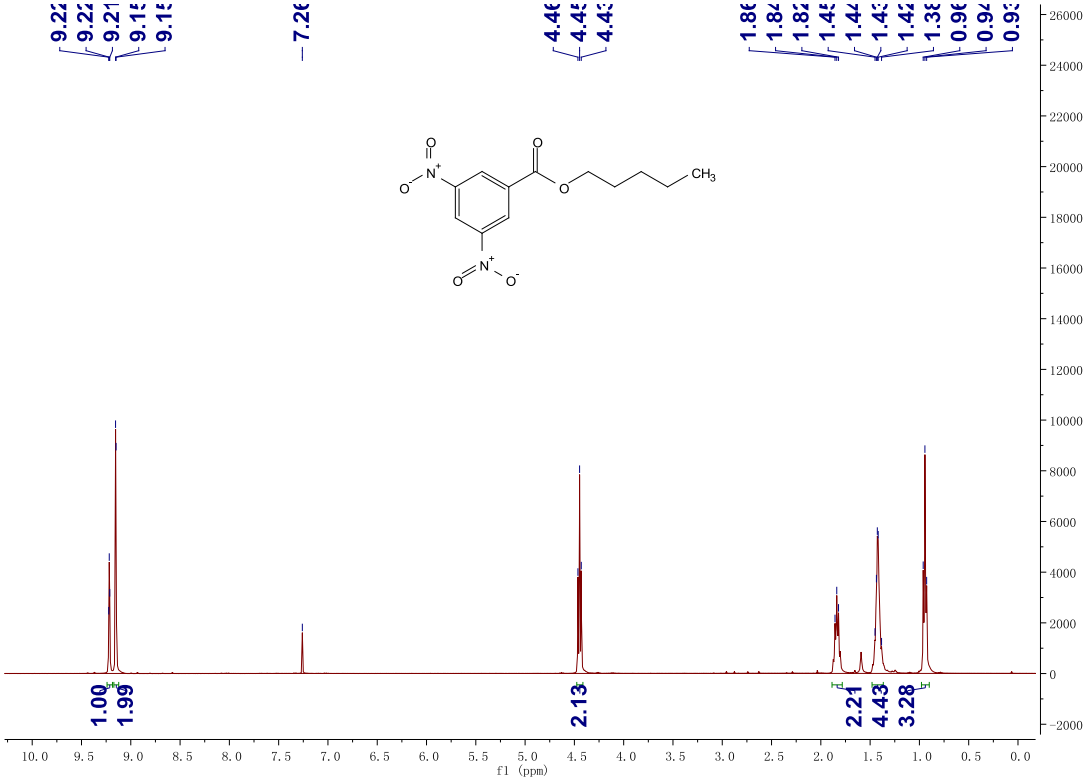


^{13}C NMR

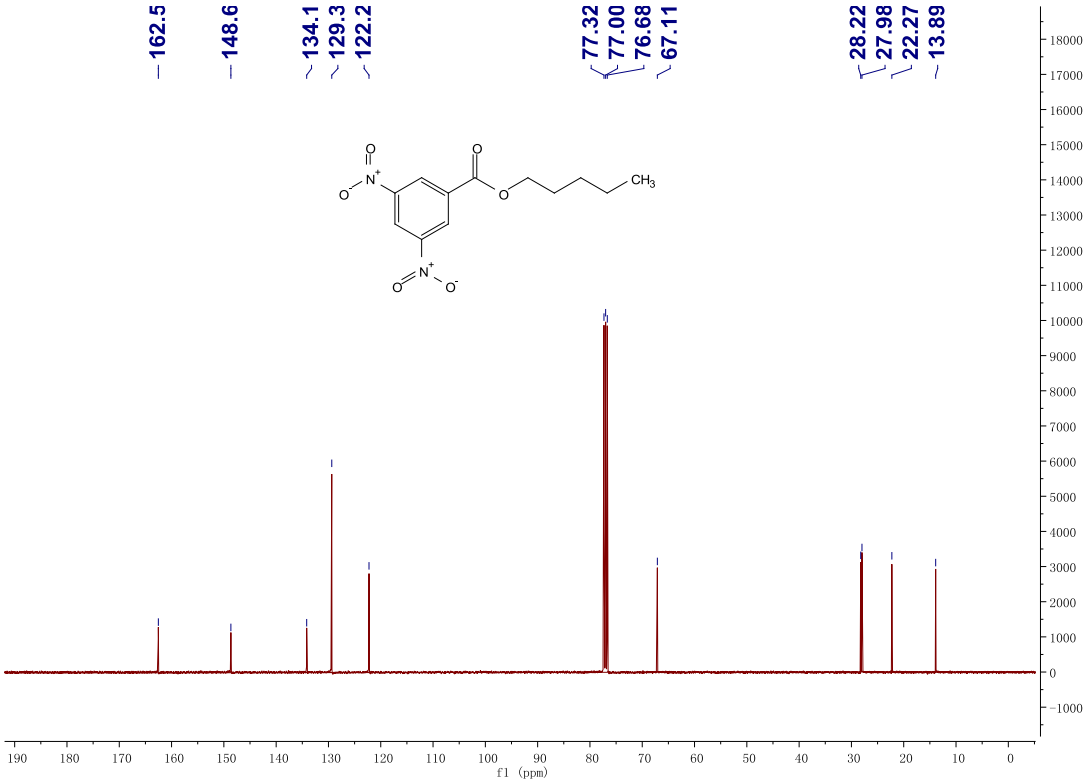


Compound 3sa

^{1}H NMR

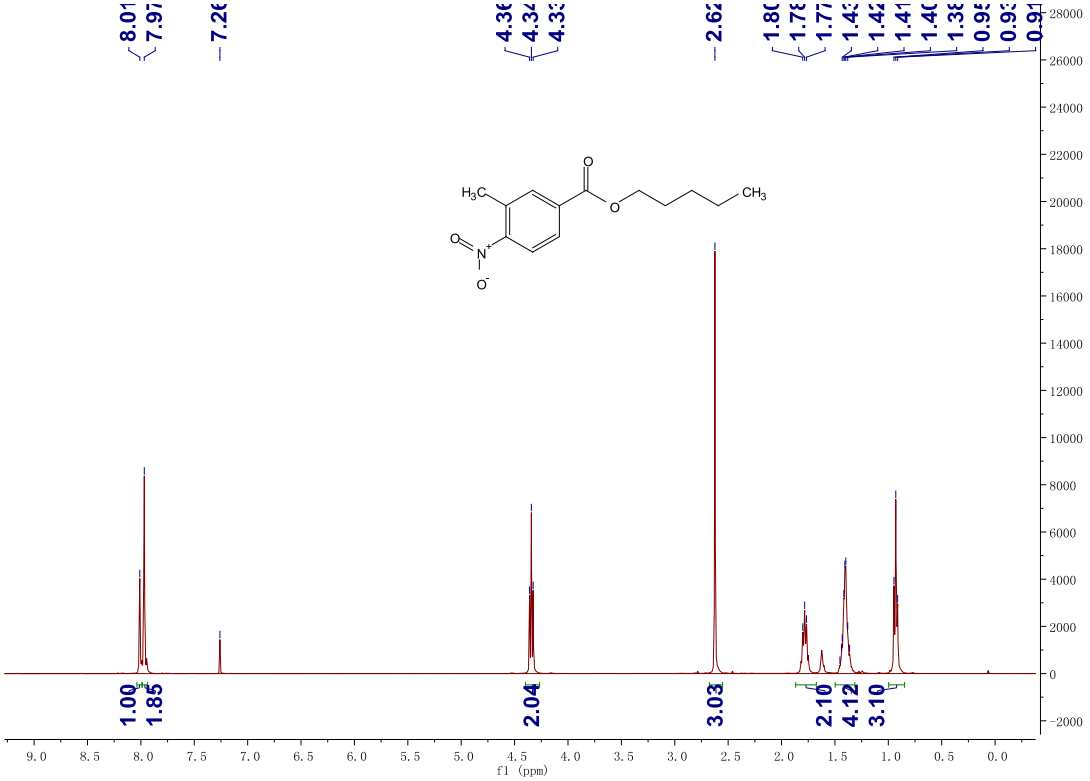


^{13}C NMR

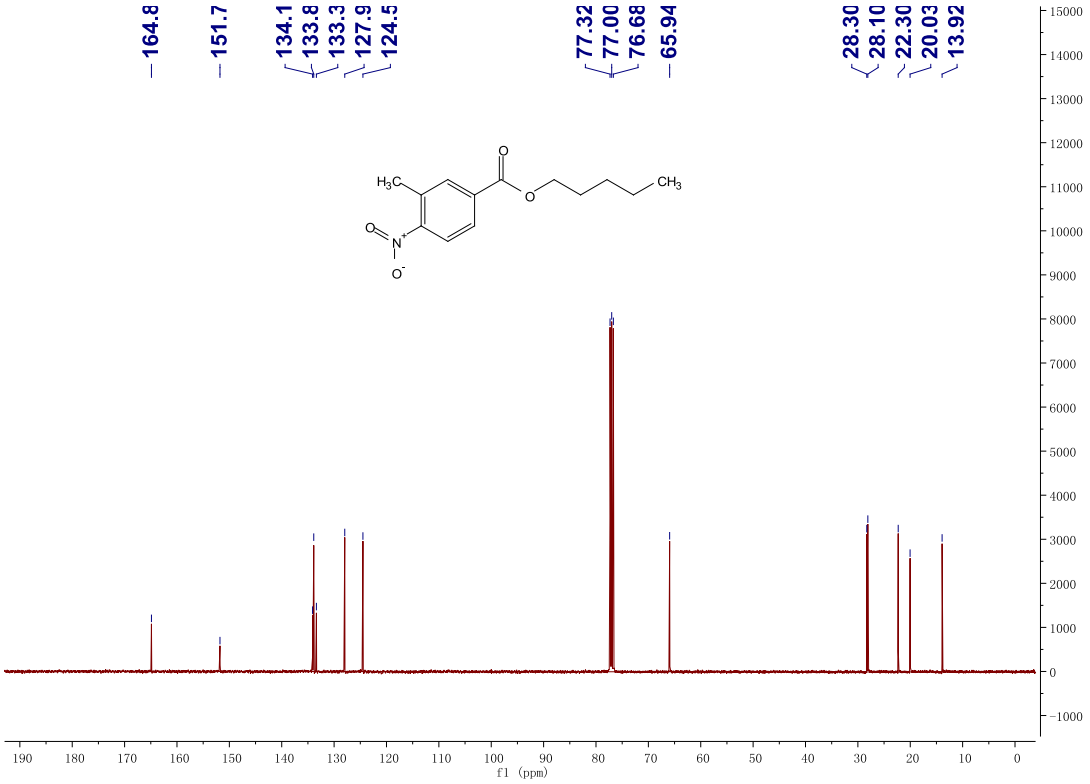


Compound 3ta

^{1}H NMR

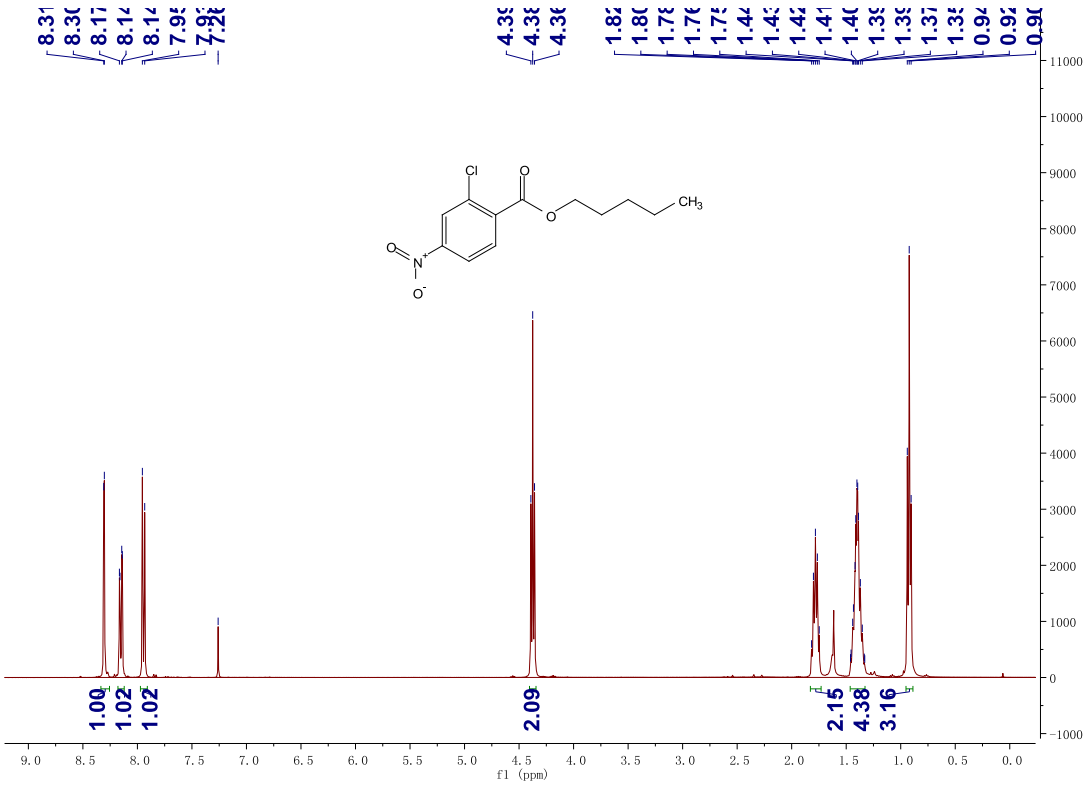


^{13}C NMR

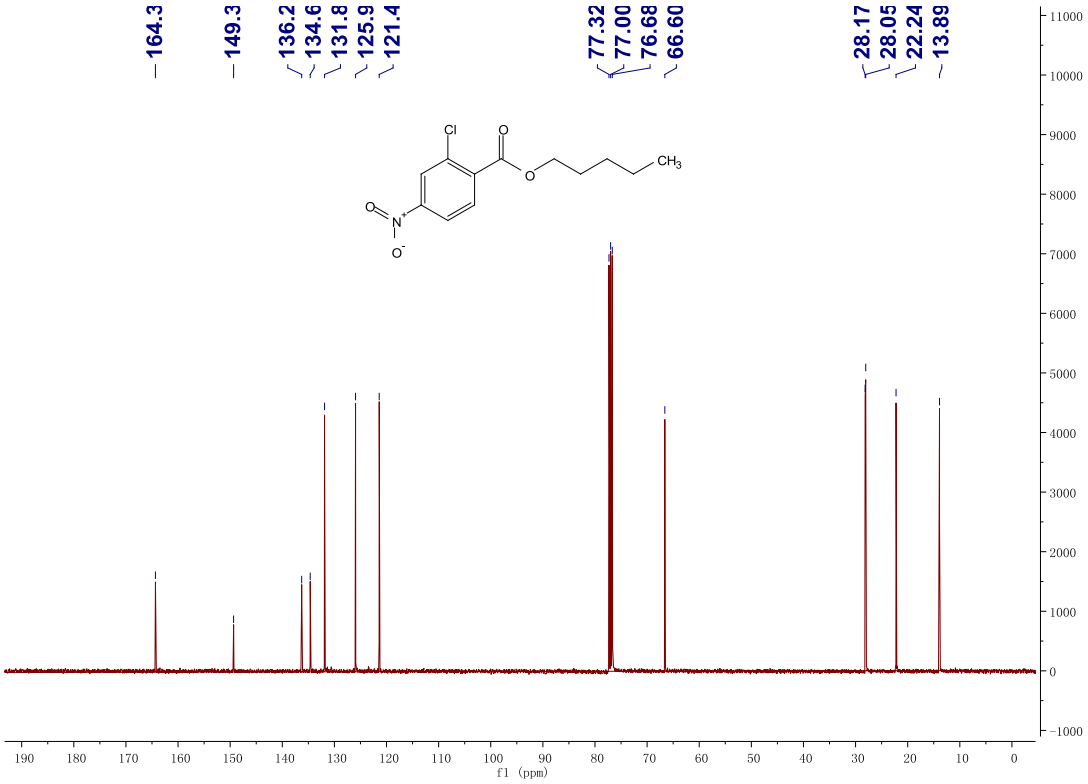


Compound 3ua

^{1}H NMR

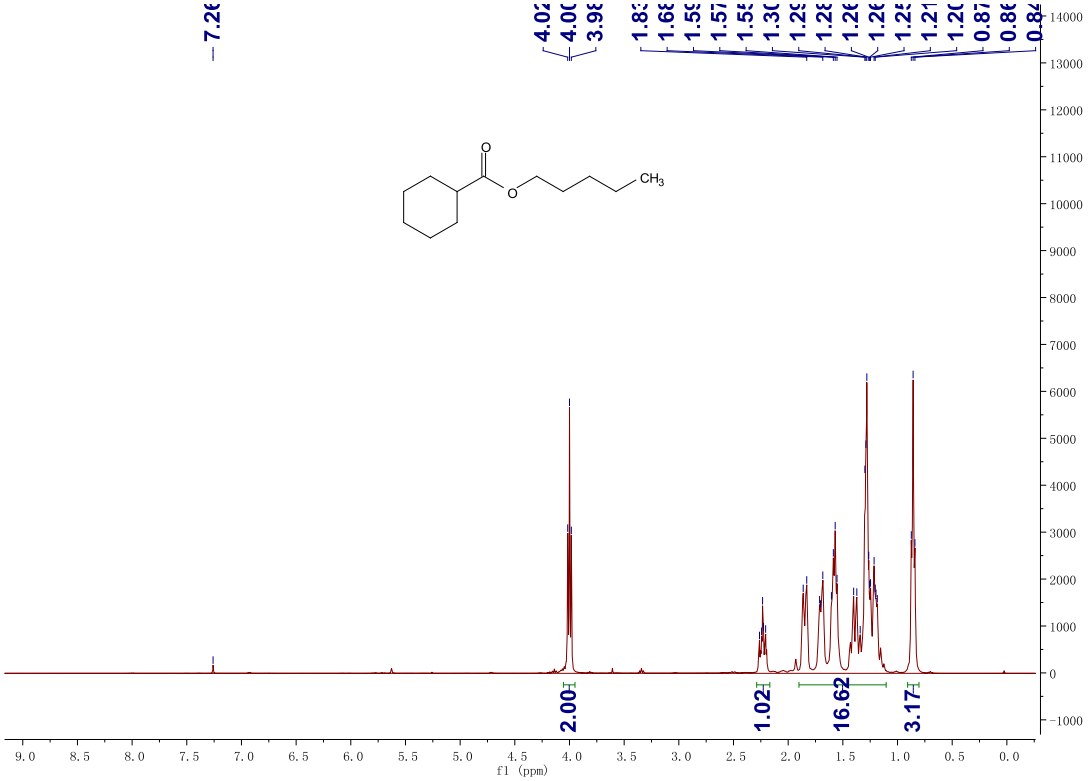


^{13}C NMR

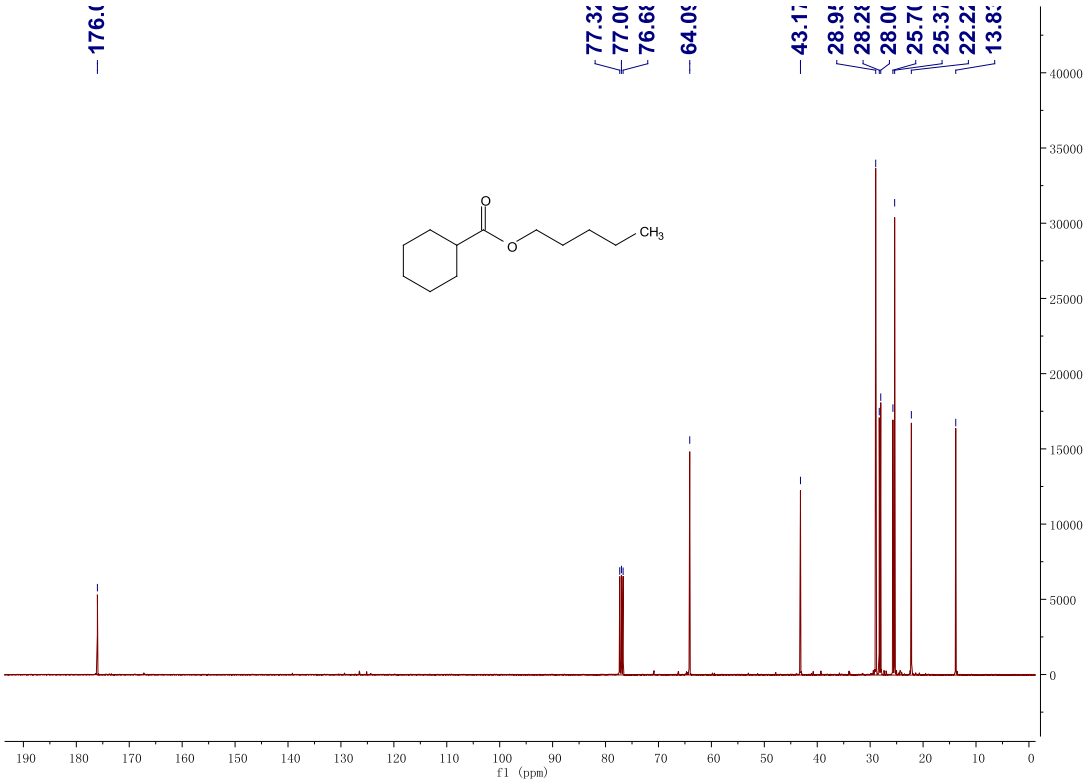


Compound 3va

^{1}H NMR

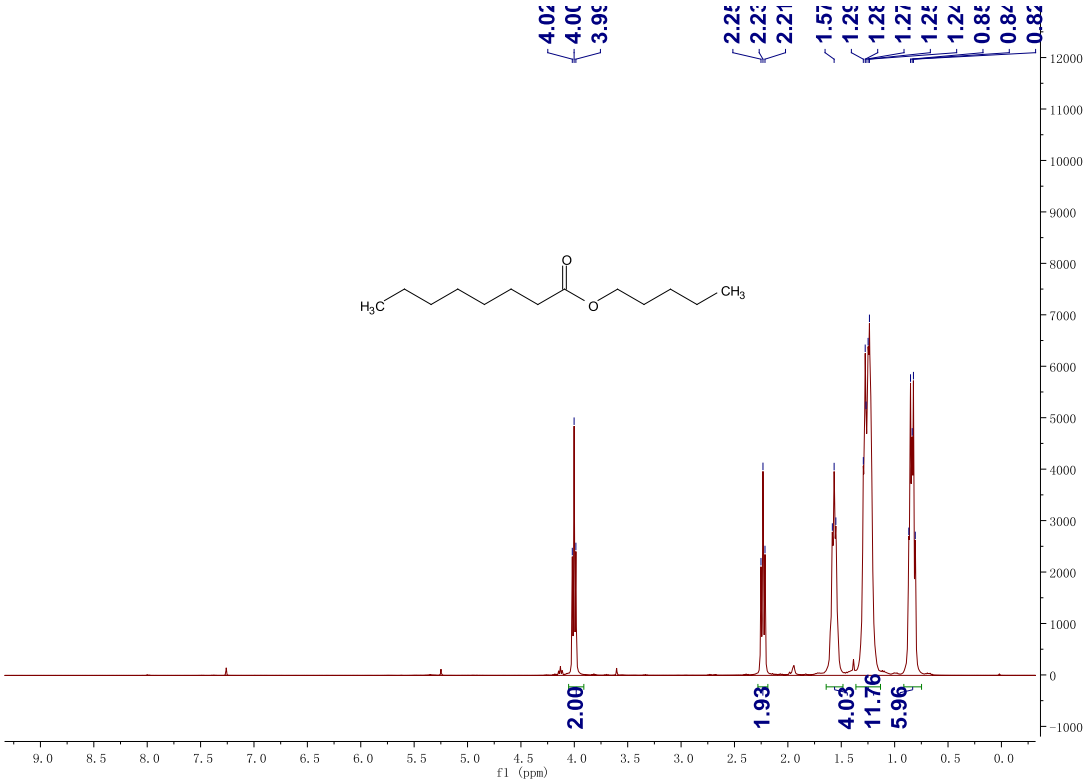


^{13}C NMR

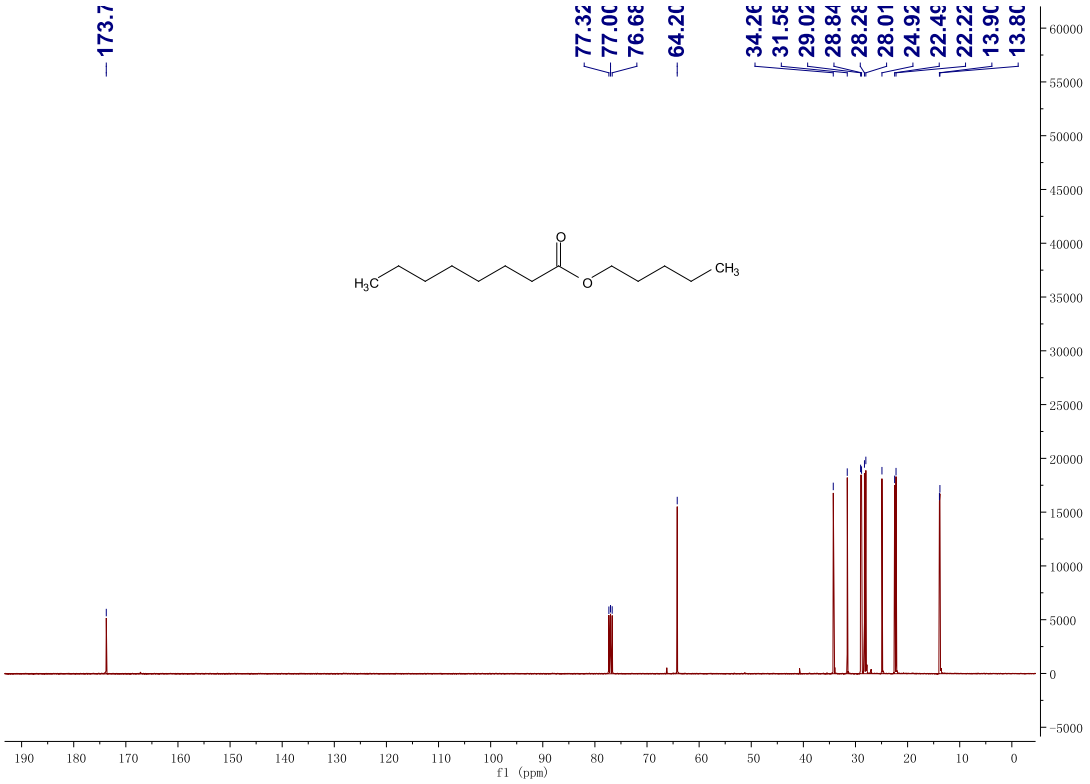


Compound 3wa

^{1}H NMR

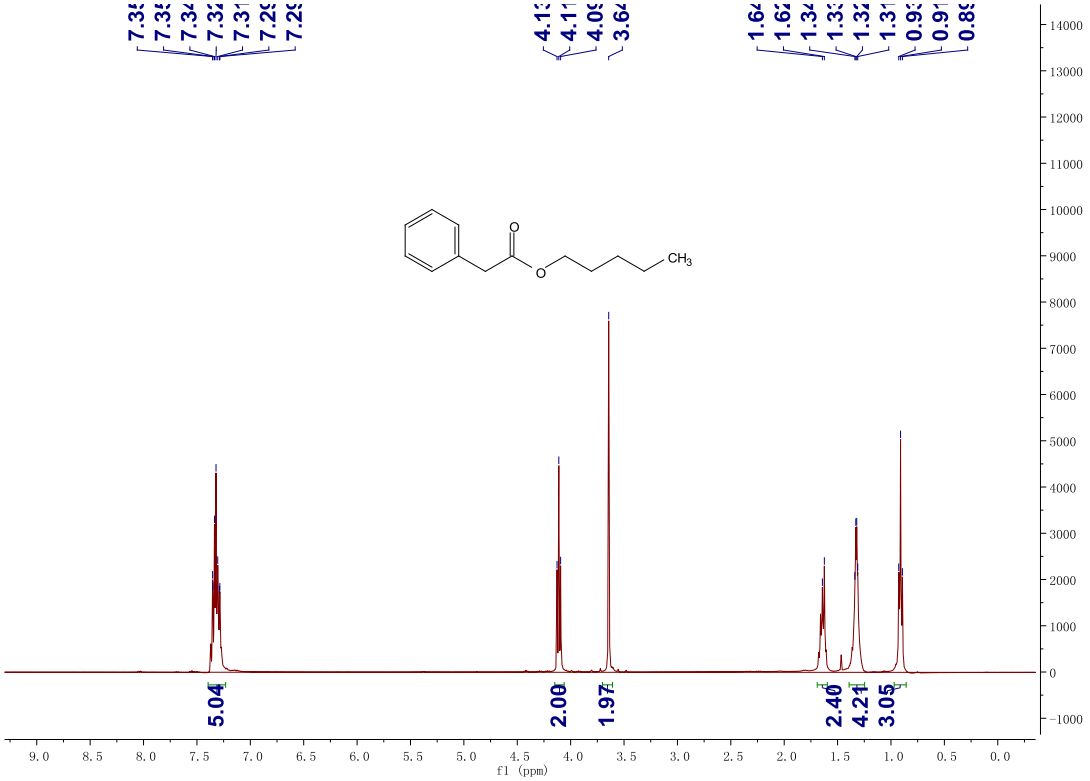


^{13}C NMR

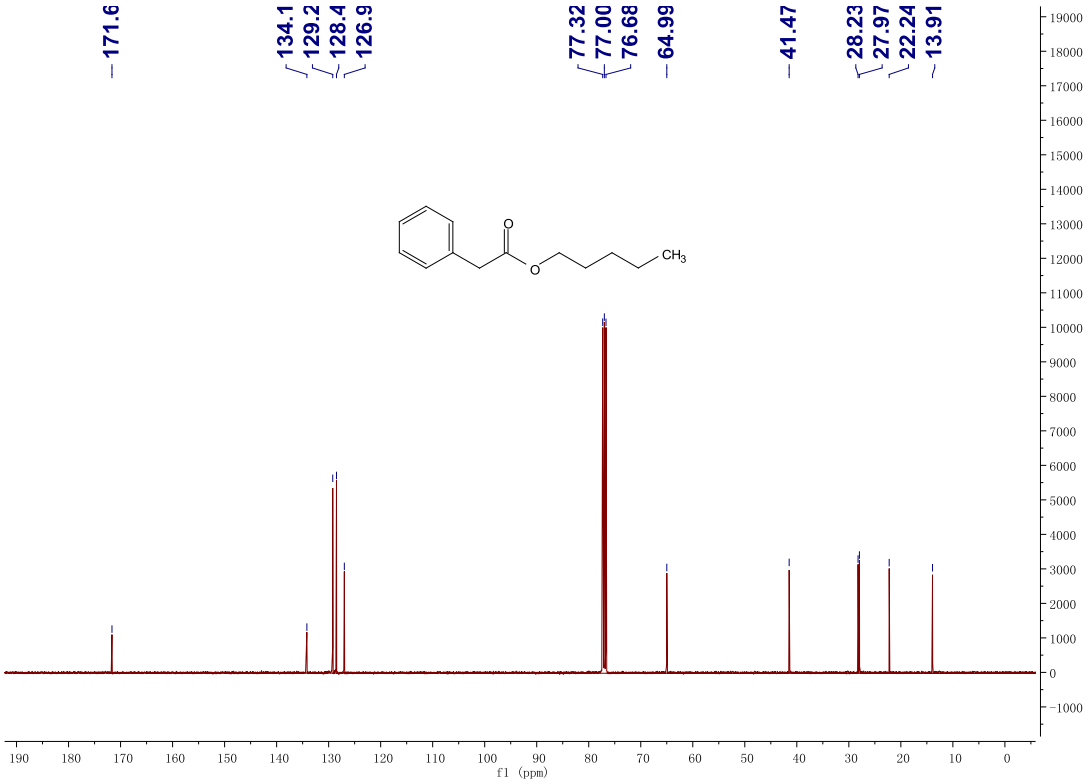


Compound 3xa

^{1}H NMR

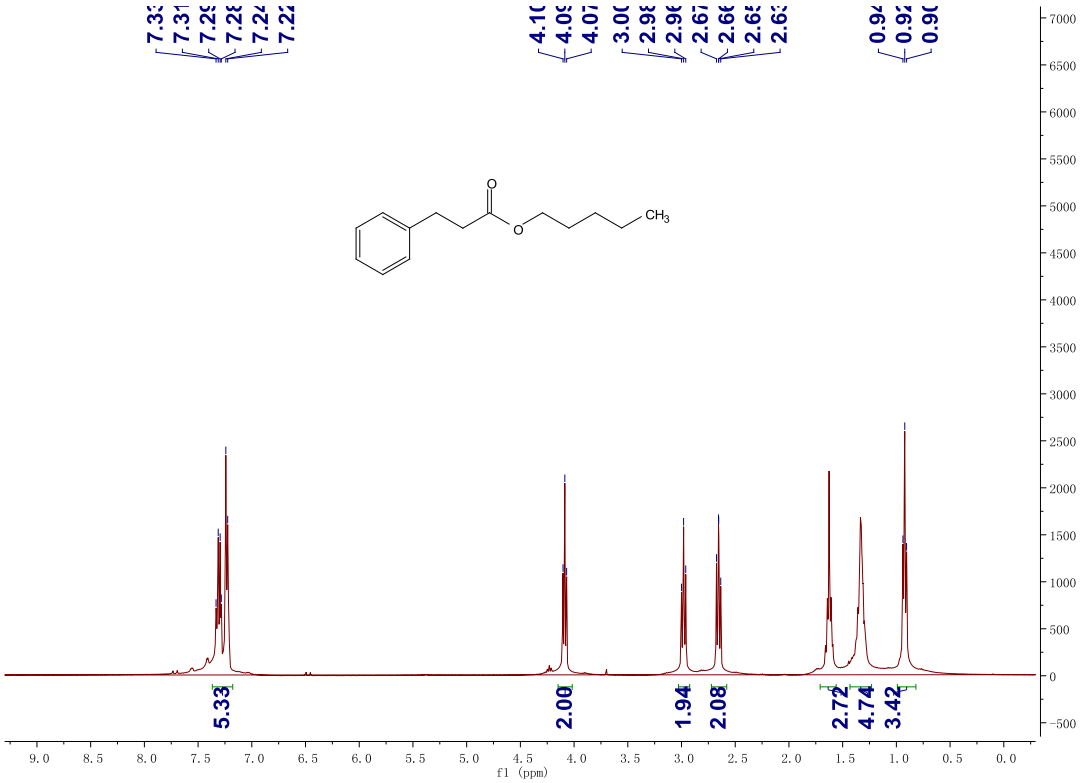


^{13}C NMR

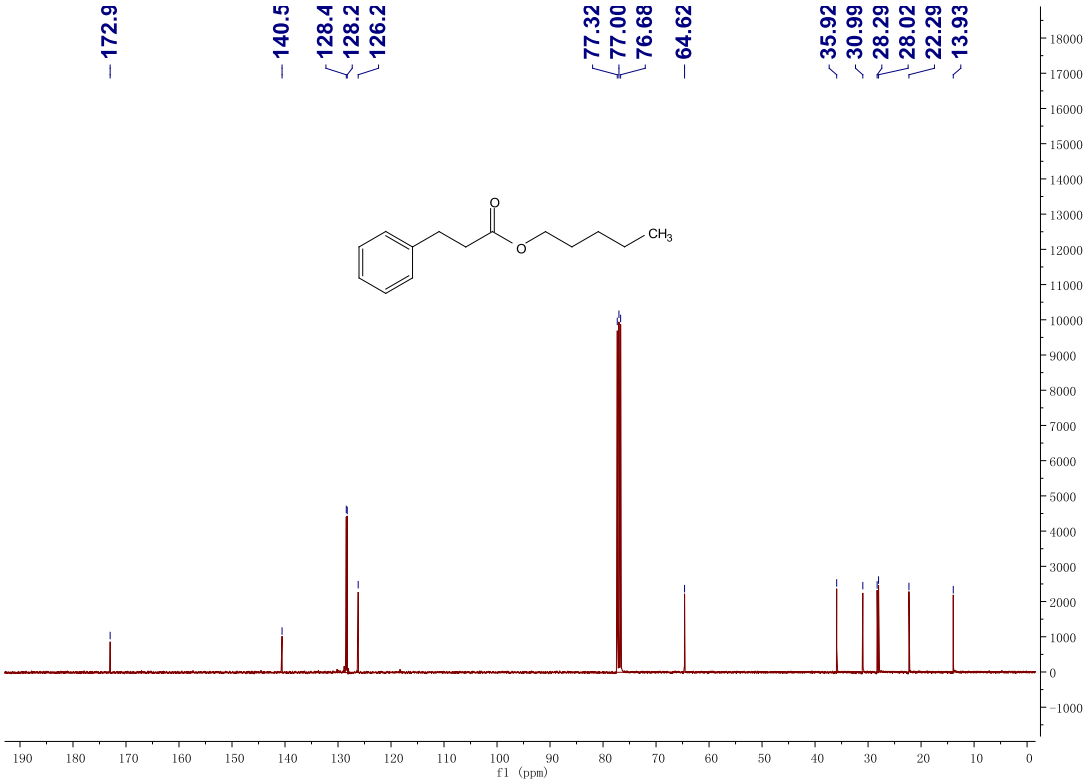


Compound 3ya

^{1}H NMR

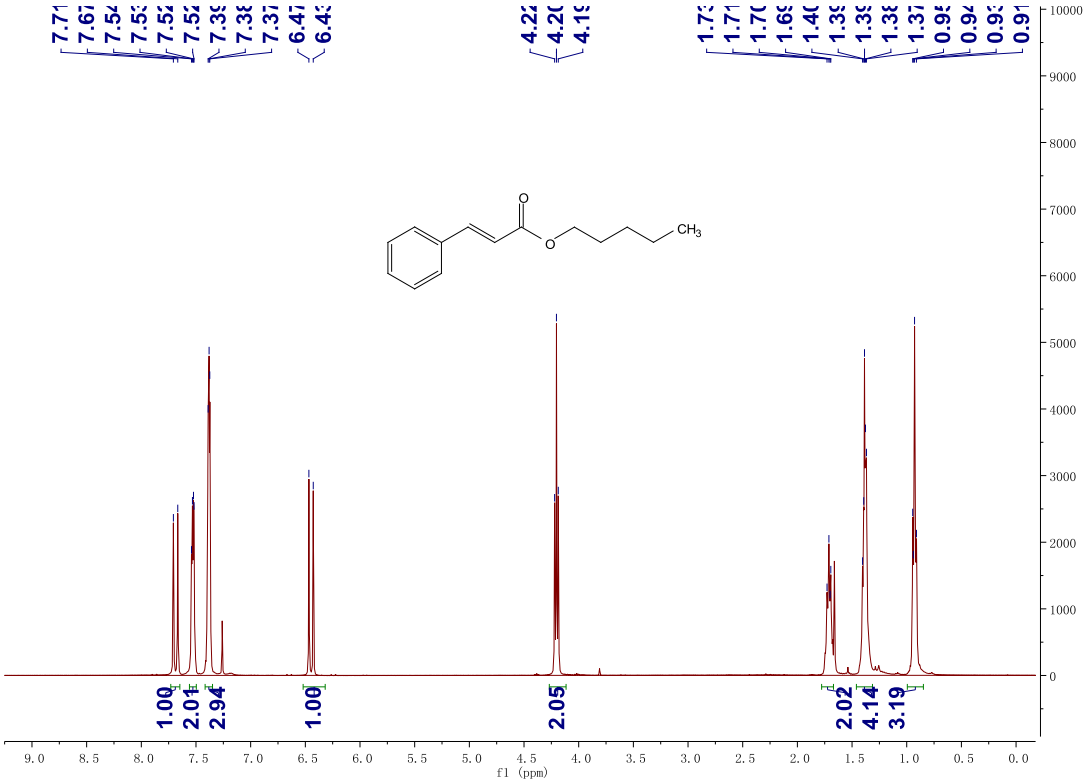


^{13}C NMR

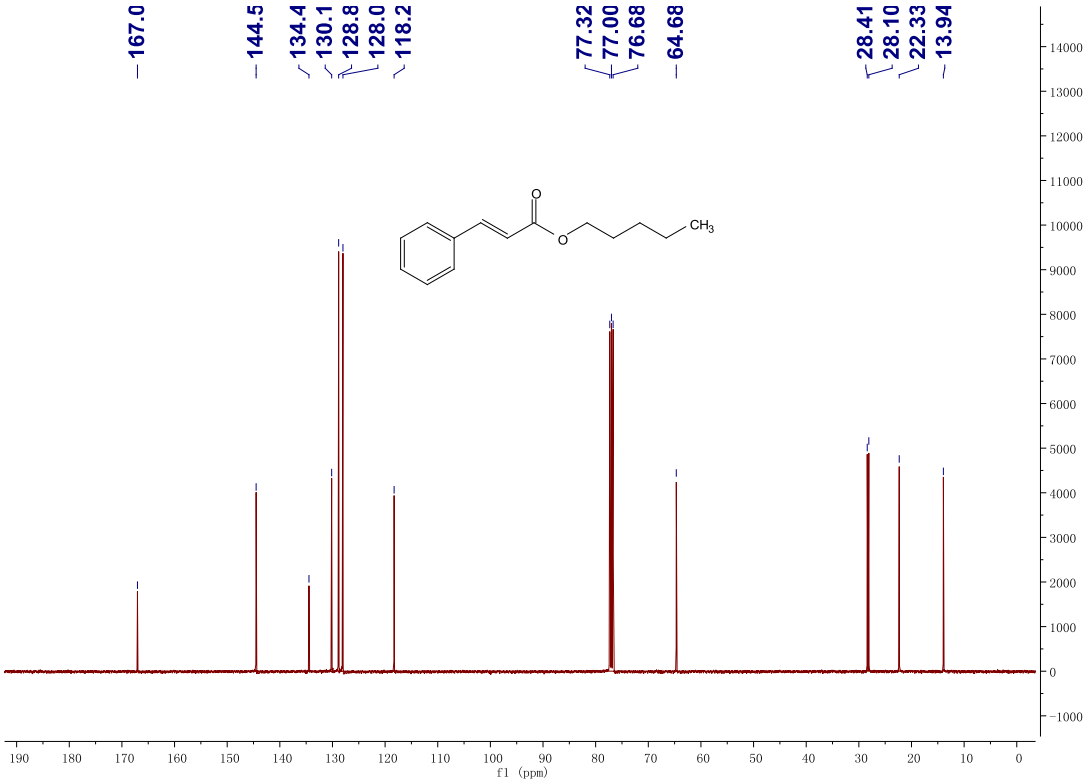


Compound 3za

^{1}H NMR

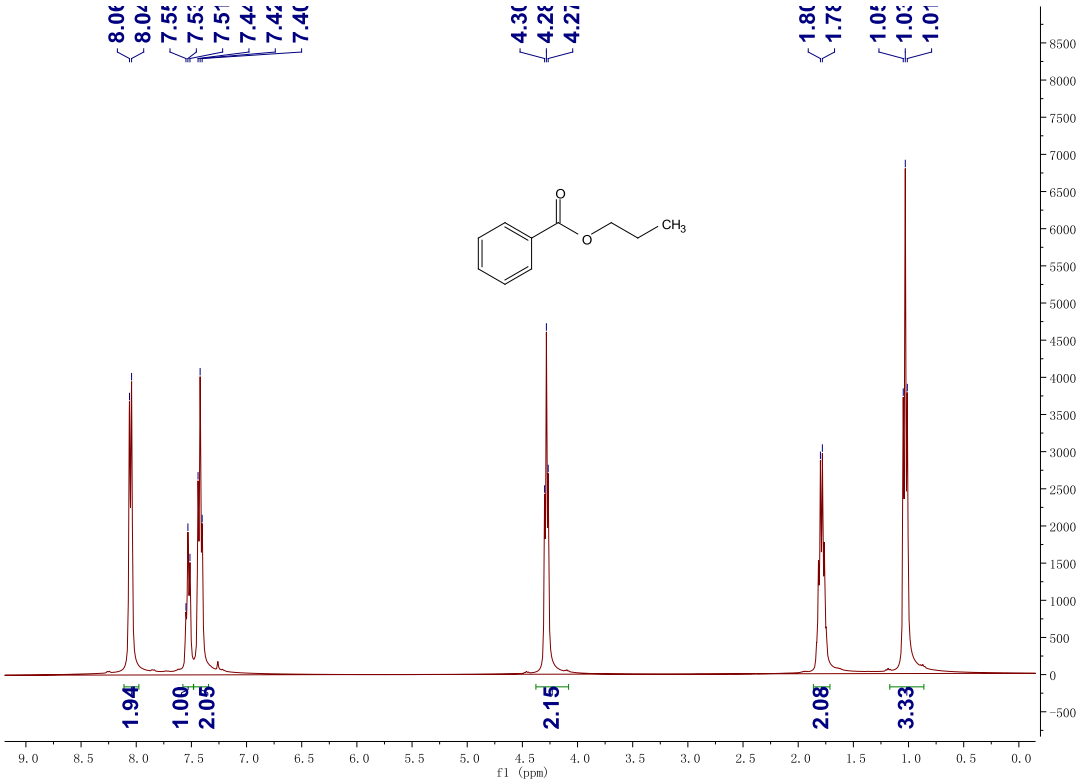


^{13}C NMR

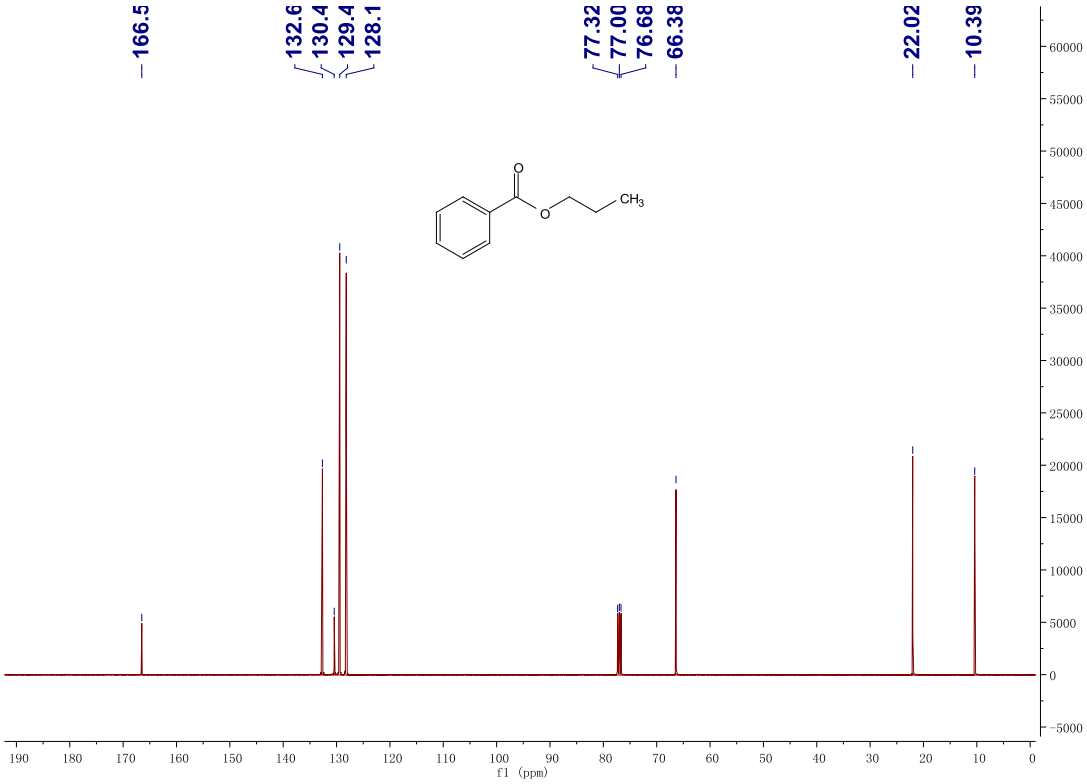


Compound 3ab

^{1}H NMR

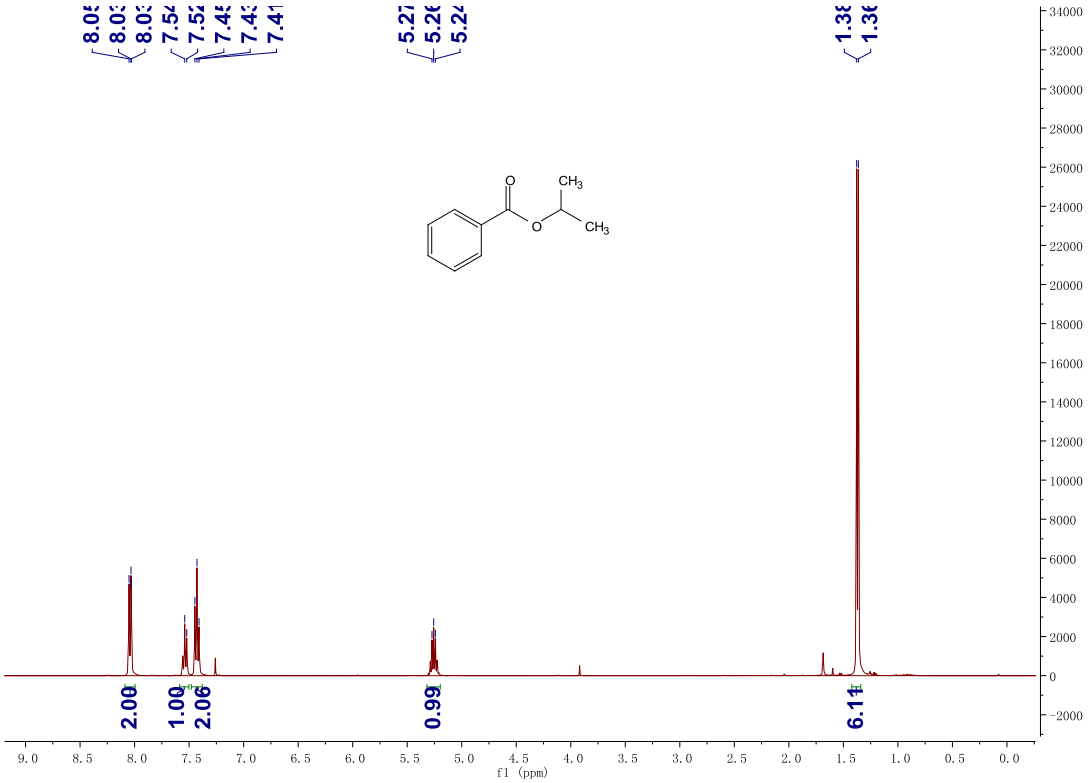


^{13}C NMR

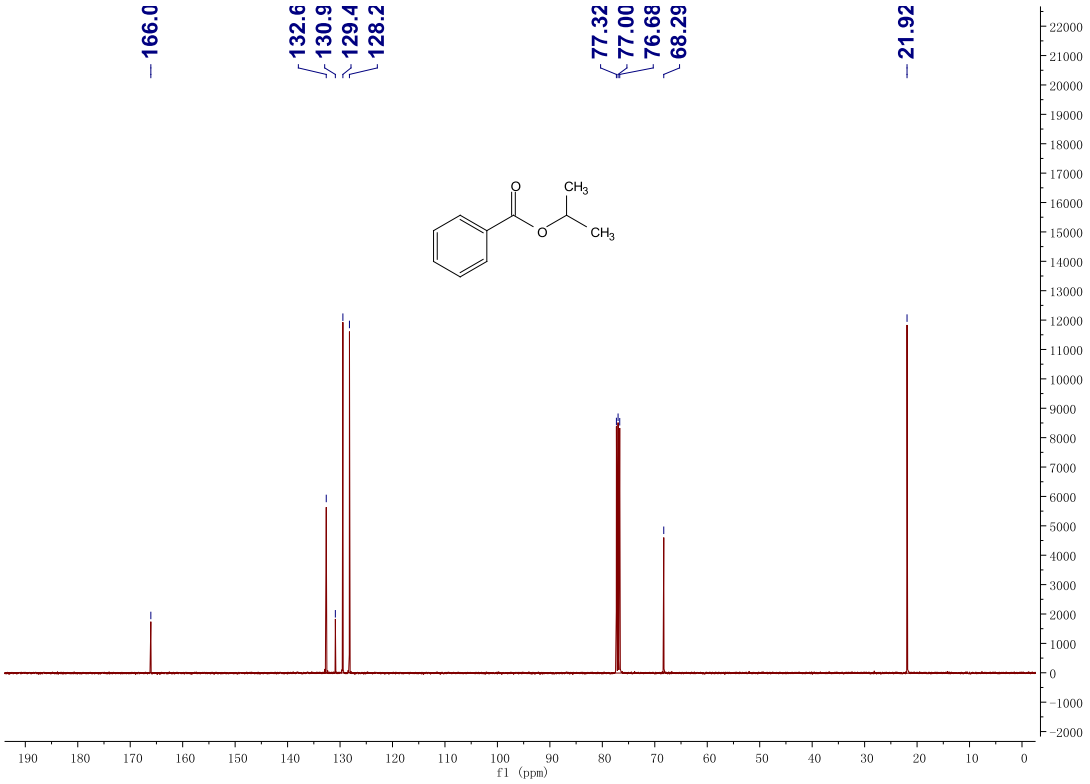


Compound 3ac

^{1}H NMR

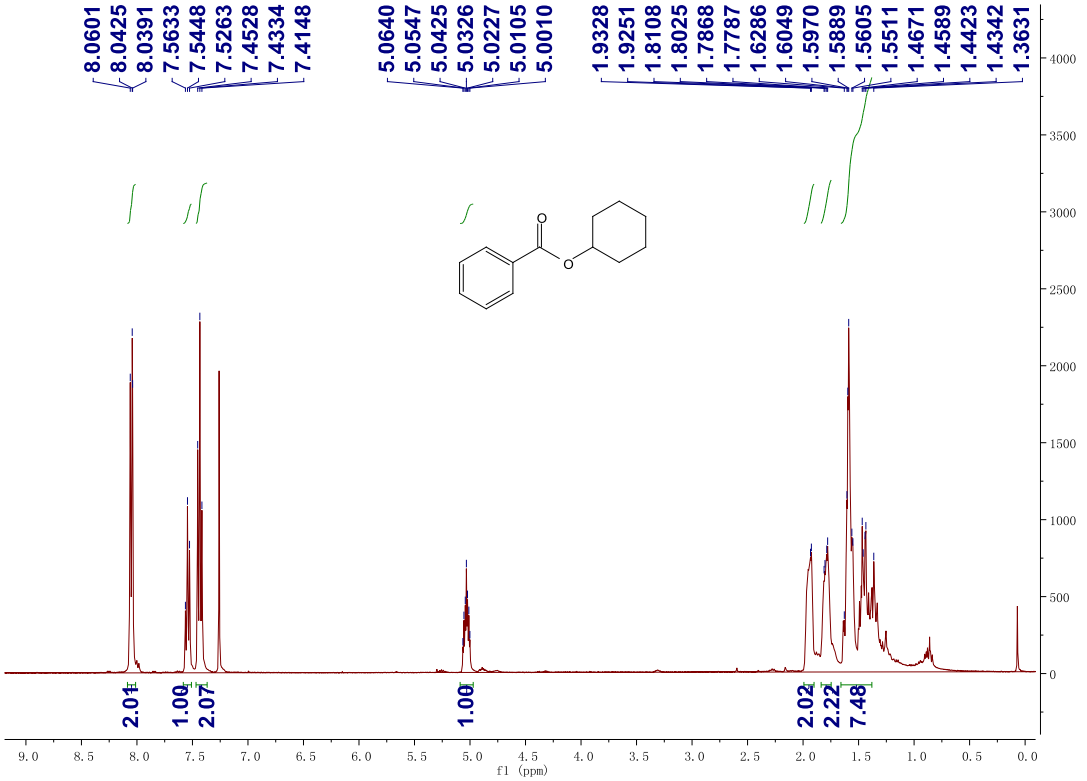


^{13}C NMR



Compound 3ad

^{1}H NMR



^{13}C NMR