

Supporting Information for
Tetraethylammonium Iodide Catalyzed Synthesis of Diaryl
Ketones *via* the Merger of Cleavage of C-C Double Bond and
Recombination of Aromatic Groups

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1. General Remarks

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. GC-MS was measured on Agilent 7890A /5975C spectrometer with a HP-5-MS column. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC inspections were on silica gel GF₂₅₄ plates.

Unless otherwise stated, all commercial reagents and solvents were used as received. Compounds **1b-1v** were synthesized according to the procedure reported in the literature.¹

2. General procedure for the synthesis of ketones from arylalkenes.

The mixture solution of arylalkene (0.2 mmol), tetraethylammonium iodide (1.3 mg, 0.005 mmol), sodium periodate (130 mg, 0.6 mmol), acetonitrile (0.8 mL) and water (0.2 mL) were stirred at 105 °C for 12 h. After the reaction, anhydrous sodium sulfate was added to the above mixture and then the mixture was purified by flash chromatography (PET/EtOAc = 1 : 0 to 10 : 1) to give the desired products.

Benzophenone (**2a**)²: White solid (33.1 mg, 91%). ¹H NMR (CDCl₃, 400 MHz) δ = 7.80-7.82 (m, 4H), 7.57-7.62 (m, 2H), 7.47-7.51 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ = 196.8, 137.6, 132.5, 130.1, 128.3. GC-MS (EI-MS): 182.1

Phenyl(*p*-tolyl)methanone (**2b**)³: White solid (37.3 mg, 95%). ¹H NMR (CDCl₃, 400 MHz) δ = 7.74-7.80 (m, 4H), 7.56-7.60 (m, 1H), 7.46-7.49 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ = 196.6, 143.3, 137.9, 134.9, 132.2, 130.4, 129.9, 129.0, 128.3, 21.7. GC-MS (EI-MS): 196.0.

Phenyl(*m*-tolyl)methanone (**2c**)⁴: White solid (36.9 mg, 94%). ¹H NMR (CDCl₃, 400 MHz) δ = 7.72-7.74 (m, 2H), 7.49-7.52 (m, 1H), 7.33-7.40 (m, 2H), 7.30-7.32 (m, 1H), 7.15-7.25 (m, 3H), 2.26 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ = 198.7, 138.6, 137.7, 136.8, 133.2, 131.0, 130.3, 130.2, 128.6, 128.5, 125.2, 20.0. GC-MS (EI-MS): 196.0.

Phenyl(*o*-tolyl)methanone (**2d**)⁴: White solid (36.1 mg, 92%). ¹H NMR (CDCl₃, 400 MHz) δ = 7.79-7.81 (m, 2H), 7.57-7.64 (m, 3H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.34-7.42 (m, 2H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ = 197.0, 138.2, 137.8, 137.6, 133.2, 132.4, 130.5, 130.1, 128.3, 128.1, 127.4, 21.0.

(4-Chlorophenyl)(phenyl)methanone (**2e**)³: White solid (38.9 mg, 90%). ¹H NMR (CDCl₃, 400 MHz) δ = 7.74-7.78 (m, 4H), 7.58-7.63 (m, 1H), 7.45-7.51 (m, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ = 195.6, 138.9, 137.2, 135.9, 132.7, 131.5, 129.9, 128.7, 128.4.

(3-Chlorophenyl)(phenyl)methanone (**2f**)³: White solid (39.8 mg, 92%). ¹H NMR (CDCl₃, 400 MHz) δ = 7.78-7.80 (m, 3H), 7.66 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.60-7.63 (m, 1H), 7.56-7.57 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.40-7.43 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ = 195.3, 139.3, 136.9, 134.6, 132.9, 132.4, 130.1, 129.9, 129.7, 128.5, 128.2.

(2-Chlorophenyl)(phenyl)methanone (**2g**)³: White solid (38.5 mg, 89%). ¹H NMR (CDCl₃, 400

MHz) δ = 7.81-7.83 (m, 2H), 7.58-7.63 (m, 1H), 7.45-7.49 (m, 4H), 7.37-7.38 (m, 2H); ^{13}C NMR (CDCl₃, 100 MHz) δ = 195.4, 138.6, 136.5, 133.8, 131.3, 131.2, 130.1, 130.0, 129.2, 128.7, 126.7.

(2,4-Dichlorophenyl)(phenyl)methanone (**2h**)⁵: White solid (42.6 mg, 85%). ^1H NMR (CDCl₃, 400 MHz) δ = 7.78-7.81 (m, 2H), 7.60-7.64 (m, 1H), 7.46-7.50 (m, 3H), 7.32-7.36 (m, 2H); ^{13}C NMR (CDCl₃, 100 MHz) δ = 194.3, 136.9, 136.7, 136.2, 134.0, 132.5, 130.2, 130.1, 128.7, 127.2, 125.7.

(4-Fluorophenyl)(phenyl)methanone (**2i**)⁶: White solid (36.5 mg, 91%). ^1H NMR (CDCl₃, 400 MHz) δ = 7.83-7.87 (m, 2H), 7.76-7.78 (m, 2H), 7.58-7.62 (m, 1H), 7.47-7.51 (m, 2H), 7.14-7.18 (m, 2H); ^{13}C NMR (CDCl₃, 100 MHz) δ = 195.3, 165.3 (d, J = 253 Hz), 137.5, 133.7 (d, J = 3 Hz), 132.6 (d, J = 9 Hz), 132.5, 129.9, 128.4, 115.4 (d, J = 22 Hz).

(4-Bromophenyl)(phenyl)methanone (**2j**)⁷: White solid (47.0 mg, 81%). ^1H NMR (CDCl₃, 400 MHz) δ = 7.78-7.81 (m, 2H), 7.69-7.71 (m, 2H), 7.62-7.66 (m, 3H), 7.49-7.53 (m, 2H); ^{13}C NMR (CDCl₃, 100 MHz) δ = 194.6, 136.1, 135.3, 131.7, 130.6, 130.5, 128.9, 127.4, 126.5.

Phenyl(4-(trifluoromethyl)phenyl)methanone (**2k**)⁸: White solid (46.1 mg, 92%). ^1H NMR (CDCl₃, 400 MHz) δ = 7.89 (d, J = 8.0 Hz, 2H), 7.80-7.82 (m, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.62-7.65 (m, 1H), 7.49-7.53 (m, 2H); ^{13}C NMR (CDCl₃, 100 MHz) δ = 195.6, 140.7, 136.7, 133.7 (d, J = 33 Hz), 133.1, 130.2, 130.1, 128.6, 125.4 (d, J = 11 Hz), 125.3 (d, J = 4 Hz).

(4-Methoxyphenyl)(phenyl)methanone (**2l**)⁹: White solid (38.6 mg, 91%). ^1H NMR (CDCl₃, 400 MHz) δ = 7.81-7.84 (m, 2H), 7.40-7.46 (m, 2H), 7.54-7.58 (m, 1H), 7.45-7.48 (m, 2H), 6.94-6.97 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (CDCl₃, 100 MHz) δ = 195.6, 163.2, 138.3, 132.6, 131.9, 130.1, 129.8, 128.2, 113.6, 55.5.

Benzo[*d*][1,3]dioxol-5-yl(phenyl)methanone (**2m**)¹⁰: White solid (43.6 mg, 96%). ^1H NMR (CDCl₃, 400 MHz) δ = 7.73-7.75 (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.48 (m, 2H), 7.36-7.38 (m, 2H), 6.84-6.87 (m, 1H), 6.06 (s, 2H); ^{13}C NMR (CDCl₃, 100 MHz) δ = 195.2, 151.5, 148.0, 138.1, 132.0, 131.9, 129.7, 128.3, 126.9, 109.9, 107.7, 101.9.

Naphthalen-1-yl(phenyl)methanone (**2n**)³: White solid (49.3 mg, 94%). ^1H NMR (CDCl₃, 400 MHz) δ = 8.10-8.12 (m, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.92-7.94 (m, 1H), 7.87-7.89 (m, 2H), 7.58-7.63 (m, 2H), 7.45-7.56 (m, 5H); ^{13}C NMR (CDCl₃, 100 MHz) δ = 198.1, 138.3, 136.4, 133.7, 133.3, 131.0, 130.5, 128.5, 128.4, 127.8, 127.3, 126.5, 125.7, 124.4.

Phenyl(thiophen-2-yl)methanone (**2o**)¹¹: Yellow oil (24.6 mg, 65%). ^1H NMR (CDCl₃, 400 MHz)

$\delta = 7.85\text{-}7.88$ (m, 2H), 7.82 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.72-7.73 (m, 1H), 7.65 (dd, $J = 4.0, 1.2$ Hz, 1H), 7.49-7.52 (m, 2H), 7.16 (dd, $J = 4.8, 4.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 188.3, 143.7, 138.0, 134.9, 134.3, 132.3, 129.2, 128.5, 128.0$.

(3-Methoxyphenyl)(thiophen-2-yl)methanone (**2p**)¹²: Yellow oil (32.0 mg, 73%). ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.72$ (dd, $J = 4.8, 1.2$ Hz, 1H), 7.67 (dd, $J = 3.6, 1.2$ Hz, 1H), 7.38-7.41 (m, 3H), 7.12-7.17 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 188.0, 159.6, 143.6, 135.6, 134.9, 134.3, 129.4, 128.0, 121.8, 118.6, 113.8, 55.5$.

(4-Chlorophenyl)(*p*-tolyl)methanone (**2q**)¹³: White solid (42.8 mg, 93%). ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.72\text{-}7.74$ (m, 2H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.44-7.50 (m, 2H), 7.29 (d, $J = 7.6$ Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 195.3, 143.6, 138.6, 136.2, 134.5, 131.2, 130.2, 129.1, 128.5, 21.7$.

(4-Chlorophenyl)(*m*-tolyl)methanone (**2r**)¹³: White solid (41.4 mg, 90%). ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.34\text{-}7.77$ (m, 2H), 7.60 (s, 1H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.45-7.47 (m, 2H), 7.35-7.40 (m, 2H), 2.42 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 195.8, 138.8, 138.4, 137.3, 136.0, 133.5, 131.5, 130.4, 128.6, 128.2, 127.2, 21.4$.

(4-Chlorophenyl)(*o*-tolyl)methanone (**2s**)¹³: White solid (42.8 mg, 93%). ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.66$ (d, $J = 8.8$ Hz, 2H), 7.30-7.36 (m, 3H), 7.17-7.22 (m, 3H), 2.25 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 197.4, 139.7, 138.1, 136.8, 136.1, 131.5, 131.2, 130.6, 128.8, 128.5, 125.3, 20.0$.

(4-Chlorophenyl)(4-fluorophenyl)methanone(**2t**)¹³: White solid (44.5 mg, 95%). ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.82$ (dd, $J = 8.4, 5.6$ Hz, 2H), 7.72 (d, $J = 8.4$ Hz, 2H), 7.46-7.48 (m, 2H), 7.15-7.19 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 194.1, 165.4$ (d, $J = 253$ Hz), 139.0, 135.8, 133.4 (d, $J = 3$ Hz), 132.5 (d, $J = 10$ Hz), 131.3, 128.7, 115.6(d, $J = 21$ Hz).

(3-Chlorophenyl)(4-chlorophenyl)methanone (**2u**)¹⁴: White solid (44.6 mg, 89%). ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.73\text{-}7.76$ (m, 3H), 7.63 (dt, $J = 7.6, 1.2$ Hz, 1H), 7.56-7.59 (m, 1H), 7.42-7.50 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 193.0, 138.4, 137.8, 134.2, 133.7, 131.6, 130.4, 128.8, 128.7, 127.8, 126.9$.


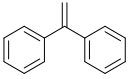

Acetophenone (**2z**)⁷: colorless oil (20.4 mg, 85%). ^1H NMR (CDCl_3 , 400 MHz) $\delta = 7.95\text{-}7.96$ (m, 2H), 7.54-7.58 (m, 1H), 7.44-7.48 (m, 2H), 2.60 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 198.2, 137.1, 133.1, 128.6, 128.3, 26.7$.

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3. Oxidative cleavage of various terminal alkenes.

Table S1 Oxidative cleavage of various terminal olefins^a

Entry	Substrate	Product	Yield(%) ^b
1	1x: 	2x	87
2	1y: 	2a	78
3	1z: 	2z	85

^a Reaction conditions: Unless otherwise noted, **1** (0.2 mmol), Et₄Ni (2.5 mol%), NaIO₄ (0.6 mmol, 3 equiv), MeCN (0.8 mL) and H₂O (0.2 mL) were stirred at 105 °C for 12 h.

^b Isolated yield.

4. Mechanism study with GC-MS and ^1H NMR.

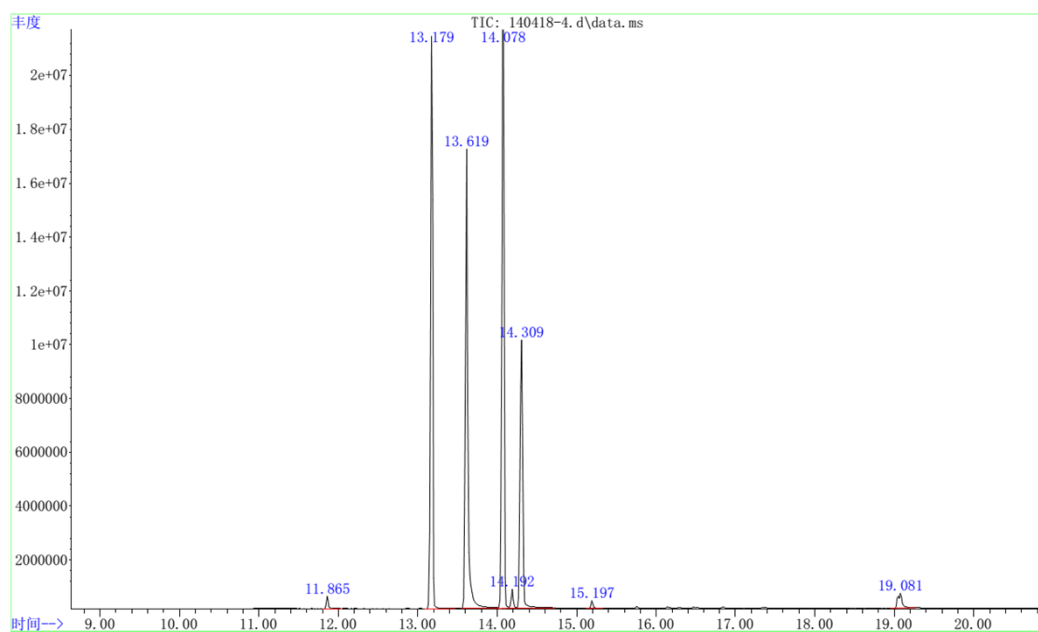


Figure S1. GC-MS spectrum of the reaction of *trans*-stilbene under the standard conditions for 2 h (13.179 min, benzophenone; 13.619 min, 2,2-diphenylacetaldehyde; 14.078 min, *trans*-stilbene; 14.192 min, *trans*-stilbene oxide; 14.309 min, 2-phenylacetophenone).

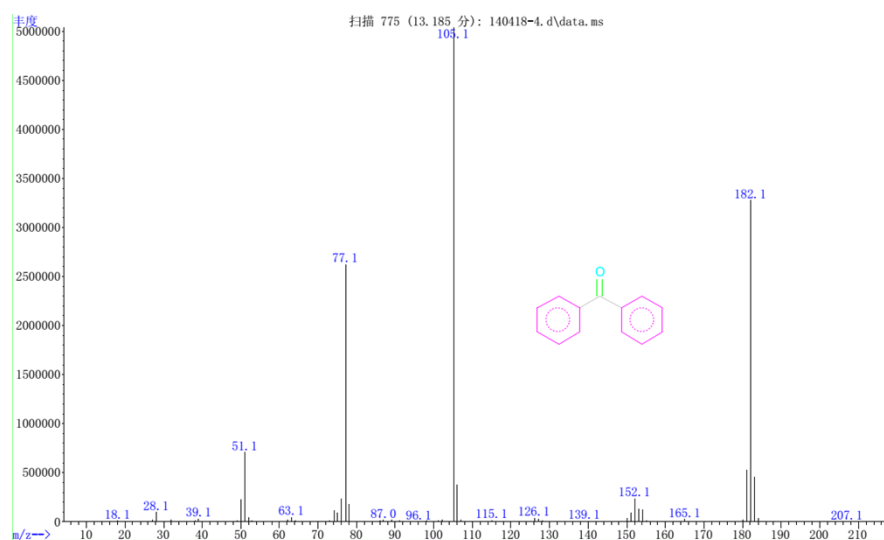


Figure S2. MS spectrum of species in 13.179 min (benzophenone).

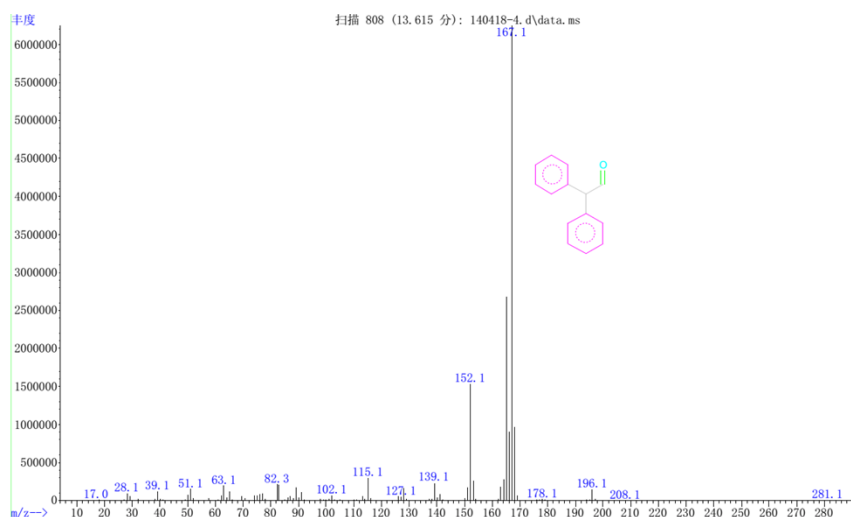


Figure S3. MS spectrum of species in 13.619 min (2,2-diphenylacetaldehyde).

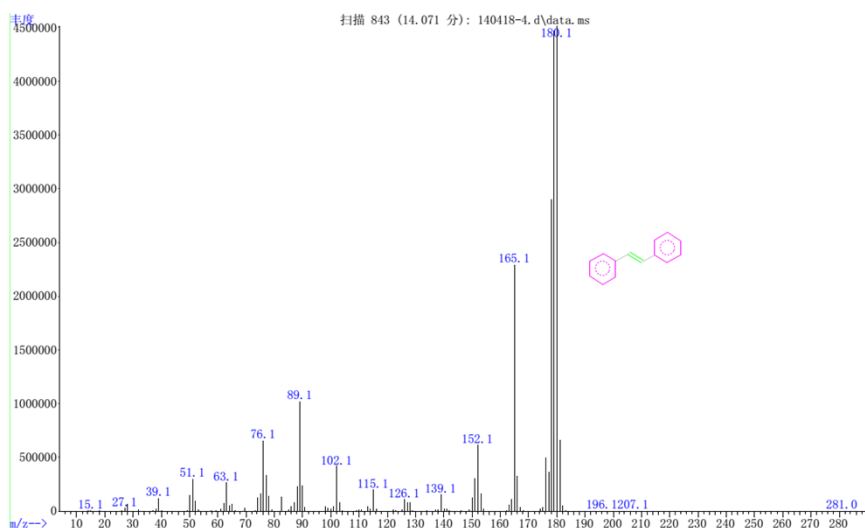


Figure S4. MS spectrum of species in 14.078 min (*trans*-stilbene).

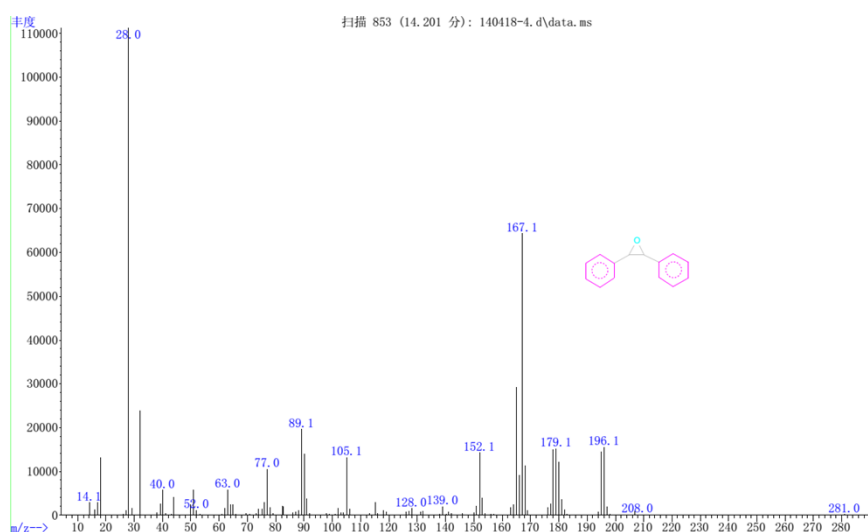


Figure S5. MS spectrum of species in 14.192 min (*trans*-stilbene oxide).

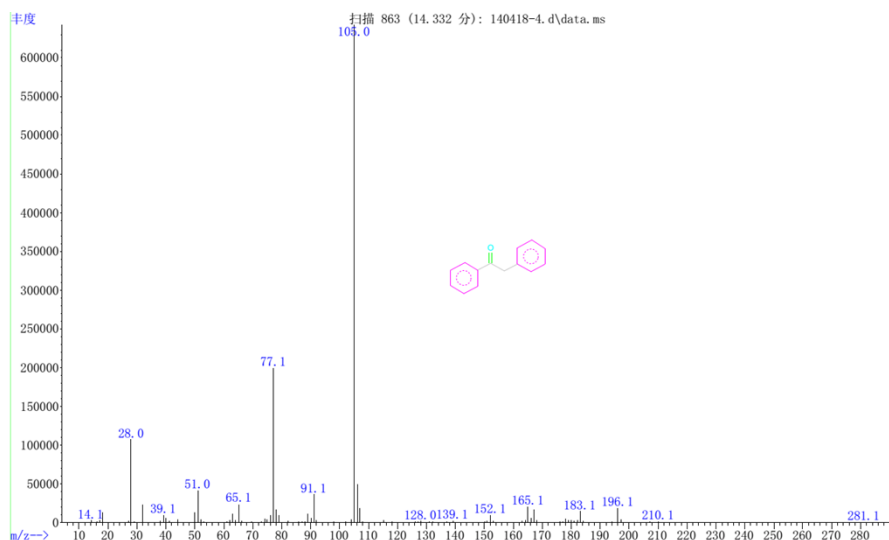


Figure S6. MS spectrum of species in 14.309 min (2-phenylacetophenone).

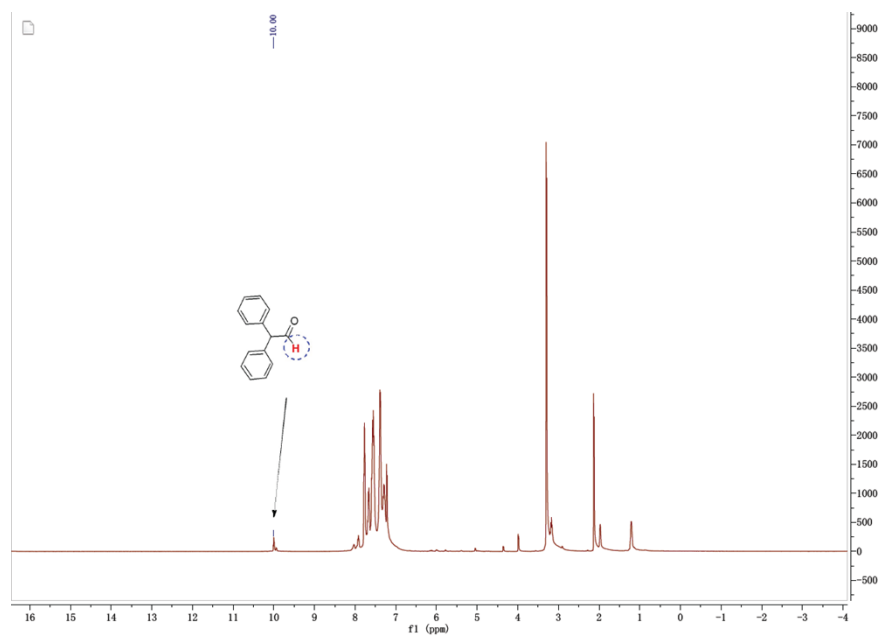
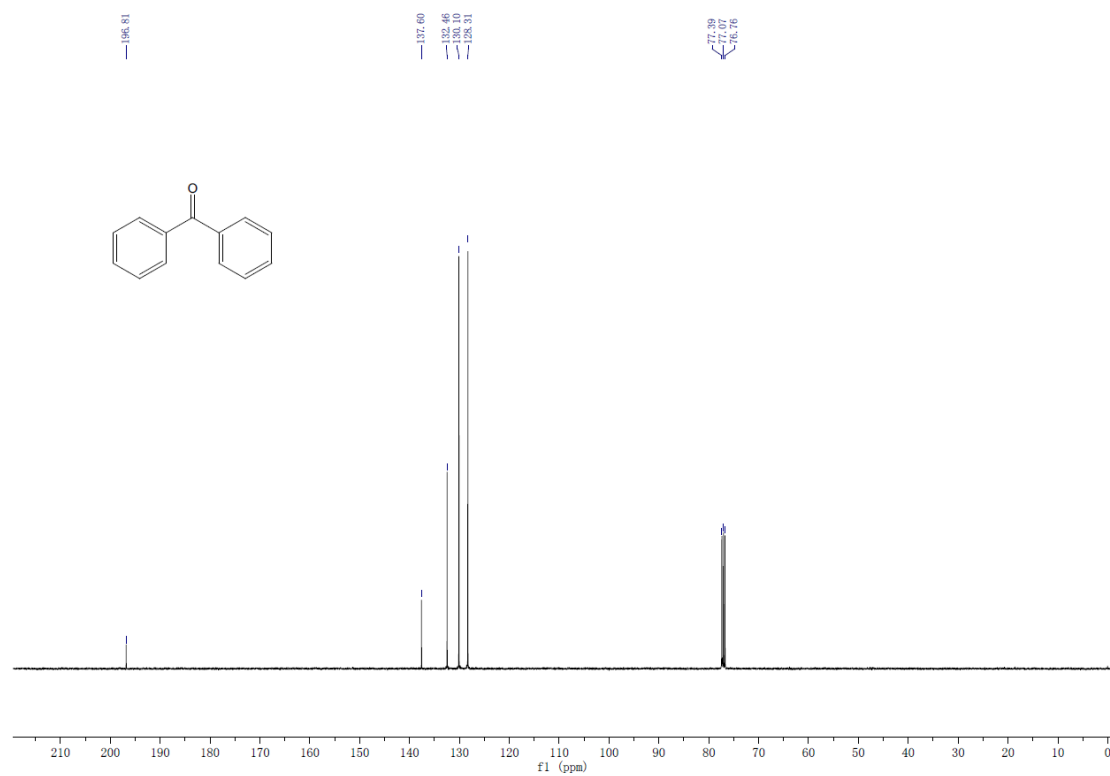
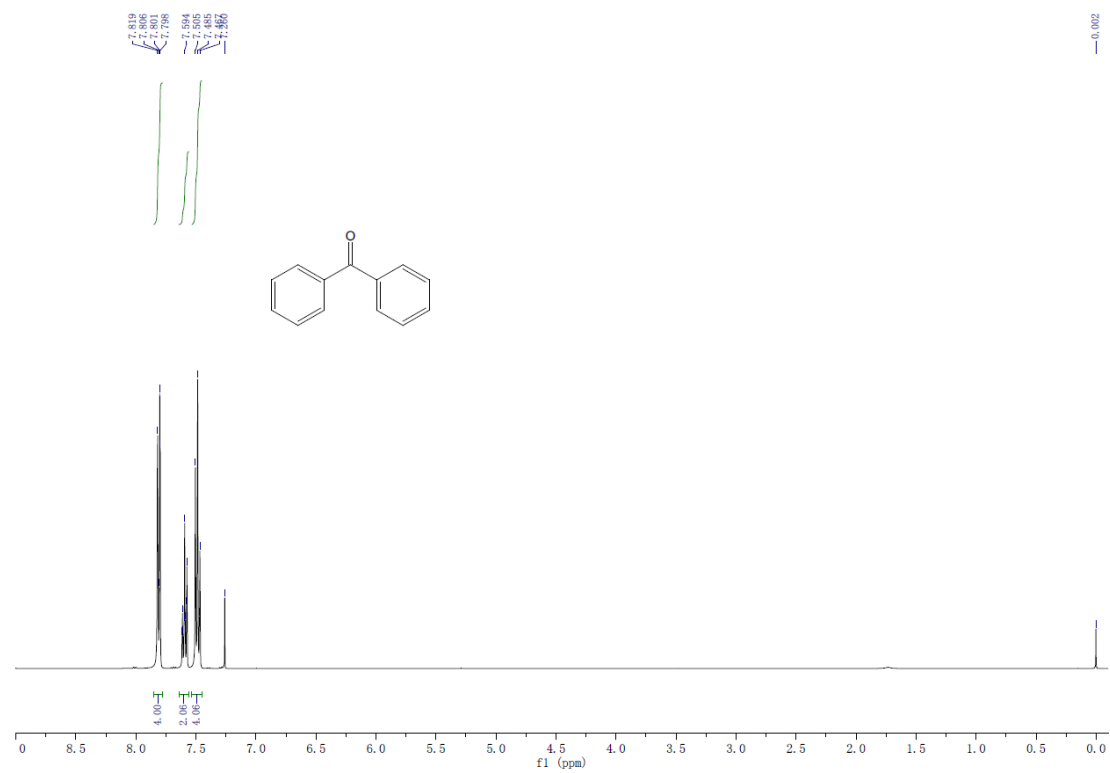


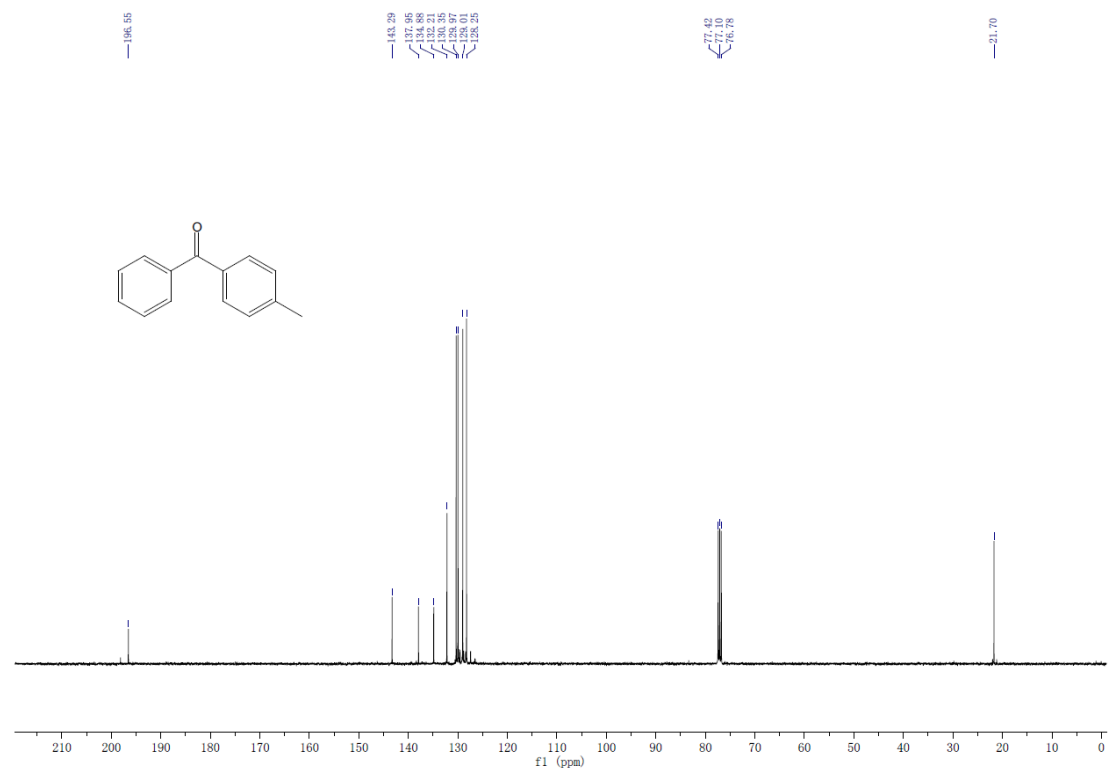
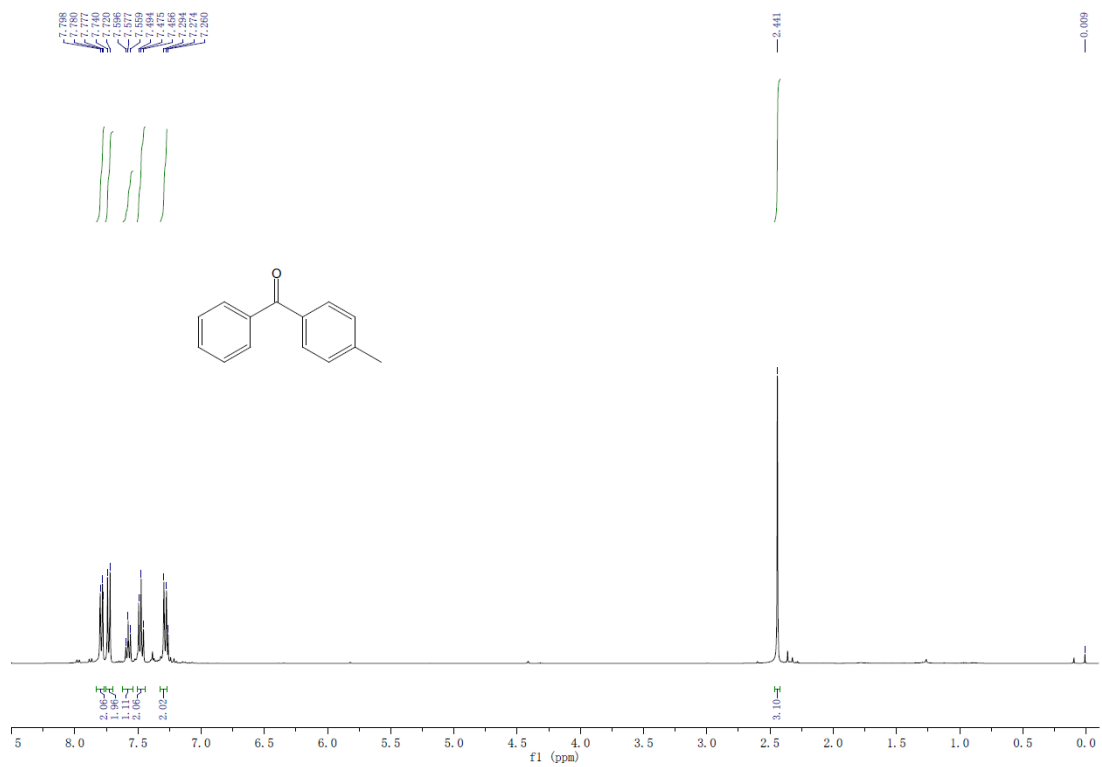
Figure S7. **1a** (0.2 mmol), Et₄Ni (0.005 mmol, 2.5 mol%), NaIO₄ (0.6 mmol, 3 equiv.), CD₃CN (0.8 mL) and D₂O (0.2 mL) were stirred at 105 °C (oil bath temperature) for 2 h in a sealed tube and then examination of the ¹H NMR.

5. NMR spectra of the products

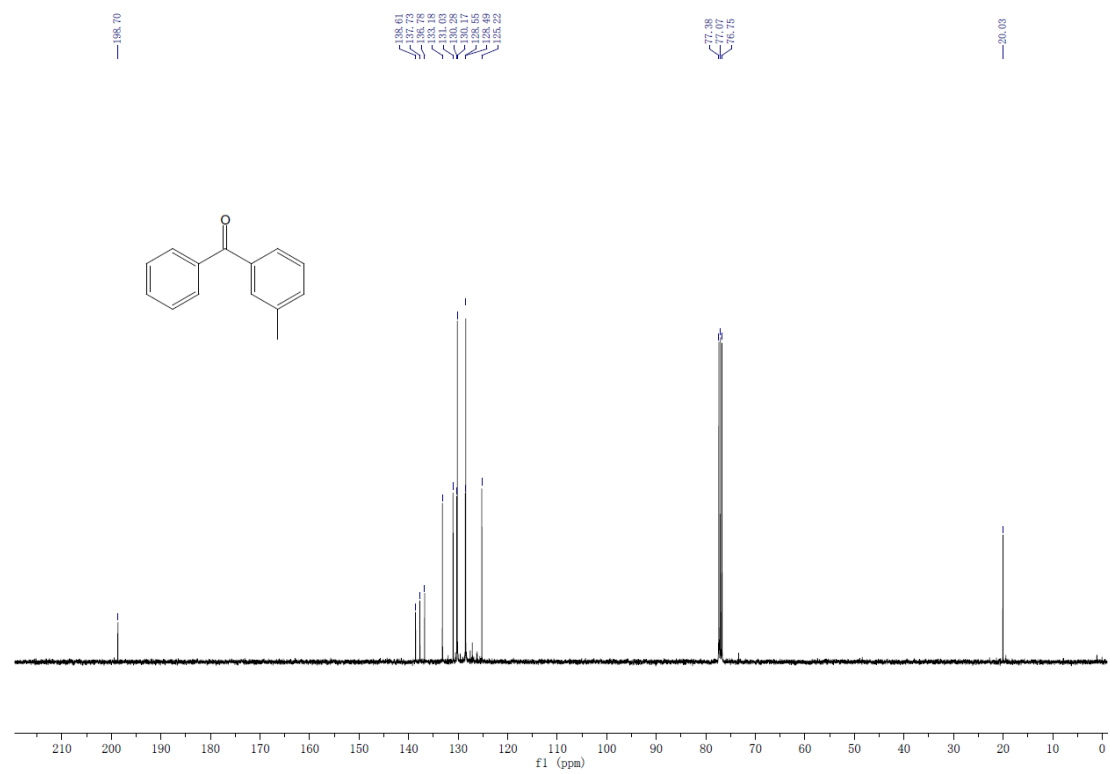
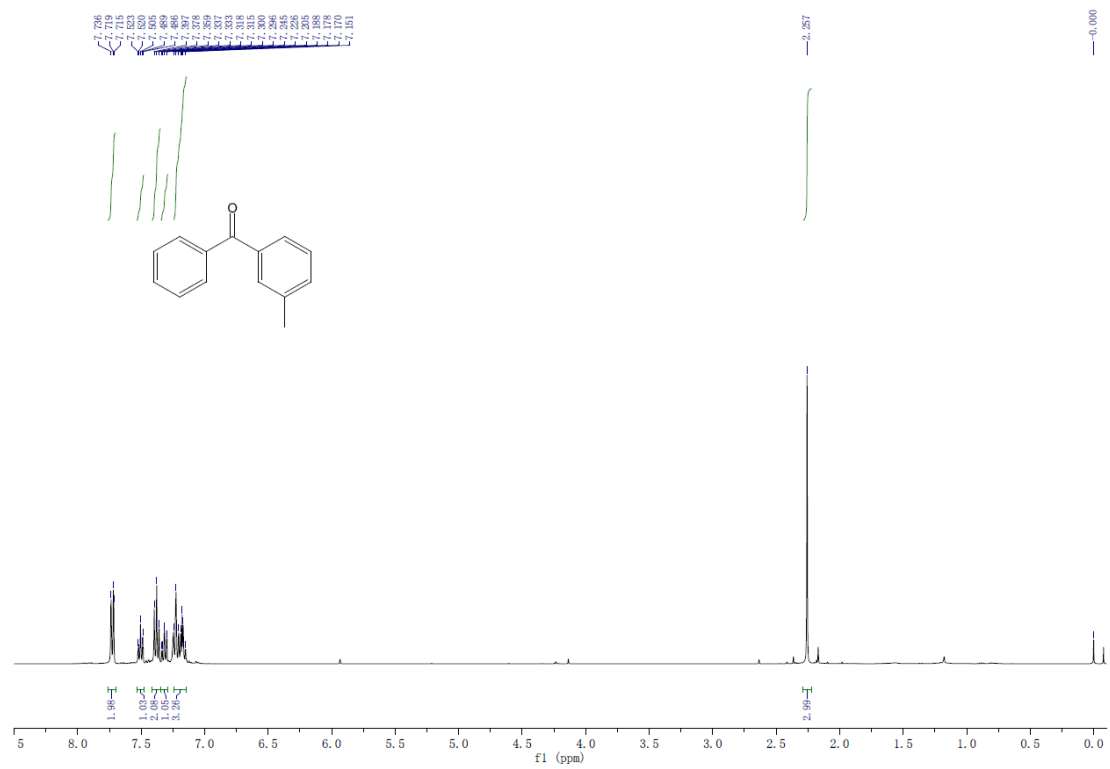
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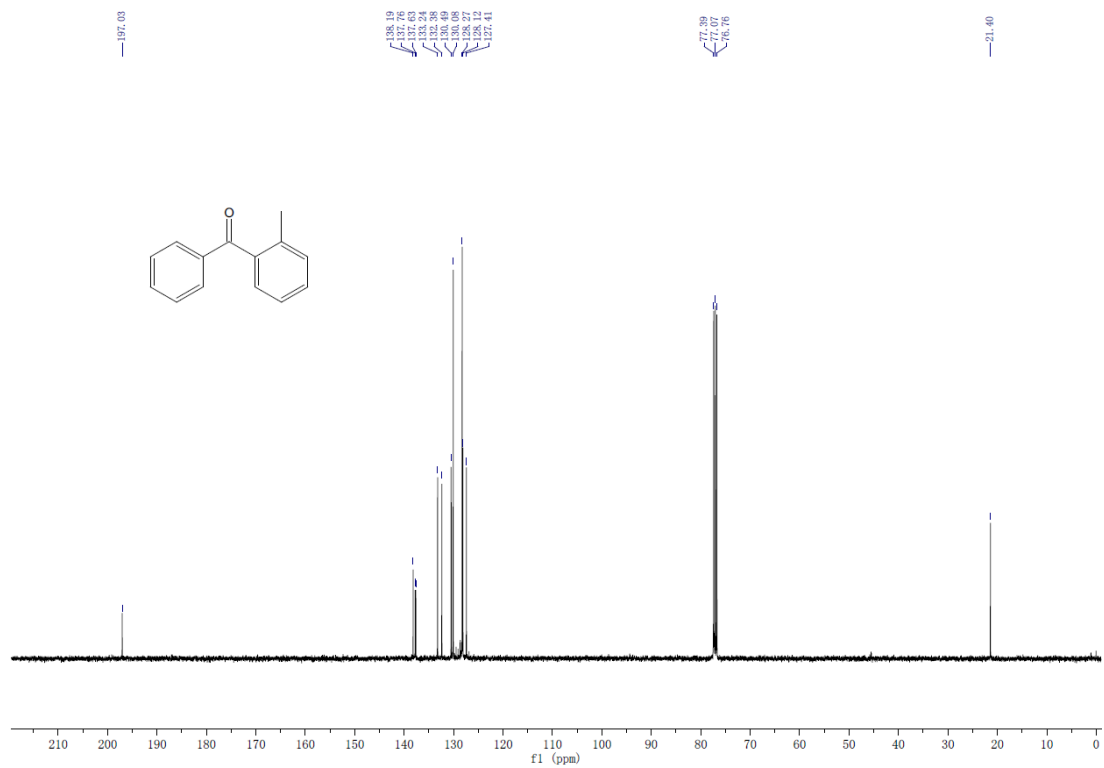
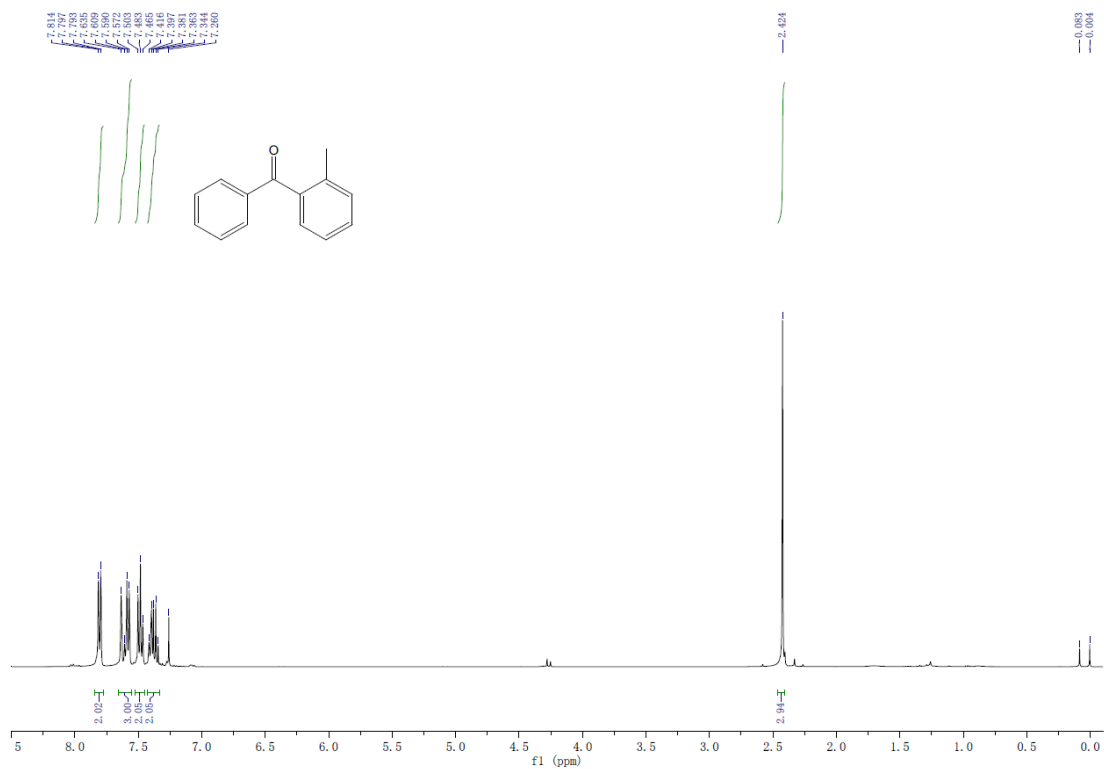
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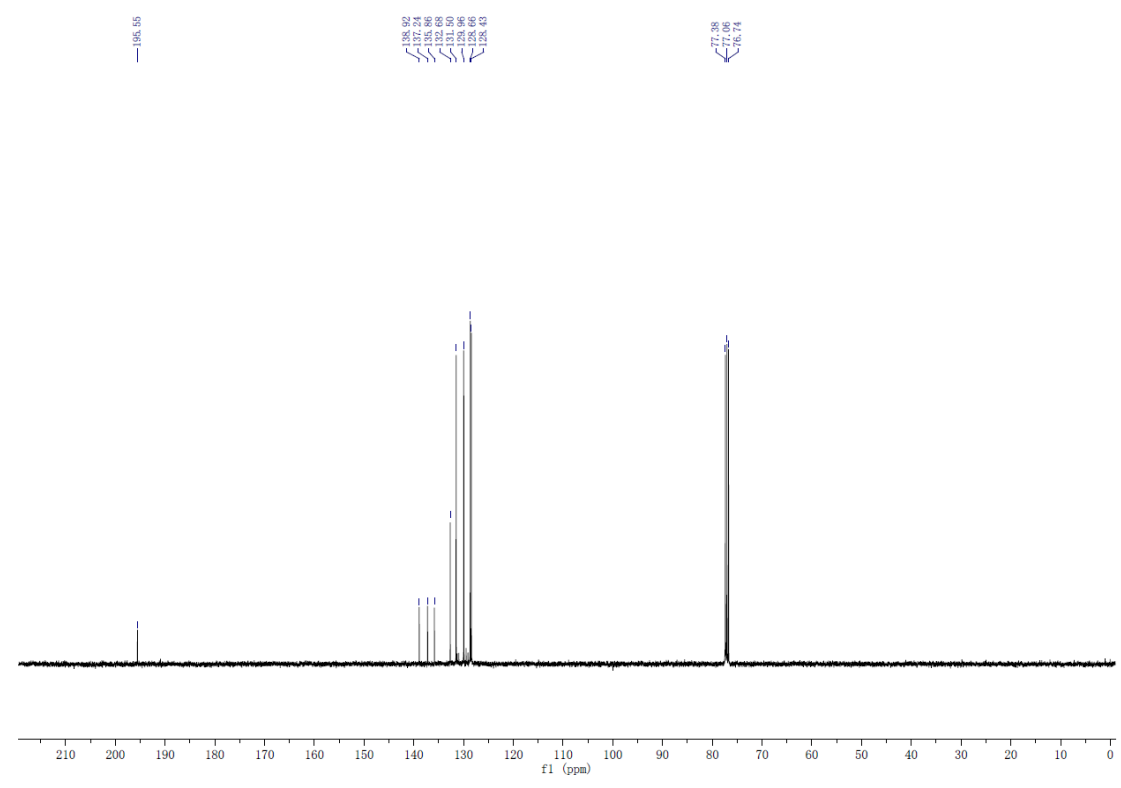
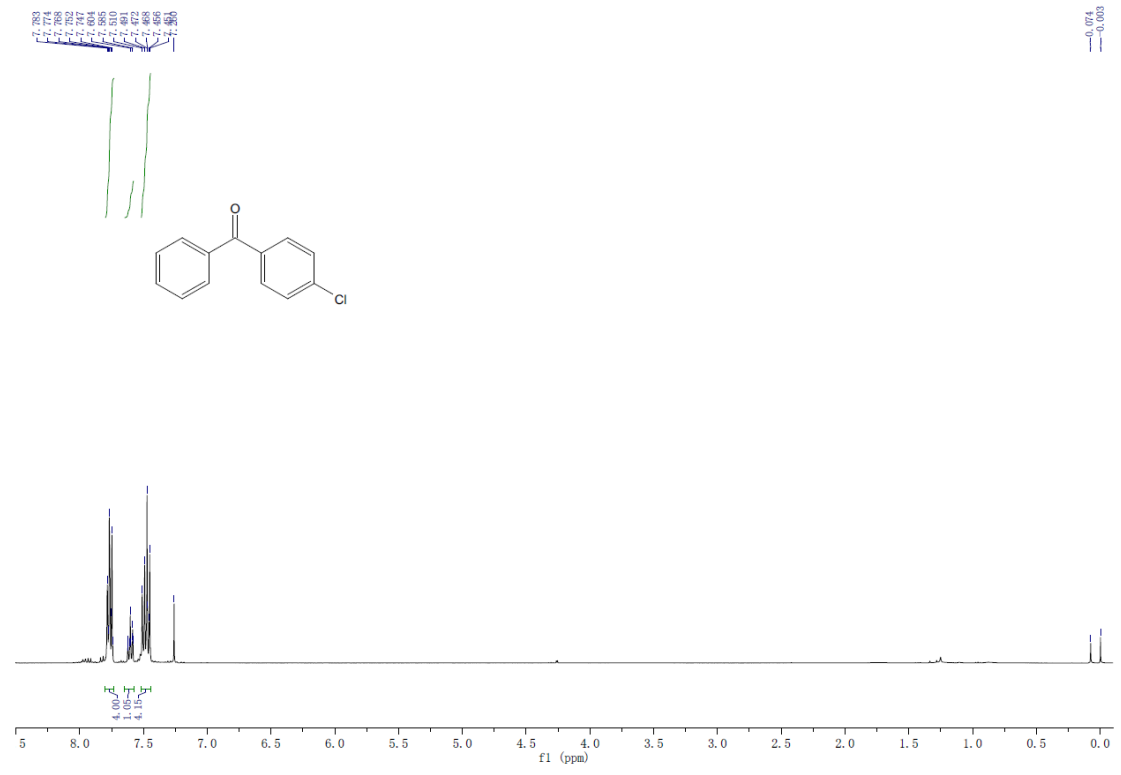
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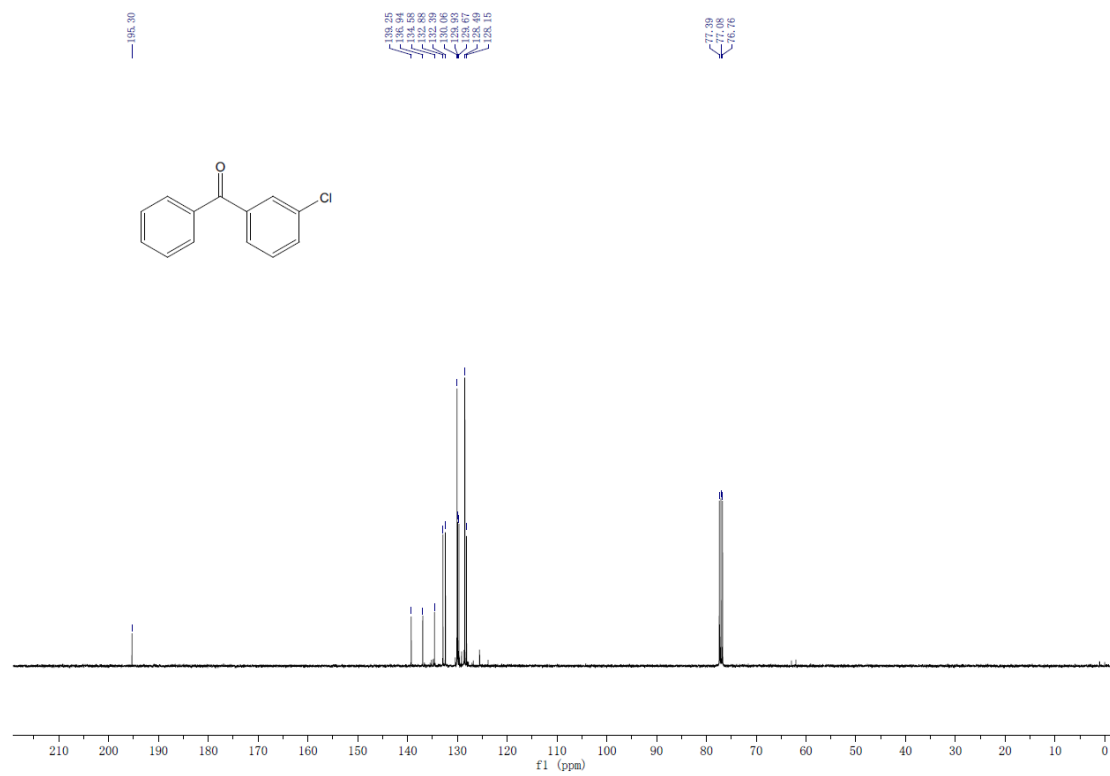
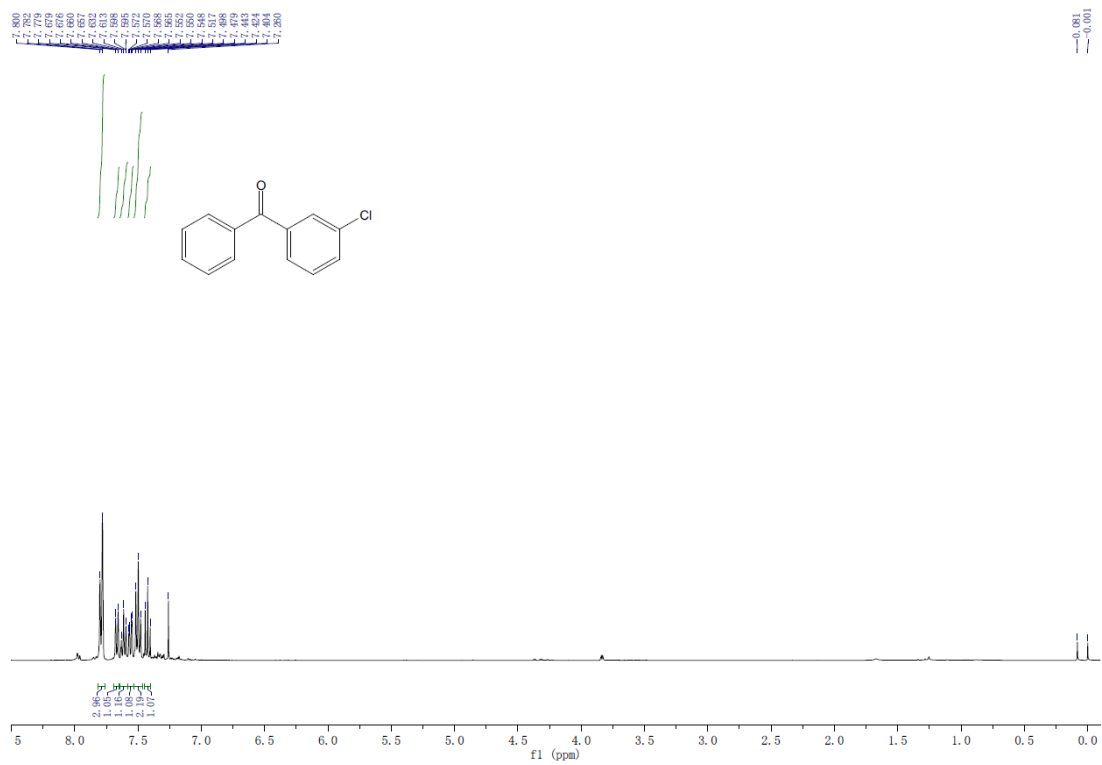
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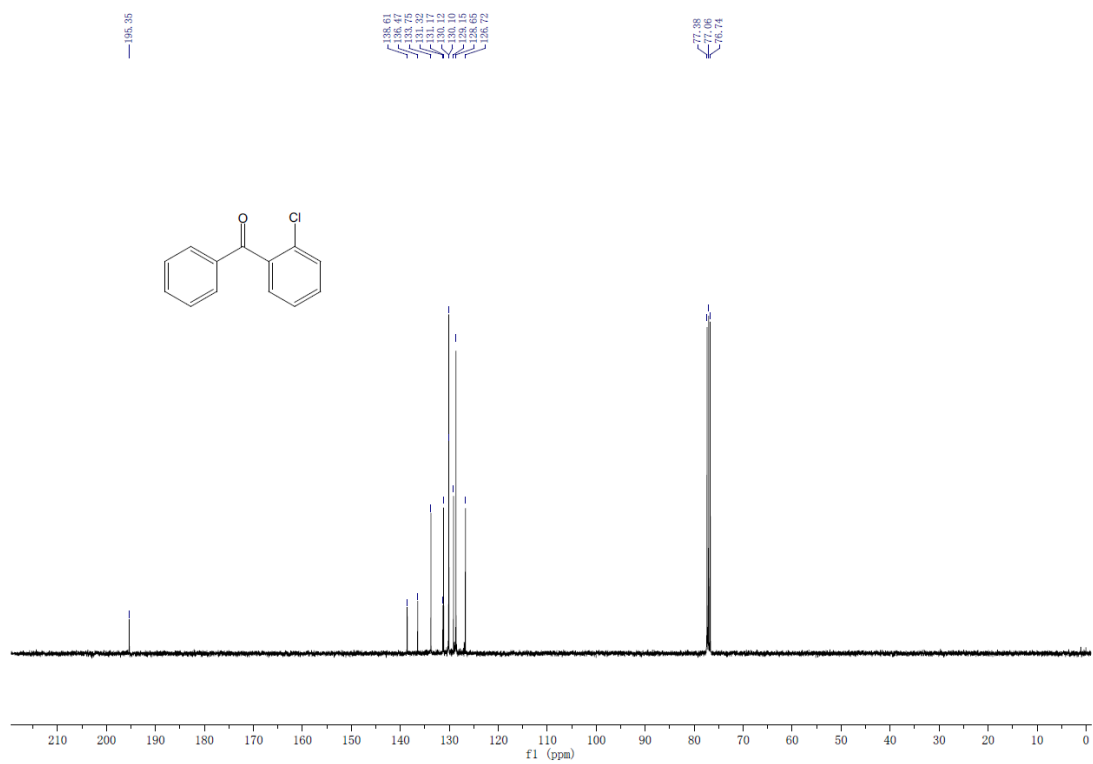
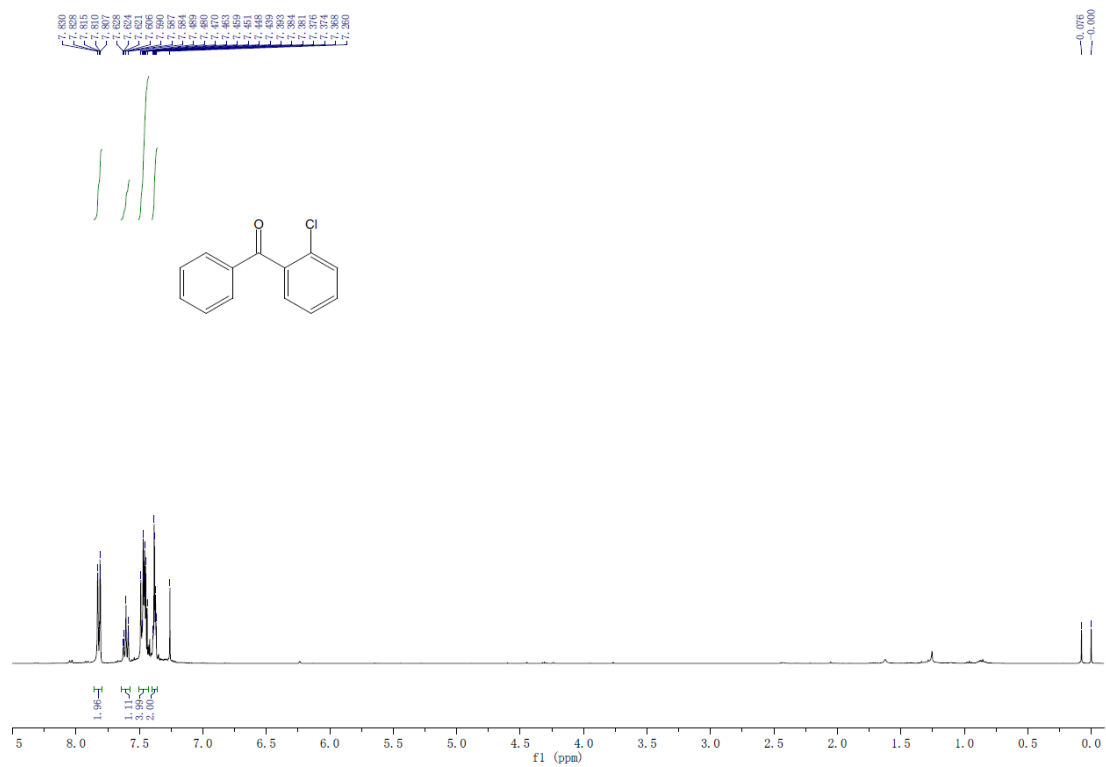
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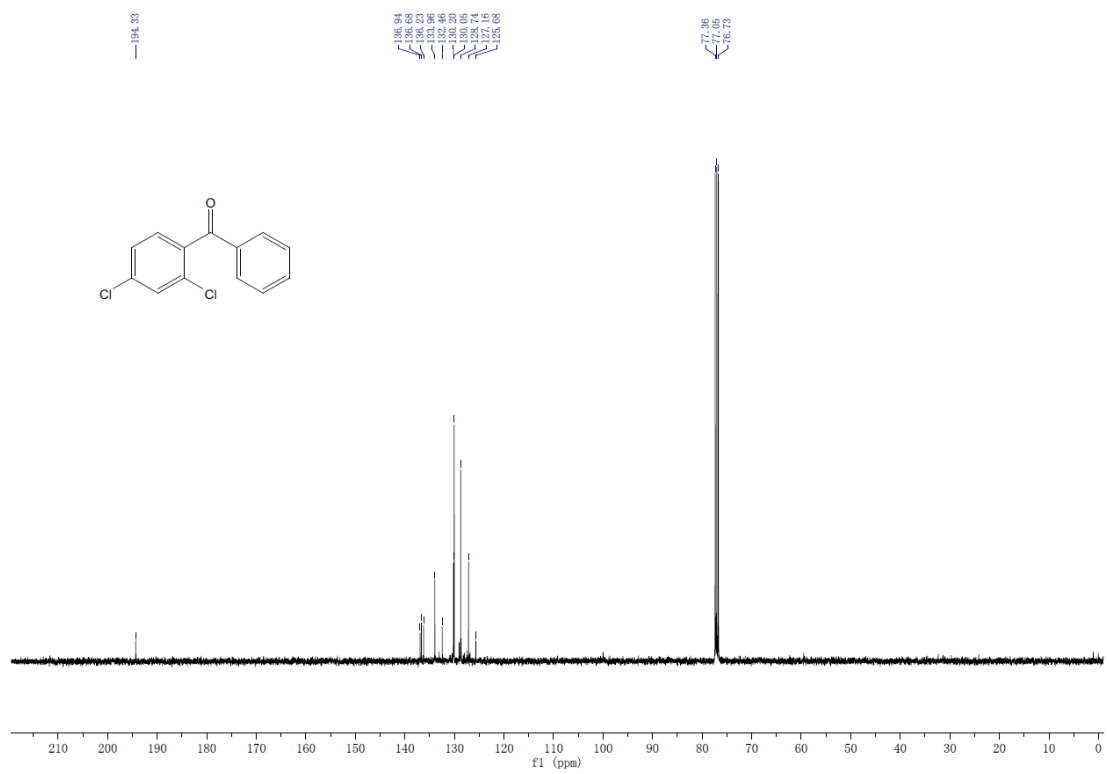
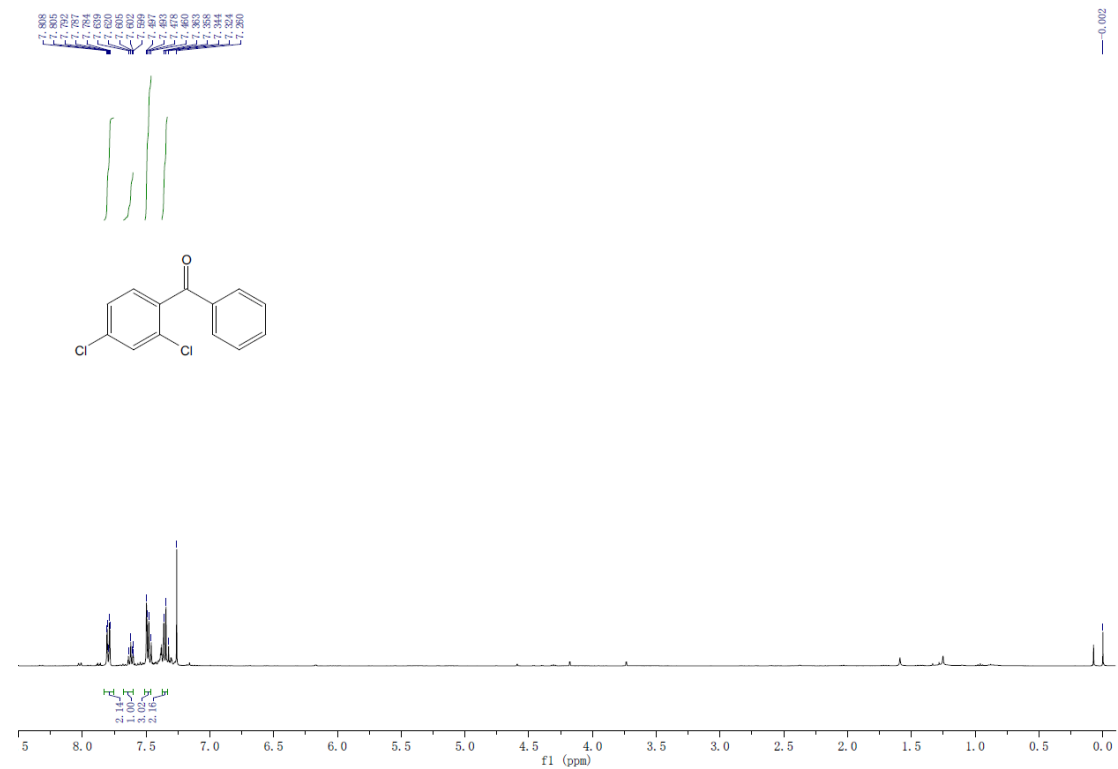
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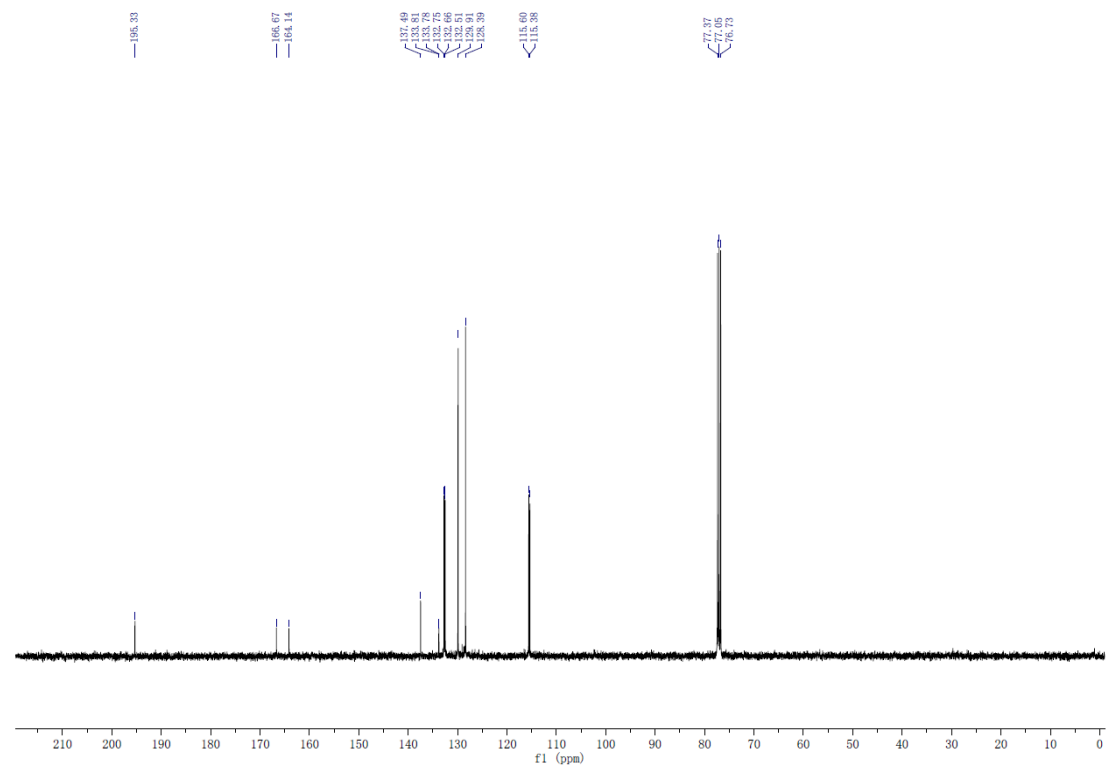
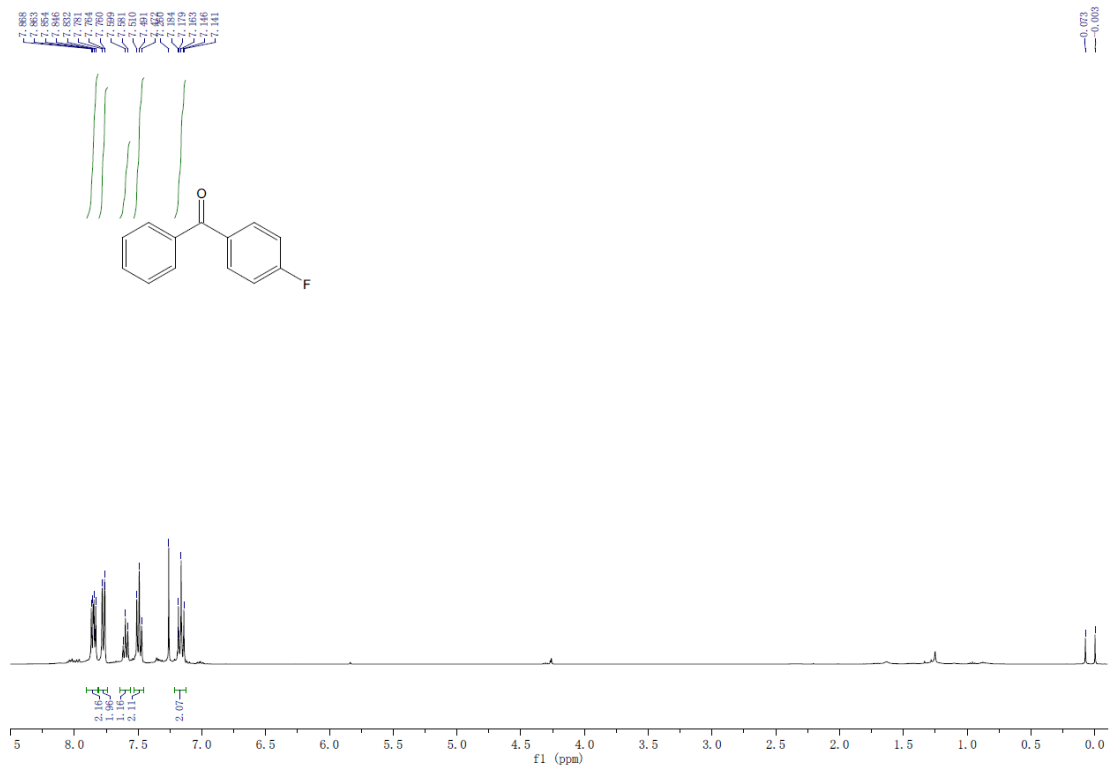
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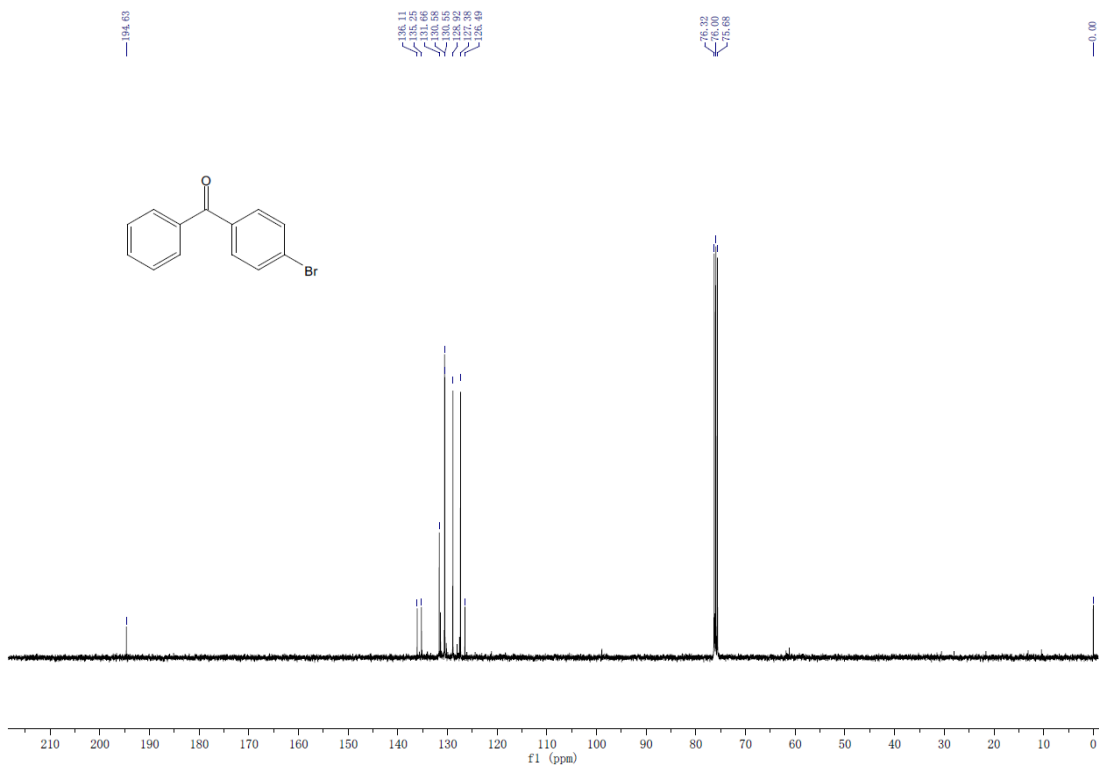
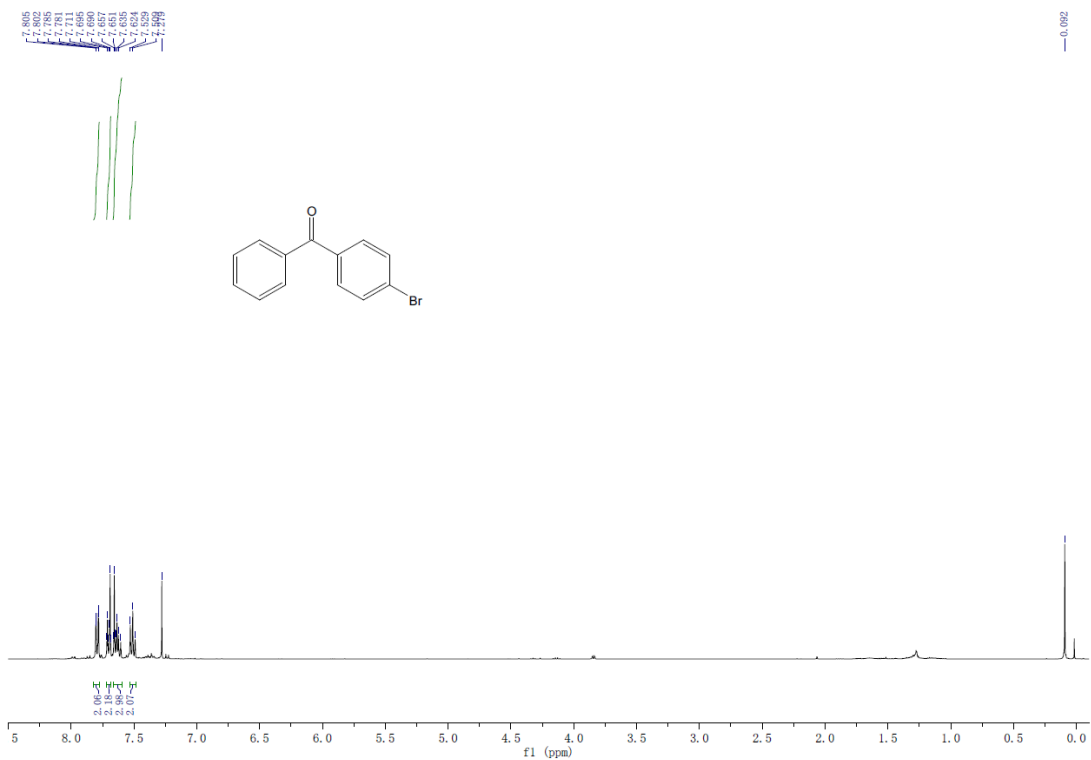
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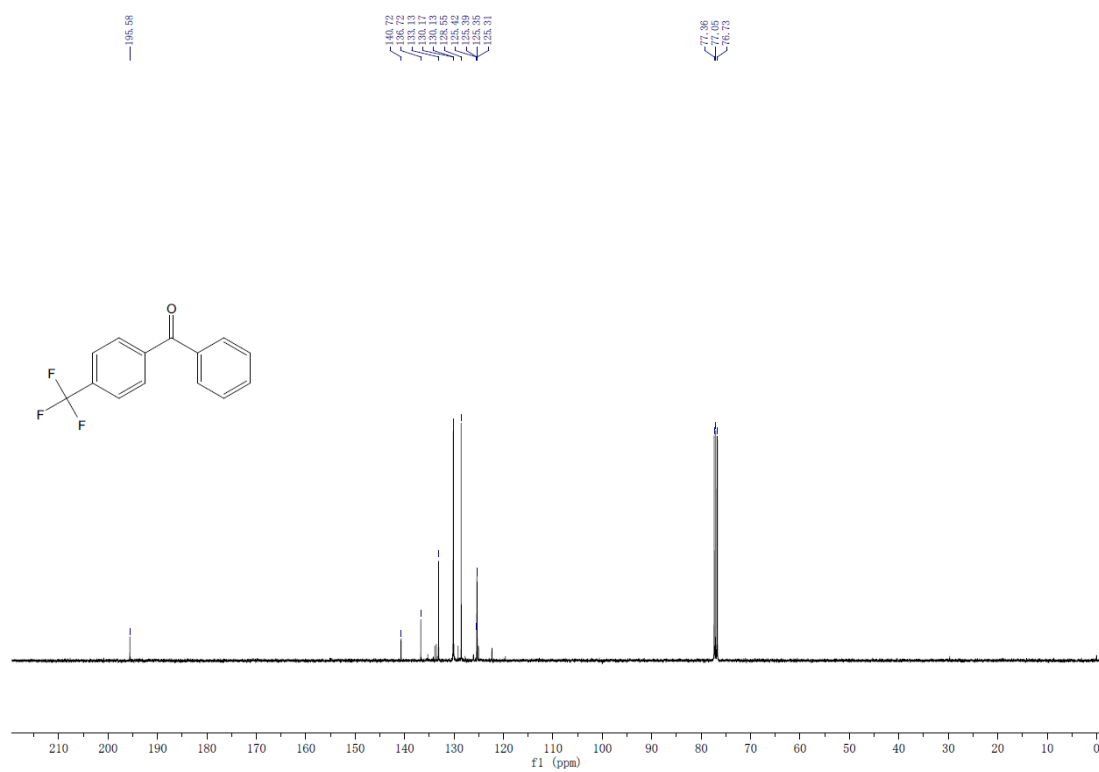
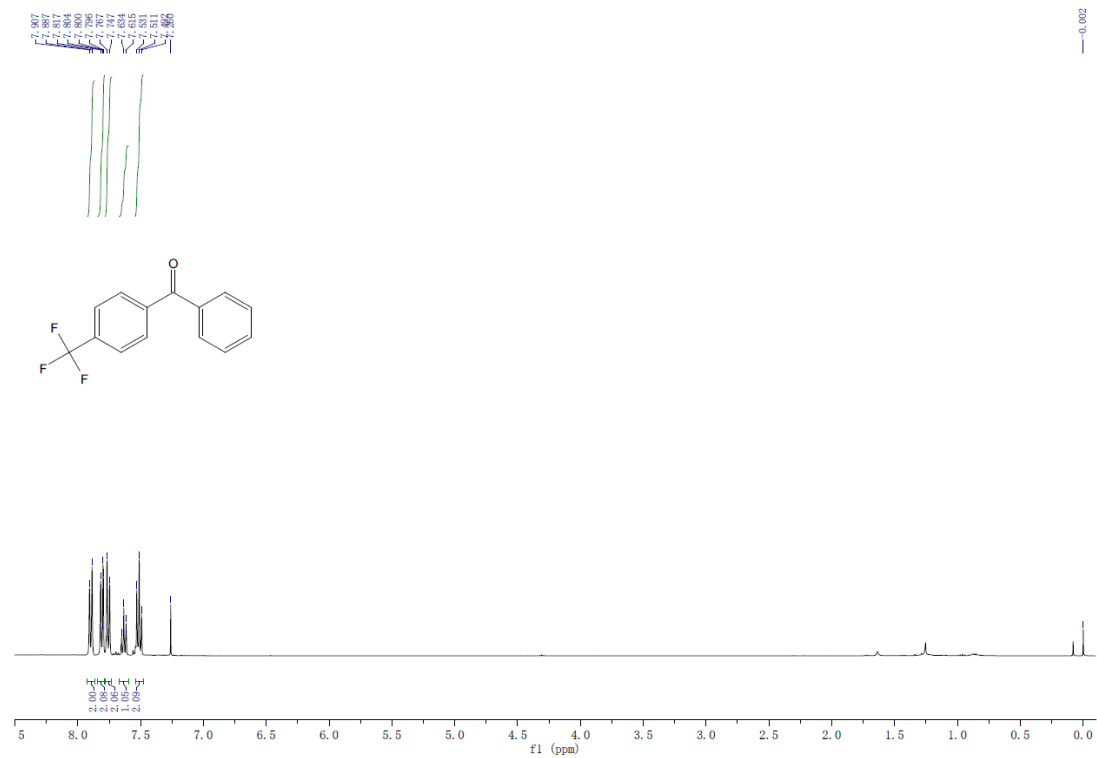
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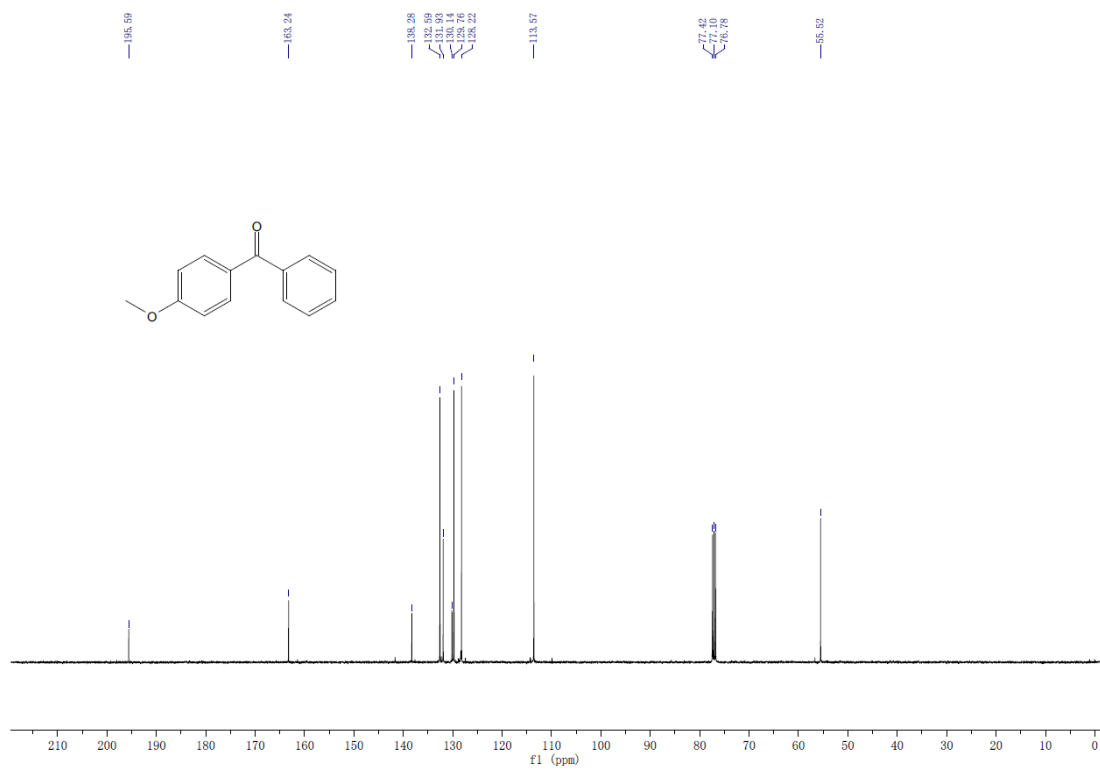
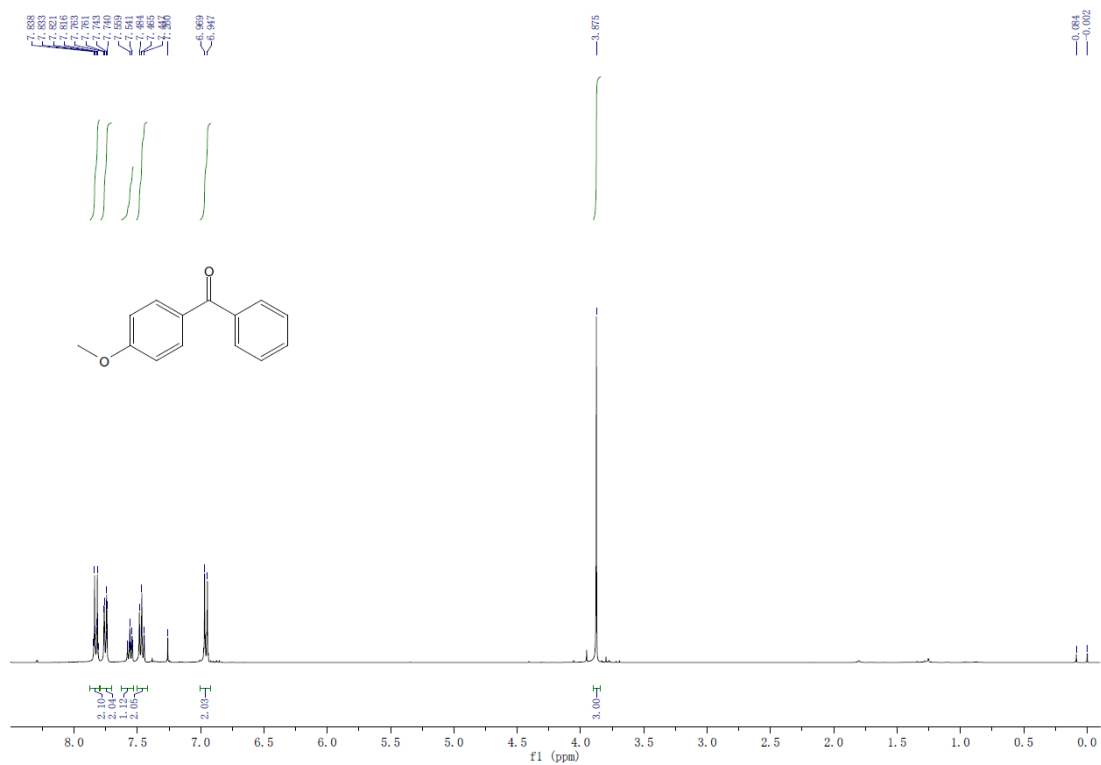
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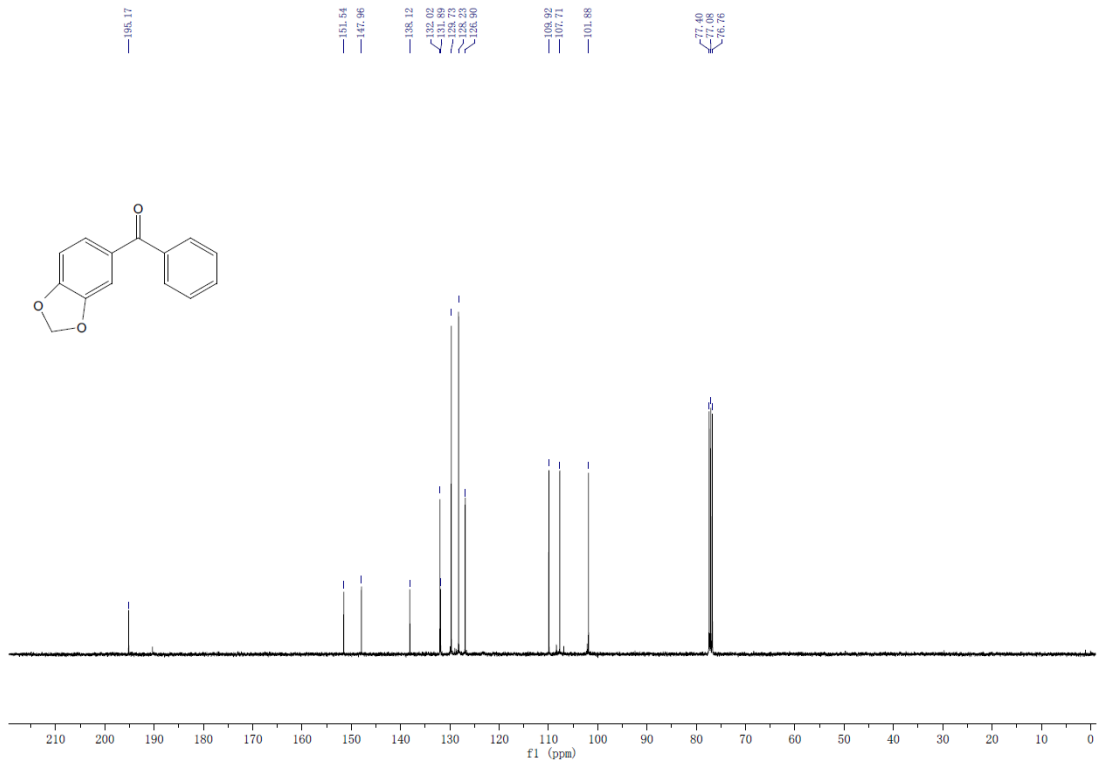
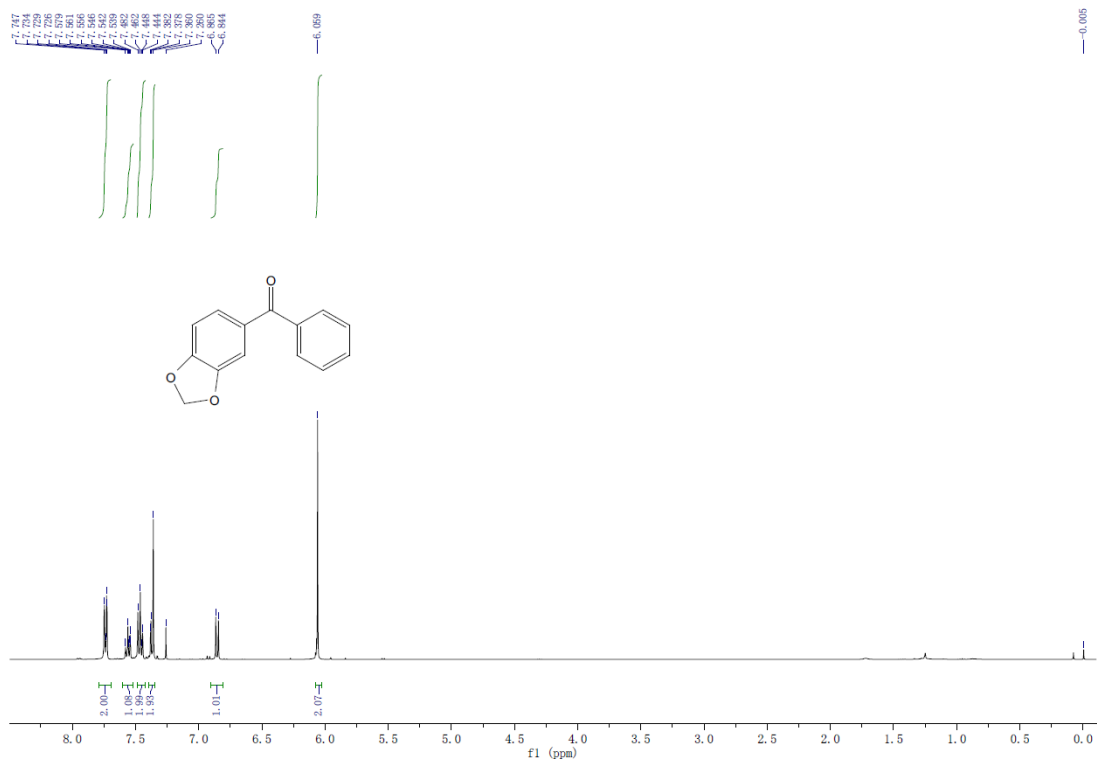
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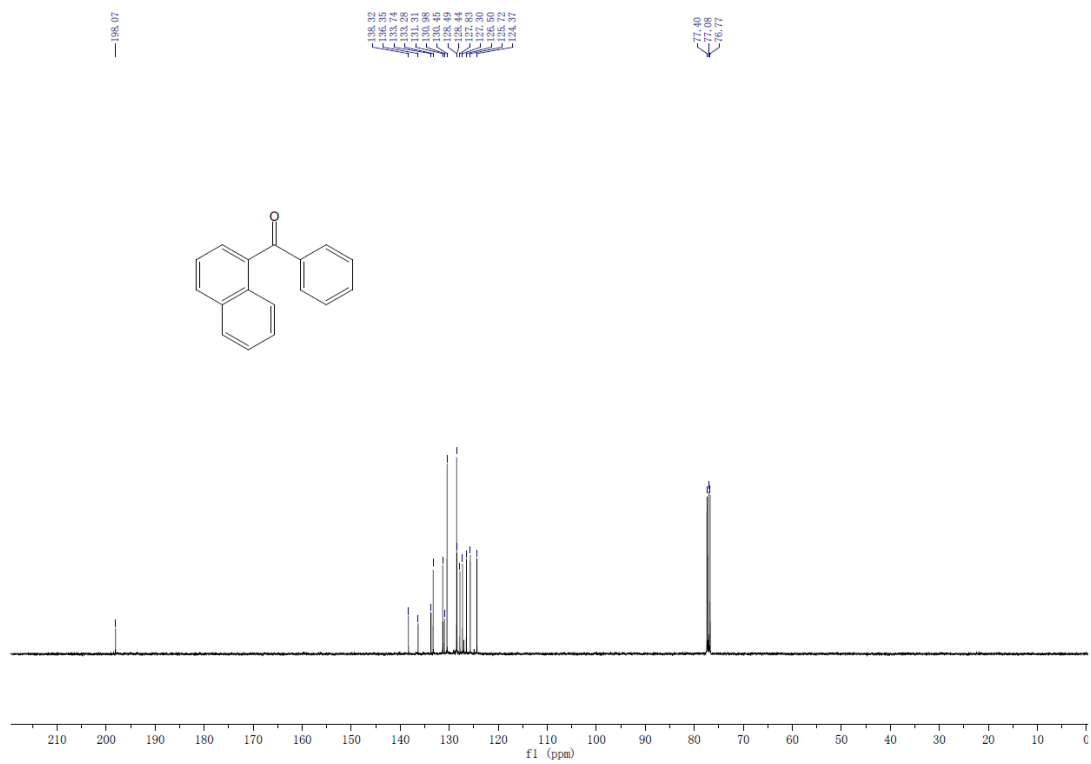
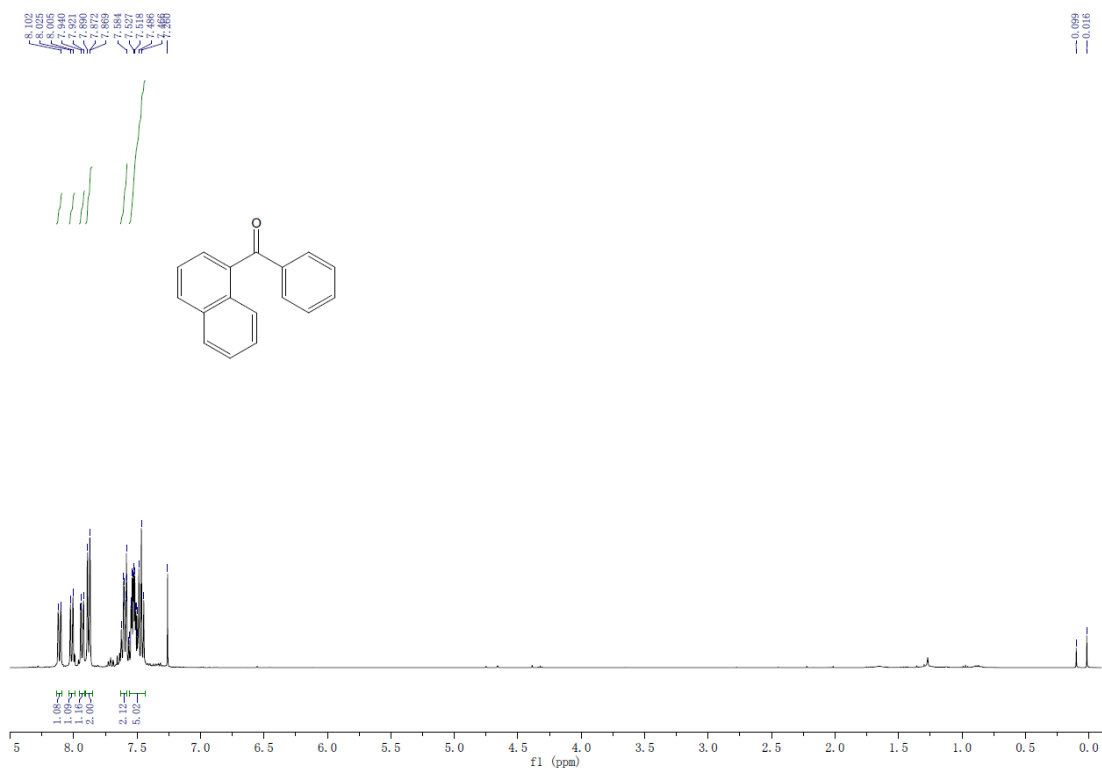
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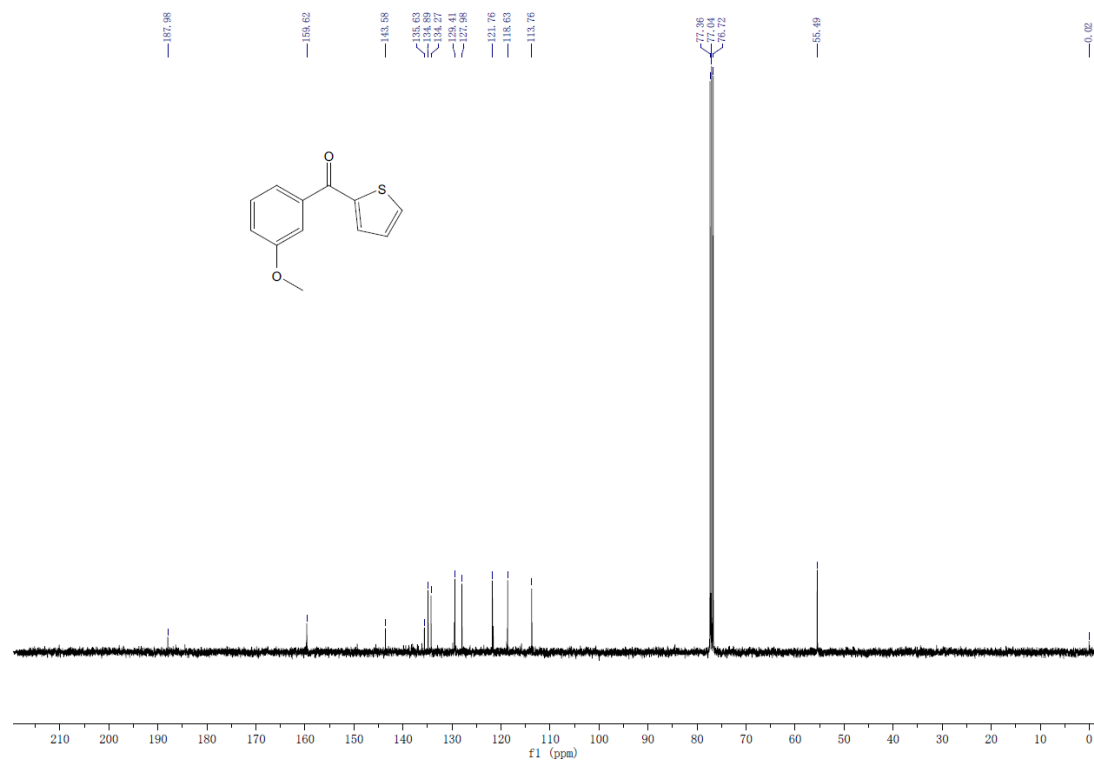
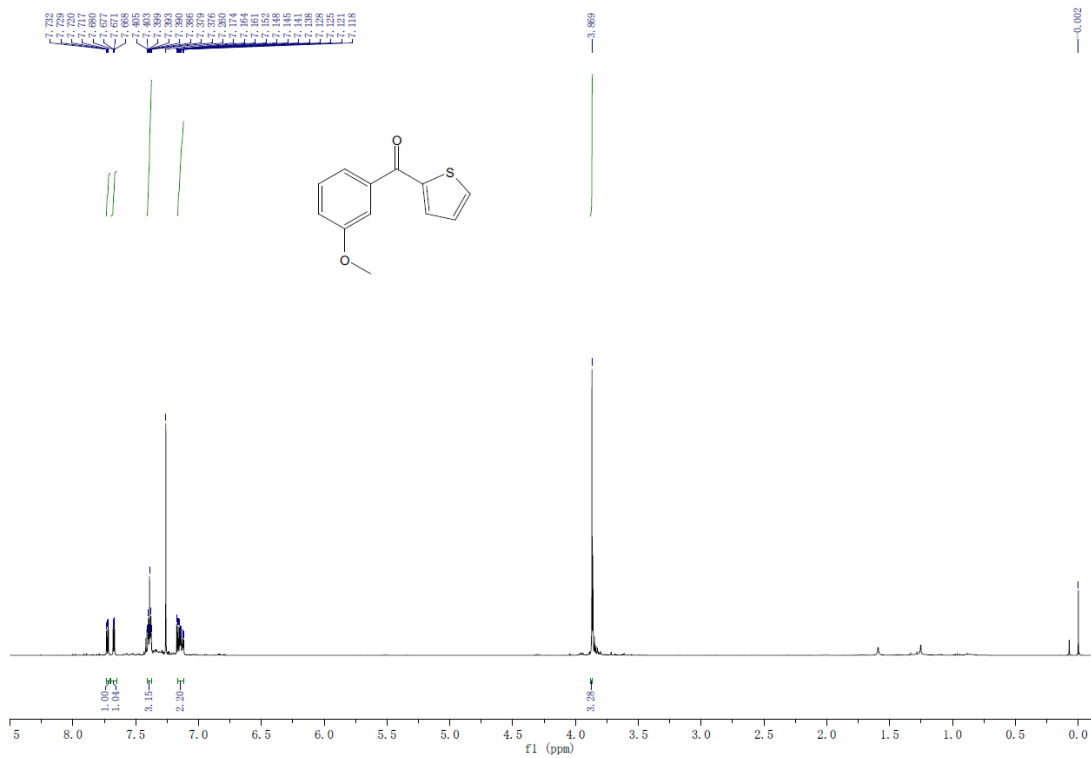
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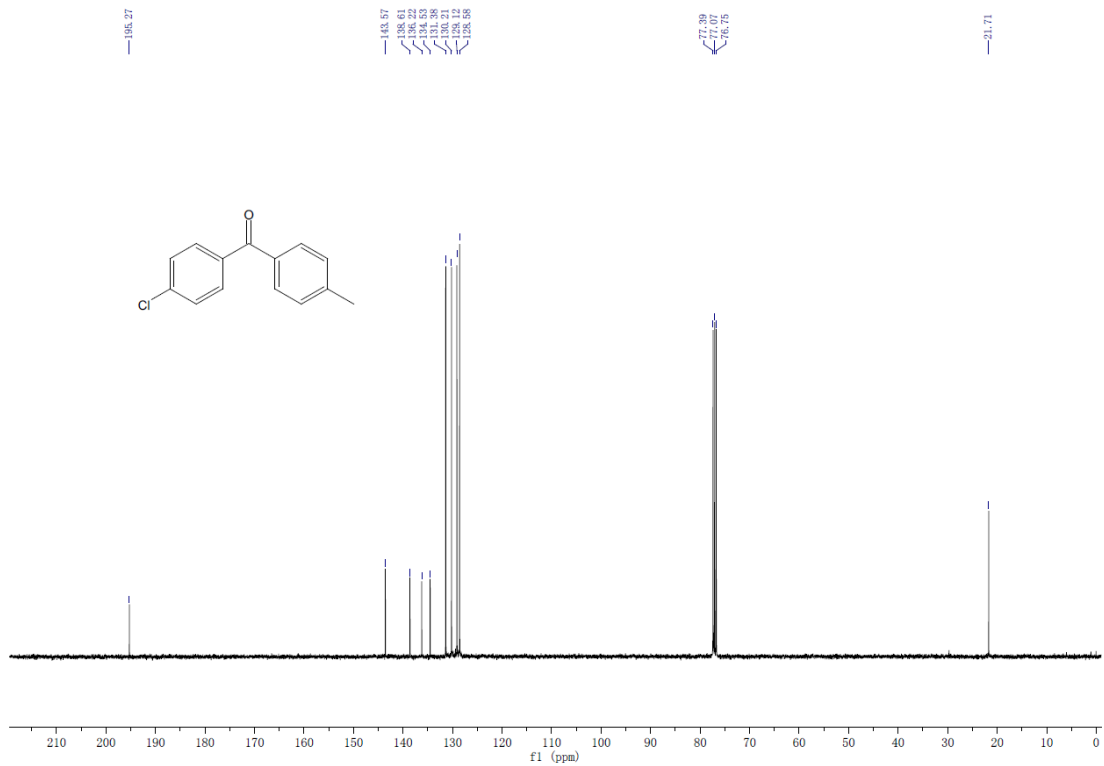
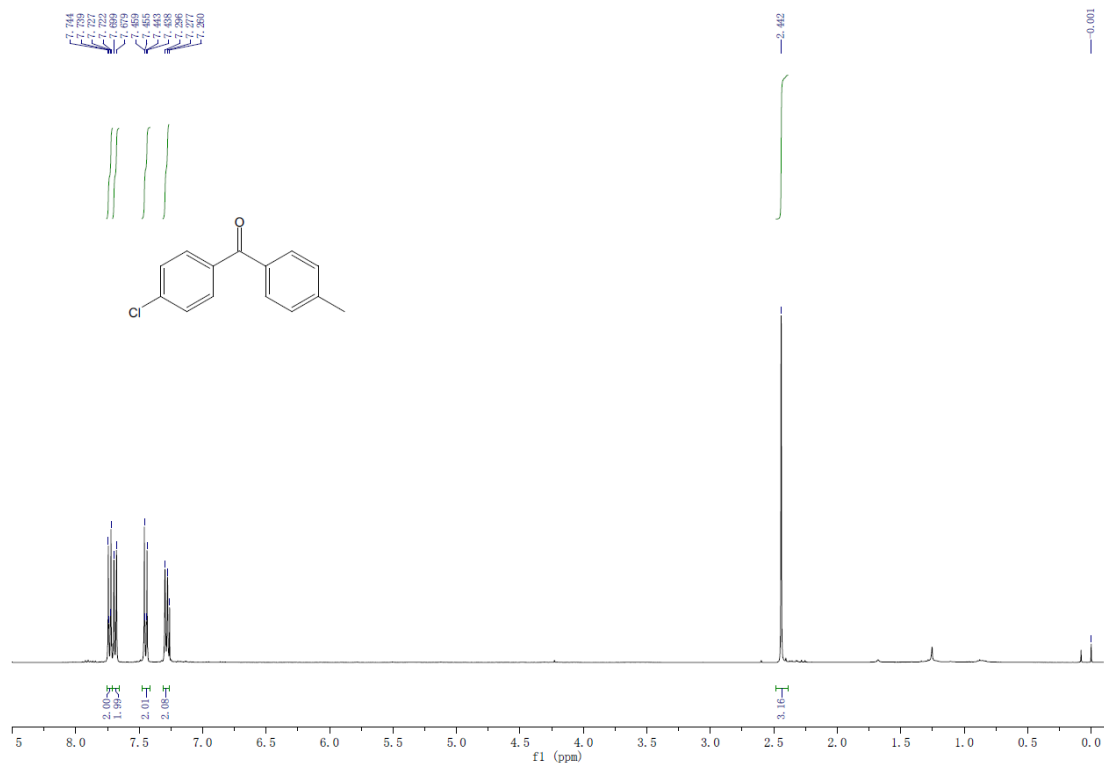
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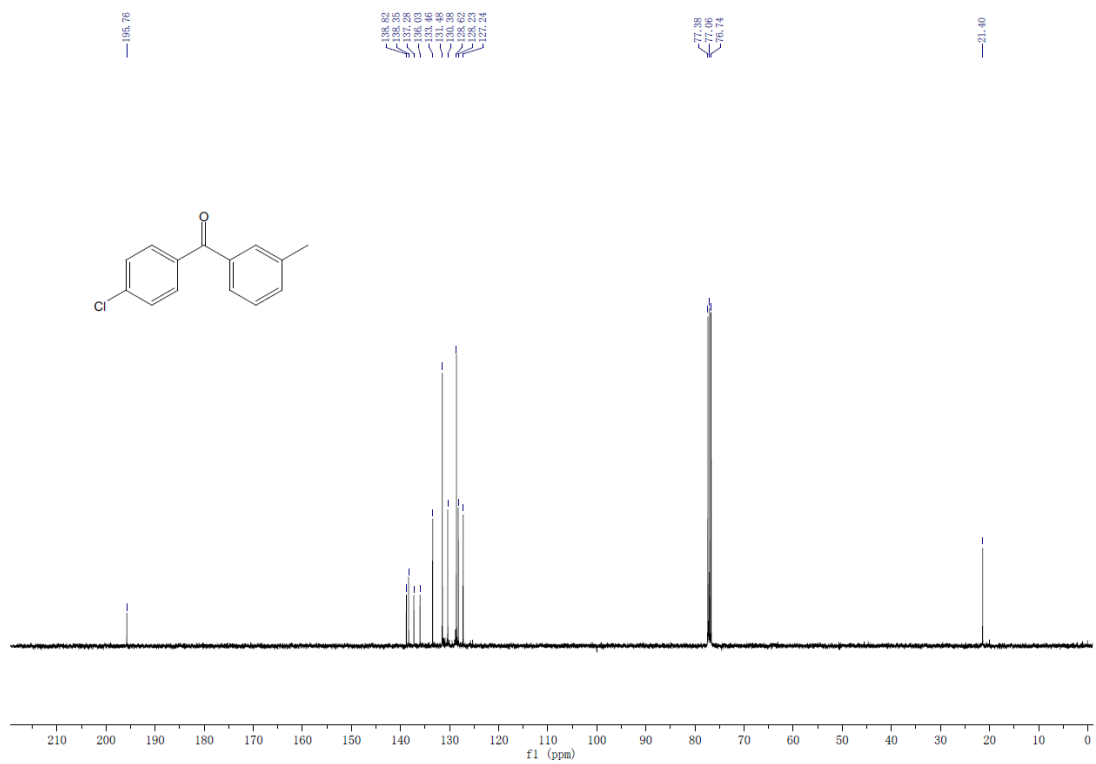
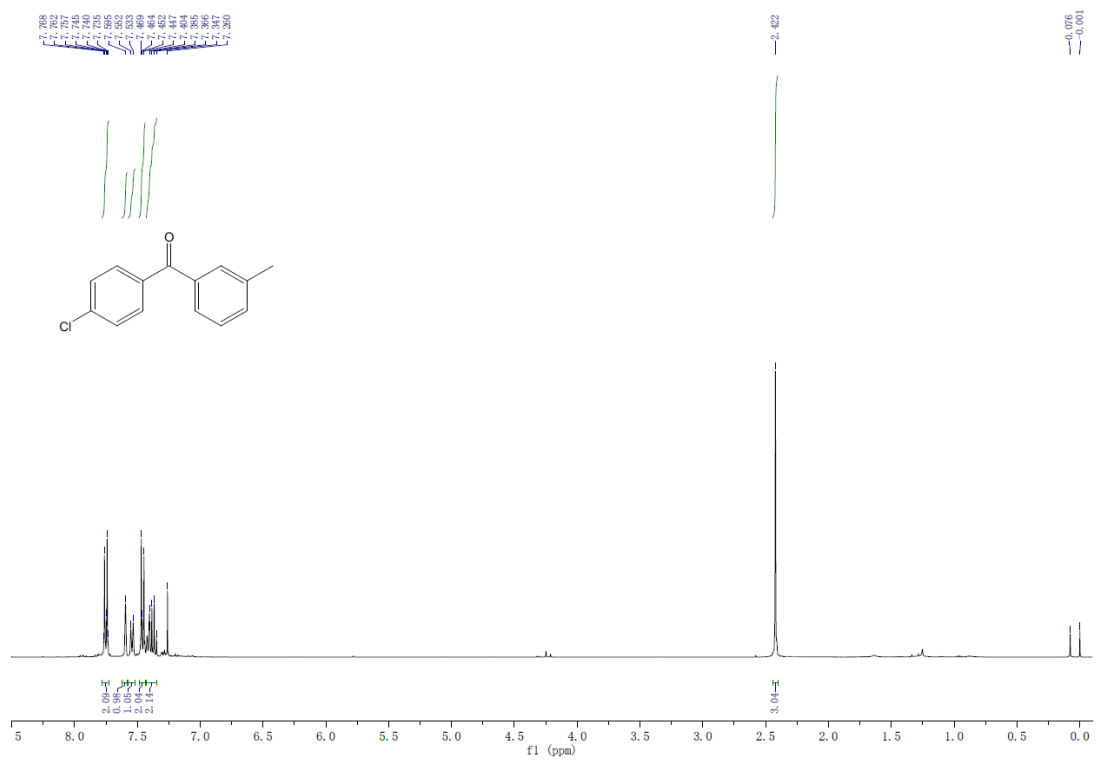
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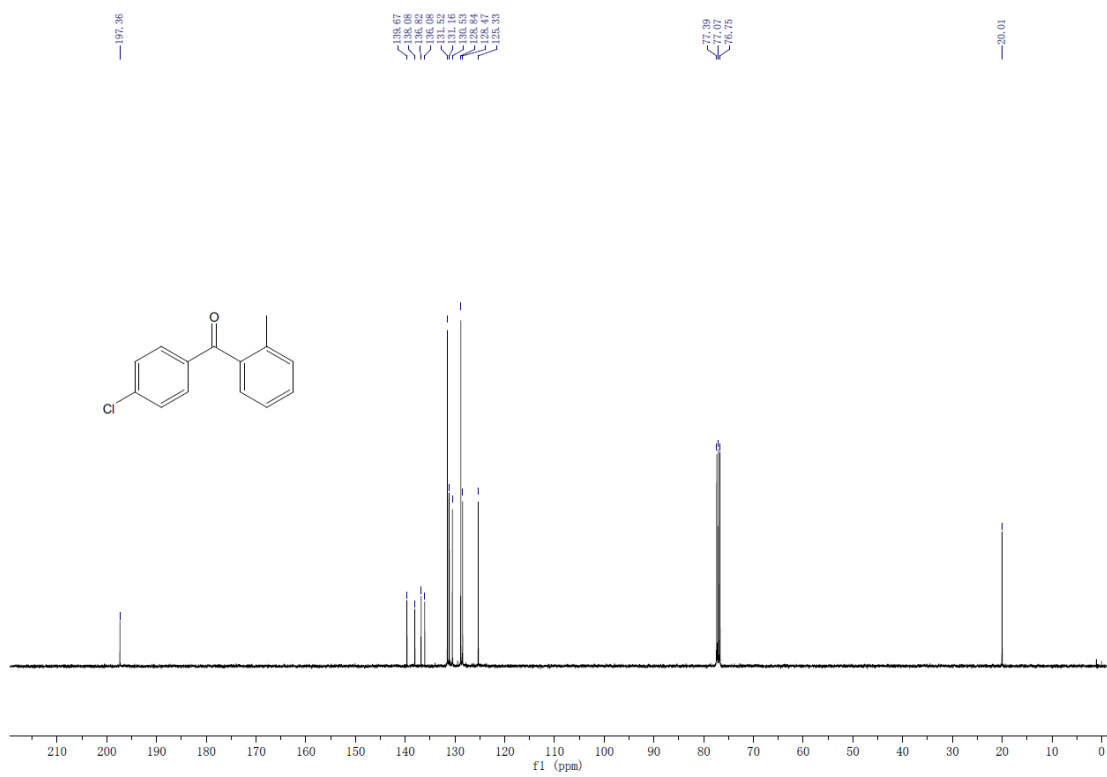
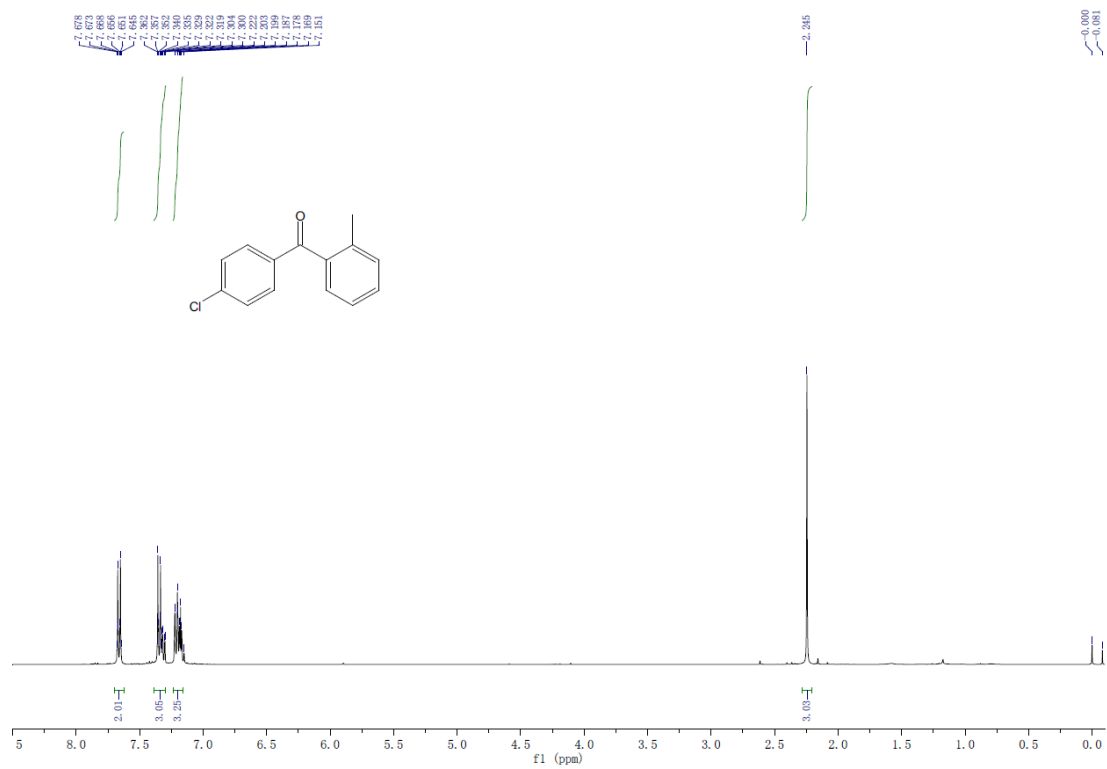
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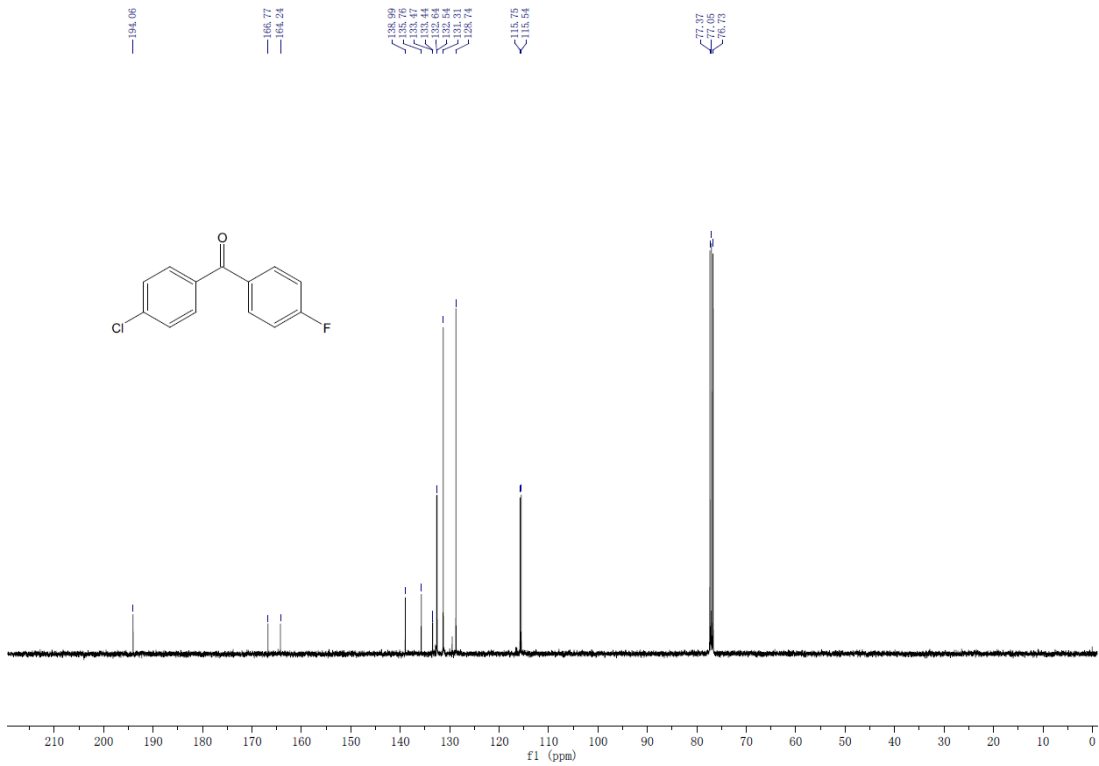
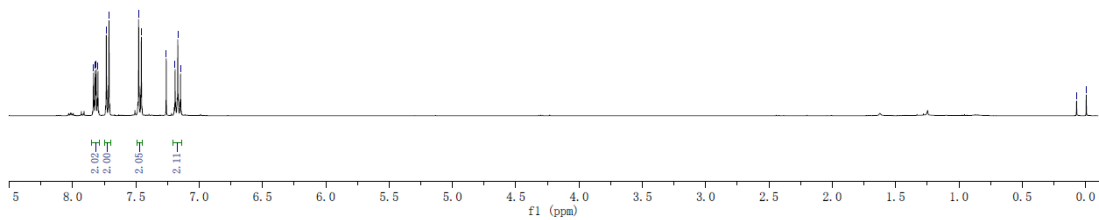
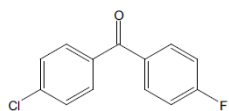
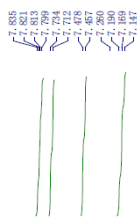
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2s



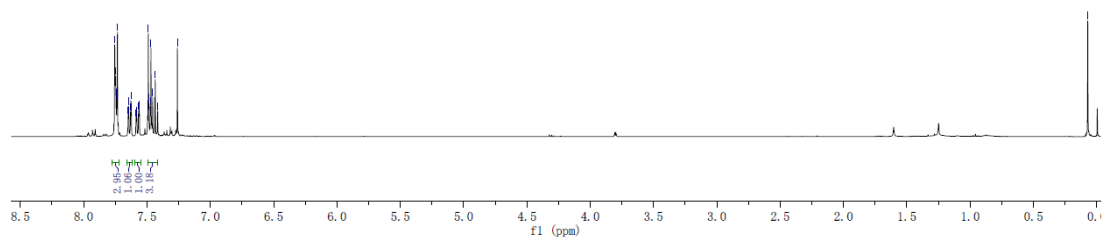
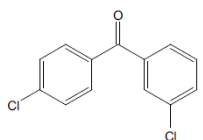
2t



2u

7.755
7.750
7.748
7.746
7.738
7.734
7.643
7.640
7.627
7.624
7.585
7.582
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7.280

0.071

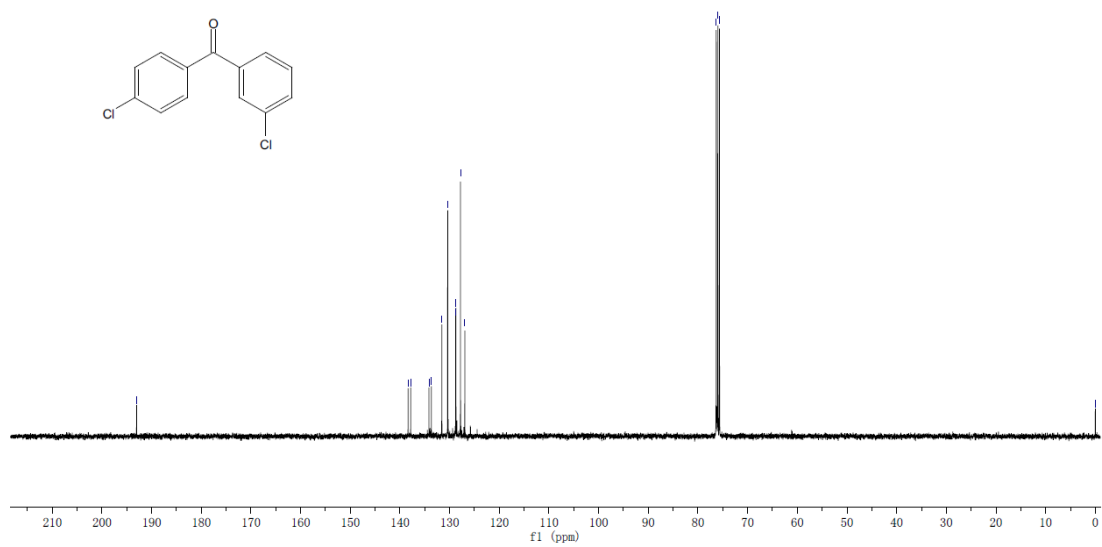
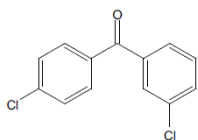


193.01

138.96
134.16
133.68
130.39
128.76
127.81
126.84

76.31
75.69

0.00



2z

