Electronic Supplementary Information

Synthesis of Isoquinolines via Visible Light-Promoted Insertion of Vinyl Isocyanides with Diaryliodonium Salts

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Table of Contents

1. General methods.

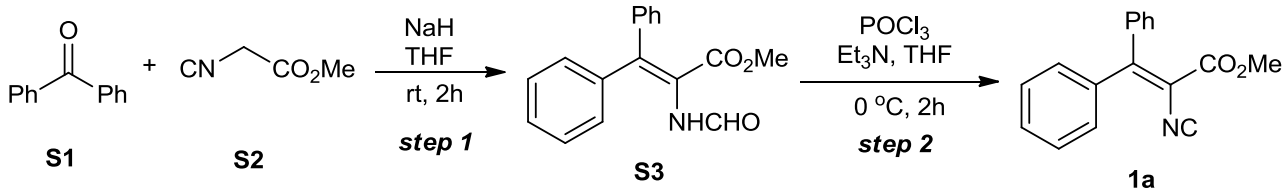
MeOH and THF were dried according to *Purification of Common Laboratory Chemicals*. Other reagents were used without further purification. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR (400 MHz), ^{13}C NMR (100MHz) and ^{19}F (376MHz) were measured on a Bruker AVANCE Ⅲ–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm^{-1}). Diaryliodonium salts **2a**-**2n** were prepared according to published literature procedures.[1,2]

[1] M. Bielawski, D. Aili and B. Olofsson, *J. Org. Chem.*, 2008, **73,** 4602.

[2] M. Bielawski, M. Zhu and B. Olofsson, *Adv. Synth. Catal. ,* 2007, **349,** 2610.

2. Synthesis of vinyl isocyanides 1a-1z.

Methyl 2-isocyano-3,3-diphenylacrylate **1a** was prepared according to the previously reported procedures:[3]



Step 1: A mixture of benzophenone (**S1**, 1.82 g, 10.0 mmol) and methyl isocyanoacetate (**S2**, 0.99 g, 10.0 mmol) in THF (10 ml) was added dropwise to a suspension of NaH (60% in oil) (0.48 g, 12.0 mmol) in THF (10.0 ml) at room temperature. After stirring for 2 h at room temperature, 10% AcOH was added to the mixture at 0 ℃ until there is no hydrogen release. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 three times and the extract was washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. Further recrystallization in MeOH afforded the product **S3** (2.0 g, 72%) as a white solid.

Step 2: THF (10.0 mL), NEt_3 (5.6 mL, 40 mmol) and **S3** (1.41 g, 5.0 mmol) were added to an oven-dried three necked flask under N_2 atmosphere and cooled to 0 ℃. $POCl_3$ (0.93 mL, 10.0 mmol) was added dropwise and the mixture was stirred for 2 h at 0 ℃ after the addition was completed. Then the mixture was quenched by sat. Na_2CO_3 and stirred for another 1 h. The mixture was extracted with CH_2Cl_2 three times, dried over Na_2SO_4 and concentracted under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give **1a** (0.93 g, 92%) as a white solid.

1b-**1d** were prepared according to procedures described for **1a**. **1w**, **1y** were also prepared with this method from 2-isocyano-1-(piperidin-1-yl)ethanone and N-benzyl-2-isocyanoacetamide.[4]

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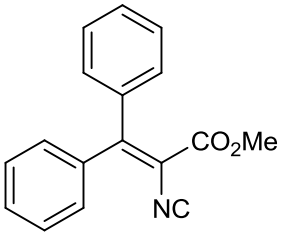
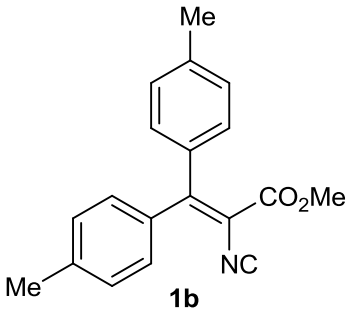
[3] M. Suzuki, K.-I. Nunami, K. Matsumoto, N. Yoneda, O. Kasuga, H. Yoshida and T. Yamaguchi, *Chem. Pharm. Bull.*, 1980, **28,** 2374.

[4] B. Beck, G. Larbig, B. Mejat, M. Magnin-Lachaux, A. Picard, E. Herdtweck and Dömling, A. *Org. Lett.*, 2003, **5,** 1047.



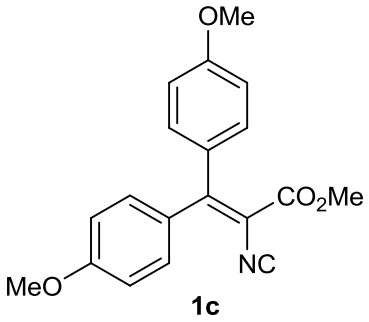
1a

Methyl 2-isocyano-3,3-diphenylacrylate (1a): for ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. m.p.: 104–106℃. IR (neat, cm^{-1}): 2113.7, 1732.9, 1568.9, 1444.3, 1245.7, 1183.9, 1110.1, 858.3, 785.3, 698.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.33 (m, 8H), 7.16 – 7.10 (m, 2H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.74, 162.24, 154.56, 137.76, 137.35, 130.28, 129.85, 129.56, 129.06, 128.42, 128.22, 113.75, 52.89. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{14}NO_2$: 264.1025; found: 264.1016.



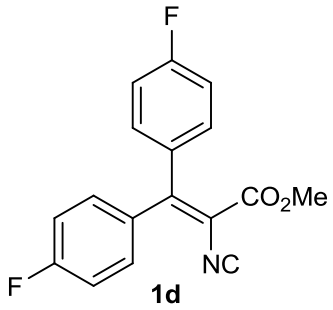
1b

Methyl 2-isocyano-3,3-dip-tolylacrylate (1b): for ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. m.p.: 94–96℃. IR (neat, cm^{-1}): 2110.1, 1723.4, 1608.4, 1431.6, 1331.1, 1267.3, 1177.5, 1110.5, 817.2, 780.8, 739.9. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 3.69 (s, 3H), 2.36 (d, *J* = 16.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.10, 162.57, 155.10, 140.76, 139.87, 135.06, 134.73, 130.10, 129.29, 129.06, 128.90, 112.66, 52.81, 21.47, 21.43. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{18}NO_2$: 292.1338; found: 292.1328.



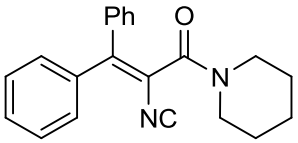
1c

Methyl 2-isocyano-3,3-bis(4-methoxyphenyl)acrylate (1c): for ***Step 1***, eluted by hexane: EtOAc = 2:1; for ***Step 2***, eluted by hexane: EtOAc = 20:1 to 5:1. m.p.: 96–98℃. IR (neat, cm^{-1}): 2110.5, 1722.2, 1602.0, 1506.7, 1434.2, 1329.0, 1243.7, 1171.9, 1107.4, 1026.6, 830.8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.45, 162.95, 161.31, 160.97, 154.69, 132.33, 131.35, 130.22, 129.83, 113.71, 113.57, 111.27, 55.38, 55.30, 52.74. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{18}NO_4$: 324.1236; found: 324.1239.



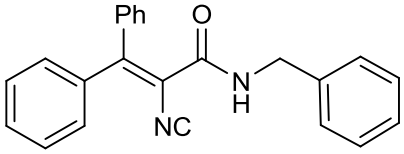
1d

Methyl 3,3-bis(4-fluorophenyl)-2-isocyanoacrylate (1d): brown oil. For ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. IR (neat, cm^{-1}): 2119.5, 1733.7, 1599.3, 1505.3, 1261.8, 1221.9, 1112.6, 993.0, 837.2. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.31 (m, 2H), 7.15 – 7.03 (m, 6H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.29, 163.74 (d, *J* = 252.6 Hz), 163.57 (d, *J* = 251.4 Hz), 161.99, 152.47, 133.46 (d, *J* = 3.5 Hz), 133.19 (d, *J* = 3.4 Hz), 132.25 (d, *J* = 8.9 Hz), 131.27 (d, *J* = 8.5 Hz), 115.82 (d, *J* = 21.7 Hz), 115.60 (d, *J* = 21.7 Hz), 113.75, 53.05. ^{19}F NMR (376 MHz, $CDCl_3$): δ –108.56 (s, 1F), –110.16 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{12}F_2NO_2$: 300.0836; found: 300.0827.



1w

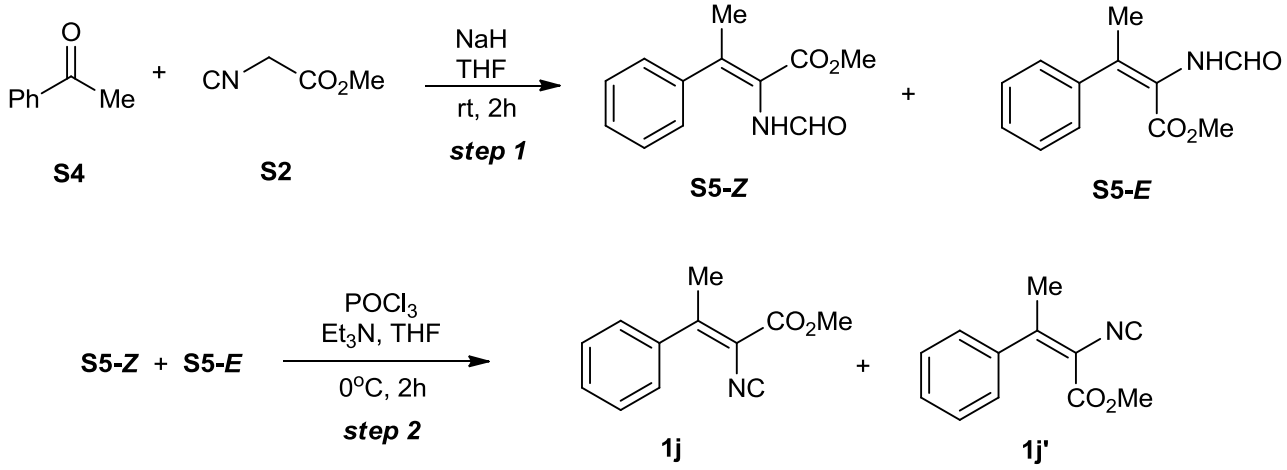
2-Isocyano-3,3-diphenyl-1-(piperidin-1-yl)prop-2-en-1-one (1w): for ***Step 1***, eluted by hexane: EtOAc = 1:2; for ***Step 2***, eluted by hexane: EtOAc = 50:1 to 20:1. m.p.: 143–145℃. IR (neat, cm^{-1}): 2116.4, 1625.9, 1437.2, 1265.6, 1108.7, 1003.5, 776.5, 701.7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.29 (m, 8H), 7.23 (d, *J* = 7.7 Hz, 2H), 3.47 (t, *J* = 5.4 Hz, 2H), 3.31 (t, *J* = 5.3 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.44 – 1.36 (m, 2H), 1.29 – 1.06 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.23, 161.48, 145.06, 136.77, 129.71, 129.60, 129.57, 129.46, 128.43, 128.41, 115.88, 47.54, 42.72, 25.48, 24.82, 24.10. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{21}H_{20}N_2NaO$: 339.1473; found: 339.1481.



1y

N-Benzyl-2-isocyano-3,3-diphenylacrylamide (1y): for ***Step 1***, eluted by hexane: EtOAc = 1:5; for ***Step 2***, eluted by hexane: EtOAc = 10:1. m.p.: 128–130℃. IR (neat, cm^{-1}): 2104.6, 1643.6, 1530.5, 1443.7, 1362.7, 1270.7, 1148.7, 1030.1, 978.2, 736.4, 696.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.21 (m, 11H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.06 – 6.94 (m, 2H), 6.05 (t, *J* = 5.6 Hz, 1H), 4.31 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.01, 161.18, 149.65, 137.39, 137.26, 136.78, 129.92, 129.72, 129.64, 129.39, 128.76, 128.63, 128.49, 127.96, 127.78, 117.25, 44.22. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{19}N_2O$: 339.1497; found: 339.1499.

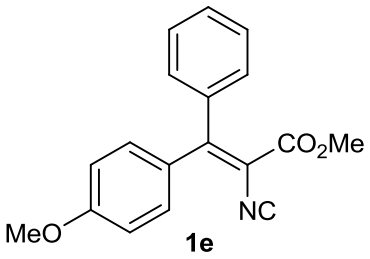
Methyl 2-isocyano-3,3-diphenylacrylate **1j** was prepared according to the modified procedure of previously reported procedures:[3]



Step 1: A mixture of acetophenone (**S4**, 1.2 g, 10.0 mmol) and methyl isocyanoacetate (**S2**, 0.99 g, 10.0 mmol) in THF (10 ml) was added dropwise to a suspension of NaH (60% in oil) (0.48 g, 12.0 mmol) in THF (10.0 ml) at room temperature. After stirring for 2 h at room temperature, 10% AcOH was added to the mixture at 0 ℃ until there is no hydrogen release. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 three times and the extract was washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. Further recrystallization in MeOH afforded the mixture of **S5-*Z*** and **S5-*E*** (1.64 g, 75%) as a white solid.

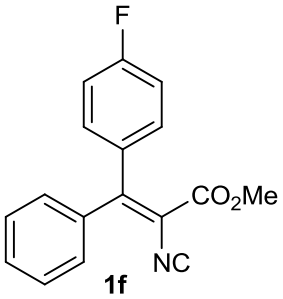
Step 2: THF (10.0 mL), NEt_3 (5.6 mL, 40 mmol) and the mixture of **S5-*Z*** and **S5-*E*** (1.1 g, 5.0 mmol) were added to an oven-dried three necked flask under N_2 atmosphere and cooled to 0 ℃. $POCl_3$ (0.93 mL, 10.0 mmol) was added dropwise and the mixture was stirred for 2 h at 0 ℃ after the addition was complete. Then, the mixture was quenched by sat. Na_2CO_3 and stirred for another 1 h. The mixture was extracted with CH_2Cl_2 three times, dried over Na_2SO_4 and concentracted under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 100/1 to 20/1) to give **1j** (0.52 g, 52%) as a yellow oil. Isomer **1j'** (0.31 g, 31%) was also separated.

1e-**1s** were also prepared according to procedures described for **1j**.



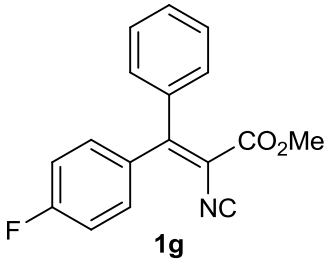
1e

(*Z*)-Methyl 2-isocyano-3-(4-methoxyphenyl)-3-phenylacrylate (1e): for ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. m.p.: 108–110℃. IR (neat, cm^{-1}): 2116.5, 1733.2, 1605.7, 1511.2, 1433.4, 1250.6, 1174.7, 1111.0, 1027.0, 828.8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.30 (m, 5H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.17, 162.55, 161.30, 154.48, 138.20, 132.15, 129.51, 129.39, 129.23, 128.17, 113.76, 112.27, 55.39, 52.78. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{16}NO_3$: 294.1130; found: 294.1124.



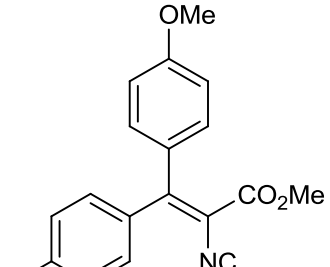
1f

(*E*)-Methyl 3-(4-fluorophenyl)-2-isocyano-3-phenylacrylate (1f): brown oil. For ***Step 1***, eluted by hexane: EtOAc = 2:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. IR (neat, cm^{-1}): 2120.7, 1734.5, 1598.5, 1506.2, 1443.6, 1261.8, 1215.5, 1114.1, 989.7, 833.3. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.30 (m, 5H), 7.12 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.04 (t, *J* = 8.5 Hz, 2H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.12, 163.44 (d, *J* = 250.7 Hz), 162.13, 153.68, 137.32, 133.72 (d, *J* = 3.5 Hz), 131.28 (d, *J* = 8.5 Hz), 130.51, 129.89, 128.56, 115.49 (d, *J* = 21.9 Hz), 113.85, 53.01. ^{19}F NMR (376 MHz, $CDCl_3$): δ –110.79 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{13}FNO_2$: 282.0930; found: 282.0922.



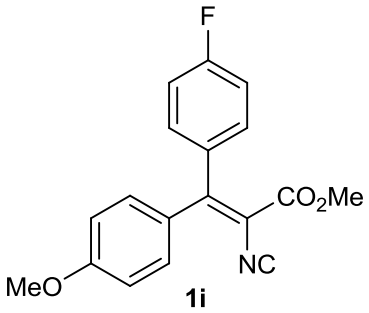
1g

(*Z*)-Methyl 3-(4-fluorophenyl)-2-isocyano-3-phenylacrylate (1g): for ***Step 1***, eluted by hexane: EtOAc = 2:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. m.p.: 111–112℃. IR (neat, cm^{-1}): 2117.7, 1739.5, 1598.4, 1506.3, 1255.7, 1220.5, 1055.8, 986.7, 831.7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.33 (m, 5H), 7.15 – 7.05 (m, 4H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.07, 163.66 (d, *J* = 252.6 Hz), 162.14, 153.34, 137.60, 133.32 (d, *J* = 3.5 Hz), 132.23 (d, *J* = 8.7 Hz), 129.77, 129.10, 128.34, 115.71 (d, *J* = 22.1 Hz), 113.76, 52.95. ^{19}F NMR (376 MHz, $CDCl_3$): δ –108.97 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{13}FNO_2$: 282.0930; found: 282.0922.



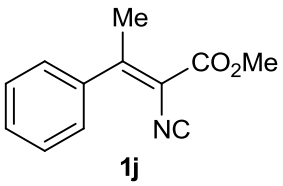
1h

(*Z*)-Methyl 3-(4-fluorophenyl)-2-isocyano-3-(4-methoxyphenyl)acrylate (1h): yellow oil. For ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. IR (neat, cm^{-1}): 2111.2, 1706.4, 1599.6, 1554.2, 1504.0, 1436.0, 1329.7, 1255.8, 1177.3, 1119.2, 831.7. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.8 Hz, 2H), 7.15 – 7.09 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.53, 163.49 (d, *J* = 251.4 Hz), 162.43, 161.47, 153.56, 134.10 (d, *J* = 3.5 Hz), 132.17, 131.36 (d, *J* = 8.5 Hz), 129.28, 115.40 (d, *J* = 21.9 Hz), 113.87, 112.32, 55.42, 52.86. ^{19}F NMR (376 MHz, $CDCl_3$): δ –110.76 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{15}FNO_3$: 312.1036; found: 312.1026.



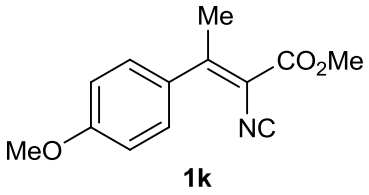
1i

(*E*)-Methyl 3-(4-fluorophenyl)-2-isocyano-3-(4-methoxyphenyl)acrylate (1i): for ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. m.p.: 104–106℃. IR (neat, cm^{-1}): 2112.4, 1726.8, 1601.7, 1505.1, 1435.0, 1245.9, 1173.7, 1109.4, 1028.9, 832.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.31, 163.67 (d, *J* = 252.5 Hz), 162.55, 161.15, 153.51, 133.77 (d, *J* = 3.4 Hz), 132.42 (d, *J* = 8.7 Hz), 131.26, 129.60, 115.62 (d, *J* = 21.9 Hz), 113.74, 112.61, 55.33, 52.90. ^{19}F NMR (376 MHz, $CDCl_3$): δ –109.17 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{15}FNO_3$: 312.1036; found: 312.1030.



1j

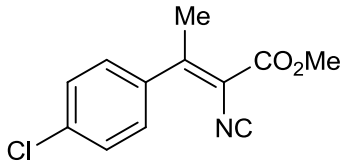
(*Z*)-methyl 2-isocyano-3-phenylbut-2-enoate (1j): yellow oil. for ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. IR (neat, cm^{-1}): 2114.0, 1727.4, 1598.6, 1434.9, 1296.8, 1254.8, 1125.5, 1053.5, 768.2, 697.8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.33 (m, 1H), 3.89 (s, 1H), 2.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.24, 161.87, 156.13, 139.48, 129.46, 128.63, 127.03, 114.49, 52.87, 21.68. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{12}H_{12}NO_2$: 202.0868; found: 202.0858.



1k

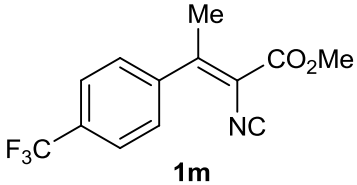
(*Z*)-Methyl 2-isocyano-3-(4-methoxyphenyl)but-2-enoate (1k): for ***Step 1***, eluted by hexane:

EtOAc = 1:2; for ***Step 2***, eluted by hexane: EtOAc = 50:1 to 10:1. m.p.: 110–112℃. IR (neat, cm^{-1}): 2114.8, 1722.5, 1588.8, 1510.5, 1425.7, 1306.7, 1246.6, 1180.7, 1122.4, 1073.5, 1022.8, 830.7. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 3.83 (d, *J* = 7.0 Hz, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.85, 162.14, 160.58, 155.67, 131.28, 129.17, 113.90, 113.55, 55.35, 52.79, 21.59. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{14}NO_3$: 232.0974; found: 232.0982.



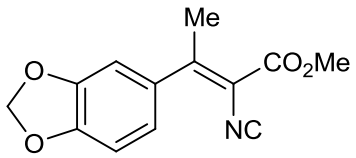
1l

(*Z*)-Methyl 3-(4-chlorophenyl)-2-isocyanobut-2-enoate (1l): for ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. m.p.: 74–76℃. IR (neat, cm^{-1}): 2119.1, 1729.3, 1428.3, 1322.8, 1258.1, 1136.9, 1087.3, 1048.0, 1010.5, 951.7, 834.5, 766.4. ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.67 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.57, 160.64, 153.54, 136.56, 135.00, 128.64, 128.03, 115.98, 52.81, 24.66. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{12}H_{11}ClNO_2$: 236.0478; found: 236.0471.



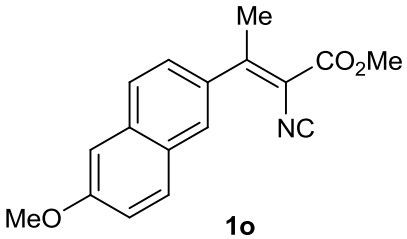
1m

(*Z*)-Methyl 2-isocyano-3-(4-(trifluoromethyl)phenyl)but-2-enoate (1m): colorless oil. For ***Step 1***, eluted by hexane: EtOAc = 2:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 50:1. IR (neat, cm^{-1}): 2116.8, 1733.6, 1437.4, 1322.3, 1250.9, 1165.1, 1122.5, 1070.0, 1015.4, 838.6. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.66 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.12, 160.38, 153.41, 142.08, 130.76 (q, *J* = 32.9 Hz), 126.98, 125.41 (q, *J* = 3.8 Hz), 123.91 (q, *J* = 272.3 Hz), 116.41, 52.89, 24.73. ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.76 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{11}F_3NO_2$: 270.0742; found: 270.0733.



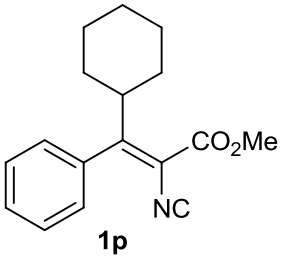
1n

(*Z*)-Methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-isocyanobut-2-enoate (1n): for ***Step 1***, eluted by hexane: EtOAc = 1:2; for ***Step 2***, eluted by hexane: EtOAc = 50:1 to 10:1. m.p.: 78–80℃. IR (neat, cm^{-1}): 2111.8, 1724.1, 1574.2, 1488.6, 1434.0, 1227.9, 1072.1, 907.4, 805.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 – 6.83 (m, 3H), 6.01 (s, 2H), 3.88 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.23, 161.96, 155.56, 148.62, 147.77, 132.88, 121.74, 114.03, 108.44, 107.87, 101.57, 52.85, 21.77. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{12}NO_4$: 246.0766; found: 246.0758.



1o

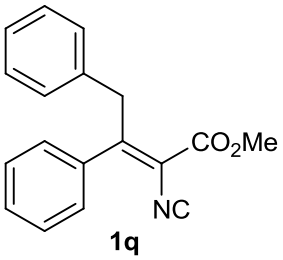
(*Z*)-Methyl 2-isocyano-3-(6-methoxynaphthalen-2-yl)but-2-enoate (1o): for ***Step 1***, eluted by hexane: EtOAc = 1:2; for ***Step 2***, eluted by hexane: EtOAc = 50:1 to 10:1. m.p.: 82–84℃. IR (neat, cm^{-1}): 2117.6, 1727.2, 1594.9, 1479.9, 1245.7, 1205.0, 1129.7, 1066.9, 852.4, 771.9. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (s, 1H), 7.77 (t, *J* = 8.9 Hz, 2H), 7.44 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.18 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.14 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.16, 162.10, 158.84, 156.12, 134.92, 134.35, 130.04, 128.23, 127.13, 127.09, 125.09, 119.66, 114.31, 105.70, 55.42, 52.87, 21.80. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{16}NO_3$: 282.1130; found: 282.1121.



1p

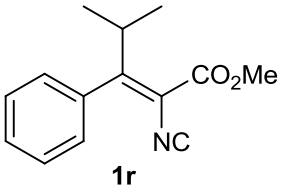
(*Z*)-Methyl 3-cyclohexyl-2-isocyano-3-phenylacrylate (1p): for ***Step 1***, eluted by hexane:

EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. m.p.: 90–92℃. IR (neat, cm^{-1}): 2125.1, 1734.7, 1438.9, 1252.8, 1231.6, 1116.7, 999.8, 844.1, 709.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.34 (m, 3H), 7.08 – 7.03 (m, 2H), 3.88 (s, 3H), 3.66 (m, 1H), 1.78 – 1.56 (m, 5H), 1.43 – 1.28 (m, 2H), 1.16 – 0.92 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.44, 165.82, 161.39, 136.54, 128.44, 128.29, 126.45, 115.39, 52.85, 40.44, 31.03, 25.91, 25.49. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{17}H_{20}NO_2$: 270.1494; found: 270.1485.



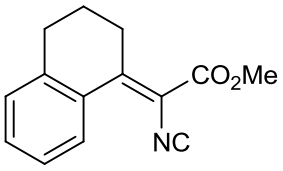
1q

(*Z*)-Methyl 2-isocyano-3,4-diphenylbut-2-enoate (1q): for ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 20:1. m.p.: 93–95℃. IR (neat, cm^{-1}): 2110.8, 1727.5, 1596.8, 1494.3, 1433.5, 1256.3, 1114.4, 1001.7, 772.6, 698.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 3H), 7.21 – 7.11 (m, 5H), 7.06 – 7.02 (m, 2H), 4.35 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.77, 161.73, 158.00, 137.84, 136.44, 129.38, 129.09, 128.58, 128.56, 127.55, 126.87, 115.38, 53.17, 39.50. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{16}NO_2$: 278.1181; found: 278.1172.



1r

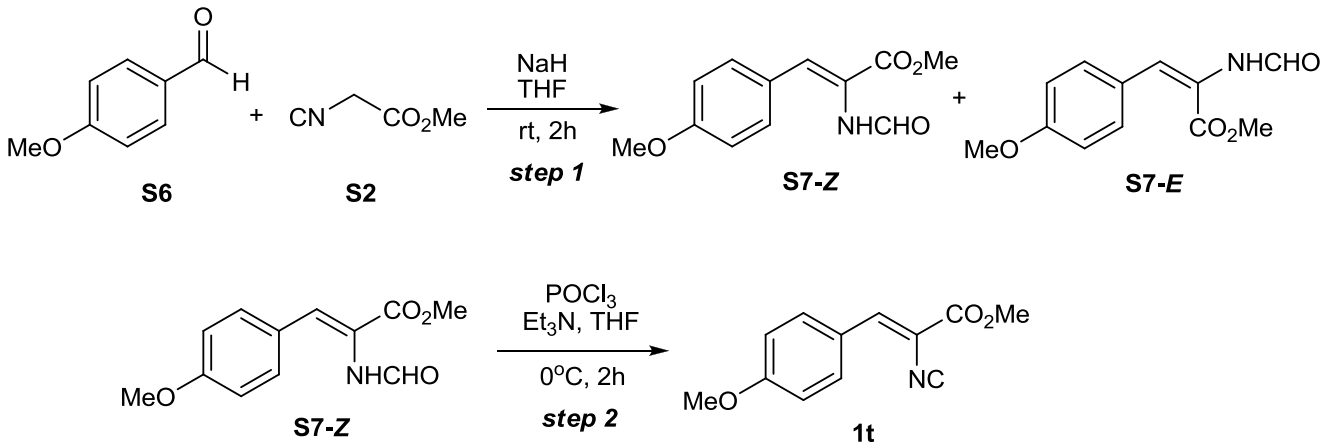
(*Z*)-Methyl 2-isocyano-4-methyl-3-phenylpent-2-enoate (1r): colorless oil. For ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 50:1. IR (neat, cm^{-1}): 2122.5, 1718.5, 1428.9, 1300.9, 1251.2, 1130.6, 1091.7, 944.7, 748.3, 704.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.35 (m, 3H), 7.08 (m, 2H), 4.07 – 3.96 (m, 1H), 3.88 (s, 3H), 1.1 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.53, 165.98, 161.36, 135.68, 128.45, 128.40, 126.78, 115.38, 52.88, 29.77, 20.84. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{16}NO_2$: 230.1181; found: 230.1173.



1s

(*Z*)-Methyl 2-(3,4-dihydronaphthalen-1(2H)-ylidene)-2-isocyanoacetate (1s): colorless oil. For ***Step 1***, eluted by hexane: EtOAc = 1:1; for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 50:1. IR (neat, cm^{-1}): 2110.4, 1718.3, 1588.1, 1453.9, 1426.1, 1319.0, 1279.5, 1255.2, 1127.2, 741.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 3.74 (s, 3H), 2.84 (t, *J* = 6.7 Hz, 2H), 2.73 (t, *J* = 6.3 Hz, 2H), 1.91 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.28, 162.52, 151.02, 141.16, 130.90, 130.81, 129.00, 128.14, 125.43, 113.31, 52.77, 30.65, 29.71, 21.17. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{14}NO_2$: 228.1025; found: 228.1018.

Methyl 2-isocyano-3,3-diphenylacrylate **1t** was prepared according to the modified procedure of previously reported procedures:[3]

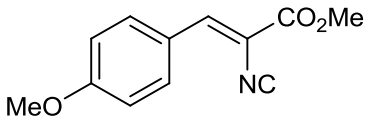


Step 1: A mixture of 4-methoxybenzaldehyde (**S6**, 1.36 g, 10.0 mmol) and methyl isocyanoacetate (**S2**, 0.99 g, 10.0 mmol) in THF (10 ml) was added dropwise to a suspension of NaH (60% in oil) (0.48 g, 12.0 mmol) in THF (10.0 ml) at room temperature. After stirring for 2 h at room

temperature, 10% AcOH was added to the mixture at 0 ℃ until there is no hydrogen release. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 three times and the extract was washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. Et_2O was added to the resulting residue. The insoluble precipitates were filtered off by suction, washed with Et_2O and dried *in vacuo* to give **S7-*Z*** (0.84 g, 41%) as a white solid.

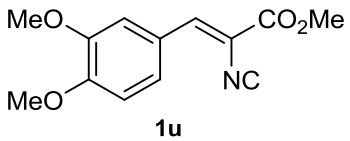
Step 2: THF (5.0 mL), NEt_3 (2.8 mL, 20 mmol) and **S7-*Z*** (0.51 g, 2.5 mmol) were added to an oven-dried three necked flask under N_2 atmosphere and cooled to 0 ℃. $POCl_3$ (0.47 mL, 5.0 mmol) was added dropwise and the mixture was stirred for 2 h at 0 ℃ after the addition was complete. Then, the mixture was quenched by sat. Na_2CO_3 and stirred for another 1 h. The mixture was extracted with CH_2Cl_2 three times, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20/1) to give **1t** (0.42 g, 90%) as a white solid.

1u, **1v** and **1x** were also prepared according to procedures described for **1t**.



1t

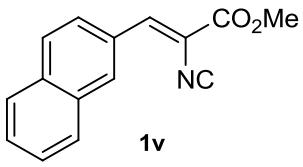
(*Z*)-Methyl 2-isocyano-3-(4-methoxyphenyl)acrylate (1t): for ***Step 2***, eluted by hexane: EtOAc = 50: 1 to 10:1. m.p.: 110–112℃. IR (neat, cm^{-1}): 2111.3, 1714.2, 1593.1, 1566.3, 1511.3, 1427.0, 1283.5, 1258.7, 1172.6, 1023.6, 964.7, 835.6. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.60 (s, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.17, 162.60, 162.29, 138.07, 133.25, 123.82, 114.62, 111.72, 55.53, 53.31. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{12}H_{12}NO_3$: 218.0817; found: 218.0810.



1u

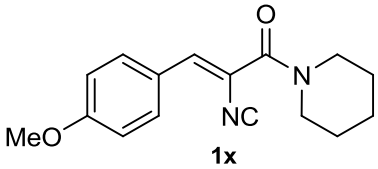
(*Z*)-Methyl 3-(3,4-dimethoxyphenyl)-2-isocyanoacrylate (1u): for ***Step 2***, eluted by hexane: EtOAc = 20: 1 to 5:1. m.p.: 109–111℃. IR (neat, cm^{-1}): 2112.0, 1727.1, 1592.6, 1511.3, 1423.1,

1258.3, 1227.4, 1151.0, 1088.2, 1016.3, 845.9, 803.9 . ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 1.5 Hz, 1H), 7.59 (s, 1H), 7.40 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H), 3.95 (s, 3H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.22, 162.24, 152.44, 149.13, 138.39, 126.74, 124.05, 112.23, 111.75, 110.99, 56.07, 56.00, 53.33. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{13}H_{14}NO_4$: 248.0923; found: 248.0914.



1v

(*Z*)-Methyl 2-isocyano-3-(naphthalen-2-yl)acrylate (1v): for ***Step 2***, eluted by hexane: EtOAc = 100:1 to 50:1. m.p.: 121–123℃. IR (neat, cm^{-1}): 2114.3, 1726.0, 1619.3, 1432.8, 1337.9, 1253.0, 1182.9, 1087.1, 963.3, 814.6, 748.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.81 (s, 1H), 7.63 – 7.50 (m, 2H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.04, 161.95, 138.50, 134.71, 132.96, 132.90, 129.14, 128.91, 128.56, 127.80, 127.05, 126.08, 114.05, 53.53. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{15}H_{12}NO_2$: 238.0868; found: 238.0860.



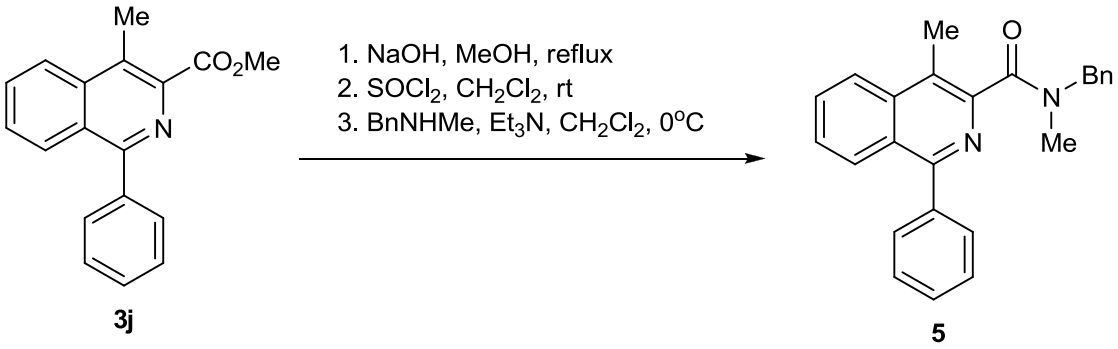
1x

(*Z*)-2-Isocyano-3-(4-methoxyphenyl)-1-(piperidin-1-yl)prop-2-en-1-one (1x): for ***Step 2***, eluted by hexane: EtOAc = 20:1 to 5:1. m.p.: 115–117℃. IR (neat, cm^{-1}): 2095.2, 1642.0, 1601.3, 1512.1, 1441.8, 1257.3, 1180.6, 1024.6, 909.9, 829.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.92 (s, 1H), 3.86 (s, 3H), 3.61 – 3.53 (m, 4H), 1.75 – 1.59 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.33, 163.08, 161.48, 134.39, 131.93, 124.46, 115.83, 114.37, 55.43, 25.69, 24.39. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{16}H_{19}N_2O_2$: 271.1447; found: 271.1447.

3. General procedure: synthesis of isoquiolines.

A 10 mL round bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with vinyl isocyanide **1** (0.2 mmol, 1.0 equiv), diaryliodonium salt **2** (0.4 mmol, 2.0 equiv) *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.01 equiv), Na_2CO_3 (0.2 mmol, 1.0 equiv). The flask was evacuated and backfilled with argon for 3 times. MeOH (4.0 mL, 0.05 M) was added with syringe under argon. The mixture was then irradiated by a 3W white LED strip. After the reaction was complete (as judged by TLC analysis), The mixture was poured into a separatory funnel containing 20 mL H_2O and 20 mL CH_2Cl_2. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure after filtration. The residue was purified by flash chromatography on silica gel to afford the desired product isoquinolines **3** or **4**.

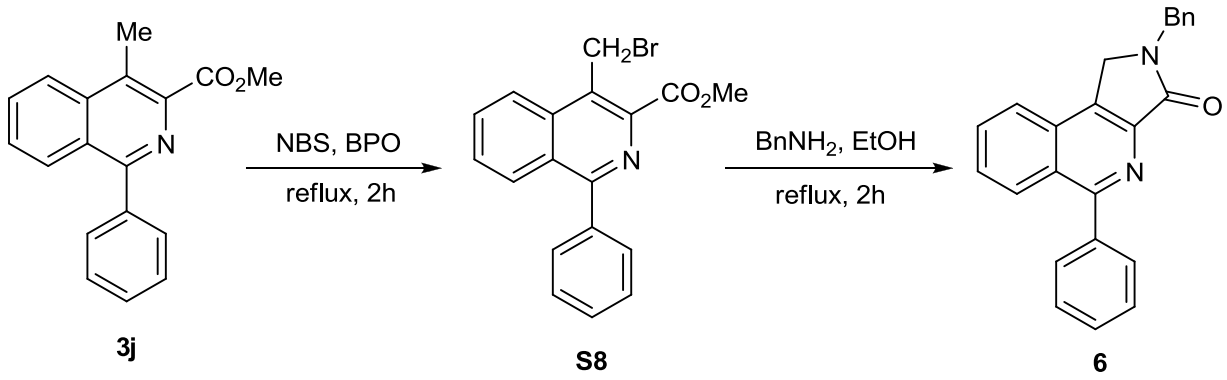
4. Synthesis of non-benzodiazepine PBR ligands 5 and 6.



3j **5**

To a stirred solution of **3j** (0.3 mmol, 83.1 mg) in 10 mL MeOH was added 0.6 mL 1.0 M NaOH aqueous solution and reflux overnight. The solvent was evaporated under reduced pressure and 10 mL H_2O was then added to the residue. $KHSO_4$ (0.3 mmol, 81.5 mg) was then added to the solution and the white solid was precipitated and filtrated to give the carboxylic acid in equivalent yield without further purification.

A solution of the carboxylic acid (0.3 mmol, 78.9 mg) in CH_2Cl_2 (10 mL) with $SOCl_2$ (0.22 mL, 10.0 mmol) was stirred at room temperature for 1h, and the solvent and excess $SOCl_2$ was evaporated under reduced pressure. The residue was diluted with CH_2Cl_2 (10 mL) and then cooled to 0-5 ℃. To the resulting mixture, N-methyl-1-phenylmethanamine (0.33 mmol, 40.0 mg) and triethylamine (0.42 mL, 3.0 mmol) were added in sequence. The reaction mixture was stirred at room temperature for 1h, washed with H_2O, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2 : EtOAc = 5 : 1) gave **5** (93.3 mg, 85% for 2 steps) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (q, *J* = 8.1Hz, 2H), 7.77 – 7.64 (m, 2H), 7.59 – 7.42 (m, 6H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.20 (m, 3H), 4.84 & 4.44 (both S, 2H, due to rotamers), 3.10 & 2.80 (both S, 3H, due to rotamers), 2.70 & 2.69 (both S, 3H, due to rotamers). ^{13}C NMR (100 MHz, $CDCl_3$, extra signals due to rotamers): δ 170.23, 169.95, 159.11, 158.90, 146.36, 146.24, 139.26, 139.18, 137.14, 136.67, 136.60, 136.55, 130.38, 130.13, 130.11, 128.74, 128.62, 128.60, 128.58, 128.43, 128.35, 128.28, 128.21, 128.16, 127.71, 127.67, 127.52, 127.33, 127.28, 126.21, 126.19, 124.15, 123.85, 123.79, 123.44, 54.63, 50.44, 35.71, 32.53, 14.50, 14.12.

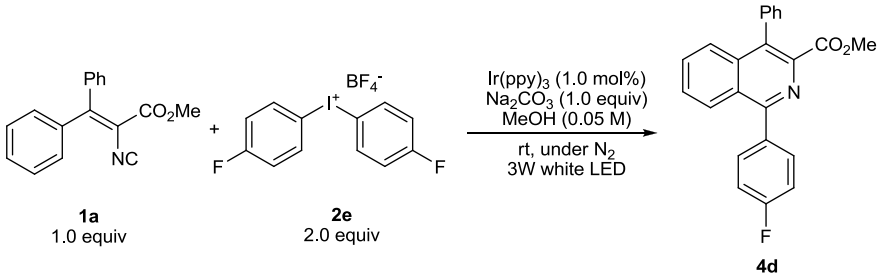


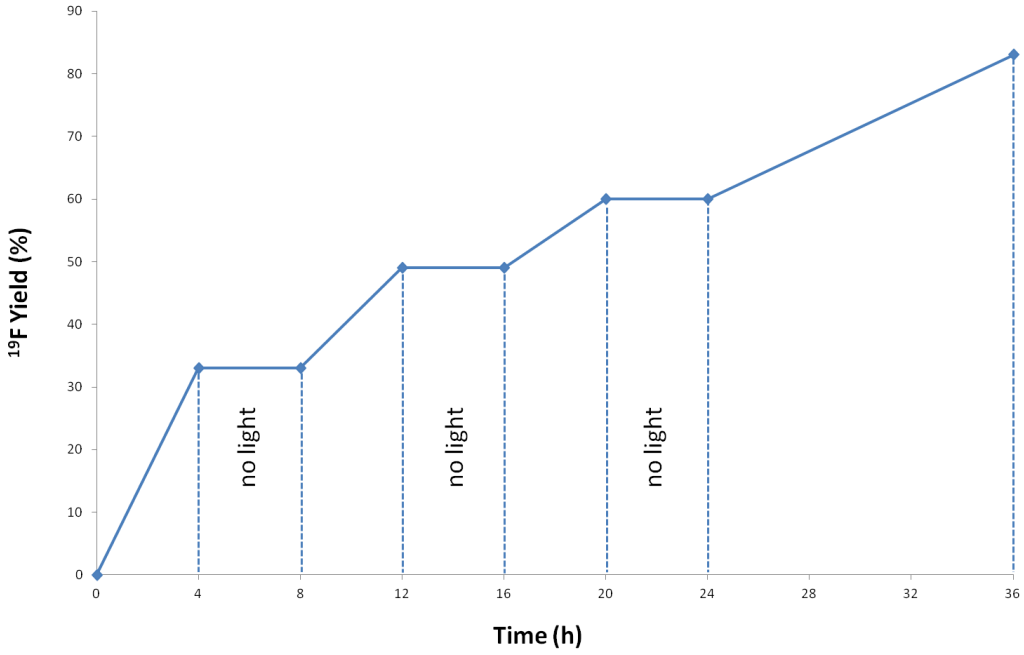
3j **S8** **6**

A mixture of **3j** (0.3 mmol, 83.1 mg) in CCl_4 (10 mL) with *N*-bromosuccinimide (0.3 mmol, 53.1 mg) and dibenzoyl peroxide (0.1 mmol, 14.5 mg) was heated at reflux for 2 h, the solvent was evaporated *in vacuo*, and the residue was purified by column chromatography (pure CH_2Cl_2) afforded **S8** (97.9 mg, 92%) as a white solid.

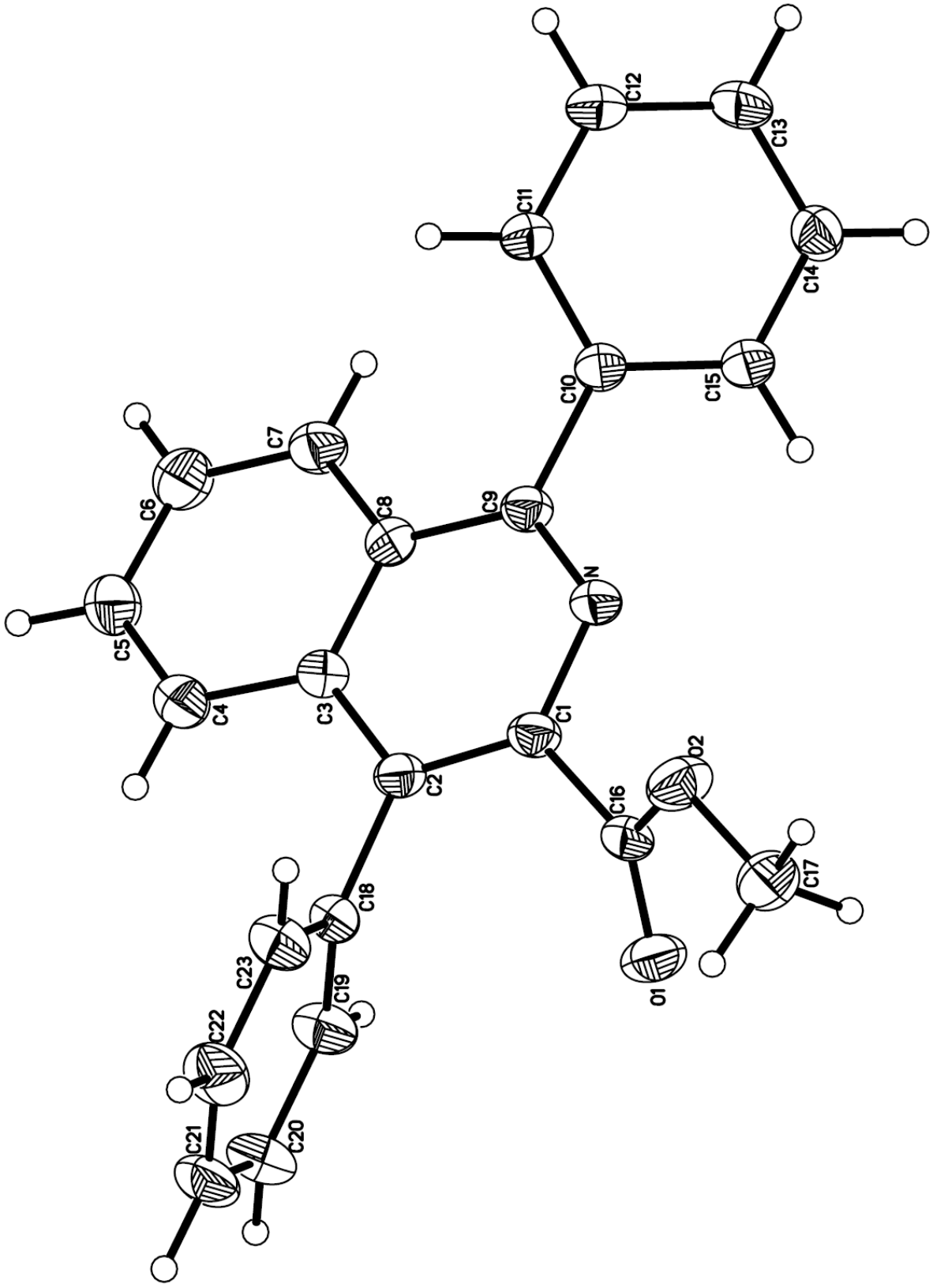
A mixture of **S8** (71.0 g, 0.20 mmol) in ethanol (10 mL) with phenylmethanamine (0.18 mL, 0.11 mL) was heated at reflux for 2 h, and then the solvent was removed under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2 : EtOAc = 4 : 1) gave **6** (64.4 mg, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 6.9 Hz, 1H), 7.86 – 7.21 (m, 13H), 4.94 (s, 2H), 4.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.74, 163.37, 143.38, 138.92, 137.00, 131.92, 131.63, 131.26, 130.34, 129.30, 128.87, 128.70, 128.31, 128.22, 127.80, 127.49, 122.72, 46.86, 46.31.

5. Result of light off/on and time profile experiment.

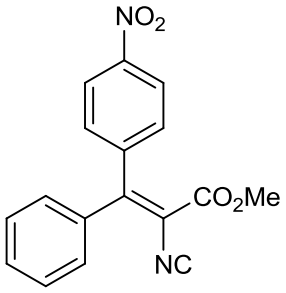


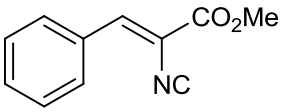


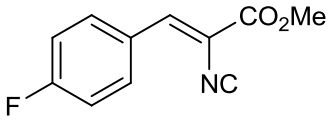
6. Single crystal X-ray analysis of 3a (CCDC 985962).

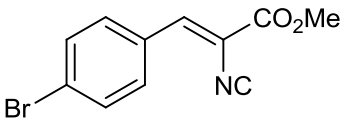


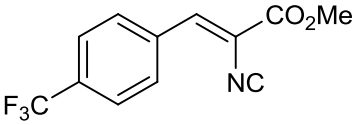
7. List of unreactive aryl aldehyde derived vinyl isocyanides.

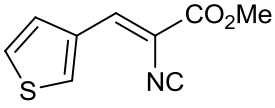




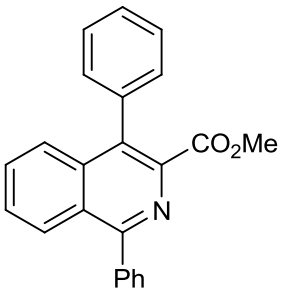






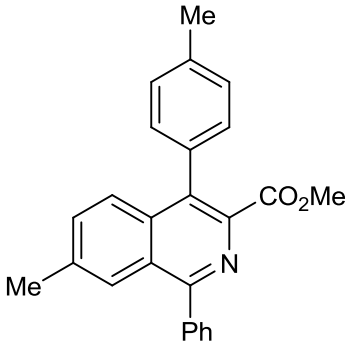


8. Data for isoquinolines.



3a

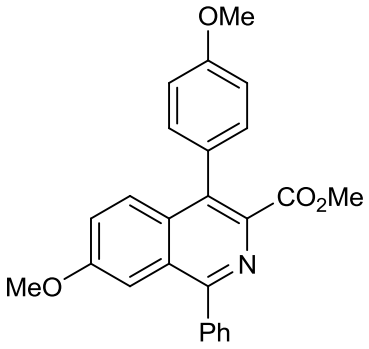
Methyl 1,4-diphenylisoquinoline-3-carboxylate (3a): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3a** (56.3 mg, 83%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 192–194℃. IR (neat, cm^{-1}): 1721.8, 1446.7, 1338.7, 1225.4, 1114.4, 1002.5, 760.0, 707.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.9 Hz, 1H), 7.80 – 7.46 (m, 11H), 7.44 – 7.38 (m, 2H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.67, 160.26, 141.39, 138.92, 136.51, 136.10, 132.73, 130.52, 130.21, 129.84, 128.91, 128.44, 128.28, 128.01, 127.74, 127.19, 126.73, 52.40. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{23}H_{18}NO_2$: 340.1338; found: 340.1335.



3b

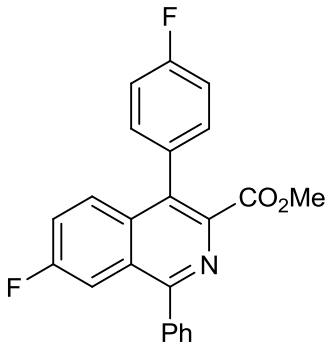
Methyl 7-methyl-1-phenyl-4-p-tolylisoquinoline-3-carboxylate (3b): According to General Procedure, methyl 2-isocyano-3,3-dip-tolylacrylate **1b** (58.2 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3b** (57.3 mg, 78%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 161–162℃. IR (neat, cm^{-1}): 1722.9, 1443.0, 1374.7, 1225.5, 1166.2, 1117.7,

1012.8, 834.7, 704.8. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.77 – 7.72 (m, 2H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.58-7.43 (m, *J* = 4H), 7.30 (q, *J* = 8.1 Hz, 4H), 3.72 (s, 3H), 2.47 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.83, 159.34, 140.63, 139.21, 138.54, 137.60, 134.91, 133.25, 132.95, 132.63, 130.18, 129.68, 129.02, 128.75, 128.44, 127.46, 126.70, 126.48, 52.40, 21.95, 21.45. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{25}H_{22}NO_2$: 368.1651; found: 368.1650.



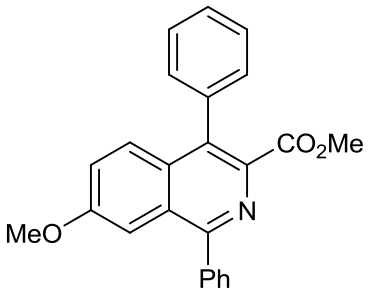
3c

Methyl 7-methoxy-4-(4-methoxyphenyl)-1-phenylisoquinoline-3-carboxylate (3c): According to General Procedure, methyl 2-isocyano-3,3-bis(4-methoxyphenyl)acrylate **1c** (64.6 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3c** (58.2 mg, 73%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 194–196℃. IR (neat, cm^{-1}): 1724.5, 1607.6, 1514.0, 1405.5, 1213.8, 1160.1, 1014.7, 850.0, 704.3. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.74 (m, 2H), 7.65 (d, *J* = 9.3 Hz, 1H), 7.58 – 7.47 (m, 3H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.04 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H), 3.81 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.88, 159.33, 159.20, 158.31, 139.86, 139.29, 132.82, 132.18, 130.93, 129.93, 128.78, 128.53, 128.37, 122.86, 113.75, 105.62, 55.46, 55.28, 52.38. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{25}H_{22}NO_4$: 400.1549; found: 400.1544.



3d

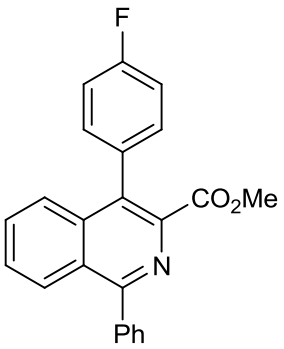
Methyl 7-fluoro-4-(4-fluorophenyl)-1-phenylisoquinoline-3-carboxylate (3d): According to General Procedure, methyl 3,3-bis(4-fluorophenyl)-2-isocyanoacrylate **1d** (59.8 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3d** (66.0 mg, 88%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 206–208℃. IR (neat, cm^{-1}): 1725.5, 1514.0, 1305.6, 1193.5, 1157.9, 1113.1, 949.2, 842.1, 709.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 9.9, 2.5 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.69 (dd, *J* = 9.3, 5.5 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.46 – 7.40 (m, 1H), 7.40 – 7.33 (m, 2H), 7.25 – 7.19 (m, 2H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.31, 162.69 (d, *J* = 248.2 Hz), 161.69 (d, *J* = 251.4 Hz), 159.78 (d, *J* = 5.5 Hz), 141.11 (d, *J* = 2.6 Hz), 138.36, 133.68, 131.73 (d, *J* = 1.4 Hz), 131.65 (d, *J* = 3.6 Hz), 131.49 (d, *J* = 8.2 Hz), 129.96, 129.56 (d, *J* = 8.7 Hz), 129.22, 128.65, 128.39 (d, *J* = 8.6 Hz), 121.06 (d, *J* = 25.0 Hz), 115.54 (d, *J* = 21.7 Hz), 111.40 (d, *J* = 22.4 Hz), 52.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.83 (s, 1F), -113.36 (s, 1F). HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{23}H_{16}F_2NO_2$: 376.1149; found: 376.1145.



3e

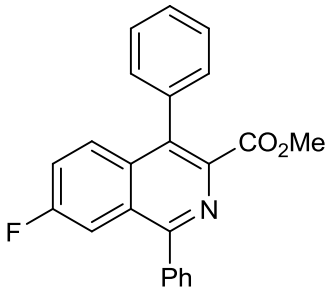
Methyl 7-methoxy-1,4-diphenylisoquinoline-3-carboxylate (3e): According to General Procedure, (*Z*)-methyl 2-isocyano-3-(4-methoxyphenyl)-3-phenylacrylate **1e** (58.6 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol)

and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3e** (58.3 mg, 79%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 144–146℃. IR (neat, cm^{-1}): 1727.9, 1617.1, 1506.7, 1406.1, 1213.9, 1164.8, 1118.4, 1007.8, 836.2, 745.9, 699.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.60 (d, *J* = 9.3 Hz, 1H), 7.58 – 7.46 (m, 6H), 7.45 (d, *J* = 2.6 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.28 (dd, *J* = 9.3, 2.6 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.64, 159.30, 158.54, 139.39, 139.24, 136.46, 133.33, 131.90, 129.95, 129.71, 128.83, 128.81, 128.57, 128.55, 128.24, 127.91, 122.96, 105.65, 55.48, 52.34. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{24}H_{20}NO_3$: 370.1443; found: 370.1440.



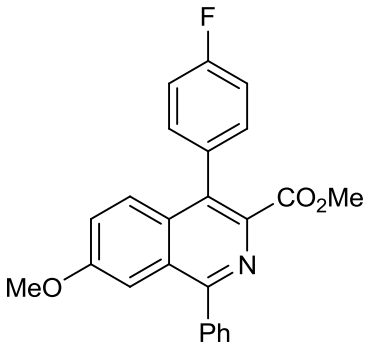
3f

Methyl 7-fluoro-1,4-diphenylisoquinoline-3-carboxylate (3f): According to General Procedure, (*E*)-methyl 3-(4-fluorophenyl)-2-isocyano-3-phenylacrylate **1f** (56.2 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3f** (61.4 mg, 86%) as a white solid after purification on Silica gel (hexane: EtOAc = 20:1). m.p.: 227–229℃. IR (neat, cm^{-1}): 1717.8, 1511.4, 1445.5, 1338.5, 1211.1, 1188.2, 1115.5, 1001.3, 841.3, 772.7, 706.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 1H), 7.79 – 7.60 (m, 5H), 7.55 – 7.47 (m, 3H), 7.43 – 7.38 (m, 2H), 7.28 – 7.21 (m, 2H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.56, 162.61 (d, *J* = 247.7 Hz), 160.51, 141.46, 138.81, 136.58, 131.95 (d, *J* = 3.5 Hz), 131.78, 131.56 (d, *J* = 8.1 Hz), 130.71, 130.20, 129.00, 128.49, 128.43, 127.85, 127.21, 126.49, 115.45 (d, *J* = 21.6 Hz), 52.51. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.77 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{17}FNO_2$: 358.1243; found: 358.1239.



3g

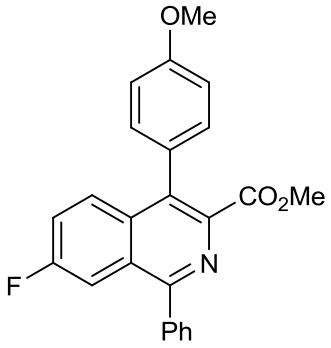
Methyl 4-(4-fluorophenyl)-1-phenylisoquinoline-3-carboxylate (3g): According to General Procedure, (*Z*)-methyl 3-(4-fluorophenyl)-2-isocyano-3-phenylacrylate **1g** (56.2 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3g** (52.1 mg, 73%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 215–217℃. IR (neat, cm^{-1}): 1718.0, 1511.4, 1445.6, 1338.4, 1221.2, 1115.3, 1001.3, 841.3, 772.4, 706.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 9.9, 2.6 Hz, 1H), 7.77 – 7.70 (m, 3H), 7.60 – 7.49 (m, 6H), 7.46 – 7.37 (m, 3H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.46, 161.66 (d, *J* = 251.4 Hz), 159.57 (d, *J* = 5.4 Hz), 140.99 (d, *J* = 2.6 Hz), 138.47, 135.81, 133.61, 132.78 (d, *J* = 1.4 Hz), 130.00, 129.85 (d, *J* = 8.7 Hz) 129.73, 129.17, 128.65, 128.39, 128.22, 120.91 (d, *J* = 24.9 Hz), 111.29 (d, *J* = 22.3 Hz), 52.48. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.11 (s, 1F). HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{23}H_{17}FNO_2$: 358.1243; found: 358.1239.



3h

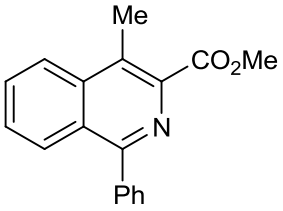
Methyl 4-(4-fluorophenyl)-7-methoxy-1-phenylisoquinoline-3-carboxylate (3h): According to General Procedure, (*E*)-methyl 3-(4-fluorophenyl)-2-isocyano-3-(4-methoxyphenyl)acrylate **1h** (62.2 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3h** (59.6 mg, 77%) as a white

solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 203–205℃. IR (neat, cm^{-1}): 1717.7, 1616.4, 1513.5, 1407.6, 1214.1, 1158.1, 1119.9, 932.3, 837.9, 705.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.60 – 7.48 (m, 4H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.30 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.24 – 7.18 (m, 2H), 3.82 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.52, 162.54 (d, *J* = 248.8 Hz), 159.37, 158.76, 139.38, 139.12, 132.39, 132.31 (d, *J* = 3.5 Hz), 131.96, 131.40 (d, *J* = 8.0 Hz), 129.91, 128.91, 128.83, 128.58, 128.31, 123.13, 115.37 (d, *J* = 21.5 Hz), 105.72, 55.50, 52.44. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.97 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{24}H_{19}FNO_3$: 388.1349; found: 388.1346.



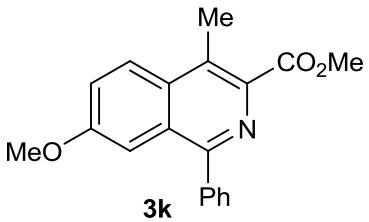
3i

Methyl 7-fluoro-4-(4-methoxyphenyl)-1-phenylisoquinoline-3-carboxylate (3i): According to General Procedure, (*Z*)-methyl 3-(4-fluorophenyl)-2-isocyano-3-(4-methoxyphenyl)acrylate **1i** (62.2 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3i** (55.7 mg, 72%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 208–210℃. IR (neat, cm^{-1}): 1726.5, 1411.8, 1249.1, 1160.9, 1076.4, 1027.8, 843.1, 711.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 4H), 7.60 – 7.49 (m, 3H), 7.46 – 7.38 (m, 1H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.70, 161.60 (d, *J* = 250.9 Hz), 159.53, 159.31 (d, *J* = 5.4 Hz), 141.44 (d, *J* = 2.5 Hz), 138.51, 133.89, 132.30 (d, *J* = 1.5 Hz), 130.98, 129.98, 129.83 (d, *J* = 8.7 Hz), 129.12, 128.63, 128.36 (d, *J* = 8.6 Hz), 127.68, 120.82 (d, *J* = 24.9 Hz), 113.90, 111.25 (d, *J* = 22.2 Hz), 55.31, 52.51. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.36 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{24}H_{19}FNO_3$: 388.1349; found: 388.1347.



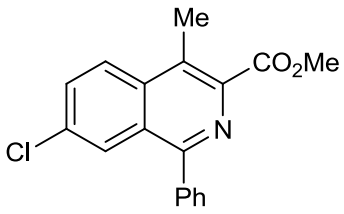
3j

Methyl 4-methyl-1-phenylisoquinoline-3-carboxylate (3j): According to General Procedure, (*Z*)-methyl 2-isocyano-3-phenylbut-2-enoate **1j** (40.2 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3j** (31.6 mg, 57%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 123–125℃. IR (neat, cm^{-1}): 1713.5, 1444.7, 1332.9, 1235.6, 1210.7, 1158.9, 1061.3, 1029.0, 705.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.71 – 7.65 (m, 2H), 7.63-7.57 (m, 1H), 7.55 – 7.45 (m, 3H), 4.01 (s, 3H), 2.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.23, 158.78, 141.24, 139.05, 136.73, 130.43, 130.19, 128.72, 128.39, 128.24, 128.13, 127.08, 124.47, 52.70, 14.41. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{18}H_{16}NO_2$: 278.1181; found: 278.1178.



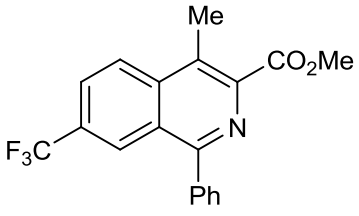
3k

Methyl 7-methoxy-4-methyl-1-phenylisoquinoline-3-carboxylate (3k): According to General Procedure, (*Z*)-methyl 2-isocyano-3-(4-methoxyphenyl)but-2-enoate **1k** (46.2 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3k** (48.5 mg, 79%) as a white solid after purification on Silica gel (hexane: EtOAc = 10:1). m.p.: 138–140℃. IR (neat, cm^{-1}): 1713.9, 1699.8, 1616.0, 1444.2, 1389.8, 1308.1, 1212.7, 1079.1, 821.2, 711.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.2 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.57 – 7.37 (m, 5H), 4.00 (s, 3H), 3.81 (s, 3H), 2.88 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$): δ 168.21, 159.10, 157.09, 139.31, 132.04, 129.91, 128.84, 128.69, 128.63, 128.46, 126.32, 122.69, 106.16, 55.41, 52.62, 14.44. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{19}H_{18}NO_3$: 308.1287; found: 308.1285.



3l

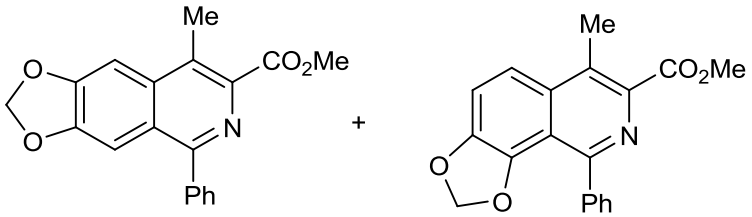
Methyl 7-chloro-4-methyl-1-phenylisoquinoline-3-carboxylate (3l): According to General Procedure, methyl 3-(4-chlorophenyl)-2-isocyanobut-2-enoate **1l** (47.0 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3l** (43.5 mg, 70%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 155–157℃. IR (neat, cm^{-1}): 1707.9, 1436.0, 1297.9, 1231.4, 1155.4, 1047.7, 965.2, 698.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.1 Hz, 1H), 8.08 (d, *J* = 2.1 Hz, 1H), 7.73 (dd, *J* = 9.1, 2.1 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.57 – 7.48 (m, 3H), 4.01 (s, 3H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.91, 157.93, 141.51, 138.38, 135.14, 134.35, 131.37, 130.07, 129.04, 128.62, 128.12, 127.85, 127.00, 126.40, 52.84, 14.45. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{15}ClNO_2$: 312.0791; found: 312.0787.



3m

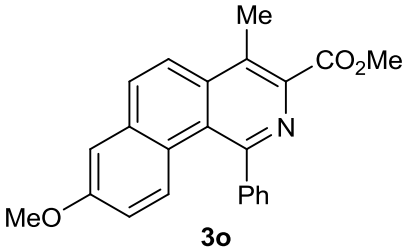
Methyl 4-methyl-1-phenyl-7-(trifluoromethyl)isoquinoline-3-carboxylate (3m): According to General Procedure, (*Z*)-methyl 2-isocyano-3-(4-(trifluoromethyl)phenyl)but-2-enoate **1m** (53.8 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3m** (36.5 mg, 53%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 108–110℃. IR (neat, cm^{-1}): 1703.7, 1361.1, 1298.4, 1229.4, 1152.9, 1077.3, 1020.1, 945.1, 753.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.33 (d, *J* = 8.9 Hz, 1H), 7.97 (dd, *J* = 8.9, 1.7 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.62 – 7.50 (m, 3H), 4.03 (s, 3H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.77, 159.61, 143.21, 138.31, 138.07, 130.13, 129.83 (q, *J* = 32.8 Hz), 129.30, 128.72, 127.55, 126.11, 126.05 (q, *J* = 3.0 Hz), 125.93 (q, *J* = 4.5 Hz), 125.87, 123.69 (q, *J* = 273.4 Hz), 52.90, 14.49. ^{19}F NMR (376

MHz, $CDCl_3$) δ -62.66 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{15}F_3NO_2$: 346.1055; found: 346.1050.



3n **3n'**

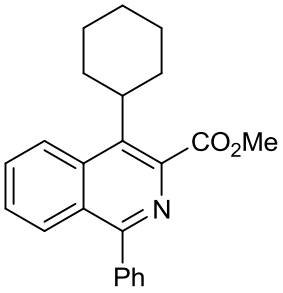
Methyl 8-methyl-5-phenyl-[1,3]dioxolo[4,5-g]isoquinoline-7-carboxylate (3n) & methyl 6-methyl-9-phenyl-[1,3]dioxolo[4,5-h]isoquinoline-7-carboxylate (3n'): According to General Procedure, (*Z*)-methyl 3-(benzo[d][1,3]dioxol-5-yl)-2-isocyanobut-2-enoate **1n** (49.0 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3n & 3n'** (44.9 mg, 70%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 193–195℃. Data for major product **3n**: IR (neat, cm^{-1}): 1705.2, 1459.0, 1253.9, 1215.5, 1042.7, 947.3, 852.3, 698.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 2H), 7.53 – 7.44 (m, 3H), 7.43 (s, 1H), 7.33 (s, 1H), 6.12 (s, 2H), 3.99 (s, 3H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.34, 156.84, 151.09, 149.00, 140.77, 139.41, 135.21, 129.92, 128.55, 128.44, 127.42, 124.76, 104.16, 102.02, 100.96, 52.68, 14.87. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{16}NO_4$: 322.1079; found: 322.1078.



3o

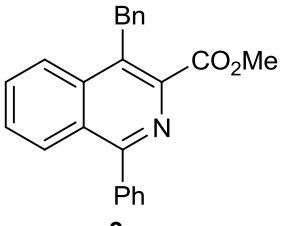
Methyl 8-methoxy-4-methyl-1-phenylbenzo[h]isoquinoline-3-carboxylate (3n): According to General Procedure, (*Z*)-methyl 2-isocyano-3-(6-methoxynaphthalen-2-yl)but-2-enoate **1o** (56.2 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3o** (50.7 mg, 71%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 184–186℃. IR (neat, cm^{-1}): 1708.9,

1609.2, 1353.0, 1232.7, 1049.9, 1023.5, 853.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.2 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.66 (d, *J* = 9.4 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.50 – 7.41 (m, 3H), 7.22 (d, *J* = 2.8 Hz, 1H), 6.82 (dd, *J* = 9.4, 2.8 Hz, 1H), 4.01 (s, 3H), 3.90 (s, 3H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.00, 158.49, 155.83, 143.61, 141.50, 136.65, 135.12, 131.70, 130.07, 129.20, 129.11, 128.43, 127.63, 125.00, 123.71, 122.02, 116.48, 108.33, 55.35, 52.63, 14.77. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{20}NO_3$: 358.1443; found: 358.1441.



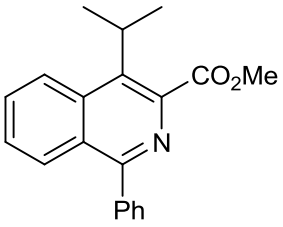
3p

Methyl 4-cyclohexyl-1-phenylisoquinoline-3-carboxylate (3p): According to General Procedure, (*Z*)-methyl 3-cyclohexyl-2-isocyano-3-phenylacrylate **1p** (53.8 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3p** (41.4 mg, 60%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 184–186℃. IR (neat, cm^{-1}): 1728.3, 1443.8, 1387.1, 1211.3, 1165.6, 1116.2, 1002.4, 780.0, 698.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.8 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.68 – 7.62 (m, 2H), 7.58 – 7.43 (m, 4H), 4.00 (s, 3H), 3.33 (t, J = 11.6 Hz, 1H), 2.21 – 1.80 (m, 7H), 1.56 – 1.37 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.67, 159.01, 143.11, 139.07, 135.77, 132.91, 130.14, 129.74, 128.67, 128.63, 128.31, 127.44, 127.23, 124.85, 52.63, 31.74, 27.50, 26.18. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{24}NO_2$: 346.1807; found: 346.1807.



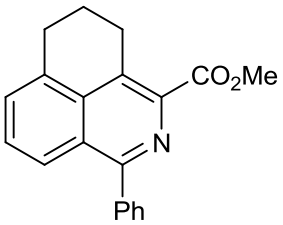
3q

Methyl 4-benzyl-1-phenylisoquinoline-3-carboxylate (3q): According to General Procedure, (*Z*)-methyl 2-isocyano-3,4-diphenylbut-2-enoate **1q** (55.4 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3q** (48.0 mg, 68%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 155–157℃. IR (neat, cm^{-1}): 1720.9, 1494.2, 1445.5, 1384.6, 1333.4, 1244.6, 1214.7, 1154.6, 1067.0, 755.3, 698.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, *J* = 8.0 Hz, 2H), 7.75 – 7.63 (m, 3H), 7.59 – 7.47 (m, 4H), 7.30 – 7.14 (m, 5H), 4.76 (s, 2H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.02, 159.74, 142.27, 139.87, 138.89, 136.47, 130.66, 130.20, 129.62, 128.85, 128.53, 128.41, 128.34, 128.13, 127.57, 126.16, 125.20, 52.82, 33.86. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{24}H_{20}NO_2$: 354.1494; found: 354.1493.



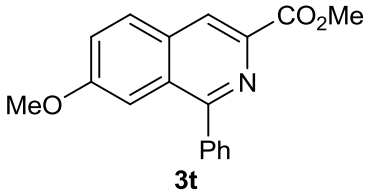
3r

Methyl 4-isopropyl-1-phenylisoquinoline-3-carboxylate (3r): According to General Procedure, (*Z*)-methyl 2-isocyano-4-methyl-3-phenylpent-2-enoate **1r** (45.8 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3r** (37.7 mg, 62%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 134–136℃. IR (neat, cm^{-1}): 1728.9, 1443.5, 1388.4, 1242.1, 1216.8, 1173.5, 1117.0, 1029.1, 960.5, 775.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.7 Hz, 1H), 8.09 (dd, *J* = 8.5, 0.6 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.67 – 7.62 (m, 2H), 7.58 – 7.44 (m, 4H), 4.00 (s, 3H), 3.82 – 3.70 (m, 1H), 1.61 (d, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.51, 159.14, 142.75, 139.01, 135.42, 134.19, 130.10, 129.77, 128.77, 128.64, 128.33, 127.55, 127.30, 124.93, 52.73, 29.65, 22.09. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{20}H_{20}NO_2$: 306.1494; found: 306.1493.



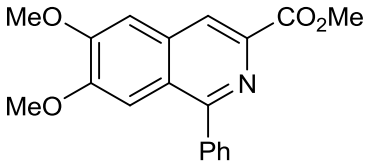
3s

Methyl 1-phenyl-5,6-dihydro-4H-benzo[de]isoquinoline-3-carboxylate (3s): According to General Procedure, (*Z*)-methyl 2-(3,4-dihydronaphthalen-1(2H)-ylidene)-2-isocyanoacetate **1s** (45.4 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3s** (39.4 mg, 65%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 150–152℃. IR (neat, cm^{-1}): 1710.1, 1383.7, 1328.6, 1213.4, 1115.6, 990.6, 766.4, 701.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 1H), 7.71 – 7.66 (m, 2H), 7.57 – 7.44 (m, 5H), 4.00 (s, 3H), 3.5 (t, *J* = 6.2 Hz, 2H), 3.14 (t, *J* = 6.2 Hz, 2H), 2.16 – 2.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.72, 158.32, 139.35, 138.25, 137.63, 133.99, 131.71, 130.14, 128.62, 128.57, 128.37, 128.24, 127.54, 125.67, 52.62, 30.58, 27.54, 22.70. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{20}H_{18}NO_2$: 304.1338; found: 304.1336.



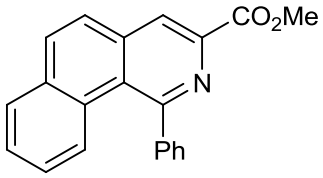
3t

Methyl 7-methoxy-1-phenylisoquinoline-3-carboxylate (3t): According to General Procedure, (*Z*)-methyl 2-isocyano-3-(4-methoxyphenyl)acrylate **1t** (43.4 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3t** (41.6 mg, 71%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 183–185℃. IR (neat, cm^{-1}): 1703.7, 1620.6, 1493.0, 1403.8, 1295.8, 1214.1, 1025.7, 1004.9, 710.9. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.95 – 7.90 (m, 1H), 7.75 – 7.70 (m, 2H), 7.56 – 7.48 (m, 3H), 7.44 – 7.39 (m, 2H), 4.03 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.71, 160.24, 159.47, 139.20, 131.93, 130.05, 129.87, 129.79, 128.82, 128.51, 123.39, 123.21, 105.84, 55.49, 52.75. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{18}H_{16}NO_3$: 294.1130; found: 294.1126.



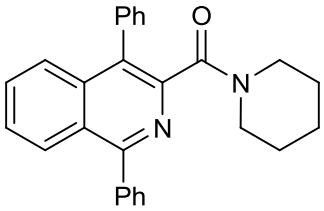
3u

Methyl 6,7-dimethoxy-1-phenylisoquinoline-3-carboxylate (3u): According to General Procedure, (*Z*)-methyl 3-(3,4-dimethoxyphenyl)-2-isocyanoacrylate **1u** (49.4 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3u** (43.3 mg, 67%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 184–186℃. IR (neat, cm^{-1}): 1705.5, 1508.4, 1422.3, 1277.7, 1258.1, 1142.2, 1009.7, 707.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.75 – 7.70 (m, 2H), 7.56 – 7.45 (m, 3H), 7.39 (s, 1H), 7.26 (s, 1H), 4.07 (s, 3H), 4.02 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.79, 158.59, 153.10, 151.78, 139.96, 139.35, 133.37, 129.84, 128.78, 128.52, 124.48, 122.13, 106.29, 105.93, 56.25, 56.03, 52.75. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{19}H_{18}NO_4$: 324.1236; found: 324.1235.



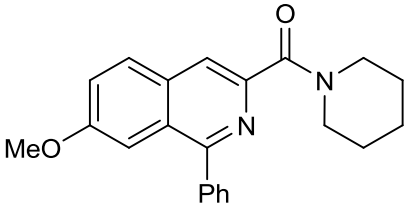
3v

Methyl 1-phenylbenzo[h]isoquinoline-3-carboxylate (3v): According to General Procedure, (*Z*)-methyl 2-isocyano-3-(naphthalen-2-yl)acrylate **1v** (47.4 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3v** (34.4 mg, 55%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 206–208℃. IR (neat, cm^{-1}): 1707.9, 1442.2, 1348.5, 1250.7, 1218.6, 1147.8, 990.9, 747.9, 697.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.99 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.62 – 7.45 (m, 6H), 7.25 – 7.18 (m, 1H), 4.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.28, 159.40, 143.38, 141.65, 138.32, 134.33, 132.73, 129.31, 129.21, 129.12, 128.75, 128.72, 128.22, 127.69, 126.34, 126.20, 125.63, 123.01, 52.91. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{21}H_{16}NO_2$: 314.1181; found: 314.1178.



3w

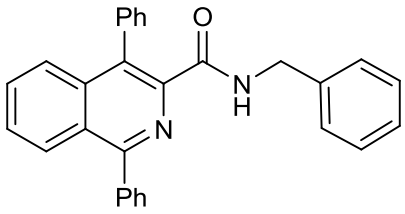
(1,4-Diphenylisoquinolin-3-yl)(piperidin-1-yl)methanone (3w): According to General Procedure, 2-isocyano-3,3-diphenyl-1-(piperidin-1-yl)prop-2-en-1-one **1w** (63.2 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3w** (65.0 mg, 83%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 227–229℃. IR (neat, cm^{-1}): 1726.7, 1630.8, 1444.5, 1230.4, 1194.8, 1157.8, 986.2, 698.2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.71 (m, 2H), 7.66 – 7.41 (m, 10H), 3.50 (t, *J* = 5.5 Hz, 2H), 3.11 (t, *J* = 5.5 Hz, 2H), 1.52 – 1.40 (m, 2H), 1.40 – 1.30 (m, 2H), 1.20 – 1.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.51, 160.43, 146.26, 139.08, 136.06, 134.93, 130.78, 130.44, 130.21, 128.74, 128.43, 128.36, 128.35, 128.23, 127.73, 127.33, 126.40, 125.90, 47.54, 42.10, 25.82, 25.15, 24.33. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{27}H_{25}N_2O$: 393.1967; found: 393.1967.



3x

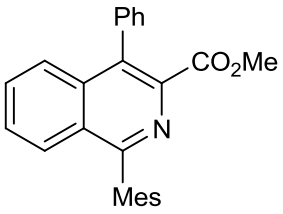
(7-Methoxy-1-phenylisoquinolin-3-yl)(piperidin-1-yl)methanone (3x): According to General Procedure, (*Z*)-2-isocyano-3-(4-methoxyphenyl)-1-(piperidin-1-yl)prop-2-en-1-one **1x** (54.0 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3x** (53.3 mg, 77%) as a white solid after purification on silica gel (hexane: EtOAc = 5:1). m.p.: 188–190℃. IR (neat, cm^{-1}): 1619.4, 1492.5, 1443.3, 1406.0, 1292.5, 1292.5, 1213.6, 1027.2, 907.7, 727.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.57 – 7.46 (m, 3H), 7.43 – 7.34 (m, 2H), 3.82 (s, 3H), 3.77 (t, *J* = 4.6 Hz, 2H), 3.61 (t, *J* = 4.9 Hz, 2H), 1.75 – 1.57 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.26, 159.20, 157.71, 145.73, 139.46, 132.69, 129.80, 129.40, 128.71, 128.48,

127.92, 123.22, 120.30, 105.32, 55.43, 48.64, 43.62, 26.58, 25.63, 24.69. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{23}N_2O_2$: 347.1760; found: 347.1757.



3y

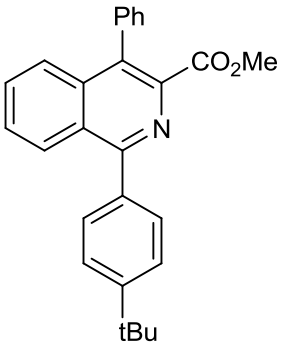
N-Benzyl-1,4-diphenylisoquinoline-3-carboxamide (3y): According to General Procedure, N-benzyl-2-isocyano-3,3-diphenylacrylamide **1y** (67.6 mg, 0.2 mmol), diphenyliodonium tetrafluoroborate **2a** (147.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **3y** (53.8 mg, 65%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 200–202℃. IR (neat, cm^{-1}): 1670.9, 1497.5, 1386.1, 1248.8, 1177.9, 979.2, 908.1, 696.3. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (t, *J* = 5.7 Hz, 1H), 8.20 – 8.13 (m, 1H), 7.76 – 7.71 (m, 2H), 7.64 – 7.46 (m, 9H), 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 4.58 (d, *J* = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.08, 158.67, 139.05, 138.94, 138.82, 137.96, 137.42, 133.68, 130.36, 130.04, 129.26, 128.93, 128.51, 128.43, 128.22, 128.06, 127.67, 127.41, 127.36, 127.35, 127.24, 127.13, 43.16. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{29}H_{23}N_2O$: 415.1810; found: 415.1808.



4a

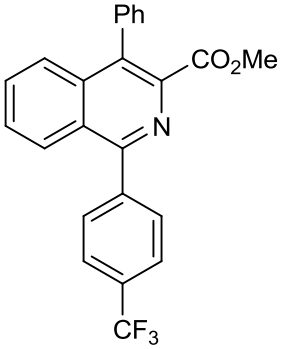
Methyl 1-mesityl-4-phenylisoquinoline-3-carboxylate (4a): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), dimesityliodonium tetrafluoroborate **2b** (180.8 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4a** (57.1 mg, 75%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 204–206℃. IR (neat, cm^{-1}): 1729.9, 1444.4, 1377.8, 1321.7, 1221.5, 1187.2, 1107.2, 1005.2, 851.6, 779.5. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 1H), 7.65 – 7.60 (m,

2H), 7.55 – 7.42 (m, 6H), 7.00 (s, 2H), 3.70 (s, 3H), 2.37 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.78, 161.09, 141.90, 138.00, 136.47, 136.11, 135.83, 134.94, 132.43, 130.70, 129.94, 128.48, 128.42, 128.28, 128.07, 128.03, 126.97, 126.71, 52.43, 21.22, 20.04. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{26}H_{24}NO_2$: 382.1807; found: 382.1808.



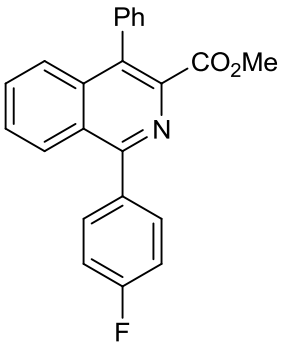
4b

Methyl 1-(4-tert-butylphenyl)-4-phenylisoquinoline-3-carboxylate (4b): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), bis(4-tert-butylphenyl)iodonium tetrafluoroborate **2c** (192.0 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4b** (63.2 mg, 80%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 173–175℃. IR (neat, cm^{-1}): 1734.9, 1721.8, 1502.7, 1386.7, 1216.3, 1188.4, 1003.6, 774.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.21 (m, 1H), 7.74 – 7.67 (m, 3H), 7.66 – 7.45 (m, 7H), 7.43 – 7.38 (m, 2H), 3.69 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.72, 160.36, 152.00, 141.43, 136.52, 136.19, 136.10, 132.47, 130.47, 129.94, 129.88, 128.28, 128.16, 127.98, 127.92, 127.21, 126.69, 125.46, 52.37, 34.80, 31.39. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{27}H_{26}NO_2$: 396.1964; found: 396.1964.



4c

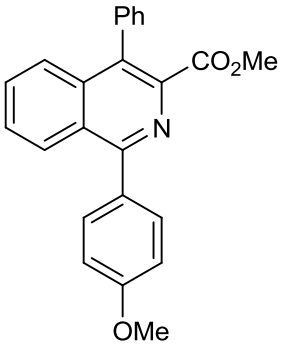
Methyl 4-phenyl-1-(4-(trifluoromethyl)phenyl)isoquinoline-3-carboxylate (4c): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), bis(4-(trifluoromethyl)phenyl)iodonium tetrafluoroborate **2d** (201.6 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4c** (73.3 mg, 90%) as a white solid after purification on Silica gel (hexane: EtOAc = 20:1). m.p.: 181–183℃. IR (neat, cm^{-1}): 1716.2, 1325.8, 1225.6, 1162.9, 1106.9, 1065.8, 853.7, 717.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 1H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.76 – 7.61 (m, 3H), 7.56 – 7.47 (m, 3H), 7.43 – 7.38 (m, 2H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.47, 158.60, 142.44 (q, *J* = 1.0 Hz), 141.52, 136.56, 135.80, 133.42, 130.97 (q, *J* = 32.3 Hz), 130.82, 130.60, 129.77, 128.70, 128.35, 128.18, 127.07, 126.98, 125.46 (q, *J* = 3.8 Hz), 124.12 (q, *J* = 272.1 Hz), 52.46. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.59 (s, 1F). HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{24}H_{17}F_3NO_2$: 408.1211; found: 408.1206.



4d

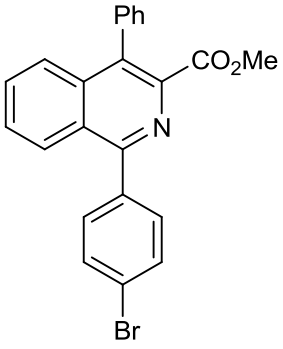
Methyl 1-(4-fluorophenyl)-4-phenylisoquinoline-3-carboxylate (4d): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), bis(4-fluorophenyl)iodonium tetrafluoroborate **2e** (161.6 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4d** (58.5 mg, 82%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 191–193℃. IR (neat, cm^{-1}): 1717.7, 1604.5, 1512.4, 1329.2, 1219.6, 1115.8, 1004.6, 849.4, 772.8. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 1H), 7.79 – 7.69 (m, 3H), 7.68 – 7.59 (m, 2H), 7.55 – 7.46 (m, 3H), 7.42 – 7.38 (m, 2H), 7.28 – 7.21 (m, 2H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.61, 163.35 (d, *J* = 248.3 Hz), 159.11, 141.41, 136.57, 135.99, 135.01 (d, *J* = 3.3 Hz), 132.87, 132.09 (d, *J* = 8.4 Hz), 130.63, 129.82, 128.45, 128.31, 128.08, 127.41, 127.13, 126.85, 115.50 (d, *J* = 21.6 Hz), 52.42.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.57 (s, 1F). HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{17}FNO_2$: 358.1243; found: 358.1239.



4e

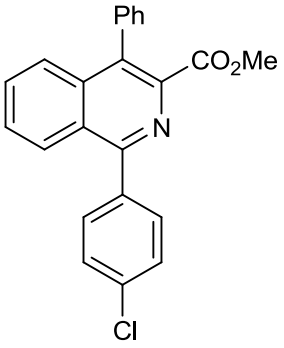
Methyl 1-(4-methoxyphenyl)-4-phenylisoquinoline-3-carboxylate (4e): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), bis(4-methoxyphenyl)iodonium tetrafluoroborate **2f** (171.2 mg, 0.4 mmol), *fac*-$Ir(ppy)_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4e** (47.9 mg, 65%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 182–184℃. IR (neat, cm^{-1}): 1729.0, 1607.5, 1514.6, 1386.0, 1335.3, 1252.4, 1229.4, 1166.8, 1112.8, 1029.7, 844.3, 771.4. ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 – 8.19 (m, 1H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.70 – 7.57 (m, 3H), 7.55 – 7.45 (m, 3H), 7.43 – 7.37 (m, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 3.90 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.75, 160.36, 159.91, 141.39, 136.58, 136.19, 132.29, 131.66, 131.47, 130.44, 129.88, 128.28, 128.17, 127.97, 127.79, 127.19, 126.71, 113.94, 55.46, 52.36. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{24}H_{20}NO_3$: 370.1443; found: 370.1441.



4f

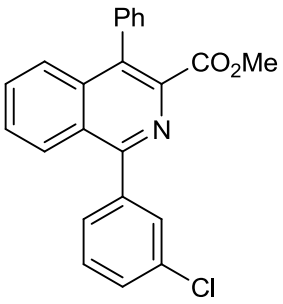
Methyl 1-(4-bromophenyl)-4-phenylisoquinoline-3-carboxylate (4f): According to General

Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), bis(4-bromophenyl)iodonium tetrafluoroborate **2g** (209.5 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4f** (63.4 mg, 76%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 178–180℃. IR (neat, cm^{-1}): 1714.8, 1440.9, 1328.6, 1222.9, 1116.8, 1070.2, 1004.3, 974.2, 766.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 1H), 7.73 – 7.59 (m, 7H), 7.55 – 7.46 (m, 3H), 7.41 – 7.37 (m, 2H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.56, 158.95, 141.46, 137.80, 136.57, 135.92, 133.06, 131.86, 131.67, 130.71, 129.80, 128.54, 128.33, 128.12, 127.27, 126.99, 126.90, 123.45, 52.45. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{23}H_{17}BrNO_2$: 418.0443; found: 418.0436.



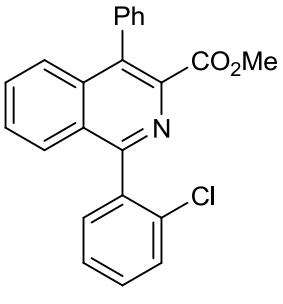
4g

Methyl 1-(4-chlorophenyl)-4-phenylisoquinoline-3-carboxylate (4g): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), bis(4-chlorophenyl)iodonium tetrafluoroborate **2h** (174.4 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4g** (64.9 mg, 87%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 183–185℃. IR (neat, cm^{-1}): 1716.5, 1440.8, 1329.1, 1222.5, 1117.1, 1088.6, 1004.5, 844.3, 766.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.10 (m, 1H), 7.74 – 7.59 (m, 5H), 7.55 – 7.46 (m, 5H), 7.42 – 7.37 (m, 2H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.57, 158.92, 141.46, 137.35, 136.57, 135.93, 135.18, 133.04, 131.59, 130.69, 129.81, 128.72, 128.53, 128.33, 128.11, 127.29, 127.03, 126.90, 52.44. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{23}H_{17}ClNO_2$: 374.0948; found: 374.0944.



4h

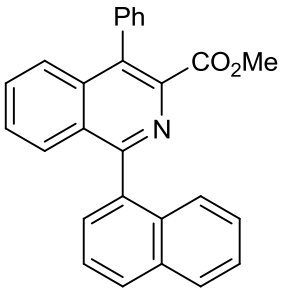
Methyl 1-(3-chlorophenyl)-4-phenylisoquinoline-3-carboxylate (4h): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), bis(3-chlorophenyl)iodonium tetrafluoroborate **2i** (174.4 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4h** (55.2 mg, 74%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 136–138℃. IR (neat, cm^{-1}): 1723.3, 1567.8, 1372.9, 1332.0, 1229.0, 1188.4, 1115.7, 888.8, 757.5, 699.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 1H), 7.78 – 7.75 (m, 1H), 7.74 – 7.60 (m, 4H), 7.56 – 7.45 (m, 5H), 7.43 – 7.38 (m, 2H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.51, 158.63, 141.41, 140.63, 136.55, 135.89, 134.55, 133.27, 130.76, 130.28, 129.79, 129.70, 129.07, 128.63, 128.41, 128.33, 128.13, 127.26, 127.03, 126.90, 52.47. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{23}H_{17}ClNO_2$: 374.0948; found: 374.0944.



4i

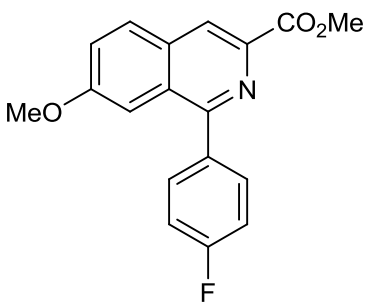
Methyl 1-(2-chlorophenyl)-4-phenylisoquinoline-3-carboxylate (4i): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), bis(2-chlorophenyl)iodonium tetrafluoroborate **2j** (174.4 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4i** (52.2 mg, 70%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 166–168℃. IR (neat, cm^{-1}): 1724.0, 1429.9, 1385.4, 1332.1, 1227.7, 1164.6, 1005.5, 917.4, 760.6. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73

– 7.68 (m, 2H), 7.68 – 7.62 (m, 1H), 7.61 – 7.37 (m, 10H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.49, 158.22, 141.37, 137.81, 135.98, 135.96, 133.73, 133.58, 131.69, 130.78, 130.18, 129.92, 129.76, 129.72, 128.56, 128.30, 128.10, 127.68, 127.43, 127.02, 126.74, 52.52. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{23}H_{17}ClNO_2$: 374.0948; found: 374.0943.



4j

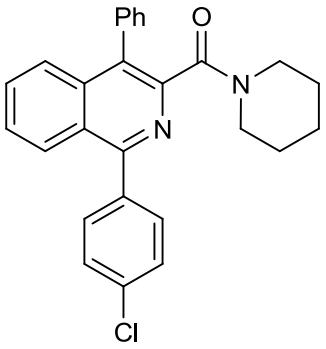
Methyl 1-(naphthalen-1-yl)-4-phenylisoquinoline-3-carboxylate (4j): According to General Procedure, methyl 2-isocyano-3,3-diphenylacrylate **1a** (52.6 mg, 0.2 mmol), dinaphthalen-1-yliodonium tetrafluoroborate **2k** (187.2 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4j** (52.1 mg, 67%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 204–206℃. IR (neat, cm^{-1}): 1724.5, 1443.1, 1324.5, 1227.4, 1163.6, 1118.6, 967.5, 768.3, 697.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.69 – 7.60 (m, 4H), 7.59 – 7.42 (m, 8H), 7.39 – 7.33 (m, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.63, 159.92, 141.64, 136.29, 136.03, 136.01, 133.70, 133.11, 132.37, 130.75, 129.89, 129.84, 129.15, 128.69, 128.35, 128.30, 128.25, 128.09, 127.95, 126.58, 126.44, 126.03, 126.01, 125.26, 52.47. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{27}H_{20}NO_2$: 390.1494; found: 390.1493.



4k

Methyl 1-(4-fluorophenyl)-7-methoxyisoquinoline-3-carboxylate (4k): According to General

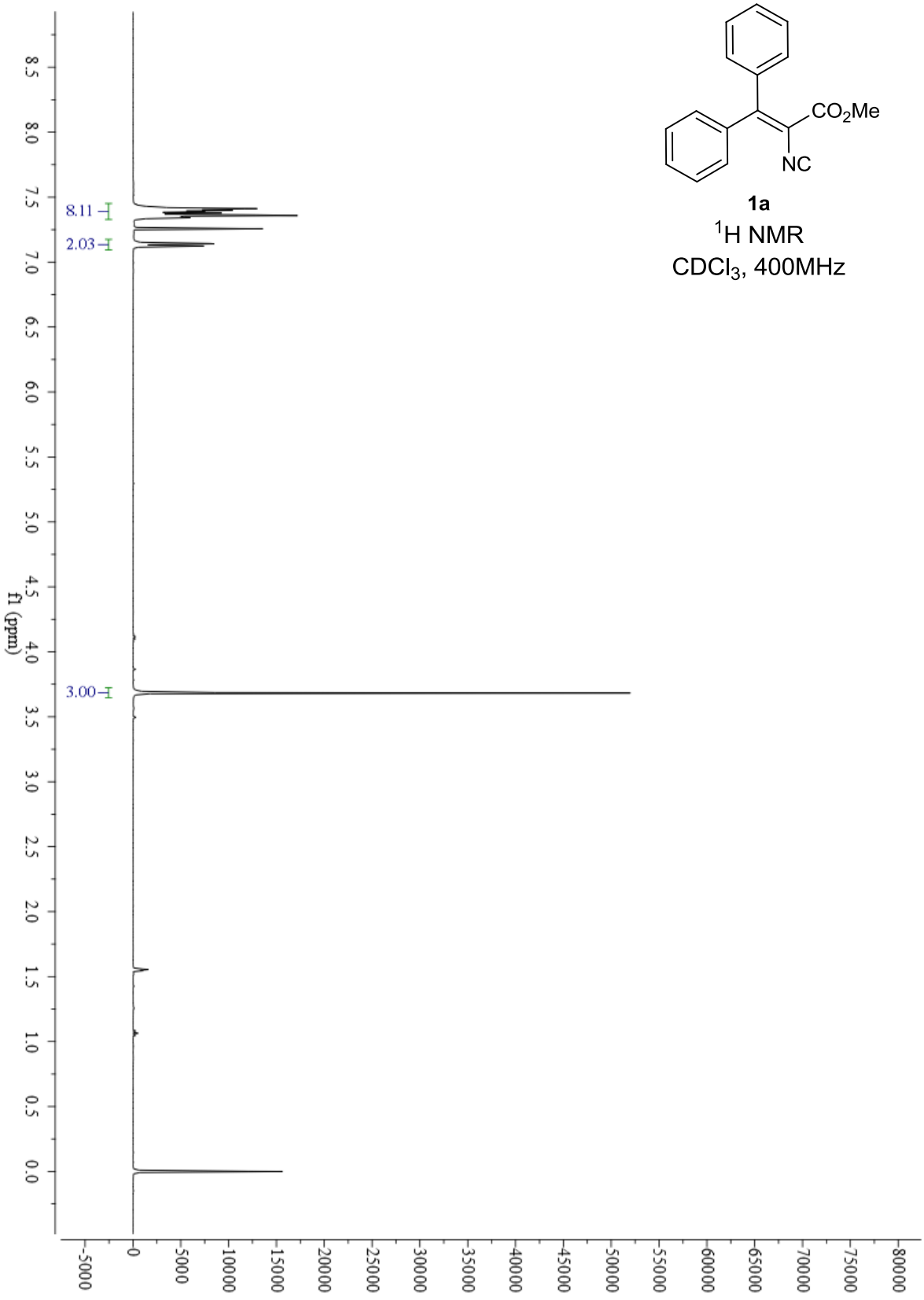
Procedure, (*Z*)-methyl 2-isocyano-3-(4-methoxyphenyl)acrylate **1t** (43.4 mg, 0.2 mmol), bis(4-fluorophenyl)iodonium tetrafluoroborate **2e** (161.6 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4k** (44.1 mg, 71%) as a white solid after purification on silica gel (hexane: EtOAc = 20:1). m.p.: 172–174℃. IR (neat, cm^{-1}): 1714.2, 1617.8, 1496.5, 1403.1, 1206.4, 1153.2, 1003.5, 909.4, 828.4, 776.4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.72 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.43 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.35 (d, *J* = 2.2 Hz, 1H), 7.23 (t, *J* = 8.7 Hz, 2H), 4.03 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.58, 163.23 (d, *J* = 247.7 Hz), 160.36, 158.35, 139.28, 135.29 (d, *J* = 3.3 Hz), 131.97, 131.73 (d, *J* = 8.3 Hz), 130.16, 129.74, 123.48, 123.31, 115.56 (d, *J* = 21.6 Hz), 105.55, 55.51, 52.77. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{18}H_{15}FNO_3$: 312.1036; found: 312.1031.

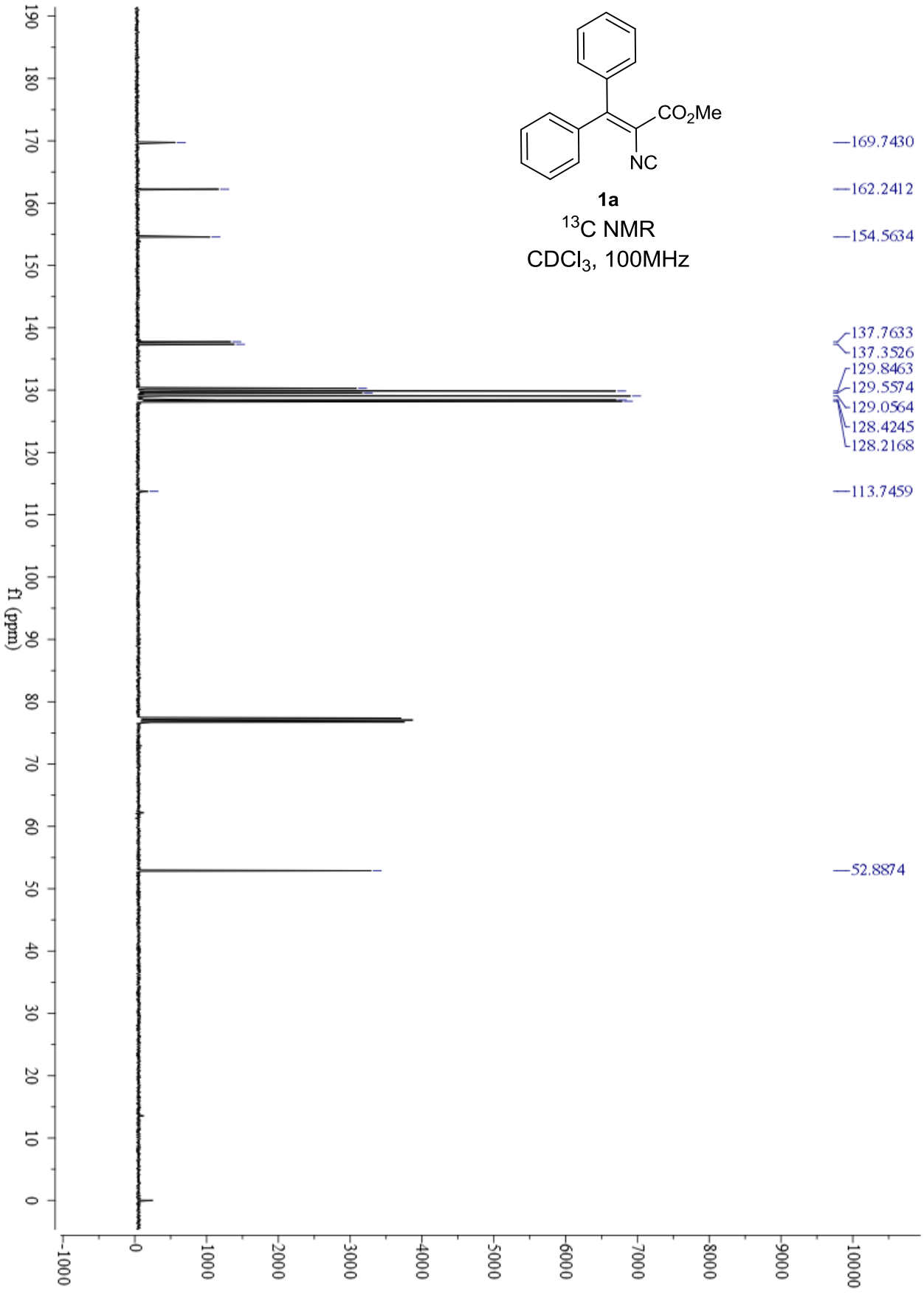


4l

(1-(4-Chlorophenyl)-4-phenylisoquinolin-3-yl)(piperidin-1-yl)methanone (4l): According to General Procedure, 2-isocyano-3,3-diphenyl-1-(piperidin-1-yl)prop-2-en-1-one **1w** (63.2 mg, 0.2 mmol), bis(4-chlorophenyl)iodonium tetrafluoroborate **2h** (174.4 mg, 0.4 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 0.002 mmol) and Na_2CO_3 (21.2 mg, 0.2 mmol) afforded **4l** (75.0 mg, 88%) as a white solid after purification on silica gel (hexane: EtOAc = 10:1). m.p.: 195–197℃. IR (neat, cm^{-1}): 1627.0, 1472.6, 1383.9, 1254.0, 1089.6, 1015.2, 907.4, 770.5, 726.0. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.60 – 7.45 (m, 8H), 3.51 (t, *J* = 5.5 Hz, 2H), 3.09 (t, *J* = 5.5 Hz, 2H), 1.50 – 1.41 (m, 2H), 1.40 – 1.32 (m, 2H), 1.18 – 1.09 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.40, 159.09, 146.33, 137.51, 136.10, 134.96, 134.76, 131.59, 130.74, 130.56, 128.66, 128.60, 128.40, 128.31, 127.54, 127.27, 126.24, 126.05, 47.53, 42.11, 25.81, 25.13, 24.30. HRMS (ESI) ([M+H]$^+$) Calcd. for $C_{27}H_{24}ClN_2O$: 427.1577; found: 427.1574.

9. NMR spectra for all compounds

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129.0564
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128.2168
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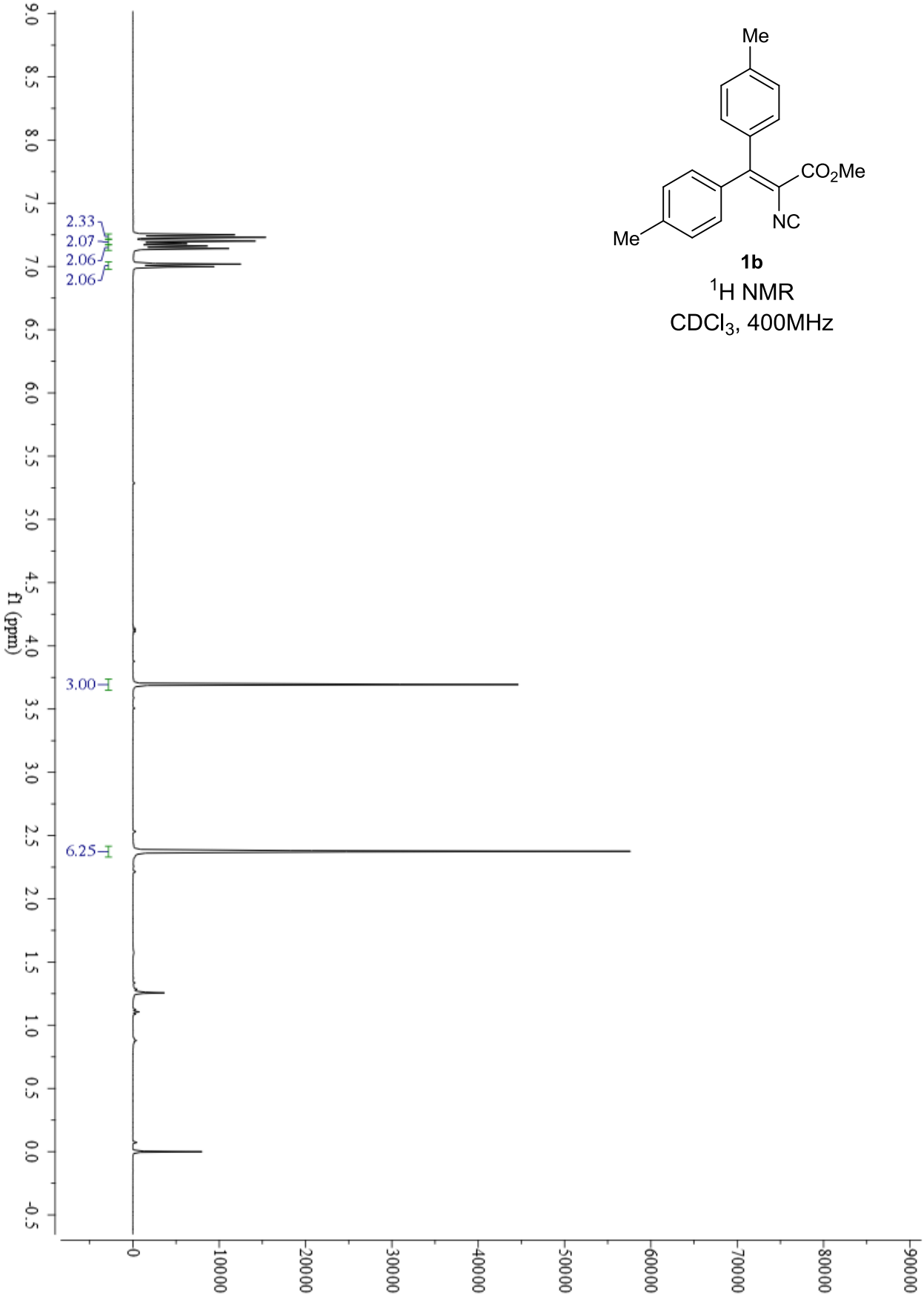
f1 (ppm)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CO2Me
NC
Me
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CDCl3, 400MHz
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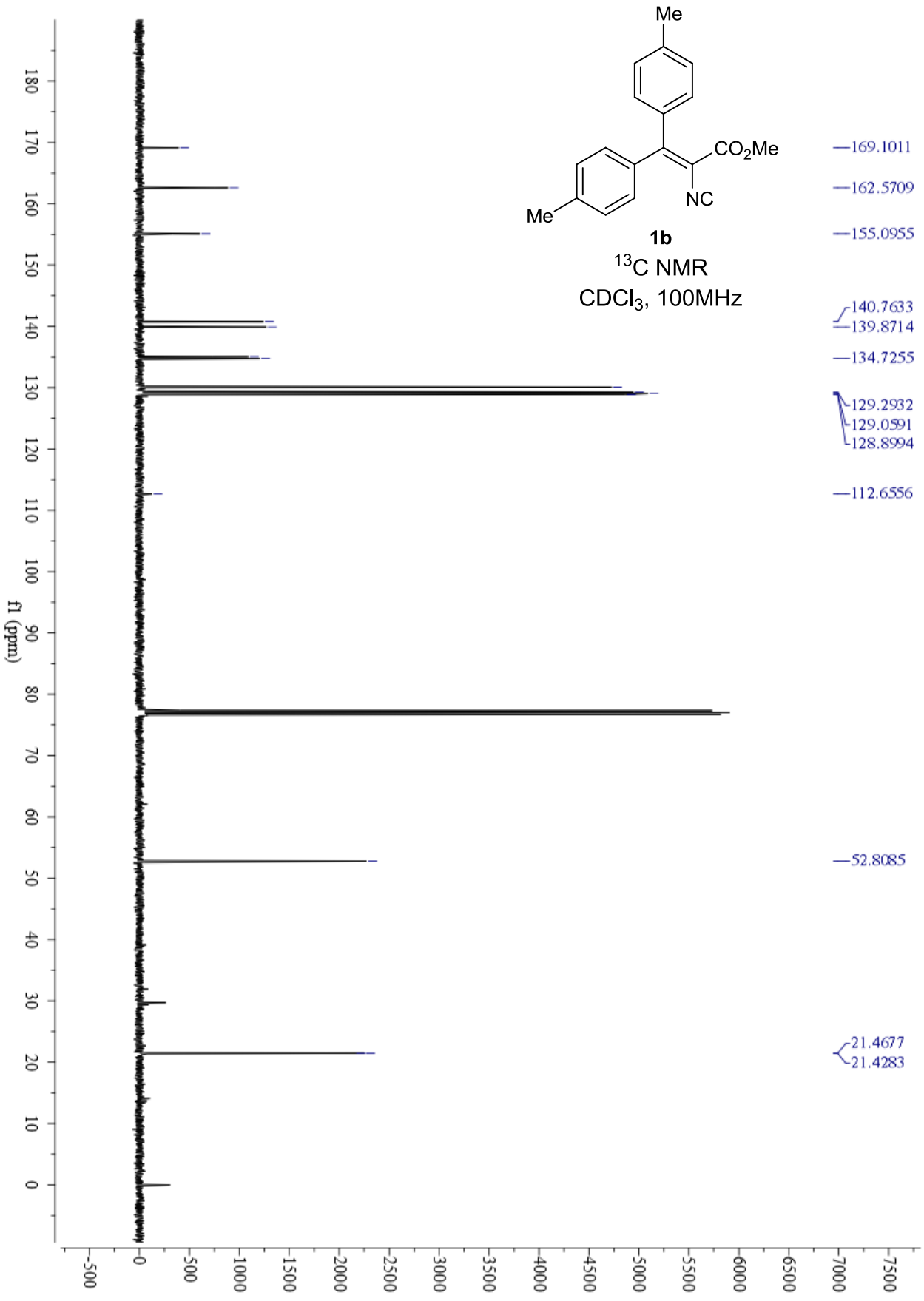
2.06
3.00
6.25
f1 (ppm)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Me
1b
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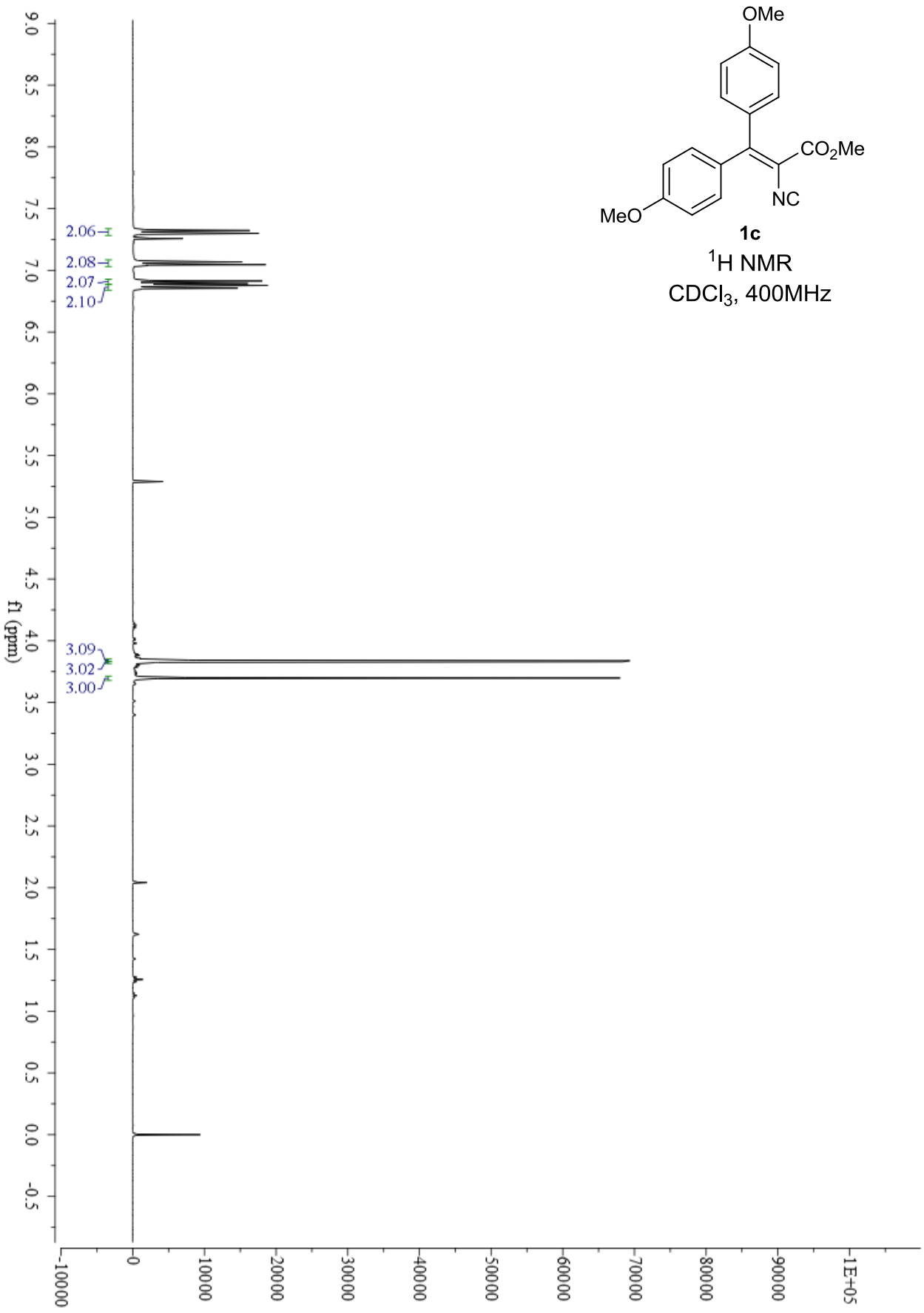
f1 (ppm)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1c
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CDCl3, 400MHz
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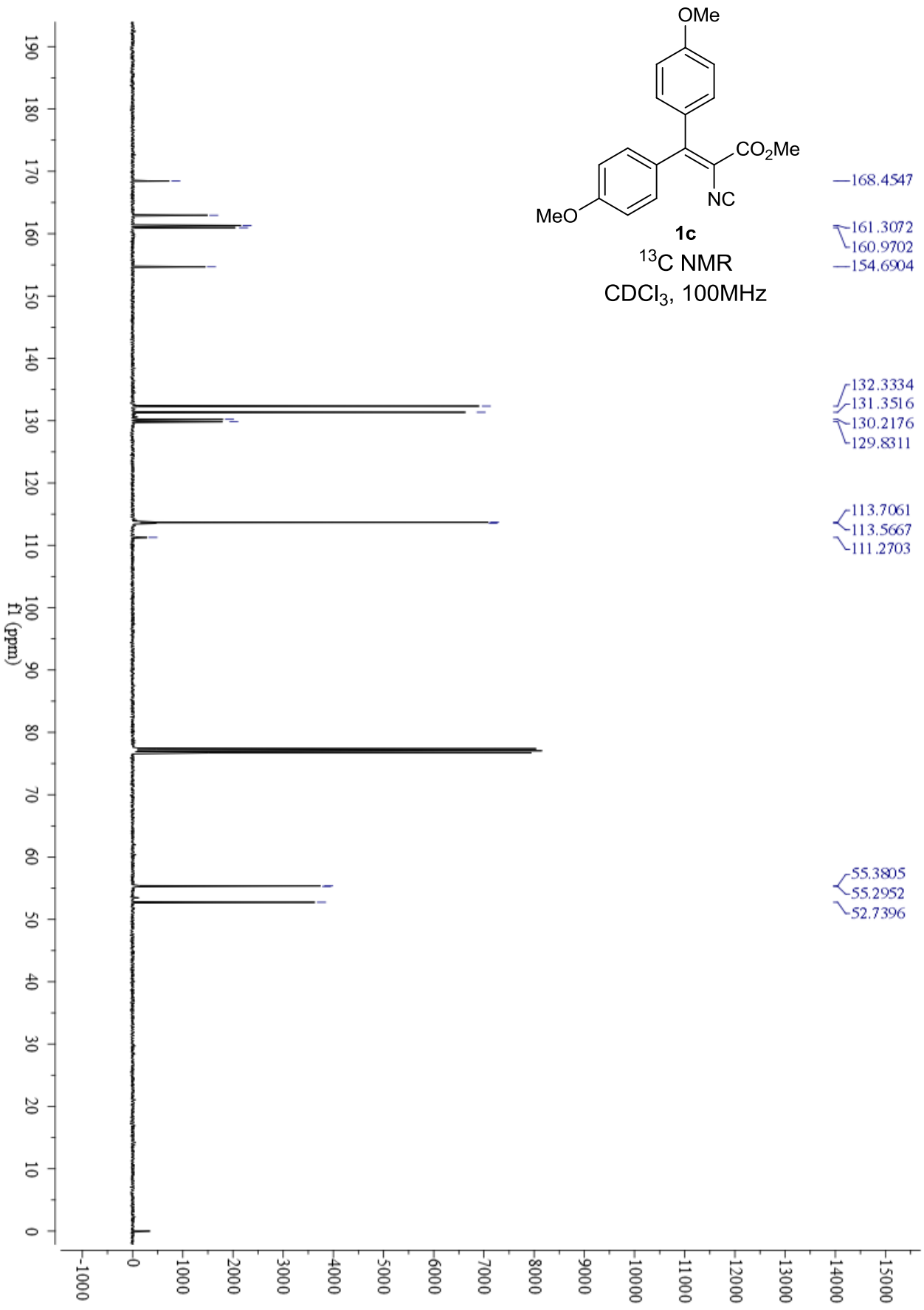
3.09
3.02
3.00
f1 (ppm)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MeO
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13C NMR
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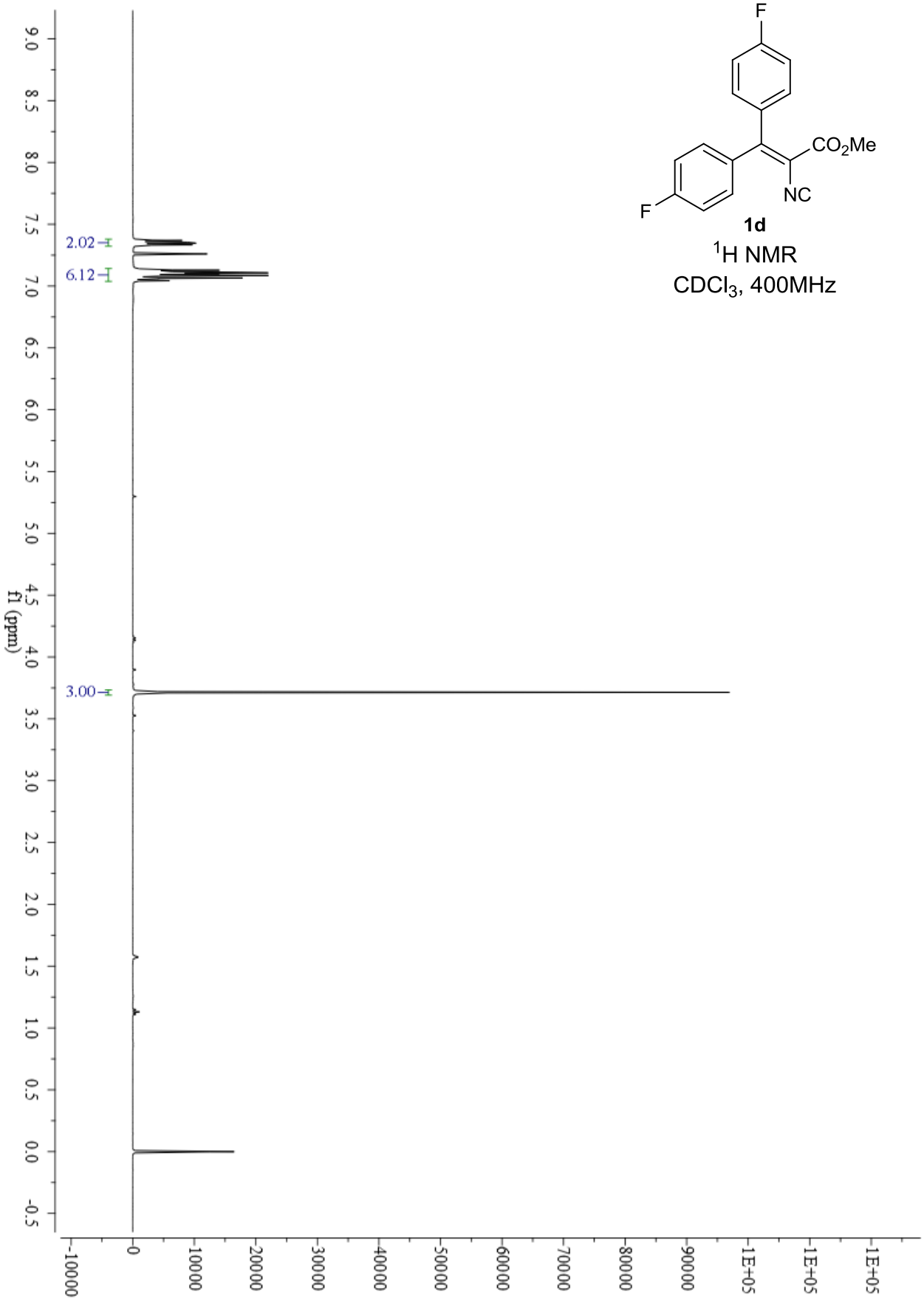
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1d
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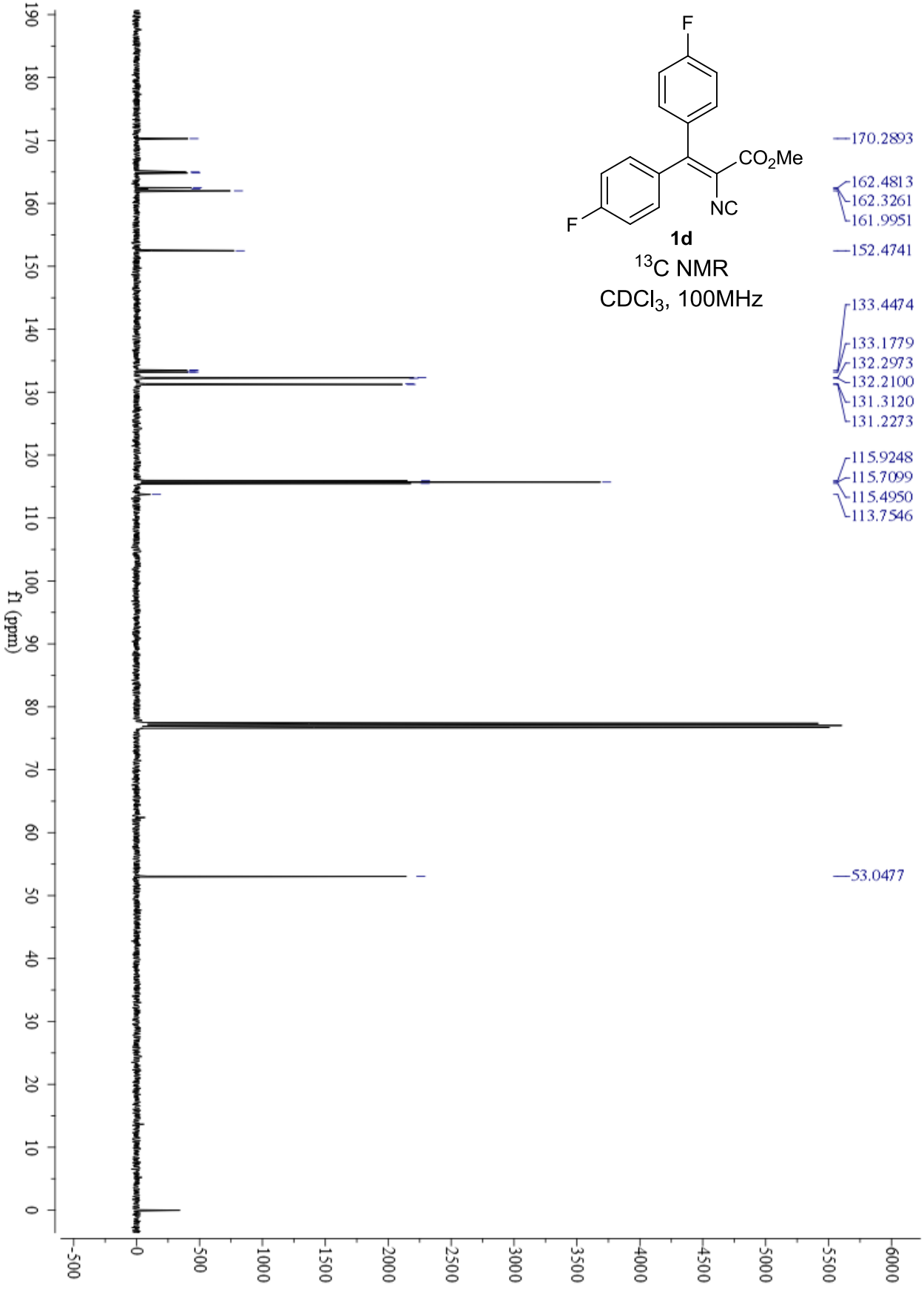
f1 (ppm)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F
1d
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133.4474
133.1779
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131.2273
115.9248
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115.4950
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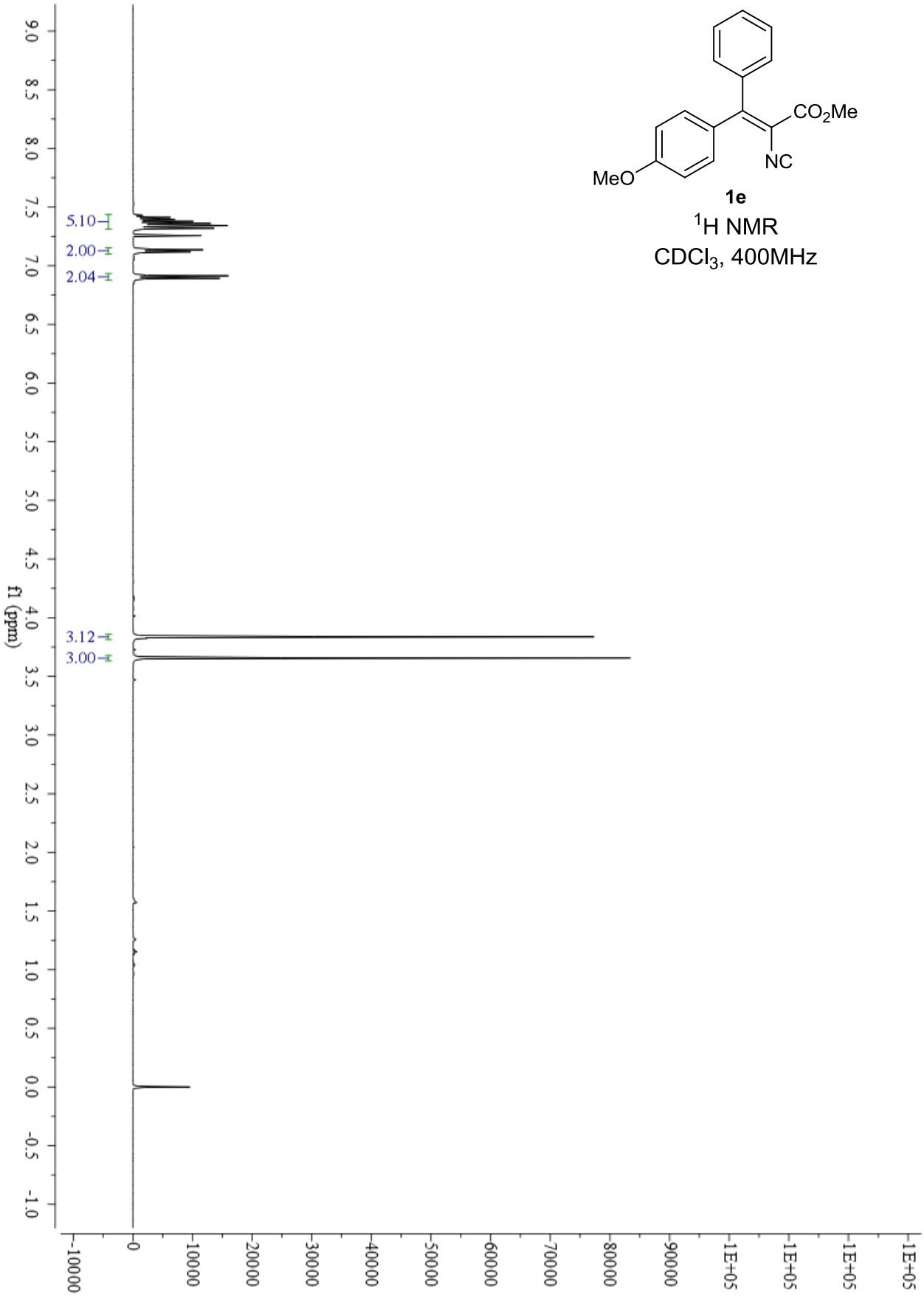
53.0477
f1 (ppm)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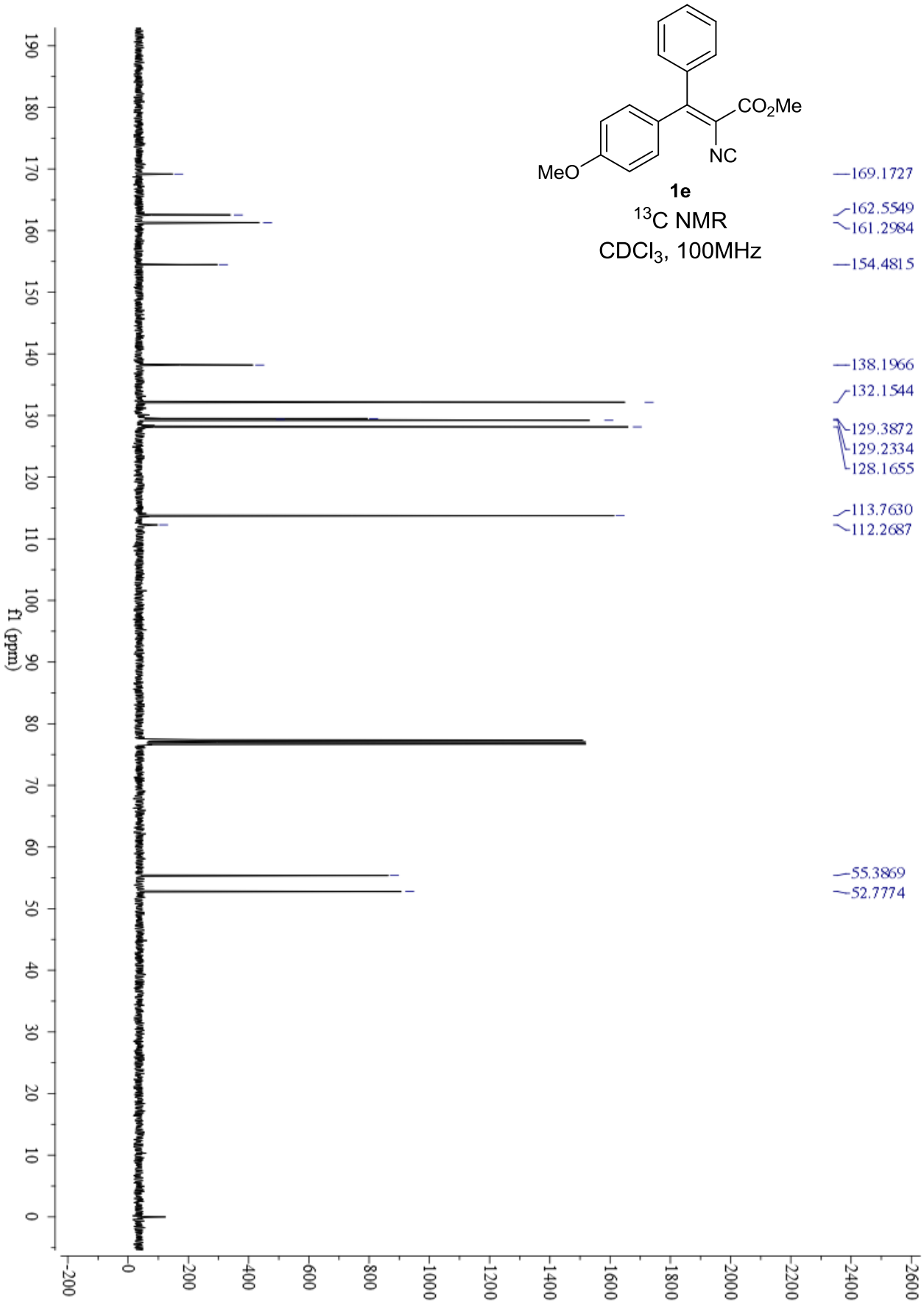
f1 (ppm)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MeO
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112.2687
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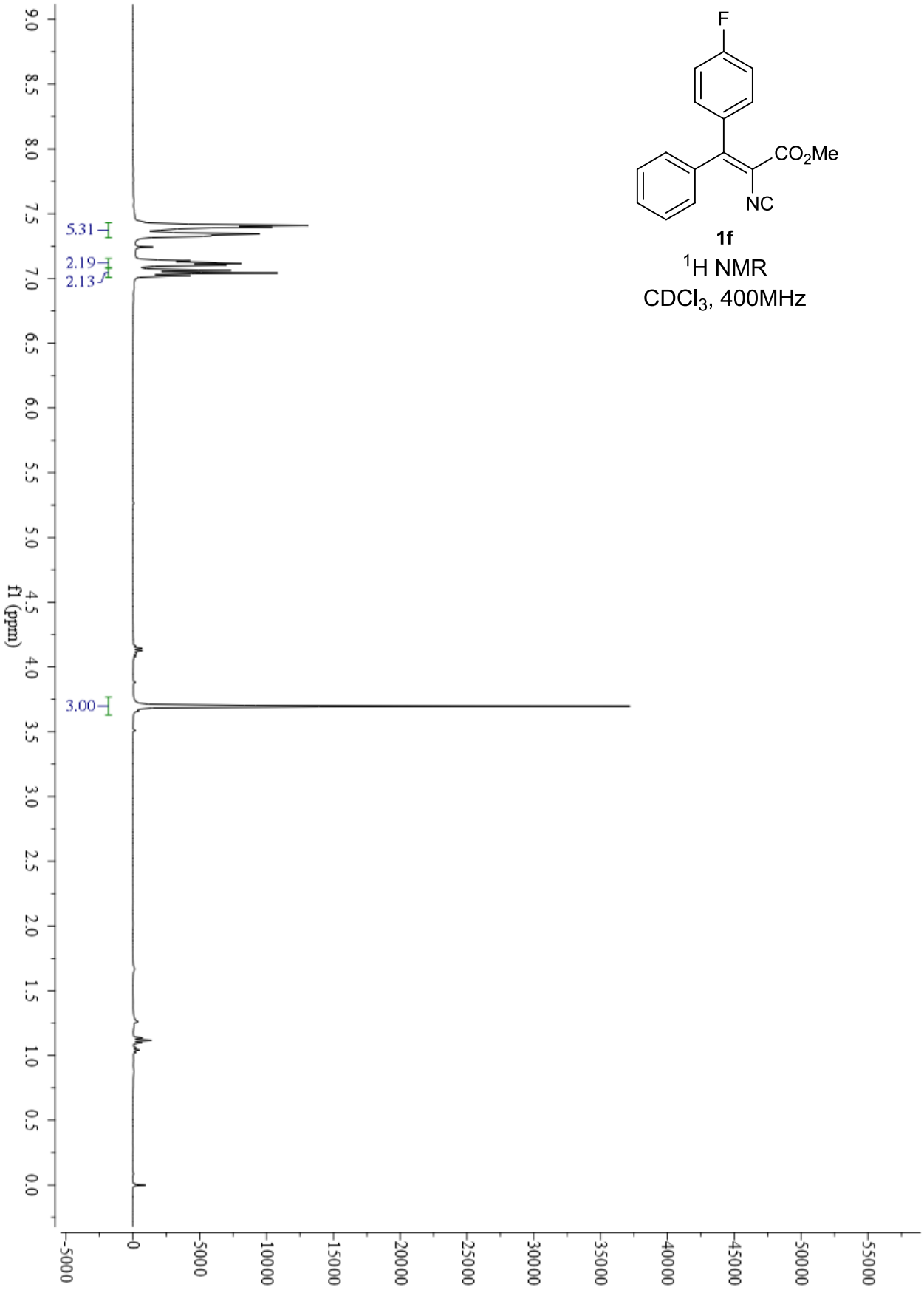
52.7774
f1 (ppm)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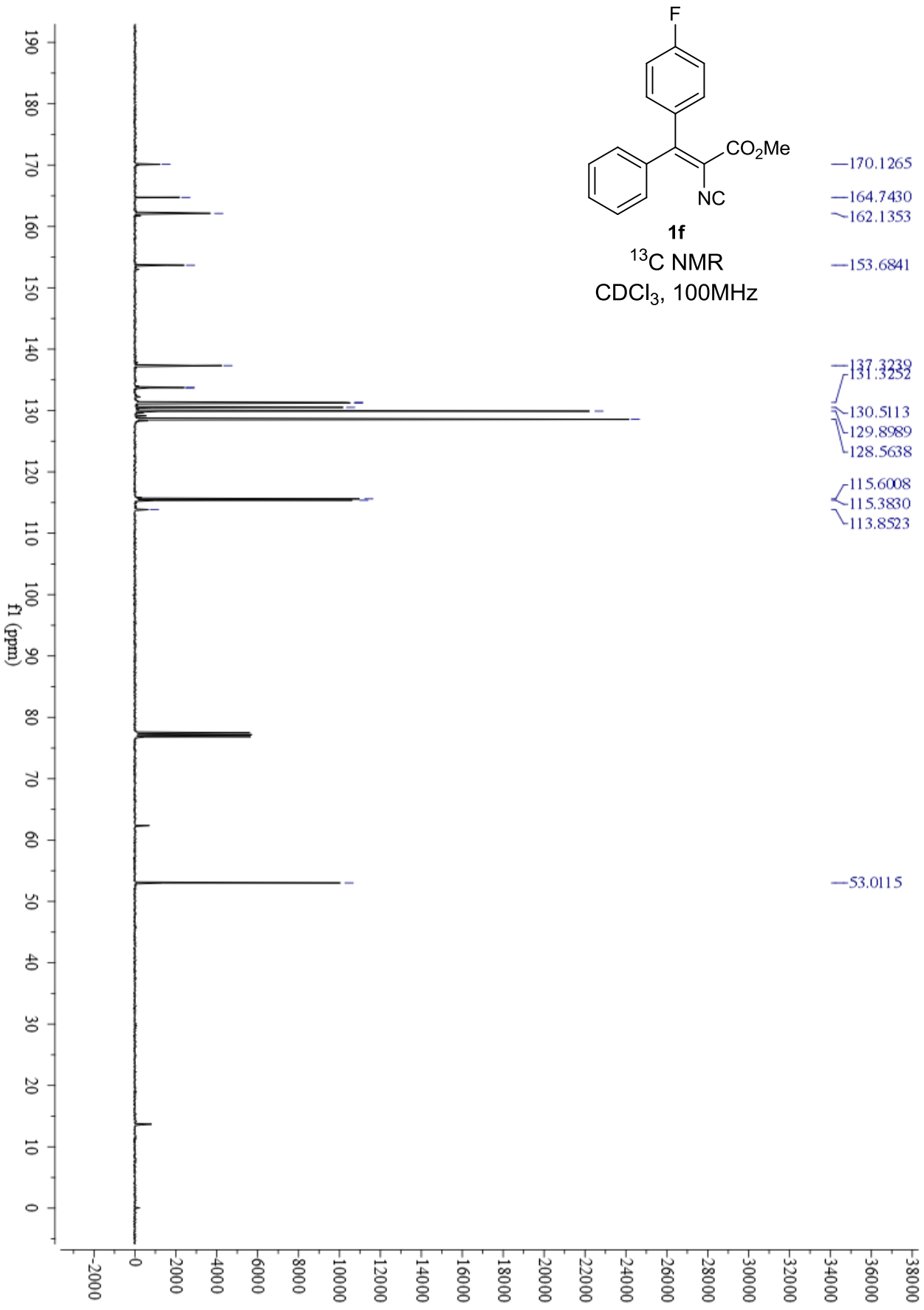
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CDCl3, 100MHz
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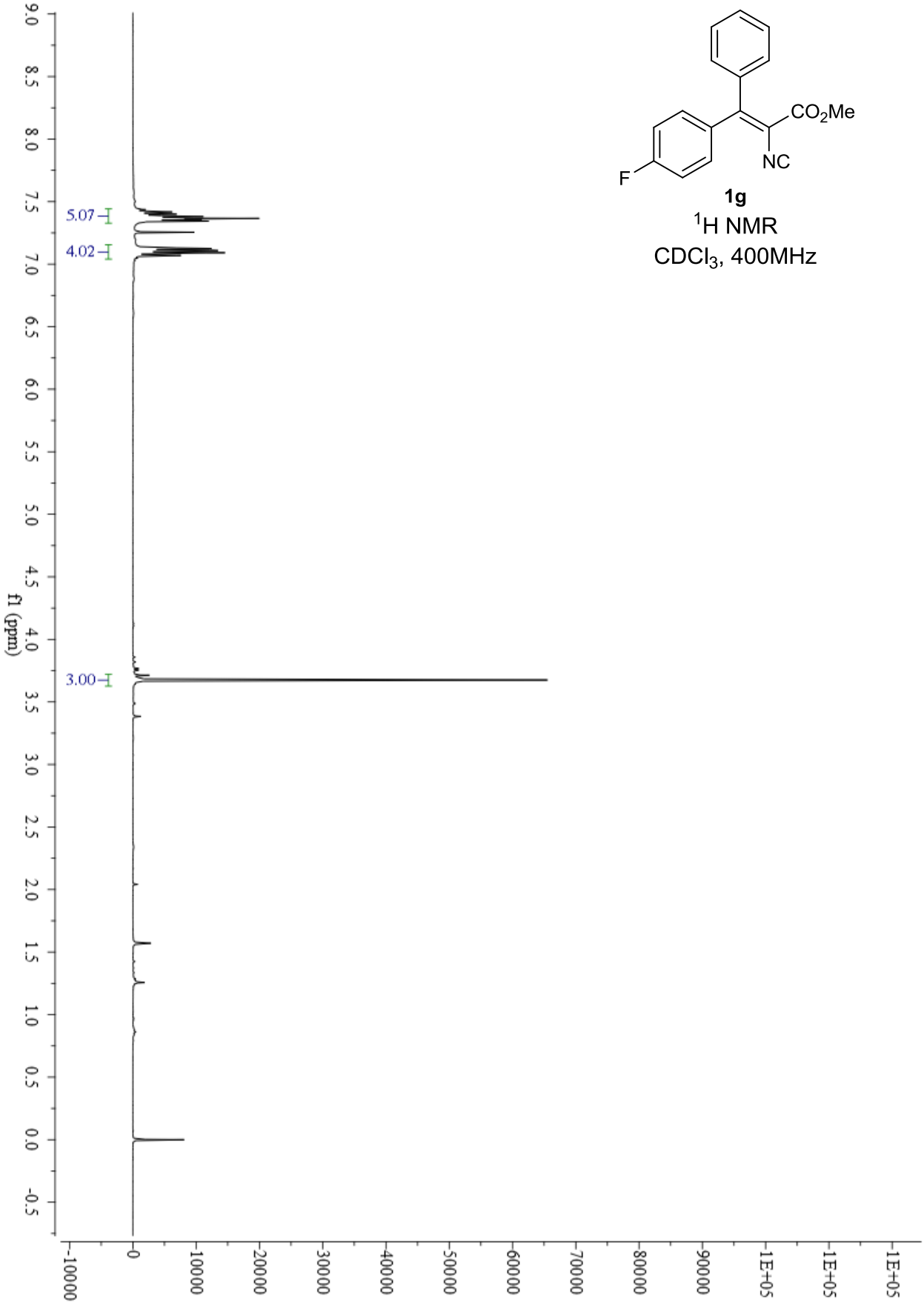
f1 (ppm)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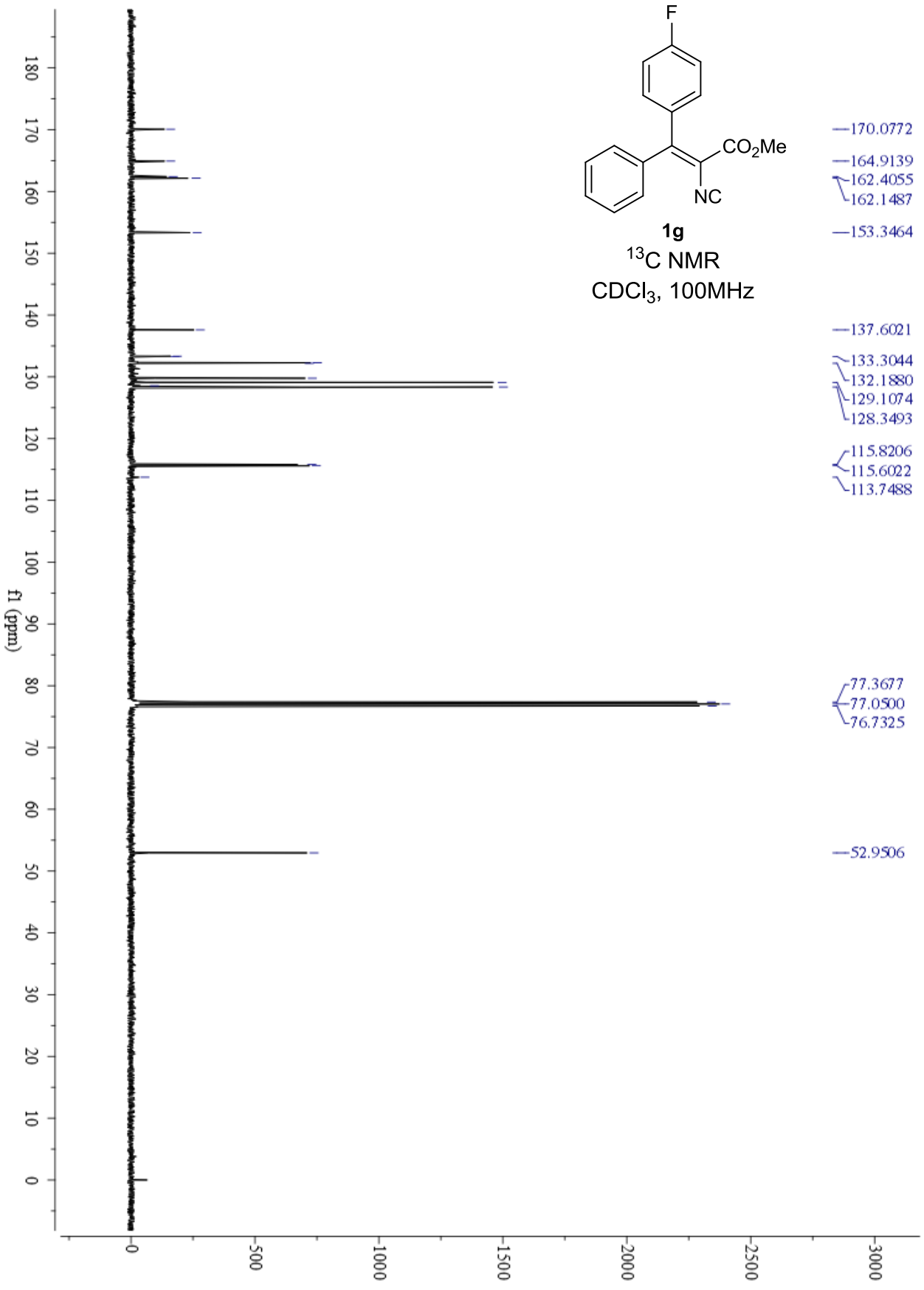
f1 (ppm)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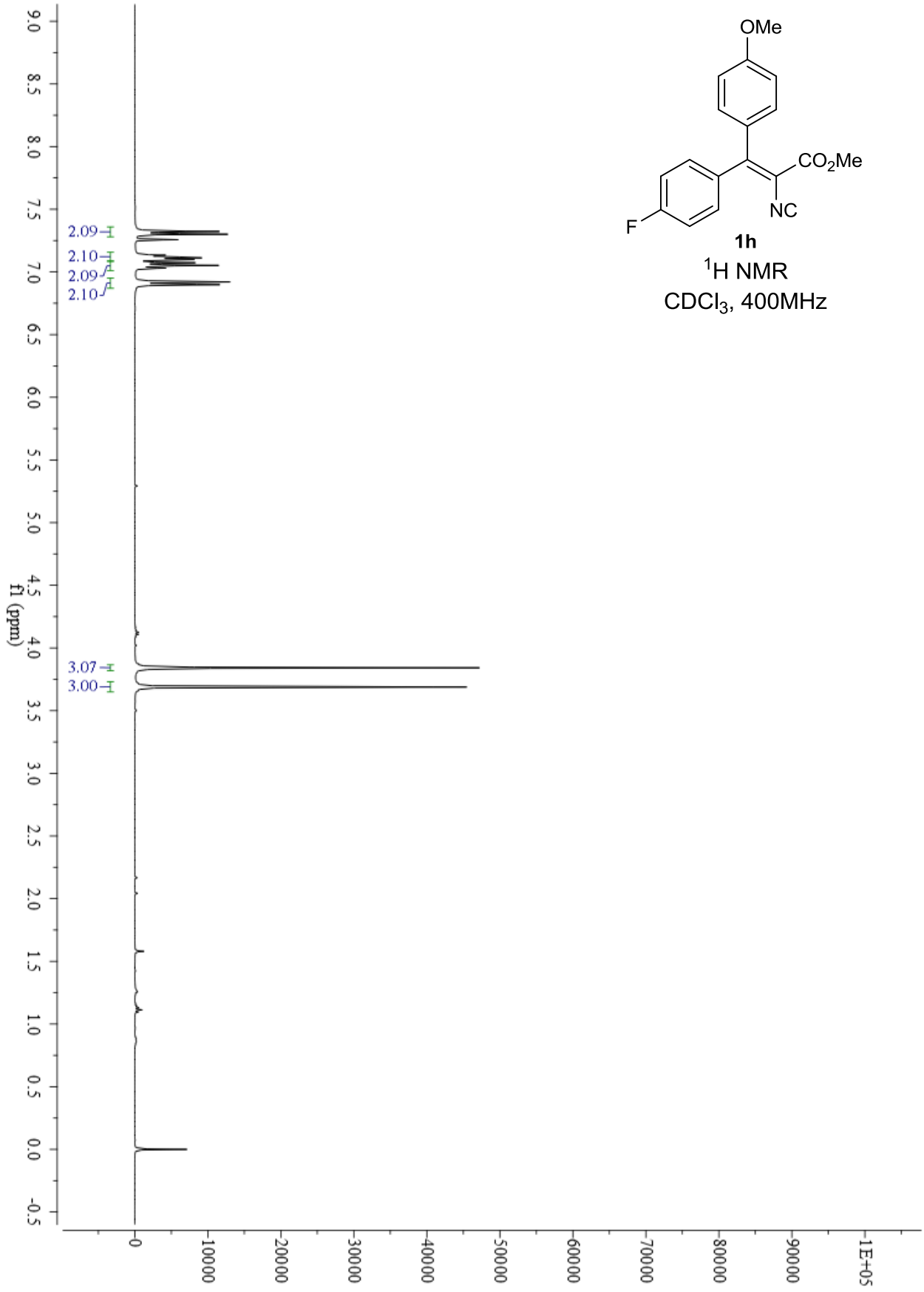
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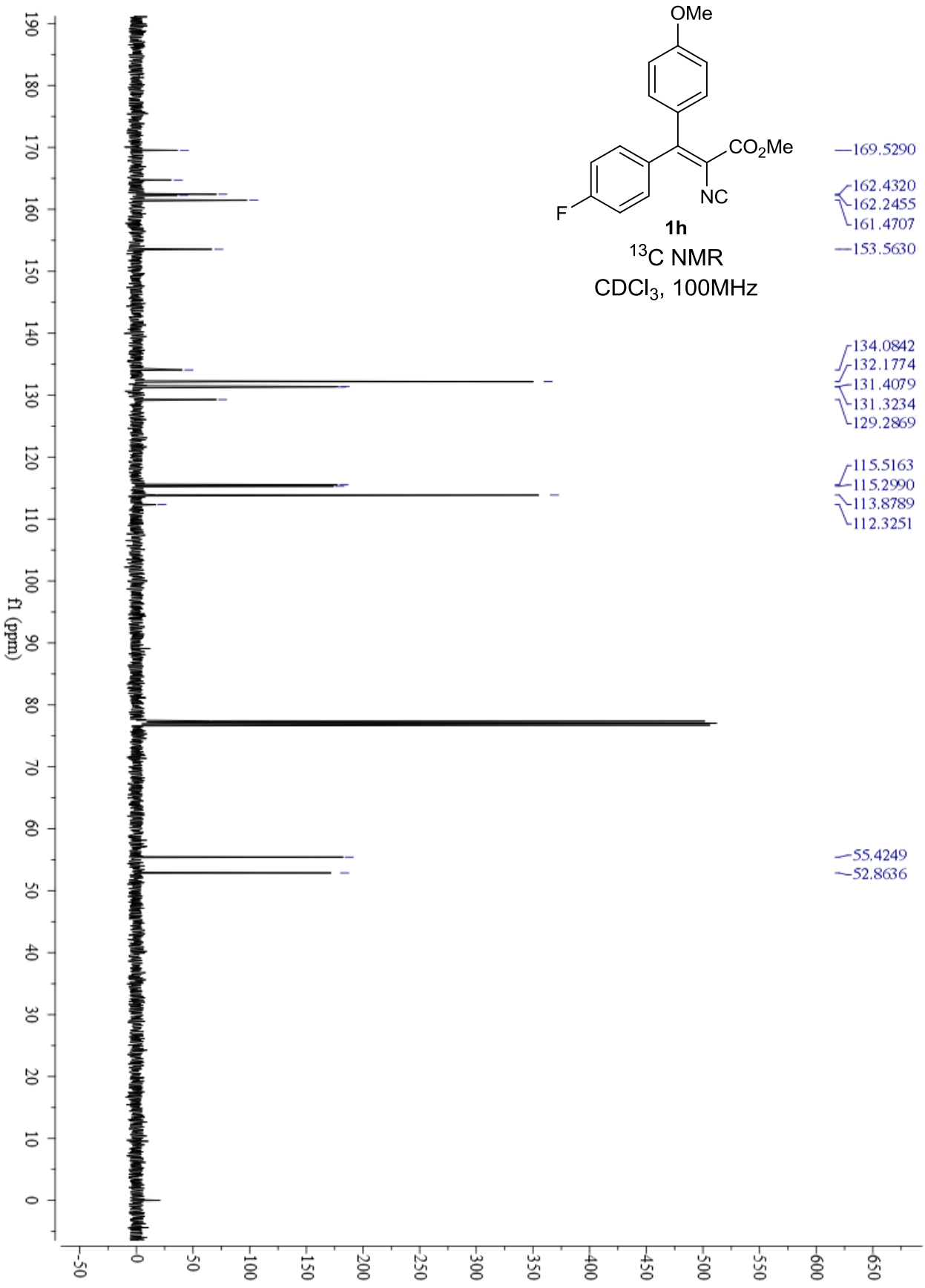
3.00
f1 (ppm)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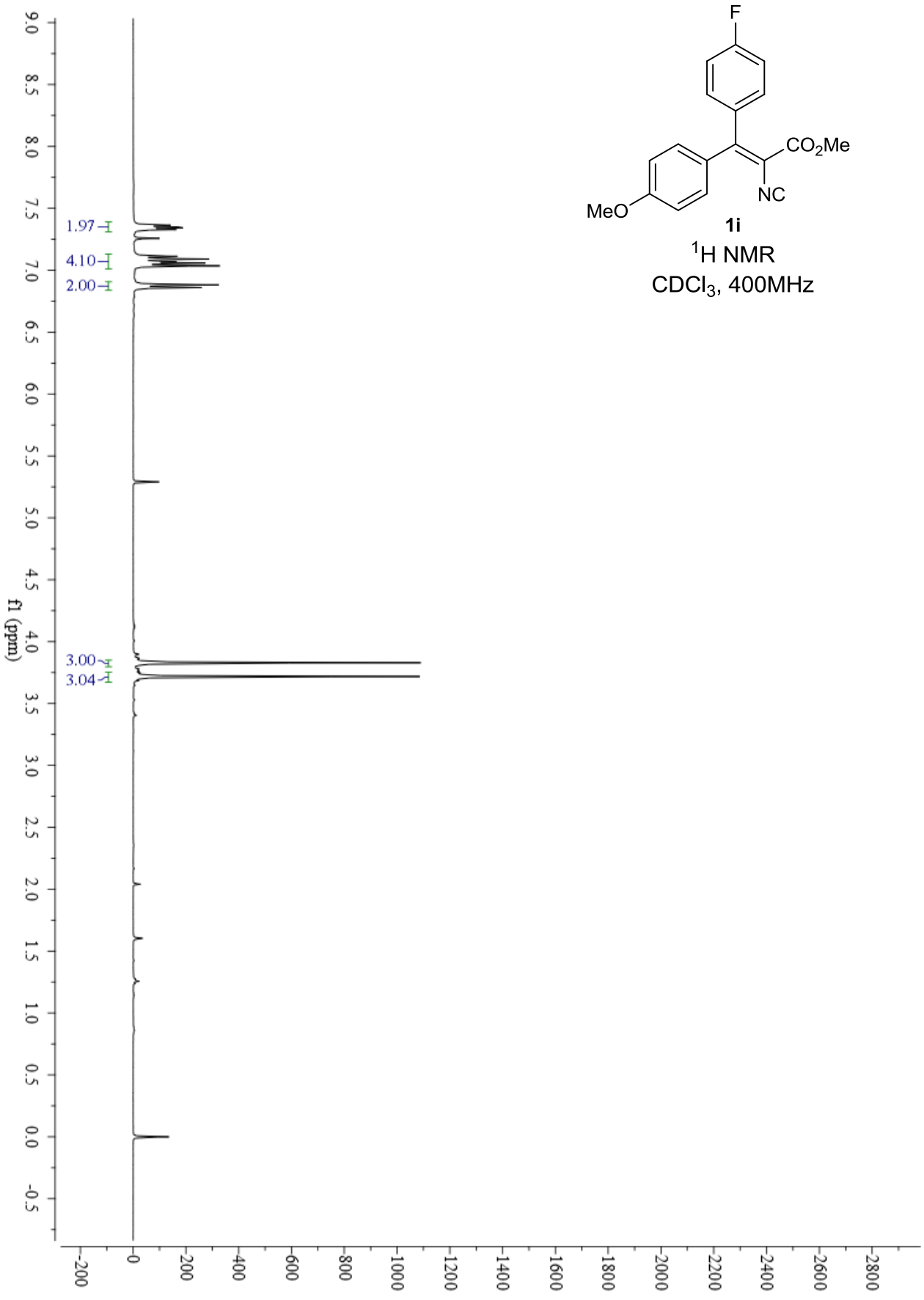
f1 (ppm)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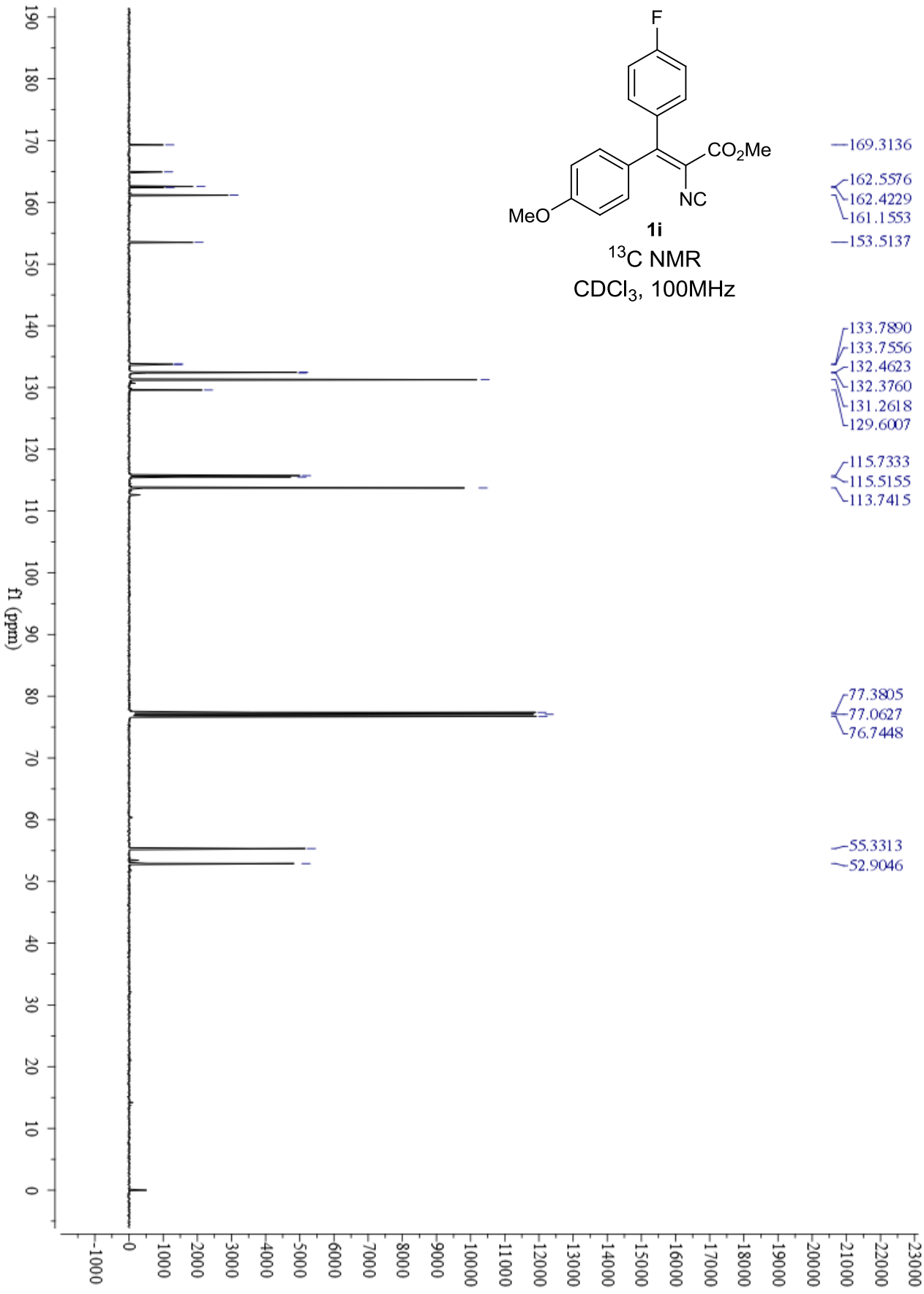
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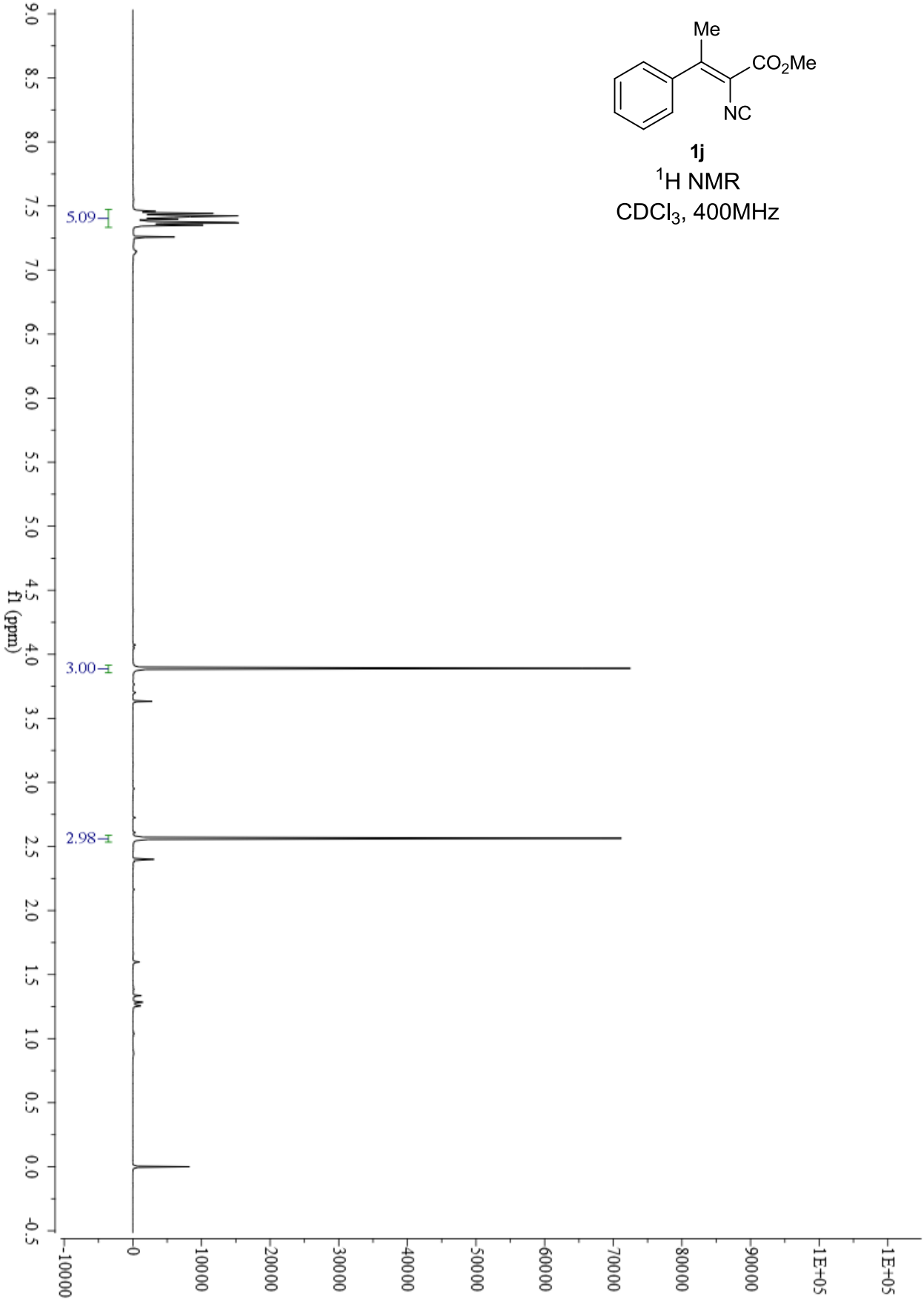
f1 (ppm)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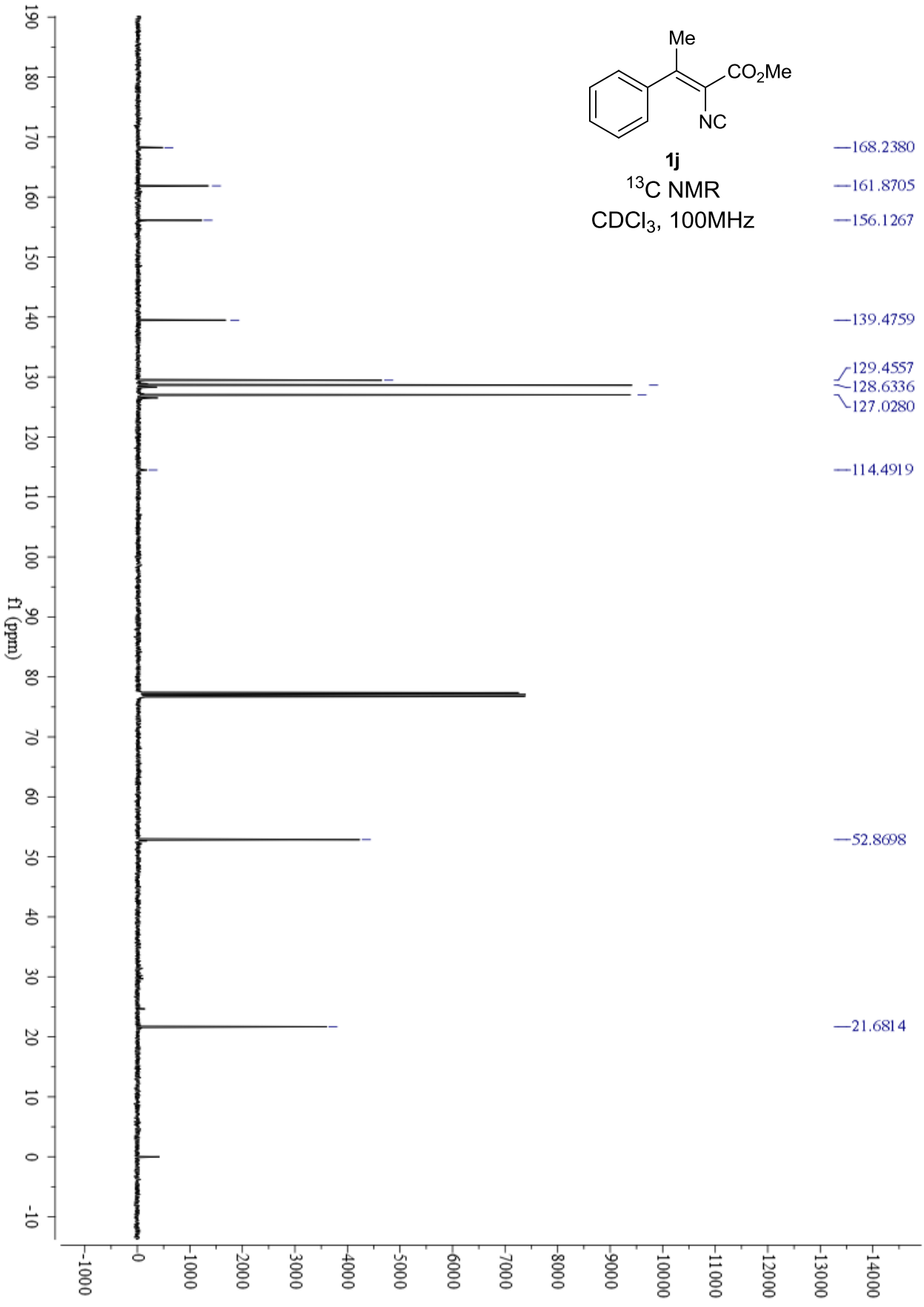
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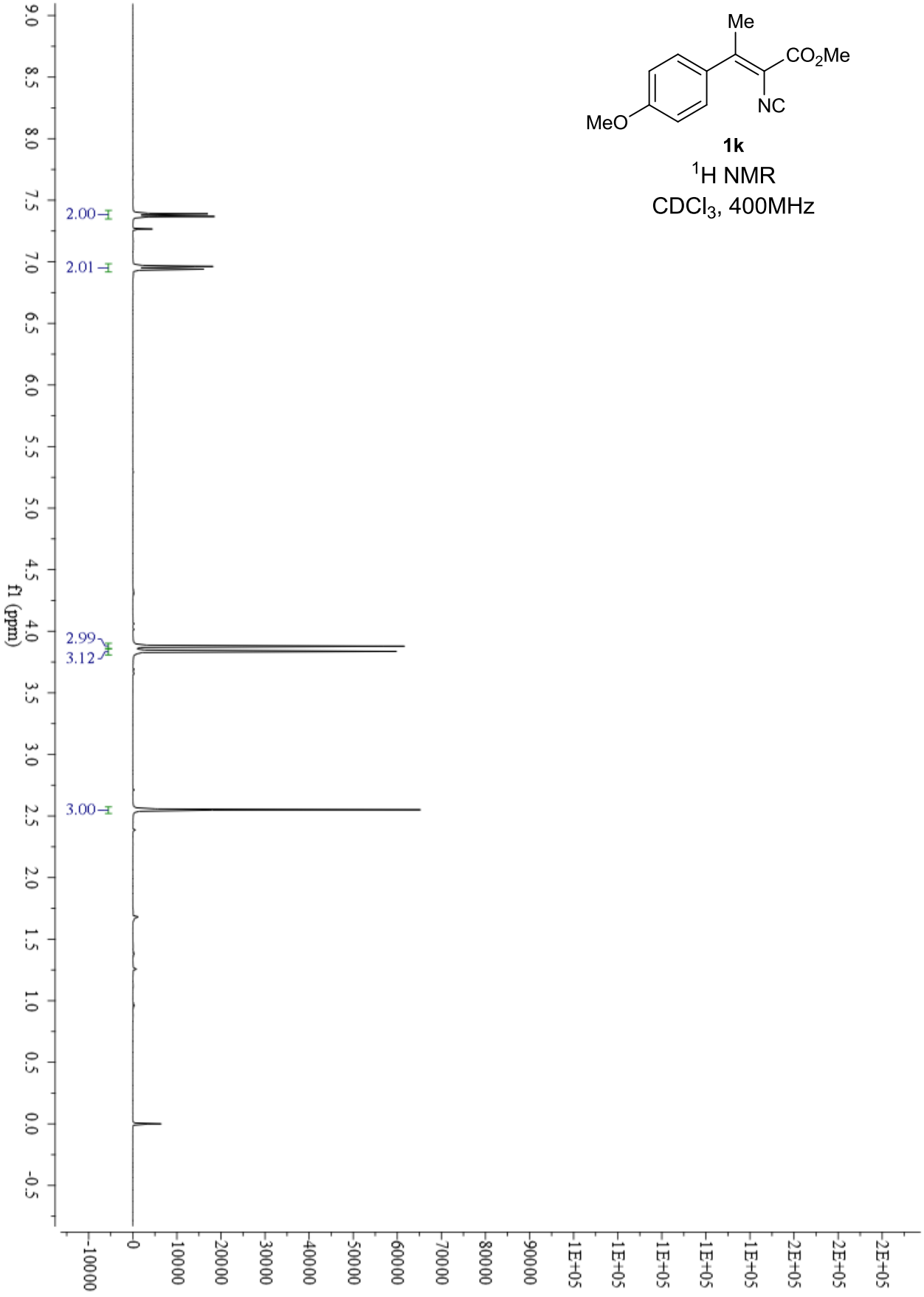
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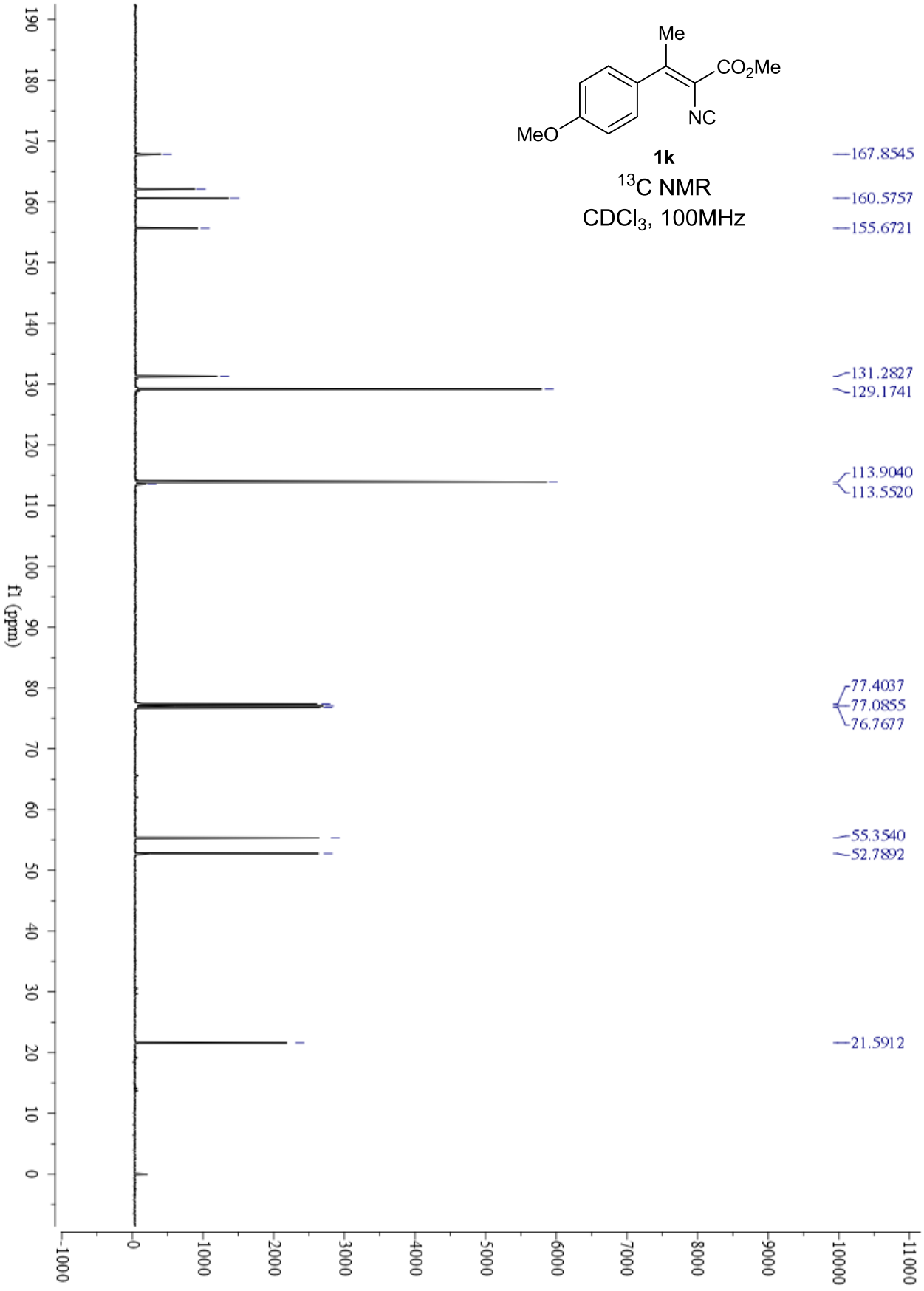
f1 (ppm)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CO2Me
NC
MeO
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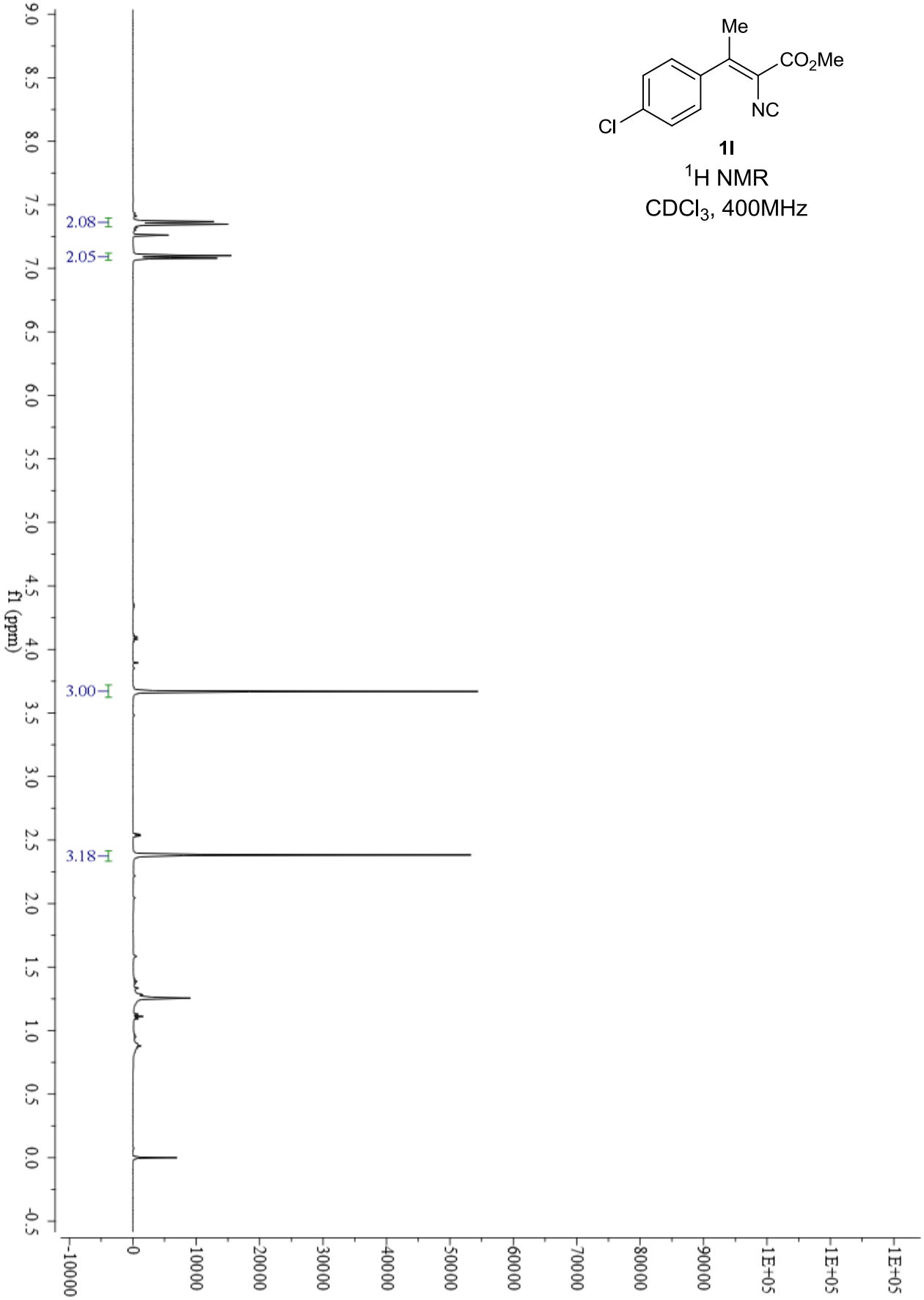
f1 (ppm)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CO2Me
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Cl
1l
1H NMR
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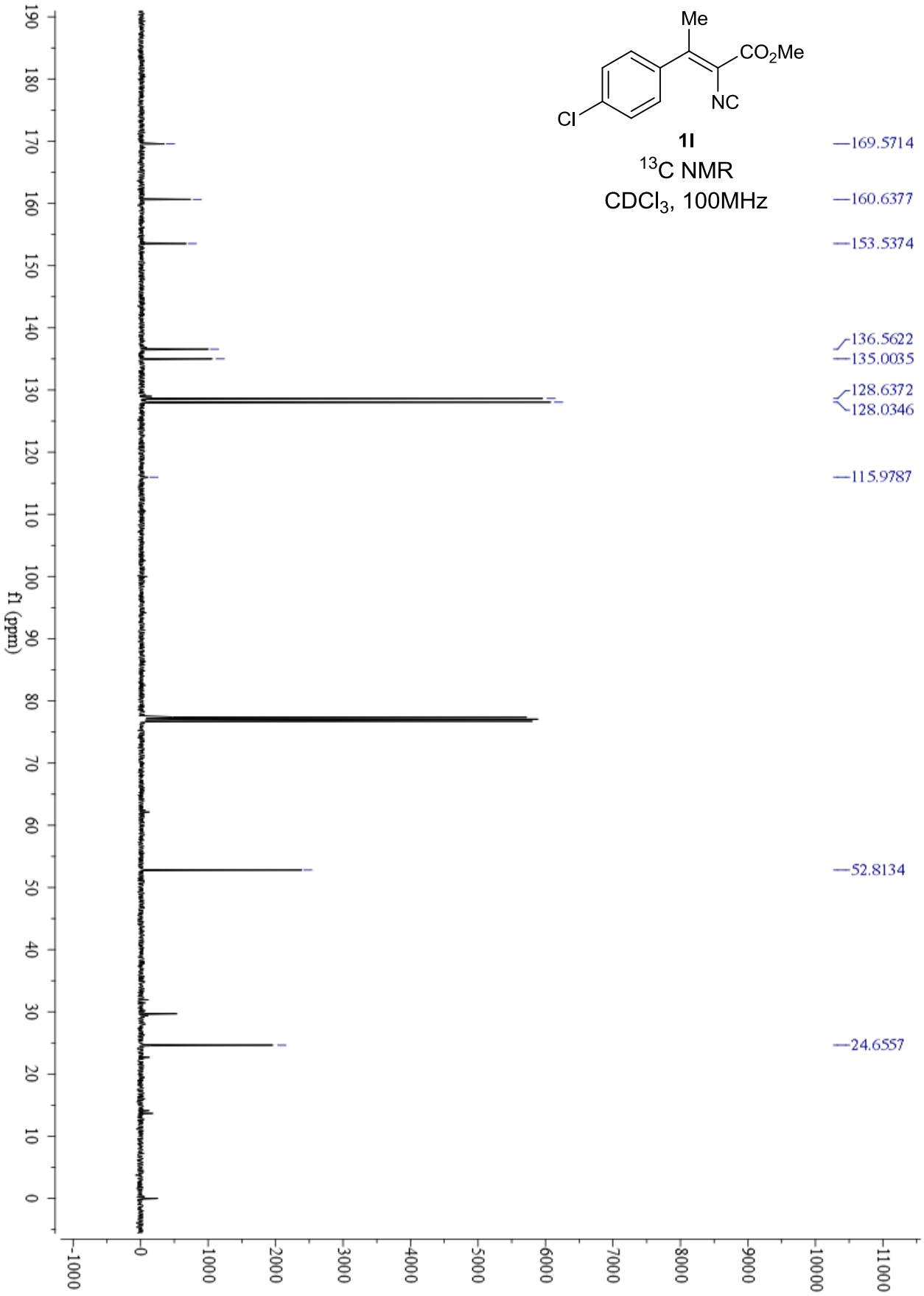
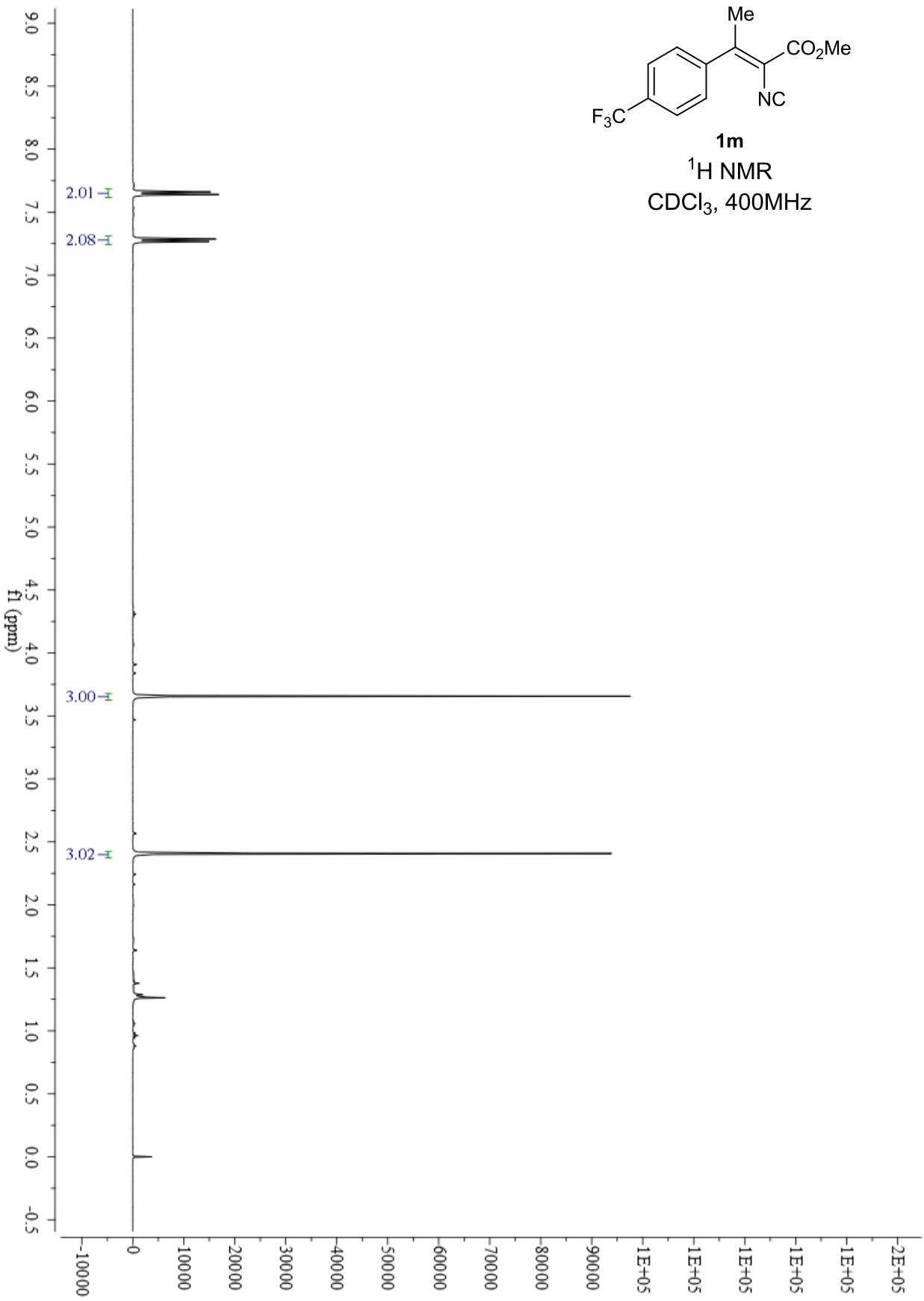
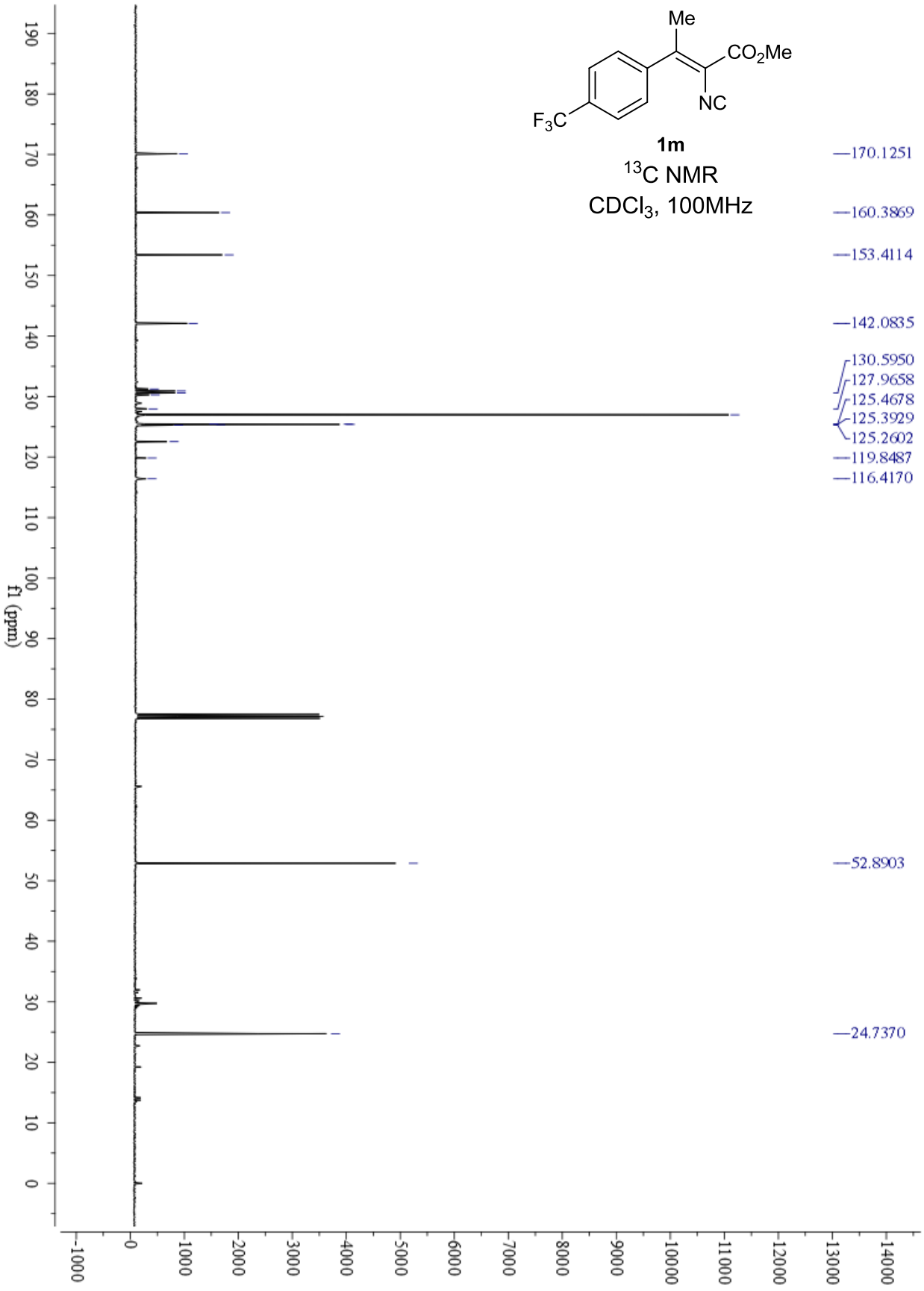
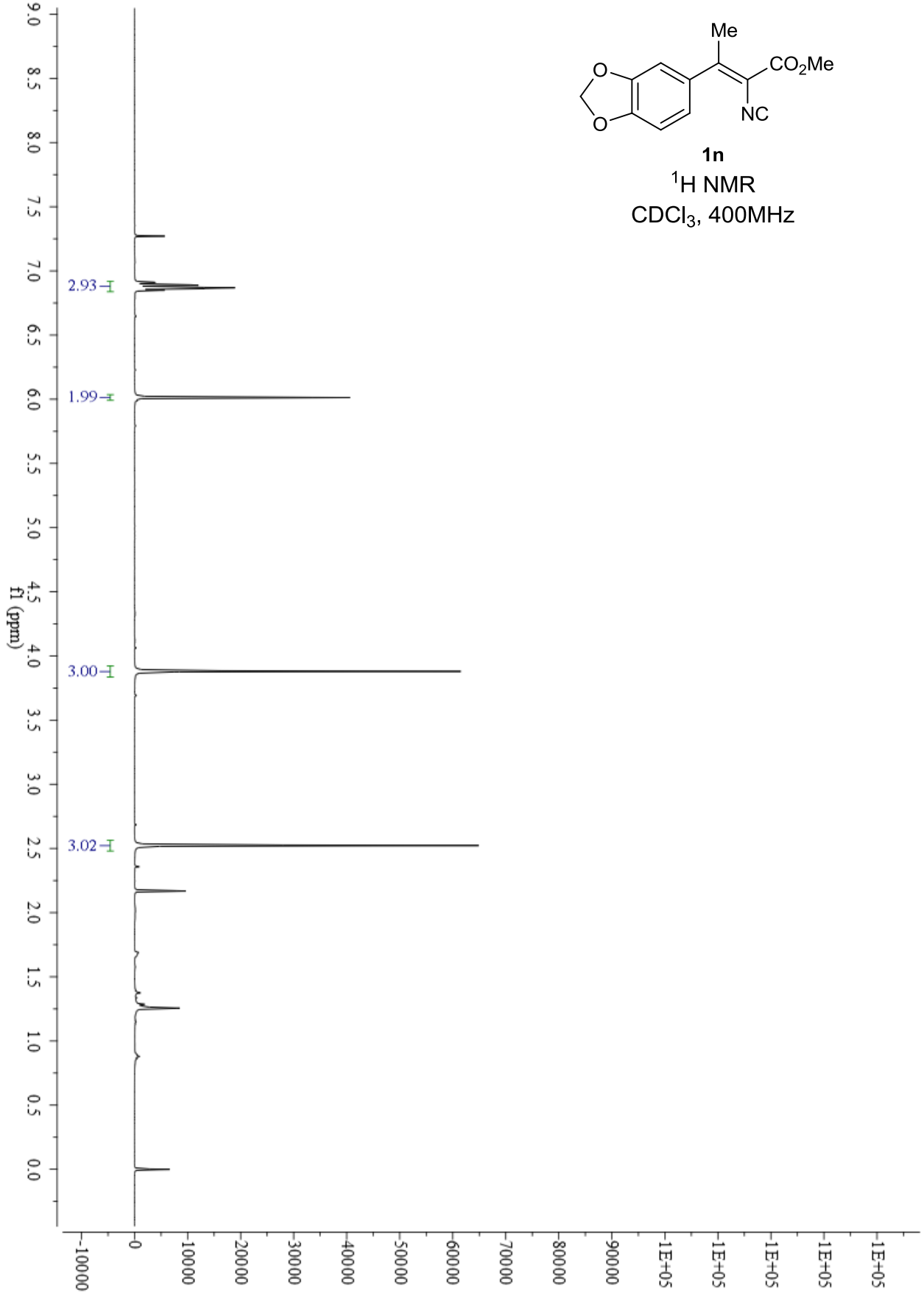
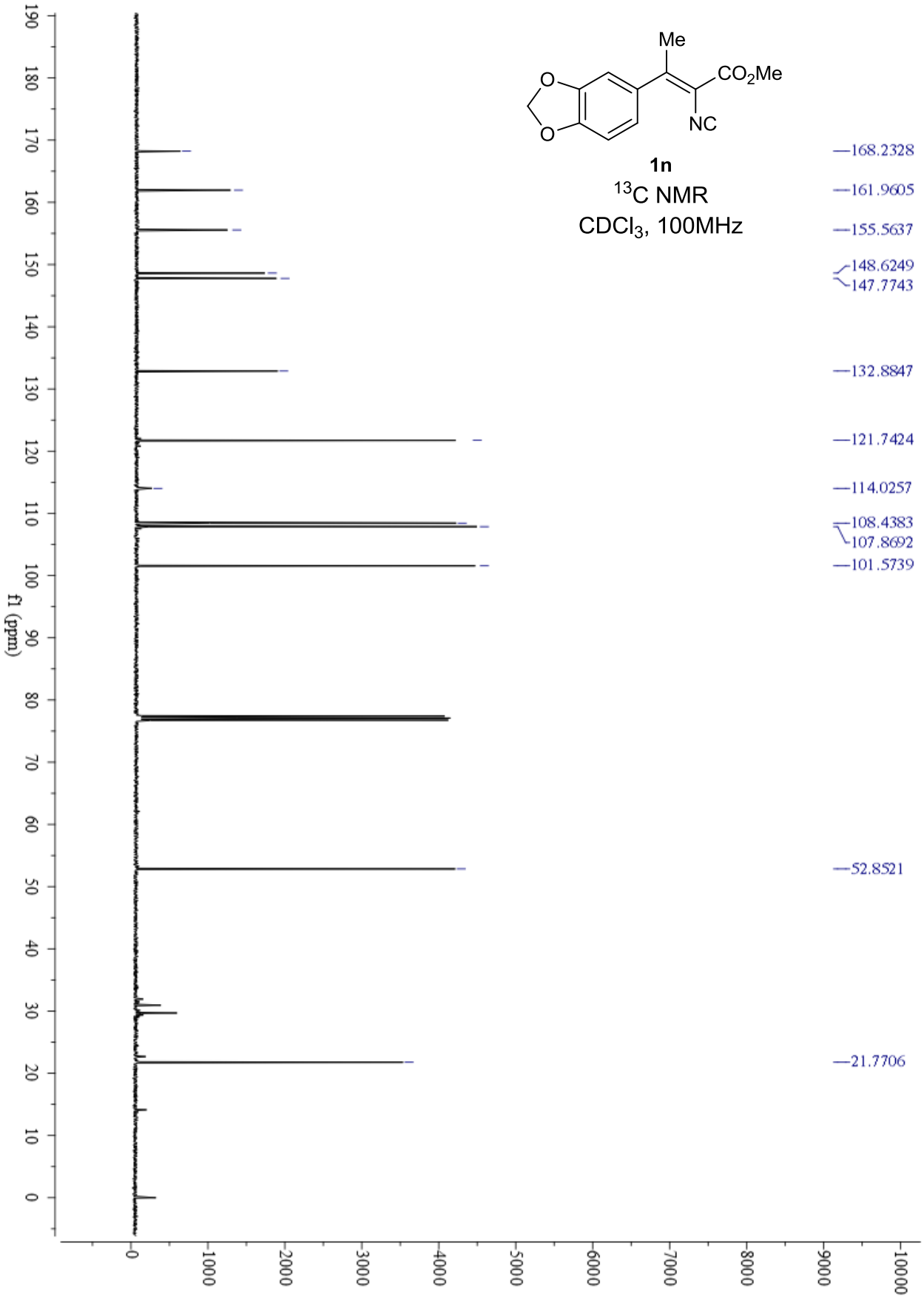
3.18
f1 (ppm)

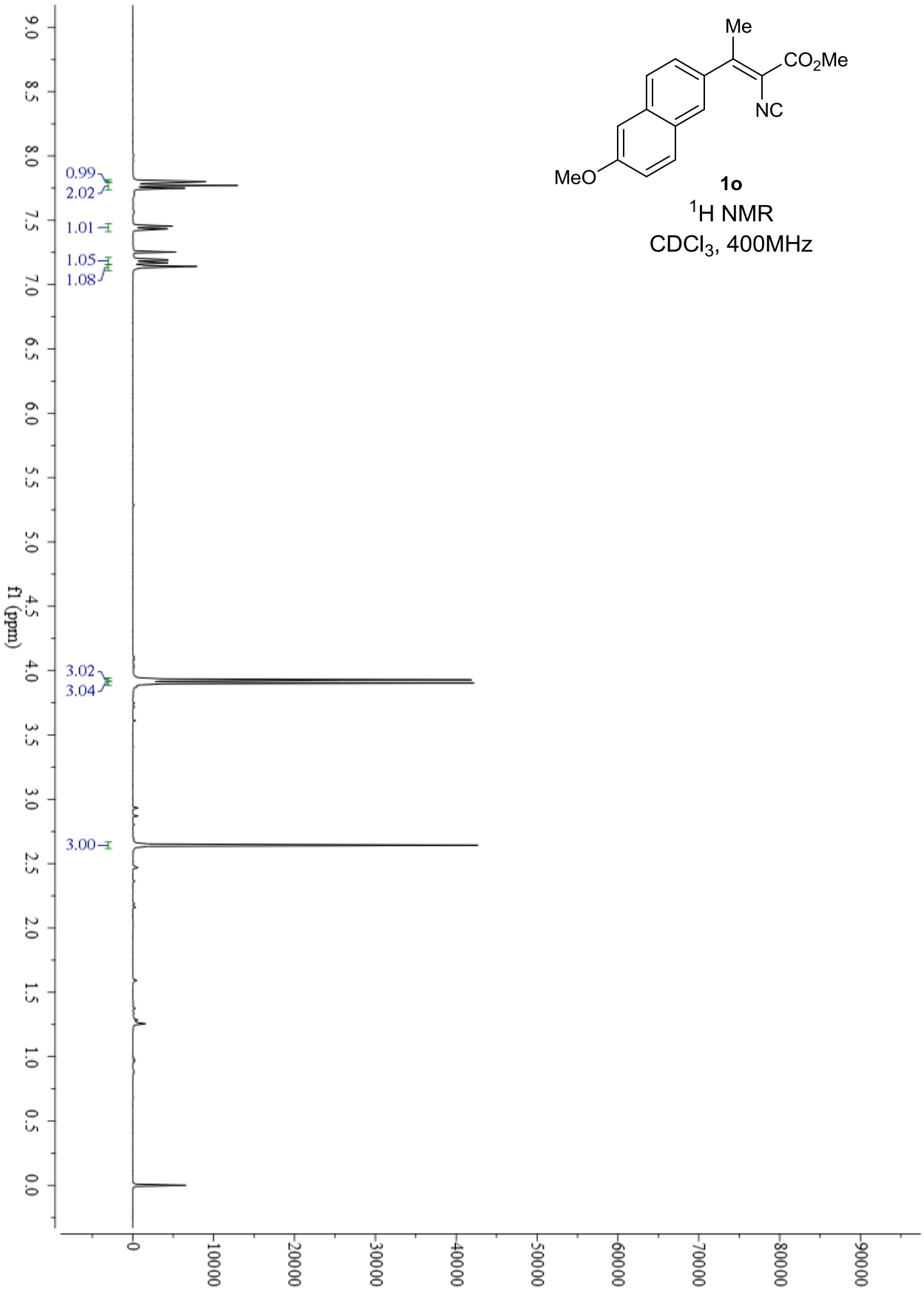

Me
CO2Me
NC
Cl
1l
13C NMR
CDCl3, 100MHz
169.5714
160.6377
153.5374
136.5622
135.0035
128.6372
128.0346
115.9787
52.8134
24.6557
f1 (ppm)

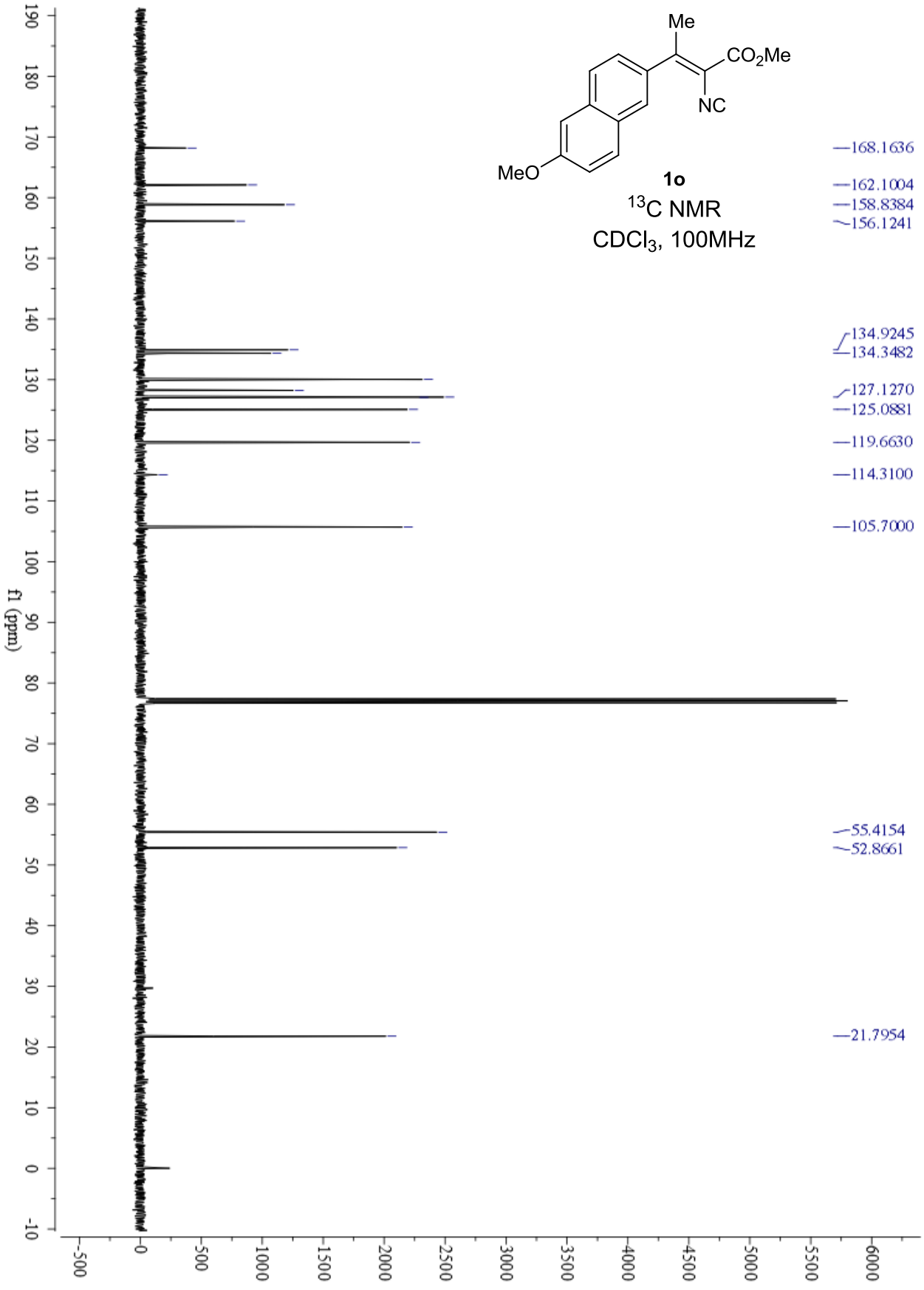

Me
CO2Me
NC
F3C
1m
1H NMR
CDCl3, 400MHz
2.01
2.08
3.00
3.02
f1 (ppm)

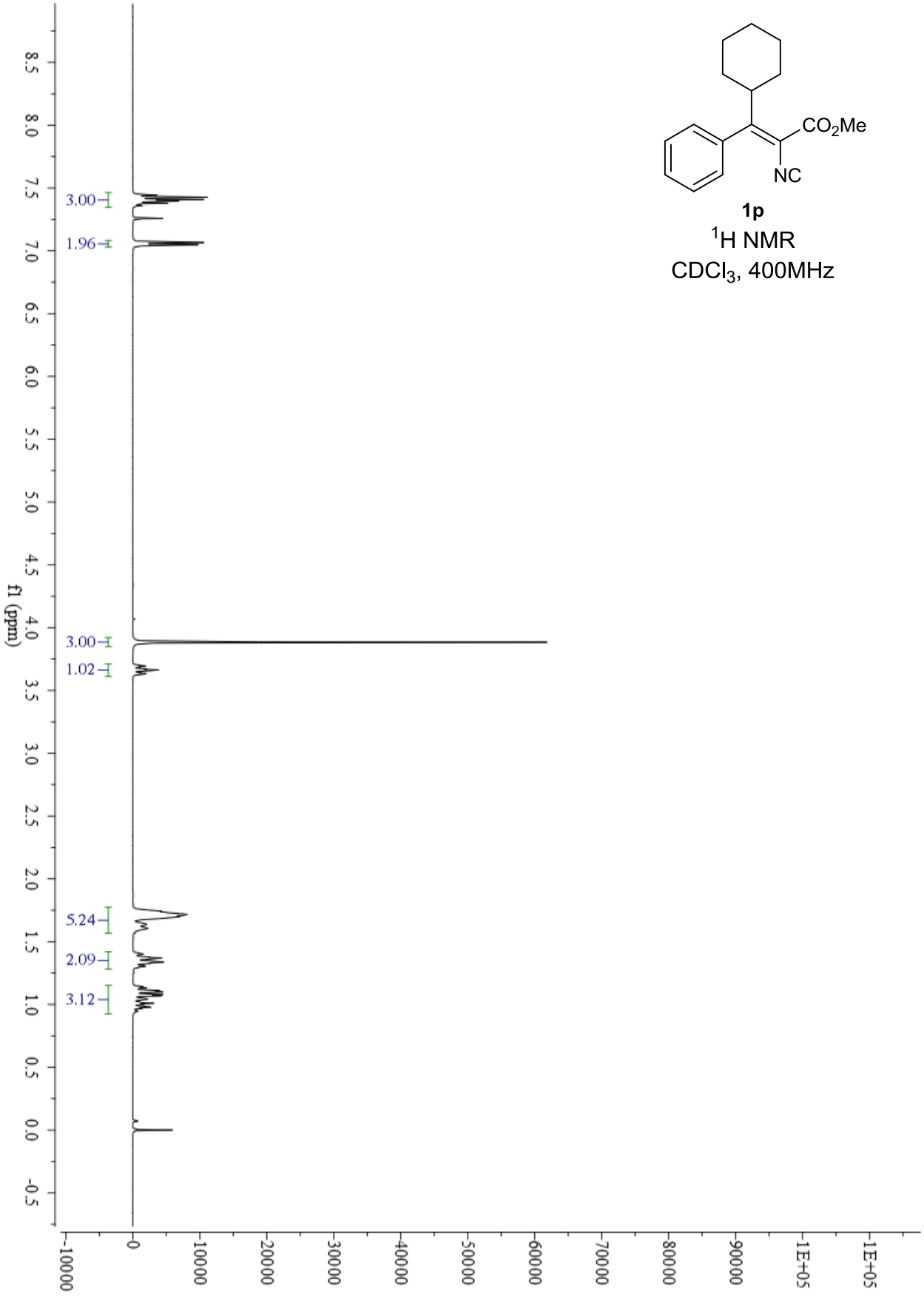

Me
CO2Me
NC
F3C
1m
13C NMR
CDCl3, 100MHz
170.1251
160.3869
153.4114
142.0835
130.5950
127.9658
125.4678
125.3929
125.2602
119.8487
116.4170
52.8903
24.7370
f1 (ppm)

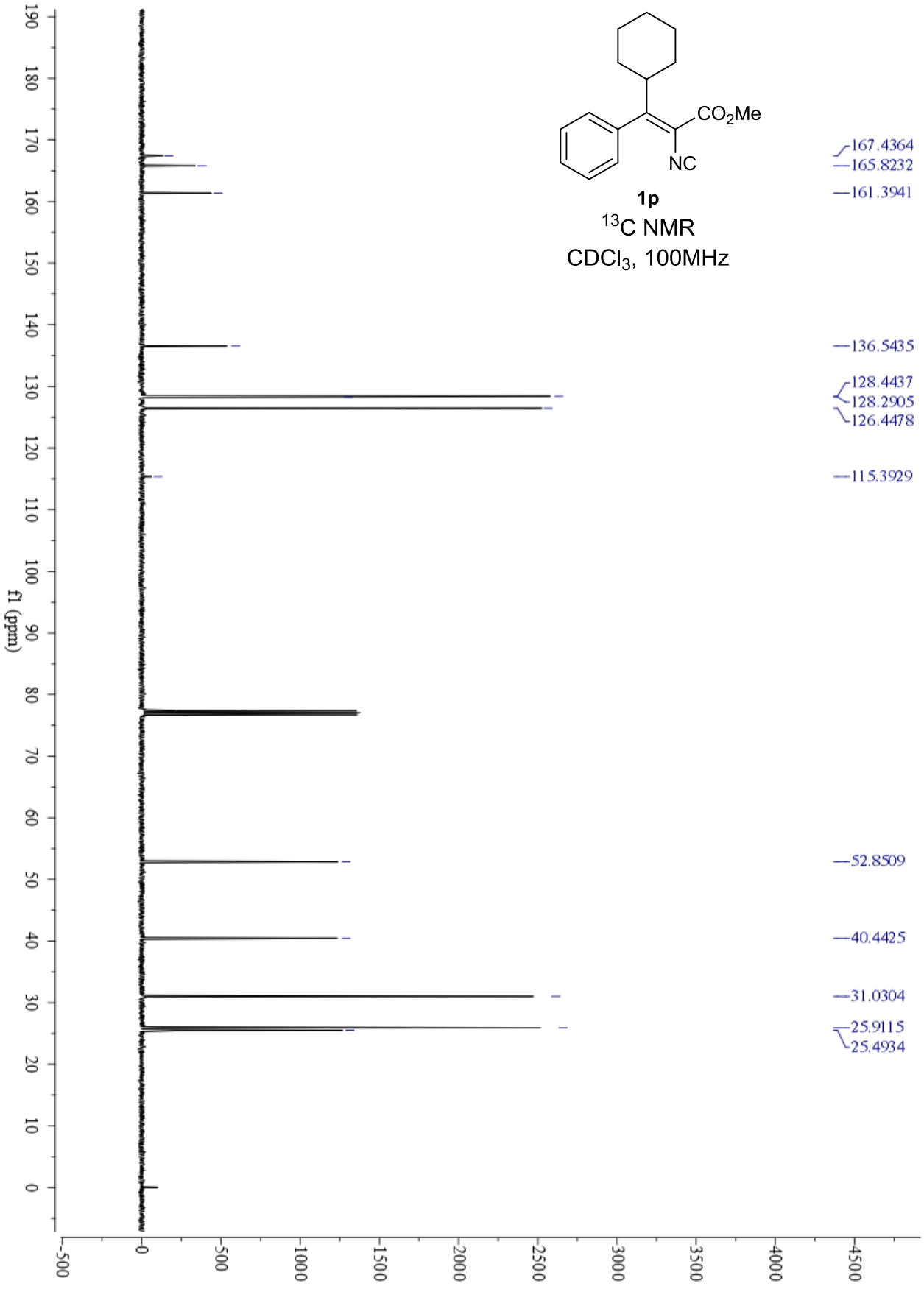

Me
CO2Me
NC
O
O
1n
1H NMR
CDCl3, 400MHz
2.93
1.99
3.00
3.02
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-10000
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
1E+05
1E+05
1E+05
1E+05
1E+05

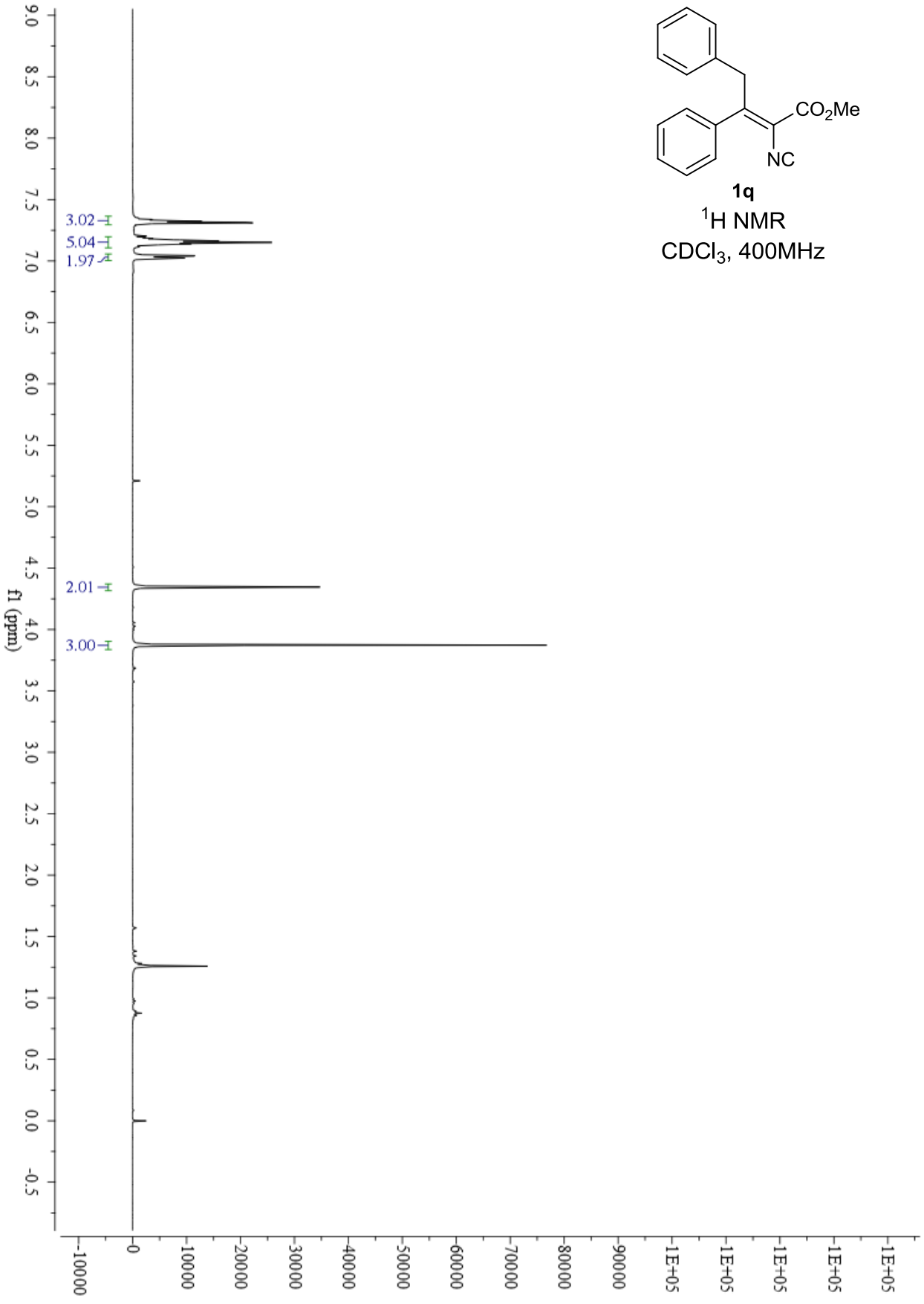

Me
CO2Me
NC
O
O
1n
13C NMR
CDCl3, 100MHz
168.2328
161.9605
155.5637
148.6249
147.7743
132.8847
121.7424
114.0257
108.4383
107.8692
101.5739
52.8521
21.7706
f1 (ppm)

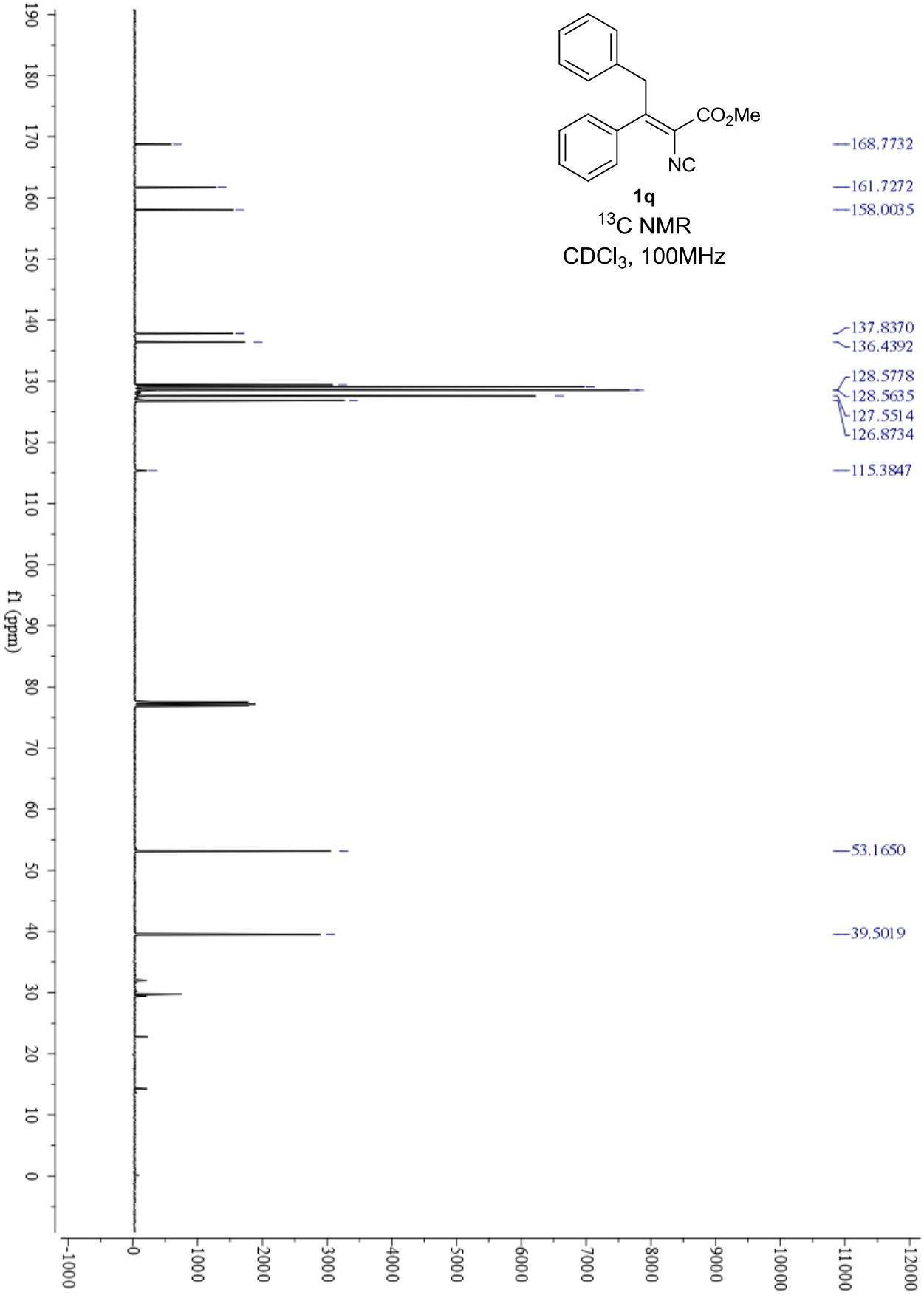

Me
CO2Me
NC
MeO
1o
1H NMR
CDCl3, 400MHz
0.99
2.02
1.01
1.05
1.08
3.02
3.04
3.00
f1 (ppm)

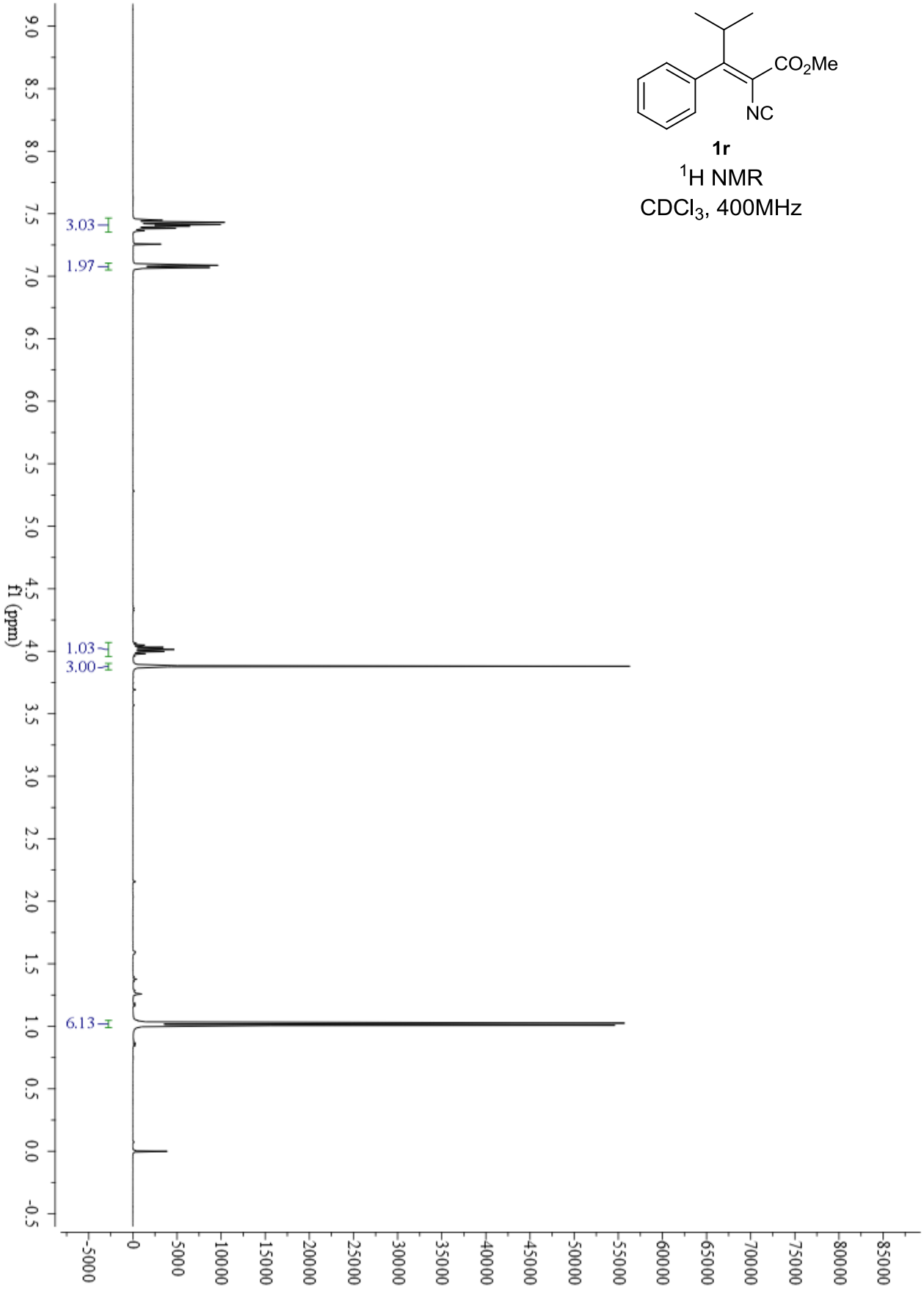

Me
CO2Me
NC
MeO
1o
13C NMR
CDCl3, 100MHz
168.1636
162.1004
158.8384
156.1241
134.9245
134.3482
127.1270
125.0881
119.6630
114.3100
105.7000
55.4154
52.8661
21.7954
f1 (ppm)

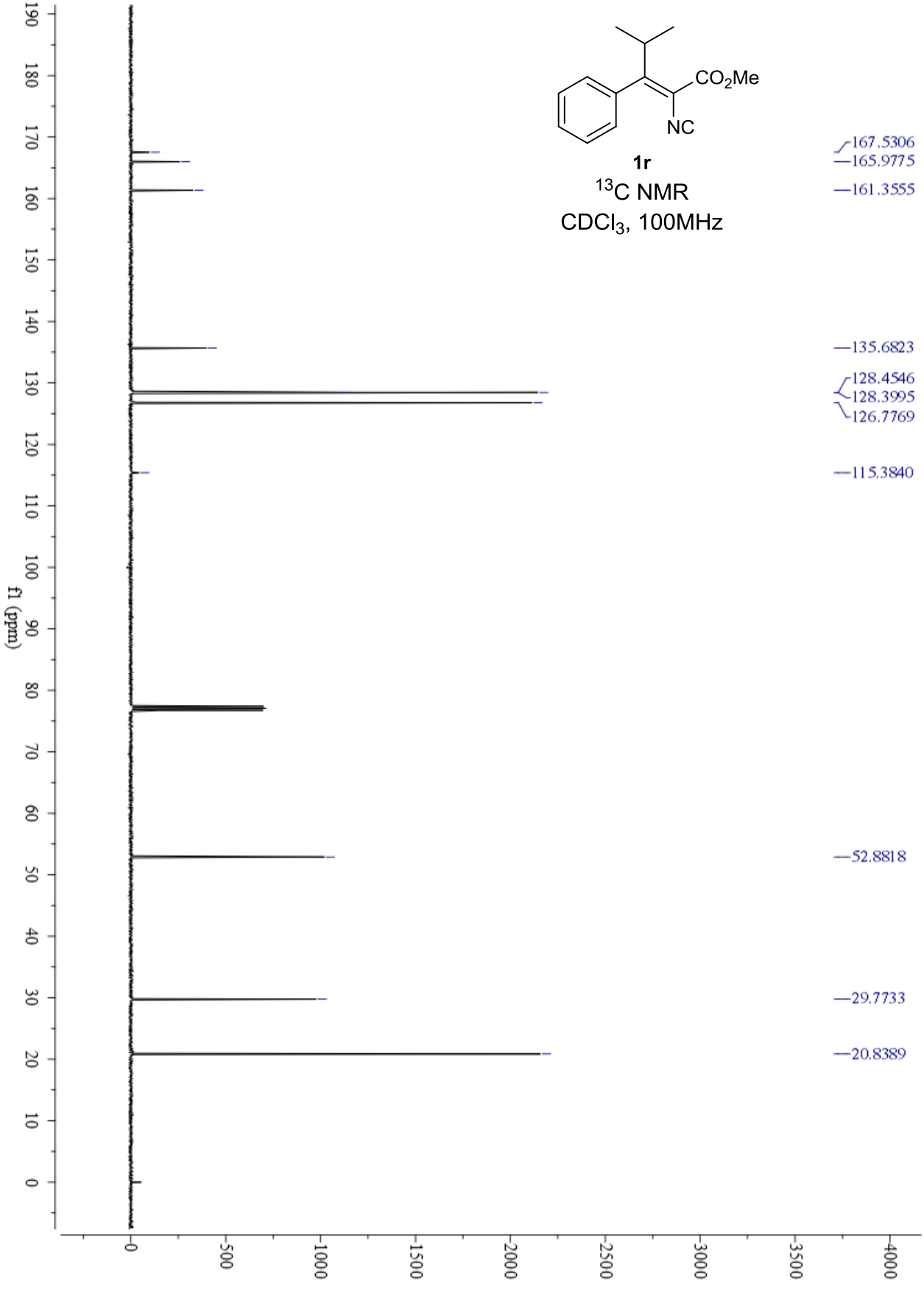

CO2Me
NC
1p
1H NMR
CDCl3, 400MHz
3.00
1.96
3.00
1.02
5.24
2.09
3.12
f1 (ppm)


CO2Me
NC
1p
13C NMR
CDCl3, 100MHz
167.4364
165.8232
161.3941
136.5435
128.4437
128.2905
126.4478
115.3929
52.8509
40.4425
31.0304
25.9115
25.4934
f1 (ppm)


CO2Me
NC
1q
1H NMR
CDCl3, 400MHz
3.02
5.04
1.97
2.01
3.00
f1 (ppm)


CO2Me
NC
1q
13C NMR
CDCl3, 100MHz
168.7732
161.7272
158.0035
137.8370
136.4392
128.5778
128.5635
127.5514
126.8734
115.3847
53.1650
39.5019
f1 (ppm)


CO2Me
NC
1r
1H NMR
CDCl3, 400MHz
3.03
1.97
1.03
3.00
6.13
f1 (ppm)


CO2Me
NC
1r
13C NMR
CDCl3, 100MHz
167.5306
165.9775
161.3555
135.6823
128.4546
128.3995
126.7769
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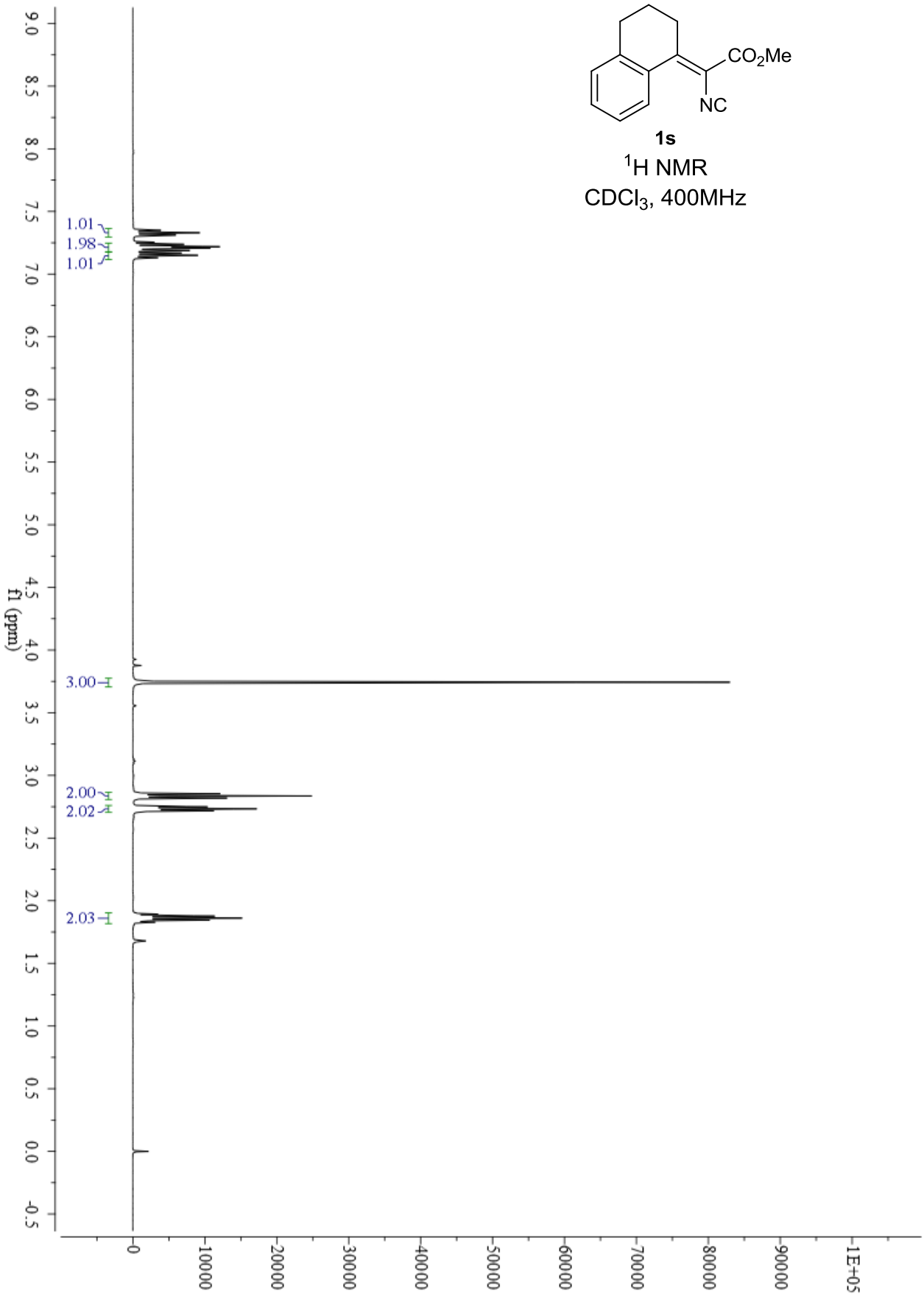
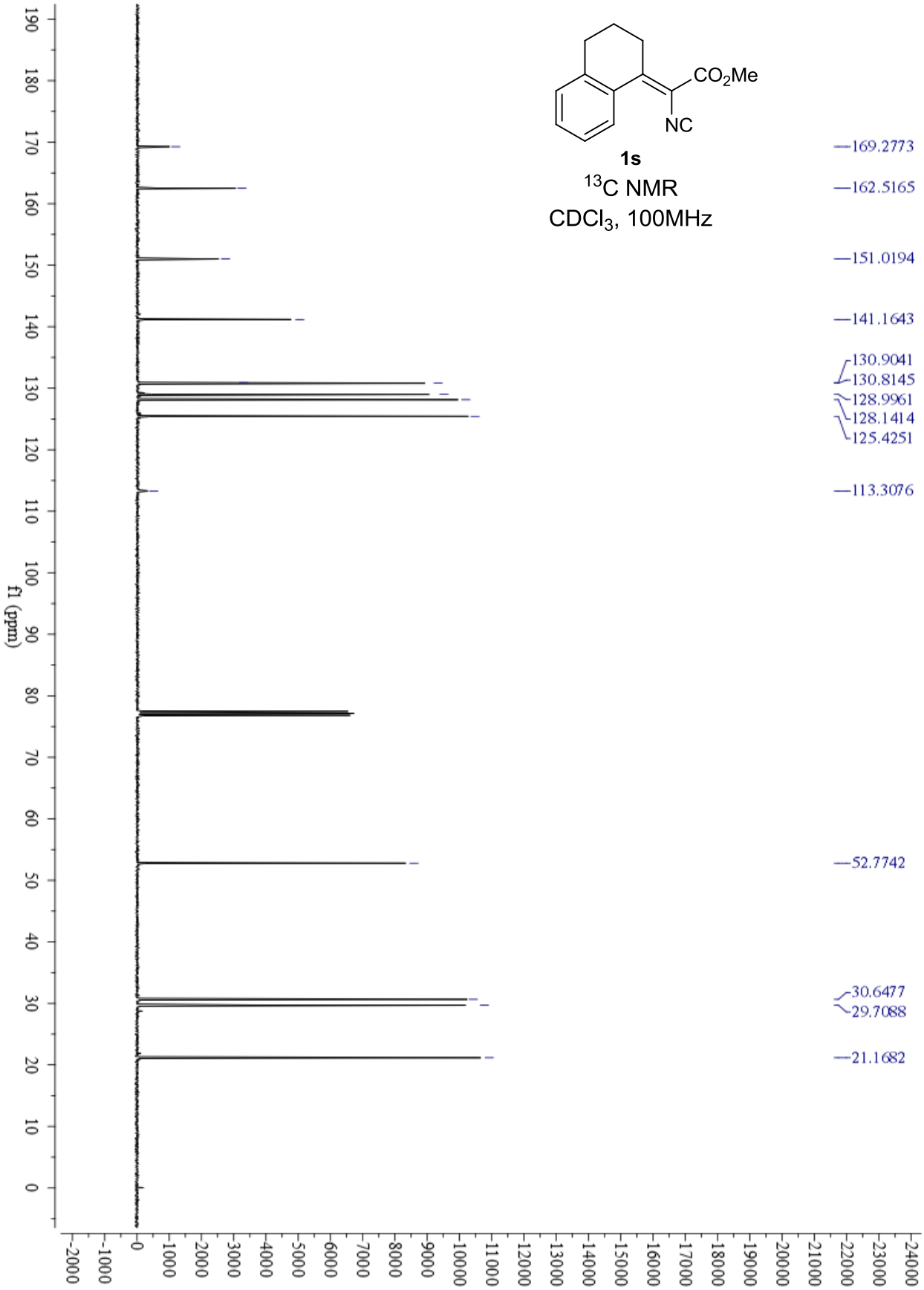
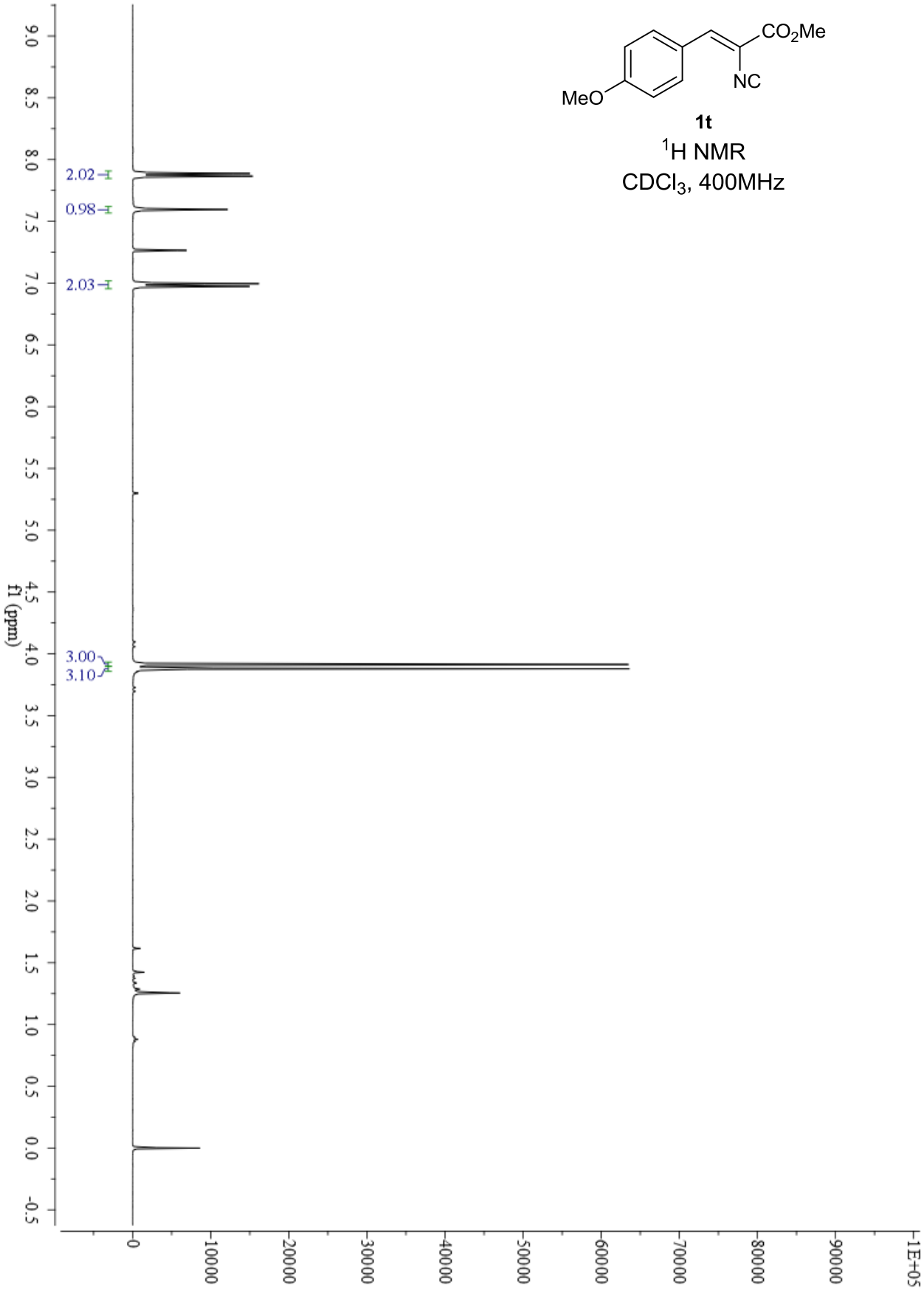
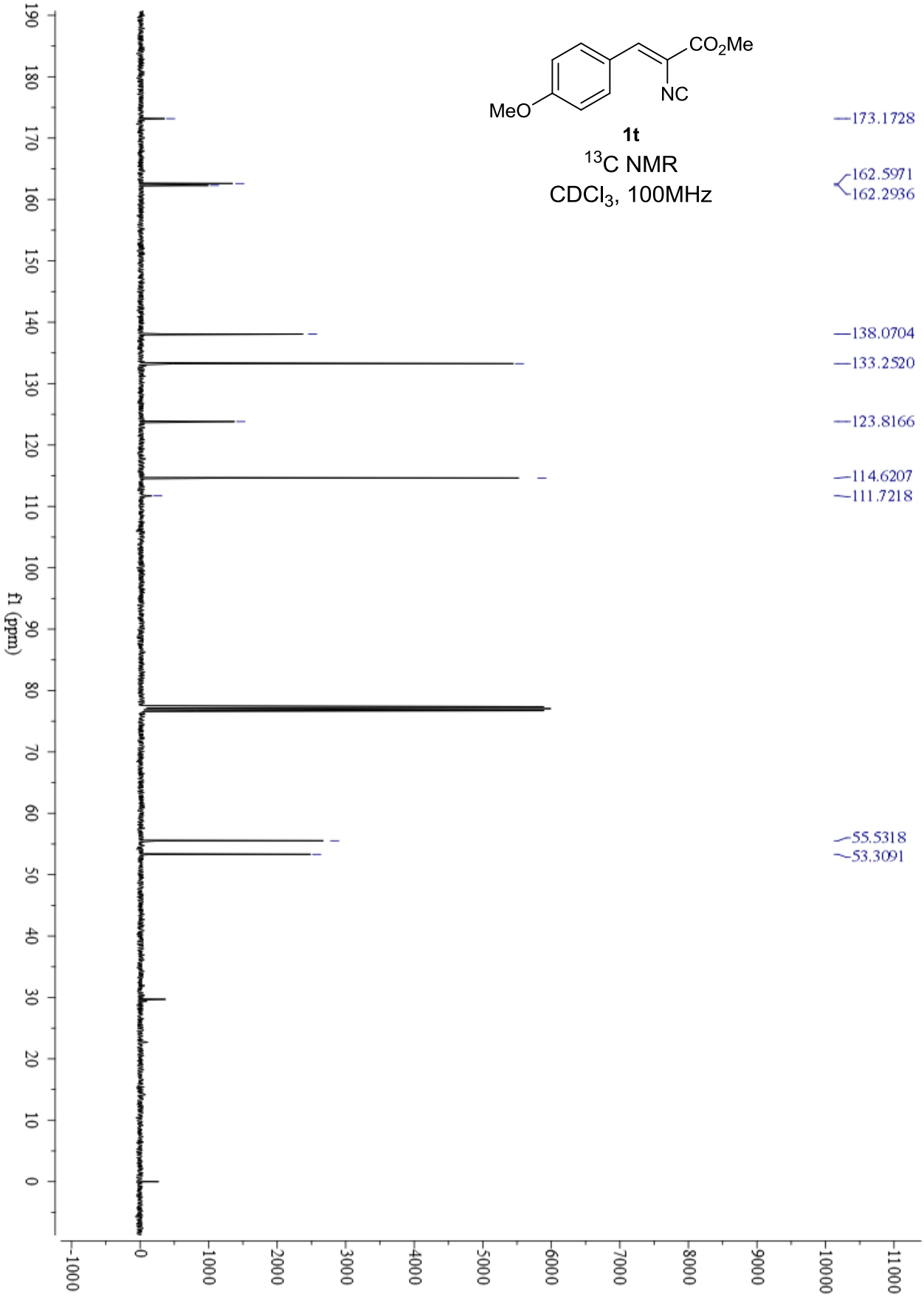
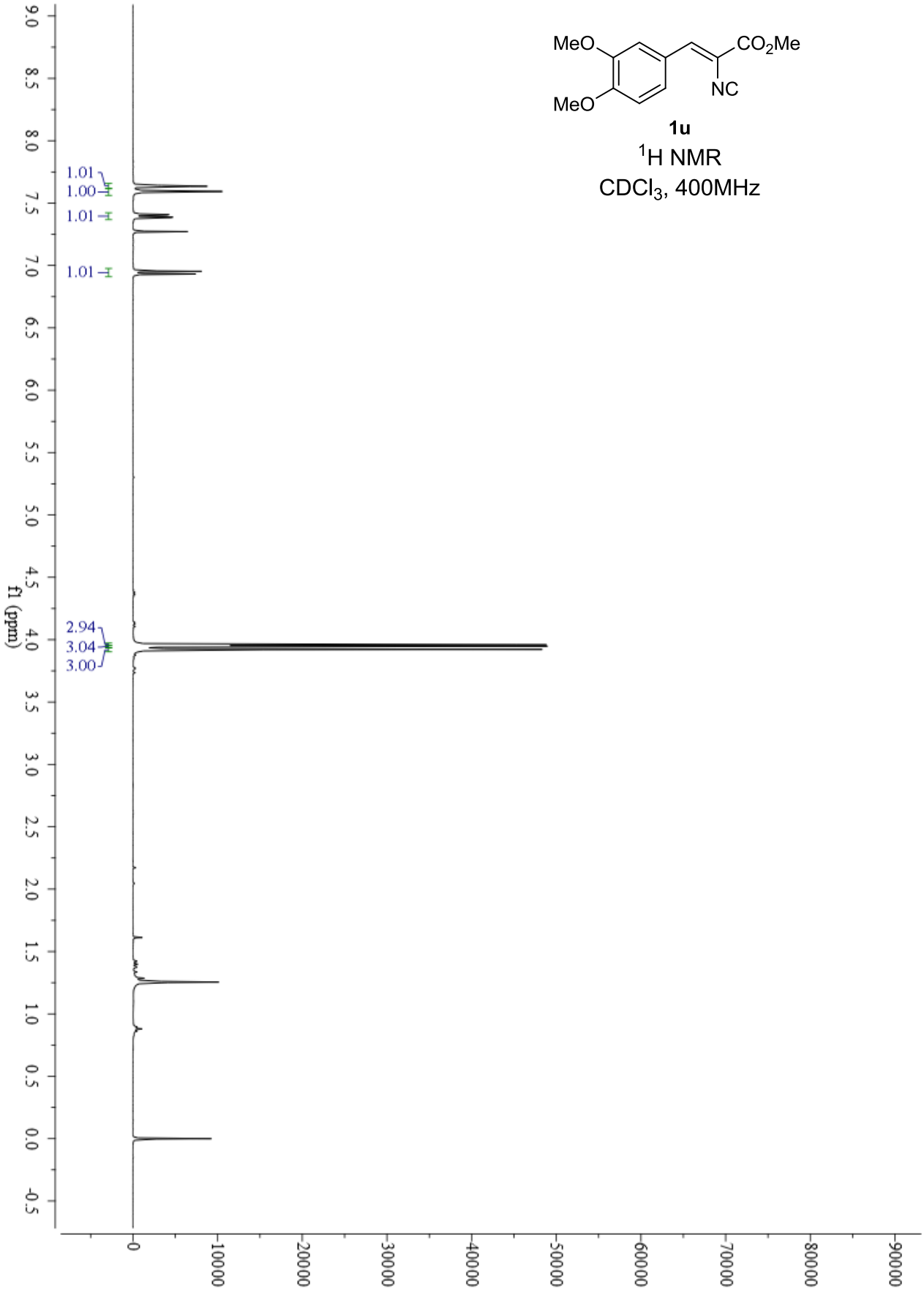
52.8818
29.7733
20.8389
f1 (ppm)

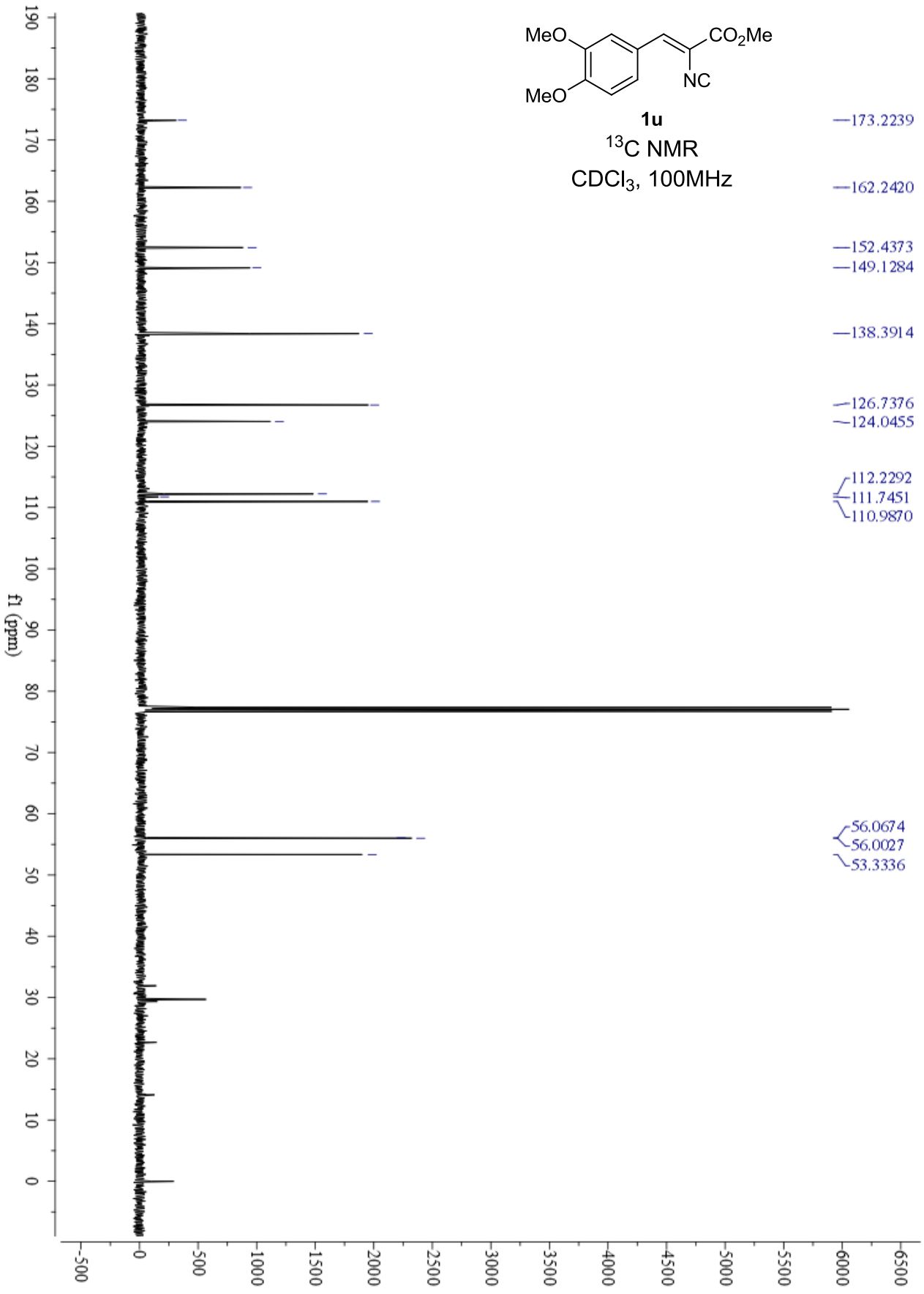

CO2Me
NC
1s
1H NMR
CDCl3, 400MHz
1.01
1.98
1.01
3.00
2.00
2.02
2.03
f1 (ppm)

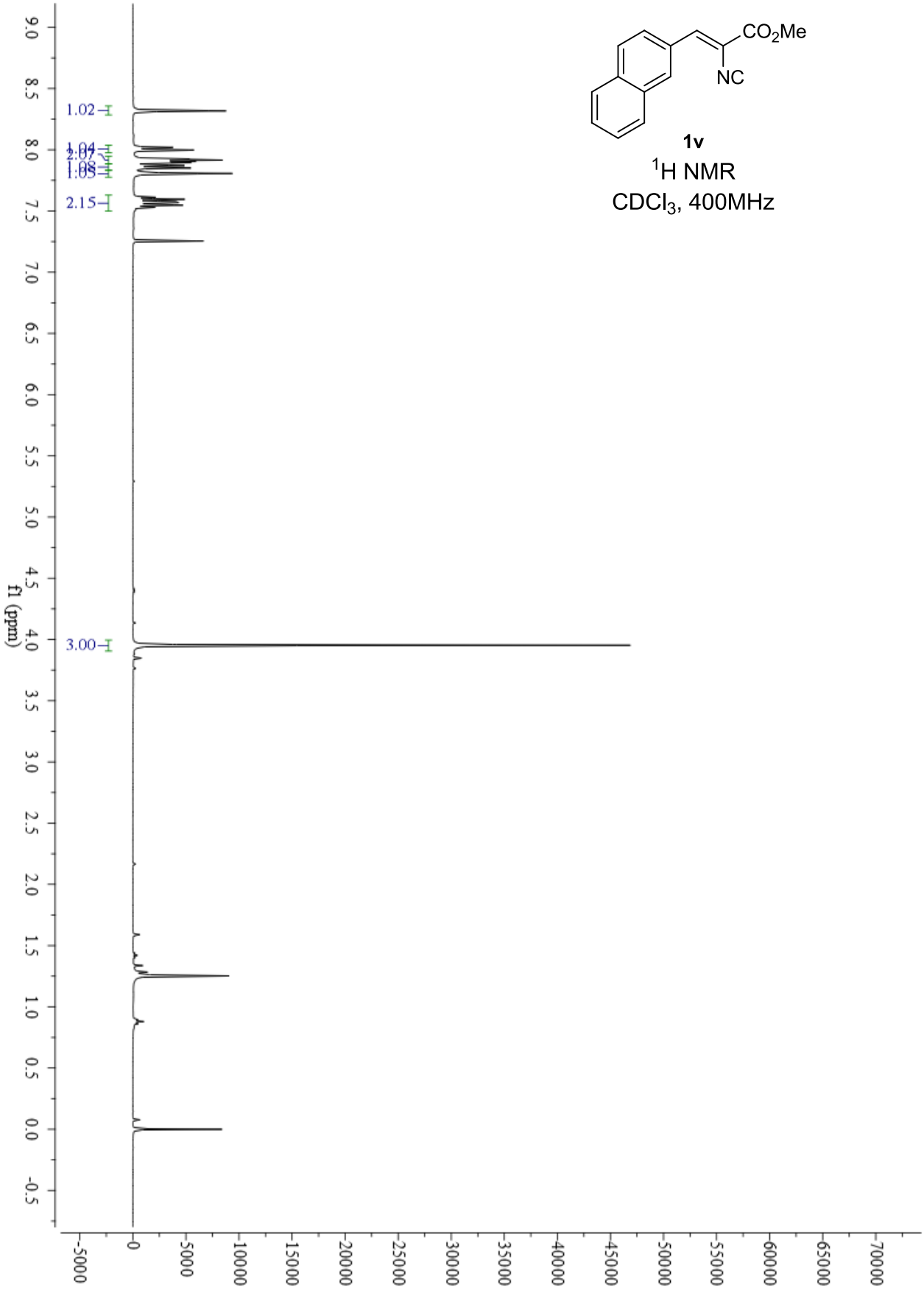

CO2Me
NC
1s
13C NMR
CDCl3, 100MHz
169.2773
162.5165
151.0194
141.1643
130.9041
130.8145
128.9961
128.1414
125.4251
113.3076
52.7742
30.6477
29.7088
21.1682
f1 (ppm)

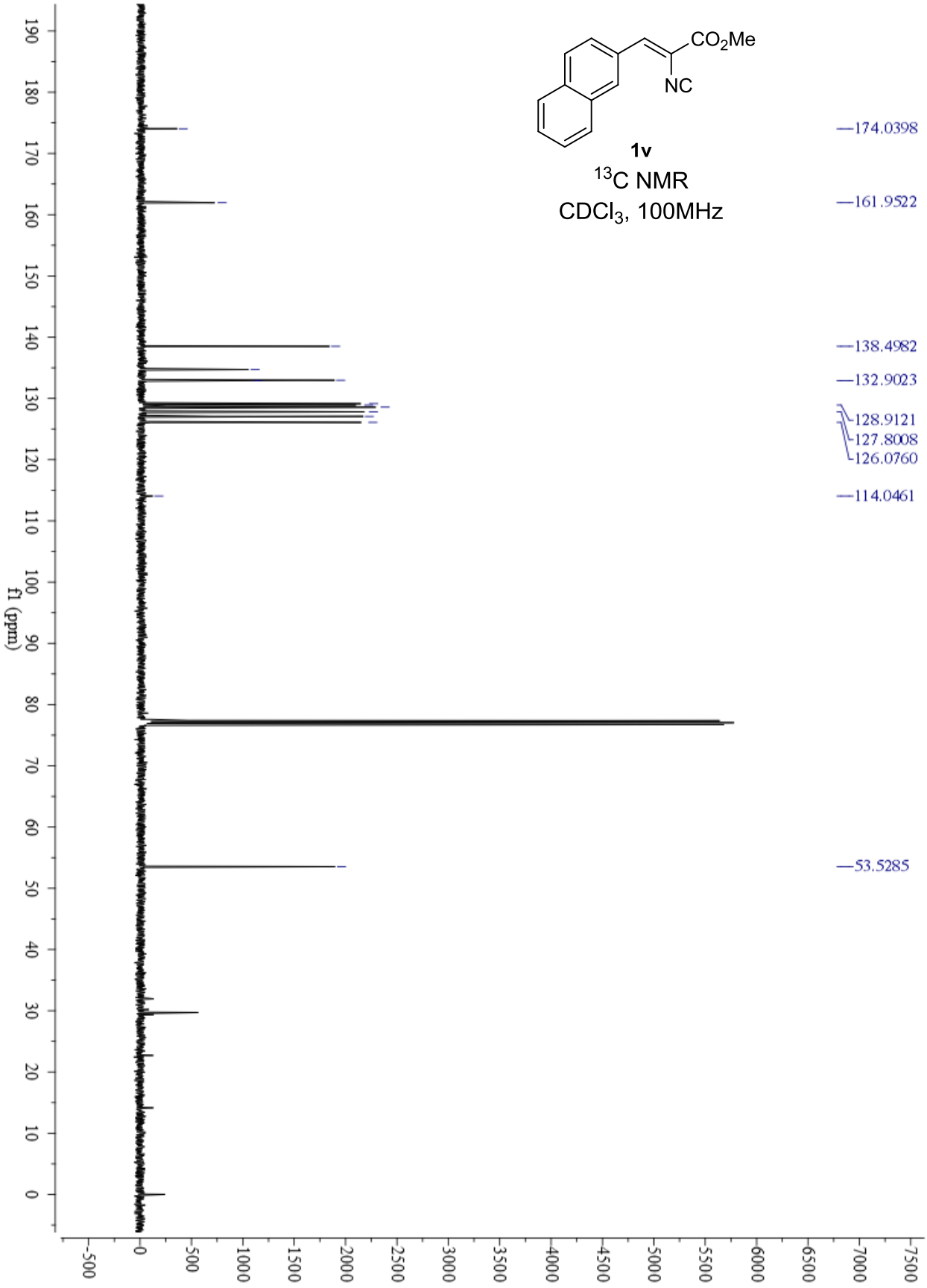

MeO
CO2Me
NC
1t
1H NMR
CDCl3, 400MHz
2.02
0.98
2.03
3.00
3.10
f1 (ppm)

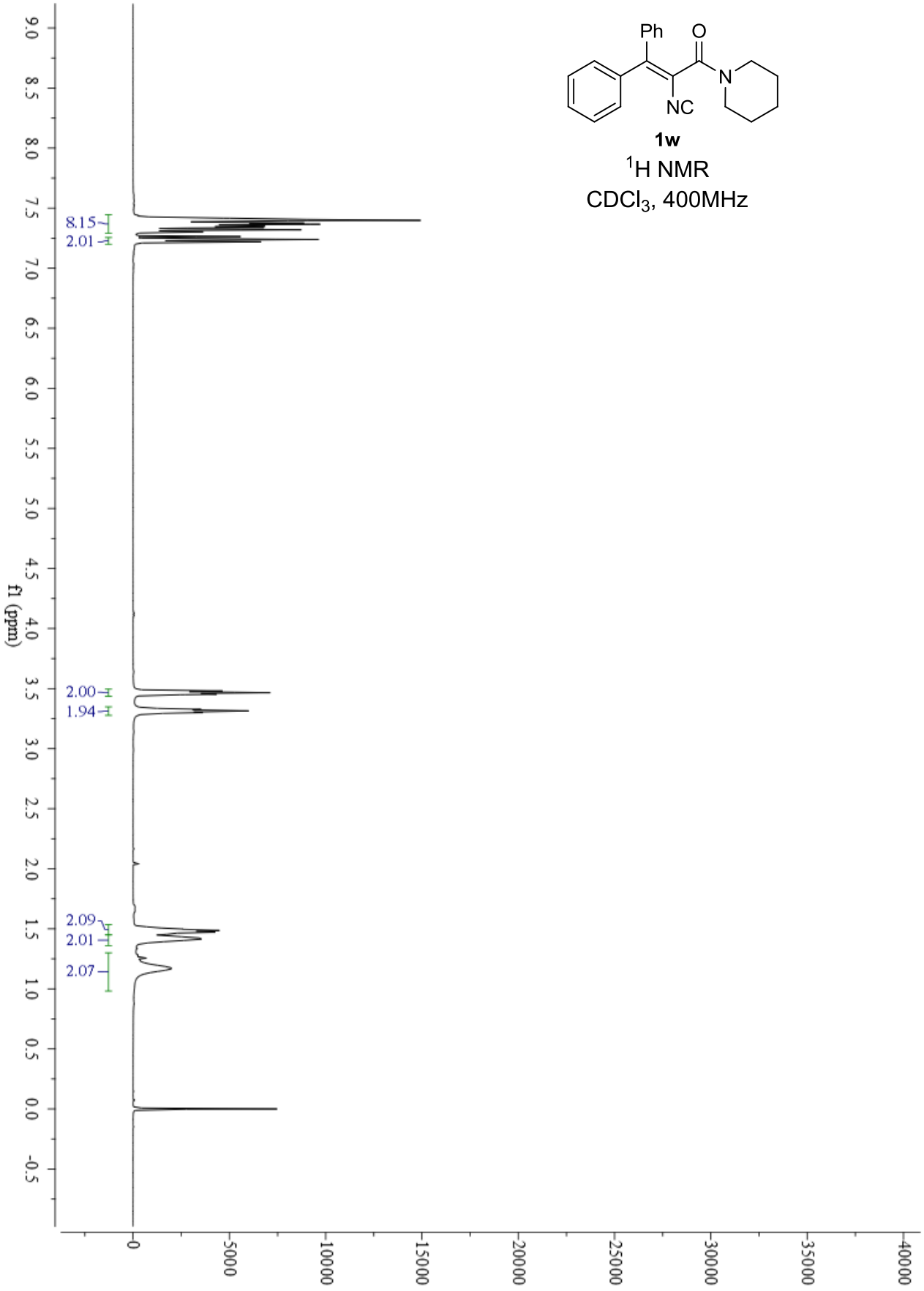

MeO
CO2Me
NC
1t
13C NMR
CDCl3, 100MHz
173.1728
162.5971
162.2936
138.0704
133.2520
123.8166
114.6207
111.7218
55.5318
53.3091
f1 (ppm)

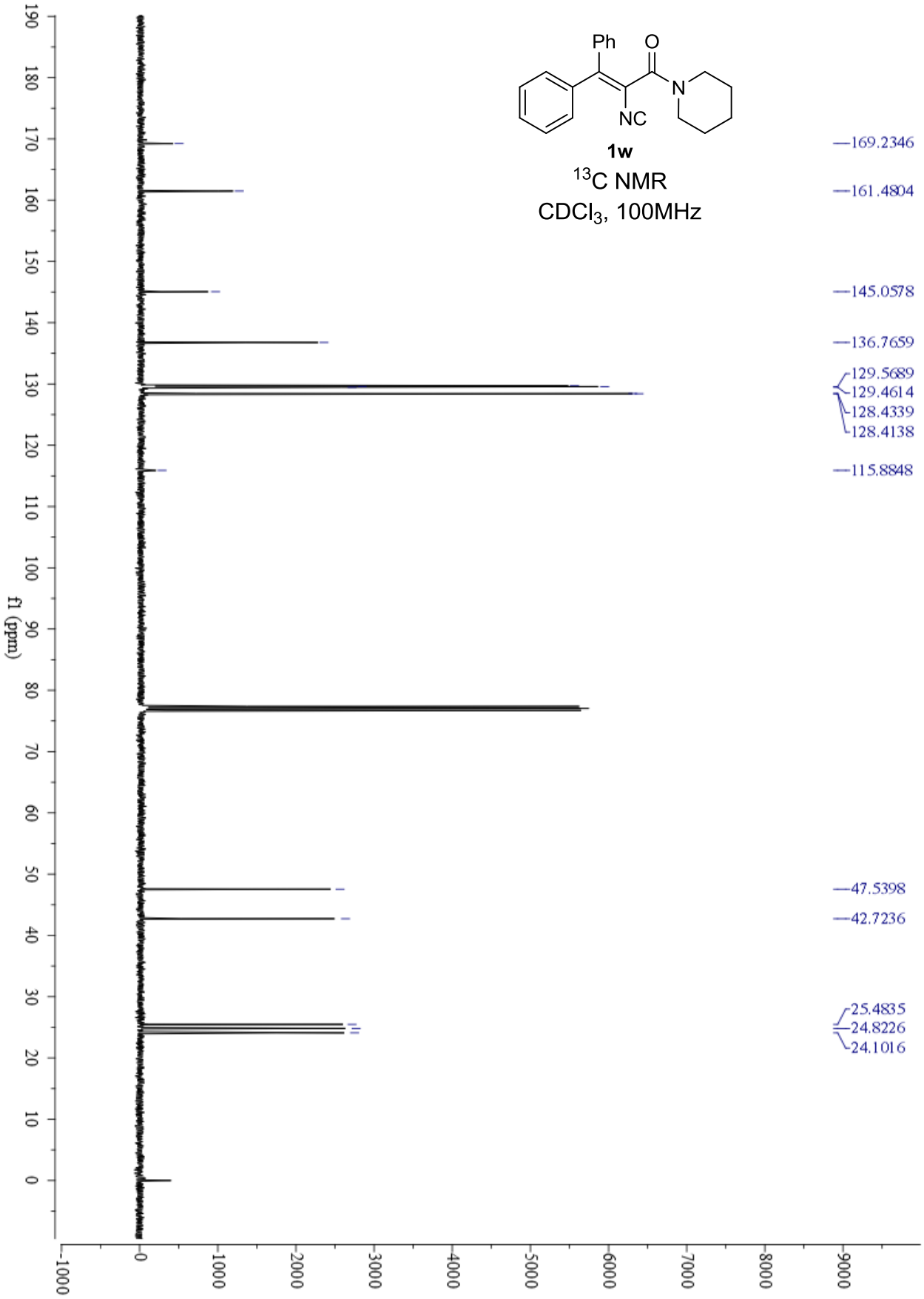

MeO
MeO
CO2Me
NC
1u
1H NMR
CDCl3, 400MHz
1.01
1.00
1.01
1.01
2.94
3.04
3.00
f1 (ppm)

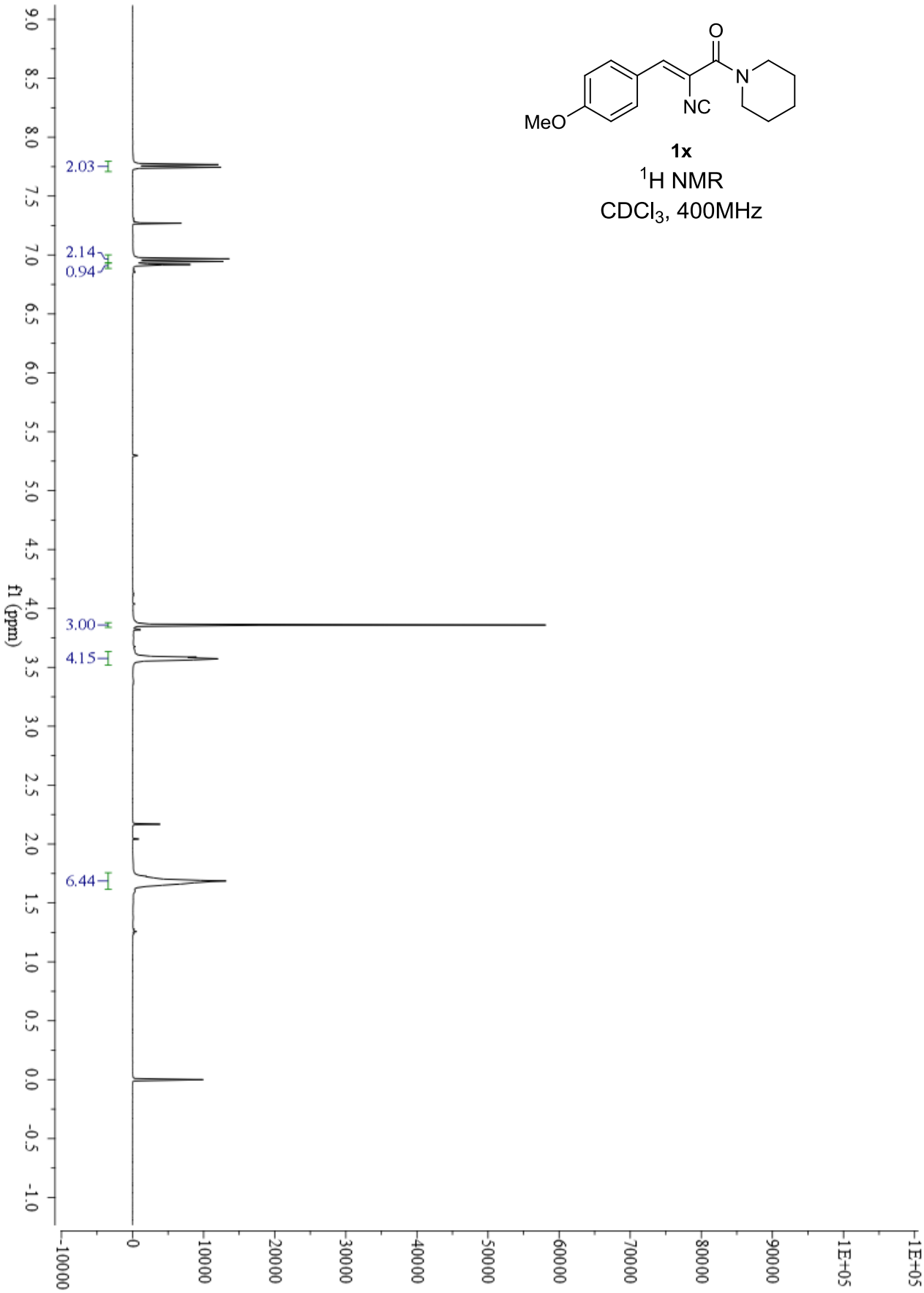

MeO
MeO
CO2Me
NC
1u
13C NMR
CDCl3, 100MHz
173.2239
162.2420
152.4373
149.1284
138.3914
126.7376
124.0455
112.2292
111.7451
110.9870
56.0674
56.0027
53.3336
f1 (ppm)

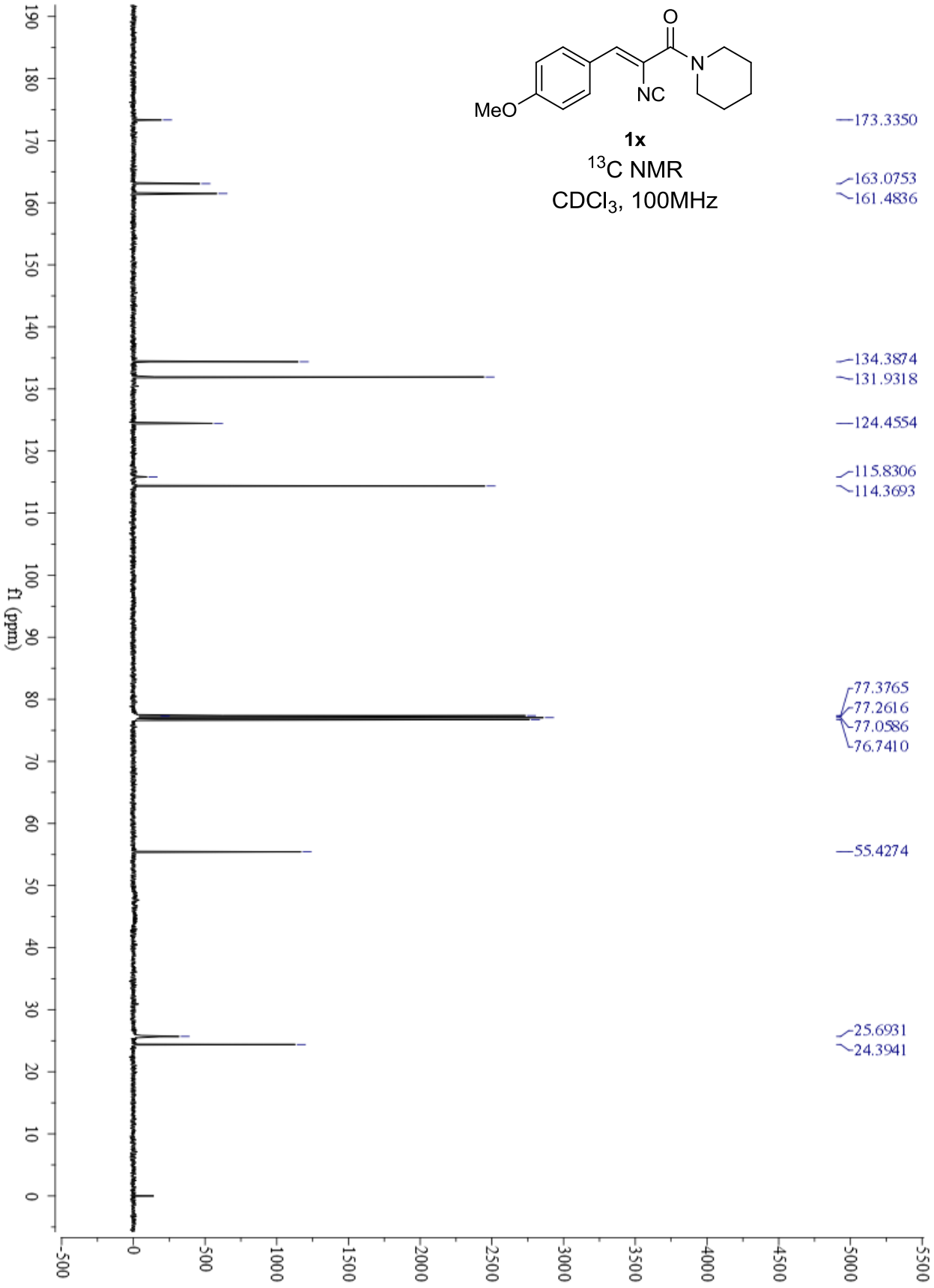

CO2Me
NC
1v
1H NMR
CDCl3, 400MHz
1.02
2.15
3.00
f1 (ppm)

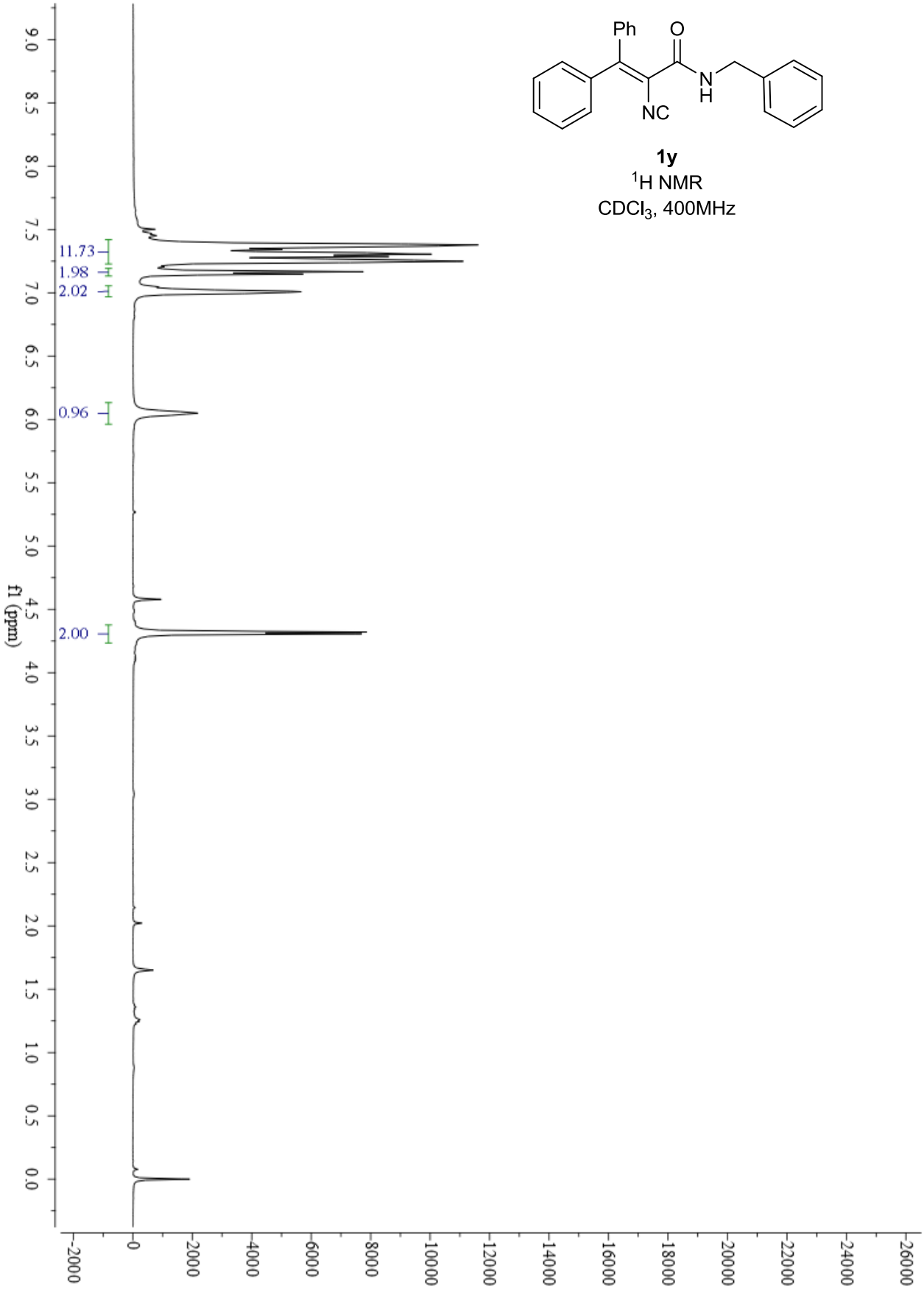

CO2Me
NC
1v
13C NMR
CDCl3, 100MHz
174.0398
161.9522
138.4982
132.9023
128.9121
127.8008
126.0760
114.0461
53.5285
f1 (ppm)


Ph
O
N
NC
1w
1H NMR
CDCl3, 400MHz
8.15
2.01
2.00
1.94
2.09
2.01
2.07
f1 (ppm)


Ph
O
N
NC
1w
13C NMR
CDCl3, 100MHz
169.2346
161.4804
145.0578
136.7659
129.5689
129.4614
128.4339
128.4138
115.8848
47.5398
42.7236
25.4835
24.8226
24.1016
f1 (ppm)


MeO
NC
O
N
1x
1H NMR
CDCl3, 400MHz
2.03
2.14
0.94
3.00
4.15
6.44
f1 (ppm)

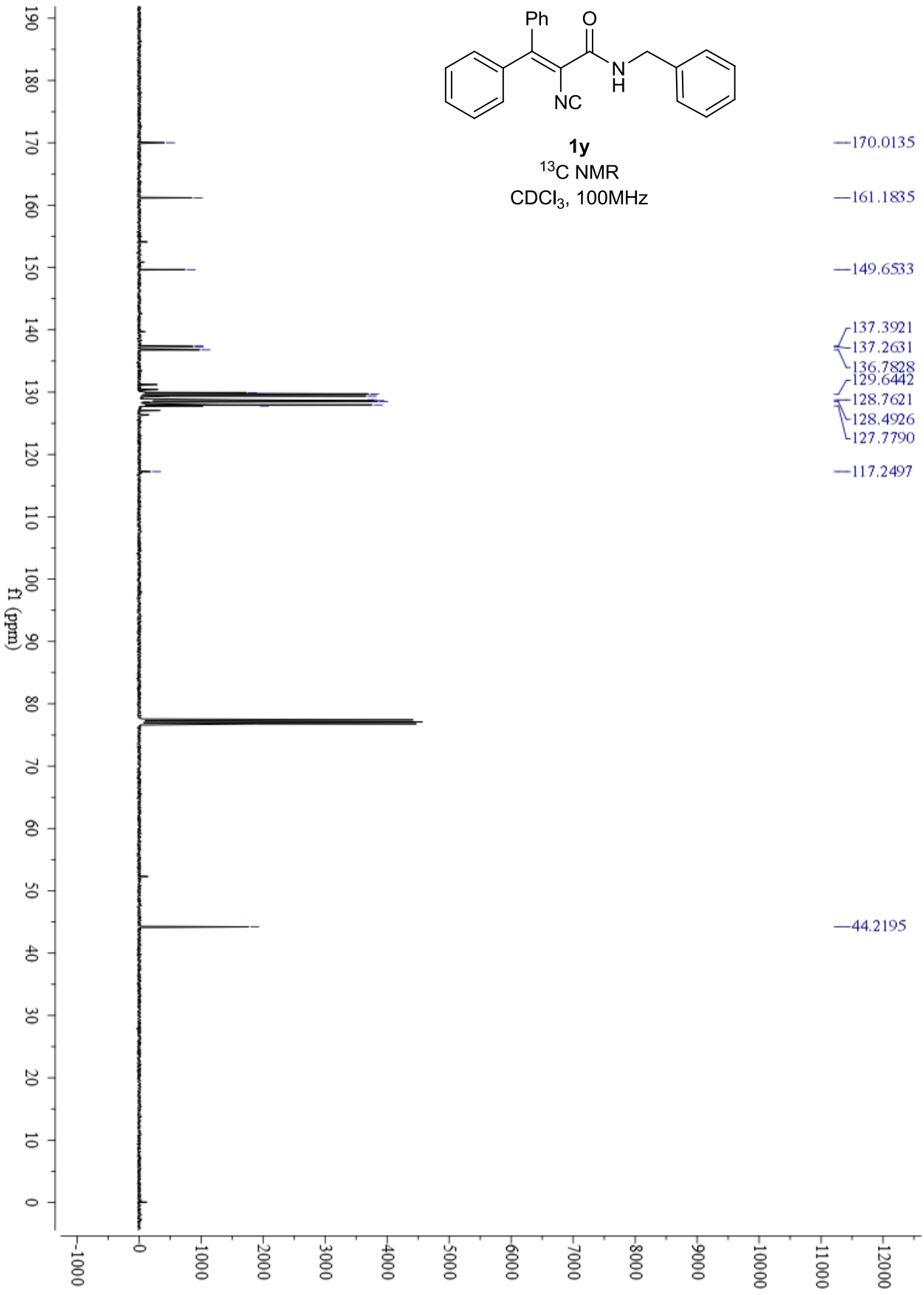

MeO
NC
O
N
1x
^{13}C NMR
$CDCl_3$, 100MHz
173.3350
163.0753
161.4836
134.3874
131.9318
124.4554
115.8306
114.3693
77.3765
77.2616
77.0586
76.7410
55.4274
25.6931
24.3941
f1 (ppm)

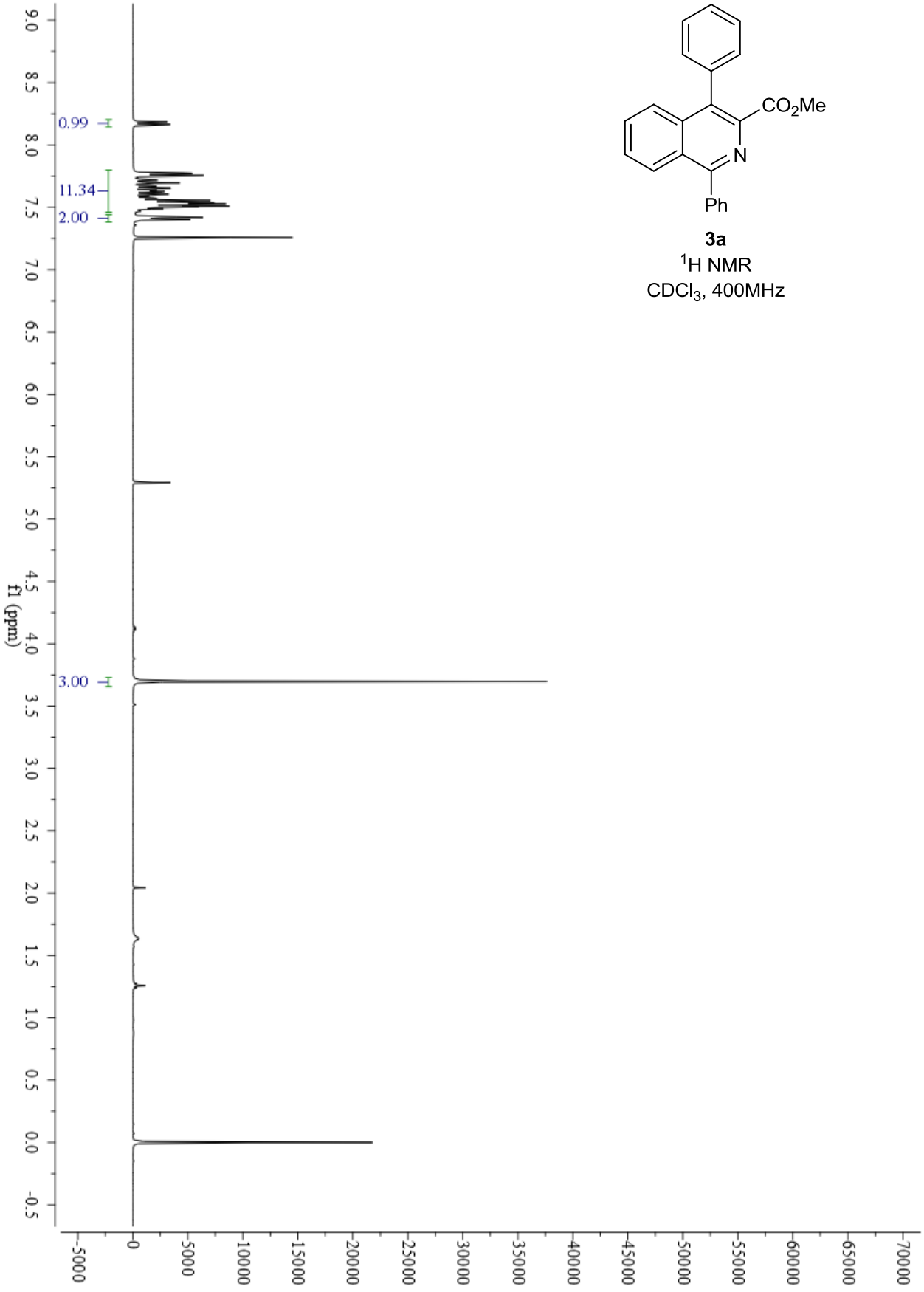


1y

^{1}H NMR

$CDCl_3$, 400MHz

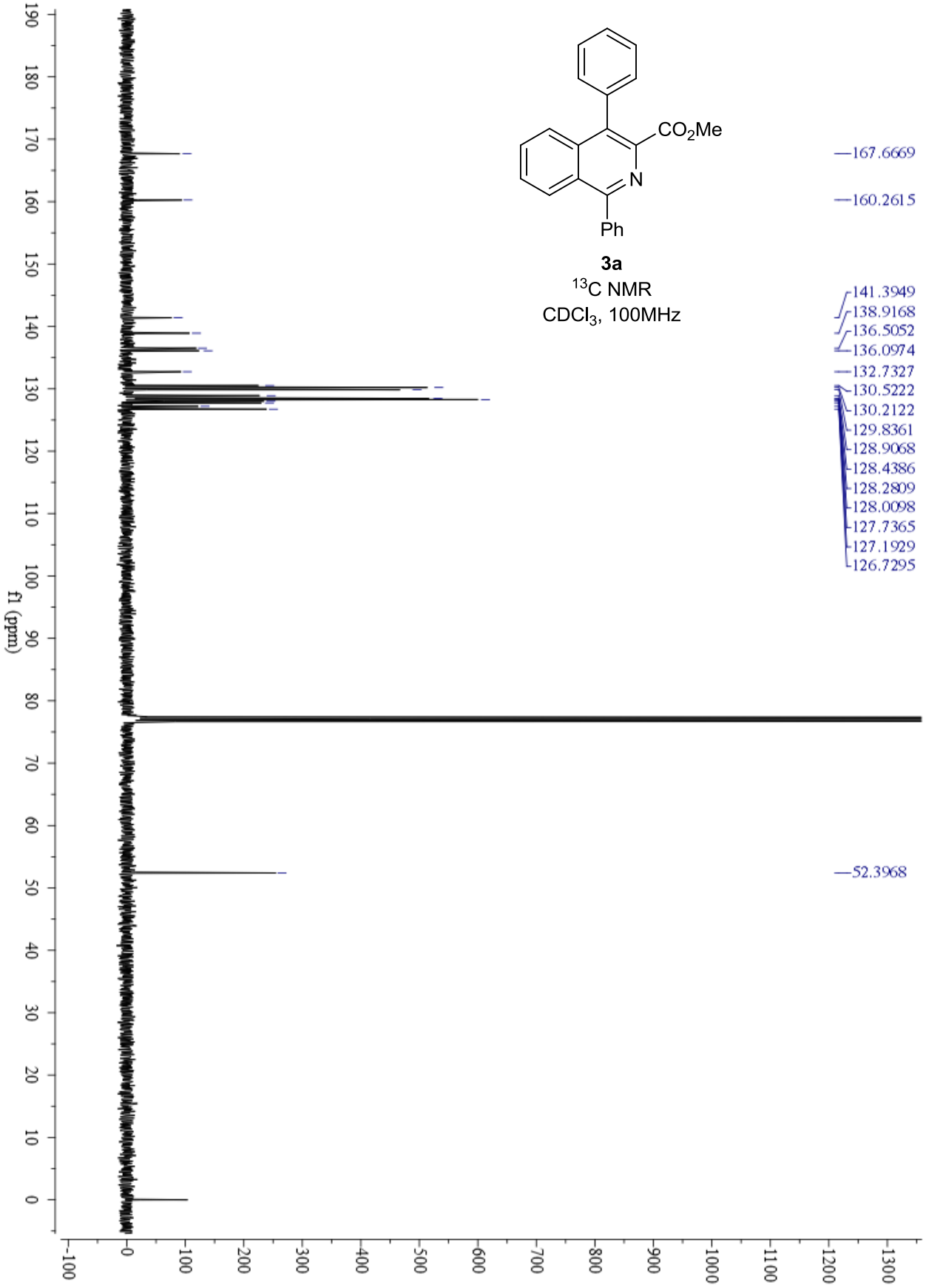

Ph
O
N
H
NC
1y
13C NMR
CDCl3, 100MHz
170.0135
161.1835
149.6533
137.3921
137.2631
136.7828
129.6442
128.7621
128.4926
127.7790
117.2497
44.2195
f1 (ppm)

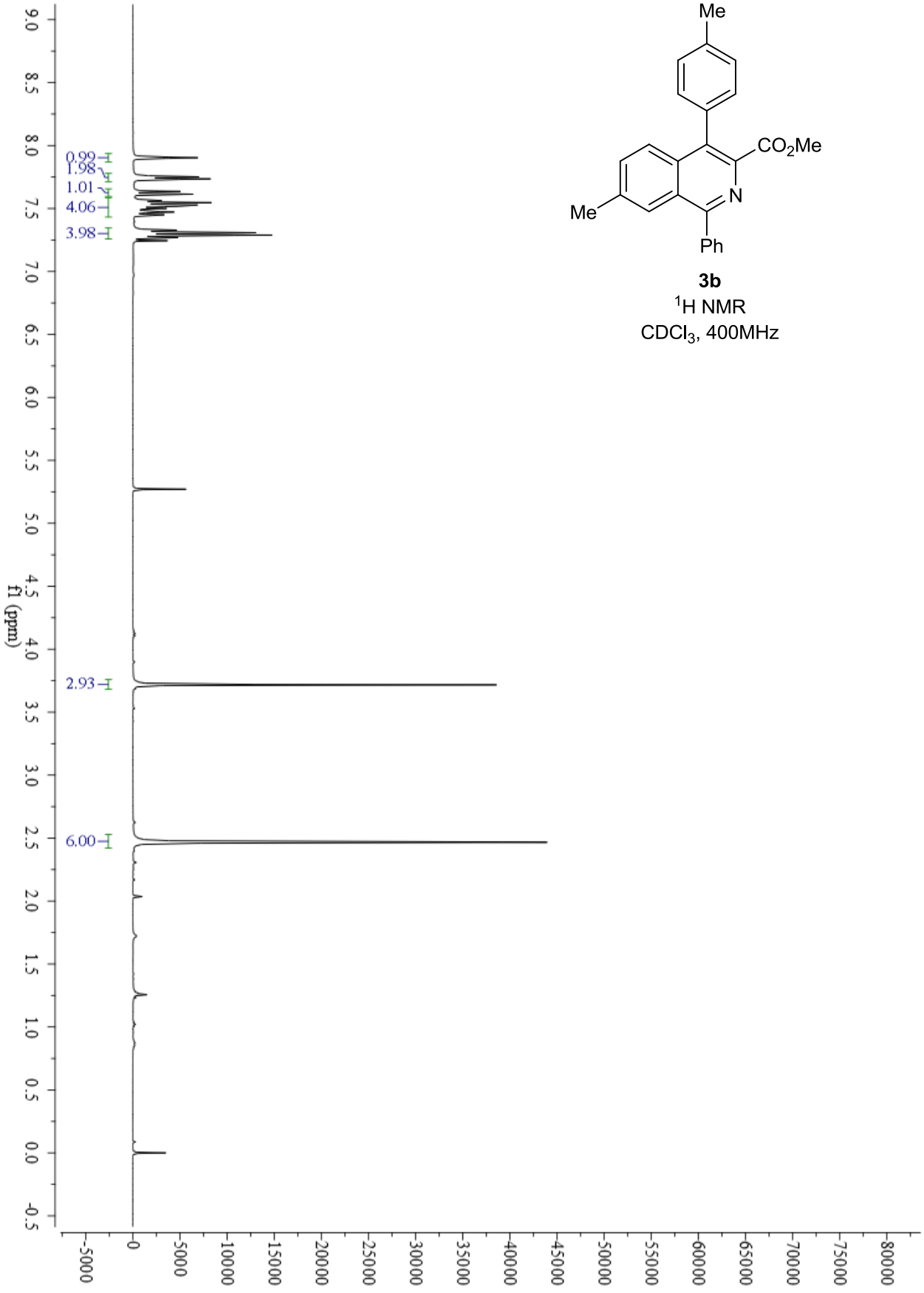


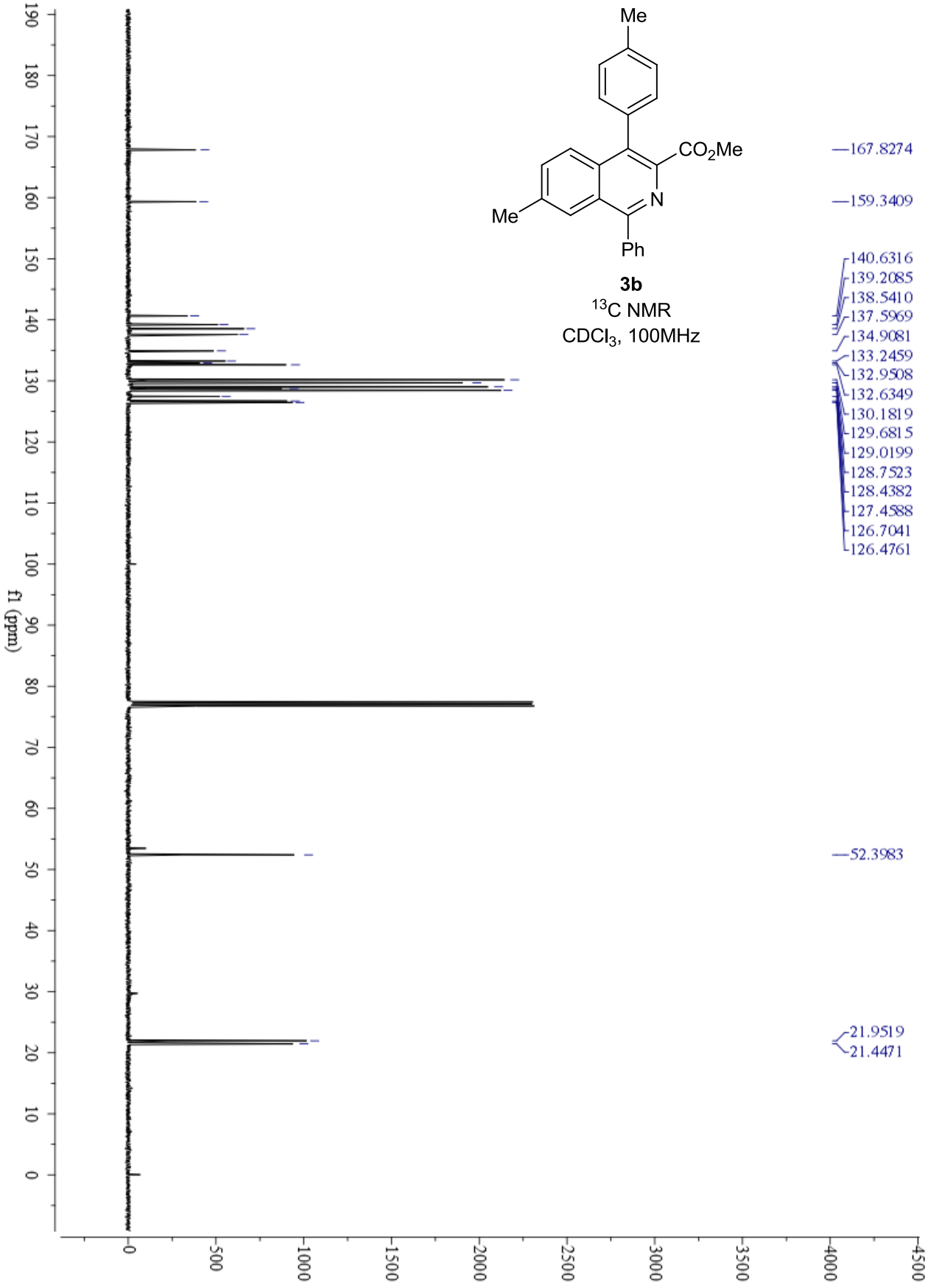
3a

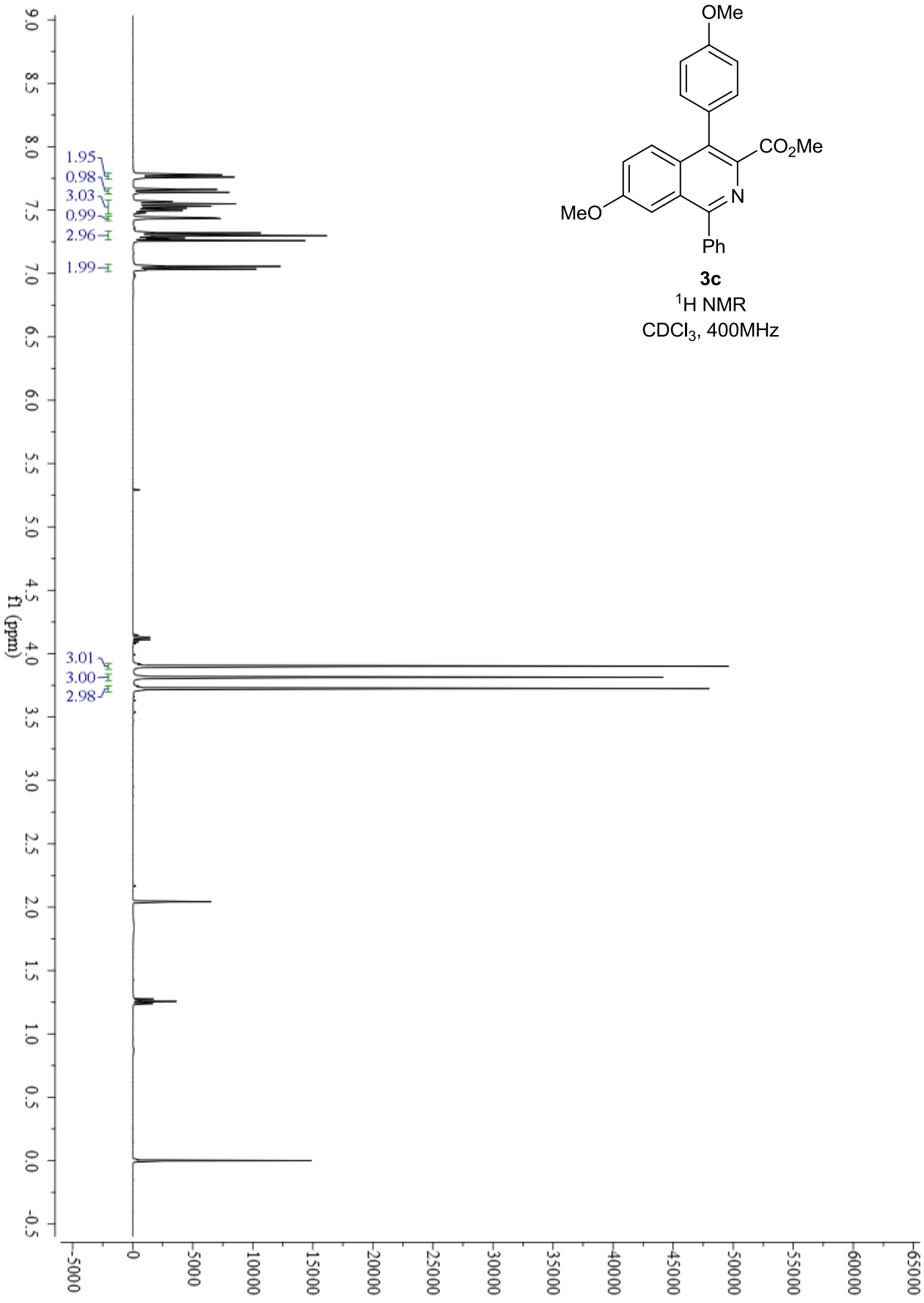
^{1}H NMR

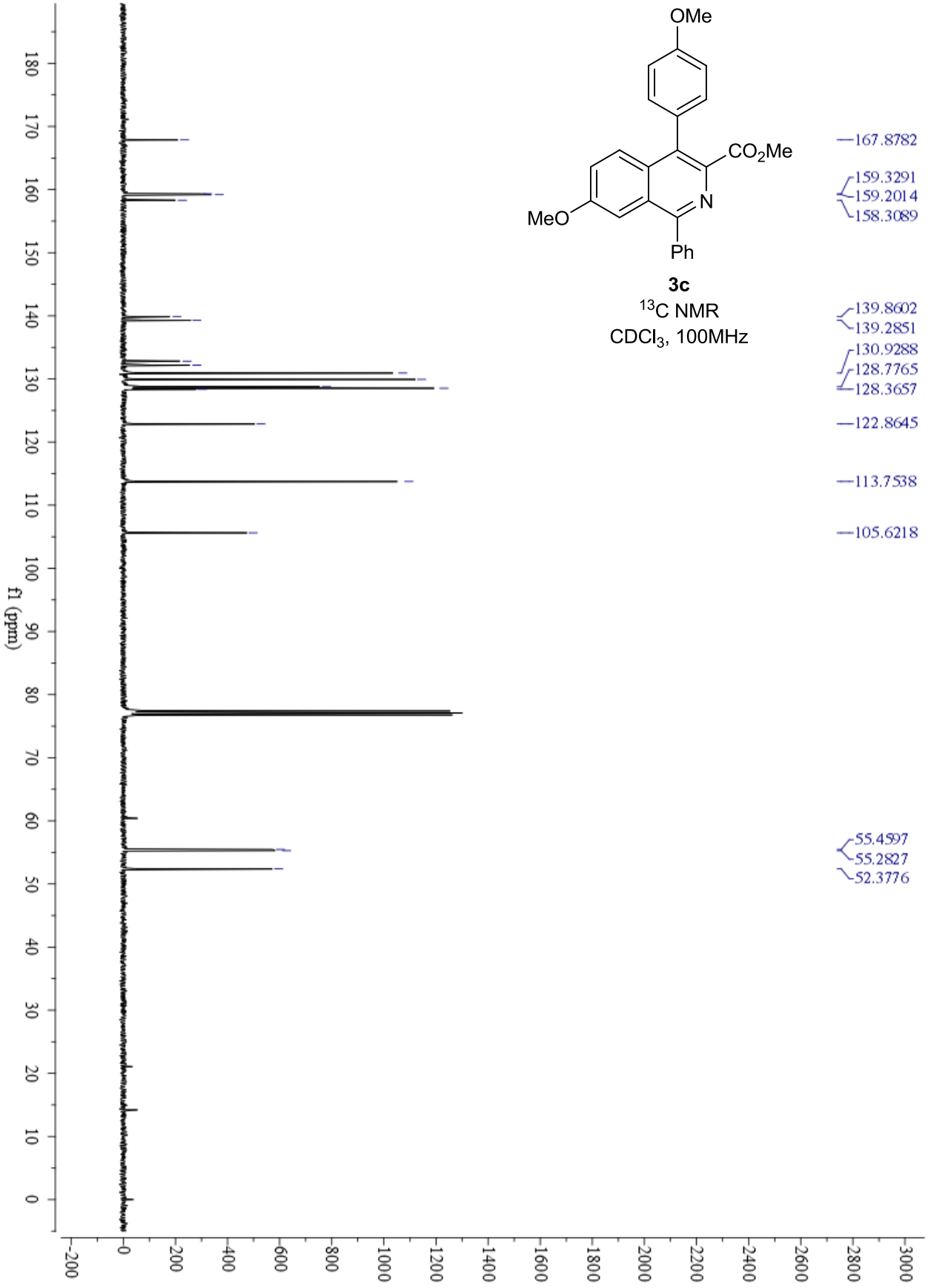
$CDCl_3$, 400MHz

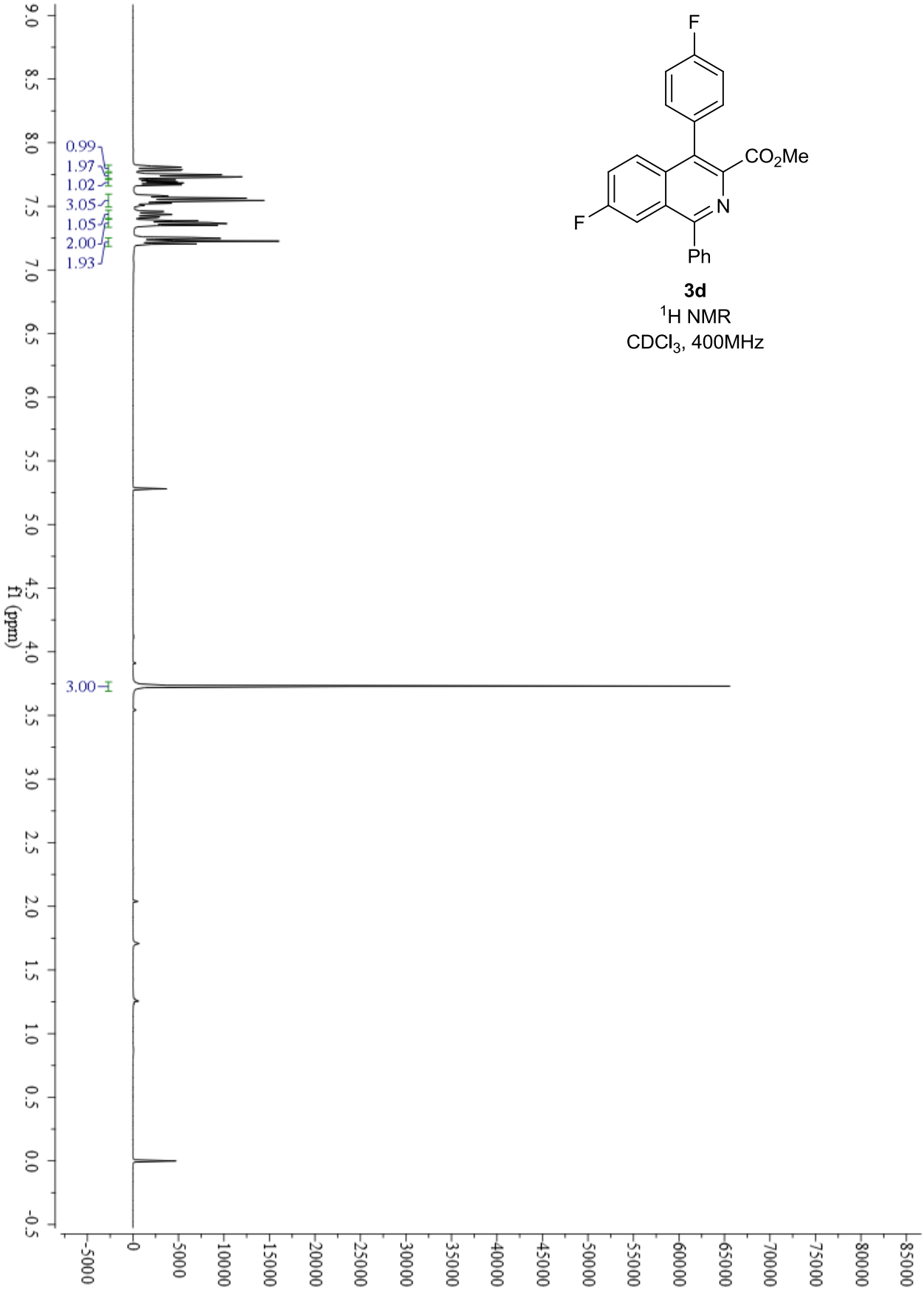

CO2Me
N
Ph
3a
13C NMR
CDCl3, 100MHz
167.6669
160.2615
141.3949
138.9168
136.5052
136.0974
132.7327
130.5222
130.2122
129.8361
128.9068
128.4386
128.2809
128.0098
127.7365
127.1929
126.7295
52.3968
f1 (ppm)

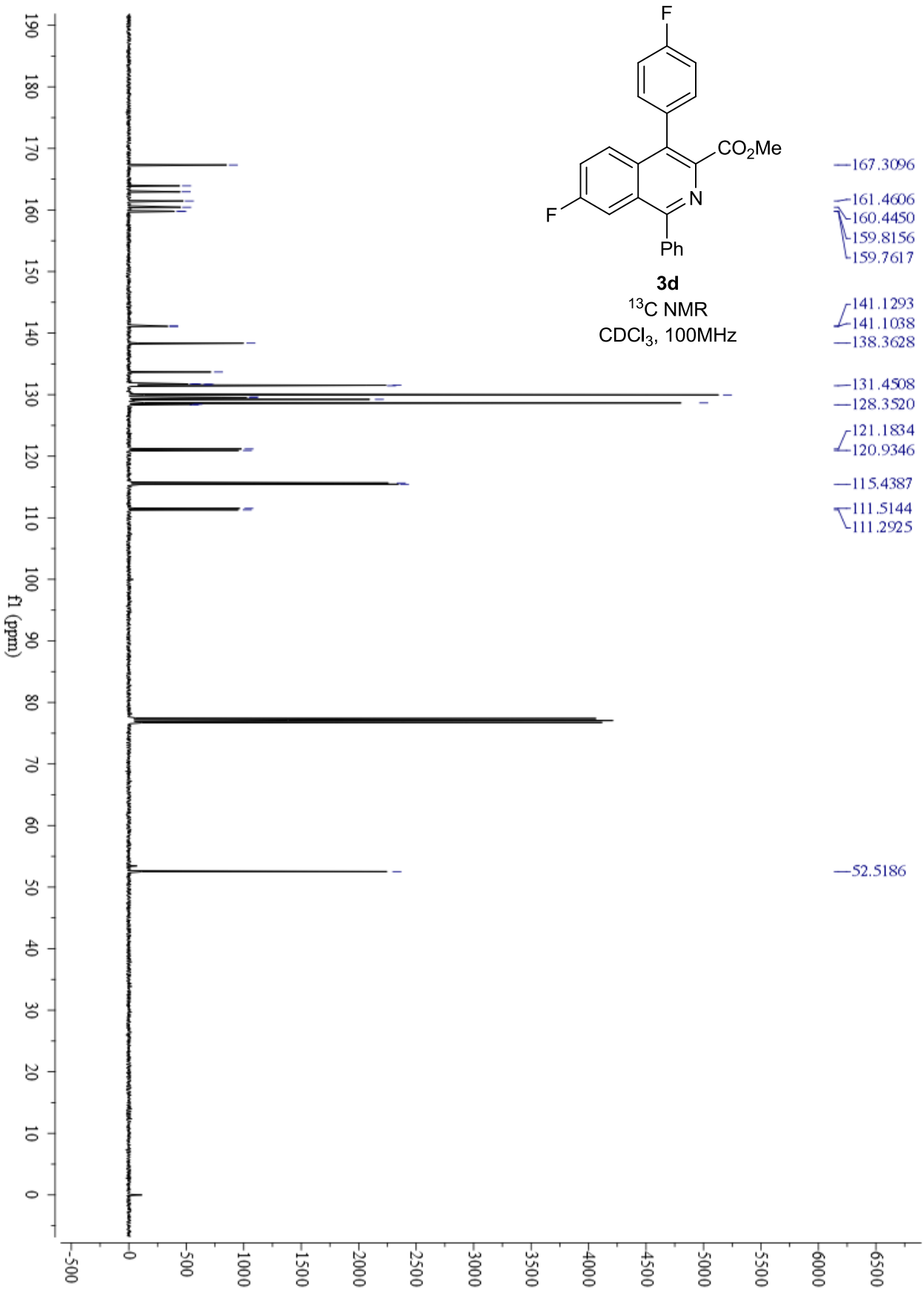

Me
CO2Me
N
Me
Ph
3b
1H NMR
CDCl3, 400MHz
0.99
1.98
1.01
4.06
3.98
2.93
6.00
f1 (ppm)

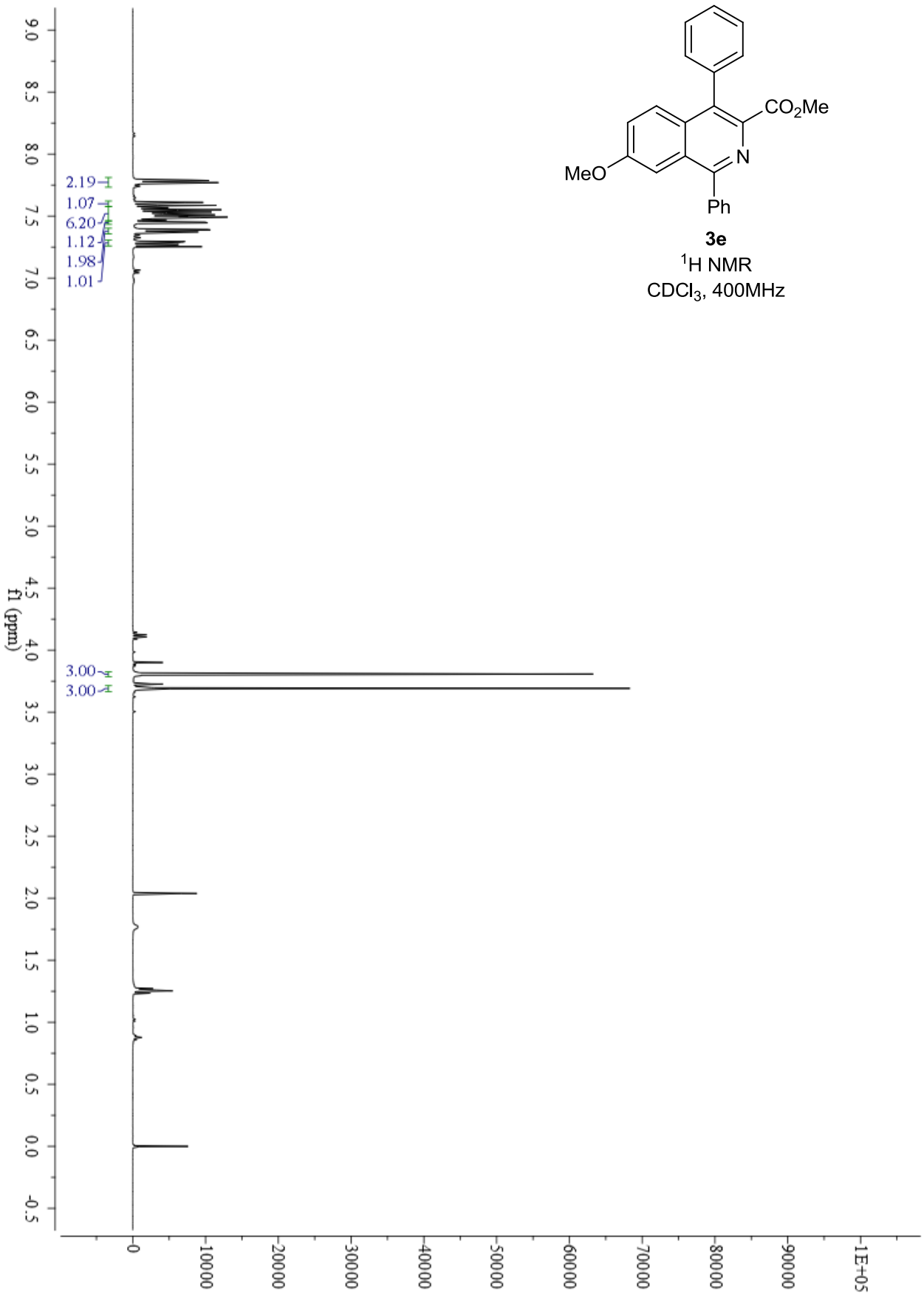

Me
CO2Me
N
Me
Ph
3b
13C NMR
CDCl3, 100MHz
167.8274
159.3409
140.6316
139.2085
138.5410
137.5969
134.9081
133.2459
132.9508
132.6349
130.1819
129.6815
129.0199
128.7523
128.4382
127.4588
126.7041
126.4761
52.3983
21.9519
21.4471
f1 (ppm)


OMe
CO2Me
N
MeO
Ph
3c
1H NMR
CDCl3, 400MHz
1.95
0.98
3.03
0.99
2.96
1.99
3.01
3.00
2.98
f1 (ppm)


OMe
CO2Me
N
MeO
Ph
3c
13C NMR
CDCl3, 100MHz
167.8782
159.3291
159.2014
158.3089
139.8602
139.2851
130.9288
128.7765
128.3657
122.8645
113.7538
105.6218
55.4597
55.2827
52.3776
f1 (ppm)


F
CO2Me
N
F
Ph
3d
1H NMR
CDCl3, 400MHz
0.99
1.97
1.02
3.05
1.05
2.00
1.93
3.00
f1 (ppm)

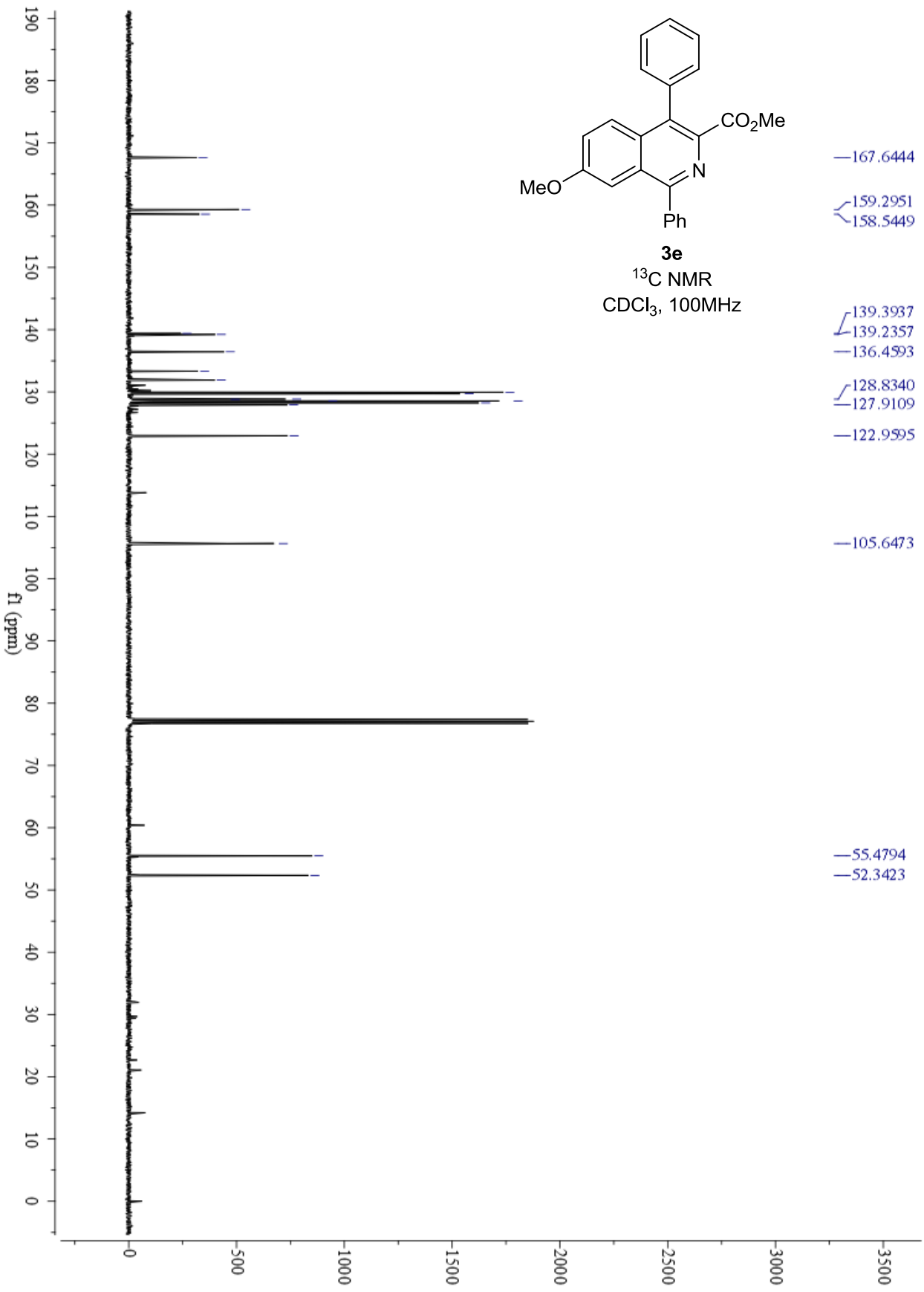

F
CO2Me
N
F
Ph
3d
13C NMR
CDCl3, 100MHz
167.3096
161.4606
160.4450
159.8156
159.7617
141.1293
141.1038
138.3628
131.4508
128.3520
121.1834
120.9346
115.4387
111.5144
111.2925
52.5186
f1 (ppm)

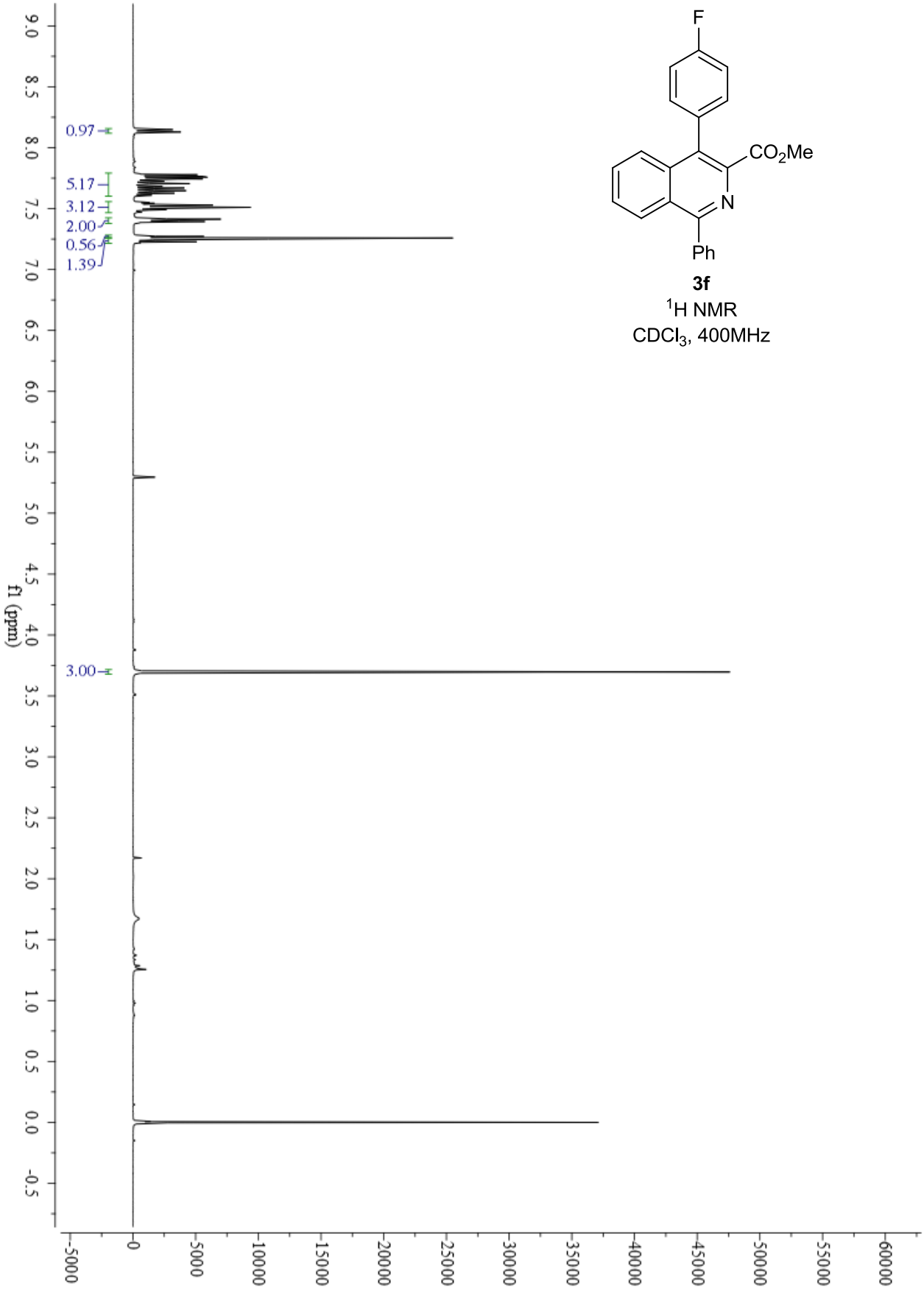


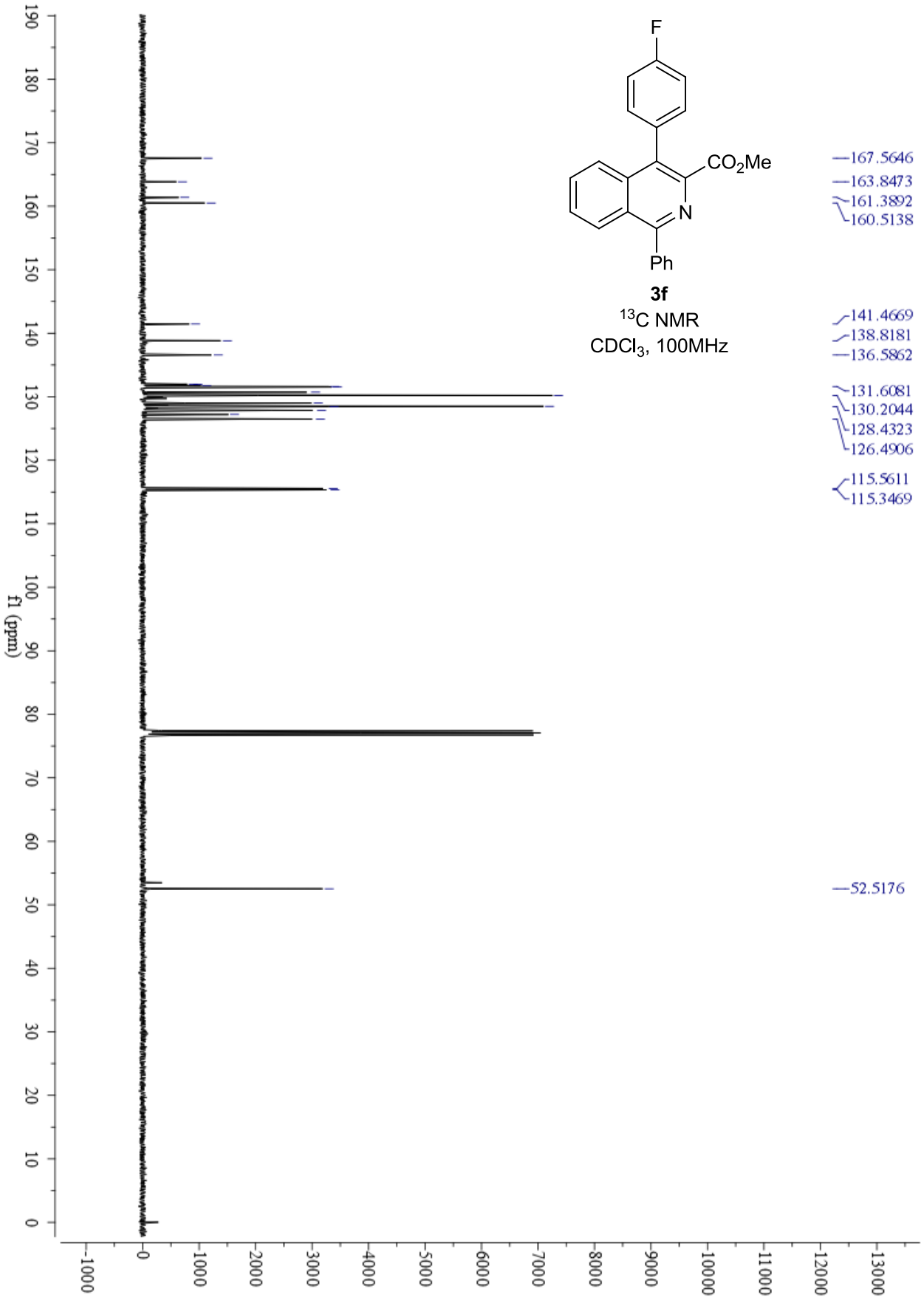
3e

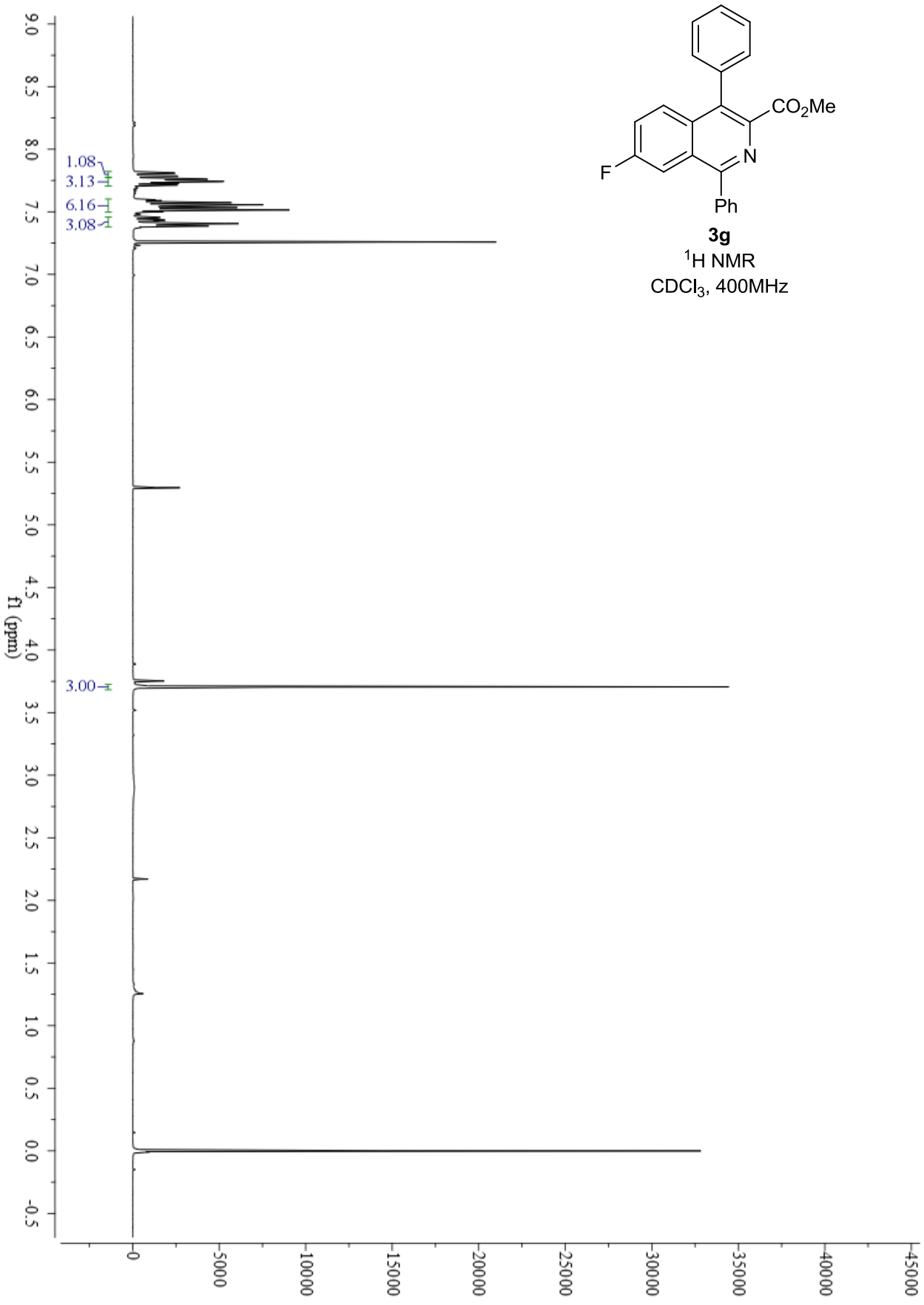
^{1}H NMR

$CDCl_3$, 400MHz


CO2Me
N
MeO
Ph
3e
13C NMR
CDCl3, 100MHz
167.6444
159.2951
158.5449
139.3937
139.2357
136.4593
128.8340
127.9109
122.9595
105.6473
55.4794
52.3423
f1 (ppm)


F
CO2Me
N
Ph
3f
1H NMR
CDCl3, 400MHz
0.97
5.17
3.12
2.00
0.56
1.39
3.00
f1 (ppm)

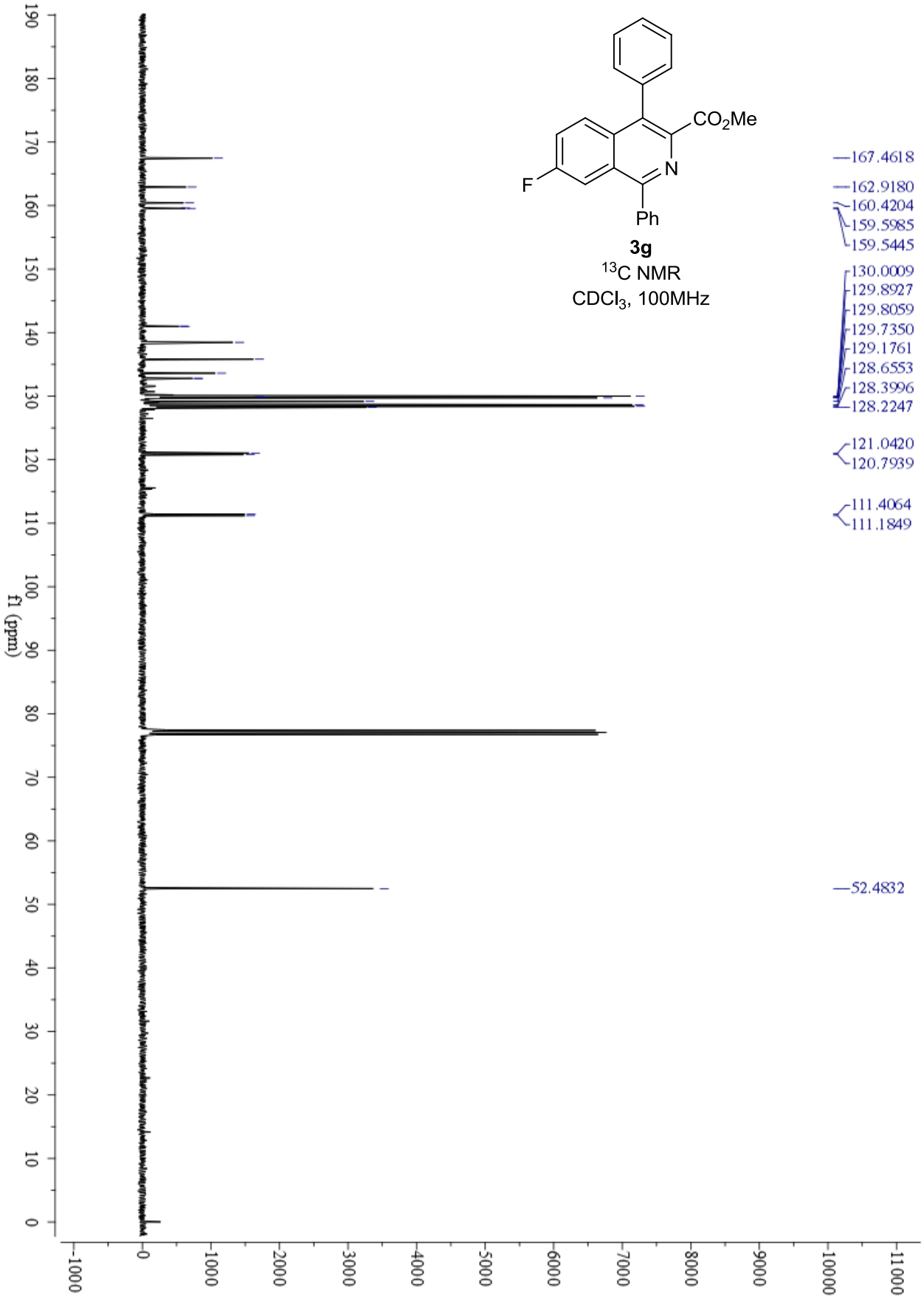

F
CO2Me
N
Ph
3f
13C NMR
CDCl3, 100MHz
167.5646
163.8473
161.3892
160.5138
141.4669
138.8181
136.5862
131.6081
130.2044
128.4323
126.4906
115.5611
115.3469
52.5176
f1 (ppm)

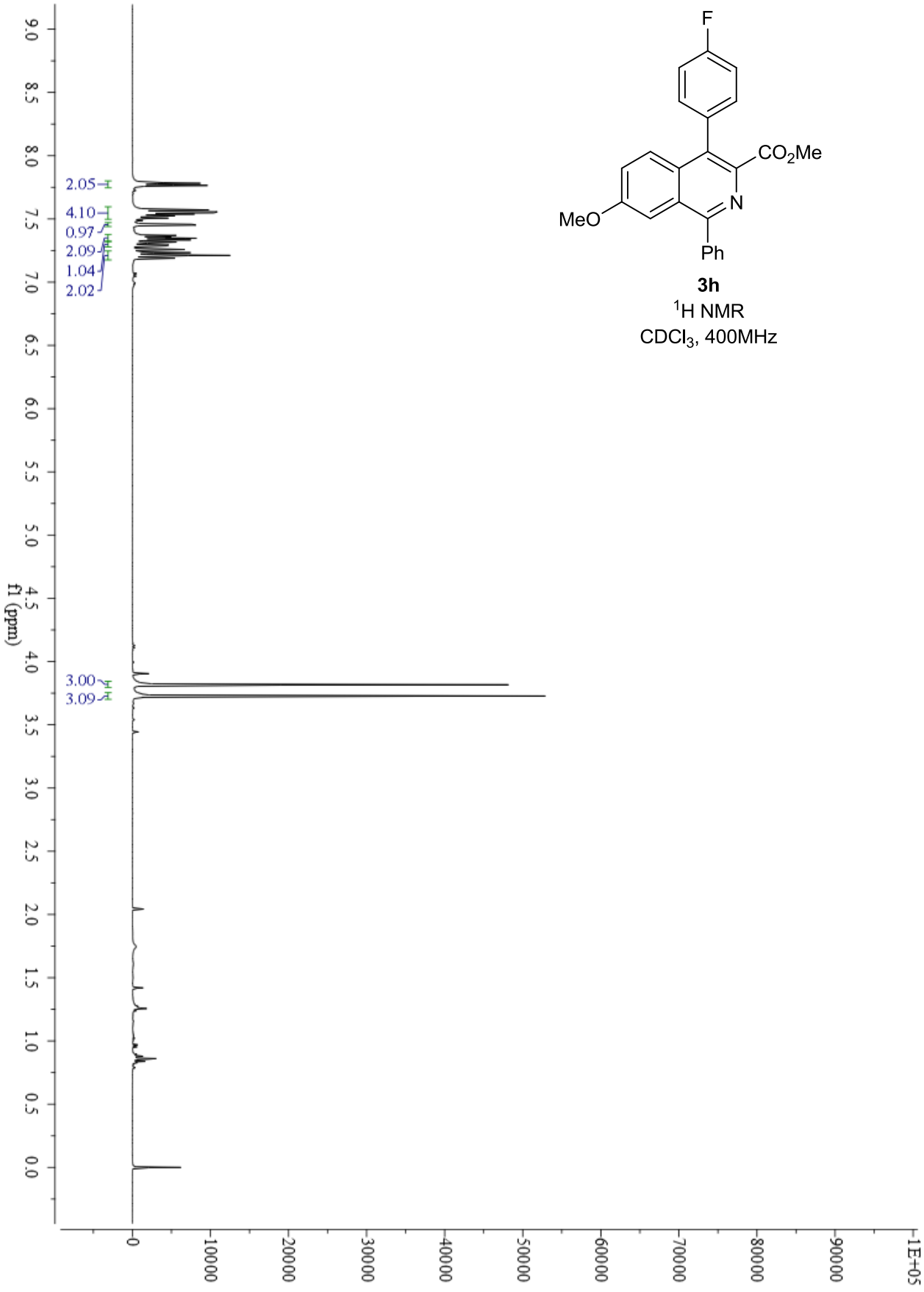


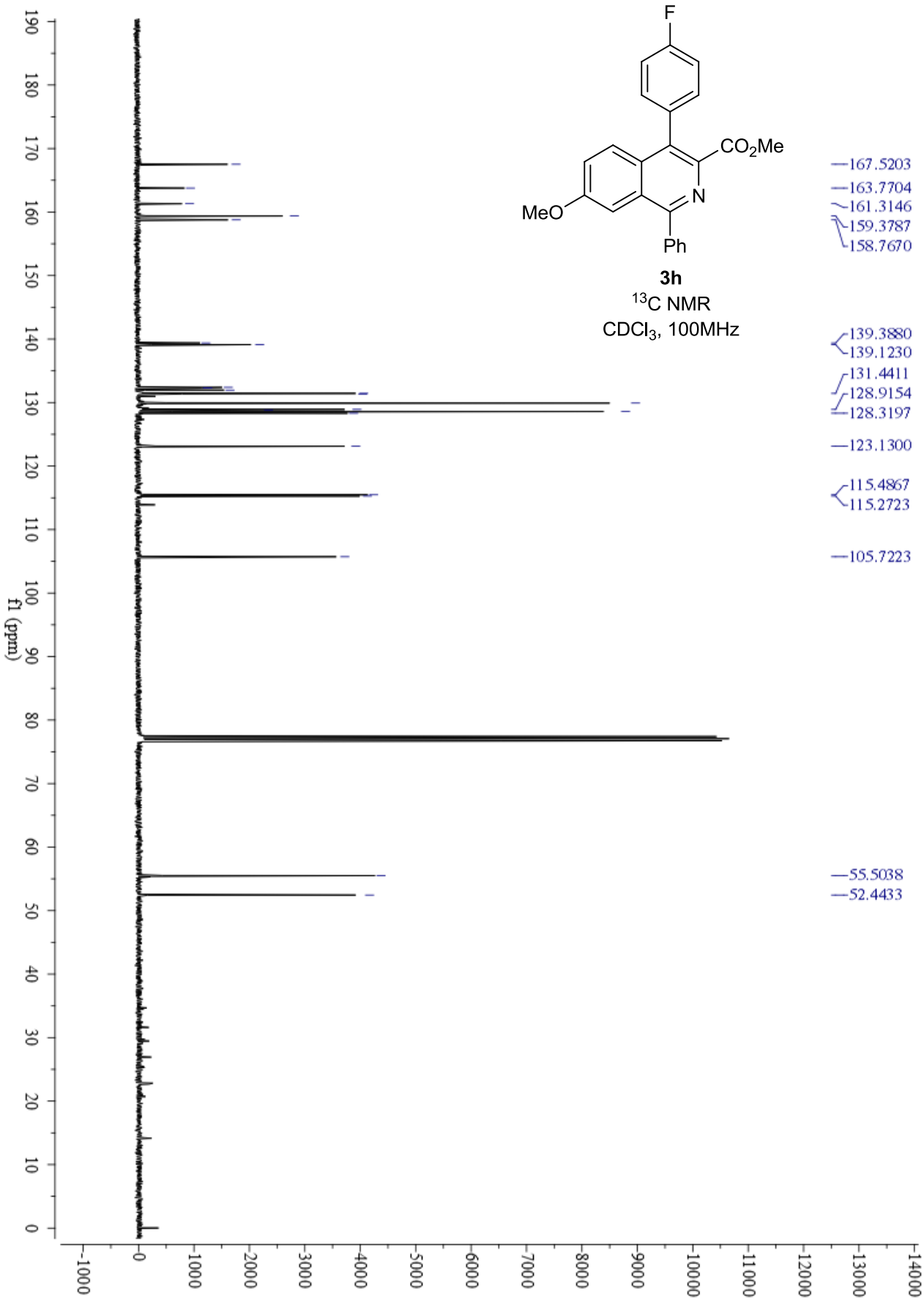
3g

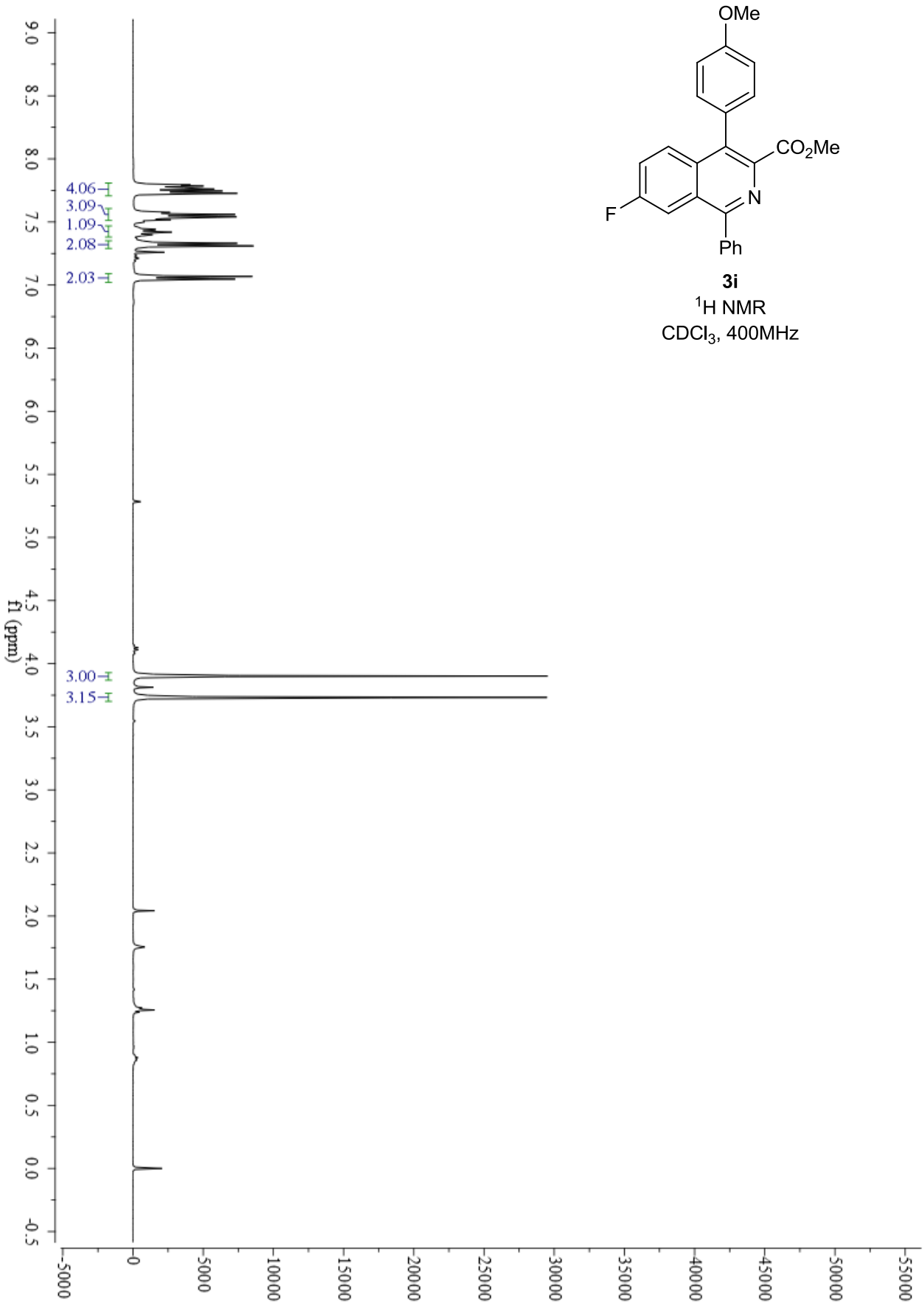
^{1}H NMR

$CDCl_3$, 400MHz


CO2Me
N
F
Ph
3g
13C NMR
CDCl3, 100MHz
167.4618
162.9180
160.4204
159.5985
159.5445
130.0009
129.8927
129.8059
129.7350
129.1761
128.6553
128.3996
128.2247
121.0420
120.7939
111.4064
111.1849
52.4832
f1 (ppm)


F
CO2Me
N
MeO
Ph
3h
1H NMR
CDCl3, 400MHz
2.05
4.10
0.97
2.09
1.04
2.02
3.00
3.09
f1 (ppm)

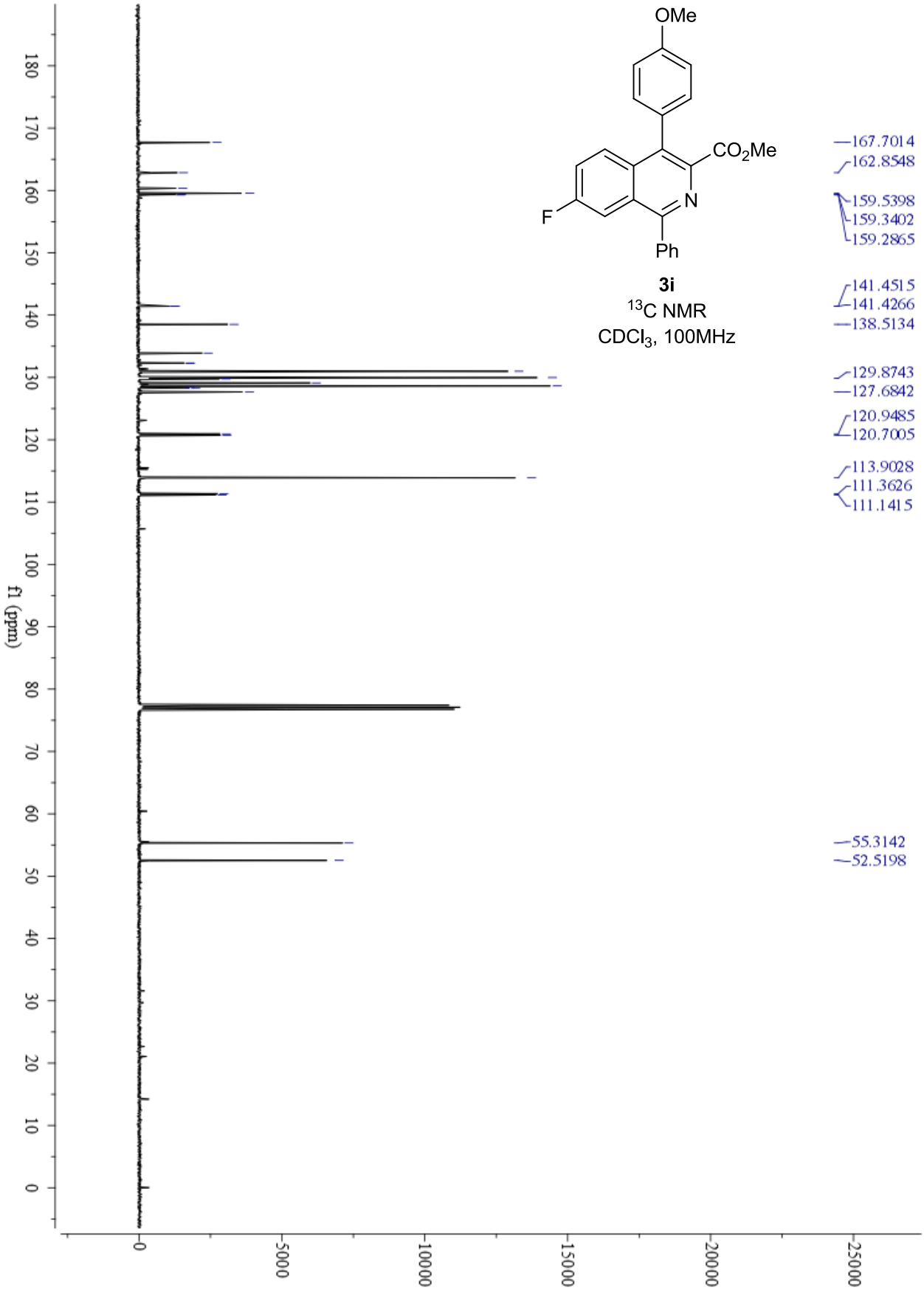

F
CO2Me
N
MeO
Ph
3h
13C NMR
CDCl3, 100MHz
167.5203
163.7704
161.3146
159.3787
158.7670
139.3880
139.1230
131.4411
128.9154
128.3197
123.1300
115.4867
115.2723
105.7223
55.5038
52.4433
f1 (ppm)

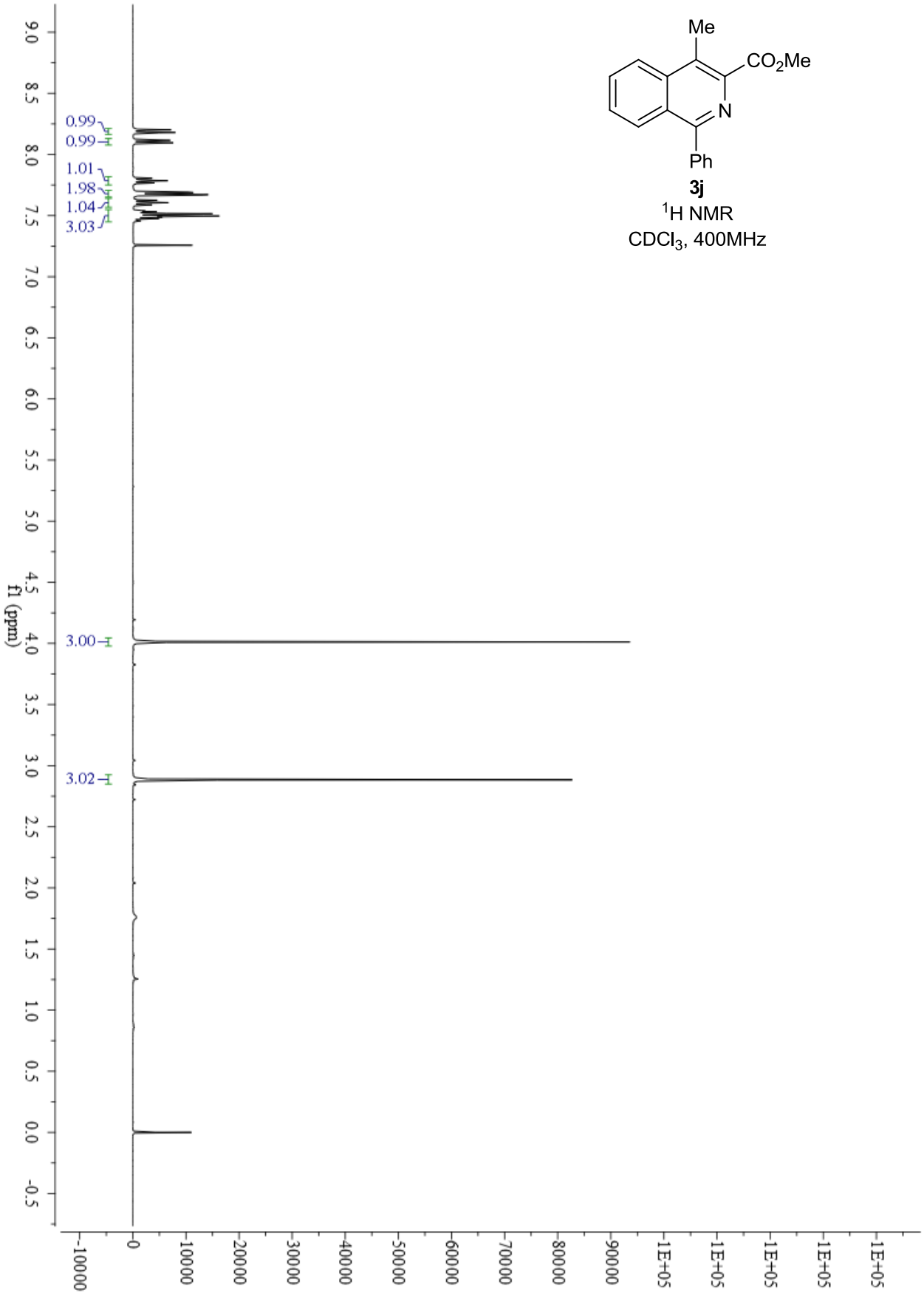


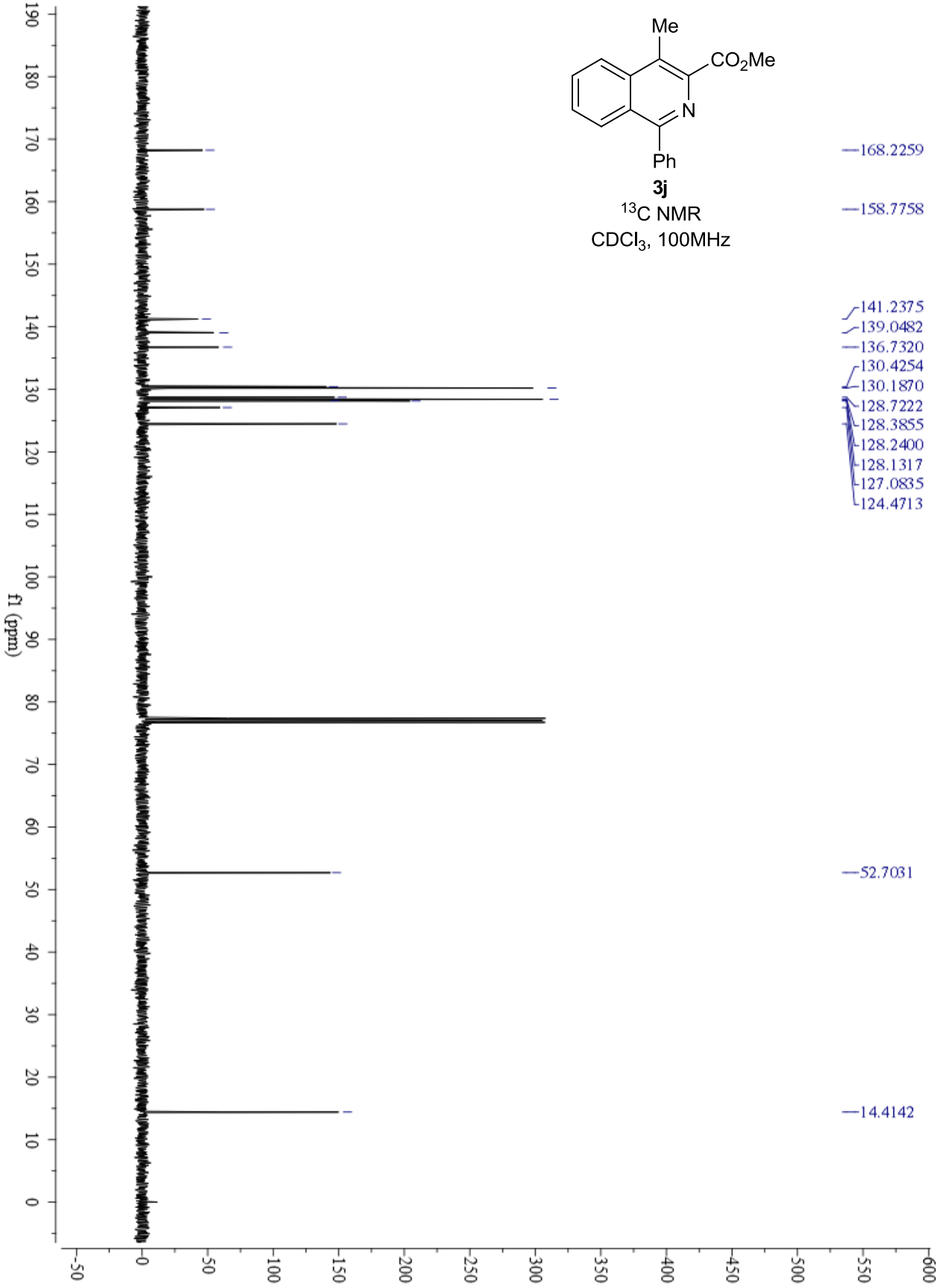
3i

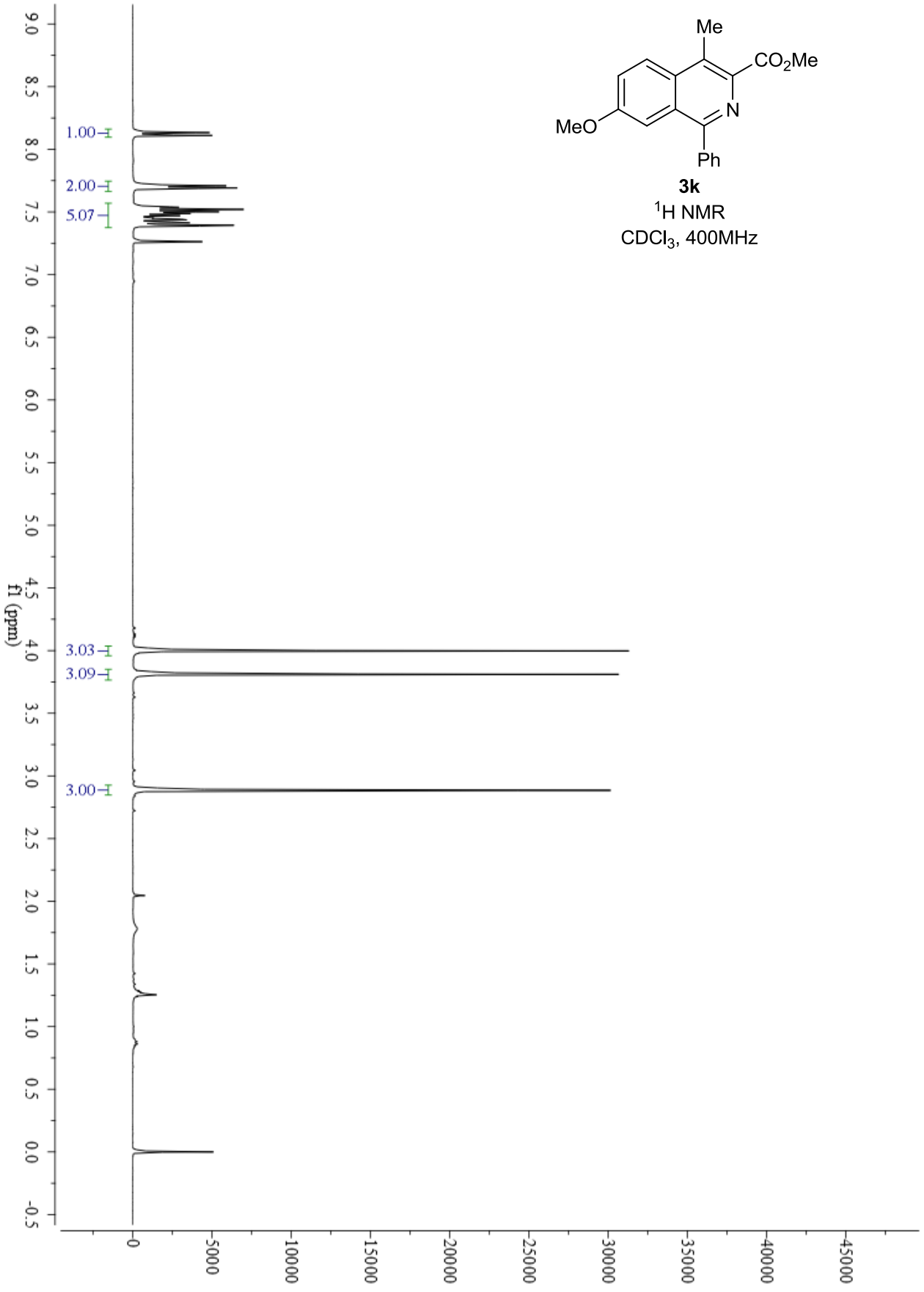
^{1}H NMR

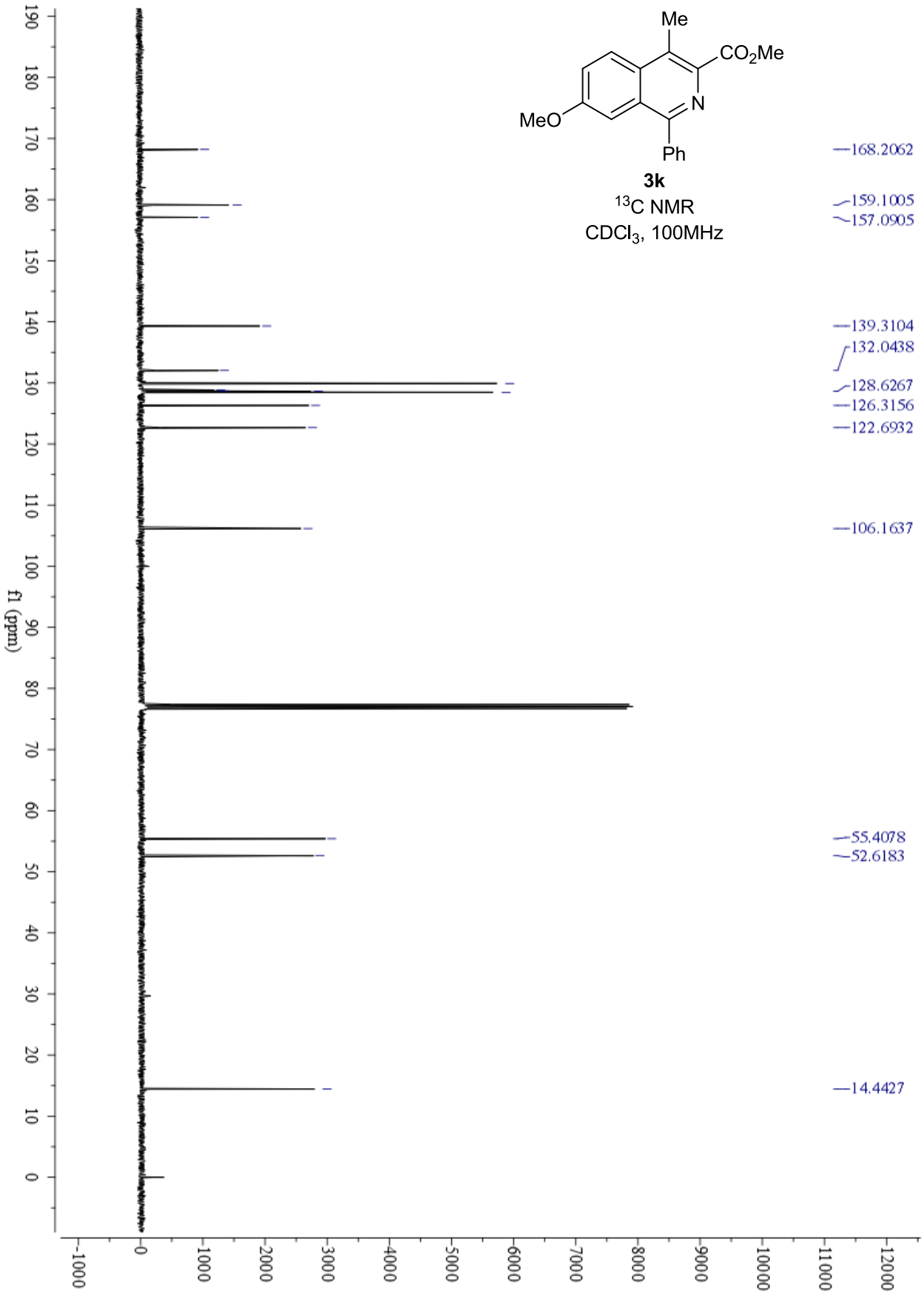
$CDCl_3$, 400MHz

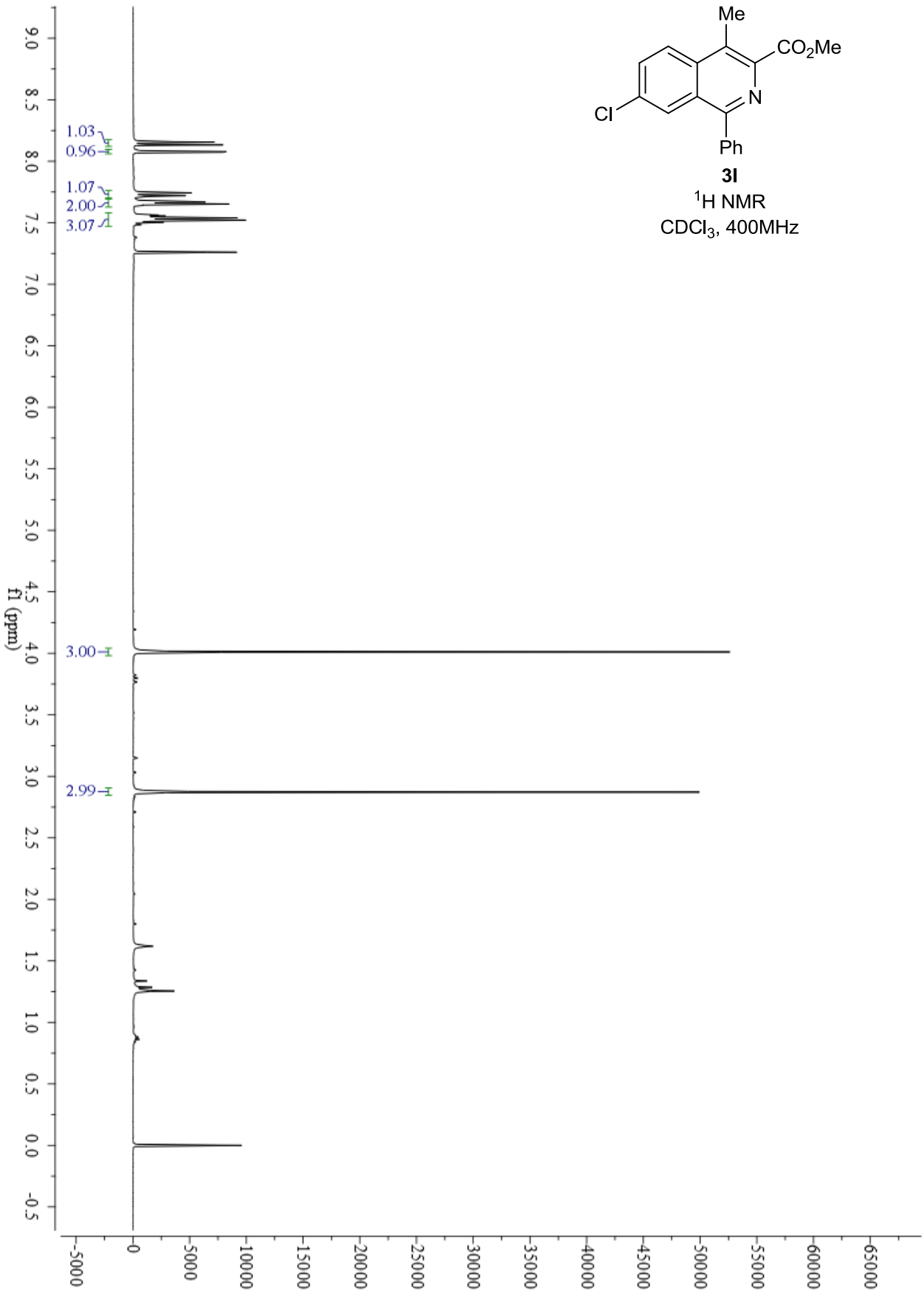

OMe
CO2Me
N
F
Ph
3i
13C NMR
CDCl3, 100MHz
167.7014
162.8548
159.5398
159.3402
159.2865
141.4515
141.4266
138.5134
129.8743
127.6842
120.9485
120.7005
113.9028
111.3626
111.1415
55.3142
52.5198
f1 (ppm)

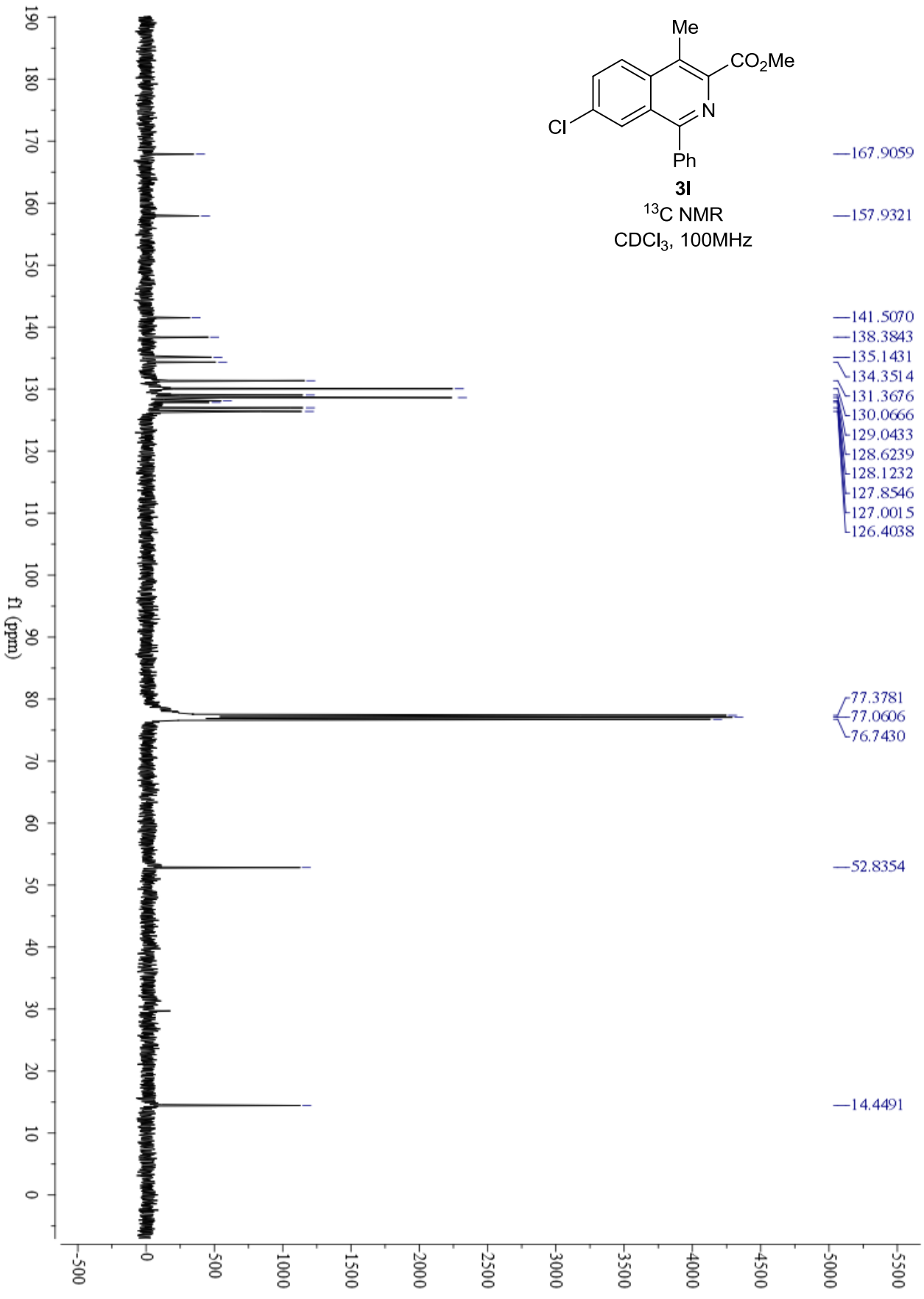

Me
CO2Me
N
Ph
3j
1H NMR
CDCl3, 400MHz
0.99
0.99
1.01
1.98
1.04
3.03
3.00
3.02
f1 (ppm)

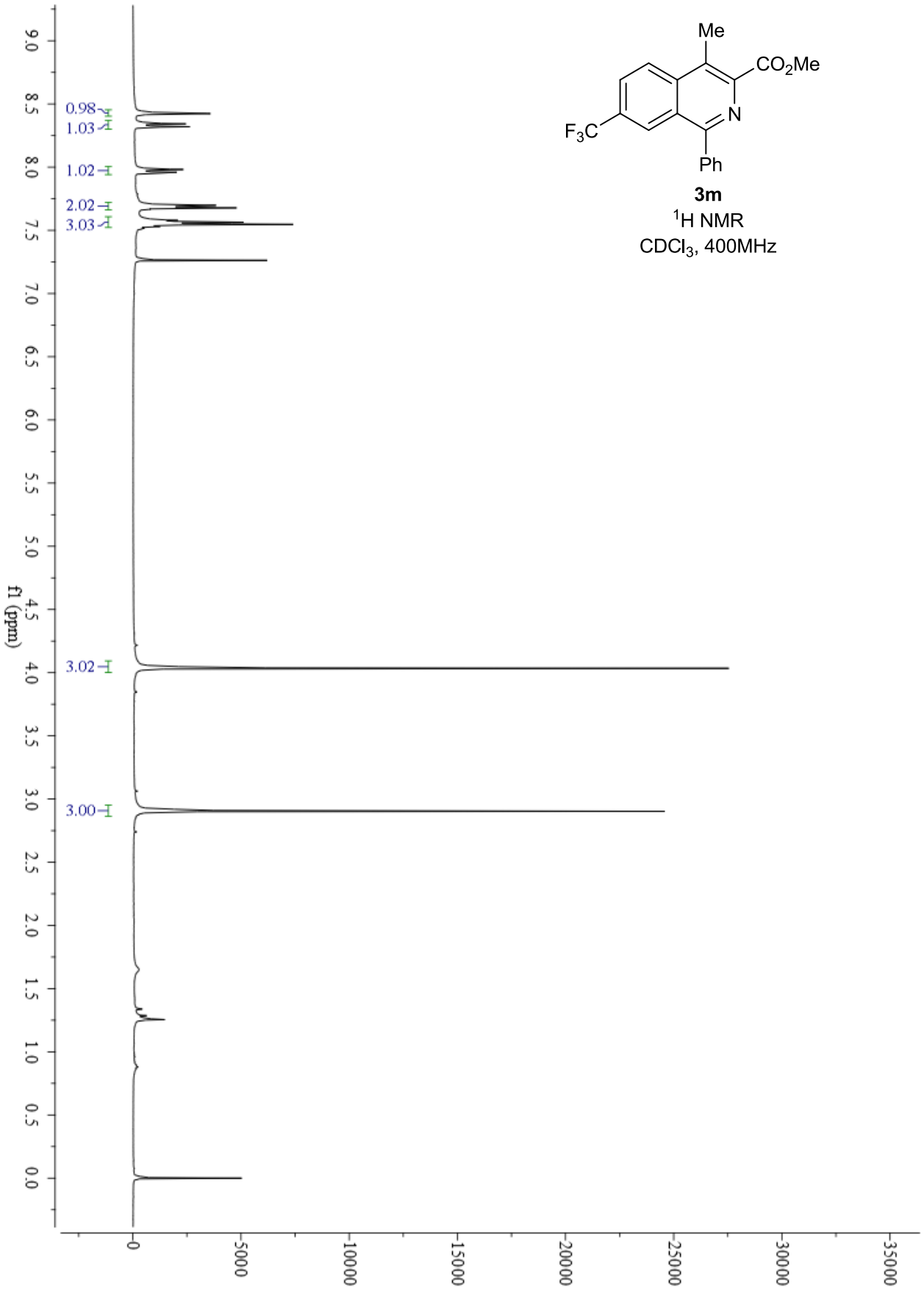

Me
CO2Me
N
Ph
3j
13C NMR
CDCl3, 100MHz
168.2259
158.7758
141.2375
139.0482
136.7320
130.4254
130.1870
128.7222
128.3855
128.2400
128.1317
127.0835
124.4713
52.7031
14.4142
f1 (ppm)

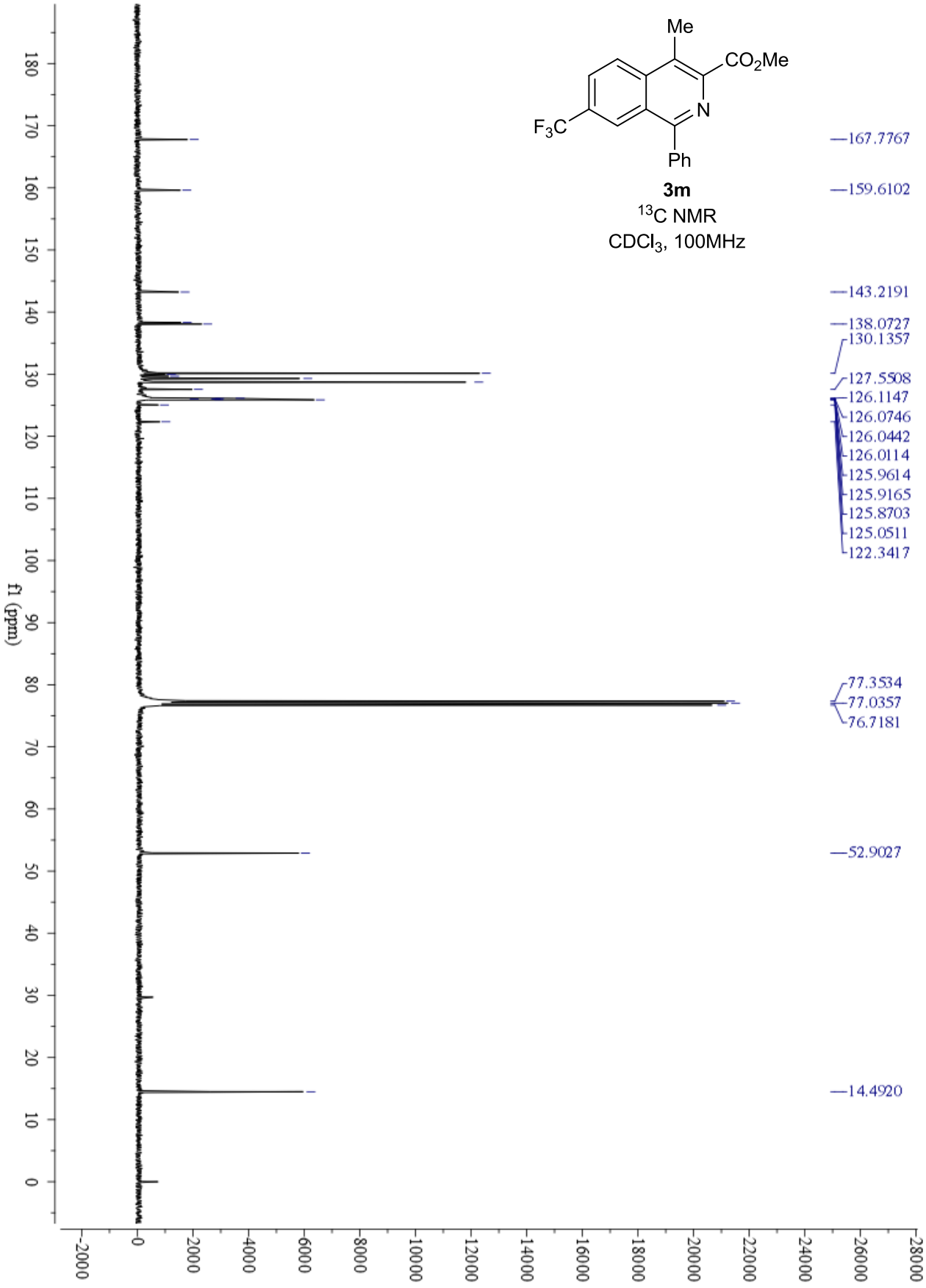

Me
CO2Me
N
MeO
Ph
3k
1H NMR
CDCl3, 400MHz
1.00
2.00
5.07
3.03
3.09
3.00
f1 (ppm)

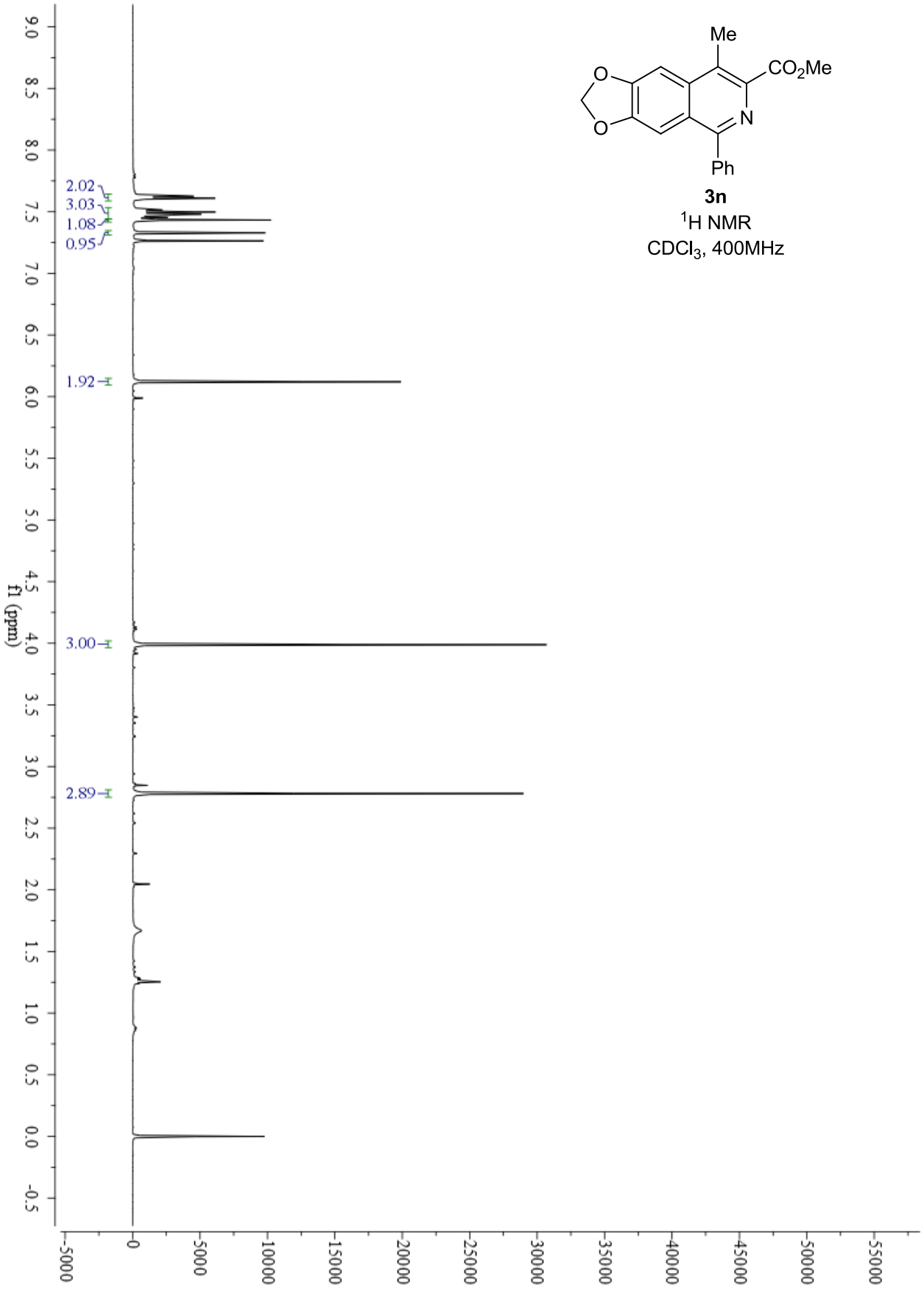

Me
CO2Me
N
MeO
Ph
3k
13C NMR
CDCl3, 100MHz
168.2062
159.1005
157.0905
139.3104
132.0438
128.6267
126.3156
122.6932
106.1637
55.4078
52.6183
14.4427
f1 (ppm)

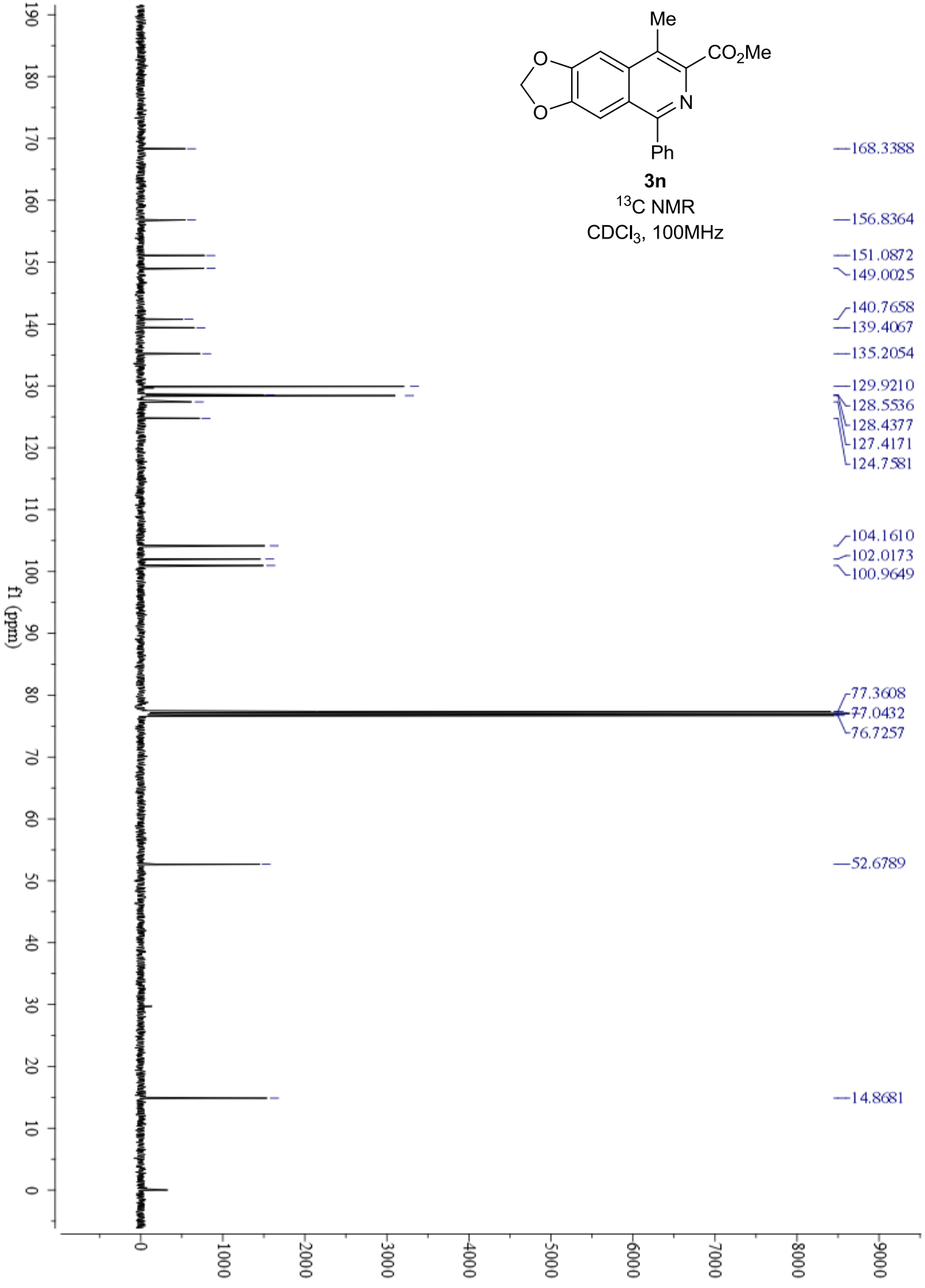

Me
CO2Me
N
Cl
Ph
3l
1H NMR
CDCl3, 400MHz
1.03
0.96
1.07
2.00
3.07
3.00
2.99
f1 (ppm)

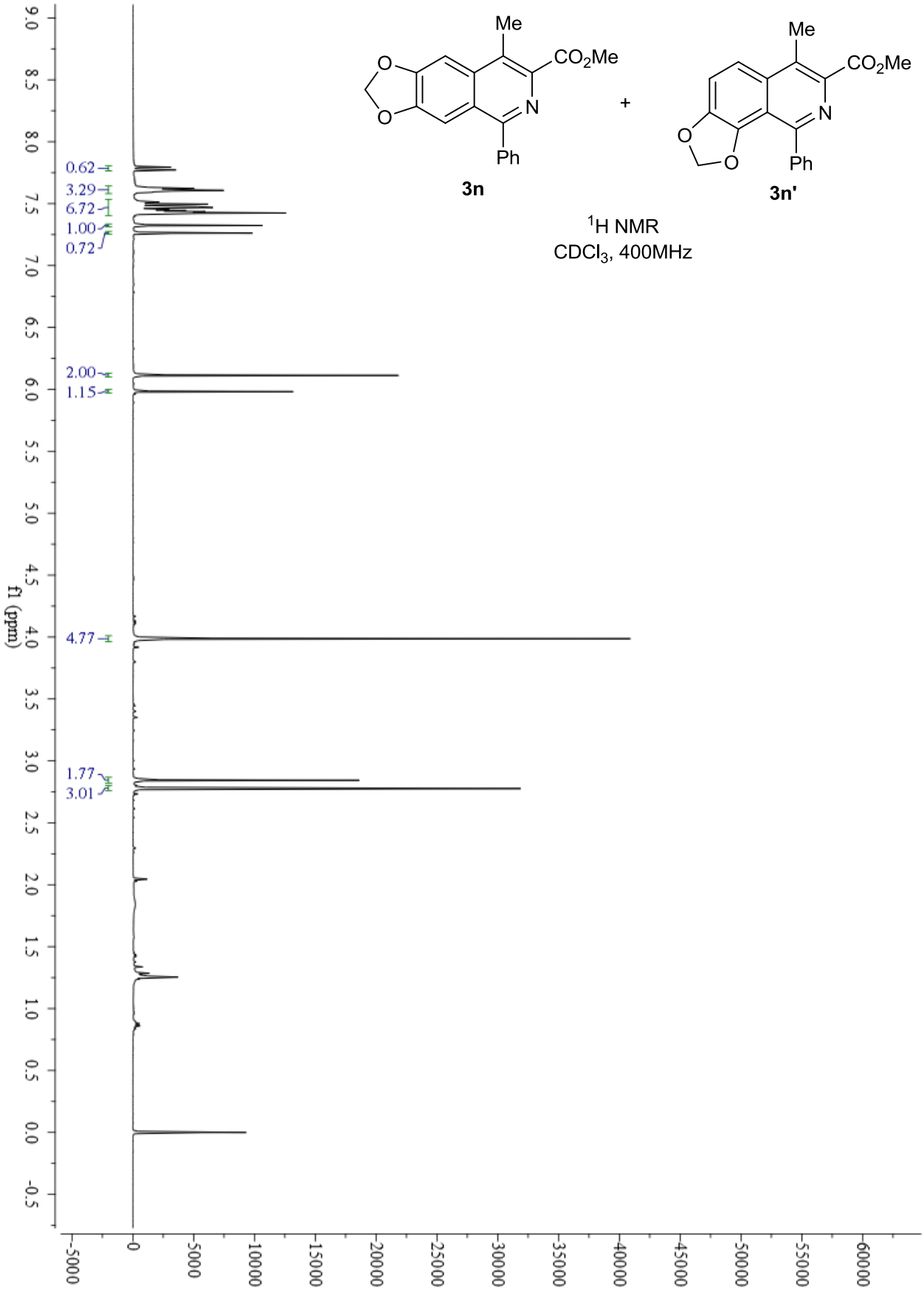

Me
CO2Me
N
Cl
Ph
3l
13C NMR
CDCl3, 100MHz
167.9059
157.9321
141.5070
138.3843
135.1431
134.3514
131.3676
130.0666
129.0433
128.6239
128.1232
127.8546
127.0015
126.4038
77.3781
77.0606
76.7430
52.8354
14.4491
f1 (ppm)

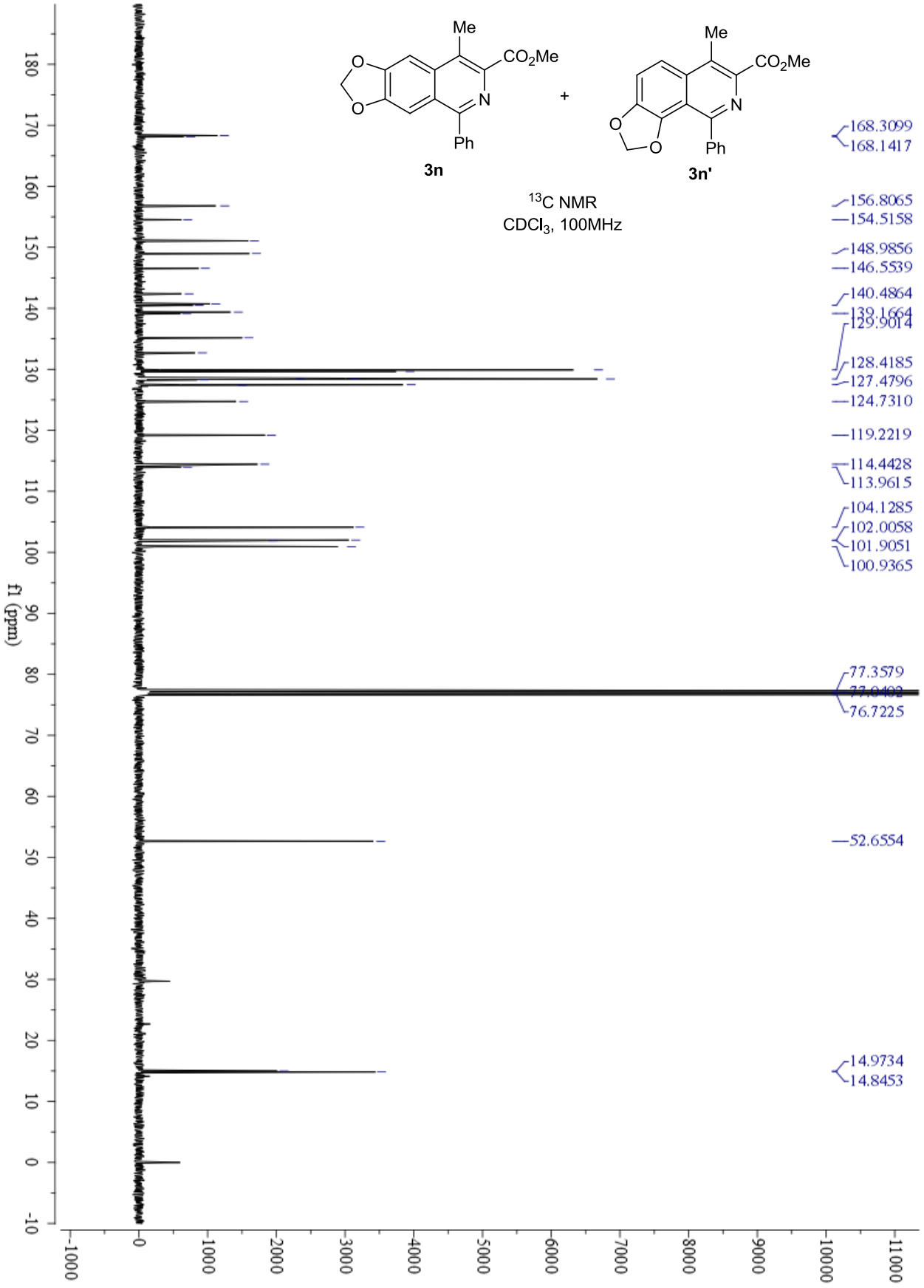

Me
CO2Me
F3C
N
Ph
3m
1H NMR
CDCl3, 400MHz
0.98
1.03
1.02
2.02
3.03
3.02
3.00
f1 (ppm)

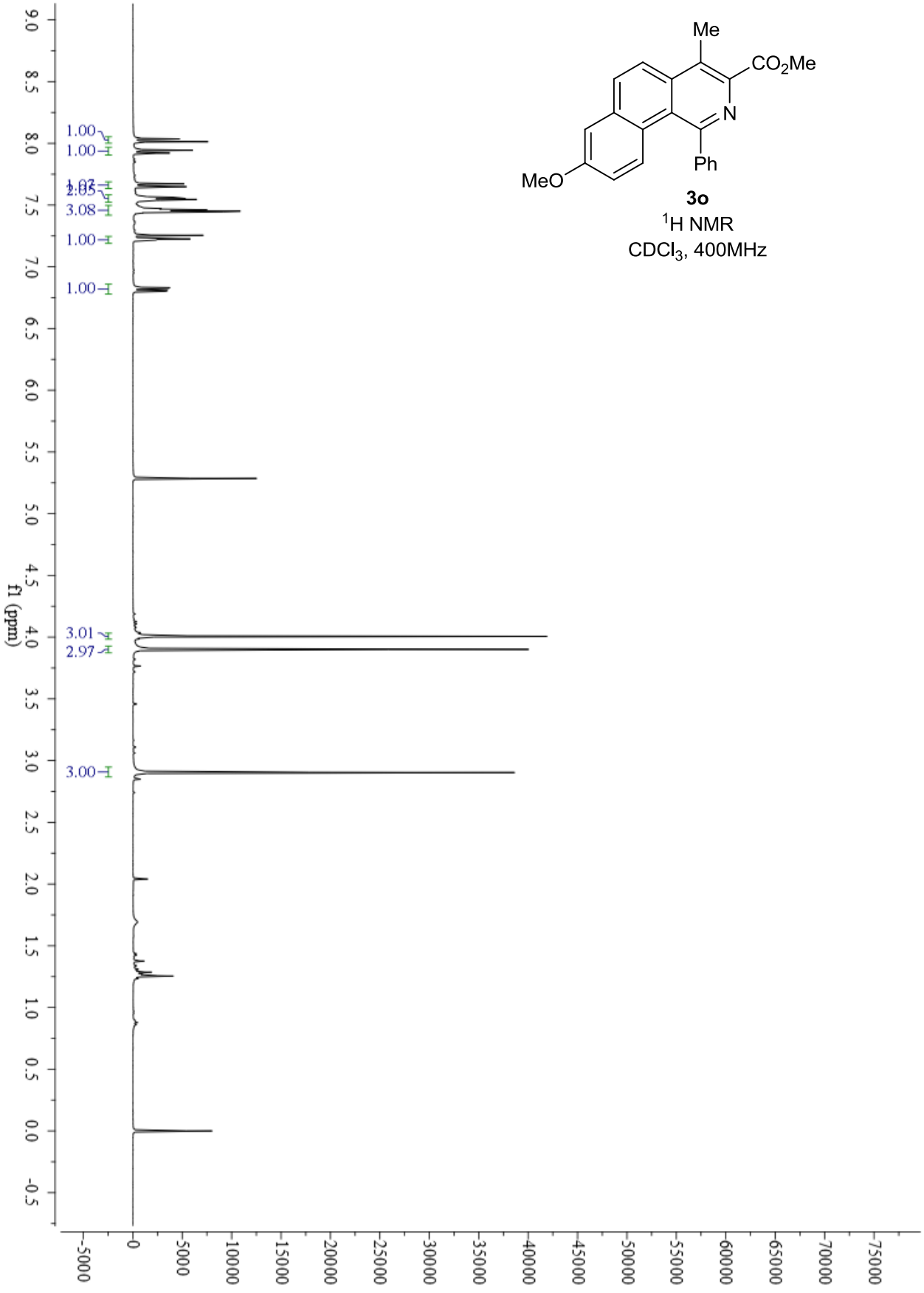

Me
CO2Me
F3C
N
Ph
3m
13C NMR
CDCl3, 100MHz
167.7767
159.6102
143.2191
138.0727
130.1357
127.5508
126.1147
126.0746
126.0442
126.0114
125.9614
125.9165
125.8703
125.0511
122.3417
77.3534
77.0357
76.7181
52.9027
14.4920
f1 (ppm)

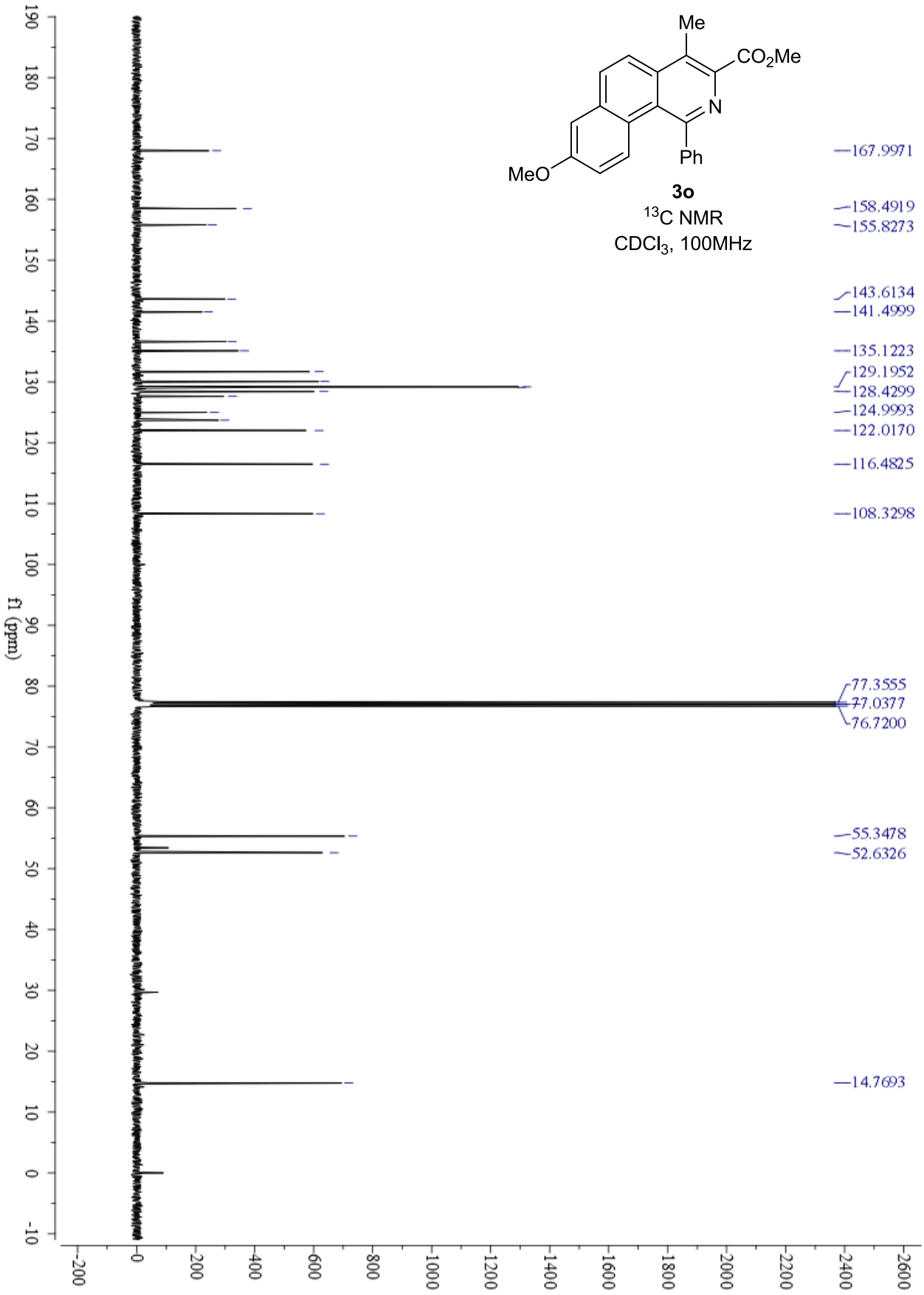

Me
CO2Me
O
O
N
Ph
3n
1H NMR
CDCl3, 400MHz
2.02
3.03
1.08
0.95
1.92
3.00
2.89
f1 (ppm)

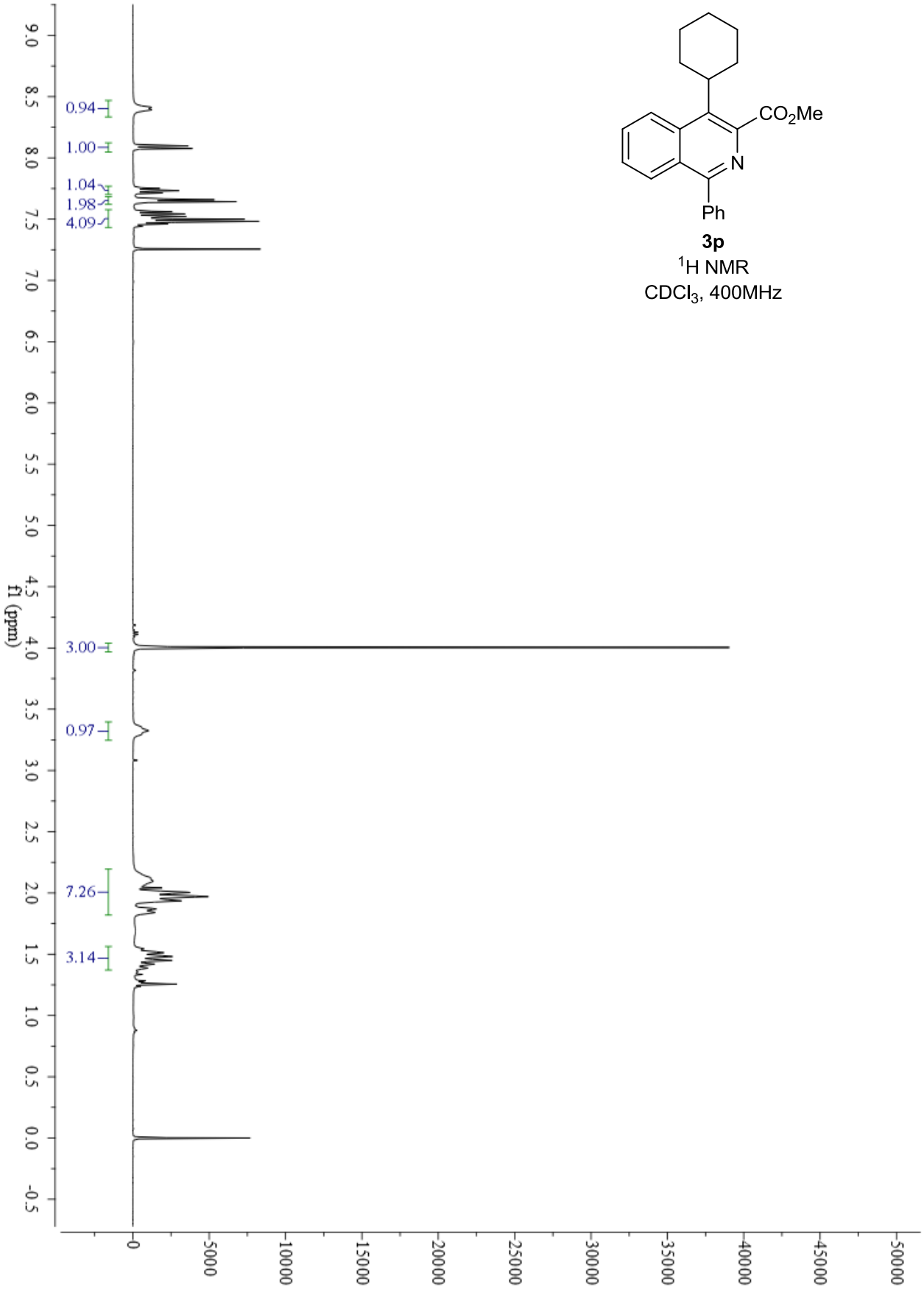

Me
CO2Me
O
O
N
Ph
3n
13C NMR
CDCl3, 100MHz
168.3388
156.8364
151.0872
149.0025
140.7658
139.4067
135.2054
129.9210
128.5536
128.4377
127.4171
124.7581
104.1610
102.0173
100.9649
77.3608
77.0432
76.7257
52.6789
14.8681
f1 (ppm)

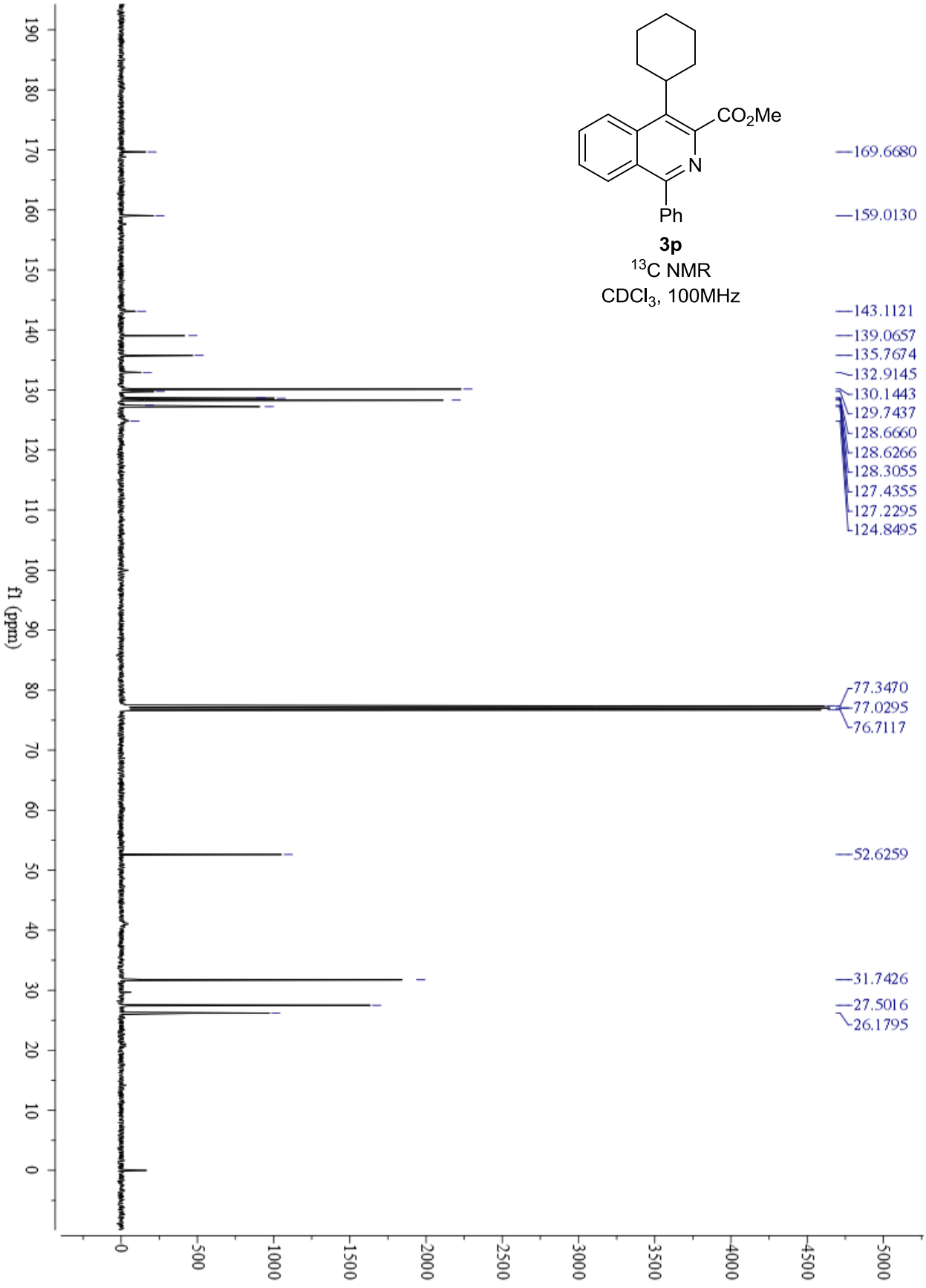

Me
CO2Me
O
O
N
Ph
3n
+
Me
CO2Me
O
O
N
Ph
3n'
1H NMR
CDCl3, 400MHz
0.62
3.29
6.72
1.00
0.72
2.00
1.15
4.77
1.77
3.01
f1 (ppm)

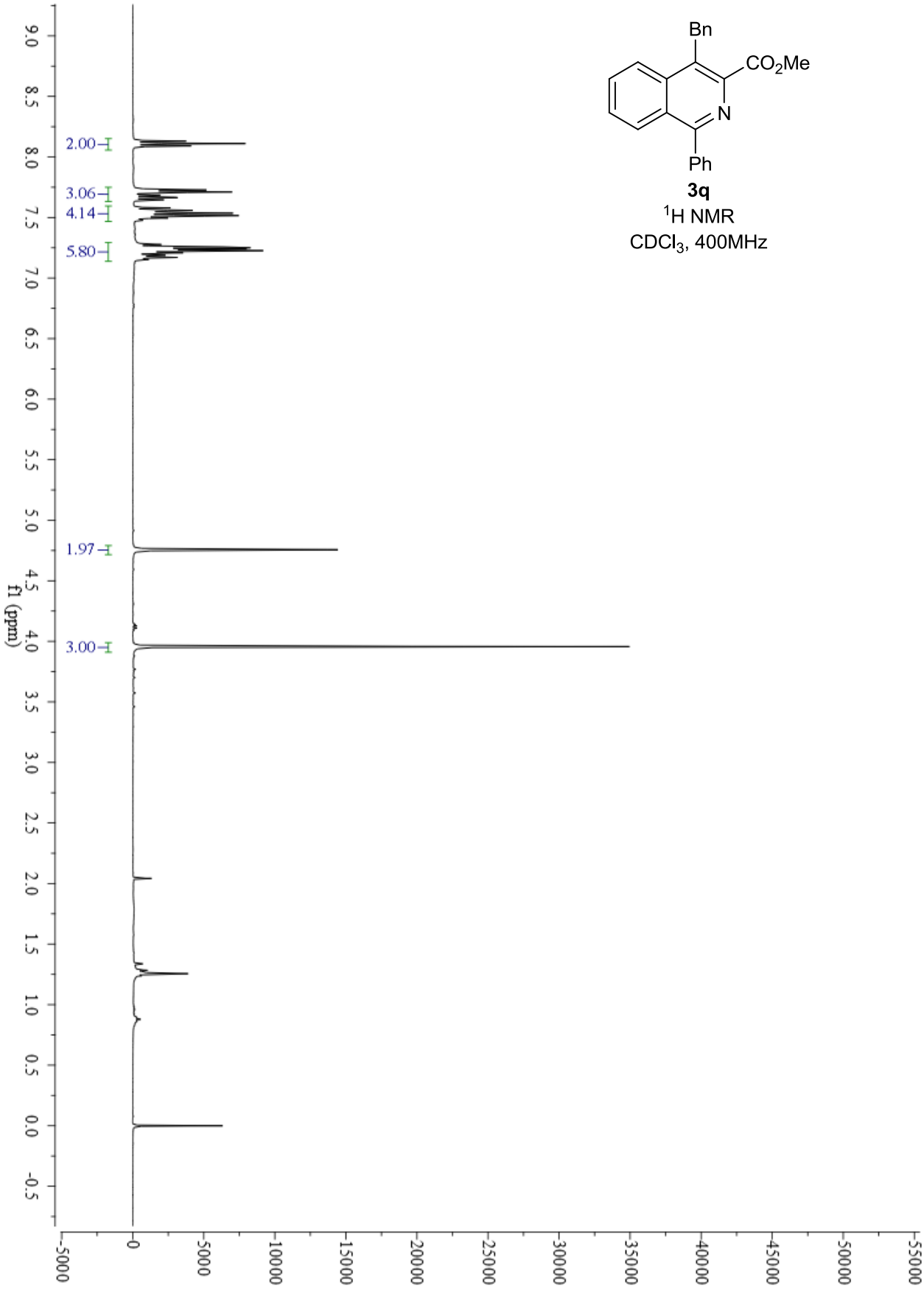

Me
CO2Me
O
O
N
Ph
3n
+
Me
CO2Me
O
O
N
Ph
3n'
13C NMR
CDCl3, 100MHz
168.3099
168.1417
156.8065
154.5158
148.9856
146.5539
140.4864
139.1664
129.9014
128.4185
127.4796
124.7310
119.2219
114.4428
113.9615
104.1285
102.0058
101.9051
100.9365
77.3579
76.7225
52.6554
14.9734
14.8453
f1 (ppm)

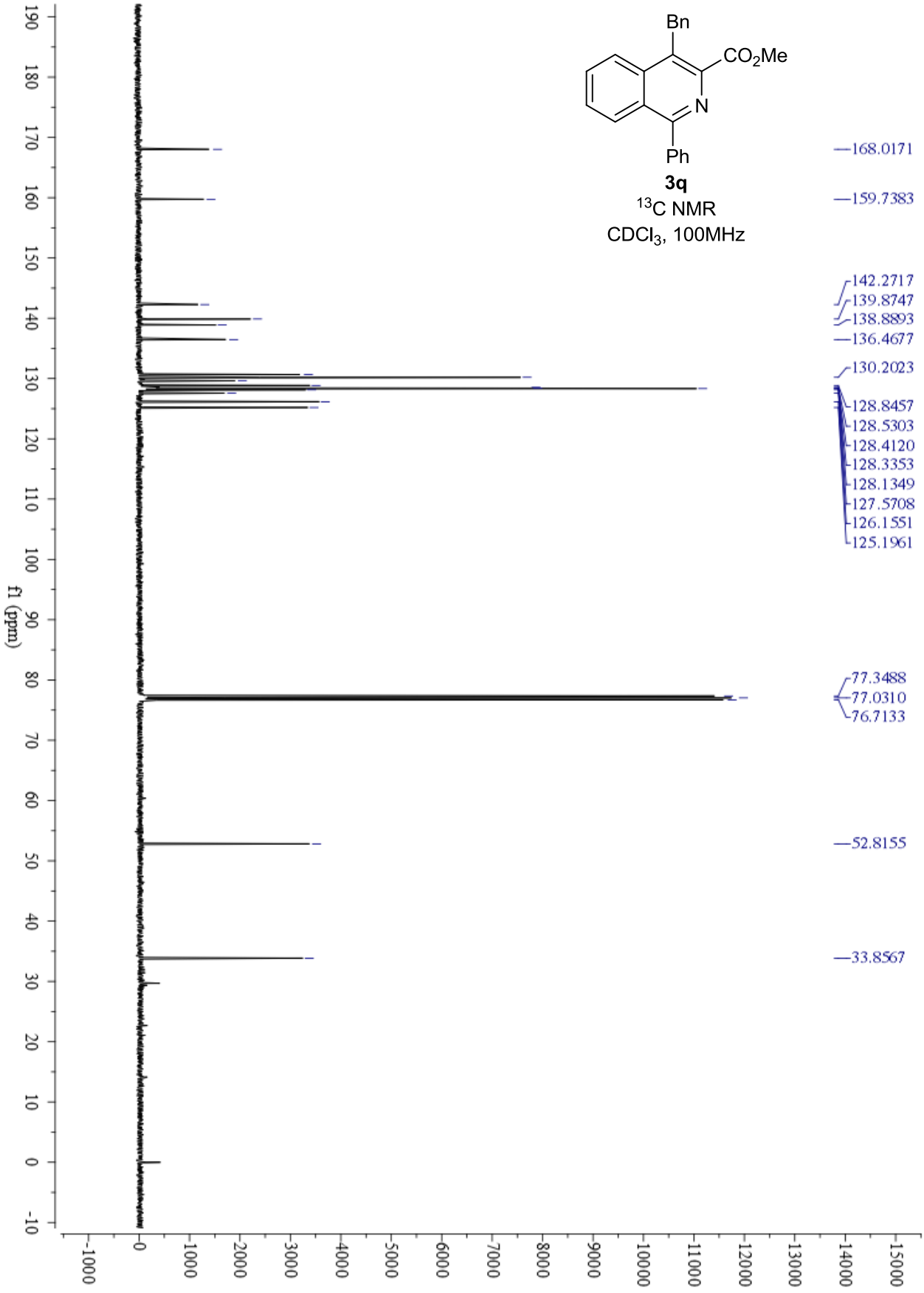

Me
CO2Me
N
Ph
MeO
3o
1H NMR
CDCl3, 400MHz
1.00
1.00
2.05
3.08
1.00
1.00
3.01
2.97
3.00
f1 (ppm)

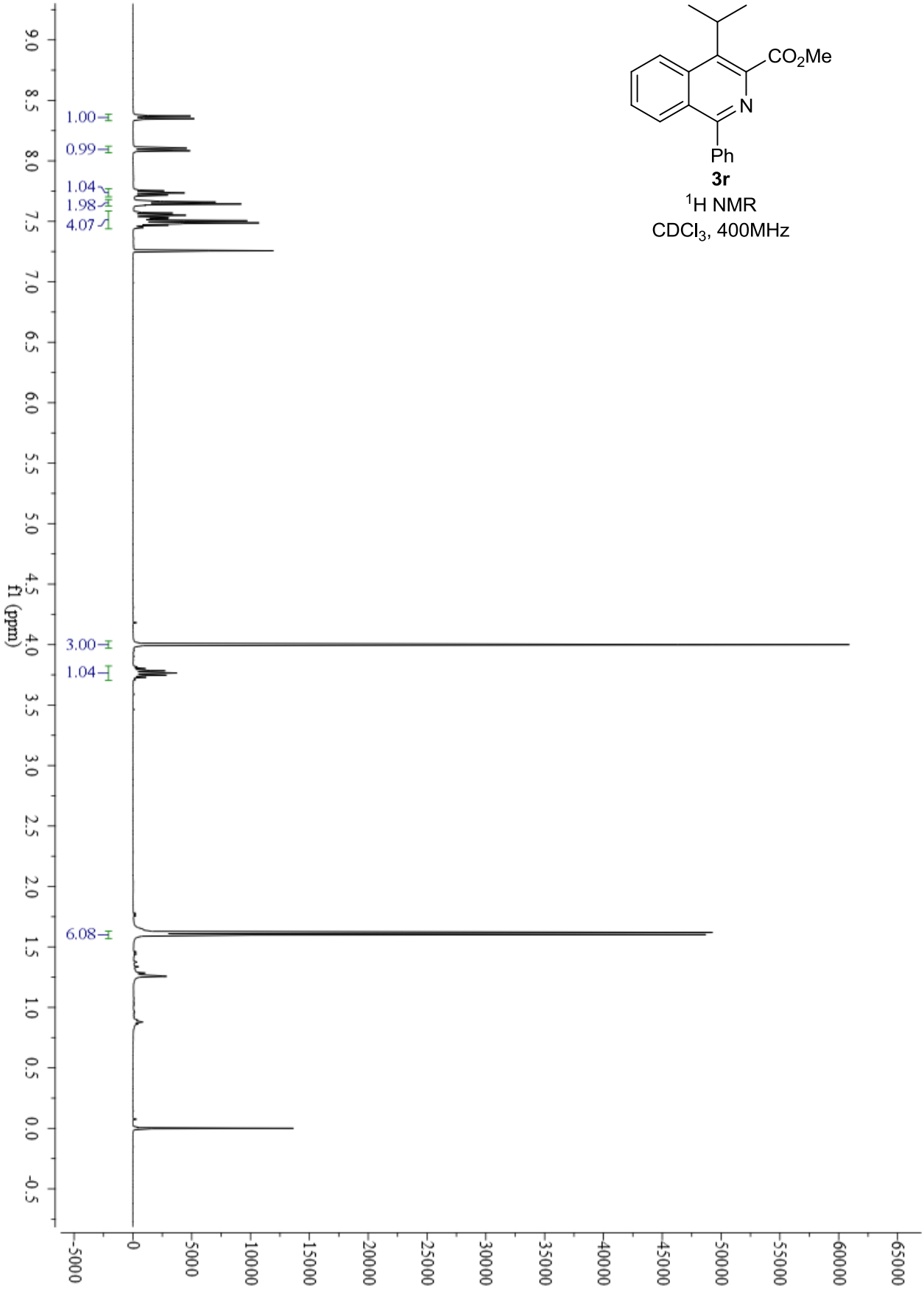

Me
CO2Me
N
Ph
MeO
3o
13C NMR
CDCl3, 100MHz
167.9971
158.4919
155.8273
143.6134
141.4999
135.1223
129.1952
128.4299
124.9993
122.0170
116.4825
108.3298
77.3555
77.0377
76.7200
55.3478
52.6326
14.7693
f1 (ppm)

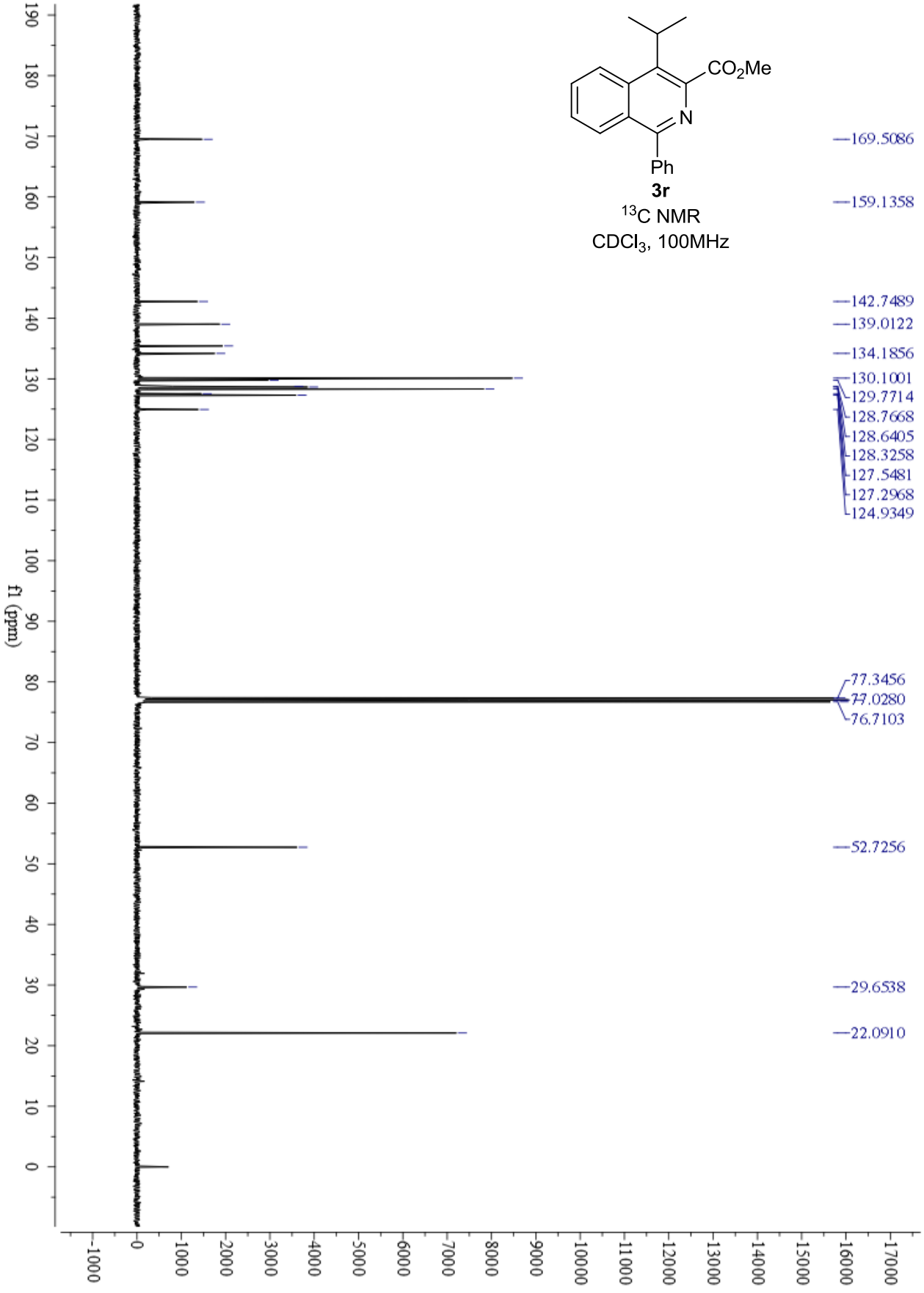

CO2Me
N
Ph
3p
1H NMR
CDCl3, 400MHz
f1 (ppm)
0.94
1.00
1.04
1.98
4.09
3.00
0.97
7.26
3.14

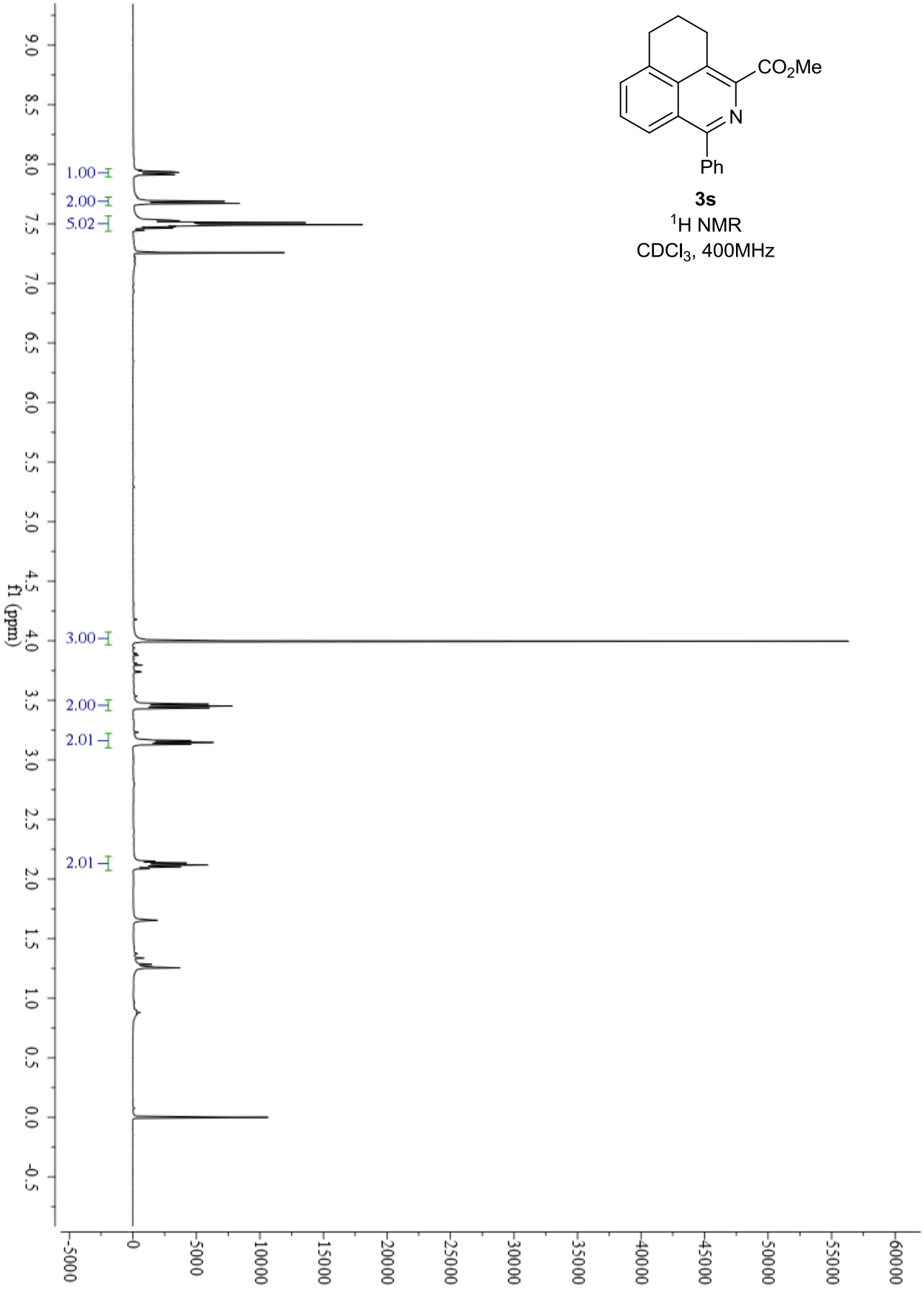

CO2Me
N
Ph
3p
13C NMR
CDCl3, 100MHz
169.6680
159.0130
143.1121
139.0657
135.7674
132.9145
130.1443
129.7437
128.6660
128.6266
128.3055
127.4355
127.2295
124.8495
77.3470
77.0295
76.7117
52.6259
31.7426
27.5016
26.1795
f1 (ppm)

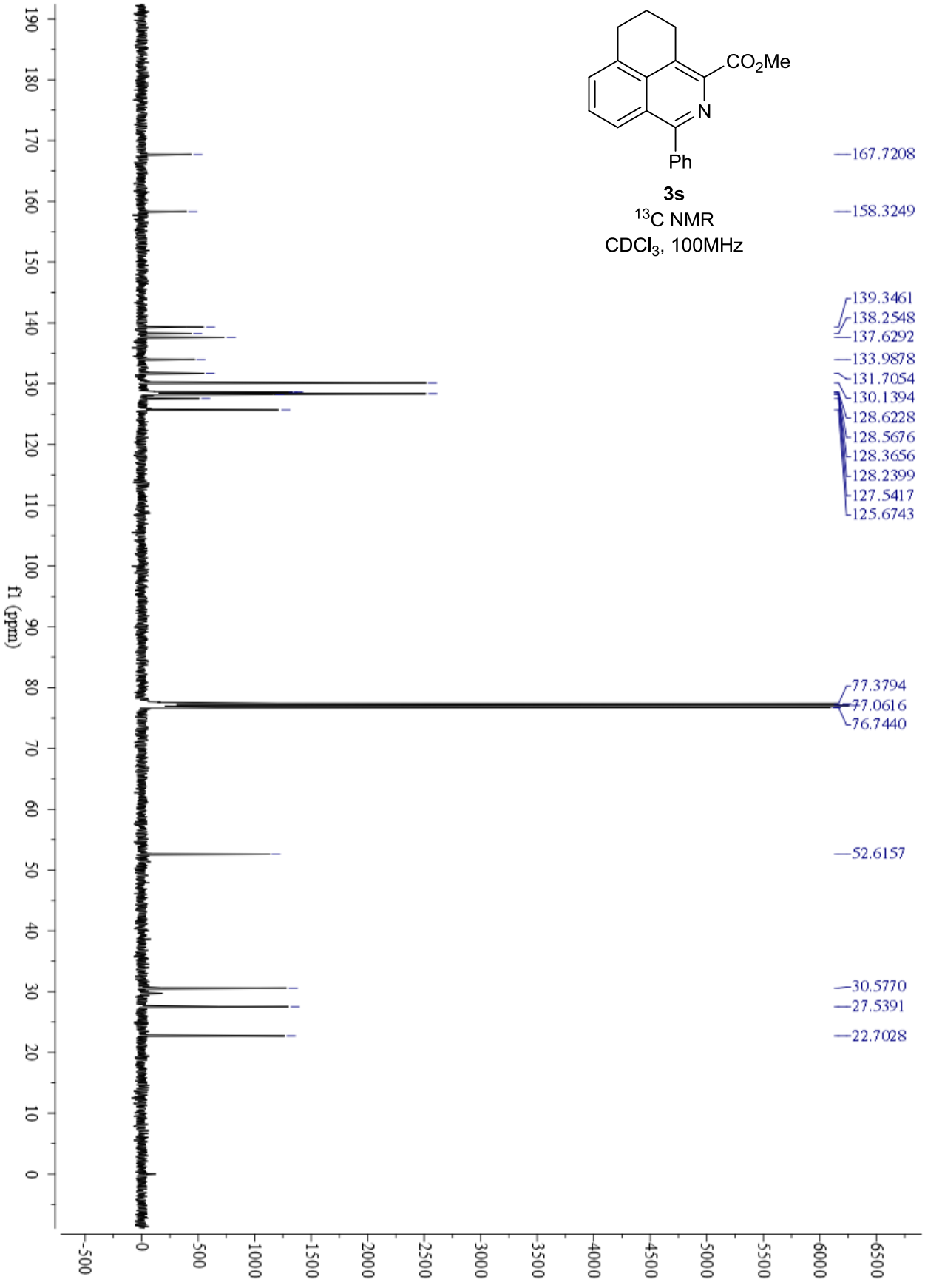

Bn
CO2Me
N
Ph
3q
1H NMR
CDCl3, 400MHz
2.00
3.06
4.14
5.80
1.97
3.00
f1 (ppm)

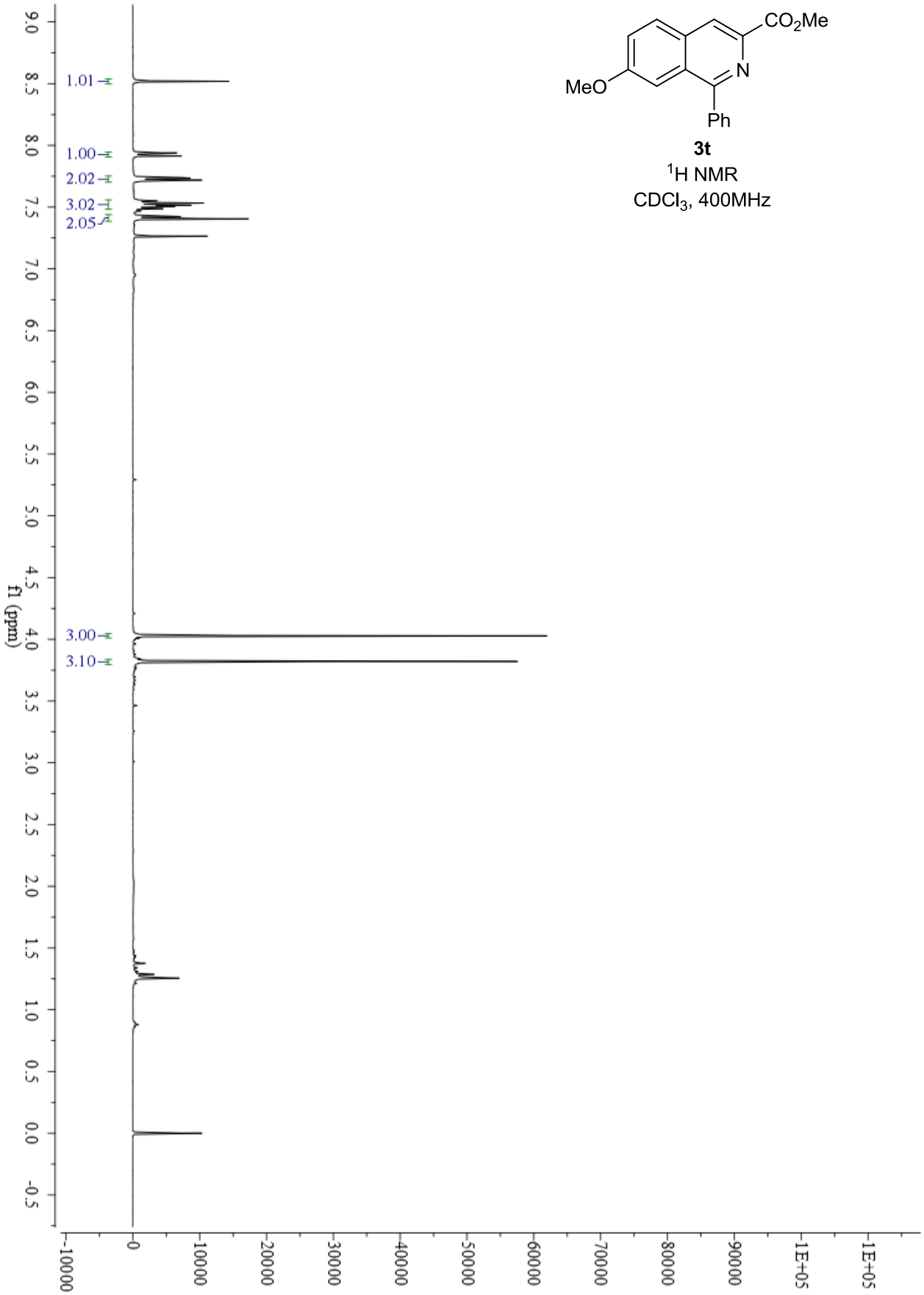

Bn
CO2Me
N
Ph
3q
13C NMR
CDCl3, 100MHz
168.0171
159.7383
142.2717
139.8747
138.8893
136.4677
130.2023
128.8457
128.5303
128.4120
128.3353
128.1349
127.5708
126.1551
125.1961
77.3488
77.0310
76.7133
52.8155
33.8567
f1 (ppm)

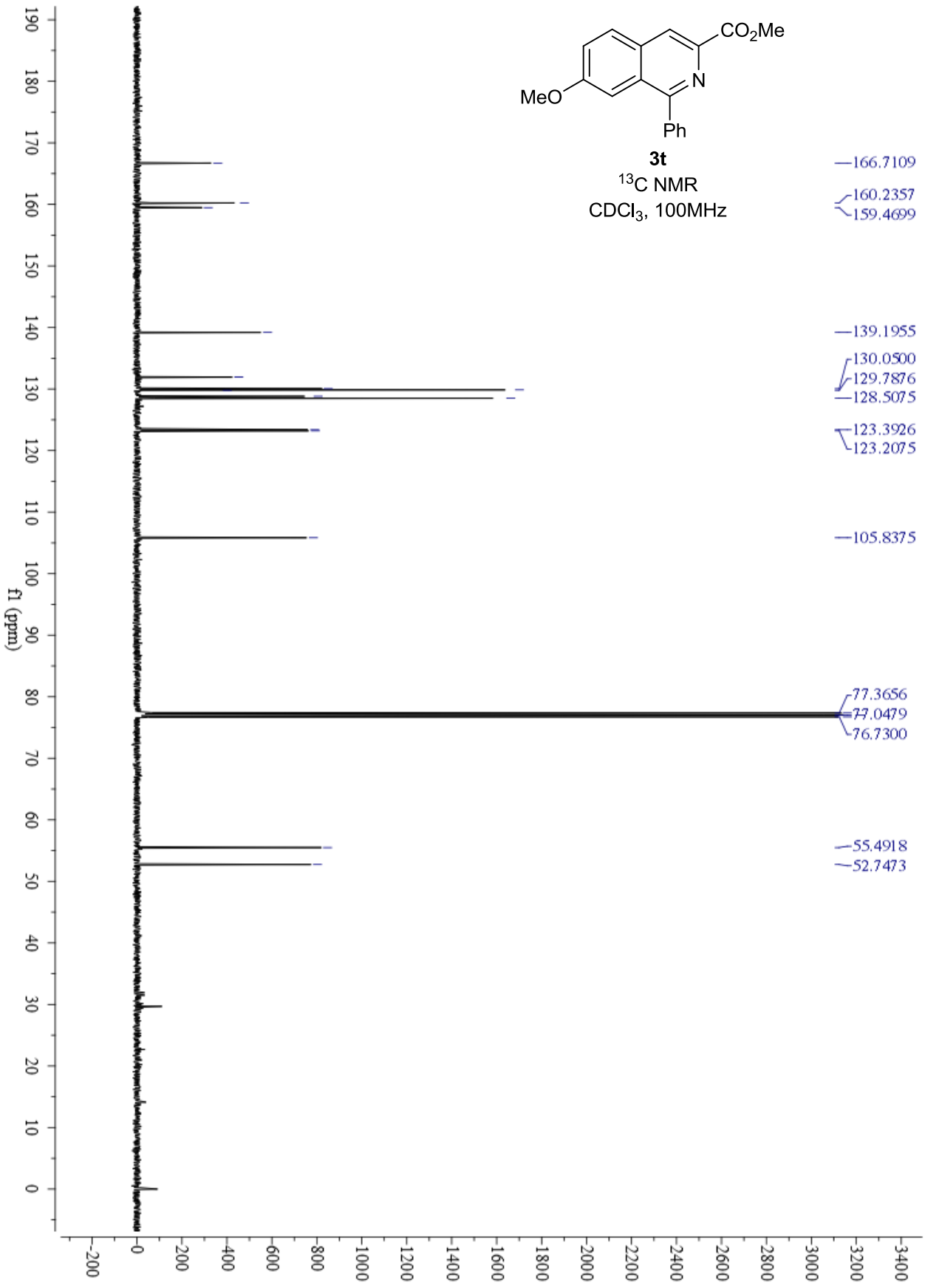

CO2Me
N
Ph
3r
1H NMR
CDCl3, 400MHz
f1 (ppm)
1.00
0.99
1.04
1.98
4.07
3.00
1.04
6.08

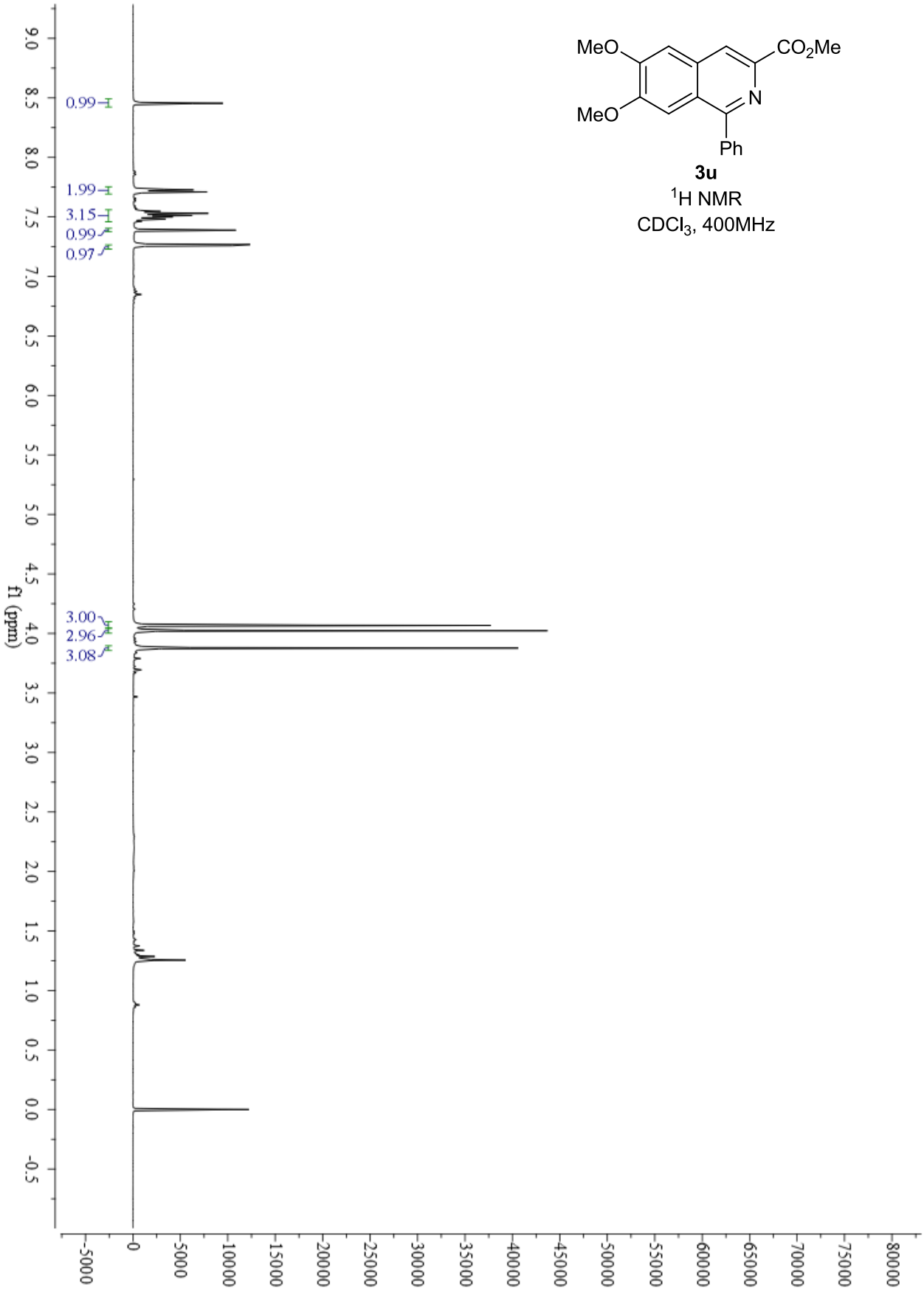

CO2Me
N
Ph
3r
13C NMR
CDCl3, 100MHz
169.5086
159.1358
142.7489
139.0122
134.1856
130.1001
129.7714
128.7668
128.6405
128.3258
127.5481
127.2968
124.9349
77.3456
77.0280
76.7103
52.7256
29.6538
22.0910
f1 (ppm)

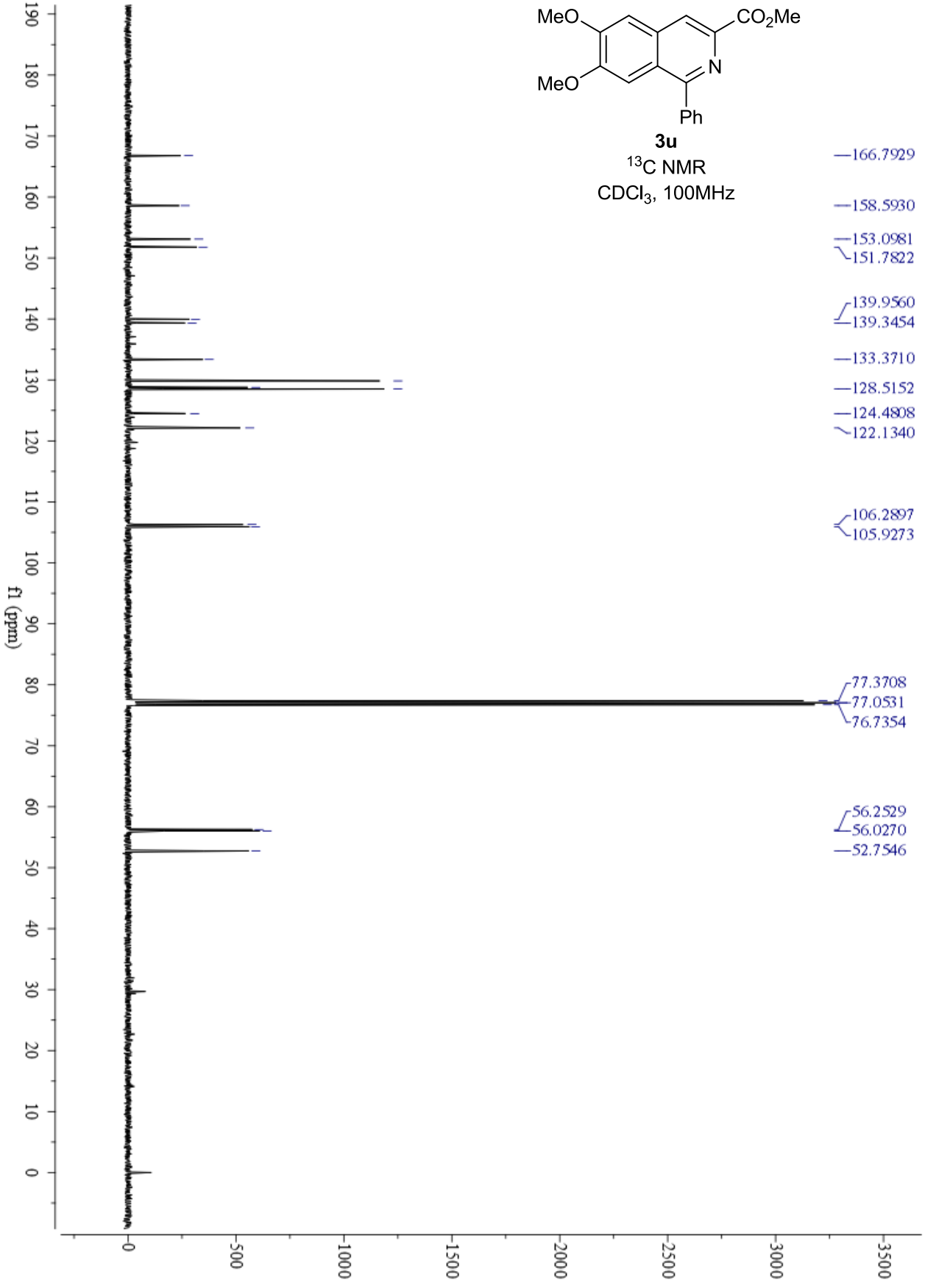

CO2Me
N
Ph
3s
1H NMR
CDCl3, 400MHz
1.00
2.00
5.02
3.00
2.00
2.01
2.01
f1 (ppm)

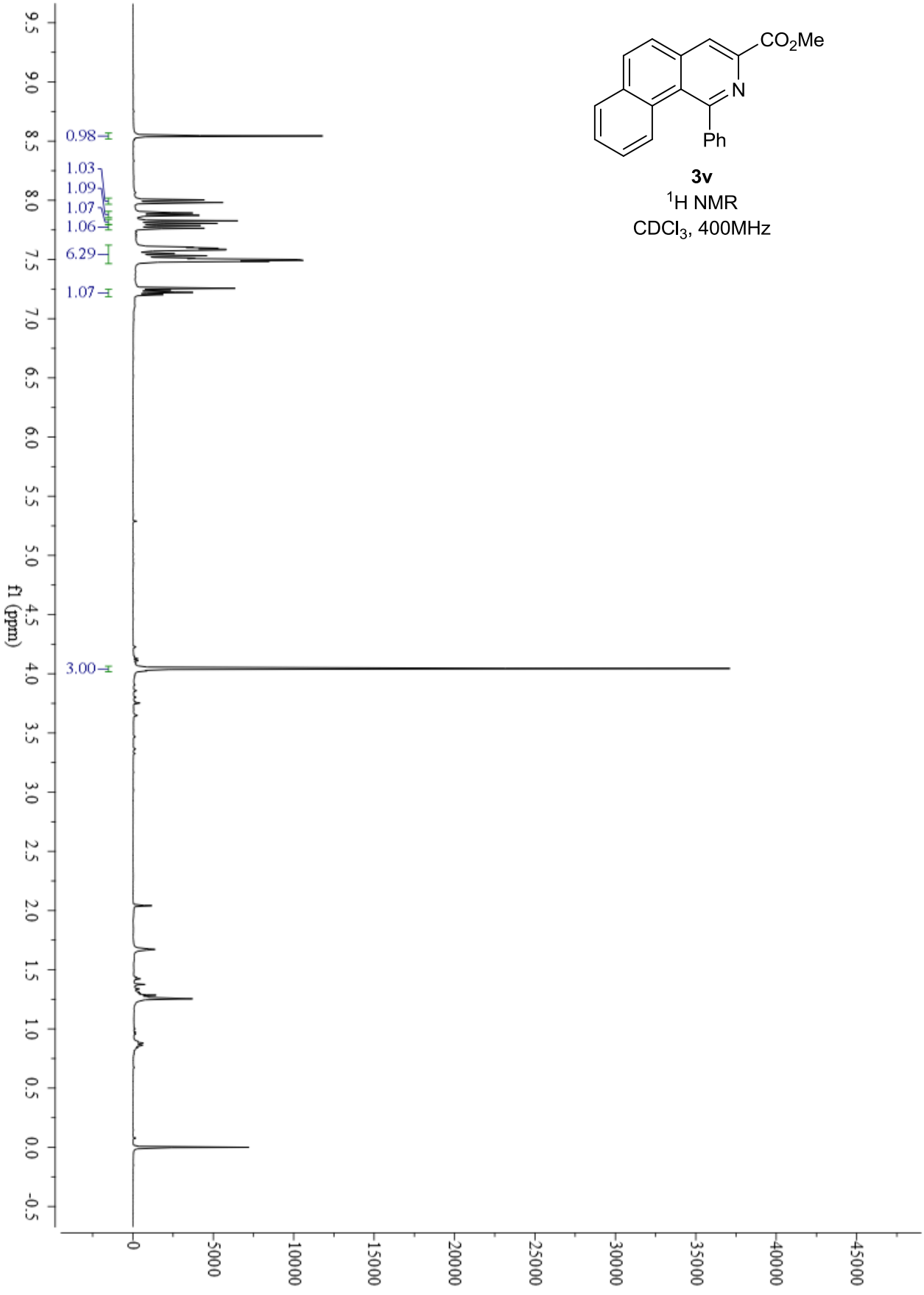

CO2Me
N
Ph
3s
13C NMR
CDCl3, 100MHz
167.7208
158.3249
139.3461
138.2548
137.6292
133.9878
131.7054
130.1394
128.6228
128.5676
128.3656
128.2399
127.5417
125.6743
77.3794
77.0616
76.7440
52.6157
30.5770
27.5391
22.7028
f1 (ppm)


CO2Me
N
MeO
Ph
3t
1H NMR
CDCl3, 400MHz
1.01
1.00
2.02
3.02
2.05
3.00
3.10
f1 (ppm)


CO2Me
N
MeO
Ph
3t
13C NMR
CDCl3, 100MHz
166.7109
160.2357
159.4699
139.1955
130.0500
129.7876
128.5075
123.3926
123.2075
105.8375
77.3656
77.0479
76.7300
55.4918
52.7473
f1 (ppm)


MeO
CO2Me
MeO
N
Ph
3u
1H NMR
CDCl3, 400MHz
0.99
1.99
3.15
0.99
0.97
3.00
2.96
3.08
f1 (ppm)

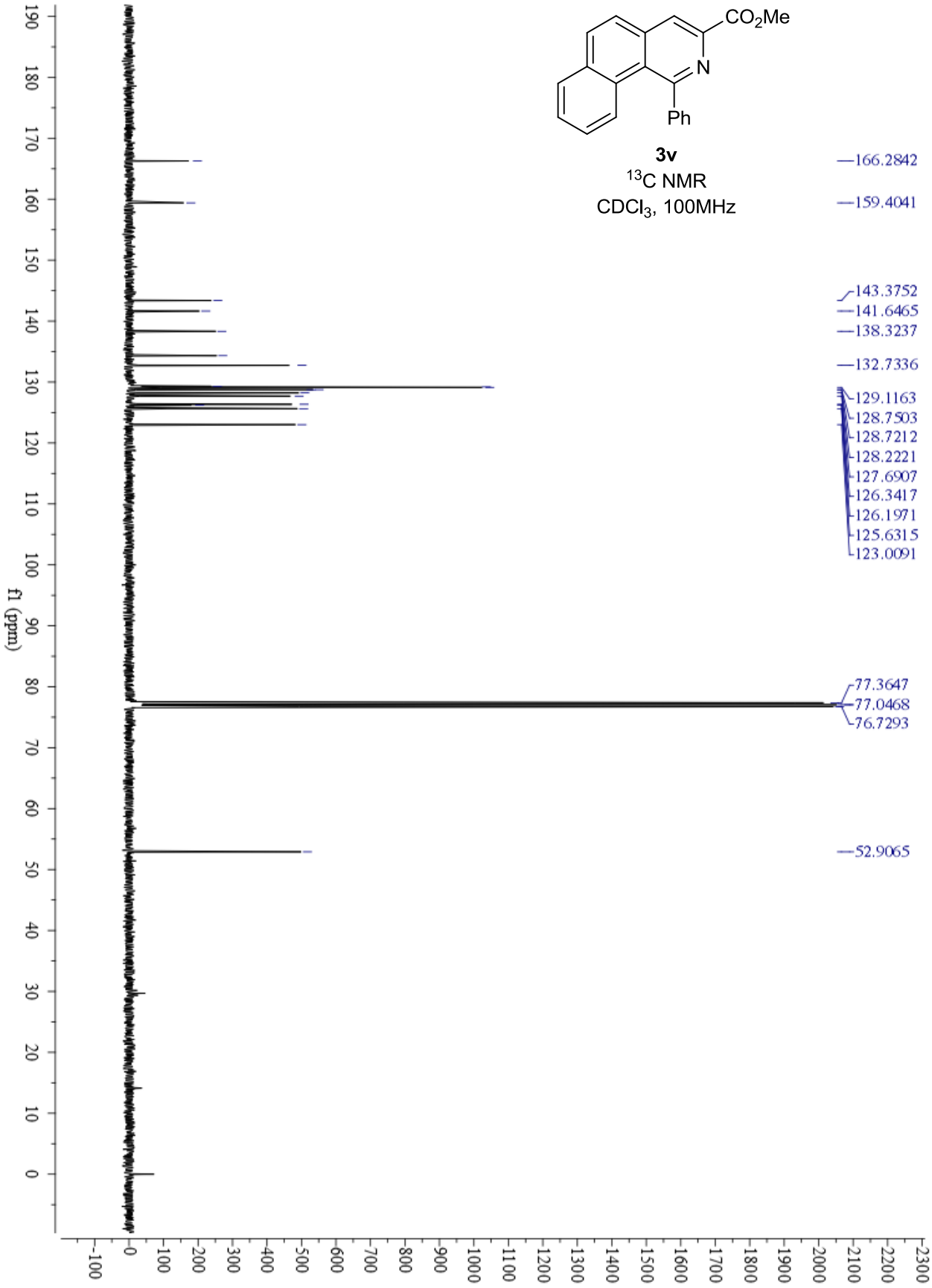

MeO
MeO
CO2Me
N
Ph
3u
13C NMR
CDCl3, 100MHz
166.7929
158.5930
153.0981
151.7822
139.9560
139.3454
133.3710
128.5152
124.4808
122.1340
106.2897
105.9273
77.3708
77.0531
76.7354
56.2529
56.0270
52.7546
f1 (ppm)

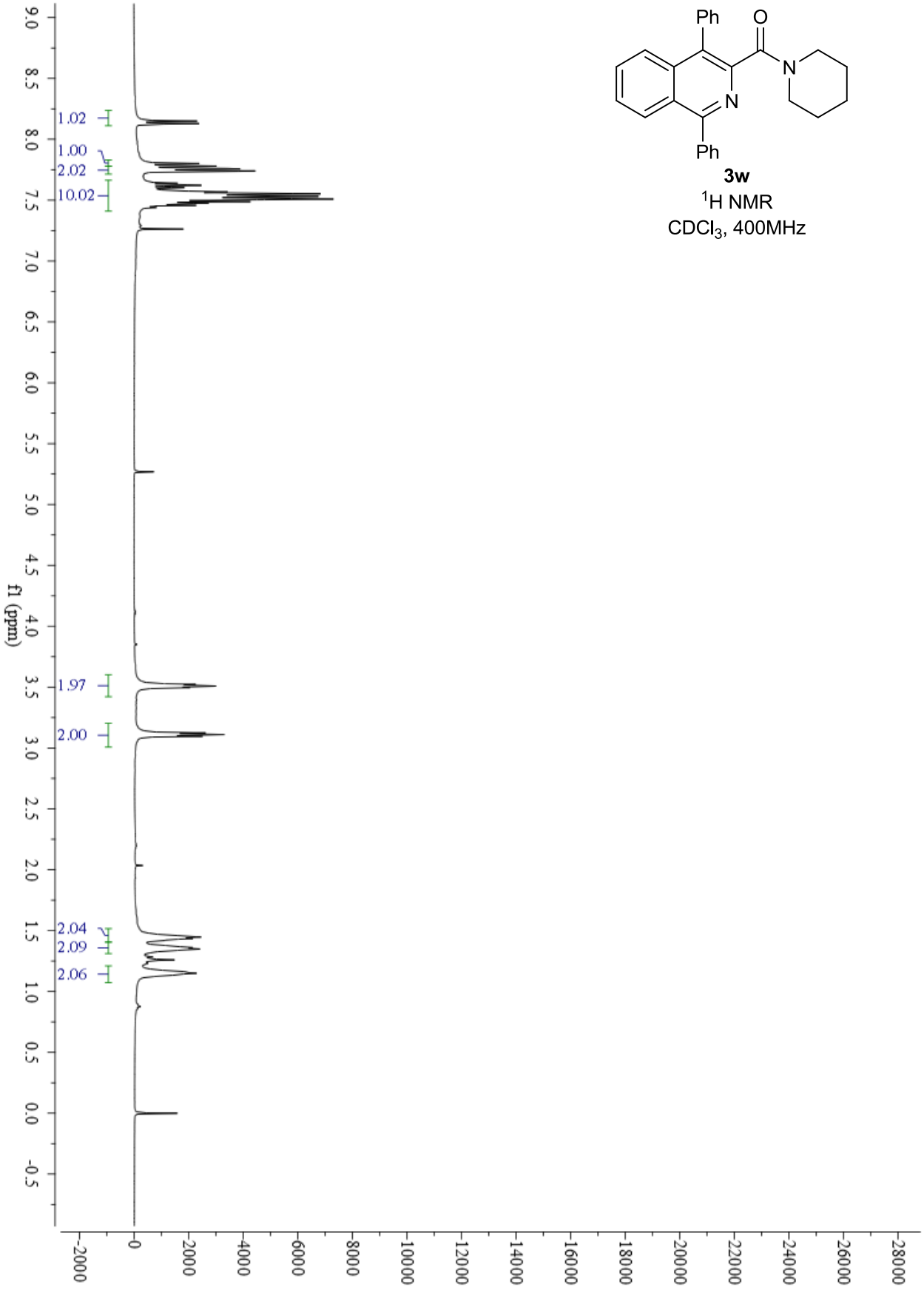


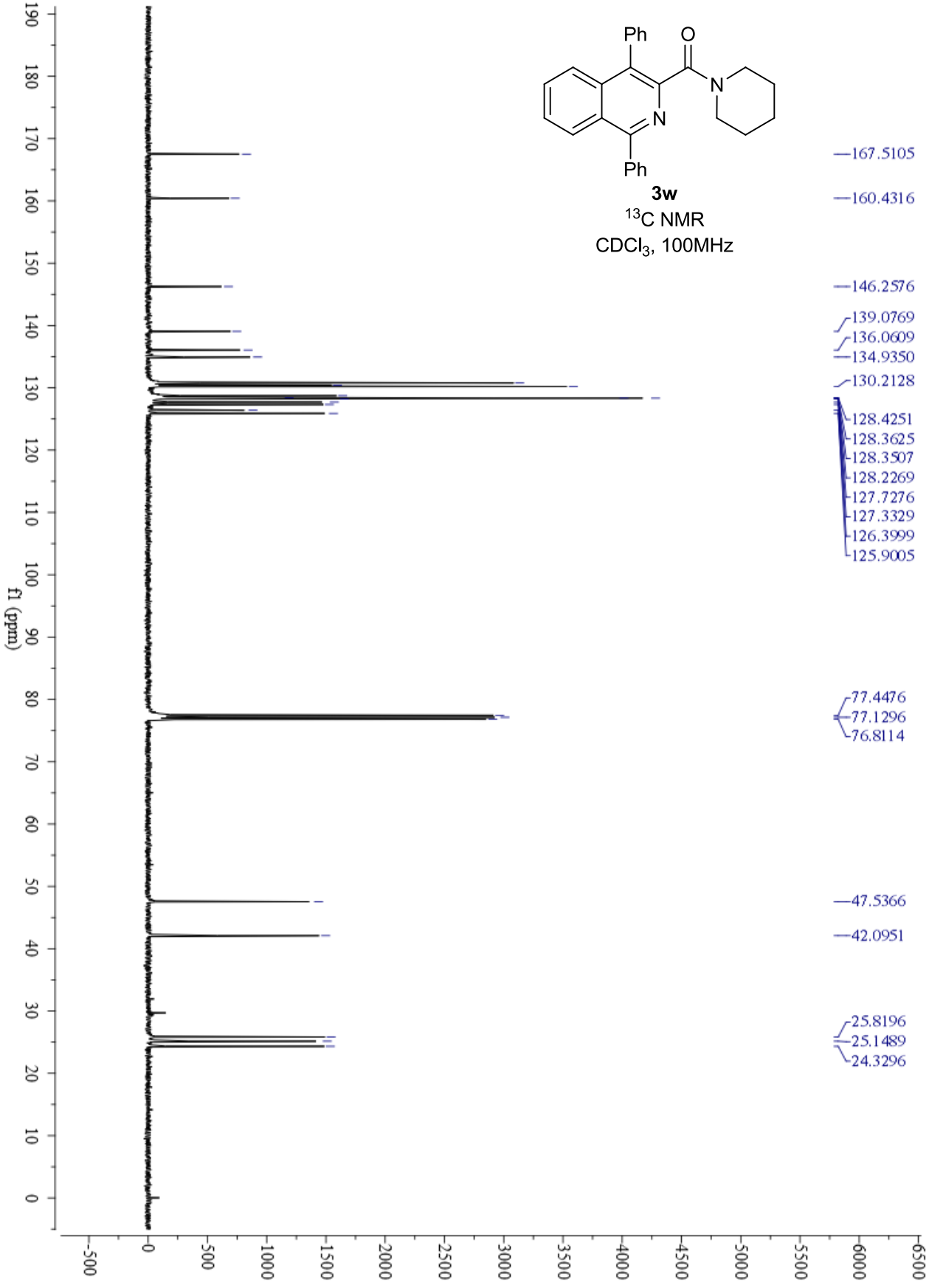
3v

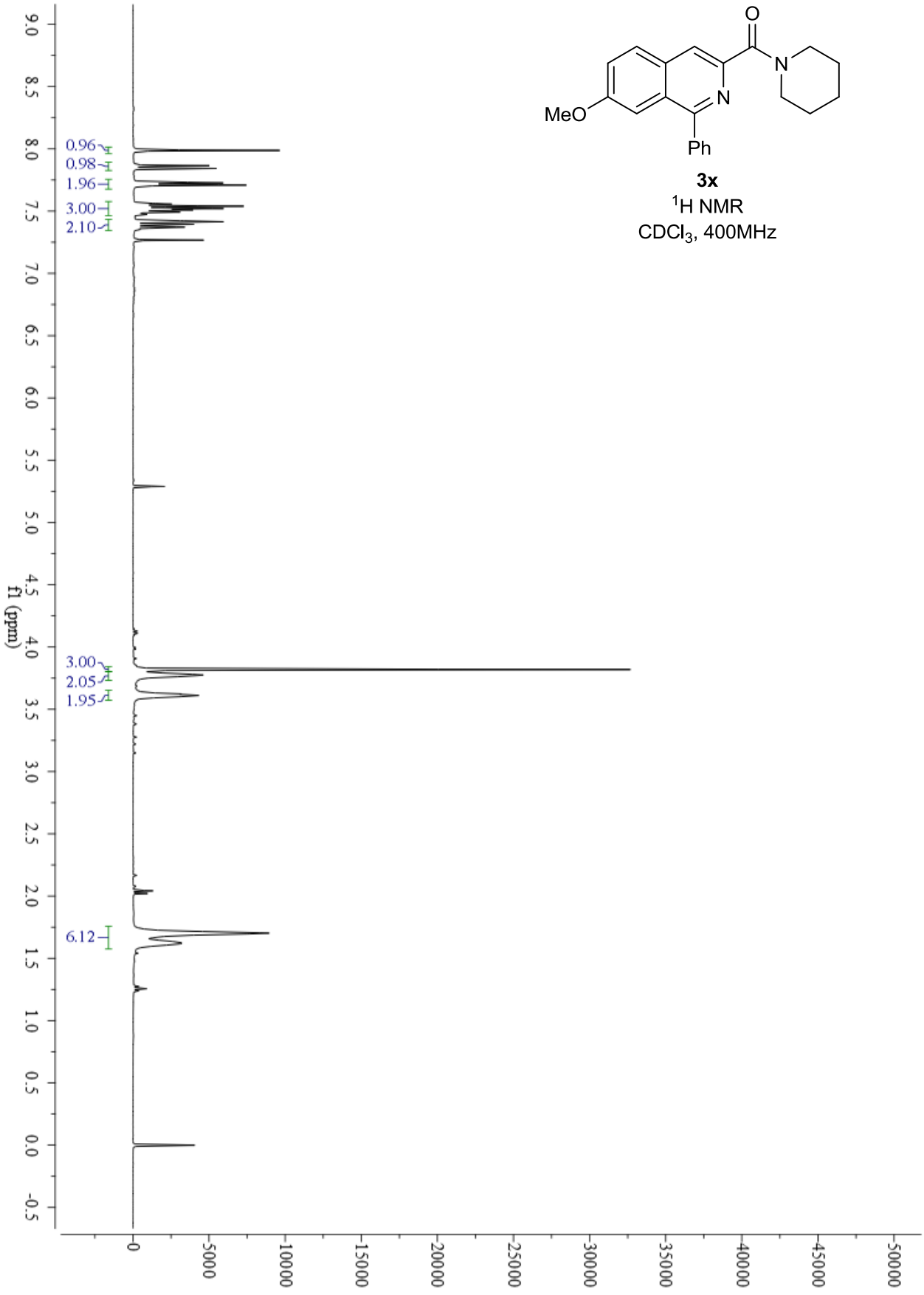
^{1}H NMR

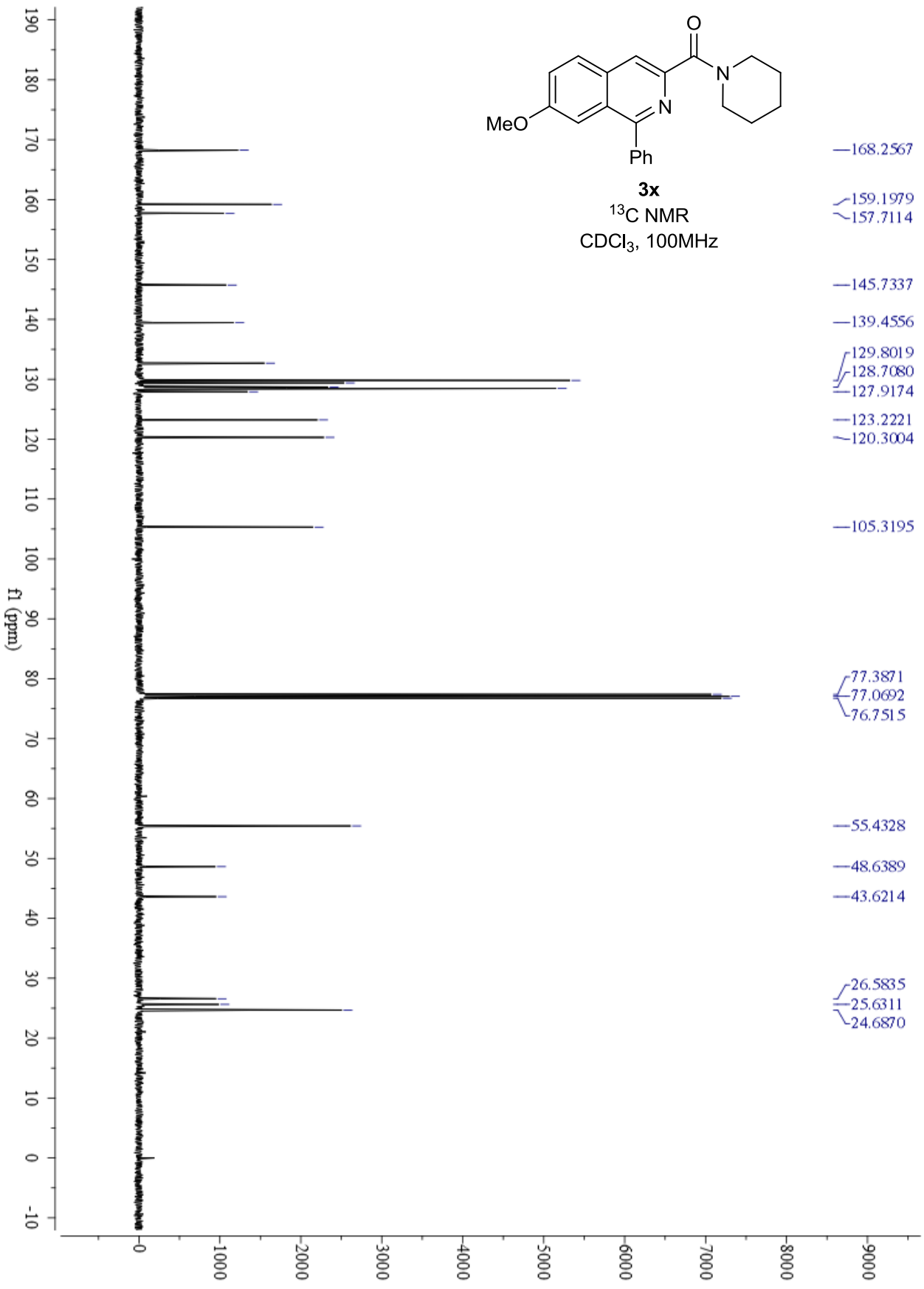
$CDCl_3$, 400MHz

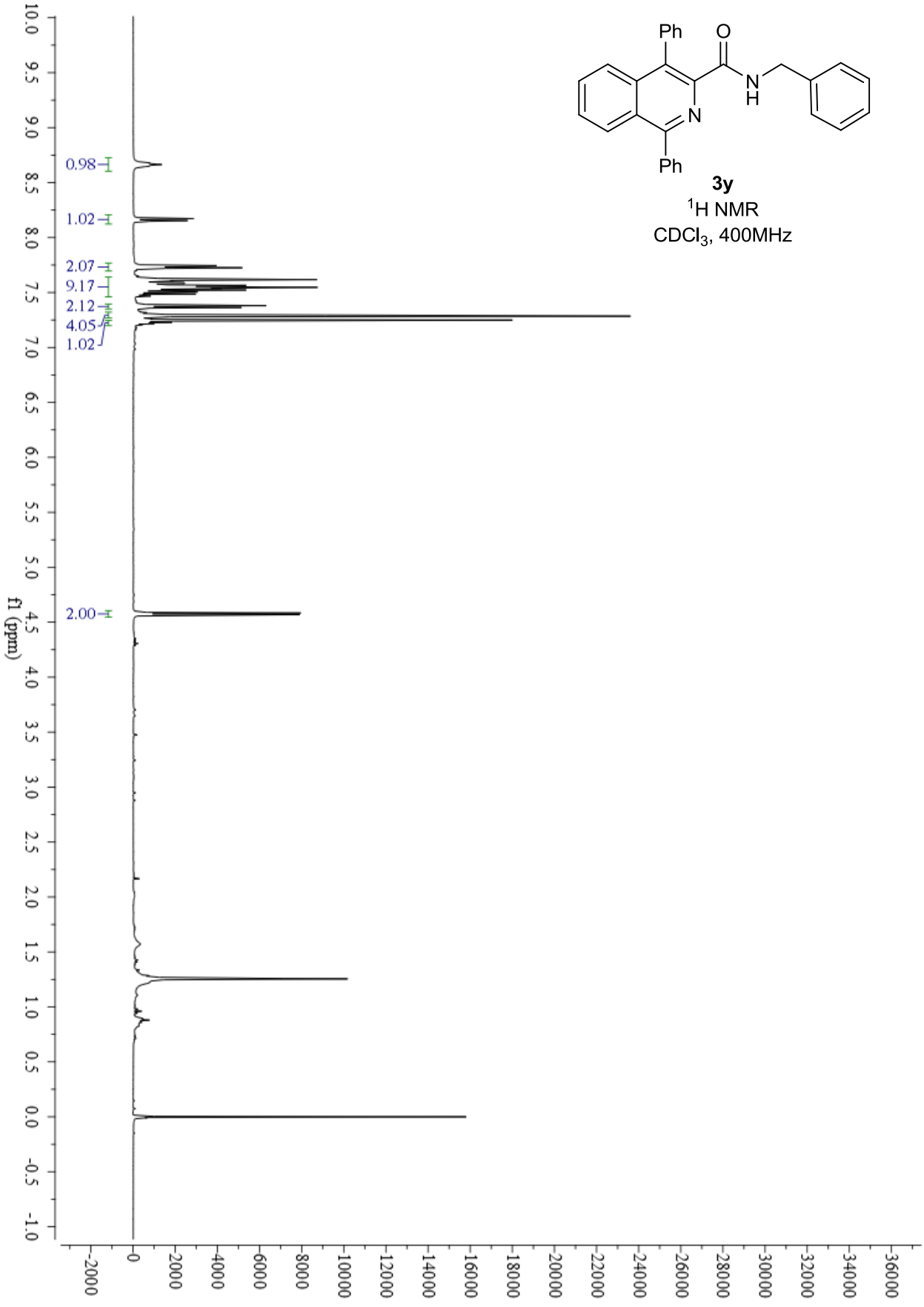

CO2Me
N
Ph
3v
13C NMR
CDCl3, 100MHz
166.2842
159.4041
143.3752
141.6465
138.3237
132.7336
129.1163
128.7503
128.7212
128.2221
127.6907
126.3417
126.1971
125.6315
123.0091
77.3647
77.0468
76.7293
52.9065
f1 (ppm)

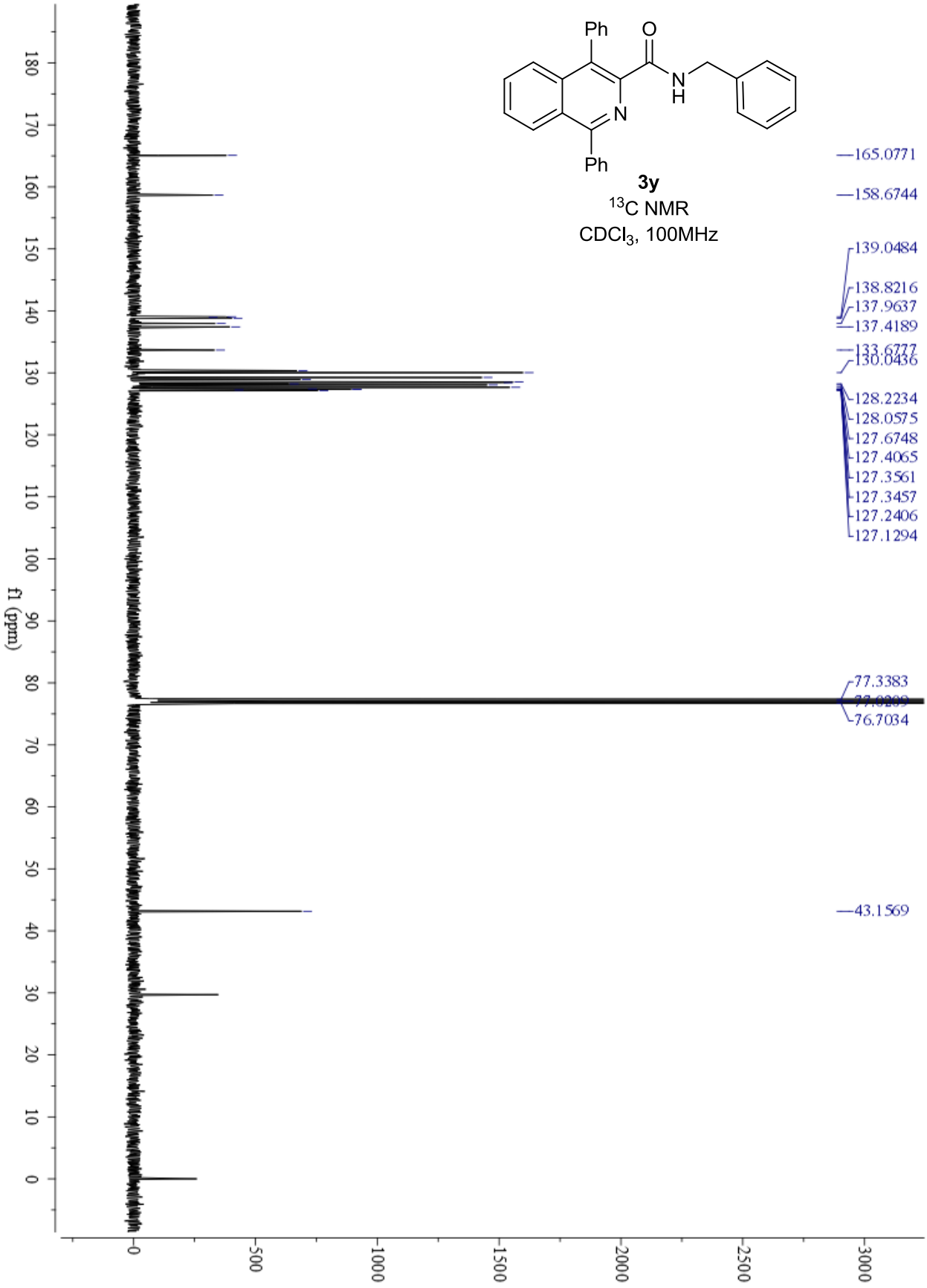

Ph
O
N
N
Ph
3w
1H NMR
CDCl3, 400MHz
f1 (ppm)
1.02
1.00
2.02
10.02
1.97
2.00
2.04
2.09
2.06

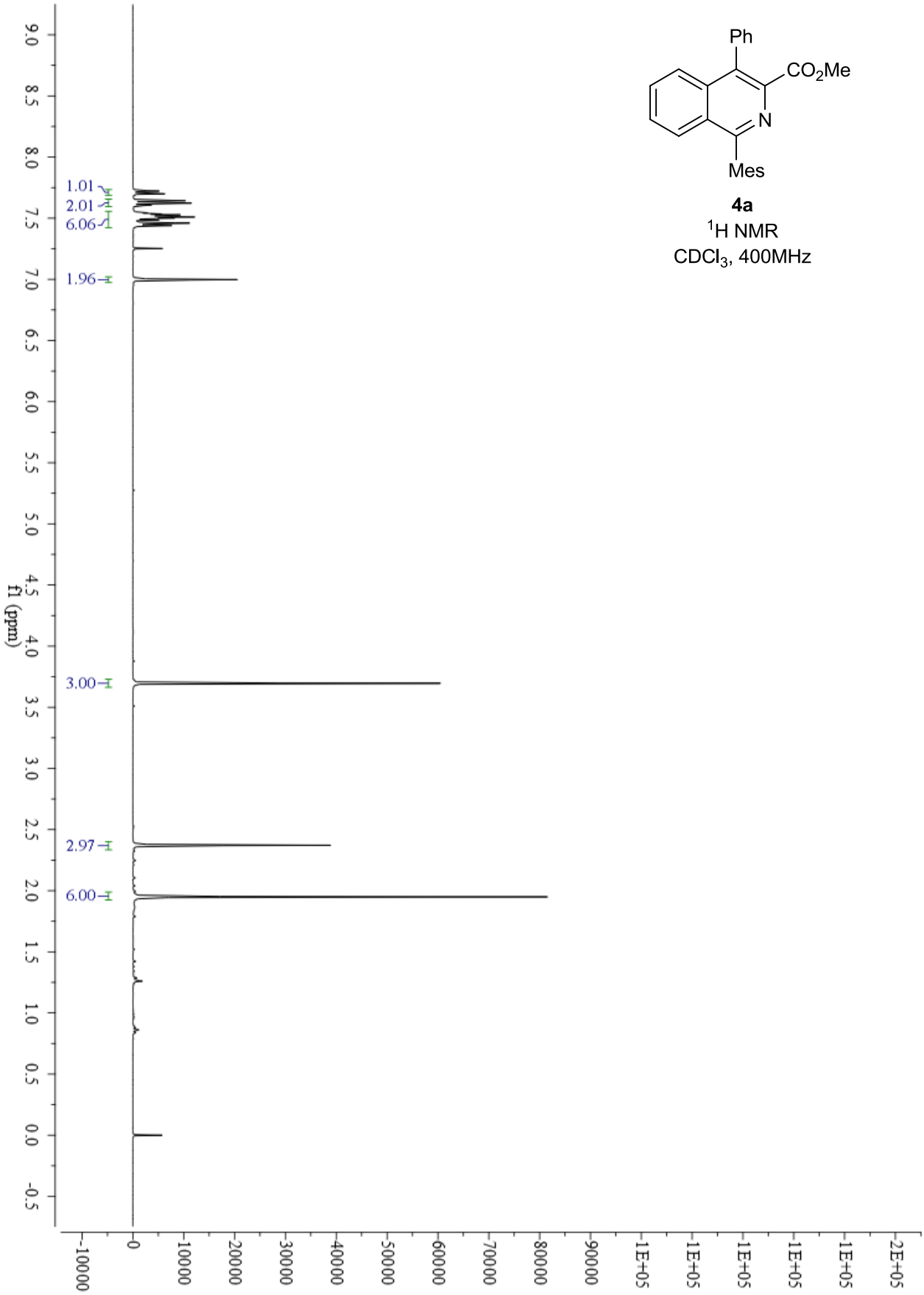

Ph
O
N
N
Ph
3w
13C NMR
CDCl3, 100MHz
167.5105
160.4316
146.2576
139.0769
136.0609
134.9350
130.2128
128.4251
128.3625
128.3507
128.2269
127.7276
127.3329
126.3999
125.9005
77.4476
77.1296
76.8114
47.5366
42.0951
25.8196
25.1489
24.3296
f1 (ppm)

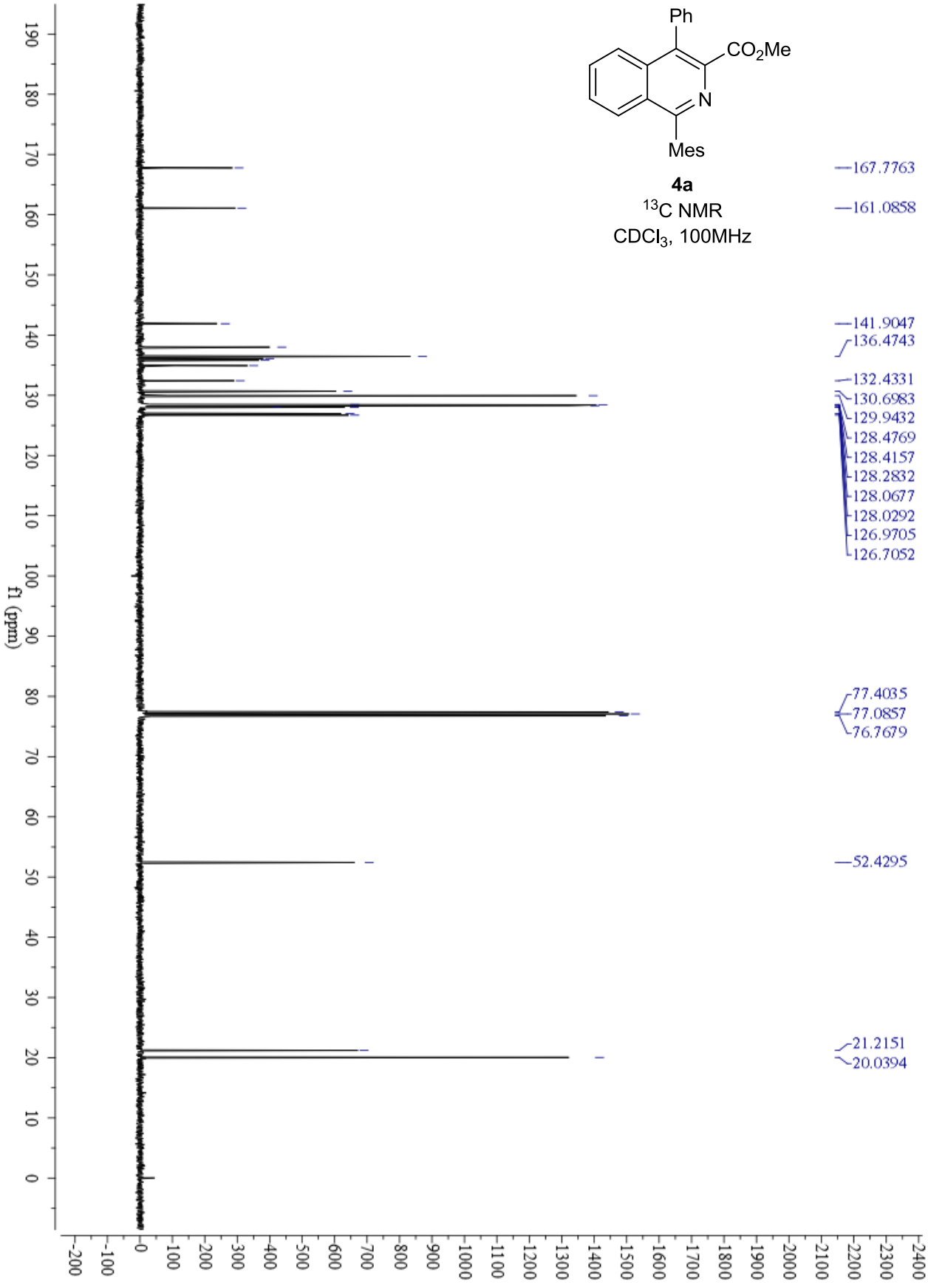

O
N
N
MeO
Ph
3x
1H NMR
CDCl3, 400MHz
0.96
0.98
1.96
3.00
2.10
3.00
2.05
1.95
6.12
f1 (ppm)

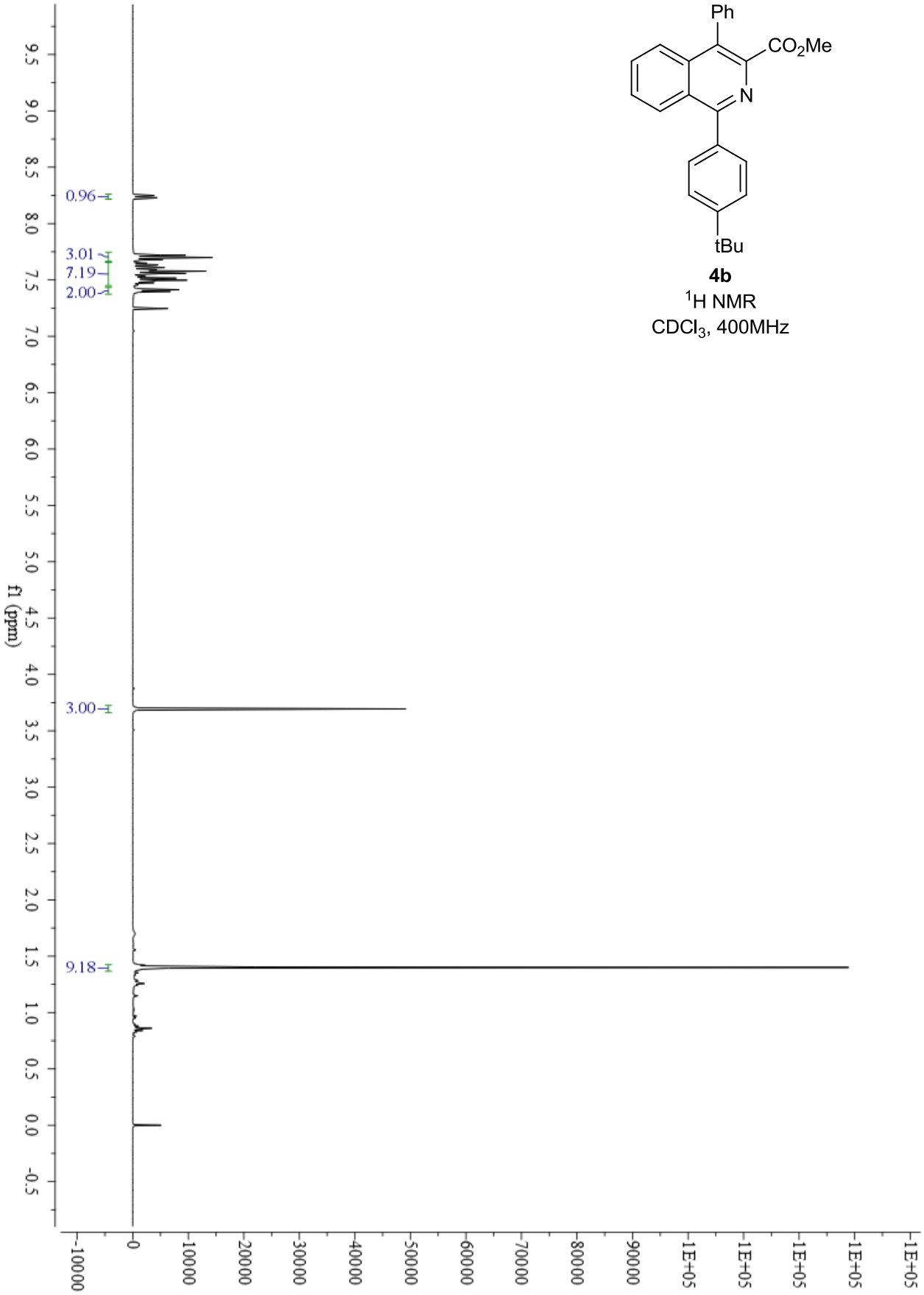

O
N
MeO
N
Ph
3x
13C NMR
CDCl3, 100MHz
168.2567
159.1979
157.7114
145.7337
139.4556
129.8019
128.7080
127.9174
123.2221
120.3004
105.3195
77.3871
77.0692
76.7515
55.4328
48.6389
43.6214
26.5835
25.6311
24.6870
f1 (ppm)

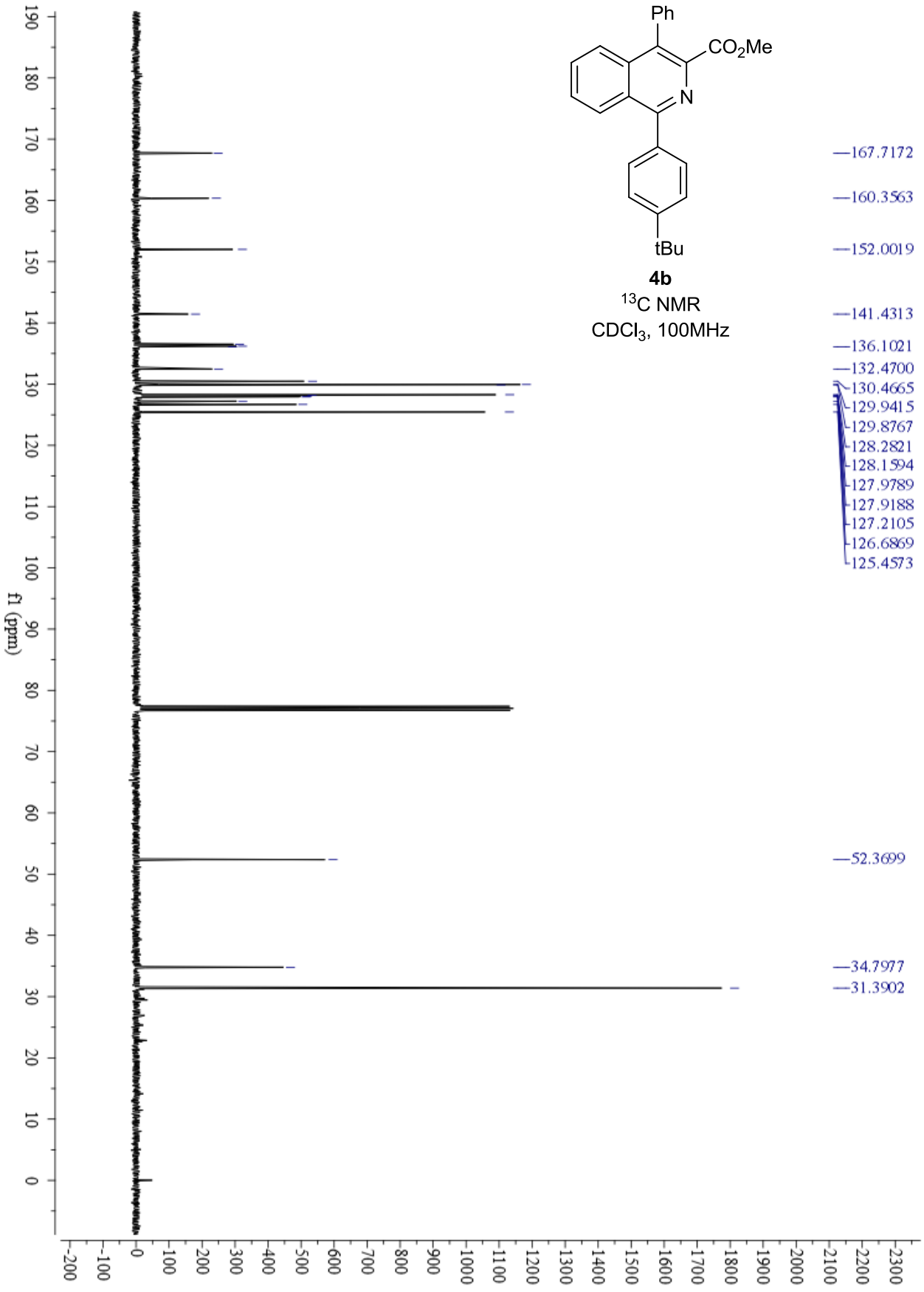

Ph
O
N
H
N
Ph
3y
1H NMR
CDCl3, 400MHz
0.98
1.02
2.07
9.17
2.12
4.05
1.02
2.00
f1 (ppm)

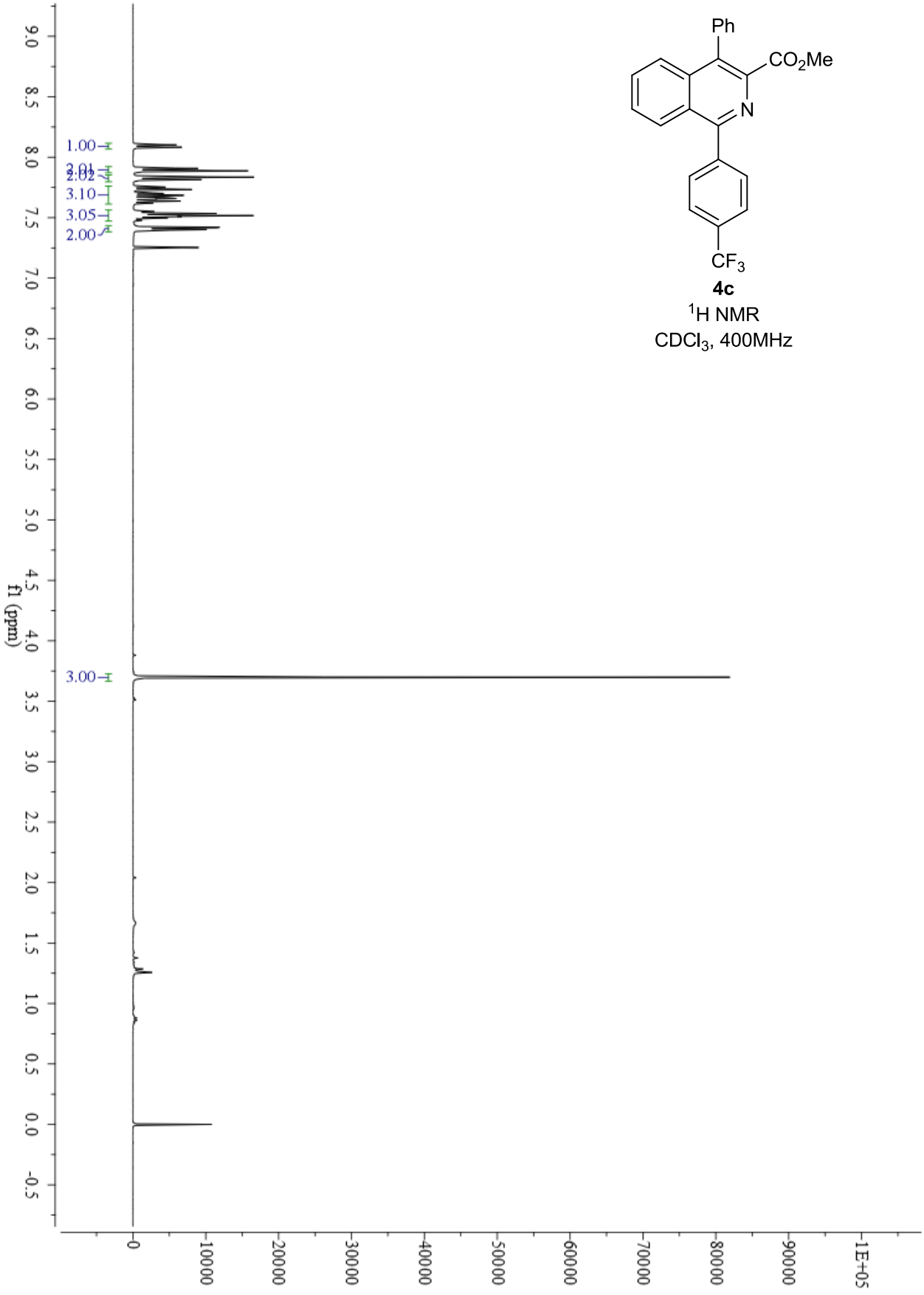

Ph
O
N
H
N
Ph
3y
13C NMR
CDCl3, 100MHz
165.0771
158.6744
139.0484
138.8216
137.9637
137.4189
133.6777
130.0436
128.2234
128.0575
127.6748
127.4065
127.3561
127.3457
127.2406
127.1294
77.3383
76.7034
43.1569
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
0
500
1000
1500
2000
2500
3000

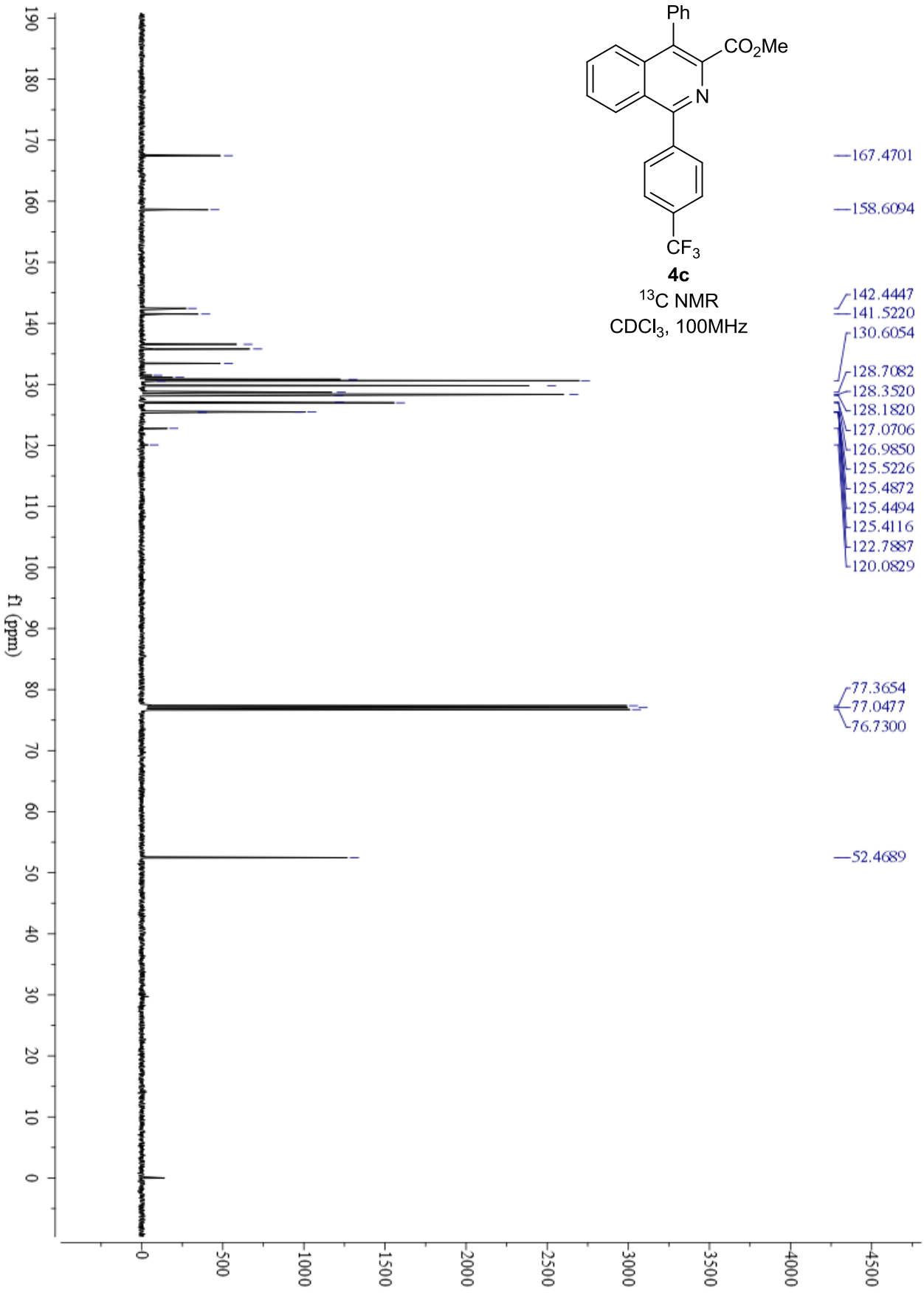

Ph
CO2Me
N
Mes
4a
1H NMR
CDCl3, 400MHz
1.01
2.01
6.06
1.96
3.00
2.97
6.00
f1 (ppm)

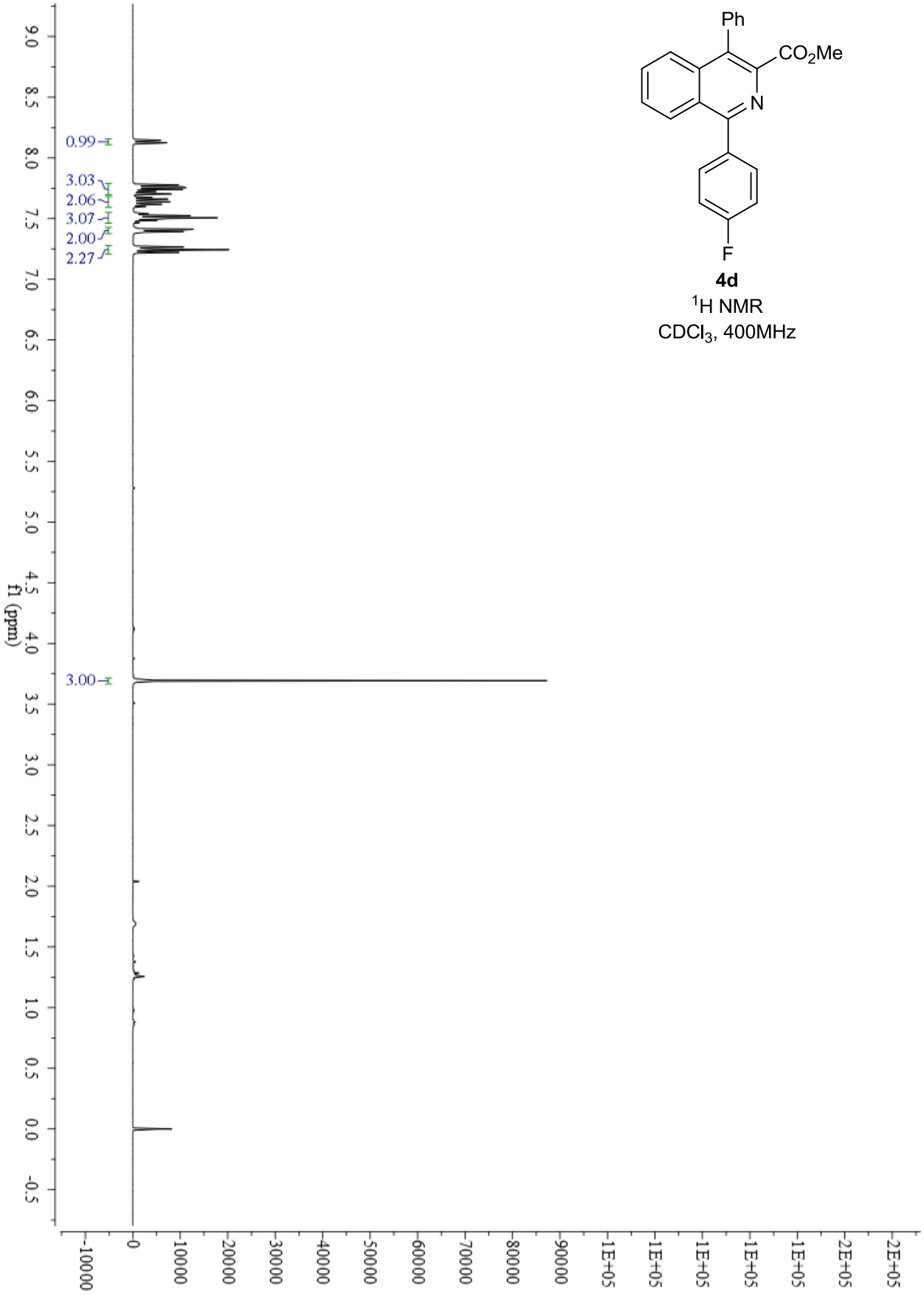

Ph
CO2Me
N
Mes
4a
13C NMR
CDCl3, 100MHz
167.7763
161.0858
141.9047
136.4743
132.4331
130.6983
129.9432
128.4769
128.4157
128.2832
128.0677
128.0292
126.9705
126.7052
77.4035
77.0857
76.7679
52.4295
21.2151
20.0394
f1 (ppm)

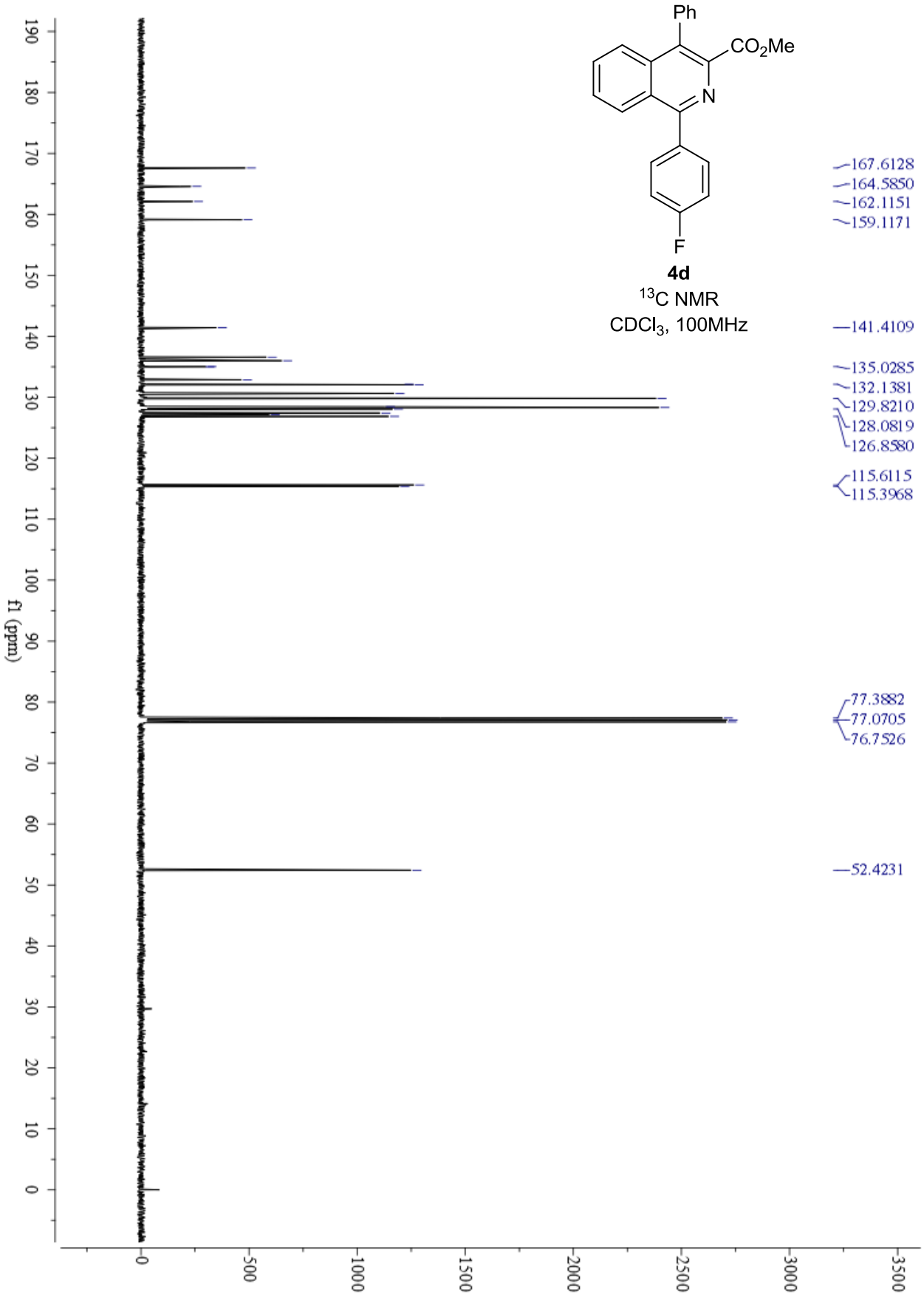

Ph
CO2Me
N
tBu
4b
1H NMR
CDCl3, 400MHz
0.96
3.01
7.19
2.00
3.00
9.18
f1 (ppm)

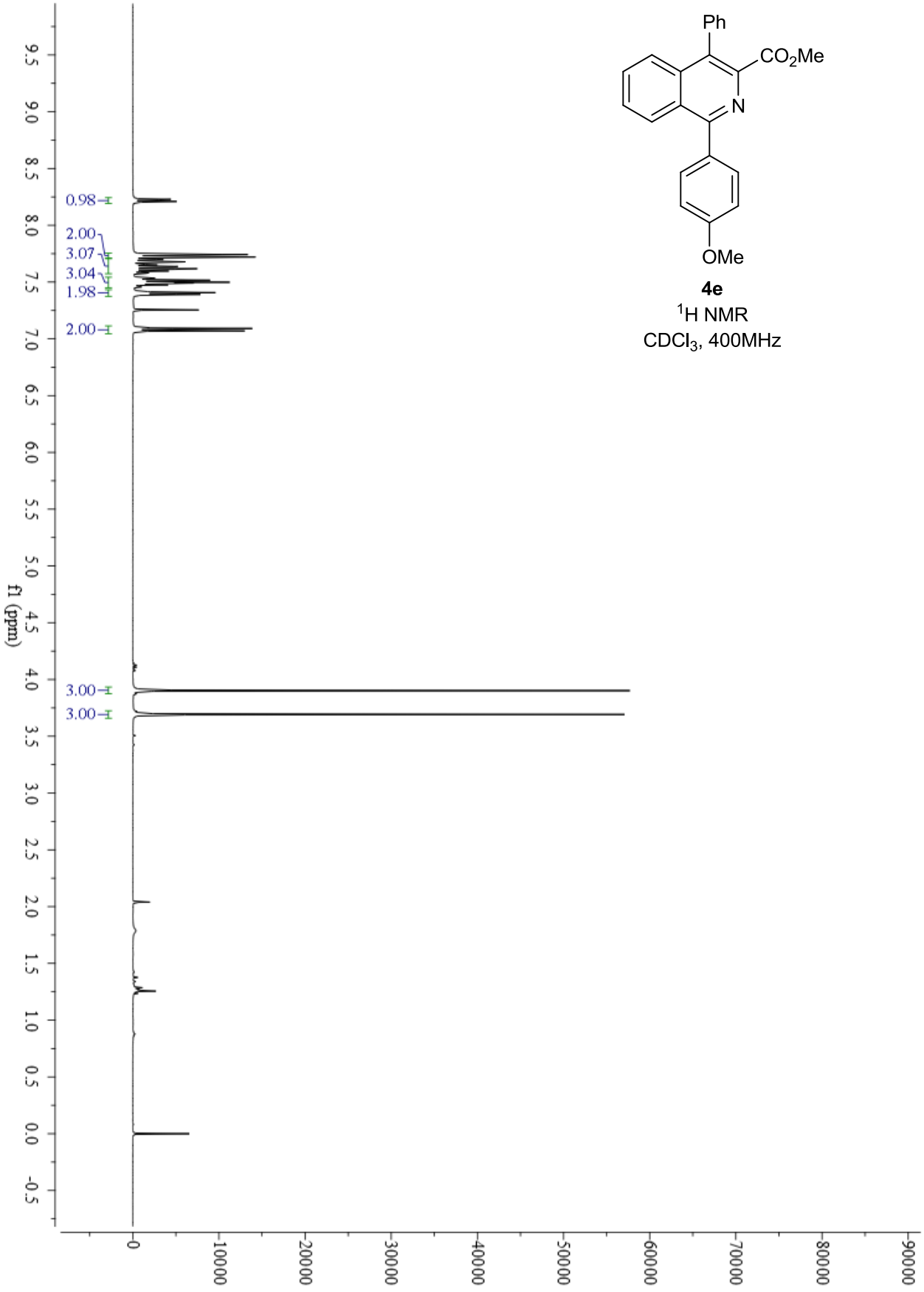

Ph
CO2Me
N
tBu
4b
13C NMR
CDCl3, 100MHz
167.7172
160.3563
152.0019
141.4313
136.1021
132.4700
130.4665
129.9415
129.8767
128.2821
128.1594
127.9789
127.9188
127.2105
126.6869
125.4573
52.3699
34.7977
31.3902
f1 (ppm)

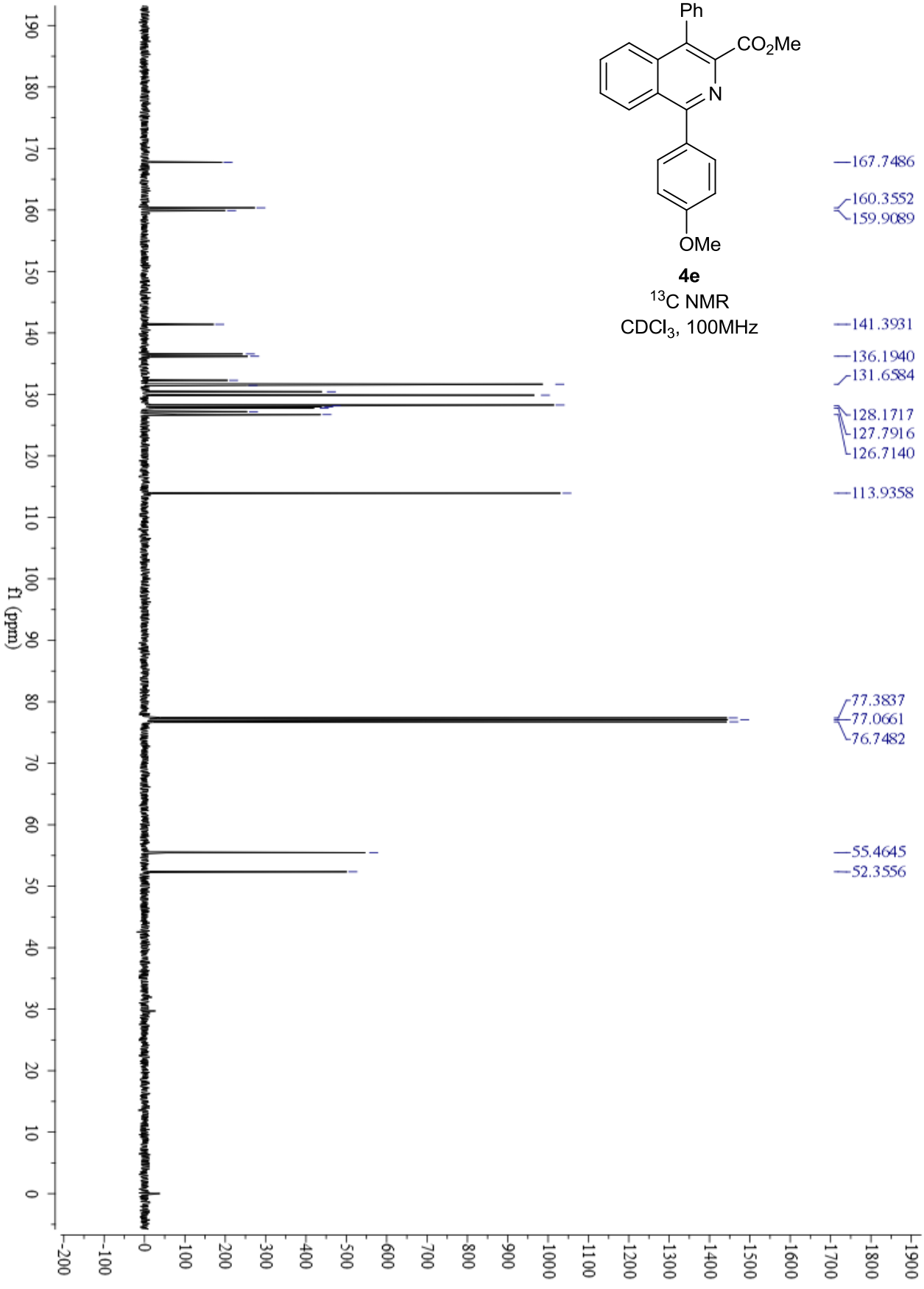

Ph
CO2Me
N
CF3
4c
1H NMR
CDCl3, 400MHz
1.00
2.01
2.02
3.10
3.05
2.00
3.00
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
1E+05

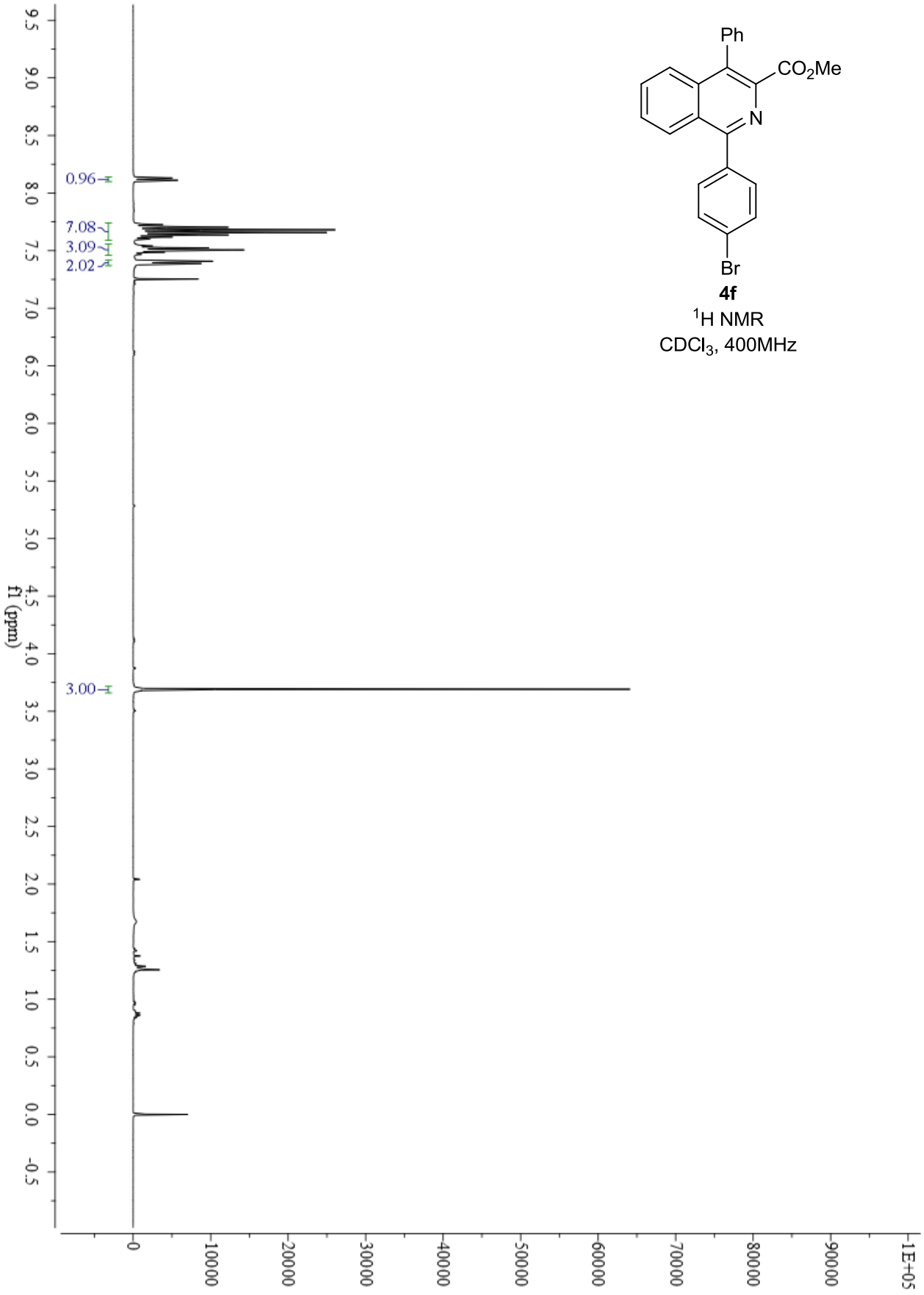

Ph
CO2Me
N
CF3
4c
13C NMR
CDCl3, 100MHz
167.4701
158.6094
142.4447
141.5220
130.6054
128.7082
128.3520
128.1820
127.0706
126.9850
125.5226
125.4872
125.4494
125.4116
122.7887
120.0829
77.3654
77.0477
76.7300
52.4689
f1 (ppm)

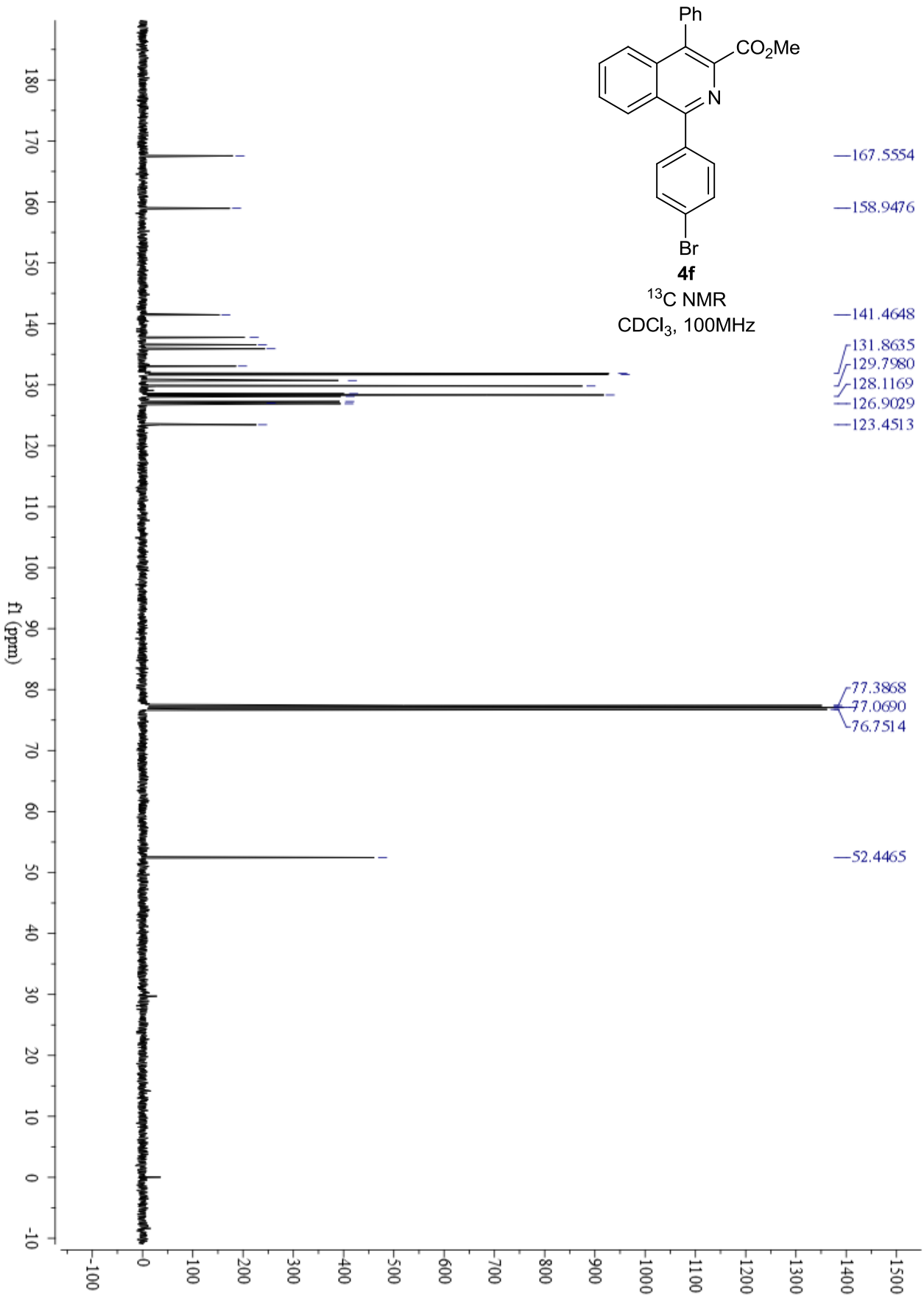

Ph
CO2Me
N
F
4d
1H NMR
CDCl3, 400MHz
0.99
3.03
2.06
3.07
2.00
2.27
3.00
f1 (ppm)


Ph
CO2Me
N
F
4d
13C NMR
CDCl3, 100MHz
167.6128
164.5850
162.1151
159.1171
141.4109
135.0285
132.1381
129.8210
128.0819
126.8580
115.6115
115.3968
77.3882
77.0705
76.7526
52.4231
f1 (ppm)


Ph
CO2Me
N
OMe
4e
1H NMR
CDCl3, 400MHz
0.98
2.00
3.07
3.04
1.98
2.00
3.00
3.00
f1 (ppm)


Ph
CO2Me
N
OMe
4e
13C NMR
CDCl3, 100MHz
167.7486
160.3552
159.9089
141.3931
136.1940
131.6584
128.1717
127.7916
126.7140
113.9358
77.3837
77.0661
76.7482
55.4645
52.3556
f1 (ppm)


Ph
CO2Me
N
Br
4f
1H NMR
CDCl3, 400MHz
0.96
7.08
3.09
2.02
3.00
f1 (ppm)


Ph
CO2Me
N
Br
4f
13C NMR
CDCl3, 100MHz
167.5554
158.9476
141.4648
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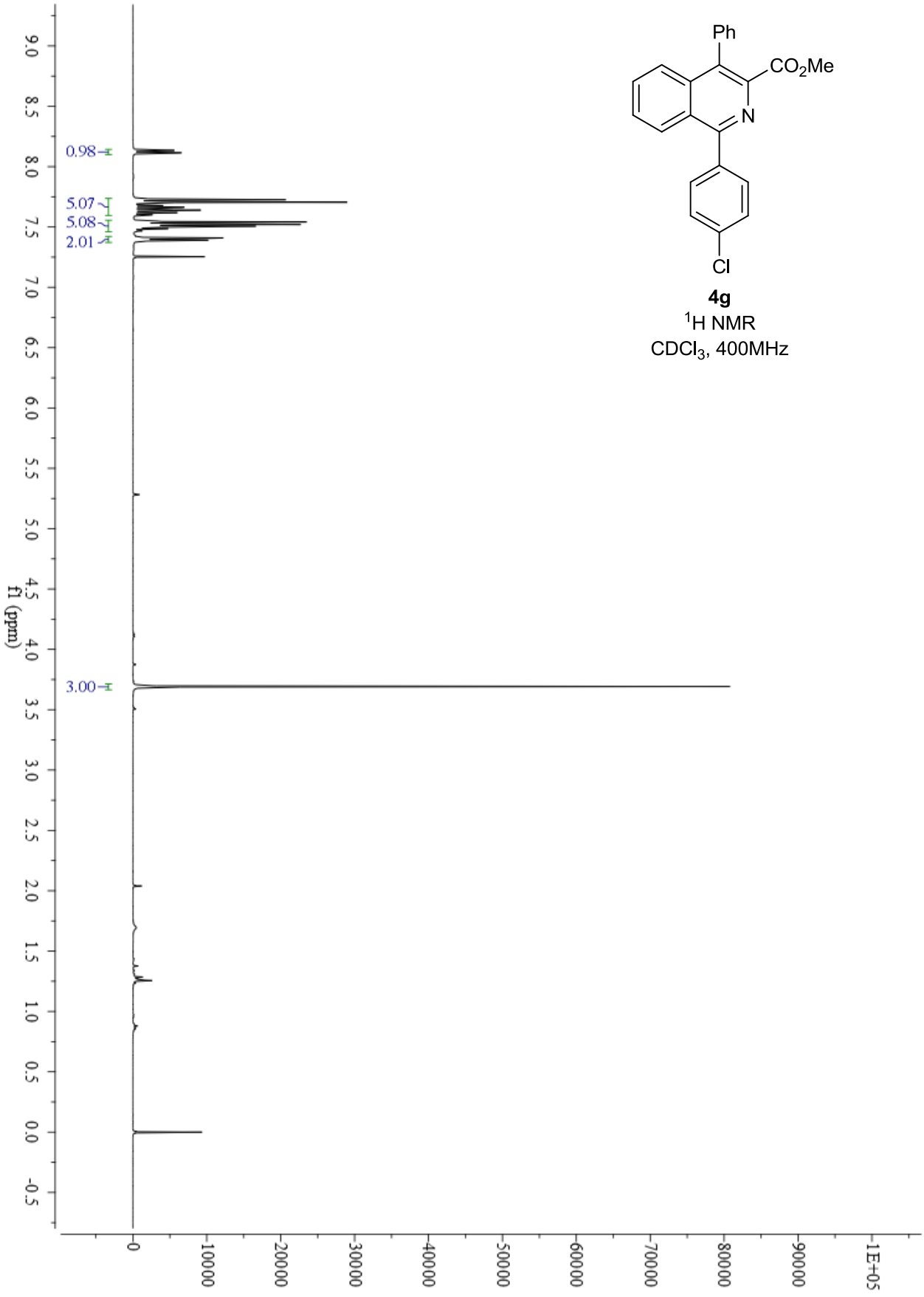
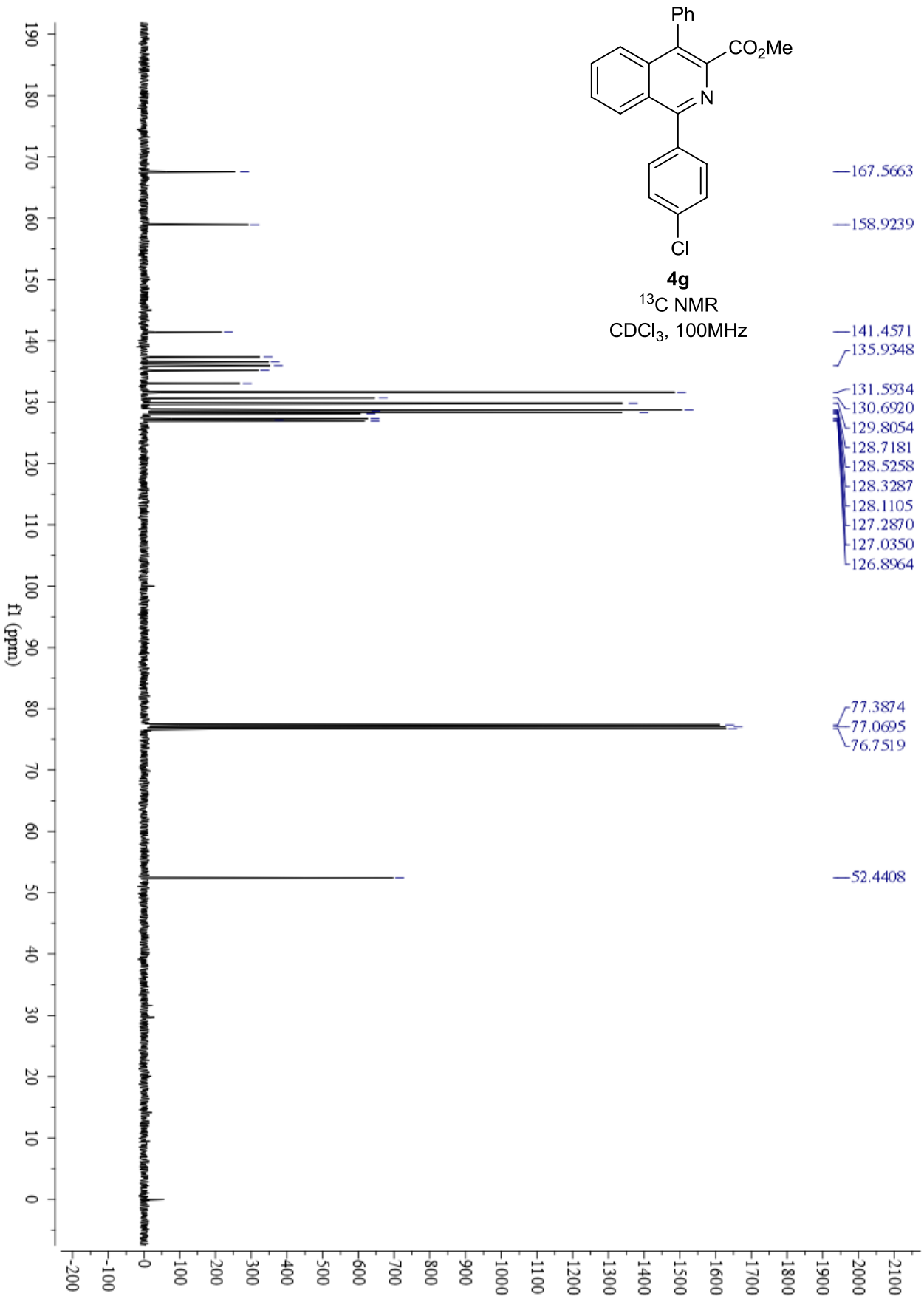
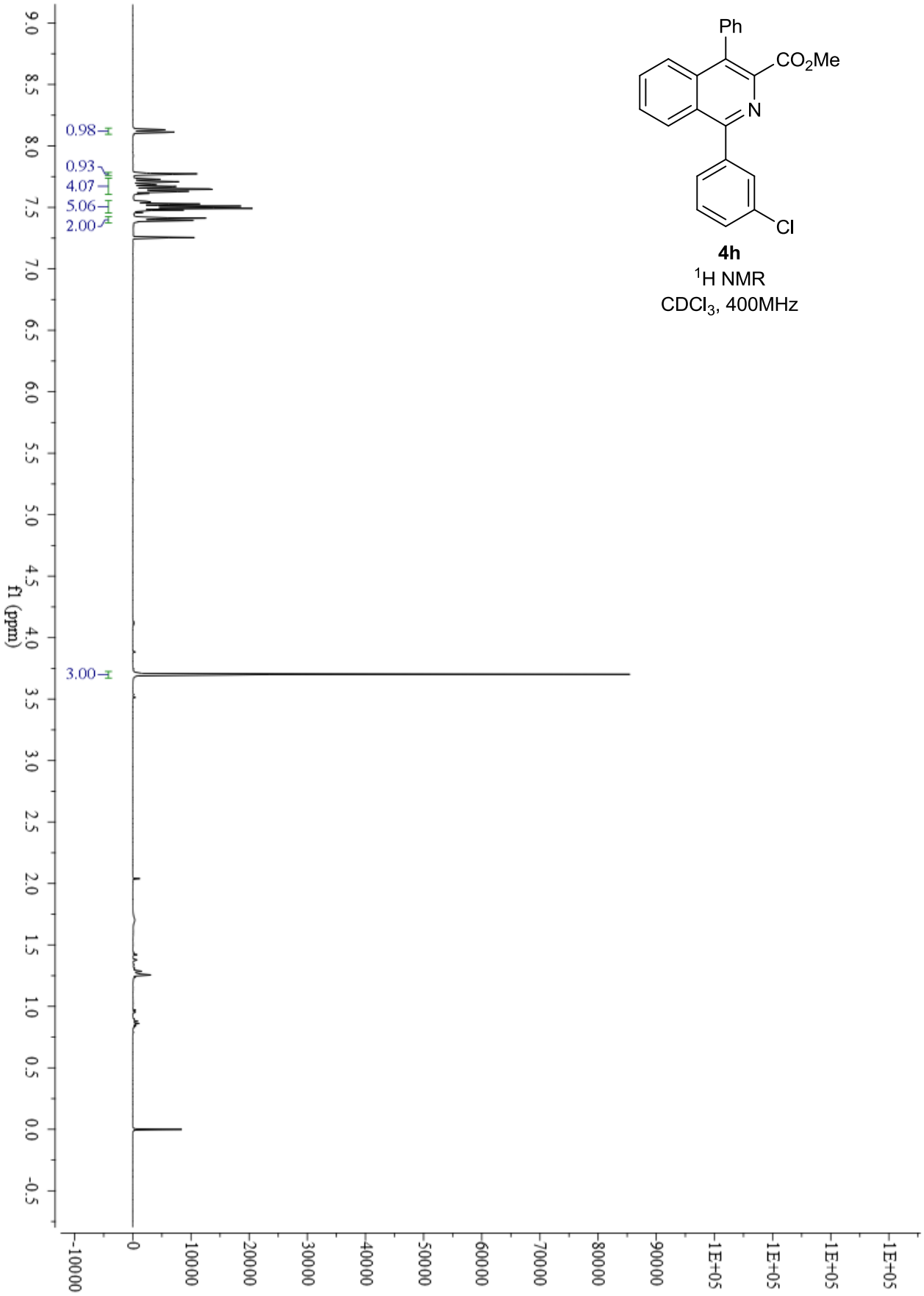
128.1169
126.9029
123.4513
77.3868
77.0690
76.7514
52.4465
f1 (ppm)


Ph
CO2Me
N
Cl
4g
1H NMR
CDCl3, 400MHz
0.98
5.07
5.08
2.01
3.00
f1 (ppm)


Ph
CO2Me
N
Cl
4g
13C NMR
CDCl3, 100MHz
167.5663
158.9239
141.4571
135.9348
131.5934
130.6920
129.8054
128.7181
128.5258
128.3287
128.1105
127.2870
127.0350
126.8964
77.3874
77.0695
76.7519
52.4408
f1 (ppm)


Ph
CO2Me
N
Cl
4h
1H NMR
CDCl3, 400MHz
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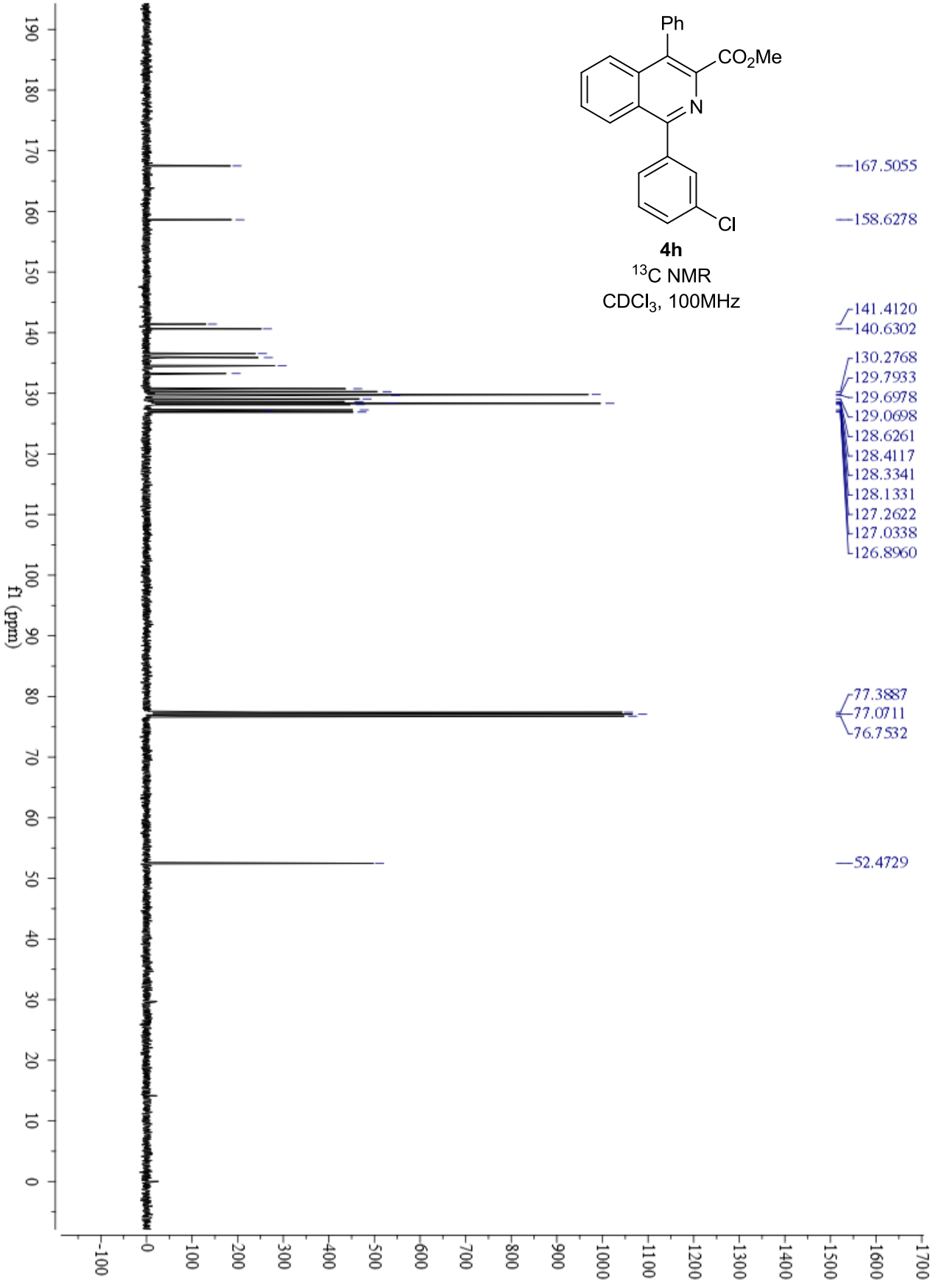
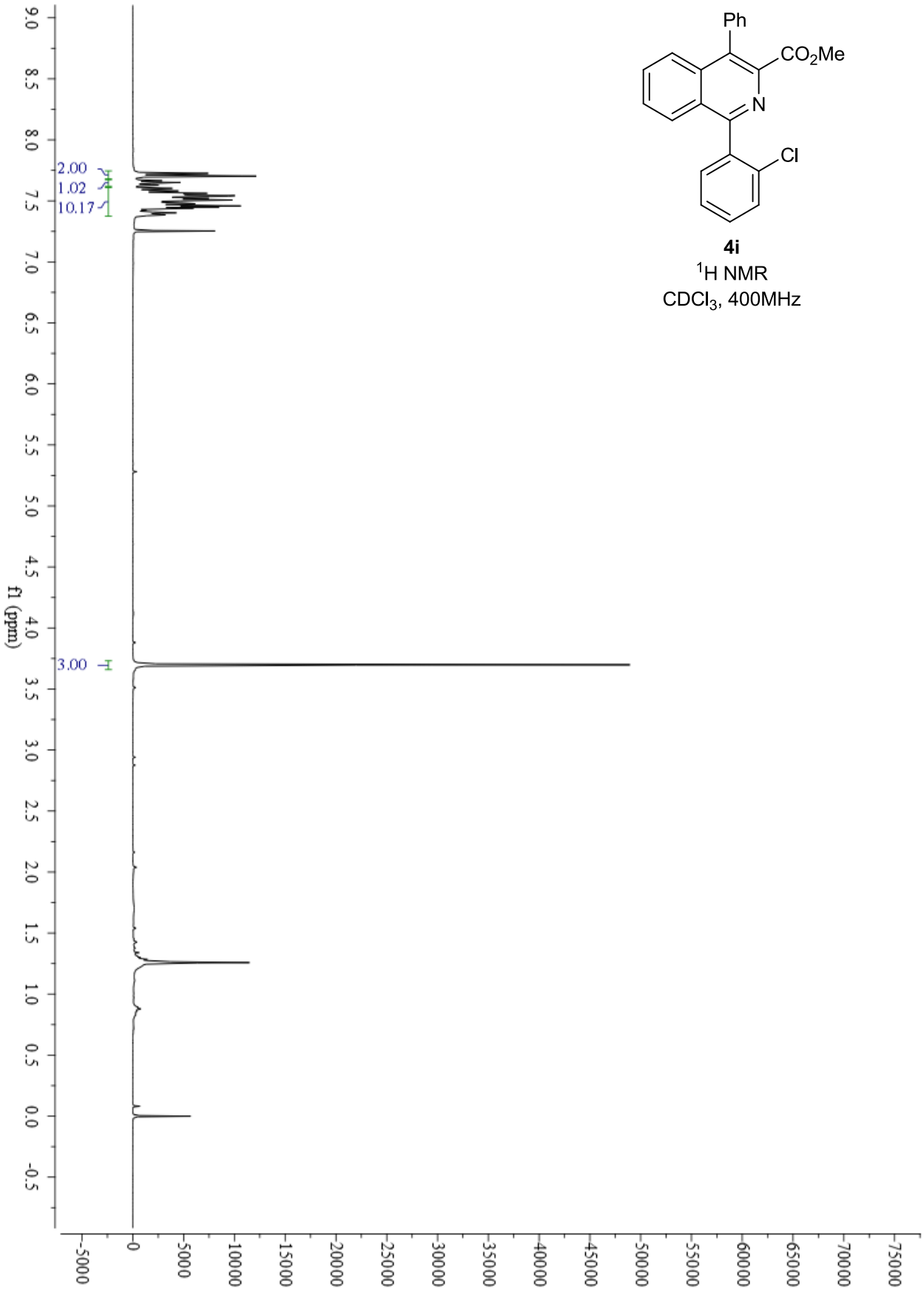
0.93
4.07
5.06
2.00
3.00
f1 (ppm)

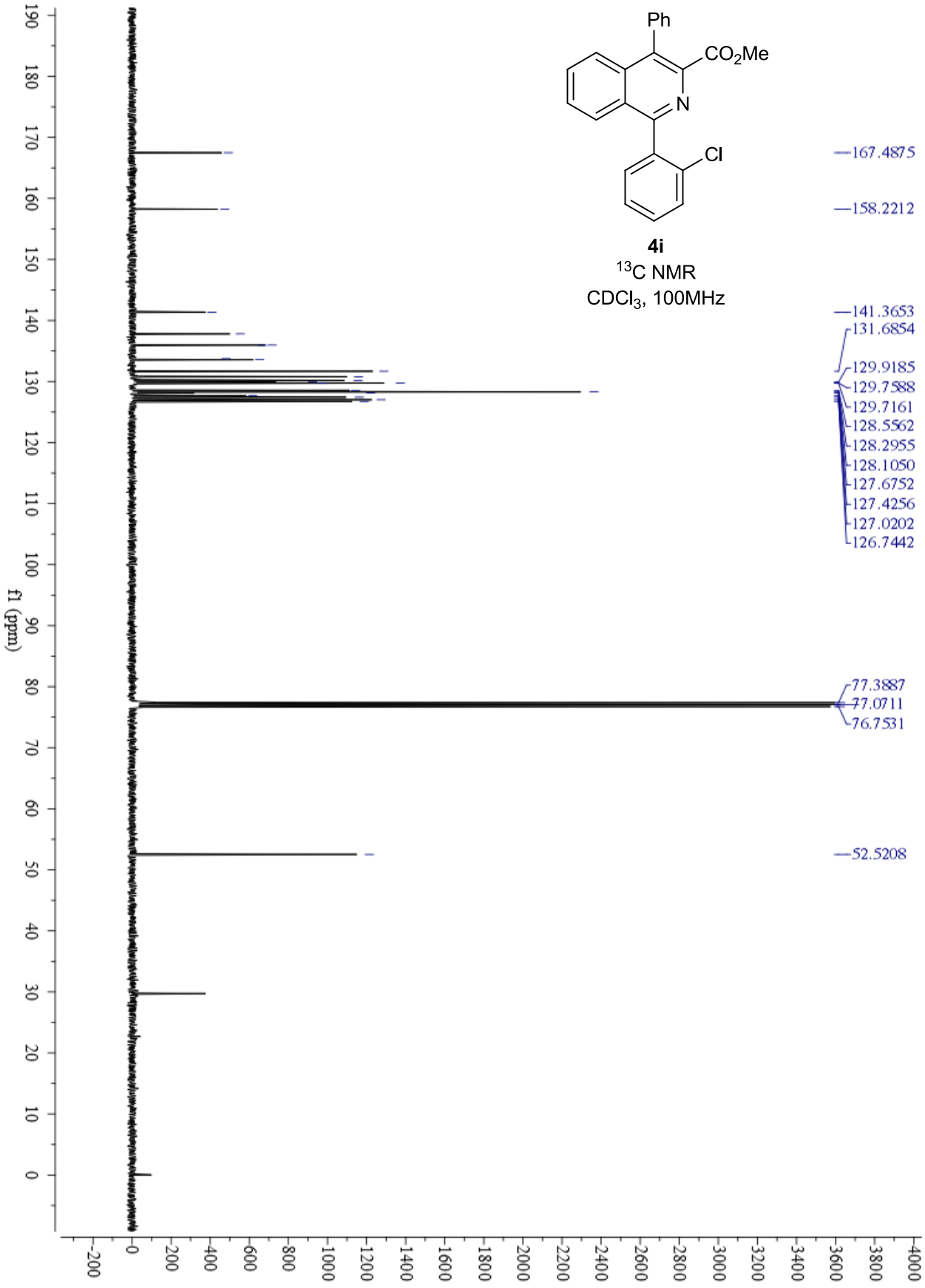

Ph
CO2Me
N
Cl
4h
13C NMR
CDCl3, 100MHz
167.5055
158.6278
141.4120
140.6302
130.2768
129.7933
129.6978
129.0698
128.6261
128.4117
128.3341
128.1331
127.2622
127.0338
126.8960
77.3887
77.0711
76.7532
52.4729
f1 (ppm)

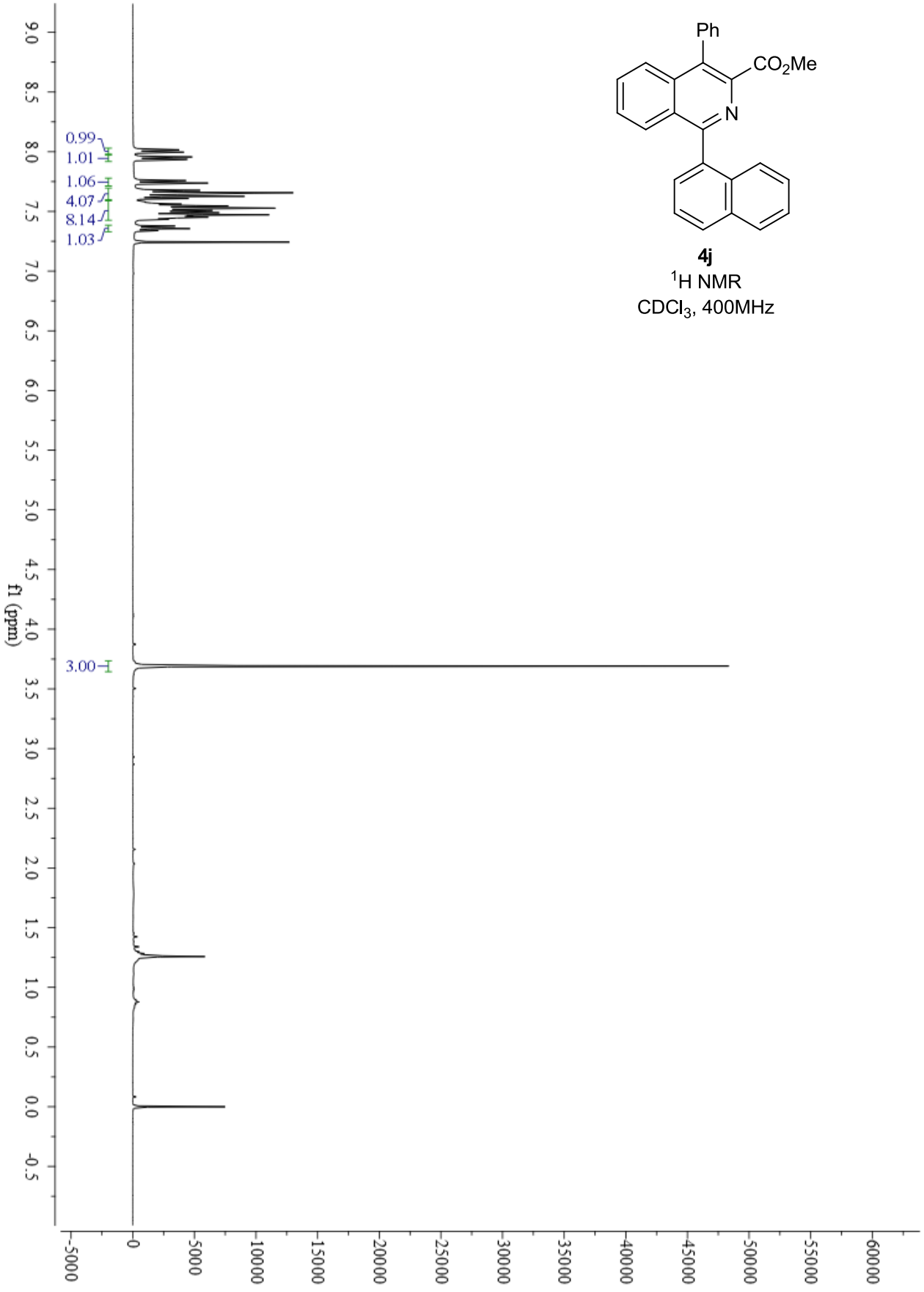


4i

^{1}H NMR

$CDCl_3$, 400MHz

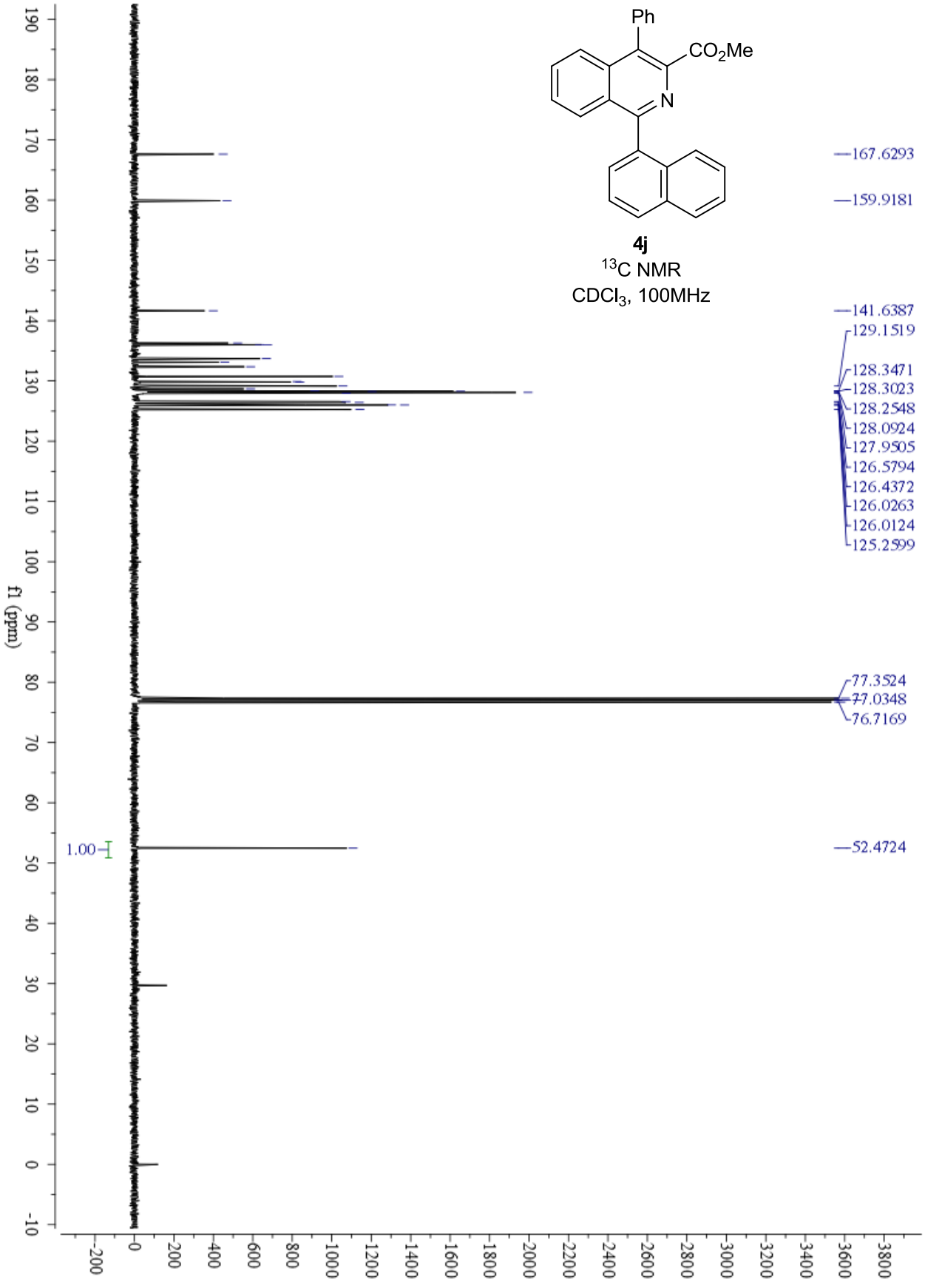

Ph
CO2Me
N
Cl
4i
13C NMR
CDCl3, 100MHz
167.4875
158.2212
141.3653
131.6854
129.9185
129.7588
129.7161
128.5562
128.2955
128.1050
127.6752
127.4256
127.0202
126.7442
77.3887
77.0711
76.7531
52.5208
f1 (ppm)

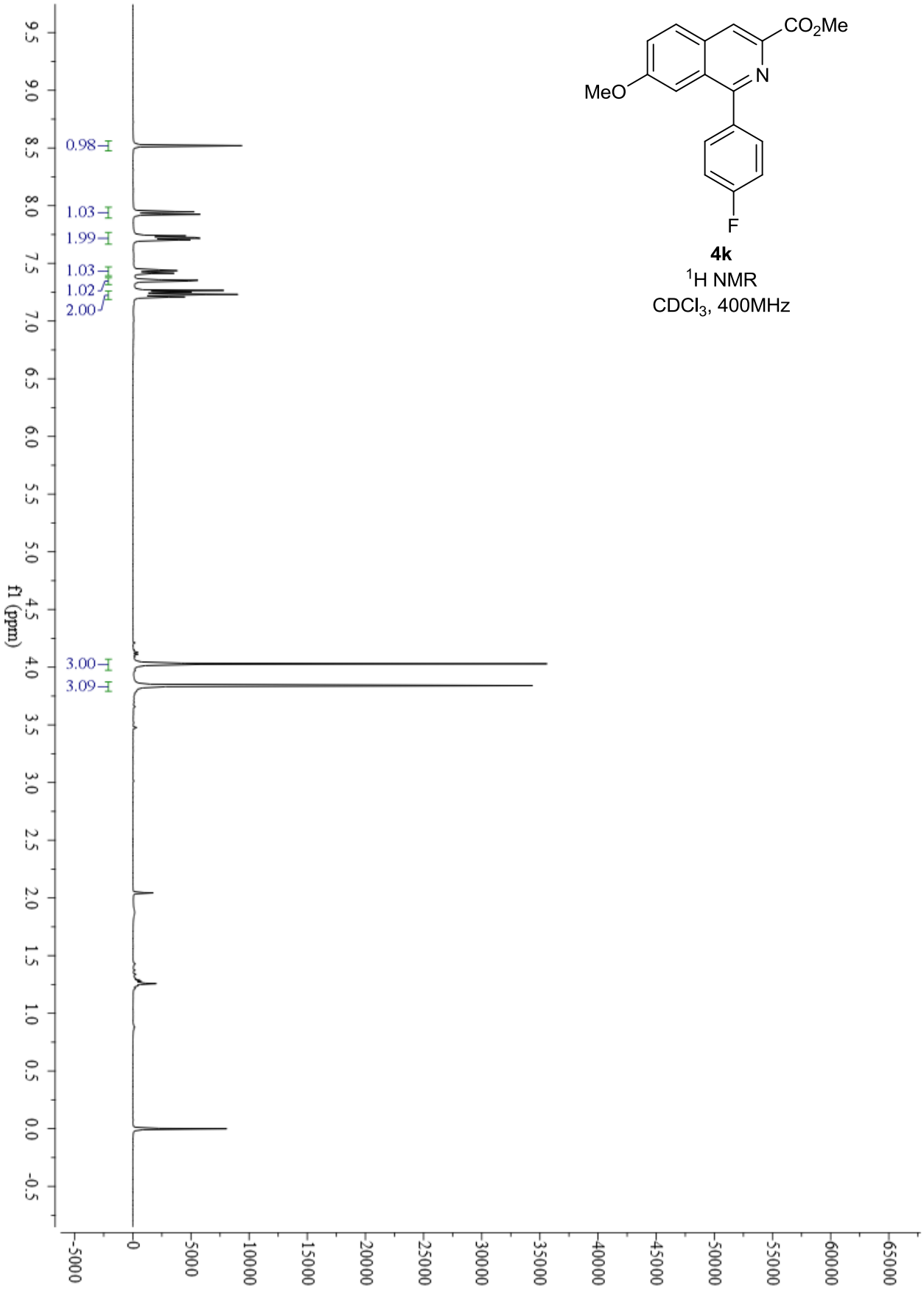


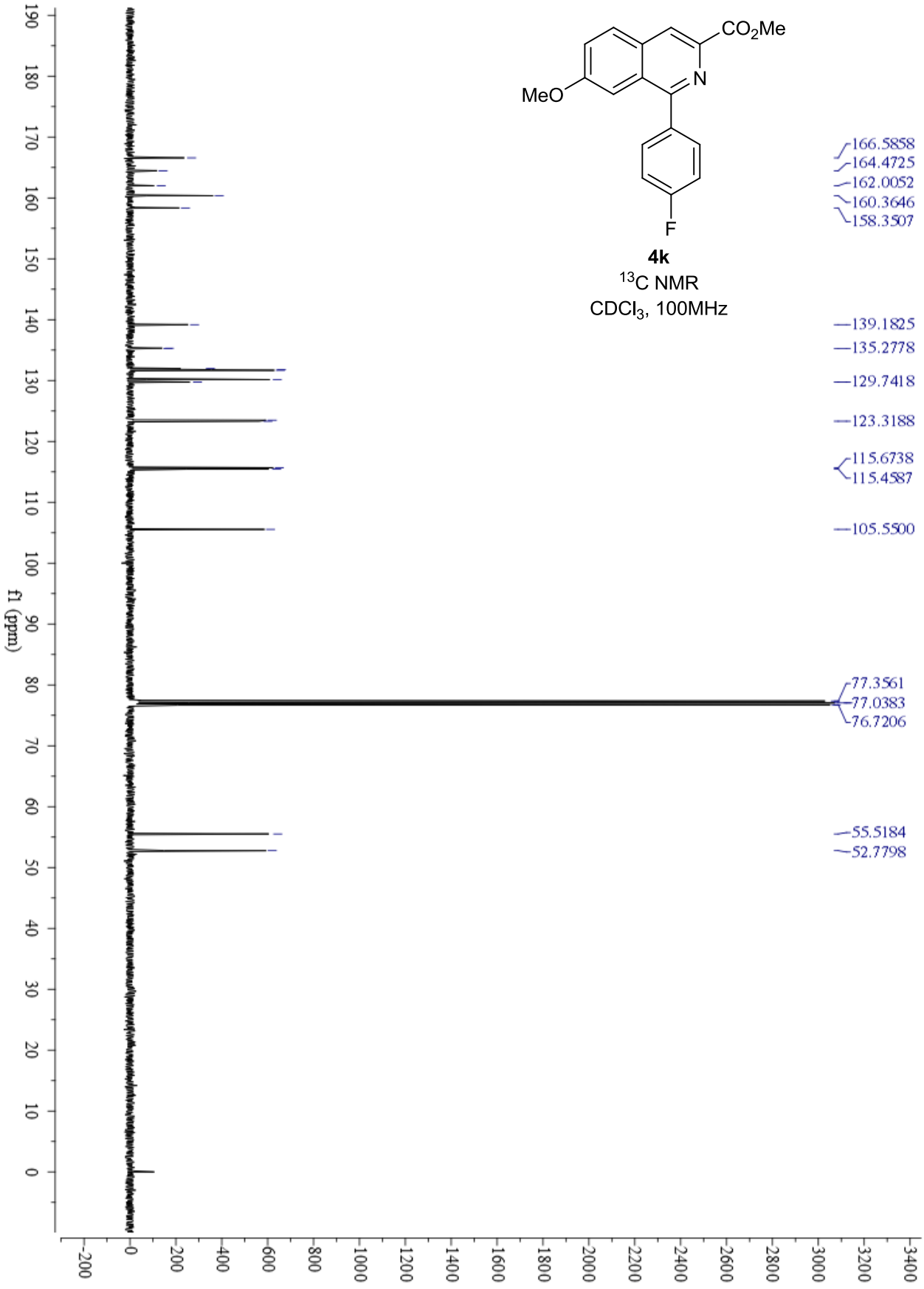
4j

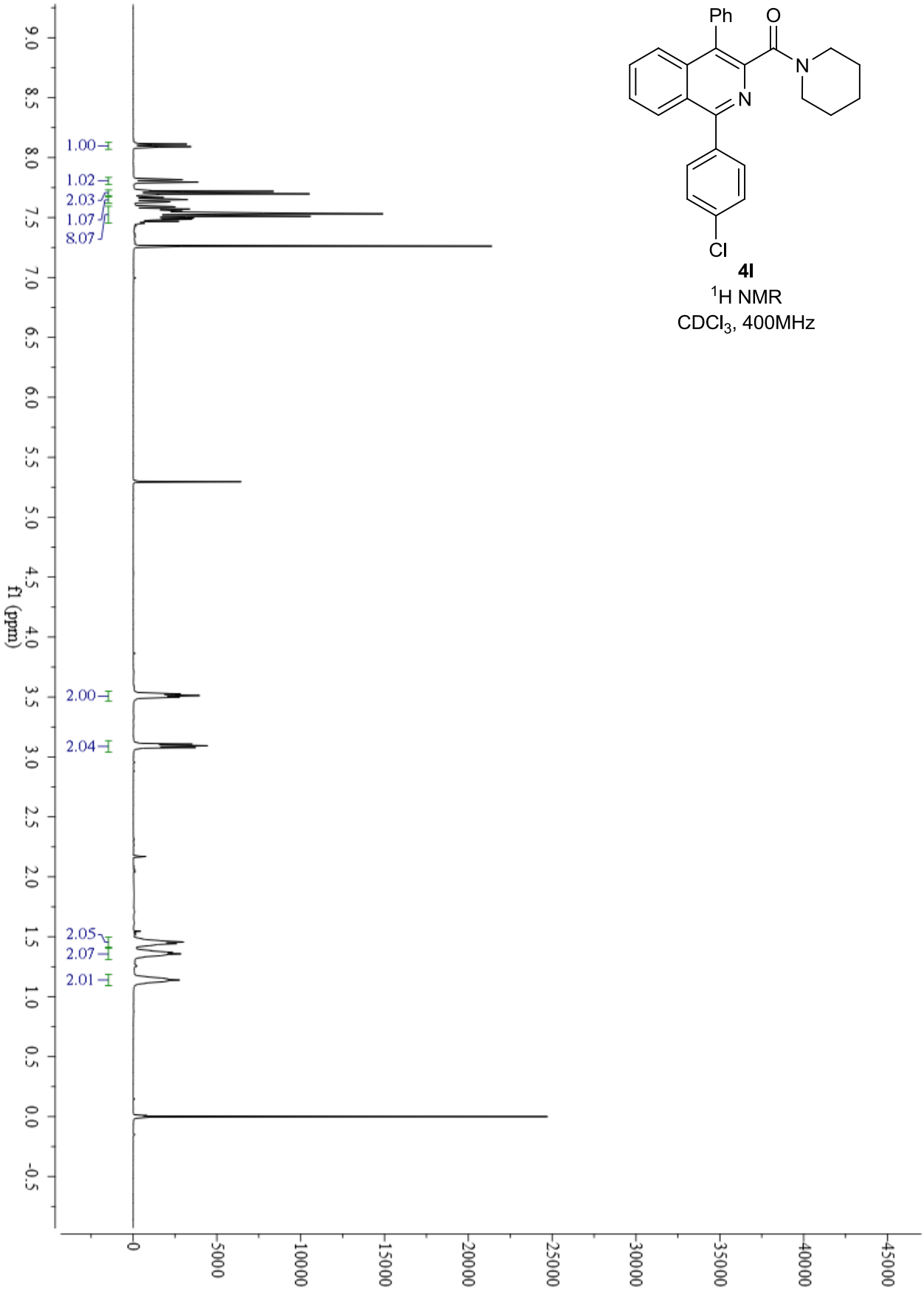
^{1}H NMR

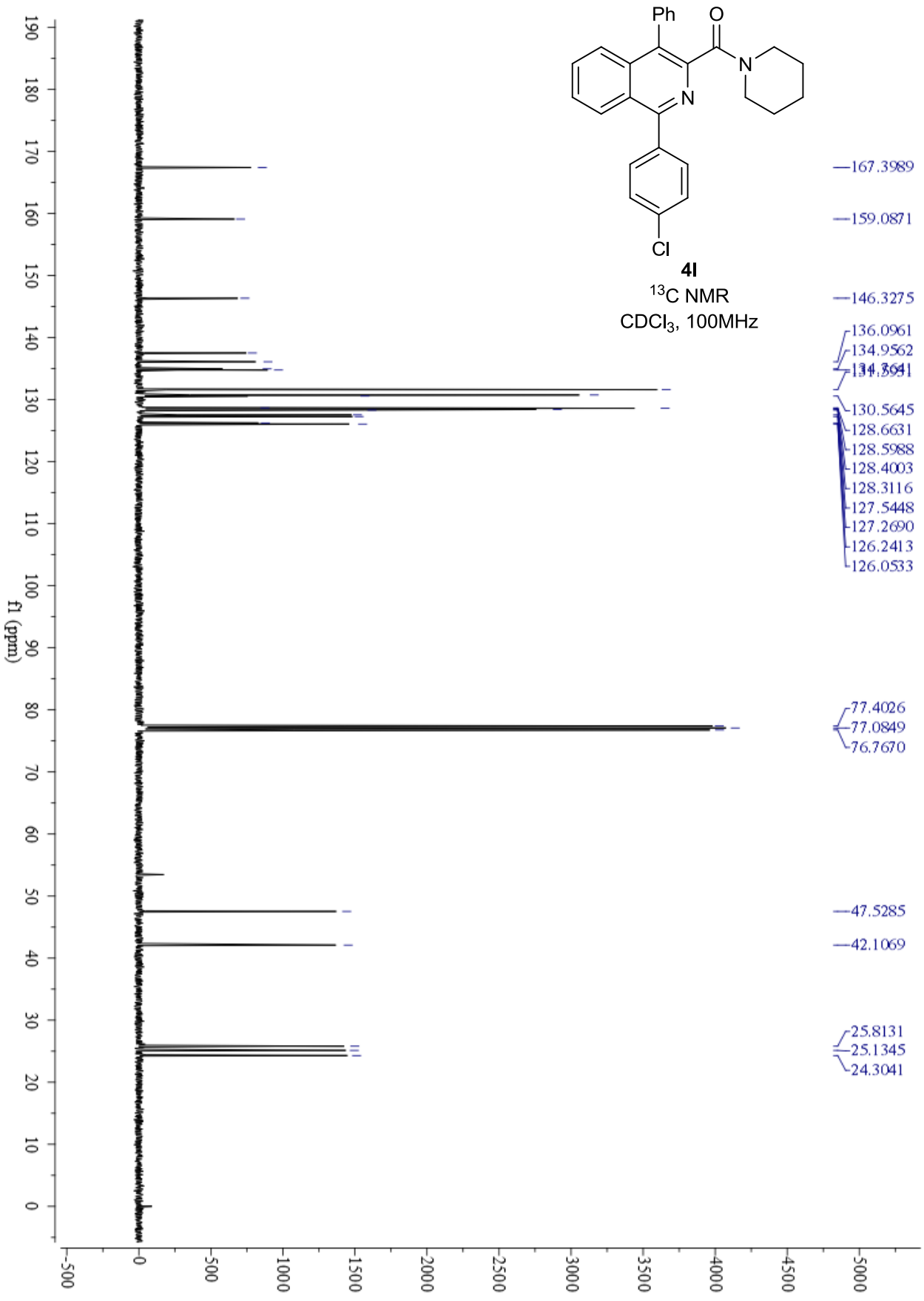
$CDCl_3$, 400MHz

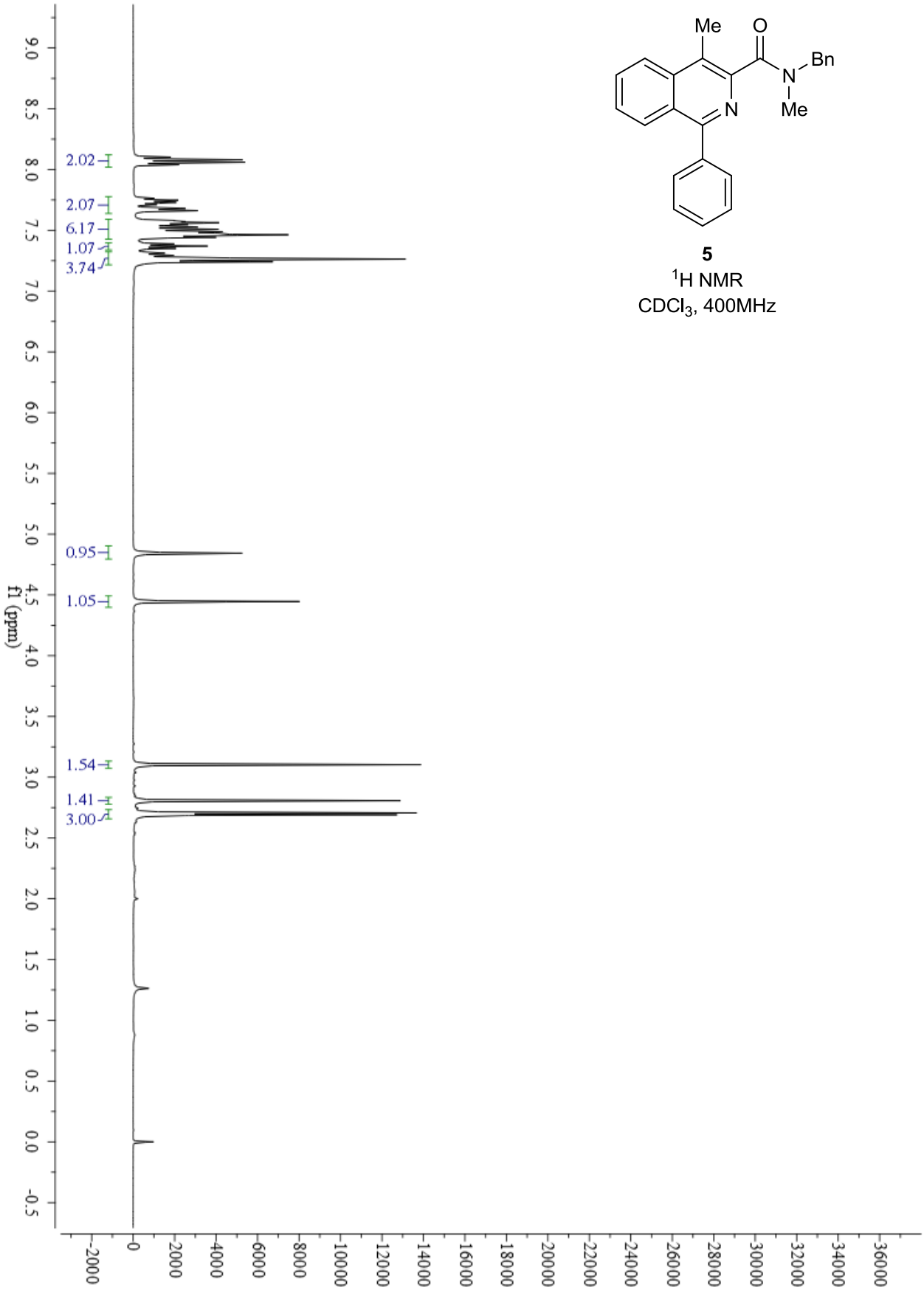

Ph
CO2Me
N
4j
13C NMR
CDCl3, 100MHz
167.6293
159.9181
141.6387
129.1519
128.3471
128.3023
128.2548
128.0924
127.9505
126.5794
126.4372
126.0263
126.0124
125.2599
77.3524
77.0348
76.7169
52.4724
1.00
f1 (ppm)


CO2Me
N
MeO
F
4k
1H NMR
CDCl3, 400MHz
0.98
1.03
1.99
1.03
1.02
2.00
3.00
3.09
f1 (ppm)


CO2Me
N
MeO
F
4k
13C NMR
CDCl3, 100MHz
166.5858
164.4725
162.0052
160.3646
158.3507
139.1825
135.2778
129.7418
123.3188
115.6738
115.4587
105.5500
77.3561
77.0383
76.7206
55.5184
52.7798
f1 (ppm)


Ph
O
N
N
Cl
4l
1H NMR
CDCl3, 400MHz
f1 (ppm)
1.00
1.02
2.03
1.07
8.07
2.00
2.04
2.05
2.07
2.01

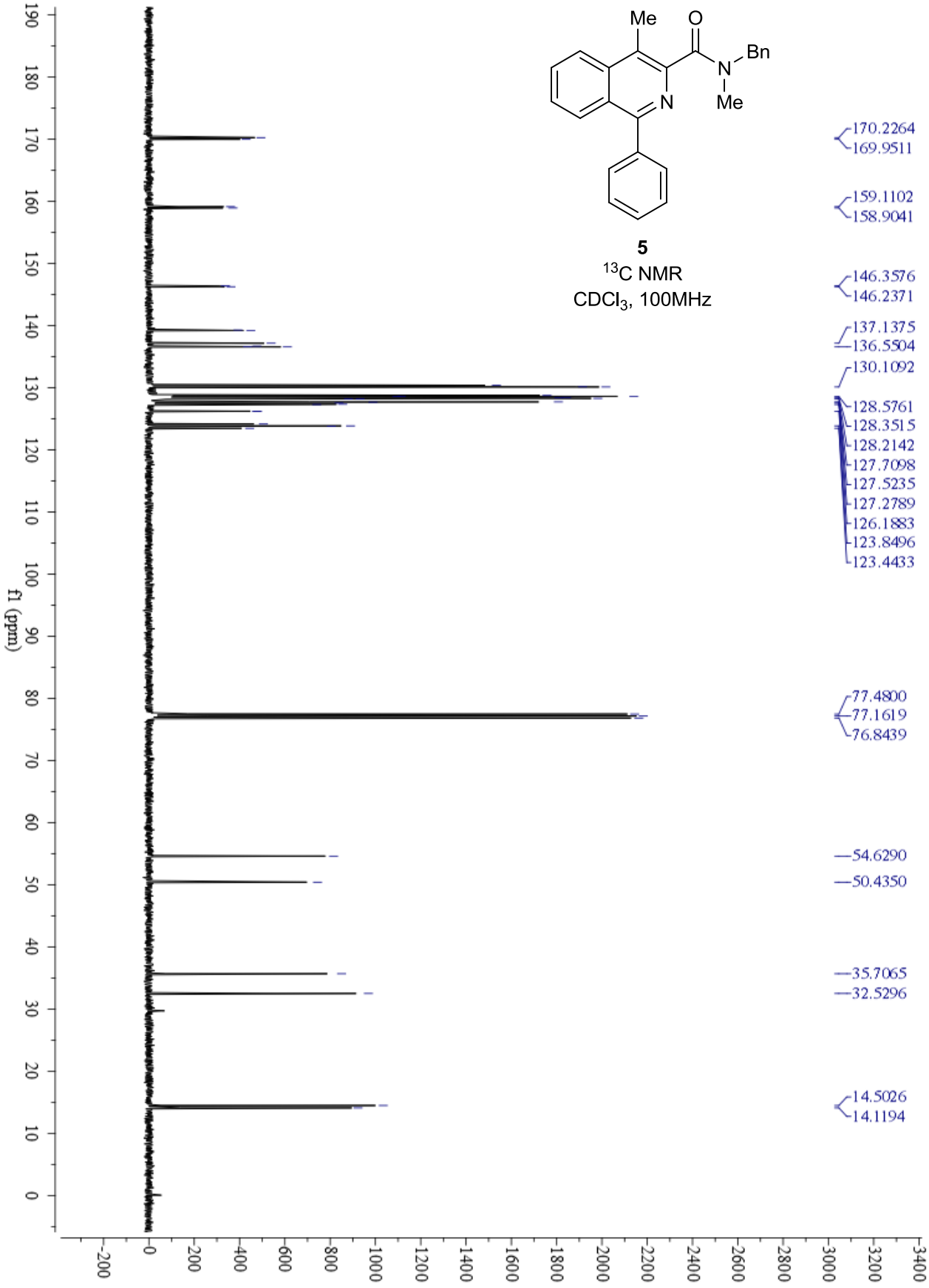

Ph
O
N
N
Cl
4l
^{13}C NMR
$CDCl_3$, 100MHz
167.3989
159.0871
146.3275
136.0961
134.9562
130.5645
128.6631
128.5988
128.4003
128.3116
127.5448
127.2690
126.2413
126.0533
77.4026
77.0849
76.7670
47.5285
42.1069
25.8131
25.1345
24.3041
f1 (ppm)

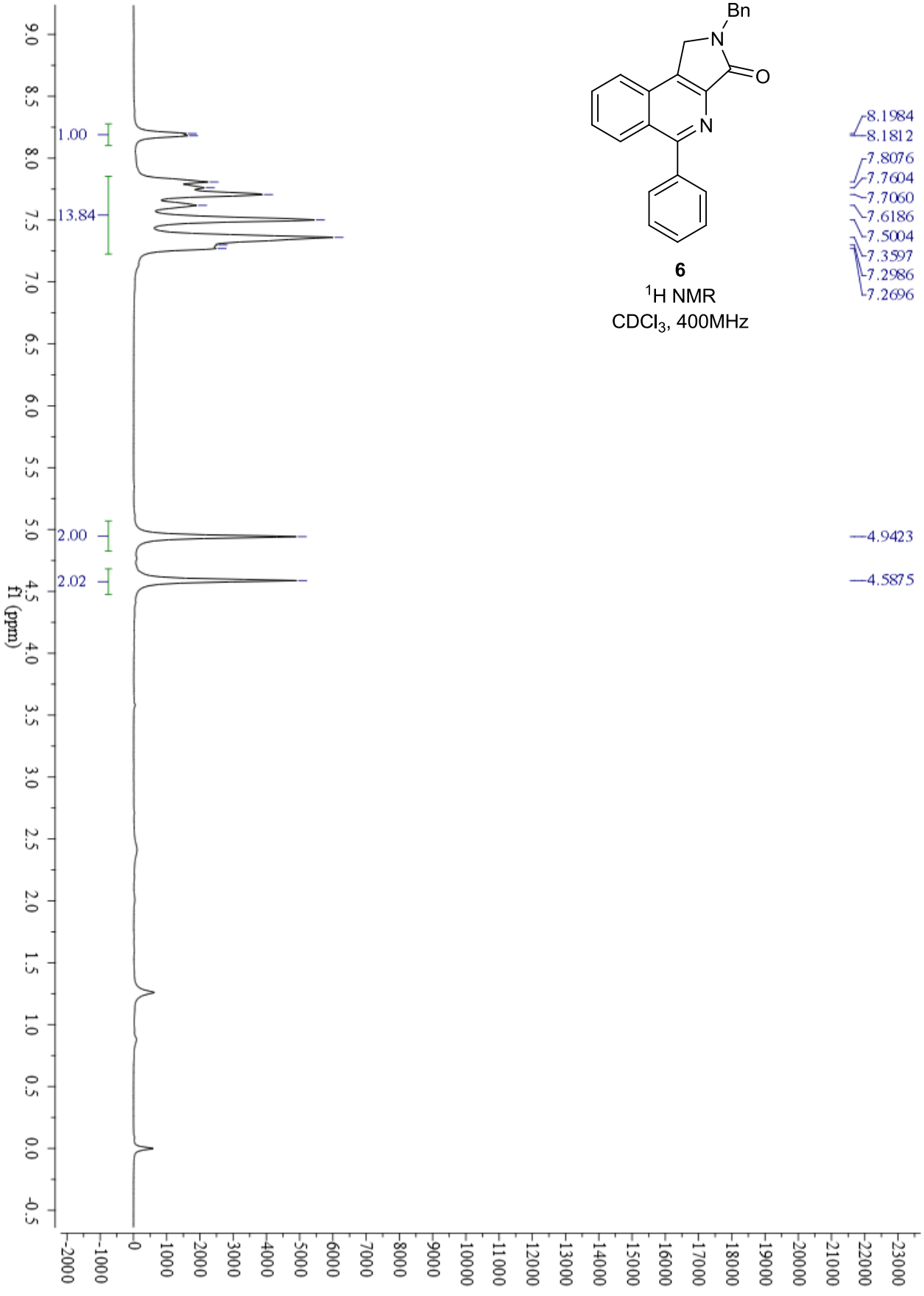


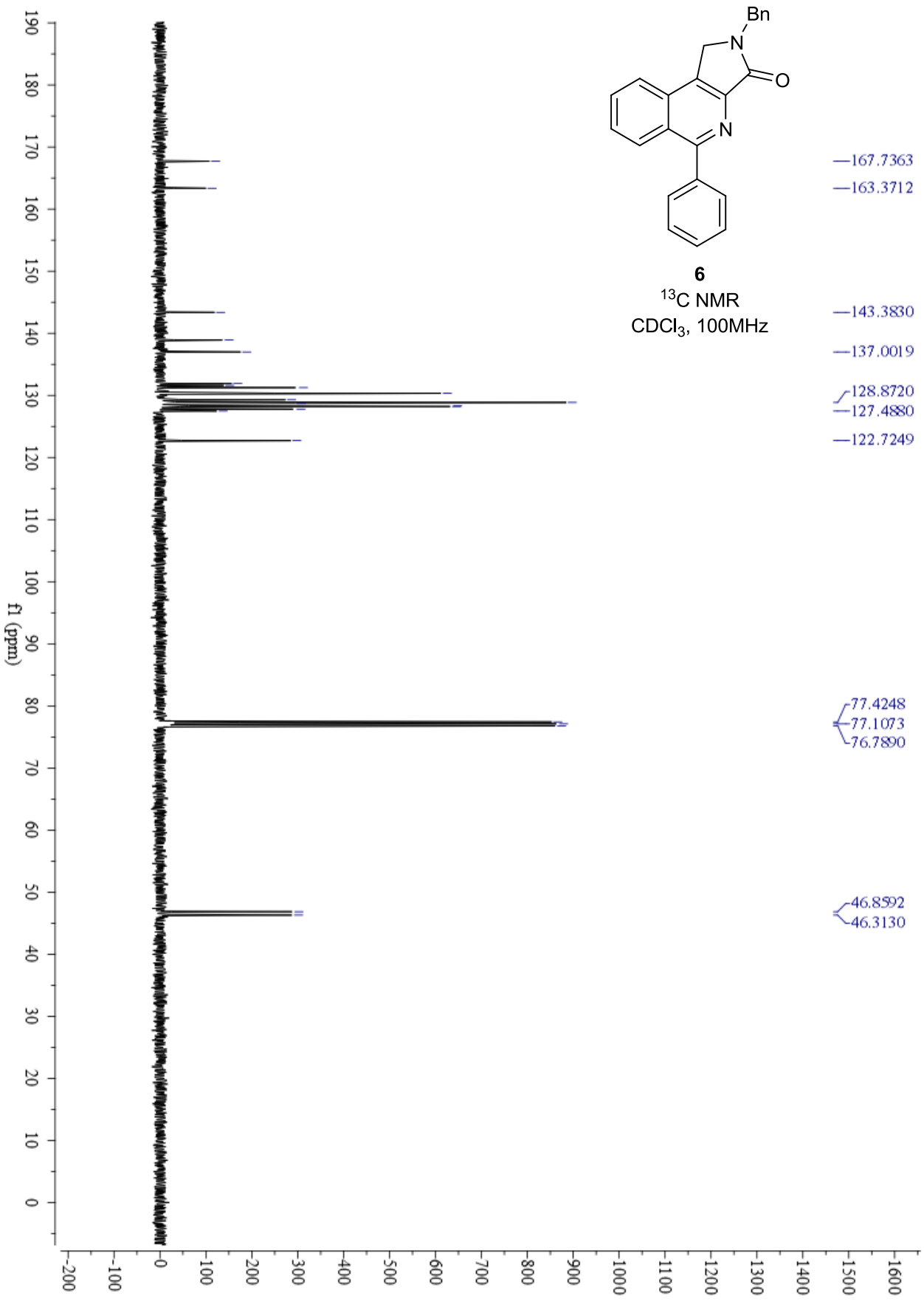
5

^{1}H NMR

$CDCl_3$, 400MHz


Me
O
Bn
N
N
Me
5
13C NMR
CDCl3, 100MHz
170.2264
169.9511
159.1102
158.9041
146.3576
146.2371
137.1375
136.5504
130.1092
128.5761
128.3515
128.2142
127.7098
127.5235
127.2789
126.1883
123.8496
123.4433
77.4800
77.1619
76.8439
54.6290
50.4350
35.7065
32.5296
14.5026
14.1194
f1 (ppm)


Bn
N
O
N
6
1H NMR
CDCl3, 400MHz
8.1984
8.1812
7.8076
7.7604
7.7060
7.6186
7.5004
7.3597
7.2986
7.2696
4.9423
4.5875
1.00
13.84
2.00
2.02
f1 (ppm)


Bn
N
O
N
6
13C NMR
CDCl3, 100MHz
167.7363
163.3712
143.3830
137.0019
128.8720
127.4880
122.7249
77.4248
77.1073
76.7890
46.8592
46.3130
f1 (ppm)