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Supporting Information

Copper-Catalyzed Oxidative Esterification of Aldehydes with Dialkyl Peroxides: Efficient Synthesis of Esters of Tertiary Alcohols

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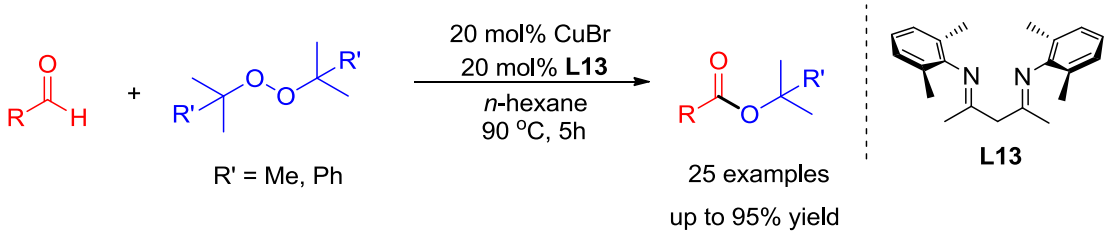

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1. General considerations

^{1}H NMR spectra were obtained with TMS as internal standard in $CDCl_3$ using a Bruker DRX 500 (500 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm), or with tetramethylsilane (TMS, δ 7.26 ppm) as the internal standard. Chemical shifts (δ) were reported as part per million (ppm) in δ scale downfield from TMS. ^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.0 ppm, the middle peak). Coupling constants (*J*) were reported in Hertz (Hz). Gas chromatography (GC) analysis was performed on an Agilent GC-6820 chromatograph equipped with a 30 m × 0.32 mm × 0.5 μm HP-Innowax capillary column and aflame ionization detector. GC-MS spectra were recorded on Thermo Trace DSQ GC-MS spectrometer using a TRB-5MS (30 m × 0.25 mm × 0.25μm) column. Melting points were determined on a Yamato melting apparatus Model MP-21. Progress of the reactions was followed by TLC (silica gel polygrams SIL G/UV 254 plates). Column chromatography was performed using Silicycle (40-60 mm) silica gel. The chemicals were purchased from commercial suppliers (Shanghai Chemical Company, China) and were used without purification prior to use.

2. Preparation of Mannich base L6 and imine L9

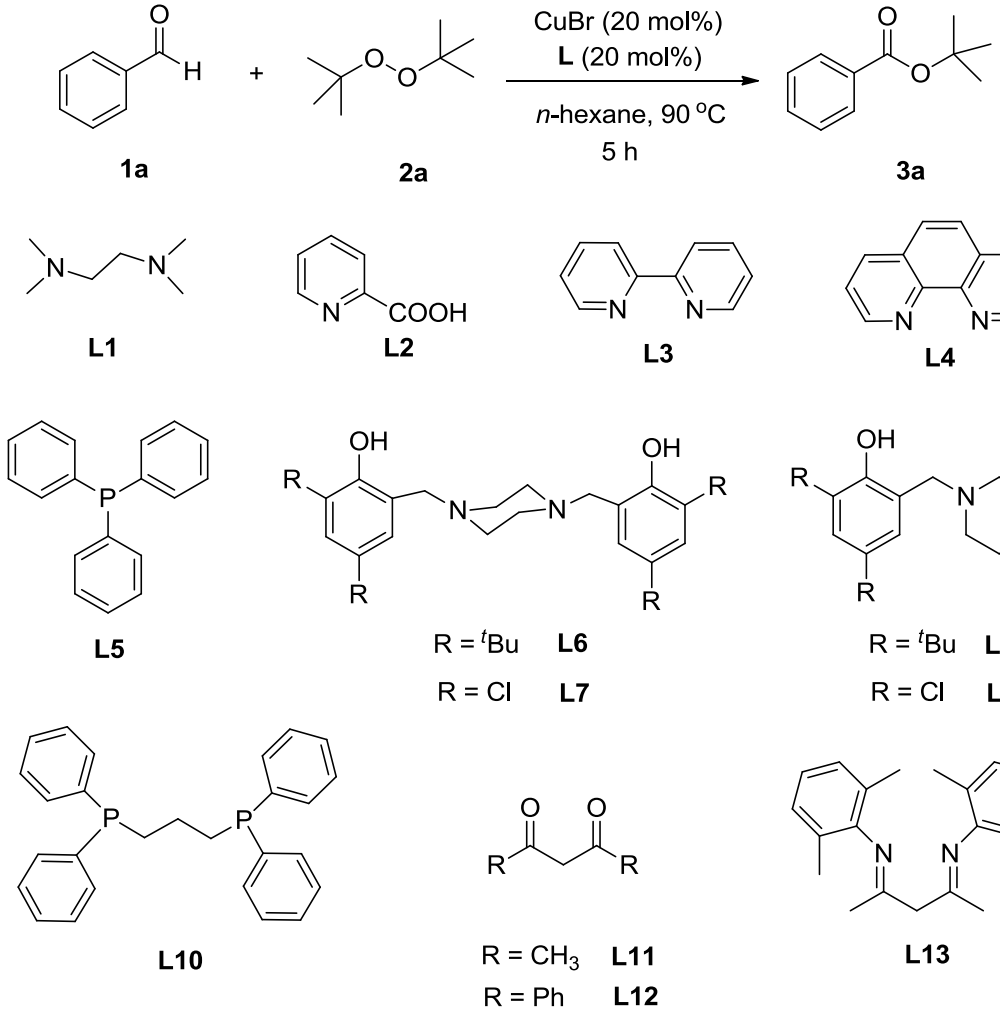
Mannich bases **L6** were prepared from their corresponding phenols, formaldehyde and amines according to the literature method without modifications.[1]

Imine **L13** was prepared from 2,4-phentanedione and 2,6-dimethylbenzenamine according to the literature method without modifications.[2]

3. General procedure for oxidative esterification reaction

A mixture of aldehyde **1** (0.5 mmol), DTBP (0.3 mL) or other peroxide (1.5 mmol), CuBr (14.4 mg, 0.1 mmol, 20 mol%) and imine **L13** (30.6 mg, 0.1 mmol, 20 mol%) in *n*-hexane (3 mL) was sealed in a Teflon septum screw-capped tube under N_2. The mixture was stirred in an oil bath at 90 ^{o}C for 5h. After cooling to room temperature, the mixture was filtered, and the filtrate was evaporated in vacuo. The residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:20 as an eluent) to afford the desire esters of tertiary alcohols **3**.

Table S1 Ligand survey for copper-catalyzed direct esterification of benzaldehyde with DTPB[a]



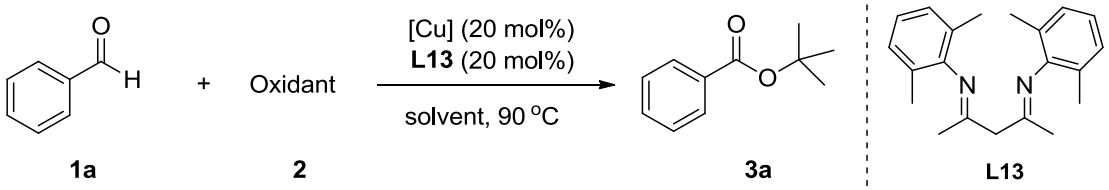
Entry	Ligand	Yield [b][%]	Entry	Ligand	Yield[b][%]
1		0	8	**L7**	<5
2	**L1**	0	9	**L8**	<5
3	**L2**	0	10	**L9**	<5
4	**L3**	0	11	**L10**	15
5	**L4**	0	12	**L11**	26
6	**L5**	0	13	**L12**	20
7	**L6**	<5	14	**L13**	92(87[c])

[a] Reaction conditions: A mixture of benzaldehyde (**1a**, 0.5 mmol), CuBr (20 mol%), ligand (20 mol%) and DTBP (**2a,** 0.3 mL) in *n*-hexane (3 mL) was stirred at 90 °C for 5 h under N_2.

[b] Yield determined by GC.

[c] Isolated yield.

Table S2 Optimization of reaction conditions for the preparation of **3a** in the presence of **L13**[a]



1a **2** **3a** **L13**

Entry	[Cu]	Oxidant	Solvent	Yield[b] (%)
1		DTBP	*n*-hexane	0
2	CuI	DTBP	*n*-hexane	82
3	CuCl	DTBP	*n*-hexane	85
4	***CuBr***	DTBP	***n-hexane***	***87***
5	CuBr	DTBP	*n*-hexane	67[d]
6	Cu_2O	DTBP	*n*-hexane	27
7	$Cu(OAc)_2$	DTBP	*n*-hexane	0
8	$CuCl_2$	DTBP	*n*-hexane	78
9	$Cu(acac)_2$	DTBP	*n*-hexane	0
10	CuBr	DTBP	toluene	<5[c]
11	CuBr	DTBP	$ClCH_2CH_2Cl$	<5[c]
12	CuBr	DTBP	cyclohexane	<5[c]
13	CuBr	DTBP	1,4-dioxane	0
14	CuBr	TBHP	*n*-hexane	<5[c]
15	CuBr	*t*-butyl perbenzoate	*n*-hexane	36
16	CuBr	O_2	*n*-hexane	0[e]
17	CuBr	H_2O_2	*n*-hexane	0[e]
18	CuBr	$K_2S_2O_4$	*n*-hexane	0[e]
19	CuBr	NHPI	*n*-hexane	0[e]
20	CuBr	DTBP	*n*-hexane	62[f]
21	CuBr	DTBP	*n*-hexane	71[g]

[a] Reaction conditions: A mixture of benzaldehyde (**1a**, 0.5 mmol), [Cu] (20 mol%), **L13** (20 mol%) and DTBP (**2a,** 0.3 mL) in *n*-hexane (3 mL) was stirred at 90 °C for 5 h under N_2.

[b] Isolated yield.

[c] Yield determined by GC.

[d] 10 mol% CuBr and 10 mol% **L13** were used.

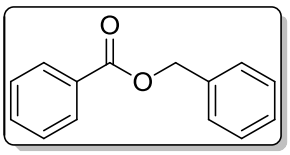
[e] 0.3ml *tert*-butanol were used in the reaction.

[f] The reaction temperature was 70 °C.

[g] 0.2 mL DTBP was used.

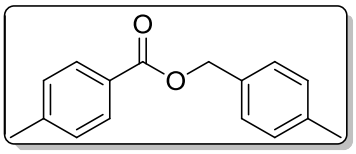
4 Characterization data of esters of tertiary Alcohols

Benzyl benzoate (Table 1, product **2a**)[3]



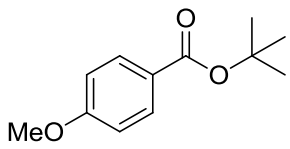
According to the general procedure A, compound **3a** was obtained in 90% yield.
Hexane: EtOAC = 20:1, R_f = 0.4
^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.12 (d, J = 7.3 Hz, 2 H), 7.58 (t, J = 7.4 Hz, 1 H), 7.49-7.35 (m, 7 H), 5.40 (s, 2 H) ppm.
GC-MS (EI, 70eV): 212.

4-Methylbenzyl 4-methylbenzoate (Table 1, **2b**)[4]



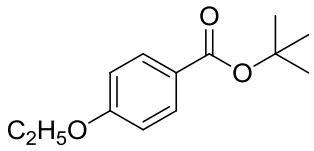
According to the general procedure A, compound **2b** was obtained in 89% yield.
Hexane: EtOAC = 20:1, R_f = 0.4
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 7.8 Hz, 2 H), 7.26-7.20 (m, 4 H), 5.32 (s, 2 H), 2.41 (s, 3 H), 2.37 (s, 3 H) ppm.
GC-MS (EI, 70eV): 240.

Tert-butyl 4-methoxybenzoate (Table 1, **3c**)[3]



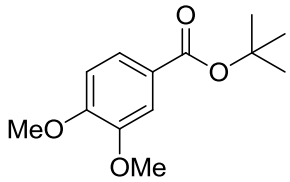
According to the general procedure, compound **3c** was obtained in 95% (98.8 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.3
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 9.0 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 3.85 (s, 3H), 1.59 (s, 9H)

Tert-butyl 4-ethoxybenzoate (Table 1, **3d**)



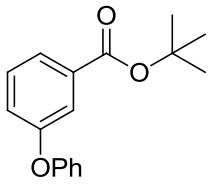
According to the general procedure, compound **3d** was obtained in 95% (103.3 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.27
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 4.08 (q, J = 7.0 Hz, 2H), 1.58 (s, 9H), 1.43 (t, J= 7.0 Hz, 3H)

Tert-butyl 3,4-dimethoxybenzoate (Table 1, **3e**)[3]



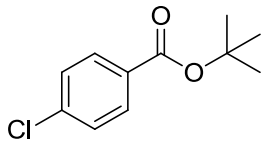
According to the general procedure, compound **3e** was obtained in 92% (109.5 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.15
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, J = 8.4, 2.0 Hz, 1H), 7.48 (d, J = 2.0 Hz, 1H), 6.83 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 1.56 (s, 9H)

Tert-butyl 3-phenoxybenzoate (Table 1, **3f**)



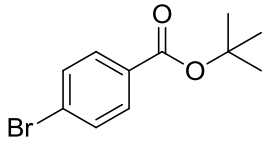
According to the general procedure, compound **3f** was obtained in 91% (123.0 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.4
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.71 (m, 1H), 7.63-7.62 (m, 1H), 7.38-7.33 (m, 3H), 7.17-7.12 (m, 2H), 7.01-6.99 (m, 2H), 1.57 (s, 9H)

Tert-butyl 4-chlorobenzoate (Table 1, **3g**)[3]



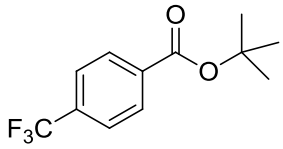
According to the general procedure, compound **3g** was obtained in 86% (91.2 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.4
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 1.62 (s, 9H)

Tert-butyl 4-bromobenzoate (Table 1, **3h**)[5]



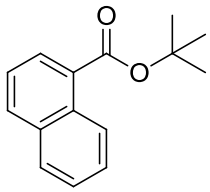
According to the general procedure, compound **3h** was obtained in 89% (114.0 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.4
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 8.6 Hz, 2H), 1.59 (s, 9H)

Tert-butyl 4-(trifluoromethyl)benzoate (Table 1, **3i**)[3]



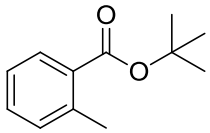
According to the general procedure, compound **3i** was obtained in 76% (93.5 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.35
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 8.6 Hz, 2H), 1.62 (s, 9H)

Tert-butyl 1-naphthoate (Table 1, **3k**)[3]



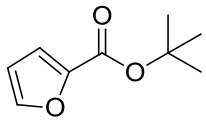
According to the general procedure, compound **3k** was obtained in 82% (93.5 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.4
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.85 (d, J = 8.2 Hz, 1H), 8.08 (dd, J = 7.3, 1.3 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.59-7.46 (m, 3H), 1.68 (s, 9H)

Tert-butyl 2-methylbenzoate (Table 1, **3l**) [3]



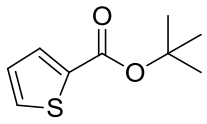
According to the general procedure, compound **3l** was obtained in 78% (74.9 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.4
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82-7.81 (m, 1H), 7.37-7.34 (m, 1H), 7.23-7.20 (m, 2H), 2.57 (s, 3H), 1.60 (s, 9H)

Tert-butyl furan-2-carboxylate (Table 1, **3o**)[3]



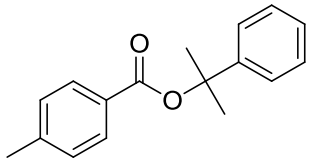
According to the general procedure, compound **3n** was obtained in 83% (69.7 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.4
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (q, J = 0.9 Hz, 1H), 7.08 (dd, J = 3.5, 0.9 Hz, 1H), 6.47 (q, J = 1.8 Hz, 1H), 1.59 (s, 9H)

Tert-butyl thiophene-2-carboxylate (Table 1, **3p**)[3]



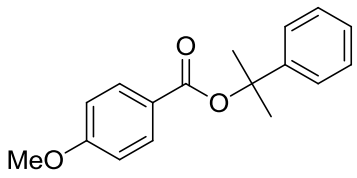
According to the general procedure, compound **3o** was obtained in 86% (79.1 mg) yield.
Hexane: EtOAC = 20:1, R_f = 0.4
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, J = 3.7, 1.3 Hz, 1H), 7.49 (dd, J = 5.0, 1.3 Hz, 1H), 7.08-7.06 (m, 1H), 1.59 (s, 9H)

2-phenylpropn-2-yl 4-methylbenzoate (Table 2, **3s**)



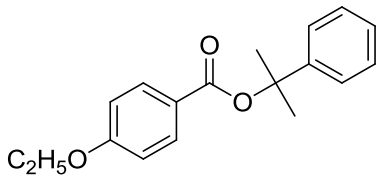
According to the general procedure, compound **3r** was obtained in 76% (96.5 mg) yield.
Colorless oil
Hexane: EtOAC = 20:1, R_f = 0.5
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.3 Hz, 2H), 7.47-7.44 (m, 2H), 7.38-7.35 (m, 2H), 7.29-7.25 (m, 3H), 2.43 (s, 3H), 1.94 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 146.0, 143.3, 129.7 (2C), 129.0 (2C), 128.4 (2C), 127.0, 125.9 (2C), 124.4, 82.0, 28.9 (2C), 21.7
GC-MS (EI, 70eV): 254.

2-phenylpropan-2-yl 4-methoxybenzoate (Table 2, **3t**)



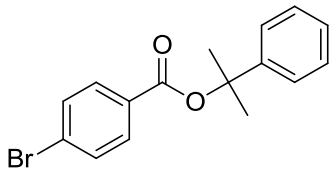
According to the general procedure, compound **3s** was obtained in 85% (114.8 mg) yield.
Colorless oil
Hexane: EtOAC = 20:1, R_f = 0.5
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.48-7.46 (m, 2H), 7.38-7.35 (m, 2H), 7.30-7.26 (m, 1H), 6.96-6.94 (m, 2H), 3.88 (s, 3H), 1.94 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 163.2, 146.1, 131.6 (2C), 128.4 (2C), 127.0 (2C), 124.3, 124.0, 113.6 (2C), 81.8, 55.5, 28.9 (2C);
GC-MS (EI, 70eV): 270.

2-phenylpropan-2-yl 4-ethoxybenzoate (Table 2, **3u**)



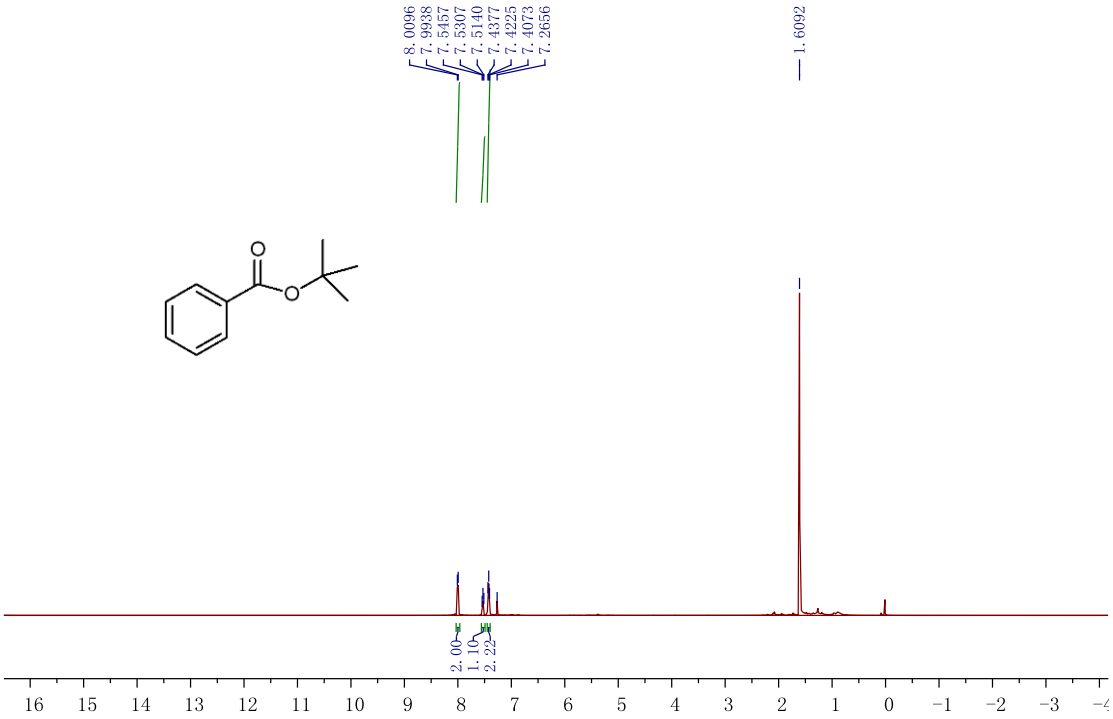
According to the general procedure, compound **3t** was obtained in 83% (117.9 mg) yield.
Colorless oil
Hexane: EtOAC = 20:1, R_f = 0.5
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04-8.02 (m, 2H), 7.47-7.45 (m, 2H), 7.38-7.35 (m, 2H), 7.29-7.27 (m, 1H), 6.94-6.92 (m, 2H), 3.88 (s, 3H), 4.11 (q, J = 7.0 Hz, 2H), 1.94 (s, 6H), 1.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 162.6, 146.1, 131.6 (2C), 128.3 (2C), 127.0 (2C), 124.3, 123.8, 114.0 (2C), 81.8, 63.7, 28.9, 14.8;
GC-MS (EI, 70eV): 284.

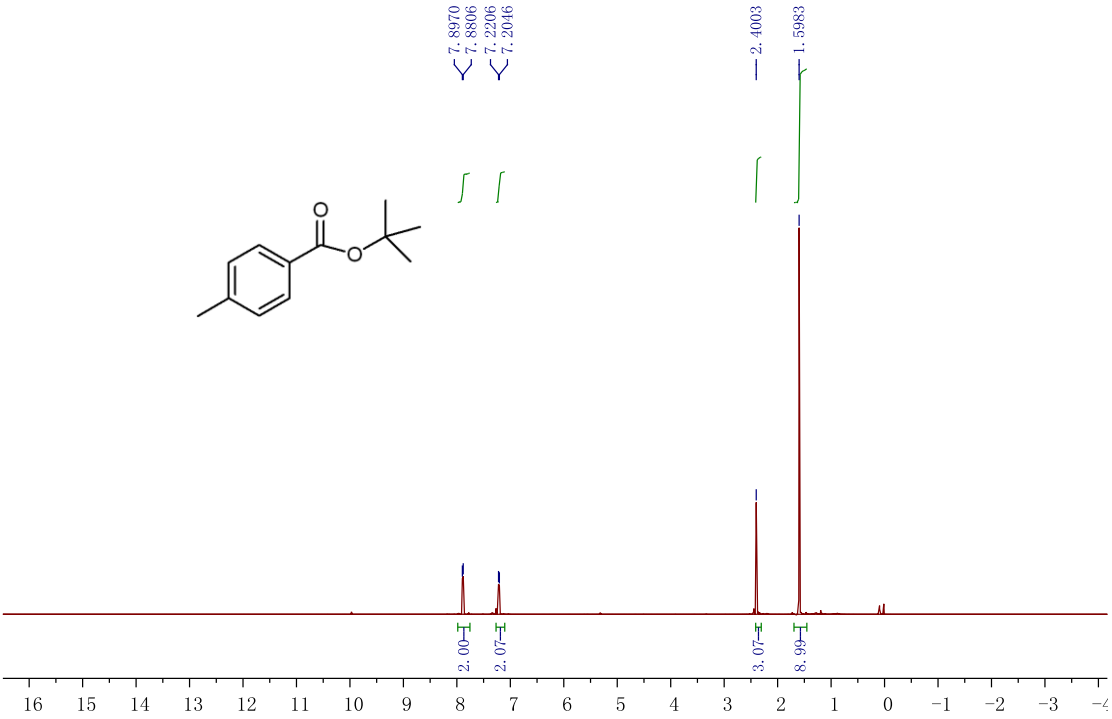
2-phenylpropn-2-yl 4-bromobenzoate (Table 2, **3v**)

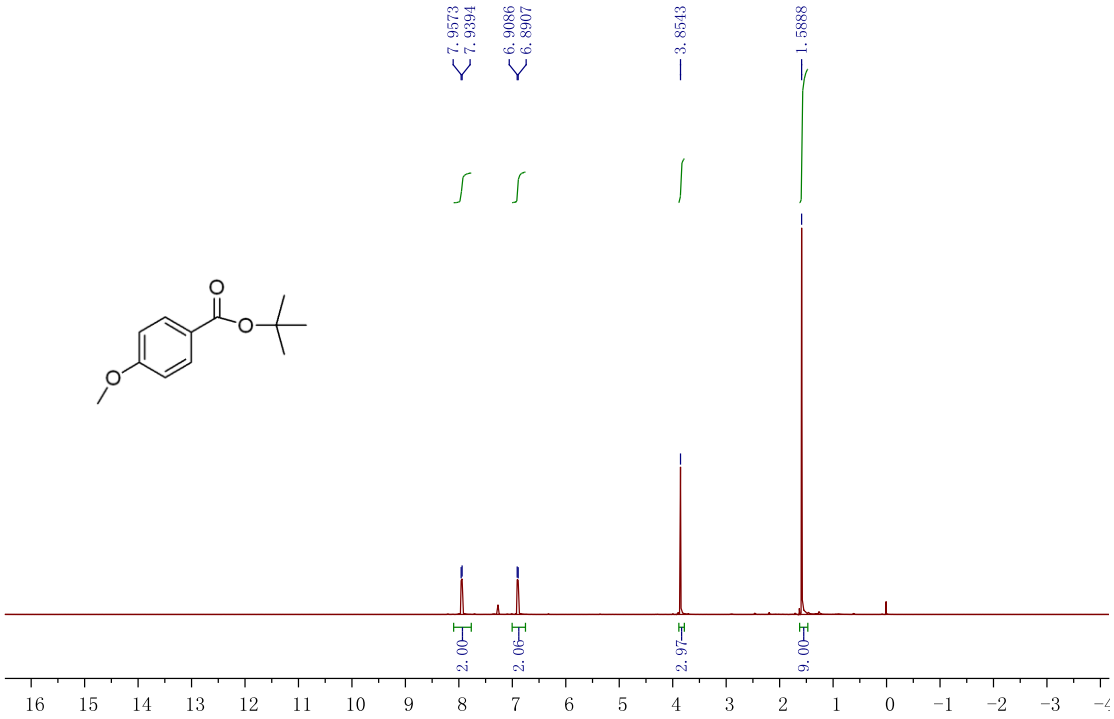


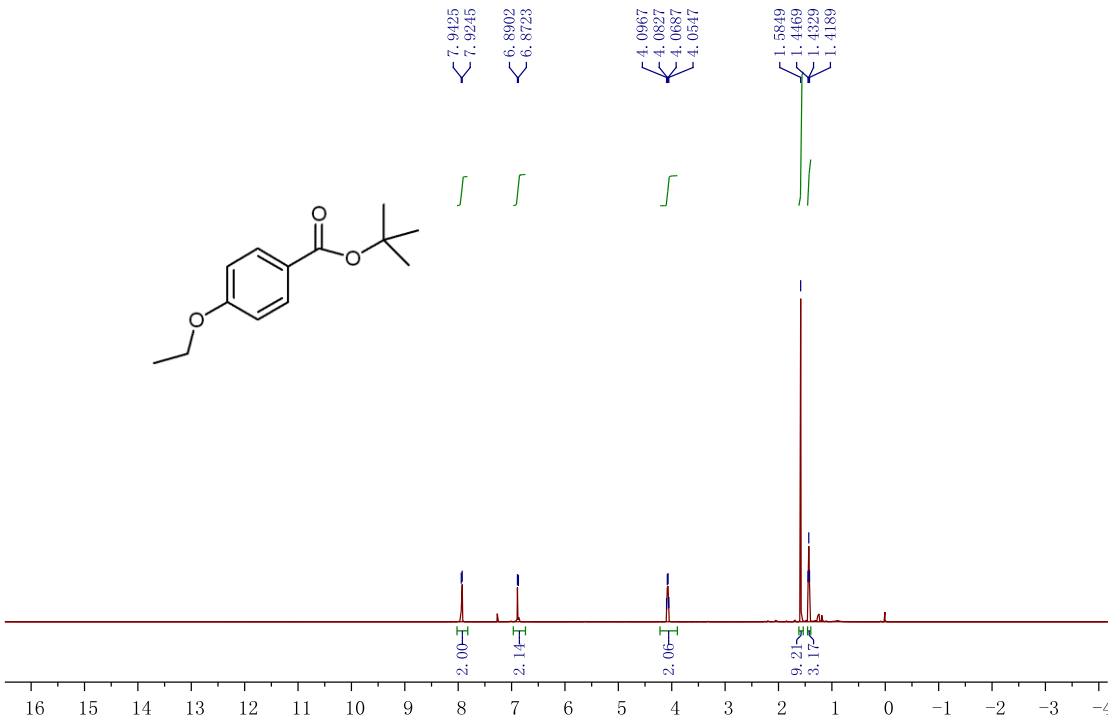
According to the general procedure, compound **3u** was obtained in 74% (117.7 mg) yield.
Colorless oil
Hexane: EtOAC = 20:1, R_f = 0.5
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.57-7.56 (m, 2H), 7.42-7.40 (m, 2H), 7.35-7.32 (m, 2H), 7.27-7.24 (m, 1H), 1.91 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 145.6, 131.6 (2C), 131.1 (2C), 130.4, 128.4 (2C), 127.8, 127.2 (2C), 124.3, 82.7, 28.7 (2C)
GC-MS (EI, 70eV): 318.

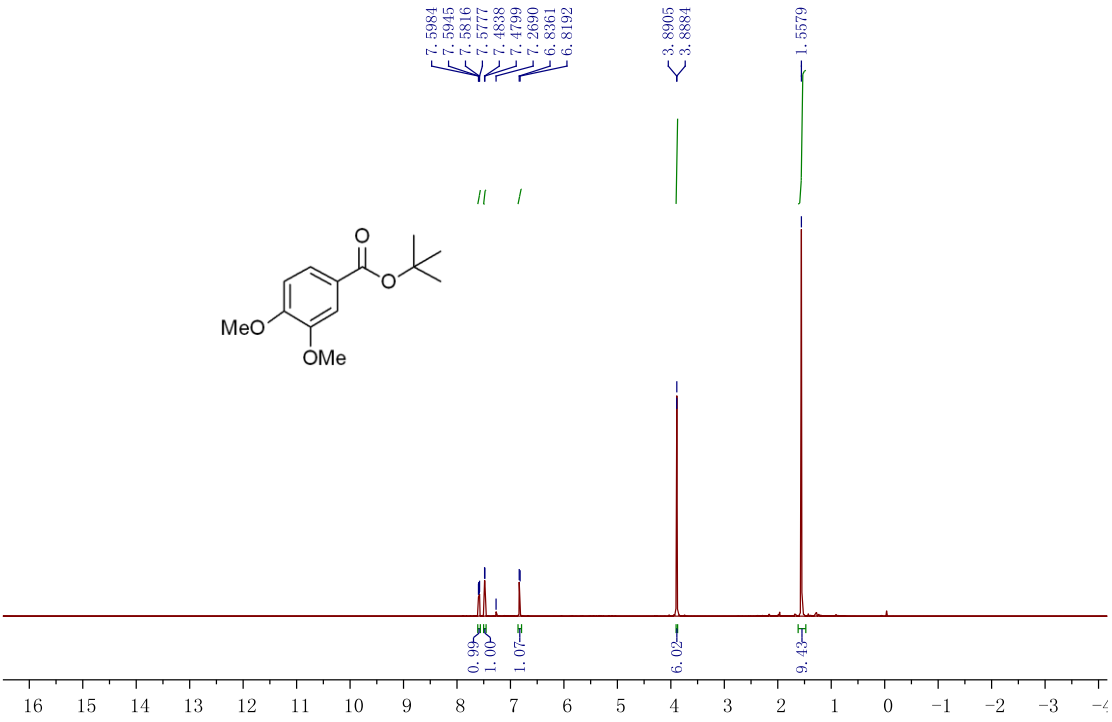
5. ^{1}H and ^{13}C NMR spectra







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7.5816
7.5777
7.4838
7.4799
7.2690
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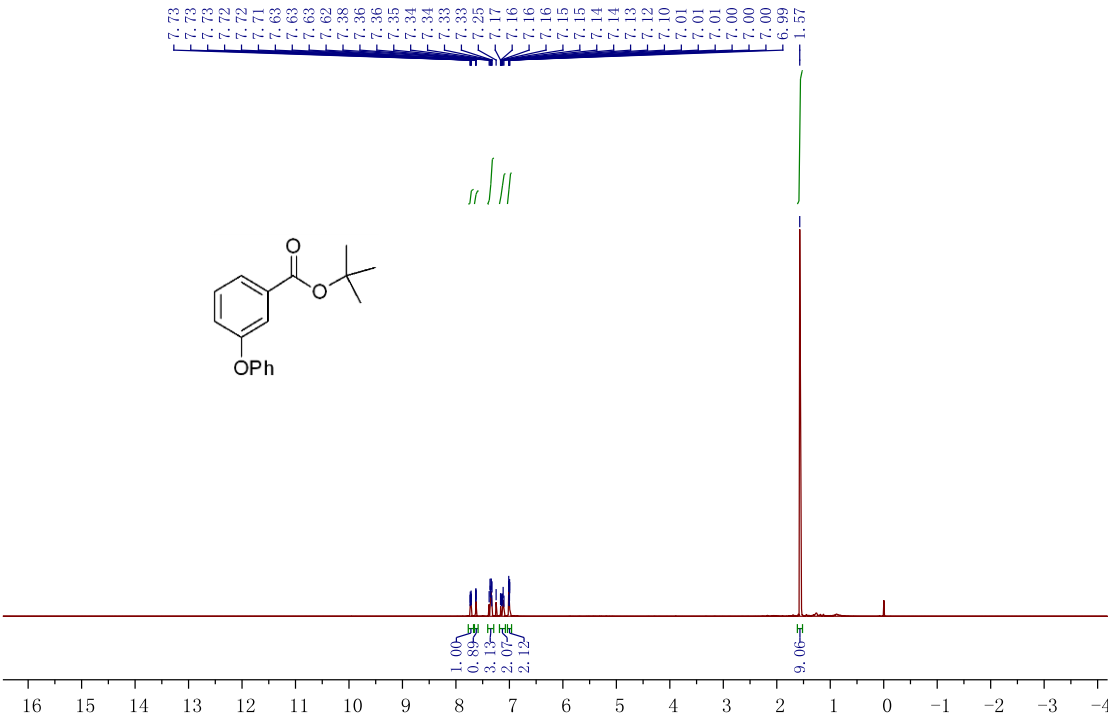
1.5579
MeO
OMe
0.99
1.00
1.07
6.02
9.43
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3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7.36
7.35
7.34
7.34
7.33
7.33
7.25
7.17
7.16
7.16
7.16
7.15
7.15
7.14
7.14
7.13
7.12
7.10
7.01
7.01
7.01
7.00
7.00
7.00
6.99
1.57
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2.12
9.06
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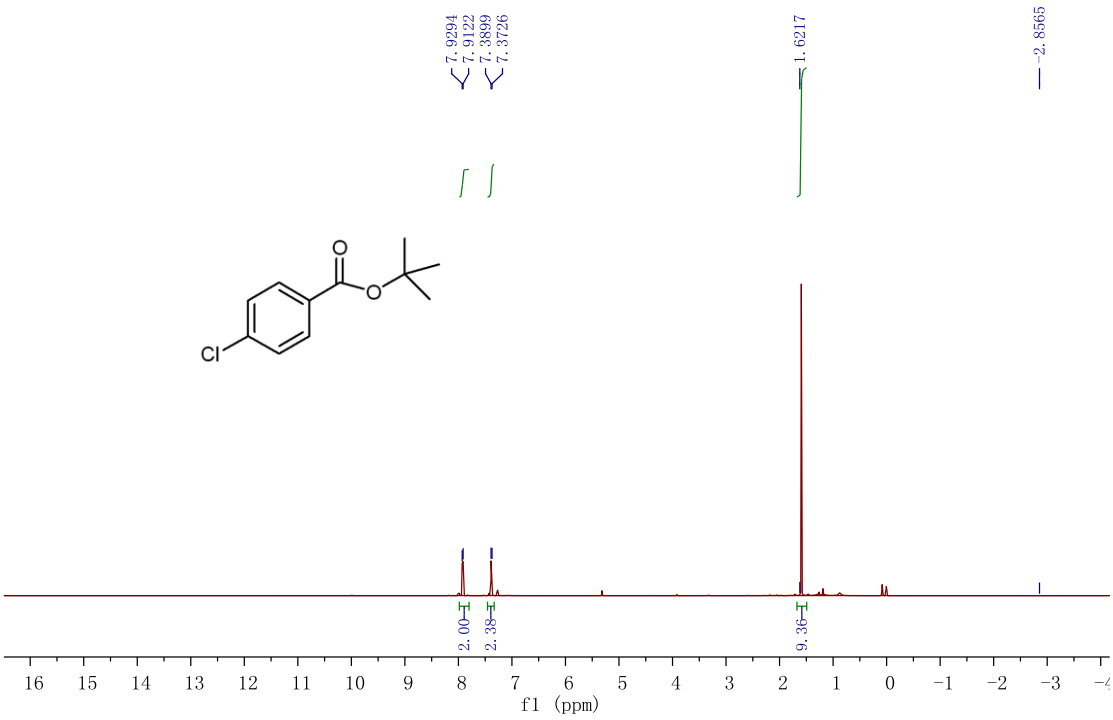
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Cl
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O
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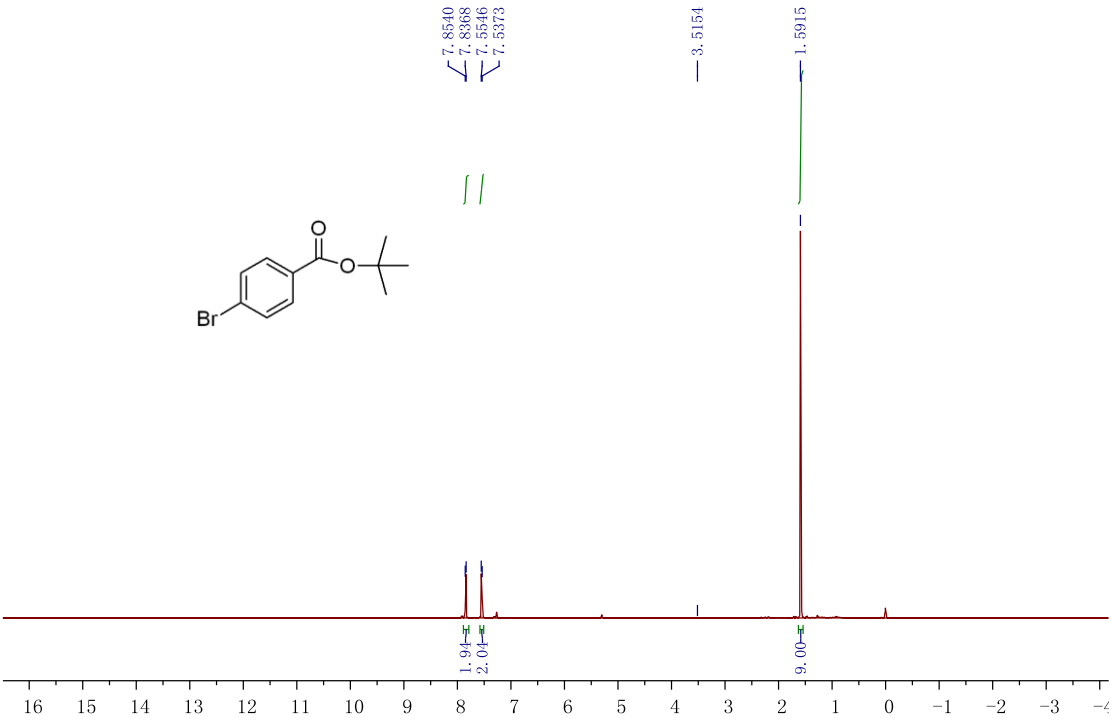
f1 (ppm)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Br
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O
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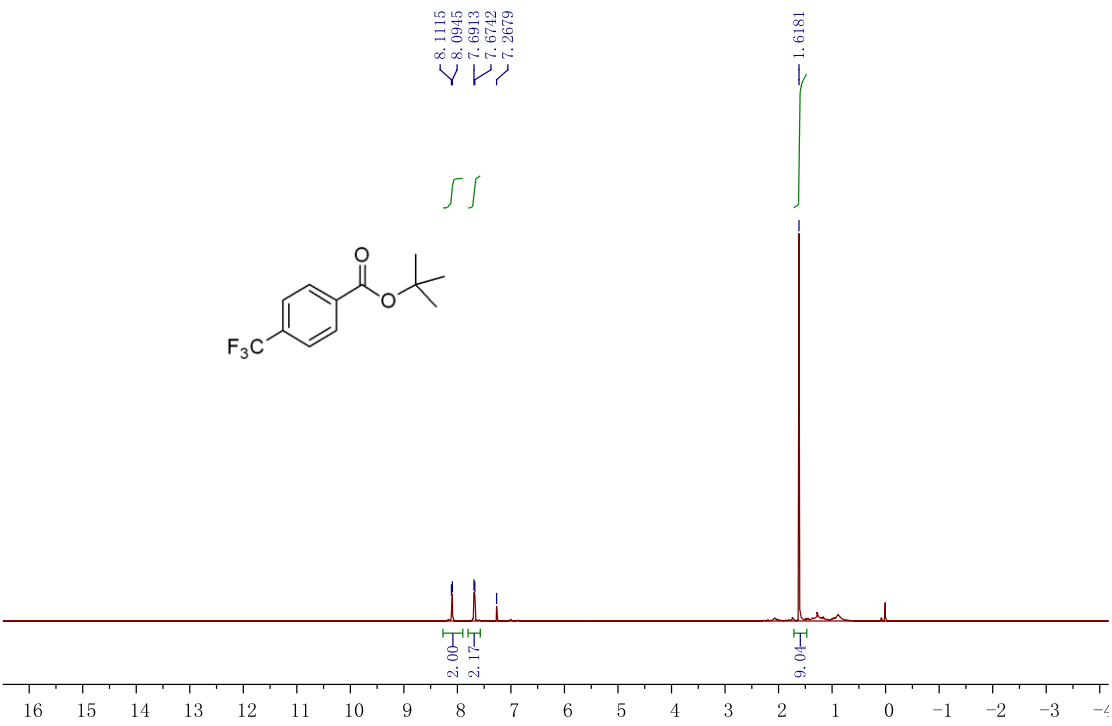
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O
O
F3C
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2.17
9.04
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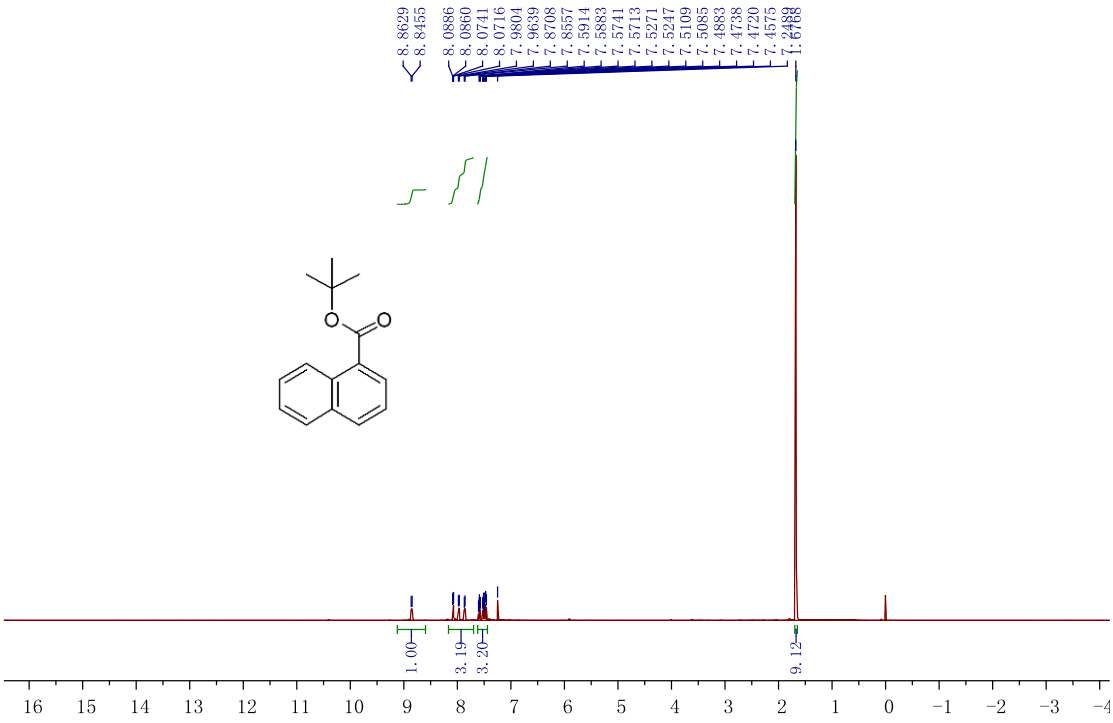
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7.4720
7.4575
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O
O
1.00
3.19
3.20
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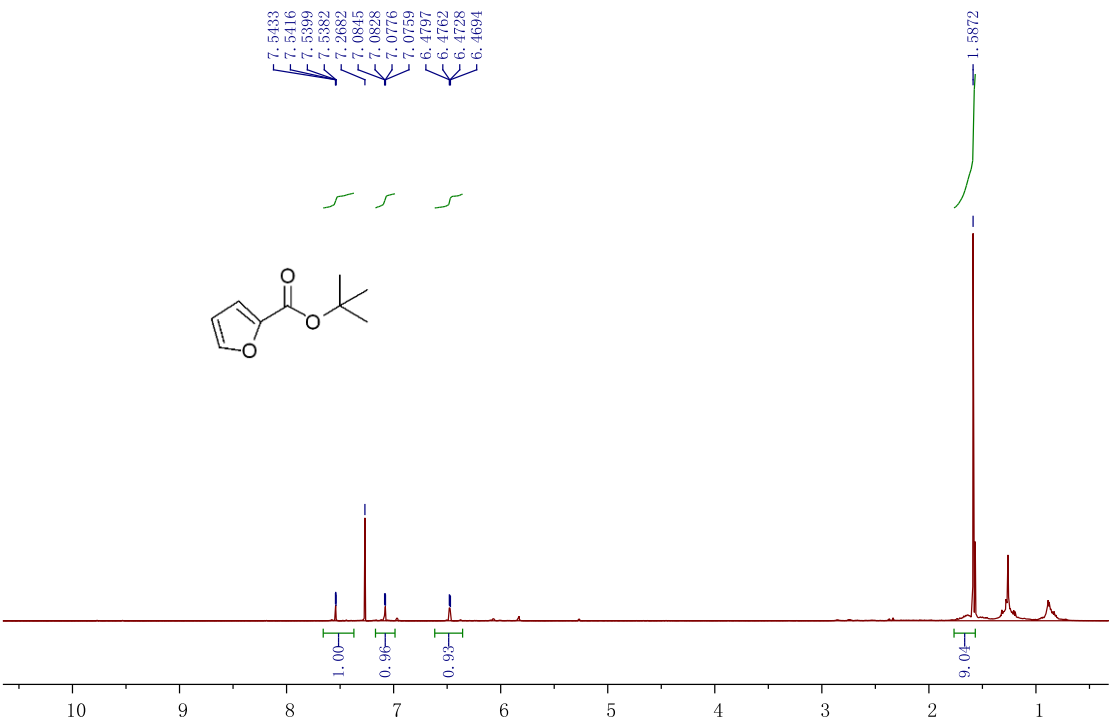
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4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6.4728
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9
8
7
6
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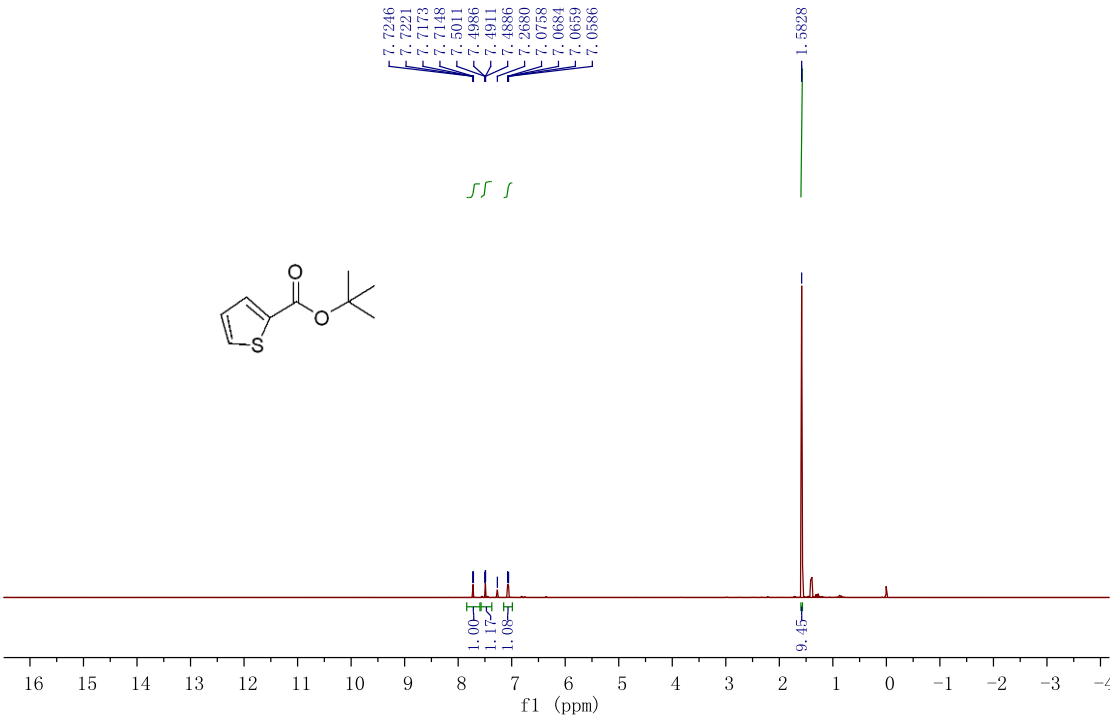
4
3
2
1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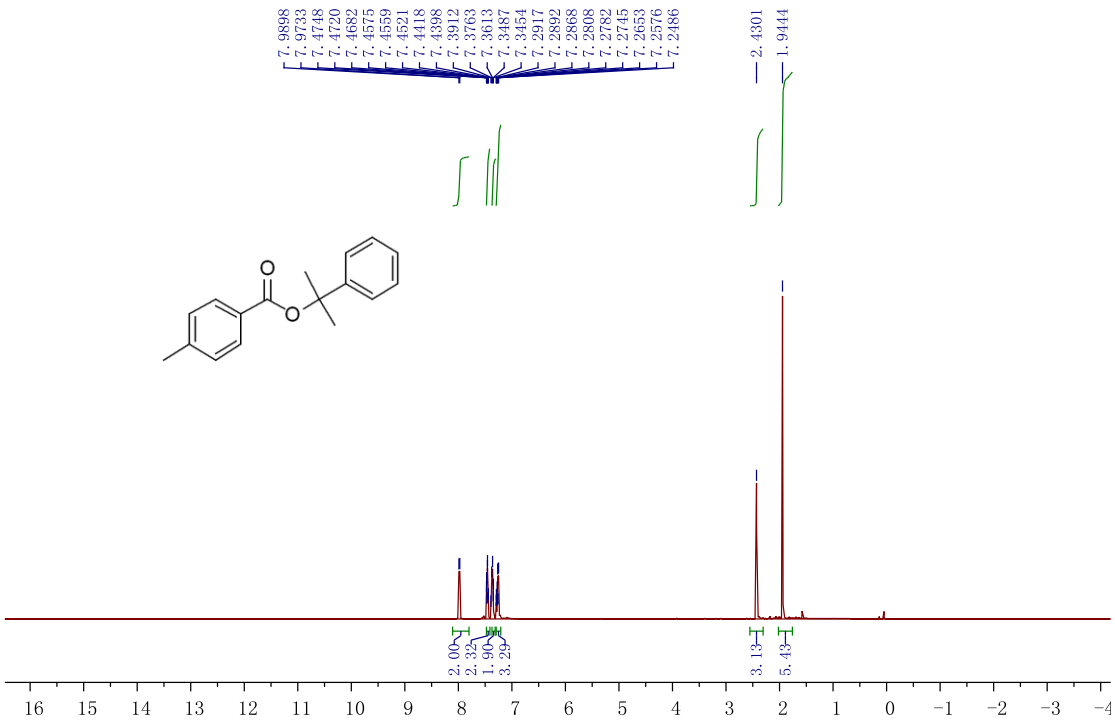
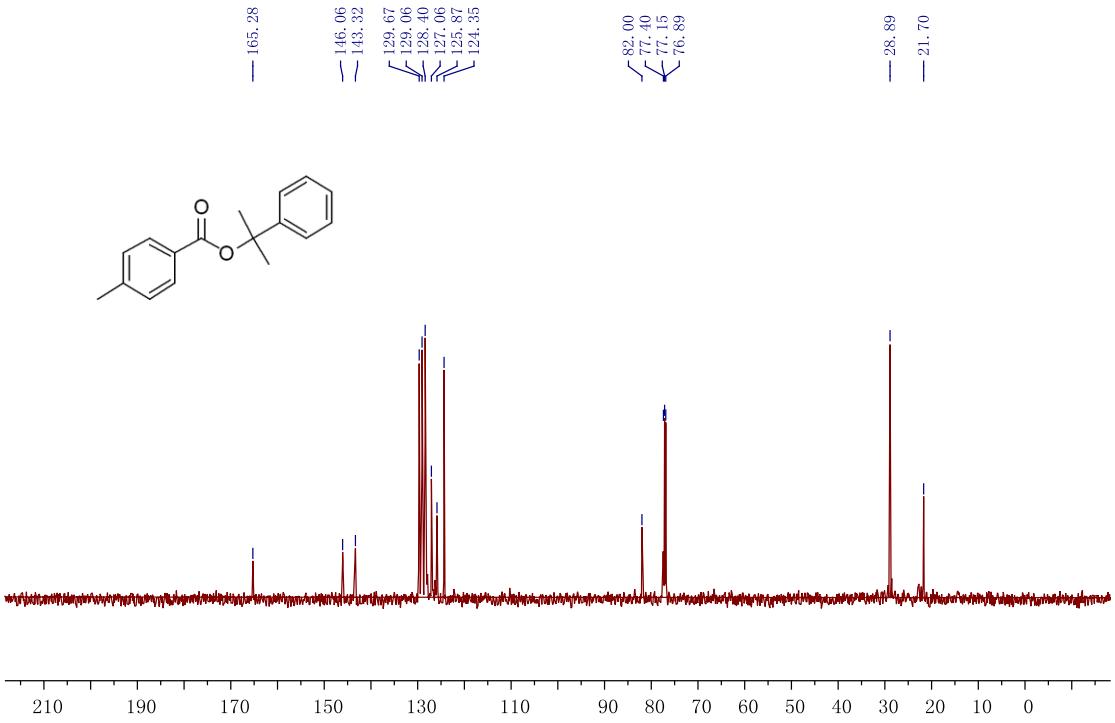
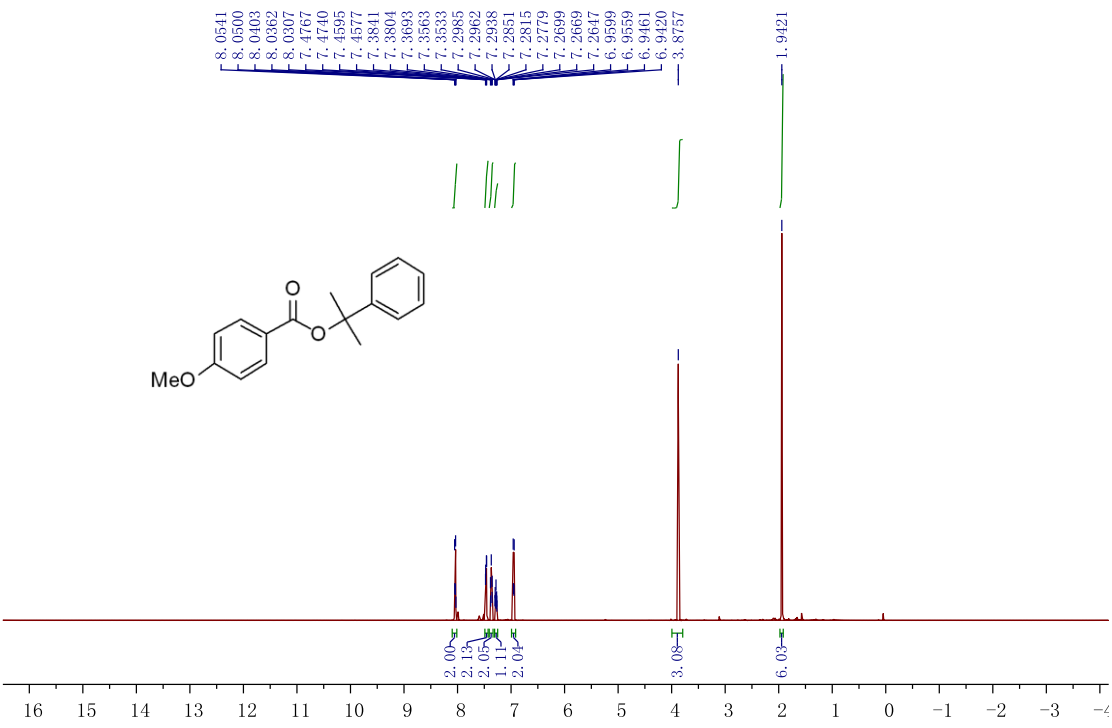
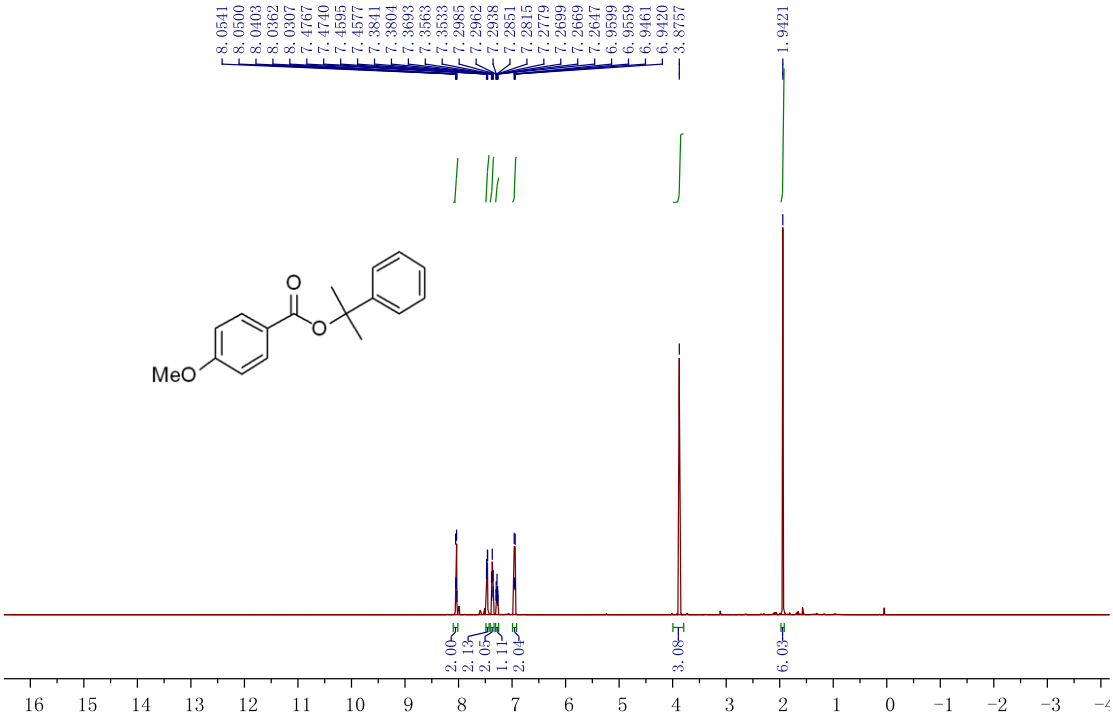
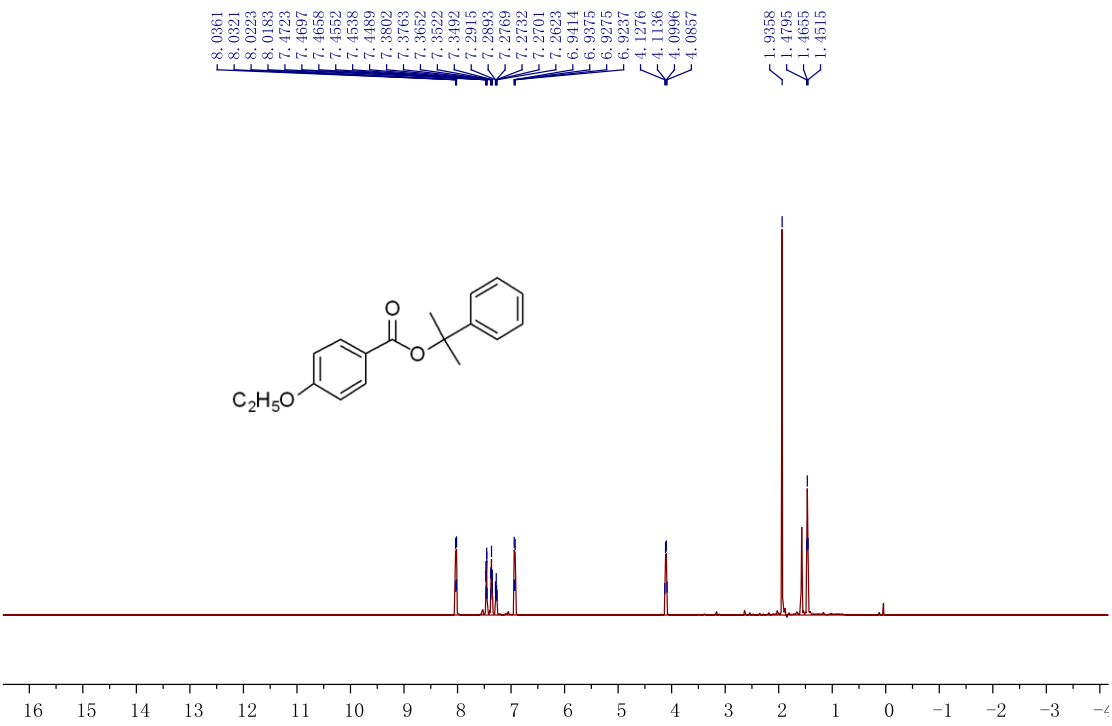
7.0586
1.5828
1.00
1.17
1.08
9.45
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

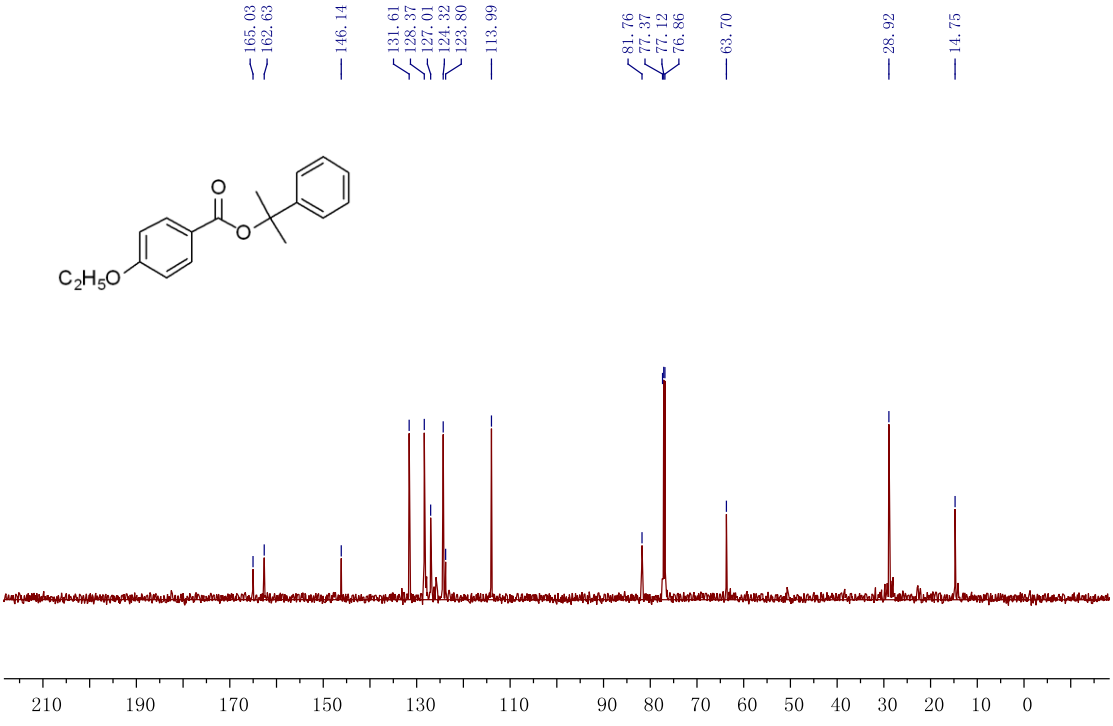


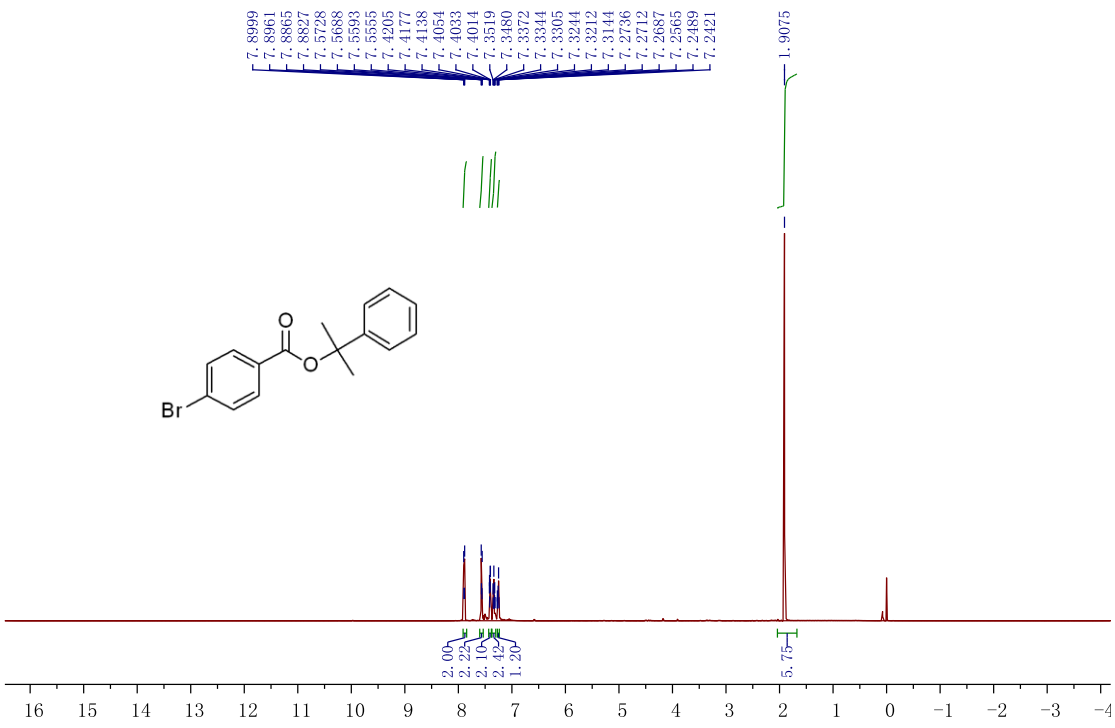


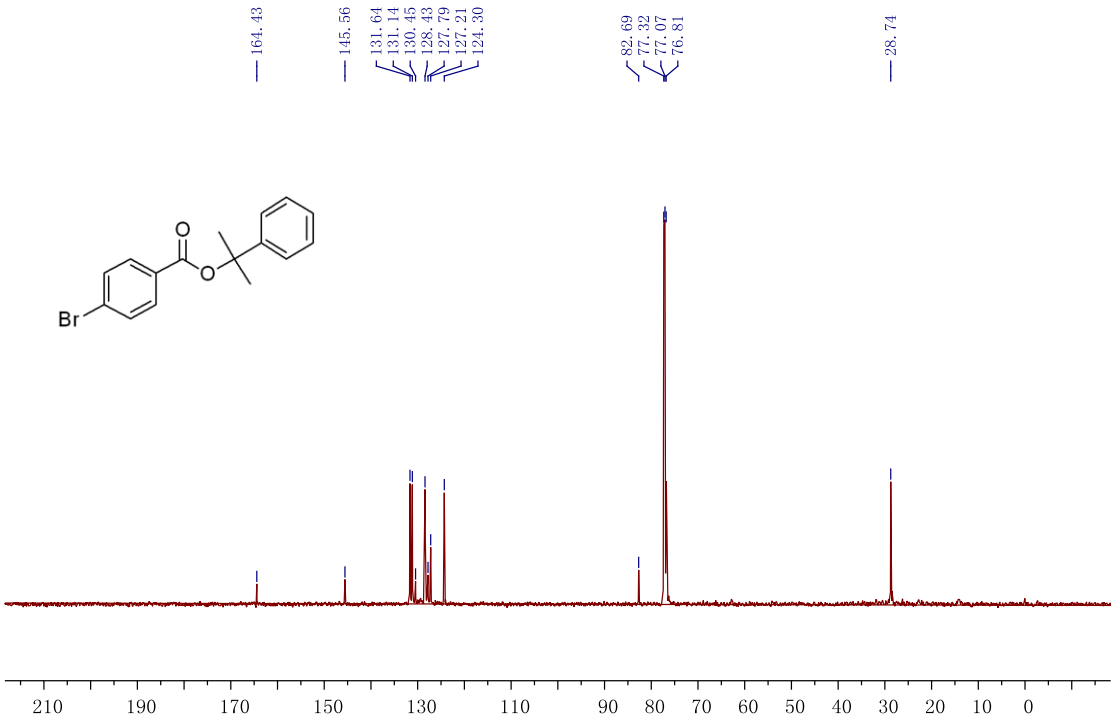


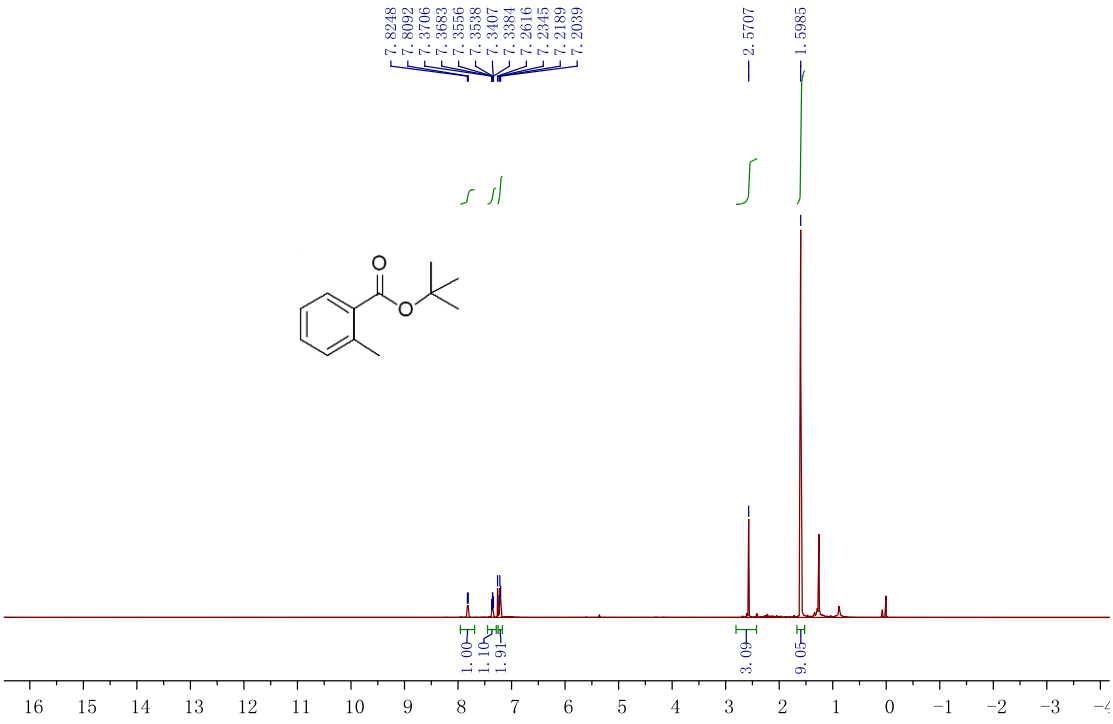








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1.5985
1.00
1.10
1.91
3.09
9.05
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3

6. References

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