Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Gold-Catalyzed Tandem Reaction of *o*-Alkynylphenols with Diazo Compounds: Access to 2,3-Disubstituted Benzofurans

Tingzhong Huang,[a] Ying Shao,[a] Shengbiao Tang[a] and Jiangtao Sun[a,*]

Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China

E-mail: jtsun@cczu.edu.cn

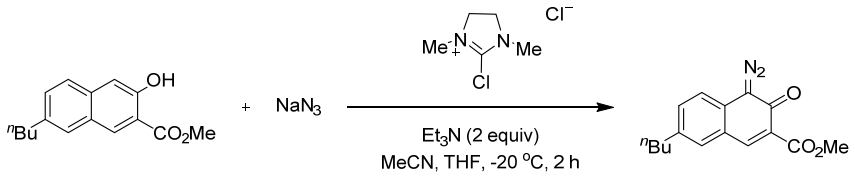
Table of Contents

General information

All of the reactions were carried out in flame-dried tube under argon atmosphere. Solvents were dried prior to use. Commercially obtained reagents were used as received. Analytical thin layer chromatography (TLC) was carried out using pre-coated (0.20 mm thickness) silica gel plates with F_{254} indicator. For column chromatography, 200-300 mesh silica gel was used. ^{1}H NMR were recorded on Bruker 500 MHz, 400 MHz, 300 MHz spectrometer in $CDCl_3$. ^{13}C NMR were recorded on Bruker 100 MHz or 75 MHz spectrometer in $CDCl_3$. ^{19}F NMR were recorded on Bruker 471 MHz, 376 MHz spectrometer in $CDCl_3$. Data for ^{1}H NMR spectra were reported relative to tetramethylsilane (TMS) as an internal standard (0 ppm), and were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets rfand m = multiplet. Data for ^{13}C NMR spectra were reported relative to $CDCl_3$ as an internal standard (77.16 ppm), and were reported in terms of chemical shift (δ ppm). High resolution mass spectra (HRMS) were performed on Agilent 6540 Q-TOF or Agilent 6230A TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus without correction.

Preparation of substrates

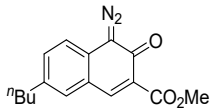
Compounds **1** were known compounds and prepared according to the literature procedures.[1]
The diazo compounds **2** were known compounds and prepared according to literature procedures.[2] **2g** is a new compound. The diazo compounds **4** were known compounds and prepared according to literature procedures.[3]



To a solution of 2-chloro-1,3-dimethylimidazolinium chloride (1.27 g, 7.5 mmol, 1.5 equiv.) in MeCN (10 mL), NaN_3 (553.0 mg, 8.5 mmol, 1.7 equiv.) was added at -20 °C, and the mixture was stirred for 30 min. Then 2-naphthol derivative (1.29 g, 5.0 mmol, 1.0 equiv.) and Et_3N (1.4 mL, 10.0 mmol, 2.0 equiv.) in THF (10 mL) were added to the mixture, which was stirred at -20 °C for 2 h. The reaction was quenched with H_2O (20 mL), and extracted with EA (50 mL). The combined organic extracts were washed with brine, dried with Na_2SO_4, filtrated, and evaporated under reduced pressure. The residue was purified by flash chromatography on a silica gel to afford corresponding

product **2g** (yellow solid, 1.13 g, 80%).

methyl 7-butyl-4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (2g)



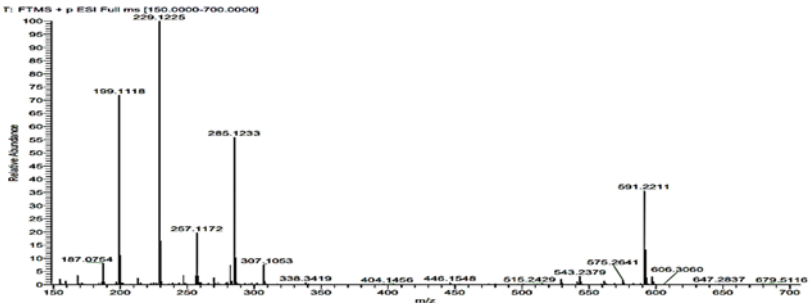
R_f = 0.2 (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.50 (s, 1H), 7.44 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.66-1.60 (m, 2H), 1.41-1.33 (m, 2H), 0.94 (t, *J* = 7.5 Hz, 3H).

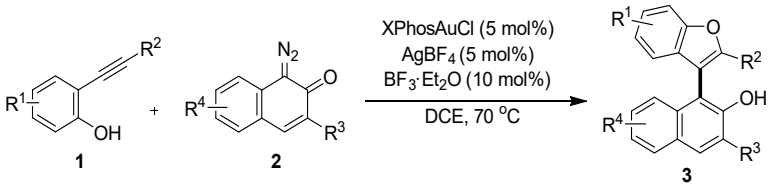
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 165.4, 145.5, 140.0, 132.8, 131.1, 126.7, 125.7, 123.8, 119.3, 79.7, 52.4, 34.9, 33.3, 22.1, 13.8.

Mp: 82-84 °C.

HRMS (ESI) calcd. For $C_{16}H_{17}N_2O_3^+$ $[M+H]^+$ m/z 285.1234, found: 285.1233.

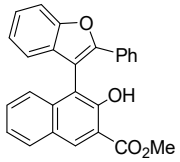


General procedure A for Scheme 2



To a flame-dried tube equipped with a stirrer was added XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%), $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) and DCE (2 mL). The mixture was stirred at rt for 10 min under argon atmosphere, then **1** (0.4 mmol, 2.0 equiv.) and **2** (0.2 mmol, 1.0 equiv.) in 2 mL of DCE was added into the reaction mixture in one portion. The reaction was stirred at 70 °C in a heating block for 1.5 h. The reaction mixture was concentrated under vacuum, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1-20:1) to give **3**.

methyl 3-hydroxy-4-(2-phenylbenzofuran-3-yl)-2-naphthoate (3a)



Prepared according to general procedure from 2-(phenylethynyl)phenol (77.6 mg, 0.4 mmol, 2.0 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 °C for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as a

yellow solid (52.8 mg, 67%).

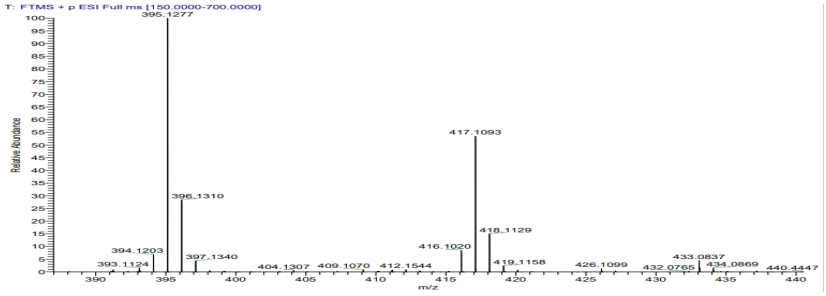
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.60 (s, 1H), 7.86-7.78 (m, 1H), 7.58-7.47 (m, 3H), 7.45-7.38 (m, 1H), 7.32-7.20 (m, 3H), 7.17-7.07 (m, 3H), 7.08-7.04 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 3.96 (s, 3H).

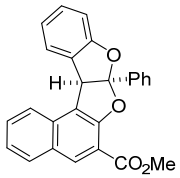
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.6, 154.3, 152.0, 136.9, 133.2, 131.0, 130.9, 129.91, 129.88, 128.64, 128.58, 128.3, 127.3, 126.0, 125.0, 124.8, 124.3, 123.0, 120.5, 114.3, 114.1, 111.4, 110.4, 52.9.

Mp: 170-172 °C.

HRMS (ESI) calcd. For $C_{26}H_{19}O_4^+$ $[M+H]^+$ m/z 395.1278, found: 395.1277.



methyl-7a-phenyl-7a,12b-dihydronaphtho[1',2':4,5]furo[2,3-b]benzofuran-6-carboxylate (3a')



Prepared according to general procedure from 2-(phenylethynyl)phenol (77.6 mg, 0.4 mmol, 2.0 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%) and $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) in 4 mL DCE at 70 °C for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as a white solid (17.3 mg, 22%).

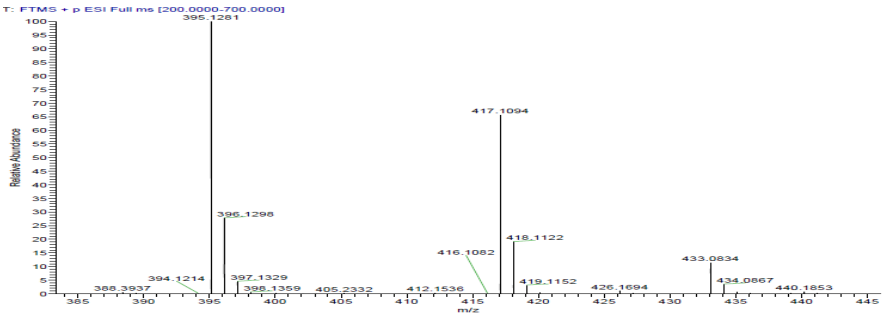
R_f = 0.3 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.05-7.99 (m, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.71-7.60 (m, 3H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.46-7.36 (m, 4H), 7.22 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.93 (td, *J* = 7.6, 0.8 Hz, 1H), 5.42 (s, 1H), 3.99 (s, 3H).

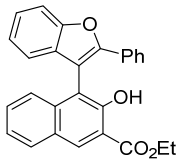
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 158.3, 154.5, 139.3, 133.6, 132.2, 130.5, 129.6, 129.4, 129.2, 128.7, 127.1, 125.2, 124.9, 124.4, 123.0, 122.8, 122.1, 121.5, 115.3, 110.8, 56.7, 52.5.

Mp: 192-194 °C.

HRMS (ESI) calcd. For $C_{26}H_{19}O_4^+$ $[M+H]^+$ m/z 395.1278, found: 395.1281.



ethyl 3-hydroxy-4-(2-phenylbenzofuran-3-yl)-2-naphthoate (3b)



Prepared according to general procedure from 2-(phenylethynyl)phenol (77.6 mg, 0.4 mmol, 2.0 equiv.), ethyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (48.4 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (44.1 mg, 54%).

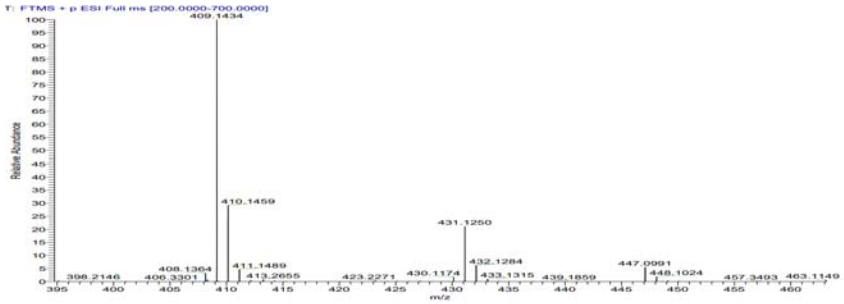
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.87 (s, 1H), 8.74-8.63 (m, 1H), 8.02-7.87 (m, 1H), 7.69-7.56 (m, 3H), 7.51-7.49 (m, 1H), 7.38-7.27 (m, 3H), 7.20-7.16 (m, 3H), 7.14 (td, *J* = 7.6, 1,2 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 4.50 (q, *J* = 7.2 Hz, 2H), 1.50 (t, *J* = 7.2 Hz, 3H).

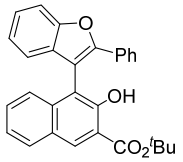
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 154.7, 154.3, 152.0, 136.8, 133.1, 131.0, 130.9, 129.84, 129.75, 128.5, 128.3, 127.2, 126.0, 124.9, 124.7, 124.2, 122.9, 120.5, 114.5, 114.0, 111.3, 110.4, 62.1, 14.4.

Mp: 123-125 ºC.

HRMS (ESI) calcd. For $C_{27}H_{21}O_4^+$ $[M+H]^+$ m/z 409.1434, found: 409.1434.



tert-butyl 3-hydroxy-4-(2-phenylbenzofuran-3-yl)-2-naphthoate (3c)



Prepared according to general procedure from 2-(phenylethynyl)phenol (77.6 mg, 0.4 mmol, 2.0 equiv.), tert-butyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (54.1 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (57.6 mg, 66%).

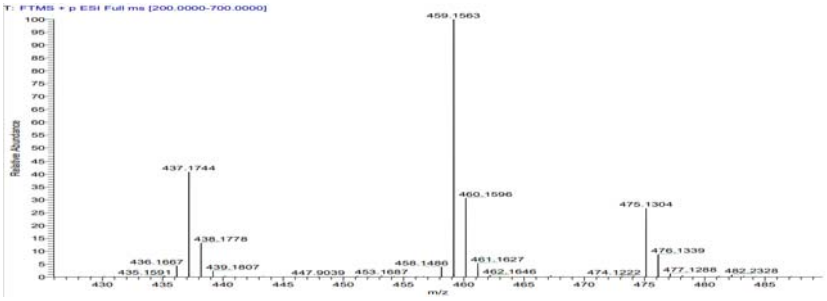
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 8.59 (s, 1H), 8.00-7.85 (m, 1H), 7.66-7.56 (m, 3H), 7.52-7.43 (m, 1H), 7.37-7.29 (m, 3H), 7.23-7.16 (m, 3H), 7.16-7.11 (m, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 1.70 (s, 9H).

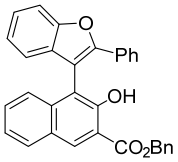
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 155.1, 154.3, 152.0, 136.7, 133.1, 131.1, 131.0, 129.8, 129.6, 128.6, 128.2, 127.2, 126.0, 124.9, 124.7, 124.1, 122.9, 120.5, 115.8, 113.9, 111.4, 110.6, 83.8, 28.4.

Mp: 182-184 ºC.

HRMS (ESI) calcd. For $C_{29}H_{25}O_4^+$ $[M+H]^+$ m/z 437.1747, found: 437.1744.



benzyl 3-hydroxy-4-(2-phenylbenzofuran-3-yl)-2-naphthoate (3d)



Prepared according to general procedure from 2-(phenylethynyl)phenol (77.6 mg, 0.4 mmol, 2 equiv.), benzyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (60.8 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (38.5 mg, 41%).

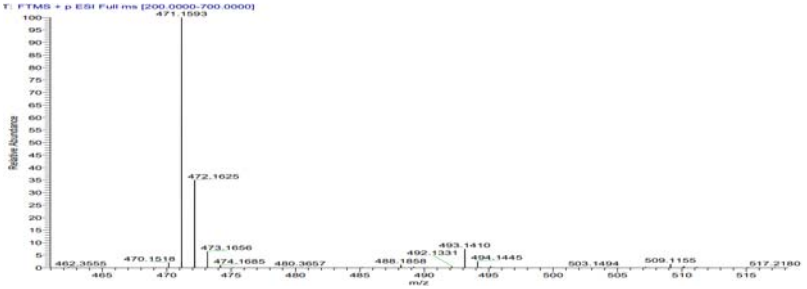
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 8.70 (s, 1H), 7.93-7.86 (m, 1H), 7.63 (d, *J* = 8.0 Hz，1H), 7.60-7.56 (m, 2H), 7.56-7.51 (m, 2H), 7.38-7.36 (m, 4H), 7.36-7.30 (m, 3H), 7.21-7.17 (m, 3 H), 7.14 (td, *J* = 7.6, 1.2 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 5.48 (s, 2H).

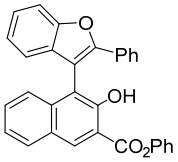
^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 154.7, 154.3, 152.1, 137.0, 135.2, 133.3, 131.0, 130.9, 129.93, 128.97, 128.93, 128.8, 128.6, 128.3, 127.3, 126.0, 125.1, 125.0, 124.8, 124.3, 123.0, 120.5, 114.3, 114.2, 111.4, 110.4, 67.7.

Mp: 87-89 ºC.

HRMS (ESI) calcd. For $C_{32}H_{23}O_4^+$ $[M+H]^+$ m/z 471.1591, found: 471.1593.



phenyl 3-hydroxy-4-(2-phenylbenzofuran-3-yl)-2-naphthoate (3e)



Prepared according to general procedure from 2-(phenylethynyl)phenol (77.6 mg, 0.4 mmol, 2.0 equiv.), phenyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (58.1 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (50.2 mg, 55%).

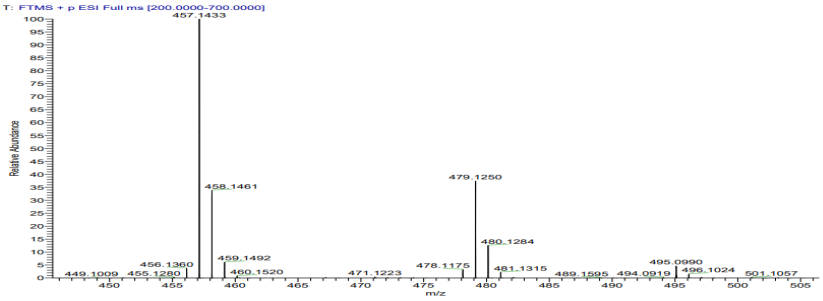
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 8.94 (s, 1H), 8.01-7.93 (m, 1H), 7.66-7.57 (m, 3H), 7.56-7.51 (m, 1H), 7.51-7.44 (m, 2H), 7.42-7.26 (m, 6H), 7.23-7.18 (m, 3H), 7.18-7.13 (m, 1H), 7.12-7.07 (d, *J* = 7.6 Hz, 1H).

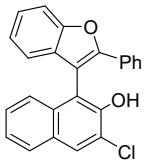
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 154.7, 154.2, 152.0, 150.2, 137.2, 133.9, 130.9, 130.8, 130.2, 130.0, 129.8, 128.5, 128.3, 127.3, 126.7, 126.0, 125.0, 124.7, 124.5, 122.9, 121.7, 120.4, 114.5, 113.7, 111.3, 110.1.

Mp: 84-86 ºC.

HRMS (ESI) calcd. For $C_{31}H_{21}O_4^+$ $[M+H]^+$ m/z 457.1434, found: 457.1433.



3-chloro-1-(2-phenylbenzofuran-3-yl)naphthalen-2-ol (3f)



Prepared according to general procedure from 2-(phenylethynyl)phenol (77.6 mg, 0.4 mmol, 2.0 equiv.), 3-chloro-1-diazonaphthalen-2(1*H*)-one (40.9 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as white solid (52.6 mg, 71%).

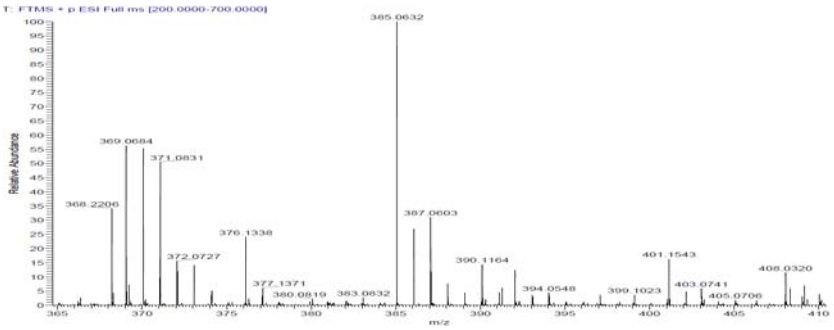
R_f = 0.3 (petroleum ether/ethyl acetate = 50:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.83-7.76 (m, 1H), 7.69-7.61 (m, 1H), 7.61-7.52 (m, 2H), 7.47 (d, J = 8.4 Hz, 1H), 7.41-7.32 (m, 2H), 7.30-7.26 (m, 1H), 7.25-7.21 (m, 3H), 7.17 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 5.69 (s, 1H).

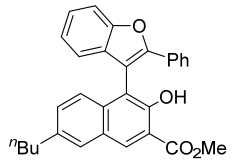
^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 152.7, 147.4, 132.1, 130.15, 130.1, 129.14, 129.1, 128.9, 128.8, 127.5, 127.3, 125.9, 125.3, 125.0, 124.8, 123.3, 122.2, 120.4, 113.3, 111.4, 108.8.

Mp: 126-128 ºC.

HRMS (ESI) calcd. For $C_{24}H_{16}ClO_2^+$ $[M+H]^+$ m/z 371.0833, found: 371.0831.



methyl 7-butyl-3-hydroxy-4-(2-phenylbenzofuran-3-yl)-2-naphthoate (3g)



Prepared according to general procedure from 2-(phenylethynyl)phenol (77.6 mg, 0.4 mmol, 2.0 equiv.), methyl 7-butyl-4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (56.8 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (60.3 mg, 67%).

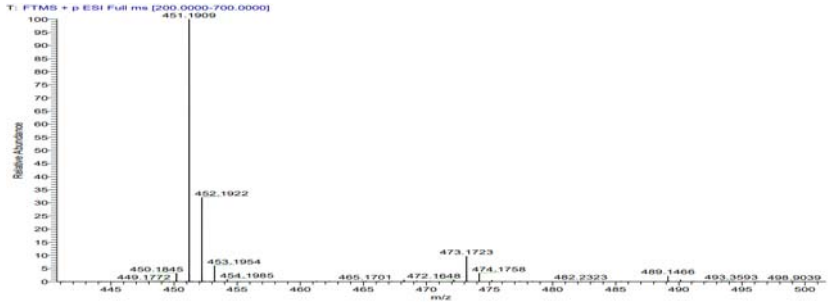
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.60 (s, 1H), 8.52 (s, 1H), 7.58 (s, 1H), 7.56-7.49 (m, 3H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.27-7.19 (m, 1H), 7.16-7.08 (m, 4H), 7.08-7.02 (m, 1H), 7.01-6.95 (m, 1H), 3.94 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.62-1.48 (m, 2H), 1.36-1.22 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H).

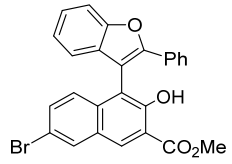
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.2, 154.0, 151.9, 138.7, 135.3, 132.5, 131.6, 131.0, 130.9, 128.5, 128.2, 127.9, 127.4, 125.9, 124.8, 124.6, 122.8, 120.4, 114.1, 113.9, 111.2, 110.5, 52.8, 35.3, 33.2, 22.4, 14.0.

Mp: 178-170 ºC.

HRMS (ESI) calcd. For $C_{30}H_{27}O_4^+$ $[M+H]^+$ m/z 451.1904, found: 451.1909.



methyl 7-bromo-3-hydroxy-4-(2-phenylbenzofuran-3-yl)-2-naphthoate (3h)



Prepared according to general procedure from 2-(phenylethynyl)phenol (77.6 mg, 0.4 mmol, 2.0 equiv.), methyl 7-bromo-4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (61.4 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and

$BF_3 \cdot Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (49.1 mg, 52%).

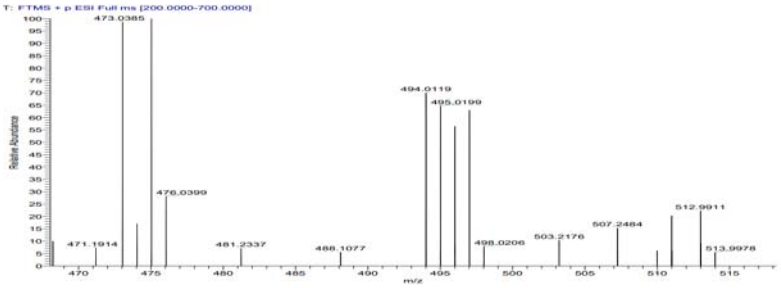
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.56 (s, 1H), 8.04 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.58-7.53 (m, 2H), 7.38 (m, 2H), 7.35-7.29 (m, 1H), 7.23-7.17 (m, 3H), 7.14 (td, *J* = 7.6, 0.8 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 4.02 (s, 3H).

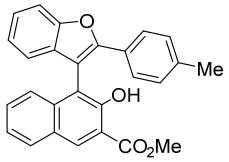
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 154.9, 154.2, 152.1, 135.2, 132.9, 132.0, 131.5, 130.8, 130.6, 128.6, 128.4, 128.2, 126.8, 125.9, 124.9, 123.0, 120.3, 118.0, 115.2, 114.7, 111.4, 109.8, 53.0.

Mp: 168-170 ºC.

HRMS (ESI) calcd. For $C_{26}H_{18}BrO_4^+$ $[M+H]^+$ m/z 473.0383, found: 473.0385.



methyl 3-hydroxy-4-(2-(p-tolyl)benzofuran-3-yl)-2-naphthoate (3i)



Prepared according to general procedure from 2-(*p*-tolylethynyl)phenol(83.2 mg, 0.4 mmol, 2.0 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3 \cdot Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (41.6 mg, 51%).

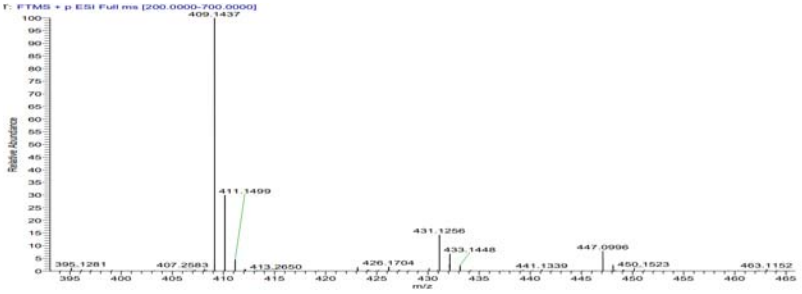
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 8.67 (s, 1H), 7.95-7.87 (m, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.53-7.43 (m, 3H), 7.39-7.26 (m, 3H), 7.17-7.09 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.04 (s, 3H), 2.25 (s, 3H).

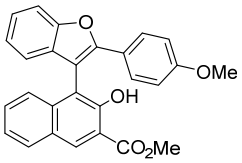
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 154.5, 154.1, 152.2, 138.2, 136.9, 133.1, 130.9, 129.8, 129.7, 129.2, 128.2, 127.2, 125.8, 125.0, 124.4, 124.2, 122.8, 120.2, 114.2, 111.2, 109.5, 52.8, 21.3.

Mp: 149-151 ºC.

HRMS (ESI) calcd. For $C_{27}H_{21}O_4^+$ $[M+H]^+$ m/z 409.1434, found: 409.1437.



methyl 3-hydroxy-4-(2-(4-methoxyphenyl)benzofuran-3-yl)-2-naphthoate (3j)



Prepared according to general procedure from 2-((4-methoxyphenyl)ethynyl)phenol (89.6 mg, 0.4 mmol, 2.0 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (45.8 mg, 54%).

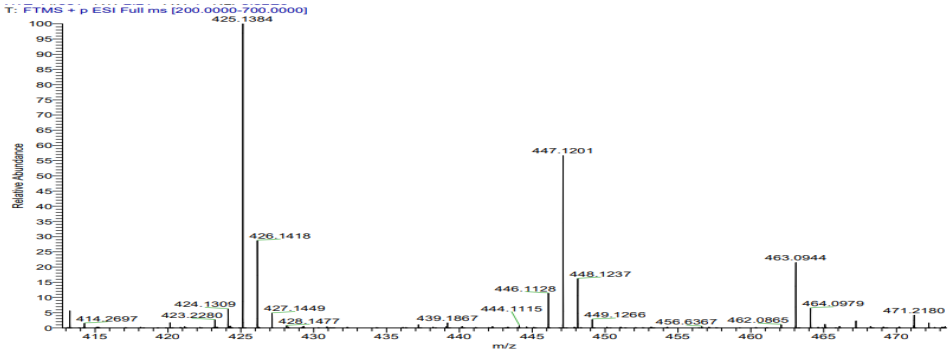
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 8.68 (s, 1H), 7.95-7.87 (m, 1H), 7.63-7.56 (m, 1H), 7.56-7.47 (m, 3H), 7.41-7.32 (m, 2H), 7.34-7.25 (m, 1H), 7.20-7.09 (m, 1H), 7.07-7.00 (m, 1H), 6.77-6.69 (m, 2H), 4.06 (s, 3H), 3.73 (s, 3H).

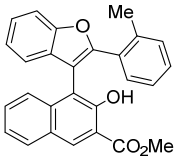
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 159.7, 154.7, 154.2, 152.2, 137.0, 133.1, 131.1, 129.9, 129.8, 127.5, 127.3, 125.1, 124.3, 124.29, 123.9, 122.9, 120.2, 114.4, 114.3, 114.1, 111.2, 108.7, 55.3, 52.9.

Mp: 208-210 ºC.

HRMS (ESI) calcd. For $C_{27}H_{21}O_5^+$ $[M+H]^+$ m/z 425.1384, found: 425.1384.



methyl 3-hydroxy-4-(2-(o-tolyl)benzofuran-3-yl)-2-naphthoate (3k)



Prepared according to general procedure from 2-(*o*-tolylethynyl)phenol (83.2 mg, 0.4 mmol, 2.0 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (45.7 mg, 56%).

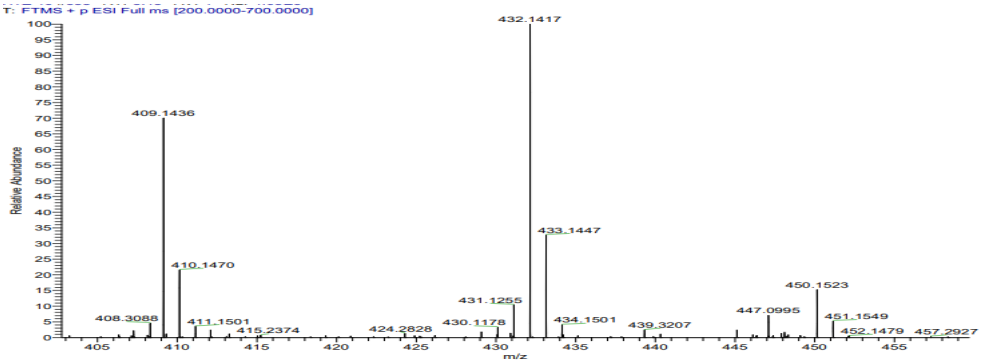
R_f = 0.3 (petroleum ether/ethyl acetate = 40:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.54 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.38-7.30 (m, 2H), 7.30-7.23 (m, 2H), 7.21-7.09 (m, 4H), 6.99-6.90 (m, 1H), 3.97 (s, 3H), 2.39 (s, 3H).

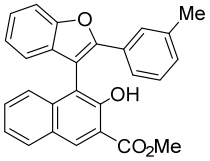
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.73, 154.72, 154.7, 137.8, 137.1, 132.9, 130.6, 130.5, 130.09, 130.06, 129.7, 129.4, 128.9, 127.0, 125.4, 124.9, 124.3, 123.9, 122.7, 120.6, 114.0, 113.9, 111.7, 111.4, 52.8, 20.6.

Mp: 90-92 ºC.

HRMS (ESI) calcd. For $C_{27}H_{21}O_4^+$ $[M+H]^+$ m/z 409.1434, found: 409.1436.



methyl 3-hydroxy-4-(2-(m-tolyl)benzofuran-3-yl)-2-naphthoate (3l)



Prepared according to general procedure from 2-(*m*-tolylethynyl)phenol (83.2 mg, 0.4 mmol, 2.0 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (44.1 mg, 54%).

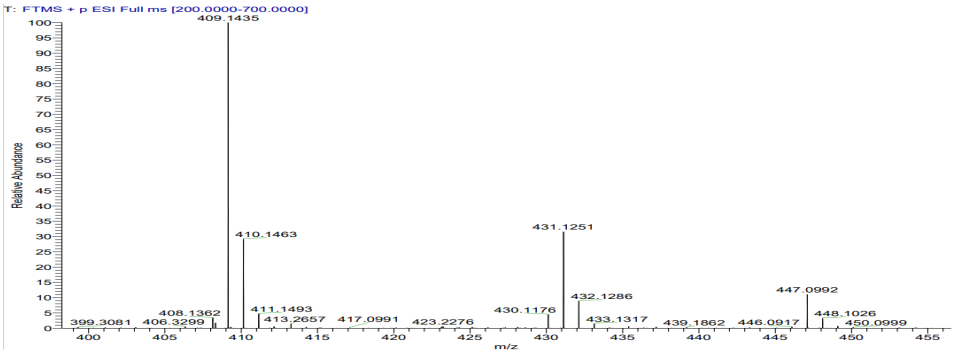
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.76 (s, 1H), 8.67 (s, 1H), 7.93-7.86 (m, 1H), 7.64-7.58 (m, 1H), 7.57-7.54 (m, 1H), 7.53-7.44 (m, 1H), 7.41-7.27 (m, 3H), 7.26-7.20 (m, 1H), 7.16-7.09 (m, 1H), 7.09-7.04 (m, 1H), 7.04-6.97 (m, 2H), 4.04 (s, 3H), 2.23 (s, 3H).

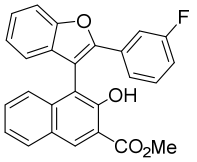
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.5, 154.2, 152.2, 138.3, 138.0, 136.9, 133.1, 130.9, 130.8, 129.8, 129.7, 129.1, 128.4, 127.2, 126.6, 125.0, 124.6, 124.2, 123.1, 122.8, 120.4, 114.2, 111.3, 110.2, 52.8, 21.5.

Mp: 154-156 ºC.

HRMS (ESI) calcd. For $C_{27}H_{21}O_4^+$ $[M+H]^+$ m/z 409.1434, found: 409.1435.



methyl 4-(2-(3-fluorophenyl)benzofuran-3-yl)-3-hydroxy-2-naphthoate (3m)



Prepared according to general procedure from 2-((3-fluorophenyl)ethynyl)phenol (84.9 mg, 0.4 mmol, 2 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (34.6 mg, 42%).

R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

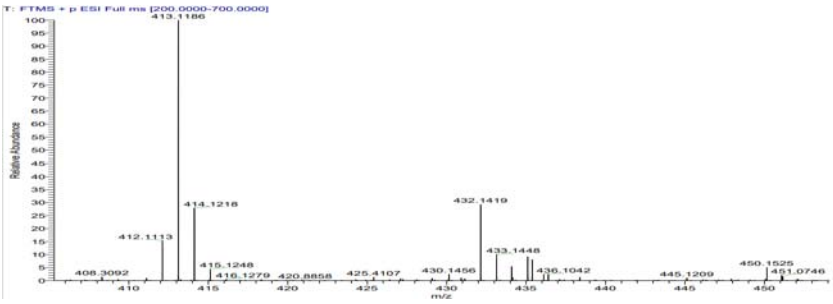
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.69 (s, 1H), 7.96-7.86 (m, 1H), 7.68-7.58 (m, 1H), 7.52-7.43 (m, 1H), 7.41-7.26 (m, 5H), 7.19-7.10 (m, 2H), 7.10-7.04 (m, 1H), 6.92-6.84 (m, 1H), 4.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 162.9 (d, *J* = 243.3 Hz), 154.6, 154.3, 150.7 (d, *J* = 3.2 Hz), 136.8, 133.5, 133.1 (d, *J* = 8.5 Hz), 130.7, 130.2 (d, *J* = 8.3 Hz), 130.0, 127.3, 125.2, 124.8, 124.4, 123.1, 121.6 (d, *J* = 2.9 Hz), 120.7, 115.3, 115.0, 114.3, 113.6, 112.9, 112.7, 111.5, 111.4, 53.0.

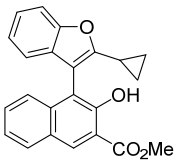
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.8.

Mp: 190-192 ºC.

HRMS (ESI) calcd. For $C_{26}H_{18}FO_4^+$ $[M+H]^+$ m/z 413.1184, found: 413.1186.



methyl 4-(2-cyclopropylbenzofuran-3-yl)-3-hydroxy-2-naphthoate (3n)



Prepared according to general procedure from 2-(cyclopropylethynyl)phenol (63.3 mg, 0.4 mmol, 2 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (35.8 mg, 50%).

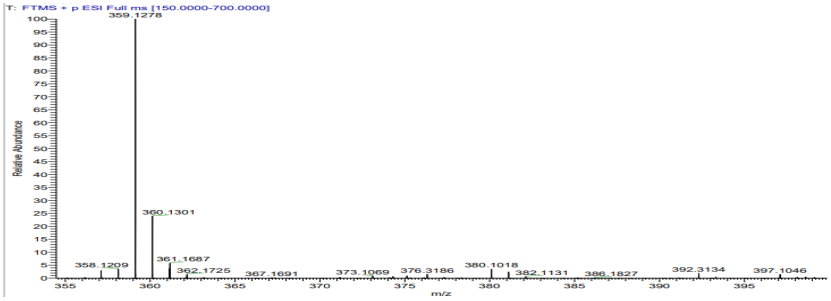
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 8.54 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.40-7.32 (m, 2H), 7.27 (m, 1H), 7.17-7.08 (m, 1H), 7.07-6.96 (m, 2H), 3.96 (s, 3H), 1.69 (m, 1H), 1.13-1.05 (m, 1H), 1.05-0.96 (m, 1H), 0.79 (m, 2H).

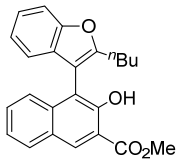
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 157.1, 154.7, 153.8, 137.3, 132.7, 130.3, 129.9, 129.4, 127.2, 125.5, 124.0, 123.2, 122.5, 119.8, 114.1, 113.8, 110.9, 109.1, 52.9, 9.2, 7.4, 7.3.

Mp: 149-151 ºC.

HRMS (ESI) calcd. For $C_{23}H_{19}O_4^+$ $[M+H]^+$ m/z 359.1278, found: 359.1278.



methyl 4-(2-butylbenzofuran-3-yl)-3-hydroxy-2-naphthoate(3o)



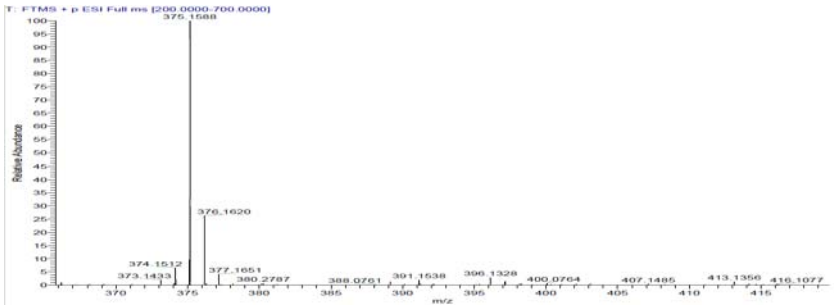
Prepared according to general procedure from 2-(hex-1-yn-1-yl)phenol (69.6 mg, 0.4 mmol, 2 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow oil (40.6 mg, 57%).

R_f = 0.5 (petroleum ether/ethyl acetate = 30:1)

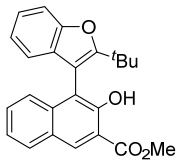
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.62 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.24-7.22 (m, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.6 Hz, 1H), 4.05 (s, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.94-1.55 (m, 2H), 1.35-1.12 (m, 2H), 0.78 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 157.5, 154.5, 154.4, 137.2, 132.7, 129.9, 129.8, 129.3, 127.0, 125.2, 124.0, 123.3, 122.4, 120.0, 114.0, 113.8, 111.0, 109.4, 52.8, 29.7, 27.2, 22.4, 13.8.

HRMS (ESI) calcd. For $C_{24}H_{23}O_4^+$ $[M+H]^+$ m/z 375.1591, found: 375.1588.



methyl 4-(2-(tert-butyl)benzofuran-3-yl)-3-hydroxy-2-naphthoate(3p)



Prepared according to general procedure from 2-(3,3-dimethylbut-1-yn-1-yl)phenol (69.6 mg, 0.4 mmol, 2 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (38.2 mg, 51%).

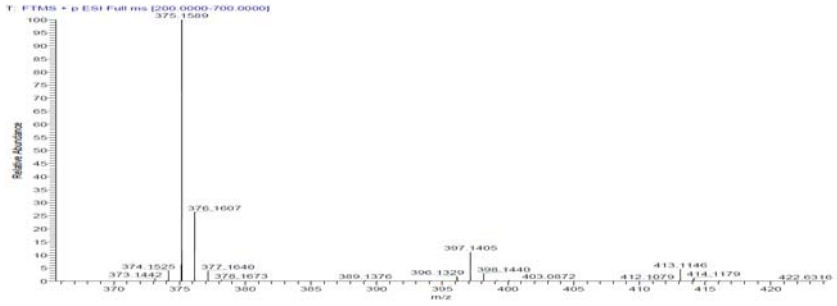
R_f = 0.5 (petroleum ether/ethyl acetate = 30:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.74 (s, 1H), 8.57 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.47 (s, 1H), 7.43-7.36 (m, 1H), 7.36-7.29 (m, 1H), 7.19 (dd, *J* = 8.0, 1.3 Hz, 1H), 6.43 (d, *J* = 0.8 Hz, 1H), 4.05 (s, 3H), 1.40 (s, 9H).

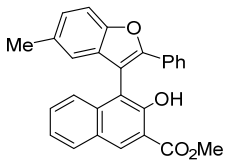
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 168.0, 154.9, 153.3, 137.3, 132.1, 130.4, 129.6, 129.2, 128.5, 127.0, 125.3, 124.3, 123.9, 120.4, 113.9, 113.2, 99.1, 52.9, 33.2, 29.0.

Mp: 79-81 ºC.

HRMS (ESI) calcd. For $C_{24}H_{23}O_4^+$ $[M+H]^+$ m/z 375.1591, found: 375.1589.



methyl 3-hydroxy-4-(5-methyl-2-phenylbenzofuran-3-yl)-2-naphthoate (3q)



Prepared according to general procedure from 4-methyl-2-(phenylethynyl)phenol (83.2 mg, 0.4 mmol, 2 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (45.7 mg, 56%).

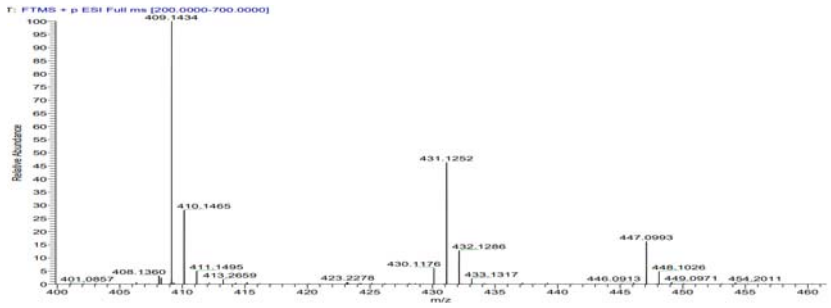
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.69 (s, 1H), 8.55 (s, 1H), 7.86-7.75 (m, 1H), 7.68-7.59 (m, 1H), 7.57-7.51 (m, 1H), 7.38-7.30 (m, 2H), 7.30-7.25 (m, 2H), 7.22-7.07 (m, 4H), 7.01-6.90 (m, 1H), 4.00 (s, 3H), 2.39 (s, 3H).

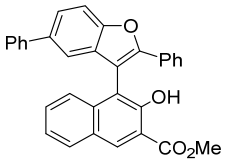
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 154.69, 154.67, 137.8, 137.0, 132.8, 130.5, 130.47, 130.1, 130.0, 129.7, 129.3, 128.9, 127.0, 125.4, 124.9, 124.2, 123.9, 122.7, 120.6, 114.0, 113.9, 111.7, 111.4, 52.7, 20.5.

Mp: 105-107 ºC.

HRMS (ESI) calcd. For $C_{27}H_{21}O_4^+$ $[M+H]^+$ m/z 409.1434, found: 409.1434.



methyl 4-(2,5-diphenylbenzofuran-3-yl)-3-hydroxy-2-naphthoate (3r)



Prepared according to general procedure from 3-(phenylethynyl)-[1,1'-biphenyl]-4-ol (108.0 mg, 0.4 mmol, 2 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (62.0 mg, 66%).

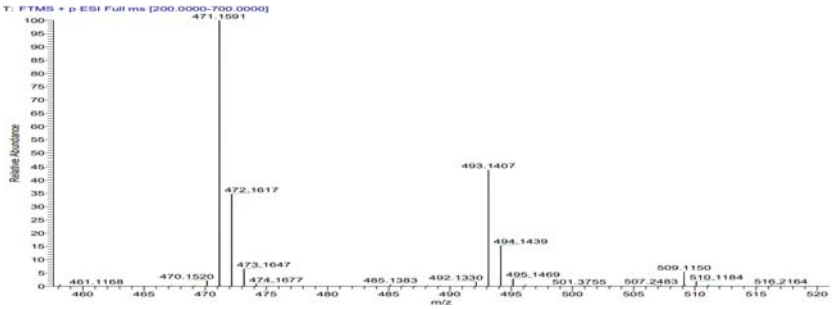
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.70 (s, 1H), 7.97-7.88 (m, 1H), 7.71-7.66 (m, 1H), 7.62-7.51 (m, 4H), 7.51-7.46 (m, 2H), 7.40-7.30 (m, 4H), 7.28-7.18 (m, 5H), 4.06 (s, 3H).

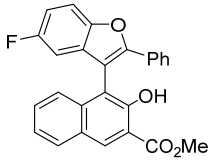
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 154.6, 153.9, 152.6, 141.7, 136.8, 136.7, 133.2, 131.3, 130.9, 129.9, 129.8, 128.6, 128.5, 128.3, 127.5, 127.2, 126.8, 125.9, 124.9, 124.4, 124.3, 118.8, 114.3, 113.9, 111.4, 110.5, 52.9.

Mp: 98-100 ºC.

HRMS (ESI) calcd. For $C_{32}H_{23}O_4^+$ $[M+H]^+$ m/z 471.1591, found: 471.1591.



methyl 4-(5-fluoro-2-phenylbenzofuran-3-yl)-3-hydroxy-2-naphthoate (3s)



Prepared according to general procedure from 4-fluoro-2-(phenylethynyl)phenol (84.8 mg, 0.4 mmol, 2 equiv.), methyl 4-diazo-3-oxo-3,4-dihydronaphthalene-2-carboxylate (45.6 mg, 0.2 mmol, 1.0 equiv.), XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified

by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as yellow solid (29.6 mg, 36%).

R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

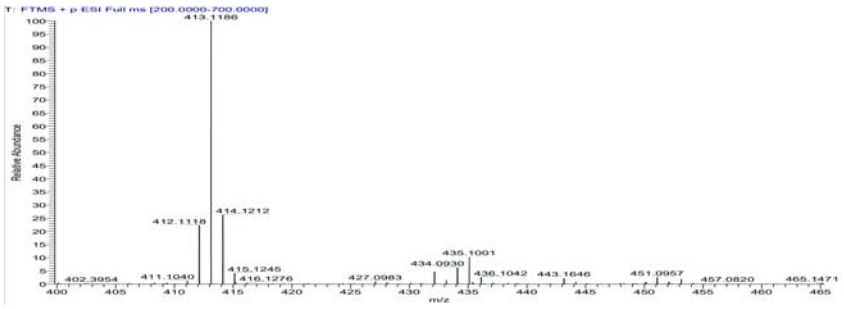
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.69 (s, 1H), 7.99-7.83 (m, 1H), 7.62-7.51 (m, 3H), 7.50-7.43 (m, 1H), 7.42-7.31 (m, 2H), 7.24-7.17 (m, 3H), 7.08-6.99 (m, 1H), 6.76-6.68 (m, 1H), 4.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 159.5 (d, *J* = 237.1 Hz), 154.6, 153.8, 150.4, 136.6, 133.4, 131.8 (d, *J* = 10.4 Hz), 130.6, 129.9 (d, *J* = 3.2 Hz), 128.5, 127.2, 126.0, 124.7, 124.3, 114.2, 113.4, 112.5, 112.2, 111.9 (d, *J* = 9.4 Hz), 110.5 (d, *J* = 4.1 Hz), 106.0, 105.8, 52.9.

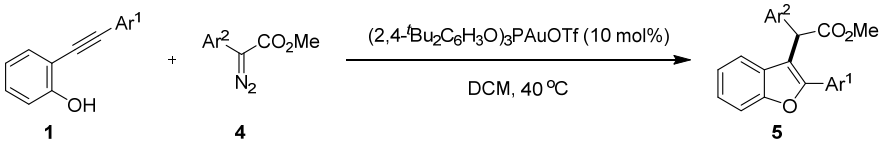
^{19}F NMR (376 MHz, $CDCl_3$) δ -120.7.

Mp: 199-201 °C.

HRMS (ESI) calcd. For $C_{26}H_{18}FO_4^+$ $[M+H]^+$ m/z 413.1184, found: 413.1186.

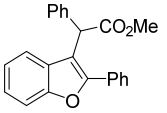


General procedure B for Scheme 3



To a dry tube was added (2,4-^{t}Bu$_2$C$_6$H$_3$O)$_3$PAuOTf (19.9 mg, 0.02 mmol, 10 mol%), **1** (0.2 mmol, 1.0 equiv.) and DCM (2 mL). Then a solution of **4** (0.24 mmol, 1.2 equiv.) in DCM (2 mL) was added via a syringe pump over 2 h under argon atmosphere. The reaction mixture was stirred at 40 °C in a heating block for 1 h. The reaction mixture was concentrated. The residue was purified by silica gel chromatography (eluent: EtOAc/Petroleum ether = 1:30-1:10) to give desired product.

methyl 2-phenyl-2-(2-phenylbenzofuran-3-yl)acetate (5a)



Prepared according to general procedure from 2-(phenylethynyl)phenol (38.8 mg, 0.2 mmol, 1.0 equiv.), methyl 2-diazo-2-phenylacetate (42.2 mg, 0.24 mmol, 1.2 equiv.), (2,4-^{t}Bu$_2$C$_6$H$_3$O)$_3$PAuOTf (19.9 mg, 0.02 mmol, 10 mol%) in 4 mL DCM at 40 °C for 3 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as white solid (48.6 mg, 71%).

R_f = 0.5 (petroleum ether/ethyl acetate = 10:1)

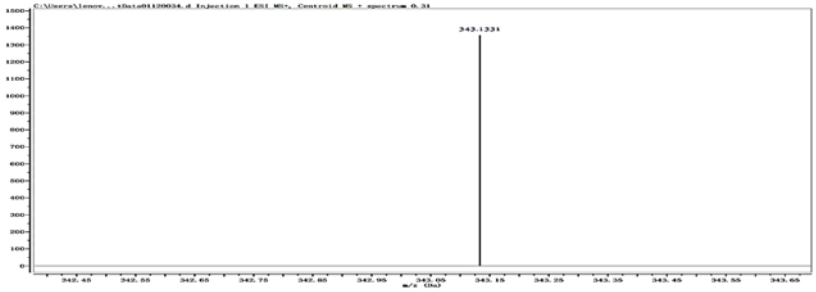
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.66 (m, 2H), 7.54-7.36 (m, 5H), 7.34-7.21 (m, 6H), 7.21-7.13

(m, 1H), 5.51 (s, 1H), 3.71 (s, 3H).

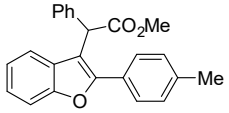
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 154.4, 153.6, 137.3, 130.3, 129.1, 128.9, 128.7, 128.6, 128.3, 128.1, 127.4, 124.6, 122.9, 122.0, 112.5, 111.3, 52.5, 47.8.

Mp: 128-130 ºC.

HRMS (ESI) calcd. For $C_{23}H_{19}O_3^+$ $[M+H]^+$ m/z 343.1329, found: 343.1331.



methyl 2-phenyl-2-(2-(p-tolyl)benzofuran-3-yl)acetate (5b)



Prepared according to general procedure from 2-(*p*-tolylethynyl)phenol (41.6 mg, 0.2 mmol, 1.0 equiv.), methyl 2-diazo-2-phenylacetate (42.2 mg, 0.24 mmol, 1.2 equiv.), (2,4-^{t}Bu$_2$C$_6$H$_3$O)$_3$PAuOTf (19.9 mg, 0.02 mmol, 10 mol%) in 4 mL DCM at 40 ºC for 3 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as a white solid (42.7 mg, 60%).

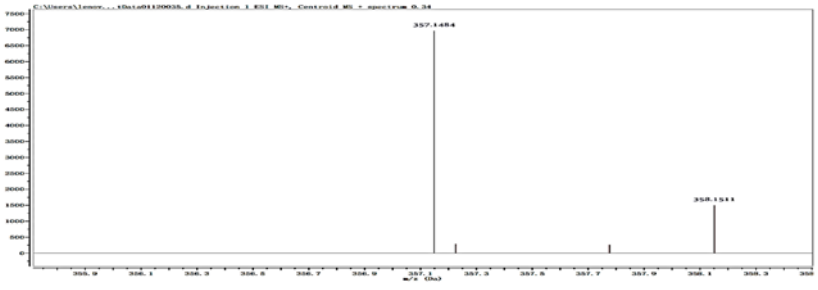
R_f = 0.3 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.31-7.19 (m, 8H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.47 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H).

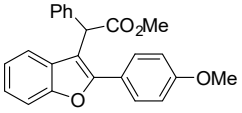
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 154.4, 153.9, 139.2, 137.4, 129.6, 128.69, 128.66, 128.3, 128.0, 127.42, 127.37, 124.4, 122.9, 121.9, 111.9, 111.3, 52.5, 47.9, 21.5.

Mp: 133-135 ºC.

HRMS (ESI) calcd. For $C_{24}H_{21}O_3^+$ $[M+H]^+$ m/z 357.1485, found: 357.1484.



methyl 2-(2-(4-methoxyphenyl)benzofuran-3-yl)-2-phenylacetate (5c)



Prepared according to general procedure from 2-((4-methoxyphenyl)ethynyl)phenol (44.8 mg, 0.2 mmol, 1.0 equiv.), methyl 2-diazo-2-phenylacetate (42.2 mg, 0.24 mmol, 1.2 equiv.), (2,4-

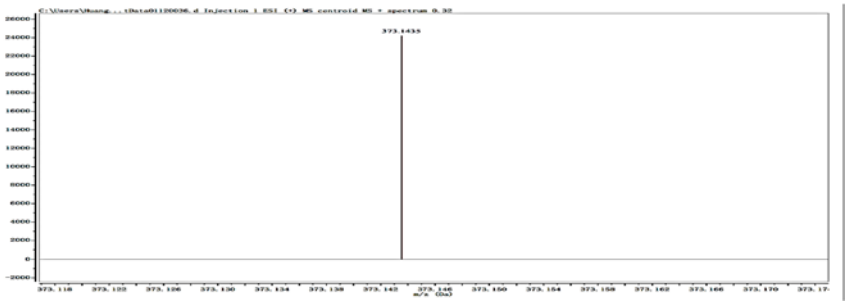
$^{t}Bu_2C_6H_3O)_3PAuOTf$ (19.9 mg, 0.02 mmol, 10 mol%) in 4 mL DCM at 40 ºC for 3 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as a colorless oil (40.9 mg, 55%).

R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

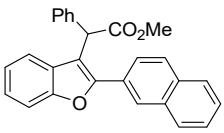
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.51-7.46 (m, 2H), 7.33-7.21 (m, 6H), 7.19-7.12 (m, 1H), 6.97 (d, *J* = 7.6 Hz, 2H), 5.47 (s, 1H), 3.79 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 160.3, 154.3, 153.8, 137.4, 129.5, 128.73, 128.65, 128.3, 127.4, 124.2, 122.82, 122.75, 121.7, 114.3, 111.3, 111.2, 55.4, 52.5, 47.9.

HRMS (ESI) calcd. For $C_{24}H_{21}O_4^+$ $[M+H]^+$ m/z 373.1434, found: 373.1435.



methyl 2-(2-(naphthalen-2-yl)benzofuran-3-yl)-2-phenylacetate (5d)



Prepared according to general procedure from 2-(naphthalen-2-ylethynyl)phenol (48.8 mg, 0.2 mmol, 1.0 equiv.), methyl 2-diazo-2-phenylacetate (42.2 mg, 0.24 mmol, 1.2 equiv.), (2,4-$^{t}Bu_2C_6H_3O)_3PAuOTf$ (19.9 mg, 0.02 mmol, 10 mol%) in 4 mL DCM at 40 ºC for 3 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as a white solid (41.6 mg, 53%).

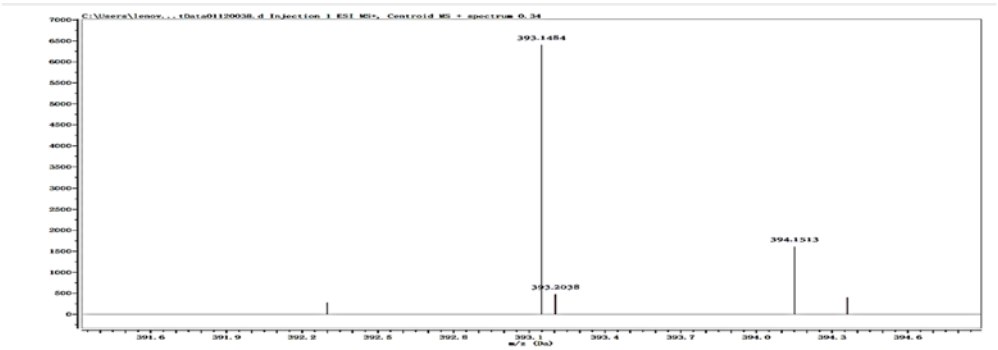
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.2 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 4H), 7.87-7.81 (m, 4H), 7.36-7.25 (m, 6H), 7.22-7.16 (m, 1H), 5.61 (s, 1H), 3.72 (s, 3H).

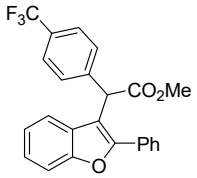
^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 154.6, 153.7, 137.4, 133.3, 133.2, 128.6, 128.5, 128.4, 127.8, 127.7, 127.6, 127.5, 127.0, 126.7, 125.2, 124.7, 123.0, 122.0, 113.0, 111.3, 52.5, 48.0.

Mp: 128-131 ºC

HRMS (ESI) calcd. For $C_{27}H_{21}O_3^+$ $[M+H]^+$ m/z 393.1485, found: 393.1484.



methyl 2-(2-phenylbenzofuran-3-yl)-2-(4-(trifluoromethyl)phenyl)acetate (5e)



Prepared according to general procedure from 2-(phenylethynyl)phenol (38.8 mg, 0.2 mmol, 1.0 equiv.), methyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (58.6 mg, 0.24 mmol, 1.2 equiv.), (2,4-$^{t}Bu_2C_6H_3O)_3PAuOTf$ (19.9 mg, 0.02 mmol, 10 mol%) in 4 mL DCM at 40 ºC for 3 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give product as a colorless oil (36.9 mg, 45%).

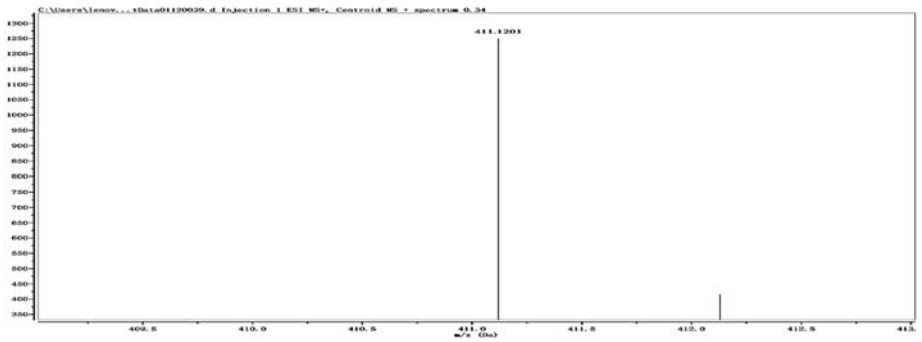
R_f = 0.4 (petroleum ether/ethyl acetate = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.65 (m, 2H), 7.54 (t, J = 8.2 Hz, 3H), 7.50-7.36 (m, 6H), 7.33-7.25 (m, 1H), 7.21-7.15 (m, 1H), 5.55 (s, 1H), 3.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 154.5, 154.0, 141.3, 130.0, 129.7 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 129.4, 129.0, 128.9, 128.3, 128.0, 125.6 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 124.9, 124.2 (q, $^1J_{C\text{-}F}$ = 270.4), 123.2, 121.6, 111.6, 111.5, 52.7, 47.6.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.4.

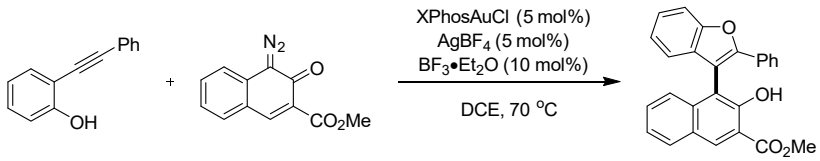
HRMS (ESI) calcd. For $C_{24}H_{18}F_3O_3^+$ $[M+H]^+$ m/z 411.1203, found: 411.1201.



Further exploration and control experiments for Scheme 4

Scheme 4a

Gram-scale reaction of 3a

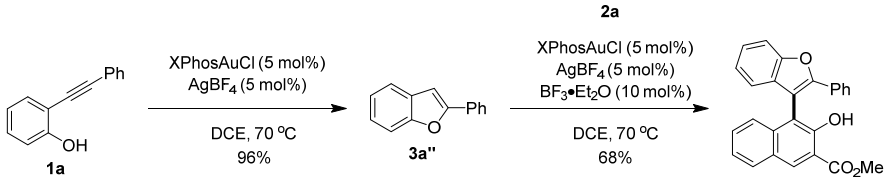


3a, 1.32 g, 67%

To a dry three-neck flask (250 mL) was added XPhosAuCl (177.5 mg, 0.25 mmol, 5 mol%), $AgBF_4$ (47.5 mg, 0.25 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (71.1 mg, 0.5 mmol, 10 mol%) in DCE (50 mL). The resulting mixture was stirred at rt for 10 min. Then a solution of **1a** (1.94 g, 10 mmol, 2.0 equiv.) and **2a** (1.14 g, 5 mmol, 1.0 equiv.) in DCE (50 mL) was added in one portion to the reaction mixture under argon atmosphere. The resulting mixture was stirred at 70 ºC in an oil bath for 1.5 h until the substrate **2a** disappeared (monitored by TLC). At this time, the reaction mixture was concentrated.

The residue was purified by silica gel column chromatography (Petroleum ether/EtOAc = 100:1-30:1) to give desired product **3a** (1.32 g, 67%).

Scheme 4b



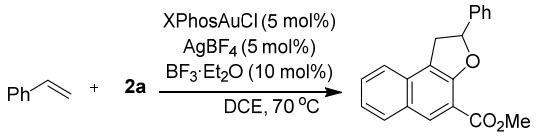
conditions	yield of **3a''**
none	96%
w/o $AgBF_4$	<5%
w/o XPhosAuCl	44%
w/o XPhosAuCl and $AgBF_4$	<5%

conditions	yield of **3a**
none	68%
w/o $AgBF_4$	0%
w/o XPhosAuCl	0%
w/o XPhosAuCl and $AgBF_4$	0%

To a 10 mL flame-dried tube equipped with a stirrer was added XPhosAuCl (28.4 mg, 0.04 mmol, 5 mol%) and $AgBF_4$ (7.8 mg, 0.04 mmol, 5 mol%) in DCE (4 mL). The resulting mixture was stirred at rt for 10 min. Then a solution of **1a** (155.2 mg, 0.8 mmol, 1.0 equiv.) in DCE (4 mL) was added in one portion to the reaction mixture under argon atmosphere. The resulting mixture was stirred at 70 °C in an oil bath for 0.5 h until the substrate **1a** disappeared (monitored by TLC). At this time, the reaction mixture was concentrated. The residue was purified by silica gel column chromatography (petroleum ether) to give desired product **3a′′** (149.0 mg, 96%). In the absence of silver salt, very low yield of **3a′′** (<5%) was observed. Without the addition of XPhosAuCl, 44% yield of **3a′′** was isolated. In the absence of neither silver nor gold salt, very low yield of **3a′′** (<5%) was observed.

To a 10 mL flame-dried tube equipped with a stirrer was added XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in DCE (2 mL). The resulting mixture was stirred at rt for 10 min. Then a solution of **3a′′** (77.6 mg, 0.4 mmol, 2.0 equiv.) and **2a** (45.6 mg, 0.2 mmol, 1.0 equiv.) in DCE (2 mL) was added in one portion to the reaction mixture under argon atmosphere. The resulting mixture was stirred at 70 °C in an oil bath for 1.5 h until the substrate **2a** disappeared (monitored by TLC). At this time, the reaction mixture was concentrated. The residue was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 100:1-50:1) to give desired product **3a** (53.6 mg, 68%). However, no **3a** was observed in the absence of either silver or gold salt.

Scheme 4c

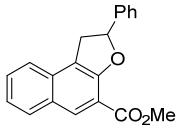


6

To a 10 mL flame-dried tube equipped with a stirrer was added XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in DCE (2 mL). The resulting mixture was stirred at rt for 10 min. Then a solution of styrene (20.8 mg, 0.2 mmol, 1.0 equiv.) and **2a** (45.6 mg, 0.2 mmol, equiv.) in DCE (2 mL) was added in one portion to the reaction mixture under argon atmosphere. The resulting mixture was stirred at 70 °C in an oil

bath for 4 h until the substrate **2a** disappeared (monitored by TLC). At this time, the reaction mixture was concentrated. The residue was purified by silica gel column chromatography (Petroleum ether: ethyl acetate) to give desired product **6** (colorless oil, 31.0 mg, 51%).

methyl 2-phenyl-1,2-dihydronaphtho[2,1-b]furan-4-carboxylate(6)

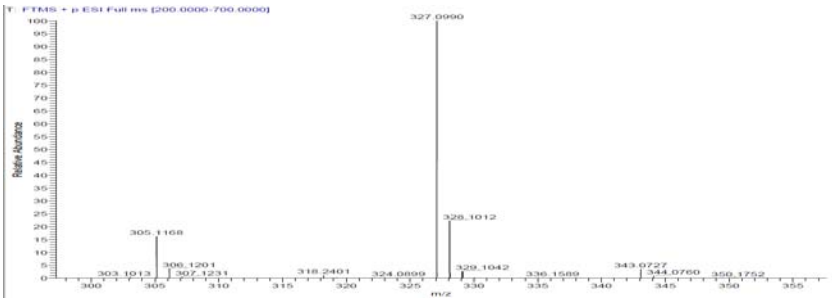


R_f = 0.4 (petroleum ether/ethyl acetate = 10:1)

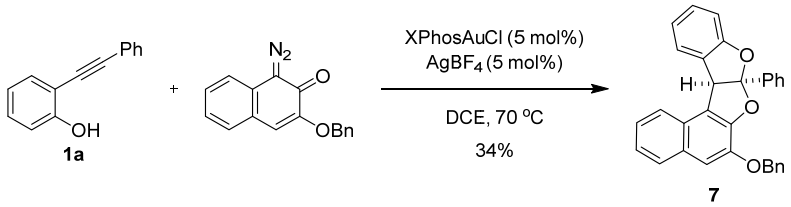
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.56-7.49 (m, 2H), 7.48-7.41 (m, 2H), 7.40-7.27 (m, 4H), 6.10 (dd, *J* = 10.0, 7.2 Hz, 1H), 3.99-3.91 (m, 4H), 3.46 (ddd, *J* = 15.6, 7.2, 0.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 155.8, 142.2, 132.8, 132.7, 130.0, 129.0, 128.7, 128.5, 128.1, 125.7, 123.8, 122.8, 120.4, 115.1, 85.1, 52.3, 37.0.

HRMS (ESI) calcd. For $C_{20}H_{17}O_3^+$ $[M+H]^+$ m/z 305.1172, found: 443.1644.

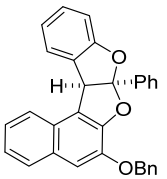


Scheme 4d



To a 10 mL flame-dried tube equipped with a stirrer was added XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%) and $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) in DCE (2 mL). The resulting mixture was stirred at rt for 10 min. Then a solution of **1a** (77.6 mg, 0.4 mmol, 2.0 equiv.) and 3-(benzyloxy)-1-diazonaphthalen-2(1H)-one (45.6 mg, 0.2 mmol, 1.0 equiv.) in DCE (2 mL) was added in one portion to the reaction mixture under argon atmosphere. The resulting mixture was stirred at 70 °C in an oil bath for 10 h until the substrate 3-(benzyloxy)-1-diazonaphthalen-2(1H)-one disappeared (monitored by TLC). At this time, the reaction mixture was concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1) to give desired product **7** (white solid, 30.1 mg, 34%).

6-(benzyloxy)-7a-phenyl-7a,12b-dihydronaphtho[1',2':4,5]furo[2,3-b]benzofuran (7)



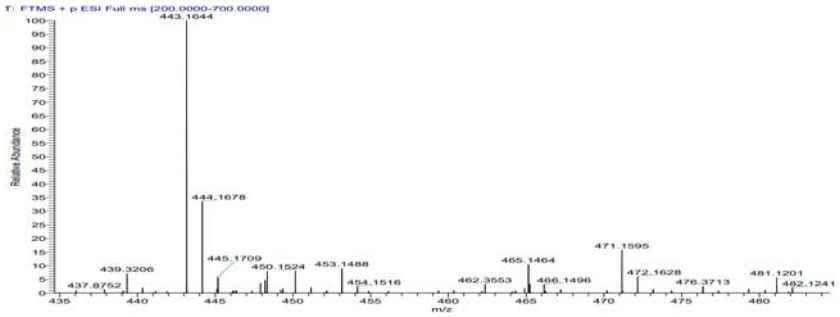
$\mathbf{R_f}$ = 0.4 (petroleum ether/ethyl acetate = 20:1)

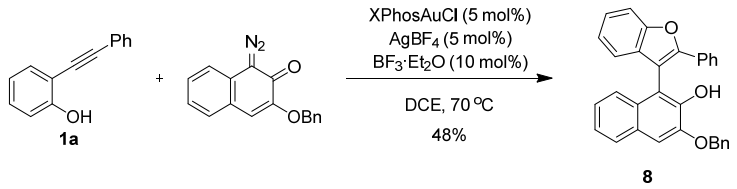
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63-7.59 (m, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.51-7.47 (m, 2H), 7.44 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.41-7.26 (m, 7H), 7.23-7.18 (m, 1H), 7.15 (s, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.91 (td, *J* = 7.6, 1.2 Hz, 1H), 5.43 (s, 1H), 5.28 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 147.8, 144.5, 139.5, 136.6, 131.1, 129.3, 129.1, 128.63, 128.62, 128.03, 127.96, 127.5, 127.3, 125.4, 125.2, 125.1, 125.0, 124.1, 122.9, 122.6, 122.1, 120.9, 110.6, 109.9, 70.9, 57.7.

Mp:167-169 ºC.

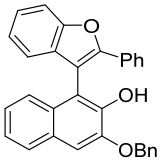
HRMS (ESI) calcd. For $C_{31}H_{23}O_3^+$ $[M+H]^+$ m/z 443.1642, found: 443.1644.





To a 10 mL flame-dried tube equipped with a stirrer was added XPhosAuCl (7.1 mg, 0.01 mmol, 5 mol%), $AgBF_4$ (1.9 mg, 0.01 mmol, 5 mol%) and $BF_3{\cdot}Et_2O$ (2.8 mg, 0.02 mmol, 10 mol%) in DCE (2 mL). The resulting mixture was stirred at rt for 10 min. Then a solution of **1a** (77.6 mg, 0.4 mmol, 2.0 equiv.) and 3-(benzyloxy)-1-diazonaphthalen-2(1H)-one (55.2 mg, 0.2 mmol, 1.0 equiv.) in DCE (2 mL) was added in one portion to the reaction mixture under argon atmosphere. The resulting mixture was stirred at 70 ºC in an oil bath for 1.5 h until the substrate **2a** disappeared (monitored by TLC). At this time, the reaction mixture was concentrated. The residue was purified by silica gel column chromatography (Petroleum ether: ethyl acetate = 10:1) to give desired product **8** (white solid, 42.4 mg, 48%).

3-(benzyloxy)-1-(2-phenylbenzofuran-3-yl)naphthalen-2-ol (8)



$\mathbf{R_f}$ = 0.3 (petroleum ether/ethyl acetate = 20:1)

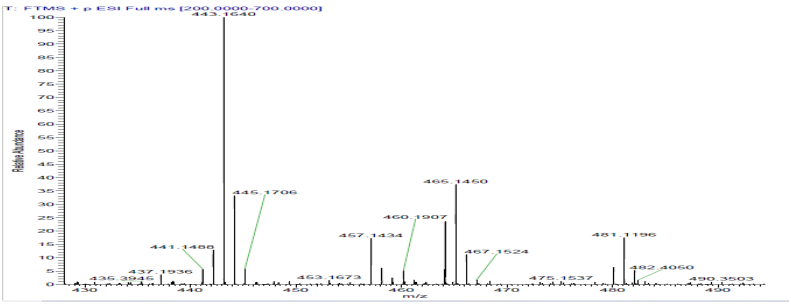
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.64-7.58 (m, 3H), 7.51-7.44 (m, 3H), 7.44-7.35 (m, 4H), 7.35-7.29 (m, 2H), 7.22-7.15 (m, 4H), 7.15-7.07 (m, 2H), 6.07 (s, 1H), 5.30 (dd, *J* = 13.2, 11.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 152.1, 146.5, 144.1, 135.9, 130.9, 130.8, 129.1, 128.9, 128.8,

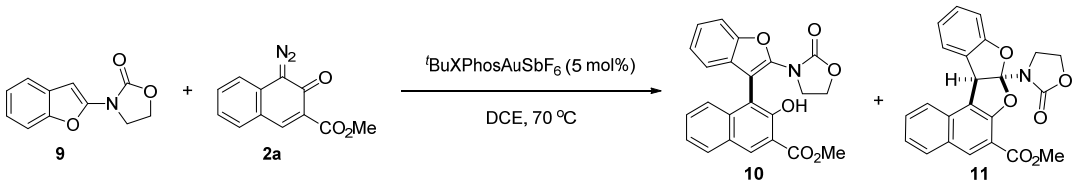
128.6, 128.5, 128.3, 128.0, 127.1, 126.0, 125.0, 124.9, 124.7, 124.3, 122.9, 120.6, 112.2, 111.3, 110.1, 107.9, 71.2.

Mp: 187-189 ºC.

HRMS (ESI) calcd. For $C_{31}H_{23}O_3^+$ $[M+H]^+$ m/z 443.1642, found: 443.1640.

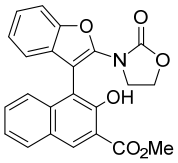


Scheme 4e



To a flame-dried tube equipped with a stirrer was added ^{t}BuPhosAuCl (6.6 mg, 0.01 mmol, 5 mol%), $AgSbF_6$ (3.4 mg, 0.01 mmol, 5 mol%) and DCE (2 mL). The mixture was stirred at rt for 10 min under argon atmosphere, then a solution of **9** (44.9 mg, 0.22 mmol, 1.1 equiv.) and **2a** (45.8 mg, 0.2 mmol, 1.0 equiv.) in 2 mL DCE was added into the reaction mixture in one portion. The reaction was stirred at 70 ºC in a heating block for 1.5 h. The reaction mixture was concentrated under vacuum, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5:1-2:1) to give **10** and **11** (ration of 3:2). When the reaction was performed for 10 h, we could only get **10**.

methyl 3-hydroxy-4-(2-(2-oxooxazolidin-3-yl)benzofuran-3-yl)-2-naphthoate (10)



To a 10 mL flame-dried tube equipped with a stirrer was added **7** (44.7 mg, 0.22 mmol, 1.1 equiv.) **2a** (45.6 mg, 0.2 mmol, 1.0 equiv.) and ^{t}BuXPhosAuSbF$_6$ (8.6 mg, 0.01 mmol, 5 mol%) in 4 mL DCE at 70 ºC for 10 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2:1) to give product as a yellow solid (43.5 mg, 54%).

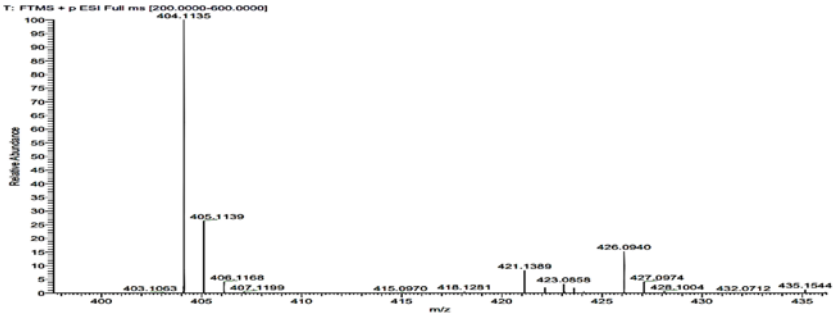
R_f = 0.4 (petroleum ether/ethyl acetate = 2:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.92 (s, 1H), 8.62 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.48-7.44 (m, 1H), 7.38-7.30 (m, 2H), 7.18-7.14 (m, 1H),7.10 (d, *J* = 7.6 Hz, 1H), 4.01-4.28 (m, 2H), 4.09-4.04 (m, 1H), 4.04 (s, 3H), 3.98-3.91 (m, 1H).

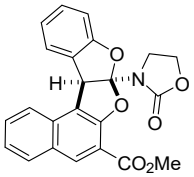
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 154.8, 154.1, 152.0, 144.5, 136.8, 133.4, 129.9, 129.3, 127.1, 125.3, 124.7, 124.4, 123.2, 120.8, 113.8, 112.0, 111.4, 105.4, 63.0, 52.9, 45.4.

Mp: 196-198 ºC.

HRMS (ESI) calcd. For $C_{23}H_{18}NO_6^+$ $[M+H]^+$ m/z 404.1129, found: 404.1135.



methyl-7a-(2-oxooxazolidin-3-yl)-7a,12b-dihydronaphtho[1',2':4,5]furo[2,3-b]benzofuran-6-carboxylate (11)



To a 10 mL flame-dried tube equipped with a stirrer was added **7** (44.7 mg, 0.22 mmol, 1.1 equiv.) **2a** (45.6 mg, 0.2 mmol, 1.0 equiv.) and ^{t}BuXPhosAuSbF$_6$ (8.6 mg, 0.01 mmol, 5 mol%) in 4 mL DCE at 70 ºC for 1.5 h. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2:1) to give product as a yellow solid (14.0 mg, 17.4%).

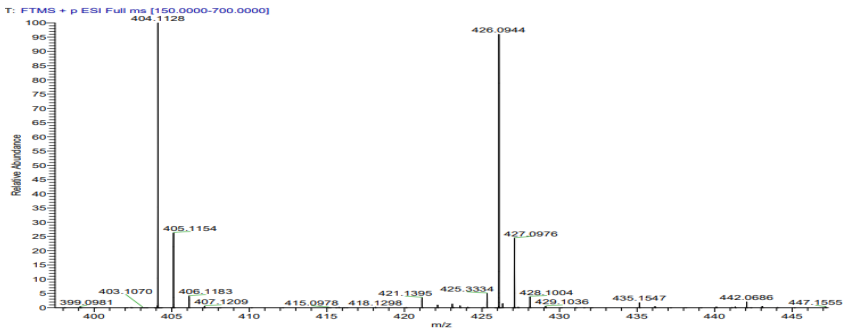
R_f = 0.3 (petroleum ether/ethyl acetate = 2:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.03 (dd, *J* = 8.4, 0.8 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.63 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 7.50-7.48 (m, 1H), 7.37 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.13-7.08 (m, 1H), 6.88-6.84 (m, 2H), 6.23 (s, 1H), 4.43-4.31 (m, 2H), 4.17-4.09 (m, 2H), 3.89 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 156.7, 155.7, 152.6, 133.5, 132.0, 130.4, 129.8, 129.4, 129.1, 126.6, 125.2, 125.0, 124.8, 123.1, 122.5, 121.8, 114.8, 110.4, 62.8, 52.3, 51.0, 43.3.

Mp: 212-214 ºC.

HRMS (ESI) calcd. For $C_{23}H_{18}NO_6^+$ $[M+H]^+$ m/z 404.1129, found: 404.1128.



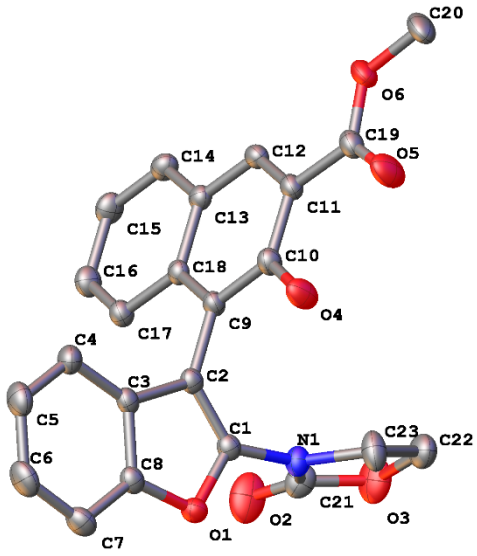
X-ray crystallographic data

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre. CCDC 2257602 (**10**) and CCDC 2257604 (**11**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/. The measurements were taken in a Bruker D8 Venture diffractometer. The data were integrated by Bruker D8 with multi-scan absorption corrections. The structure solution and refinement were processed by SHELXL (2018/3).

X-ray crystallographic data for 10 and 11

Method of crystallization: A solution of **10** in ethyl acetate and petroleum ether was evaporated the solvent slowly at room temperature.

Crystal data and structure for 10 (thermal ellipsoids are shown at the 50% level)



X-ray structure of **10**.

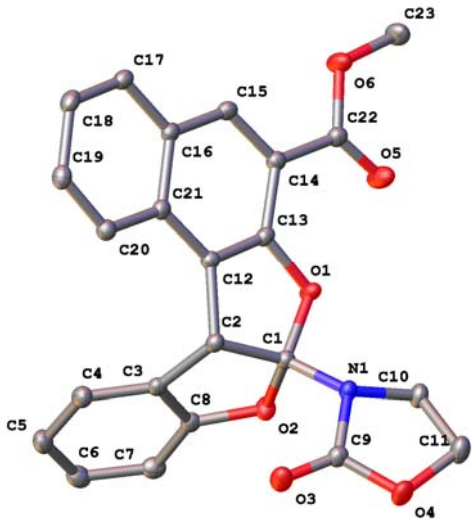
Empirical formula	$C_{23}H_{17}NO_6$	
Formula weight	403.38	
Temperature	213.00 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 11.6847(3) Å	α = 90 °
	b = 13.9633(3) Å	β = 90 °
	c = 23.2986(6) Å	γ = 90 °
Volume	3801.33(16) $Å^3$	
Z	8	
Density (calculated)	1.410 Mg/m^3	
Absorption coefficient	0.546 mm^{-1}	
F(000)	1680	
Crystal size	0.07 x 0.07 x 0.05 mm^3	

θ range for data collection	3.301 to 54.980°
Index ranges	-14<=h<=14, -12<=k<=17, -28<=l<=28
Reflections collected	41038
Independent reflections	3619 [R(int) = 0.0505]
Completeness to θ = 53.594°	99.8 %
Max. and min. transmission	0.7508 and 0.6058
Data / restraints / parameters	3619 / 0 / 273
Goodness-of-fit on F^2	1.192
Final R indices [I > 2σ(I)]	R_1 = 0.0433, wR_2 = 0.1405
R indices (all data)	R_1 = 0.0525, wR_2 = 0.1499
Largest diff. peak and hole	0.256 and -0.294 e.$Å^{-3}$

X-ray crystallographic data for 11

Method of crystallization: A solution of **11** in ethyl acetate and dichloromethane was evaporated the solvent slowly at room temperature.

Crystal data and structure for 11 (thermal ellipsoids are shown at the 50% level)



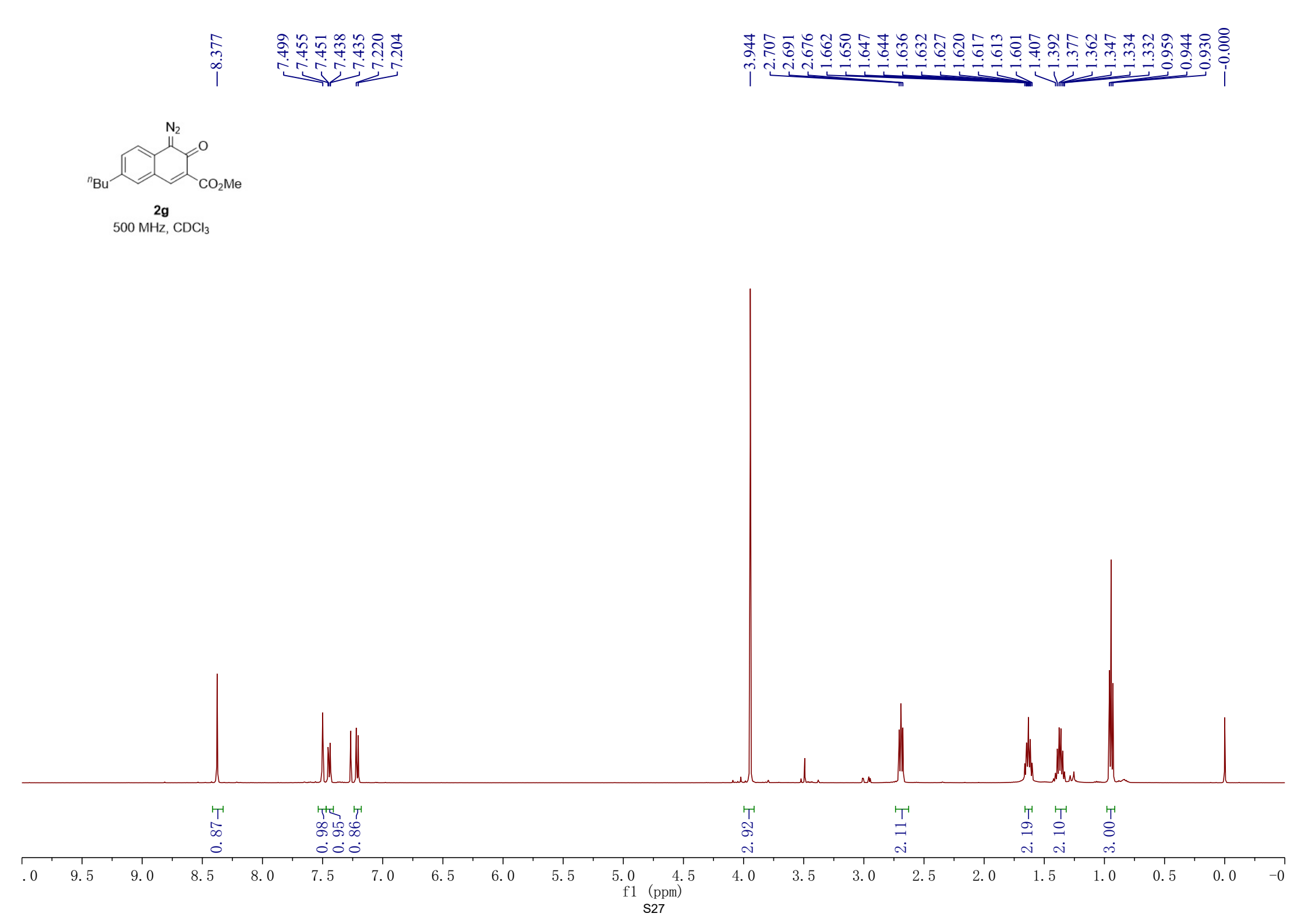
X-ray structure of **11**.

Empirical formula	$C_{23}H_{17}NO_6$	
Formula weight	403.38	
Temperature	214.00 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.4331(2) Å	α = 90 °
	b = 11.3391(2) Å	β = 96.5160(10) °
	c = 17.0360(3) Å	γ = 90 °
Volume	1810.45(6) $Å^3$	
Z	4	
Density (calculated)	1.480 Mg/m^3	

Absorption coefficient	0.573 mm^{-1}
F(000)	840
Crystal size	0.08 x 0.07 x 0.07 mm^3
θ range for data collection	4.460 to 54.936°.
Index ranges	-11<=h<=11, -12<=k<=13, -20<=l<=18
Reflections collected	13399
Independent reflections	3429 [R(int) = 0.0399]
Completeness to θ = 53.594°	99.5 %
Max. and min. transmission	0.7508 and 0.6293
Data / restraints / parameters	3425 / 0 / 272
Goodness-of-fit on F^2	1.062
Final R indices [I > 2σ(I)]	R_1 = 0.0401, wR_2 = 0.0988
R indices (all data)	R_1 = 0.0543, wR_2 = 0.1064
Largest diff. peak and hole	0.212 and -0.305 e.$Å^{-3}$

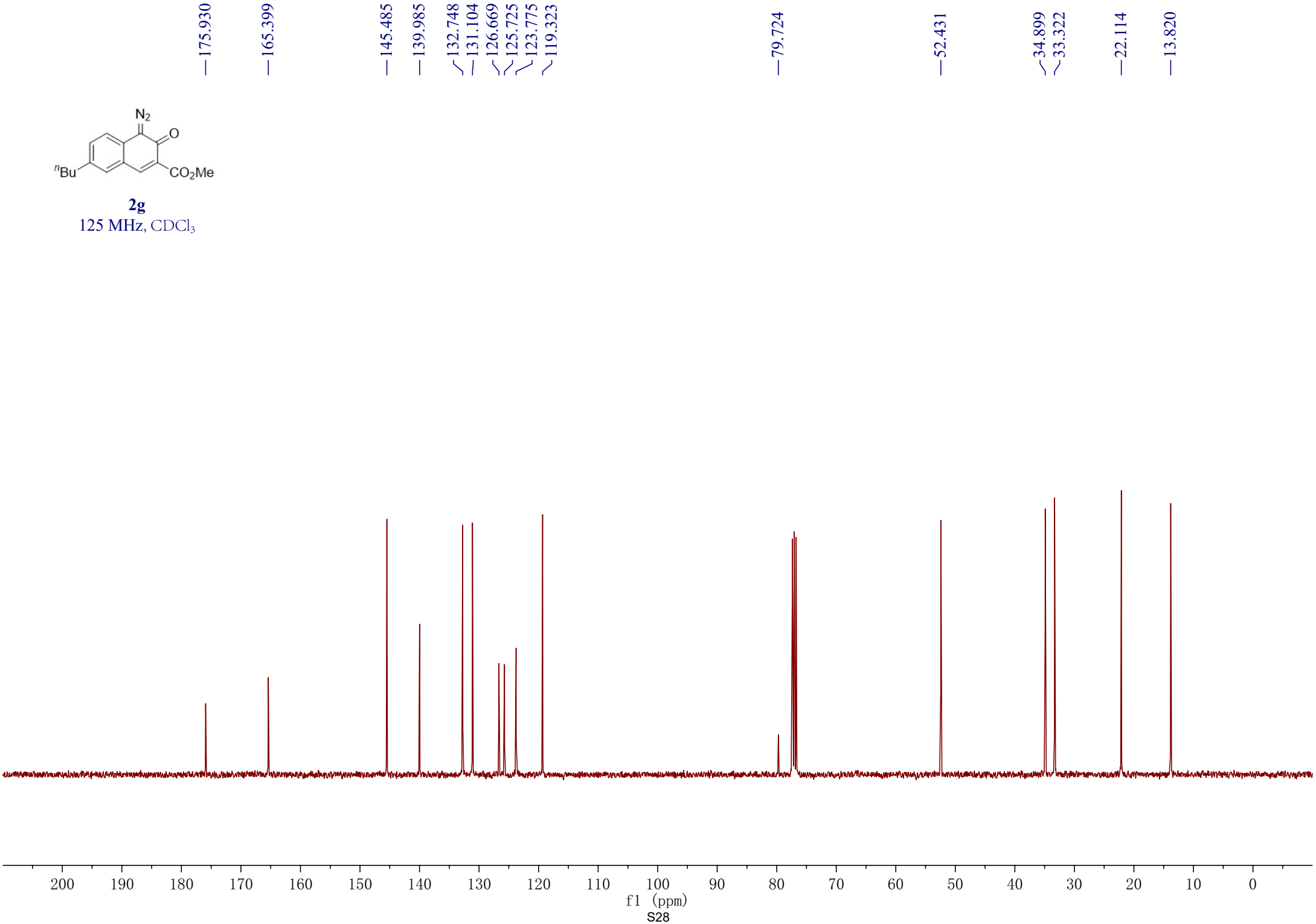
References

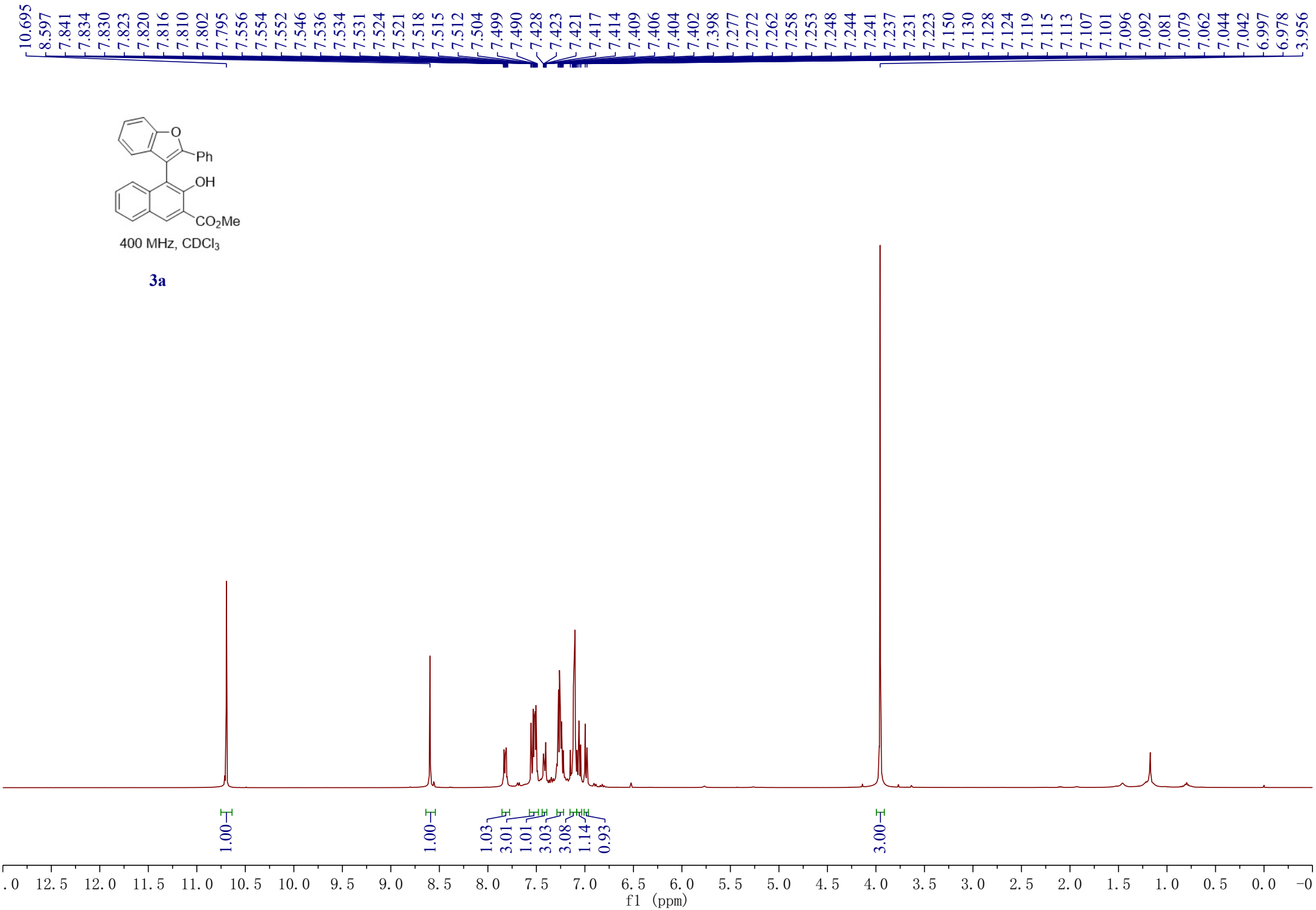
1. (a) Wang, Z.; Cao, T.; Zhu, S. Gold-Catalyzed Enynal and Enynol Coupling by Selectively Steering Two Transient Vinyl-Gold Intermediates. *Org. Lett*. **2022**, *24*, 9296-9300. (b) Zhang, Y.; Xin, Z.; Xue, J.; Li, Y. Gold-catalyzed Alkyne Hydroxylation: Synthesis of 2-Substituted Benzo[b]furan Compounds. *Chinese J. Chem*. **2008**, *26*, 1461-1464. (c) Xia, Z.; Corcé, V.; Zhao, F.; Przybylski, C.; Espagne, A.; Jullien, L.; Saux, T.; Gimbert, Y.; Dossmann, H.; Ollivier, C.; Fensterbank, L. Photosensitized Oxidative Addition to Gold(I) Enables Alkynylative Cyclization of *o*-Alkylnylphenols with Iodoalkynes. *Nat. Chem*. **2019**, *11*, 797-805.
2. (a) Niu, C.; Zhou, Y.; Chen, Q.; Zhu, Y.; Tang, S.; Yu, Z.; Sun, J. Atroposelective Synthesis of N-Arylindoles via Enantioselective N–H Bond Insertion. *Org. Lett.* **2022**, *24*, 7428-7433. (b) Li, Z.; Chen, Y.; Wang, C.; Xu, G.; Shao, Y.; Zhang, X.; Tang, S.; Sun, J. Construction of C−C Axial Chirality via Asymmetric Carbene Insertion into Arene C−H Bonds. *Angew. Chem. Int. Ed.* **2021**, *60*, 25714-25718. (c) Zhang, J.; Jiang, F.; Chen, Y.; Xiang, S.; Tan, B. Synthesis of Structurally Diversified BINOLs and NOBINs via Palladium-Catalyzed C−H Arylation with Diazoquinones. *Sci. China Chem.* **2021**, *64*, 1515-1521.
3. Su, J.; Li, Q.; Shao, Y.; Sun, J. Catalytic Transformations of 2-Pyridones by Rhodium-Mediated Carbene Transfer. *Org. Lett.* **2022**, *21*, 1637-1641.

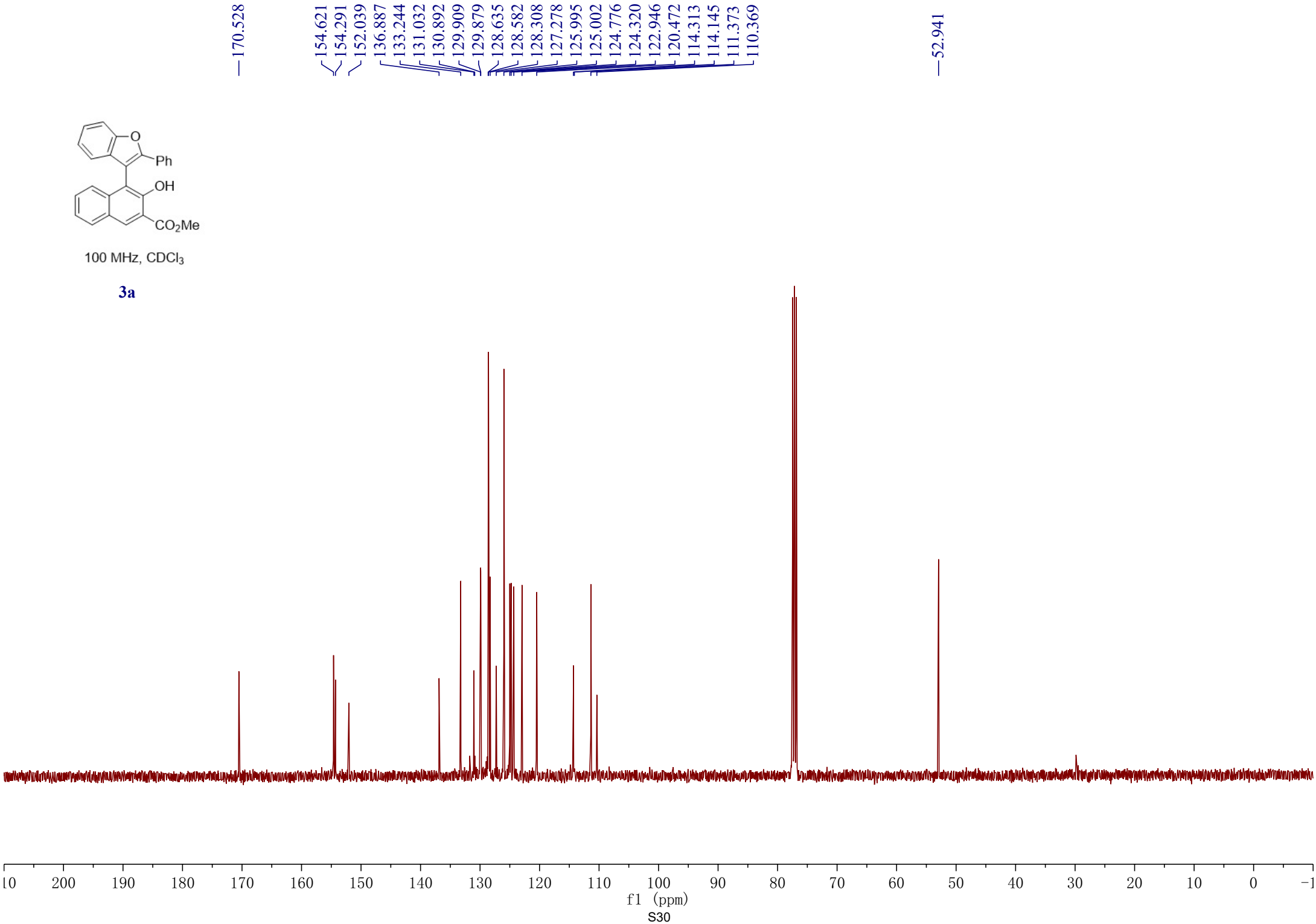

8.377
7.499
7.455
7.451
7.438
7.435
7.220
7.204
3.944
2.707
2.691
2.676
1.662
1.650
1.647
1.644
1.636
1.632
1.627
1.620
1.617
1.613
1.601
1.407
1.392
1.377
1.362
1.347
1.334
1.332
0.959
0.944
0.930
-0.000
N2
O
nBu
CO2Me
2g
500 MHz, CDCl3
0.87
0.98
0.95
0.86
2.92
2.11
2.19
2.10
3.00
f1 (ppm)

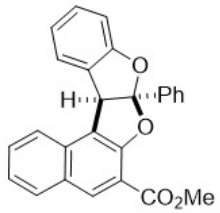
2g

125 MHz, $CDCl_3$




10.695
8.597
7.841
7.834
7.830
7.823
7.820
7.816
7.810
7.802
7.795
7.556
7.554
7.552
7.546
7.536
7.534
7.531
7.524
7.521
7.518
7.515
7.512
7.504
7.499
7.490
7.428
7.423
7.421
7.417
7.414
7.409
7.406
7.404
7.402
7.398
7.277
7.272
7.262
7.258
7.253
7.248
7.244
7.241
7.237
7.231
7.223
7.150
7.130
7.128
7.124
7.119
7.115
7.113
7.107
7.101
7.096
7.092
7.081
7.079
7.062
7.044
7.042
6.997
6.978
3.956
O
Ph
OH
CO2Me
400 MHz, CDCl3
3a
1.00
1.00
1.03
3.01
1.01
3.03
3.08
1.14
0.93
3.00
f1 (ppm)

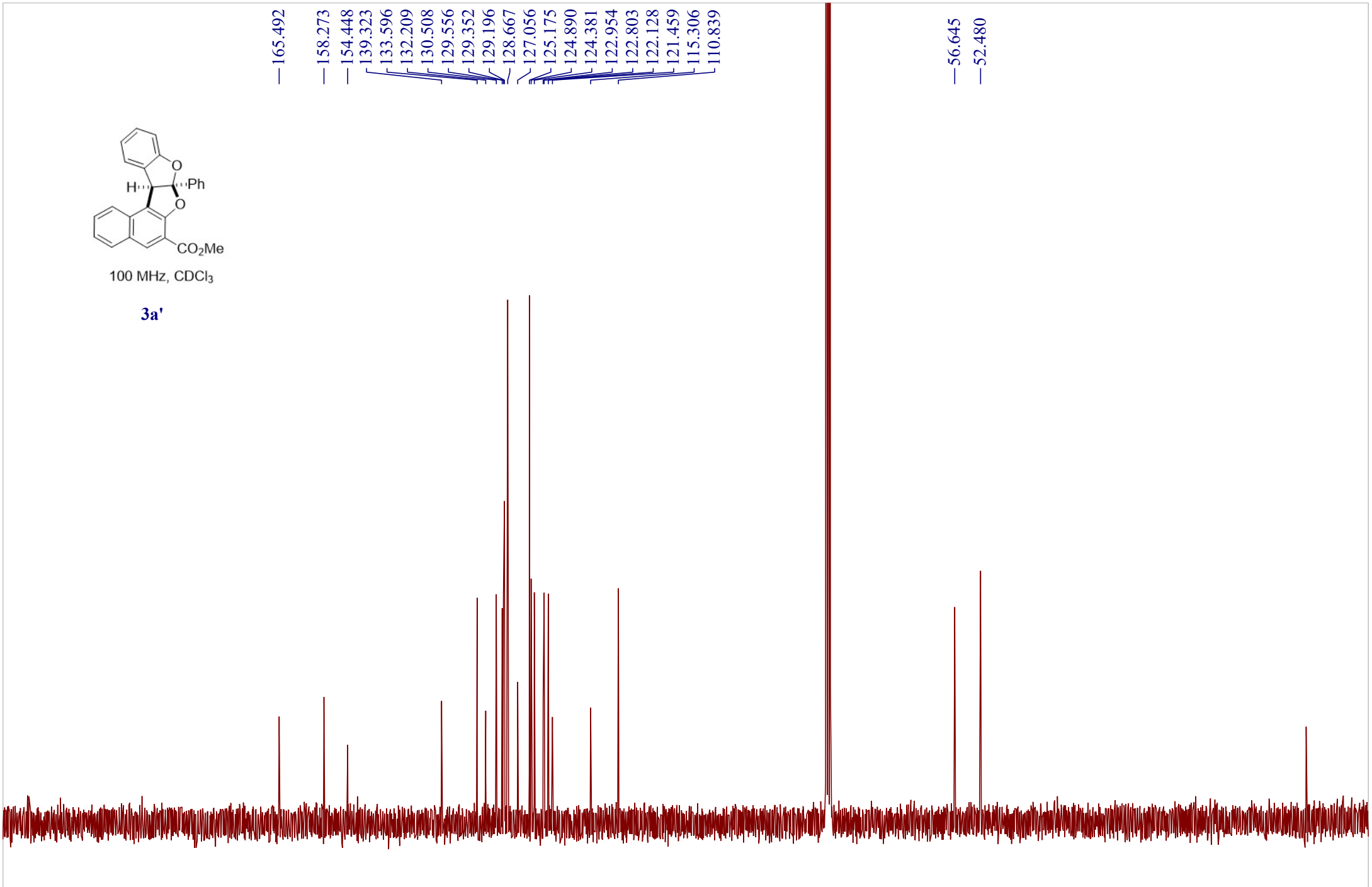

170.528
154.621
154.291
152.039
136.887
133.244
131.032
130.892
129.909
129.879
128.635
128.582
128.308
127.278
125.995
125.002
124.776
124.320
122.946
120.472
114.313
114.145
111.373
110.369
52.941
O
Ph
OH
CO2Me
100 MHz, CDCl3
3a
f1 (ppm)

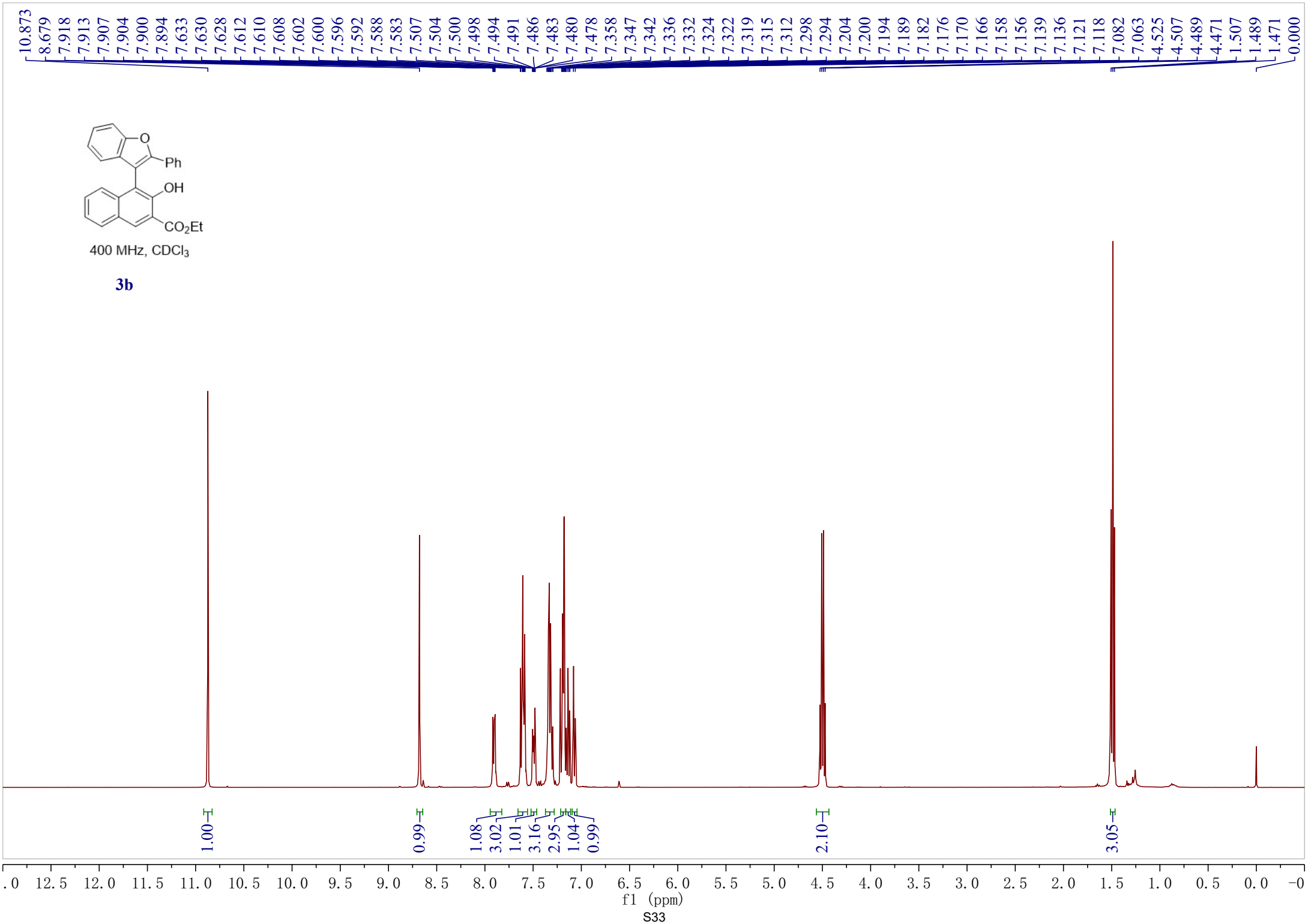


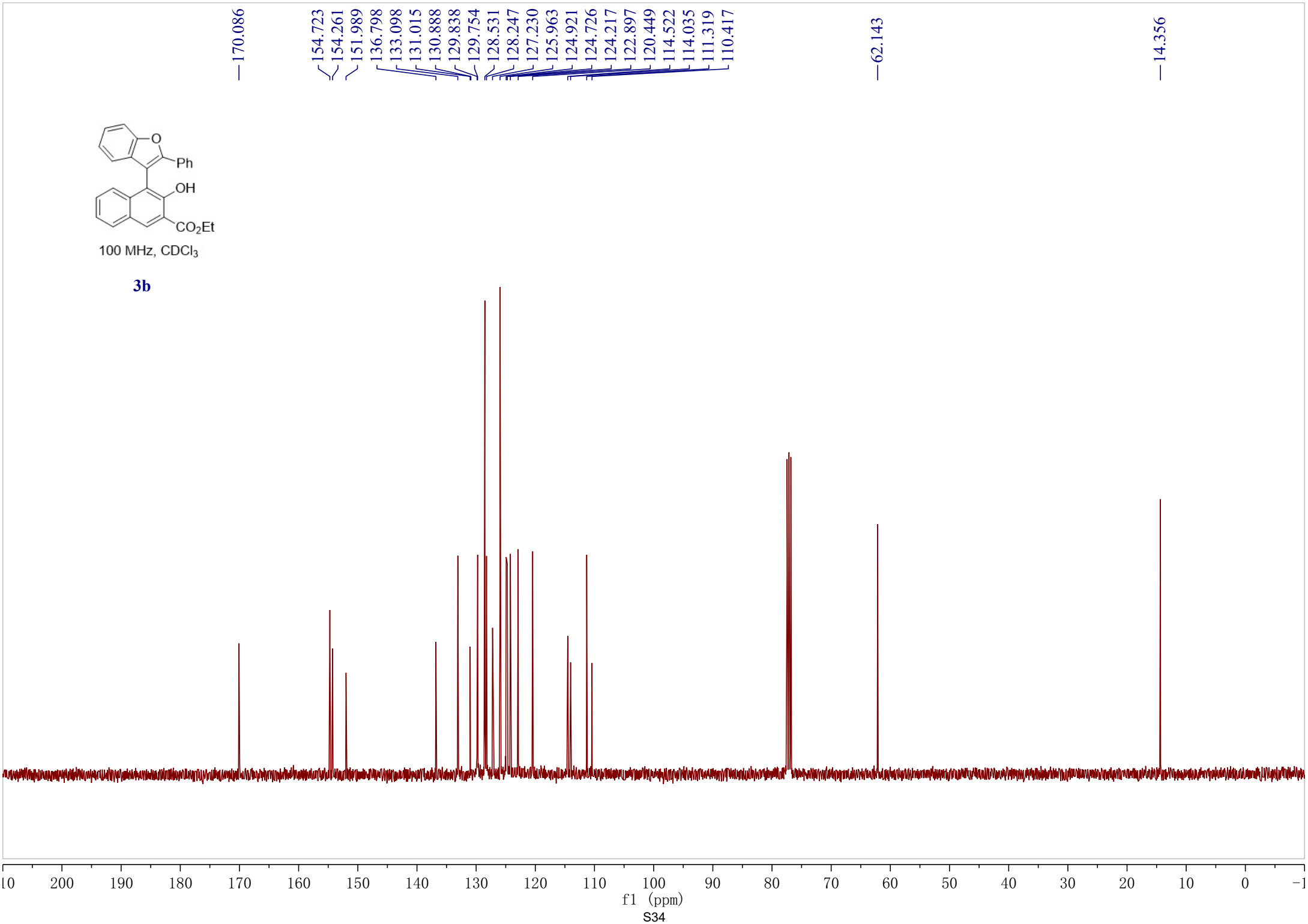
400 MHz, $CDCl_3$

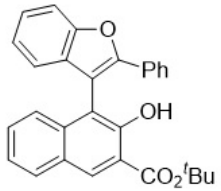
3a'

f1 (ppm)


165.492
158.273
154.448
139.323
133.596
132.209
130.508
129.556
129.352
129.196
128.667
127.056
125.175
124.890
124.381
122.954
122.803
122.128
121.459
115.306
110.839
56.645
52.480
O
H
Ph
O
CO2Me
100 MHz, CDCl3
3a'
f1 (ppm)

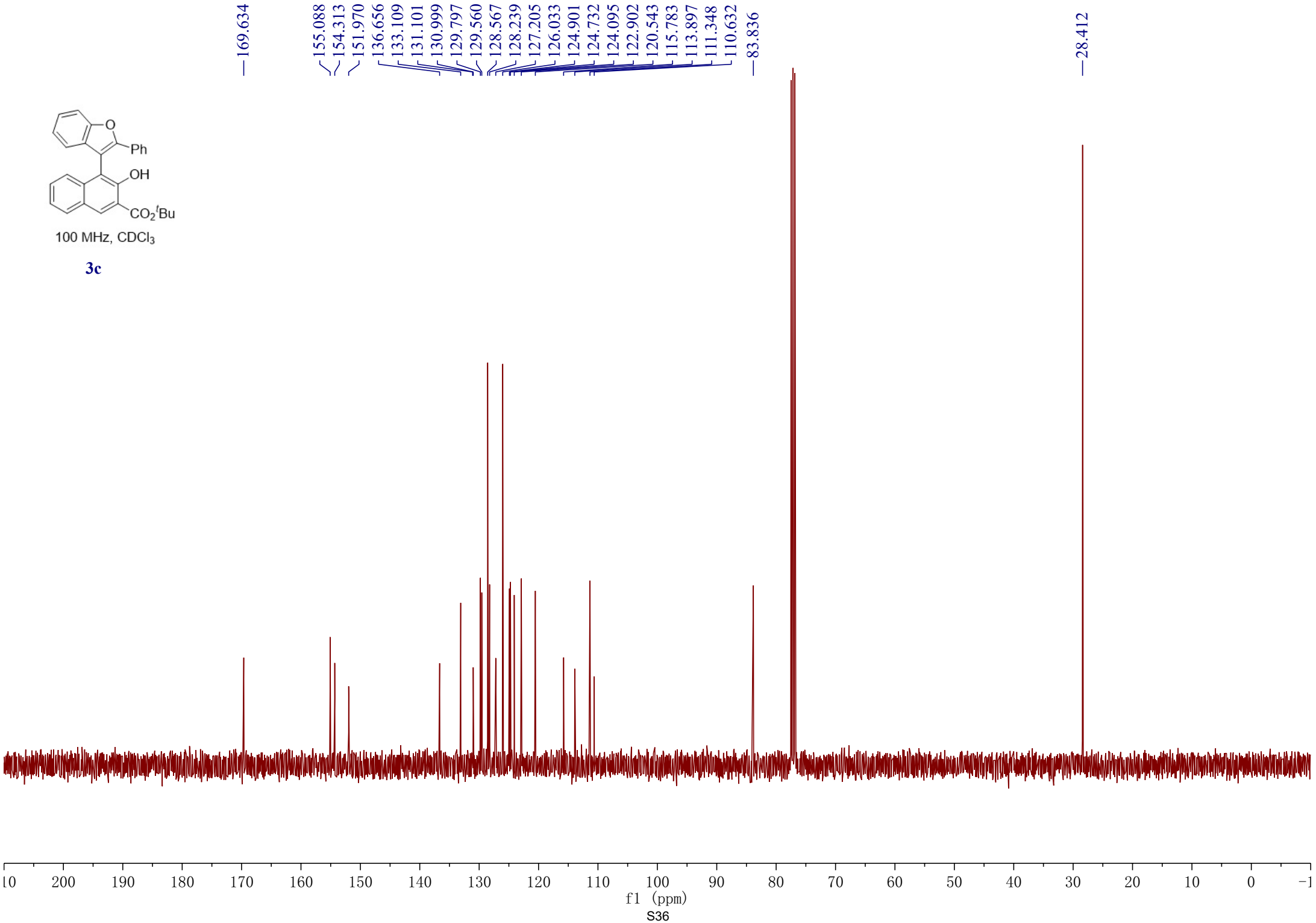

10.873
8.679
7.918
7.913
7.907
7.904
7.900
7.894
7.633
7.630
7.628
7.612
7.610
7.608
7.602
7.600
7.596
7.592
7.588
7.583
7.507
7.504
7.500
7.498
7.494
7.491
7.486
7.483
7.480
7.478
7.358
7.347
7.342
7.336
7.332
7.324
7.322
7.319
7.315
7.312
7.298
7.294
7.204
7.200
7.194
7.189
7.182
7.176
7.170
7.166
7.158
7.156
7.139
7.136
7.121
7.118
7.082
7.063
4.525
4.507
4.489
4.471
1.507
1.489
1.471
0.000
O
Ph
OH
CO2Et
400 MHz, CDCl3
3b
1.00
0.99
1.08
3.02
1.01
3.16
2.95
1.04
0.99
2.10
3.05
f1 (ppm)

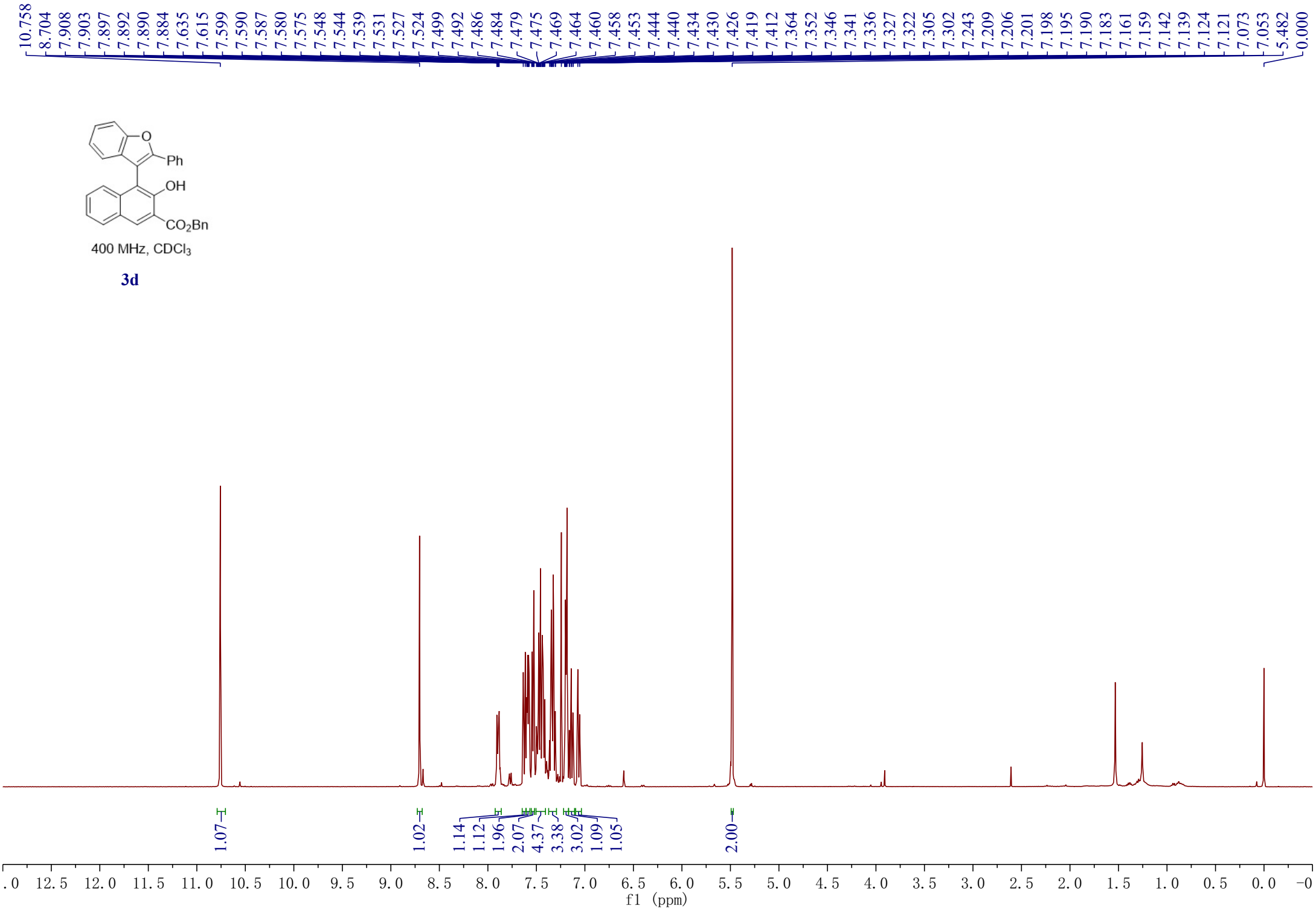

170.086
154.723
154.261
151.989
136.798
133.098
131.015
130.888
129.838
129.754
128.531
128.247
127.230
125.963
124.921
124.726
124.217
122.897
120.449
114.522
114.035
111.319
110.417
62.143
14.356
O
Ph
OH
CO2Et
100 MHz, CDCl3
3b
f1 (ppm)

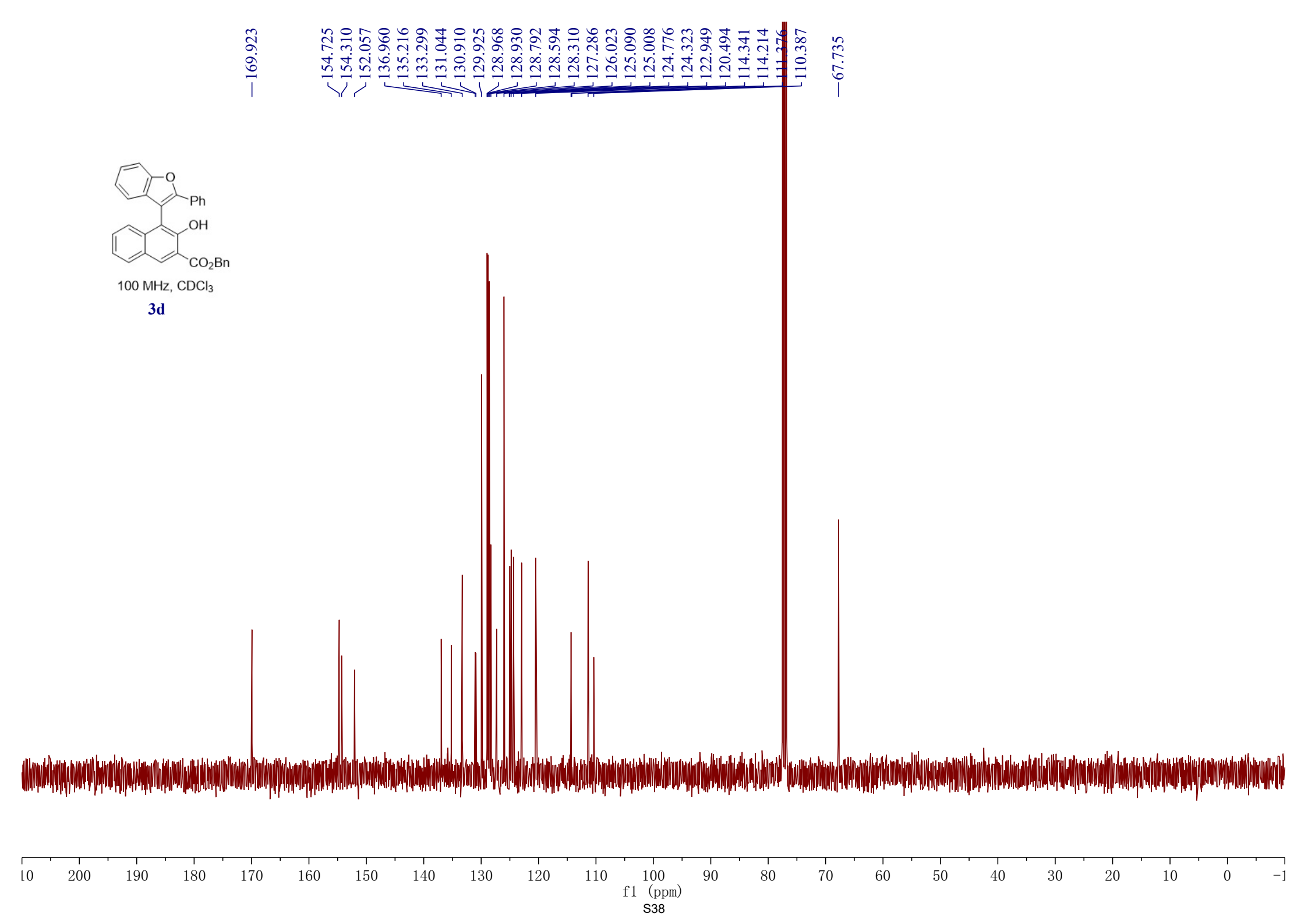


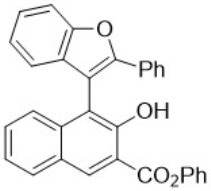
400 MHz, $CDCl_3$

3c


169.634
155.088
154.313
151.970
136.656
133.109
131.101
130.999
129.797
129.560
128.567
128.239
127.205
126.033
124.901
124.732
124.095
122.902
120.543
115.783
113.897
111.348
110.632
83.836
28.412
O
Ph
OH
CO2tBu
100 MHz, CDCl3
3c
f1 (ppm)

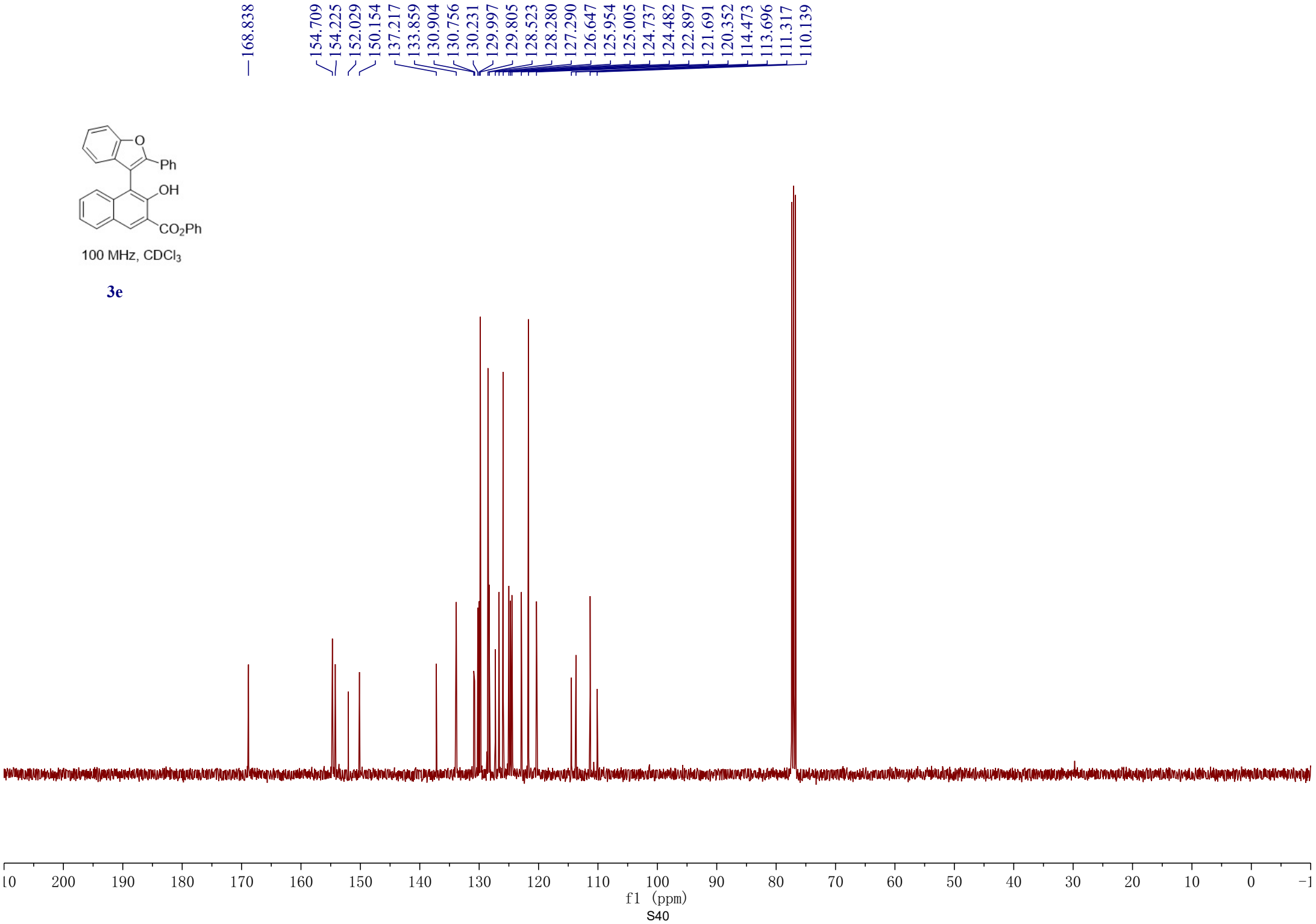

10.758
8.704
7.908
7.903
7.897
7.892
7.890
7.884
7.635
7.615
7.599
7.590
7.587
7.580
7.575
7.548
7.544
7.539
7.531
7.527
7.524
7.499
7.492
7.486
7.484
7.479
7.475
7.469
7.464
7.460
7.458
7.453
7.444
7.440
7.434
7.430
7.426
7.419
7.412
7.364
7.352
7.346
7.341
7.336
7.327
7.322
7.305
7.302
7.243
7.209
7.206
7.201
7.198
7.195
7.190
7.183
7.161
7.159
7.142
7.139
7.124
7.121
7.073
7.053
5.482
0.000
O
Ph
OH
CO2Bn
400 MHz, CDCl3
3d
1.07
1.02
1.14
1.12
1.96
2.07
4.37
3.38
3.02
1.09
1.05
2.00
f1 (ppm)

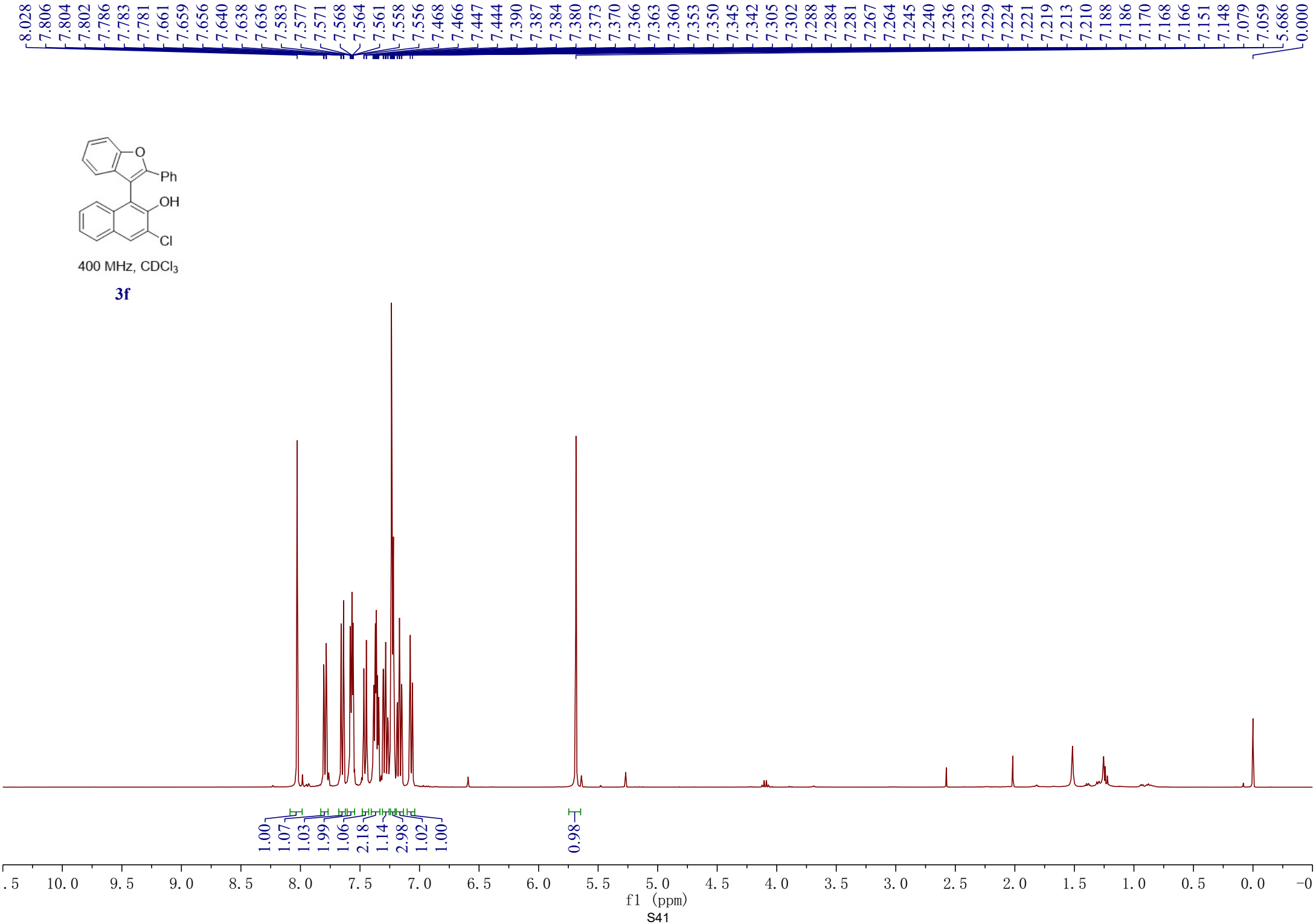

169.923
154.725
154.310
152.057
136.960
135.216
133.299
131.044
130.910
129.925
128.968
128.930
128.792
128.594
128.310
127.286
126.023
125.090
125.008
124.776
124.323
122.949
120.494
114.341
114.214
111.376
110.387
67.735
O
Ph
OH
CO2Bn
100 MHz, CDCl3
3d
f1 (ppm)

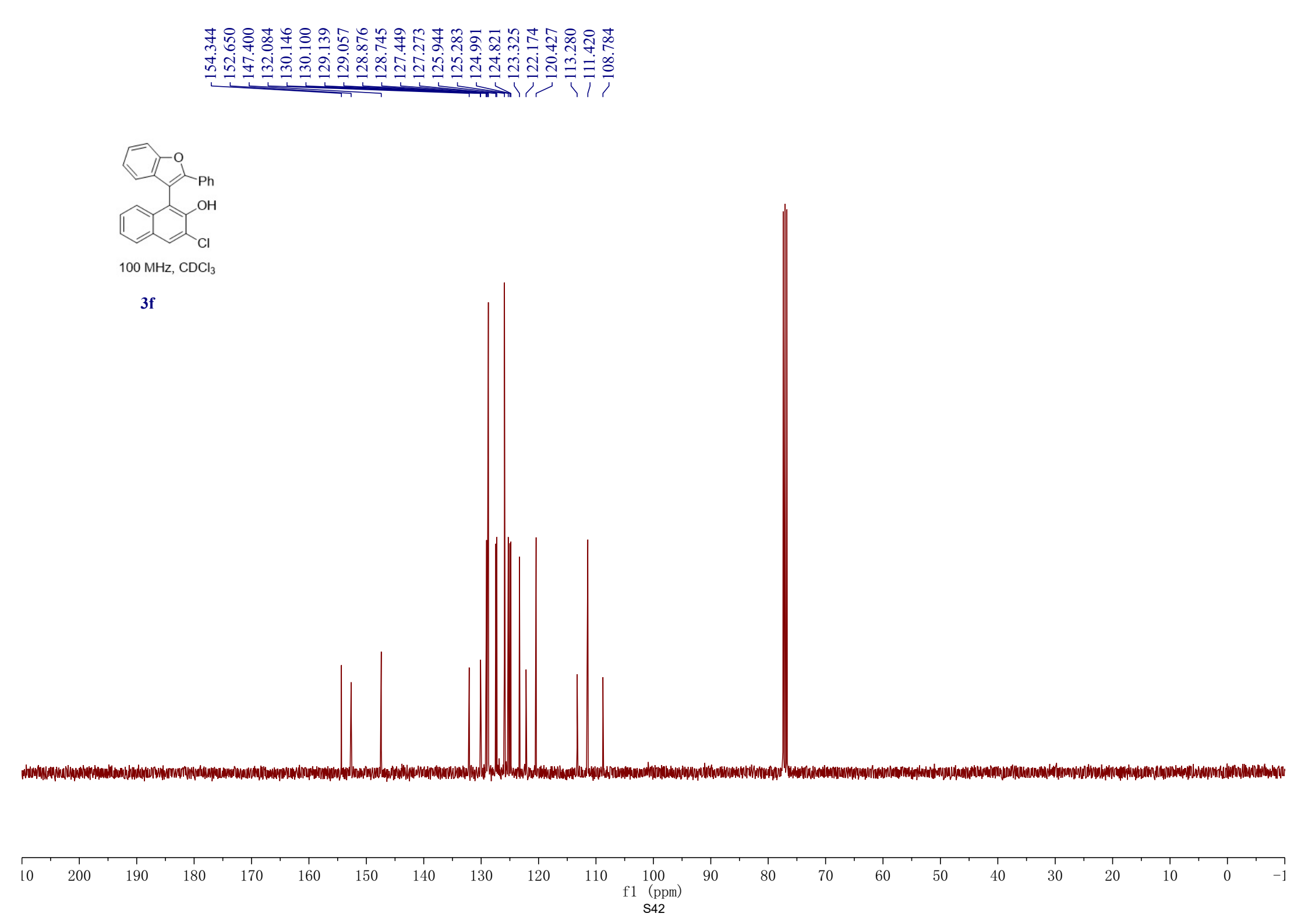


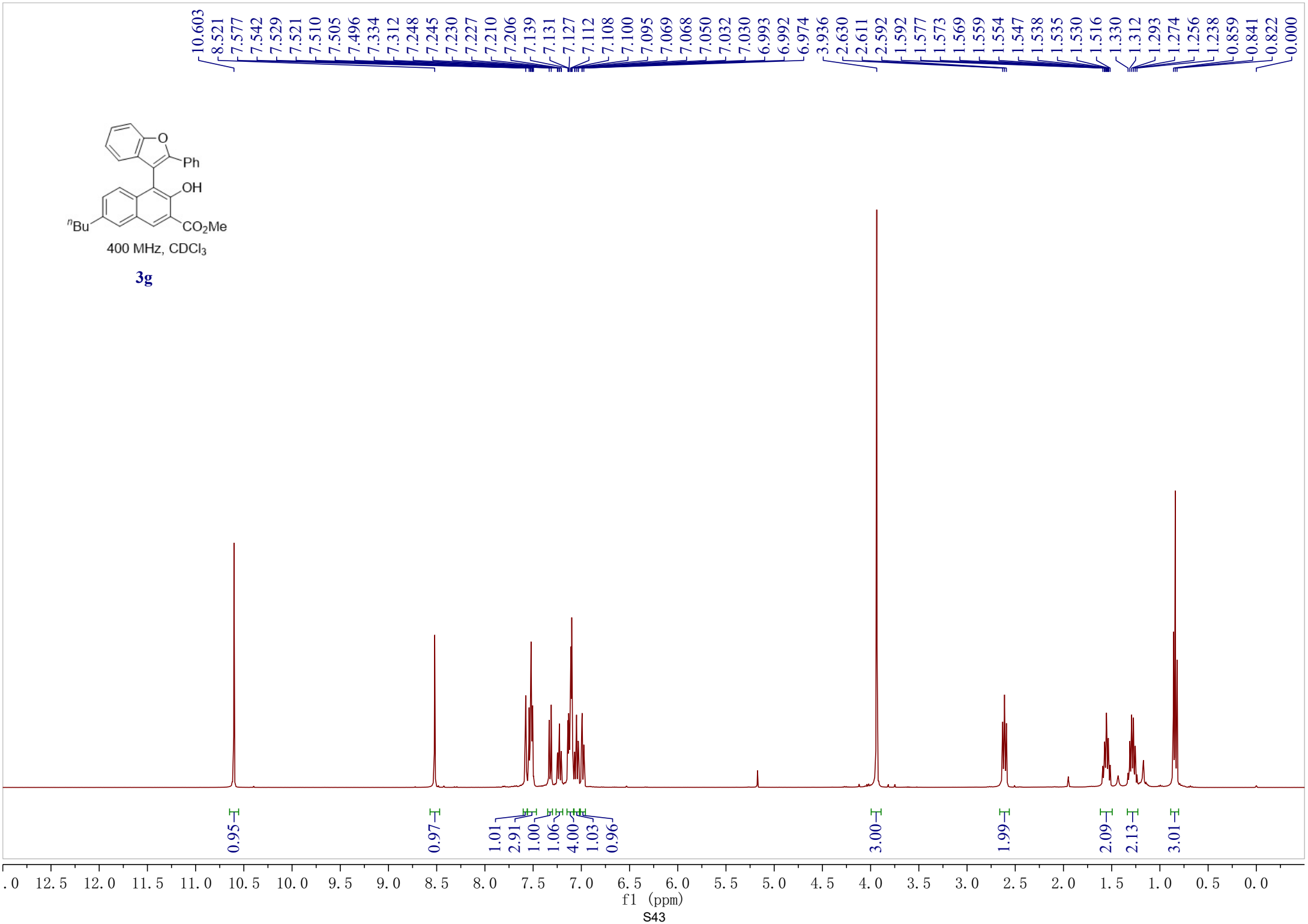
400 MHz, $CDCl_3$

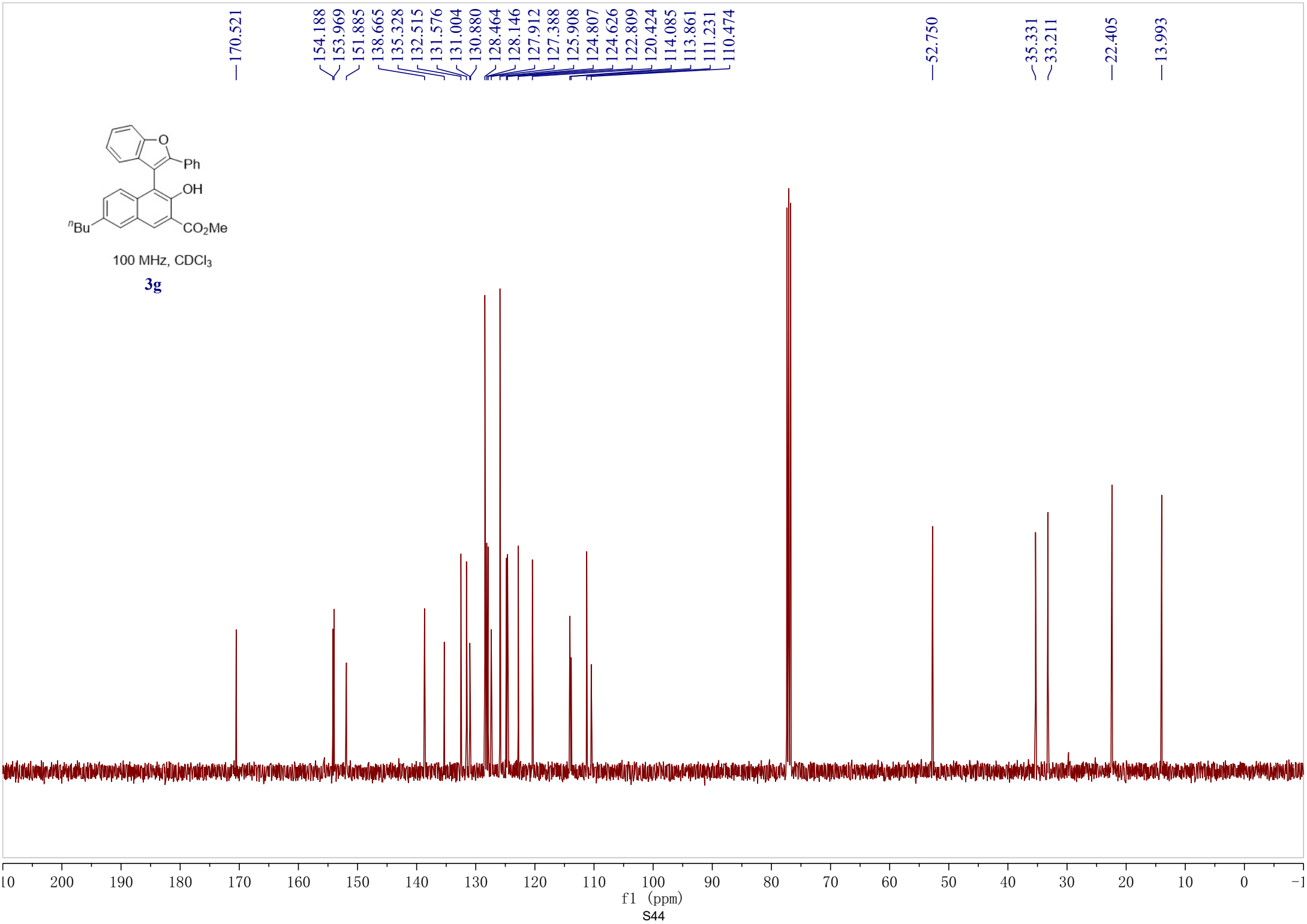
3e

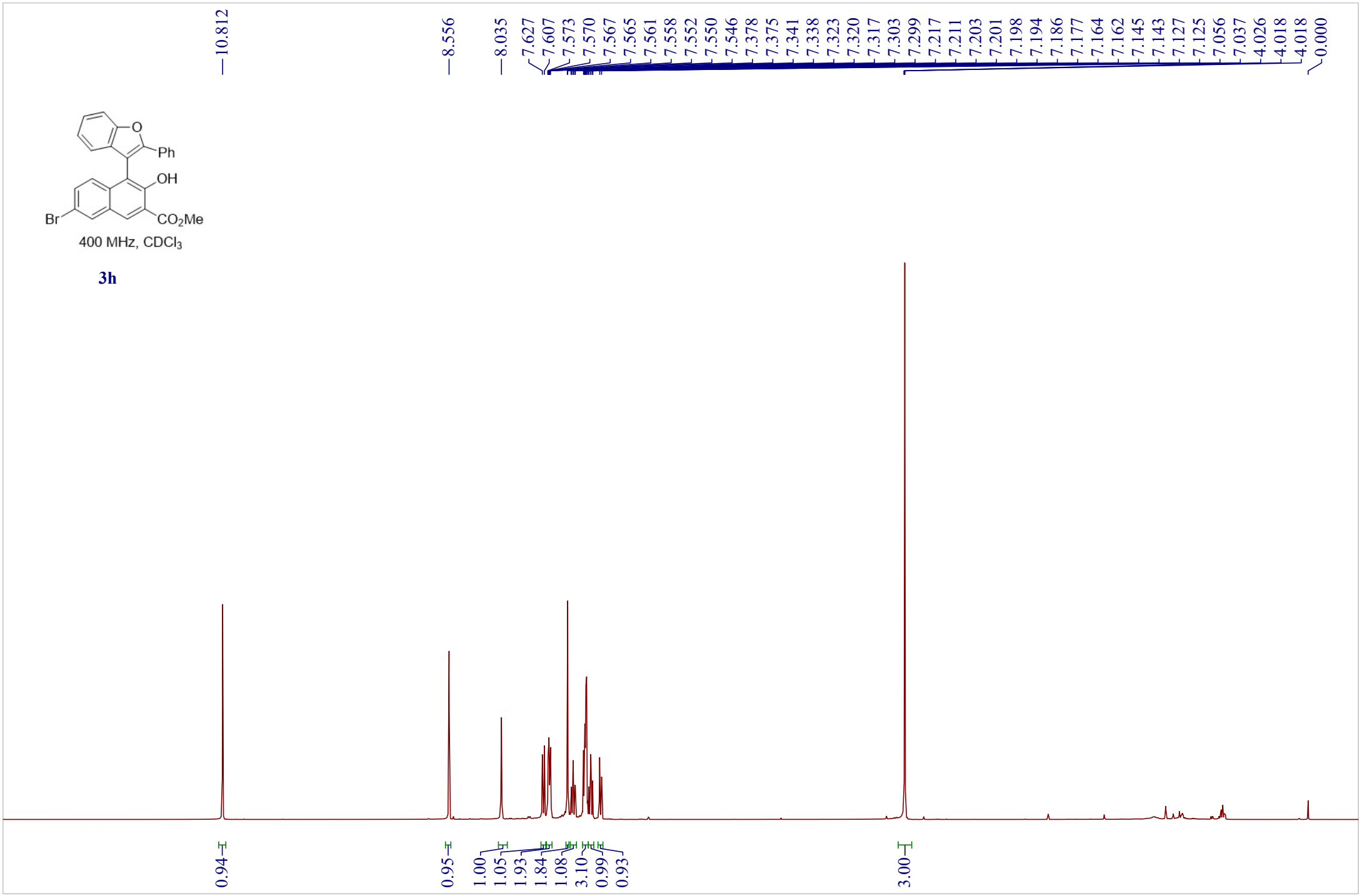

168.838
154.709
154.225
152.029
150.154
137.217
133.859
130.904
130.756
130.231
129.997
129.805
128.523
128.280
127.290
126.647
125.954
125.005
124.737
124.482
122.897
121.691
120.352
114.473
113.696
111.317
110.139
O
Ph
OH
CO2Ph
100 MHz, CDCl3
3e
f1 (ppm)

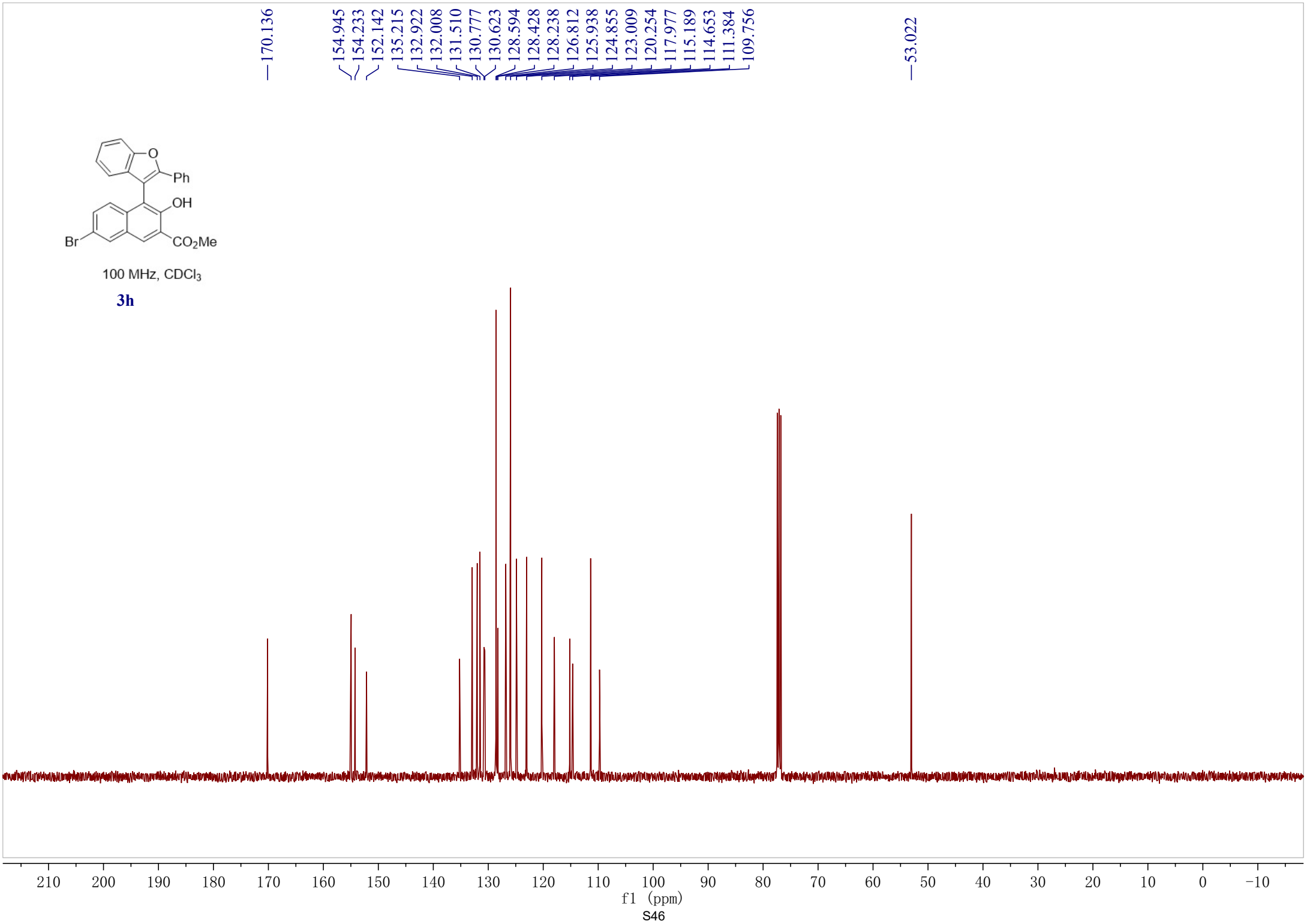

8.028
7.806
7.804
7.802
7.786
7.783
7.781
7.661
7.659
7.656
7.640
7.638
7.636
7.583
7.577
7.571
7.568
7.564
7.561
7.558
7.556
7.468
7.466
7.447
7.444
7.390
7.387
7.384
7.380
7.373
7.370
7.366
7.363
7.360
7.353
7.350
7.345
7.342
7.305
7.302
7.288
7.284
7.281
7.267
7.264
7.245
7.240
7.236
7.232
7.229
7.224
7.221
7.219
7.213
7.210
7.188
7.186
7.170
7.168
7.166
7.151
7.148
7.079
7.059
5.686
0.000
O
Ph
OH
Cl
400 MHz, CDCl3
3f
1.00
1.07
1.03
1.99
1.06
2.18
1.14
2.98
1.02
1.00
0.98
10.0
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
f1 (ppm)

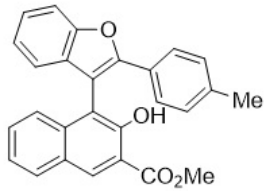

154.344
152.650
147.400
132.084
130.146
130.100
129.139
129.057
128.876
128.745
127.449
127.273
125.944
125.283
124.991
124.821
123.325
122.174
120.427
113.280
111.420
108.784
O
Ph
OH
Cl
100 MHz, CDCl3
3f
f1 (ppm)


10.603
8.521
7.577
7.542
7.529
7.521
7.510
7.505
7.496
7.334
7.312
7.248
7.245
7.230
7.227
7.210
7.206
7.139
7.131
7.127
7.112
7.108
7.100
7.095
7.069
7.068
7.050
7.032
7.030
6.993
6.992
6.974
3.936
2.630
2.611
2.592
1.592
1.577
1.573
1.569
1.559
1.554
1.547
1.538
1.535
1.530
1.516
1.330
1.312
1.293
1.274
1.256
1.238
0.859
0.841
0.822
0.000
O
Ph
OH
nBu
CO2Me
400 MHz, CDCl3
3g
0.95
0.97
1.01
2.91
1.00
1.06
4.00
1.03
0.96
3.00
1.99
2.09
2.13
3.01
f1 (ppm)


170.521
154.188
153.969
151.885
138.665
135.328
132.515
131.576
131.004
130.880
128.464
128.146
127.912
127.388
125.908
124.807
124.626
122.809
120.424
114.085
113.861
111.231
110.474
52.750
35.331
33.211
22.405
13.993
O
Ph
OH
nBu
CO2Me
100 MHz, CDCl3
3g
f1 (ppm)

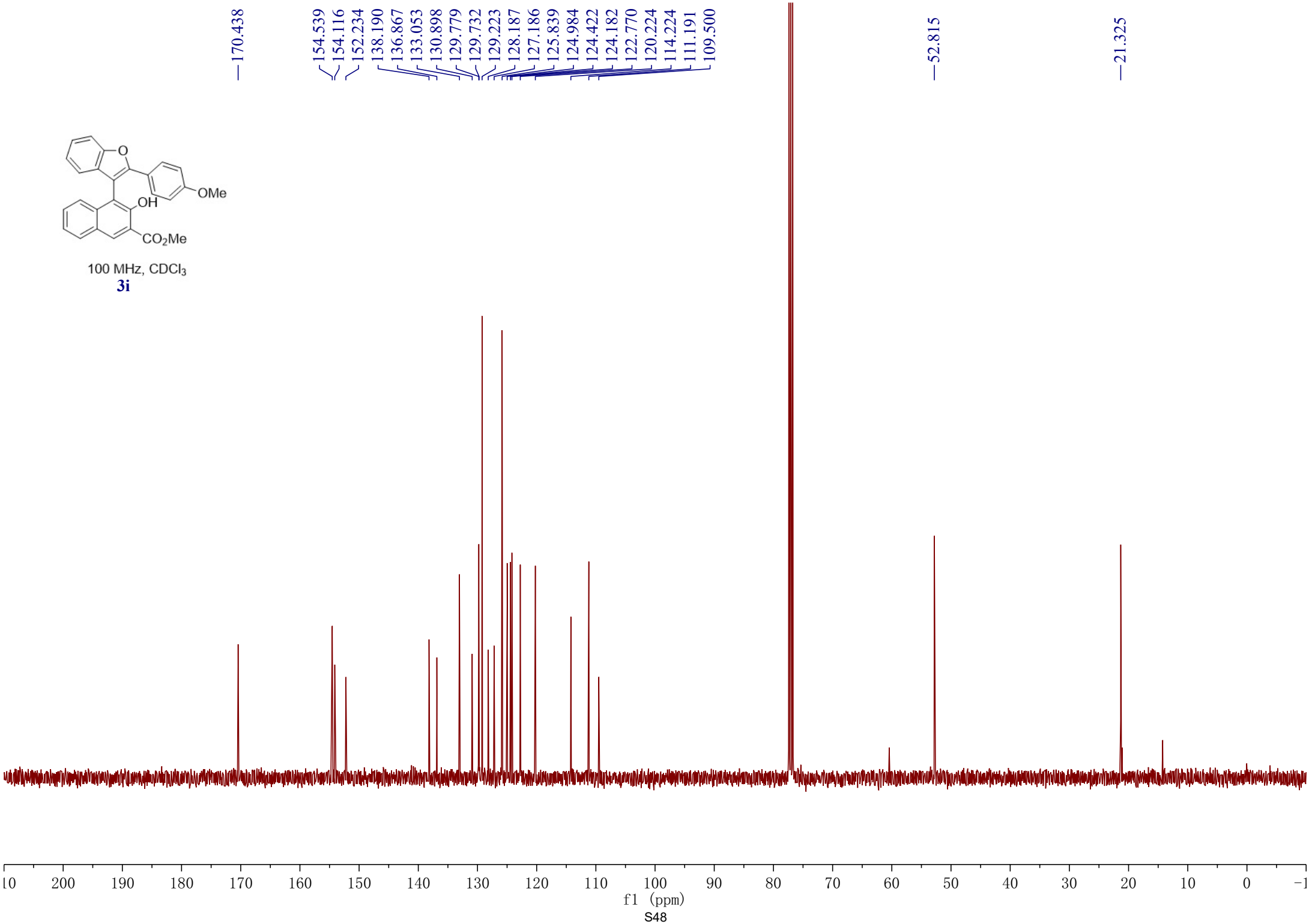

10.812
8.556
8.035
7.627
7.607
7.573
7.570
7.567
7.565
7.561
7.558
7.552
7.550
7.546
7.378
7.375
7.341
7.338
7.323
7.320
7.317
7.303
7.299
7.217
7.211
7.203
7.201
7.198
7.194
7.186
7.177
7.164
7.162
7.145
7.143
7.127
7.125
7.056
7.037
4.026
4.018
4.018
0.000
O
Ph
OH
Br
CO2Me
400 MHz, CDCl3
3h
0.94
0.95
1.00
1.05
1.93
1.84
1.08
3.10
0.99
0.93
3.00
f1 (ppm)

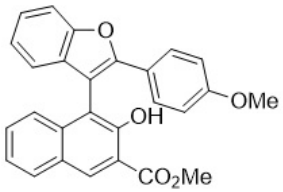

170.136
154.945
154.233
152.142
135.215
132.922
132.008
131.510
130.777
130.623
128.594
128.428
128.238
126.812
125.938
124.855
123.009
120.254
117.977
115.189
114.653
111.384
109.756
53.022
O
Ph
OH
Br
CO2Me
100 MHz, CDCl3
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



400 MHz, $CDCl_3$

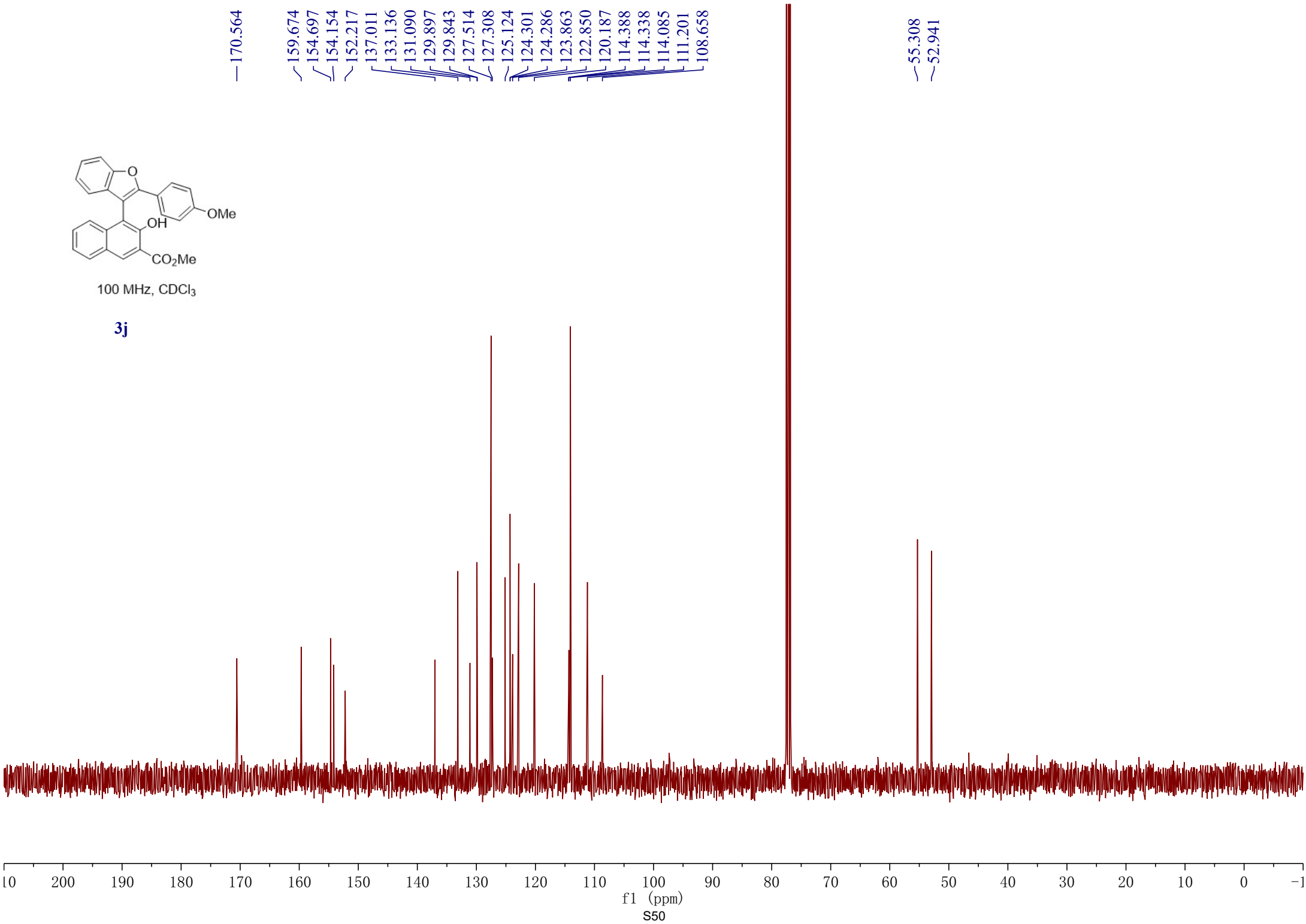
3i

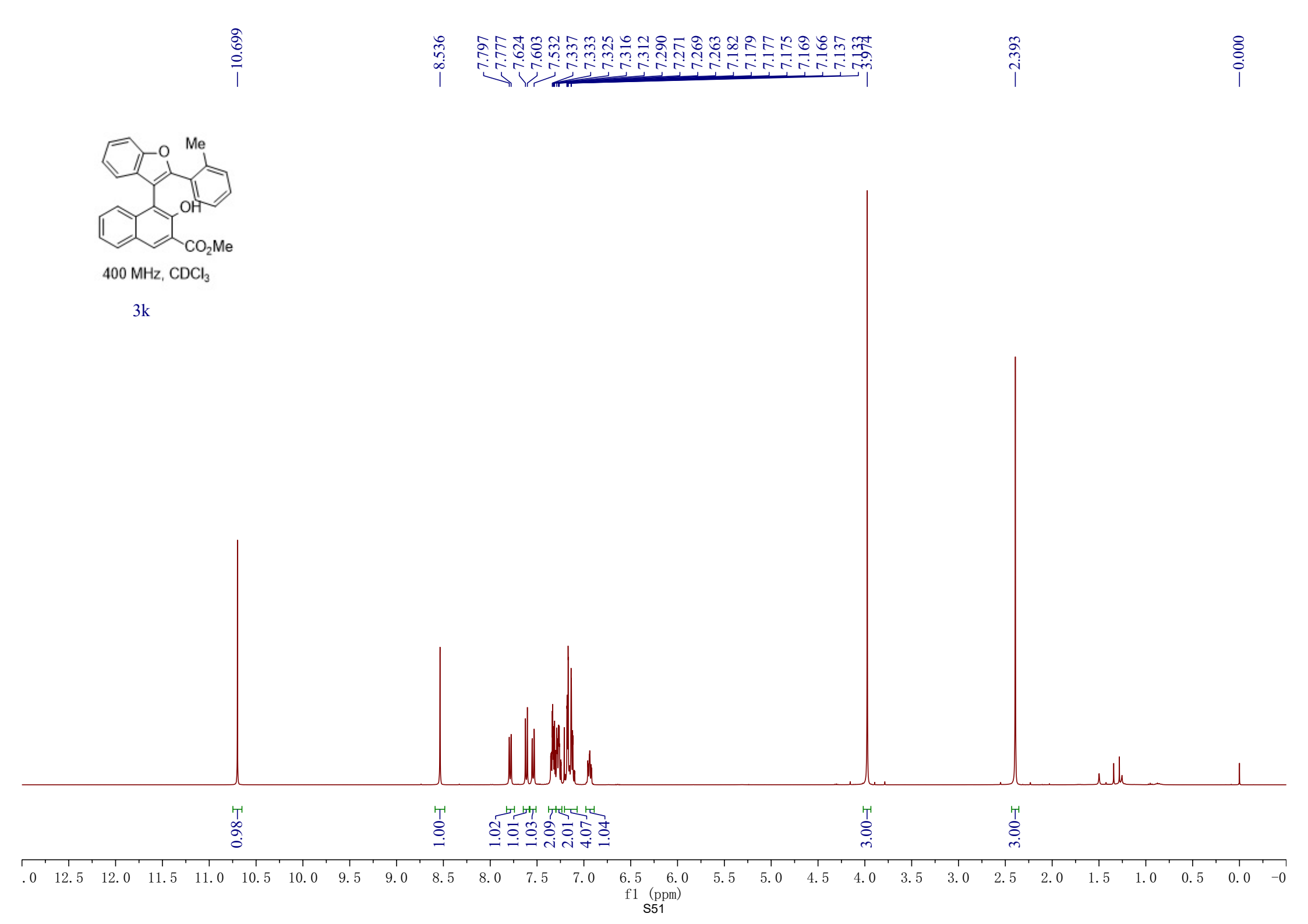

170.438
154.539
154.116
152.234
138.190
136.867
133.053
130.898
129.779
129.732
129.223
128.187
127.186
125.839
124.984
124.422
124.182
122.770
120.224
114.224
111.191
109.500
52.815
21.325
O
OMe
OH
CO2Me
100 MHz, CDCl3
3i
f1 (ppm)



400 MHz, $CDCl_3$

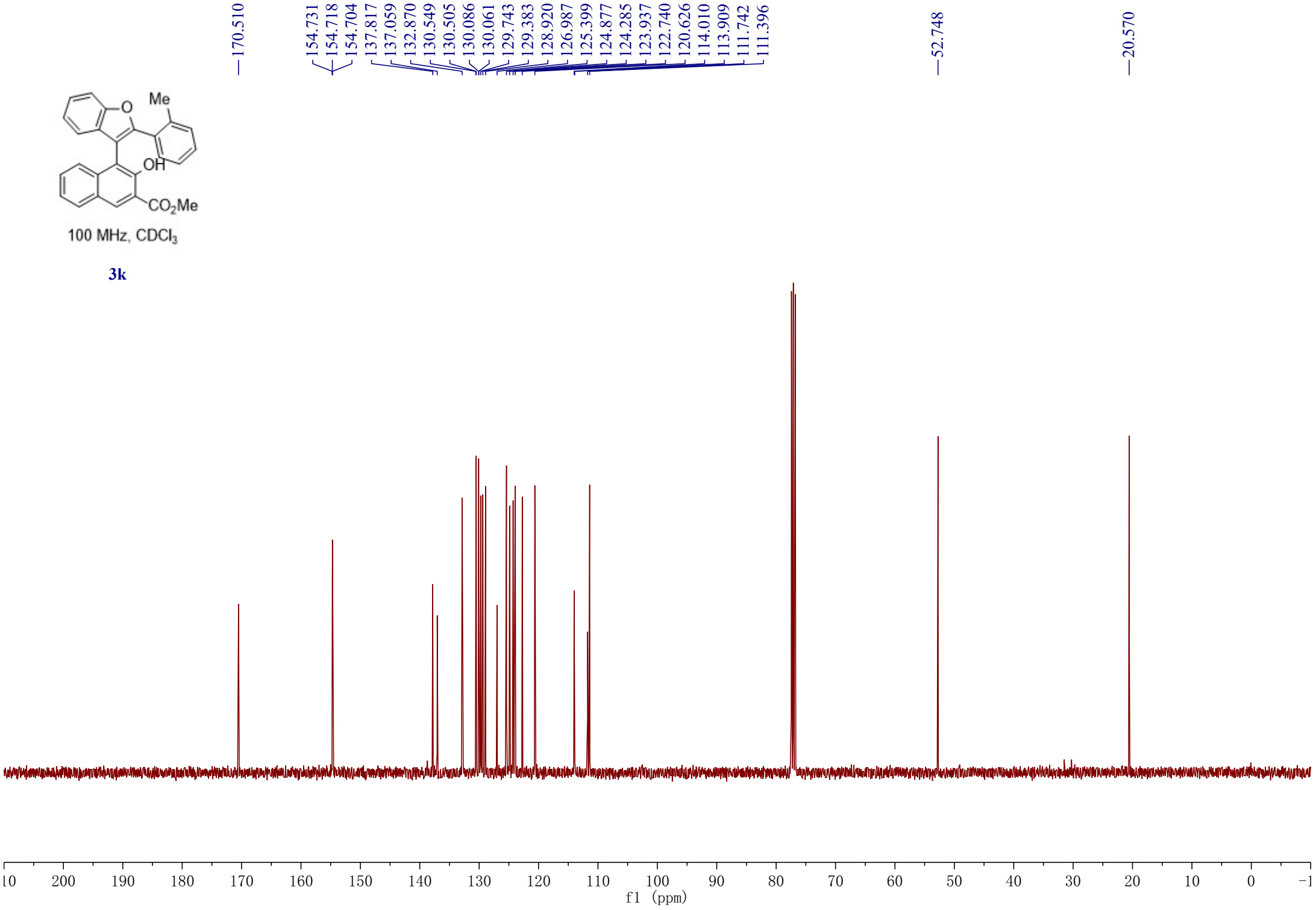
3j

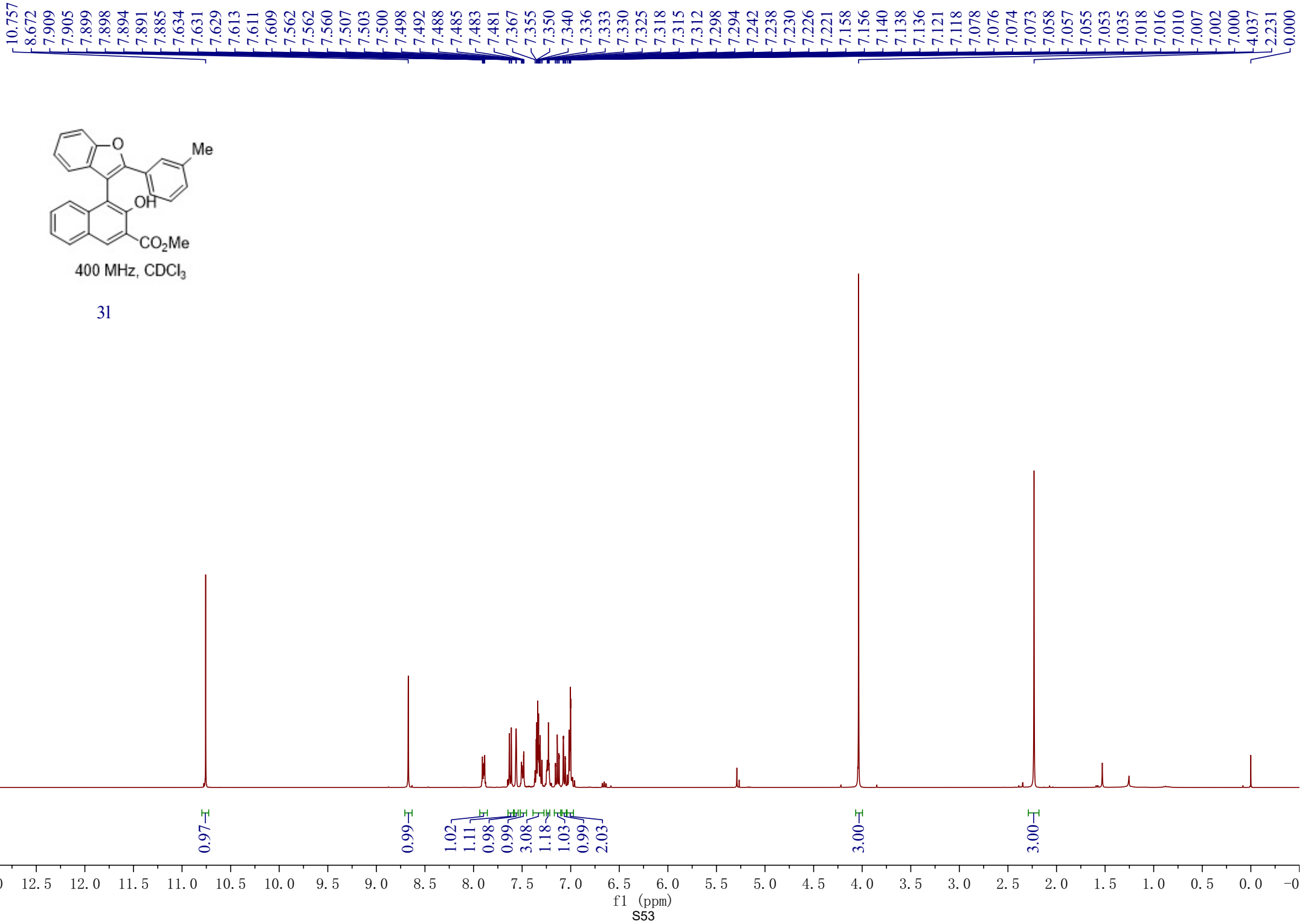

170.564
159.674
154.697
154.154
152.217
137.011
133.136
131.090
129.897
129.843
127.514
127.308
125.124
124.301
124.286
123.863
122.850
120.187
114.388
114.338
114.085
111.201
108.658
55.308
52.941
O
OMe
OH
CO2Me
100 MHz, CDCl3
3j
f1 (ppm)

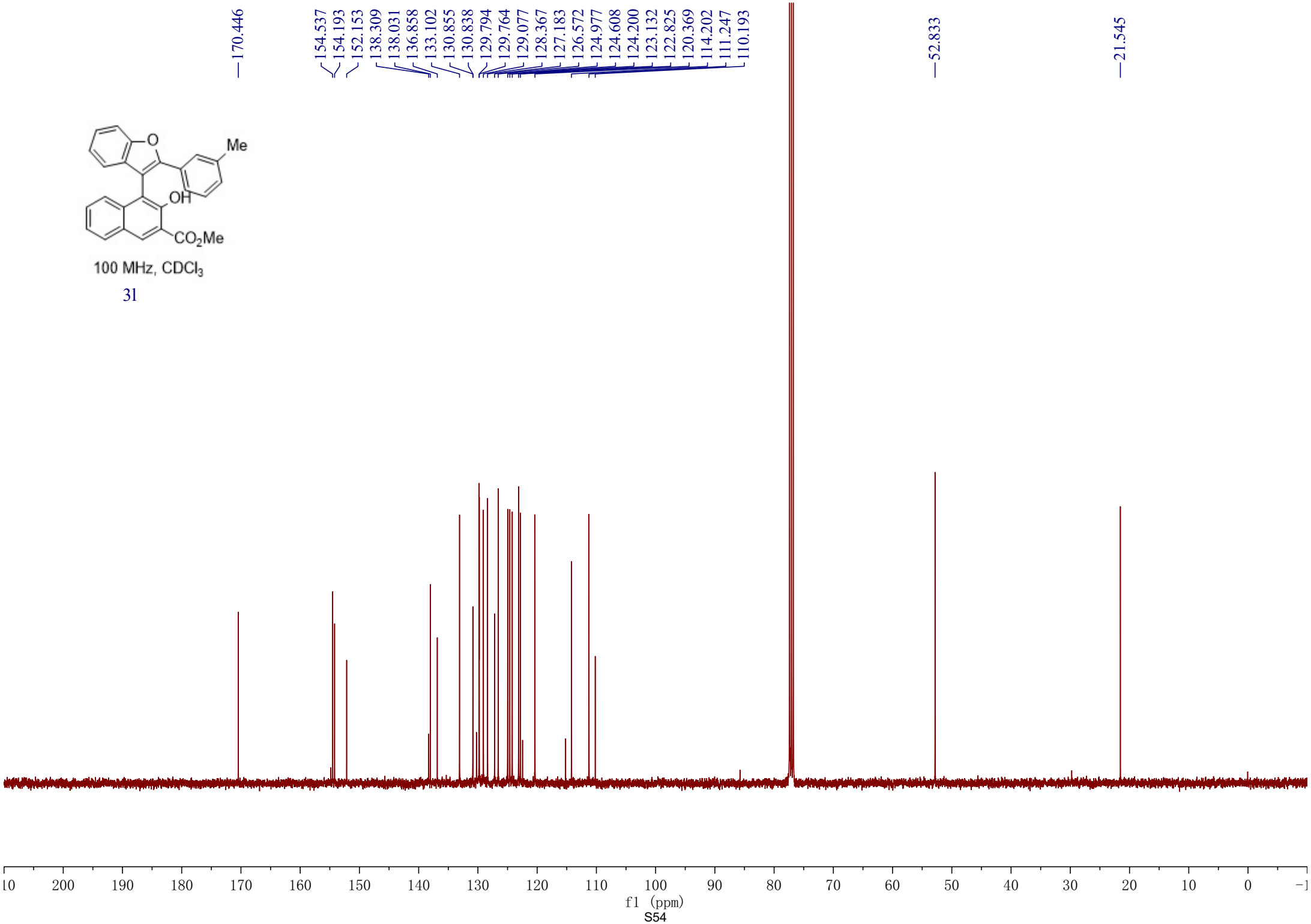

10.699
8.536
7.797
7.777
7.624
7.603
7.532
7.337
7.333
7.325
7.316
7.312
7.290
7.271
7.269
7.263
7.182
7.179
7.177
7.175
7.169
7.166
7.137
7.133
3.974
2.393
0.000
Me
O
OH
CO2Me
400 MHz, CDCl3
3k
0.98
1.00
1.02
1.01
1.03
2.09
2.01
4.07
1.04
3.00
3.00
f1 (ppm)

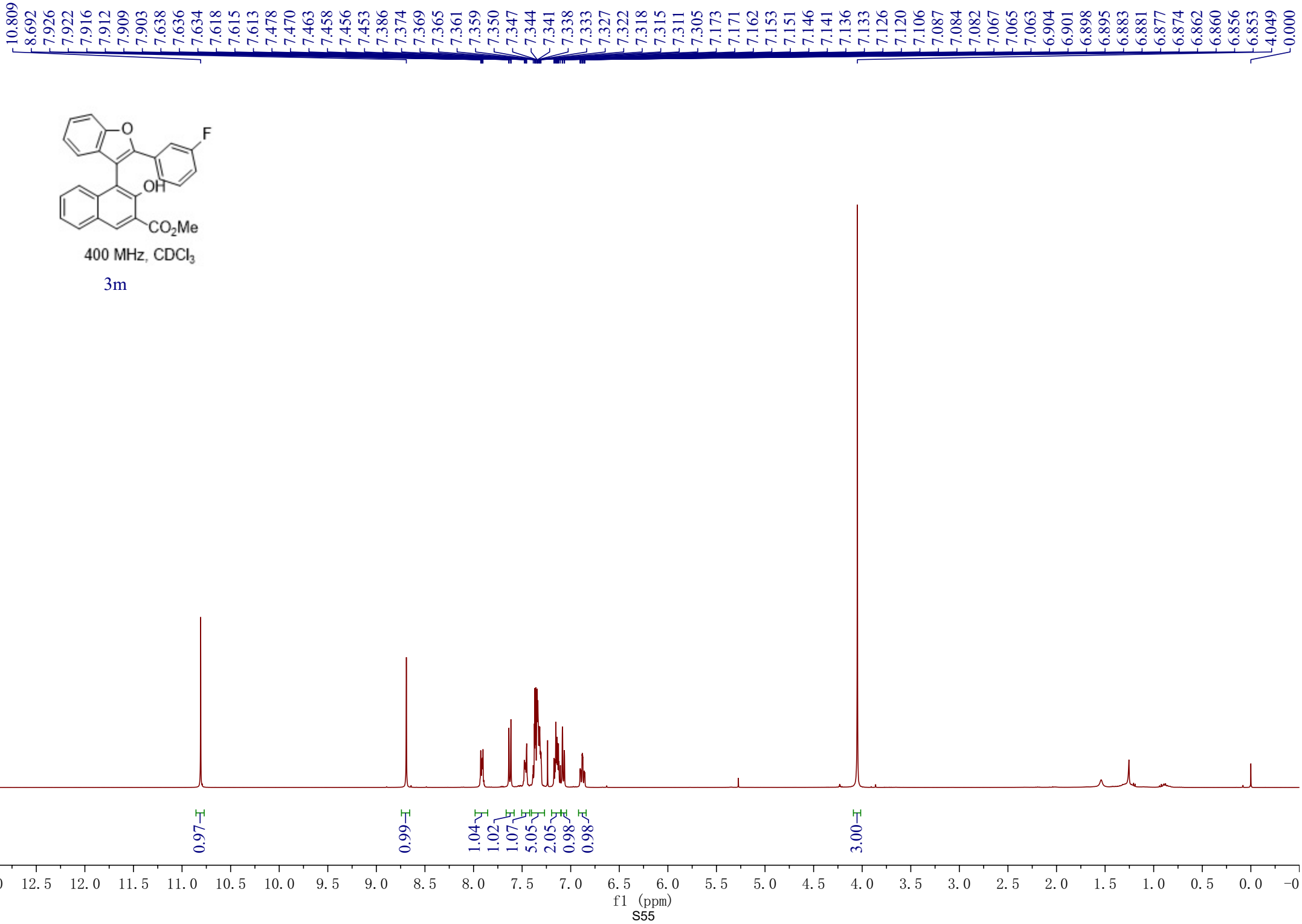
100 MHz, $CDCl_3$

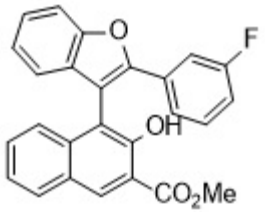
3k




10.757
8.672
7.909
7.905
7.899
7.898
7.894
7.891
7.885
7.634
7.631
7.629
7.613
7.611
7.609
7.562
7.562
7.560
7.507
7.503
7.500
7.498
7.492
7.488
7.485
7.483
7.481
7.367
7.355
7.350
7.340
7.336
7.333
7.330
7.325
7.318
7.315
7.312
7.298
7.294
7.242
7.238
7.230
7.226
7.221
7.158
7.156
7.140
7.138
7.136
7.121
7.118
7.078
7.076
7.074
7.073
7.058
7.057
7.055
7.053
7.035
7.018
7.016
7.010
7.007
7.002
7.000
4.037
2.231
0.000
O
Me
OH
CO2Me
400 MHz, CDCl3
31
0.97
0.99
1.02
1.11
0.98
0.99
3.08
1.18
1.03
0.99
2.03
3.00
3.00
f1 (ppm)


170.446
154.537
154.193
152.153
138.309
138.031
136.858
133.102
130.855
130.838
129.794
129.764
129.077
128.367
127.183
126.572
124.977
124.608
124.200
123.132
122.825
120.369
114.202
111.247
110.193
52.833
21.545
O
Me
OH
CO2Me
100 MHz, CDCl3
31
f1 (ppm)


10.809
8.692
7.926
7.922
7.916
7.912
7.909
7.903
7.638
7.636
7.634
7.618
7.615
7.613
7.478
7.470
7.463
7.458
7.456
7.453
7.386
7.374
7.369
7.365
7.361
7.359
7.350
7.347
7.344
7.341
7.338
7.333
7.327
7.322
7.318
7.315
7.311
7.305
7.173
7.171
7.162
7.153
7.151
7.146
7.141
7.136
7.133
7.126
7.120
7.106
7.087
7.084
7.082
7.067
7.065
7.063
6.904
6.901
6.898
6.895
6.883
6.881
6.877
6.874
6.862
6.860
6.856
6.853
4.049
0.000
O
F
OH
CO2Me
400 MHz, CDCl3
3m
0.97
0.99
1.04
1.02
1.07
5.05
2.05
0.98
0.98
3.00
f1 (ppm)

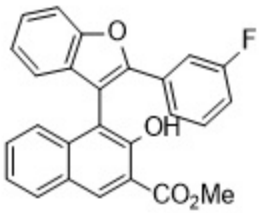


100 MHz, $CDCl_3$

3m

170.507
164.101
161.668
154.608
154.319
150.740
150.708
136.747
133.509
133.118
133.033
130.702
130.180
130.097
130.012
127.314
125.240
124.805
124.421
123.136
121.673
121.644
120.711
115.255
115.043
114.346
113.606
112.942
112.705
111.509
111.465
52.972

f1 (ppm)

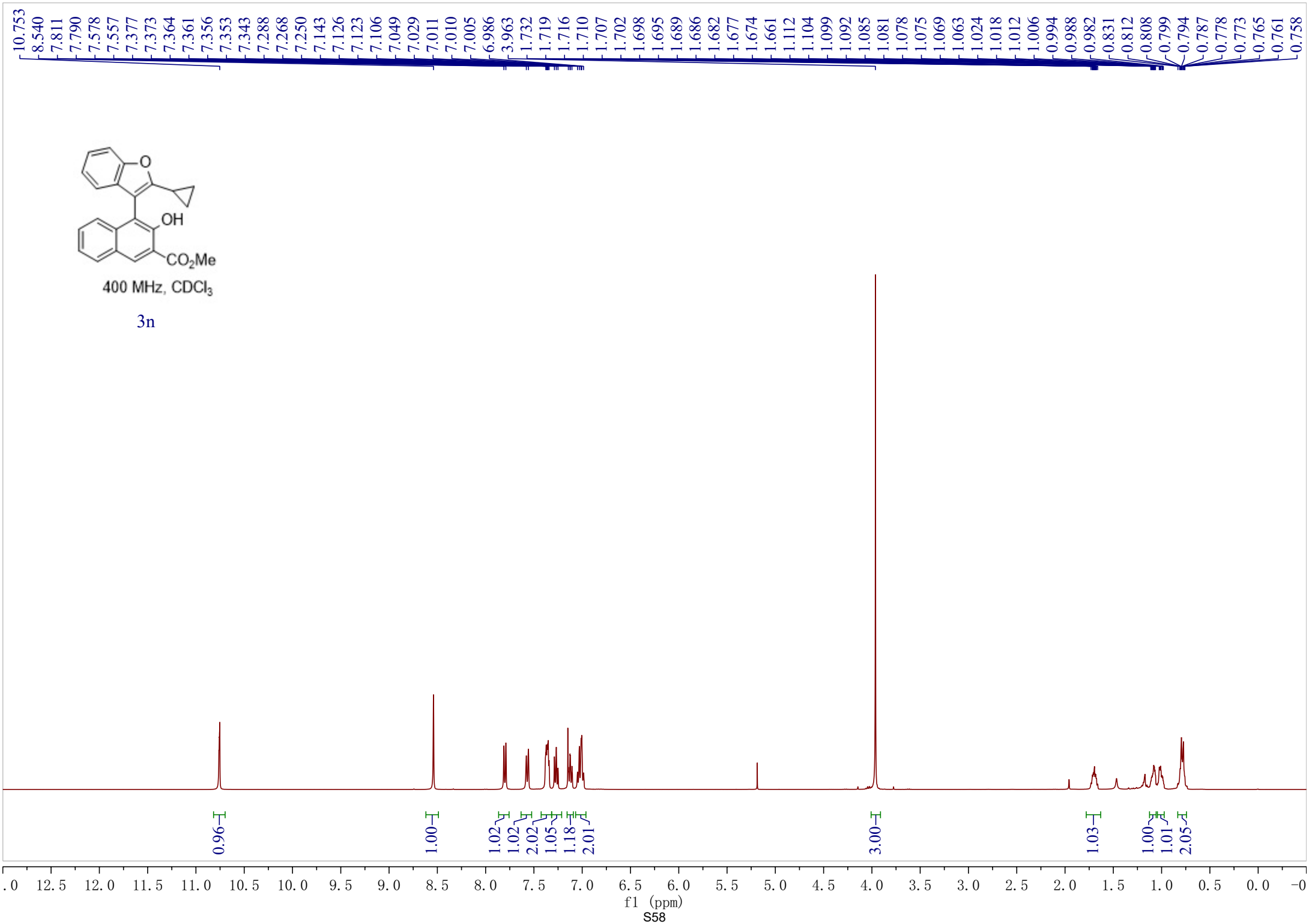


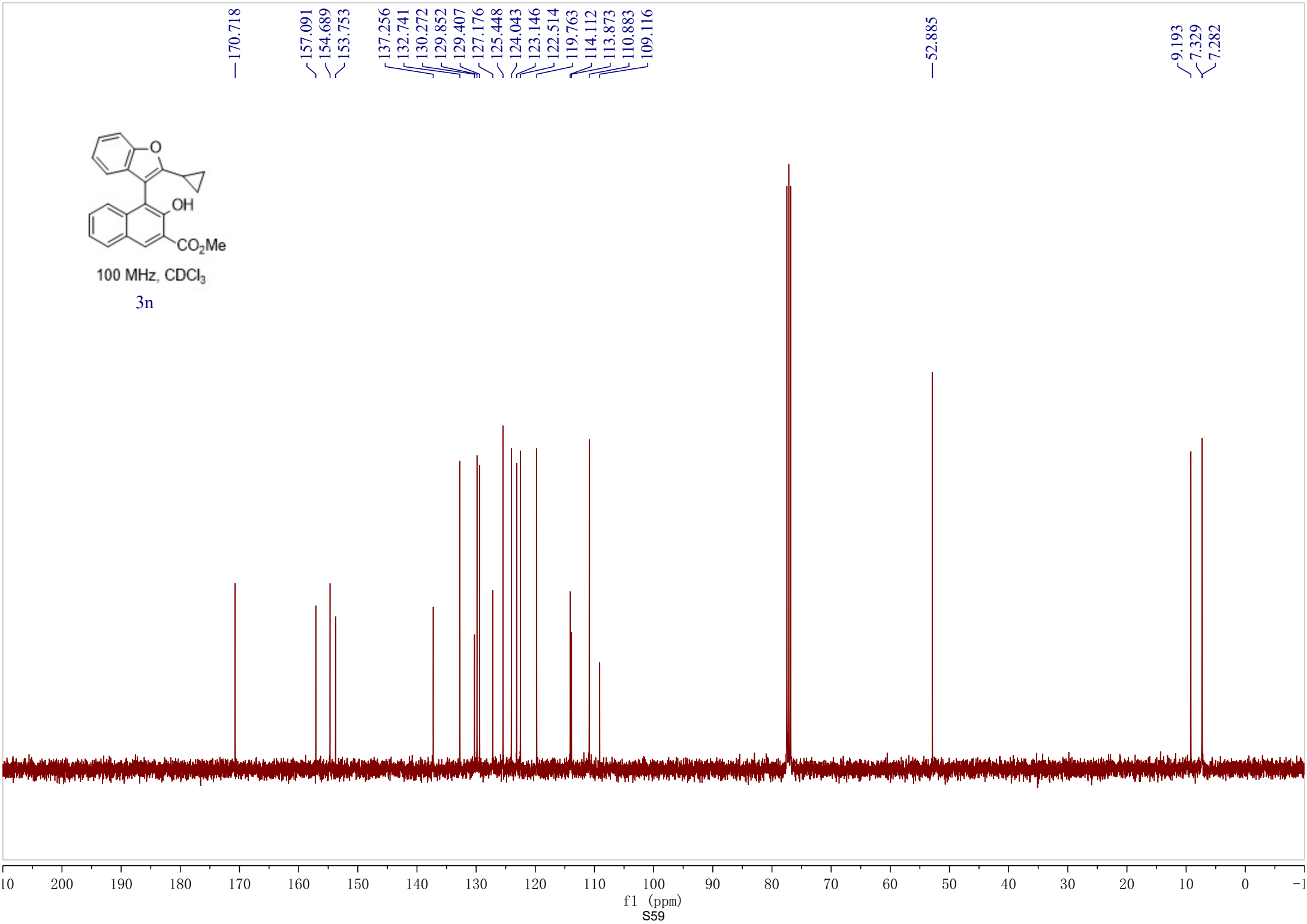
100 MHz, $CDCl_3$

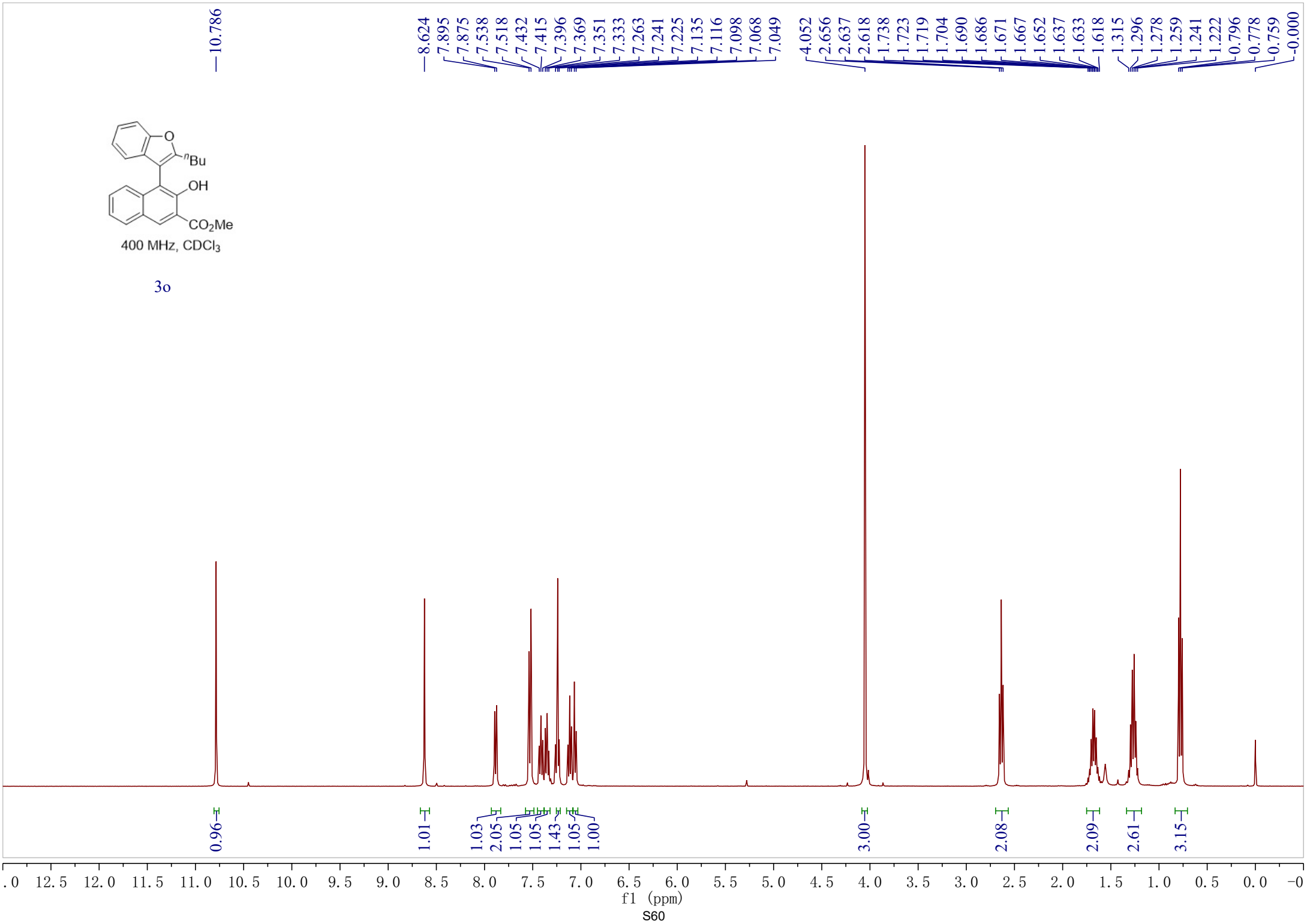
3m

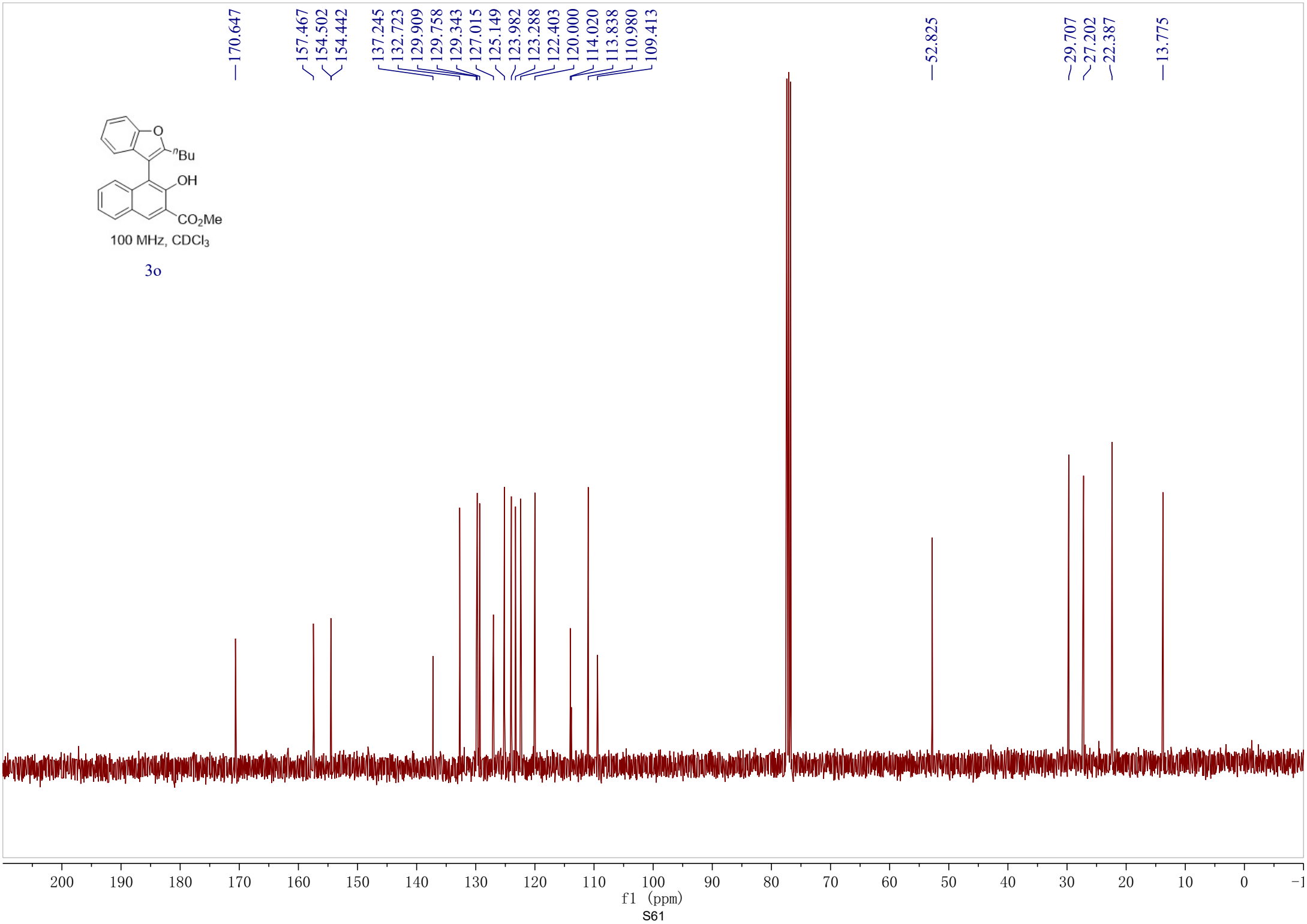
-112.767

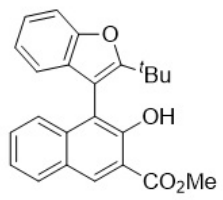
f1 (ppm)


10.753
8.540
7.811
7.790
7.578
7.557
7.377
7.373
7.364
7.361
7.356
7.353
7.343
7.288
7.268
7.250
7.143
7.126
7.123
7.106
7.049
7.029
7.011
7.010
7.005
6.986
3.963
1.732
1.719
1.716
1.710
1.707
1.702
1.698
1.695
1.689
1.686
1.682
1.677
1.674
1.661
1.112
1.104
1.099
1.092
1.085
1.081
1.078
1.075
1.069
1.063
1.024
1.018
1.012
1.006
0.994
0.988
0.982
0.831
0.812
0.808
0.799
0.794
0.787
0.778
0.773
0.765
0.761
0.758
O
OH
CO2Me
400 MHz, CDCl3
3n
0.96
1.00
1.02
1.02
2.02
1.05
1.18
2.01
3.00
1.03
1.00
1.01
2.05
f1 (ppm)


170.718
157.091
154.689
153.753
137.256
132.741
130.272
129.852
129.407
127.176
125.448
124.043
123.146
122.514
119.763
114.112
113.873
110.883
109.116
52.885
9.193
7.329
7.282
O
OH
CO2Me
100 MHz, CDCl3
3n
f1 (ppm)

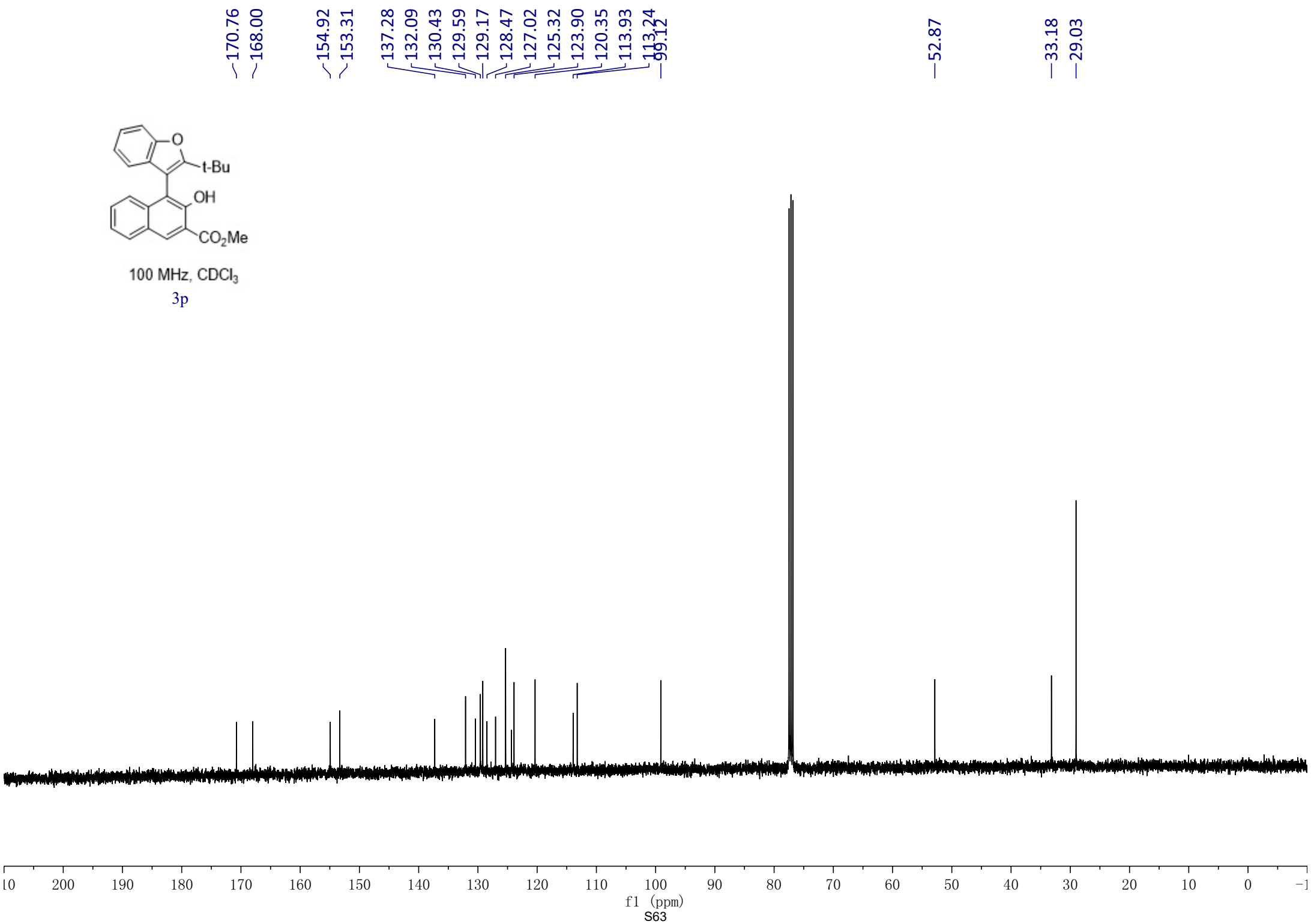

10.786
8.624
7.895
7.875
7.538
7.518
7.432
7.415
7.396
7.369
7.351
7.333
7.263
7.241
7.225
7.135
7.116
7.098
7.068
7.049
4.052
2.656
2.637
2.618
1.738
1.723
1.719
1.704
1.690
1.686
1.671
1.667
1.652
1.637
1.633
1.618
1.315
1.296
1.278
1.259
1.241
1.222
0.796
0.778
0.759
-0.000
O
nBu
OH
CO2Me
400 MHz, CDCl3
3o
0.96
1.01
1.03
2.05
1.05
1.05
1.43
1.05
1.00
3.00
2.08
2.09
2.61
3.15
f1 (ppm)

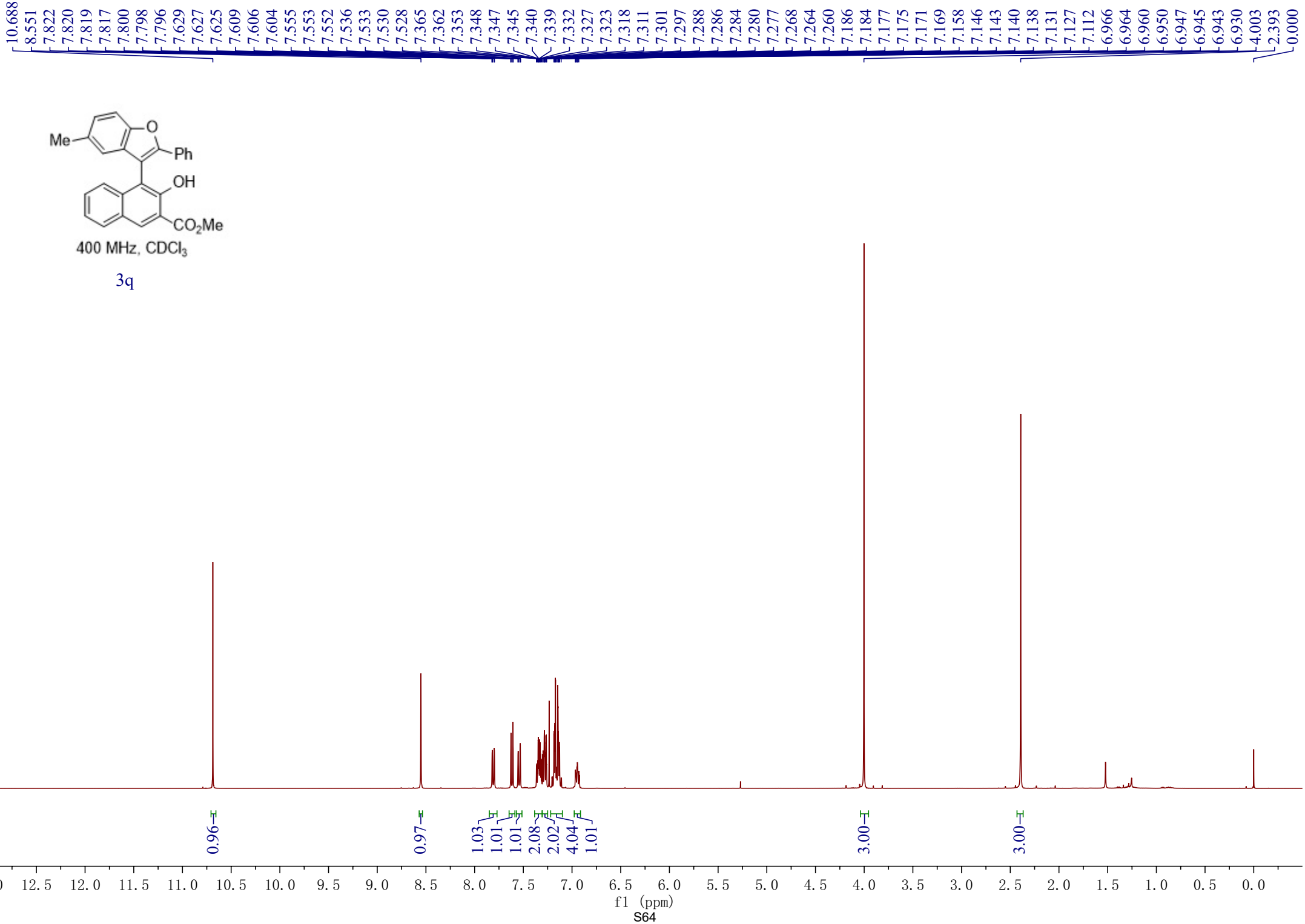

170.647
157.467
154.502
154.442
137.245
132.723
129.909
129.758
129.343
127.015
125.149
123.982
123.288
122.403
120.000
114.020
113.838
110.980
109.413
52.825
29.707
27.202
22.387
13.775
O
nBu
OH
CO2Me
100 MHz, CDCl3
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

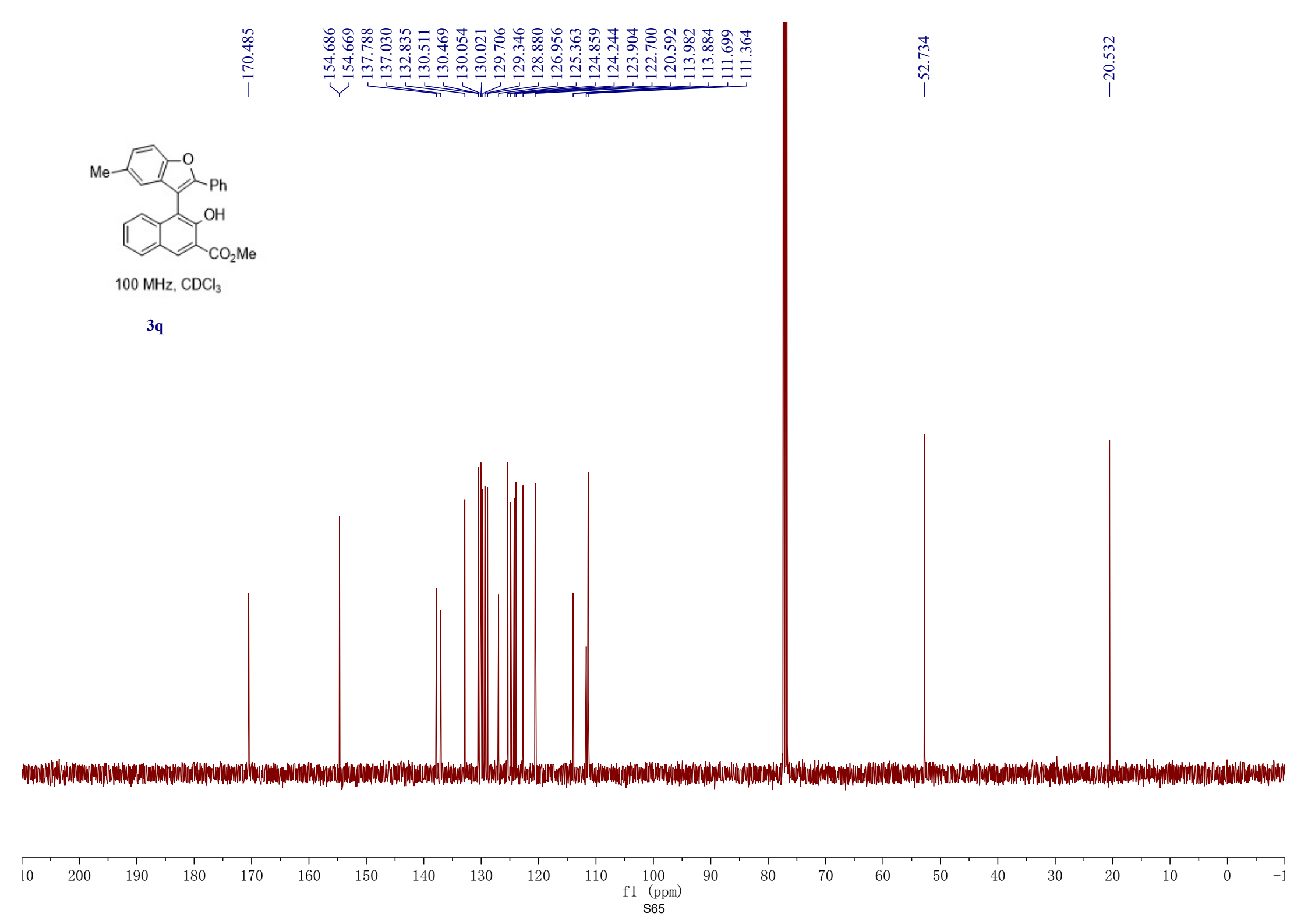


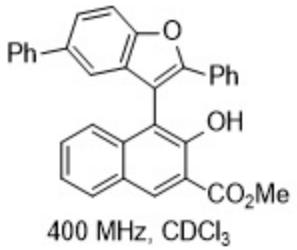
400 MHz, $CDCl_3$

3p


170.76
168.00
154.92
153.31
137.28
132.09
130.43
129.59
129.17
128.47
127.02
125.32
123.90
120.35
113.93
113.24
99.12
52.87
33.18
29.03
O
t-Bu
OH
CO2Me
100 MHz, CDCl3
3p
f1 (ppm)

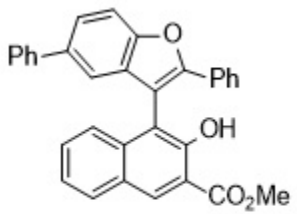

10.688
8.551
7.822
7.820
7.819
7.817
7.800
7.798
7.796
7.629
7.627
7.625
7.609
7.606
7.604
7.555
7.553
7.552
7.536
7.533
7.530
7.528
7.365
7.362
7.353
7.348
7.347
7.345
7.340
7.339
7.332
7.327
7.323
7.318
7.311
7.301
7.297
7.288
7.286
7.284
7.280
7.277
7.268
7.264
7.260
7.186
7.184
7.177
7.175
7.171
7.169
7.158
7.146
7.143
7.140
7.138
7.131
7.127
7.112
6.966
6.964
6.960
6.950
6.947
6.945
6.943
6.930
4.003
2.393
0.000
Me
O
Ph
OH
CO2Me
400 MHz, CDCl3
3q
0.96
0.97
1.03
1.01
1.01
2.08
2.02
4.04
1.01
3.00
3.00
f1 (ppm)


170.485
154.686
154.669
137.788
137.030
132.835
130.511
130.469
130.054
130.021
129.706
129.346
128.880
126.956
125.363
124.859
124.244
123.904
122.700
120.592
113.982
113.884
111.699
111.364
52.734
20.532
Me
O
Ph
OH
CO2Me
100 MHz, CDCl3
3q
f1 (ppm)



400 MHz, $CDCl_3$

3r

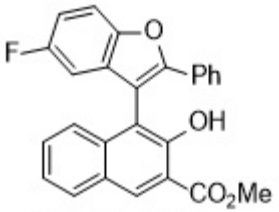


100 MHz, $CDCl_3$

3r

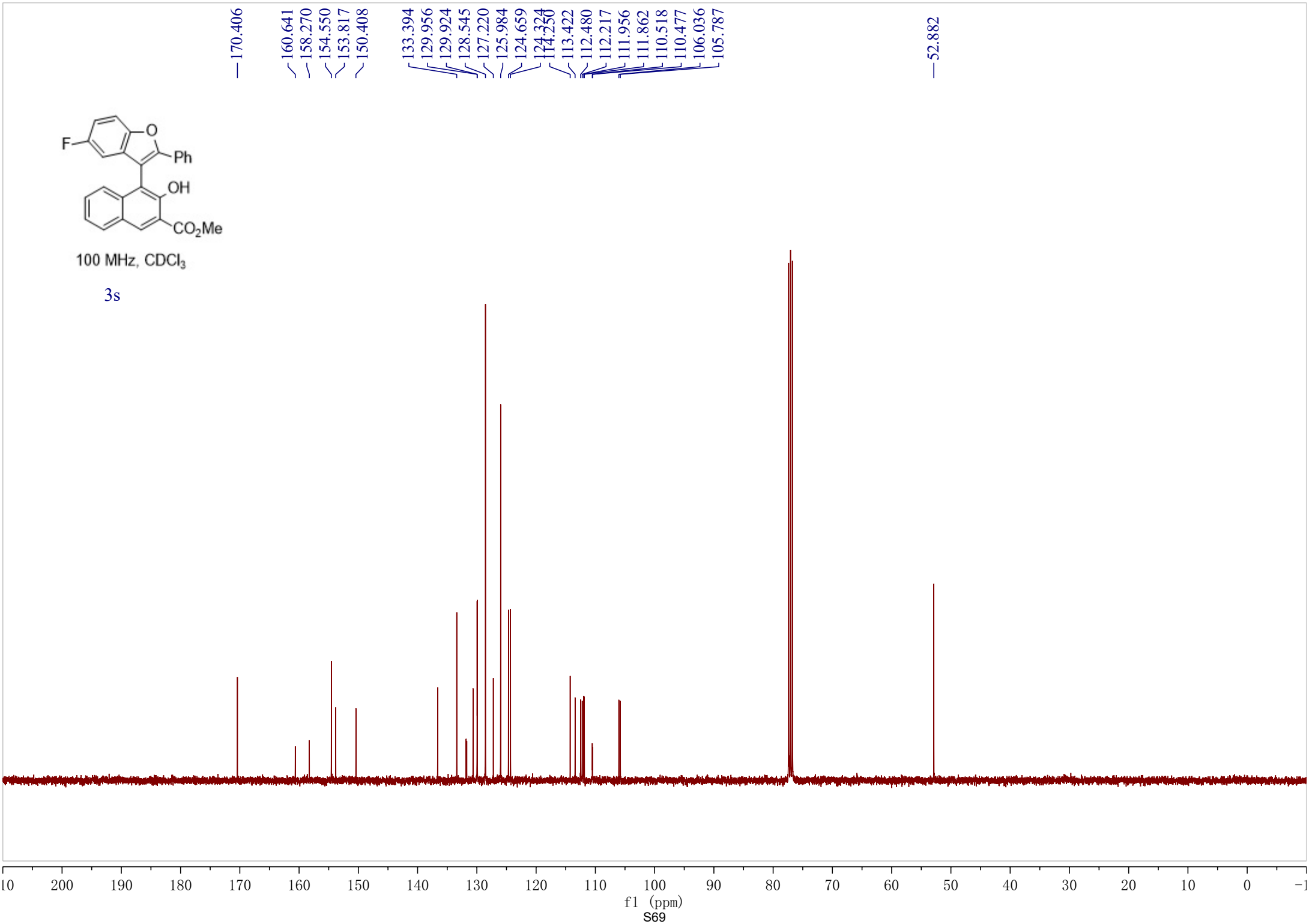
170.435
154.587
153.886
152.641
141.696
136.820
136.652
133.228
131.324
130.888
129.884
129.838
128.573
128.518
128.301
127.484
127.222
126.747
125.937
124.891
124.442
124.275
118.811
114.268
113.928
111.417
110.484
52.855

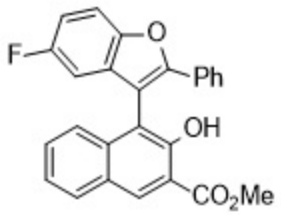
f1 (ppm)



400 MHz, $CDCl_3$

3s


170.406
160.641
158.270
154.550
153.817
150.408
133.394
129.956
129.924
128.545
127.220
125.984
124.659
124.324
124.250
113.422
112.480
112.217
111.956
111.862
110.518
110.477
106.036
105.787
52.882
F
O
Ph
OH
CO2Me
100 MHz, CDCl3
3s
f1 (ppm)

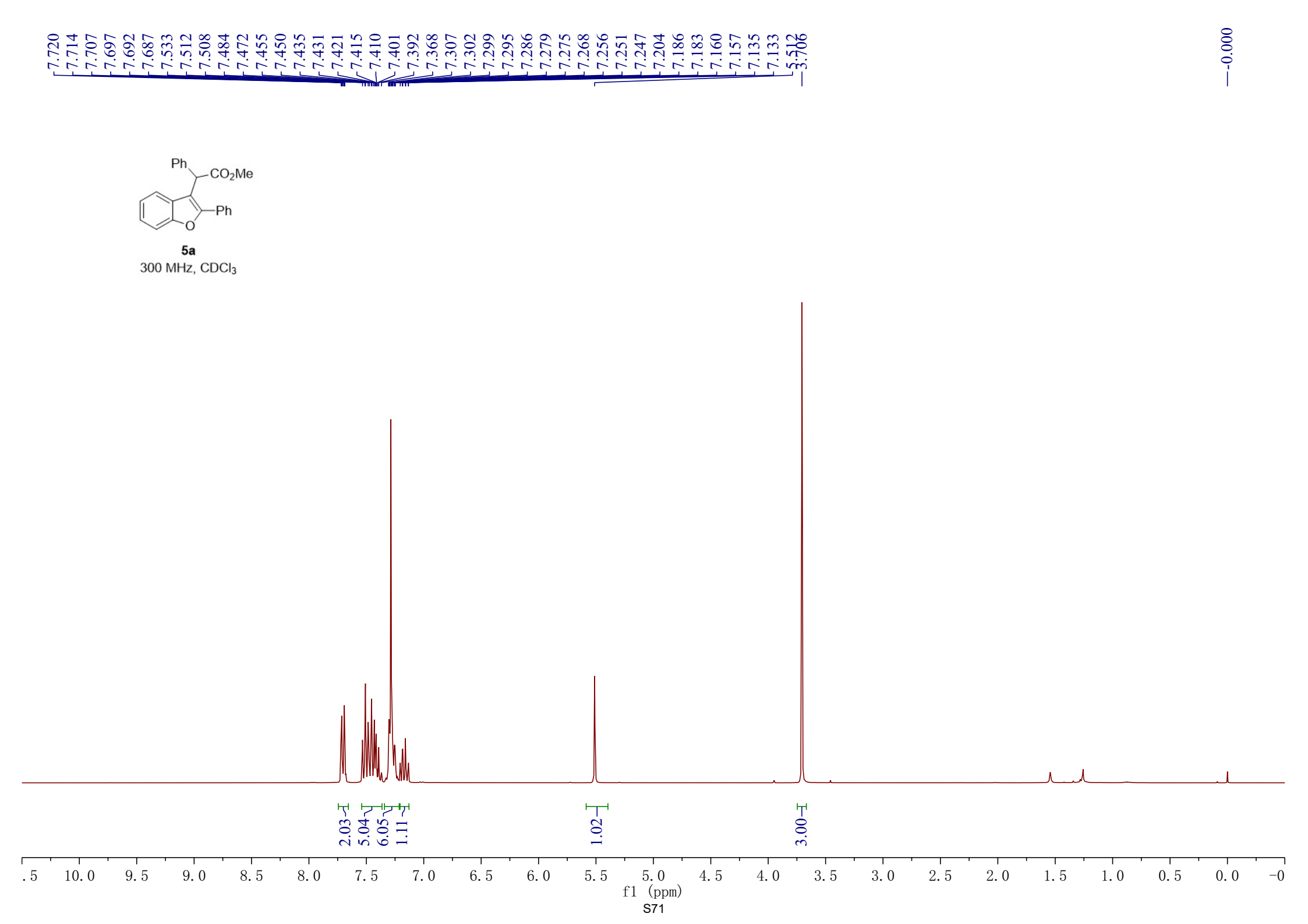


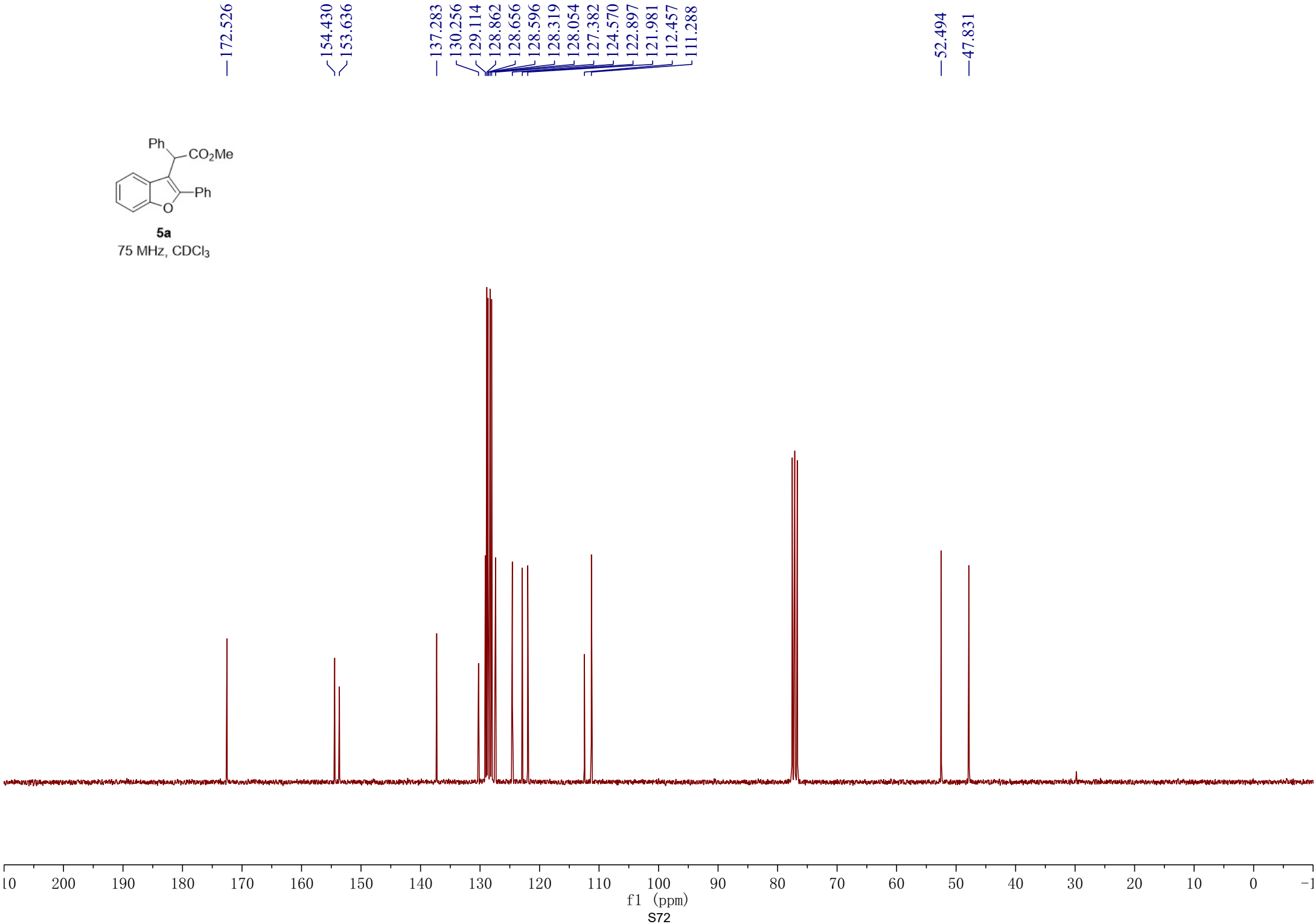
376 MHz, $CDCl_3$

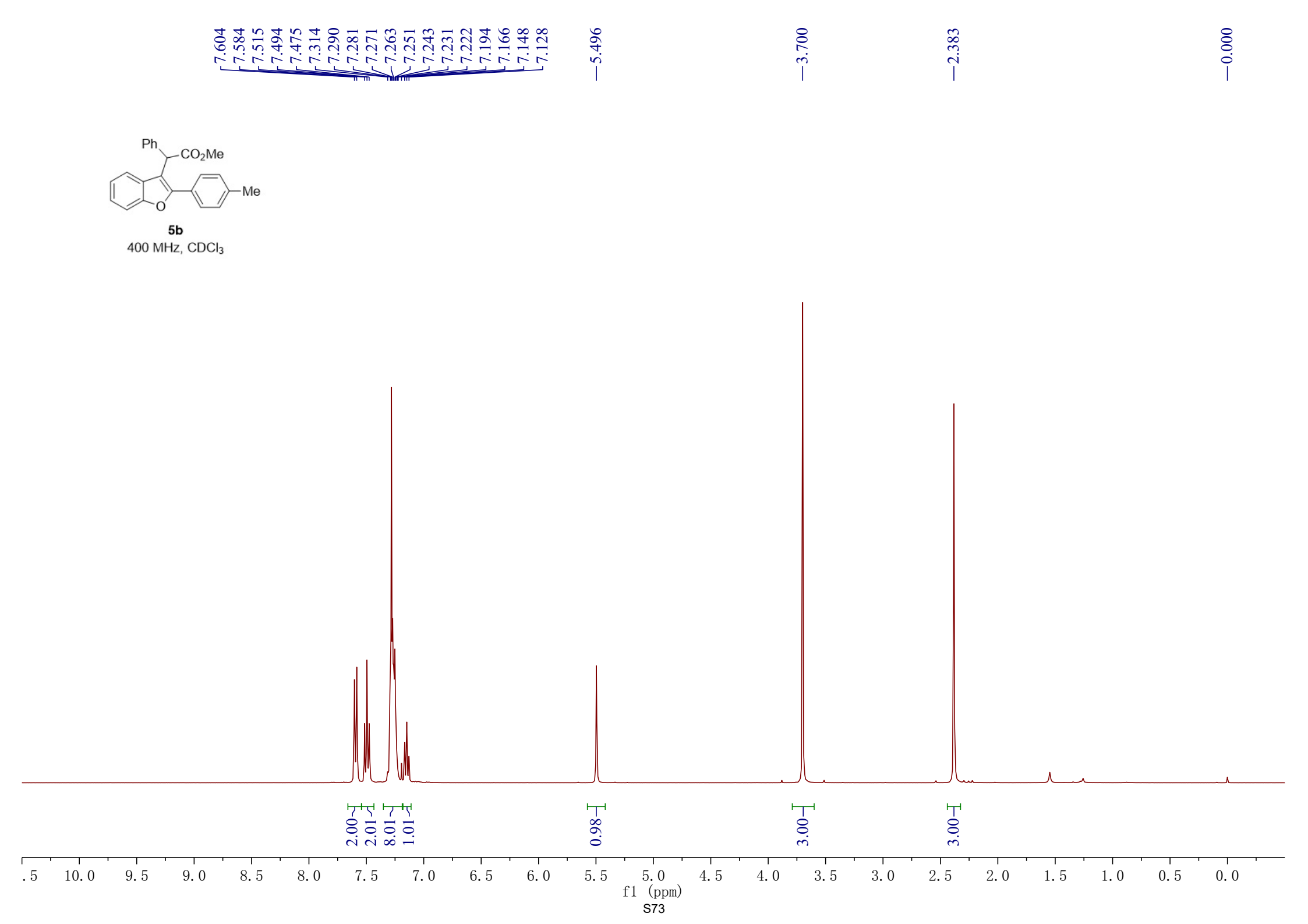
3s

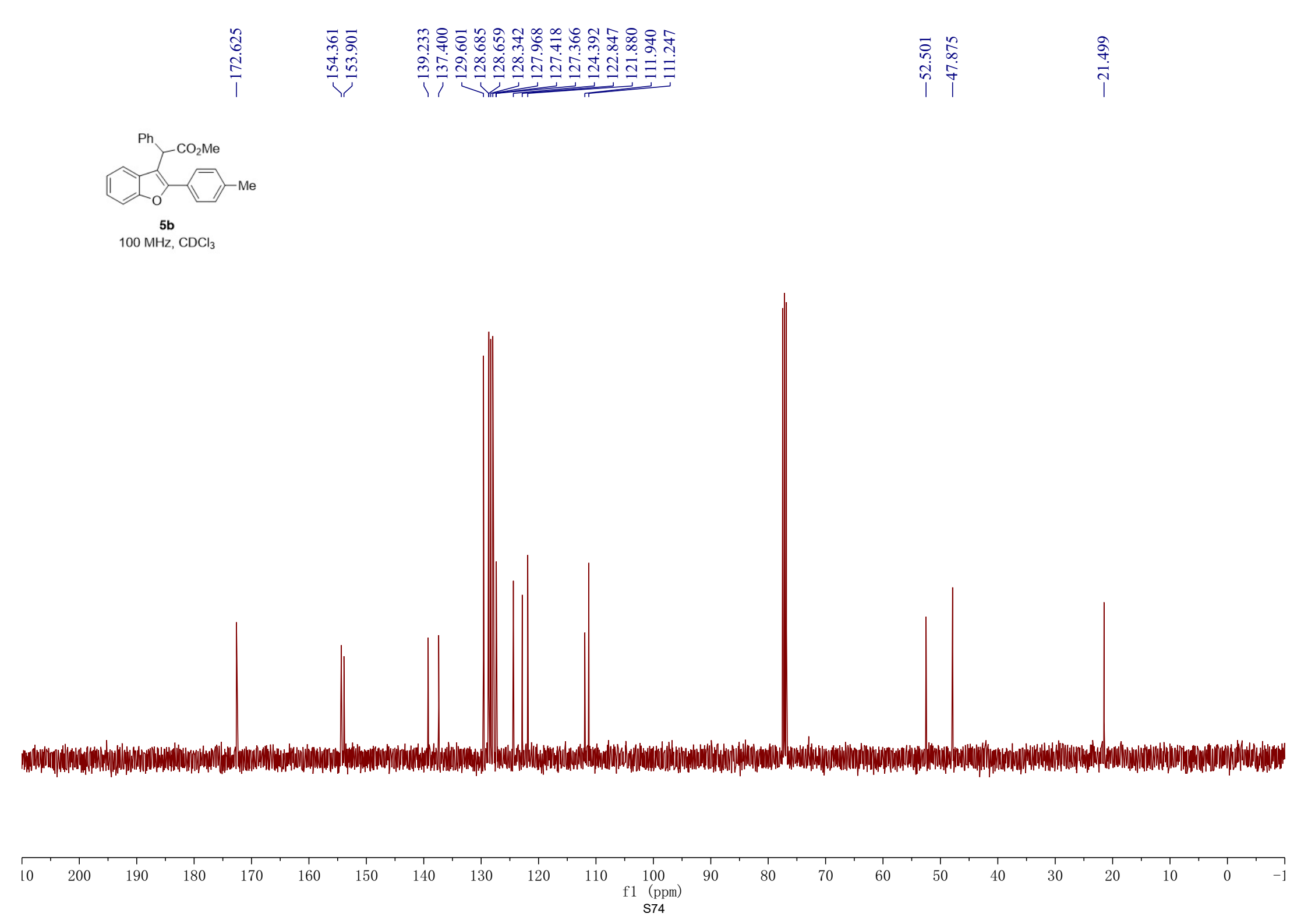
-120.744

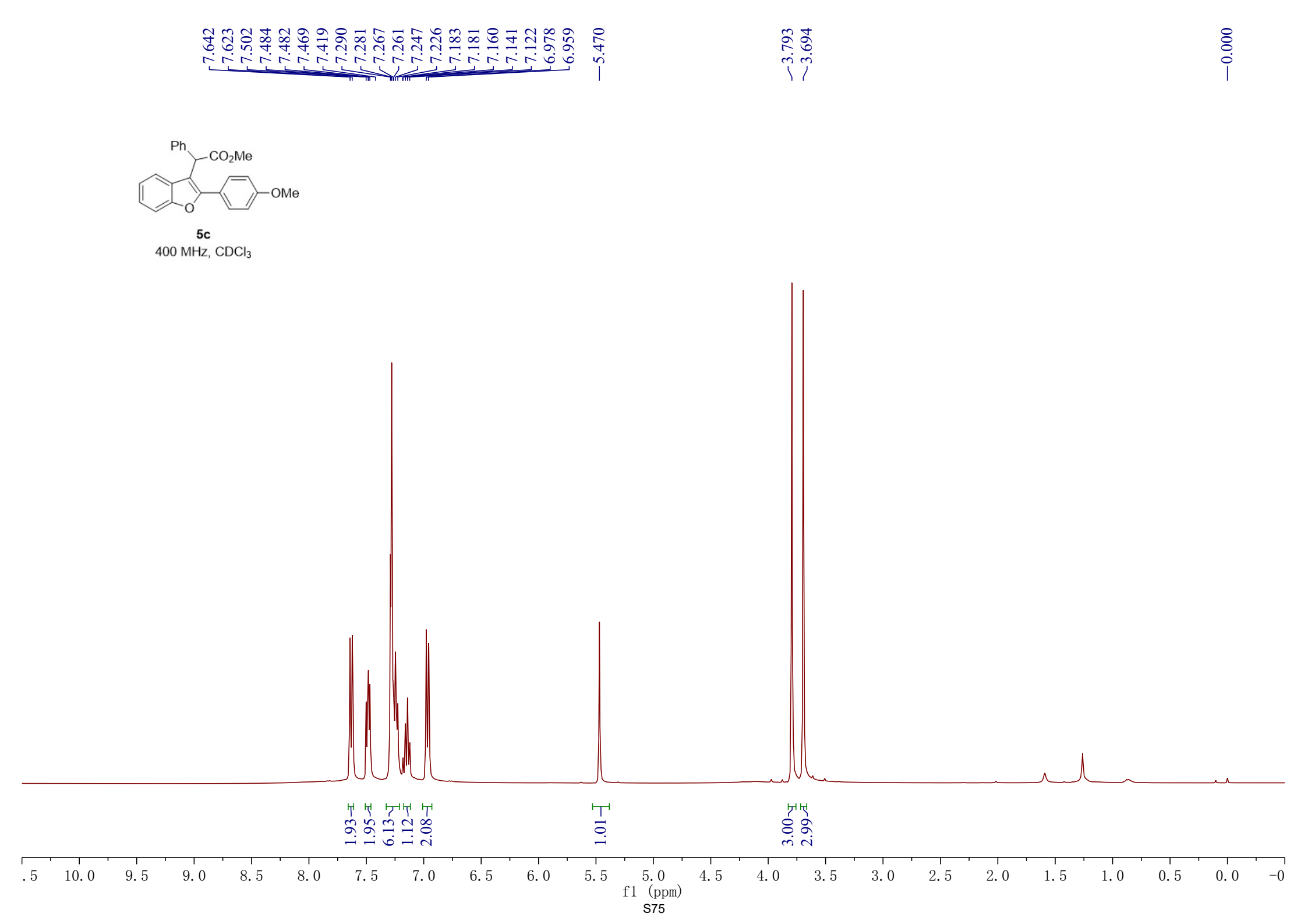
f1 (ppm)

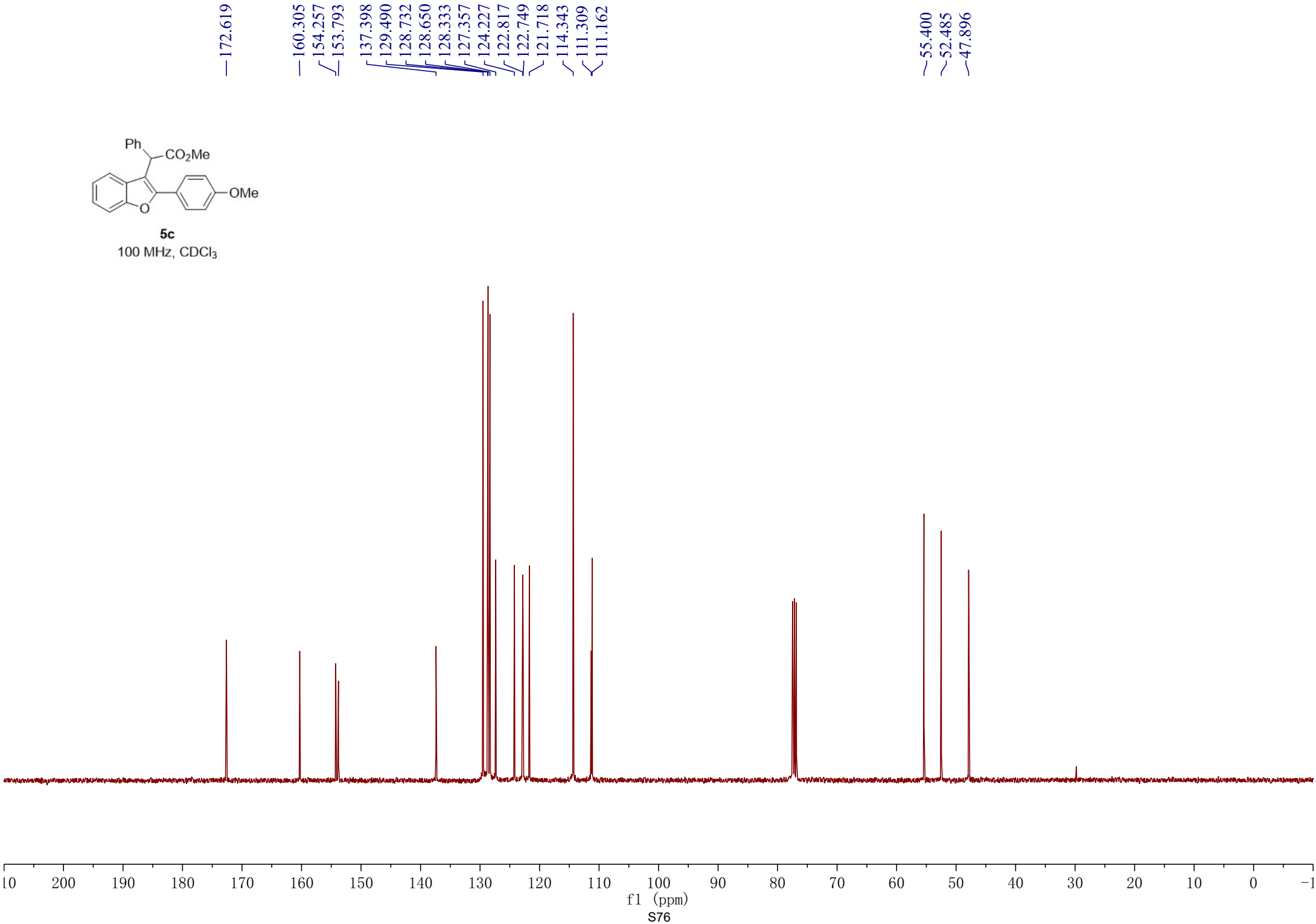

7.720
7.714
7.707
7.697
7.692
7.687
7.533
7.512
7.508
7.484
7.472
7.455
7.450
7.435
7.431
7.421
7.415
7.410
7.401
7.392
7.368
7.307
7.302
7.299
7.295
7.286
7.279
7.275
7.268
7.256
7.251
7.247
7.204
7.186
7.183
7.160
7.157
7.135
7.133
5.512
3.706
-0.000
Ph
CO2Me
Ph
O
5a
300 MHz, CDCl3
2.03
5.04
6.05
1.11
1.02
3.00
f1 (ppm)

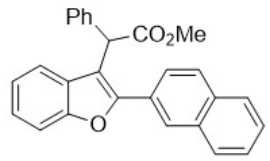

172.526
154.430
153.636
137.283
130.256
129.114
128.862
128.656
128.596
128.319
128.054
127.382
124.570
122.897
121.981
112.457
111.288
52.494
47.831
Ph
CO2Me
Ph
O
5a
75 MHz, CDCl3
f1 (ppm)


7.604
7.584
7.515
7.494
7.475
7.314
7.290
7.281
7.271
7.263
7.251
7.243
7.231
7.222
7.194
7.166
7.148
7.128
5.496
3.700
2.383
0.000
Ph
CO2Me
Me
O
5b
400 MHz, CDCl3
2.00
2.01
8.01
1.01
0.98
3.00
3.00
f1 (ppm)


172.625
154.361
153.901
139.233
137.400
129.601
128.685
128.659
128.342
127.968
127.418
127.366
124.392
122.847
121.880
111.940
111.247
52.501
47.875
21.499
Ph
CO2Me
Me
O
5b
100 MHz, CDCl3
f1 (ppm)

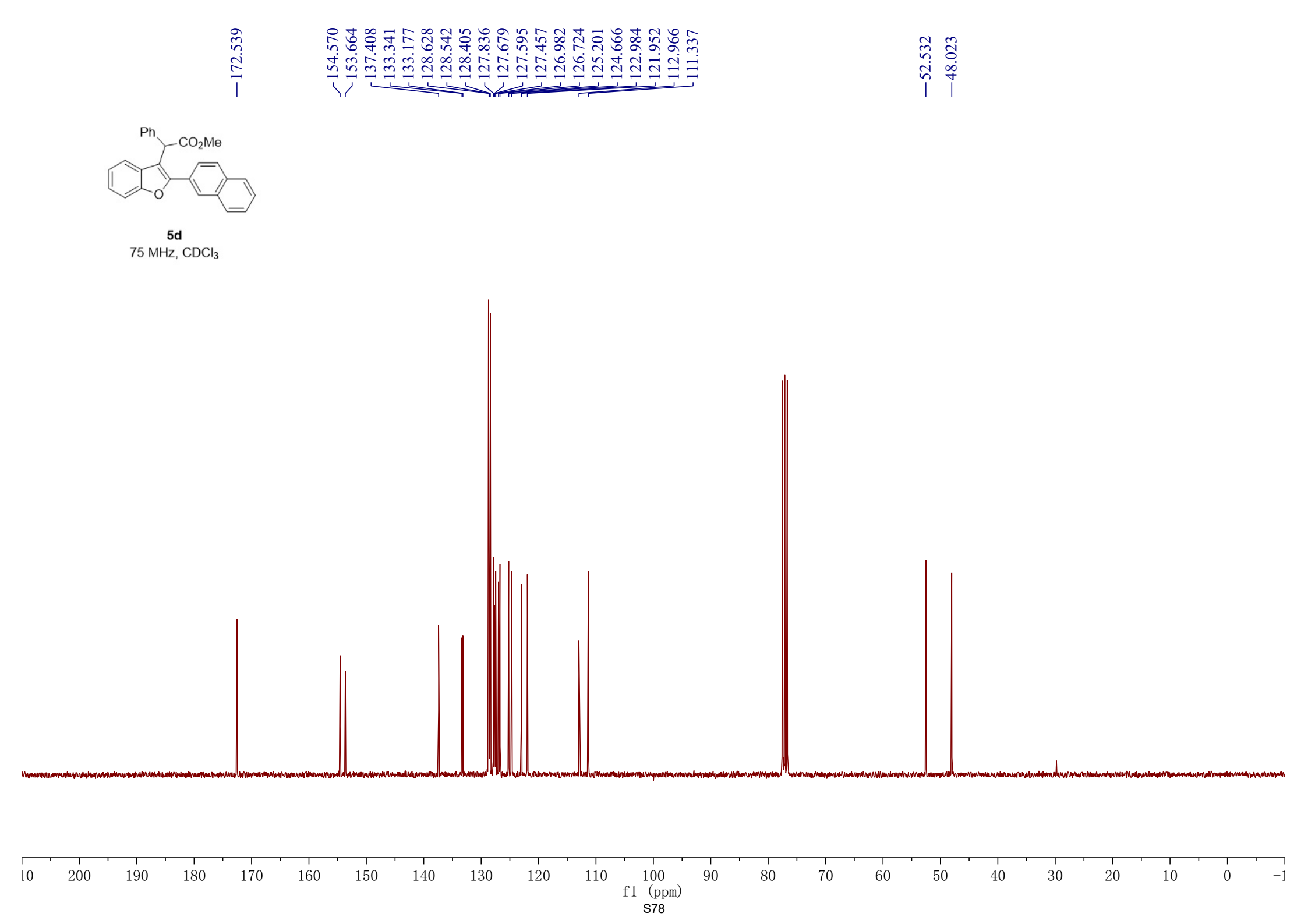

7.642
7.623
7.502
7.484
7.482
7.469
7.419
7.290
7.281
7.267
7.261
7.247
7.226
7.183
7.181
7.160
7.141
7.122
6.978
6.959
5.470
3.793
3.694
0.000
Ph
CO2Me
OMe
O
5c
400 MHz, CDCl3
1.93
1.95
6.13
1.12
2.08
1.01
3.00
2.99
f1 (ppm)

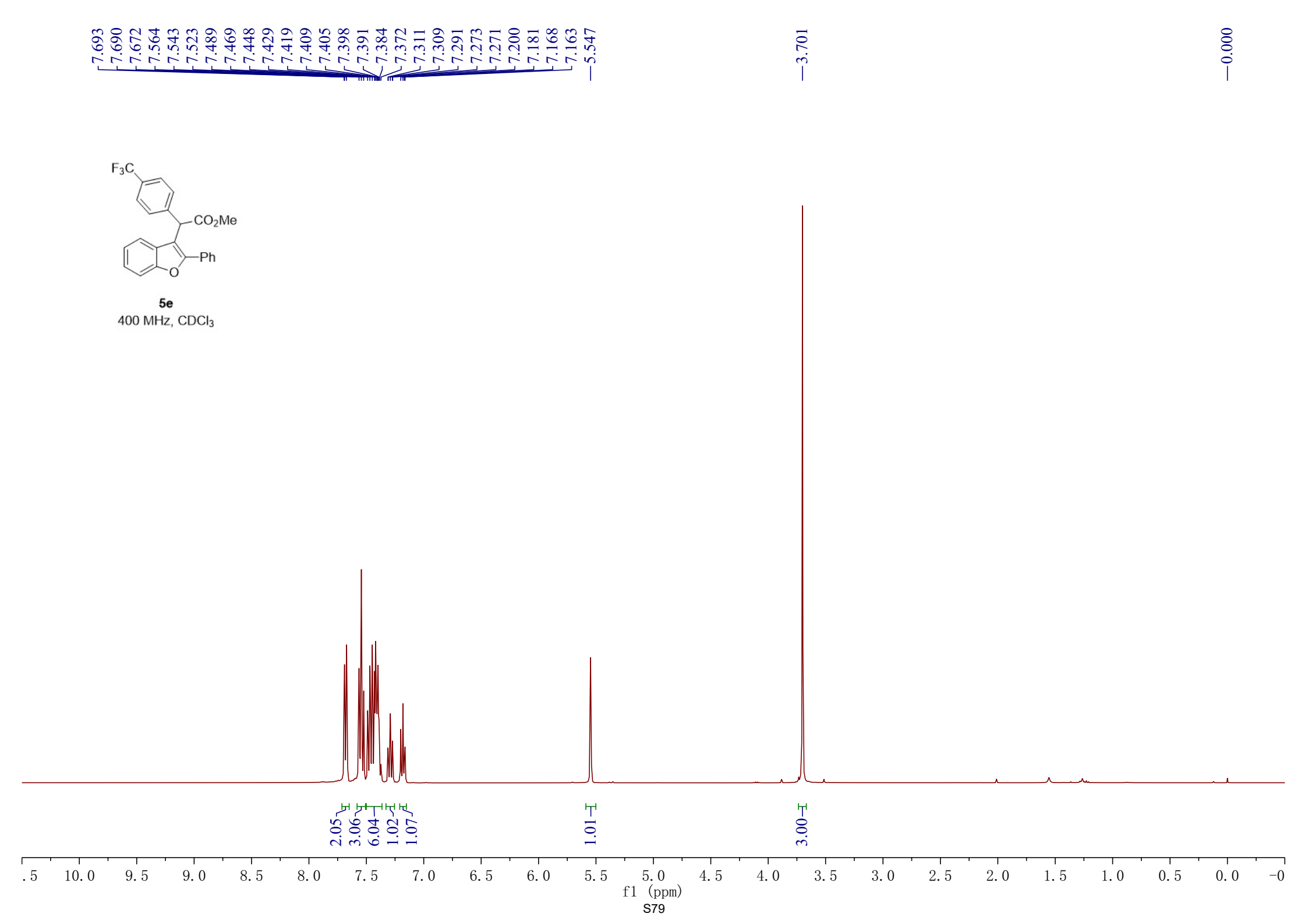

172.619
160.305
154.257
153.793
137.398
129.490
128.732
128.650
128.333
127.357
124.227
122.817
122.749
121.718
114.343
111.309
111.162
55.400
52.485
47.896
Ph
CO2Me
OMe
O
5c
100 MHz, CDCl3
f1 (ppm)

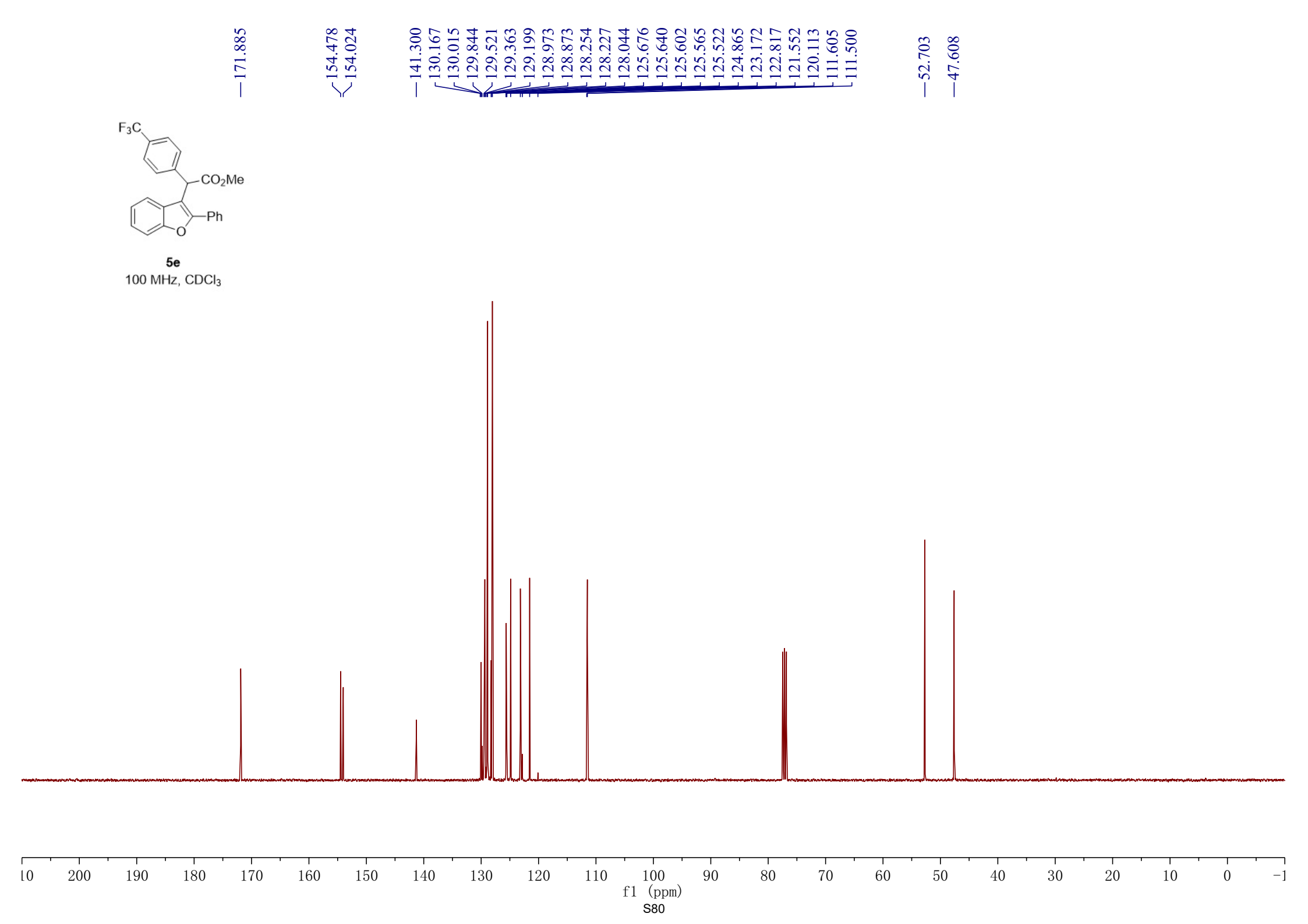


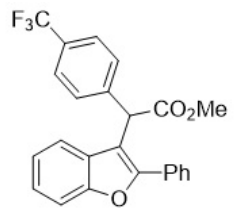
5d

300 MHz, $CDCl_3$


172.539
154.570
153.664
137.408
133.341
133.177
128.628
128.542
128.405
127.836
127.679
127.595
127.457
126.982
126.724
125.201
124.666
122.984
121.952
112.966
111.337
52.532
48.023
Ph
CO2Me
O
5d
75 MHz, CDCl3
f1 (ppm)


7.693
7.690
7.672
7.564
7.543
7.523
7.489
7.469
7.448
7.429
7.419
7.409
7.405
7.398
7.391
7.384
7.372
7.311
7.309
7.291
7.273
7.271
7.200
7.181
7.168
7.163
5.547
3.701
0.000
F3C
CO2Me
Ph
O
5e
400 MHz, CDCl3
2.05
3.06
6.04
1.02
1.07
1.01
3.00
f1 (ppm)


171.885
154.478
154.024
141.300
130.167
130.015
129.844
129.521
129.363
129.199
128.973
128.873
128.254
128.227
128.044
125.676
125.640
125.602
125.565
125.522
124.865
123.172
122.817
121.552
120.113
111.605
111.500
52.703
47.608
F3C
CO2Me
Ph
O
5e
100 MHz, CDCl3
f1 (ppm)

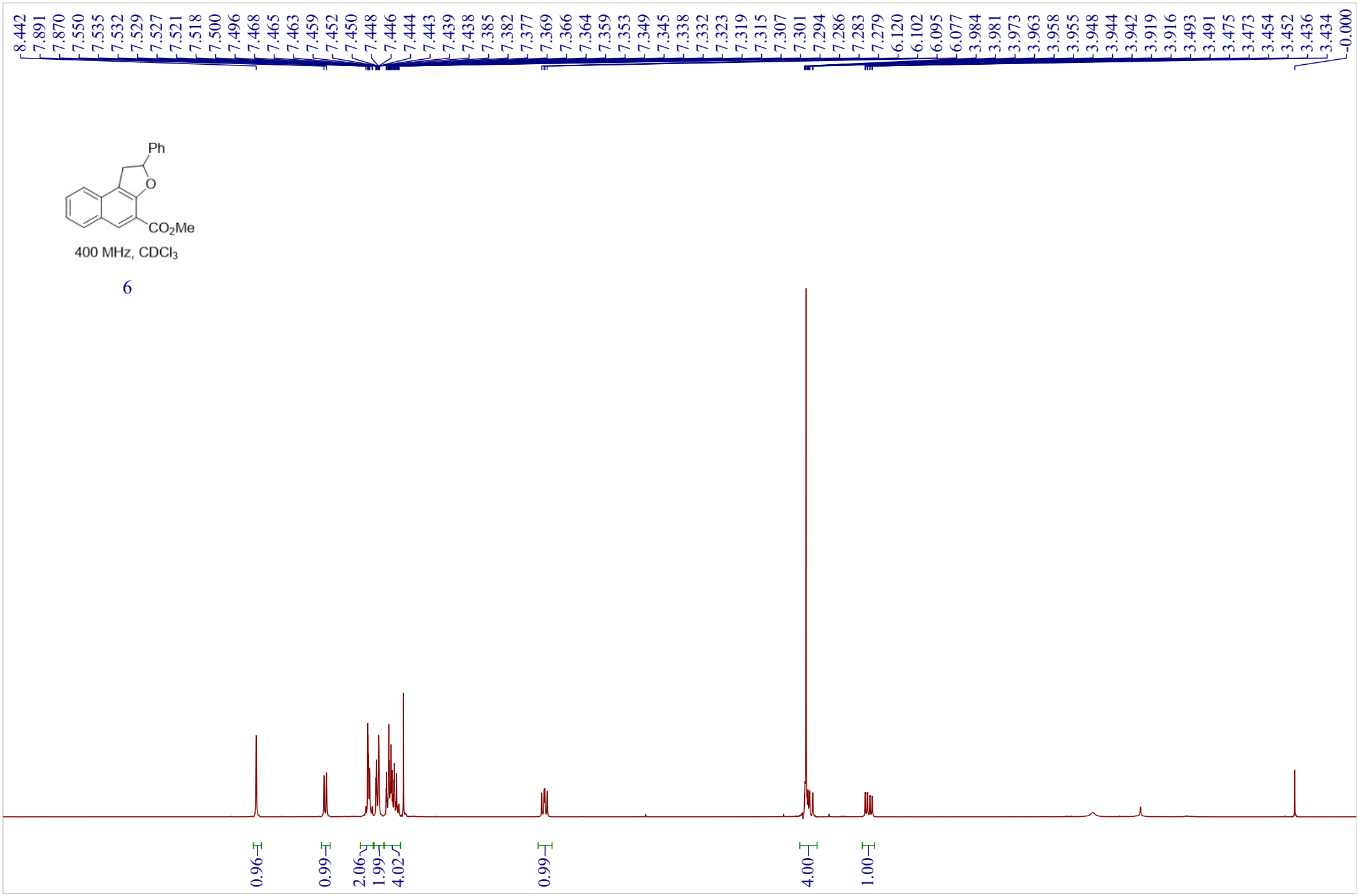


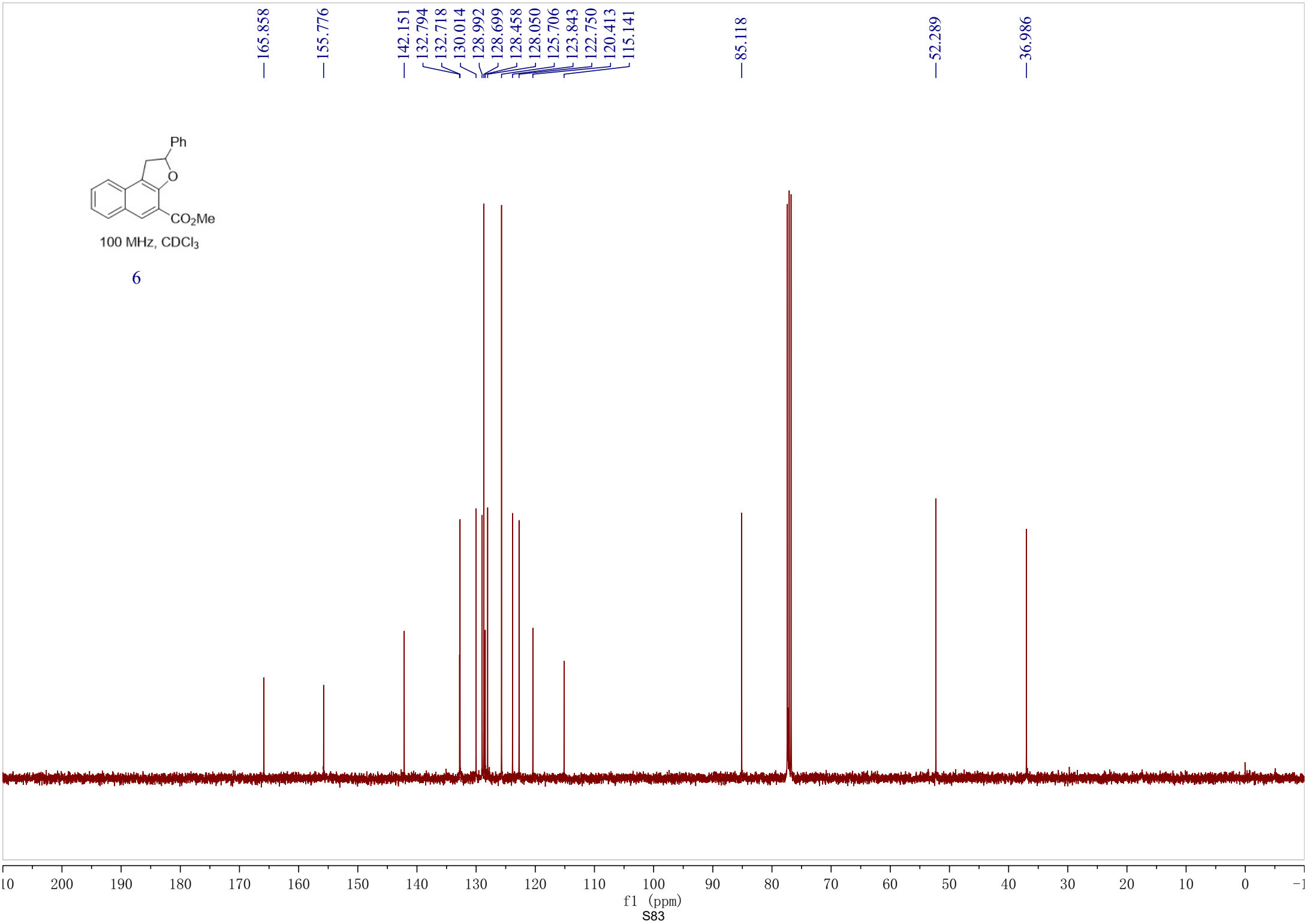
5e
471 MHz, $CDCl_3$

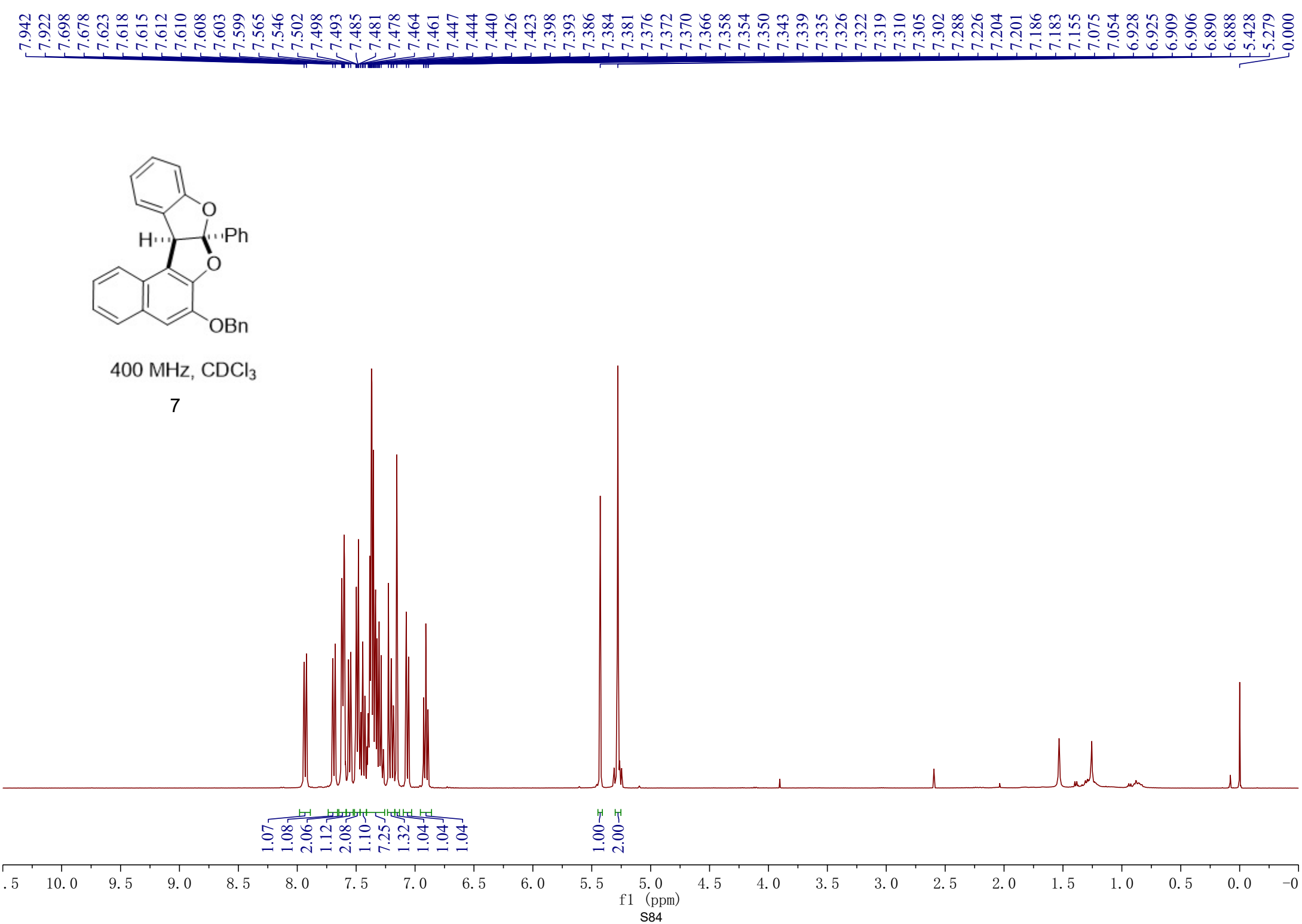
-62.411

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22

f1 (ppm)


8.442
7.891
7.870
7.550
7.535
7.532
7.529
7.527
7.521
7.518
7.500
7.496
7.468
7.465
7.463
7.459
7.452
7.450
7.448
7.446
7.444
7.443
7.439
7.438
7.385
7.382
7.377
7.369
7.366
7.364
7.359
7.353
7.349
7.345
7.338
7.332
7.323
7.319
7.315
7.307
7.301
7.294
7.286
7.283
7.279
6.120
6.102
6.095
6.077
3.984
3.981
3.973
3.963
3.958
3.955
3.948
3.944
3.942
3.919
3.916
3.493
3.491
3.475
3.473
3.454
3.452
3.436
3.434
-0.000
Ph
O
CO2Me
400 MHz, CDCl3
6
0.96
0.99
2.06
1.99
4.02
0.99
4.00
1.00
f1 (ppm)

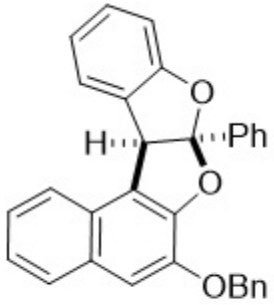

165.858
155.776
142.151
132.794
132.718
130.014
128.992
128.699
128.458
128.050
125.706
123.843
122.750
120.413
115.141
85.118
52.289
36.986
Ph
O
CO2Me
100 MHz, CDCl3
6
f1 (ppm)


7.942
7.922
7.698
7.678
7.623
7.618
7.615
7.612
7.610
7.608
7.603
7.599
7.565
7.546
7.502
7.498
7.493
7.485
7.481
7.478
7.464
7.461
7.447
7.444
7.440
7.426
7.423
7.398
7.393
7.386
7.384
7.381
7.376
7.372
7.370
7.366
7.358
7.354
7.350
7.343
7.339
7.335
7.326
7.322
7.319
7.310
7.305
7.302
7.288
7.226
7.204
7.201
7.186
7.183
7.155
7.075
7.054
6.928
6.925
6.909
6.906
6.890
6.888
5.428
5.279
0.000
O
H
Ph
O
OBn
400 MHz, CDCl3
7
1.07
1.08
2.06
1.12
2.08
1.10
7.25
1.32
1.04
1.04
1.04
1.00
2.00
f1 (ppm)

158.337
147.820
144.501
139.482
136.566
131.125
129.303
129.053
128.634
128.617
128.026
127.963
127.458
127.269
125.397
125.106
125.083
125.038
124.135
122.873
122.640
122.055
120.857
110.612
109.901

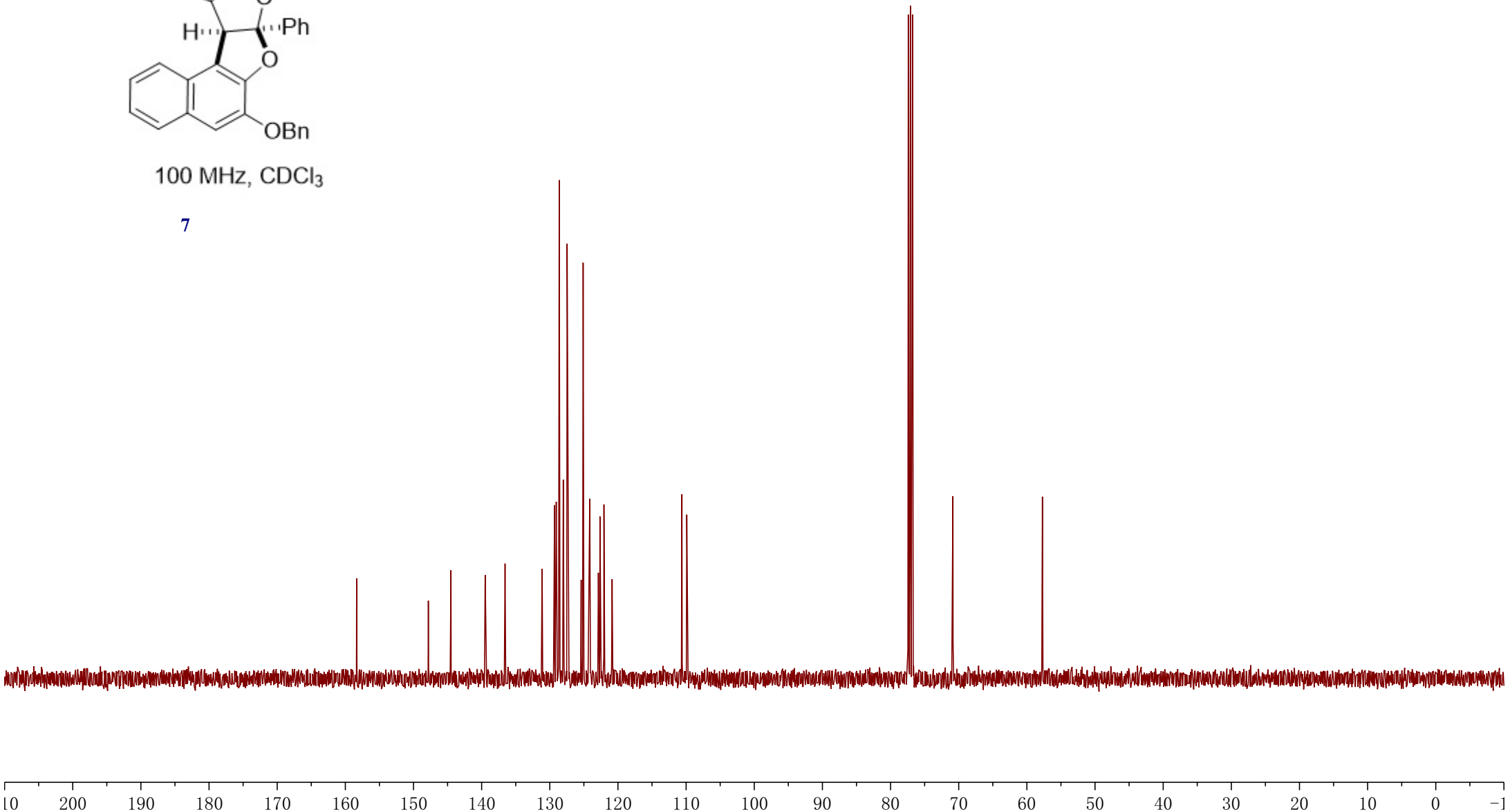
70.848

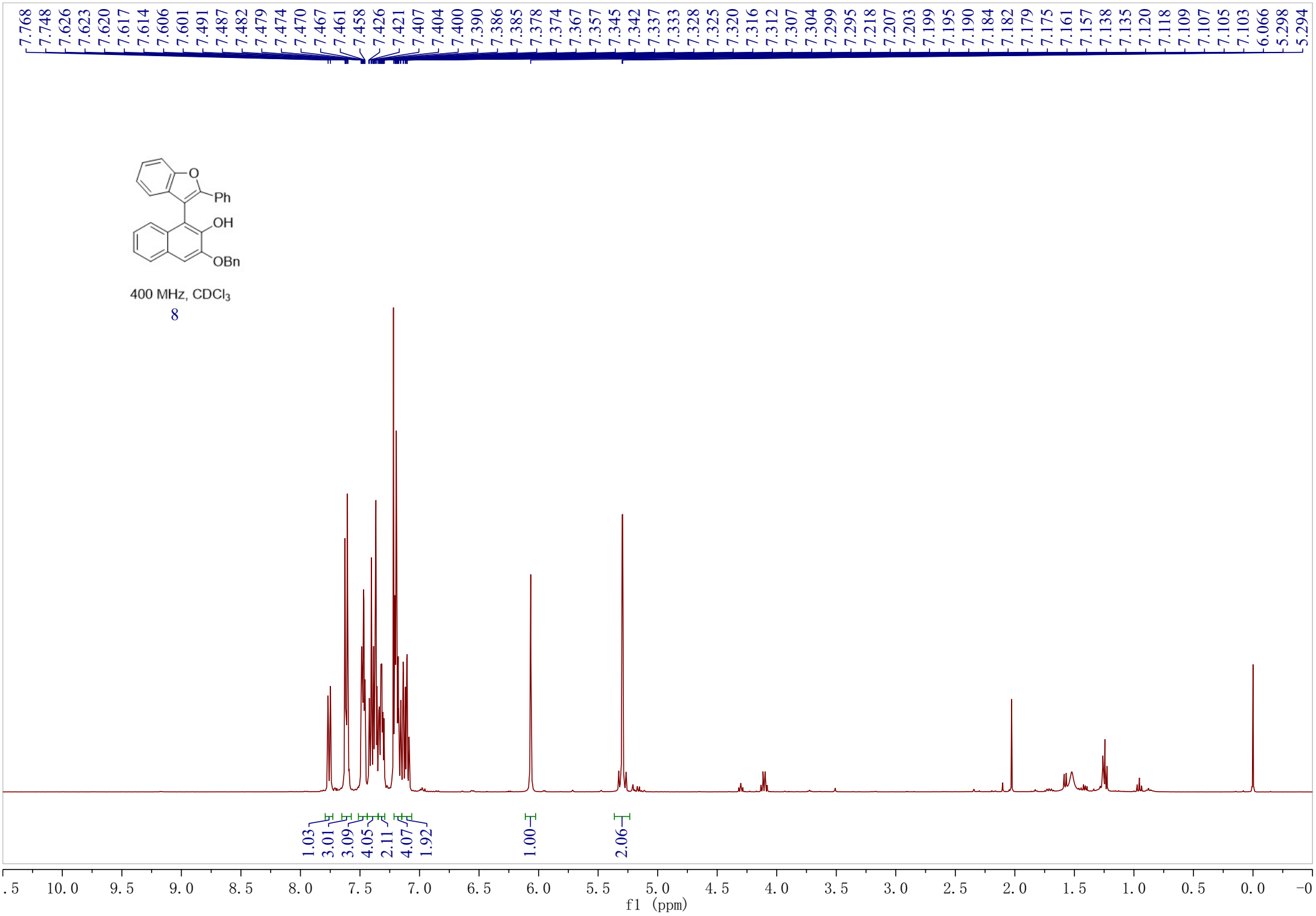
57.719

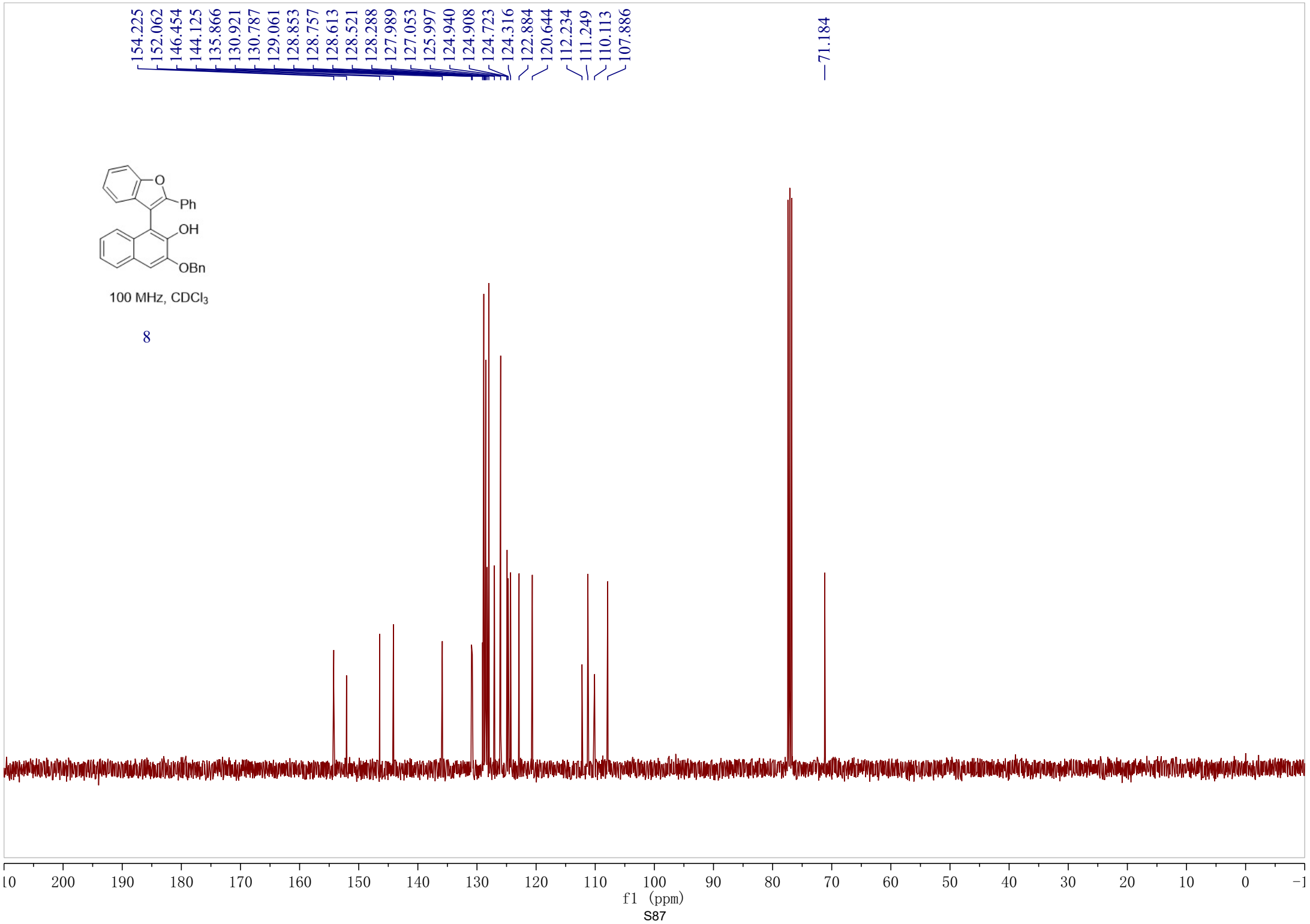


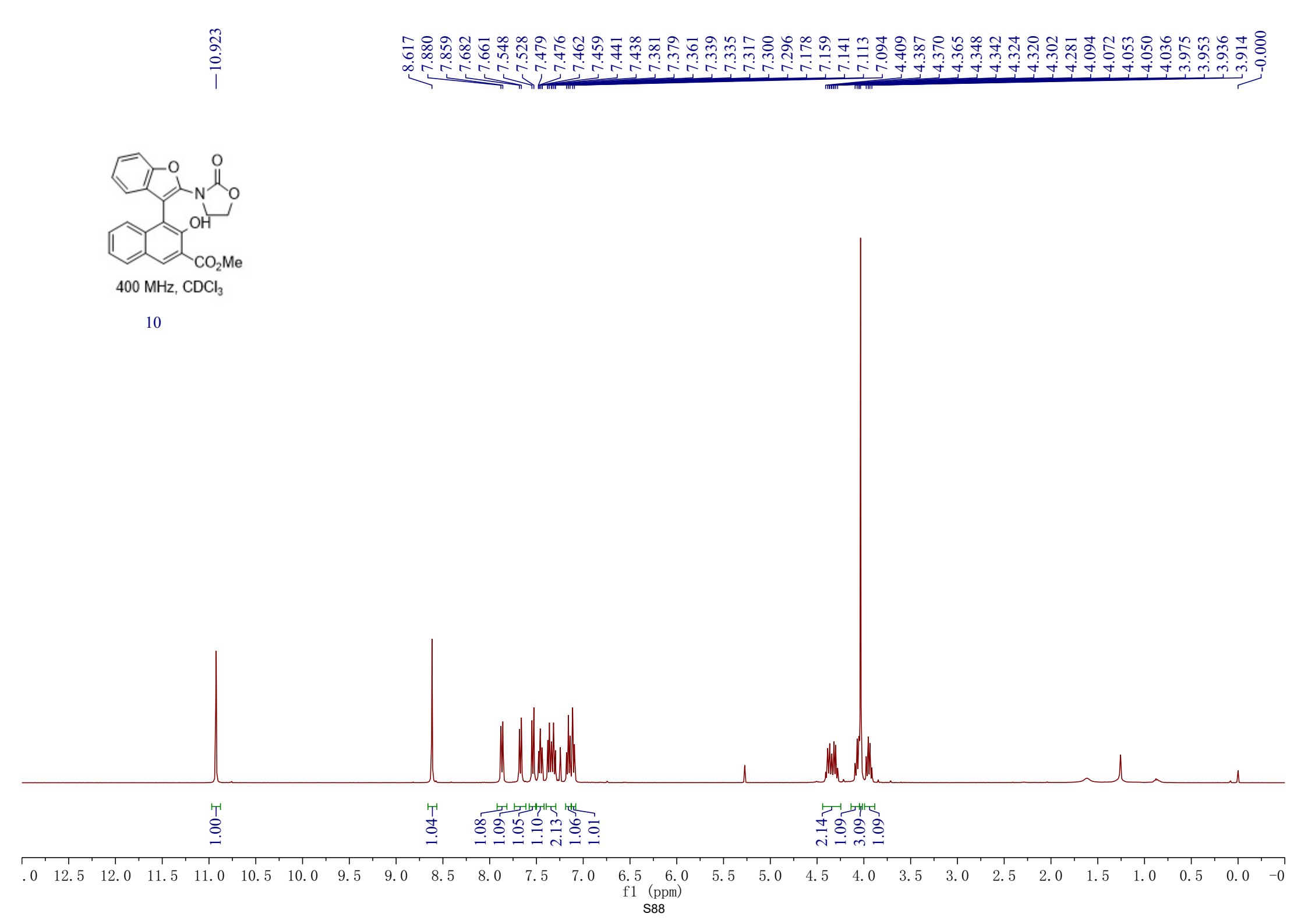
100 MHz, $CDCl_3$

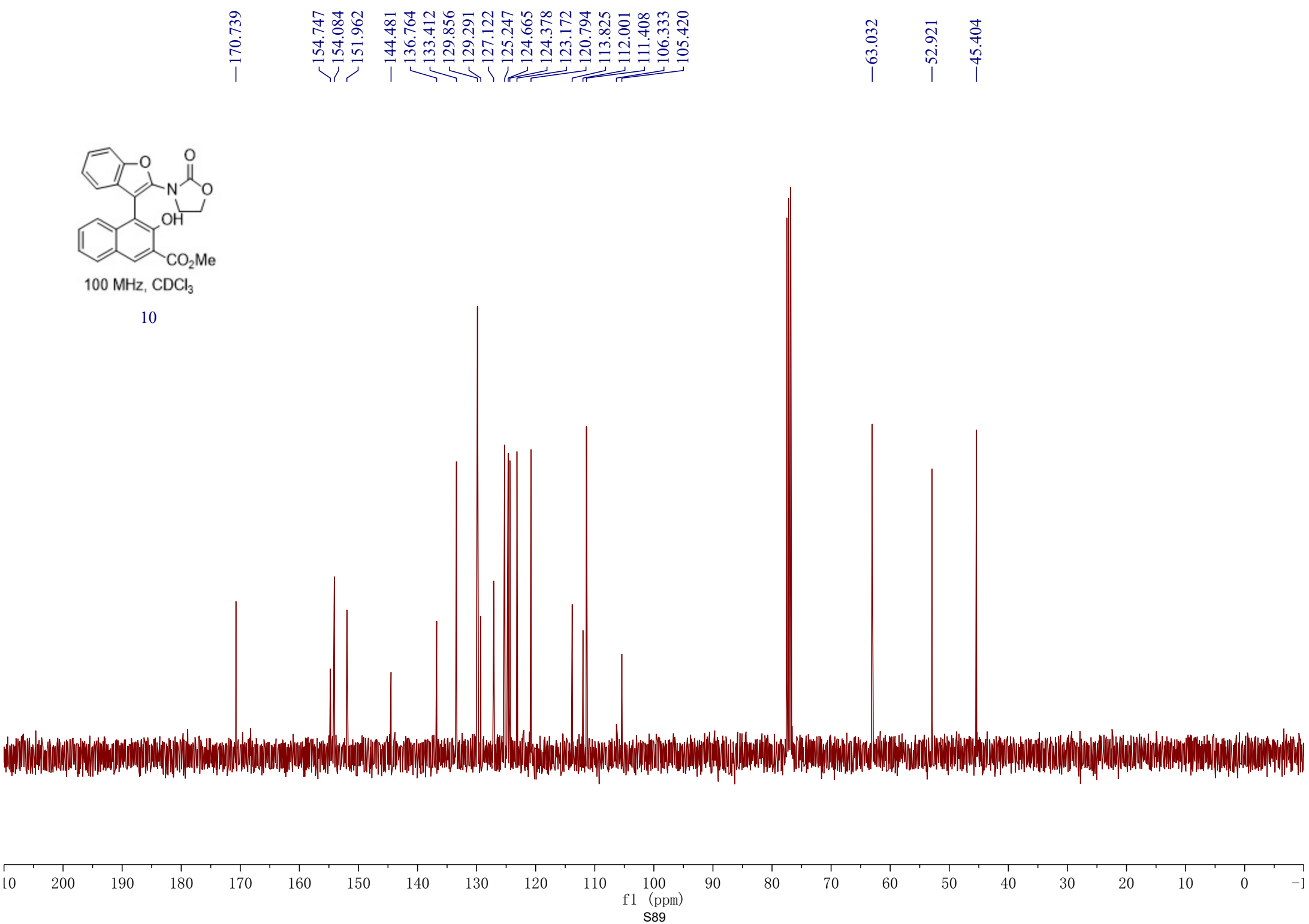
7

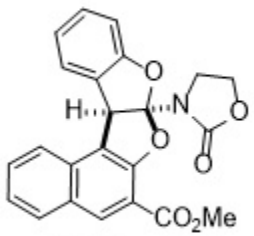



7.768
7.748
7.626
7.623
7.620
7.617
7.614
7.606
7.601
7.491
7.487
7.482
7.479
7.474
7.470
7.467
7.461
7.458
7.426
7.421
7.407
7.404
7.400
7.390
7.386
7.385
7.378
7.374
7.367
7.357
7.345
7.342
7.337
7.333
7.328
7.325
7.320
7.316
7.312
7.307
7.304
7.299
7.295
7.218
7.207
7.203
7.199
7.195
7.190
7.184
7.182
7.179
7.175
7.161
7.157
7.138
7.135
7.120
7.118
7.109
7.107
7.105
7.103
6.066
5.298
5.294
O
Ph
OH
OBn
400 MHz, CDCl3
8
1.03
3.01
3.09
4.05
2.11
4.07
1.92
1.00
2.06
10.0
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
f1 (ppm)


154.225
152.062
146.454
144.125
135.866
130.921
130.787
129.061
128.853
128.757
128.613
128.521
128.288
127.989
127.053
125.997
124.940
124.908
124.723
124.316
122.884
120.644
112.234
111.249
110.113
107.886
71.184
O
Ph
OH
OBn
100 MHz, CDCl3
8
f1 (ppm)

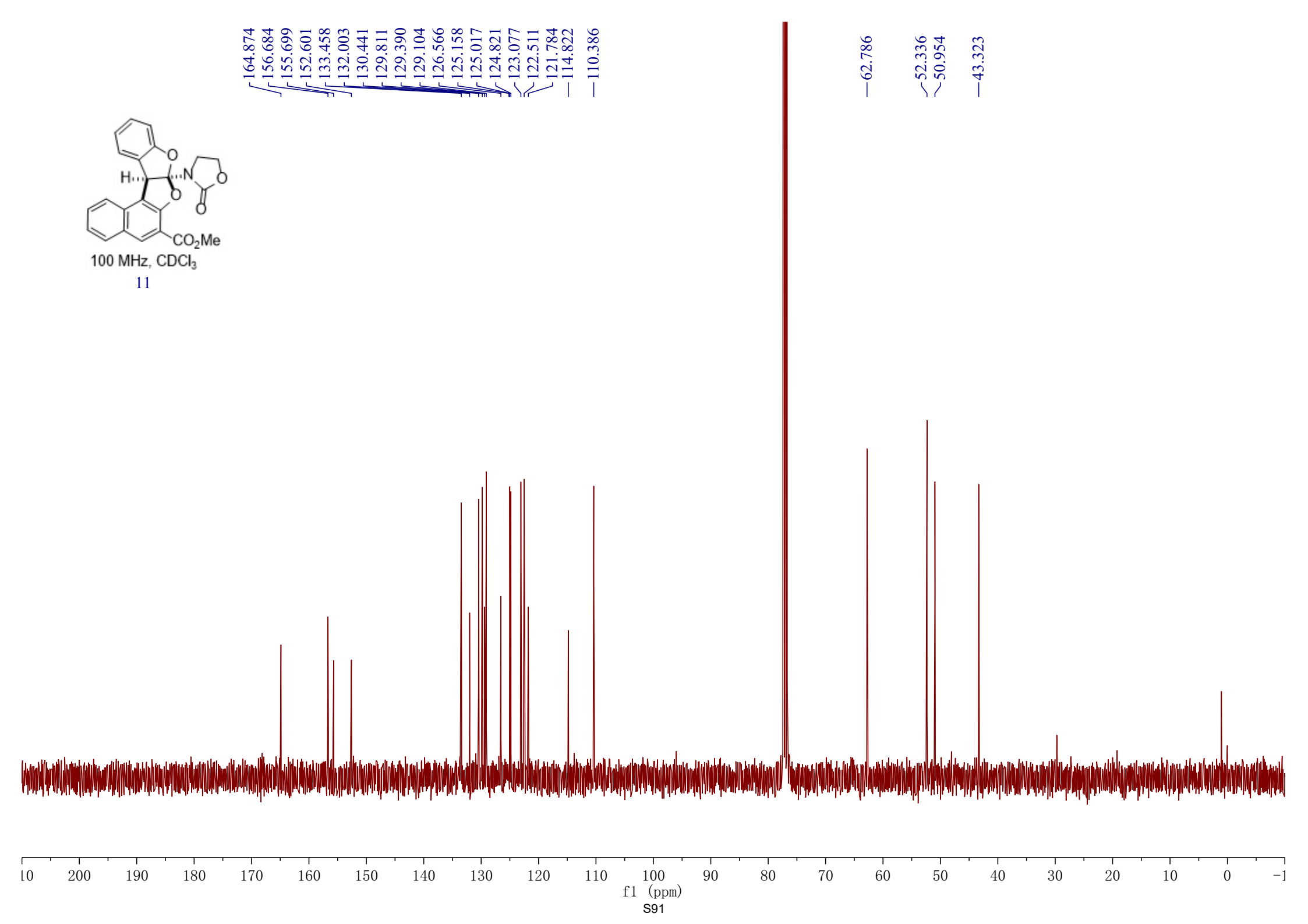

10.923
8.617
7.880
7.859
7.682
7.661
7.548
7.528
7.479
7.476
7.462
7.459
7.441
7.438
7.381
7.379
7.361
7.339
7.335
7.317
7.300
7.296
7.178
7.159
7.141
7.113
7.094
4.409
4.387
4.370
4.365
4.348
4.342
4.324
4.320
4.302
4.281
4.094
4.072
4.053
4.050
4.036
3.975
3.953
3.936
3.914
-0.000
O
O
N
O
OH
CO2Me
400 MHz, CDCl3
10
1.00
1.04
1.08
1.09
1.05
1.10
2.13
1.06
1.01
2.14
1.09
3.09
1.09
f1 (ppm)


170.739
154.747
154.084
151.962
144.481
136.764
133.412
129.856
129.291
127.122
125.247
124.665
124.378
123.172
120.794
113.825
112.001
111.408
106.333
105.420
63.032
52.921
45.404
O
O
N
O
OH
CO2Me
100 MHz, CDCl3
10
f1 (ppm)



400 MHz, $CDCl_3$

11


164.874
156.684
155.699
152.601
133.458
132.003
130.441
129.811
129.390
129.104
126.566
125.158
125.017
124.821
123.077
122.511
121.784
114.822
110.386
62.786
52.336
50.954
43.323
CO2Me
100 MHz, CDCl3
11
f1 (ppm)