Iridium-Catalyzed Triple C(sp^3)-H Borylations: Construction of Triborylated sp^3-Carbon Centers

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Electronic Supplementary Information (ESI)

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(A) General

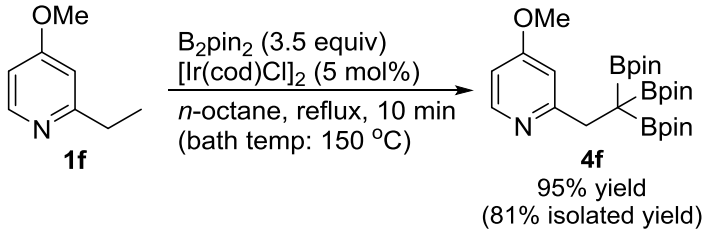
Infrared (IR) spectra were recorded on a JASCO FT/IR 460 Plus Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL ECA-500 spectrometer, operating at 500 MHz (^{1}H) or 125 MHz (^{13}C). Chemical shifts in $CDCl_3$ were reported in the scale relative to $CHCl_3$ (7.26 ppm) for ^{1}H NMR and to $CDCl_3$ (77.0 ppm) for ^{13}C NMR as internal references. ESI mass spectra were measured on a Thermo Scientific Exactive. Column chromatography was performed with silica gel Kanto 60 (230-400 mesh ASTM). Dry toluene was purified under argon using the Ultimate Solvent System (Glass Counter Inc.). *n*-Octane was purified by distillation with CaH. $[Ir(cod)Cl]_2$, pinB-Bpin, and CsF were purchased from Aldrich, Inc., Tokyo Chemical Industry Co., Ltd. (TCI), and Nacalai Tesque, Inc., respectively. A cylinder of CO_2 was purchased from Hokkaido Air Water, Inc. In general, reactions were carried out under an argon atmosphere unless otherwise noted. The X-ray intensities were measured on a Rigaku VariMax with RAPID using CuKα radiation.

(B) Synthesis of Substrates

2-Ethylpyridine (**1a**) was purchased from Tokyo Chemical Industry Co., Ltd. (TCI), and used as received. 2-Ethyl-4-nitropyridine (**1b**) was prepared by the reduction of the corresponding *N*-oxide[1] using PCl_3 as a reductant. 4-Cyano-2-ethylpyridine (**1c**)[2] and 2-ethyl-4-methylpyridine (**1e**)[3] were prepared according to the reported procedures. 4-Chloro-2-ethylpyridine (**1d**), 2-Ethyl-4-methoxypyridine (**1f**), and 4-Benzyloxy-2-ethylpyridine (**1g**) were prepared from the corresponding *N*-Oxide[1,4] using $Mo(CO)_6$ as a reductant.[5] 2-Ethyl-5-methoxypyridine (**1h**),[6] 2-Ethyl-6-metoxypyridine (**1i**),[7] 3-ethylisoquinoline (**1j**),[8] 1-ethylisoquinoline (**1k**),[9] and 2-ethylquinoline (**1l**)[10] were synthesized following the reported methods. 2-[2-(Triethylsilyl)ethyl]pyridine (**1m**) was synthesized from 2-ethylpyridine and Et_3SiH in the presence of $[Ir(cod)Cl]_2$ under a reflux condition.[11]

(C) General Procedure of C(sp^3)-H Borylation

(C-1) Using 3.5 equiv of pinB-Bpin

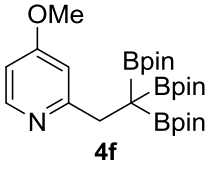


To a 10 mL test tube combined with condenser were placed 2-ethyl-4-methoxypyridiene (**1f**) (13.3 mg,

[1] Zhang, C. X.; Liang, H.-C.; Kim, E.-i.; Shearer, J.; Halton, M. E.; Kim, E.; Kaderli, S.; Incarvito, C. D.; Zuberbühler, A. D.; Rheingold, A. L.; Karlin, K. D. *J. Am. Chem. Soc.* **2003**, *125*, 634.
[2] Bose, D. S.; Sunder, K. S. *Synth. Commun.* **1999**, *29*, 4235.
[3] Kaiser, E. M.; Bartling, G. J.; Thomas, W. R.; Nichols, S. B.; Nash, D. R. *J. Org. Chem.* **1973**, *38*, 71.
[4] Ochiai, E. *J. Org. Chem.* **1953**, *18*, 534.
[5] Yoo, B. W.; Choi, J. W.; Yoon, C. M. *Tetrahedron Lett.* **2006**, *47*, 125.
[6] Gonzalez, J.; Jewell, T. M.; Li, H.; Linton, A.; Tatlock, J. H. PTC Patent WO2006/018725 A1, 2006.
[7] Brameld, K. A.; Carter, D. S.; Chin, E.; Javier de Vicente, F.; Li, J.; Schoenfeld, R. C.; Sjogren, E. B.; Talamas, F. X. PTC Patent WO2010/010017 A1, 2010.
[8] Kido, K.; Watanabe, Y. *Chem. Pharm. Bull.* **1987**, *35*, 4964.
[9] Dime, D. S.; McLean, S. *J. Org. Chem.* **1981**, *46*, 4999.
[10] Qian, B.; Guo, S.; Shao, J.; Zhu, Q.; Yang, L.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2010**, *132*, 3650.
[11] Mita, T.; Michigami, K.; Sato, Y. *manuscript in preparation*.

0.097 mmol, 1.0 equiv), pinB-Bpin (87.4 mg, 0.34 mmol, 3.5 equiv), and $[Ir(cod)Cl]_2$ (3.4 mg, 5 μmol, 5 mol%), then evacuated and backfilled with argon (x3). *n*-Octane (1 mL) was added to this mixture, which was stirred under reflux (bath temp: 150 °C) just for 10 min. The reaction mixture was directly concentrated under high vacuum to afford the crude product. Yield of **4f** was determined at this stage using 1,1,2,2-tetrachloroethane in ^{1}H NMR analysis as an internal standard (95% yield). The crude product was then purified by open column chromatography (Silica gel had been heated at 110 °C before use. hexane-AcOEt with 3% Et_3N, 8:1 to 3:1) to afford **4f** as white solids (40.4 mg, 0.078 mmol, 81% yield). Small quantity of pinacol boron residues could not be removed. See copies of ^{1}H and ^{13}C NMR spectra (section (J)).

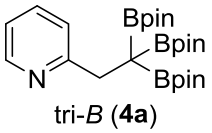
4-Methoxy-2-[2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (4f):



4f

mp. 133-134 °C; IR ($CHCl_3$): 2975, 2929, 1626, 1578, 1497, 1343, 1276, 1145, 1061, 860 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.27 (d, J = 6.3 Hz, 1H), 6.75-6.73 (m, 2H), 3.88 (s, 3H), 3.33 (s, 2H), 1.18 (s, 36H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.2, 166.6, 142.0, 109.9, 105.8, 81.1, 55.8, 36.3, 25.6 ppm. The signal of triborylated carbon was not identified due to quadrupolar broadening from the boron nuclei.; HRMS (ESI) *m/z* calcd for $C_{26}H_{44}B_3NO_7$ [M+H$^+$]: 516.3475. Found: 516.3475.

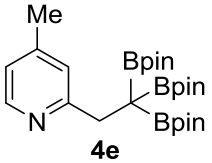
2-[2,2,2-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (4a):



tri-*B* (**4a**)

1a (*d* = 0.93 g/mL, 11.5 μL, 0.10 mmol) was used as a substrate. Reaction conditions: 2 equiv of pinB-Bpin and stirred for 1.5 h. The crude product was purified by open column chromatography (Silica gel had been heated at 110 °C before use. hexane-AcOEt with 3% Et_3N, 8:1 to 4:1) to afford **4a** as white solids (8.4 mg, 0.017 mmol, 17% yield). mp. 124-125 °C; IR ($CHCl_3$): 2977, 1620, 1480, 1451, 1343, 1274, 1142, 1067, 1015, 860 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.48 (d, J = 6.8 Hz, 1H), 7.73 (td, J = 6.8 and 1.5 Hz, 1H), 7.34 (d, J = 6.8 Hz, 1H), 7.23 (t, J = 6.8 Hz, 1H), 3.41 (s, 2H), 1.19 (s, 36H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.3, 141.9, 139.1, 123.0, 121.4, 81.4, 36.5, 25.4 ppm. The signal of triborylated carbon was not identified due to quadrupolar broadening from the boron nuclei.; HRMS (ESI) *m/z* calcd for $C_{25}H_{42}B_3NO_6$ [M+H$^+$]: 486.3370. Found: 486.3375.

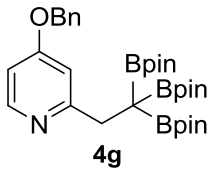
4-Methyl-2-[2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (4e):



4e

1e (12.1 mg, 0.10 mmol) was used as a substrate. Reaction conditions: stirred for 30 min. The crude product was purified by open column chromatography (Silica gel had been heated at 110 °C before use. hexane-AcOEt with 3% Et_3N, 8:1 to 4:1) to afford **4e** as white solids (37.5 mg, 0.075 mmol, 75% yield). mp. 138-139 °C; IR ($CHCl_3$): 2976, 2928, 1631, 1573, 1464, 1343, 1272, 1144, 1015, 860 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.32 (d, J = 5.7 Hz, 1H), 7.14 (s, 1H), 7.05 (d, J = 5.7 Hz, 1H), 3.35 (s, 2H), 2.39 (s, 3H), 1.19 (s, 36H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.0, 151.6, 140.6, 123.3, 122.8, 81.2, 36.1, 25.6, 21.3 ppm. The signal of triborylated carbon was not identified due to quadrupolar broadening from the boron nuclei.; HRMS (ESI) *m/z* calcd for $C_{26}H_{44}B_3NO_6$ [M+H$^+$]: 500.3526. Found: 500.3531.

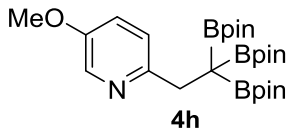
4-Benzyloxy-2-[2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (4g):



4g

1g (21.2 mg, 0.099 mmol) was used as a substrate. Reaction conditions: stirred for 10 min. The crude product was purified by open column chromatography (Silica gel had been heated at 110 ^{o}C before use. hexane-AcOEt with 3% Et_3N, 15:1 to 5:1) to afford **4g** as white solids (37.9 mg, 0.064 mmol, 64% yield). Small quantity of pinacol boron residues could not be removed. See copies of ^{1}H and ^{13}C NMR spectra (section (J)). mp. 46-47 ^{o}C; IR ($CHCl_3$): 2976, 2929, 1625, 1577, 1495, 1343, 1275, 1144, 1057, 861 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.29-8.28 (m, 1H), 7.41-7.34 (m, 5H), 6.81-6.80 (m, 2H), 5.15 (s, 2H), 3.33 (s, 2H), 1.19 (s, 36H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.3, 166.6, 142.1, 134.8, 128.8, 128.6, 127.4, 110.4, 107.0, 81.1, 70.5, 36.4, 25.6 ppm. The signal of triborylated carbon was not identified due to quadrupolar broadening from the boron nuclei.; HRMS (ESI) *m/z* calcd for $C_{32}H_{48}B_3NO_7$ [M+H$^+$]: 592.3788. Found: 592.3788.

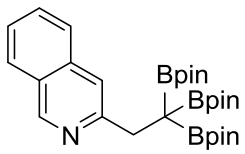
5-Methoxy-2-[2,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (4h):



4h

1h (13.6 mg, 0.099 mmol) was used as a substrate. Reaction conditions: stirred for 30 min. The crude product was purified by open column chromatography (Silica gel had been heated at 110 ^{o}C before use. hexane-AcOEt with 3% Et_3N, 8:1 to 3:1) to afford **4h** as white solids (39.4 mg, 0.077 mmol, 77% yield). Small quantity of pinacol boron residues could not be removed. See copies of ^{1}H and ^{13}C NMR spectra (section (J)). mp. 136-137 ^{o}C; IR ($CHCl_3$): 2978, 2929, 1644, 1605, 1466, 1343, 1282, 1142, 1016, 859 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 2.9 Hz, 1H), 7.28 (dd, *J* = 8.6 and 2.9 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 3.84 (s, 3H), 3.31 (s, 2H), 1.19 (s, 36H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.4, 154.5, 128.3, 125.7, 123.0, 81.5, 56.0, 35.4, 25.3 ppm. The signal of triborylated carbon was not identified due to quadrupolar broadening from the boron nuclei.; HRMS (ESI) *m/z* calcd for $C_{26}H_{44}B_3NO_7$ [M+H$^+$]: 516.3475. Found: 516.3476.

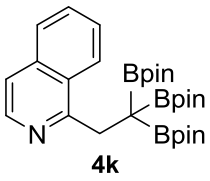
3-[2,2,2-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]isoquinoline (4j):



4j

1j (15.9 mg, 0.10 mmol) was used as a substrate. Reaction conditions: stirred for 30 min. The crude product was purified by open column chromatography (Silica gel had been heated at 110 ^{o}C before use. hexane-AcOEt with 3% Et_3N, 20:1 to 10:1) to afford **4j** as white solids (28.1 mg, 0.053 mmol, 52% yield). Small quantity of pinacol boron residues could not be removed. See copies of ^{1}H and ^{13}C NMR spectra (section (J)). mp. 106-107 ^{o}C; IR ($CHCl_3$): 2978, 2929, 1644, 1605, 1466, 1343, 1282, 1142, 1016, 859 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.15 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.63 (s, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 3.53 (s, 2H), 1.19 (s, 36H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.1, 146.3, 137.5, 131.4, 128.2, 126.7, 126.4, 126.2, 118.4, 81.7, 35.4, 25.2 ppm. The signal of triborylated carbon was not identified due to quadrupolar broadening from the boron nuclei.; HRMS (ESI) *m/z* calcd for $C_{29}H_{44}B_3NO_6$ [M+H$^+$]: 536.3526. Found: 536.3527.

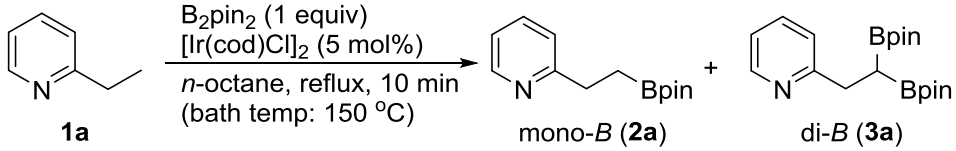
1-[2,2,2-Tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]isoquinoline (4k):



4k

1k (16.2 mg, 0.10 mmol) was used as a substrate. Reaction conditions: stirred for 1 h. The crude product was purified by open column chromatography (Silica gel had been heated at 110 °C before use. hexane-AcOEt with 3% Et_3N, 10:1 to 5:1) to afford **4k** as white solids (24.3 mg, 0.045 mmol, 44% yield). mp. 212-213 °C; IR ($CHCl_3$): 2976, 2929, 1637, 1577, 1469, 1434, 1343, 1284, 1143, 1015 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.36 (d, J = 6.6 Hz, 1H), 8.29 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.81 (td, J = 7.8 and 1.1 Hz, 1H), 7.68 (td, J = 7.8 and 1.1 Hz, 1H), 7.63 (d, J = 6.6 Hz, 1H), 3.86 (s, 2H), 1.23 (s, 36H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 136.7, 133.1, 132.6, 128.2, 127.04, 126.96, 126.1, 120.8, 81.2, 35.0, 25.7 ppm. The signal of triborylated carbon was not identified due to quadrupolar broadening from the boron nuclei.; HRMS (ESI) *m/z* calcd for $C_{29}H_{44}B_3NO_6$ [M+H$^+$]: 536.3526. Found: 536.3533.

(C-2) Using an Excess Amount (10 equiv) of 2-Ethylpyridiene



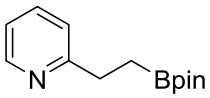
1a (10 equiv)

mono-*B* (**2a**) 131% yield

di-*B* (**3a**) 9% yield

To a 20 mL round-bottom flask combined with condenser were placed $[Ir(cod)Cl]_2$ (10.1 mg, 15 μmol, 5 mol%) and pinB-Bpin (76.2mg, 0.3 mmol, 1.0 equiv), then evacuated and backfilled with argon (x3). *n*-Octane (3 mL) and 2-ethylpyridiene (d = 0.93 g/mL, 346 μL, 3.0 mmol, 10 equiv) were added to this mixture. The resulting solution was stirred under reflux (bath temp: 150 °C) for 10 min. The reaction mixture was directly concentrated under high vacuum to afford the crude product. Yields of **2a** and **3a** were determined at this stage using 1,1,2,2-tetrachloroethane (δ = 5.9 ppm in $CDCl_3$, 2H) in ^1H NMR analysis as an internal standard (**2a**: 131%, **3a**: 9%). Monoborylated compound **2a** was too unstable to purify by silica gel column chromatography. However, it was purified by bulb-to-bulb distillation (126%), but it still contained small amount of pinacol boron residues. See copies of ^1H and ^{13}C NMR spectra (section (J)). Diborylated compound **3a** was isolated after flash column chromatography (Silica gel, hexane-AcOEt). Total yield exceeding 100% is probably because borylation is also promoted by HBpin, which should be generated after one catalytic cycle. When HBpin was used instead of B_2pin_2, monoborylation only proceeded with low conversion even after 4 h (38%). These results suggest that HBpin also works as a borylating reagent but is much less reactive than B_2pin_2.

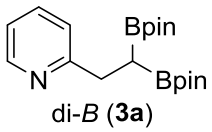
2-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (2a):



mono-*B* (**2a**)

IR (neat): 2978, 2933, 1620, 1475, 1457, 1372, 1333, 1148, 984, 850 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.52 (d, J = 5.5 Hz, 1H), 7.65 (t, J = 7.6 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.16 (dd, J = 7.6 and 5.5 Hz, 1H), 2.97 (t, J = 7.7 Hz, 2H), 1.23 (s, 12H), 1.06 (t, J = 7.7 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.6, 146.1, 137.7, 122.7, 121.3, 81.6, 31.8, 25.2 ppm The signal of borylated carbon was not identified.; HRMS (ESI) *m/z* calcd for $C_{13}H_{20}BNO_2$ [M+H$^+$]: 234.1665. Found: 234.1661.

2-[2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]pyridine (3a):

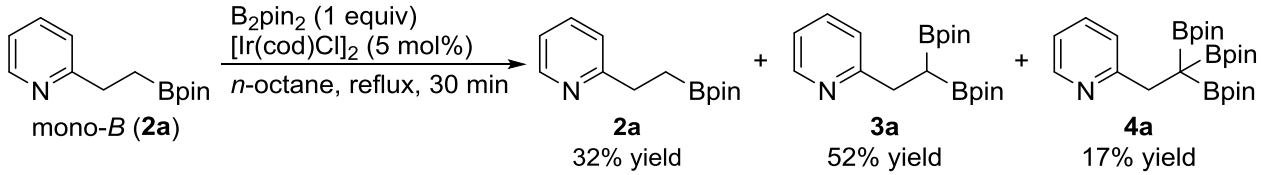


di-*B* (**3a**)

White solids. mp. 69-70 °C; IR ($CHCl_3$): 2978, 1619, 1485, 1450, 1363, 1304, 1147, 1077, 970, 854 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.55 (d, J = 5.2 Hz, 1H), 7.73 (td, J = 7.8 and 1.3 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.26-7.24 (m, 1H), 3.18 (d, J = 8.2 Hz, 2H), 1.25 (s, 12H), 1.24 (s, 12H), 0.92 (t, J = 8.2 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.8, 143.4, 139.0, 123.0, 121.8, 81.5, 33.7, 25.7, 25.4 ppm. The signal of diborylated carbon was not identified.; HRMS (ESI) *m*/*z* calcd for $C_{19}H_{31}B_2NO_4$ [M+Na^+]: 382.2337. Found: 382.2330.

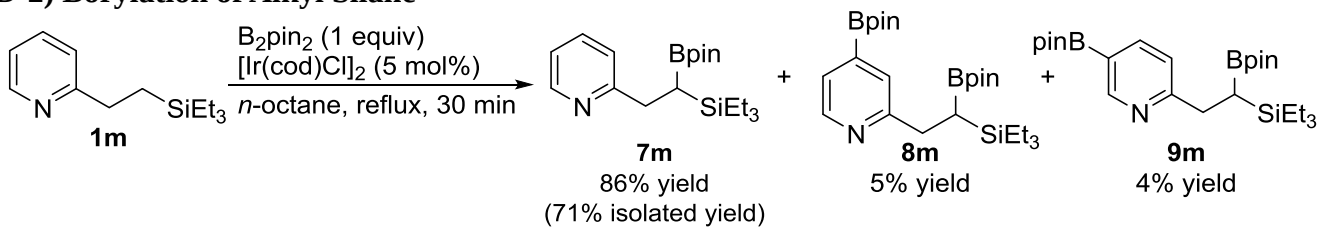
(D) Borylation of Secondary C(sp^3)-H Bonds

(D-1) Borylation of Alkyl Boronate Ester



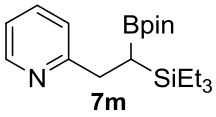
To a 10 mL test tube combined with condenser were placed $[Ir(cod)Cl]_2$ (3.4 mg, 5 μmol, 5 mol%) and pinB-Bpin (25.4 mg, 0.1 mmol, 1.0 equiv), then evacuated and backfilled with argon (x3). *n*-Octane (1 mL) and 2-ethylpyridiene (d = 0.93 g/mL, 115 μL, 1.0 mmol, 10 equiv) were added to this mixture. The resulting solution was stirred under reflux (bath temp: 150 °C). After 10 min, the reaction mixture was concentrated under high vacuum for 2 h. To this residue were added $[Ir(cod)Cl]_2$ (4.6 mg, 5 μmol, 5 mol%) and pinB-Bpin (34.5 mg, 0.1 mmol, 1.0 equiv), then evacuated and backfilled with argon (x3). *n*-Octane (1.4 mL) was added to this mixture. The resulting solution was stirred under reflux (bath temp: 150 °C) for 30 min. The reaction mixture was directly concentrated under high vacuum to afford the crude product. Yields of **2a**, **3a**, and **4a** were determined at this stage using 1,1,2,2-tetrachloroethane in ^1H NMR analysis as an internal standard (32%, 52%, and 17% yields, respectively).

(D-2) Borylation of Alkyl Silane



To a 10 mL test tube combined with condenser were placed 2-[2-(triethylsilyl)ethyl]pyridine (**1m**) (21.9 mg, 0.099 mmol, 1.0 equiv), pinB-Bpin (26.2 mg, 0.10 mmol, 1.0 equiv), and $[Ir(cod)Cl]_2$ (3.4 mg, 5 μmol, 5 mol%), then evacuated and backfilled with argon (x3). *n*-Octane (1 mL) was added to this mixture, which was stirred under reflux (bath temp: 150 °C) for 30 min. The reaction mixture was directly concentrated under high vacuum to afford the crude product. Yields of **7m**, **8m**, and **9m** were determined at this stage using 1,1,2,2-tetrachloroethane in ^1H NMR analysis as an internal standard (86%, 5%, and 4% yields, respectively). The crude product was then purified by flash column chromatography (Silica gel, hexane-Et_2O 10:1 to 5:1) to afford **7m** as colorless oil (24.5 mg, 0.071 mmol, 71% yield).

2-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(triethylsilyl)ethyl]pyridine (7m):

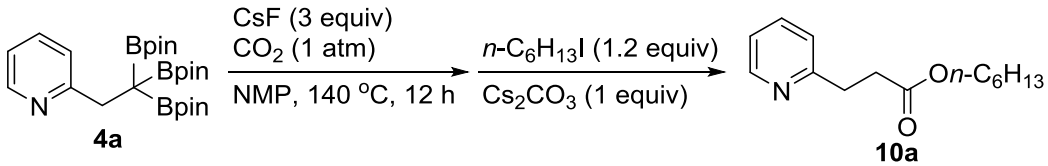


7m

IR (neat): 2952, 2875, 1590, 1472, 1350, 1306, 1246, 1146, 1008, 734 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.47 (d, J = 5.6 Hz, 1H), 7.51 (td, J = 7.6 and 1.7 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.02 (dd, J = 7.6 and 5.6 Hz, 1H), 3.03 (dd, J = 15.1 and 12.6 Hz, 1H), 2.87 (dd, J = 15.1 and 3.7 Hz, 1H), 1.15 (s, 6H), 1.08 (s, 6H), 1.03-0.97 (m, 10H), 0.64 (q, J = 7.8 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.9, 148.6, 135.7, 122.3, 120.5, 82.5, 33.9, 25.0, 24.7, 7.6, 3.5 ppm; HRMS (ESI) *m/z* calcd for $C_{19}H_{34}BNO_2Si$ [M+H^+]: 348.2530. Found: 348.2529.

(E) Carboxylation of Borylated Compounds

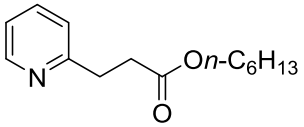
(E-1) Carboxylation of Triborylated Compounds



4a **10a**
54% yield

CsF (45.6 mg, 0.30 mmol, 3.0 equiv) was placed on the bottom of a test tube and was heated under vacuum for 10 min to be completely dry, to which **4a** (48.5 mg, 0.10 mmol, 1.0 equiv) was added, then evacuated and backfilled with CO_2 (x3). To this mixture was added NMP (1.5 mL), which was stirred at 140 °C under 1 atm of CO_2 (balloon). After 12 h, the reaction mixture was cooled to room temperature, then treated with Cs_2CO_3 (32.6 mg, 0.10 mmol, 1.0 equiv) and *n*-$C_6H_{13}I$ (d = 1.437 g/mL, 17.7 μL, 0.12 mmol, 1.2 equiv) and stirred at 50 °C for 30 min. Water (5 mL) and brine (5 mL) were added and the mixture was filtered through a Celite pad. The filtrate was extracted with ethyl acetate (10 mL x3). The combined organic layer was washed with brine (x1), and then dried over with Na_2SO_4. After removal of solvent under reduced pressure, the crude product was then purified by flash column chromatography (Silica gel, hexane-AcOEt 8:1 to 3:1) to afford **10a** as colorless oil (12.8 mg, 0.054 mmol, 54% yield).
Carboxylation of diborylated compound **3a** also gave a small amount of **10a** with this procedure (0.8 mg, 0.0034 mmol, 4% yield).

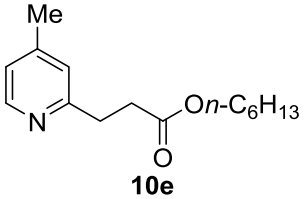
Hexyl 3-(pyridin-2-yl)propanoate (10a):



10a

IR (neat): 2956, 2930, 2859, 1735, 1593, 1570, 1474, 1434, 1169, 751 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.51 (d, J = 5.0 Hz, 1H), 7.58 (td, J = 7.6 and 1.7 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.11 (dd, J = 7.6 and 5.0 Hz, 1H), 4.05 (t, J = 6.9 Hz, 2H), 3.11 (t, J = 7.4 Hz, 2H), 2.79 (t, J = 7.4 Hz, 2H), 1.60-1.55 (m, 2H), 1.32-1.23 (m, 6H), 0.87 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.1, 160.1, 149.3, 136.3, 122.9, 121.3, 64.6, 33.5, 32.9, 31.4, 28.5, 25.5, 22.5, 14.0 ppm; HRMS (ESI) *m/z* calcd for $C_{14}H_{21}NO_2$ [M+Na^+]: 258.1470. Found: 258.1464.

Hexyl 3-(4-methylpyridin-2-yl)propanoate (10e):

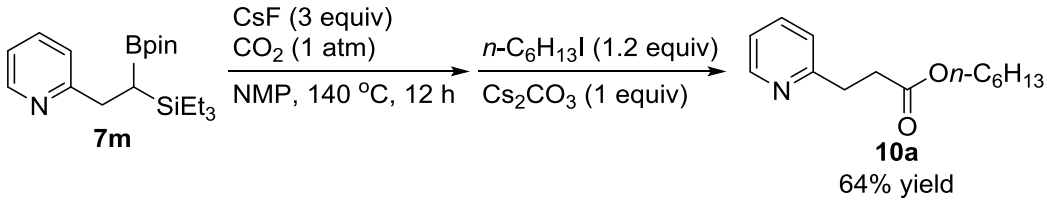


10e

4e (49.9 mg, 0.10 mmol) was used as a substrate. The crude product was purified by flash column chromatography (Silica gel, hexane-AcOEt 8:1 to 4:1) to afford **10e** as colorless oil (14.4 mg, 0.058 mmol, 58% yield). IR (neat): 2956, 2930, 2859, 1736, 1606, 1562, 1451, 1361, 1169, 822 cm^{-1}; ^1H NMR (500

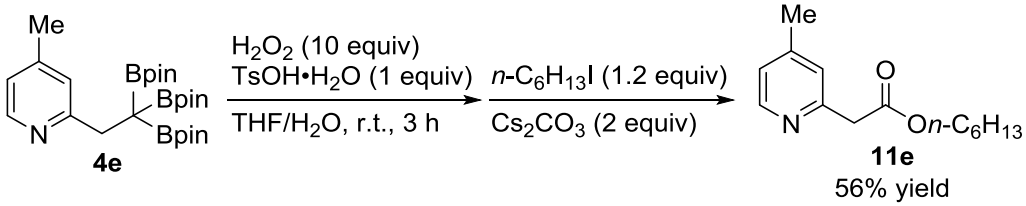
MHz, $CDCl_3$): δ = 8.36 (d, J = 4.9 Hz, 1H), 7.00 (s, 1H), 6.93 (d, J = 4.9 Hz, 1H), 4.05 (t, J = 6.9 Hz, 2H), 3.05 (t, J = 7.4 Hz, 2H), 2.78 (t, J = 7.4 Hz, 2H), 2.30 (s, 3H), 1.60-1.54 (m, 2H), 1.32-1.23 (m, 6H), 0.87 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.2, 159.8, 149.0, 147.3, 123.8, 122.3, 64.6, 33.5, 32.8, 31.4, 28.5, 25.5, 22.5, 20.9, 14.0 ppm; HRMS (ESI) *m/z* calcd for $C_{15}H_{23}NO_2$ [M+Na$^+$]: 272.1627. Found: 272.1620.

(E-2) Carboxylation of Compound 7m



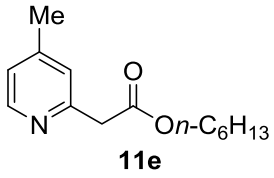
To a 10 mL test tube was placed compound **7m** (34.7 mg, 0.10 mmol, 1.0 equiv), then evacuated and backfilled with CO_2 (x3). To this test tube were added NMP (1.5 mL) and flame-dried CsF (45.6 mg, 0.30 mmol, 3 equiv), which was stirred at 140 ^{o}C under 1 atm of CO_2 (balloon). After 12 h, the reaction mixture was cooled to room temperature, then treated with Cs_2CO_3 (32.6 mg, 0.10 mmol, 1.0 equiv) and *n*-$C_6H_{13}I$ (d = 1.437 g/mL, 17.7 μL, 0.12 mmol, 1.2 equiv) and stirred at 50 ^{o}C for 30 min. Water (5 mL) and brine (5 mL) were added and the mixture was filtered through a Celite pad. The filtrate was extracted with ethyl acetate (10 mL x3). The combined organic layer was washed with brine (x1), and then dried over with Na_2SO_4. After removal of solvent under reduced pressure, the crude product was then purified by flash column chromatography (Silica gel, hexane-AcOEt 8:1 to 3:1) to afford **10a** as colorless oil (15.0 mg, 0.064 mmol, 64% yield).

(F) Oxidation of Triborylated Compounds



To a 10 mL round-bottom flask was placed substrate **4e** (49.9 mg, 0.10 mmol, 1.0 equiv) and TsOH·H_2O (19.0 mg, 0.10 mmol, 1.0 equiv), then evacuated and backfilled with argon (x3). THF (1 mL) and 30% H_2O_2 aq. (78.2 μL, 1.0 mmol, 10 equiv) were added to this mixture, which was stirred at room temperature for 3 h. The reaction mixture was concentrated under high vacuum to remove volatile materials such as THF and H_2O. To this residue were added DMF (1.5 mL), *n*-$C_6H_{13}I$ (d = 1.437 g/mL, 17.7 μL, 0.12 mmol, 1.2 equiv), and Cs_2CO_3 (65.2 mg, 0.20 mmol, 2.0 equiv), and then stirred at 50 ^{o}C for 30 min. Water (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL x3). The combined organic layer was washed with brine (x1), and then dried over with Na_2SO_4. After removal of solvent under reduced pressure, the crude product was then purified by flash column chromatography (Silica gel, CH_2Cl_2-AcOEt 20:1 to 5:1) to afford **11e** as colorless oil (13.1 mg, 0.056 mmol, 56% yield).

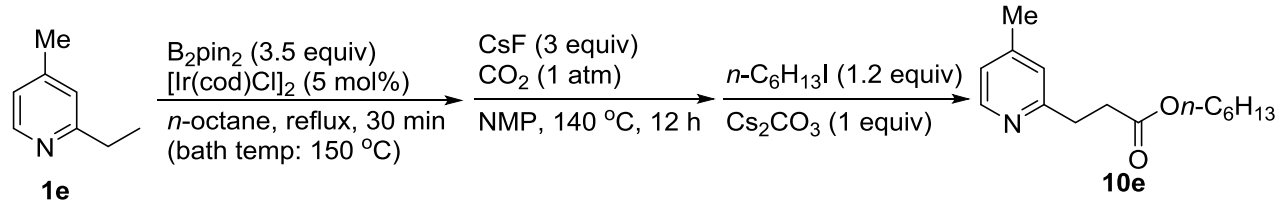
Hexyl 2-(4-methylpyridin-2-yl)acetate (11e):



11e

IR (neat): 2956, 2930, 2859, 1738, 1606, 1562, 1458, 1266, 1155, 996 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 8.40 (d, J = 5.2 Hz, 1H), 7.11 (s, 1H), 7.00 (d, J = 5.2 Hz, 1H), 4.11 (t, J = 6.9 Hz, 2H), 3.79 (s, 2H), 2.33 (s, 3H), 1.64-1.58 (m, 2H), 1.33-1.22 (m, 6H), 0.87 (t, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.9, 154.3, 149.2, 147.7, 124.7, 123.1, 65.1, 43.9, 31.3, 28.5, 25.5, 22.5, 21.0, 14.0 ppm; HRMS (ESI) *m/z* calcd for $C_{14}H_{21}NO_2$ [M+Na^+]: 258.1470. Found: 258.1464.

(G) Carboxylation of Unactivated C(sp^3)-H Bonds (Sequential Procedure)



1e **10e**
40% yield

To a 10 mL test tube combined with condenser were placed a substrate **1e** (12.1 mg, 0.10 mmol, 1.0 equiv), pinB-Bpin (88.9 mg, 0.35 mmol, 3.5 equiv), $[Ir(cod)Cl]_2$ (3.4 mg, 5 μmol, 5 mol%), and then evacuated and backfilled with argon (x3). *n*-Octane (1 mL) was added to this mixture, which was stirred under reflux (bath temp: 150 °C) for 30 min. The reaction mixture was filtered through a Celite pad. The filtrate was concentrated under high vacuum, followed by the introduction of CO_2 (balloon). To the residue were added NMP (1.5 mL) and flame-dried CsF (45.6 mg, 0.30 mmol, 3 equiv). The mixture was heated at 140 °C under 1 atm of CO_2 for 12 h. After cooling to room temperature, the resulting residue was treated with Cs_2CO_3 (32.6 mg, 0.10 mmol, 1.0 equiv) and *n*-$C_6H_{13}I$ (*d* = 1.437 g/mL, 17.7 μL, 0.12 mmol, 1.2 equiv), and then stirred at 50 °C for 30 min. Water (5 mL) and brine (5 mL) were added and the mixture was filtered through a Celite pad. The filtrate was extracted with ethyl acetate (10 mL x3). The combined organic layer was washed with brine (x1), and then dried over with Na_2SO_4. After removal of solvent under reduced pressure, the crude product was then purified by flash column chromatography (Silica gel, hexane-AcOEt 8:1 to 4:1) to afford **10e** as colorless oil (10.0 mg, 0.040 mmol, 40% yield).

(H) Preparation of Single Crystals

Dry hexane was added to triborylated compound **4a** (entry 2, Table 1) until it was completely dissolved. After 2 days, colorless block prisms appeared and were washed with hexane several times. It was then dried under reduced pressure. One of the big crystals was cut to be an appropriate size for mounting (0.175 x 0.130 x 0.127 mm). X-ray crystallographic analysis was carried out by the Rigaku Corporation (See section (I)).

Experimental

Data Collection

A colorless block crystal of $C_{25}H_{42}B_3NO_6$ having approximate dimensions of 0.175 x 0.130 x 0.127 mm was mounted in a loop. All measurements were made on a Rigaku R-AXIS RAPID II diffractometer using multi-layer mirror monochromated Cu-Kα radiation.

The crystal-to-detector distance was 127.00 mm.

Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with dimensions:

a = 17.5820(3) Å
b = 10.16276(18) Å β = 107.583(8)^o
c = 16.1577(3) Å
V = 2752.20(14) Å^3

For Z = 4 and F.W. = 485.04, the calculated density is 1.171 g/cm^3. The reflection conditions of:

h0l: l = 2n
0k0: k = 2n

uniquely determine the space group to be:

$P2_1/c$ (#14)

The data were collected at a temperature of -180 $\pm$ 1^{o}C to a maximum 2θ value of 136.4^o. A total of 252 oscillation images were collected. A sweep of data was done using ω scans from 80.0 to 260.0^o in 5.0^o step, at χ=54.0^o and ϕ = 0.0^o. The exposure rate was 30.0 [sec./^{o}]. A second sweep was performed using ω scans from 80.0 to 260.0^o in 5.0^o step, at χ=54.0^o and ϕ = 90.0^o. The exposure rate was 30.0 [sec./^{o}].

Another sweep was performed using ω scans from 80.0 to 260.0° in 5.0° step, at χ=54.0° and ϕ = 180.0°. The exposure rate was 30.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 5.0° step, at χ=54.0° and ϕ = 270.0°. The exposure rate was 30.0 [sec./°]. Another sweep was performed using ω scans from 80.0 to 260.0° in 5.0° step, at χ=0.0° and ϕ = 0.0°. The exposure rate was 30.0 [sec./°]. The crystal-to-detector distance was 127.00 mm. Readout was performed in the 0.100 mm pixel mode.

Data Reduction

Of the 44334 reflections were collected, where 5015 were unique (R_{int} = 0.0248); equivalent reflections were merged.

The linear absorption coefficient, μ, for Cu-Kα radiation is 6.404 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.796 to 0.922. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[1] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[2] on F^2 was based on 5015 observed reflections and 328 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.0367$$

$$wR2 = [\Sigma \, (w \, (Fo^2 - Fc^2)^2) / \Sigma \, w(Fo^2)^2]^{1/2} = 0.0975$$

The standard deviation of an observation of unit weight[3] was 1.07. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.34 and -0.26 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[4]. Anomalous

dispersion effects were included in Fcalc[5]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley[6]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[7]. All calculations were performed using the CrystalStructure[8] crystallographic software package except for refinement, which was performed using SHELXL-97[9].

References

(1) SIR2008: M.C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G.L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi, R. Spagna (2007)

(2) Least Squares function minimized: (SHELXL97)

$\Sigma w(F_o^2-F_c^2)^2$ where w = Least Squares weights.

(3) Standard deviation of an observation of unit weight:

$[\Sigma w(F_o^2-F_c^2)^2/(N_o-N_v)]^{1/2}$

where: N_o = number of observations
N_v = number of variables

(4) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(5) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(6) Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(7) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(8) CrystalStructure 4.0: Crystal Structure Analysis Package, Rigaku Corporation (2000-2011). Tokyo 196-8666, Japan.

(9) SHELX97: Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{25}H_{42}B_3NO_6$
Formula Weight	485.04
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.175 X 0.130 X 0.127 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 17.5820(3) Å b = 10.16276(18) Å c = 16.1577(3) Å β = 107.583(8) ^{o} V = 2752.20(14) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.171 g/cm^3
F_{000}	1048.00
μ(CuKα)	6.404 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID II
Radiation	CuKα (λ = 1.54187 Å) multi-layer mirror monochromated
Voltage, Current	40kV, 30mA
Temperature	-180.0^{o}C
Detector Aperture	460 x 256 mm
Data Images	252 exposures
ω oscillation Range (χ=54.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=90.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=180.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
ω oscillation Range (χ=54.0, ϕ=270.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
ω oscillation Range (χ=0.0, ϕ=0.0)	80.0 - 260.0^{o}
Exposure Rate	30.0 sec./^{o}
Detector Position	127.00 mm
Pixel Size	0.100 mm

$2\theta_{max}$	136.4°
No. of Reflections Measured	Total: 44334 Unique: 5015 (R_{int} = 0.0248)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.796 - 0.922)

C. Structure Solution and Refinement

Structure Solution	Direct Methods
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w $(Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\sigma^2(Fo^2) + (0.0513 \cdot P)^2 + 1.0259 \cdot P]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2\theta_{max}$ cutoff	136.4^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5015
No. Variables	328
Reflection/Parameter Ratio	15.29
Residuals: R1 (I>2.00σ(I))	0.0367
Residuals: R (All reflections)	0.0379
Residuals: wR2 (All reflections)	0.0975
Goodness of Fit Indicator	1.067
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.34 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.26 $e^-/Å^3$

Table 1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
O1	0.81515(5)	1.12378(8)	0.63235(5)	1.658(15)
O2	0.87667(5)	1.01316(8)	0.54679(5)	1.528(14)
O3	0.70963(5)	1.13750(8)	0.40115(5)	1.625(15)
O4	0.79075(5)	0.77408(8)	0.45584(5)	1.689(15)
O5	0.63176(5)	0.94865(8)	0.37006(5)	1.617(15)
O6	0.70021(5)	0.70330(8)	0.52208(5)	1.684(15)
N7	0.61169(6)	1.11000(9)	0.48290(6)	1.541(17)
C8	0.67546(6)	0.95688(11)	0.59158(7)	1.539(19)
C9	0.55309(7)	1.09502(12)	0.59659(8)	1.79(2)
C10	0.61056(7)	1.05690(11)	0.55828(7)	1.544(19)
C11	0.72730(6)	0.95382(11)	0.52916(7)	1.441(19)
C12	1.01655(7)	1.06562(13)	0.61673(8)	1.97(2)
C13	0.56100(7)	1.20764(12)	0.44578(8)	1.87(2)
C14	0.78985(7)	1.03201(13)	0.32414(8)	1.87(2)
C15	0.89994(7)	1.15050(12)	0.66813(7)	1.581(19)
C16	0.93150(7)	1.11685(11)	0.59042(7)	1.548(19)
C17	0.63816(7)	0.99514(12)	0.28835(7)	1.81(2)
C18	0.70950(7)	1.09587(12)	0.31589(7)	1.70(2)
C19	0.80084(7)	0.63248(12)	0.46523(8)	1.87(2)
C20	0.49871(7)	1.19113(12)	0.55754(8)	2.05(2)
C21	0.69934(8)	1.21751(13)	0.25845(8)	2.19(2)
C22	0.91227(8)	1.29185(12)	0.69861(9)	2.16(2)
C23	0.72073(7)	0.58828(12)	0.47914(8)	1.75(2)
C24	0.72590(8)	0.46909(12)	0.53720(9)	2.19(2)
C25	0.50394(7)	1.25081(12)	0.48169(8)	2.11(2)
C26	0.93136(8)	1.05785(13)	0.74501(8)	2.18(2)
C27	0.65352(8)	0.87645(13)	0.23774(8)	2.28(2)
C28	0.92211(8)	1.22975(12)	0.52580(8)	2.03(2)
C29	0.65380(8)	0.56886(13)	0.39452(8)	2.37(2)
C30	0.87313(7)	0.61077(13)	0.54480(9)	2.41(2)
C31	0.55873(7)	1.05717(14)	0.23707(8)	2.40(2)
C32	0.81686(9)	0.57714(14)	0.38507(9)	2.72(3)
B33	0.67458(8)	1.03591(13)	0.43933(8)	1.50(2)
B34	0.80703(8)	1.03034(13)	0.56805(8)	1.44(2)
B35	0.73923(7)	0.81064(13)	0.50094(8)	1.48(2)

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}
H8A	0.65236	0.87080	0.59394	1.847
H8B	0.70803	0.98036	0.64966	1.847
H9	0.55133	1.05608	0.64806	2.144
H12A	1.01884	0.98190	0.64490	2.367
H12B	1.05093	1.12679	0.65593	2.367
H12C	1.03369	1.05578	0.56601	2.367
H13	0.56470	1.24645	0.39501	2.240
H14A	0.83182	1.09389	0.34887	2.244
H14B	0.79181	1.00579	0.26774	2.244
H14C	0.79655	0.95610	0.36102	2.244
H20	0.45898	1.21590	0.58151	2.459
H21A	0.74478	1.27405	0.27998	2.627
H21B	0.65192	1.26378	0.25908	2.627
H21C	0.69492	1.19134	0.20009	2.627
H22A	0.89195	1.30383	0.74697	2.593
H22B	0.88448	1.34926	0.65212	2.593
H22C	0.96820	1.31217	0.71608	2.593
H24A	0.76397	0.48570	0.59286	2.630
H24B	0.74248	0.39387	0.51110	2.630
H24C	0.67452	0.45233	0.54437	2.630
H25	0.46940	1.31864	0.45588	2.532
H26A	0.92330	0.96838	0.72524	2.613
H26B	0.90329	1.07336	0.78665	2.613
H26C	0.98730	1.07341	0.77161	2.613
H27A	0.60833	0.81849	0.22477	2.730
H27B	0.70011	0.83053	0.27203	2.730
H27C	0.66177	0.90570	0.18461	2.730
H28A	0.93471	1.19917	0.47527	2.434
H28B	0.95764	1.30003	0.55226	2.434
H28C	0.86809	1.26107	0.50924	2.434
H29A	0.65021	0.64493	0.35831	2.848
H29B	0.60419	0.55683	0.40692	2.848
H29C	0.66482	0.49259	0.36500	2.848
H30A	0.86115	0.64109	0.59575	2.891
H30B	0.91788	0.65888	0.53806	2.891
H30C	0.88582	0.51870	0.55063	2.891
H31A	0.51647	0.99477	0.23142	2.884

Table 2. Atomic coordinates and B_{iso} involving hydrogens/B_{eq} (continued)

atom	x	y	z	B_{eq}
H31B	0.56080	1.08191	0.18044	2.884
H31C	0.54903	1.13381	0.26712	2.884
H32A	0.86703	0.60980	0.38159	3.269
H32B	0.77502	0.60370	0.33434	3.269
H32C	0.81867	0.48283	0.38848	3.269

Table 3. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	0.0156(4)	0.0229(4)	0.0250(4)	-0.0005(3)	0.0069(3)	-0.0044(3)
O2	0.0167(4)	0.0201(4)	0.0214(4)	-0.0004(3)	0.0059(3)	-0.0030(3)
O3	0.0193(4)	0.0232(4)	0.0198(4)	-0.0006(3)	0.0066(3)	0.0003(3)
O4	0.0233(4)	0.0179(4)	0.0252(4)	0.0020(3)	0.0106(3)	0.0004(3)
O5	0.0199(4)	0.0240(4)	0.0175(4)	-0.0014(3)	0.0056(3)	0.0003(3)
O6	0.0199(4)	0.0195(4)	0.0257(4)	-0.0002(3)	0.0087(3)	-0.0027(3)
N7	0.0160(5)	0.0197(5)	0.0225(5)	-0.0012(4)	0.0053(4)	-0.0027(4)
C8	0.0167(5)	0.0223(6)	0.0197(5)	-0.0011(4)	0.0057(4)	-0.0009(4)
C9	0.0192(6)	0.0251(6)	0.0248(6)	-0.0057(5)	0.0084(5)	-0.0075(5)
C10	0.0177(5)	0.0191(6)	0.0214(6)	-0.0053(4)	0.0051(4)	-0.0056(4)
C11	0.0164(5)	0.0204(6)	0.0184(5)	0.0009(4)	0.0059(4)	0.0001(4)
C12	0.0170(6)	0.0288(6)	0.0288(6)	0.0009(5)	0.0064(5)	-0.0032(5)
C13	0.0204(6)	0.0222(6)	0.0271(6)	0.0009(5)	0.0053(5)	-0.0004(5)
C14	0.0206(6)	0.0293(6)	0.0222(6)	0.0011(5)	0.0082(5)	0.0031(5)
C15	0.0147(5)	0.0226(6)	0.0223(6)	-0.0011(4)	0.0048(4)	-0.0023(5)
C16	0.0172(6)	0.0191(6)	0.0224(6)	-0.0010(4)	0.0058(5)	-0.0024(5)
C17	0.0219(6)	0.0282(6)	0.0183(6)	-0.0000(5)	0.0055(5)	0.0022(5)
C18	0.0202(6)	0.0257(6)	0.0188(6)	0.0006(5)	0.0061(5)	0.0017(5)
C19	0.0244(6)	0.0177(6)	0.0312(6)	0.0019(5)	0.0116(5)	-0.0001(5)
C20	0.0181(6)	0.0268(6)	0.0344(7)	-0.0032(5)	0.0103(5)	-0.0126(5)
C21	0.0287(7)	0.0291(7)	0.0257(6)	0.0023(5)	0.0086(5)	0.0060(5)
C22	0.0239(6)	0.0266(7)	0.0326(7)	-0.0032(5)	0.0101(5)	-0.0091(5)
C23	0.0201(6)	0.0200(6)	0.0269(6)	0.0010(5)	0.0079(5)	-0.0035(5)
C24	0.0257(6)	0.0227(6)	0.0368(7)	-0.0015(5)	0.0124(5)	0.0004(5)
C25	0.0193(6)	0.0228(6)	0.0355(7)	0.0029(5)	0.0045(5)	-0.0047(5)
C26	0.0242(6)	0.0339(7)	0.0235(6)	-0.0007(5)	0.0055(5)	0.0014(5)
C27	0.0327(7)	0.0331(7)	0.0214(6)	-0.0044(5)	0.0094(5)	-0.0031(5)
C28	0.0248(6)	0.0256(6)	0.0281(6)	-0.0009(5)	0.0100(5)	0.0028(5)
C29	0.0282(7)	0.0274(7)	0.0321(7)	-0.0006(5)	0.0055(5)	-0.0069(5)
C30	0.0196(6)	0.0253(6)	0.0450(8)	0.0022(5)	0.0073(6)	0.0049(6)
C31	0.0217(6)	0.0406(8)	0.0252(6)	-0.0005(5)	0.0013(5)	0.0056(6)
C32	0.0410(8)	0.0267(7)	0.0445(8)	0.0001(6)	0.0261(7)	-0.0068(6)
B33	0.0164(6)	0.0206(6)	0.0204(6)	0.0018(5)	0.0059(5)	-0.0004(5)
B34	0.0184(6)	0.0176(6)	0.0182(6)	0.0030(5)	0.0049(5)	0.0026(5)
B35	0.0150(6)	0.0222(7)	0.0172(6)	0.0010(5)	0.0019(5)	0.0005(5)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2$

$$+ 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table 4. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
O1	C15	1.4525(14)	O1	B34	1.3827(15)
O2	C16	1.4581(13)	O2	B34	1.3791(18)
O3	C18	1.4404(15)	O3	B33	1.4339(17)
O4	C19	1.4523(15)	O4	B35	1.3742(17)
O5	C17	1.4383(15)	O5	B33	1.4480(14)
O6	C23	1.4592(16)	O6	B35	1.3852(16)
N7	C10	1.3378(16)	N7	C13	1.3475(15)
N7	B33	1.6600(19)	C8	C10	1.5013(15)
C8	C11	1.5506(18)	C9	C10	1.3900(19)
C9	C20	1.3791(16)	C11	B33	1.6879(16)
C11	B34	1.5596(16)	C11	B35	1.5579(18)
C12	C16	1.5178(17)	C13	C25	1.374(2)
C14	C18	1.5235(18)	C15	C16	1.5564(18)
C15	C22	1.5128(17)	C15	C26	1.5232(17)
C16	C28	1.5263(17)	C17	C18	1.5754(17)
C17	C27	1.5264(19)	C17	C31	1.5281(16)
C18	C21	1.5236(18)	C19	C23	1.5580(19)
C19	C30	1.5264(16)	C19	C32	1.514(2)
C20	C25	1.3951(19)	C23	C24	1.5179(18)
C23	C29	1.5235(16)			

Table 5. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
C8	H8A	0.970	C8	H8B	0.970
C9	H9	0.930	C12	H12A	0.960
C12	H12B	0.960	C12	H12C	0.960
C13	H13	0.930	C14	H14A	0.960
C14	H14B	0.960	C14	H14C	0.960
C20	H20	0.930	C21	H21A	0.960
C21	H21B	0.960	C21	H21C	0.960
C22	H22A	0.960	C22	H22B	0.960
C22	H22C	0.960	C24	H24A	0.960
C24	H24B	0.960	C24	H24C	0.960
C25	H25	0.930	C26	H26A	0.960
C26	H26B	0.960	C26	H26C	0.960
C27	H27A	0.960	C27	H27B	0.960
C27	H27C	0.960	C28	H28A	0.960
C28	H28B	0.960	C28	H28C	0.960
C29	H29A	0.960	C29	H29B	0.960
C29	H29C	0.960	C30	H30A	0.960
C30	H30B	0.960	C30	H30C	0.960
C31	H31A	0.960	C31	H31B	0.960
C31	H31C	0.960	C32	H32A	0.960
C32	H32B	0.960	C32	H32C	0.960

Table 6. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C15	O1	B34	106.74(10)	C16	O2	B34	107.17(9)
C18	O3	B33	108.86(9)	C19	O4	B35	106.97(10)
C17	O5	B33	109.98(9)	C23	O6	B35	107.55(10)
C10	N7	C13	120.83(12)	C10	N7	B33	113.46(9)
C13	N7	B33	125.52(10)	C10	C8	C11	108.24(9)
C10	C9	C20	119.37(12)	N7	C10	C8	112.38(11)
N7	C10	C9	120.38(10)	C8	C10	C9	127.24(11)
C8	C11	B33	105.75(9)	C8	C11	B34	111.18(9)
C8	C11	B35	111.51(10)	B33	C11	B34	107.05(9)
B33	C11	B35	107.31(9)	B34	C11	B35	113.55(9)
N7	C13	C25	121.09(12)	O1	C15	C16	102.18(8)
O1	C15	C22	109.63(10)	O1	C15	C26	106.55(10)
C16	C15	C22	114.85(11)	C16	C15	C26	113.09(10)
C22	C15	C26	109.91(9)	O2	C16	C12	109.82(9)
O2	C16	C15	101.77(10)	O2	C16	C28	107.06(8)
C12	C16	C15	114.24(9)	C12	C16	C28	110.08(11)
C15	C16	C28	113.29(10)	O5	C17	C18	103.33(8)
O5	C17	C27	107.92(10)	O5	C17	C31	108.73(11)
C18	C17	C27	114.22(11)	C18	C17	C31	113.85(10)
C27	C17	C31	108.43(9)	O3	C18	C14	107.93(8)
O3	C18	C17	103.42(10)	O3	C18	C21	108.08(10)
C14	C18	C17	112.71(10)	C14	C18	C21	109.51(11)
C17	C18	C21	114.73(9)	O4	C19	C23	102.33(10)
O4	C19	C30	106.00(9)	O4	C19	C32	109.09(11)
C23	C19	C30	113.32(11)	C23	C19	C32	115.22(10)
C30	C19	C32	110.12(11)	C9	C20	C25	119.29(13)
O6	C23	C19	101.64(9)	O6	C23	C24	108.82(11)
O6	C23	C29	107.19(9)	C19	C23	C24	115.55(10)
C19	C23	C29	113.25(11)	C24	C23	C29	109.70(10)
C13	C25	C20	118.85(11)	O3	B33	O5	107.40(10)
O3	B33	N7	106.49(9)	O3	B33	C11	122.01(9)
O5	B33	N7	110.38(10)	O5	B33	C11	112.59(9)
N7	B33	C11	97.04(9)	O1	B34	O2	112.10(10)
O1	B34	C11	121.42(12)	O2	B34	C11	126.45(11)
O4	B35	O6	111.88(11)	O4	B35	C11	125.19(11)
O6	B35	C11	122.88(11)				

Table 7. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C10	C8	H8A	110.0	C10	C8	H8B	110.0
C11	C8	H8A	110.0	C11	C8	H8B	110.1
H8A	C8	H8B	108.4	C10	C9	H9	120.3
C20	C9	H9	120.3	C16	C12	H12A	109.5
C16	C12	H12B	109.5	C16	C12	H12C	109.5
H12A	C12	H12B	109.5	H12A	C12	H12C	109.5
H12B	C12	H12C	109.5	N7	C13	H13	119.5
C25	C13	H13	119.5	C18	C14	H14A	109.5
C18	C14	H14B	109.5	C18	C14	H14C	109.5
H14A	C14	H14B	109.5	H14A	C14	H14C	109.5
H14B	C14	H14C	109.5	C9	C20	H20	120.4
C25	C20	H20	120.4	C18	C21	H21A	109.5
C18	C21	H21B	109.5	C18	C21	H21C	109.5
H21A	C21	H21B	109.5	H21A	C21	H21C	109.5
H21B	C21	H21C	109.5	C15	C22	H22A	109.5
C15	C22	H22B	109.5	C15	C22	H22C	109.5
H22A	C22	H22B	109.5	H22A	C22	H22C	109.5
H22B	C22	H22C	109.5	C23	C24	H24A	109.5
C23	C24	H24B	109.5	C23	C24	H24C	109.5
H24A	C24	H24B	109.5	H24A	C24	H24C	109.5
H24B	C24	H24C	109.5	C13	C25	H25	120.6
C20	C25	H25	120.6	C15	C26	H26A	109.5
C15	C26	H26B	109.5	C15	C26	H26C	109.5
H26A	C26	H26B	109.5	H26A	C26	H26C	109.5
H26B	C26	H26C	109.5	C17	C27	H27A	109.5
C17	C27	H27B	109.5	C17	C27	H27C	109.5
H27A	C27	H27B	109.5	H27A	C27	H27C	109.5
H27B	C27	H27C	109.5	C16	C28	H28A	109.5
C16	C28	H28B	109.5	C16	C28	H28C	109.5
H28A	C28	H28B	109.5	H28A	C28	H28C	109.5
H28B	C28	H28C	109.5	C23	C29	H29A	109.5
C23	C29	H29B	109.5	C23	C29	H29C	109.5
H29A	C29	H29B	109.5	H29A	C29	H29C	109.5
H29B	C29	H29C	109.5	C19	C30	H30A	109.5
C19	C30	H30B	109.5	C19	C30	H30C	109.5
H30A	C30	H30B	109.5	H30A	C30	H30C	109.5
H30B	C30	H30C	109.5	C17	C31	H31A	109.5

Table 7. Bond angles involving hydrogens (°) (continued)

atom	atom	atom	angle	atom	atom	atom	angle
C17	C31	H31B	109.5	C17	C31	H31C	109.5
H31A	C31	H31B	109.5	H31A	C31	H31C	109.5
H31B	C31	H31C	109.5	C19	C32	H32A	109.5
C19	C32	H32B	109.5	C19	C32	H32C	109.5
H32A	C32	H32B	109.5	H32A	C32	H32C	109.5
H32B	C32	H32C	109.5				

Table 8. Torsion Angles(°)
(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C15	O1	B34	O2	-12.18(12)	C15	O1	B34	C11	166.01(9)
B34	O1	C15	C16	26.62(10)	B34	O1	C15	C22	148.87(9)
B34	O1	C15	C26	-92.24(10)	C16	O2	B34	O1	-9.26(12)
C16	O2	B34	C11	172.67(9)	B34	O2	C16	C12	146.24(8)
B34	O2	C16	C15	24.85(9)	B34	O2	C16	C28	-94.26(10)
C18	O3	B33	O5	-16.45(12)	C18	O3	B33	N7	-134.70(8)
C18	O3	B33	C11	115.68(10)	B33	O3	C18	C14	-94.06(10)
B33	O3	C18	C17	25.56(10)	B33	O3	C18	C21	147.59(8)
C19	O4	B35	O6	-14.08(10)	C19	O4	B35	C11	163.58(8)
B35	O4	C19	C23	27.30(9)	B35	O4	C19	C30	-91.66(10)
B35	O4	C19	C32	149.80(8)	C17	O5	B33	O3	-1.00(12)
C17	O5	B33	N7	114.70(10)	C17	O5	B33	C11	-138.07(9)
B33	O5	C17	C18	16.07(11)	B33	O5	C17	C27	137.38(9)
B33	O5	C17	C31	-105.20(9)	C23	O6	B35	O4	-6.84(10)
C23	O6	B35	C11	175.43(8)	B35	O6	C23	C19	22.92(9)
B35	O6	C23	C24	145.29(8)	B35	O6	C23	C29	-96.14(9)
C10	N7	C13	C25	-3.48(15)	C13	N7	C10	C8	-175.84(8)
C13	N7	C10	C9	4.69(15)	C10	N7	B33	O3	-142.27(8)
C10	N7	B33	O5	101.46(10)	C10	N7	B33	C11	-15.86(10)
B33	N7	C10	C8	8.81(12)	B33	N7	C10	C9	-170.67(8)
C13	N7	B33	O3	42.63(13)	C13	N7	B33	O5	-73.64(13)
C13	N7	B33	C11	169.05(9)	B33	N7	C13	C25	171.29(9)
C10	C8	C11	B33	-13.66(10)	C10	C8	C11	B34	102.19(8)
C10	C8	C11	B35	-129.98(8)	C11	C8	C10	N7	3.57(11)
C11	C8	C10	C9	-176.99(9)	C10	C9	C20	C25	-1.83(16)
C20	C9	C10	N7	-2.00(16)	C20	C9	C10	C8	178.61(9)
C8	C11	B33	O3	130.96(11)	C8	C11	B33	O5	-99.08(11)
C8	C11	B33	N7	16.48(9)	C8	C11	B34	O1	-20.90(14)
C8	C11	B34	O2	157.01(10)	C8	C11	B35	O4	-170.64(8)
C8	C11	B35	O6	6.78(12)	B33	C11	B34	O1	94.15(12)
B33	C11	B34	O2	-87.94(13)	B34	C11	B33	O3	12.33(15)
B34	C11	B33	O5	142.29(10)	B34	C11	B33	N7	-102.16(10)
B33	C11	B35	O4	74.00(12)	B33	C11	B35	O6	-108.58(11)
B35	C11	B33	O3	-109.90(12)	B35	C11	B33	O5	20.06(14)
B35	C11	B33	N7	135.61(9)	B34	C11	B35	O4	-44.09(14)
B34	C11	B35	O6	133.32(10)	B35	C11	B34	O1	-147.62(10)
B35	C11	B34	O2	30.29(16)	N7	C13	C25	C20	-0.42(16)

Table 8. Torsion angles (°) (continued)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
O1	C15	C16	O2	-31.05(9)	O1	C15	C16	C12	-149.33(8)
O1	C15	C16	C28	83.53(10)	C22	C15	C16	O2	-149.66(8)
C22	C15	C16	C12	92.06(11)	C22	C15	C16	C28	-35.07(12)
C26	C15	C16	O2	83.08(10)	C26	C15	C16	C12	-35.20(13)
C26	C15	C16	C28	-162.34(8)	O5	C17	C18	O3	-25.12(10)
O5	C17	C18	C14	91.17(10)	O5	C17	C18	C21	-142.58(9)
C27	C17	C18	O3	-142.08(9)	C27	C17	C18	C14	-25.79(12)
C27	C17	C18	C21	100.46(11)	C31	C17	C18	O3	92.62(11)
C31	C17	C18	C14	-151.08(9)	C31	C17	C18	C21	-24.83(15)
O4	C19	C23	O6	-30.18(10)	O4	C19	C23	C24	-147.80(8)
O4	C19	C23	C29	84.47(10)	C30	C19	C23	O6	83.49(11)
C30	C19	C23	C24	-34.13(14)	C30	C19	C23	C29	-161.87(9)
C32	C19	C23	O6	-148.41(9)	C32	C19	C23	C24	93.97(12)
C32	C19	C23	C29	-33.76(13)	C9	C20	C25	C13	3.01(16)

Table 9. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O1	C8	2.8923(13)	O1	C10	3.4975(14)
O1	C28	3.1010(18)	O1	B33	3.4606(14)
O2	O3	3.4036(11)	O2	O4	3.0006(11)
O2	C14	3.4628(14)	O2	C26	3.0867(15)
O2	B33	3.4592(15)	O2	B35	3.0891(15)
O3	C10	3.5809(16)	O3	C13	2.9993(17)
O3	C31	3.2380(13)	O3	B34	2.9327(14)
O4	O5	3.2468(11)	O4	C14	3.3733(16)
O4	C29	3.1125(15)	O4	B33	3.3158(16)
O4	B34	3.1366(15)	O5	O6	3.4515(11)
O5	C8	3.4274(14)	O5	C10	3.3590(15)
O5	C13	3.3003(16)	O5	C14	3.2000(17)
O5	B35	2.7560(14)	O6	C8	2.8960(14)
O6	C30	3.0965(15)	N7	C17	3.5135(16)
N7	C20	2.7436(18)	N7	B34	3.3895(16)
C9	C13	2.7334(19)	C10	C25	2.7436(16)
C10	B34	3.4206(19)	C12	C22	3.444(2)
C12	C26	2.902(2)	C12	B34	3.5450(18)
C14	C27	2.8587(17)	C14	B33	3.139(2)
C21	C27	3.5513(19)	C21	C31	2.8932(19)
C21	B33	3.592(2)	C22	C28	2.918(2)
C22	B34	3.5467(17)	C24	C30	2.9321(19)
C24	C32	3.490(2)	C24	B35	3.5397(18)
C26	B34	3.0423(16)	C27	B33	3.5559(19)
C28	B34	3.082(2)	C29	C32	2.918(2)
C29	B35	3.1129(18)	C30	B35	3.0270(18)
C31	B33	3.2945(16)	C32	B35	3.542(2)

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
O1	H8B	2.463	O1	H22A	2.663
O1	H22B	2.570	O1	H22C	3.246
O1	H26A	2.576	O1	H26B	2.558
O1	H26C	3.220	O1	H28C	2.809
O2	H12A	2.543	O2	H12B	3.251
O2	H12C	2.718	O2	H14A	3.162
O2	H14C	2.962	O2	H26A	2.787
O2	H28A	2.581	O2	H28B	3.234
O2	H28C	2.585	O3	H13	2.752
O3	H14A	2.573	O3	H14B	3.226
O3	H14C	2.599	O3	H21A	2.621
O3	H21B	2.557	O3	H21C	3.227
O3	H28C	3.074	O3	H31C	2.995
O4	H14C	2.424	O4	H27B	2.971
O4	H29A	2.821	O4	H30A	2.604
O4	H30B	2.517	O4	H30C	3.214
O4	H32A	2.645	O4	H32B	2.569
O4	H32C	3.242	O5	H13	3.317
O5	H14C	2.946	O5	H27A	2.617
O5	H27B	2.558	O5	H27C	3.225
O5	H29A	3.115	O5	H31A	2.570
O5	H31B	3.235	O5	H31C	2.638
O6	H8A	2.355	O6	H8B	3.468
O6	H24A	2.585	O6	H24B	3.248
O6	H24C	2.634	O6	H29A	2.593
O6	H29B	2.575	O6	H29C	3.234
O6	H30A	2.791	N7	H8A	2.977
N7	H8B	3.018	N7	H9	3.203
N7	H25	3.207	N7	H31C	3.333
C8	H9	2.796	C9	H8A	2.878
C9	H8B	2.847	C9	H25	3.237
C10	H13	3.168	C10	H20	3.234
C11	H14C	3.296	C12	H22C	3.225
C12	H26A	2.911	C12	H26C	2.704
C12	H28A	2.674	C12	H28B	2.680
C12	H28C	3.322	C13	H20	3.227
C13	H31C	2.928	C14	H21A	2.616

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C14	H21B	3.316	C14	H21C	2.721
C14	H27B	2.567	C14	H27C	2.955
C14	H28A	3.403	C15	H12A	2.814
C15	H12B	2.731	C15	H12C	3.395
C15	H28A	3.388	C15	H28B	2.827
C15	H28C	2.702	C16	H22A	3.399
C16	H22B	2.785	C16	H22C	2.773
C16	H26A	2.689	C16	H26B	3.383
C16	H26C	2.827	C17	H13	3.536
C17	H14A	3.398	C17	H14B	2.822
C17	H14C	2.705	C17	H21A	3.423
C17	H21B	2.794	C17	H21C	2.804
C18	H13	3.525	C18	H27A	3.420
C18	H27B	2.780	C18	H27C	2.804
C18	H31A	3.411	C18	H31B	2.862
C18	H31C	2.718	C19	H24A	2.776
C19	H24B	2.818	C19	H24C	3.411
C19	H29A	2.693	C19	H29B	3.386
C19	H29C	2.833	C20	H13	3.225
C21	H14A	2.661	C21	H14B	2.674
C21	H14C	3.319	C21	H27C	3.380
C21	H31B	2.751	C21	H31C	2.820
C22	H12B	3.201	C22	H26A	3.313
C22	H26B	2.667	C22	H26C	2.668
C22	H28B	2.716	C22	H28C	2.937
C23	H30A	2.669	C23	H30B	3.383
C23	H30C	2.869	C23	H32A	3.406
C23	H32B	2.785	C23	H32C	2.790
C24	H29A	3.316	C24	H29B	2.662
C24	H29C	2.673	C24	H30A	2.872
C24	H30C	2.800	C24	H32C	3.290
C25	H9	3.238	C26	H12A	2.661
C26	H12B	2.968	C26	H22A	2.597
C26	H22B	3.310	C26	H22C	2.739
C27	H14B	2.676	C27	H14C	2.814
C27	H21C	3.378	C27	H29A	3.066
C27	H31A	2.667	C27	H31B	2.639

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C27	H31C	3.312	C27	H32B	3.559
C28	H12A	3.311	C28	H12B	2.787
C28	H12C	2.574	C28	H14A	3.140
C28	H22B	2.626	C28	H22C	3.050
C29	H24A	3.315	C29	H24B	2.714
C29	H24C	2.620	C29	H27B	3.553
C29	H32B	2.620	C29	H32C	3.057
C30	H24A	2.608	C30	H24B	3.111
C30	H32A	2.607	C30	H32B	3.317
C30	H32C	2.743	C31	H13	3.172
C31	H21B	2.621	C31	H21C	2.969
C31	H27A	2.605	C31	H27B	3.310
C31	H27C	2.701	C32	H24B	3.307
C32	H27B	3.452	C32	H29A	2.912
C32	H29C	2.732	C32	H30A	3.319
C32	H30B	2.702	C32	H30C	2.649
B33	H8A	3.130	B33	H8B	3.318
B33	H13	2.826	B33	H14A	3.545
B33	H14C	2.915	B33	H27B	3.549
B33	H31C	3.145	B34	H8A	3.299
B34	H8B	2.532	B34	H12A	3.586
B34	H14C	3.379	B34	H26A	2.809
B34	H26B	3.452	B34	H28A	3.502
B34	H28C	2.858	B35	H8A	2.520
B35	H8B	3.138	B35	H14C	3.113
B35	H24A	3.593	B35	H27B	3.558
B35	H29A	2.901	B35	H29B	3.524
B35	H30A	2.815	B35	H30B	3.386
H8A	H9	2.899	H8B	H9	2.853
H9	H20	2.319	H12A	H26A	2.417
H12A	H26C	2.460	H12A	H28A	3.482
H12A	H28B	3.589	H12B	H22C	2.732
H12B	H26A	3.225	H12B	H26C	2.511
H12B	H28A	3.104	H12B	H28B	2.634
H12C	H28A	2.400	H12C	H28B	2.796
H12C	H28C	3.472	H13	H21B	3.040
H13	H25	2.304	H13	H31A	3.591

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H13	H31C	2.305	H14A	H21A	2.430
H14A	H21B	3.510	H14A	H21C	3.010
H14A	H27B	3.511	H14A	H28A	2.521
H14A	H28C	3.002	H14B	H21A	2.873
H14B	H21B	3.569	H14B	H21C	2.555
H14B	H27B	2.417	H14B	H27C	2.492
H14C	H21A	3.502	H14C	H21C	3.586
H14C	H27B	2.258	H14C	H27C	3.150
H14C	H28A	3.564	H20	H25	2.339
H21B	H31A	3.564	H21B	H31B	2.523
H21B	H31C	2.275	H21C	H27C	2.957
H21C	H31B	2.539	H21C	H31C	3.126
H22A	H26A	3.488	H22A	H26B	2.421
H22A	H26C	2.837	H22B	H26B	3.502
H22B	H26C	3.570	H22B	H28A	3.577
H22B	H28B	2.400	H22B	H28C	2.411
H22C	H26A	3.595	H22C	H26B	3.046
H22C	H26C	2.574	H22C	H28B	2.600
H22C	H28C	3.314	H24A	H29B	3.513
H24A	H29C	3.567	H24A	H30A	2.317
H24A	H30B	3.557	H24A	H30C	2.460
H24B	H29A	3.580	H24B	H29B	3.003
H24B	H29C	2.549	H24B	H30A	3.288
H24B	H30C	2.720	H24B	H32C	2.853
H24C	H29A	3.504	H24C	H29B	2.435
H24C	H29C	2.881	H27A	H29A	2.711
H27A	H31A	2.436	H27A	H31B	2.831
H27A	H31C	3.501	H27B	H29A	2.648
H27B	H31A	3.516	H27B	H31B	3.539
H27B	H32B	2.695	H27C	H31A	3.014
H27C	H31B	2.508	H27C	H31C	3.561
H29A	H32B	2.378	H29A	H32C	3.294
H29B	H32B	3.571	H29C	H32B	2.420
H29C	H32C	2.617	H30A	H32A	3.507
H30A	H32C	3.585	H30B	H32A	2.465
H30B	H32B	3.530	H30B	H32C	3.088
H30C	H32A	2.807	H30C	H32B	3.555

Table 10. Intramolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H30C	H32C	2.554			

Table 11. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
O5	C9[1]	3.4797(16)	O5	C20[1]	3.2047(17)
O6	C20[1]	3.5099(14)	N7	C9[1]	3.4837(15)
N7	C20[1]	3.5769(15)	C9	O5[1]	3.4797(16)
C9	N7[1]	3.4837(15)	C9	C10[1]	3.5460(15)
C10	C9[1]	3.5460(15)	C10	C20[1]	3.3726(16)
C12	C14[2]	3.3939(17)	C14	C12[2]	3.3939(17)
C20	O5[1]	3.2047(17)	C20	O6[1]	3.5099(14)
C20	N7[1]	3.5769(15)	C20	C10[1]	3.3726(16)

Symmetry Operators:

(1) -X+1,-Y+2,-Z+1 (2) -X+2,-Y+2,-Z+1

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
O1	H21A[1]	3.175	O1	H21C[1]	3.255
O1	H24B[2]	3.390	O2	H12C[3]	2.834
O3	H24B[2]	3.108	O5	H9[4]	3.143
O5	H20[4]	2.590	O6	H20[4]	2.912
O6	H25[4]	3.116	O6	H27C[5]	3.107
N7	H9[4]	3.446	N7	H20[4]	3.580
C8	H20[4]	3.535	C9	H21B[1]	3.036
C9	H21C[1]	3.348	C9	H31A[4]	3.479
C9	H31B[1]	3.539	C10	H20[4]	3.552
C10	H21B[1]	3.599	C10	H21C[1]	3.456
C12	H12C[3]	3.073	C12	H14A[3]	3.025
C12	H14B[3]	3.401	C12	H14C[3]	3.204
C12	H22A[6]	3.518	C12	H28A[3]	3.310
C13	H9[4]	3.402	C13	H24B[2]	3.584
C13	H24C[2]	3.284	C13	H27A[7]	3.573
C14	H12A[3]	3.251	C14	H12B[3]	3.162
C14	H12C[3]	3.201	C14	H22A[8]	2.985
C16	H12C[3]	3.283	C20	H8A[4]	3.084
C20	H21B[1]	3.574	C20	H29B[4]	3.285
C20	H31B[1]	3.024	C21	H8B[8]	3.564
C21	H9[8]	3.528	C21	H22A[8]	3.454
C21	H29C[2]	3.432	C22	H12A[9]	3.121
C22	H14A[1]	3.364	C22	H14B[1]	3.375
C22	H24A[2]	3.303	C22	H26A[9]	3.308
C22	H26C[9]	3.320	C22	H30C[2]	3.252
C24	H14B[5]	3.560	C24	H21C[5]	3.278
C24	H22B[10]	3.095	C24	H27C[5]	3.192
C24	H28C[10]	3.407	C25	H8A[4]	2.923
C25	H24C[2]	3.518	C25	H27A[7]	3.394
C25	H29B[4]	3.570	C25	H31B[1]	3.502
C26	H22C[6]	3.013	C26	H32A[5]	3.250
C26	H32C[5]	3.499	C27	H8A[11]	3.418
C27	H25[12]	3.274	C28	H12C[3]	3.453
C28	H24B[2]	3.516	C28	H30B[3]	3.466
C28	H30C[2]	3.057	C28	H32C[2]	3.522
C29	H20[4]	3.055	C29	H31A[12]	3.161
C29	H31B[12]	3.600	C30	H22B[10]	3.147

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
C30	H26C^{6}	3.251	C30	H28B^{10}	3.477
C30	H28C^{10}	3.597	C31	H9^{4}	3.269
C31	H20^{8}	3.471	C31	H29B^{7}	3.097
C32	H21A^{10}	3.560	C32	H26B^{11}	2.939
B33	H20^{4}	3.420	B35	H20^{4}	3.345
H8A	C20^{4}	3.084	H8A	C25^{4}	2.923
H8A	C27^{5}	3.418	H8A	H20^{4}	3.048
H8A	H25^{4}	2.810	H8A	H27A^{5}	3.124
H8A	H27B^{5}	3.422	H8A	H27C^{5}	3.150
H8B	C21^{1}	3.564	H8B	H21A^{1}	3.203
H8B	H21B^{1}	3.452	H8B	H21C^{1}	3.459
H8B	H32B^{5}	2.983	H9	O5^{4}	3.143
H9	N7^{4}	3.446	H9	C13^{4}	3.402
H9	C21^{1}	3.528	H9	C31^{4}	3.269
H9	H21B^{1}	2.789	H9	H21C^{1}	3.520
H9	H29C^{5}	3.505	H9	H31A^{4}	2.623
H9	H31C^{4}	3.190	H12A	C14^{3}	3.251
H12A	C22^{6}	3.121	H12A	H12C^{3}	3.273
H12A	H14A^{3}	2.709	H12A	H14B^{3}	3.202
H12A	H14C^{3}	3.336	H12A	H22A^{6}	2.671
H12A	H22B^{6}	3.478	H12A	H22C^{6}	2.786
H12A	H28A^{3}	2.963	H12B	C14^{3}	3.162
H12B	H14A^{3}	3.063	H12B	H14B^{3}	2.987
H12B	H14C^{3}	2.902	H12B	H32A^{3}	3.185
H12C	O2^{3}	2.834	H12C	C12^{3}	3.073
H12C	C14^{3}	3.201	H12C	C16^{3}	3.283
H12C	C28^{3}	3.453	H12C	H12A^{3}	3.273
H12C	H12C^{3}	2.390	H12C	H14A^{3}	2.799
H12C	H14B^{3}	3.470	H12C	H14C^{3}	2.861
H12C	H28A^{3}	2.773	H12C	H30B^{3}	3.581
H13	H24B^{2}	3.463	H13	H24C^{2}	3.334
H13	H27A^{7}	3.159	H13	H29B^{2}	3.223
H13	H29C^{2}	3.179	H13	H31A^{7}	3.289
H14A	C12^{3}	3.025	H14A	C22^{8}	3.364
H14A	H12A^{3}	2.709	H14A	H12B^{3}	3.063
H14A	H12C^{3}	2.799	H14A	H22A^{8}	2.441
H14B	C12^{3}	3.401	H14B	C22^{8}	3.375

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H14B	C24[11]	3.560	H14B	H12A[3]	3.202
H14B	H12B[3]	2.987	H14B	H12C[3]	3.470
H14B	H22A[8]	2.704	H14B	H22B[8]	3.186
H14B	H24A[11]	2.720	H14C	C12[3]	3.204
H14C	H12A[3]	3.336	H14C	H12B[3]	2.902
H14C	H12C[3]	2.861	H20	O5[4]	2.590
H20	O6[4]	2.912	H20	N7[4]	3.580
H20	C8[4]	3.535	H20	C10[4]	3.552
H20	C29[4]	3.055	H20	C31[1]	3.471
H20	B33[4]	3.420	H20	B35[4]	3.345
H20	H8A[4]	3.048	H20	H29A[4]	2.786
H20	H29B[4]	2.594	H20	H31B[1]	2.873
H20	H31C[1]	3.311	H21A	O1[8]	3.175
H21A	C32[2]	3.560	H21A	H8B[8]	3.203
H21A	H22A[8]	2.905	H21A	H26B[8]	3.163
H21A	H29C[2]	3.156	H21A	H32B[2]	3.463
H21A	H32C[2]	2.808	H21B	C9[8]	3.036
H21B	C10[8]	3.599	H21B	C20[8]	3.574
H21B	H8B[8]	3.452	H21B	H9[8]	2.789
H21B	H29C[2]	2.855	H21C	O1[8]	3.255
H21C	C9[8]	3.348	H21C	C10[8]	3.456
H21C	C24[11]	3.278	H21C	H8B[8]	3.459
H21C	H9[8]	3.520	H21C	H22A[8]	3.315
H21C	H24A[11]	2.997	H21C	H24B[11]	3.509
H21C	H24C[11]	2.837	H22A	C12[9]	3.518
H22A	C14[1]	2.985	H22A	C21[1]	3.454
H22A	H12A[9]	2.671	H22A	H14A[1]	2.441
H22A	H14B[1]	2.704	H22A	H21A[1]	2.905
H22A	H21C[1]	3.315	H22A	H24A[2]	3.361
H22A	H26A[9]	3.559	H22A	H26C[9]	3.534
H22A	H28A[1]	3.535	H22B	C24[2]	3.095
H22B	C30[2]	3.147	H22B	H12A[9]	3.478
H22B	H14B[1]	3.186	H22B	H24A[2]	2.470
H22B	H24B[2]	2.862	H22B	H26A[9]	3.573
H22B	H26C[9]	3.180	H22B	H30A[2]	3.093
H22B	H30C[2]	2.383	H22C	C26[9]	3.013
H22C	H12A[9]	2.786	H22C	H26A[9]	2.442

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H22C	H26B^{9}	3.495	H22C	H26C^{9}	2.758
H22C	H30C^{2}	3.363	H24A	C22^{10}	3.303
H24A	H14B^{5}	2.720	H24A	H21C^{5}	2.997
H24A	H22A^{10}	3.361	H24A	H22B^{10}	2.470
H24A	H27C^{5}	2.873	H24A	H28C^{10}	3.447
H24B	O1^{10}	3.390	H24B	O3^{10}	3.108
H24B	C13^{10}	3.584	H24B	C28^{10}	3.516
H24B	H13^{10}	3.463	H24B	H21C^{5}	3.509
H24B	H22B^{10}	2.862	H24B	H28C^{10}	2.596
H24C	C13^{10}	3.284	H24C	C25^{10}	3.518
H24C	H13^{10}	3.334	H24C	H21C^{5}	2.837
H24C	H25^{4}	3.437	H24C	H27C^{5}	2.752
H24C	H31B^{5}	3.407	H25	O6^{4}	3.116
H25	C27^{7}	3.274	H25	H8A^{4}	2.810
H25	H24C^{4}	3.437	H25	H27A^{7}	2.824
H25	H27C^{7}	2.845	H25	H29B^{4}	3.150
H25	H31A^{7}	3.589	H25	H31B^{7}	3.404
H26A	C22^{6}	3.308	H26A	H22A^{6}	3.559
H26A	H22B^{6}	3.573	H26A	H22C^{6}	2.442
H26A	H32A^{5}	3.083	H26B	C32^{5}	2.939
H26B	H21A^{1}	3.163	H26B	H22C^{6}	3.495
H26B	H32A^{5}	2.611	H26B	H32B^{5}	3.157
H26B	H32C^{5}	2.593	H26C	C22^{6}	3.320
H26C	C30^{9}	3.251	H26C	H22A^{6}	3.534
H26C	H22B^{6}	3.180	H26C	H22C^{6}	2.758
H26C	H30A^{9}	2.952	H26C	H30B^{9}	3.145
H26C	H30C^{9}	3.109	H27A	C13^{12}	3.573
H27A	C25^{12}	3.394	H27A	H8A^{11}	3.124
H27A	H13^{12}	3.159	H27A	H25^{12}	2.824
H27A	H31C^{12}	3.378	H27B	H8A^{11}	3.422
H27C	O6^{11}	3.107	H27C	C24^{11}	3.192
H27C	H8A^{11}	3.150	H27C	H24A^{11}	2.873
H27C	H24C^{11}	2.752	H27C	H25^{12}	2.845
H28A	C12^{3}	3.310	H28A	H12A^{3}	2.963
H28A	H12C^{3}	2.773	H28A	H22A^{8}	3.535
H28A	H30B^{3}	3.030	H28A	H32C^{2}	3.565
H28B	C30^{2}	3.477	H28B	H30B^{3}	3.004

Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

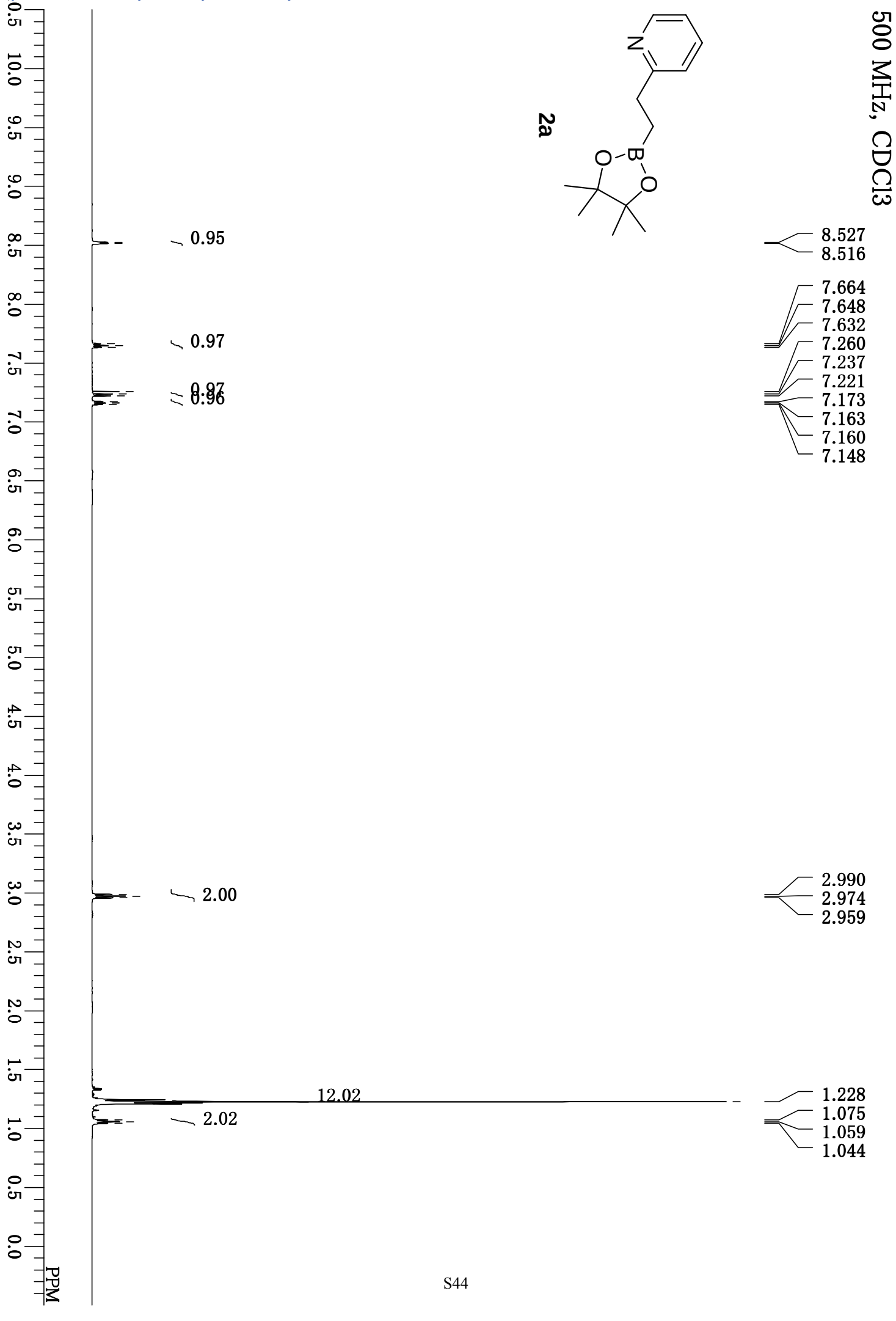
atom	atom	distance	atom	atom	distance
H28B	H30C^{2}	2.552	H28B	H32A^{3}	3.081
H28B	H32C^{2}	3.538	H28C	C24^{2}	3.407
H28C	C30^{2}	3.597	H28C	H24A^{2}	3.447
H28C	H24B^{2}	2.596	H28C	H30C^{2}	2.697
H28C	H32C^{2}	2.935	H29A	H20^{4}	2.786
H29A	H31A^{12}	3.233	H29A	H31C^{12}	3.479
H29B	C20^{4}	3.285	H29B	C25^{4}	3.570
H29B	C31^{12}	3.097	H29B	H13^{10}	3.223
H29B	H20^{4}	2.594	H29B	H25^{4}	3.150
H29B	H31A^{12}	2.651	H29B	H31B^{12}	2.828
H29B	H31C^{12}	3.347	H29C	C21^{10}	3.432
H29C	H9^{11}	3.505	H29C	H13^{10}	3.179
H29C	H21A^{10}	3.156	H29C	H21B^{10}	2.855
H29C	H31A^{12}	3.096	H30A	H22B^{10}	3.093
H30A	H26C^{6}	2.952	H30B	C28^{3}	3.466
H30B	H12C^{3}	3.581	H30B	H26C^{6}	3.145
H30B	H28A^{3}	3.030	H30B	H28B^{3}	3.004
H30C	C22^{10}	3.252	H30C	C28^{10}	3.057
H30C	H22B^{10}	2.383	H30C	H22C^{10}	3.363
H30C	H26C^{6}	3.109	H30C	H28B^{10}	2.552
H30C	H28C^{10}	2.697	H31A	C9^{4}	3.479
H31A	C29^{7}	3.161	H31A	H9^{4}	2.623
H31A	H13^{12}	3.289	H31A	H25^{12}	3.589
H31A	H29A^{7}	3.233	H31A	H29B^{7}	2.651
H31A	H29C^{7}	3.096	H31B	C9^{8}	3.539
H31B	C20^{8}	3.024	H31B	C25^{8}	3.502
H31B	C29^{7}	3.600	H31B	H20^{8}	2.873
H31B	H24C^{11}	3.407	H31B	H25^{12}	3.404
H31B	H29B^{7}	2.828	H31C	H9^{4}	3.190
H31C	H20^{8}	3.311	H31C	H27A^{7}	3.378
H31C	H29A^{7}	3.479	H31C	H29B^{7}	3.347
H32A	C26^{11}	3.250	H32A	H12B^{3}	3.185
H32A	H26A^{11}	3.083	H32A	H26B^{11}	2.611
H32A	H28B^{3}	3.081	H32B	H8B^{11}	2.983
H32B	H21A^{10}	3.463	H32B	H26B^{11}	3.157
H32C	C26^{11}	3.499	H32C	C28^{10}	3.522
H32C	H21A^{10}	2.808	H32C	H26B^{11}	2.593

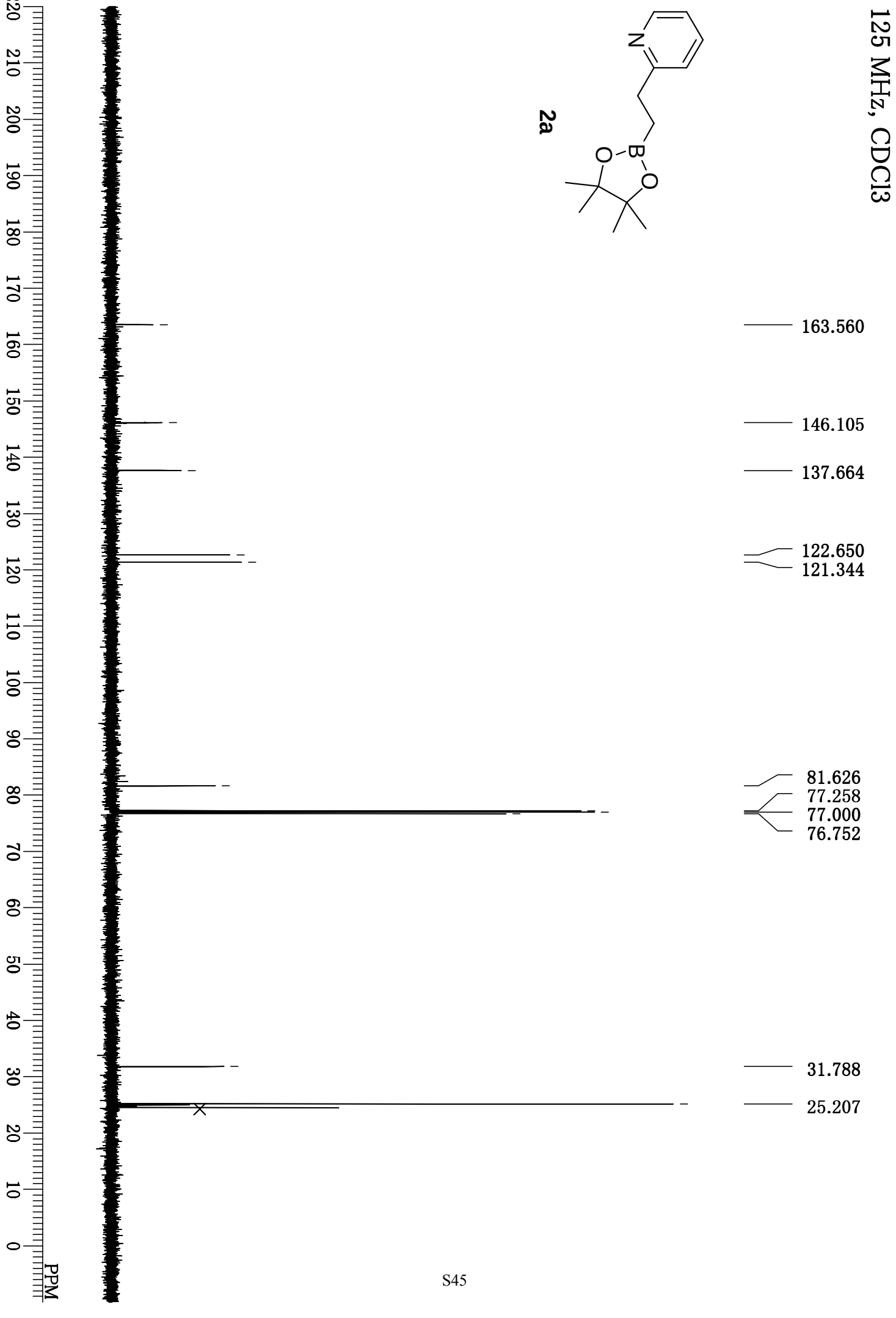
Table 12. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H32C	H28A[10]	3.565	H32C	H28B[10]	3.538
H32C	H28C[10]	2.935			

Symmetry Operators:

(1) X,-Y+1/2+2,Z+1/2
(2) X,Y+1,Z
(3) -X+2,-Y+2,-Z+1
(4) -X+1,-Y+2,-Z+1
(5) X,-Y+1/2+1,Z+1/2
(6) -X+2,Y+1/2-1,-Z+1/2+1
(7) -X+1,Y+1/2,-Z+1/2
(8) X,-Y+1/2+2,Z+1/2-1
(9) -X+2,Y+1/2,-Z+1/2+1
(10) X,Y-1,Z
(11) X,-Y+1/2+1,Z+1/2-1
(12) -X+1,Y+1/2-1,-Z+1/2

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76.752
31.788
25.207
PPM
220
210
200
190
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150
140
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70
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10
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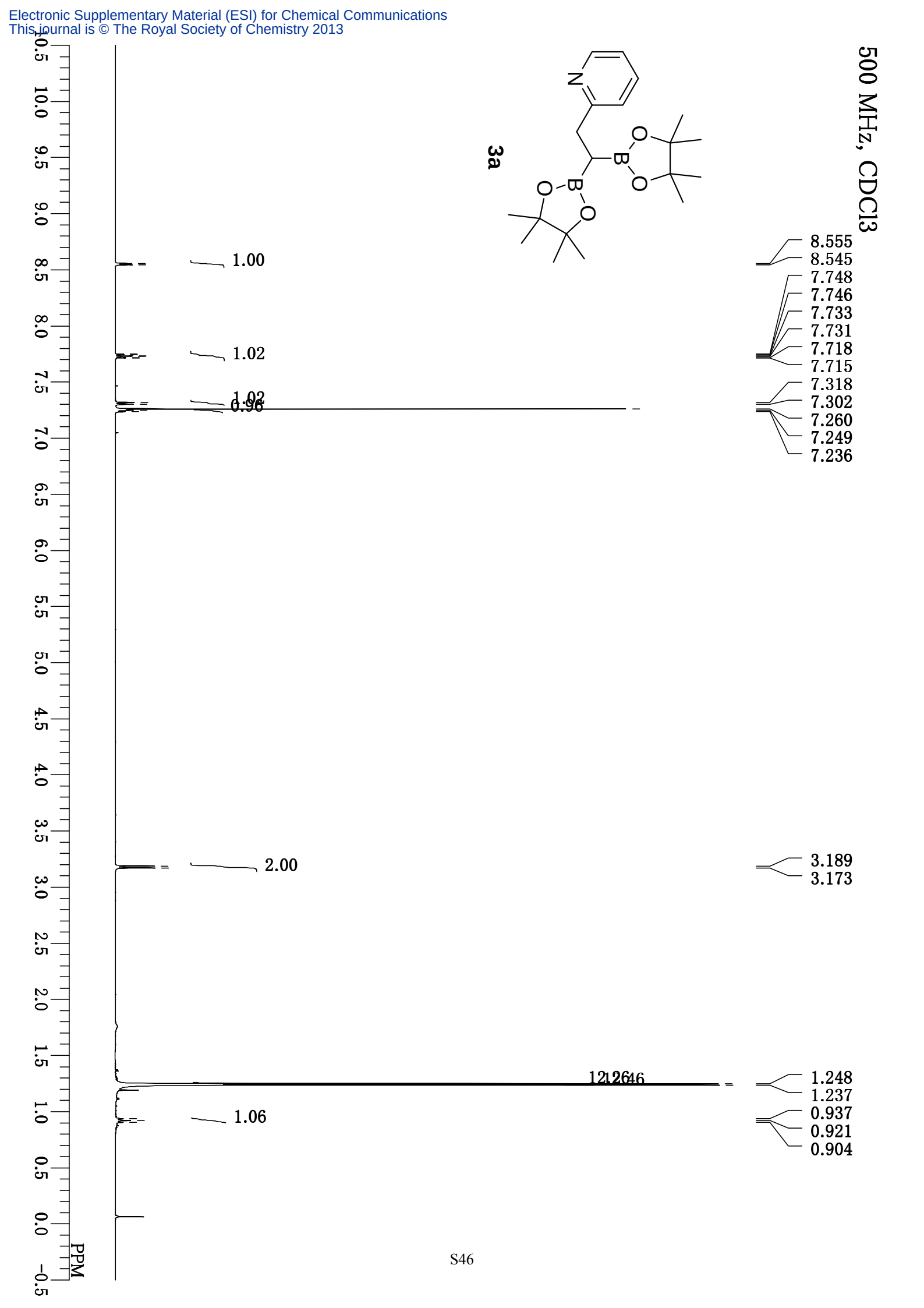

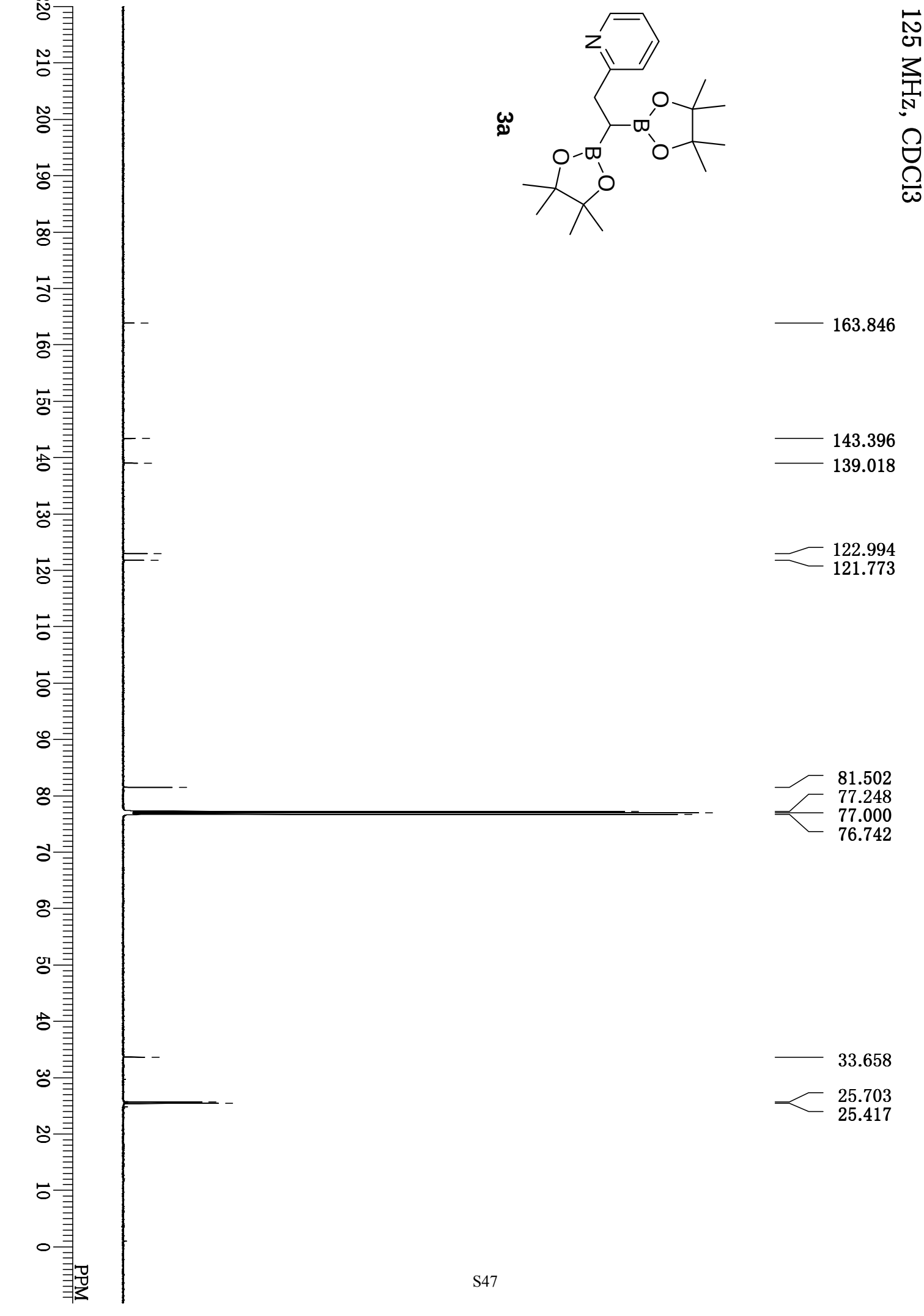
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O
B
O
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81.502
77.248
77.000
76.742
33.658
25.703
25.417
220
210
200
190
180
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140
130
120
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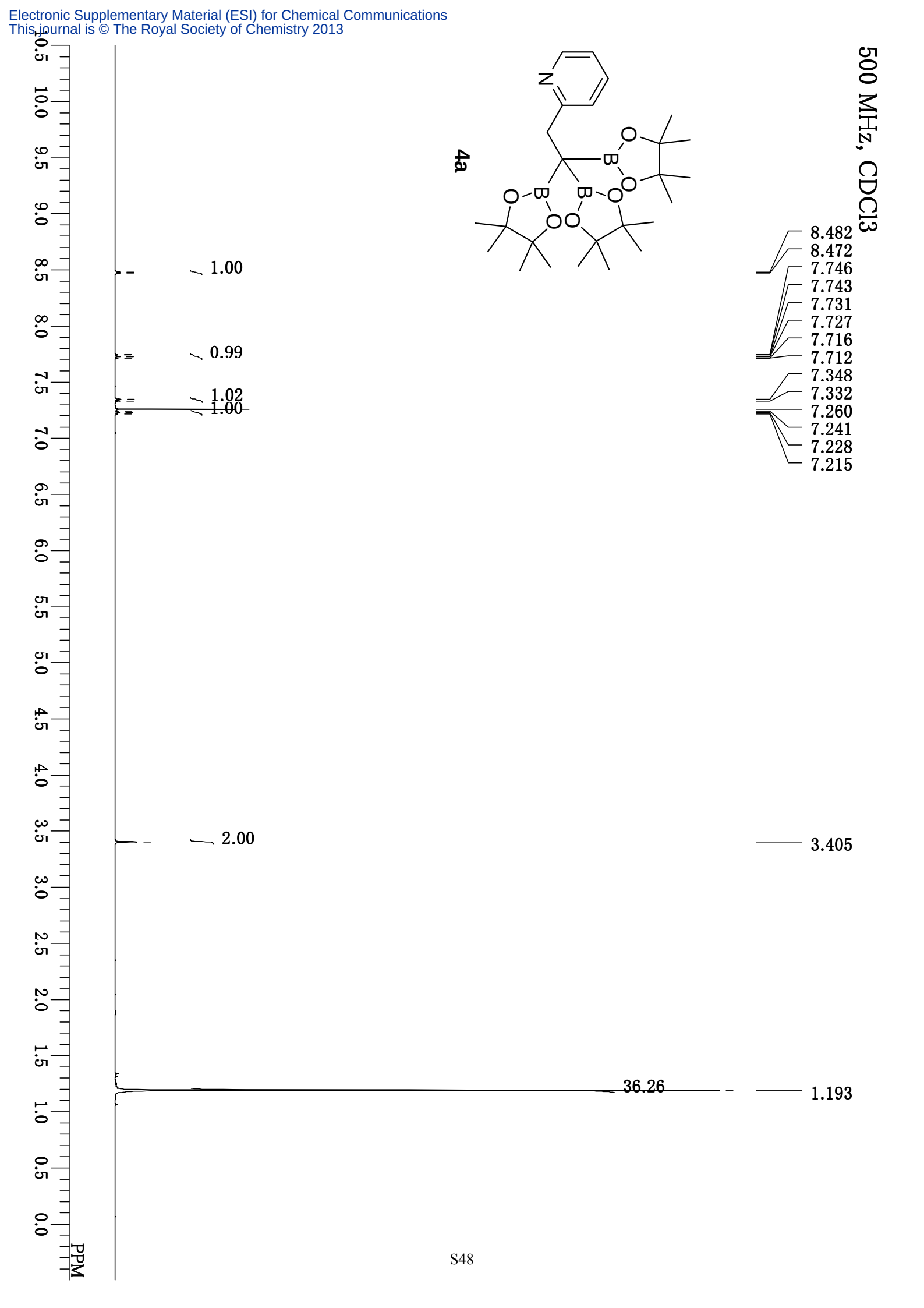
100
90
80
70
60
50
40
30
20
10
0
PPM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7.332
7.260
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2.00
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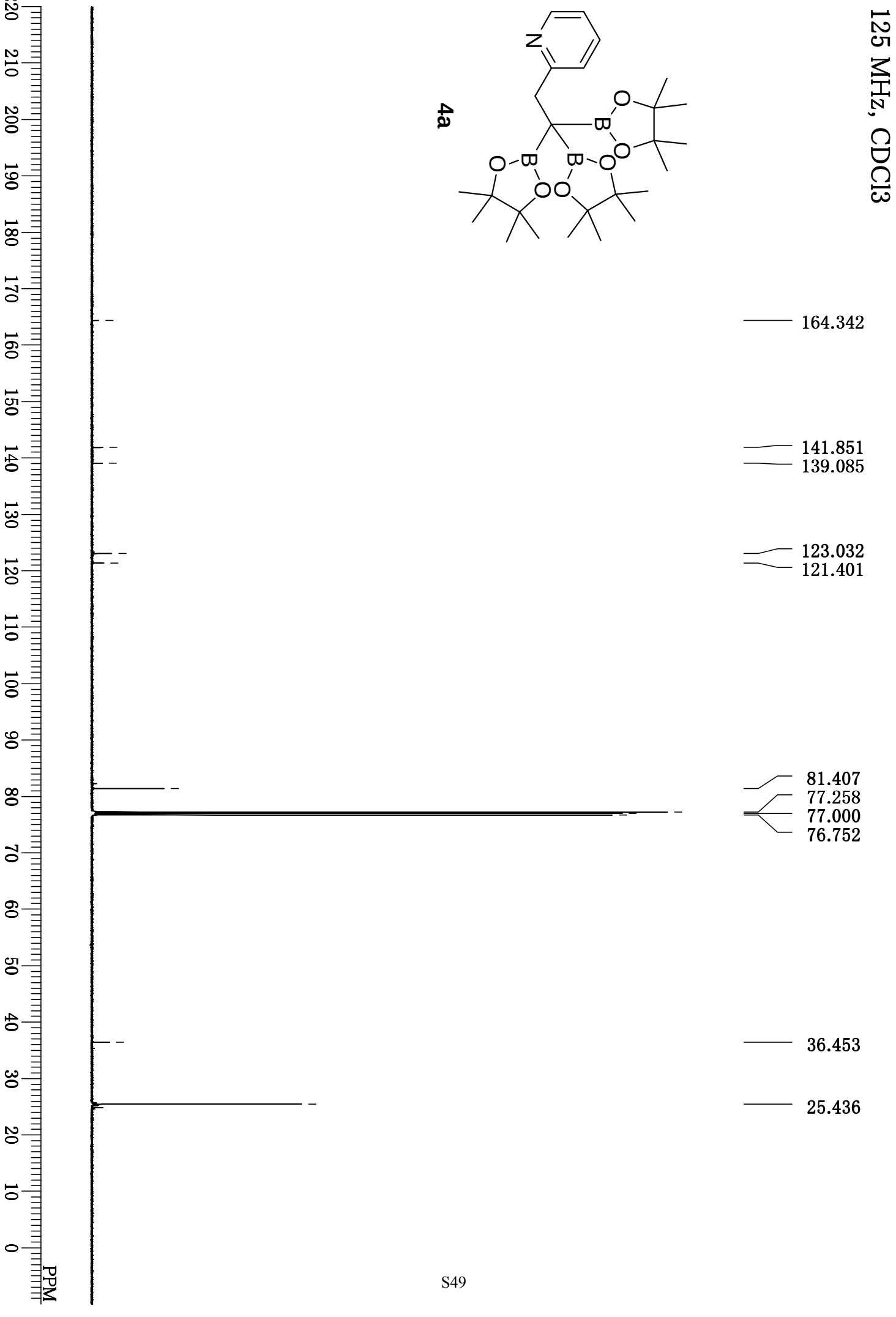
125 MHz, CDCl3
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B
O
B
O
B
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O
O
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77.258
77.000
76.752
36.453
25.436
220
210
200
190
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50
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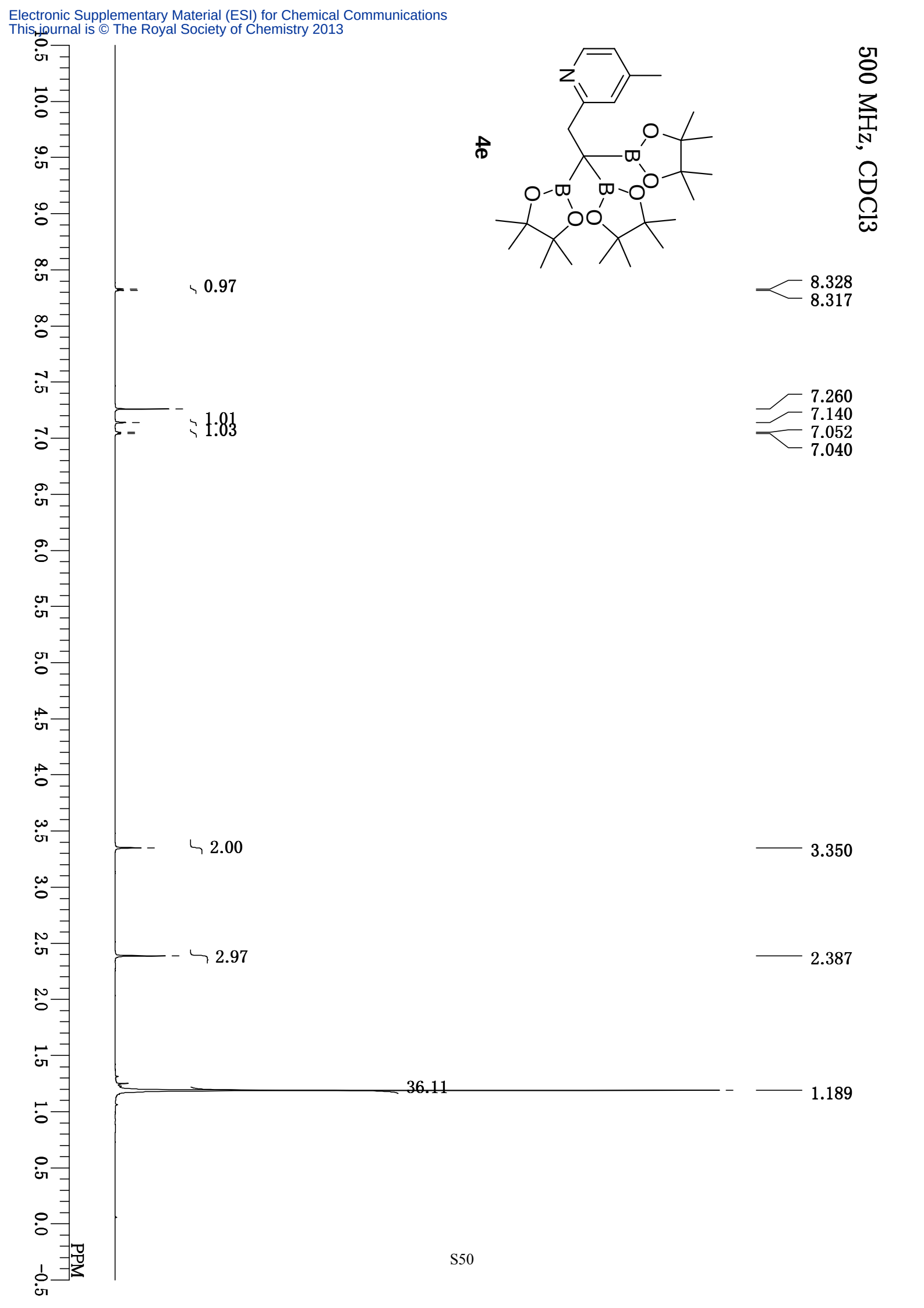
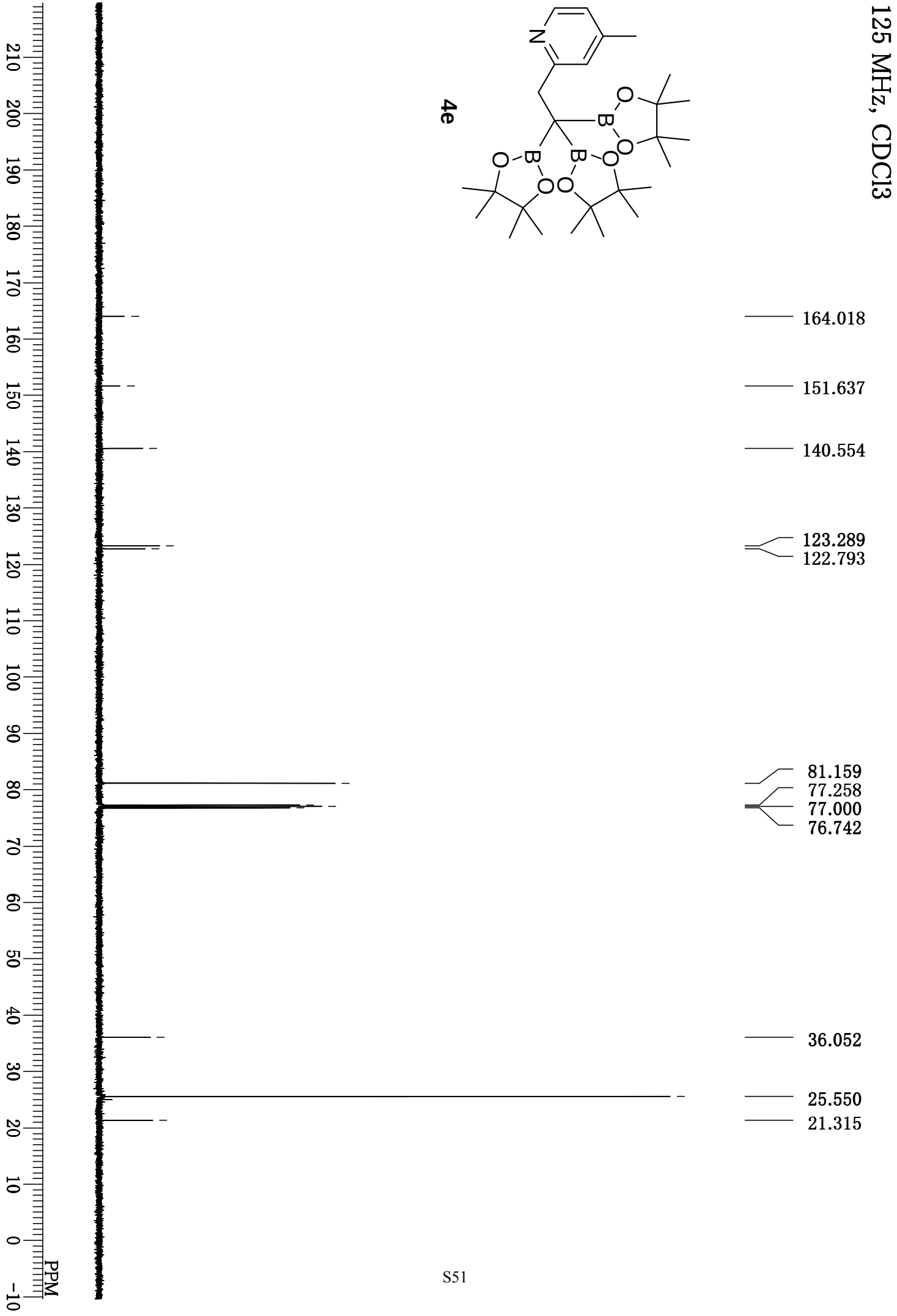
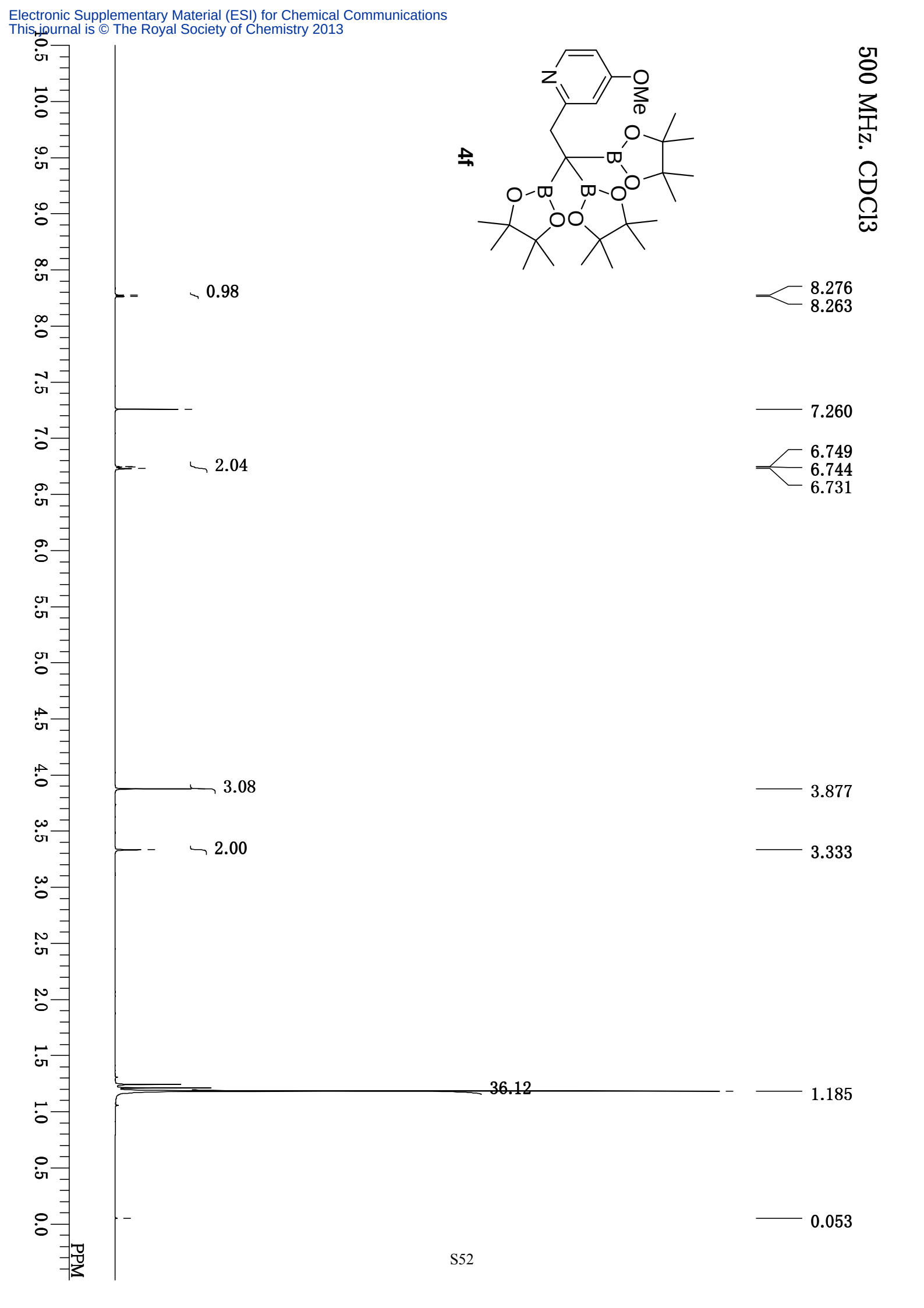
PPM






500 MHz. CDCl3
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OMe
B
O
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6.731
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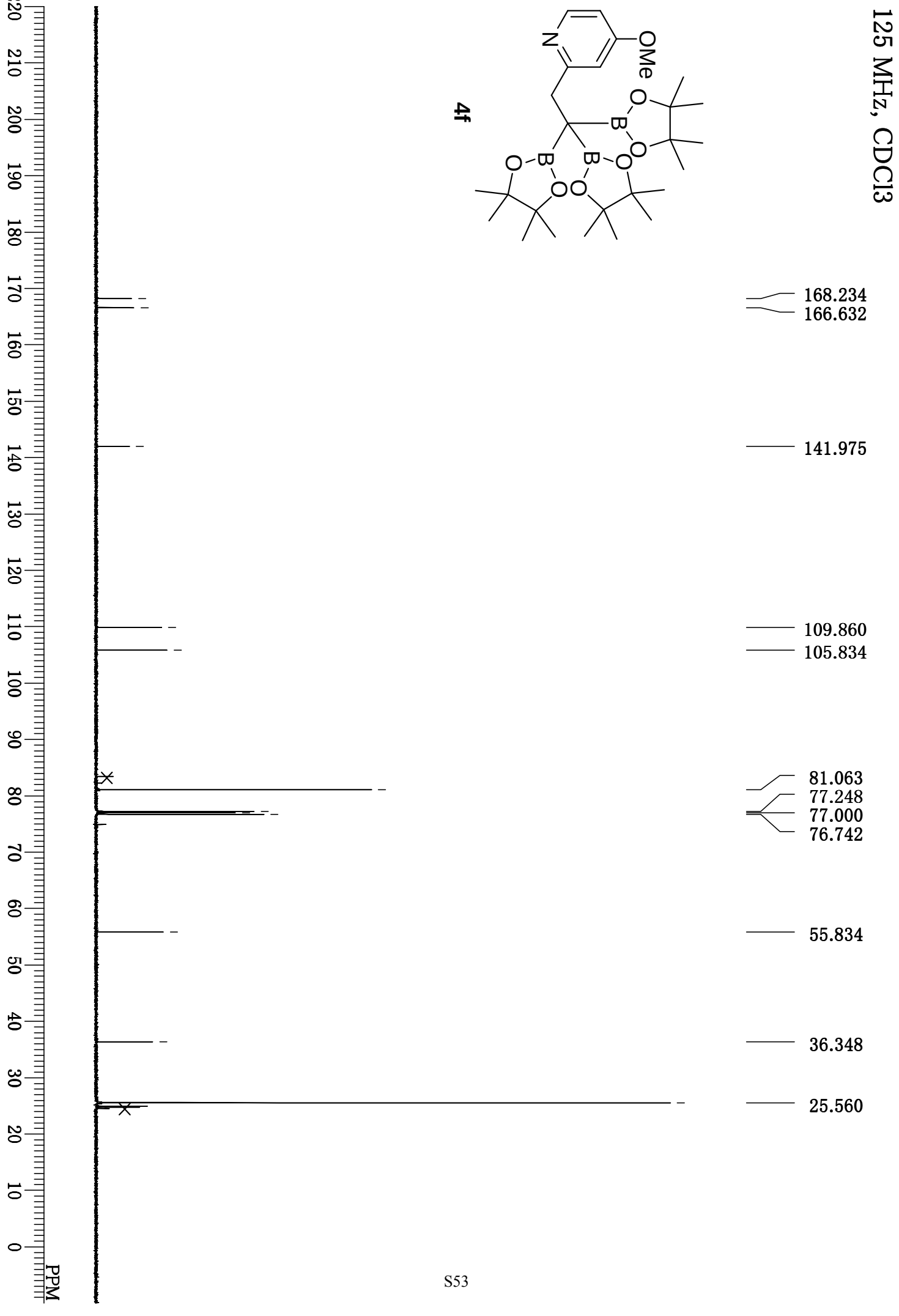
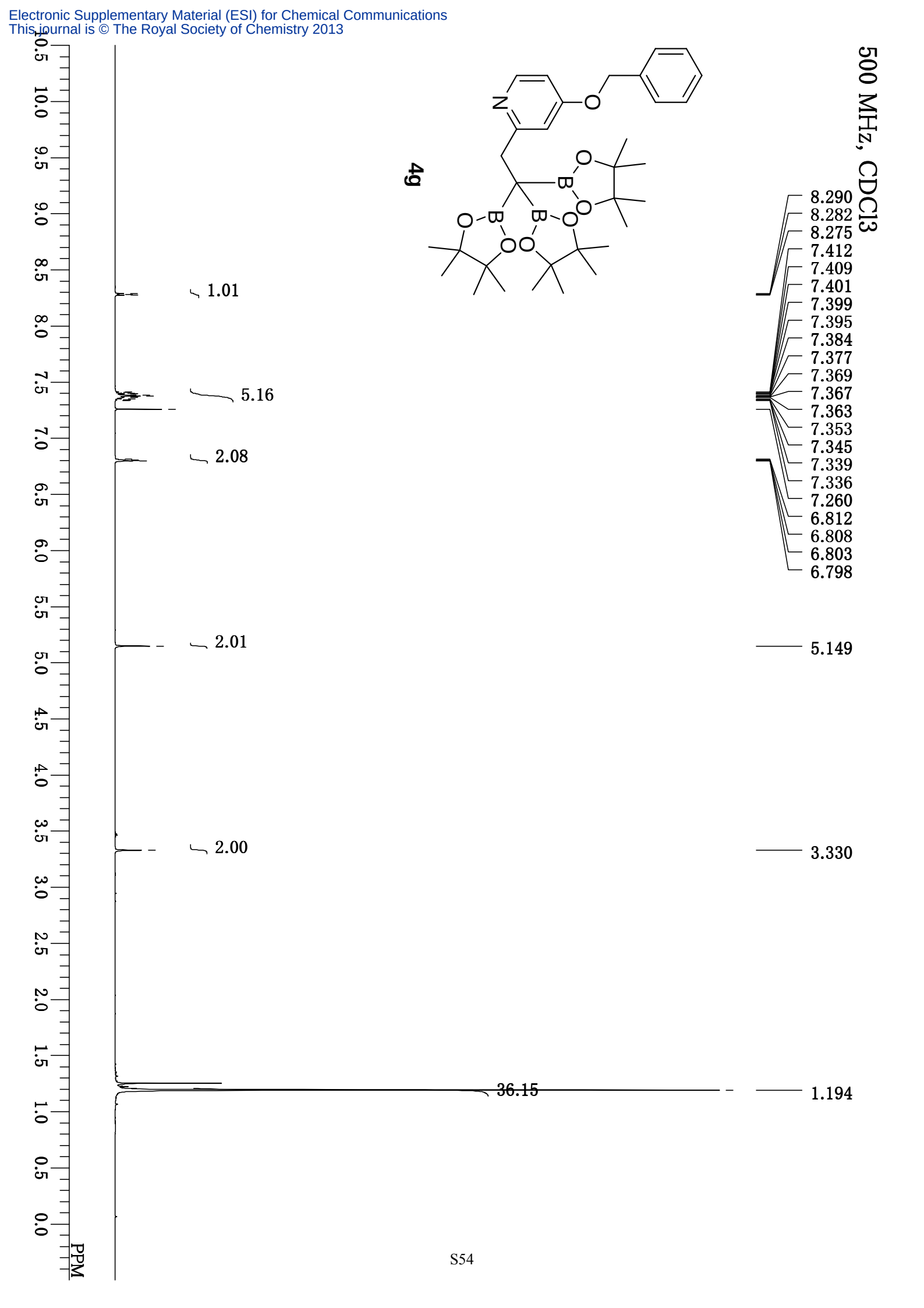
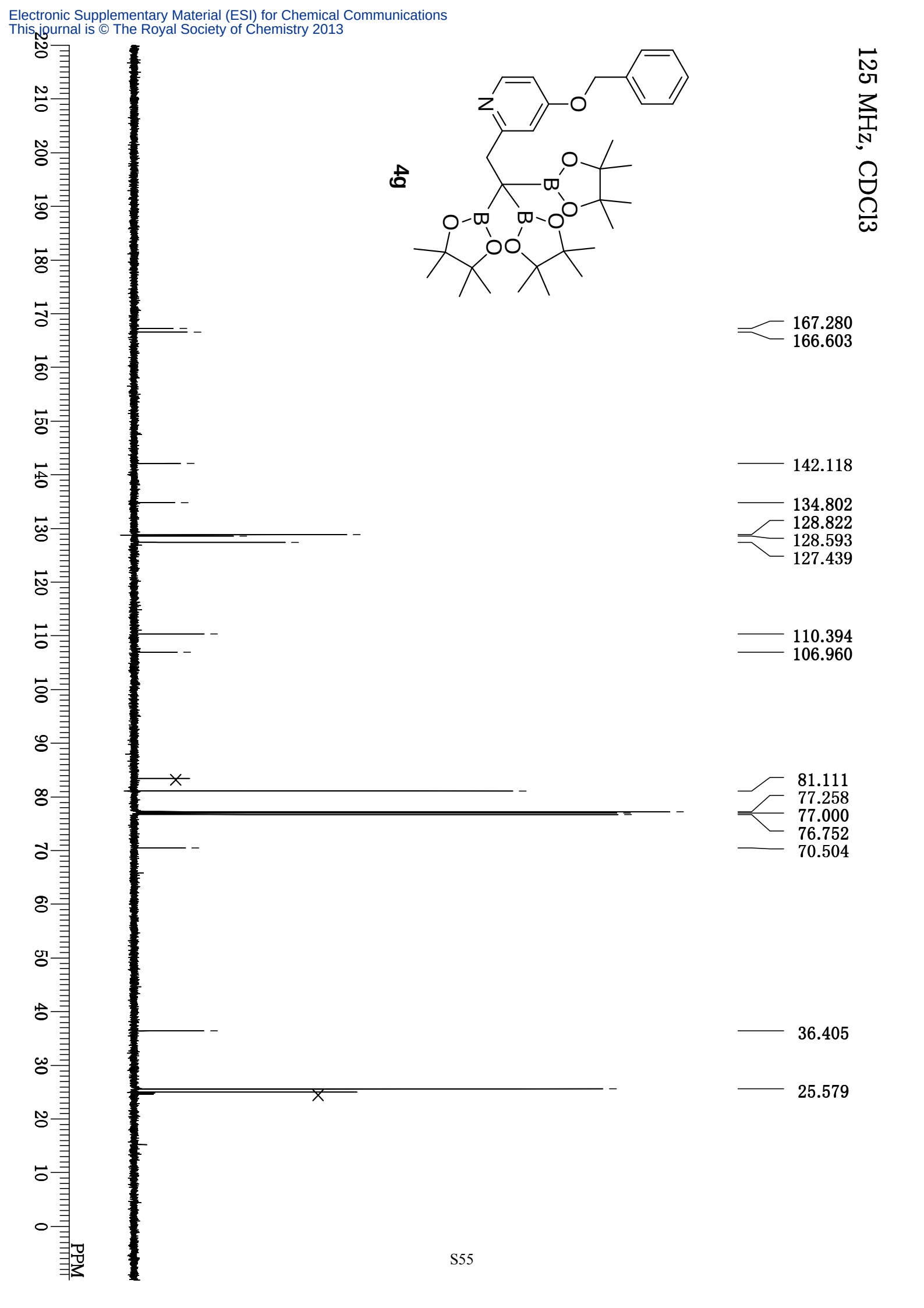
3.333
1.185
0.053
PPM



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76.752
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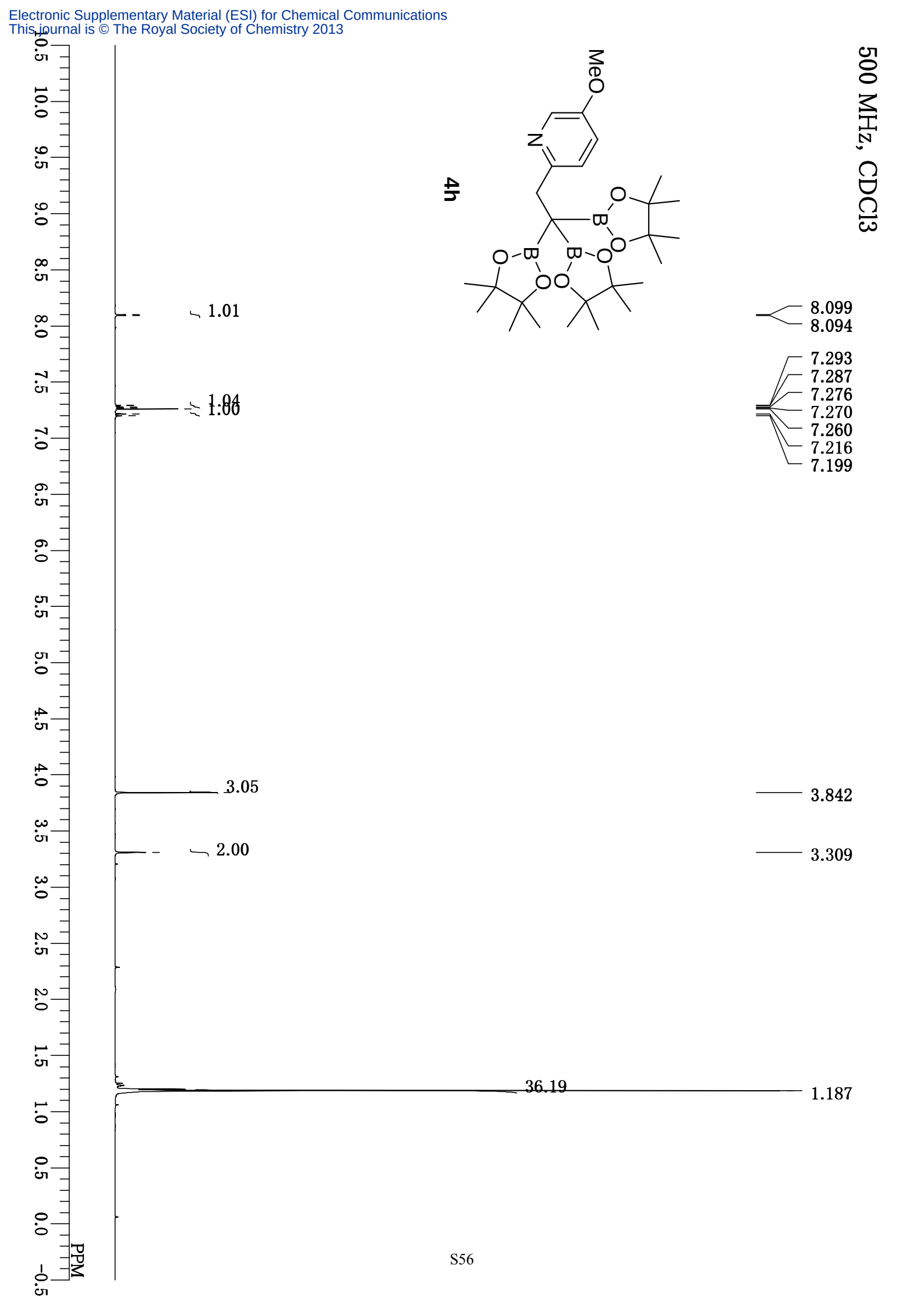
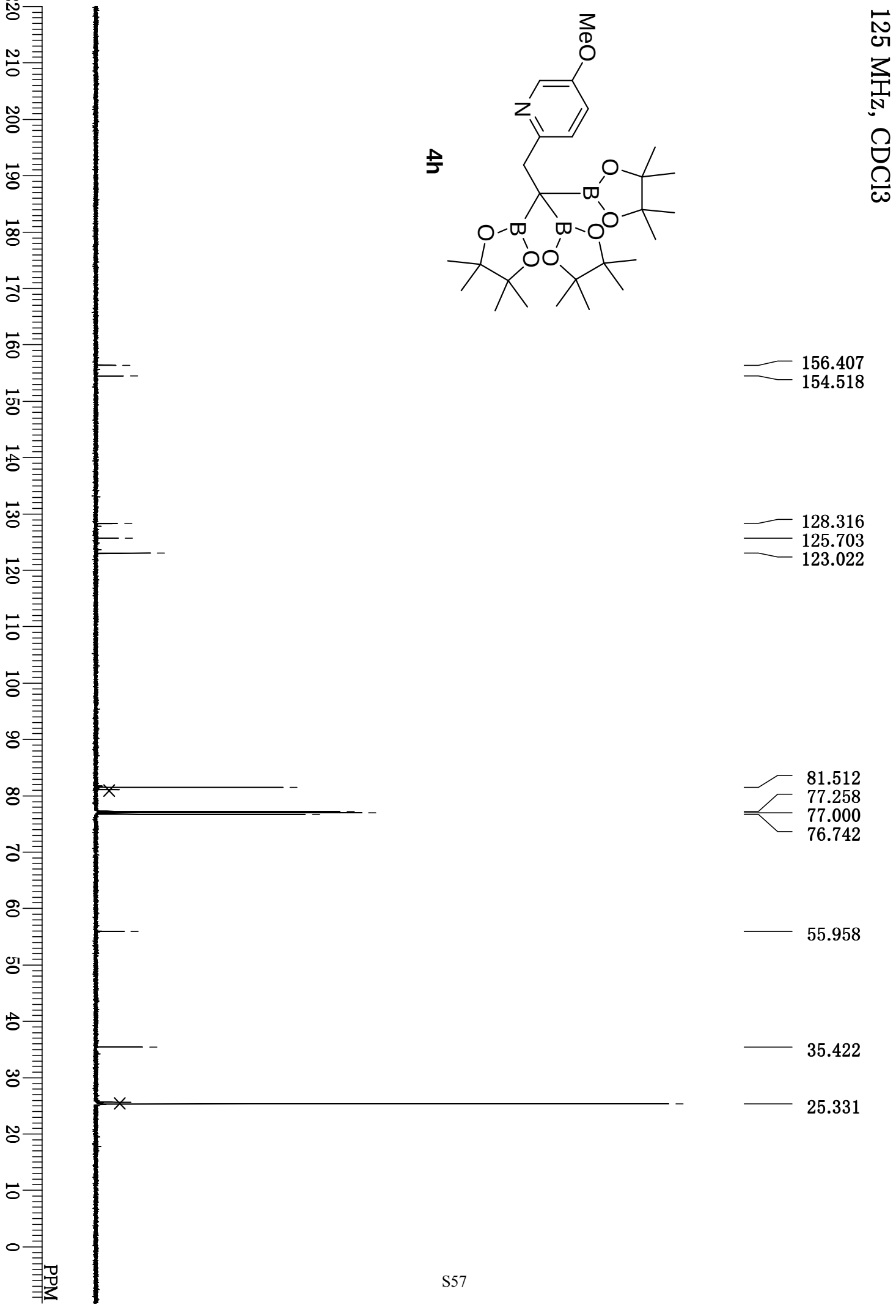
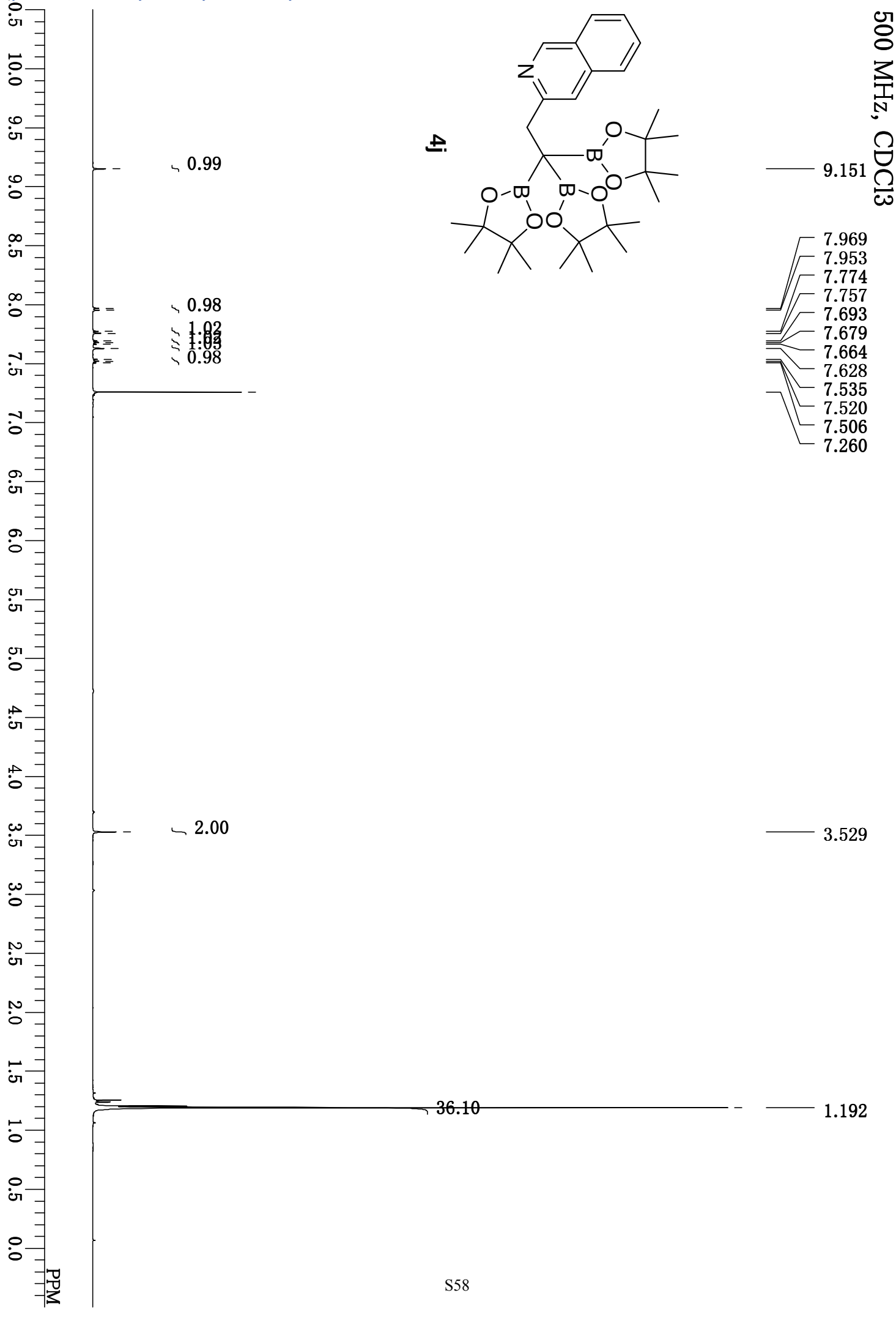
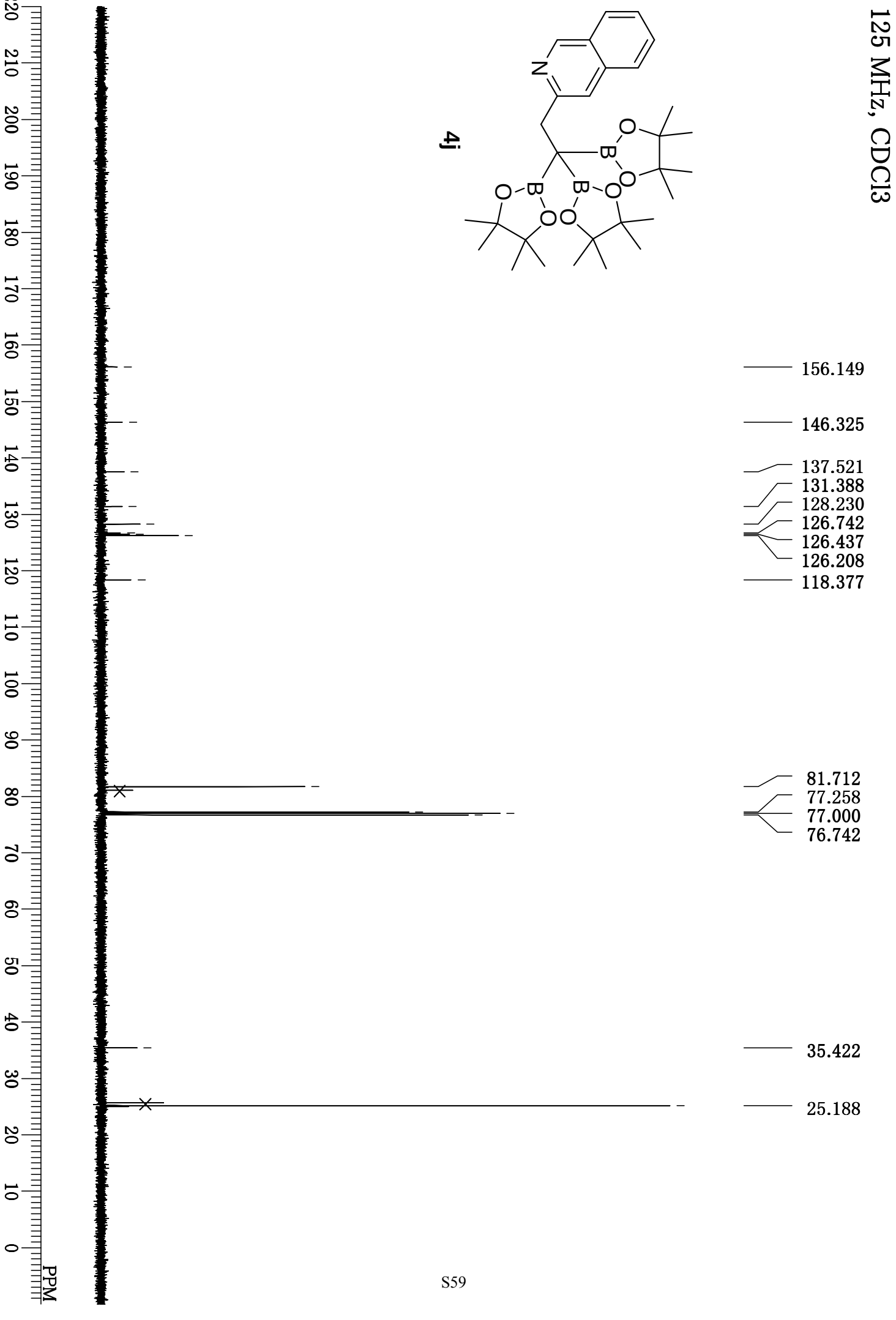
25.579
PPM





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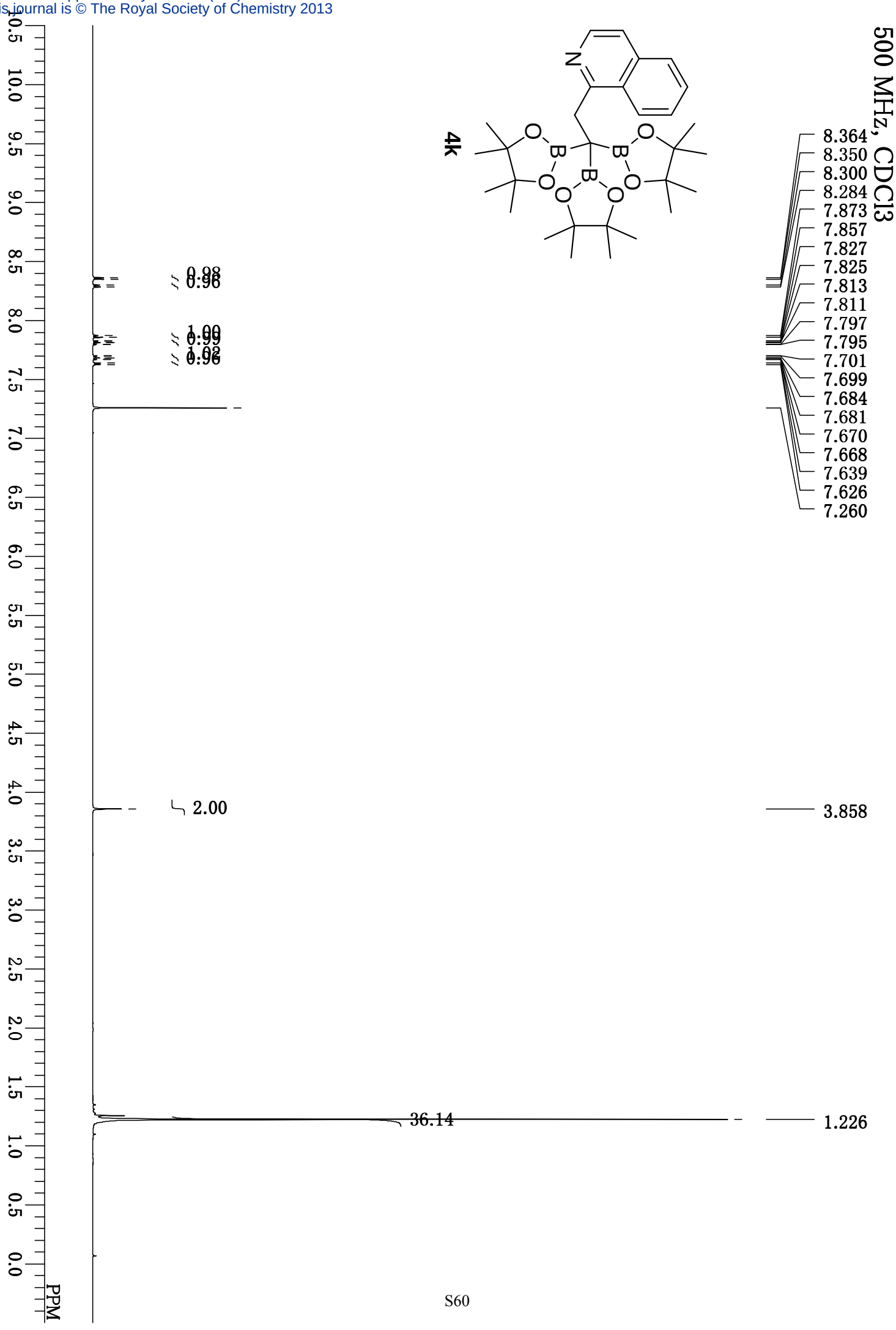
25.188
PPM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7.797
7.795
7.701
7.699
7.684
7.681
7.670
7.668
7.639
7.626
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2.00
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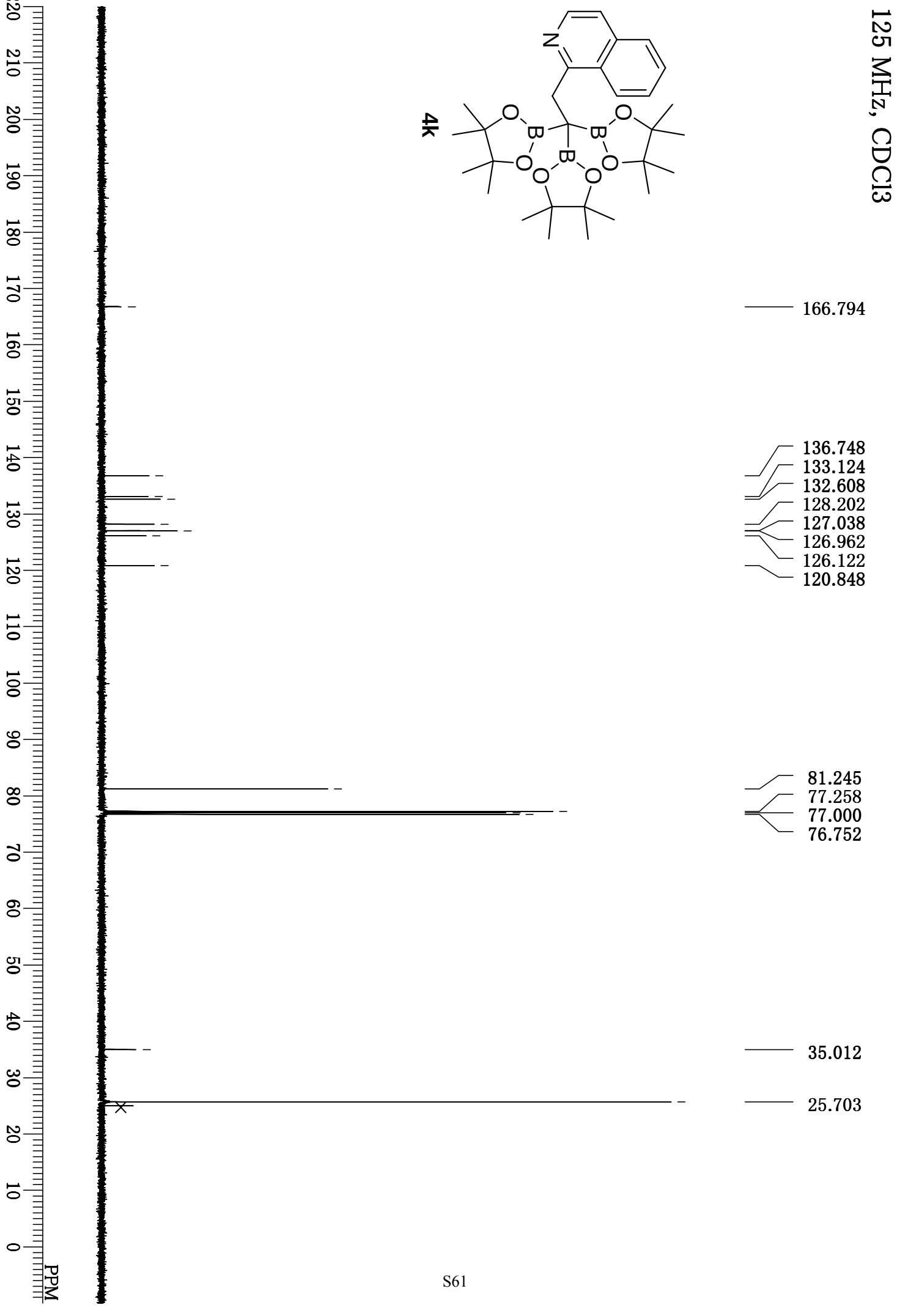
1.226
PPM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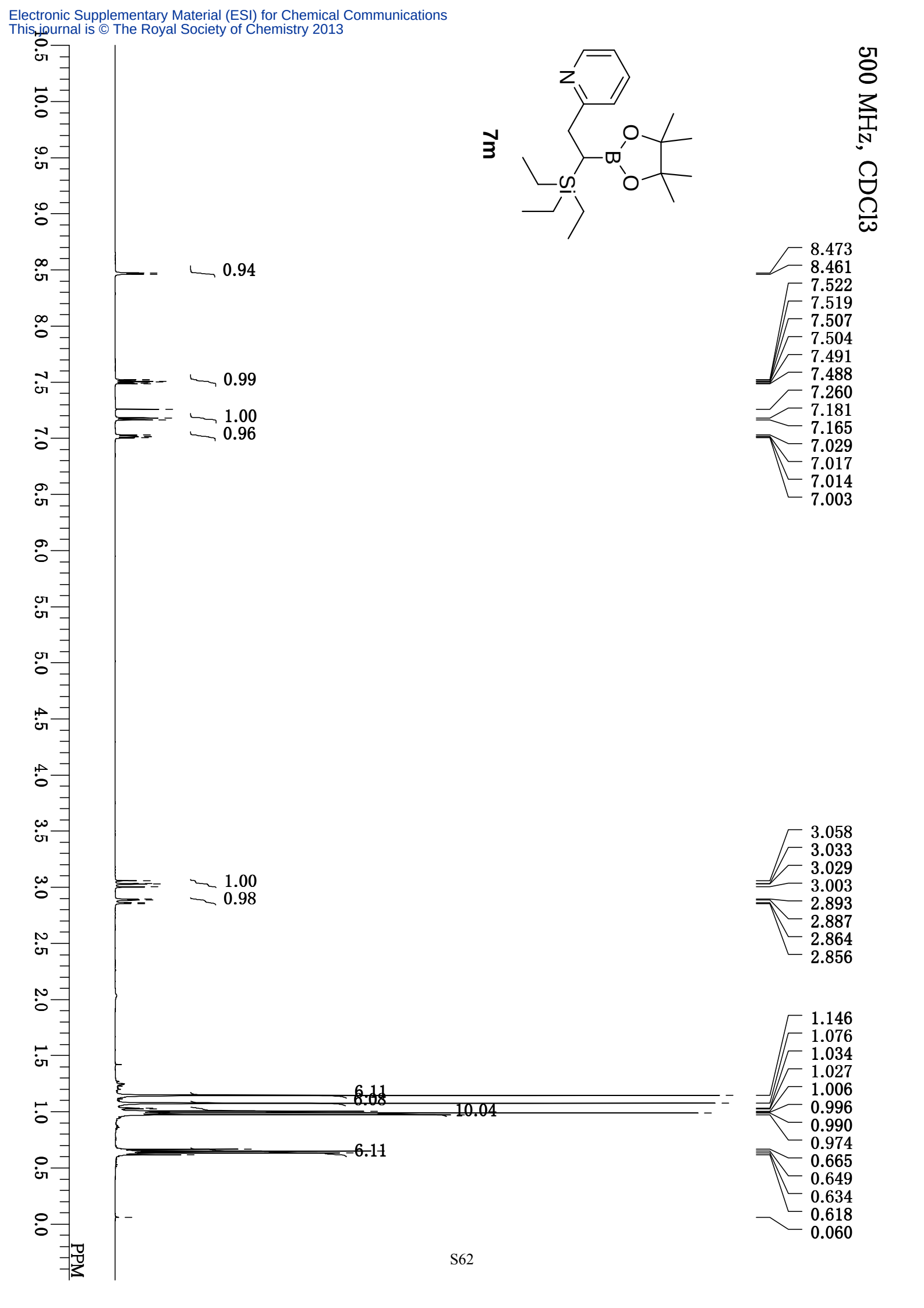
PPM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3.003
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2.864
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1.146
1.076
1.034
1.027
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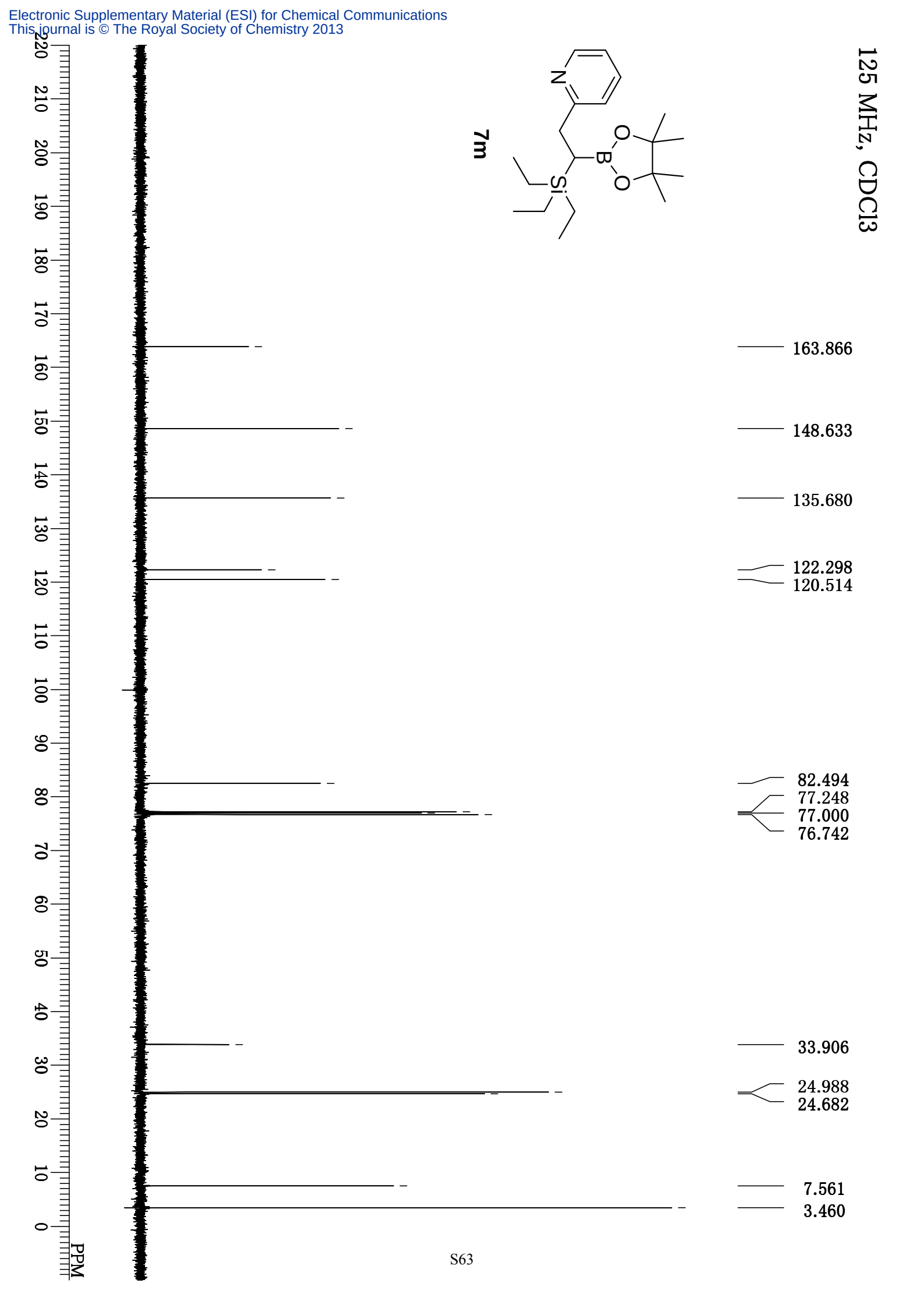

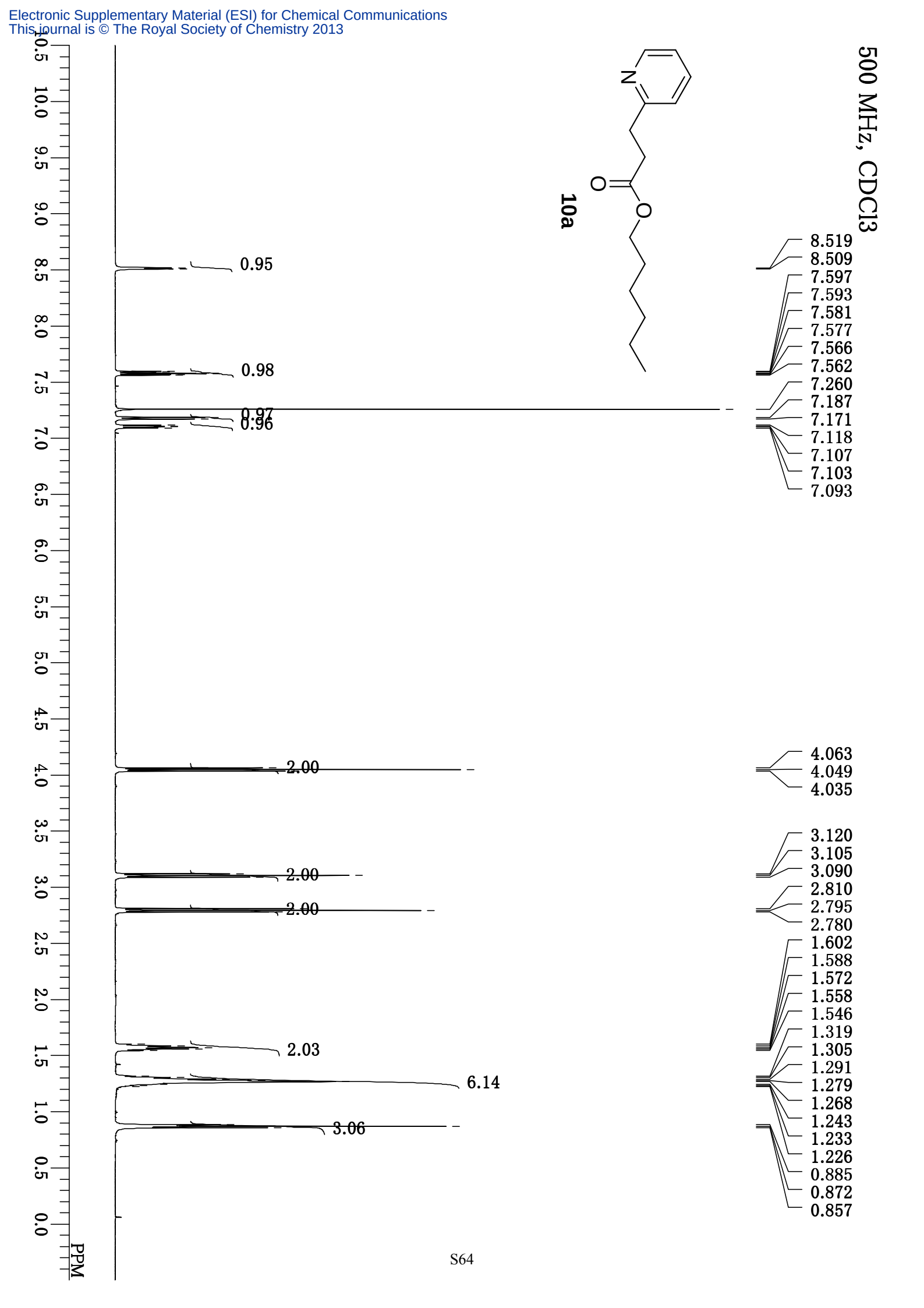

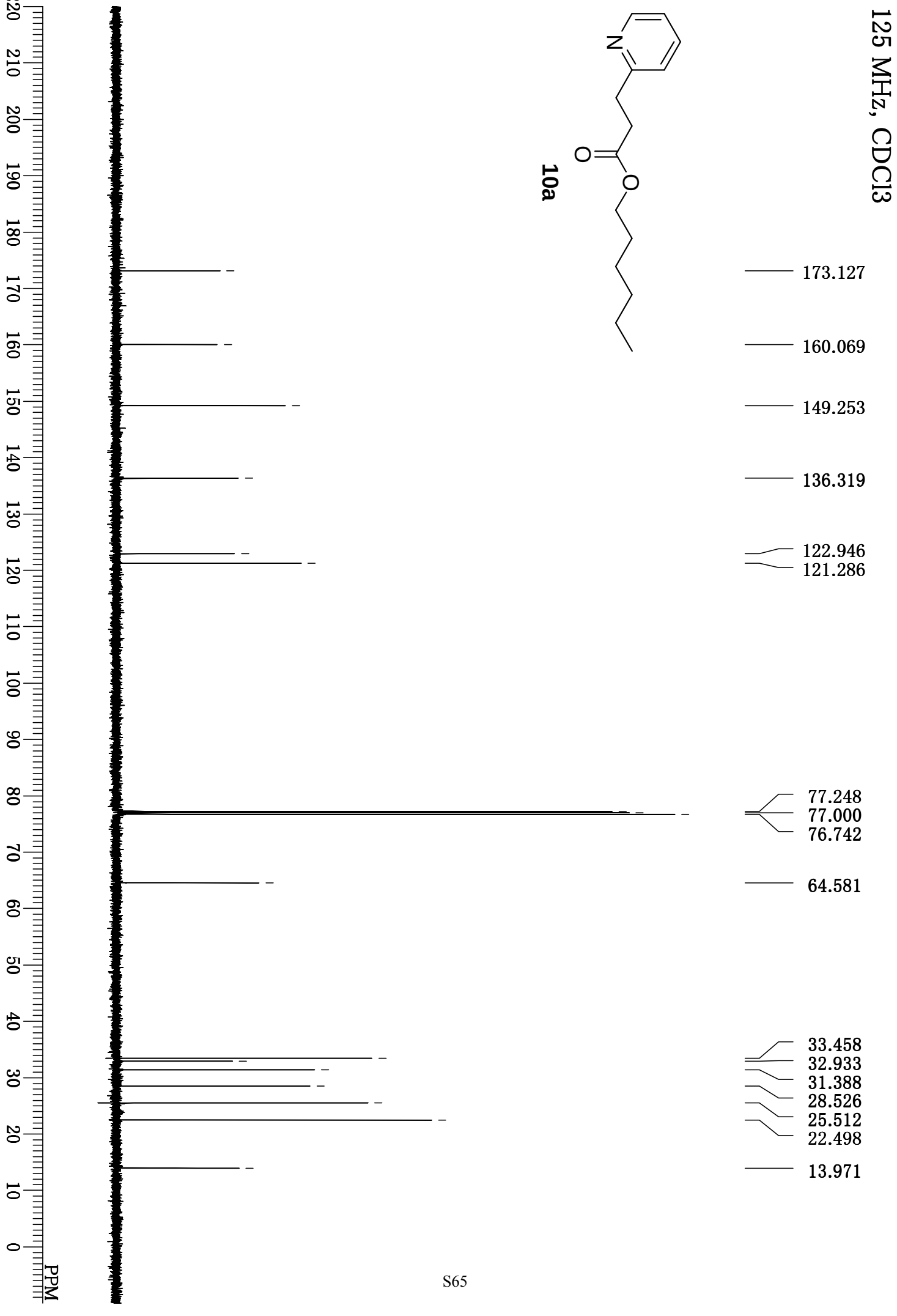

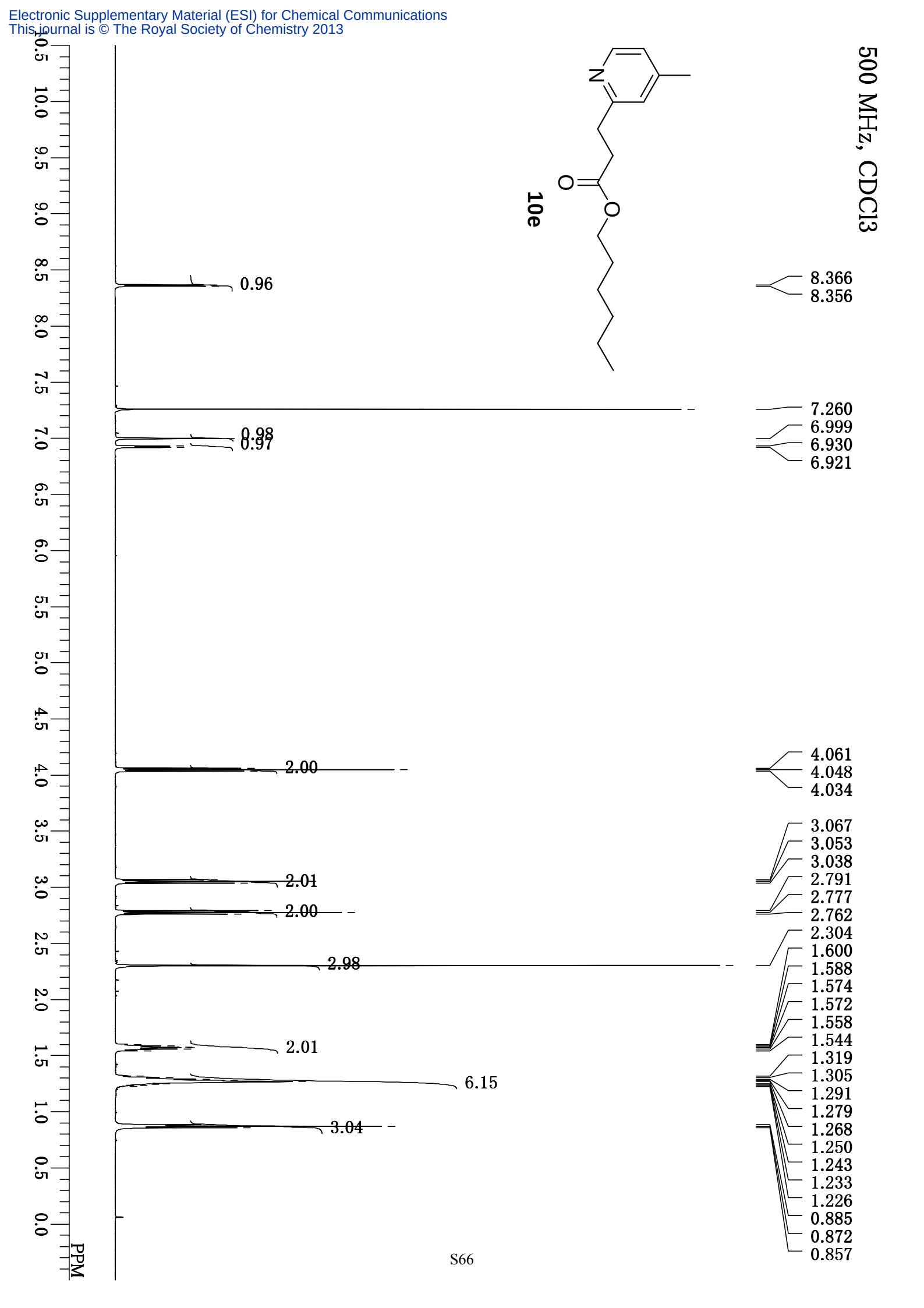

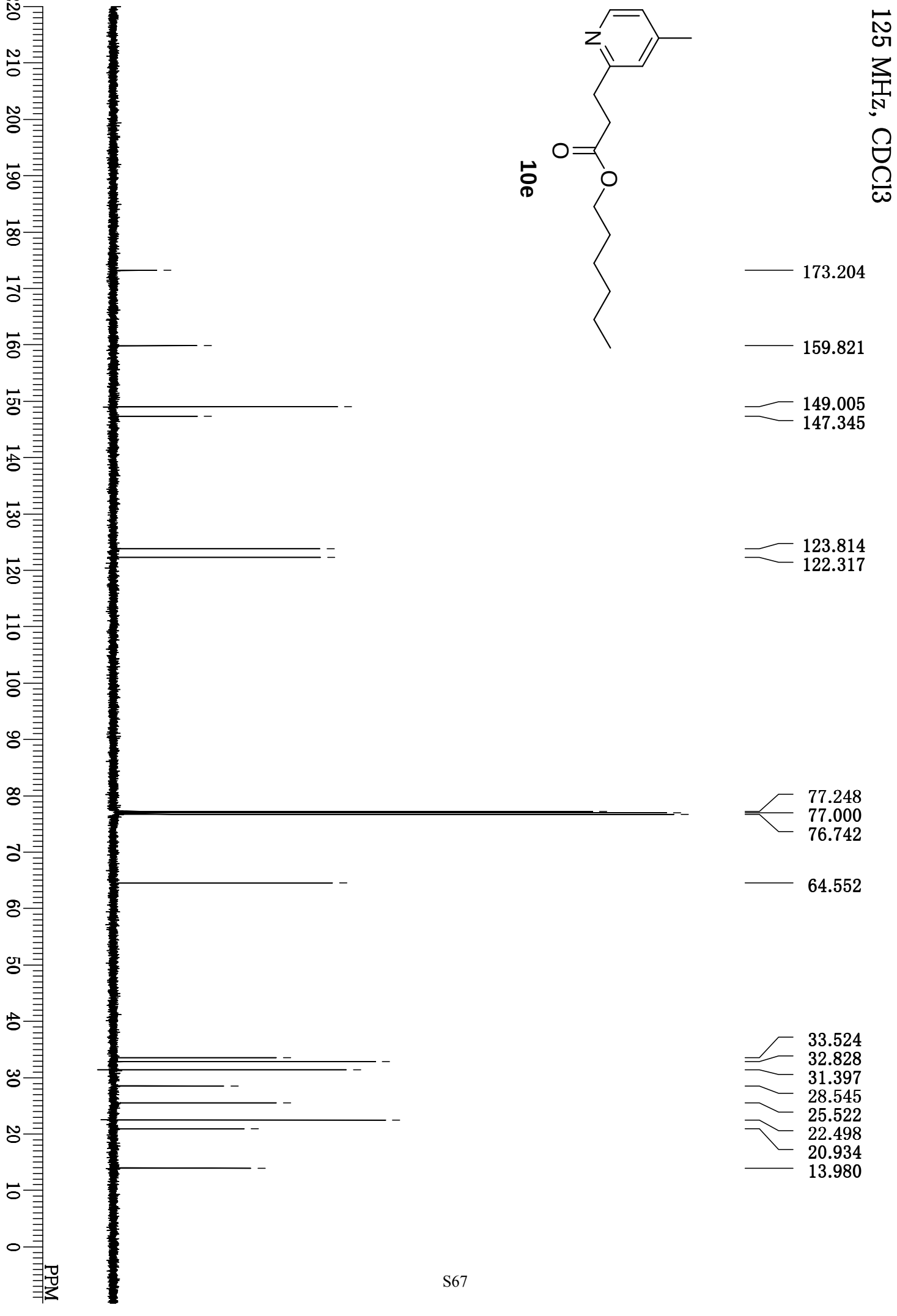
125 MHz, CDCl3
10e
N
O
O
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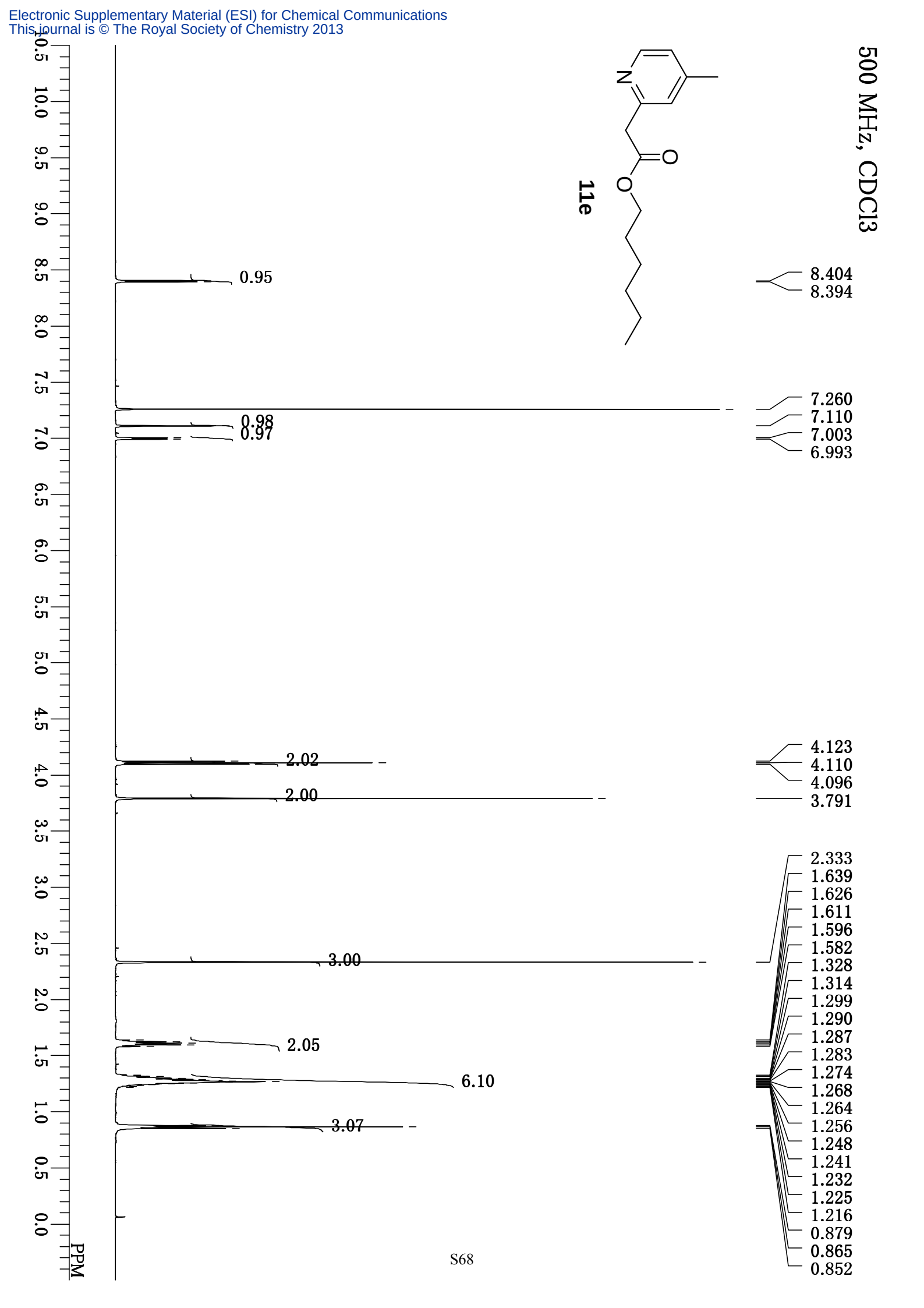
159.821
149.005
147.345
123.814
122.317
77.248
77.000
76.742
64.552
33.524
32.828
31.397
28.545
25.522
22.498
20.934
13.980
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM


500 MHz, CDCl3
11e
N
O
O
PPM
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.95
0.98
0.97
2.02
2.00
3.00
2.05
6.10
3.07
8.404
8.394
7.260
7.110
7.003
6.993
4.123
4.110
4.096
3.791
2.333
1.639
1.626
1.611
1.596
1.582
1.328
1.314
1.299
1.290
1.287
1.283
1.274
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1.248
1.241
1.232
1.225
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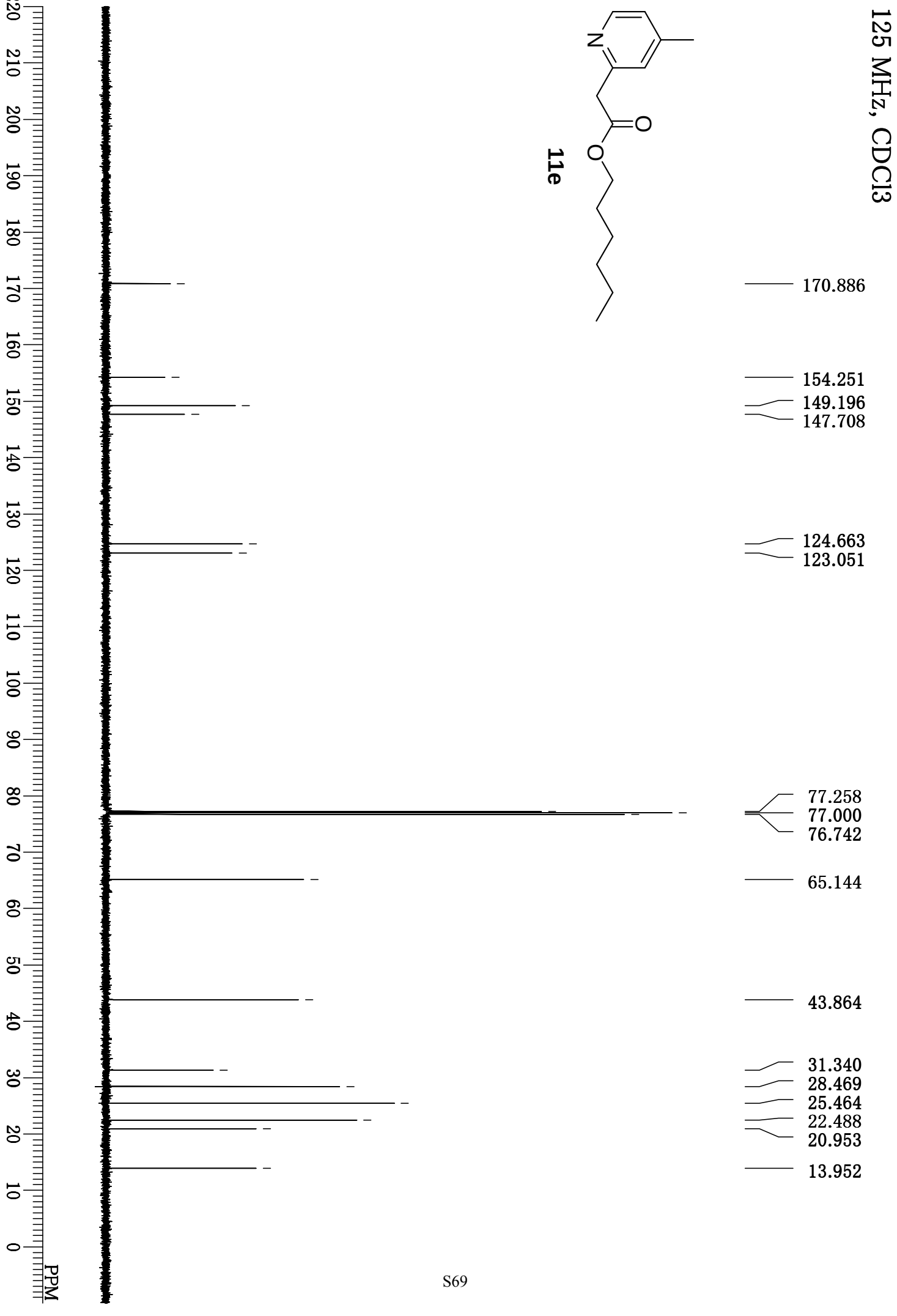
0.852


125 MHz, CDCl3
11e
N
O
O
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154.251
149.196
147.708
124.663
123.051
77.258
77.000
76.742
65.144
43.864
31.340
28.469
25.464
22.488
20.953
13.952
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
PPM