Sequential Protocol for C(sp^3)-H Carboxylation with CO_2: Transition Metal-Catalyzed Benzylic C-H Silylation and Fluoride-Mediated Carboxylation

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Supporting Information

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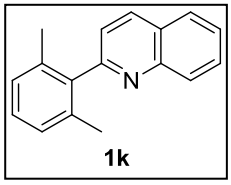
(A) General

Infrared (IR) spectra were recorded on a JASCO FT/IR 460 Plus Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL ECA-500 spectrometer, operating at 500 MHz (^{1}H) or 125 MHz (^{13}C). Chemical shifts in $CDCl_3$ were reported in the scale relative to $CHCl_3$ (7.26 ppm) for ^{1}H NMR and to $CDCl_3$ (77.0 ppm) for ^{13}C NMR as internal references. EI mass spectra were measured on a JEOL JMS-T100GCv. Column chromatography was performed with silica gel Kanto 60 (230-400 mesh ASTM). Dry toluene and DMF were purified under argon using the Ultimate Solvent System (Glass Counter Inc.). $[Ir(cod)Cl]_2$, $Ru_3(CO)_{12}$, and Et_3SiH were purchased from Aldrich, Inc. Norbornene and CsF were purchased from Tokyo Kasei, Co. Ltd. and Nacalai Tesque, Inc., respectively. All of these materials were used as received. A cylinder of CO_2 was purchased from Hokkaido Air Water, Inc.

(B) Synthesis of Substrates

8-Methylquinoline (**1b**) and 5-methylquinoxaline (**1f**) were purchased from Aldrich, Inc. and Tokyo Kasei, Co. Ltd., respectively. 4,8-Dimethylquinoline (**1d**), 5,8-dimethylquinoline (**1e**), and 2,4-dimethylbenzoxazol (**1l**) were synthesized by reported methods.[1,2,3] The other materials (**1c**,[4] **1g**,[5], **1h**[4], **1i**[6], **1j**[7], and **1k**) were prepared by Suzuki-Miyaura cross-coupling reactions of *N*-heteroaryl bromides with aryl boronic acids.[8]



1k

2-(2,6-Dimethylphenyl)quinoline (1k): Colorless solid. mp. 79.4-80.8 ºC; IR (neat): 3057, 2921, 1599, 1501, 1463, 1423, 1304, 1121, 1045, 834, 760 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.75 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.59 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 2H), 2.08 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.5, 148.1, 140.6, 136.3, 135.7, 129.5, 129.5, 128.0, 127.7, 127.6, 126.7, 126.4, 122.6, 20.2 ppm; HRMS (EI): *m/z* calcd for $C_{17}H_{14}N^+$ [M^+]: 232.1126, Found: 232.1124.

(C) C-H Silylation Reactions

(C-1) General Procedure - Method A

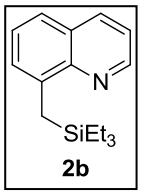
To a 10 mL test tube combined with condenser was placed a substrate **1** (0.4 mmol, 1.0 equiv), then evacuated and backfilled with argon (x3). To the reaction tube was added 0.20 mL of toluene (2.0 M), $[Ir(cod)Cl]_2$ (13.4 mg, 20 μmol, 5 mol %), and Et_3SiH (**method A1**: 232.6 mg, 320 μL, 2.0 mmol, 5.0 equiv; **method A2**: 325.6 mg, 450 μL, 2.8 mmol, 7.0 equiv). The resulting mixture was stirred under

1 O'Murchu, C. *Synthesis* **1989**, 880.
2 Ranu, B. C.; Hajra, A.; Dey, S. S.; Jana, U. *Tetrahedron* **2003**, *59*, 813.
3 Lee, J. J.; Kim, J.; Jun, Y. M.; Lee, B. M.; Kim, B. H. *Tetrahedron* **2009**, *65*, 8821.
4 Kakiuchi, F.; Tsuchiya, K.; Matsumoto, M.; Mizushima, E.; Chatani, N. *J. Am. Chem. Soc.* **2004**, *126*, 12792.
5 Böhm, V. P. W.; Weskamp, T.; Gstöttmayr, C. W. K.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1602.
6 Ackermann, L.; Potukuchi, H. K.; Kapdi, A. R.; Schulzke, C. *Chem. Eur. J.* **2010**, *16*, 3300.
7 Zheng, X.; Song, B.; Xu, B. *Eur. J. Org. Chem.* **2010**, 4376.
8 Petitjean, A.; Khoury, R. G.; Kyritsakas, N.; Lehn, J.-M. *J. Am. Chem. Soc.* **2004**, *126*, 6637.

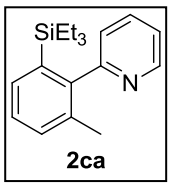
reflux for 20 h. After monitoring the progress of the reaction by a TLC, the reaction mixture was passed through a short pad of silica-gel. The solvent was removed and dried under reduced pressure. The yields of the corresponding products were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard, then purified by flash silica-gel column chromatography.

(C-2) General Procedure - Method B

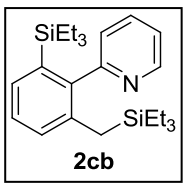
To a 10 mL sealed tube was placed a substrate **1** (0.3 mmol, 1.0 equiv), then evacuated and backfilled with argon (x3). To the reaction tube was added $Ru_3(CO)_{12}$ (11.5 mg, 18 μmol, 6 mol %), norbornene (**method B1**: 141.2 mg, 1.5 mmol, 5.0 equiv; **method B2**: 197.7 mg, 2.1 mmol, 7.0 equiv), 0.15 mL of toluene (2.0 M), and Et_3SiH (**method B1**: 174.4 mg, 240 μL, 1.5 mmol, 5.0 equiv; **method B2**: 244.2 mg, 335 μL, 2.1 mmol, 7.0 equiv). The system was closed and stirred at 150 ºC for 20 h. After monitoring the progress of the reaction by a TLC, the reaction mixture was passed through a short pad of silica-gel. The solvent was removed and dried under reduced pressure. The yields of the corresponding products were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard, then purified by flash silica-gel column chromatography.



8-Triethylsilylmethylquinoline (2b)[4]: 8-Methylquinoline (57.3 mg, 0.4 mmol) was used as a substrate. By using the **method A1** ($[Ir(cod)Cl]_2$: 13.4 mg, 20 μmol, 5 mol %; Et_3SiH: 232.6 mg, 2.0 mmol, 5.0 equiv; toluene: 0.2 mL, reflux for 20 h) and **method B1** ($Ru_3(CO)_{12}$: 11.5 mg, 18 μmol, 6 mol %; Et_3SiH: 232.6 mg, 2.0 mmol, 5.0 equiv; norbornene: 141.2 mg, 1.5 mmol, 5.0 equiv; toluene: 0.2 mL, 150 ºC in closed sealed tube for 20 h), **2b** was obtained in 98% (0.39 mmol) and 93% yields (0.37 mmol), respectively. **2b** was purified by flash silica-gel column chromatography (hexane/ethyl acetate, 40:1).



2-(2-Methyl-6-triethylsilylphenyl)pyridine (2ca)[4]: 2-(*o*-Tolyl)pyridine (67.7 mg, 0.4 mmol) was used as a substrate. By using the **method A2** ($[Ir(cod)Cl]_2$: 13.4 mg, 20 μmol, 5 mol %; Et_3SiH: 325.6 mg, 2.8 mmol, 7.0 equiv; toluene: 0.2 mL, reflux for 20 h), **2ca** was obtained in 99% yield (0.39 mmol). **2ca** was purified by silica-gel column chromatography (hexane/ethyl acetate, 40:1).

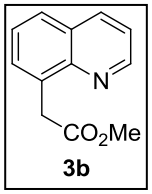


2-(2-Triethylsilyl-6-triethylsilylmethylphenyl)pyridine (2cb)[4]: 2-(*o*-Tolyl)pyridine (50.8 mg, 0.3 mmol) was used as a substrate. By using the **method B2** ($Ru_3(CO)_{12}$: 11.5 mg, 18 μmol, 6 mol %; Et_3SiH: 244.2 mg, 2.1 mmol, 7.0 equiv; norbornene: 197.7 mg, 2.1 mmol, 7.0 equiv; toluene: 0.2 mL, 150 ºC in closed sealed tube for 20 h), **2cb** was obtained in quantitative yield (0.3 mmol). **2cb** was purified by silica-gel column chromatography (hexane/ethyl acetate, 40:1).

(D) Carboxylation Reactions

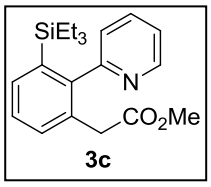
To a 10 mL test tube was placed a benzylsilane **2** (0.1 mmol, 1.0 equiv), then evacuated and backfilled with CO_2 (x3). To the reaction tube was added 1.0 mL of DMF (0.1 M) and flame-dried CsF. The

resultant mixture was then stirred at 100 ºC for 1 h under 1 atm of CO_2 (balloon). After monitoring the progress of the reaction by a TLC, the reaction mixture was cooled to room temperature, then treated with Cs_2CO_3 (65.1 mg, 2.0 equiv) and MeI (28.4 mg, 12.5 μL, 2.0 equiv) and stirred at room temperature for 30 min. 20 mL of water was added and the product was extracted with ethyl acetate (5 mL x3). The combined organic layer was washed with water (x1) and brine (x1), and then dried over with Na_2SO_4. After removal of solvent under reduced pressure, the yields of corresponding esters **3** and protodesilylation compounds were determined by ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.



3b

Methyl 2-(quinolin-8-yl)acetate (3b): 8-Triethylsilylmethylquinoline (25.7 mg, 0.1 mmol) was treated with CsF (45.6 mg, 0.3 mmol, 3.0 equiv) in DMF (1.0 mL) at 100 ºC for 1 h, followed by the esterification with Cs_2CO_3 (65.1 mg, 2.0 equiv) and MeI (28.4 mg, 2.0 equiv) at room temperature for 30 min, affording 91% (0.091 mmol) of the ester **3b** and 9% (8.8 μmol) of protodesilylation product **1b**.



3c

Methyl 2-{2-(pyridin-2-yl)-3-triethylsilylphenyl}acetate (3c): 2-(2-Triethylsilyl-6-triethylsilylmethyl)pyridine (39.8 mg, 0.1 mmol) was treated with CsF (76.0 mg, 0.5 mmol, 5.0 equiv) in DMF (1.0 mL) at 100 ºC for 1 h, followed by the esterification with Cs_2CO_3 (65.1 mg, 2.0 equiv) and MeI (28.4 mg, 2.0 equiv) at room temperature for 30 min, affording 82% (0.082 mmol) of the ester **3c** and 11% (0.011 mmol) of protodesilylation product **2ca**.

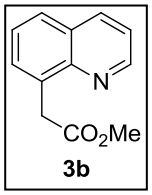
(E) Sequential Reactions (Silylation-Carboxylation)

(E-1) General Procedure of Silylation (method A1) -Carboxylation Sequence

To a 10 mL test tube combined with condenser was placed a substrate **1** (0.4 mmol, 1.0 equiv), then evacuated and backfilled with argon (x3). To the reaction tube was added 0.20 mL of toluene (2.0 M), $[Ir(cod)Cl]_2$ (13.4 mg, 20 μmol, 5 mol %), and Et_3SiH (232.6 mg, 320 μL, 2.0 mmol, 5.0 equiv). The resulting mixture was stirred under reflux for 20 h. After monitoring the progress of the C-H silylation reaction by a TLC, the system was directly pumped up at room temperature to remove volatile materials such as toluene and Et_3SiH, followed by the introduction of CO_2 (balloon). To the residue was added 4.0 mL of DMF (0.1 M) and flame-dried CsF (182.3 mg, 1.2 mmol, 3.0 equiv). The mixture was heated at 100 °C under 1 atm of CO_2 for 2 h. The reaction mixture was then cooled down to room temperature and treated with Cs_2CO_3 (260.6 mg, 0.8 mmol, 2.0 equiv) and MeI (113.6 mg, 50 μL, 0.8 mmol, 2.0 equiv), and then stirred at room temperature for 30 min. 40 mL of water was added and iridium impurity was filtered off. The filtrate was extracted with ethyl acetate (10 mL x3) and the combined organic layer was washed with water (x1) and brine (x1), and then dried over with Na_2SO_4. After removal of solvent under reduced pressure, the residue was purified by flash silica-gel column chromatography to give the corresponding ester **3** and protodesilylation compound.

(E-1) General Procedure of Silylation (method B2) -Carboxylation Sequence

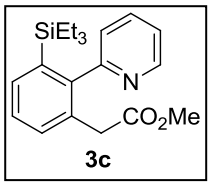
To a 10 mL sealed tube was placed a substrate **1** (0.3 mmol, 1.0 equiv), then evacuated and backfilled with argon (x3). To the reaction tube was added $Ru_3(CO)_{12}$ (11.5 mg, 0.018 mmol, 6 mol %), norbornene (197.7 mg, 2.1 mmol, 7.0 equiv), 0.15 mL of toluene (2.0 M), and Et_3SiH (244.2 mg, 0.34 mL, 2.1 mmol, 7.0 equiv). The system was closed and stirred at 150 ºC for 20 h. After monitoring the progress of the C-H silylation reaction by a TLC, the system was directly pumped up at room temperature to remove volatile materials such as toluene, Et_3SiH, and norbornene, followed by the introduction of CO_2 (balloon). To the residue was added 3.0 mL of DMF (0.1 M) and flame-dried CsF (227.9 mg, 1.5 mmol, 5.0 equiv). The mixture was heated at 100 °C under 1 atm of CO_2 for 2 h. The reaction mixture was then cooled down to room temperature and treated with Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv) and MeI (85.2 mg, 38 μL, 0.6 mmol, 2.0 equiv), and then stirred at room temperature for 30 min. 40 mL of water was added and ruthenium impurity was filtered off. The filtrate was extracted with ethyl acetate (10 mL x3) and the combined organic layer was washed with water (x1) and brine (x1), and then dried over with Na_2SO_4. After removal of solvent under reduced pressure, the residue was purified by flash silica-gel column chromatography to give the corresponding ester **3** and protodesilylation compound.



3b

Methyl 2-(quinolin-8-yl)acetate (3b): 8-Methylquinoline (57.3 mg, 0.4 mmol) was used as a substrate. After the silylation by using the **method A1** ($[Ir(cod)Cl]_2$: 13.4 mg, 20 μmol, 5 mol %; Et_3SiH: 232.6 mg, 2.0 mmol, 5.0 equiv; toluene: 0.2 mL, reflux for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (182.3 mg, 1.2 mmol, 5.0 equiv) in DMF (4.0 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (260.6 mg, 0.8 mmol, 2.0 equiv) and MeI (113.6 mg, 0.8 mmol, 2.0 equiv) at room temperature for 30 min, affording the corresponding ester **3b** (pale yellow oil, 70.2 mg, 0.35 mmol, 87%) and protodesilylation starting material **1b** (4.8 mg, 0.034 mmol, 8%). These compounds were purified by flash silica-gel column chromatography (hexane/ethyl acetate, 4:1).

IR (neat): 2951, 1738, 1595, 1500, 1435, 1343, 1261, 1173, 1002, 796 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.92 (dd, *J* = 4.4, 1.5 Hz, 1H), 8.14 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.76 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.50 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.40 (dd, *J* = 8.1, 4.4 Hz, 1H), 4.30 (s, 2H), 3.71 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.6, 149.7, 146.6, 136.1, 133.3, 130.2, 128.3, 127.4, 126.2, 121.1, 51.9, 36.9 ppm; HRMS (EI): *m/z* calcd for $C_{12}H_{11}NO_2$ $[M+H^+]$: 201.0790, Found: 201.0790.

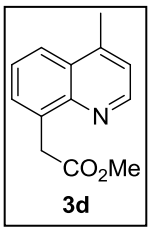


3c

Methyl 2-{2-(pyridin-2-yl)-3-triethylsilylphenyl}acetate (3c): 2-(*o*-Tolyl)pyridine (50.8 mg, 0.3 mmol) was used as a substrate. After the silylation by using the **method B2** ($Ru_3(CO)_{12}$: 11.5 mg, 18 μmol, 6 mol %; Et_3SiH: 244.2 mg, 2.1 mmol, 7.0 equiv; norbornene: 197.7 mg, 2.1 mmol, 7.0 equiv; toluene: 0.15 mL, 150 ºC in closed sealed tube for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (227.9 mg, 1.5 mmol, 5.0 equiv) in DMF (3.0 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv) and MeI (85.2 mg, 0.6 mmol, 2.0 equiv) at room temperature for 30 min, affording the corresponding ester **3c** (pale yellow solid, 83.0 mg, 0.24 mmol, 81%) and protodesilylation compound **2ca** (11.9 mg, 0.042 mmol, 14%). These compounds were purified by flash silica-gel column chromatography (hexane/ethyl acetate, 4:1).

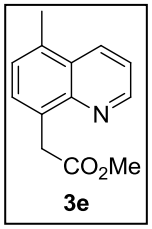
mp. 53.2-54.0 ºC; IR (neat): 2952, 1740, 1587, 1417, 1336, 1259, 1236, 1160, 1006, 754, 730 cm^{-1}; ^1H

NMR (500 MHz, $CDCl_3$) δ = 8.66 (d, *J* = 4.5 Hz, 1H), 7.69 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.37-7.32 (m, 2H), 7.30-7.28 (m, 2H), 3.55 (s, 3H), 3.39 (s, 2H), 0.80 (t, *J* = 8.0 Hz, 9H), 0.35 (q, *J* = 8.0 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.1, 160.2, 148.9, 147.1, 136.1, 135.5, 134.6, 131.9, 130.8, 127.4, 125.4, 122.4, 51.7, 38.9, 7.4, 3.7 ppm; HRMS (EI): *m/z* calcd for $C_{20}H_{27}NO_2Si$ [M+H$^+$]: 341.1811, Found: 341.1809.



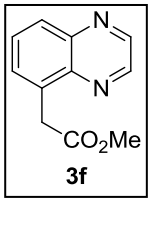
Methyl 2-(4-methylquinolin-8-yl)acetate (3d): 4,8-Dimethylquinoline (62.9 mg, 0.4 mmol) was used as a substrate. After the silylation by using the **method A1** ([Ir(cod)Cl]$_2$: 13.4 mg, 20 μmol, 5 mol %; Et_3SiH: 232.6 mg, 2.0 mmol, 5.0 equiv; toluene: 0.2 mL, reflux for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (182.3 mg, 1.2 mmol, 5.0 equiv) in DMF (4.0 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (260.6 mg, 0.8 mmol, 2.0 equiv) and MeI (113.6 mg, 0.8 mmol, 2.0 equiv) at room temperature for 30 min, affording the corresponding ester **3d** (pale brown oil, 68.9 mg, 0.32 mmol, 80%) and protodesilylation starting material **1d** (9.0 mg, 0.057 mmol, 14%). These compounds were purified by flash silica-gel column chromatography (hexane/ethyl acetate, 2:1).

IR (neat): 2951, 1739, 1597, 1510, 1435, 1340, 1260, 1164, 1016, 842, 766 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.76 (d, *J* = 4.3 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.51 (dd, *J* = 8.5, 7.1 Hz, 1H), 7.21 (d, *J* = 4.3 Hz, 1H), 4.29 (s, 2H), 3.70 (s, 3H), 2.68 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.7, 149.3, 146.4, 144.3, 133.8, 129.9, 128.3, 125.8, 123.4, 121.9, 51.8, 37.3, 18.8 ppm; HRMS (EI): *m/z* calcd for $C_{13}H_{13}NO_2$ [M+H$^+$]: 215.0946, Found: 215.0947.



Methyl 2-(5-methylquinolin-8-yl)acetate (3e): 5,8-Dimethylquinoline (62.9 mg, 0.4 mmol) was used as a substrate. After the silylation by using the **method A1** ([Ir(cod)Cl]$_2$: 13.4 mg, 20 μmol, 5 mol %; Et_3SiH: 232.6 mg, 2.0 mmol, 5.0 equiv; toluene: 0.2 mL, reflux for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (182.3 mg, 1.2 mmol, 5.0 equiv) in DMF (4.0 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (260.6 mg, 0.8 mmol, 2.0 equiv) and MeI (113.6 mg, 0.8 mmol, 2.0 equiv) at room temperature for 30 min, affording the corresponding ester **3e** (pale brown oil, 77.7 mg, 0.36 mmol, 90%) and protodesilylation starting material **1e** (4.3 mg, 0.027 mmol, 7%). These compounds were purified by flash silica-gel column chromatography (hexane/ethyl acetate, 2:1).

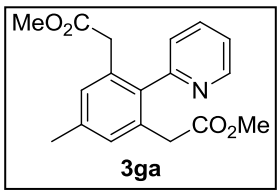
IR (neat): 2951, 1739, 1599, 1503, 1435, 1344, 1266, 1168, 1015, 795 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.92 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.31 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.52 (d, *J* = 6.9 Hz, 1H), 7.42 (dd, *J* = 8.5, 4.2 Hz, 1H), 7.33 (d, *J* = 6.9 Hz, 1H), 4.25 (s, 2H), 3.70 (s, 3H), 2.67 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.9, 149.2, 146.9, 134.2, 132.6, 131.4, 129.9, 127.7, 126.6, 120.7, 51.9, 37.0, 18.6 ppm; HRMS (EI): *m/z* calcd for $C_{13}H_{13}NO_2$ [M+H$^+$]: 215.0946, Found: 215.0950.



Methyl 2-(quinoxalin-5-yl)acetate (3f): 5-Methylquinoxaline (57.7 mg, 0.4 mmol) was used as a substrate. After the silylation by using the **method A1** ([Ir(cod)Cl]$_2$: 26.9 mg, 40 μmol, 10 mol %; Et_3SiH: 232.6 mg, 2.0 mmol, 5.0 equiv; toluene: 0.2 mL, reflux for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (182.3 mg, 1.2 mmol, 5.0 equiv) in DMF (4.0 mL) at 100 ºC for 2 h, followed by the esterification

with Cs_2CO_3 (130.3 mg, 0.4 mmol, 1.0 equiv) and MeI (113.6 mg, 0.8 mmol, 2.0 equiv) at room temperature for 30 min, affording the corresponding ester **3f** (colorless solid, 36.1 mg, 0.18 mmol, 42%) and protodesilylation starting material **1f** (17.0 mg, 0.12 mmol 29%). These compounds were purified by flash silica-gel column chromatography (hexane/ethyl acetate, 2:1).

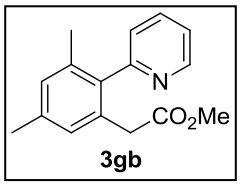
mp. 72.7-74.1 ºC; IR (neat): 2954, 1735, 1496, 1443, 1359, 1231, 1065, 999, 886, 773 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.85 (m, 2H), 8.06 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.74 (dd, *J* = 8.2, 6.8 Hz, 1H), 7.70 (d, *J* = 6.8 Hz, 1H), 4.28 (s, 2H), 3.70 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.1, 144.9, 144.1, 143.1, 141.7, 133.7, 130.8, 129.7, 129.0, 52.1, 36.2 ppm; HRMS (EI): *m/z* calcd for $C_{11}H_{10}N_2O_2$ [$M+H^+$]: 202.0742, Found: 202.0741.



3ga

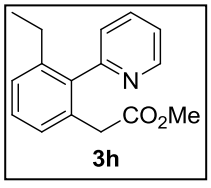
Dimethyl 2,2'-{5-methyl-2-(pyridin-2-yl)-1,3-phenylene}diacetate (3ga): 2-Mesitylpyridine (59.2 mg, 0.3 mmol) was used as a substrate. The silylation was carried out with the **method B2** ($Ru_3(CO)_{12}$: 11.5 mg, 18 μmol, 6 mol %; Et_3SiH: 244.2 mg, 2.1 mmol, 7.0 equiv; norbornene: 197.7 mg, 2.1 mmol, 7.0 equiv; toluene: 0.15 mL, 150 ºC in closed sealed tube for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (227.9 mg, 1.5 mmol, 5.0 equiv) in DMF (3.0 mL) at 100 ºC for 2 h. After the esterification with Cs_2CO_3 (293.3 mg, 0.9 mmol, 3.0 equiv) and MeI (212.9 mg, 1.5 mmol, 5.0 equiv) at room temperature for 30 min, DMF and other volatile materials were evaporated under reduced pressure, and then purified by flash silica-gel column chromatography (hexane/ethyl acetate, 2:1). The di-ester **3ga** (pale brown oil, 50.8 mg, 0.16 mmol, 54%) and mono-ester **3gb** (0.053 mmol, 18%) were obtained. The yield of **3gb** was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

IR (neat): 2952, 1737, 1587, 1460, 1433, 1336, 1259, 1158, 1017, 754 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.68 (ddd, *J* = 4.0, 1.8, 1.0 Hz, 1H), 7.73 (ddd, *J* = 7.6, 6.0, 1.8 Hz, 1H), 7.29-7.26 (m, 2H), 7.10 (s, 2H), 3.56 (s, 6H), 3.39 (s, 4H), 2.37 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.9, 157.9, 149.5, 138.2, 138.0, 136.1, 132.5, 130.2, 125.5, 122.2, 51.8, 39.0, 21.1 ppm; HRMS (EI): *m/z* calcd for $C_{18}H_{17}NO_4^+$ [M^+]: 312.1236, Found: 312.1236.



3gb

Methyl 2-{3,5-dimethyl-2-(pyridin-2-yl)phenyl}acetate (3gb): Pale brown oil. IR (neat): 2952, 1739, 1613, 1587, 1435, 1338, 1266, 1158, 1025, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.69 (dd, *J* = 5.6, 2.0 Hz, 1H), 7.73 (ddd, *J* = 7.6, 5.6, 2.0 Hz, 1H), 7.26-7.23 (m, 2H), 7.02 (s, 1H), 7.00 (s, 1H), 3.55 (s, 3H), 3.39 (s, 2H), 2.34 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.2, 158.9, 149.6, 137.8, 137.7, 136.0, 132.1, 130.0, 128.5, 125.1, 121.8, 51.8, 39.0, 21.1, 20.2 ppm; HRMS (EI): *m/z* calcd for $C_{16}H_{15}NO_2^+$ [M^+]: 254.1181, Found: 254.1180.

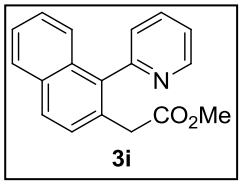


3h

Methyl 2-{3-ethyl-2-(pyridin-2-yl)phenyl}acetate (3h): 2-(2-Ethyl-6-methylphenyl)-pyridine (59.2 mg, 0.3 mmol) was used as a substrate. After the silylation by using the **method B2** ($Ru_3(CO)_{12}$: 11.5 mg, 18 μmol, 6 mol %; Et_3SiH: 244.2 mg, 2.1 mmol, 7.0 equiv; norbornene: 197.7 mg, 2.1 mmol, 7.0 equiv; toluene: 0.15 mL, 150 ºC in closed sealed tube for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF

(227.9 mg, 1.5 mmol, 5.0 equiv) in DMF (3.0 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv) and MeI (85.2 mg, 0.6 mmol, 2.0 equiv) at room temperature for 30 min, affording the corresponding ester **3h** (pale brown oil, 62.5 mg, 0.24 mmol, 82%) and protodesilylation starting material **1h** (3.2 mg, 0.016 mmol, 5%) were obtained. These compounds were purified by silica-gel column chromatography (hexane/ethyl acetate, 10:1).

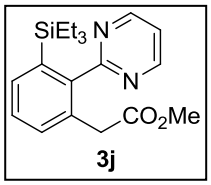
IR (neat): 2966, 1739, 1584, 1454, 1426, 1338, 1258, 1160, 1025, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.70 (dd, *J* = 5.4, 2.0 Hz, 1H), 7.74 (ddd, *J* = 8.0, 7.4, 1.2 Hz, 1H), 7.32 (dd, *J* = 8.0, 7.4 Hz, 1H), 7.29-7.24 (m, 3H), 7.19 (dd, *J* = 7.4, 1.2 Hz, 1H), 3.55 (s, 3H), 3.40 (s, 2H), 2.37 (q, *J* = 7.4 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.1, 158.7, 149.6, 142.3, 140.2, 136.0, 132.3, 128.4, 127.8, 127.5, 125.1, 122.0, 51.8, 39.1, 26.5, 15.3 ppm; HRMS (EI): *m/z* calcd for $C_{16}H_{15}NO_2^+$ [M^+]: 254.1181, Found: 254.1183.



3i

Methyl 2-{1-(pyridin-2-yl)naphthalen-2-yl}acetate (3i): 2-(2-Methylnaphthalen-1-yl)pyridine (65.7mg, 0.3 mmol) was used as a substrate. After the silylation by using the **method B2** ($Ru_3(CO)_{12}$: 11.5 mg, 0.018 mmol, 6 mol %; Et_3SiH: 244.2 mg, 2.1 mmol, 7.0 equiv; norbornene: 197.7 mg, 2.1 mmol, 7.0 equiv; toluene: 0.15 mL, 150 ºC in closed sealed tube for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (227.9 mg, 1.5 mmol, 5.0 equiv) in DMF (3.0 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv) and MeI (85.2 mg, 0.6 mmol, 2.0 equiv) at room temperature for 30 min, affording the corresponding ester **3i** (pale brown oil, 49.8 mg, 0.18 mmol, 90%) and protodesilylation starting material **1i** (2.6 mg, 0.012 mmol, 6%) were obtained. These compounds were purified by silica-gel column chromatography (hexane/ethyl acetate, 5:1).

IR (neat): 3053, 2951, 1737, 1587, 1509, 1433, 1388, 1166, 1015, 753 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.81 (ddd, *J* = 4.0, 1.8, 1.3 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.84 (ddd, *J* = 8.6, 5.8, 1.8 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.47-7.42 (m, 2H), 7.39-7.33 (m, 3H), 3.62 (d, *J* = 2.9 Hz, *gem*-coupling, 2H), 3.60 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.9, 157.9, 149.9, 137.8, 136.2, 132.7, 132.4, 129.8, 128.6, 127.9, 127.9, 126.3, 126.0, 125.8, 125.6, 122.3, 51.9, 39.1 ppm; HRMS (EI): *m/z* calcd for $C_{18}H_{13}NO_2^+$ [M^+]: 276.1025, Found: 276.1026.

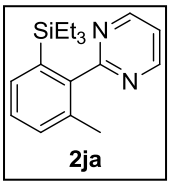


3j

Methyl 2-{2-(pyrimidin-2-yl)-3-triethylsilylphenyl}acetate (3j): 2-(*o*-Tolyl)-pyrimidine (51.1 mg, 0.3 mmol) was used as a substrate. After the silylation by using the **method B2** ($Ru_3(CO)_{12}$: 11.5 mg, 18 μmol, 6 mol %; Et_3SiH: 244.2 mg, 2.1 mmol, 7.0 equiv; norbornene: 197.7 mg, 2.1 mmol, 7.0 equiv; toluene: 0.15 mL, 150 ºC in closed sealed tube for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (227.9 mg, 1.5 mmol, 5.0 equiv) in DMF (3.0 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv) and MeI (85.2 mg, 0.6 mmol, 2.0 equiv) at room temperature for 30 min, affording the corresponding ester **3j** (pale brown solid, 51.3 mg, 0.15 mmol, 50%) and protodesilylation compound **2ja** (0.014 mmol, 5%) were obtained. **3j** was purified by silica-gel column chromatography (hexane/ethyl acetate, 4:1). The yield of **2ja** was determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard.

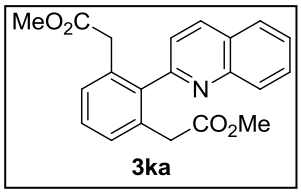
mp. 44.0-45.0 ºC; IR (neat): 2952, 2874, 1739, 1556, 1455, 1403, 1264, 1160, 1007, 725 cm^{-1}; ^1H NMR

(500 MHz, $CDCl_3$) δ = 8.82 (d, *J* = 5.1 Hz, 2H), 7.56 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.39 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.29 (t, *J* = 5.1 Hz, 1H), 3.56 (s, 3H), 3.51 (s, 2H), 0.81 (t, *J* = 7.9 Hz, 9H), 0.40 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.8, 168.7, 156.6, 145.4, 136.3, 134.8, 131.8, 131.4, 127.8, 119.4, 51.8, 39.4, 7.5, 3.8 ppm; HRMS (EI): *m/z* calcd for $C_{19}H_{26}N_2O_2Si$ [M+H$^+$]: 342.1764, Found: 342.1756.



2ja

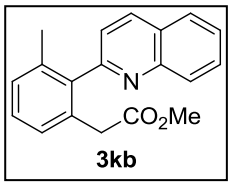
2-(2-Methyl-6-triethylsilylphenyl)pyrimidine (2ja): Pale yellow oil. IR (neat): 2952, 1567, 1556, 1447, 1397, 1240, 1148, 1004, 865, 728 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.84 (d, *J* = 5.2 Hz, 2H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.32-7.29 (m, 1H), 7.27-7.25 (m, 1H), 2.07 (s, 3H), 0.81 (t, *J* = 7.9 Hz, 9H), 0.38 (q, *J* = 7.9 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 169.6, 156.7, 145.4, 135.1, 135.0, 133.2, 130.9, 127.6, 119.3, 20.1, 7.5, 3.6 ppm; HRMS (EI): *m/z* calcd for $C_{17}H_{24}N_2Si$ [M+H$^+$]: 284.1709, Found: 284.1704.



3ka

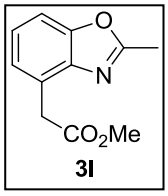
Dimethyl 2,2'-{2-(quinolin-2-yl)-1,3-phenylene}diacetate (3ka): 2-(2,6-Dimethylphenyl)quinoline (55.7 mg, 0.24 mmol) was used as a substrate. After the silylation by using the **method B2** ($Ru_3(CO)_{12}$: 9.2 mg, 14 μmol, 6 mol %; Et_3SiH: 194.3 mg, 1.7 mmol, 7.0 equiv; norbornene: 157.3 mg, 1.7 mmol, 7.0 equiv; toluene: 0.12 mL, 150 ºC in closed sealed tube for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (181.3 mg, 1.2 mmol, 5.0 equiv) in DMF (2.4 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (233.4 mg, 0.7 mmol, 3.0 equiv) and MeI (169.4 mg, 1.2 mmol, 5.0 equiv) at room temperature for 30 min, affording the corresponding di-ester **3ka** (pale brown solid, 24.5 mg, 0.070 mmol, 29%), the mono-ester **3kb** (pale brown oil, 28.6 mg, 0.098 mmol, 41%), and protodesilylation starting material **1k** (9.0 mg, 0.039 mmol, 16%) were obtained. These compounds were purified by silica-gel column chromatography (hexane/ethyl acetate, 4:1).

mp. 75.0-76.0 ºC; IR (neat): 2951, 1739, 1600, 1503, 1435, 1337, 1256, 1160, 1018, 839, 761 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.7 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.76 (ddd, *J* = 8.7, 6.8, 1.1 Hz, 1H), 7.62-7.58 (m, 1H), 7.44 (d, *J* = 8.7 Hz, 1H), 7.40 (dd, *J* = 8.7, 6.8 Hz, 1H), 7.35 (d, *J* = 6.8 Hz, 2H), 3.53 (s, 6H), 3.46 (s, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.7, 158.4, 147.9, 141.1, 136.2, 132.8, 129.8, 129.6, 129.5, 128.7, 127.6, 126.8, 123.1, 51.8, 39.0 ppm; HRMS (EI): *m/z* calcd for $C_{21}H_{17}NO_4^+$ [M$^+$]: 348.1236, Found: 348.1236.



3kb

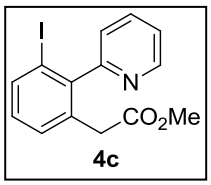
Methyl 2-{3-methyl-2-(quinolin-2-yl)phenyl}acetate (3kb): IR (neat): 2951, 1738, 1600, 1502, 1434, 1250, 1159, 1044, 836, 760 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.75 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.59 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.31 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.24 (m, 2H), 3.51 (s, 3H), 3.47 (s, 2H), 2.11 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.0, 159.4, 148.0, 140.8, 136.2, 136.2, 132.3, 129.7, 129.5, 129.3, 128.4, 128.1, 127.6, 126.8, 126.6, 123.0, 51.8, 39.0, 20.4 ppm; HRMS (EI): *m/z* calcd for $C_{19}H_{15}NO_2^+$ [M$^+$]: 290.1181, Found: 290.1181.



3l

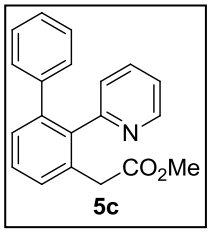
Methyl 2-(2-methylbenzo[*d*]oxazol-4-yl)acetate (3l): 2,4-Dimethylbenzoxazol (44.2 mg, 0.3 mmol) was used as a substrate. When employing the **method A1** ($[Ir(cod)Cl]_2$: 13.4 mg, 20 μmol, 5 mol %; Et_3SiH: 232.6 mg, 2.0 mmol, 5.0 equiv; toluene: 0.2 mL, reflux for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (182.3 mg, 1.2 mmol, 5.0 equiv) in DMF (4.0 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (260.6 mg, 0.8 mmol, 2.0 equiv) and MeI (113.6 mg, 0.8 mmol, 2.0 equiv) at room temperature for 30 min, 8% (0.025 mmol) of the ester **3l** and 72% (0.22 mmol) of protodesilylation starting material **1l** were observed. These yields were determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. On the other hand, after the silylation by using the **method B1** ($Ru_3(CO)_{12}$: 11.5 mg, 18 μmol, 6 mol %; Et_3SiH: 174.4 mg, 1.5 mmol, 5.0 equiv; norbornene: 141.2 mg, 1.5 mmol, 5.0 equiv; toluene: 0.15 mL, 150 ºC in closed sealed tube for 20 h), toluene was removed under reduced pressure and the residue was treated with CsF (136.7 mg, 0.9 mmol, 3.0 equiv) in DMF (3.0 mL) at 100 ºC for 2 h, followed by the esterification with Cs_2CO_3 (195.5 mg, 0.6 mmol, 2.0 equiv) and MeI (85.2 mg, 0.6 mmol, 2.0 equiv) at room temperature for 30 min, affording the corresponding ester **3l** (pale yellow oil, 44.2 mg, 0.22 mmol, 72%) and protodesilylation starting material **1l** (4.2 mg, 0.029 mmol, 10%) were obtained. These compounds were purified by flash silica-gel column chromatography (hexane/ethyl acetate, 4:1).
IR (neat): 2952, 1582, 1433, 1341, 1246, 1165, 1042, 923, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.0 Hz, 1H), 7.24 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 4.00 (s, 2H), 3.71 (s, 3H), 2.63 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.6, 163.6, 150.8, 140.8, 125.5, 124.8, 124.3, 109.1, 52.1, 35.9, 14.6 ppm; HRMS (EI): *m/z* calcd for $C_{11}H_{11}NO_3$ $[M+H^+]$: 205.0739, Found: 205.0733.

(F) Derivatization of the Product



4c

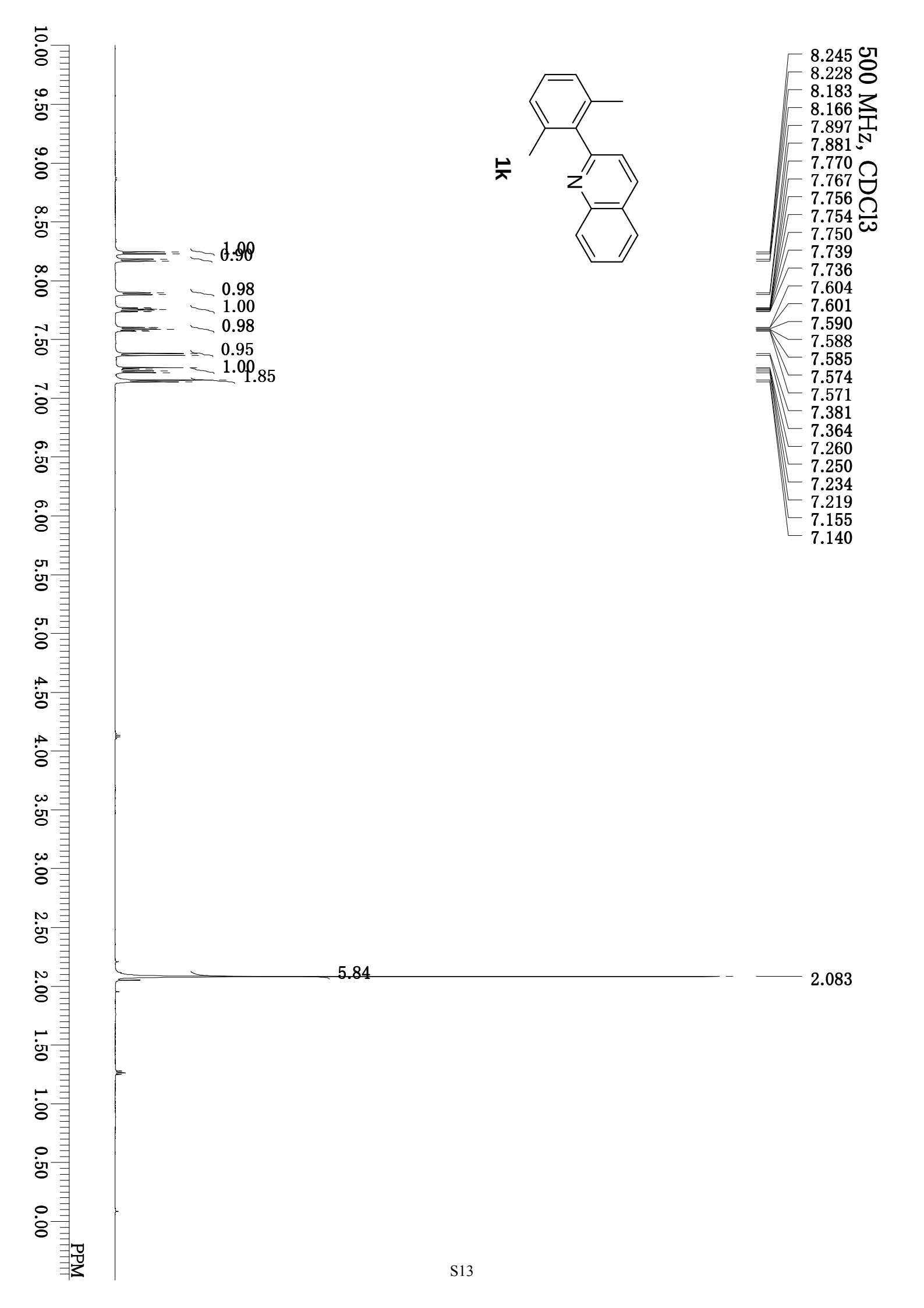
Methyl 2-{3-iodo-2-(pyridin-2-yl)phenyl}acetate (4c): To a solution of the ester **3c** (34.2 mg, 0.1 mmol, 1.0 equiv) in 0.5 mL of CH_2Cl_2 was added a solution of ICl (95.9 mg, 0.6 mmol, 6.0 equiv) in 0.5 mL of CH_2Cl_2 under Ar atmosphere and stirred under reflux for 20 h. After cooling to room temperature, the reaction was quenched by 5 mL of sat. Na_2SO_3 aq., and then the product was extracted with CH_2Cl_2 (5 mL x3). The combined organic layer was washed with brine (10 mL x1) and dried over Na_2SO_4. After concentration, the crude product was purified by flash silica-gel column chromatography (hexane/ethyl acetate, 10:1) to afford **4c** as pale yellow amorphous solid in quantitative yield (35.6 mg, 0.1 mmol).
IR (neat): 2950, 1737, 1589, 1564, 1423, 1336, 1249, 1161, 1022, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.71 (d, *J* = 4.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.78 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.34-7.28 (m, 3H), 7.07 (dd, *J* = 8.0, 7.5 Hz, 1H), 3.55 (s, 3H), 3.46 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 171.3, 160.7, 149.4, 144.9, 138.1, 136.2, 133.9, 130.4, 129.9, 125.2, 122.7, 98.9, 51.9, 39.8 ppm; HRMS (EI): *m/z* calcd for $C_{14}H_{11}INO_2$ $[M^+]$: 351.9835, Found: 351.9834.

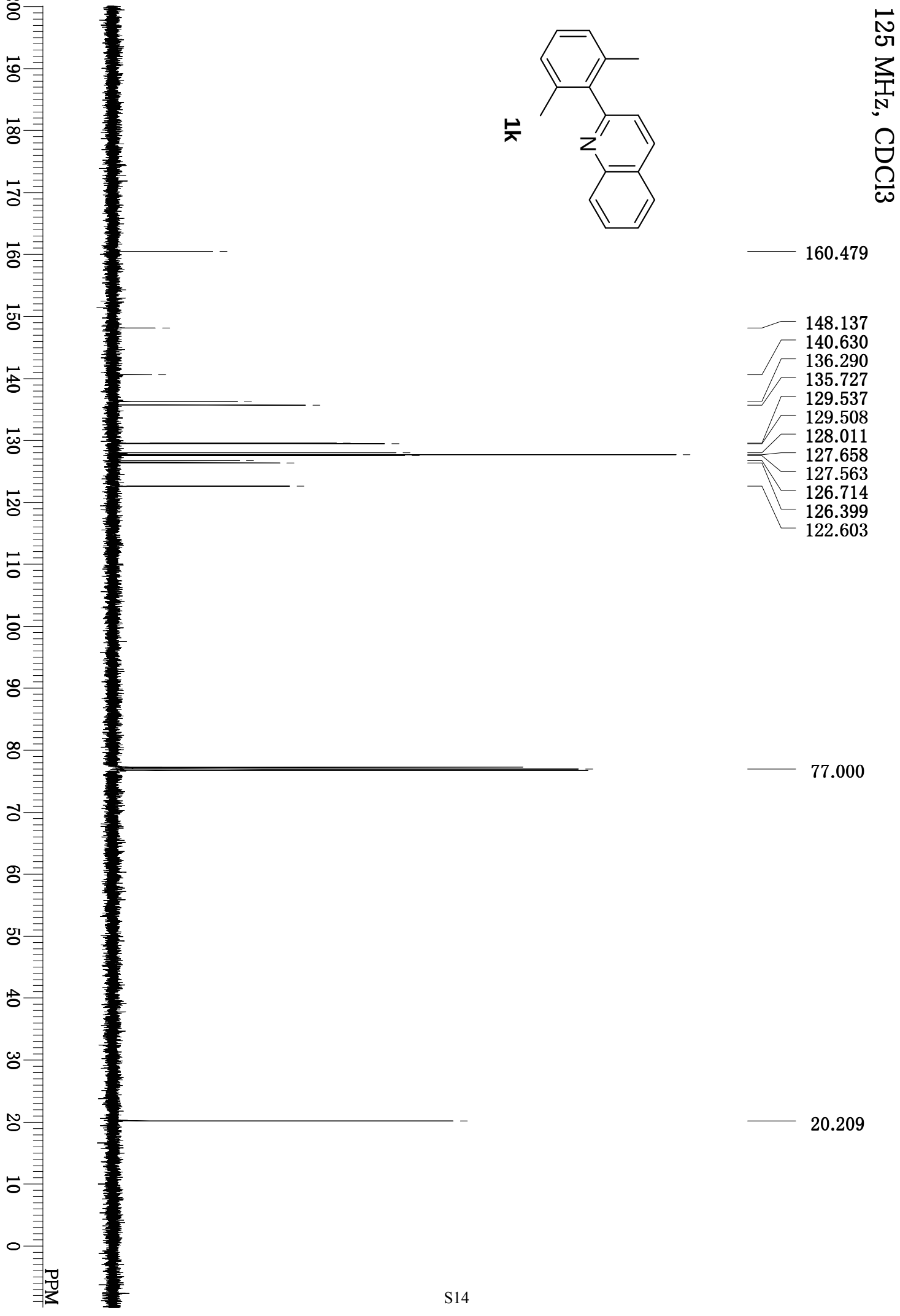


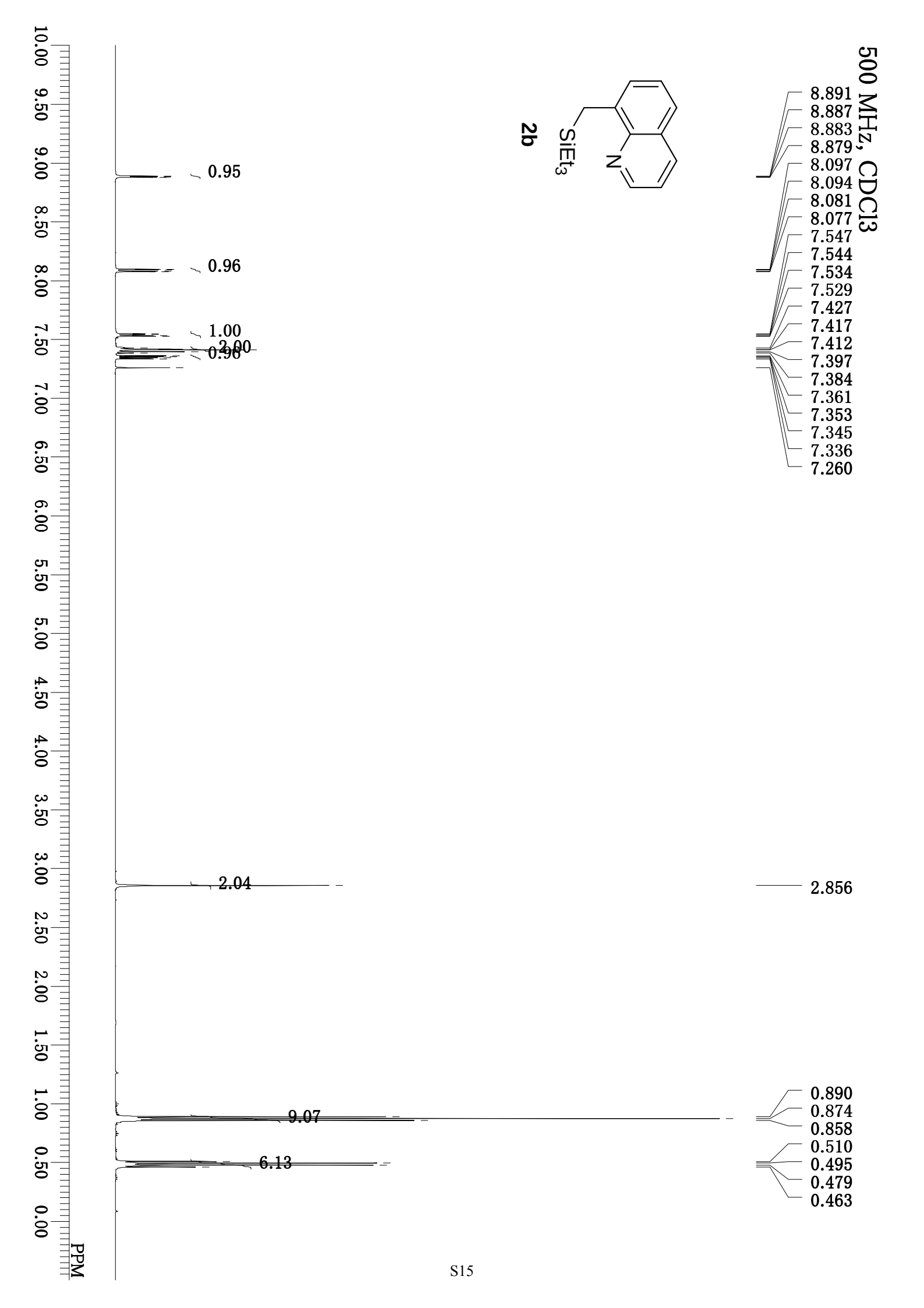
5c

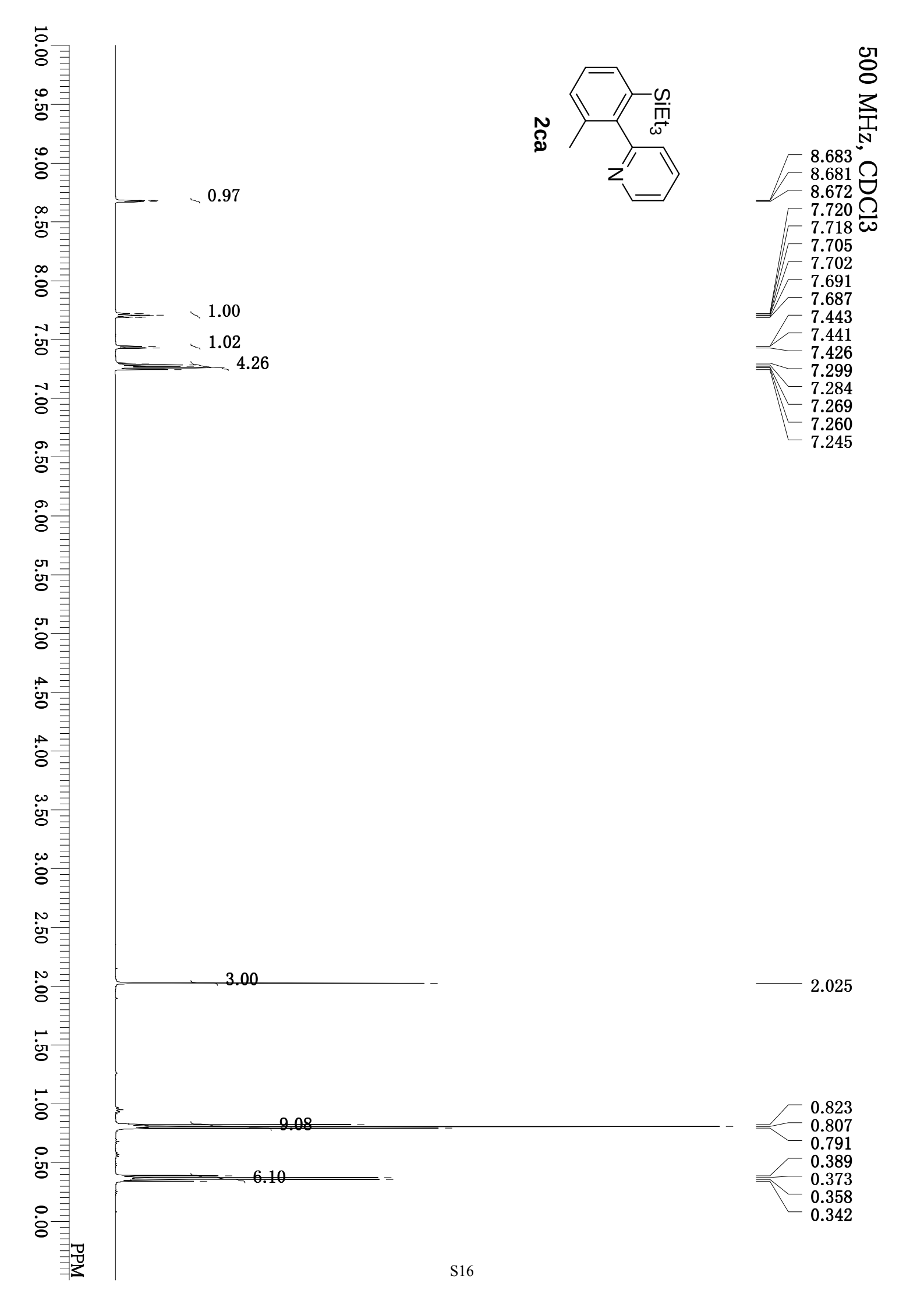
Methyl 2-{1-phenyl-2-(pyridin-2-yl)phenyl}acetate (5c): To a solution of **4c** (36.8 mg, 0.1 mmol, 1.0 equiv) in DMF (1.0 mL) was added $PhB(OH)_2$ (19.0 mg, 0.16 mmol, 1.5 equiv), K_2CO_3 (43.1 mg, 0.31 mmol, 3.0 equiv), and $Pd(PPh_3)_4$ (6.0 mg, 5 μmol, 5 mol %). The resulting mixture was then stirred at 100 ºC for 15 h under Ar atmosphere. After cooling to room temperature, the reaction mixture was quenched by 10 mL of water and extracted with ethyl acetate (4 mL x3). The solvent was removed under reduced pressure and the residue was purified by flash silica-gel column chromatography (hexane/ethyl acetate, 4:1) to give **5c** as pale yellow oil in 83% yield (21.6 mg, 0.87 mmol).

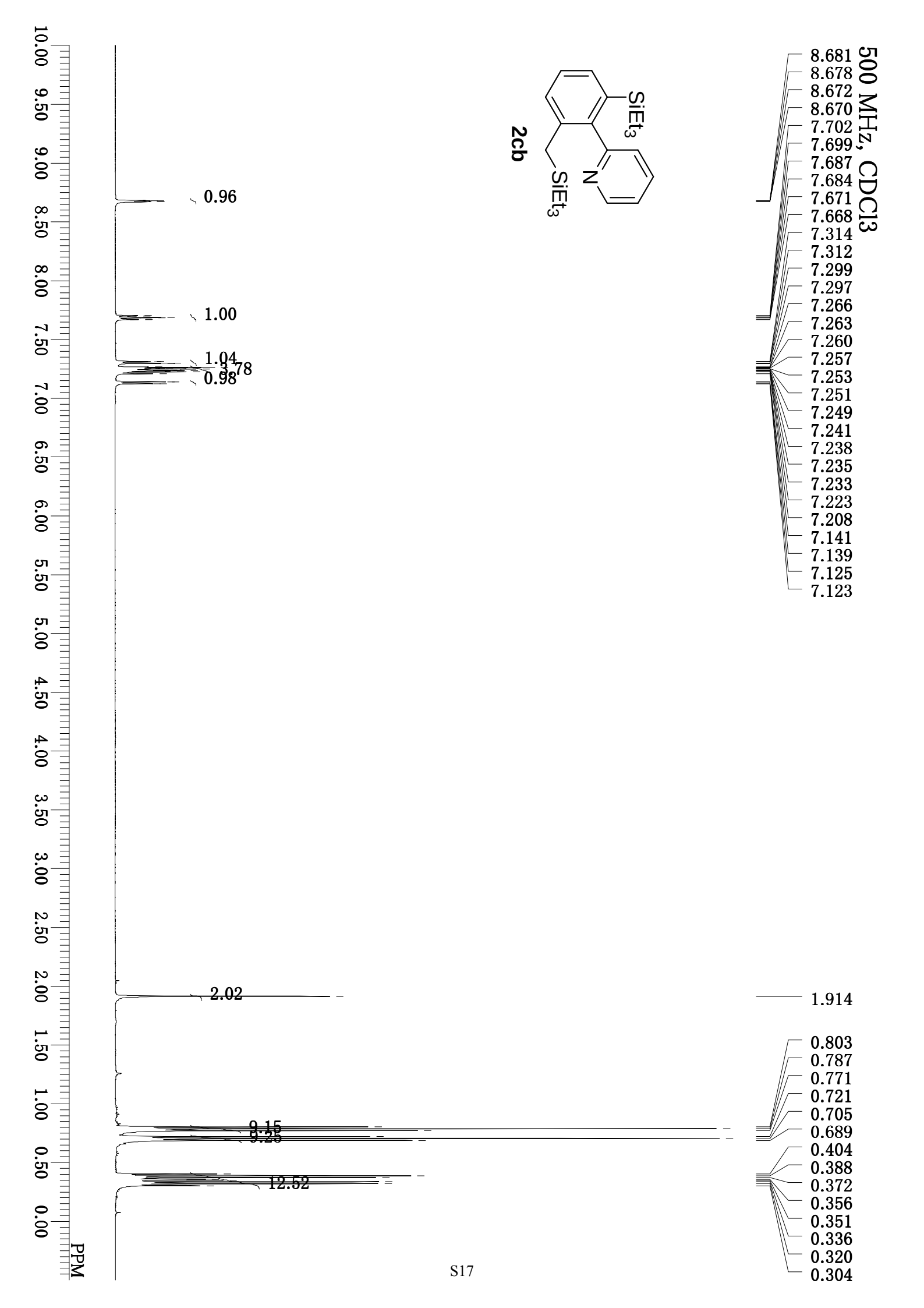
IR (neat): 2951, 1738, 1585, 1423, 1339, 1259, 1160, 1025, 761, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 8.62 (dd, *J* = 4.0, 1.1 Hz, 1H), 7.46-7.36 (m, 4H), 7.15-7.12 (m, 3H), 7.11-7.05 (m ,3H), 6.85 (dt, *J* = 8.0, 1.1 Hz, 1H), 3.66 (s, 2H), 3.53 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ = 172.0, 158.6, 148.8, 141.6, 141.3, 139.4, 135.5, 133.1, 129.8, 129.6, 129.2, 128.3, 127.6, 126.4, 121.5, 51.7, 39.1 ppm; HRMS (EI): *m/z* calcd for $C_{20}H_{16}NO_2^+$ $[M^+]$: 302.1181, Found: 302.1176.


500 MHz, CDCl3
1k
N
8.245
8.228
8.183
8.166
7.897
7.881
7.770
7.767
7.756
7.754
7.750
7.739
7.736
7.604
7.601
7.590
7.588
7.585
7.574
7.571
7.381
7.364
7.260
7.250
7.234
7.219
7.155
7.140
1.00
0.90
0.98
1.00
0.98
0.95
1.00
1.85
5.84
2.083
PPM

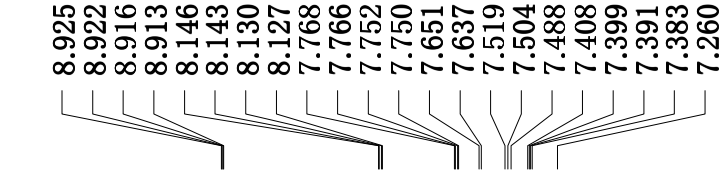

125 MHz, CDCl3
1k
N
160.479
148.137
140.630
136.290
135.727
129.537
129.508
128.011
127.658
127.563
126.714
126.399
122.603
77.000
20.209
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM

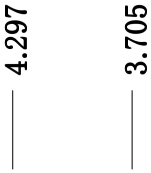

500 MHz, CDCl3
2b
SiEt3
N
8.891
8.887
8.883
8.879
8.097
8.094
8.081
8.077
7.547
7.544
7.534
7.529
7.427
7.417
7.412
7.397
7.384
7.361
7.353
7.345
7.336
7.260
0.95
0.96
1.00
2.00
0.96
2.04
9.07
6.13
2.856
0.890
0.874
0.858
0.510
0.495
0.479
0.463
PPM

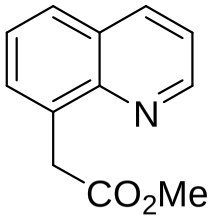

500 MHz, CDCl3
SiEt3
N
2ca
8.683
8.681
8.672
7.720
7.718
7.705
7.702
7.691
7.687
7.443
7.441
7.426
7.299
7.284
7.269
7.260
7.245
0.97
1.00
1.02
4.26
3.00
9.08
6.10
2.025
0.823
0.807
0.791
0.389
0.373
0.358
0.342
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
PPM


500 MHz, CDCl3
2cb
SiEt3
N
SiEt3
8.681
8.678
8.672
8.670
7.702
7.699
7.687
7.684
7.671
7.668
7.314
7.312
7.299
7.297
7.266
7.263
7.260
7.257
7.253
7.251
7.249
7.241
7.238
7.235
7.233
7.223
7.208
7.141
7.139
7.125
7.123
0.96
1.00
1.04
3.78
0.98
2.02
9.15
9.28
12.52
1.914
0.803
0.787
0.771
0.721
0.705
0.689
0.404
0.388
0.372
0.356
0.351
0.336
0.320
0.304
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
PPM

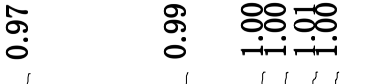
500 MHz, CDCl3

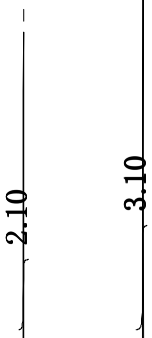


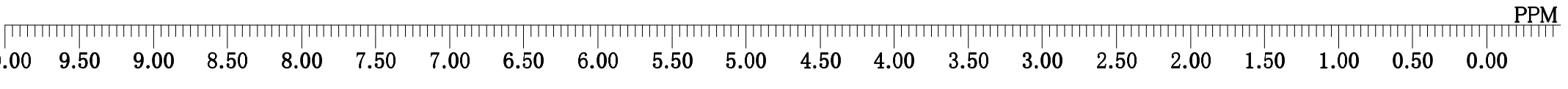




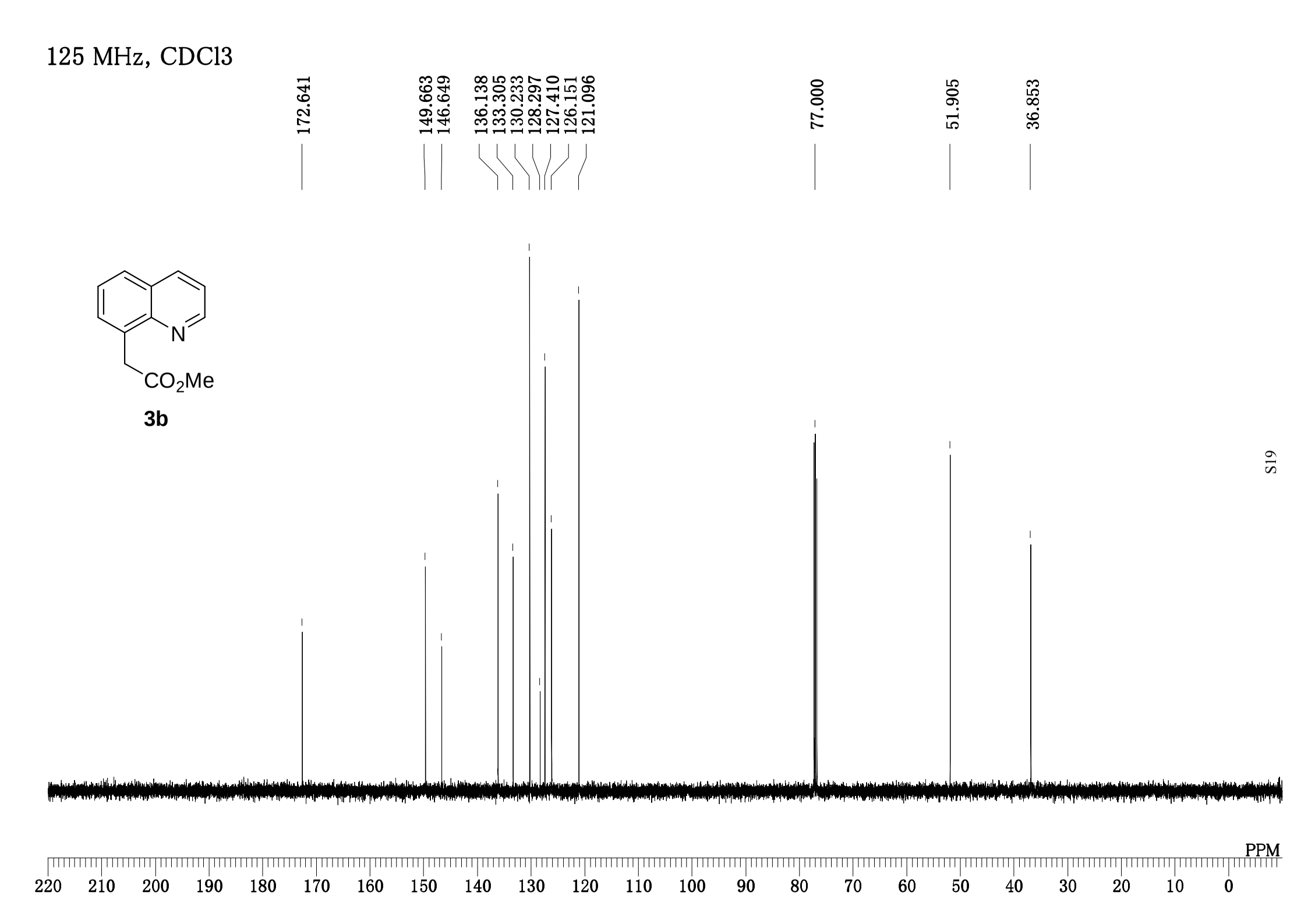
3b

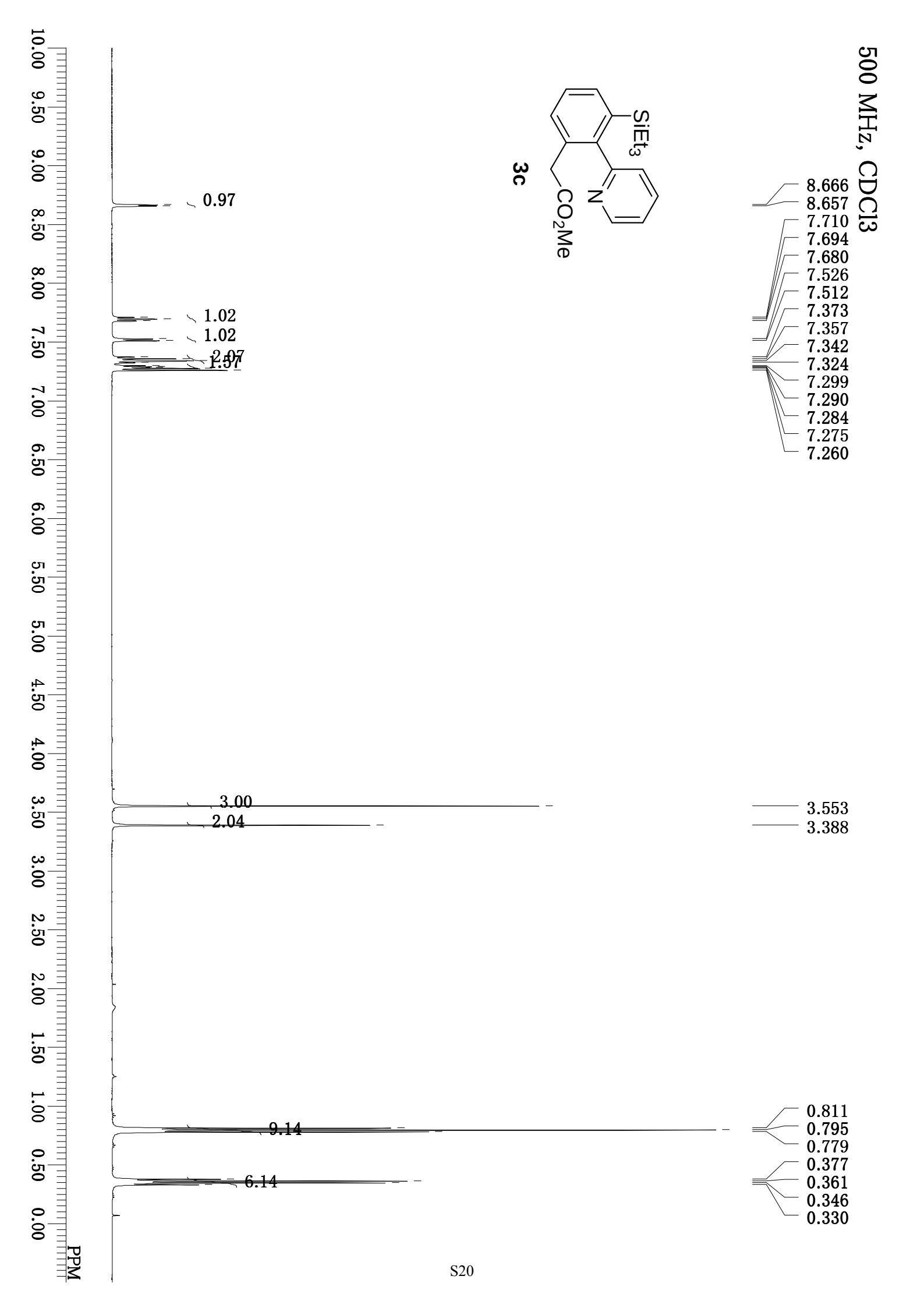




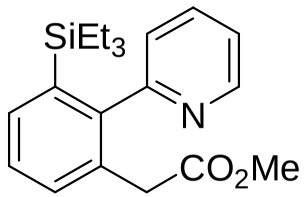


125 MHz, CDCl3



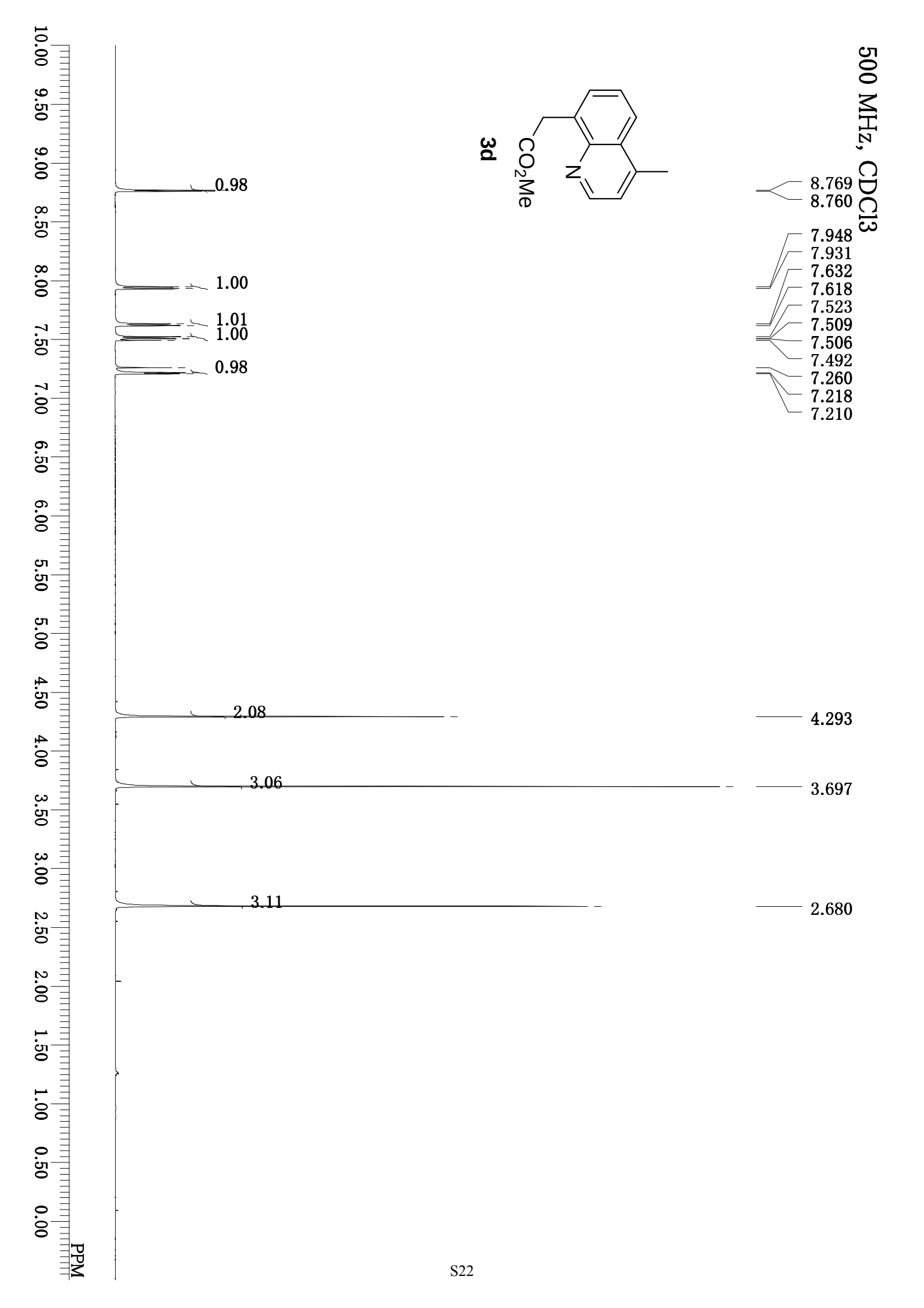

500 MHz, CDCl3
3c
SiEt3
N
CO2Me
8.666
8.657
7.710
7.694
7.680
7.526
7.512
7.373
7.357
7.342
7.324
7.299
7.290
7.284
7.275
7.260
3.553
3.388
0.811
0.795
0.779
0.377
0.361
0.346
0.330
0.97
1.02
1.02
2.07
1.57
3.00
2.04
9.14
6.14
PPM

125 MHz, CDCl3

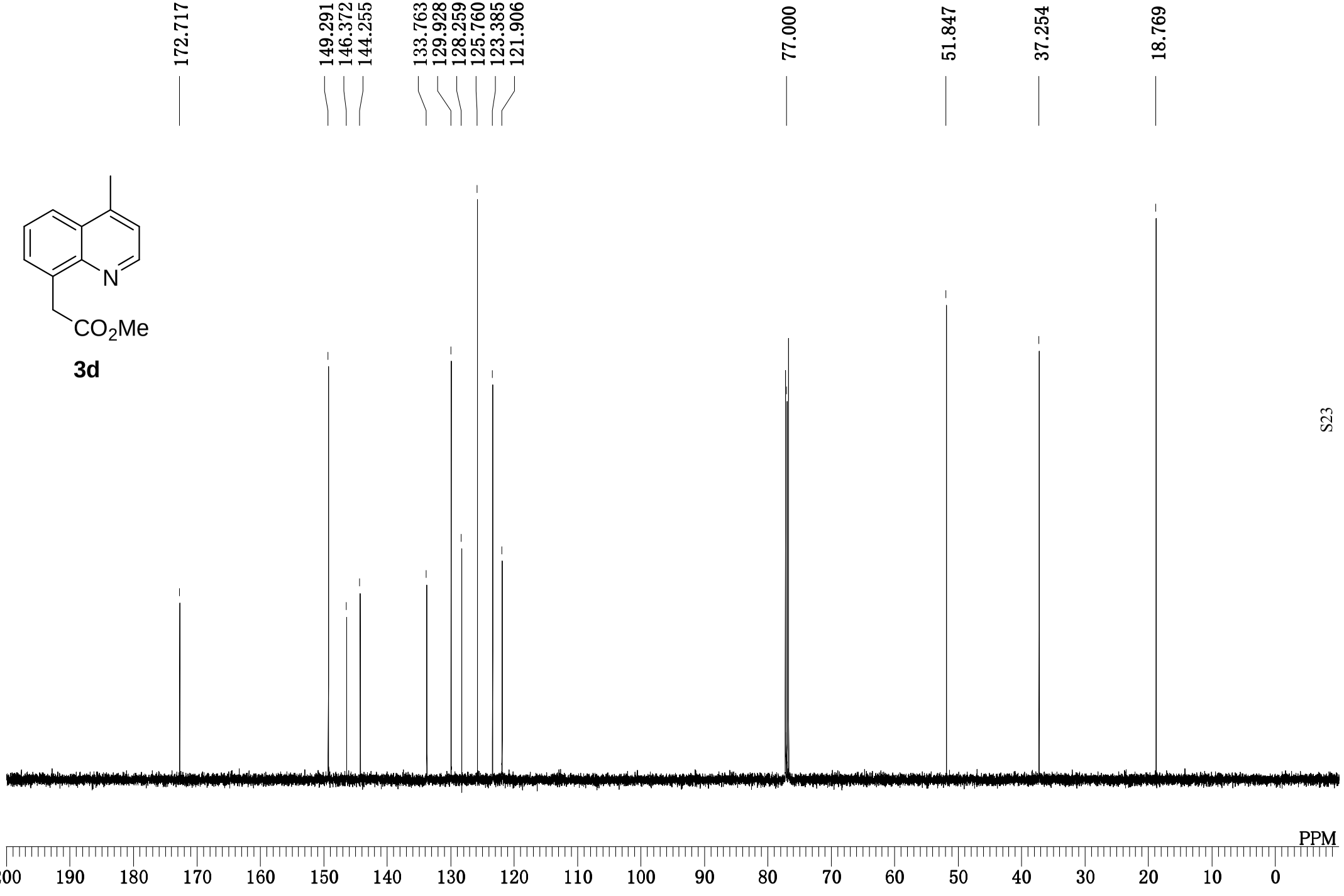


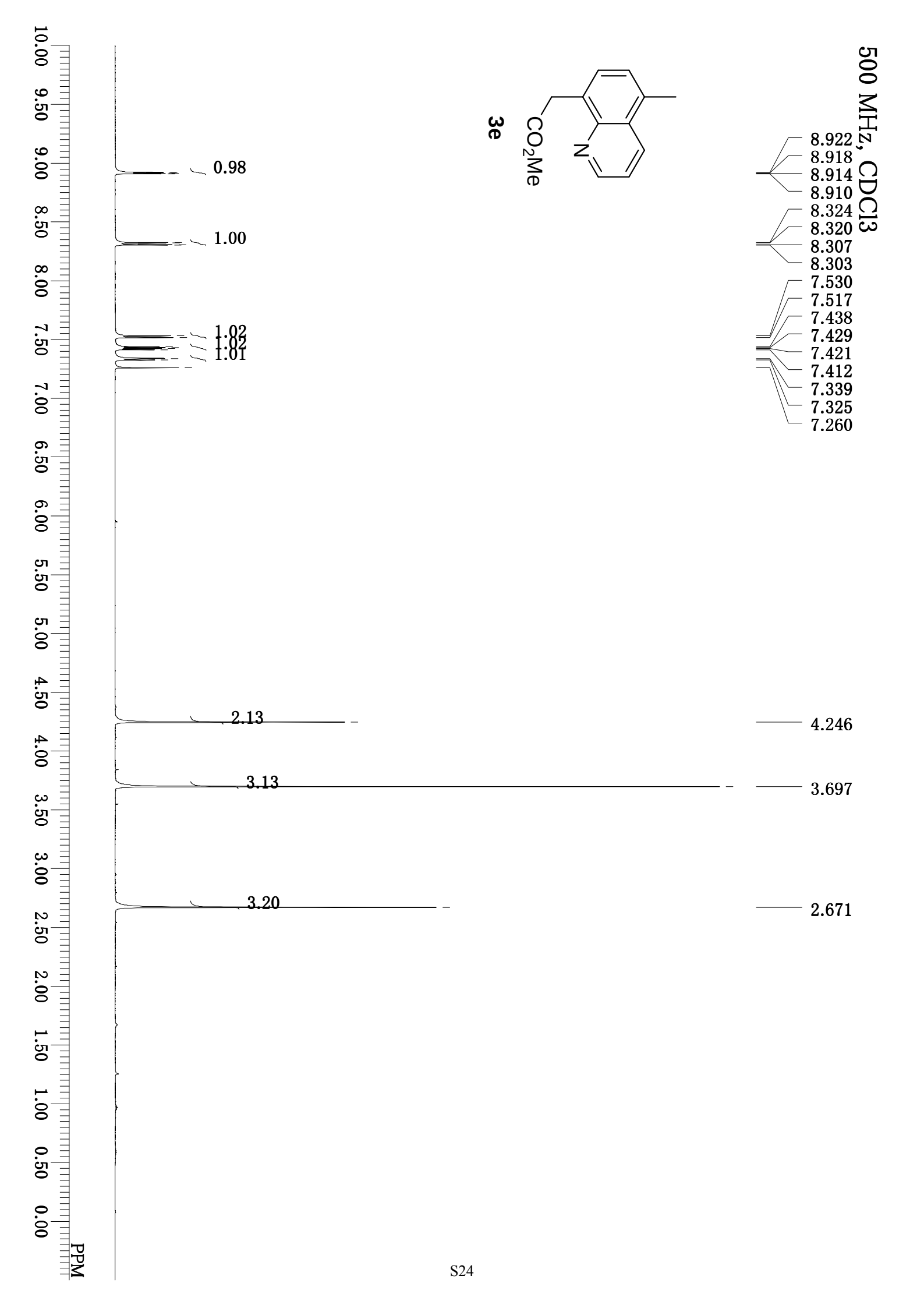
3c

PPM

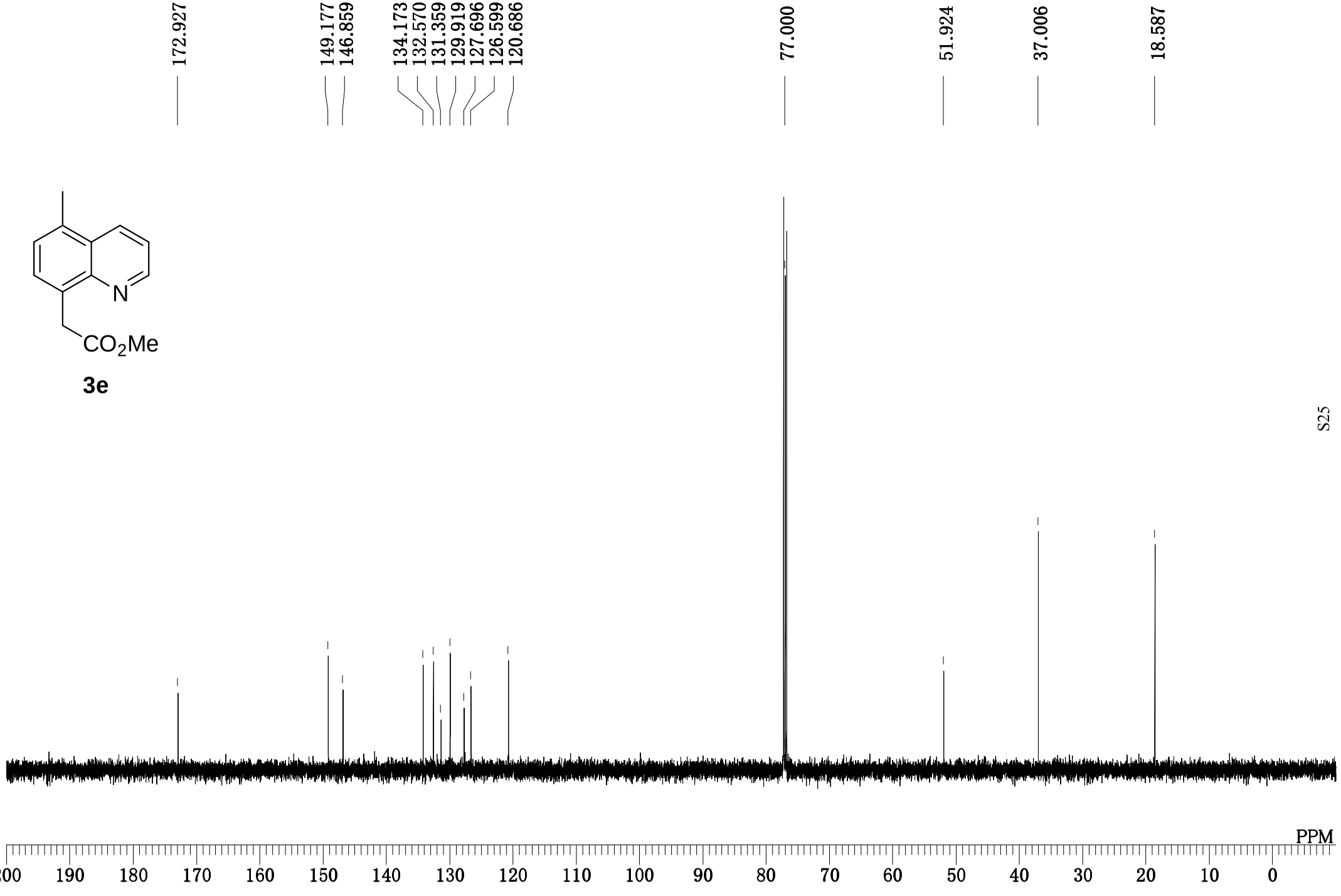

500 MHz, CDCl3
3d
CO2Me
N
8.769
8.760
7.948
7.931
7.632
7.618
7.523
7.509
7.506
7.492
7.260
7.218
7.210
4.293
3.697
2.680
0.98
1.00
1.01
1.00
0.98
2.08
3.06
3.11
PPM

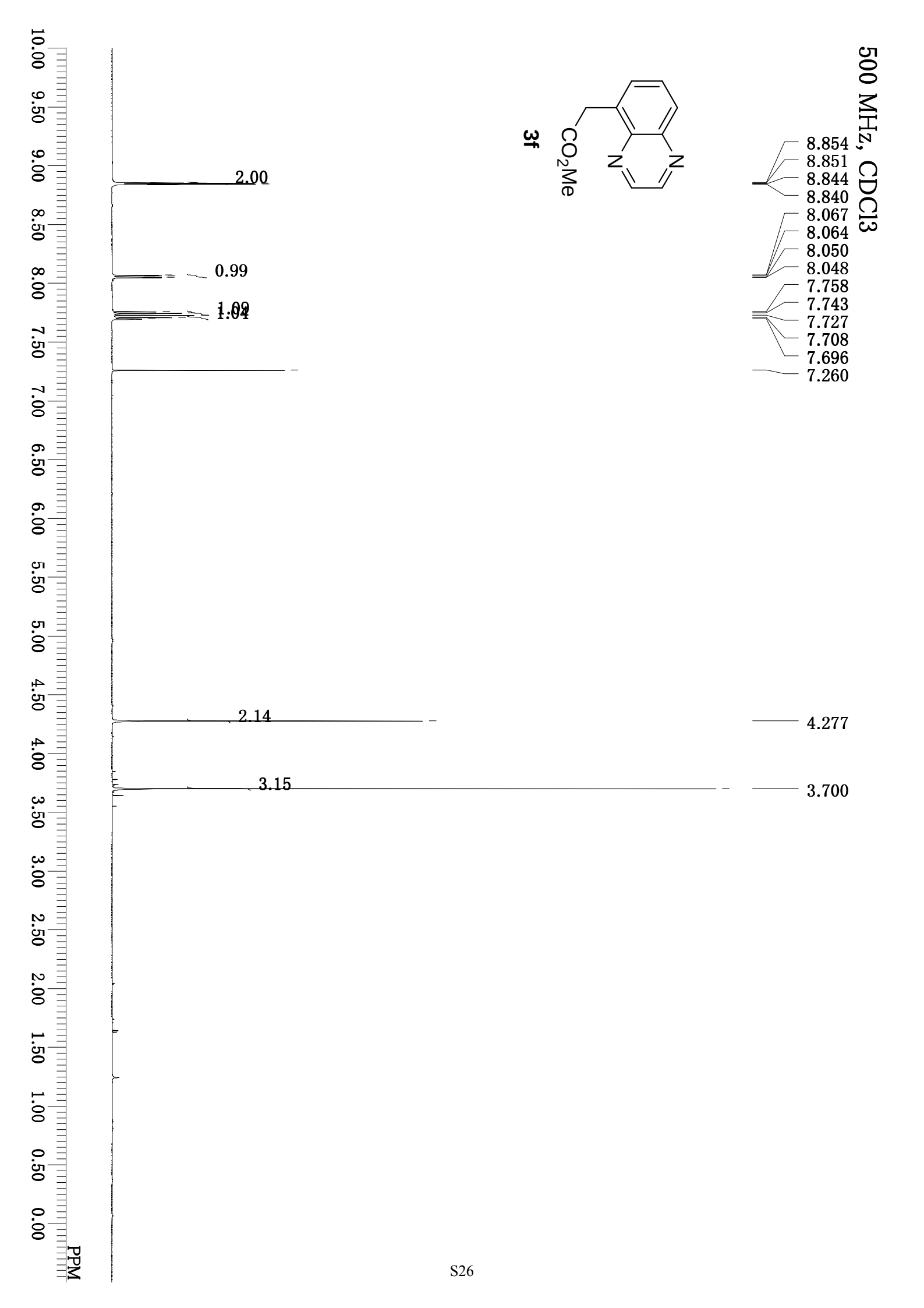
125 MHz, CDCl3

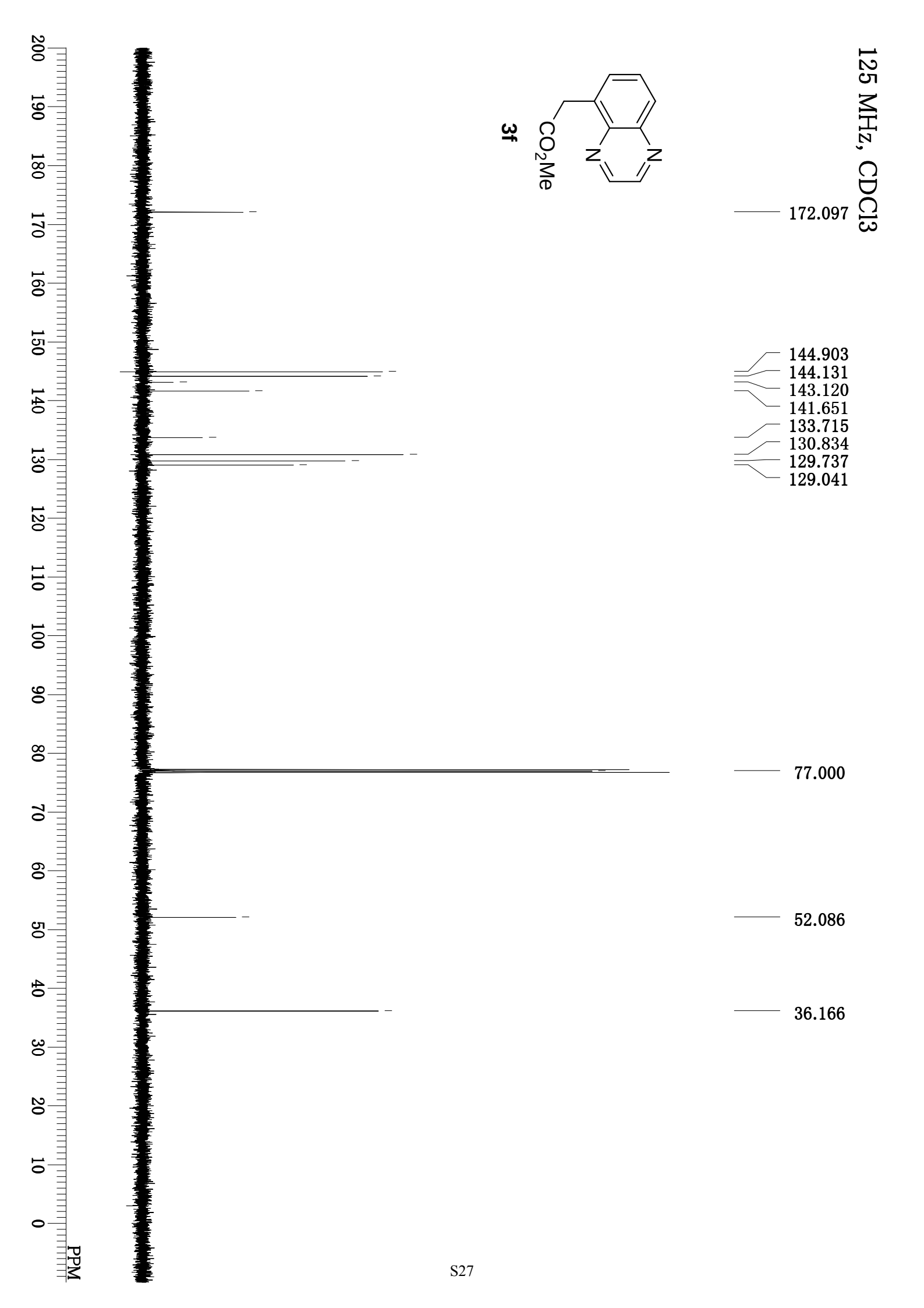



500 MHz, CDCl3
3e
CO2Me
N
8.922
8.918
8.914
8.910
8.324
8.320
8.307
8.303
7.530
7.517
7.438
7.429
7.421
7.412
7.339
7.325
7.260
0.98
1.00
1.02
1.02
1.01
2.13
3.13
3.20
4.246
3.697
2.671
PPM

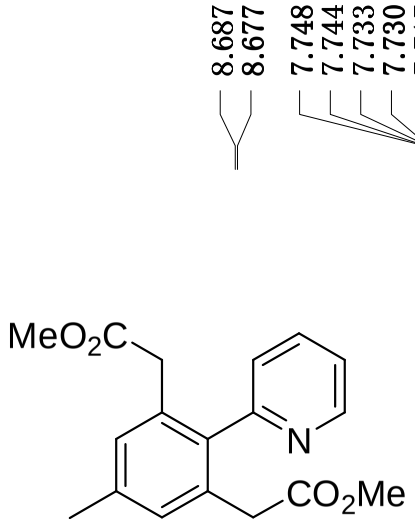
125 MHz, CDCl3




500 MHz, CDCl3
3f
CO2Me
N
N
8.854
8.851
8.844
8.840
8.067
8.064
8.050
8.048
7.758
7.743
7.727
7.708
7.696
7.260
4.277
3.700
2.00
0.99
1.09
1.04
2.14
3.15
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
PPM


125 MHz, CDCl3
3f
CO2Me
N
N
172.097
144.903
144.131
143.120
141.651
133.715
130.834
129.737
129.041
77.000
52.086
36.166
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM

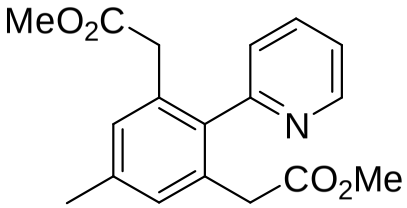
500 MHz, CDCl3



3ga

125 MHz, CDCl3

171.925
157.856
149.548
138.169
138.026
136.052
132.504
130.157
125.541
122.154
77.000
51.828
39.009
21.105

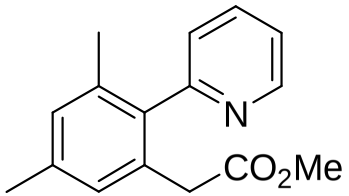


3ga

PPM

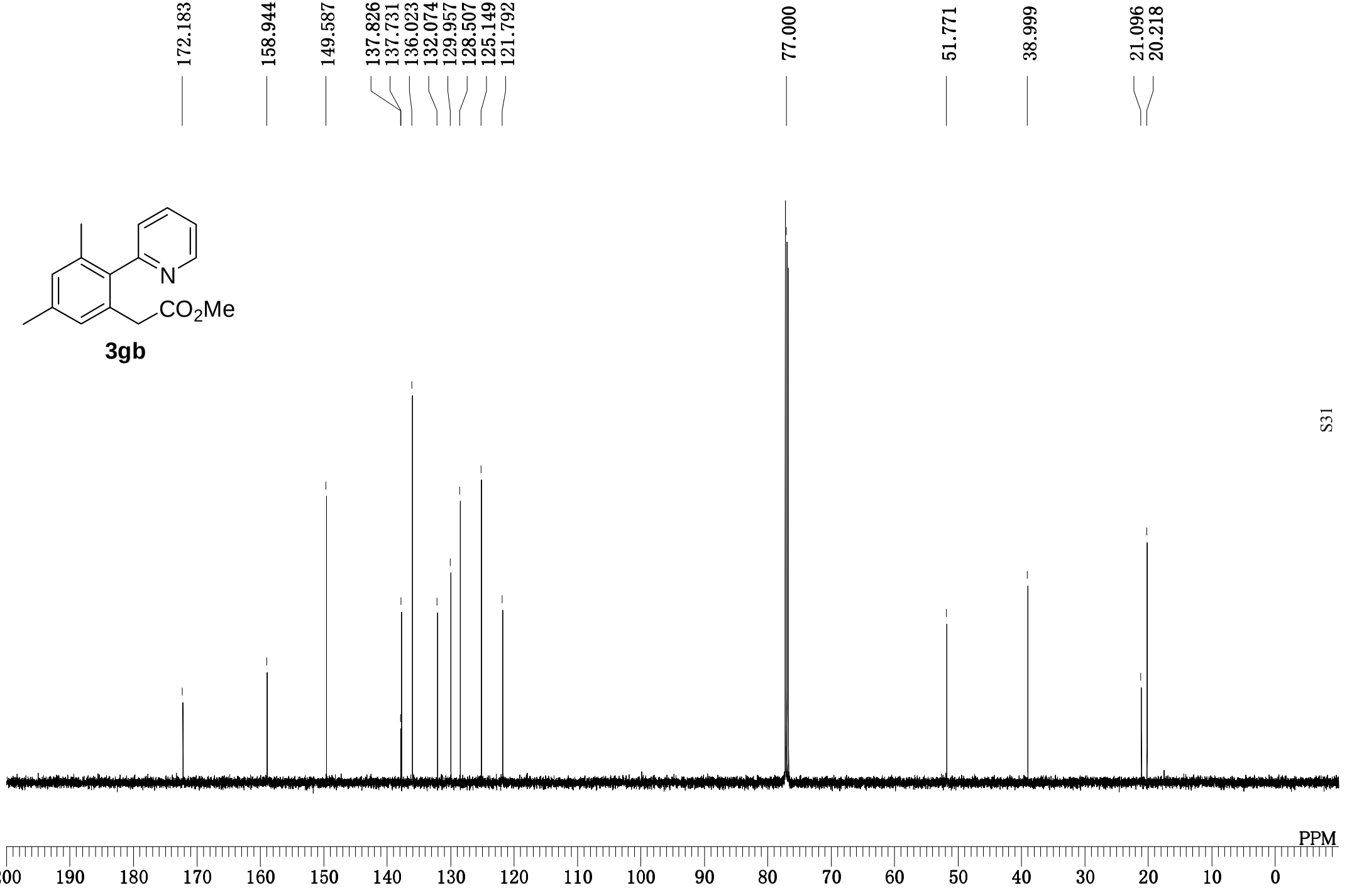
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

500 MHz, CDCl3

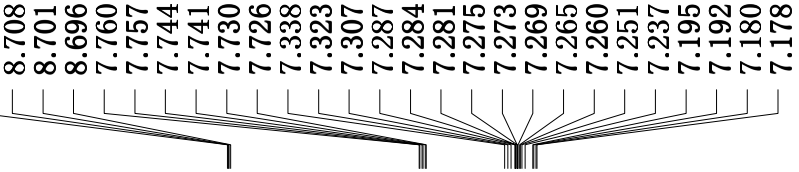


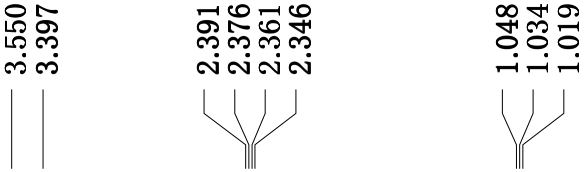
3gb

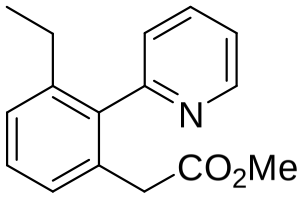
125 MHz, CDCl3



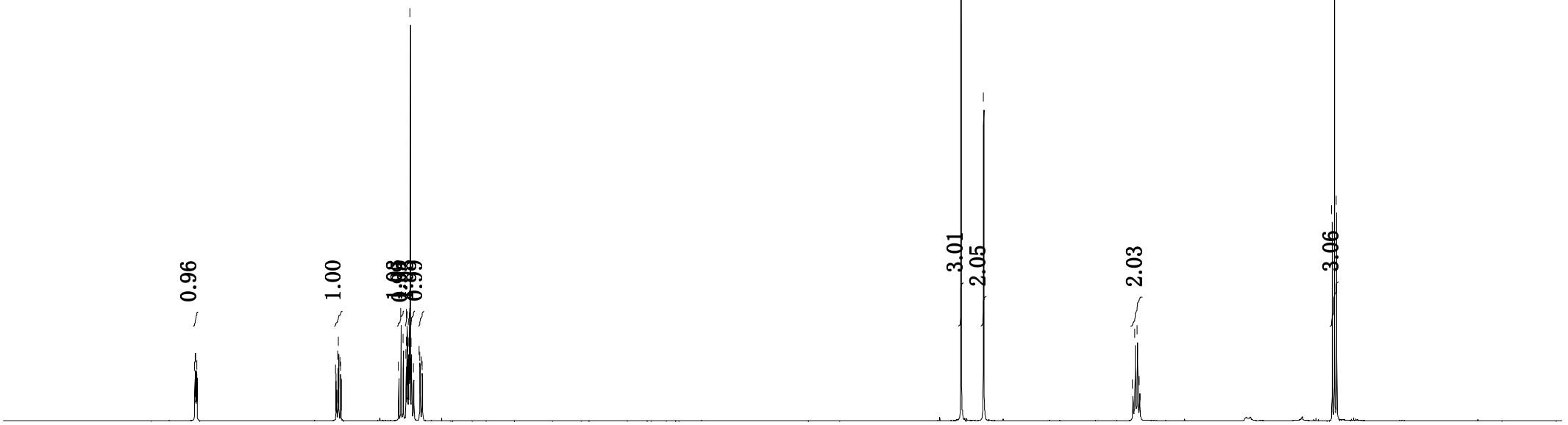
500 MHz, CDCl3

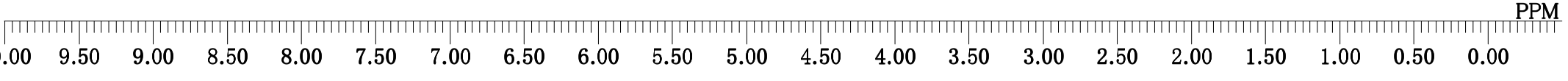






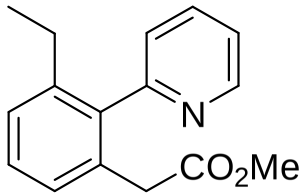
3h





125 MHz, CDCl3

172.068
158.696
149.558
142.290
140.163
135.966
132.265
128.402
127.773
127.467
125.121
121.973
77.000
51.790
39.076
26.533
15.268

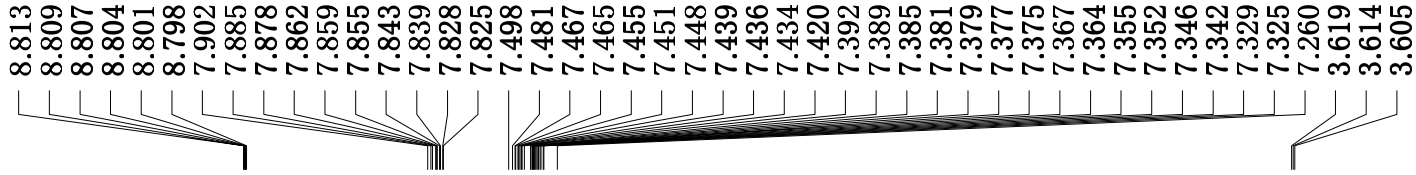


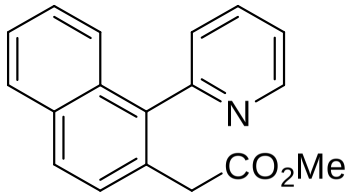
3h

PPM

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

500 MHz, CDCl3

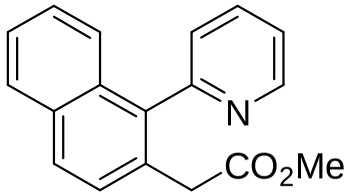




3i

125 MHz, CDCl3

171.944
157.895
149.873
137.769
136.195
132.704
132.360
129.814
128.621
127.935
127.916
126.370
126.046
125.817
125.645
122.345
77.000
51.943
39.142

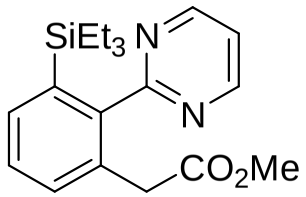


3i

PPM

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

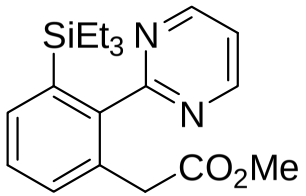
500 MHz, CDCl3



3j

125 MHz, CDCl3

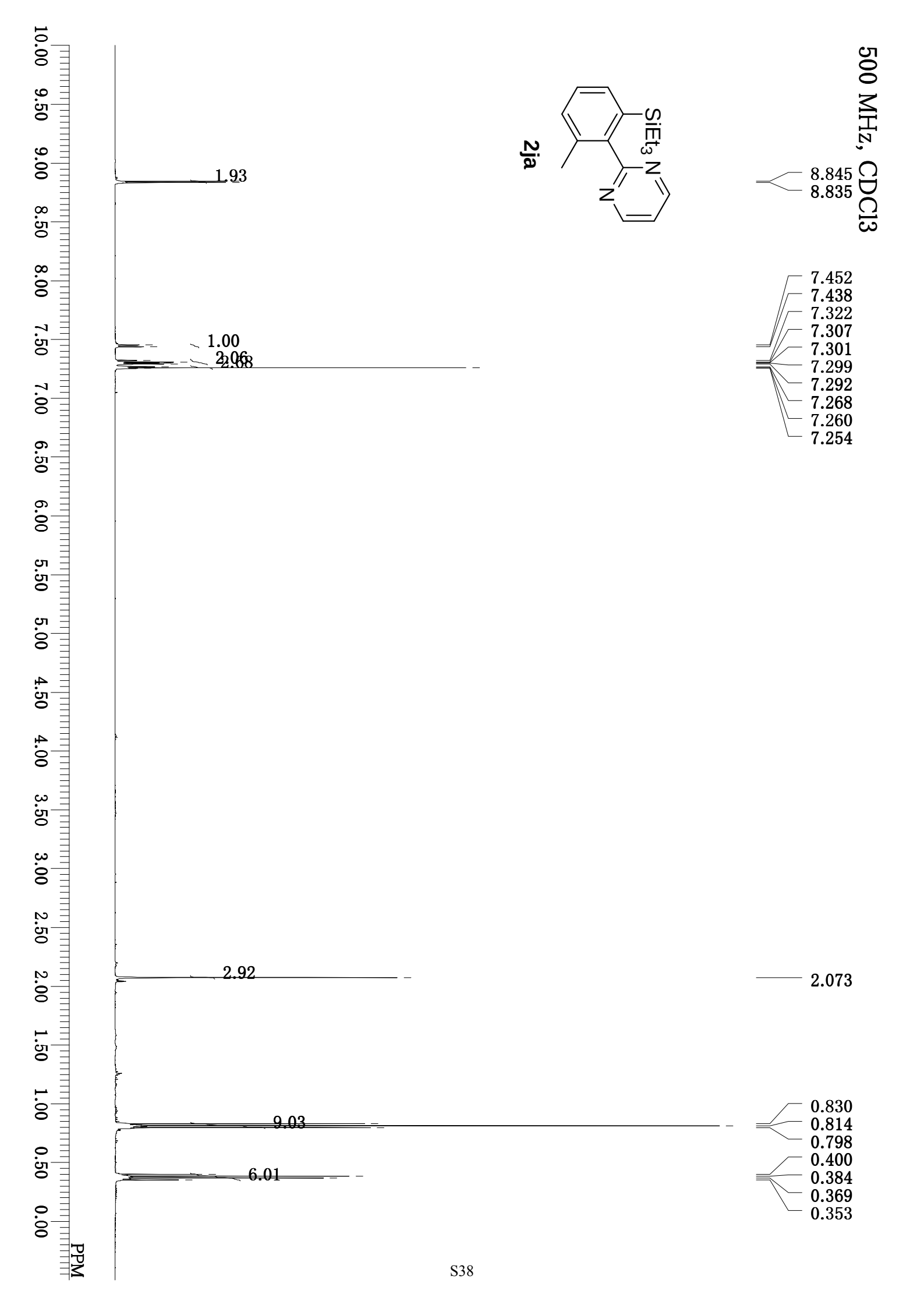
171.801
168.682
156.588
145.399
136.338
134.812
131.845
131.388
127.839
119.388
77.000
51.819
39.400
7.532
3.822

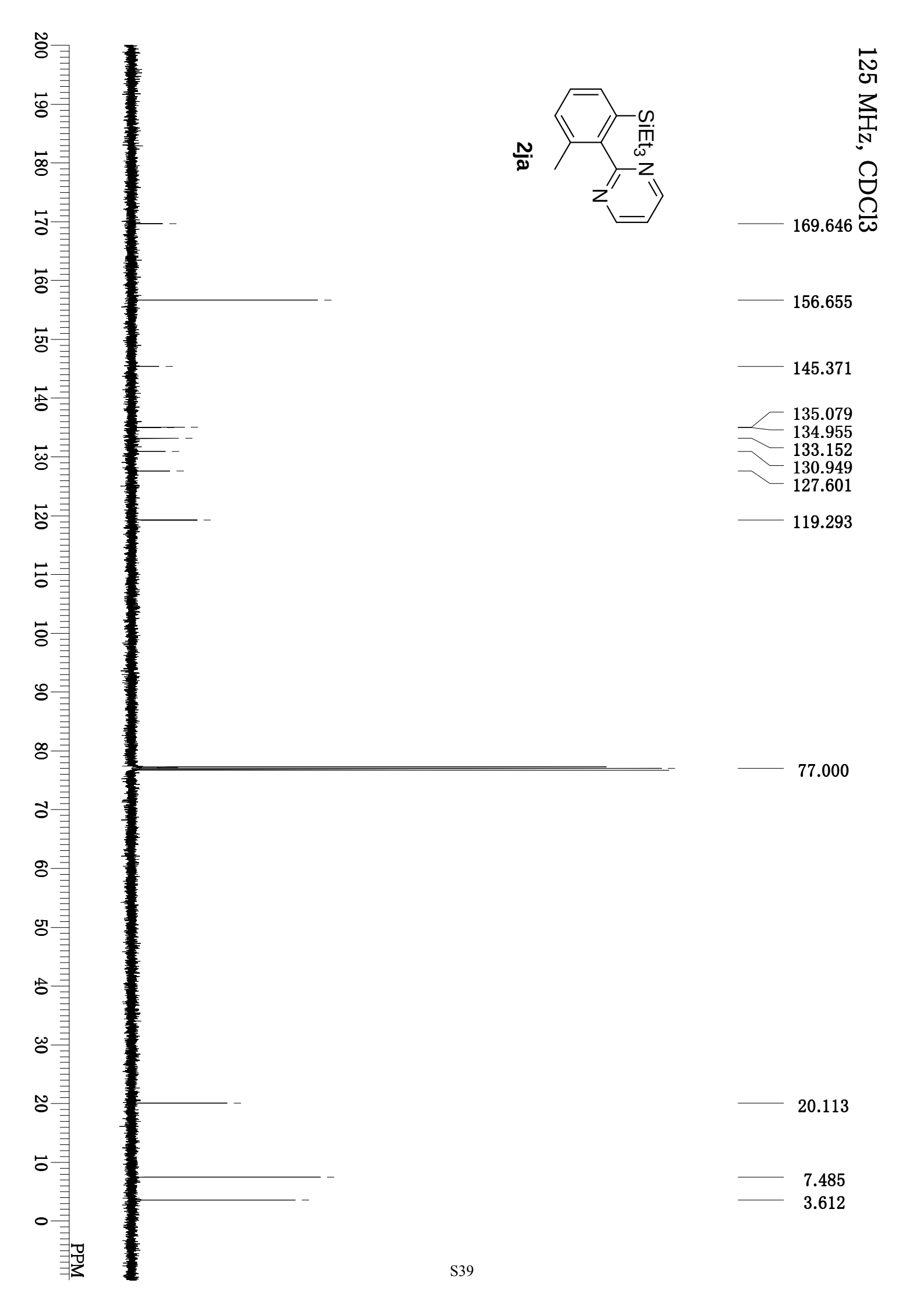


3j

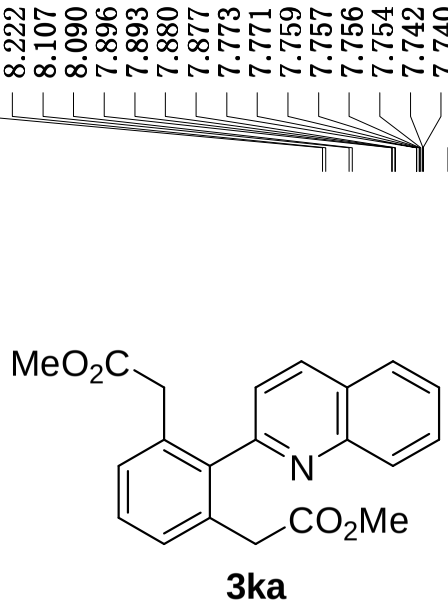
PPM

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

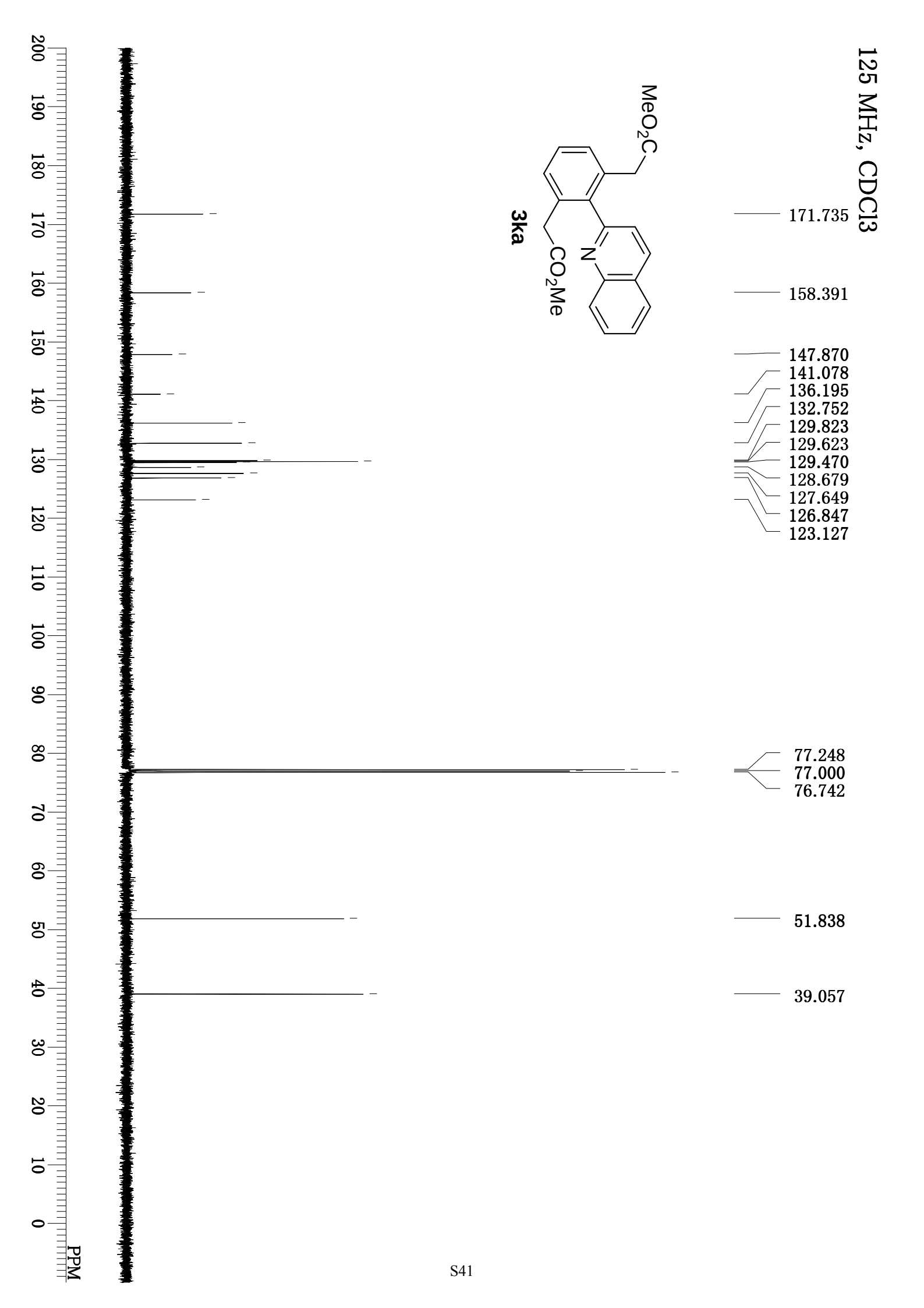

500 MHz, CDCl3
2ja
SiEt3
N
N
8.845
8.835
7.452
7.438
7.322
7.307
7.301
7.299
7.292
7.268
7.260
7.254
2.073
0.830
0.814
0.798
0.400
0.384
0.369
0.353
1.93
1.00
2.06
2.08
2.92
9.03
6.01
10.00
9.50
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
PPM


125 MHz, CDCl3
2ja
SiEt3
N
N
169.646
156.655
145.371
135.079
134.955
133.152
130.949
127.601
119.293
77.000
20.113
7.485
3.612
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

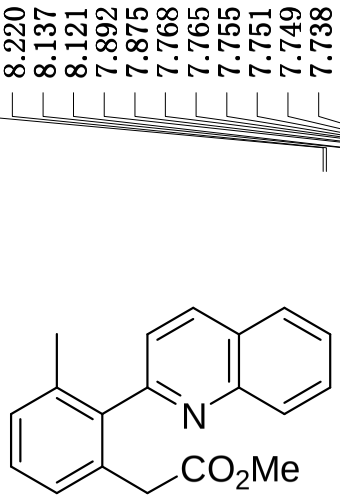
500 MHz, CDCl3



3ka


125 MHz, CDCl3
MeO2C
N
CO2Me
3ka
171.735
158.391
147.870
141.078
136.195
132.752
129.823
129.623
129.470
128.679
127.649
126.847
123.127
77.248
77.000
76.742
51.838
39.057
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

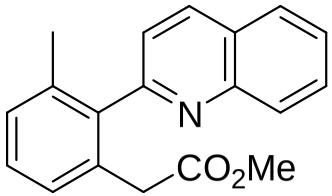
500 MHz, CDCl3



3kb

125 MHz, CDCl3

171.954
159.430
147.984
140.792
136.204
136.157
132.313
129.652
129.499
129.318
128.364
128.068
127.601
126.771
126.618
122.984
77.000
51.752
39.009
20.390

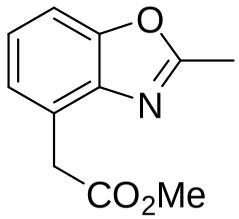


3kb

PPM

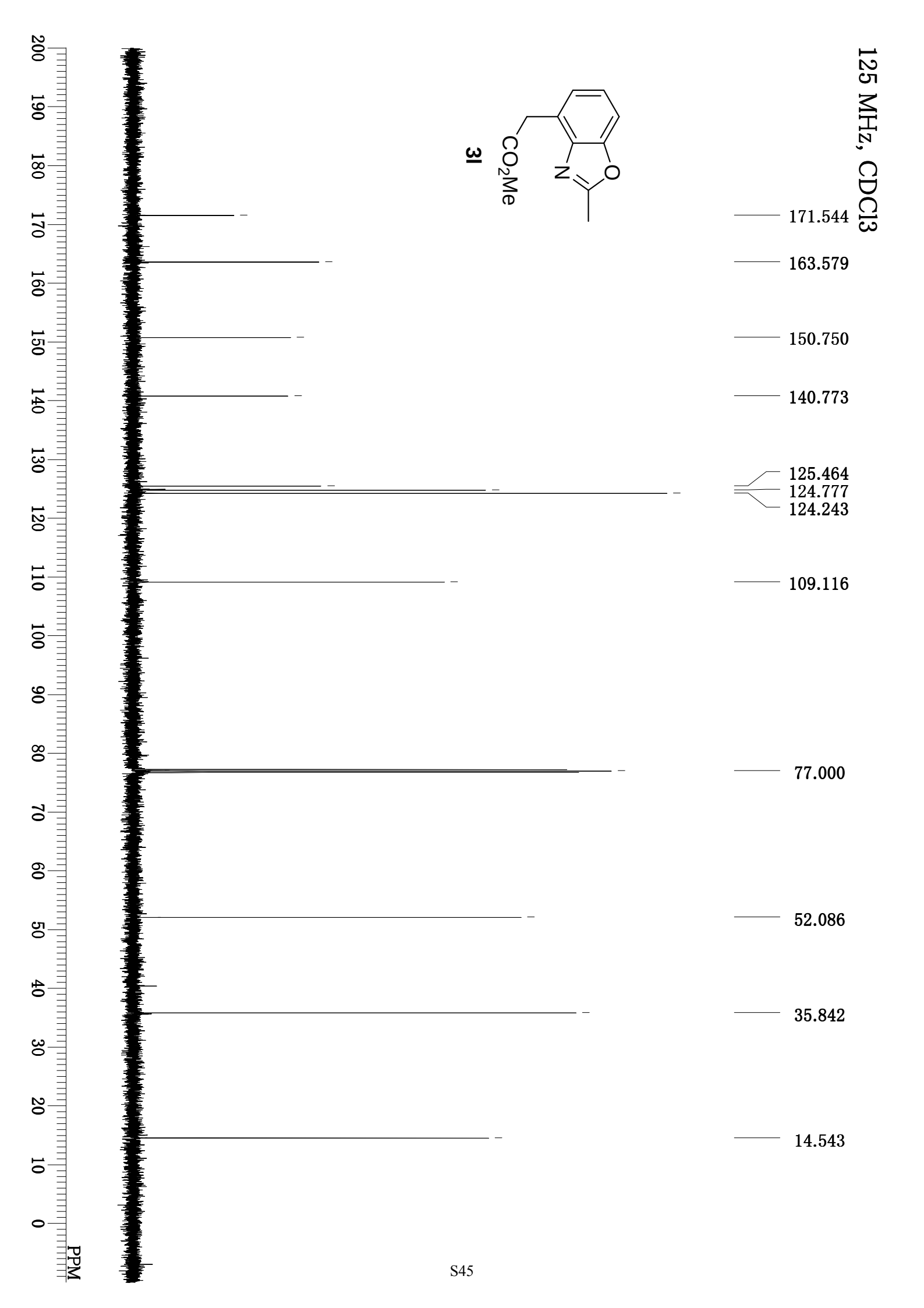
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

500 MHz, CDCl3

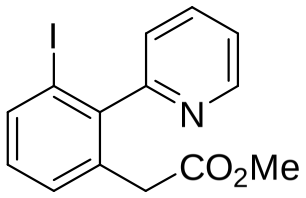


3l

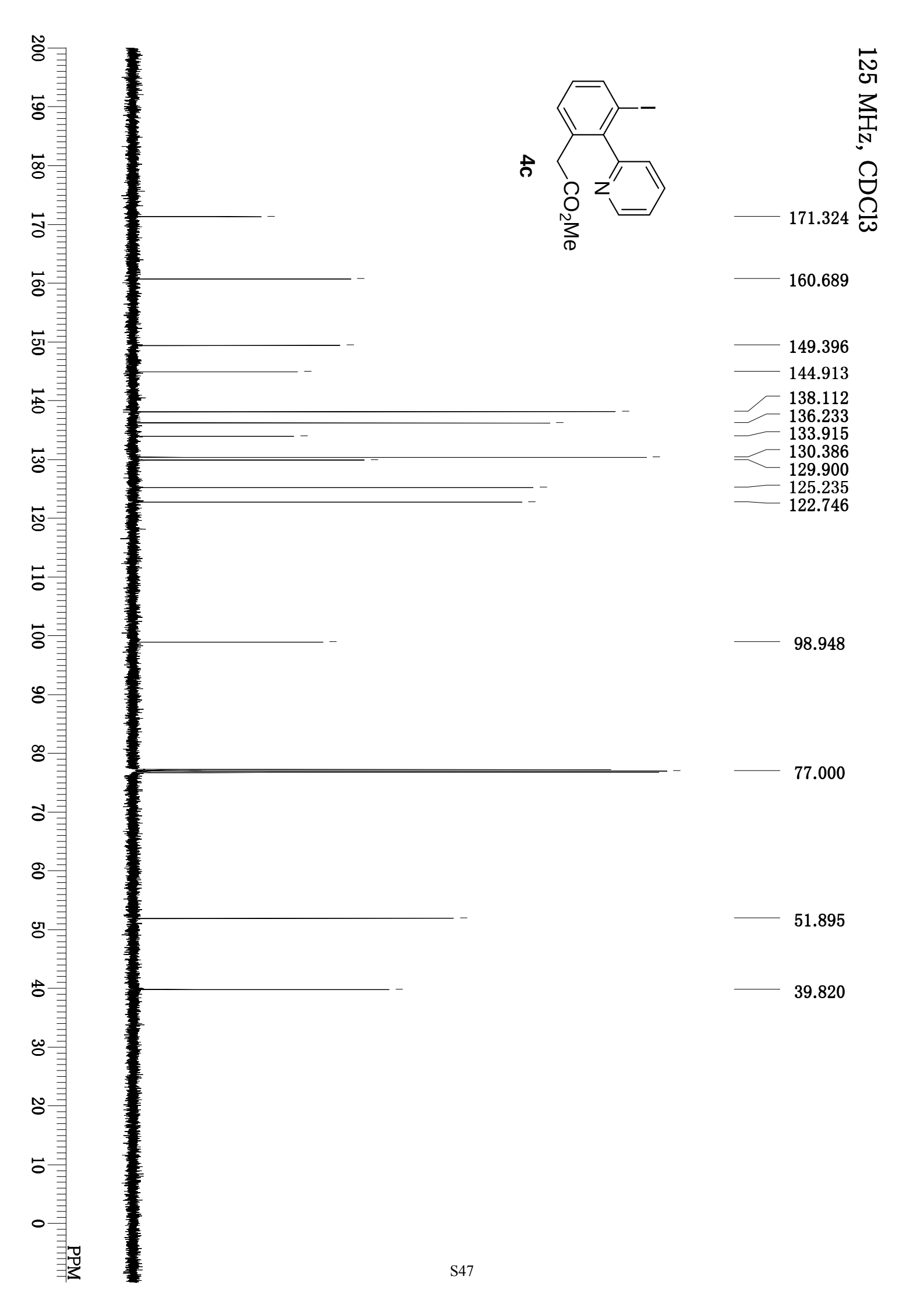
PPM


125 MHz, CDCl3
3l
CO2Me
N
O
171.544
163.579
150.750
140.773
125.464
124.777
124.243
109.116
77.000
52.086
35.842
14.543
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

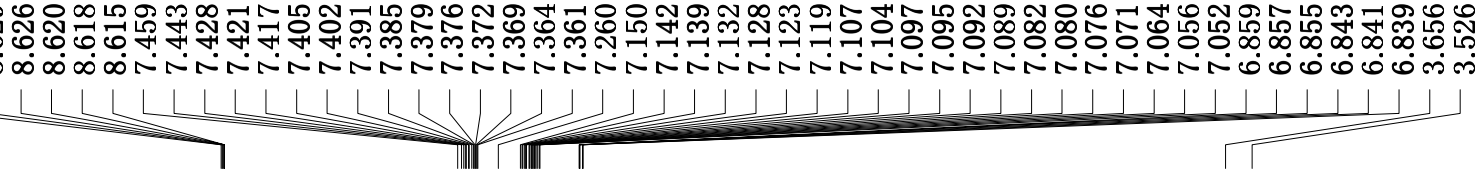
500 MHz, CDCl3

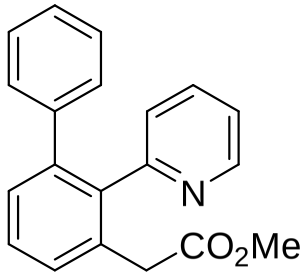


4c


125 MHz, CDCl3
4c
I
N
CO2Me
171.324
160.689
149.396
144.913
138.112
136.233
133.915
130.386
129.900
125.235
122.746
98.948
77.000
51.895
39.820
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

500 MHz, CDCl3

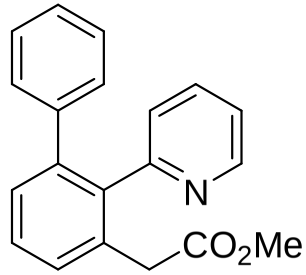




5c

125 MHz, CDCl3

172.011
158.581
148.795
141.584
141.279
139.438
135.508
133.114
129.823
129.623
129.222
128.335
127.610
126.361
121.496
77.000
51.743
39.104



5c

PPM

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