Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Transesterification of (hetero)aryl esters with phenols by an Earth-abundant metal catalyst

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General information

Unless otherwise stated, reactions were performed in oven-dried reaction tube under air atmosphere. Reaction progress was monitored by thin-layer chromatography (TLC). Thin layer chromatography (TLC) was performed on pre-coated silica gel GF254 plates and visualized by UV fluorescence quenching. Silica gel (particle size 40–60 nm) was used for flash chromatography. ^{1}H NMR spectras were recorded on a Bruker Avance 600 MHz in $CDCl_3$ and are reported relative to residual solvent peak at δ 7.26 ppm. ^{13}C NMR spectras were recorded on a Bruker Avance 600 MHz spectrometer (126 MHz) in $CDCl_3$ and are reported relative to residual solvent peak at δ 77.16 ppm. Data for 1H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). All chemical shifts are reported in ppm using TMS the internal standard. The structures of known compounds were further corroborated by comparing their ^{1}H NMR data with those of literature. GC-MS analyses were obtained on a Thermo DSQ II gas chromatograph. ICP-MS analysis was conducted at the Agilent 7700ce ICP-MS spectrometer. The TEM images were recorded on a JEOL-2100F transmission electron microscope employing an accelerating voltage of 200 kV. The samples were suspended in ethanol and dried on holey carbon-coated Cu grids. The solid-state NMR experiments were performed on a Bruker Avance III 400 WB spectrometer equipped with a 9.39 T magnet at 297 K. The ^{1}H-^{13}C cross-polarization magic angle spinning (CP/MAS) NMR spectra were recorded using a Bruker 4 mm standard bore MAS probe head with the ZrO_2 rotors spinning at 5.0 kHz rate with a Larmor frequency of 100.62 MHz. The spinning sidebands were suppressed by total sideband suppression (TOSS) technique. The TEM images were recorded on a JEOL-2100F transmission electron microscope employing an accelerating voltage of 200 kV. The samples were suspended in ethanol and dried on holey carbon-coated Cu grids.

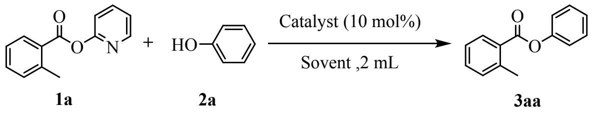
K_2CO_3 was purchased from TCI (sublimed grade, 99.99% trace metals basis) and used directly. Phenol substrates were purchased from TCI and used as received (unless noted).

Part I. Reaction optimizations, trace metal analysis, and preliminary mechanistic investigation

1. Reaction optimization

Procedure for reaction condition optimization: pyridin-2-yl 2-methylbenzoate **1a** and phenol **2a** were used as the model reaction. In a typical reaction, pyridin-2-yl 2-methylbenzoate (21.30 mg, 0.10 mmol), phenol (15.98 mg, 0.17 mmol), catalyst (1.38 mg, 0.01 mmol), and the solvent (2.0 mL) were charged in a 25 mL ovendried reaction tube. Reaction was carried out 60 ℃ for 48 h in an oil bath under air condition. After being cooled to room temperature, the reaction solution was evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5~1:15 as an eluent) to afford the desired product **3**. All the products were also confirmed by comparing the ^{1}H NMR and ^{13}C NMR data with authentic samples.

Table S1. Condition optimization of novel transesterification[a]



Entry	Catalyst	Base	T(°C)	Solvent	yield(%)[b]
1	Pd/γ-Al_2O_3	K_2CO_3	60	1,4-dioxane	99
2	K_2CO_3		60	1,4-dioxane	100
3	K_3PO_4		60	1,4-dioxane	81
4	$KOBu^t$		60	1,4-dioxane	79
5	KOH		60	1,4-dioxane	70
6	$KOCH_3$		60	1,4-dioxane	92
7	Cs_2CO_3		60	1,4-dioxane	93
8	NaOH		60	1,4-dioxane	NP
9	Na_2CO_3		60	1,4-dioxane	NP
10	$NaOC_2H_5$		60	1,4-dioxane	NP
11	NaOAc		60	1,4-dioxane	NP
12	Li_2CO_3		60	1,4-dioxane	NP
13	$Ca(OH)_2$		60	1,4-dioxane	NP
14	NEt_3		60	1,4-dioxane	NP
15	NaOH		60	DMSO	48
16	Li_2CO_3		60	DMSO	77
17	$Ca(OH)_2$		60	DMSO	NP
18	NEt_3		60	DMSO	NP
19	KI		120	DMSO	67
20	CsI		120	DMSO	55
21	NaI		120	DMSO	53
22	LiI		120	DMSO	56
23	—		60	1,4-dioxane	NP

24	K_2CO_3	60	CH_3CN	76
25	K_2CO_3	60	toluene	91
26	K_2CO_3	60	PhCl	79
27	K_2CO_3	60	DMF	93
28	K_2CO_3	60	DMSO	94
29	K_2CO_3	60	THF	91
30	K_2CO_3	60	H_2O	78
31	K_2CO_3	20	1,4-dioxane	31
32	K_2CO_3	40	1,4-dioxane	42
33	K_2CO_3	80	1,4-dioxane	92
34	K_2CO_3	60	1,4-dioxane	97[d]

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.17 mmol), catalyst (10 mol%), solvent (2 mL), 60 °C, 48 h; [b] Isolated yield; [c] Catalyst (100 mol%); [d] **1a** (0.1 mmol), **2a** (0.1 mmol).

The results from Table S1 reveal that there is a high degree of tunability in the reaction conditions for the novel transesterification reaction. All potassium bases, such as KOH, K_3PO_4, $KOCH_3$, $KOBu^t$ and Cs_2CO_3 could catalyze the transesterification reaction smoothly (entries 3-7). But reactions in the presence of other bases as potential catalysts, such as NaOH, Na_2CO_3, $NaOC_2H_5$, NaOAc, Li_2CO_3, $Ca(OH)_2$, and strongly basic amines TEA, did not proceed (entries 8-14). Aim to confirm if this transformation is solubility controlled, NaOH, Li_2CO_3, $Ca(OH)_2$ and TEA were chosen for reacting in DMSO (entries 15-18). The experiment results showed that NaOH, and Li_2CO_3 could catalyze the transesterification reaction to give desired product in DMSO, whereas $Ca(OH)_2$ and TEA could not. Non-basic alkali metal salts, including KI, CsI, NaI and LiI, could catalyze the transesterification reaction smoothly at 120 °C (entries 19-22). The use of other solvents, such as DMF, DMSO, CH_3CN, PhCl, toluene and H_2O, led to the formation of **3aa** in lower yields (entries 24-30). Both a decrease and increase in the reaction temperature (20 ℃, 40 ℃ and 80 ℃) reduced the yield of **3aa** (entries 31-33). When the reactants in a ratio 1:1, the yield of **3aa** represents a slight decline (entry 34).

2. Trace metal analysis by ICP-MS

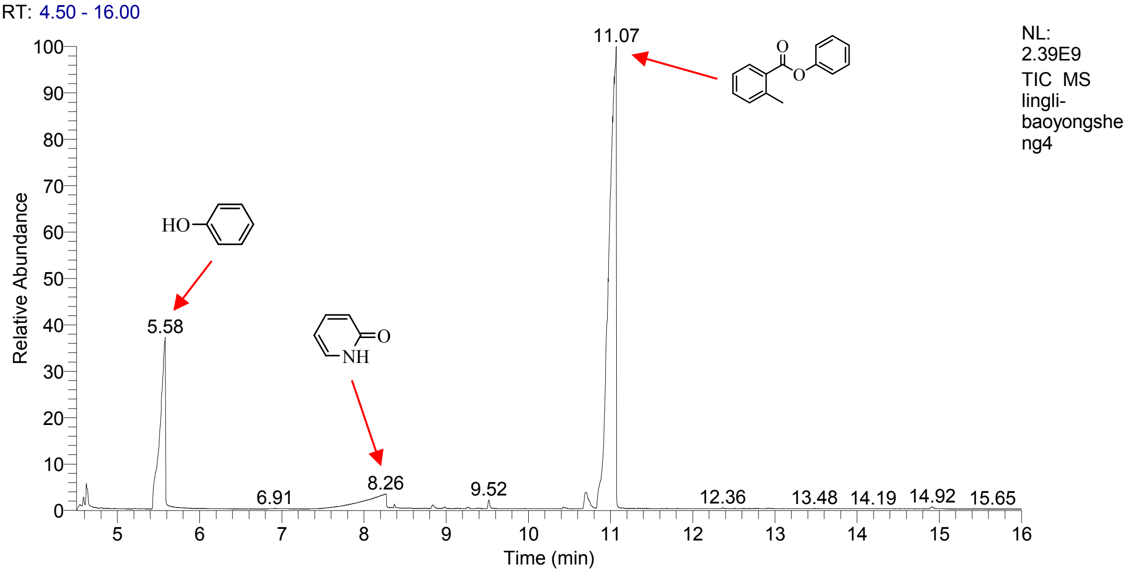
ICP-MS trace metal analysis. To provide further support against involvement of adventitious trace metal species in the K_2CO_3-catalyzed transesterification of aryl ester with phenol, inductively coupled plasma mass spectrometry (ICP-MS) was performed on samples of K_2CO_3 and a standard reaction mixture that was run under optimized conditions in the glove box. Each sample was added to a 100 mL DigiTUBE digestion tube (SCP Science) followed by addition of 3.0 mL of Plasma Pure chloroazotic acid (SCP Science) and heating to 75°C for 36 hours. After digestion, each sample was diluted using Milli Q water to 100 mL and sample analysis was performed on an Agilent 7700ce ICP-MS spectrometer. The results are given in Table S2. The results from quantitative analysis revealed that most metal contaminants were present below the instrument's lowest limit of detection (i.e., in 0.1 ppm range or lower). On the other hand, the model reaction was conducted in new glassware, and almost the same result (100% isolated yield) was obtained. These results indicated that this hydroxylation reaction is promoted by K_2CO_3 itself rather than catalyzed by the presence of trace metal impurities.

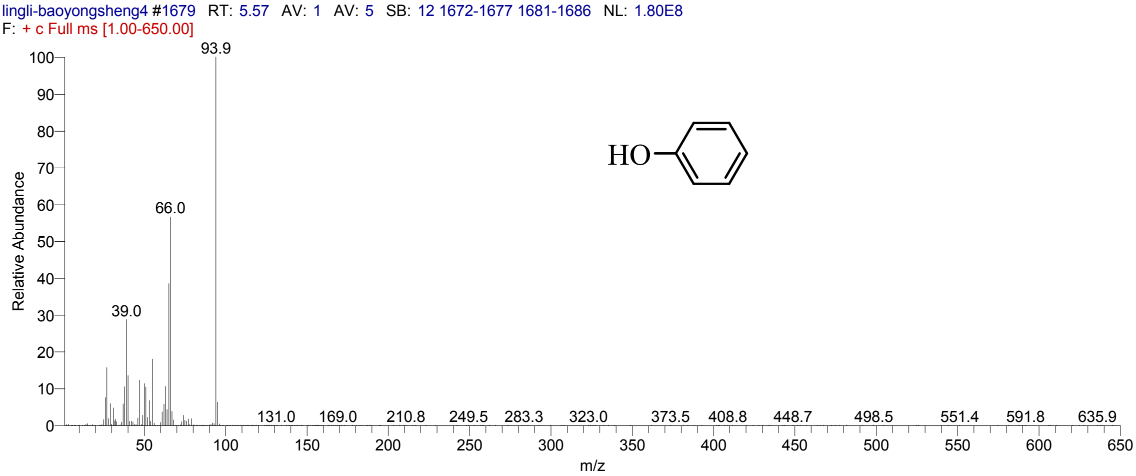
Table S2: ICP-MS analysis on the contents (ppm) of elements in K_2CO_3 and model reaction solution.

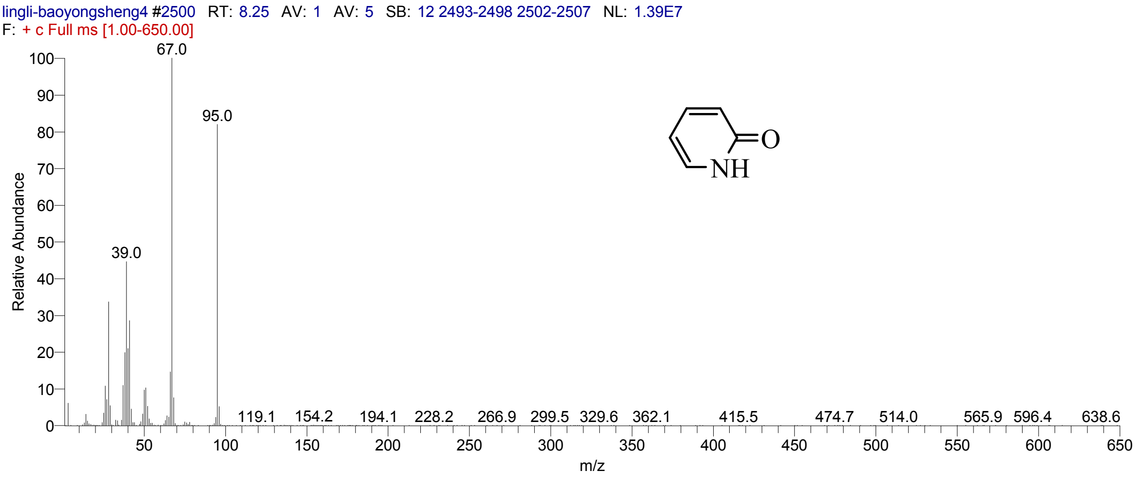
Transition-metal	Pd	Cu	Fe	Ru	Ir	Ni	Ag	Au
K_2CO_3	<0.1	<0.1	<0.1	<0.1	<0.1	0.13	<0.1	<0.1
Model reaction solution	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

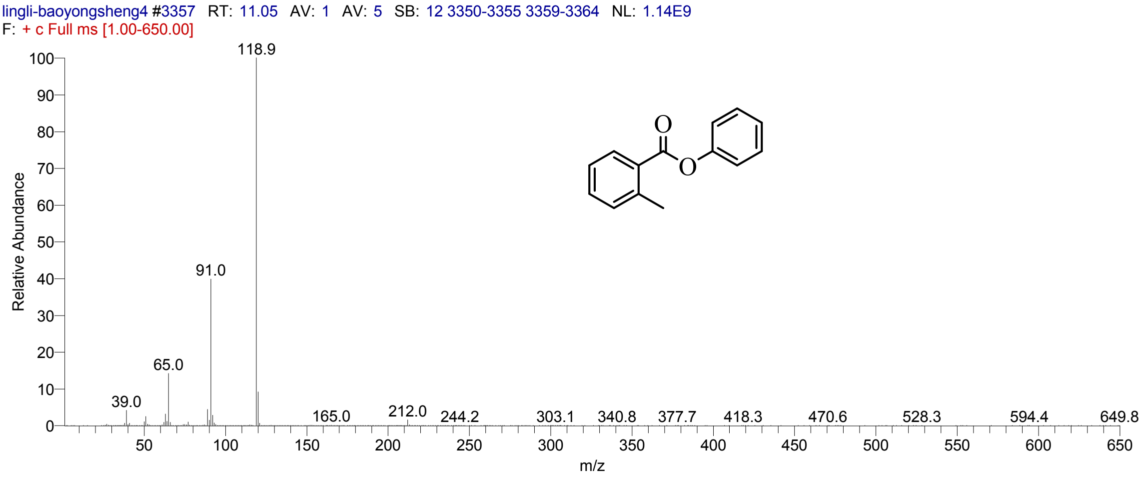
3. GC-MS analysis of reaction of 1a with 2a and reaction of 4r with 2a

GC-MS analysis of reaction of 1a with 2a

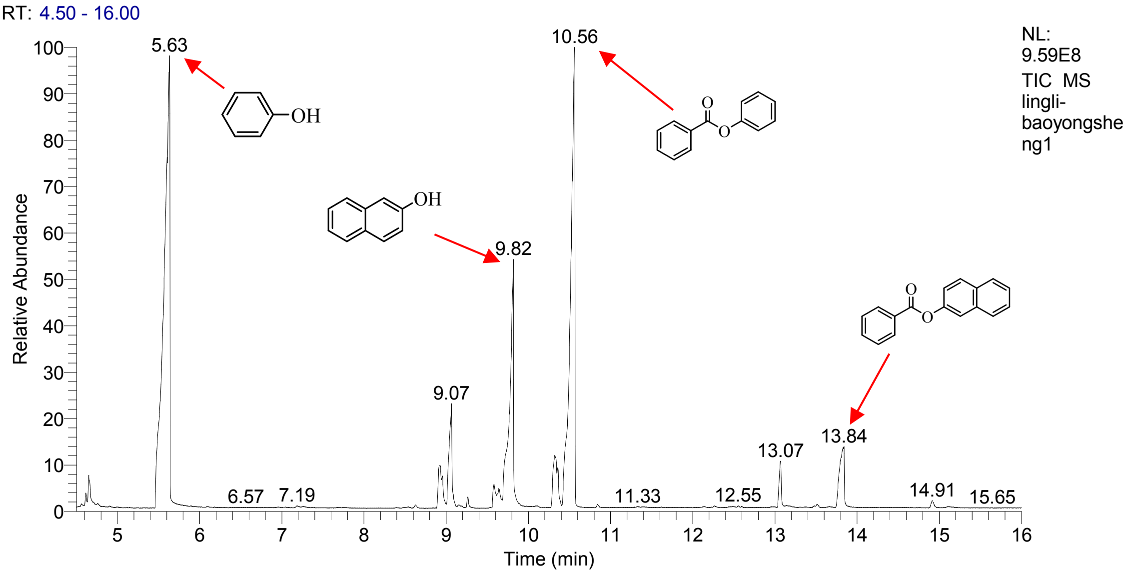


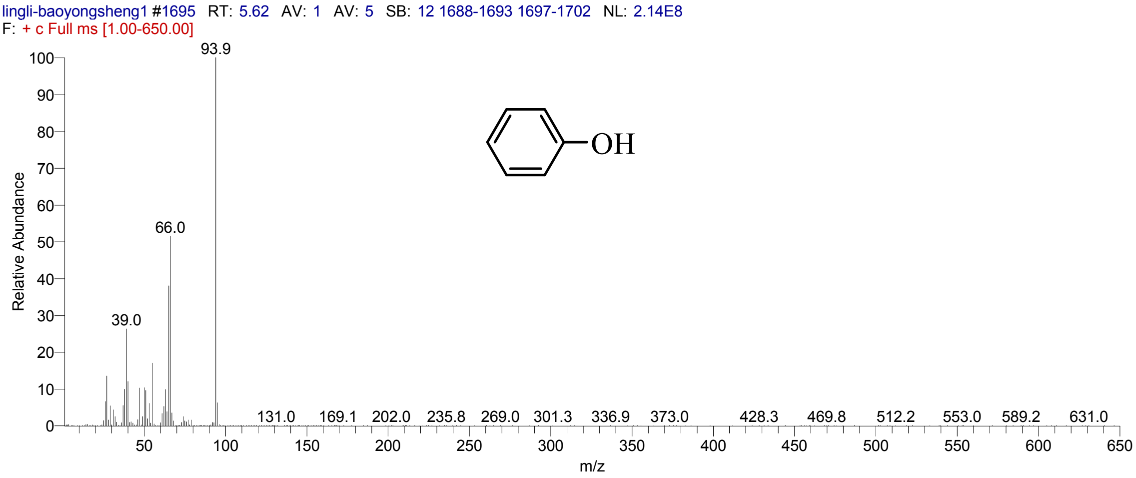






GC-MS analysis of reaction of 4r with 2a

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39.0
131.0
169.1
202.0
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373.0
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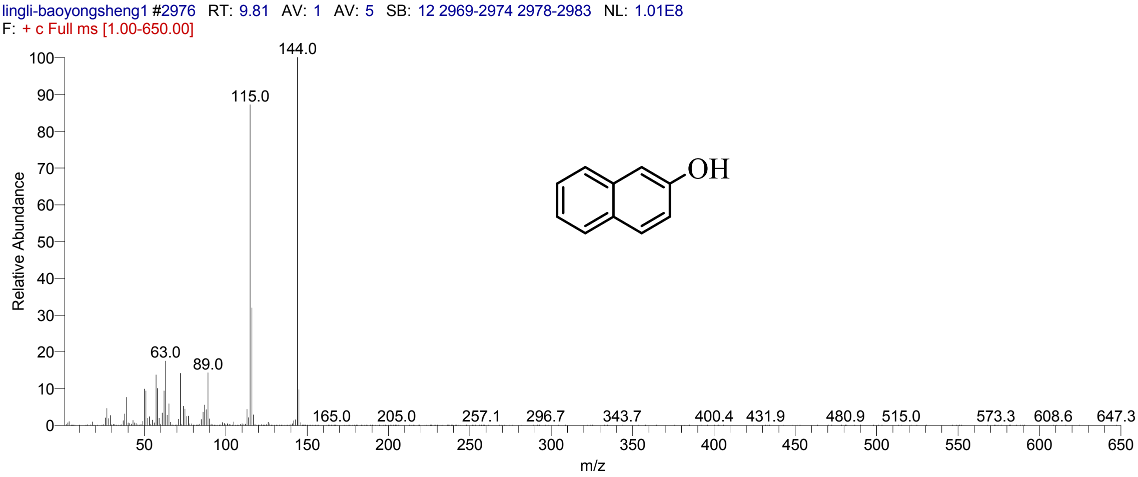
469.8
512.2
553.0
589.2
631.0
OH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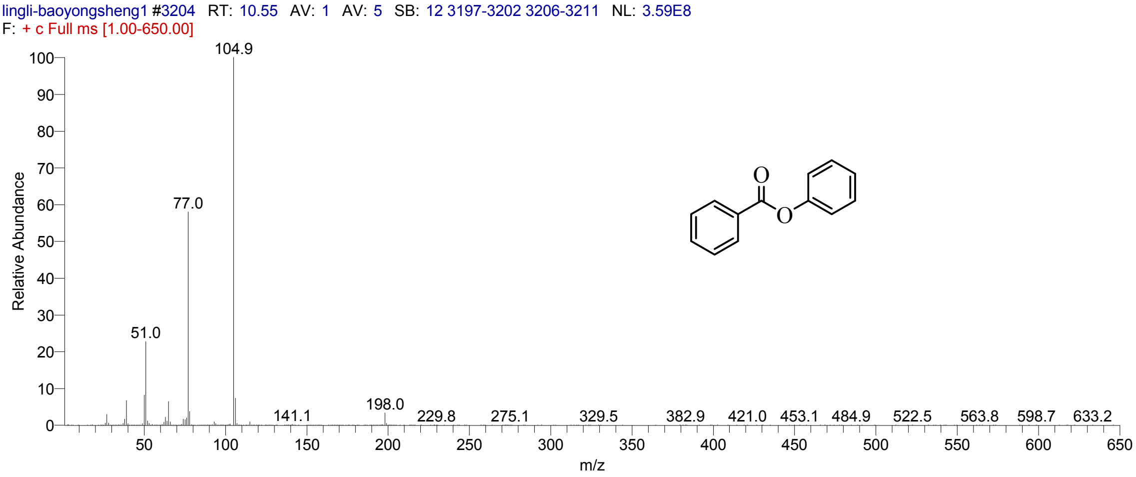
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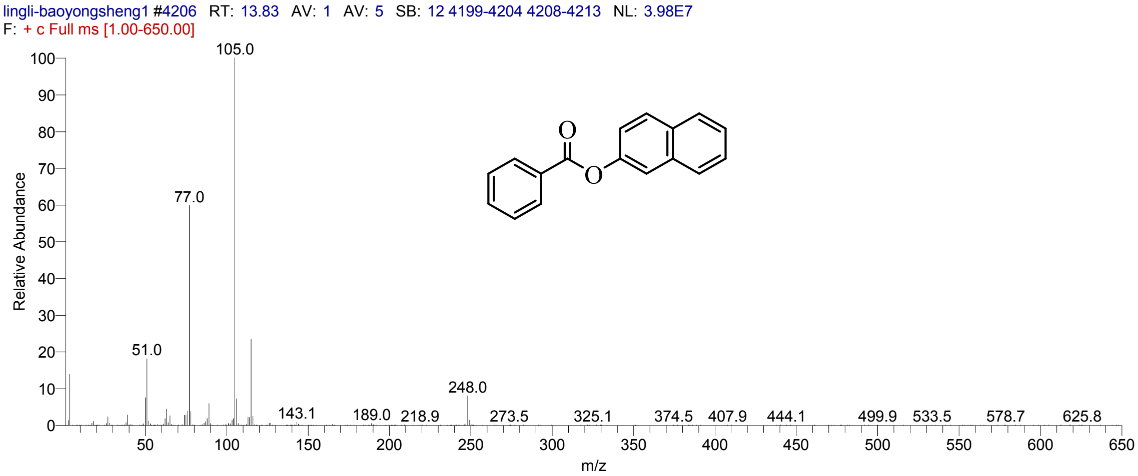
O



4. The solid state NMR spectra of used K_2CO_3

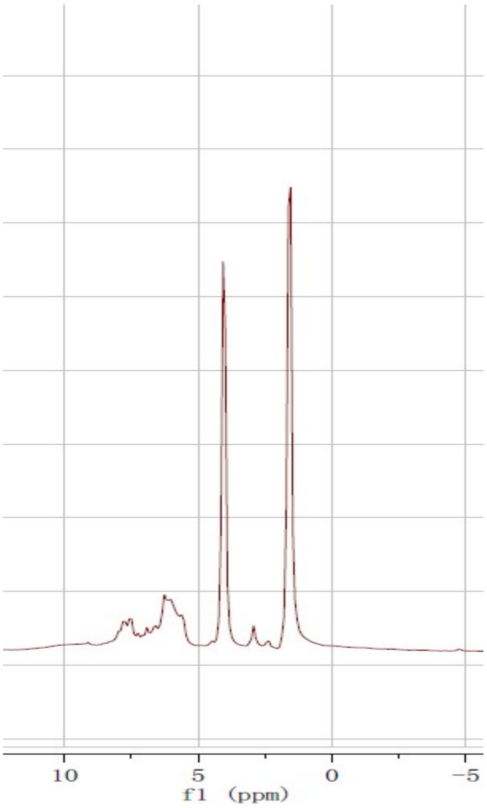


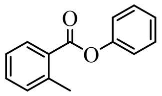
Figure S1. The solid state ^{1}H NMR of used K_2CO_3 catalyst

Part II. Experimental and analytics

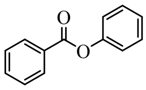
1. General procedure for K_2CO_3-catalyzed transesterification

In a typical reaction, Aryl ester (0.10 mmol), phenol (0.17 mmol), catalyst (0.01 mmol or 0.02 mmol), and the solvent 1,4-dioxane (2.0 mL) were charged in a 25 mL ovendried reaction tube. Reaction was carried out 60 ℃ or 120 ℃ for 48 h in an oil bath under air condition. After being cooled to room temperature, the reaction solution was evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5~1:15 as an eluent) to afford the desired product **3**. All the products were also confirmed by comparing the ^{1}H NMR and ^{13}C NMR data with authentic samples.

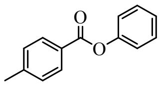
2. Characterization Data for the Products



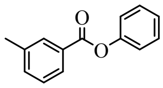
phenyl 2-methylbenzoate **3aa**.[1] Yield: 100% (21.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 2.67 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 151.0, 141.4, 132.8, 132.0, 131.2, 129.5, 128.6, 126.0, 125.9, 121.9, 22.0.



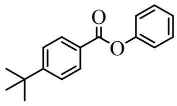
phenyl benzoate **3ba**.[2] Yield: 78% (15.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 151.0, 133.6, 130.2, 129.6, 129.5, 128.6, 125.9, 121.8.



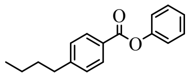
phenyl 4-methylbenzoate **3ca**.[3] Yield: 79% (16.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.40 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.3, 151.1, 144.4, 130.2, 129.5, 129.3, 126.9, 125.8, 121.8, 21.8.



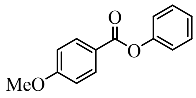
phenyl 3-methylbenzoate **3da**.[3] Yield: 85% (18.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.35 – 7.29 (m, 2H), 7.29 – 7.25 (m, 1H), 7.23 – 7.18 (m, 2H), 2.68 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 151.0, 141.4, 132.7, 132.0, 131.2, 129.5, 128.6, 126.0, 125.9, 121.9, 22.0.



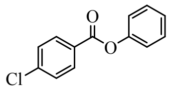
phenyl 4-(tert-butyl)benzoate **3ea**.[3] Yield: 61% (15.5 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.17 – 8.07 (m, 2H), 7.56 – 7.50 (m, 2H), 7.45 – 7.38 (m, 2H), 7.28 – 7.25 (m, 1H), 7.23 – 7.18 (m, 2H), 1.37 (s, 9H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 165.2, 157.4, 151.1, 130.1, 129.5, 126.8, 125.8, 125.6, 121.8, 35.2, 31.1.



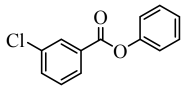
phenyl 4-butylbenzoate **3fa**.[4] Yield: 70% (17.8 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.25 – 8.01 (m, 2H), 7.46 – 7.38 (m, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.23 – 7.19 (m, 2H), 2.70 (t, J = 7.2 Hz, 2H), 1.69 – 1.60 (m, 2H), 1.43 – 1.33 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 165.3, 151.1, 149.4, 130.3, 129.5, 128.7, 127.0, 125.8, 121.8, 35.8, 33.3, 22.3, 13.9.



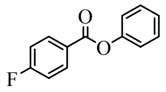
phenyl 4-methoxybenzoate **3ga**.[3] Yield: 79% (17.9 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.21 – 8.13 (m, 2H), 7.43 (t, J = 7.9 Hz, 2H), 7.27 (t, J = 5.6 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 164.9, 163.9, 151.1, 132.3, 129.5, 125.7, 121.9, 121.8, 113.9, 55.5.



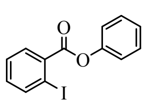
phenyl 4-chlorobenzoate **3ha**.[3] Yield: 70% (16.3 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.14 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 7.9 Hz, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 164.4, 150.8, 140.2, 131.6, 129.6, 129.0, 128.1, 126.1, 121.6.



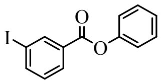
phenyl 3-chlorobenzoate **3ia**.[5] Yield: 74% (17.2 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.19 (s, 1H), 8.09 (d, J = 7.5 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.50 – 7.40 (m, 3H), 7.29 (t, J = 7.3 Hz, 1H), 7.21 (d, J = 7.6 Hz, 2H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 164.0, 150.7, 134.8, 133.6, 131.4, 130.2, 129.9, 129.6, 128.3, 126.1, 121.6.



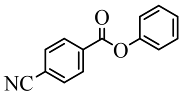
phenyl 4-fluorobenzoate **3ja**.[3] Yield: 85% (18.4 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.27 – 8.19 (m, 2H), 7.47 – 7.38 (m, 2H), 7.31 – 7.26 (m, 1H), 7.24 – 7.15 (m, 4H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 167.0, 165.3, 164.2, 150.9, 132.8 (d, J=9.3 Hz), 129.5, 126.0, 125.8 (d, J=3.0 Hz), 121.7, 115.8 (d, J=22.1 Hz).



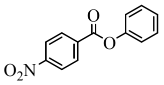
phenyl 2-iodobenzoate **3ka**.[2] Yield: 68% (22.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (dd, J = 8.0, 1.0 Hz, 1H), 8.04 (dd, J = 7.8, 1.7 Hz, 1H), 7.48 (td, J = 7.6, 1.1 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.30 – 7.25 (m, 3H), 7.22 (td, J = 7.7, 1.7 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9, 150.7, 141.7, 134.3, 133.2, 131.5, 129.6, 128.1, 126.2, 121.6, 94.6.



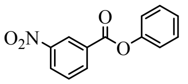
phenyl 3-iodobenzoate **3la**.[6] Yield: 89% (28.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.54 (t, J = 1.6 Hz, 1H), 8.22 – 8.13 (m, 1H), 8.00 – 7.94 (m, 1H), 7.49 – 7.40 (m, 2H), 7.33 – 7.25 (m, 2H), 7.23 – 7.17 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 150.7, 142.4, 139.0, 131.5, 130.3, 129.6, 129.3, 126.1, 121.6, 93.9.



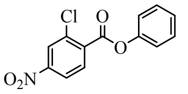
phenyl 4-cyanobenzoate **3ma**.[7] Yield: 28% (6.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (d, J = 8.2 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.45 (t, J = 7.8 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 150.6, 133.4, 132.4, 130.7, 129.7, 126.4, 121.5, 117.9, 117.0.



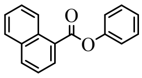
phenyl 4-nitrobenzoate **3na**.[1] Yield: 95% (23.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 – 8.29 (m, 4H), 7.50 – 7.42 (m, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.25 – 7.22 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.4, 150.5, 135.0, 131.3, 129.7, 126.5, 123.8, 121.4, 120.7.



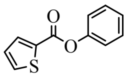
phenyl 3-nitrobenzoate **3oa**.[1] Yield: 29% (7.1mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.05 (t, J = 1.9 Hz, 1H), 8.56 – 8.52 (m, 1H), 8.50 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.35 – 7.29 (m, 1H), 7.27 – 7.24 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1, 150.5, 148.4, 135.8, 131.4, 129.9, 129.7, 128.0, 126.4, 125.1, 121.5.



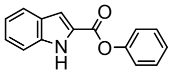
phenyl 2-chloro-4-nitrobenzoate **3pa**.[8] Yield: 69% (19.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (d, J = 2.2 Hz, 1H), 8.26 – 8.22 (m, 1H), 8.18 (d, J = 8.5 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.36 – 7.30 (m, 1H), 7.28 – 7.26 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7, 150.3, 149.8, 135.5, 135.2, 132.5, 129.7, 126.6, 126.3, 121.6, 121.3.



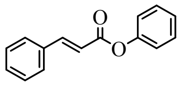
phenyl 1-naphthoate **3qa**.[9] Yield: 89% (22.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.04 (d, J = 8.6 Hz, 1H), 8.46 (d, J = 7.2 Hz, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.62 (t, J = 7.7 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.45 (t, J = 7.5 Hz, 2H), 7.32 – 7.25 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 151.1, 134.4, 134.0, 131.8, 131.3, 129.6, 128.8, 128.2, 126.5, 126.0, 125.9, 125.8, 124.6, 122.0.



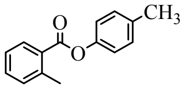
phenyl thiophene-2-carboxylate **3ra**.[10] Yield: 82% (16.7 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.98 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.31 – 7.25 (m, 1H), 7.24 – 7.20 (m, 2H), 7.18 (dd, *J* = 5.0, 3.8 Hz, 1H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 160.6, 150.6, 134.7, 133.5, 132.9, 129.5, 128.0, 126.0, 121.7.



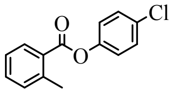
phenyl 1*H*-indole-2-carboxylate **3sa**.[7] Yield: 89% (21.1 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 9.25 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.40 – 7.32 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.22 (m, 2H), 7.21 – 7.15 (m, 1H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 160.7, 150.5, 137.4, 129.6, 127.5, 126.4, 126.1, 125.9, 122.8, 121.7, 121.1, 112.1, 110.3.



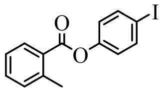
phenyl cinnamate **3ta**.[11] Yield: 36% (8.1 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.87 (d, *J* = 16.0 Hz, 1H), 7.57 (s, 2H), 7.47 – 7.35 (m, 5H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 165.4, 150.9, 146.6, 134.2, 130.7, 129.5, 129.0, 128.3, 125.8, 121.7, 117.4.



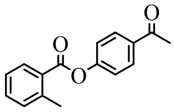
4-methylphenyl 2-methylbenzoate **3ab**.[12] Yield: 100% (22.6 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.14 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.17 (m, 2H), 7.13 – 7.00 (m, 2H), 2.67 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 166.1, 148.7, 141.3, 135.5, 132.7, 131.9, 131.2, 130.0, 128.8, 125.9, 121.5, 22.0, 20.9.



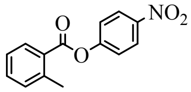
4-chlorophenyl 2-methylbenzoate **3ac**.[13] Yield: 100% (24.6 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.48 (td, *J* = 7.5, 1.4 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.20 – 7.09 (m, 2H), 2.66 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 165.5, 149.4, 141.5, 133.0, 132.1, 131.2, 129.6, 128.1, 126.0, 123.3, 22.0.



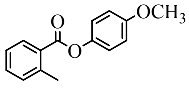
4-iodophenyl 2-methylbenzoate **3ad**.[14] Yield: 79% (26.7 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.48 (td, *J* = 7.6, 1.3 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.01 – 6.95 (m, 2H), 2.66 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 165.4, 150.8, 141.5, 138.6, 133.0, 132.1, 131.2, 128.1, 126.0, 124.1, 89.8, 22.0.



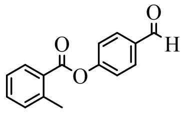
4-acetylphenyl 2-methylbenzoate **3ae**.[15] Yield: 87% (22.1 mg). ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.17 (d, *J* = 7.9 Hz, 1H), 8.07 – 8.03 (m, 2H), 7.50 (td, *J* = 7.5, 1.3 Hz, 1H), 7.36 – 7.30 (m, 4H), 2.68 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$) δ 196.9, 165.1, 154.7, 141.6, 134.7, 133.1, 132.1, 131.3, 130.0, 128.0, 126.0, 122.1, 26.6, 22.0.



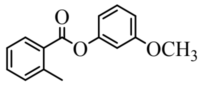
4-nitrophenyl 2-methylbenzoate **3af**.[16] Yield: 77% (19.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 – 8.30 (m, 2H), 8.21 – 8.12 (m, 1H), 7.53 (td, *J* = 7.6, 1.3 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 2.68 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.6, 155.8, 145.4, 141.9, 133.5, 132.2, 131.3, 127.4, 126.1, 125.3, 122.8, 22.0.



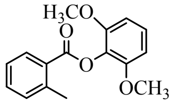
4-methoxyphenyl 2-methylbenzoate **3ag**.[17] Yield: 91% (22.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 – 8.06 (m, 1H), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H), 7.31 (t, *J* = 8.1 Hz, 2H), 7.16 – 7.07 (m, 2H), 7.00 – 6.84 (m, 2H), 3.81 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2, 157.3, 144.4, 141.2, 132.6, 131.9, 131.1, 128.7, 125.9, 122.6, 114.5, 55.6, 21.9.



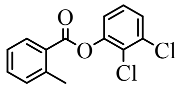
4-formylphenyl 2-methylbenzoate **3ah**.[15] Yield: 82% (19.7 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 8.03 – 7.88 (m, 2H), 7.51 (td, *J* = 7.6, 1.1 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.37 – 7.29 (m, 2H), 2.68 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 191.0, 165.0, 155.7, 141.7, 134.0, 133.2, 132.2, 131.3, 131.3, 127.8, 126.1, 122.7, 22.0.



3-methoxyphenyl 2-methylbenzoate **3ai**.[18] Yield: 88% (21.3 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 1H), 7.47 (td, *J* = 7.5, 1.3 Hz, 1H), 7.36 – 7.27 (m, 3H), 6.85 – 6.78 (m, 2H), 6.76 (t, *J* = 2.3 Hz, 1H), 3.82 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 160.6, 151.9, 141.4, 132.8, 132.0, 131.2, 129.9, 128.6, 125.9, 114.1, 111.8, 107.8, 55.5, 22.0.

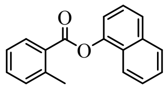


2,6-dimethoxyphenyl 2-methylbenzoate **3aj**. Yield: 84% (22.8 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.9 Hz, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 6H), 2.67 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 152.6, 140.9, 132.3, 131.6, 131.4, 129.0, 128.9, 126.2, 125.8, 105.0, 56.2, 21.7; MS (EI) m/z (%) 272.1(M^+, 0.3), 119.0(100), 91.0(54), 65.0(26), 39.0(11); Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92; Found: C, 70.60; H, 5.88.

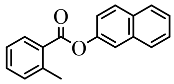


2,3-dichlorophenyl 2-methylbenzoate **3ak**. Yield: 100% (28.0 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.51 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.27 (t, *J* = 8.1 Hz, 1H), 7.19 (dd, *J* = 8.1, 1.5 Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (151

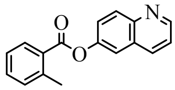
MHz, $CDCl_3$) δ 164.5, 148.6, 141.8, 134.0, 133.2, 132.1, 131.5, 127.8, 127.5, 127.5, 126.7, 126.1, 122.3, 21.9; MS (EI) m/z (%) 280.0(M^+, 0.2), 118.9(100), 90.9(35), 65.0(12), 38.9(2); Anal. Calcd for $C_{14}H_{10}Cl_2O_2$: C, 59.81; H, 3.59; Found: C, 59.90; H, 3.56.



naphthalen-1-yl 2-methylbenzoate **3al**.[19] Yield: 93% (24.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.89 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.55 – 7.46 (m, 4H), 7.41 – 7.33 (m, 3H), 2.71 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 146.9, 141.8, 134.8, 132.9, 132.2, 131.3, 128.3, 128.1, 127.1, 126.5, 126.5, 126.1, 126.0, 125.5, 121.3, 118.3, 22.1.



naphthalen-2-yl 2-methylbenzoate **3am**.[20] Yield: 100% (26.2 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.89 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 2.2 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.37 – 7.30 (m, 3H), 2.70 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 147.5, 140.4, 132.8, 131.8, 131.0, 130.5, 130.2, 128.4, 127.5, 126.8, 126.6, 125.5, 124.9, 124.7, 120.4, 117.7, 21.0.



quinolin-6-yl 2-methylbenzoate **3an**. Yield: 88% (23.1 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.22 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.19 (d, *J* = 9.1 Hz, 1H), 8.17 – 8.12 (m, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.59 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.51 (td, *J* = 7.5, 1.3 Hz, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.37 – 7.32 (m, 2H), 2.71 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 150.2, 148.8, 146.3, 141.6, 135.9, 133.0, 132.1, 131.3, 131.1, 128.6, 128.2, 126.0, 125.1, 121.6, 118.7, 22.0; MS (EI) m/z (%) 263.0(M^+, 3),118.9(100), 91.0(39), 65.0(17), 39.0(5); Anal. Calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.60; H, 5.00; N, 5.29.

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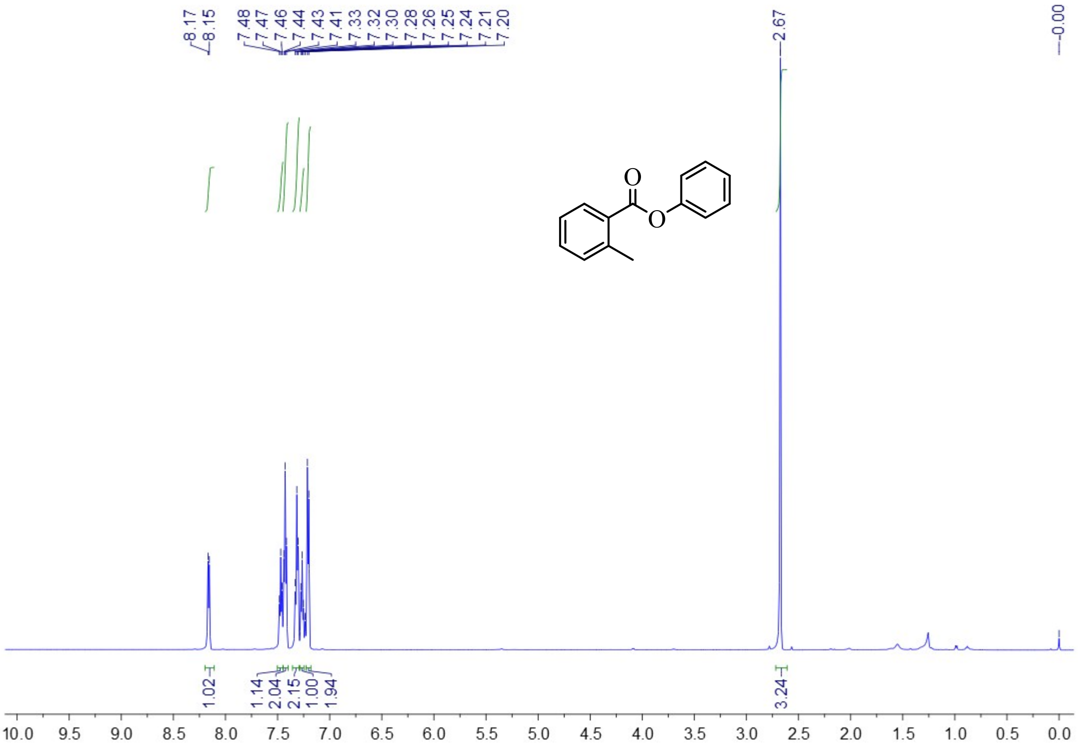
[20] CAS Registry Number: 666212-54-0.

3. 10 Gram-scale synthesis of 3aa

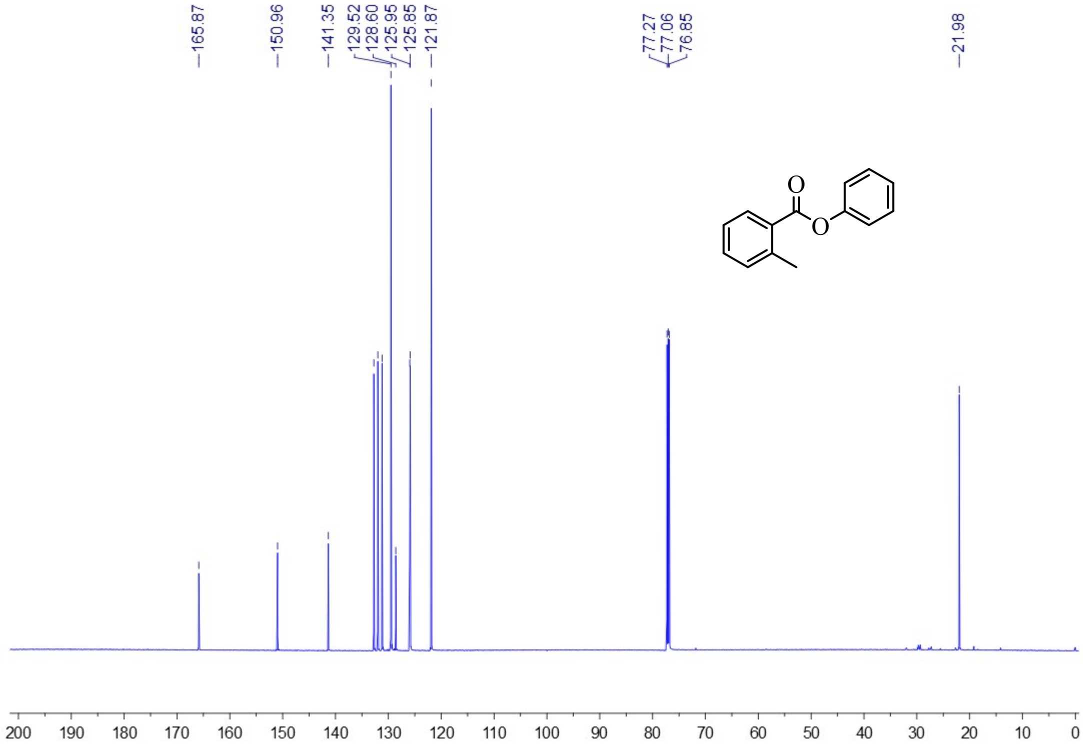
In a 10 gram-scale reaction, pyridin-2-yl 2-methylbenzoate **1a** (10 g, 47.0 mmol), phenol **2a** (7.51 g, 79.9 mmol), K_2CO_3 (0.65 g, 4.7 mmol), and the solvent (150 mL) were charged in a 250 mL ovendried round flask. Reaction was carried out 60 ℃ for 48 h in an oil bath under air condition. After being cooled to room temperature, the reaction solution was evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:5~1:15 as an eluent) to afford the desired product **3aa** (9.85 g, 99% yield）.

Part III. ^{1}H NMR and ^{13}C NMR Spectra of the Products

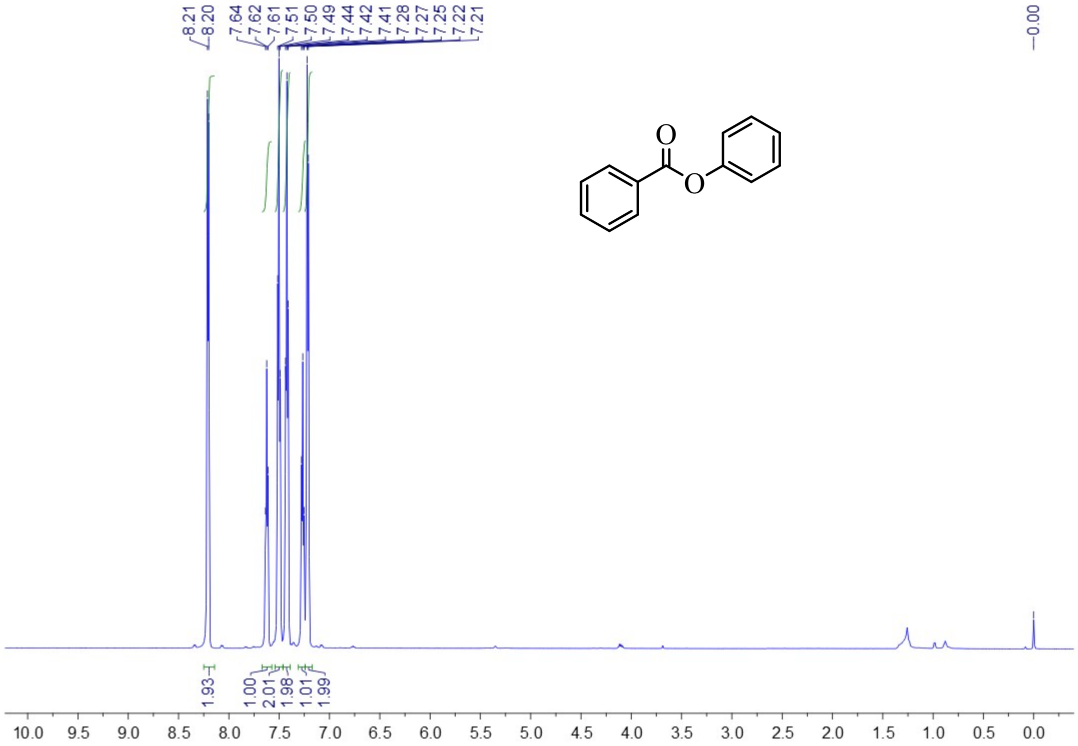
^{1}H NMR of phenyl 2-methylbenzoate **3aa**



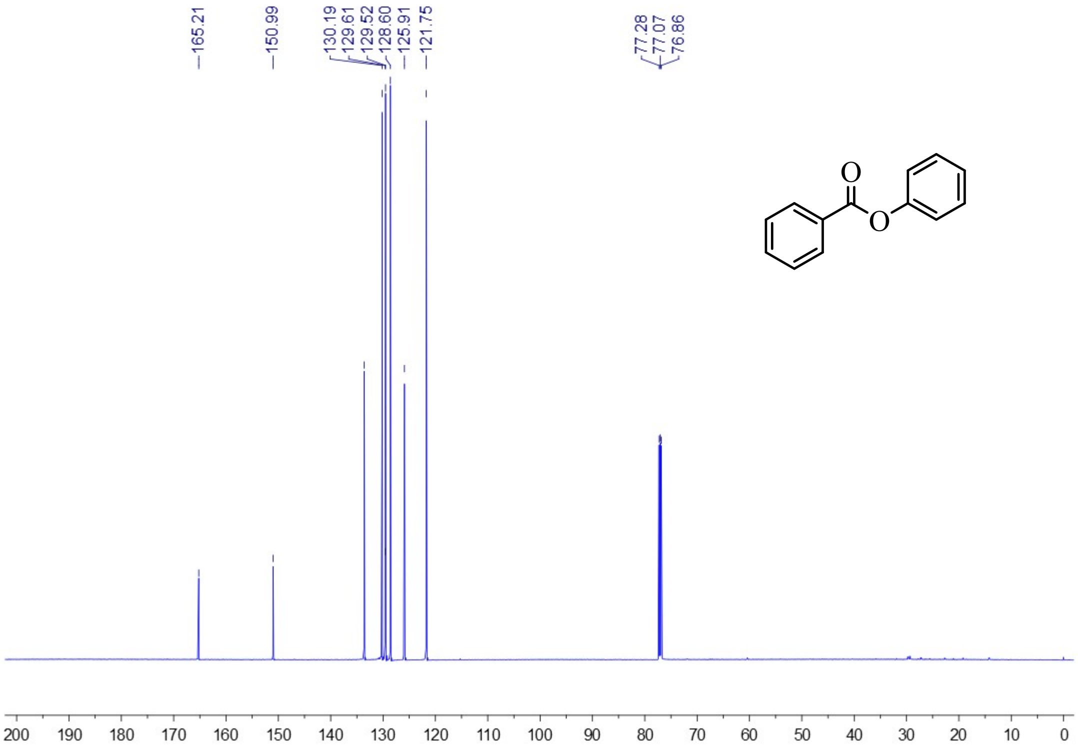
^{13}C NMR of phenyl 2-methylbenzoate **3aa**



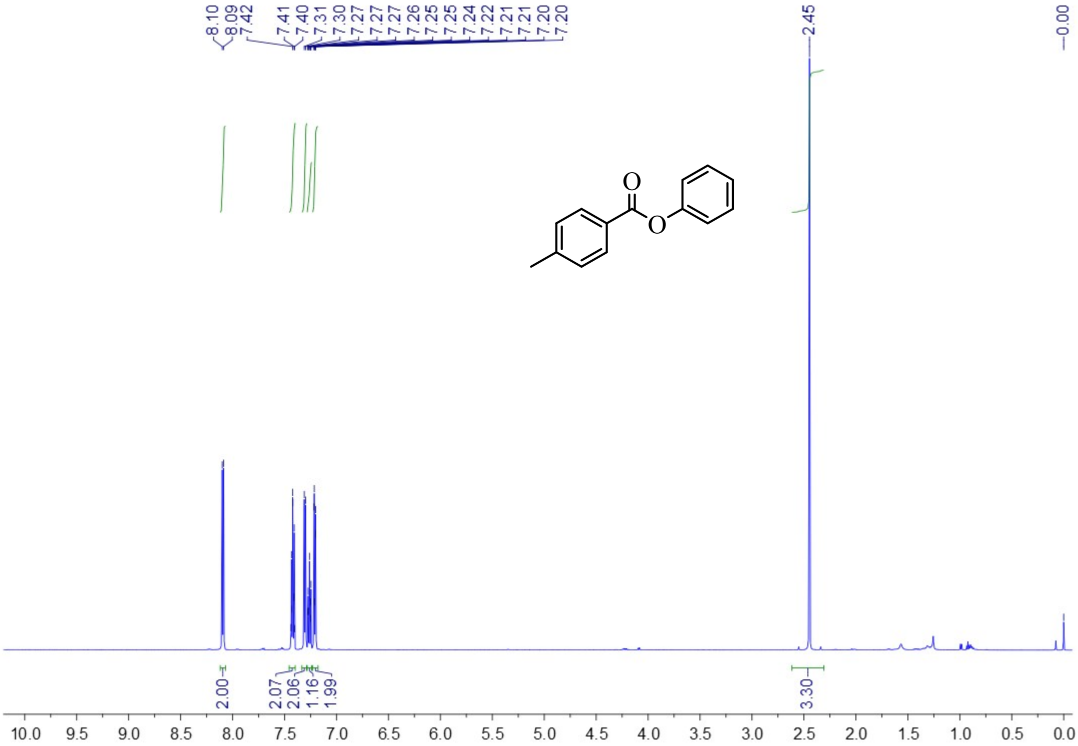
^{1}H NMR of phenyl benzoate **3ba**



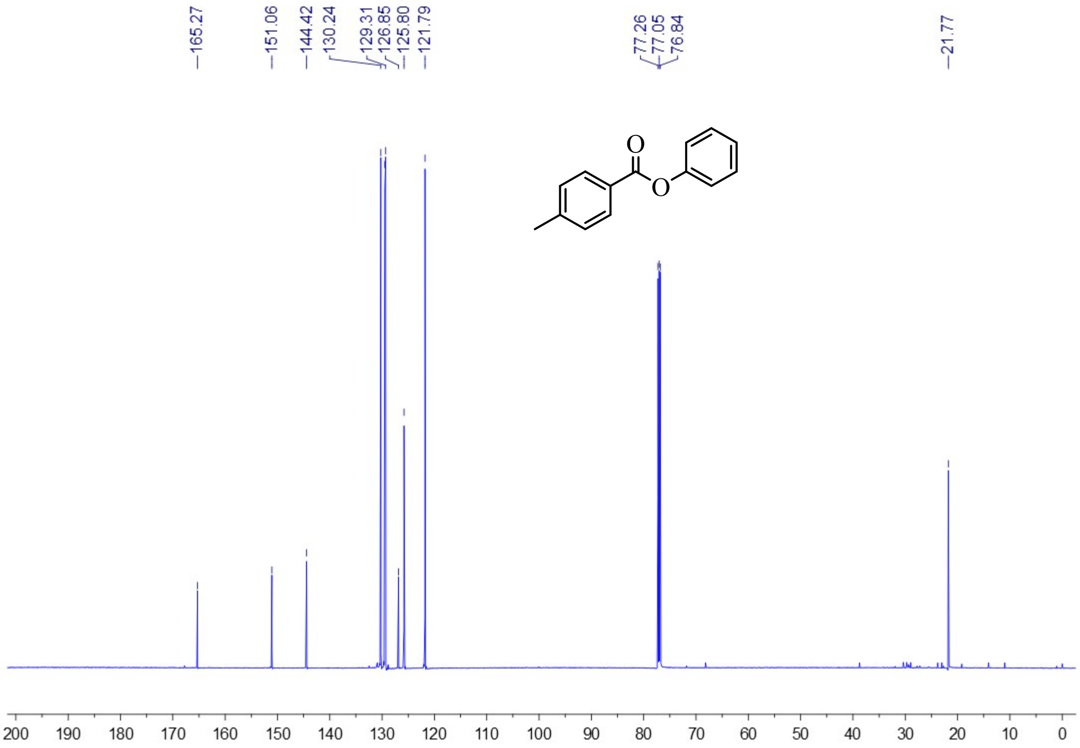
^{13}C NMR of phenyl benzoate **3ba**



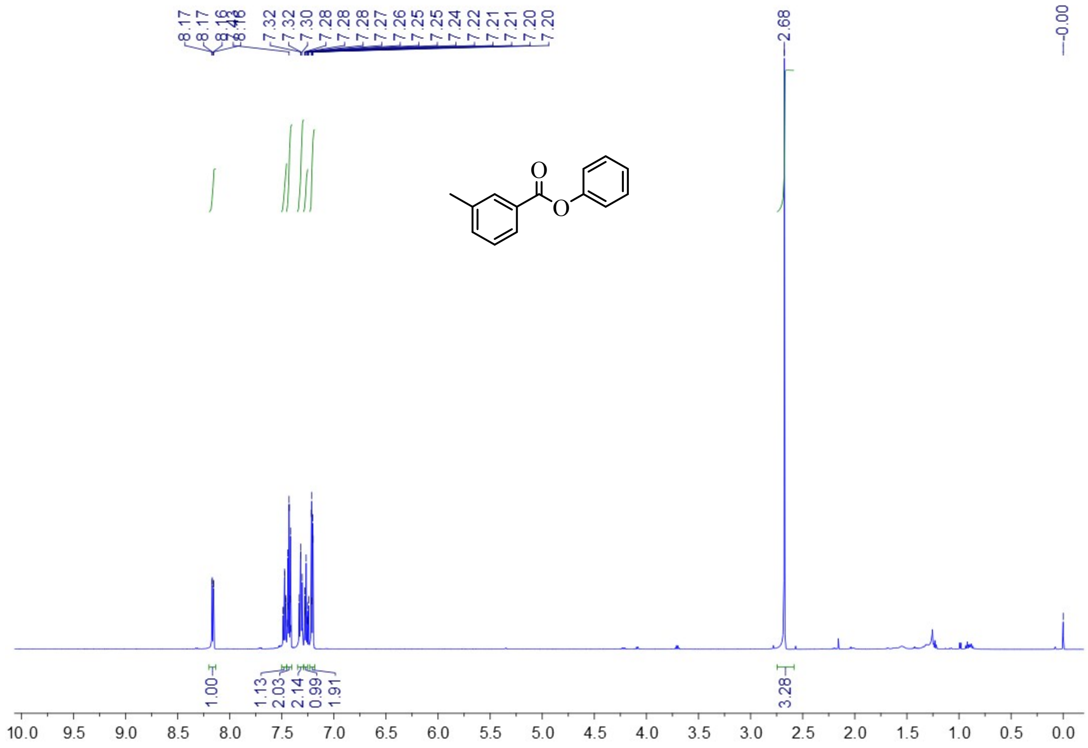
^{1}H NMR of phenyl 4-methylbenzoate **3ca**



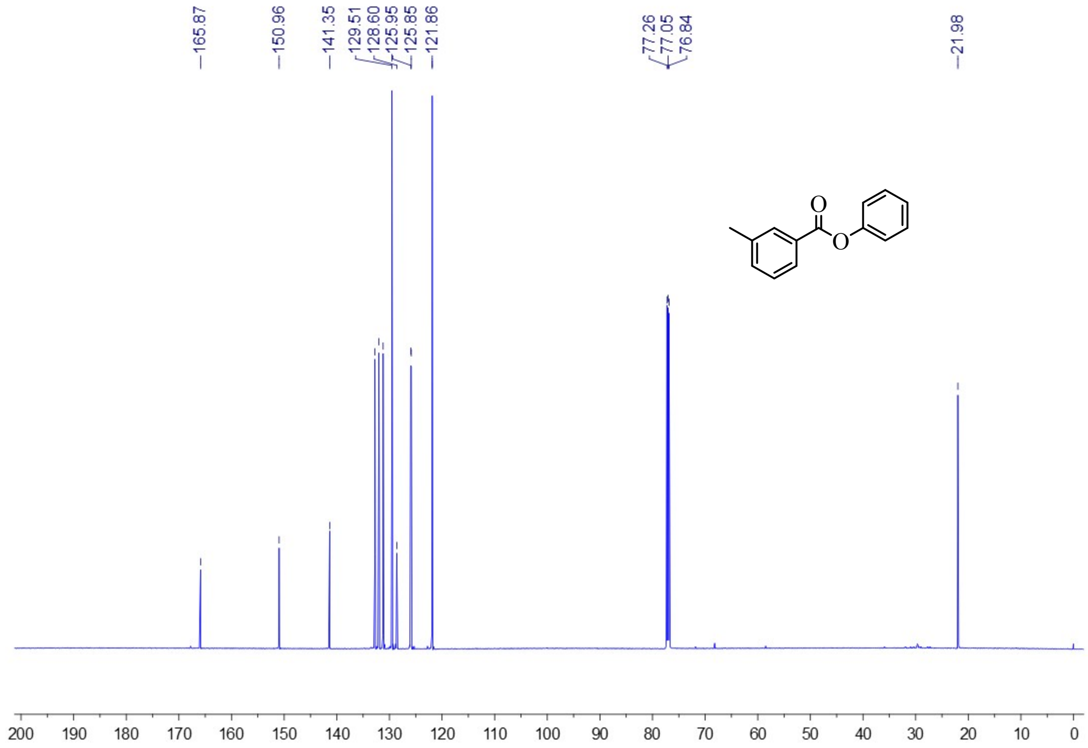
^{13}C NMR of phenyl 4-methylbenzoate **3ca**



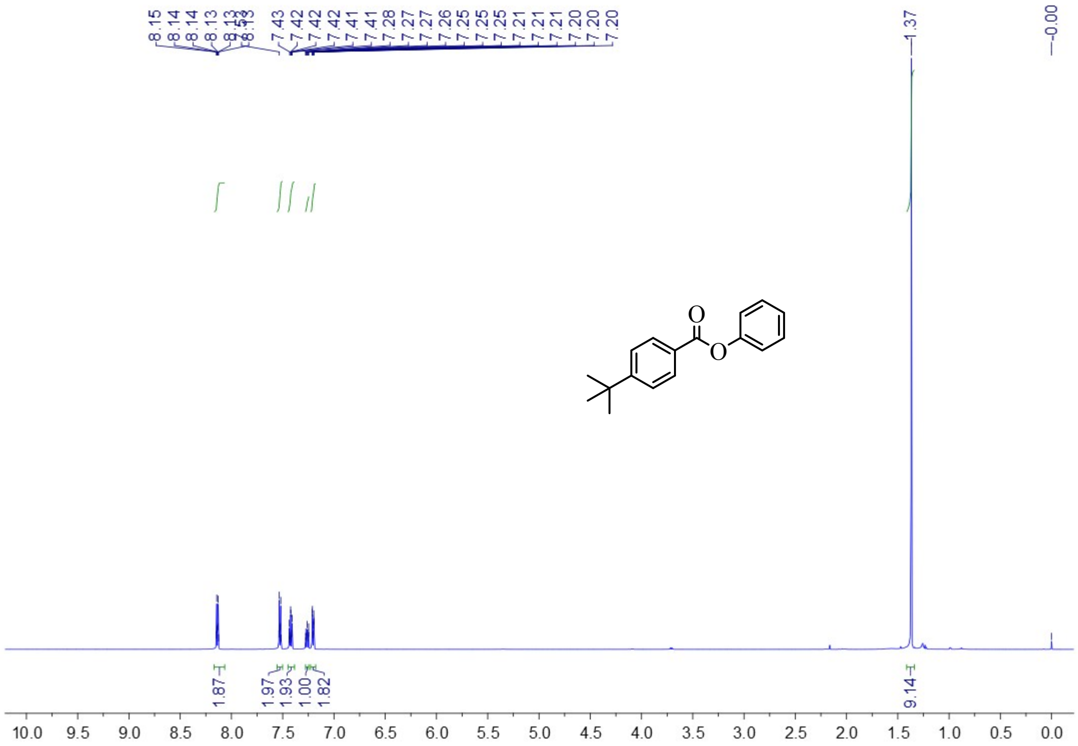
^{1}H NMR of phenyl 3-methylbenzoate **3da**



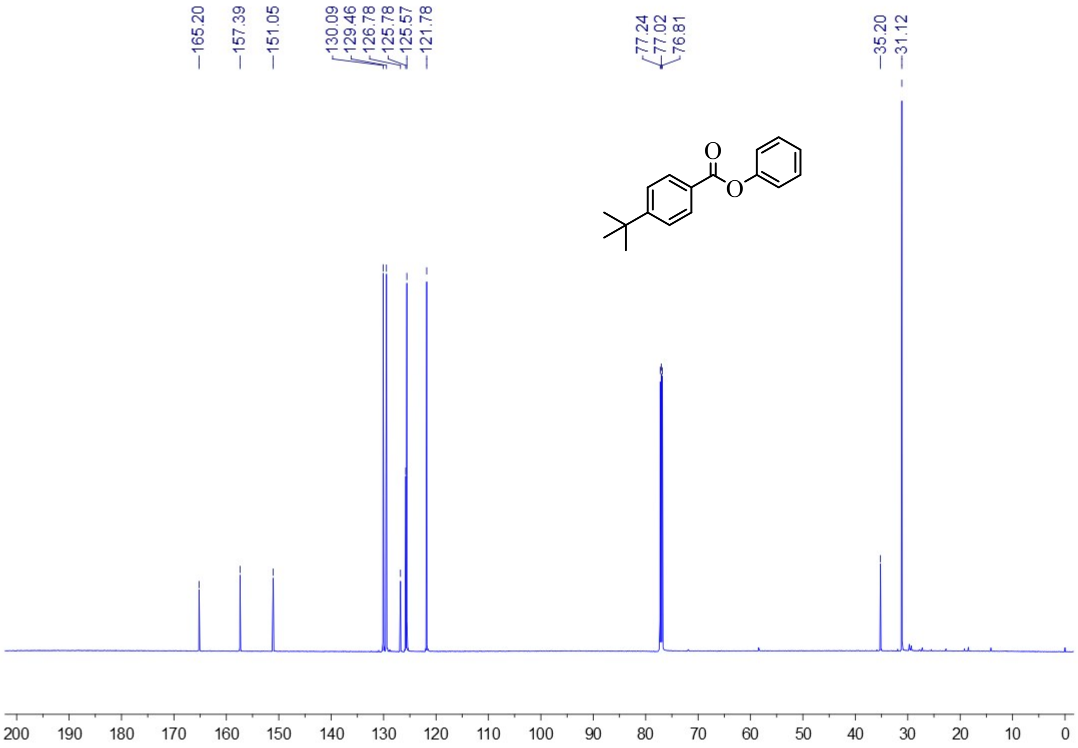
^{13}C NMR of phenyl 3-methylbenzoate **3da**



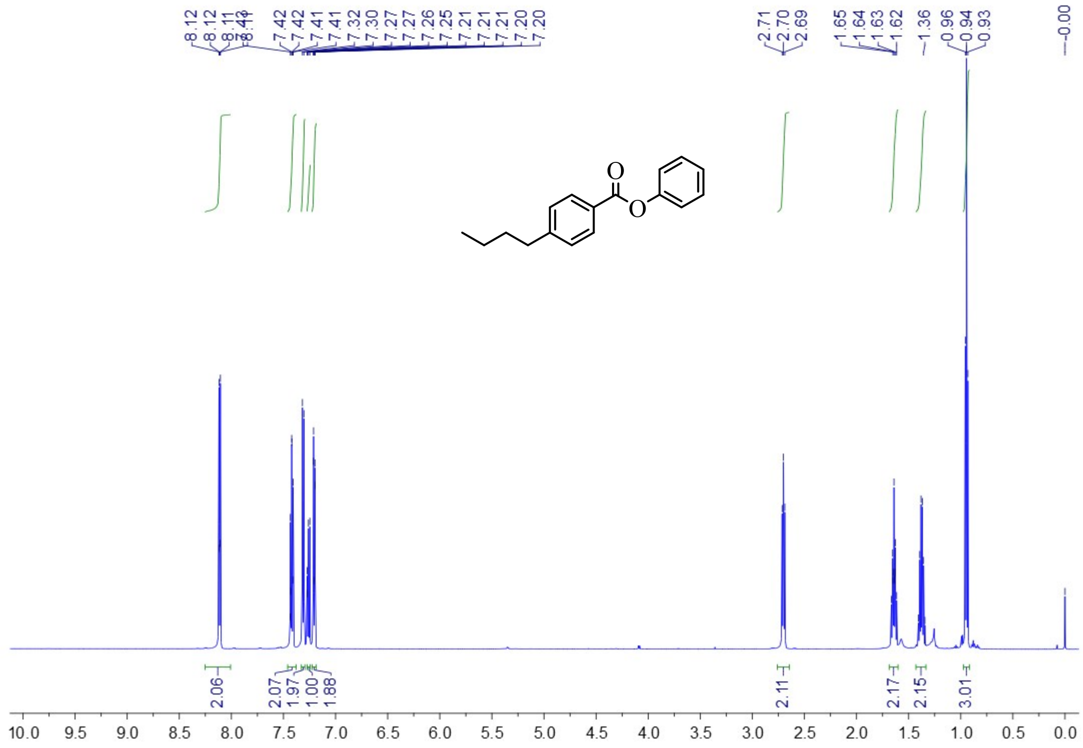
^{1}H NMR of phenyl 4-(tert-butyl)benzoate **3ea**



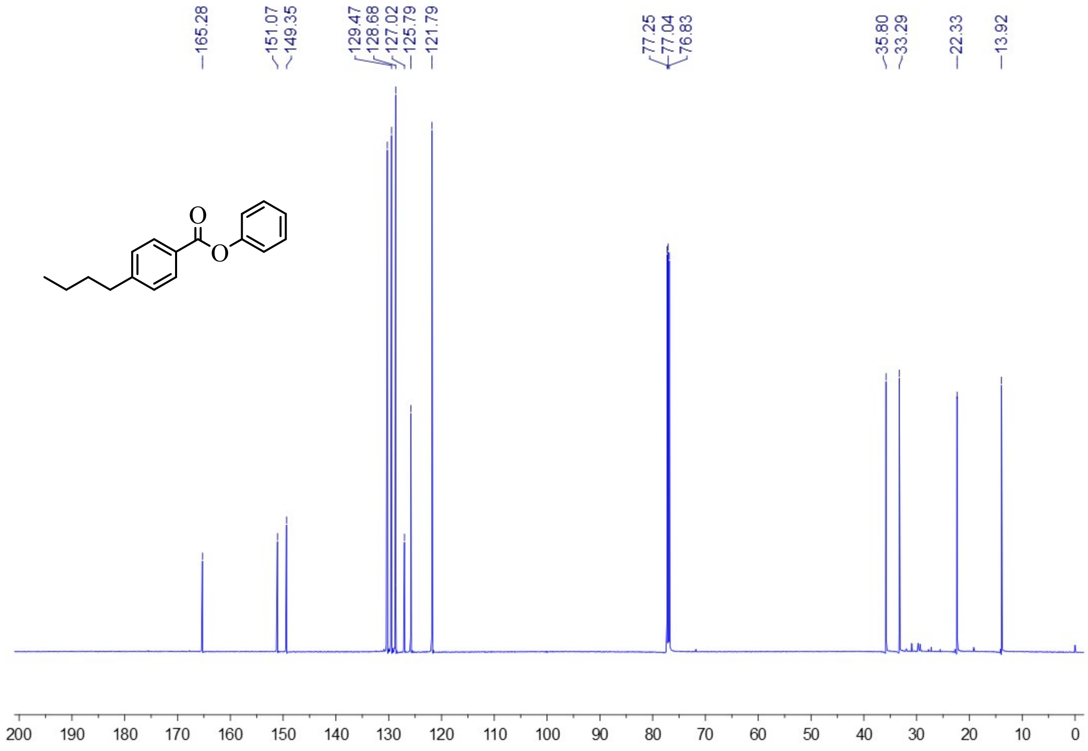
^{13}C NMR of phenyl 4-(tert-butyl)benzoate **3ea**



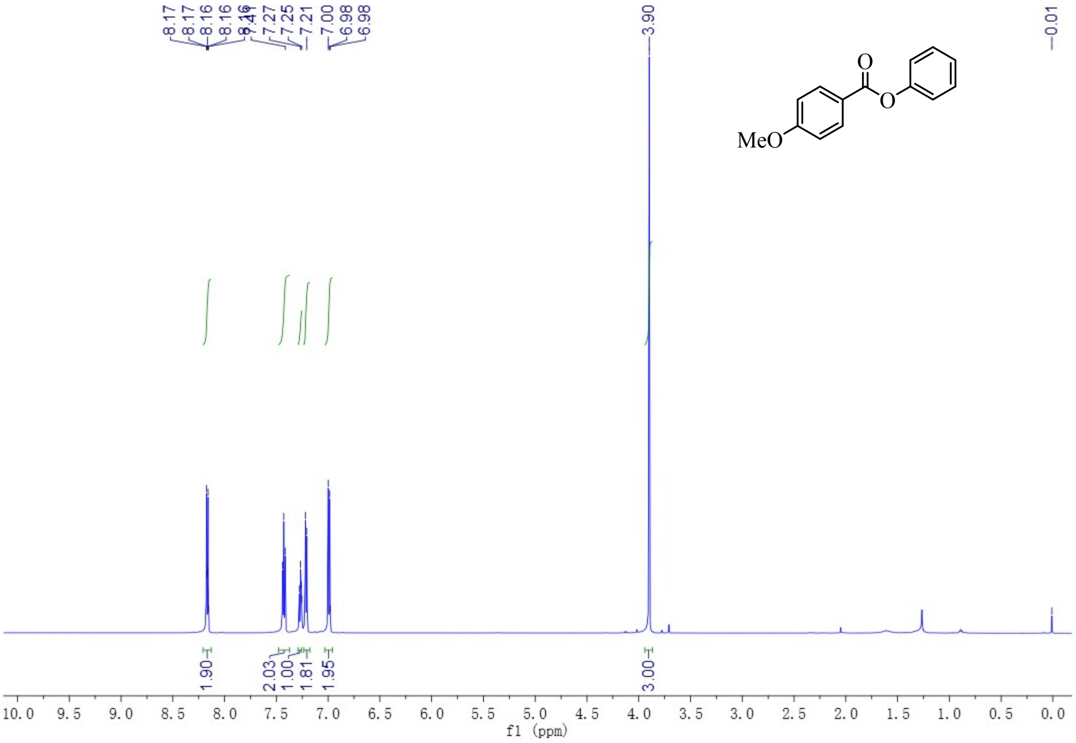
^{1}H NMR of phenyl 4-butylbenzoate **3fa**



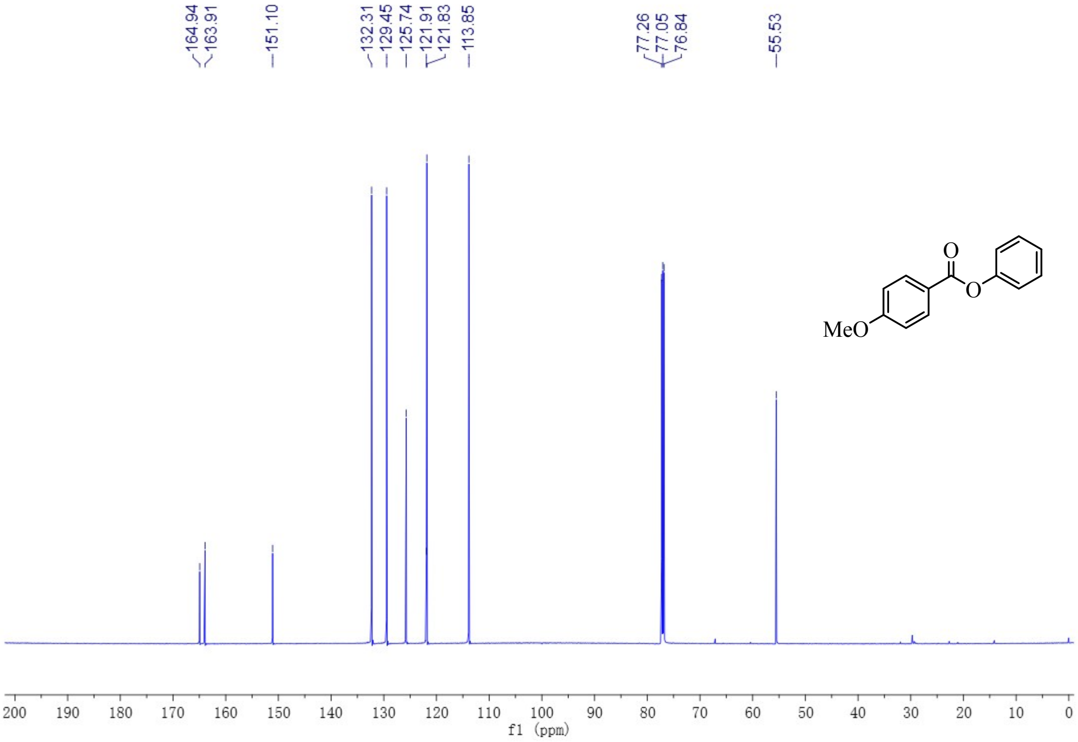
^{13}C NMR of phenyl 4-butylbenzoate **3fa**



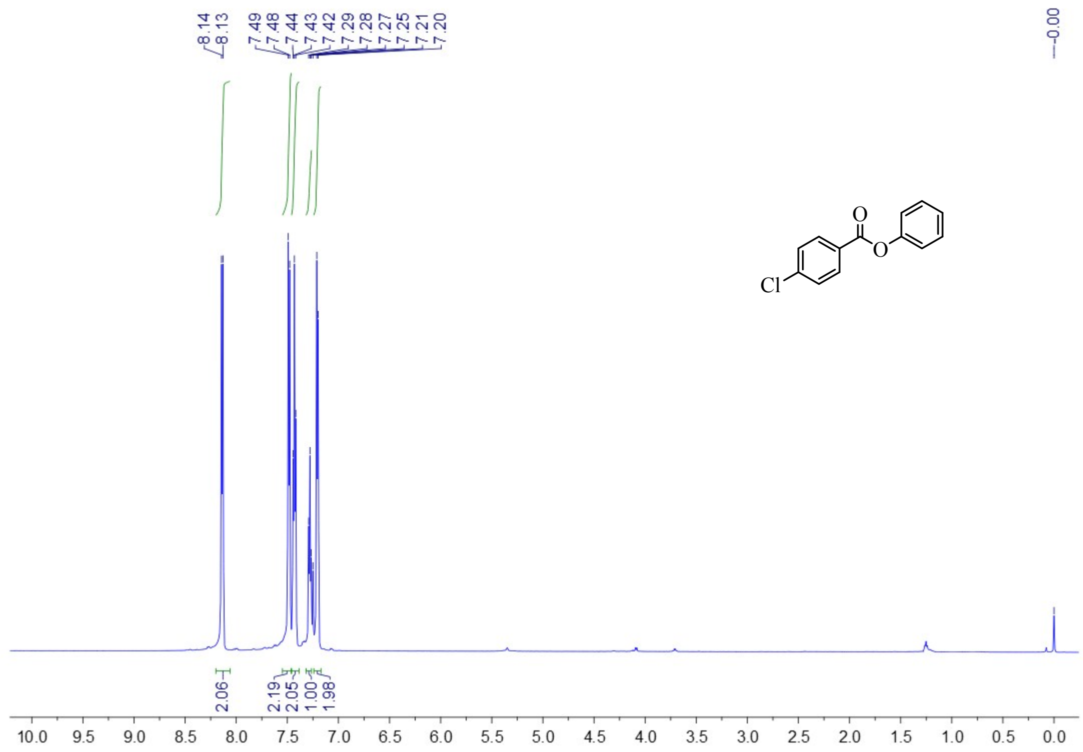
^{1}H NMR of phenyl 4-methoxybenzoate **3ga**



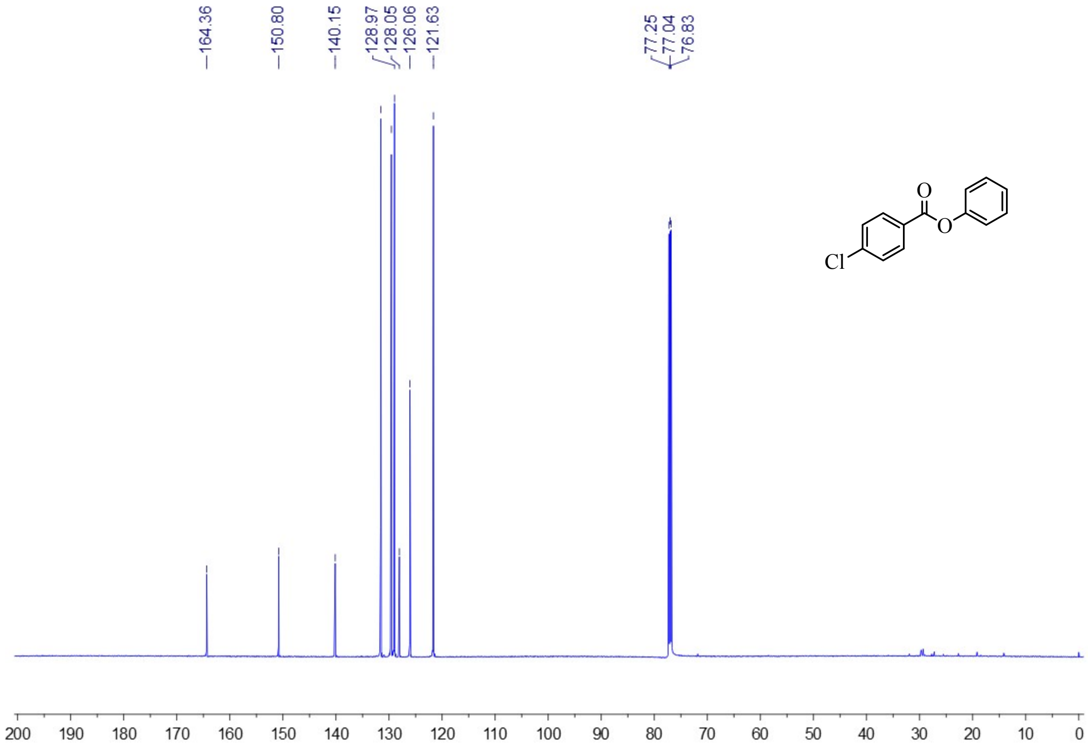
^{13}C NMR of phenyl 4-methoxybenzoate **3ga**



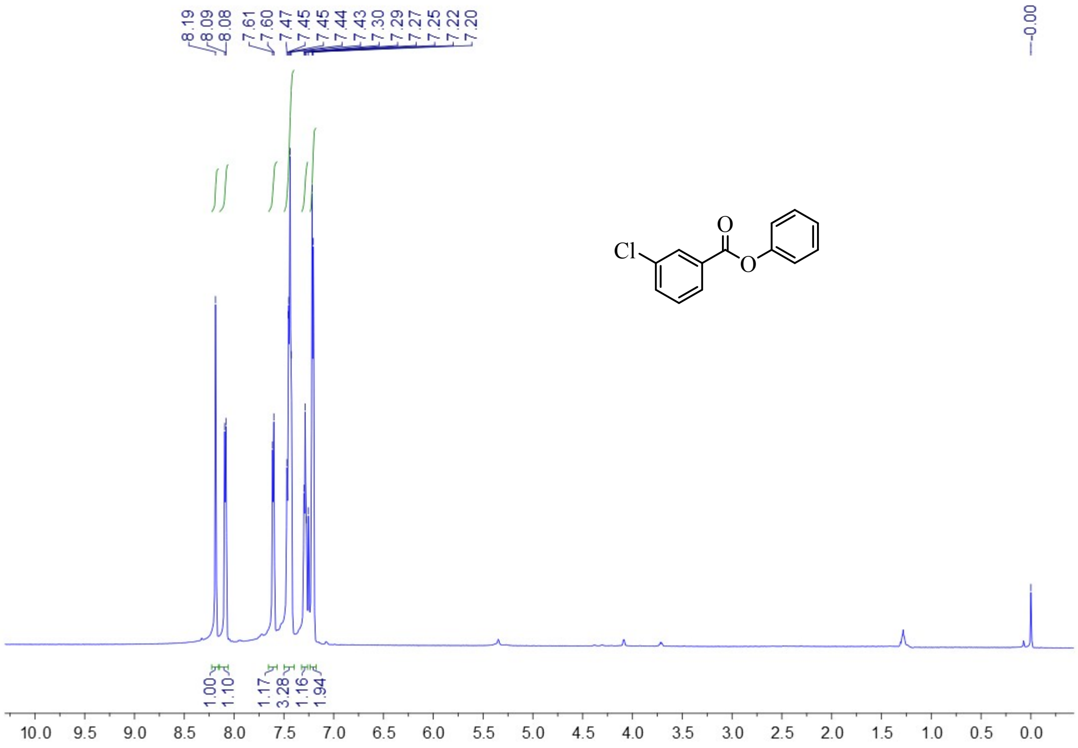
^{1}H NMR of phenyl 4-chlorobenzoate **3ha**



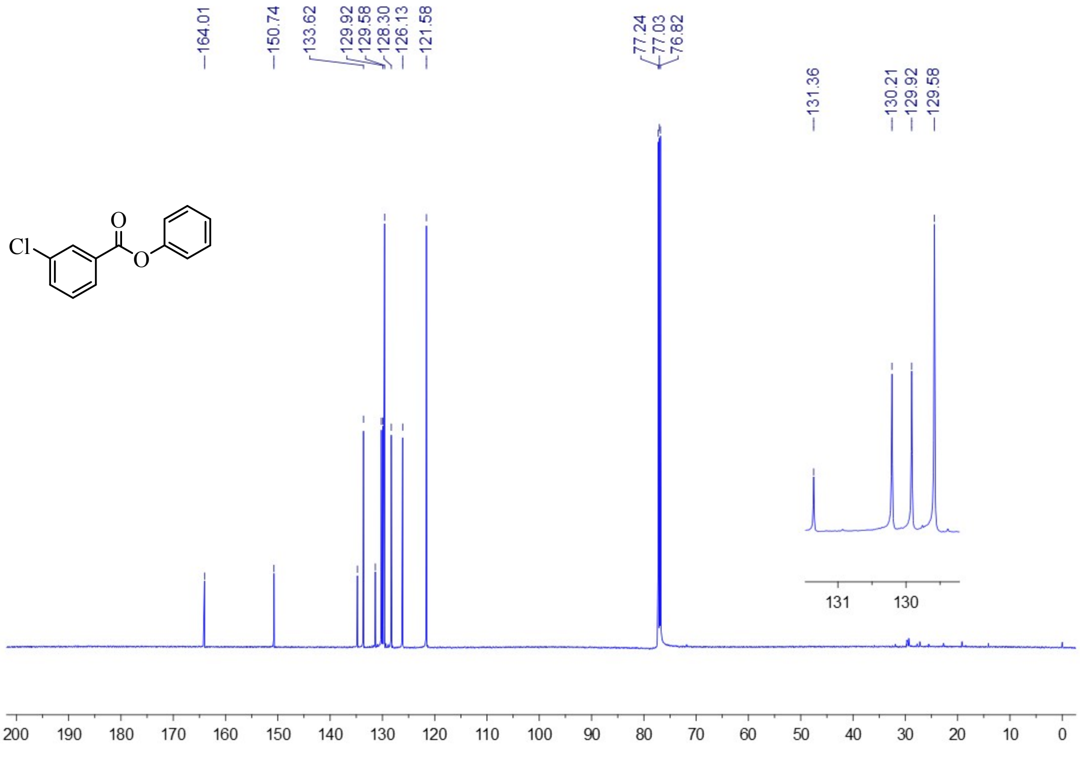
^{13}C NMR of phenyl 4-chlorobenzoate **3ha**



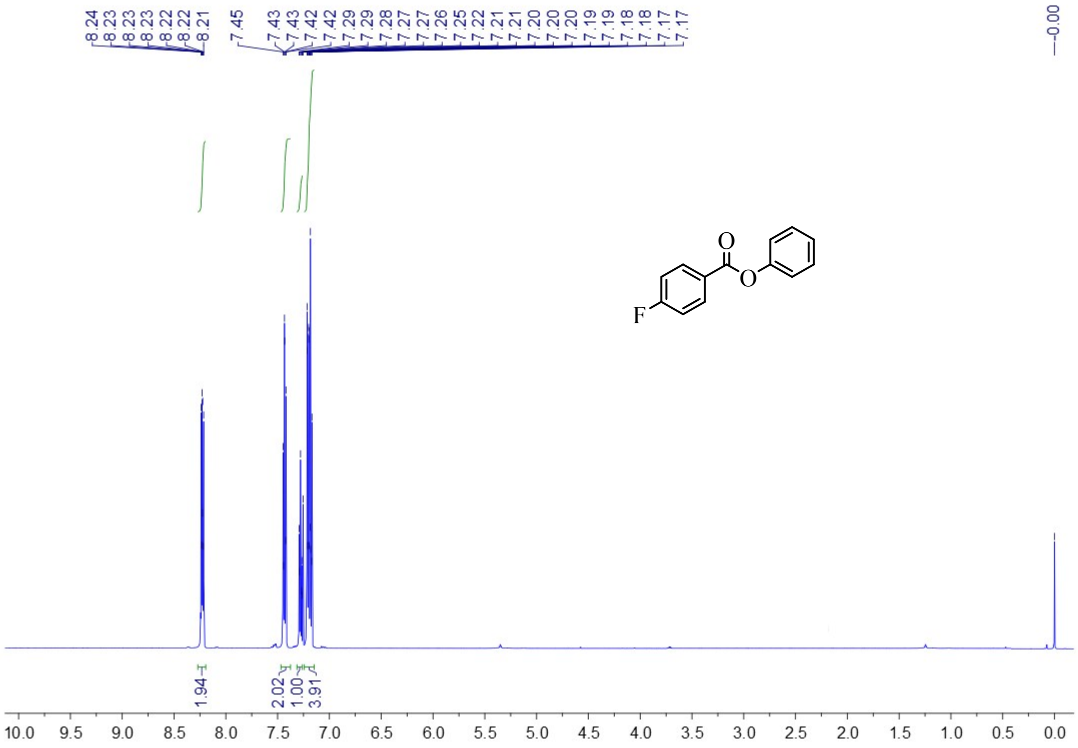
^{1}H NMR of phenyl 3-chlorobenzoate **3ia**



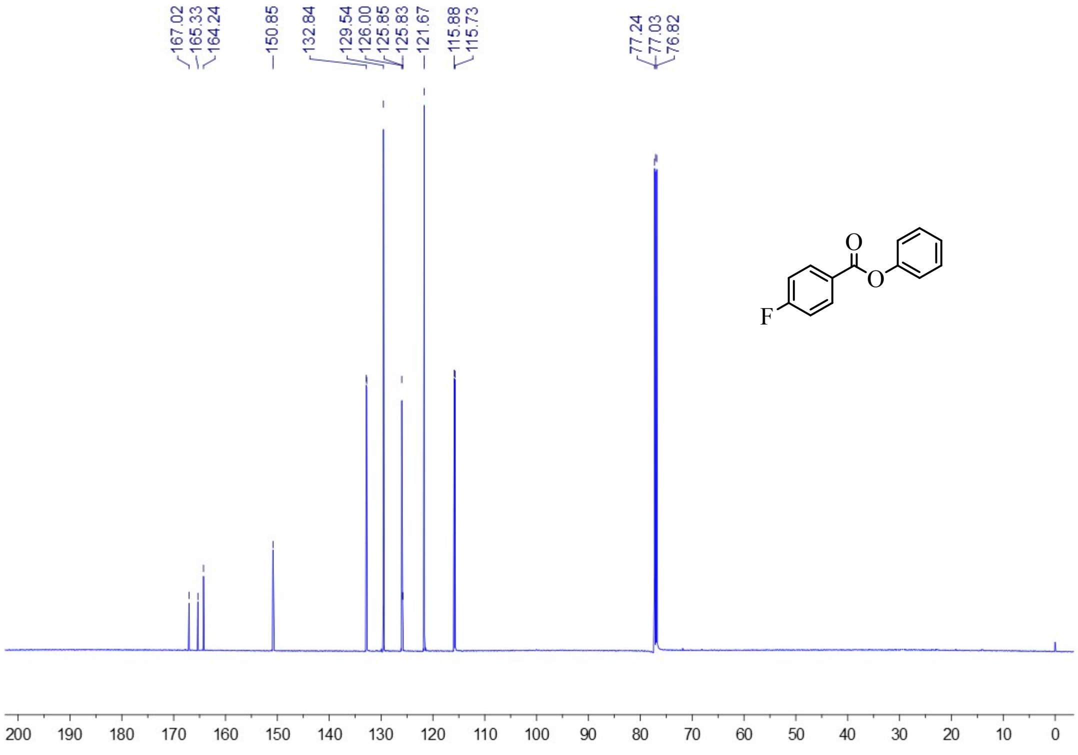
^{13}C NMR of phenyl 3-chlorobenzoate **3ia**



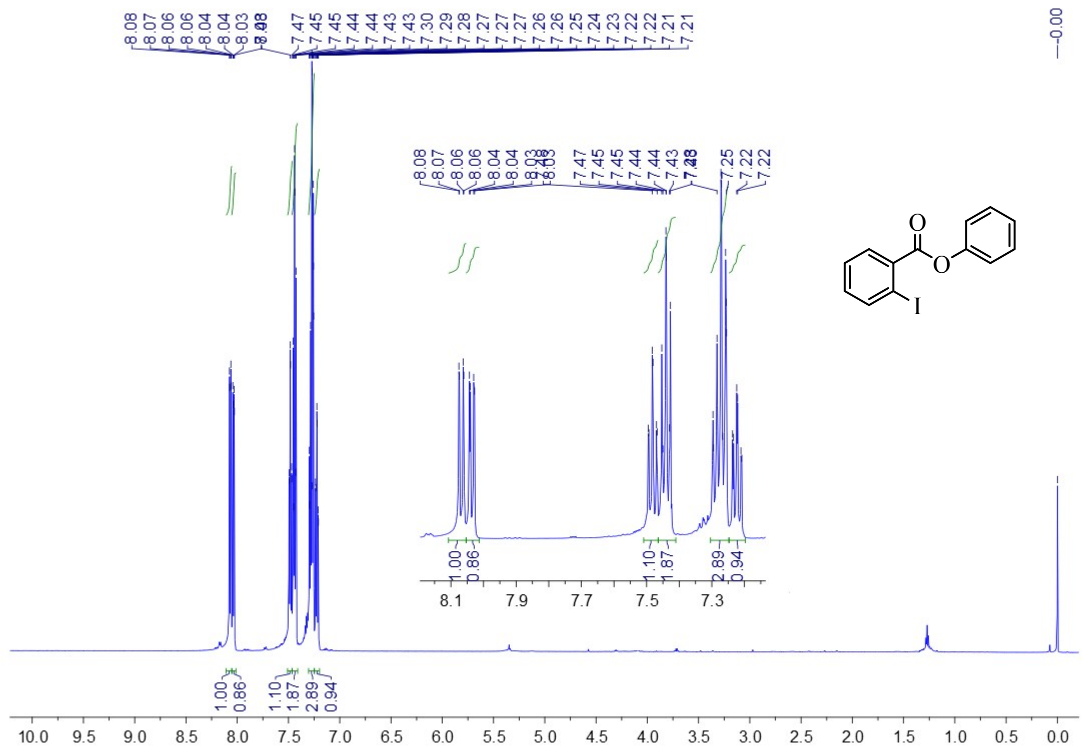
^{1}H NMR of phenyl 4-fluorobenzoate **3ja**



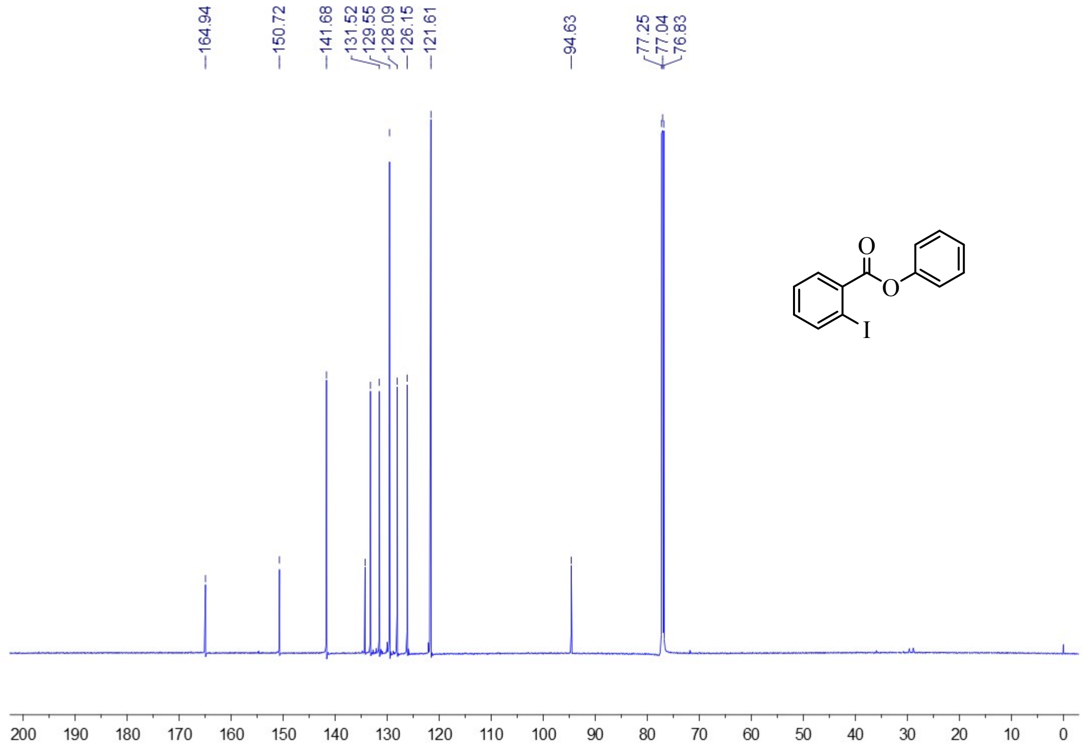
^{13}C NMR of phenyl 4-fluorobenzoate **3ja**



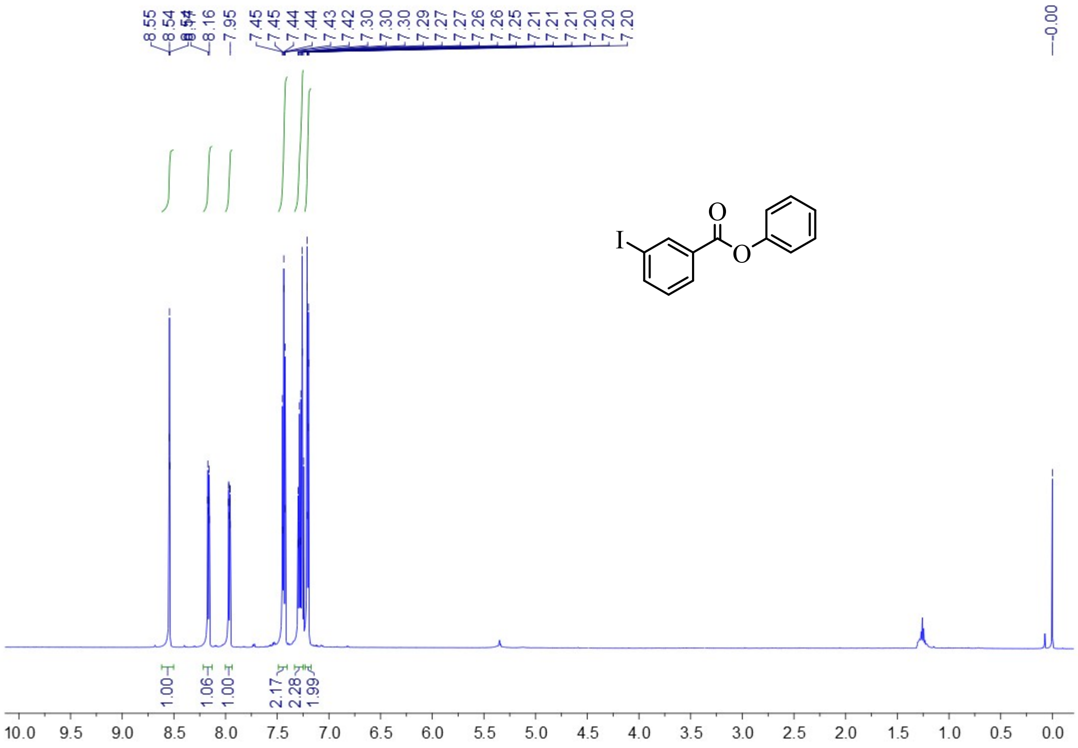
^{1}H NMR of phenyl 2-iodobenzoate **3ka**



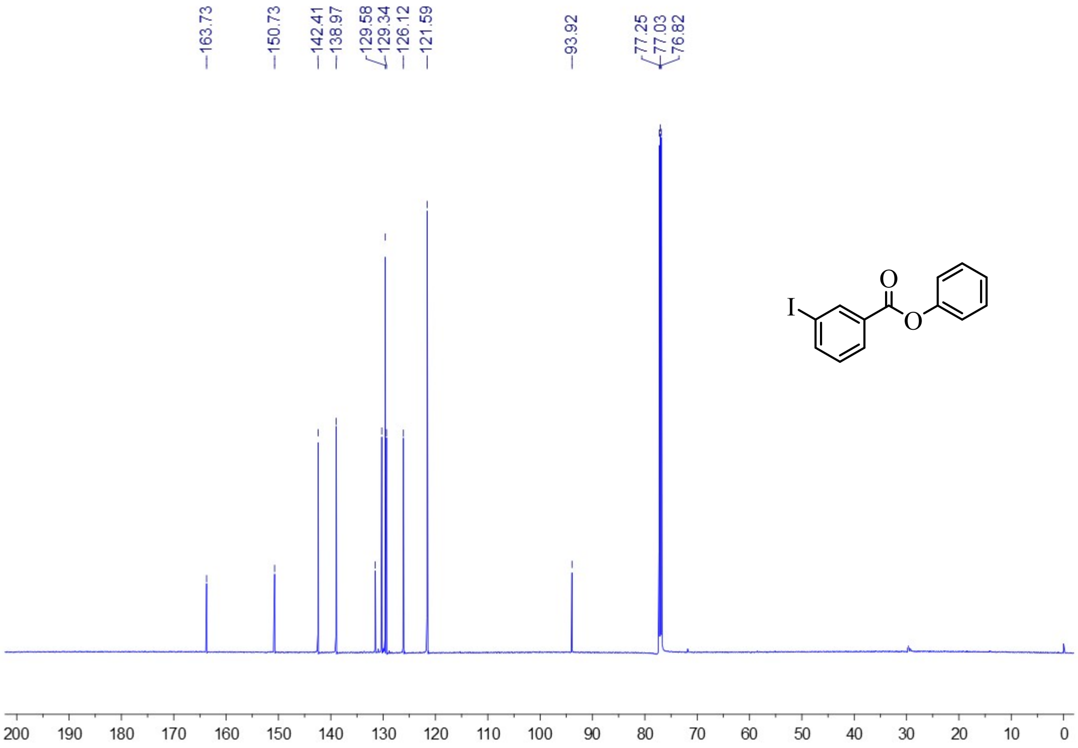
^{13}C NMR of phenyl 2-iodobenzoate **3ka**



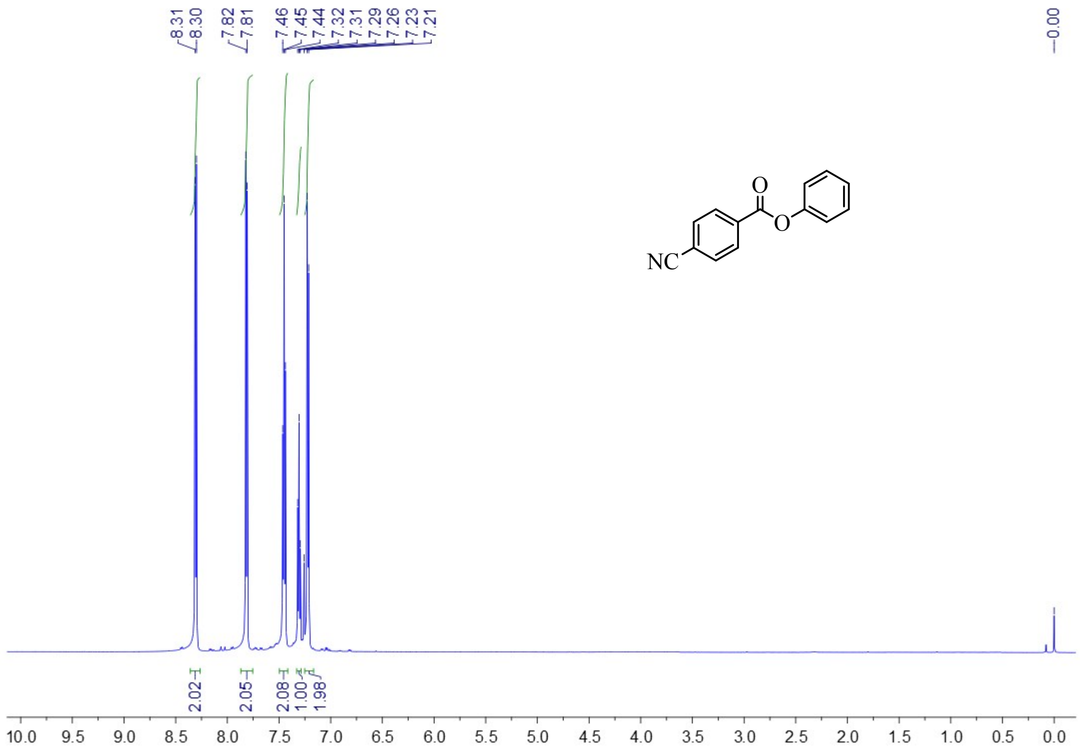
^{1}H NMR of phenyl 3-iodobenzoate **3la**



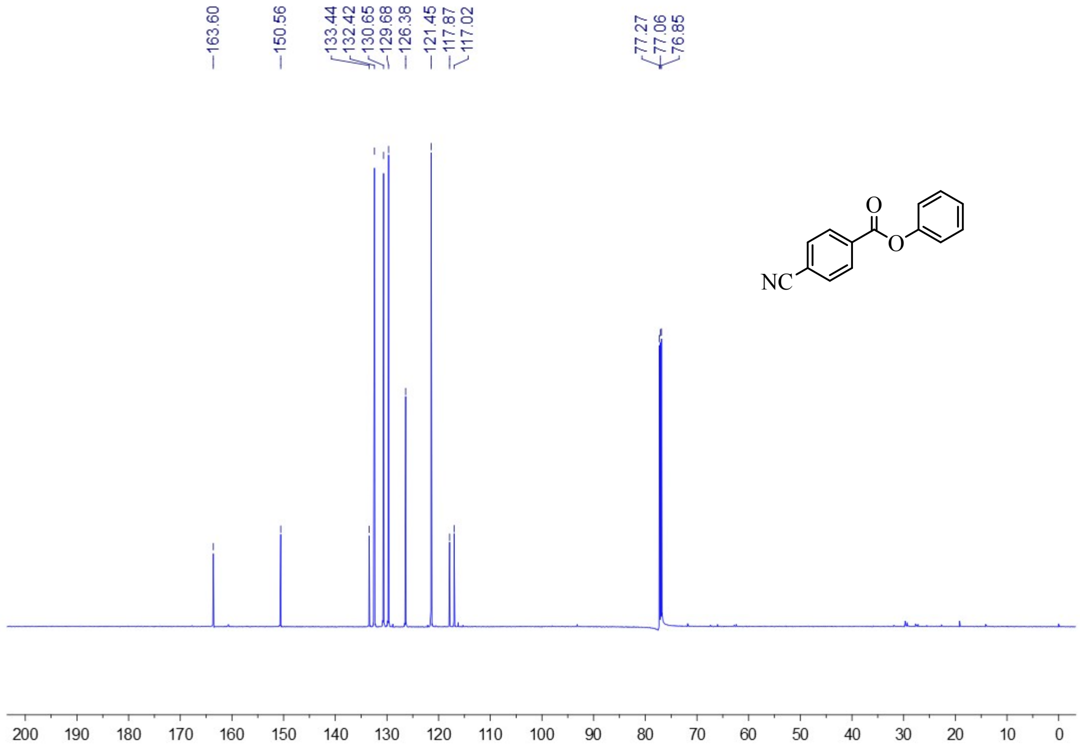
^{13}C NMR of phenyl 3-iodobenzoate **3la**



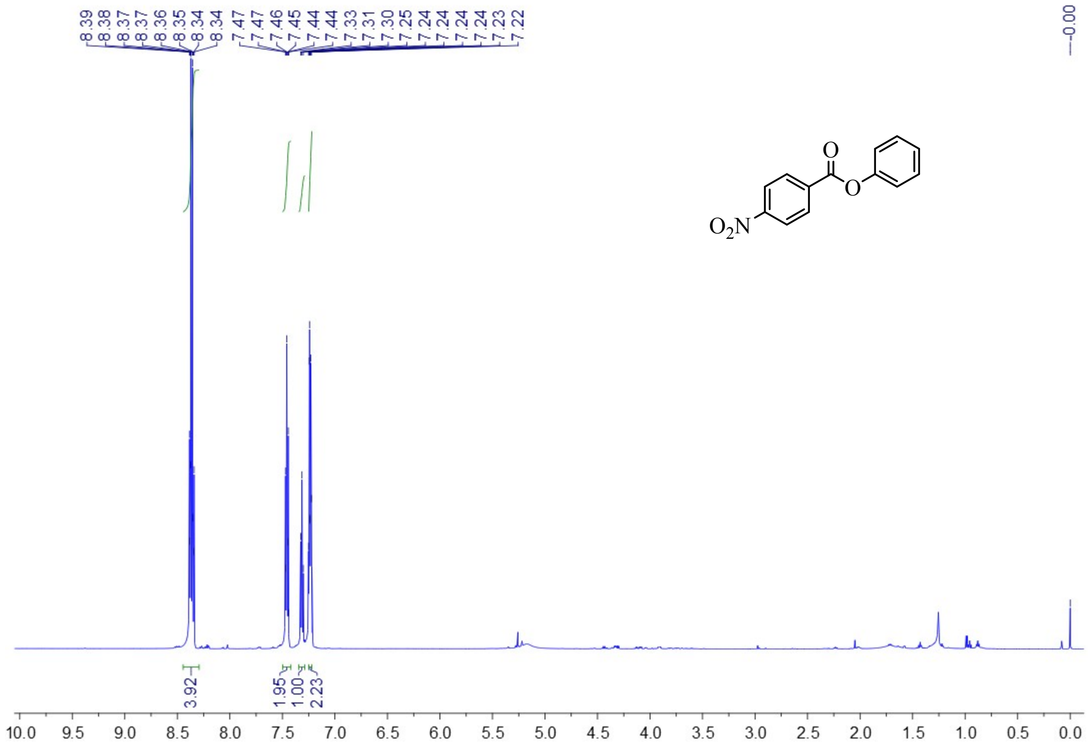
^{1}H NMR of phenyl 4-cyanobenzoate **3ma**



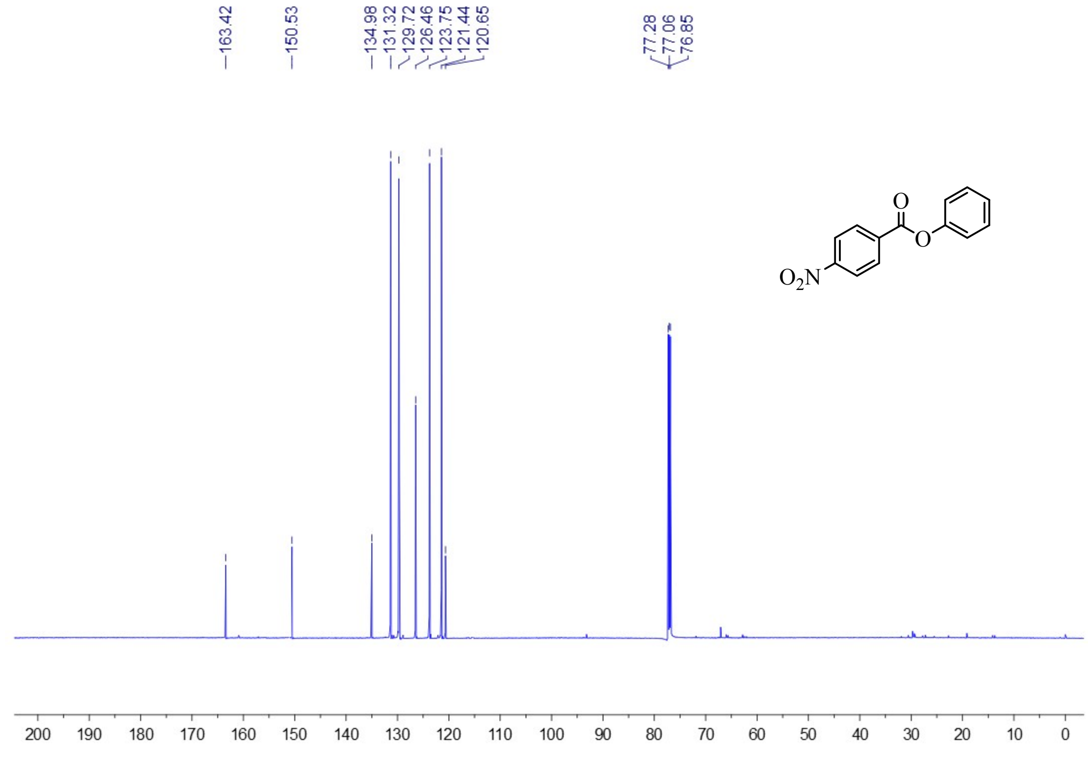
^{13}C NMR of phenyl 4-cyanobenzoate **3ma**



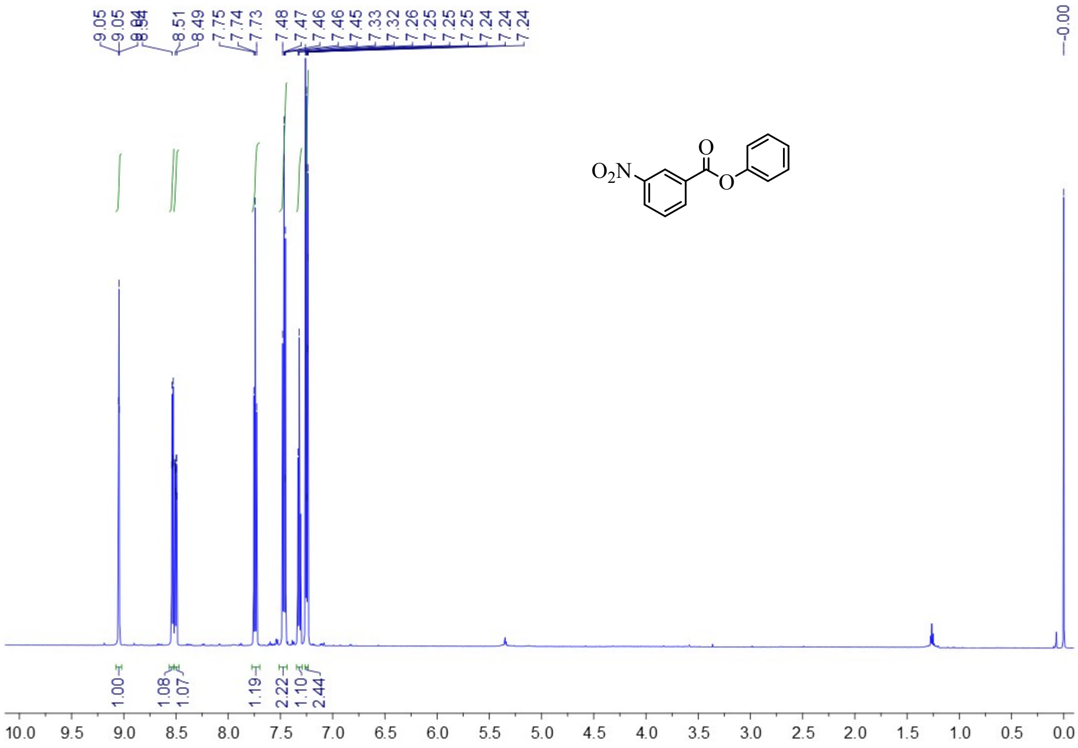
^{1}H NMR of phenyl 4-nitrobenzoate **3na**



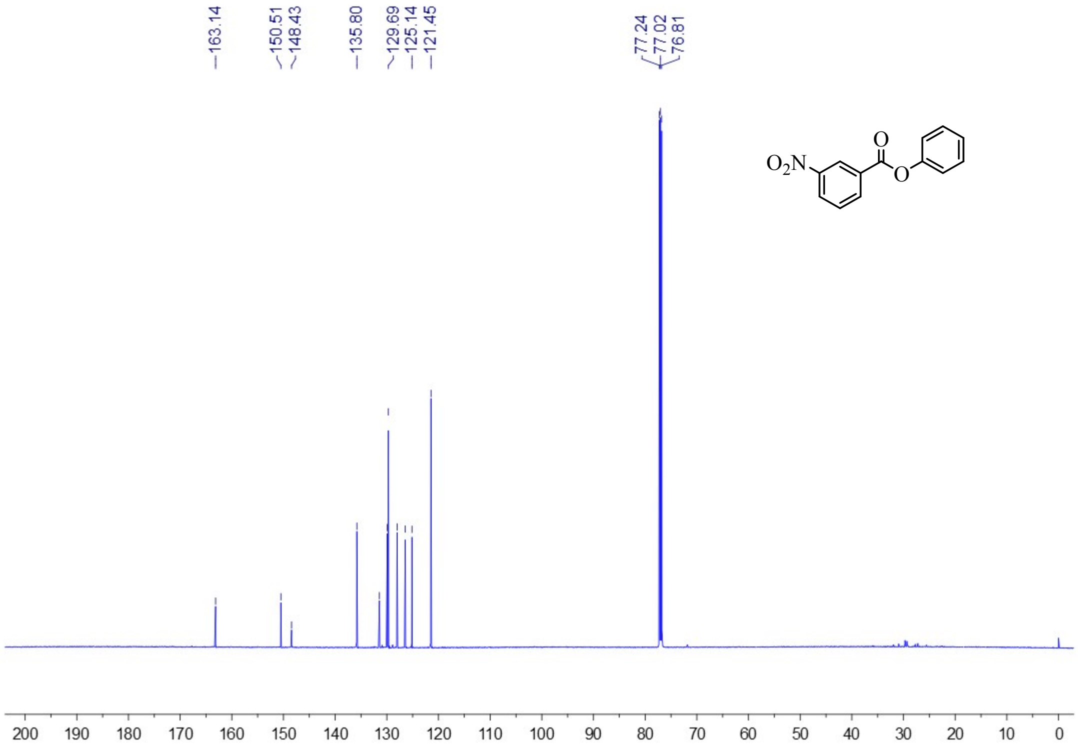
^{13}C NMR of phenyl 4-nitrobenzoate **3na**



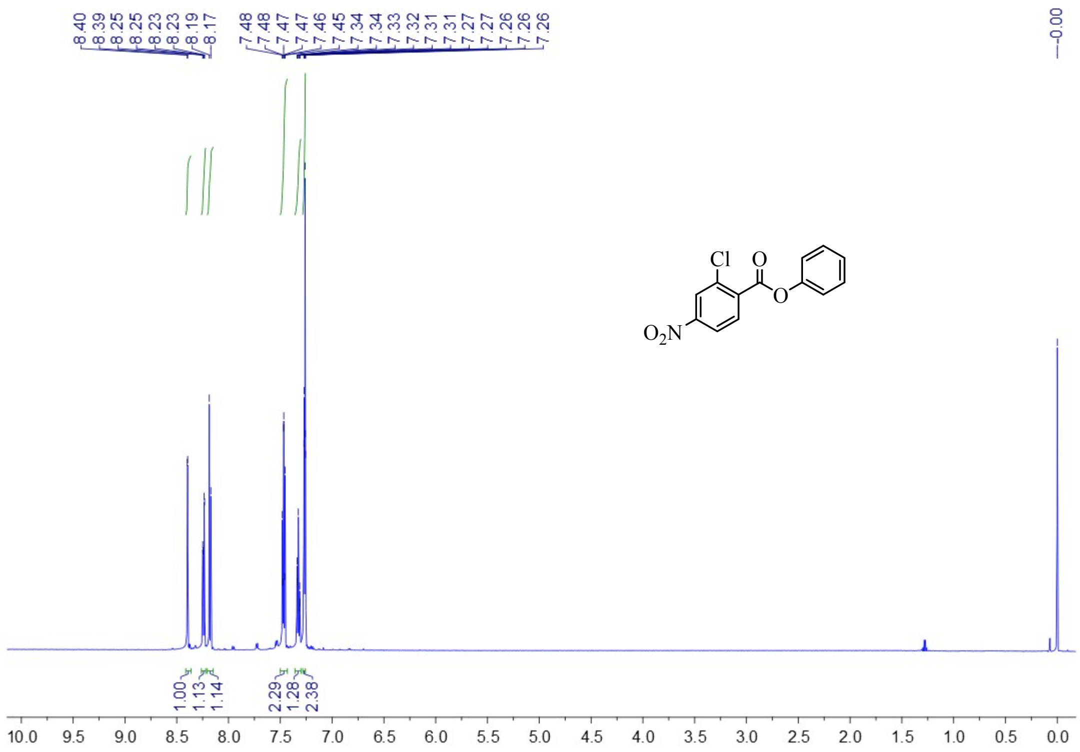
^{1}H NMR of phenyl 3-nitrobenzoate **3oa**



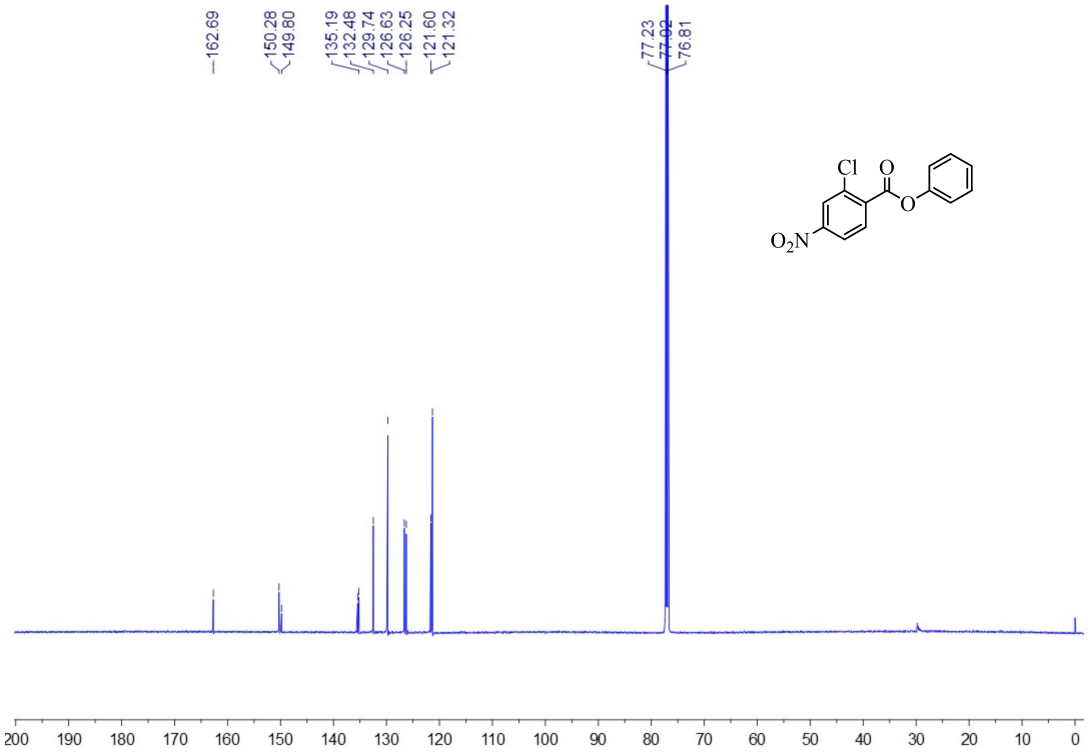
^{13}C NMR of phenyl 3-nitrobenzoate **3oa**



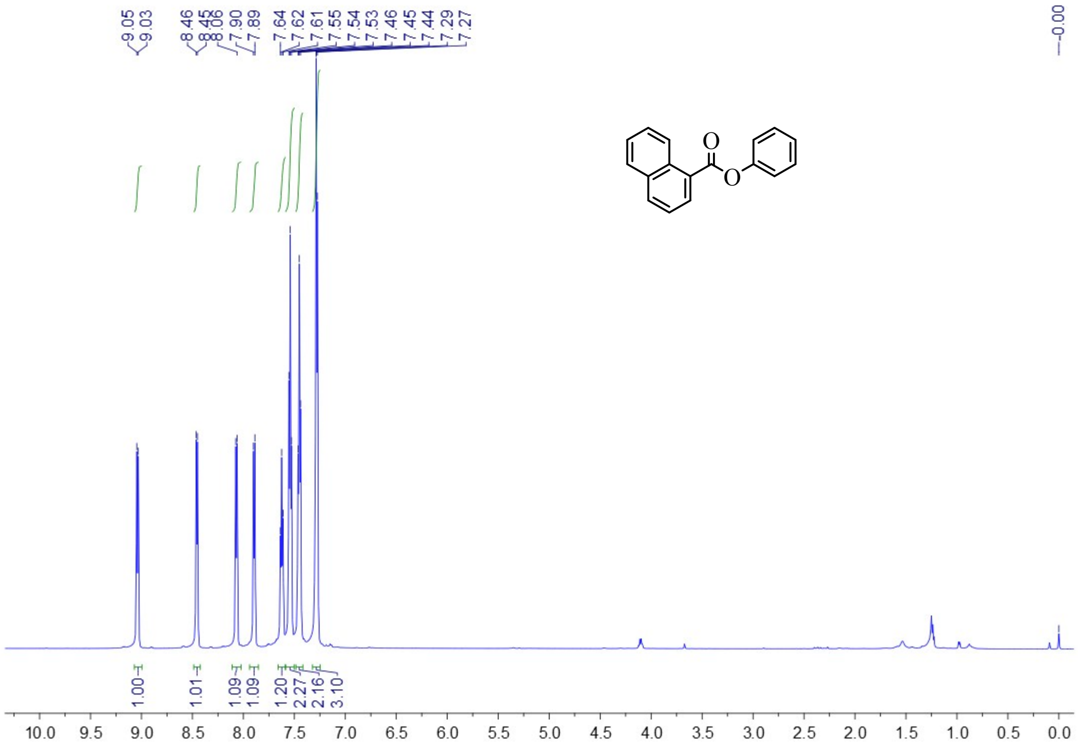
^{1}H NMR of phenyl 2-chloro-4-nitrobenzoate **3pa**



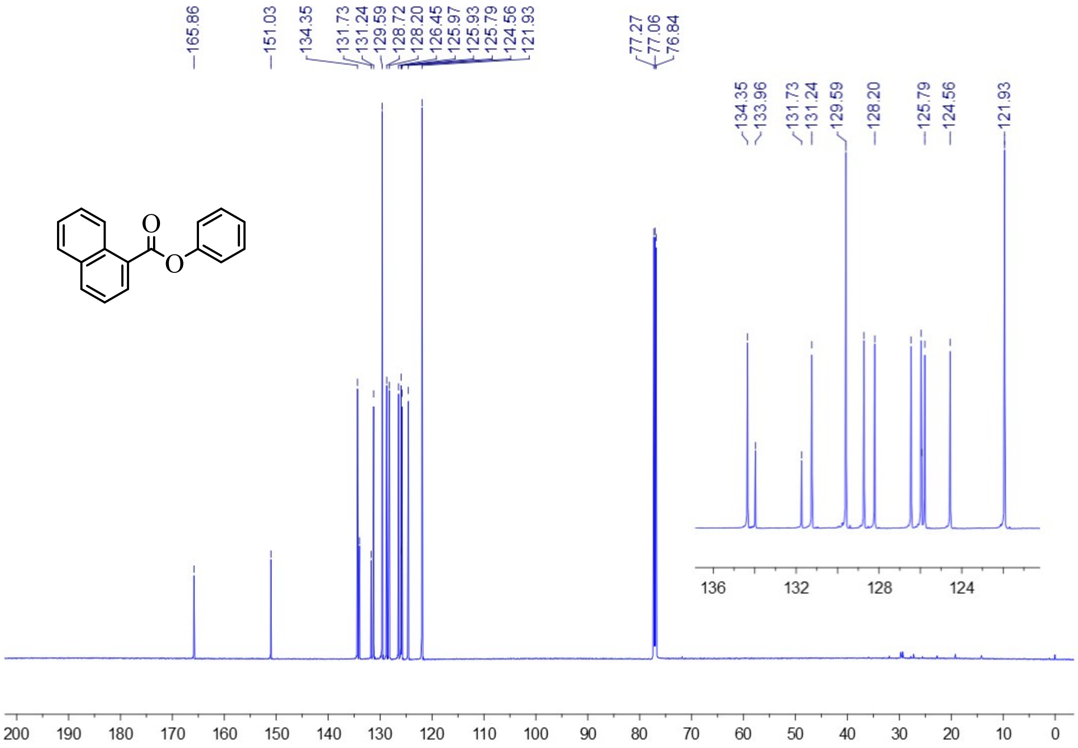
^{13}C NMR of phenyl 2-chloro-4-nitrobenzoate **3pa**



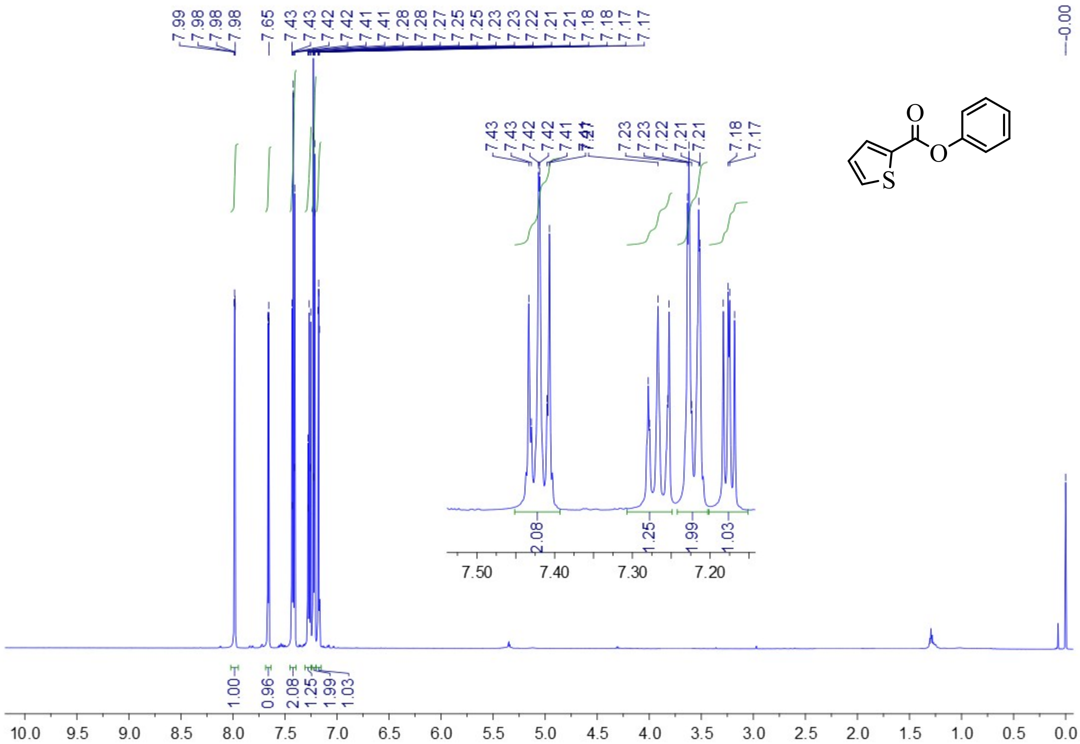
^{1}H NMR of phenyl 1-naphthoate **3qa**



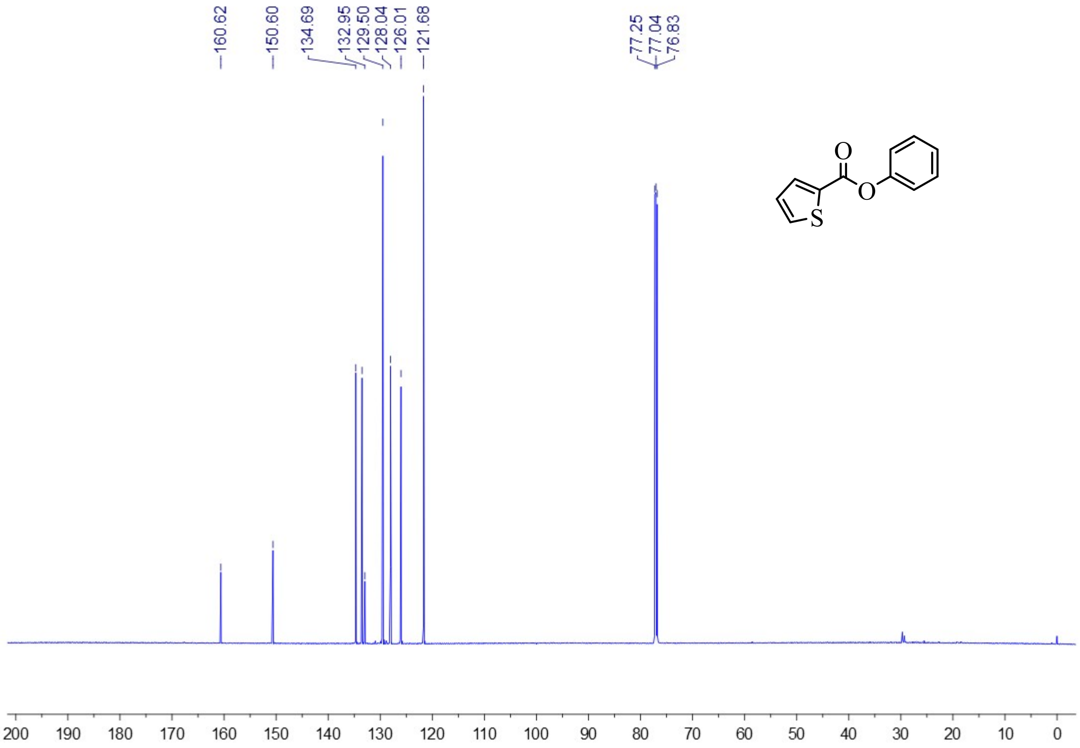
^{13}C NMR of phenyl 1-naphthoate **3qa**



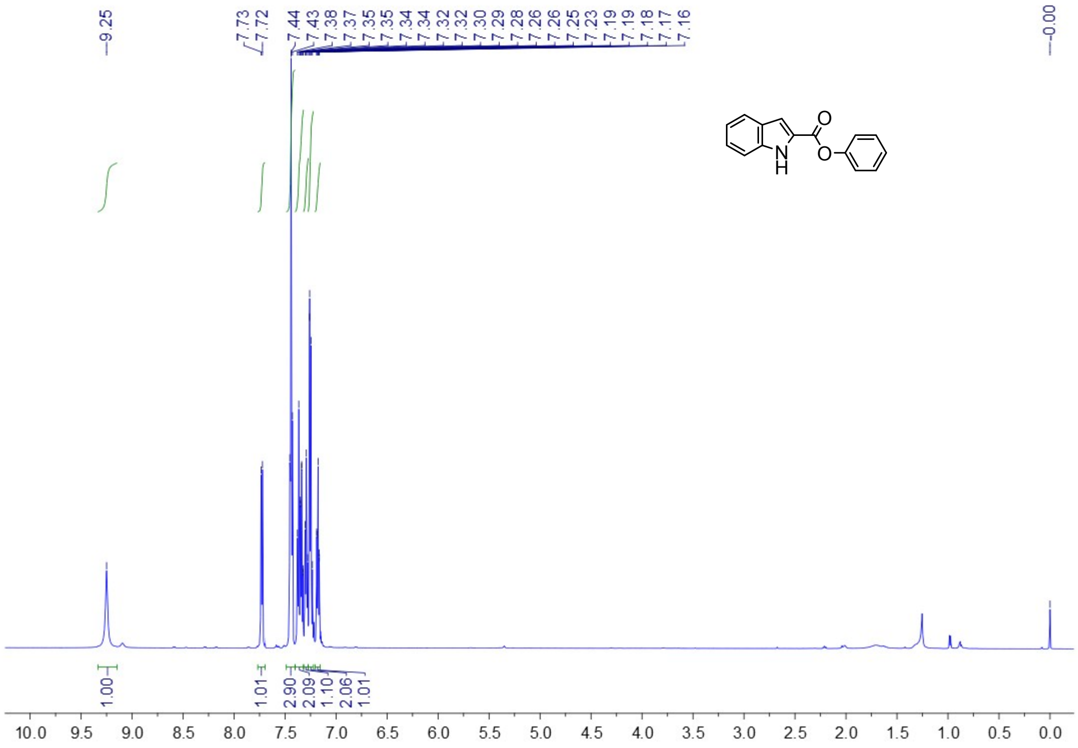
^{1}H NMR of phenyl thiophene-2-carboxylate **3ra**



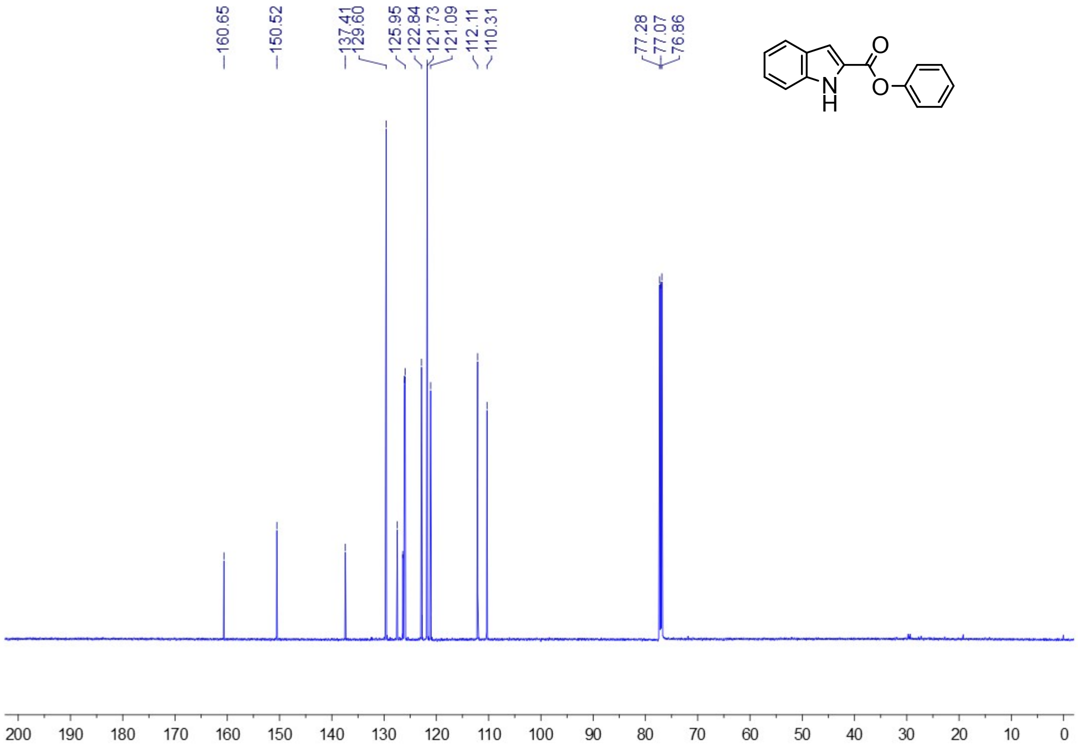
^{13}C NMR of phenyl thiophene-2-carboxylate **3ra**



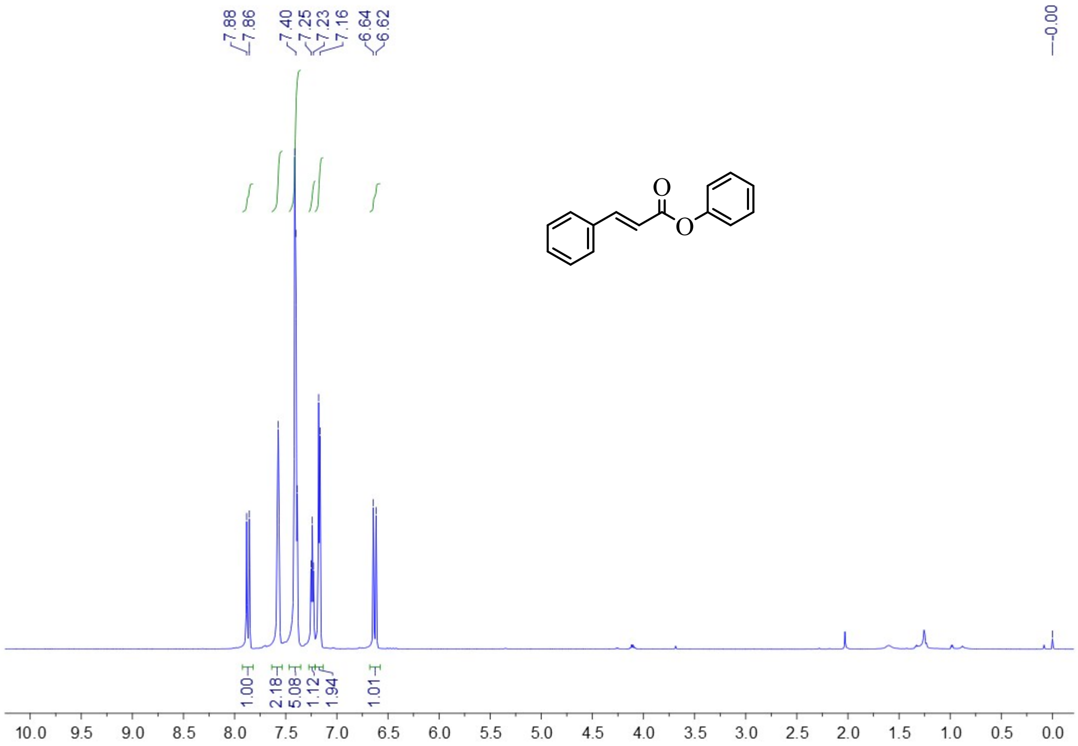
^{1}H NMR of phenyl *1H*-indole-2-carboxylate **3sa**



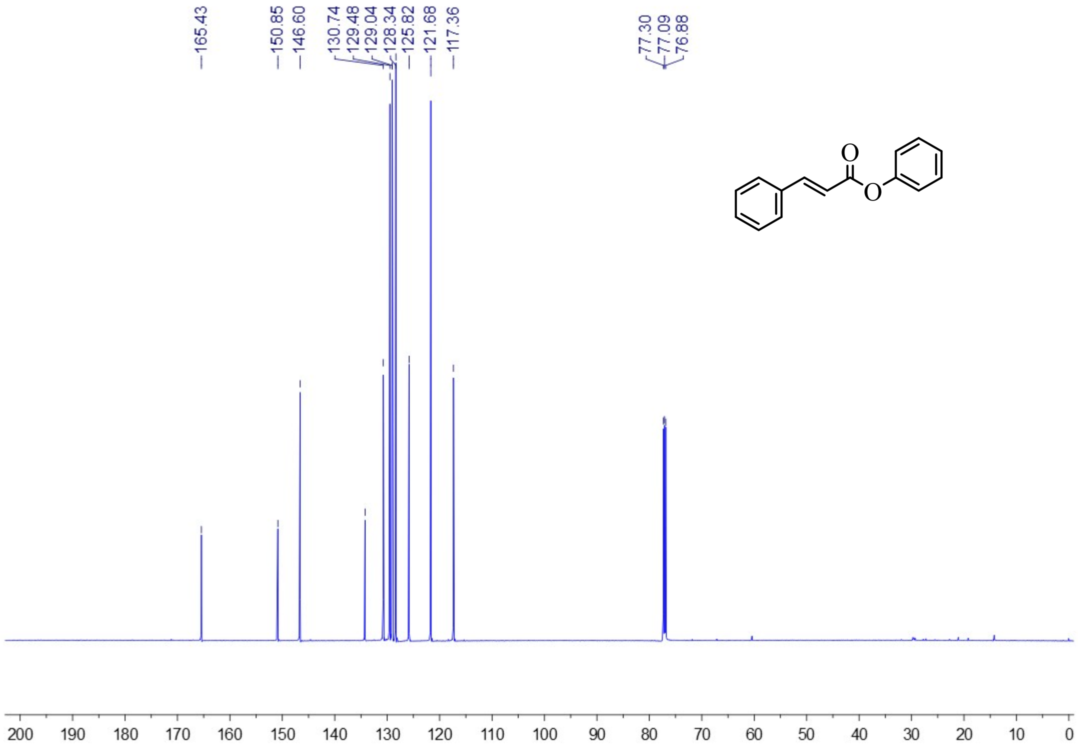
^{13}C NMR of phenyl 1H-indole-2-carboxylate **3sa**



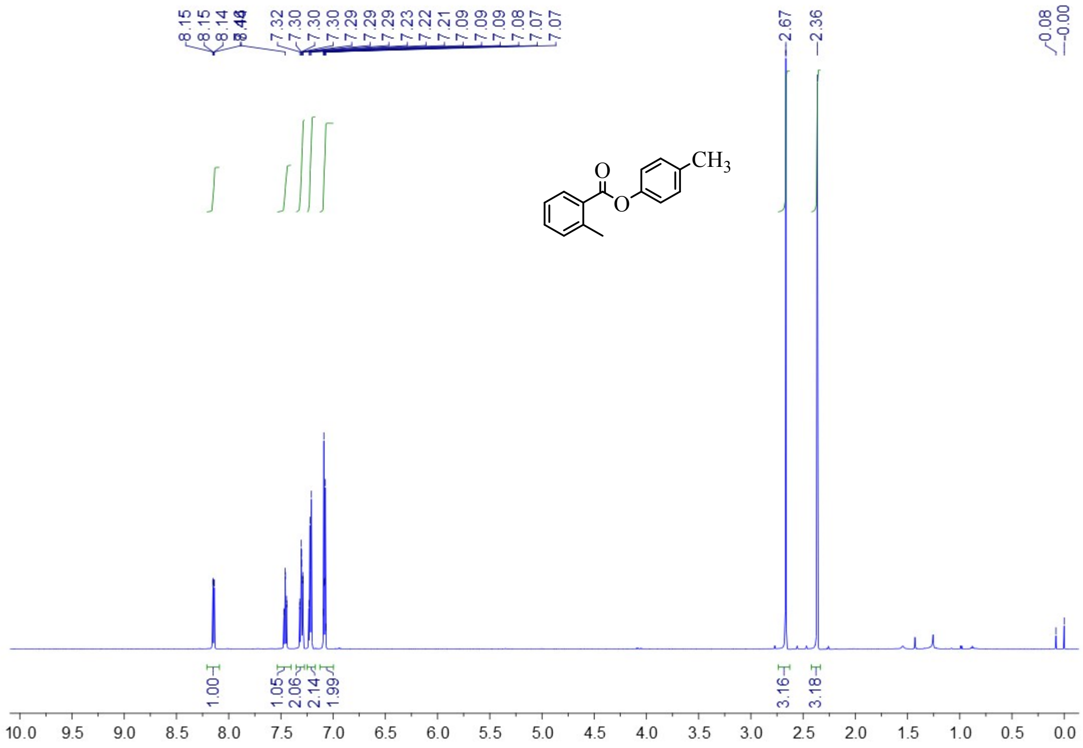
^{1}H NMR of phenyl cinnamate **3ta**



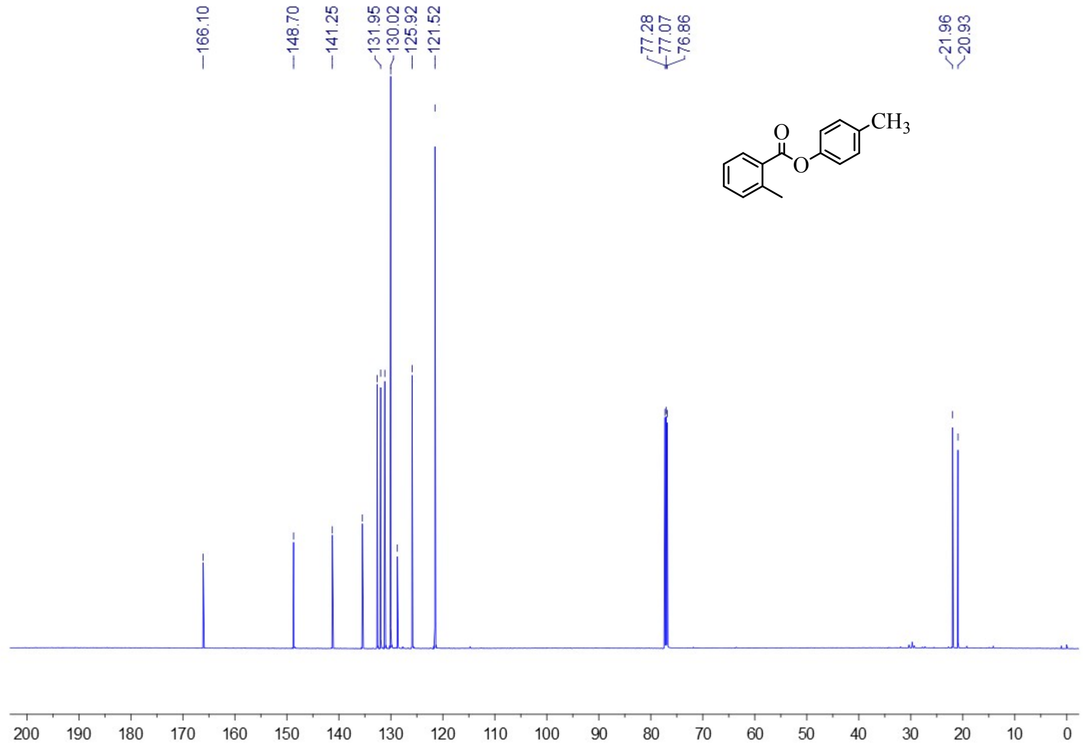
^{13}C NMR of phenyl cinnamate **3ta**



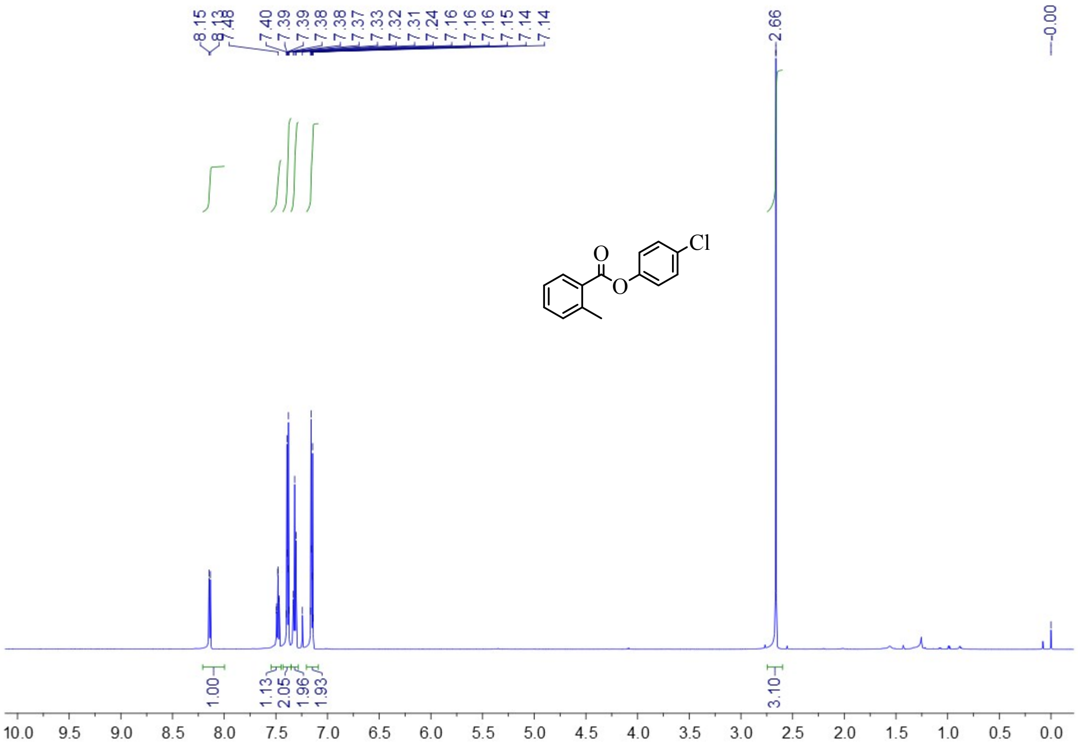
^{1}H NMR of 4-methylphenyl 2-methylbenzoate **3ab**



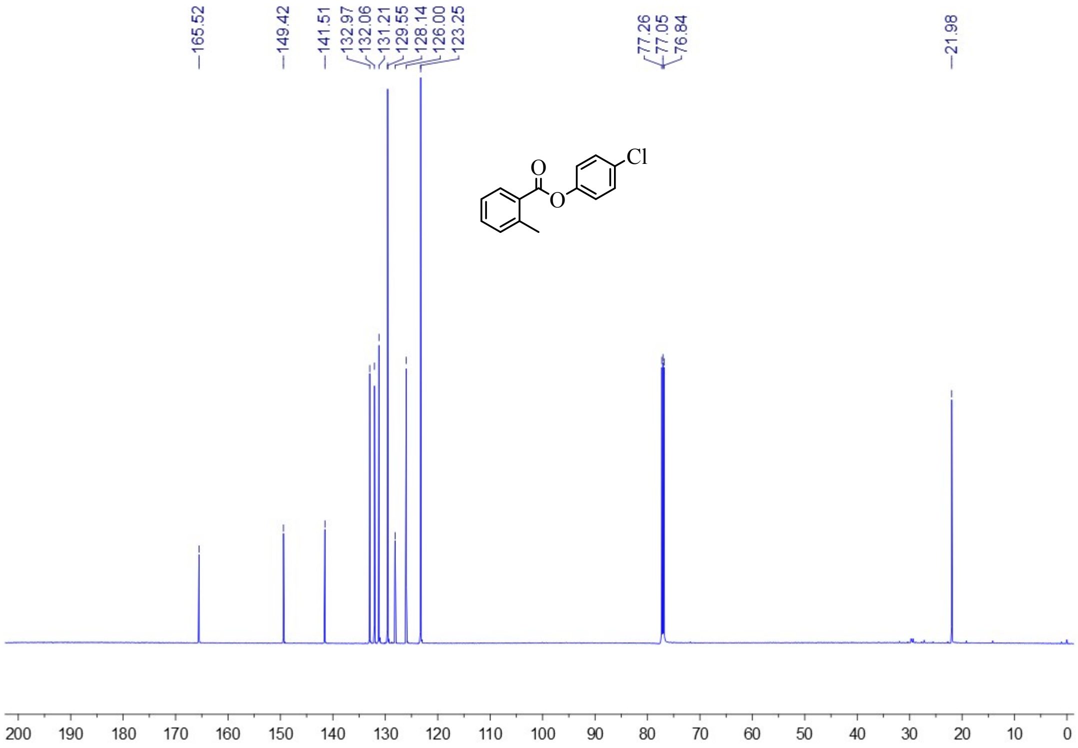
^{13}C NMR of 4-methylphenyl 2-methylbenzoate **3ab**



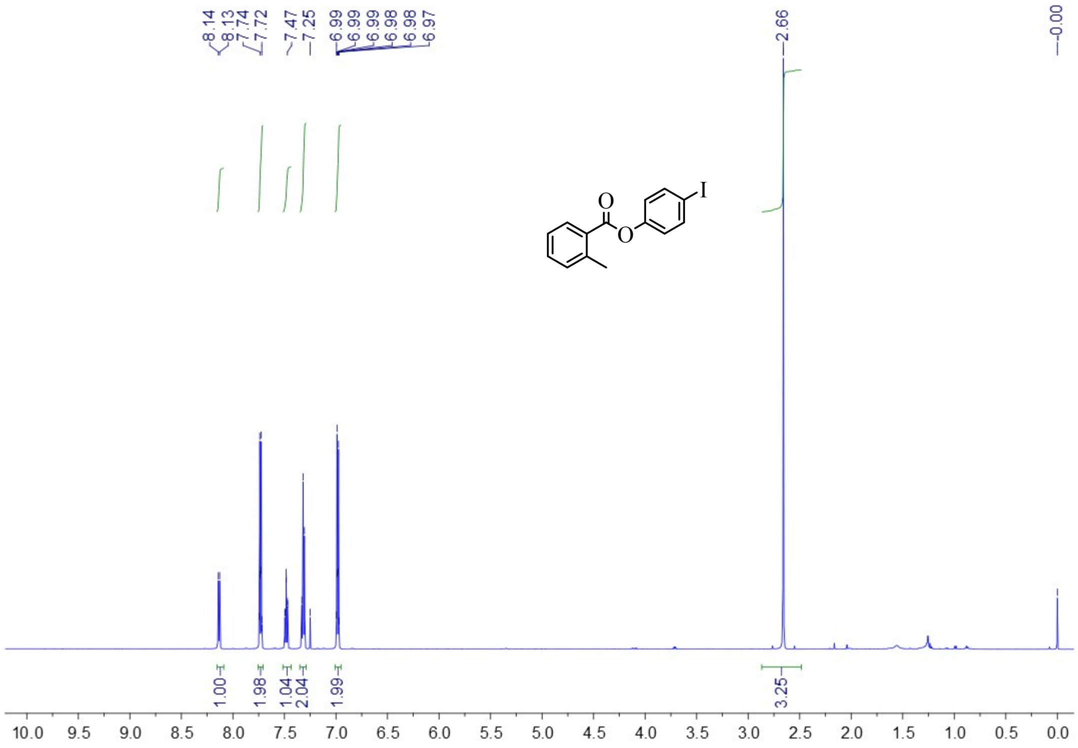
^{1}H NMR of 4-chlorophenyl 2-methylbenzoate **3ac**



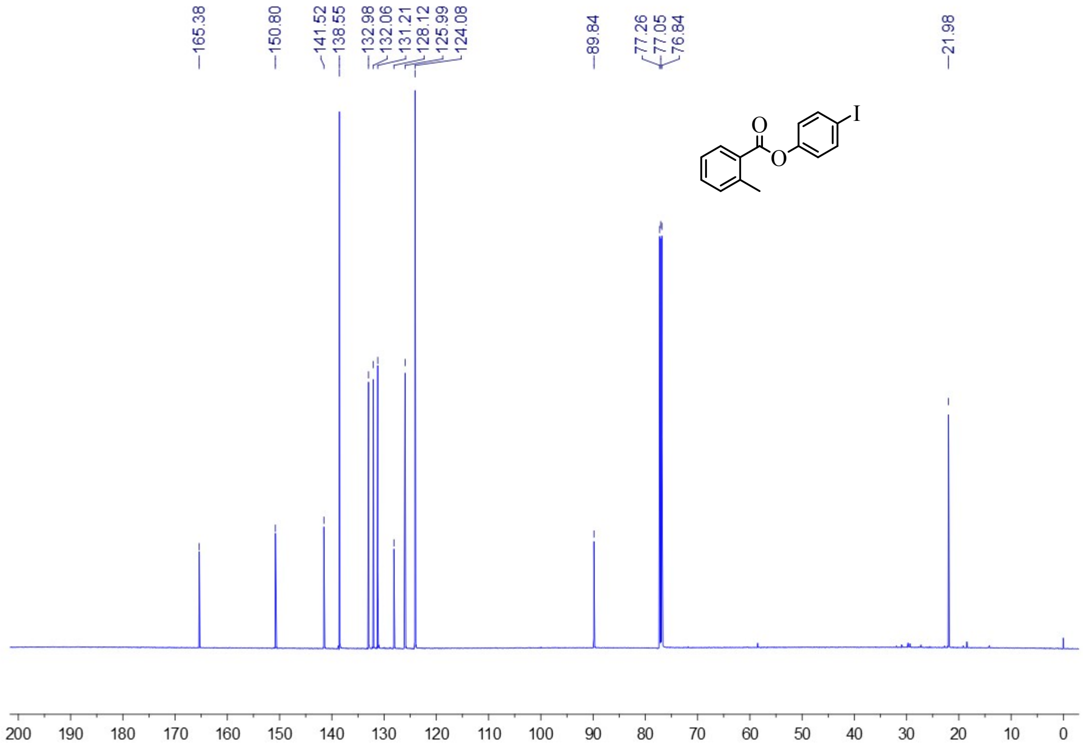
^{13}C NMR of 4-chlorophenyl 2-methylbenzoate **3ac**



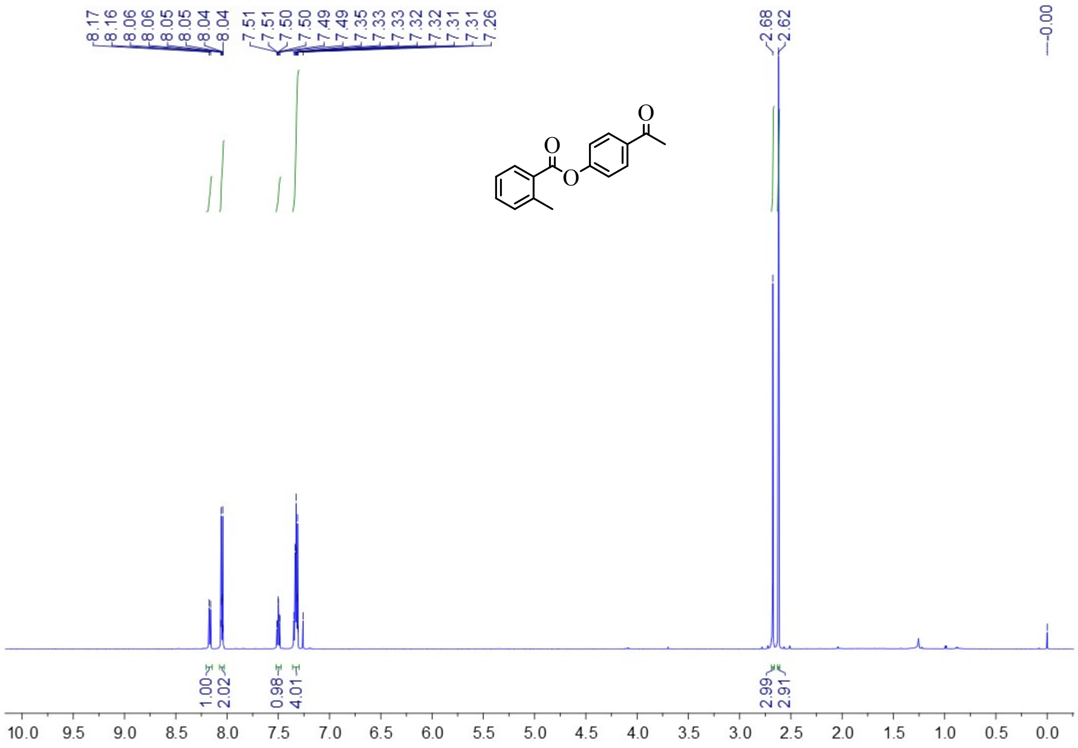
^{1}H NMR of 4-iodophenyl 2-methylbenzoate **3ad**



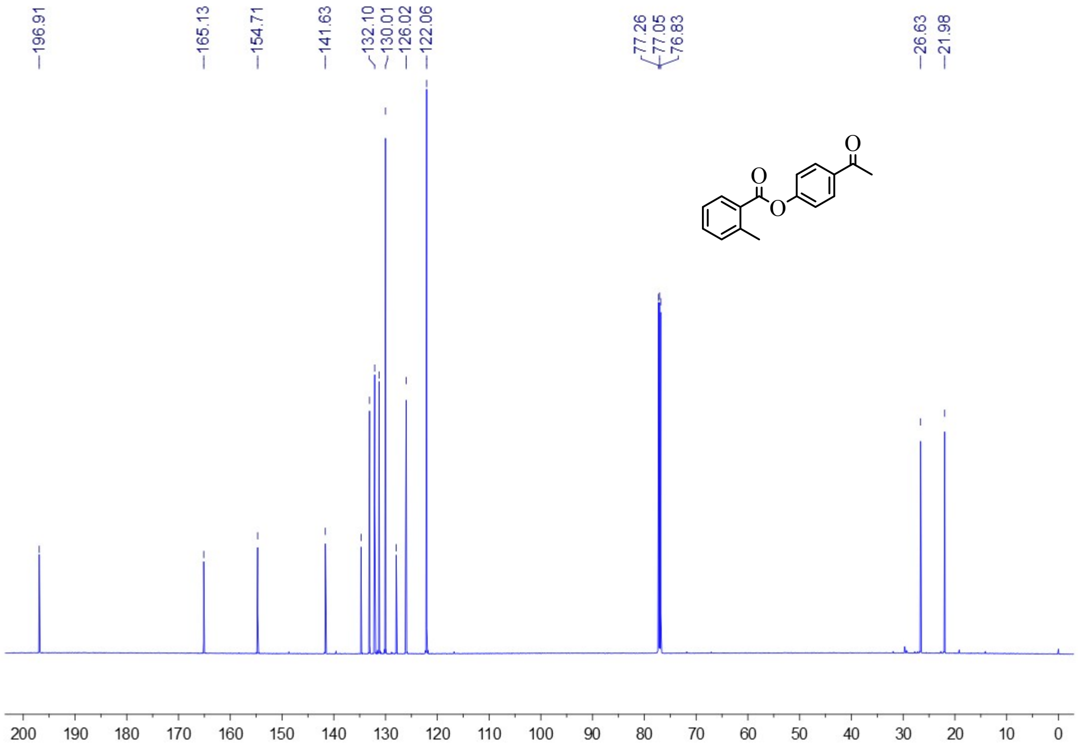
^{13}C NMR of 4-iodophenyl 2-methylbenzoate **3ad**



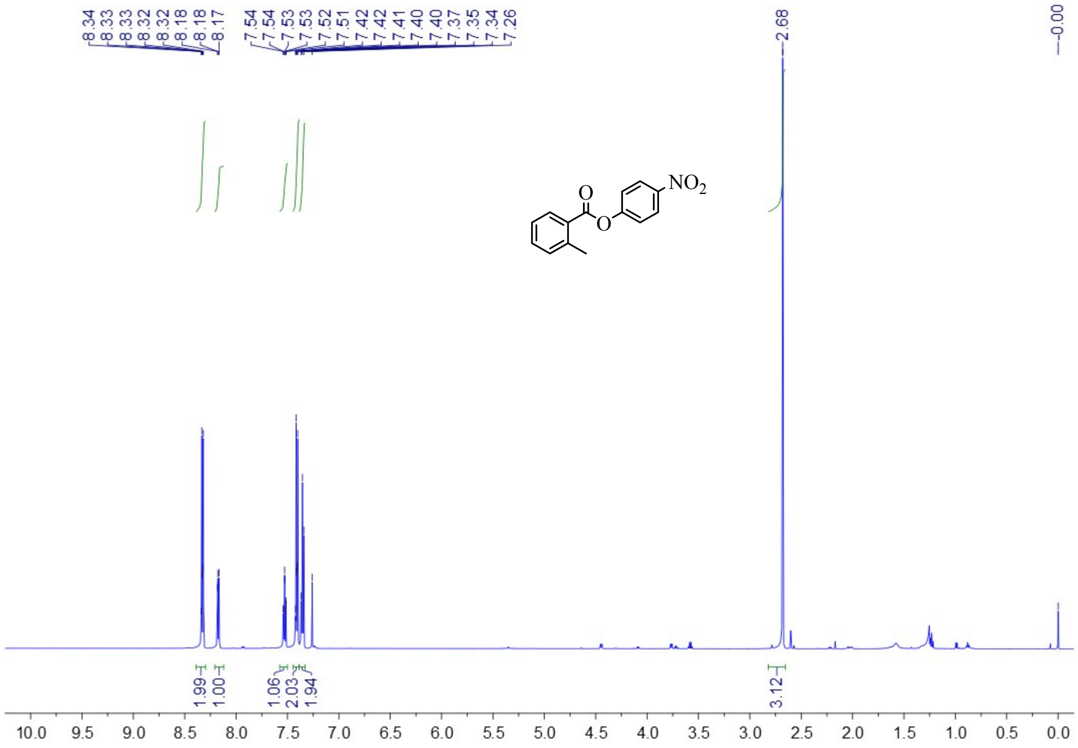
^{1}H NMR of 4-acetylphenyl 2-methylbenzoate **3ae**



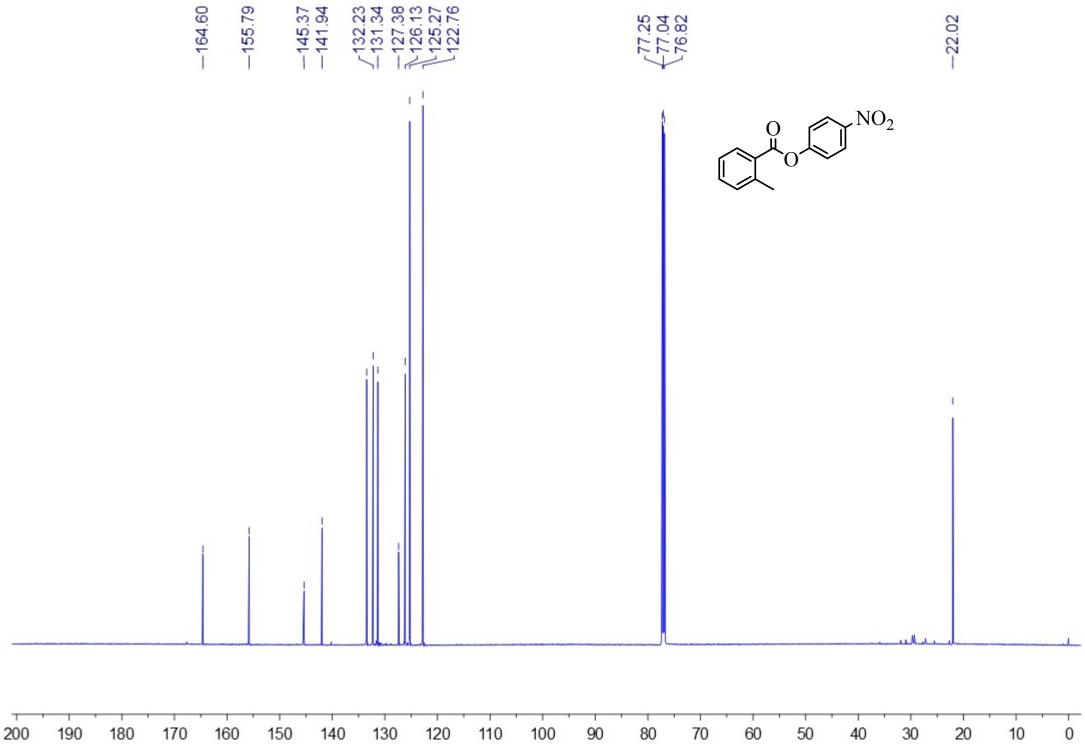
^{13}C NMR of 4-acetylphenyl 2-methylbenzoate **3ae**



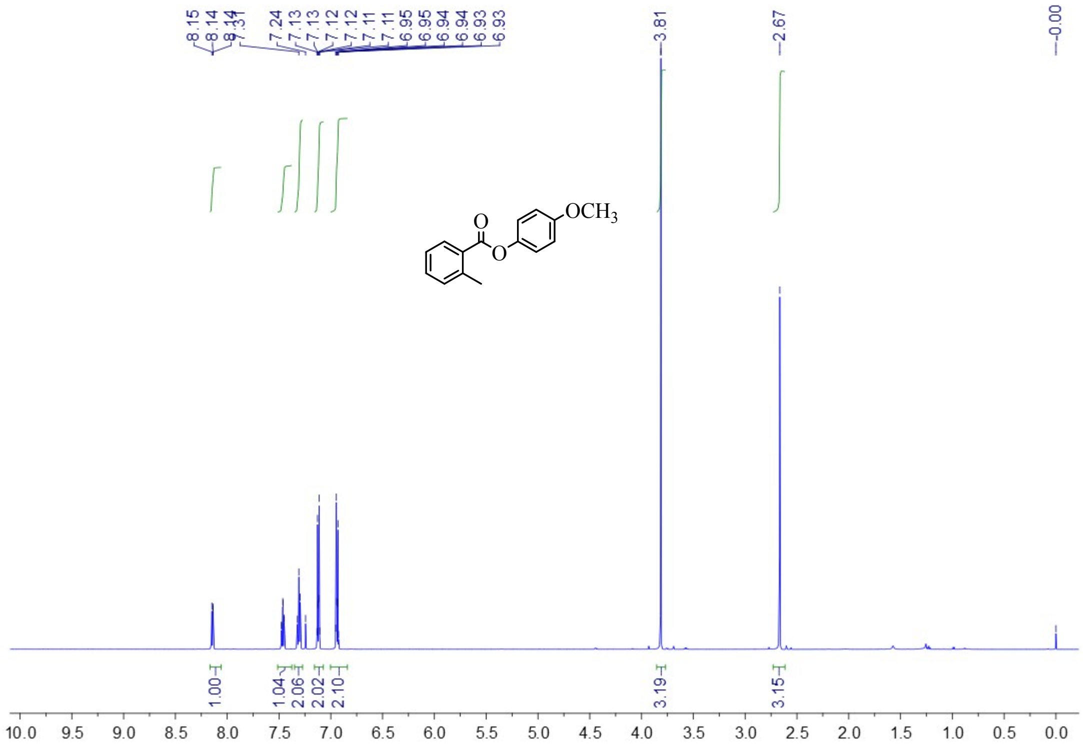
^{1}H NMR of 4-nitrophenyl 2-methylbenzoate **3af**



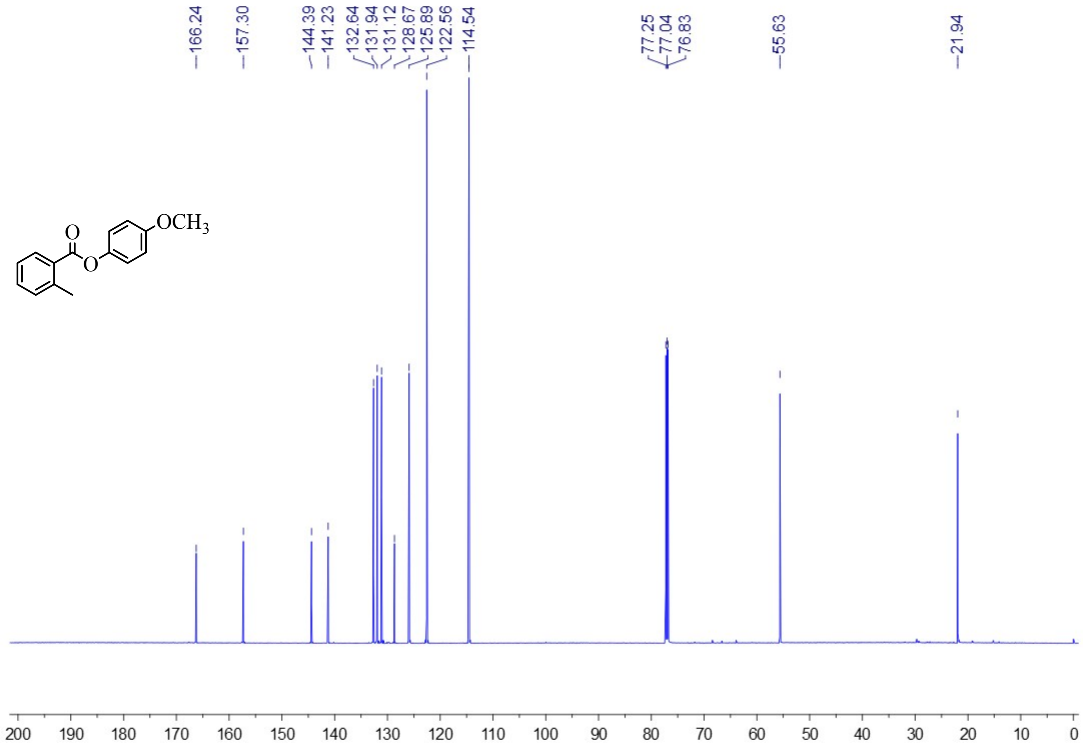
^{13}C NMR of 4-nitrophenyl 2-methylbenzoate **3af**



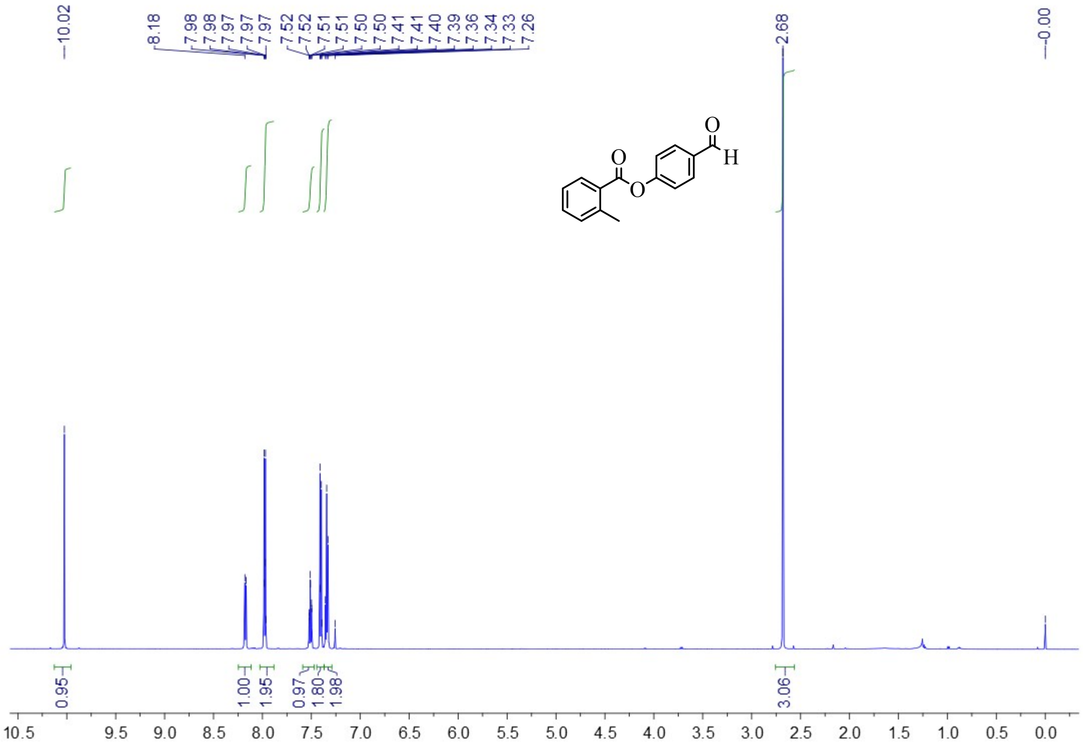
^{1}H NMR of 4-methoxyphenyl 2-methylbenzoate **3ag**



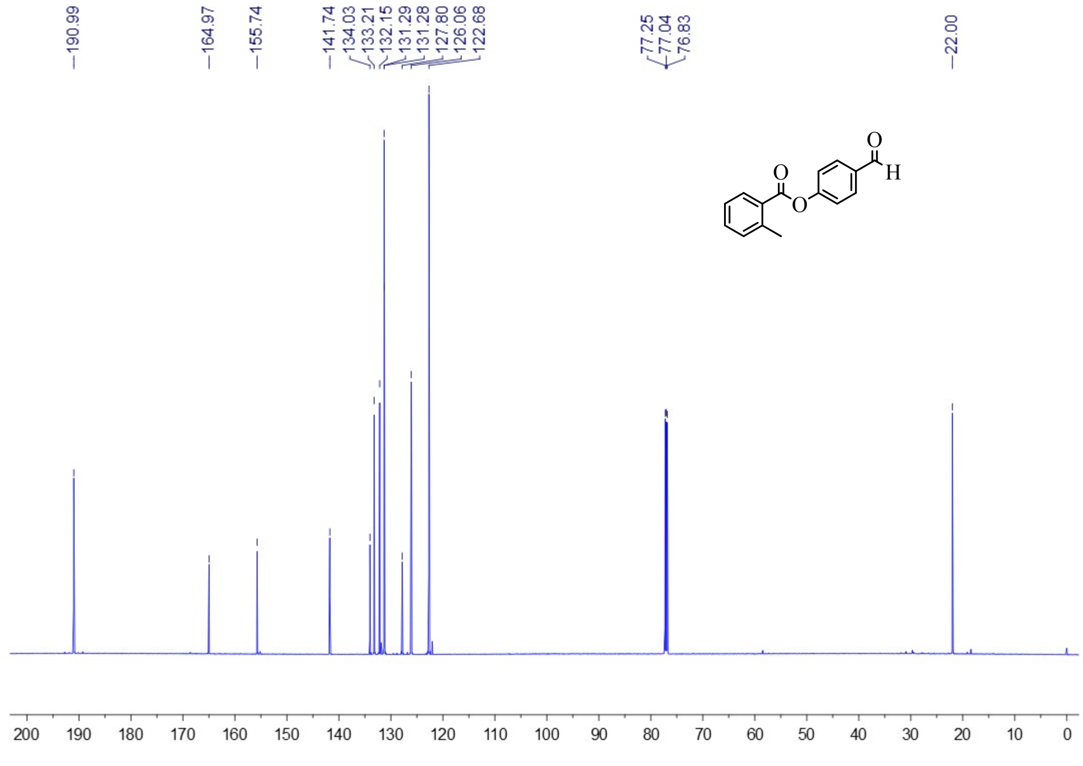
^{13}C NMR of 4-methoxyphenyl 2-methylbenzoate **3ag**



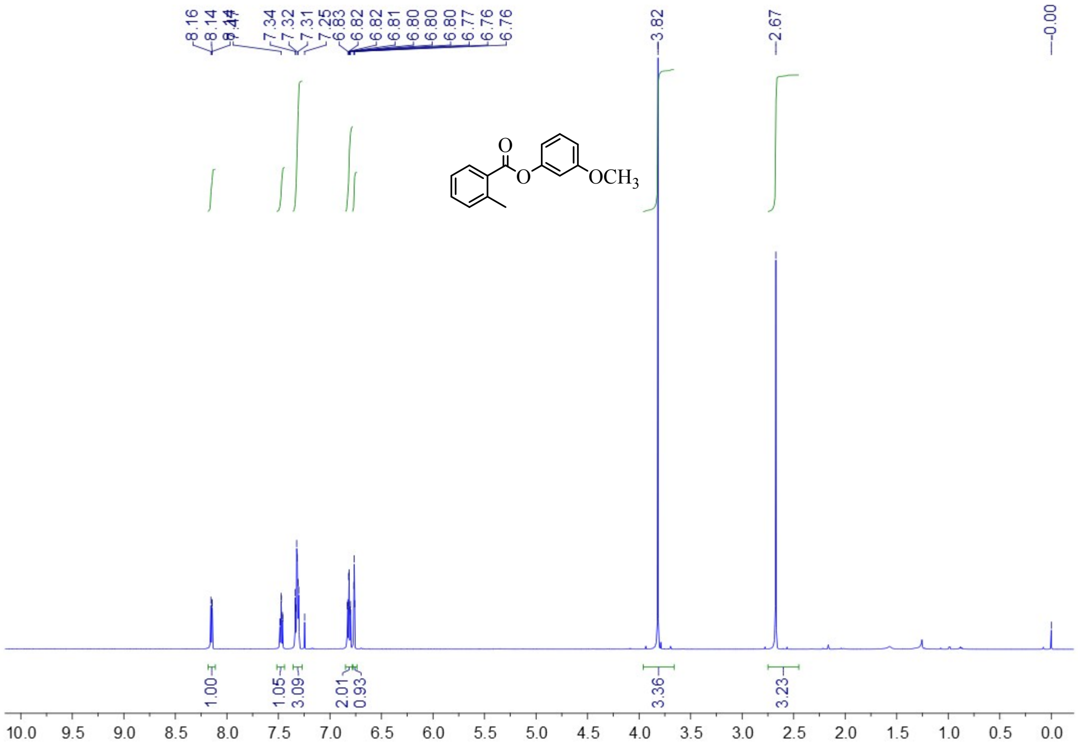
^{1}H NMR of 4-formylphenyl 2-methylbenzoate **3ah**



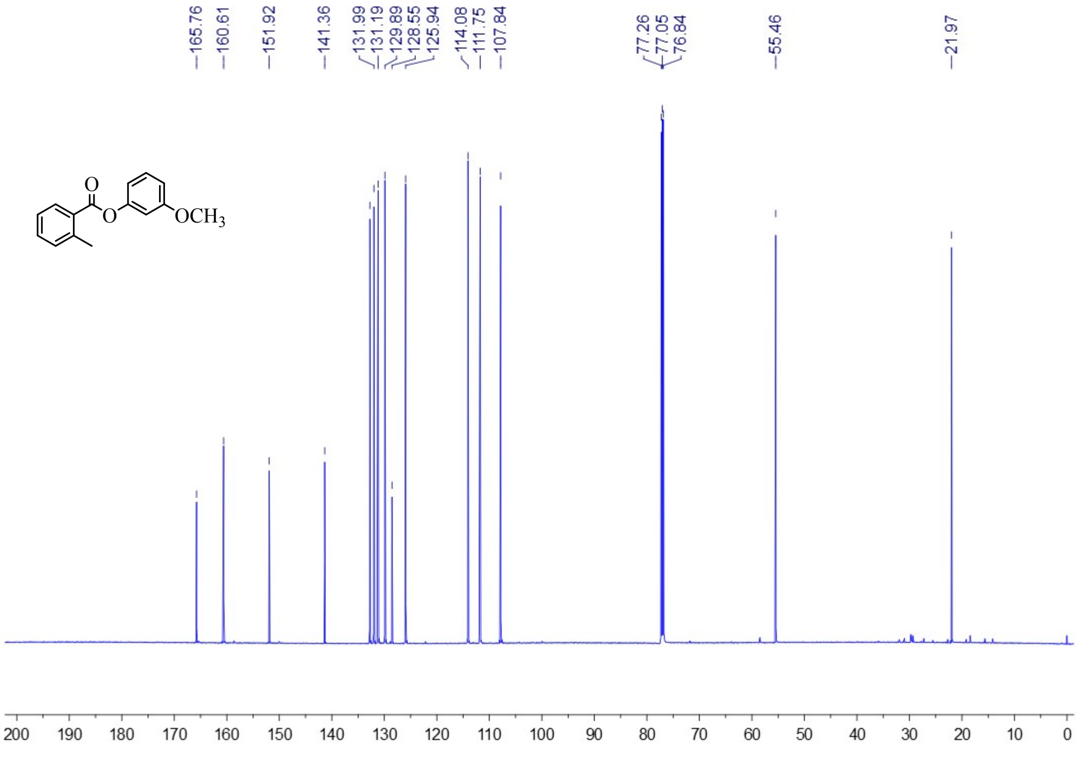
^{13}C NMR of 4-formylphenyl 2-methylbenzoate **3ah**



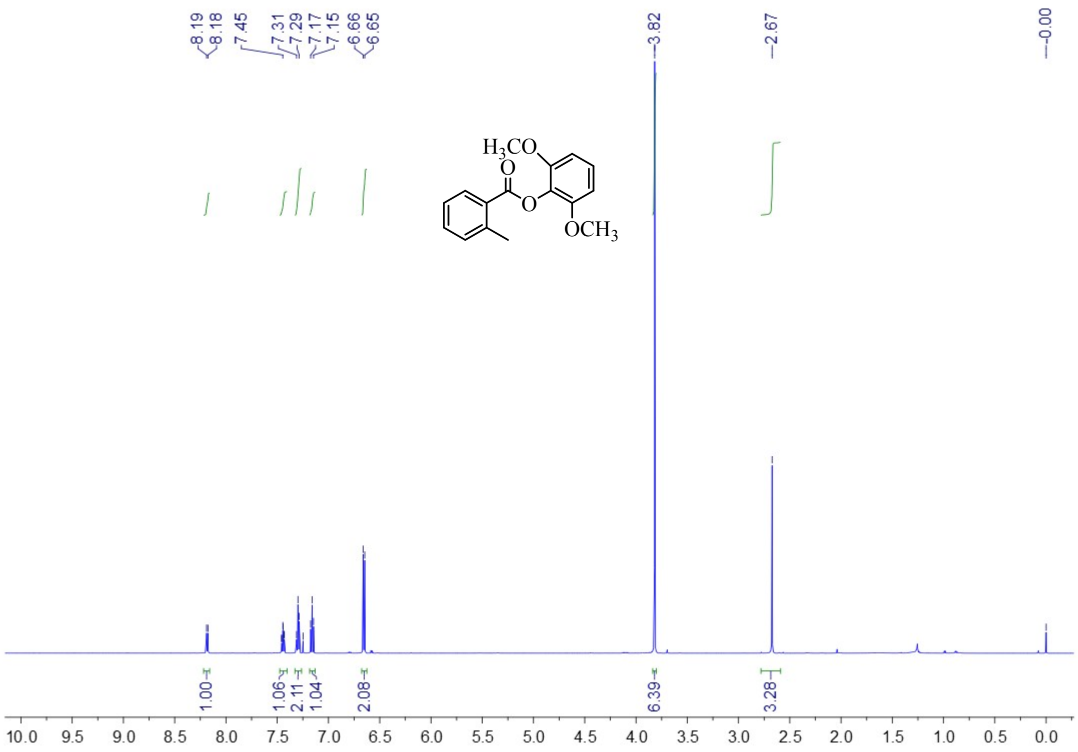
^{1}H NMR of 3-methoxyphenyl 2-methylbenzoate **3ai**



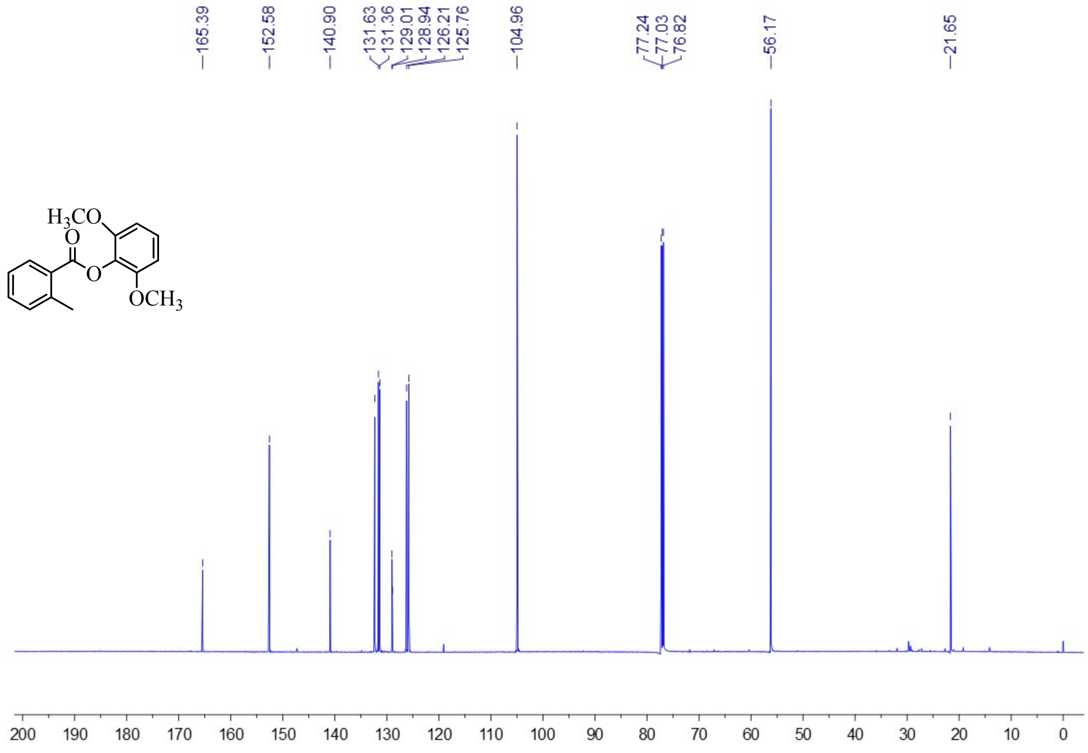
^{13}C NMR of 3-methoxyphenyl 2-methylbenzoate **3ai**



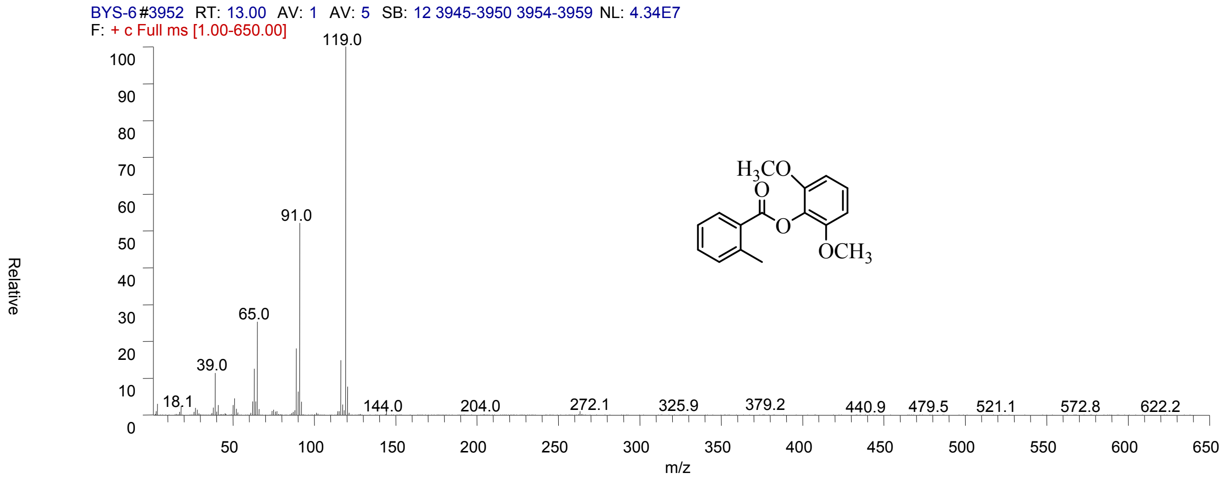
^{1}H NMR of 2,6-dimethoxyphenyl 2-methylbenzoate **3aj**



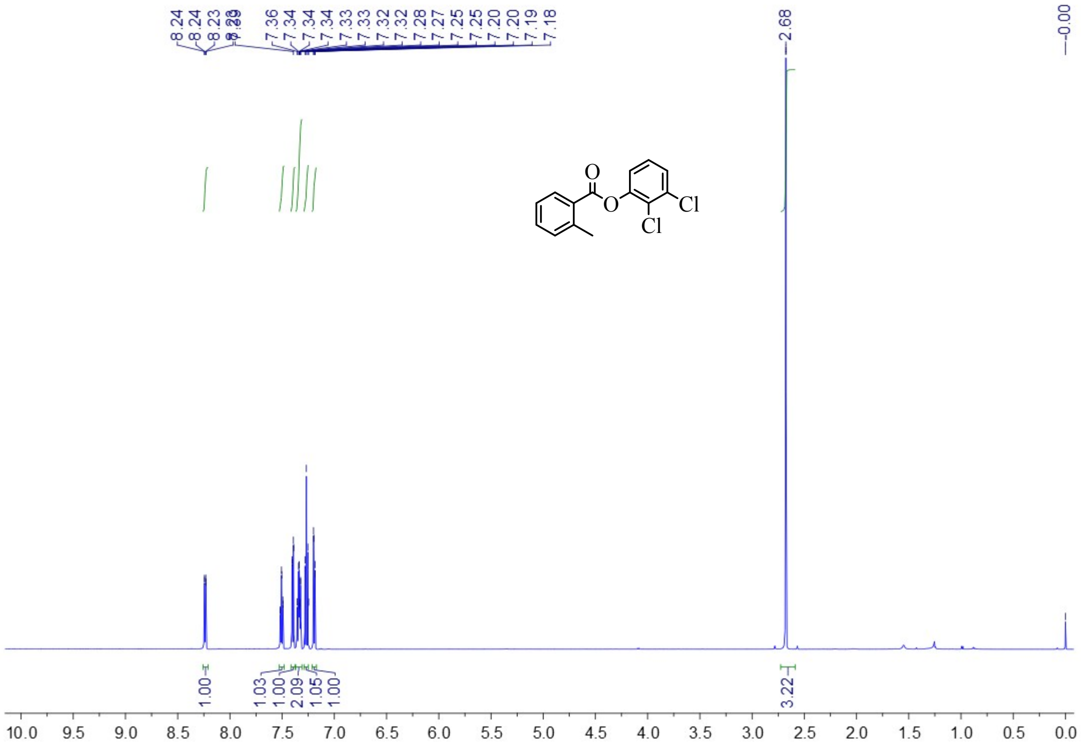
^{13}C NMR of 2,6-dimethoxyphenyl 2-methylbenzoate **3aj**



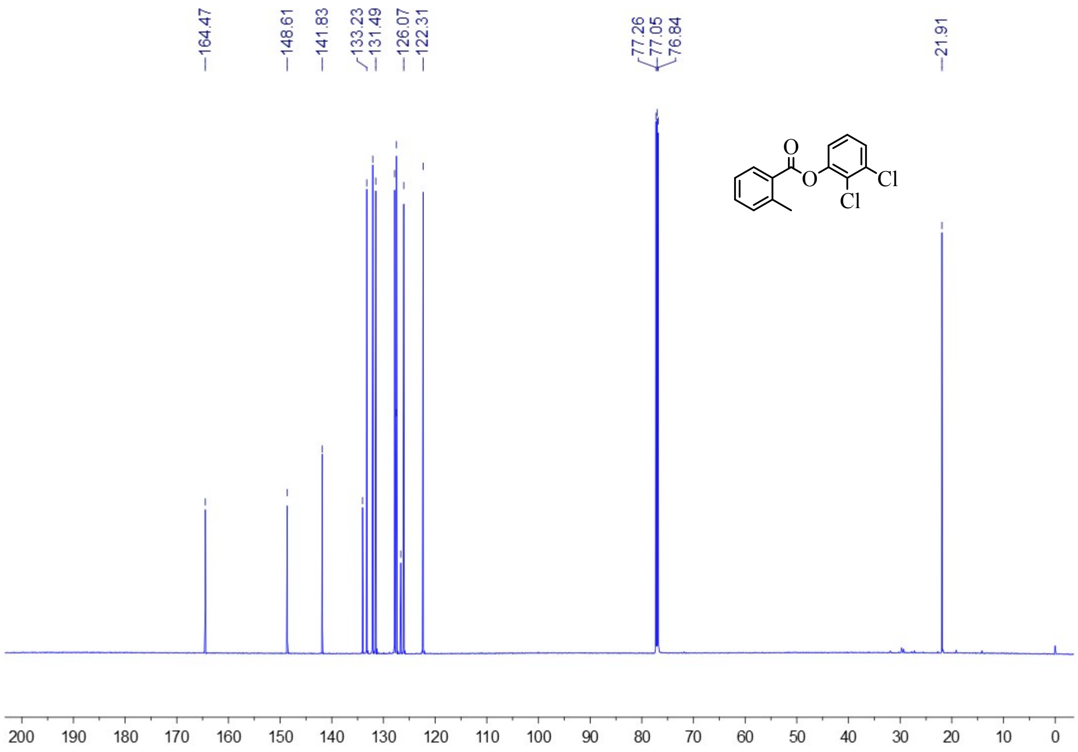
MS(EI) of 2,6-dimethoxyphenyl 2-methylbenzoate **3aj**



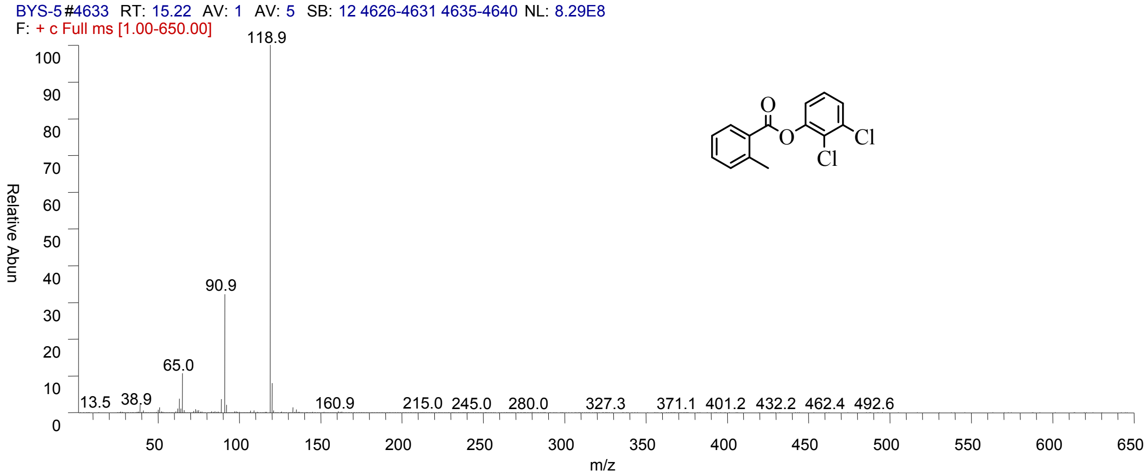
^{1}H NMR of 2,3-dichlorophenyl 2-methylbenzoate **3ak**



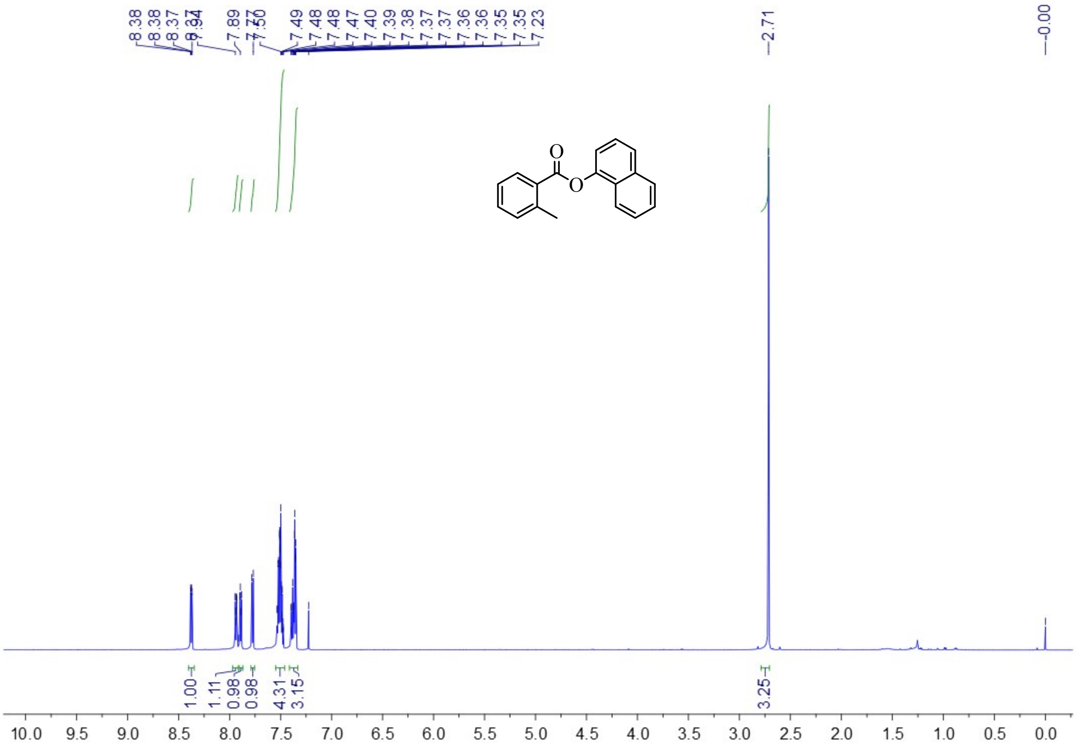
^{13}C NMR of 2,3-dichlorophenyl 2-methylbenzoate **3ak**



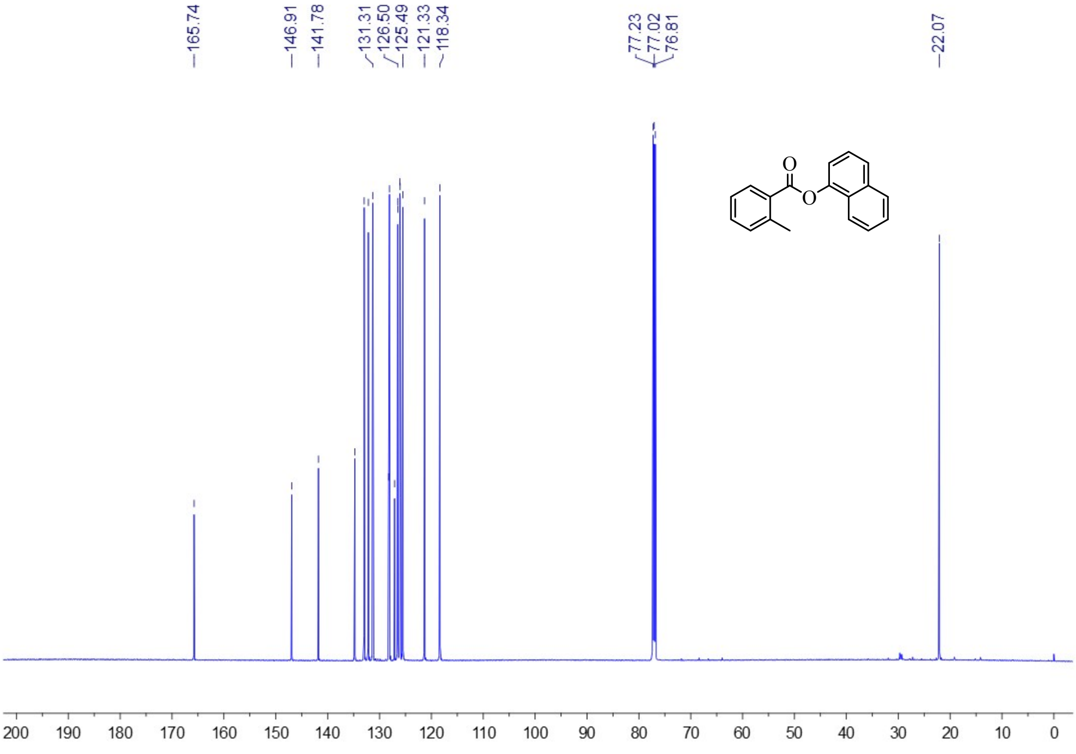
MS(EI) of 2,3-dichlorophenyl 2-methylbenzoate **3ak**



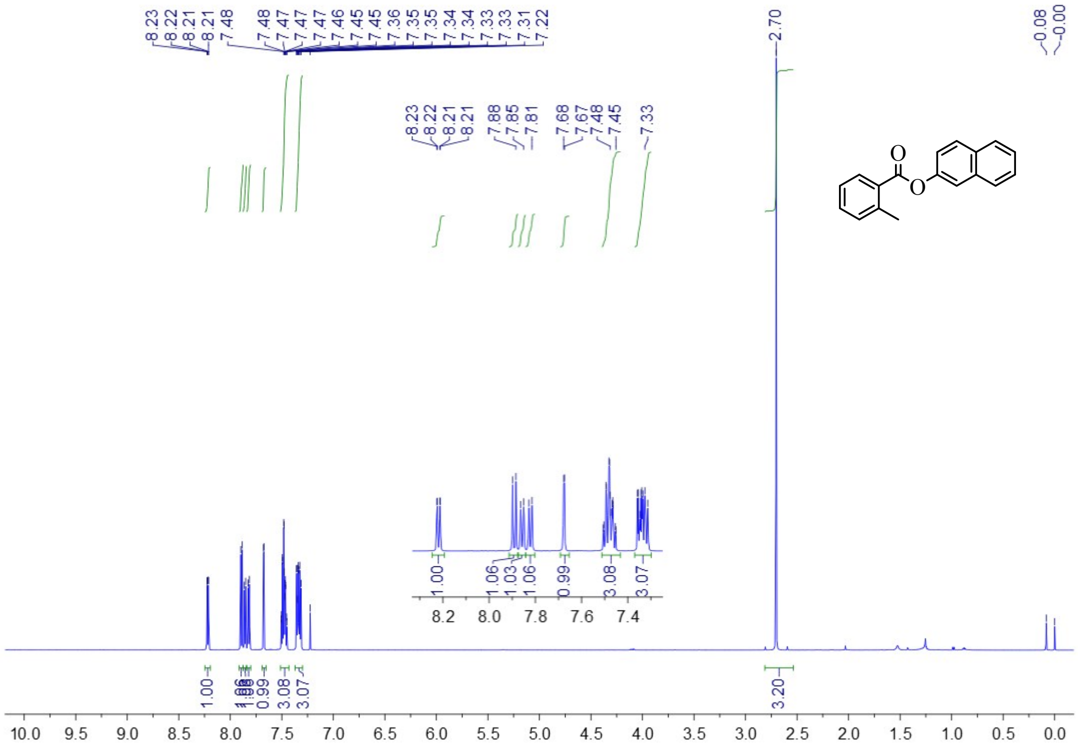
^{1}H NMR of naphthalen-1-yl 2-methylbenzoate **3al**



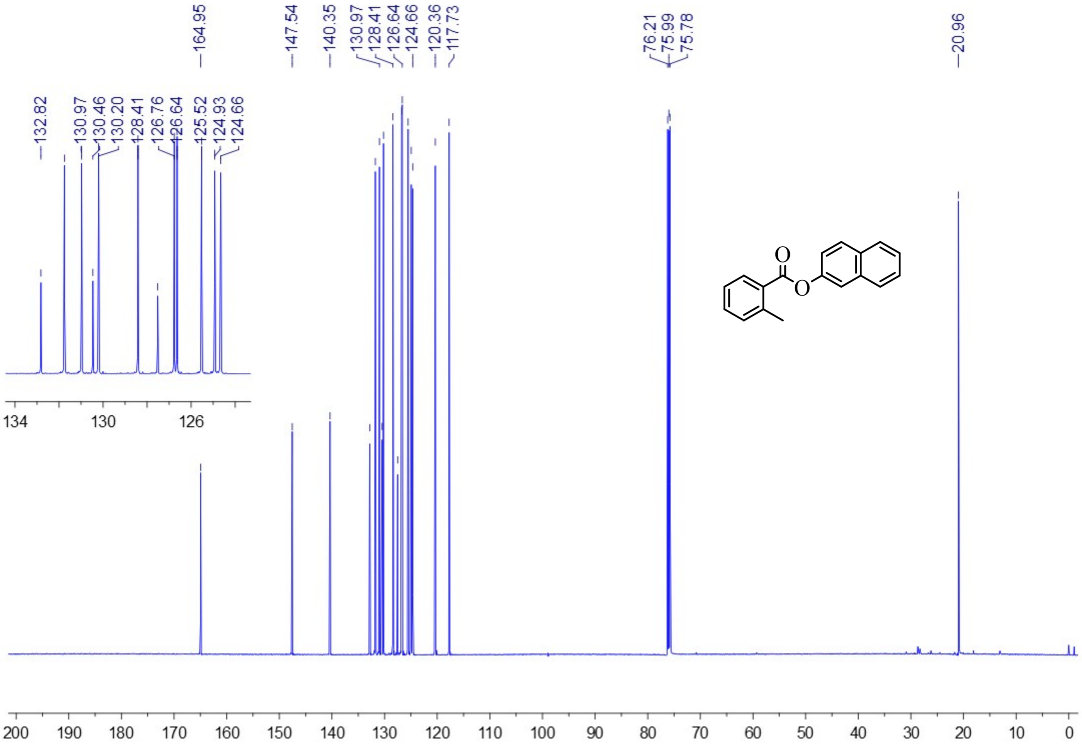
^{13}C NMR of naphthalen-1-yl 2-methylbenzoate **3al**



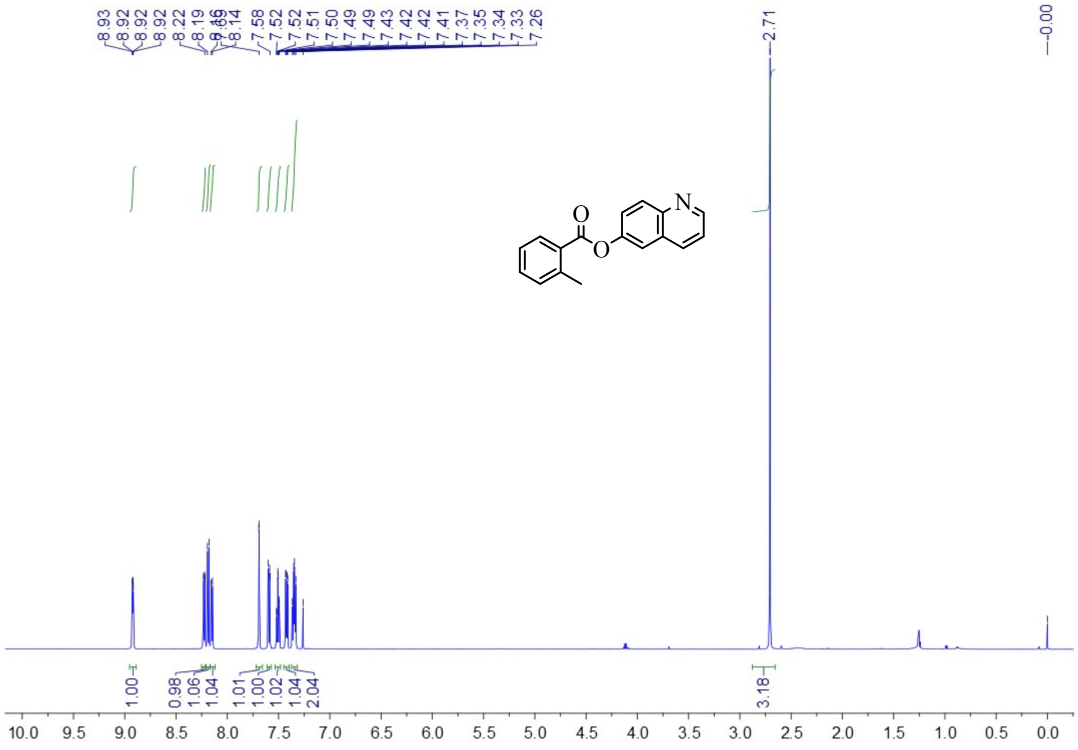
^{1}H NMR of naphthalen-2-yl 2-methylbenzoate **3am**



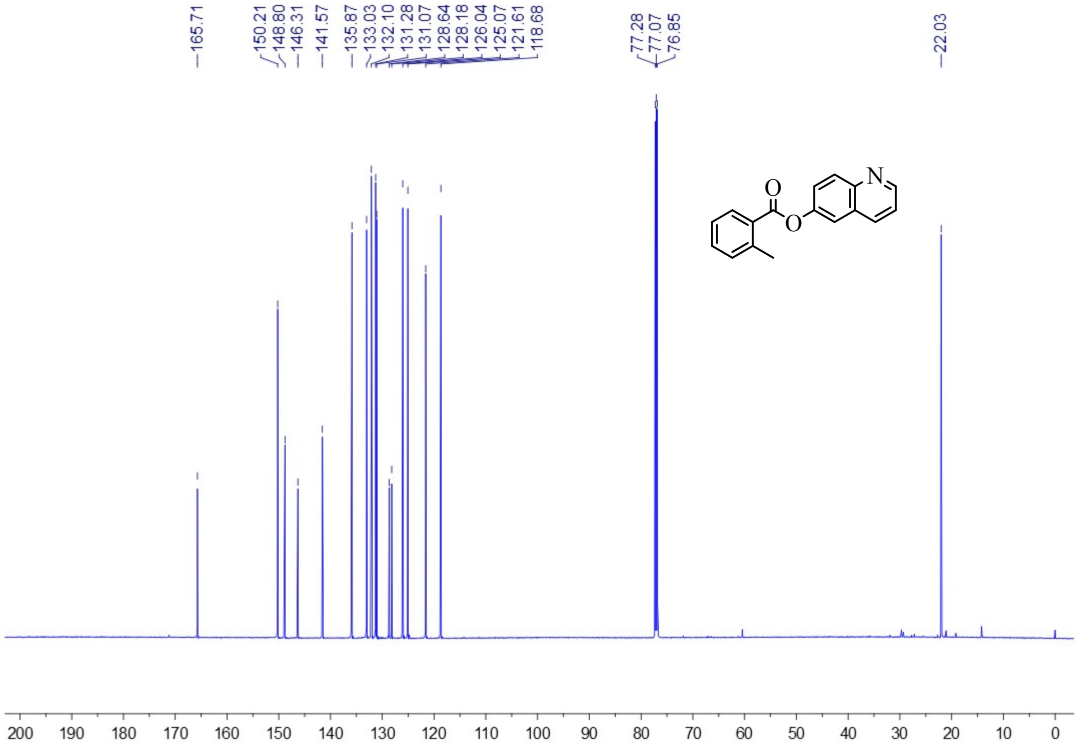
^{13}C NMR of naphthalen-2-yl 2-methylbenzoate **3am**



^{1}H NMR of quinolin-6-yl 2-methylbenzoate **3an**



^{13}C NMR of quinolin-6-yl 2-methylbenzoate **3an**



MS(EI) of quinolin-6-yl 2-methylbenzoate **3an**