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

Copper Catalyzed Oxidative *ortho*-C–H Benzoxylation of 2-Phenylpyridines with Benzyl Alcohols and Benzyl Amines as Benzoxylation Sources

Ashok B. Khemnar and Bhalchandra M. Bhanage*

Department of Chemistry, Institute of Chemical Technology,

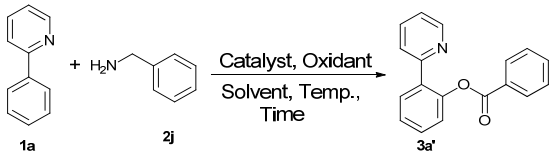
N. Parekh Marg, Matunga, Mumbai–400019. India.

Tel.: +91-22-33612601; fax: +91-22-33611020

bm.bhanage@gmail.com, bm.bhanage@ictmumbai.edu.in

Contents:

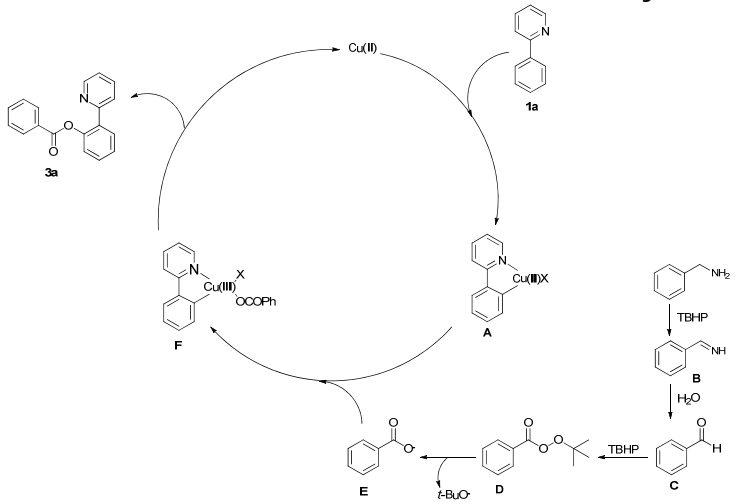
1. Optimization study for the benzoxylation of 2-phenylpyridine with benzyl amine.[a]



Entry	Catalyst	Oxidant	Solvent	Yield (%)[b]
1	CuI	TBHP	PhCl	08
2	CuBr	TBHP	PhCl	Trace
3	CuCl	TBHP	PhCl	Trace
4	$CuCO_3.Cu(OH)_2$	TBHP	PhCl	04
5	Cu_2O	TBHP	PhCl	06
6	CuO	TBHP	PhCl	00
7	$CuBr_2$	TBHP	PhCl	03
8	$Cu(OAc)_2$	TBHP	PhCl	30
9	$Cu(OAc)_2$	TBHP (aq.)	PhCl	13
10	$Cu(OAc)_2$	TBPB	PhCl	05
11	$Cu(OAc)_2$	DTBP	PhCl	10
12	$Cu(OAc)_2$	*m*-CPBA	PhCl	00
13	$Cu(OAc)_2$	H_2O_2	PhCl	00
14	$Cu(OAc)_2$	TBHP	PhCN	trace
15	$Cu(OAc)_2$	TBHP	DCE	00
16	$Cu(OAc)_2$	TBHP	DCB	05
17	$Cu(OAc)_2$	TBHP	H_2O	00[c]
18	$Cu(OAc)_2$	TBHP	PhCl	45[d]
19	$Cu(OAc)_2$	TBHP	-	00[e]

[a] Reaction Conditions: **1a** (0.5 mmol), **2a** (1 mmol), catalyst (0.1 mmol), Oxidant (2 mmol), Solvent (2 mL), 120 ^oC, 17 h. [b] GC yield. [c] temp. 100 °C. [d] TBHP (2.5 mmol). [e] benzyl amine (1 mL). DCE = 1,2-dichloroethane, DCB = 1,2-dichlorobenzene.

2. Plausible reaction mechanism of **1a** with **2j**.[1]

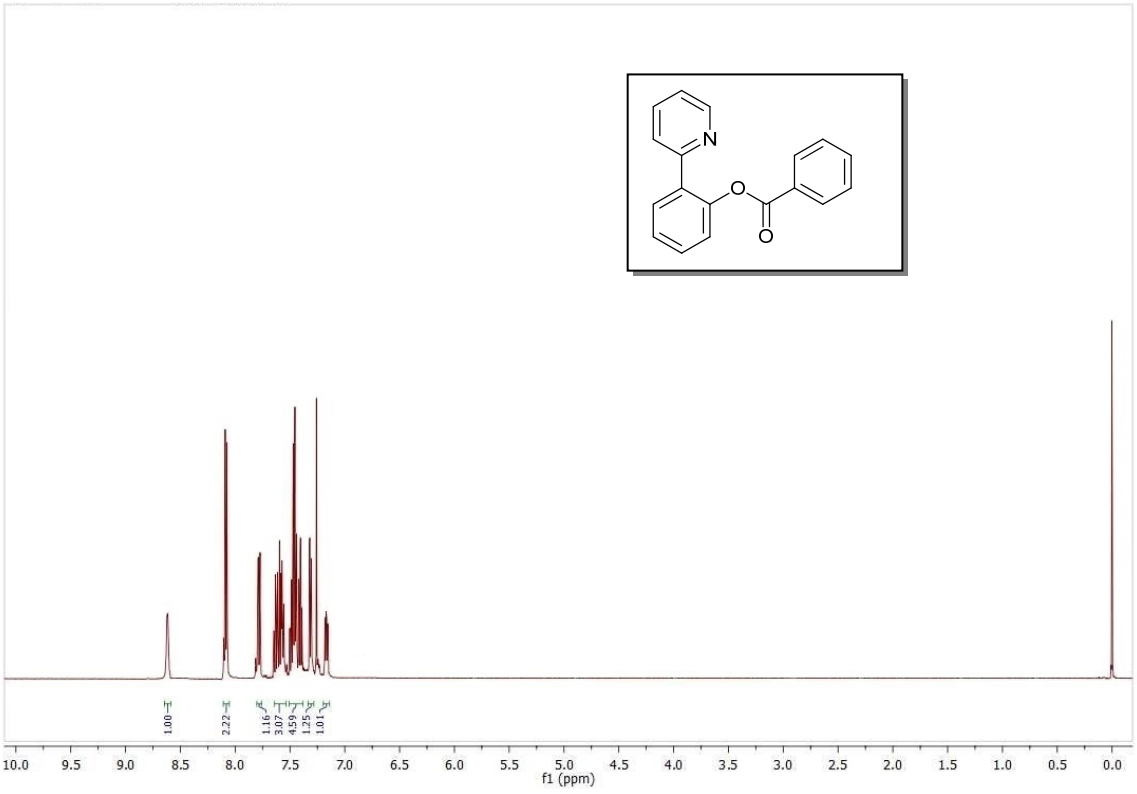


References:

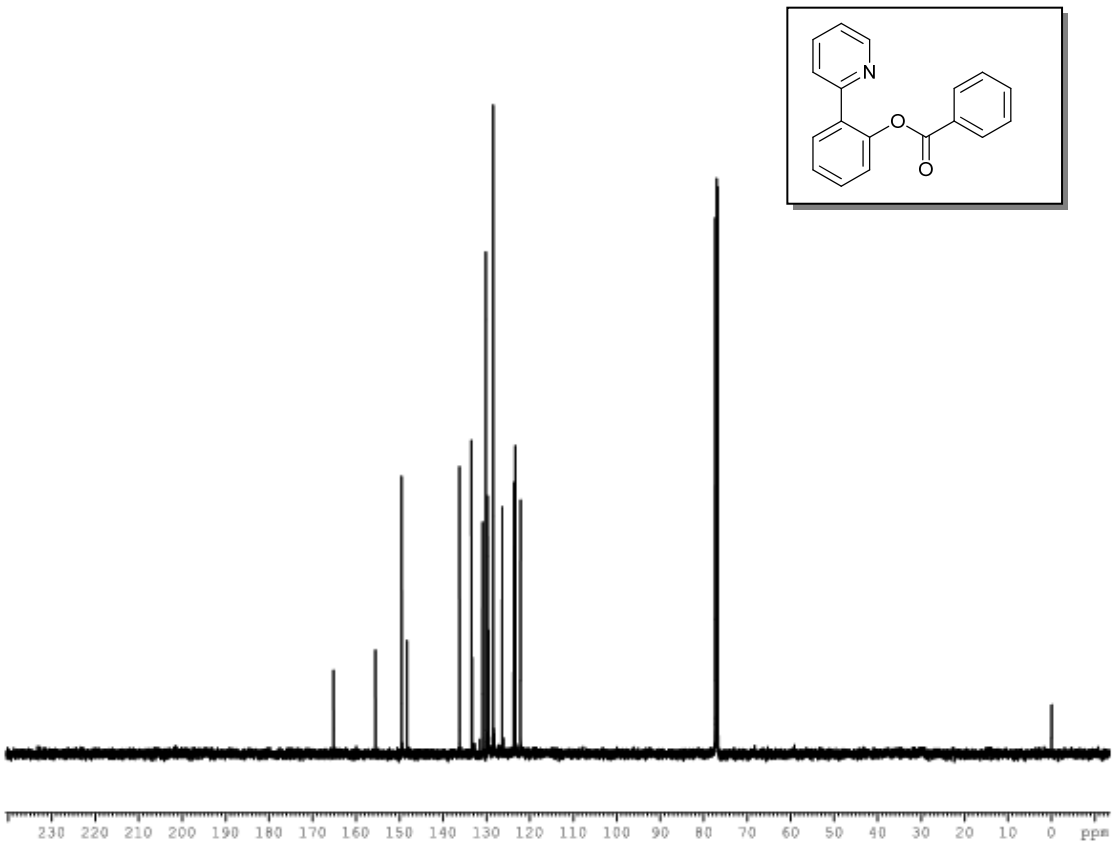
1. a) Q. Zhang, F. Yang and Y. Wu, *Chem. Commun.*, 2013, **49**, 6837–6839; b) S. K. Rout, S. Guin, A. Gogoi, G. Majji and B. K. Patel, *Org. Lett.*, 2014, **16**, 1614–1617.

3. Copies of ^{1}H NMR and ^{13}C NMR Spectra:

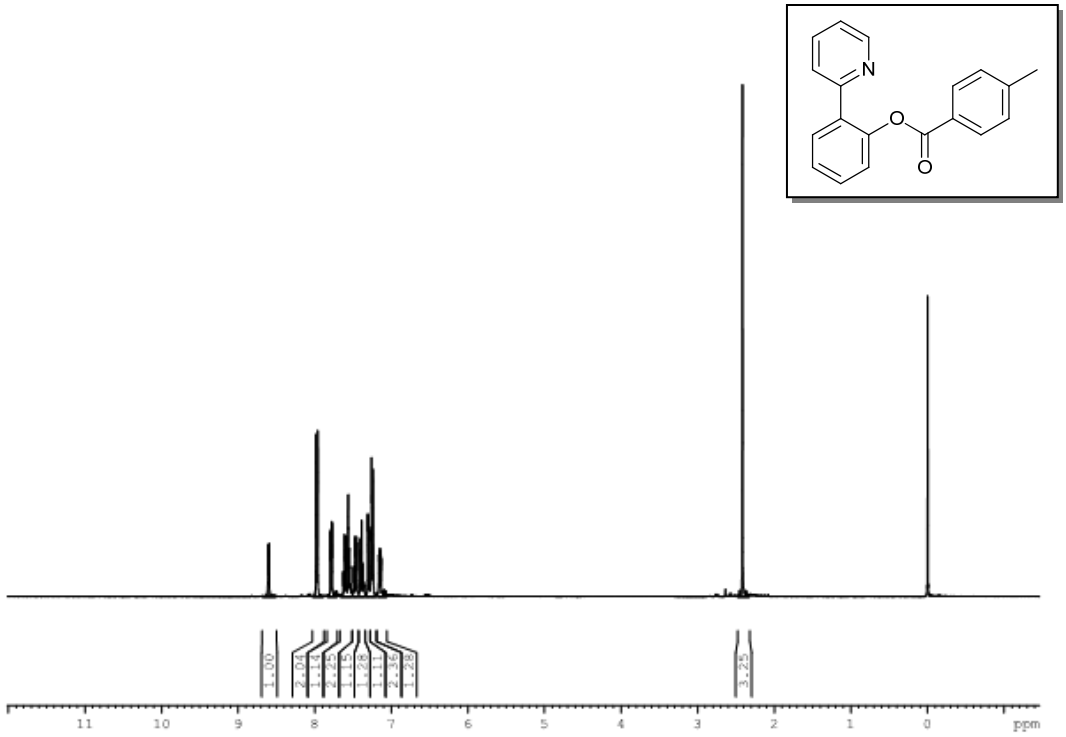
2-(pyridin-2-yl)phenyl benzoate (3a) (^{1}H NMR)



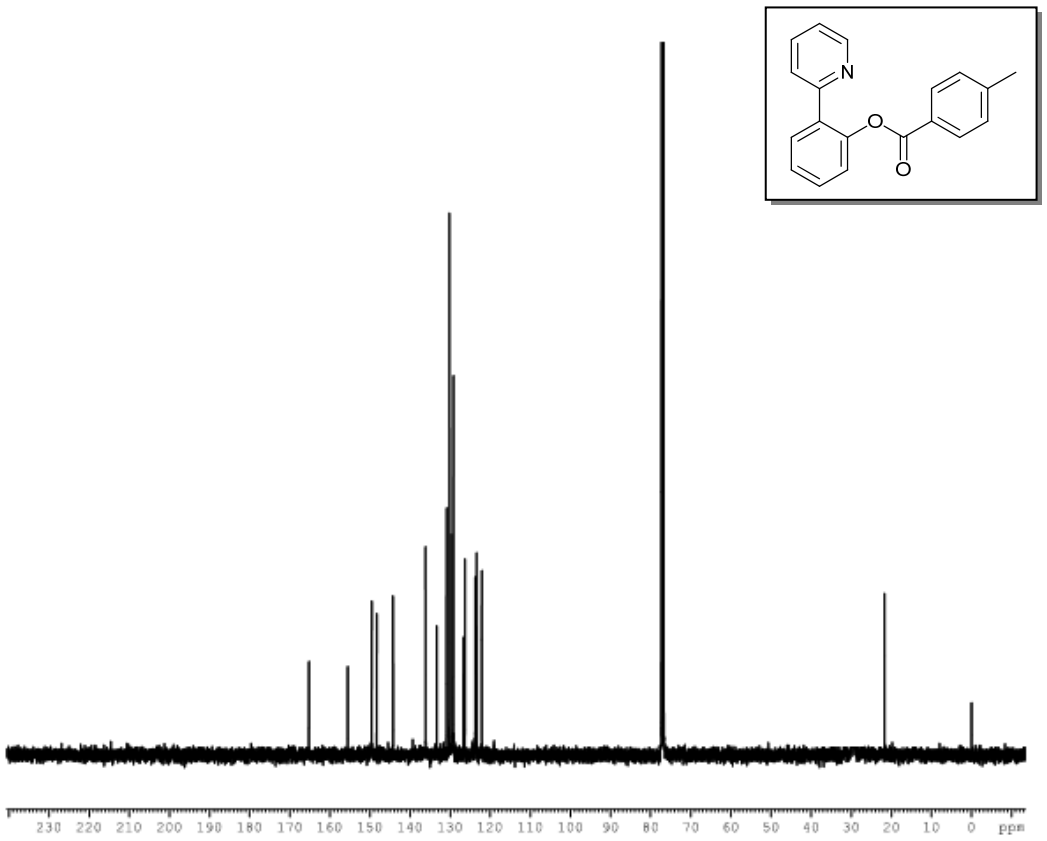
2-(pyridin-2-yl)phenyl benzoate (3a) (^{13}C NMR)



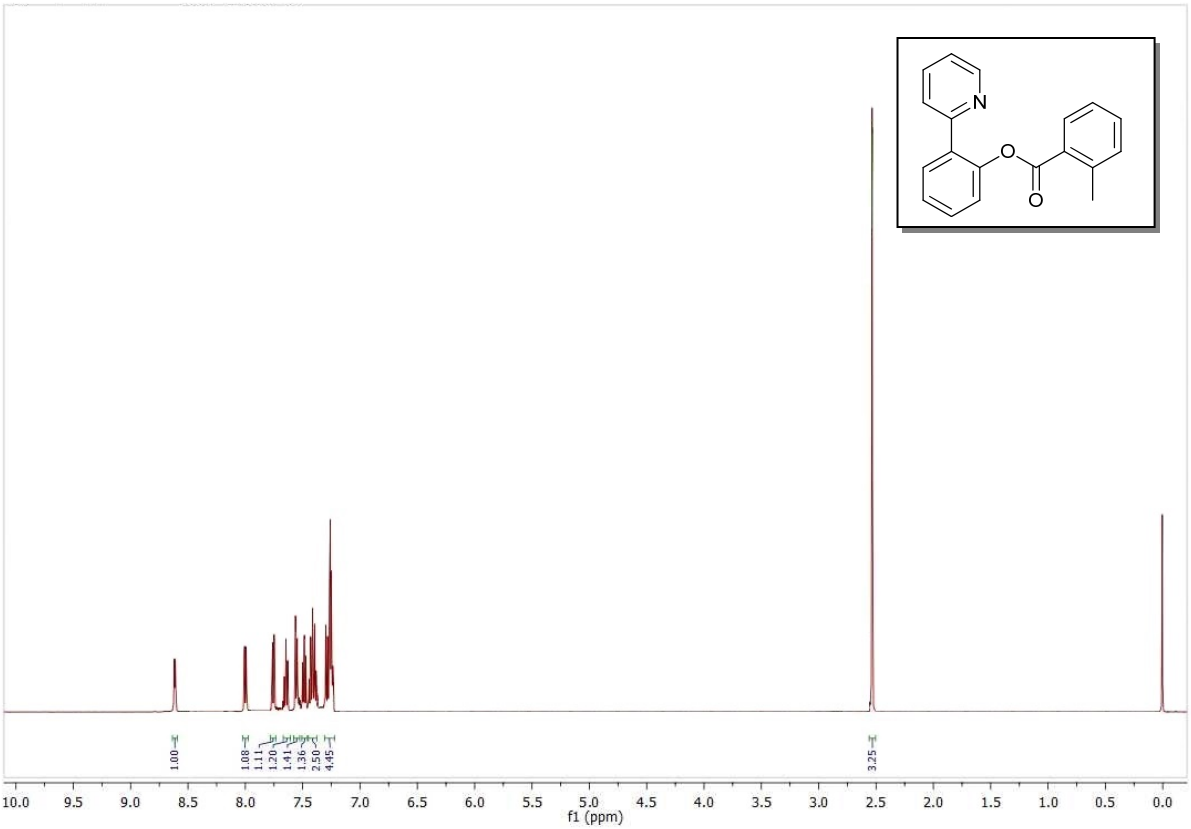
2-(pyridin-2-yl)phenyl 4-methylbenzoate (3b) (^{13}H NMR)



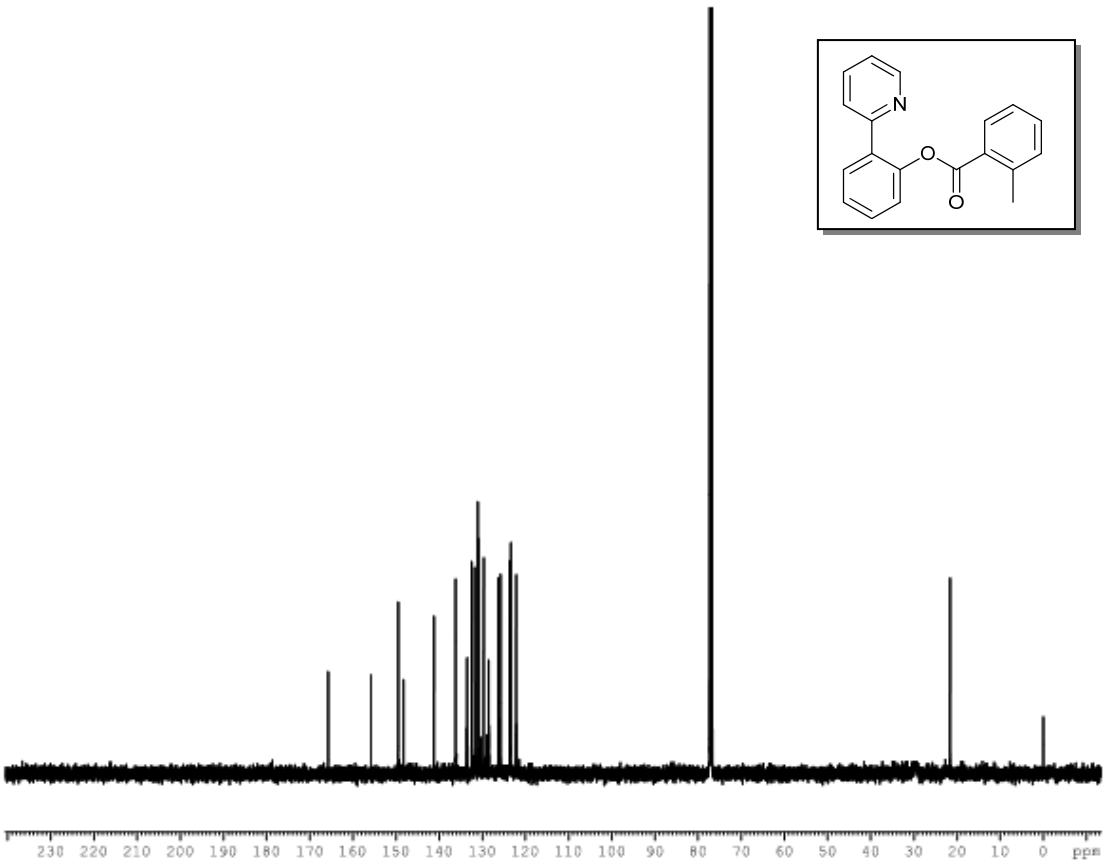
2-(pyridin-2-yl)phenyl 4-methylbenzoate (3b) (^{13}C NMR)



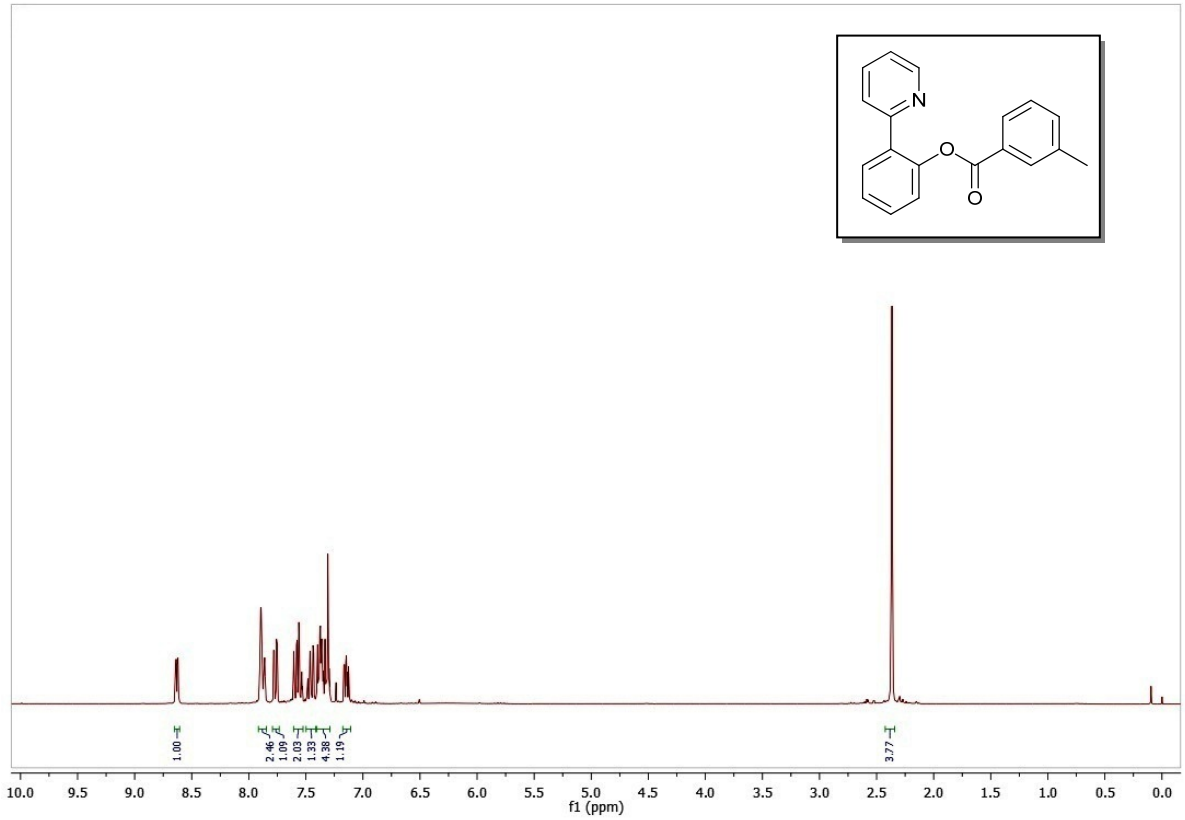
2-(pyridin-2-yl)phenyl 2-methylbenzoate (3c) (^{1}H NMR)



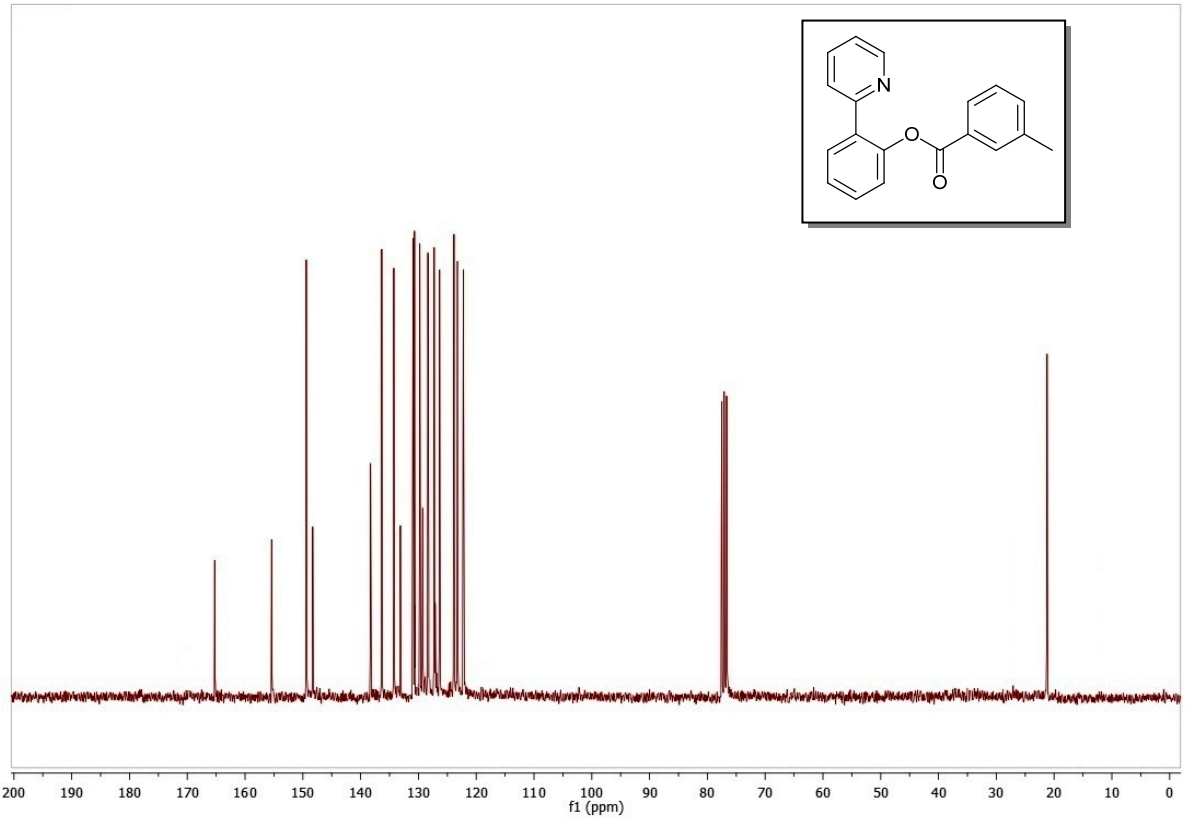
2-(pyridin-2-yl)phenyl 2-methylbenzoate (3c) (^{13}C NMR)



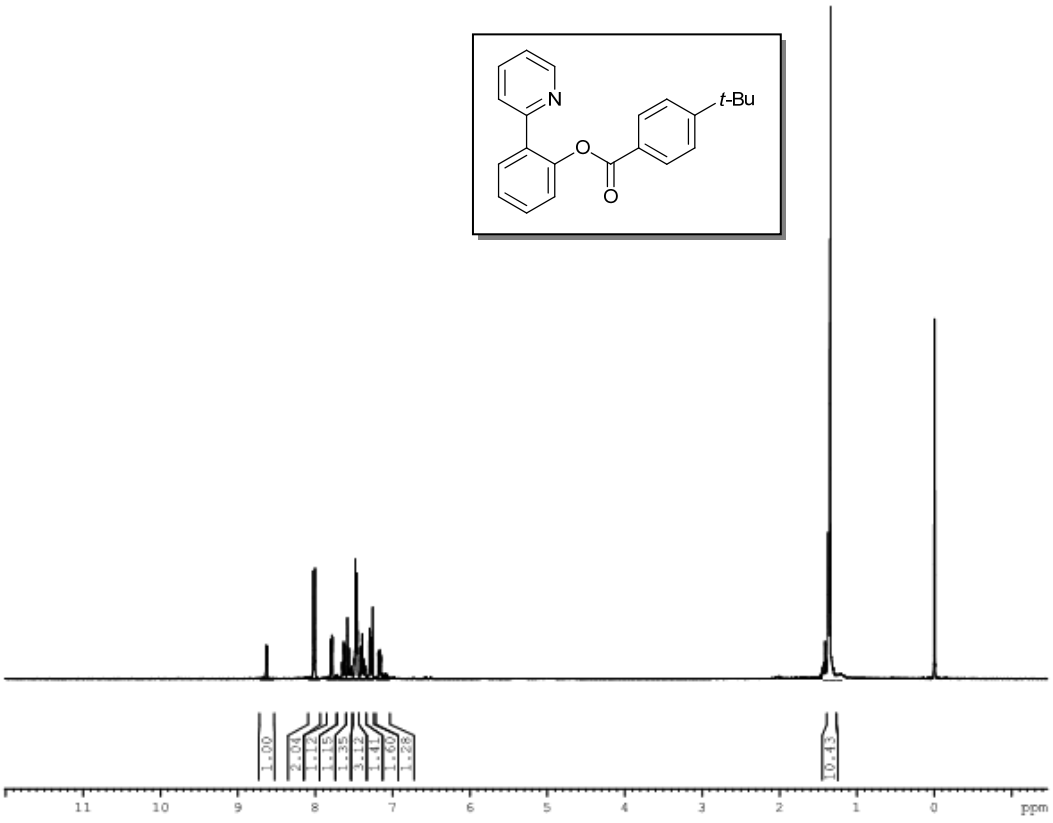
2-(pyridin-2-yl)phenyl 3-methylbenzoate (3d) (^{1}H NMR)



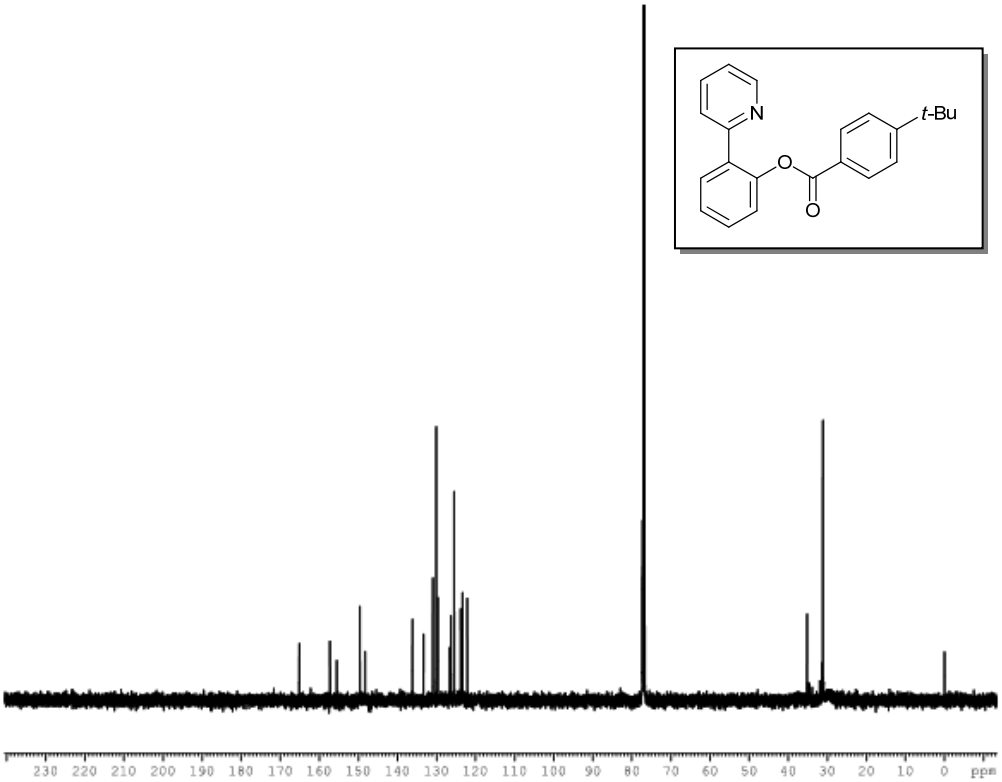
2-(pyridin-2-yl)phenyl 3-methylbenzoate (3d) (^{13}C NMR)



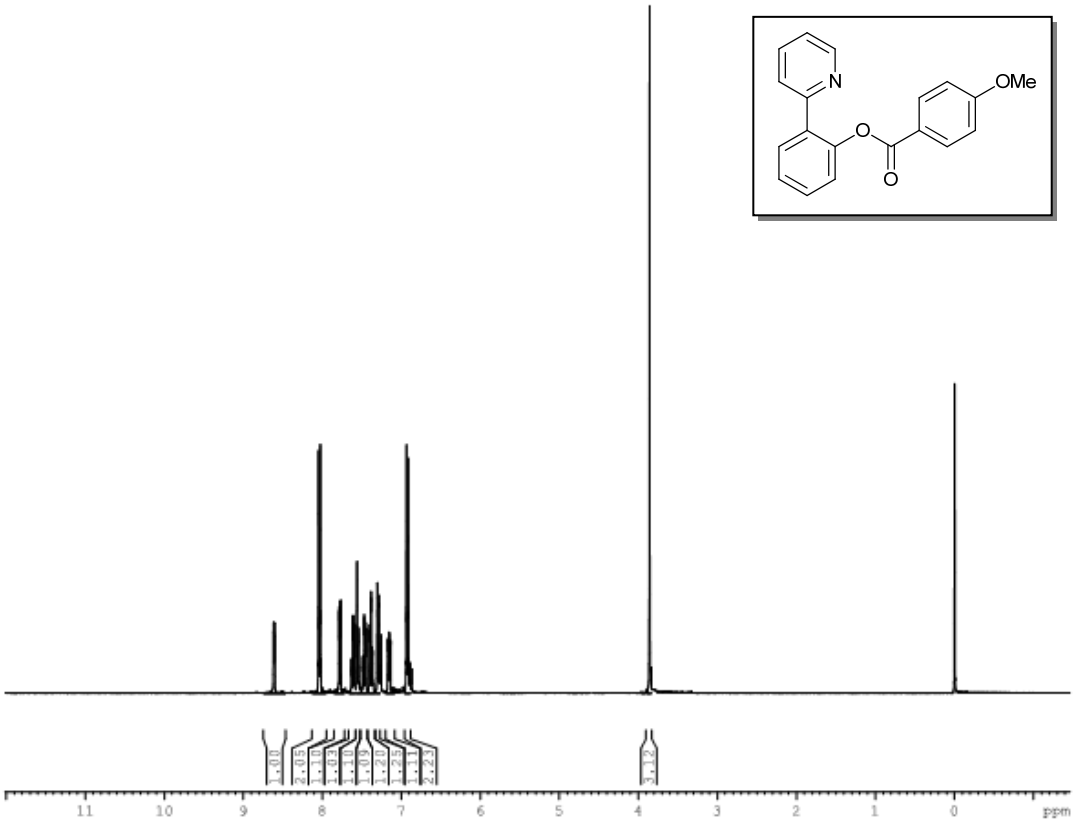
2-(pyridin-2-yl)phenyl 4-(*tert*-butyl)benzoate (3e) (^{1}H NMR)



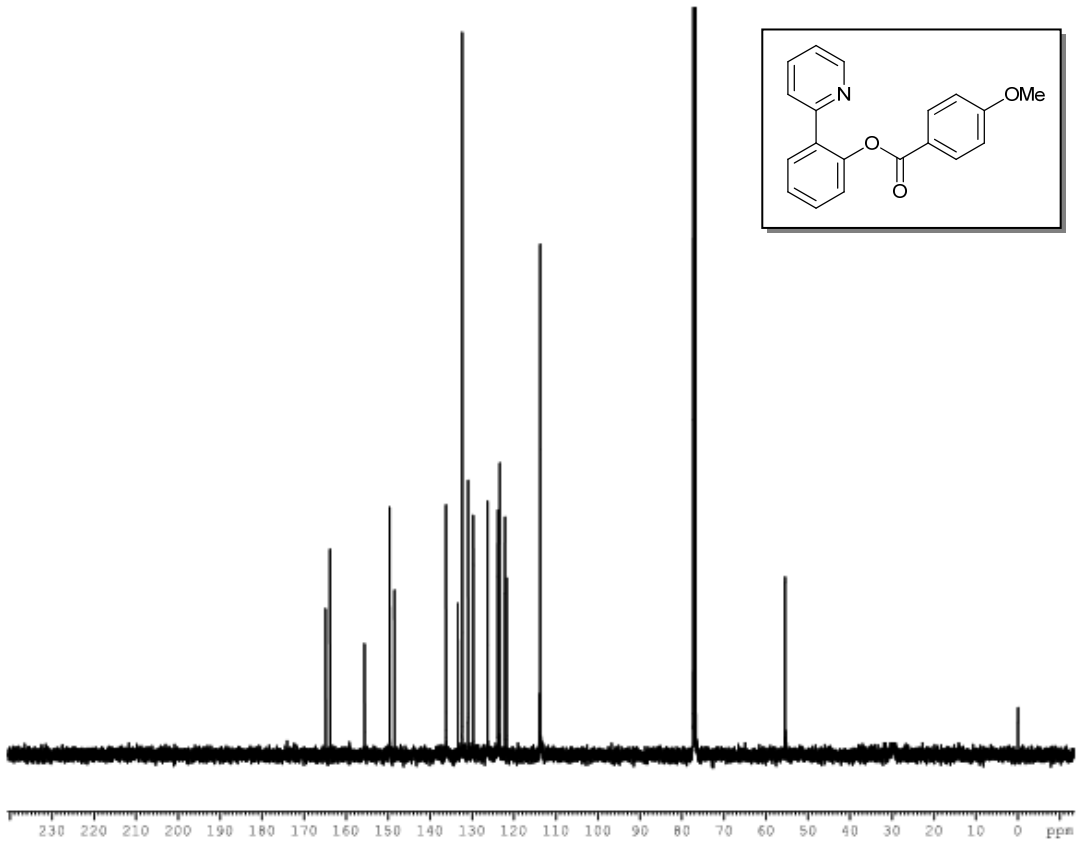
2-(pyridin-2-yl)phenyl 4-(*tert*-butyl)benzoate (3e) (^{13}C NMR)



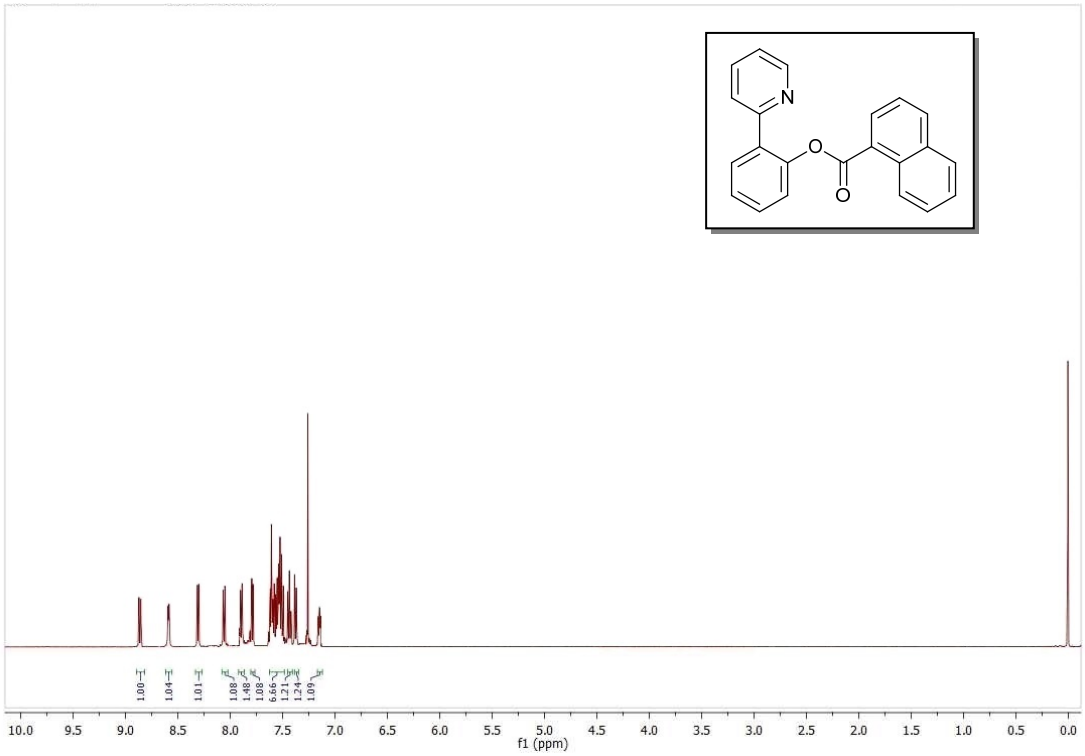
2-(pyridin-2-yl)phenyl 4-methoxybenzoate (3f) (^{1}H NMR)



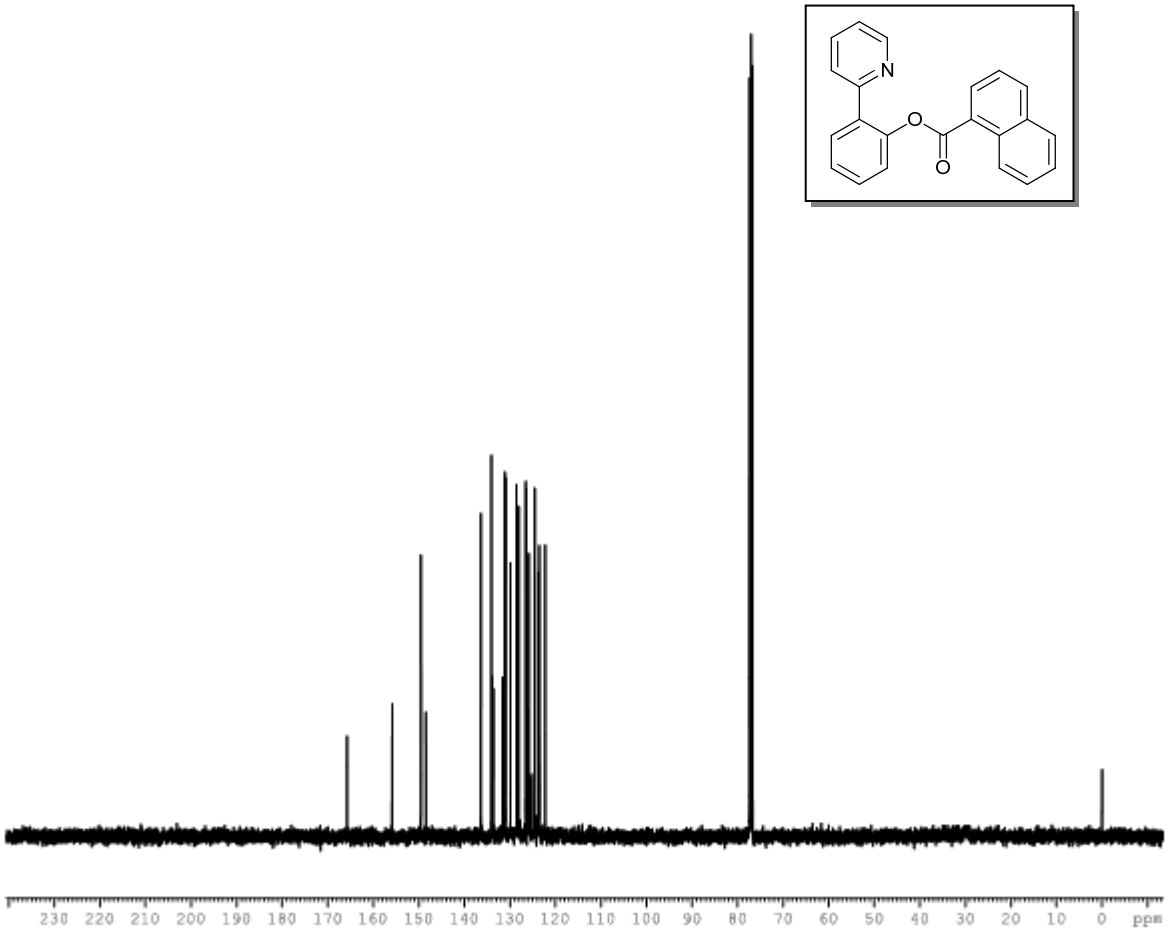
2-(pyridin-2-yl)phenyl 4-methoxybenzoate (3f) (^{13}C NMR)



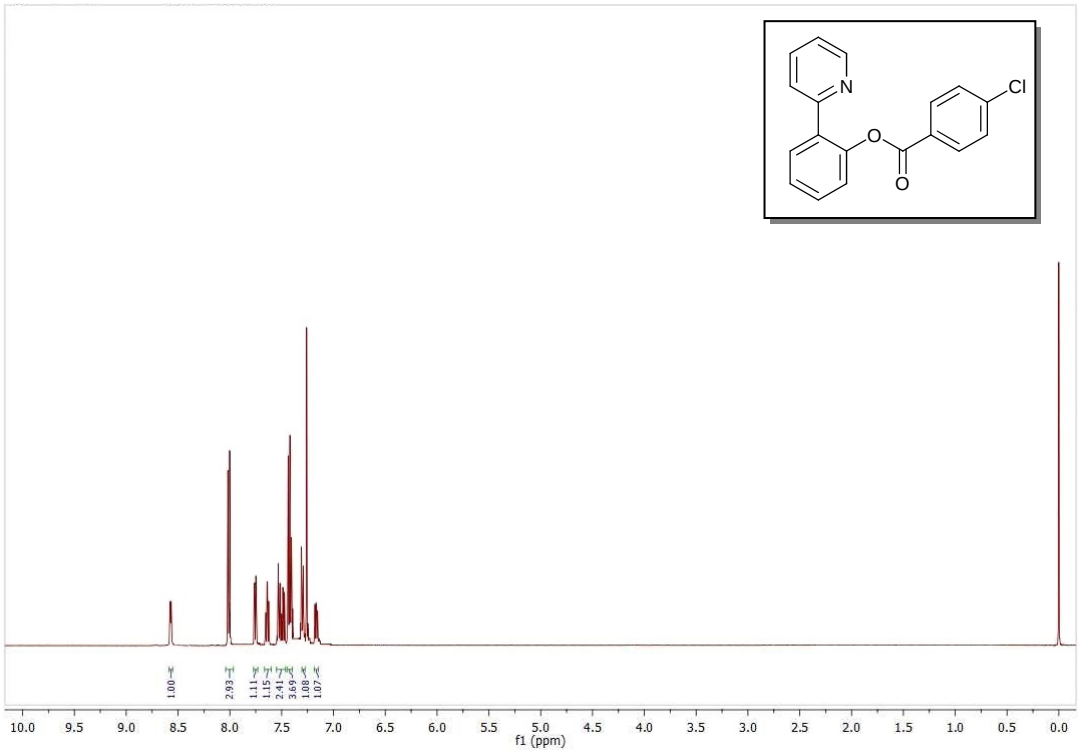
2-(pyridin-2-yl)phenyl 1-naphthoate (3g) (^{1}H NMR)



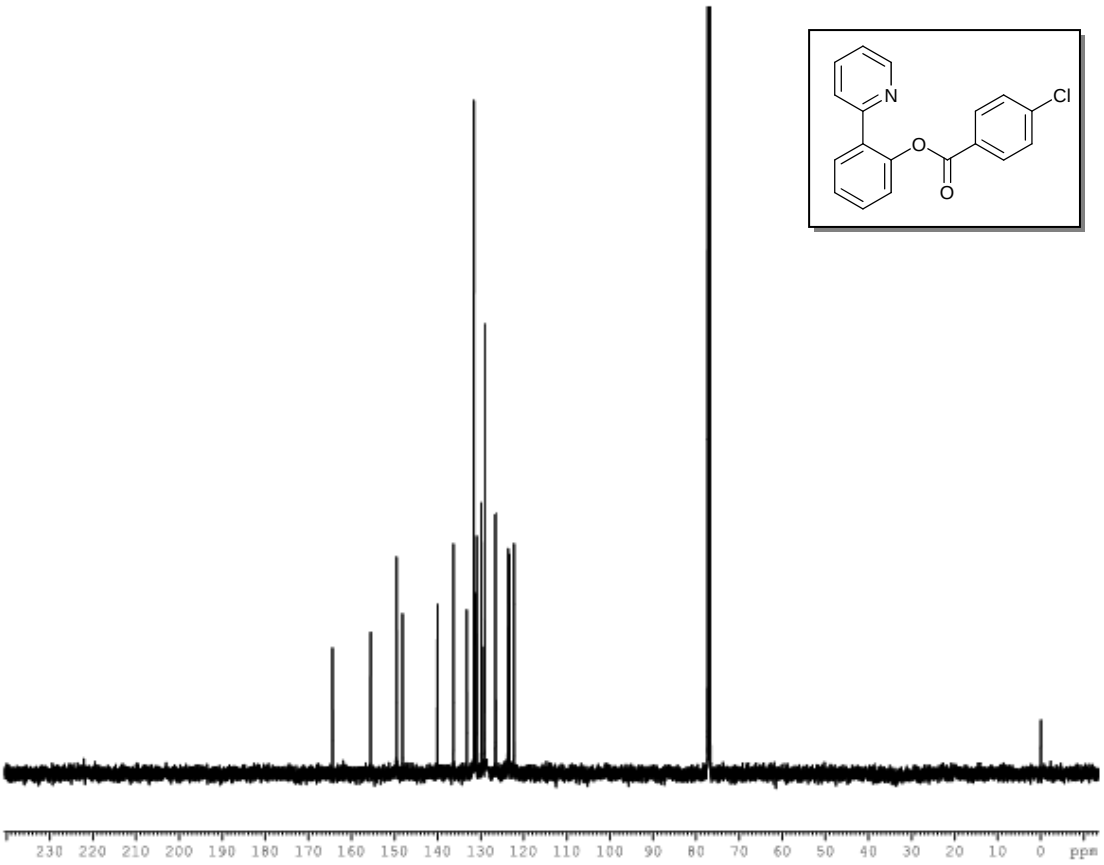
2-(pyridin-2-yl)phenyl 1-naphthoate (3g) (^{13}C NMR)



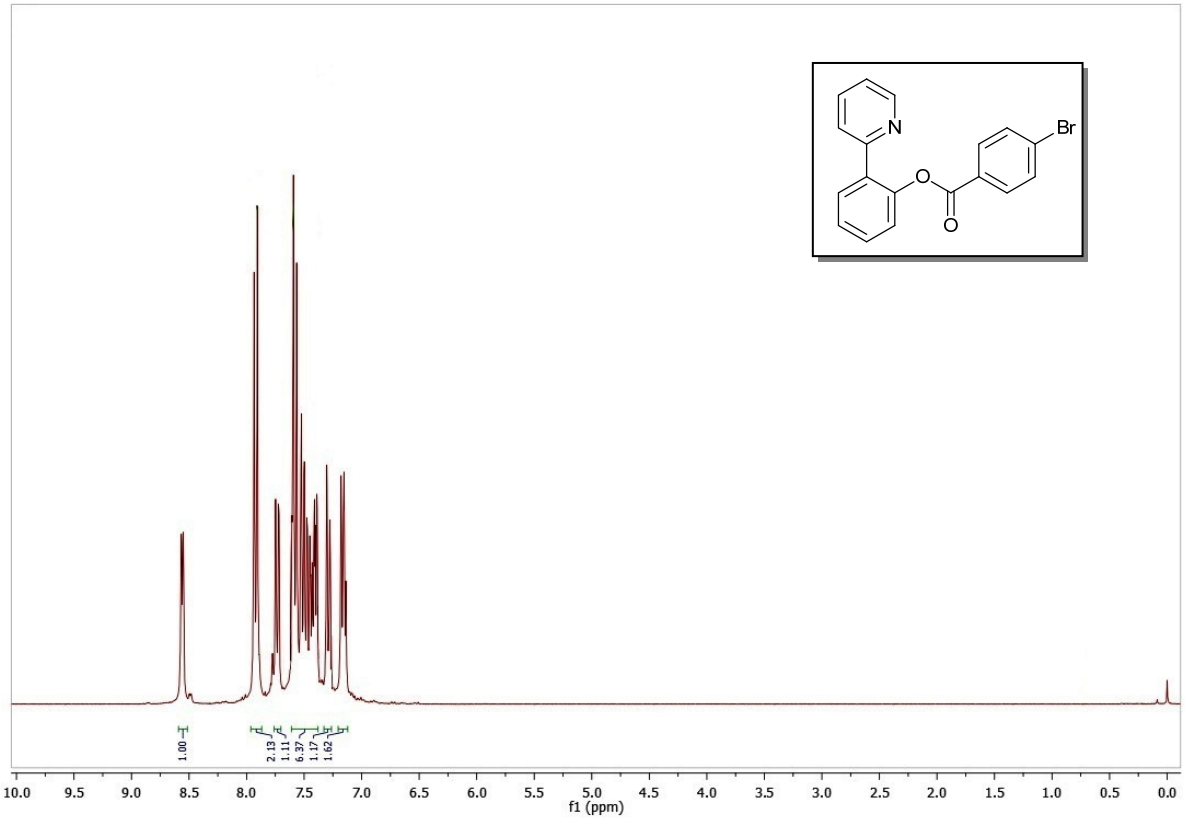
2-(pyridin-2-yl)phenyl 4-chlorobenzoate (3h) (^{1}H NMR)



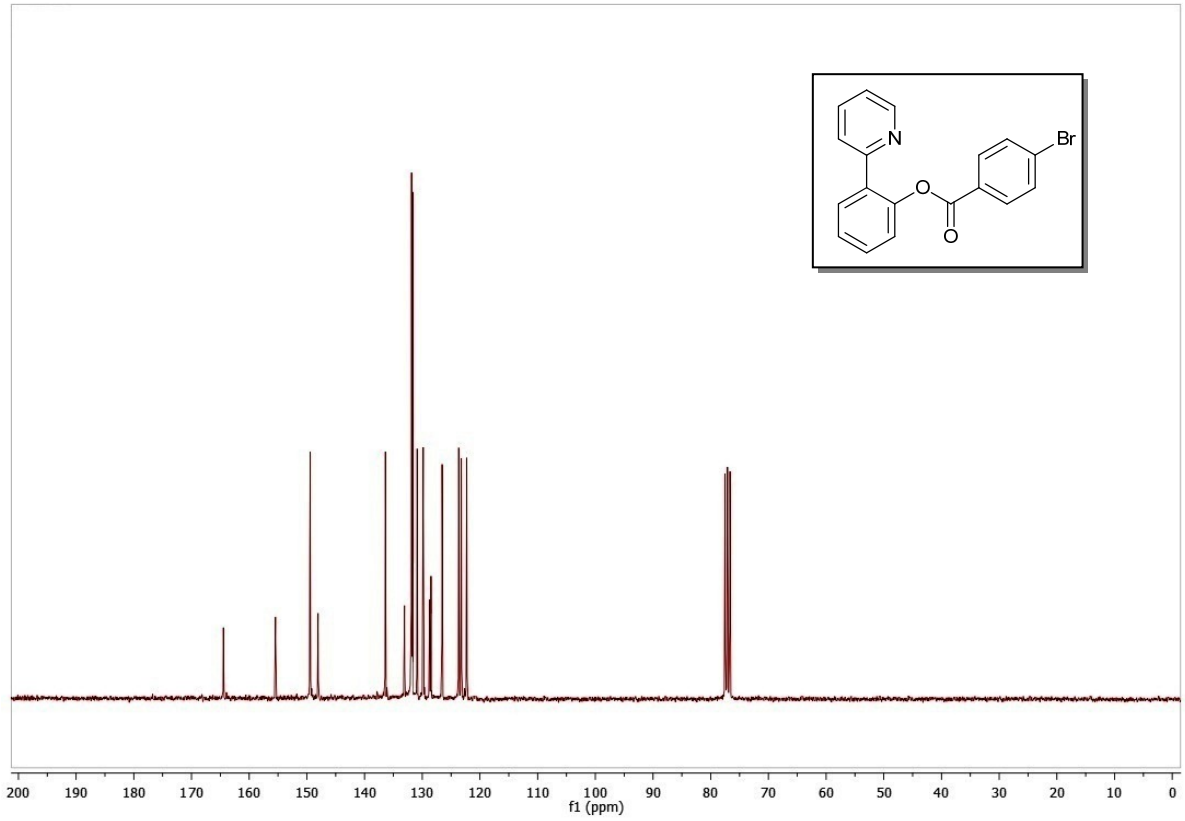
2-(pyridin-2-yl)phenyl 4-chlorobenzoate (3h) (^{13}C NMR)



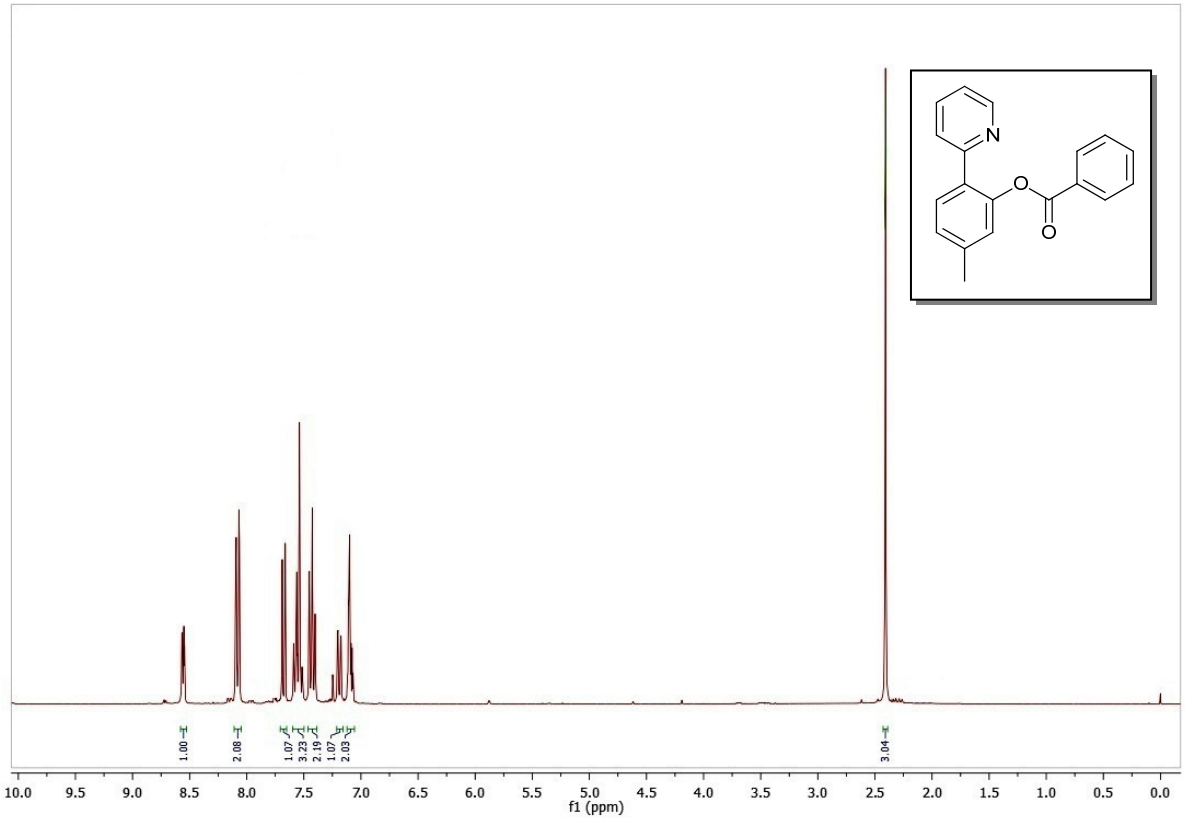
2-(pyridin-2-yl)phenyl 4-bromobenzoate (3i) (^{1}H NMR)



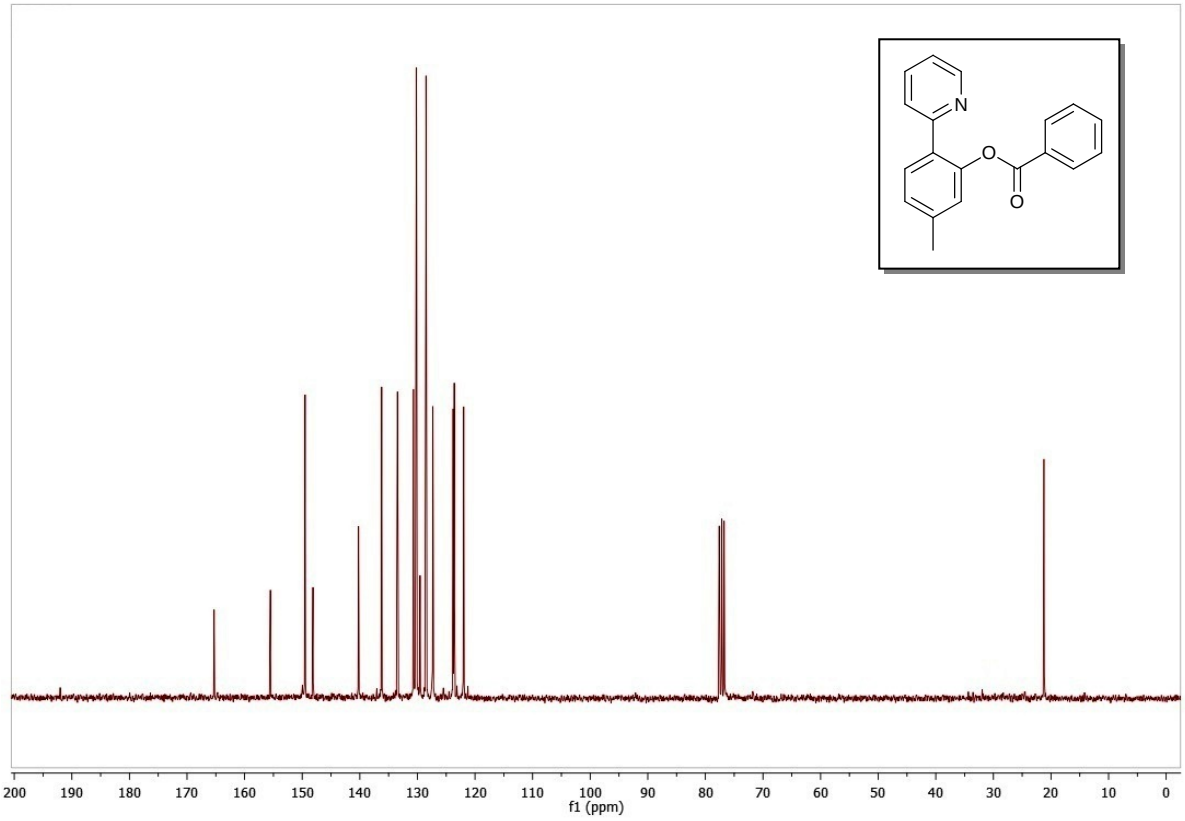
2-(pyridin-2-yl)phenyl 4-bromobenzoate (3i) (^{13}C NMR)



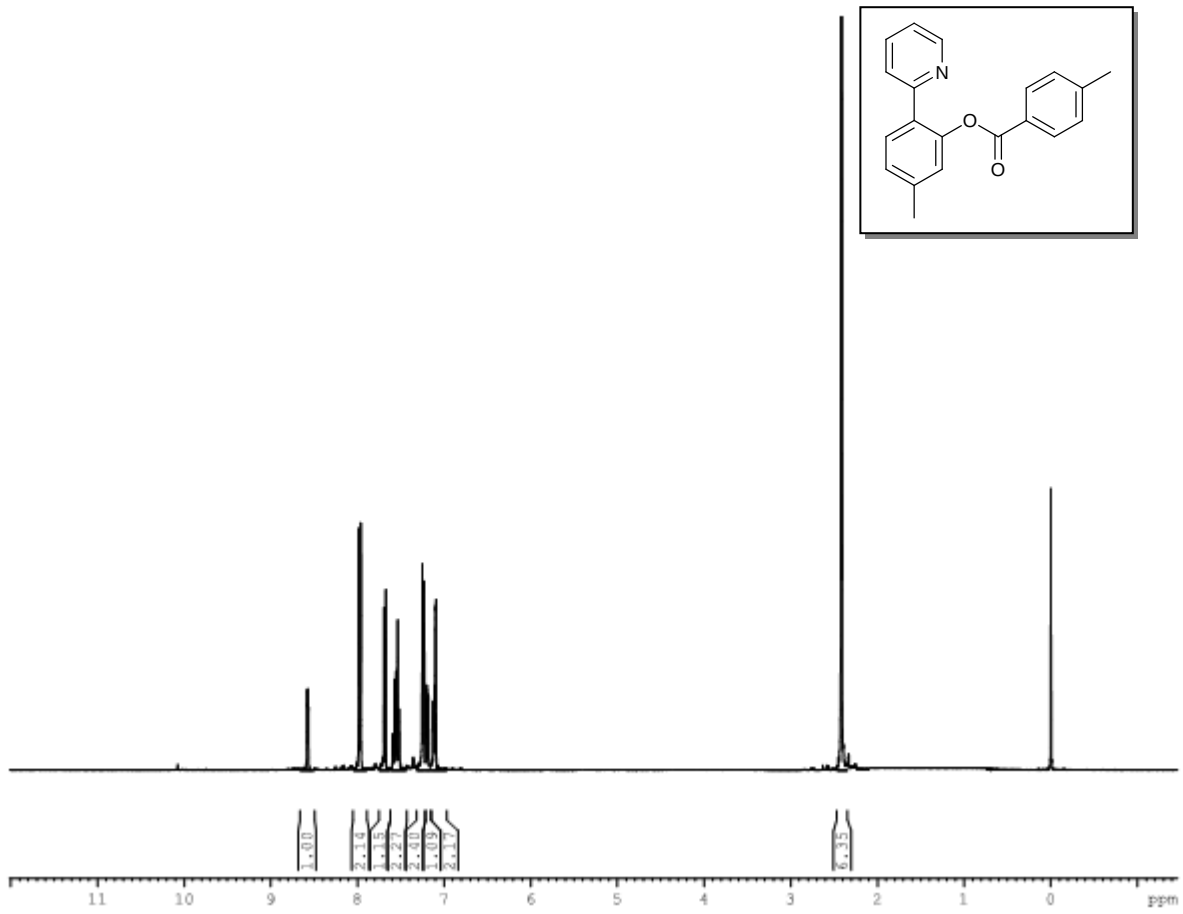
5-methyl-2-(pyridin-2-yl)phenyl benzoate (3j) (^{1}H NMR)



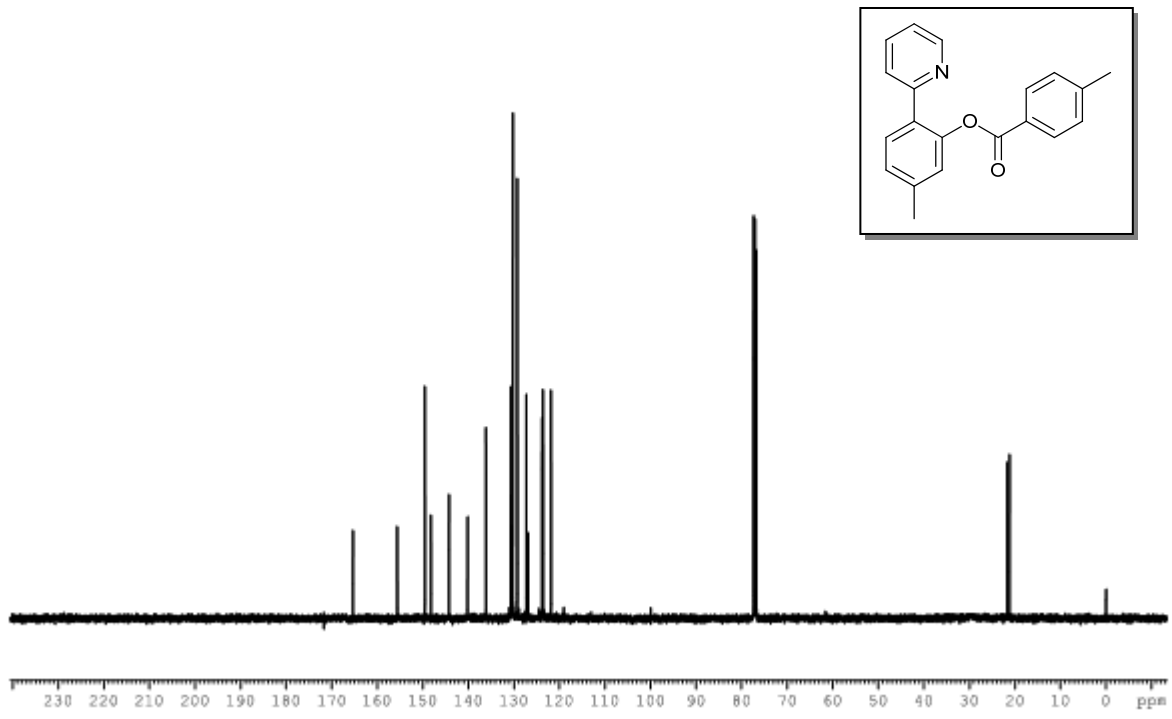
5-methyl-2-(pyridin-2-yl)phenyl benzoate (3j) (^{13}C NMR)



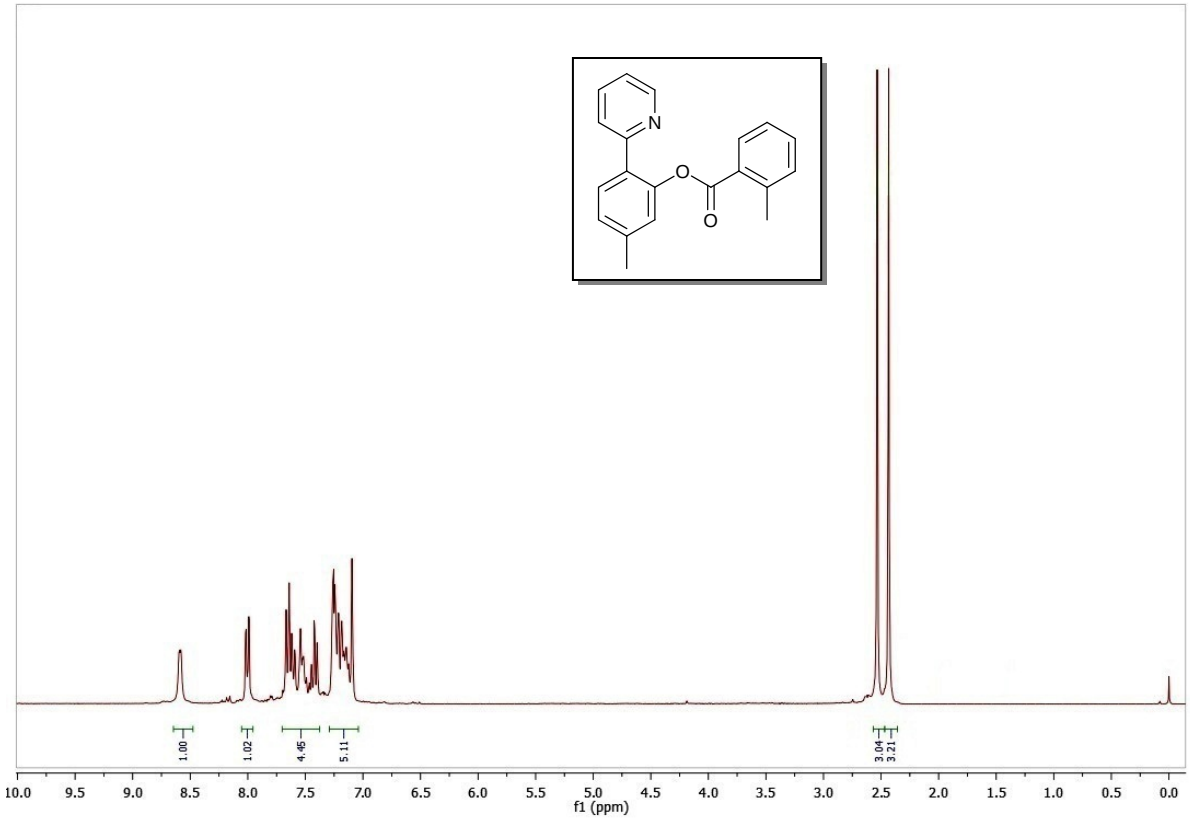
5-methyl-2-(pyridin-2-yl)phenyl 4-methylbenzoate (3k) (^{1}H NMR)



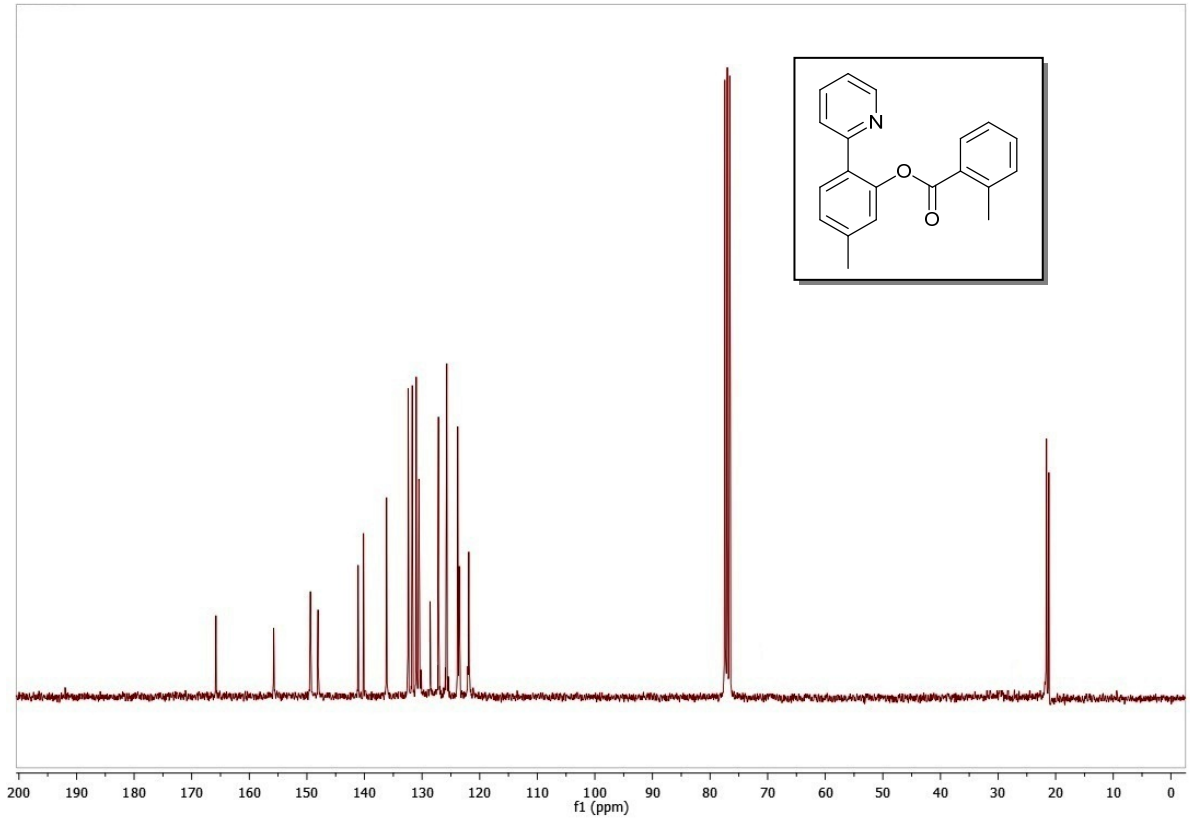
5-methyl-2-(pyridin-2-yl)phenyl 4-methylbenzoate (3k) (^{13}C NMR)



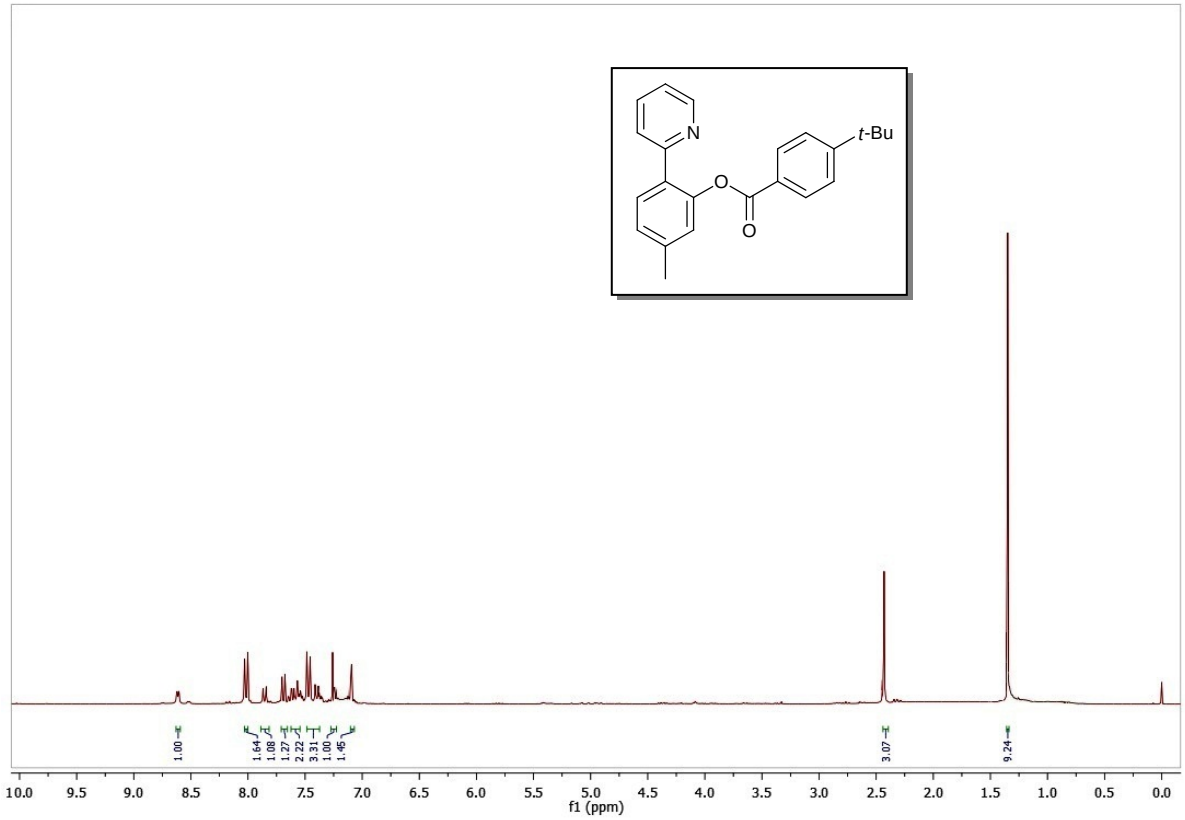
5-methyl-2-(pyridin-2-yl)phenyl 2-methylbenzoate (3l) (^{1}H NMR)



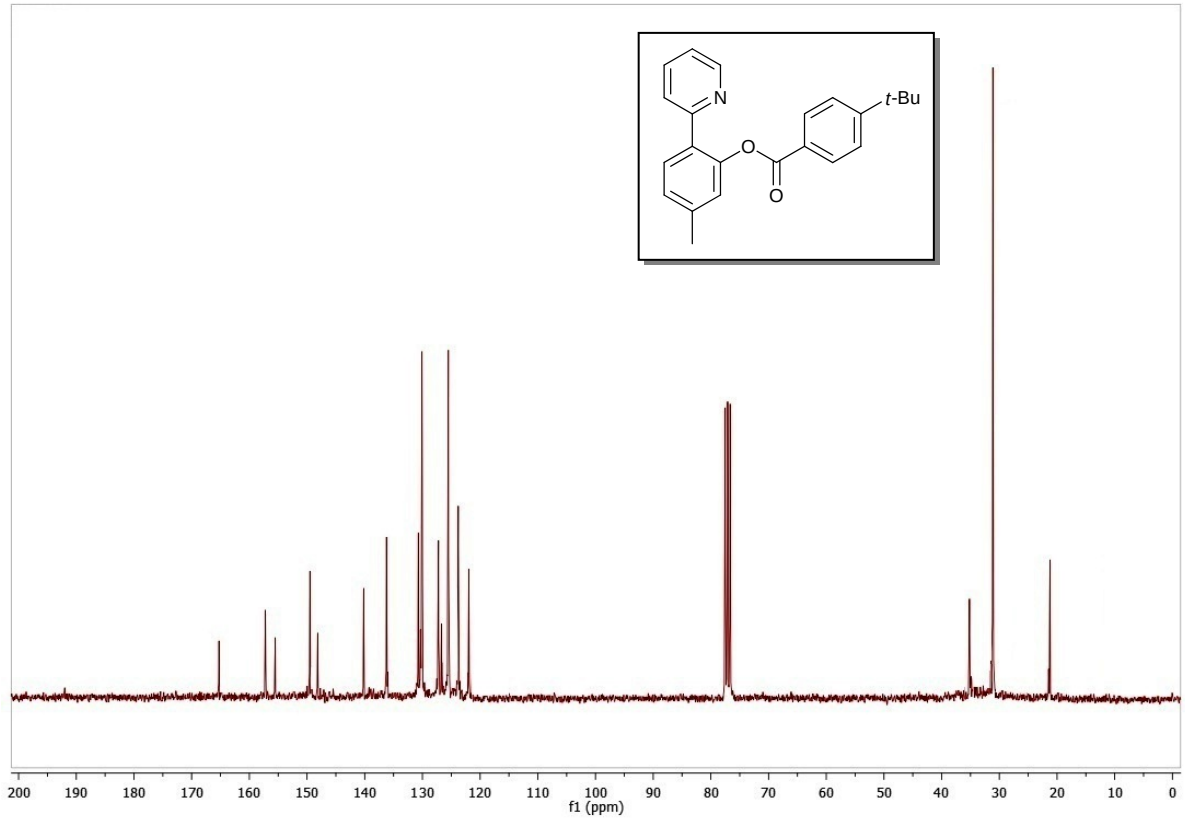
5-methyl-2-(pyridin-2-yl)phenyl 2-methylbenzoate (3l) (^{13}C NMR)



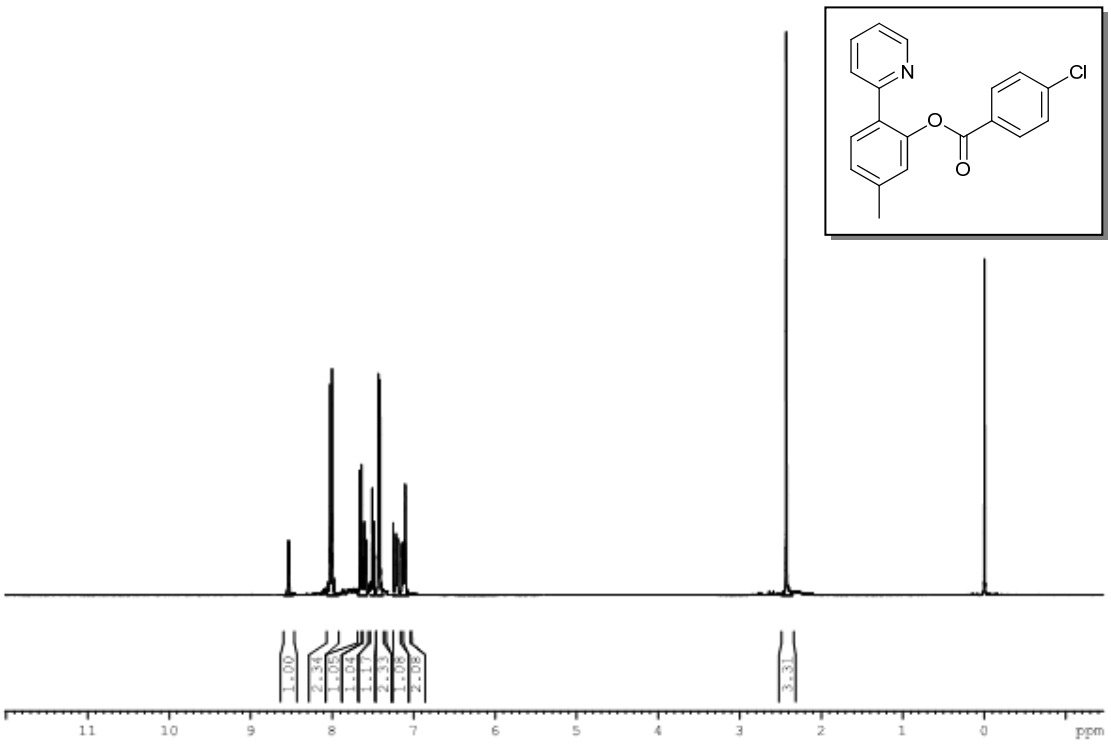
5-methyl-2-(pyridin-2-yl)phenyl 4-(*tert*-butyl)benzoate (3m) (^{1}H NMR)



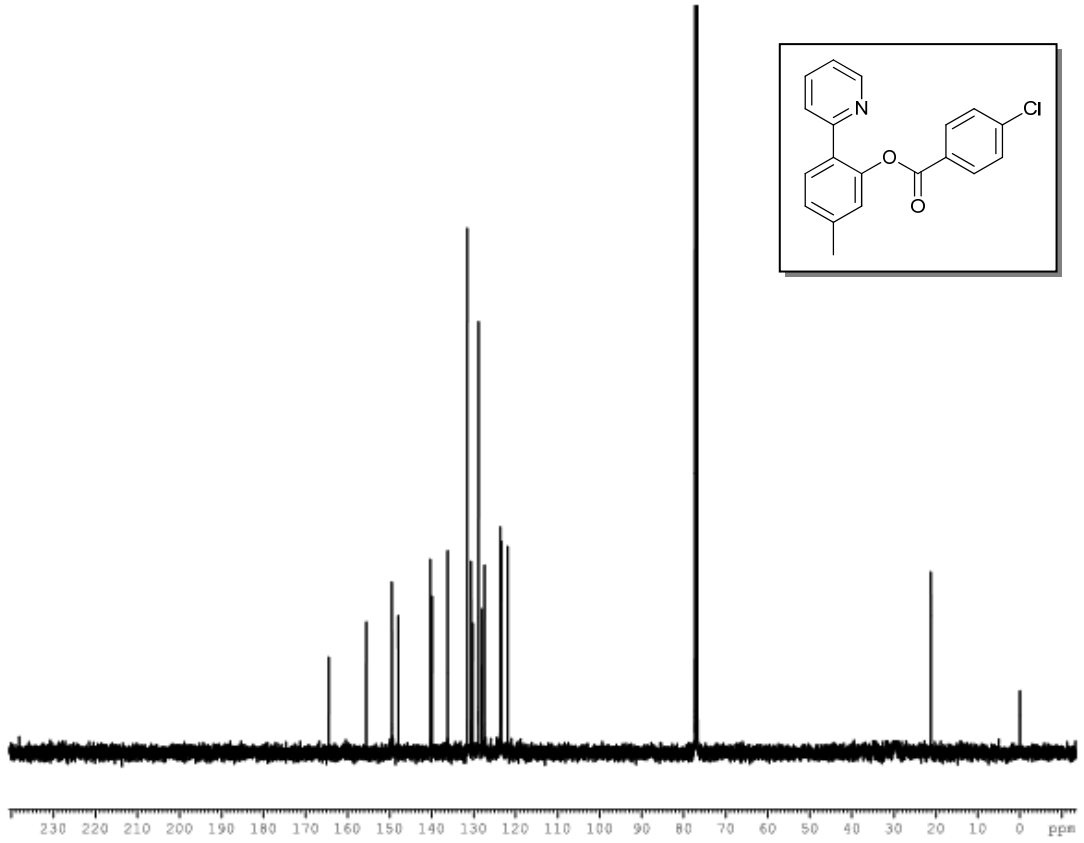
5-methyl-2-(pyridin-2-yl)phenyl 4-(*tert*-butyl)benzoate (3m) (^{13}C NMR)



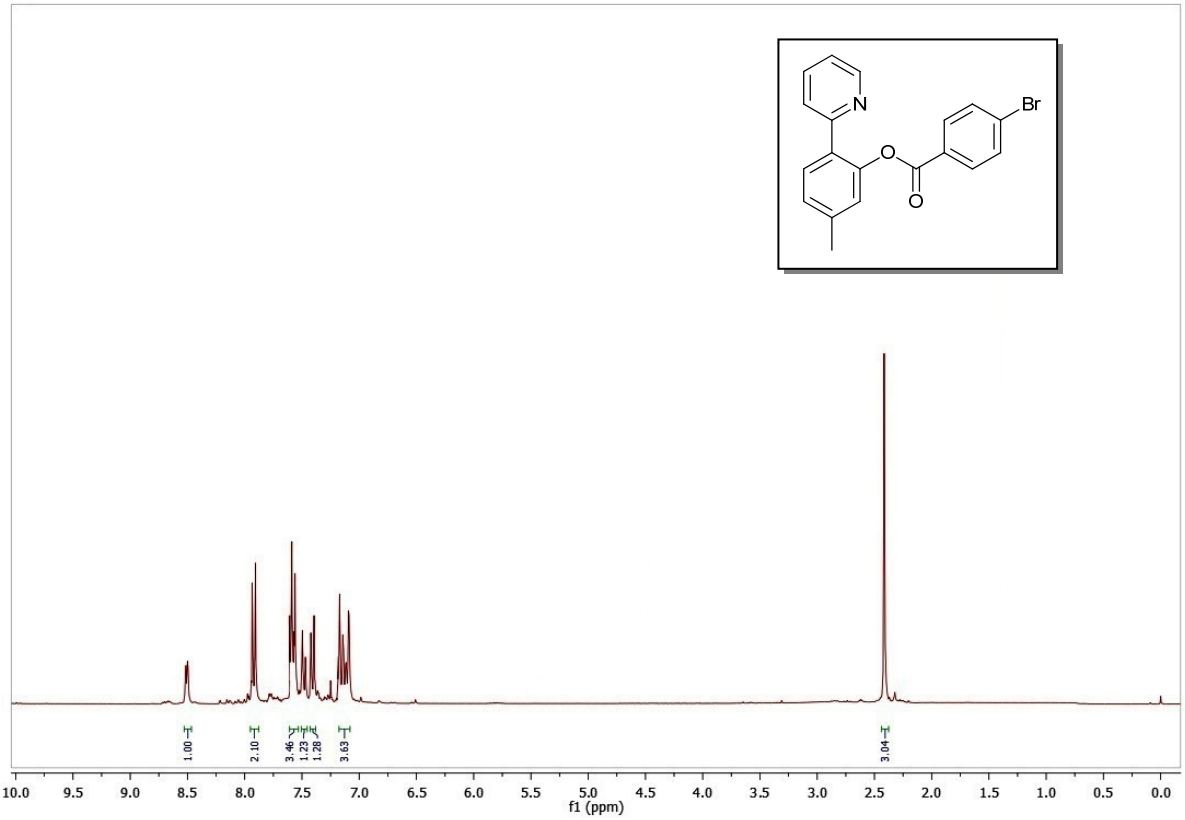
5-methyl-2-(pyridin-2-yl)phenyl 4-chlorobenzoate (3n) (^{1}H NMR)



5-methyl-2-(pyridin-2-yl)phenyl 4-chlorobenzoate (3n) (^{13}C NMR)



5-methyl-2-(pyridin-2-yl)phenyl 4-bromobenzoate (3o) (^{1}H NMR)



5-methyl-2-(pyridin-2-yl)phenyl 4-bromobenzoate (3o) (^{13}C NMR)