Supporting Information

Ir/Co Dual Catalyzed Hydroacylation of Electron-Deficient Alkenes Overcoming Redox Potential Limitations

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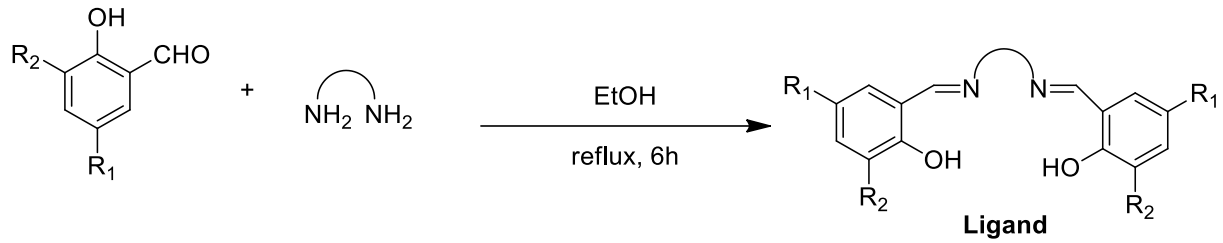
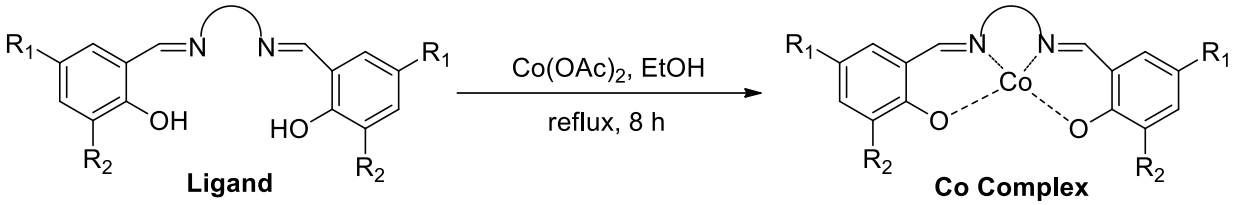
General Information

The Ligand and Co complex were prepared according to the reported literature.[1] CH_3CN, were extra dry solvent purchased from chemical energy. If no special indicated, other reagents and solvents were used as commercially available without further purification. All the reactions were carried out under Ar atmosphere. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel. NMR spectra were measured on a Bruker Avance-400 spectrometer in the solvents indicated; chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm or $CHCl_3$ resonance in $CDCl_3$ as 7.26 ppm, $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. Coupling constants are reported in Hz with multiplicities denoted as br (broad), s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). HRMS were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. The emission spectra were recorded using a HITACHI F-7000 FL Spectrophotometer. Cyclic voltammetry experiments were studied on a CHI660E Electrochemical Workstation equipped with the conventional three electrode system under argon atmosphere. The measurements were performed in solvent of CH_3CN containing 0.1 M n-Bu_4PF_6. The working electrode was a glassy carbon disk electrode (d = 0.3 cm). The auxiliary and reference electrode consisted of a Pt tablets and an saturated calomel electrode (SCE), respectively. Wattecs Parallel Light Reactor System (Connecting with a circulating cooling pump, Blue LED Light source, 10 W every position).

General Procedure for Preparation of Co(salen) Complex

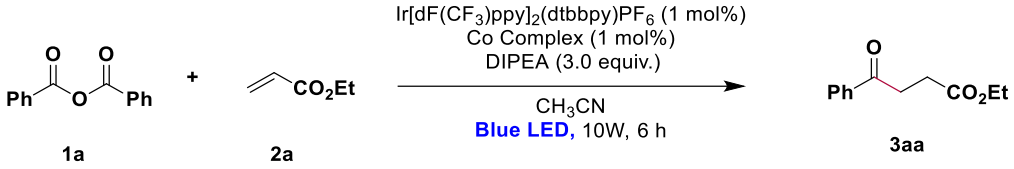


A mixture of 2-hydroxybenzaldehyde (20 mmol) and diamine (10 mmol) was heated to reflux in ethanol (50 mL) for 6 h, and then much of the solid was formed. This solid was filtered and washed by n-hexane, and further dried to give the corresponding ligand.[1-2]



Ligand (1 mmol) in EtOH (15 mL) was heated to reflux under argon. After 10 min, dry $Co(OAc)_2$ (1 mmol) was added, and the mixture was refluxed 2 for another 8 h. Then the reaction was cooled to room temperature and the precipitate filtered. The solid was washed with cold EtOH (3×15 mL) and dried over to give the cobalt(II) complex. Following is the Co(salen) complexes synthesized in our laboratories.[3]

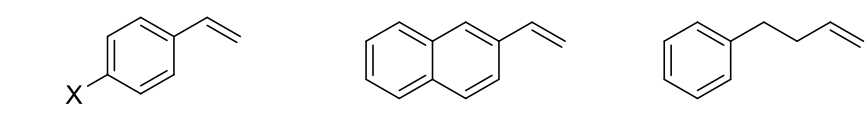
General procedure for synthesis of 3



1a 2a 3aa

To a Schlenk tube containing a stirring bar was addedIr[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.002 mmol, 1 mol%) and **Co-5** (0.002 mmol, 1 mol%). Then, **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.4 mmol, 2.0 equiv.), DIPEA (0.6 mmol, 3.0 equiv.), and solvent of CH_3CN were added to the reaction tube via syringe under Ar atmosphere. The reaction mixture was stirred for 6 h under blue LED irradiation (the equipment see below picture). Once the reaction was finished, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel to afford the compound **3aa**.

Wattecs Parallel Light Reactor System (Connecting with a circulating cooling pump, Blue LED Light source, 10 W every position)

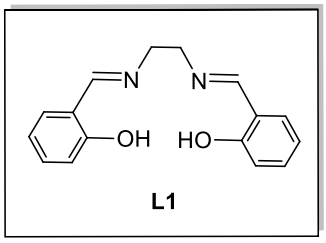


Scheme S1. Low-active substrates

Characterization Data for Products

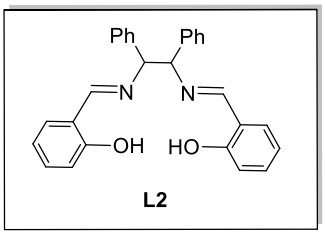
Characterization Data for Products

2,2'-((1*E*,1'*E*)-((Z)-ethene-1,2-diylbis(azanylylidene))bis(methanylylidene))diphenol **L1**[1]



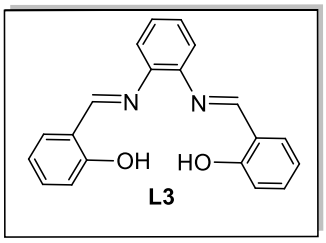
According to the general procedure, **L1** (yellow solid, 6.07 g, mp: 198-200 °C) was filtered by funnel in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.25 (s, 2H), 8.36 (s, 2H), 7.34-7.24 (m, 4H), 6.99-6.86 (m, 4H), 3.93 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4 (2C), 160.9 (2C), 132.3 (4C), 131.4 (2C), 118.6 (2C), 116.9 (2C), 59.6 (2C). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{17}N_2O_2^+$, 269.1285; found, 269.1290.

2,2'-((1*E*,1'*E*)-((1,2-diphenylethane-1,2-diyl)bis(azanylylidene))bis(methanylylidene))diphenol **L2**[4]



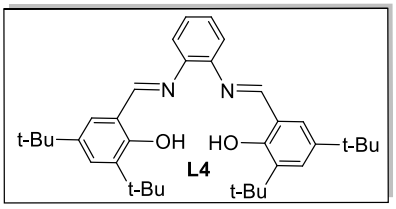
According to the general procedure, **L2** (yellow solid, 8.25 g, mp: 182-185 °C) was filtered by funnel in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.48 (s, 2H), 8.36 (s, 2H), 7.35-7.27 (m, 12H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.86 (t, *J* = 7.2 Hz, 2H), 4.84 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0 (2C), 160.8 (2C), 139.2 (2C), 132.4 (2C), 131.6 (2C), 128.2 (4C), 127.7 (4C), 127.5 (2C), 118.6 (2C), 118.4 (2C), 116.7 (2C), 79.9 (2C). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{28}H_{25}N_2O_2^+$, 421.1911; found, 421.1919.

2,2'-((1*E*,1'*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))diphenol **L3**[1]



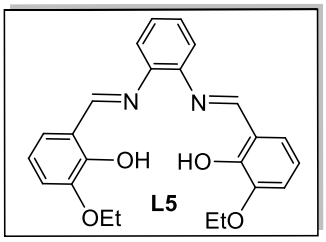
According to the general procedure, **L3** (orange solid, 6.07 g, mp: 171-173 °C) was filtered by funnel in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.10 (s, 2H), 8.65 (s, 2H), 7.41-7.34 (m, 6H), 7.28-7.24 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.96-6.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (2C), 161.3 (2C), 142.5 (2C), 133.3 (2C), 132.3 (2C), 127.6 (2C), 119.7 (2C), 119.2 (2C), 118.9 (2C), 117.5 (2C). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}N_2O_2^+$, 317.1285; found, 317.1984

6,6'-((1*E*,1'*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(2,4-di-tert-butylphenol) **L4**[5]



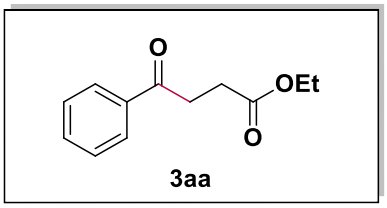
According to the general procedure, **L4** (yellow solid, 8.43 g, mp: 191-193 °C) was filtered by funnel in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.55 (s, 2H), 8.66 (s, 2H), 7.44 (d, *J* = 2.0 Hz, 4H), 7.31-7.30 (m, 2H), 7.24-7.21 (m, 4H), 1.44 (s, 18H), 1.32 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7 (2C), 158.6 (2C), 142.7 (2C), 140.3 (2C), 137.2 (2C), 128.2 (2C), 127.3 (2C), 126.8 (2C), 119.8 (2C), 118.3 (2C), 35.1 (2C), 34.1 (2C), 31.5 (6C), 29.4 (6C). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{36}H_{49}N_2O_2^+$, 541.3789; found, 541.3791.

6,6'-((1*E*,1'*E*)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(2-ethoxyphenol) **L5**[6]



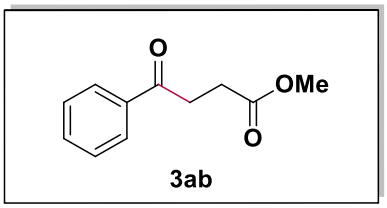
According to the general procedure, **L5** (orange solid, 6.07 g, mp: 222-224 °C) was filtered by funnel in 75% yield. 1H NMR (400 MHz, CDCl3) δ 13.13 (s, 2H), 8.59 (s, 2H), 7.32-7.30 (m, 2H), 7.00-6.96 (m, 4H), 6.84-6.81 (m, 2H), 4.14-4.09 (m, 4H), 1.42 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (2C), 151.9 (2C), 147.7 (2C), 142.5 (2C), 127.5 (2C), 124.1 (2C), 120.4 (2C), 119.4 (2C), 118.4 (2C), 117.1 (2C), 64.8 (2C), 14.8 (2C). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{24}H_{25}N_2O_4^+$, 405.1809; found, 405.1810.

Ethyl 4-oxo-4-phenylbutanoate **3aa**[7]



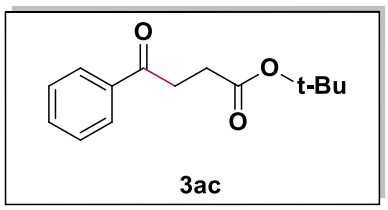
According to the general procedure, **3aa** (colourless liquid, 41.2 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 50:1) in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.60-7.56 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.19-4.12 (m, 2H), 3.33 (t, *J* = 6.8 Hz, 2H), 2.77 (t, *J* = 6.8 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 172.9, 136.7, 133.2, 128.6 (2C), 128.0 (2C), 60.6, 33.4, 28.3, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{15}O_3^+$, 207.1016; found, 207.1015.

Methyl 4-oxo-4-phenylbutanoate **3ab**[8]



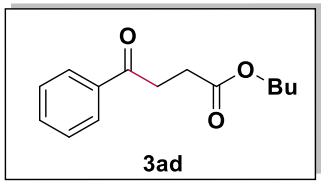
According to the general procedure, **3ab** (colourless liquid, 38.4 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 50:1) in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 3.71 (s, 3H), 3.33 (t, *J* = 6.4 Hz, 2H), 2.77 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 173.3, 136.5, 133.2, 128.6 (2C), 128.0 (2C), 51.8, 33.4, 28.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{13}O_3^+$, 193.0859; found, 193.0865.

Tert-butyl 4-oxo-4-phenylbutanoate **3ac**[8]



According to the general procedure, **3ac** (yellow liquid, 46.9 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 50:1) in 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.26 (t, *J* = 6.4 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 172.1, 136.8, 133.1, 128.5 (2C), 128.0 (2C), 80.6, 33.5, 29.5, 28.1 (3C). HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}O_3^+$, 235.1329; found, 235.1335.

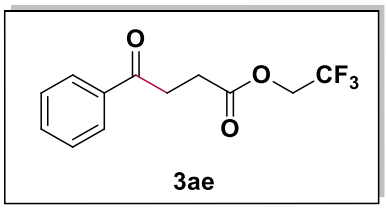
Pentyl 4-oxo-4-phenylbutanoate **3ad**[8]



According to the general procedure, **3ad** (colourless liquid, 49.6 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 1H),

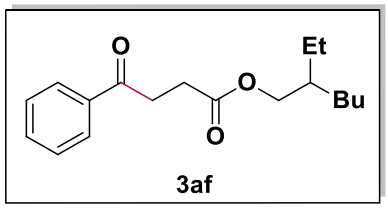
7.39 (t, *J* = 7.6 Hz, 2H), 4.03 (t, *J* = 6.4 Hz, 2H), 3.24 (t, *J* = 6.4 Hz, 2H), 2.69 (t, *J* = 6.8 Hz, 2H), 1.56−1.51 (m, 2H), 1.33−1.28 (m, 2H), 0.85 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 172.9, 136.6, 133.2, 128.6 (2C), 128.0 (2C), 64.6, 33.4, 30.6, 28.3, 19.1, 13.7. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{19}O_3^+$, 235.1329; found, 235.1338.

2,2,2-Trifluoroethyl 4-oxo-4-phenylbutanoate **3ae**[9]



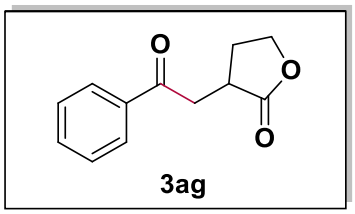
According to the general procedure, **3ae** (yellow liquid, 52.0 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 4.44-4.39 (m, 2H), 3.29 (t, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 171.4, 136.3, 133.4, 128.7 (2C), 128.0 (2C), 122.9 (q, $^1J_{C\text{-}F}$=275.5 Hz), 66.7 (q, $^2J_{C\text{-}F}$ = 36.4 Hz), 33.1, 27.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -73.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{12}F_3O_3^+$, 261.0733; found, 261.0738.

2-Ethylhexyl 4-oxo-4-phenylbutanoate **3af**



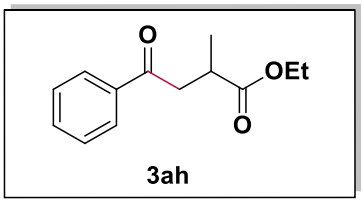
According to the general procedure, **3af** (colourless liquid, 60.9 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.59-7.56 (m, 1H), 7.49−7.45 (m, 2H), 4.03-4.01 (m, 2H), 3.32 (t, *J* = 6.4 Hz, 2H), 2.78 (t, *J* = 6.8 Hz, 2H), 1.69-1.54 (m, 2H), 1.39-1.27 (m, 9H), 0.90−0.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 166.0, 129.6, 126.2, 121.6 (2C), 121.0 (2C), 60.1, 31.7, 26.4, 23.4, 21.9, 21.3, 16.7, 15.9, 7.0, 4.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{27}O_3^+$, 291.1955; found, 291.1965.

(*R*)-3-(2-Oxo-2-phenylethyl)dihydrofuran-2(3*H*)-one **3ag**[9]



According to the general procedure, **3ag** (white solid, 40.8 mg, mp: 71-73 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.47-4.26 (m, 2H), 3.67 (d, *J* = 15.2 Hz, 1H), 3.23-3.14 (m, 2H), 2.67-2.62 (m, 1H), 2.01-1.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 179.1, 136.1, 133.5, 128.7 (2C), 128.0 (2C), 66.8, 39.3, 35.2, 29.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{13}O_3^+$, 205.0859; found, 205.0861.

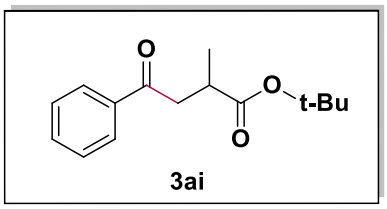
Ethyl 2-methyl-4-oxo-4-phenylbutanoate **3ah**[8]



According to the general procedure, **3ah** (yellow liquid, 44.0 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 50:1) in 80%

yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 4.18-4.13 (m, 2H), 3.52-3.46 (m, 1H), 3.15-2.99 (m, 2H), 1.29-1.24 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 175.9, 133.1, 128.6 (2C), 128.0 (2C), 60.6, 41.9, 35.1, 17.3 14.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}O_3^+$, 221.1172; found, 221.1176.

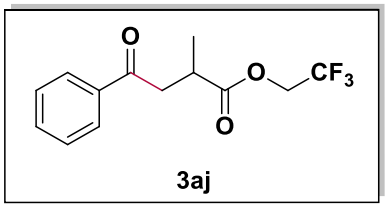
Tert-butyl 2-methyl-4-oxo-4-phenylbutanoate **3ai**[10]



3ai

According to the general procedure, **3ai** (white solid, 49.6 mg, mp: 55-57 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 50:1) in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.2 Hz 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.46-3.40 (m, 1H), 3.07-2.92(m, 2H), 1.44 (s, 9H), 1.25 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 175.1, 137.0, 133.0, 128.5 (2C), 128.0 (2C), 80.3, 41.9, 36.0, 28.0 (3C), 17.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{21}O_3^+$, 249.1485; found, 249.1494.

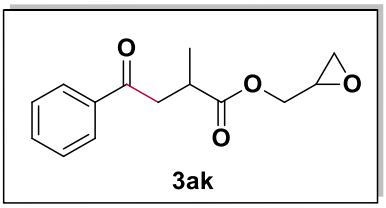
2,2,2-Trifluoroethyl 2-methyl-4-oxo-4-phenylbutanoate **3aj**



3aj

According to the general procedure, **3aj** (yellow liquid, 54.8 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 4.62-4.53 (m, 1H), 4.45-4.40 (m, 1H), 3.52−3.46 (m, 1H), 3.24-3.19 (m, 1H), 3.14-3.08 (m, 1H), 1.33 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 174.4, 136.4, 133.3, 128.6 (2C), 128.0 (2C), 123.0 (q, $^1J_{C\text{-}F}$=273.9 Hz), 60.4 (q, $^2J_{C\text{-}F}$=36.4 Hz), 41.7, 34.6, 17.0. ^{19}F NMR (376 MHz, $CDCl_3$) : δ -73.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{14}F_3O_3^+$, 275.0890; found, 275.0895.

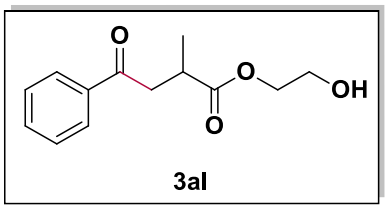
Oxiran-2-ylmethyl 2-methyl-4-oxo-4-phenylbutanoate **3ak**



3ak

According to the general procedure, **3ak** (colourless liquid, 49.6 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 8:1) in 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz 2H), 4.37-4.33 (m, 1H), 3.97-3.86 (m, 1H), 3.45-3.39 (m, 1H), 3.12-2.97 (m, 3H), 2.76-2.75 (m, 1H), 2.63-2.55 (m, 1H), 1.24 (d, *J* = 7.2 Hz 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.9, 175.6, 136.5, 133.2, 128.6 (2C), 128.0 (2C), 64.6, 49.3, 44.6, 41.9, 34.9, 17.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}O_4^+$, 249.1121; found, 249.1125.

2-Hydroxyethyl 2-methyl-4-oxo-4-phenylbutanoate **3al**

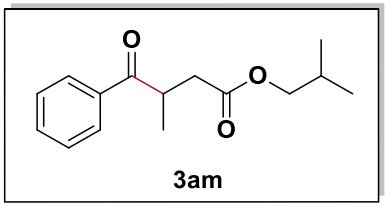


3al

According to the general procedure, **3al** (yellow liquid, 47.2 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.2 Hz,

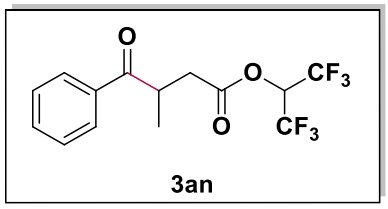
1H), 7.40 (t, *J* = 7.2 Hz, 2H), 4.30-4.10 (m, 2H), 3.75 (t, *J* = 4.4 Hz, 2H), 3.44 -3.37(m, 1H), 3.08-3.02 (m, 2H), 1.24 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 176.3, 136.4, 133.4, 128.6 (2C), 128.1 (2C), 66.2, 61.1, 42.3, 35.1, 17.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}O_4^+$, 237.1121; found, 237.1127.

Isobutyl 3-methyl-4-oxo-4-phenylbutanoate **3am**



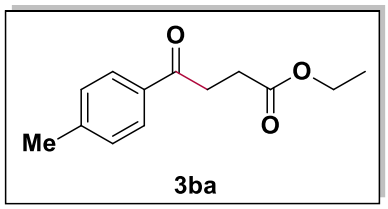
According to the general procedure, **3am** (yellow liquid, 49.6 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 3.91-3.86 (m, 1H), 3.76 (d, *J* = 6.8 Hz, 2H), 2.95-2.88 (m, 1H), 2.43-2.38 (m, 1H), 1.83-1.77 (m, 1H), 1.16 (d, *J* = 7.2 Hz, 3H), 0.81 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 172.4, 135.9, 133.0, 128.7 (2C), 128.4 (2C), 70.7, 37.5, 37.2, 27.6, 19.0 (2C), 17.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{21}O_3^+$, 249.1485; found, 249.1495.

1,1,1,3,3,3-Hexafluoropropan-2-yl 3-methyl-4-oxo-4-phenylbutanoate **3an**



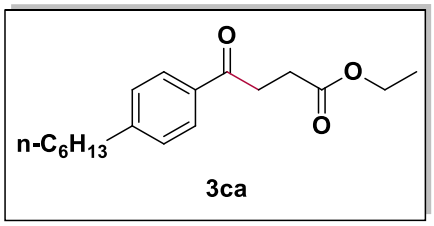
According to the general procedure, **3an** (white solid, 68.4 mg, mp: 57-59 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.0 Hz, 2H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 5.83-5.77 (m, 1H), 3.54-3.47 (m, 1H), 3.33−3.16 (m, 2H), 1.37 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 172.8, 136.2, 133.5, 128.7 (2C), 128.0 (2C), 124.6-117.6 (m, 2C), 67.3-65.9 (m,2C), 41.6, 34.5, 16.8. ^{19}F NMR (376 MHz, $CDCl_3$) : δ -73.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{13}F_6O_3^+$, 343.0763; found, 343.0765.

Ethyl 4-oxo-4-(p-tolyl)butanoate **3ba**[8]



According to the general procedure, **3ba** (white solid, 44.0 mg, mp: 53-55 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 4.12-4.06 (m, 2H), 3.22 (t, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 173.0, 144.0, 134.1, 129.3 (2C), 128.1 (2C), 60.6, 33.3, 28.3, 21.6, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}O_3^+$, 221.1172; found, 221.1175.

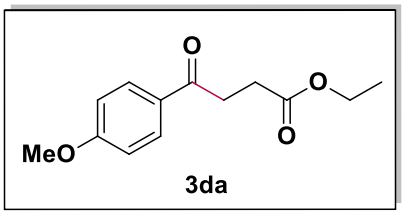
Ethyl 4-(4-hexylphenyl)-4-oxobutanoate **3ca**



According to the general procedure, **3ca** (white solid, 60.9 mg, mp: 87-89 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.19−4.13 (m, 2H), 3.30 (t, *J* = 6.4 Hz, 2H), 2.75

(t, *J* = 6.4, 2H), 2.66 (t, *J* = 7.6 Hz, 2H), 1.66-1.61 (m, 2H) 1.32-1.25 (m, 9H) 0.88 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 173.0, 148.9, 134.3, 128.6 (2C), 128.2 (2C), 60.6, 36.0, 33.3, 31.8, 31.1, 29.2, 28.4, 22.6, 14.2, 14.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{27}O_3^+$, 291.1955; found, 291.1960.

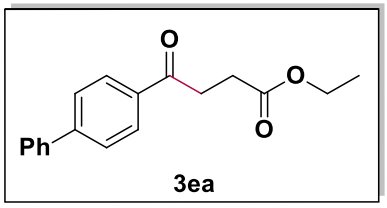
Ethyl 4-(4-methoxyphenyl)-4-oxobutanoate **3da**[8]



3da

According to the general procedure, **3da** (colourless liquid, 47.2 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.19–4.13 (m, 2H), 3.87 (s, 3H), 2.27 (t, *J* = 6.4 Hz, 2H), 2.74 (t, *J* = 6.8 Hz, 2H), 1.29-1.25 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 173.0, 163.6, 130.3 (2C), 129.8 113.7 (2C), 60.6, 55.4, 33.0, 28.4, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{17}O_4^+$, 237.1121; found, 237.1123.

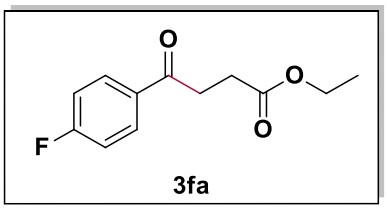
Ethyl 4-([1,1'-biphenyl]-4-yl)-4-oxobutanoate **3ea**[8]



3ea

According to the general procedure, **3ea** (colourless liquid, 56.4 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 39% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 4.20-4.15 (m, 2H), 3.35 (t, *J* = 6.8 Hz, 2H), 2.79 (t, *J* = 6.4 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 172.9, 145.9, 139.9, 135.4, 128.9 (2C), 128.6 (2C), 128.2, 127.3 (4C), 60.6, 33.5, 28.4, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{19}O_3^+$, 283.1329; found, 283.1331.

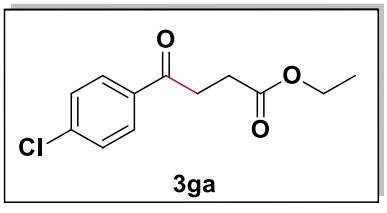
Ethyl 4-(4-fluorophenyl)-4-oxobutanoate **3fa**[8]



3fa

According to the general procedur, **3fa** (yellow liquid, 44.8 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 4.12-4.06 (m, 2H), 3.21 (t, *J* = 6.4 Hz, 2H), 2.69 (t, *J* = 6.4 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 172.8, 165.8 (d, $^1J_{C\text{-}F}$ = 254.4 Hz), 133.0 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 130.6 (d $^3J_{C\text{-}F}$ = 9.3 Hz, 2C), 115.7 (d, $^2J_{C\text{-}F}$ = 21.8 Hz, 2C), 60.7, 33.3, 28.2, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ -105.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}FO_3^+$, 225.0921; found, 225.0925.

Ethyl 4-(4-chlorophenyl)-4-oxobutanoate **3ga**[8]



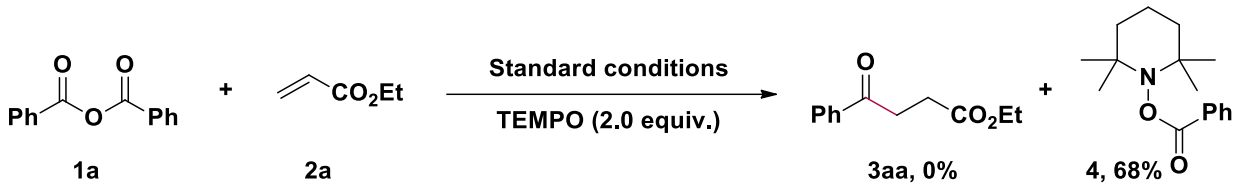
3ga

According to the general procedure, **3ga** (yellow solid, 48.1 mg, mp: 48-50 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 30:1) in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.44

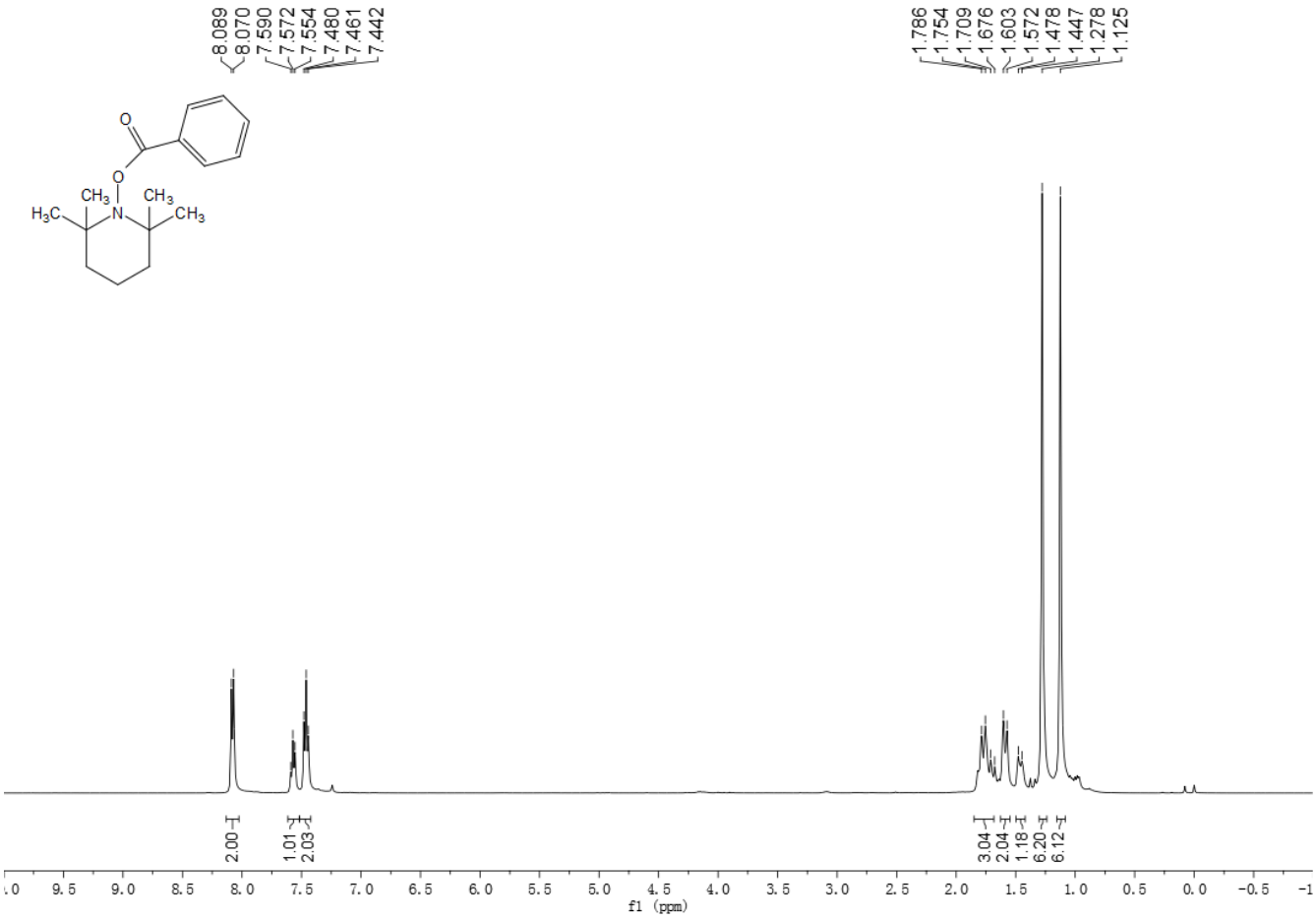
(d, *J* = 8.8 Hz, 2H), 4.19−4.13 (m, 2H), 3.28 (t, *J* = 6.4 Hz, 2H), 2.76 (t, *J* = 6.8, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 172.7, 139.6, 134.9, 129.4 (2C), 128.9 (2C), 60.7, 33.3, 28.2, 14.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{14}ClO_3^+$, 241.0626; found, 241.0628.

Mechanistic studies

1) Free radical trapping experiment



When TEMPO (2.0 equiv.) was added to the reaction, it was observed that the desired transformation was totally inhibited, but the acyl-TEMPO adduct **4** was observed and isolated in 68% yield. **4**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 1.79-1.68 (m, 3H), 1.59 (d, *J* = 12.4 Hz, 2H), 1.46 (d, *J* = 12.4 Hz, 1H), 1.28 (s, 6H), 1.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 132.3, 129.2, 129.0 (2C), 127.9 (2C), 59.9 (2C), 38.6 (2C), 31.4 (2C), 20.3 (2C), 16.5. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{24}NO_2^+$, 262.1802; found, 262.1806.



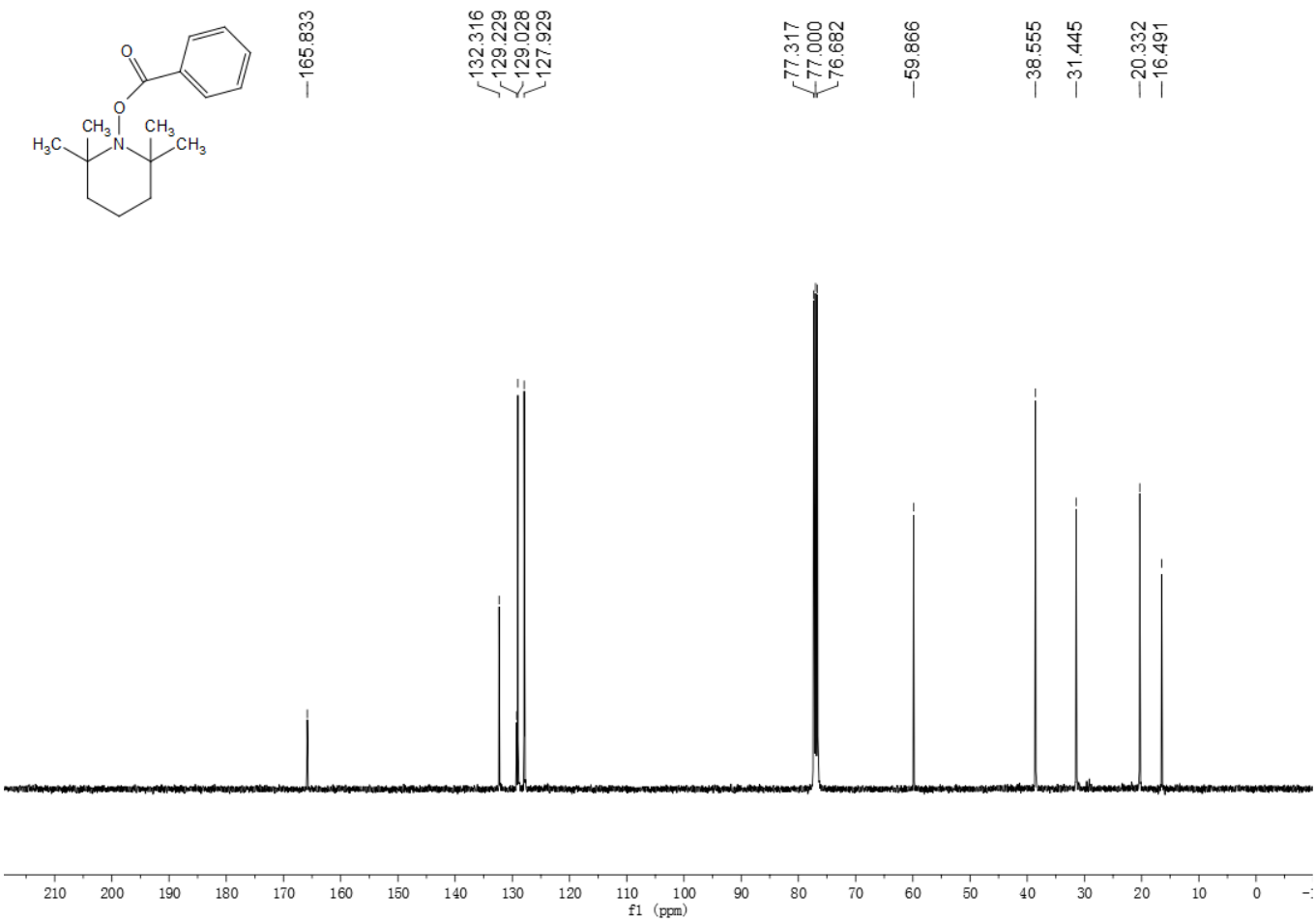


Figure S1. ^{1}H and ^{13}C NMR spectra of acyl-TEMPO adduct **4**.

2) Light on/off experiments

The light on/off experiments were conducted by using Wattecs Parallel Light Reactor (Blue LED, 445 nm–450 nm, 10 W every position, temperature range from 28 ºC to 30 ºC), which equipped with a circulating cooling pump to keep the temperature constant. The reaction system was alternately treated with light and dark at a time interval of 3 hours and the results were summarized in table S1 and Figure S1. These results confirmed the essential role of continuous irradiation for the high yield transformation,

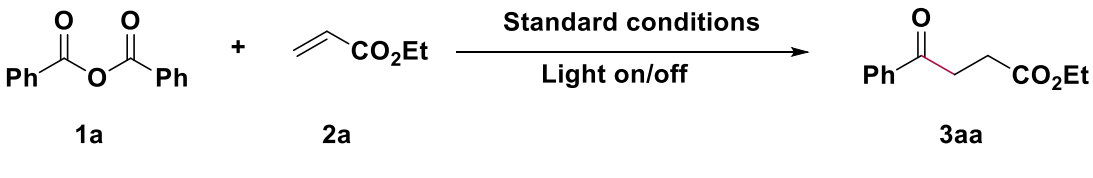


Table S1. Results of light on/off experiments.

entry[a]	time (h.)			yield (%)
1	0	light →	3	43
2	3	dark →	6	45
3	6	light →	9	58
4	9	dark →	12	59

[a] Reaction condition: **1a** (0.2 mmol), **2a** (0.4 mmol), Ir[dF(CF_3)ppy(dtbbpy)]PF_6 (1 mol%), Co Salen complex (1 mmol%), DIPEA (3.0 equiv.), in CH_3CN (2ml), irradiation with blue LEDs (445~450 nm, 10 W), ^1H NMR yield was reported using $Cl_2CHCHCl_2$ as an internal standard.

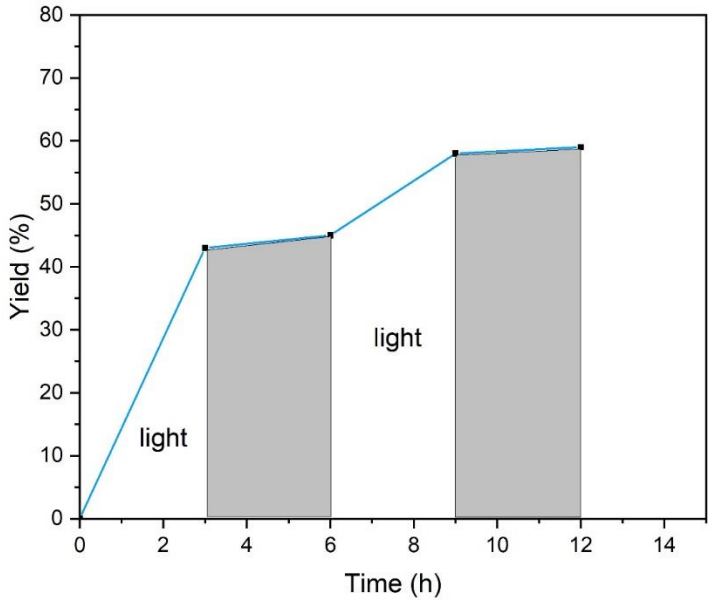
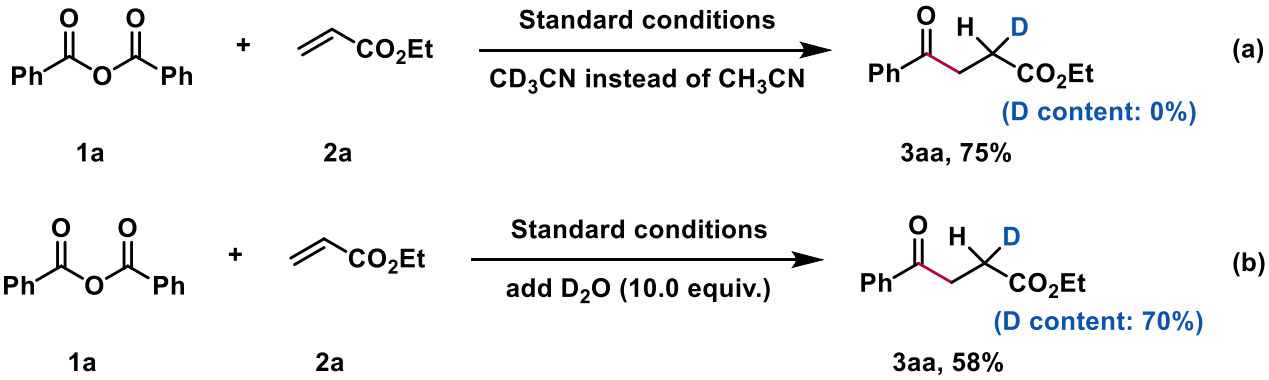


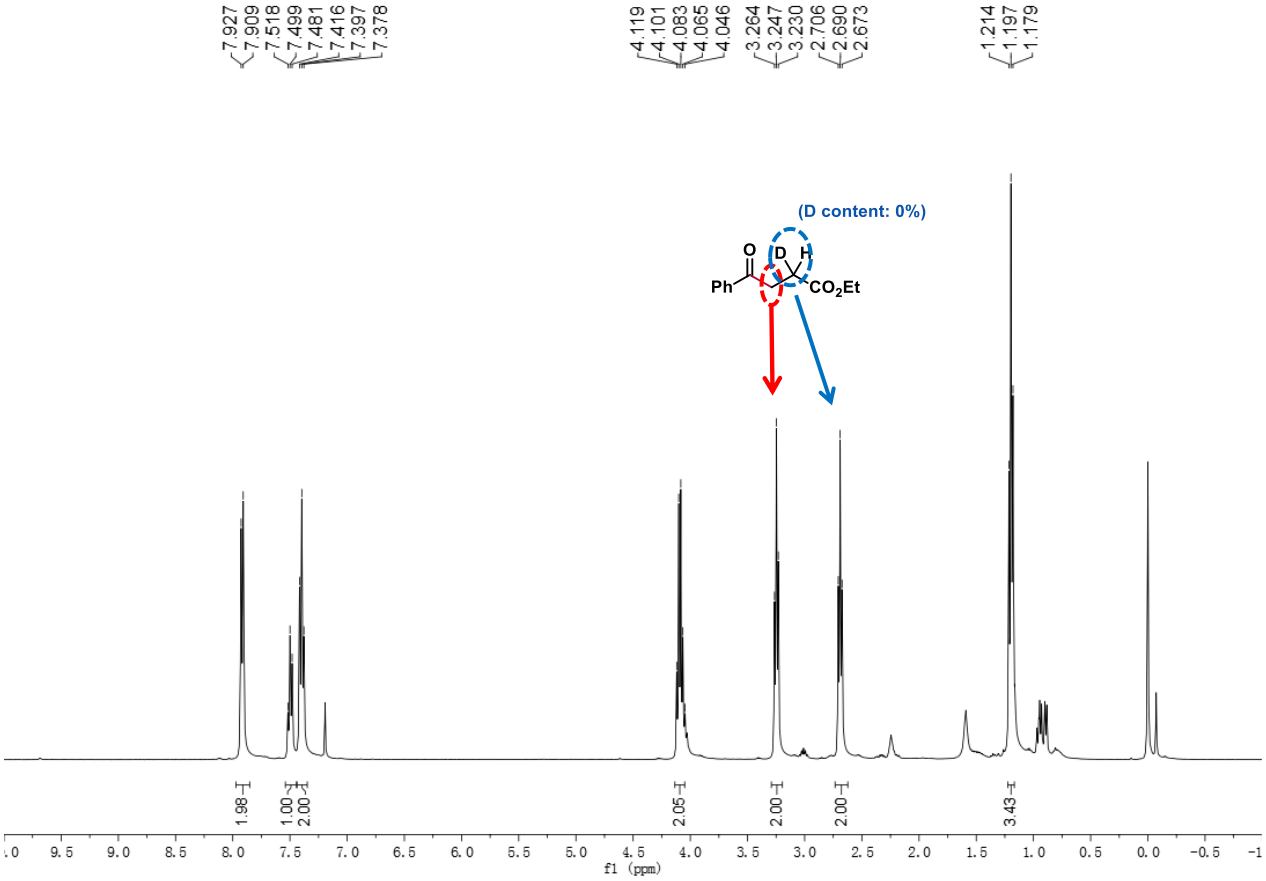
Figure S2. Time-yield plot of optical switch control experiments.

3) Deuteration experiments



Scheme S2. Deuteration experiments.

The experimental results showed that no deuterated products were formed when utilizing CD_3CN as the solvent (Scheme S2a). However, upon the introduction of D_2O (10 equivalents) into the reaction mixture, the formation of **D-3aa** was observed, yielding a deuteration content of 70% (Scheme S2b). These findings suggest that a carbon anion intermediate is likely involved in the reaction, with the hydrogen source being DIPEA.



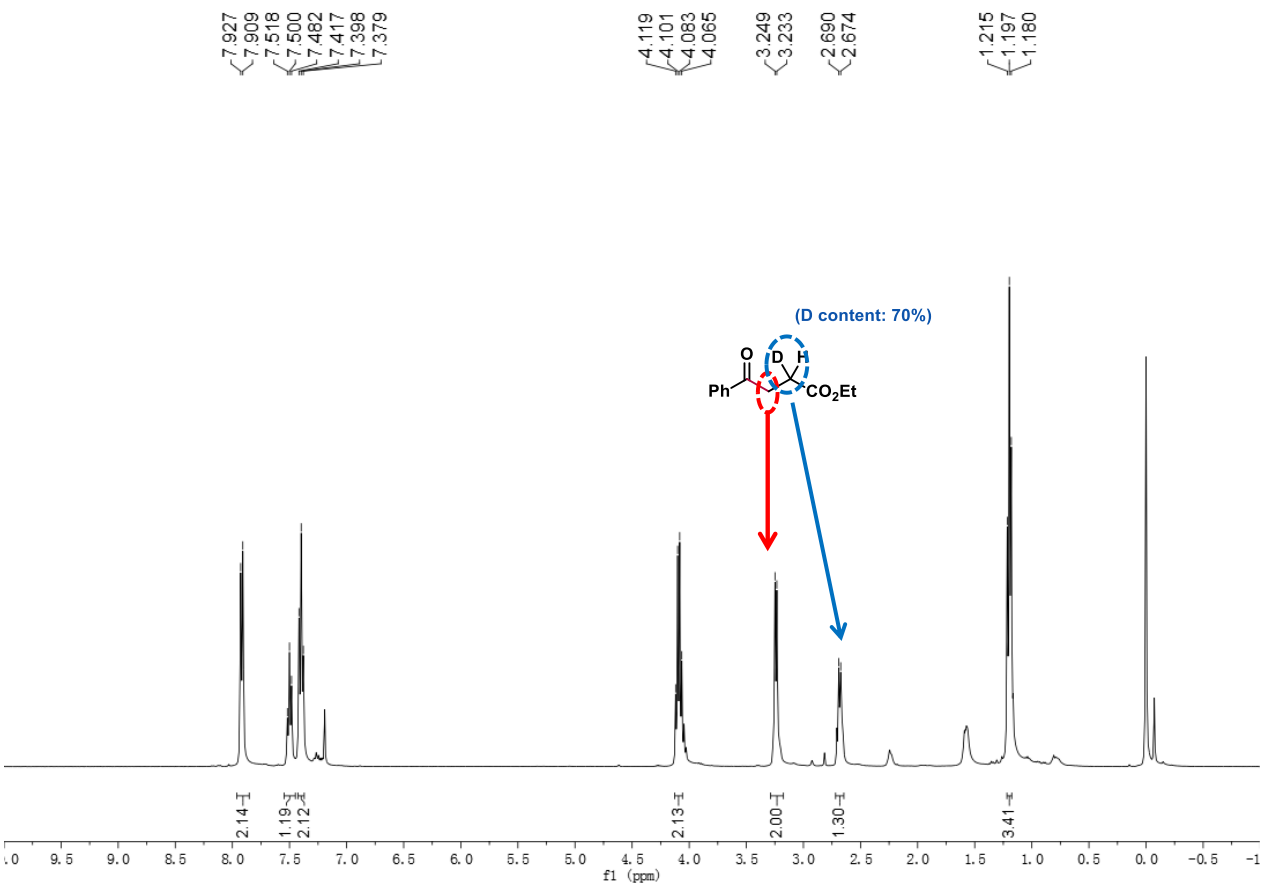


Figure S3. ^{1}H NMR analysis of deuteration experiment.

4) Fluorescence quenching experiment

The photocatalyst and substrate samples were dissolved in acetonitrile (CH_3CN) separately. A solution of Ir[dF(CF_3)ppy(dtbbpy)]PF_6 was prepared at a concentration of 5×10^{-4} mol/L, while **1a**, **2a**, and DIPEA were prepared at a concentration of 0.02 mol/L. The **Co-5** complex was prepared at a concentration of 0.001 mol/L. For the fluorescence test, 2.5 mL of the Ir[dF(CF_3)ppy(dtbbpy)]PF_6 solution was taken in glove box and the cuvette was sealed with a PTFE stopper, further sealed with parafilm. 5 μL of a quenching agent was added to the solution incrementally. The photocatalysts' luminescence was excited at a wavelength of 400 nm, and the emitted luminescence was measured at 523 nm.

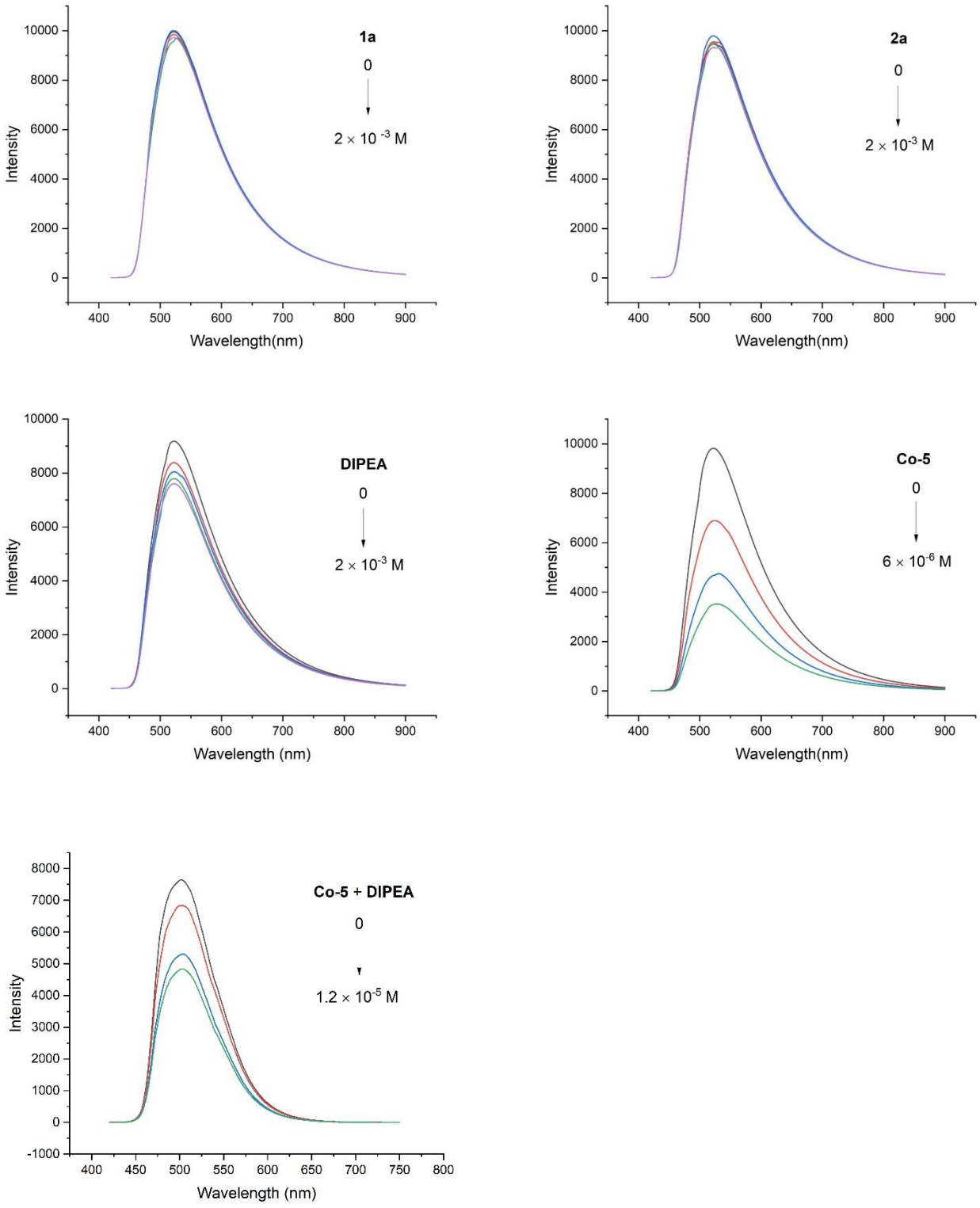


Figure S4. Fluorescence quenching spectra of **1a**, **2a**, DIPEA, **Co-5,** and **Co-5 + DIPEA**.

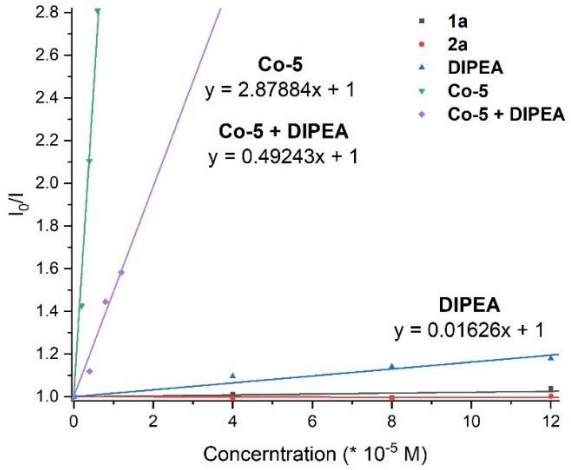


Figure S5. Stern-Volmer plots of **1a**, **2a**, DIPEA, **Co-5**, and **Co-5**+**DIPEA**

The emission quenching plots of **Co-2** and **Co-4** towards Ir[dF(CF_3)ppy(dtbbpy)]PF_6 were also detected. In these reactions, the solution of Ir[dF(CF_3)ppy(dtbbpy)]PF_6 was prepared at a concentration of 5×10^{-5} mol/L, while **Co-2** and **Co-4** were prepared at a concentration of $1*10^{-4}$ mol/L. 10 μL of a quenching agent was added to the solution incrementally. Other conditions were as same as the above mentioned. Below graphs corresponding to the emission quenching plots and the Stern-Volmer plots.

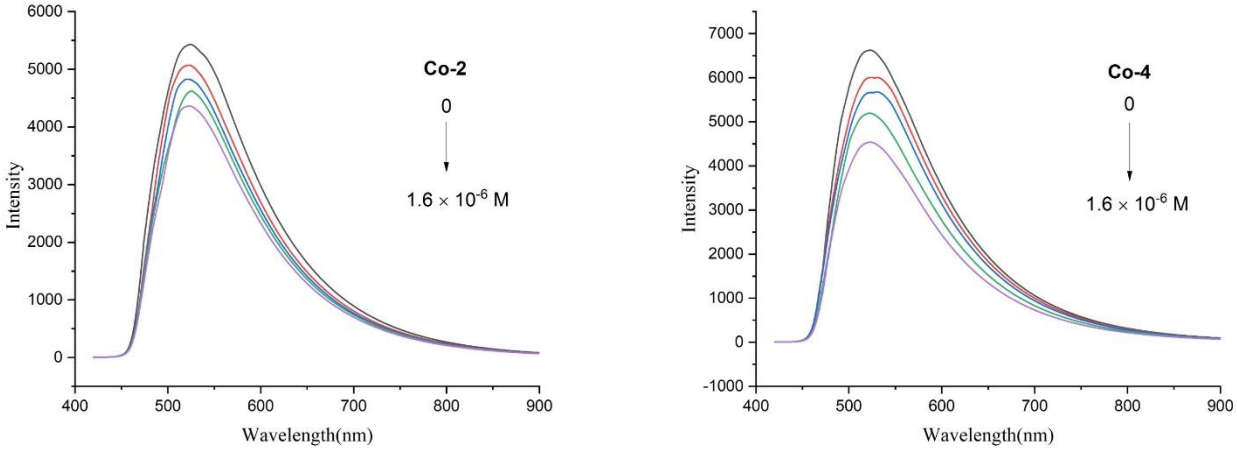


Figure S6. Fluorescence quenching spectra of **Co-2** and **Co-4**.

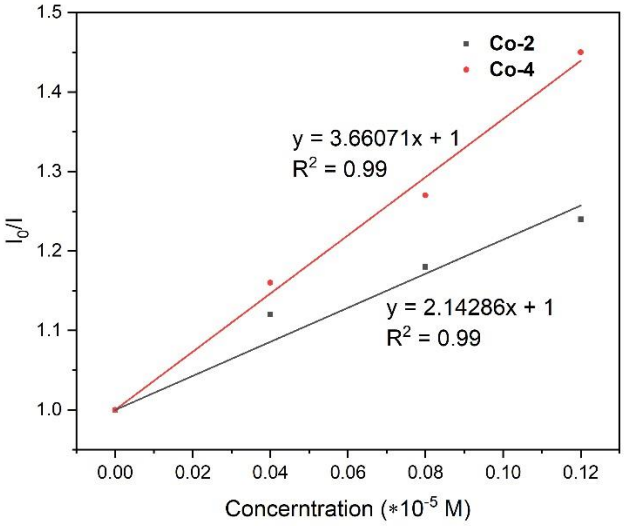


Figure S7. Stern-Volmer plots of **Co-2** and **Co-5.**

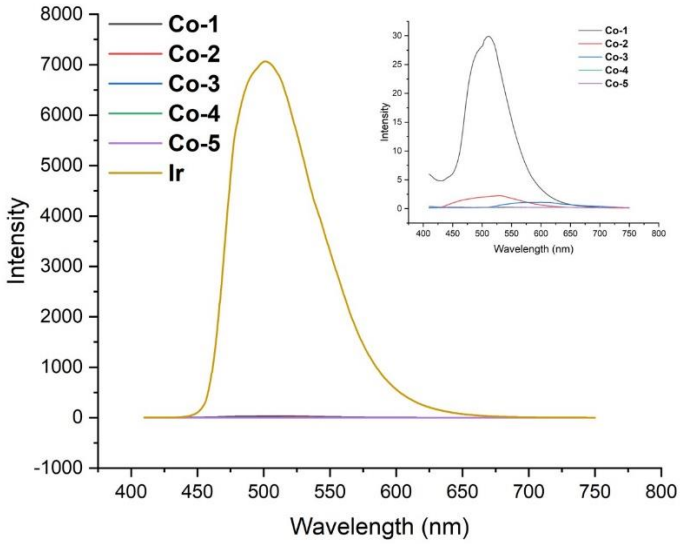


Figure S8. Emission spectrum of **Co-1~Co-5** and **Ir** in a concentration of $1*10^{-4}$ M in CH_3CN.

Stern-Volmer Kinetic Analysis

Stern-Volmer constants were determined using Stern–Volmer kinetics (eq 1).

$$I_0/I = Ksv \bullet [Q] + 1 \quad (1)$$

$$Ksv = k_q \bullet \tau_0 \quad (2)$$

Where I_0 is the luminescence intensity without the quencher, I is the intensity in the presence of the quencher, and Ksv is the Stern-Volmer constant. As shown in equation 2, the actual bimolecular rate of quenching (k_q) can be readily calculated from Ksv using the lifetime (τ_0) of the corresponding photocatalyst (2300 ns for Ir[dF(CF_3)ppy(dtbbpy)]PF_6 in acetonitrile).[14] The Ksv value was read as 2.87884*10^5 M^{-1} from the Stern-Volmer plot of **Co-5**, thus, the k_q value was calculated as 1.25*10^{11} $M^{-1}s^{-1}$. For **Co-2** and **Co-4**, the Ksv value was read as 2.14286*10^5 M^{-1} and 3.66071*10^5 M^{-1}, respectively, which gave the corresponding k_q values as 9.3*10^{10} $M^{-1}s^{-1}$ and 1.59*10^{11} $M^{-1}s^{-1}$, respectively.

5) Cyclic Voltammetry (CV) Experiments

For the electrochemical measurements a three-electrode system connected to an electrochemical station was used. The working electrode was a glassy carbon disk electrode (d = 0.3 cm). The auxiliary and reference electrode consisted of a Pt tablets and an saturated calomel electrode (SCE), respectively. All electrochemical measurements were performed in 0.1 M n-Bu_4PF_6 CH_3CN solution under dry argon atmosphere.

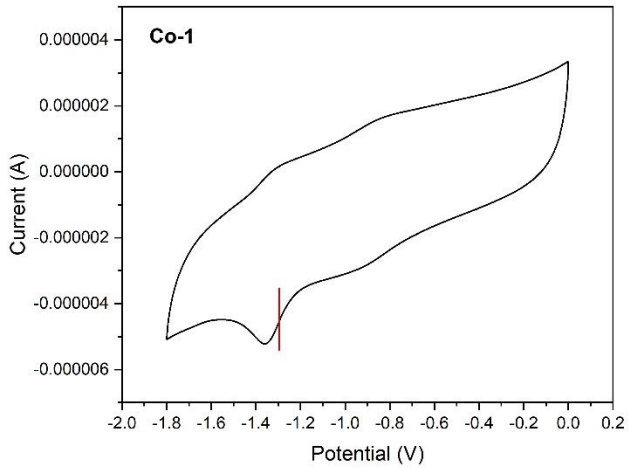


Figure S9. Cyclic voltammogram (CV) of 3 mM **Co-1** in 0.1 M *n*-Bu_4PF_6 CH_3CN solution under Ar. Conditions: working electrode: glassy carbon electrode; reference electrode: SCE; scan rate = 50 mV/s. $E_{p/2}$ = - 1.30 V vs. SCE. This value is in accordance with the literature report (E = -1.23 V vs SCE).[11]

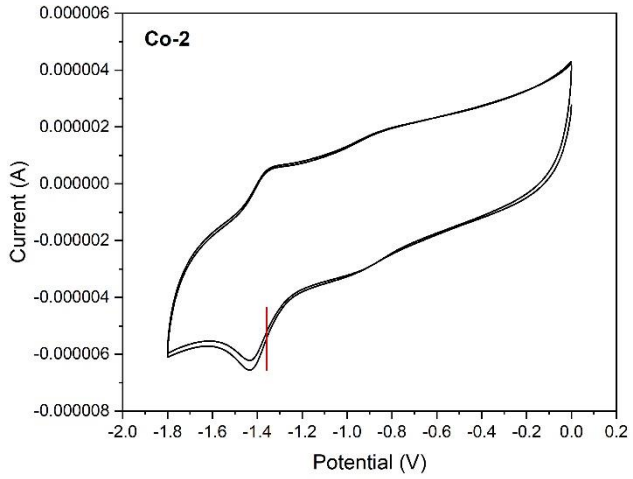


Figure S10. Cyclic voltammogram (CV) of 3 mM **Co-2** in 0.1 M n-Bu_4PF_6 CH_3CN solution under Ar. Conditions: working electrode: glassy carbon electrode; reference electrode: SCE; scan rate = 100 mV/s. $E_{p/2}$ = - 1.36 V vs. SCE.

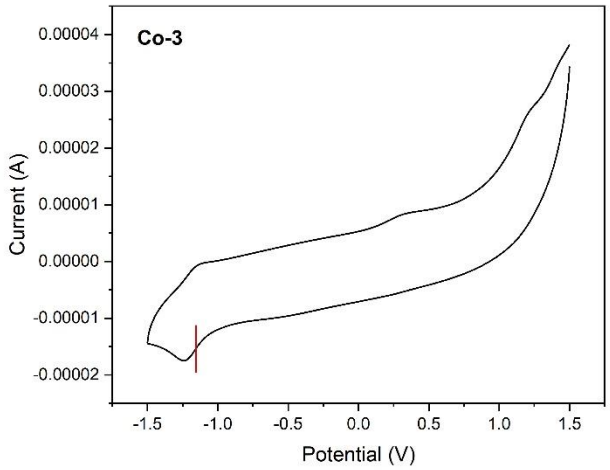


Figure S11. Cyclic voltammogram (CV) of 3 mM **Co-3** in 0.1 M n-Bu_4PF_6 CH_3CN solution under Ar. Conditions: working electrode: glassy carbon electrode; reference electrode: SCE; scan rate = 100 mV/s. $E_{p/2}$ = - 1.15 V vs. SCE.

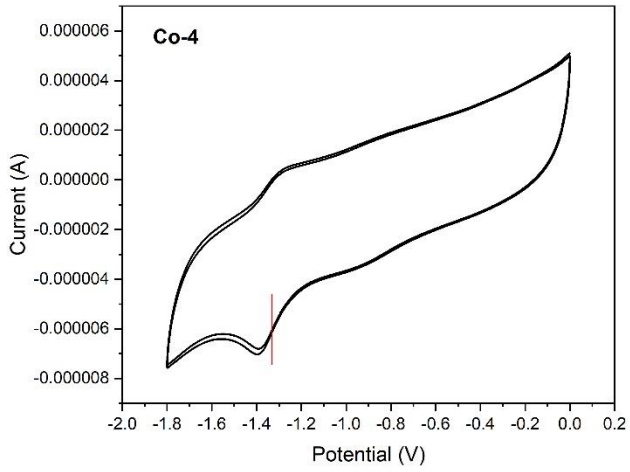


Figure S12. Cyclic voltammogram (CV) of 3 mM **Co-4** in 0.1 M n-Bu_4PF_6 CH_3CN solution under Ar. Conditions: working electrode: glassy carbon electrode; reference electrode: SCE; scan rate = 100 mV/s. $E_{p/2}$ = -1.33 V vs. SCE. This value is in accordance with the literature report (E = -1.36 V vs SCE).[12]

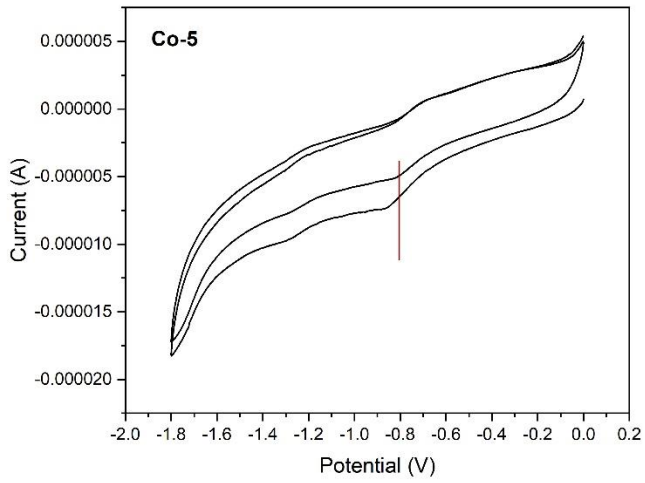


Figure S13. Cyclic voltammogram (CV) of 1 mM **Co-5** in 0.1 M n-Bu_4PF_6 CH_3CN solution under Ar. Conditions: working electrode: glassy carbon electrode; reference electrode: SCE; scan rate = 100 mV/s. $E_{p/2}$ = -0.80 V vs. SCE.

6) UV-vis spectrum

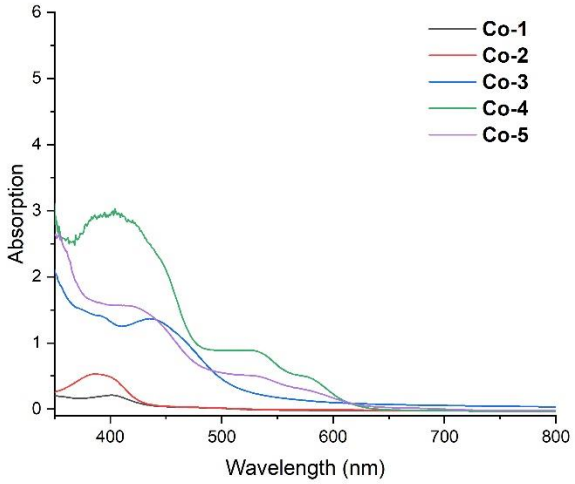


Figure S14. UV-vis spectrum of Co-1~Co-5 in a concentration of $1*10^{-4}$ M in CH_3CN

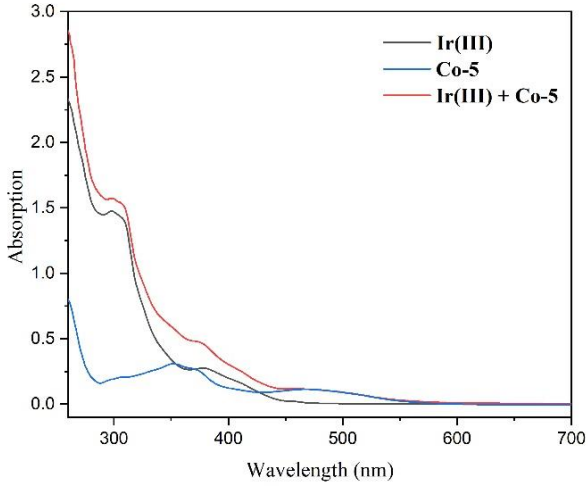
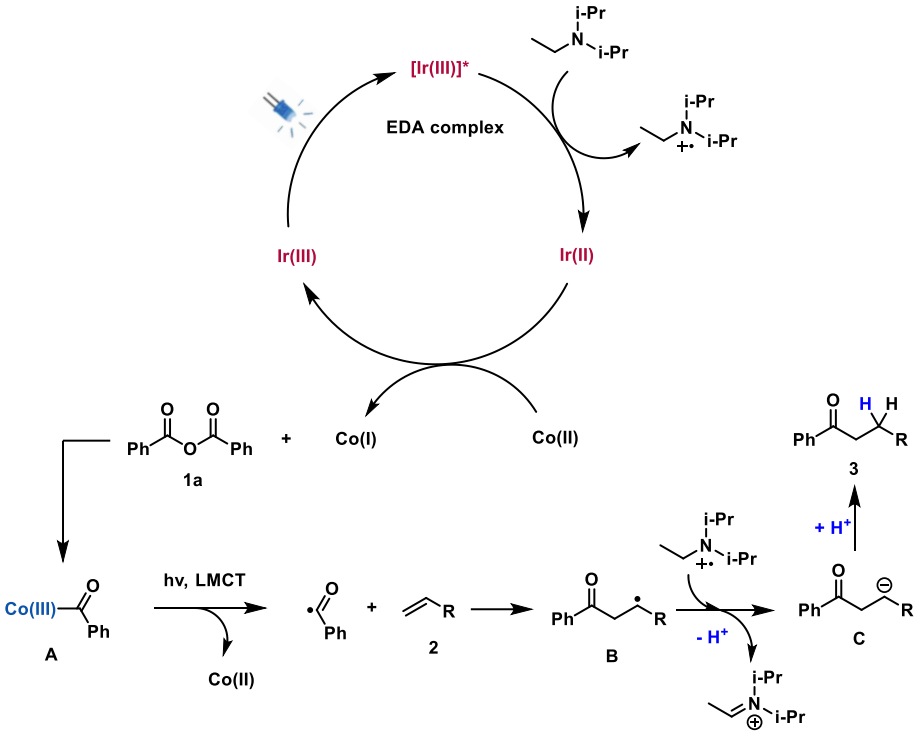
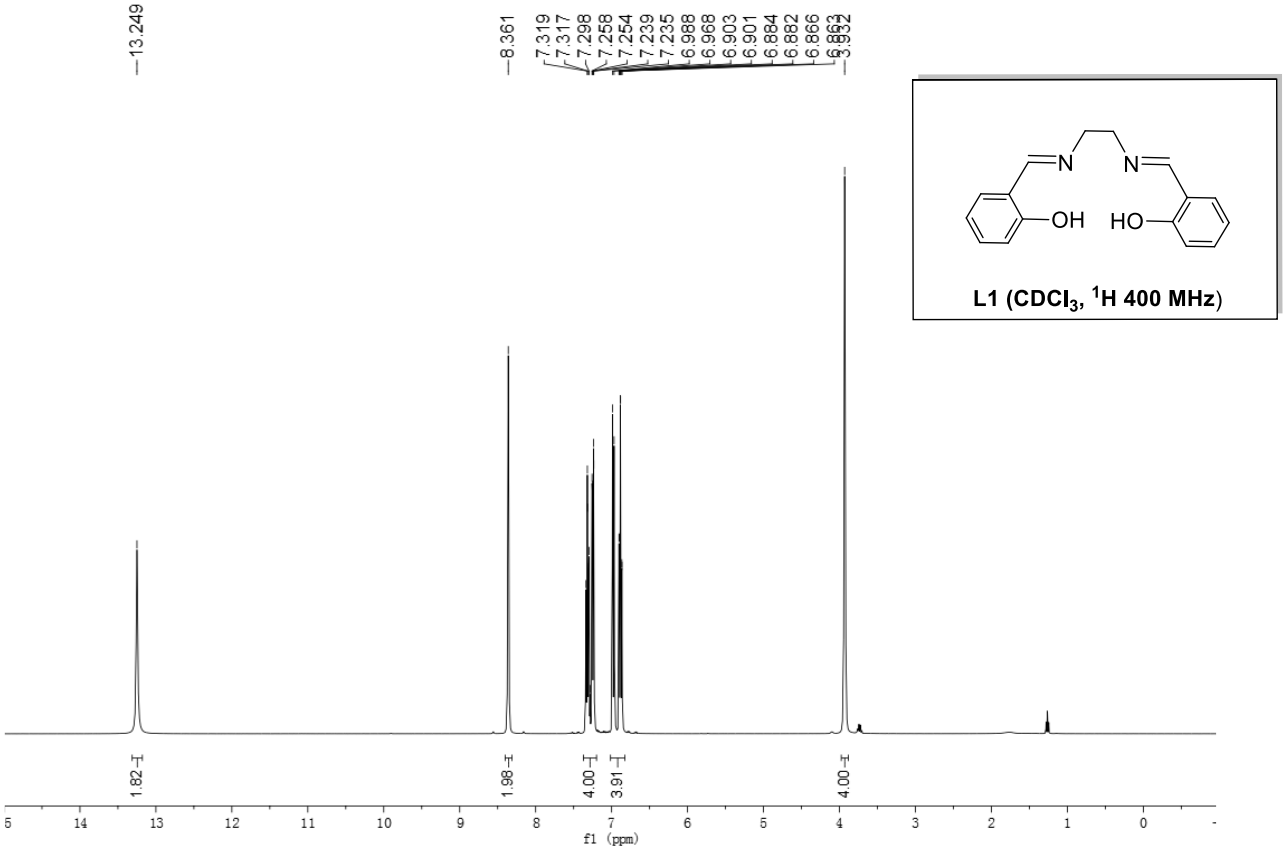


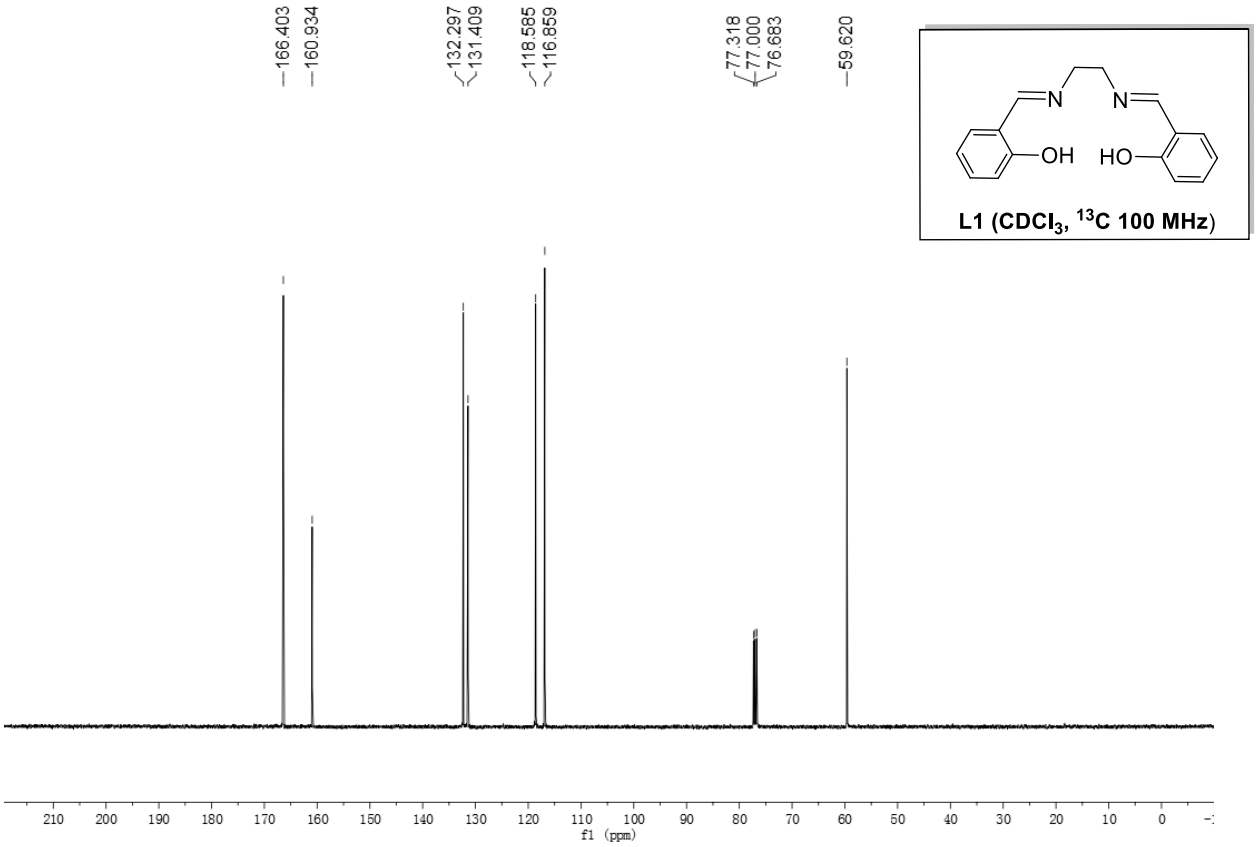
Figure S15. UV-vis spectrum of Ir[dF(CF_3)ppy(dtbbpy)]PF_6, **Co-5**, Ir[dF(CF_3)ppy(dtbbpy)]PF_6 and **Co-5** in CH_3CN

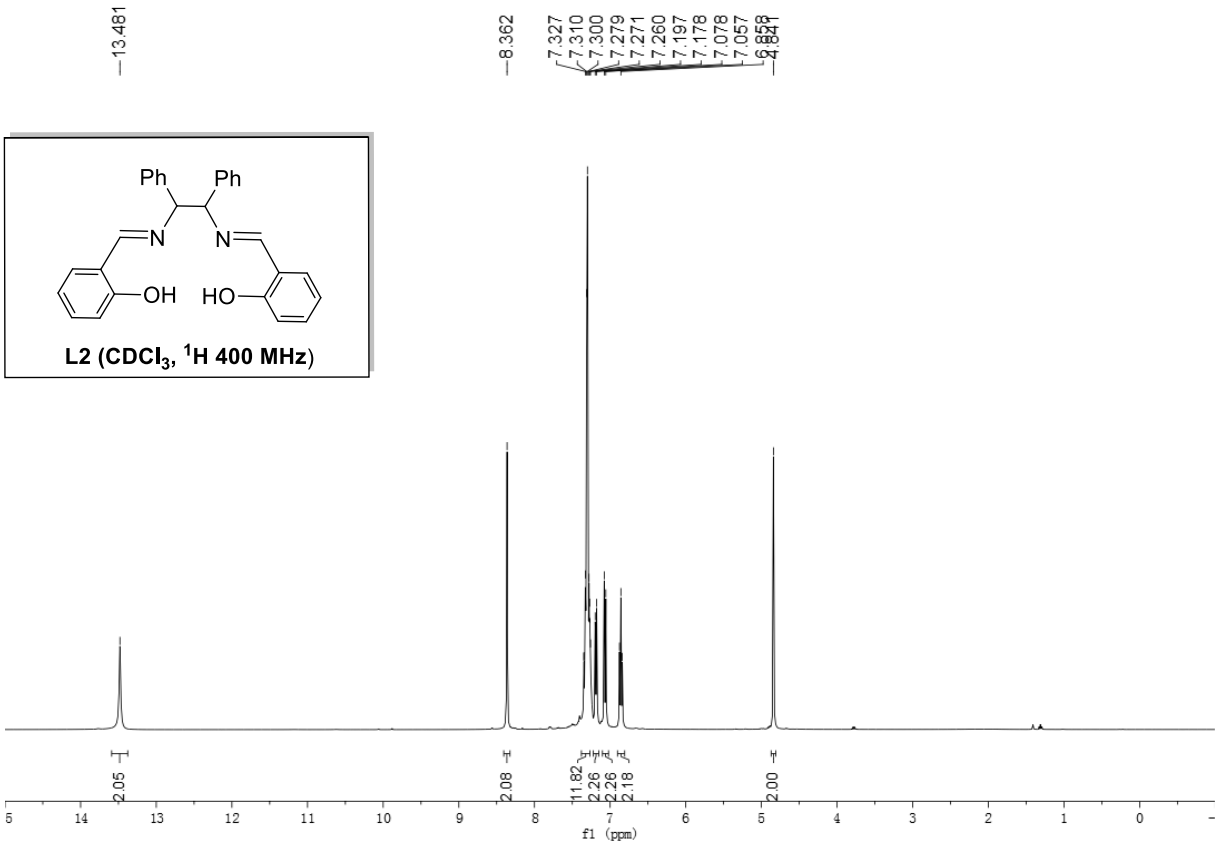


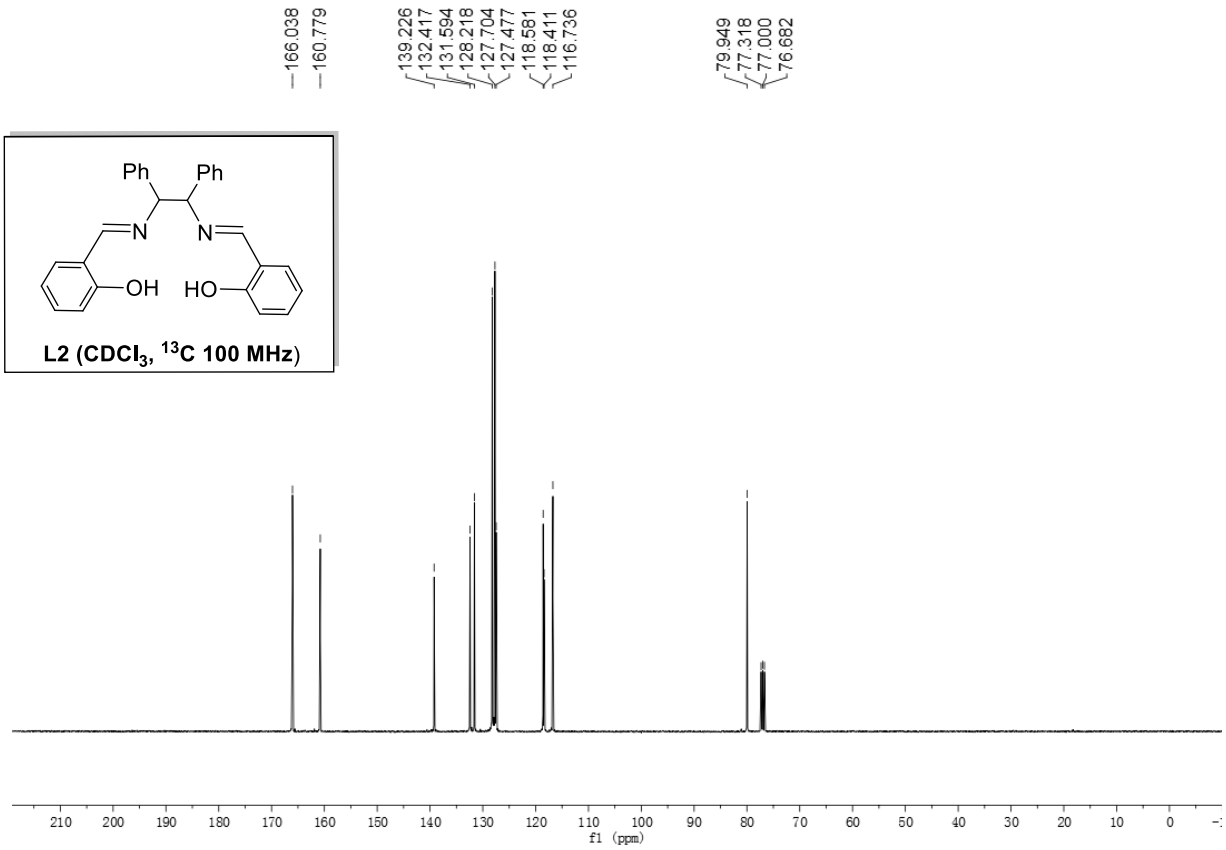
Scheme S3. Common mechanism of DIPEA as sacrificial reagent.

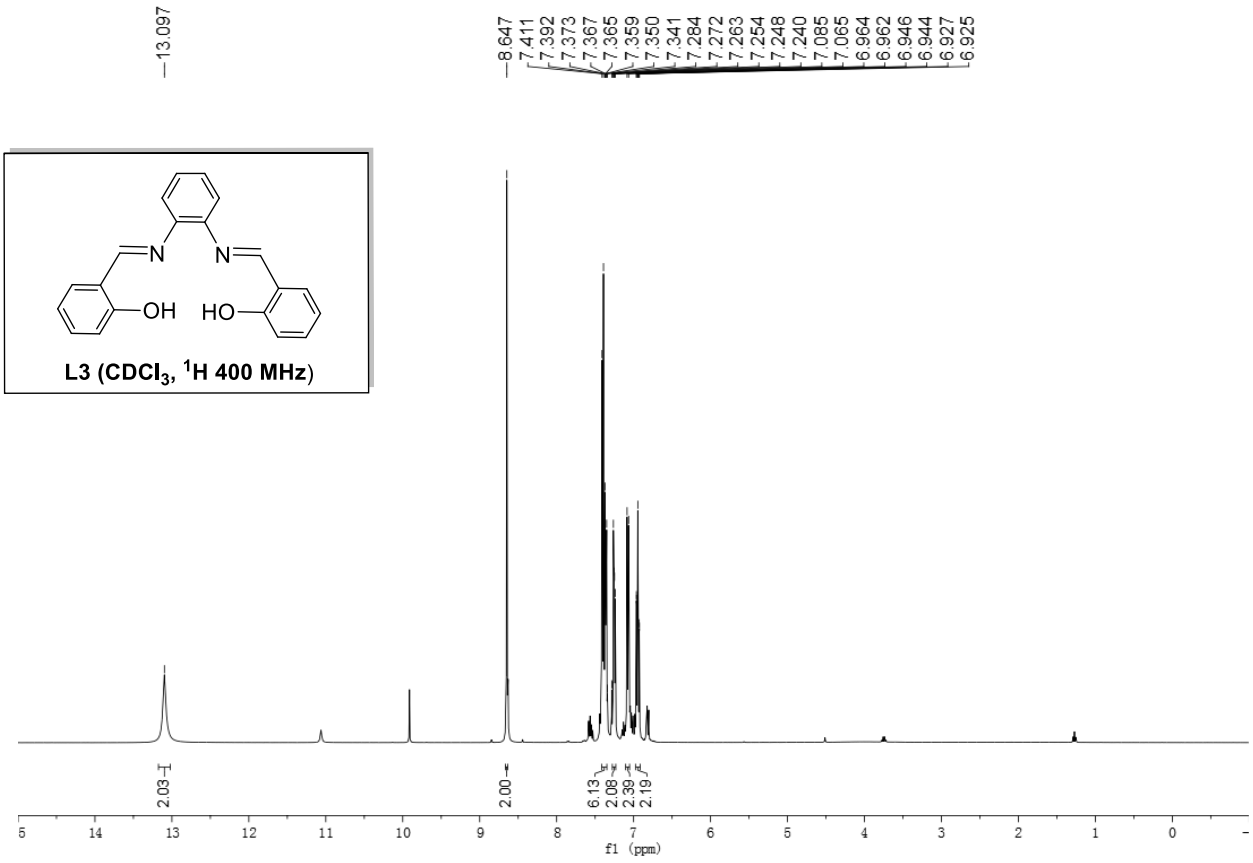
Spectra

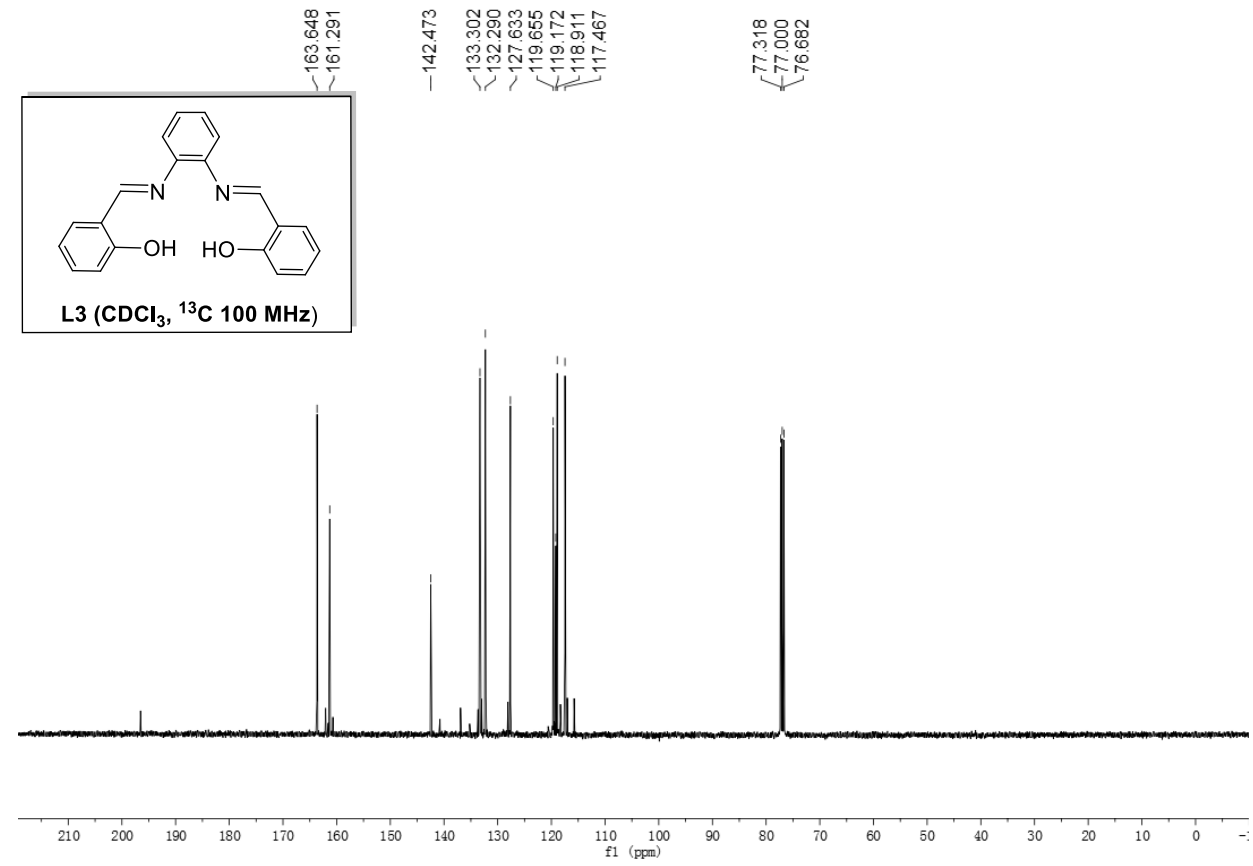

13.249
8.361
7.319
7.317
7.298
7.258
7.254
7.239
7.235
6.988
6.968
6.903
6.901
6.884
6.882
6.866
3.932
1.82
1.98
4.00
3.91
4.00
f1 (ppm)
L1 (CDCl3, 1H 400 MHz)

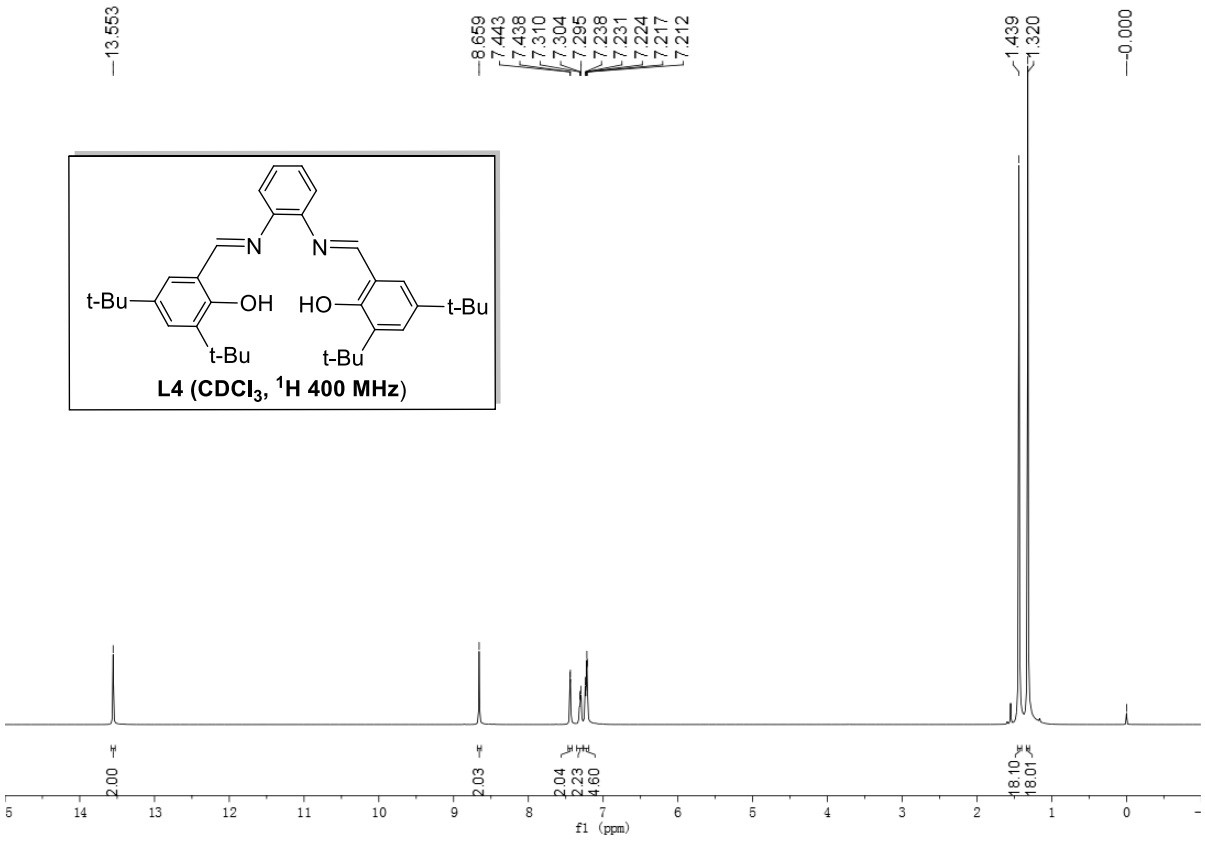

166.403
160.934
132.297
131.409
118.585
116.859
77.318
77.000
76.683
59.620
f1 (ppm)
L1 (CDCl3, 13C 100 MHz)

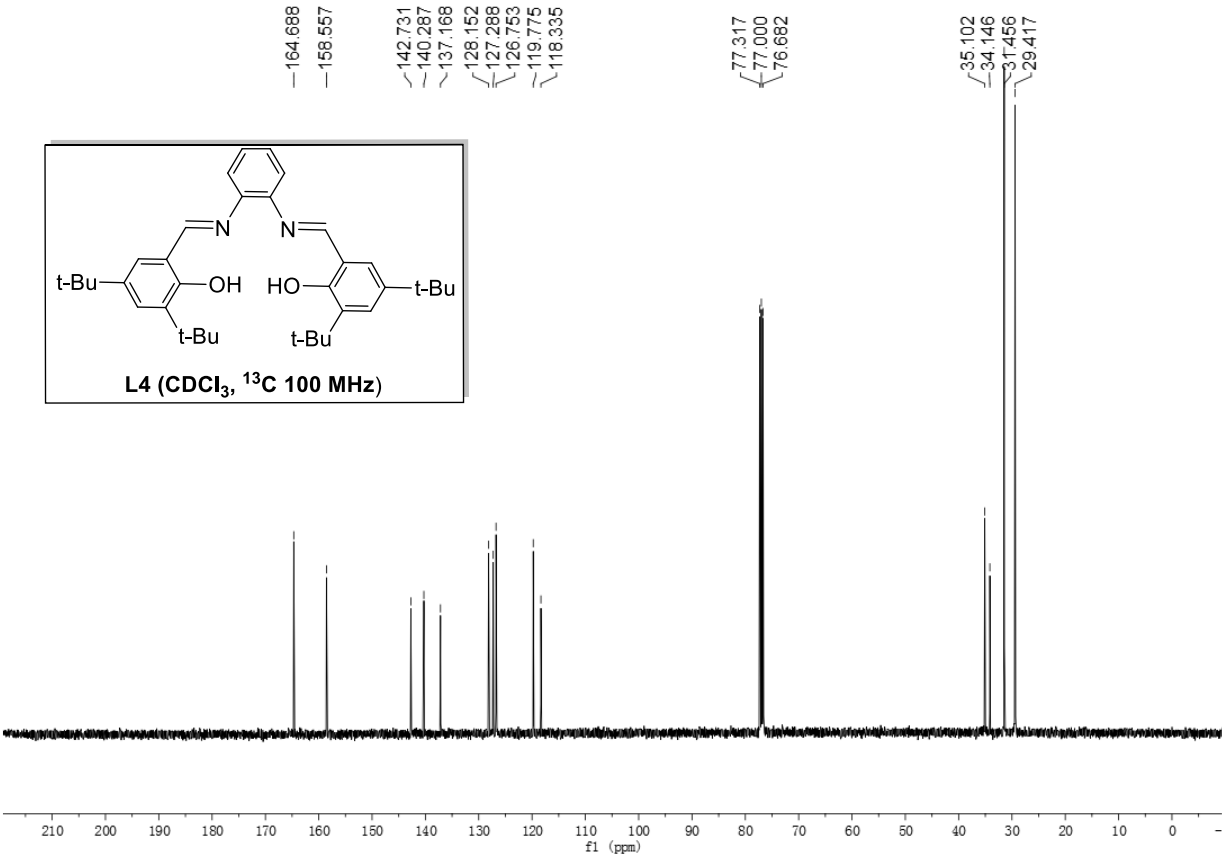

13.481
8.362
7.327
7.310
7.300
7.279
7.271
7.260
7.197
7.178
7.078
7.057
Ph
Ph
N
N
OH
HO
L2 (CDCl3, 1H 400 MHz)
2.05
2.08
11.82
2.26
2.26
2.18
2.00
f1 (ppm)

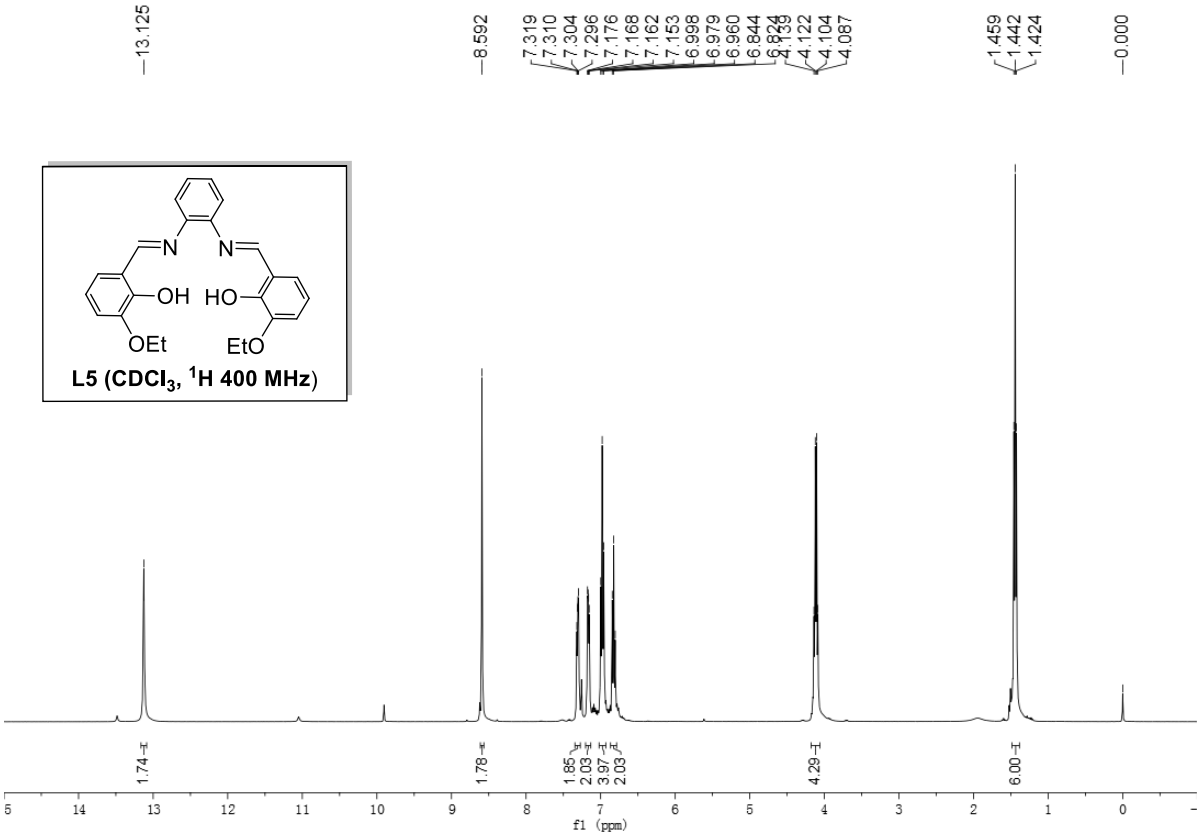

166.038
160.779
139.226
132.417
131.594
128.218
127.704
127.477
118.581
118.411
116.736
79.949
77.318
77.000
76.682
Ph
Ph
N
N
OH
HO
L2 (CDCl3, 13C 100 MHz)
f1 (ppm)

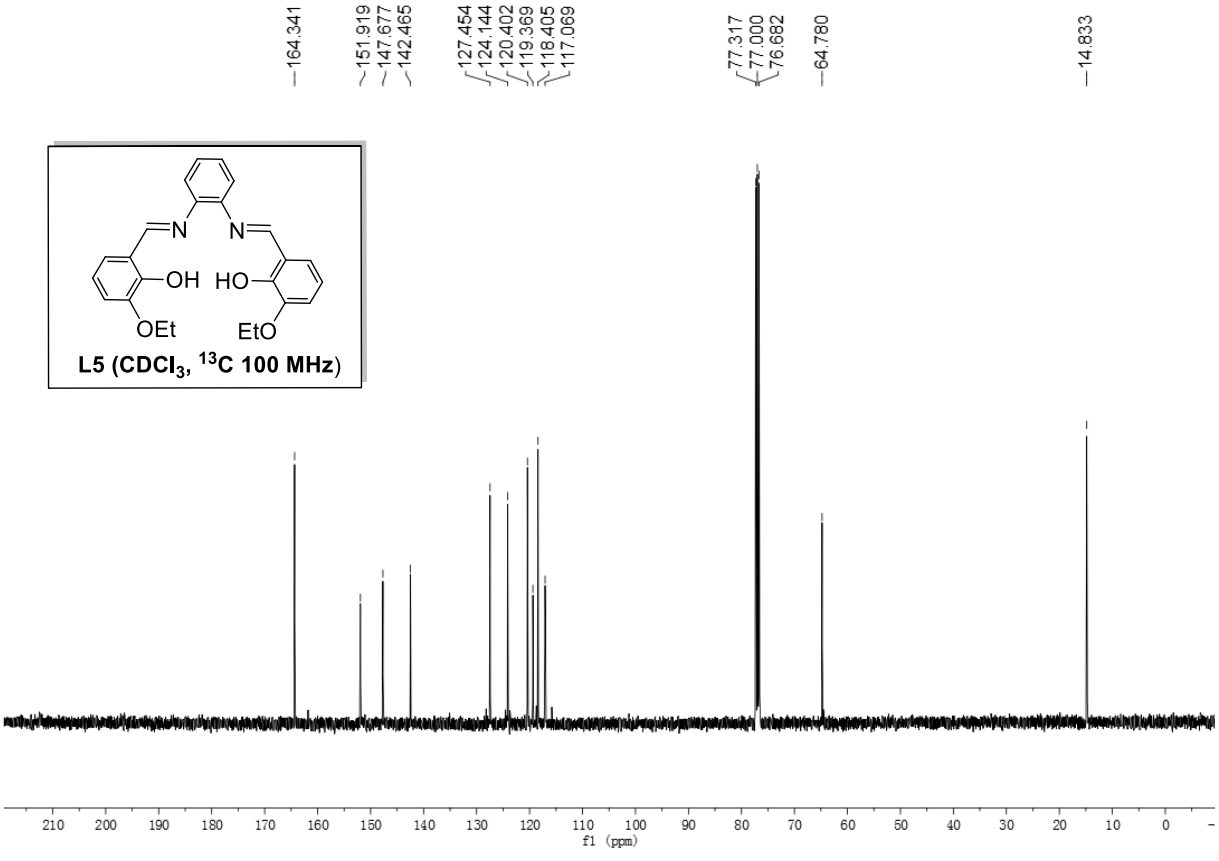

13.097
8.647
7.411
7.392
7.373
7.367
7.365
7.359
7.350
7.341
7.284
7.272
7.263
7.254
7.248
7.240
7.085
7.065
6.964
6.962
6.946
6.944
6.927
6.925
N
N
OH
HO
L3 (CDCl3, 1H 400 MHz)
2.03
2.00
6.13
2.08
2.39
2.19
f1 (ppm)

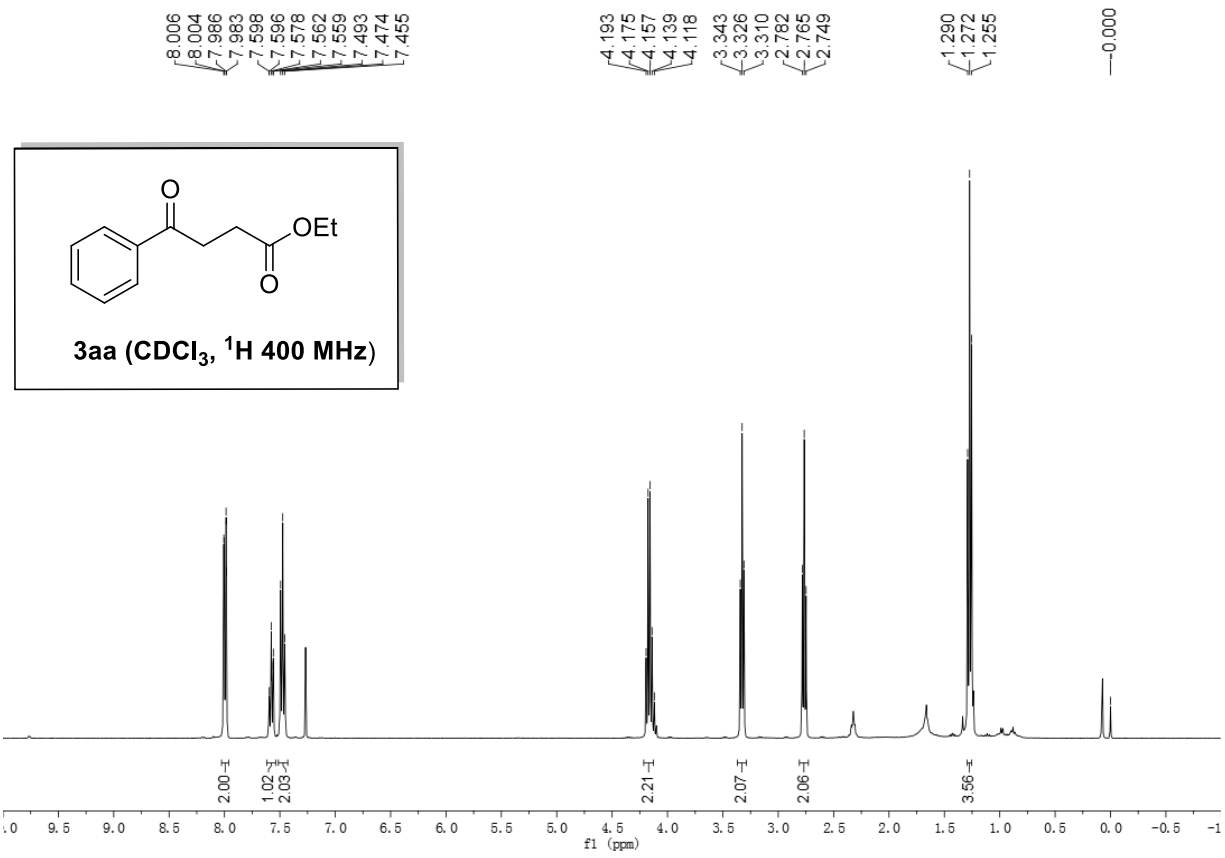

163.648
161.291
142.473
133.302
132.290
127.633
119.655
119.172
118.911
117.467
77.318
77.000
76.682
N
N
OH
HO
L3 (CDCl3, 13C 100 MHz)
f1 (ppm)

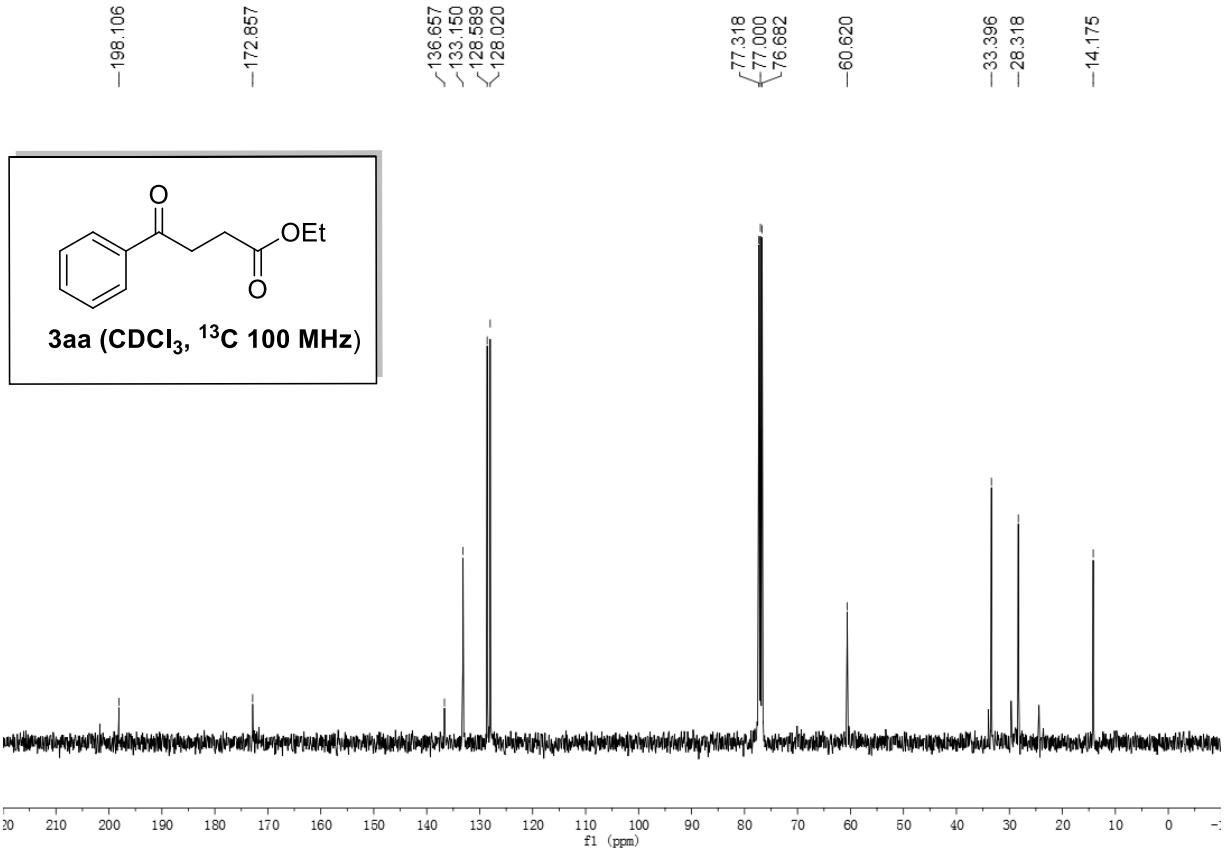

13.553
8.659
7.443
7.438
7.310
7.304
7.295
7.238
7.231
7.224
7.217
7.212
1.439
1.320
0.000
t-Bu
OH
HO
t-Bu
t-Bu
t-Bu
L4 (CDCl3, 1H 400 MHz)
2.00
2.03
2.04
2.23
4.60
18.10
18.01
f1 (ppm)

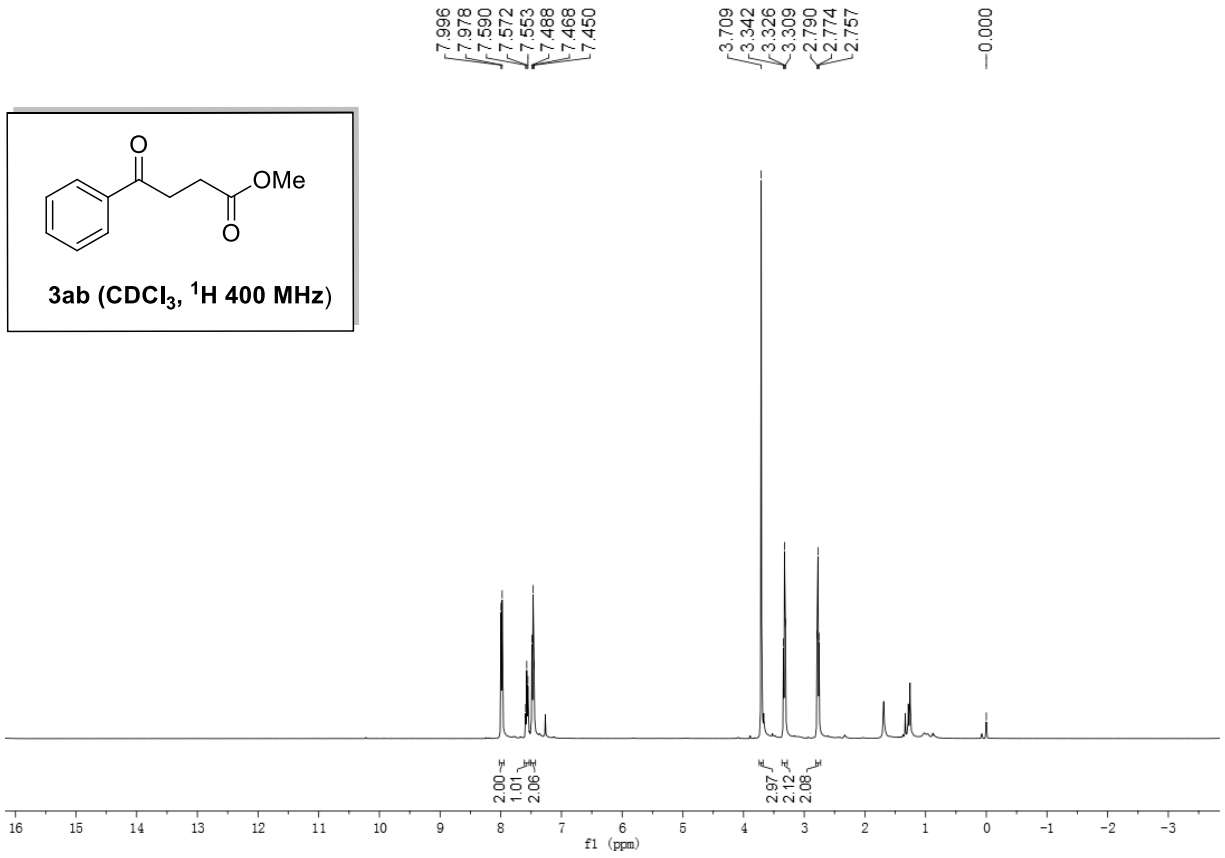

164.688
158.557
142.731
140.287
137.168
128.152
127.288
126.753
119.775
118.335
77.317
77.000
76.682
35.102
34.146
31.456
29.417
t-Bu
OH
HO
t-Bu
t-Bu
t-Bu
L4 (CDCl3, 13C 100 MHz)
f1 (ppm)

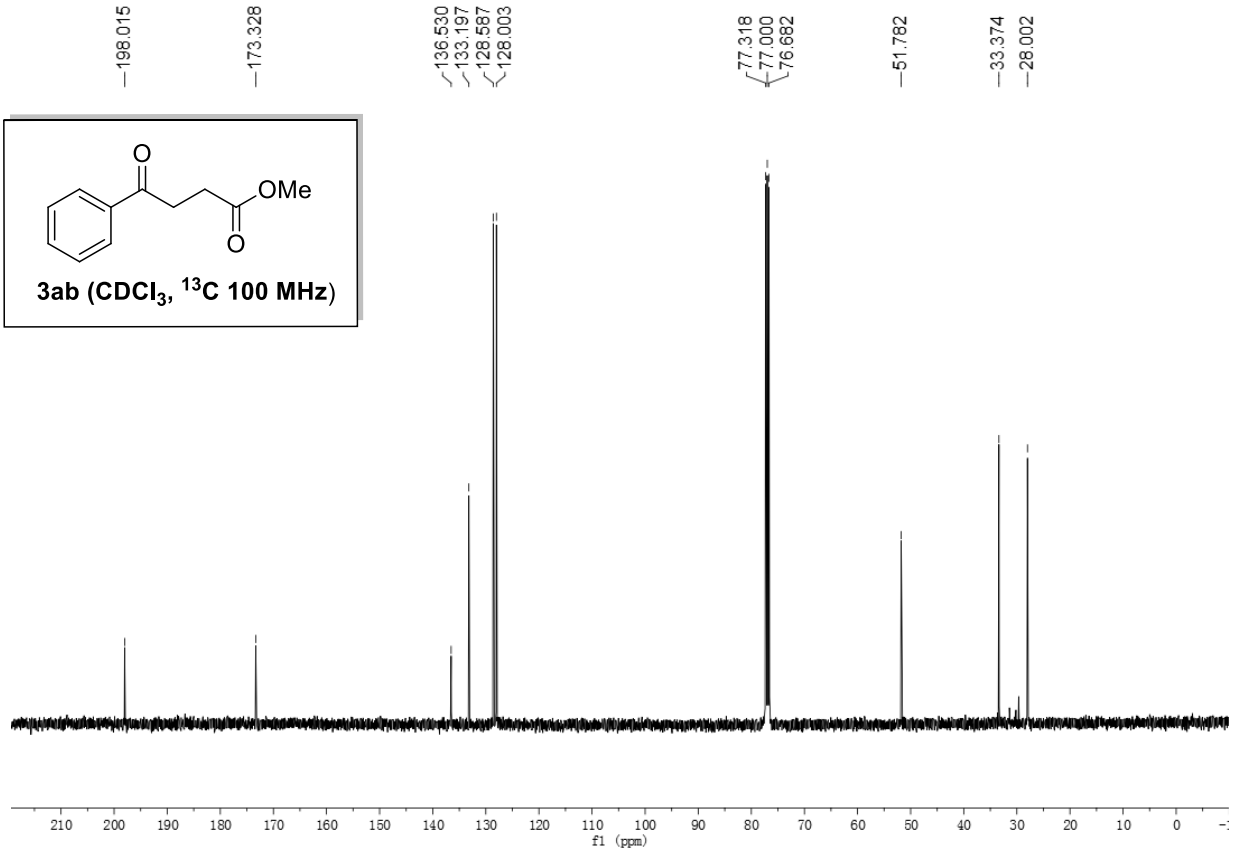

13.125
8.592
7.319
7.310
7.304
7.296
7.176
7.168
7.162
7.153
6.998
6.979
6.960
6.844
6.824
6.139
4.122
4.104
4.087
1.459
1.442
1.424
0.000
OH
HO
OEt
EtO
L5 (CDCl3, 1H 400 MHz)
1.74
1.78
1.85
2.03
3.97
2.03
4.29
6.00
f1 (ppm)

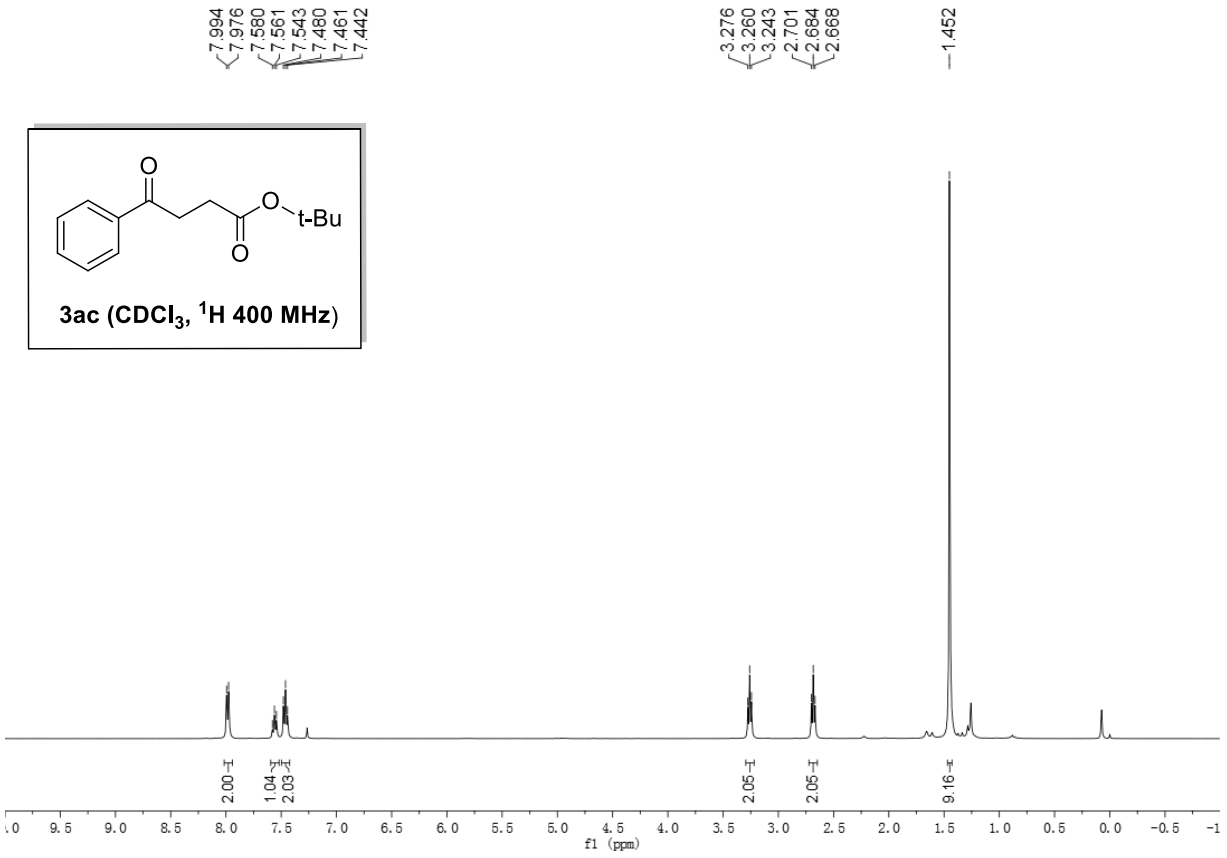

164.341
151.919
147.677
142.465
127.454
124.144
120.402
119.369
118.405
117.069
77.317
77.000
76.682
64.780
14.833
OH
HO
OEt
EtO
L5 (CDCl3, 13C 100 MHz)
f1 (ppm)

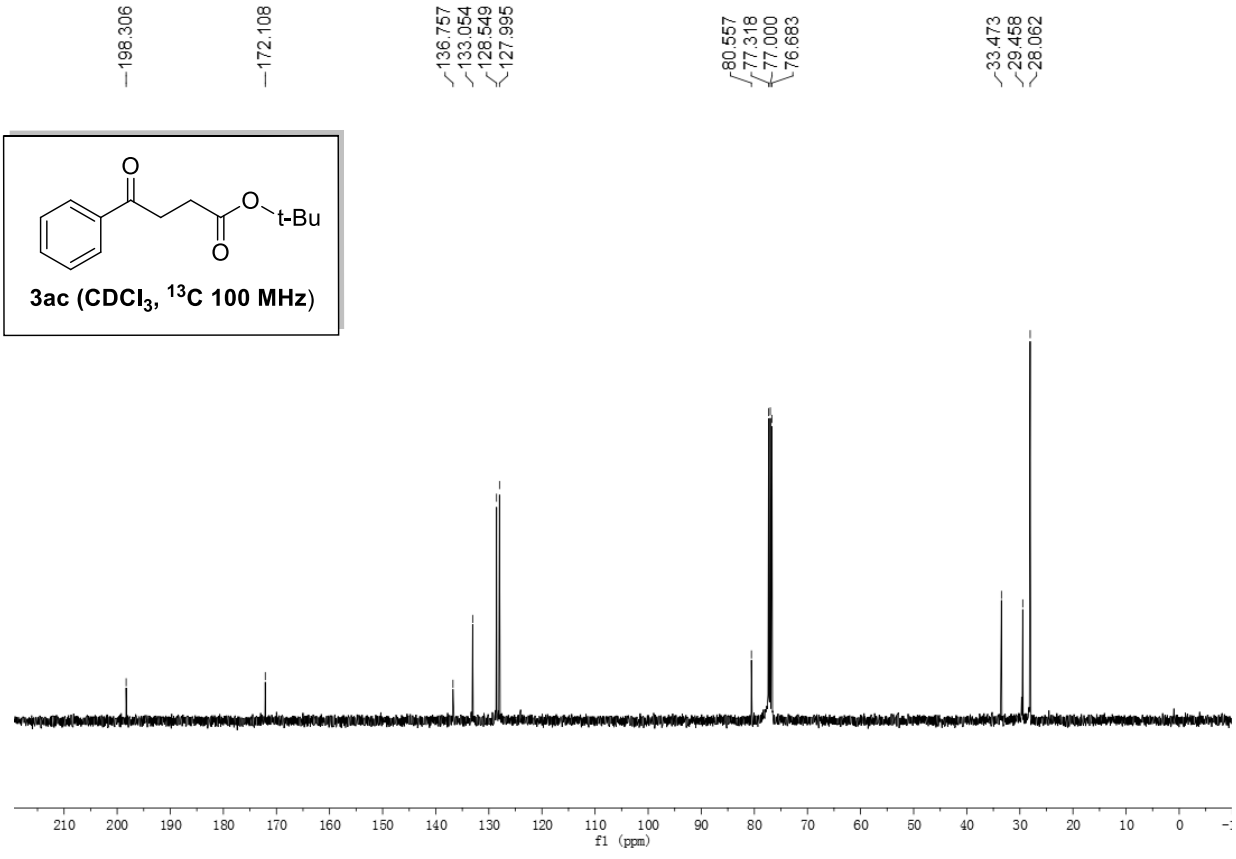

8.006
8.004
7.986
7.983
7.598
7.596
7.578
7.562
7.559
7.493
7.474
7.455
4.193
4.175
4.157
4.139
4.118
3.343
3.326
3.310
2.782
2.765
2.749
1.290
1.272
1.255
0.000
O
OEt
O
3aa (CDCl3, 1H 400 MHz)
2.00
1.02
2.03
2.21
2.07
2.06
3.56
f1 (ppm)

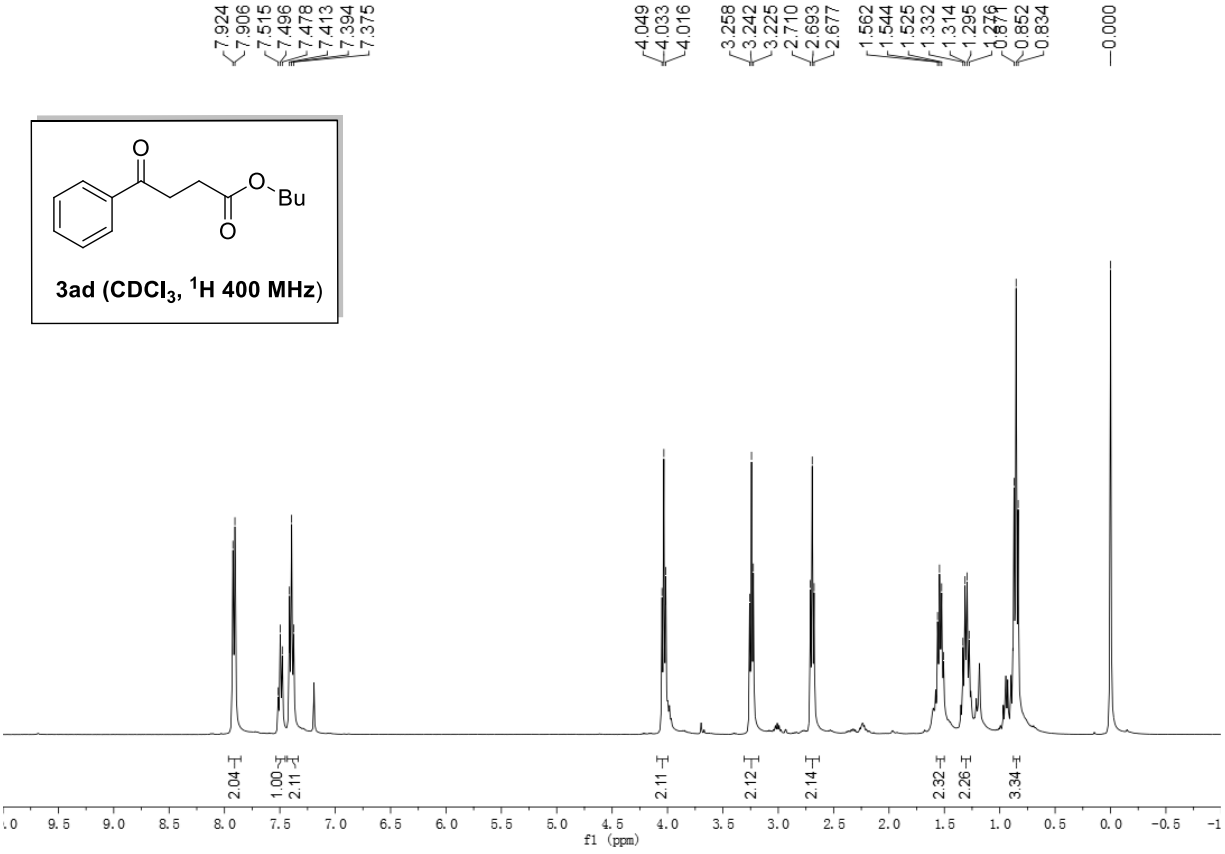

198.106
172.857
136.657
133.150
128.589
128.020
77.318
77.000
76.682
60.620
33.396
28.318
14.175
O
OEt
O
3aa (CDCl3, 13C 100 MHz)
f1 (ppm)

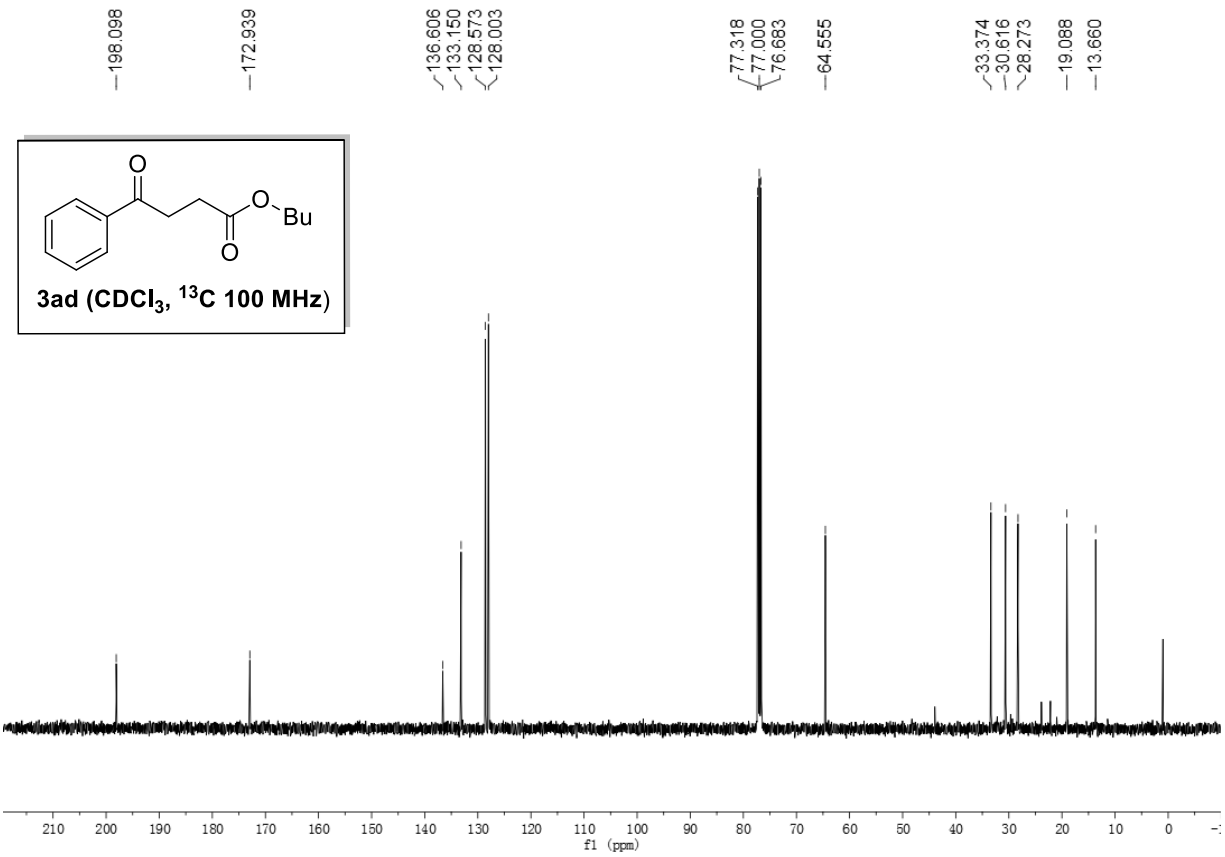

7.996
7.978
7.590
7.572
7.553
7.488
7.468
7.450
3.709
3.342
3.326
3.309
2.790
2.774
2.757
0.000
O
OMe
O
3ab (CDCl3, 1H 400 MHz)
2.00
1.01
2.06
2.97
2.12
2.08
f1 (ppm)


198.015
173.328
136.530
133.197
128.587
128.003
77.318
77.000
76.682
51.782
33.374
28.002
O
OMe
O
3ab (CDCl3, 13C 100 MHz)
f1 (ppm)


7.994
7.976
7.580
7.561
7.543
7.480
7.461
7.442
3.276
3.260
3.243
2.701
2.684
2.668
1.452
O
O
O
t-Bu
3ac (CDCl3, 1H 400 MHz)
2.00
1.04
2.03
2.05
2.05
9.16
f1 (ppm)


198.306
172.108
136.757
133.054
128.549
127.995
80.557
77.318
77.000
76.683
33.473
29.458
28.062
O
O
O
t-Bu
3ac (CDCl3, 13C 100 MHz)
f1 (ppm)


7.924
7.906
7.515
7.496
7.478
7.413
7.394
7.375
4.049
4.033
4.016
3.258
3.242
3.225
2.710
2.693
2.677
1.562
1.544
1.525
1.332
1.314
1.295
0.871
0.852
0.834
0.000
O
O
Bu
O
3ad (CDCl3, 1H 400 MHz)
2.04
1.00
2.11
2.11
2.12
2.14
2.32
2.26
3.34
f1 (ppm)


198.098
172.939
136.606
133.150
128.573
128.003
77.318
77.000
76.683
64.555
33.374
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28.273
19.088
13.660
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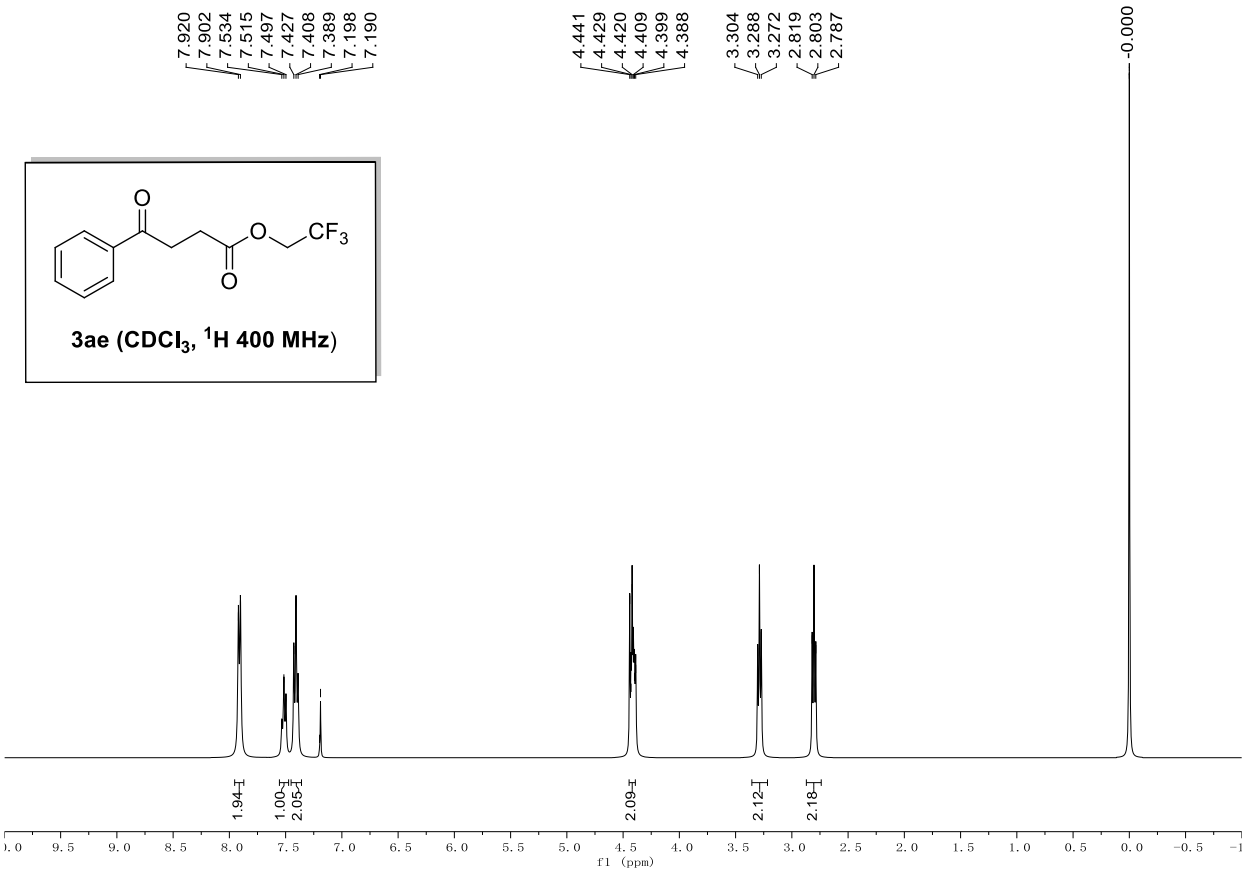
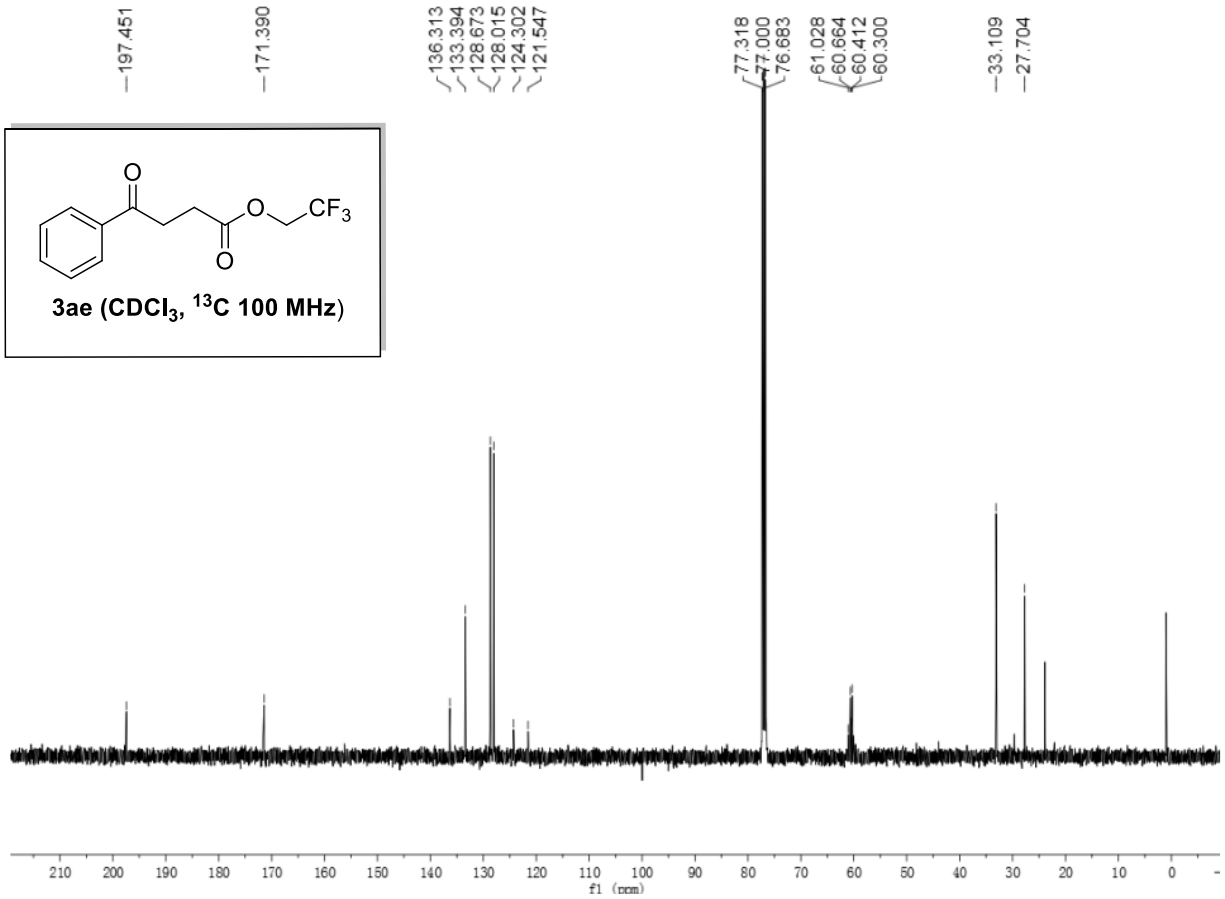
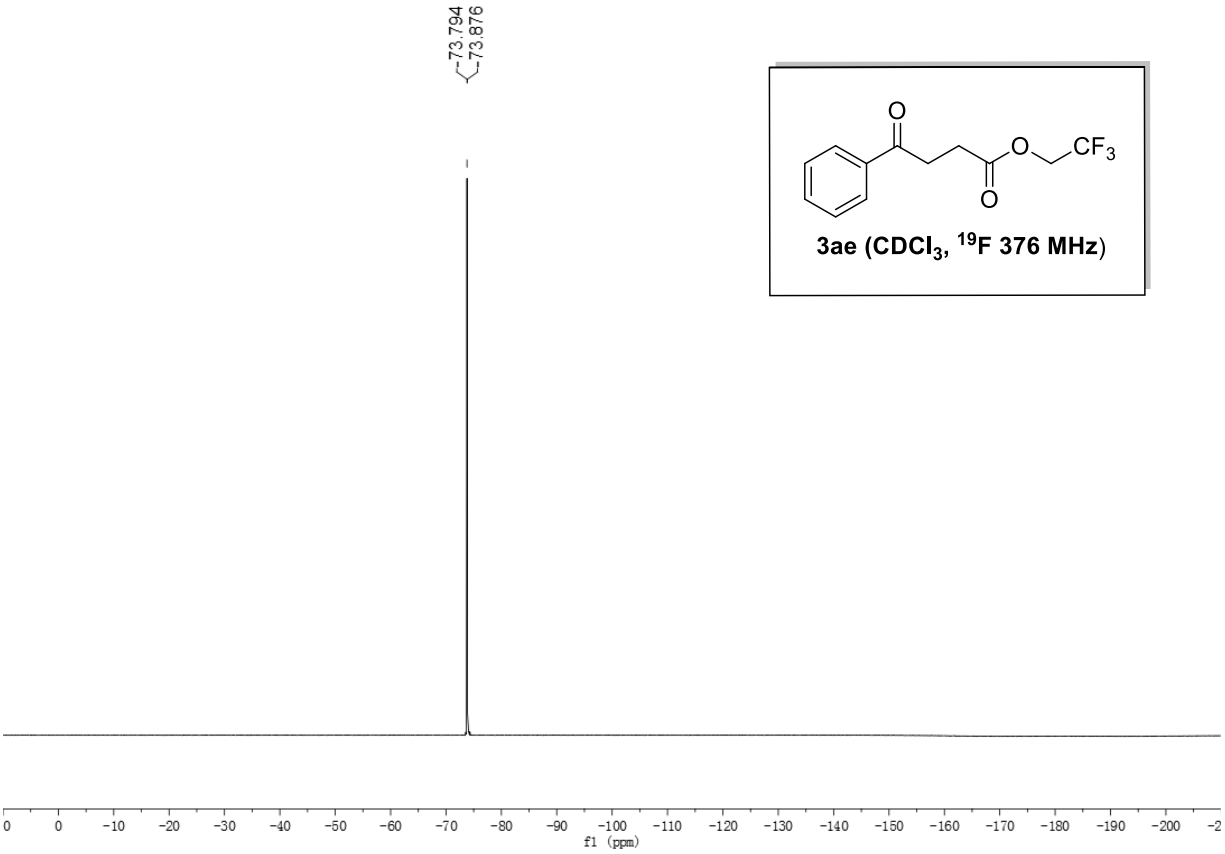
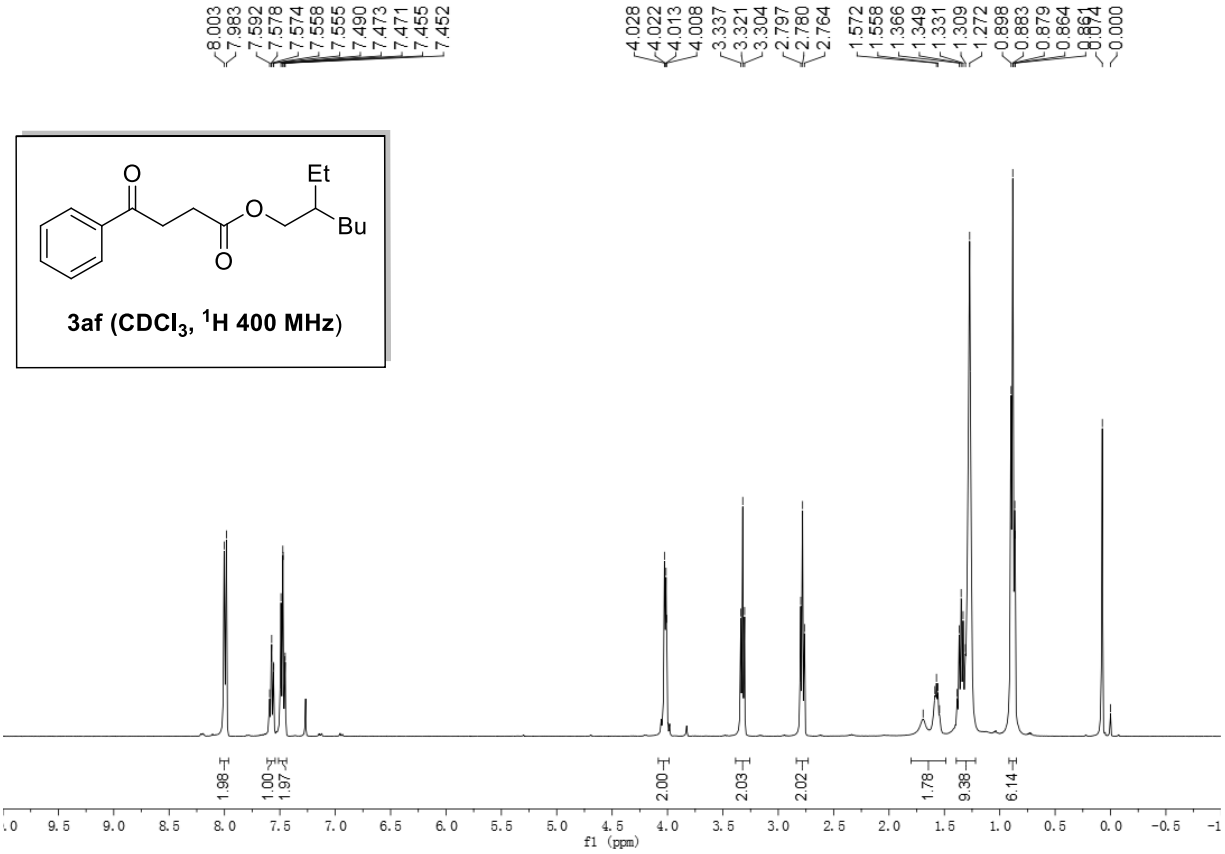
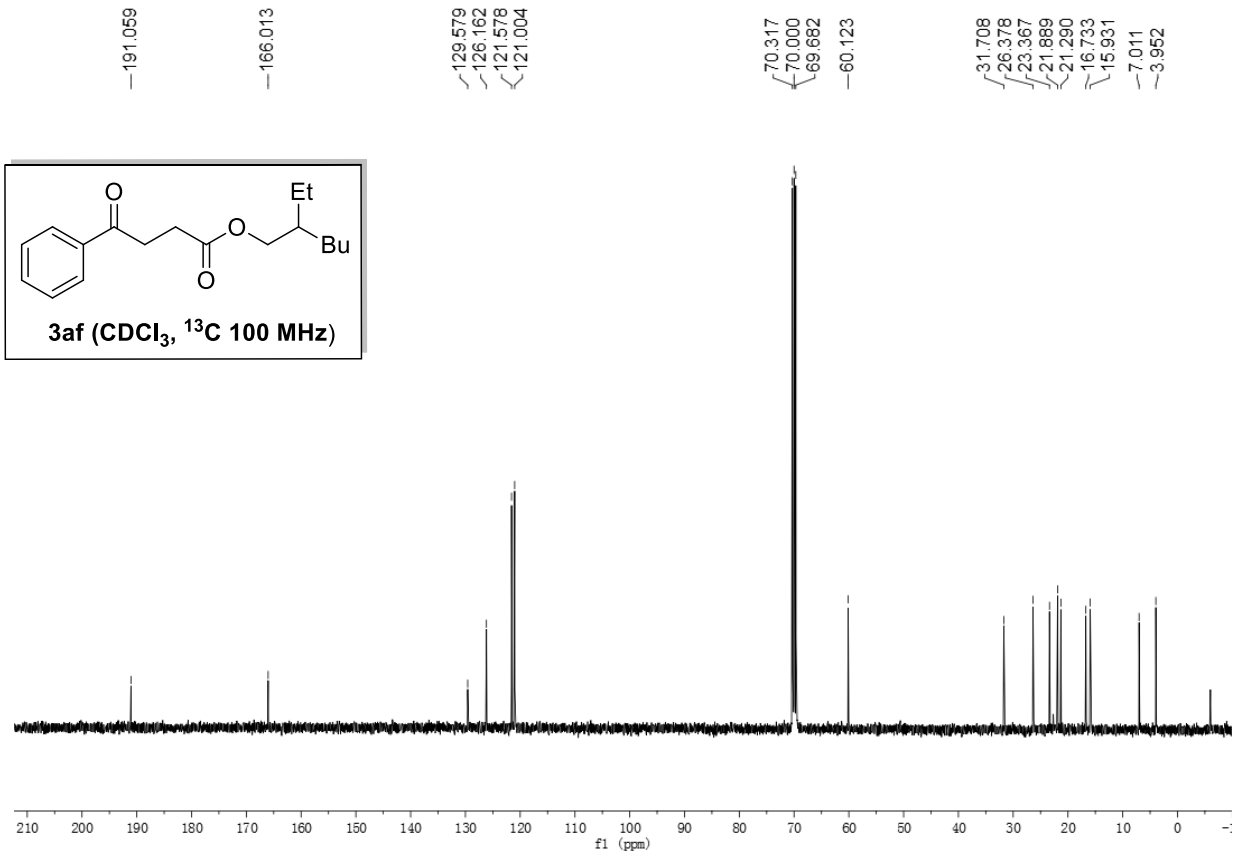
O
Bu
O
3ad (CDCl3, 13C 100 MHz)
f1 (ppm)

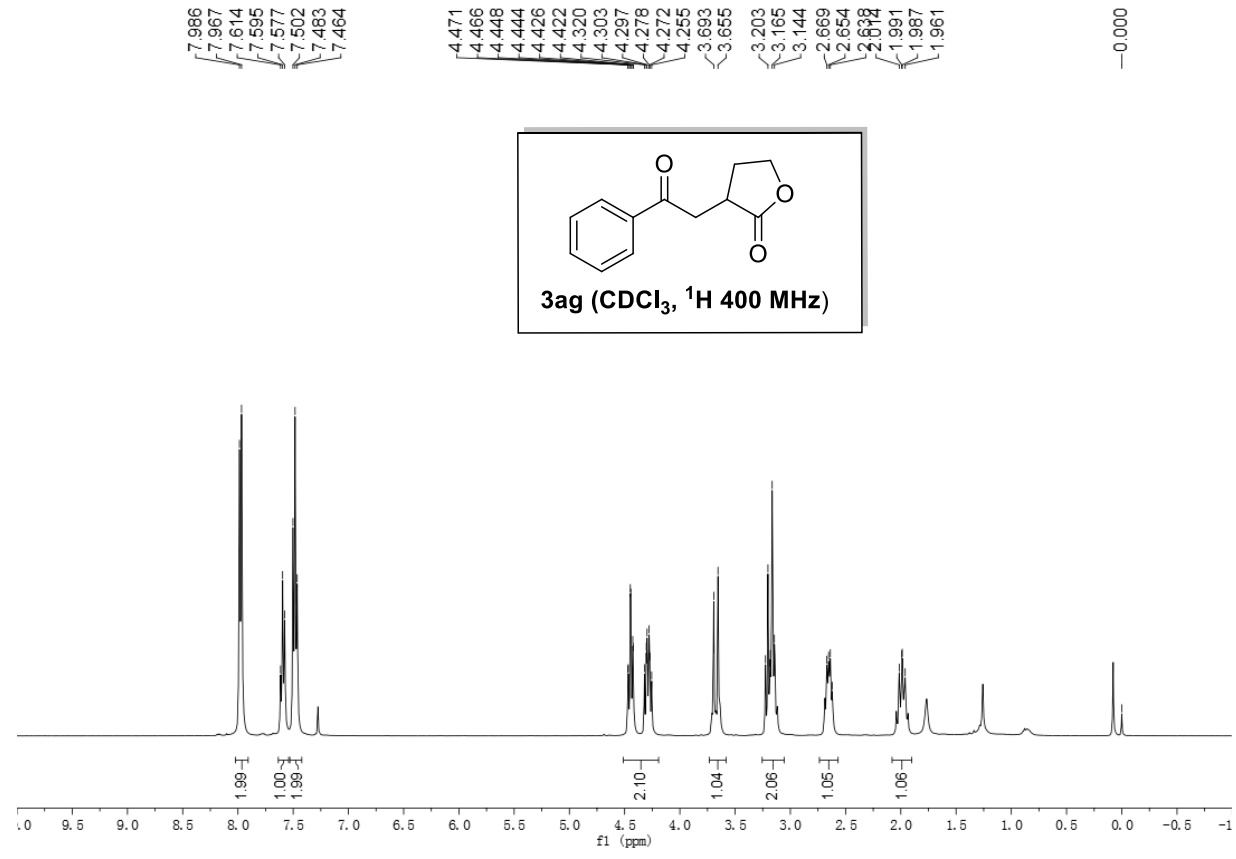

7.920
7.902
7.534
7.515
7.497
7.427
7.408
7.389
7.198
7.190
4.441
4.429
4.420
4.409
4.399
4.388
3.304
3.288
3.272
2.819
2.803
2.787
-0.000
O
O
O
CF3
3ae (CDCl3, 1H 400 MHz)
1.94
1.00
2.05
2.09
2.12
2.18
f1 (ppm)

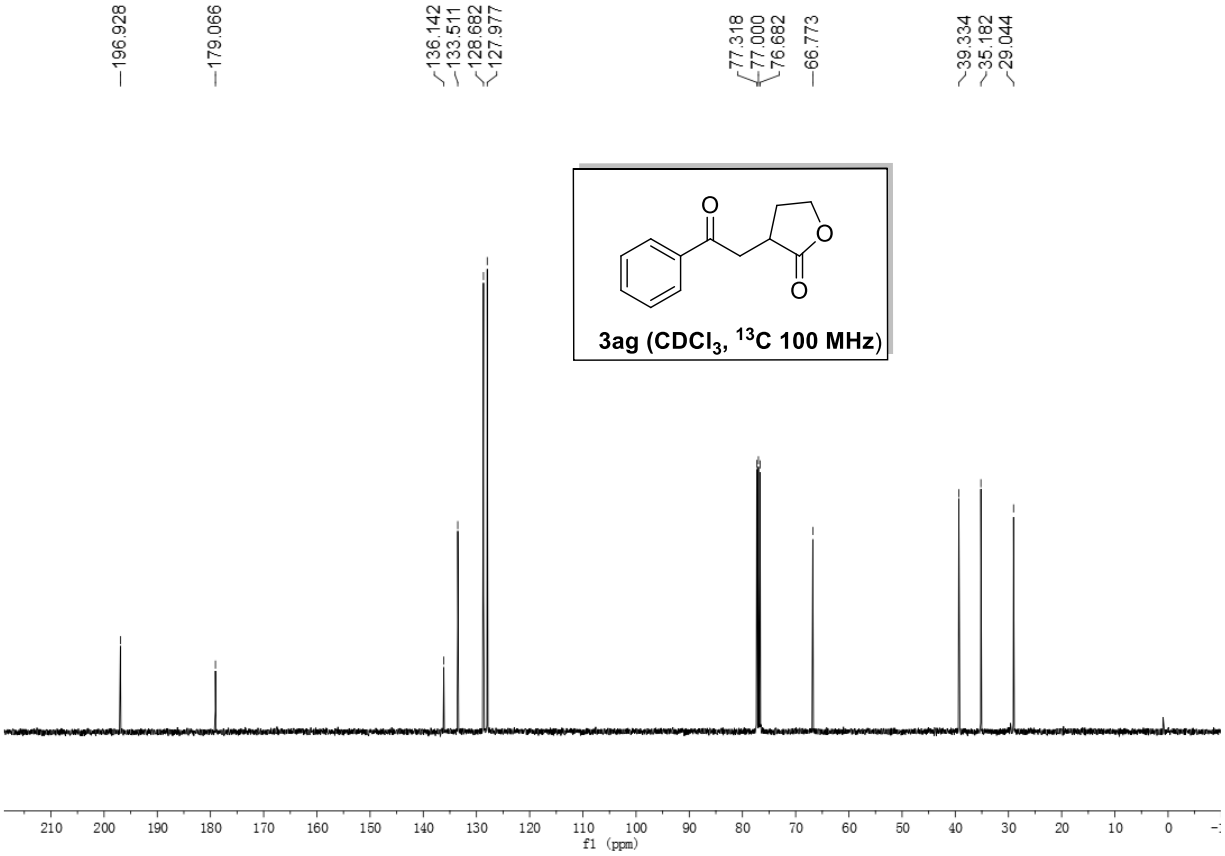

197.451
171.390
136.313
133.394
128.673
128.015
124.302
121.547
77.318
77.000
76.683
61.028
60.664
60.412
60.300
33.109
27.704
O
O
O
CF3
3ae (CDCl3, 13C 100 MHz)
f1 (ppm)

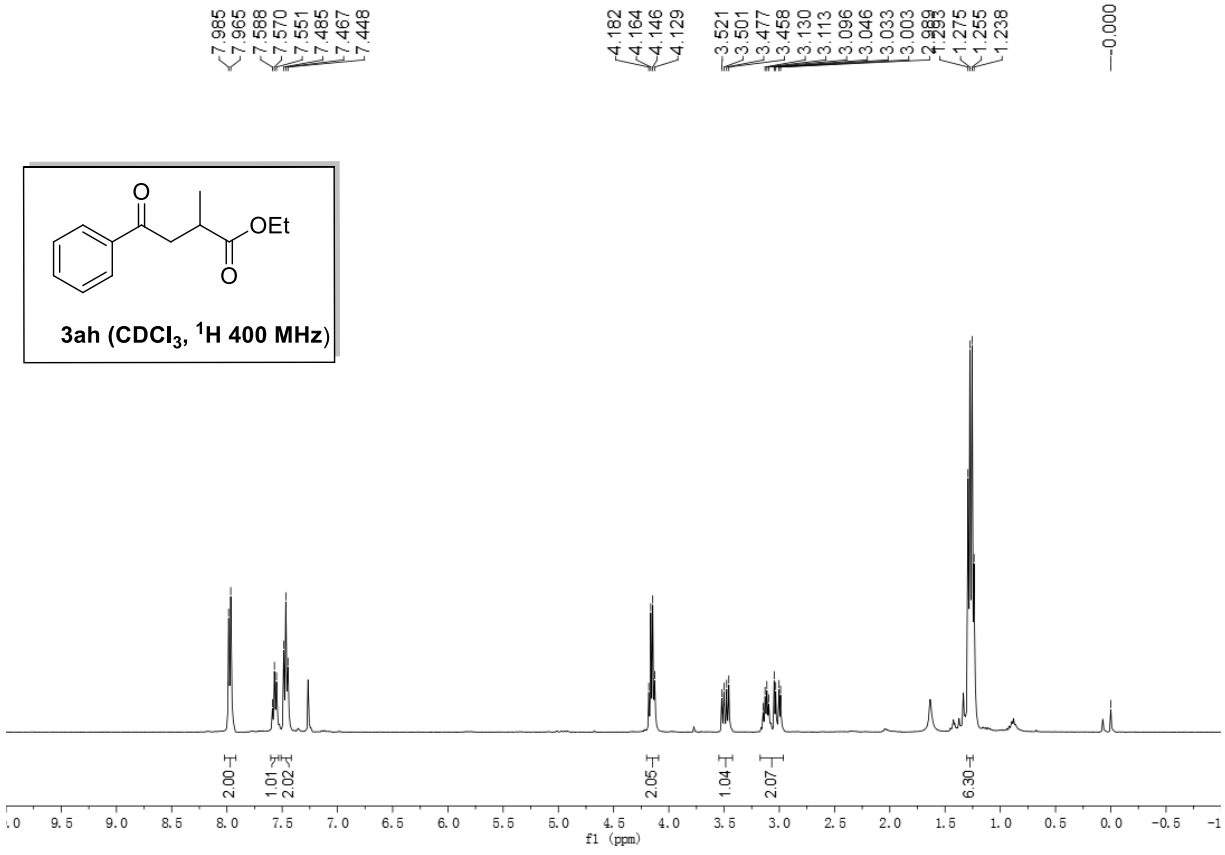

73.794
73.876
O
O
O
CF3
3ae (CDCl3, 19F 376 MHz)
f1 (ppm)

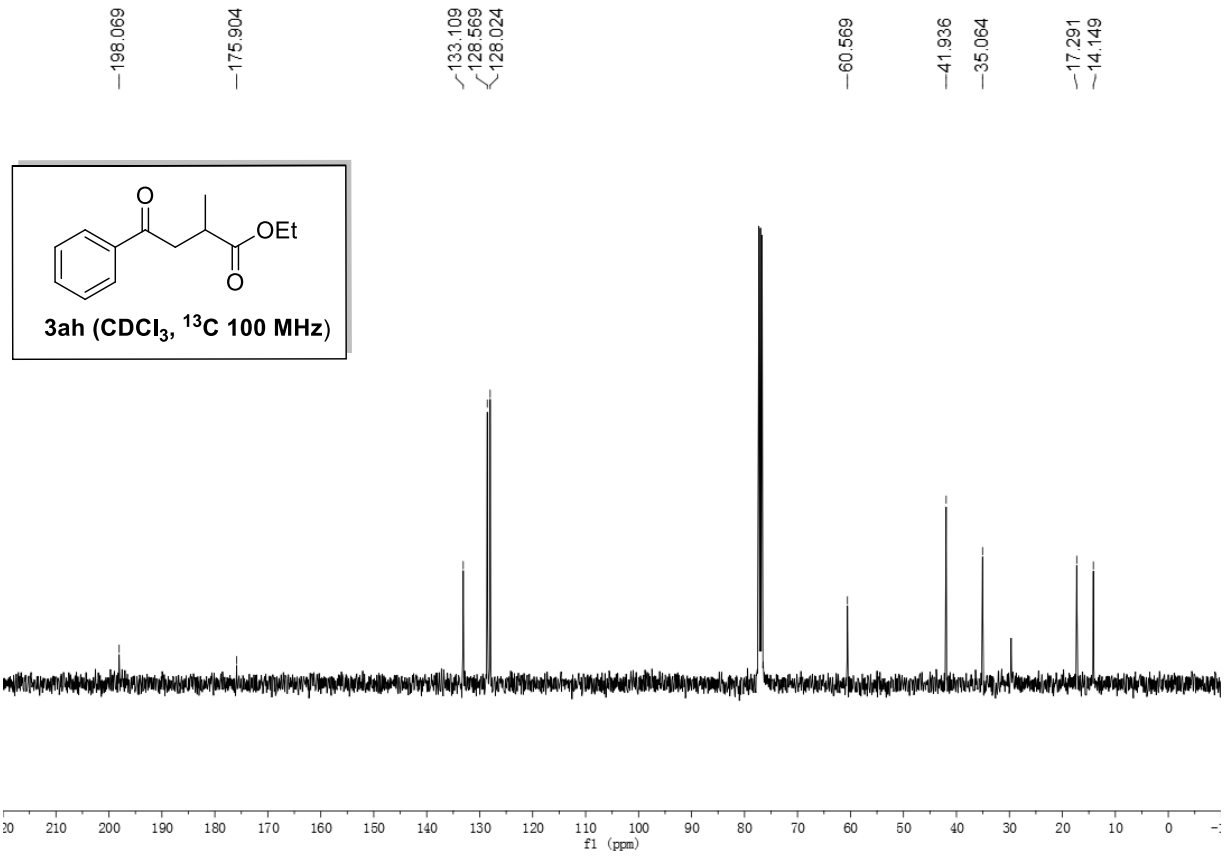

8.003
7.983
7.592
7.578
7.574
7.558
7.555
7.490
7.473
7.471
7.455
7.452
4.028
4.022
4.013
4.008
3.337
3.321
3.304
2.797
2.780
2.764
1.572
1.558
1.366
1.349
1.331
1.309
1.272
0.898
0.883
0.879
0.864
0.861
0.000
O
O
O
Et
Bu
3af (CDCl3, 1H 400 MHz)
1.98
1.00
1.97
2.00
2.03
2.02
1.78
9.38
6.14
f1 (ppm)

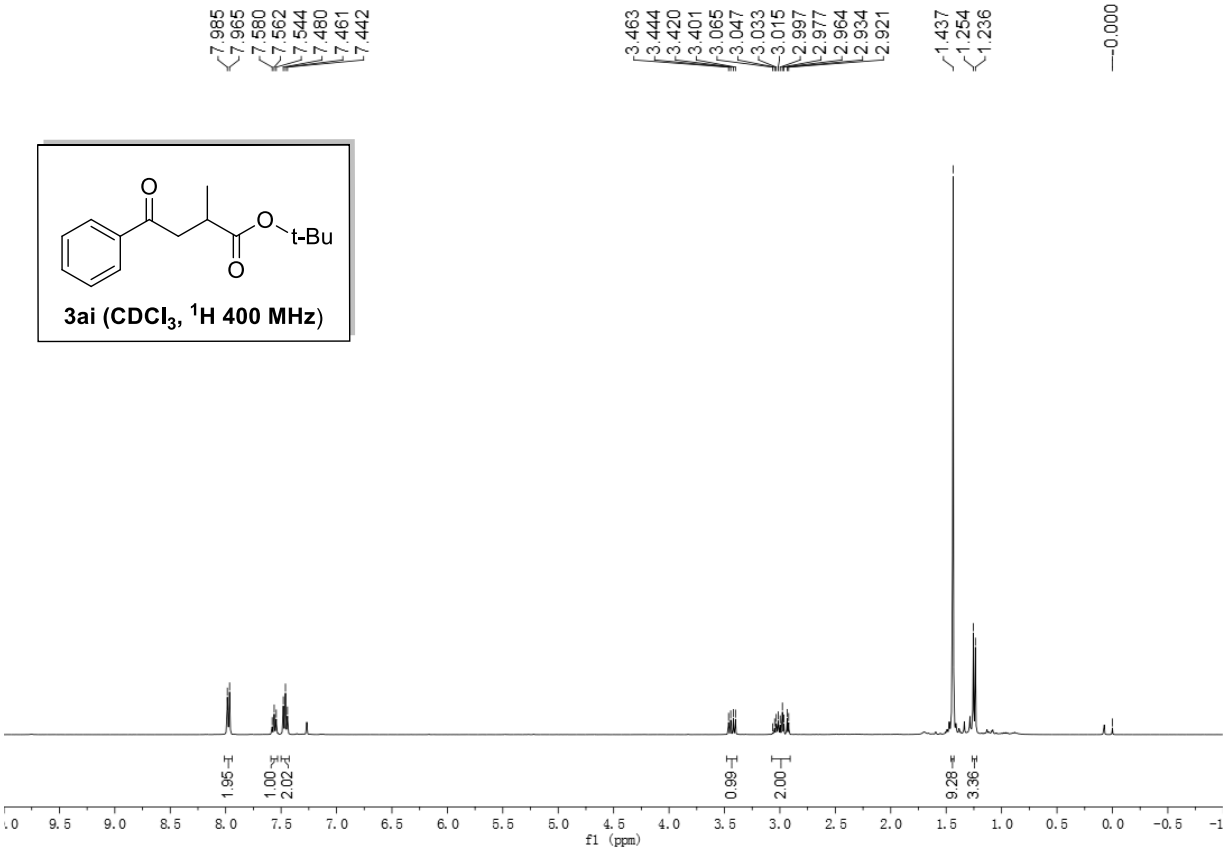

191.059
166.013
129.579
126.162
121.578
121.004
70.317
70.000
69.682
60.123
31.708
26.378
23.367
21.889
21.290
16.733
15.931
7.011
3.952
O
Et
O
Bu
O
3af (CDCl3, 13C 100 MHz)
f1 (ppm)

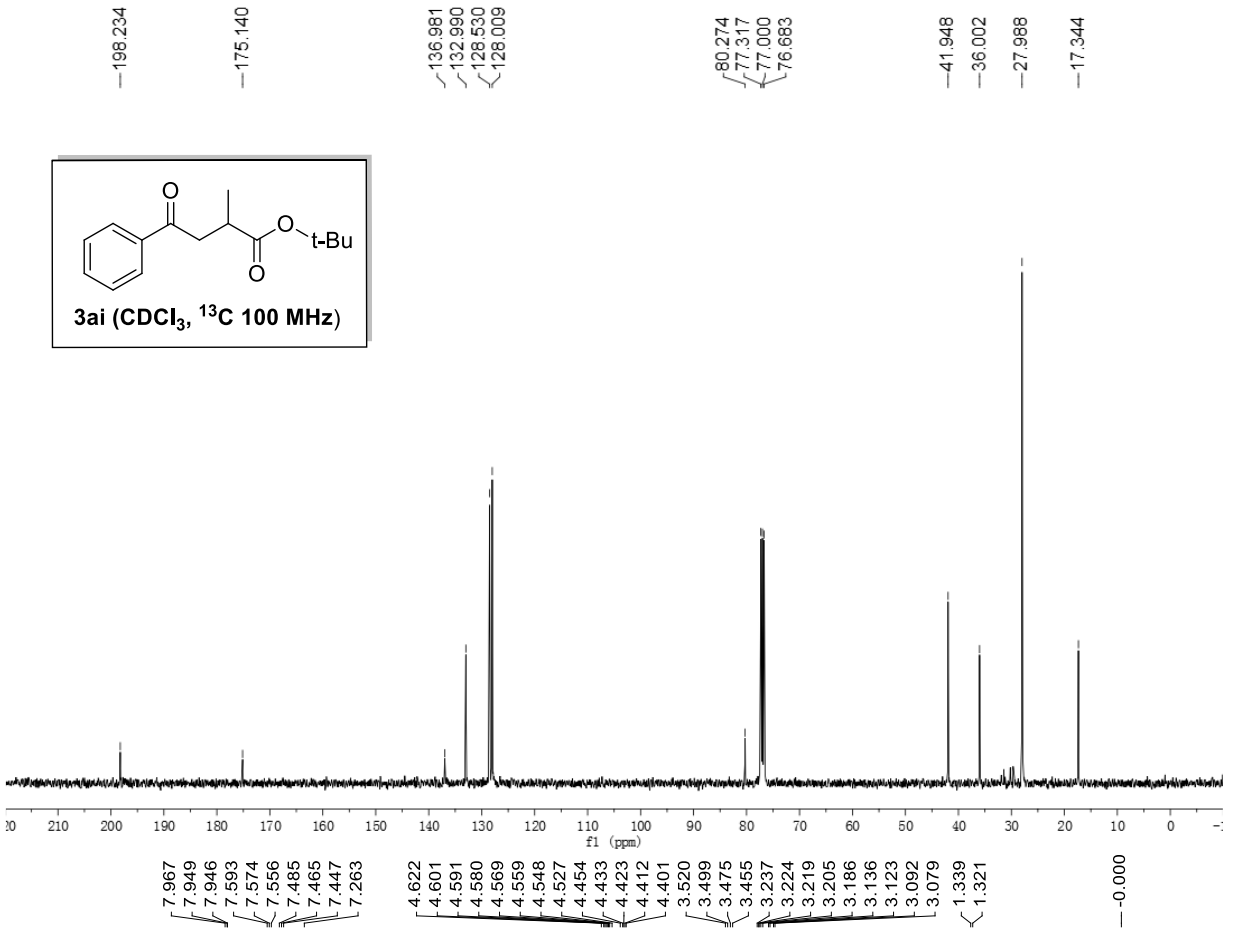

7.986
7.967
7.614
7.595
7.577
7.502
7.483
7.464
4.471
4.466
4.448
4.444
4.426
4.422
4.320
4.303
4.297
4.278
4.272
4.255
3.693
3.655
3.203
3.165
3.144
2.669
2.654
1.991
1.987
1.961
0.000
O
O
O
3ag (CDCl3, 1H 400 MHz)
1.99
1.00
1.99
2.10
1.04
2.06
1.05
1.06
f1 (ppm)

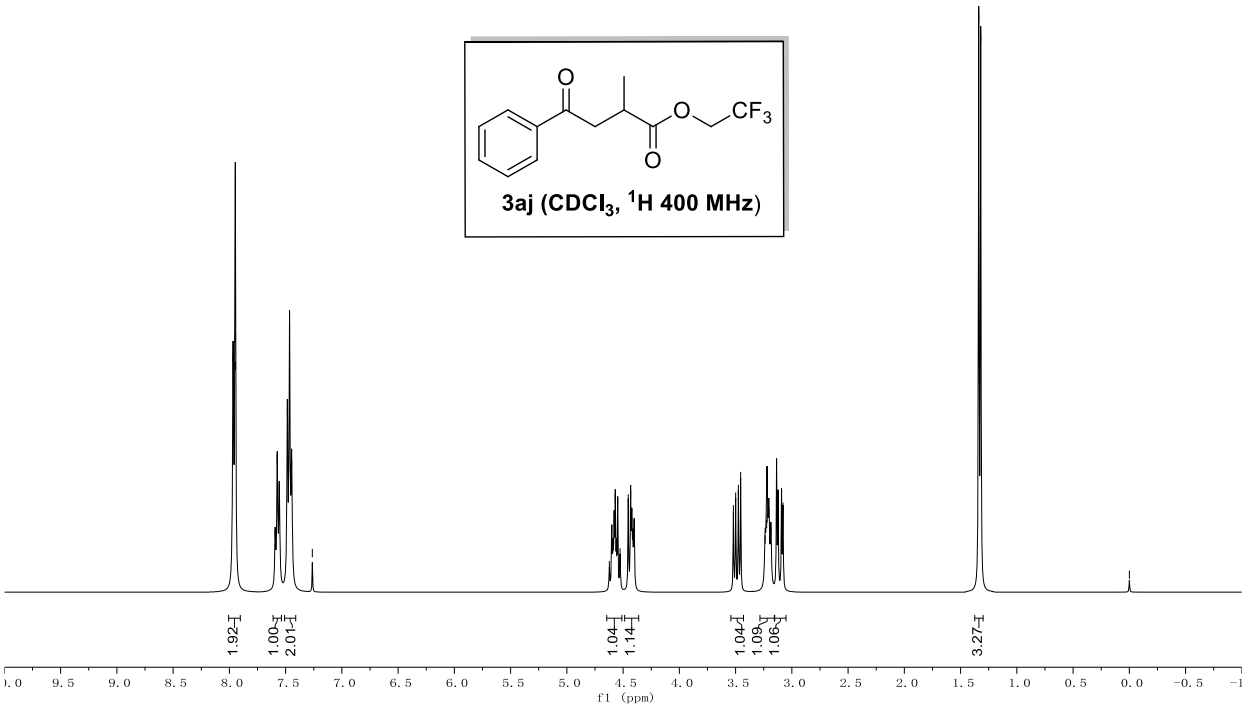

196.928
179.066
136.142
133.511
128.682
127.977
77.318
77.000
76.682
66.773
39.334
35.182
29.044
O
O
O
3ag (CDCl3, 13C 100 MHz)
f1 (ppm)

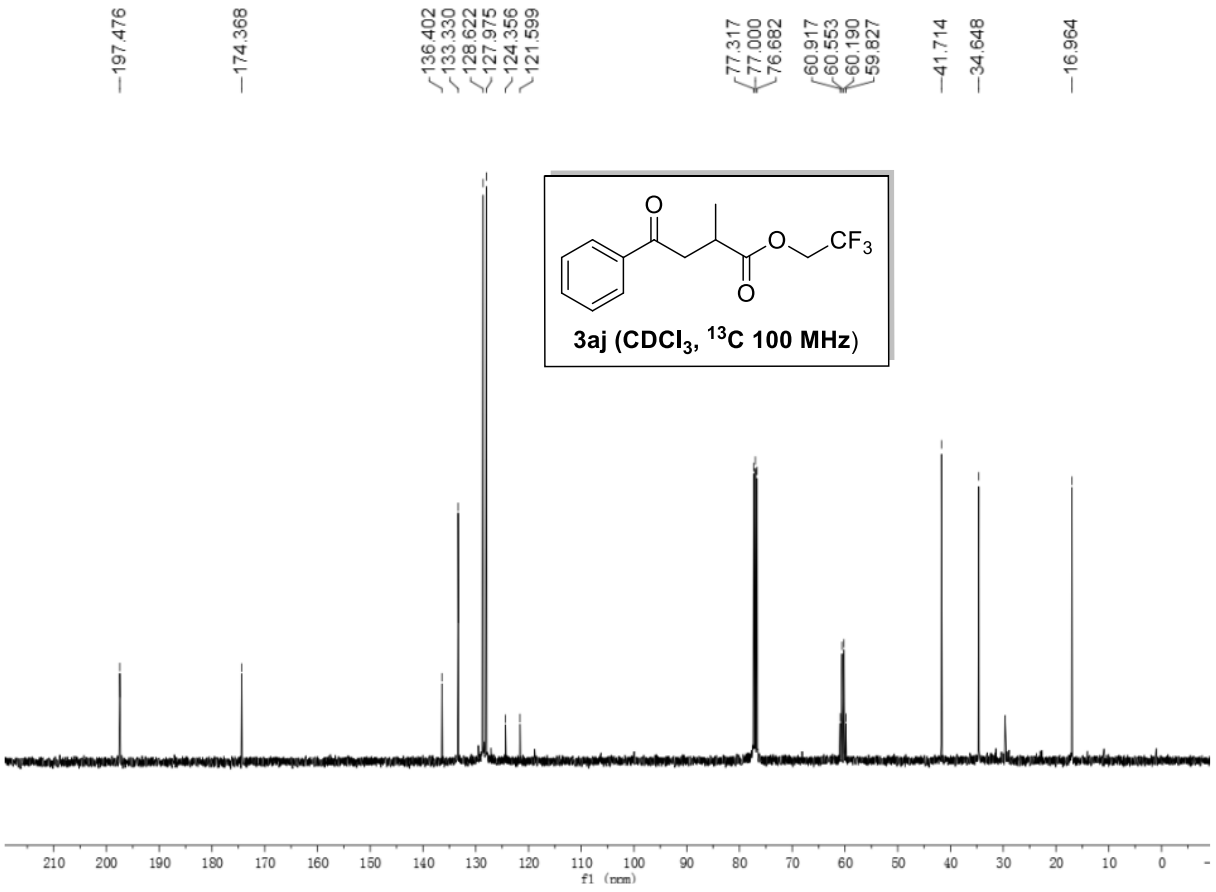

7.985
7.965
7.588
7.570
7.551
7.485
7.467
7.448
4.182
4.164
4.146
4.129
3.521
3.501
3.477
3.458
3.130
3.113
3.096
3.046
3.033
3.003
1.275
1.255
1.238
0.000
O
OEt
O
3ah (CDCl3, 1H 400 MHz)
2.00
1.01
2.02
2.05
1.04
2.07
6.30
f1 (ppm)

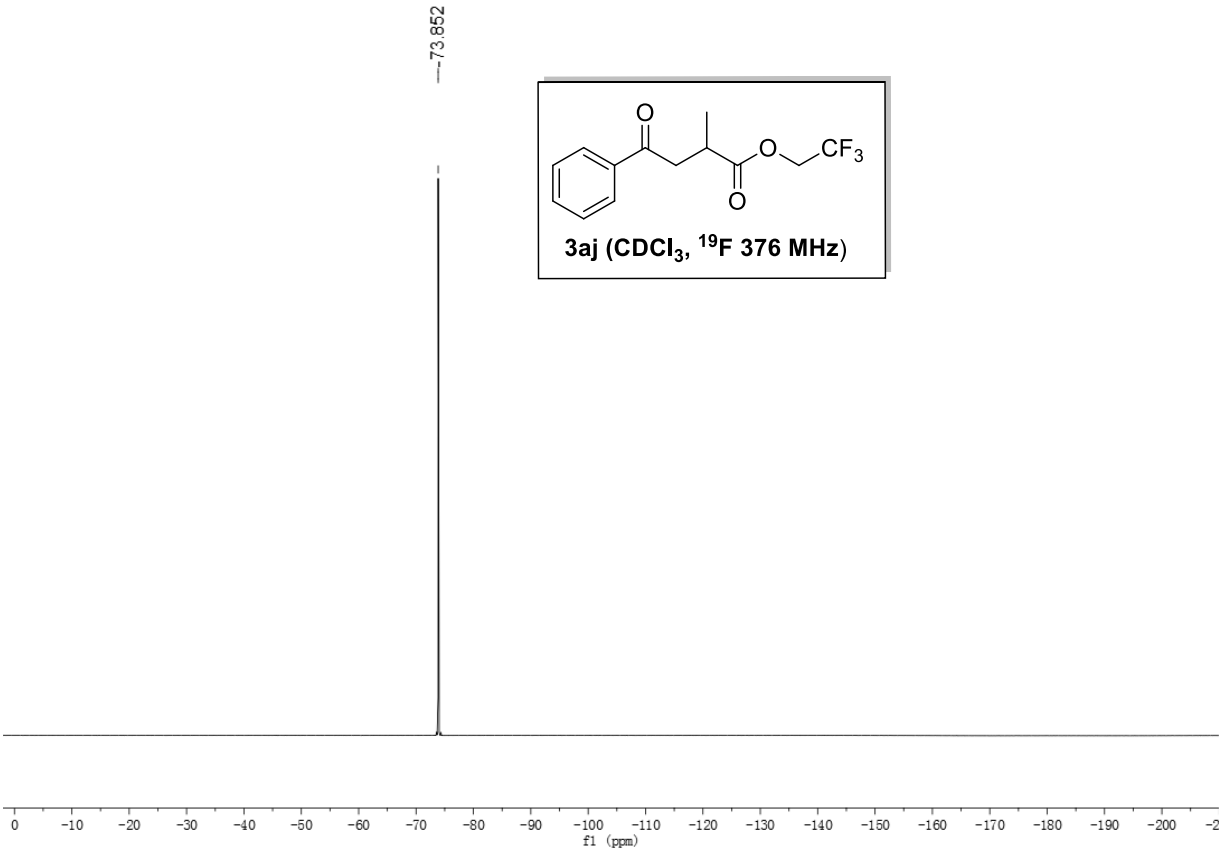

198.069
175.904
133.109
128.569
128.024
60.569
41.936
35.064
17.291
14.149
OEt
O
O
3ah (CDCl3, 13C 100 MHz)
f1 (ppm)

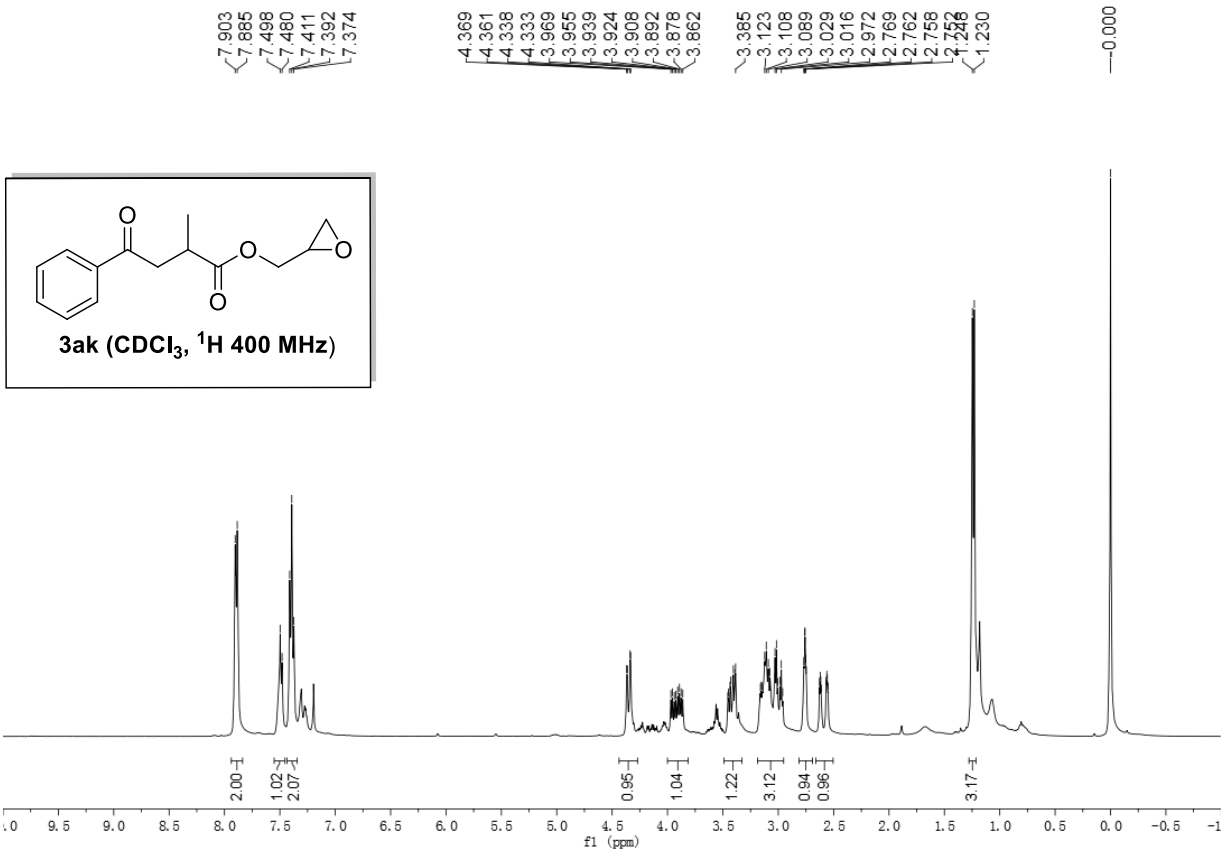

7.985
7.965
7.580
7.562
7.544
7.480
7.461
7.442
3.463
3.444
3.420
3.401
3.065
3.047
3.033
3.015
2.997
2.977
2.964
2.934
2.921
1.437
1.254
1.236
0.000
t-Bu
O
O
O
3ai (CDCl3, 1H 400 MHz)
1.95
1.00
2.02
0.99
2.00
9.28
3.36
f1 (ppm)

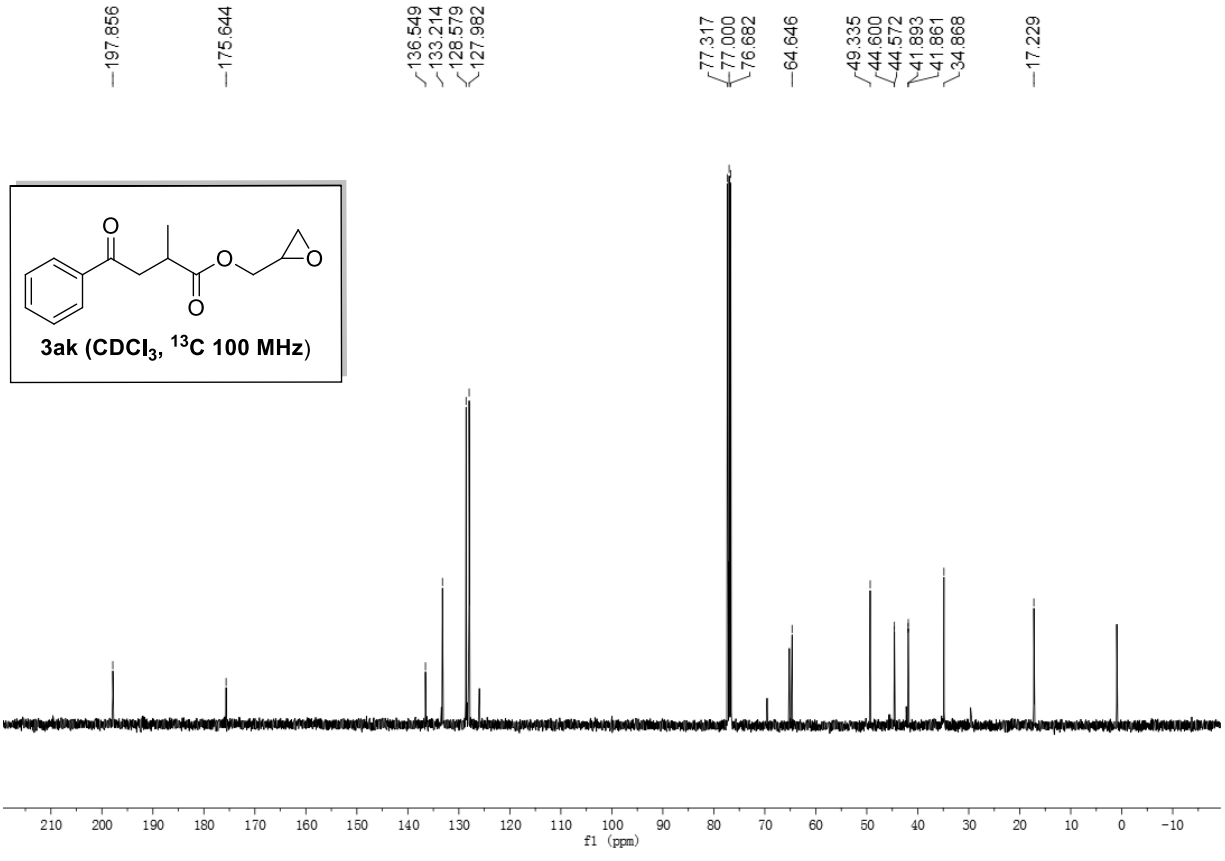

198.234
175.140
136.981
132.990
128.530
128.009
80.274
77.317
77.000
76.683
41.948
36.002
27.988
17.344
O
O
O
t-Bu
3ai (CDCl3, 13C 100 MHz)
f1 (ppm)
7.967
7.949
7.946
7.593
7.574
7.556
7.485
7.465
7.447
7.263
4.622
4.601
4.591
4.580
4.569
4.559
4.548
4.527
4.454
4.433
4.423
4.412
4.401
3.520
3.499
3.475
3.455
3.237
3.224
3.219
3.205
3.186
3.136
3.123
3.092
3.079
1.339
1.321
-0.000

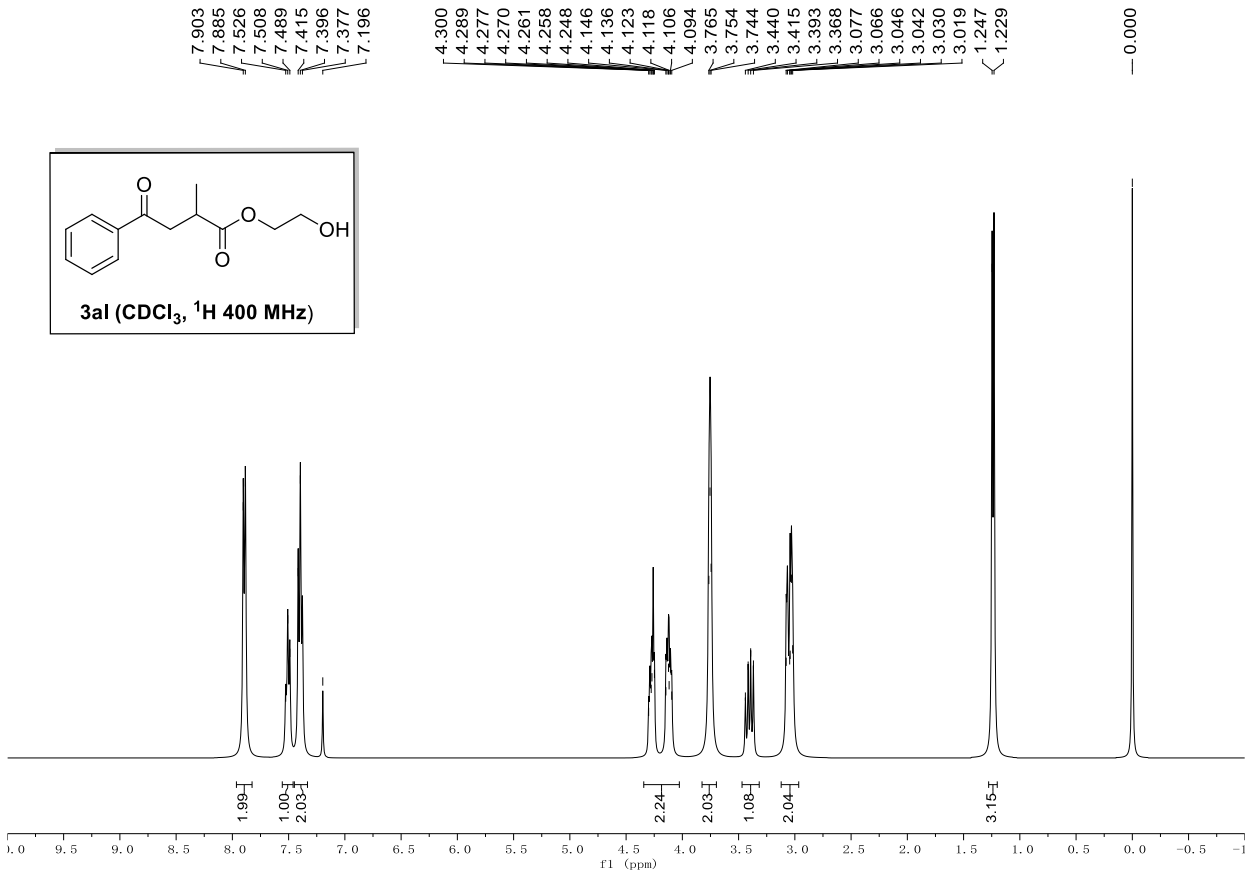

O
O
O
CF3
3aj (CDCl3, 1H 400 MHz)
1.92
1.00
2.01
1.04
1.14
1.04
1.09
1.06
3.27
f1 (ppm)

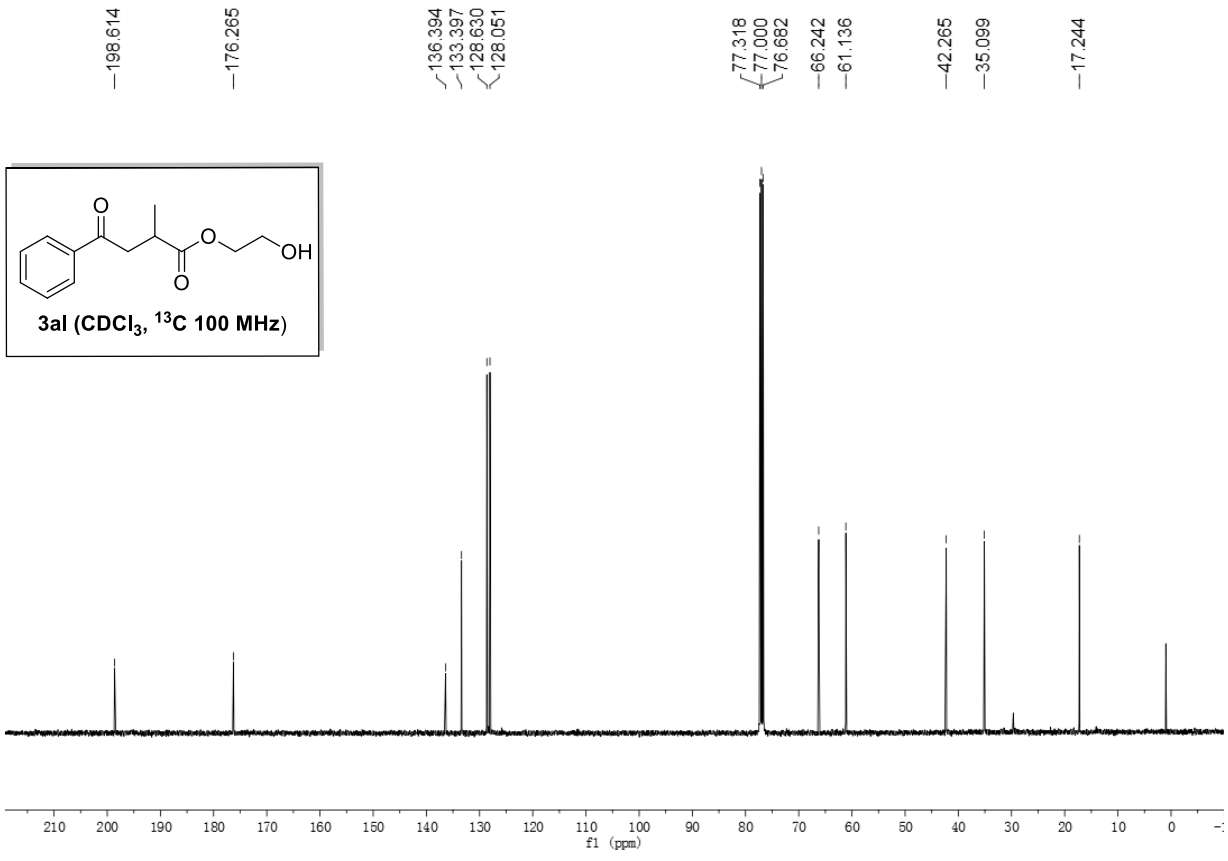

197.476
174.368
136.402
133.330
128.622
127.975
124.356
121.599
77.317
77.000
76.682
60.917
60.553
60.190
59.827
41.714
34.648
16.964
O
O
O
CF3
3aj (CDCl3, 13C 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

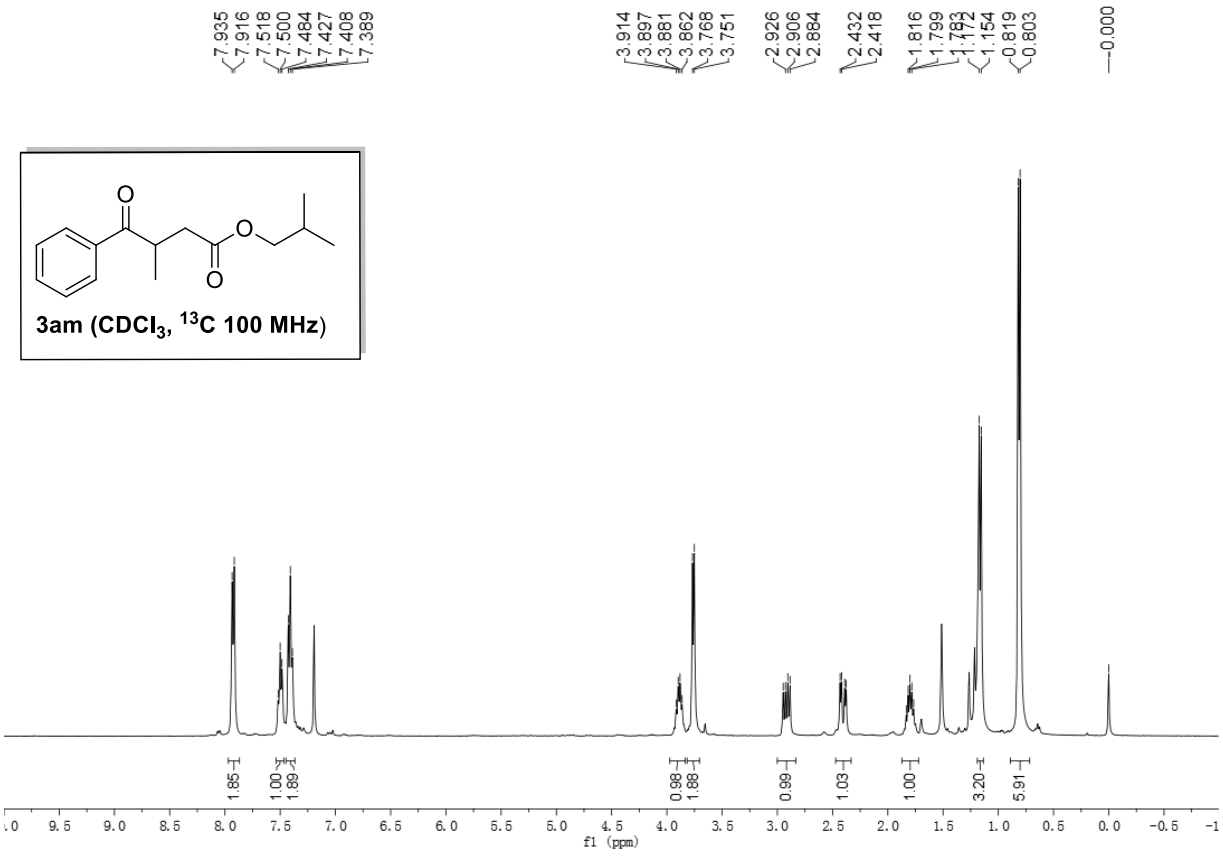

73.852
O
O
O
CF3
3aj (CDCl3, 19F 376 MHz)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

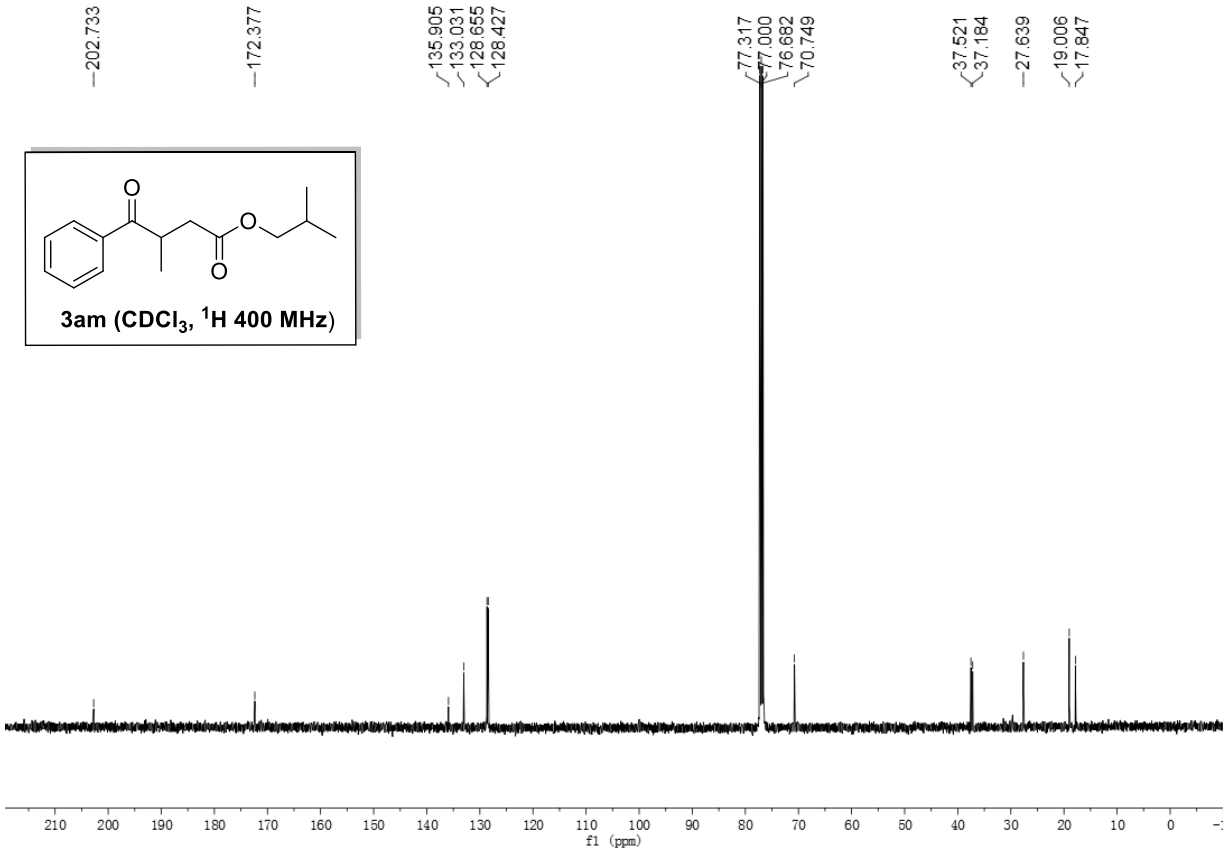

7.903
7.885
7.498
7.480
7.411
7.392
7.374
4.369
4.361
4.338
4.333
3.969
3.955
3.939
3.924
3.908
3.892
3.878
3.862
3.385
3.123
3.108
3.089
3.029
3.016
2.972
2.769
2.762
2.758
1.230
0.000
3ak (CDCl3, 1H 400 MHz)
2.00
1.02
2.07
0.95
1.04
1.22
3.12
0.94
0.96
3.17
f1 (ppm)

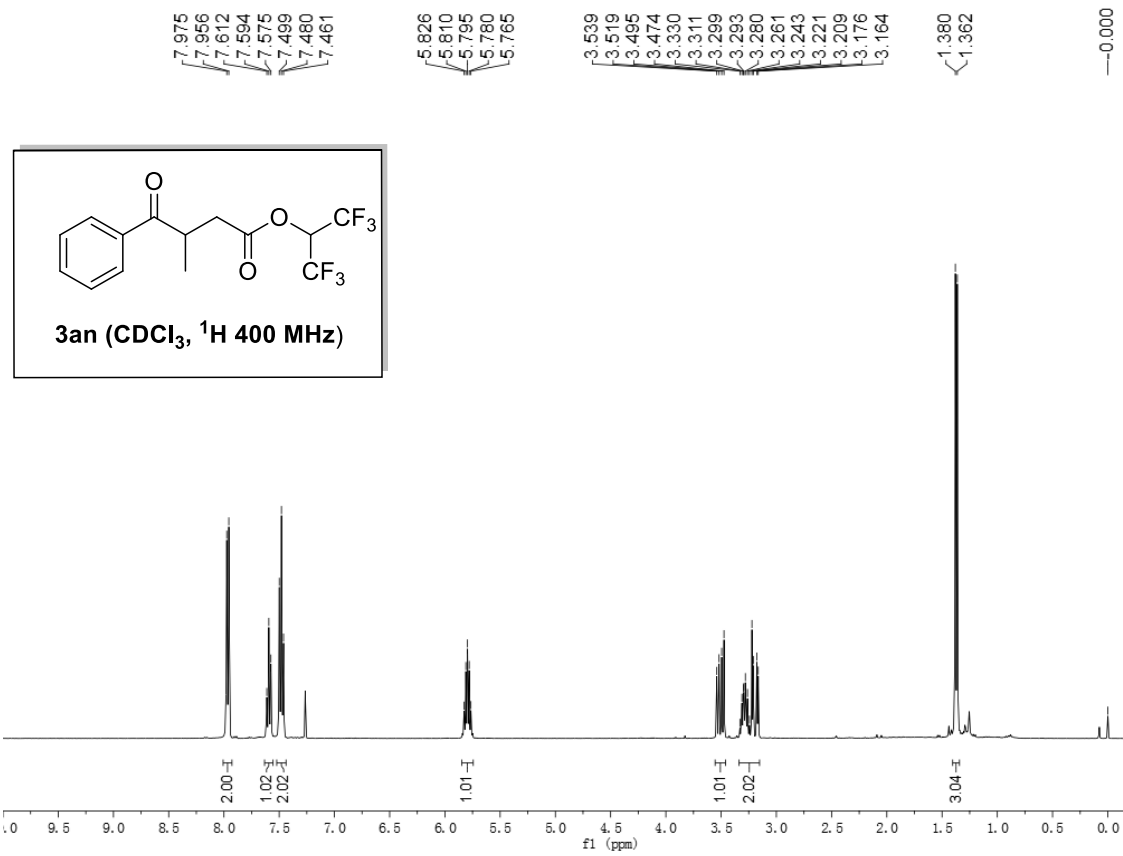

197.856
175.644
136.549
133.214
128.579
127.982
77.317
77.000
76.682
64.646
49.335
44.600
44.572
41.893
41.861
34.868
17.229
3ak (CDCl3, 13C 100 MHz)
f1 (ppm)

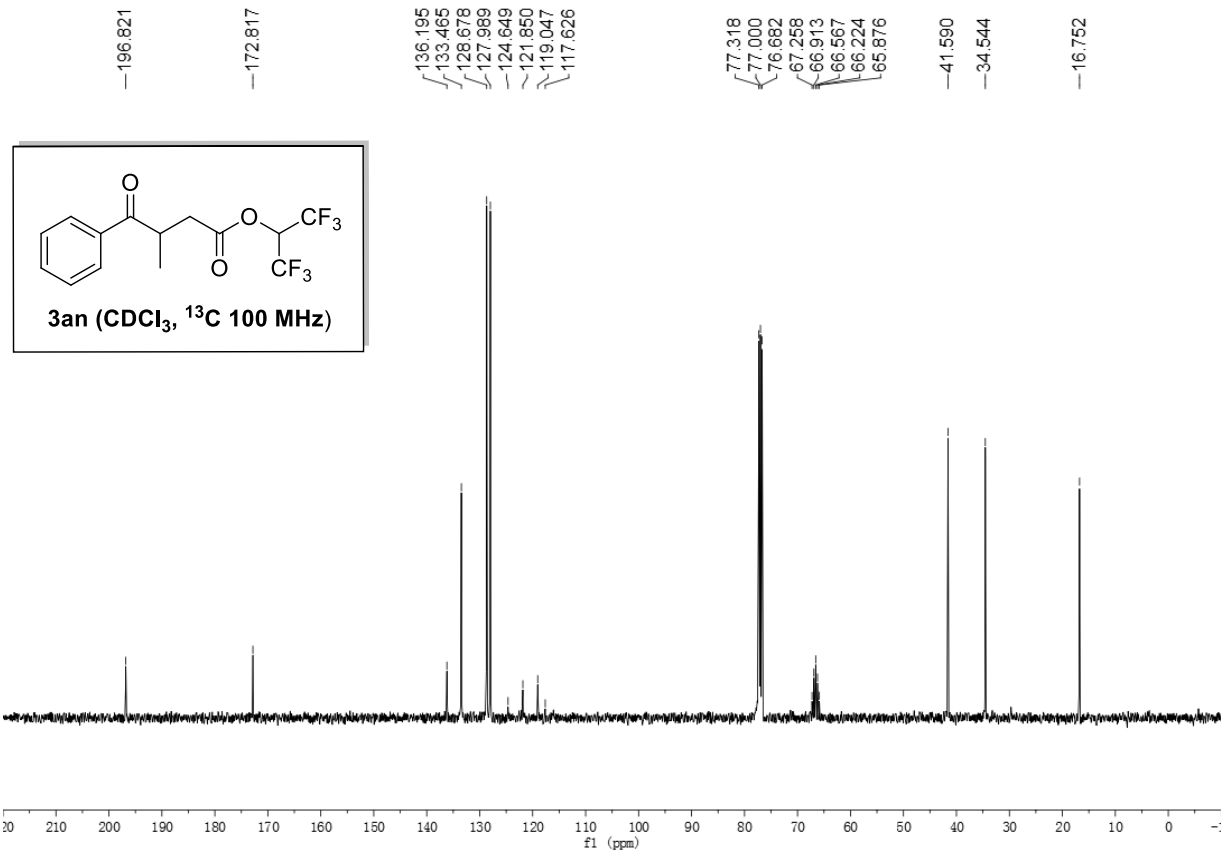

7.903
7.885
7.526
7.508
7.489
7.415
7.396
7.377
7.196
4.300
4.289
4.277
4.270
4.261
4.258
4.248
4.146
4.136
4.123
4.118
4.106
4.094
3.765
3.754
3.744
3.440
3.415
3.393
3.368
3.077
3.066
3.046
3.042
3.030
3.019
1.247
1.229
0.000
O
O
O
OH
3al (CDCl3, 1H 400 MHz)
1.99
1.00
2.03
2.24
2.03
1.08
2.04
3.15
f1 (ppm)

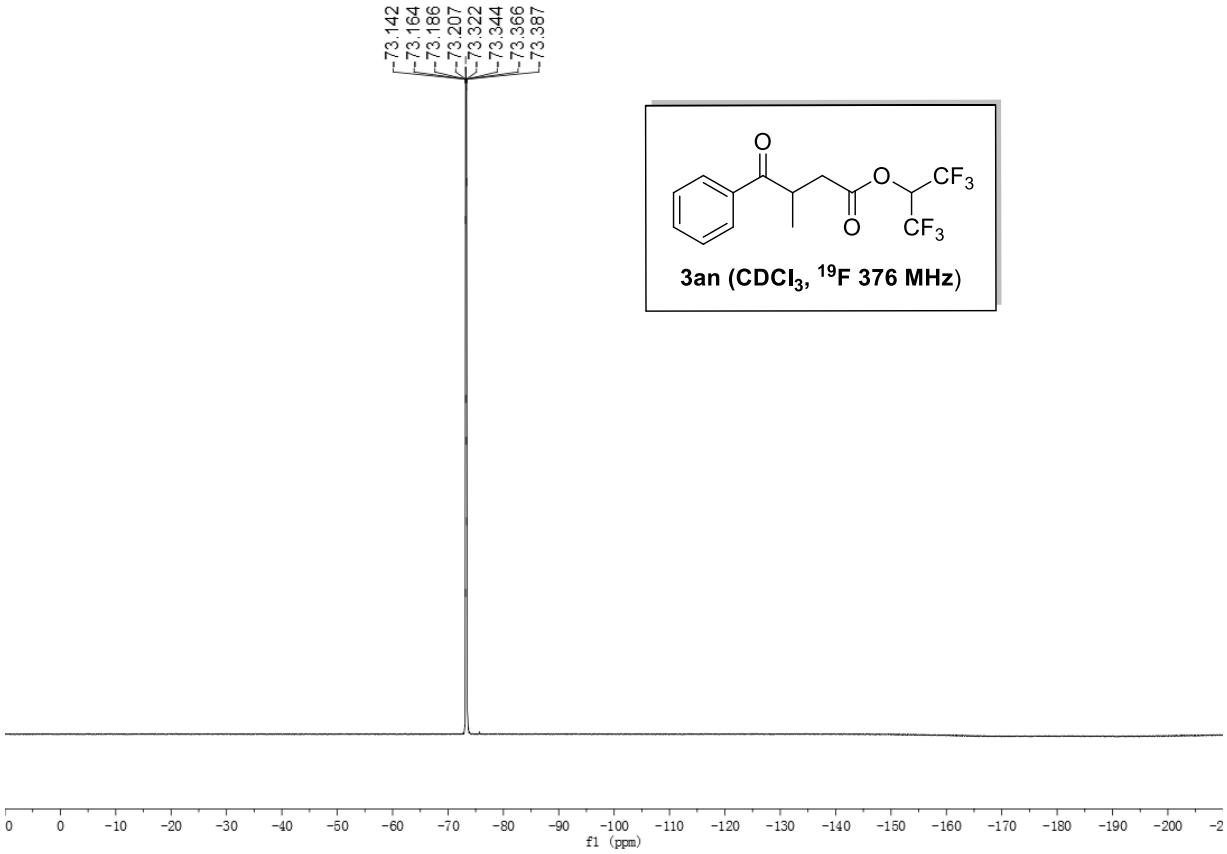

198.614
176.265
136.394
133.397
128.630
128.051
77.318
77.000
76.682
66.242
61.136
42.265
35.099
17.244
O
O
O
OH
3al (CDCl3, 13C 100 MHz)
f1 (ppm)

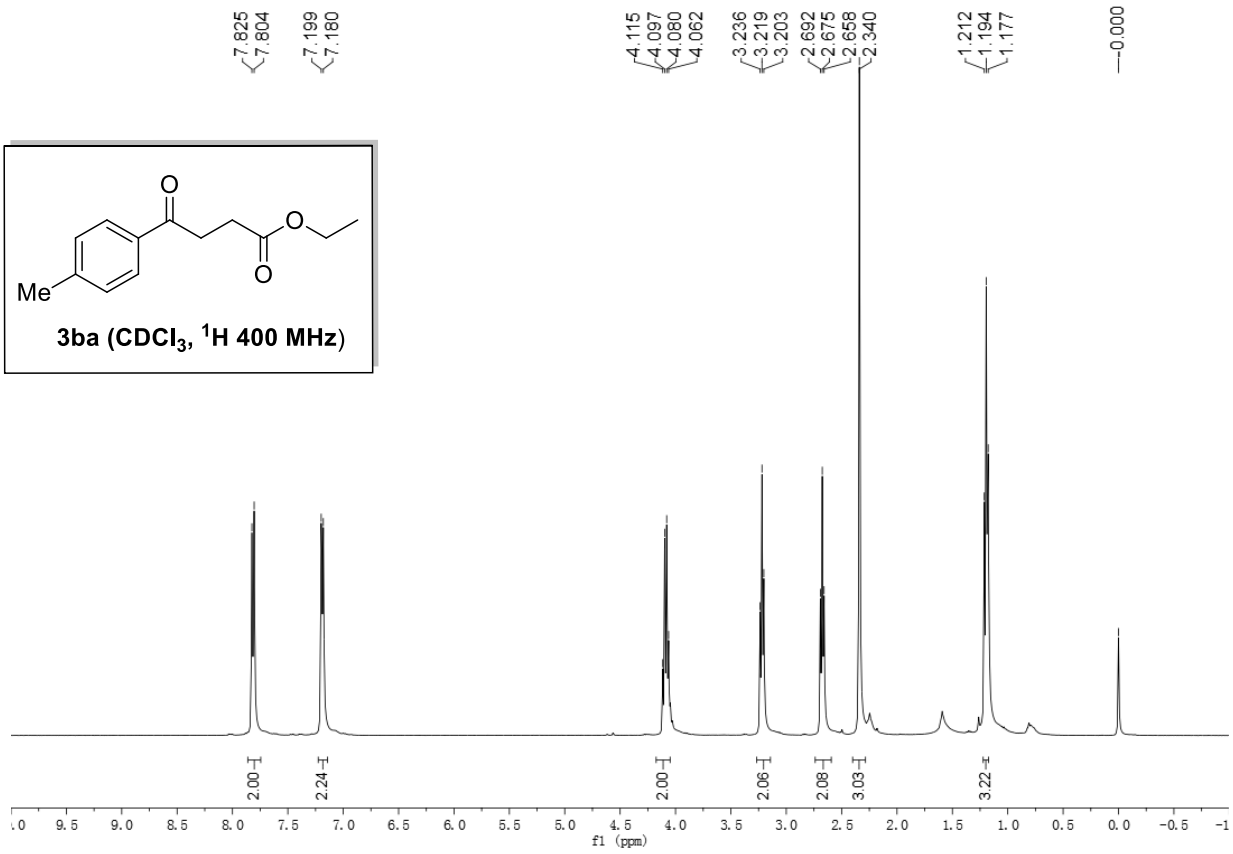

7.935
7.916
7.518
7.500
7.484
7.427
7.408
7.389
3.914
3.897
3.881
3.862
3.768
3.751
2.926
2.906
2.884
2.432
2.418
1.816
1.799
1.783
1.172
1.154
0.819
0.803
0.000
3am (CDCl3, 13C 100 MHz)
1.85
1.00
1.89
0.98
1.88
0.99
1.03
1.00
3.20
5.91
f1 (ppm)

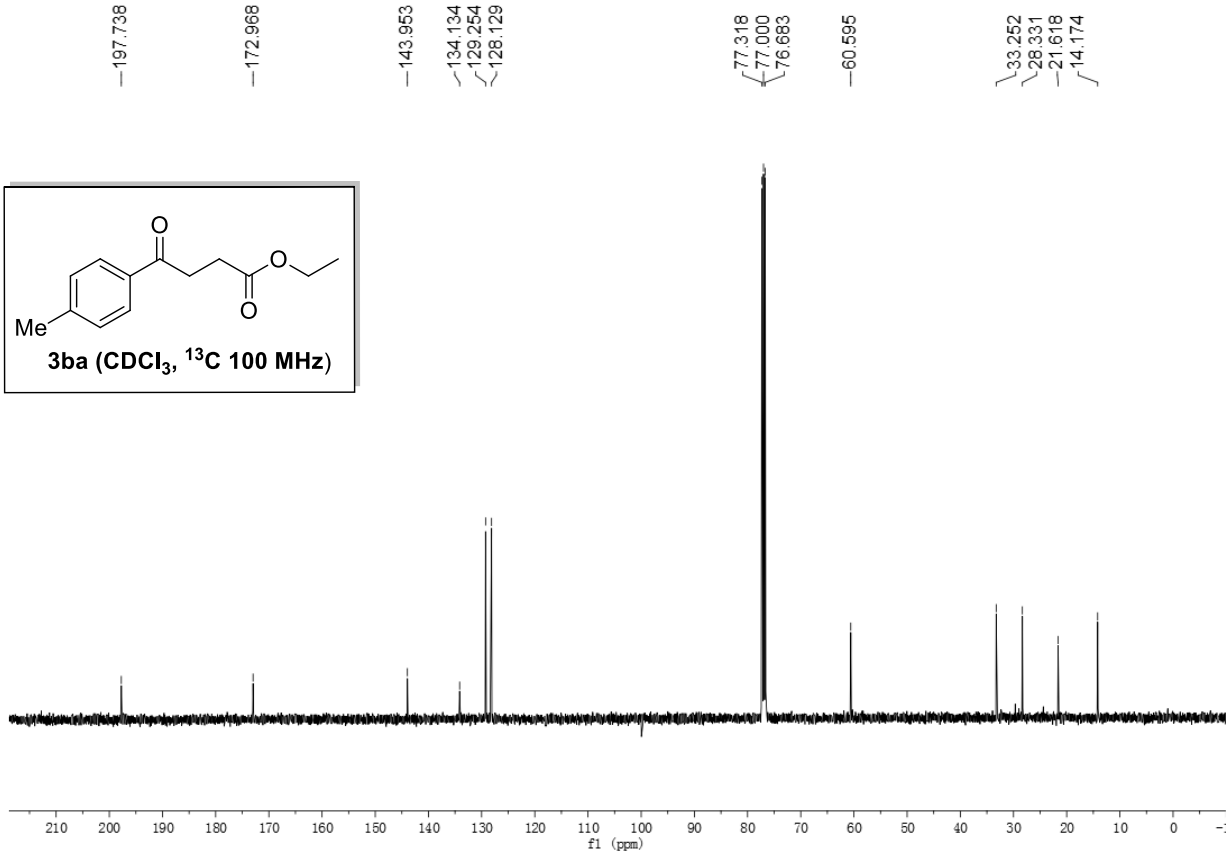

202.733
172.377
135.905
133.031
128.655
128.427
77.317
77.000
76.682
70.749
37.521
37.184
27.639
19.006
17.847
3am (CDCl3, 1H 400 MHz)
f1 (ppm)


7.975
7.956
7.612
7.594
7.575
7.499
7.480
7.461
5.826
5.810
5.795
5.780
5.765
3.539
3.519
3.495
3.474
3.330
3.311
3.299
3.293
3.280
3.261
3.243
3.221
3.209
3.176
3.164
1.380
1.362
0.000
O
O
O
CF3
CF3
3an (CDCl3, 1H 400 MHz)
2.00
1.02
2.02
1.01
1.01
2.02
3.04
f1 (ppm)

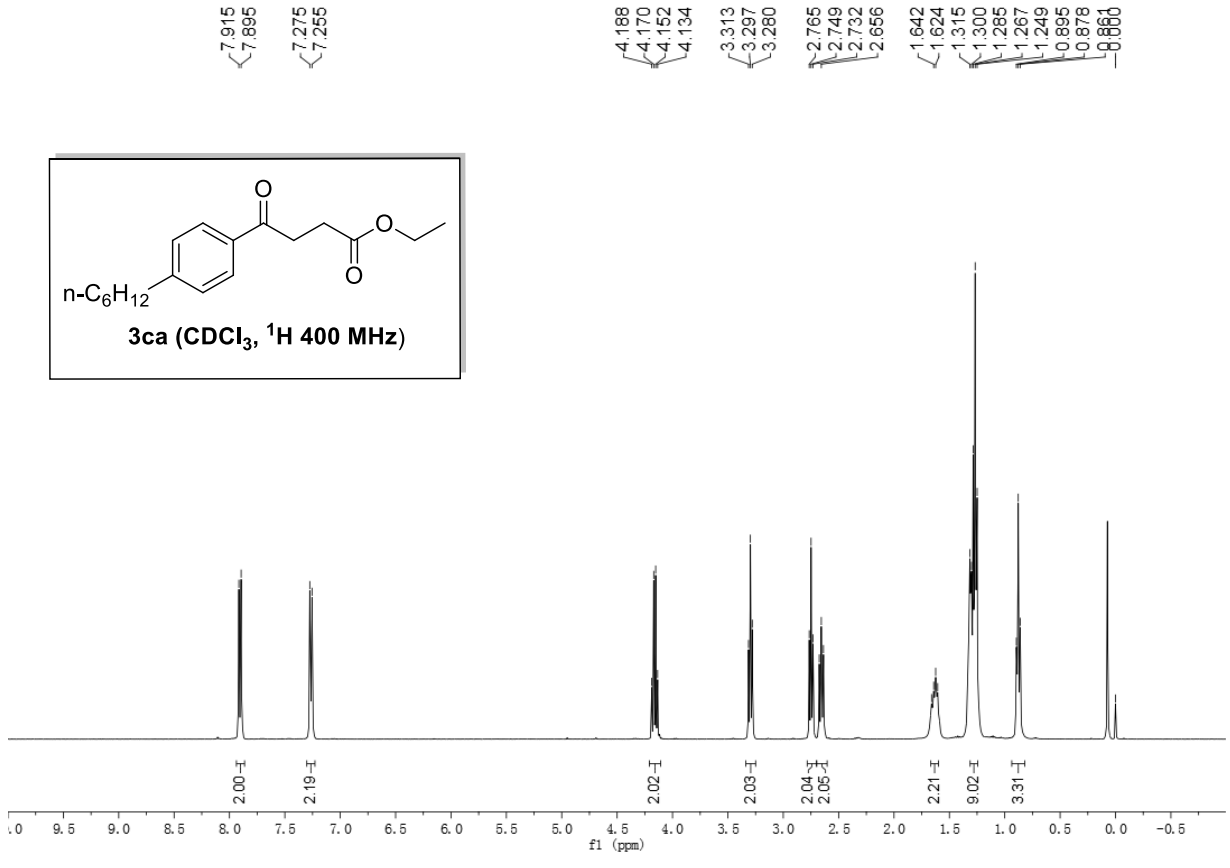

196.821
172.817
136.195
133.465
128.678
127.989
124.649
121.850
119.047
117.626
77.318
77.000
76.682
67.258
66.913
66.567
66.224
65.876
41.590
34.544
16.752
O
O
O
CF3
CF3
3an (CDCl3, 13C 100 MHz)
f1 (ppm)


73.142
73.164
73.186
73.207
73.322
73.344
73.366
73.387
O
O
O
CF3
CF3
3an (CDCl3, 19F 376 MHz)
f1 (ppm)

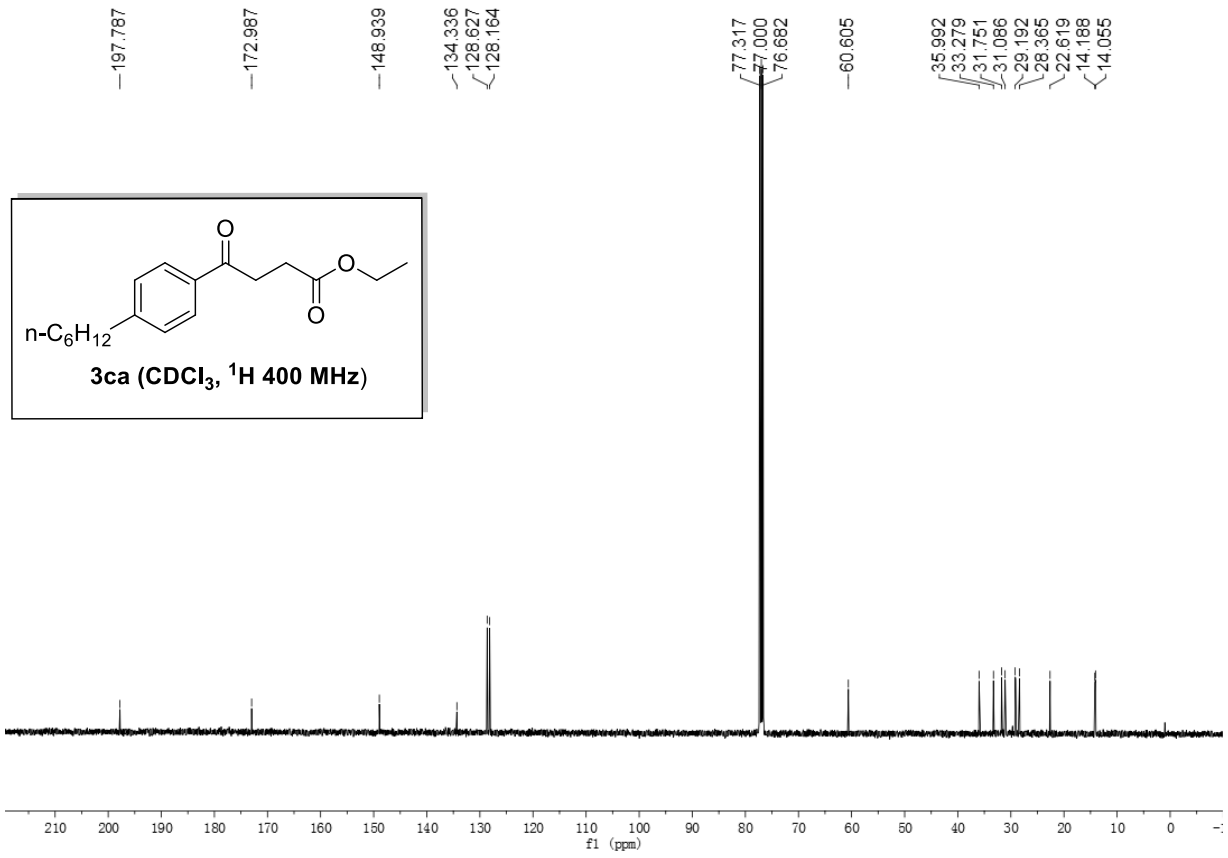

7.825
7.804
7.199
7.180
4.115
4.097
4.080
4.062
3.236
3.219
3.203
2.692
2.675
2.658
2.340
1.212
1.194
1.177
0.000
O
O
O
Me
3ba (CDCl3, 1H 400 MHz)
2.00
2.24
2.00
2.06
2.08
3.03
3.22
f1 (ppm)

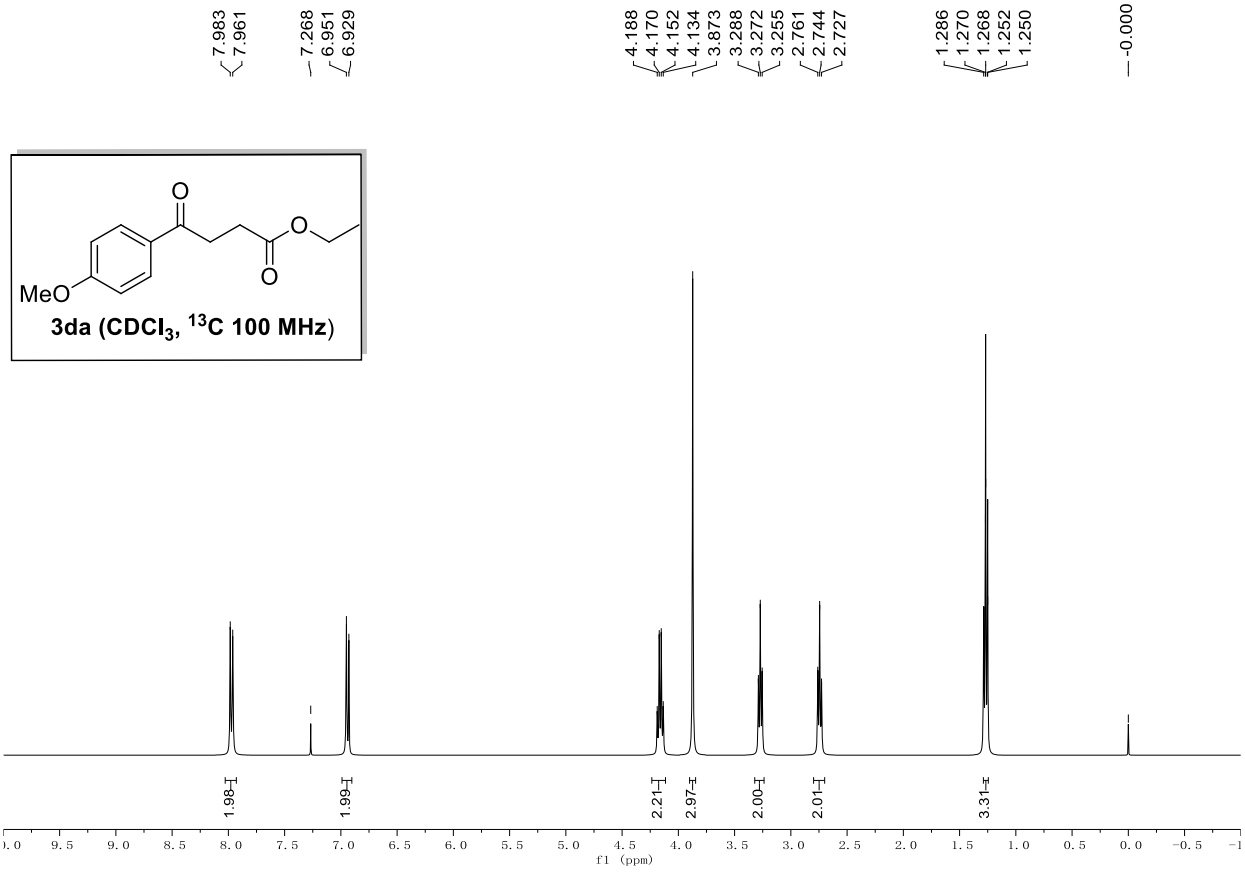


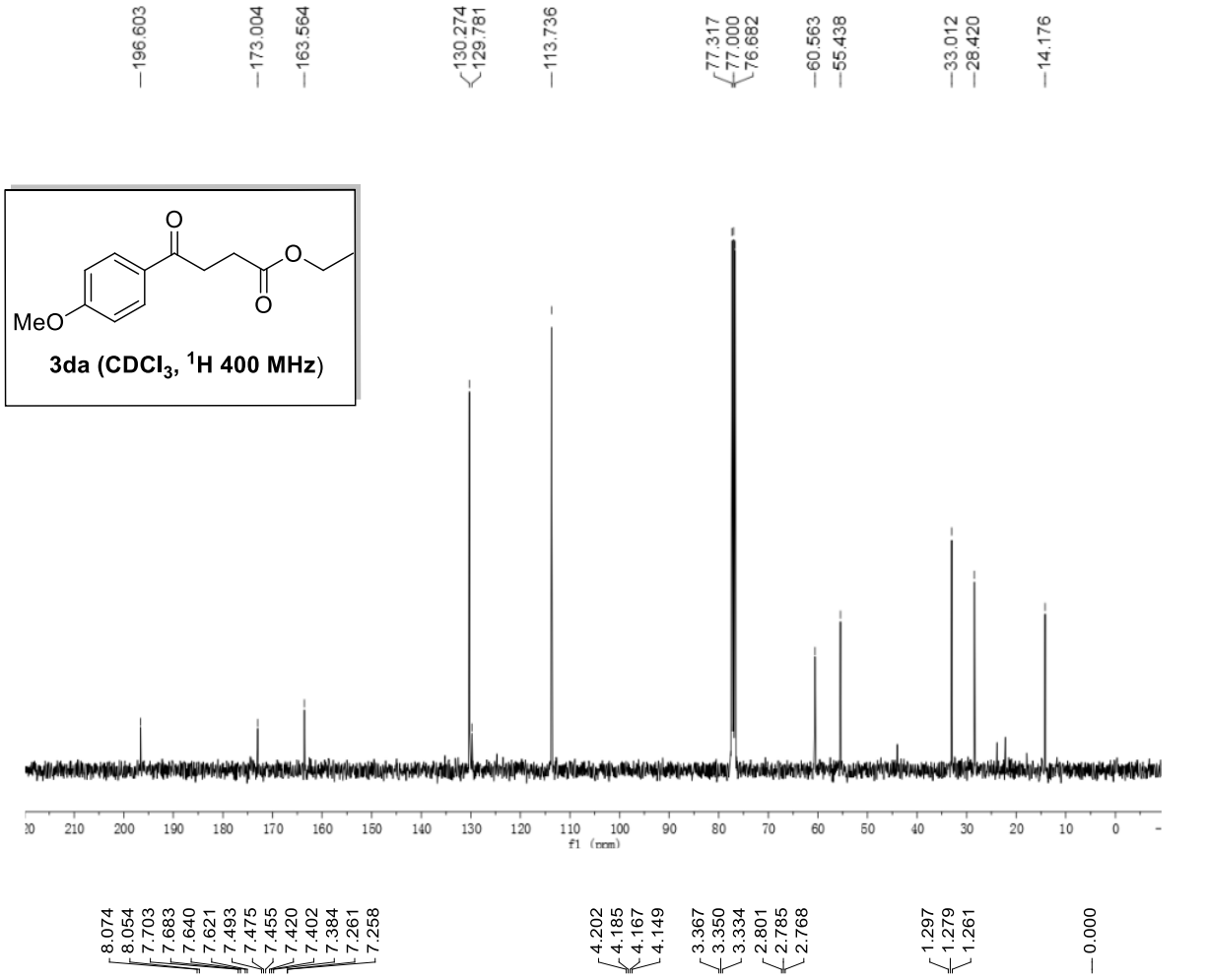
3ba ($CDCl_3$, ^{13}C 100 MHz)

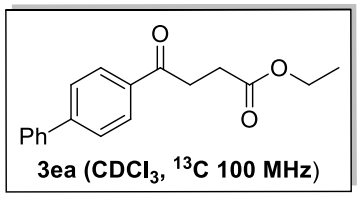


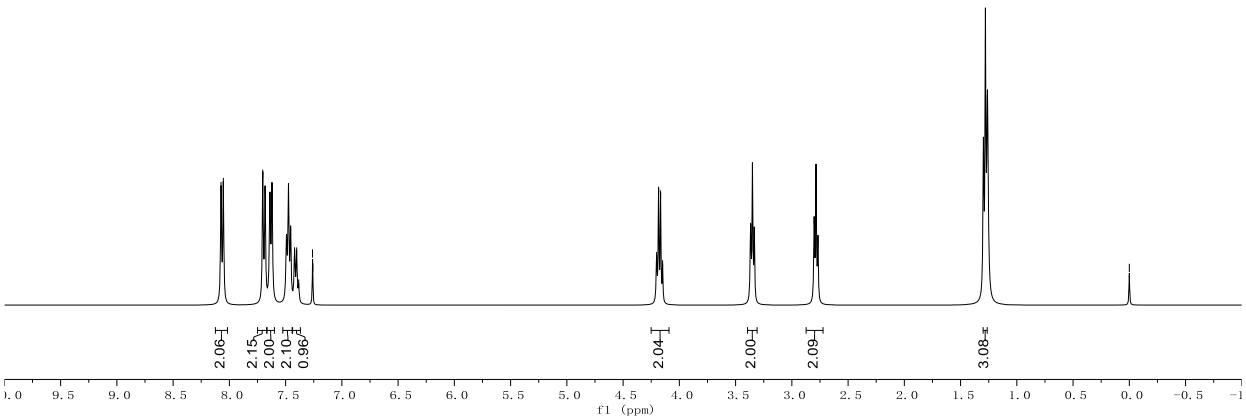
3ca ($CDCl_3$, ^{1}H 400 MHz)

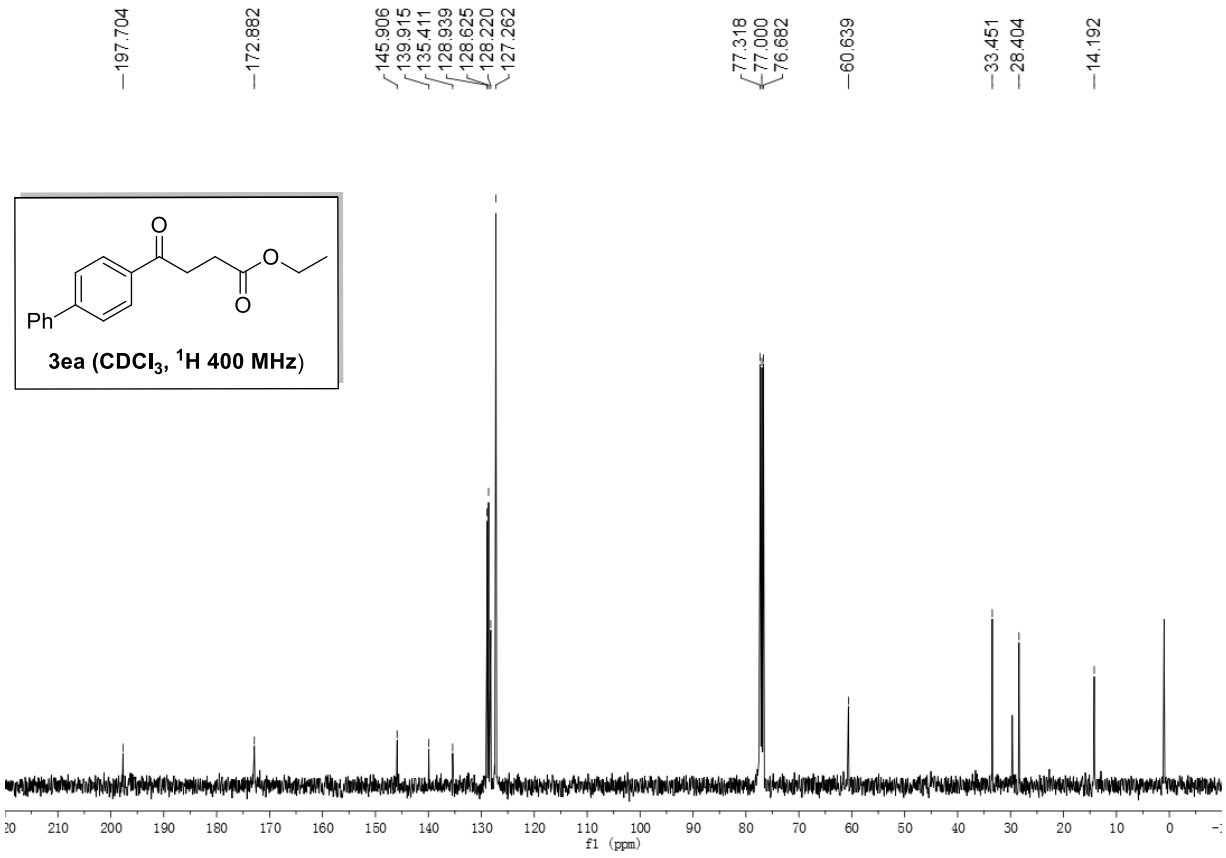

197.787
172.987
148.939
134.336
128.627
128.164
77.317
77.000
76.682
60.605
35.992
33.279
31.751
31.086
29.192
28.365
22.619
14.188
14.055
n-C6H12
3ca (CDCl3, 1H 400 MHz)
f1 (ppm)

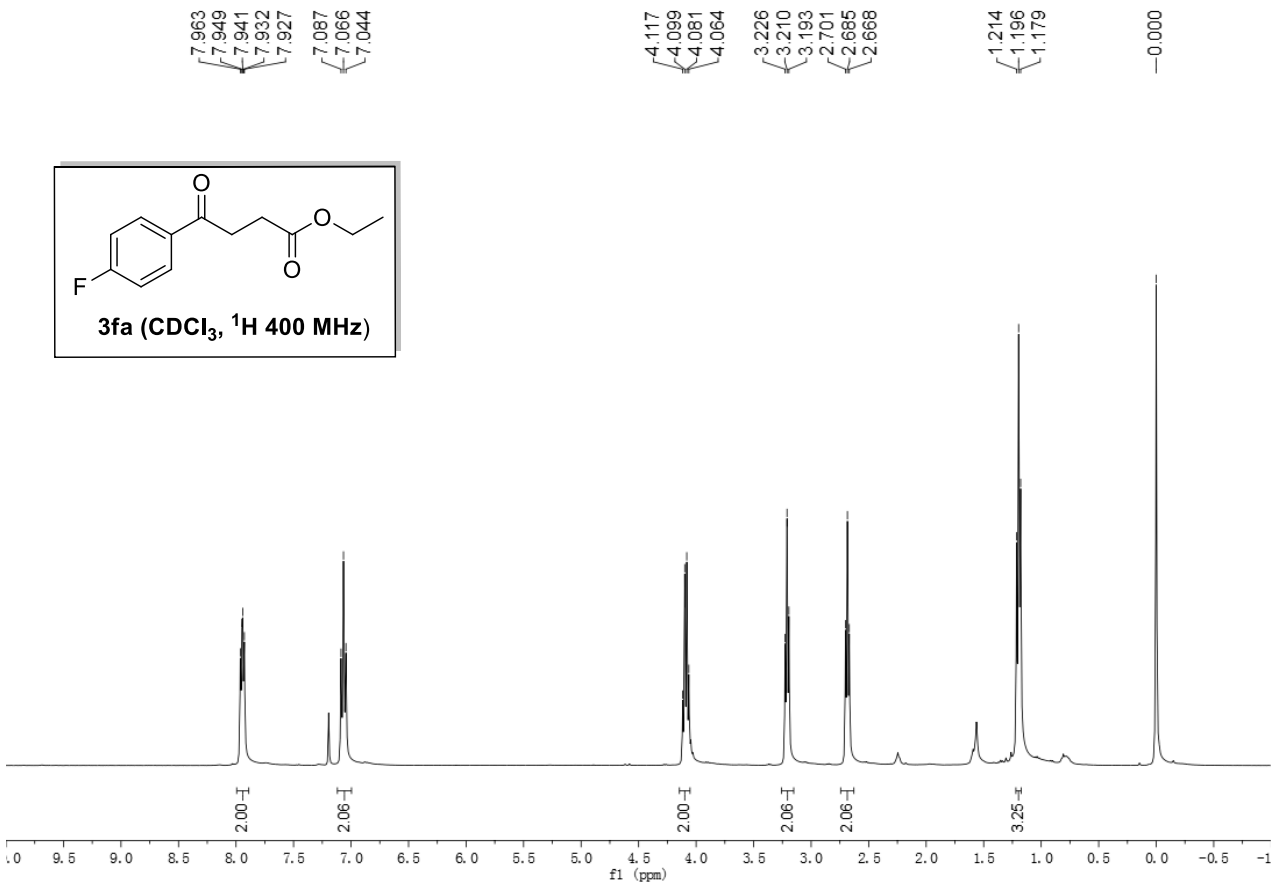

7.983
7.961
7.268
6.951
6.929
4.188
4.170
4.152
4.134
3.873
3.288
3.272
3.255
2.761
2.744
2.727
1.286
1.270
1.268
1.252
1.250
-0.000
MeO
3da (CDCl3, 13C 100 MHz)
1.98
1.99
2.21
2.97
2.00
2.01
3.31
f1 (ppm)

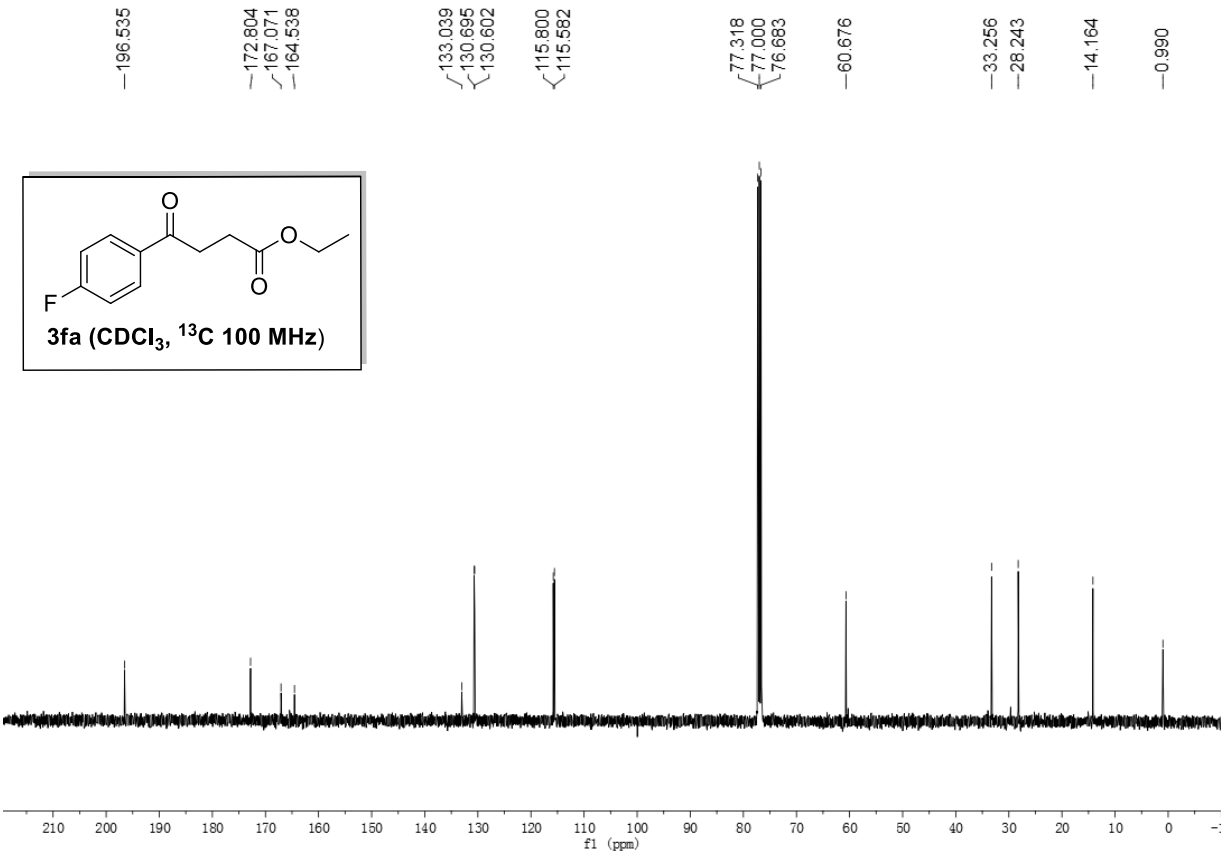

196.603
173.004
163.564
130.274
129.781
113.736
77.317
77.000
76.682
60.563
55.438
33.012
28.420
14.176
MeO
3da (CDCl3, 1H 400 MHz)
f1 (ppm)
8.074
8.054
7.703
7.683
7.640
7.621
7.493
7.475
7.455
7.420
7.402
7.384
7.261
7.258
4.202
4.185
4.167
4.149
3.367
3.350
3.334
2.801
2.785
2.768
1.297
1.279
1.261
0.000

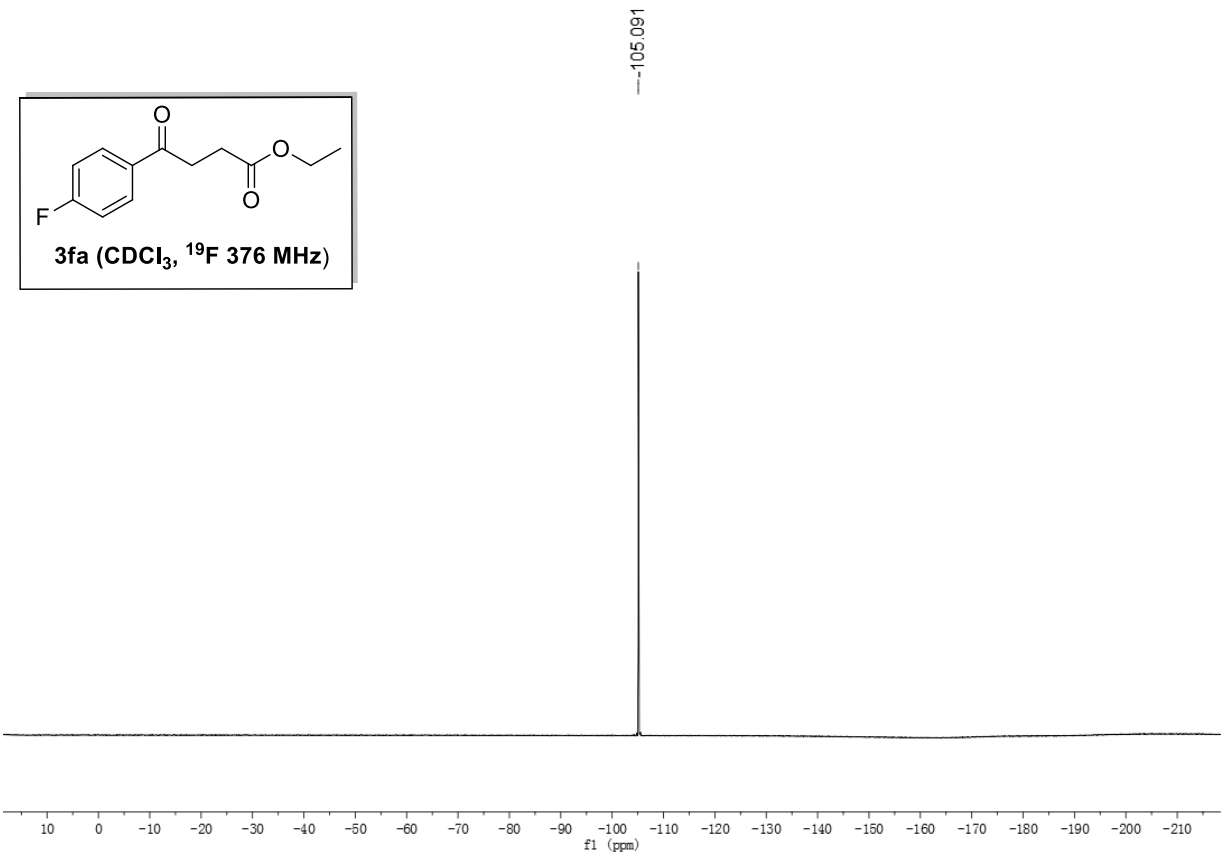

Ph
3ea (CDCl3, 13C 100 MHz)

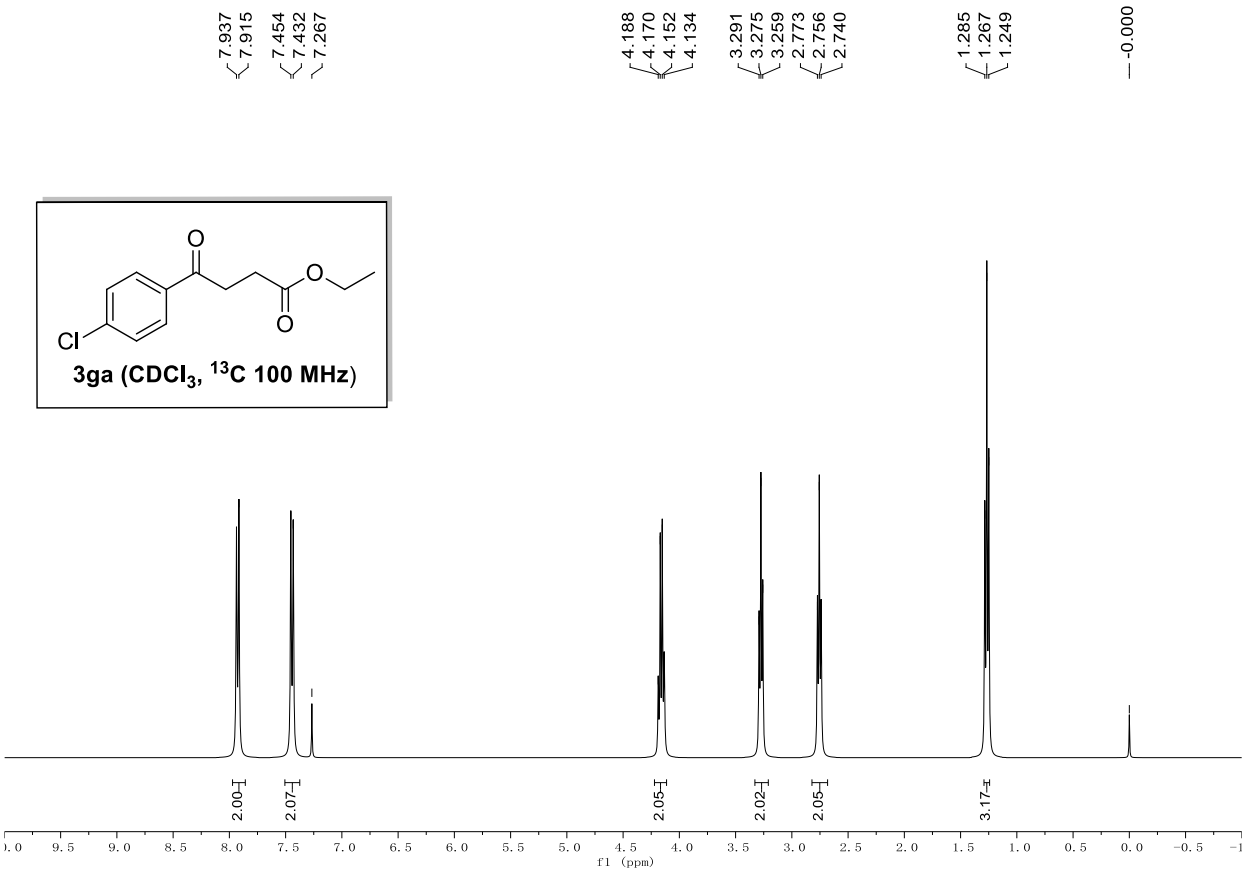

2.06
2.15
2.00
2.10
0.96
2.04
2.00
2.09
3.08
f1 (ppm)

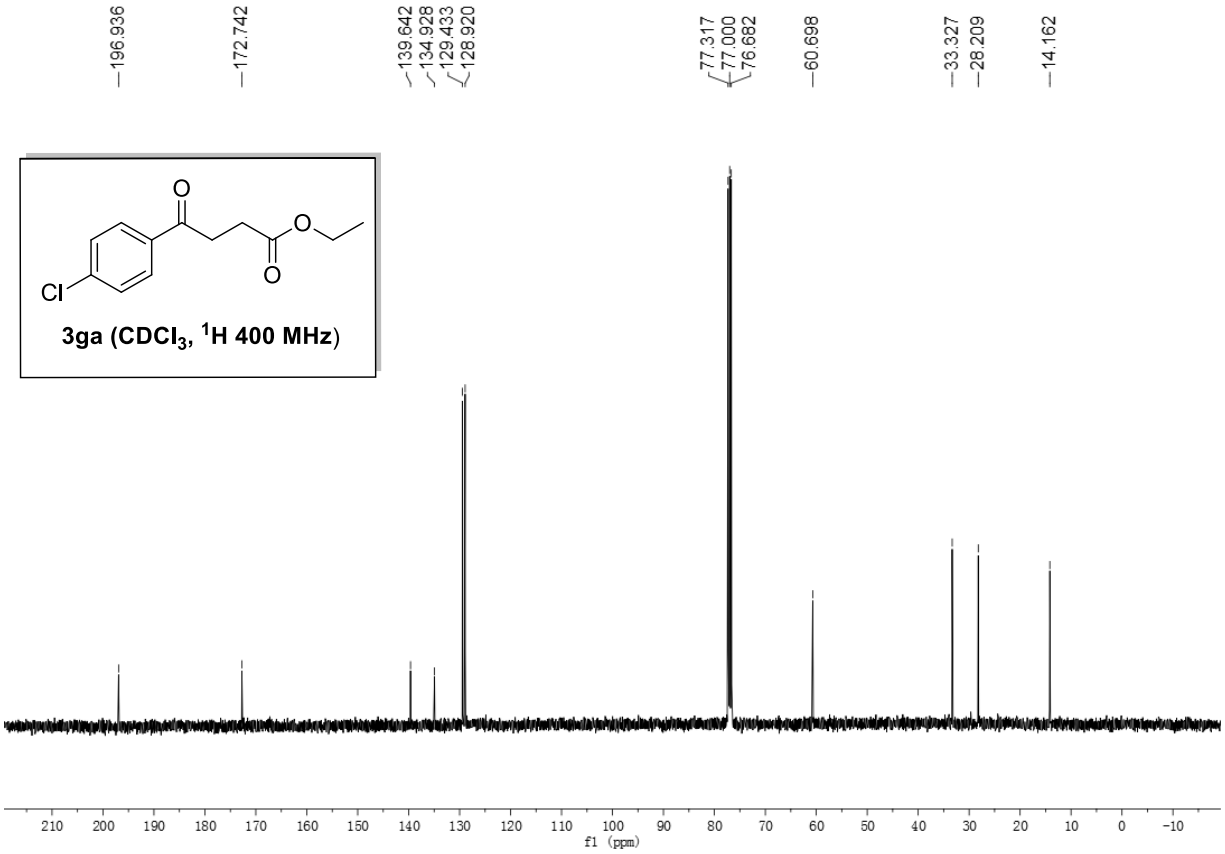

197.704
172.882
145.906
139.915
135.411
128.939
128.625
128.220
127.262
77.318
77.000
76.682
60.639
33.451
28.404
14.192
Ph
O
O
O
3ea (CDCl3, 1H 400 MHz)
f1 (ppm)


7.963
7.949
7.941
7.932
7.927
7.087
7.066
7.044
4.117
4.099
4.081
4.064
3.226
3.210
3.193
2.701
2.685
2.668
1.214
1.196
1.179
0.000
F
O
O
O
3fa (CDCl3, 1H 400 MHz)
2.00
2.06
2.00
2.06
2.06
3.25
f1 (ppm)


196.535
172.804
167.071
164.538
133.039
130.695
130.602
115.800
115.582
77.318
77.000
76.683
60.676
33.256
28.243
14.164
0.990
O
O
O
F
3fa (CDCl3, 13C 100 MHz)
f1 (ppm)


-105.091
O
O
O
F
3fa (CDCl3, 19F 376 MHz)
f1 (ppm)


7.937
7.915
7.454
7.432
7.267
4.188
4.170
4.152
4.134
3.291
3.275
3.259
2.773
2.756
2.740
1.285
1.267
1.249
-0.000
O
O
O
Cl
3ga (CDCl3, 13C 100 MHz)
2.00
2.07
2.05
2.02
2.05
3.17
f1 (ppm)


196.936
172.742
139.642
134.928
129.433
128.920
77.317
77.000
76.682
60.698
33.327
28.209
14.162
O
O
O
Cl
3ga (CDCl3, 1H 400 MHz)
f1 (ppm)

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