Electronic Supplementary Material (ESI) for Green Chemistry.

Visible-light induced oxidative Csp3-H activation of methyl aromatics to methyl esters

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1. General Information

All manipulations were carried out by standard Schlenk techniques. Unless otherwise noted, analytical grade solvents and commercially available reagents were used to conduct the reactions. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (boiling point is between 60-90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient using petroleum ether and ethyl acetate. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. GC-MS spectra were recorded on a Varian GC-MS 3900-2100T. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance III 400 MHz NMR spectrometer with tetramethylsilane as an internal standard. The chemical shifts (δ) were given in part per million relative to internal tetramethyl silane (TMS, 0 ppm for ^{1}H), $CDCl_3$ (77.3 ppm for ^{13}C). The photocatalyst Acr^{+} Mes ClO_4^{-} is commercial available from the company of TokyoChemicalIndustry (TCI). The CAS number is 674783-97-2. The source of the blue LEDs is common LED lights. The power of each blue light is 3W. There is 3.0 cm distance between the reactor and LEDs. This reaction could be well-performed using a round bottle (25 mL). Below you will add two pictures of our instrument.

2. General Procedures for Synthesizing Ester Derivatives

2.1 Visible Light Mediated Aerobic Oxidative Direct Esterification in the Presence of HCl

In a dried schlenk tube, methyl arenes **1** (0.3 mmol), Acr^+ - Mes ClO_4^- (7 mol%, 0.021 mmol) and HCl (20 mol%, 0.06 mmol) were stirred in 2.0 mL ROH for 30 hours at room temperature under an atmospheric pressure oxygen atmosphere s irradiated by blue LEDs. After completion of the reaction, the mixture was diluted by ethyl acetate. The pure product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate. The yields of EtOH and iPrOH were determined by NMR.

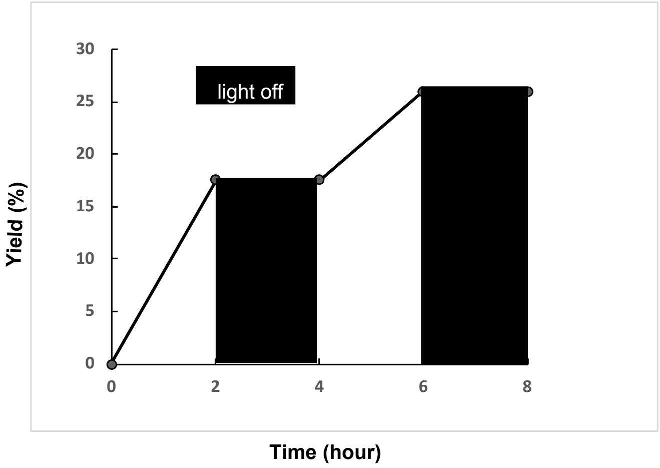
2.2 Procedure for the Gram-Scale Synthesis of Methyl Ester

In a dried schlenk tube, 1-(*tert*-butyl)-4-methylbenzene **1f** (10 mmol), Acr^+ - Mes ClO_4^- (7 mol%) and HCl (20 mol%) were stirred in 10 mL MeOH for 30 hours at room temperature under an atmospheric pressure oxygen atmosphere s irradiated by blue LEDs. After completion of the reaction, as indicated by TLC and GC-MS, the mixture was diluted by ethyl acetate. The pure product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate.

3. Mechanism Studies

3.1 Time Profile of Photocatalytic Reaction with and without Visible Light.

A solution of the *p*-xylene **1a** (0.3 mmol), and Acr^+ - Mes ClO_4^- (7 mol%, 0.021 mmol) were stirred in 2 mL MeOH at room temperature under an atmospheric pressure oxygen atmosphere. The process of photocatalytic reaction with and without light was monitored by GC using biphenyl as internal standard.



3.2 Radical-inhibiting Experiment

In a dried schlenk tube, *p*-xylene **1a** (0.3 mmol), Acr$^+$ - Mes ClO$_4^-$ (7 mol%, 0.021 mmol) 2,2,6,6-tetramethlpiperidinooxy (TEMPO, 0.6 mmol) and HCl (20 mol%, 0.06 mmol) were stirred in 2.0 mL MeOH for 30 hours at room temperature under an atmospheric pressure oxygen atmosphere s irradiated by blue LEDs. After completion of the reaction, the mixture was detected by GC.

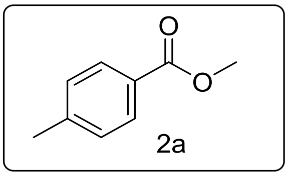
3.3 Visible Light Mediated Aerobic Oxidative Direct Esterification between Aldehyde 6 and MeOH

In a dried schlenk tube, p-tolualdehyde **6** (0.3 mmol), Acr$^+$ - Mes ClO$_4^-$ (7 mol%, 0.021 mmol) and HCl (20 mol%, 0.06 mmol) were stirred in 2.0 mL MeOH for 30 hours at room temperature under an atmospheric pressure oxygen atmosphere s irradiated by blue LEDs. After completion of the reaction, as indicated by TLC and GC-MS, the mixture was diluted by ethyl acetate. The pure product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl acetate.

3.4 Visible Light Mediated Aerobic Oxidative Direct Esterification between 4-methylphenylene 7 and MeOH

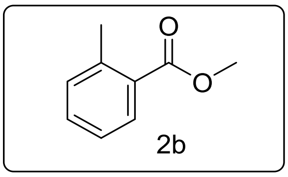
In a dried schlenk tube, 4-methylphenylene **7** (0.3 mmol), Acr$^+$ - Mes ClO$_4^-$ (7 mol%, 0.021 mmol) and HCl (20 mol%, 0.06 mmol) were stirred in 2.0 mL MeOH for 30 hours at room temperature under an atmospheric pressure oxygen atmosphere s irradiated by blue LEDs. After completion of the reaction, as indicated by TLC and GC-MS, the mixture was diluted by ethyl acetate. The pure product was obtained by flash column chromatography on silica gel using petroleum ether and ethyl ace

Characterization of Products



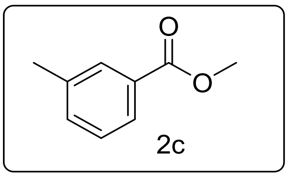
2a

Methyl 4-methylbenzoate (**2a**): [1] 32.9 mg (yield: 73%, light yellow oil). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.73 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.0, 143.5, 129.6, 129.0, 127.4, 51.8, 21.5.



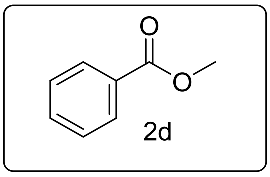
2b

Methyl 2-methylbenzoate (**2b**): [1] 39.2 mg (yield: 87%, colorless oil). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 – 7.87 (m, 1H), 7.40 (m, 1H), 7.24 (dd, *J* = 10.0, 4.6 Hz, 2H), 3.89 (s, 3H), 2.60 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 168.3, 140.4, 132.2, 131.9, 130.8, 129.8, 125.9, 52.1, 22.0.



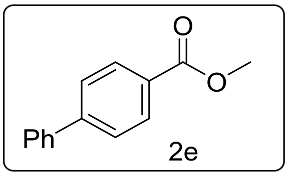
2c

Methyl 3-methylbenzoate (**2c**): [1] 21.2 mg (yield: 47%, colorless oil). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 – 7.80 (m, 2H), 7.34 (m, 2H), 3.91 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.6, 138.4, 133.9, 130.4, 130.3, 128.5, 126.9, 52.3, 21.5.



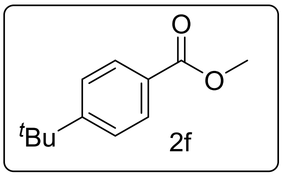
2d

Methyl benzoate (**2d**): [1] 8.6 mg (yield: 21%, colorless oil). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 (m, 2H), 7.60 – 7.51 (m, 1H), 7.47 – 7.38 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.3, 133.1, 130.4, 129.8, 128.6, 52.3.



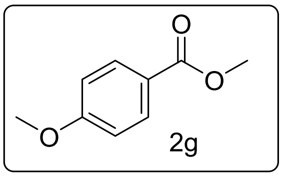
2e

Methyl [1,1'-biphenyl]-4-carboxylate(**2e**):[1] 42.6 mg (yield: 67%, colorless powder). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.14 – 8.07 (m, 2H), 7.70 – 7.59 (m, 4H), 7.47 (dd, *J* = 10.1, 4.7 Hz, 2H), 7.43 – 7.37 (m, 1H), 3.94 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.3, 145.9, 140.3, 130.4, 129.2, 129.1, 128.4, 127.6, 127.3, 52.4.



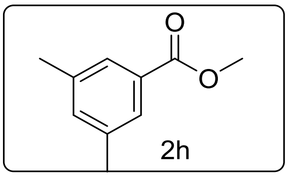
2f

Methyl 4-(tert-butyl)benzoate (**2f**):[2] 44.4 mg (yield: 77%, colorless solid). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.4, 156.7, 129.7, 127.6, 125.6, 52.2, 35.3, 31.4.



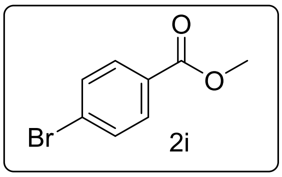
2g

Methyl 4-methoxybenzoate (**2g**):[1] 32.4 mg (yield: 65%, colorless solid). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.1, 163.6, 131.8, 122.8, 113.8, 55.7, 52.2.



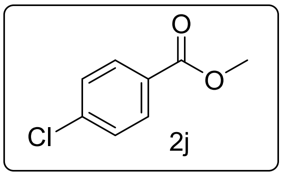
2h

Methyl 3,5-dimethylbenzoate (**2h**):[3] 31.0 mg (yield: 63%, colorless oil). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.66 (s, 2H), 7.18 (s, 1H), 3.90 (s, 3H), 2.35 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.7, 138.3, 134.8, 130.2, 127.5, 52.3, 21.4.



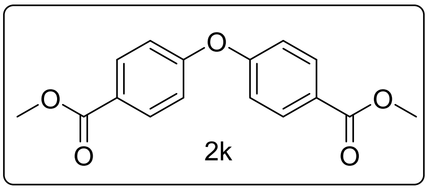
2i

Methyl 4-bromobenzoate (**2i**):[1] 39.8 mg (yield: 62%, colorless solid). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 (d, *J* = 7.9 Hz, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.6, 132.0, 131.4, 129.3, 128.3, 52.6.



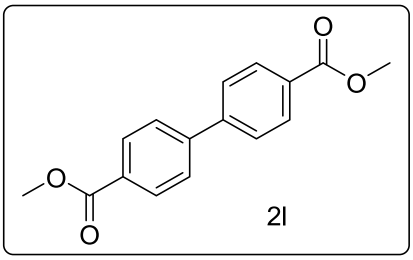
2j

Methyl 4-chlorobenzoate (**2j**):[2] 25.5 mg (yield: 50%, colorless oil). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.5, 139.6, 131.2, 129.0, 128.8, 52.6.



2k

Dimethyl 4,4'-oxydibenzoate (**2k**):[2] 77.2 mg (yield: 90%, colorless solid). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, *J* = 8.7 Hz, 4H), 7.06 (d, *J* = 8.7 Hz, 4H), 3.91 (s, 6H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 166.6, 160.3, 132.1, 125.9, 118.8, 52.4.



2l

Dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate (**2l**):[2] 61.6 mg (yield: 76%, colorless solid). ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, *J* = 8.5 Hz, 4H), 7.69 (d, *J* = 8.5 Hz, 4H), 3.95 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.1, 144.6, 130.5, 130.0, 127.5, 52.5.

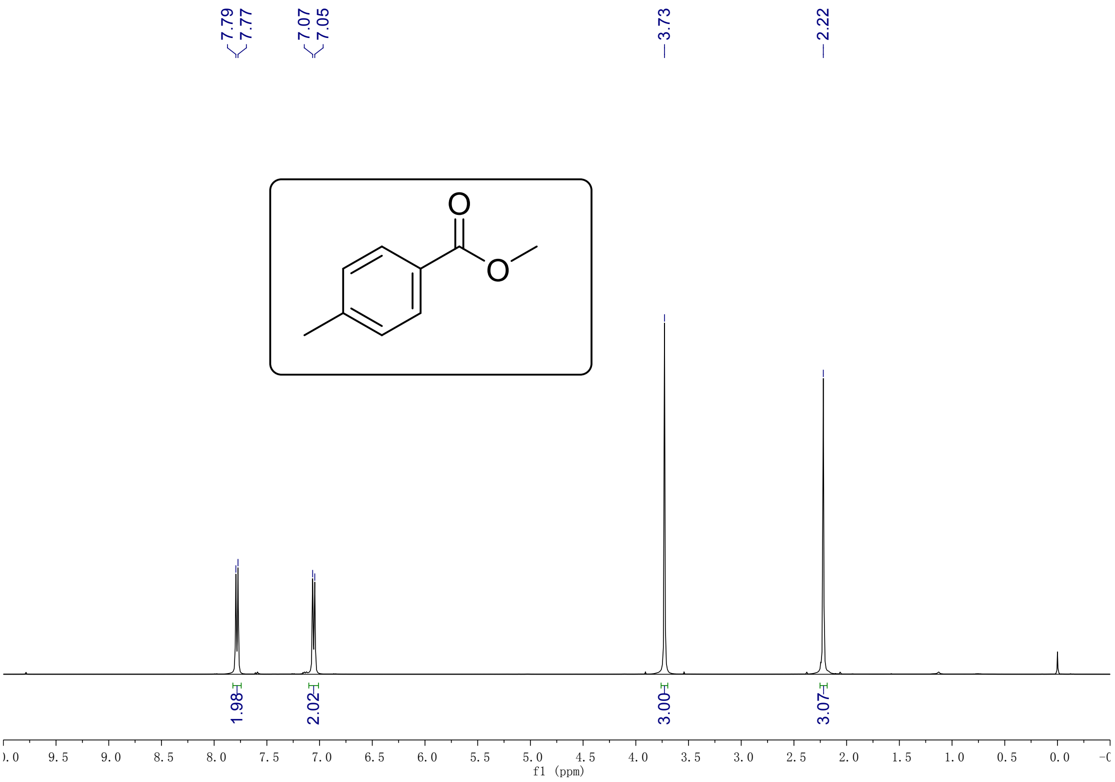
Reference

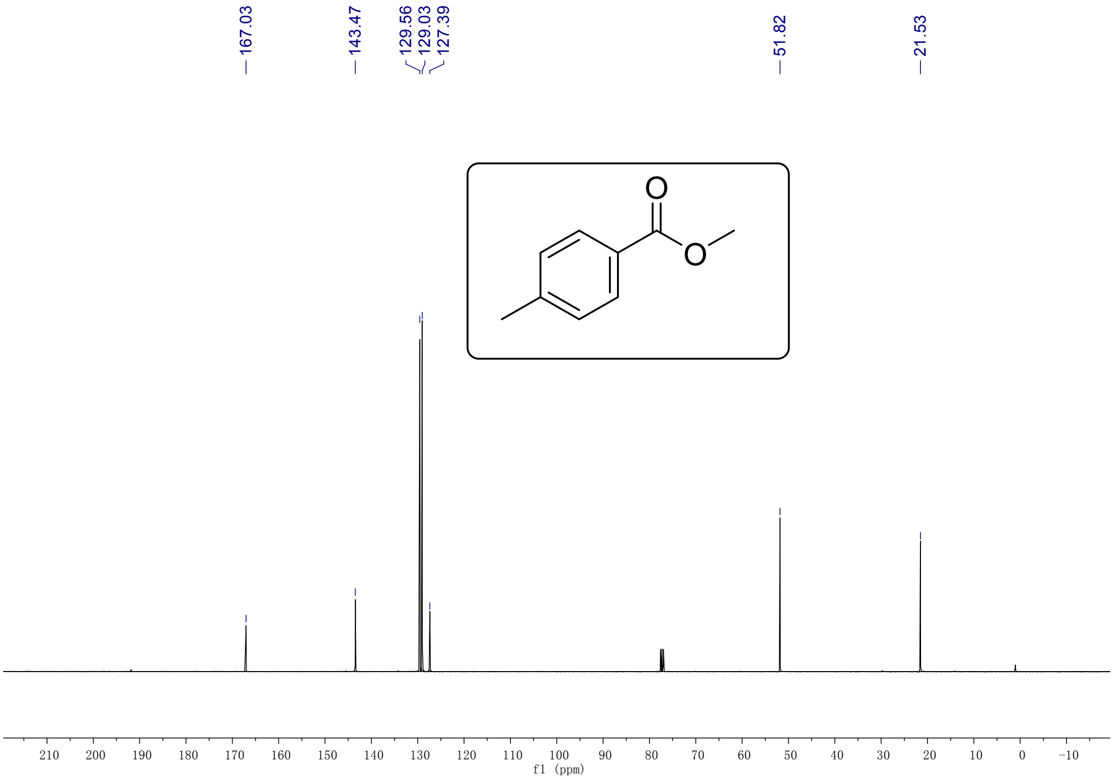
[1] Liu, H.; Chen, G.; Jiang, H.; Li, Y.; Luque, R., *ChemSusChem.* **2012,** *5* , 1892-1896.

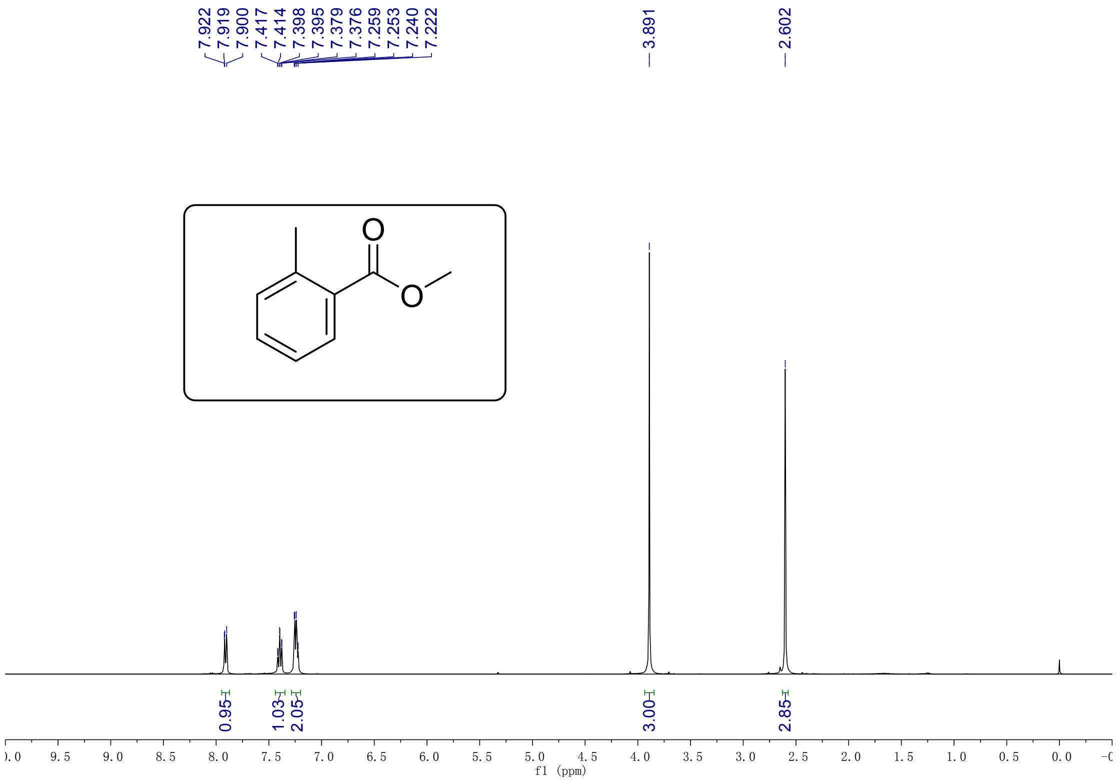
[2] Tada, N.; Ikebata, Y.; Nobuta, T.; Hirashima, S.-i.; Miura, T.; Itoh, A., *Photochem. Photobiol. Sci.* **2012,** *11* , 616-619.

[3] Aavula, S. K.; Chikkulapalli, A.; Hanumanthappa, N.; Jyothi, I.; Vinod Kumar, C. H.; Manjunatha, S. G., *Tetrahedron Letters.* **2013,** *54* , 5690-5694.

NMR Spectra of Products



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2.05
3.00
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9.0
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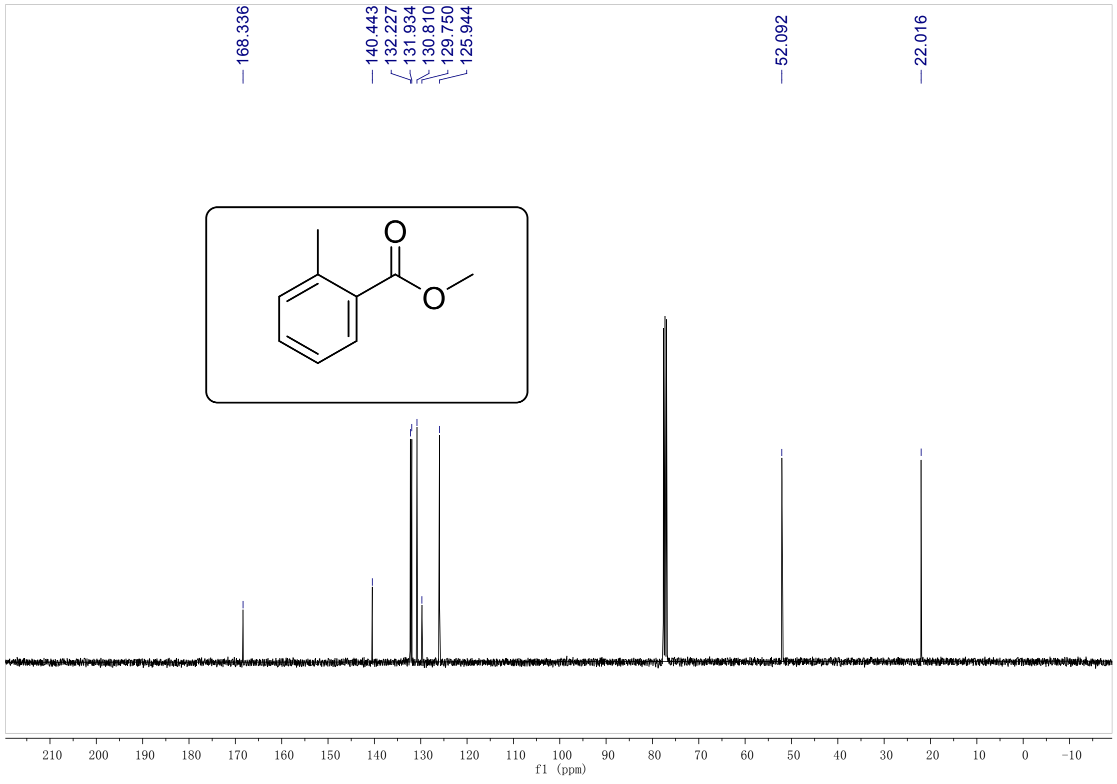
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30
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10
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f1 (ppm)


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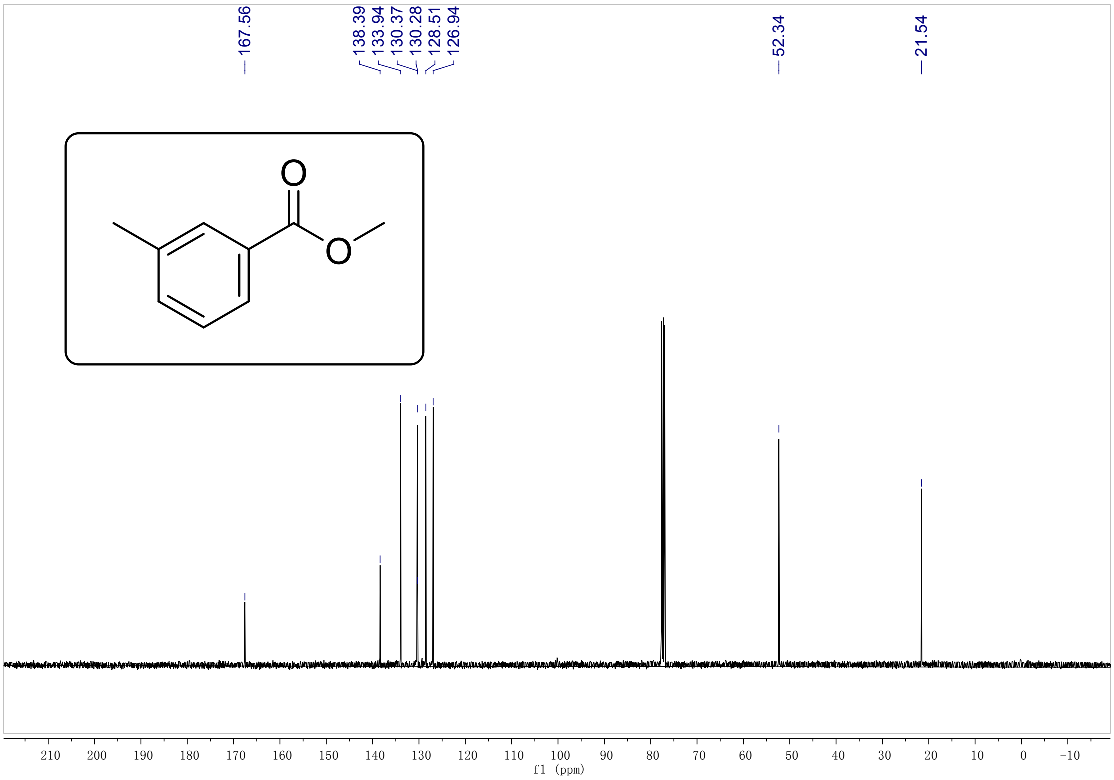
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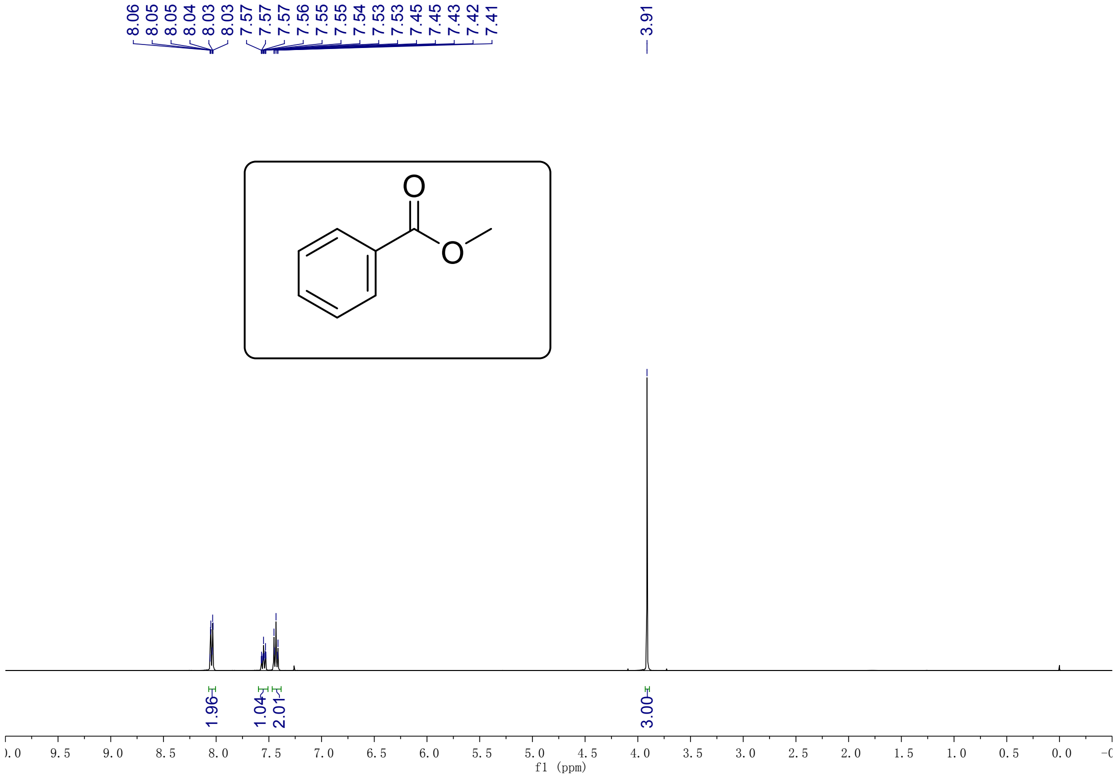
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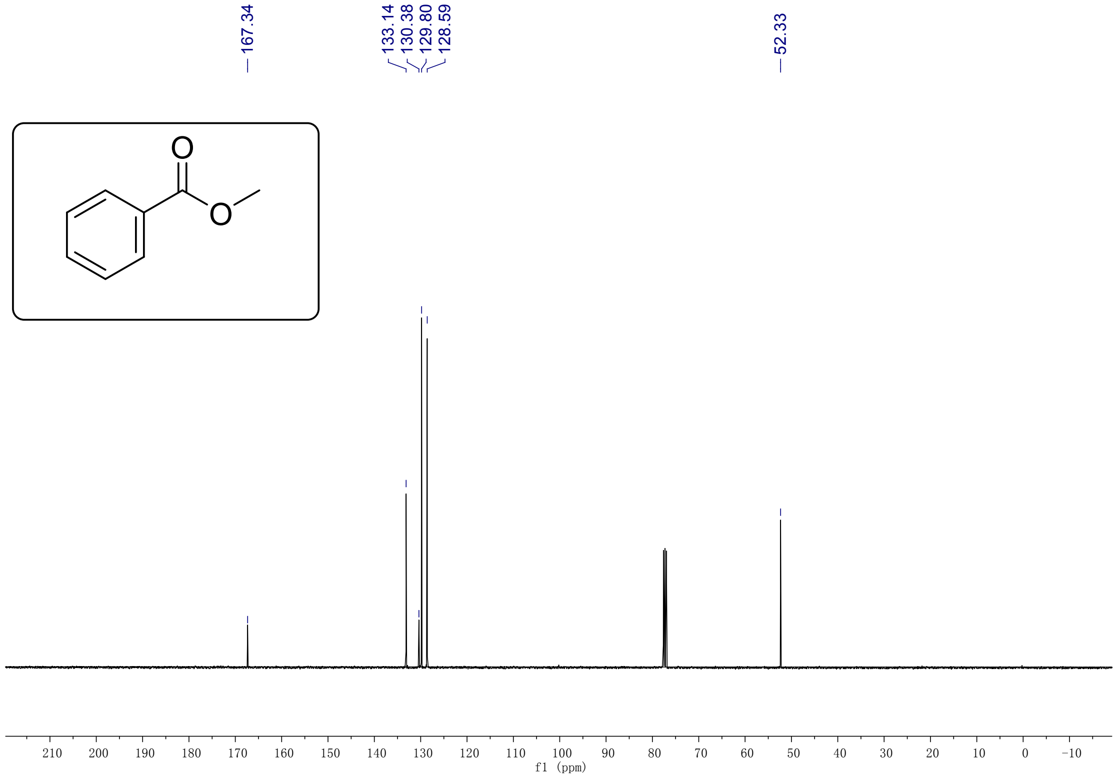
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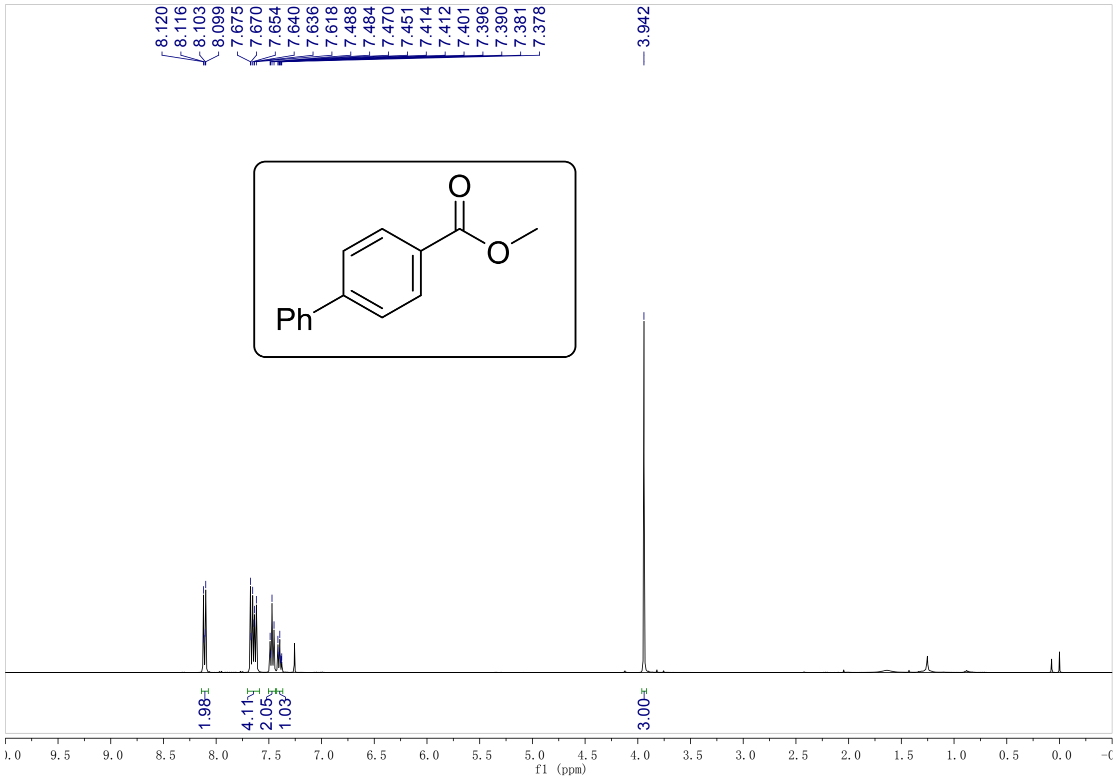
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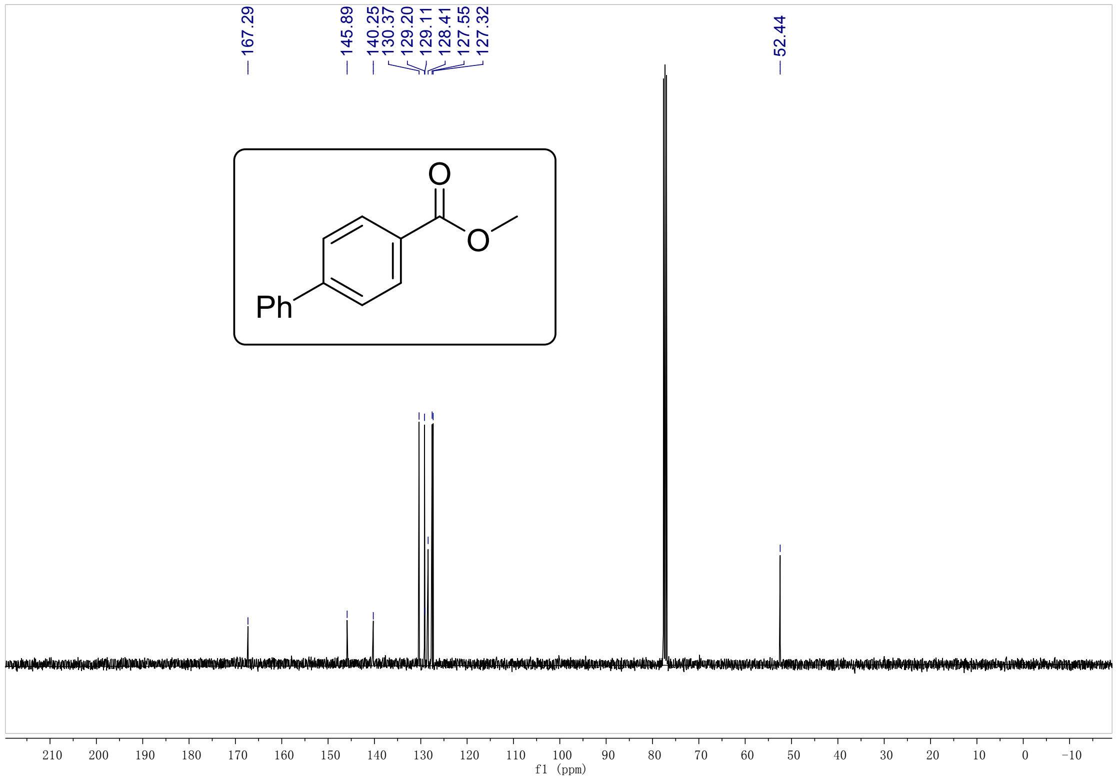
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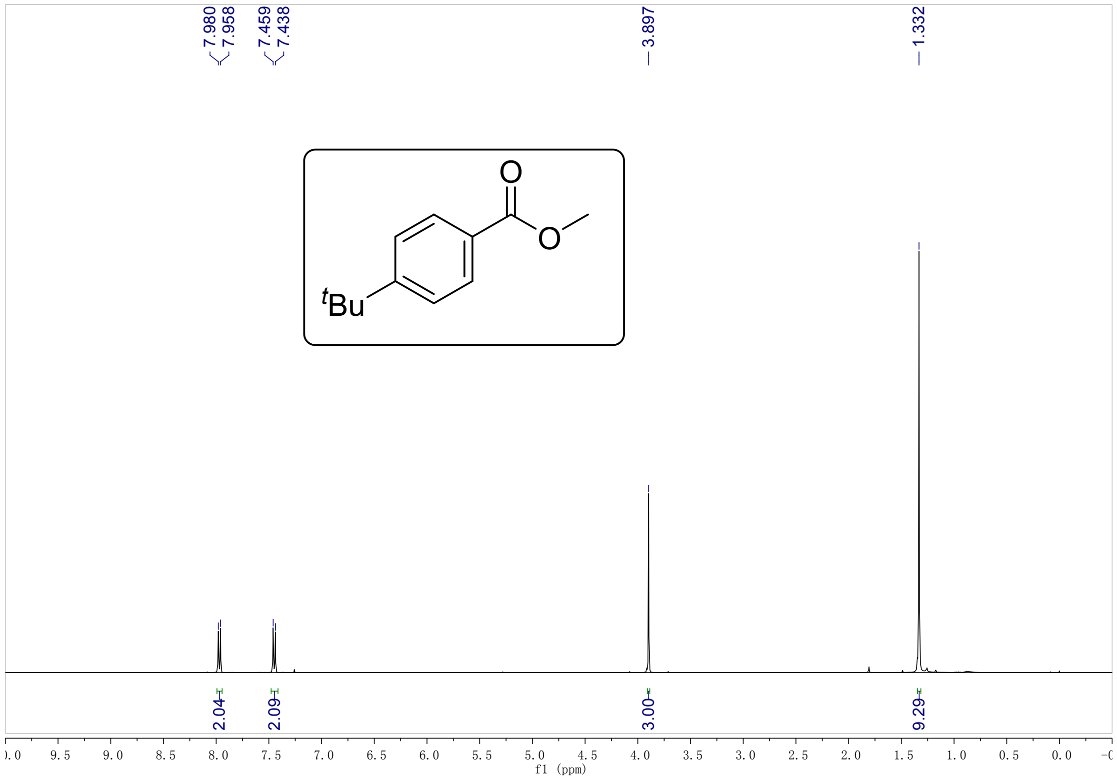
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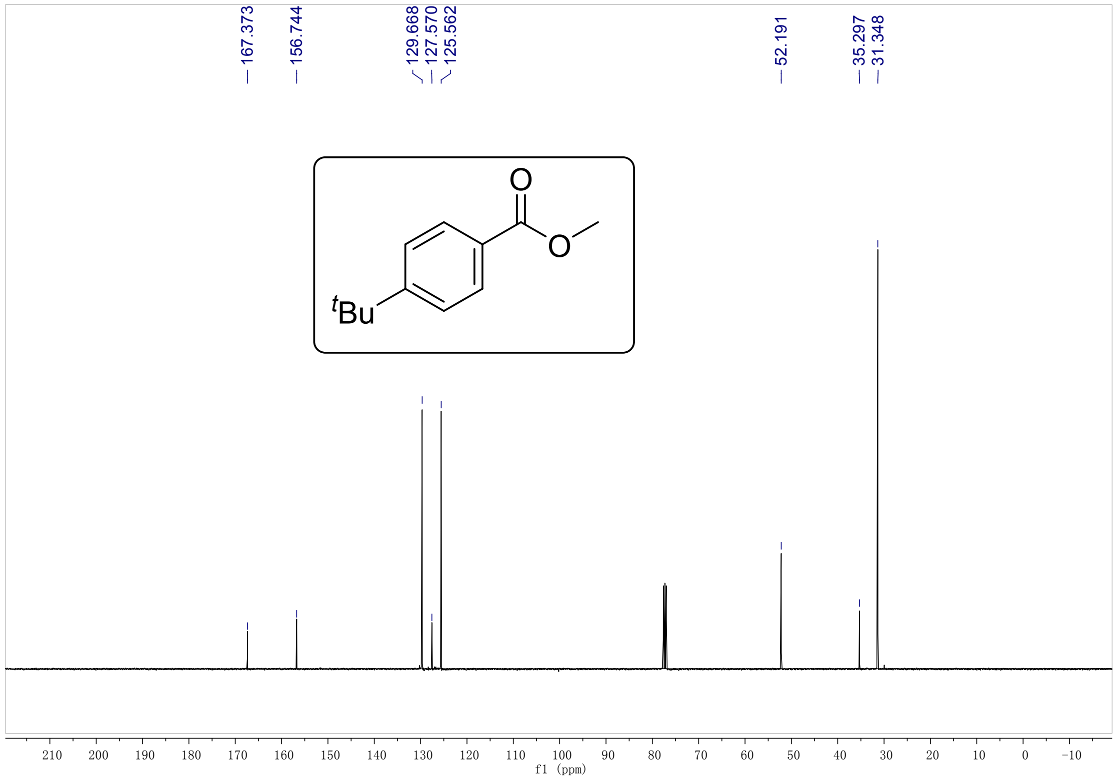
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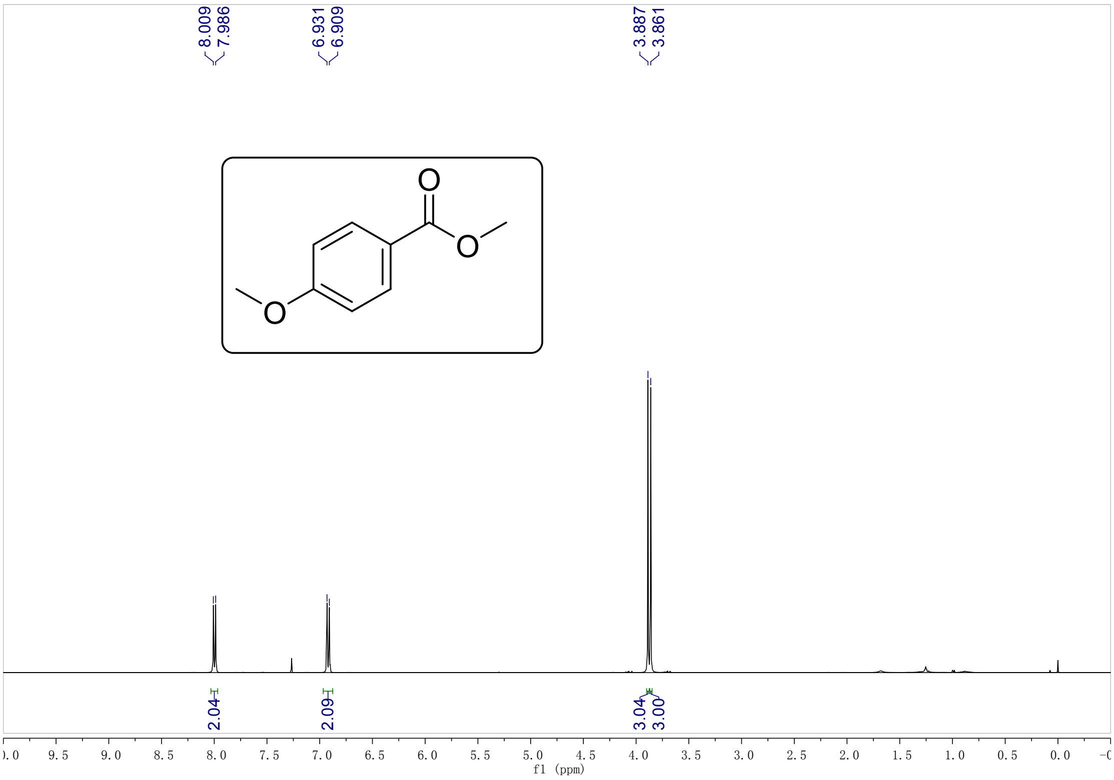
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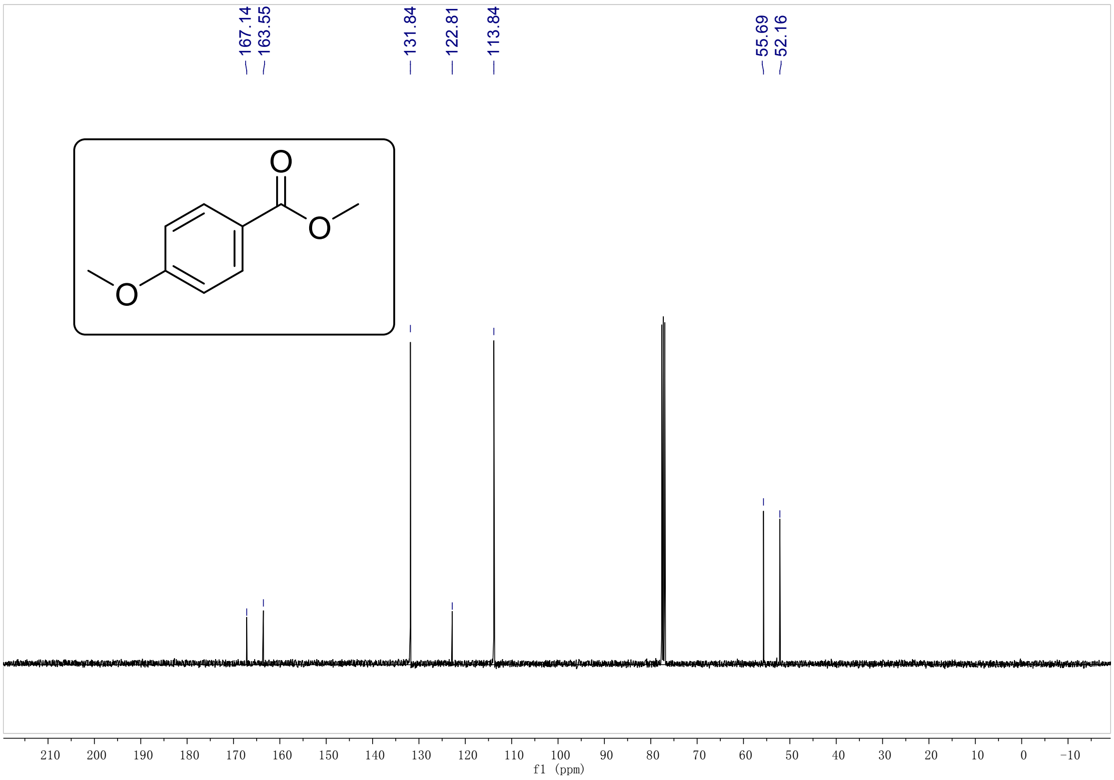
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40
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20
10
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f1 (ppm)


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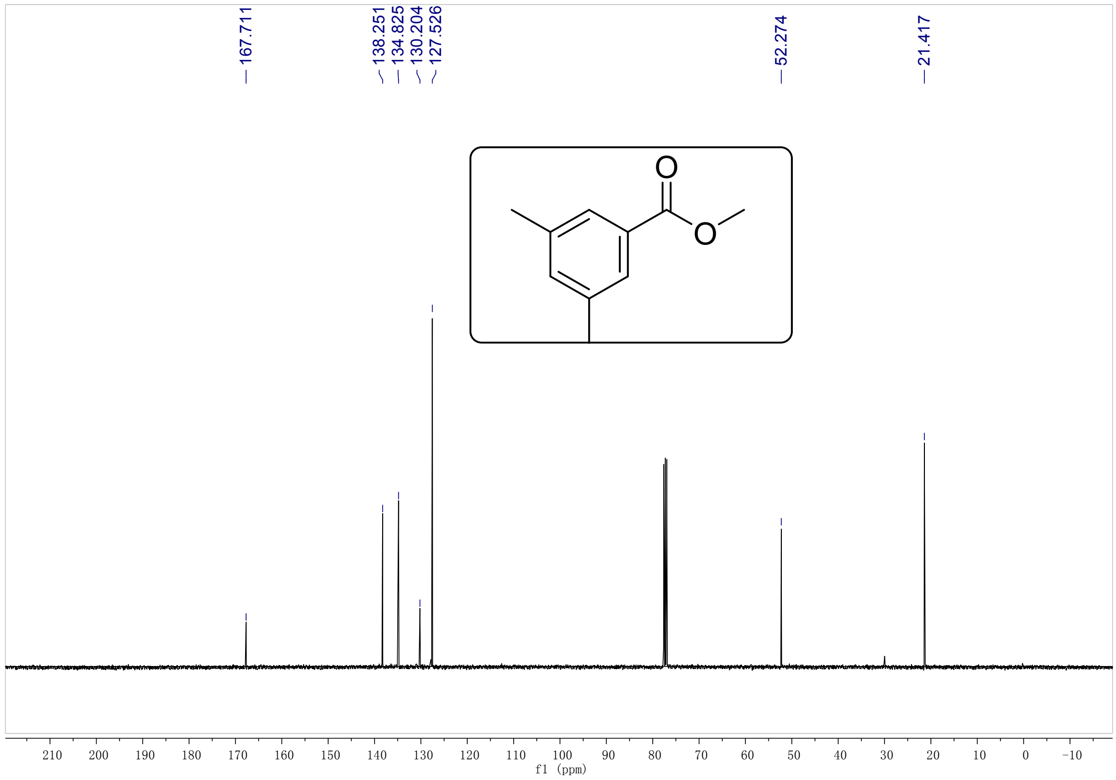
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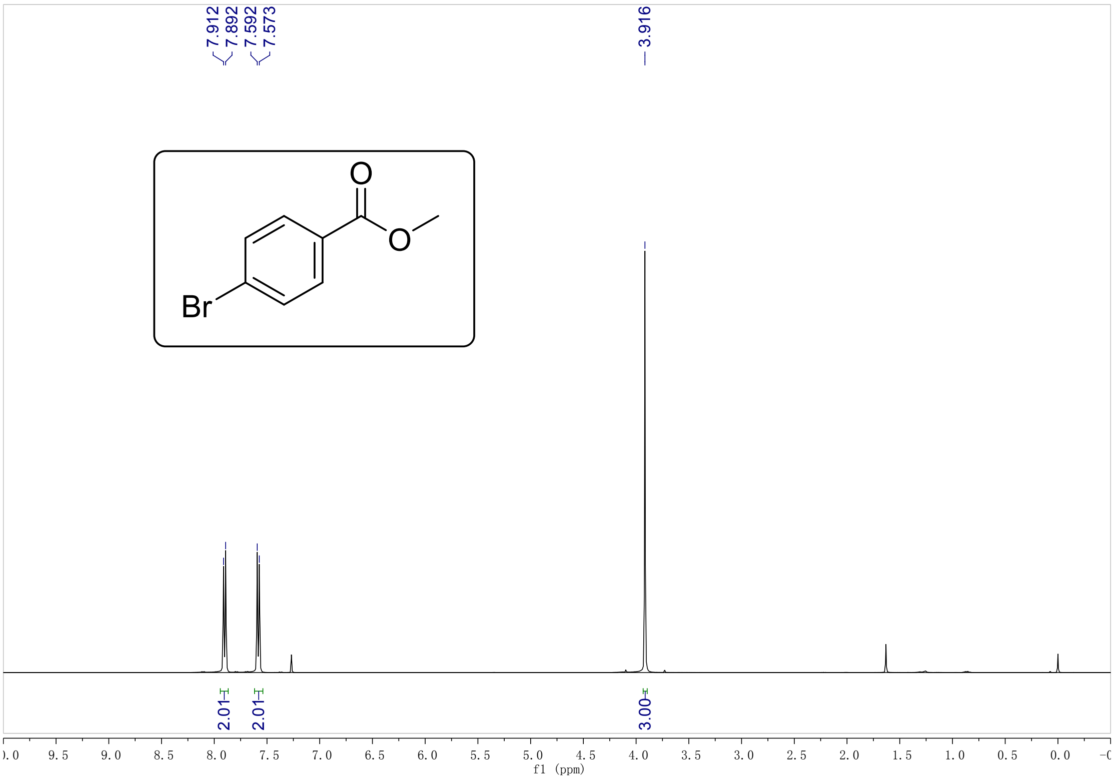
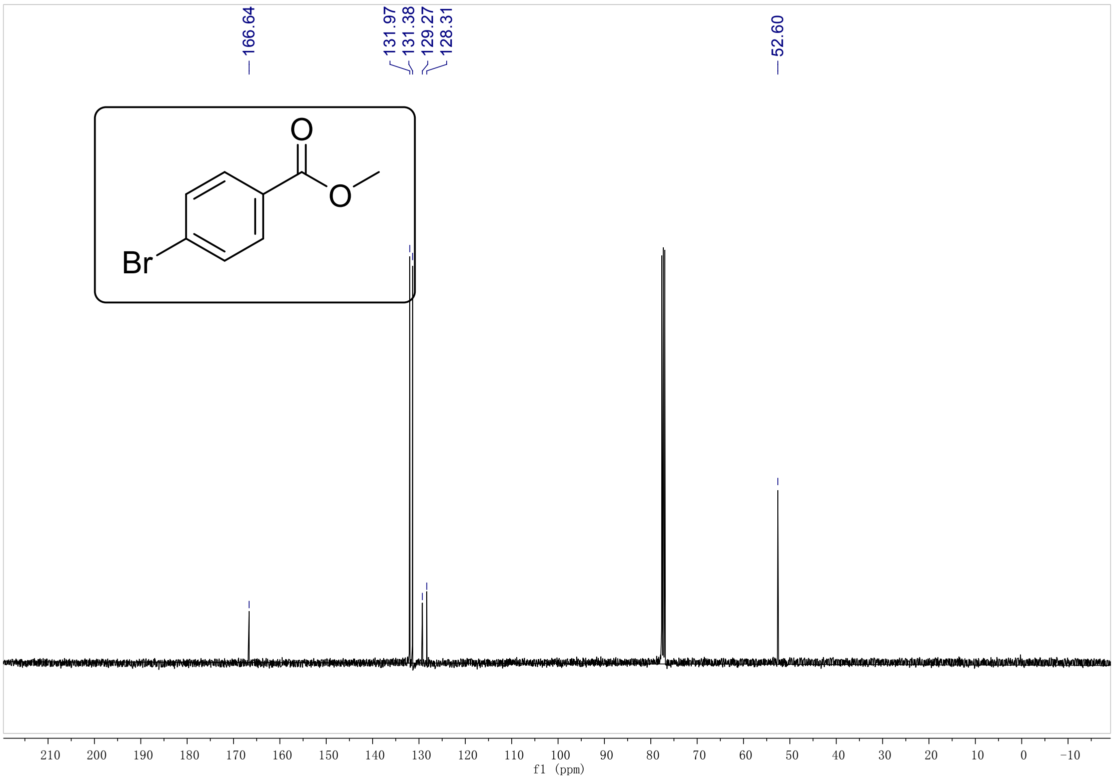
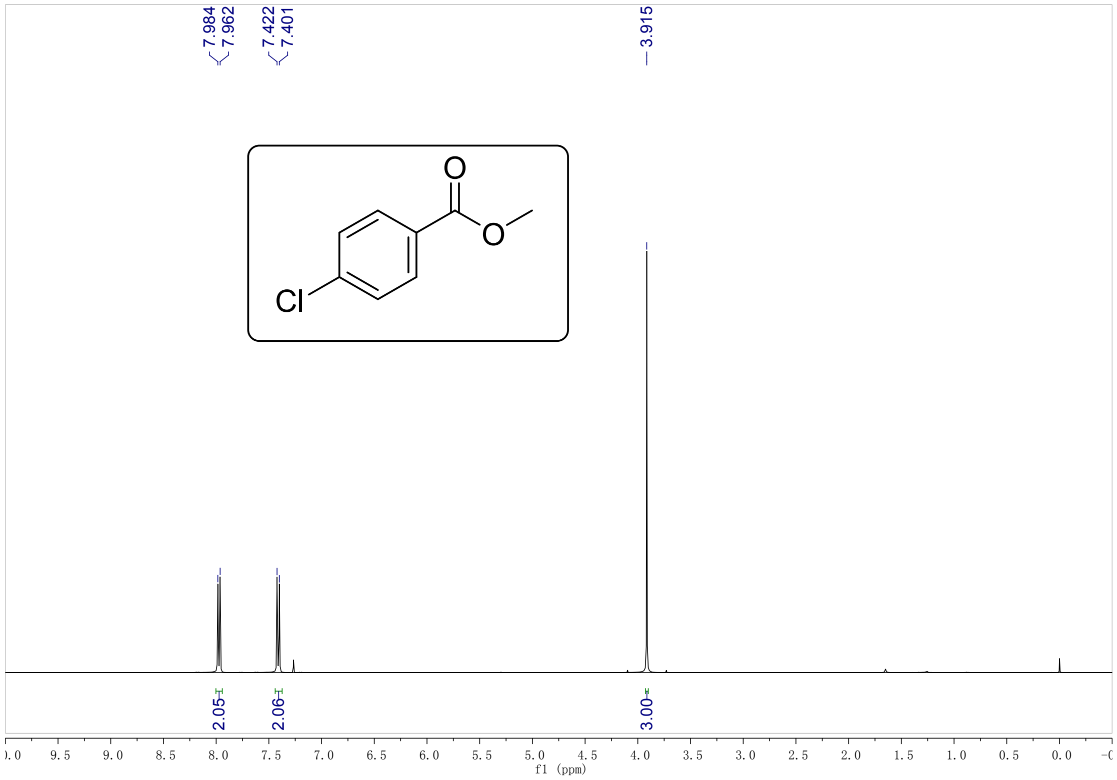
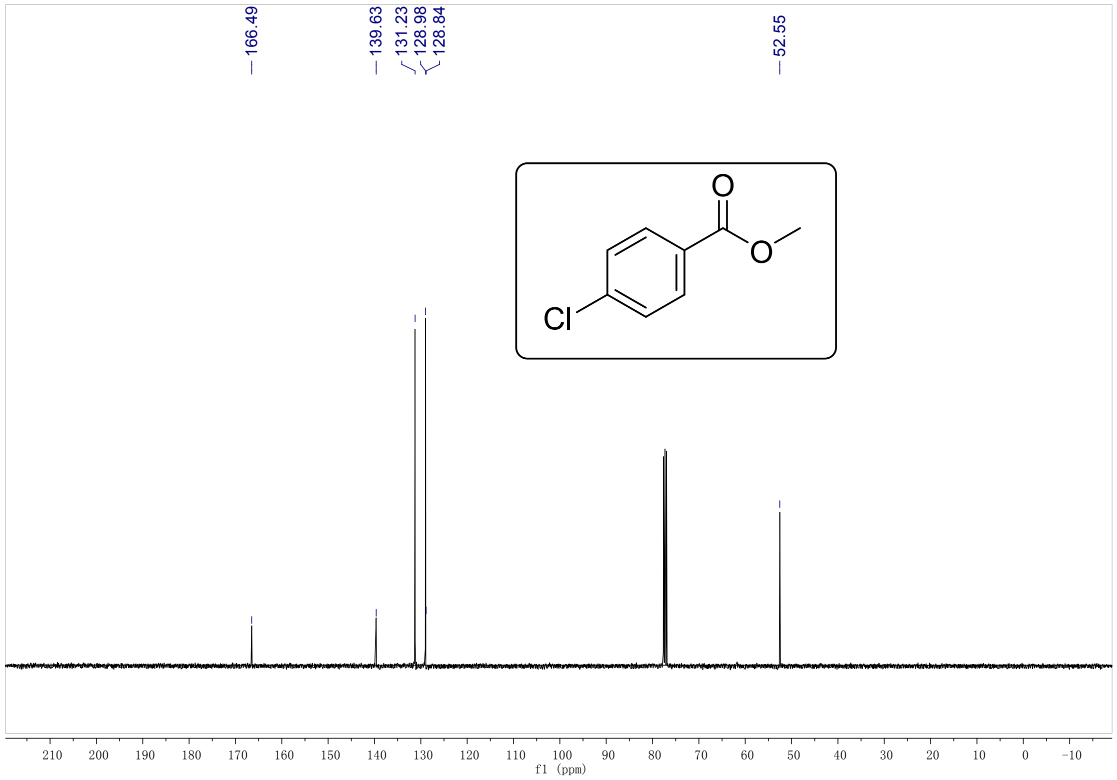
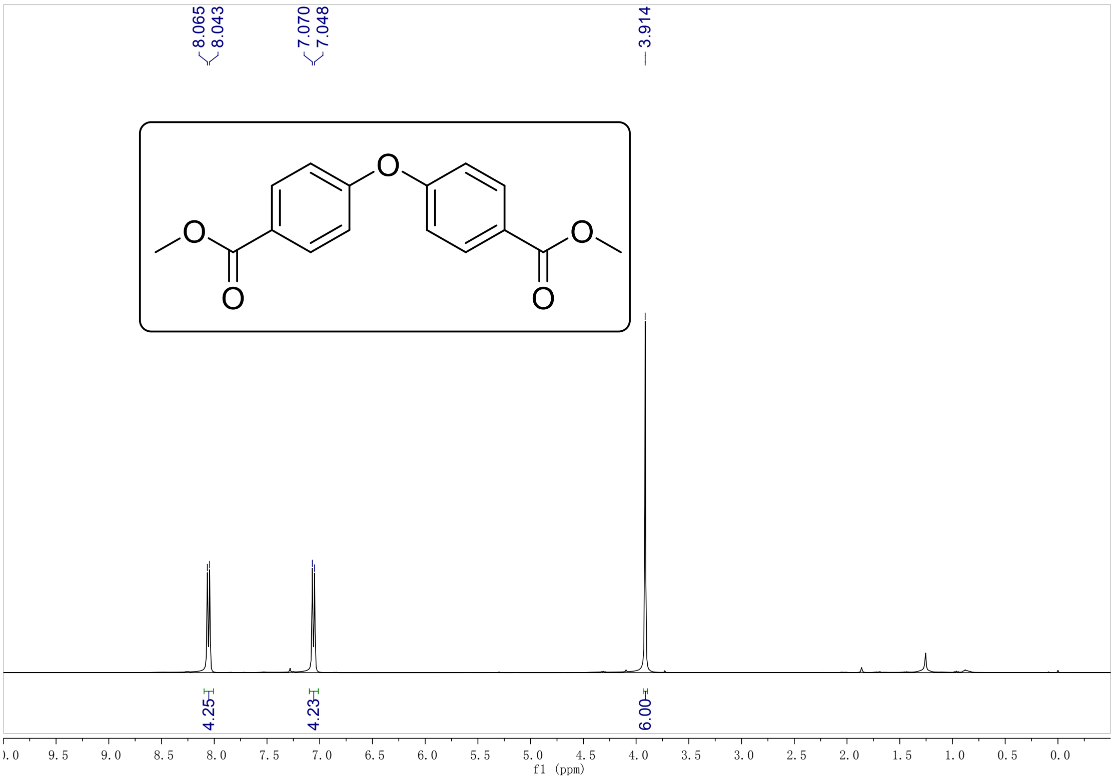
70
60
50
40
30
20
10
0
-10
f1 (ppm)

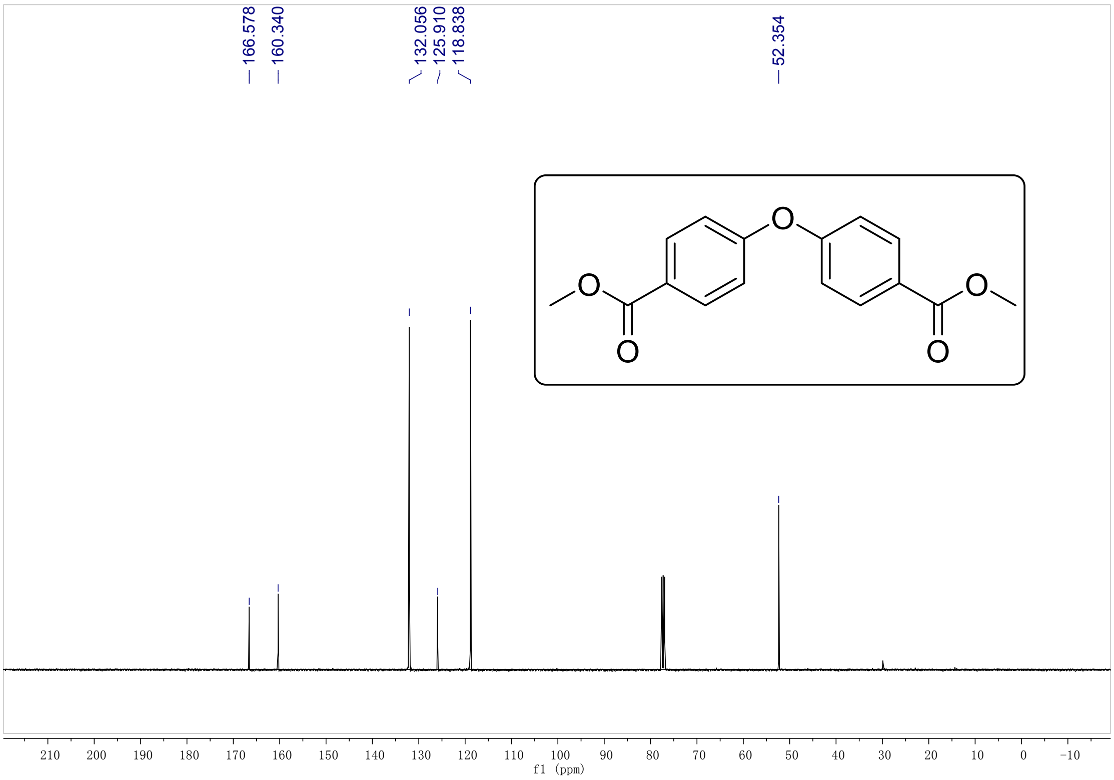

7.912
7.892
7.592
7.573
3.916
Br
O
O
2.01
2.01
3.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

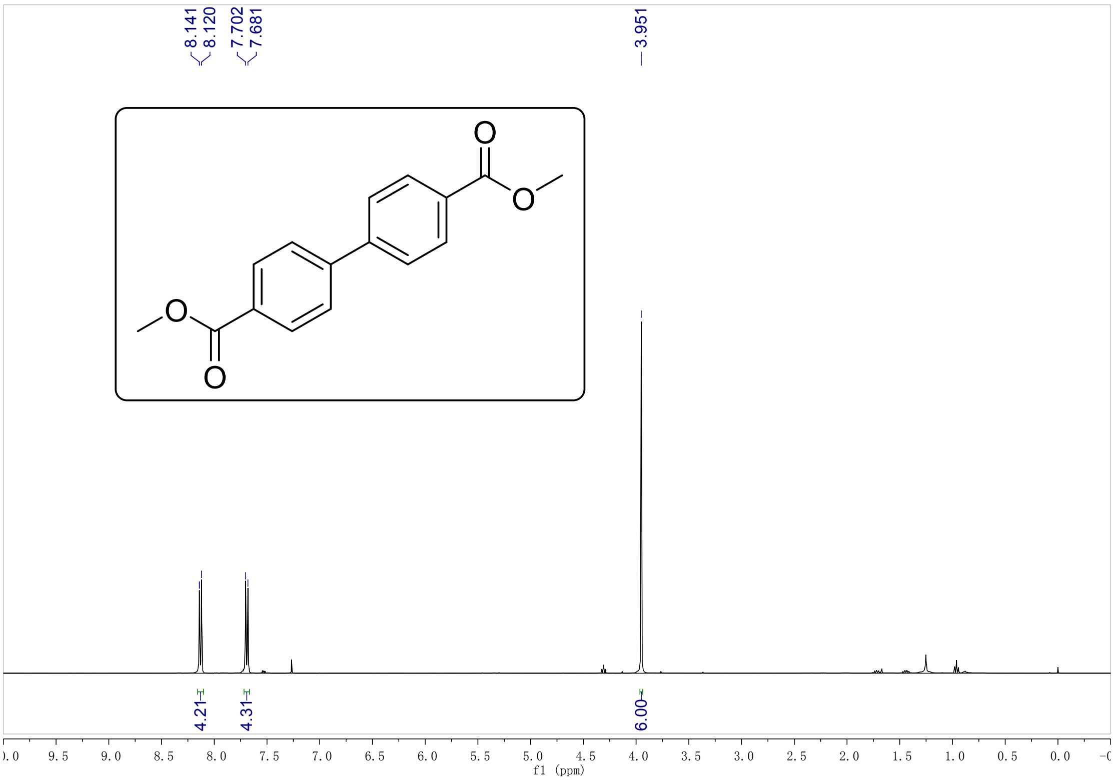

166.64
131.97
131.38
129.27
128.31
52.60
Br
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

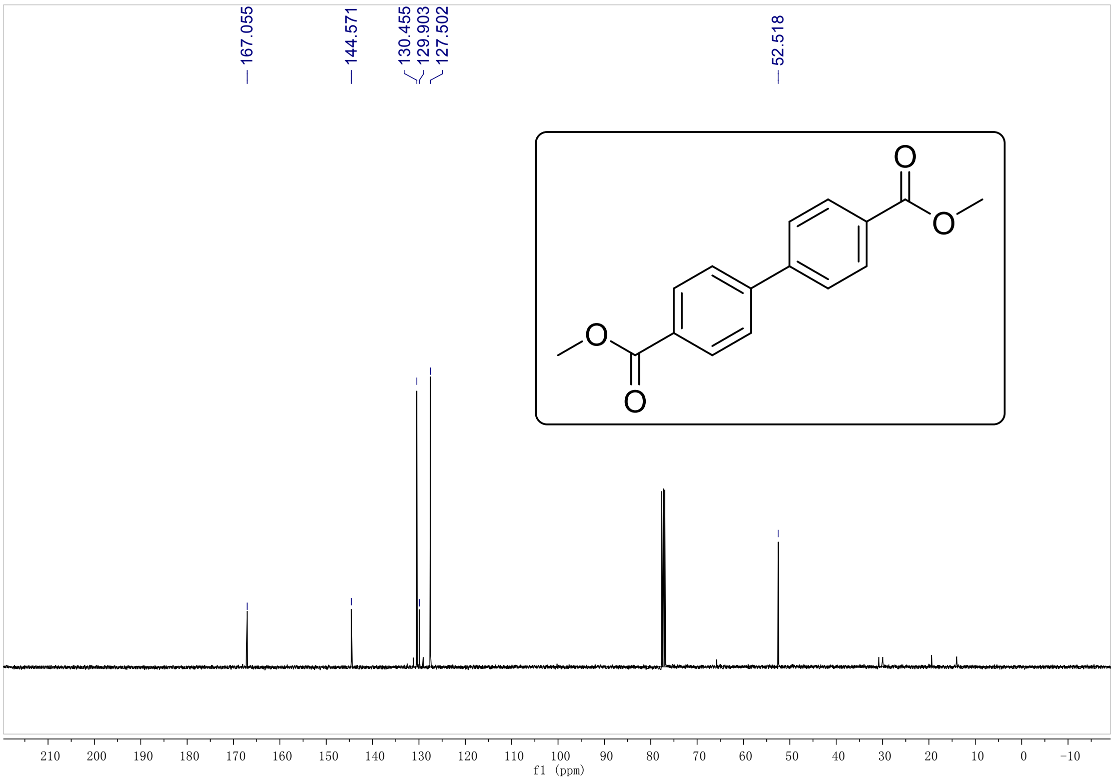

7.984
7.962
7.422
7.401
3.915
O
O
Cl
2.05
2.06
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.49
139.63
131.23
128.98
128.84
52.55
O
O
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.065
8.043
7.070
7.048
3.914
O
O
O
O
O
4.25
4.23
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.578
160.340
132.056
125.910
118.838
52.354
O
O
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.141
8.120
7.702
7.681
3.951
4.21
4.31
6.00
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
O
O
O


167.055
144.571
130.455
129.903
127.502
52.518
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
O
O
O
O