

Supporting information

Aerobic oxidative acylation of nitroarenes with arylacetic esters under mild conditions: Facile access to diarylketones

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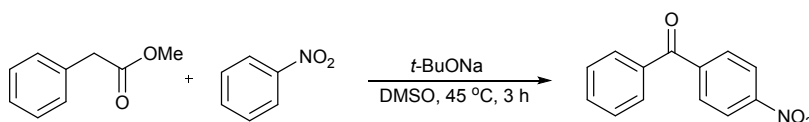
1) General information

All solvents and reagents were purchased from the suppliers and used without further purification unless otherwise stated. Yields reported are for isolated yields unless otherwise stated. ^1H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded in CDCl_3 at room temperature on Bruker Avance III 400 spectrometer using TMS as the internal reference. MS spectra were performed on a Agilent 6890/5973 GC-MS (EI), EVOQ GC-TQ(EI), or Waters UPLC_Xevo_TQD (ESI). Elemental analyses were measured on a Perkin Elmer 2400 series analyzer. The melting point (m.p.) was determined using an open glass tube. TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (mesh 200-300) at increased pressure.

2) General procedure for cascade oxidative reaction

To a predried 10 mL round-bottom flask were sequentially added phenylacetates **1** (0.2 mmol), nitroarenes **2** (0.4 mmol), dry DMSO (0.5 mL), and *t*-BuONa (0.4 mmol). The reaction system became dark purple on adding the base. The resulting mixture was stirred at 45°C for the specific time. Then it was cooled to room temperature, to which added aqueous HCl (1 M) to pH=6-7, and the resulting mixture was extracted with ethyl acetate, dried over anhydrous Na_2SO_4 , and concentrated with rotary evaporation. Then the resulting residue was subjected to column chromatography on silica gel using co-solvent (ethyl acetate/ petroleum ether=1/40, v/v) as eluent to give the corresponding diarylketones.

3) Screening parameters



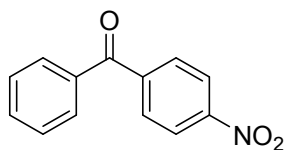
Entry	Ester (equiv)	Nitrobenzene (equiv)	DMSO (mL)	Base (equiv)	Yield(%)
1	1	0.5	0.5	2	60
2	1	1	0.5	2	71
3	1	1.5	0.5	2	75
4	1	2	0.5	2	80
5	1	3	0.5	2	80
6	1	2	0.1	2	62
7	1	2	1	2	74
8	1	2	0.5	1	58
9	1	2	0.5	1.5	70
10	1	2	0.5	3	80

^aReactions were carried out using methyl phenylacetate (0.2 mmol) and nitrobenzene (specified amount) and

base (specified amount) in dry DMSO (specified) for 3 h.

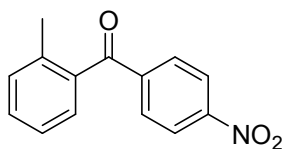
4) Characterization data

(4-Nitro-phenyl)-phenyl-methanone (3aa)¹



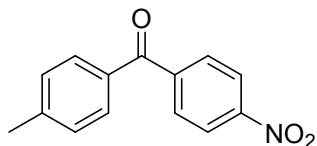
Yellow solid, m. p. 132-134 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 8.6 Hz, 2H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 194.8, 149.8, 142.9, 136.3, 133.5, 130.7 (2C), 130.1 (2C), 128.7 (2C), 123.6 (2C). MS (EI): *m/z* 227.1 [M]⁺⁺.

(4-Nitrophenyl)(*o*-tolyl)methanone (3ab)²



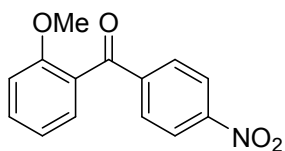
Yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.38-7.28 (m, 3H), 2.38 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 196.6, 150.2, 142.8, 137.7, 137.0, 131.6, 131.4, 130.9 (2C), 129.2, 125.5, 123.7 (2C), 20.3. MS (EI): *m/z* 241.1 [M]⁺⁺.

(4-Nitrophenyl)(*p*-tolyl)methanone (3ac)³



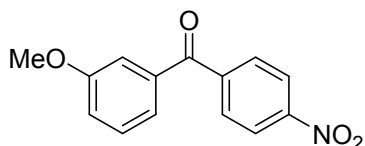
Yellow solid, m. p. 122-123 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.6, 149.7, 144.6, 143.3, 133.6, 130.6 (2C), 130.4 (2C), 129.4 (2C), 123.5 (2C), 21.8. MS (EI): *m/z* 241.1 [M]⁺⁺.

(2-Methoxyphenyl)(4-nitrophenyl)methanone (3ad)²



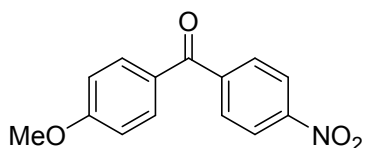
Yellow solid, m. p. 88-90 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 8.2 Hz, 2H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 3.69 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.8, 157.7, 150.0, 143.2, 133.4, 130.3 (2C), 127.4, 123.4(2C), 121.0, 111.6, 55.5. MS (EI): *m/z* 257.2 [M]⁺⁺.

(3-Methoxyphenyl)(4-nitrophenyl)methanone (3ae)⁴



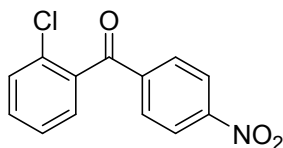
Yellow solid, m. p. 75-76 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 8.3 Hz, 2H), 7.42 (t, J = 7.9 Hz, 1H), 7.37 (s, 1H), 7.31 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 8.2 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.6, 159.9, 149.8, 142.9, 137.6, 130.7 (2C), 129.6, 123.5 (2C), 122.9, 119.9, 114.3, 55.6. MS (EI): m/z 257.2 $[\text{M}]^{+}$.

(4-Methoxyphenyl)(4-nitrophenyl)methanone (3af)⁴



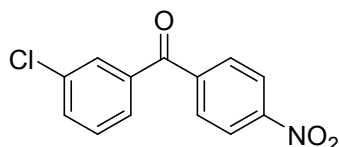
White solid, m. p. 127-129 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, J = 7.6 Hz, 2H), 7.89 (d, J = 7.6 Hz, 2H), 7.82 (d, J = 7.6 Hz, 2H), 7.00 (d, J = 7.6 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.5, 164.0, 149.6, 143.8, 132.7 (2C), 130.4 (2C), 129.0, 123.5 (2C), 114.0 (2C), 55.6. MS (ESI): m/z 258.2 $[\text{M}+\text{H}]^{+}$.

(2-Chlorophenyl)(4-nitrophenyl)methanone (3ag)⁵



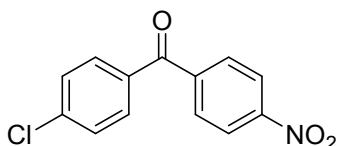
Yellow solid, m. p. 100-102 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, J = 8.4 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H), 7.50 (s, 2H), 7.45 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.7, 150.5, 141.2, 137.3, 132.2, 131.5, 130.8 (2C), 130.4, 129.5, 127.2, 123.9 (2C). MS (EI): m/z 261.0 $[\text{M}]^{+}$, 263.0.

(3-Chlorophenyl)(4-nitrophenyl)methanone (3ah)



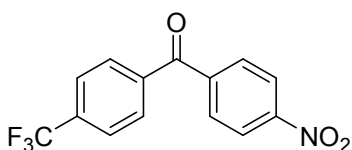
Yellow solid, m. p. 91-92 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.36 (d, J = 8.5 Hz, 2H), 7.94 (d, J = 8.5 Hz, 2H), 7.79 (s, 1H), 7.67 (d, J = 7.7 Hz, 1H), 7.63 (d, J = 8.1 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.4, 150.1, 142.1, 137.9, 135.1, 133.4, 130.7 (2C), 130.0, 129.9, 128.2, 123.7 (2C). MS (EI): m/z 261.0 $[\text{M}]^{+}$, 263.0. Anal. Calcd for $\text{C}_{13}\text{H}_8\text{ClNO}_3$ C 59.67, H 3.08, N 5.35%; Found: C 59.53, H 3.25, N 5.51%.

(4-Chlorophenyl)(4-nitrophenyl)methanone (3ai)³



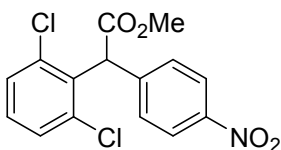
Yellow solid, m. p. 103-105 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.35 (d, J = 8.3 Hz, 2H), 7.92 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.6, 149.9, 142.5, 140.1, 134.6, 131.5 (2C), 130.6 (2C), 129.1 (2C), 123.7 (2C). MS (EI): m/z 261.0 $[\text{M}]^{+}$, 263.0.

(4-Nitrophenyl)(4-(trifluoromethyl)phenyl)methanone (3aj)⁶



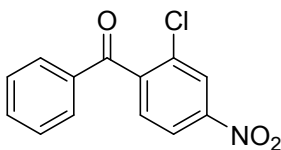
White solid, m. p. 112-114 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.37 (d, J = 8.2 Hz, 2H), 7.96 (d, J = 8.1 Hz, 2H), 7.92 (d, J = 7.9 Hz, 2H), 7.81 (d, J = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.7, 150.2, 141.8, 139.3, 134.9, 134.5, 130.8, 130.3, 125.84, 125.80, 125.77, 125.73, 123.8, 122.1. MS (EI): m/z 295.0 $[\text{M}]^{+}$.

Methyl 2-(2,6-dichlorophenyl)-2-(4-nitrophenyl)acetate (4ak)



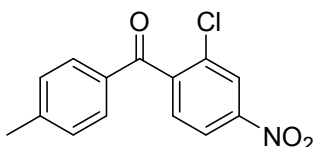
White solid, m. p. 153-155 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.26 (t, J = 8.0 Hz, 1H), 5.86 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.3, 147.1, 142.3, 136.0 (2C), 134.1, 130.3 (2C), 129.8, 129.2 (2C), 123.4 (2C), 53.0, 51.8. MS (ESI): m/z 340.0 $[\text{M}+\text{H}]^{+}$. Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{Cl}_2\text{NO}_4$ C 57.97, H 3.26, N 4.12%; Found: C 57.81, H 3.38, N 4.33%.

(2-Chloro-4-nitrophenyl)(phenyl)methanone (3ba)⁷



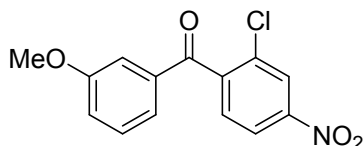
Yellow solid, m. p. 93-94 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.36 (s, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.57 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.3, 148.9, 144.5, 135.3, 134.6, 132.6, 130.0 (2C), 129.6, 129.0 (2C), 125.3, 121.9. MS (EI): m/z 261.0 $[\text{M}]^{+}$, 263.0.

(2-Chloro-4-nitrophenyl)(p-tolyl)methanone (3bc)⁷



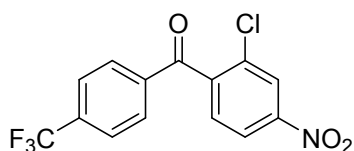
Yellow solid, m. p. 113-115 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.34 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.55 (d, J = 8.3 Hz, 1H), 7.30 (d, J = 7.8 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.9, 148.8, 145.9, 144.8, 132.8, 132.5, 130.2 (2C), 129.8 (2C), 129.5, 125.3, 121.9, 21.9. MS (EI): m/z 275.0 $[\text{M}]^{+}$, 277.0.

(2-Chloro-4-nitrophenyl)(3-methoxyphenyl)methanone (3be)



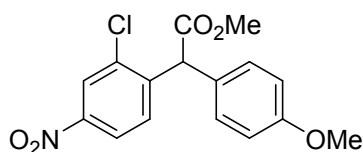
Yellow solid, m. p. 110-112 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H), 8.24 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 8.3 Hz, 1H), 7.42 (s, 1H), 7.39 (t, J = 8.2 Hz, 1H), 7.21 (t, J = 8.2 Hz, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.1, 160.1, 148.9, 144.5, 136.6, 132.6, 130.0, 129.6, 125.3, 123.2, 121.9, 121.3, 113.4, 55.6. MS (EI): m/z 291.0 $[\text{M}]^{+}$, 293.0. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{ClNO}_4$ C 57.65, H 3.46, N 4.80%; Found: C 57.80, H 3.65, N 4.63%.

(2-Chloro-4-nitrophenyl)(4-(trifluoromethyl)phenyl)methanone (3bj)



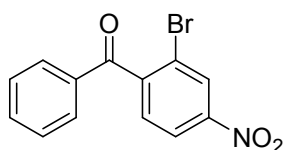
Yellow solid, m. p. 98-100 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.38 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 192.4, 149.2, 143.5, 138.0, 135.8, 135.5, 132.6, 130.2, 129.9, 126.14, 126.10, 126.06, 126.03, 125.5, 124.7, 122.2. MS (EI): m/z 329.0 $[\text{M}]^{+}$. Anal. Calcd for $\text{C}_{14}\text{H}_7\text{ClF}_3\text{NO}_3$ C 51.01, H 2.14, N 4.25%; Found: C 51.20, H 2.00, N 4.38%.

Methyl 2-(2-chloro-4-nitrophenyl)-2-(4-methoxyphenyl)acetate (4bf)



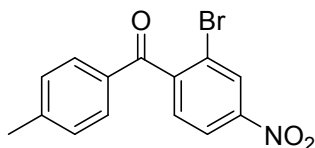
Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.26 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.20 (d, J = 7.6 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 5.44 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.5, 159.4, 147.3, 144.1, 135.0, 130.9, 130.0 (2C), 127.6, 124.7, 121.8, 114.6 (2C), 55.3, 53.1, 52.9. MS (ESI): m/z 336.1 $[\text{M}+\text{H}]^{+}$. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{ClNO}_5$ C 57.24, H 4.20, N 4.17%; Found: C 57.40, H 4.42, N 4.45%.

(2-Bromo-4-nitrophenyl)(phenyl)methanone (3ca)⁸



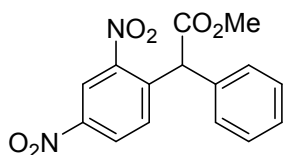
White solid, m. p. 101 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.53 (s, 1H), 8.30 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.54 – 7.49 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.0, 148.7, 146.6, 134.9, 134.6, 130.1 (2C), 129.4, 129.0 (2C), 128.3, 122.4, 120.2.

(2-Bromo-4-nitrophenyl)(p-tolyl)methanone (3cc)



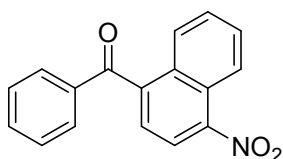
Yellow solid, m. p. 129-132 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.52 (s, 1H), 8.29 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 8.4 Hz, 1H), 7.30 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 193.6, 148.6, 146.9, 146.0, 132.5, 130.3 (2C), 129.8 (2C), 129.3, 128.3, 122.4, 120.1, 21.9. MS (ESI): m/z 320.0 $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{BrNO}_3$ C 52.52, H 3.15, N 4.38%; Found: C 52.40, H 3.28, N 4.57%.

Methyl 2-(2,4-dinitrophenyl)-2-phenylacetate (4da)



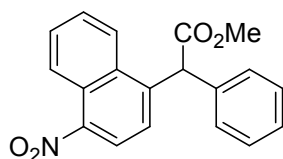
Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.86 (s, 1H), 8.31 (d, J = 8.8 Hz, 1H), 7.44 – 7.36 (m, 4H), 7.26 (d, J = 6.8 Hz, 2H), 5.76 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.9, 148.9, 147.0, 140.4, 135.3, 133.3, 129.6 (2C), 129.1 (2C), 128.6, 127.0, 120.3, 53.3, 53.0. MS (ESI): m/z 317.1 $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_6$ C 56.97, H 3.82, N 8.86%; Found: C 56.80, H 4.01, N 9.03%.

(4-Nitronaphthalen-1-yl)(phenyl)methanone (3ea)⁹



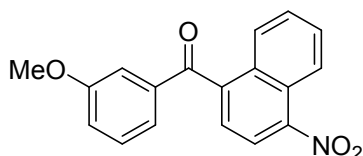
Yellow solid, m. p. 85-87 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.67 – 7.59 (m, 3H), 7.49 (t, J = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 196.5, 148.0, 142.7, 136.9, 134.3, 131.9, 130.4 (2C), 129.7, 128.9 (2C), 128.4, 126.2, 125.3, 124.3, 123.3, 122.2.

Methyl 2-(4-nitronaphthalen-1-yl)-2-phenylacetate (4ea)



Yellow solid, m. p. 106-108 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, J = 8.8 Hz, 1H), 8.12 (t, J = 10.0 Hz, 2H), 7.71 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.42-7.30 (m, 6H), 5.83 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.2, 146.6, 141.3, 136.7, 132.5, 129.1 (2C), 128.9, 128.9 (2C), 128.1, 128.0, 125.4, 125.1, 123.9, 123.7, 123.1, 53.9, 52.8. MS (ESI): m/z 322.1 $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_4$ C 71.02, H 4.71, N 4.36%; Found: C 70.85, H 4.55, N 4.57%.

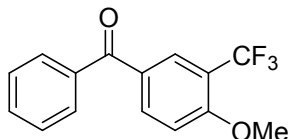
(3-Methoxyphenyl)(4-nitronaphthalen-1-yl)methanone (3ee)



Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, J = 8.8 Hz, 1H), 8.20 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 7.76 (t, J = 7.8 Hz, 1H), 7.61 (q, J = 6.8 Hz, 2H), 7.49 (s, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 7.2 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 3.86 (s, 3H).

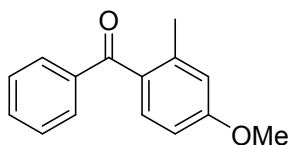
^{13}C NMR (101 MHz, CDCl_3) δ 196.3, 160.0, 148.0, 142.7, 138.2, 131.9, 129.8, 129.7, 128.4, 126.2, 125.3, 124.3, 123.7, 123.3, 122.2, 120.9, 113.8, 55.6. MS (ESI): m/z 308.2 $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{NO}_4$ C 70.35, H 4.26, N 4.56%; Found: C 70.21, H 4.45, N 4.39%.

(4-Methoxy-3-(trifluoromethyl)phenyl)(phenyl)methanone (3ca)



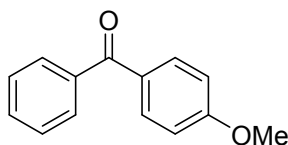
Yellow solid, m. p. 63-65°C. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (s, 1H), 8.02 (d, J = 8.7 Hz, 1H), 7.75 (d, J = 7.4 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.5 Hz, 2H), 7.09 (d, J = 8.7 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.5, 160.8, 137.4, 135.9, 132.5, 129.8, 129.73, 129.69, 129.6, 129.5, 128.5, 127.8, 124.5, 121.8, 118.9, 118.6, 113.9, 111.5, 56.3. MS (ESI): m/z 281.1 $[\text{M}+\text{H}]^+$. Anal. Calcd for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{O}_2$ C 64.29, H 3.96%; Found: C 64.42, H 3.81 %.

(4-Methoxy-2-methylphenyl)(phenyl)methanone (3da)¹⁰



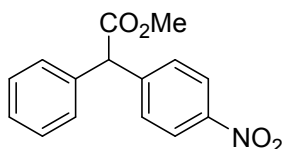
Yellow liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 1H), 6.82 (s, 1H), 6.73 (d, J = 8.5 Hz, 1H), 3.83 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.7, 161.3, 140.7, 138.8, 132.5, 132.1, 130.7, 130.0(2C), 128.3(2C), 116.8, 110.2, 55.3, 20.8. MS (ESI): m/z 227.2 $[\text{M}+\text{H}]^+$.

(4-Methoxyphenyl)(phenyl)methanone(3ea)¹¹



Yellow solid, m. p. 122-123°C. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 7.1 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.6, 163.3, 138.3, 132.6, 131.9, 130.2, 129.7, 128.2, 113.6, 77.4, 77.1, 76.8, 55.5. MS (ESI): *m/z* 213.2 [M+H]⁺.

Methyl 2-(4-nitrophenyl)-2-phenylacetate(4aa)



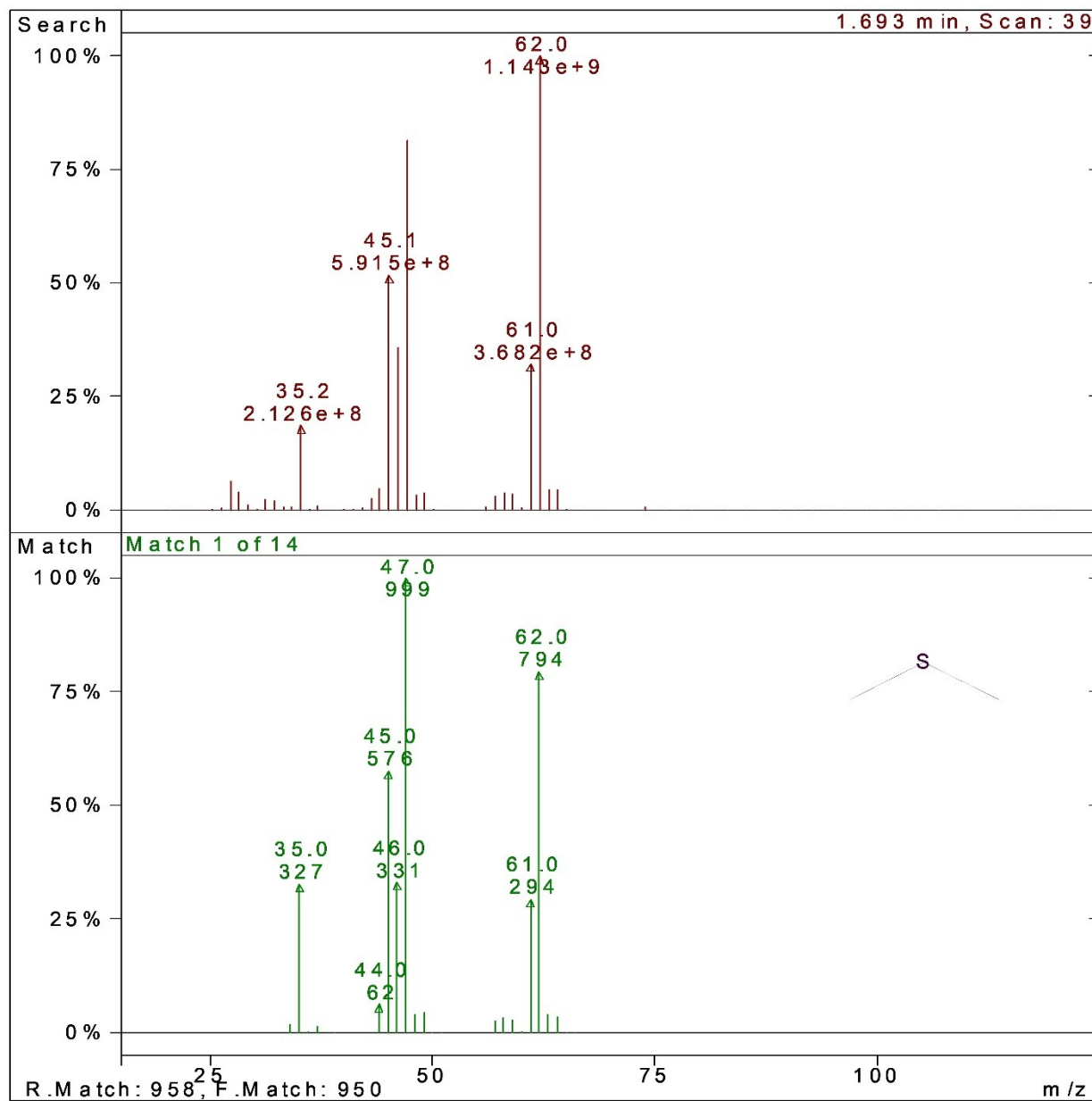
Yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.7 Hz, 2 H), 7.49 (d, *J* = 8.7 Hz, 2 H), 7.39-7.26 (m, 5 H), 5.12 (s, 1 H), 3.77 (s, 3 H). ¹³C NMR (101 MHz, CDCl₃) δ 171.9, 147.2, 145.9, 137.2, 129.6 (2C), 129.1 (2C), 128.5 (2C), 127.9, 123.8 (2C), 56.7, 52.7. MS (EI): *m/z* 271.1 [M]⁺. Anal. Calcd for C₁₅H₁₃NO₄ C 66.41, H 4.83, N 5.16%; Found: C 66.28, H 5.00, N 5.32%.

References

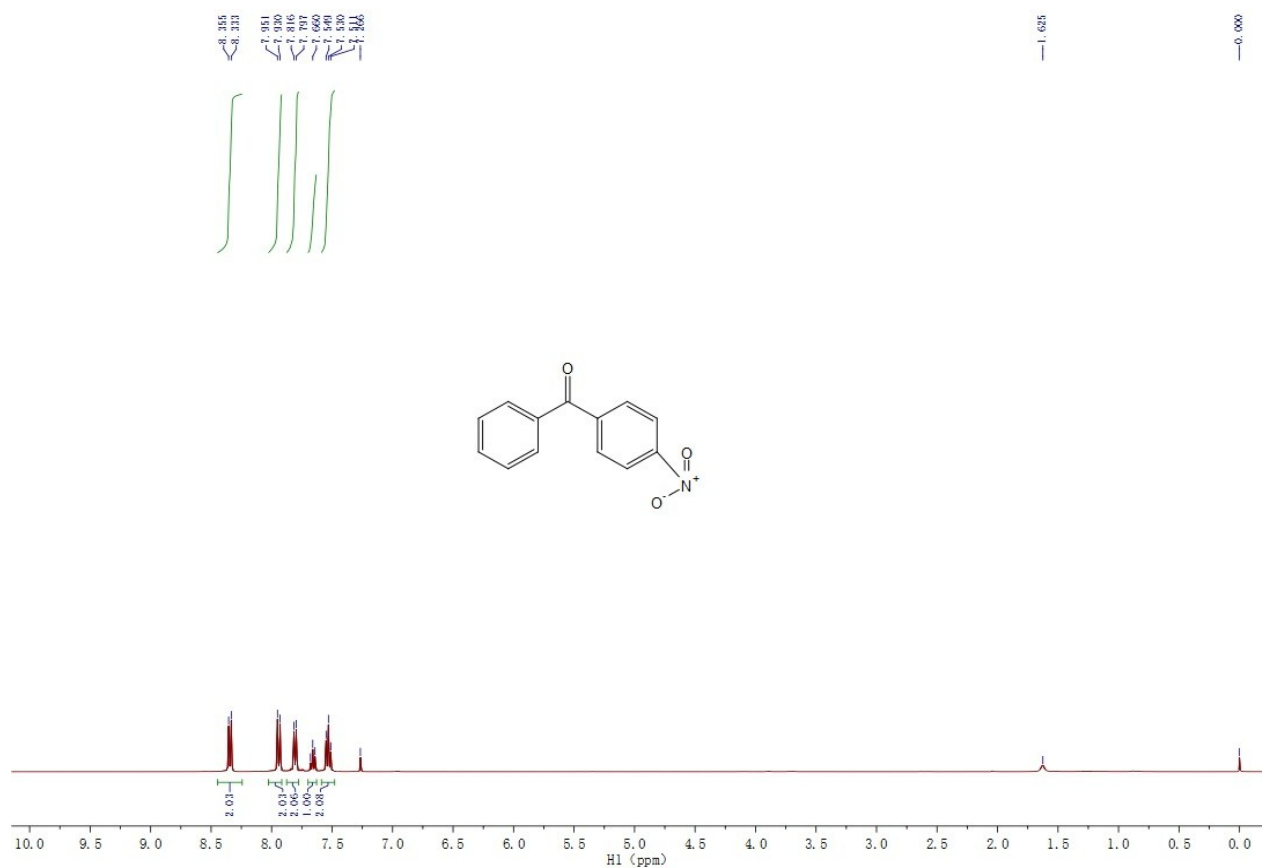
1. **see ref 12.** S. Barroso, G. Blay, L. Cardona, I. Fernández, B. García, and J. R. Pedro, *J. Org. Chem.*, 2004, **69**, 6821
2. C. Qin, J. Chen, H. Wu, J. Cheng, Q. Zhang, B. Zuo, W. Su and J. Ding, *Tetrahedron Lett.*, 2008, **49**, 1884.
3. **see ref 13.** M. Cai, J. Peng, W. Hao and G. Ding, *Green Chem.*, 2011, **13**, 190.
4. Y. Suzuki, S. Ota, Y. Fukuta, Y. Ueda and M. Sato, *J. Org. Chem.*, 2008, **73**, 2420.
5. Z. Vejdělek, M. Rajšner, A. Dlabač, M. Ryska, J. Holubek, E. Svátek and M. Protiva, *Coll. Czech. Chem. Commun.*, 1980, **45**, 3593.
6. H. Zheng, J. Ding, J. Chen, M. Liu, W. Gao and H. Wu, *Synlett* 2011, (11), 1626
7. **see ref 14.** J. Mahdi, H. Ankati, J. Gregory, B. Tenner and E. R. Biehl. *Tetrahedron Lett.*, 2011, **52**, 2594.
8. K. Inamoto, M. Katsuno, T. Yoshino, Y. Arai, K. Hiroya and T. Sakamoto, *Tetrahedron*, 2007, **63**, 2695.
9. M. Makosza, J. Winiarski, *J. Org. Chem.*, 1984, **49**, 1494.
10. Fei He, H. Wu, J. Chen and W. Su, *Synth. Commun.* 2008, **38**, 255.
11. D. Xing, B. Guan, G. Cai, Z. Fang, L. Yang and Z. Shi, *Org. Lett.*, 2006, **8**, 693.

5) GC-MS spectrum of dimethyl sulfide generated in the argon reaction condition

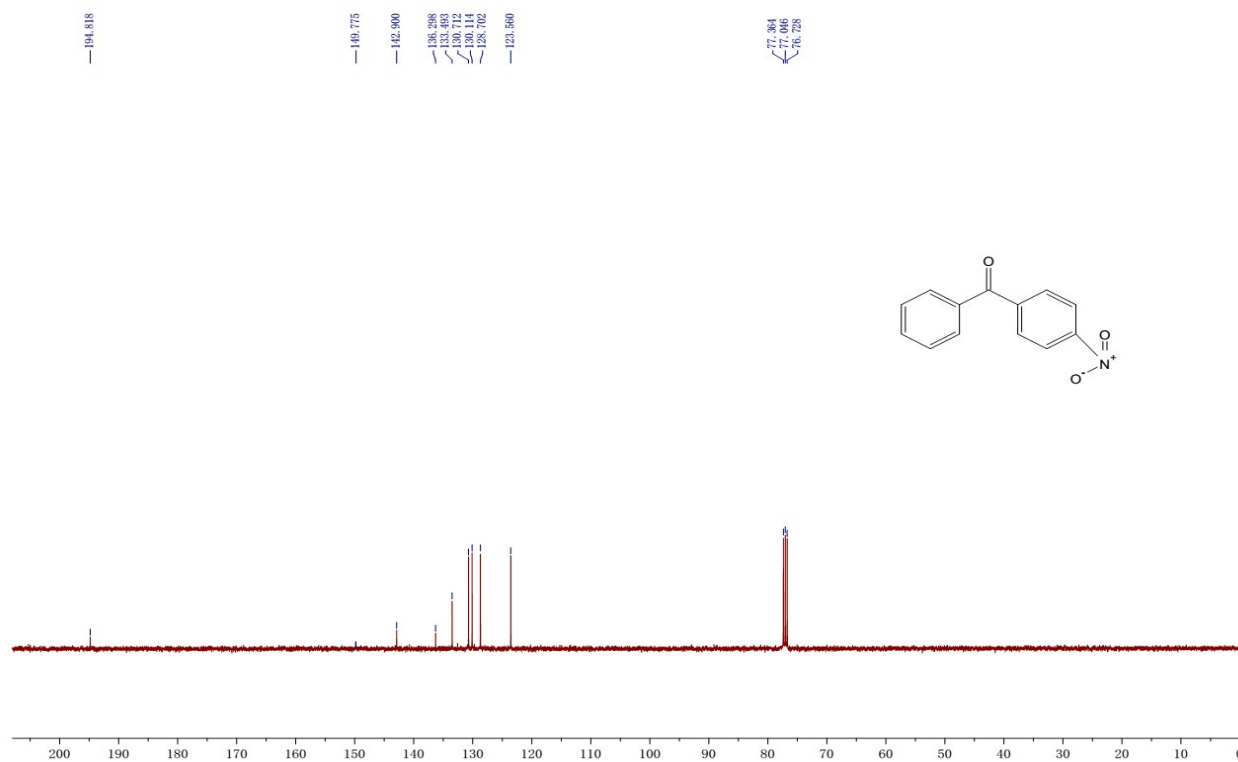
(Top: spectrum of our sample; Bottom: spectrum searched in the data library)



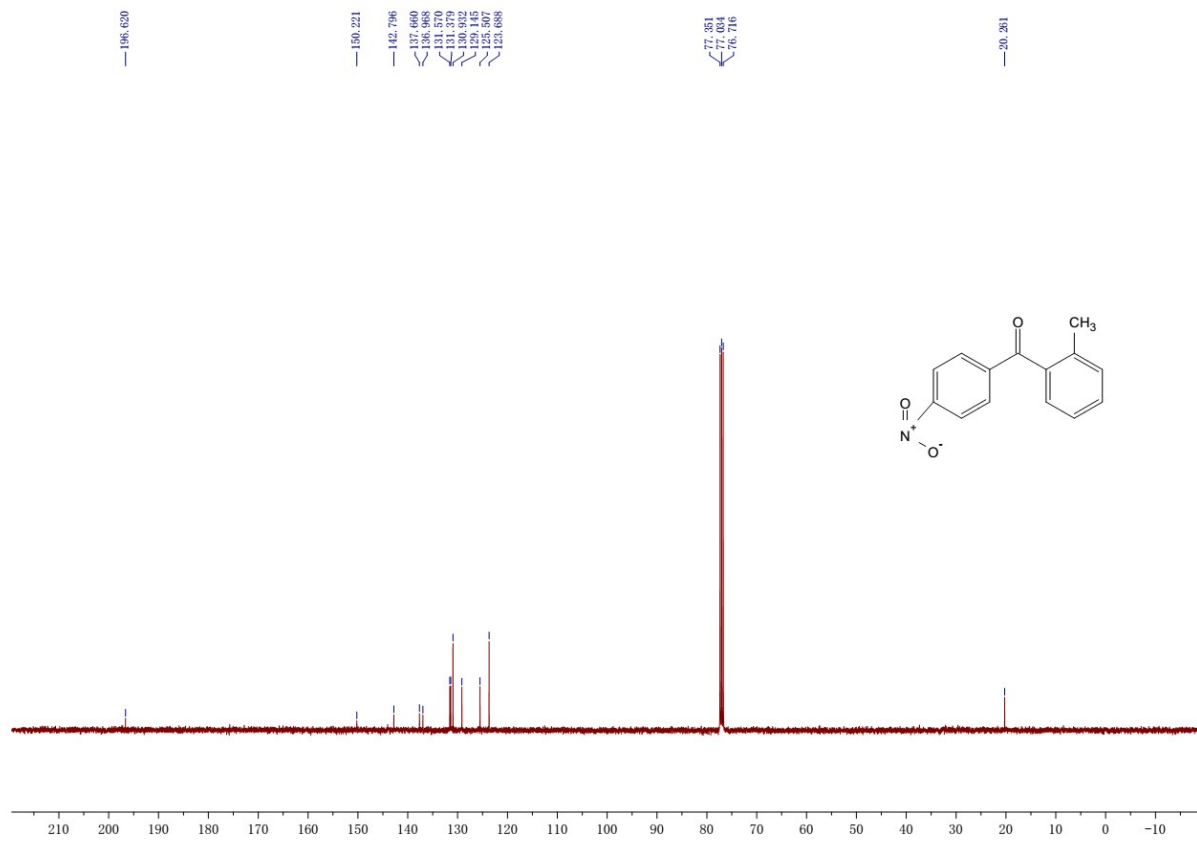
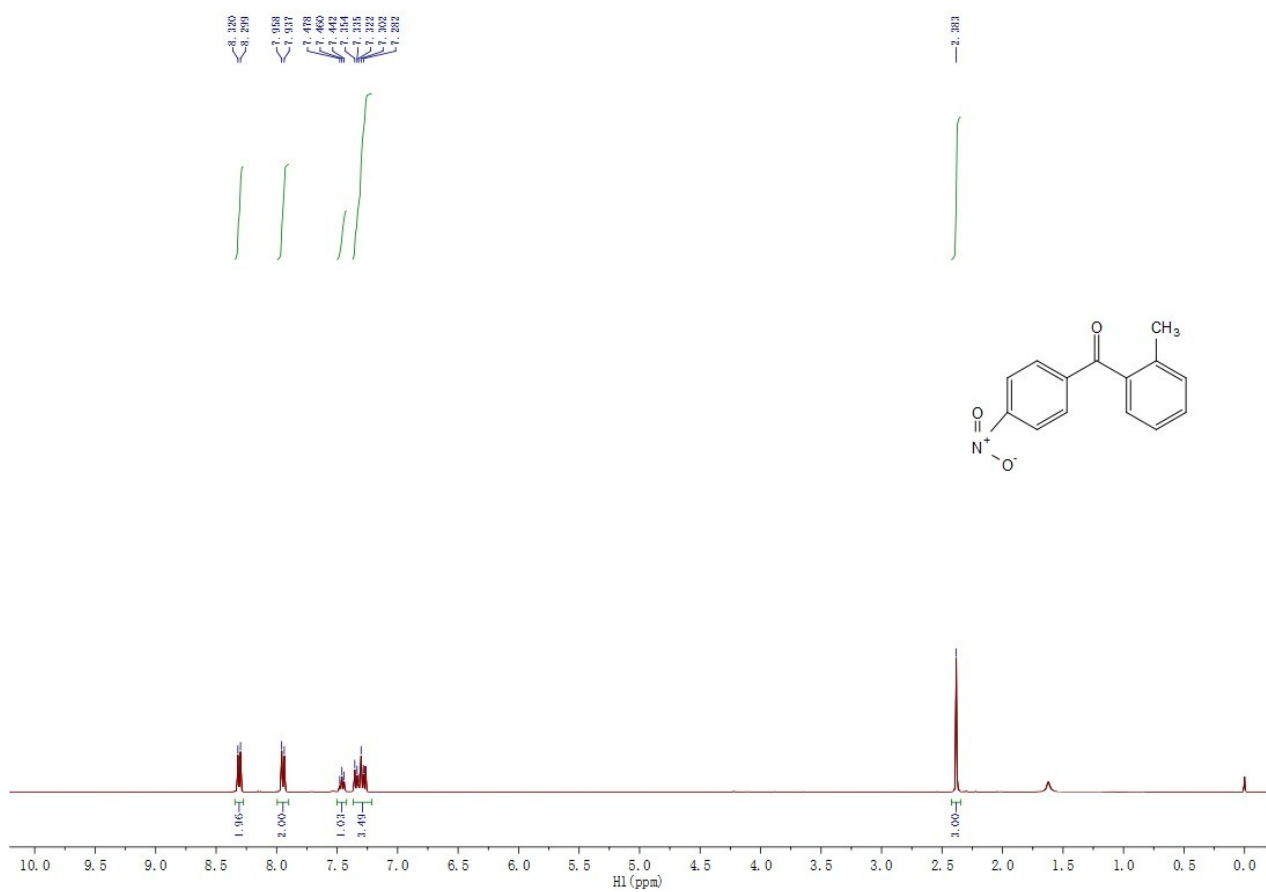
6) Copies of ^1H - and ^{13}C -NMR spectra



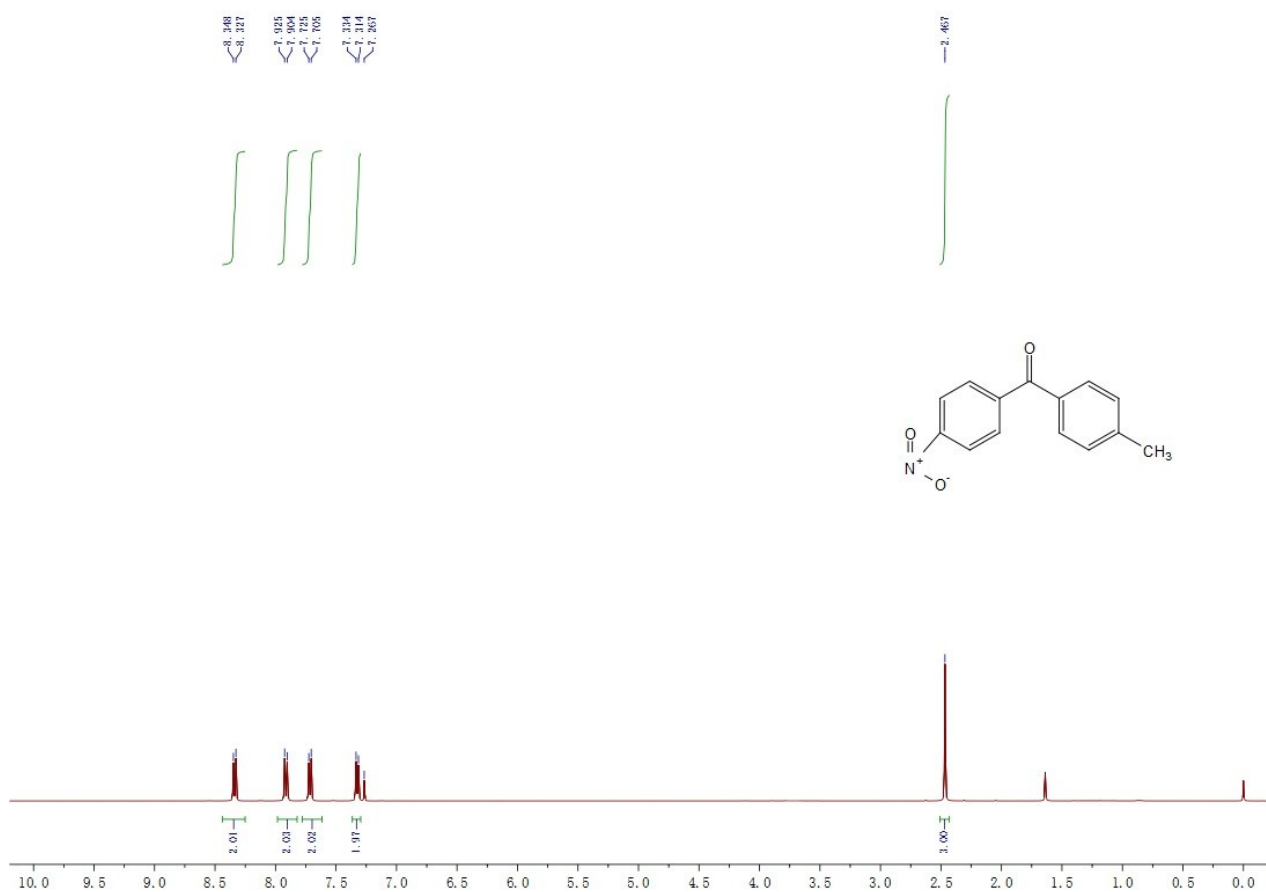
^1H NMR spectrum of **3aa**



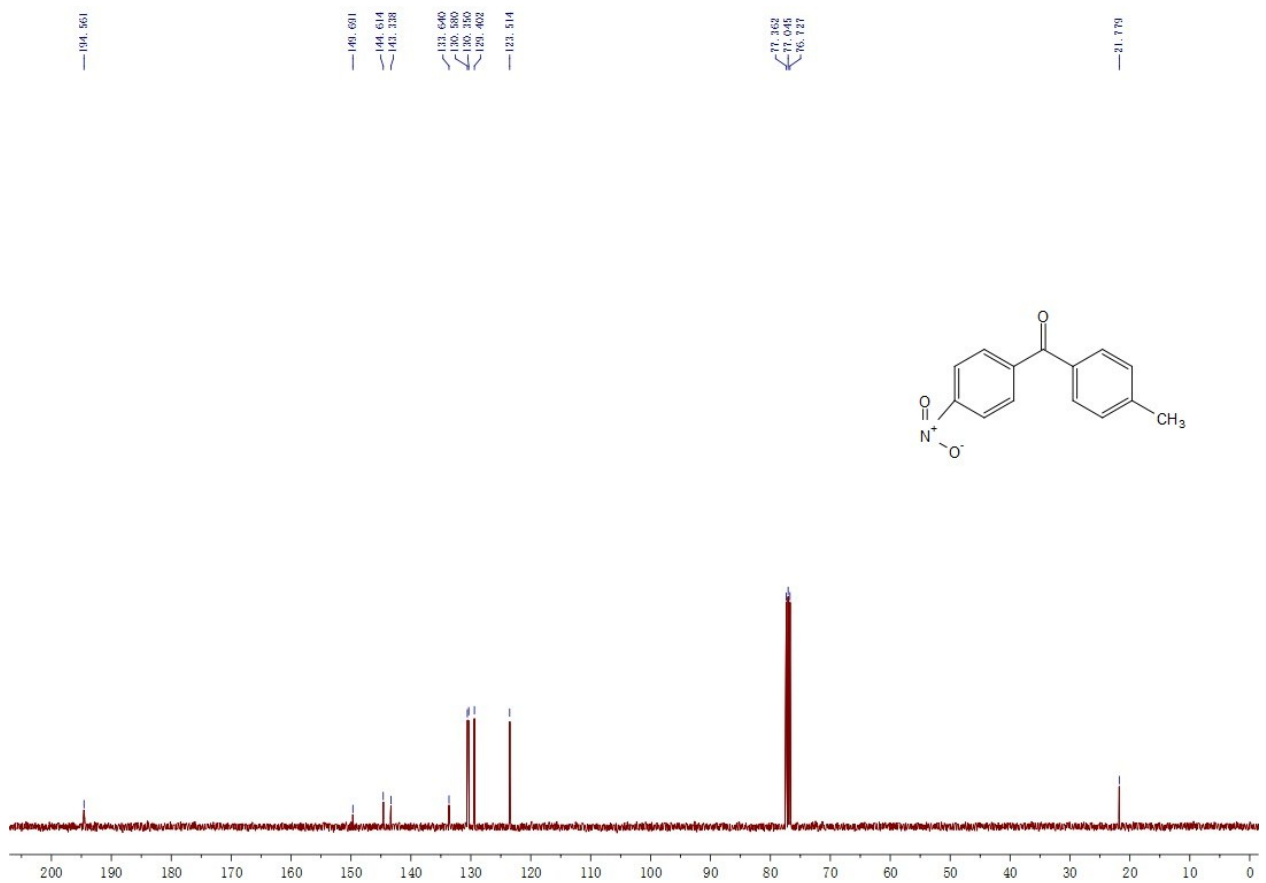
^{13}C NMR spectrum of **3aa**



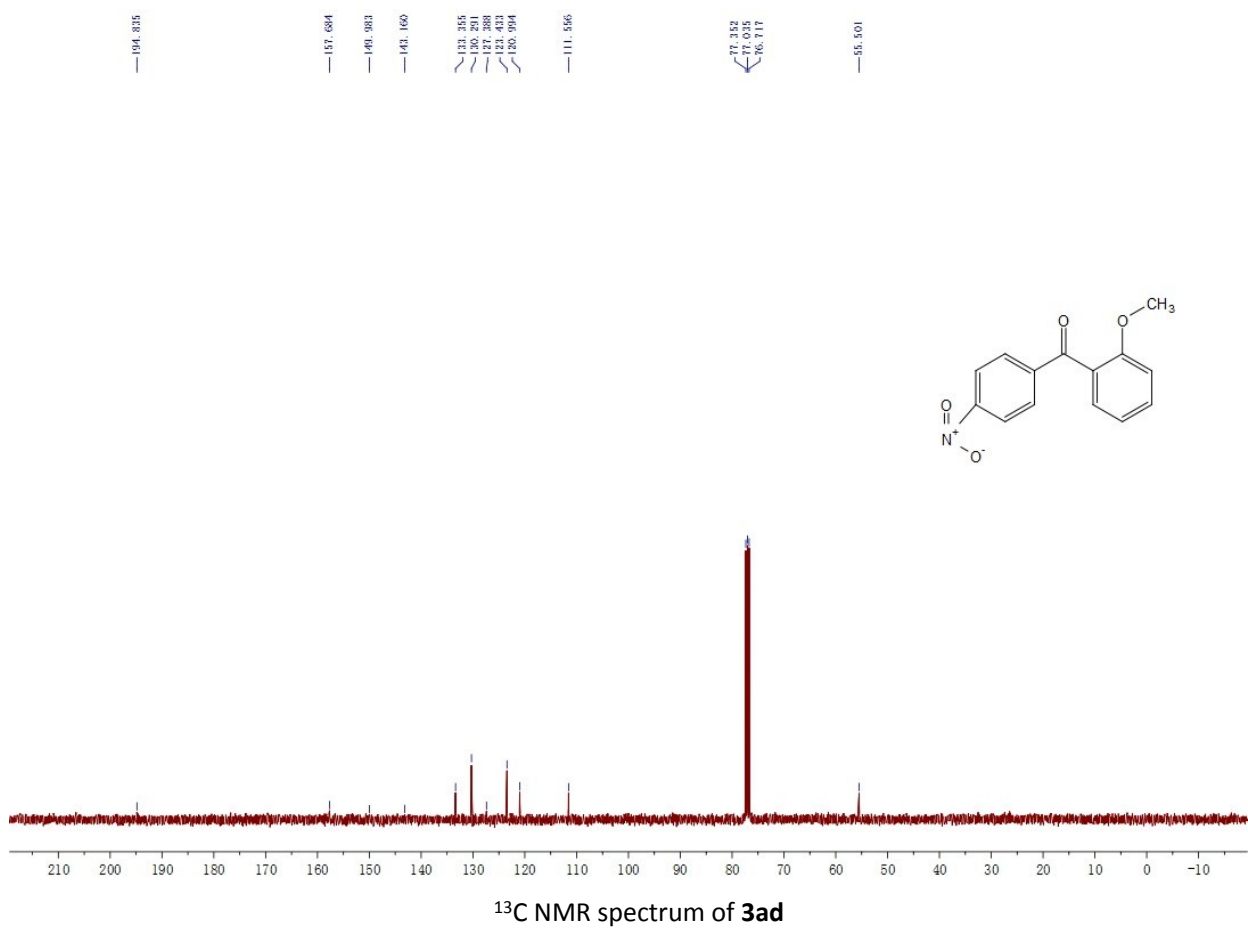
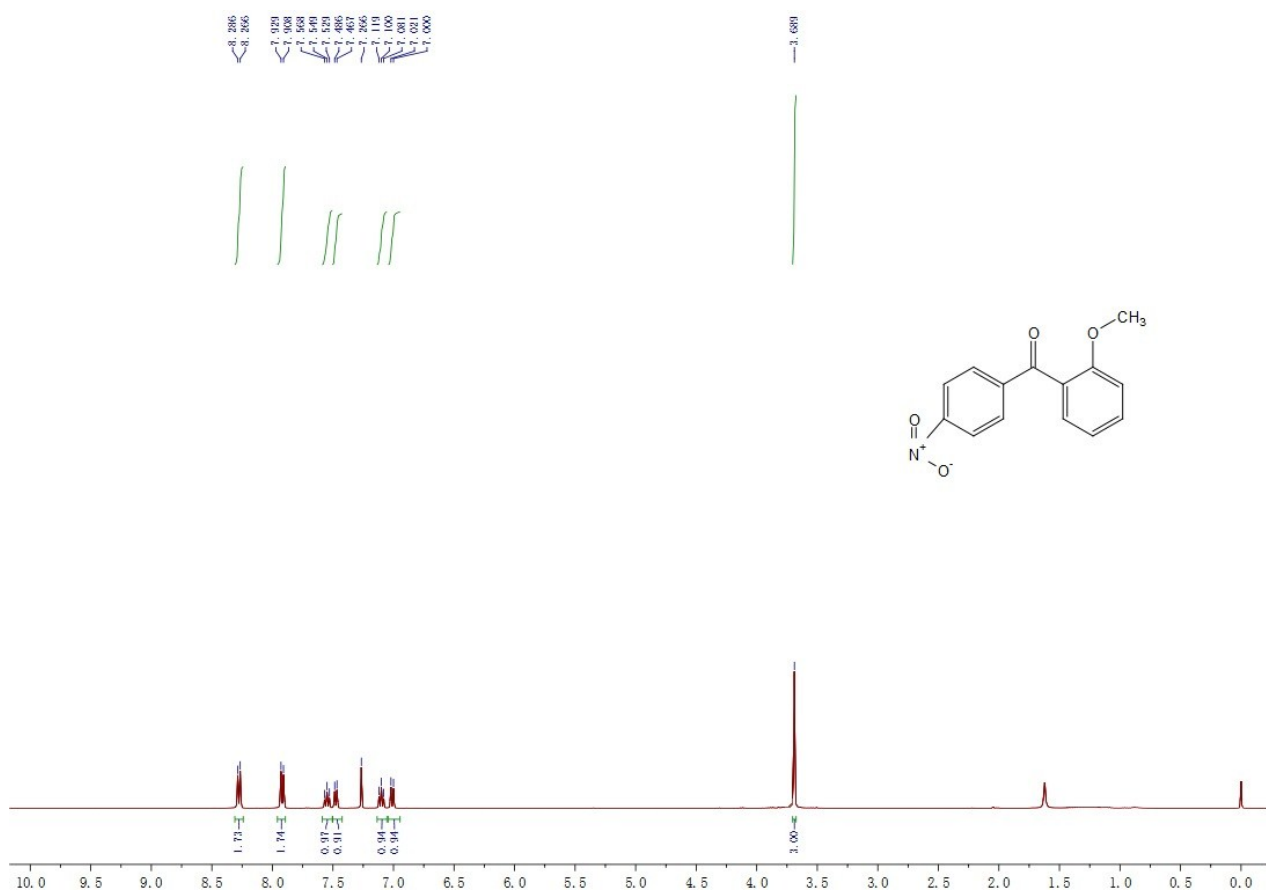
¹³C NMR spectrum of **3ab**

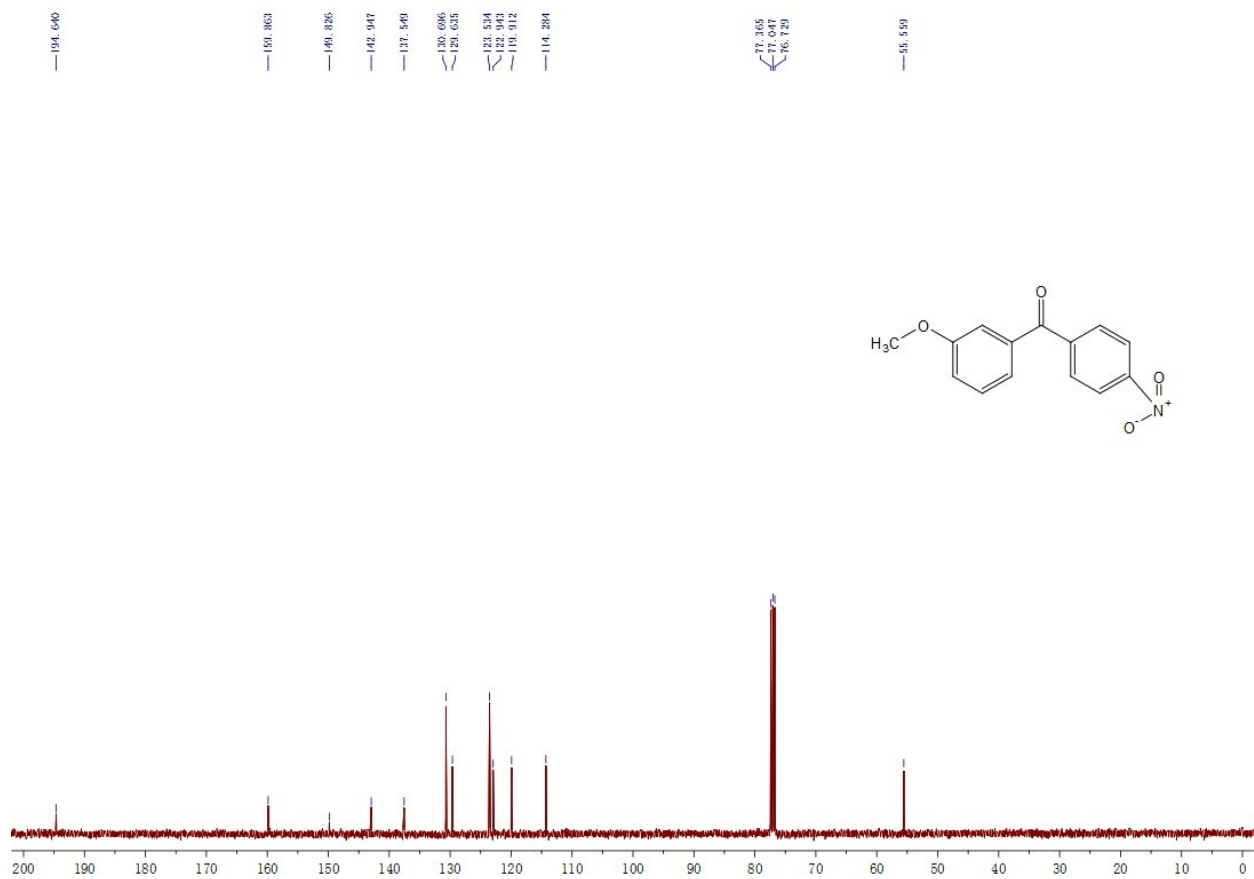


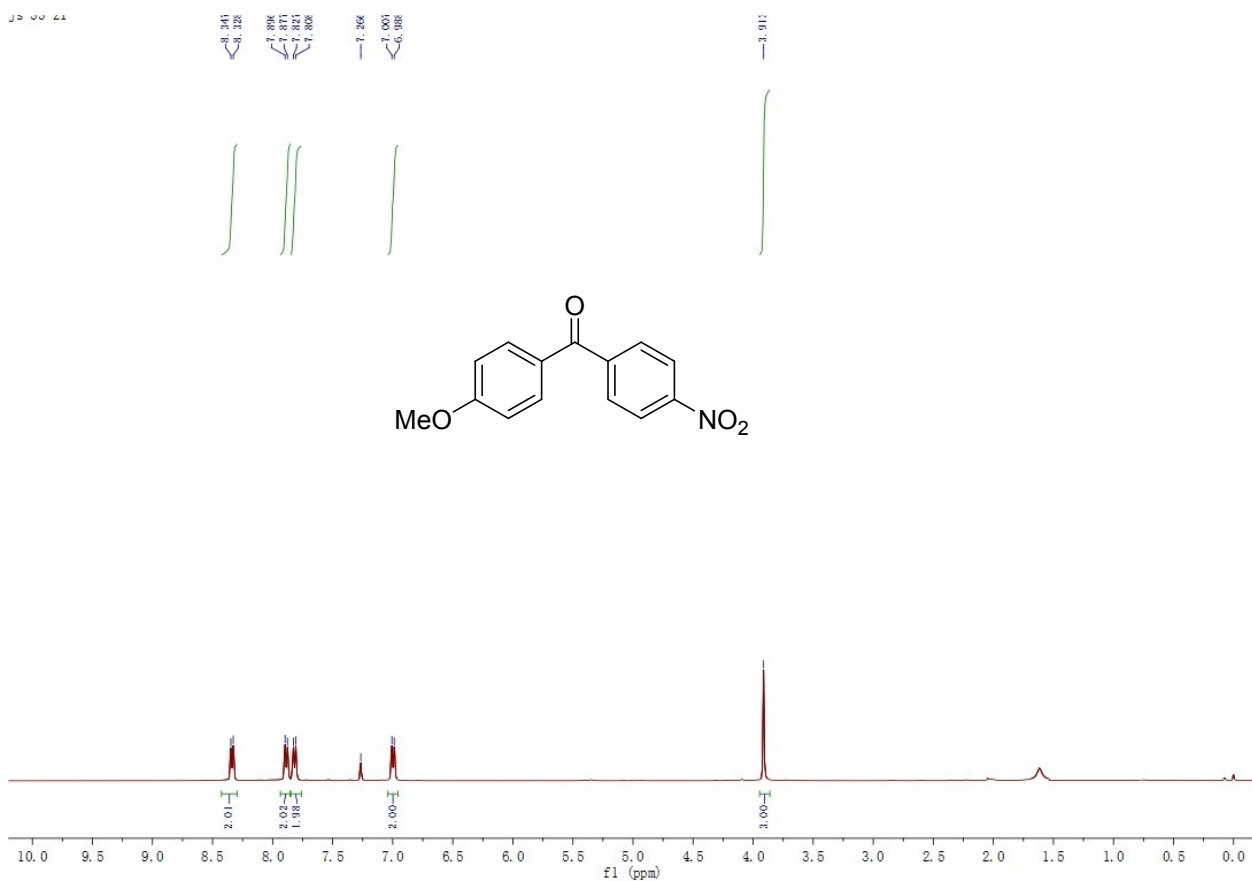
¹H NMR spectrum of **3ac**



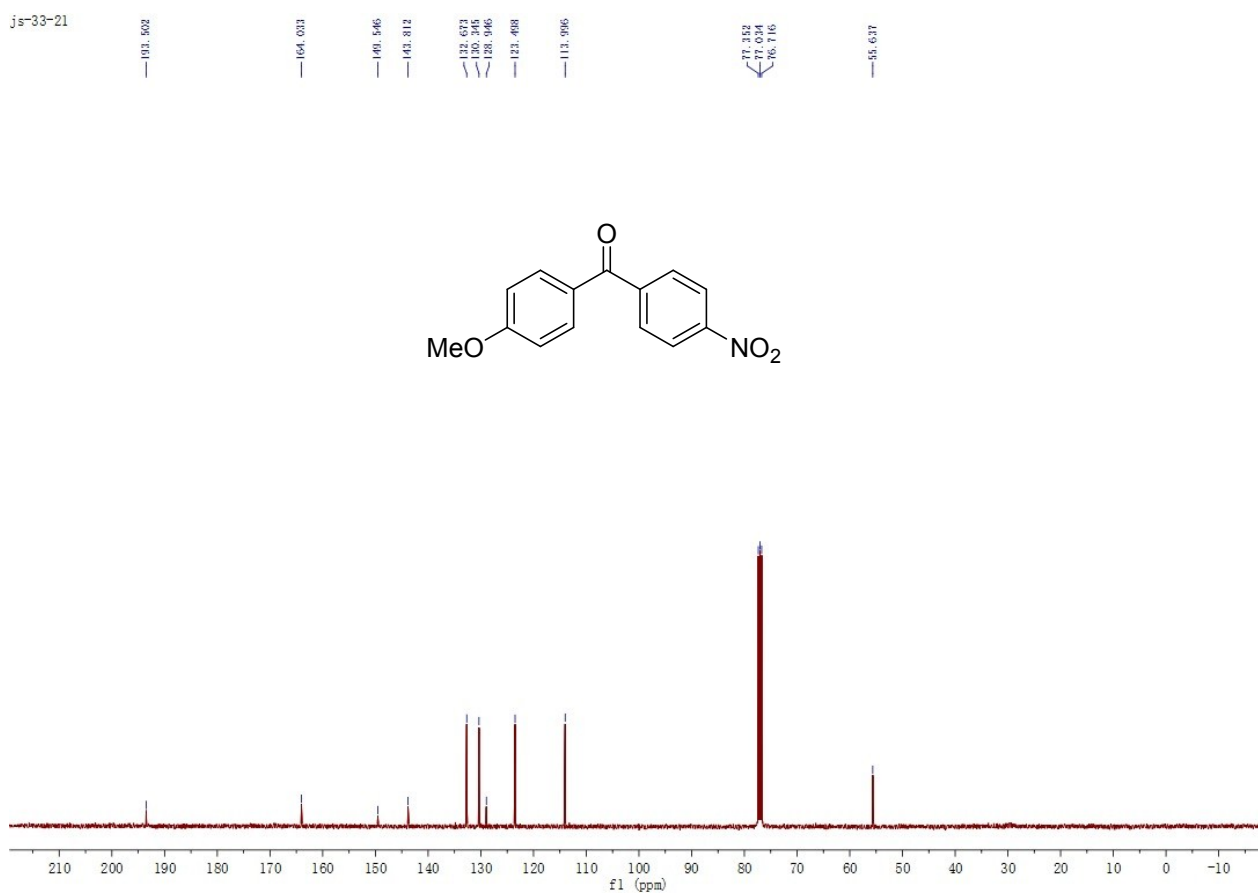
¹³C NMR spectrum of **3ac**



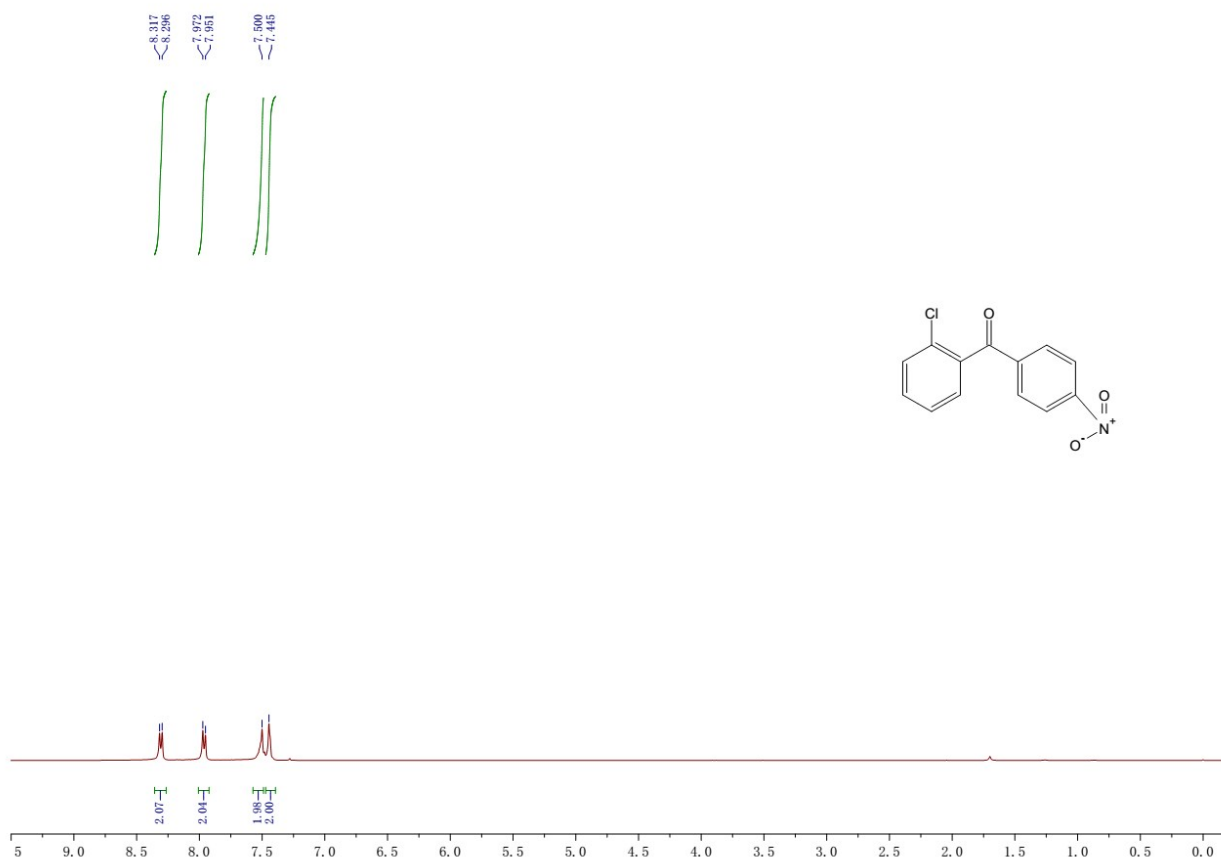




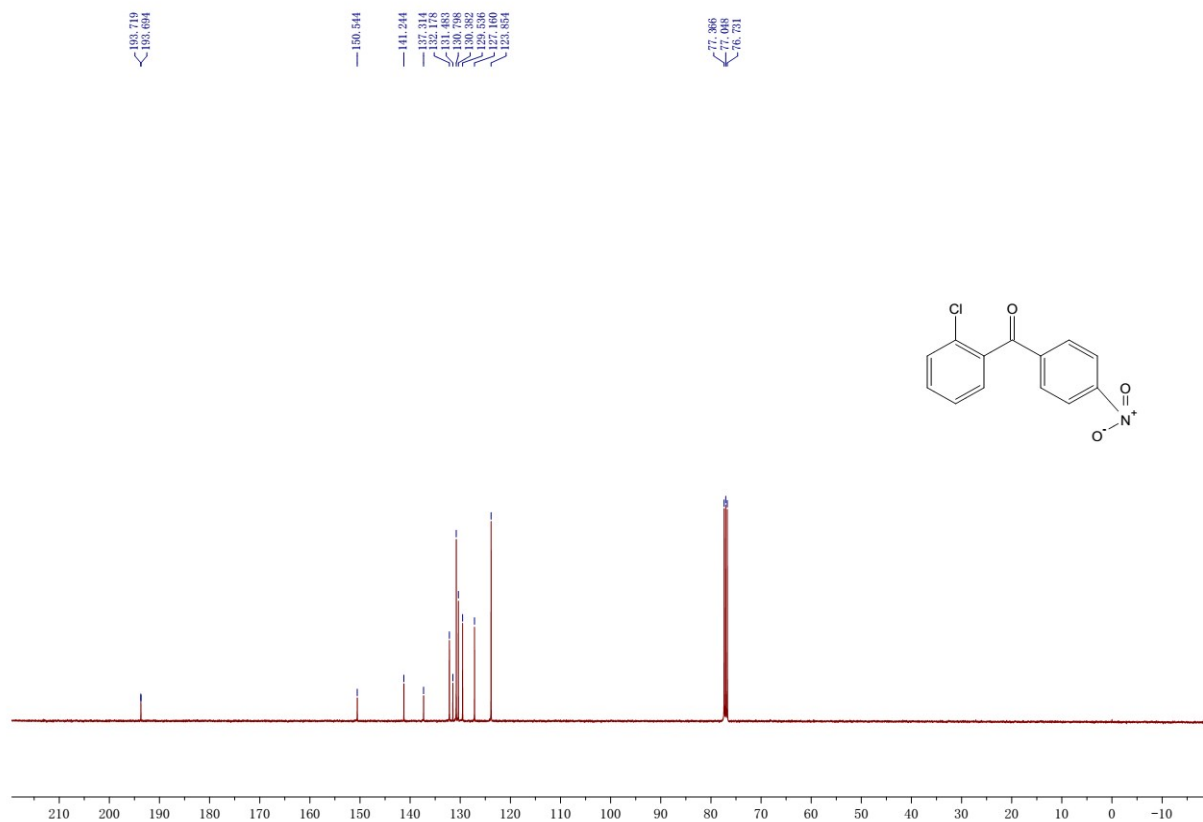
¹H NMR spectrum of **3af**



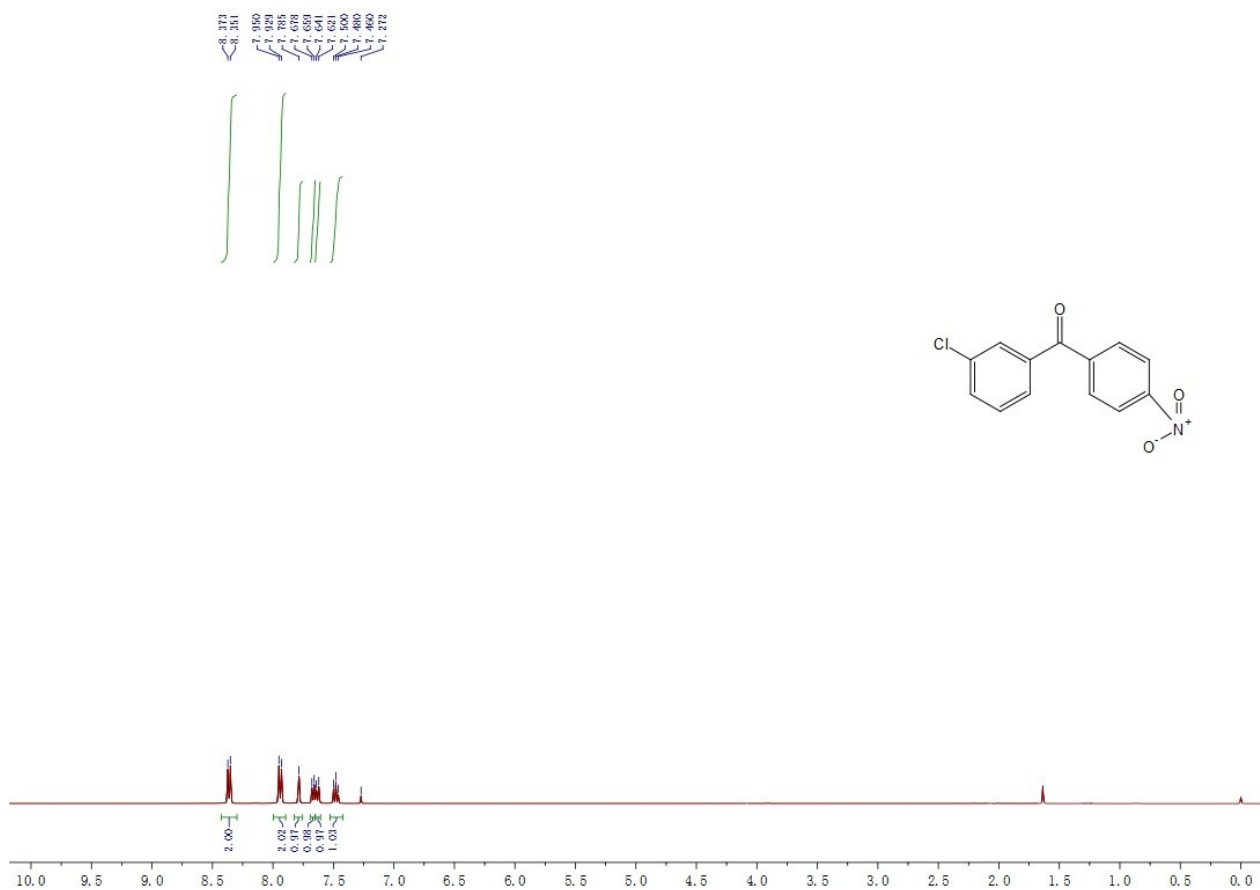
¹³C NMR spectrum of **3af**



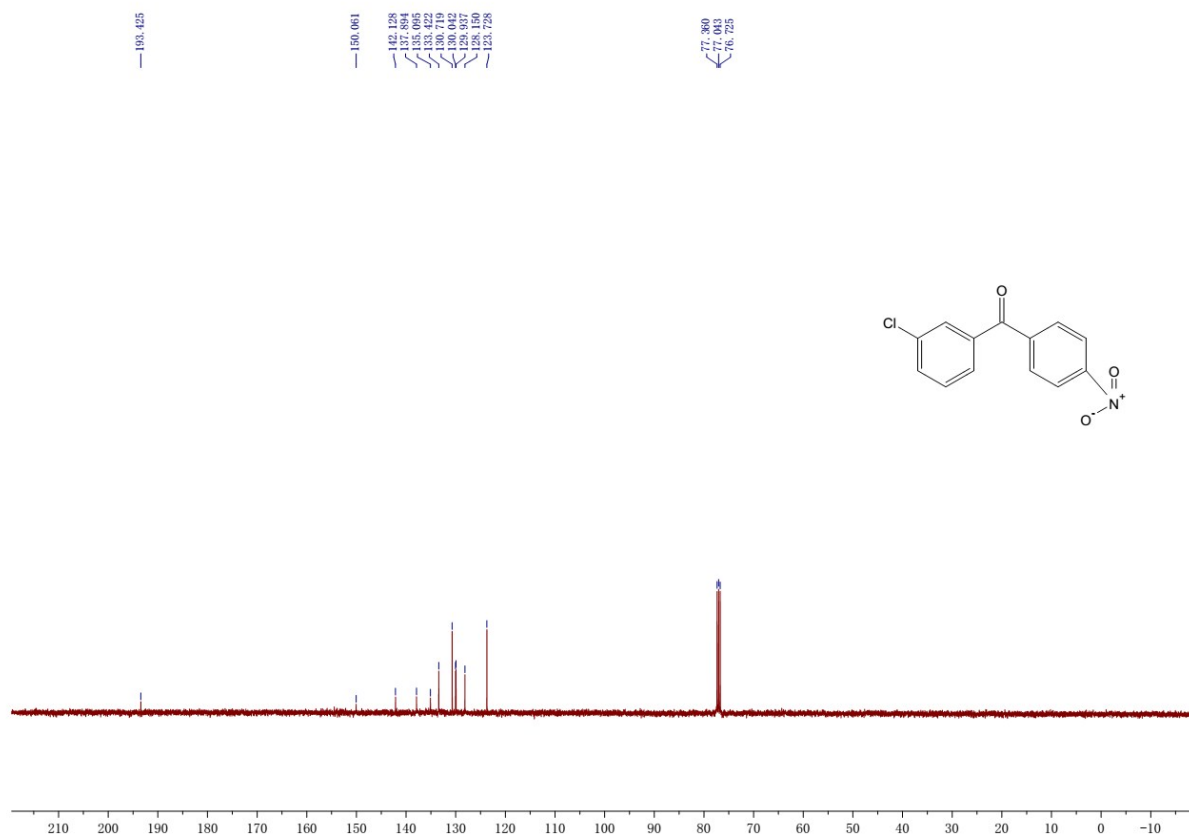
¹H NMR spectrum of **3ag**



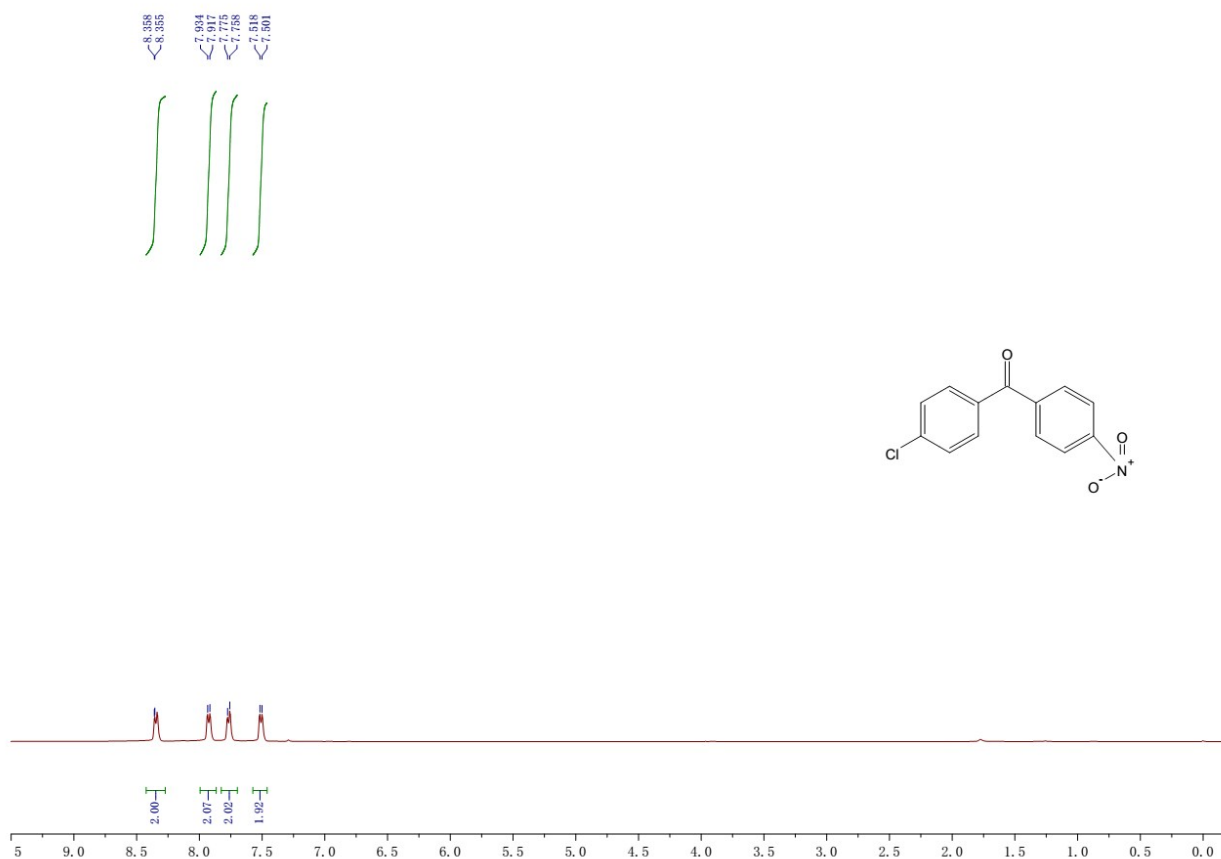
¹³C NMR spectrum of **3ag**



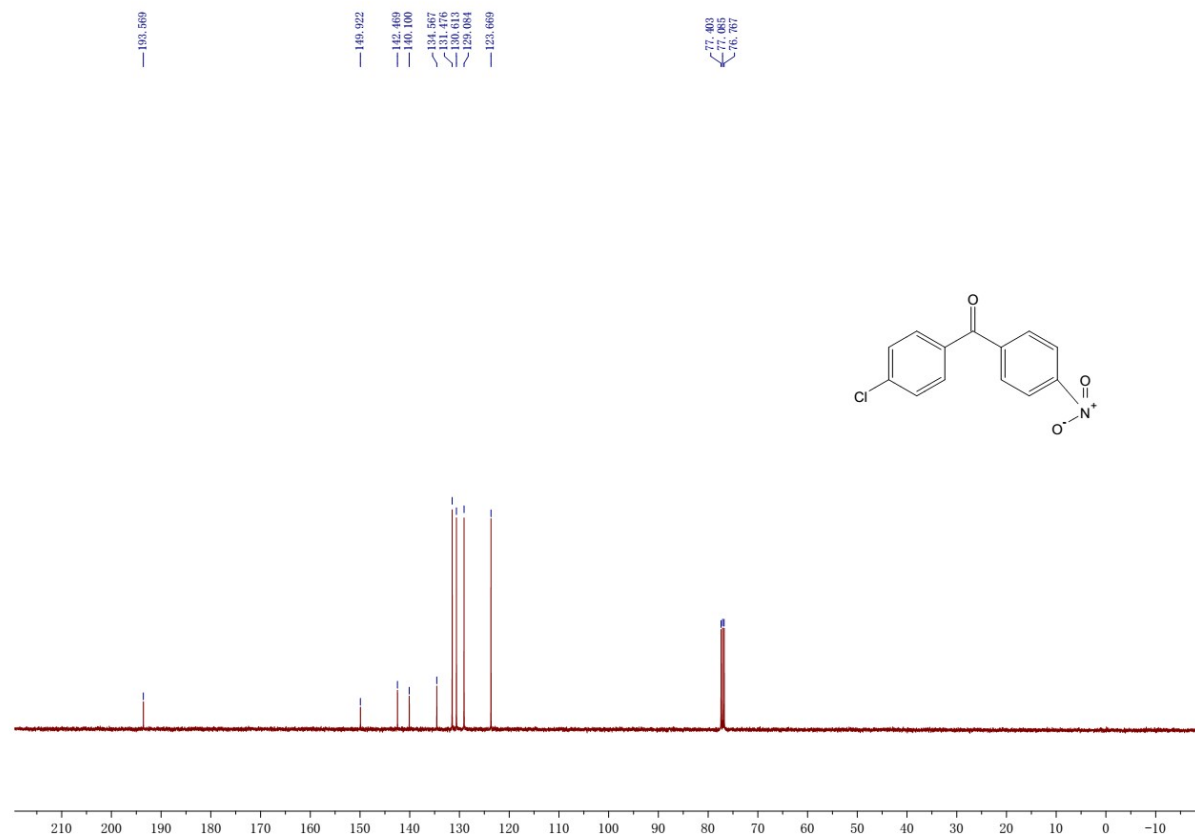
¹H NMR spectrum of **3ah**



¹³C NMR spectrum of **3ah**



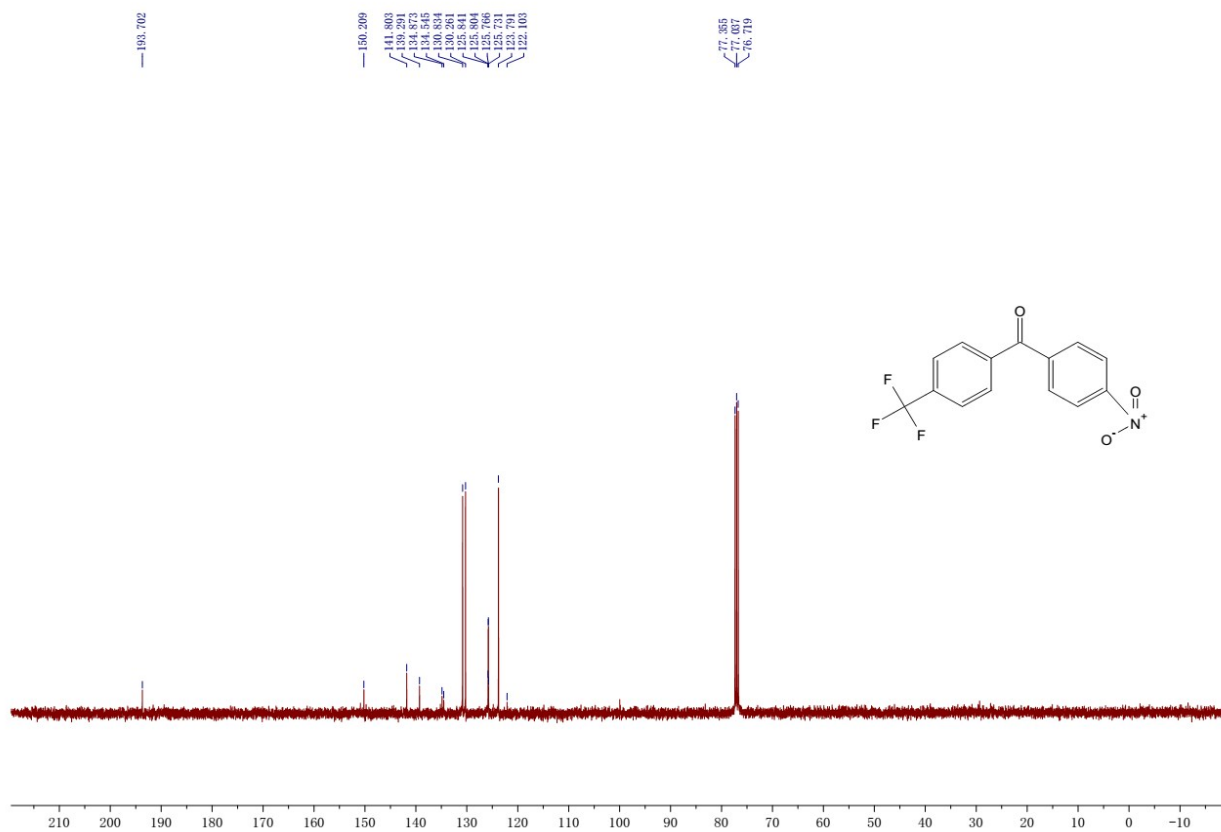
¹H NMR spectrum of **3ai**



¹³C NMR spectrum of **3ai**



¹H NMR spectrum of **3aj**



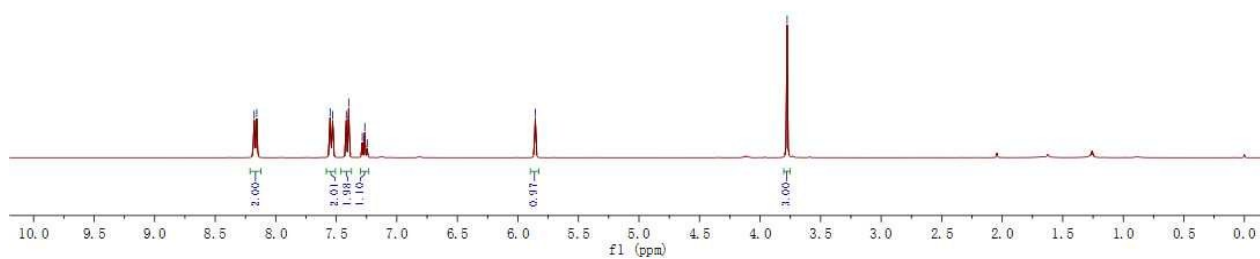
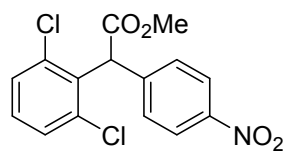
¹³C NMR spectrum of **3aj**

js-33-30

8.178
8.157
7.551
7.529
7.417
7.397
7.285
7.264
7.245

5.866

3.777

¹H NMR spectrum of **4ak**

js-33-30

170.270

147.127

142.310

135.984

134.122

130.292

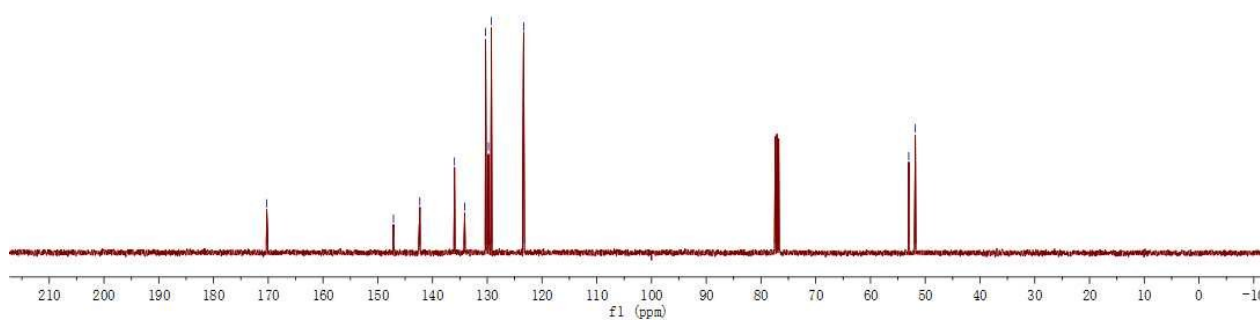
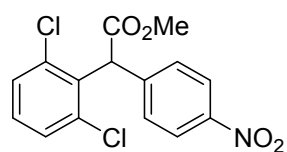
129.774

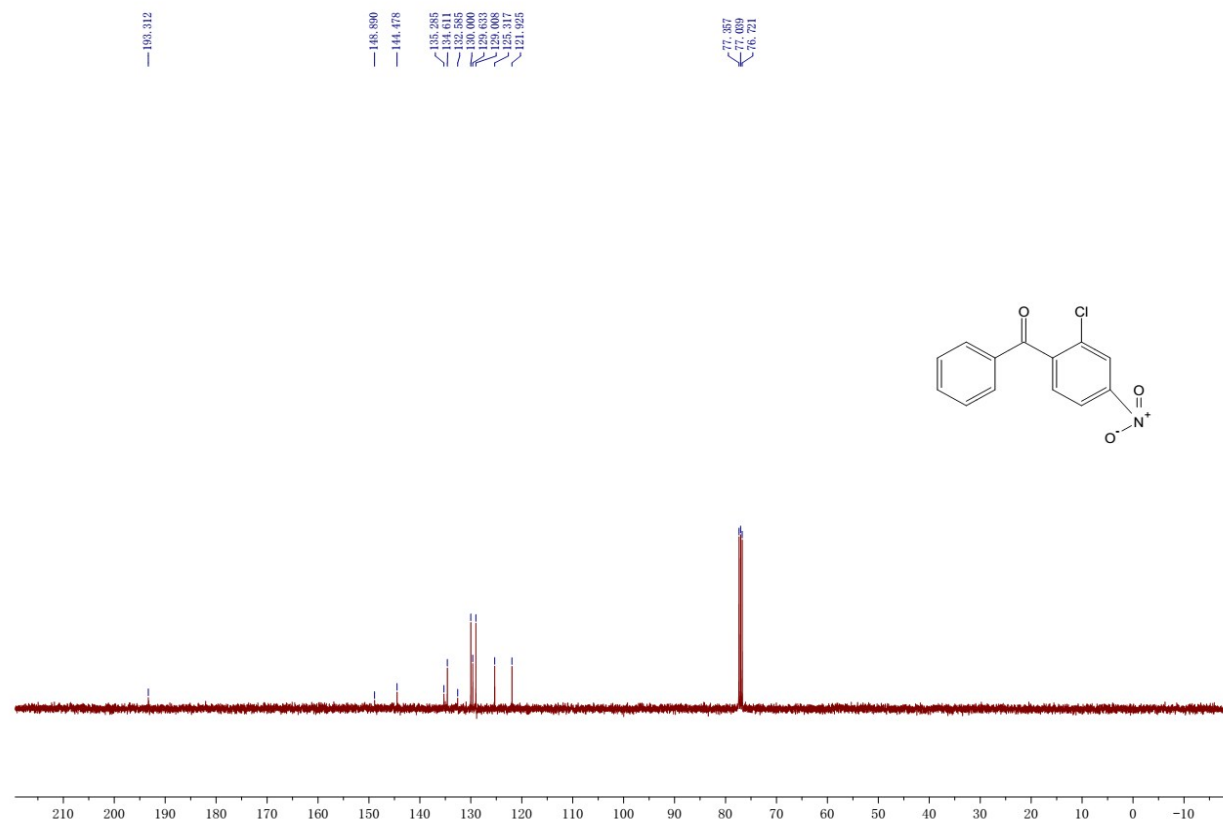
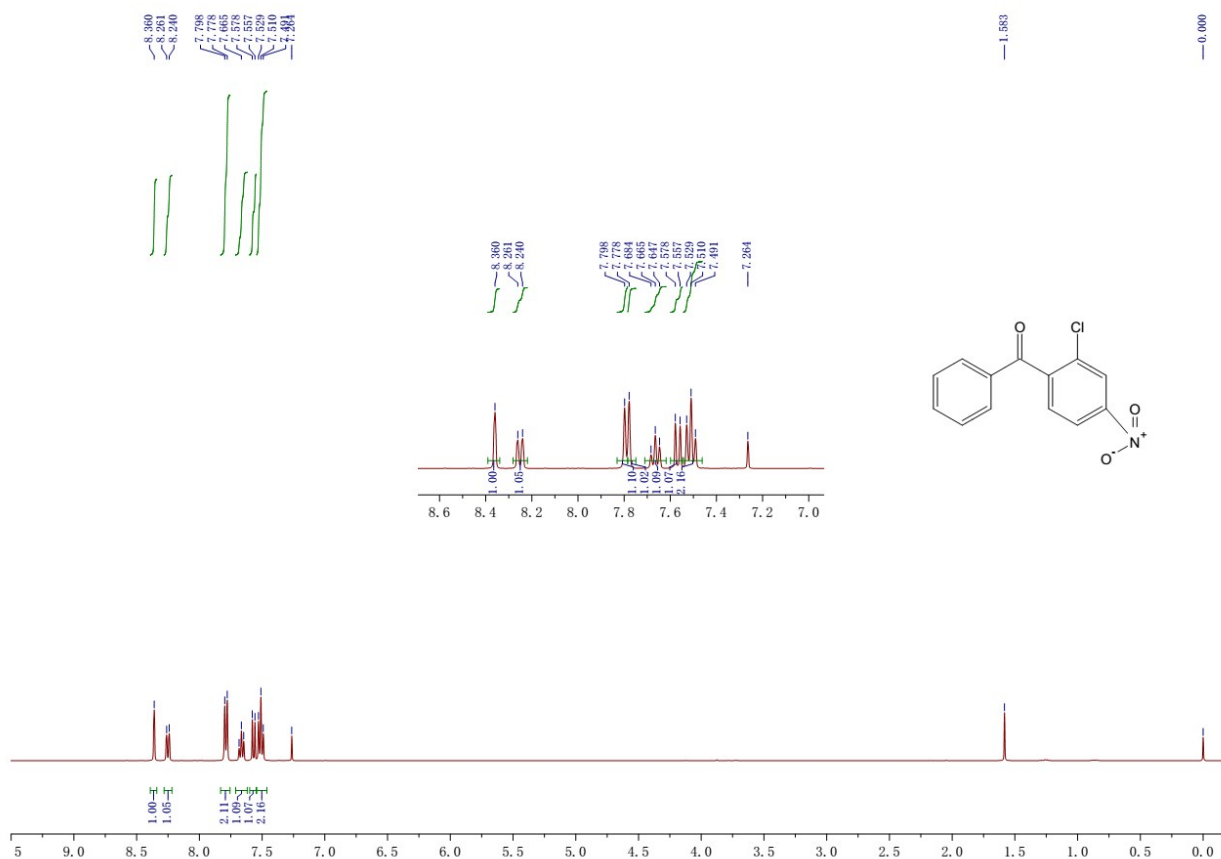
123.241

123.352

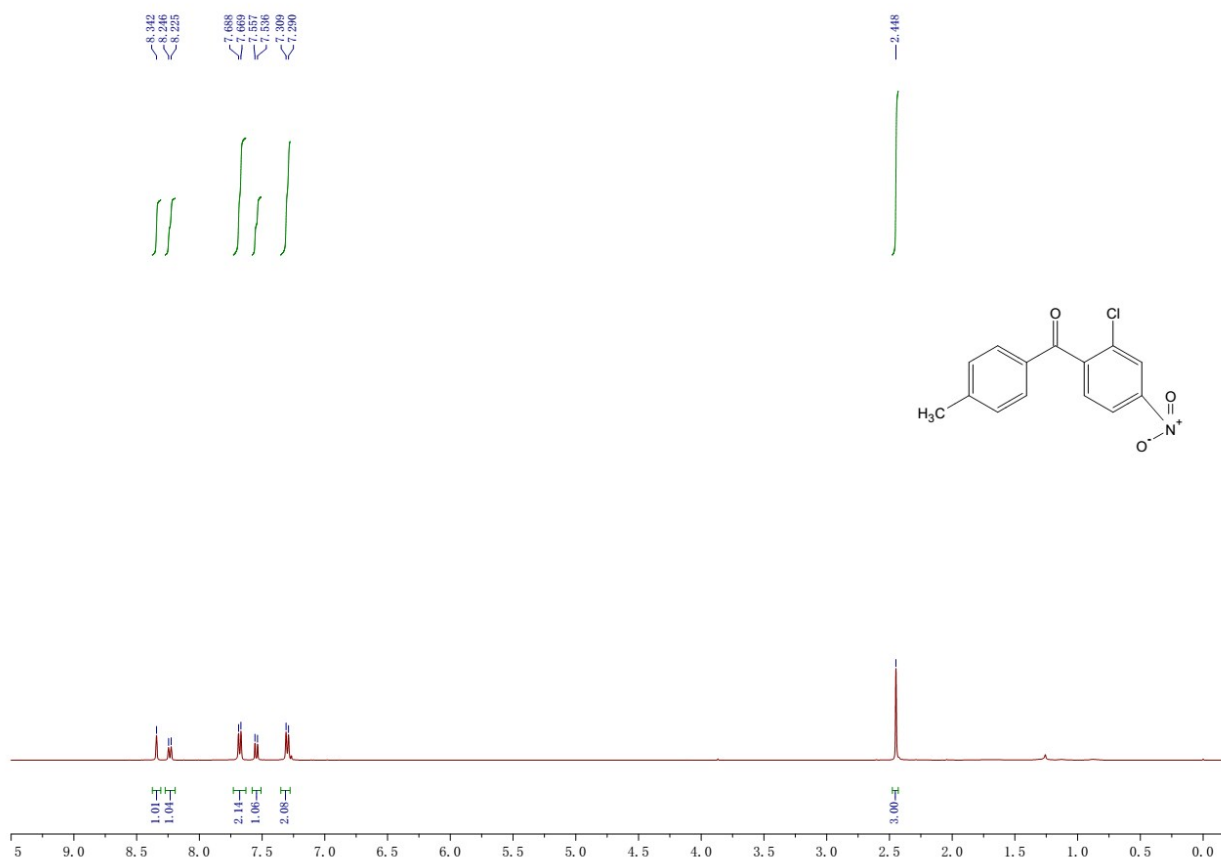
53.014

51.815

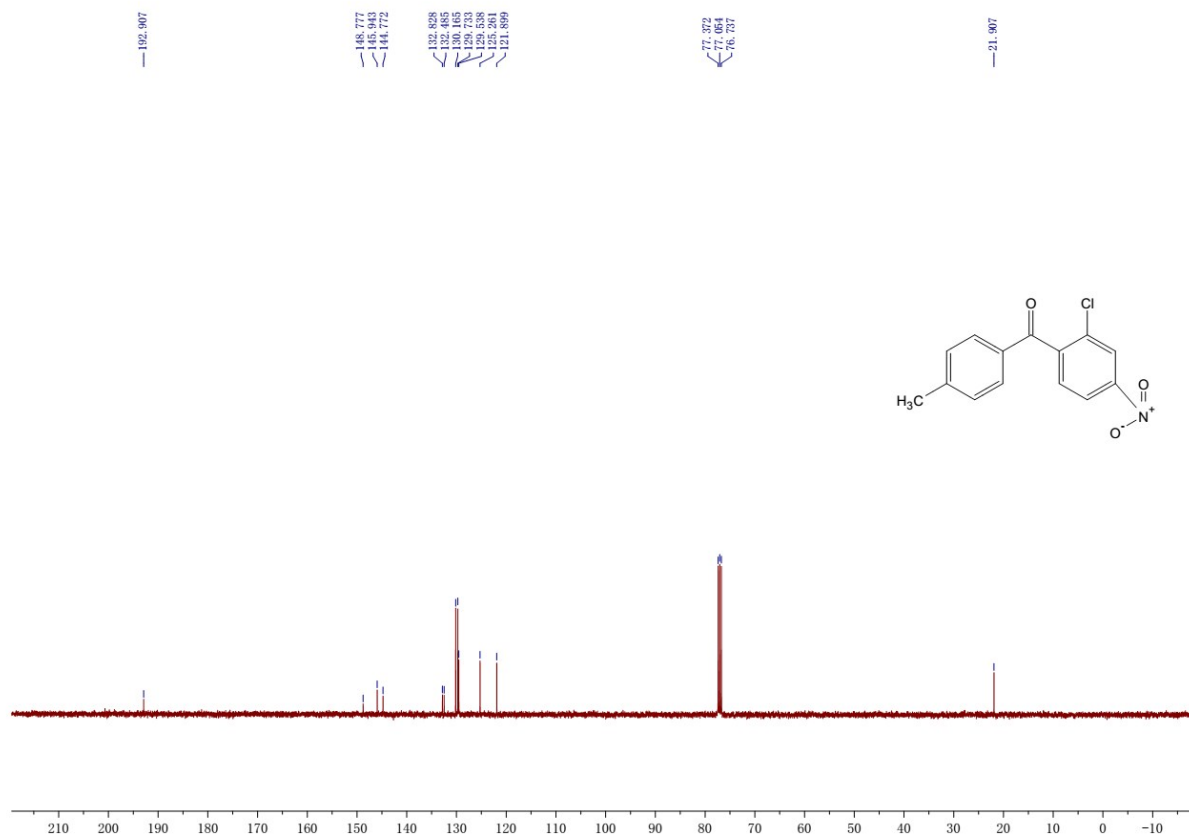
¹³C NMR spectrum of **4ak**



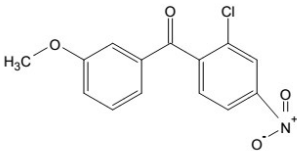
¹³C NMR spectrum of 3ba



¹H NMR spectrum of **3bc**



¹³C NMR spectrum of **3bc**



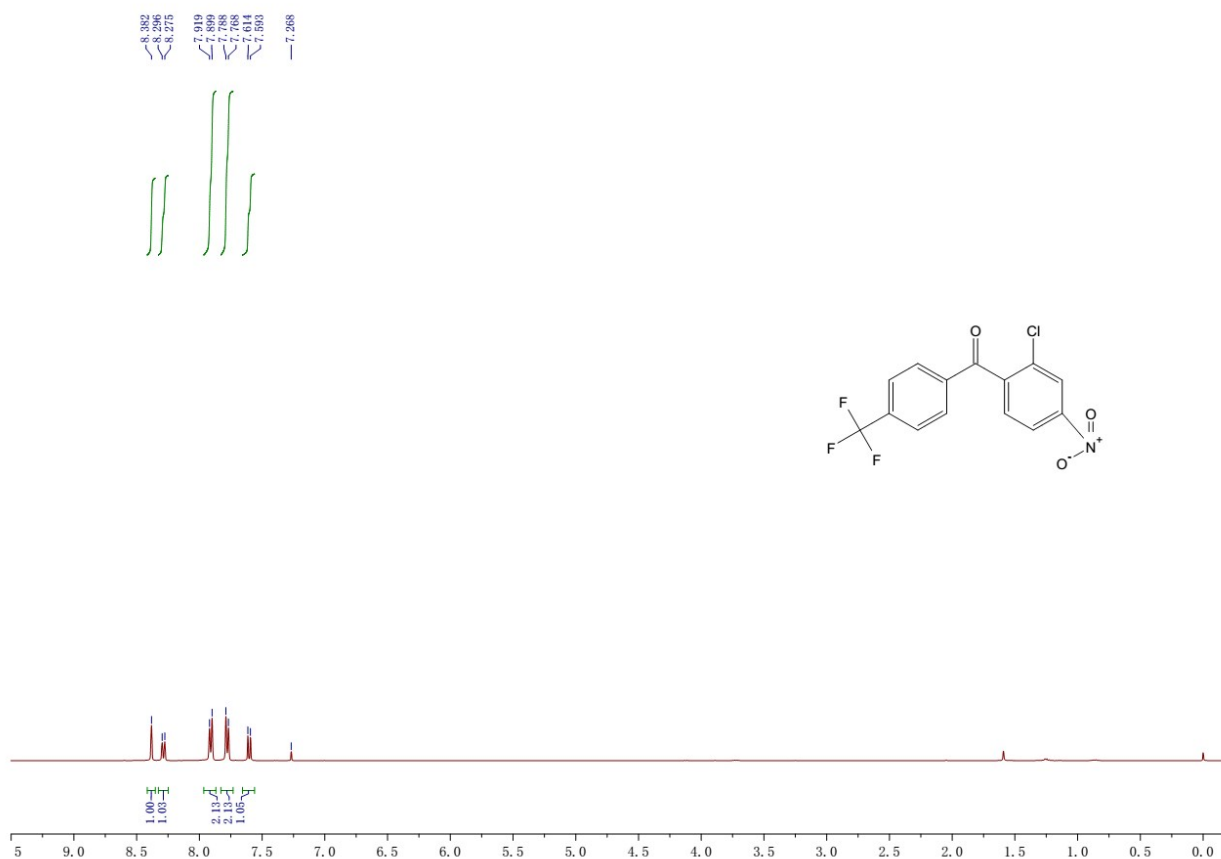
Chemical structure of 4-(4-methoxybenzoyl)-2-chloro-5-nitrobenzoic acid:

COc1ccc(cc1)C(=O)c2ccc(cc2Cl)[N+](=O)[O-]

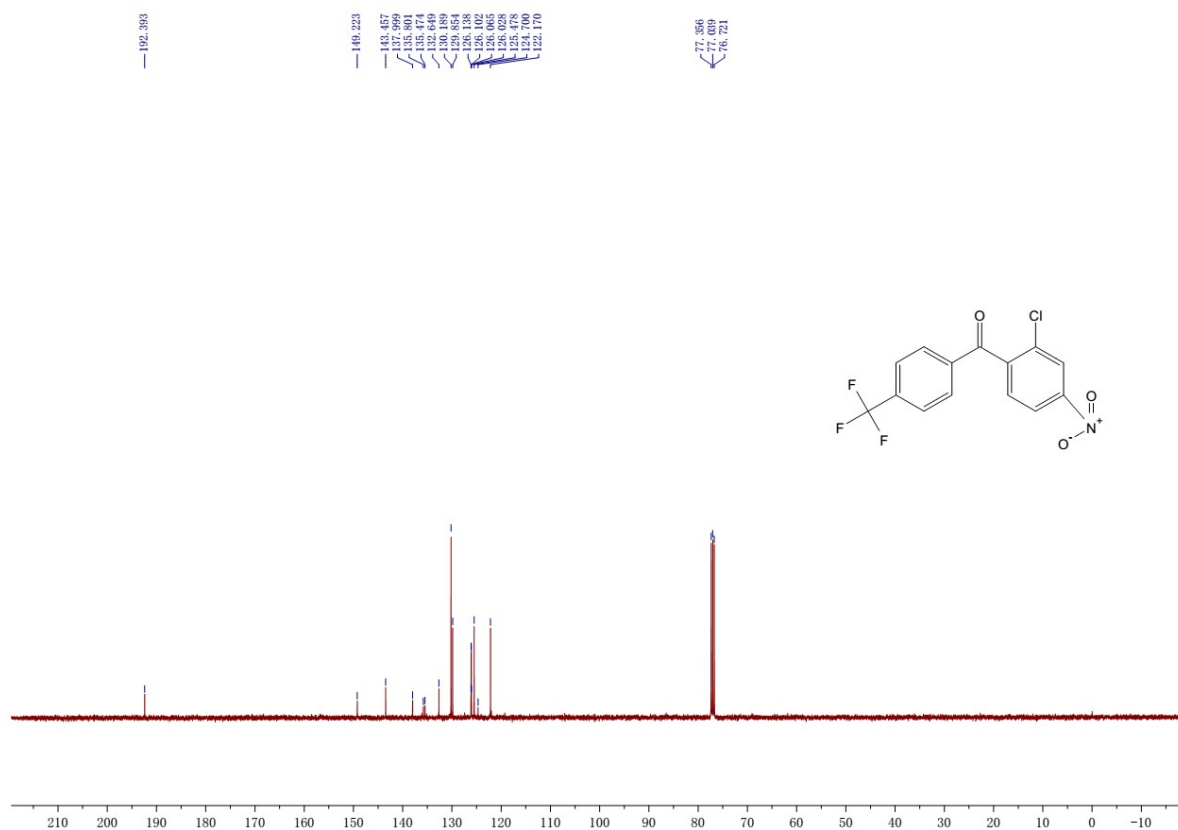
¹³C NMR peaks (ppm):

Peak Label	Chemical Shift (ppm)
193.131	193.131
160.112	160.112
148.847	148.847
144.500	144.500
136.582	136.582
132.553	132.553
129.961	129.961
128.531	128.531
125.292	125.292
123.210	123.210
121.863	121.863
121.253	121.253
113.417	113.417
77.281	77.281
77.063	77.063
76.745	76.745
55.571	55.571

25 / 37

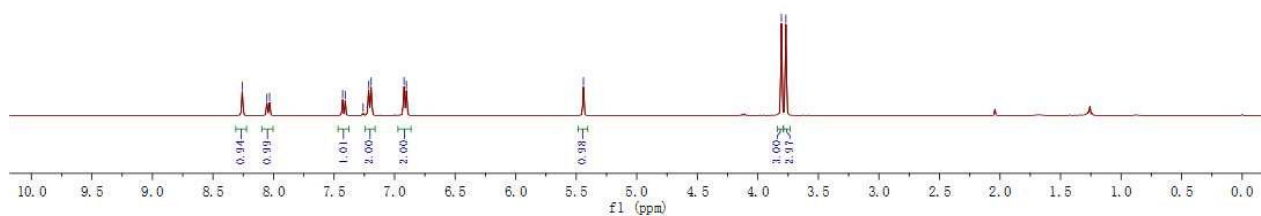
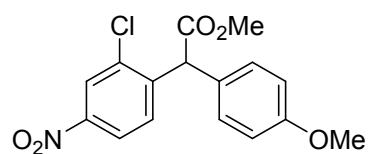
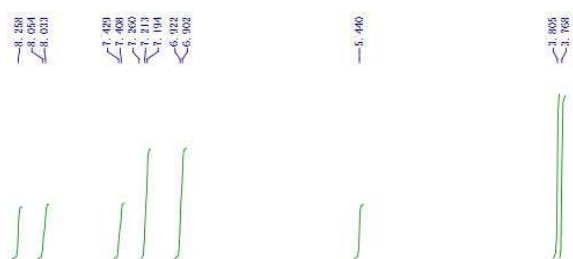


¹H NMR spectrum of **3bj**

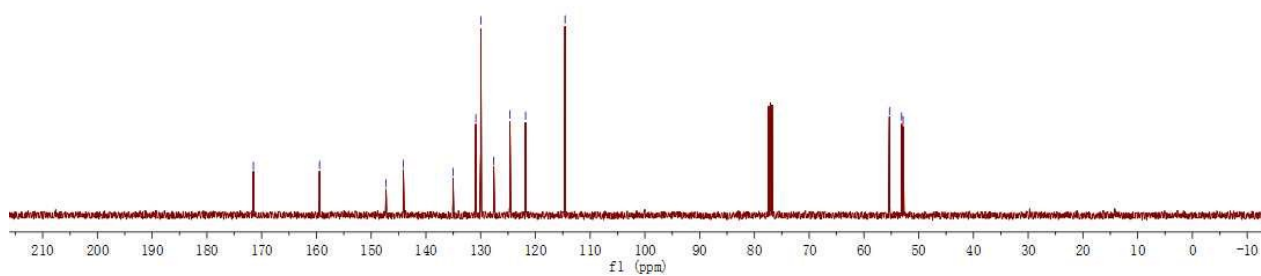
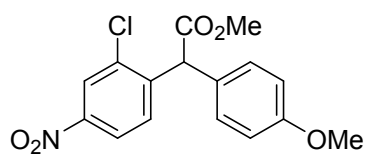


¹³C NMR spectrum of **3bj**

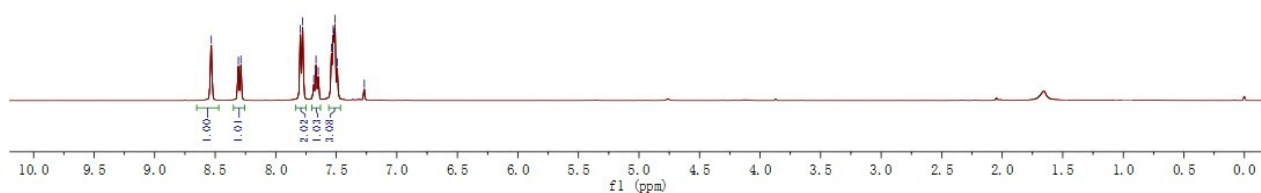
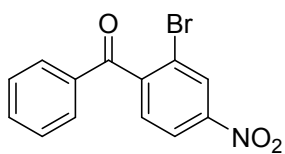
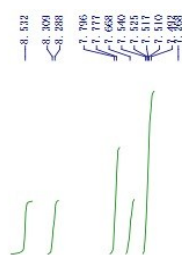
js-33-26

¹H NMR spectrum of **4bf**

js-33-26

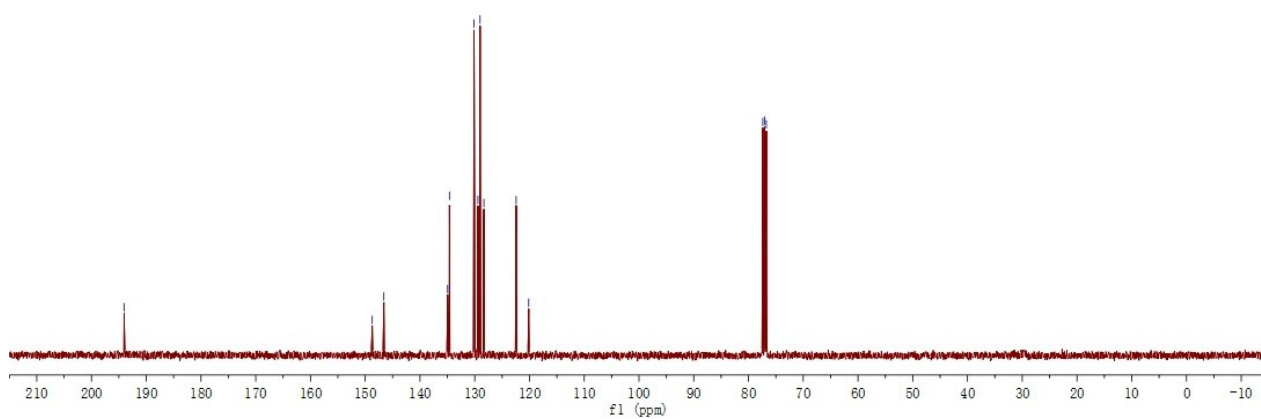
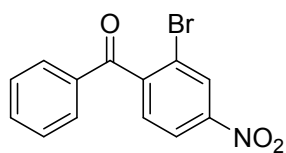
¹³C NMR spectrum of **4bf**

js-33-11



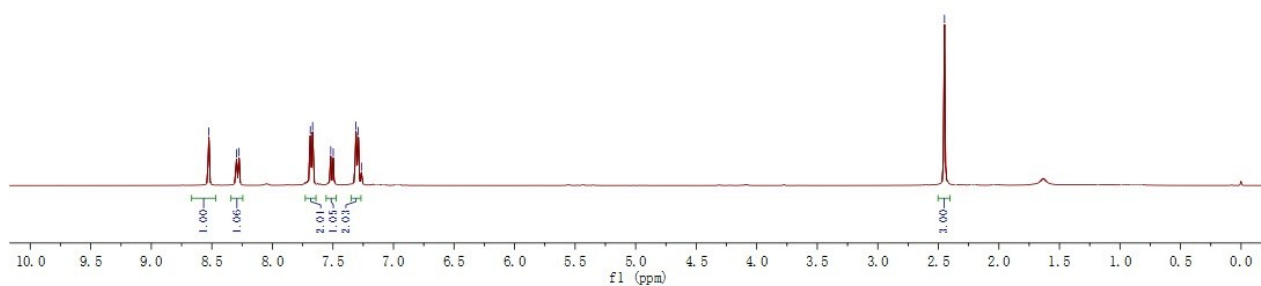
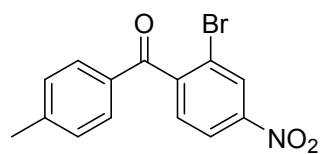
¹H NMR spectrum of 3ca

js-33-11



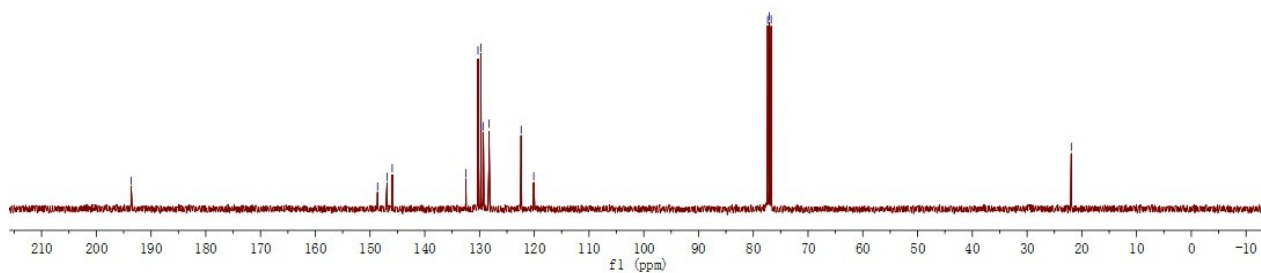
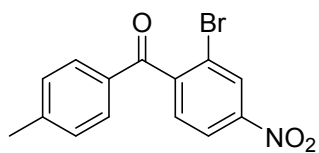
¹³C NMR spectrum of 3ca

js-33-14



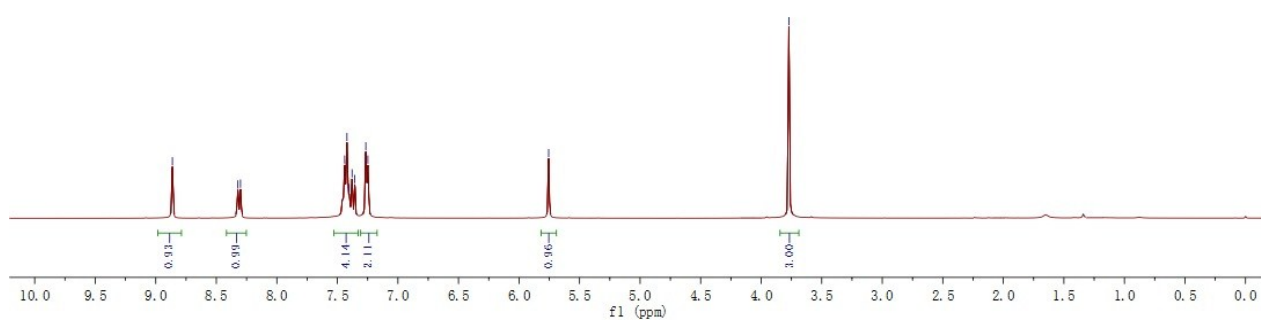
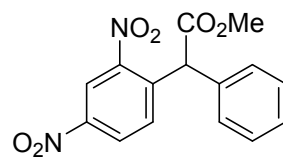
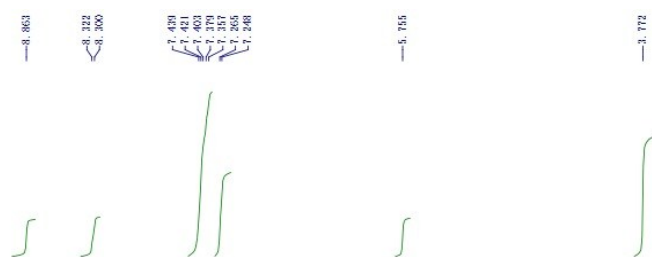
¹H NMR spectrum of **3cc**

js-33-14

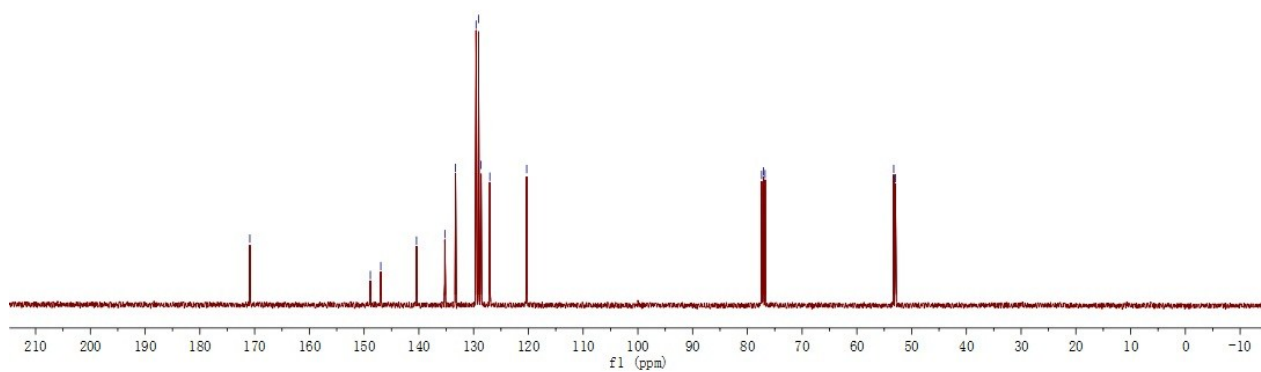
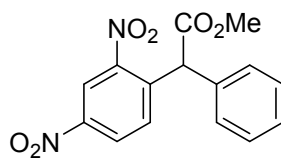


¹³C NMR spectrum of **3cc**

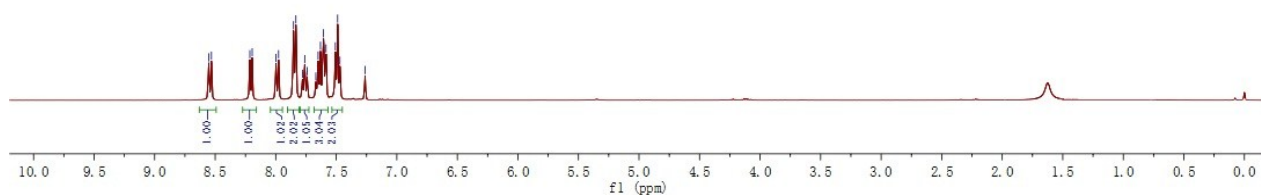
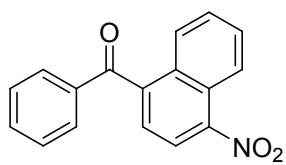
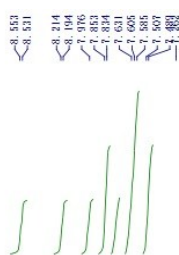
js-33-6

¹H NMR spectrum of **4da**

js-33-6

¹³C NMR spectrum of **4da**

js-33-7-1



¹H NMR spectrum of **3ea**

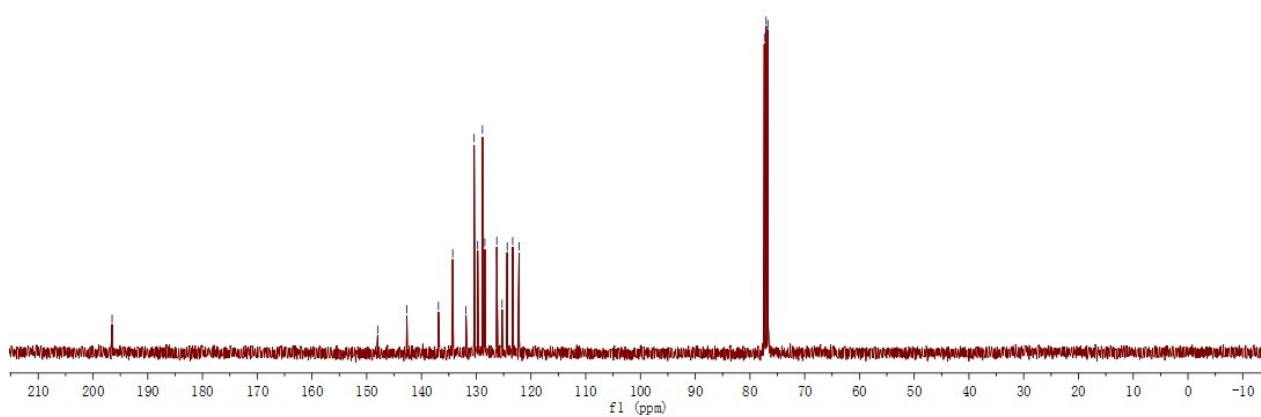
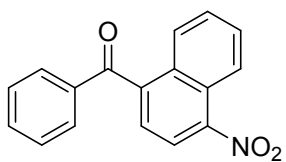
js-33-7-1

196.502

147.907

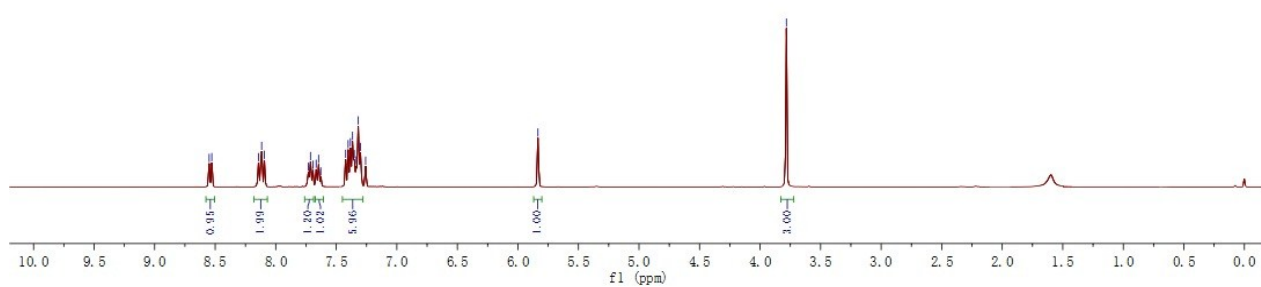
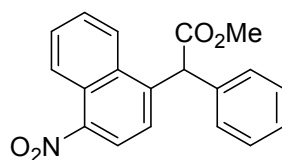
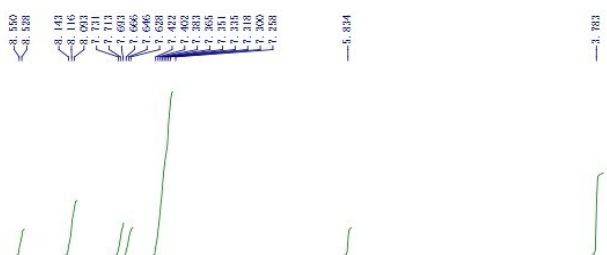
142.655, 136.551, 135.389, 131.864, 130.379, 129.735, 129.685, 128.429, 126.238, 125.275, 124.339, 123.174, 122.176

77.807, 77.002, 76.711

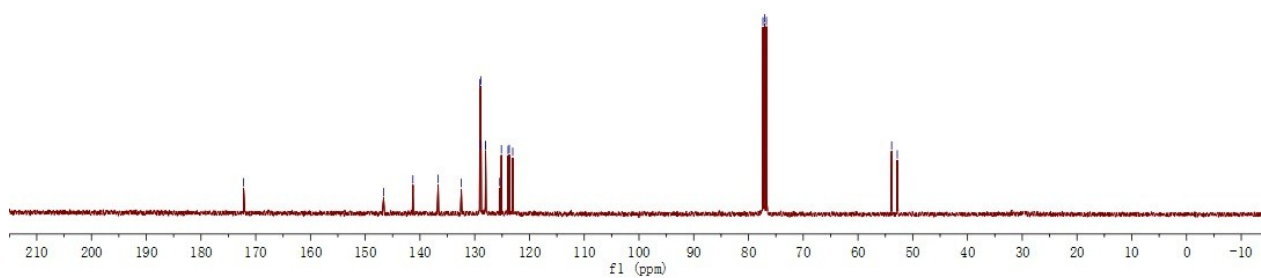
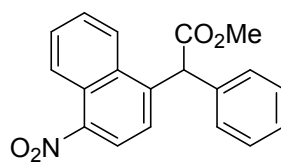


¹³C NMR spectrum of **3ea**

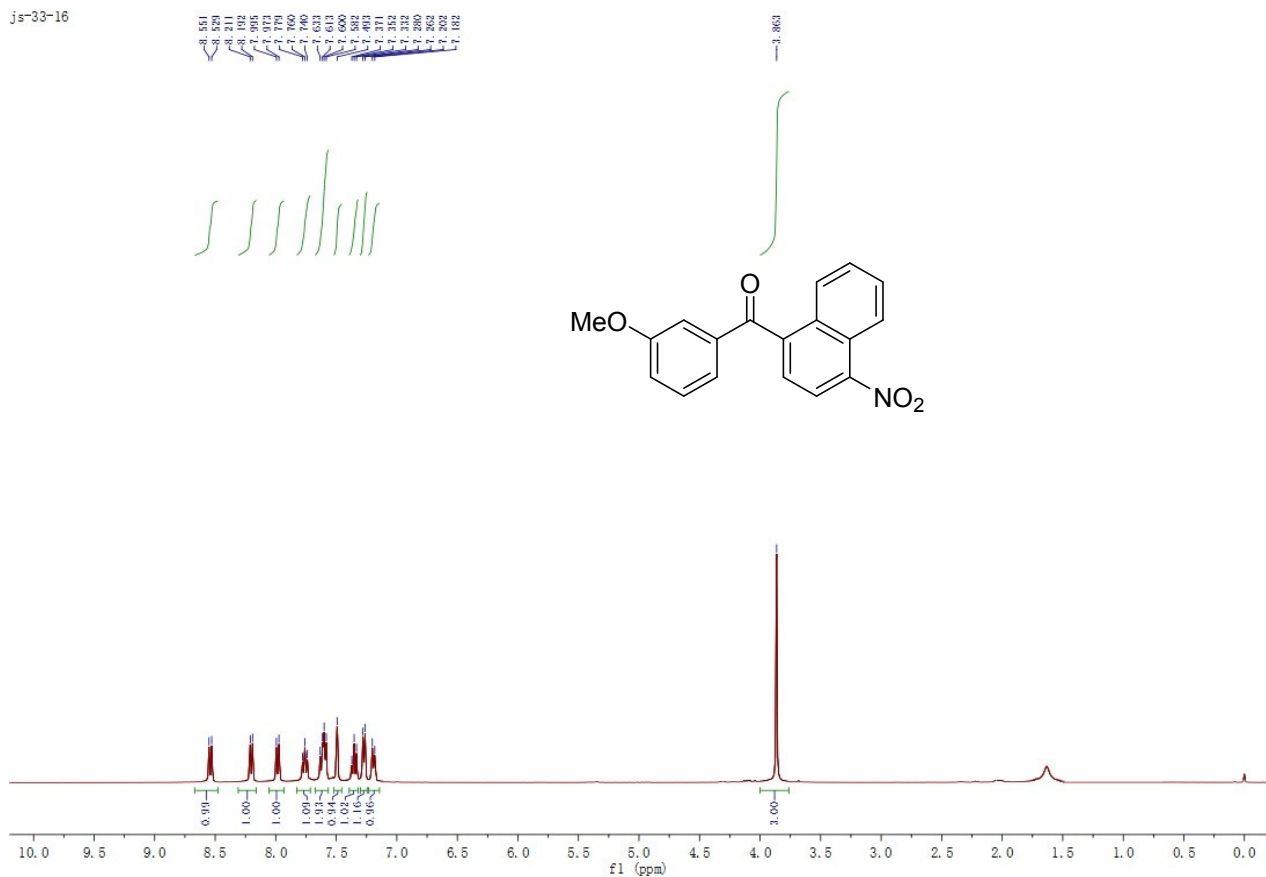
js-33-7-2

¹H NMR spectrum of 4ea

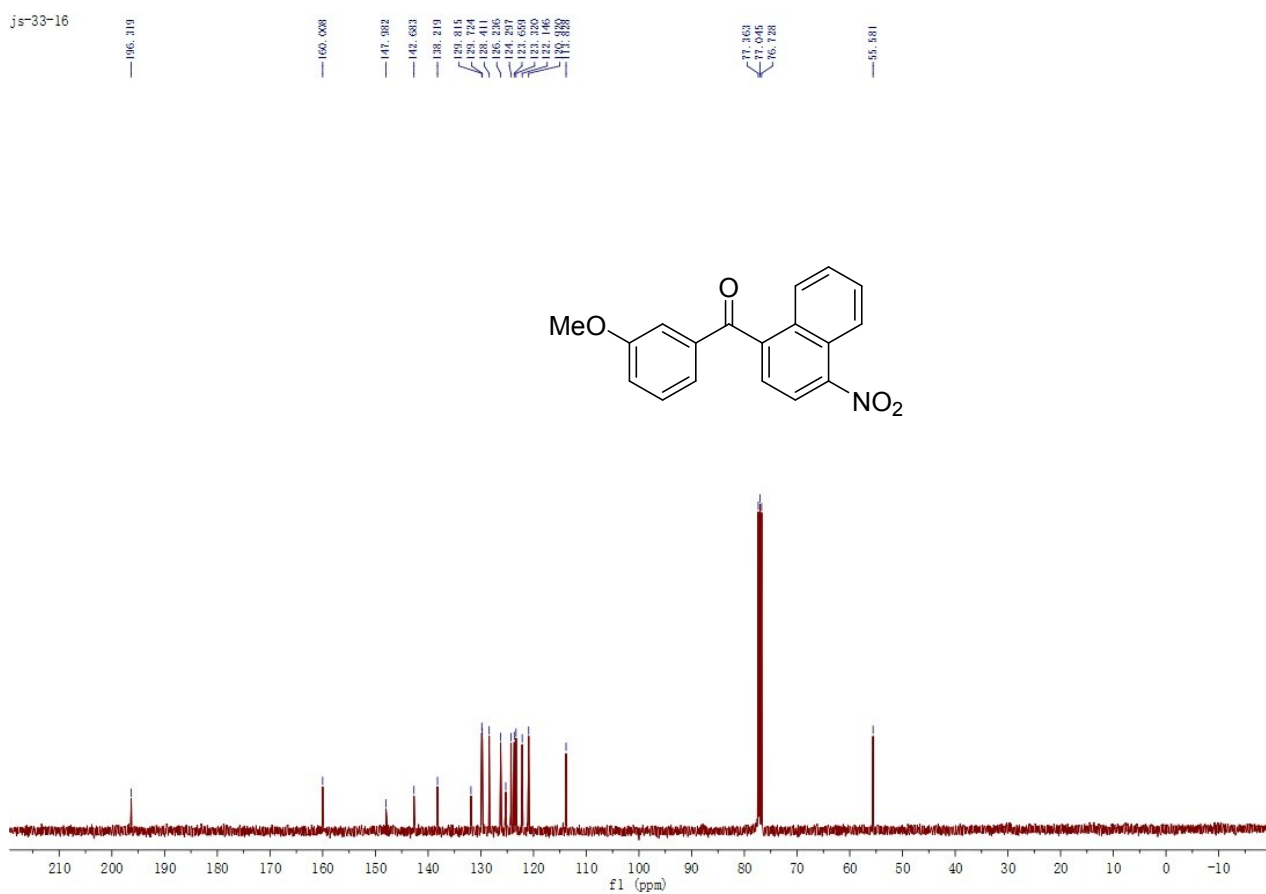
js-33-7-2

¹³C NMR spectrum of 4ea

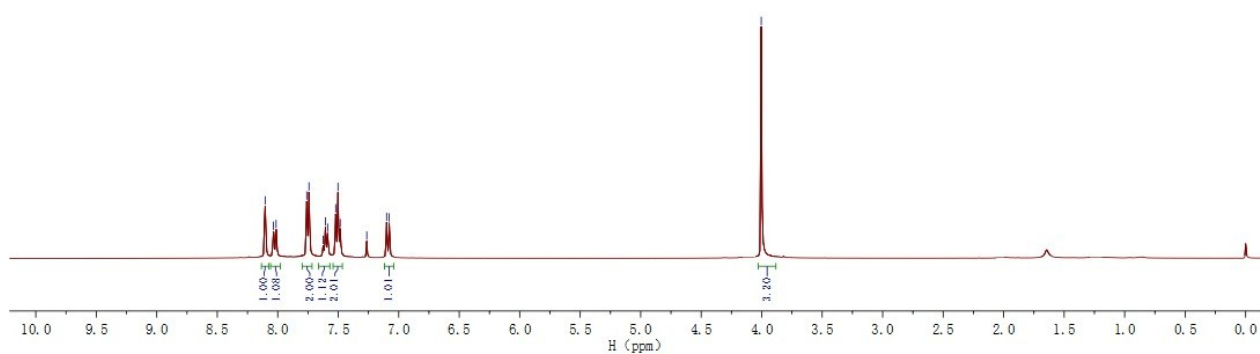
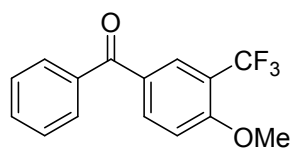
js-33-16

¹H NMR spectrum of **3ee**

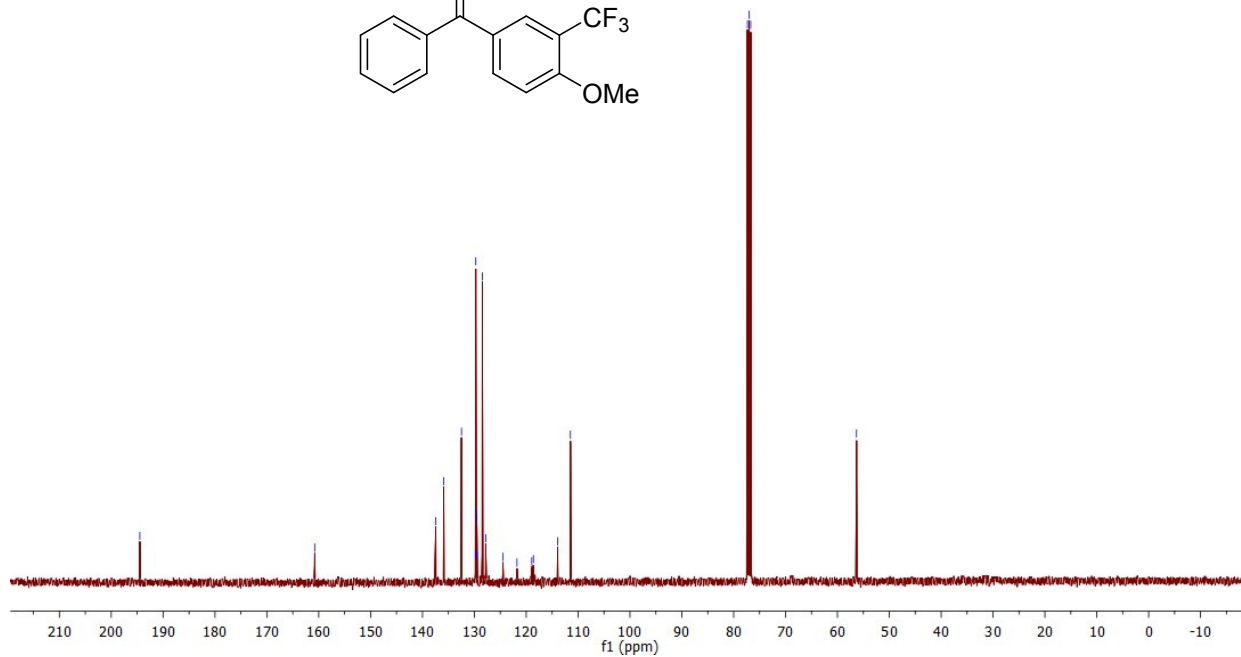
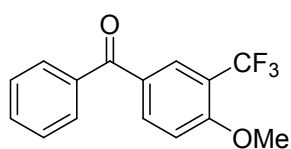
js-33-16

¹³C NMR spectrum of **3ee**

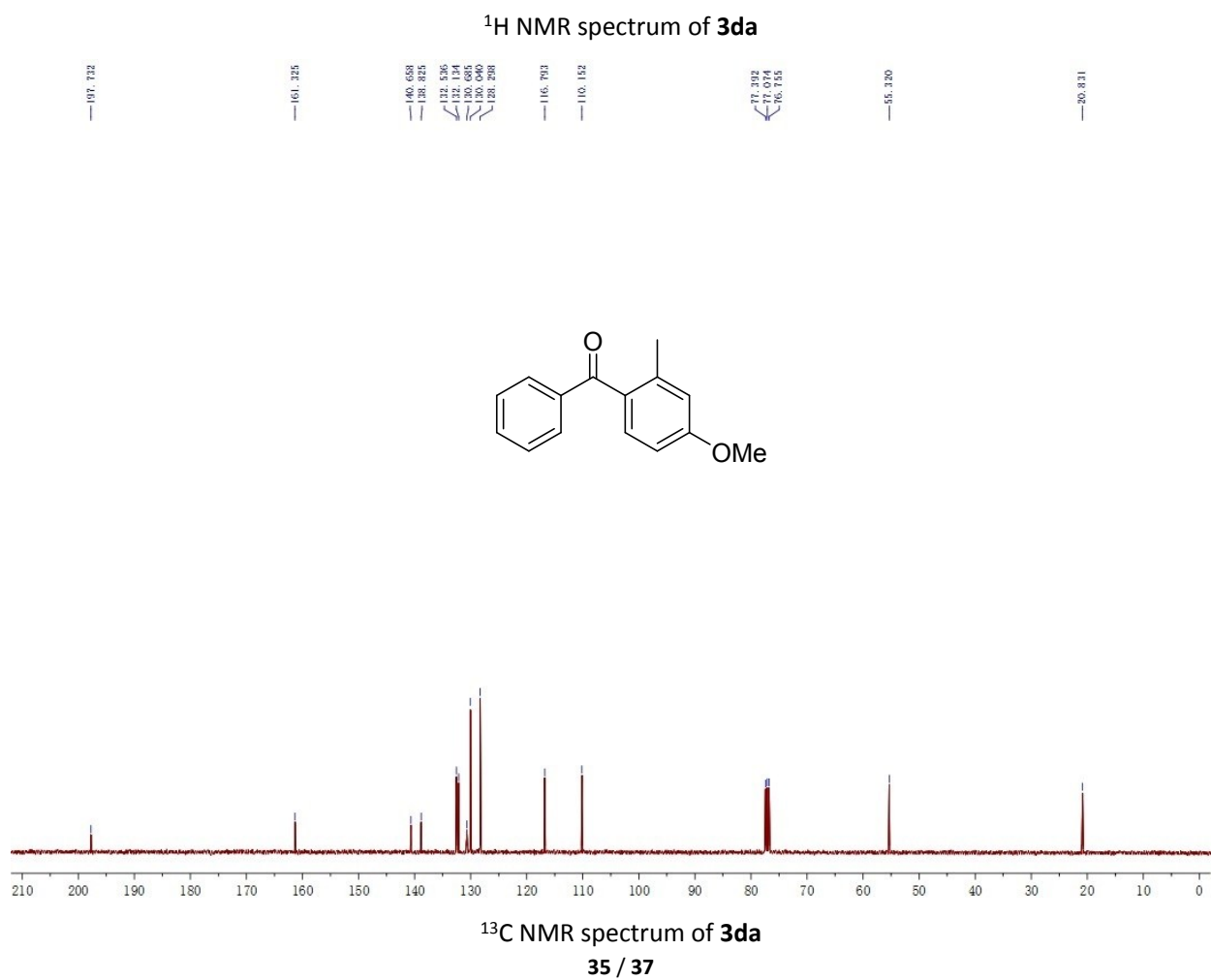
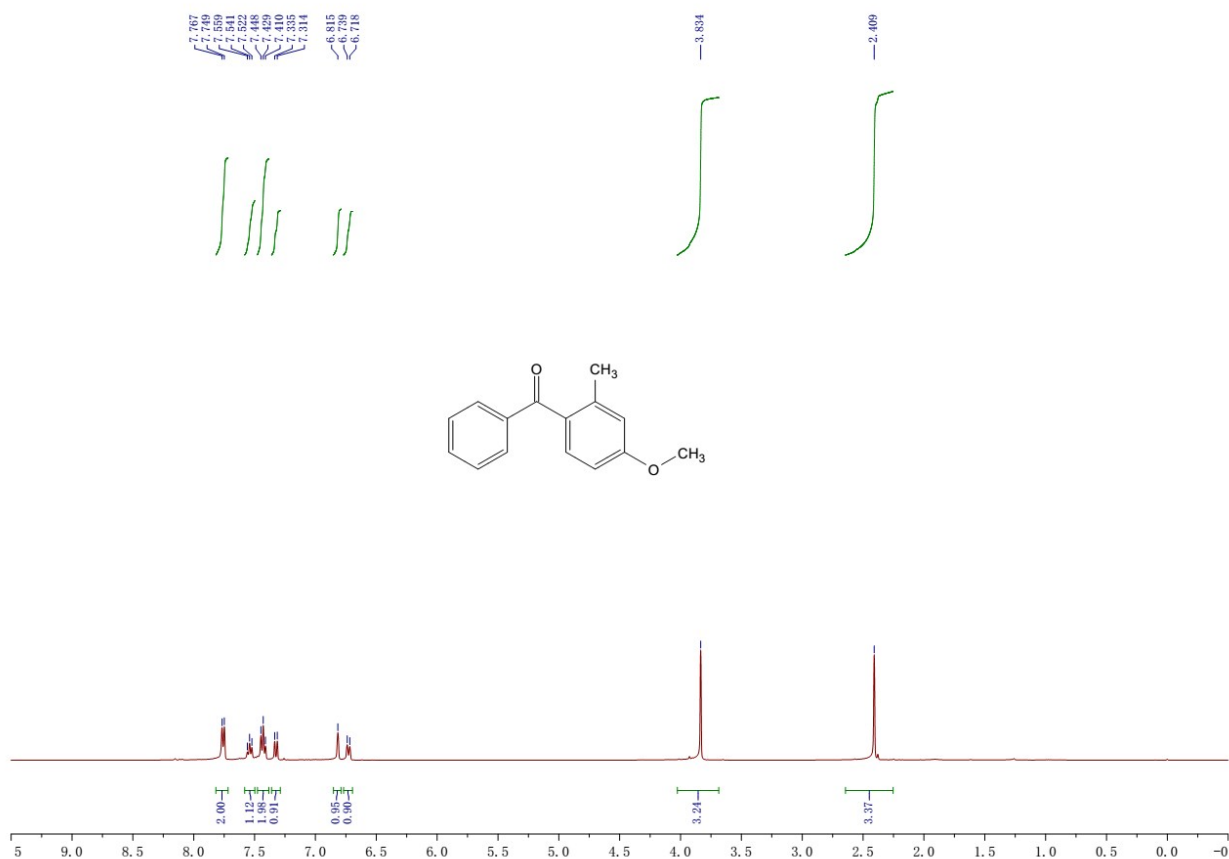
js-23-7-1

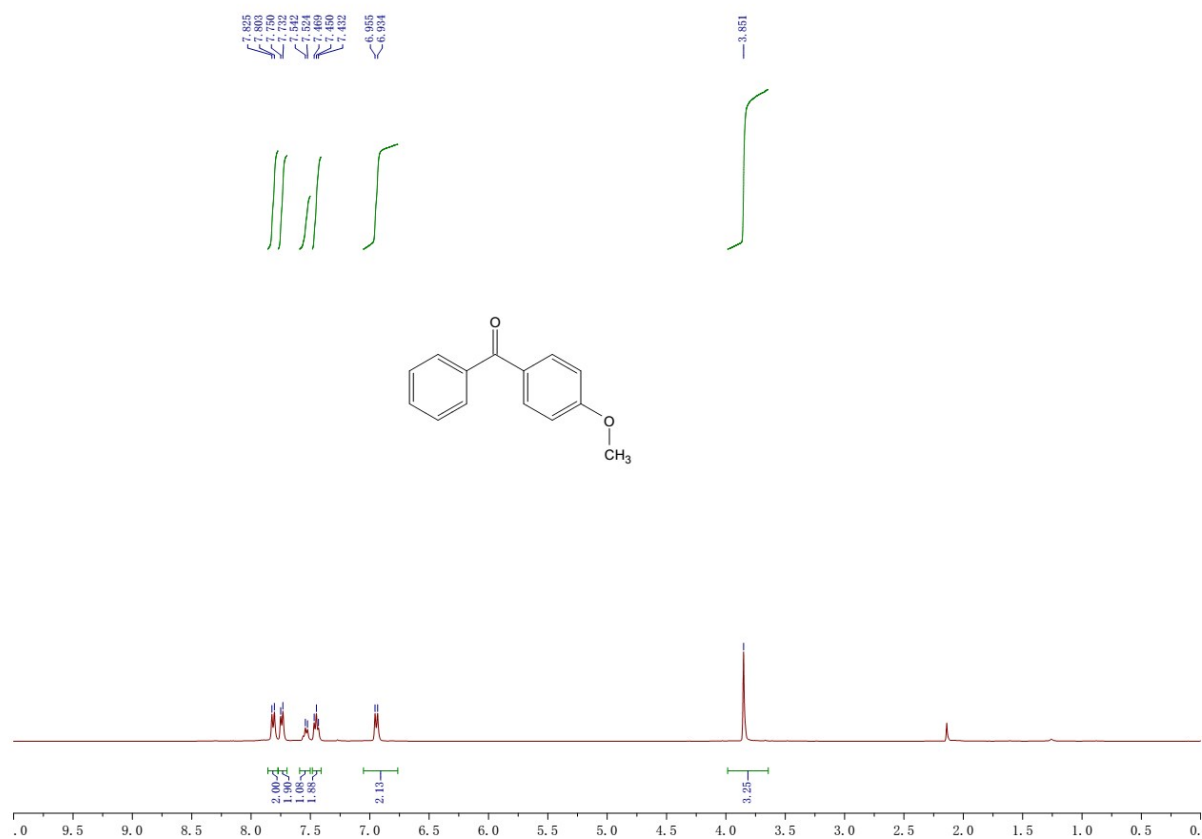


¹H NMR spectrum of 3ca

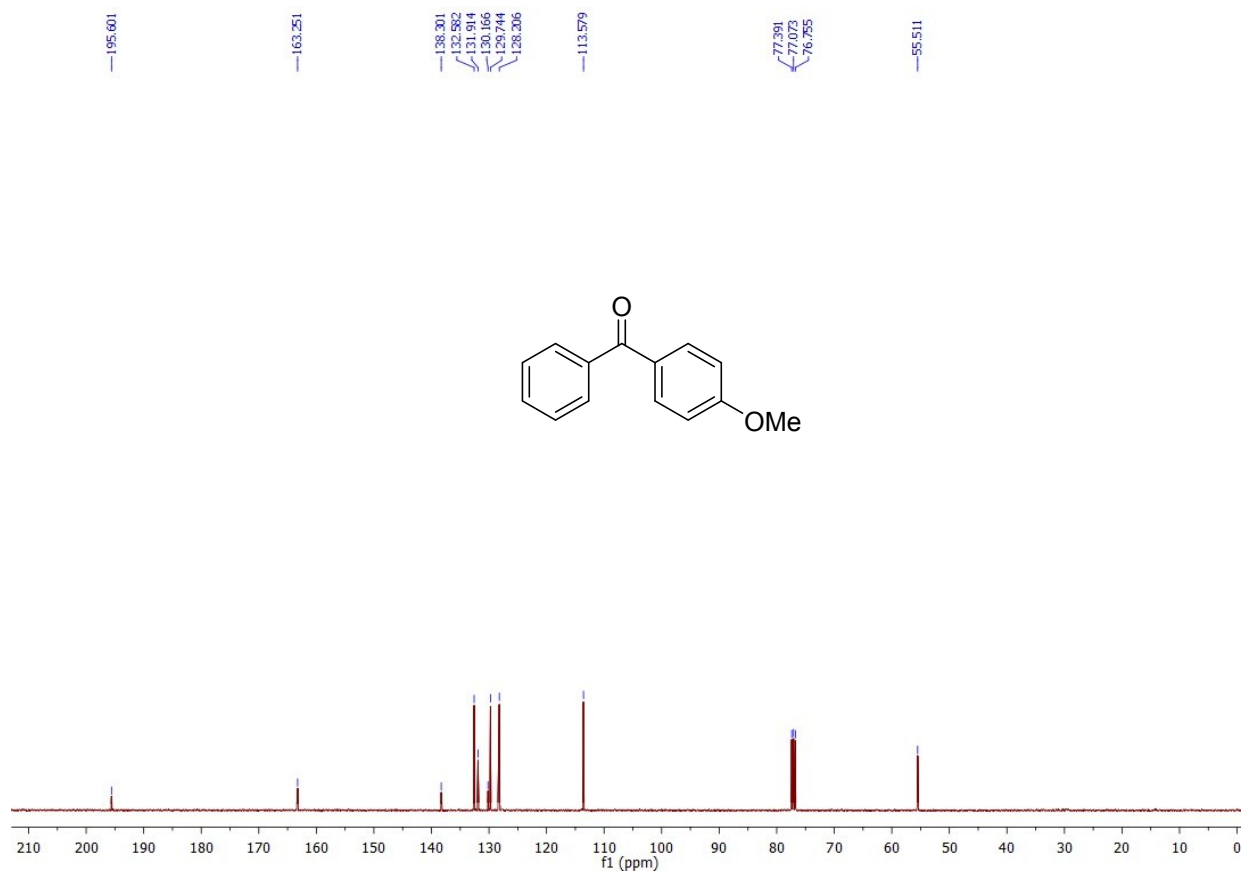


¹³C NMR spectrum of 3ca

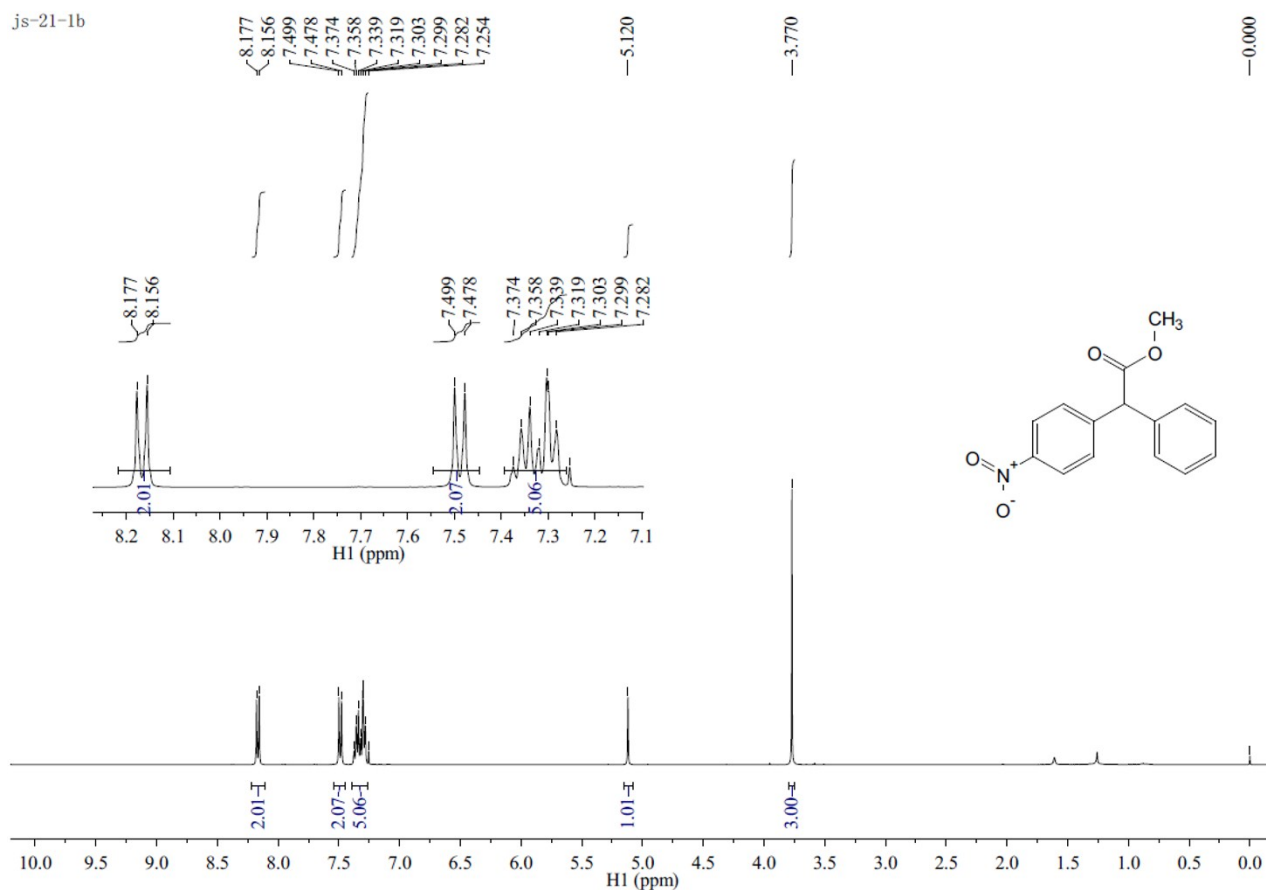




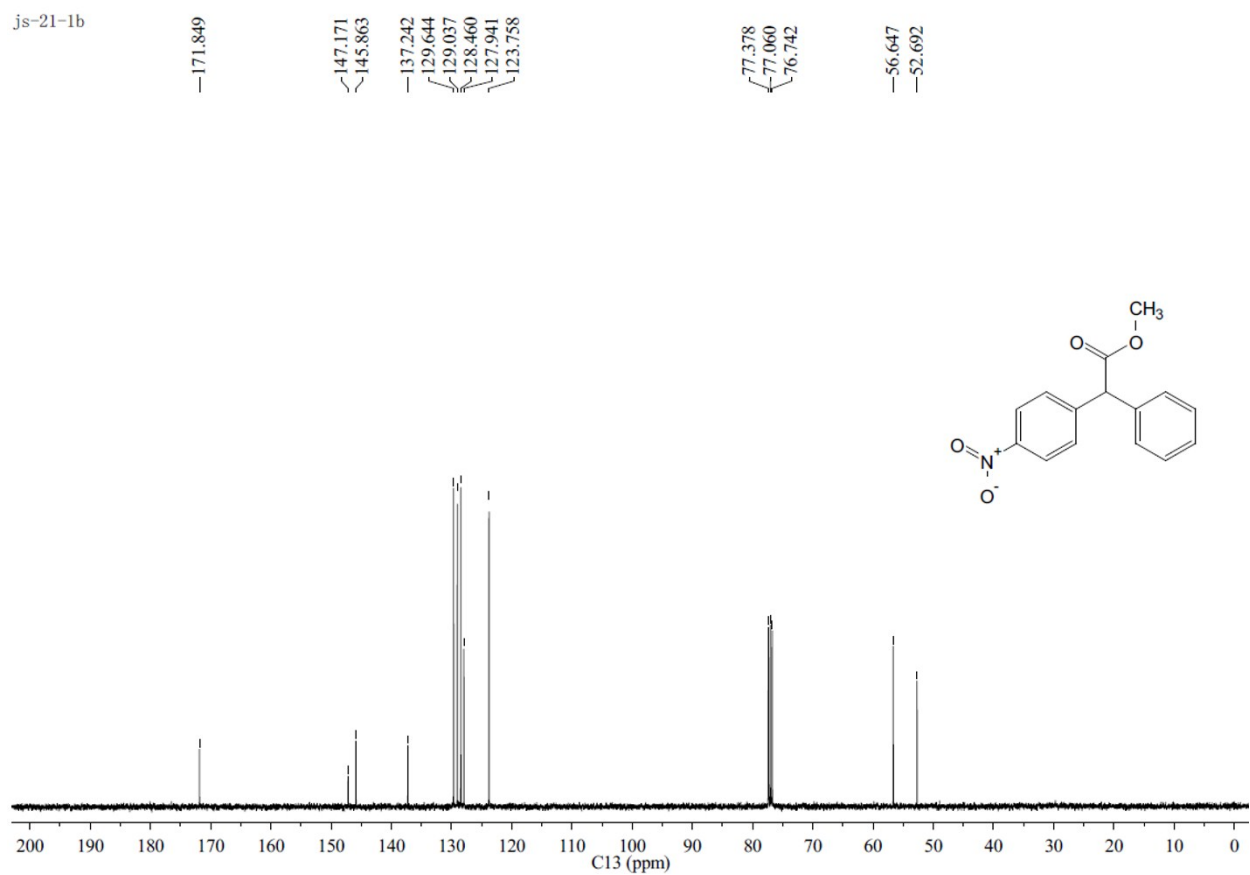
¹H NMR spectrum of **3ea**



¹³C NMR spectrum of **3ea**



¹H NMR spectrum of 4aa



¹³C NMR spectrum of 4aa