Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible-Light Enabled Photochemical Reduction of 1,2-Dicarbonyl Compounds by Hünig's Base

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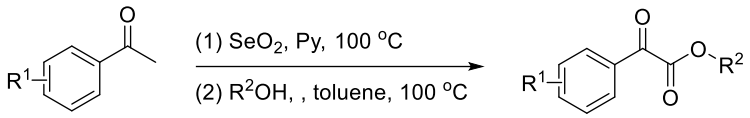
General Information

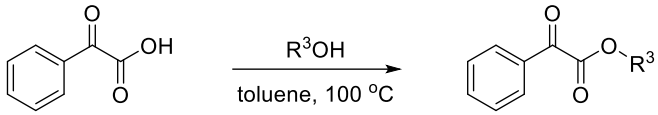
Substrates of α-ketoesters and α-ketoamide were prepared according to the reported literature.[1] CH_3CN, ethanol and THF were extra dry solvent purchased from chemical energy. If no special indicated, other reagents and solvents were used as commercially available without further purification. All the reactions were carried out under argon 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 77.00 ppm, and DMSO-d_6 resonance in the ^1H spectrum as 2.50 ppm and ^{13}C spectrum as 39.50 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.

General procedure for preparation of substrates 1b–1q.



Following a literature procedure,[1a] a mixture of substituted acetophenone (20.0 mmol) and selenium dioxide (4.4 g, 40 mmol) in dry pyridine (20 mL) was stirred at 100 °C under a nitrogen atmosphere for 15 h, and then removal of pyridine under reduced pressure. Next, the corresponding alcohol (40.0 mmol) in toluene (20 mL) was added to the residue and stirred at 100 °C until the full conversion of the starting material by TLC monitoring. Toluene were removed under vacuum, and the residue was purified on silica chromatography by gradient elution (Ethyl acetate/Petroleum ether) to give the pure α-keto esters.

General procedure for preparation of substrates 1r–1t.



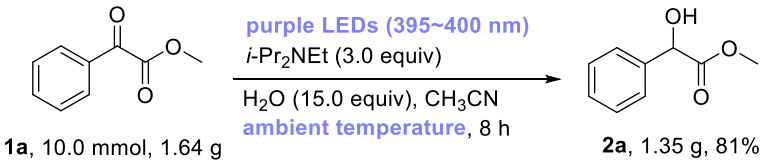
Following a literature procedure,[1a] a mixture of substituted benzoylformic acid (2.25 g, 15 mmol) and corresponding alcohol (30 mmol) in toluene (20 mL) was stirred at 100 °C until the full conversion of the starting material by TLC monitoring. Toluene were removed under vacuum, and the residue was purified on silica chromatography by gradient elution (Ethyl acetate/Petroleum ether) to give the pure α-keto esters.

General Procedure for synthesis of α-hydroxyesters 2.

To a Schlenk tube containing a stirring bar was added α-keto esters **1** (0.20 mmol, 1.0 equiv). Then, *i*-Pr_2EtN (0.60 mmol, 3.0 equiv), H_2O (3.00 mmol, 15.0 equiv), and 2.0 mL CH_3CN were added to the reaction tube via syringe under Ar atmosphere. The reaction mixture was stirred for 6 h at Wattecs Parallel Light Reactor (Purple LED Light source (390–395 nm), 10 W every position) at ambient temperature (the temperature range from 28 ^oC to 32 ^oC). Finally, the solvent was removed in vacuum and the residue was purified by column chromatography on silica gel to afford the compound **2**.

Wattecs Parallel Light Reactor (Purple LED Light source, 10 W every position, 390-395 nm)

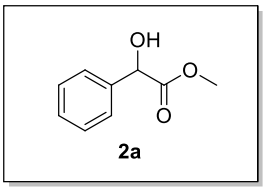
Gram-scale reaction



Scheme S1. Gram-scale reaction. (Reaction conditions: 10.0 mmol of α-keto esters **1a**, 3.0 equiv *i*-Pr$_2$EtN, 15.0 equiv H_2O, 100 mL CH_3CN, purple LEDs, 8 h irradiation at ambient temperature).

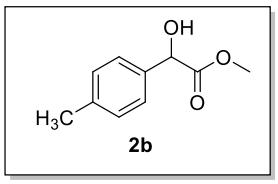
Characterization data for products

Methyl 2-hydroxy-2-phenylacetate **2a**[1a]



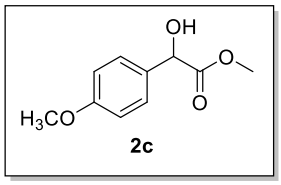
According to the general procedure, **2a** (white solid, 27.9 mg, mp: 50–51 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.32 (m, 5H), 5.18 (d, *J* = 5.2 Hz, 1H), 3.76 (s, 3H), 3.49 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 138.2, 128.6 (2C), 128.5, 126.6 (2C), 72.9, 53.0. MS: m/z: $[M]^+$, 166.0.

Methyl 2-hydroxy-2-(p-tolyl)acetate **2b**[1a]



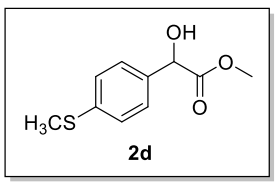
According to the general procedure, **2b** (white solid, 31.6 mg, mp: 51–52 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 5.14 (d, *J* = 5.2 Hz, 1H), 3.75 (s, 3H), 3.47 (d, *J* = 5.6 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 138.3, 135.3, 129.3 (2C), 126.5 (2C), 72.7, 52.9, 21.1. MS: m/z: $[M]^+$, 180.0.

Methyl 2-hydroxy-2-(4-methoxyphenyl)acetate **2c**[1a]



According to the general procedure, **2c** (yellow oil, 33.9 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.13 (d, *J* = 5.6 Hz, 1H), 3.80 (s, 3H), 3.75 (s, 3H), 3.48 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 159.7, 130.4, 127.9 (2C), 114.0 (2C), 72.4, 55.2, 52.9. MS: m/z: $[M]^+$, 196.0.

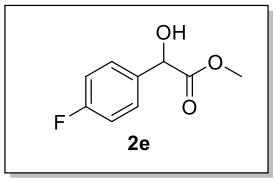
Methyl 2-hydroxy-2-(4-(methylthio)phenyl)acetate **2d**[2]



According to the general procedure, **2d** (white solid, 34.2 mg, mp: 54–55 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 81% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.34 (d, *J* = 8.4

Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.07 (d, *J* = 5.2 Hz, 1H), 5.11 (d, *J* = 5.2 Hz, 1H), 3.60 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.0, 137.8, 136.2, 127.3 (2C), 125.7 (2C), 71.9, 51.8, 14.6. MS: m/z: $[M]^+$, 212.0.

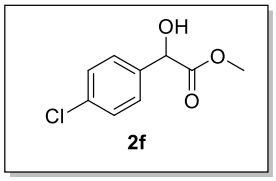
Methyl 2-(4-fluorophenyl)-2-hydroxyacetate **2e**[1a]



2e

According to the general procedure, **2e** (white solid, 32.9 mg, mp: 45–46 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 5:1) in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.38 (m, 2H), 7.05 (t, *J* = 8.8 Hz, 2H), 5.17 (s, 1H), 3.76 (s, 3H), 3.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 162.7 (d, $^1J_{C\text{-}F}$ = 245.4 Hz), 134.0, 128.3 (d, $^3J_{C\text{-}F}$ = 8.2 Hz, 2C), 115.5 (d, $^2J_{C\text{-}F}$ = 21.5 Hz, 2C), 72.1, 53.1. ^{19}F NMR (376 MHz, $CDCl_3$): -113.52. MS: m/z: $[M]^+$, 184.0.

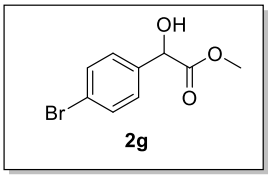
Methyl 2-(4-chlorophenyl)-2-hydroxyacetate **2f**[1a]



2f

According to the general procedure, **2c** (white solid, 36.3 mg, mp: 56–57 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.33 (m, 4H), 5.16 (d, *J* = 5.2 Hz, 1H), 3.77 (s, 3H), 3.54 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 136.6, 134.4, 128.8 (2C), 127.9 (2C), 72.2, 53.2. MS: m/z: $[M]^+$, 200.0.

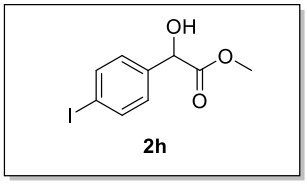
Methyl 2-(4-bromophenyl)-2-hydroxyacetate **2g**[1a]



2g

According to the general procedure, **2g** (white solid, 38.7 mg, mp: 55–56 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.15 (d, *J* = 5.2 Hz, 1H), 3.77 (s, 3H), 3.54 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 137.1, 131.7 (2C), 128.2 (2C), 122.5, 72.2, 53.2. MS: m/z: $[M]^+$, 244.0.

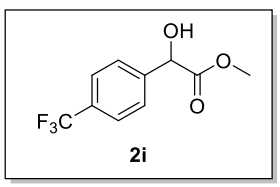
Methyl 2-hydroxy-2-(4-iodophenyl)acetate **2h**[3]



2h

According to the general procedure, **2h** (yellow oil, 48.4 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 83% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.18 (d, *J* = 5.2 Hz, 1H), 5.13 (d, *J* = 5.2 Hz, 1H), 3.60 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.6, 139.4, 137.0 (2C), 128.9 (2C), 94.1, 71.8, 51.9. MS: m/z: $[M]^+$, 292.0.

Methyl 2-hydroxy-2-(4-(trifluoromethyl)phenyl)acetate **2i**[4]

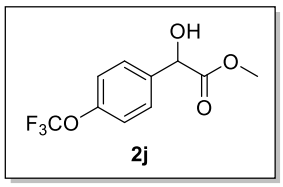


2i

According to the general procedure, **2i** (white oil, 32.8 mg, mp: 149–150 °C)

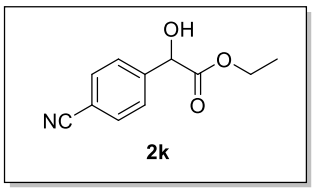
was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 66% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 5.25 (d, *J* = 4.8 Hz, 1H), 3.78 (s, 3H), 3.61 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 141.9, 130.5 (q, $^{2}J_{C\text{-}F}$ = 32.3 Hz, 2C), 126.9 (2C), 125.5 (q, $^{3}J_{C\text{-}F}$ = 3.2 Hz, 2C), 123.9 (q, $^{1}J_{C\text{-}F}$ = 270.7 Hz), 72.2, 53.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.64. MS: m/z: $[M]^+$, 234.0.

Methyl 2-hydroxy-2-(4-(trifluoromethoxy)phenyl)acetate **2j**



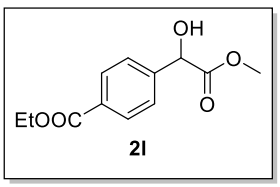
According to the general procedure, **2j** (yellow oil, 28.7 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 40:1) in 85% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.54 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.24 (d, *J* = 5.2 Hz, 1H), 5.23 (d, *J* = 5.6 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.6, 147.9, 139.0, 128.6 (2C), 120.8 (2C), 120.0 (q, $^{1}J_{C\text{-}F}$ = 254.6 Hz), 71.6, 51.9. ^{19}F NMR (376 MHz, DMSO-d_6): δ -56.86. HRMS (ESI-TOF) m/z: [M + H - H_2O]$^+$, calcd for $C_{10}H_8F_3O_3^+$: 233.0420; found: 233.0410.

Ethyl 2-(4-cyanophenyl)-2-hydroxyacetate **2k**[5]



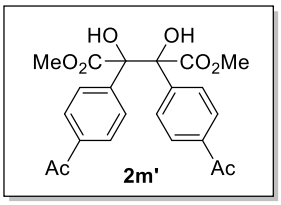
According to the general procedure, **2k** (yellow solid, 28.3 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 4:1) in 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 5.16 (s, 1H), 4.25–4.08 (m, 2H), 3.69 (s, 1H), 1.67 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 143.3, 132.2 (2C), 127.1 (2C), 118.5, 112.1, 72.1, 62.8, 13.9. MS: m/z: $[M]^+$, 191.1.

Ethyl 4-(2-ethoxy-1-hydroxy-2-oxoethyl)benzoate **2l**



According to the general procedure, **2l** (white solid, 25.9 mg, mp: 55–56 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 4:1) in 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 5.15 (d, *J* = 4.8 Hz, 1H), 4.22–4.09 (m, 2H), 3.85 (s, 3H), 3.59 (d, *J* = 5.2 Hz, 1H), 1.15 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 166.7, 143.2, 130,1, 129.8 (2C), 126.5 (2C), 72.4, 62.5, 51.2, 14.0. HRMS (ESI-TOF) m/z: [M + H - H_2O]$^+$, calcd for $C_{12}H_{13}O_4^+$: 221.0808; found: 221.0815.

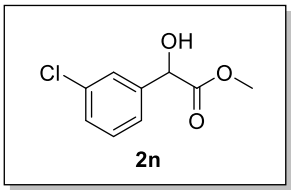
Dimethyl 2,3-bis(4-acetylphenyl)-2,3-dihydroxysuccinate **2m'**



According to the general procedure, **2m'** (*meso* + *dl*: white solid, 32.7 mg, mp: 67–68 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 1:1) in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (peaks are

reported for the mixture of both the *meso* and *dl* isomers) δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 5H), 7.21 (d, *J* = 8.4 Hz, 4H), 5.38 (s, 2H), 5.22 (s, 0.5 H), 3.84 (s, 1.5H), 3.79 (s, 6H), 1.60 (s, 6H), 1.28 (s, 1.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.3, 152.4, 152.0, 128.0, 127.5, 127.3, 127.1, 126.9, 77.2, 76.9, 51.9, 51.8, 24.8, 24.5. HRMS (ESI-TOF) m/z: $[M - H_2O + H]^+$ calcd for $C_{22}H_{21}O_7^+$, 397.1282; found, 397.1280.

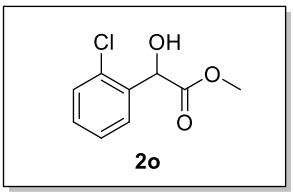
Methyl 2-(3-chlorophenyl)-2-hydroxyacetate **2n**[6]



2n

According to the general procedure, **2n** (yellow solid, 27.8 mg, mp: 48–49 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (brs, 1H), 7.31 (brs, 3H), 5.16 (d, *J* = 4.8 Hz, 1H), 3.78 (s, 3H), 3.58 (d, *J* = 5.2 Hz, 1H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 140.0, 134.5, 129.8, 128.6, 126.7, 124.7, 72.1, 53.3. MS: m/z: $[M]^+$, 200.0.

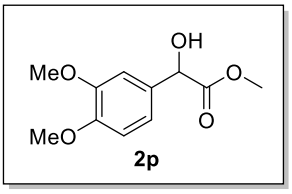
Methyl 2-(2-chlorophenyl)-2-hydroxyacetate **2o**[4]



2o

According to the general procedure, **2o** (yellow oil, 34.3 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 12:1) in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.39 (m, 2H), 7.29–7.27 (m, 2H), 5.58 (d, *J* = 5.2 Hz, 1H), 3.77 (s, 3H), 3.65 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 136.0, 133.5, 129.9, 129.8, 128.8, 127.1, 70.3, 53.1. MS: m/z: $[M]^+$, 200.0.

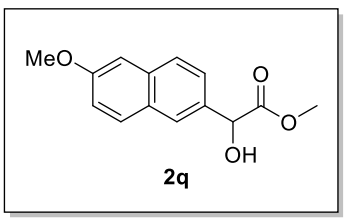
Methyl 2-(3,4-dimethoxyphenyl)-2-hydroxyacetate **2p**[6]



2p

According to the general procedure, **2p** (yellow oil, 38.5 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 2:1) in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97–6.94 (m, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.13 (d, *J* = 5.6 Hz, 1H), 3.88 (d, *J* = 4.0 Hz, 6H), 3.76 (s, 3H), 3.55 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 149.1, 149.0, 130.6, 119.1, 110.8, 109.3, 72.6, 55.8 (2C), 52.9. MS: m/z: $[M]^+$, 226.1.

Methyl 2-hydroxy-2-(6-methoxynaphthalen-2-yl)acetate **2q**

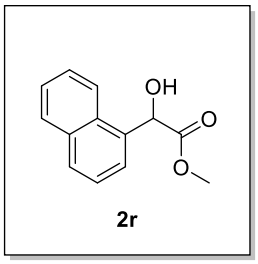


2q

According to the general procedure, **2q** (white solid, 40.9 mg, mp: 117–118 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 8:1) in 83% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84–7.78 (m, 3H), 7.50–7.47 (m, 1H), 7.30 (d, *J* = 2.4 Hz, 1H), 7.18–7.15 (m, 1H), 6.14 (d, *J* = 4.4 Hz, 1H), 5.27 (d, *J* = 4.8 Hz, 1H), 3.87 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.1, 157.4, 134.7, 133.9, 129.4, 128.0, 126.8, 125.4, 125.1, 118.8, 105.8, 72.5, 55.2, 51.7. HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$, calcd for

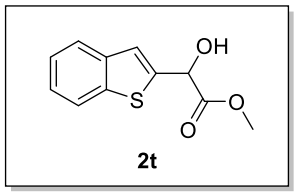
$C_{14}H_{13}O_3^+$: 229.0859; found: 229.0855.

Methyl 2-hydroxy-2-(naphthalen-1-yl)acetate **2r**[7]



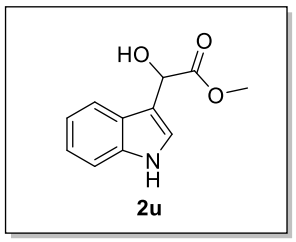
According to the general procedure, **2r** (white solid, 39.0 mg, mp: 77–78 ºC) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.89–7.84 (m, 2H), 7.56–7.43 (m, 4H), 5.80 (d, *J* = 4.0 Hz, 1H), 3.71 (s, 3H), 3.64 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 134.0, 133.9, 130.9, 129.4, 128.8, 126.6, 125.9 (2C), 125.2, 123.6, 71.4, 53.0. MS: m/z: $[M]^+$, 216.1.

Methyl 2-(benzo[b]thiophen-2-yl)-2-hydroxyacetate **2t**



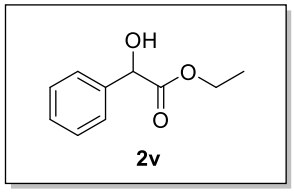
According to the general procedure, **2t** (yellow oil, 25.7 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 58% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.93 (d, *J* = 7.2 Hz, 1H), 7.82–7.80 (m, 1H), 7.41 (brs, 1H), 7.38–7.32 (m, 2H), 6.61 (d, *J* = 5.2 Hz, 1H), 5.55 (d, *J* = 5.2 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 171.7, 143.6, 139.0, 138.9, 124.4 (2C), 123.6, 122.4, 121.7, 69.0, 52.1. HRMS (ESI-TOF) m/z: $[M + H - H_2O]^+$, calcd for $C_{11}H_9O_2S^+$: 205.0318; found: 205.0310.

Methyl 2-hydroxy-2-(1H-indol-3-yl)acetate **2u**[8]



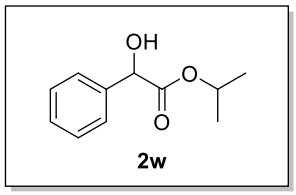
According to the general procedure, **2u** (yellow oil, 31.1 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 3:1) in 76% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.06 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.37–7.32 (m, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 5.71 (d, *J* = 5.2 Hz, 1H), 5.37 (d, *J* = 5.2 Hz, 1H), 3.60 (s, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 173.6, 136.2, 125.5, 124.0, 121.2, 119.3, 118.8, 113.4, 111.5, 66.6, 51.5. MS: m/z: $[M]^+$, 205.0.

Ethyl 2-hydroxy-2-phenylacetate **2v**[9]



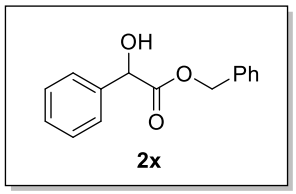
According to the general procedure, **2v** (yellow oil, 28.5 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.30 (m, 5H), 5.16 (d, *J* = 5.6 Hz, 1H), 4.29–4.16 (m, 2H), 3.54 (d, *J* = 5.6 Hz, 1H), 1.22 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 138.4, 128.5 (2C), 128.3, 126.5 (2C), 72.9, 62.2, 14.0. MS: m/z: $[M]^+$, 180.0.

Isopropyl 2-hydroxy-2-phenylacetate **2w**[9]



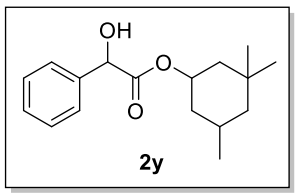
According to the general procedure, **2w** (white solid, 21.3 mg, mp: 34–35 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 55% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.41–7.27 (m, 5H), 5.97 (s, 1H), 5.07 (d, *J* = 5.2 Hz, 1H), 4.93–4.86 (m, 1H), 1.18 (d, *J* = 6.0 Hz, 3H), 1.06 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 172.1, 139.7, 128.2 (2C), 127.8, 126.5 (2C), 72.5, 67.8, 21.5, 21.3. MS: m/z: $[M]^+$, 194.0.

Benzyl 2-hydroxy-2-phenylacetate **2x**[9]



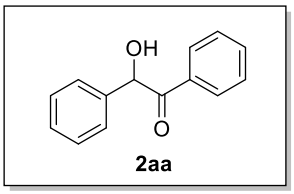
According to the general procedure, **2x** (white solid, 40.9 mg, mp: 88–89 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 6.8 Hz, 2H), 7.35–7.30 (m, 6H), 7.20 (d, *J* = 2.4 Hz, 2H), 5.23 (d, *J* = 12.4 Hz, 2H), 5.12 (d, *J* = 12.4 Hz, 1H), 3.53 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 138.1, 134.9, 128.5 (5C), 128.4, 127.9 (2C), 126.5 (2C), 72.9, 67.6. MS: m/z: $[M]^+$, 242.0.

3,3,5-Trimethylcyclohexyl 2-hydroxy-2-phenylacetate **2y**[1a]



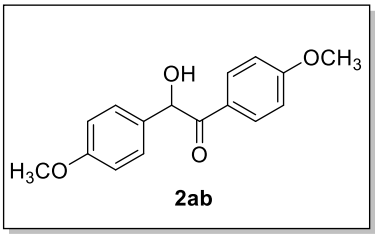
According to the general procedure, **2y**, a mixture of diastereomers (yellow oil, 48.6 mg), was isolated by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.30 (m, 5H), 5.11 (d, *J* = 4.8 Hz, 1H), 4.99–4.91 (m, 1H), 3.53 (d, *J* = 5.6 Hz, 1H), 2.04–2.01 (m, 0.5H), 1.75–1.68 (m, 2H), 1.51–1.47 (m, 0.5H), 1.33–1.12 (m, 2H), 0.98–0.89 (m, 9H), 0.84–0.70 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 138.6, 128.4 (2C), 128.2, 126.4 (2C), 73.5, 72.9, 47.3, 43.3, 40.1, 39.7, 32.9, 32.8, 32.3, 27.0, 26.9. 25.4, 25.4, 22.2, 22.1. MS: m/z: $[M]^+$, 276.2.

2-Hydroxy-1,2-diphenylethan-1-one **2aa**[10]



According to the general procedure, **2aa** (white solid, 32.8 mg, mp: 120–121 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.33–7.26 (m, 5H), 5.96 (d, *J* = 6.0 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 139.0, 133.9, 133.5, 129.9, 129.1 (4C), 128.6 (2C), 128.5, 127.7, 76.2. MS: m/z: $[M]^+$, 212.0.

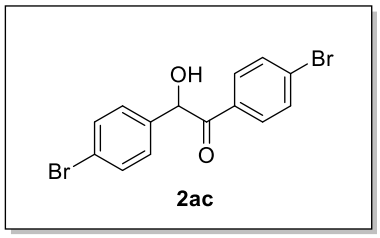
2-Hydroxy-1,2-bis(4-methoxyphenyl)ethan-1-one **2ab**[10]



According to the general procedure, **2ab** (white solid, 50.4 mg, mp: 107–108 °C) was obtained by column chromatography with the eluting

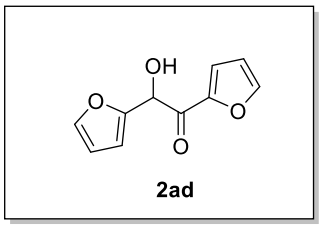
(petroleum ether/ethyl acetate = 5:1) in 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.86–6.83 (m, 4H), 5.85 (d, *J* = 6.0 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 163.9, 159.5, 131.7, 131.5 (2C), 128.9 (2C), 126.1, 114.4 (2C), 113.8 (2C)., 75.1, 55.4, 55.1. MS: m/z: $[M]^+$, 272.0.

1,2-Bis(4-bromophenyl)-2-hydroxyethan-1-one **2ac**[10]



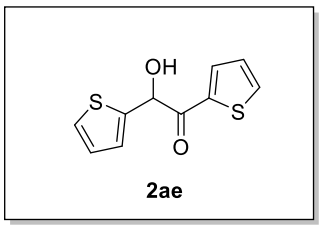
According to the general procedure, **2ac** (white solid, 51.8 mg, mp: 100–101 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.00 (d, *J* = 7.6 Hz, 2H), 7.58–7.45 (m, 4H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.20 (d, *J* = 5.6 Hz, 1H), 6.10 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 198.8, 139.2, 134.6, 133.3, 131.4 (2C), 129.4 (2C), 128.9 (2C), 128.6 (2C), 120.9, 74.9. MS: m/z: $[M]^+$, 370.0.

1,2-Di(furan-2-yl)-2-hydroxyethan-1-one **2ad**[11]



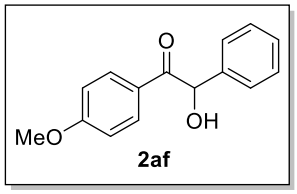
According to the general procedure, **2ad** (yellow solid, 21.3 mg, mp: 111–112 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 55% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (s, 1H), 7.60 (s, 1H), 7.53 (d, *J* = 3.6 Hz, 1H), 6.71–6.70 (m, 1H), 6.42 (s, 2H), 6.14 (d, *J* = 6.4 Hz, 1H), 5.80 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 184.9, 152.4, 149.6, 148.3, 143.0, 120.4, 112.5, 110.7, 108.5, 69.5. MS: m/z: $[M]^+$, 192.0.

2-Hydroxy-1,2-di(thiophen-2-yl)ethan-1-one **2ae**[11]



According to the general procedure, **2ae** (yellow solid, 23.5 mg, mp: 100–101 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 52% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.15 (d, *J* = 3.6 Hz, 1H), 8.04 (d, *J* = 5.2 Hz, 1H), 7.47 (d, *J* = 5.2 Hz, 1H), 7.24 (t, *J* = 4.8 Hz, 1H), 7.11 (d, *J* = 3.2 Hz, 1H), 6.98-6.96 (m, 1H), 6.57 (d, *J* = 4.8 Hz, 1H), 6.11 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.1, 143.0, 140.1, 135.7, 134.6, 128.6, 126.8, 126.3, 125.9, 72.6. MS: m/z: $[M]^+$, 224.0.

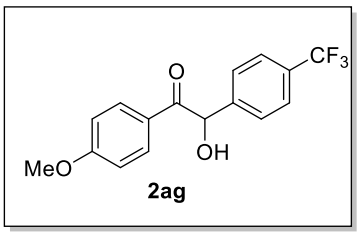
2-Hydroxy-1-(4-methoxyphenyl)-2-phenylethan-1-one **2af**[12]



According to the general procedure, **2af** (white solid, 34.6 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 4:1) in 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 2H),

7.45–7.19 (m, 4H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.82 (d, *J* = 6.0 Hz, 1H), 4.60 (d, J = 6..0 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 191.7, 164.0, 139.5, 132.0 (2C), 129.1 (2C), 128.7, 127.7 (2C), 126.1, 113.9 (2C), 75.8, 55.5. MS: m/z: $[M]^+$, 242.1.

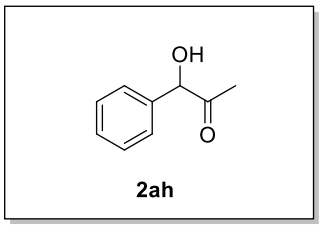
2-Hydroxy-1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-one **2ag**[13]



2ag

According to the general procedure, **2ag** (white solid, 45.9 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 4:1) in 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.88 (s, 1H), 4.65 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 164.4, 143.3, 131.6 (2C), 130.5 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 128.0 (2C), 126.0 (q, $^3J_{C\text{-}F}$ = 3.7 Hz, 2C), 128.5, 123.8 (q, $^1J_{C\text{-}F}$ = 270.5 Hz), 114.1 (2C), 75.0, 55.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.69. MS: m/z: $[M]^+$, 310.1.

1-Hydroxy-1-phenylpropan-2-one **2ah**[12]



2ah

According to the general procedure, **2ah** (white oil, 18.0 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 60% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40–7.28 (m, 5H), 6.04 (d, *J* = 4.4 Hz, 1H), 5.05 (d, *J* = 4.4 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 208.7, 139.4, 128.4 (2C), 127.8, 126.6 (2C), 79.2, 25.0. MS: m/z: $[M]^+$, 150.0.

Mechanistic studies

Determination the absorbtion of 1a at visible-light region

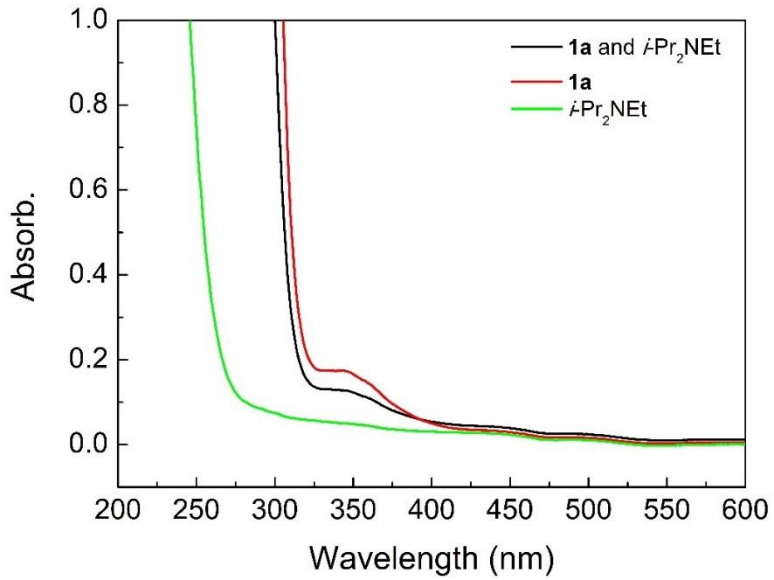
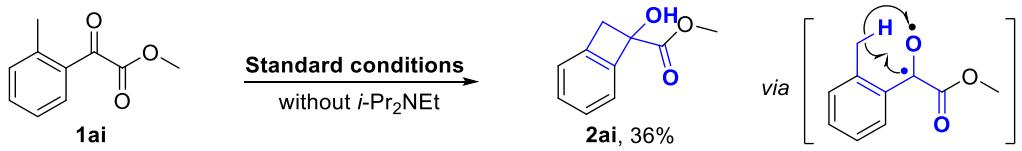


Figure S1. UV-vis spectra of *i*-Pr_2NEt, **1a**, and mixture of **1a** with *i*-Pr_2NEt in CH_3CN.

According to the above UV-vis spectra (Figure S1), the absorption of **1a** stretched to visible light region (~ 400 nm) and *i*-Pr_2NEt did not show any aborsorbtion in visible light region. However, the mixture of **1a** and *i*-Pr_2NEt showed slight blue shift. So, we deduced that a complexation between the two compounds may occur.

Norrish-Yang photocyclization experiment



Scheme S2. Norrish-Yang photocyclization experiment.

Substrate **1ai** (71.2 mg, 0.4 mmol, 1.0 equiv), H_2O (108 mg, 6.0 mmol, 15.0 equiv) were added to reaction tube. Then the solvent CH_3CN (4.0 mL) was added under Ar atmosphere. The reaction mixture was stirred under purple LED irradiation for 6.0 h. The volatile materials were then evaporated under vacuum and the residue was further purified by flash column chromatography with the eluent of petroleum ether/ethyl acetate (10:1) to afford the cyclization product **2ai** (yellow oil, 25.8 mg) in 36% yield. **2ai**[14]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7,20 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 4.04 (s,1H), 3.79 (d, *J* = 14.0 Hz, 1H), 3.75 (s, 3H), 3.36 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 145.3, 142.9, 130.0, 127.7, 123.4, 121.1, 78.1, 53.1, 45.6. MS: m/z: $[M]^+$, 178.0.

Deuterium labelling experiments

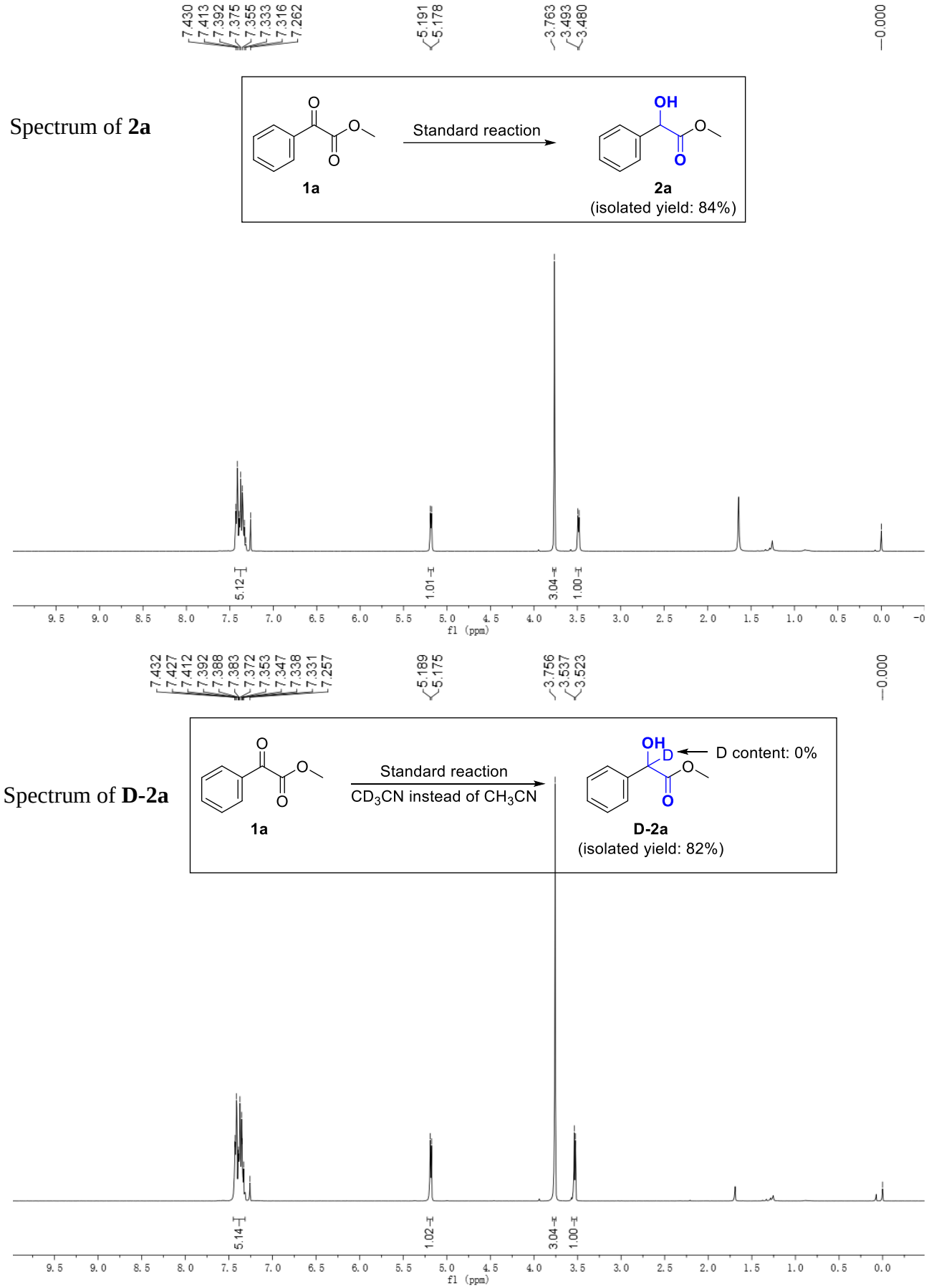
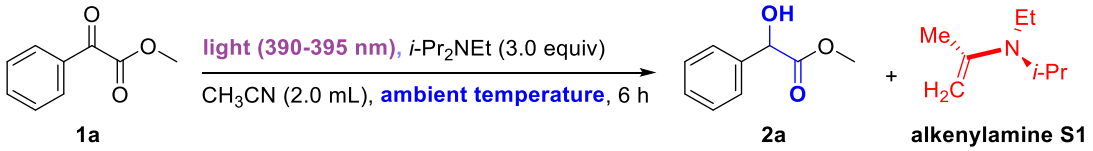


Figure S2. ^{1}H NMR spectra of **2a** and D-**2a**.

Determination the presence of alkenylamine S1.



To determine the formation of alkenylamine in the reaction, a control experiment of standard reaction without H_2O was performed. After the reaction was finished, a GC-MS analysis of the crude mixture was performed. Indeed, a peak corresponding to the alkenylamine **S1** was found (see Figure S3, m/z: 127.00 corresponds to the molecular ion peak, m/z: 112.00 corresponds to the fragment peak that loses a methyl group, m/z: 84.00 corresponds to the fragment peak that loses an isopropyl group, and m/z: 70.00 corresponds to the fragment peak that loses a methyl group and an isopropyl group).

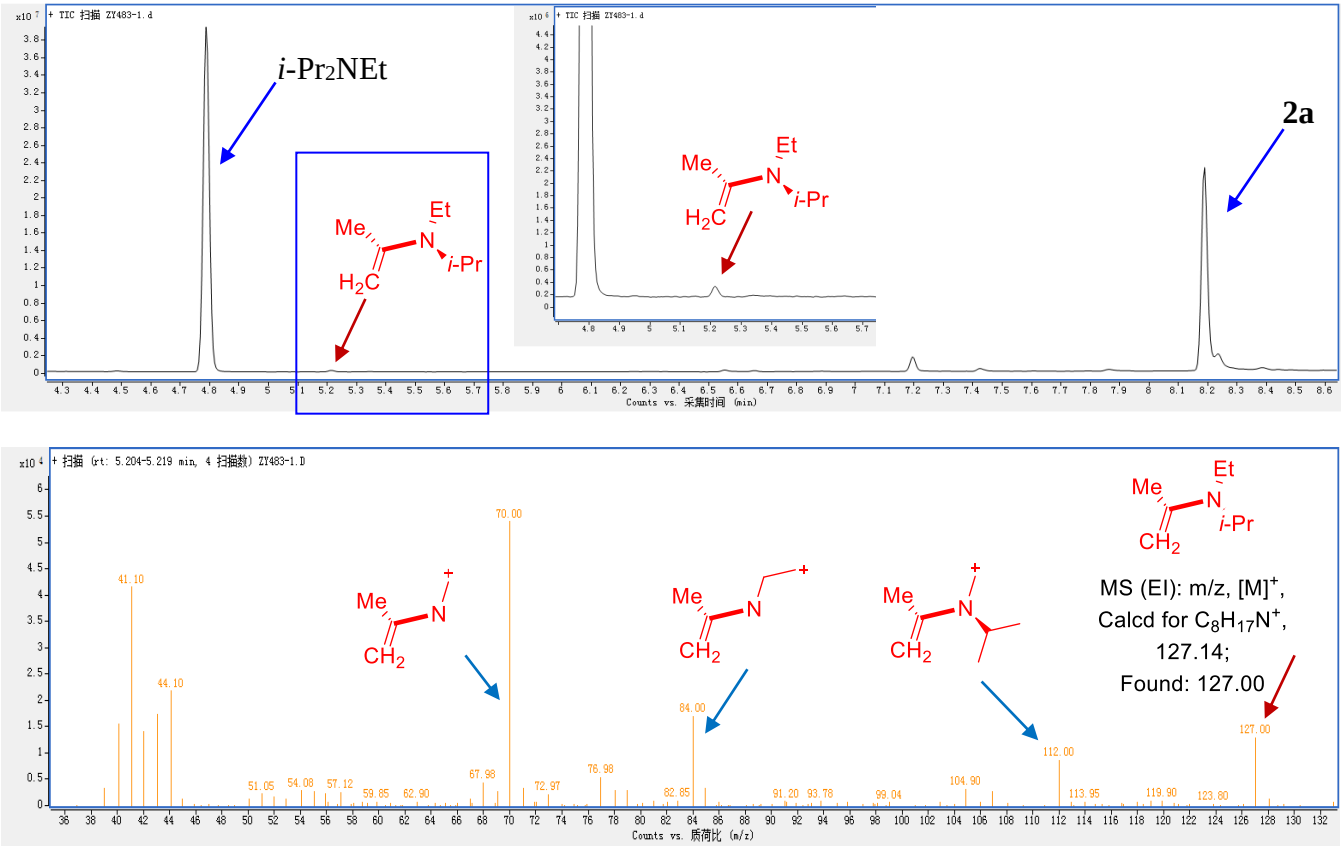
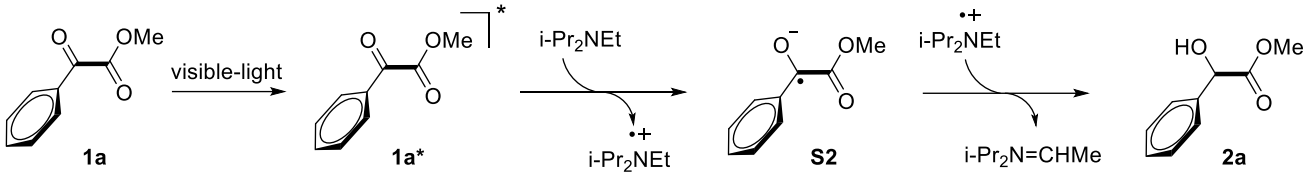


Figure S3. GC spectrum of crude mixture and MS analysis of alkenylamine **S1**.

Another plausible reaction mechanism



Scheme S3. A plausible reaction mechanism.

References

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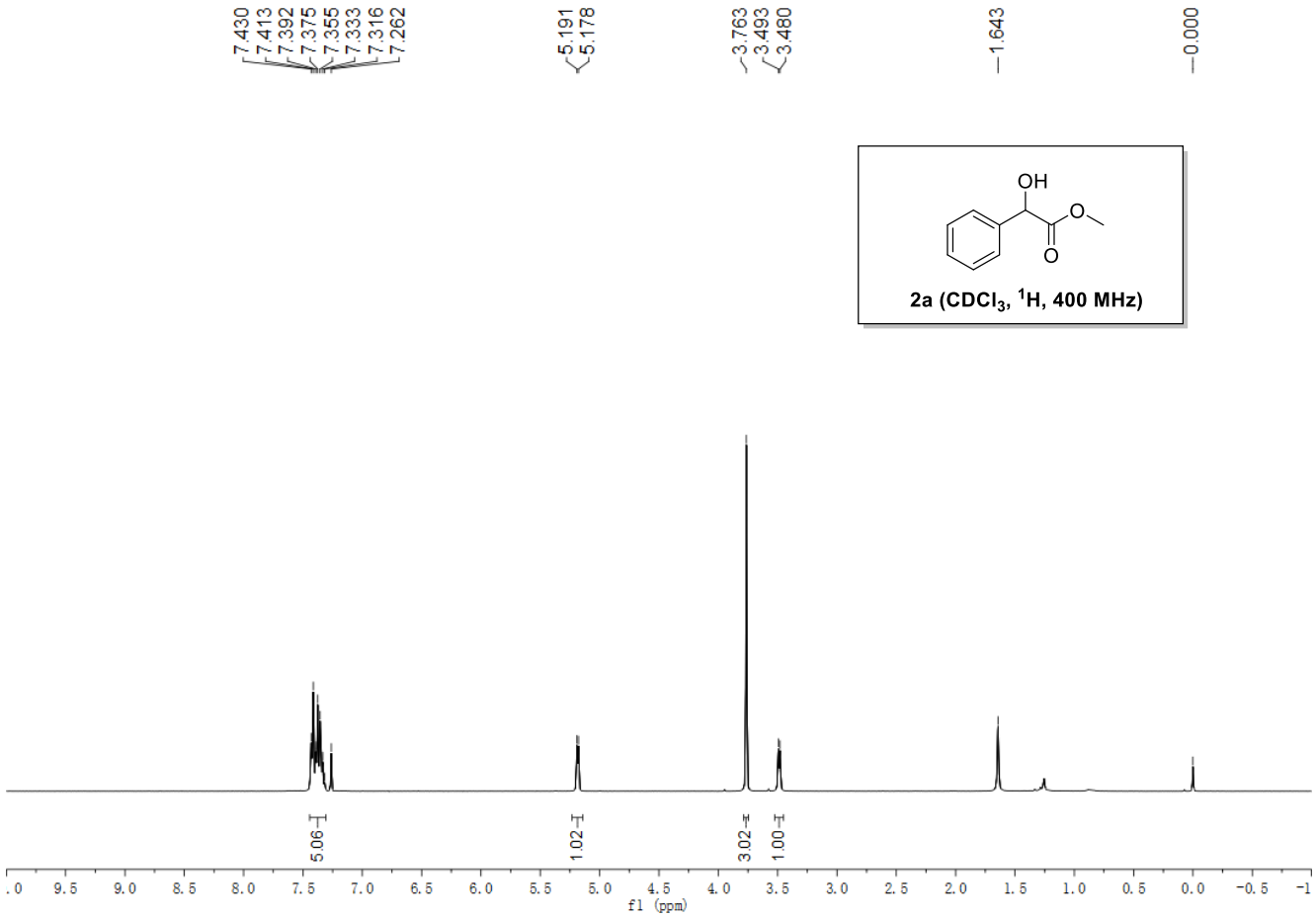
Spectrum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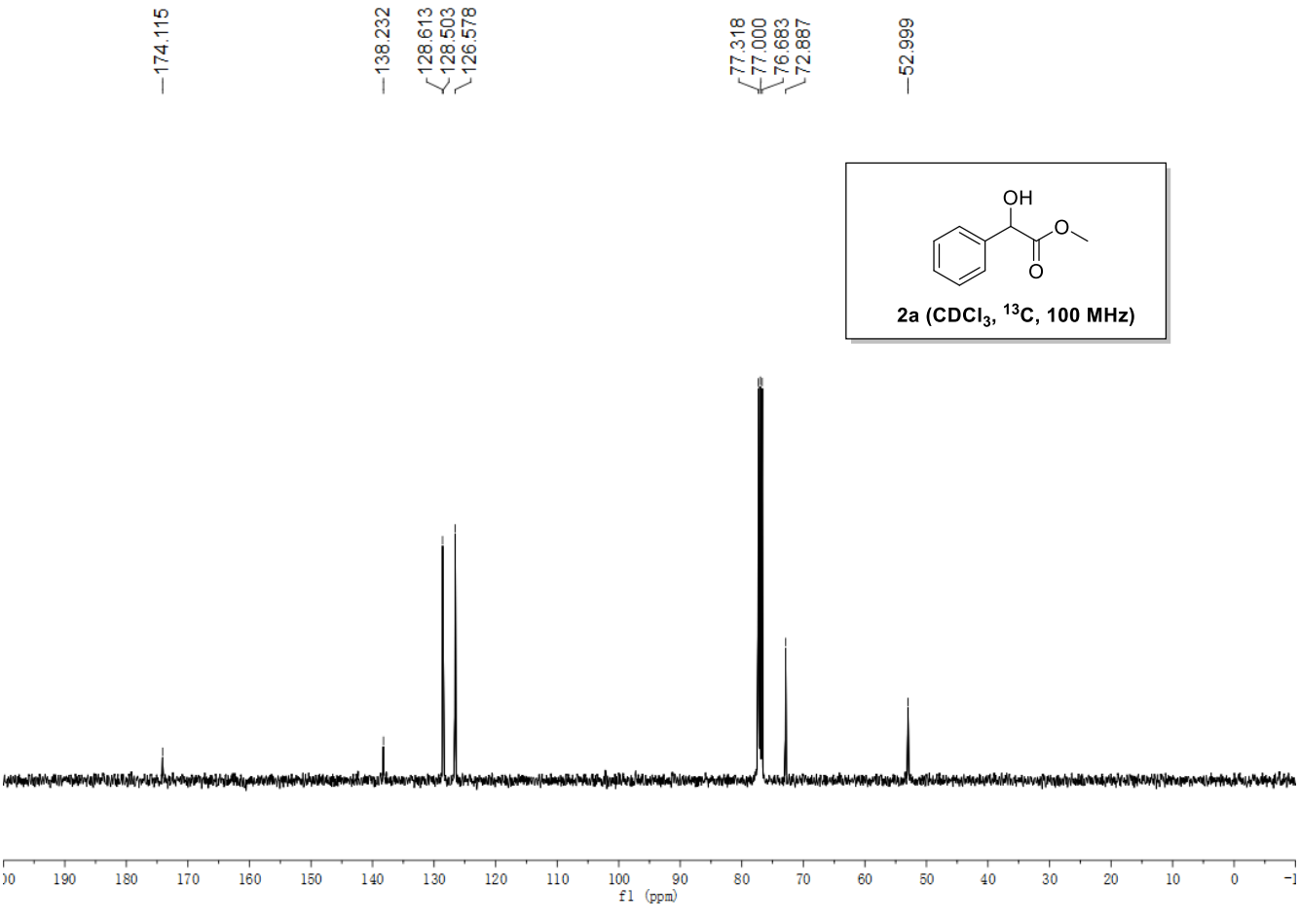
7.392
7.375
7.355
7.333
7.316
7.262
5.191
5.178
3.763
3.493
3.480
1.643
0.000
OH
O
O
2a (CDCl3, 1H, 400 MHz)
5.06
1.02
3.02
1.00
f1 (ppm)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126.578
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77.000
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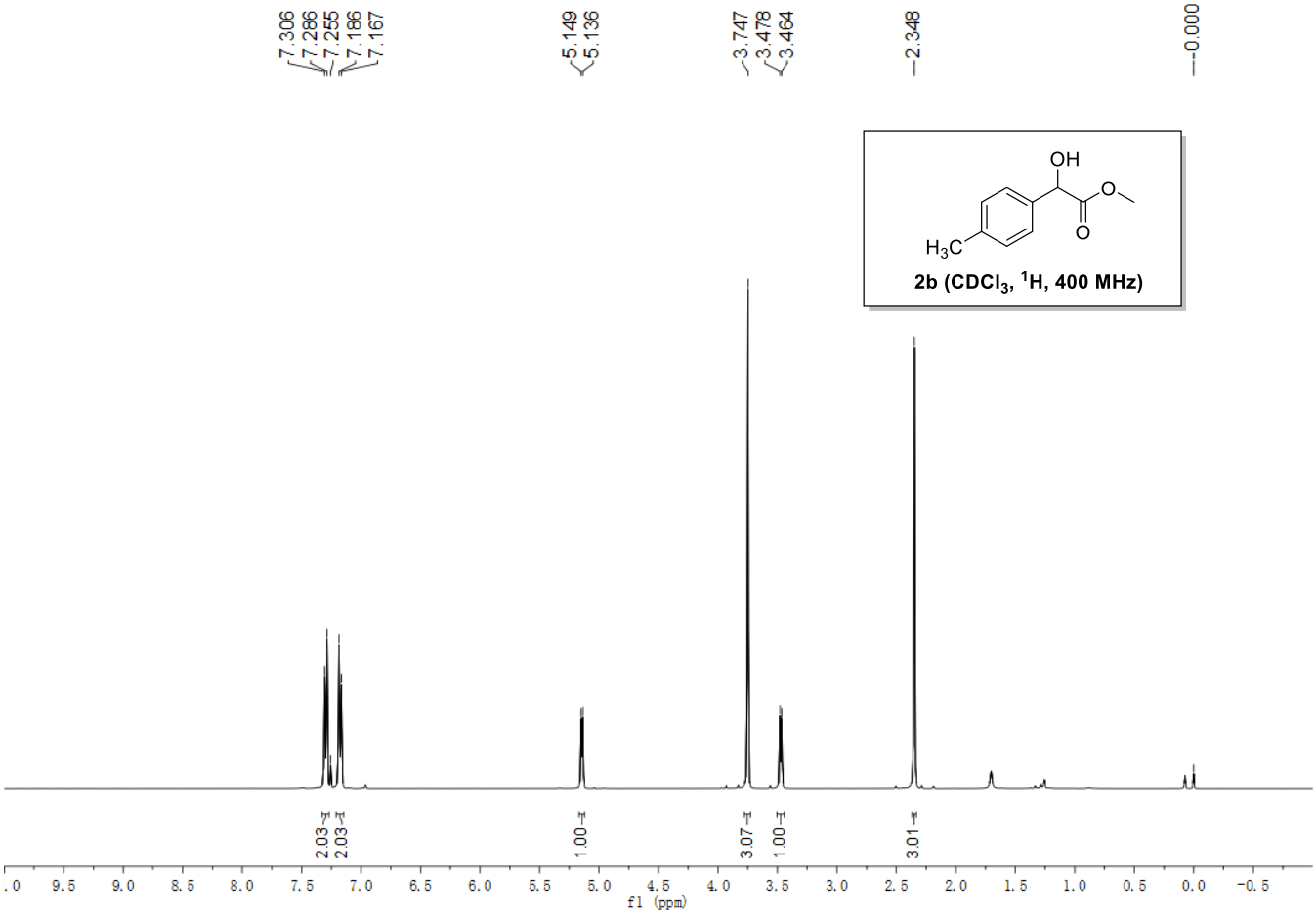
52.999
OH
O
O
2a (CDCl3, 13C, 100 MHz)
f1 (ppm)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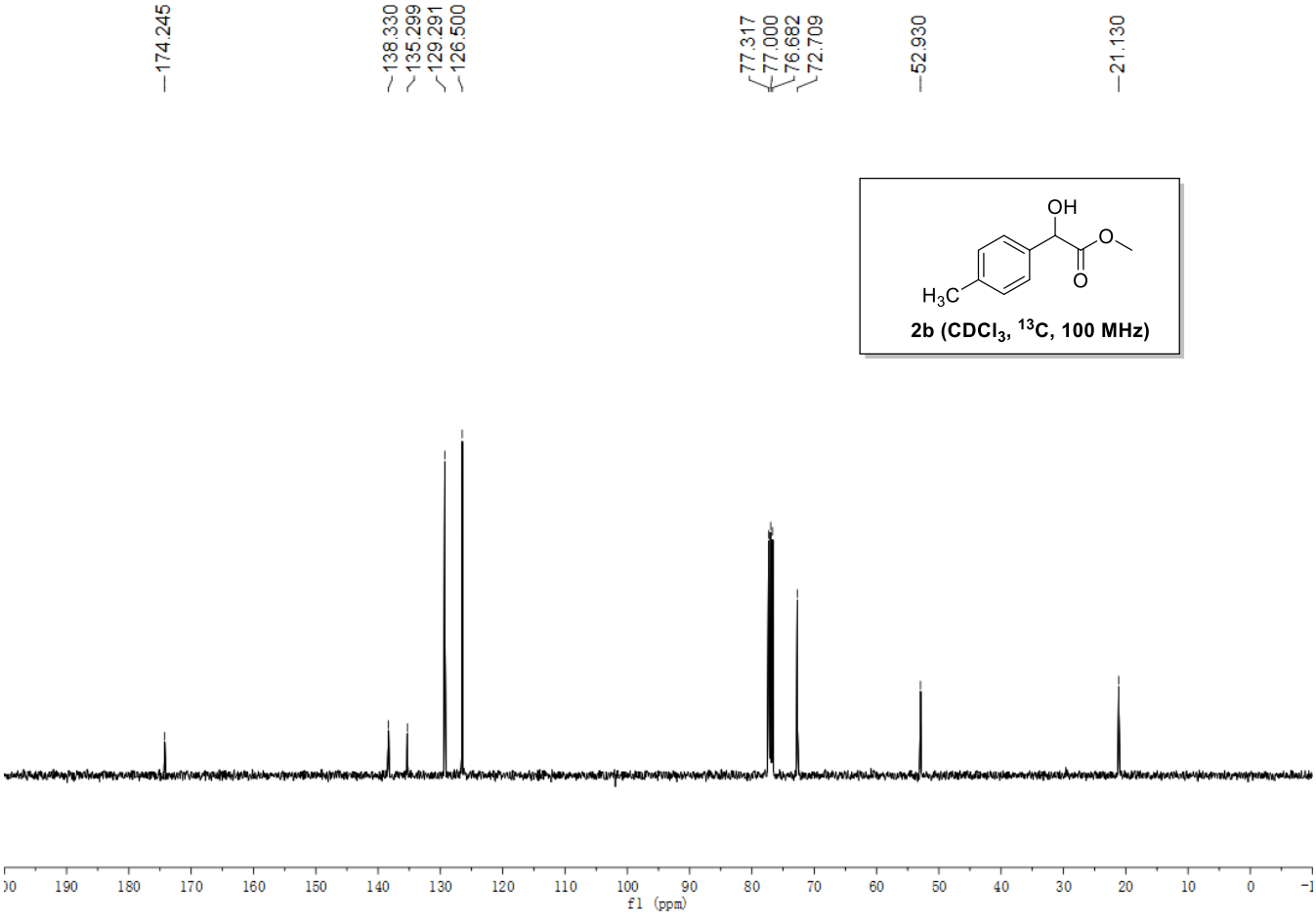
7.286
7.255
7.186
7.167
5.149
5.136
3.747
3.478
3.464
2.348
0.000
OH
O
O
H3C
2b (CDCl3, 1H, 400 MHz)
2.03
2.03
1.00
3.07
1.00
3.01
f1 (ppm)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138.330
135.299
129.291
126.500
77.317
77.000
76.682
72.709
52.930
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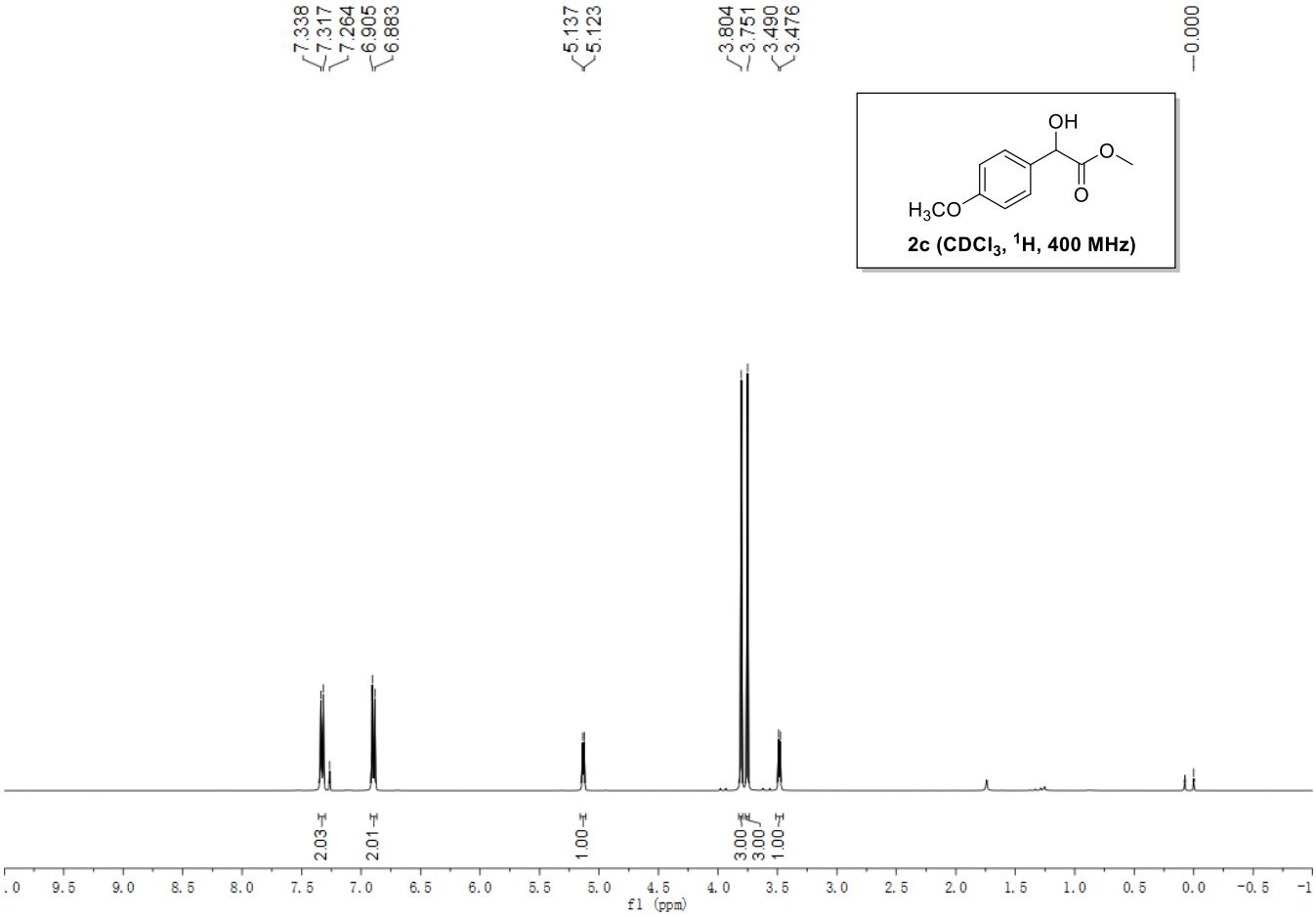
OH
O
O
H3C
2b (CDCl3, 13C, 100 MHz)
f1 (ppm)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7.317
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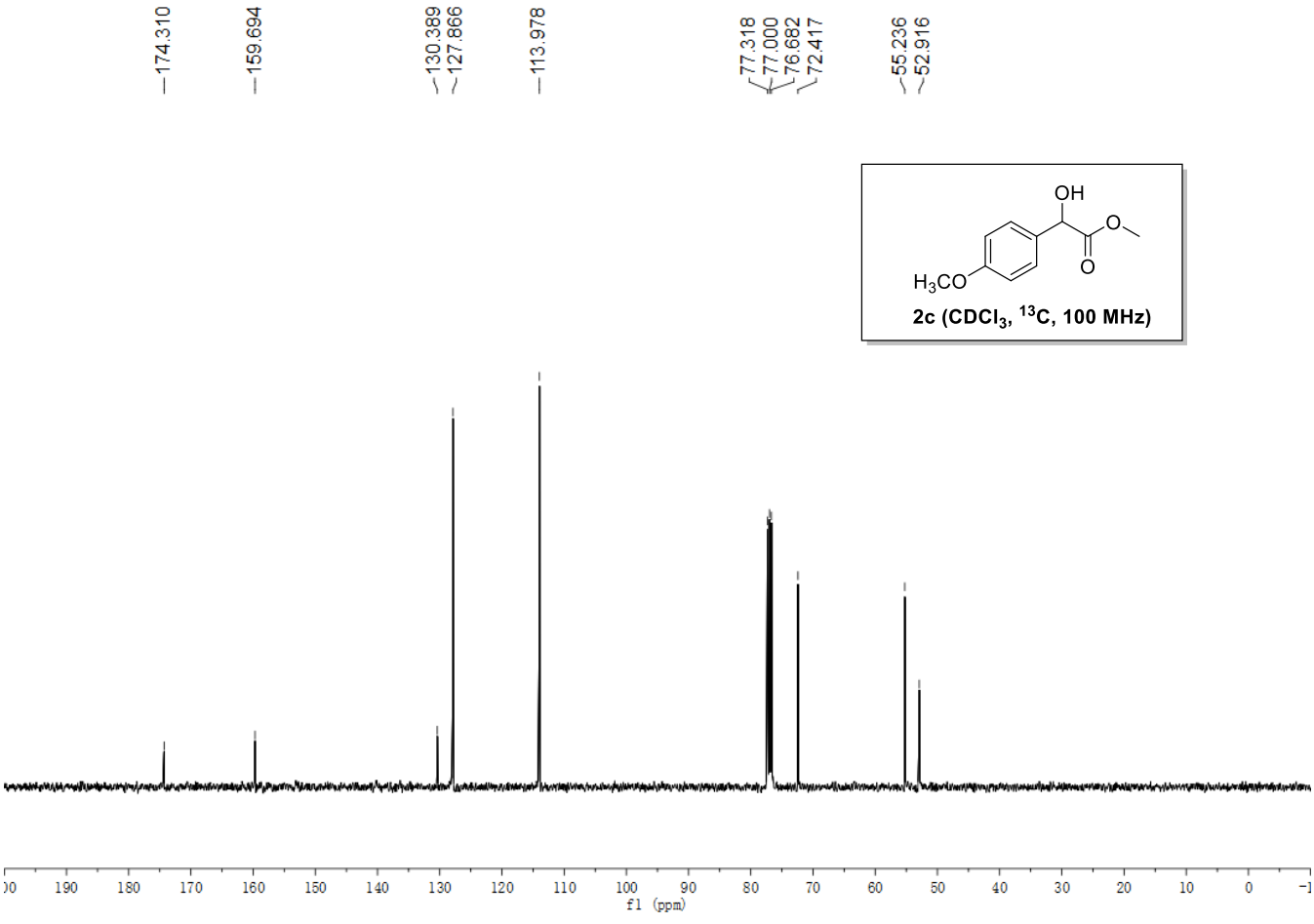
6.883
5.137
5.123
3.804
3.751
3.490
3.476
0.000
OH
O
O
H3CO
2c (CDCl3, 1H, 400 MHz)
2.03
2.01
1.00
3.00
3.00
1.00
f1 (ppm)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127.866
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77.318
77.000
76.682
72.417
55.236
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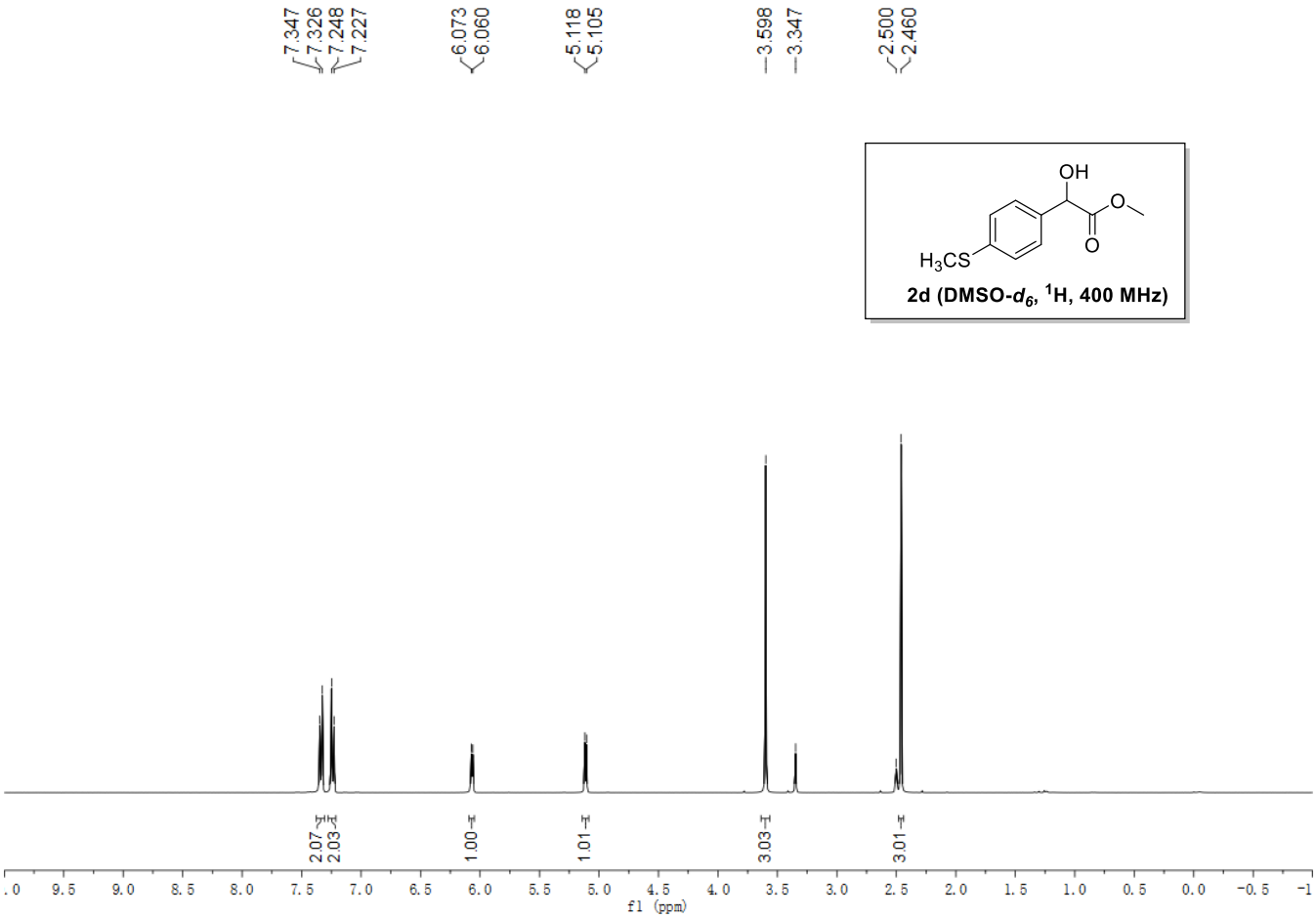
OH
O
O
H3CO
2c (CDCl3, 13C, 100 MHz)
f1 (ppm)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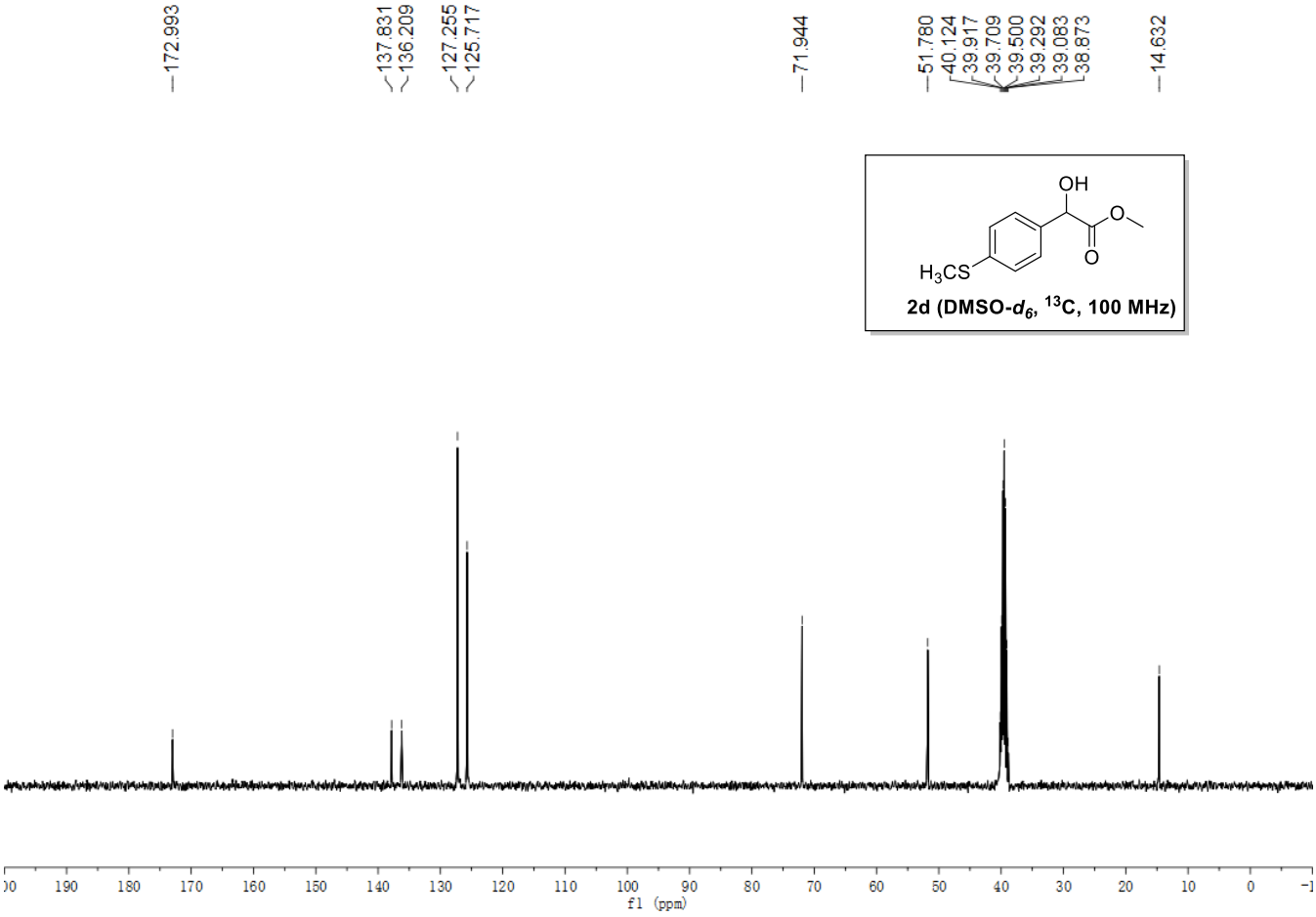
7.227
6.073
6.060
5.118
5.105
3.598
3.347
2.500
2.460
OH
O
O
H3CS
2d (DMSO-d6, 1H, 400 MHz)
2.07
2.03
1.00
1.01
3.03
3.01
f1 (ppm)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136.209
127.255
125.717
71.944
51.780
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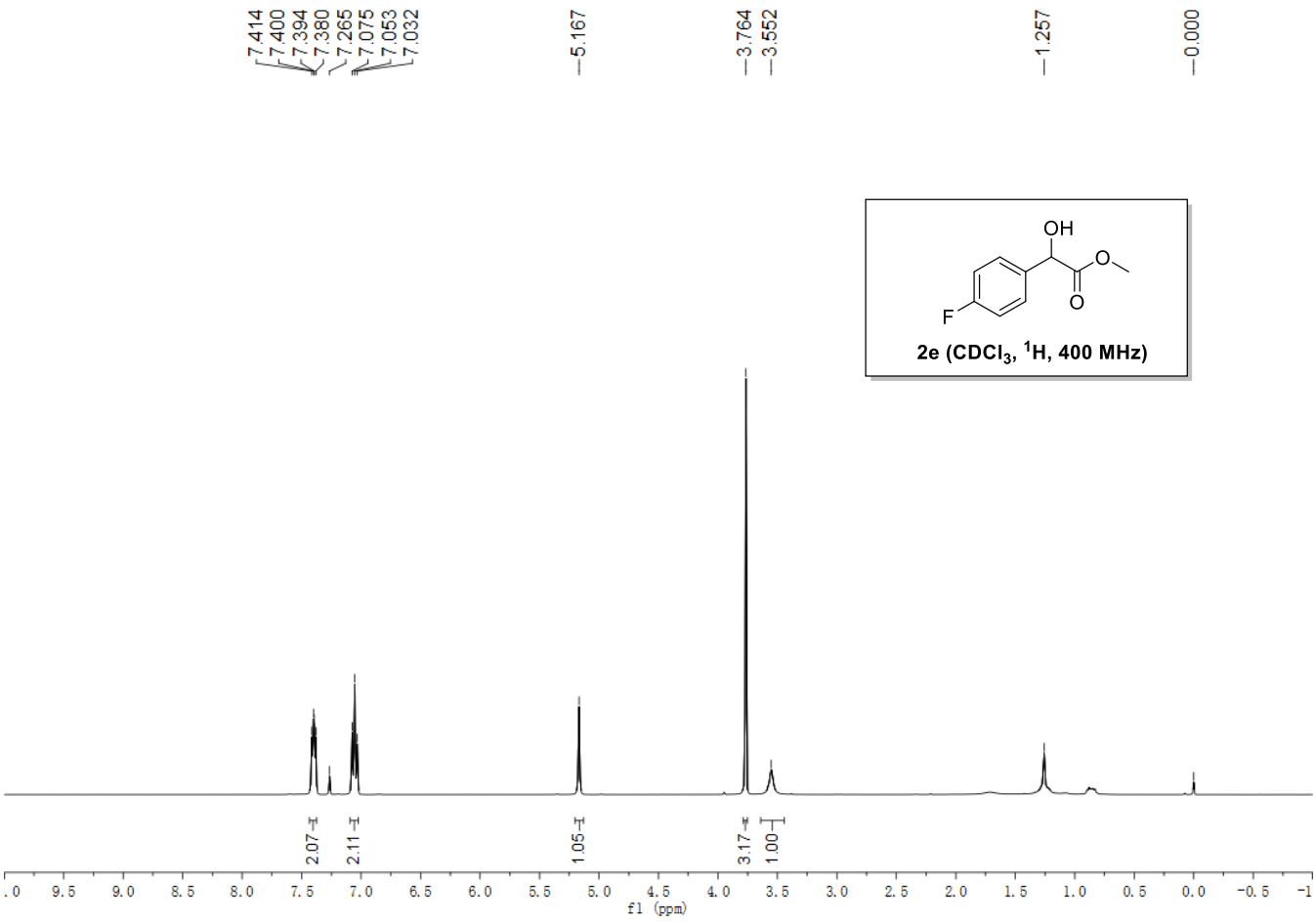
39.709
39.500
39.292
39.083
38.873
14.632
OH
O
O
H3CS
2d (DMSO-d6, 13C, 100 MHz)
f1 (ppm)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7.380
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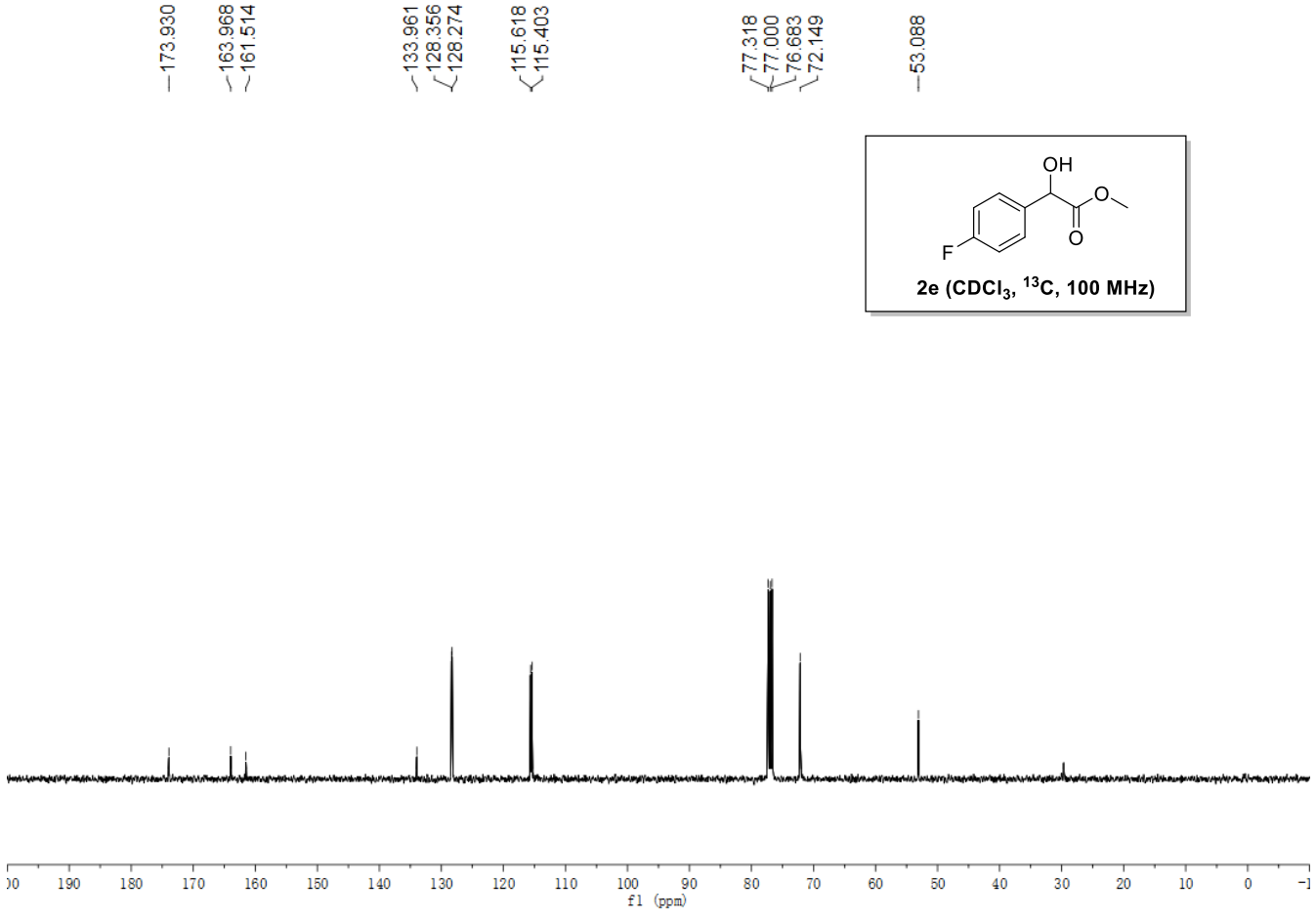
1.257
0.000
OH
O
O
F
2e (CDCl3, 1H, 400 MHz)
2.07
2.11
1.05
3.17
1.00
f1 (ppm)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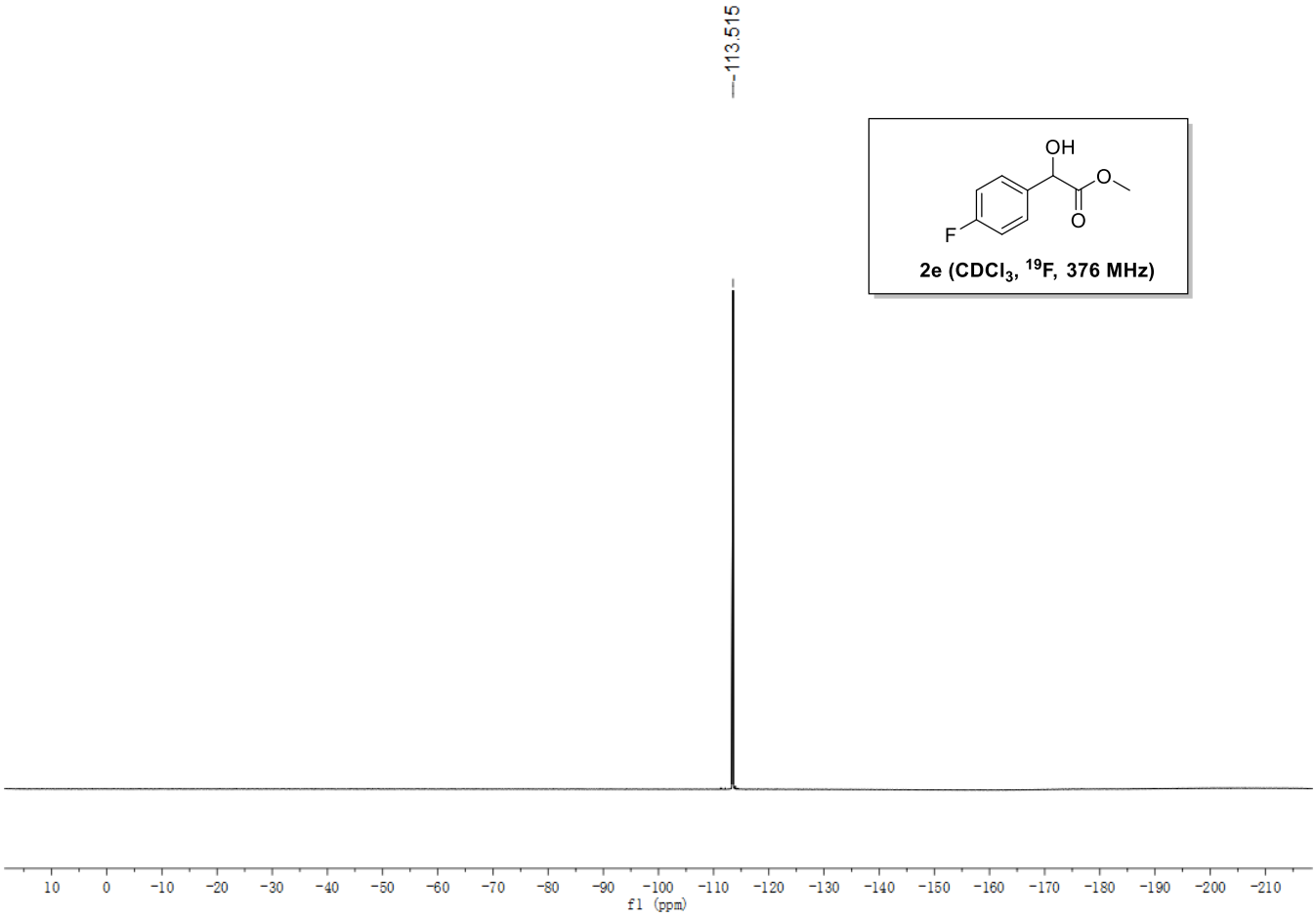
OH
O
O
F
2e (CDCl3, 13C, 100 MHz)
f1 (ppm)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OH
O
O
F
2e (CDCl3, 19F, 376 MHz)
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f1 (ppm)


7.384
7.378
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7.351
7.334
7.329
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3.768
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3.536
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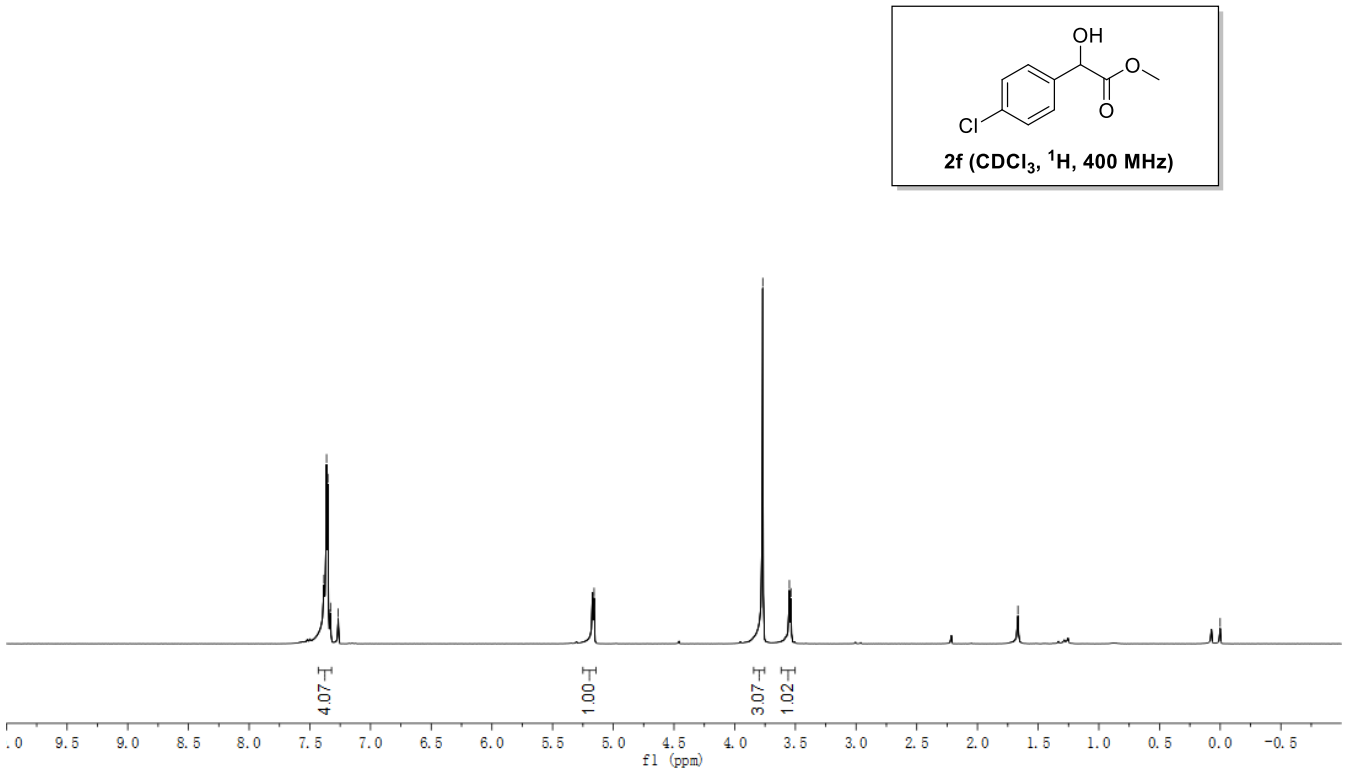
0.000


OH
O
O
Cl
2f (CDCl3, 1H, 400 MHz)
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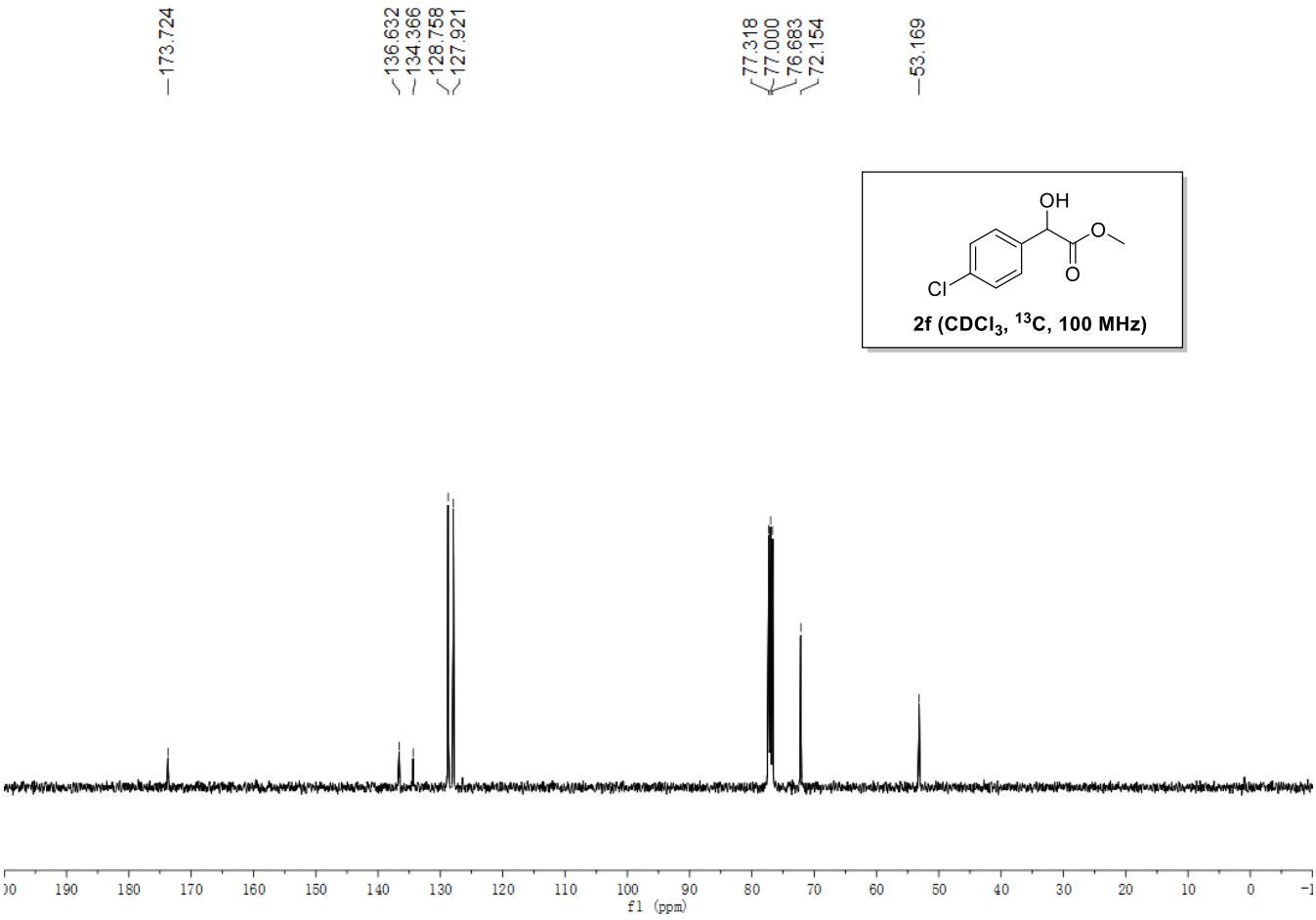
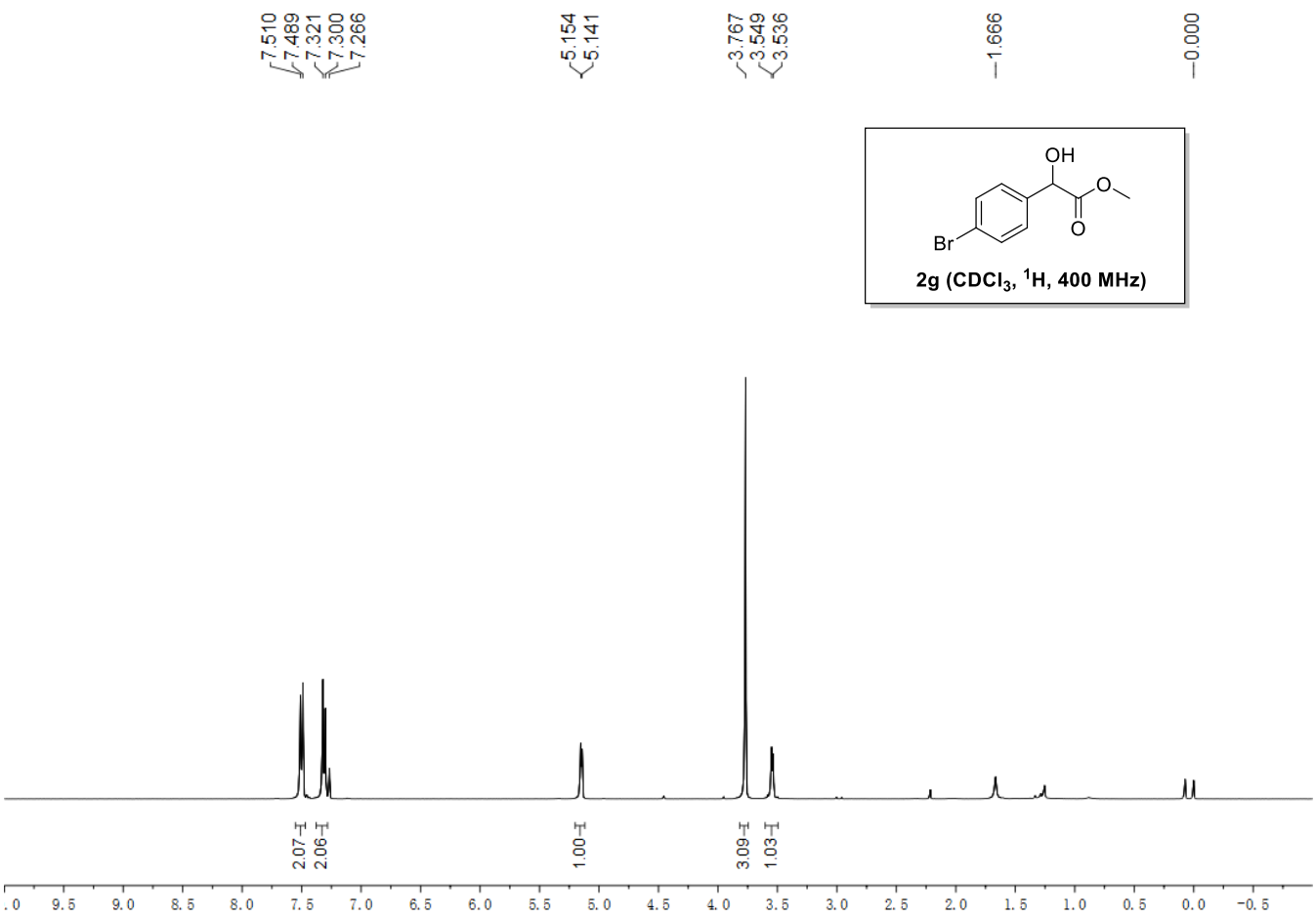
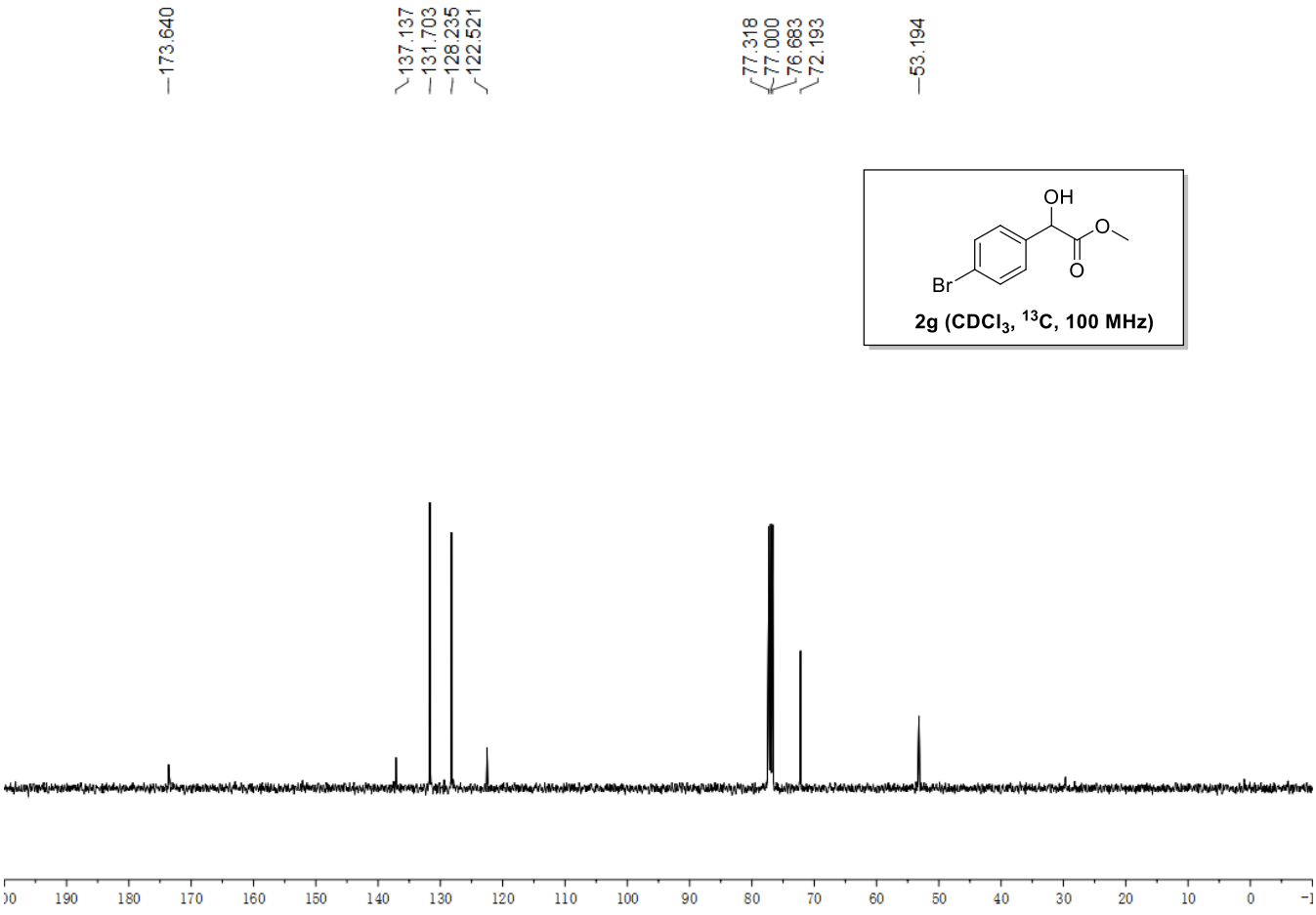
1.00
3.07
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



2f ($CDCl_3$, ^{13}C, 100 MHz)



2g ($CDCl_3$, ^{1}H, 400 MHz)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131.703
128.235
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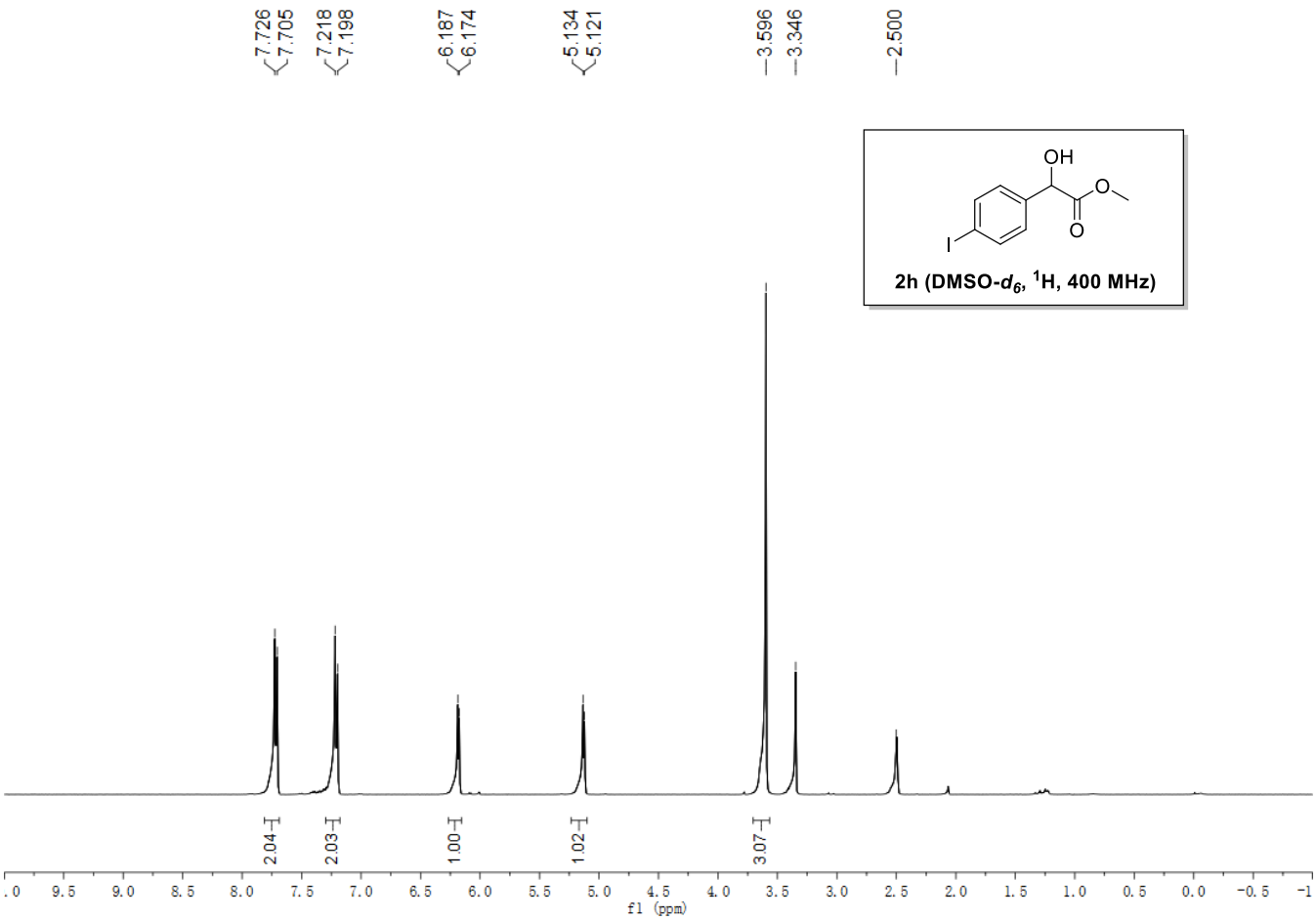
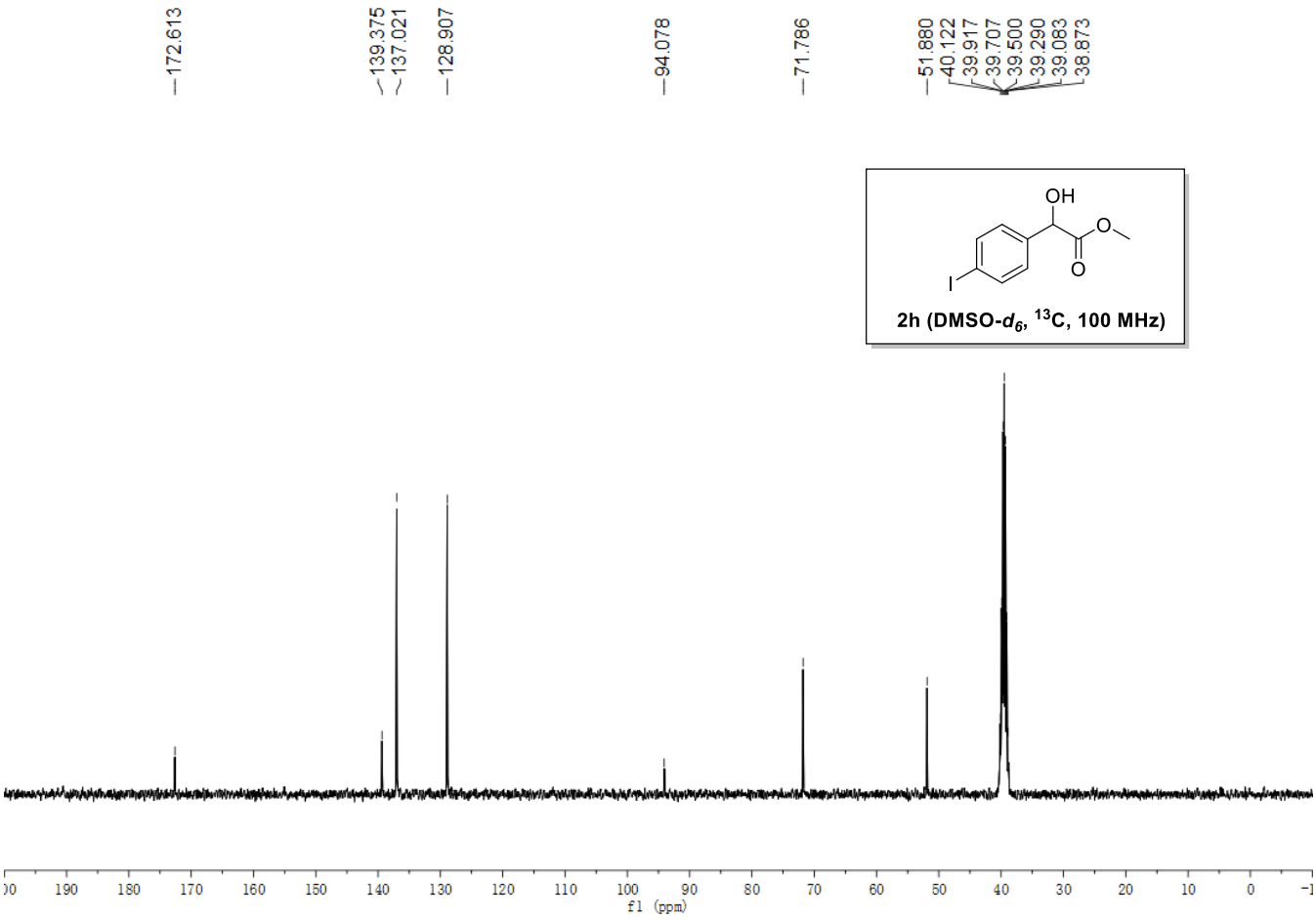
77.000
76.683
72.193
53.194
OH
O
O
Br
2g (CDCl3, 13C, 100 MHz)


7.726
7.705
7.218
7.198
6.187
6.174
5.134
5.121
3.596
3.346
2.500
OH
O
O
I
2h (DMSO-d6, 1H, 400 MHz)
2.04
2.03
1.00
1.02
3.07
f1 (ppm)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128.907
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71.786
51.880
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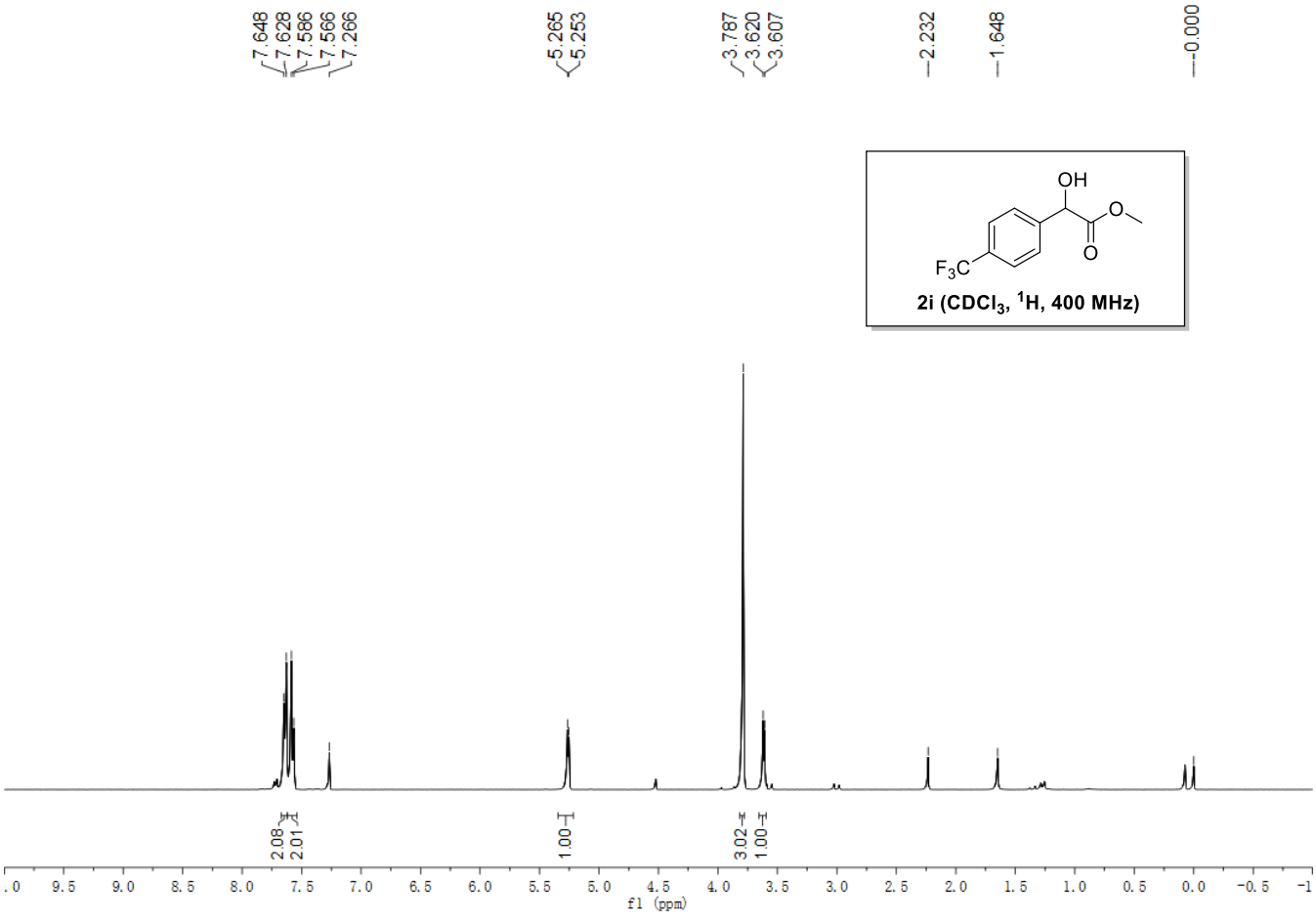
39.083
38.873
OH
O
O
I
2h (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)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7.586
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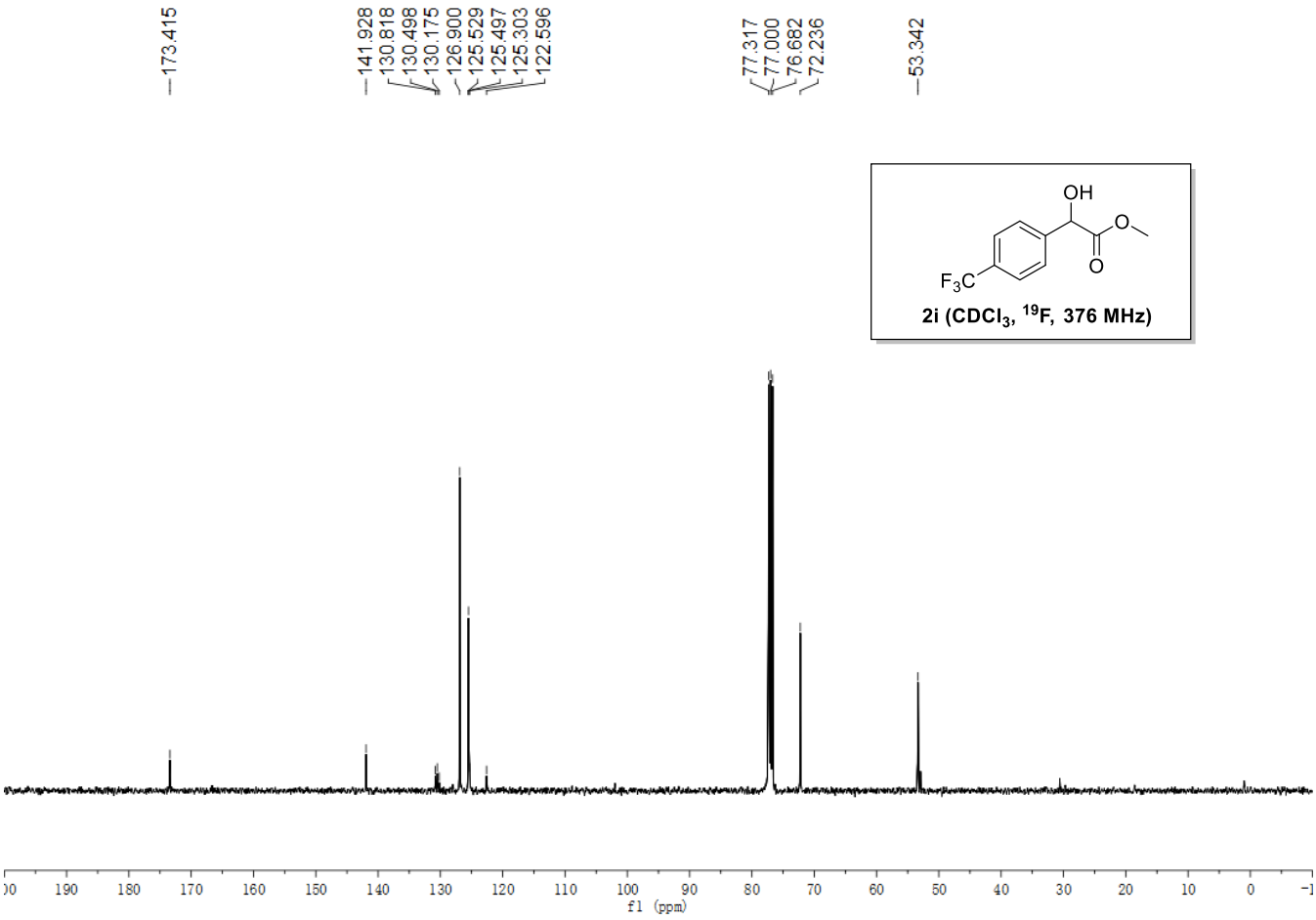
5.265
5.253
3.787
3.620
3.607
2.232
1.648
0.000
OH
O
O
F_3C
2i ($CDCl_3$, ^{1}H, 400 MHz)
2.08
2.01
1.00
3.02
1.00
f1 (ppm)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130.175
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125.529
125.497
125.303
122.596
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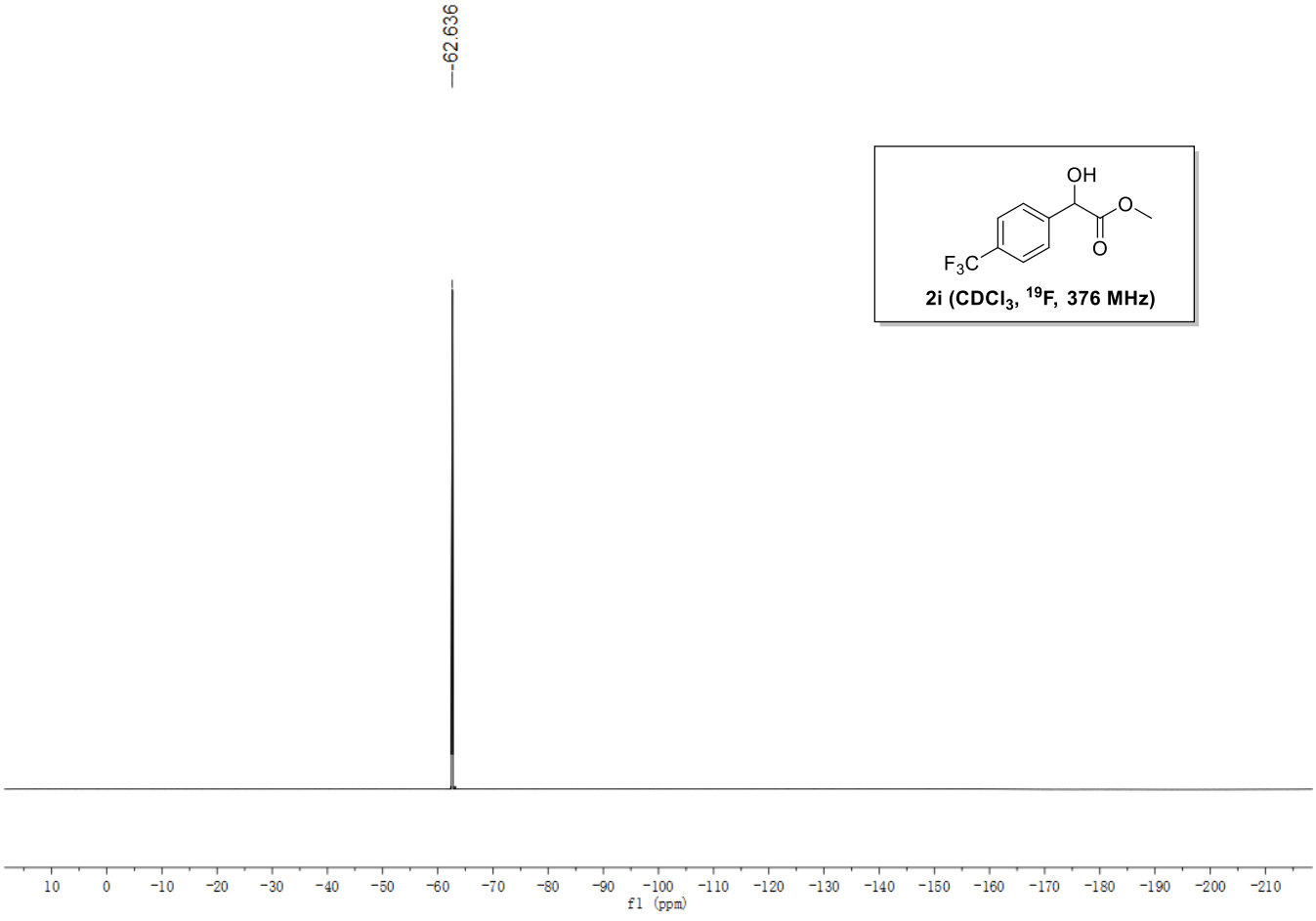
77.000
76.682
72.236
53.342
OH
O
O
F3C
2i (CDCl3, 19F, 376 MHz)
f1 (ppm)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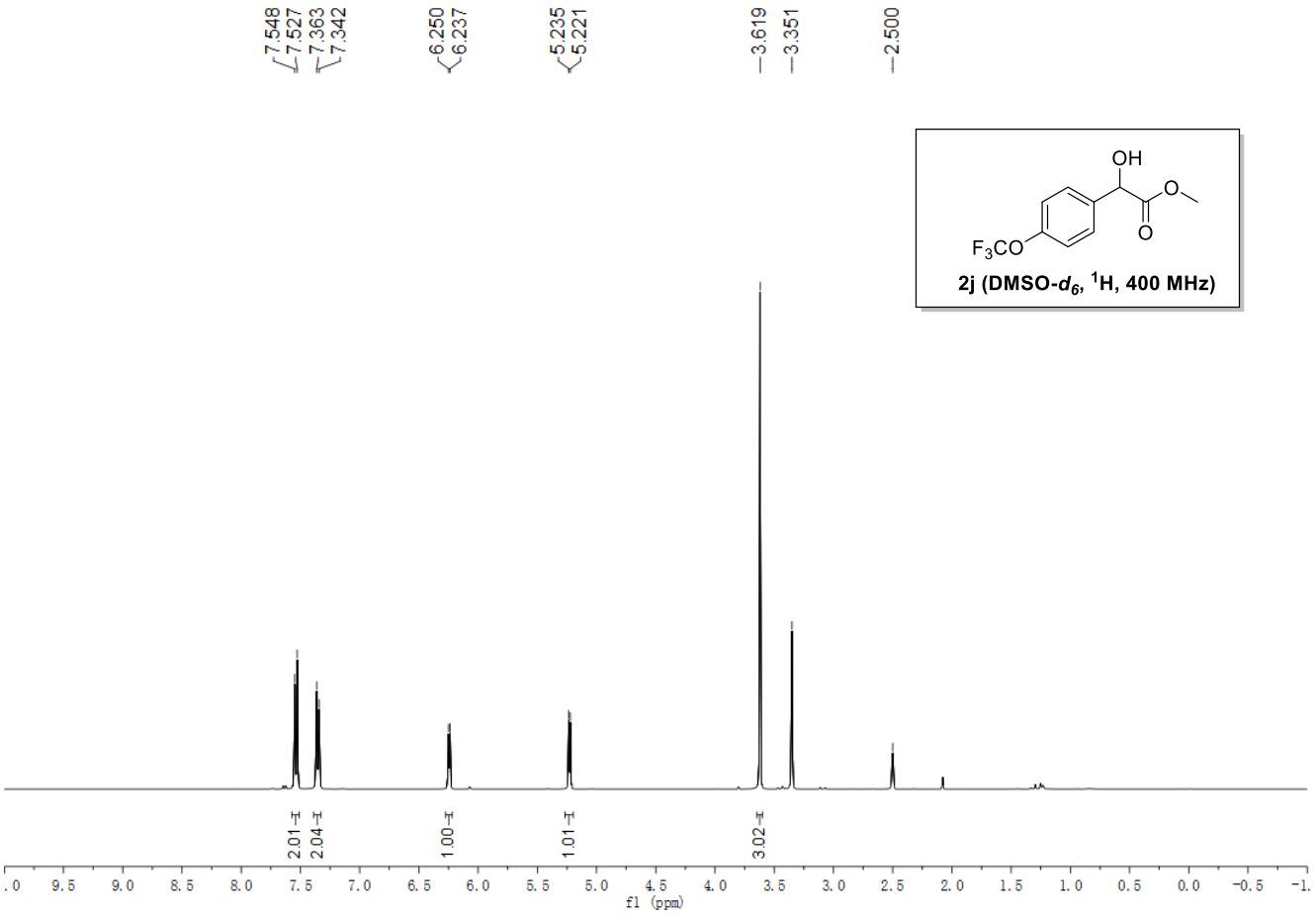
f1 (ppm)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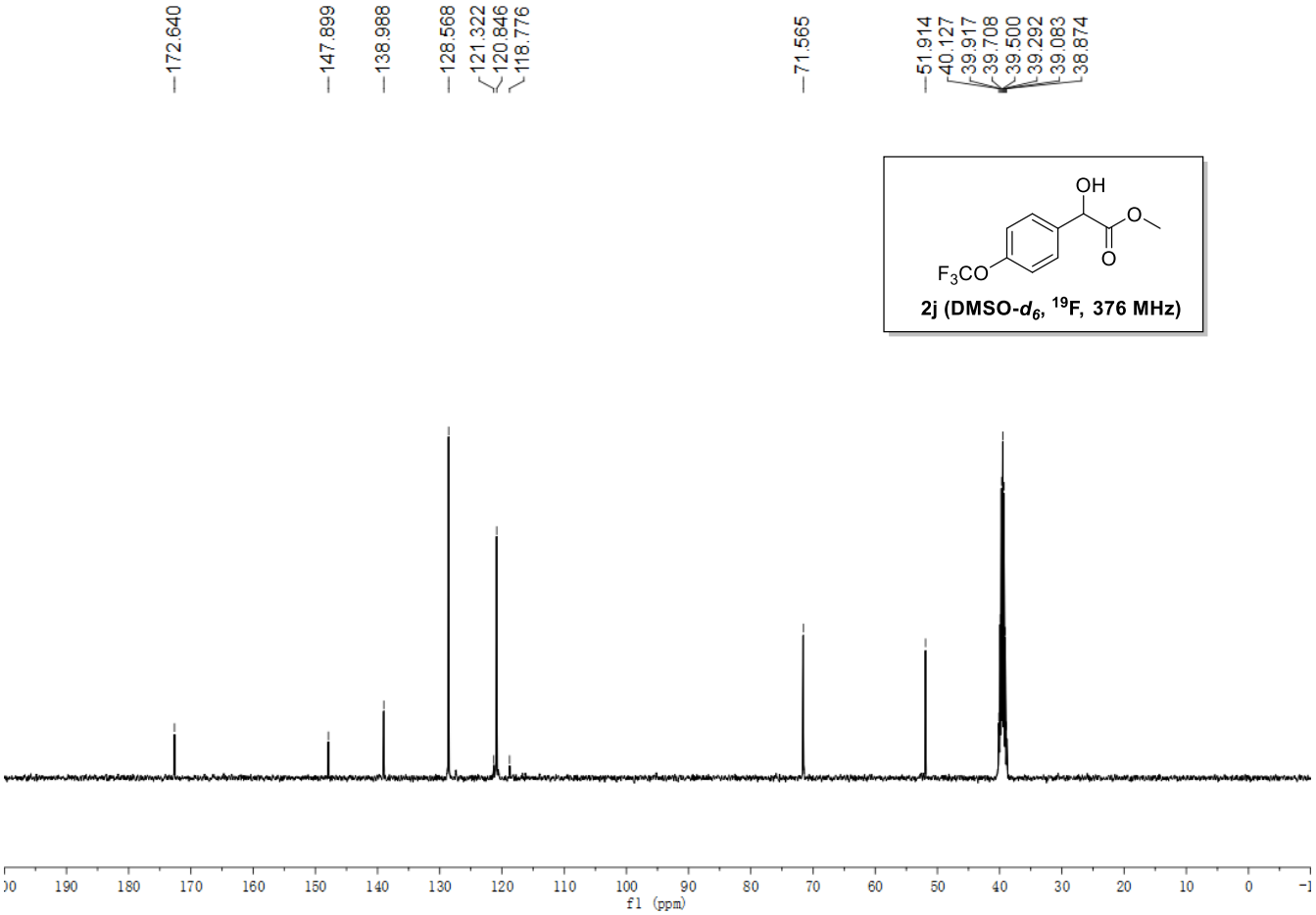
6.250
6.237
5.235
5.221
3.619
3.351
2.500
OH
O
O
F3CO
2j (DMSO-d6, 1H, 400 MHz)
2.01
2.04
1.00
1.01
3.02
f1 (ppm)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120.846
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39.083
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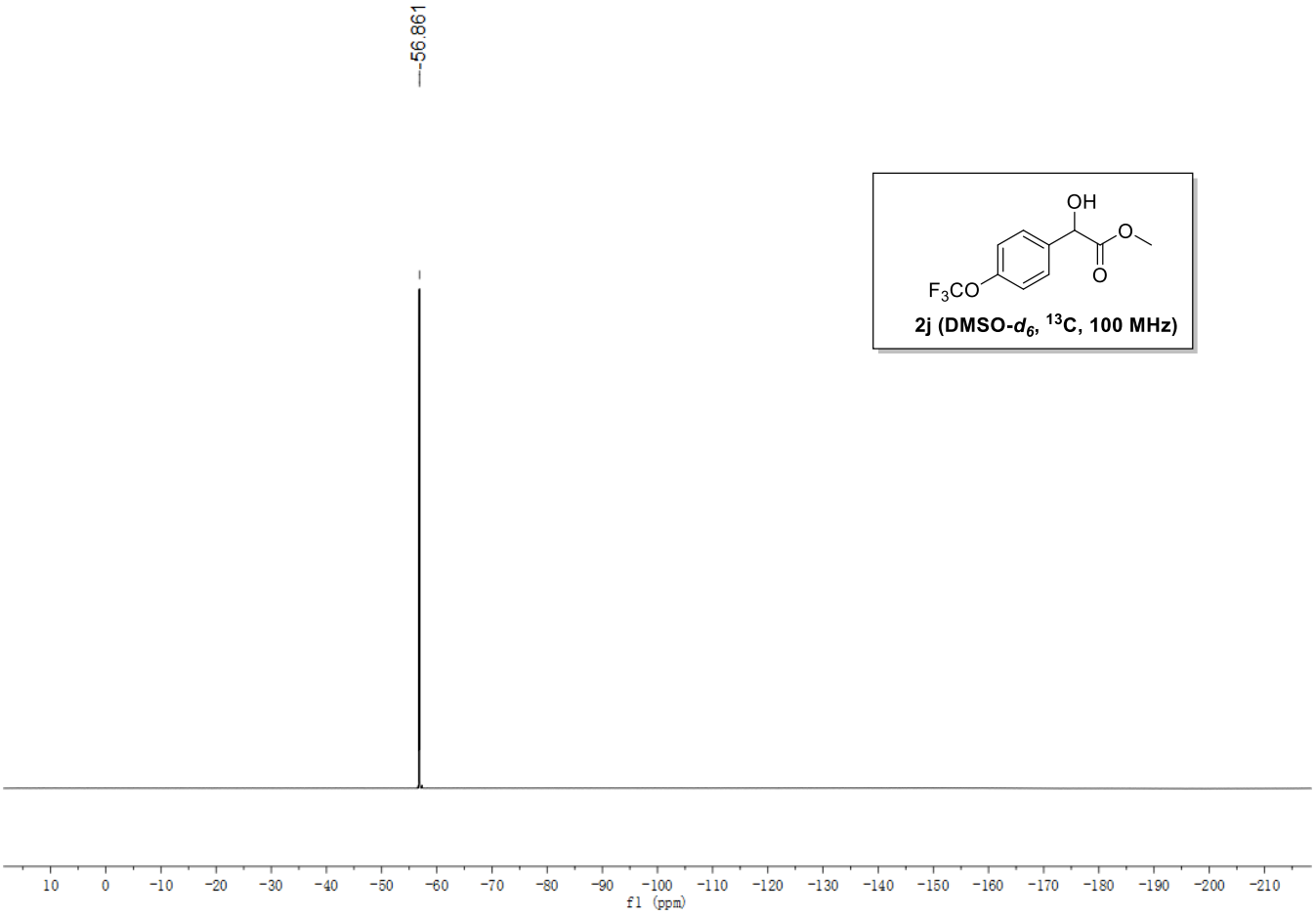
O
O
F3CO
2j (DMSO-d6, 19F, 376 MHz)
f1 (ppm)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O
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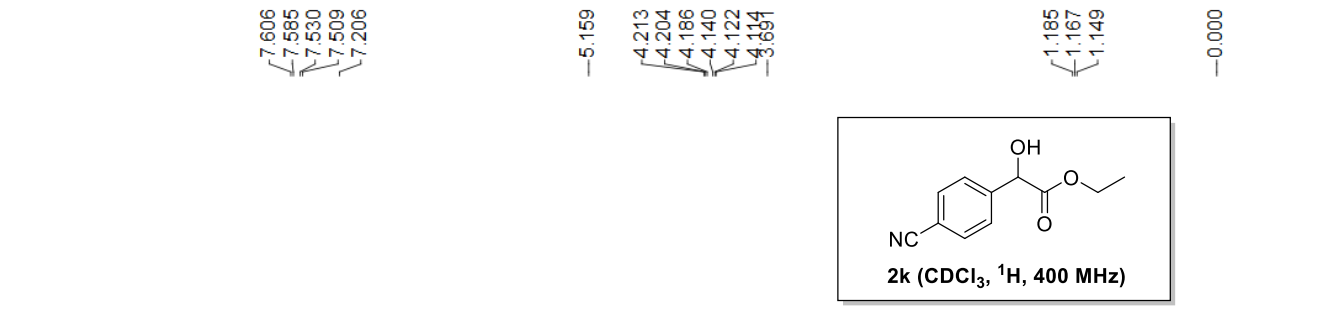
f1 (ppm)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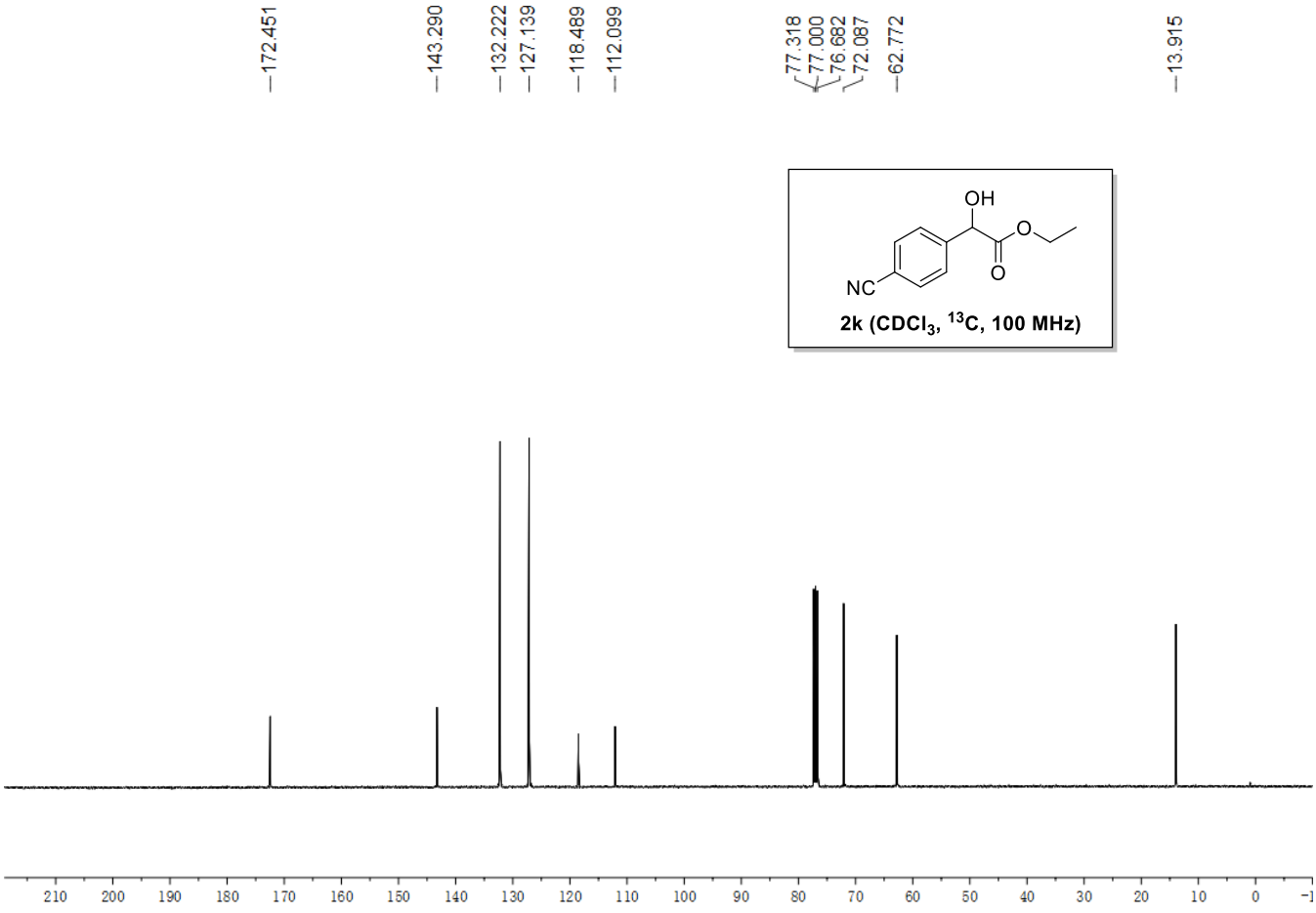
5.159
4.213
4.204
4.186
4.140
4.122
4.114
3.691
1.185
1.167
1.149
0.000
OH
O
O
NC
2k (CDCl3, 1H, 400 MHz)
2.00
2.07
1.00
2.15
1.03
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1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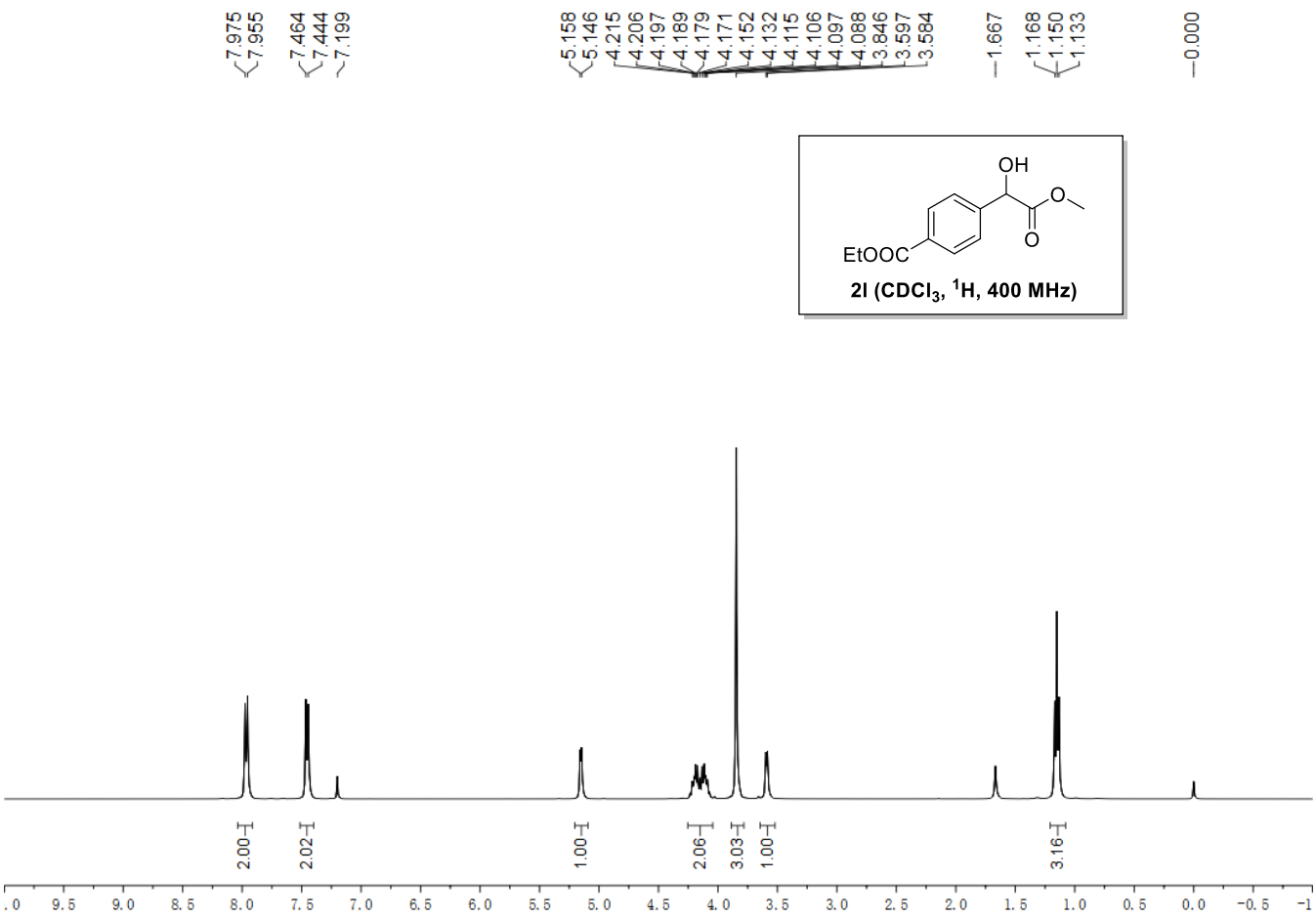
O
O
NC
2k (CDCl3, 13C, 100 MHz)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4.171
4.152
4.132
4.115
4.106
4.097
4.088
3.846
3.597
3.584
1.667
1.168
1.150
1.133
0.000
OH
O
O
EtOOC
2l (CDCl3, 1H, 400 MHz)
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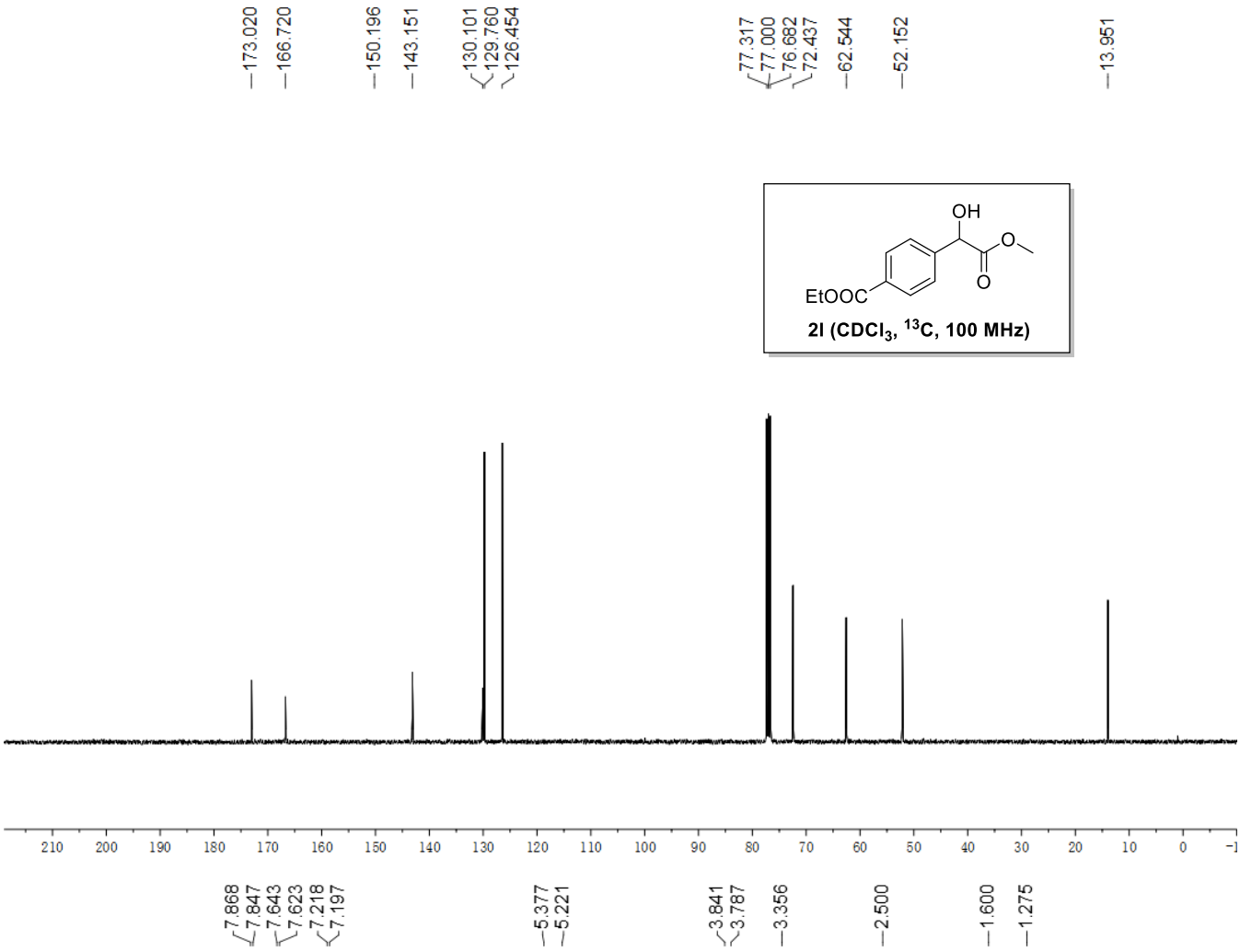
2.02
1.00
2.06
3.03
1.00
3.16


173.020
166.720
150.196
143.151
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77.000
76.682
72.437
62.544
52.152
13.951
OH
O
O
EtOOC
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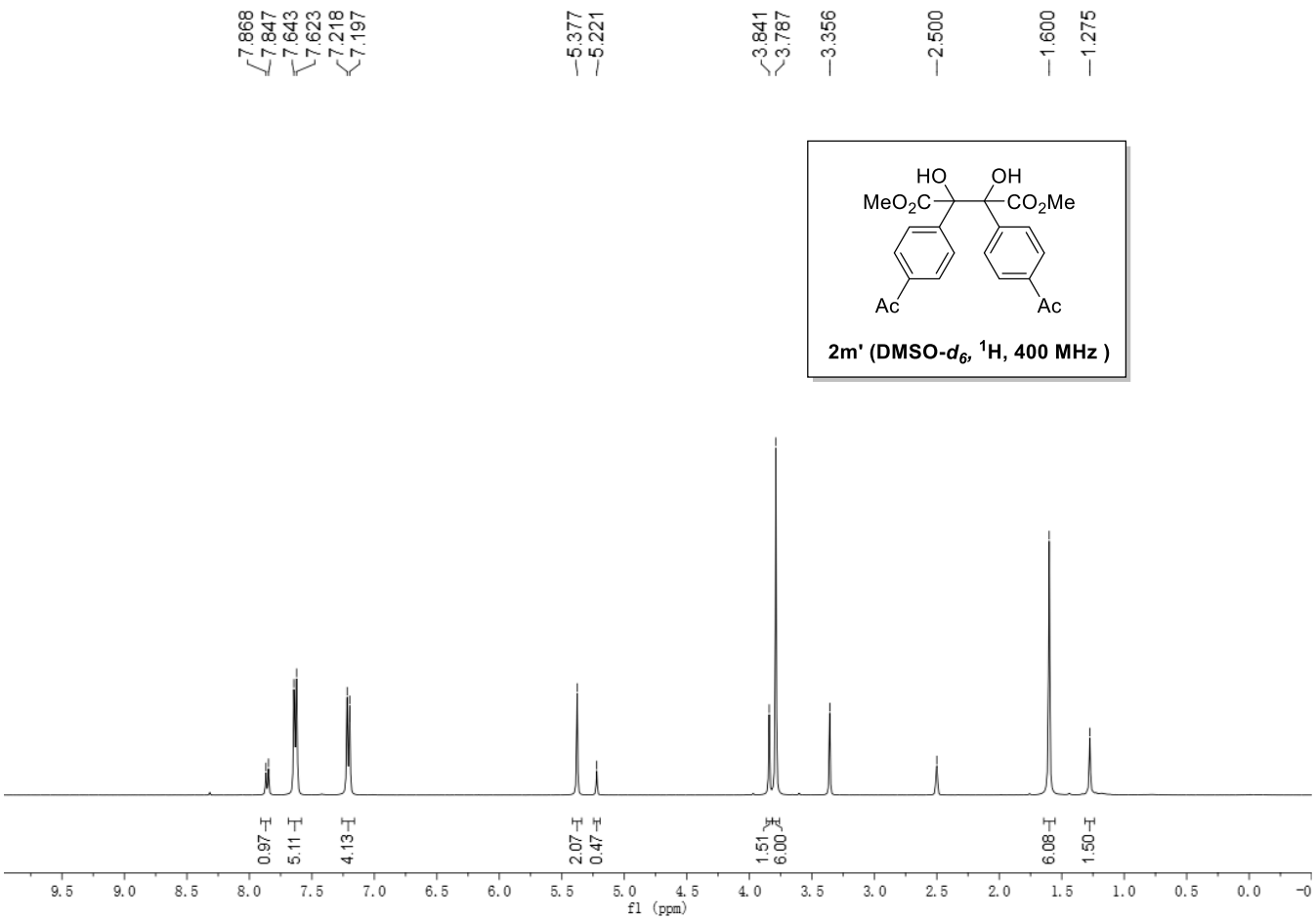
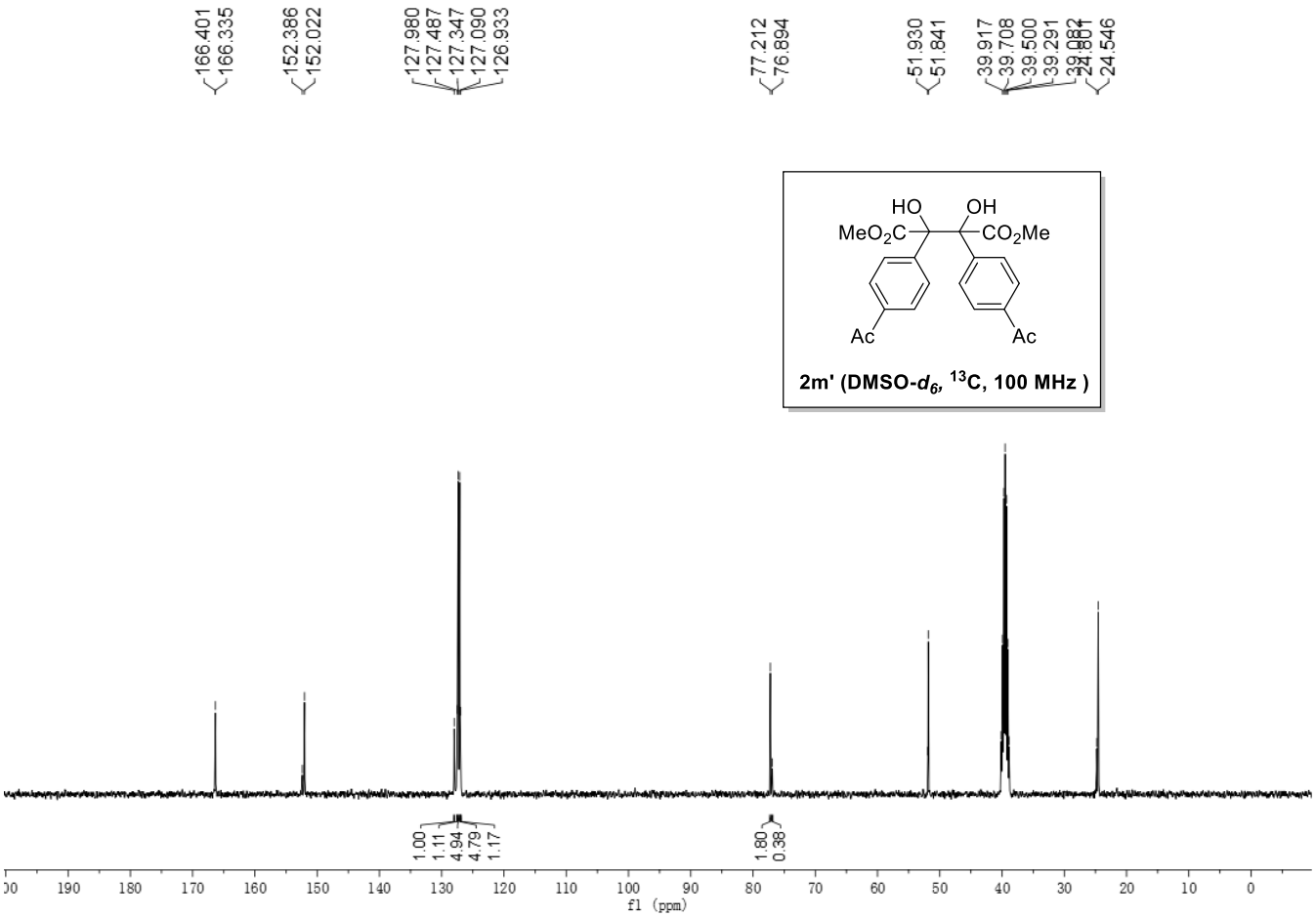
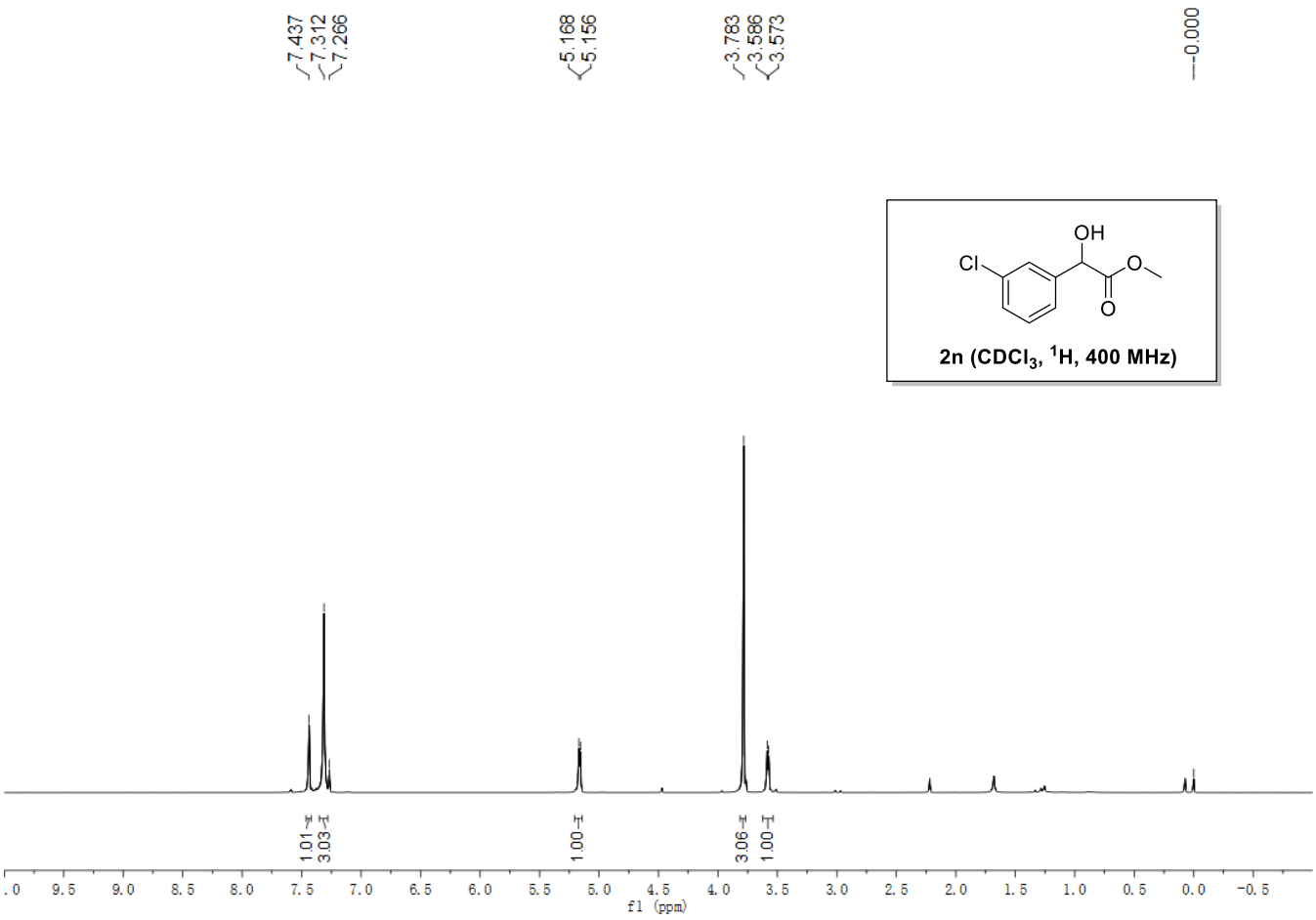
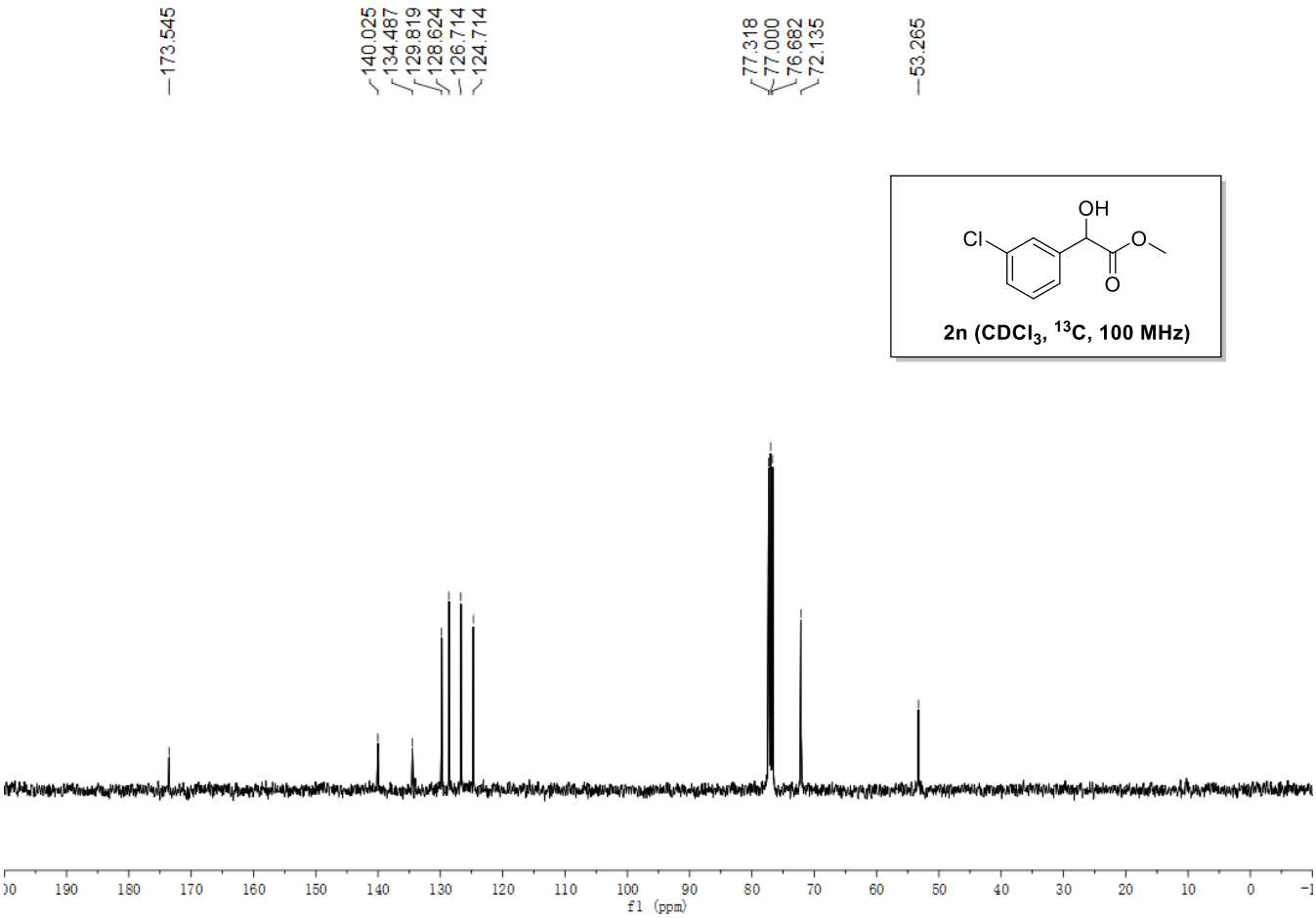
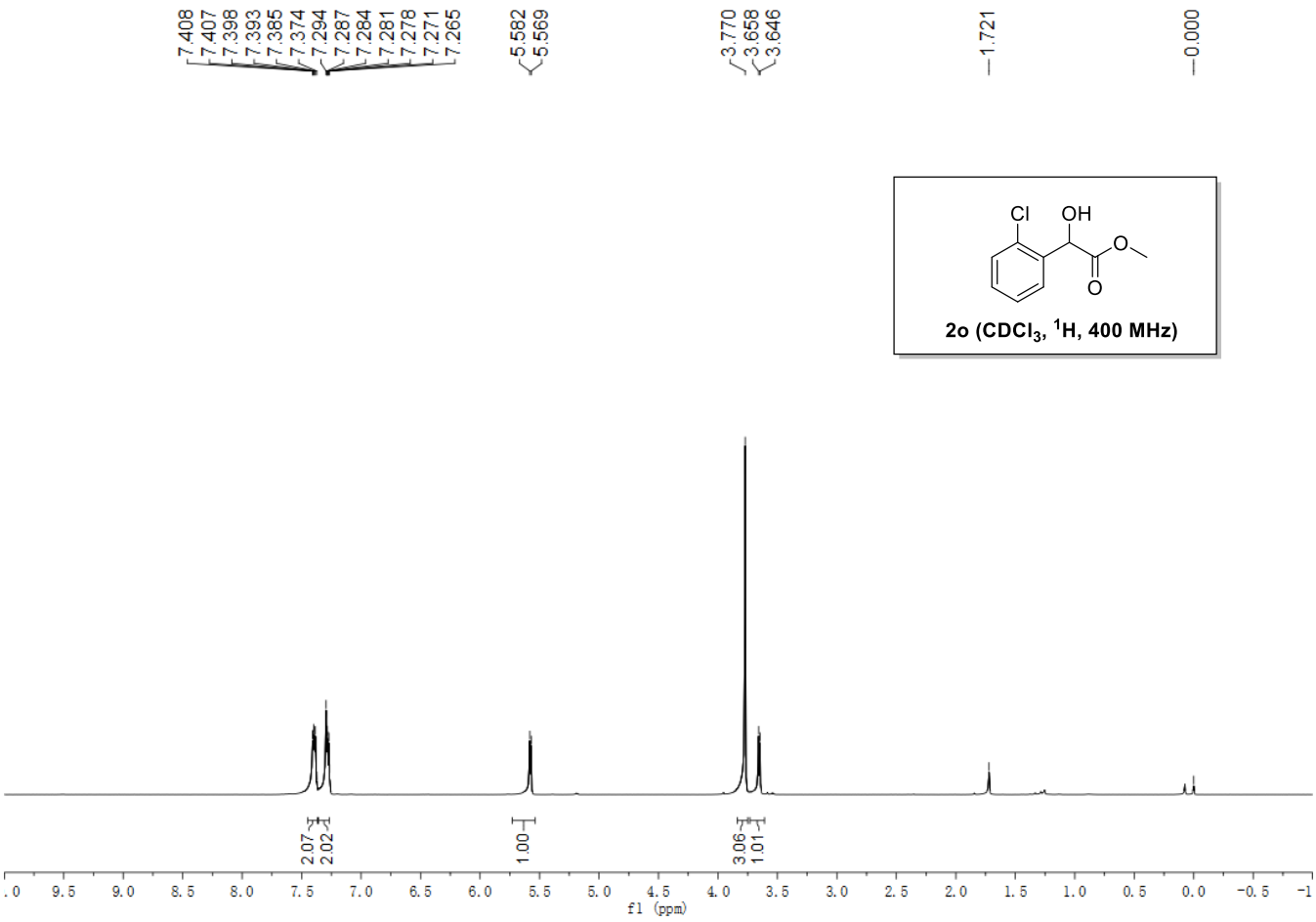

7.868
7.847
7.643
7.623
7.218
7.197
5.377
5.221
3.841
3.787
3.356
2.500
1.600
1.275
HO
OH
MeO2C
CO2Me
Ac
Ac
2m' (DMSO-d6, 1H, 400 MHz)
0.97
5.11
4.13
2.07
0.47
1.51
6.00
6.08
1.50
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)


166.401
166.335
152.386
152.022
127.980
127.487
127.347
127.090
126.933
77.212
76.894
51.930
51.841
39.917
39.708
39.500
39.291
24.546
HO
OH
MeO2C
CO2Me
Ac
Ac
2m' (DMSO-d6, 13C, 100 MHz)
1.00
1.11
4.94
4.79
1.17
1.80
0.38
f1 (ppm)

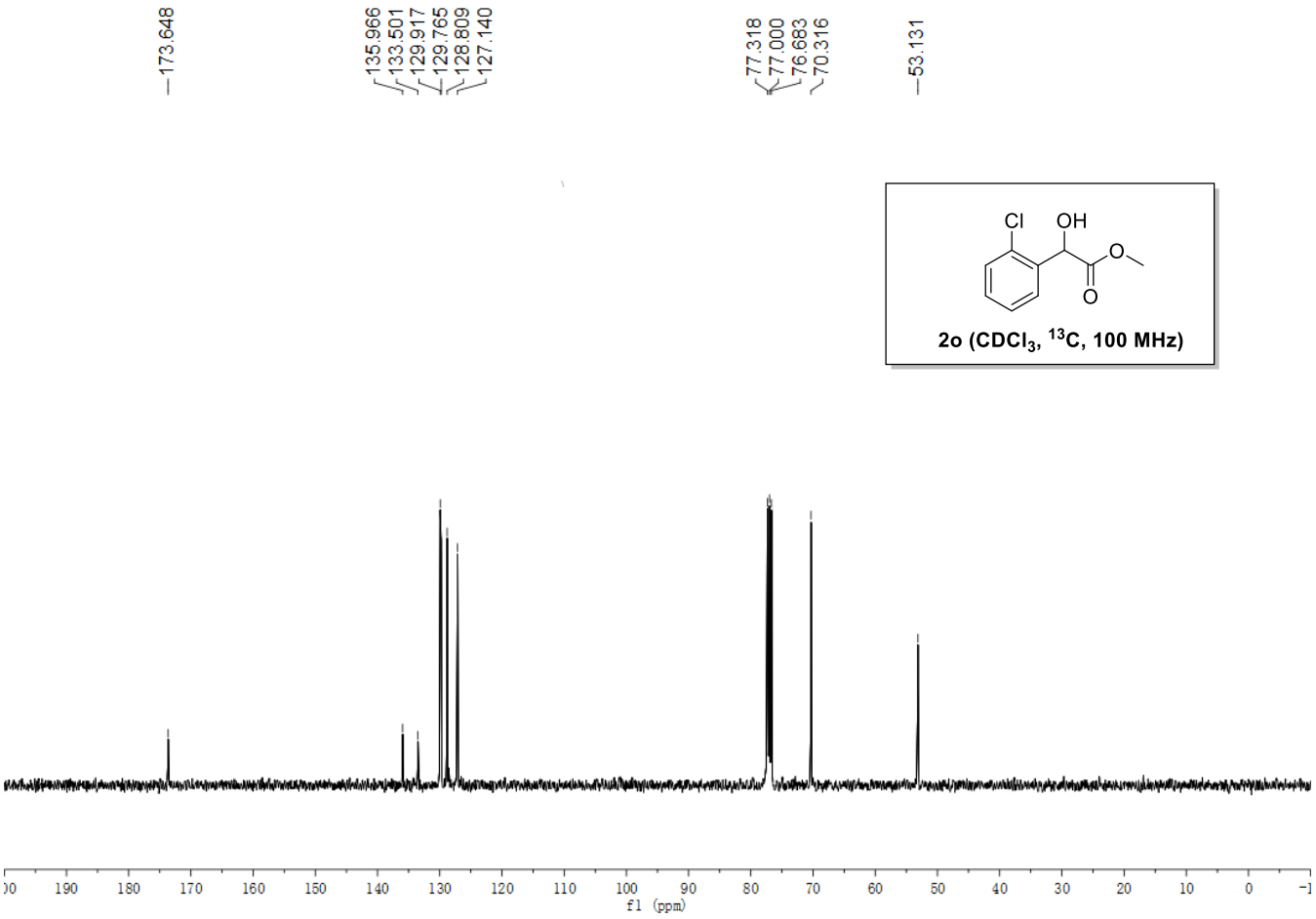

7.437
7.312
7.266
5.168
5.156
3.783
3.586
3.573
0.000
OH
Cl
O
O
2n (CDCl3, 1H, 400 MHz)
1.01
3.03
1.00
3.06
1.00
f1 (ppm)



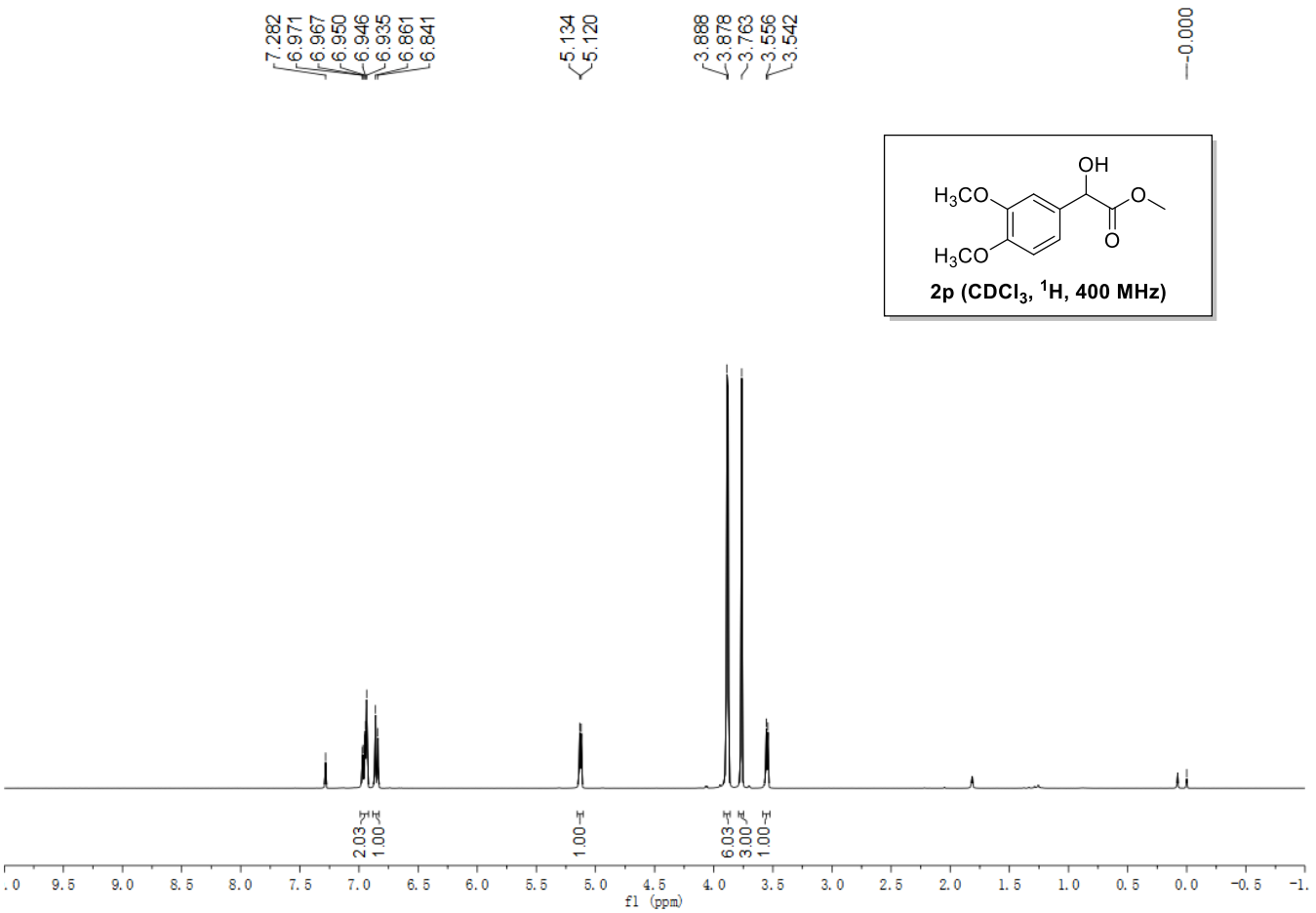
2n ($CDCl_3$, ^{13}C, 100 MHz)



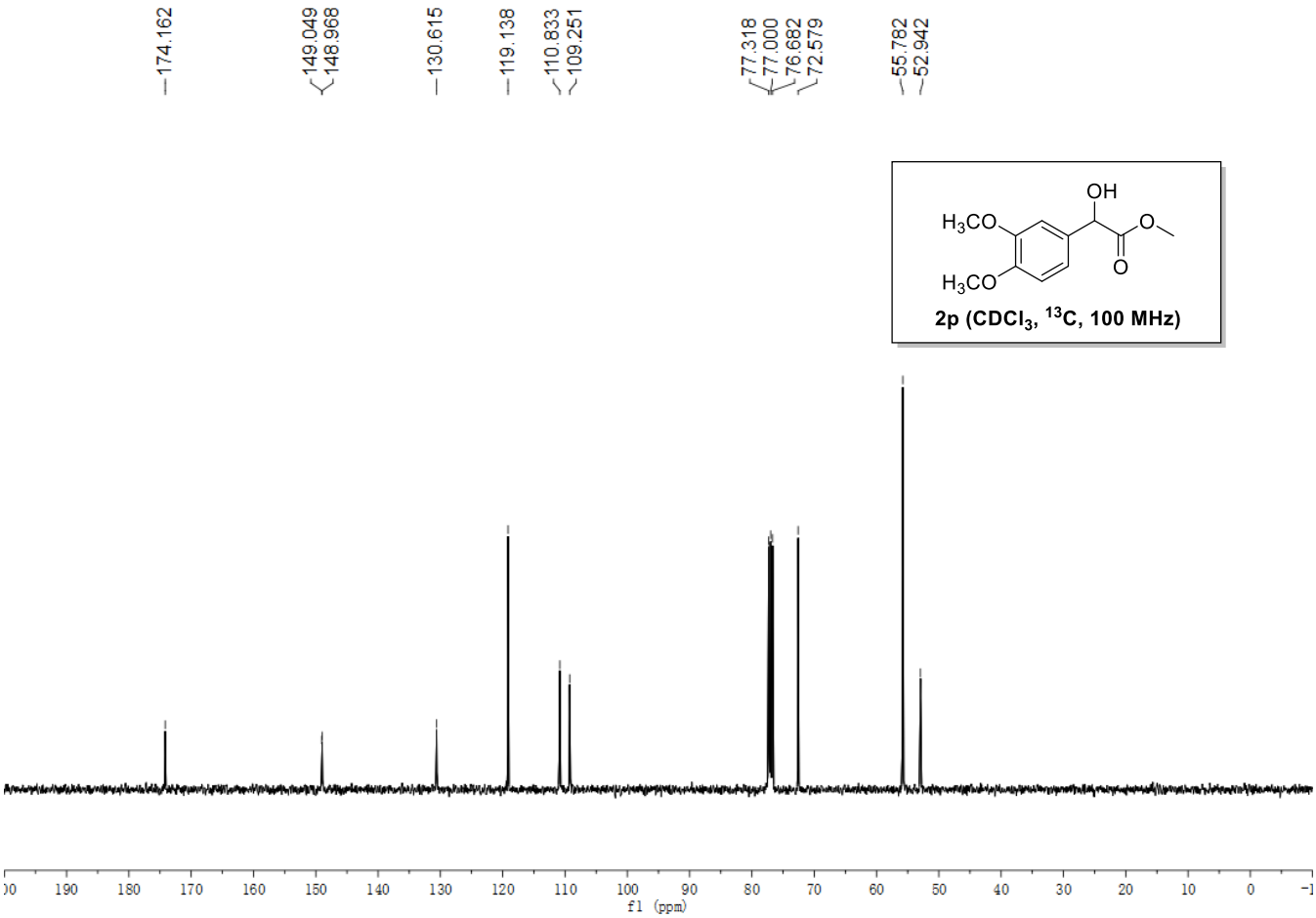
2o ($CDCl_3$, ^{1}H, 400 MHz)

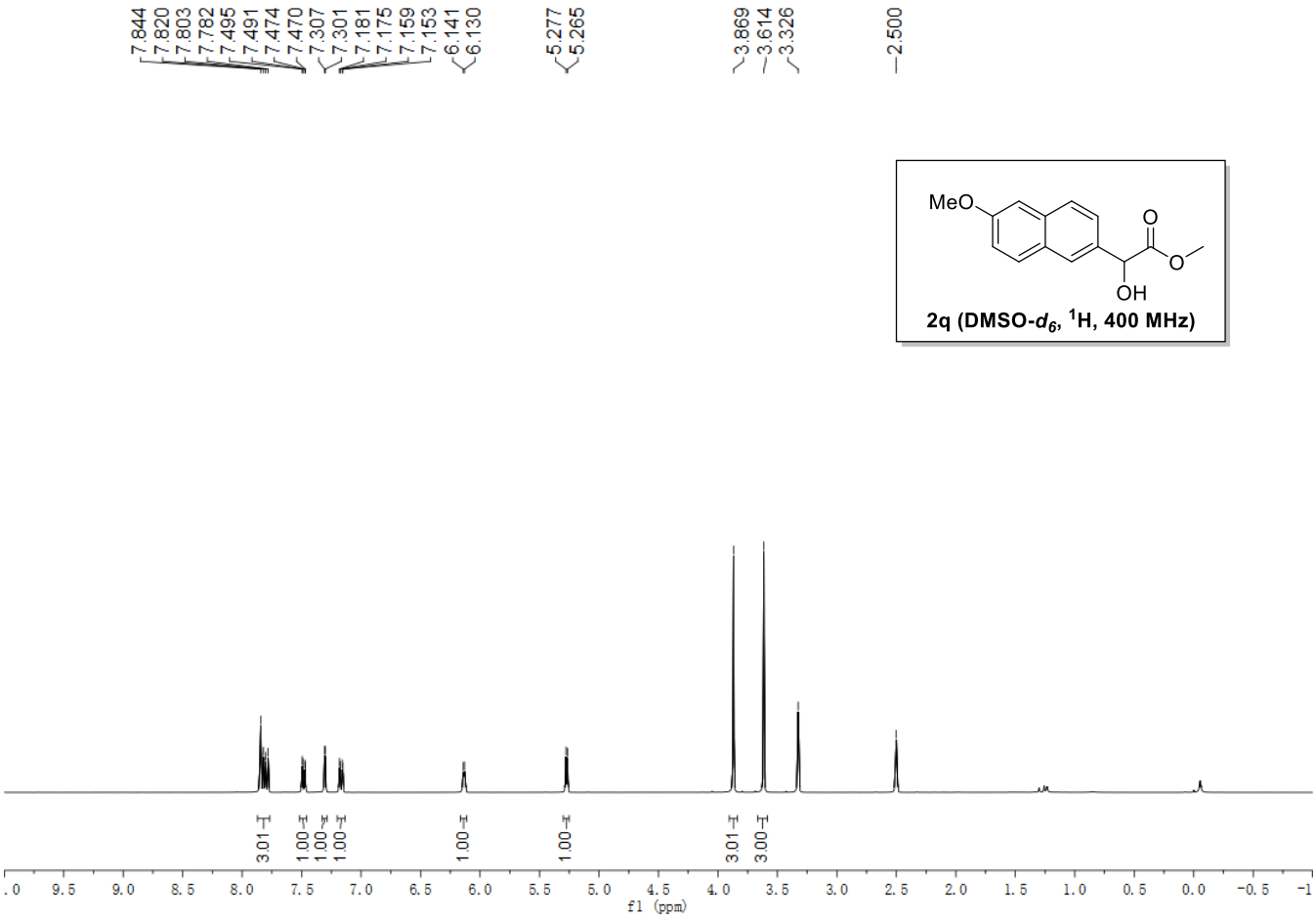


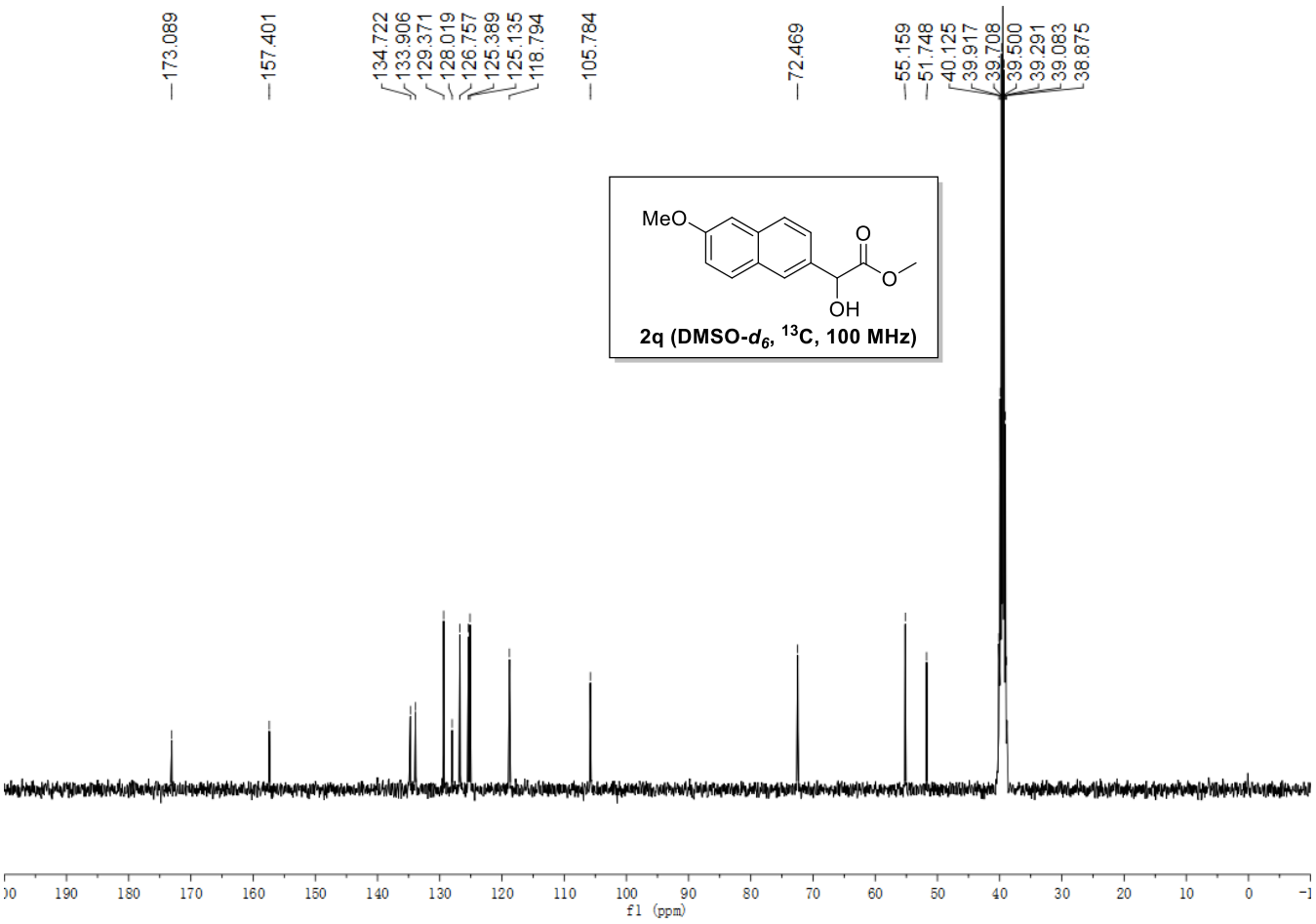
2o ($CDCl_3$, ^{13}C, 100 MHz)

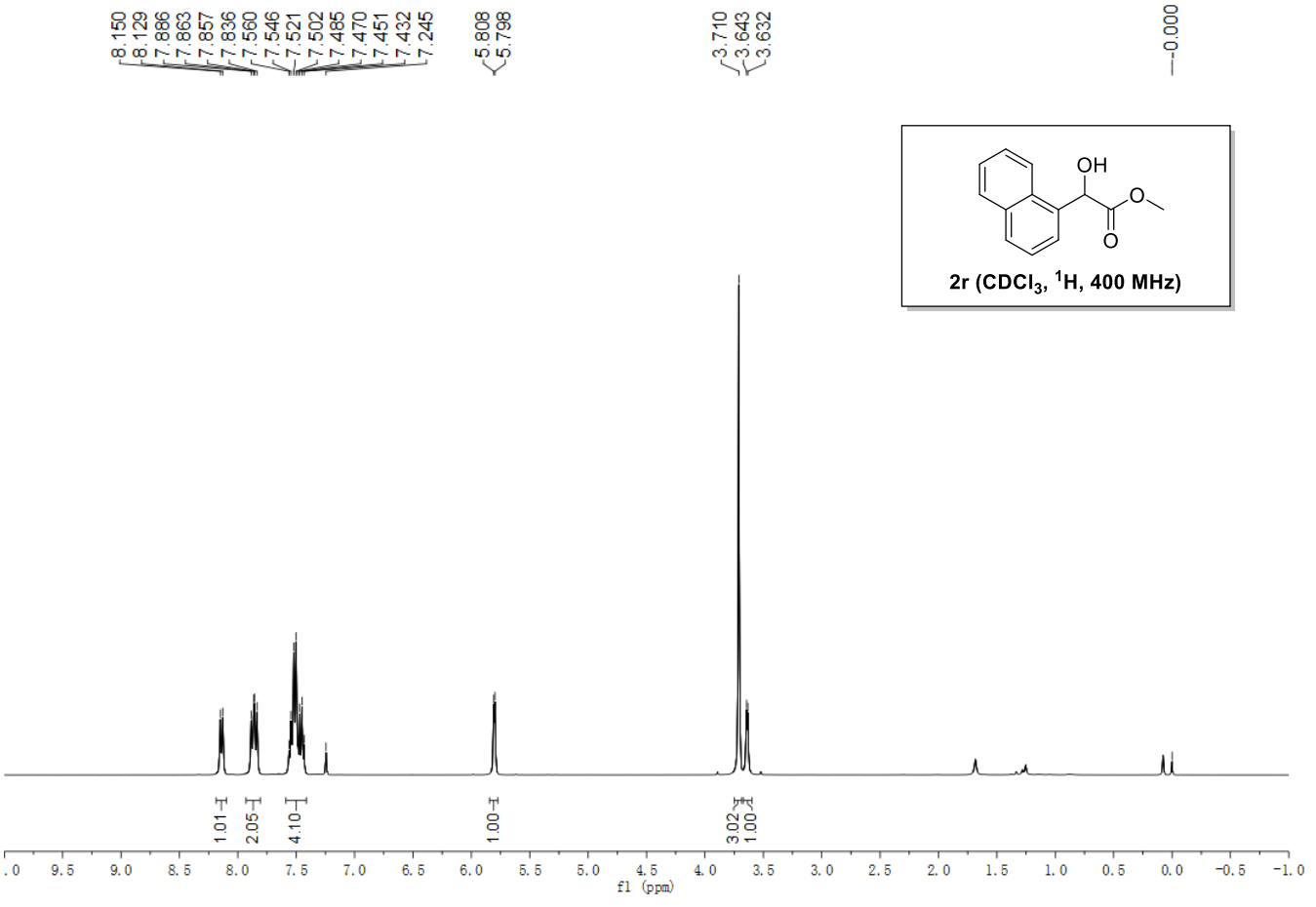


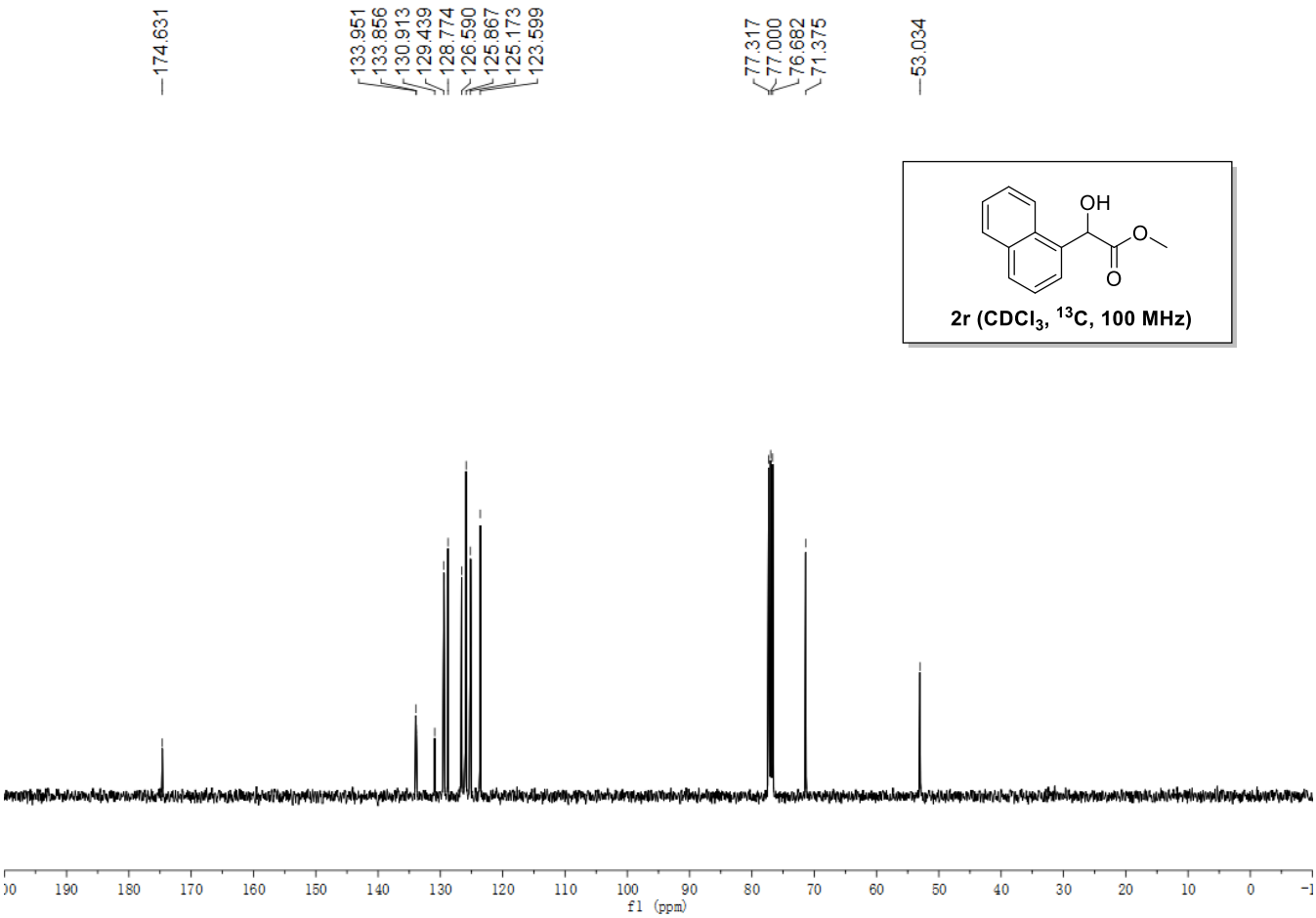
2p ($CDCl_3$, ^{1}H, 400 MHz)


174.162
149.049
148.968
130.615
119.138
110.833
109.251
77.318
77.000
76.682
72.579
55.782
52.942
OH
H3CO
H3CO
O
O
2p (CDCl3, 13C, 100 MHz)
f1 (ppm)

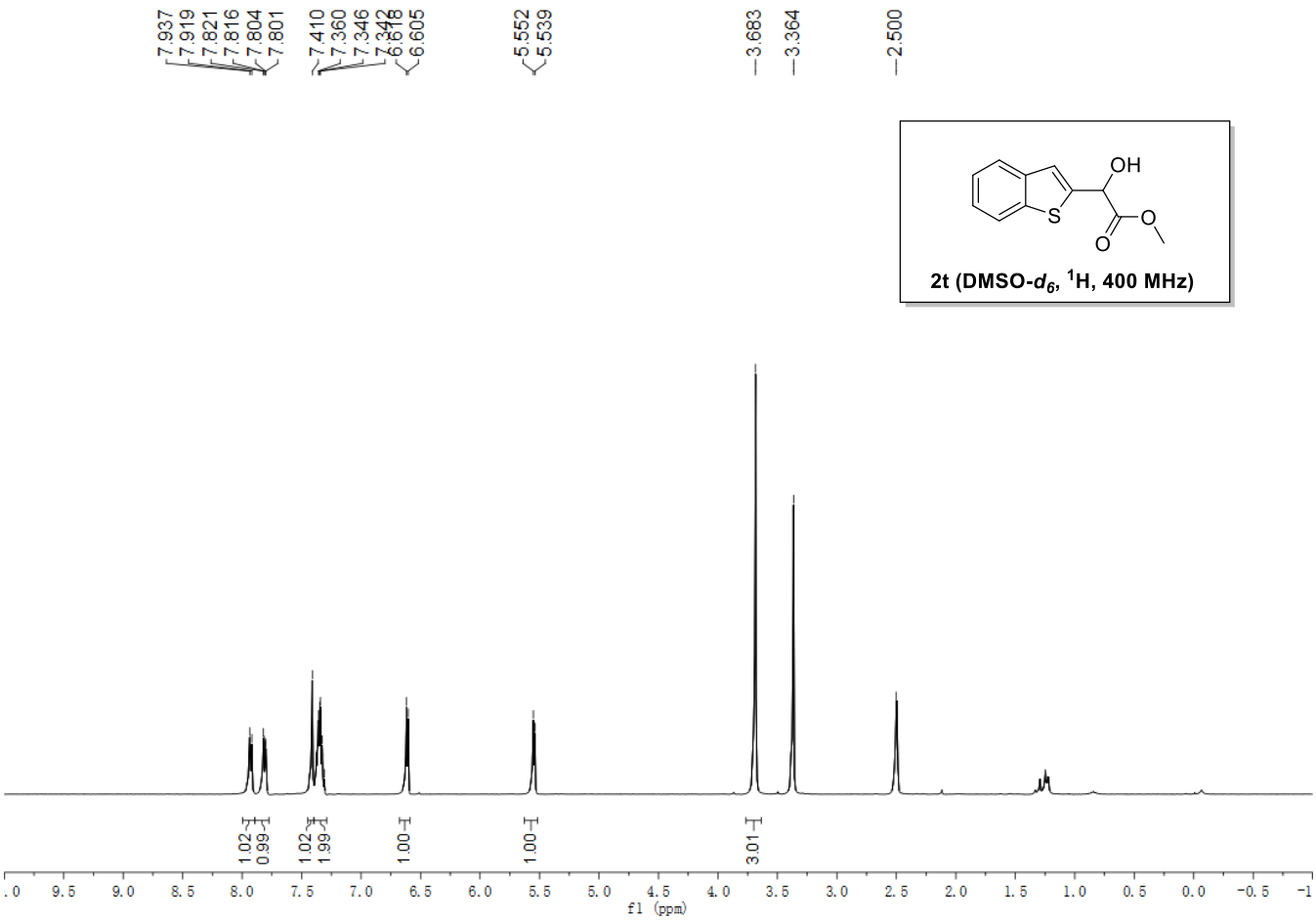

7.844
7.820
7.803
7.782
7.495
7.491
7.474
7.470
7.307
7.301
7.181
7.175
7.159
7.153
6.141
6.130
5.277
5.265
3.869
3.614
3.326
2.500
MeO
O
O
OH
2q (DMSO-d6, 1H, 400 MHz)
3.01
1.00
1.00
1.00
1.00
1.00
3.01
3.00
f1 (ppm)


173.089
157.401
134.722
133.906
129.371
128.019
126.757
125.389
125.135
118.794
105.784
72.469
55.159
51.748
40.125
39.917
39.708
39.500
39.291
39.083
38.875
MeO
O
O
OH
2q (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

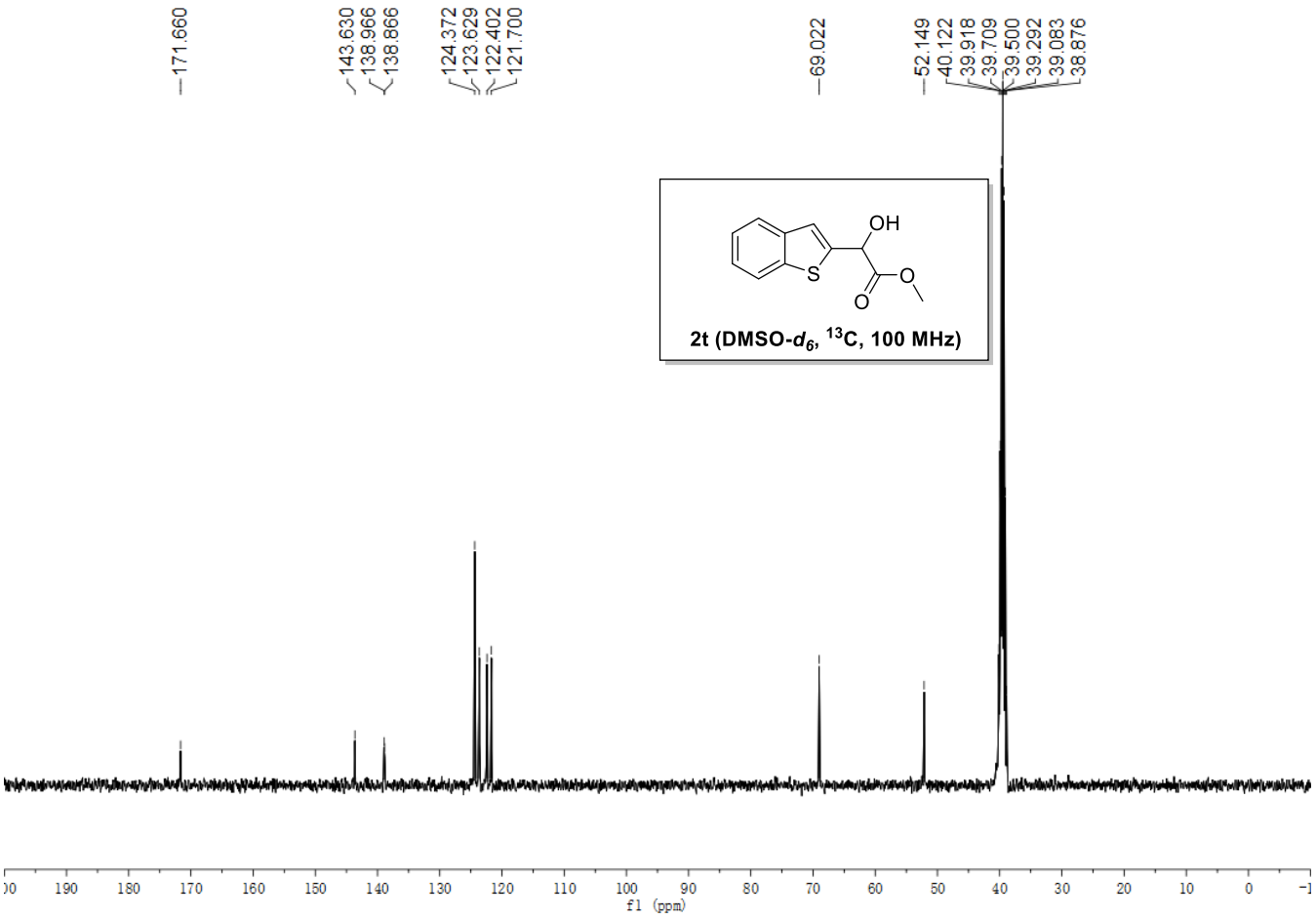

8.150
8.129
7.886
7.863
7.857
7.836
7.560
7.546
7.521
7.502
7.485
7.470
7.451
7.432
7.245
5.808
5.798
3.710
3.643
3.632
0.000
OH
O
O
2r (CDCl$_3$, ^{1}H, 400 MHz)
1.01
2.05
4.10
1.00
3.02
1.00
f1 (ppm)

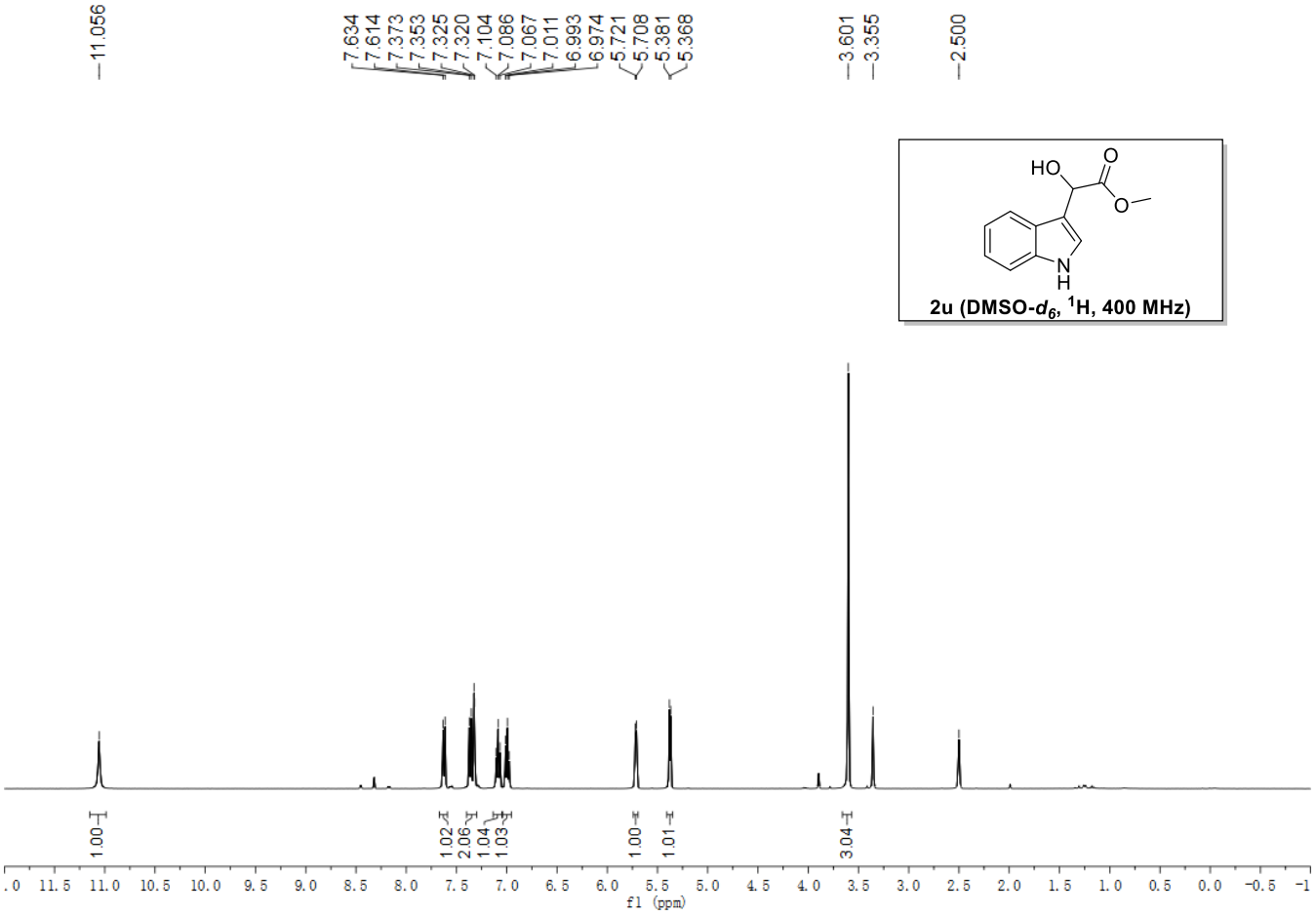


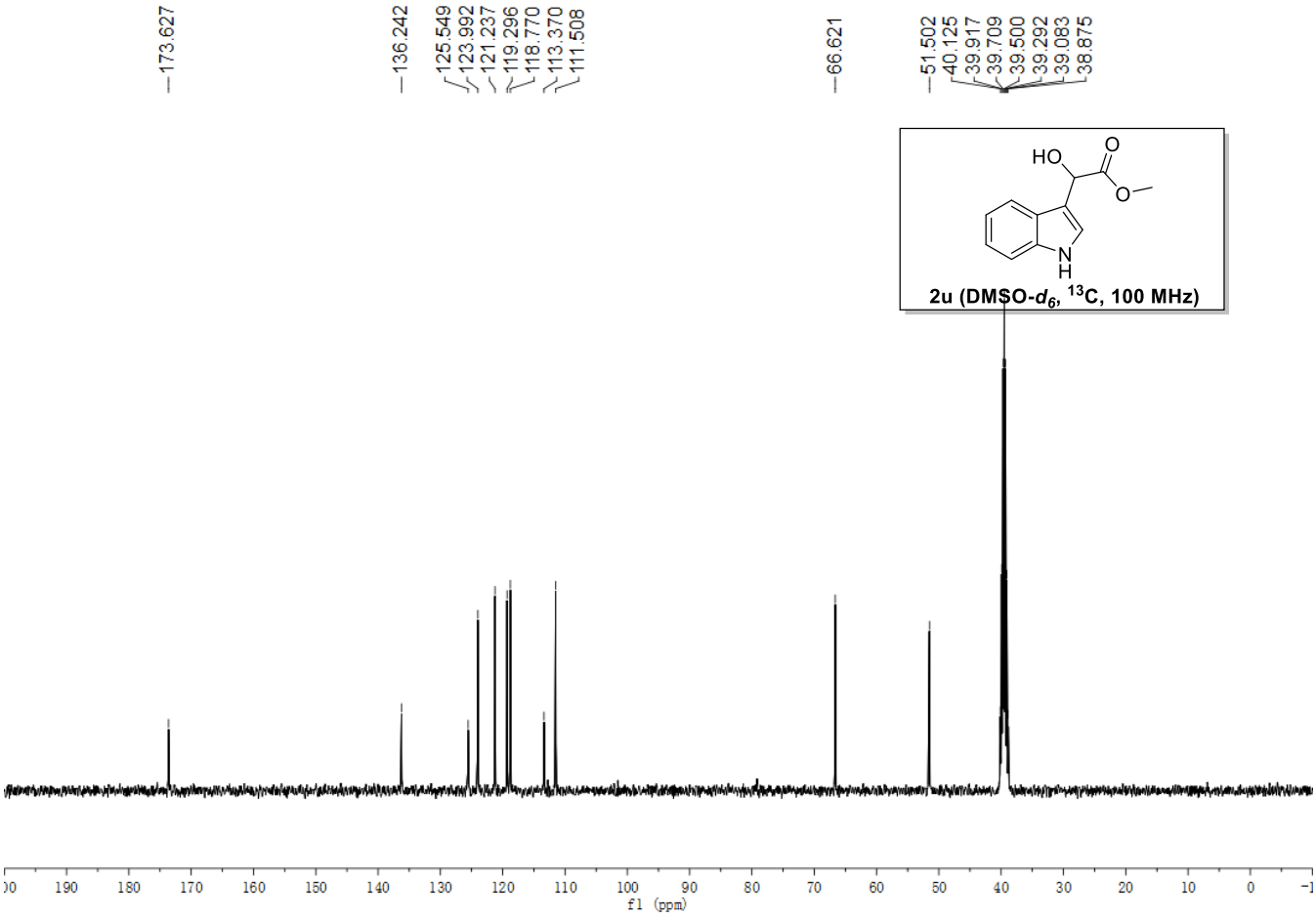
2r ($CDCl_3$, ^{13}C, 100 MHz)

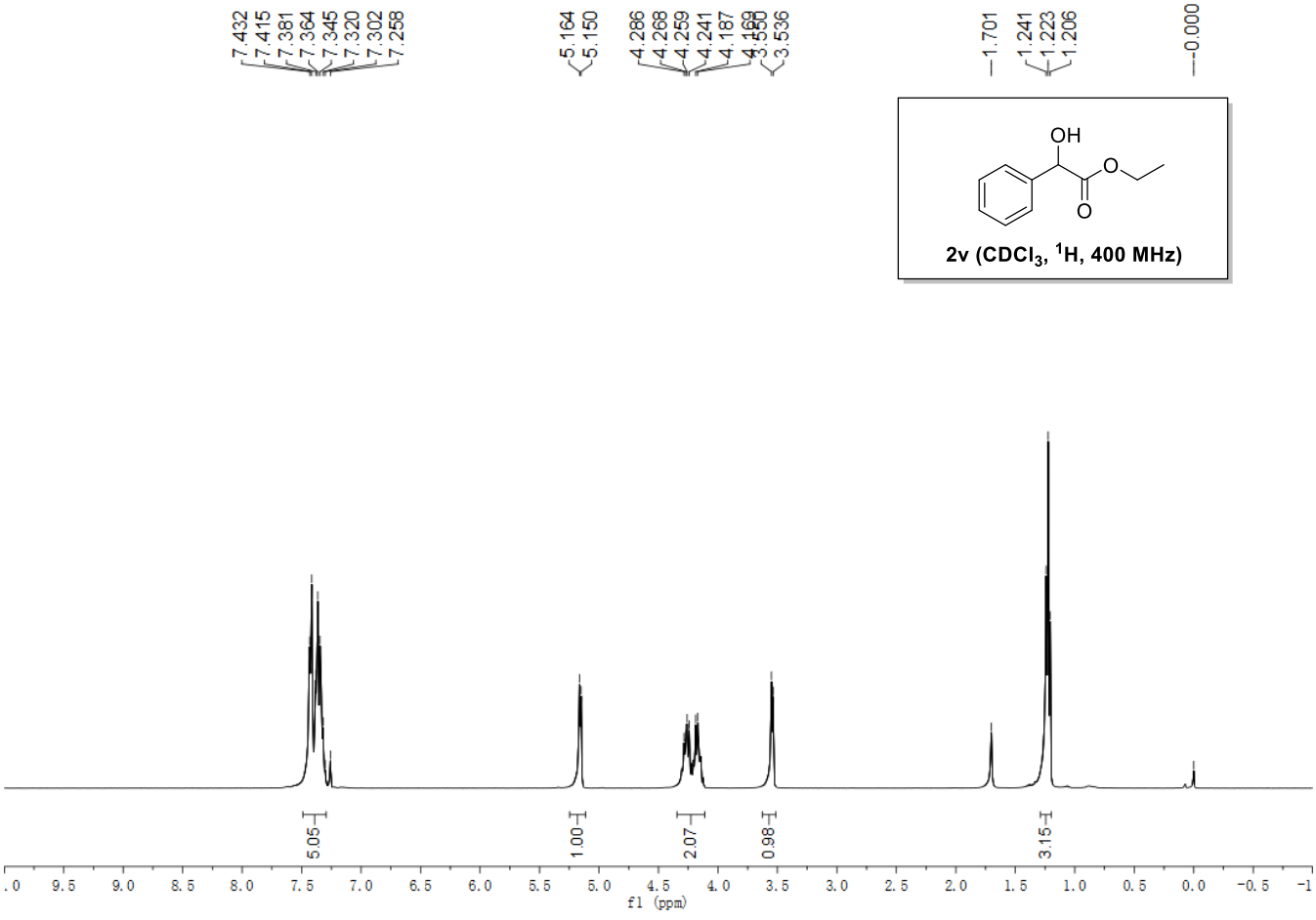


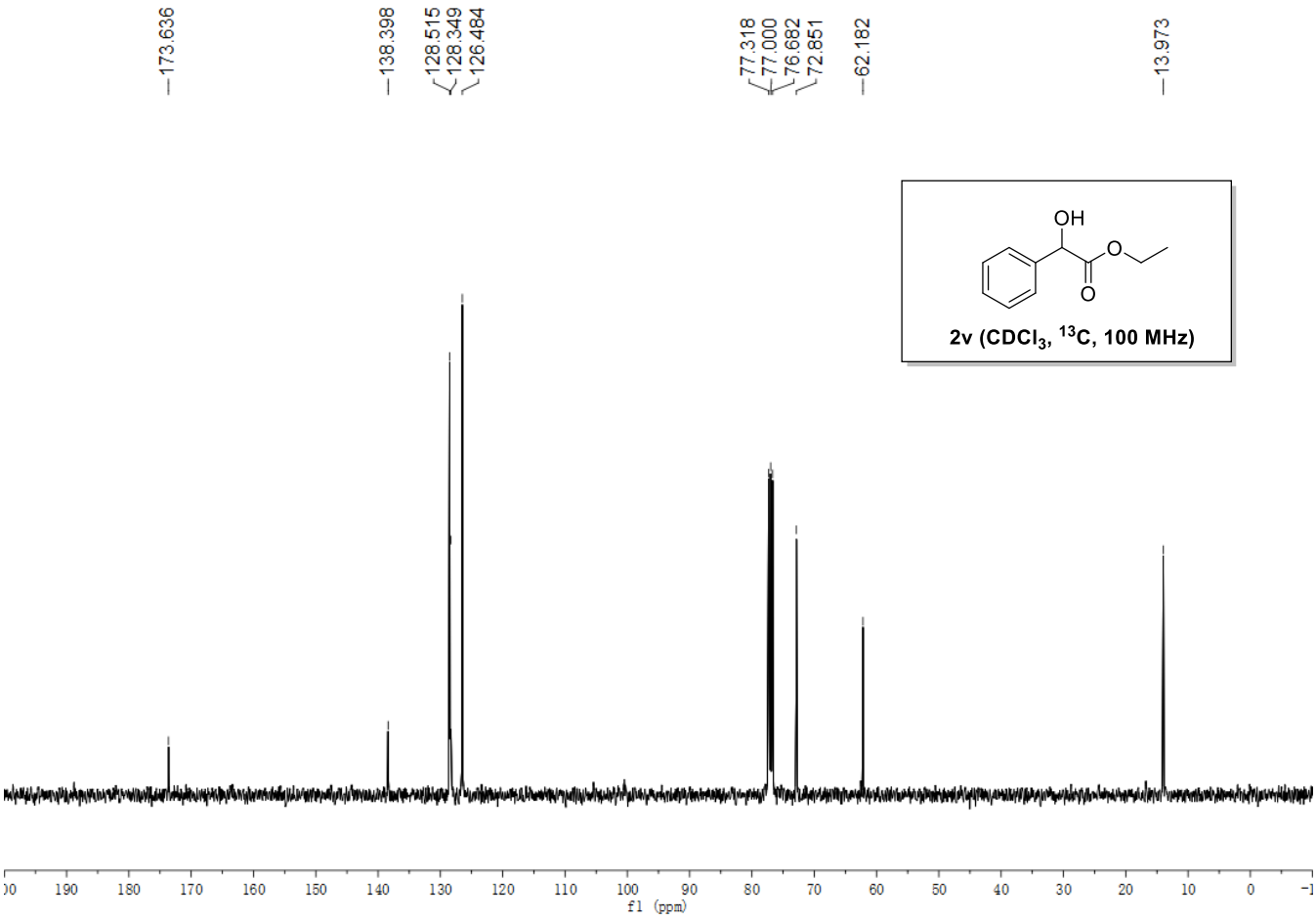
2t (DMSO-d_6, ^1H, 400 MHz)

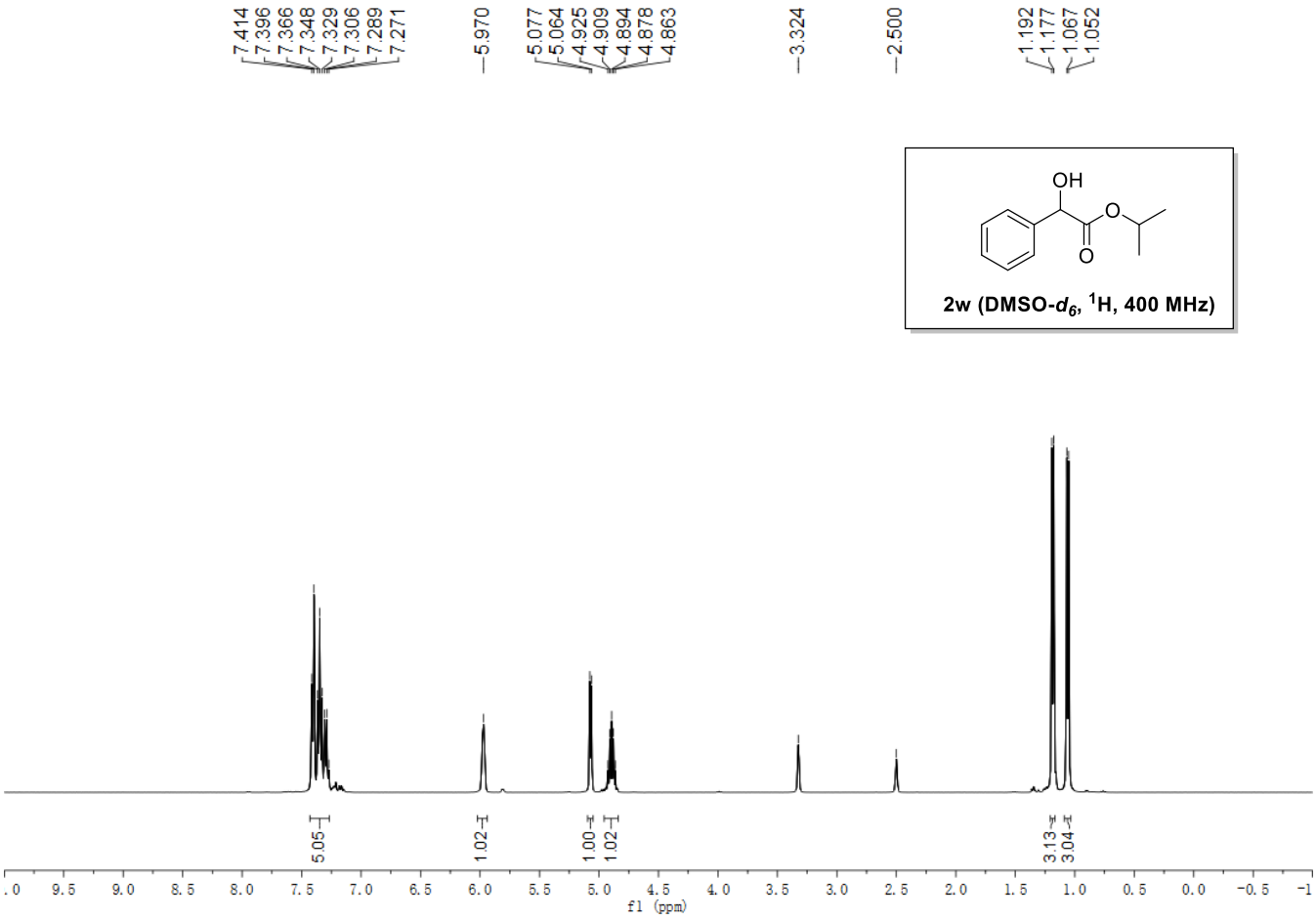

171.660
143.630
138.966
138.866
124.372
123.629
122.402
121.700
69.022
52.149
40.122
39.918
39.709
39.500
39.292
39.083
38.876
OH
S
O
O
2t (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

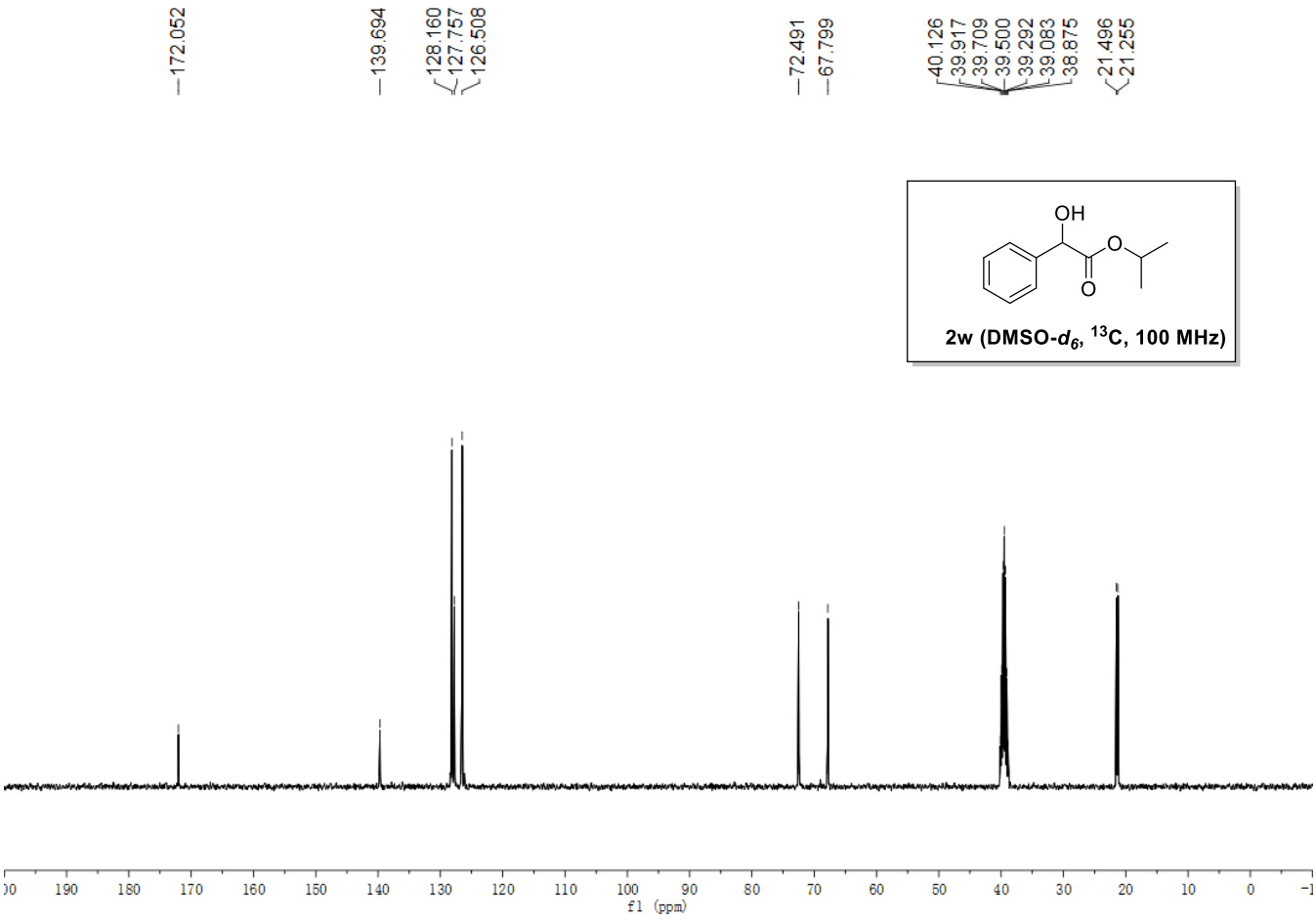

11.056
7.634
7.614
7.373
7.353
7.325
7.320
7.104
7.086
7.067
7.011
6.993
6.974
5.721
5.708
5.381
5.368
3.601
3.355
2.500
HO
O
O
N
H
2u (DMSO-d_6, ^{1}H, 400 MHz)
1.00
1.02
2.06
1.04
1.03
1.00
1.01
3.04
f1 (ppm)

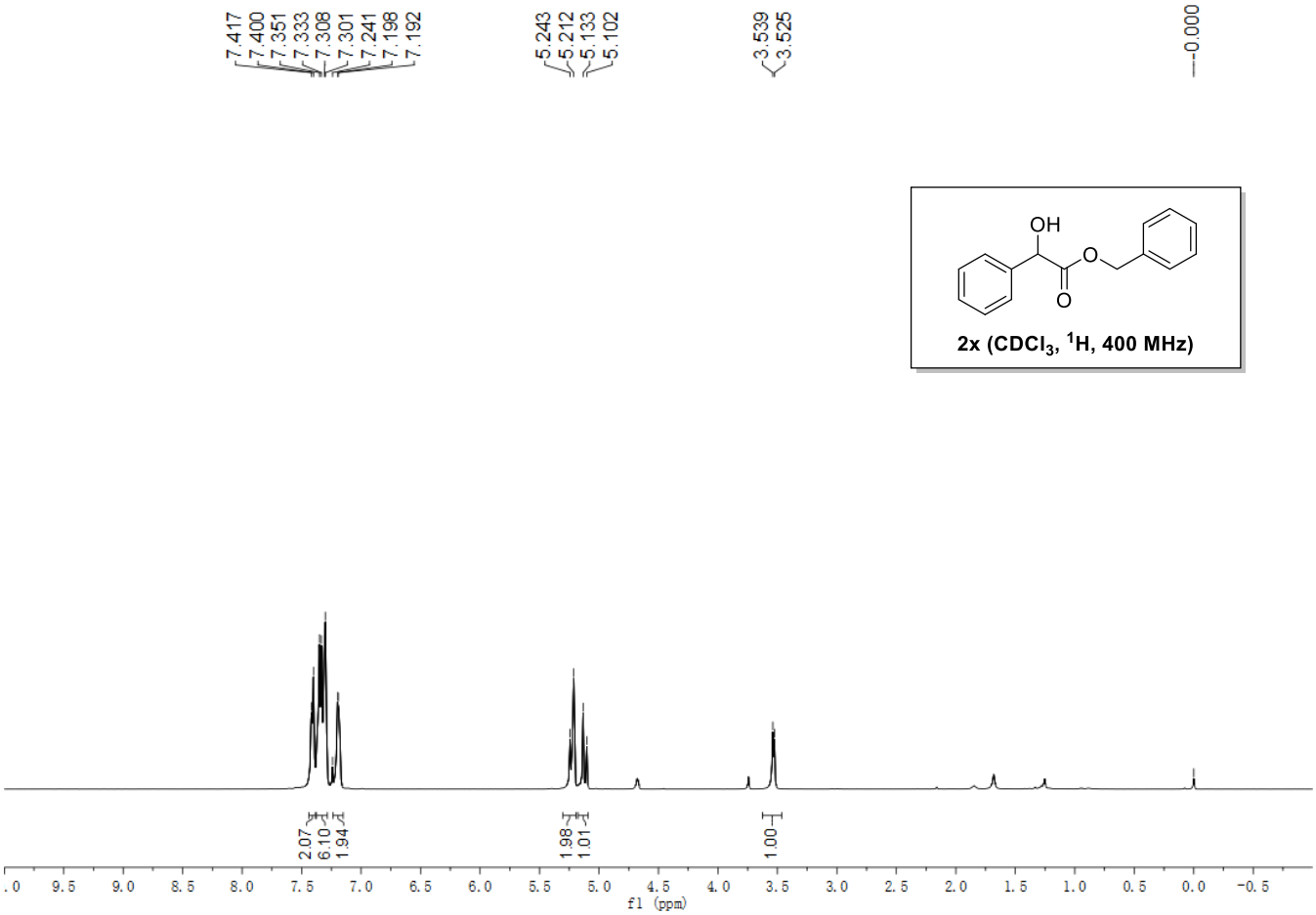

173.627
136.242
125.549
123.992
121.237
119.296
118.770
113.370
111.508
66.621
51.502
40.125
39.917
39.709
39.500
39.292
39.083
38.875
HO
O
O
N
H
2u (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

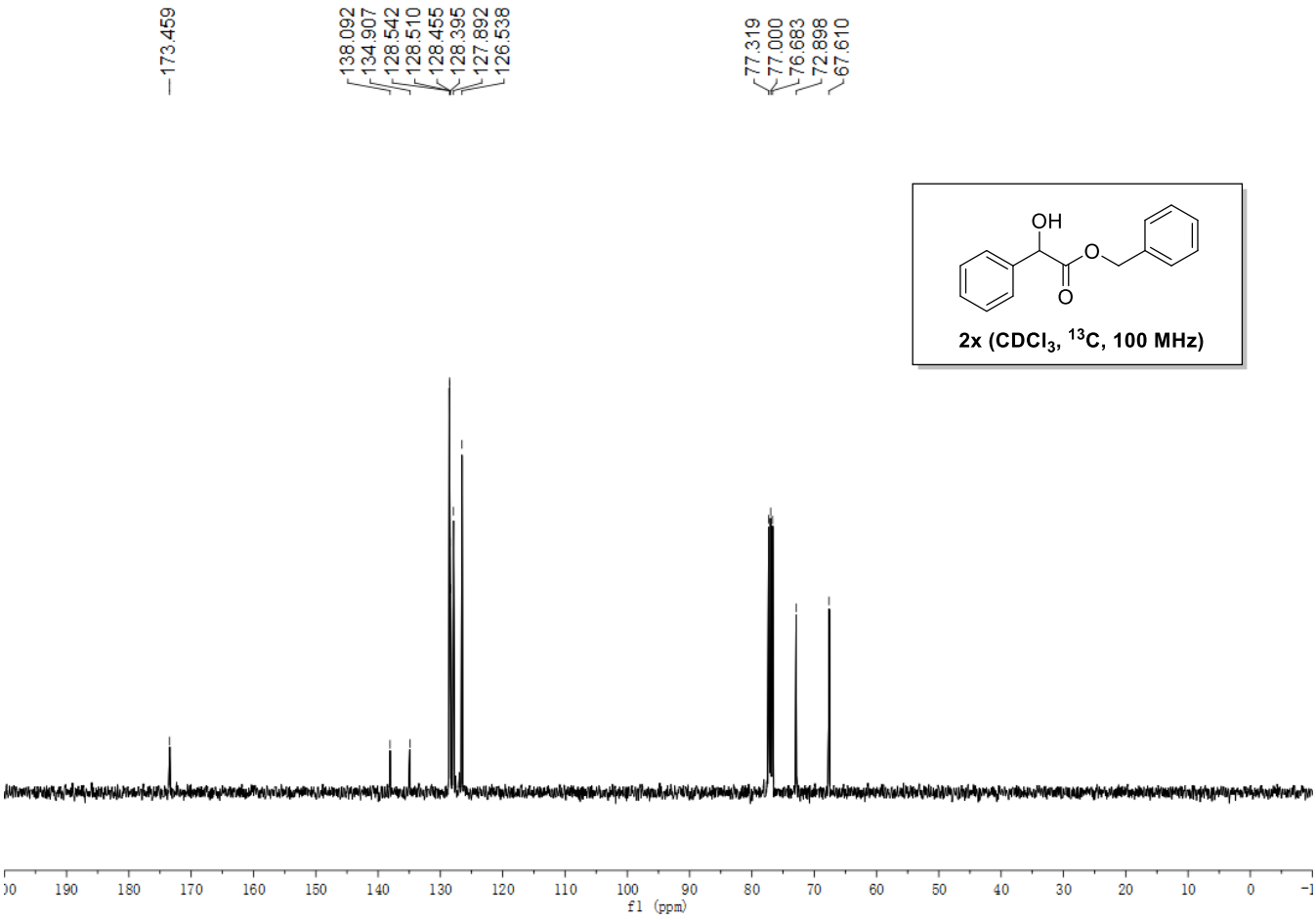

7.432
7.415
7.381
7.364
7.345
7.320
7.302
7.258
5.164
5.150
4.286
4.268
4.259
4.241
4.187
3.550
3.536
1.701
1.241
1.223
1.206
0.000
OH
O
O
2v ($CDCl_3$, ^{1}H, 400 MHz)
5.05
1.00
2.07
0.98
3.15
f1 (ppm)

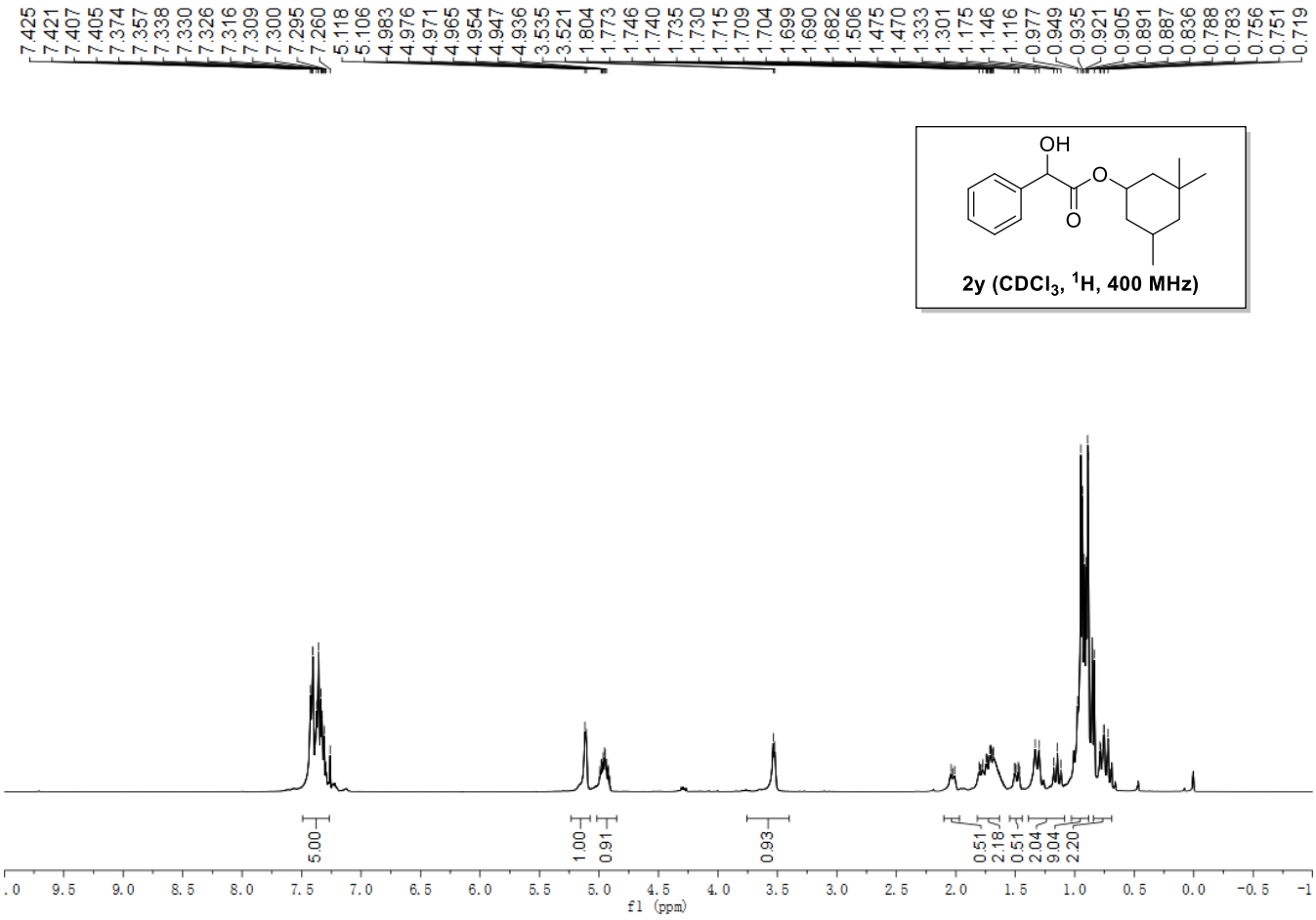

173.636
138.398
128.515
128.349
126.484
77.318
77.000
76.682
72.851
62.182
13.973
OH
O
O
2v (CDCl3, 13C, 100 MHz)
f1 (ppm)

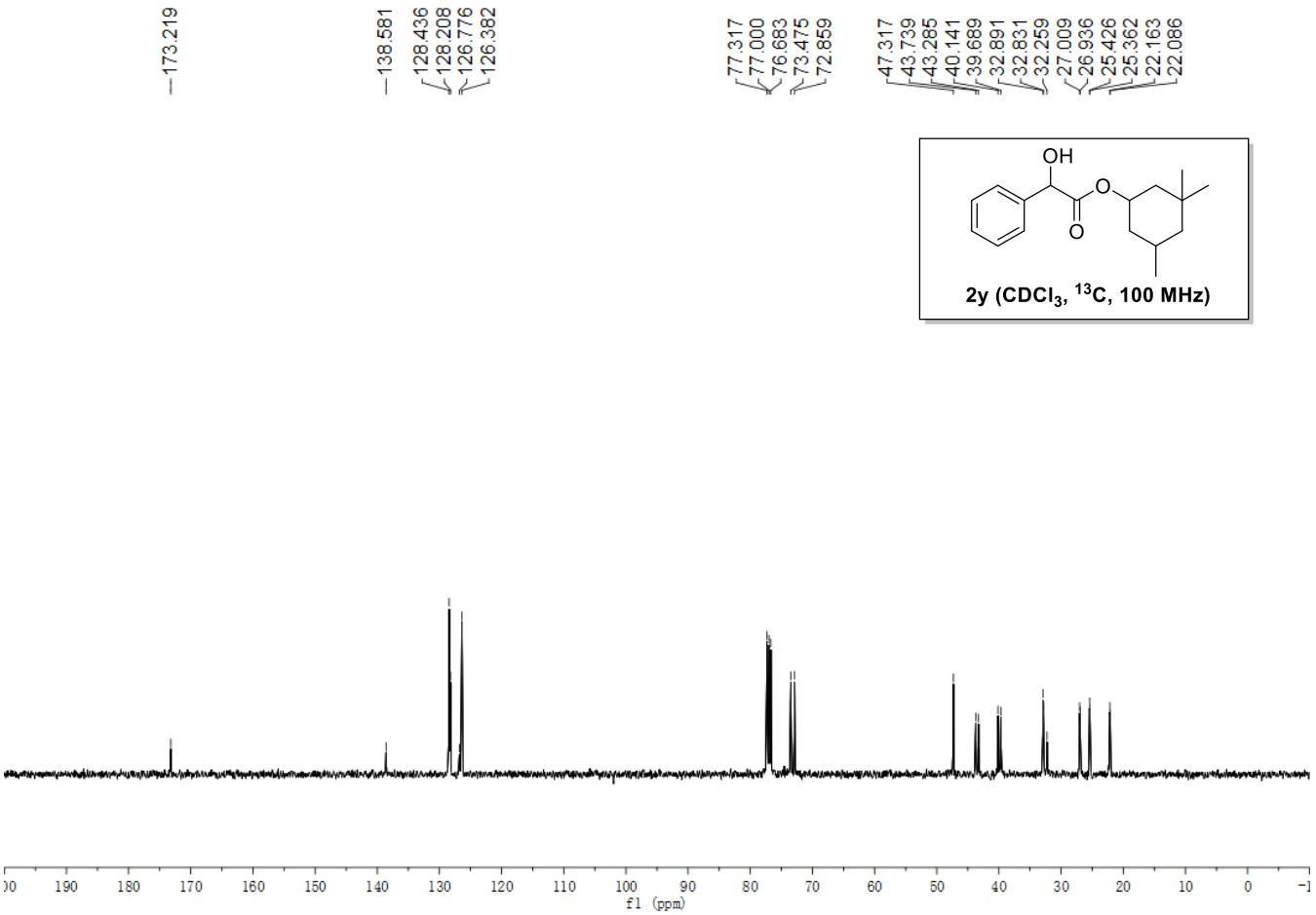

7.414
7.396
7.366
7.348
7.329
7.306
7.289
7.271
5.970
5.077
5.064
4.925
4.909
4.894
4.878
4.863
3.324
2.500
1.192
1.177
1.067
1.052
OH
O
O
2w (DMSO-d6, 1H, 400 MHz)
5.05
1.02
1.00
1.02
3.13
3.04
f1 (ppm)


172.052
139.694
128.160
127.757
126.508
72.491
67.799
40.126
39.917
39.709
39.500
39.292
39.083
38.875
21.496
21.255
OH
O
O
2w (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

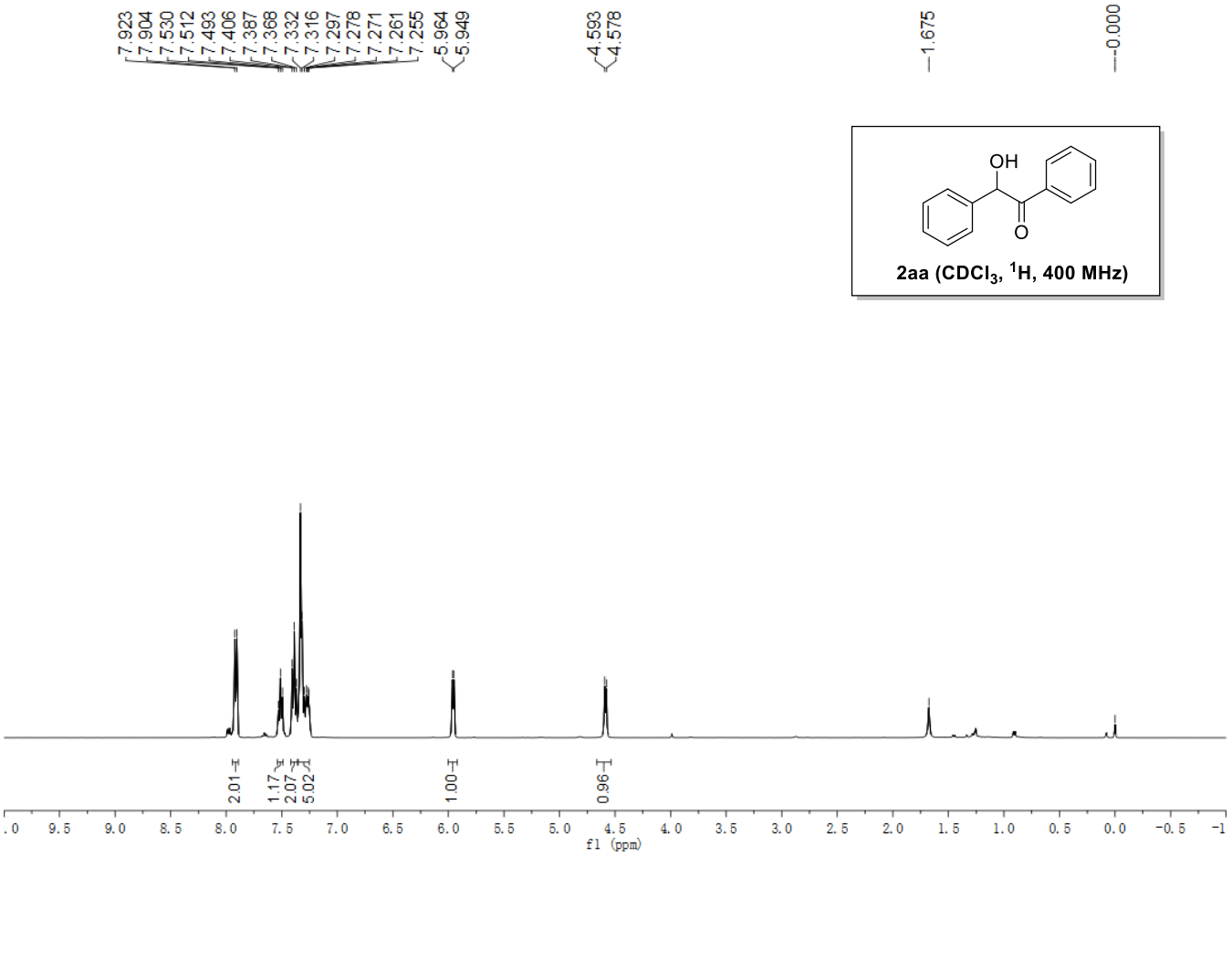

7.417
7.400
7.351
7.333
7.308
7.301
7.241
7.198
7.192
5.243
5.212
5.133
5.102
3.539
3.525
0.000
OH
O
O
2x ($CDCl_3$, ^{1}H, 400 MHz)
2.07
6.10
1.94
1.98
1.01
1.00
f1 (ppm)


173.459
138.092
134.907
128.542
128.510
128.455
128.395
127.892
126.538
77.319
77.000
76.683
72.898
67.610
OH
O
O
2x (CDCl3, 13C, 100 MHz)
f1 (ppm)

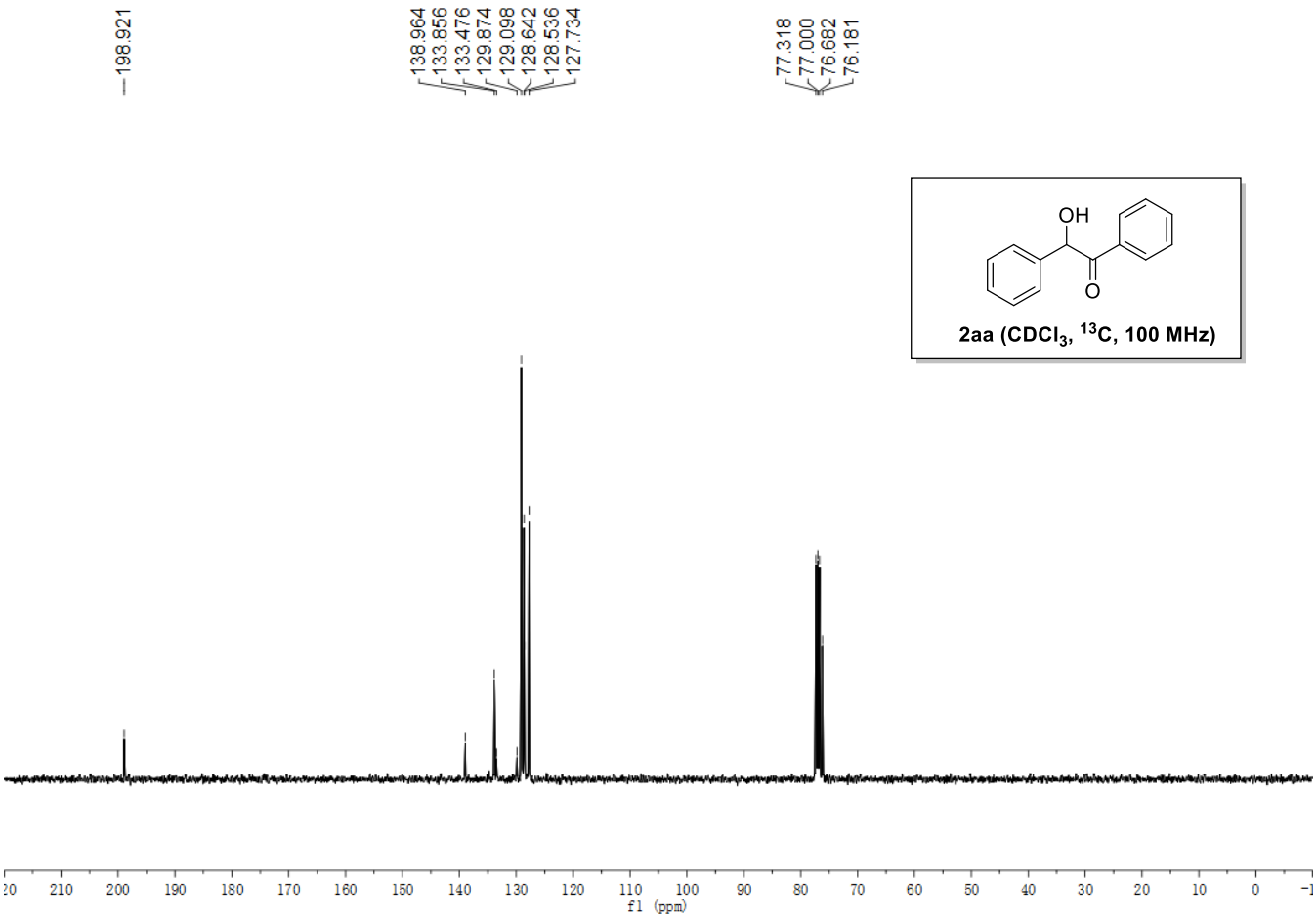

7.425
7.421
7.407
7.405
7.374
7.357
7.338
7.330
7.326
7.316
7.309
7.300
7.295
7.260
5.118
5.106
4.983
4.976
4.971
4.965
4.954
4.947
4.936
3.535
3.521
1.804
1.773
1.746
1.740
1.735
1.730
1.715
1.709
1.704
1.699
1.690
1.682
1.506
1.475
1.470
1.333
1.301
1.175
1.146
1.116
0.977
0.949
0.935
0.921
0.905
0.891
0.887
0.836
0.788
0.783
0.756
0.751
0.719
OH
O
O
2y (CDCl3, 1H, 400 MHz)
5.00
1.00
0.91
0.93
0.51
2.18
0.51
2.04
9.04
2.20
f1 (ppm)

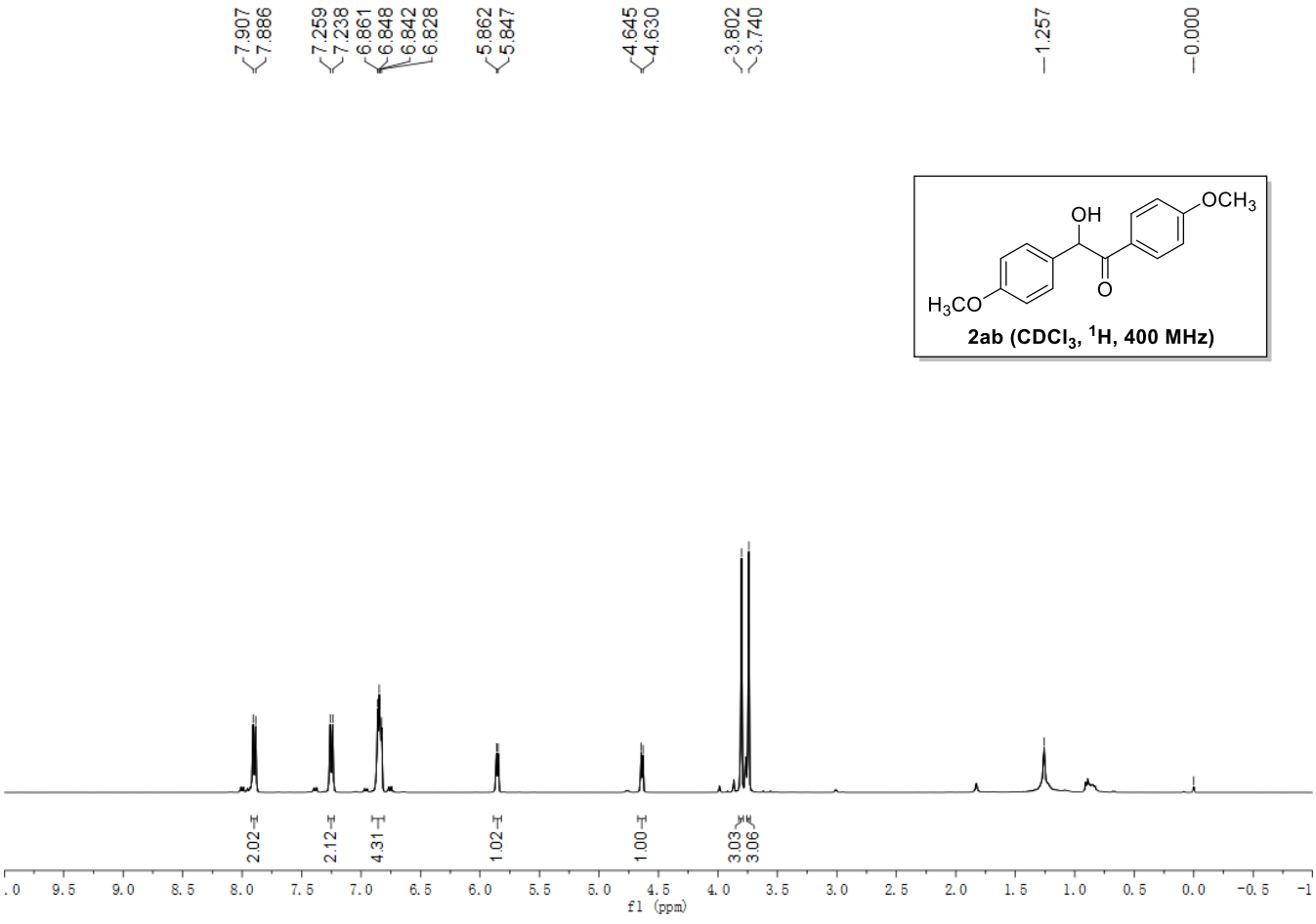


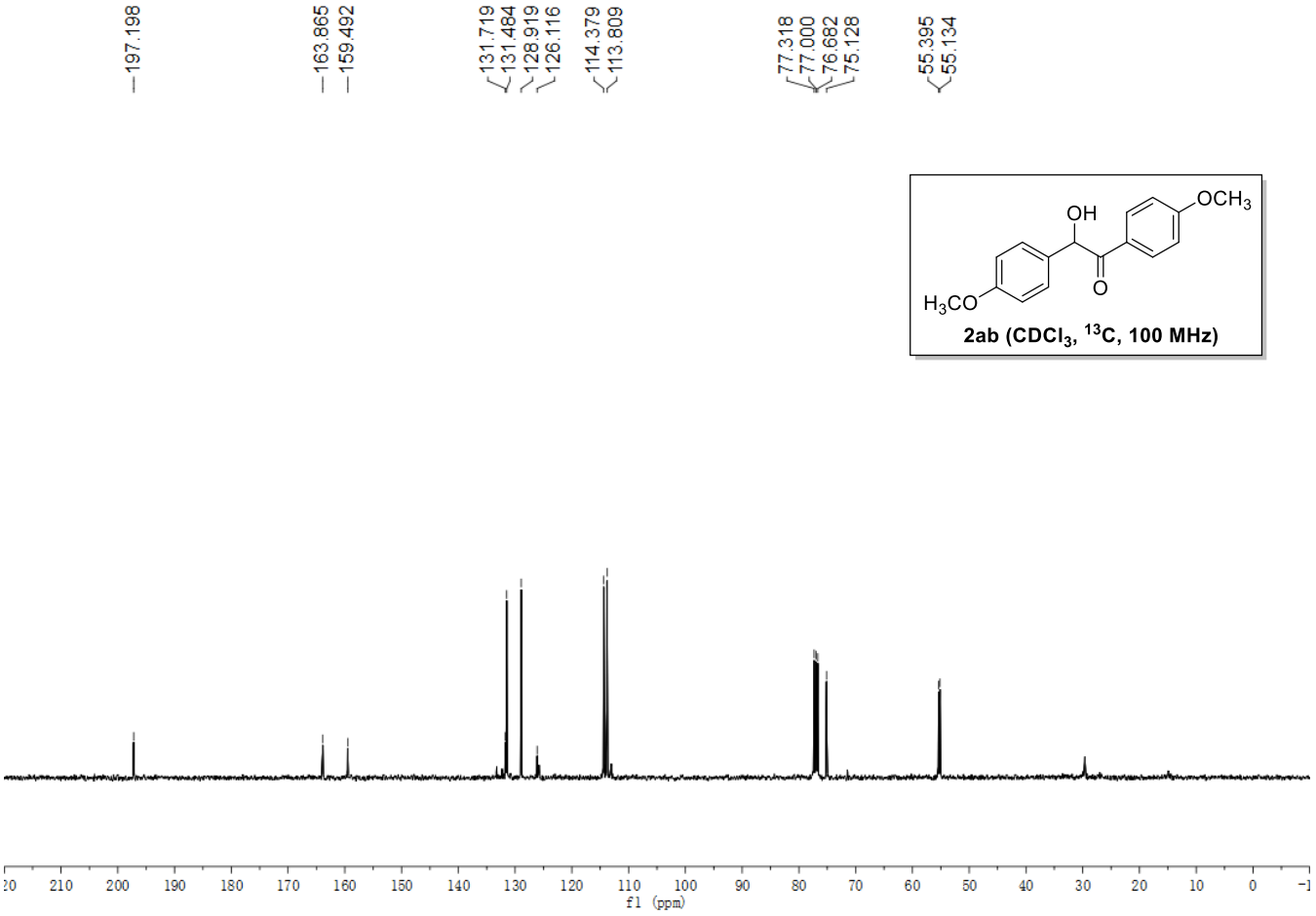
2y ($CDCl_3$, ^{13}C, 100 MHz)



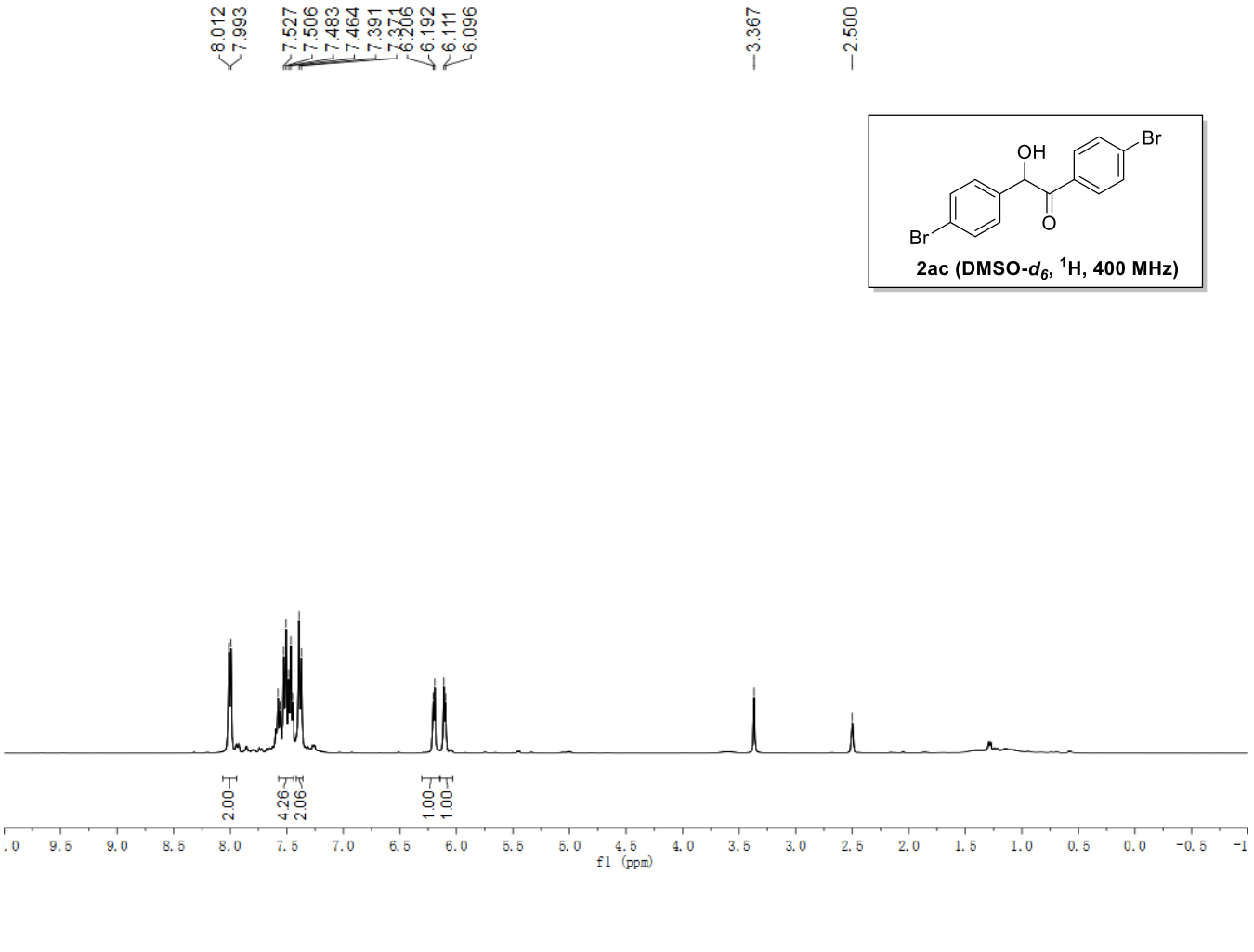
2aa ($CDCl_3$, ^{1}H, 400 MHz)


198.921
138.964
133.856
133.476
129.874
129.098
128.642
128.536
127.734
77.318
77.000
76.682
76.181
OH
O
2aa (CDCl3, 13C, 100 MHz)
f1 (ppm)

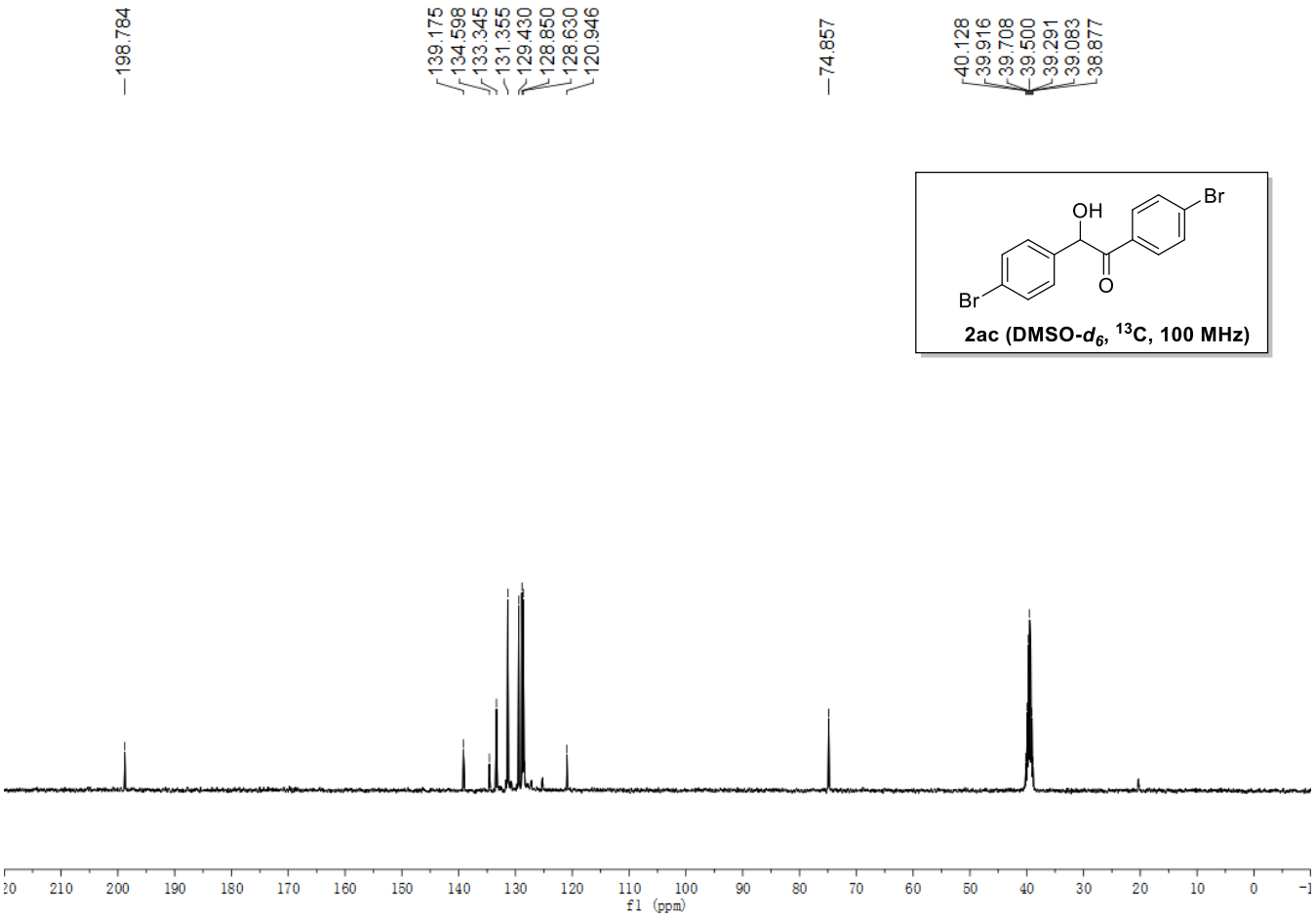

7.907
7.886
7.259
7.238
6.861
6.848
6.842
6.828
5.862
5.847
4.645
4.630
3.802
3.740
1.257
0.000
OCH3
OH
O
H3CO
2ab (CDCl3, 1H, 400 MHz)
2.02
2.12
4.31
1.02
1.00
3.03
3.06
f1 (ppm)

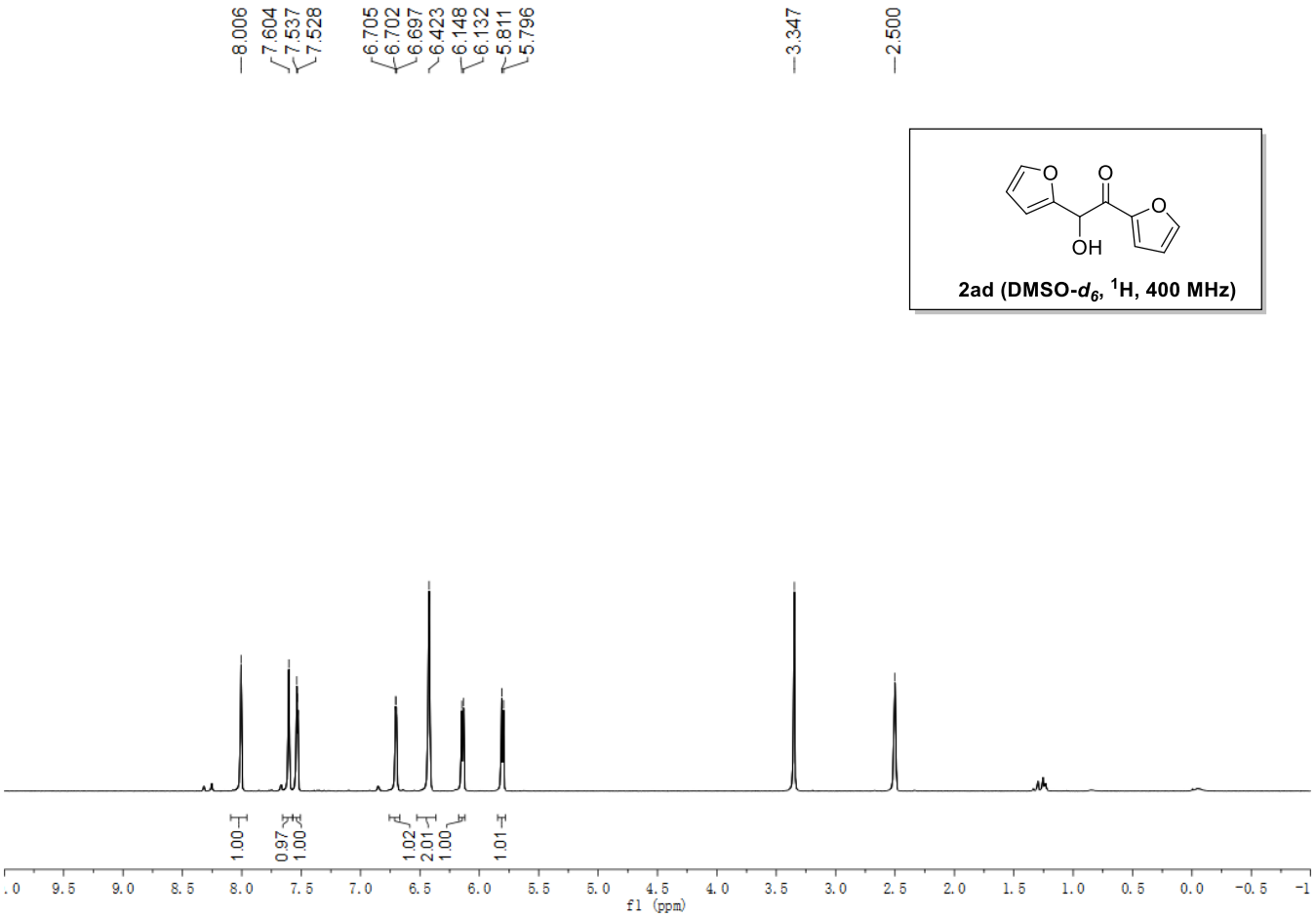


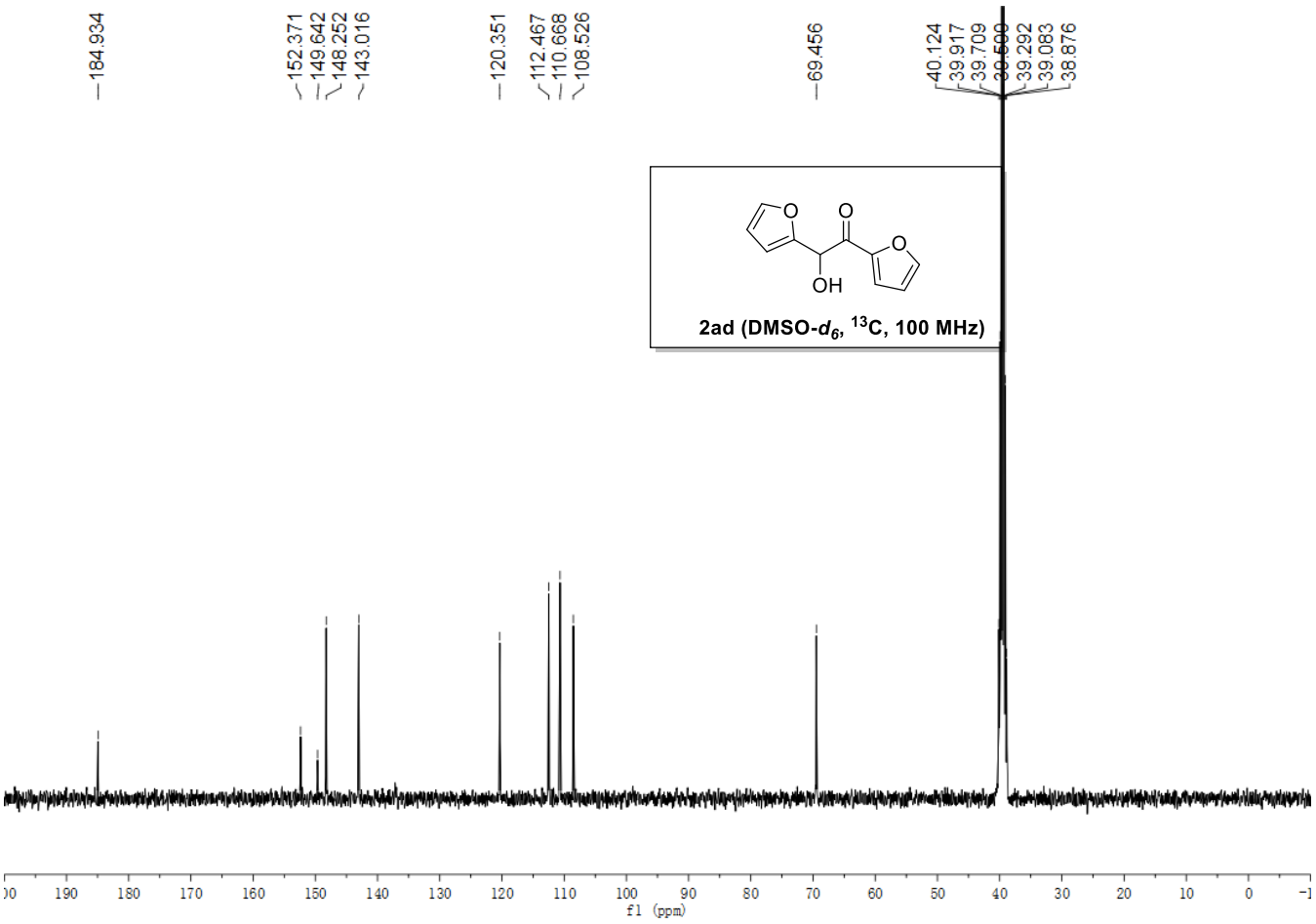
2ab ($CDCl_3$, ^{13}C, 100 MHz)



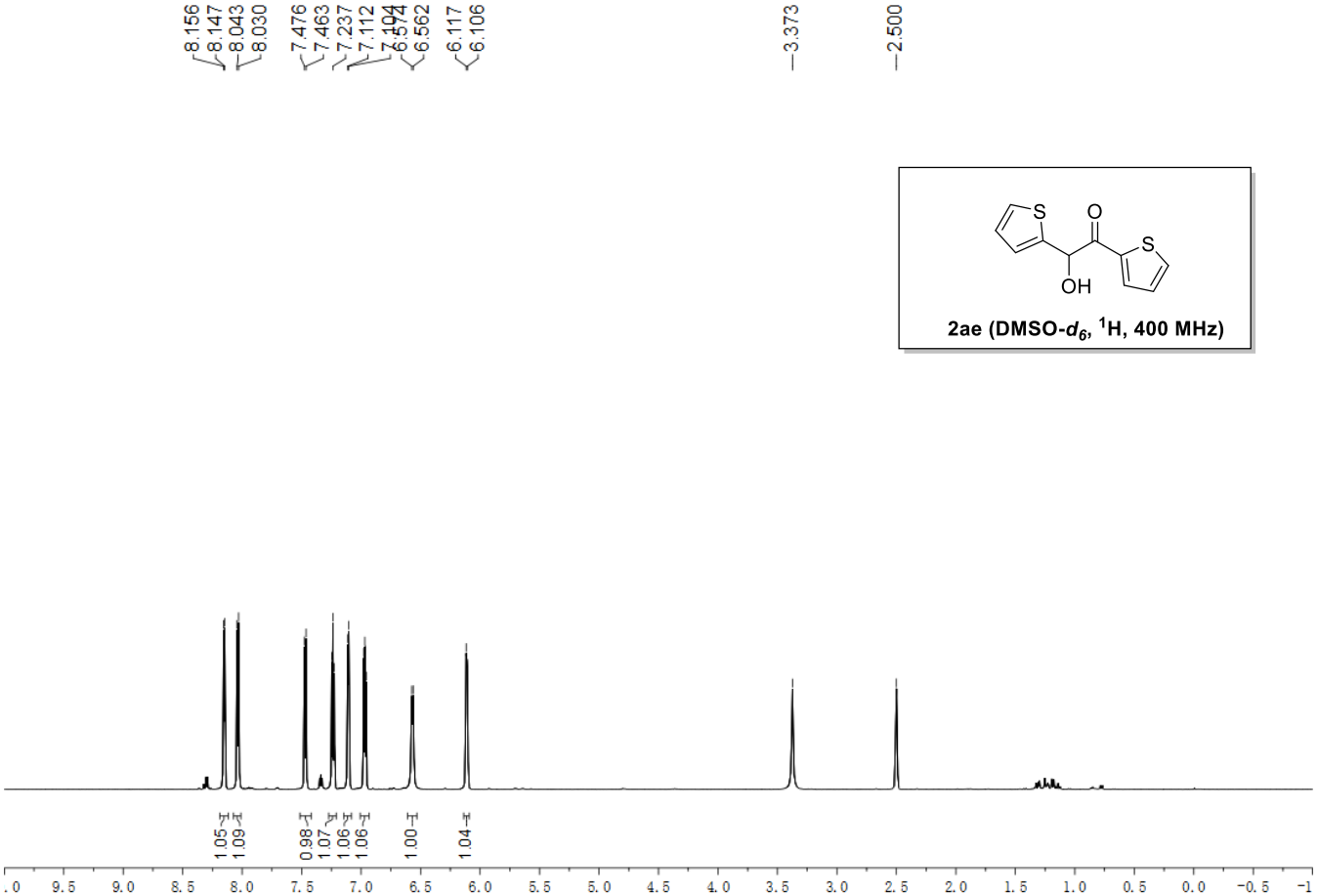
2ac (DMSO-d_6, ^1H, 400 MHz)


198.784
139.175
134.598
133.345
131.355
129.430
128.850
128.630
120.946
74.857
40.128
39.916
39.708
39.500
39.291
39.083
38.877
OH
Br
Br
O
2ac (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

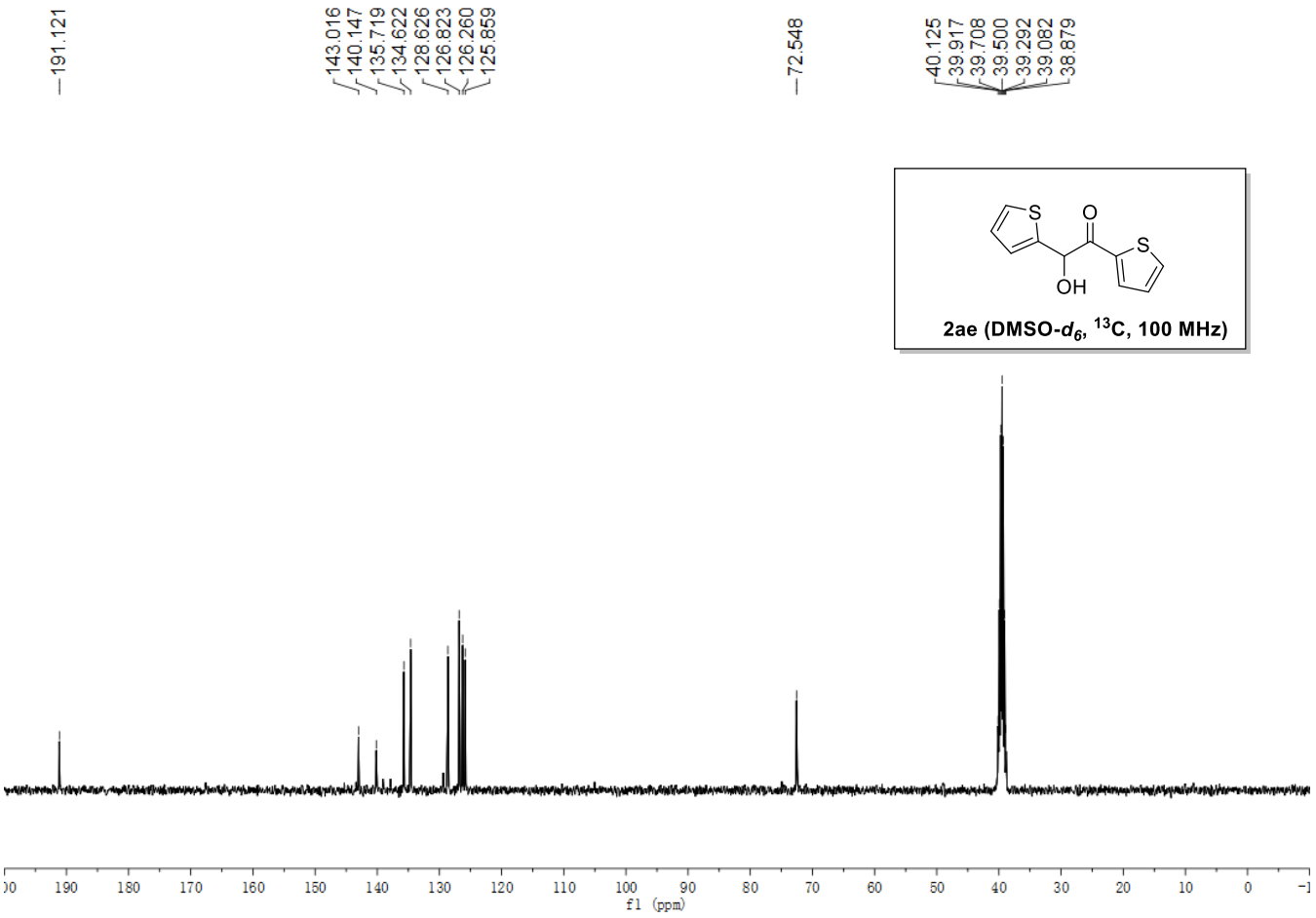

8.006
7.604
7.537
7.528
6.705
6.702
6.697
6.423
6.148
6.132
5.811
5.796
3.347
2.500
O
O
O
OH
2ad (DMSO-d_6, ^{1}H, 400 MHz)
1.00
0.97
1.00
1.02
2.01
1.00
1.01
f1 (ppm)

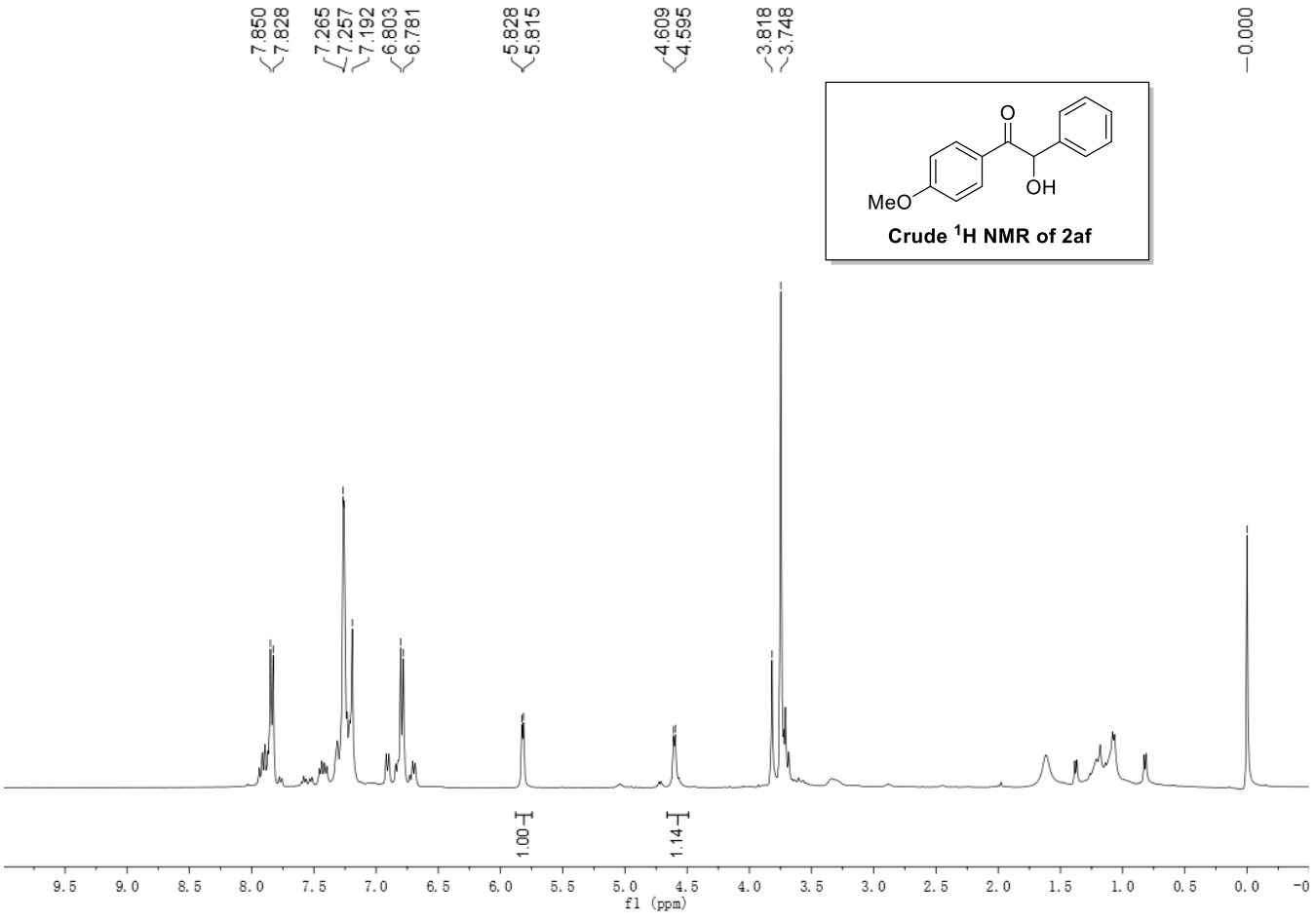


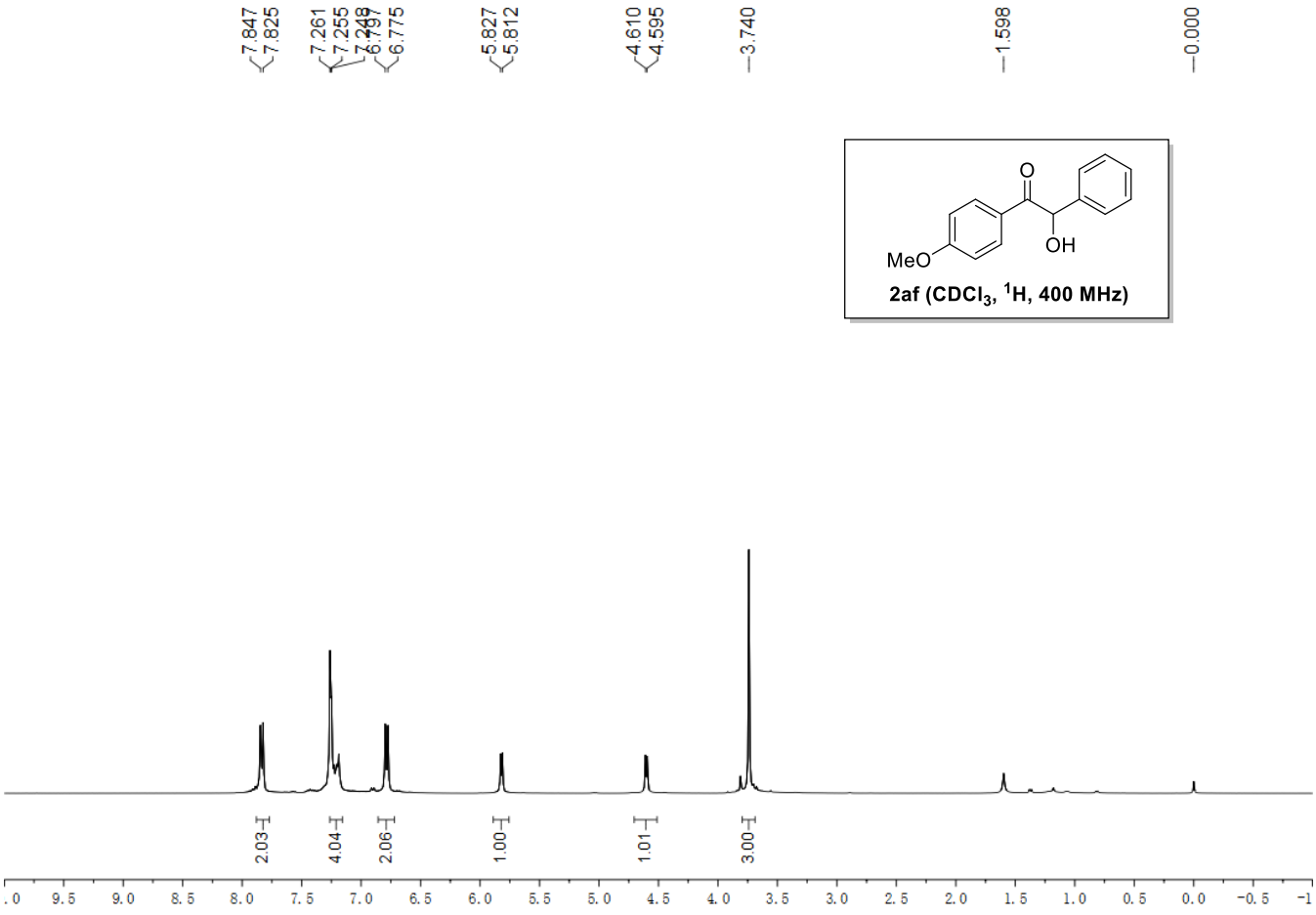
2ad (DMSO-d_6, ^{13}C, 100 MHz)

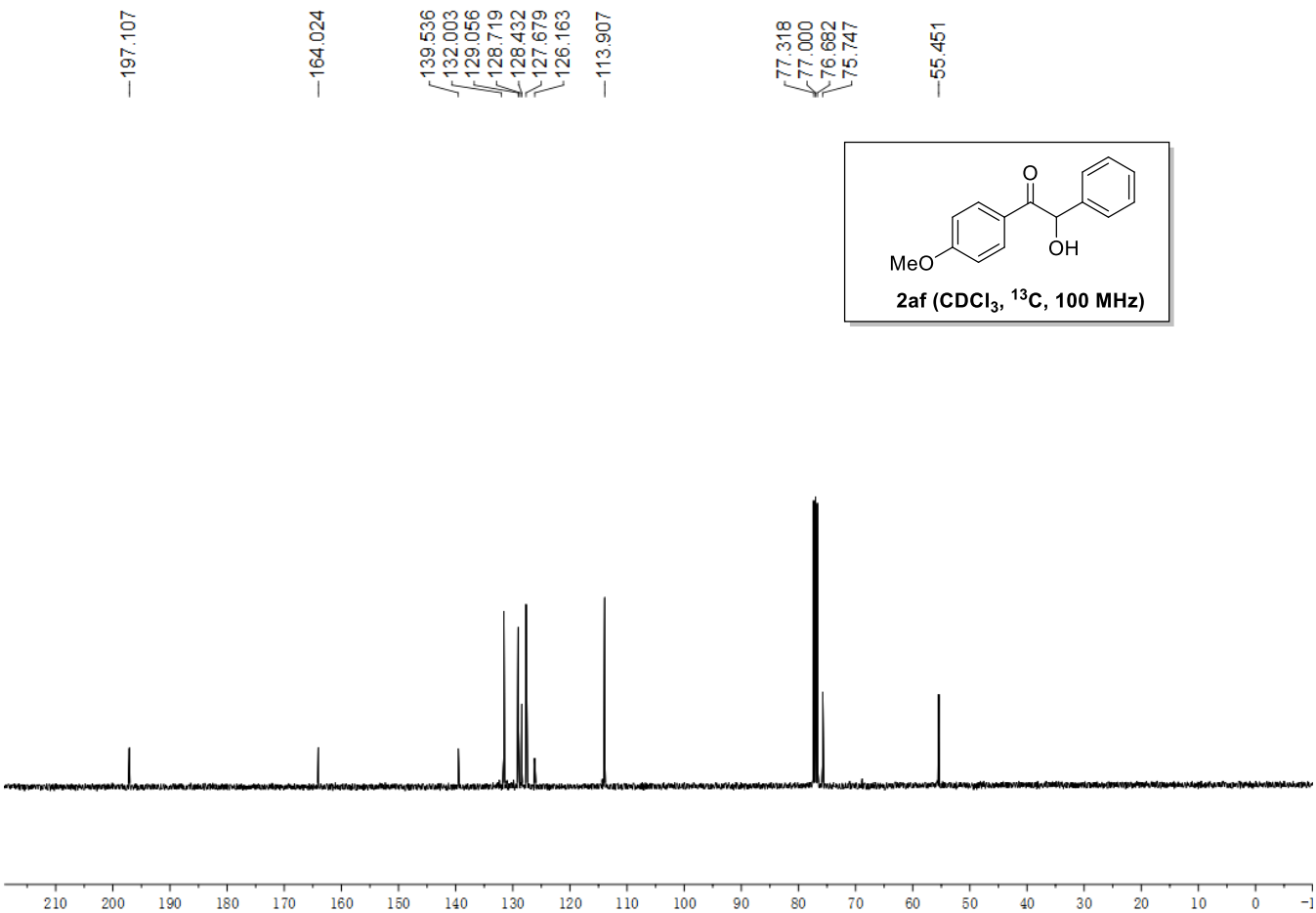


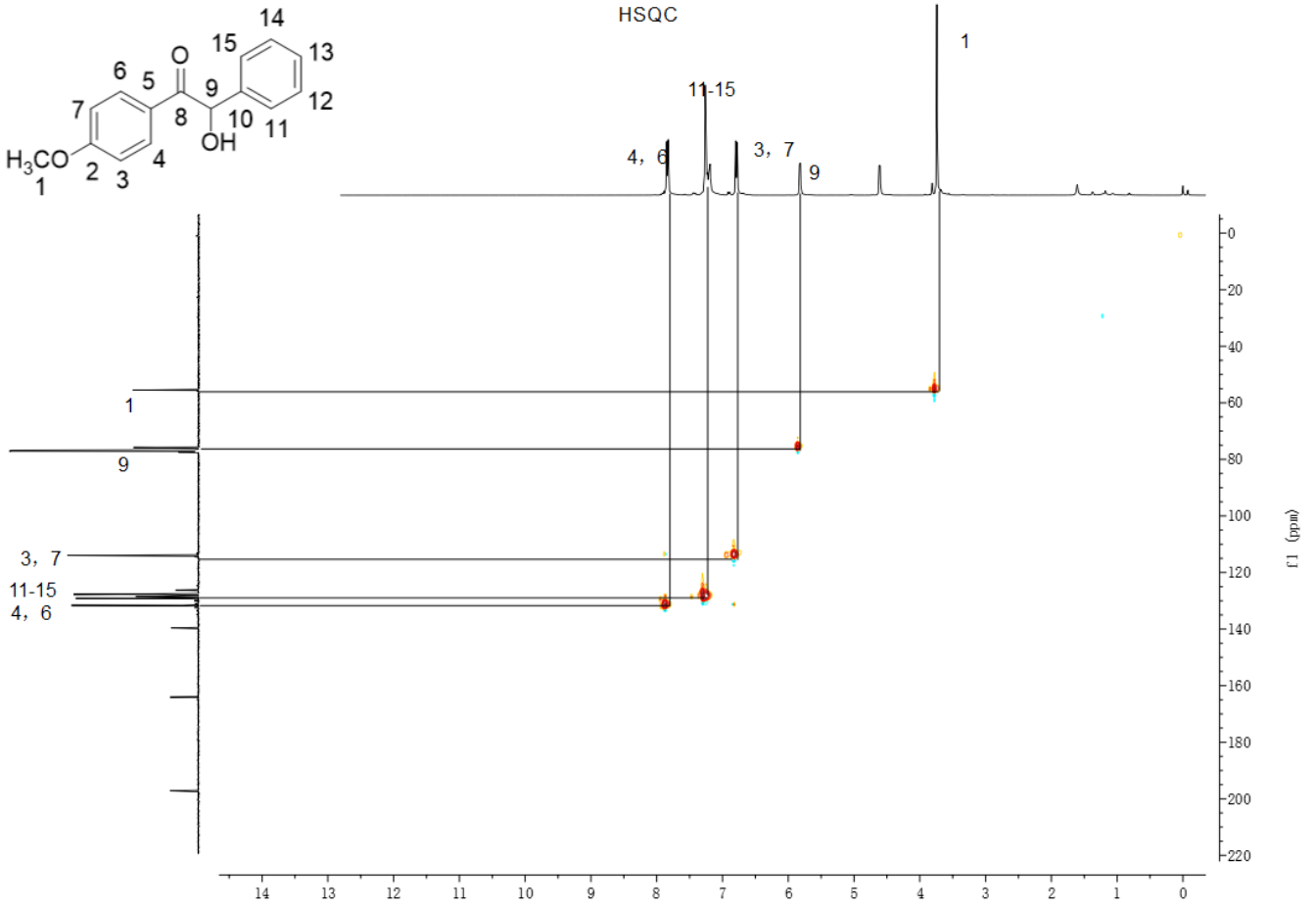
2ae (DMSO-d_6, ^{1}H, 400 MHz)

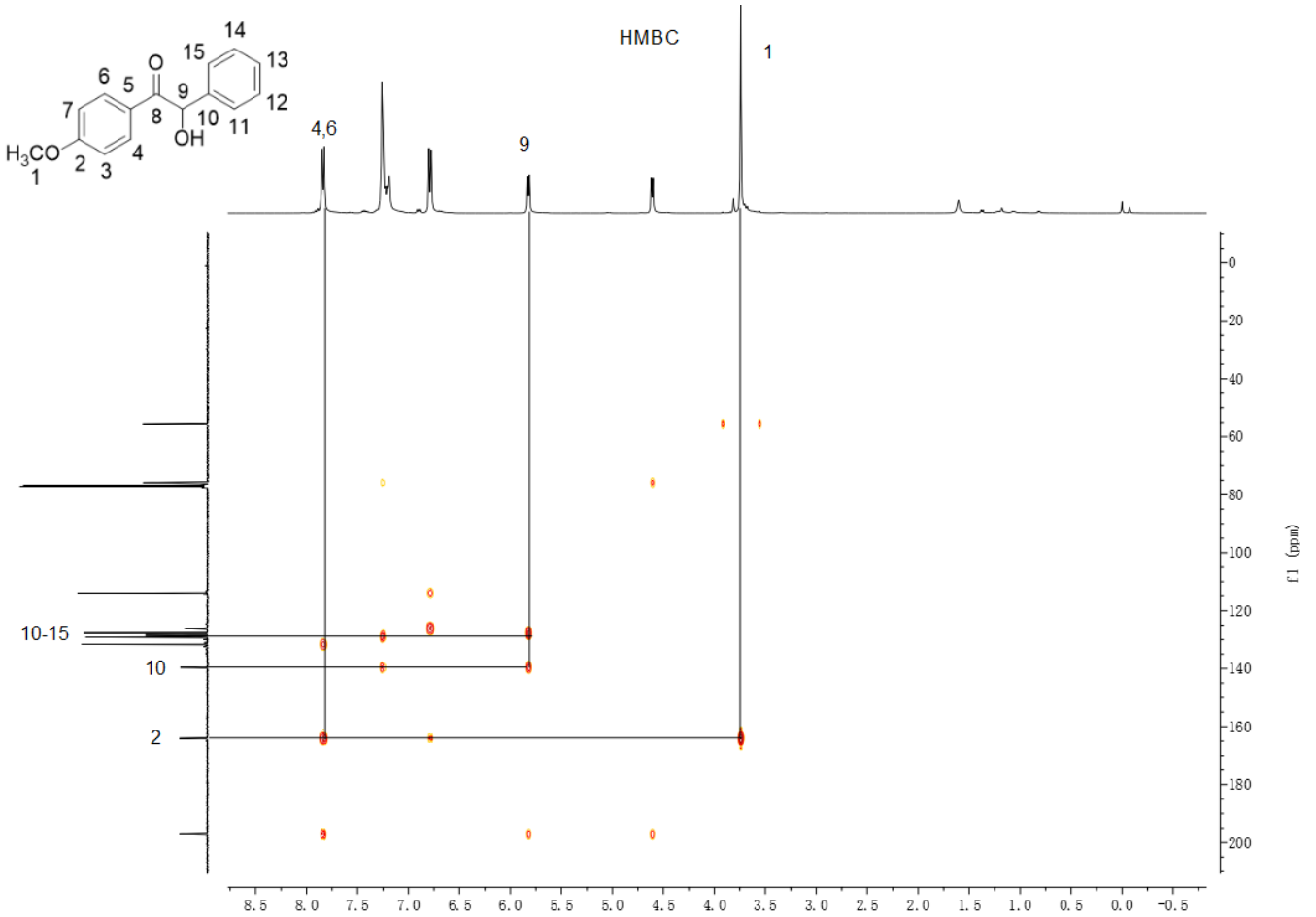

191.121
143.016
140.147
135.719
134.622
128.626
126.823
126.260
125.859
72.548
40.125
39.917
39.708
39.500
39.292
39.082
38.879
S
O
S
OH
2ae (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

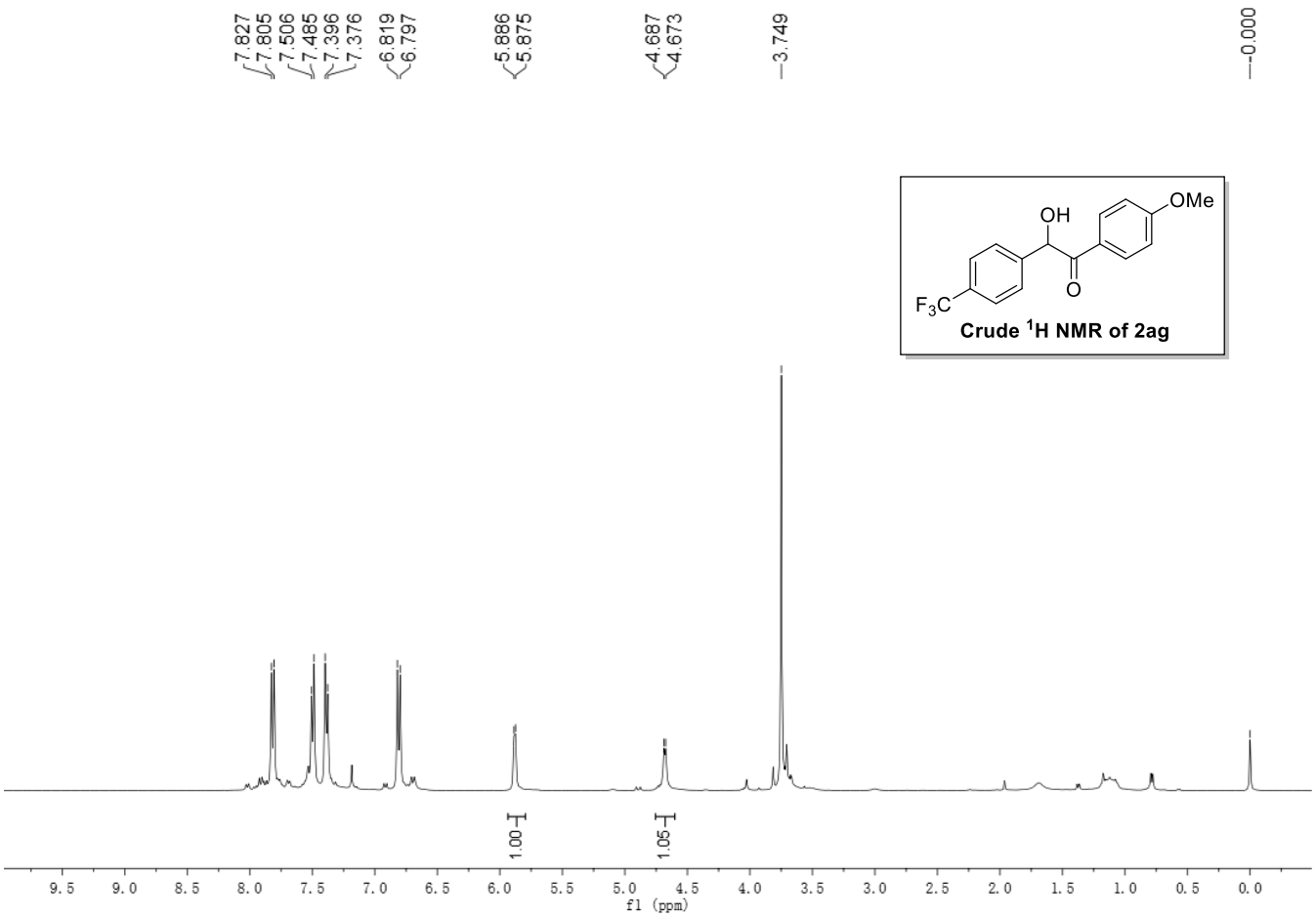

7.850
7.828
7.265
7.257
7.192
6.803
6.781
5.828
5.815
4.609
4.595
3.818
3.748
0.000
O
OH
MeO
Crude ^{1}H NMR of 2af
1.00
1.14
f1 (ppm)

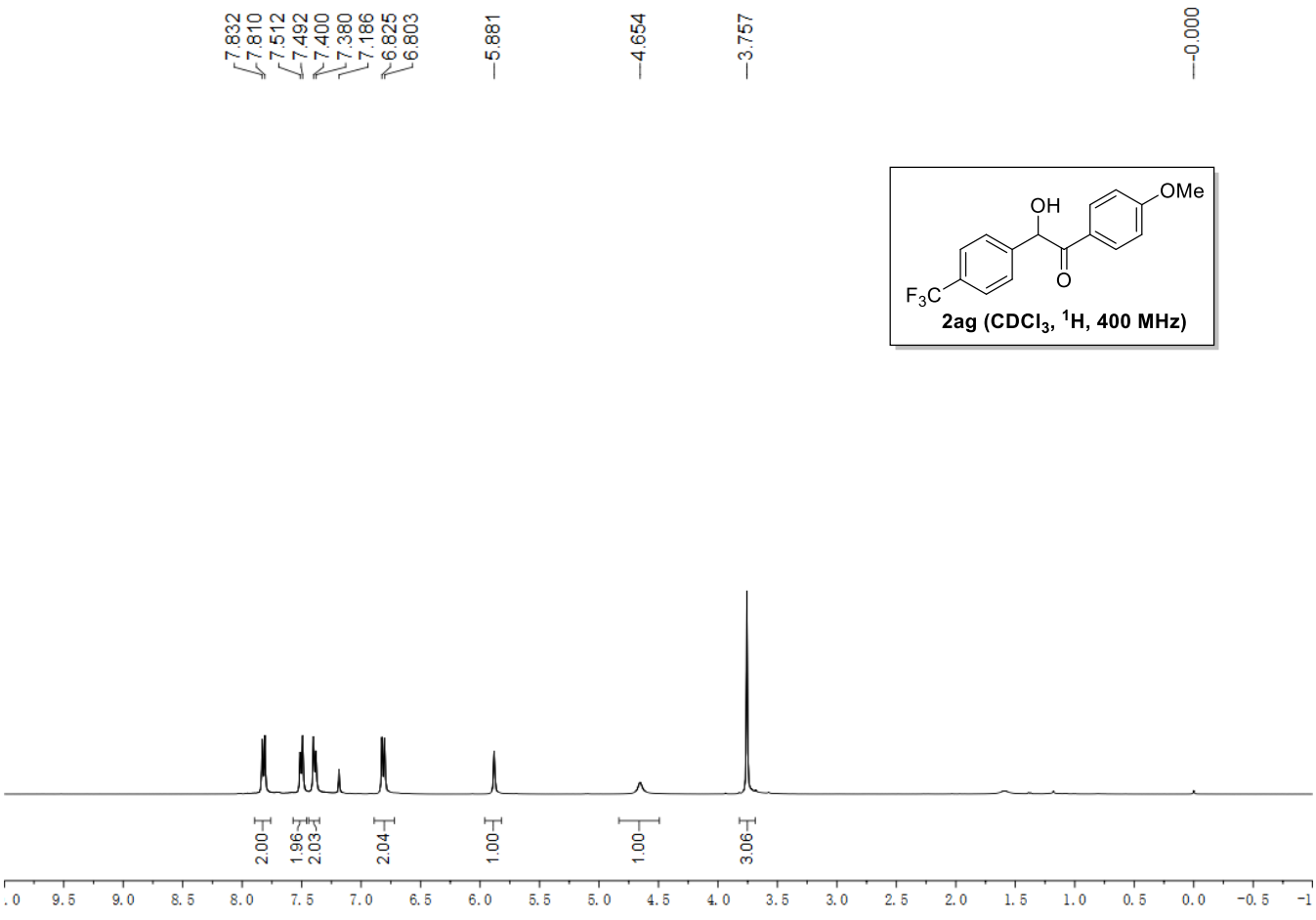

7.847
7.825
7.261
7.255
7.248
6.797
6.775
5.827
5.812
4.610
4.595
3.740
1.598
0.000
O
OH
MeO
2af (CDCl3, 1H, 400 MHz)
2.03
4.04
2.06
1.00
1.01
3.00

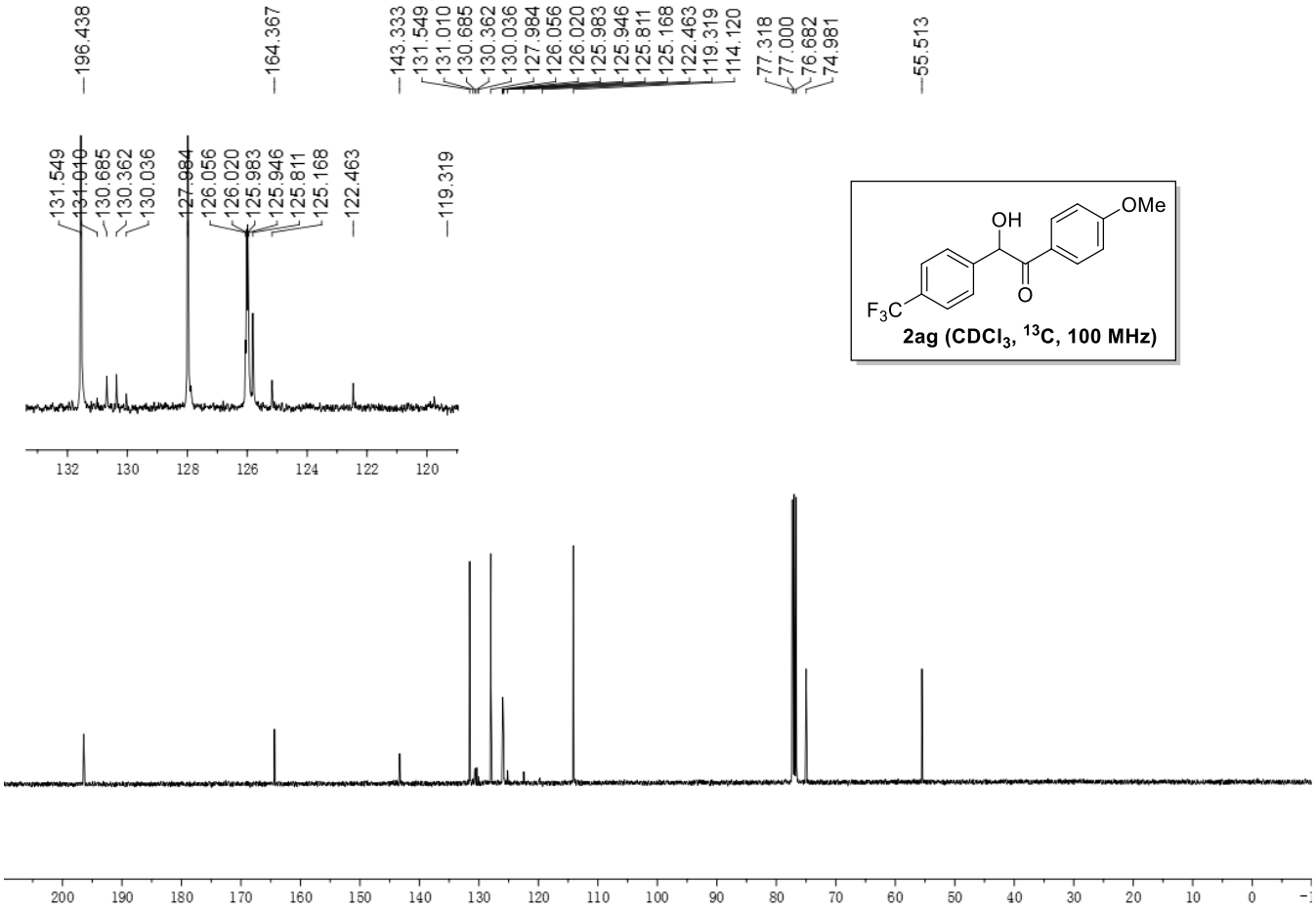

197.107
164.024
139.536
132.003
129.056
128.719
128.432
127.679
126.163
113.907
77.318
77.000
76.682
75.747
55.451
O
OH
MeO
2af (CDCl3, 13C, 100 MHz)

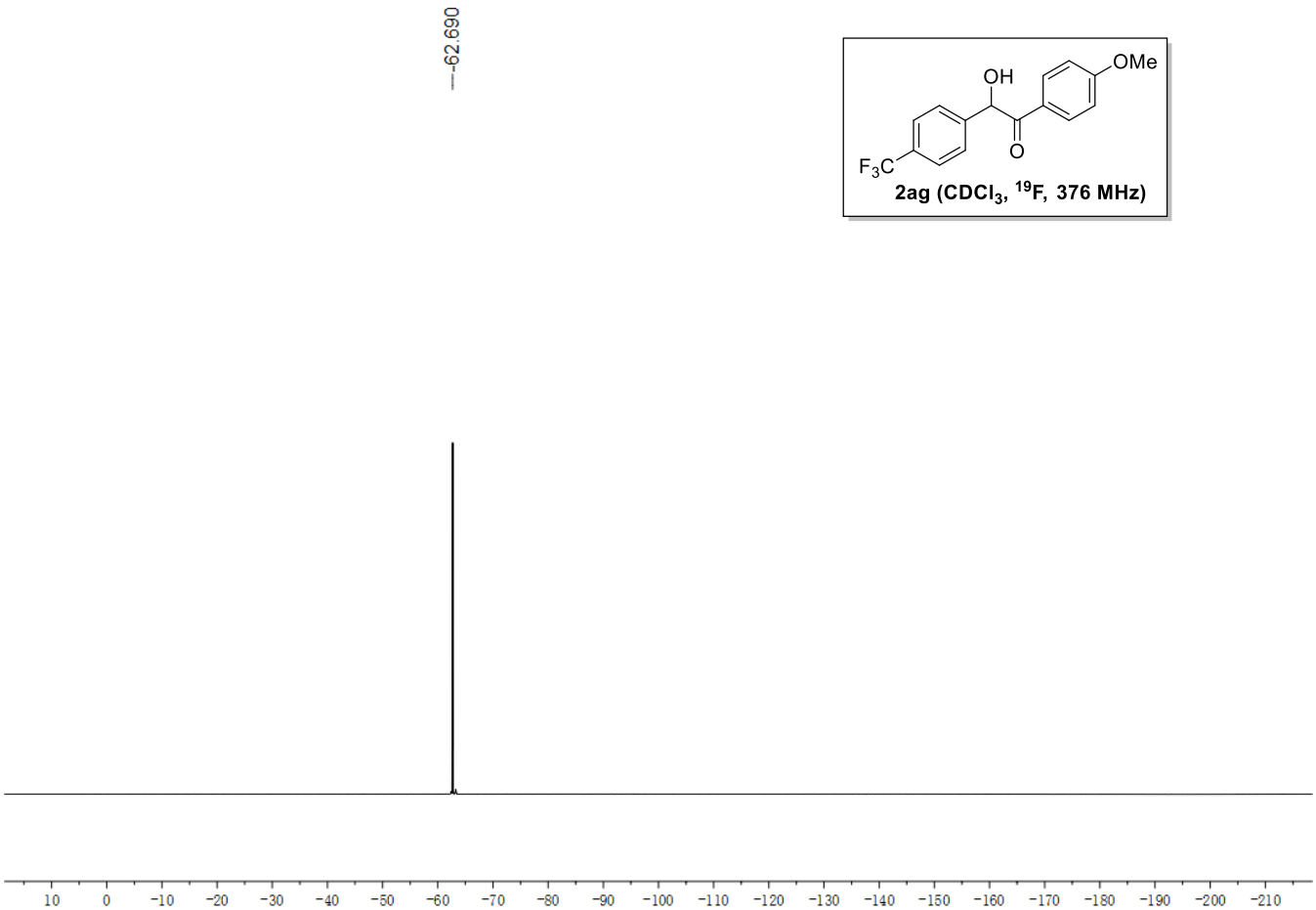

HSQC
1
11-15
4，6
3，7
9
1
9
3，7
11-15
4，6
f1 (ppm)

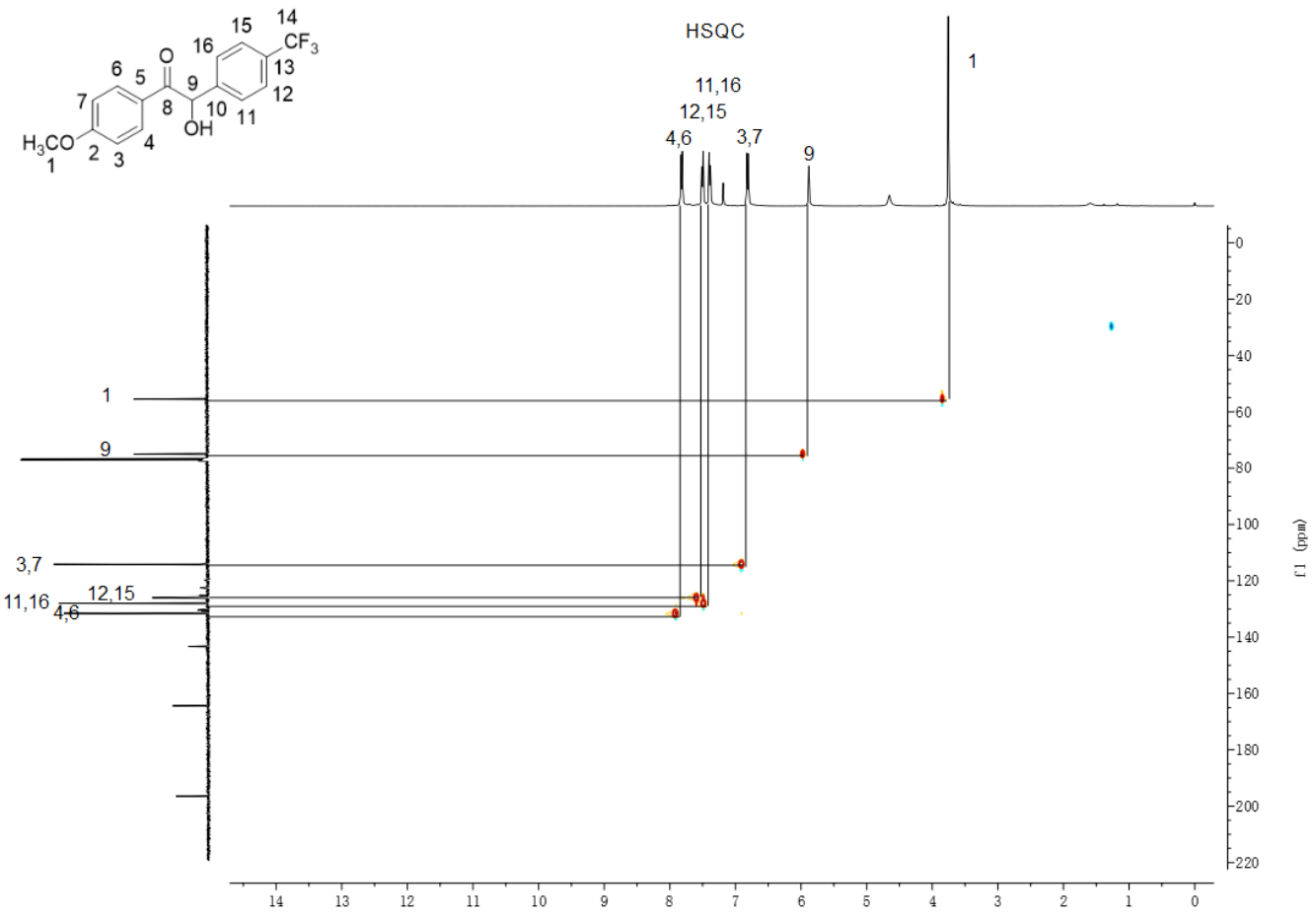

HMBC
1
4,6
9
10-15
10
2
f1 (ppm)

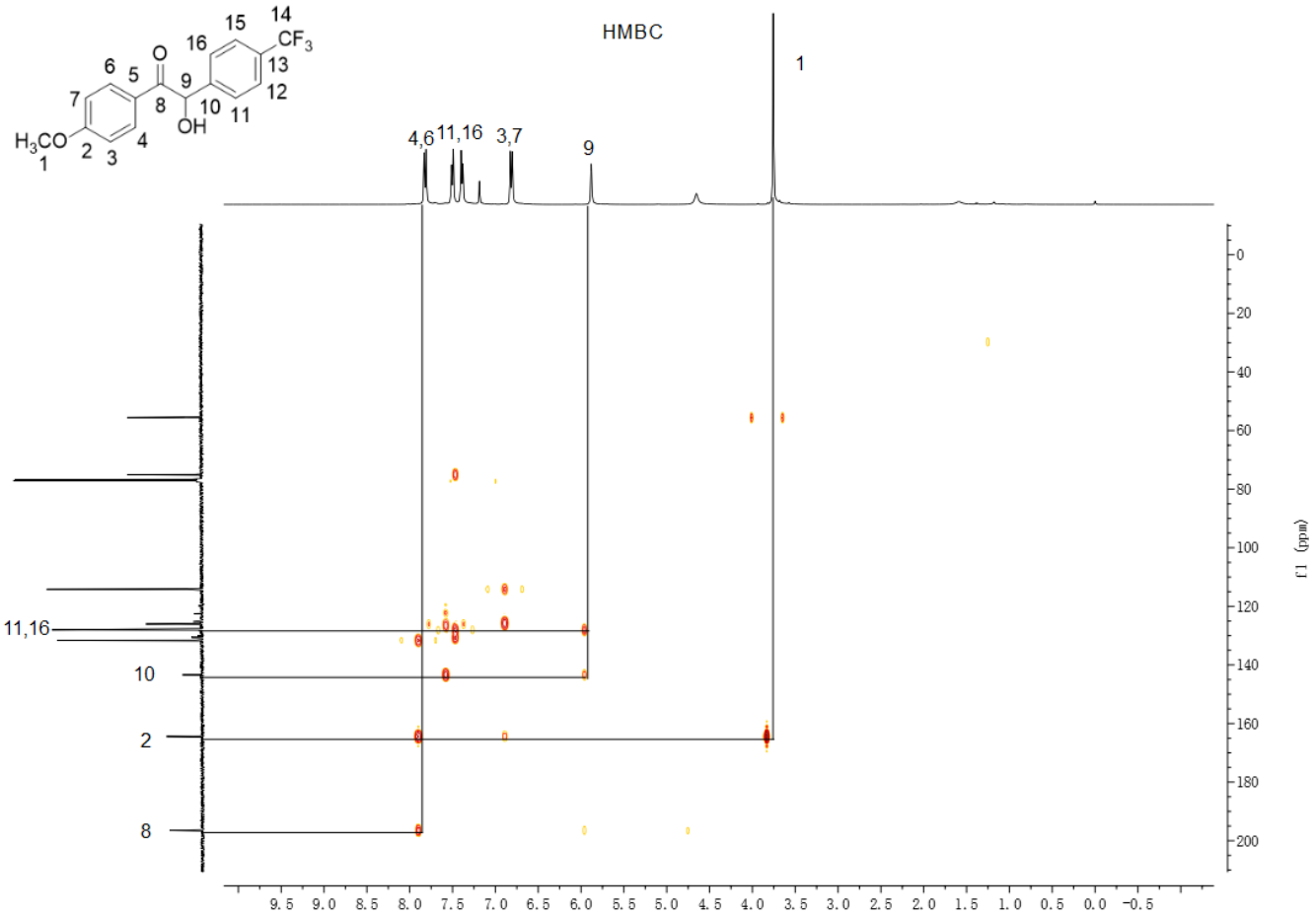

7.827
7.805
7.506
7.485
7.396
7.376
6.819
6.797
5.886
5.875
4.687
4.673
3.749
0.000
OH
OMe
O
F3C
Crude 1H NMR of 2ag
1.00
1.05
f1 (ppm)

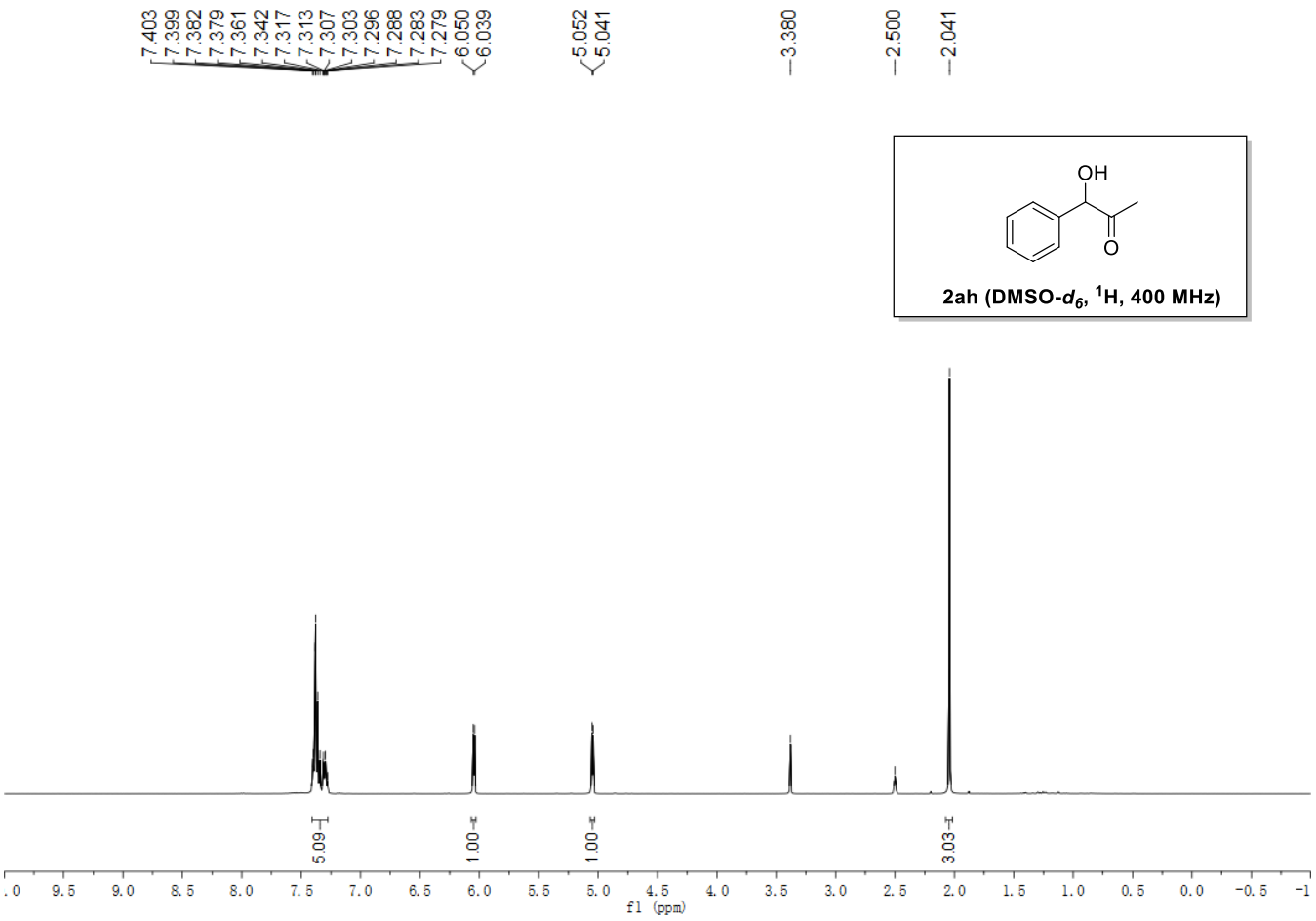

7.832
7.810
7.512
7.492
7.400
7.380
7.186
6.825
6.803
5.881
4.654
3.757
0.000
OH
OMe
O
F3C
2ag (CDCl3, 1H, 400 MHz)
2.00
1.96
2.03
2.04
1.00
1.00
3.06

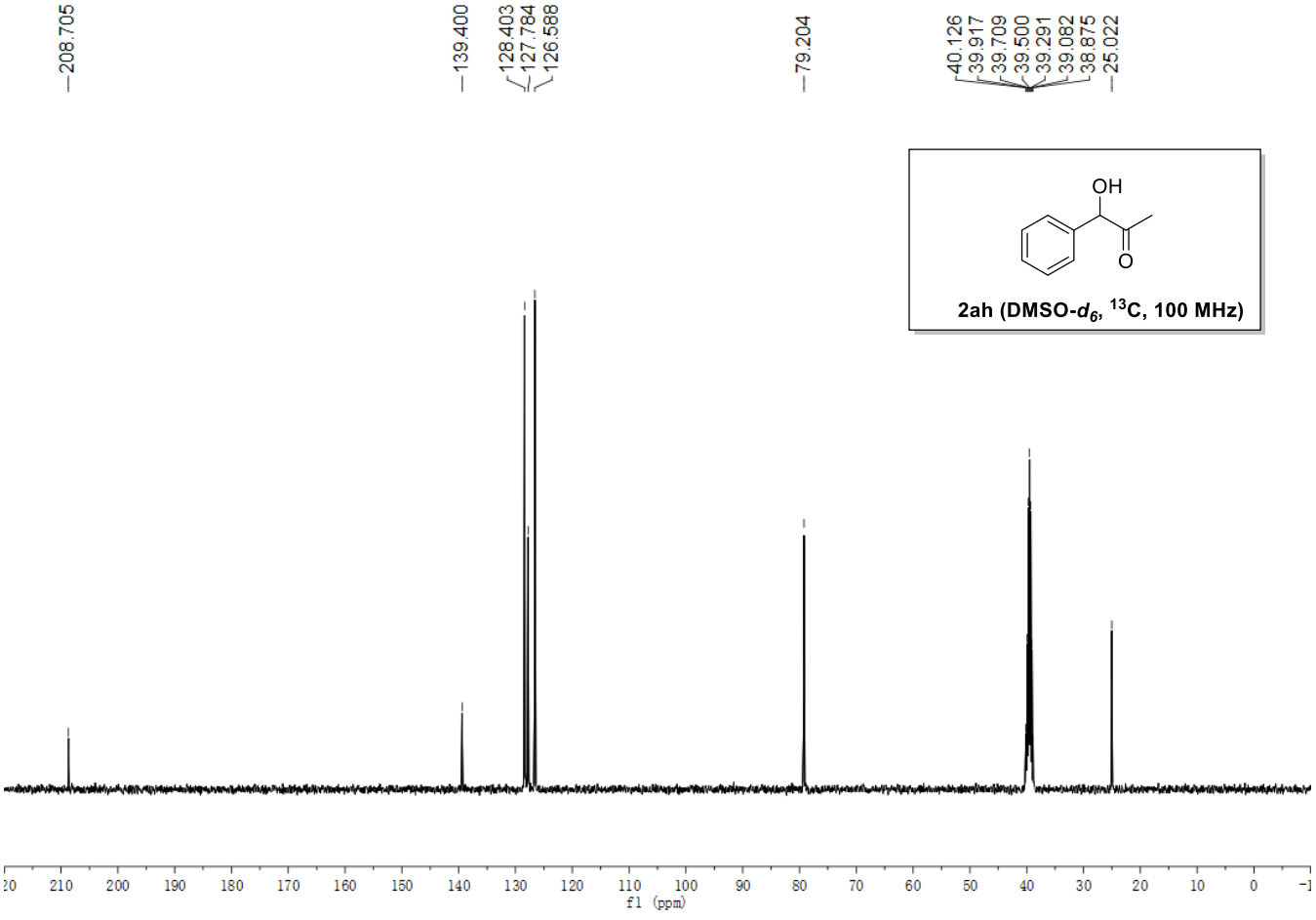

196.438
164.367
143.333
131.549
131.010
130.685
130.362
130.036
127.984
126.056
126.020
125.983
125.946
125.811
125.168
122.463
119.319
114.120
77.318
77.000
76.682
74.981
55.513
OH
OMe
O
F3C
2ag (CDCl3, 13C, 100 MHz)

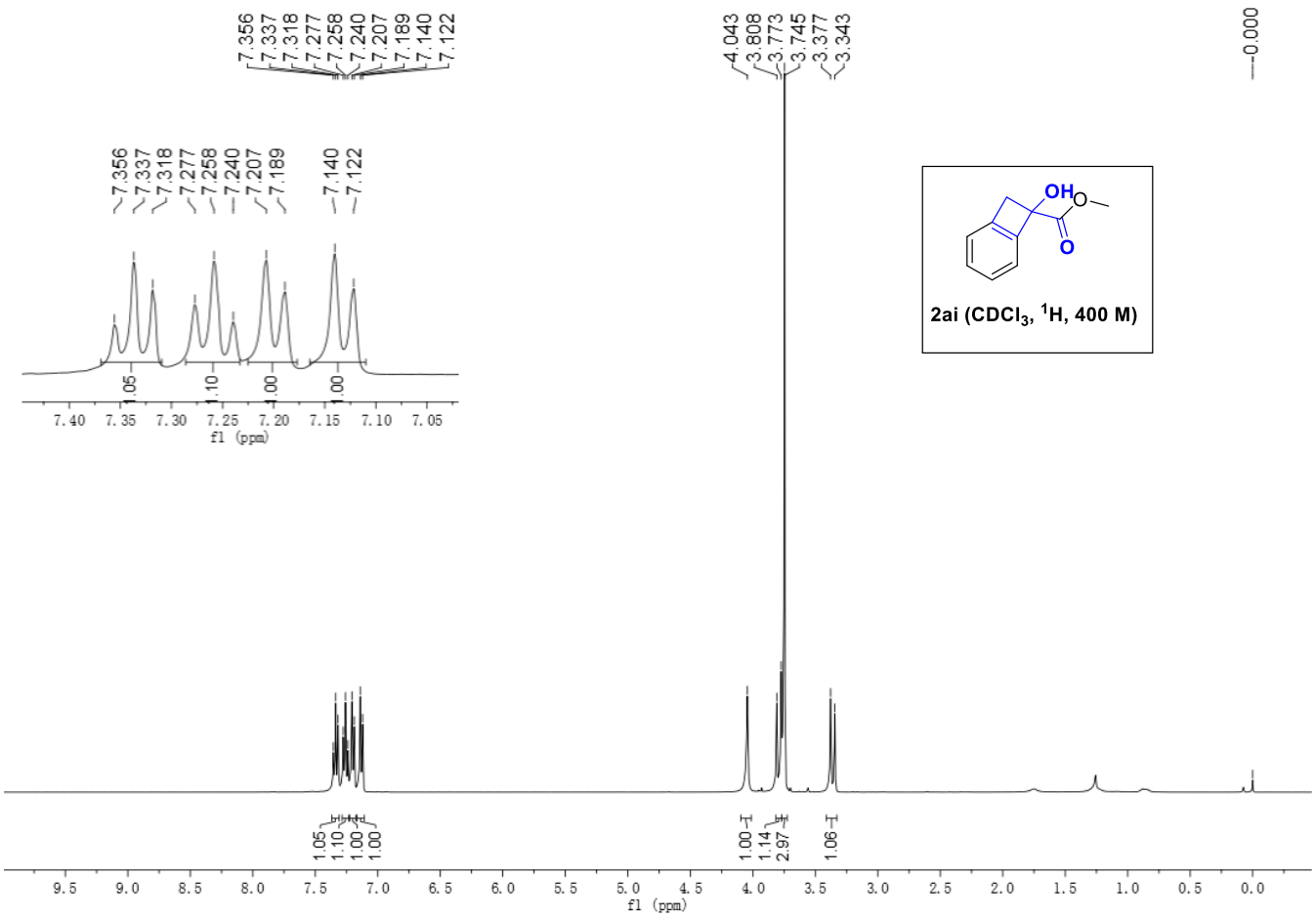

62.690
OH
OMe
O
F3C
2ag (CDCl3, 19F, 376 MHz)

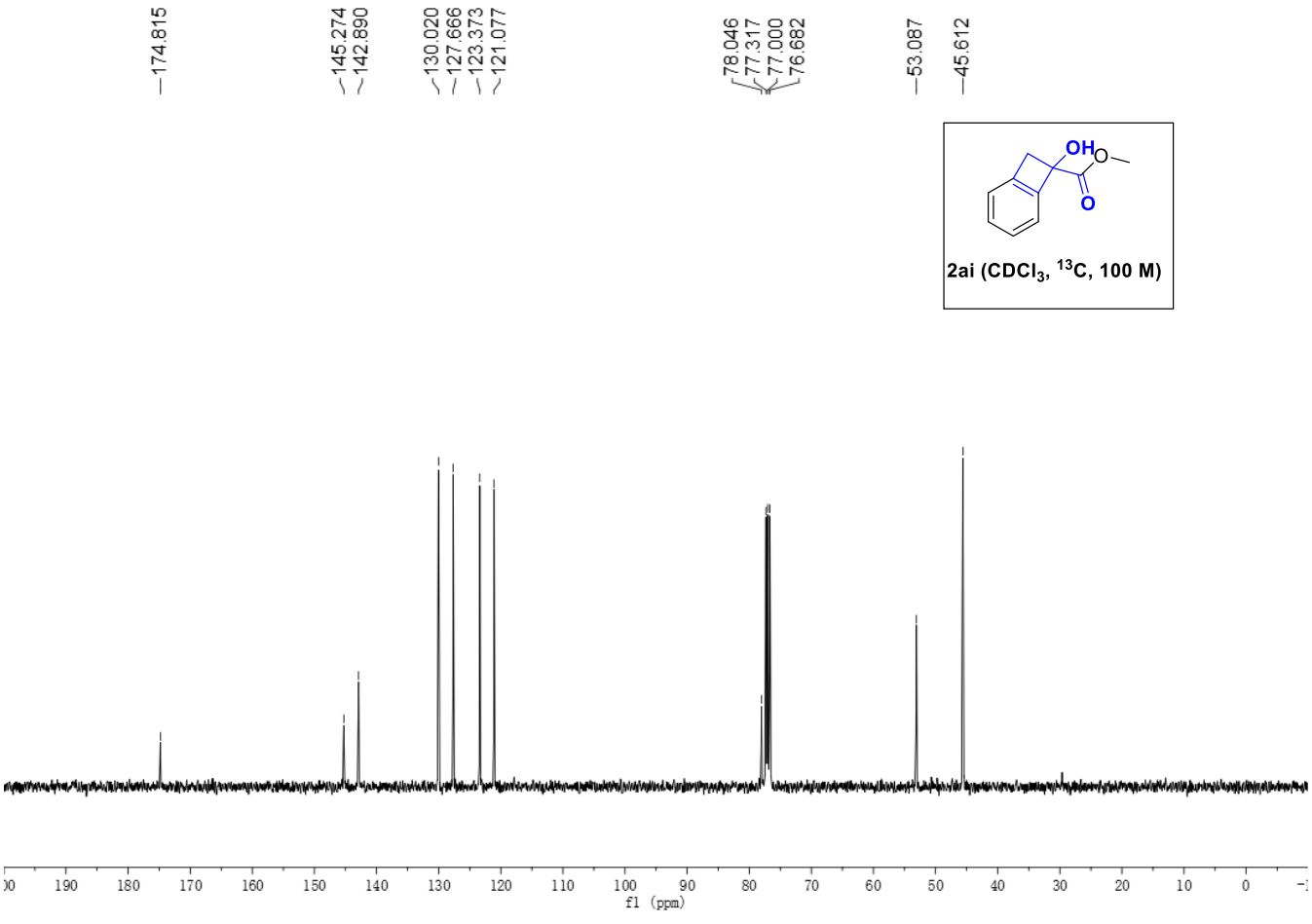

HSQC
1
11,16
12,15
4,6
3,7
9
f1 (ppm)


HMBC
1
4,6
11,16
3,7
9
10
2
8
f1 (ppm)


7.403
7.399
7.382
7.379
7.361
7.342
7.317
7.313
7.307
7.303
7.296
7.288
7.283
7.279
6.050
6.039
5.052
5.041
3.380
2.500
2.041
OH
O
2ah (DMSO-d_6, ^{1}H, 400 MHz)
5.09
1.00
1.00
3.03
f1 (ppm)


208.705
139.400
128.403
127.784
126.588
79.204
40.126
39.917
39.709
39.500
39.291
39.082
38.875
25.022
OH
O
2ah (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)


7.356
7.337
7.318
7.277
7.258
7.240
7.207
7.189
7.140
7.122
4.043
3.808
3.773
3.745
3.377
3.343
0.000
OH
O
O
2ai (CDCl3, 1H, 400 M)
f1 (ppm)


174.815
145.274
142.890
130.020
127.666
123.373
121.077
78.046
77.317
77.000
76.682
53.087
45.612
OH
O
O
2ai (CDCl3, 13C, 100 M)
f1 (ppm)