Supporting Information

Z-Selective Ethenolysis With a Ruthenium Metathesis Catalyst: Experiment and Theory

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Table of Contents

List of Figures

General Information

All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenk technique, or in a Vacuum Atmospheres Glovebox under a nitrogen atmosphere unless otherwise specified. Commercially available reagents were used as received unless otherwise noted. Substrates for ethenolysis and olefin cross metathesis were degassed with argon prior to use. Proton peaks in the ^{1}H NMR spectra corresponding to the *E*- and *Z*-isomers of all ethenolysis substrates were confirmed by HSQC analysis. THF was purified by passage through solvent purification columns and further degassed with bubbling argon.[1] C_6D_6 was purified by passage through a solvent purification column. $CDCl_3$ and acetone-d_6 were used as received. Benzylidene-bis (tricyclohexylphosphine)dichlororuthenium (**S1**), (1,3-Bis(2,4,6-trimethylphenyl)- 2-imidazolidinylidene) dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium (**S2**), and **5** were obtained from Materia, Inc. Catalyst **3** was synthesized according to a previous report.[2]

^{1}H and ^{13}C NMR spectra were recorded on a Varian 500 MHz spectrometer. Chemical shifts are reported in ppm downfield from Me_4Si by using the residual solvent peak as an internal standard. Spectra were analyzed and processed using MestReNova Ver. 7.1. High-resolution mass spectra were provided by the California Institute of Technology Mass Spectrometry Facility using JEOL JMS-600H High Resolution Mass Spectrometer. Gas chromatography data were obtained using Agilent 6850 FID gas chromatograph equipped with HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent).

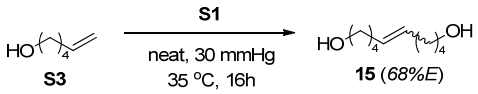
Synthesis of 12: Representative Procedure for synthesis of *E*-dominant symmetric internal olefin (metathesis homocoupling of terminal olefin):

A 50 ml Schlenk flask was charged with **14** (4.2 g, 23 mmol) and **S1** (190 mg, 0.23 mmol). The flask was sealed and placed on a vacuum line (Buchi Vacuum Controller B-721), and the mixture was stirred at 35 ˚C for 16 h under vacuum (30 mmHg). The reaction was

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, 15, 1518.

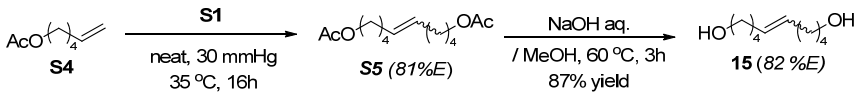
[2] Endo, K.; Grubbs, R. H. *J. Am. Chem. Soc*. **2011**, *133*, 8525.

quenched by adding tris(hydroxymethyl)phosphine[3] (840 mg, 6.8 mmol), THF (20 ml) and water (10 ml). After stirring at 60 ˚C for 4 h, the mixture was extracted with diethyl ether and the organic solution was washed with water, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/20) to give pure **12** (2.6 g, 7.7 mmol, 68% yield, 78 %*E*) as a colorless oil. ^{1}H NMR of *E*-isomer (500 MHz, $CDCl_3$): δ 5.41-5.37 (m, 2H), 4.04 (t, *J* = 6.8 Hz, 4H), 2.04 (s, 6H), 1.98-1.94 (m, 4H), 1.66-1.55 (m, 4H), 1.43-1.19 (m, 16H). ^{1}H NMR of *Z*-isomer (500 MHz, $CDCl_3$): δ 5.35-5.30 (m, 2H), 4.04 (t, *J* = 6.8 Hz, 4H), 2.04 (s, 6H), 2.02-1.99 (m, 4H), 1.66-1.55 (m, 4H), 1.43-1.19 (m, 16H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.3, 130.4, 64.7, 32.6, 29.6, 29.2, 29.1, 28.7, 26.0, 21.1. HRMS (EI+): Calc for $C_{20}H_{36}O_4$ (M^+): 340.2614. Found: 340.2607.



Synthesis of 15

This compound was prepared from **S3** (2.9 g, 29 mmol) as described in the synthesis of **12**. The crude product was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/1 ~ 3/1) to give pure **15** (1.7 g, 9.9 mmol, 67% yield, 68 %*E*) as a colorless oil. ^{1}H NMR (500 MHz, acetone-d_6): δ 5.47-5.32 (m, 2H), 3.58-3.48 (m, 4H), 3.42 (br s, 1H), 2.86-2.82 (m, 1H), 2.09-1.95 (m, 4H), 1.58-1.33 (m, 8H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 130.5, 63.0, 32.4, 32.3, 25.8. HRMS (EI+): Calc for $C_{10}H_{20}O_2$ (M^+): 172.1463. Found: 172.1467.

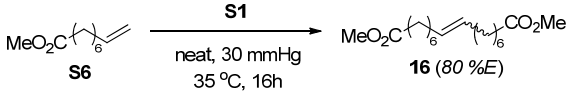


Synthesis of S5 and 15

S5 was prepared from **S4** (5.4 g, 38 mmol) as described in the synthesis of **12**. The crude product was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/9) to give pure **S5** (4.3 g, 17 mmol, 88% yield, 81 %*E*) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.44-5.32 (m, 2H), 4.05 (t, *J* = 6.7 Hz, 4H), 2.04 (s, 6H), 2.12-1.95 (m, 4H), 1.70-1.57 (m, 4H), 1.49-1.32 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.4, 130.4, 64.6, 32.2, 28.2, 26.0, 21.2. HRMS (EI+): Calc for $C_{14}H_{25}O_4$ ([M+H]$^+$): 257.1753. Found: 257.1745.

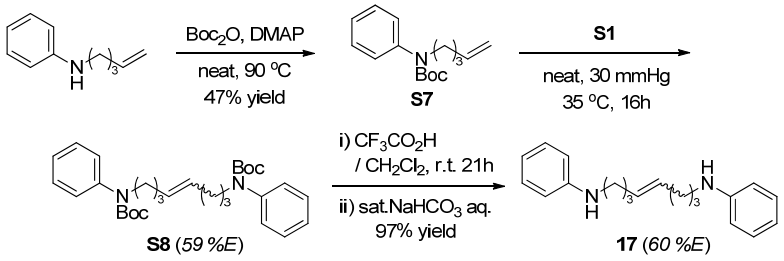
[3] Pederson, R. L.; Fellows, I. M.; Ung, T . A.; Ishihara, H.; Hajela, S. P. *Adv. Synth. Catal.* **2002**, *344*, 728.

To a solution of **S5** (4.3 g, 17 mmol, 81 %*E*) in methanol (50 ml) was slowly added a 10 *N* sodium hydroxide aqueous solution (50 ml). After stirring at 60 °C for 3 h, the mixture was extracted with dichloromethane and the organic solution was washed with a saturated ammonium chloride solution, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/1 ~ 3/1) to give pure **15** (2.5 g, 15 mmol, 87% yield, 82 %*E*) as a colorless oil.



Synthesis of 16

16 was prepared from **S6** (3.3 g, 19 mmol) as described in the synthesis of **12**. The crude product was purified by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/9 ~ 1/4) to give pure **16** (2.7 g, 8.6 mmol, 89% yield, 80 %*E*) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.42-5.29 (m, 2H), 3.66 (s, 6H), 2.30 (t, *J* = 7.6 Hz, 4H), 2.05-1.89 (m, 4H), 1.69-1.55 (m, 4H), 1.40-1.23 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.4, 130.4, 51.6, 34.2, 32.6, 29.5, 29.1, 28.8, 25.0. HRMS (FAB+): Calc for $C_{18}H_{33}O_4$ ([M+H]$^+$): 313.2379. Found: 313.2388.



Synthesis of S7, S8 , and **17**

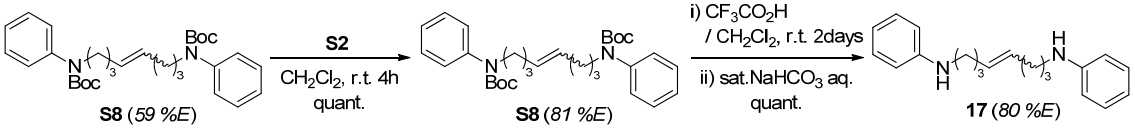
N-(Pent-4-enyl)aniline[4] (2.2 g, 14 mmol), di-*tert*-butyl dicarbonate (4.5 g, 21 mmol) and 4-(dimethylamino)pyridine (170 mg, 1.4 mmol) were combined and the mixture was stirred at 90 °C for 17 h. Di-*tert*-butyl dicarbonate (4.5 g, 21 mmol) was added to the mixture. After addition, the mixture was stirred for an additional 5 h at 90 °C and concentrated *in vacuo*. To the resulting residue was added di-*tert*-butyl dicarbonate (2.5 g, 12 mmol) and the mixture was stirred overnight at 90 °C. The mixture was concentrated *in vacuo* and then the crude product was purified by flash column chromatography (SiO_2; chloroform/*n*-

[4] Yorimitsu, H.; Wakabayashi, K.; Shinokubo, H.; Oshima. K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1963.

hexane=1/1 ~ ethyl acetate/*n*-hexane=1/9) to give pure **S7** (1.7 g, 6.4 mmol, 47% yield, 60 %*E*) as a red oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 8.3, 7.4 Hz, 2H), 7.23-7.14 (m, 3H), 5.77 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.03-4.88 (m, 2H), 3.68-3.58 (m, 2H), 2.09-2.00 (m, 2H), 1.64 (tt, *J* = 9.2, 6.5 Hz, 2H), 1.42 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.9, 142.7, 138.01, 128.9, 127.3, 126.1, 115.1, 80.2, 49.7, 31.1, 28.5, 27.8. HRMS (FAB+): Calc for $C_{16}H_{23}O_2N$ (M^+): 261.1729. Found: 261.1735.

S8 was prepared from **S7** (8.8 g, 33 mmol) as described in the synthesis of **12**. The crude product was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/100 ~ 1/50 ~ 1/20 ~ 1/10 ~ 1/7) to give pure **S8** (5.4 g, 11 mmol, 62% yield, 59 %*E*) as a pale yellow solid. ^{1}H NMR (500 MHz, C_6D_6): δ 7.14-7.06 (m, 8H), 7.01-6.93 (m, 2H), 5.35-5.18 (m, 2H), 3.73-3.54 (m, 4H), 1.97-1.81 (m, 4H), 1.59 (dq, *J* = 9.3, 7.5 Hz, 4H), 1.40 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 154.9, 142.8, 130.0, 128.8, 127.2, 126.1, 80.1, 49.8, 29.9, 28.5, 24.6. HRMS (FAB+): Calcd for $C_{30}H_{42}O_4N_2$ (M^+): 494.3145. Found: 494.3165.

To a solution of **S8** (4.0 g, 8.1 mmol, 59 %*E*) in dichloromethane (20 ml) was slowly added trifluoroacetic acid (20 ml) and the mixture was stirred for 21 h at room temperature. The reaction mixture was concentrated *in vacuo*, and chloroform and a saturated sodium bicarbonate solution was added to the resulting residue. The mixture was extracted with chloroform and the organic solution was dried over Na_2SO_4 and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (SiO_2; diethyl ether/*n*-hexane=1/4) to give pure **17** (2.3 g, 7.9 mmol, 97% yield, 60 %*E*) as an orange oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (ddd, *J* = 8.6, 7.4, 1.2 Hz, 4H), 6.72-6.66 (m, 2H), 6.63-6.56 (m, 4H), 5.54-5.39 (m, 2H), 3.66 (br, 2H), 3.16-3.07 (m, 4H), 2.25-2.03 (m, 4H), 1.75-1.63 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 148.5, 130.3, 129.4, 117.3, 112.9, 43.6, 30.2, 29.4. HRMS (FAB+): Calcd for $C_{20}H_{27}N_2$ ($[M+H]^+$): 295.2174. Found: 295.2170.



Alternative Synthesis of 17

To a solution of **S8** (1.0 g, 2.0 mmol, 59 %*E*) in dichloromethane (5.0 ml) was added **S2** (18 mg, 0.021 mmol) and the mixture was stirred for 4 h at room temperature. The reaction was quenched by adding tris(hydroxymethyl)phosphine (77 mg, 0.62 mmol), THF (20 ml) and water (20 ml). After stirring at 60 °C for 14 h, the mixture was extracted with diethyl

ether and the organic solution was washed twice with water, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product **S8** (1.1 g, quant., 81 %*E*) was used in the next step without further purification.

17 (80 %*E*) was prepared from **S8** (81 %*E*) as described in the synthesis of **17** (60 %*E*).

Synthesis of 18

18 was prepared from **S9** (4.0 g, 41 mmol) as described in the synthesis of **12**. The crude product was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/3) to give pure **18** (1.2 g, 7.1 mmol, 35% yield, 72 %*E*) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.44-5.25 (m, 2H), 2.49-2.40 (m, 4H), 2.33-2.15 (m, 4H), 2.10 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 208.4, 129.5, 43.4, 30.0, 26.7. HRMS (FAB+): Calc for $C_{10}H_{17}O_2$ ($[M+H]^+$): 169.1229. Found: 169.1235.

Representative procedure for ethenolysis at 1 atm

In a glovebox, *cis*-5-decene (19 µl, 0.10 mmol) and *trans*-5-decene (76 µl, 0.40 mmol) were combined in a 5 ml vial with a screw-cap septum top and a magnetic stir bar. A solution of the appropriate catalyst (**2** or **4**) was prepared in THF. THF and the desired volume of the catalyst solution were added to the 5-decene [THF total 160 µl and **4** (1.6 mg, 0.0025 mmol)]. (Before adding the catalyst, an aliquot was taken for ^{1}H NMR analysis to check the *E*/*Z* ratio at the starting point.) The reaction solution was sealed, removed from the glovebox, equipped with an ethylene balloon, and then purged with ethylene before heating. After the reaction solution equipped with the ethylene balloon was allowed to stir at 35 °C for 4 h, the vial was left open to air and NMR analysis was performed.

Representative procedure for ethenolysis at 5 atm

Formation of purely *E* 5-decene (11): In a glovebox, *cis*-5-decene (88 mg, 120 µl, 0.63 mmol) and *trans*-5-decene (350 mg, 470 µl, 2.5 mmol) were combined in a 5 ml vial. A solution of **4** in THF was prepared, and the appropriate amount of THF and the catalyst solution were added to the 4:1 *E*:*Z* 5-decene mixture [THF total 972 µl and **4** (9.9 mg, 0.016 mmol)], and then the reaction mixture was transferred into a Fisher-Porter bottle (before adding the catalyst, an aliquot was taken for ^{1}H NMR analysis to check the *E*/*Z* ratio at the

starting point). The Fisher-Porter bottle was equipped with a stir bar and the top of it was equipped with a pressure gauge. The system was sealed and taken out of the glovebox to the ethylene line. The vessel was then purged with ethylene (ultra-high purity 99.95% from Matheson Tri Gas), pressurized to 5 atm, and placed in an oil bath at 35 °C. After the reaction solution was allowed to stir for 4 h, the vessel was left open to air and the reaction solution was concentrated *in vacuo*. The crude mixture was then dissolved in hexane and loaded onto a silica gel column for purification (100% *n*-hexane as the eluting solvent). Upon concentration of the fractions containing product, 5-decene was obtained as a colorless oil (310 mg, 2.2 mmol, 72% yield, >95 %*E*).

Formation of purely *E* compound 12:

In a glovebox, **12** (1.0 g, 3.0 mmol, 78% *E*) was added to a 5 ml vial. A solution of **4** in THF was prepared, and the appropriate amount of THF and the catalyst solution were added to the solution [THF total 750 μl and **4** (9.5 mg, 0.015 mmol)], and then the reaction mixture was transferred into a Fisher-Porter bottle (before adding the catalyst, an aliquot was taken for ^{1}H NMR analysis to check the *E*/*Z* ratio at the starting point). The Fisher-Porter bottle was equipped with a stir bar and the top of it was equipped with a pressure gauge. The system was sealed and taken out of the glovebox to the ethylene line. The vessel was then purged with ethylene (ultra-high purity 99.95% from Matheson Tri Gas), pressurized to 5 atm, and placed in an oil bath at 35 °C. After the reaction solution was allowed to stir for 4 h, the vessel was left open to air and the reaction solution was concentrated *in vacuo*. The crude mixture was then dissolved in hexane and purified by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/20). Upon concentration of the fractions containing product, **12** (790 mg, 2.3 mmol, 77% yield, >95 %*E*) and **14** (240 mg, 1.3 mmol, 21% yield) were obtained as colorless oils.

Procedure for the ethenolysis of methyl oleate:

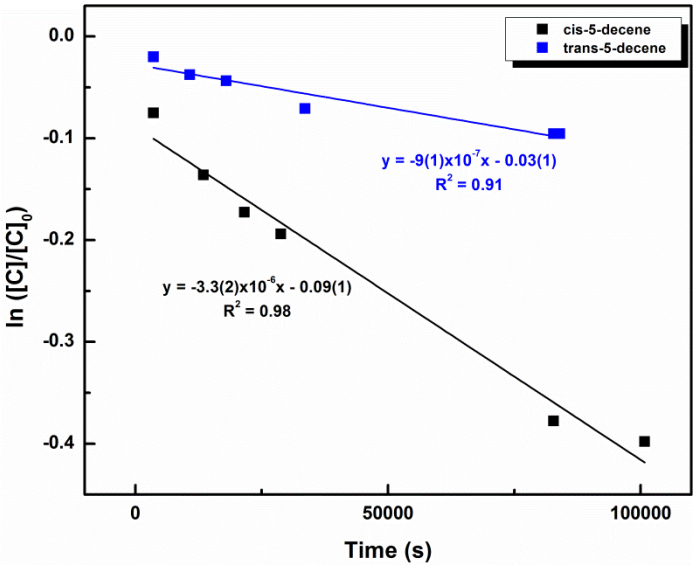
Ethenolysis reactions were carried out using research-grade methyl oleate (>99%) that was purified by storage over actived alumina followed by filtration. The experiments were set up in a glovebox under an atmosphere of argon. Methyl oleate (10 g, 34 mmol) was charged in a Fisher-Porter bottle equipped with a stir bar, pressure gauge and dip-tube adapted to the bottle. A solution of the appropriate ruthenium catalyst (**2** or **4**) was prepared in dry dichloromethane, and the desired volume of this solution was added to the methyl oleate. The reaction vessel was sealed, removed from the glovebox and then attached to an ethylene line. The reaction vessel purged three times with ethylene (polymer purity 99.9%

from Matheson Tri Gas), pressurized to 150 psi, and placed in an oil bath at 40 ˚C. The reaction was monitored by collecting samples via the dip-tube at different routine intervals and immediately quenched by the addition of a solution of tris(hydroxymethyl)phosphine (1.0 mL, 1.0 M) in isopropanol. The samples were then heated to 60 ˚C for 1 hour, diluted with distilled water, extracted with hexanes, and analyzed by GC. The GC analyses were run using a flame ionization detector. Column: Rtx-5 from Restek, 30 m - 0.25 mm i.d. - 0.25 µm film thickness. GC and column conditions: injection temperature, 250 ˚C; detector temperature, 280 ˚C; oven temperature, starting temperature, 100 ˚C; hold time, 1 min. The ramp rate was 10 ˚C/min to 250ºC, hold time 12 min; carrier gas helium.

Kinetic measurement procedure:

In a glovebox, **4** (23 mg, 0.036 mmol) and anthracene (internal standard, 69 mg, 0.49 mmol) were dissolved in 5 mL of C_6D_6 (ca. 0.0072 M in catalyst). A portion (13 uL) of this solution was added to a J. Young NMR tube followed by C_6D_6 (570 uL) and olefin (10 uL, 0.095 mmol). The tube was quickly sealed, removed from the glovebox, cooled to -78 °C and freeze-pump-thawed (x3). After the final freeze-pump-thaw cycle, the NMR tube was backfilled with an atmosphere of ethylene, sealed, and allowed to warm to RT. An initial NMR spectrum was taken at RT to get initial concentrations after which the tube was placed in a 50 °C oil bath. Over a period of ca. 24 h the NMR tube was periodically removed from the oil bath and the reaction was analyzed by NMR spectrometry.

The ethenolysis of cis-5-decene reached a maximum of 30% while that of trans-5-decene was 10%. Therefore, the first-order kinetic plots below only take into account the early stages of the reaction, before equilibrium is established.



Alternatively, at these low concentrations, the method of initial rates can be used to compute the ratio of d[cis-5-decene]/dt to d[trans-5-decene]/dt. As shown in the table below, the ratio of the rates derived from the method of initial rates is similar to the ratio of the rate constants obtained from the linear fits in the figure above.

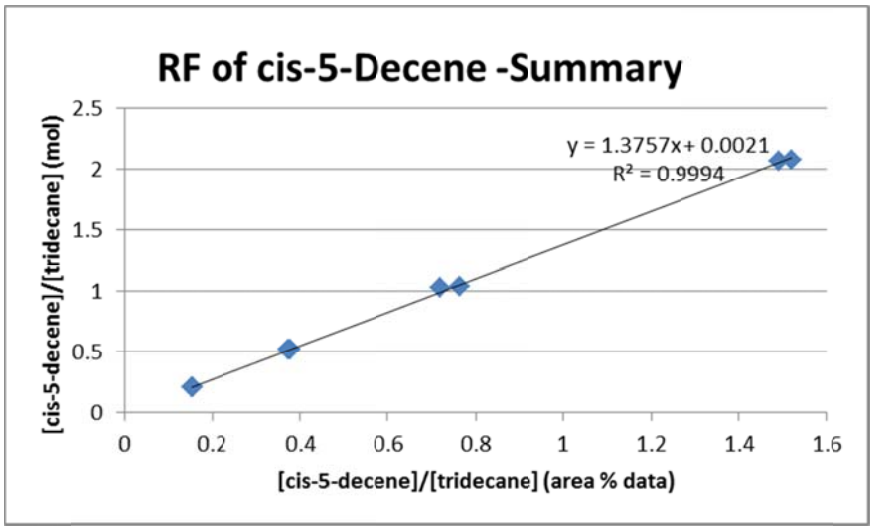
d[cis-5-decene]/dt	d[trans-5-decene]/dt	ratio
1.5×10^{-6}	4.3×10^{-7} M s^{-1}	3.4

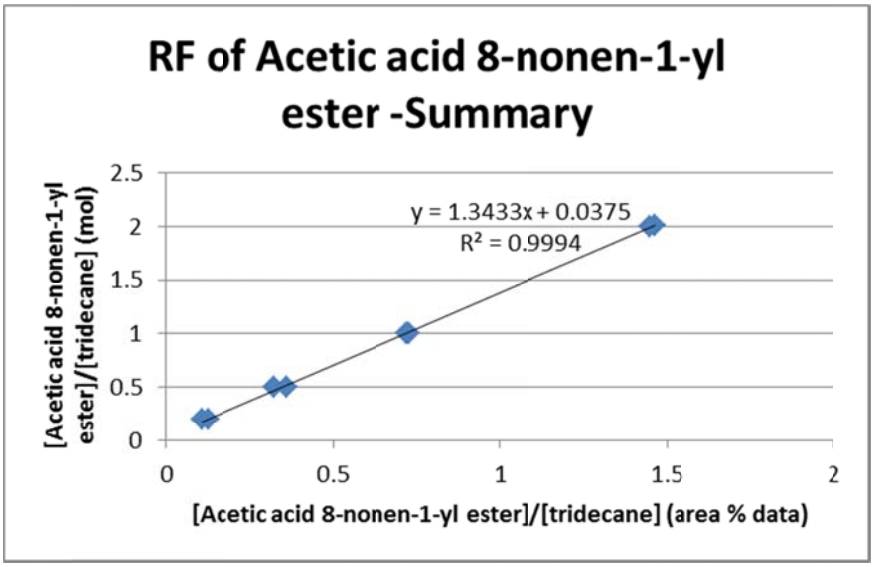
GC Data Analysis for Cross Metathesis

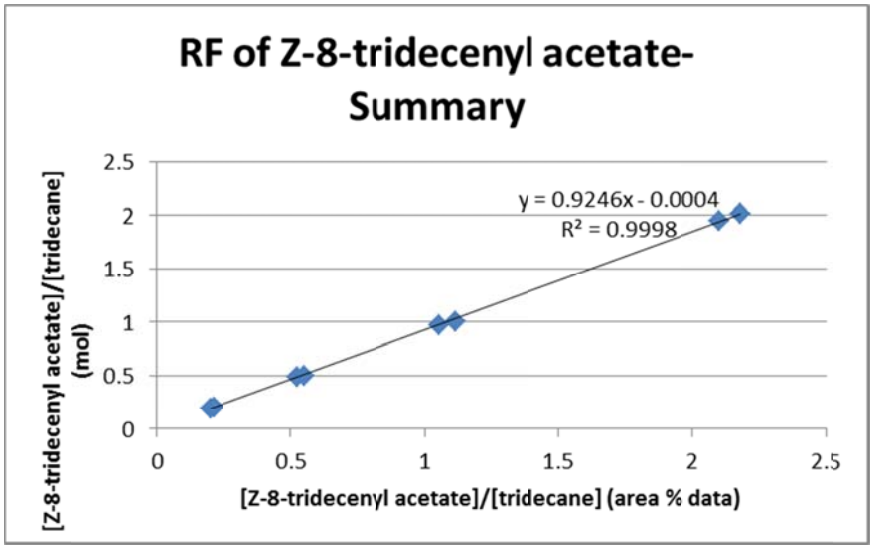
To obtain accurate conversion data, GC response factors for all starting materials and products (ethylene and 1-hexene excluded) were obtained and GC data was analyzed according to the literature.[5] Tridecane was used as an internal standard. Samples for GC analysis were obtained by adding ca. 10-30 µl of the reaction mixture to 1 ml of ethyl vinyl ether. The resulting sample was shaken, allowed to stand for 5 min, and then analyzed via GC.

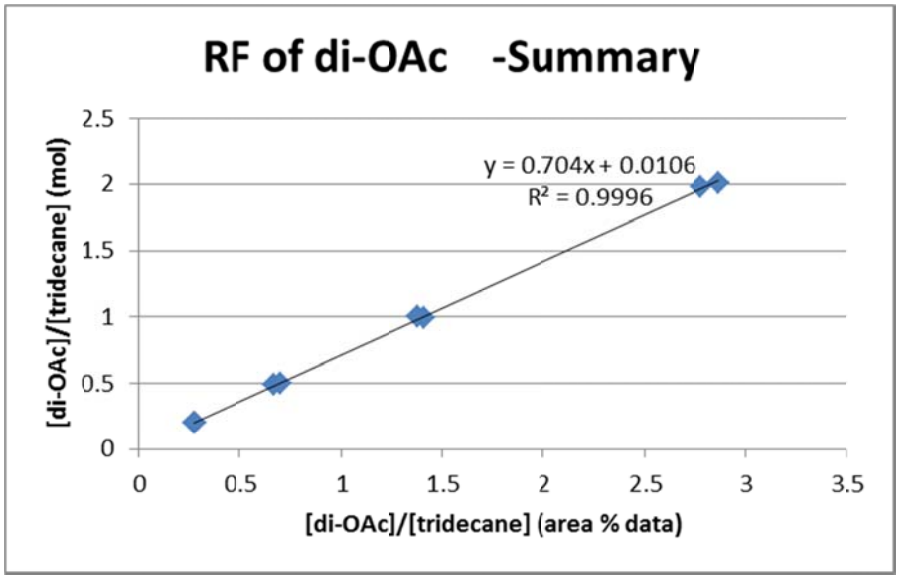
GC instrument conditions: inlet temperature: 250 °C; detector temperature: 250 °C; hydrogen flow: 30 ml/min; air flow: 400 ml/min.; constant col + makeup flow: 25 ml/min.
GC Method: A) 50 °C for 4 min, followed by a temperature increase of 6 °C/min to 300 °C and a subsequent isothermal period at 300 °C for 5 min. or B) 50 °C for 2 min, followed by a temperature increase of 12 °C/min to 110 °C and a subsequent isothermal period at 110 °C for 2 min. ~ a temperature increase of 6 °C/min to 115 °C and a subsequent isothermal period at 115 °C for 0.5 min. ~ a temperature increase of 5 °C/min to 140 °C. ~ a temperature increase of 12 °C/min to 210 °C and a subsequent isothermal period at 210 °C for 2 min. ~ a temperature increase of 6 °C/min to 250 °C ~ a temperature increase of 15 °C/min to 300 °C and a subsequent isothermal period at 300 °C for 5 min.

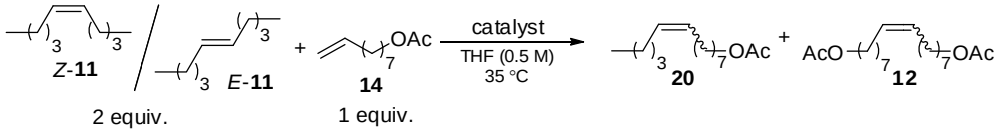
[5] Ritter, T.; Hejl, A.; Wenzel, A. G.; Funk, T. W.; Grubbs, R. H. *Organometallics* **2006**, *25*, 5740.


RF of cis-5-Decene -Summary
y = 1.3757x + 0.0021
R² = 0.9994
[cis-5-decene]/[tridecane] (mol)
[cis-5-decene]/[tridecane] (area % data)
0
0.5
1
1.5
2
2.5
0.2
0.4
0.6
0.8
1.2
1.4
1.6


RF of Acetic acid 8-nonen-1-yl ester -Summary
y = 1.3433x + 0.0375
R² = 0.9994
[Acetic acid 8-nonen-1-yl ester]/[tridecane] (mol)
[Acetic acid 8-nonen-1-yl ester]/[tridecane] (area % data)
0
0.5
1
1.5
2
2.5


RF of Z-8-tridecenyl acetate-Summary
y = 0.9246x - 0.0004
R² = 0.9998
[Z-8-tridecenyl acetate]/[tridecane] (mol)
[Z-8-tridecenyl acetate]/[tridecane] (area % data)
0
0.5
1
1.5
2
2.5



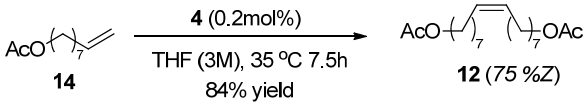


Representative procedure for cross metathesis of 14 with *cis*-5-decene (*Z*-11) or *trans*-5-decene (*E*-11) with catalyst 4:

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with *cis*-5-decene (370 µl, 280 mg, 2.0 mmol) or *trans*-5-decene (370 µl, 280 mg, 2.0 mmol), 8-noneyl acetate (210 µl, 180 mg, 1.0 mmol) and tridecane (120 µl, 92 mg, 0.50 mmol). A solution of catalyst **4** was prepared in THF. THF and the desired volume of the catalyst solution were added to the reaction mixture [THF total 1.3 mL and **4** (1.3 mg, 0.0020 mmol)]. (Before adding the catalyst, an aliquot was taken for GC analysis to check the molar ratio of each compound at the starting point.) The vial was sealed with a screw-cap and then stirred at 35 °C. After the reaction solution was allowed to stir for 6 h, an aliquot was taken for GC analysis to obtain the yield. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring overnight at room temperature, the mixture was concentrated *in vacuo*. The resulting mixture was separable by flash column chromatography (SiO_2; *n*-hexane ~ ethyl

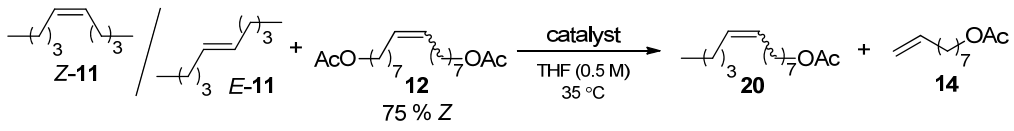
acetate/*n*-hexane=1/40 ~ 1/30 ~ 1/9) to give pure **20**, **14**, and **12** as colorless oils. The NMR data for **20** matched literature precedence.[6]

Procedure for cross metathesis of 14 with *cis*-5-decene (*Z*-11) or *trans*-5-decene (*E*-11) with catalyst 2: According to the above procedure, *cis*-5-decene (190 µl, 140 mg, 1.0 mmol) or *trans*-5-decene (190 µl, 140 mg, 1.0 mmol), 8-noneyl acetate (105 µl, 90 mg, 0.5 mmol) and tridecane (60 µl, 46 mg, 0.25 mmol) were added to a 5 mL vial. A solution of catalyst **2** was prepared in THF. THF and the desired volume of the catalyst solution were added to the reaction mixture [THF total 0.65 mL and **2** (8.2 mg, 0.013 mmol)]. These reactions were worked up according to the above procedure.



Synthesis of *Z*-12

In a glovebox, a 20 ml vial was charged with **14** (3.2 g, 17 mmol) and **4** (22 mg, 0.035 mmol) and THF (6.0 ml). The vial was sealed with a screw-cap and then stirred at 35 °C for 7.5 h. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring for overnight at room temperature, the mixture was concentrated *in vacuo*. The resulting residue was purified by flash column chromatography (SiO_2; ethyl acetate/*n*-hexane=1/50 ~ 1/20 ~ 1/4) to give pure **12** (2.5 g, 7.3 mmol, 84% yield, 75 %*Z*) as a colorless oil. The NMR data for **12** matched that reported earlier in the supporting information.



Representative procedure for cross metathesis of *cis*-5-decene (*Z*-11) or *trans*-5-decene (*E*-11) with 12 *without ethylene* in the presence of catalyst 4:

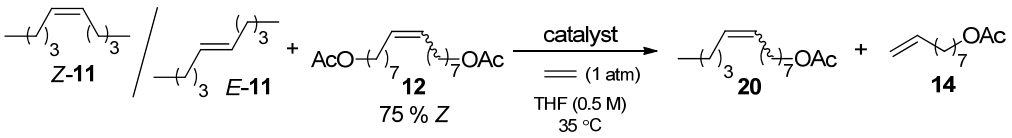
In a glovebox, a 5 ml vial with a magnetic stir bar was charged with *cis*-5-decene (95 µl, 70 mg, 0.5 mmol) or *trans*-5-decene (95 µl, 70 mg, 0.5 mmol), **12** (170 mg, 0.50 mmol, 75 %Z) and tridecane (61 µl, 46 mg, 0.25 mmol). A solution of catalyst **4** was prepared in THF. THF and the desired volume of the catalyst solution were added to reaction mixture [THF total

[6] Keitz, B. K.; Endo, K.; Patel, P. R.; Herbert, M. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **2012**, 134, 693.

675 µl and **4** (3.2 mg, 0.0050 mmol)]. (Before adding the catalyst, an aliquot was taken for GC analysis to check the molar ratio of each compound at the starting point.) The vial was sealed with a screw-cap and then stirred at 35 °C. After the reaction solution was allowed to stir for 2 h, an aliquot was taken for GC analysis to obtain the yield. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring for overnight at room temperature, the mixture was concentrated *in vacuo*. The resulting mixture was separable by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/40 ~ 1/30 ~ 1/9) to give pure **20**, **14**, and **12** as colorless oils.

Procedure for cross metathesis of *cis*-5-decene (*Z*-11) or *trans*-5-decene (*E*-11) with 12 *without ethylene* in the presence of catalyst 2:

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with *cis*-5-decene (95 µl, 70 mg, 0.5 mmol) or *trans*-5-decene (95 µl, 70 mg, 0.5 mmol), **12** (170 mg, 0.50 mmol, 75 %Z) and tridecane (61 µl, 46 mg, 0.25 mmol). A solution of catalyst **4** was prepared in THF. THF and the desired volume of the catalyst solution were added to reaction mixture [THF total 675 µl and **2** (8.2 mg, 0.013 mmol)]. These reactions were worked up according to the above procedure.



Representative procedure for cross metathesis of *cis*-5-decene (*Z*-11) or *trans*-5-decene (*E*-11) with 12 *with ethylene* in the presence of catalyst 4:

In a glovebox, a 5 ml vial with a magnetic stir bar was charged with *cis*-5-decene (94 µl, 70 mg, 0.50 mmol) or *trans*-5-decene (94 µl, 70 mg, 0.50 mmol), **12** (170 mg, 0.50 mmol, 75 %Z) and tridecane (61 µl, 46 mg, 0.25 mmol). A solution of catalyst **4** was prepared in THF. THF and the desired volume of the catalyst solution were added to reaction mixture [THF total 675 µl and **4** ((3.2 mg, 0.0050 mmol))]. (Before adding the catalyst, an aliquot was taken for GC analysis to check the molar ratio of each compound at the starting point.) The reaction solution was sealed with a screw-cap septum top, removed from the glovebox, equipped with an ethylene balloon, and then purged with ethylene before heating. After the reaction solution equipped with the ethylene balloon was allowed to stir at 35 °C for 2 h, the vial was brought in the glovebox again. The reaction mixture was stirred at 35 °C while open to the glovebox atmosphere. After the reaction solution was allowed to stir for 4.5 h,

an aliquot was taken for GC analysis to obtain the yield. The vessel was removed from the glovebox and left open to air, and then the reaction solution was transferred to a 50 ml flask with using ethyl vinyl ether (ca. 10 ml). After stirring for overnight at room temperature, the mixture was concentrated *in vacuo*. The resulting mixture was separable by flash column chromatography (SiO_2; *n*-hexane ~ ethyl acetate/*n*-hexane=1/40 ~ 1/30 ~ 1/9) to give pure **20**, **14**, and **12** as colorless oils.

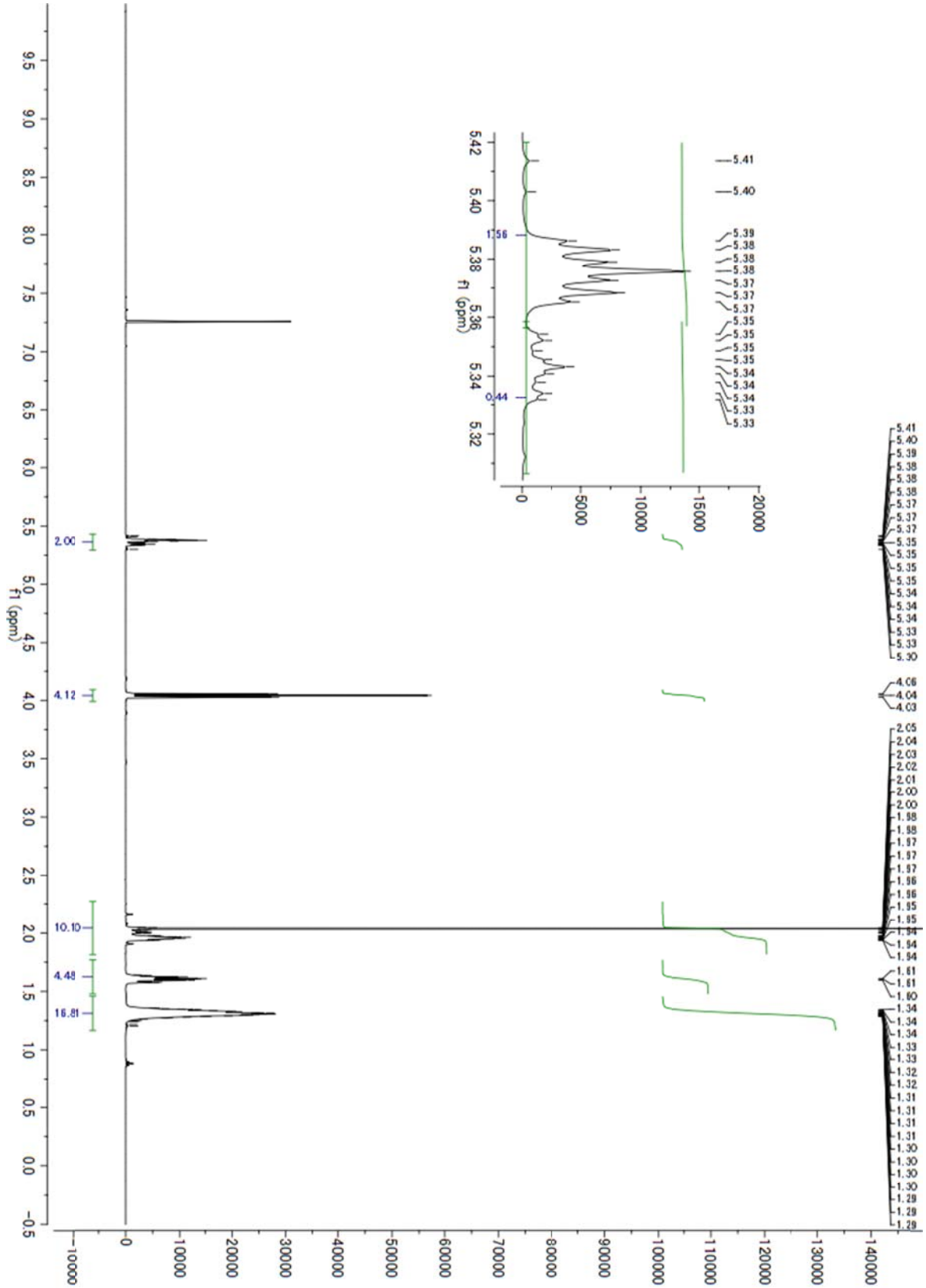


Figure S1. ^{1}H NMR (500 MHz) spectrum of **12** in $CDCl_3$.

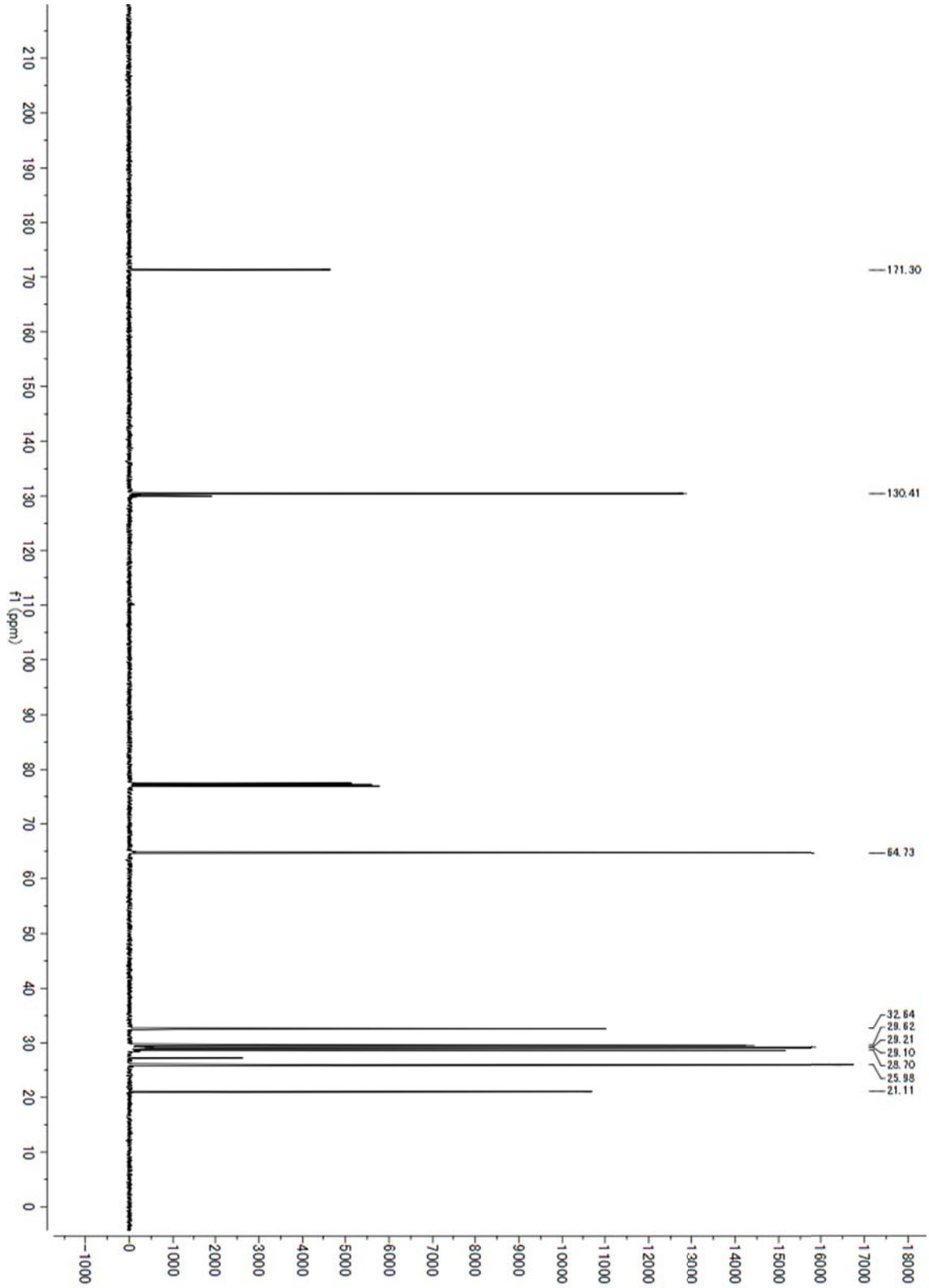


Figure S2. ^{13}C NMR (126 MHz) spectrum of **12** in $CDCl_3$.

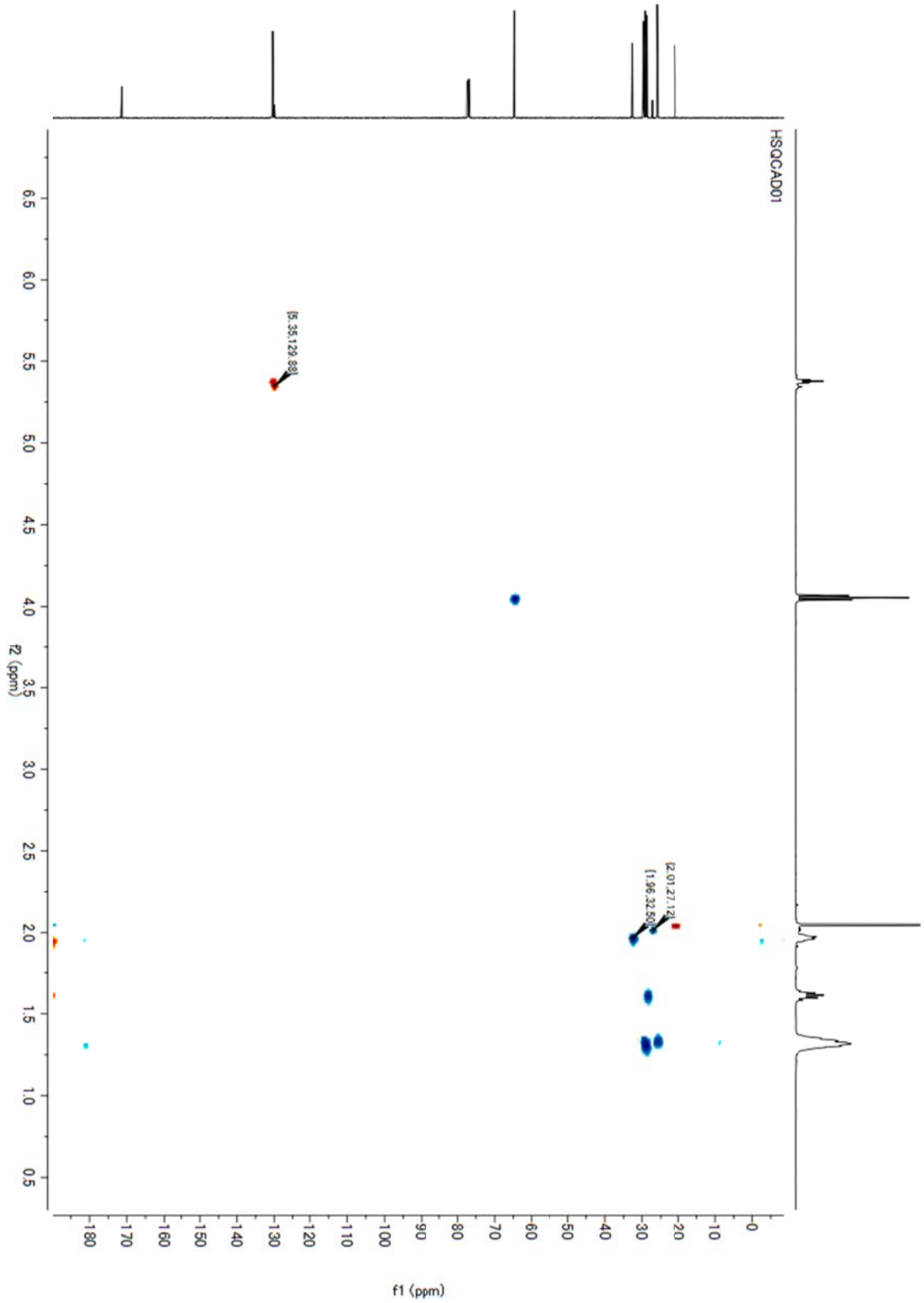


Figure S3. ^{1}H-^{13}C HSQC of **12** in $CDCl_3$.

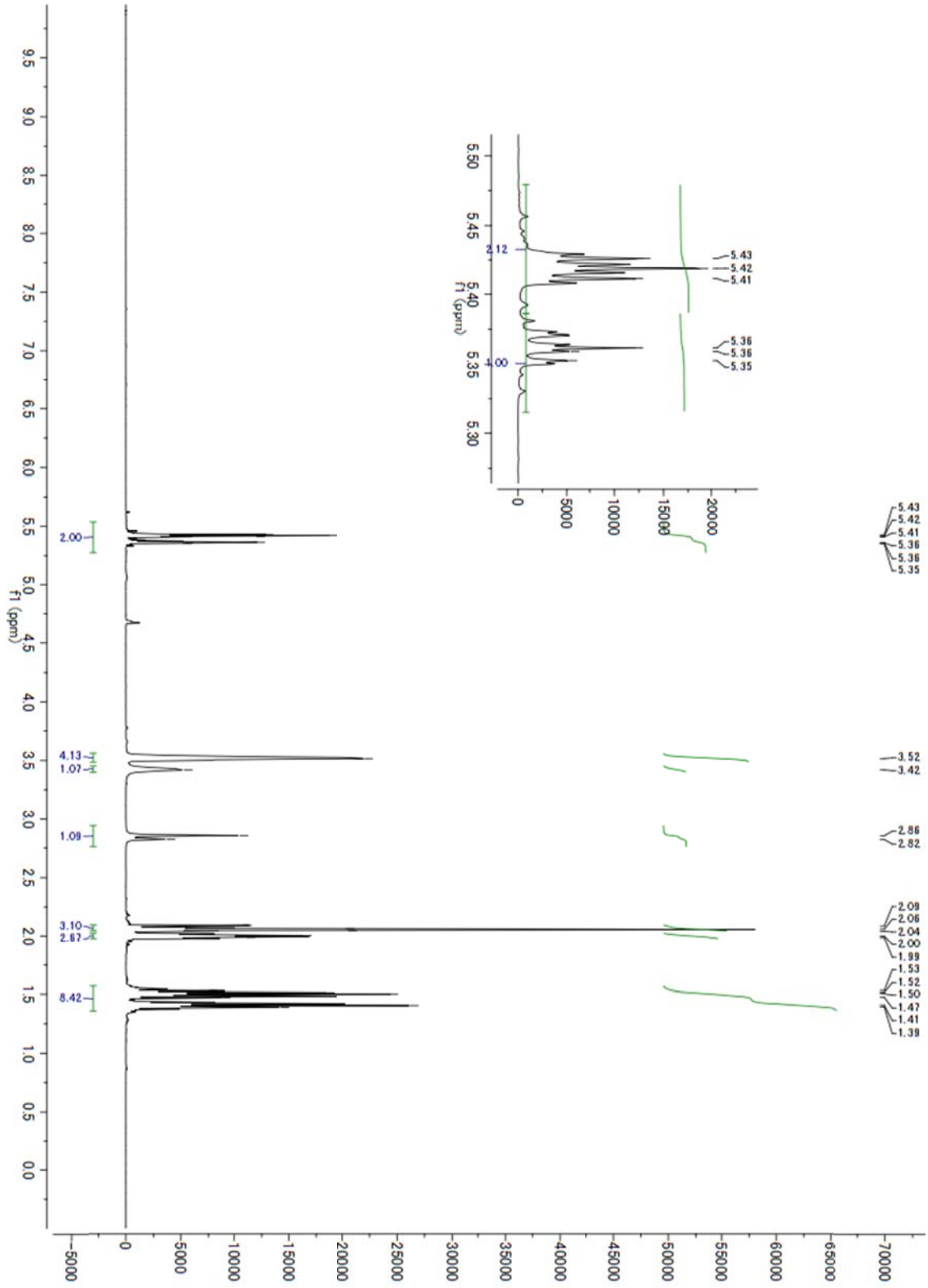


Figure S4. ^{1}H NMR (500 MHz) spectrum of **15** in acetone-d_6.

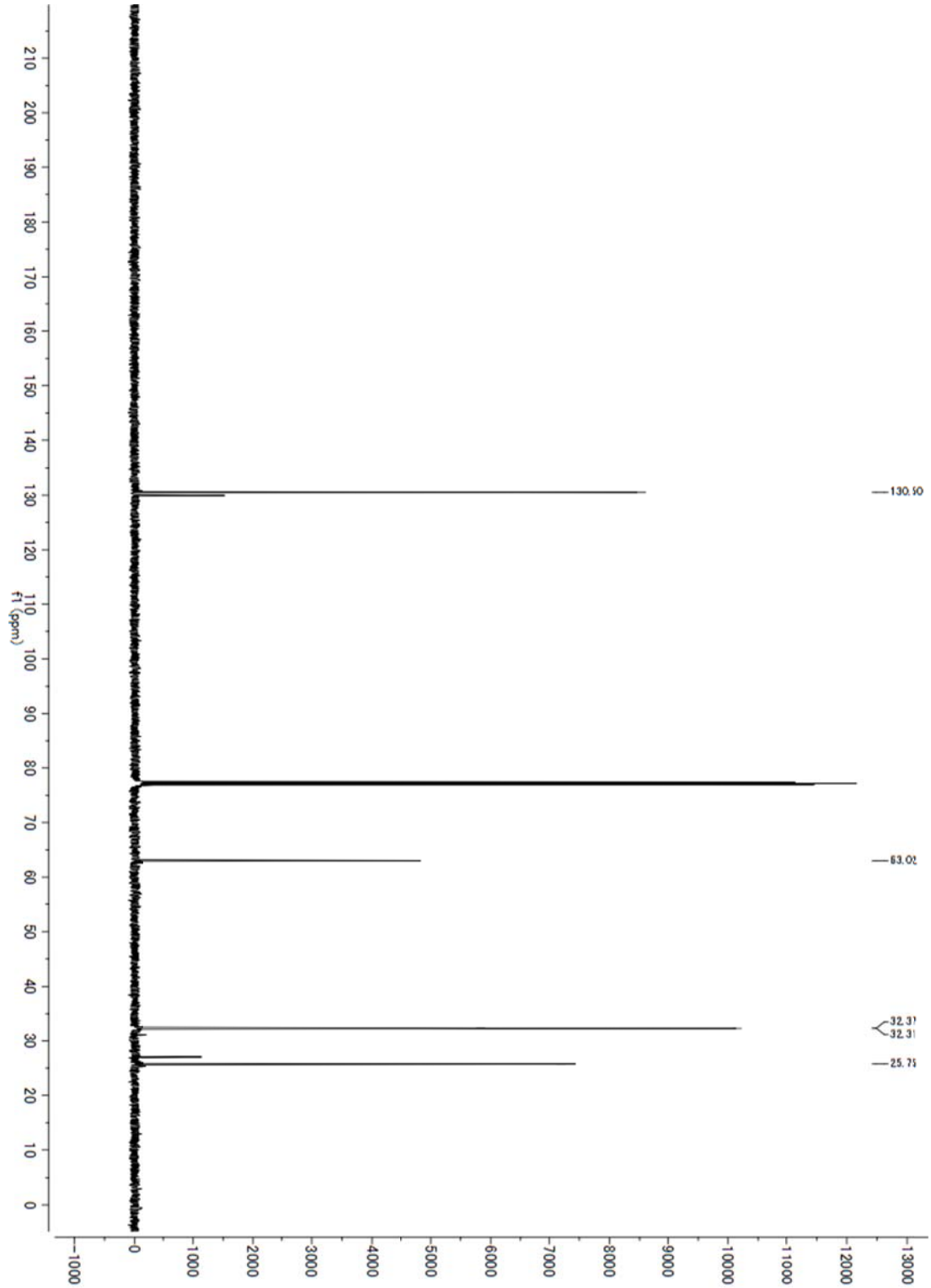


Figure S5. ^{13}C NMR (126 MHz) spectrum of **15** in $CDCl_3$.

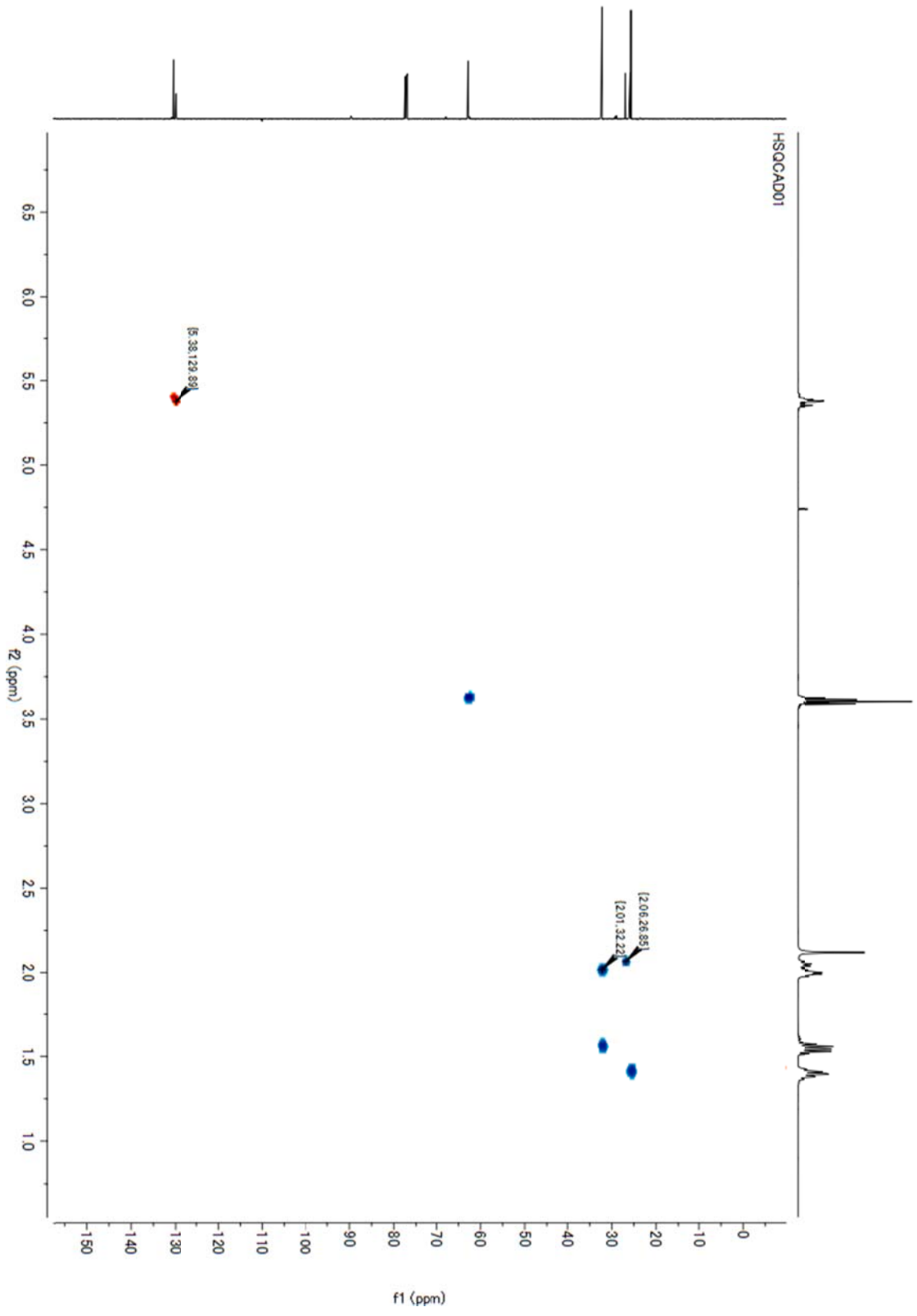


Figure S6. ^{1}H-^{13}C HSQC of **15** in $CDCl_3$.

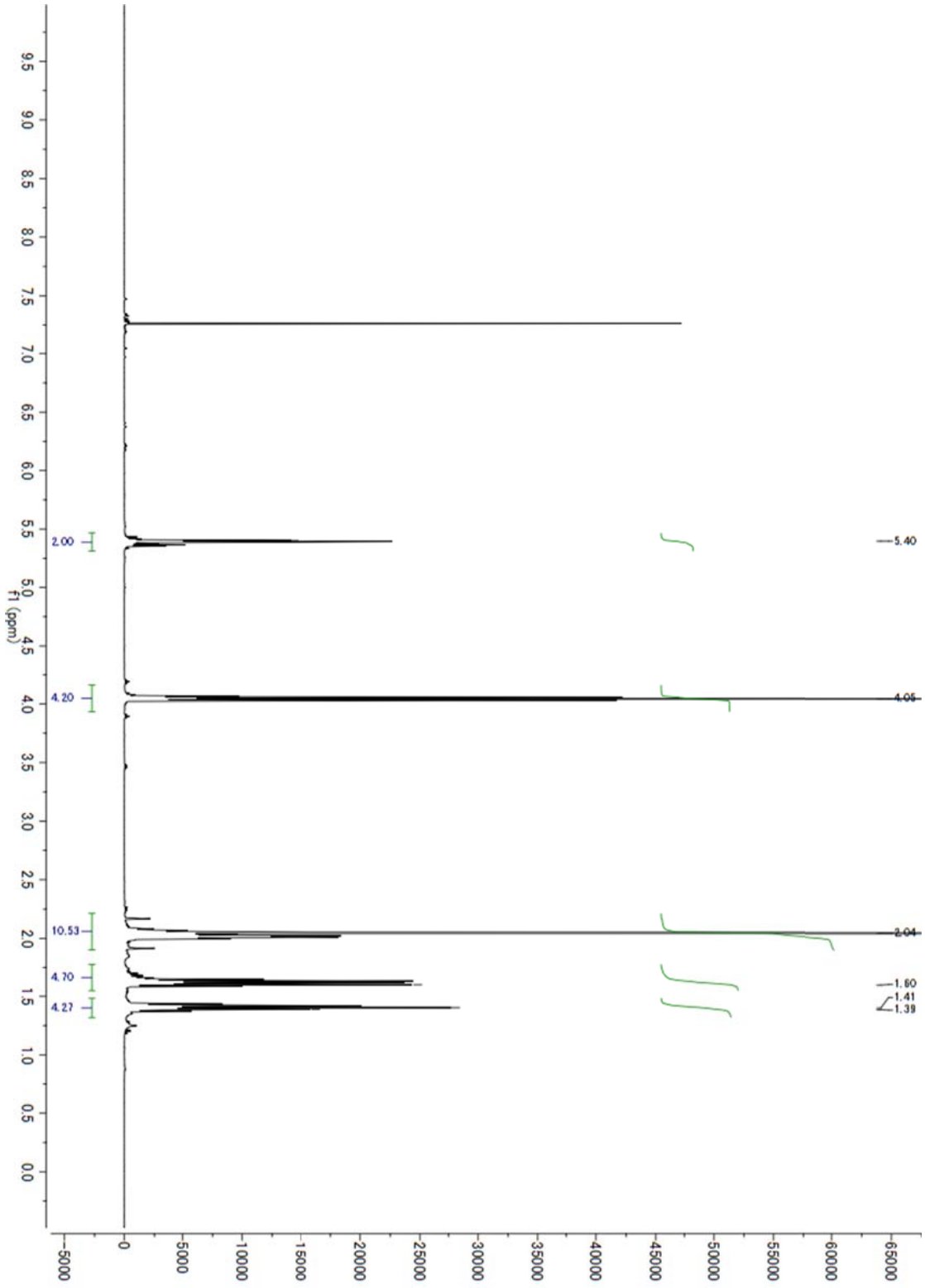


Figure S7. ^{1}H NMR (500 MHz) spectrum of **S5** in $CDCl_3$.

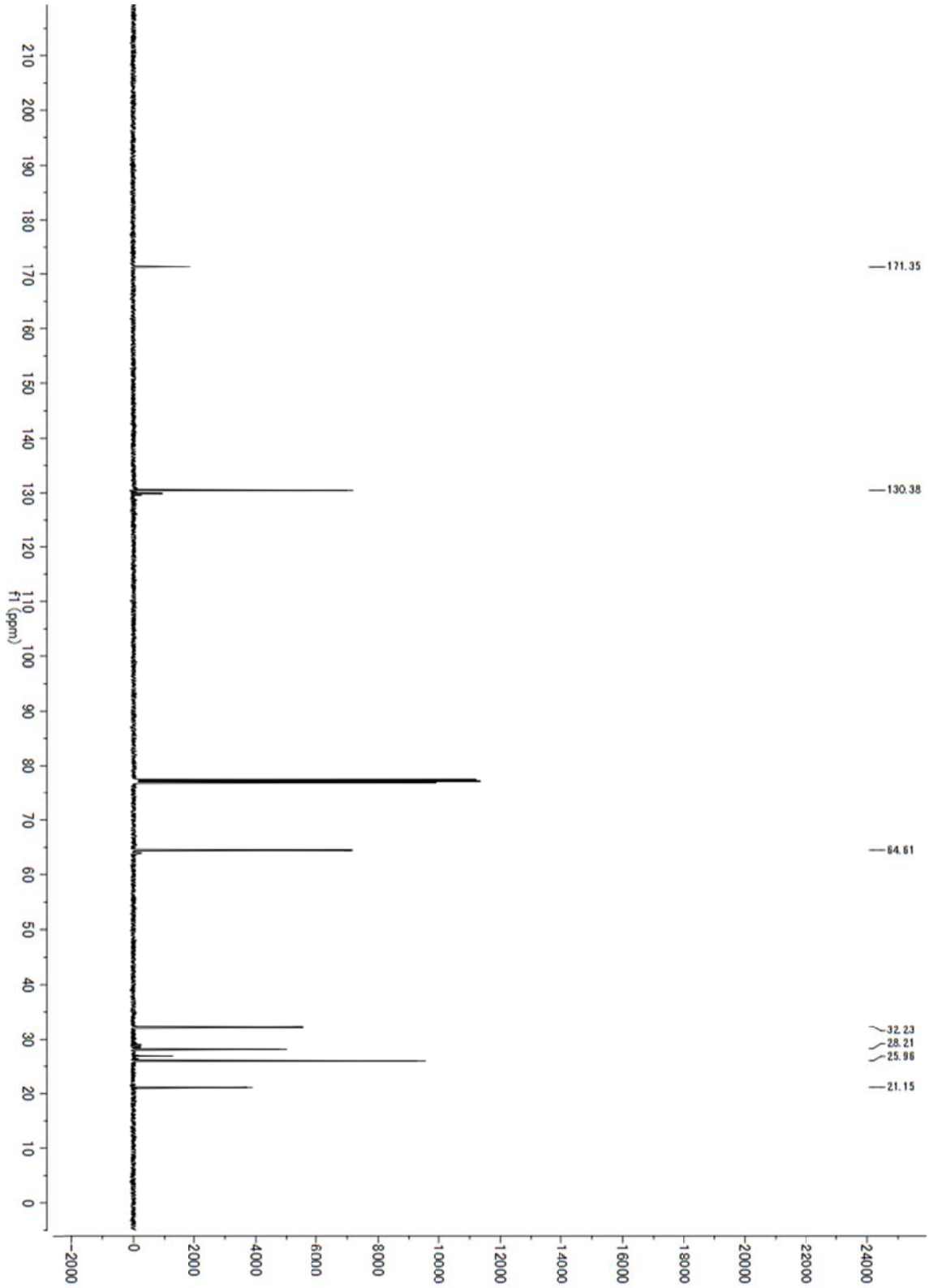


Figure S8. ^{13}C NMR (126 MHz) spectrum of **S5** in $CDCl_3$.

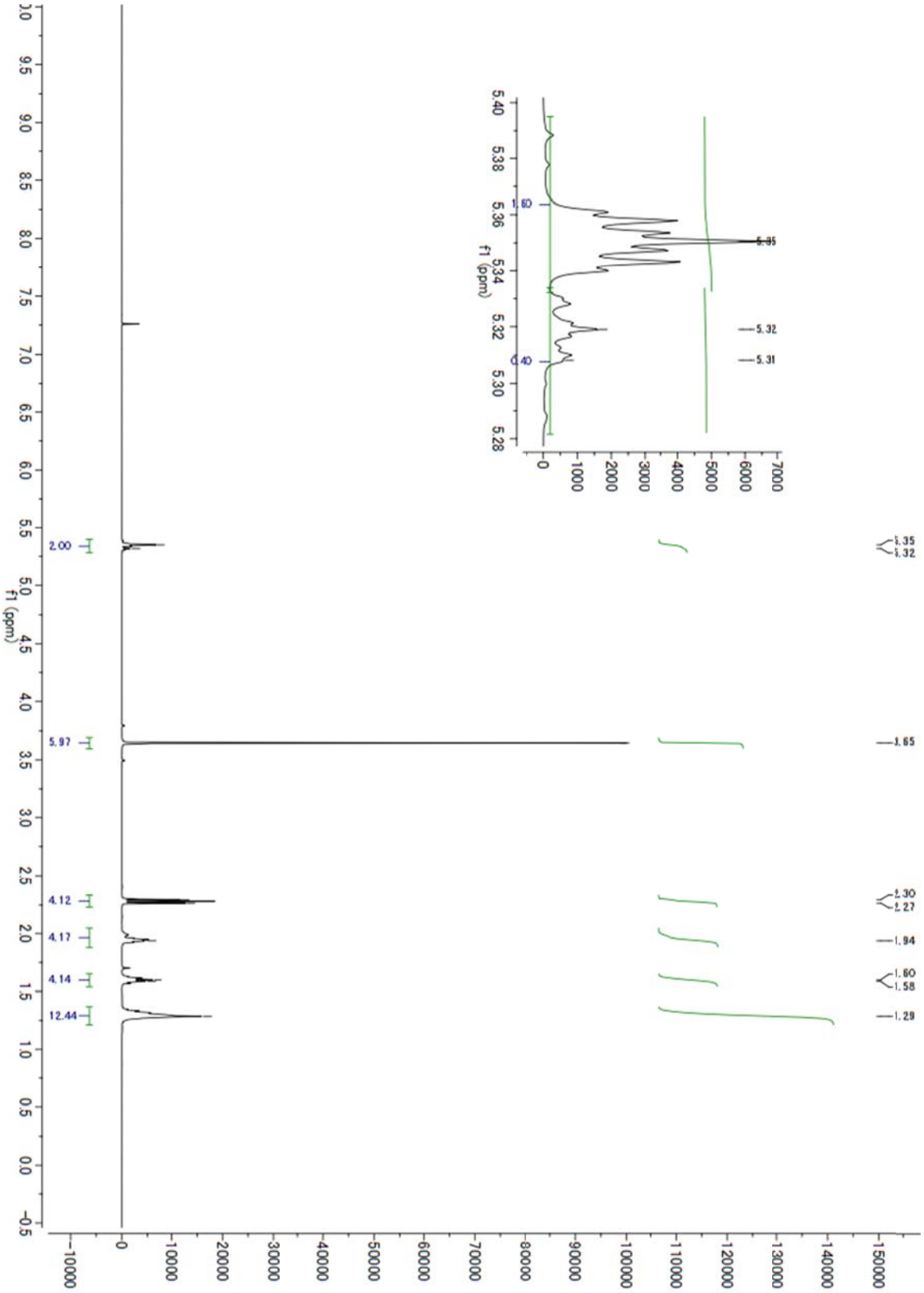


Figure S9. ^{1}H NMR (500 MHz) spectrum of **16** in $CDCl_3$.

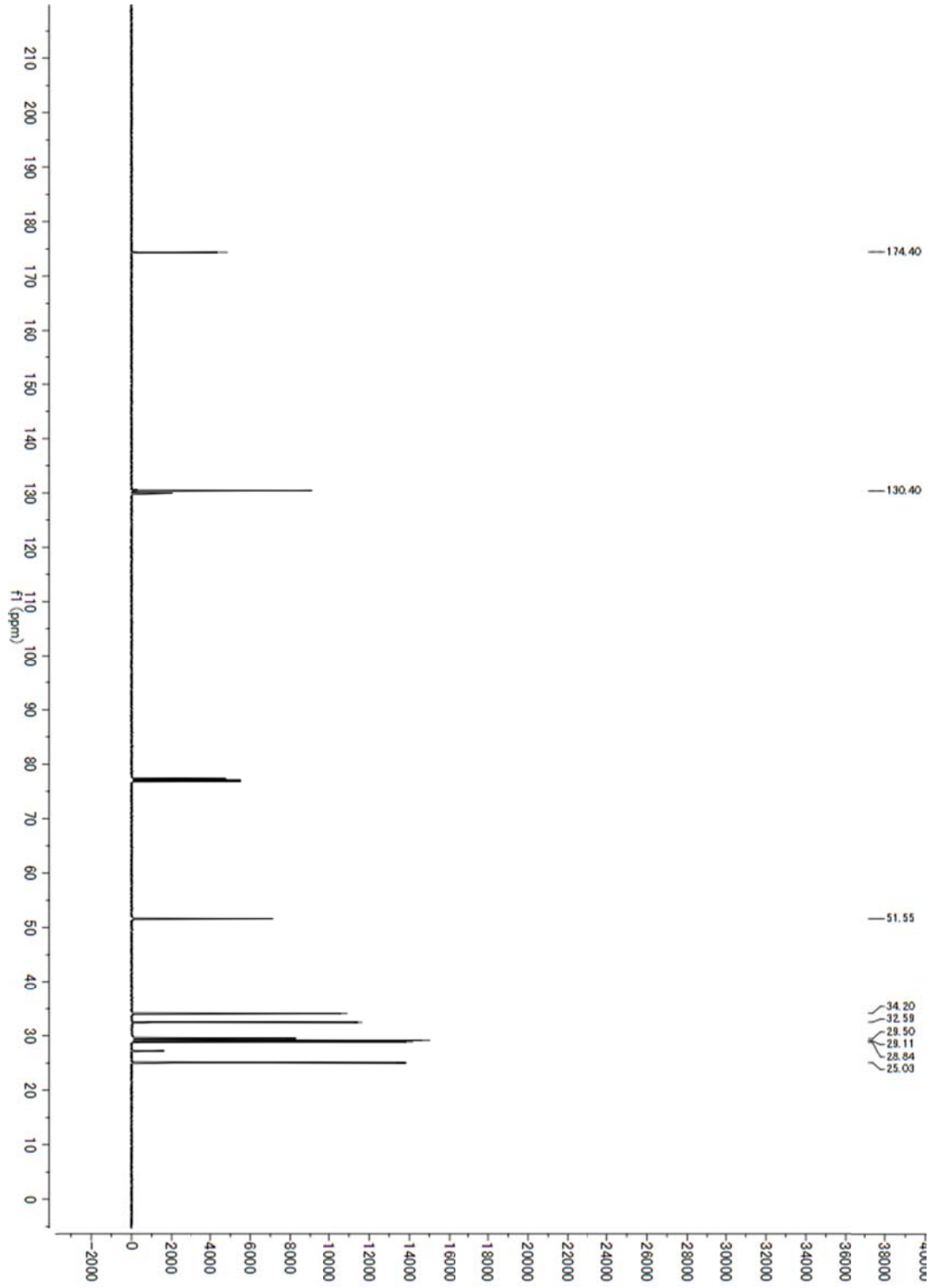


Figure S10. ^{13}C NMR (126 MHz) spectrum of **16** in $CDCl_3$.

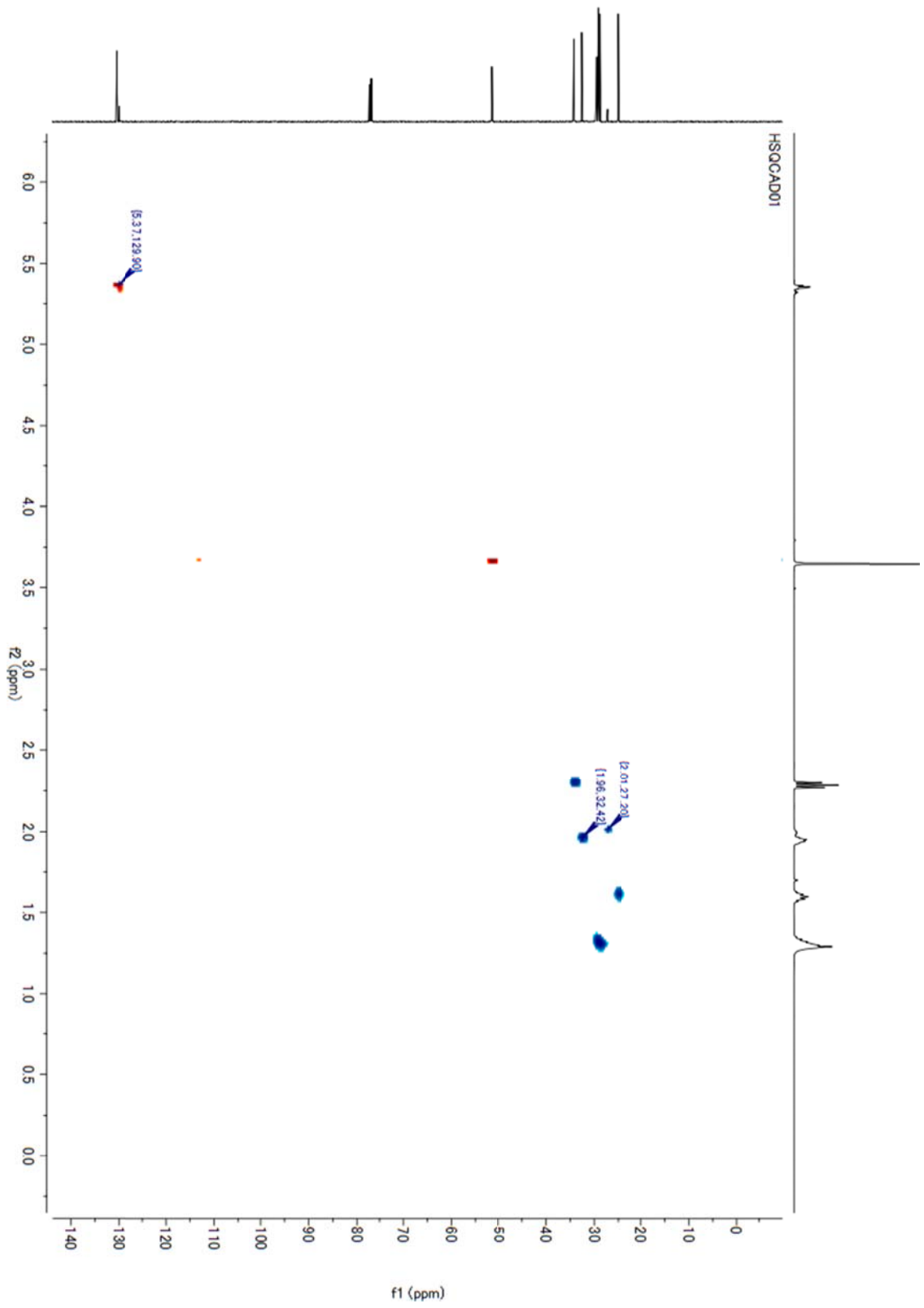


Figure S11. ^{1}H-^{13}C HSQC of **16** in $CDCl_3$.

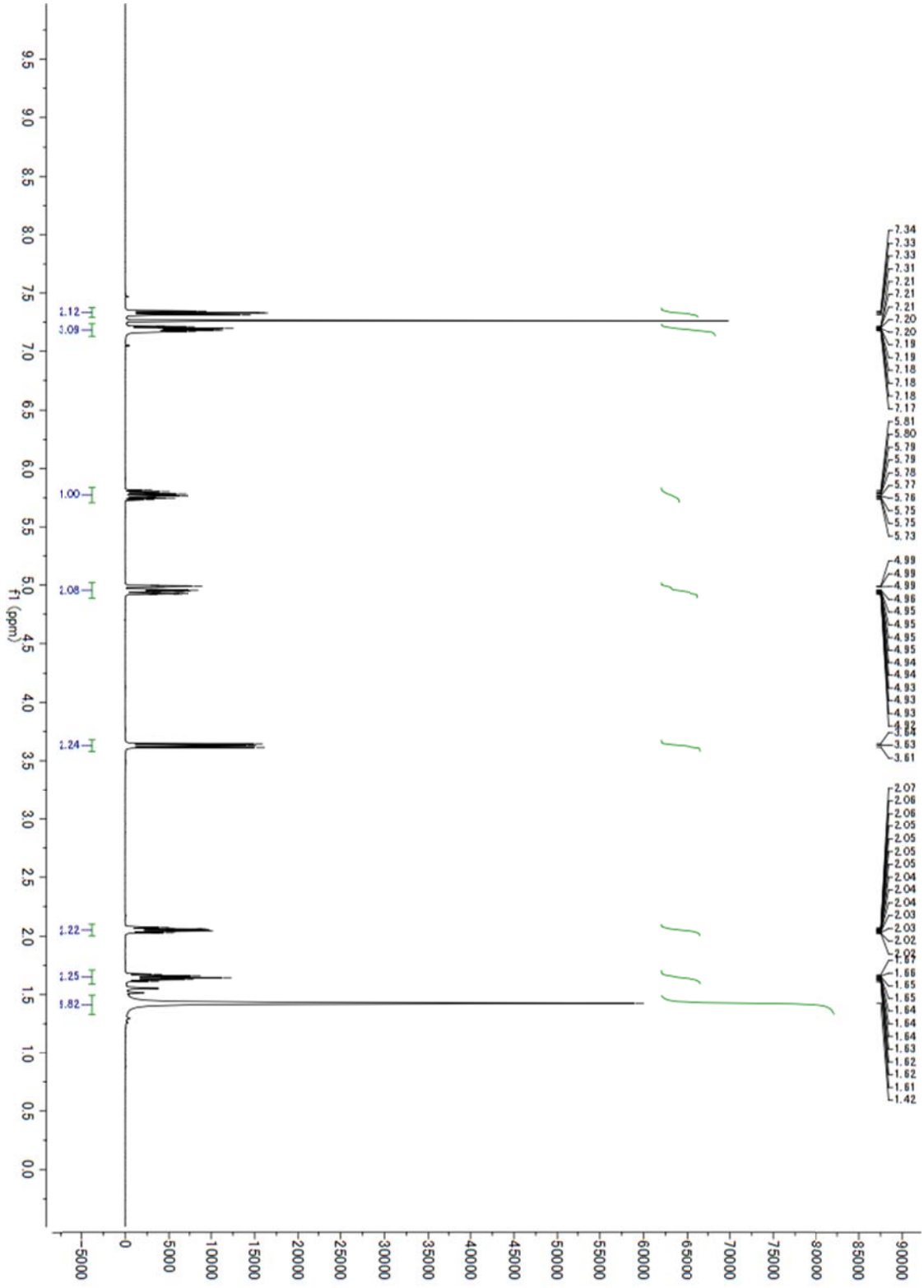


Figure S12. ^{1}H NMR (500 MHz) spectrum of **S7** in $CDCl_3$.

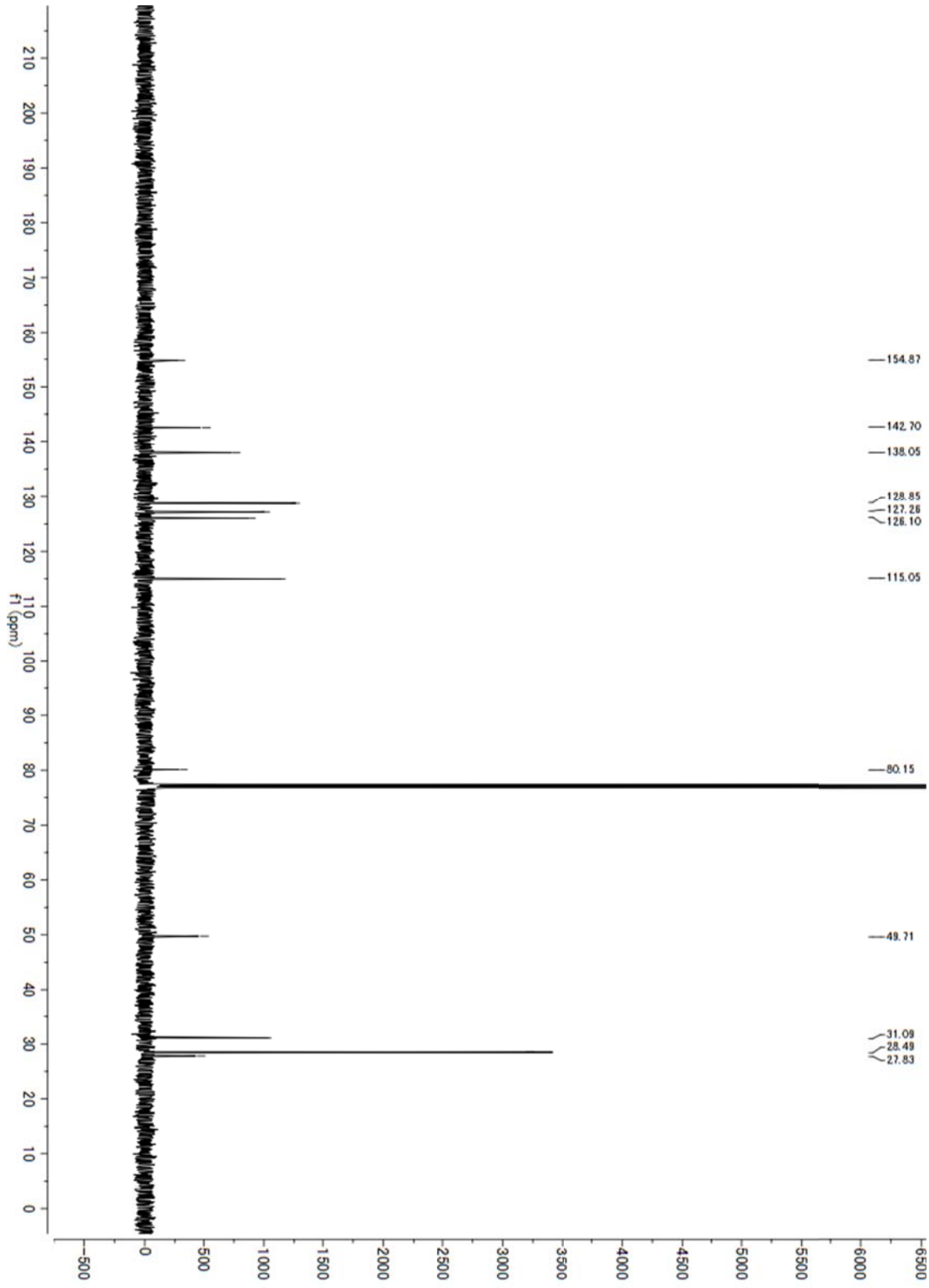


Figure S13. ^{13}C NMR (126 MHz) spectrum of **S7** in $CDCl_3$.

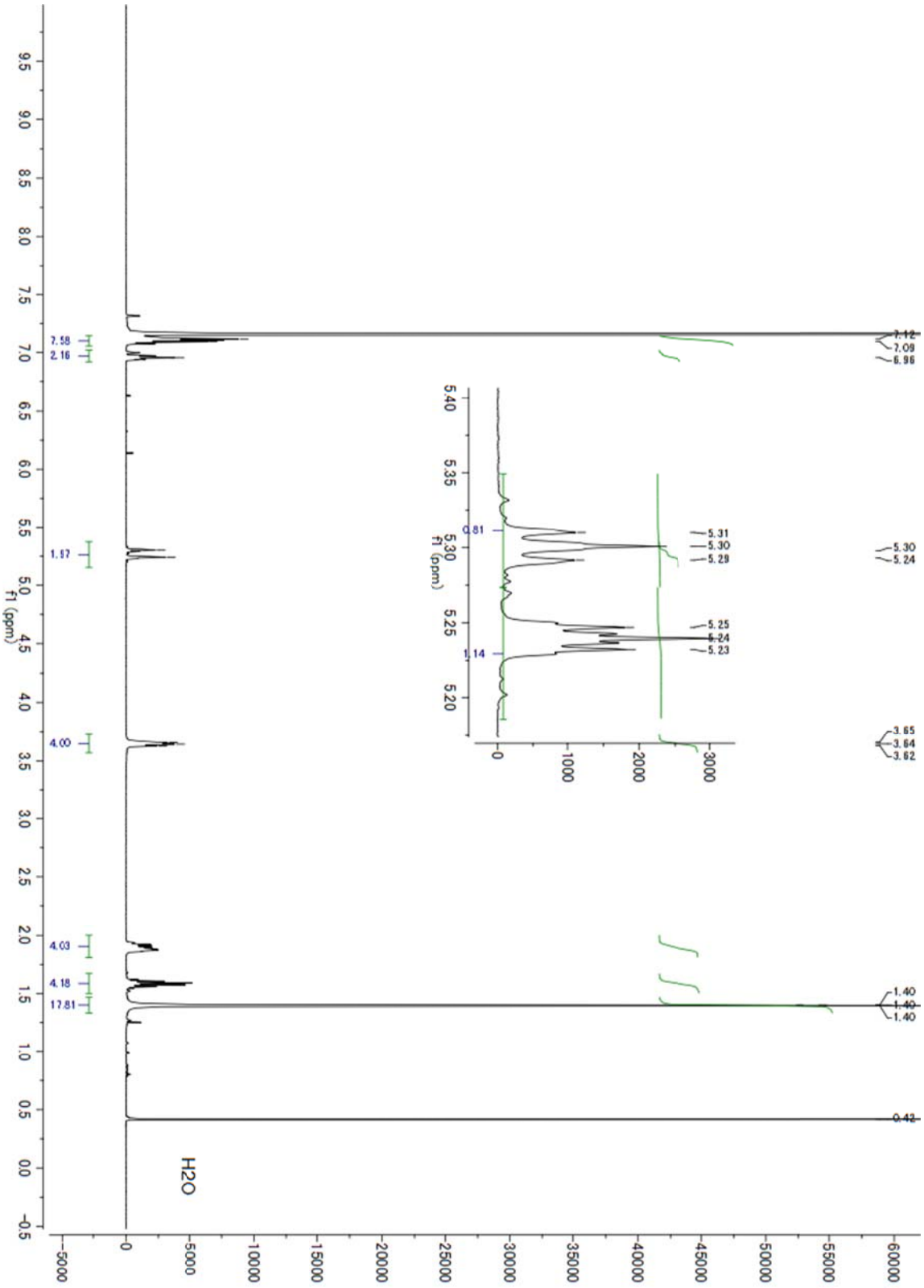


Figure S14. ^{1}H NMR (500 MHz) spectrum of **S8** in C_6D_6.

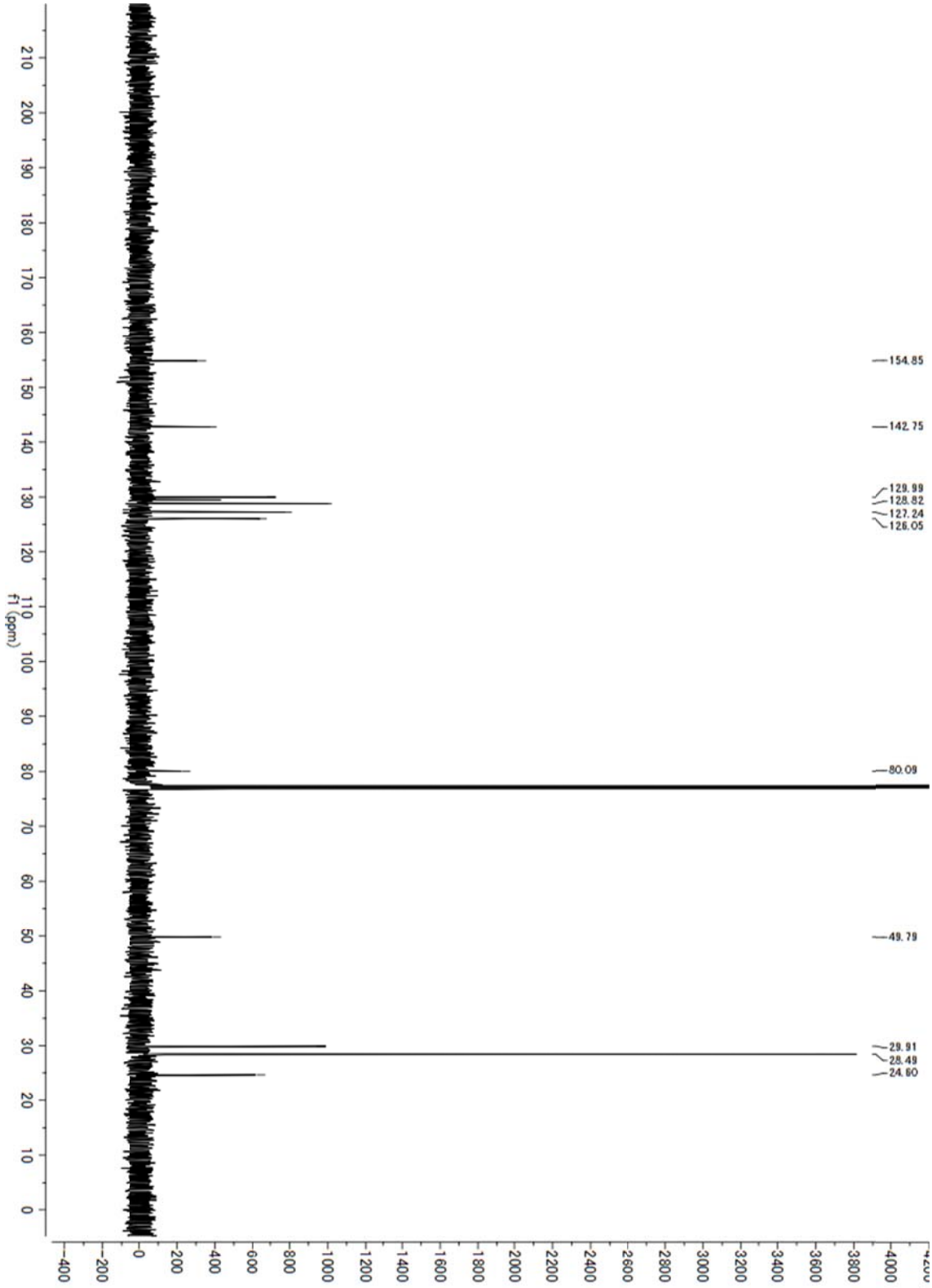


Figure S15. ^{13}C NMR (126 MHz) spectrum of **S8** in $CDCl_3$.

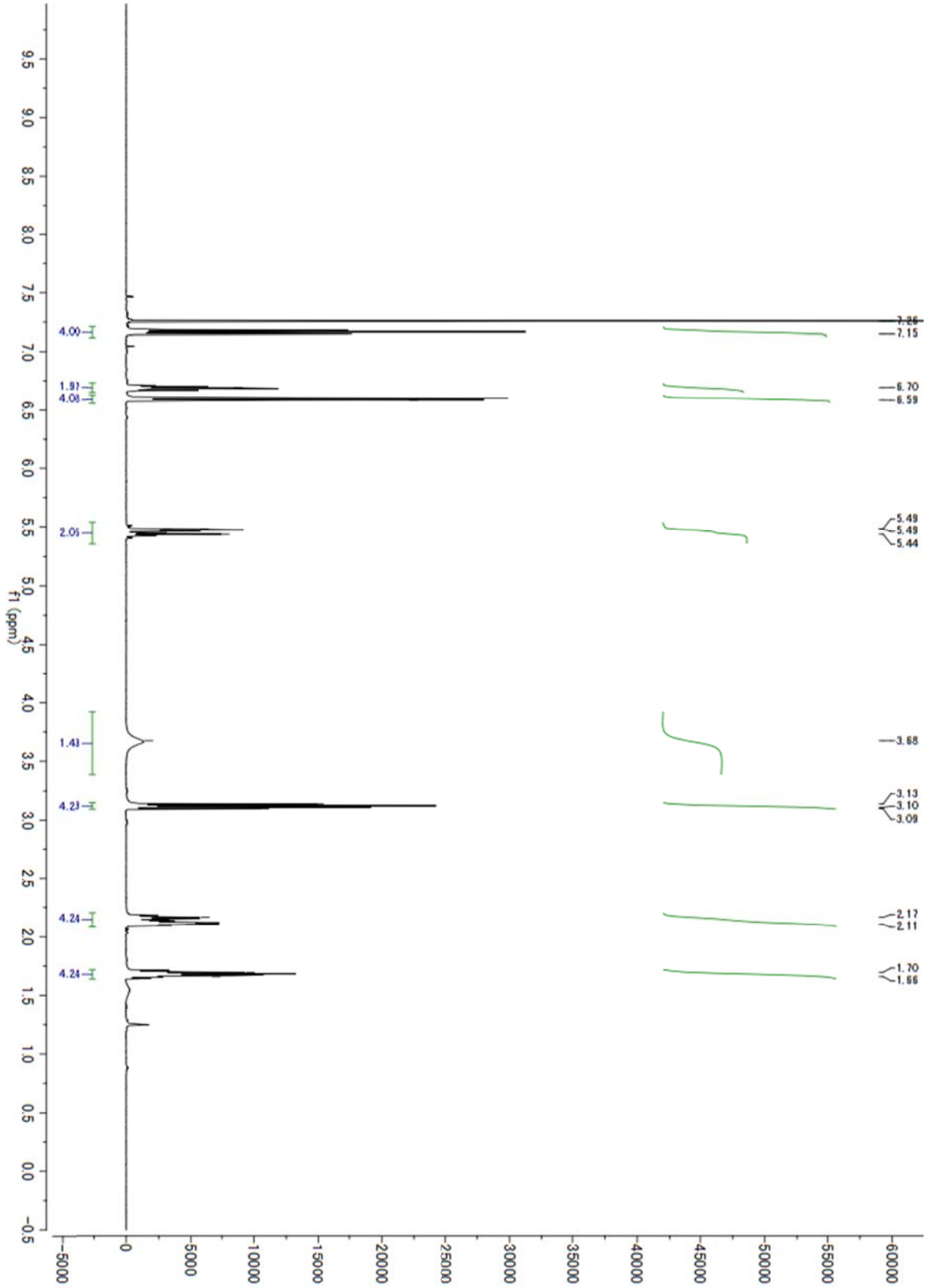


Figure S16. ^{1}H NMR (500 MHz) spectrum of **17** in $CDCl_3$.

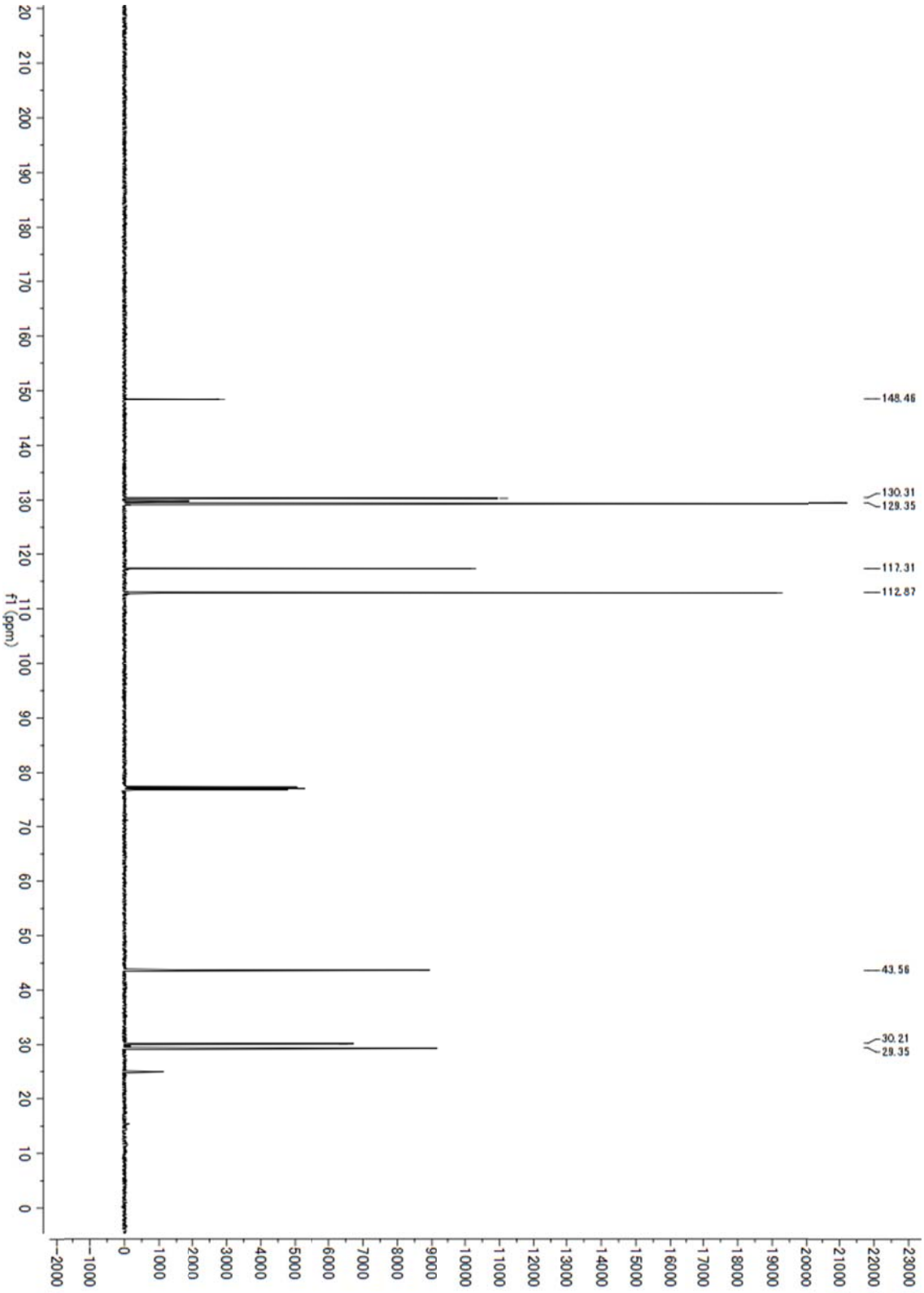


Figure S17. ^{13}C NMR (126 MHz) spectrum of **17** in $CDCl_3$.

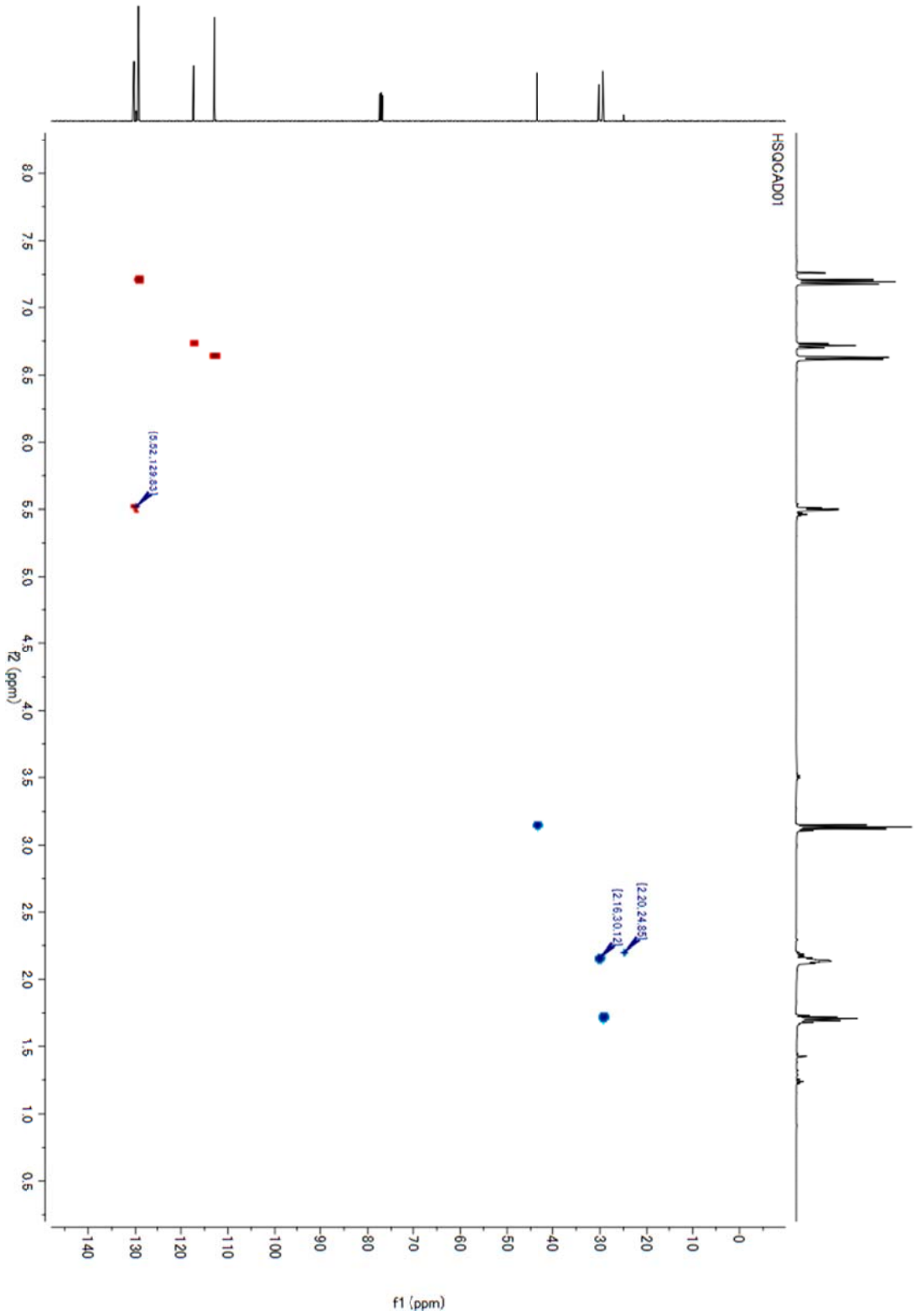


Figure S18. ^{1}H-^{13}C HSQC of **17** in $CDCl_3$.

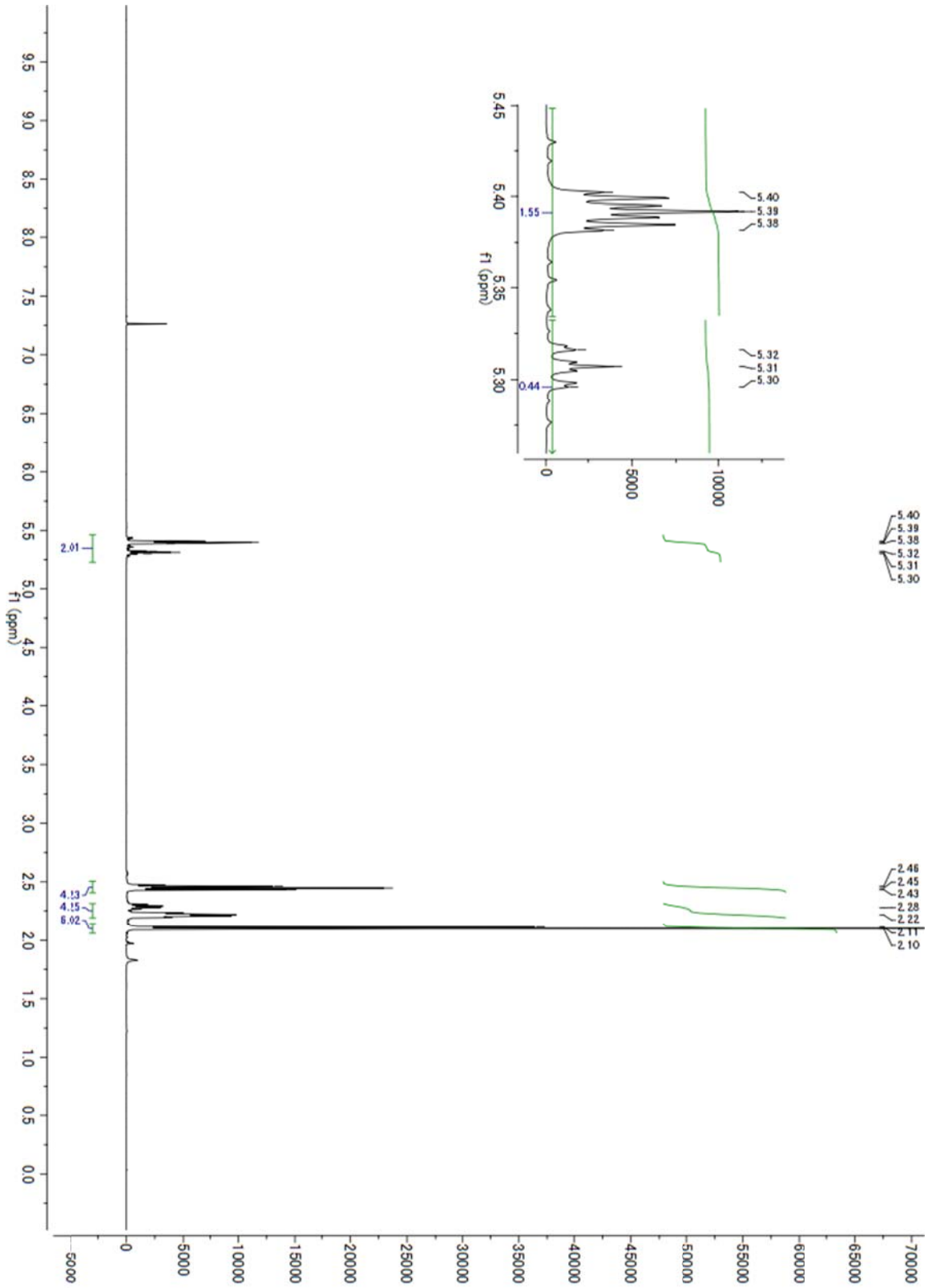


Figure S19. ^{1}H NMR (500 MHz) spectrum of **18** in $CDCl_3$.

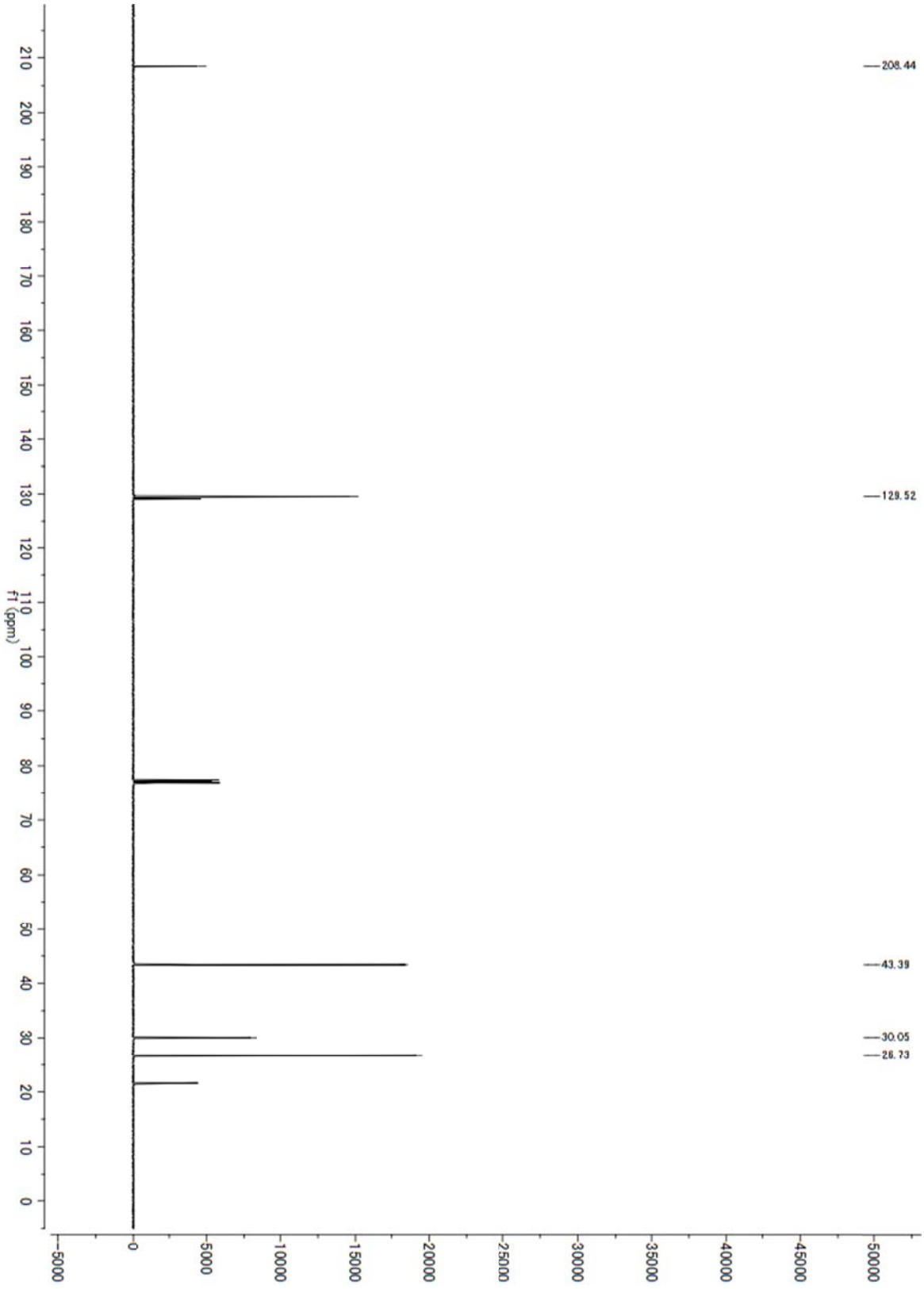


Figure S20. ^{13}C NMR (126 MHz) spectrum of **18** in $CDCl_3$.

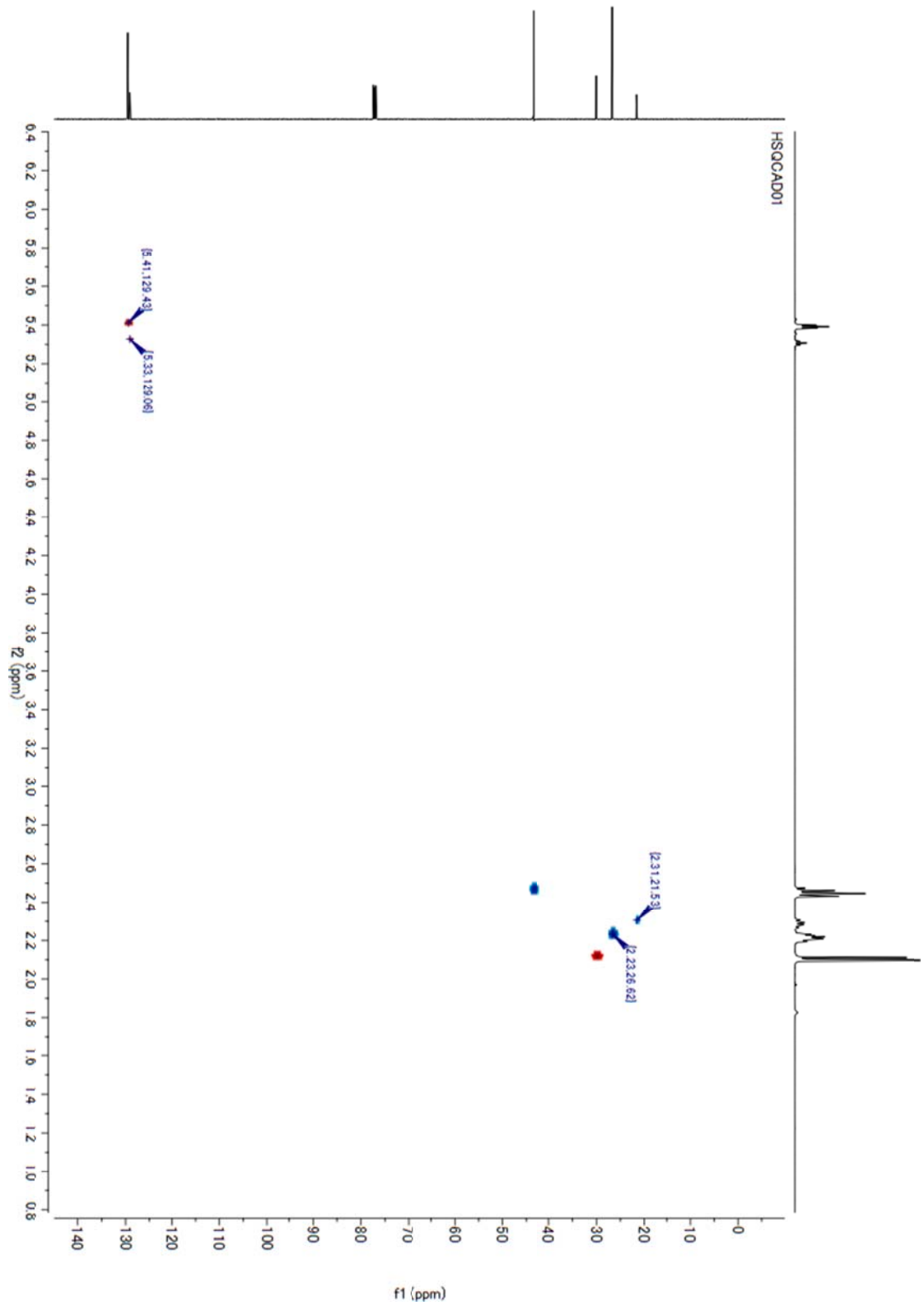


Figure S21. ^{1}H-^{13}C HSQC of **18** in $CDCl_3$.

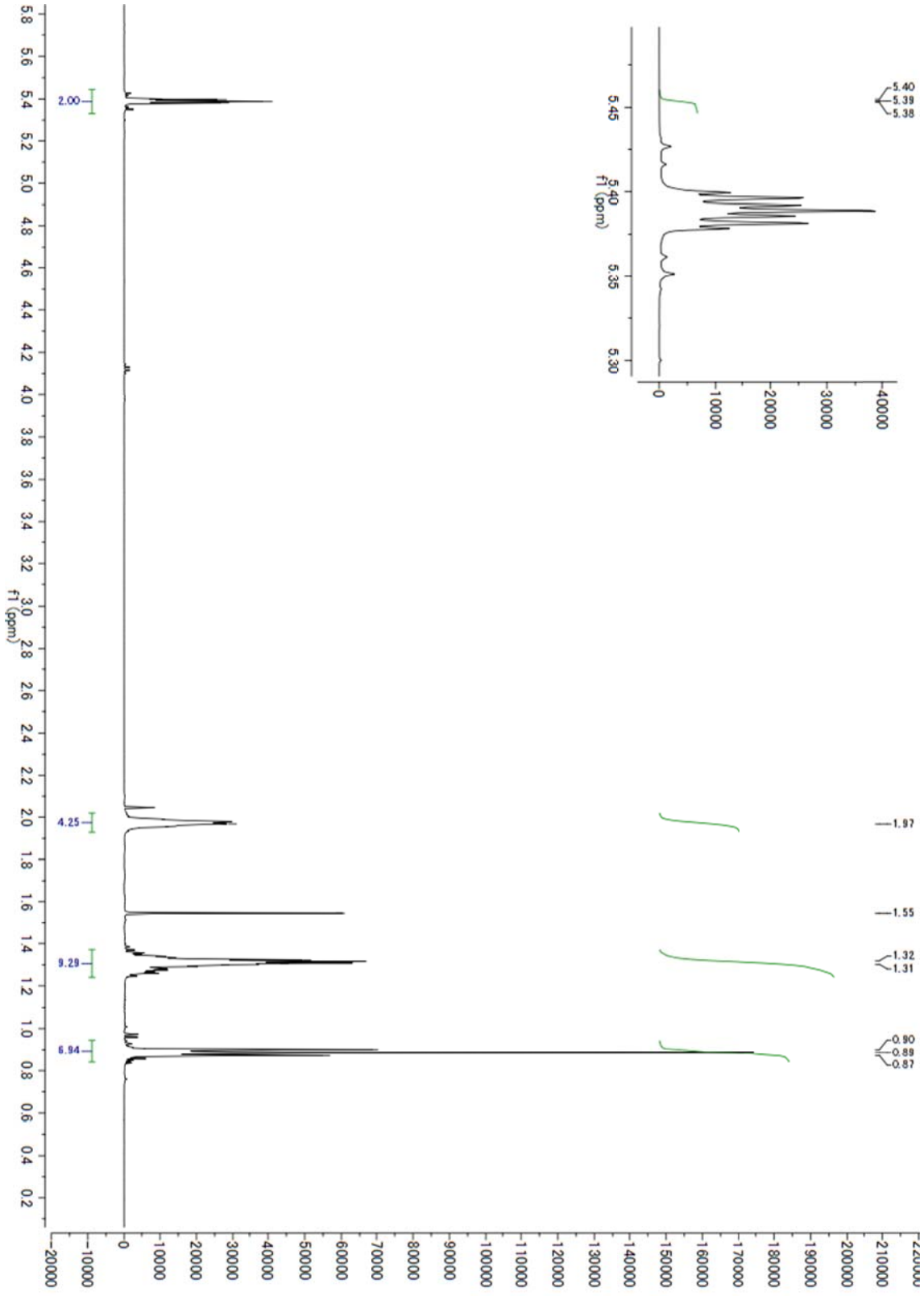


Figure S22. ^{1}H NMR (500 MHz) spectrum of the purely *E*-isomer of **11** in $CDCl_3$.

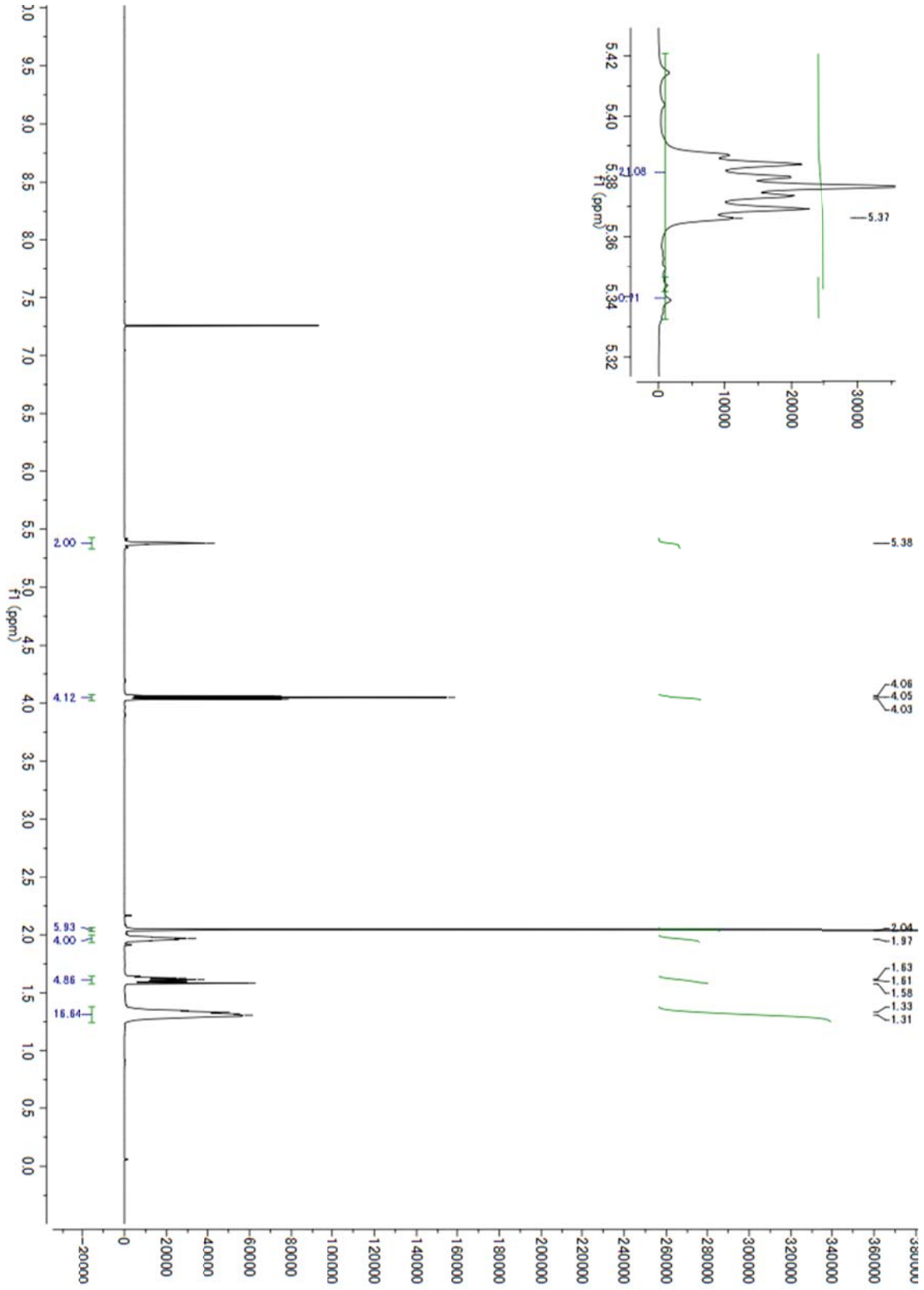


Figure S23. ^{1}H NMR (500 MHz) spectrum of the purely *E*-isomer of **12** in $CDCl_3$.