

B(C₆F₅)₃-Catalyzed Formal (4+1)-Annulation of *ortho*-Quinone Methides with Diazoacetates: Access to 2,3-Dihydrobenzofurans

Guangyang Xu, Shengbiao Tang, Ying Shao and Jiangtao Sun*

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 or jtsun08@gmail.com

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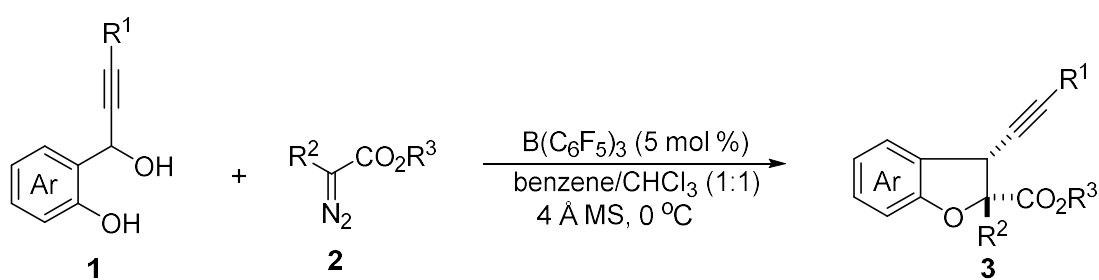
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General information

All of the reactions were carried out in flame-dried tubes. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used. ^1H NMR were recorded on Bruker 300 MHz or 400 MHz spectrometer in CDCl_3 . ^{13}C NMR were recorded on Bruker 75 MHz, 100 MHz or 125MHz spectrometer in CDCl_3 . Chemical shifts are expressed in parts per million (ppm) and reported relative to CDCl_3 peaks [$\delta = 7.26$ ppm (^1H NMR); $\delta = 77.1$ ppm (^{13}C NMR)]. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, and m = multiplet. Coupling constants (J) are reported in Hertz (Hz). HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus.

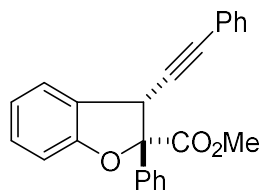
Diazo compounds **2**¹ and 2-(1-hydroxyprop-2-yn-1-yl)phenol derivatives **1**² were known compounds and prepared according to the literature procedures. $\text{B}(\text{C}_6\text{F}_5)_3$ was prepared according to the literature procedures.³

General procedure for Scheme 3



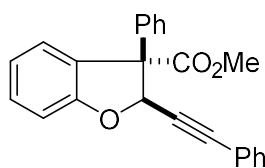
To a dry tube was added $\text{B}(\text{C}_6\text{F}_5)_3$ (0.01 mmol, 0.05 eq), 4Å molecular sieve (60 mg) and benzene/ CHCl_3 (3 mL, 1:1) under an argon atmosphere, then **1** (0.2 mmol, 1 eq) and **2** (0.3 mmol, 1.5 eq) in benzene/ CHCl_3 (3 mL, 1:1) was added via a syringe pump over 30 min at 0 °C. The reaction mixture was stirred for further 1.5 h. The reaction mixture was concentrated and purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether =1:30~1:15 or CH_2Cl_2 : Petroleum ether =1:5~1:1) to

give products **3**.



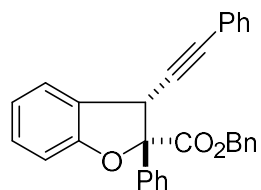
methyl 2-phenyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3a)

3a was prepared via general procedure as colorless oil (51 mg, 72%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). ¹H NMR (400 MHz, CDCl₃) δ 7.83-7.76 (m, 2H), 7.47-7.37 (m, 4H), 7.37-7.27 (m, 5H), 7.27-7.22 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 4.95 (s, 1H), 3.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.6, 158.1, 139.3, 131.8, 129.5, 128.6, 128.5, 128.3, 126.2, 126.0, 124.8, 122.7, 122.0, 110.4, 93.8, 86.1, 85.4, 53.0, 46.9. HRMS (ESI) calcd. for C₂₄H₁₉O₃ [M+H]⁺: 355.1329, found: 355.1326.



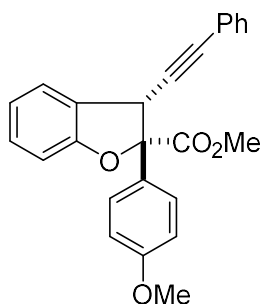
methyl 3-phenyl-2-(phenylethynyl)-2,3-dihydrobenzofuran-3-carboxylate (4a)

4a was prepared as colorless oil (18 mg, 25%) using Ph₃PAuCl/AgSbF₆ (5 mol %) as catalyst and 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**) in CH₂Cl₂ at rt. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.36-7.30 (m, 4H), 7.25-7.14 (m, 3H), 7.11-7.06 (m, 2H), 7.06-6.95 (m, 4H), 6.42 (s, 1H), 3.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 172.1, 159.0, 138.7, 131.8, 130.3, 128.6, 128.2, 128.03, 128.02, 127.9, 127.2, 126.3, 121.9, 121.7, 110.7, 91.0, 83.8, 80.0, 66.5, 53.3. HRMS (ESI) calcd. for C₂₄H₁₉O₃ [M+H]⁺: 355.1329, found: 355.1332.



benzyl 2-phenyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3b)

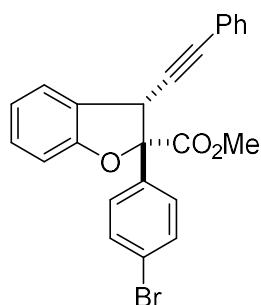
3b was prepared via general procedure as colorless oil (52 mg, 60%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). ¹H NMR (300 MHz, CDCl₃) δ 7.83-7.75 (m, 2H), 7.43-7.14 (m, 13H), 7.14-7.02 (m, 3H), 6.96 (td, *J* = 7.4, 0.9 Hz, 1H), 5.17 (dd, *J* = 29.2, 12.7 Hz, 2H), 4.98 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 168.9, 158.2, 139.1, 135.2, 131.8, 129.5, 128.6, 128.4, 128.33, 128.31, 128.2, 128.0, 127.6, 126.3, 126.2, 124.7, 122.6, 121.9, 110.4, 93.8, 86.2, 85.4, 67.5, 46.8. HRMS (ESI) calcd. for C₃₀H₂₃O₃ [M+H]⁺: 431.1642, found: 431.1637.



methyl

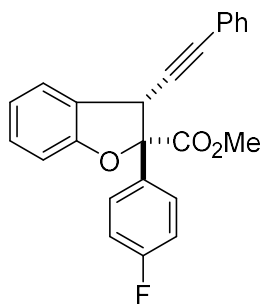
2-(4-methoxyphenyl)-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3c)

3c was prepared via general procedure as colorless oil (55 mg, 71%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). ¹H NMR (300 MHz, CDCl₃) δ 7.73-7.66 (m, 2H), 7.46-7.40 (m, 2H), 7.35-7.27 (m, 4H), 7.27-7.20 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.99-6.88 (m, 3H), 4.91 (s, 1H), 3.80 (s, 3H), 3.75 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.8, 159.7, 158.1, 131.7, 131.2, 129.5, 128.5, 128.3, 127.5, 126.0, 124.8, 122.7, 122.0, 113.7, 110.4, 93.7, 86.0, 85.5, 55.3, 52.9, 46.9. HRMS (ESI) calcd. for C₂₅H₂₁O₄ [M+H]⁺: 385.1434, found: 385.1439.



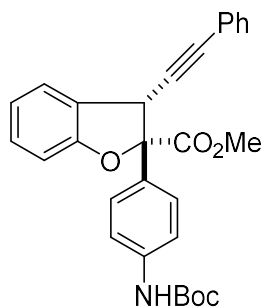
methyl 2-(4-bromophenyl)-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3d)

3d was prepared via general procedure as colorless oil (50 mg, 58%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). ^1H NMR (300 MHz, CDCl_3) δ 7.70-7.62 (m, 2H), 7.55-7.50 (m, 2H), 7.47-7.40 (m, 2H), 7.35-7.28 (m, 4H), 7.26-7.22 (m, 1H), 7.05 (d, $J = 8.0$ Hz, 1H), 6.98 (td, $J = 7.5, 0.9$ Hz, 1H), 4.88 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 169.1, 158.0, 138.4, 131.7, 131.5, 129.6, 128.6, 128.4, 128.0, 125.7, 124.8, 122.8, 122.5, 122.2, 110.4, 93.3, 86.3, 84.9, 53.1, 47.1. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{18}\text{BrO}_3$ $[\text{M}+\text{H}]^+$: 433.0434, found: 433.0430.



methyl 2-(4-fluorophenyl)-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3e)

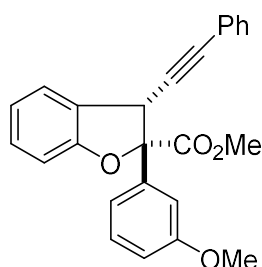
3e was prepared via general procedure as colorless oil (42 mg, 56%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). ^1H NMR (400 MHz, CDCl_3) δ 7.81-7.73 (m, 2H), 7.46-7.41 (m, 2H), 7.36-7.29 (m, 4H), 7.28-7.23 (m, 1H), 7.11-7.14 (m, 3H), 6.98 (td, $J = 7.5, 0.7$ Hz, 1H), 4.90 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 169.4, 163.8, 161.8, 158.0, 135.1, 131.7, 129.6, 128.6, 128.4, 128.1, 128.06, 125.8, 124.8, 122.5, 122.1, 115.3, 115.2, 110.4, 93.3, 86.3, 85.1, 53.0, 47.2. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{18}\text{FO}_3$ $[\text{M}+\text{H}]^+$: 373.1234, found: 373.1232.



methyl

2-(4-((tert-butoxycarbonyl)amino)phenyl)-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3f)

3f was prepared via general procedure as colorless oil (56 mg, 60%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). ¹H NMR (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.47-7.34 (m, 4H), 7.34-7.27 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.53 (s, 1H), 4.89 (s, 1H), 3.74 (s, 3H), 1.50 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 169.6, 158.0, 152.6, 138.7, 133.6, 131.7, 129.5, 128.4, 128.3, 127.0, 126.0, 124.8, 122.7, 122.0, 118.2, 110.5, 93.6, 86.0, 85.5, 80.8, 52.9, 46.8, 28.3. HRMS (ESI) calcd. for C₂₉H₂₈NO₅ [M+H]⁺: 470.1962, found: 470.1966.

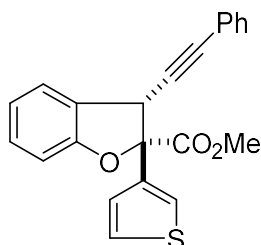


methyl

2-(3-methoxyphenyl)-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3g)

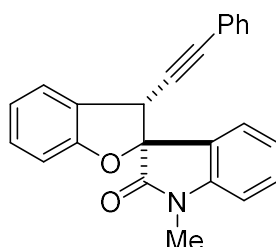
3g was prepared via general procedure as colorless oil (39 mg, 51%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.40 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.36-7.28 (m, 6H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.95 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 169.4, 159.5, 158.1, 140.8, 131.7, 129.5, 129.4, 128.5, 128.3, 126.0, 124.7, 122.7, 122.0, 118.6,

114.0, 112.1, 110.4, 93.7, 86.1, 85.4, 55.3, 52.9, 46.8. HRMS (ESI) calcd. for $C_{25}H_{21}O_4$ $[M+H]^+$: 385.1434, found: 385.1437.



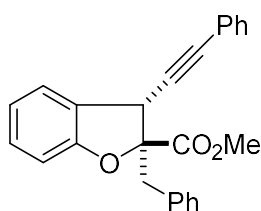
methyl 3-(phenylethynyl)-2-(thiophen-3-yl)-2,3-dihydrobenzofuran-2-carboxylate (3h)

3h was prepared via general procedure as colorless oil (36 mg, 50%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). 1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, $J = 3.0, 1.3$ Hz, 1H), 7.44-7.38 (m, 3H), 7.35-7.28 (m, 5H), 7.27-7.23 (m, 1H), 7.05 (d, $J = 8.0$ Hz, 1H), 6.98 (d, $J = 7.5$, 1H), 4.85 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.1, 158.2, 140.2, 131.7, 129.6, 128.5, 128.3, 126.2, 125.7, 124.9, 122.8, 122.6, 122.0, 110.4, 92.4, 86.1, 85.0, 52.9, 46.9. HRMS (ESI) calcd. for $C_{22}H_{17}O_3S$ $[M+H]^+$: 361.0893, found: 361.0897.



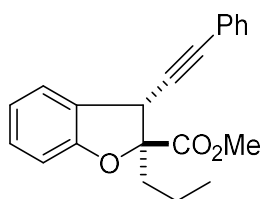
1'-methyl-3-(phenylethynyl)-3H-spiro[benzofuran-2,3'-indolin]-2'-one (3i)

3i was prepared via general procedure as colorless oil (54 mg, 77%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). 1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, $J = 7.5$ Hz, 1H), 7.43-7.32 (m, 4H), 7.30-7.21 (m, 4H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 4.99 (s, 1H), 3.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 159.0, 144.7, 131.9, 131.1, 129.5, 128.4, 128.2, 127.2, 126.6, 124.6, 124.2, 123.2, 122.7, 122.0, 110.3, 108.6, 89.2, 85.1, 83.4, 44.9, 26.1. HRMS (ESI) calcd. for $C_{24}H_{18}NO_2$ $[M+H]^+$: 352.1332, found: 352.1336.



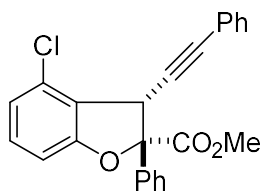
methyl 2-benzyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3j)

3j was prepared via general procedure as colorless oil (40 mg, 54%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.33 (m, 2H), 7.31-7.27 (m, 2H), 7.26-7.16 (m, 5H), 6.94-6.83 (m, 5H), 5.51 (s, 1H), 3.77 (s, 3H), 3.59 (d, *J* = 13.3 Hz, 1H), 3.20 (d, *J* = 13.3 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 171.5, 158.9, 135.5, 131.9, 130.5, 129.5, 128.9, 128.2, 128.15, 127.2, 126.9, 126.87, 121.8, 120.8, 110.5, 87.9, 83.9, 79.1, 63.8, 52.5, 42.8. HRMS (ESI) calcd. for C₂₅H₂₁O₃ [M+H]⁺: 369.1485, found: 369.1488.



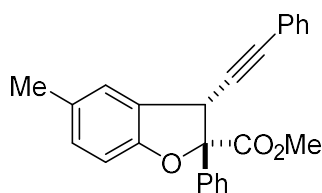
methyl 3-(phenylethynyl)-2-propyl-2,3-dihydrobenzofuran-2-carboxylate (3k)

3k was prepared via general procedure as colorless oil (36 mg, 57%) using 45 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1a**). ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.36 (m, 2H), 7.33-7.20 (m, 5H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.1 Hz, 1H), 5.40 (s, 1H), 3.74 (s, 3H), 2.11-1.97 (m, 2H), 1.52-1.40 (m, 1H), 1.30-1.20 (m, 1H), 0.92 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 171.9, 158.8, 131.9, 129.3, 128.9, 128.3, 128.2, 125.7, 121.9, 121.2, 110.6, 87.9, 84.2, 79.6, 62.4, 52.3, 39.3, 17.9, 14.3. HRMS (ESI) calcd. for C₂₁H₂₁O₃ [M+H]⁺: 321.1485, found: 321.1482.



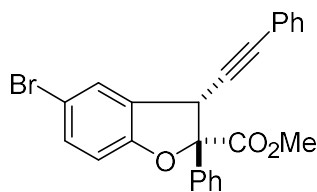
methyl 4-chloro-2-phenyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3l)

3l was prepared via general procedure as colorless oil (31 mg, 40%) using 52 mg of 3-chloro-2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1b**). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.46-7.32 (m, 5H), 7.32-7.27 (m, 3H), 7.17 (t, *J* = 8.1 Hz, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 4.96 (s, 1H), 3.81 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 168.9, 158.7, 138.6, 131.7, 131.0, 130.7, 128.8, 128.5, 128.4, 128.3, 126.1, 124.2, 122.6, 109.2, 94.1, 86.2, 83.8, 53.1, 46.4. HRMS (ESI) calcd. for C₂₄H₁₈ClO₃ [M+H]⁺: 389.0939, found: 389.0943.



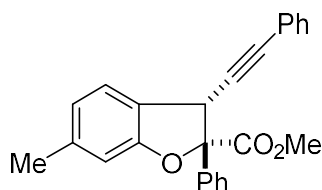
methyl 5-methyl-2-phenyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3m)

3m was prepared via general procedure as colorless oil (52 mg, 71%) using 48 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)-4-methylphenol (**1c**). ¹H NMR (300 MHz, CDCl₃) δ 7.82-7.74 (m, 2H), 7.48-7.43 (m, 2H), 7.40-7.28 (m, 6H), 7.12 (s, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 4.90 (s, 1H), 3.75 (s, 3H), 2.29 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 169.7, 156.0, 139.4, 131.8, 131.4, 129.9, 128.5, 128.4, 128.3, 126.2, 125.8, 125.2, 122.7, 110.0, 93.8, 86.0, 85.6, 52.9, 46.9, 20.9. HRMS (ESI) calcd. for C₂₅H₂₁O₃ [M+H]⁺: 369.1485, found: 369.1481.



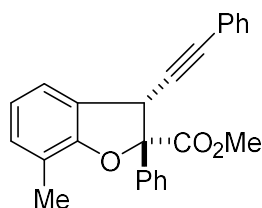
methyl 5-bromo-2-phenyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3n)

3n was prepared via general procedure as colorless oil (50 mg, 58%) using 61 mg of 4-bromo-2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenol (**1d**). ^1H NMR (300 MHz, CDCl_3) δ 7.78-7.71 (m, 2H), 7.49-7.28 (m, 10H), 6.94 (d, $J = 8.5$ Hz, 2H), 4.94 (s, 1H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 169.2, 157.3, 138.7, 132.4, 131.8, 128.8, 128.7, 128.4, 128.39, 127.8, 126.1, 122.3, 113.8, 112.0, 94.4, 86.6, 84.4, 53.0, 46.6. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{18}\text{BrO}_3$ $[\text{M}+\text{H}]^+$: 433.0434, found: 433.0428.



methyl 6-methyl-2-phenyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3o)

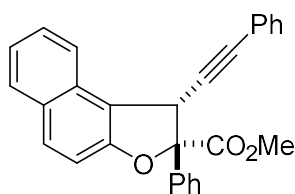
3o was prepared via general procedure as colorless oil (46 mg, 62%) using 48 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)-5-methylphenol (**1e**). ^1H NMR (400 MHz, CDCl_3) δ 7.80-7.75 (m, 2H), 7.46-7.33 (m, 5H), 7.32-7.28 (m, 3H), 7.19 (d, $J = 7.6$ Hz, 1H), 6.89 (s, 1H), 6.77 (d, $J = 7.6$ Hz, 1H), 4.90 (s, 1H), 3.75 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 169.6, 158.3, 139.9, 139.4, 131.7, 128.5, 128.4, 128.3, 126.2, 124.3, 123.0, 122.8, 122.7, 111.1, 94.0, 85.9, 85.7, 52.9, 46.7, 21.7. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$: 369.1485, found: 369.1489.



methyl 7-methyl-2-phenyl-3-(phenylethynyl)-2,3-dihydrobenzofuran-2-carboxylate

(3p)

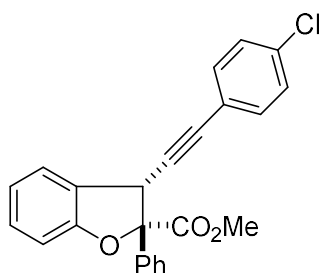
3p was prepared via general procedure as colorless oil (30 mg, 41%) using 48 mg of 2-(1-hydroxy-3-phenylprop-2-yn-1-yl)-6-methylphenol (**1f**). ¹H NMR (300 MHz, CDCl₃) δ 7.83-7.76 (m, 2H), 7.46-7.33 (m, 5H), 7.33-7.27 (m, 3H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 4.94 (s, 1H), 3.74 (s, 3H), 2.41 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 169.7, 156.6, 139.5, 131.7, 130.7, 128.5, 128.4, 128.3, 128.28, 126.2, 125.2, 122.8, 122.0, 121.8, 120.6, 93.4, 85.9, 85.7, 52.9, 47.3, 15.3. HRMS (ESI) calcd. for C₂₅H₂₁O₃ [M+H]⁺: 369.1485, found: 369.1480.



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

(3q)

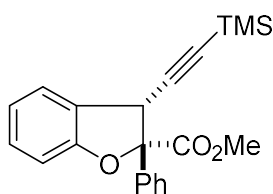
3q was prepared via general procedure as colorless oil (45 mg, 55%) using 55 mg of 1-(1-hydroxy-3-phenylprop-2-yn-1-yl)naphthalen-2-ol (**1g**). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.80 (t, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.42-7.29 (m, 7H), 7.29-7.25 (m, 3H), 5.25 (s, 1H), 3.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.5, 155.7, 139.5, 131.7, 130.9, 130.2, 130.0, 128.9, 128.7, 128.4, 128.37, 128.3, 127.3, 126.2, 123.7, 122.7, 122.5, 116.8, 112.5, 94.7, 86.6, 85.3, 53.1, 46.5. HRMS (ESI) calcd. for C₂₈H₂₁O₃ [M+H]⁺: 405.1485, found: 405.1488.



methyl 3-((4-chlorophenyl)ethynyl)-2-phenyl-2,3-dihydrobenzofuran-2-carboxylate

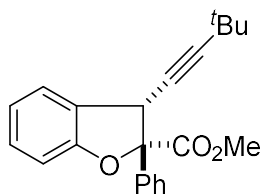
(3r)

3r was prepared via general procedure as colorless oil (47 mg, 60%) using 52 mg of 2-(3-(4-chlorophenyl)-1-hydroxyprop-2-yn-1-yl)phenol (**1h**). ¹H NMR (400 MHz, CDCl₃) δ 7.80-7.45 (m, 2H), 7.43-7.34 (m, 5H), 7.33-7.22 (m, 4H), 7.07 (d, *J* = 8.0 Hz, 1H), 6.96 (td, *J* = 7.5, 0.7 Hz, 1H), 4.93 (s, 1H), 3.74 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 169.5, 158.1, 139.2, 134.5, 133.0, 129.6, 128.7, 128.6, 128.4, 126.1, 125.7, 124.7, 122.0, 121.1, 110.5, 93.7, 86.5, 85.0, 53.0, 46.9. HRMS (ESI) calcd. for C₂₄H₁₈ClO₃ [M+H]⁺: 389.0939, found: 389.0934.



methyl 2-phenyl-3-((trimethylsilyl)ethynyl)-2,3-dihydrobenzofuran-2-carboxylate (3s)

3s was prepared via general procedure as colorless oil (41 mg, 59%) using 44 mg of 2-(1-hydroxy-3-(trimethylsilyl)prop-2-yn-1-yl)phenol (**1i**). ¹H NMR (400 MHz, CDCl₃) δ 7.76-7.70 (m, 2H), 7.40-7.31 (m, 3H), 7.27-7.19 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 4.75 (s, 1H), 3.75 (s, 3H), 0.18 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 169.4, 158.1, 139.4, 129.4, 128.5, 128.3, 126.2, 125.9, 124.7, 121.9, 110.3, 101.6, 93.7, 90.8, 52.7, 47.2, 0.0. HRMS (ESI) calcd. for C₂₁H₂₃O₃Si [M+H]⁺: 351.1411, found: 351.1416.



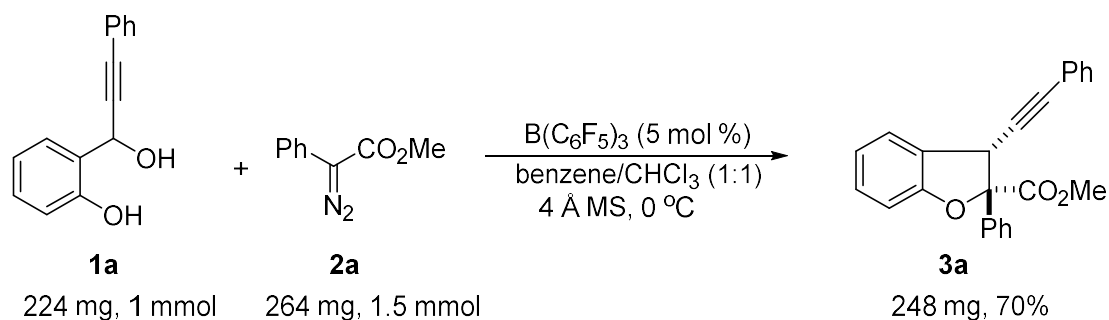
methyl

3-(3,3-dimethylbut-1-yn-1-yl)-2-phenyl-2,3-dihydrobenzofuran-2-carboxylate (3t)

3t was prepared via general procedure as colorless oil (43 mg, 64%) using 41 mg of 2-(1-hydroxy-4,4-dimethylpent-2-yn-1-yl)phenol (**1j**). ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 7.4 Hz, 2H), 7.40-7.29 (m, 3H), 7.26-7.17 (m, 2H), 7.01 (d, *J* = 8.0 Hz,

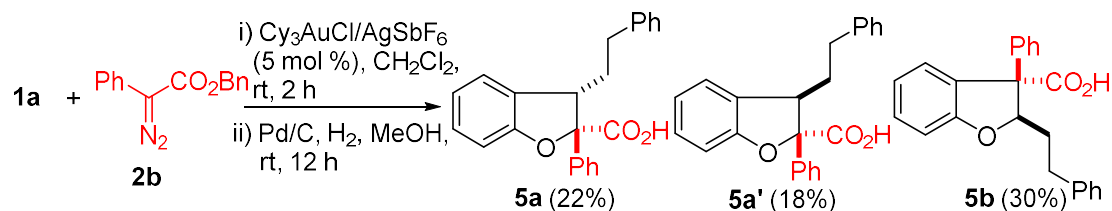
1H), 6.93 (t, $J = 7.4$ Hz, 1H), 4.70 (s, 1H), 3.74 (s, 3H), 1.23 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3) δ 169.6, 158.1, 139.7, 129.1, 128.4, 128.2, 127.0, 126.2, 124.5, 121.7, 110.1, 94.9, 93.7, 74.5, 52.6, 46.4, 31.1, 27.5. HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{23}\text{O}_3$ $[\text{M}+\text{H}]^+$: 335.1642, found: 335.1645.

Preparation of 3a in 1 mmol scale



To a dry tube was added $\text{B(C}_6\text{F}_5)_3$ (26.6 mg, 0.05 mmol, 0.05 eq), 4 Å molecular sieve (300 mg) and benzene/ CHCl_3 (15 mL, 1:1) under an argon atmosphere, then **1** (224 mg, 1 mmol, 1 eq) and **2** (264 mg, 1.5 mmol, 1.5 eq) in benzene/ CHCl_3 (15 mL, 1:1) was added via a syringe pump over 30 min at 0 °C. The reaction mixture was stirred for further 1.5 h. The reaction mixture was concentrated and purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether =1:30~1:15) to give products **3a** (248 mg, 70%) as colorless oil.

Further exploration of Scheme 4



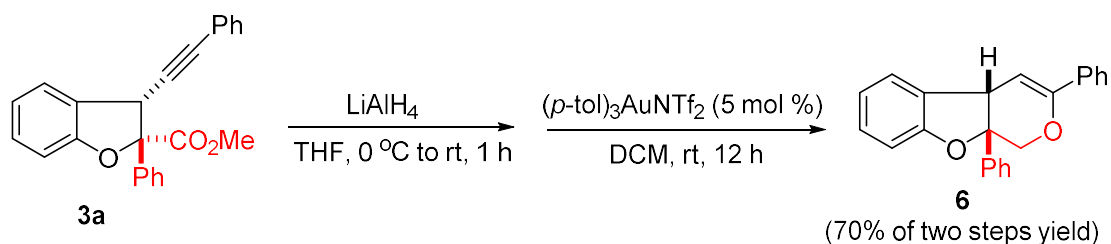
To a schlenk tube was added Cy_3PAuCl (10.2 mg, 0.02 mmol, 0.05 eq), AgSbF_6 (6.9 mg, 0.02 mmol, 0.05 eq), **1a** (90 mg, 0.4 mmol, 1 eq) and CH_2Cl_2 (6 mL) under argon atmosphere. After the mixture was stirred at rt for 0.5 h, **2b** (151 mg, 0.6 mmol, 1.5 eq) in CH_2Cl_2 (6 mL) was added in a portion. The reaction mixture was stirred for further 1.5 h. The reaction solution was concentrated, the crude residue was purified by

column chromatography (silica gel, eluted with EtOAc: Petroleum ether =1:50~1:20) to obtain a mixture of three isomers which was used to next step. To a flask was added the above mixture of three isomers, MeOH (15 mL) and 10% Pd/C (15 mg), the mixture was degassed and refilled with H₂ for three times. The mixture was stirred under a H₂ balloon at rt for 12 h. The reaction mixture was filtered through a pad of celite and washed the cake with MeOH; the filtrate was concentrated under vacuum. The crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether =1:8~1:3) to give **5a**, **5a'** and **5b**.

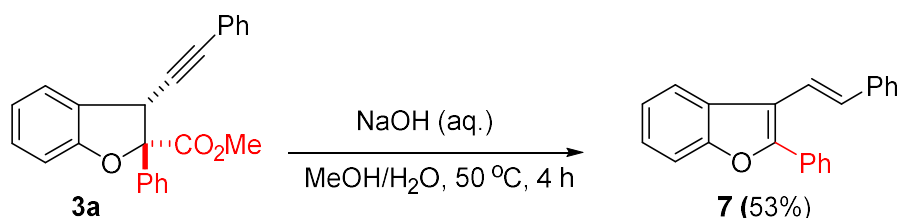
5a was obtained as a white solid (30 mg, 22%), mp: 142-144 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.66-7.59 (m, 2H), 7.33-7.21 (m, 6H), 7.16 (t, *J* = 7.2 Hz, 4H), 7.06 (d, *J* = 7.9 Hz, 1H), 6.93 (td, *J* = 7.4, 0.9 Hz, 1H), 3.78 (dd, *J* = 9.3, 4.2 Hz, 1H), 2.87-2.74 (m, 1H), 2.70-2.56 (m, 1H), 2.44-2.28 (m, 1H), 2.10-1.94 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 172.7, 156.7, 141.0, 139.4, 129.0, 128.9, 128.6, 128.4, 128.35, 126.1, 125.9, 125.4, 122.1, 110.6, 93.5, 52.5, 33.5, 32.4. HRMS (ESI) calcd. for C₂₃H₂₁O₃ [M+H]⁺: 345.1485, found: 345.1490.

5a' was obtained as a white solid (25 mg, 18%), mp: 180-182 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 6.9 Hz, 2H), 7.46-7.34 (m, 3H), 7.31-7.23 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 2H), 7.12-7.05 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.2 Hz, 2H), 4.14 (dd, *J* = 8.4, 4.8 Hz, 1H), 2.52-2.40 (m, 1H), 2.32-2.23 (m, 1H), 1.65-1.54 (m, 1H), 1.45-1.36 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 175.7, 156.8, 141.4, 134.1, 129.7, 128.9, 128.7, 128.6, 128.3, 128.2, 126.1, 125.8, 125.6, 122.3, 110.5, 94.2, 48.0, 33.6, 31.8. HRMS (ESI) calcd. for C₂₃H₂₁O₃ [M+H]⁺: 345.1485, found: 345.1488.

5b was obtained as a white solid (41 mg, 30%), mp: 156-158 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.5 Hz, 1H), 7.34-7.24 (m, 4H), 7.24-7.18 (m, 2H), 7.13 (t, *J* = 7.1 Hz, 1H), 7.08 (d, *J* = 7.1 Hz, 2H), 7.01-6.92 (m, 4H), 5.32 (dd, *J* = 10.5, 2.8 Hz, 1H), 2.90-2.79 (m, 1H), 2.76-2.63 (m, 1H), 1.59-1.48 (m, 1H), 1.37-1.27 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 178.6, 159.5, 141.5, 137.4, 130.2, 128.53, 128.5, 128.4, 127.9, 127.87, 127.6, 127.2, 125.9, 121.3, 110.3, 87.4, 64.6, 33.7, 32.7. HRMS (ESI) calcd. for C₂₃H₂₁O₃ [M+H]⁺: 345.1485, found: 345.1488.



To a suspension of LAH (27 mg, 0.7 mmol, 7 eq) in anhydrous THF (2 mL) was added dropwise a solution of **3a** (35 mg, 0.1 mmol, 1 eq) in THF (1 mL) at 0 °C, then the mixture was allowed to rt and stirred for 1 h. The reaction was quenched with H₂O and extracted with EtOAc; the organic layer was dried over Na₂SO₄, concentrated under vacuum to give alcohol product which was pure enough and used directly. To a solution of the above alcohol (0.1 mmol, 1 eq) in DCM (5 mL) was added (*p*-tol)₃PAuNTf₂ (3.9 mg, 0.005 mmol, 0.05 eq) under argon atmosphere, then stirred at rt for 12 h. The reaction solution was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:100~1:50) to give **6** as a white solid (23 mg, 70% of two steps yield), mp: 41-43 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (t, *J* = 8.0 Hz, 4H), 7.42-7.28 (m, 6H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 5.85 (d, *J* = 4.4 Hz, 1H), 4.25 (s, 2H), 4.21 (d, *J* = 4.4 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 157.7, 152.7, 142.2, 134.7, 130.9, 128.6, 128.5, 128.3, 128.0, 125.2, 124.8, 124.3, 121.3, 110.6, 99.0, 86.9, 70.5, 46.1. HRMS (ESI) calcd. for C₂₃H₁₉O₂ [M+H]⁺: 327.1380, found: 327.1385.

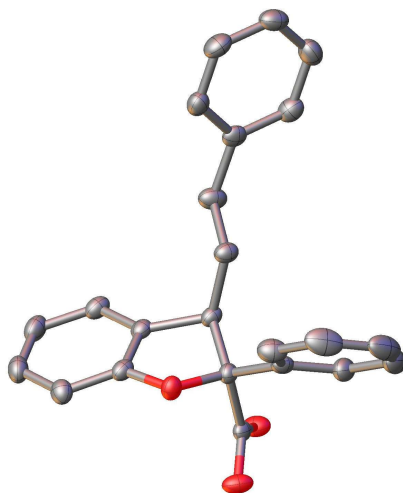


To a solution of **3a** (35 mg, 0.1 mmol, 1 eq) in MeOH (1.5 mL) was added a solution of NaOH (16 mg, 0.4 mmol, 4 eq) in H₂O (3.5 mL), the resulting solution was stirred at 50 °C for 4 h. The reaction was cooled, acidified with HCl and extracted with EtOAc; the organic layer was dried over Na₂SO₄, concentrated under vacuum to give crude product, which was purified by column chromatography (silica gel, eluted with

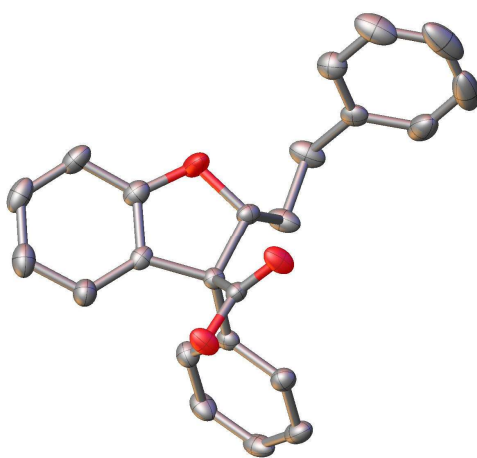
EtOAc: Petroleum ether =1:100) to give **7⁴** as sticky colorless oil (16 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 8.00-7.95 (m, 1H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.59-7.48 (m, 5H), 7.46-7.27 (m, 8H). ¹³C NMR (75 MHz, CDCl₃) δ 154.5, 153.4, 137.8, 131.1, 130.9, 128.8, 128.0, 127.8, 127.6, 126.3, 124.9, 123.2, 121.0, 119.9, 114.6, 111.4.

X-ray structure of **5a'** and **5b**

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1923042, **5a'**) and (CCDC 1922985, **5b**). The data can be obtained free of charge via the internet at <https://www.ccdc.cam.ac.uk/structures/>.



X-ray structure of **5a'**

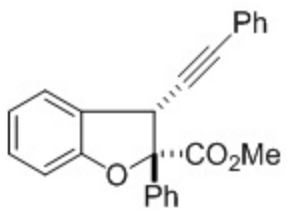


X-ray structure of **5b**

References

1. (a) Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063. (b) Chan, W.-W.; Yeung, S.-H.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y. *Org. Lett.* **2010**, *12*, 604. (c) Peng, C.; Wang, Y.; Wang, J. *J. Am. Chem. Soc.* **2008**, *130*, 1566. (d) Murphy, G. K.; Abbas, F. Z.; Poulton, A. V. *Adv. Synth. Catal.* **2014**, *356*, 2919. (e) Zhang, Y.; Yao, Y.; He, L.; Liu, Y.; Shi, L. *Adv. Synth. Catal.* **2017**, *359*, 2754. (f) Lee, E. C.; Fu, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 12066.
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3. Wang, C.; Erker G.; Kehr, G.; Wedeking, K.; Fröhlich, R. *Organometallics* **2005**, *24*, 4760.
4. Nakamura, M.; Ilies, L.; Otsubo, S.; Nakamura, E. *Angew. Chem. Int. Ed.* **2006**, *45*, 944.

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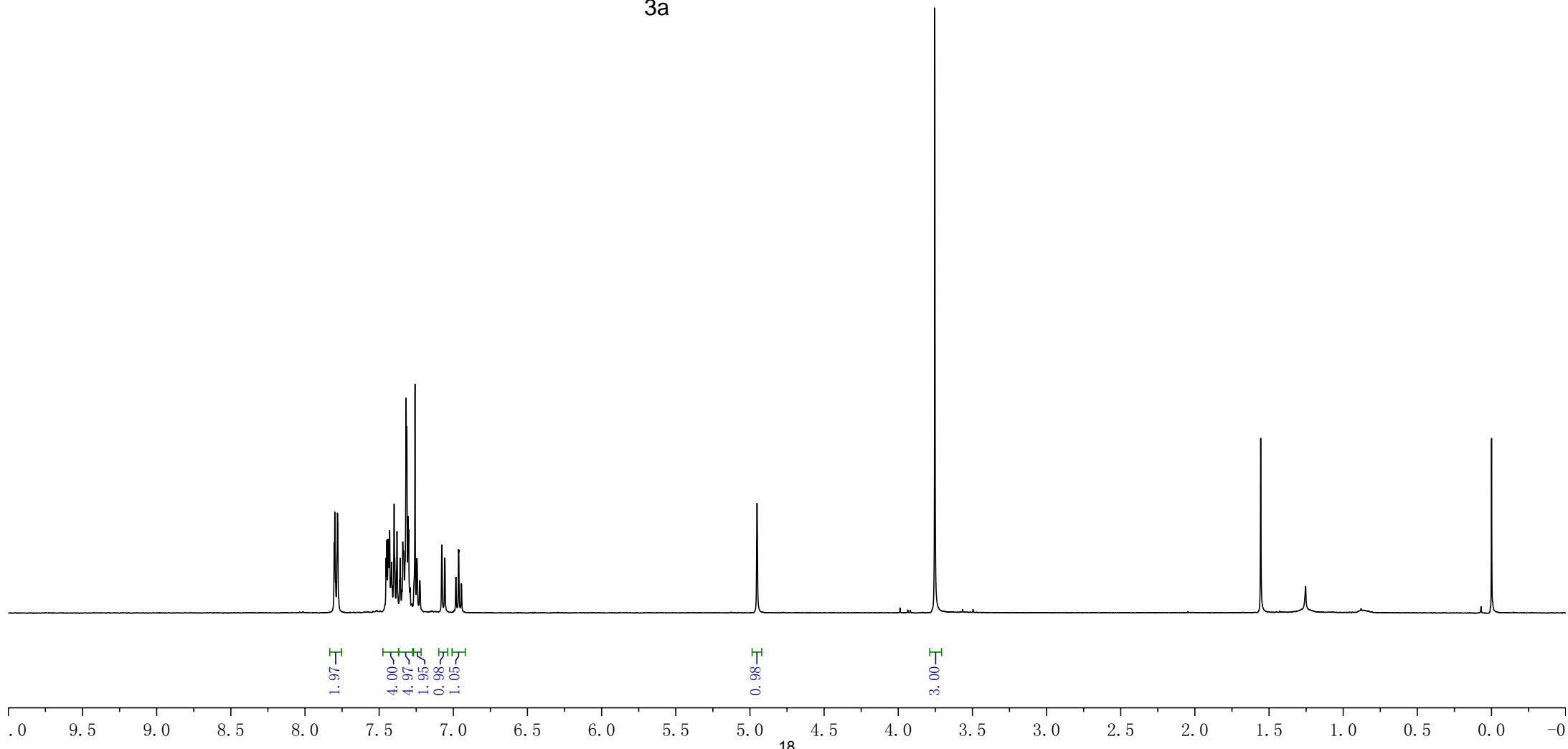
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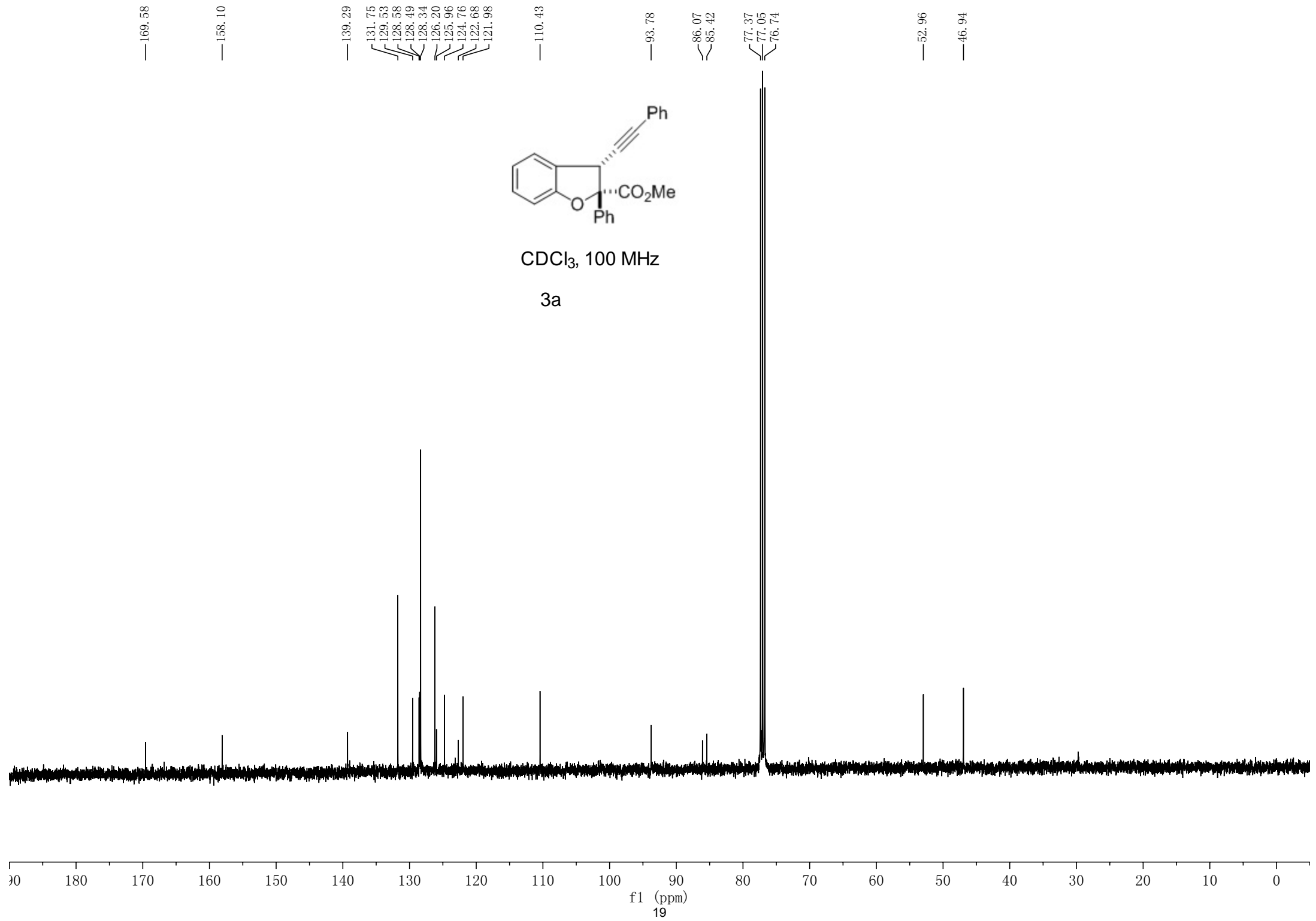
3a

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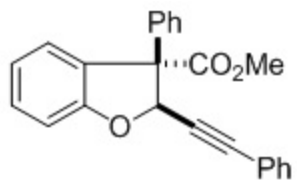
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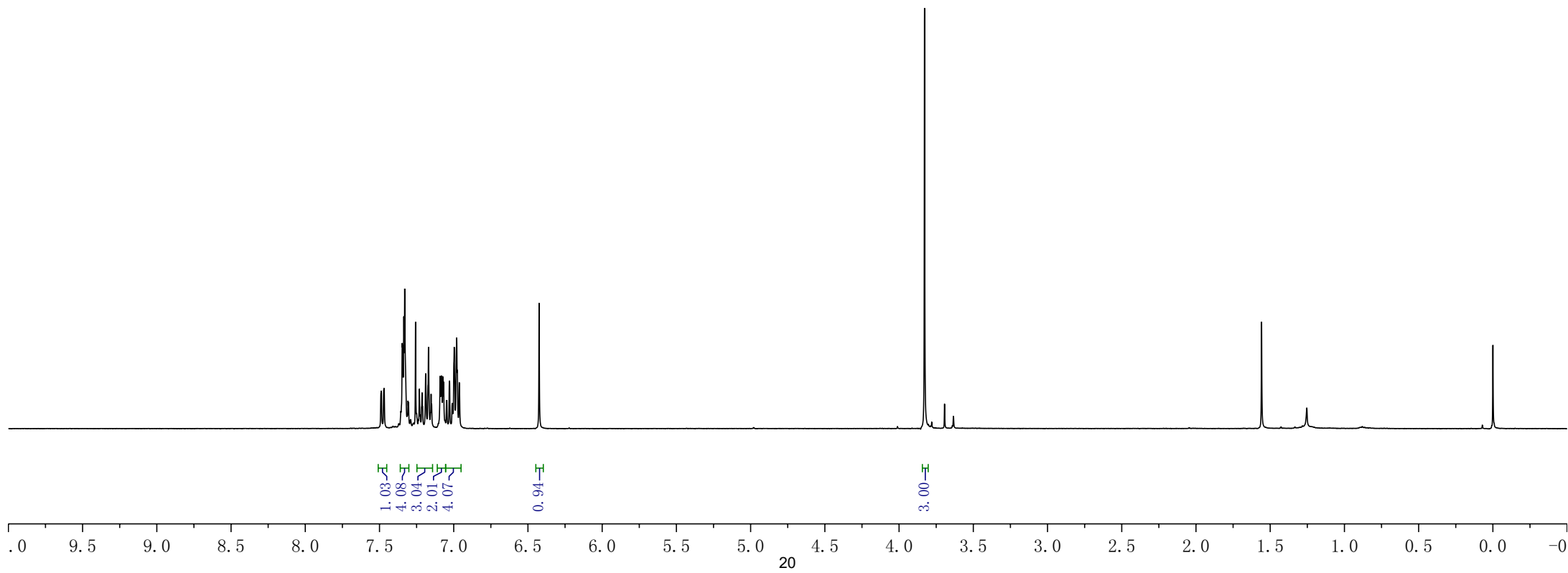
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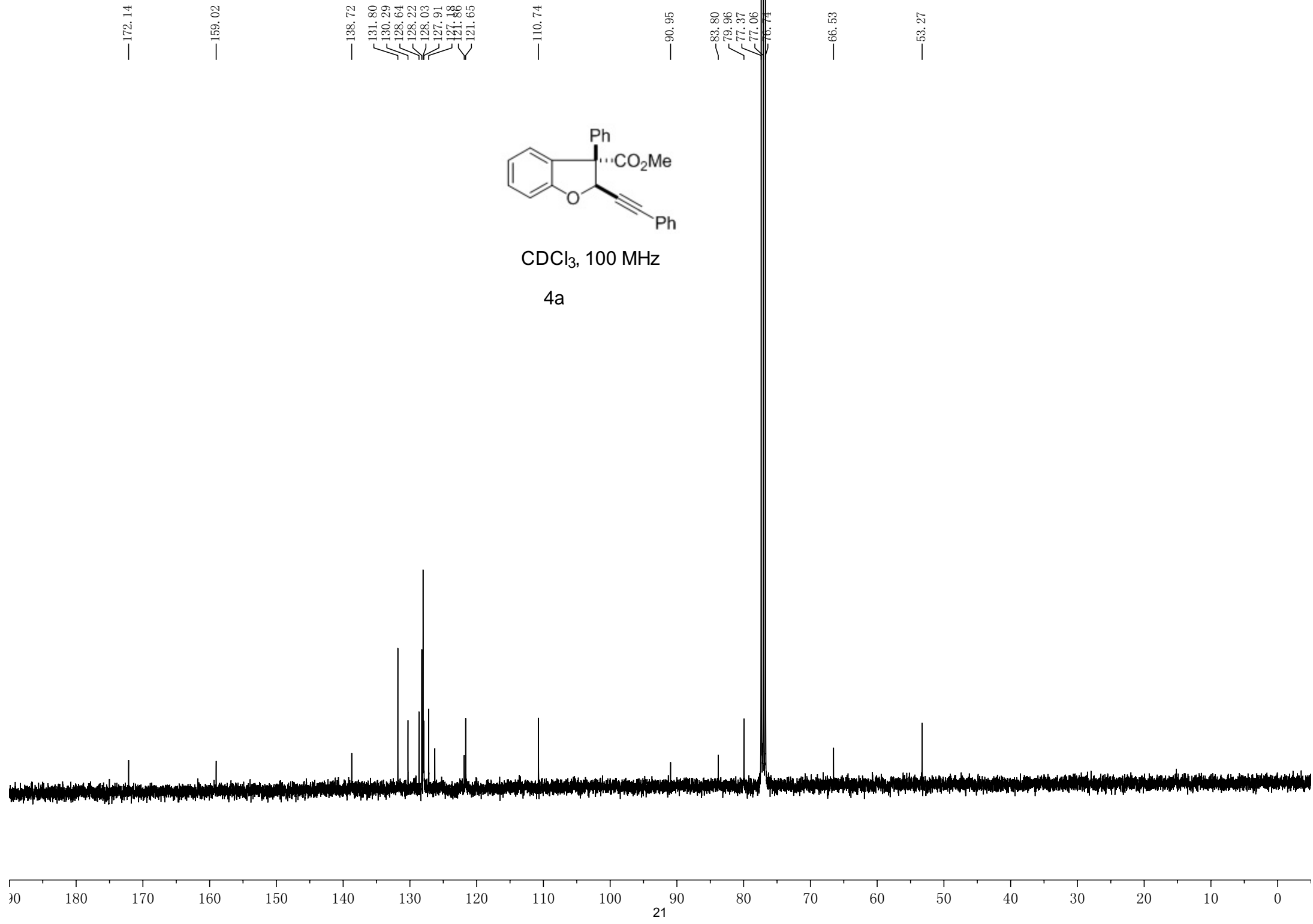
4a

3.83

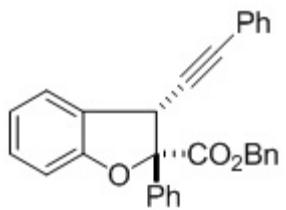
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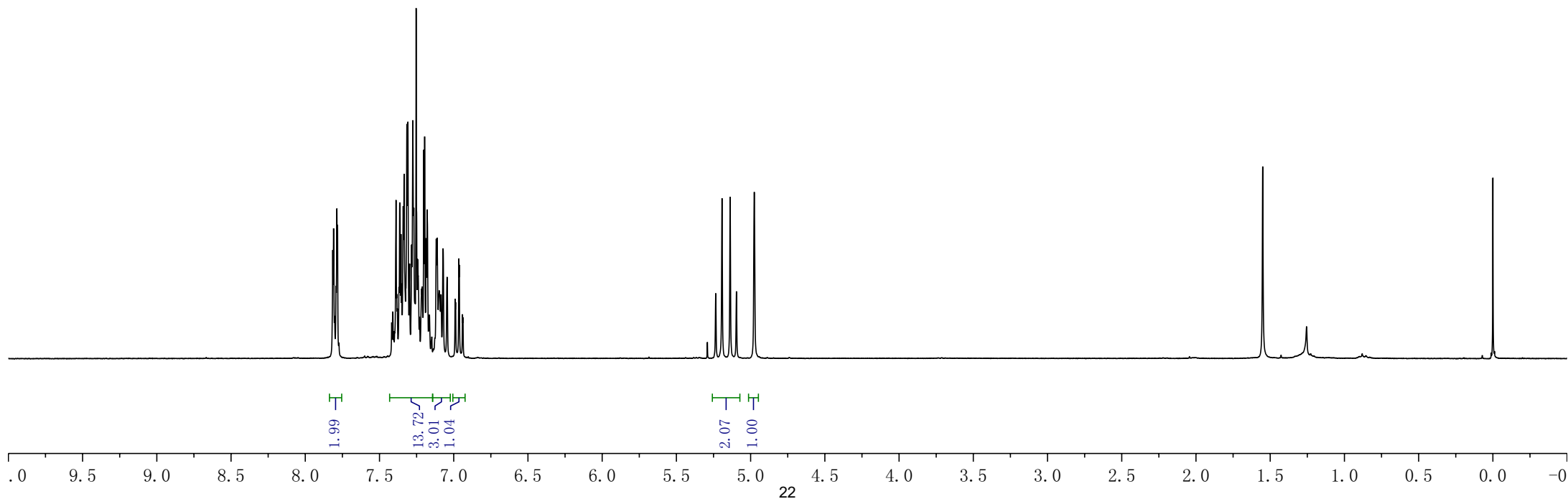
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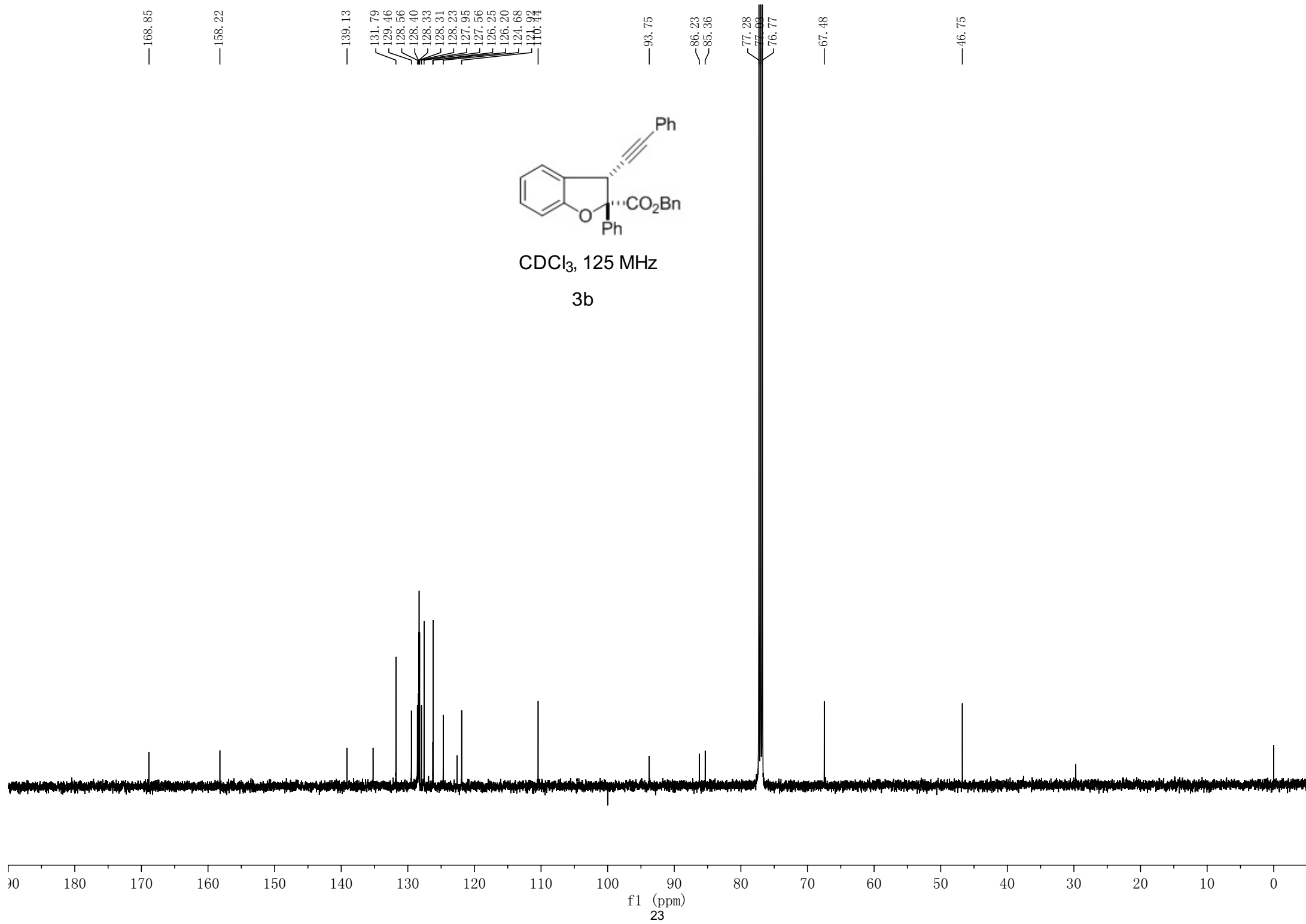


CDCl₃, 300 MHz
3b

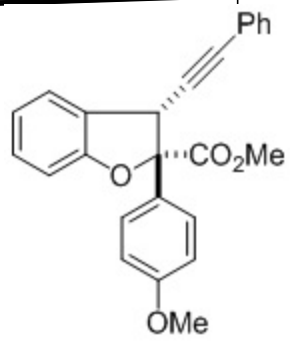
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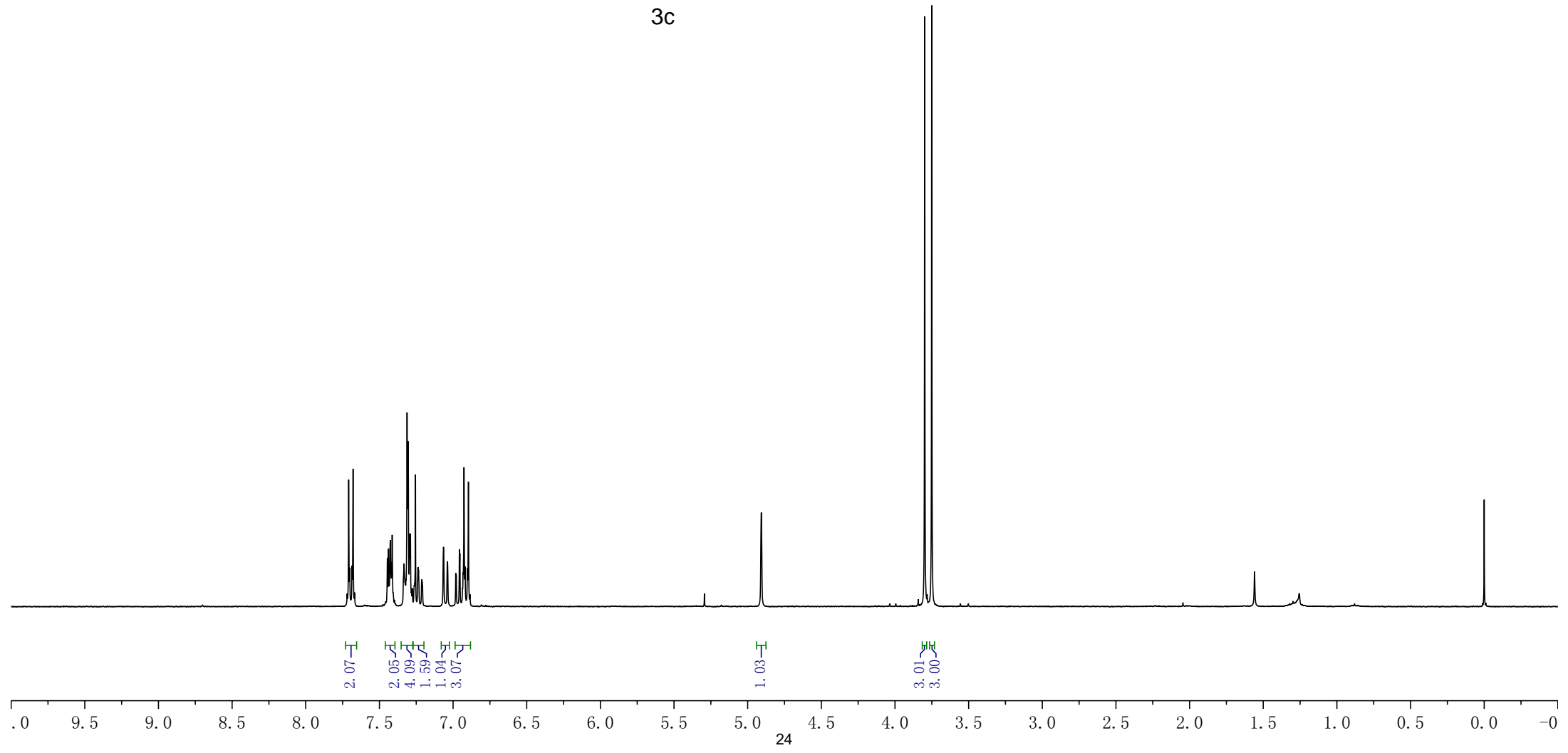
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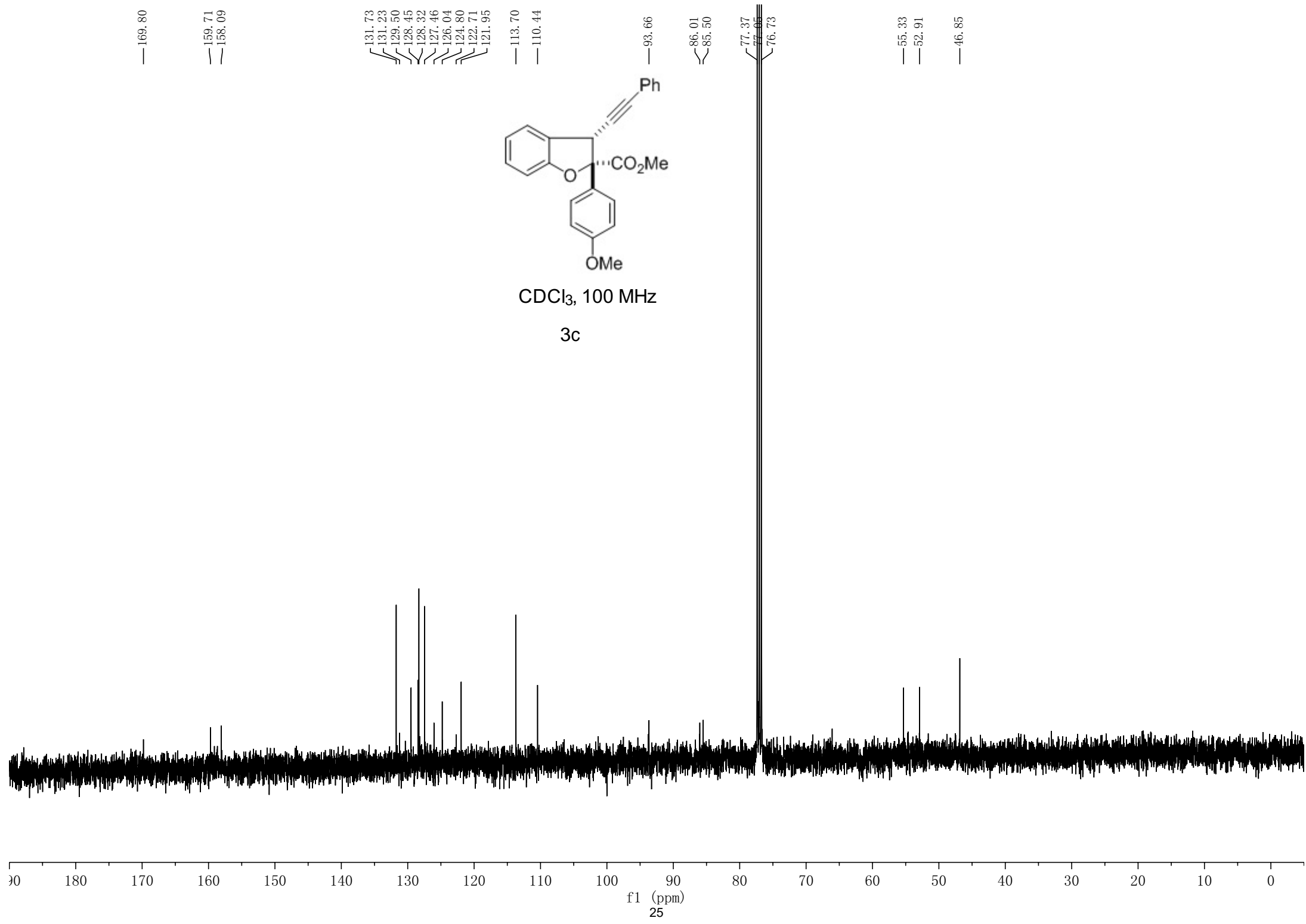
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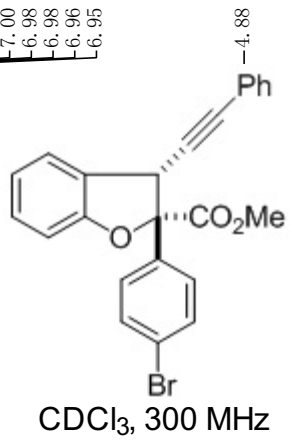
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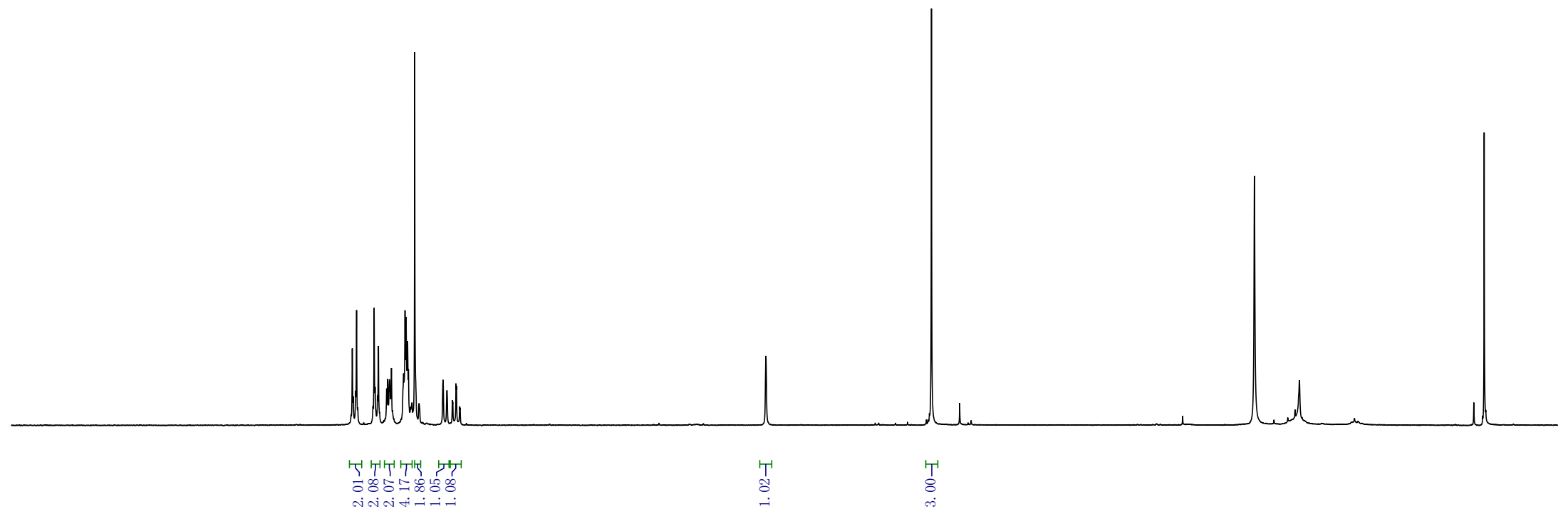


3d

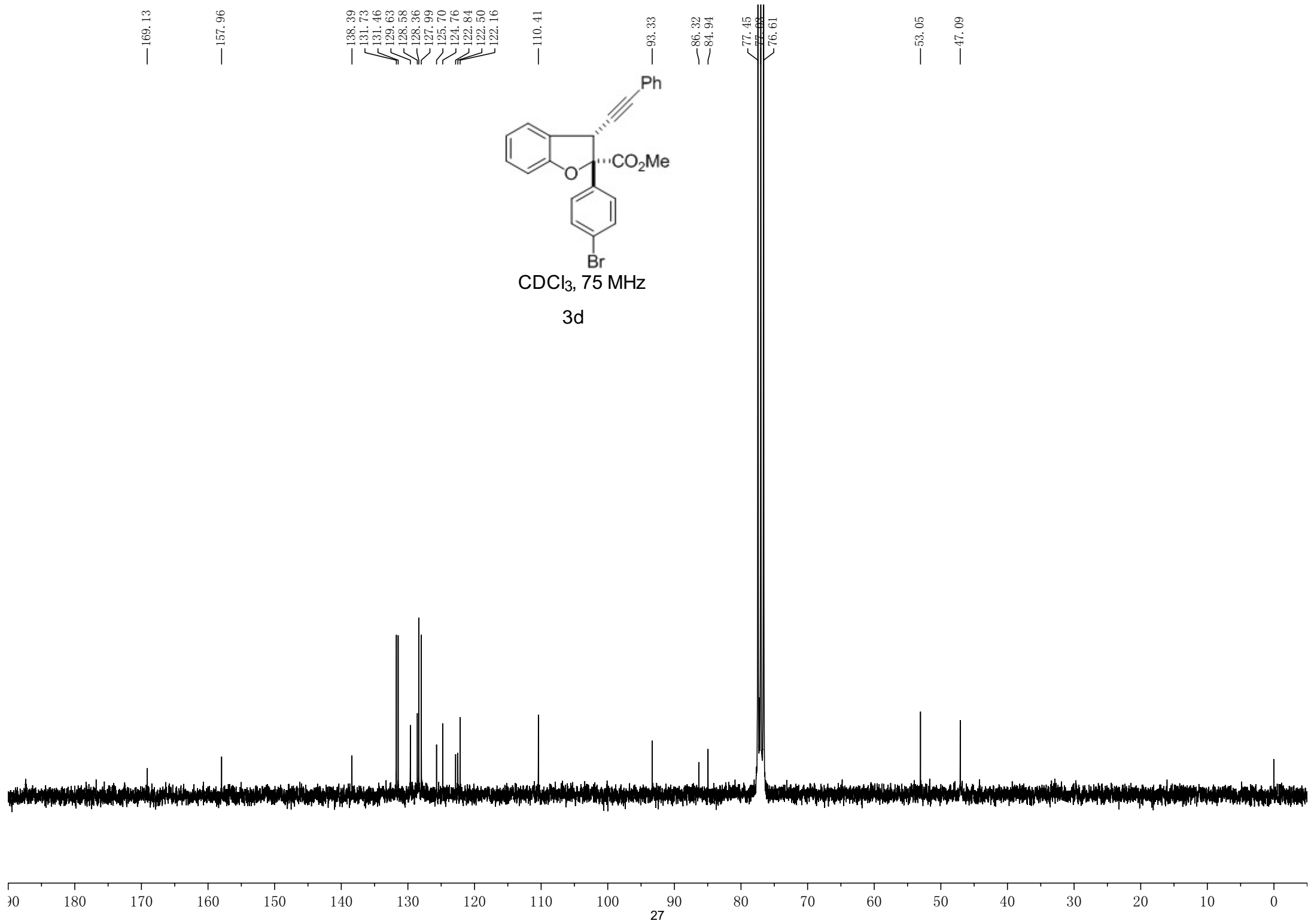
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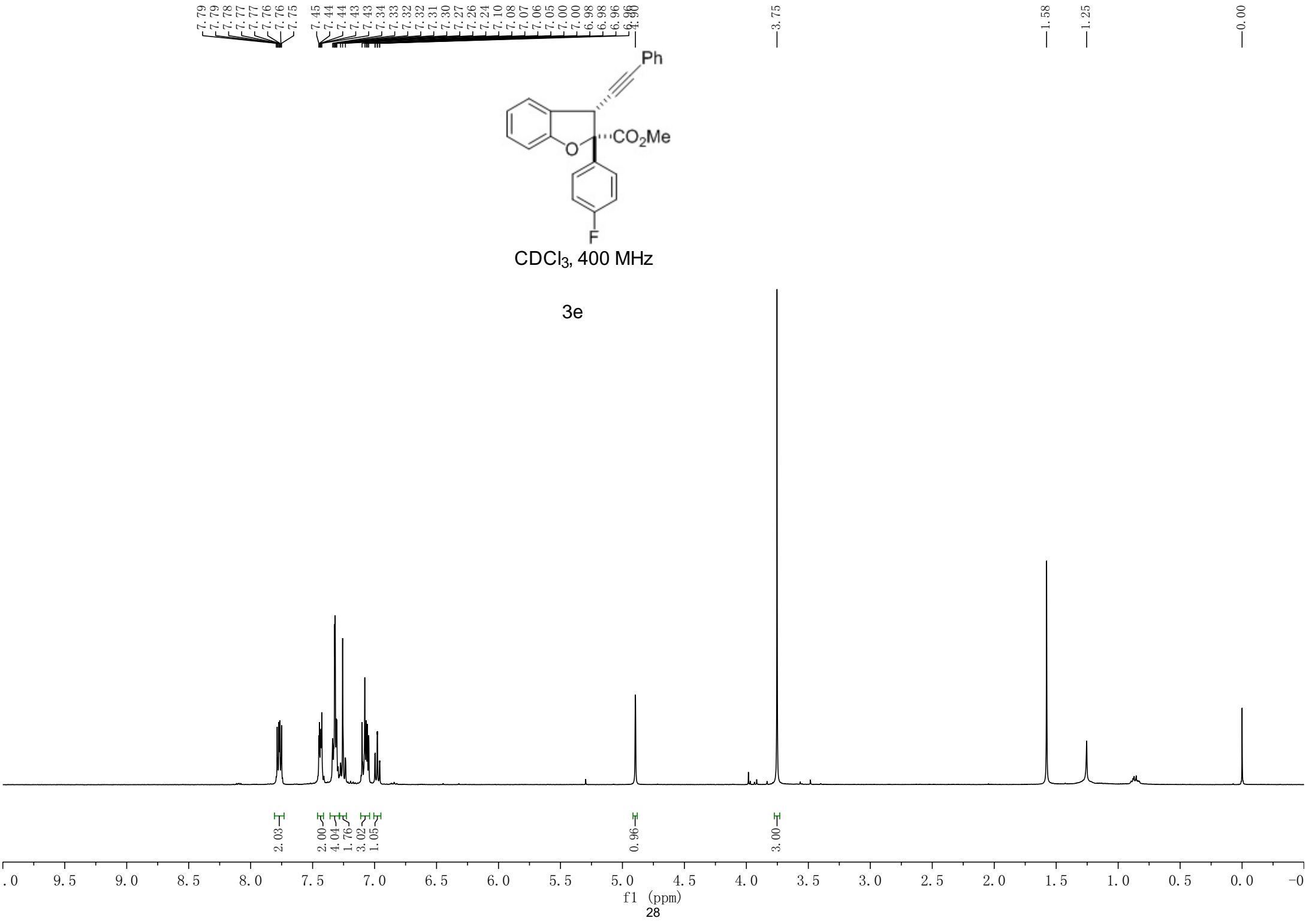
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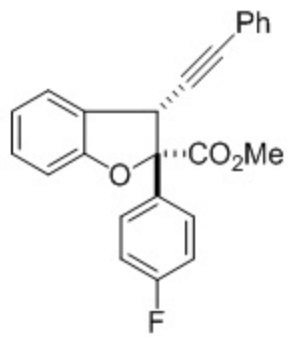
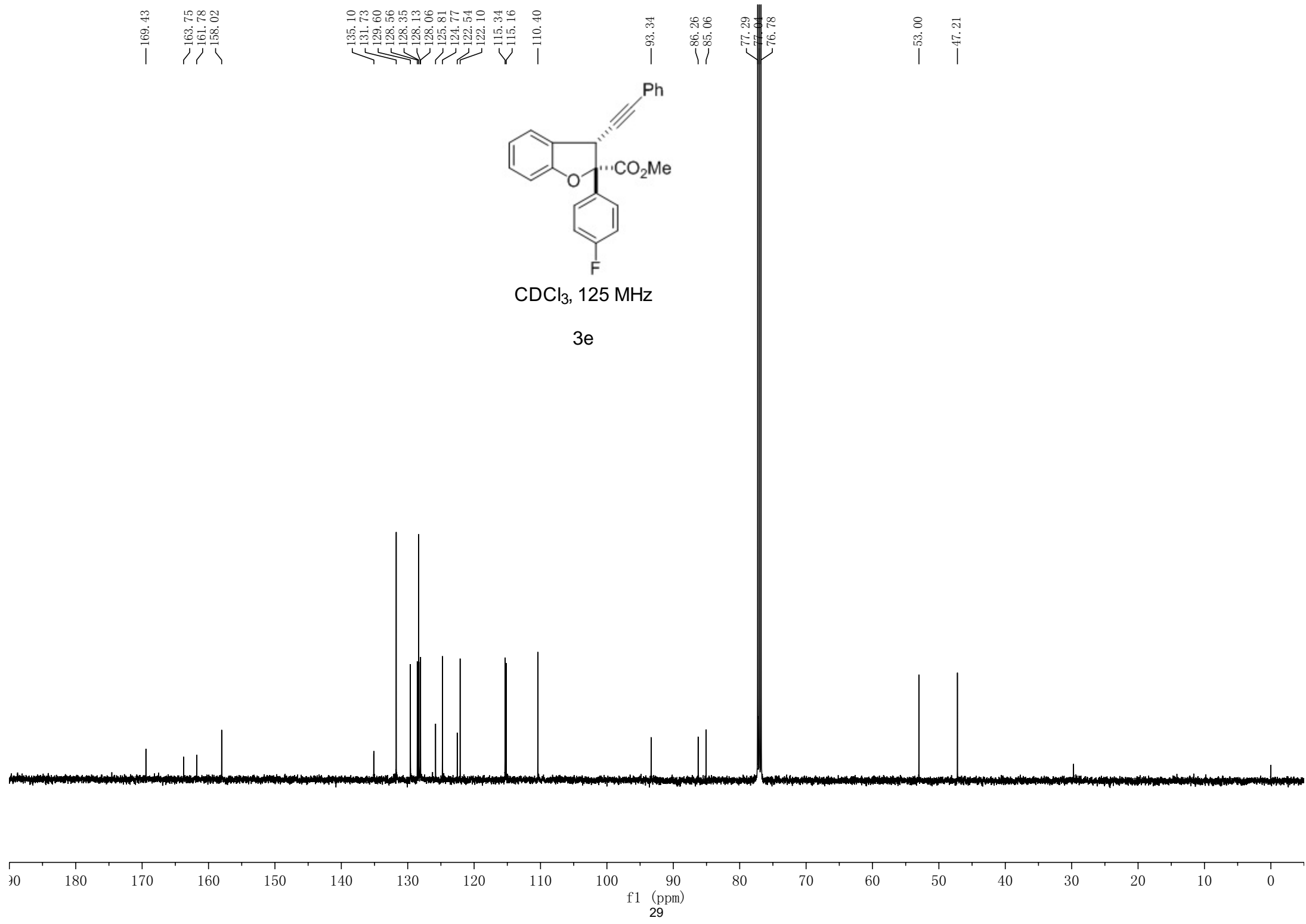
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.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0



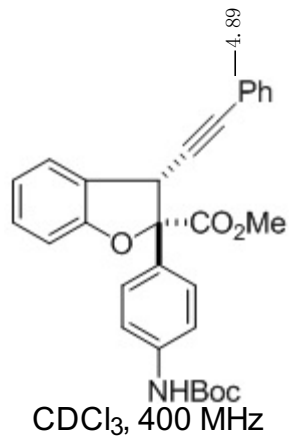




CDCl₃, 125 MHz

3e

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6.55

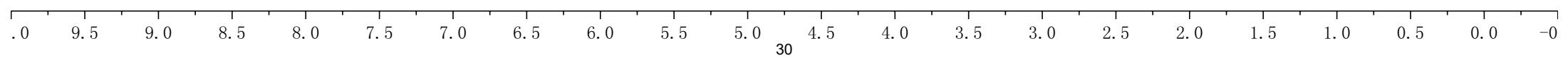


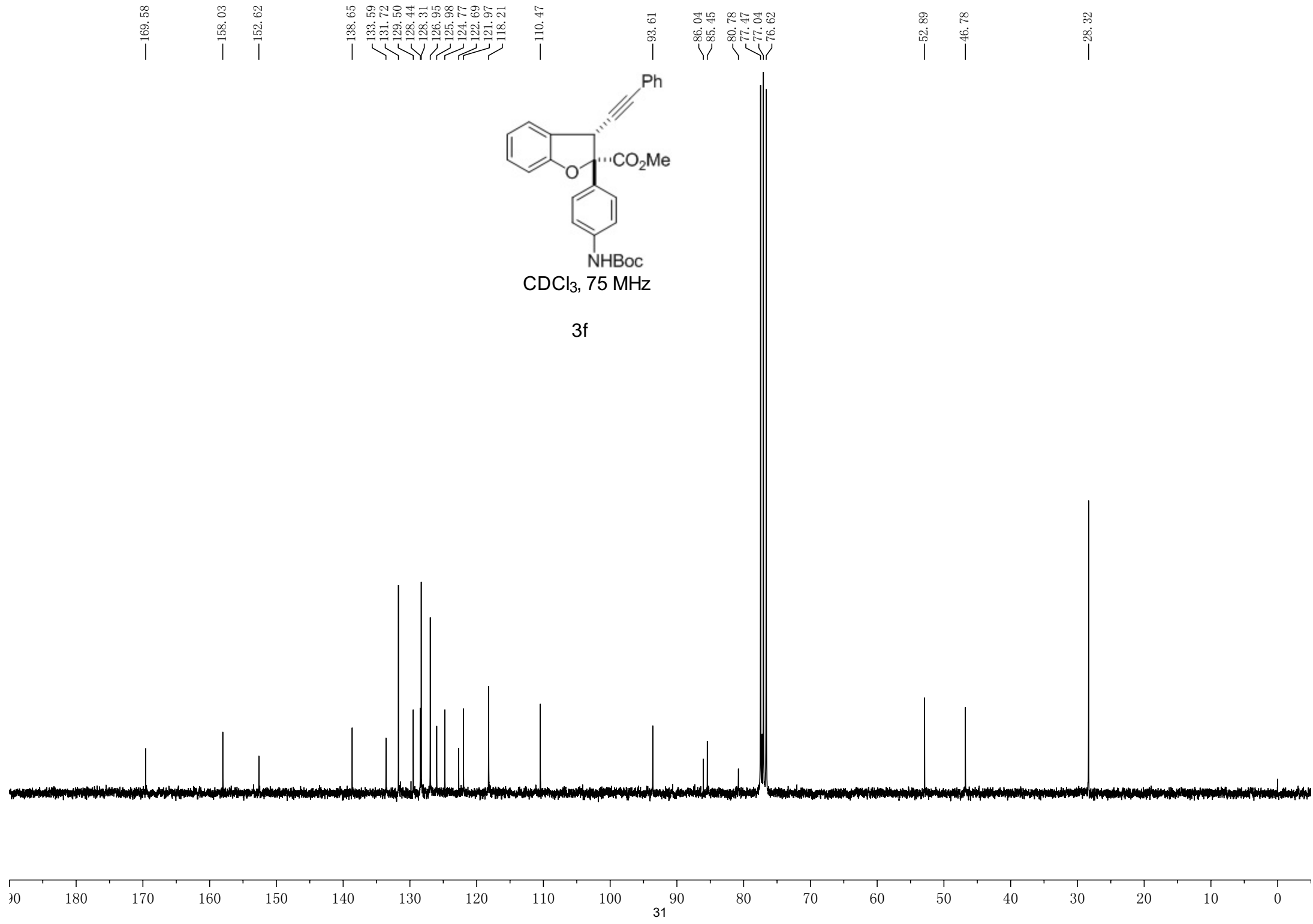
3f

3.74

1.60
1.50

-0.00





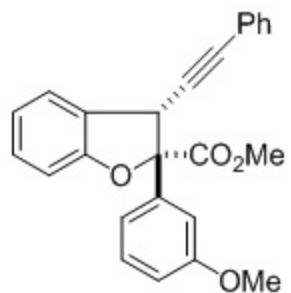
7.45
7.44
7.43
7.42
7.39
7.37
7.35
7.34
7.34
7.33
7.31
7.31
7.30
7.30
7.29
7.28
7.26
7.24
7.22
7.07
7.05
6.98
6.96
6.95
6.89
6.89
6.87
6.87

4.95

3.82
3.75

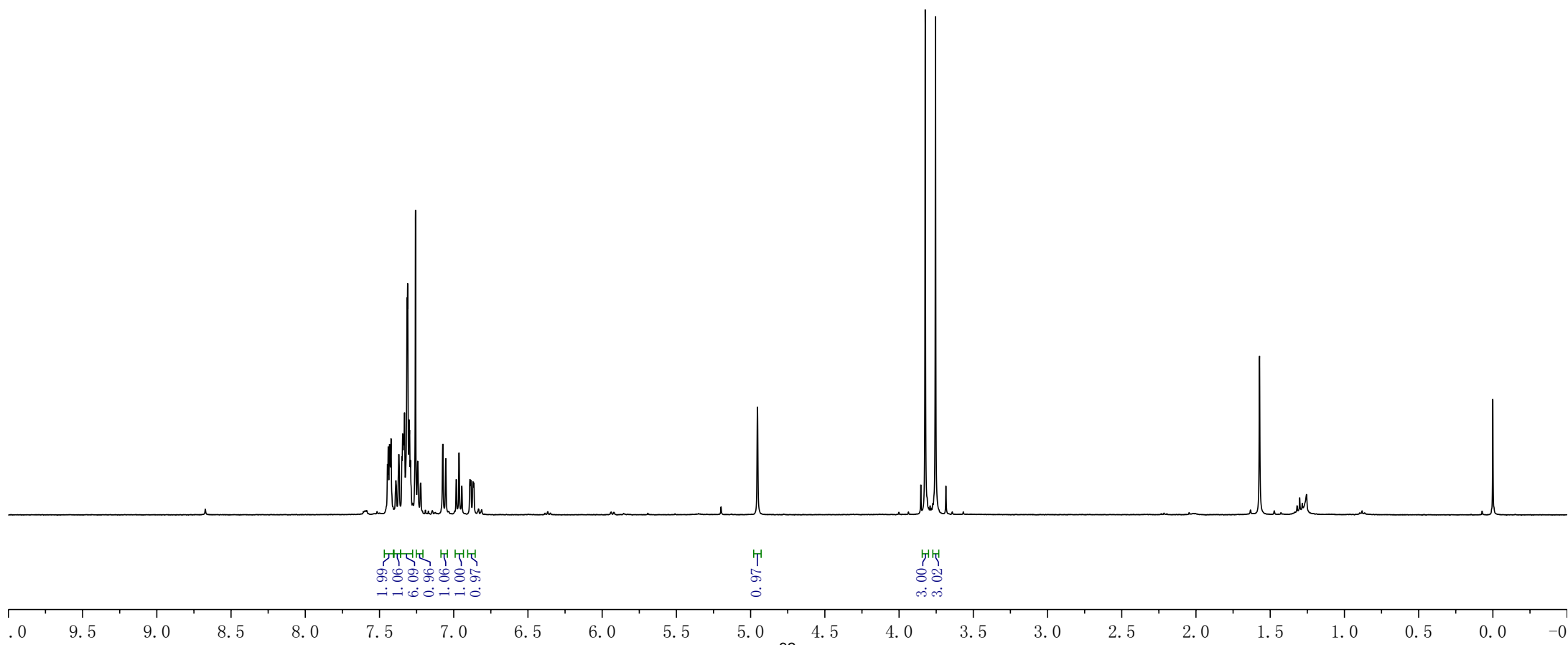
1.57

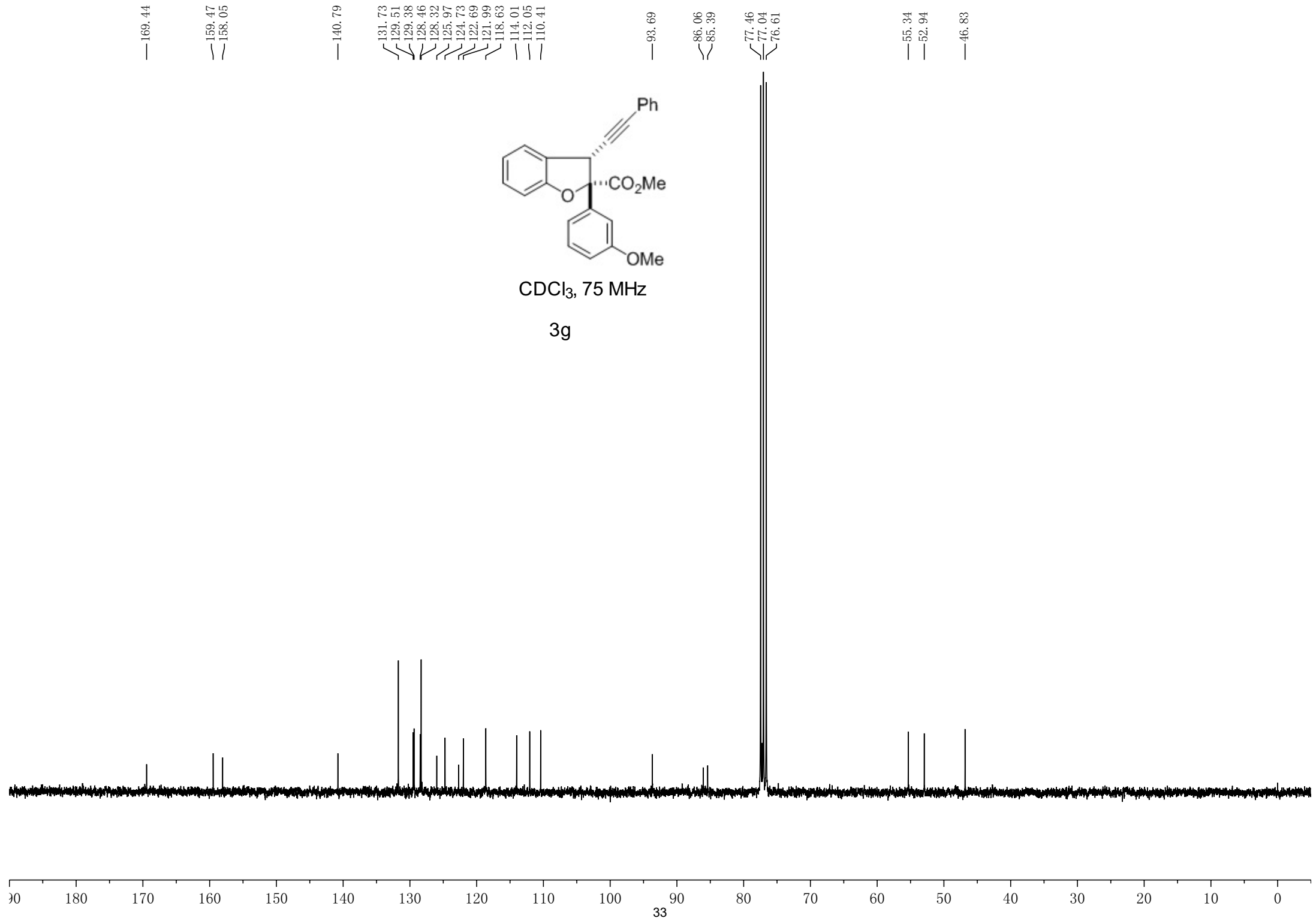
0.00



CDCl₃, 400 MHz

3g





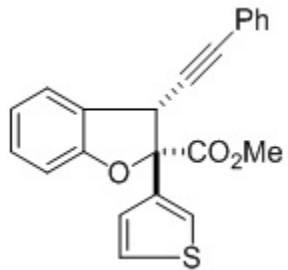
7.55
7.55
7.54
7.43
7.41
7.41
7.40
7.40
7.39
7.38
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.26
7.26
7.25
7.23
7.06
7.04
6.99
6.97
6.96

4.85

3.79

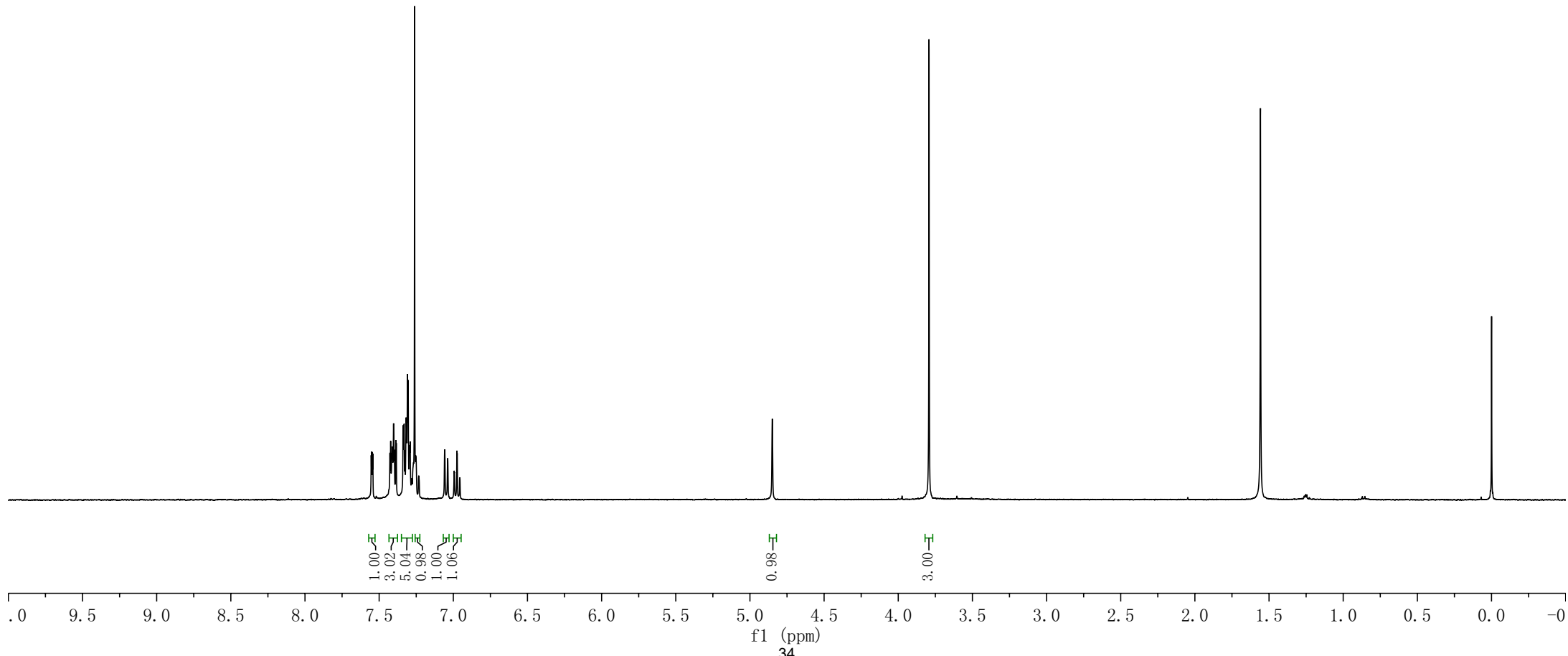
1.56

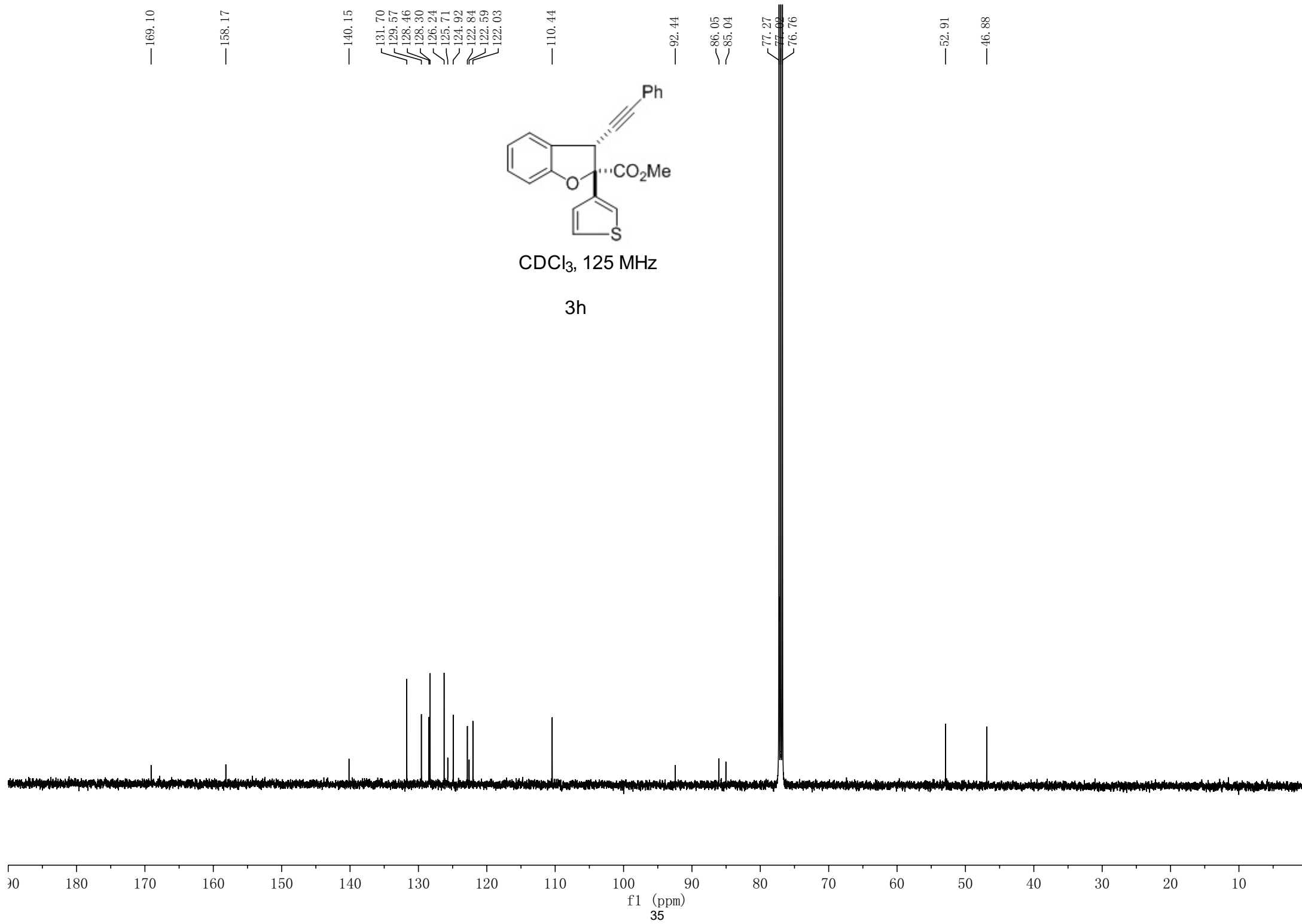
-0.00



CDCl₃, 400 MHz

3h





7.47
7.46
7.42
7.40
7.39
7.37
7.35
7.27
7.25
7.24
7.15
7.13
7.12
7.12
7.04
7.03
7.01
6.94
6.92
6.87
6.85

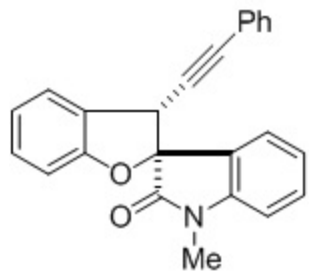
5.28

4.99

3.19

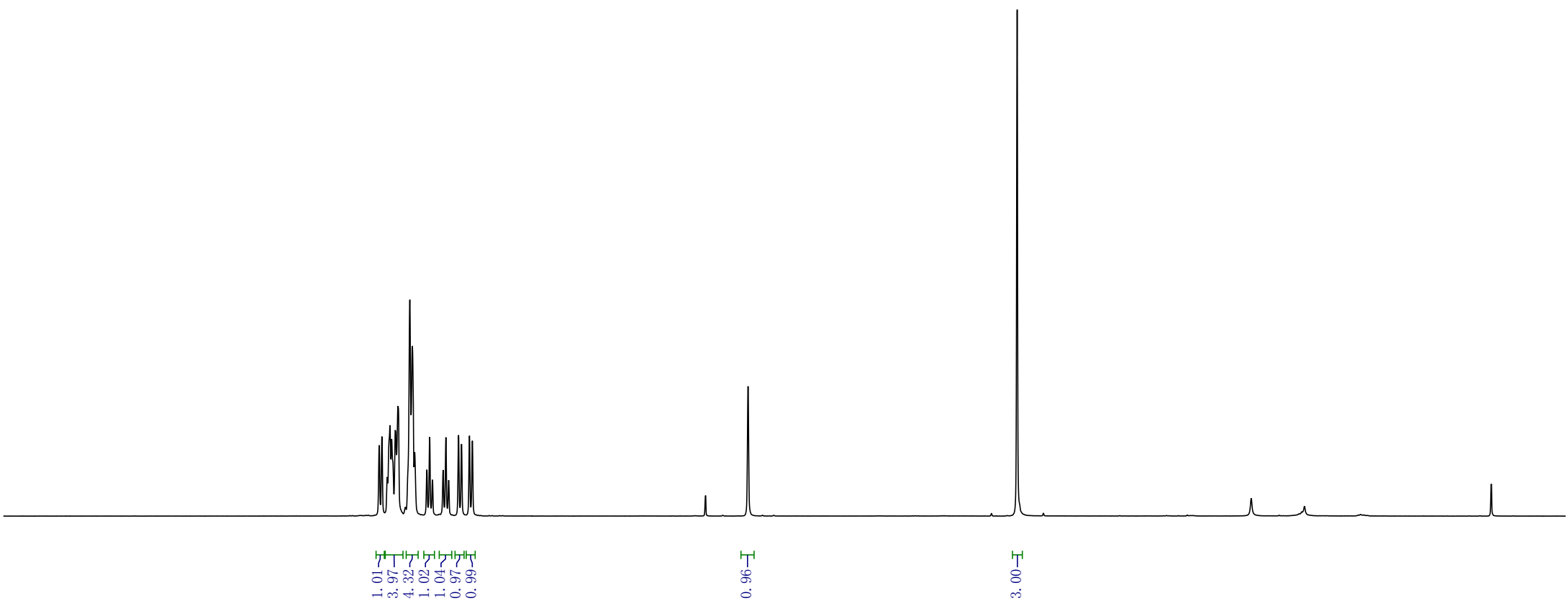
1.61

-0.00



CDCl₃, 400 MHz

3i



1.01
3.97
4.32
1.02
1.04
0.97
0.99
0.96
3.00
1.61

0.0 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 -0.0

36

— 172.56

— 158.99

— 144.72

131.87

131.08

129.48

128.41

128.22

127.18

126.60

124.61

124.16

123.24

122.65

122.00

110.26

108.55

— 89.24

85.10

83.44

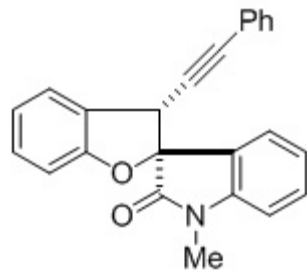
77.50

77.08

76.65

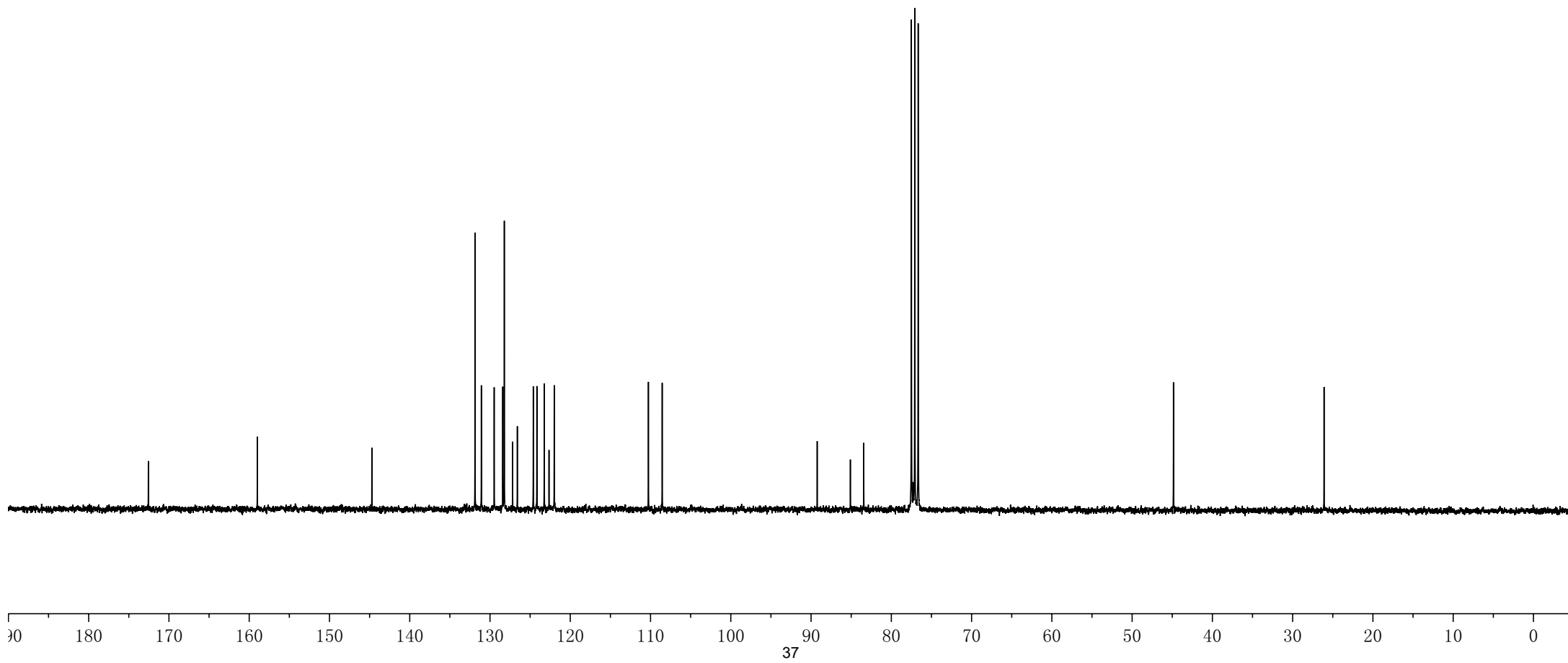
— 44.85

— 26.09



CDCl₃, 75 MHz

3i



7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.31
7.29
7.29
7.28
7.27
7.26
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.19
7.17
6.92
6.92
6.91
6.89
6.88
6.87
6.86
6.85
6.83

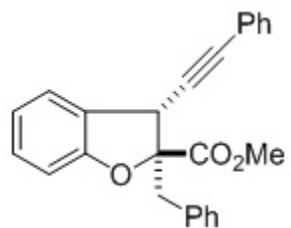
5.51

3.77
3.61
3.57

3.22
3.18

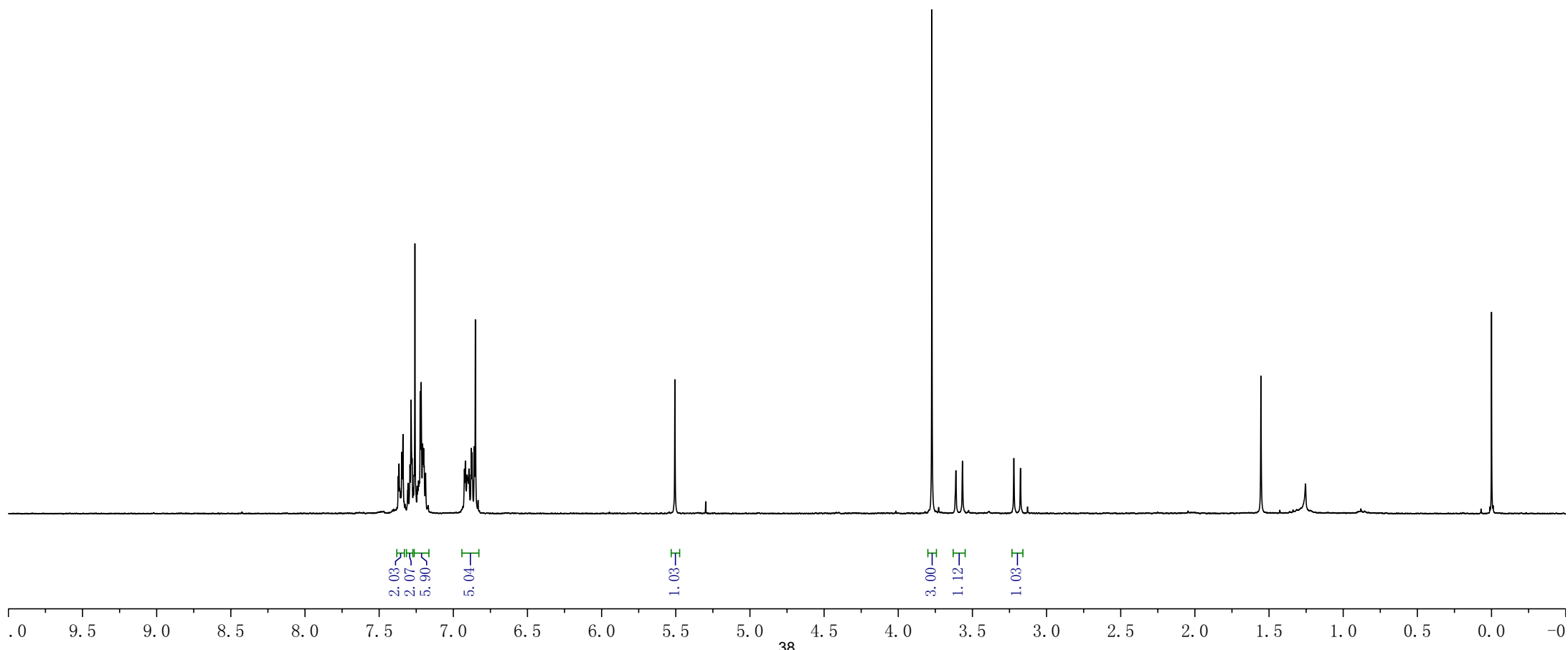
1.55

0.00



CDCl₃, 300 MHz

3j



— 171.52

— 158.87

135.47
131.89
130.48
129.45
128.85
128.24
128.15
127.16
126.94
126.87
121.81
120.82

— 110.50

— 87.87

— 83.93

79.09

77.46

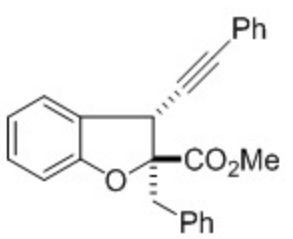
77.01

76.61

— 63.79

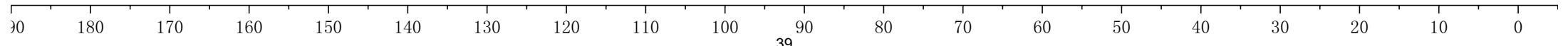
— 52.45

— 42.83



CDCl₃, 75 MHz

3j



7.42
7.40
7.40
7.38
7.38
7.31
7.30
7.29
7.27
7.26
7.25
7.25
7.24
7.23
7.21
7.21
6.98
6.96
6.94
6.91
6.89

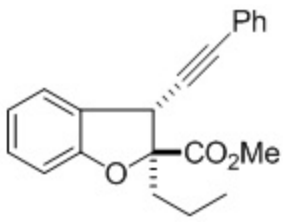
5.40

3.74

2.11
2.10
2.08
2.07
2.06
2.05
2.04
2.04
2.03
2.02
1.99
1.98

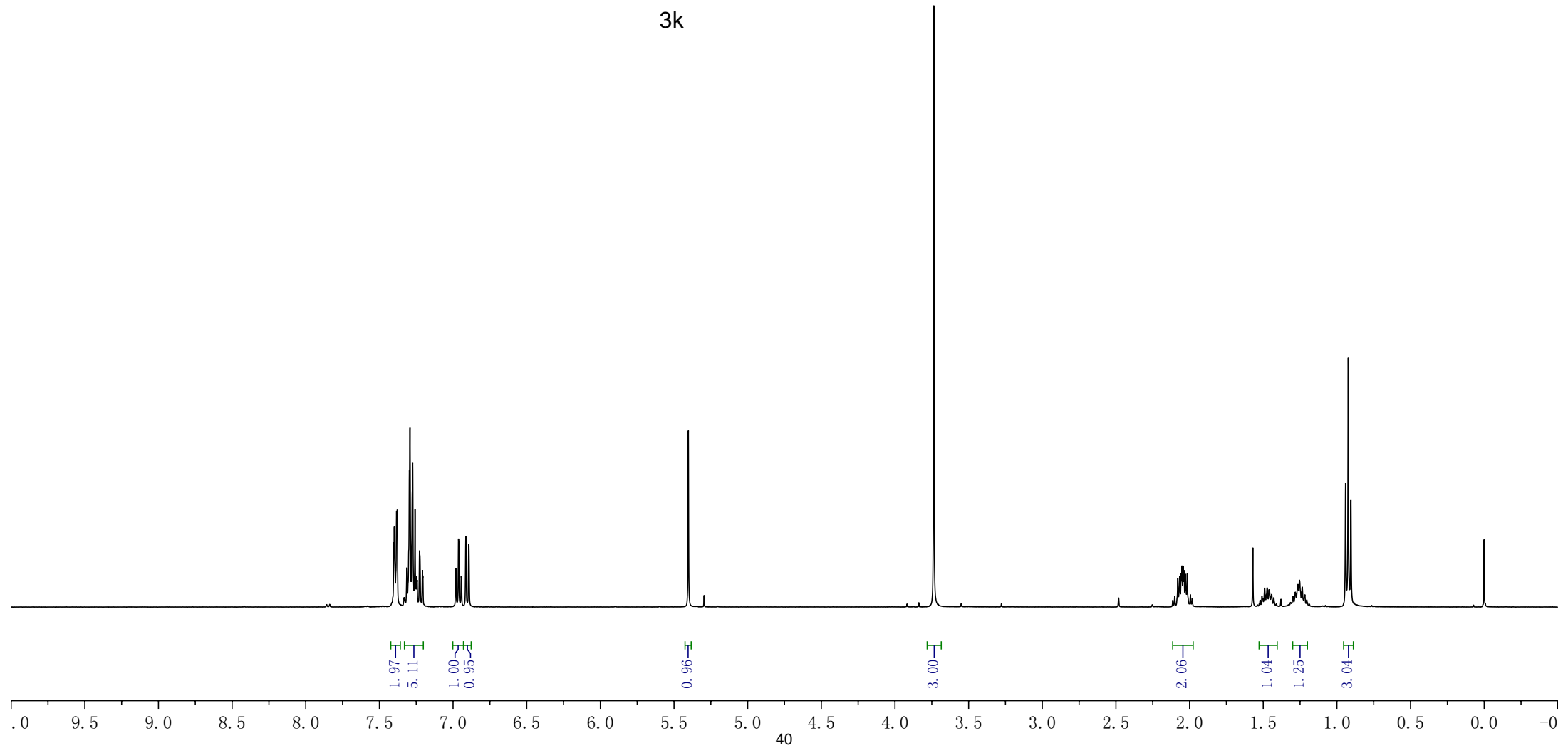
1.57
1.49
1.47
1.26
1.25
0.94
0.92
0.90

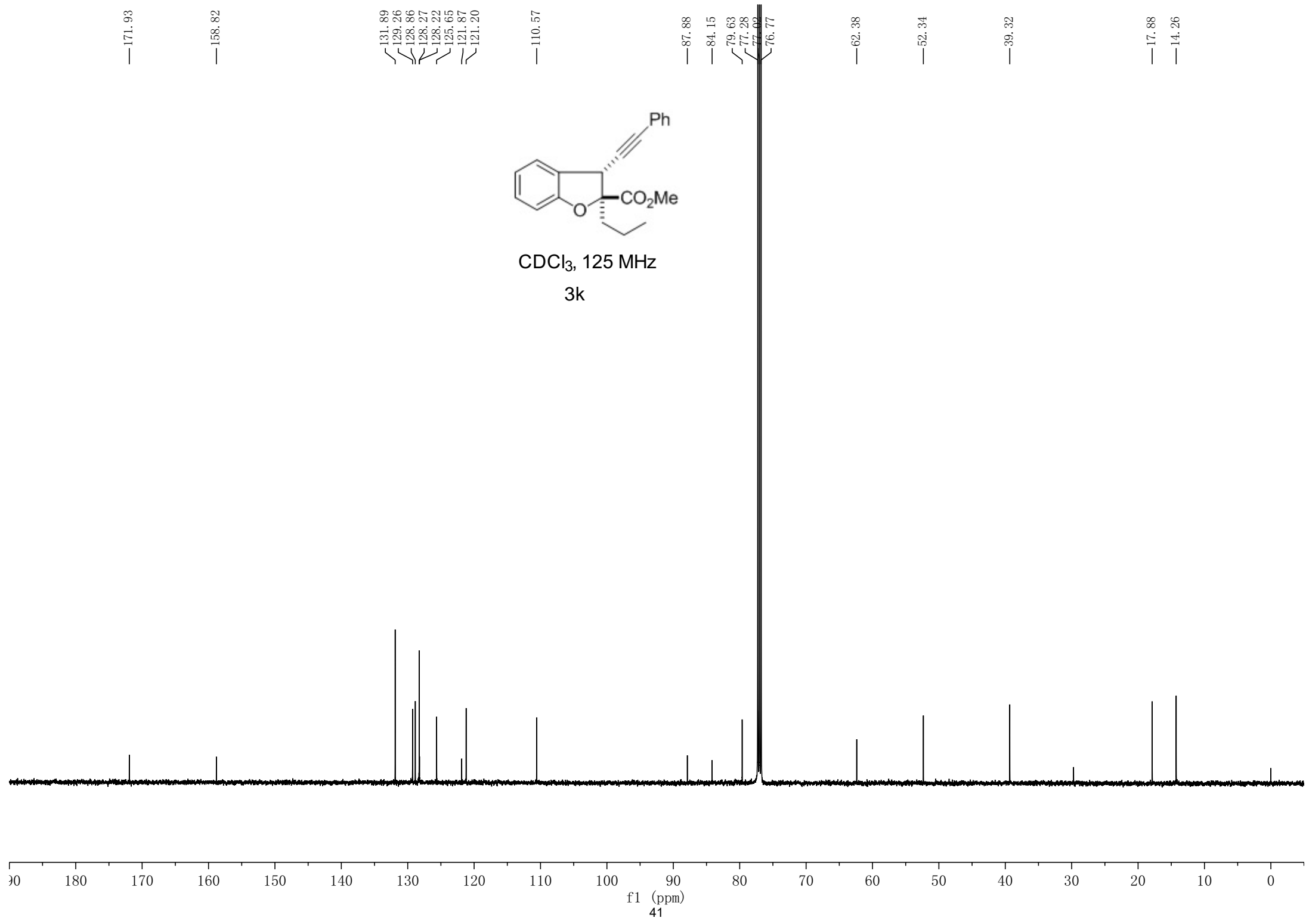
0.00



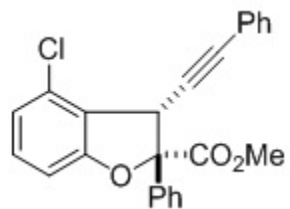
CDCl₃, 400 MHz

3k





7.77
7.75
7.44
7.43
7.42
7.41
7.41
7.39
7.37
7.36
7.35
7.34
7.33
7.32
7.30
7.30
7.29
7.27
7.26
7.19
7.17
7.15
7.00
6.98
6.93
6.91
4.96



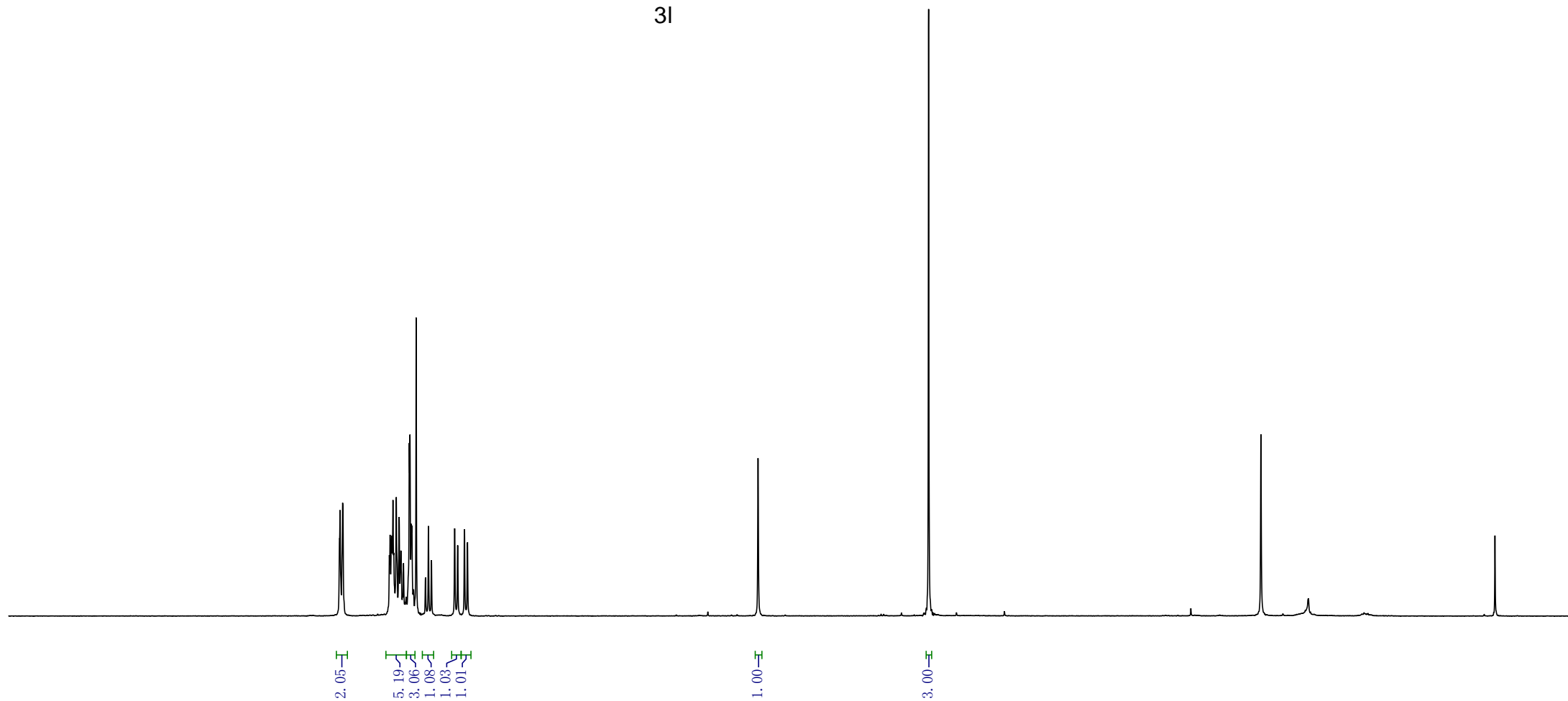
CDCl₃, 400 MHz

3I

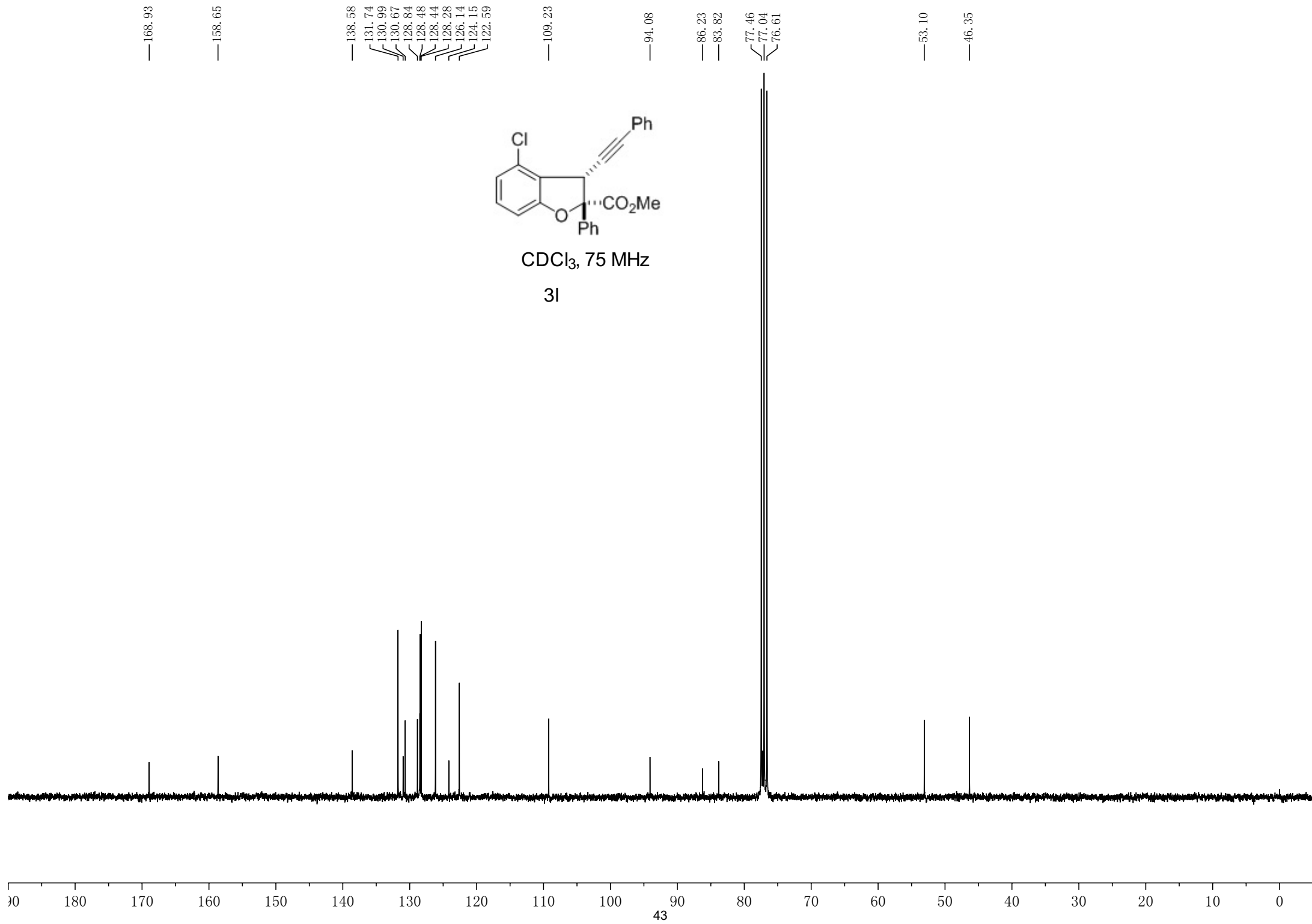
3.81

1.57

0.00



2.05
5.19
3.06
1.08
1.03
1.01
1.00
3.00
1.00



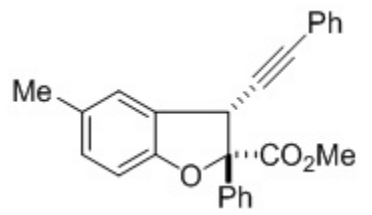
7.80
7.79
7.79
7.78
7.77
7.77
7.46
7.46
7.44
7.44
7.43
7.41
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.33
7.32
7.31
7.30
7.30
7.30
7.26
7.12
7.02
6.96
6.96
6.96
6.96

3.75

2.29

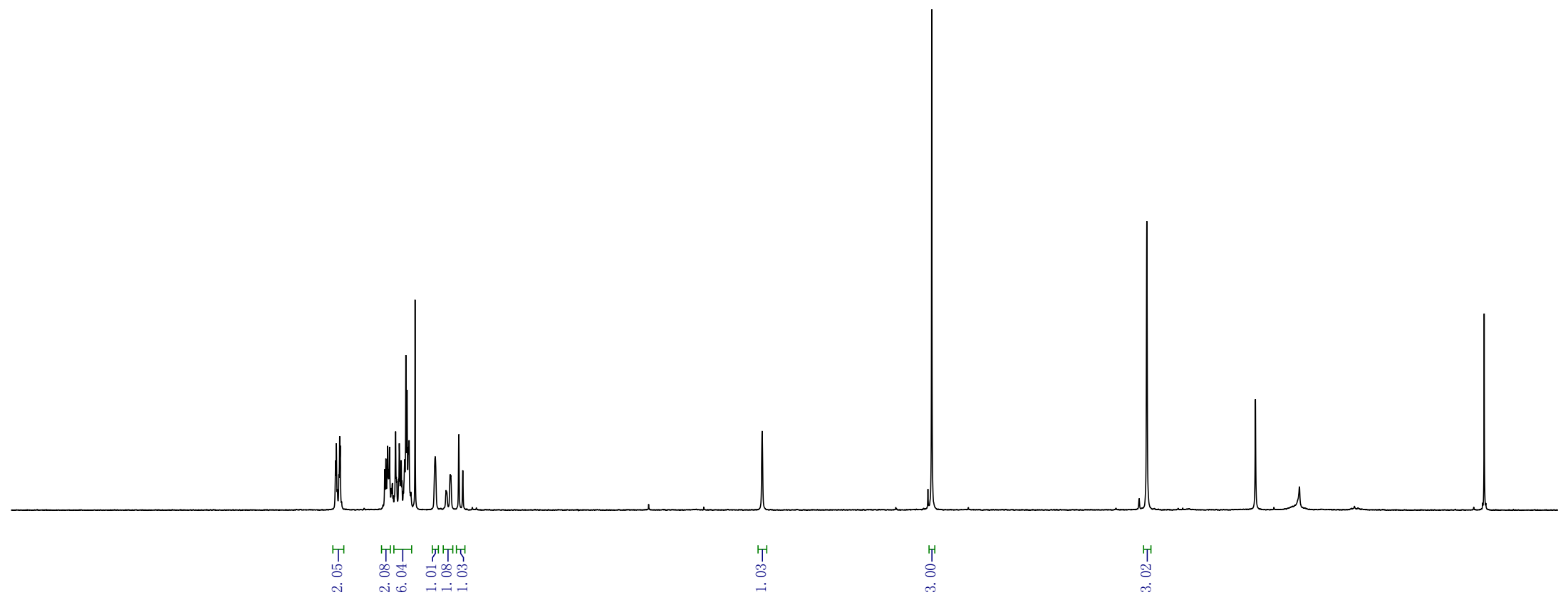
1.55

0.00

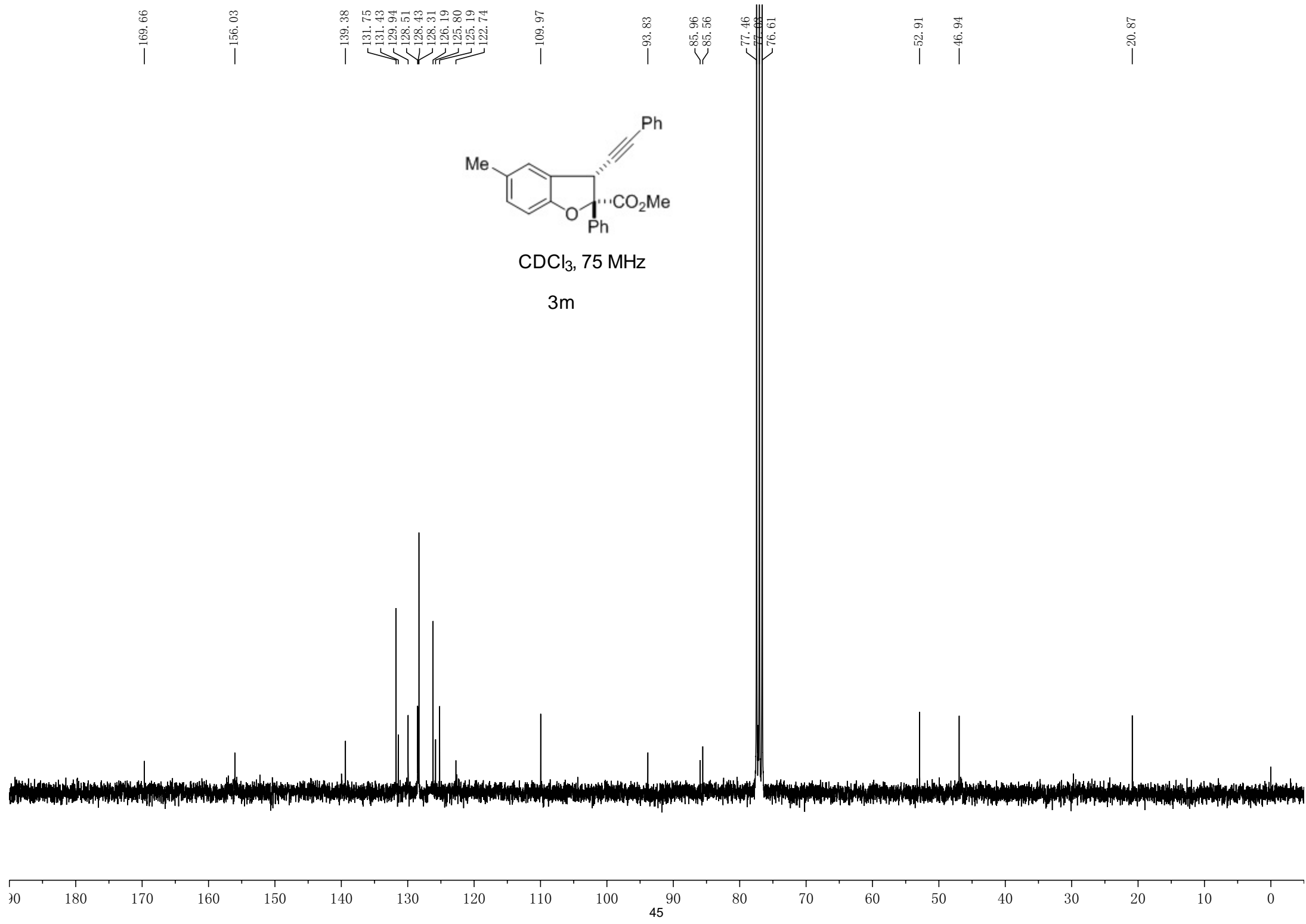


CDCl₃, 300 MHz

3m



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 -0.0



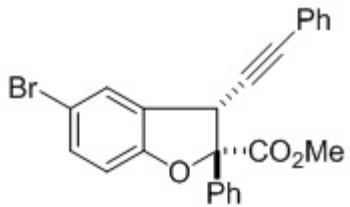
7.76
7.76
7.75
7.74
7.74
7.73
7.44
7.43
7.43
7.33
6.88
6.92

4.94

3.75

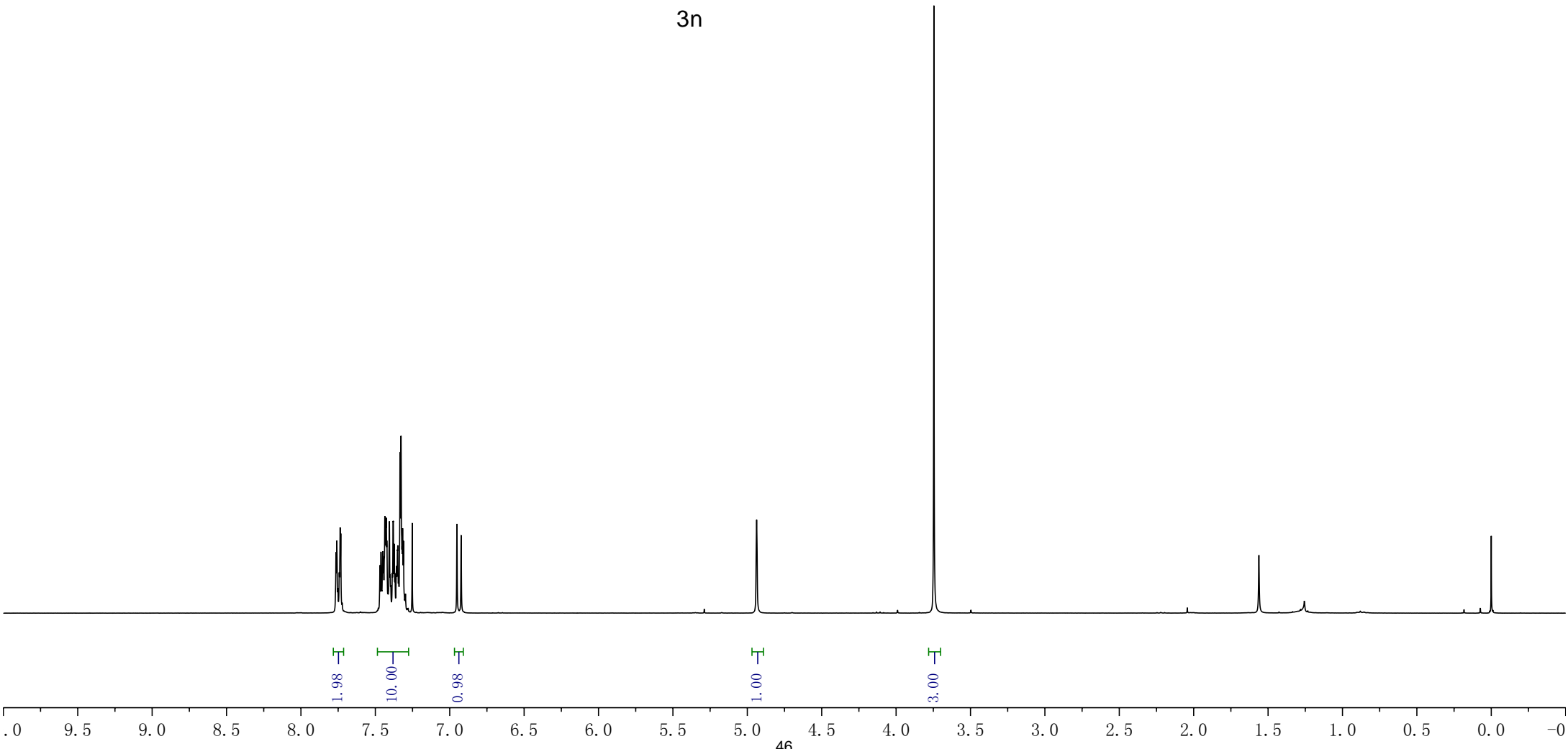
1.56

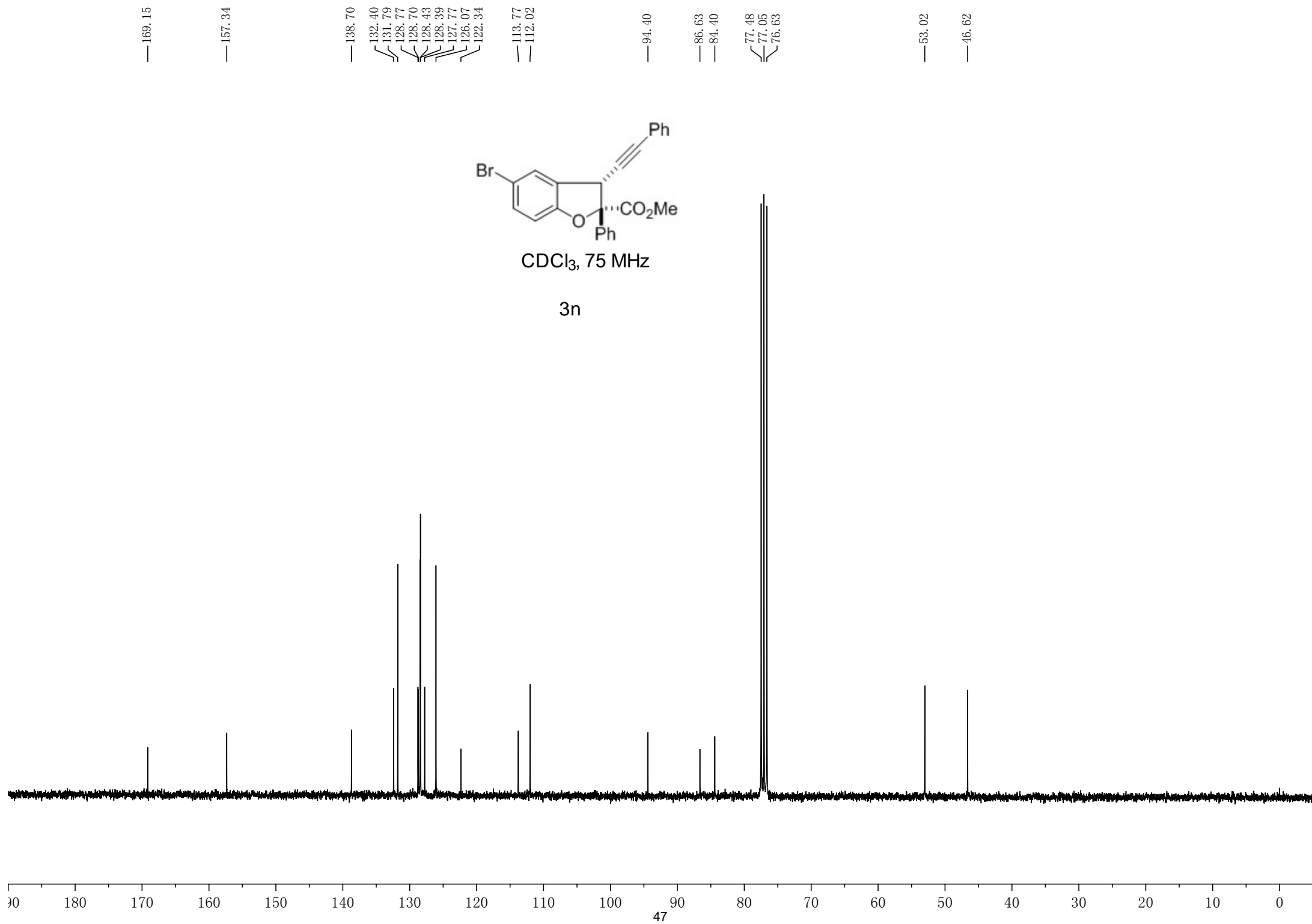
0.00



CDCl₃, 300 MHz

3n





7.79
7.79
7.78
7.77
7.76
7.39
7.31
7.30
7.30
6.88
6.78
6.76

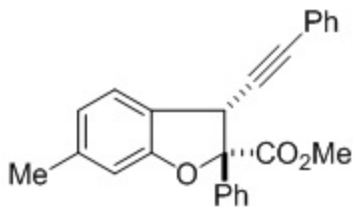
4.90

3.75

2.35

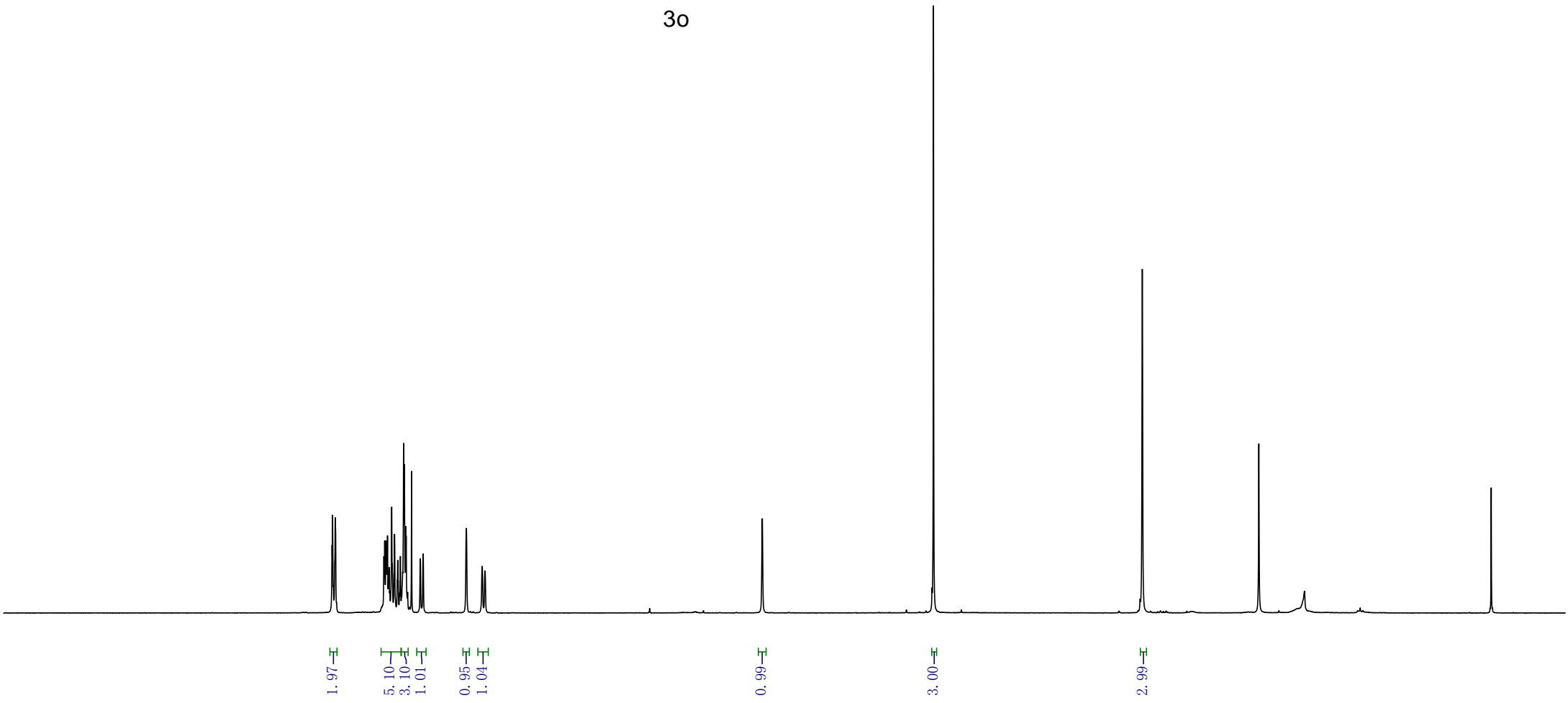
1.56

0.00

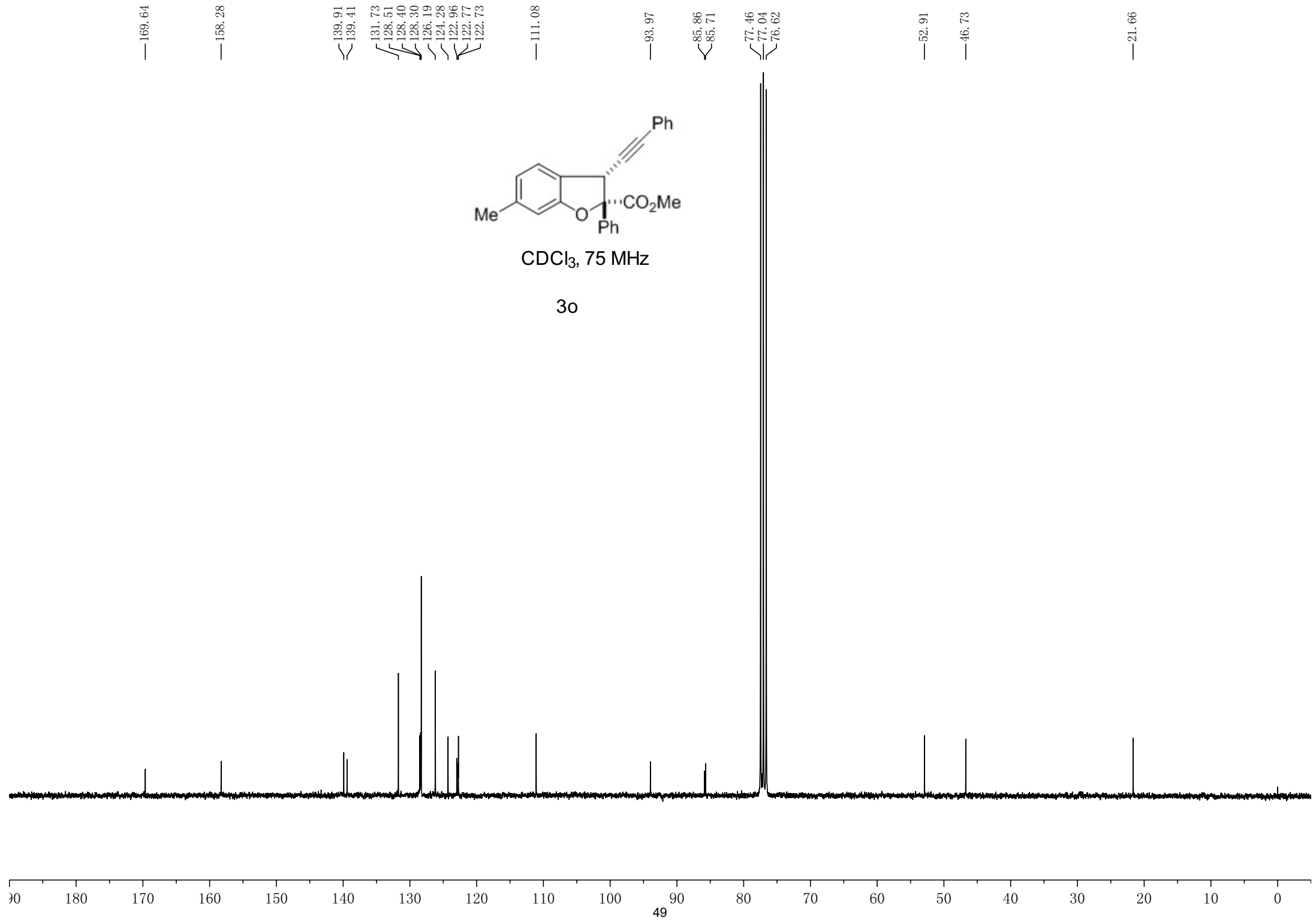


CDCl₃, 400 MHz

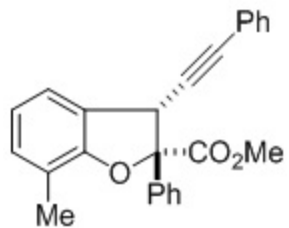
30



10 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0



7.81
7.80
7.79
7.78
7.77
7.46
7.45
7.44
7.43
7.42
7.40
7.39
7.38
7.37
7.36
7.36
7.33
7.31
7.30
7.30
7.29
7.26
7.16
7.13
7.04
6.88
3.99



CDCl₃, 300 MHz

3p

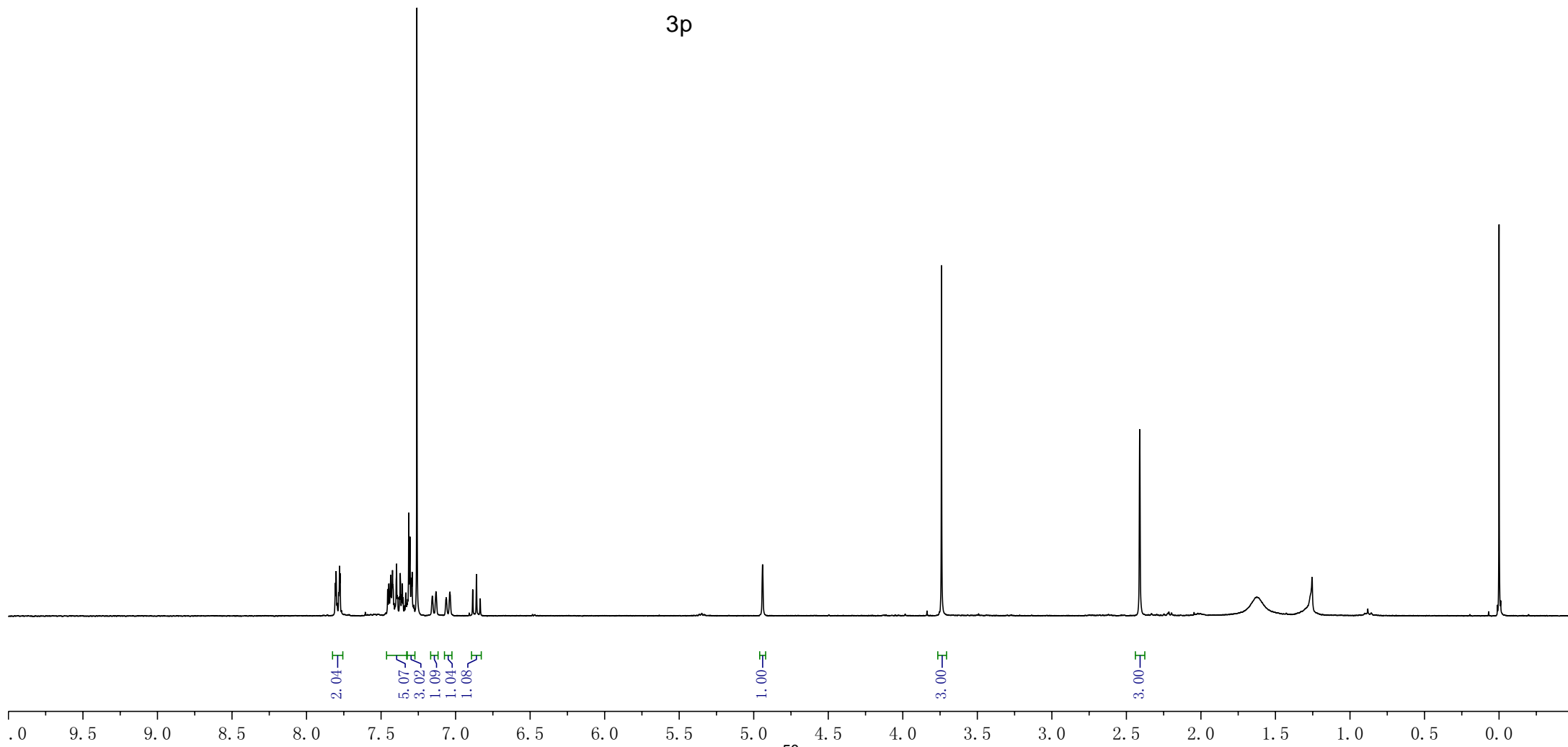
3.74

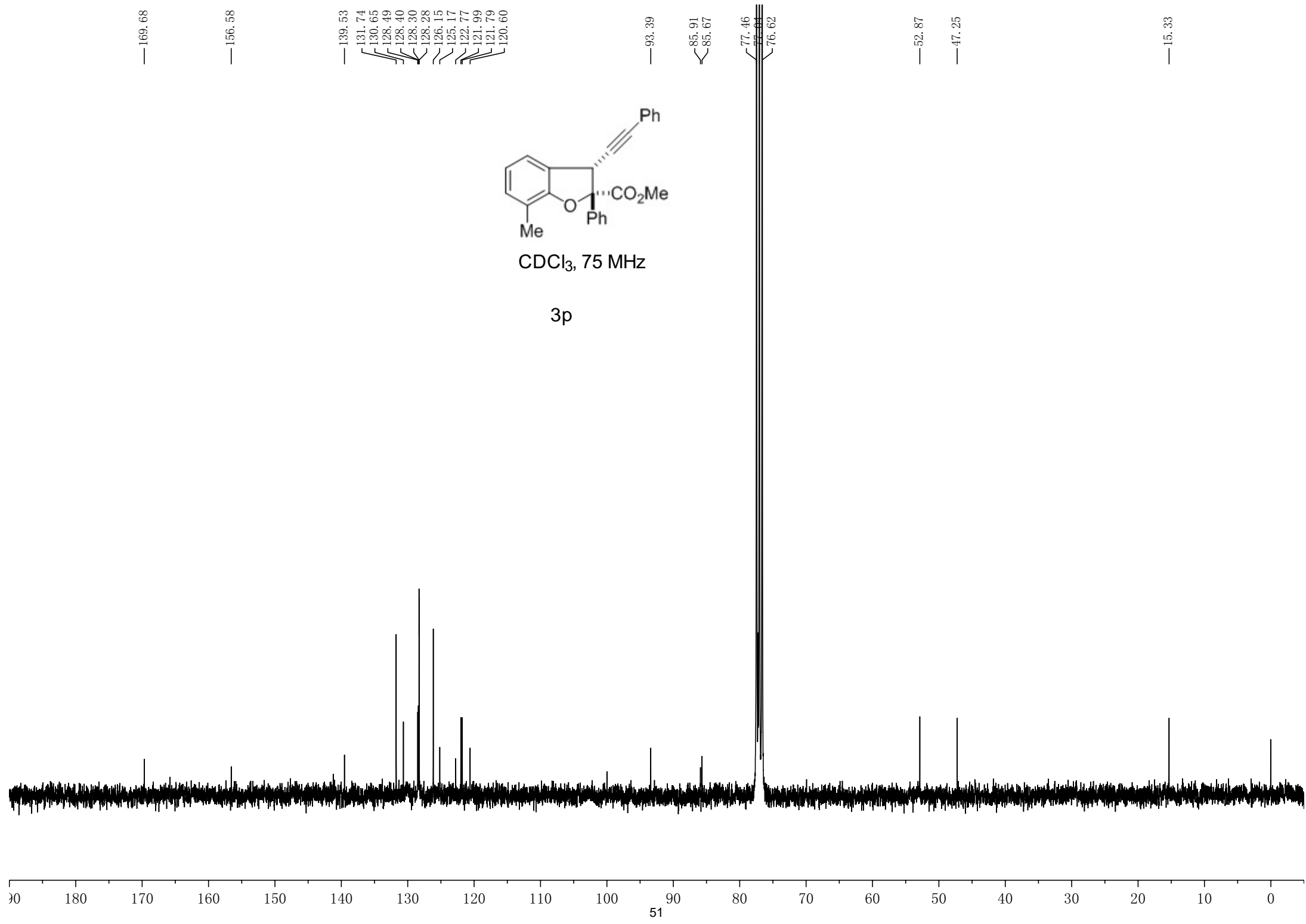
2.41

1.63

1.25

0.00





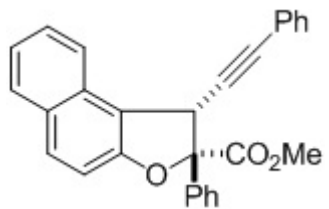
7.94
7.92
7.86
7.84
7.82
7.80
7.78
7.52
7.50
7.48
7.40
7.39
7.38
7.38
7.36
7.33
7.31
7.30
7.28
7.27
7.27
7.26
7.25

5.25

3.82

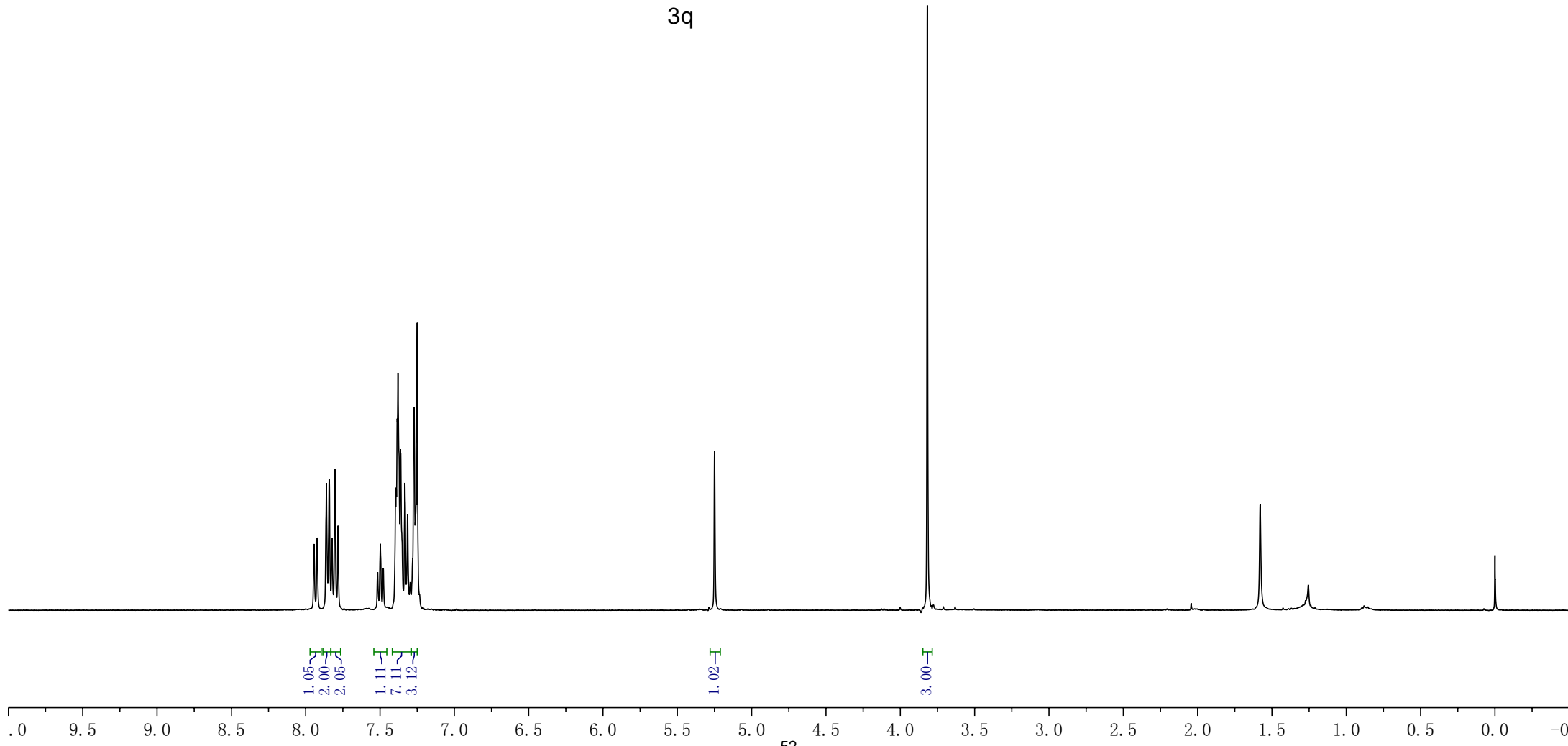
1.58

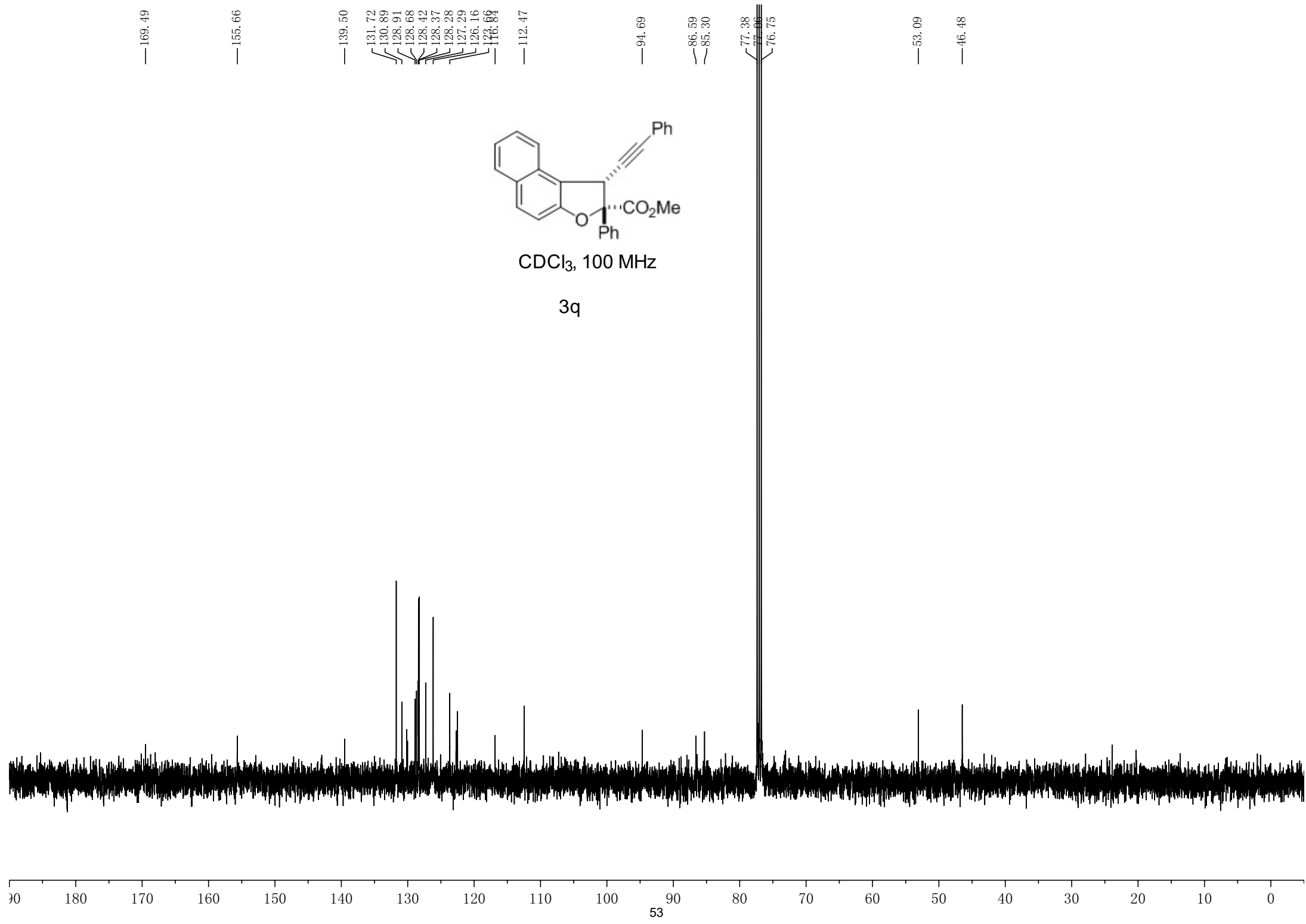
0.00



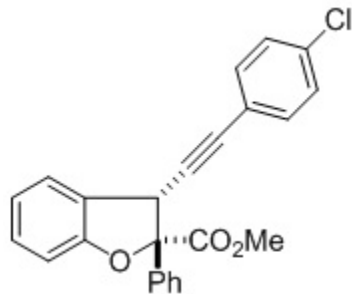
CDCl₃, 400 MHz

3q





7.78
7.78
7.78
7.76
7.76
7.41
7.40
7.38
7.37
7.36
7.35
7.35
7.34
7.32
7.30
7.29
7.29
7.28
7.27
7.26
7.25
7.23
7.08
7.06
6.98
6.96
6.96
3.94



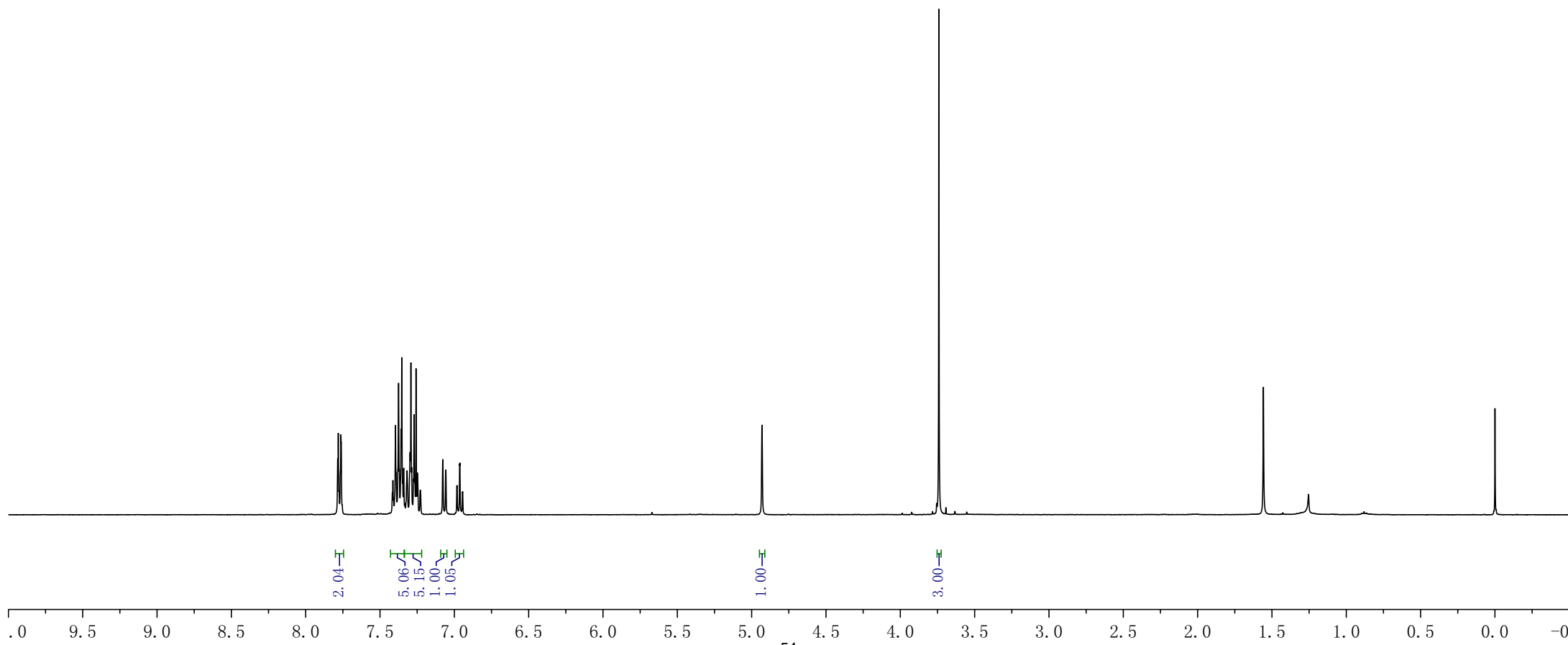
CDCl₃, 400 MHz

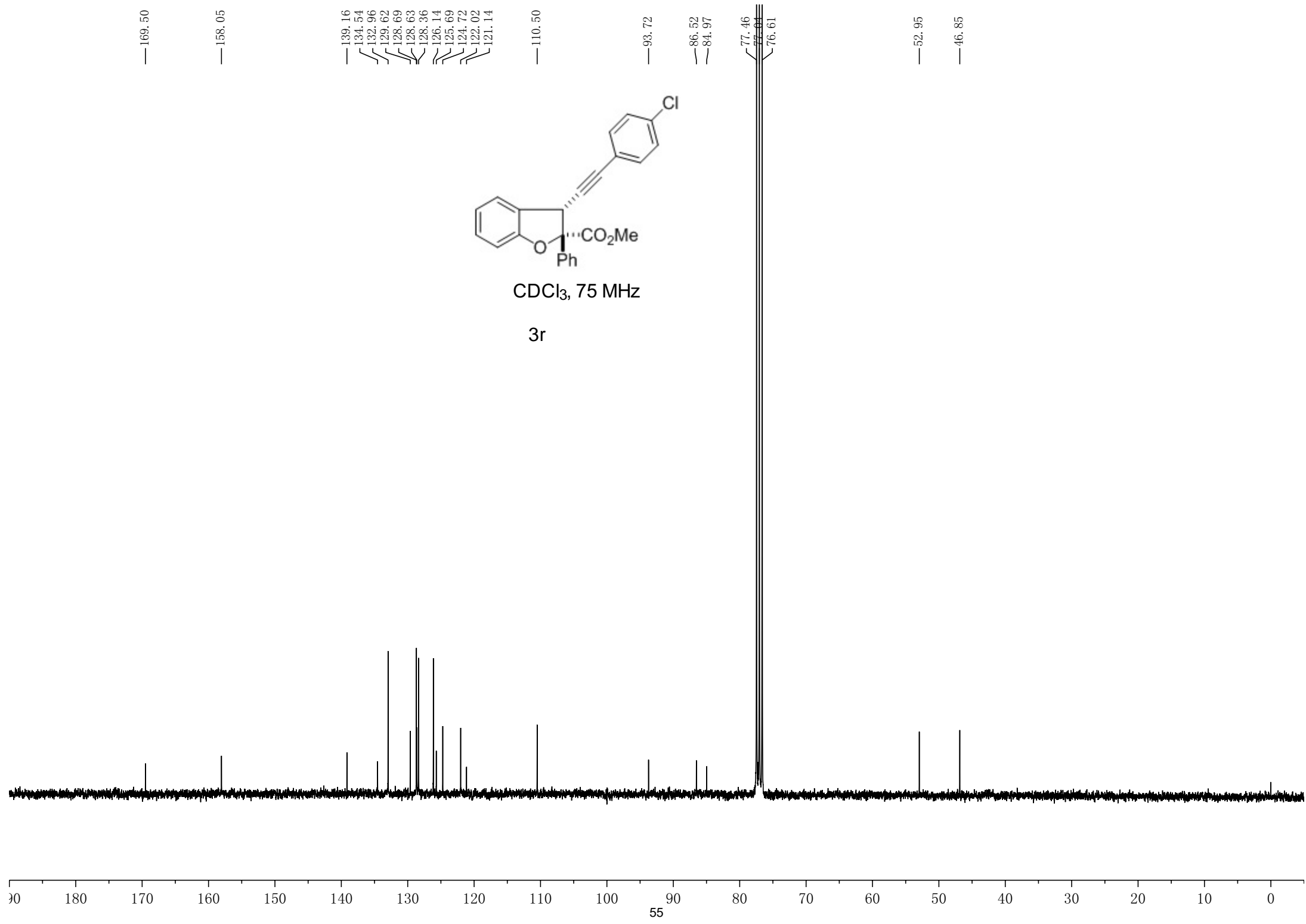
3r

3.74

1.56

0.00





7.74
7.74
7.72
7.71
7.39
7.38
7.36
7.34
7.33
7.32
7.26
7.25
7.22
7.20
7.04
7.02
6.96
6.94
6.93

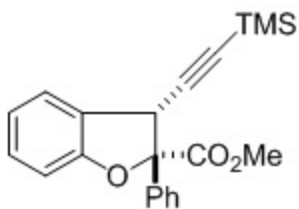
4.75

3.75

1.56

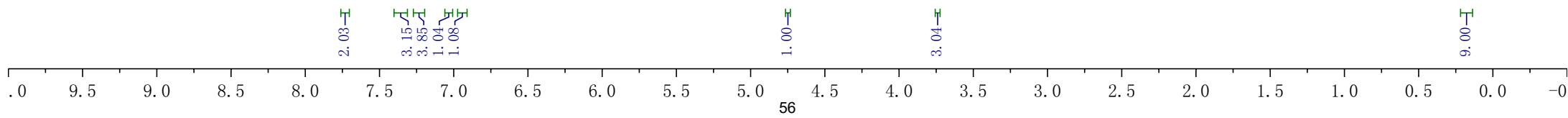
0.18

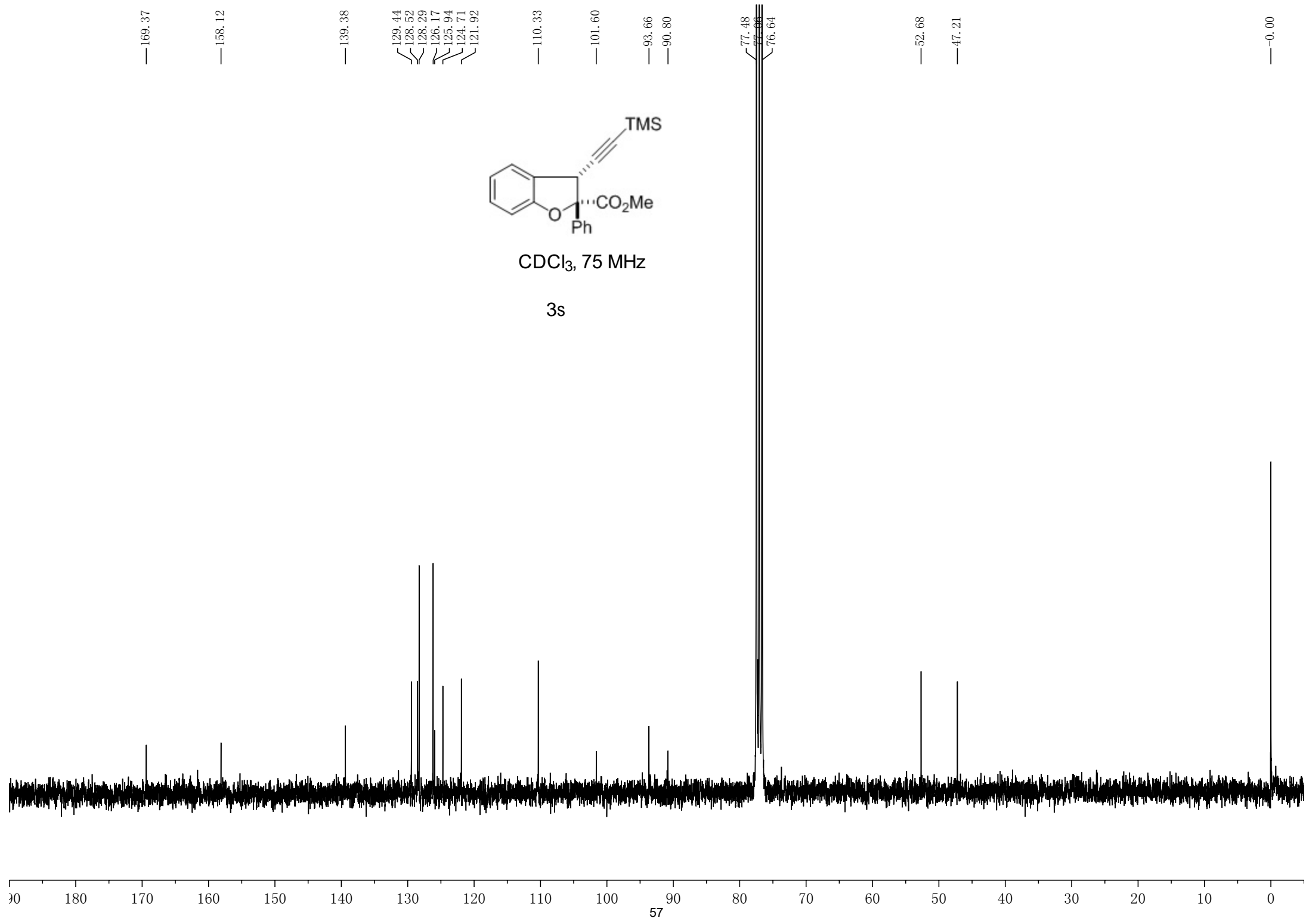
-0.00



CDCl₃, 400 MHz

3s





7.74
7.73
7.39
7.37
7.35
7.33
7.31
7.30
7.25
7.24
7.22
7.20
7.19
7.02
7.00
6.95
6.93
6.91

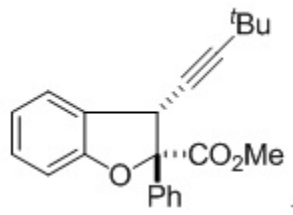
4.70

3.74

1.59

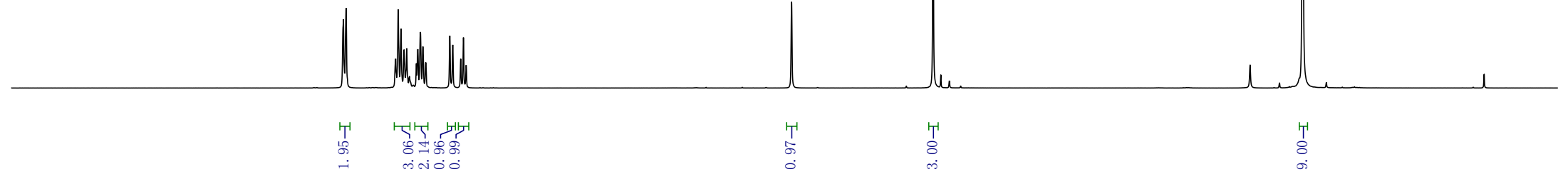
1.23

0.00



CDCl₃, 400 MHz

3t



10 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

— 169.61

— 158.07

— 139.67

129.13

128.37

128.19

126.95

126.16

124.53

121.73

— 110.13

94.90

93.68

77.48

77.06

76.63

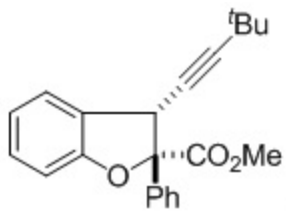
74.50

— 52.61

— 46.40

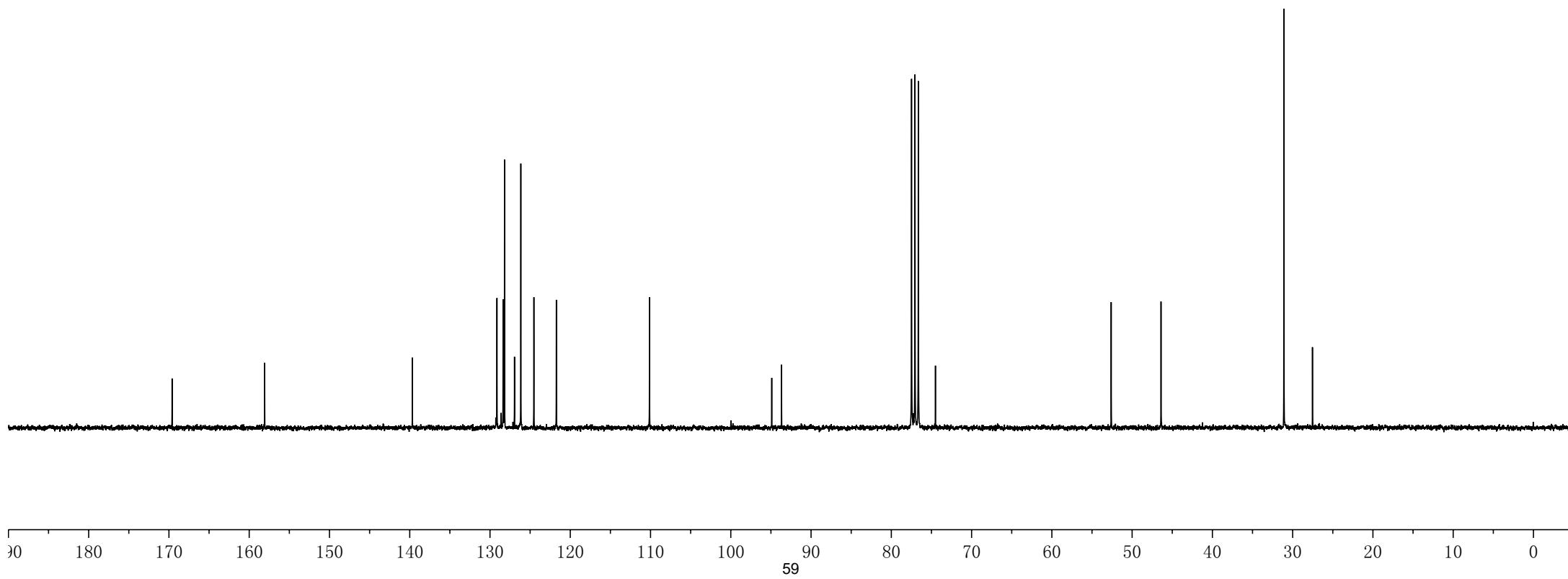
— 31.09

— 27.53



CDCl₃, 75 MHz

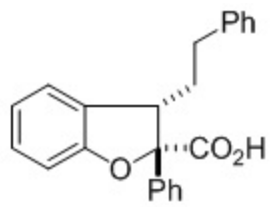
3t



7.65
7.64
7.62
7.61
7.60
7.33
7.32
7.31
7.30
7.27
7.25
7.24
7.23
7.21
7.19
7.16
7.14
7.08
7.05
6.96
6.94
6.93
6.91
6.91

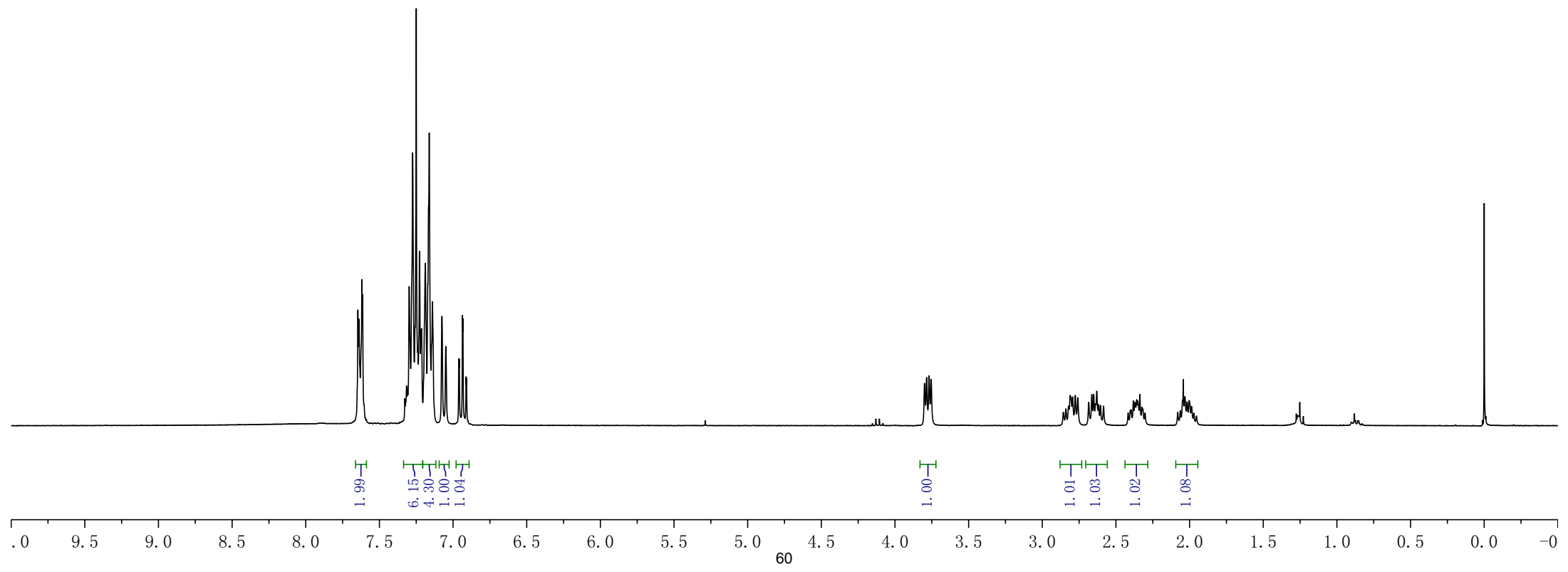
3.80
3.79
3.77
3.75
2.81
2.79
2.78
2.76
2.68
2.66
2.65
2.63
2.38
2.37
2.36
2.35
2.34
2.06
2.05
2.04
2.03
2.02
2.00
1.99
1.97
1.95

0.00



CDCl₃, 300 MHz

5a



— 172.66

— 156.69

— 141.00
— 139.39

128.96
128.87
128.55
128.44
128.35
126.12
125.92
125.43
122.11

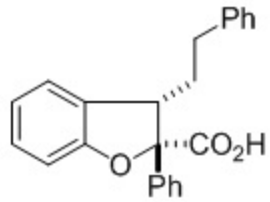
— 110.57

— 93.53

77.48
77.05
76.63

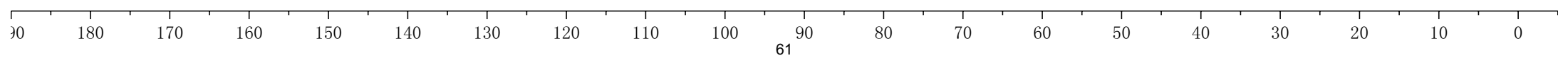
— 52.52

33.50
32.35



CDCl₃, 75 MHz

5a



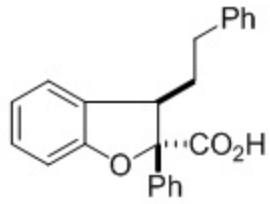
7.68
7.66
7.43
7.42
7.40
7.39
7.38
7.37
7.35
7.29
7.27
7.26
7.24
7.17
7.15
7.13
7.11
7.10
7.09
7.08
7.03
7.01
7.00
6.82
6.81

4.15
4.14
4.13
4.12

2.50
2.48
2.46
2.45
2.43
2.42
2.31
2.29
2.28
2.27
2.27
2.26
2.25
2.23
2.04

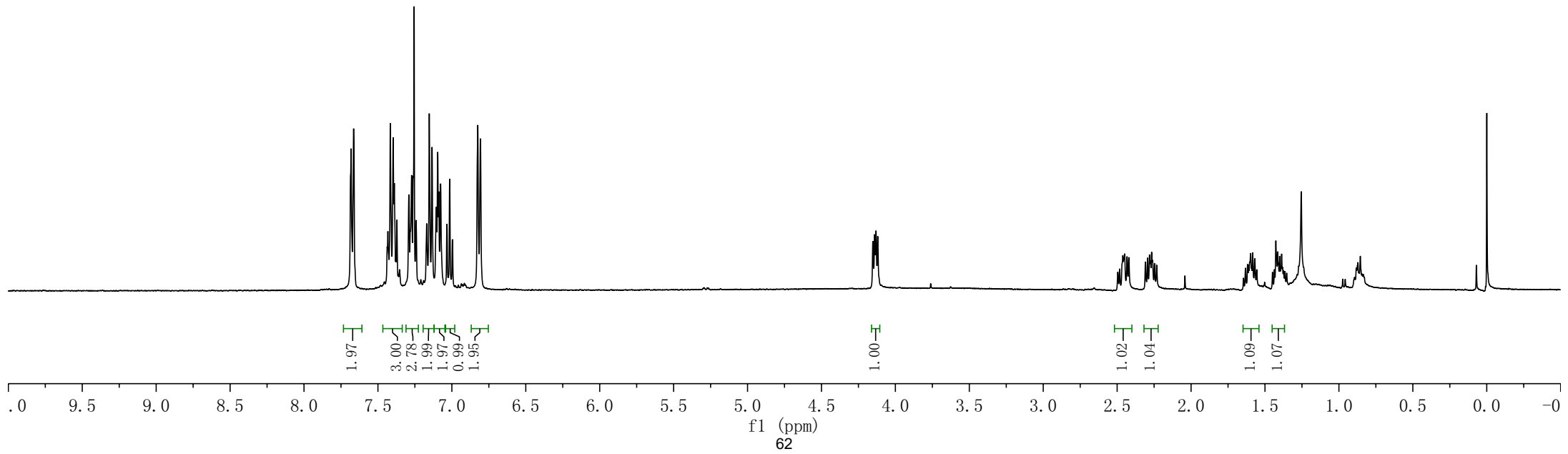
1.60
1.58
1.43
1.42
1.39
0.97
0.96
0.89
0.88
0.87
0.86

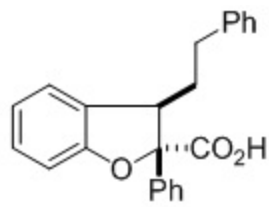
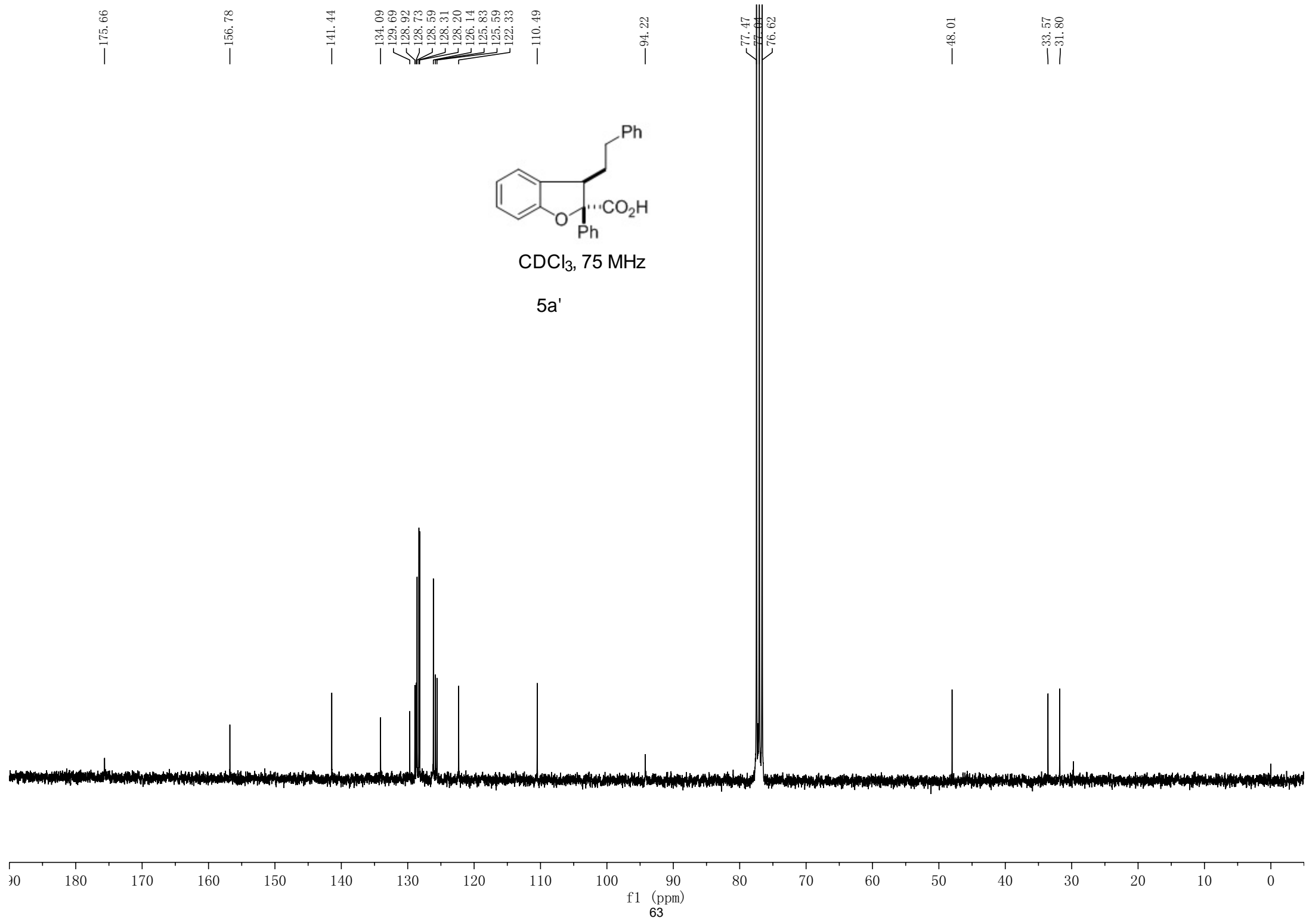
-0.00



CDCl₃, 400 MHz

5a'





CDCl₃, 75 MHz

5a'

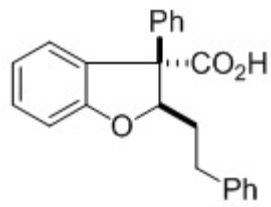
7.50
7.48
7.33
7.31
7.29
7.28
7.26
7.25
7.23
7.21
7.19
7.15
7.13
7.11
7.09
7.07
7.00
6.98
6.96
6.95
6.94

5.34
5.33
5.31
5.31

2.88
2.87
2.86
2.85
2.84
2.82
2.81
2.73
2.72
2.71
2.70
2.69
2.68
2.68
2.66

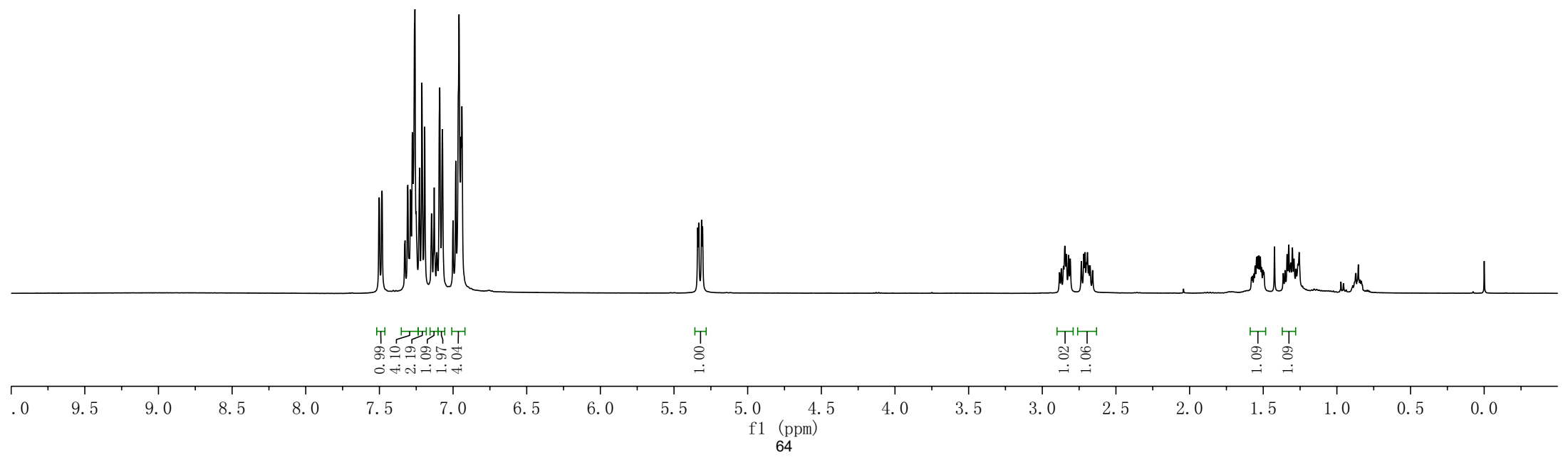
1.55
1.54
1.53
1.52
1.42
1.34
1.33
1.31
1.30
1.29
0.86

-0.00



CDCl₃, 400 MHz

5b



— 178.59

— 159.46

— 141.50

— 137.42

130.20

128.53

128.50

128.35

127.90

127.87

127.89

121.52

— 110.33

— 87.38

77.50

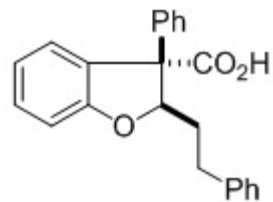
77.08

76.65

— 64.55

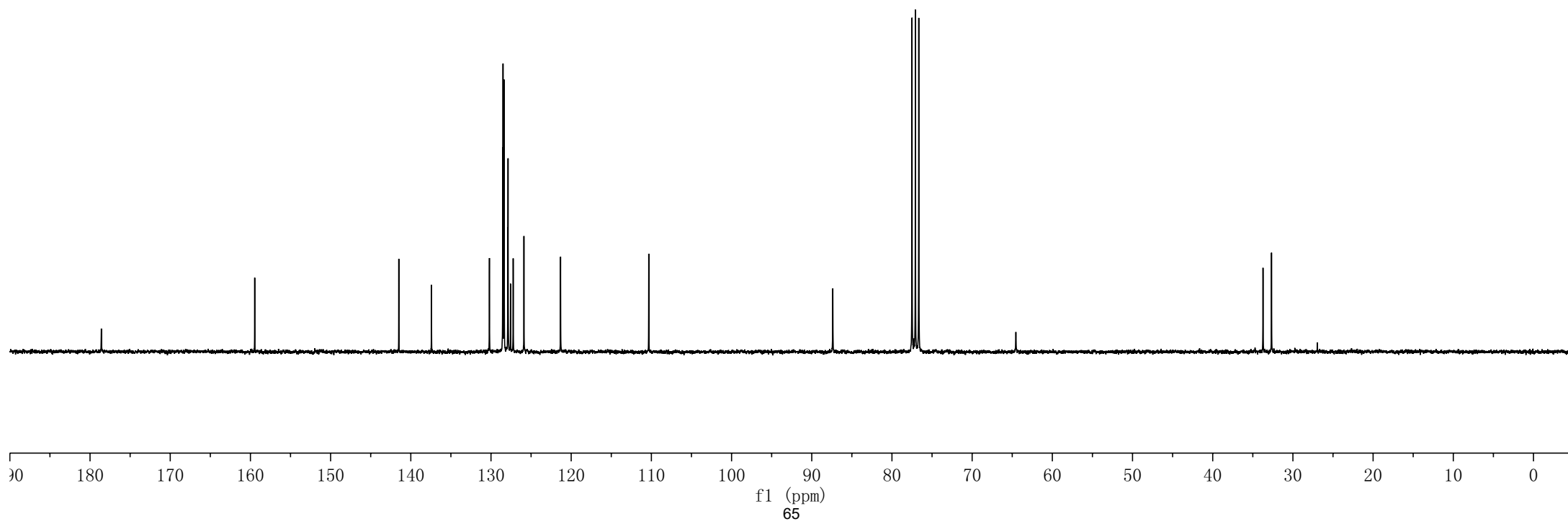
33.73

32.67



CDCl₃, 75 MHz

5b



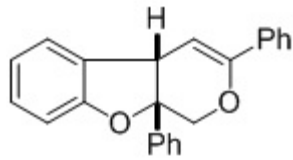
7.63
7.61
7.58
7.40
7.38
7.36
7.34
7.32
7.32
7.31
7.30
7.26
7.22
7.20
7.17
7.16
7.14
6.95
6.93
6.91
6.89
6.87

5.85
5.84

4.25
4.21
4.20

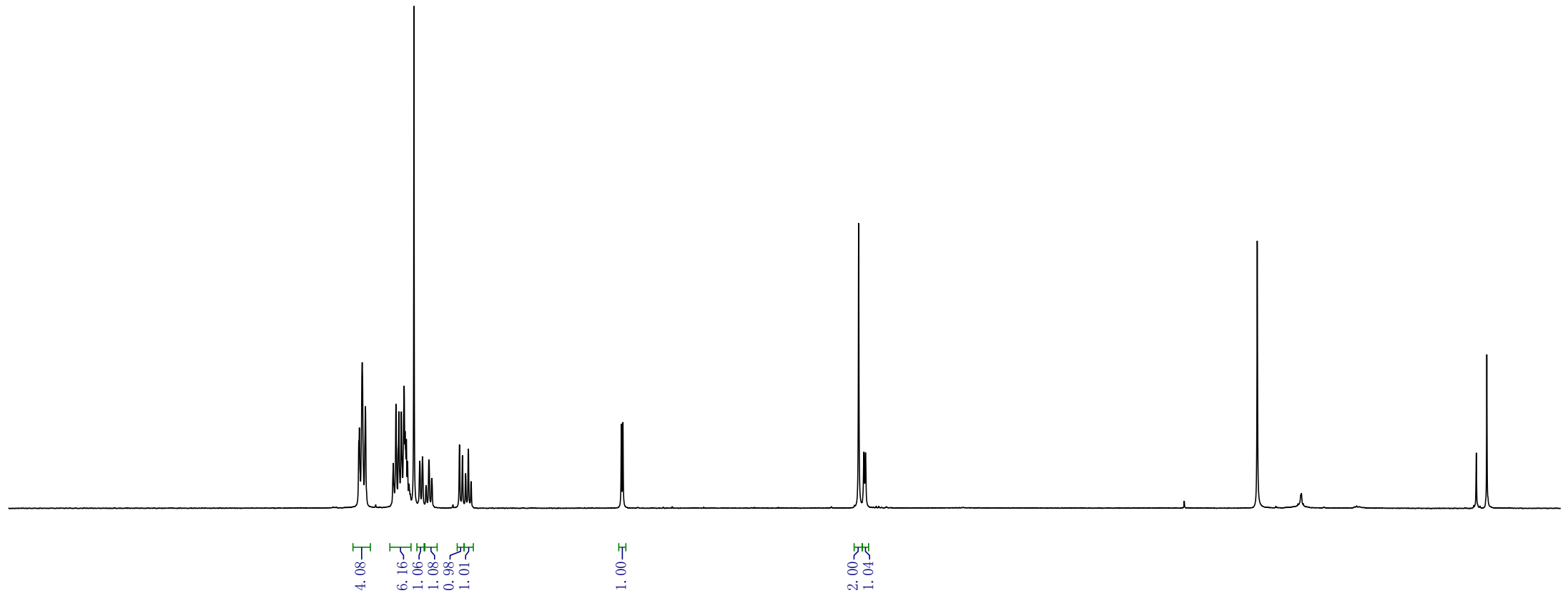
1.55

0.00

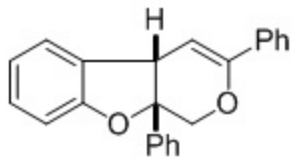


CDCl₃, 400 MHz

6

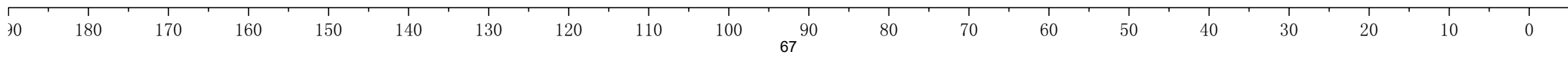


—157.71 —152.73 —142.23
134.71 130.85 128.55 128.53 128.25 127.98 125.19 124.81 124.34 121.29
—110.56 —99.00 —86.93 77.45 77.00 76.61 70.49 —46.09



CDCl₃, 75 MHz

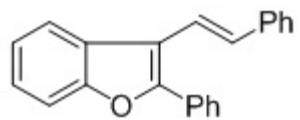
6



7.99
7.98
7.97
7.97
7.84
7.82
7.56
7.56
7.55
7.54
7.52
7.50
7.45
7.43
7.41
7.39
7.37
7.36
7.36
7.34
7.34
7.31
7.29
7.27
7.25

—1.56

—-0.00



CDCl₃, 400 MHz

7

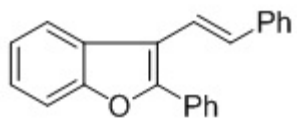


.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

154.51
153.37

137.80
131.11
130.85
128.79
128.01
127.83
127.61
126.29
124.85
123.15
121.03
119.93
114.57
111.44

77.45
77.00
76.61



CDCl₃, 75 MHz

7

