Supporting Information

Transition-metal-free $K_2S_2O_8$-promoted oxidative C-C triple bond cleavage and esterification leading to α-keto esters

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1. General considerations

All reactions were carried out under nitrogen atmosphere. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (600 MHz/151 MHz/565 NMR) in $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. Chemical shifts (δ) were reported in ppm, and coupling constants (J) were given in Hertz (Hz). Data were reported as s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF ESI mass spectrometer or a Micromass CI-TOF mass spectrometer.

2. Preparation of the starting materials

The chemicals and solvents were purchased from commercial supplierseither Aldrich (USA), Energy Chemical (Shanghai) or Shanghai Chemical Company (P. R. China). All solvents were dried and freshly distilled in N_2 prior to use. Products were purified by flash chromatographyon 200-300 mesh silica gel.

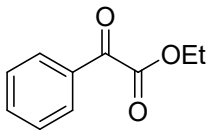
3. General procedure for the synthesis of 2a

In a 15 mL pressure-resistant tube, a magnetic stirrer was added, and 1,3-diphenylprop-2-en-1-one (1, 0.20 mmol), EtOH (2, 2 mL), $K_2S_2O_8$ (4 equiv, 0.80 mmol), $NaNO_2$ (2 equiv, 0.40 mmol) were added. The

reaction was performed at 110 ^{o}C for 18 h. After the reaction was completed, the mixture was concentrated to obtain the crude product, which was further purified by rapid chromatography (silica gel, petroleum ether / ethyl acetate = 30 : 1) to obtain the desired product **3a** in a yield of 71 %.

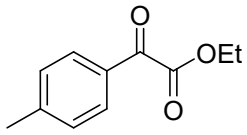
4. Characterization Data for Products

Ethyl 2-oxo-2-phenylacetate (3a) [1]



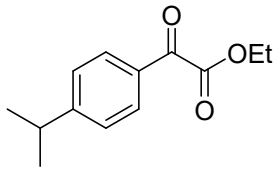
Yellow liquid，(25 mg, 71% yield) **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.04 – 7.99 (m, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 4.46 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 186.4, 163.8, 134.9, 132.5, 130.0, 128.9, 62.3, 14.1. The characterization data matched the literature.

Ethyl 2-oxo-2-(*p*-tolyl)acetate (3b) [1]



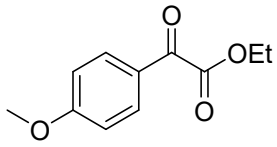
Yellow liquid，(27 mg, 69% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.83 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.36 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 186.1, 164.0, 146.2, 130.1, 130.0, 129.6, 62.2, 21.9, 14.1. The characterization data matched the literature.

Ethyl 2-(4-isopropylphenyl)-2-oxoacetate (3c) [3]



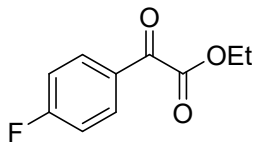
Yellow liquid，(31 mg, 70% yield). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.98 – 7.90 (m, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 (dd, *J* = 8.7, 5.6 Hz, 3H), 1.29 (dd, *J* = 9.4, 4.6 Hz, 7H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 186.1, 164.0, 156.8, 130.3, 130.3, 127.0, 62.2, 34.4, 23.5, 14.1. The characterization data matched the literature.

Ethyl 2-(4-methoxyphenyl)-2-oxoacetate (3d) [1]



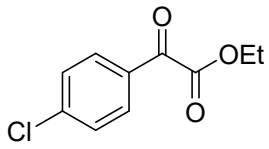
Yellow liquid，(27 mg, 66% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.99 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 184.9, 165.0, 164.1, 132.5, 125.4, 114.2, 62.1, 55.6, 14.1. The characterization data matched the literature.

Ethyl 2-(4-fluorophenyl)-2-oxoacetate(3e) [1]



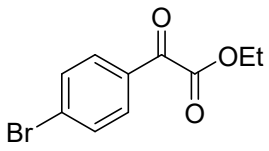
Yellow liquid，(31 mg, 66% yield).**^{1}H NMR (600 MHz, $CDCl_3$) δ** 8.12 – 8.05 (m, 2H), 7.19 (t, *J* = 8.5 Hz, 2H), 4.45 (q, *J* = 7.2 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 184.6, 167.7, 166.0, 163.4, 133.0 (d, *J* = 9.8 Hz), 116.3 (d, *J* = 21.9 Hz), 62.5, 14.1. **^{19}F NMR (565 MHz, $CDCl_3$) δ** -101.24. The characterization data matched the literature.

Ethyl 2-(4-chlorophenyl)-2-oxoacetate (3f) [1]



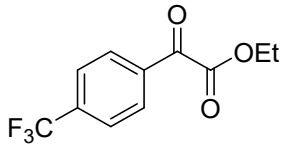
Yellow liquid，(30 mg, 71% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.91 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.40 – 4.35 (m, 2H), 1.35 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 184.9, 163.2, 141.6, 131.4, 129.3, 62.5, 14.1. The characterization data matched the literature.

Ethyl 2-(4-bromophenyl)-2-oxoacetate(3g) [1]



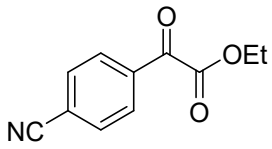
Yellow liquid，(30 mg, 71% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.93 – 7.87 (m, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 4.45 (d, *J* = 7.1 Hz, 2H), 1.42 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 185.1, 163.2, 132.3, 131.5, 131.4, 130.5, 62.6, 14.1. The characterization data matched the literature.

Ethyl 2-oxo-2-(4-(trifluoromethyl)phenyl)acetate(3h) [2]



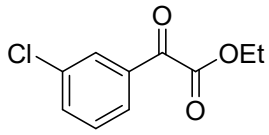
Yellow liquid，(30 mg, 67% yield).**^{1}H NMR (600 MHz, $CDCl_3$) δ** 8.09 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 4.40 (d, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 185.0, 162.8, 130.4, 130.0, 128.9, 125.9 (d, *J* = 4.0 Hz), 62.8, 14.1. **^{19}F NMR (565 MHz, $CDCl_3$) δ** -63.39. The characterization data matched the literature.

Ethyl 2-(4-cyanophenyl)-2-oxoacetate(3i) [1]



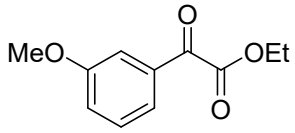
Yellow liquid，(30 mg, 72% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 8.15 (dd, *J* = 8.2, 1.3 Hz, 22H), 7.74 (dd, *J* = 8.3, 1.3 Hz, 2H), 4.42 (m, *J* = 7.1, 1.2 Hz, 2H), 1.42 (m, *J* = 7.1, 1.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 165.0, 134.3, 132.2, 130.1, 118.0, 116.3, 61.8, 14.3. The characterization data matched the literature.

Ethyl 2-(3-chlorophenyl)-2-oxoacetate (3j)[1]



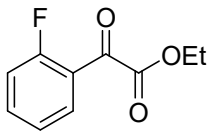
Yellow liquid，(31 mg, 74% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 8.01 (dd, *J* = 4.1, 2.4 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 184.8, 163.0, 134.8, 130.2, 129.8, 128.2, 62.6, 14.1. The characterization data matched the literature.

Ethyl 2-(3-methoxyphenyl)-2-oxoacetate (3k) [1]



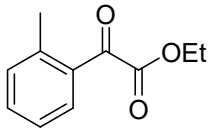
Yellow liquid，(29 mg, 69% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.96 – 7.90 (m, 1H), 7.64 (td, *J* = 7.4, 1.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.17 (dd, *J* = 10.4, 8.7 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 186.3, 163.8, 159.9, 133.7, 129.9, 123.1, 121.8, 113.2, 62.3, 55.5, 14.1. The characterization data matched the literature.

Ethyl 2-(2-fluorophenyl)-2-oxoacetate (3l)



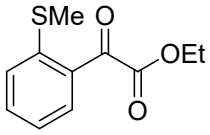
Yellow liquid，(27 mg, 68% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.96 – 7.90 (m, 1H), 7.64 (td, *J* = 7.4, 1.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.17 (dd, *J* = 10.4, 8.7 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 184.1, 164.1, 163.6, 161.8, 136.7, 136.7, 130.8, 124.9, 124.8, 116.6, 116.5, 62.5, 13.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{10}FO_3$ 197.0614, found 197.0614.

Ethyl 2-oxo-2-(o-tolyl)acetate (3m) [1]



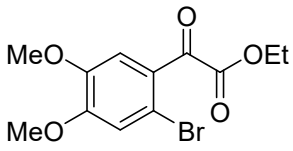
Yellow liquid，(27 mg, 69% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.69 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.32 (dd, *J* = 12.0, 7.7 Hz, 2H), 4.43 (d, *J* = 7.2 Hz, 2H), 2.61 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 188.8, 164.6, 141.3, 133.6, 132.3, 132.2, 131.2, 125.9, 62.2, 21.4, 14.1. The characterization data matched the literature.

Ethyl 2-(2-(methylthio)phenyl)-2-oxoacetate(3n)



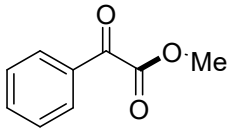
Yellow liquid，(32 mg, 67% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.84 – 7.75 (m, 1H), 7.58 – 7.52 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.24 (m, 1H), 4.43 (m, *J* = 7.0, 1.3 Hz, 2H), 2.47 (d, *J* = 1.3 Hz, 3H), 1.41 (m, *J* = 7.2, 1.4 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 187.0, 164.0, 144.4, 133.8, 133.1,130.3, 126.5, 124.2, 62.4, 16.5, 14.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}SO_3$ 225.0585, found 225.0580.

Ethyl 2-(2-bromo-4,5-dimethoxyphenyl)-2-oxoacetate (3o)



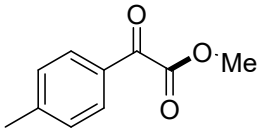
Yellow liquid，(42 mg, 66% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.25 (s, 1H), 6.98 (s, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 3.84 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 186.4, 163.7, 153.7, 148.6, 126.7, 116.1, 115.3, 113.8, 62.7, 56.5, 56.2, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}BrO_5$ 317.0025, found 317.0031.

Methyl 2-oxo-2-phenylacetate (3p) [2]



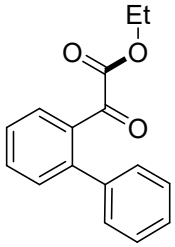
Yellow liquid，(23 mg, 70% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 8.02 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 3.98 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 186.0, 164.0, 135.0, 132.4, 130.1, 128.9, 52.8. The characterization data matched the literature.

Methyl 2-oxo-2-(p-tolyl)acetate(3q) [2]



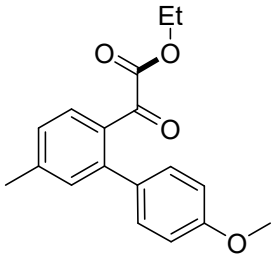
Yellow liquid，(26 mg, 67% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.91 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.97 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 185.71, 164.25, 146.37, 130.23, 130.00, 129.65, 52.71, 21.93. The characterization data matched the literature.

Ethyl 2-([1,1'-biphenyl]-2-yl)-2-oxoacetate (3r)



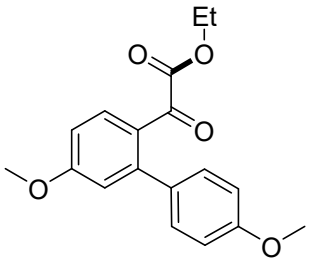
Yellow liquid，(39 mg, 77% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.74 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.55 (td, *J* = 7.6, 1.1 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.26 – 7.23 (m, 2H), 3.65 (q, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 189.6, 162.5, 143.0, 139.4, 134.5, 132.8, 130.3, 130.1, 129.6, 128.7, 128.2, 127.6, 62.1, 13.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{15}O_3$ 255.1021, found 255.1022.

Ethyl 2-(4'-methoxy-5-methyl-[1,1'-biphenyl]-2-yl)-2-oxoacetate (3s)



Yellow liquid，(44 mg, 73% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.72 (d, *J* = 7.9 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 3H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H), 3.77 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.06 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 189.5, 163.0, 159.8, 143.7, 143.0, 133.7, 132.0, 131.7, 130.8, 130.8, 130.5, 130.2, 128.5, 128.0, 114.0, 61.9, 55.3, 21.7, 13.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O_4$ 299.1283, found 299.1282.

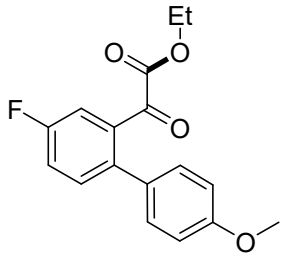
Ethyl 2-(4',5-dimethoxy-[1,1'-biphenyl]-2-yl)-2-oxoacetate (3t)



Yellow liquid，(46 mg, 74% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.84 (d, *J* = 8.7 Hz, 1H), 7.26 – 7.23 (m, 2H), 6.97 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.95 – 6.92 (m, 2H), 6.87 (d, *J* = 2.5 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.77 – 3.72 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz,**

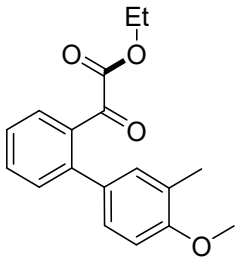
$CDCl_3$) δ 188.3, 163.5, 163.1, 159.9, 145.6, 132.9, 131.9, 130.7, 130.1, 128.4, 126.9, 115.3, 113.9, 113.0, 61.8, 55.6, 55.3, 13.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O_5$ 315.1232, found 315.1236.

Ethyl 2-(4-fluoro-4'-methoxy-[1,1'-biphenyl]-2-yl)-2-oxoacetate (3u)



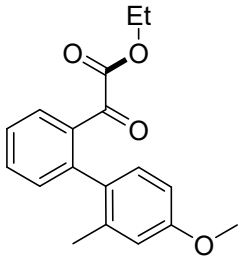
Yellow liquid，(40 mg, 67% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.41 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.32 (dd, *J* = 8.5, 5.2 Hz, 1H), 7.23 (td, *J* = 8.2, 2.7 Hz, 1H), 7.14 – 7.10 (m, 2H), 6.90 – 6.83 (m, 2H), 3.76 (s, 3H), 3.71 (q, *J* = 7.2 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 187.4, 161.5, 161.1, 159.9, 158.9, 137.8, 137.8, 134.8, 134.7, 130.9, 130.8, 129.8, 129.7, 118.9, 118.7, 115.7, 115.5, 113.1, 61.2, 54.3, 12.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}FO_4$ 303.1033, found 303.1027.

Ethyl 2-(4'-methoxy-3'-methyl-[1,1'-biphenyl]-2-yl)-2-oxoacetate (3v)



Yellow liquid，(37 mg, 67% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.79 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.60 (td, *J* = 7.6, 1.3 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.16 – 7.06 (m, 2H), 6.85 (d, *J* = 8.1 Hz, 1H), 3.86 (s, 3H), 3.77 (q, *J* = 7.2 Hz, 2H), 2.25 (s, 3H), 1.04 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 189.9, 162.7, 158.0, 143.0, 134.5, 132.7, 131.7, 131.4, 130.2, 129.9, 128.3, 127.1, 127.0, 109.9, 61.9, 55.4, 16.1, 13.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O_4$ 299.1283, found 299.1282.

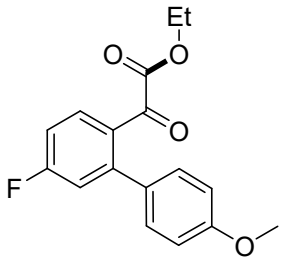
Ethyl 2-(4'-methoxy-2'-methyl-[1,1'-biphenyl]-2-yl)-2-oxoacetate (3w)



Yellow liquid，(38 mg, 69% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.86 (d, *J* = 7.7 Hz, 1H), 7.60 (dd, *J* = 10.9, 4.1 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 1.9 Hz, 1H), 6.74 (dd, *J* = 8.3, 2.3 Hz, 1H), 3.82 (s, 3H), 3.78 – 3.71 (m, 2H),

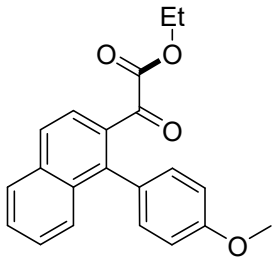
2.15 (s, 3H), 1.09 (t, J = 7.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 189.6, 163.5, 159.7, 142.4, 138.4, 134.9, 132.6, 132.4, 131.0, 130.7, 129.9, 127.4, 115.8, 110.6, 62.0, 55.2, 20.5, 13.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O_4$ 299.1283, found 299.1286.

Ethyl 2-(5-fluoro-4'-methoxy-[1,1'-biphenyl]-2-yl)-2-oxoacetate (3x)



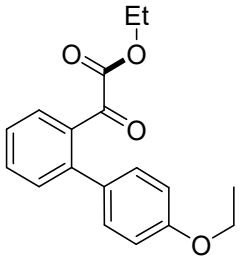
Yellow liquid，(38 mg, 70% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.83 (m, J = 8.1, 6.0, 1.5 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.19 – 7.09 (m, 2H), 6.95 (dd, J = 8.6, 1.7 Hz, 2H), 3.84 (d, J = 1.6 Hz, 3H), 3.77 (m, J = 7.2, 1.5 Hz, 2H), 1.06 (m, J = 7.2, 1.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 188.4, 165.9, 164.2, 162.6, 160.3, 145.8 (d, J = 9.0 Hz) , 133.1 (d, J = 9.8 Hz), 133.0, 130.7, 117.0 (d, J = 22.1 Hz), 114.6 (d, J = 22.1 Hz), 114.3, 62.2, 55.4, 13.7. **^{19}F NMR (565 MHz, $CDCl_3$) δ** -105.16. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{16}FO_4$ 303.1033, found 303.1032.

Ethyl 2-(1-(4-methoxyphenyl)naphthalen-2-yl)-2-oxoacetate(3y)



Yellow liquid，(38 mg, 71% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.93 (t, *J* = 9.5 Hz, 2H), 7.85 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.47 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.02 (dd, *J* = 8.5, 1.4 Hz, 2H), 3.89 (d, *J* = 1.2 Hz, 3H), 3.79 (m, *J* = 7.2, 1.3 Hz, 2H), 1.11 (m, *J* = 7.1, 1.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 190.5, 163.6, 160.0, 142.0, 135.6, 133.3, 132.3, 132.0, 128.3, 128.2, 128.2, 127.3, 127.0, 125.2, 113.7, 62.0, 55.4, 13.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{18}O_4Na$ 357.1103, found 357.1093.

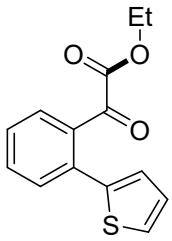
Ethyl 2-(4'-ethoxy-[1,1'-biphenyl]-2-yl)-2-oxoacetate(3z)



Yellow liquid，(38 mg, 68% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.93 (t, *J* = 9.5 Hz, 1H), 7.85 (dd, *J* = 8.6, 1.2 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.47 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.33 – 7.27

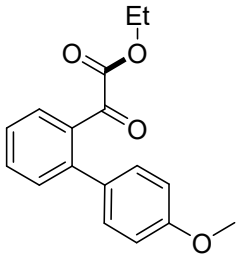
(m, 2H), 7.02 (dd, *J* = 8.5, 1.4 Hz, 2H), 3.89 (d, *J* = 1.2 Hz, 3H), 3.79 (m, *J* = 7.2, 1.3 Hz, 1H), 1.11 (m, *J* = 7.1, 1.2 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 189.9, 162.7, 159.3, 142.8, 134.5, 132.8, 131.7, 130.8, 130.2, 130.0, 127.2, 114.7, 63.6, 62.0, 14.8, 13.7. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{18}H_{19}O_4$ 299.1283, found 299.1282.

Ethyl 2-oxo-2-(2-(thiophen-2-yl)phenyl)acetate(3aa)



Yellow liquid，(38 mg,71% yield). **^{1}H NMR (600 MHz, $CDCl_3$) δ** 7.76 (d, *J* = 7.7 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 5.2 Hz, 1H), 7.04 (m, *J* = 5.1, 3.5, 1.3 Hz, 1H), 6.93 (d, *J* = 3.5 Hz, 1H), 3.91 (m, *J* = 7.2, 1.4 Hz, 2H), 1.11 (m, *J* = 7.2, 1.4 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 189.3, 162.0, 141.2, 135.1, 132.7, 130.3, 130.2, 129.5, 128.2, 127.9, 127.7, 62.3, 13.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}SO_3$ 261.0585, found 261.0577.

Ethyl 2-(4'-methoxy-[1,1'-biphenyl]-2-yl)-2-oxoacetate (3ab)



Yellow liquid，(40 mg, 71% yield). **^{1}H NMR (600 MHz, CDCl3) δ** 7.79 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.61 (m, *J* = 7.6, 1.3 Hz, 1H), 7.46 (m, *J* = 7.6, 1.0 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 6.96 – 6.93 (m, 2H), 3.84 (s, 3H), 3.79 (q, *J* = 7.2 Hz, 2H). **^{13}C NMR (151 MHz, CDCl3) δ** 189.8, 162.7, 159.8, 142.7, 134.5, 132.7, 131.8, 130.8, 130.2, 130.0, 127.2, 114.1, 62.0, 55.3, 13.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{17}O_4$ 285.1172, found 285.1180.

5. References

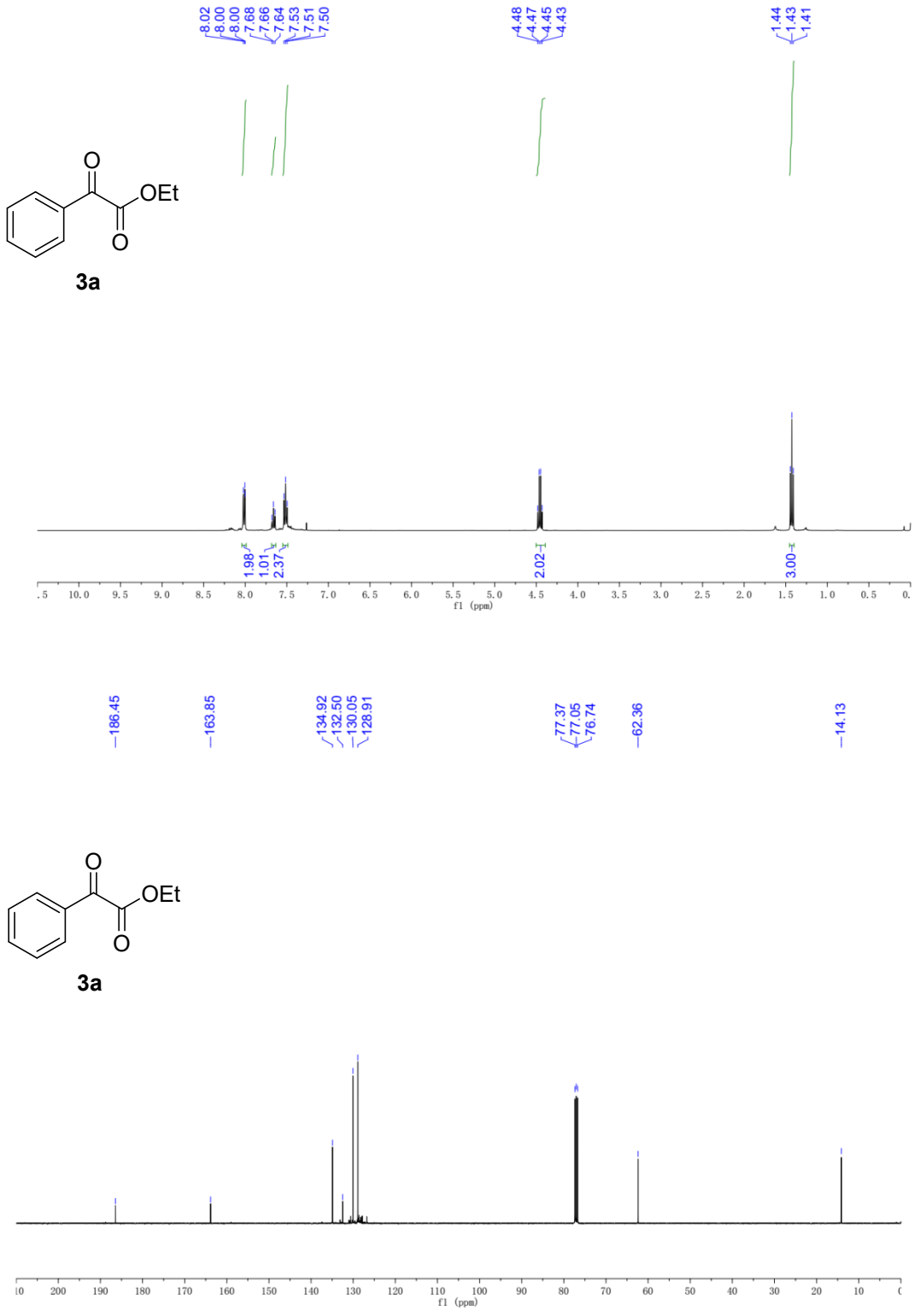
[1] Q. Yu, Y. Zhang and J.-P. Wan, Ambient and aerobic carbon–carbon bond cleavage toward α-ketoester synthesis by transition-metal-free photocatalysis, Green Chem., 2019, **21**, 3436–3441.

[2] R. Liu, Q. Liu, H. Meng, H. Ding, J. Hao, Z. Ji, H. Yue and W. Wei, Metal-free visible-light-induced aerobic oxidation of α-diazoesters leading to α-ketoesters in air, Org. Chem. Front., 2021, **8**, 1970–1975.

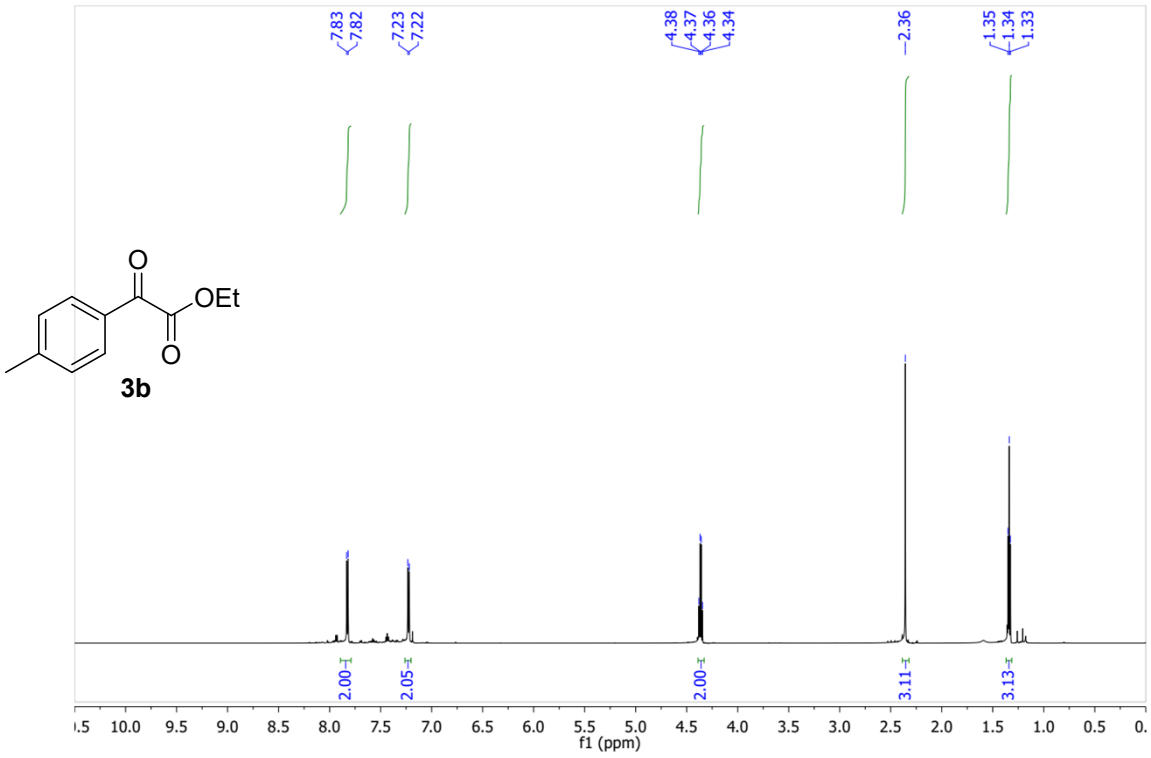
[3] S-E Wang, L-F Wang, Q-Q He and R-H Fan, Destruction and Construction: Application of Dearomatization Strategy in Aromatic Carbon–Nitrogen Bond Functionalization, Angew Chem Int Ed, 2015, **54,** 13655-13658.

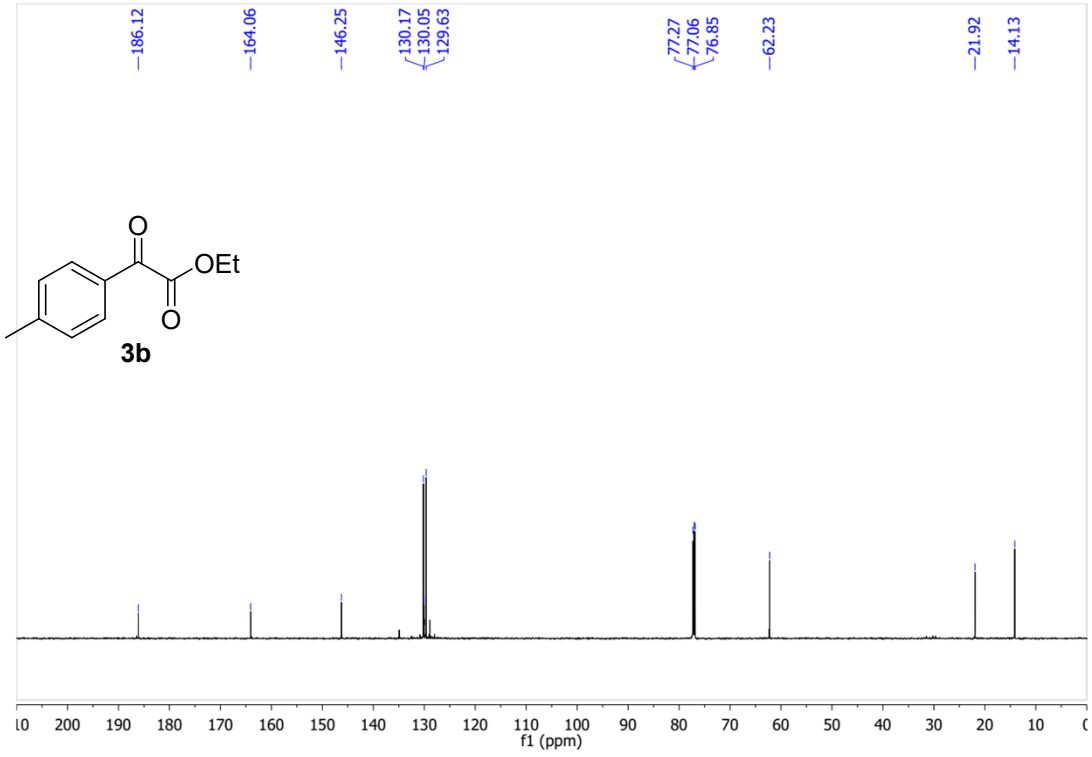
6. NMR spectra of compound

^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3a**

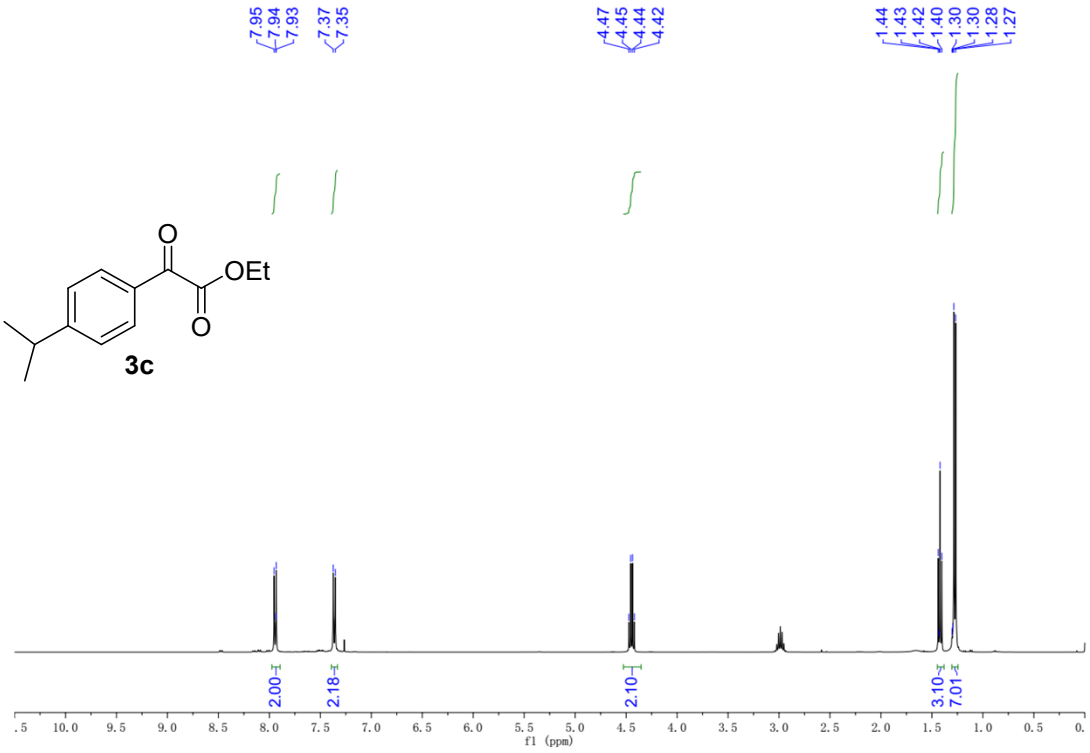


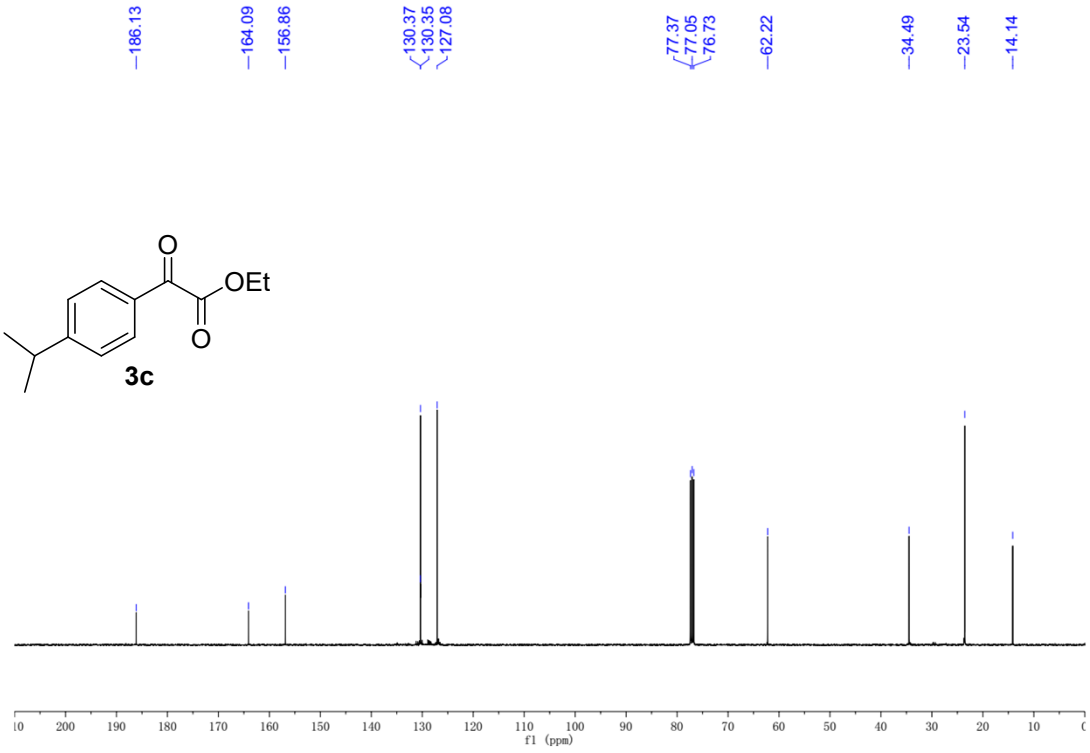
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3b**



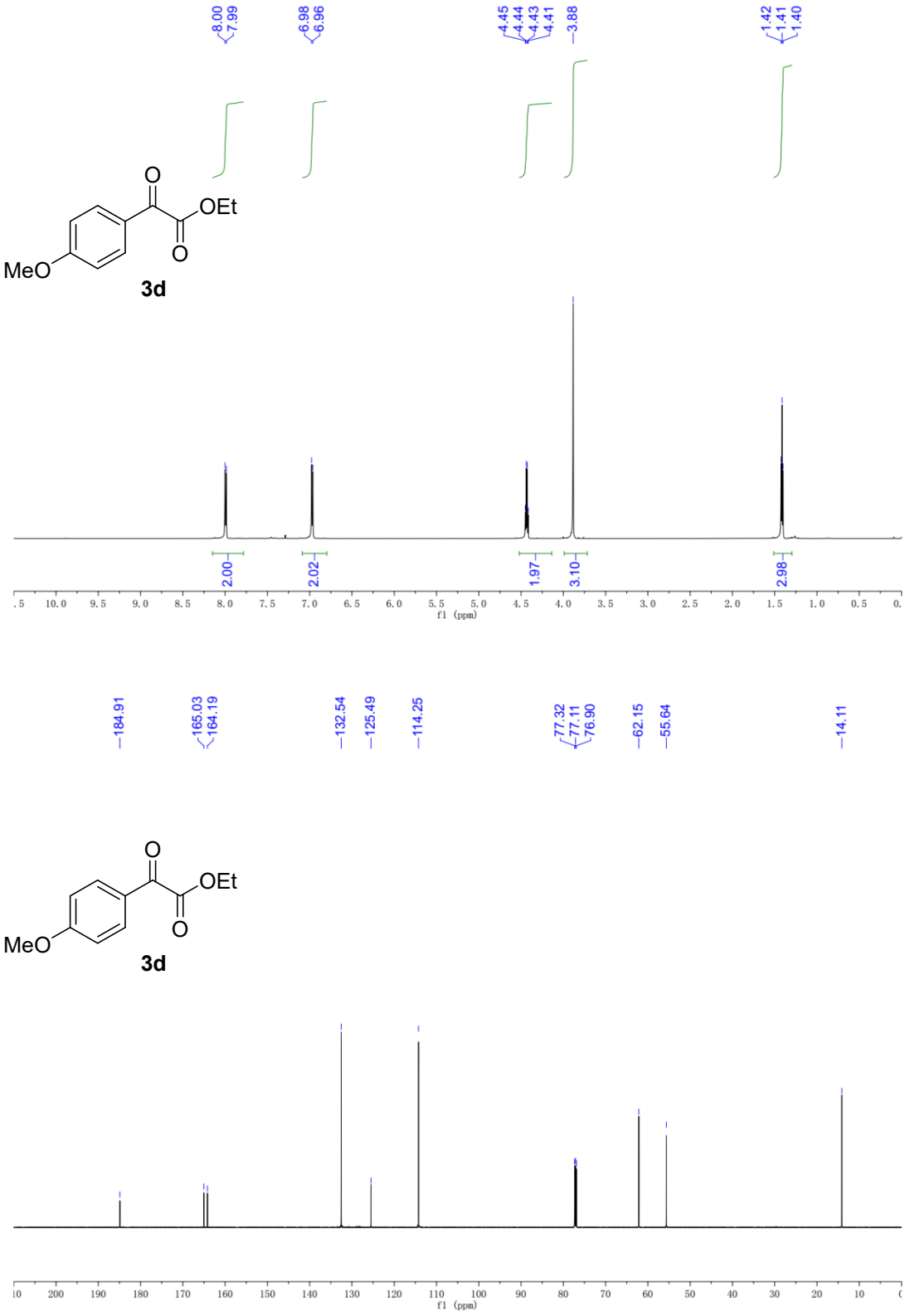


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3c**

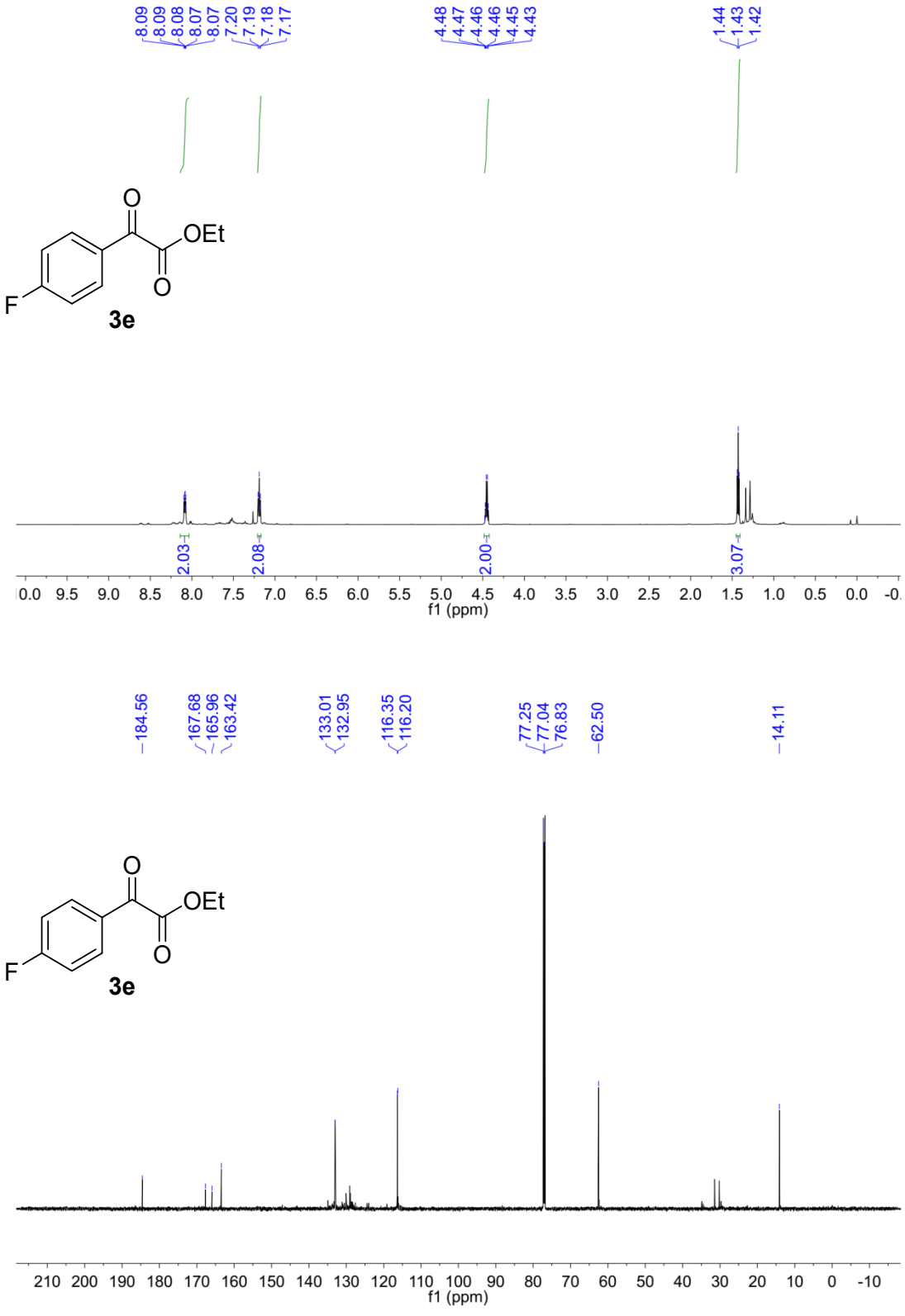




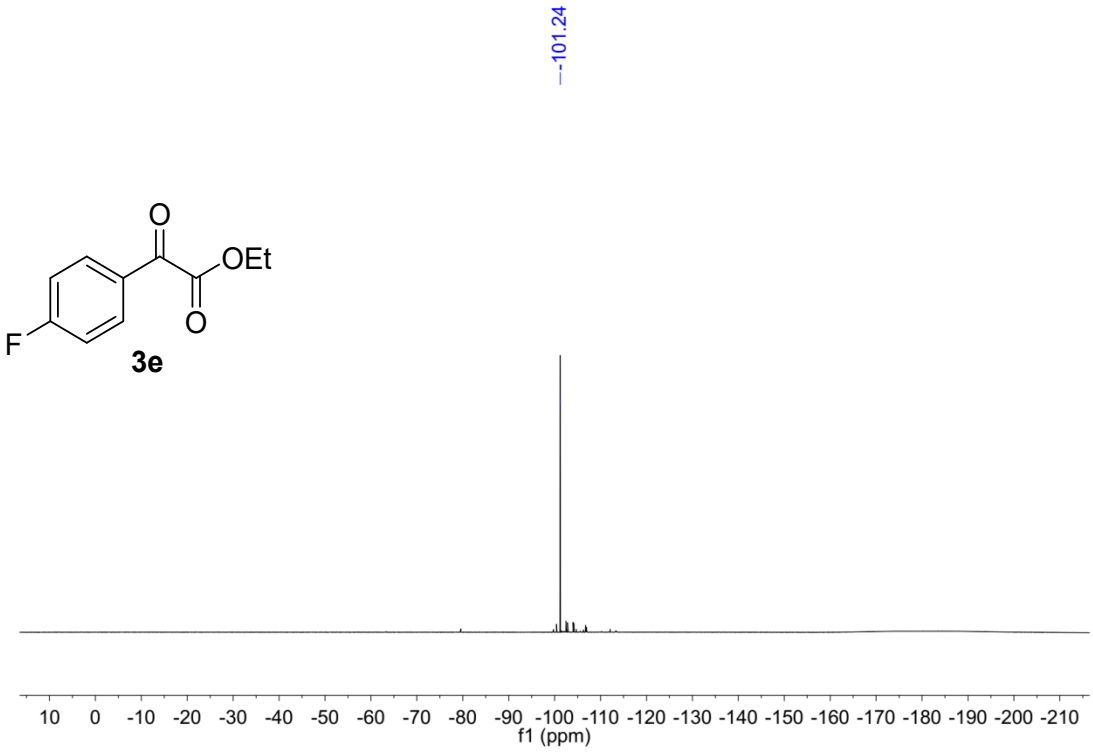
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3d**



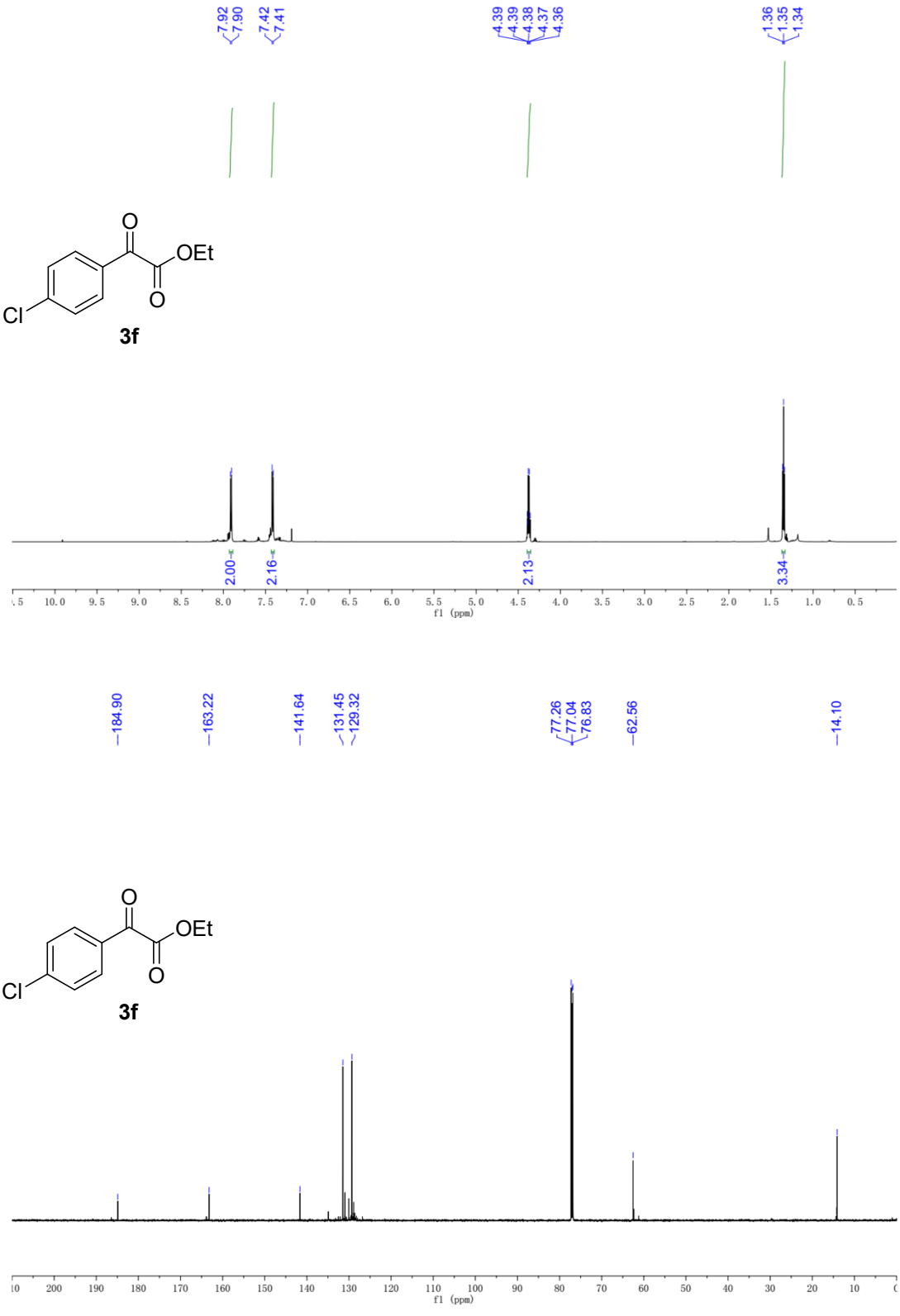
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3e**



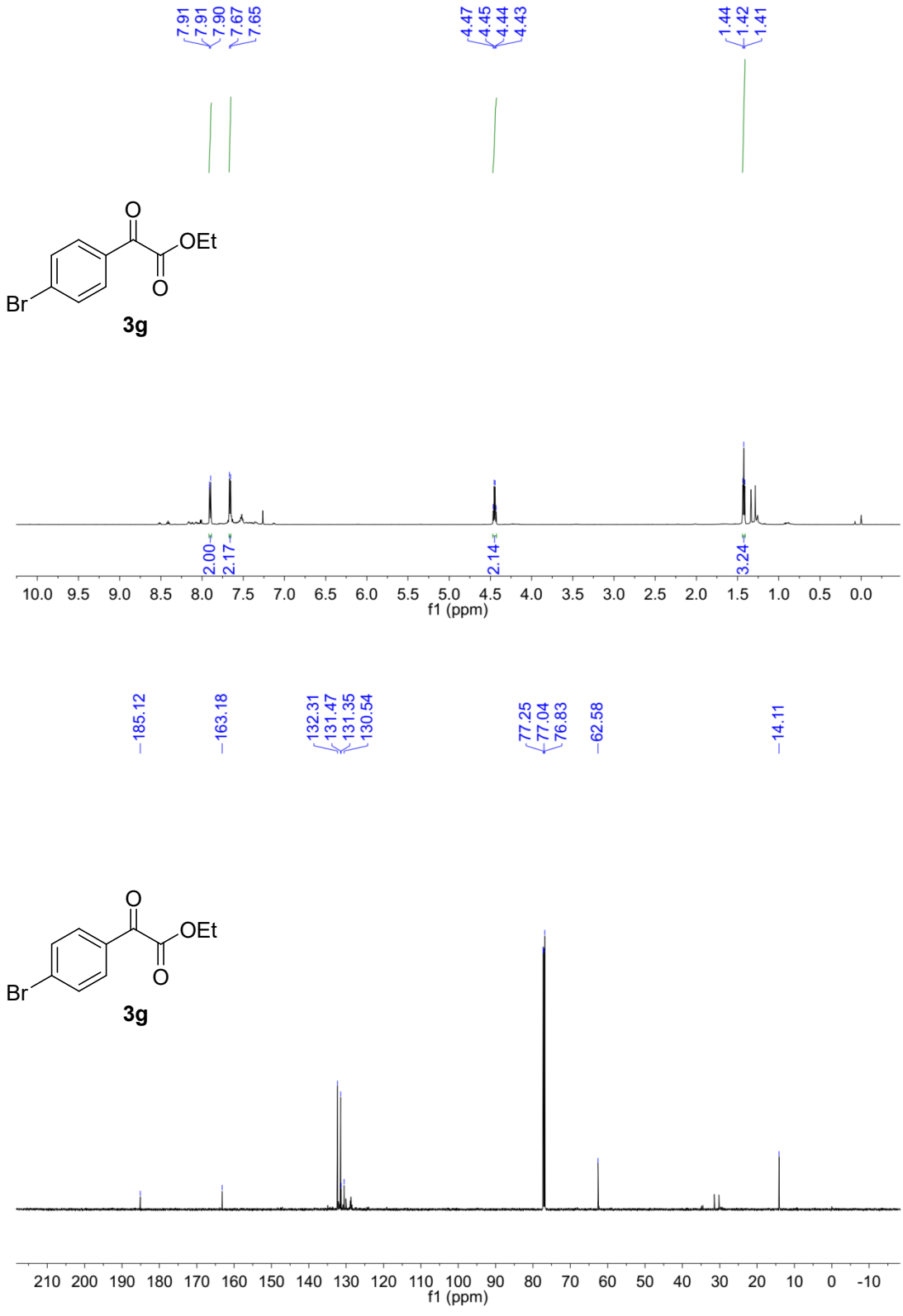
^{19}F NMR (600 MHz, $CDCl_3$) of **3e**



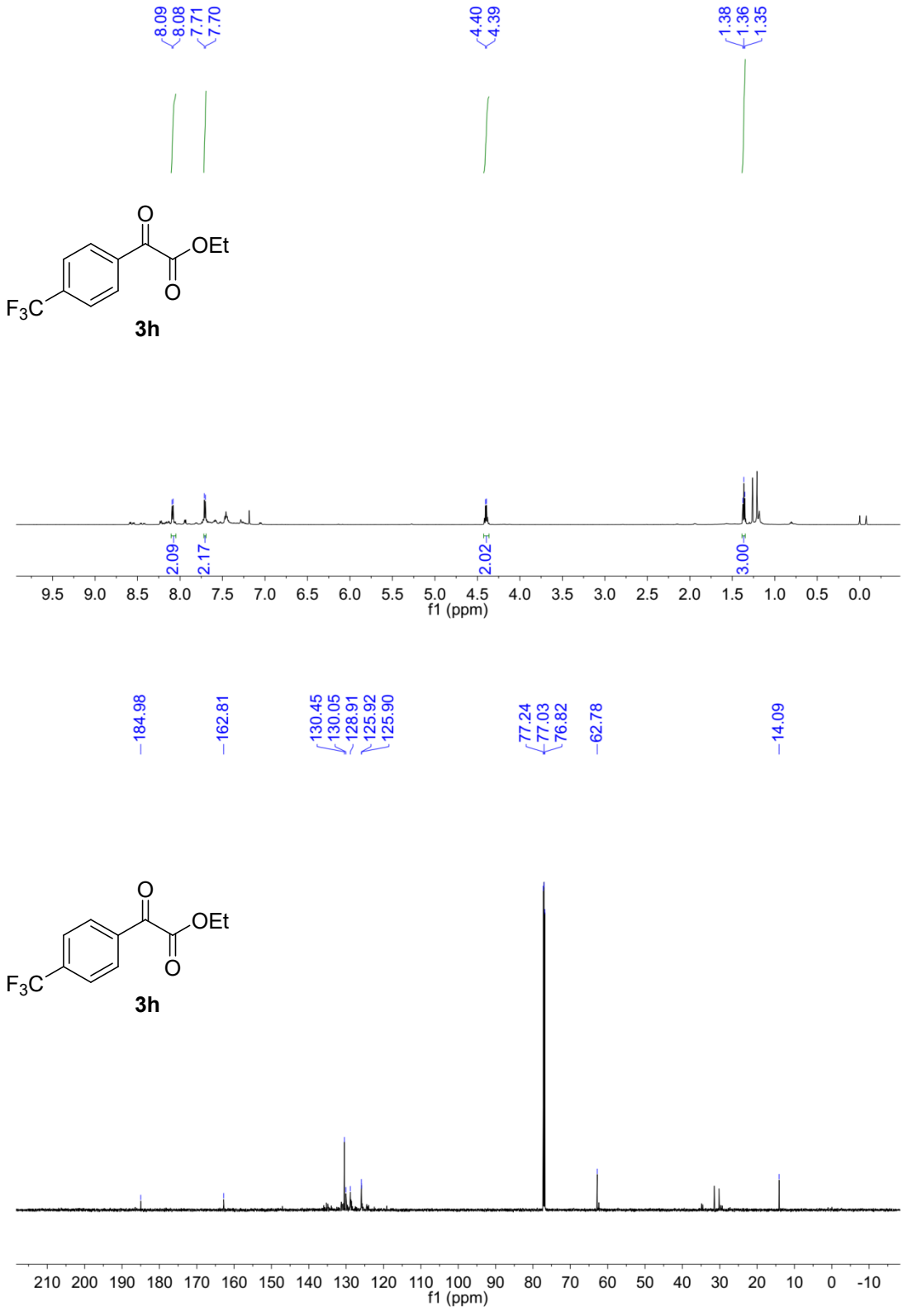
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3f**



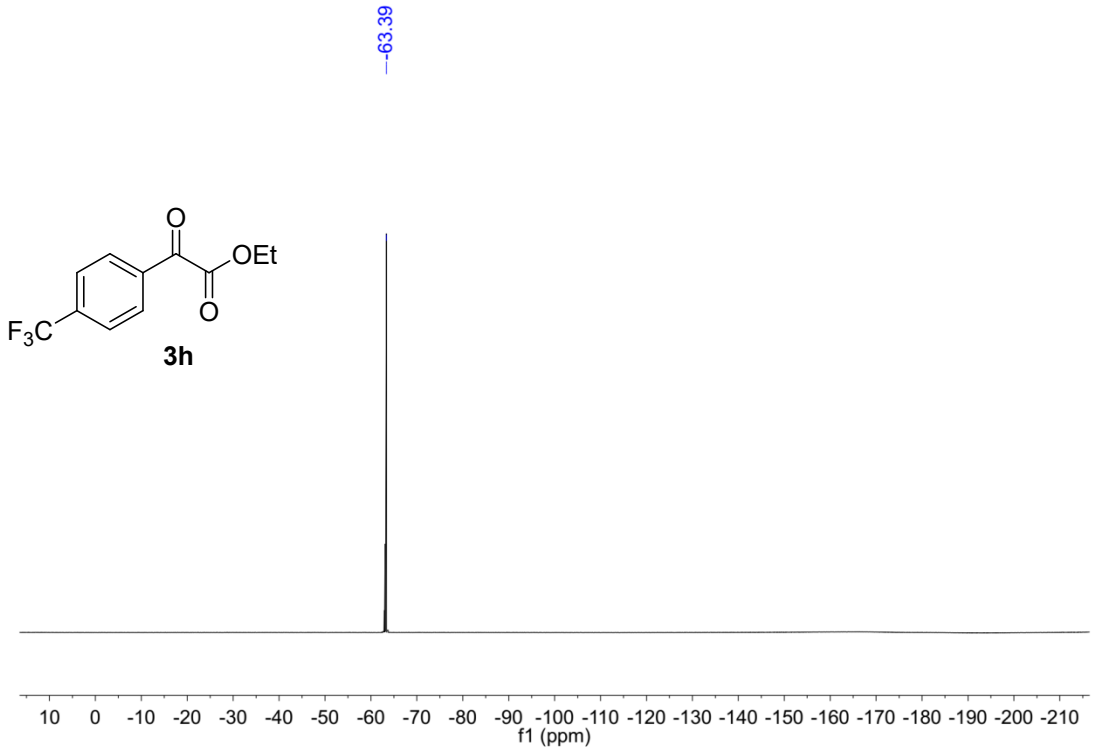
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3g**



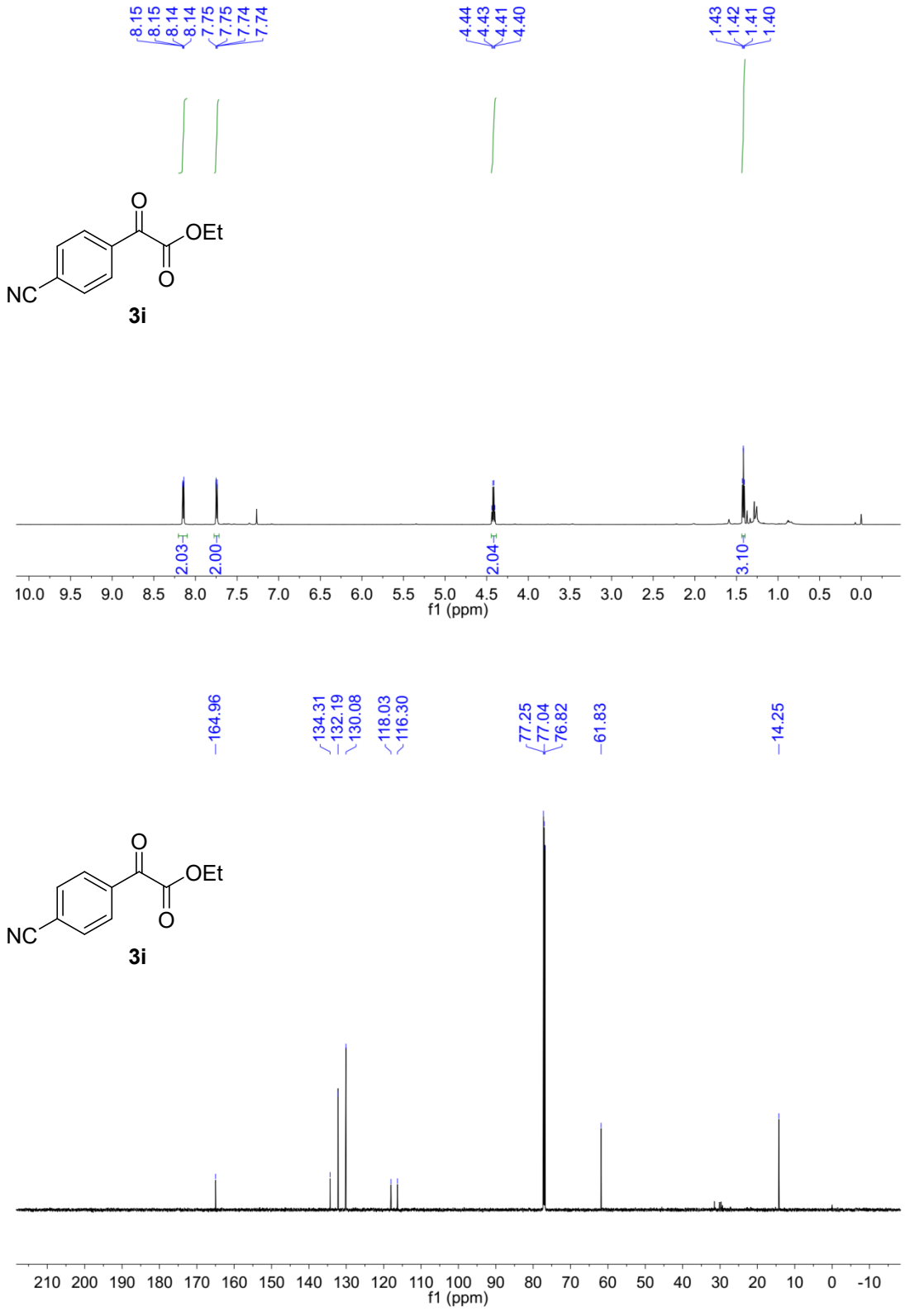
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3h**



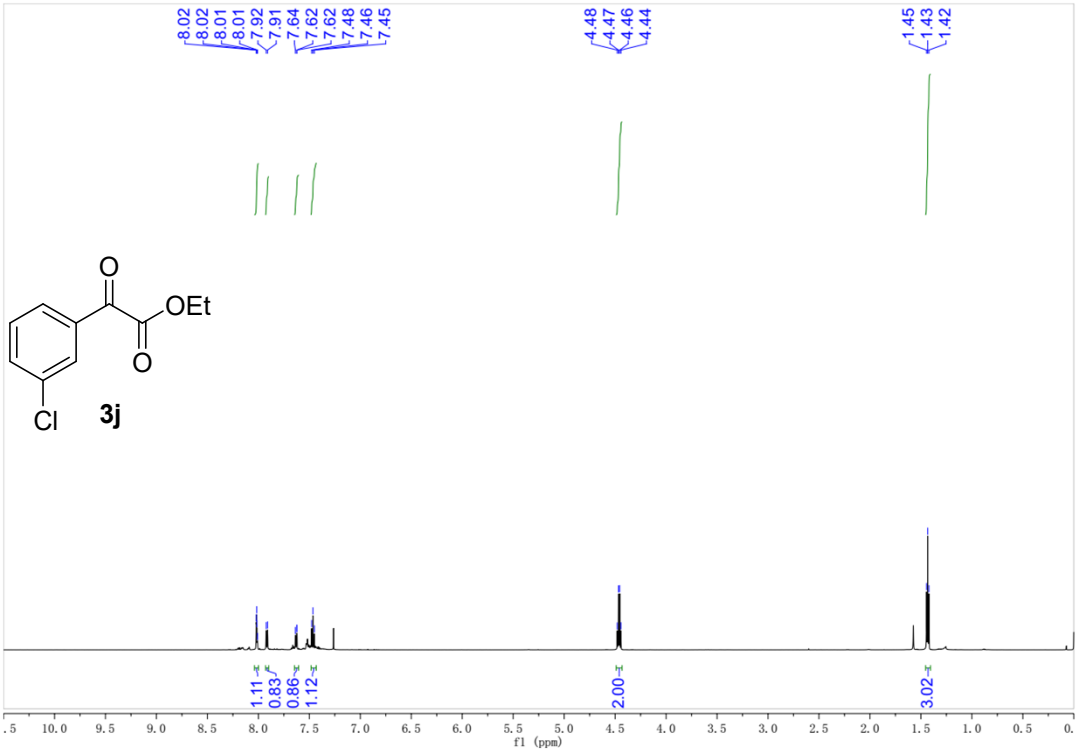
^{19}F NMR of **3h** in $CDCl_3$ (600 MHz, $CDCl_3$)

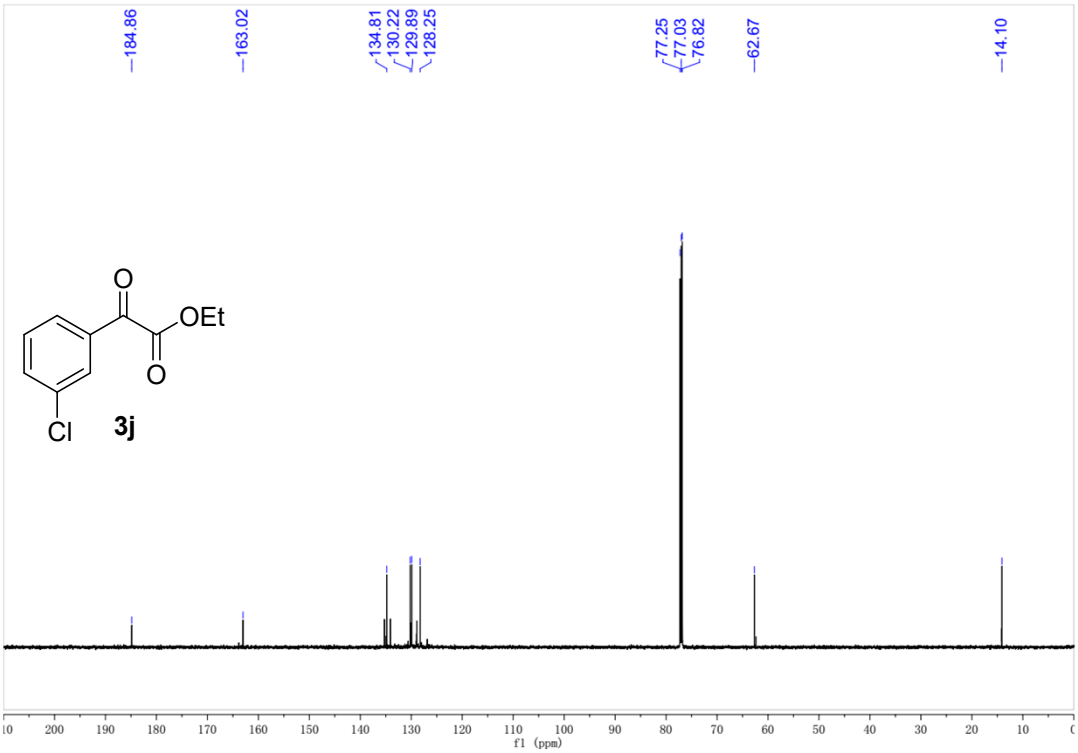


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3i**

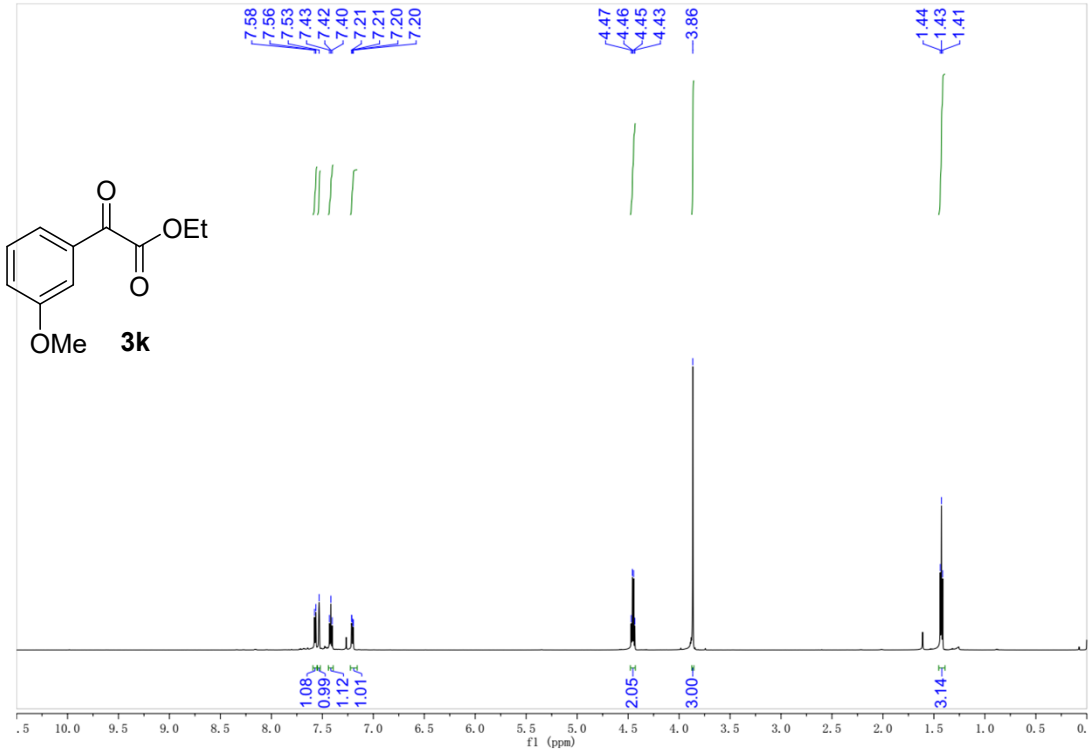


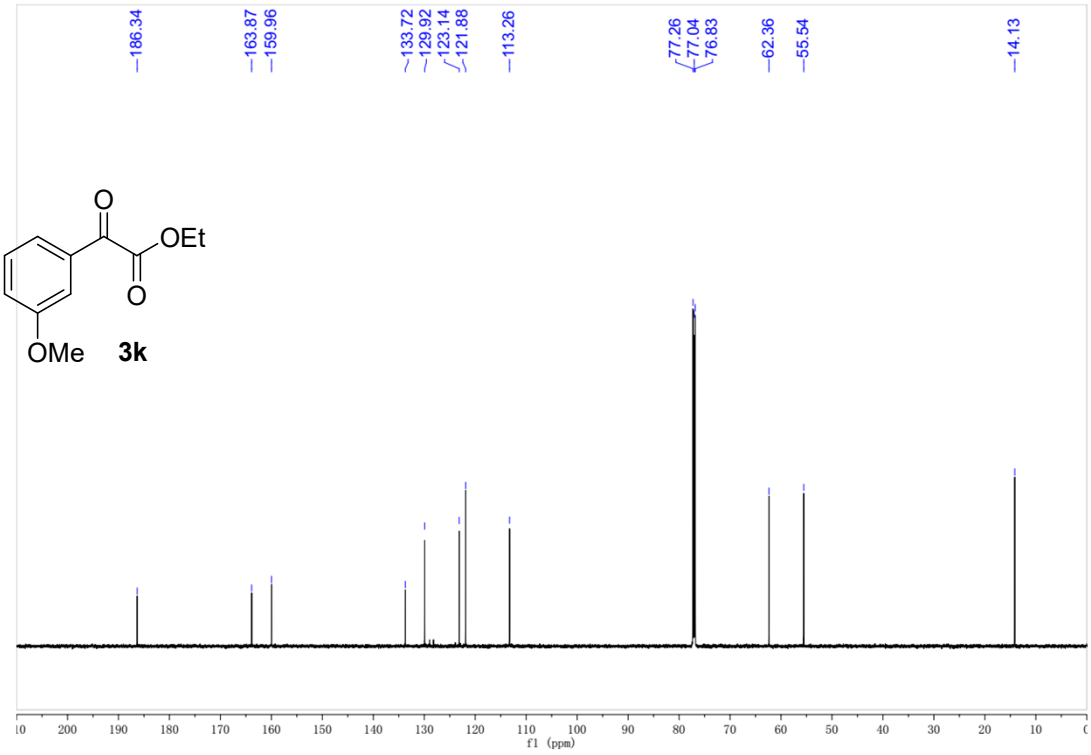
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3j**



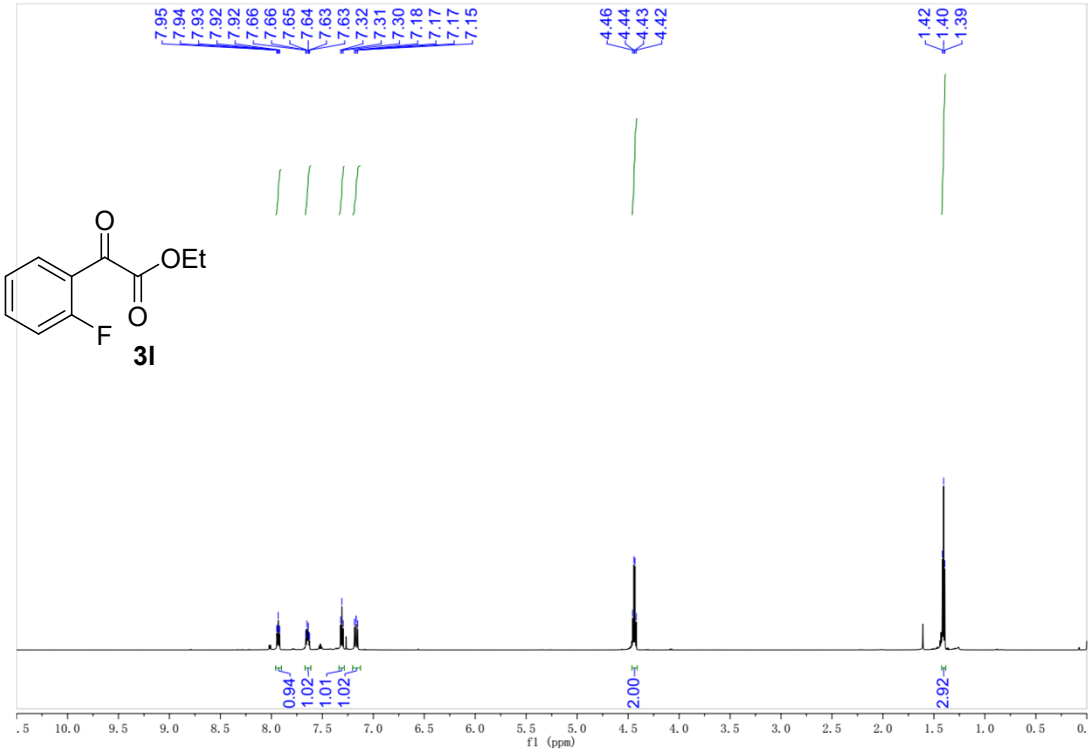


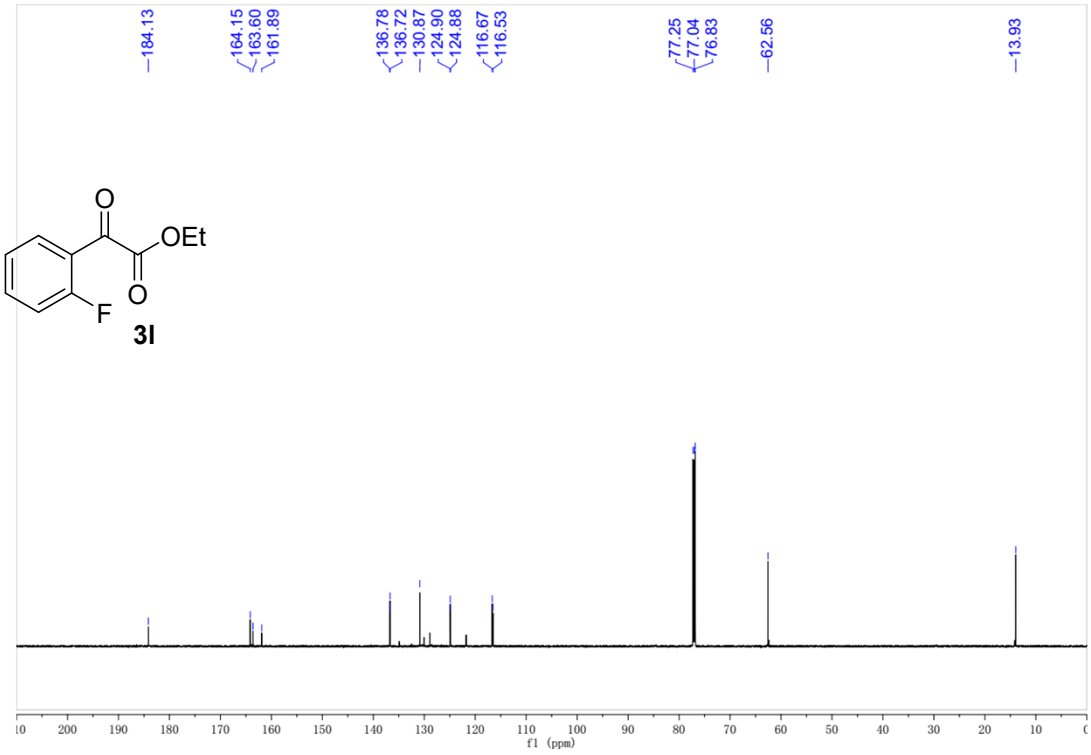
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3k**



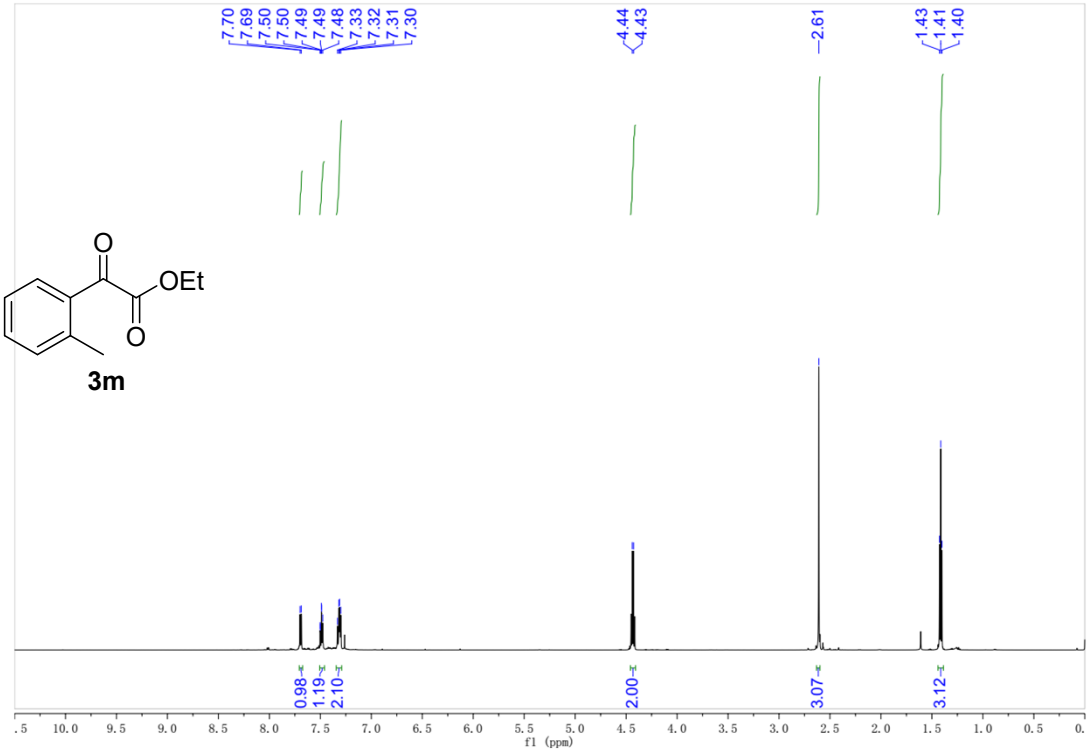


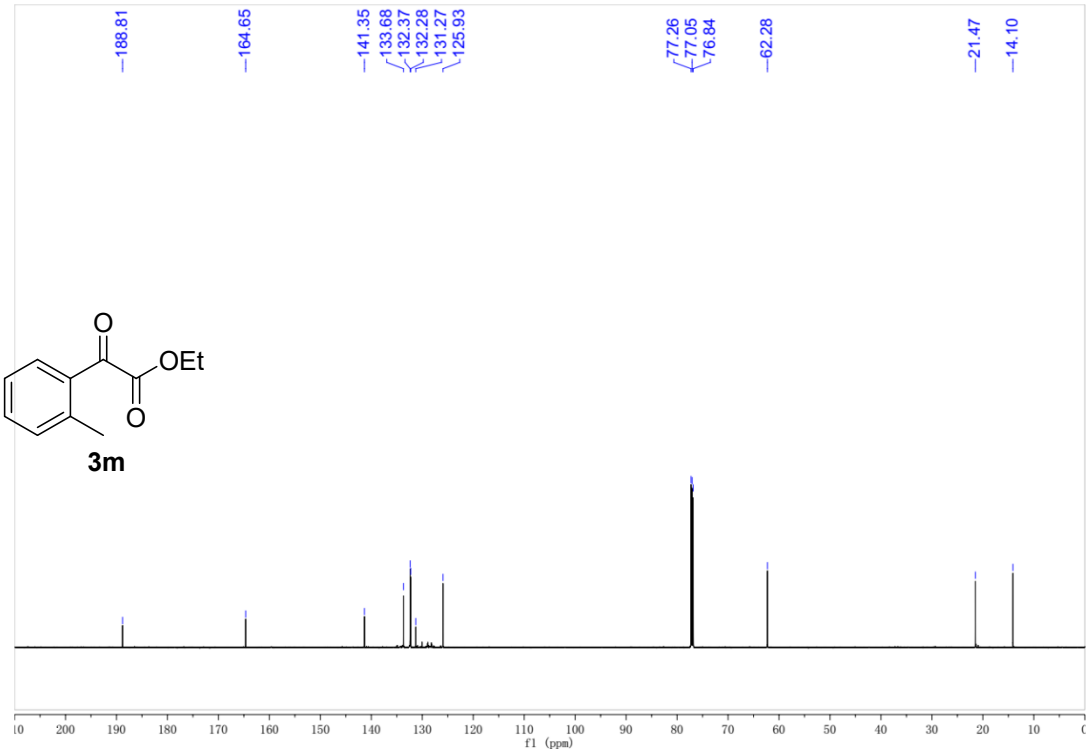
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3l**



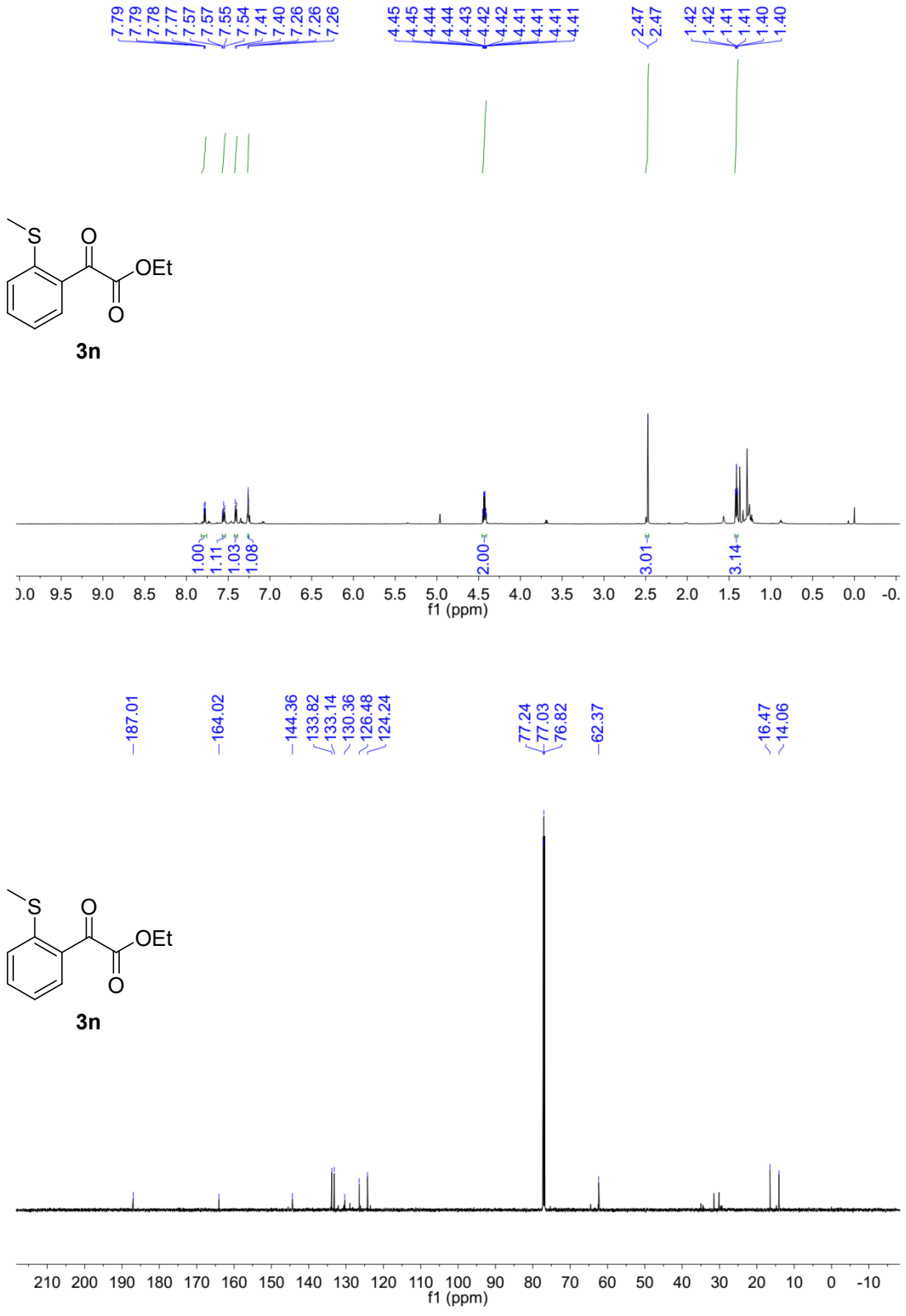


^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3m**

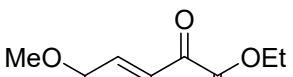


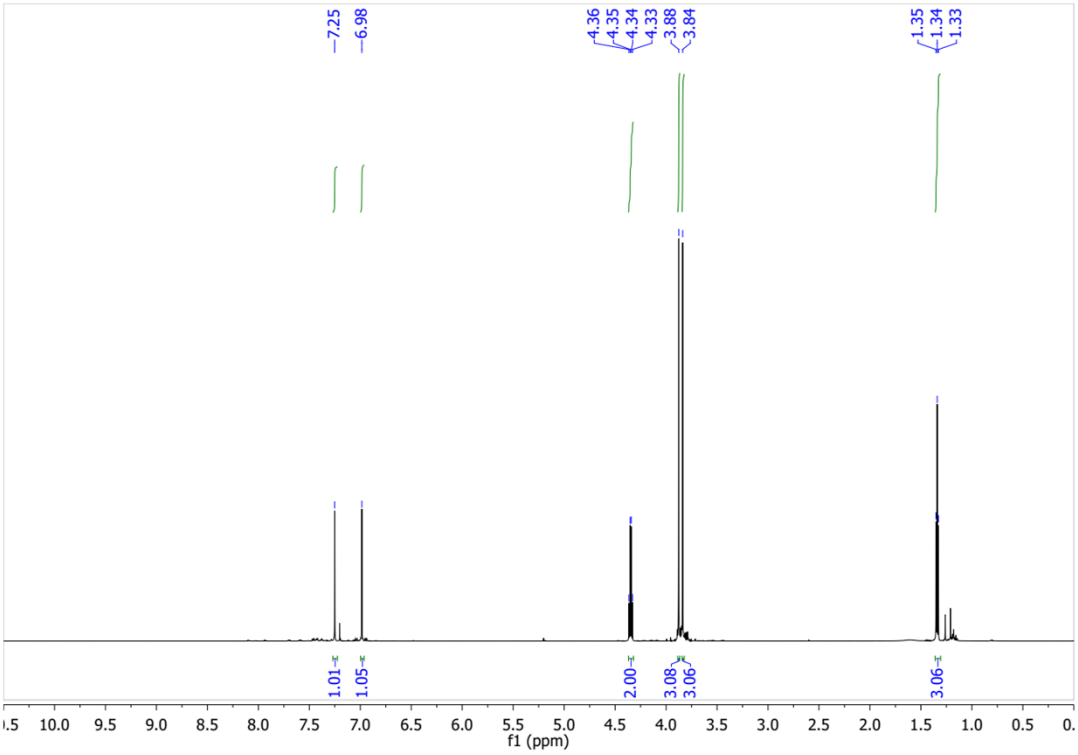


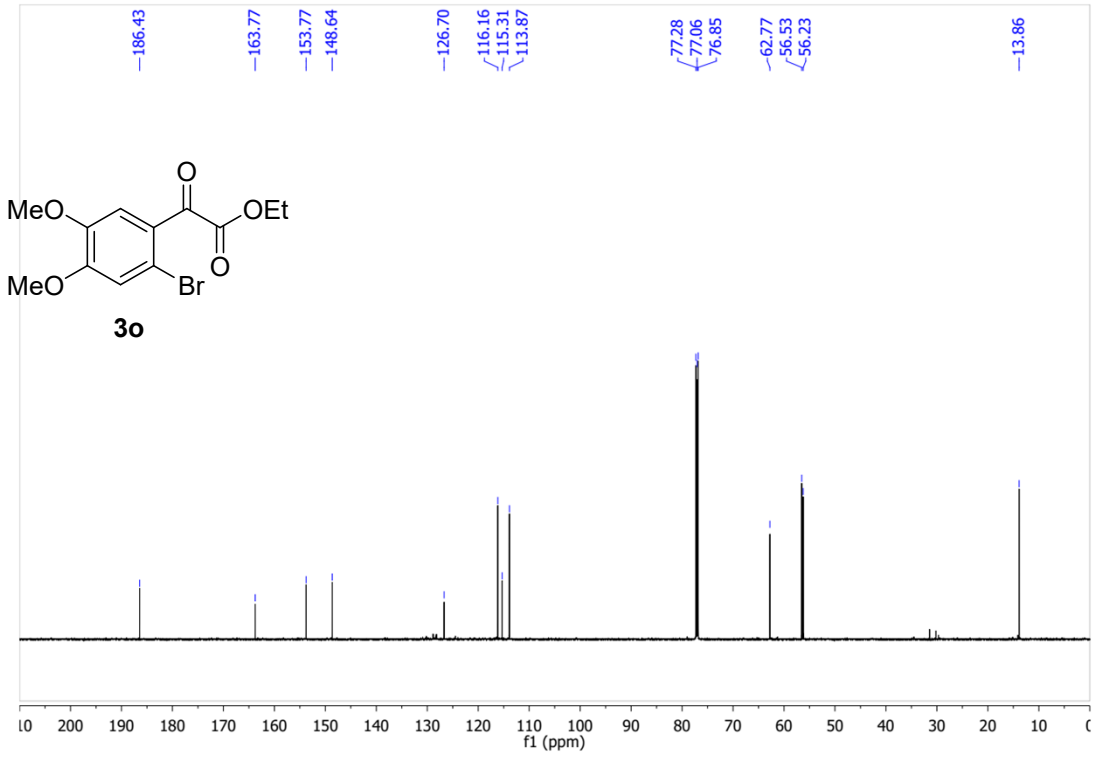
^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3n**



^{1}H NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3o**

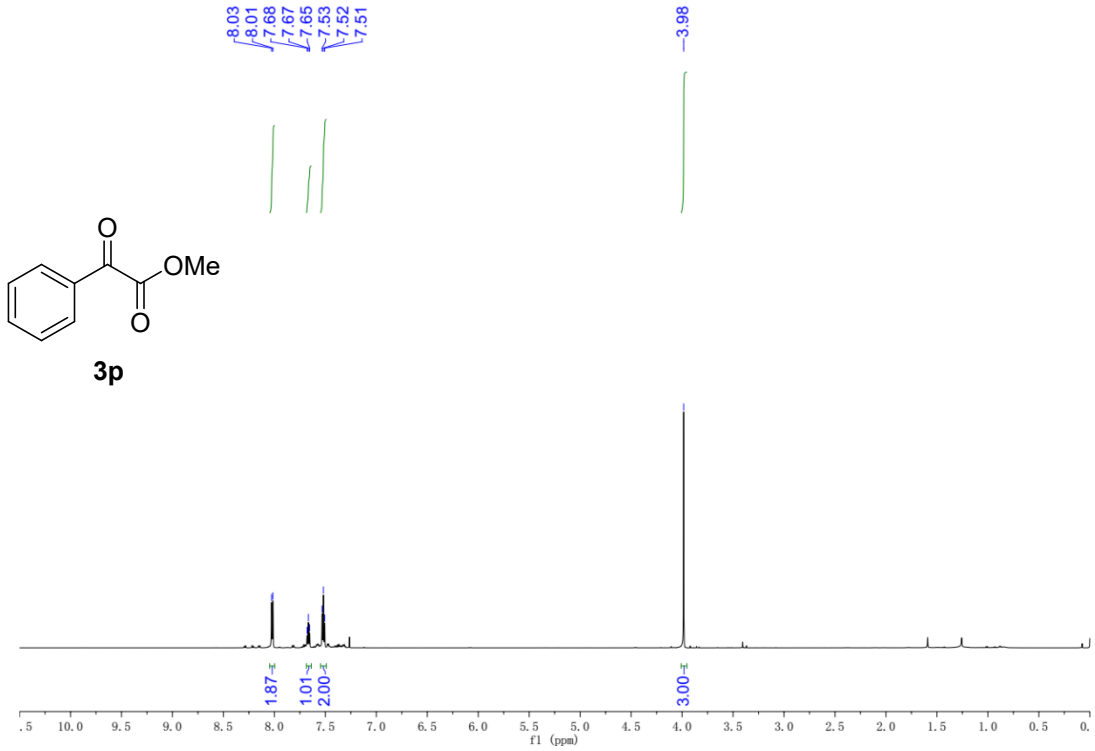




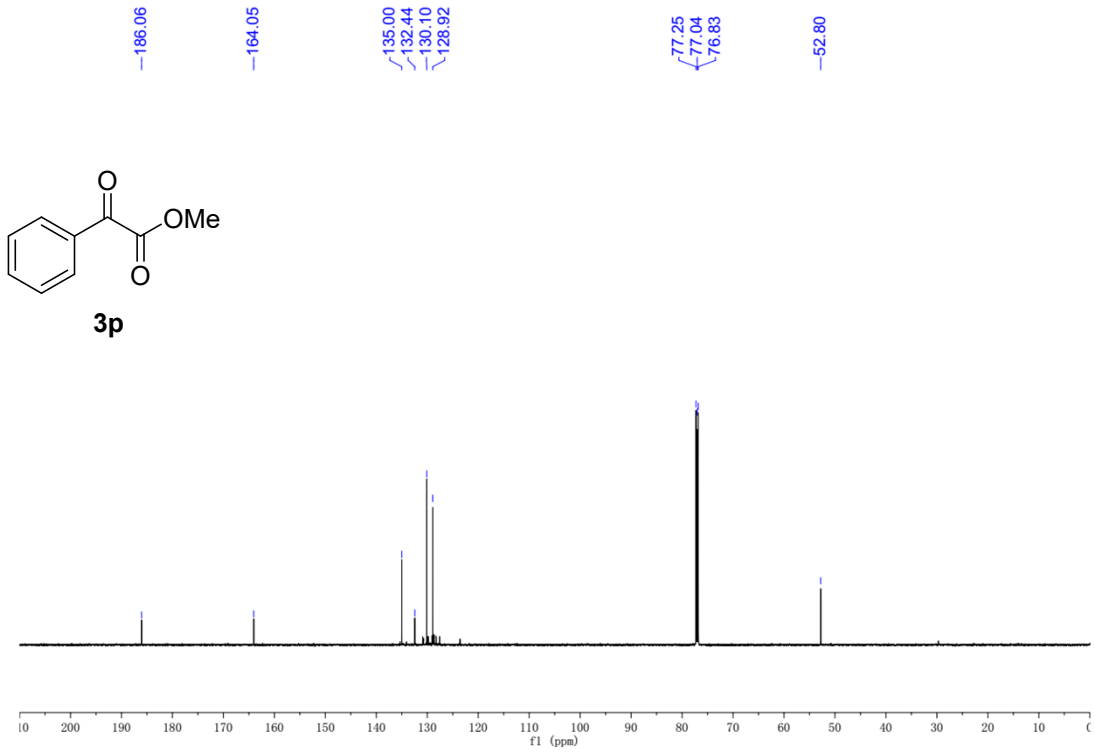


3o

NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3p**

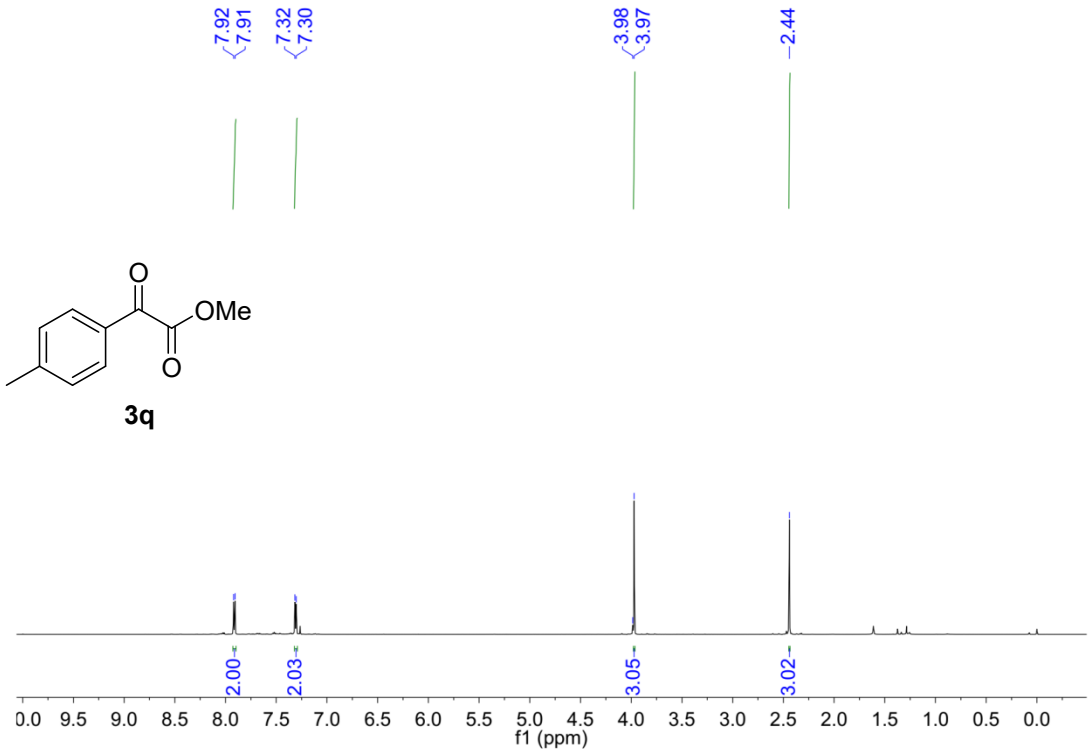


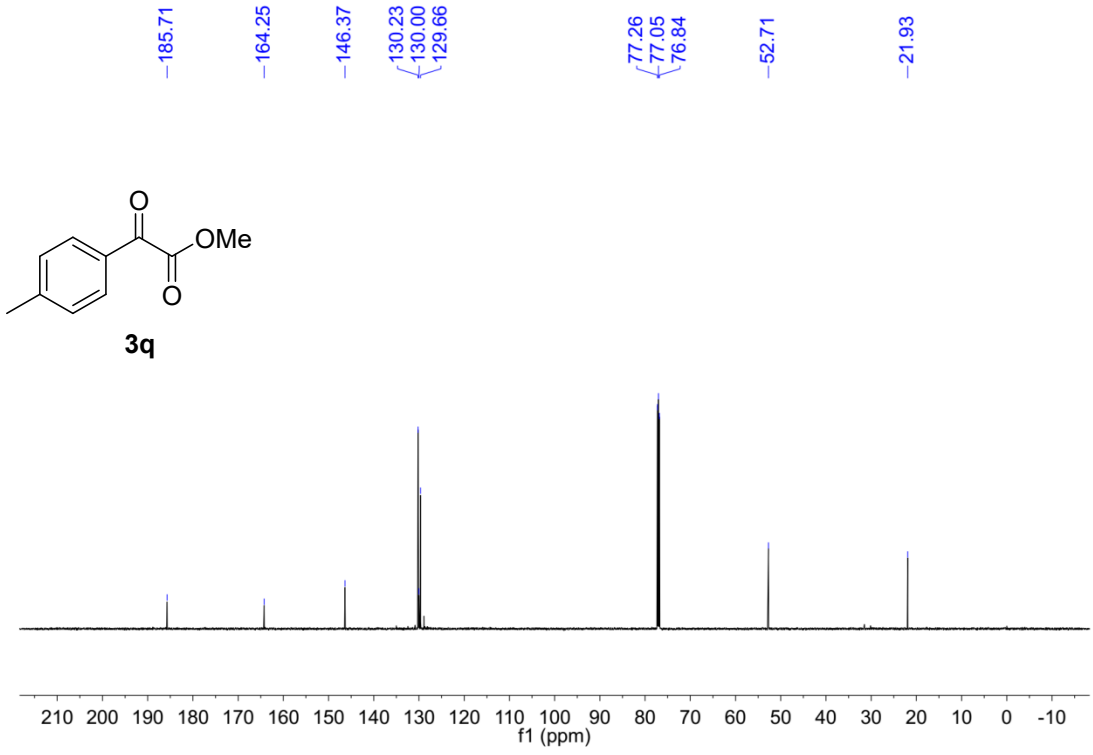
3p



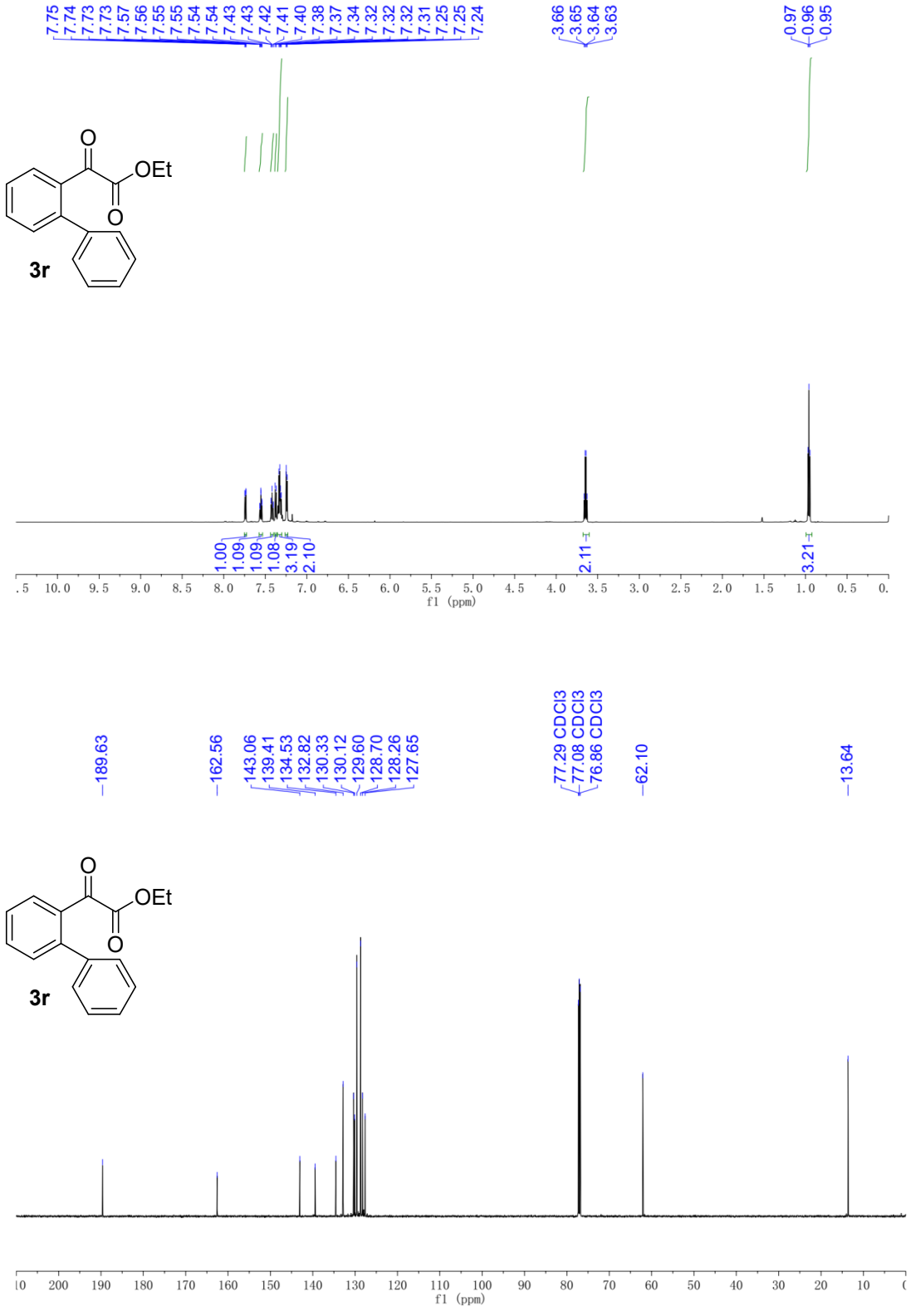
3p

NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3q**

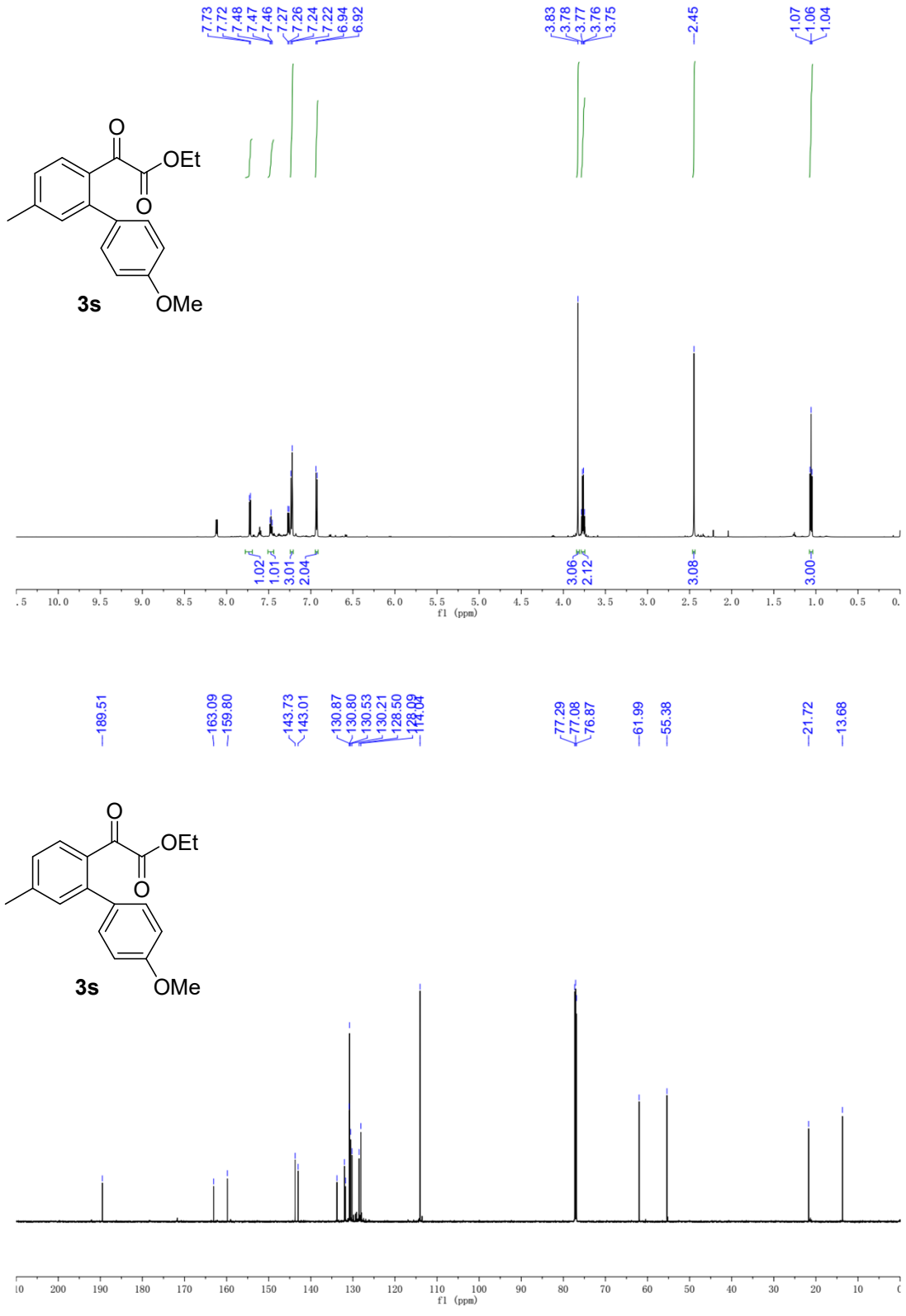




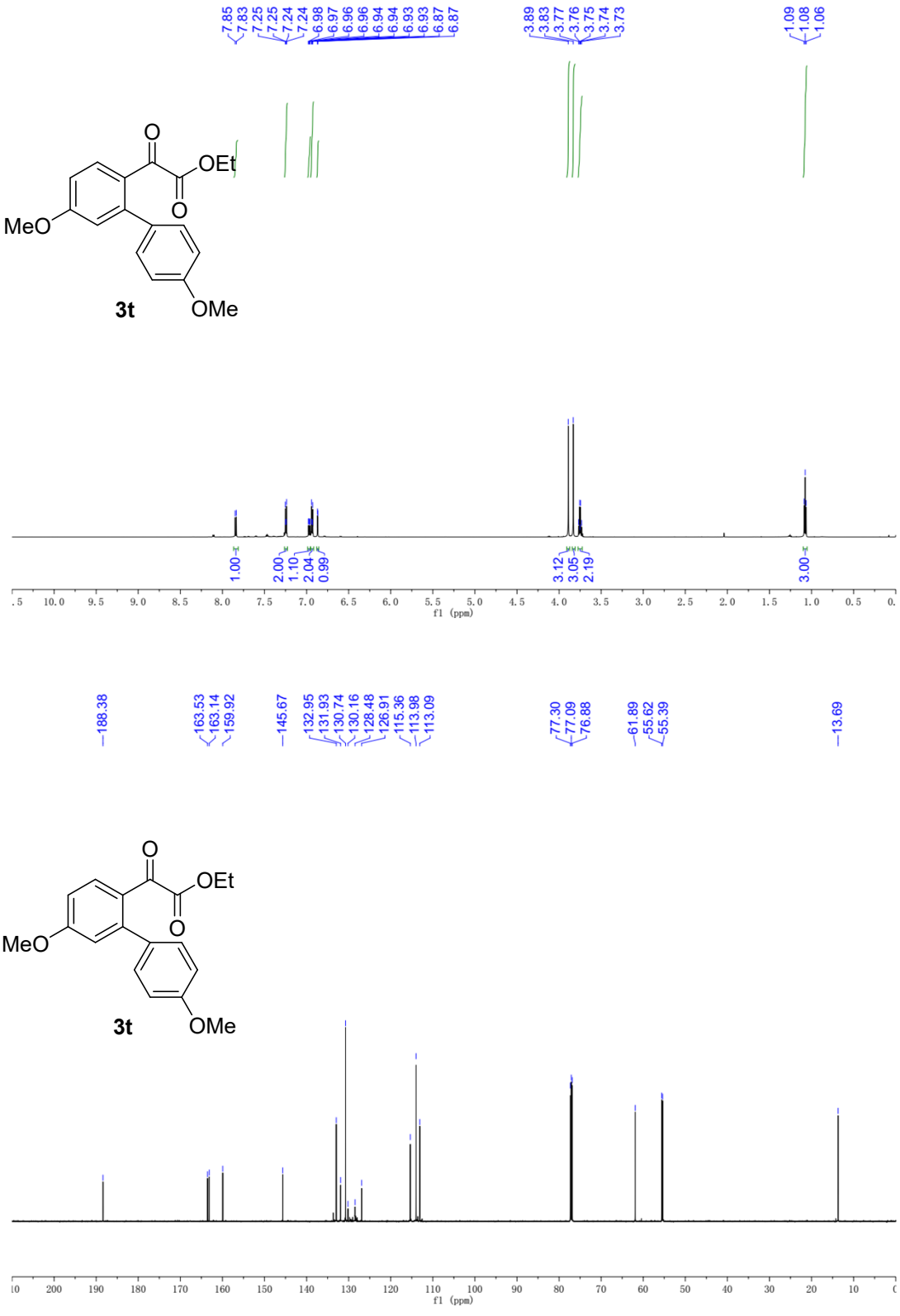
NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3r**



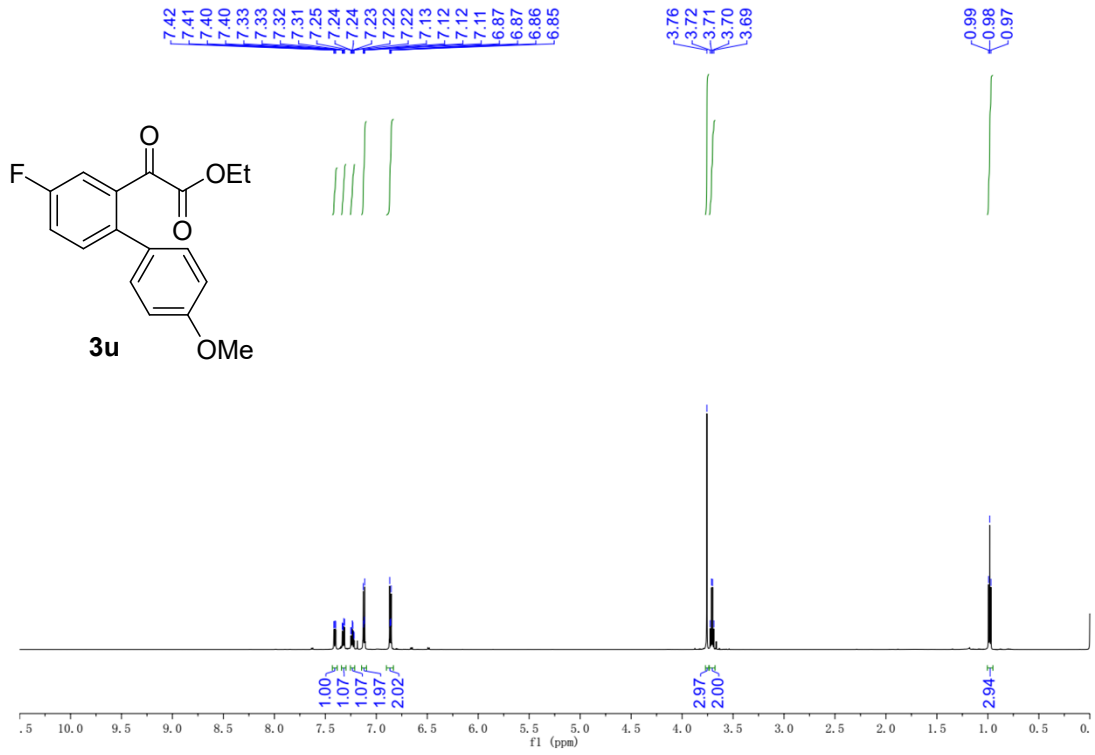
NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3s**

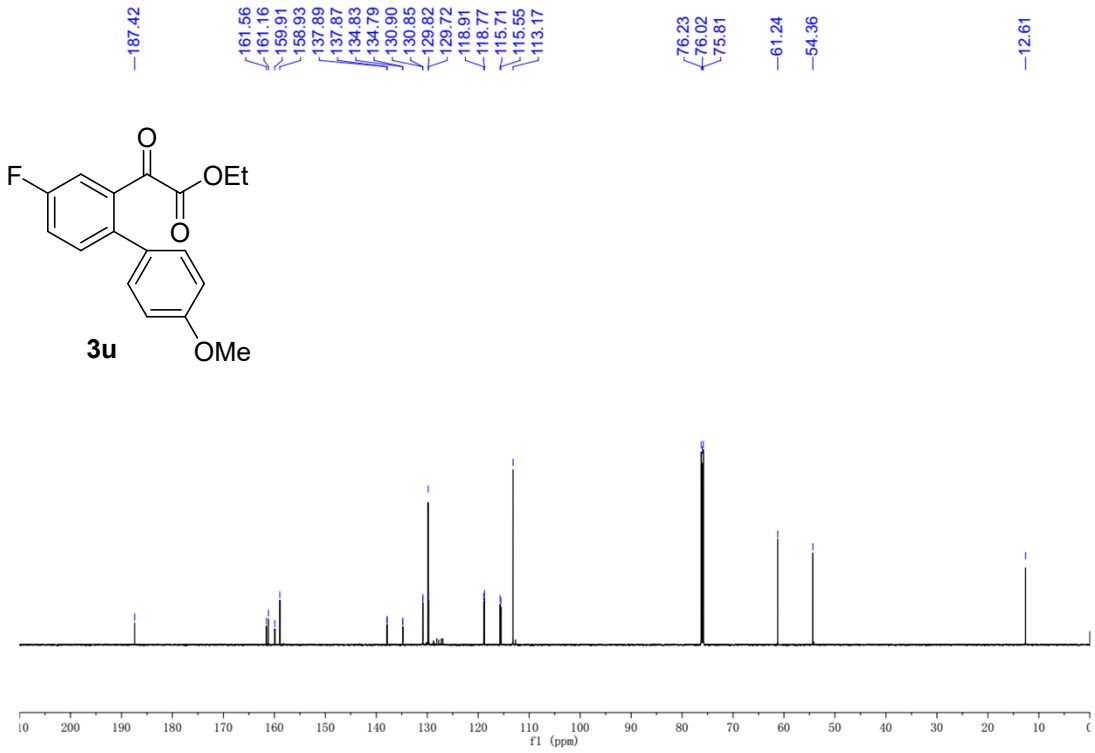


NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3t**

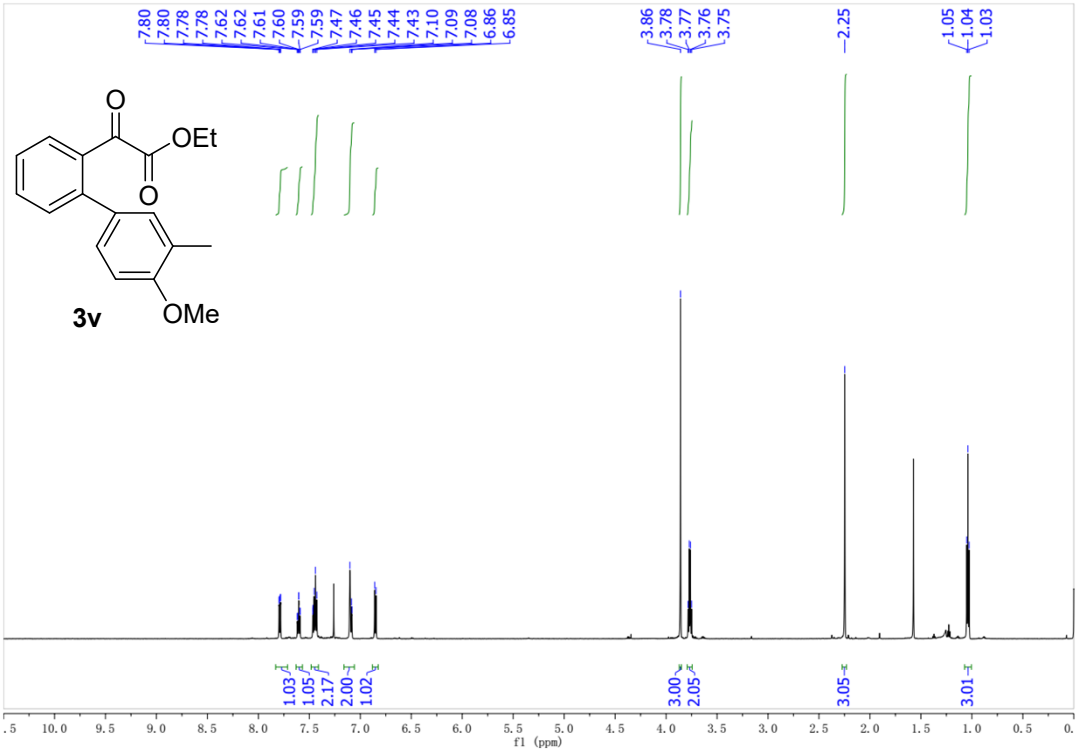


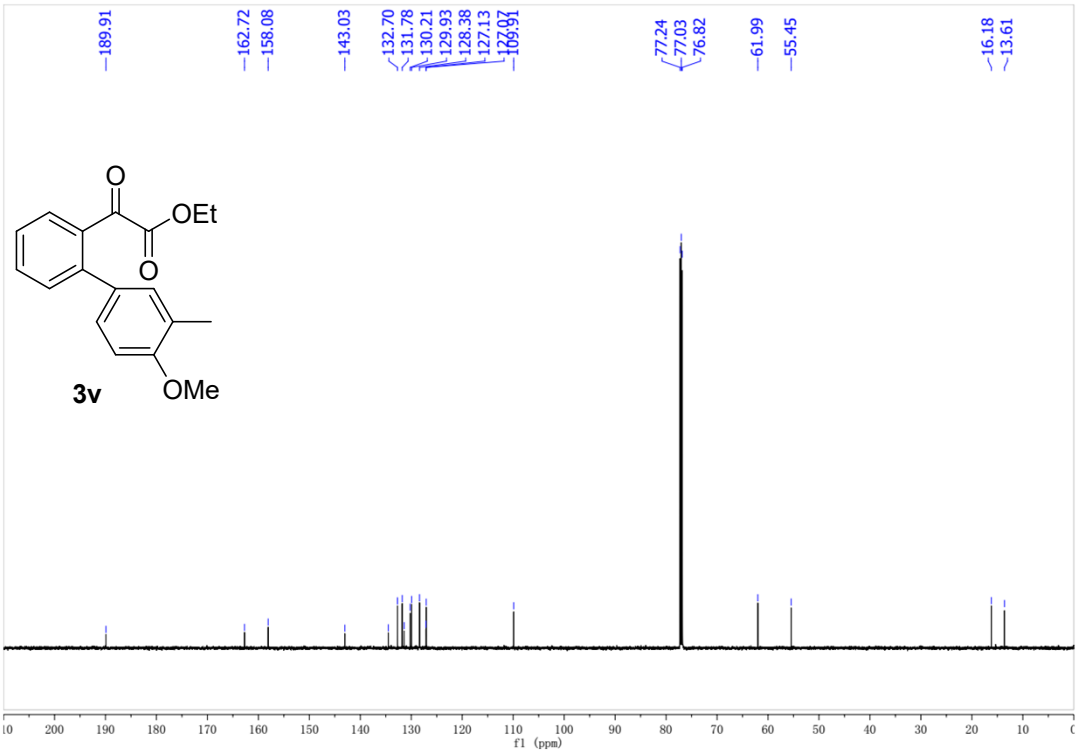
NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3u**



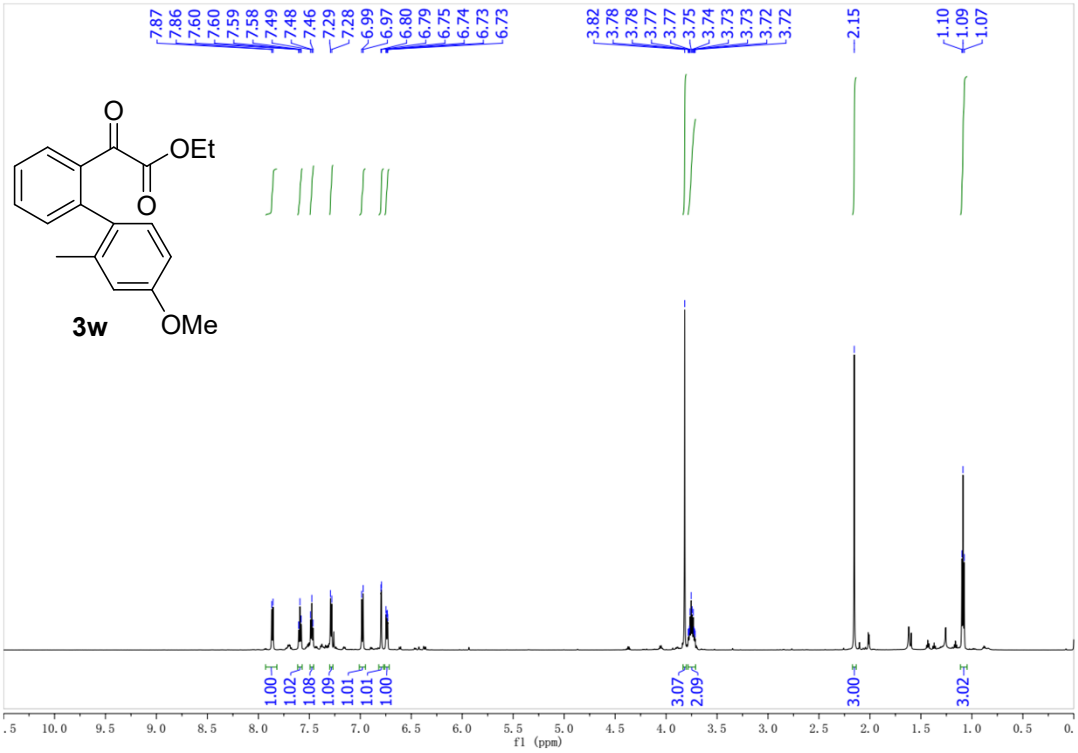


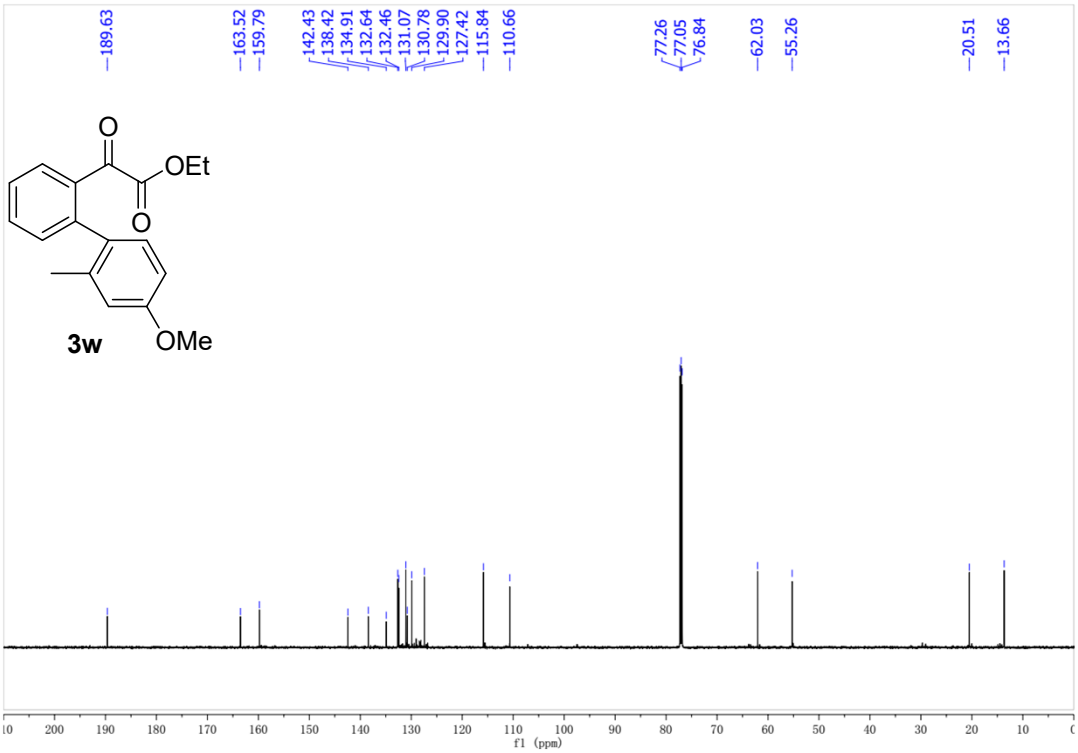
NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3v**



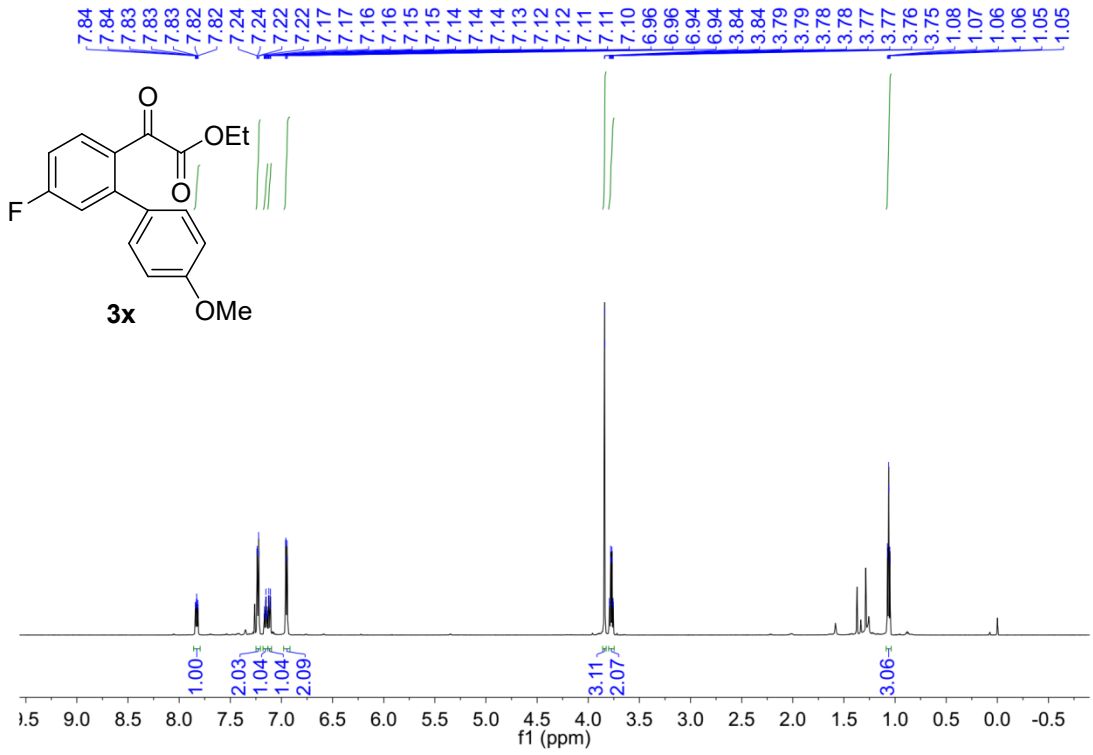


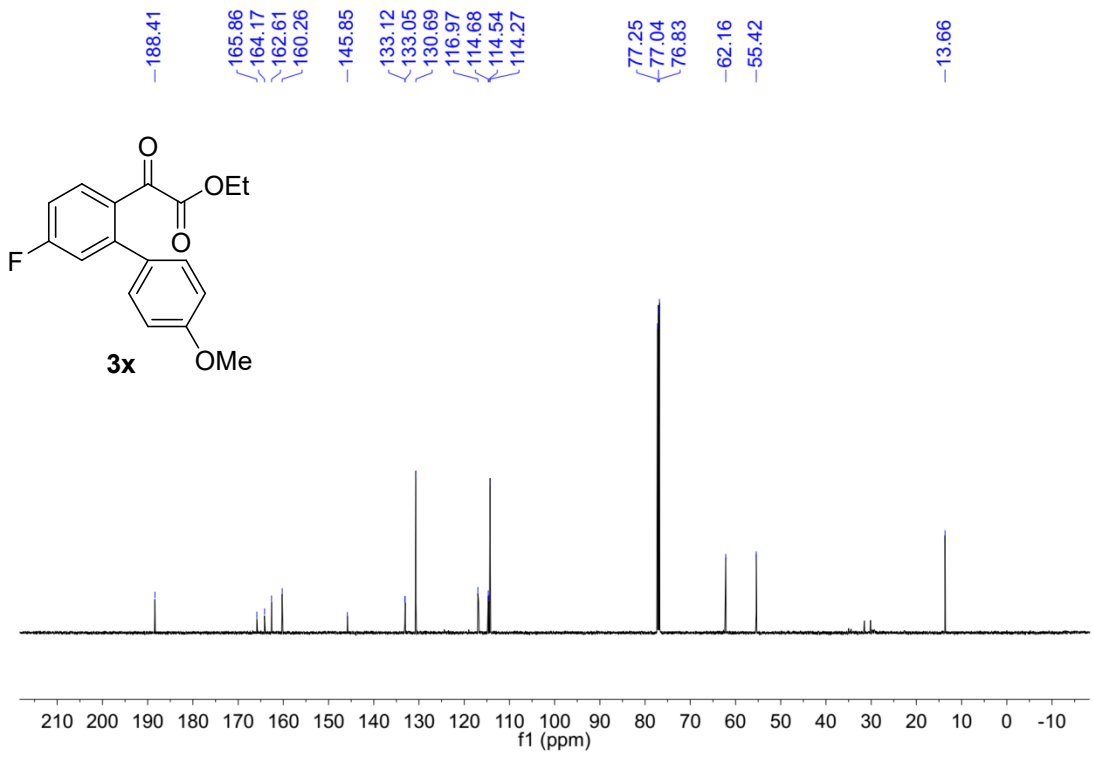
NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3w**



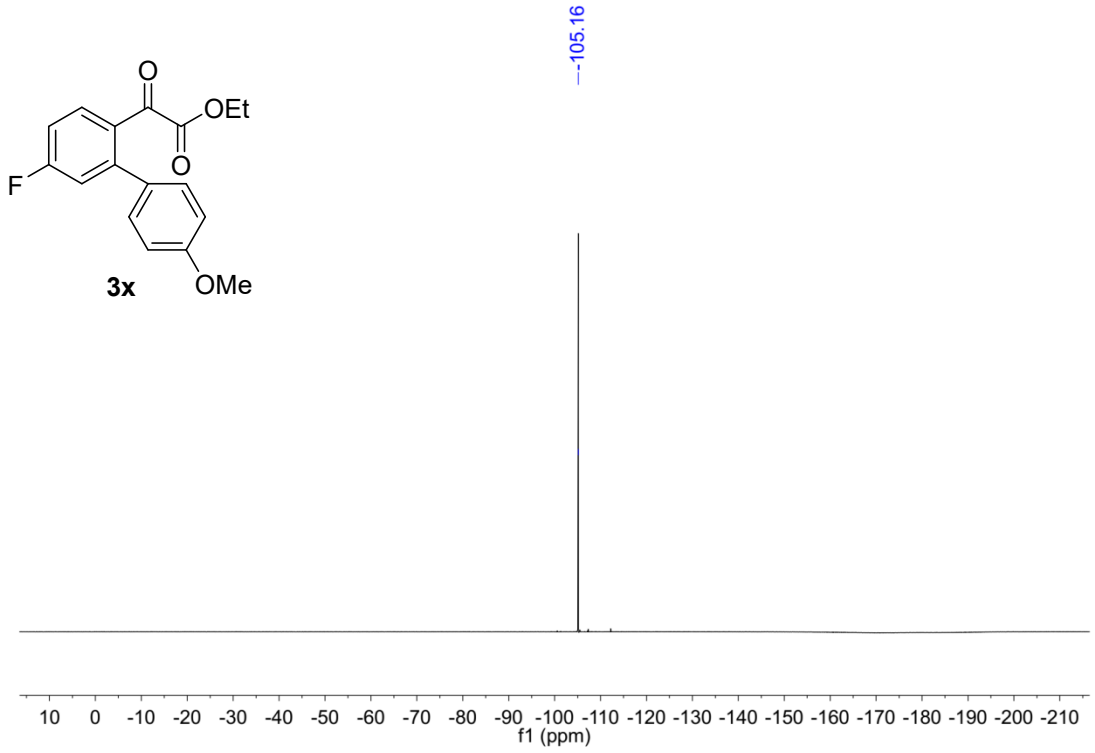


NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3x**

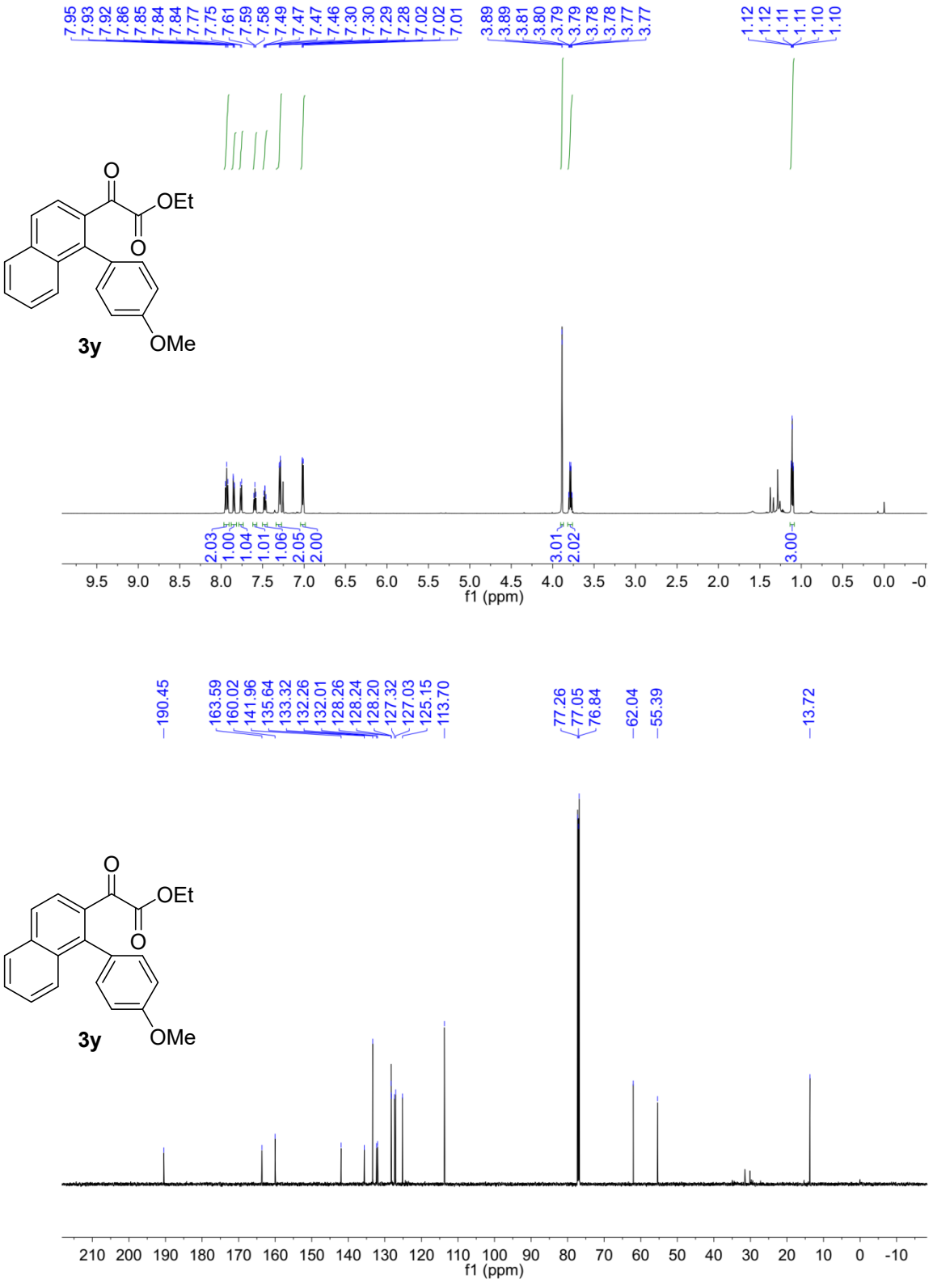




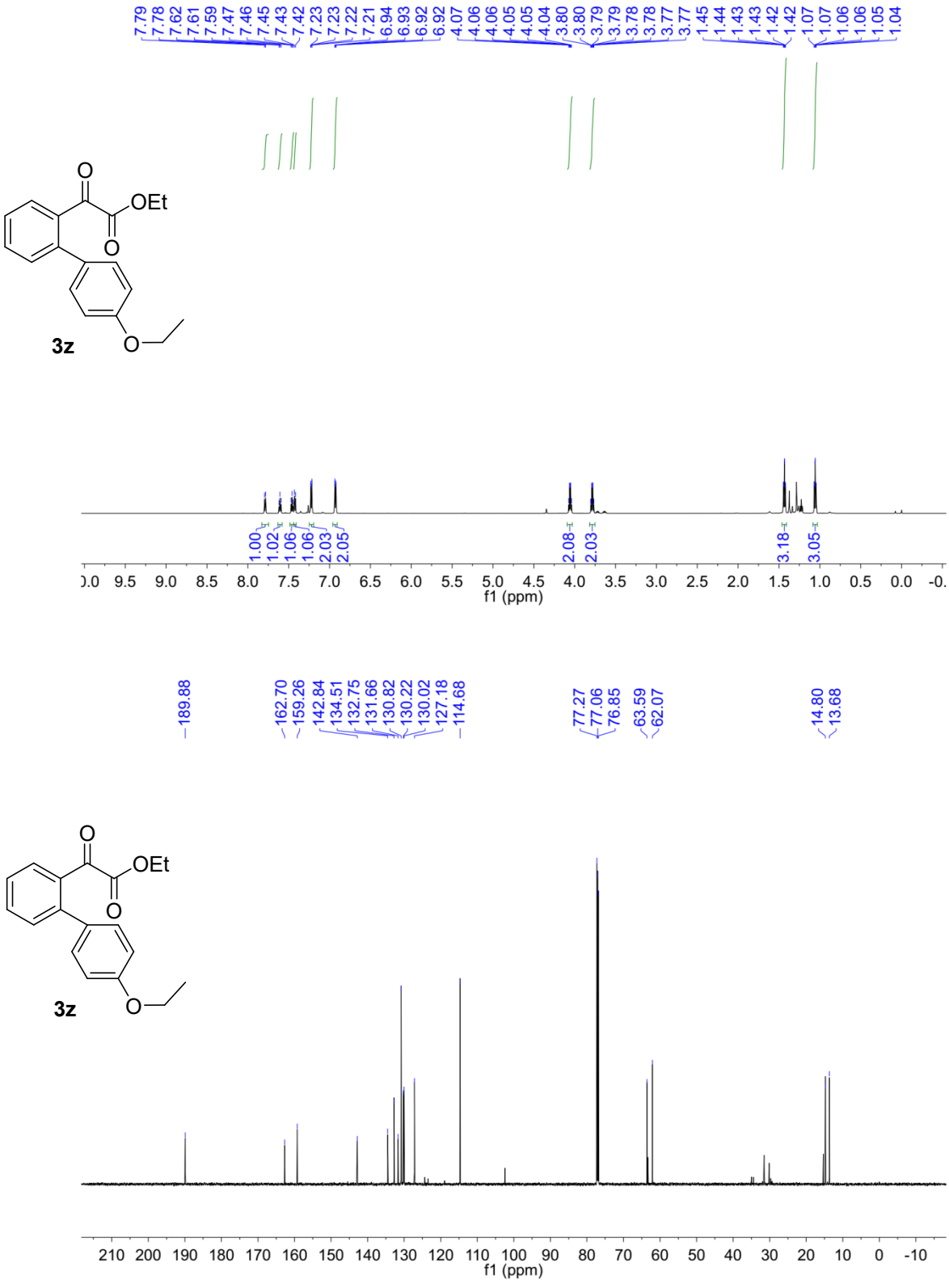
^{19}F NMR of **3x** in $CDCl_3$ (600 MHz, $CDCl_3$)



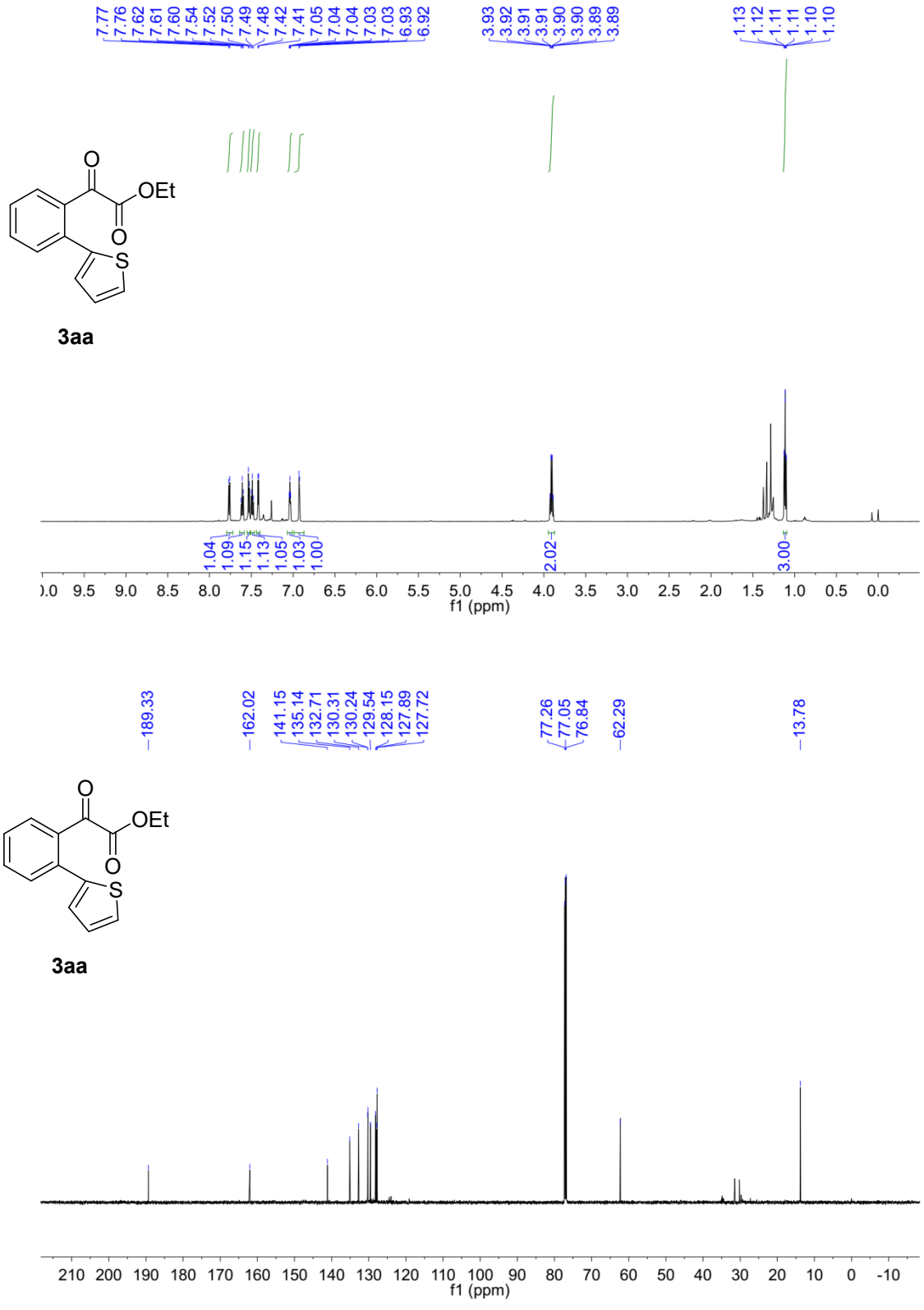
NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3y**



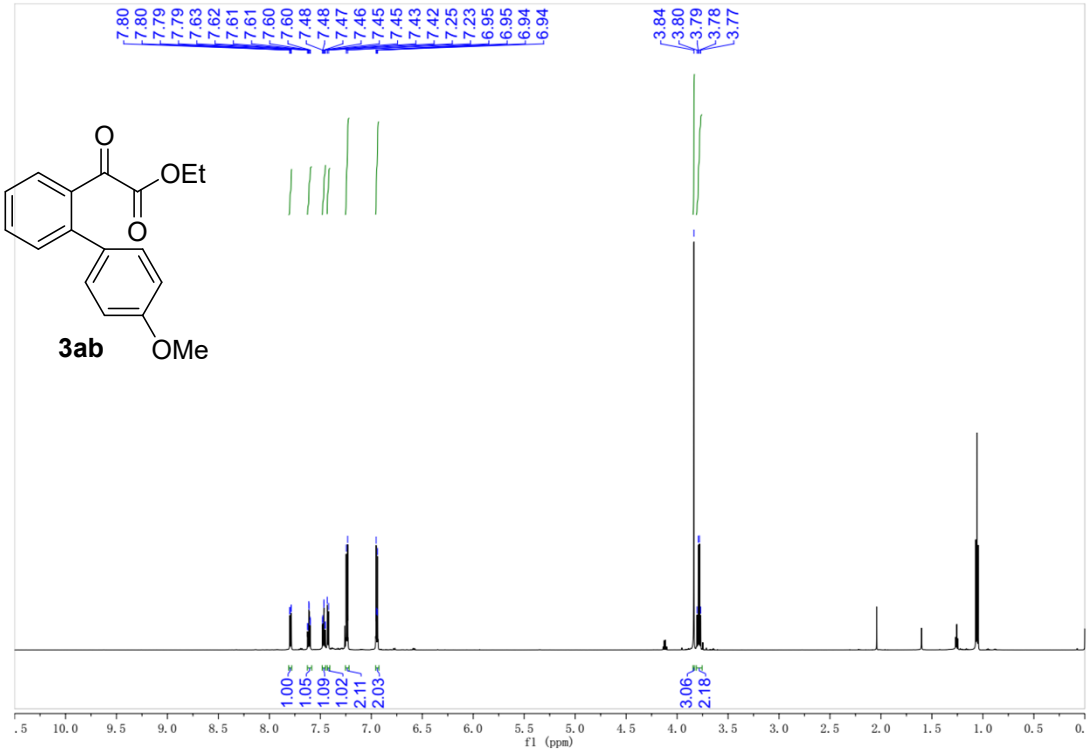
NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3z**

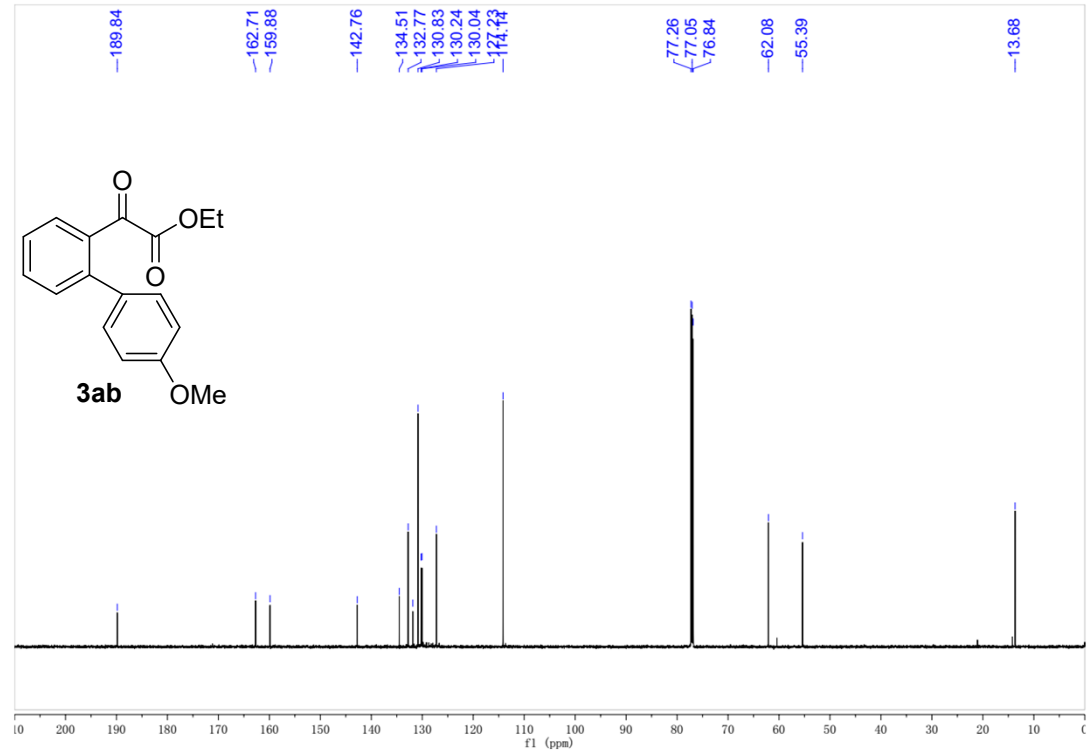


NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3aa**



NMR (600 MHz, $CDCl_3$) and ^{13}C NMR (151 MHz, $CDCl_3$) of **3ab**


7.80
7.80
7.79
7.79
7.63
7.62
7.61
7.61
7.60
7.60
7.48
7.47
7.46
7.45
7.45
7.43
7.42
7.25
7.23
6.95
6.95
6.94
6.94
3.84
3.80
3.79
3.78
3.77
O
OEt
O
3ab
OMe
1.00
1.05
1.09
1.02
2.11
2.03
3.06
2.18
f1 (ppm)


189.84
162.71
159.88
142.76
134.51
132.77
130.83
130.24
130.04
77.26
77.05
76.84
62.08
55.39
13.68
O
OEt
O
3ab
OMe
f1 (ppm)