Supporting Information

Pd(II)-Catalyzed Oxidative Alkoxycarbonylation of 2-Phenoxypyridine Derivatives with CO and Alcohols

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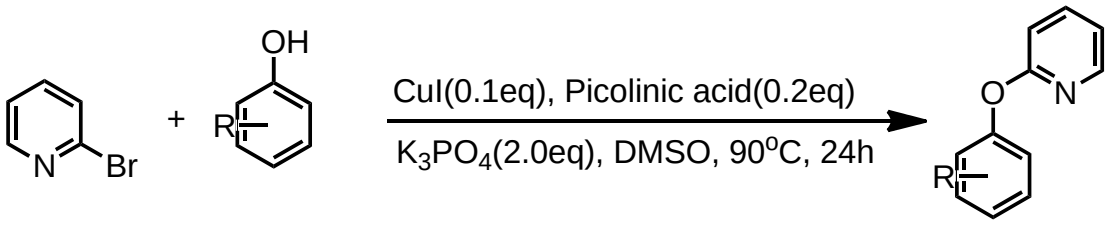
A: General Information

Dioxane was dried by sodium and freshly distilled. The other materials and solvents were purchased from Aladdin and other commercial suppliers and used without additional purification. NMR spectra were recorded on a Bruke Avance operating for ^{1}H NMR at 400 MHz, and ^{13}C NMR at 100 MHz using TMS as internal standard. Chemical shifts were given relative to $CDCl_3$(7.26 ppm for ^{1}H NMR, 77.16ppm for ^{13}C NMR). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or a low-resolution MS instrument using EI ionization.

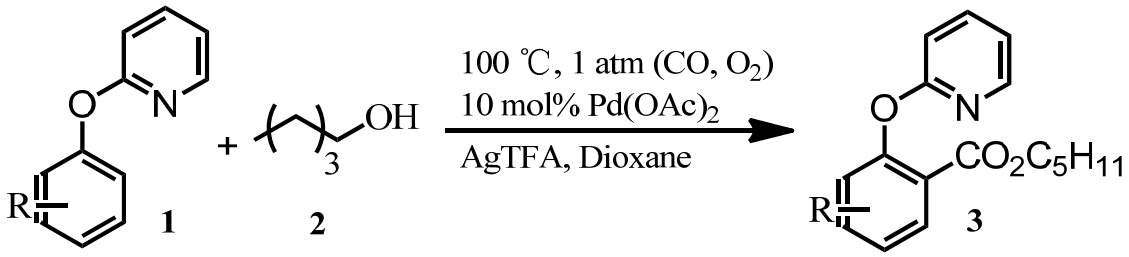
B: **General Procedure for the Preparation of Starting Materials:**

All substrates were prepared according to the following literature:[1]

[1]



C: General Procedure for carbonylation of 1 with CO and Alcohol:

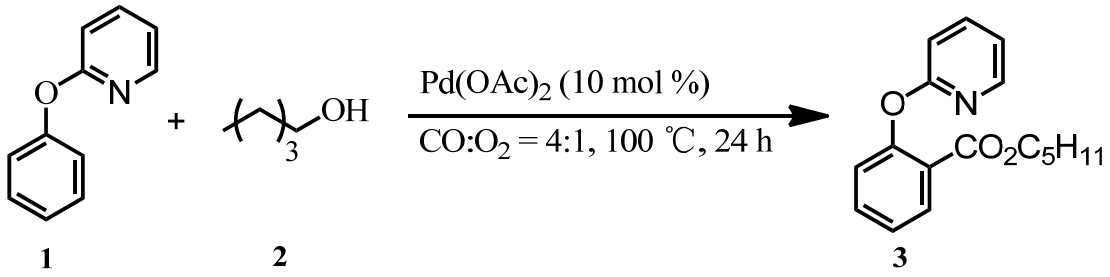


A mixture of substrate (0.4 mmol), $Pd(OAc)_2$ (10 mmol%), AgTFA (0.4 mmol), alcohol (6.0 mmol) and Dioxane (2.0 mL) in a 50 mL Schlenk tube (purged with

[1] Maiti, D. and Buchwald, S.L, *J. Org. Chem.* 2010**, 75**, 1791-1794

$CO:O_2$ = 4:1) was heated at 100 °C for 24 hours. The reaction mixture was cooled to RT, and concentrated *in vacuo*. The residue was purified by silica gel chromatography to yield the desired product.

D: **Optimization of Reaction Conditions:**

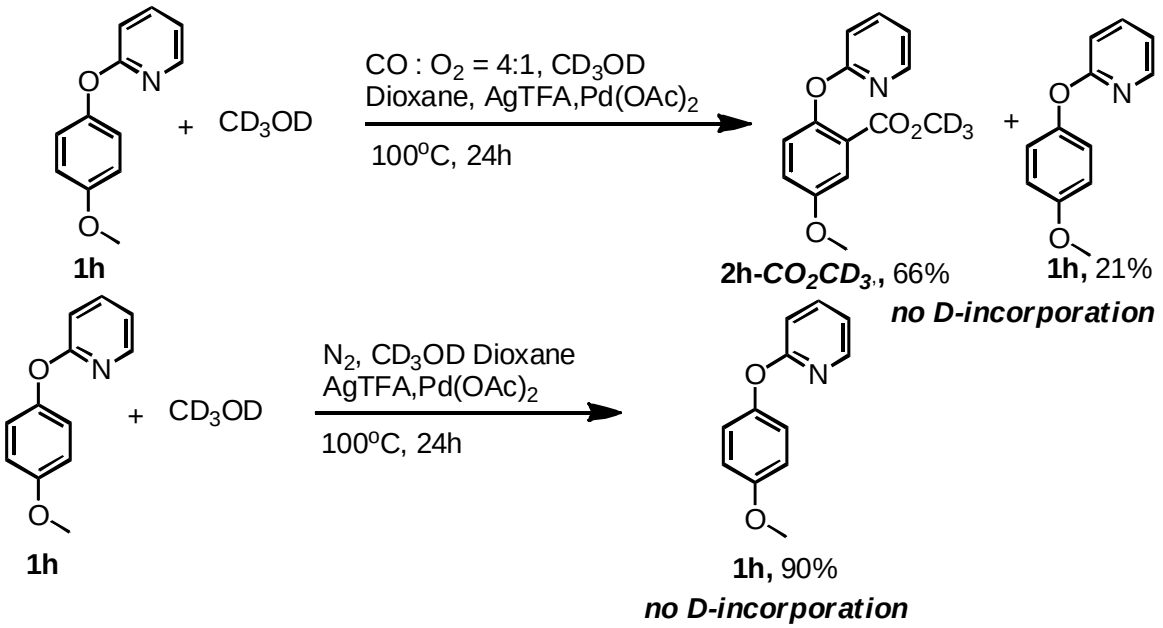


1 **2** **3**

entry	oxidant	Additive	Solvent	yield (%)
1	$CuBr_2$	None	Dioxane	Trace
2	$K_2S_2O_8$	None	Dioxane	N.R[5]
3	$CuSO_4$	None	Dioxane	55
4	AgTFA[1]	None	Dioxane	75
5	$CuSO_4$	NaTFA	Dioxane	Trace
6	$CuSO_4$	NaOAc	Dioxane	N.R
7	$CuSO_4$	$LiCO_3$	Dioxane	N.R
8	AgOTf[2]	None	Dioxane	Trace
9	$CuBr_2$	KOAc	Dioxane	N.R
10	$CuBr_2$	NaTFA	Dioxane	Trace
11	$CuBr_2$	None	DCM[4]	N.R
12	$CuBr_2$	None	Toluene	N.R
13	$CuBr_2$	None	DCE	N.R
14	AgOAc[3]	None	Dioxane	N,R
15	Ag_2CO_3	None	Dioxane	N.R

[1] TFA = Trifluoroacetyl, [2] Tf = Trifloromethanesulfonyl, [3] Ac = Acetyl, [4] DCM = Dichloromethane, [5] N.R = no reaction

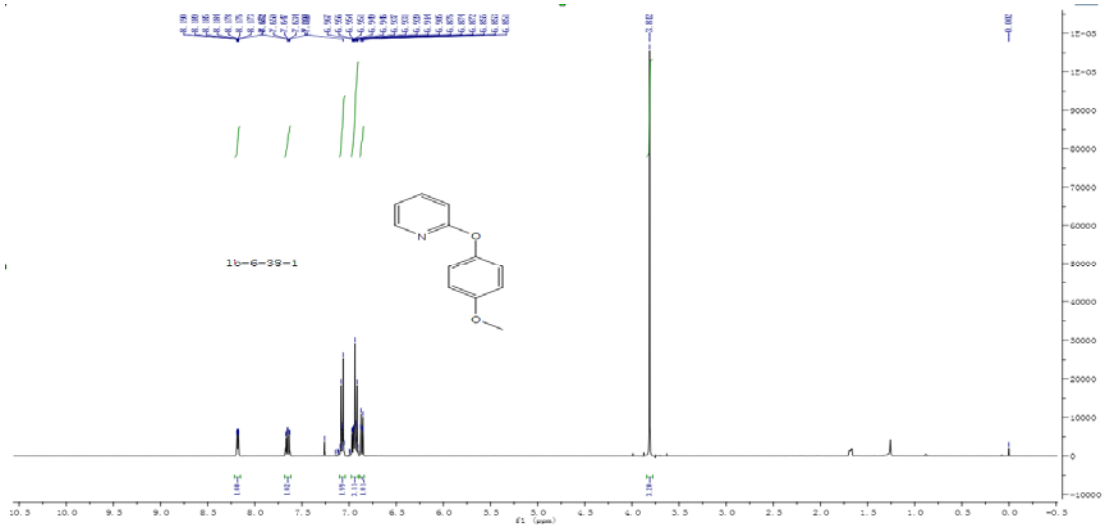
E: Deuterium Labeling Experiments

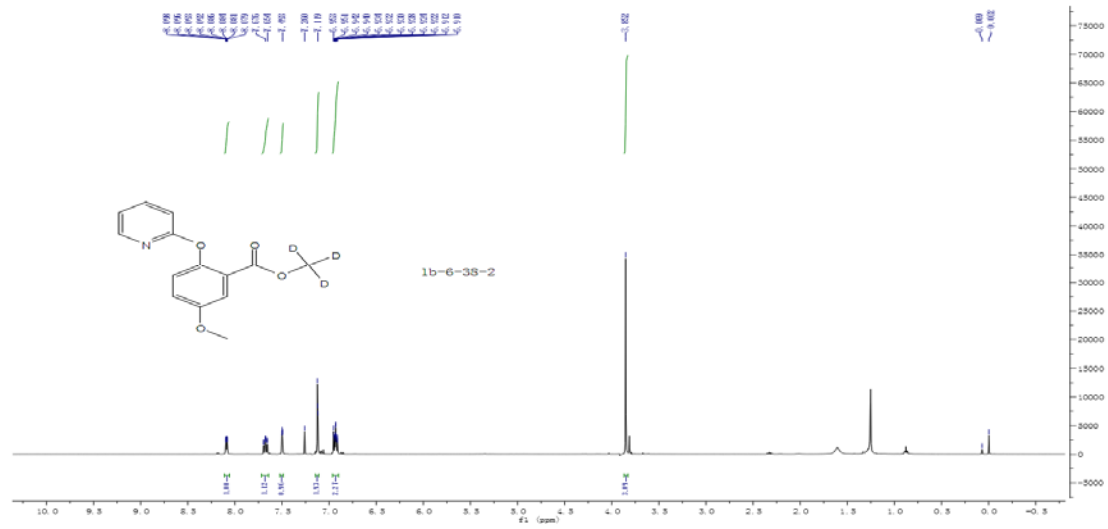


Experiment procedure

Following our general procedure, a mixture of 2-(4-Methoxyphenoxy)pyridine (0.4 mmol), $Pd(OAc)_2$ (10 mmol%), AgTFA (0.4 mmol), CD_3OD (6.0 mmol) and Dioxane (2.0 mL) in a 50 mL Schlenk tube (purged with $CO:O_2$ = 4:1 or N_2) was stirred in a preheated oil bath at 100 °C for 24 h. After the removal of solvent, the crude reaction mixture was carefully pre-adsorbed on silica on the rotary evaporator. After 0purification by flash chromatography (Ethyl acetate/Petroleum ether = 1/5) , the **2h** was obtained in 66% yield, R_f = 0.32.

^{1}H NMR of Deuterium Labeling Experiments


1b-6-39-1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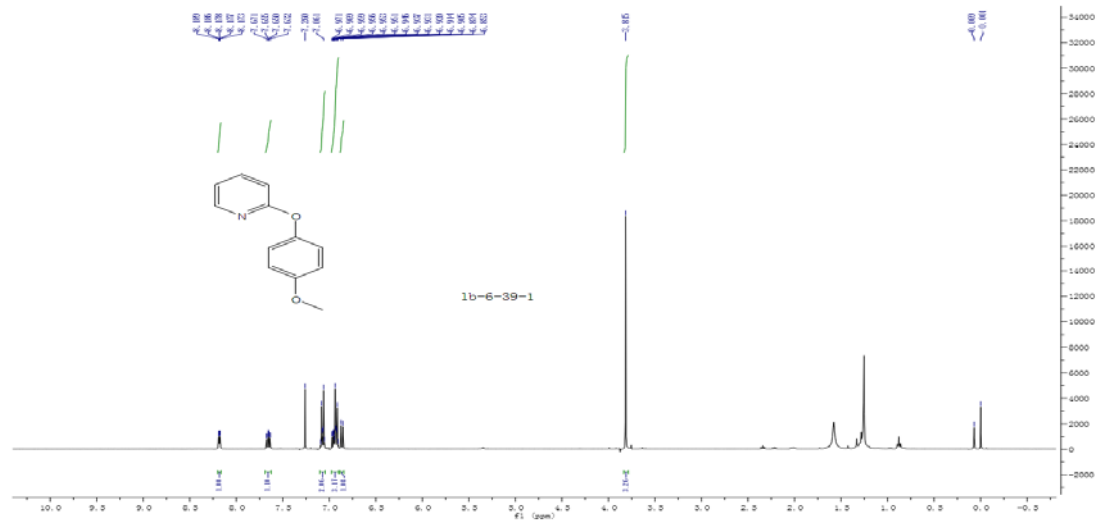
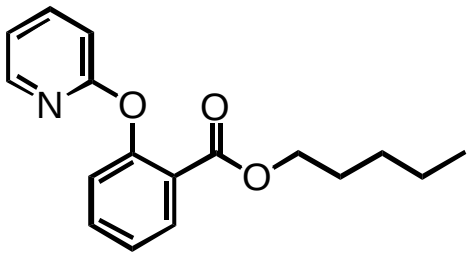
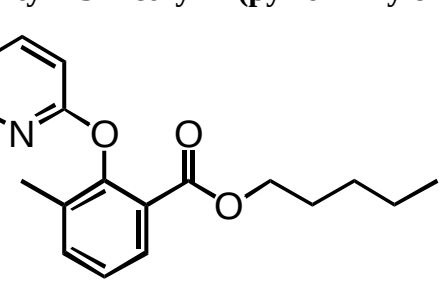

1b-6-39-1

F: Characterization Data of Products

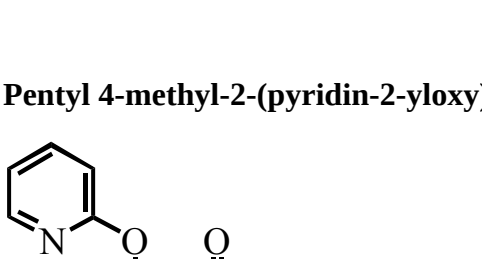
Pentyl 2-(pyridin-2-yloxy)benzoate (2a). Synthesized according to general procedure C, yield : 75%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 4.4 Hz, 1H), 8.01 (d, J =7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 7.19 (d, J =8.4 Hz, 1H), 6.96 (m, 2H), 4.09 (t, J = 6.0 Hz, 2H), 1.49-1.45 (m, 2H), 1.25-1.19 (m, 4H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 164.5, 153.4, 147.9, 139.9, 134.2, 132.5, 125.7, 125.4, 124.7, 118.6, 111.7, 65.7, 28.7, 28.6, 22.9, 14,5. HRMS (EI-TOF) calc. for $C_{17}H_{19}NO_3$ (M^+): 285.1365, found: 285.1356.



Pentyl 3-methyl-2-(pyridin-2-yloxy)benzoate (2b). Synthesized according to general procedure C, yield: 30%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz 1H), 7.83 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.70-7.65 (m, 1H), 7.44 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.96-6.90 (m, 2H), 4. 07 (t, J = 6.8 Hz, 2H), 2.18 (s, 3H), 1.48-1.41 (m, 2H), 1.28-1.15 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 163.5, 150.9, 147.3, 139.2, 135.1, 133.0, 129.4, 125.1, 125.0, 117.6, 110.5, 65.1, 28.1, 27.9, 22.3, 16.6, 13.9. HRMS (EI-TOF) calc. for $C_{18}H_{21}NO_3$ (M^+): 299.1521, found: 299.1528

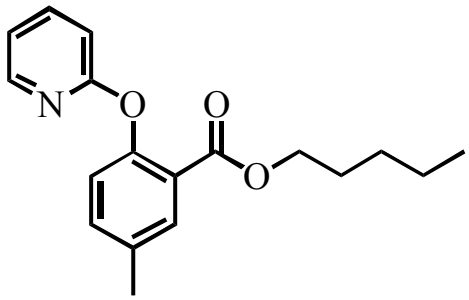


Pentyl 4-methyl-2-(pyridin-2-yloxy)benzoate (2c). Synthesized according to general procedure C, yield : 50%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 4.8 Hz, 1H), 7.92 (d, J = 7.6 Hz, 1 H), 7.69-7.65 (m, 1H), 7.10 (d, J = 8.0 Hz, 1H), 6.99 (s, 1H), 6.95-6.91

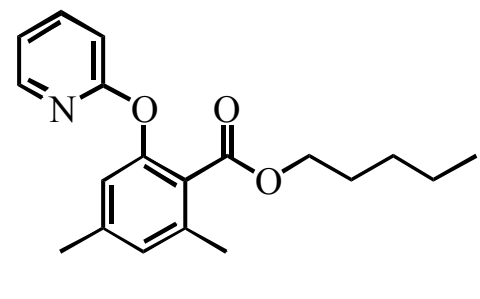


(m, 2H), 4. 07 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H), 1.49-1.42(m, 2H), 1.21-1.17 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 164.0, 152.8, 147.3, 144.8, 139.2, 137.8, 126.1, 124.5, 121.7, 117.8, 111.0, 64.9, 28.1, 27.9, 22.3, 21.5, 13.9. HRMS (EI-TOF) calc. for $C_{18}H_{21}NO_3$ (M^+): 299.1521, found: 299.1520.

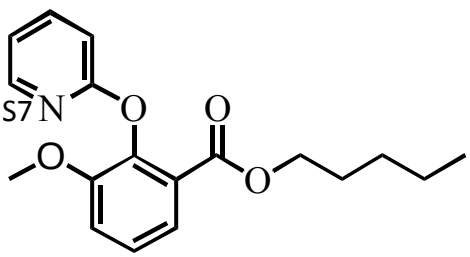
Pentyl 5-methyl-2-(pyridin-2-yloxy)benzoate (2d). Synthesized according to general procedure C, yield : 50%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 4.8 Hz, 1H), 7.80 (s, 1 H), 7.69-7.64 (m, 1H), 7.36 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 6.95-6.91 (m, 2H), 4. 07 (t, J = 6.6 Hz, 2H), 2.40 (s, 3H), 1.48-1.42 (m, 2H), 1.28-1.13 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 164.1, 150.5, 147.2, 139.1, 134.8, 134.3, 132.1, 124.3, 123.9, 117.7, 111.0, 65.0, 28.1, 27.9, 22.2, 20.7, 13.9. HRMS (EI-TOF) calc. for $C_{18}H_{21}NO_3$ (M^+): 299.1521, found: 299.1526.



Pentyl 2,4-dimethyl-6-(pyridin-2-yloxy)benzoate (2e). Synthesized according to general procedure C, yield : 67%, yellow oil. ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 3.6 Hz, 1H), 7.67-7.62 (m, 1H), 6.95 (t, J = 6.0 Hz, 1 H), 6.89 (s, 1H), 6.88 (d, J = 11.2 Hz, 1H), 6.78(s, 1H), 4. 09 (t, J = 6.6 Hz, 2H), 2.37 (s, 3 H), 2.31(s, 1H), 1.48-1.41 (m, 2H), 1.19-1.14 (m, 4H), 0.81 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 163.8, 151.2, 147.5, 141.0, 139.1, 137.7, 128.0, 124.5, 120.6, 118.1, 111.2, 65.0, 28.1, 27.9, 22.2, 21.3, 19.9, 13.8. HRMS (EI-TOF) calc. for $C_{19}H_{23}NO_3$ (M^+): 313.1678, found: 313.1675.

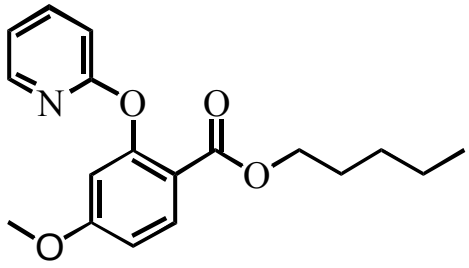


Pentyl 3-methoxy-2-(pyridin-2-yloxy)benzoate (2f). Synthesized according to general procedure C, yield : 44%, yellow oil.

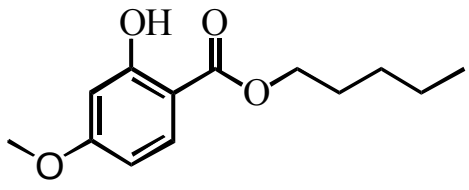


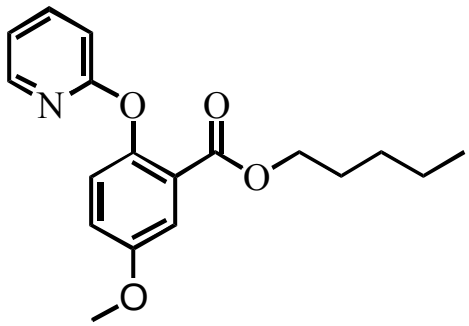
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 4.0 Hz, 1H), 7.71-7.67 (m, 1H), 7.58 (d, *J* = 7.6 Hz, 1 H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 6.2 Hz, 1H), 4.10 (t, *J* = 6.6 Hz, 2H), 3.77 (s, 3 H), 1.48-1.41 (m, 2H), 1.24-1.13 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 163.5, 152.8, 147.1, 142.0, 139.1, 126.1, 125.5, 122.9, 117.7, 116.2, 110.5, 65.2, 56.3, 28.1, 27.9, 27.3, 13.9. HRMS (EI-TOF) calc. for $C_{18}H_{21}NO_4$ (M^+): 315.1471, found: 315.1476.

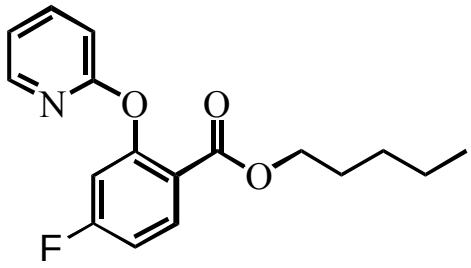
Pentyl 4-methoxy-2-(pyridin-2-yloxy)benzoate (2g). Synthesized according to general procedure C, yield : 24%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 4.0 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 6.96-6.93 (m, 2H), 6.82 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 4.05 (t, *J*= 6.6 Hz, 2H), 3.84 (s, 3H), 1.48-1.41 (m, 2H), 1.28-1.17 (m, 4 H), 0.84 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 163.9, 154.7, 147.3, 139.2, 133.5, 117.9, 116.8, 111.2, 111.0, 109.3, 64.8, 55.6, 28.2, 28.0, 22.3, 13.9. HRMS (EI-TOF) calc. for $C_{18}H_{21}NO_4$ (M^+): 315.1471, found:315.1466.

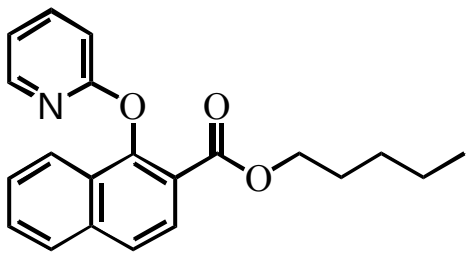


Pentyl 2-hydroxy-4-methoxybenzoate (3g). Synthesized according to general procedure C, yield :73% , yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.08 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 6.45 (s, 1H), 6.42 (dd, J_1= 8.8 Hz,J_2 = 2.4 Hz, 1H), 4.30 (t, *J*= 6.6 Hz, 2H), 3.82 (s, 3H), 1.79-1.73 (m, 2H), 1.43-1.33 (m, 4H), 0.93 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 165.5, 163.8, 131.1, 107.4, 105.7, 100.6, 65.1, 55.4, 28.3, 28.1, 22.3, 14.0. HRMS (EI-TOF) calc. for $C_{13}H_{18}O_4$ (M^+): 238.1205, found: 238.1210.



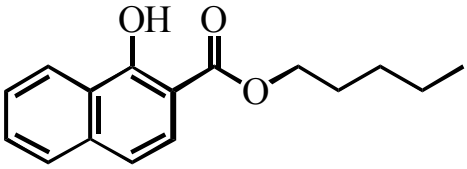
Pentyl 5-methoxy-2-(pyridin-2-yloxy)benzoate (2h). Synthesized according to general procedure C, yield : 92%, yellow oil. 
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 4.4 Hz, 1H), 7.68-7.64 (m, 1H), 7.51 (s, 1H), 7.10 (d, J= 0.8 Hz, 2H), 6.93-6.90 (m, 2H), 4.08(t, J= 6.8 Hz, 2H), 3.85 (s, 3 H), 1.47-1.37 (m, 2H), 1.25-1.12 (m, 4H), 0.83 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 164.2, 156.4, 147.2, 146.2, 139.1, 125.2, 119.9, 117.7, 115.6, 110.9, 65.2, 55.7, 28.0, 27.9, 22.2, 13.9. HRMS (EI-TOF) calc. for $C_{18}H_{21}NO_4$ (M^+): 315.1471, found: 315.1470.

Pentyl 4-fluoro-2-(pyridin-2-yloxy)benzoate (2i). Synthesized according to general procedure C, yield : 37%, yellow oil. 
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 4.0 Hz, 1H), 8.04 (dd, J_1 = 8.8 Hz, J_2 = 6.8 Hz, 1H), 7.73-7.69 (m, 1H), 7.02-6.96 (m, 3H), 6.91 (dd, J_1 = 9.4 Hz, J_2 = 2.2 Hz, 1H), 4. 08(t, J = 6.8 Hz, 2 H), 1.50-1.44(m, 2H), 1.26-1.16 (m, 4H), 0.84 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4 (d, J_{C-F} = 253.2 Hz), 164.6, 163.4, 154.6 (d, J_{C-F} = 11.6 Hz), 147.2, 139.5, 135.6 (d, J_{C-F} = 10.1 Hz), 121.0 (d, J_{C-F} = 3.5 Hz), 118.4, 112.4(d, J_{C-F} = 21.3 Hz), 111.7 (d, J_{C-F} = 23.4 Hz), 111.3, 65.2, 28.1, 27.9, 22.2, 13.9. HRMS (EI-TOF) calc. for $C_{17}H_{18}FNO_3$ (M^+): 303.1271, found: 303.1271.

Pentyl 1-(pyridin-2-yloxy)-2-naphthoate (2j). Synthesized according to general procedure C, yield : 15% , yellow oil. 
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 2.0 Hz, 1H), 8.03 (d, J = 2.4 Hz, 1H), 7.89(d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.74-7.70 (m, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.48 (t, J =7.0 Hz,

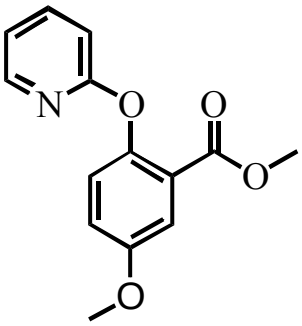
1H), 7.06 (d, *J* =8.4 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 1.52-1.45 (m, 2H), 1.29-1.18 (m, 4H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 164.4, 150.2, 147.4, 139.3, 136.7, 128.3, 127.8, 126.8, 126.7, 125.2, 123.7, 120.5, 117.9, 110.5, 65.2, 28.1, 28.0, 22.3, 13.9. HRMS (EI-TOF) calc. for $C_{21}H_{21}NO_3$ (M^+): 335.1521, found: 335.1528.

Pentyl 1-hydroxy-2-naphthoate (3j). Synthesized according to general procedure C,



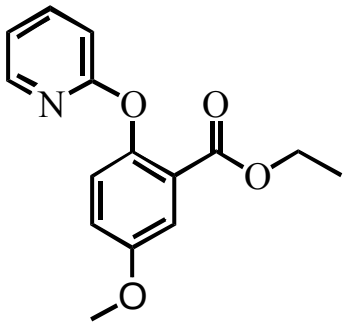
yield : 84%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.09 (s, 1 H), 8.41 (d, *J* = 8.4 Hz, 1H), 7.79-7.76 (m, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 4.39 (t, *J* = 6.8 Hz, 2H), 1.86-1.79(m, 2H), 1.49-1.38 (m, 4H), 0.95 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ HRMS (EI-TOF) calc. for $C_{16}H_{18}O_3$ (M^+): 258.1256, found: 258.1526.

Methyl 5-methoxy-2-(pyridin-2-yloxy)benzoate (2k). Synthesized according to



general procedure C, yield : 64%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 5.2 Hz, 1 H), 7.69-7.65 (m, 1 H), 7.49 (s, 1H), 7.14-7.09 (m, 2H), 6.95-6.90 (m, 2H), 3.85 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.5, 164.2, 156.3, 147.2, 146.5, 139.2, 125.2, 124.5, 120.1, 117.8, 115.4, 110.9, 55.7, 52.0. HRMS (EI-TOF) calc. for $C_{15}H_{14}O_4$ (M^+): 258.0845, found: 258.0844.

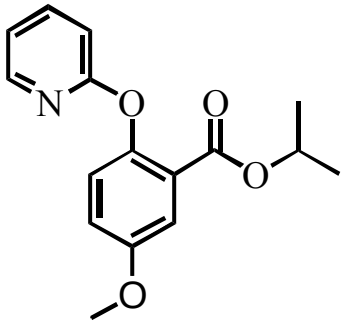
Ethyl 5-methoxy-2-(pyridin-2-yloxy)benzoate (2l). Synthesized according to



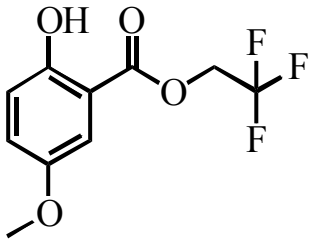
general procedure C, yield : 67%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 4.8 Hz, 1H), 7.66-7.64 (m, 1H), 7.51 (s, 1H), 7.14-7.09 (m, 2H), 6.94-6.90 (m, 2H), 4.72(q, *J* = 8.2 Hz, 2H), 3.85 (s, 3H), 1.05 (t, *J* =7.0 HZ, 3H). ^{13}C NMR (100 MHz, $CDCl_3$):

δ 165.2, 164.2, 156.4, 147.2, 146.1, 139.1, 125.2, 119.9, 117.7, 115.6, 110.8, 61.0, 55.7, 13.8. HRMS (EI-TOF) calc. for $C_{15}H_{15}NO_4$ (M^+): 273.1001, found: 273.1000.

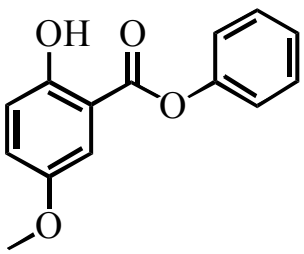
Isopropyl 5-methoxy-2-(pyridin-2-yloxy)benzoate (2m). Synthesized according to general procedure C, yield : 71%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 7.68-7.64 (m, 1H), 7.50 (s, 1 H), 7.10 (d, J = 2.0 Hz, 2H), 6.93-6.89 (m, 2H),5.06-5.00 (m, 1H), 3.85 (s, 3H), 1.04 (d, J= 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 164.3, 156.5, 147.2, 145.9, 139.1, 125.8, 125.1, 119.7, 117.6, 115.6, 110.9, 68.5, 55.7, 21.4. HRMS (EI-TOF) calc. for $C_{16}H_{17}NO_4$ (M^+): 287.1158, found: 287.1167.



2,2,2-Trifluoroethyl 2-hydroxy-5-methoxybenzoate (2n). Synthesized according to general procedure C, yield : 50%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.30 (d, J = 6.8 Hz, 1H), 7.14 (dd, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 1H), 6.95 (d, J = 9.2 Hz, 1H), 4.72 (q, J = 8.2 Hz, 2H),3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.7, 157.1, 152.8, 125.7, 123.4 (d, $J_{C\text{-}F}$ = 275.5 Hz), 119.4, 112.4, 111.0, 61.3 (q, $J_{C\text{-}F}$ = 36.9 Hz), 56.5. HRMS (EI-TOF) calc. for $C_{10}H_9F_3O_4$ (M^+): 250.0453, found: 250.0458.

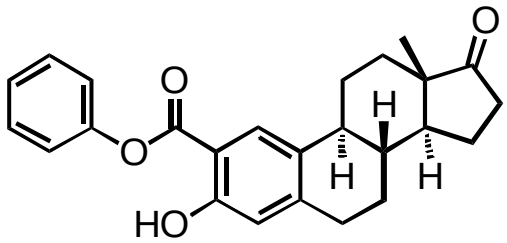


Phenyl 2-hydroxy-5-methoxybenzoate (2o). Synthesized according to general procedure C, yield : 48%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (s, 1H), 7.52 (d, J = 3.2 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.32(d, J = 7.4 Hz, 1H), 7.22(d, J = 7.6 Hz, 2H), 7.17 (dd, J_1 = 9.2 Hz, J_2 = 3.0 Hz, 1H), 6.98 (d, J = 9.2 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 156.8, 152.2, 150.1, 129.6, 126.4, 125.0, 121.7, 118.8, 111.9, 111.2, 55.9.



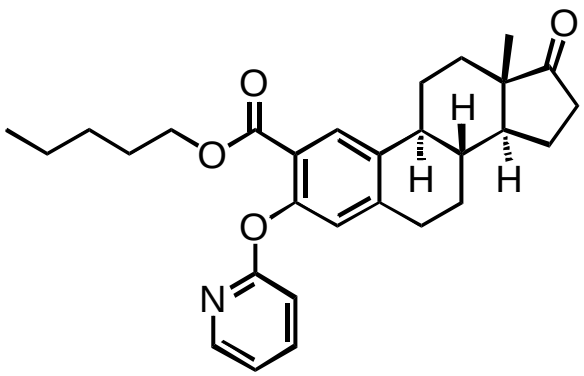
HRMS (EI-TOF) calc. for $C_{14}H_{12}O_4$ (M^+): 244.0736, found: 244.0739.

(*8R,9S,13S,14S*)-Phenyl 3-hydroxy-13-methyl-17-oxo-7, 8, 9, 11, 12, 13, 14, 15, 16, 17-decahydro-6H-cyclopenta[a] phenanthrene-2-carboxylate (5a).



Synthesized according to general procedure C, yield : 53%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.27 (s, 1H), 7.97 (s, 1H), 7.45 (t, *J* =7.8 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2 H), 6.78 (s, 1H), 2.97-2.93 (m, 2H), 2.56-2.46 (m, 2 H), 2.24 (dt, J_1 =10.8 Hz, J_2 = 4.0 Hz, 1H), 2.20-2.13 (m, 1H), 2.12-1.96 (m, 3H), 1.62-1.42 (m, 6H), 0.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.3, 169.5, 160.5, 150.7, 147.4, 132.2, 130.2, 127.4, 126.9, 122.3, 117.8, 110.0, 50.9, 48.5, 44.2, 38.6, 36.4, 31.9, 30.3, 26.7, 26.4, 22.1, 14.4. HRMS (EI-TOF) calc. for $C_{25}H_{26}O_4$ (M^+): 390.1831, found: 390.1835.

(*8R,9S,13S,14S*)-Pentyl 13-methyl-17-oxo-3-(pyridin-2-yloxy)-7, 8, 9, 11, 12, 13, 14, 15, 16, 17-decahydro-6H-cyclopenta[a]phenanthrene-2-carboxylate (5b).

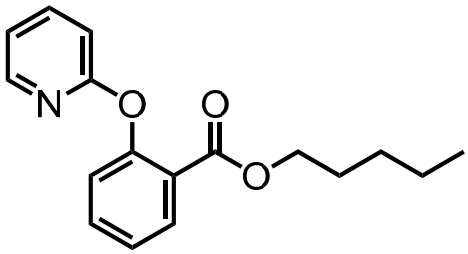


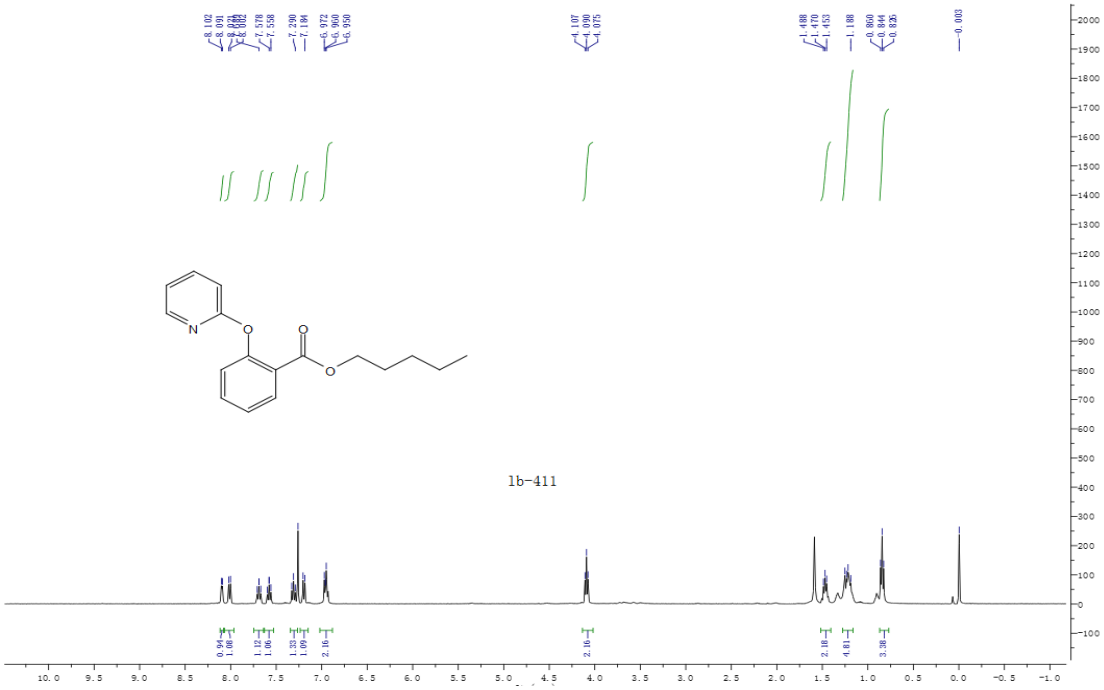
Synthesized according to general procedure C, yield : 52%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (dd, J_1 = 4.8 Hz, J_2 = 1.0 Hz, 1H), 7.94 (s, 1H), 7.67 (dt, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 6.96-6.91 (m, 3H), 4.05 (t, *J* = 6.8 Hz, 2H), 2.95 (t, *J* =4.4 Hz, 2H), 2.55-2.48 (m, 2H), 2.32 (dt, J_1 = 10.8 Hz, J_2 = 4.0 Hz, 1H), 2.18-2.11 (m, 1H), 2.05-1.97 (m, 3H), 1.57-1.50 (m, 2H), 1.46-1.39 (m, 3H), 1.25-1.36 (m, 7H), 0.92 (s, 3H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 220.1, 166.3, 164.7, 151.2, 147.8, 143.8, 139.7, 137.4, 129.7, 124.6, 122.5, 118.3, 111.7, 65.5, 51.0, 48.5, 44.6, 38.4, 36.4, 32.0, 30.0, 28.7, 28.6, 26.7, 26.2, 22.8,

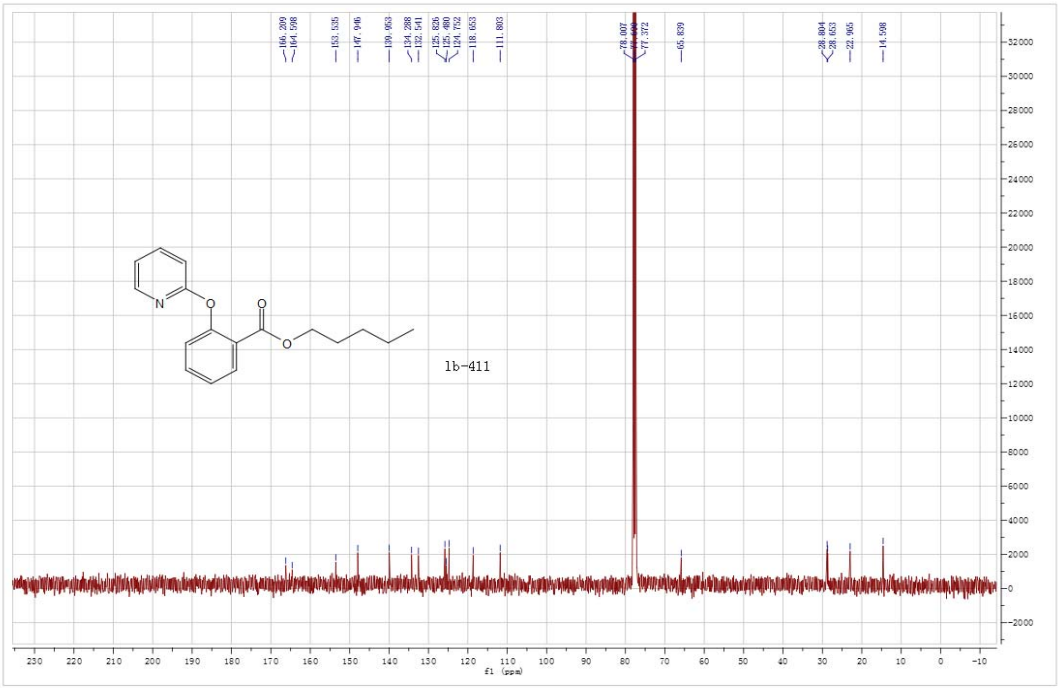
22.2, 14.5, 14.4. HRMS (EI-TOF) calc. for $C_{29}H_{35}NO_4$ (M^+): 461.2566, found: 461.2566.

G: NMR Analysis of Products

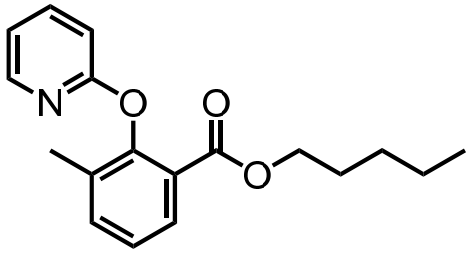
Pentyl 2-(pyridin-2-yloxy)benzoate (2a)

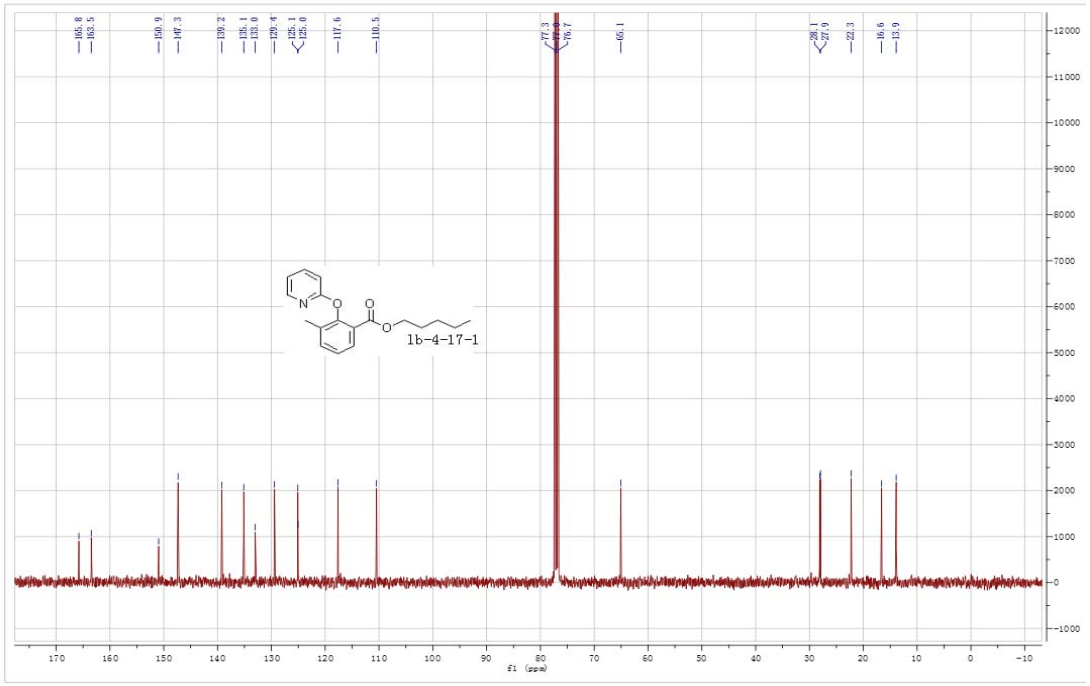


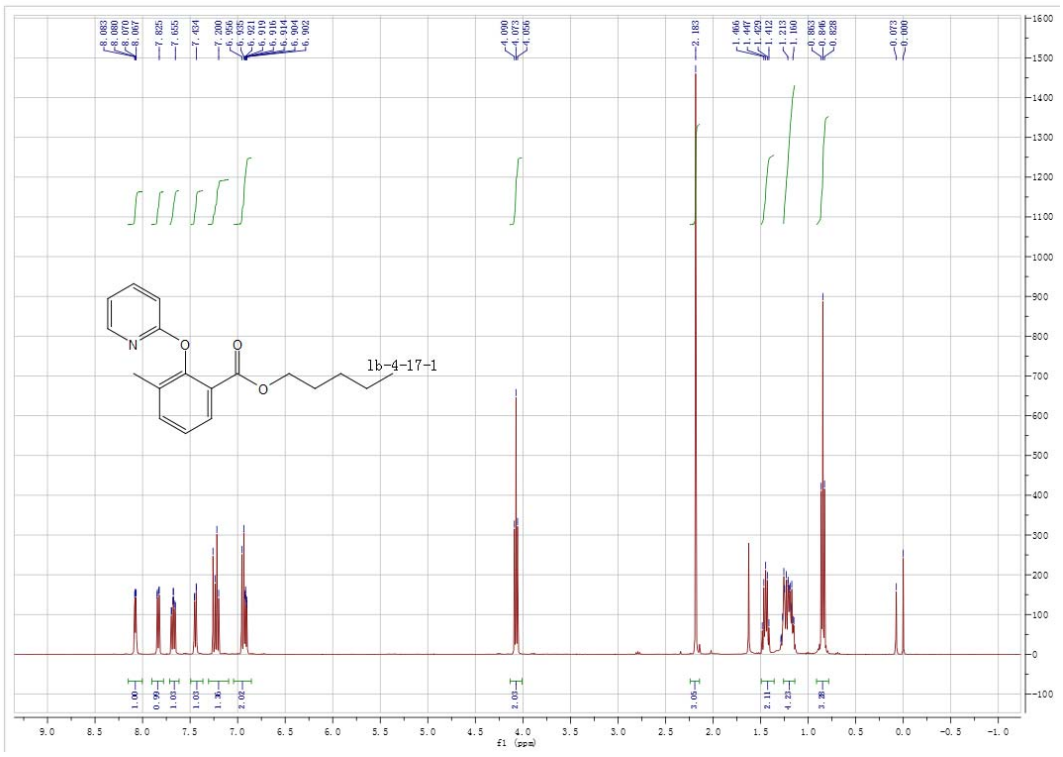




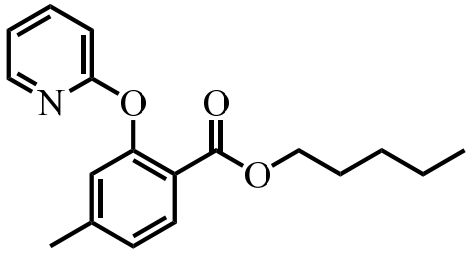
Pentyl 3-methyl-2-(pyridin-2-yloxy)benzoate (2b)

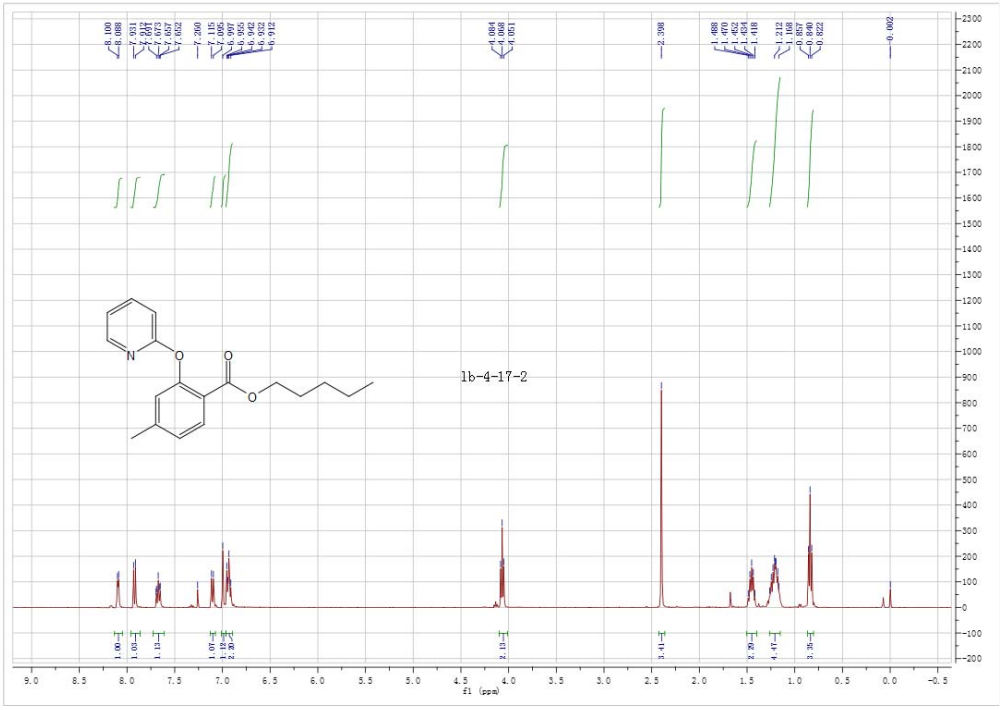


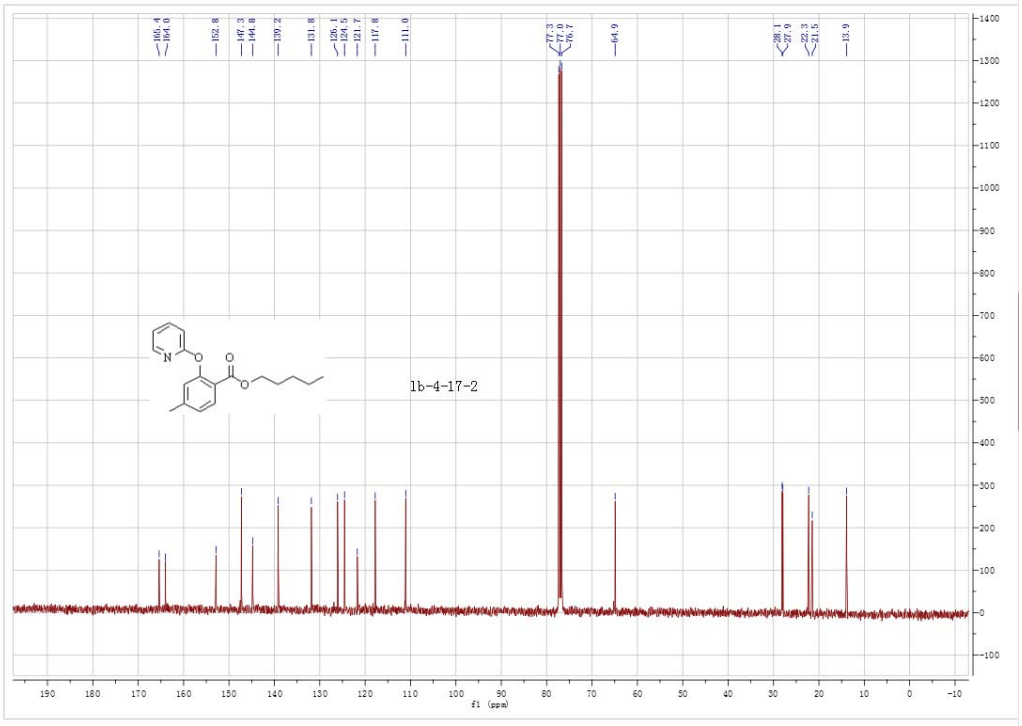




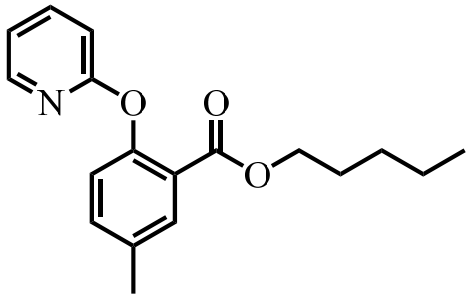
Pentyl 4-methyl-2-(pyridin-2-yloxy)benzoate (2c)

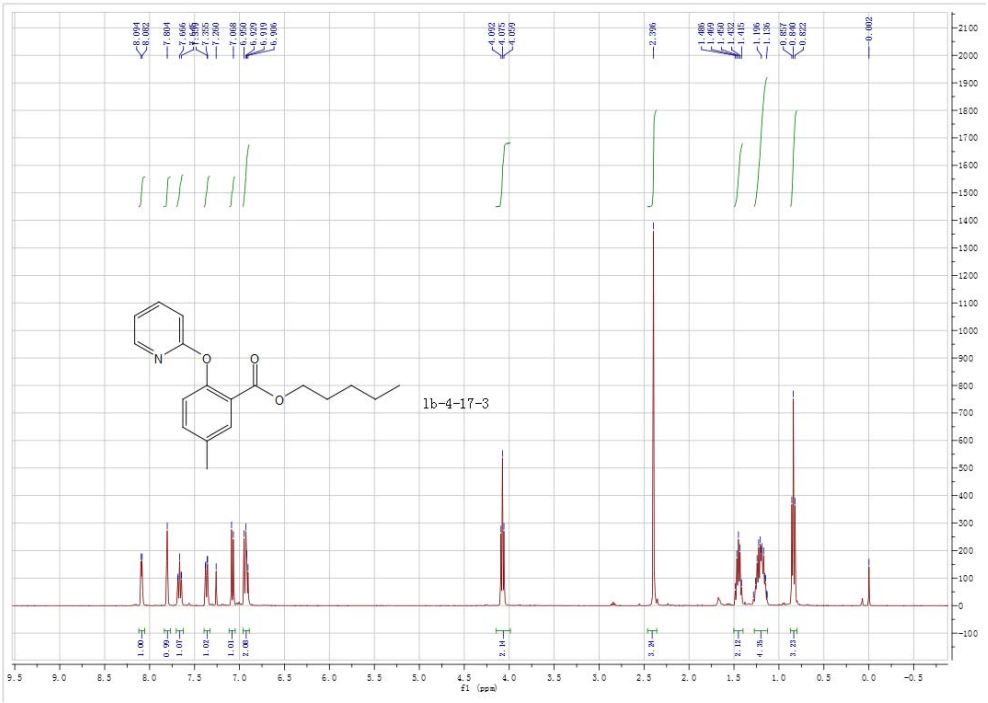


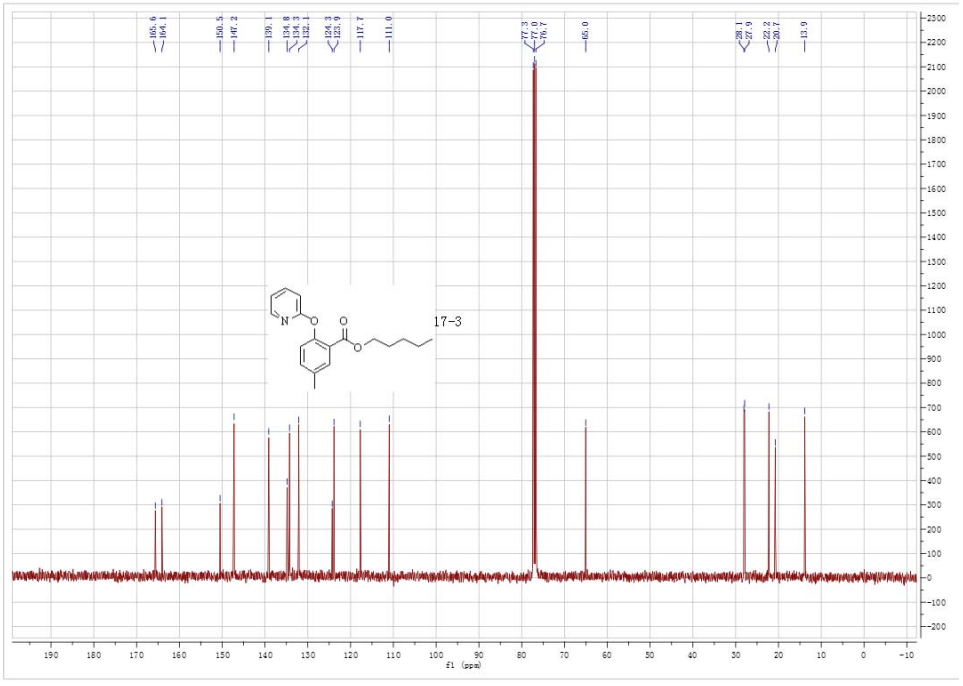




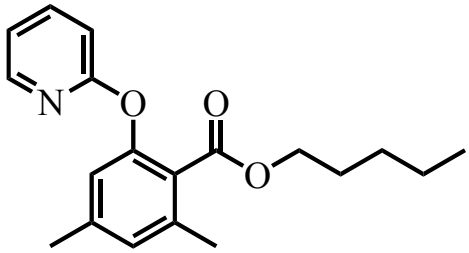
Pentyl 5-methyl-2-(pyridin-2-yloxy)benzoate (2d)

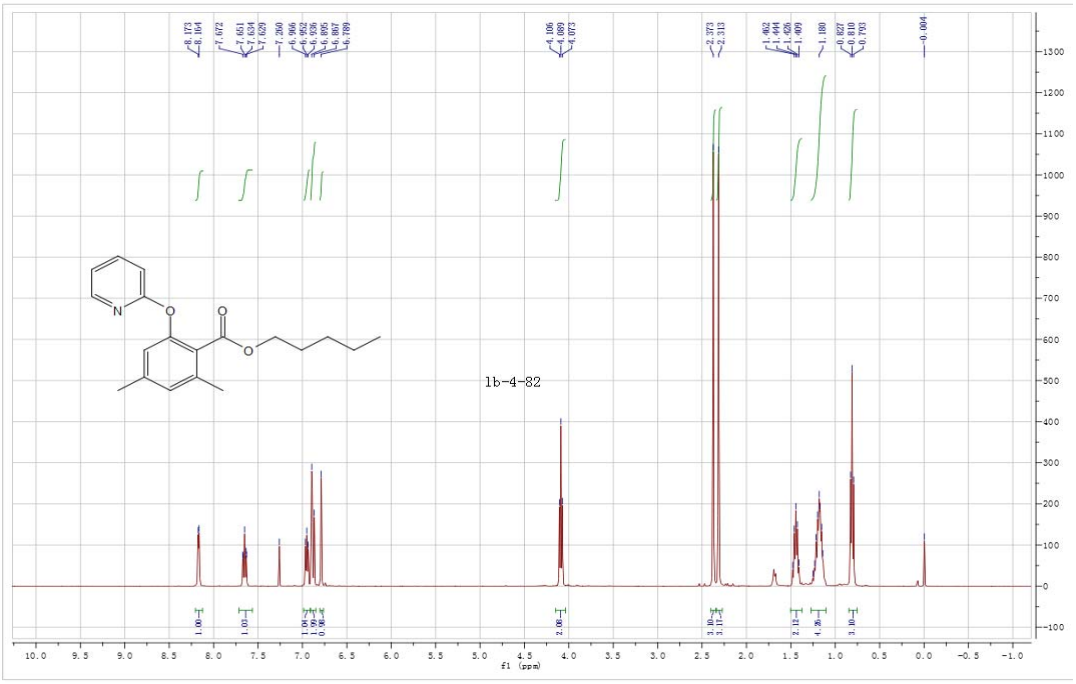


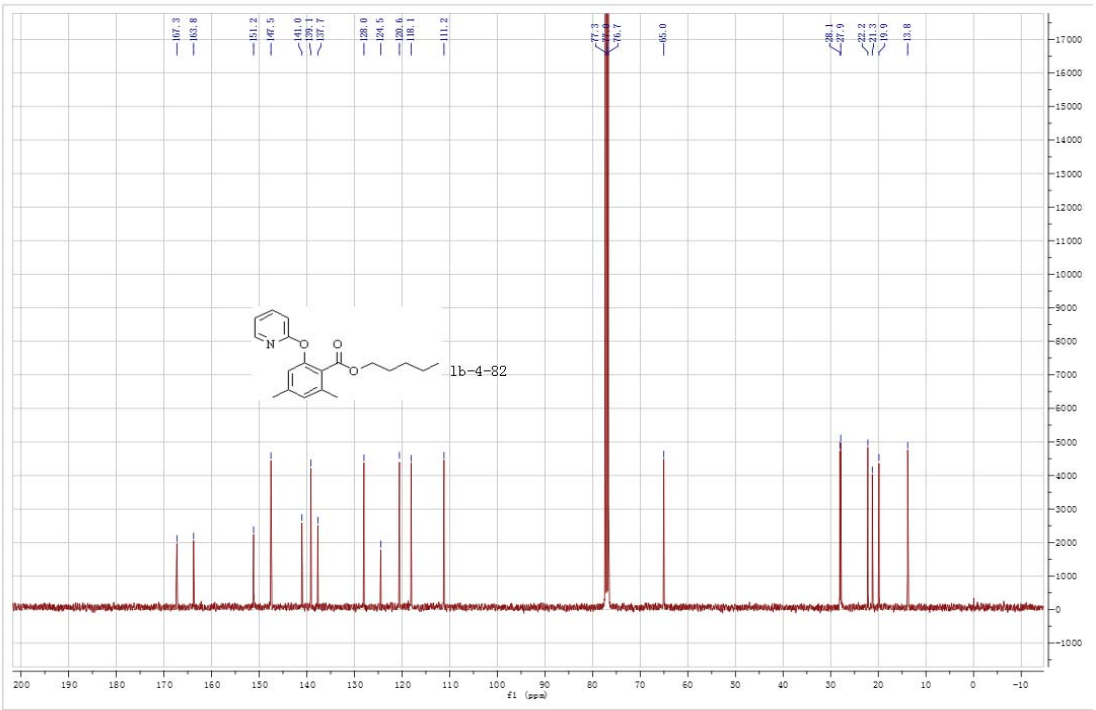




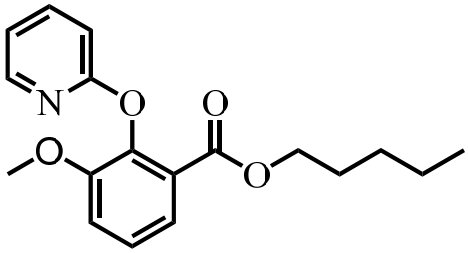
Pentyl 2,4-dimethyl-6-(pyridin-2-yloxy)benzoate (2e)

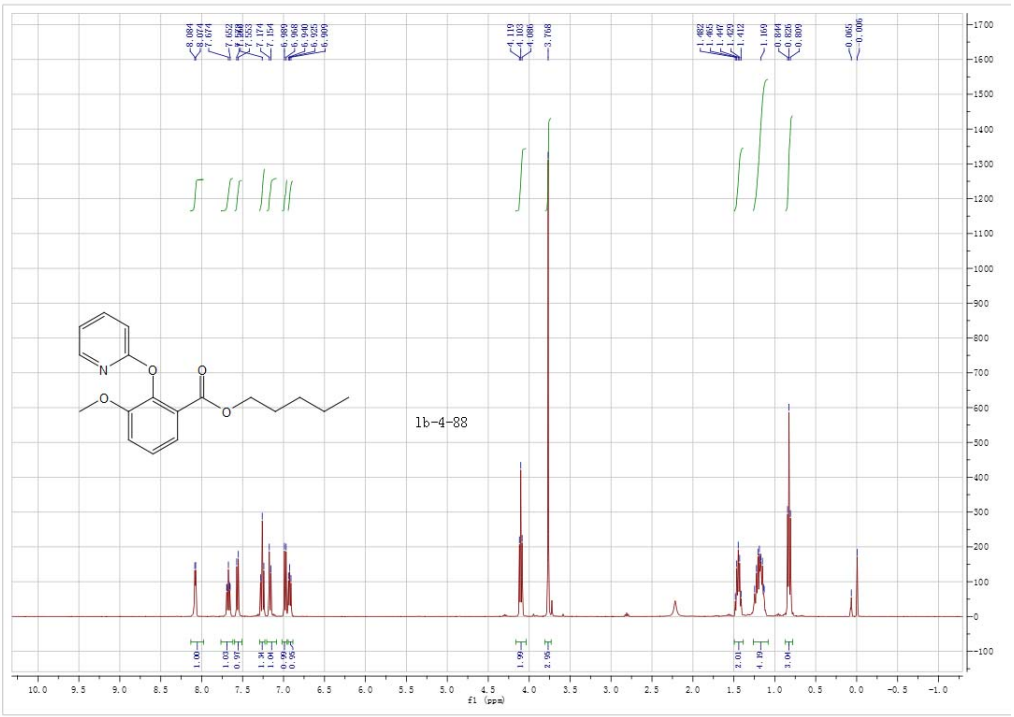


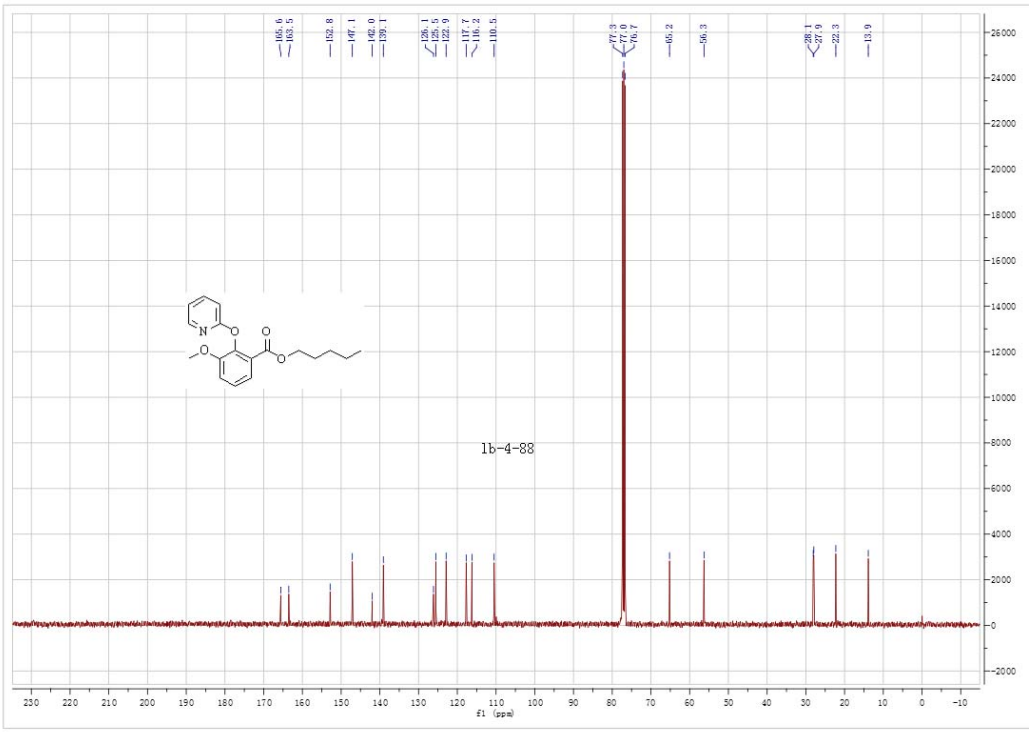




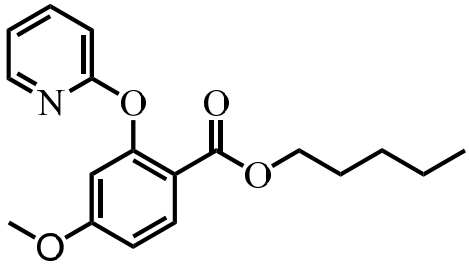
Pentyl 3-methoxy-2-(pyridin-2-yloxy)benzoate (2f)

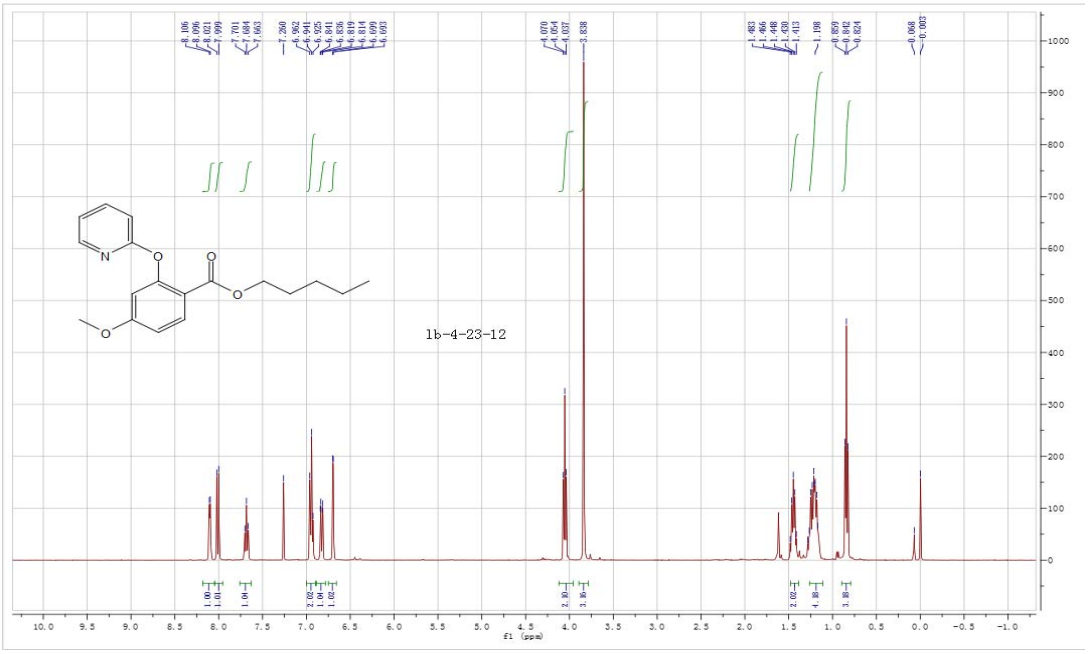


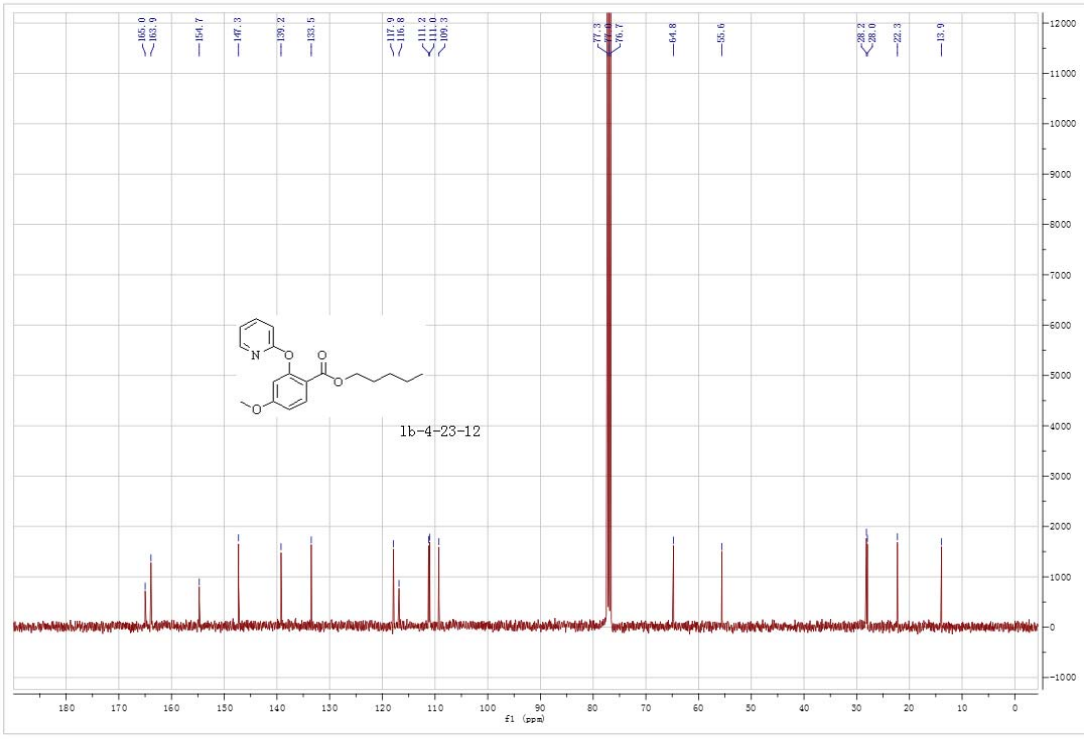




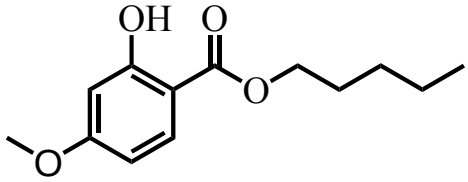
Pentyl 4-methoxy-2-(pyridin-2-yloxy)benzoate (2g)

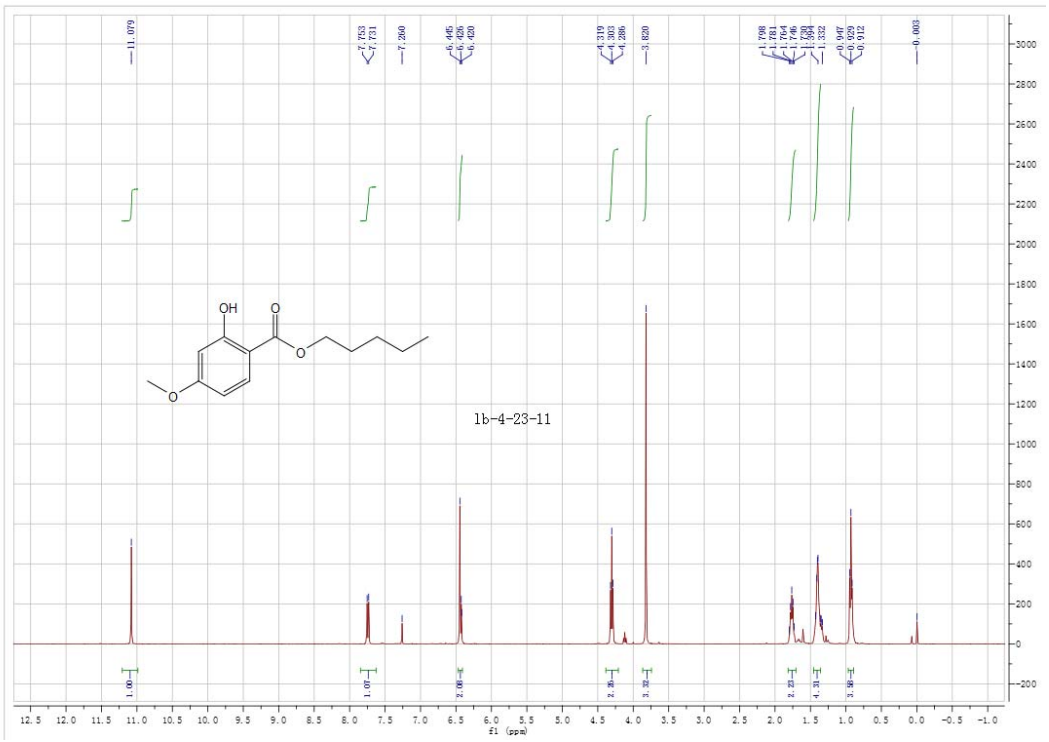


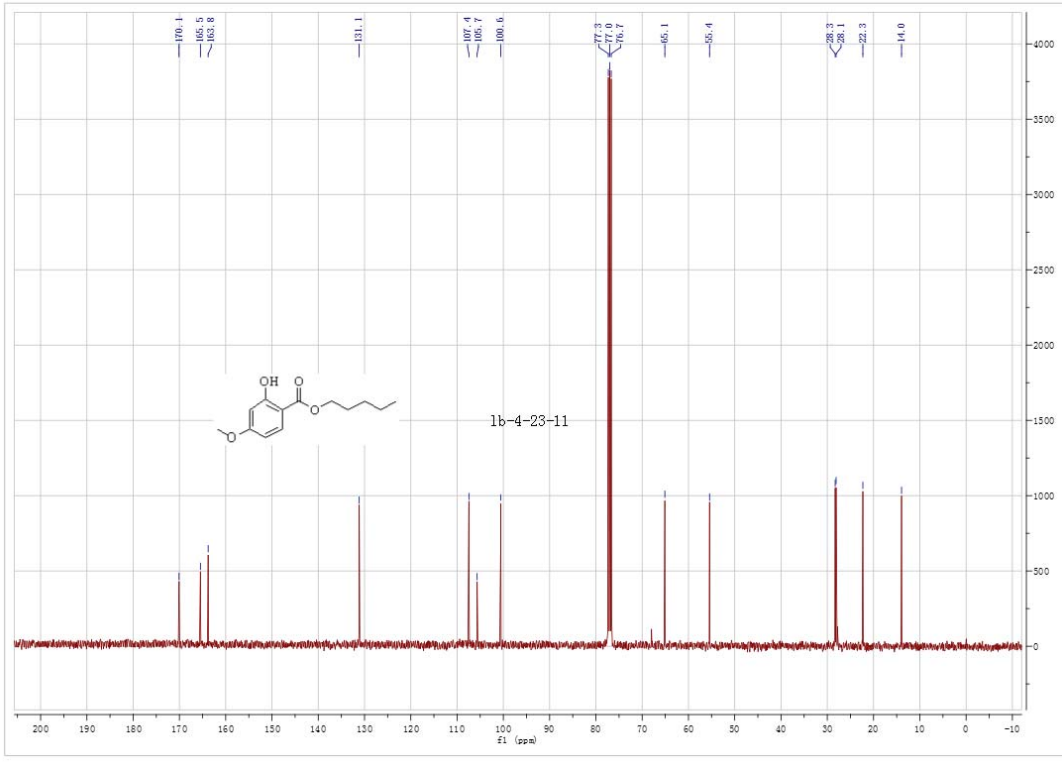




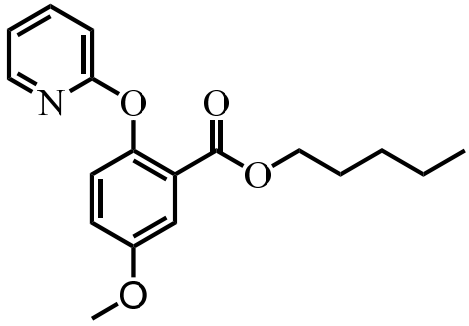
Pentyl 2-hydroxy-4-methoxybenzoate (3g)

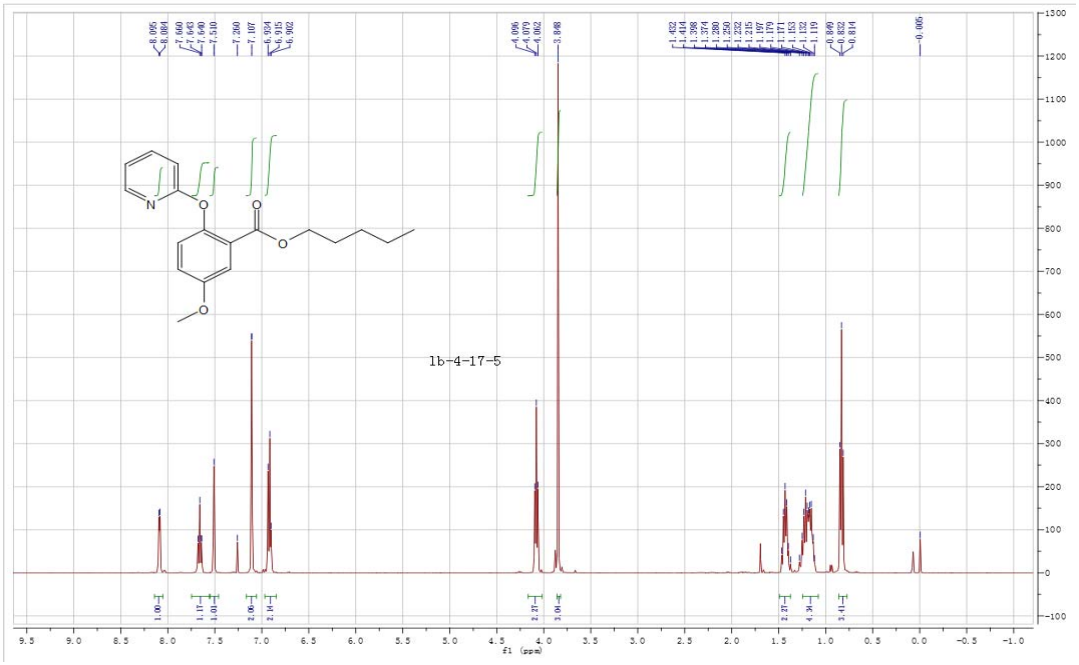


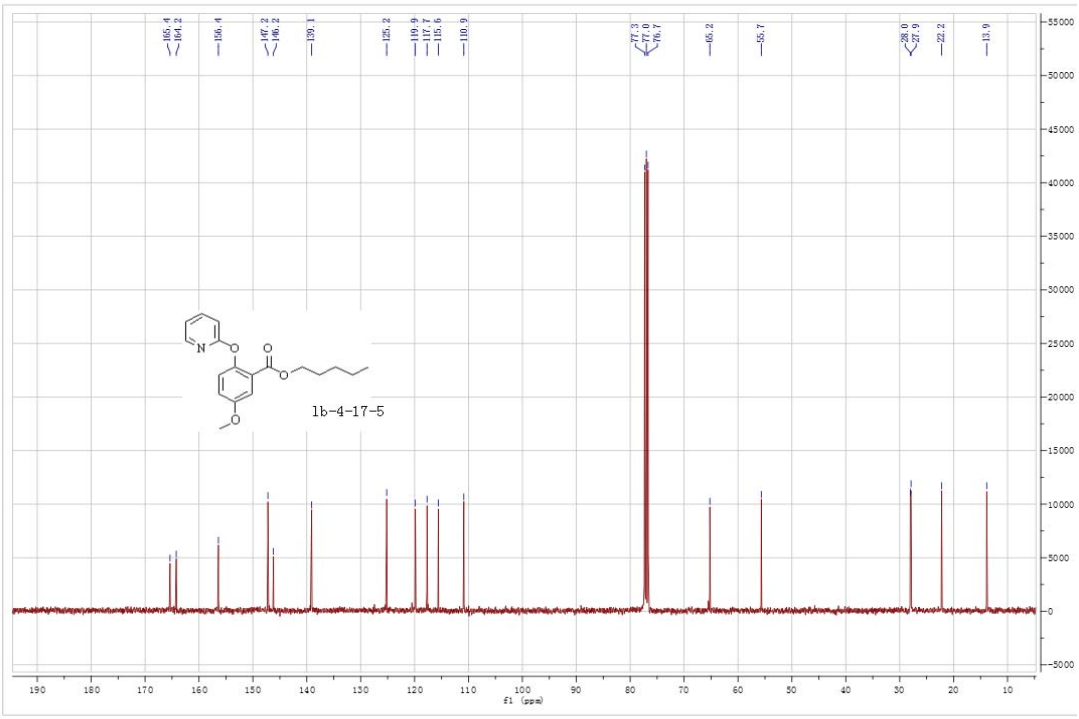




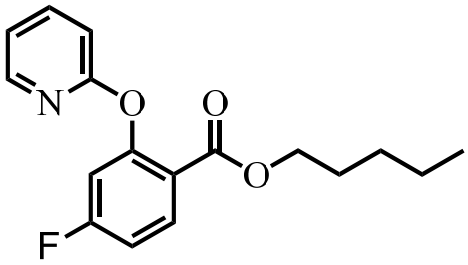
Pentyl 5-methoxy-2-(pyridin-2-yloxy)benzoate (2h)

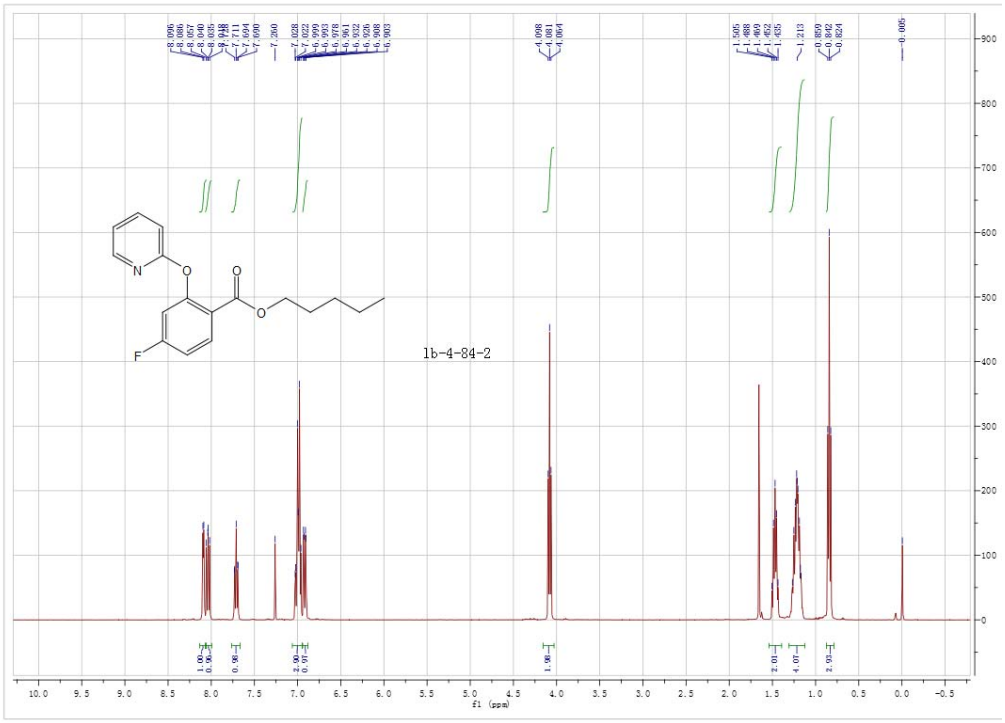


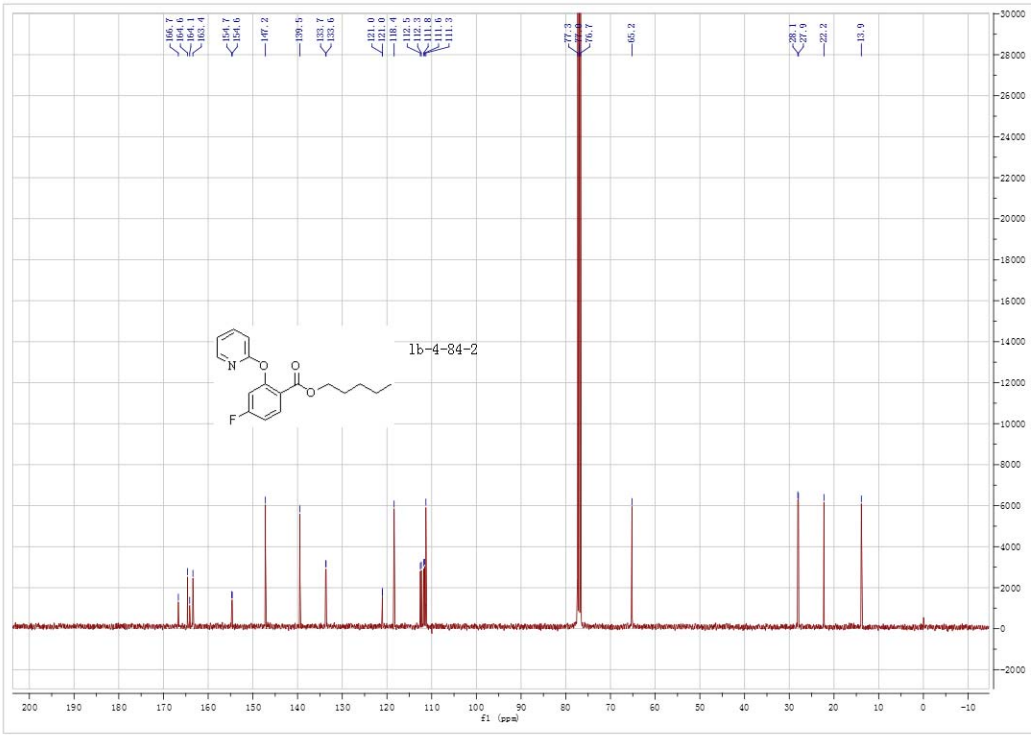




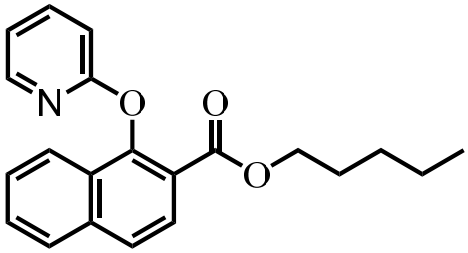
Pentyl 4-fluoro-2-(pyridin-2-yloxy)benzoate (2i)

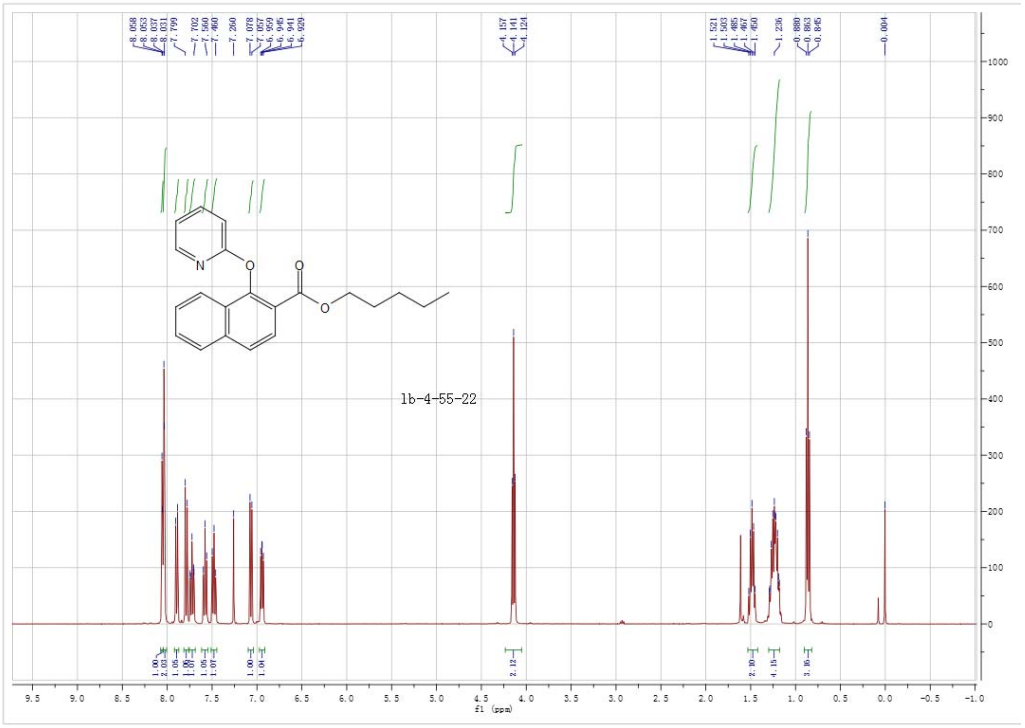


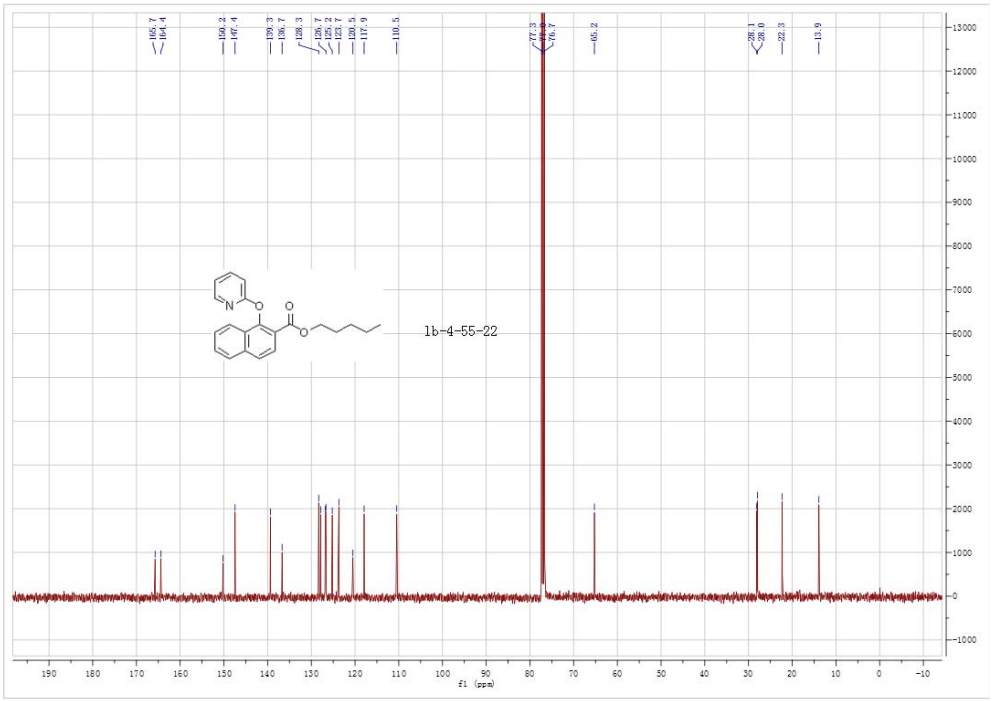




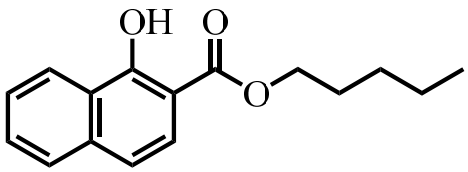
Pentyl 1-(pyridin-2-yloxy)-2-naphthoate (2j)

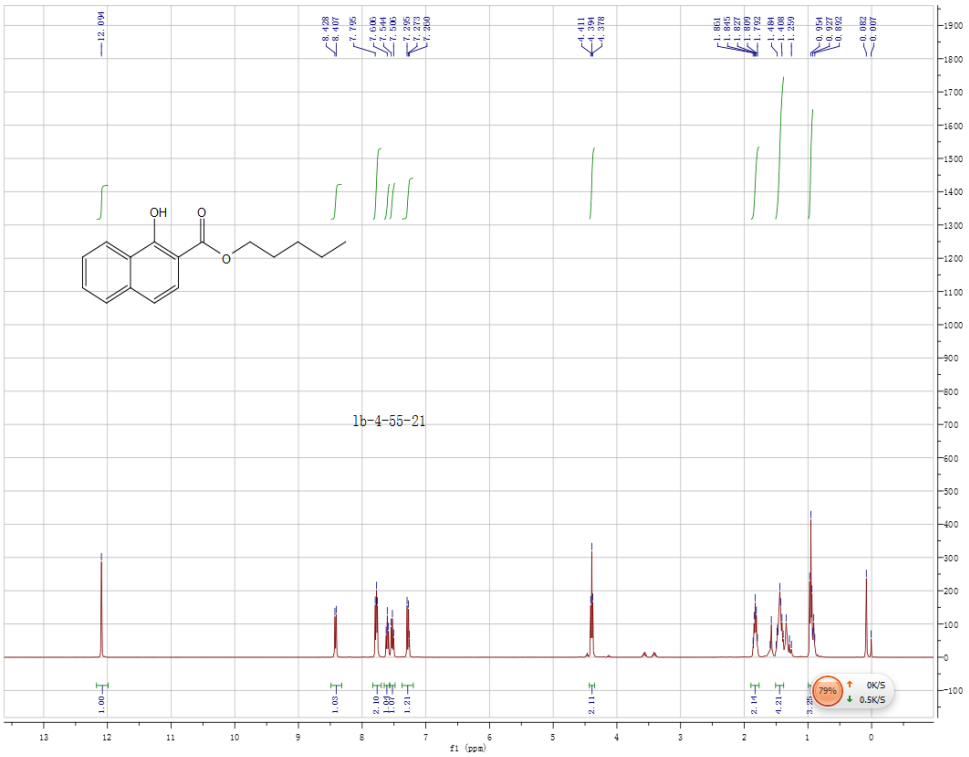


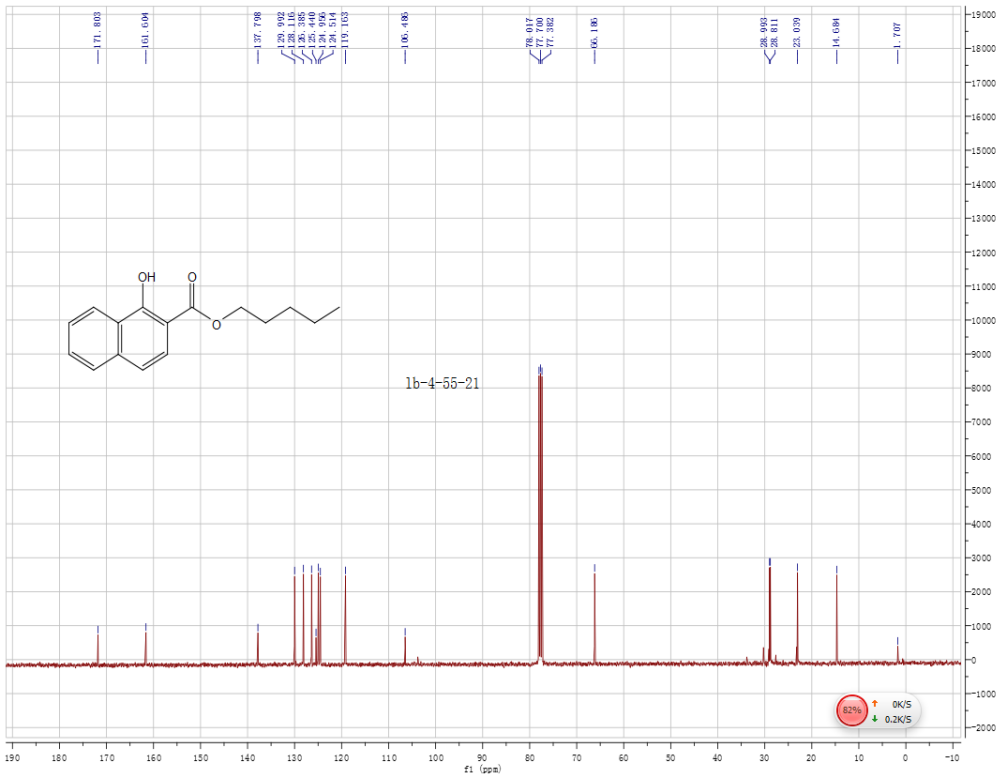




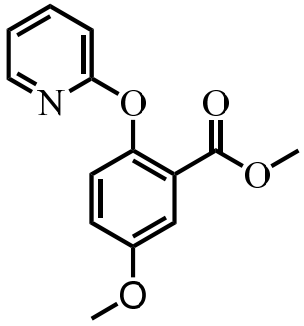
Pentyl 1-hydroxy-2-naphthoate (3j)

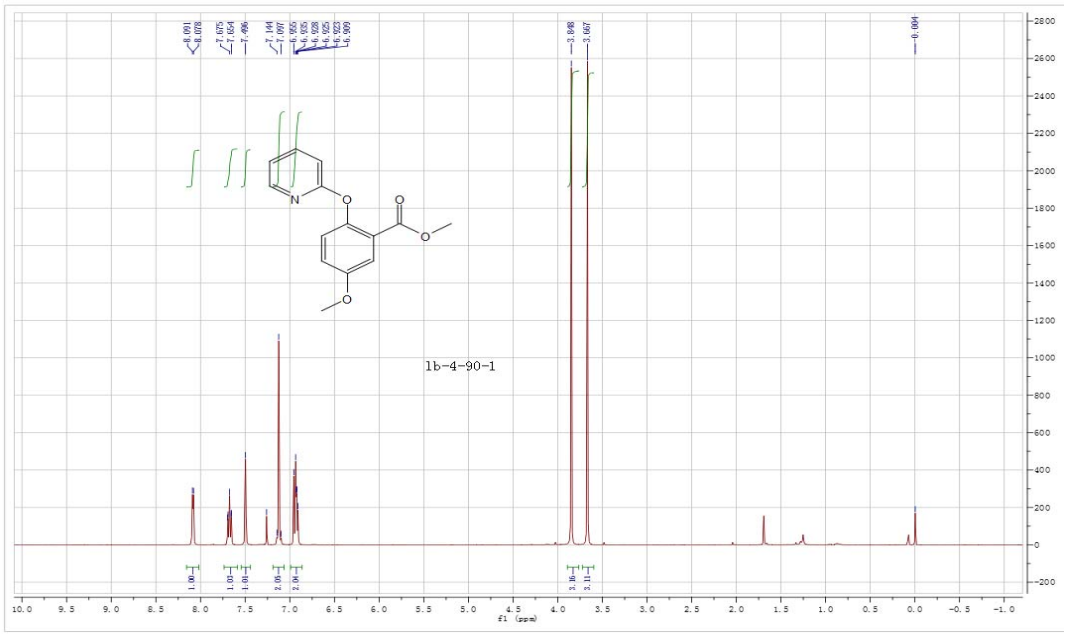


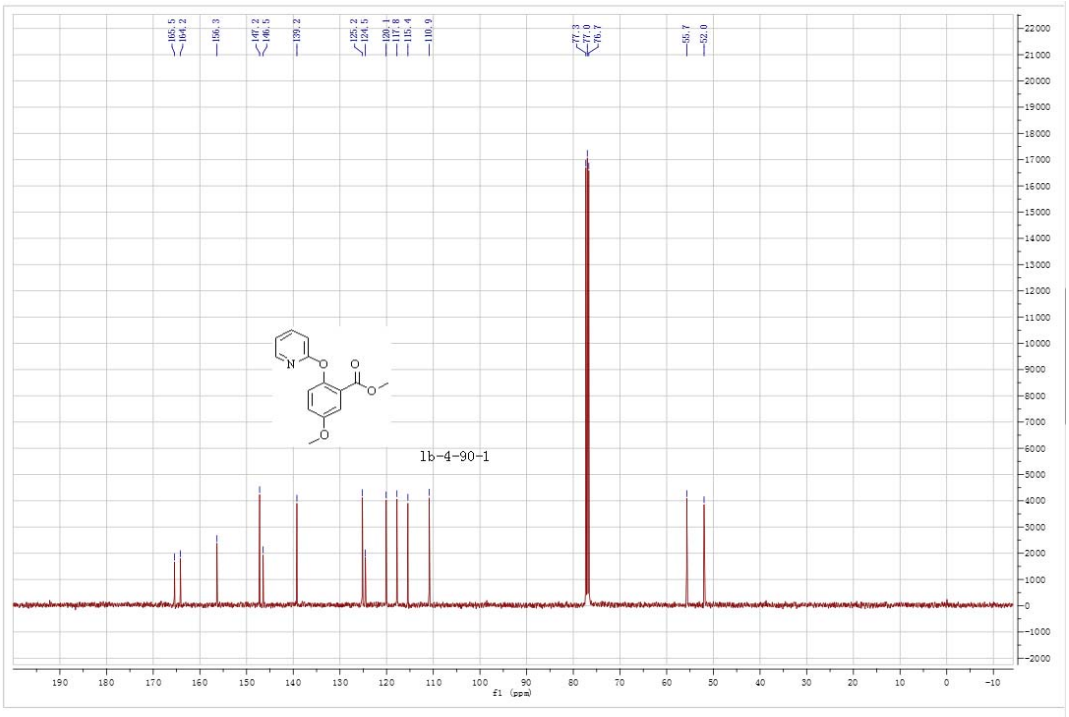




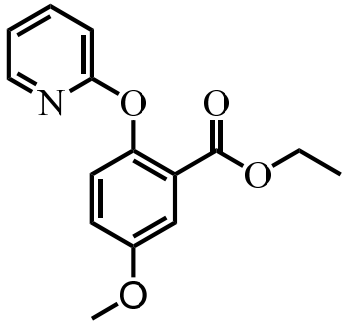
Methyl 5-methoxy-2-(pyridin-2-yloxy)benzoate (2k)

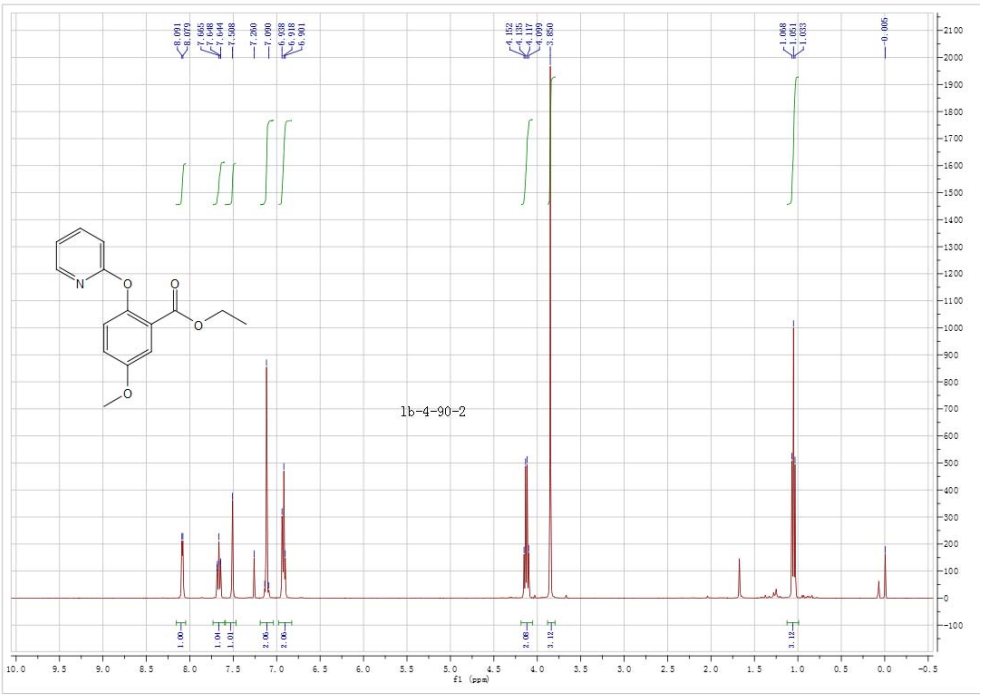


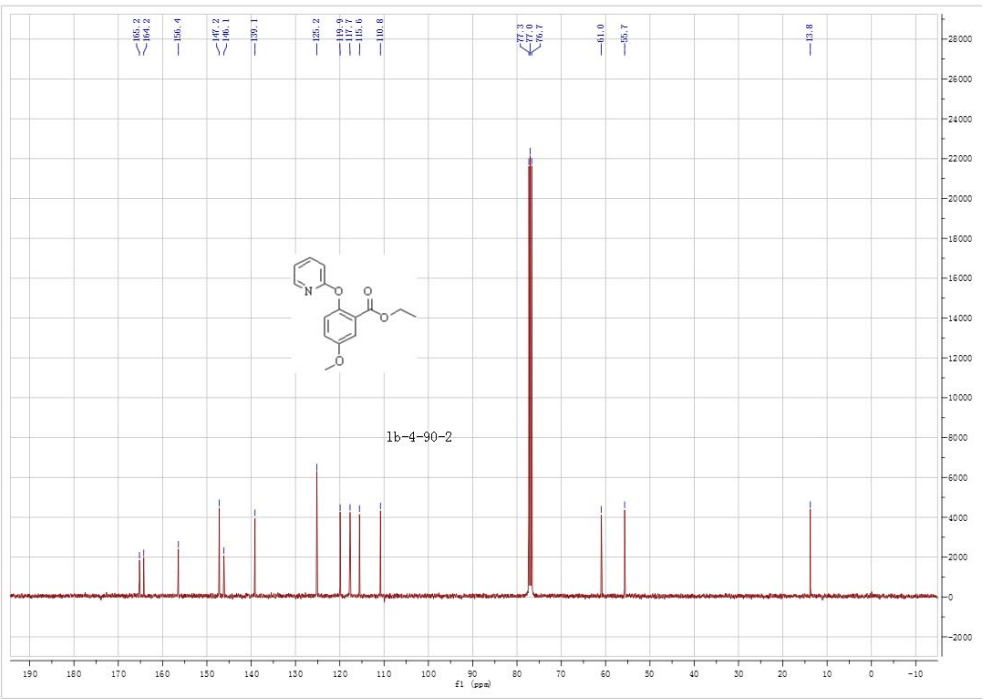




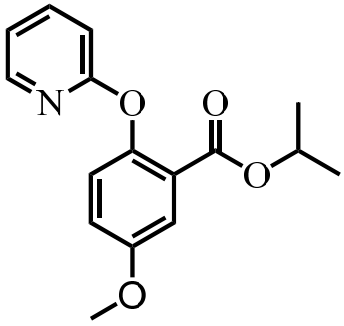
Ethyl 5-methoxy-2-(pyridin-2-yloxy)benzoate (2l)

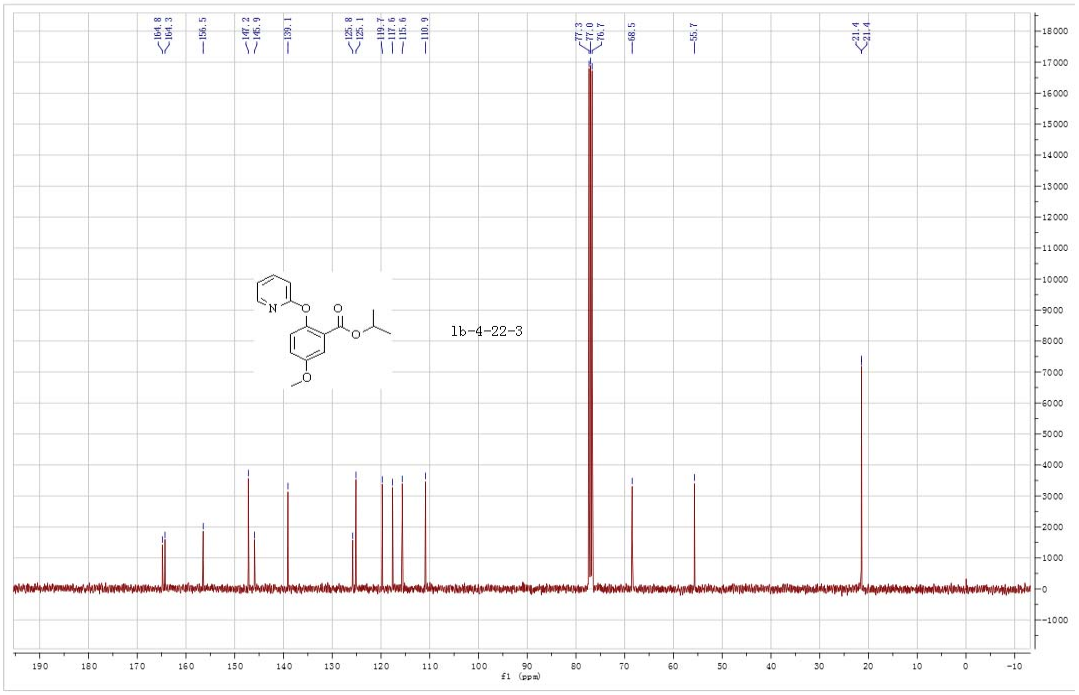


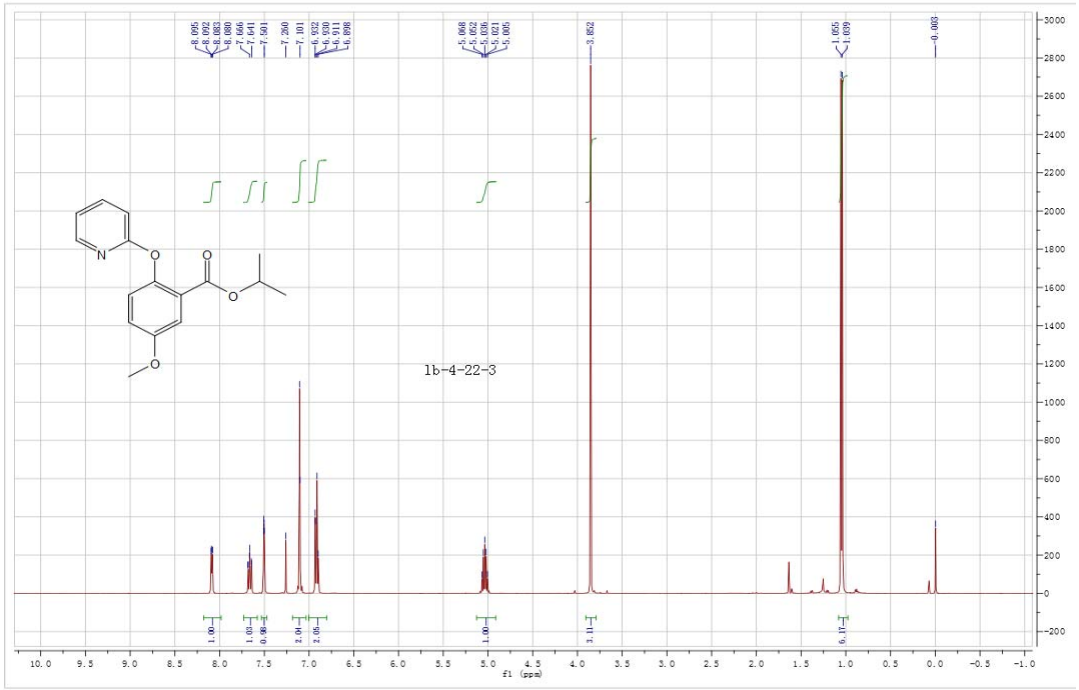




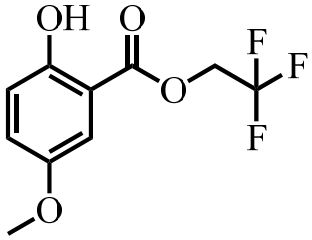
Isopropyl 5-methoxy-2-(pyridin-2-yloxy)benzoate (2m)

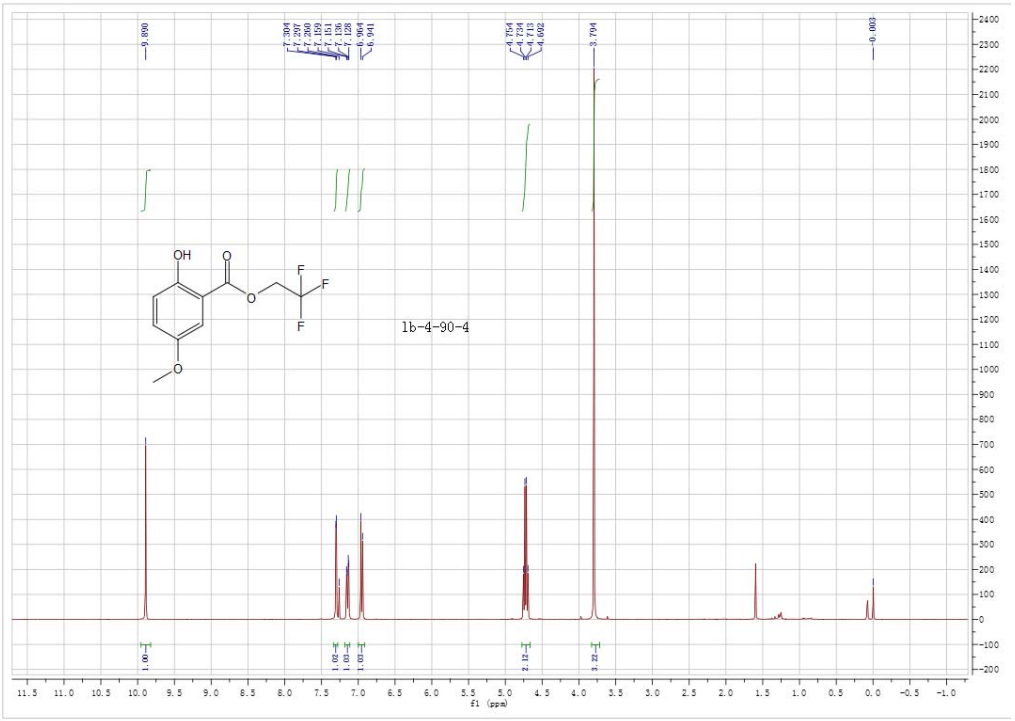


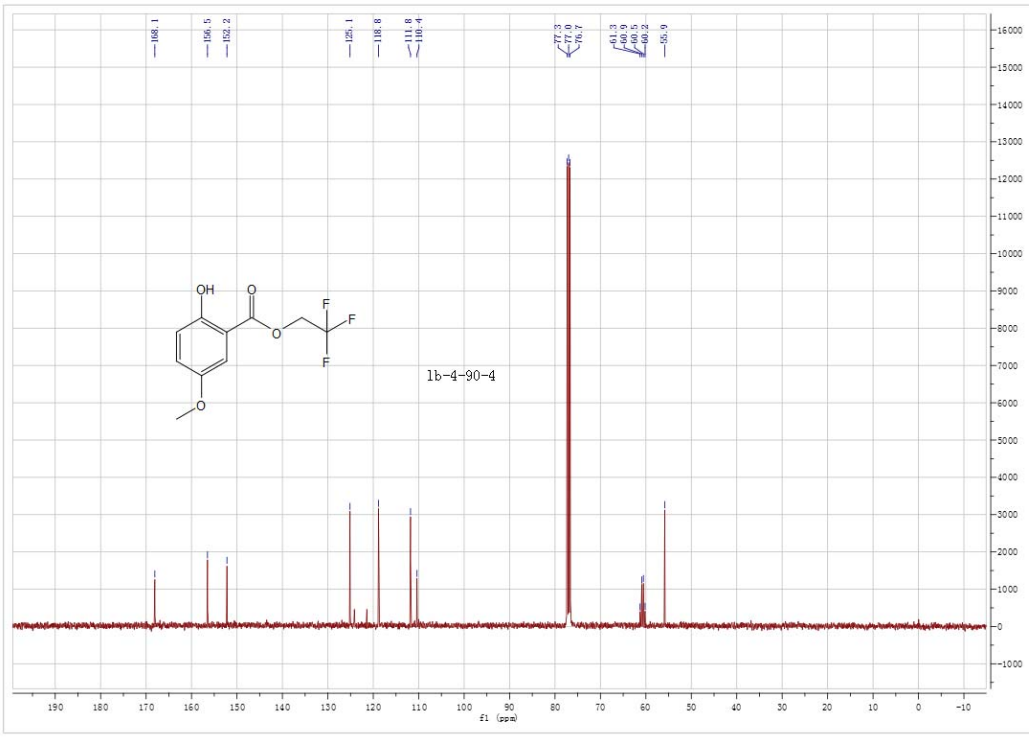




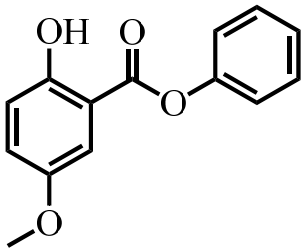
2,2,2-Trifluoroethyl 2-hydroxy-5-methoxybenzoate (2n)

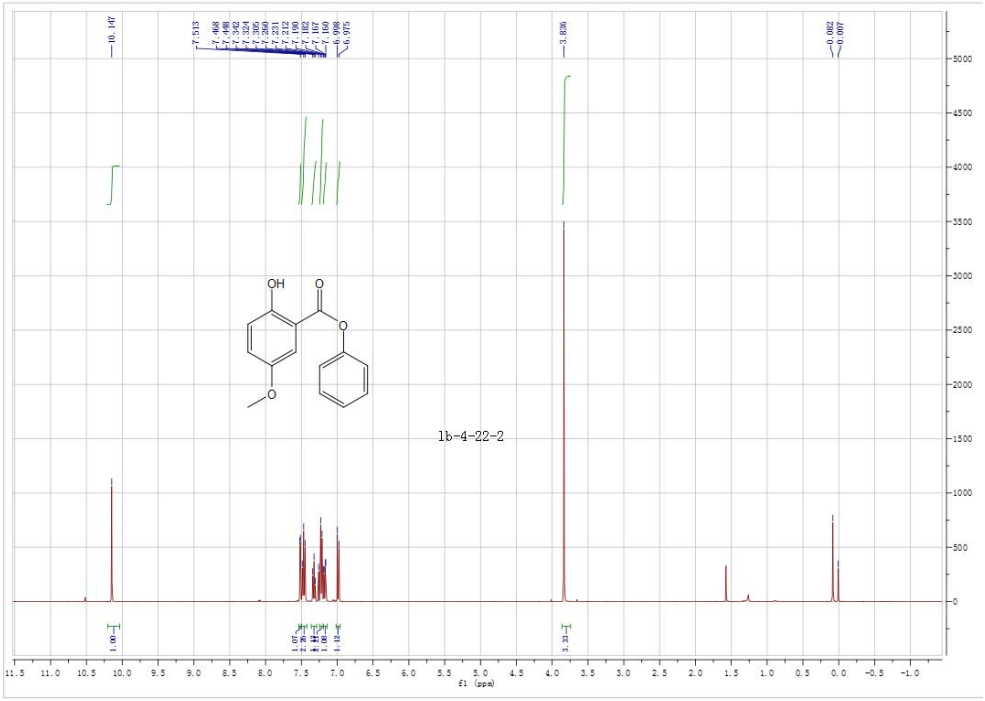


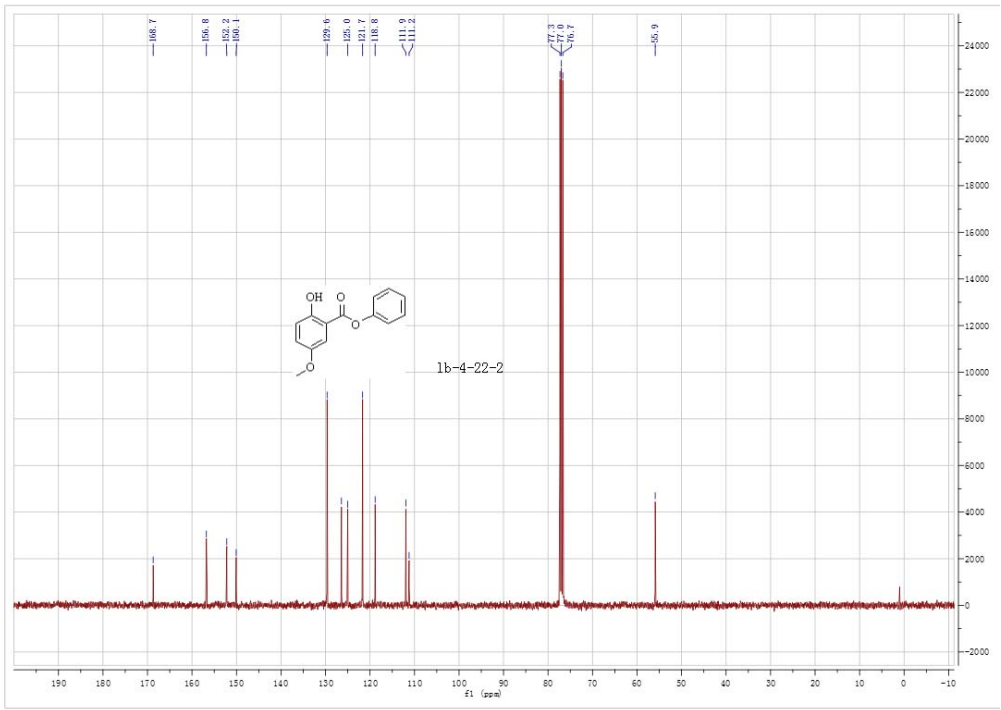




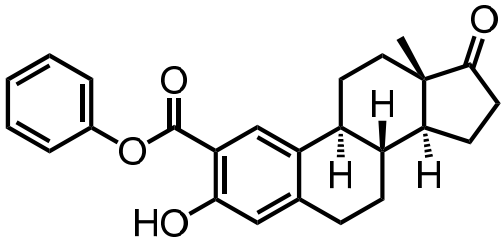
Phenyl 2-hydroxy-5-methoxybenzoate (2o)

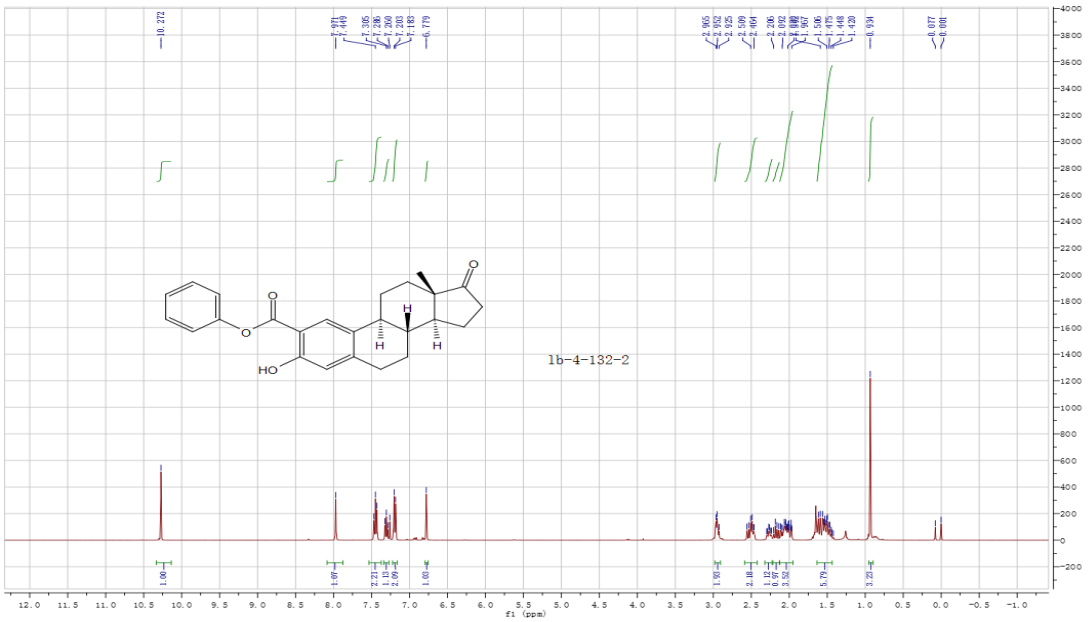


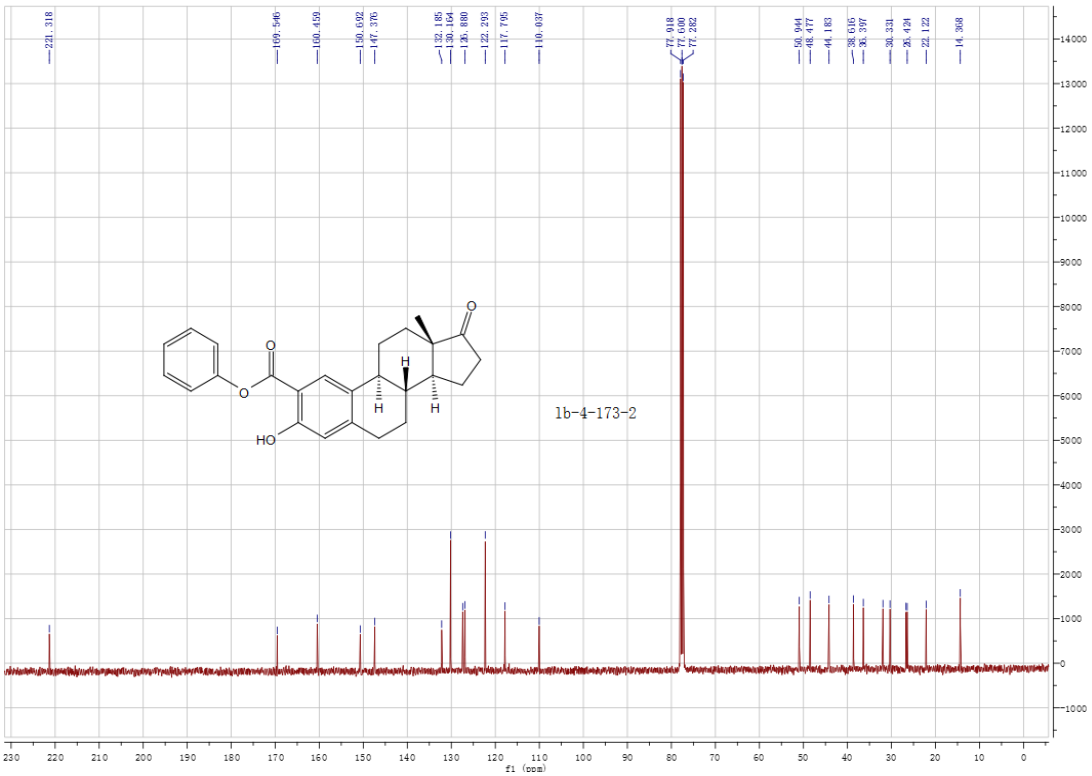




(*8R*,*9S*,*13S*,*14S*)-Phenyl 3-hydroxy-13-methyl-17-oxo-7, 8, 9, 11, 12, 13, 14, 15, 16, 17-decahydro-6H-cyclopenta[a] phenanthrene-2-carboxylate (5a)







(*8R,9S,13S,14S*)-Pentyl 13-methyl-17-oxo-3-(pyridin-2-yloxy)-7, 8, 9, 11, 12, 13, 14, 15, 16, 17-decahydro-6H-cyclopenta[a]phenanthrene-2-carboxylate (5b)